Extending the Scope of Chromium−Manganese Redox-Coupled Reactions: A One-Pot Synthesis of Benzoxazoles

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A critically important strategy for synthetic chemistry is the development of "domino" processes: those capable of concatenating multiple transformations into a single step. Such transformations not only provide an increase in synthetic efficiency, but also imply the development of a significant degree of mechanistic understanding. We report herein a new domino reaction, in which a chromium−manganese redox couple is employed both to catalytically reduce an *o*-hydroxy nitroarene and to oxidatively cyclize a subsequently formed imine. We find that the reaction is most effective for starting *o*-hydroxy nitroarenes with a strongly electron-withdrawing group at the *para* position.

Advancing the "state of the art" in organic synthesis is tied to the development of new methodology which can produce the maximum increase in structural complexity in the fewest number of steps. One strategic approach to this goal is to employ reactions that generate mechanistic intermediates able to subsequently carry out further bond-forming steps.[1] Examples of spectacular successes employing such "domino" or cascade transformations include the Johnson polyene cyclization reaction,[2] various multiring radical closures,[3] and cascade pericyclic processes.[4] Many organometallic reactions represent an alternative implementation of this strategy, in that the initial formation of an organometallic species sets up the formation of additional bonds.[5] While such reactions are, in one sense, exercises in mechanistic engineering, they also require that a fundamental understanding of mechanism has been reached in order to be successful.

In the course of a broad program in the development of new methods for the design and synthesis of biologically active structures, we recently reported the development of a catalytic reduction of nitroarenes.[6] This method employs a chromium/manganese redox couple in a manner analogous to that described by Fürstner and co-workers[7] for Nozaki−Hiyama−Kishi[8] coupling reactions, and by Boeckman and Hudack[9] for the Takai−Utimoto[10] condensation. Our working model for the catalytic cycle for this reaction (Scheme 1) suggested that reduction of the nitroarene to aryl hexamethyldisilazane involves oxidation (conversion) of Cr(II) to Cr(III). Subsequent reduction of the Cr(III) species must occur via oxidation of Mn(0); however, it was not clear to us what oxidation state of manganese would be produced. It occurred to us that we could both shed light on the mechanism of this transformation and extend its synthetic utility by incorporating functionality which could use the (presumed) oxidized Mn species produced in the reaction to form additional bonds in a "domino" sense.

The primary oxidized Mn species we suspected of being present were Mn(II) oxide (MnO) and Mn(IV) oxide (MnO_2), as well as $MnCl_2$. Therefore, we conceived of a scheme to test this as follows (Scheme 2). Subjecting an *o*-nitro phenol **1** to the catalytic reduction conditions would allow for the formation of hexamethyldisilazane **2**. As this occurred, the oxidized chromium species would be rereduced to Cr(II) by manganese, yielding an oxidized Mn species. We assumed in situ conversion of hexamethyldisilazane **2** to *o*-hydroxy aniline **3**, or a related N- or O-silylated species, could occur. If the reaction were carried out in the presence of an aldehyde, subsequent conversion to the imine, **4**, would be expected. This imine would then undergo ready equilibration with aminal **5**. By analogy to reports of the ability of Mn(IV) to convert imines such as **4** to benzoxazoles[11] via what is essentially

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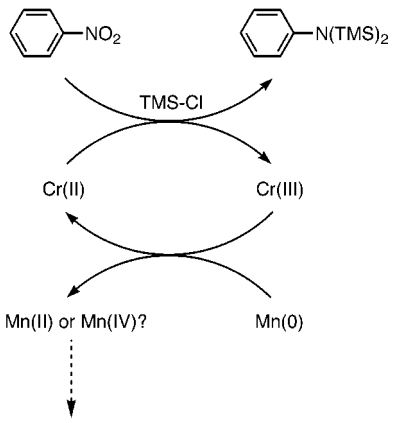
Scheme 1



a dehydrogenation reaction,[12] we anticipated that the end product of this reaction would be either a benzoxazole (**6**), if Mn(IV) was indeed produced in situ, or, if Mn(II) were the species produced, an imine (since Mn(II) was deemed insufficiently reactive to carry out the final aminal oxidation).

