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Regioselective Halogenations and Subsequent Suzuki−Miyaura Coupling onto Bicyclic 2-Pyridones

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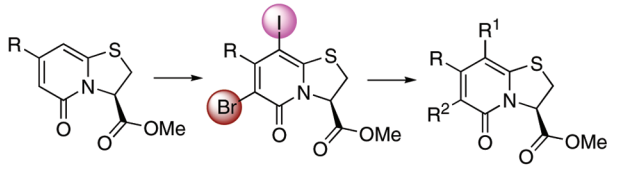

R = Me, CH_2-naphthyl, R^1 = I, Ph, 4-MeOPh, 4-carboxyPh, 5-indol
R^2 = I, Br, Ph, 5-indol

A selective synthesis of 6-bromo-8-iodo dihydro thiazolo ring-fused 2-pyridones is described. These halogenated 2-pyridones are selectively arylated by sequential Suzuki−Miyaura couplings. This approach can advantageously be used to synthesize focused libraries of substituted ring-fused 2-pyridones, a class of compounds with novel antibacterial properties.

2-Pyridones are heterocycles, which can be found in a variety of natural products and biologically active molecules (Figure 1) such as militarinone A+D,[1] leporin A,[2] tenellin,[2] cytisine,[3] camptothecin, and ricinine. These products possess different biological properties such as neurotrophic activity, antifeedant, and nicotine agonist properties.

Substituted bicyclic 2-pyridones are known to act as inhibitors of pilus assembly in uropathogenic *Escherichia coli* (so-called pilicides).[4] In addition, it has been seen that by fine-tuning the substitution pattern onto these latter bicyclic 2-pyridones, an inhibitory effect on Aβ-peptide aggregation involved in Alzheimer's disease is evident.[5] A very recent study reveals that these amyloid inhibitors also act as inhibitors for functional amyloids, curli, in uropathogenic *Escherichia coli*. These compounds have been named curlicides (e.g., FN075, Figure 1).[6] In that study, it was also concluded that the R^1-substituent (e.g., 3-CF_3Ph, Figure 1)

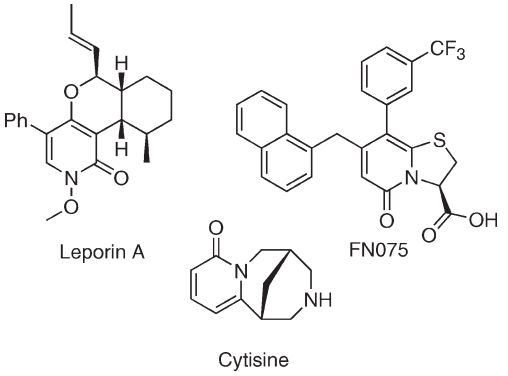

FIGURE 1. Examples of biologically active bicyclic 2-pyridones.

was of great importance for discriminating between compounds with selective curlicide or pilicide properties. The desired framework can be synthesized via an acyl ketene imine cyclocondensation (Scheme 1).[7] Starting from commercially available nitriles to construct the imine part and by preparing various acyl Meldrum's acid derivatives, the two substituents R^1 and R^2 can be directly introduced in the 2-pyridone forming reaction. Although this method has proven to be robust and reliable in library synthesis[8,9] it suffers from the fact that the substituents must already be introduced in the synthesis of the building-blocks and later fine-tuning of structure activity relationships can therefore be ineffective and time-consuming. In both the pilicide and the curlicide projects the R^1-substituent has proven to be of great importance for biological activity. Therefore, in order to synthesize focused libraries of pilicides and curlicides more effectively, a strategy that allows for a later introduction of substituents would be highly desirable.

Halogenations of ring-fused 2-pyridones are known to proceed well with high yields.[10] However, selective halogenations where two active positions in the 2-pyridone ring are available are scarcely reported. Inspired by such a report on selective halogenation of a related bicyclic 2-pyridone framework,[11] we saw a possibility of synthesizing pyridones **3a** and **3b** in larger amounts. These 2-pyridones could then be halogenated and subsequently substituted with a variety of substituents with transition metal-mediated cross couplings.

