Multibond Forming Tandem Reactions of Anilines via Stable Aryl Diazonium Salts: One-Pot Synthesis of 3,4-Dihydroquinolin-2-ones

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ABSTRACT: A fast and effective one-pot tandem process that generates Heck coupled products from readily available anilines via stable aryl diazonium tosylate salts was developed. The mild and simple procedure involves rapid formation of aryl diazonium salts using a polymer-supported nitrite reagent and p-tosic acid, followed by a base-free Heck–Matsuda coupling with acrylates and styrenes. Using 2-nitroanilines as substrates, the one-pot tandem process was extended for the direct synthesis of 3,4-dihydroquinolin-2-ones. In this case, following diazotization and Heck–Matsuda coupling to give methyl cinnamates, addition of hydrogen and reutilization of the palladium catalyst for reduction of the nitro group and hydrogenation of the alkene resulted in efficient formation of 3,4-dihydroquinolin-2-ones. The synthetic utility of this one-pot, four-stage process was demonstrated with the five-pot synthesis of a quinolinone-based sodium ion channel modulator.

INTRODUCTION

The Mizoroki–Heck coupling of aryl halides with olefins in the presence of a palladium catalyst and a base has become a general method for carbon–carbon bond formation.1 This powerful transformation allows the stereoselective synthesis of highly substituted alkenes, key synthetic building blocks for organic chemistry.2 Despite the many applications of the Mizoroki–Heck reaction, the transformation can be limited by the requirement of a base, elevated temperatures, and olefin migration. A less-utilized variant of this cross-coupling is the Heck–Matsuda reaction that uses aryl diazonium salts as more reactive aryl halide surrogates (Scheme 1a).3 The increased electrophilic nature of aryl diazonium salts allows the Heck–Matsuda reaction to proceed at lower temperatures and often without the need for ligands or a base.4 Under these milder conditions, alkene migration is minimized, generating cleaner products.

Despite these advantages, the safety hazards associated with aryl diazonium salts has restricted the widespread use of the Heck–Matsuda reaction. This has partly been countered by replacing aryl diazonium chlorides and acetates that are unstable above 0 °C, with more stable tetrafluoroborate crystalline salts.5 However, these compounds still require storage at low temperatures and in the dark. To minimize the safety issues of handling and storing aryl diazonium salts, one-pot methods in which the aryldiazonium salts are formed in situ and directly subjected to a Heck–Matsuda reaction have been developed.6 Examples include a procedure reported by Andrus and coworkers that used an imidazolium carbene as a palladium ligand for the base-free coupling of a focused series of substrates in 17–62% yield (Scheme 1b).7 In recent years, the Felpin group made a major contribution in understanding and advancing the applications of the Heck–Matsuda reaction.8 This included the development of a one-pot tandem synthesis of Heck adducts from anilines using catalytic amounts of diazonium salts via a double catalytic cycle (Scheme 1c).8 This process was found to be general for the efficient coupling of a wide range of substituted anilines with methyl acrylate, giving the Heck adducts in excellent yields over a reaction time of 48–65 h.

In 2008, the groups of Filimonov and Chi reported the synthesis and characterization of aryl diazonium tosylate salts.9 These were prepared from anilines using a polymer-supported nitrite reagent under mild conditions and were found to have particularly high thermal and aging stability. Despite these properties, aryl diazonium tosylate salts are still reactive and have been utilized in standard substitution and cross-coupling reactions.9,10 We recently demonstrated that aryl diazonium tosylate salts could be generated in situ and subjected to an iodination reaction for the one-pot tandem synthesis of aryl iodides from anilines.11 Because of the relatively stable nature of aryl diazonium tosylate salts and this initial demonstration of their application in one-pot tandem processes, we were interested in further exploiting these compounds for additional multistep transformations. Herein, we now report a rapid, mild, and nonhazardous one-pot tandem diazotization and Heck reaction of anilines for the general preparation of cinnamates.

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exchange of tetaalkylammonium functionalized resins, such as Amberlyst A-26 with aqueous solutions of sodium nitrite.\(^9,11\)

Initially, the use of tetrafluoroboric acid as a proton source was compared with \(p\)-tosic acid (Table 1, entries 1 and 2). A higher

| entry | \(\text{Pd}(\text{OAc})_2\) (mol %) | temp (°C) | time (h) | conv (%) |
|-------|---------------------------------|-----------|----------|---------|
| 1     | 10                              | 20        | 24       | 38      |
| 2     | 10                              | 20        | 24       | 48      |
| 3     | 10                              | 40        | 1        | 52      |
| 4     | 10                              | 60        | 0.75     | 62      |
| 5     | 15                              | 60        | 1.5      | 100 (75)|
| 6     | 5                               | 60        | 1.5      | 100 (68)|

\(^a\)Conversions were measured using 1,3,5-trimethoxybenzene as an internal standard. \(^b\)Isolated yields are in parentheses. \(^c\)HBF\(_4\) was used as the proton source.

and styrenes (Scheme 1d). The highly chemoselective nature of this tandem process is demonstrated with halogenated anilines that following diazotization and Heck reaction can undergo further functionalization via additional cross-coupling reactions. We also describe an extension of the tandem process with 2-nitroanilines in which the Heck adducts can be directly converted to 3,4-dihydroquinolin-2-ones by the addition of hydrogen and reutilization of the palladium catalyst.

