Supporting Information for

Copper-Catalyzed Oxidative Decarboxylative C-H Arylation of Benzoxazoles with 2-Nitrobenzoic Acids

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I. General Considerations.

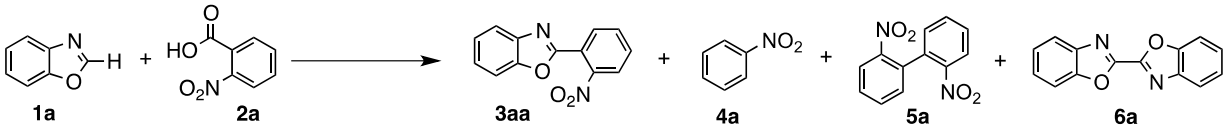
^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on an Agilent 400 MHz spectrometer or a Varian INOVA 600 MHz spectrometer. Chemical shifts (δ) are given in parts per million and referenced to the residual solvent signal;[1] all coupling constants are reported in Hz. High resolution mass spectra were obtained on a Termo Finnigan Linear Trapping Quadrupole mass spectrometer. Melting points were taken on a Mel-Temp melting point apparatus. Column chromatography was performed using Silicycle Silia Flash P60 silica gel. All commercial reagents were used without further purification unless otherwise noted.

II. General Method for Screening of Reaction Conditions

2-nitrobenzoic acid (33 mg, 0.2 mmol), CuCl (2 mg, 0.02 mmol), phen (4 mg, 0.02 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), Ag_2O (93 mg, 0.4 mmol), and 4 Å molecular sieves (200 mg), were combined in a 25 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with N_2 three times before a solution of benzoxazole (36 mg, 0.3 mmol) in dry DMF (2.0 mL, 0.15 M) was added. The reaction mixture was stirred under N_2 at 110°C for 23 h. Upon completion, the mixture was cooled to room temperature and diluted with ethyl acetate (40 mL). The mixture was filtered through celite and the filtrate added to a roundbottom flask containing hexamethylbenzene standard (5 mg, 0.03 mmol). A small portion of the solution (1 mL) was removed for analysis by GC, and for the remainder of the mixture, the solvent was removed (by rotary evaporation to ~2mL, then by vacuum line) and the crude mixture dissolved in $CDCl_3$ for ^1H NMR analysis.

The nitobenzene yields given are not true yields due to the volatility of nitrobenzene, but they are included here for completeness.

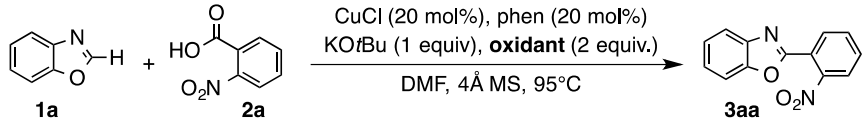
Table S1. Optimization of the Reaction Conditions for the Cu-Catalyzed Decarboxylative Arylation of Benzoxazole with 2-Nitrobenzoic Acid.



entry	[Cu]	[Ag]	base	ligand	**3aa** yield (%)[b]	**4a** yield (%)[b]	**5a** yield (%)[b]	**6a** yield (%)[b]
1	CuCl	Ag_2CO_3	KO*t*Bu	phen	55	1	21	13
2	CuCl	Ag_2CO_3	Cs_2CO_3	phen	6	21	ND	ND
3	CuCl	Ag_2O	KO*t*Bu	phen	39	17	7	9
4	CuCl	Ag_2O	Cs_2CO_3	phen	67	24	12	ND
5	**CuCl**	**Ag_2O**	**Cs_2CO_3**	**phen**	**71**	**25**	**ND**	**ND**
6	$CuCl_2$	Ag_2O	Cs_2CO_3	phen	13	16	ND	13
7	$CuBr_2$	Ag_2O	Cs_2CO_3	phen	26	5	5	12
8	$Cu(OAc)_2$	Ag_2O	Cs_2CO_3	phen	29	19	ND	3
9	$Cu(OTf)_2$	Ag_2O	Cs_2CO_3	phen	43	22	9	ND
11	CuBr	Ag_2O	Cs_2CO_3	phen	48	14	4	ND
12	CuI	Ag_2O	Cs_2CO_3	phen	55	23	16	ND
13	Cu(OAc)	Ag_2O	Cs_2CO_3	phen	6	23	8	ND
14	Cu(OTf)	Ag_2O	Cs_2CO_3	phen	59	30	ND	ND
15	Cu_2O	Ag_2O	Cs_2CO_3	phen	26	39	ND	ND
16	CuCl	Ag_2O	Cs_2CO_3	bpy	25	48	7	4
17	CuCl	Ag_2O	Cs_2CO_3	OMebpy	46	23	ND	ND
18	CuCl	Ag_2O	Cs_2CO_3	*t*Bubpy	30	26	7	ND
19	CuCl	Ag_2O	Cs_2CO_3	neocuproine	16	55	ND	9
20	CuCl	Ag_2O	Cs_2CO_3	bathophen	52	17	ND	ND
21	CuCl	Ag_2O	Cs_2CO_3	terpyridine	ND	13	ND	ND
22	CuCl	Ag_2O	Cs_2CO_3	pyridine	9	31	ND	ND
23	CuCl	Ag_2O	Cs_2CO_3	none	12	62	ND	ND
24	CuCl	none	Cs_2CO_3	phen	22	12	12	ND
25	none	Ag_2O	Cs_2CO_3	phen	ND	16	ND	ND

[a]Yields were determined by ^1H NMR analysis. ND indicates a product not detected.

Table S2. Evaluation of Oxidants for the Cu-Catalyzed Decarboxylative Arylation of Benzoxazole with 2-Nitrobenzoic Acid

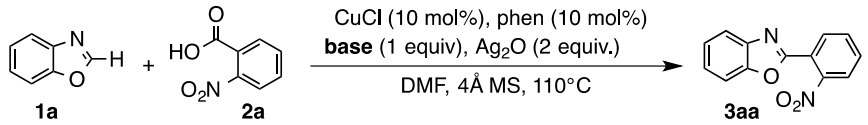


1a **2a** **3aa**

entry	oxidant	**3aa** yield (%)[a]
1	air	ND
2	$K_2S_2O_8$	ND
3	*t*BuOOH	ND
4	*t*BuOO*t*Bu	ND
5	BzOOBz	ND
6	I_2	ND
7	Ag_2CO_3	16
8	Ag_2O	10
9[b]	Ag_2O	17
10[c]	Ag_2O	43

[a]Yields were determined by ^{1}H NMR analysis. ND indicates a product not detected. [b] with Cs_2CO_3 in place of KO*t*Bu. [c]with 10 mol% CuCl and 10 mol% phen at 110°C.

