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SYNTHESIS OF 5-SUBSTITUTED 7-AZAOXINDOLES *VIA* PALLADIUM-CATALYZED REACTIONS

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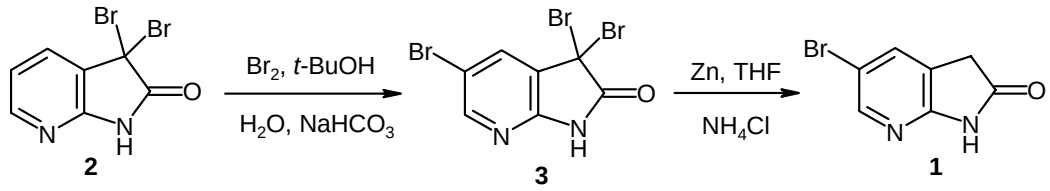
Abstract - A synthesis of 5-substituted 1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-ones (5-substituted 7-azaoxindoles) *via* palladium-catalyzed Suzuki coupling, Stille coupling, and carbonylation reactions is described.

Azaoxindoles have attracted considerable interest in medicinal chemistry as a useful scaffold for generating potential drug molecules.[1,2] During our effort in developing structure-activity relationships of oxindoles as c-Raf1 kinase inhibitors,[3] we discovered that the oxindole ring core can be replaced by 7-azaoxindole.[4,5] We knew from our earlier work on oxindoles that introduction of diverse substitutions at the 5-position led to improvement in their physical properties without sacrificing potency of their biological activities. Thus, we decided to also incorporate substitution at the 5-position of the 7-azaoxindole. Synthesis of 7-azaoxindole has been disclosed;[6] however, on the onset of our program, synthesis of 5-substituted 7-azaoxindole was relatively unknown. Herein we report the synthesis of 5-substituted 7-azaoxindole *via* palladium-catalyzed coupling reactions that allow diverse modifications at the 5-position of the 5-bromo-7-azaoxindole (**1**).

Scheme 1

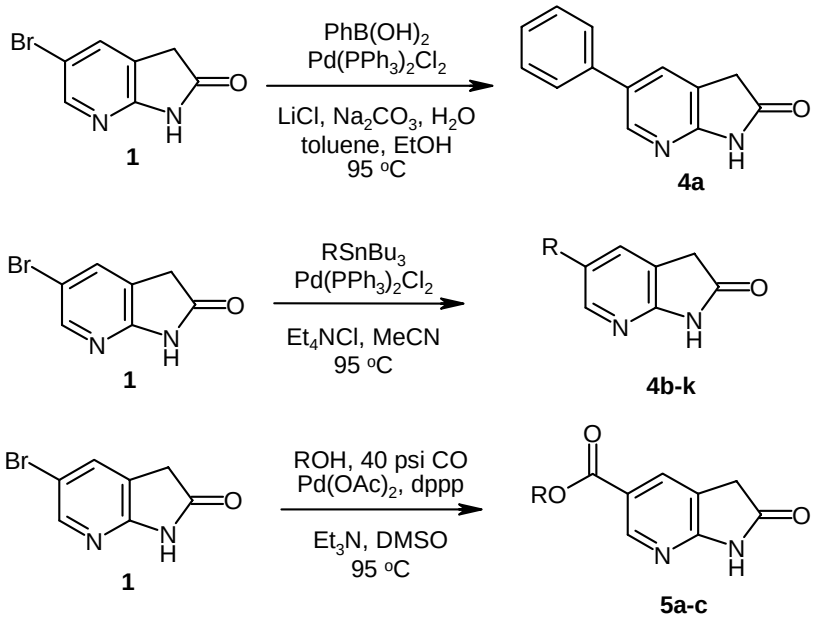


As outlined in Scheme 1, 3,3-dibromo-7-azaxoindole (**2**)[6] was brominated in the presence of bromine and sodium bicarbonate solution in *tert*-butanol at pH 6.5-7 to give 3,3,5-tribromo-7-azaoxindole (**3**) in 98% yield.[7] Facile reduction of **3** in the presence of excess zinc dust in a saturated ammonium chloride and