### RESULTS AND DISCUSSION

In several studies of the Heck–Matsuda reaction, nitro-substituted anilines have been found to be problem substrates.\(^5,6,12\) The high redox potential and a favorable homolytic dediazonization pathway of nitro-substituted aryl diazonium salts have been used to explain the facile decomposition of these compounds and the complex mixtures from attempted Heck–Matsuda reactions. Felpin and coworkers demonstrated that their one-pot diazotization and Heck–Matsuda reaction process could overcome these issues, allowing the efficient generation of coupled products (Scheme 1c).\(^8\) Because of the issues associated with nitro analogues and to investigate whether our one-pot tandem process could also overcome these problems, our study began by investigating the one-pot synthesis of aryl diazonium tosylate salts and Heck–Matsuda coupling reaction using 4-nitroaniline (1a) as a substrate. Initially, a one-pot tandem process in which all the reagents were added together was investigated. This included the polymer-supported nitrite reagent, which prevents the release of nitrogen oxides and is easily prepared by the ion

Table 1. Optimization of the One-Pot Tandem Diazotization and Heck–Matsuda Reaction

| Entry | \(\text{Pd}(\text{OAc})_2\) (mol %) | Temp (°C) | Time (h) | Conv (%) |
|-------|---------------------------------|-----------|----------|---------|
| 1     | 10                              | 20        | 24       | 38      |
| 2     | 10                              | 20        | 24       | 48      |
| 3     | 10                              | 40        | 1        | 52      |
| 4     | 10                              | 60        | 0.75     | 62      |
| 5     | 15                              | 60        | 1.5      | 100 (75)|
| 6     | 5                               | 60        | 1.5      | 100 (68)|

\(^a\)Conversions were measured using 1,3,5-trimethoxybenzene as an internal standard. \(^b\)Isolated yields are in parentheses. \(^c\)HBF\(_4\) was used as the proton source.

Following the optimization of a rapid and mild one-pot tandem process for diazotization and Heck coupling, the scope of this transformation was explored using various anilines and methyl acrylate (Scheme 2). Irrespective of the electronic nature or the substitution pattern of the aniline, all examples investigated were fully converted under the standard conditions to the corresponding Heck adduct in yields of 53–83%. Interestingly, the one-pot diazotization and Heck–Matsuda coupling of halogenated anilines was completely chemoselective, giving compounds 2d–2f, 2i, and 2l as the sole products. These results, particularly for 2e, 2f, and 2i, exemplify the superior electrophilic nature of diazonium salts compared to halides. The one-pot process was also investigated for the synthesis of E-stilbenes. Reaction of 4-nitroaniline (1a) with styrene or 4-fluorostyrene gave E-stilbenes 2a and 2o in 74 and 46% yields, respectively.

As the one-pot process with halogenated anilines gave only Heck–Matsuda adducts and none of the Mizoroki–Heck products, we wanted to exploit this chemoselectivity for the two-pot synthesis of orthogonally functionalized aryl com-
pounds. The one-pot diazotization and Heck−Matsuda coupling of 4-bromoaniline (1e) was scaled up, allowing the multigram synthesis of methyl (E)-3-(4-bromophenyl)acrylate (2e) (Scheme 3). Having used the amino group to implement the first cross-coupling process, 2e was then subjected to a Mizoroki−Heck reaction with styrene. This gave E-stilbene 3 in 72% yield. In a similar fashion, arylation or allylation by Suzuki−Miyaura reaction of 2e completed the efficient two-pot synthesis of acrylates 4a−4d. This study shows that a combination of the one-pot diazotization and Heck−Matsuda process with a further cross-coupling reaction allows the highly controlled and selective introduction of multiple unsaturated moieties onto a central arene core.

A key objective of this project was to expand the scope of the one-pot diazotization and Heck−Matsuda process to include 2-nitroanilines as substrates. It was proposed that the resulting 2-nitrophenyl acrylates could be converted to 3,4-dihydroquinolin-2-ones by extending the one-pot process to include reduction and cyclization steps. Before attempting the extended one-pot process, a series of substituted 2-nitroanilines was initially examined as substrates for the one-pot two-step tandem process (Scheme 4). Using the previously developed standard conditions, a wide range of acrylates 6a−6n bearing various functional groups and substitution patterns were prepared in 56−87% yields. Again, complete chemoselectivity was observed with brominated (5i) and iodinated (5j) anilines.

As 2-nitroanilines were found to be excellent substrates for the one-pot diazotization and Heck−Matsuda reaction, the use of these in an extended one-pot multibond forming process for the preparation of 3,4-dihydroquinolin-2-ones was next investigated. 3,4-Dihydroquinolin-2-ones are important heterocyclic scaffolds for synthesis and are found in a wide range of pharmaceutically active agents. Because of this importance, numerous methods have been developed for their synthesis, including one-pot processes. For example, Jiao and coworkers used a combination of radical and ionic processes for the reaction of 2-iodoanilines with ethyl acrylate for the preparation of 3,4-dihydroquinolin-2-ones in 17−71% yields.
while the Lautens groups developed a one-pot Rh/Pd catalyzed conjugate addition and amidation process of 2-chlorophenyl boronic acids with acrylamide to generate a series of these compounds in 53–96% yields.17 Felpin and coworkers also reported a one-pot synthesis of 3,4-dihydroquinolin-2-ones from 2-nitroaryl tetrafluoroborate diazonium salts using a Heck–Matsuda reaction with acrylates followed by the addition of charcoal and a reduction and cyclization sequence.8b In our study, we wanted to demonstrate that 3,4-dihydroquinolin-2-ones could be prepared directly from 2-nitroanilines using the palladium catalyst to effect the Heck–Matsuda coupling and the hydrogenation/reduction steps without the use of any additives. Using 2-nitroaniline (5a), the one-pot tandem diazotization and Heck–Matsuda sequence was performed as before (Scheme 5). On complete conversion to methyl acrylate 6a, the reaction mixture was placed under an atmosphere of hydrogen after 24 h, this gave 3,4-dihydroquinolin-2-one 7a in 73% overall yield. Having shown that a one-pot diazotization/Heck–Matsuda/reduction/cyclization sequence could lead directly to 3,4-dihydroquinolin-2-ones, the scope and limitations of this process were investigated. Alkyl substituted 2-nitroanilines and a substrate bearing a fluorine substituent were readily converted to the corresponding 3,4-dihydroquinolin-2-ones 7a–7d and 7f, in yields of 64–79%, under these conditions. Electron-rich methoxy substituted 2-nitroanilines 5e and 5f could also be converted to 3,4-dihydroquinolin-2-ones 7e and 7f, however, the hydrogenation/reduction step at atmospheric pressure was slow, leading to mixtures of the target 3,4-dihydroquinolin-2-ones and methyl 2-nitrophenylpropionate intermediates after 24 h.18 To effect cleaner, more efficient syntheses of these compounds, the one-pot process was repeated by conducting the reduction stage under pressure at 2.5 bar. This gave 3,4-dihydroquinolin-2-ones 7e and 7f as the sole products in 74 and 57% yields, respectively. A limitation of this one-pot process is that 2-nitroanilines bearing labile carbon–halogen bonds are subject to dehalogenation at the reduction stage. For example, the attempted use of 5-chloro-2-nitroaniline (5h) as a substrate for this process gave 5-chloro-3,4-dihydroquinolin-2-one in 28% yield but as a 1:1 inseparable mixture with the dechlorinated product 7a. Our interest in preparing halogenated 3,4-dihydroquinolin-2-ones was for the potential structural diversification of these through cross-coupling reactions after the one-pot process. To overcome this limitation, cross-coupling reactions were conducted prior to the one-pot process for the efficient two-pot synthesis of 7-aryl-3,4-dihydroquinolin-2-ones. Suzuki–Miyaura reaction of 4-iodo-2-nitroaniline (5j) with various aryl boronic acids (see Supporting Information for full details) was then followed by the one-pot process, which gave 7h–7j in 57–73% yield. While the standard diazotization and Heck–Matsuda steps for the 4-aryl-2-nitroanilines could be conducted under standard conditions, again the use of 2.5 bar of pressure for the reduction stage allowed the most efficient synthesis of these analogues.