Table S3. Evaluation of Bases for the Cu-Catalyzed Decarboxylative Arylation of Benzoxazole with 2-Nitrobenzoic Acid



1a **2a** **3aa**

entry	base	**3aa** yield (%)[a]
1	KO*t*Bu	43
2	Cs_2CO_3	52
3[b]	KO*t*Bu and Cs_2CO_3	23
4	K_2CO_3	43
5	Na_2CO_3	45
6	NaOAc	10
7	$NaHCO_3$	34
8	none	20

[a]Yields were determined by ^{1}H NMR analysis. ND indicates a product not detected. [b]with 20 mol% (0.04 mmol) of KO*t*Bu and 1 equiv (0.2 mmol) of Cs_2CO_3

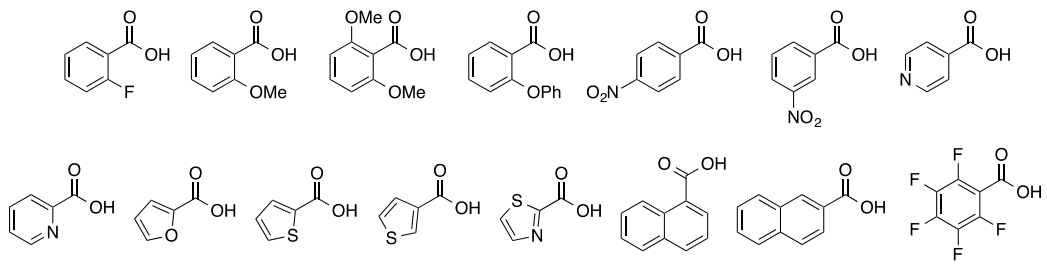
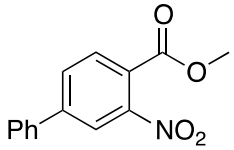
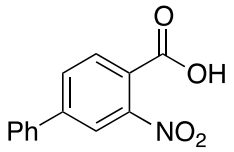


Chart S1. Carboxylic Acids that do not Undergo the Cu-Catalyzed Decarboxylative Arylation of Benzoxazole with 2-Nitrobenzoic Acid Under the Standard Conditions.

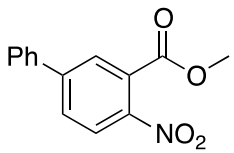
III. Synthesis and Characterization of Substituted Benzoic Acids



methyl-4-phenyl-2-nitrobenzoate. Methyl-4-chloro-2-nitrobenzoate (4.99 g, 23.15 mmol), cesium carbonate (8.16 g, 25.0 mmol), and phenyl boronic acid (2.79 g, 22.9 mmol) were combined in a 100 mL Schlenk tube on the benchtop. $Pd_2(dba)_3$ (0.176 g, 0.19 mmol), PCy_3 (0.218 g, 0.78 mmol) and dioxane (33 mL) were added to the tube in a glove box. The tube was removed and from the glovebox and heated at 80°C under nitrogen for 24 h. Upon completion the reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated and purified by silica column chromatography (gradient elution 1:1 hexanes:ethyl acetate to 100% ethyl acetate) to afford the title compound as a white solid in 15% yield (0.89 g, 3.46 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (s, 1H), 7.84 (m, 2H), 7.60 (d, J = 6.8 Hz, 2H), 7.47 (m, 3H), 3.93 (s, 3H, OCH_3). The product was used without further purification or characterization.

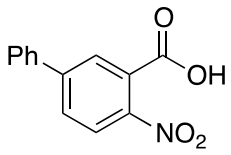


4-phenyl-2-nitrobenzoic acid (2d). To a mixture of methyl-4-phenyl-2-nitrobenzoate (0.89 g, 3.46 mmol) and LiOH (0.86 g, 35.91 mmol) was added 10 mL of a 3:1:1 mixture of THF:MeOH:water and the reaction was allowed to stir at room temperature for 3 h. After reaching completion (as determined by TLC) the reaction mixture was quenched with 1 N HCl (250 mL) and extracted with ethyl acetate (3x 250 mL). The combined organics were washed with brine, dried over Na_2SO_4 and the solvent removed under vacuum. The crude material was recrystallized from ethyl acetate/hexanes to yield 0.48 g (1.97 mmol, 57%) of the title compound as a white crystalline powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (s, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.49 (m, 3H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 13.89 (s, 1H, OH), 8.25 (d, J = 1.6 Hz, 1H), 8.01 (dd, J = 8.0, 2.0 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 6.8 Hz, 1H), 7.49 (m, 3 H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 165.39, 149.65, 144.22, 136.84, 130.81, 130.33, 129.24, 129.18, 127.17, 124.94, 121.42. The spectral data are consistent with those reported in the literature.[2]



methyl-5-phenyl-2-nitrobenzoate. Methyl-5-chloro-2-nitrobenzoate (2.49 g, 11.55 mmol), cesium carbonate (4.06 g, 12.46 mmol), and phenyl boronic acid (1.40 g, 11.48 mmol) were combined in a 100 mL Schlenk tube on the benchtop. $Pd_2(dba)_3$ (0.096 g, 0.10 mmol), PCy_3 (0.116 g, 0.42 mmol) and dioxane (16 mL) were added to the tube in a glove box. The tube was

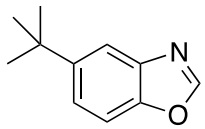
removed and from the glovebox and heated at 80°C under nitrogen for 24 h. Upon completion the reaction mixture was diluted with ethyl acetate and filtered through celite. The filtrate was concentrated and purified by silica column chromatography (2% ethyl acetate in hexanes gradient elution 1:1 hexanes:ethyl acetate to 100% ethyl acetate) to afford the title compound as a white solid in 62% yield (1.83 g, 7.11 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (d, *J* = 8.4 Hz, 1H), 7.89 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2 H), 7.48 (m, 3H), 3.95 (s, 3H). The product was used without further purification or characterization.



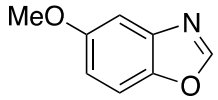
5-phenyl-2-nitrobenzoic acid (2j). Methyl-5-phenyl-2-nitrobenzoate (1.83 g, 7.11 mmol) and LiOH (1.71 g, 71.4 mmol) were combined in a 3:1:1 mixture of THF:MeOH:water (22 mL) and the mixture was allowed to stir for 3 h. After reaching completion the reaction mixure was quenched with 1 N HCl (250 mL) and extracted with ethyl acetate (3 x 250 mL). The combined organics were washed with brine, dried over Na_2SO_4 and the solvent removed under vacuum. The crude material was recrystallized from ethyl acetate/hexanes to yield the title compound as a white crystalline powder in 70% yield (1.21 g, 4.98 mmol) mp = 193.2-195.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (d, *J* = 8.8 Hz, 2 H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.61 (m, 2H), 7.49 (m, 3H). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 14.0 (br s, 1H); 8.06 (m, 3 H), 7.81 (d, *J* = 6.8 Hz, 2H), 7.51 (m, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 166.08, 146.71, 144.83, 137.14, 129.83, 129.25, 129.16, 128.80, 127.47, 127.30, 124.69. FTIR (ATR, cm^{-1}): 2861 (br), 1694, 1519, 1349, 689, 753. HRMS (ESI) $[M-H]^-$ calcd. 242.04588 found 242.04705.

