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A modular synthesis of functionalised phenols enabled by controlled boron speciation†

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A modular synthesis of functionalised biaryl phenols from two boronic acid derivatives has been developed *via* one-pot Suzuki–Miyaura cross-coupling, chemoselective control of boron solution speciation to generate a reactive boronic ester *in situ*, and oxidation. The utility of this method has been further demonstrated by application in the synthesis of drug molecules and components of organic electronics, as well as within iterative cross-coupling.

Introduction

The biaryl phenol moiety is a privileged structure that has found wide-ranging applications within the pharmaceutical, agrochemical, and material industries (Fig. 1a).[1] For example, the basic biaryl phenol skeleton represents the principle architecture of (i) the breast cancer treatment raloxifene[2] and the non-steroidal anti-inflammatory drug (NSAID) diflunisal,[3] (ii) the fungicide bitertanol,[4] and (iii) components of the E7 liquid crystal blend.[5] Biaryl phenols are also of continued interest within academic research, particularly in total synthesis where many structurally unique natural products, such as (+)-Cavicularin[6] and Biphenomycin A,[7] feature this motif.

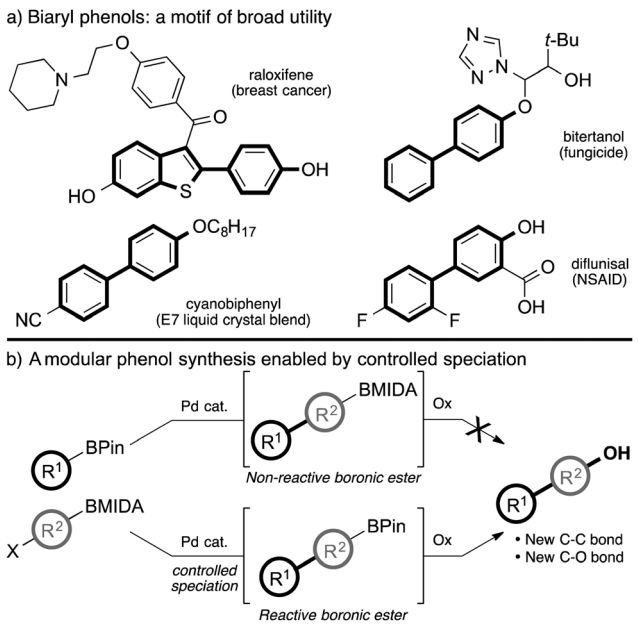

Fig. 1 (a) Importance of biaryl phenols. (b) A modular biaryl phenol synthesis enabled by chemoselective boron speciation.

Of the methods available for the synthesis of biaryl phenols, Suzuki–Miyaura cross-coupling[8] of, for example, halophenols with boronic acid derivatives is perhaps the most direct method. However, many of these processes can be problematic, with diminished yields due to issues with boronate formation from the free phenol.[9] Use of a protected phenol or suitable latent hydroxyl may therefore be preferable in these cases.

We considered a novel approach towards the synthesis of biaryl phenols using two boron species in which a reactive boronic ester takes part in a Suzuki–Miyaura cross-coupling to establish the required C–C bond and a protected boronic ester acts as a latent hydroxyl unit (Fig. 1b).[10] We have previously demonstrated the formal homologation of aryl boronic acid pinacol esters (BPin) using boronic acid *N*-methyliminodiacetic acid (BMIDA) esters[11] *via* chemoselective control of boron solution speciation.[12] This method provides a one step synthesis of a new reactive BPin ester primed for further reaction, such as further Suzuki–Miyaura cross-coupling, while avoiding ancillary deprotection and isolation steps. Herein we show how this controlled speciation process can be smoothly coupled to an oxidative event providing a one-pot, step-efficient, modular synthesis of functionalised biaryl phenols.

Results and discussion

To probe the appropriateness of controlled speciation in this context, we established the reactivity of aryl BPin and BMIDA

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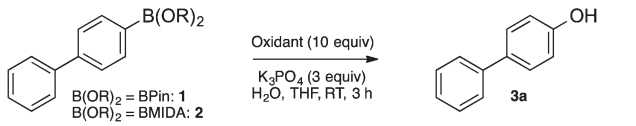
Table 1 Selection and optimisation of oxidant

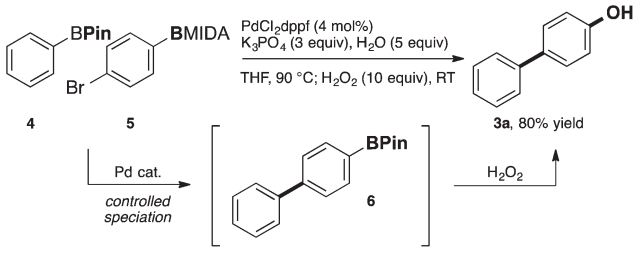


Entry	Boronic ester	Oxidant	**3a**[a] (%)
1	1	30% aq. H_2O_2	98
2	2	30% aq. H_2O_2	10
3	1	UHP[b]	87
4	2	UHP[b]	2
5	1	Sat. aq. Oxone®	9
6	2	Sat. aq. Oxone®	—
7	1	NaOCl	—
8	2	NaOCl	—
9	1	$NaBO_3{\cdot}4H_2O$	18
10	2	$NaBO_3{\cdot}4H_2O$	1

[a] Determined by HPLC analysis using an internal standard.[15] [b] UHP = urea-hydrogen peroxide.

esters towards oxidation using oxidants known to be effective for similar transformations (Table 1). BPin esters are very labile towards oxidation[10] while BMIDA esters have previously been shown to withstand common neutral or acidic oxidative conditions such as Swern, TPAP/NMO, and DMP oxidations as well as the comparatively harsh Jones oxidation.[13] However, tolerance of oxidation in basic media was anticipated to be low as BMIDA esters are readily hydrolysed to liberate the readily oxidisable parent boronic acid.[14] As expected, biphenyl BPin **1**, with available p orbital, was efficiently oxidized with peroxide (entries 1 and 3), however, little oxidation was observed with Oxone®, NaOCl, or $NaBO_3$ (entries 5, 7, and 9). BMIDA **2** was surprisingly inert, even under basic reaction conditions and with the more nucleophilic peroxide oxidants, due to the occupied p orbital (entries 2, 4, 6, 8, and 10). A small quantity of oxidation is observed if there is sufficient hydrolysis of the BMIDA to the parent oxidatively labile boronic acid (*e.g.*, entry 2). These results further demonstrate the remarkable resilience of BMIDA esters towards oxidation as well as confirm the requirement for use of a more reactive boronic ester in the designed process.