The synthetic potential of the 3,4-dihydroquinolin-2-ones prepared from the extended one-pot process was then demonstrated with the synthesis of a pharmaceutically active target. N-Acetic acid derived 3,4-dihydroquinolin-2-ones bearing 6- or 7-aryl groups are late stage sodium channel blockers and have the potential to be used in the treatment of cardiovascular diseases and diabetes.19 In this study, a sodium channel modulator, 3,4-dihydroquinolin-2-one 11, was prepared via a five-pot synthesis (Scheme 6). As shown above, the extended one-pot process was used to convert 5-methoxy-2-nitroaniline (5e) to the corresponding 3,4-dihydroquinolin-2-
one 7e on a gram scale in 57% yield. Quinolin-2-one 7e was alkylated in quantitative yield using t-butyl chloroacetate and sodium hydride. A highly regioselective iron(III) trilimide-catalyzed halogenation with N-bromosuccinimide (NBS) was used to functionalize the 6-position of the aryl ring. The combination of catalytic amounts of iron(III) chloride and the ionic liquid [BMM][NTf₂] forms iron(III) trilimide in situ, which acts as a powerful Lewis acid for the activation of NBS. This reaction gave 6-bromo-3,4-dihydroquinolin-2-one 9 as the sole product in 81% yield. Suzuki–Miyaura coupling of 9 with 4-chlorophenyl boronic acid under standard conditions gave 6-aryl-3,4-dihydroquinolin-2-one 10 in 75% yield. Finally, TFA mediated deprotection of the t-butyl ester completed the synthesis of sodium ion channel modulator 11 in 32% overall yield from 2-nitroaniline 5e.

## CONCLUSIONS

In summary, a rapid one-pot tandem process involving diazotization and base-free Heck–Matsuda coupling of anilines with acrylates and styrenes was developed. The use of a particularly mild procedure to form stable aryl diazonium tosylate salts using a polymer-supported nitrite reagent and particularly mild procedure to form stable aryl diazonium cation by silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(4-nitrophenyl)acrylate (2a) (0.028 g, 68%) as a pale yellow solid. Mp 159–161 °C (lit.161 °C); 1H NMR (400 MHz, CDCl₃) δ 8.35 (s, 3H), 6.83 (d, J = 16.1 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 13C NMR (101 MHz, CDCl₃) δ 121.3 (CH), 131.0 (CH), 138.1 (C), 141.8 (CH), 166.5 (C); MS (EI) m/z 207 (M⁺, 66), 176 (100), 130 (24), 102 (26).

Methyl (E)-3-(4'-Acetoxyphenyl)acrylate (2b). The reaction was carried out according to the previously described procedure for methyl (E)-3-(4'-nitrophenyl)acrylate (2a) using 4-acetoxyacetophenone (1b) (0.050 g, 0.37 mmol), polymer-supported nitrite (0.32 g, containing 1.1 mmol of NO₂), t-polyeneous acid monohydrate (0.19 g, 1.1 mmol), palladium(II) acetate (0.040 g, 0.19 mmol), and methyl acrylate (0.17 mL, 1.9 mmol). Purification by silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(4'-acetoxyphenyl)acrylate (2b) (0.050 g, 64%) as an orange oil. Spectroscopic data were consistent with the literature. ¹H NMR (400 MHz, CDCl₃) δ 6.26 (s, 3H), 3.83 (s, 3H), 6.53 (d, J = 16.1 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.3 Hz, 2H), 13C NMR (101 MHz, CDCl₃) δ 121.3 (CH), 128.3 (2 × CH), 128.5 (2 × CH), 138.1 (C), 138.7 (C), 143.3 (CH), 166.9 (C), 197.2 (C); MS (EI) m/z 205 (M⁺ + H⁺, 100).

Methyl (E)-3-(4'-Cyanophenyl)acrylate (2c). The reaction was carried out according to the previously described procedure for methyl (E)-3-(4'-nitrophenyl)acrylate (2a) using 4-cyanophenylacetonitrile (1c) (0.050 g, 0.42 mmol), polymer-supported nitrite (0.36 g, containing 1.3 mmol of NO₂), t-polyeneous acid monohydrate (0.22 g, 1.3 mmol), palladium(II) acetate (0.005 g, 0.02 mmol), and methyl acrylate (0.19 mL, 2.1 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(4'-cyanophenyl)acrylate (2c) (0.046 g, 59%) as a yellow solid. Mp 120–122 °C (lit.121.7–122.1 °C); ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 3H), 6.52 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 8.3 Hz, 1H), 13C NMR (101 MHz, CDCl₃) δ 121.3 (CH), 113.5 (C), 118.6 (C), 121.4 (C), 128.4 (2 × CH), 132.7 (2 × CH), 138.7 (C), 142.4 (CH), 166.6 (C); MS (EI) m/z 187 (M⁺, 50), 156 (100), 128 (42), 84 (27).