IV. Synthesis and Characterization of Substituted Benzoxazoles.

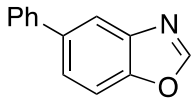
General procedure for the synthesis of substituted benzoxazoles. A mixture of the appropriately substituted 2-amino-phenol (7 mmol) and triethylorthoformate (20 mL, 120 mmol) was heated under reflux (at 150 °C). Upon completion, as determined by TLC, the triethylorthoformate was removed under vacuum and the product was purified by silica column chromatography eluting with hexanes/ethyl acetate to afford the title compound.



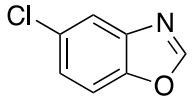
5-*tert*-butylbenzoxazole (1c). The title compound was synthesized according to the general procedure and isolated as a yellow oil in quantitative yield (3.38 g, 19.3 mmol) after purification by silica column chromatography (R_f = 0.64 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.07 (s, 1H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.46 (m, 2H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.75, 148.30, 148.12, 140.11, 123.52, 117.13, 110.20, 35.08, 31.92. The spectral data are consistent with those reported in the literature.[3,4]



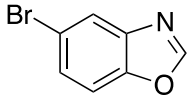
5-methoxybenzoxazole (1d). The title compound was synthesized according to the general procedure and isolated as a light pink solid in 92% yield (0.484 g, 3.25 mmol) after purification by silica column chromatography (R_f = 0.31 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 2.8 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.47, 153.34, 144.69, 140.97, 114.58, 111.16, 103.24, 56.01. The spectral data are consistent with those reported in the literature.[4]



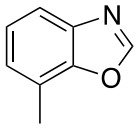
5-phenylbenzoxazole (1e). The title compound was synthesized according to the general procedure and isolated as a light pink solid in 76% yield (583 mg, 2.99 mmol) after purification by silica column chromatography (R_f = 0.57 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (s, 1H), 7.99 (m, 1H), 7.64 (m, 4H), 7.46 (m, 2H), 7.38 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.21, 149.60, 140.96, 140.78, 138.67, 129.01, 127.62, 127.47, 125.39, 119.18, 111.11. The spectral data are consistent with those reported in the literature.[3]



5-chlorobenzoxazole (1f). The title compound was synthesized according to the general procedure and isolated as a tan solid in 80% yield (4.29 g, 27.9 mmol) after purification by silica column chromatography (R_f = 0.60 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (s, 1H), 7.76 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.78, 148.67, 141.28, 130.29, 126.15, 120.72, 111.83. The spectral data are consistent with those reported in the literature.[3]

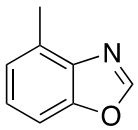


5-bromobenzoxazole (1g). The title compound was synthesized according to the general procedure and isolated as an orange solid in 62% yield (0.65 g, 3.28 mmol) after purification by silica column chromatography (R_f = 0.60 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.92 (d, *J* = 3.2 Hz, 1H), 7.47 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.62, 149.07, 141.71, 128.87, 123.73, 117.53, 112.33. The spectral data are consistent with those reported in the literature.[3]

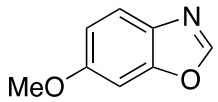


7-methylbenzoxazole (1h). The title compound was synthesized according to the general procedure and isolated as an orange solid in 55% yield (0.59 g, 4.43 mmol) after purification by silica column chromatography (R_f = 0.37 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400

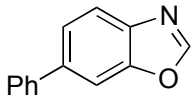
MHz): δ = 8.07 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.6, Hz 1 H), 7.15 (d, *J* = 7.6 Hz, 1H), 2.52 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.34, 149.30, 139.66, 126.54, 124.60, 121.66, 117.93, 15.28. The spectral data are consistent with those reported in the literature.[4]



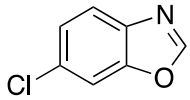
4-methylbenzoxazole (1i). The title compound was synthesized according to the general procedure and isolated as a light yellow oil in 12% yield (523.2 mg, 3.93 mmol) after purification by silica column chromatography (R_f = 0.41 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.17 (dt, *J* = 7.6, 0.8 Hz, 1H), 2.64 (s, 1H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.86, 149.83, 139.35, 131.13; 125.40, 125.18, 108.37, 16.59. The spectral data are consistent with those reported in the literature.[3]



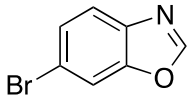
6-methoxybenzoxazole (1j). The title compound was synthesized according to the general procedure and isolated as a white solid in 72% yield (0.607 g, 4.07 mmol) after purification by silica column chromatography (R_f = 0.24 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.63, 151.70, 150.99, 133.78, 120.61, 113.78, 95.43, 56.00. The spectral data are consistent with those reported in the literature.[5]



6-phenylbenzoxazole (1k). The title compound was synthesized from 6-bromobenzoxazole **(2o)** and phenylboronic acid according to the following procedure: 6-bromobenzoxazole (1.01g, 5.01 mmol), phenylboronic acid (0.65 g, 5.29 mmol), Cs_2CO_3 (1.80g, 5.52 mmol), $Pd_2(dba)_3$ (38.9 mg, 0.038 mmol), tricyclohexylphosphine (46.3 mg, 0.17 mmol), were combined in a 50 mL Schlenk tube under N_2. Dioxane (15 mL) was added and the reaction mixture stirred under N_2 at 80°C for 1d. The crude reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. After removal of the solvent, the crude product was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.282 in 10% ethyl acetate in hexanes) followed by recrystallization from hexanes / ethyl acetate to give 329 mg (1.69 mmol, 33% y) of the title compound as a light pink solid (mp = 118.0-119.3°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (s 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.62 (m, 3H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.99, 150.74, 140.80, 139.74, 139.48, 129.05, 127.72, 127.63, 124.40, 120.61, 109.61. FTIR (ATR, cm^{-1}): 3092, 1507, 1471, 1426, 1076, 828, 767, 754, 699. HRMS (ESI) $[M+H]^+$ calcd. 196.07264, found 196.07563.