With chemoselective boronic ester oxidation demonstrated, we sought to generate a one-pot protocol for the synthesis of biaryl phenols (Scheme 1). PhBPin (**4**) was reacted with



Scheme 1 Modular biaryl phenol synthesis enabled by chemoselective boron speciation.

haloaryl BMIDA **5** under conditions that promote chemoselective generation of a reactive BPin intermediate (**6**). Subsequent one-pot treatment with H_2O_2 generated the desired phenolic product **3a** in 80% isolated yield.

Having identified effective conditions for the modular phenol synthesis, we sought to ascertain the generality of our protocol through application to a diverse range of BPin and BMIDA components (Fig. 2). A library of functionalised phenolic products was rapidly prepared from commercial building blocks and with typically high levels of synthetic efficiency, especially for BMIDA units with electron-withdrawing functionality. For those reactions in which the cross-coupling was found to be slow, use of a more active catalyst system

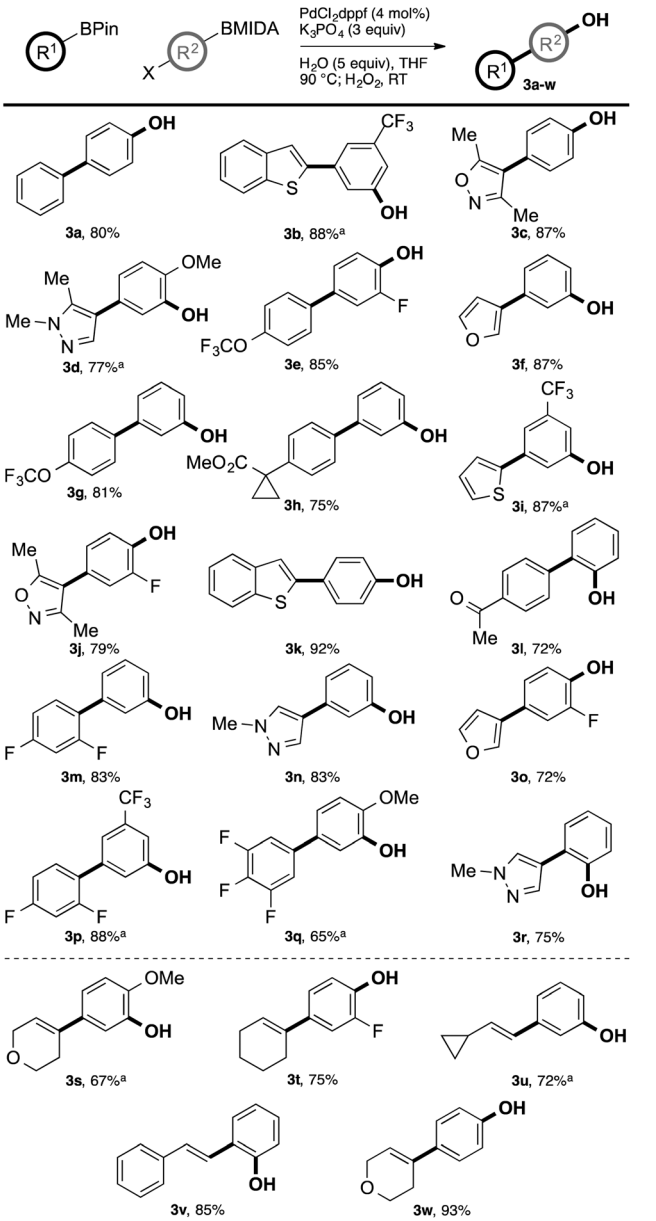


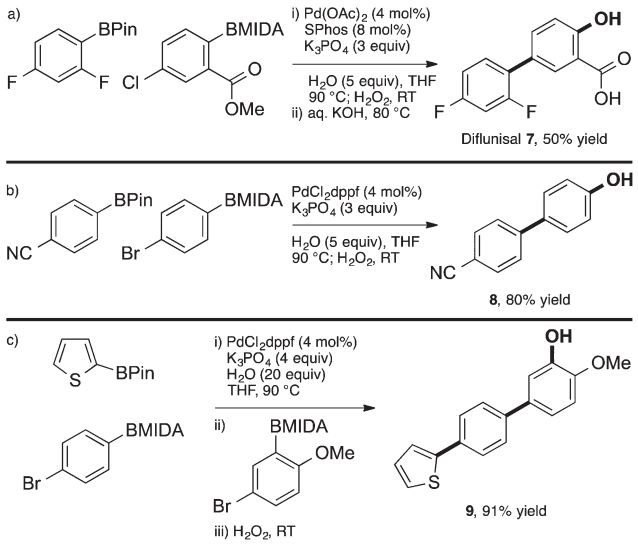
Fig. 2 Scope of the modular phenol synthesis. Yields are isolated yields of pure products. [a]Using $Pd(OAc)_2$ (4 mol%) and SPhos (8 mol%) as the catalyst.

($Pd(OAc)_2$/SPhos) was beneficial. In addition to the formation of biaryl phenols (**3a–r**), the synthesis of styrenyl phenols was similarly effective (**3s–w**).

In addition to the chemoselectivity control with regards to boron, this procedure also exhibits remarkable chemoselectivity for common functionality.[16] The mildly basic reaction conditions preclude oxidations that proceed *via* an electrophilic H_2O_2 mechanism. Consequently, the *in situ* generated biaryl BPin intermediate is chemoselectively oxidised in the presence of oxidatively labile functionality including olefinic moieties such as styrenes (**3s–u**, **w**) and stilbenes (**3v**), electron-rich heterocycles such as furans (**3f**, **3o**), and heteroatoms such as sp^2-nitrogen (**3c**, **3d**, **3j**, **3n**, **3r**) and sulfur (**3b**, **3i**, **3k**). This latter aspect enables preparation of the biaryl phenolic core of raloxifene (**3k**).[2] In addition, the reaction tolerates functional groups that are potentially labile *via* a nucleophilic H_2O_2 mechanism, such as esters and ketones (**3h**, **3l**).

To further demonstrate the synthetic utility of our method, we have applied this protocol towards the preparation of commercialised products and within iterative synthesis (Scheme 2).