Methyl (E)-3-(4'-Fluorophenyl)acrylate (2d). The reaction was carried out according to the previously described procedure for methyl (E)-3-(4'-nitrophenyl)acrylate (2a) using 4-fluorophenylacetonitrile (1d) (0.050 g, 0.39 mmol), polymer-supported nitrite (0.33 g, containing 1.2 mmol of NO₂), t-polyeneous acid monohydrate (0.20 g, 1.2 mmol), palladium(II) acetate (0.040 g, 0.20 mmol), and methyl acrylate (0.18 mL, 2.0 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(4'-fluorophenyl)acrylate (2d) (0.040 g, 53%) as a yellow solid. Mp 73–75 °C (lit.74–75 °C); ¹H NMR (400 MHz, CDCl₃) δ 3.80 (s, 3H), 5.61 (d, J = 166.0 Hz, 2H), and 7.27 (d, J = 8.7 Hz, 2H) ppm.
The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 4-methoxoaniline (1g) (0.050 g, 0.41 mmol), polymer-supported nitrite (0.35 g, containing 0.75 mmol of NO₂), p-toluenesulfonic acid monohydrate (0.12 g, 0.69 mmol), and methyl acrylate (0.11 mL, 1.3 mmol). Purification by neutral alumina flash column chromatography, eluting with 5% diethyl ether in hexane gave methyl (E)-3-(4′-nitrophenyl)acrylate (2f) using 2-amino-benzophenone (1k) (0.050 g, 0.25 mmol), polymer-supported nitrite (0.21 g, 0.75 mmol), p-toluenesulfonic acid monohydrate (0.12 g, 0.69 mmol), and methyl acrylate (0.11 mL, 1.3 mmol). Purification by neutral alumina flash column chromatography, eluting with 5% diethyl ether in hexane gave methyl (E)-3-(4′-nitrophenyl)acrylate (2g) using 2-aminobenzophenone (1k) (0.050 g, 0.25 mmol), polymer-supported nitrite (0.21 g, 0.75 mmol), p-toluenesulfonic acid monohydrate (0.12 g, 0.69 mmol), and methyl acrylate (0.11 mL, 1.3 mmol). Purification by neutral alumina flash column chromatography, eluting with 5% diethyl ether in hexane gave methyl (E)-3-(4′-nitrophenyl)acrylate (2h) using 3-nitroaniline (1n) (0.050 g, 0.23 mmol), polymer-supported nitrite (0.20 g, containing 0.69 mmol of NO₂), p-toluenesulfonic acid monohydrate (0.12 g, 0.69 mmol), p-toluenesulfonic acid monohydrate (0.12 g, 0.69 mmol), palladium(II) acetate (0.0030 g, 0.015 mmol), and methyl acrylate (0.11 mL, 1.3 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 2% diethyl ether in hexane gave methyl (E)-3-(4′-nitrophenyl)acrylate (2i) using 2-trifluoromethoxyaniline (1i) (0.040 mL, 0.31 mmol), polymer-supported nitrite (0.27 g, containing 0.93 mmol of NO₂), p-toluenesulfonic acid monohydrate (0.16 g, 0.93 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.14 mL, 1.6 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(3′-fluoromethyl)phenyl)acrylate (2j) (0.059 g, 83%) as a yellow oil. Spectroscopic data were consistent with the literature.¹⁶ H NMR (400 MHz, CDCl₃) δ 3.83 (s, 3H), 6.41 (d, J = 16.0 Hz, 1H), 7.70 (br d, J = 8.0 Hz, 1H), 8.06 (dq, J = 16.0, 2.0 Hz, 1H);¹³C NMR (101 MHz, CDCl₃) δ 51.9 (CH₃), 122.2 (CH), 123.9 (q, J°F = 274.0 Hz, CH), 126.2 (q, J°C = 5.6 Hz, CH), 127.9 (CH), 128.9 (q, J°C = 30.4 Hz, C), 129.6 (CH), 132.1 (q, J°C = 1.0 Hz, CH), 133.4 (q, J°C = 1.3 Hz, C), 140.3 (q, J°C = 1.9 Hz, CH), 166.5 (C); MS (EI) m/z 231 (M + Na⁺, 10).
methoxy-5-methylaniline (1m) (0.050 g, 0.36 mmol), polymer-supported nitrite (0.31 g, containing 1.1 mmol of NO₃), p-toluenesulfonic acid monohydrate (0.19 g, 1.1 mmol), and methyl acrylate (0.16 mL, 1.8 mmol). Purification by neutral alumina flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4a) (0.044 g, 88%) as a pale yellow solid. Mp 146–148 °C (lit. 152–154 °C). H NMR (400 MHz, CDCl₃) δ 8.33 (s, 3H), 6.49 (d, J = 16.0 Hz, 1H), 7.35–7.41 (m, 2H), 7.43–7.50 (m, 2H), 7.67 (s, d, J = 16.0 Hz, 1H). MS (ESI) 𝑚/𝑧 261 (M + Na⁺, 100).

**Methyl (E)-3′-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4b).** The reaction was carried out according to the previously described procedure for methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4a) using methyl (E)-3-[(4′-bromophenyl)acrylate (2e) (0.50 g, 0.21 mmol), 2-methylphenyl boronic acid (0.44 g, 0.21 mmol), [1′,1′-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (0.011 mmol) and cesium fluoride (0.064 g, 0.42 mmol). Purification by silica gel flash column chromatography, eluting with 20% diethyl ether in hexane gave methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4b) (0.044 g, 83%) as a white solid. Mp 55–57 °C; IR (neat) 2974, 1708, 1632, 1313, 1169, 993, 765 cm⁻¹. H NMR (400 MHz, CDCl₃) δ 2.22 (s, 3H), 3.81 (s, 3H), 1.57–2.08 (m, 4H), 5.23 (s, d, J = 16.0 Hz, 1H), 7.45–7.50 (m, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 16.0 Hz, 1H). MS (ESI) 𝑚/𝑧 204 (CH₃), 187 (2H), 185 (2H), 178 (2H), 168 (2H), 154 (2H), 132 (2H), 113 (2H), 66 (2H), 51.7 (CH₃), 117.7 (CH₃), 127.1 (2 × CH), 127.6 (2 × CH), 127.9 (CH), 128.6 (2 × CH), 128.9 (2 × CH), 133.4 (C), 140.2 (C), 143.1 (C), 144.4 (CH), 167.5 (C); MS (ESI) 𝑚/𝑧 261 (M + Na⁺, 100).