(1) (a) Schmidt, K.; Riese, U.; Li, Z.; Hamburger, M. *J. Nat. Prod.* **2003**, *66*, 378–383. (b) Schmidt, K.; Günther, W.; Stoyanova, S.; Schubert, B.; Li, Z.; Hamburger, M. *Org. Lett.* **2002**, *4*, 197–199.
(2) Eley, K. L.; Halo, L. M.; Song, Z.; Powles, H.; Cox, R. J.; Bailey, A. M.; Lazarus, C. M.; Simpson, T. J. *ChemBioChem* **2007**, *8*, 289–297.
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(8) Emtenäs, H.; Åhlin, K.; Pinkner, J. S.; Hultgren, S. J.; Almqvist, F. *J. Comb. Chem.* **2002**, *4*, 630–639.
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(10) (a) Padwa, A.; Sheehan, S. M.; Straub, C. S. *J. Org. Chem.* **1999**, *64*, 8648–8659. (b) Otten, P. A.; London, R. E.; Levy, L. A. *Bioconjugate Chem.* **2001**, *12*, 203–212. (c) Pemberton, N.; Åberg, V.; Almstedt, H.; Westermark, A.; Almqvist, F. *J. Org. Chem.* **2004**, *69*, 7830–7835.
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SCHEME 1. Cyclocondensation between a Δ^2-Thiazoline and an Acyl Ketene Source

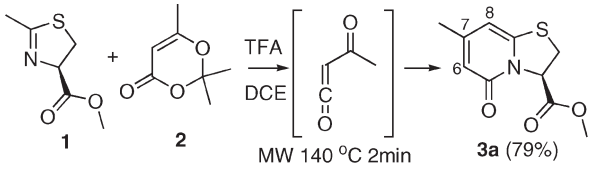
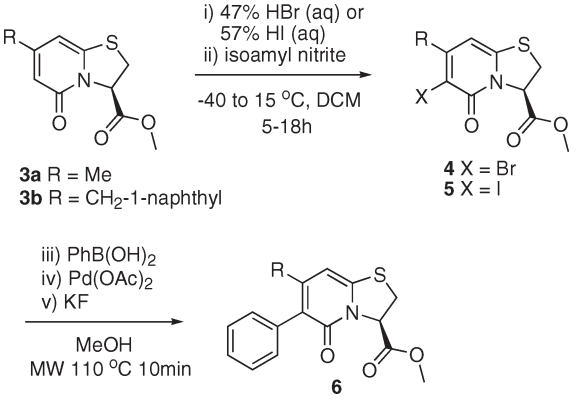


TABLE 1. Selective Iodination Followed by Suzuki−Miyaura Coupling in the 6-Position



entry	R	X	yield (%)	product
1	Me	Br	82	**4a**
2	CH_2-1-naphthyl	Br	85	**4b**
3	Me	I	75	**5a**
4	CH_2-1-naphthyl	I	73	**5b**
5	Me		83	**6a**
6	CH_2-1-naphthyl		86	**6b**

Hence the bicyclic 2-pyridones **3a** and **3b** were synthesized. The methyl-substituted analogue **3** was synthesized via a cyclocondensation between a commercially available acyl ketene source **2** and the Δ^2-thiazoline **1**[7] in 79% yield (Scheme 1). The CH_2-1-naphthyl analogue **3b** was prepared according to a previously published procedure.[7]

The subsequent bromination of these 2-pyridones, by using HBr (aq 47%) and isoamyl nitrite in dichloromethane, was expected to selectively occur in position 8. This was based upon what had been reported for analogues, where the sulfur in the fused five-membered ring was exchanged for a methylene group.[11] However, to our surprise we only observed bromination in position 6 with the more electron-rich dihydro thiazolo fused system (Table 1). Still, the yields were good and the selectivity was excellent in both cases and initial Suzuki−Miyaura couplings were therefore applied on these 6-bromo analogues. Under ligand free conditions ($Pd(OAc)_2$, phenyl boronic acid, and microwave assisted heating) the coupling reactions with the 6-bromo pyridones **4** did not perform well and only approximately 20% conversion of the starting material was observed.