Diflunisal[3,17] **7** was prepared in 50% overall yield over two steps (Scheme 2a). The yield-limiting issue of this process was found to be the *in situ* generation of a protodeboronation-prone boronic acid intermediate.[18] Additionally, **8**, a component of the E7 liquid crystal blend,[5] was isolated in 80% yield with no reaction observed at the oxidatively labile nitrile functionality (Scheme 2b). Furthermore, high levels of chemoselective control can be achieved in a one-pot iterative cross-coupling[11,19] with three different boron species (Scheme 2c). Synthesis of the triaryl phenol **9** involves the formation of two C–C bonds, recycling of pinacol over multiple boron species, and chemoselective oxidation to provide the desired triaryl phenol product in 91% isolated yield.



Scheme 2 (a) Synthesis of diflunisal **7**. (b) Synthesis of E7 cyanobiphenyl **8**. (c) Synthesis of triaryl phenol 9 *via* one-pot iterative cross-coupling and oxidation.

Conclusions

In summary, chemoselective control of boron solution speciation provides expedient access to oxidatively labile pinacol boronic esters, which enables a modular, iterative synthesis of phenolic frameworks. The reaction is tolerant of a diverse range of useful functionality: pH control renders electrophilic oxidations inactive while the mild reaction conditions prevent nucleophilic oxidation of any functionality other than BPin. This approach is highly applicable as shown through the preparation of commercialised drug molecules and materials as well as within iterative cross-coupling processes. This study further demonstrates the utility of speciation control as a method for chemoselective bond formation.

Experimental section

Materials and methods

Purification of starting materials. All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Purification was carried out according to standard laboratory methods.[20] Dry THF was obtained from a PureSolv SPS-400-5 solvent purification system. This solvent was transferred to and stored in a septum-sealed oven-dried flask over previously activated 4 Å molecular sieves and purged with and stored under N_2. CH_2Cl_2, Et_2O, EtOAc, MeCN, and petroleum ether 40–60° for purification purposes were used as obtained from suppliers without further purification. K_3PO_4 was dried in a Heraeus Vacutherm oven at 60 °C under vacuum for a minimum of 24 hours before use.

Experimental details. Reactions were carried out using conventional glassware (preparation of intermediates) or in capped 5 mL microwave vials (optimisation reactions and reactions for Table 1, Scheme 1, Fig. 2, and Scheme 2). The glassware was oven-dried (150 °C) and purged with N_2 before use. Purging refers to a vacuum/nitrogen-refilling procedure. Room temperature was generally 18 °C. Reactions were carried out at elevated temperatures using a temperature-regulated hotplate/stirrer.

Purification of products. Thin layer chromatography was carried out using Merck silica plates coated with fluorescent indicator UV254. These were analysed under 254 nm UV light or developed using potassium permanganate solution. Normal phase flash chromatography was carried out using ZEOprep 60 HYD 40–63 μm silica gel. Reverse phase flash chromatography was carried out using IST Isolute C18 cartridges.

Analysis. Fourier Transformed Infra-Red (FTIR) spectra were obtained on a Shimadzu IRAffinity-1 machine. ^{19}F NMR spectra were obtained on a Bruker AV 400 spectrometer at 376 MHz. ^{11}B NMR spectra were obtained on a Bruker AV 400 spectrometer at 128 MHz. ^{1}H and ^{13}C, NMR spectra were obtained on either a Bruker AV 400 at 400 MHz and 101 MHz, respectively, or Bruker DRX 500 at 500 MHz and 126 MHz, respectively. Chemical shifts are reported in ppm and coupling

constants are reported in Hz: $CDCl_3$ is referenced at 7.26 (^{1}H) and 77.0 (^{13}C), DMSO-d6 referenced at 2.50 (^{1}H) and 39.5 (^{13}C), and CD_3CN referenced at 1.94 (^{1}H) and 118.3, 1.3 (^{13}C). High-resolution mass spectra were obtained through analysis at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Reversed phase HPLC data was obtained on an Agilent 1200 series HPLC using a Machery-Nagel Nucleodur C18 column, which was maintained at a constant temperature of 40 °C. Analysis was performed using a gradient method, eluting with 5–80% MeCN–H_2O over 16 minutes at a flow rate of 2 mL min^{-1}. Samples for HPLC analysis were prepared through the addition of 2 mL of caffeine standard to the completed reaction mixture, the resulting solution was then stirred before the removal of a 200 μL aliquot. The aliquot was diluted to 1 mL with MeCN, a 200 μL aliquot of the diluted solution was then filtered through cotton wool and further diluted with 800 μL MeCN and 500 μL H_2O for HPLC analysis against established conversion factors.

Synthetic procedures

General procedure A. For example, synthesis of compound 3a. To an oven-dried 5 mL microwave vial was added 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (69.3 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), and K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.). The vial was then capped and purged with N_2 before addition of THF (0.9 mL, 0.25 M) and H_2O (20 μL, 1.13 mmol, 5 equiv.). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 °C, and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 °C and quenched with sodium metabisulphite (176 mg, 0.904 mmol, 4 equiv.) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2 × 10 mL) and brine (10 mL). The aqueous washings were re-extracted with EtOAc (10 mL), the combined organics were filtered through a hydrophobic frit packed with Celite®, and concentrated under vacuum before being purified by column chromatography (C18 silica gel, 0–60% H_2O in MeCN) to afford the title compound as a white solid (31 mg, 80%).

General procedure B. For example, synthesis of compound 3b. To an oven dried 5 mL microwave vial was added 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (86 mg, 0.226 mmol, 1 equiv.), (benzo[*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2 mg, 0.009 mmol, 4 mol%), SPhos (7.4 mg, 0.018 mmol, 8 mol%), and K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.). The vial was then capped and purged with N_2 before addition of THF (0.9 mL, 0.25 M) and H_2O (20 μL, 1.13 mmol, 5 equiv.). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 °C, and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 °C and quenched with sodium metabisulphite (176 mg, 0.904 mmol, 4 equiv.) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2 × 10 mL) and brine (10 mL). The aqueous washings were re-extracted with EtOAc (10 mL), the combined organics filtered through a hydrophobic frit packed with Celite®, and concentrated under vacuum before being purified by column chromatography (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as an orange solid (58 mg, 88%).