THF solution provided **1** in quantitative yield. Alternatively, compound (**1)** can be obtained *via* a two-step sequence from 7-azaindole (bromination and reduction) as reported by Viaud *et al*. in 80% overall yield.[8]

As shown in Scheme 2, palladium-catalyzed Suzuki, Stille and carbonylation reactions were employed to introduce substitution at the 5-position of 5-bromo-7-azaoxindole (**1**).[9] Suzuki coupling reaction of **1** was carried out with $PhB(OH)_2$ under several standard conditions such as [$Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$, Na_2CO_3, toluene/EtOH, reflux], [$Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$, Na_2CO_3, Et_4NCl, MeCN, reflux], and [$Pd(OAc)_2$, dppf, Et_3N, DMF, 95 ^oC]. In all cases, the reactions were sluggish and incomplete, and only 0-5% product was obtained. The addition of LiCl was found to be crucial for the success of the Suzuki reaction. When LiCl (3 eqv.) was added to the reaction conditions [**1**, $PhB(OH)_2$, $Pd(PPh_3)_2Cl_2$, Na_2CO_3, LiCl, toluene/EtOH, 95 ^oC, 18 h], a complete Suzuki transformation was observed. As illustrated in Table 1, compound (**4a**) was obtained from **1** in 51% yield.

Scheme 2



Stille coupling reaction of **1** could be achieved with most tin reagents in 36-66% yield [$RSnBu_3$, $Pd(PPh_3)_2Cl_2$, Et_4NCl, MeCN, 95 ^oC, 22 h].[10] However, compounds (**4g**, **4h** and **4i**) were isolated in poor yield (23, 28 and 12% respectively), and we did not observe any product formation (**4j** and **4k**) when electron deficient tin reagents such as 2-tributylstannylpyrazine and 5-tributylstannylpyrimidine were used (Entries 9 and 10).

Ester functionality at the 5-position of **1** can be readily incorporated *via* palladium-catalyzed carbonylation reaction in the presence of alcohol in 24-53% yield [ROH, 40 psi CO, $Pd(OAc)_2$, dppp, Et_3N, DMSO, 95 ^oC, 18 h]. High pressure and high temperature were required for the carbonylation

reaction of **1** because we did not observe any product formation when the reaction was carried out with an atmospheric pressure of carbon monoxide or when the reaction was carried out at room temperature.

Table I. Synthesis of 5-Sustituted 7-Azaoxindole *via* Palladium-Catalyzed Reactions.

Entry	Product	R	Reagent	Procedure[a]	Yield (%)[b]
1	**4a**	Ph	$PhB(OH)_2$	A	51
2	**4b**	PhC≡C	$PhC{\equiv}CSnBu_3$	B	66
3	**4c**	1-Ethoxyvinyl	(1-Ethoxyvinyl)$SnBu_3$	B	55
4	**4d**	COMe	(1-Ethoxyvinyl)$SnBu_3$	B	25[c]
5	**4e**	4-Benzenesulfonamide	(4-Benzenesulfonamide)$SnBu_3$[11]	B	29
6	**4f**	2-Furan	(2-Furyl)$SnBu_3$	B	36
7	**4g**	3-Pyridine	(3-Pyridinyl)$SnBu_3$	B	23
8	**4h**	2-Thiophene	(2-Thienyl)$SnBu_3$	B	28
9	**4i**	3-Thiophene	(3-Thienyl)$SnBu_3$	B	12
10	**4j**	2-Pyrazine	(2-Pyrazinyl)$SnBu_3$	B	0
11	**4k**	5-Pyrimidine	(5-Pyrimidinyl)$SnBu_3$	B	0
12	**5a**	Et	EtOH	C	26
13	**5b**	*i*-Bu	*i*-BuOH	C	53
14	**5c**	Benzyl	$PhCH_2OH$	C	24

a) Typical procedures are provided in the experimental procedure session. Procedure A is the Suzuki reaction, Procedure B is the Stille reaction, and Procedure C is the carbonylation reaction. *b)* Satisfactory spectroscopic data were obtained for all products. *c*) Compound (**4d**) was isolated from **4c** during silica gel column chromatography purification.