This problem could be solved by preparing the 6-iodo analogues **5** instead, via the same strategy (changing HBr for HI (aq 57%) in the halogenation procedure). This time the following ligand free Suzuki−Miyaura coupling resulted in a 83% and 86% yield of the coupling products, respectively (Table 1).

SCHEME 2. Selective Halogenations of the 2-Pyridones

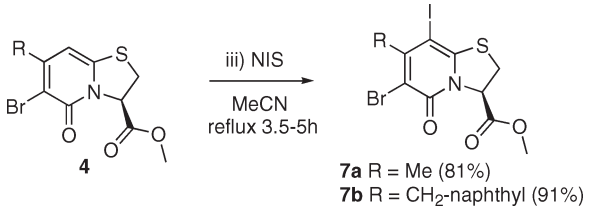
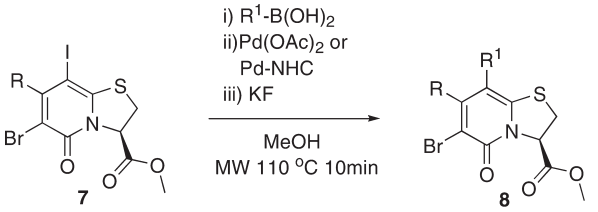
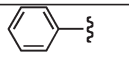
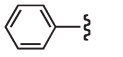
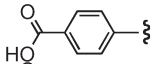
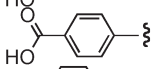
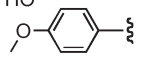
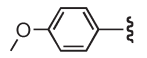
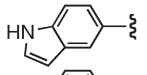
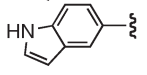


TABLE 2. Regioselective Suzuki−Miyaura Couplings



entry	R	R^1	yield (%)	catalyst	product
1	Me		85[a]	$Pd(OAc)_2$	**8a**
2	CH_2-1-naphthyl		66[a]	$Pd(OAc)_2$	**8b**
3	Me		67[a,b]	$Pd(OAc)_2$	**8c**
4	CH_2-1-naphthyl		45[a,b]	$Pd(OAc)_2$	**8d**
5	Me		83	Pd-NHC	**8e**
6	CH_2-1-naphthyl		62	Pd-NHC	**8f**
7	Me		83	Pd-NHC	**8g**
8	CH_2-1-naphthyl		61	Pd-NHC	**8h**

[a]Using Pd-NHC instead of $Pd(OAc)_2$ did not increase the yield. [b] 120 °C was used instead of 110 °C.

With this result in mind the 6-bromo-8-iodo analogues **7** were prepared in order to solve the previous selectivity problem. In addition, it was possible to synthesize compounds **7a** and **7b** in gram scale by selective bromination of the 6-position, as previously described, followed by iodination of the 8-position with NIS in acetonitrile (Scheme 2).

Regioselective Suzuki−Miyaura couplings of bromo- and iodo-substituted monocyclic 2-pyridones are reported in the literature.[12] However, no examples are reported for these types of couplings with bromo- and iodo-substituted ring-fused 2-pyridones. In addition, dihydrothiazolo fused 2-pyridones are known to be problematic in Suzuki−Miyaura couplings.[13] Still, with our previous results in hand (Table 1), we were hoping to see a regioselective coupling in the 8-position under ligand free conditions by using the 6-bromo-8-iodo analogues **7**.