Characterisation data

3a: [1,1′-Biphenyl]-4-ol. Prepared according to General procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (69.3 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.) and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (C18 silica gel, 0–60% H_2O in MeCN) to afford the title compound as a white solid (31 mg, 80%). ν_{max} (solid): 3399, 3098, 3062, 1597, 1485 cm^{-1}. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.56–7.59 (m, 2H), 7.48–7.51 (m, 2H), 7.42 (t, J = 8.2 Hz, 2H), 7.30 (tt, J = 8.0, 2.0 Hz, 1H), 6.99 (s, 1H), 6.89 (d, J = 8.3 Hz, 2H). ^{13}C NMR (DMSO-d6, 126 MHz): δ 157.1, 140.2, 130.9, 128.7, 127.7, 126.3, 125.9, 115.8. HRMS: exact mass calculated for $[M - H]^-$ ($C_{12}H_9O$) requires m/z 169.0659, found m/z 169.0658.

3b: 3-(Benzo[*b*]thiophen-2-yl)-5-(trifluoromethyl)phenol. Prepared according to General procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (86 mg, 0.226 mmol, 1 equiv.), (benzo[*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2 mg, 0.01 mmol, 4 mol%), SPhos (7.4 mg, 0.02 mmol, 8 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.) and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as an orange solid (58 mg, 88%). ν_{max} (solid): 3305, 3067, 3052, 2923, 1610, 1450, 1439, 1351, 1327 cm^{-1}. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.93 (d, J = 7.5 Hz, 1H), 7.86 (dd, J = 6.9, 1.6 Hz, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.37–7.46 (m, 3H), 7.10 (s, 1H). ^{13}C NMR (CD_3CN, 126 MHz): δ 157.9, 141.9, 140.5, 139.4, 136.6, 132.2 (d, $^2J_{C-F}$ = 32.4 Hz), 132.1 (d, $^2J_{C-F}$ = 32.4 Hz), 125.2, 125.0, 124.0, 123.9 (d, $^1J_{C-F}$ = 271.8 Hz) 122.3, 121.4, 116.6, 114.3 (d, $^3J_{C-F}$ = 3.2 Hz) 111.9 (d, $^3J_{C-F}$ = 3.2 Hz). ^{19}F NMR (CD_3CN, 376 MHz): δ −64.2 (s, 3F). HRMS: exact mass calculated for $[M - H]^-$ ($C_{15}H_8F_3OS$) requires m/z 293.0253, found m/z 293.0245.

3c: 4-(3,5-Dimethylisoxazol-4-yl)phenol. Prepared according to General procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoxazole (75.6 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as a white solid (37 mg, 87%). ν_{max} (solid): 3194, 3025, 2926, 1612, 1591, 1424 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz): δ 7.18 (d, J = 8.8 Hz, 2H), 7.05 (br. s., 1H), 6.90 (d, J = 8.8 Hz, 2H), 2.35 (s, 3H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 165.0, 158.9, 155.6, 130.4, 122.3, 116.4, 115.8, 11.5, 10.7. HRMS: exact mass calculated for $[M + H]^+$ ($C_{11}H_{12}NO_2$) requires m/z 190.0863, found m/z 190.0861.

3d: 5-(1,5-Dimethyl-1*H*-pyrazol-4-yl)-2-methoxyphenol. Prepared according to General procedure B using 5-bromo-2-methoxyphenylboronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv.), 1,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (83 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 20–70% EtOAc in petroleum ether) to afford the desired product as a white solid (42 mg, 77%). ν_{max} (film): 3341, 3204, 2920, 2851, 1464, 1034 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53 (s, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.85 (dd, J = 8.2, 2.0 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.3, 144.9, 136.4, 134.5, 126.8, 120.1, 118.9, 113.8, 110.6, 55.6, 35.9, 9.8. HRMS: exact mass calculated for $[M + H]^+$ ($C_{12}H_{15}N_2O_2$) requires m/z 219.1128, found m/z 219.1126.

3e: 3-Fluoro-4′-(trifluoromethoxy)-[1,1′-biphenyl]-4-ol. Prepared according to General procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (86 mg, 0.375 mmol, 1.5 equiv.), Pd(dppf)-Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–10% EtOAc in petroleum ether) to afford the title compound as a white solid (58 mg, 85%). ν_{max} (film): 3395, 1503, 1256, 1200, 1159, 1117 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.58 (m, 2H), 7.23–7.35 (m, 4H), 7.10 (t, J = 8.5 Hz, 1H), 5.23 (br. s., 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.2 (d, $^1J_{C-F}$ = 237.0 Hz), 148.6, 143.3 (d, $^2J_{C-F}$ = 14.6 Hz), 138.5, 133.1 (d, $^3J_{C-F}$ = 5.9 Hz), 128.0, 123.4 (d, $^3J_{C-F}$ = 5.9 Hz), 121.3, 120.5 (q, $^1J_{C-F}$ = 257.5 Hz), 117.7, 114.2 (d, $^2J_{C-F}$ = 20.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −57.8 (s, 3F), −140.4 (s, 1F). HRMS: exact mass calculated for $[M]^+$ ($C_{13}H_8F_4O_2$) requires m/z 272.0455, found m/z 272.0459.

3f: 3-(Furan-3-yl)phenol. Prepared according to General procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65.8 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as a white solid (32 mg, 87%). ν_{max} (solid): 3477, 3401, 3150, 3127, 1591, 1513, 1457 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (s, 1H), 7.47–7.50 (m, 1H), 7.26 (t, J = 7.9 Hz, 1H), 7.09 (td, J = 7.8, 1.1 Hz, 1H), 6.97–6.99 (m, 1H), 6.72–6.79 (m, 1H), 6.65–6.71 (m, 1H), 4.88 (br. s., 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.9, 143.7, 138.7, 134.1, 130.1, 126.1, 118.6, 113.9, 112.8, 108.9. HRMS: exact mass calculated for $[M - H]^-$ ($C_{10}H_7O_2$) requires m/z 159.0452, found m/z 159.0448.