6-chlorobenzoxazole (1l). The title compound was synthesized according to the general procedure and isolated as a white solid in 62% yield (662 mg, 4.31 mmol) after purification by silica column chromatography (R_f = 0.33 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.09 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.13, 150.28, 138.92, 131.56, 125.54, 121.27, 111.77. The spectral data are consistent with those reported in the literature.[6]

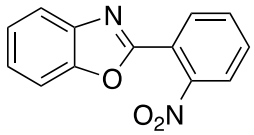


6-bromobenzoxazole (1m). The title compound was synthesized according to the general procedure and isolated as a light pink solid in 48% yield (2.5 g, 12.6 mmol) after purification by silica column chromatography (R_f = 0.33 in 10:1 hexanes:ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ =153.00, 150.59, 139.35, 128.27, 121.74, 118.89, 114.68. The spectral data are consistent with those reported in the literature.[7]

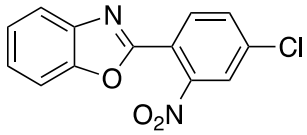
V. Representative Procedure for the Decarboxylative Arylation of Benzoxazoles with Benzoic Acids. 2-nitrobenzoic acid (99 mg, 0.6 mmol), CuCl (6 mg, 0.06 mmol), phen (11 mg, 0.06 mmol), Cs_2CO_3 (195 mg, 0.6 mmol), Ag_2O (279 mg, 1.2 mmol), and 4Å molecular sieves (600 mg), were combined in a 50 mL Schlenk tube fitted with a septum and a stir bar. The tube was evacuated and backfilled with N_2 three times before a solution of benzoxazole (107 mg, 0.9 mmol) in dry DMF (6.0 mL, 0.15 M) was added. The reaction mixture was stirred under N_2 at 110°C for 23 h. Upon completion, the mixture was cooled to room temperature and diluted with EtOAC (40 mL). The mixture was filtered through celite and the solvent removed (by rotary evaporation to ~6 mL, then by vacuum line). The crude mixture was purified by silica column chromatography to yield the title compound in 68% yield (97.9 mg, 0.41 mmol).

VI. Characterization of Decarboxylative Arylation Products.

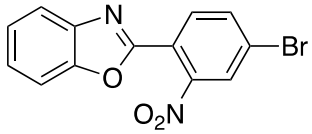
<u>Arylation Products in Table 2 (3aa-3al)</u>



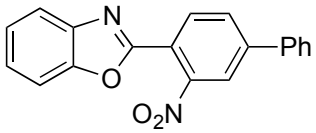
2-(2-nitrophenyl)-benzoxazole (3aa). The crude material was purified by silica column chromatography (10% ethyl acetate in hexanes, R_f = 0.18 in 10% ethyl acetate in hexanes to yield 97.9 mg (0.41 mmol, 68% y) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.83 (m, 1H), 7.71 (m, 2H), 7.58 (m, 1H), 7.40 (m, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.93, 151.17, 149.34, 141.69, 132.48, 131.98, 131.56, 126.17, 125.09, 124.35, 121.65, 120.85, 120.81, 111.09. The spectral data are consistent with those reported in the literature.[7]



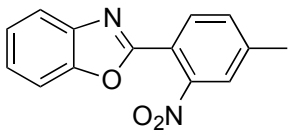
2-(4-chloro-2-nitrophenyl)-benzoxazole (3ab). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.55 in 10% ethyl acetate in hexanes) to yield 137.0 mg (0.49 mmol, 81% y) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.81 (m, 1H), 7.71 (dd, *J* = 8.0 Hz, 2.0, 1H), 7.57 (m, 1H), 7.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.83,151.05, 149.49, 141.56, 138.06, 132.51, 132.35, 126.38, 125.21, 124.56, 120.88, 119.69, 111.07. The spectral data are consistent with those reported in the literature.[7]



2-(4-bromo-2-nitrophenyl)-benzoxazole (3ac). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.55 in 10% ethyl acetate in hexanes) to yield 145.5 mg (0.46 mmol, 76% y) of the title compound as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.81 (m, 1H), 7.59 (m, 1H), 7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.75, 150.88, 149.25, 141.40, 135.32, 132.24, 127.17, 126.25, 125.61, 125.08, 120.73, 119.90, 110.93. The spectral data are consistent with those reported in the literature.[7]

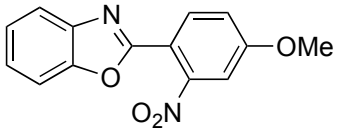


2-(4-phenyl-2-nitrophenyl)-benzoxazole (3ad). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.04 in 5% ethyl acetate in hexanes) to yield 129.6 mg (0.41 mmol, 54% y) of the title compound as a white solid (mp = 96.3-97.1°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.31 (d, *J* = 2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.4, 2 Hz, 1H), 7.83 (m, 1H), 7.67 (m, 2H), 7.59 (m, 1H), 7.49 (m, 3 H), 7.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.20, 151.16, 147.84, 145.91, 141.61, 137.88, 130.18, 130.07, 129.37, 129.31, 127.48, 126.16, 125.14, 125.07, 122.38, 120.77, 111.09. FTIR (ATR, cm^{-1}): 1534, 1450, 1356, 1240, 760, 743, 730, 696. HRMS (ESI) $[M+H]^+$ calcd. 317.09262, found 317.09195.

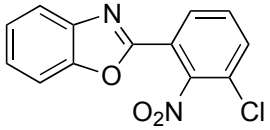


2-(4-methyl-2-nitropheny)-benzoxazole (3ae). The crude material was purified by silica column chromatography (gradient elution of 5% ethyl acetate in hexanes to 100% ethyl acetate, R_f = 0.08 in 5% ethyl acetate in hexanes) to yield 70.5 mg (0.277 mmol, 46% y) of the title compound as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, *J* = 8.0 Hz, 1H), 7.77 (m, 1H), 7.79 (m, 1H), 7.63 (d, *J* =0.8 Hz, 1H), 7.50 (m, 2H), 7.35 (m, 2H), 2.48 (s, 3H). ^{13}C NMR

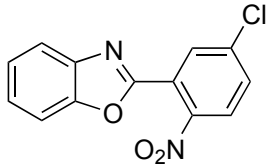
($CDCl_3$, 100 MHz): δ = 158.98, 150.91, 149.11, 143.26, 141.59, 132.95, 131.11, 125.84, 124.86, 124.56, 120.60, 120.54, 118.46, 110.86. The spectral data are consistent with those reported in the literature.[7]



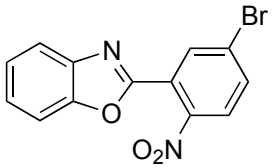
2-(4-methoxy-2-nitrophenyl)-benzoxazole (3af). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.21 in 10% ethyl acetate in hexanes) to yield 34.1 mg (0.13 mmol, 21%) of the title compound as an orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, *J* = 4.4 Hz, 1 H), 7.75 (m, 1H), 7.52 (m, 1H), 7.34 (m, 3 H), 7.19 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.92 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.09, 159.03, 150.97, 150.34, 141.74, 132.64, 125.71, 124.87, 120.49, 117.90, 113.38, 110.87, 109.86, 56.29. The spectral data are consistent with those reported in the literature.[7]