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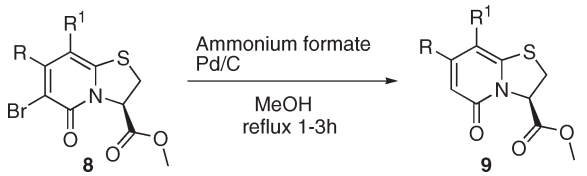
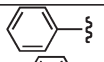
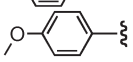
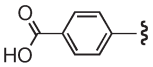
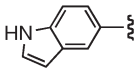
TABLE 3. Catalytic Transfer Hydrogenation of the 6-Bromopyridones



entry	R	R^1	Yield (%)	product
1	CH_2-1-naphthyl		94	**9a**
2	CH_2-1-naphthyl		91	**9b**
3	CH_2-1-naphthyl		94	**9c**
4	CH_2-1-naphthyl		96	**9d**

Indeed, in the case of phenylboronic acid and 4-carboxyphenylboronic acid, this was possible and the 8-coupled 2-pyridones **8a**−**d** were obtained in acceptable yields (Table 2). When *p*-methoxy-substituted phenyl boronic acid or the indol analogues were used, the reaction was not feasible under ligand free conditions. However, these boronic acids could be introduced to the 2-pyridone scaffold without affecting the regioselectivity, by exchanging $Pd(OAc)_2$ with the commercially available Pd-source PEPPSI-iPr (Pd-NHC), which was used in 5 mol % (the addition of more Pd-NHC catalyst in these cases did not increase the yields). In all the couplings, small amounts of the deiodinated product **4** were observed as a byproduct, but no double coupled products were seen.

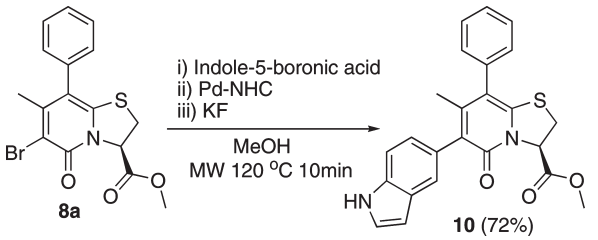
The yields decreased by approximately 20% when the more sterically hindered CH_2-1-naphthyl-substituted 2-pyridones were reacted, as compared to the methyl substitution (Table 2). Adding more than 1 equiv of the boronic acid only yielded the dicoupled product as a byproduct.

The 6-bromo pyridones **8b**, **8d**, **8f**, and **8h** were easily dehalogenated by catalytic transfer hydrogenation (ammonium formate and Pd/C) to give **9a**−**d** in excellent yields (Table 3).

However, if further substitution in position 6 is desired this can be accomplished by using Pd-NHC as a palladium source. The 6-indole derivative **10** was synthesized in a 72% yield by allowing **8a** to be coupled in a second Suzuki−Miyaura coupling, in the pressence of 5 mol % of Pd-NHC and KF in dry methanol at 120 °C for 10 min, under microwave irradiation (Scheme 3). Ligand free $Pd(OAc)_2$ only gave a 20% conversion of the starting material by using the same conditions.

In conclusion, we have shown that dihydro thiazolofused 2-pyridones can be halogenated with complete regioselectivity in position 6. This halogenation selectivity, which is opposite to what has been described earlier for ring-fused 2-pyridones, can be used with advantage to synthesize 6-bromo-8-iodo-substituted bicyclic 2-pyridones in gram scale. Methods to selectively couple these dihalogenated 2-pyridones have been developed. These new methodologies now allow for a faster and more efficient exploration of the effect that the substitution patterns have on these scaffolds in various biological systems.

SCHEME 3. Second Suzuki−Miyaura Coupling



Experimental Section

General Procedure for the Preparation of 6-Bromo Bicyclic 2-Pyridones 4a,b. The dihydro thiazolo ring-fused 2-pyridone **3a** or **3b** (4.33 mmol) and 47% HBr (aq) (4.33 mmol) in DCM (25 mL) were cooled to −40 °C with an acetone/CO_2 (s) bath and isoamylnitrite (8.66 mmol) was added, then the reaction was stirred for 6 h (−40 to 5 °C). The reaction mixture was diluted with DCM and washed with saturated $NaHCO_3$ (aq) and 10% $Na_2S_2O_5$ (aq). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The crude product was purified with column chromatography on silica gel (heptane:EtOAc) to give products **4a**,**b**.