3g: 4′-(Trifluoromethoxy)-[1,1′-biphenyl]-3-ol. Prepared according to General procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (97.7 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (C18 silica gel, 0–60% H_2O in MeCN) to afford the title compound as a pale yellow solid (47 mg, 81%). ν_{max} (solid): 3304, 3047, 2928, 1597, 1485, 1457 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz): δ 7.72–7.68 (m, 2H), 7.37 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 7.9 Hz, 1H), 7.15–7.12 (m, 1H), 7.09–7.07 (m, 2H), 6.89–6.83 (m, 1H). ^{13}C NMR (CD_3CN, 126 MHz): δ 157.4, 148.5, 141.0, 140.0, 130.2, 128.6, 121.3, 120.6 (d, $^1J_{C-F}$ = 255.3 Hz), 118.6, 114.7, 113.8, 29.4. ^{19}F NMR (CD_3CN, 376 MHz): δ −57.8 (s, 3F). HRMS: exact mass calculated for $[M - H]^-$ ($C_{13}H_8F_3O$) requires m/z 253.0482, found m/z 253.0482.

3h: Methyl 1-(3′-hydroxy-[1,1′-biphenyl]-4-yl)cyclopropane-1-carboxylate. Prepared according to General procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1-carboxylate (102.4 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as a white solid (45 mg, 75%). ν_{max} (solid): 3440, 3040, 2954, 2926, 2852, 1698, 1590 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.27–7.32 (m, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.01–7.07 (m, 1H), 6.80 (dd, J = 8.0, 2.5 Hz, 1H), 3.66 (s, 3H), 1.63–1.66 (m, 2H), 1.22–1.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.2, 155.9,

142.6, 139.6, 138.8, 130.9, 129.9, 126.9, 119.7, 114.2, 114.0, 52.5, 28.7, 16.8. HRMS: exact mass calculated for $[M - H]^-$ ($C_{17}H_{15}O_3$) requires *m*/*z* 267.1027, found *m*/*z* 267.1019.

3i: 3-(Thiophen-2-yl)-5-(trifluoromethyl)phenol. Prepared according to General procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (95 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–15% Et_2O in petroleum ether) to afford the title compound as a brown solid (53 mg, 87%). ν_{max} (film): 3318, 1599, 1115, 1099 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44–7.47 (m, 1H), 7.35–7.39 (m, 2H), 7.26 (t, J = 2.0 Hz, 1H), 7.13 (dd, J = 5.0, 3.5 Hz, 1H), 7.00–7.03 (m, 1H), 5.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 156.2, 142.3, 136.9, 132.7 (q, $^2J_{C-F}$ = 33.1 Hz), 128.2, 126.0, 124.4, 123.7 (q, $^1J_{C-F}$ = 272.1 Hz), 116.0, 115.3, 111.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.9 (s, 3F). HRMS: exact mass calculated for $[M - H]^-$ ($C_{11}H_6F_3OS$) requires *m*/*z* 243.0097, found *m*/*z* 243.0097.

3j: 4-(3,5-Dimethylisoxazol-4-yl)-2-fluorophenol. Prepared according to General procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-4-(3,5-dimethylisoxazol-4-yl)-1,3,2-dioxaborolane (84 mg, 0.375 mmol, 1.5 equiv.), $Pd(dppf)Cl_2$·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 10–20% Et_2O in petroleum ether) to afford the title compound as a white solid (41 mg, 79%). ν_{max} (film): 3075, 1460, 1410, 1308, 1244, 1213, 1121 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.13–7.08 (m, 1H), 7.00 (dd, J = 11.5, 2.0 Hz, 1H), 6.94 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 5.98 (br. s., 1H), 2.42 (s, 3H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.8, 158.2, 150.6 (d, $^1J_{C-F}$ = 237.0 Hz), 142.8 (d, $^2J_{C-F}$ = 16.2 Hz), 125.2 (d, J_{C-F} = 2.7 Hz), 122.4 (d, $^3J_{C-F}$ = 8.1 Hz), 117.3 (d, $^3J_{C-F}$ = 5.4 Hz), 115.9 (d, $^2J_{C-F}$ = 18.8 Hz), 115.2, 11.0, 10.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −139.3 (s, 1F). HRMS: exact mass calculated for $[M + H]^+$ ($C_{11}H_{11}FNO_2$) requires *m*/*z* 208.0768, found *m*/*z* 208.0768.

3k: 4-(Benzo[*b*]thiophen-2-yl)phenol. Prepared according to General procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 2-(benzo[*b*]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv.), $Pd(dppf)Cl_2$·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as an off-white solid (47 mg, 92%). ν_{max} (solid): 3388, 3052, 3042, 2923, 1610, 1597, 1507 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz): δ 9.78 (s, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.63 (s, 1H), 7.57–7.61 (m, 2H), 7.35 (dt, J = 7.5, 1.3 Hz, 1H), 7.27–7.31 (m, 1H), 6.86 (d, J = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 126 MHz): δ 158.5, 144.3, 141.2, 138.5, 128.0, 125.1, 125.0, 124.5, 123.7, 122.7, 118.3, 116.4. HRMS: exact mass calculated for $[M - H]^-$ ($C_{14}H_9OS$) requires *m*/*z* 225.0380, found *m*/*z* 225.0385.

3l: 1-(2′-Hydroxy-[1,1′-biphenyl]-4-yl)ethanone. Prepared according to General procedure A using 2-bromophenylboronic acid MIDA ester (92 mg, 0.25 mmol, 1 equiv.), 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (92 mg, 0.375 mmol, 1.5 equiv.), $Pd(dppf)Cl_2$·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 5–20% EtOAc in petroleum ether) to afford the title compound as a white solid (38 mg, 72%). ν_{max} (film): 3285, 1667, 1479, 1277, 1190, 1179, 1155 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.11–8.05 (m, 2H), 7.63–7.68 (m, 2H), 7.29–7.34 (m, 2H), 7.08–6.98 (m, 2H), 2.67 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 197.4, 152.0, 142.1, 135.6, 129.9, 129.3, 128.9, 128.5, 126.7, 120.7, 115.8, 26.2. HRMS: exact mass calculated for $[M + H]^+$ ($C_{14}H_{13}O_2$) requires *m*/*z* 213.0910, found *m*/*z* 213.0909.