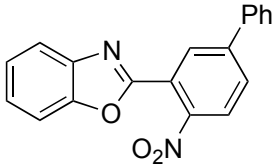
2-(3-chloro-2-nitrophenyl)-benzoxazole (3ag). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.13 in 5% ethyl acetate in hexanes) to yield 36.9 mg (0.13 mmol, 19% y) of the title compound as a yellow solid (mp = 126.5-128.6°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 (t, *J* = 8.4 Hz, 2H), 7.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.69, 150.75, 141.59, 133.11, 131.05, 128.28, 126.83, 126.67, 125.34, 121.20, 120.91, 111.07, 110.15. FTIR (ATR, cm^{-1}): 2926, 1546, 1371, 743. HRMS (ESI) $[M+H]^+$ calcd. 275.02234, found 275.02169.



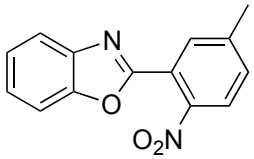
2-(3-chloro-6-nitrophenyl)-benzoxazole (3ah). The crude material was purified by silica column chromatography (gradient elution of 2% ethyl acetate in hexanes to 20% ethyl acetate in hexanes, R_f = 0.32 in 10% ethyl acetate in hexanes) to yield 28.8 mg (0.10 mmol, 18% y) of the title compound as a tan solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.82 (m, 1H), 7.64 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.58 (m, 1H), 7.42 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.68, 151.16, 147.43, 141.50, 138.94, 131.83, 131.15, 126.55, 125.78, 125.30, 123.24, 121.00, 111.17. The spectral data are consistent with those reported in the literature.[7]



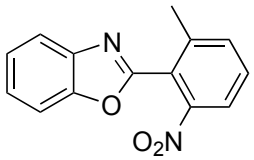
2-(3-bromo-6-nitrophenyl)-benzoxazole (3ai). The crude material was purified by silica column chromatography (gradient elution of 2% ethyl acetate in hexanes to 10% ethyl acetate in hexanes, R_f = 0.39 in 10% ethyl acetate in hexanes) to yield 67.1 mg (0.35 mmol, 59% y) of the title compound as a light orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (d, *J* =2.0 Hz, 1H), 7.79 (m, 3H), 7.57 (m, 1H), 7.41 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.46, 151.08, 147.85, 141.44, 134.82, 134.26, 126.87, 126.50, 125.71, 125.25, 123.09, 120.93, 111.10.
The spectral data are consistent with those reported in the literature.[7]



2-(5-phenyl-2-nitrophenyl)-benzoxazole (3aj). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.04 in 5% ethyl acetate in hexanes) to yield 131.9 mg (0.42 mmol, 70% y) of the title compound as a light tan solid (mp = 98.3-101.4°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.24 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 1.6 Hz, 1H), 7.94 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.83 (m, 1H), 7.66 (m, 2H), 7.59 (m, 1H), 7.51 (m, 3H), 7.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.75, 151.09, 149.75, 145.28, 141.73, 137.65, 131.79, 130.39, 129.44, 129.37, 127.25, 126.10, 125.05, 122.57, 120.77, 119.61, 111.02. FTIR (ATR, cm^{-1}): 2964, 1550, 1521, 1450, 1344, 1243, 1055, 740, 694. HRMS (ESI) $[M+H]^+$ calcd. 317.09262, found 317.09194.

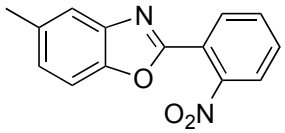


2-(5-methyl-2-nitrophenyl)-benzoxazole (3ak). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.37 in 10% ethyl acetate in hexanes) to yield 29.6 mg (0.116 mmol, 19% y) of the title compound as a yellow solid (mp = 115.2-116.3°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, *J* = 1.2 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.82 (m, 1H), 7.57 (m, 1H), 7.47 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.40 (m, 2H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.49, 151.22, 147.11, 143.97, 141.64, 132.37, 132.22, 126.05, 125.02, 124.62, 121.92, 120.74, 111.08, 21.49. The spectral data are consistent with those reported in the literature.[7]

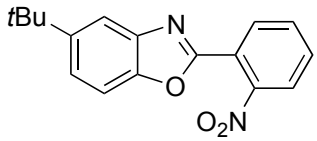


2-(2-methyl-6-nitrophenyl)-benzoxazole (3al). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.28 in 20% ethyl acetate in hexanes) to yield 56.5 mg (0.22 mmol, 37% y) of the title compound as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.81 (m, 1H), 7.59 (m, 3H), 7.40 (m, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.77, 151.01, 149.70, 141.69, 141.56, 135.54, 131.19, 125.80, 124.87, 123.07, 122.41, 120.68, 111.08, 20.15. The spectral data are consistent with those reported in the literature.[7]

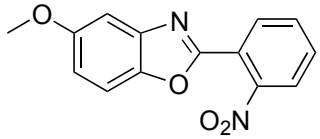
Arylation Products in Table 3 (3ba-3ma)



5-methyl-2-(2-nitrophenyl)-benzoxazole (3ba). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.18 in 10% ethyl acetate in hexanes) to yield 103.4 mg (0.41 mmol, 68% y) of the title compound as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (dd, *J*= 7.2, 1.6 Hz, 1H), 7.86 (dd, *J*= 8.0, 1.2 Hz, 1H), 7.67 (m, 2H), 7.57 (d, *J*= 0.8 Hz, 1H), 7.42 (d, *J*= 8.4 Hz, 1H), 7.19 (dd, *J*= 8.8, 1.2 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.78, 149.28, 141.72, 134.84, 132.26, 131.67, 131.32, 127.16, 125.66, 124.12, 121.58, 120.48, 110.26, 21.47. The spectral data are consistent with those reported in the literature.[7]

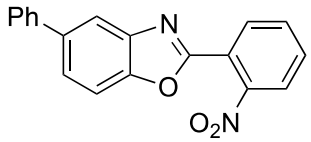


5-*tert*-butyl-2-(2-nitrophenyl)-benzoxazole (3ca). The crude material was purified by silica column chromatography (15:1 hexanes: ethyl acetate, R_f = 0.19 in 10:1 hexanes:ethyl acetate) to yield 71 mg (0.24 mmol, 44% y) of the title compound as a light yellow solid (mp = 63.6-64.7°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.85 (m, 2H), 7.68 (m, 2H), 7.48 (m, 2H), 1.39 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.90, 149.30, 149.16, 148.68, 141.62, 132.38, 131.80, 131.14, 124.23, 124.40, 121.67, 117.25, 110.18, 35.13, 31.87. FTIR (ATR, cm^{-1}): 2961, 1537, 1375, 1041, 815, 760, 696. HRMS (ESI) $[M+H]^+$ calcd. 279.12392, found 297.12339.