For our initial experiments, we examined the reactivity of methyl 4-nitro-3-hydroxybenzoate[13] with benzaldehyde, using conditions identical to those developed for our reduction chemistry (Table 1). In the absence of Mn metal and TMSCl, employing an excess of $CrCl_2$ to reduce the nitroarene, no benzoxazole product is observed. However, carrying out the reaction with substoichiometric amounts of $CrCl_2$ and an excess of Mn and TMSCl allowed us to isolate the desired benzoxazole **7**, albeit in low yield (entry 2). The overall mass recovery in this instance was poor, suggesting to us that product could be potentially entrained within the sludge of manganese salts generated in the reaction. Indeed, reducing the number of equivalents of Mn(0) and TMSCl employed to 6 and 4 equiv, respectively, provided **7** in significantly higher yield (73%, entry 3).

While the above result strongly suggested that some material present in the reaction mixture was capable of effecting the desired oxidative cyclization, we were concerned that a coating of oxides present on the surface of the Mn chips used in the reaction could be a complicating factor in our analysis of whether this was the result of a material produced in the Cr/Mn catalytic cycle. Therefore, we cleaned the Mn by sonication in acidic ethanol prior to use, and reran the reaction. No change in yield was observed, lending support to the conclusion that an oxidized Mn species produced during the reaction was the active cyclization reagent. To examine the dependence of benzoxazole formation on various potential components of the reaction mixture, we reacted methyl 3-hydroxy-4-aminobenzoate[14] with benzaldehyde in DMF in the presence of a series of reagents (Table 2). While none of the conditions attempted provided **7** in a yield comparable to the one-pot procedure, complete conversion of starting materials was observed for the reaction employing MnO_2 and TMSCl (entry 3). Unexpectedly, although the intermediate imine was the primary species oberved in the crude ^{1}H NMR spectrum in the reaction employing MnO as oxidant in the presence of TMSCl (entry 4), we also obtained a small amount of benzoxazole following flash chromatography. For MnO to act as the oxidant in benzoxazole formation, it would be converted to Mn(0), suggesting the possibility of a "bicatalytic" mechanism for the nitroarene reduction/benzoxazole cyclization sequence. However, we have observed that reactions employing substoichiometric amounts of Cr *and* substoichiometric quantities of Mn do not proceed to completion. At this stage we cannot rule out the possibility that the MnO we employed was contaminated with small amounts of MnO_2, and further studies will be required to fully resolve this question.

Requirement for the aldehyde oxidation state in the reaction was established by subjecting either 2-hydroxynitrobenzene or 4-nitro-3-hydroxybenzoic acid and benzoyl chloride to the above reaction conditions (Scheme 3). In both cases, benzoyl protection of the phenolic hydroxyl with concomitant nitro reduction was the sole product observed.

To determine the scope of the reaction, the ability of a series of aldehydes to provide benzoxazole products with methyl 3-hydroxy-4-nitrobenzoate was first examined (Table 3). Both aryl and alkyl aldehydes participate readily in the reaction, providing the desired benzoxazoles in moderate to excellent yield. The sole exception to this was salicylaldehyde (entry 10), an unsurprising result given its propensity to strongly chelate a wide variety of transition metals. For entries 1−9, crude NMR spectra indicated that only the desired benzoxazoles and, in lower yielding reactions, uncyclized imines were present.

While we have only begun to examine the range of *o*-nitrophenols which will undergo the cyclization reaction, we have observed that compounds lacking a strongly electron-withdrawing group *para* to the nitro group do not provide the benzoxazole product or provide it in substantially reduced yield (Table 4). This was somewhat unexpected, since the presence of a para electron-withdrawing group should significantly decrease the nucleophilicity (and hence the imine-forming ability) of the amine functionality. However, such an electron-withdrawing group would be expected to also shift the imine−aminal equilibrium shown in Scheme 2 toward the aminal form, and it is perhaps this effect which dominates in the reaction. While an *ortho* electron-withdrawing group would also be expected to favor the oxidative cyclization, others have noted that such benzoxazoles have poor stability.[15] Indeed, in our hands reaction of methyl 2-nitro-3-hydroxybenzoate with benzaldehyde under our standard conditions produced the desired benzoxazole in only 25% isolated yield, despite the fact that benzoxazole was the only material observed in the crude NMR.