3m: 2′,4′-Difluoro-[1,1′-biphenyl]-3-ol. Prepared according to General procedure A using 3-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv.), 2-(2,4-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (90 mg, 0.375 mmol, 1.5 equiv.), $Pd(dppf)Cl_2$·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–10% Et_2O in petroleum ether) to afford the title compound as a white solid (43 mg, 83%). ν_{max} (film) 3260, 1597, 1479, 1306, 1265, 1229, 1192, 1140, 1099 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.41 (td, J = 8.8, 6.5 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.10 (dq, J = 7.6, 1.5 Hz, 1H), 7.00–7.04 (m, 1H), 6.86–7.00 (m, 3H), 5.06 (s, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.5 (dd, $^1J_{C-F}$ = 250.4 Hz, $^3J_{C-F}$ = 5.4), 159.2 (dd, $^1J_{C-F}$ = 250.4 Hz, $^3J_{C-F}$ = 5.4), 155.0, 136.1, 130.9 (dd, $^3J_{C-F}$ = 6.7, 5.4 Hz), 129.3, 124.4 (dd, $^2J_{C-F}$ = 18.9 Hz, J_{C-F} = 5.4 Hz), 121.0, 115.5, 114.3, 111.0 (dd, $^2J_{C-F}$ = 21.5 Hz, J_{C-F} = 2.7 Hz), 103.9 (dd, $^2J_{C-F}$ = 24.2, 26.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −111.3 (d, J = 7.5 Hz, 1F), −113.2 (d, J = 7.5 Hz, 1F). HRMS: exact mass calculated for $[M + H]^+$ ($C_{12}H_9F_2O$) requires *m*/*z* 207.0616, found *m*/*z* 207.0619.

3n: 3-(1-Methyl-1*H*-pyrazol-4-yl)phenol. Prepared according to General procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (71.2 mg, 0.339 mmol, 1.5 equiv.), $Pd(dppf)Cl_2$·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h,

the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 20–80% Et_2O in petroleum ether) to afford the title compound as a yellow solid (33 mg, 83%). ν_{max} (solid): 3107, 2926, 2855, 1616, 1569, 1588, 1374 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz): δ 7.79 (s, 1H), 7.72 (s, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.03 (td, J = 7.6, 1.4 Hz, 1H), 6.98–6.96 (m, 1H), 6.94 (br. s., 1H), 6.74–6.61 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (DMSO-d_6, 126 MHz): δ 157.7, 135.9, 133.8, 129.7, 127.6, 122.0, 115.9, 113.0, 111.8, 38.6. HRMS: exact mass calculated for $[M + H]^+$ ($C_{10}H_{11}N_2O$) requires m/z 175.0866, found m/z 175.0864.

3o: 2-Fluoro-4-(furan-3-yl)phenol. Prepared according to General procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (83 mg, 0.25 mmol, 1 equiv.), 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 mg, 0.375 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–10% EtOAc in petroleum ether) to afford the title compound as off-white solid (32 mg, 72%). ν_{max} (film): 3362, 1520, 1497, 1279, 1250, 1231, 1155, 1117, 1086, 1049, 1016 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.67 (dd, J = 1.4, 1.0 Hz, 1H), 7.48 (t, J = 1.7 Hz, 1H), 7.22 (dd, J = 11.5, 2.0 Hz, 1H), 7.18 (ddd, J = 8.4, 2.1, 1.0 Hz, 1H), 7.07–6.99 (m, 1H), 6.64 (dd, J = 1.8, 0.9 Hz, 1H), 5.14 (br. s., 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.7 (d, $^1J_{C–F}$ = 237.0 Hz), 143.3, 141.9 (d, $^2J_{C–F}$ = 13.5 Hz), 137.6, 125.4 (d, $^2J_{C–F}$ = 8.1 Hz), 124.9 (d, $J_{C–F}$ = 2.7 Hz), 121.8 (d, $^3J_{C–F}$ = 5.4 Hz), 117.1, 112.6 (d, $^3J_{C–F}$ = 18.8 Hz), 108.3. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −140.7 (s, 1F). HRMS: exact mass calculated for $[M + H]^+$ ($C_{10}H_8FO_2$) requires m/z 179.0503, found m/z 179.0502.

3p: 3-(2,4-Difluorophenyl)-5-(trifluoromethyl)phenol. Prepared according to General procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (95 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(2,4-difluorophenyl)-1,3,2-dioxaborolane (90 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–20% Et_2O in petroleum ether) to afford the title compound as a brown solid (60 mg, 88%). ν_{max} (film): 3331, 1607, 1364, 1271, 1121, 1103 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43 (td, J = 8.7, 6.3 Hz, 1H), 7.34 (s, 1H), 7.19 (d, J = 1.5 Hz, 1H), 7.14–7.11 (m, 1H), 7.03–6.92 (m, 2H), 5.30 (br. s, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.8 (dd, $^1J_{C–F}$ = 250.0 Hz, $^3J_{C–F}$ = 11.0 Hz), 159.7 (dd, $^1J_{C–F}$ = 250.0 Hz, $^3J_{C–F}$ = 11.0 Hz), 155.8, 137.4, 132.4 (q, $^2J_{C–F}$ = 33.1 Hz), 131.4 (dd, $^3J_{C–F}$ = 7.5, 7.5 Hz), 123.6 (dd, $^2J_{C–F}$ = 13.5 Hz, $J_{C–F}$ = 5.4 Hz), 123.7 (q, $^1J_{C–F}$ = 272.1 Hz), 119.3, 118.2, 111.9 (dd, $^2J_{C–F}$ = 21.5 Hz, $J_{C–F}$ = 3.0 Hz), 111.7, 104.6 (dd, $^2J_{C–F}$ = 25.7, 25.7 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.8 (s, 3F), −109.7 (d, J = 8.0 Hz, 1F), −113.1 (d, J = 8.0 Hz, 1F). HRMS: exact mass calculated for $[M + H]^+$ ($C_{13}H_8F_5O$) requires m/z 275.0490, found m/z 275.0490.

3q: 3′,4′,5′-Trifluoro-3-methoxy-[1,1′-biphenyl]-4-ol. Prepared according to General procedure B using 5-bromo-2-methoxyphenylboronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane (97 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 5–20% EtOAc in petroleum ether) to afford the title compound as an off-white solid (41 mg, 65%). ν_{max} (film): 3530, 2941, 2361, 1503, 1263, 1231, 1211, 1136, 1038, 1022 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.17–7.12 (m, 2H), 7.10 (d, J = 2.5 Hz, 1H), 7.01 (dd, J = 8.1, 2.5 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.73 (br. s., 1H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.5 (ddd, $^1J_{C–F}$ = 248.9 Hz, $^2J_{C–F}$ = 10.0 Hz, $^3J_{C–F}$ = 4.1 Hz), 147.1, 146.2, 139.0 (dt, $^1J_{C–F}$ = 251.1 Hz, $^2J_{C–F}$ = 15.6 Hz), 137.1 (td, $^3J_{C–F}$ = 8.0 Hz, $J_{C–F}$ = 4.3 Hz), 131.8, 118.7, 113.2, 111.1, 110.7 (dd, $^2J_{C–F}$ = 15.8 Hz, $^3J_{C–F}$ = 6.0 Hz), 56.2. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −134.5 (d, J = 20.4 Hz, 2F), −163.6 (t, J = 20.4 Hz, 1F). HRMS: exact mass calculated for $[M - H]^-$ ($C_{13}H_8F_3O_2$) requires m/z 253.0482, found m/z 253.0477.