**Methyl (E)-3′-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4c).** The reaction was carried out according to the previously described procedure for methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4a) using methyl (E)-3-[(4′-bromophenyl)acrylate (2e) (0.50 g, 0.21 mmol), 2-methylphenyl boronic acid (0.36 g, 0.21 mmol), [1′,1′-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (0.0090 g, 0.011 mmol) and cesium fluoride (0.064 g, 0.42 mmol). Purification by silica gel flash column chromatography, eluting with 20% diethyl ether in hexane gave methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4c) (0.045 g, 75%) as a white solid. Mp 118–121 °C; IR (neat) 2974, 1723, 1316, 1173, 1135, 806 cm⁻¹. H NMR (400 MHz, CDCl₃) δ 3.82 (s, 3H), 3.93 (s, 3H), 6.46 (d, J = 16.0 Hz, 1H), 7.03 (s, J = 8.8 Hz, 1H), 7.30–7.38 (m, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 16.0 Hz, 1H). MS (ESI) 𝑚/𝑧 261 (M + Na⁺, 100).

**Methyl (E)-3′-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4d).** The reaction was carried out according to the previously described procedure for methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4a) using methyl (E)-3-[(4′-bromophenyl)acrylate (2e) (0.50 g, 0.21 mmol), 2-methylphenyl boronic acid (0.36 g, 0.21 mmol), [1′,1′-bis(diphenylphosphino)ferrocene]palladium(II) dichloride (0.0090 g, 0.011 mmol) and cesium fluoride (0.064 g, 0.42 mmol). Purification by silica gel flash column chromatography, eluting with 20% diethyl ether in hexane gave methyl (E)-3-[(1′,1′′-biphenyl)-4′-yl]-acrylate (4d) (0.027 g, 64%) as a yellow oil. IR (neat) 2970, 1715, 1635, 1371, 1271, 1204, 1166, 983, 826 cm⁻¹. H NMR (400 MHz, CDCl₃) δ 3.41 (d, J = 6.8 Hz, 2H), 3.80 (s, 3H), 5.06–5.13 (m, 2H), 5.95 (dd, 1H), 7.00–7.03 (m, 4H), 7.15–7.19 (m, 2H), 7.45–7.54 (m, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H). MS (ESI) 𝑚/𝑧 309 (M + Na⁺, 100).
Methyl (E)-3-(2′-Nitrophenyl)acrylate (6a).6a The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 4,5-dimethyl-2-nitroaniline (5d) (0.050 g, 0.33 mmol), polymer-supported nitrite (0.26 g, containing 0.99 mmol of NO₂), p-toluene sulfonic acid monohydrate (0.17 g, 0.099 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.15 mL, 1.6 mmol). Purification by neutral alumina flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(2′-nitrophenyl)acrylate (6a) (0.070 g, 84%) as a yellow solid. Mp 68° 70°C (lit.73 71° 72°C); 1H NMR (400 MHz, CDCl3) δ 7.10 (d, J = 15.6 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 15.8 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 15.6 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 21.5 (CH3), 52.0 (CH3), 122.6 (CH), 125.1 (CH), 129.7 (CH), 130.8 (CH), 140.8 (CH), 144.9 (C), 146.1 (C), 166.3 (C); MS (ESI) m/z 244 (M + Na+, 100); HRMS (ESI) calc for C11H9NaNO3 (M + Na+) 244.0580, found 244.0577.

Methyl (E)-3-(4′-Methyl-2′-nitrophenyl)acrylate (6b).6b The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 4,5-dimethyl-2-nitroaniline (5e) (0.050 g, 0.33 mmol), polymer-supported nitrite (0.26 g, containing 0.99 mmol of NO₂), p-toluene sulfonic acid monohydrate (0.16 g, 0.90 mmol), palladium(II) acetate (0.0030 g, 0.015 mmol), and methyl acrylate (0.14 mL, 1.5 mmol). Purification by neutral alumina flash column chromatography, eluting with 20% diethyl ether in hexane gave methyl (E)-3-(4′-fluoro-2′-nitrophenyl)acrylate (6b) (0.062 g, 87%) as a pale yellow solid. Mp 87° 89°C (lit.90° 91°C); 1H NMR (400 MHz, CDCl3) δ 296 (s, 3H), 3.90 (s, 3H), 6.30 (d, J = 15.8 Hz, 1H); 1H NMR (101 MHz, CDCl3) δ 3.85 (s, 3H), 6.40 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.62 (m, 1H), 7.70 (m, 1H), 7.85 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 15.8 Hz, 1H), 8.03 (d, J = 15.8 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 13.9 (CH3), 56.1 (CH3), 109.5 (CH), 120.9 (CH), 121.0 (CH), 122.4 (C), 130.0 (CH), 139.5 (C), 140.9 (C), 160.9 (C), 166.5 (C); MS (ESI) m/z 260 (M + Na+, 100).

Methyl (E)-3-(5′-Methoxy-2′-fluoro-2′-nitrophenyl)acrylate (6f).33 The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 4-fluoro-2-nitroaniline (5g) (0.050 g, 0.32 mmol), polymer-supported nitrite (0.27 g, containing 0.99 mmol of NO₂), p-toluene sulfonic acid monohydrate (0.16 g, 0.90 mmol), palladium(II) acetate (0.0030 g, 0.016 mmol), and methyl acrylate (0.14 mL, 1.6 mmol). Purification by neutral alumina flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(5′-methoxy-2′-fluoro-2′-nitrophenyl)acrylate (6f) (0.054 g, 77%) as an orange solid. Scoprosopic data were consistent with the literature.33 Mp 98° 100°C; 1H NMR (400 MHz, CDCl3) δ 3.82 (s, 3H), 3.92 (s, 3H), 6.29 (d, J = 15.8 Hz, 1H), 6.95-7.00 (m, 2H), 8.10-8.15 (m, 1H), 8.20 (d, J = 15.8 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 52.0 (CH3), 56.1 (CH3), 114.2 (CH), 114.9 (CH), 122.7 (CH), 127.7 (CH), 133.8 (C), 141.1 (C), 141.5 (CH), 163.5 (C), 166.3 (C); MS (ESI) m/z 260 (M + Na+, 100).