In summary, we have demonstrated a procedure for the one-pot preparation of benzoxazoles, which employs a domino reaction process made possible by a Cr/Mn redox couple. Highest yields are obtained for *o*-hydroxynitroarenes substituted with an electron-withdrawing group at the *para* position. This reaction should be a

(12) $Pb(OAc)_4$ has also been reported to convert imines such as **4** to benzoxazoles: Stephen, F. F.; Bower, J. D. *J. Chem. Soc.* **1949**, 2971−2972. Stephen, F. F.; Bower, J. D. *J. Chem. Soc.* **1950**, 1722−1726.

(13) Prepared from 3-hydroxy-4-nitrobenzoic acid according to: Samih, F.; Prudhomme, M.; Dauphin, G.; Jeminet, G. *Tetrahedron* **1990**, *46*, 5177−5186.

(14) Methyl 3-hydroxy-4-nitrobenzoate was reduced using a procedure analogous to: Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839−842.

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Scheme 2

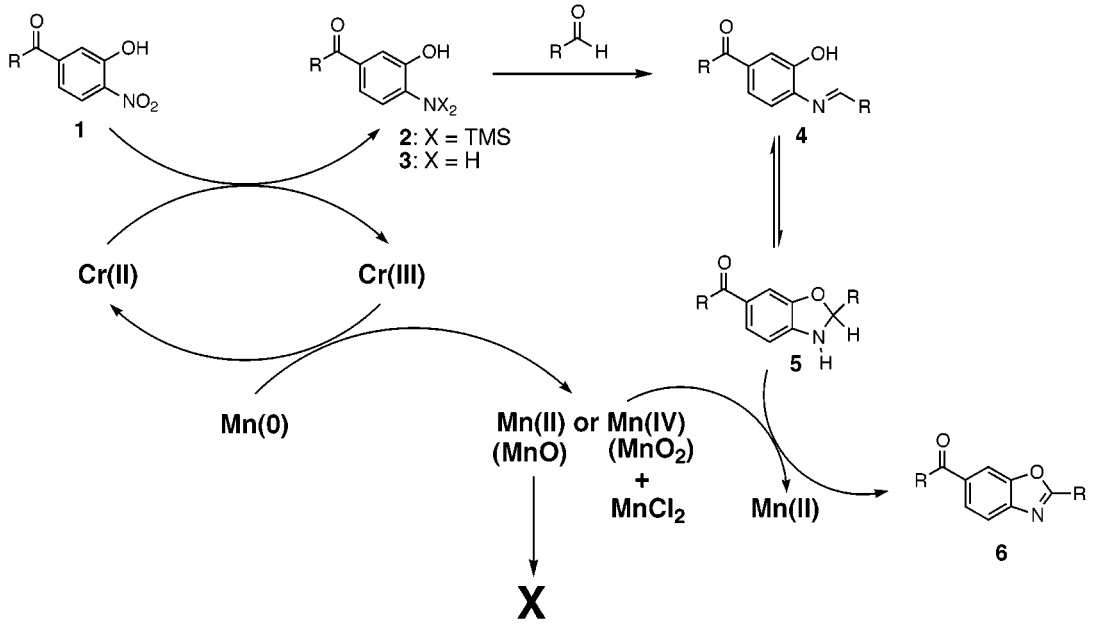
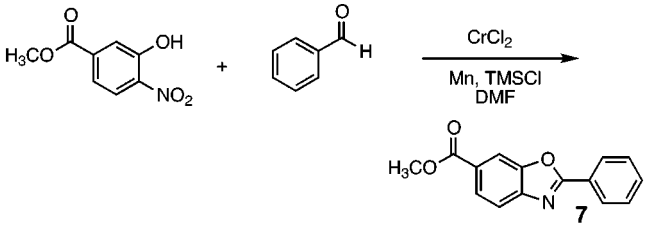
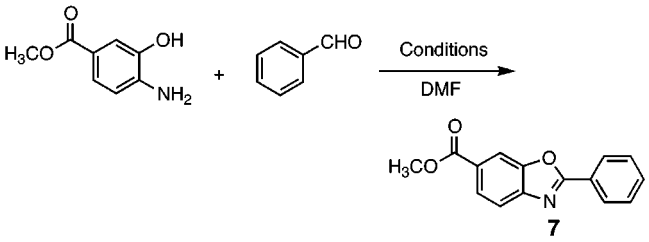


Table 1



entry	$CrCl_2$, equiv	Mn, equiv	TMSCl, equiv	% yield of **7**
1	16	0	0	0
2	0.25	16	16	30
3	0.25	6	4	73