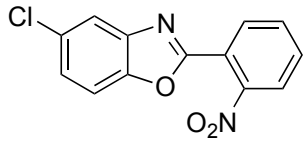


5-methoxy-2-(2-nitrophenyl)-benzoxazole (3da). The crude material was purified by silica column chromatography (12% ethyl acetate in hexanes, R_f = 0.50 in 1:1 hexanes:ethyl acetate) to

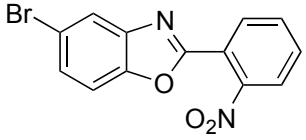
yield 100.4 mg (0.37 mmol, 62% y) of the title compound as a pink solid (mp = 175.4-175.6°C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.20 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 1.6 Hz, 1H), 7.92 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.50 (m, 4 H), 7.29 (d, J = 2.8 Hz, 1H), 7.00 (dd, J = 8.8, 2.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 158.70, 157.25, 148.63, 144.85, 141.90, 132.97, 132.80, 130.87, 124.33, 119.72, 114.89, 111.35, 103.08, 55.83. FTIR (ATR, cm^{-1}): 1539, 1484, 1379, 1264, 1188, 1146, 1025, 828, 799, 764, 692. HRMS (ESI) $[M+H]^+$ calcd. 271.07188, found 271.07127.



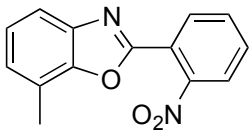
5-phenyl-2-(2-nitrophenyl)-benzoxazole (3ea). The crude material was purified by silica column chromatography (20:1 hexanes:ethyl acetate, R_f = 0.21 in 10:1 hexanes:ethyl acetate) to yield 132.9 mg (0.42 mmol, 70% y) of the title compound as a white solid (mp = 116.0-117.3°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (dd, J = 6.8, 1.2 Hz, 1H), 8.01 (dd, J = 1.6, 0.8 Hz, 1H), 7.90 (dd, J = 8.0, 1.6 Hz, 1H), 7.70 (m, 2H), 7.63 (m, 4H), 7.47 (m, 2H), 7.38 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.50, 159.40, 150.55, 149.17, 142.21, 140.78, 138.89, 132.46, 132.00, 131.42, 128.99, 127.51, 125.72, 124.26, 121.34, 119.08, 111.02. FTIR (ATR, cm^{-1}): 3059, 1534, 1367, 762, 701. HRMS (ESI) $[M+H]^+$ calcd. 317.09262, found 317.09216.



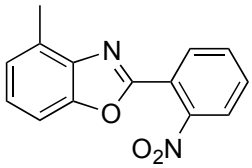
5-chloro-2-(2-nitrophenyl)-benzoxazole (3fa). The crude material was purified by silica column chromatography (20:1 hexanes:ethyl acetate, R_f = 0.19 in 10:1 hexanes:ethyl acetate) to yield 79.2 mg (0.29 mmol, 48% y) of the title compound as a yellow solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 7.75 (dd, J = 6.4, 2.0 Hz, 1H), 7.70 (dd, J = 6.8 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.48 (m, 2H), 7.42 (d, J = 8.8 Hz, 1H), 7.09 (dd, J = 8.8, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.77, 149.11, 148.62, 142.13, 133.34, 133.28, 131.33, 129.48, 126.44, 124.55, 120.05, 119.46, 112.60. The spectral data are consistent with those reported in the literature.[7]



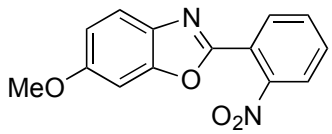
5-bromo-2-(2-nitrophenyl)-benzoxazole (3ga). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.28 in 10% ethyl acetate in hexanes) to yield 131.7 mg (0.41 mmol, 69% y) of the title compound as a light orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (dd, J = 7.6, 2.0 Hz, 1H), 7.96 (d, J = 1.6 Hz, 1H), 7.92 (dd, J = 7.6, 1.2 Hz, 1H), 7.74 (m, 2H), 7.52 (dd, J = 8.8, 2.0 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.13, 150.15, 149.30, 143.20, 132.64, 132.36, 131.67, 129.24, 124.48, 123.82, 121.22, 117.91, 112.33. The spectral data are consistent with those reported in the literature.[7]



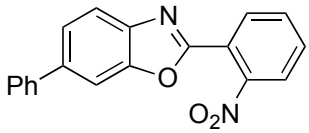
7-methyl-2-(2-nitrophenyl)-benzoxazole (3ha). The crude material was purified by silica column chromatography (gradient elution of 5% ethyl acetate in hexanes to 10% ethyl acetate in hexanes, R_f = 0.21 in 10% ethyl acetate in hexanes) to yield 71.6 mg (0.28 mmol, 47% y) of the title compound as a white solid (mp = 136.9-138.1°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.23 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.43, 150.27, 149.19, 141.07, 132.25, 131.70, 131.33, 126.90, 124.86, 124.12, 121.66, 121.56. 117.93, 15.06. FTIR (ATR, cm^{-1}): 2923, 1545, 1374, 770, 749, 698. HRMS (ESI) $[M+H]^+$ calcd. 255.07697, found 255.07640.



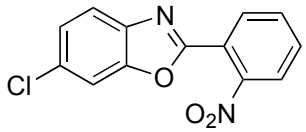
4-methyl-2-(2-nitrophenyl)-benzoxazole (3ia). The crude material was purified by silica column chromatography (17:1 hexanes : ethyl acetate, R_f = 0.20 in 10:1 hexanes:ethyl acetate) to yield 69.9 mg (0.27 mmol, 46% y) of the title compound as a white solid (mp =104.3-108.8°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.12 (dd, *J* = 7.6 Hz, 1.6, 1H), 7.90 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.70 (m, 2H), 7.38 (dq, *J* = 8.4, 0.8 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.18 (dquint, *J* = 7.2, 1.2 Hz, 1H), 2.66 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.27, 151.00, 149.26, 141.02, 132.55, 131.81, 131.82, 131.41, 125.84, 125.54, 124.38, 124.37, 122.07, 108.34, 16.65. FTIR (ATR, cm^{-1}): 2919, 1527, 1376, 1240, 1030, 777, 749, 696. HRMS (ESI) $[M+H]^+$ calcd. 255.07697, found 255.07640.