3r: 2-(1-Methyl-1*H*-pyrazol-4-yl)phenol. Prepared according to General procedure A using 2-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (71.2 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 20–80% Et_2O in petroleum ether) to afford the title compound as a yellow solid (30 mg, 75%). ν_{max} (solid): 3060, 2928, 2852, 1566, 1457, 1355 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz): δ 7.96 (s, 1H), 7.82 (s, 1H), 7.51 (dd, J = 7.7, 1.7 Hz, 1H), 7.20 (s, 1H), 7.05–7.11 (m, 1H), 6.87–6.93 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (CD_3CN, 126 MHz): δ 153.0, 137.3, 129.4, 127.4, 127.0, 120.2, 119.8, 118.3, 115.8, 38.3. HRMS: exact mass calculated for $[M + H]^+$ ($C_{10}H_{11}N_2O$) requires m/z 175.0866, found m/z 175.0864.

3s: 5-(3,6-Dihydro-2*H*-pyran-4-yl)-2-methoxyphenol. Prepared according to General procedure B using (5-bromo-2-methoxyphenyl)boronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv.), 2-(3,6-dihydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 10–20% EtOAc in petroleum ether) to afford the title compound as an off-white solid (35 mg, 67%). ν_{max} (film): 3302, 2916, 1510, 1276, 1118, 1028,

1014 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.00 (d, J = 2.2 Hz, 1H), 6.89 (dd, J = 8.4, 2.2 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.03 (tt, J = 3.0, 1.5 Hz, 1H), 5.60 (br. s, 1H), 4.31 (q, J = 2.8 Hz, 2H), 3.92 (t, J = 5.5 Hz, 2H), 3.89 (s, 3H), 2.45–2.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.5, 145.0, 133.5, 132.9, 120.6, 115.9, 110.6, 109.9, 65.4, 64.0, 55.5, 26.7. HRMS: exact mass calculated for $[M + H]^+$ ($C_{12}H_{15}O_3$) requires m/z 207.1016, found m/z 207.1012.

3t: 3-Fluoro-2′,3′,4′,5′-tetrahydro-[1,1′-biphenyl]-4-ol. Prepared according to General procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv.), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (78 mg, 0.375 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–10% EtOAc in petroleum ether) to afford the title compound as an off-white solid (36 mg, 75%). ν_{max} (film): 3314, 2928, 2859, 2359, 1593, 1516, 1431, 1290, 1267 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.13 (dd, J = 12.5, 2.0 Hz, 1H), 7.08 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 6.99–6.89 (m, 1H), 6.10–6.04 (m, 1H), 5.18 (d, J = 3.5 Hz, 1H), 2.41–2.30 (m, 2H), 2.27–2.13 (m, 2H), 1.84–1.72 (m, 2H), 1.71–1.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.4 (d, $^1J_{C-F}$ = 237.0 Hz), 141.5 (d, $^2J_{C-F}$ = 16.2 Hz), 135.7 (d, $^3J_{C-F}$ = 8.1 Hz), 134.6 (d, J_{C-F} = 2.7 Hz), 123.7, 120.6 (d, $^3J_{C-F}$ = 5.4 Hz), 116.2, 111.5 (d, $^2J_{C-F}$ = 18.8 Hz), 26.9, 25.3, 22.5, 21.6. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −141.4 (s, 1F). HRMS: exact mass calculated for $[M + H]^+$ ($C_{12}H_{14}FO$) requires m/z 193.1023, found m/z 193.1023.

3u: (*E*)-3-(2-Cyclopropylvinyl)phenol. Prepared according to General procedure B using 3-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv.), (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 mg, 0.375 mmol, 1.5 equiv.), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–15% EtOAc in petroleum ether) to afford the title compound as an off-white solid (29 mg, 72%). ν_{max} (film): 3321, 3005, 2359, 1649, 1607, 1580, 1491, 1449, 1277, 1252, 1229, 1153 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.17 (t, J = 8.0 Hz, 1H), 6.94–6.88 (m, 1H), 6.77–6.84 (m, 1H), 6.68 (ddd, J = 8.0, 2.5, 1.0 Hz, 1H), 6.43 (d, J = 15.7 Hz, 1H), 5.73 (dd, J = 15.7, 8.8 Hz, 1H), 4.99 (s, 1H), 1.64–1.52 (m, 1H), 0.89–0.81 (m, 2H), 0.57–0.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.2, 139.1, 135.1, 129.2, 126.5, 118.0, 113.1, 111.7, 14.0, 6.8. HRMS: exact mass calculated for $[M + H]^+$ ($C_{11}H_{13}O$) requires m/z 161.0959, found m/z 161.0959.

3v: (*E*)-2-Styrylphenol. Prepared according to General procedure A using 2-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (78.0 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as a yellow solid (38 mg, 85%). ν_{max} (solid): 3526, 3042, 2927, 1584, 1497, 1454, 1329 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.57 (m, 3H), 7.35–7.41 (m, 3H), 7.28 (s, 1H), 7.11–7.19 (m, 2H), 6.97 (dt, J = 7.5, 0.8 Hz, 1H), 6.82 (dd, J = 8.2, 0.9 Hz, 1H), 4.97 (br. s., 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.0, 137.6, 130.2, 128.7, 127.7, 127.3, 126.6, 124.7, 123.0, 121.2, 116.0. HRMS: exact mass calculated for $[M - H]^-$ ($C_{14}H_{11}O$) requires m/z 195.0815, found m/z 195.0821.