Table 2



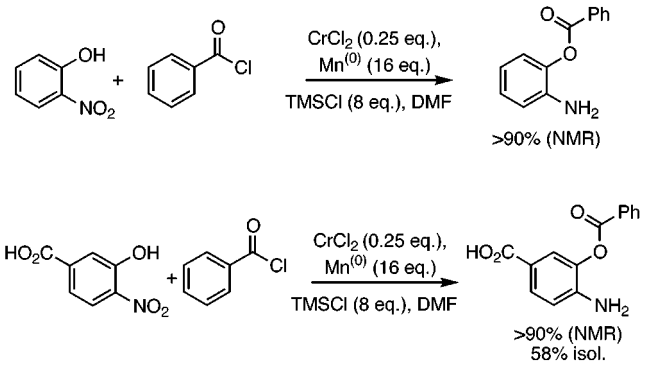
	equiv of reagent					
entry	MnO	MnO_2	$MnCl_2$	TMSCl	$CrCl_3$	% yield of **7**
1	4	0	0	0	0	0
2	0	4	0	0	0	0
3	0	4	0	8	0	44
4	4	0	0	8	0	17
5	2	0	2	8	2	0

useful alternative to other currently available methods for benzoxazole formation, particularly in cases where chemoselectivity and sensitivity to the harsh conditions typically employed[16] are issues. This methodology should also be extensible to the one-pot synthesis of a wide range of heterocycles, and efforts to examine this are currently underway.

Experimental Section

General Experimental Details. Unless otherwise indicated, all starting materials were purchased from the Aldrich Chemical Co. and used as obtained from the manufacturer. $CrCl_2$ was purchased from Strem and stored in a drybox under N_2 prior to use. Mn chips (Aldrich) were manually broken into pieces ca. 3 mm × 3 mm immediately prior to use. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were acquired using Bruker Avance-400 or AMX-400 instruments. High-resolution mass spectra were acquired at the University of California, Irvine, mass spectrometry laboratory with electron impact ionization.

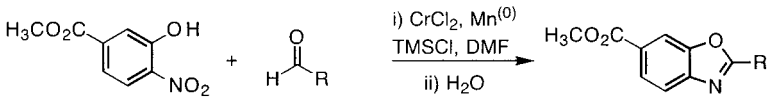
Scheme 3

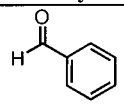
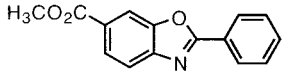
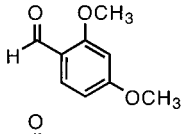
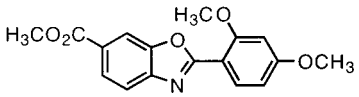
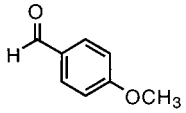
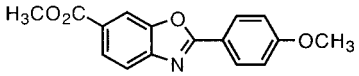
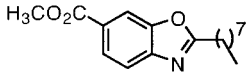
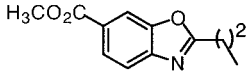
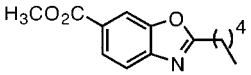
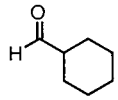
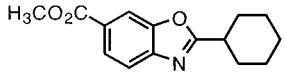
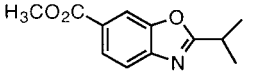
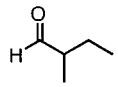
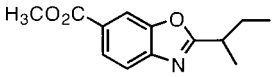
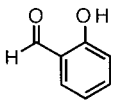
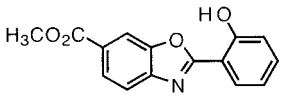


Preparation of 2-phenyl-6-(methoxycarbonyl)benzoxazole (small scale procedure): methyl 3-hydroxy-4-nitrobenzoate (99 mg, 0.5 mmol), manganese chips (165 mg, 3 mmol), and chromium chloride (13 mg, 0.1 mmol) were taken up in 3 mL of anhydrous DMF in a flame-dried, nitrogen-purged round-bottom flask. TMSCl (0.25 mL, 2 mmol) was slowly added dropwise (Caution: on larger scale, this step produces a noticeable exotherm and should be carried out at 0 °C). After allowing this mixture to stir at room temperature for 15 min, benzaldehyde (53 mg, 0.5 mmol) was added, and stirring was allowed to continue at room temperature for 18 h. The reaction was then quenched with water (3 mL), and the mixture was allowed to stir for an additional 1 h. The resulting