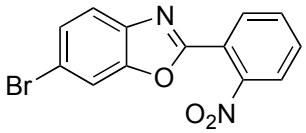
6-methoxy-2-(2-nitrophenyl)-benzoxazole (3ja). The crude material was purified by silica column chromatography (17:1 hexanes:ethyl acetate R_f = 0.20 in 5:1 hexanes:ethyl acetate) to yield 96.8 mg (0.36 mmol, 60% y) as a yellow solid (mp = 148.1-150.7°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.70 (m, 3H); 7.07 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.01, 157.78, 152.08, 149.08, 135.38, 132.36, 131.58, 131.15, 124.19, 121.45, 120.81, 113.86, 95.30, 56.06. FTIR (ATR, cm^{-1}): 3018, 2831, 1738, 1533, 1327, 1373, 1023, 820, 764, 691. HRMS (ESI) $[M+H]^+$ calcd. 271.07188, found 271.07135.



6-phenyl-2-(2-nitrophenyl)-benzoxazole (3ka). The crude material was purified by silica column chromatography (gradient elution of 2% ethyl acetate in hexanes to 5% ethyl acetate in hexanes, R_f =0.18 in 10% ethyl acetate in hexanes) to yield 16.6 mg (0.05 mmol, 9% y) of the title compound as a tan solid (mp = 148.4-149.3 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.91 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.24 (m, 3H), 7.66 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.27, 151.82, 149.35, 141.03, 140.74, 140.14, 132.49, 132.00, 131.52, 129.10, 127.82, 127.63, 124.78, 124.37, 121.58, 120.78, 109.54. FTIR (ATR, cm^{-1}): 3274, 1764, 1733, 1481, 761, 699.

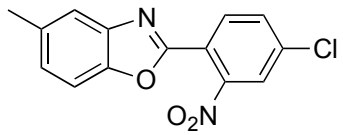


6-chloro-2-(2-nitrophenyl)-benzoxazole (3la). The crude material was purified by silica column chromatography (20:1 hexanes: ethyl acetate, R_f = 0.21 in 10:1 hexanes:ethyl acetate) to yield 79.2 mg (0.29 mmol, 48% y) of the title compound as a yellow solid. ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 8.14 (m, 2H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.90 (m, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.60, 151.00, 148.97, 140.31, 133.82, 133.76, 131.72, 131.20, 126.30, 124.96, 121.75, 119.88, 112.15. The spectral data are consistent with those reported in the literature.[7]

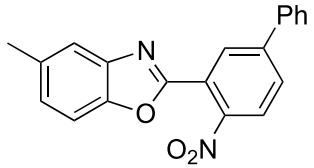


6-bromo-2-(2-nitrophenyl)-benzoxazole (3ma). The crude material was purified by silica column chromatography (16:1 hexanes:ethyl acetate, R_f = 0.11 in 10:1 hexanes:ethyl acetate) to yield 80.2 mg (0.25 mmol, 42% y) of the title compound as a light yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.66-7.77 (m, 4H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.39, 151.52, 149.25, 140.86, 132.57, 132.28, 131.52, 128.62, 124.43, 121.78, 121.13, 119.23, 114.60. The spectral data are consistent with those reported in the literature.[7]

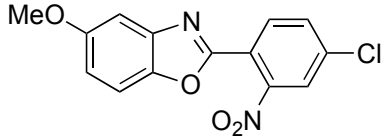
<u>Arylation Proudcts in Table 4 (3bb-3jj)</u>



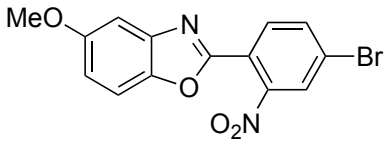
5-methyl-2-(4-chloro-2-nitrophenyl)-benzoxazole (3bb). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.50 in 10% ethyl acetate in hexanes) to yield 100.3 mg (0.35 mmol, 51% y) of the title compound as a tan solid (mp = 100.1-101.5°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.97, 149.59, 149.47, 141.89, 138.00, 135.28, 132.56, 132.41, 127.68, 124.62, 120.78, 119.96, 110.53, 21.72. FTIR (ATR, cm^{-1}): 1541, 1476, 1361, 1197, 801. HRMS (ESI) $[M+H]^+$ calcd. 289.03799, found 289.03741.



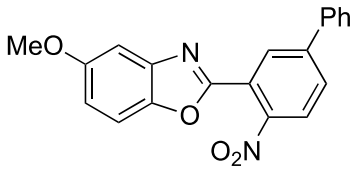
5-methyl-2-(4-phenyl-2-nitrophenyl)-benzoxazole (3bj). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.41 in 10% ethyl acetate in hexanes) to yield 131 mg (0.40 mmol, 60% y) of the title compound as a light yellow solid (mp = 94.0-94.9°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.30 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.68 (m, 2H), 7.62 (m, 1H), 7.50 (m 4H), 7.22 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.76, 149.70, 149.36, 145.11, 141.93, 137.68, 134.94, 131.71, 130.31, 129.42, 129.32, 127.27, 127.23, 122.50, 120.57, 119.73, 110.36, 21.61. FTIR (ATR, cm^{-1}): 2920, 1530, 1354, 853, 812, 762, 732, 696. HRMS (ESI) $[M+H]^+$ calcd. 331.10827, found 331.10756.



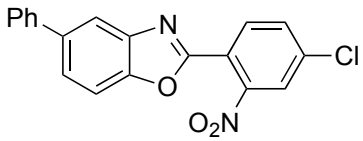
5-methoxy-2-(4-chloro-2-nitrophenyl)-benzoxazole (3db). The crude material was purified by silica column chromatography (15:1 hexanes:ethyl acetate, R_f = 0.18 in 5:1 hexanes:ethyl acetate) to yield 139.6 mg (0.46 mmol, 77% y) of the title compound as a light orange solid (mp = 150.1-151.0 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 2.8 Hz, 1H), 6.99 (dd, *J* = 8.8 Hz, 2.4, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.33, 157.84, 149.41, 145.70, 142.43, 137.87, 132.39, 132.11, 124.45, 119.57, 115.49, 111.24, 103.20, 56.06. FTIR (ATR, cm^{-1}): 3016, 1541, 1363, 1277, 1196, 1149, 880, 827, 810. HRMS (ESI) $[M+H]^+$ calcd. 305.03291, found 305.03223.



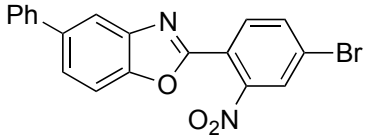
5-methoxy-2-(4-bromo-2-nitrophenyl)-benzoxazole (3dc). The crude material was purified by silica column chromatography (15:1 hexanes:ethyl acetate, R_f = 0.18 in 5:1 hexanes:ethyl acetate) to yield 109.3 mg (0.31 mmol, 52% y) as a light orange solid (mp = 167.9-169.0°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (d, *J*, = 8.4 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.46, 157.87, 149.38, 145.75, 142.47, 135.39, 132.21, 127.28, 125.61, 120.04, 115.56, 111.29, 103.24, 56.10. FTIR (ATR, cm^{-1}): 3076, 1540, 1483, 1433, 1364, 1277, 1196, 1149, 827, 809. HRMS (ESI) $[M+H]^+$ calcd. 348.98239, found 348.98169.