3w: 4-(3,6-Dihydro-2*H*-pyran-4-yl)phenol. Prepared according to General procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv.), 2-(3,6-dihydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (71.2 mg, 0.339 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv.), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–30% Et_2O in petroleum ether) to afford the title compound as a white solid (48 mg, 93%). ν_{max} (solid): 3271, 2924, 2872, 1610, 1588, 1515, 1442 cm^{-1}. ^1H NMR (CD_3CN, 500 MHz): δ 7.30 (d, J = 8.8 Hz, 2H), 6.91 (br. s., 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.06 (tt, J = 2.9, 1.5 Hz, 1H), 4.23 (q, J = 2.8 Hz, 2H), 3.86 (t, J = 5.5 Hz, 2H), 2.47–2.42 (m, 2H). ^{13}C NMR (CD_3CN, 126 MHz): δ 156.3, 133.3, 132.1, 125.8, 120.4, 115.1, 65.4, 64.0, 26.9. HRMS: exact mass calculated for $[M + H]^+$ ($C_{11}H_{13}O_2$) requires m/z 177.0910, found m/z 177.0906.

7: 2′,4′-Difluoro-4-hydroxy-[1,1′-biphenyl]-3-carboxylic acid (diflunisal). To a solution of methyl 2′,4′-difluoro-4-hydroxy-[1,1′-biphenyl]-3-carboxylate (13 mg, 0.049 mmol, 1 equiv.) in THF (1 mL) and water (1 mL) was added KOH (3 mg, 0.054 mmol, 1.1 equiv.). The reaction was heated to 80 °C for 3 h before being allowed to cool to room temperature and concentrated under vacuum. The residue was partitioned between EtOAc (10 mL) and 2 M HCl (5 mL) and the aqueous extracted with EtOAc (2 × 10 mL). The combined organics were dried through a hydrophobic frit and evaporated to dryness to afford the desired product (12 mg, 98%) as a white solid. ν_{max} (film): 2961, 2614, 1668, 1618, 1587, 1483, 1449, 1300, 1267, 1236, 1209 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): δ 7.94–7.91 (m, 1H), 7.70–7.67 (m, 1H), 7.59 (td, J = 8.9, 6.6 Hz, 1H), 7.35 (ddd, J = 11.4, 9.1, 2.5 Hz, 1H), 7.21–7.16 (m, 1H), 7.08 (d, J = 8.5 Hz, 1H). Exchangeable protons were not observed. ^{13}C NMR (DMSO-d_6, 101 MHz): δ 171.5, 160.7, 160.1, 161.5 (dd, $^1J_{C-F}$ = 250.0 Hz, $^3J_{C-F}$ = 11.0 Hz), 159.0 (dd, $^1J_{C-F}$ = 250.0 Hz, $^3J_{C-F}$ = 11.0 Hz), 135.8, 131.5 (dd, $^3J_{C-F}$ = 5.4 Hz, $^3J_{C-F}$ = 8.8 Hz), 130.3, 125.1, 123.7 (dd, $^2J_{C-F}$ = 17.6 Hz, J_{C-F} = 2.7 Hz), 117.6, 113.2, 112.0 (dd, $^2J_{C-F}$ = 20.5 Hz, J_{C-F} = 2.7 Hz), 104.5 (dd, $^2J_{C-F}$ = 26.5, 26.5 Hz). ^{19}F NMR (DMSO-d_6, 376 MHz): δ −111.40 (d, J = 8.2 Hz, 1F), −114.17 (d, J = 8.2 Hz, 1F). HRMS: exact mass

calculated for $[M - H]^-$ ($C_{13}H_7F_2O_3$) requires m/z 249.0369, found m/z 249.0370.

8: 4′-Hydroxy-[1,1′-biphenyl]-4-carbonitrile. Prepared according to General procedure A using 4-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv.), 2-(4-cyanophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (86 mg, 0.375 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv.), THF (1 mL, 0.25 M), H_2O (22.5 μL, 1.25 mmol, 5 equiv.), and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.). After 27 h, the reaction mixture was subjected to the purification outlined in the General procedure (silica gel, 0–15% Et_2O in petroleum ether) to afford the desired product as a white solid (39 mg, 80%). ν_{max} (film): 3375, 2228, 1601, 1587, 1491, 1204, 1179 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz) δ 9.79 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.82 (dd, J = 22.4, 8.7 Hz, 4H), 6.89 (d, J = 8.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 101 MHz): δ 158.3, 144.6, 132.7, 128.8, 128.3, 126.5, 119.1, 116.0, 108.7. HRMS: exact mass calculated for $[M - H]^-$ ($C_{13}H_8NO$) requires m/z 194.0611, found m/z 194.0606.

9: 4-Methoxy-4′-(thiophen-2-yl)-[1,1′-biphenyl]-3-ol. To an oven dried 5 mL microwave vial was added 4-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv.), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv.), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), and K_3PO_4 (159 mg, 1 mmol, 4 equiv.). The vial was then capped and purged with N_2 before addition of THF (1 mL, 0.25 M) and H_2O (90 μL, 5 mmol, 20 equiv.). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature before adding (5-bromo-2-methoxyphenyl)boronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv.). The vial was then recapped and purged again with N_2 before being heated to 90 °C for a further 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 °C and 30 wt% aq. H_2O_2 (195 μL, 2.5 mmol, 10 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 °C and quenched with sodium metabisulphite (190 mg, 1 mmol, 4 equiv.) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2 × 10 mL) and brine (10 mL). The aqueous extracts were extracted with EtOAc (10 mL), the combined organics filtered through a hydrophobic frit packed with Celite® and concentrated under vacuum before being purified by column chromatography (silica gel, 10–20% Et_2O in petroleum ether) to afford the title compound as an off-white solid (64 mg, 91%). ν_{max} (film): 3377, 2980, 1502, 1263, 1219 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.55–7.49 (m, 2H), 7.23 (ddd, J = 4.8, 4.3, 1.1 Hz, 2H), 7.10–7.06 (m, 2H), 6.99 (dd, J = 8.6, 2.4 Hz, 1H), 6.89–6.85 (m, 2H), 6.74 (d, J = 8.6 Hz, 1H), 5.65 (br. s., 1H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.6, 146.0, 145.4, 143.7, 127.4, 127.1, 127.0, 123.4, 122.3, 121.6, 117.4, 115.3, 112.8, 111.4, 55.6 HRMS: exact mass calculated for $[M + H]^+$ ($C_{17}H_{15}O_2S$) requires m/z 283.0787, found m/z 283.0788.

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