(16) The most common methods for benzoxazole synthesis rely on the reaction of an *o*-hydroxyaniline with a carboxylic acid in the presence of polyphosphoric acid; for lead references and mechanistic analysis, see: So, Y.-H.; Heeschen, J. P. *J. Org. Chem.* **1997**, *62*, 3552−3561. For other synthetic approaches to benzoxazoles, see: (a) Terashima, M.; Ishii, M.; Kanaoka, Y. *Synthesis* **1982**, 484−485. (b) Perry, R. J.; Wilson, B. D.; Miller, R. J. *J. Org. Chem.* **1992**, *57*, 2883−2887. (c) Kondo, T.; Yang, S.; Huh, K.-T.; Kobayashi, M.; Kotachi, S.; Watanabe, Y. *Chem. Lett.* **1991**, 1275−1278.

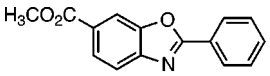
Table 3. Dependence of the Reaction on Aldehyde Structure



Entry	Aldehyde	Product	Yield (%)
1			73
2			47
3			35
4			76
5			67
6			55
7			81
8			57
9			62
10			0

mixture was then poured into 10 mL of water and extracted with 3 × 15 mL ethyl acetate. We have observed that care must be taken during the extraction procedure not to overzealously agitate the mixture, as intractable emulsions can result. The combined organic extracts were dried over sodium sulfate and filtered, and solvent was removed in vacuo. Purification of the crude product by flash chromatography (silica gel; elution with 4:1 hexane:ethyl acetate) provided 2-phenyl-6-(methoxycarbonyl)benzoxazole as a white solid (92 mg, 73%).

Preparation of 2-phenyl-6-(methoxycarbonyl)benzoxazole (large scale procedure; unoptimized): methyl 3-hydroxy-4-nitrobenzoate (10 g, 50 mmol), manganese chips (16.5 g, 300 mmol), and chromium chloride (2 g, 15 mmol) were taken up in 180 mL of anhydrous DMF in a 500 mL flame-dried, nitrogen-purged three-neck round-bottom flask equipped with an overhead stirrer and an addition funnel. The mixture was cooled to 0 °C in an ice bath, and TMSCl (25 mL, 200 mmol) was added dropwise via an addition funnel over the course of 1.0 h. The mixture was stirred an additional 30 min at 0 °C, and then benzaldehyde (6.4 g, 60 mmol) was added dropwise over ca. 5 min via syringe. The reaction was allowed to warm to room temperature, and stirring was allowed to continue for an additional 12 h. 200 mL water was then added, and this mixture was stirred at room temperature for 1 h. Subsequent workup and purification was analogous to that described above. The yield of 2-phenyl-6-(methoxycarbonyl)benzoxazole at this scale was 5.2 g (41%).

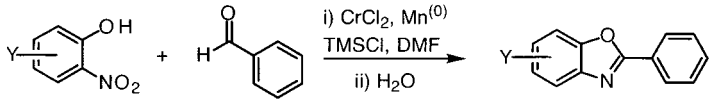


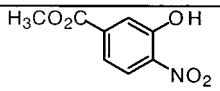
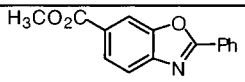
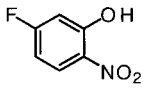
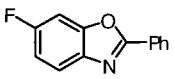
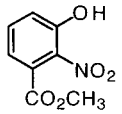
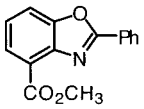
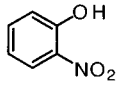
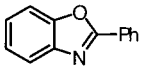
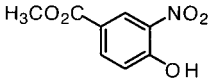
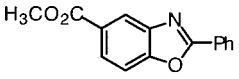
6-Carbomethoxy-2-phenyl benzoxazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30−8.32 (m, 3H); 8.1 (dd, J = 1.2, 7.1 Hz, 1H); 7.8 (d, 8.3 Hz, 1H); 7.5 (m, 3H); 4.0 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 165.5, 150.4, 146.0, 132.1, 129.0, 127.9, 127.0, 126.5, 126.3, 119.5, 112.2, 52.3. FTIR (thin film): 1714, 1613, 1549, 1482, 1431, 1286, 1231, 1199, 1121, 1085 cm^{-1}. HRMS: Calculated for $C_{15}H_{11}NO_3$ (M^+) 253.0739 found 253.0745.