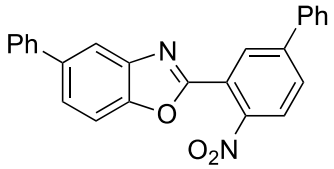
5-methoxy-2-(5-phenyl-2-nitrophenyl)-benzoxazole (3dj). The crude material was purified by silica column chromatography (12:1 hexanes:ethyl acetate, R_f = 0.08 in 10:1 hexanes:ethyl acetate) to yield 104.5 mg (0.30 mmol, 50% y) of the title compound as a yellow solid (mp = 146.5-147.1°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.20 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.50 (m, 4H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.33, 157.78, 149.73, 145.81, 145.20, 142.63, 137.74, 131.61, 130.34, 129.47, 129.37, 127.29, 122.55, 119.60, 115.19, 111.22, 103.25, 56.11. FTIR (ATR, cm^{-1}): 2935, 1529, 1477, 1363, 1184, 1150, 1023, 759, 695. HRMS (ESI) $[M+H]^+$ calcd. 347.10318, found 347.10253.



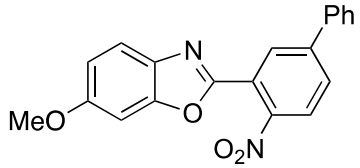
5-phenyl-2-(4-chloro-2-nitrophenyl)-benzoxazole (3eb). The crude material was purified by silica column chromatography (12:1 hexanes:ethyl acetate, R_f = 0.21 in 5:1 hexanes:ethyl acetate) to yield 104.3 mg (0.30 mmol, 50% y) of the title compound as a white solid (mp = 176.5-177.9°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 0.8 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.72 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.63 (m, 4H), 7.47 (t, *J* = 8.4 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.46, 150.62, 149.54, 142.23, 140.82, 139.23, 138.18, 132.58, 132.41, 129.07, 127.62, 126.07, 125.42, 124.64, 119.69, 119.28, 111.18. FTIR (ATR, cm^{-1}): 3084, 1538, 1363, 1042, 766, 704. HRMS (ESI) $[M+H]^+$ calcd. 351.05364, found 351.05298.



5-phenyl-2-(4-bromo-2-nitrophenyl)-benzoxazole (3ec). The crude material was purified by silica column chromatography (30:1 hexanes:ethyl acetate, R_f = 0.21 in 5:1 hexanes:ethyl acetate) to yield 96.5 mg (0.24 mmol, 41% y) of the title compound as an orange solid (mp = 175.3-177.3°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (m, 2H), 7.86 (dd, *J* = 8.4, 2 Hz, 1H), 7.62 (m, 4H), 7.47 (m, 2H), 7.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.50, 150.57, 149.42, 142.20, 140.75, 139.18, 135.51, 132.41, 129.04, 127.57, 127.37, 126.05, 125.85, 125.38, 120.02, 119.23, 111.09. FTIR (ATR, cm^{-1}): 3076, 1531, 1466, 1361, 815, 755, 696. HRMS (ESI) $[M+H]^+$ calcd. 395.00313, found 395.00240.



5-phenyl-2-(5-phenyl-2-nitrophenyl)-benzoxazole (3ej). The crude material was purified by silica column chromatography (12:1 hexanes:ethyl acetate R_f = 0.15 in 5:1 hexanes:ethyl acetate) to yield 112.6 mg (0.29 mmol, 48% y) of the title compound as a yellow solid (mp = 169.4 – 170.5°C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.34 (d, *J* = 2.0 Hz, 1H), 8.03 (m, 2 H), 7.88 (dd, *J* = 8.4, 2 Hz, 1H), 7.69 (m, 2H), 7.64 (m, 4H), 7.50 (m, 5H), 7.39 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.77, 150.70, 147.86, 145.91, 142.27, 140.89, 139.00, 137.87, 130.15, 130.10, 129.327, 129.31, 129.02, 127.59, 127.52, 127.47, 125.79, 125.13, 122.30, 119.15, 111.08. FTIR (ATR, cm^{-1}): 3031, 1519, 1346, 755, 746, 689. HRMS (ESI) $[M+H]^+$ calcd. 393.12393, found 393.12409.



6-methoxy-2-(5-phenyl-2-nitrophenyl)-benzoxazole (3jj). The crude material was purified by silica column chromatography (5% ethyl acetate in hexanes, R_f = 0.39 in 10% ethyl acetate in hexanes) to yield 182.5 mg (0.53 mmol, 87% y) of the title compound as an oily orange solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.31 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 8.54 Hz, 2H), 7.48 (m, 2H), 7.02 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.71, 157.81, 147.91, 145.88, 142.54, 138.05, 130.07, 130.00, 129.40, 129.31, 127.53, 125.09, 122.38, 115.22, 111.31, 111.11, 103.31, 56.15. FTIR (ATR, cm^{-1}): 2921, 1483, 1530, 1152, 732. HRMS (ESI) $[M+H]^+$ calcd. 347.10318, found 347.10247.

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(1) Gottlieb, H. E.; Kotlyar, V.; Abraham, N. *J. Org. Chem.* **1997**, *62*, 7512-7515.
(2) Pellicani, R. Z.; Stefanachi, A.; Niso, M.; Carotti, A.; Leonetti, F.; Nicolotti, O.; Perrone, R.; Berardi, F.; Cellamare, S.; Colabufo, N. A. *J. Med. Chem.* **2012**, *55*, 424-436.
(3) Guo, S.; Qian, B.; Xie, Y.; Xia, C.; Huang, H. *Org. Lett.* **2011**, *13*, 522-525.
(4) Lee, J. J.; Kim, J.; Jun, Y. M.; Lee, B. M.; Kim, B. H. *Tetrahedron. Lett.* **2009**, *65*, 8821-8831.
(5) Filloux, C. M.; Rovis, T. *J. Am. Chem. Soc.* **2015**, *137*, 508-517.
(6) Liu, Q.; Wu, P.; Yang, Y.; Zeng, Z.; Liu, J.; Yi, H.; Lei, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 4666-4670.
(7) Yang, K.; Wang, P.; Zhang, C.; Kadi, A. A.; Fun, H.-K.; Zhang, Y.; Lu, H. *Eur. J. Org. Chem.* **2014**, 7586-7589.