In conclusion, we have developed facile procedures of introducing diverse substitutions at the 5-position of the readily available 5-bromo-7-azaoxindole (**1**) *via* palladium-catalyzed Suzuki coupling, Stille coupling and carbonylation reactions.

EXPERIMENTAL

Melting points were determined on a Mel-temp II apparatus and are uncorrected. Proton NMR spectra were obtained with a VARIAN Unity Plus NMR spectrophotometers at 300 or 400 MHz. IR spectra were obtained with a Bruker DuraScope Vector 22. MS spectra were recorded on a Micromass Platform II mass spectrometers using either Atmospheric Chemical Ionization (APCI) or Electrospray Ionization

(ESI). Microanalysis data were obtained from Atlantic MicroLab, Inc. in Georgia, U.S.A. Organic solvents and reagents were purchased and used without further purification. All anhydrous reactions were performed in oven-dried glassware under an atmosphere of argon or nitrogen. All solutions were dried over anhydrous magnesium sulfate and evaporated on a Büchi rotatory evaporator. Analytical TLC was carried out on precoated plates (Merck Silica Gel 60 F-254), and spots were visualized with UV light. Column chromatography was performed on Merck Silica gel 60 (230-400 mesh) with stated solvent system under pressure.

5-Phenyl-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4a)

To a stirred mixture of **1** (213 mg, 1.0 mmol) and $PhB(OH)_2$ (183 mg, 1.5 mmol) in toluene (6 mL) and EtOH (6 mL) were added 1 M Na_2CO_3 (2.5 mL, 2.5 mmol), LiCl (127 mg, 3.0 mmol) and $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) under N_2. The reaction mixture was heated to reflux at 95 ^oC for 18 h. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with brine (20 mL). The aqueous layer was thoroughly extracted with $CHCl_3$. The combined organic layers were dried, filtered and evaporated. The resulting product was purified by column chromatography (eluent: ethyl acetate/hexane, 1/1) to provide **4a** (108 mg, 51.4%) as a yellow solid: mp 207-209 ^oC (decomp) (EtOAc). IR (Neat) υ: 3170, 1714, 1619, 1588, 1443, 1305, 1206, 892, 751, 696 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 11.04 (s, 1H), 8.32 (s, 1H), 7.83 (s, 1H), 7.60 (d, 2H, *J* = 7.4 Hz), 7.44 (t, 2H, *J* = 7.4 Hz), 7.32 (t, 1H, *J* = 7.4 Hz), 3.58 (s, 2H). ^{13}C NMR (DMSO-d_6) δ: 176.54, 158.44, 144.89, 138.31, 130.97, 130.53, 129.72, 127.98, 127.00, 121.41, 36.04. MS (-ve APCI): 209 (M-H). *Anal*. Calcd for $C_{13}H_{10}N_2O+0.25H_2O$: C, 72.71; H, 4.93; N, 13.05. Found: C, 72.72; H, 4.93; N, 12.95.

5-Phenylethynyl-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4b)

To a stirred mixture of **1** (213 mg, 1.0 mmol) in MeCN (4 mL) were added phenylethylnyltributyltin (0.42 mL, 1.2 mmol), Et_4NCl hydrate (166 mg, 1.0 mmol), and $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol) under N_2. The reaction mixture was heated to reflux at 95 ^oC for 22 h. The reaction mixture was diluted with Et_2O (100 mL) and washed with 2M KF solution (20 mL). The aqueous layer was thoroughly extracted with Et_2O. The combined organic layers were dried, filtered and evaporated. Trituation of the product with Et_2O provided **4b** (155 mg, 66%) as a yellow solid: mp 195-197 ^oC (Et_2O). IR (Neat) υ: 3142, 3052, 1719, 1697, 1618, 1465, 1312, 1230, 750 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 11.23 (s, 1H), 8.25 (d, 1H, *J* = 1.6 Hz), 7.68 (s, 1H), 7.51-7.53 (m, 2H), 7.39-7.42 (m, 3H), 3.57 (s, 2H). ^{13}C NMR (DMSO-d_6) δ: 176.39, 168.59, 158.72, 150.00, 134.51, 131.93, 129.46, 122.92, 121.38, 113.17, 91.01, 87.67, 35.80. MS (-ve APCI): 233 (M-H). *Anal*. Calcd for $C_{15}H_{10}N_2O$: C, 76.91; H, 4.30; N, 11.96. Found: C, 75.66; H, 4.56; N, 11.23.