6-Carbomethoxy-2-(2,4-dimethoxyphenyl)benzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and 2,4-dimethoxybenzaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H); 8.15 (d, J = 8.8 Hz, 1H); 8.07 (dd, J = 1.3, 7.1 Hz, 1H); 7.8 (d, J = 8.4 Hz, 1H); 6.66 (dd, J = 2.1, 6.5 Hz, 1H); 6.63 (d, J = 2.1 Hz, 1H); 4.05 (s, 3H); 4.0 (s, 3H); 3.9 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 164.3, 164.1, 160.3, 149.7, 146.3, 132.8, 126.3, 126.0, 119.3, 111.8, 108.4, 105.5, 99.1, 56.2, 55.6, 52.2. FTIR (thin film): 1718, 1614, 1574, 1455, 1429, 1287, 1267, 1235, 1214, 1191, 1169, 1138, 1082 cm^{-1}. HRMS: Calculated for $C_{17}H_{15}NO_5$ (M^+) 313.0950 found 313.0939.

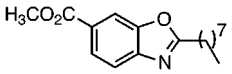
6-Carbomethoxy-2-(4-methoxyphenyl)benzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and 4-methoxybenzaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26−8.23 (3H, m); 8.10 (1H, dd, J = 8.4, 1.5 Hz); 7.76 (1H, d, J = 8 Hz);

Table 4. Dependence of the Reaction on *o*-Hydroxy Nitroarene Structure

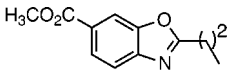


Entry	*o*-hydroxy nitroarene	Benzoxazole Product	Benzoxazole: Imine (NMR)	Isolated Yield of Benzoxazole (%)
1			>95:5	73
2			75:25	31
3			>95:5	25
4			13:87	13
5			7:93	0

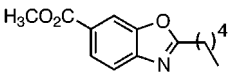
7.07 (2H, m); 3.99 (3H, s); 3.93 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 165.5, 162.8, 150.3, 146.3, 129.8, 126.5, 126.3, 119.0, 114.4, 112.0, 55.5, 52.3. FTIR (thin film) 2954, 1768, 1614, 1502, 1436, 1349 cm^{-1} HRMS: Calculated for $C_{16}H_{13}NO_4$ (M^+): 283.0845; found 283.0837



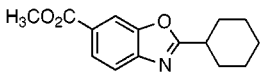
6-Carbomethoxy-2-octylbenzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and nonanal. ^{1}H NMR (400 MHz, $CDCl_3$): d 8.18 (d, J = 1.2 Hz, 1H); 8.05 (dd, J = 1.4 Hz, 7.0 Hz, 1H); 7.69 (d, J = 8.3 Hz, 1H); 4.0 (s, 3H); 2.95 (t, J = 7.6 Hz, 2H); 1.88 (q, J = 7.4 Hz, 2H), 1.28−1.46 (m, 10H); 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): d 170.2, 166.7, 150.4, 145.3, 126.5, 125.9, 119.0, 111.9, 52.3, 31.7, 29.1, 29.0, 28.7, 26.6, 22.6, 14.0. FTIR (thin film): 2923, 2852, 1721, 1607, 1566, 1467, 1434, 1378, 1290, 1216, 1198, 1119, 1079 cm^{-1}. HRMS: Calculated for $C_{17}H_{23}NO_3$ (M^+) 289.1678 found 289.1682.



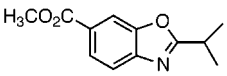
6-Carbomethoxy-2-propylbenzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and butanal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 1.3 Hz, 1H), 8.05−8.02 (dd, J = 1.51, 6.7 Hz, 1H), 7.69−7.67 (d, J = 8.2 Hz, 1H), 3.95 (s, 3H), 2.96−2.92 (t, J = 7.4 Hz, 2H), 1.96−1.91 (m, 2H), 1.08−1.04 (t, J = 7.42 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): ^{d} 170.0, 166.7, 150.4, 145.3, 126.5, 125.8, 119.0, 111.9, 52.2, 30.6, 20.0, 13.7. FTIR (thin film): 2923, 1722, 1640, 1585, 1434, 1291, 1276, 1209, 842 cm^{-1}. HRMS: calculated for $C_{12}H_{13}NO_3$ (M^+) 219.0895; found 219.0885.