Methyl (E)-3-(4′-Fluoro-2′-nitrophenyl)acrylate (6g).33 The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 4-fluoro-2-nitroaniline (5g) (0.050 g, 0.32 mmol), polymer-supported nitrite (0.27 g, containing 0.99 mmol of NO₂), p-toluene sulfonic acid monohydrate (0.16 g, 0.90 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.14 mL, 1.6 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(4′-fluoro-2′-nitrophenyl)acrylate (6g) (0.056 g, 78%) as a pale yellow solid. Scoprosopic data were consistent with the literature.33 Mp 87° 89°C; 1H NMR (400 MHz, CDCl3) δ 3.83 (s, 3H), 6.31 (d, J = 16.0 Hz, 1H), 7.36 (s, 1H), 7.84 (s, 1H), 8.11 (d, J = 16.0 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 19.6 (CH3), 19.9 (CH3), 51.9 (CH3), 121.8 (CH2), 125.8 (CH2), 128.1 (C), 129.9 (CH), 139.8 (C), 140.6 (CH), 143.5 (C), 146.0 (C), 166.5 (C); MS (ESI) m/z 258 (M + Na+, 100); HRMS (ESI) calc for C12H9NNaO5 (M + Na+) 258.0737, found 258.0738.

Methyl (E)-3-(5′-Methoxy-2′-chloro-2′-nitrophenyl)acrylate (6h).6h The reaction was carried out according to the previously described procedure for methyl (E)-3-(4′-nitrophenyl)acrylate (2a) using 5-chloro-2-nitroaniline (5h) (0.070 g, 0.40 mmol), polymer-supported nitrite (0.34 g, containing 1.2 mmol of NO₂), p-toluene sulfonic acid monohydrate (0.21 g, 1.2 mmol), palladium(II) acetate (0.0040 g, 0.020 mmol), and methyl acrylate (0.18 mL, 2.0 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3-(5′-chloro-2′-nitrophenyl)acrylate (6h) (0.066 g, 68%) as a yellow solid. Mp 110° 113°C; IR (neat) 2961, 1715, 1516, 1343, 1279, 1250,
Methyl (E)-3′-(4′-Bromo-2′-nitrophenyl)acrylate (6). The reaction was carried out according to the previously described procedure for methyl (E)-3′-(4′-nitrophenyl)acrylate (2a) using 4-bromo-2-nitroaniline (0.050 g, 0.25 mmol), polymer-supported nitrite (0.16 mmol, 0.23 mmol), and methyl acrylate (0.10 mL, 1.2 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 10% diethyl ether in hexane gave methyl (E)-3′-(4′-Bromo-2′-nitrophenyl)acrylate (6) (0.050 g, 76%) as a yellow solid. 

**Experimental Details:**

1. **Preparation of Polymer-Supported Nitrite:**
   - Polymer-supported nitrite was prepared by coupling polymer-supported chloride (0.050 g, 0.25 mmol) with sodium nitrite (0.20 mmol) in a mixture of acetonitrile and water (1:1). The reaction mixture was stirred for 2 h, and then the solvent was evaporated. The residue was washed with water (15 mL) and then dried under vacuum.

2. **Coupling Reaction:**
   - Polymer-supported nitrite (0.050 g, 0.25 mmol) and methyl acrylate (0.10 mL, 1.2 mmol) were dissolved in acetonitrile and stirred for 2 h. The solvent was evaporated, and the residue was purified by flash column chromatography using a gradient of diethyl ether:hexane (0:100 to 10:90). The product was recrystallized from hexane to yield a yellow solid.

3. **Analytical Data:**
   - **1H NMR (400 MHz, CDCl3):** δ 7.85 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H).
   - **13C NMR (101 MHz, CDCl3):** δ 136.8 (C), 148.9 (C), 159.2 (C).
   - **MS (ESI):** m/z 306 (M + Na+, 100).

4. **Final Yield:**
   - The final yield of methyl (E)-3′-(4′-Bromo-2′-nitrophenyl)acrylate (6) was 0.050 g, 76% as a yellow solid. 

5. **Methyl (E)-3′-(4′-Nitrophenyl)-2′-methoxy-3′-(4′-methoxy-3′,1′-biphenyl)-4′-yl)acrylate (6m).** The reaction was carried out according to the previously described procedure for methyl (E)-3′-(4′-nitrophenyl)acrylate (2a) using 4′-methoxy-3′-nitro-1′,1′-biphenyl acrylate (0.040 g, 0.16 mmol), polymer-supported nitrite (0.14 g, containing 0.48 mmol of NO2), p-toluene sulfonic acid monohydrate (0.083 g, 0.48 mmol), and palladium(II) acetate (0.0020 g, 0.0080 mmol), methyl acrylate (0.072 mL, 0.80 mmol). Purification by neutral alumina and then silica gel flash column chromatography, eluting with 35% diethyl ether in hexane gave methyl (E)-3′-(4′-methoxy-3′-nitro-1′,1′-biphenyl)-4′-yl)acrylate (6m) (0.040 g, 16%)

**Note:** The exact conditions and yields for each step are detailed in the original journal article. The above highlights provide a concise overview of the key steps involved in the synthesis of methyl (E)-3′-(4′-Bromo-2′-nitrophenyl)acrylate (6) and methyl (E)-3′-(4′-Nitrophenyl)-2′-methoxy-3′-(4′-methoxy-3′,1′-biphenyl)-4′-yl)acrylate (6m).
The reaction was carried out according to the previously described procedure for 3,4-dihydro-1H-quinolin-2-one (7a) using 4,5-dimethyl-2-nitroaniline (5d) (0.050 g, 0.32 mmol), polymer-supported nitrite (0.27 g, containing 0.96 mmol of NO₂), p-toluenesulfonic acid monohydrate (0.17 g, 0.96 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (1.1 mL, 14.1 mmol). Purification by silica gel flash column chromatography, eluting with 10% ethyl acetate in hexane gave 6,7-dimethyl-3,4-dihydro-1H-quinolin-2-one (7d) (0.041 g, 84%), as an orange solid. Mp 124 °C. The reaction mixture was cooled to room temperature, filtered through a pad of Celite, washed with methanol (20 mL), and concentrated in vacuo. Purification by silica gel flash column chromatography, eluting with 20% ethyl acetate in hexane gave 3,4-dihydro-1H-quinolin-2-one (7b) (0.046 g, 73%) as a white solid. Mp 152–154 °C (lit. 164–166 °C). 1H NMR (400 MHz, CDCl₃) δ 6.65 (dd, J = 7.6, 6.0 Hz, 2H), 2.86 (s, J = 7.6 Hz, 1H), 3.77 (s, J = 2.6 Hz, 3H), 7.52 (d, J = 8.0 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 6.24 (CH₃), 114.8 (CH), 115.2 (CH), 135.0 (C), 159.1 (C), 172.0 (C). HRMS (EI) calcd for C₁₆H₉FN₂O₂ [M⁺] 248.0734, found 248.0739.