5-(1-Ethoxyvinyl)-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4c)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4c**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 55% yield as a yellow solid; mp 138-140 ^{o}C (decomp) (EtOAc). IR (Neat) υ: 3094, 2974, 2836, 2724, 1720, 1615, 1478, 1327, 1223, 1150, 1053 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.09 (s, 1H), 8.32 (s, 1H), 7.76 (s, 1H), 4.71 (s, 1H), 4.27 (s, 1H), 3.90 (q, 2H, *J* = 7 Hz), 3.58 (s, 2H), 1.36 (t, 3H, *J* = 7 Hz). ^{13}C NMR (DMSO-d$_6$) δ: 176.61, 159.11, 157,61, 143.69, 129.27, 126.49, 120.78, 82.97, 63.66, 35.90, 14.99. MS (+ve ESI): 205 (M+H). *Anal*. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.13; H, 5.96; N, 13.51.

5-Acetyl-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4d)

This compound was prepared from **1** according to the method used for the product (**4c**). The expected derivative (**4d**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 25% yield as a yellow solid: mp 118-220 ^{o}C (decomp) (EtOAc). IR (Neat) υ: 3152, 3081, 2959, 2887, 1713, 1672, 1610, 1453, 1300, 1226, 1145 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.41 (s, 1H), 8.72 (d, 1H, *J* = 1.6 Hz), 7.97 (s, 1H), 3.60 (s, 2H), 2.52 (s, 3H). ^{13}C NMR (DMSO-d$_6$) δ: 196.74, 176.85, 162.45, 149.76, 131.03, 127.76, 121.38, 35.78, 27.21. MS (-ve APCI): 175 (M-H). *Anal*. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 60.84; H, 4.67; N, 15.81.

4-(2-Oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridin-5-yl)benzenesulfonamide (4e)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4e**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 29% yield as a white solid: mp 273-275 ^{o}C (decomp) (EtOAc). IR (Neat) υ: 3350, 3245, 2975, 2821, 2765, 1714, 1626, 1312, 1150 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.12 (s, 1H), 8.41 (d, *J* = 2 Hz, 1H), 7.91 (d, *J* = 2 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.36 (s, 2H), 3.60 (s, 2H). MS (-ve ESI) 290 (M+H). *Anal*. Calcd for $C_{13}H_{11}N_3O_3S$: C, 53.97; H, 3.83; N, 14.52. Found: C, 53.97; H, 3.85; N, 14.55.

5-(2-Furyl)-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4f)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4f**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 36% yield as a peach solid: mp 219-220 ^{o}C (EtOAc). IR (Neat) υ: 3082, 1704, 1602, 1424, 1306, 1217 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.09 (s, 1H), 8.40 (d, 1H, *J* = 1.8 Hz), 7.84 (s, 1H), 7.72 (d, 1H, *J* = 1.8 Hz), 6.89 (d, 1H, *J* = 3.5 Hz), 6.57 (dd, 1H, *J* = 3.3 and 1.8 Hz), 3.58 (s, 2H). ^{13}C NMR (DMSO-d$_6$) δ: 176.41, 158.20, 151.75, 143.43, 142.10, 127.88, 121.60, 121.56, 112.69, 105.84, 35.93. MS (+ve APCI): 201 (M+H). *Anal*. Calcd for $C_{11}H_8N_2O_2$: C, 66.00; H, 4.03; N, 13.99. Found: C, 65.61; H, 4.13; N, 13.91.