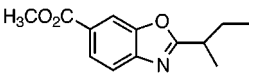
6-Carbomethoxy-2-pentylbenzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and hexanal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 0.9 Hz, 1H), 8.04−8.02 (dd, J = 1.5, 6.87 Hz, 1H), 7.69−7.67 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H), 2.97−2.93 (t, J = 7.6 Hz, 2H), 1.94−1.86 (m, 2H), 1.47−1.35 (m, 4H), 0.93−0.89 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 166.7, 150.4, 145.3, 125.9, 119.0, 111.9, 52.3, 31.2, 29.6, 28.7, 26.2, 22.2, 13.8. FTIR (thin film): 3257, 2920, 2884, 2857, 1714, 1654, 1583, 1288, 1200, 821, 807 cm^{-1}. HRMS: calculated for $C_{14}H_{17}NO_3$ (M^+) 247.1208; found 247.1202.



6-Carbomethoxy-2-cyclohexylbenzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and cyclohexanecarboxaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 1 Hz, 1H); 8.04 (dd, J = 1 Hz, 7.1 Hz, 1H); 7.7 (d, J = 8.3 Hz, 1H); 3.96 (s, 3H); 2.97 (m, 1H); 2.18 (m, 2H); 1.88 (m, 2H); 1.72 (m, 3H); 1.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 166.7, 150.2, 145.3, 126.5, 125.8, 119.1, 111.9, 52.2, 38.0, 30.3, 25.6, 25.5. FTIR (thin film): 2933, 2855, 1722, 1606, 1561, 1434, 1349, 1292, 1211, 1156, 1116, 1078 cm^{-1}. HRMS: Calculated for $C_{15}H_{17}NO_3$ (M^+) 259.1208 found 259.1210.

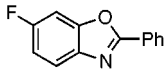


6-Carbomethoxy-2-isopropylbenzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and isobutyraldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.05−8.03 (d, J = 8.33 Hz, 1H), 7.71−7.69 (d, J = 8.31 Hz, 1H), 3.95 (s, 3H), 3.31−3.24 (m, 1H), 1.49−1.47 (d, J = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 166.6, 150.3, 145.2, 126.5, 125.8, 119.1, 111.9, 52.2, 28.9, 20.1. FTIR (thin film): 3052, 2975, 2891, 2878, 1714, 1654, 1582, 1295, 1218, 816, 803 cm^{-1}. HRMS: calculated for $C_{12}H_{13}NO_3$ (M^+) 219.0895; found 219.0893.



6-Carbomethoxy-2-(*sec*-butyl)benzoxazole: Prepared as above, from methyl 3-hydroxy-4-nitrobenzoate and 2-methylbutanal. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (1H, s); 8.03 (1H, d, J = 8 Hz); 7.69 (1H, d, J = 8 Hz); 3.94 (3H, s); 3.08 (1H, sextuplet, J = 6 Hz); 1.99−1.74 (2H, m); 1.44 (3H, d, J = 7 Hz); 0.96

(3H, t, $J = 7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 166.7, 150.3, 145.2, 126.5, 125.8, 119.1, 112.0, 52.3, 35.8, 27.9, 17.7, 11.5. FTIR (thin film) 2969, 1728, 1607, 1564, 1434, 1213, 1077, 775, 747 cm^{-1}. HRMS: Calculated for $C_{13}H_{15}NO_3$ (M^+) 233.1052; found 233.1056.



6-Flouro-2-phenyl benzoxazole: Prepared as above, from 1-fluoro-3-hydroxy-4-nitrobenzene and benzaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23−8.26 (m, 2H); 7.70−7.74 (m, 1H); 7.55−7.58 (m, 3H); 7.33−7.35 (dd, $J = 2.4$ Hz, 5.6 Hz, 1H); 7.13−7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.9, 127.4, 126.8, 120.3, 120.2, 112.4, 98.8, 98.5. FTIR (Thin film): 1623, 1556, 1479, 1452, 1345, 1289, 1255, 1127, 1103, 1049, 1022 cm^{-1}. HRMS: Calculated for $C_{13}H_9FNO$ (M^+) 213.0590 found 213.0591

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Supporting Information Available: Full spectroscopic characterization for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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