7-Methyloxy-3,4-dihydro-1H-quinolin-2-one (7a). The reaction was carried out according to the previously described procedure for 3,4-dihydro-1H-quinolin-2-one (7a) using 4-methoxy-2-nitroaniline (5e) (0.40 g, 2.4 mmol), polymer-supported nitrite (2.0 g, containing 7.1 mmol of NO₂), p-toluenesulfonic acid monohydrate (1.2 g, 7.1 mmol), palladium(II) acetate (0.127 g, 0.12 mmol), and methyl acrylate (1.1 mL, 12 mmol). After the first two steps were complete (2 h), the vessel was transferred to a Parr Shaker Hydrogenation apparatus and hydrogenated at 2.5 bar and rt, for 24 h. Purification by silica gel flash column chromatography, eluting with 50% ethyl acetate in hexane gave 7-methoxy-3,4-dihydro-1H-quinolin-2-one (7e) (0.31 g, 74%) as a white solid. Mp 141–144 °C (lit. 145 °C). 1H NMR (400 MHz, CDCl₃) δ 2.62 (dd, J = 7.6, 6.0 Hz, 2H), 2.86 (s, J = 7.6 Hz, 1H), 3.77 (s, J = 2.6 Hz, 3H), 6.41 (d, J = 2.5 Hz, 1H), 6.52 (d, J = 8.3 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 2.94 (br, Jₕ = 2.2 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 24.6 (CH₃), 31.1 (CH), 55.5 (CH₂), 101.7 (CH), 108.3 (CH), 115.8 (CH), 126.8 (CH), 138.3 (C), 159.3 (C), 172.5 (C); MS (EI) m/z 270 (M + Na⁺, 100).

6-Methoxy-3,4-dihydro-1H-quinolin-2-one (6f). The reaction was carried out according to the previously described procedure for 6-methoxy-3,4-dihydro-1H-quinolin-2-one (6a) using 5-methyl-2-nitroaniline (5c) (0.050 g, 0.33 mmol), polymer-supported nitrite (0.28 g, containing 0.99 mmol of NO₂), p-toluenesulfonic acid monohydroxide (0.17 g, 0.99 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.15 mL, 1.6 mmol). Purification by silica gel flash column chromatography, eluting with 40% ethyl acetate in hexane gave 6,7-dimethyl-3,4-dihydro-1H-quinolin-2-one (6d) (0.043 g, 82%) as an orange solid. Mp 196–198 °C (lit. 200 °C). 1H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 2.90 (dd, J = 8.8, 5.2 Hz, 2H), 7.60 (dd, J = 8.8, 5.2 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 21.7 (CH₂), 21.9 (CH₂), 116.3 (CH), 123.5 (C), 127.9 (C), 128.5 (C), 135.0 (C), 172.0 (C). MS (EI) m/z 261 (M⁺, 100), 132 (62), 106 (23), 91 (20).

6,7-Dimethyl-3,4-dihydro-1H-quinolin-2-one (6d). The reaction was carried out according to the previously described procedure for 3,4-dihydro-1H-quinolin-2-one (7a) using 4-fluoro-2-nitroaniline (5g) (0.050 g, 0.32 mmol), polymer-supported nitrite (0.27 g, containing 0.96 mmol of NO₂), p-toluenesulfonic acid monohydroxide (0.17 g, 0.96 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.15 mL, 1.6 mmol). Purification by silica gel flash column chromatography, eluting with 40% ethyl acetate in hexane gave 6,7-dimethyl-3,4-dihydro-1H-quinolin-2-one (6d) (0.043 g, 82%) as an orange solid. Mp 196–198 °C (lit. 200 °C). 1H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 2.90 (dd, J = 8.8, 5.2 Hz, 2H), 7.60 (dd, J = 8.8, 5.2 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 21.7 (CH₂), 21.9 (CH₂), 116.3 (CH), 123.5 (C), 127.9 (C), 128.5 (C), 135.0 (C), 172.0 (C); MS (EI) m/z 261 (M⁺, 100), 132 (62), 106 (23), 91 (20).

6-Methyl-3,4-dihydro-1H-quinolin-2-one (7c). The reaction was carried out according to the previously described procedure for 3,4-dihydro-1H-quinolin-2-one (7a) using 4-fluoro-2-nitroaniline (5g) (0.050 g, 0.32 mmol), polymer-supported nitrite (0.27 g, containing 0.96 mmol of NO₂), p-toluenesulfonic acid monohydroxide (0.17 g, 0.96 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.15 mL, 1.6 mmol). Purification by silica gel flash column chromatography, eluting with 40% ethyl acetate in hexane gave 6,7-dimethyl-3,4-dihydro-1H-quinolin-2-one (6d) (0.043 g, 82%) as an orange solid. Mp 196–198 °C (lit. 200 °C). 1H NMR (400 MHz, CDCl₃) δ 2.20 (s, 3H), 2.90 (dd, J = 8.8, 5.2 Hz, 2H), 7.60 (dd, J = 8.8, 5.2 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 21.7 (CH₂), 21.9 (CH₂), 116.3 (CH), 123.5 (C), 127.9 (C), 128.5 (C), 135.0 (C), 172.0 (C); MS (EI) m/z 261 (M⁺, 100), 132 (62), 106 (23), 91 (20).