5-(3-Pyridinyl)-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4g)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4g**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 23% yield as a yellow solid: mp 257-258 ^{o}C (decomp) (EtOAc). IR (Neat) υ: 3009, 1713, 1626, 1464, 1218 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.13 (s, 1H), 8.84 (d, 1H, *J* = 1.2 Hz), 8.52 (d, 1H, *J* = 4.4 Hz), 8.39 (s, 1H), 8.03 (d, 1H, *J* = 8.0 Hz), 7.91 (s, 1H), 7.44 (dd, 1H, *J* = 8.0 and 4.8 Hz), 3.60 (s, 2H). ^{13}C NMR (DMSO-d$_6$) δ: 176.49, 159.00, 149.02, 147.92, 145.21, 134.40, 133.91, 131.00, 127.44, 124.58, 121.63, 36.01. MS (+ve APCI): 212 (M+H). *Anal*. Calcd for $C_{12}H_9N_3O$: C, 68.24; H, 4.29; N, 19.89. Found: C, 68.04; H, 4.35; N, 19.78.

5-(2-Thienyl)-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4h)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4h**) was obtained after purification by column chromatography (eluent: ethyl acetate/hexane, 1/1) in 28% yield as a yellow solid: mp 249-250 ^{o}C (EtOAc). IR (Neat) υ: 3071, 1704, 1615, 1589, 1305, 1221, 681 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.12 (s, 1H), 8.38 (s, 1H), 7.86 (s, 1H), 7.55 (d, 1H, *J* = 5.0 Hz), 7.49 (d, 1H, *J* = 3.6 Hz), 7.15 (dd, 1H, *J* = 5.0 Hz and 3.6 Hz), 3.63 (s, 2H). ^{13}C NMR (DMSO-d$_6$) δ: 176.42, 158.41, 143.51, 141.11, 129.86, 129.17, 125.97, 124.80, 124.11, 121.76, 35.96. MS (+ve APCI): 217 (M+H). *Anal*. Calcd for $C_{11}H_8N_2OS$: C, 61.09; H, 3.73; N, 12.95; S, 14.83. Found: C, 60.8; H, 3.81; N, 12.73; S, 14.82.

5-(3-Thienyl)-1,3-dihydro-2*H*-pyrrolo[2,3-*b*]pyridin-2-one (4i)

This compound was prepared from **1** according to the method used for the product (**4b**). The expected derivative (**4i**) was obtained after trituation with MeOH in 12% yield as a yellow solid: mp 235-237 ^{o}C (decomp) (MeOH). IR (Neat) υ: 3093, 2918, 1706, 1615, 1591, 1305, 1226, 783 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.03 (s, 1H), 8.48 (d, 1H, *J* = 1.8 Hz), 7.90 (m, 1H), 7.83 (s, 1H), 7.63 (dd, 1H, *J* = 5.0 and 3.0 Hz), 7.54 (dd, 1H, *J* = 5.0 and 1.1 Hz), 3.58 (s, 2H). ^{13}C NMR (DMSO-d$_6$) δ: 176.49, 157.97, 144.29, 139.33, 130.34, 127.98, 126.47, 125.92, 121.41, 120.82, 35.96. MS (-ve APCI): 215 (M-H). *Anal*. Calcd for $C_{11}H_8N_2OS$: C, 61.09; H, 3.73; N, 12.95. Found: C, 60.91; H, 3.80; N, 12.83.

Ethyl 2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-5-carboxylate (5a)

To a mixture of **1** (213 mg, 1.0 mmol) in DMSO (1 mL) and EtOH (2 mL) in Parr bomb were added Et_3N (0.31 mL, 2.25 mmol), $Pd(OAc)_2$ (33.7 mg, 0.15 mmol), and 1,4-(bisdiphenylphosphino)propane (dppp) (61.9 mg, 0.15 mmol). Carbon monoxide gas (40 psi) was applied and the reaction mixture was vigorously stirred and heated at 95 ^{o}C for 18 h. The reaction mixture was diluted with Et_2O (50 mL) and washed with water (10 mL). The aqueous layer was thoroughly extracted with Et_2O. The combined organic layers were dried, filtered and evaporated. Trituation of the crude product with MeOH yielded **5a** (53 mg, 25.7%) as a tan solid: mp 218-220 ^{o}C (MeOH). IR (Neat) υ: 3013, 2998, 2831, 1702, 1622, 1405, 1288, 1256, 1150, 1021, 775 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 11.39 (s, 1H), 8.62 (s, 1H), 7.95 (s,

1H), 4.27 (q, 2H, *J* = 7 Hz), 3.59 (s, 2H), 1.28 (t, 3H, *J* = 7 Hz). ^{13}C NMR (DMSO-d_6) δ: 176.80, 165.64, 162.57, 149.51, 132.29, 121.34, 120.33, 61.35, 35.81, 14.83. MS (-ve APCI): 205 (M-H). *Anal*. Calcd for $C_{10}H_{10}N_2O_3.H_2O$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.84, H, 5.10; N, 12.11.

Isobutyl 2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-5-carboxylate (5b)

This compound was prepared from **1** according to the method used for the product (**5a**). The expected derivative (**5b**) was obtained after trituation with MeOH in 53% yield as a yellow solid: mp 148-150 ^{o}C (MeOH). IR (Neat) υ: 3109, 2964, 2848, 1712, 1618, 1407, 1282, 1247, 1145, 778 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 11.41 (s, 1H), 8.65 (s, 1H), 7.97 (s, 1H), 4.03 (d, 2H, *J* = 6.5 Hz), 3.61 (s, 2H), 1.99 (m, 1H), 0.94 (d, 6H, *J* = 6.5 Hz). MS (-ve APCI): 177 (M-C_4H_9). *Anal*. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.86; H, 6.28; N, 11.50.

Benzyl 2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-5-carboxylate (5c)

This compound was prepared from **1** according to the method used for the product (**5a**). The expected derivative (**5c**) was obtained after trituation with MeOH in 24% yield as an off-white solid: mp 176-178 ^{o}C (MeOH). IR (Neat) υ: 3098, 3041, 2832, 1735, 1702, 1626, 1446, 1372, 1259, 1211, 1145 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ: 11.43 (s, 1H), 8.67 (d, 1H, *J* = 1.8 Hz), 7.99 (s, 1H), 7.46-7.35 (m, 5H), 5.32 (s, 2H), 3.60 (s, 2H). ^{13}C NMR (DMSO-d_6) δ: 176.80, 165.52, 162.88, 149.71, 136.75, 132.36, 129.21, 128.82, 128.64, 121.45, 120.06, 66.77, 35.98. MS (-ve APCI): 177 (M-C_7H_7). *Anal*. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.51; N, 10.44. Found: C, 67.20; H, 4.57; N, 10.39.

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11. 4-(Tributyltin)benzenesulfonamide was prepared as follows: A mixture of 1 g (4.2 mmol) of 4-bromobenzenesulfonamide, 3.65 g (6.3 mmol) of bis(tributyltin), and 0.046 g of $Pd(PPh_3)_4$ in MeCN (25 mL) and toluene (3 mL) was heated to reflux for 18 h. After cooling to rt, the reaction mixture was diluted with ethyl acetate (10 mL) and the excess bis(tributyltin) was removed *via* separatory funnel. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 2/1) to afforded 4-(tributyltin)benzenesulfonamide (970 mg, 52%) as a pale yellow oil. ^1H NMR (DMSO-d_6) δ: 7.73 (d, 2H, *J* = 8.0 Hz), 7.61 (d, 2H, *J* = 8.0 Hz), 7.28 (s, 2H), 1.48 (m, 6H), 1.26 (m, 6H), 1.07 (m, 6H), 0.82 (t, 9H, *J* = 7.3 Hz). ^{13}C NMR (DMSO-d_6) δ: 147.81, 144.50, 137.22, 125.24, 29.21, 27.33, 14.20, 9.96. MS (-ve ES): 445 (M-H).