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acrylate (0.14 mL, 1.6 mmol). Purification by silica gel flash column chromatography, eluting with 10% ethyl acetate in hexane gave 7-fluoro-3,4-dihydro-1H-quinoxalin-2-one (7g) (0.037 g, 70%) as a pale yellow solid. Spectroscopic data were consistent with the literature.1 Mp 176–178 °C; 1H NMR (400 MHz, CDCl3) δ 2.64 (d, J = 8.8, 8.0 Hz, 2H), 2.94 (d, J = 8.0, 7.2 Hz, 2H), 6.95 (d, J = 9.2, 2.4 Hz, 1H), 6.68 (t, J = 8.2, 2.4 Hz, 1H), 7.09 (dd, J = 8.2, 6.0 Hz, 1H), 9.23 (br s, 1H); 13C NMR (101 MHz, CDCl3) δ 26.7 (CH), 30.7 (CH), 130.1 (d, J13C−F = 25.7 Hz, CH), 109.5 (d, J13C−F = 21.4 Hz, CH), 119.2 (d, J13C−F = 3.2 Hz, CH), 129.0 (d, J13C−F = 9.3 Hz, CH), 138.6 (d, J13C−F = 16.6 Hz, CH), 162.1 (d, J13C−F = 245.3 Hz, CH), 172.2 (C); MS (EI) m/z 188 (M + Na+, 100).

7-Phenyl-3,4-dihydro-1H-quinoxalin-2-one (7h). The reaction was carried out according to the previously described procedure for 7-methoxy-3,4-dihydro-1H-quinoxalin-2-one (7e) using 4-phenyl-2-nitroaniline (5i) (0.050 g, 0.32 mmol), palladium(II) acetate (0.0040 g, 0.016 mmol), and methyl acrylate (0.14 mL, 1.6 mmol). Purification by silica gel flash column chromatography, eluting with 60% ethyl acetate in hexane gave 7-phenyl-3,4-dihydro-1H-quinoxalin-2-one (7h) (0.030 g, 71%) as a white solid. Mp 178–181 °C; IR (neat) 2976, 1674, 1483, 1391, 820, 760 cm−1; 1H NMR (400 MHz, CDCl3) δ 2.68 (t, J = 7.6 Hz, 2H), 3.01 (t, J = 7.6 Hz, 2H), 7.02 (s, 1H), 7.19–7.25 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 8.86 (br s, 1H); 13C NMR (101 MHz, CDCl3) δ 25.1 (CH), 30.8 (CH), 114.1 (CH), 121.9 (CH), 122.7 (C), 127.1 (2 × CH), 127.5 (CH), 128.3 (CH), 128.8 (2 × CH), 137.8 (C), 140.4 (C), 141.0 (C), 172.0 (C); MS (EI) m/z 223 (M+100), 195 (38), 168 (14), 152 (10), 83 (51), 75 (30); HRMS (EI) calc for C19H17N2O3 (M+) 223.0997, found 223.0989.

7′-(4-Methoxyphenyl)-3,4-dihydro-1H-quinoxalin-2-one (7i). The reaction was carried out according to the previously described procedure for 7-methoxy-3,4-dihydro-1H-quinoxalin-2-one (7e) using 4′-(4-methoxyphenyl)-2-nitroaniline (5m) (0.040 g, 0.16 mmol), polymer-supported nitrite (0.14 g, containing 0.48 mmol of NO2), p-toluene sulfonic acid monohydrate (0.17 g, 0.96 mmol), palladium(II) acetate (0.040 g, 0.16 mmol), and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) ([BMIM]Nt3) (0.3 μL, 0.011 mmol) were stirred for 0.5 h at room temperature. This was added to a solution of tert-buty1 2-(‘-methoxy-3′-dihydro-1H-quinoxalin-2-one-1′-yl)acetate (8) (0.045 g, 0.15 mmol) and N-bromosuccinimide (0.027 g, 0.15 mmol) in toluene (0.5 mL). The reaction mixture was stirred at 40 °C for 24 h, cooled to room temperature, and concentrated in vacuo. Purification by silica gel flash chromatography, eluting with 30% ethyl acetate in hexane gave tert-buty1 2-(‘-bromo-3′-dihydro-1H-quinoxalin-2-one-1′-yl)acetate (9) (0.045 g, 81%) as a pale yellow solid. Mp 70–72 °C; IR (neat) 2977, 1740, 1678, 1605, 1413, 1354, 1152, 748 cm−1; 1H NMR (400 MHz, CDCl3) δ 1.44 (s, 9H), 2.66 (d, J = 9.2, 8.0 Hz, 2H), 2.85 (d, J = 9.2, 8.0 Hz, 2H), 3.76 (s, 3H), 4.53 (s, 2H), 6.31 (d, J = 2.4 Hz, 1H), 6.52 (d, J = 8.4, 2.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 24.6 (CH3), 28.0 (3 × CH3), 31.8 (CH3), 45.0 (CH3), 55.4 (CH3), 82.1 (C), 102.0 (CH), 107.0 (CH), 118.4 (C), 128.5 (CH), 140.7 (C), 159.2 (C), 167.7 (C), 170.6 (C); MS (EI) m/z 291 (M+100), 235 (80), 218 (45), 190 (12), 189 (100), 145 (47), 121 (18), 109 (58); HRMS (EI) calc for C25H29BrNO3 (M+) 291.1484, found 291.1493.
8.8 Hz, 2H); 1^3^C NMR (101 MHz, CDCl_3) δ 24.5 (CH_3), 28.0 (3 × CH_2), 31.8 (CH_3), 45.0 (CH_2), 55.8 (CH_3), 82.3 (C), 99.0 (CH, 118.4 (C), 123.9 (C), 128.3 (2 × CH), 129.9 (CH), 130.7 (2 × CH), 132.8 (C), 136.1 (C), 140.1 (C), 155.7 (C), 167.8 (C), 170.4 (C); MS (EI) m/z 401 (M^+), 375, 345 (100), 272 (34), 258 (11), 84 (12), 57 (18). HRMS (EI) calcd for C_{12}H_{12}ClINO_3: M^+ 401.1394, found 401.1378.

2-(4′-(4″-Chlorophenyl)-7′-methoxy-3′,4′-dihydro-1H-quinolin-2′-one-1′-yl)acetic Acid (11). Trifluoroacetic acid (0.050 mL, 0.65 mmol) was added dropwise to a solution of tert-

2H), 2.93

220 (33), 248 (18), 165 (10), 109 (17), 97 (22), 69 (23), 55 (49).

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