(3*R*)-6-Bromo-7-naphthalen-1-ylmethyl-5-oxo-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic Acid Methyl Ester (4b). Compound **4b** (1.5 g, 81%) was isolated as a pale yellow foam: $[\alpha]_D$ −107 (*c* 0.5, $CHCl_3$). IR λ 1750, 1643, 1575, 1487, 1212. ^{1}H NMR (400 MHz, CDCl3) δ 7.86−7.91 (m, 1H), 7.77−7.84 (m, 2H), 7.48−7.53 (m, 2H), 7.42−7.47 (m, 1H), 7.31−7.35 (m, 1H), 5.64 (s, 1H), 5.57 (dd, J = 8.5, 2.6 Hz,1H), 4.30−4.51 (m, 2H), 3.81 (s, 3H), 3.66 (dd, J = 11.8, 8.5 Hz, 1H), 3.47 (dd, J = 11.8, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 158.1, 153.4, 145.7, 134.0, 133.2, 132.2, 128.9, 128.2, 128.0, 126.7, 126.1, 125.7, 124.0, 111.4, 101.8, 63.9, 53.6, 40.2, 32.3. HRMS (ES^+) calcd [M + H^+] for $C_{20}H_{16}BrNO_3S$ 430.0113, obsd 430.0110.

General Procedure for the Preparation of 6-Bromo-8-iodo Bicyclic 2-Pyridones 7a,b. To the 6-bromo bicyclic 2-pyridone **4a** or **4b** (3.25 mmol) in MeCN (35 mL) was added NIS (3.58 mmol) and the reaction was refluxed for 3.5 h. The solvent was evaporated and the crude material was diluted with EtOAc (150 mL) and washed with saturated $NaHCO_3$ (aq) and 10% $Na_2S_2O_5$ (aq). The organic phase was dried (Na_2SO_4), filtered, and concentrated, and the crude material was purified with column chromatography on silca gel (heptane:EtOAc) to give compounds **7a**,**b**.

(3*R*)-6-Bromo-8-iodo-7-naphthalen-1-ylmethyl-5-oxo-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic Acid Methyl Ester (4b). Compound **4b** (1.65 g, 91%) was isolated as a pale yellow foam: $[\alpha]_D$ −127 (*c* 0.5, $CHCl_3$). IR λ 1750, 1628, 1553, 1466. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.59−7.65 (m, 1H), 7.52−7.58 (m, 1H), 7.33−7.38 (m, 1H), 6.86−6.91 (m, 1H), 5.98 (dd, J = 8.8, 2.5 Hz, 1H), 4.76 (s, 2H), 3.88 (s, 3H), 3.86 (dd, J = 11.8, 8.8 Hz, 1H), 3.59 (dd, J = 11.8, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 157.5, 153.5, 151.9, 134.0, 131.9, 130.8, 129.1, 127.6, 126.5, 126.0, 125.8, 123.9,123.0, 112.8, 67.1, 66.3, 53.8, 44.6, 31.5. HRMS (ES^+) calcd [M + H^+] for $C_{20}H_{15}BrINO_3S$ 555.9087, obsd 555.9081.

General Procedure for the Preparation of 6-Bromo-8-aryl Bicyclic 2-Pyridones 8a−h. A mixture of 6-bromo-8-iodo-bicyclic 2-pyridone **7a** or **7b** (0.1 mmol), boronic acid (0.1 mmol), KF (0.2 mmol), and $Pd(OAc)_2$ (0.01 mmol) or PEPPSI-iPr (0.005 mmol) in dry MeOH (1.3 mL, dried over 3 Å MS) was heated in the microwave oven at 110 °C for 10 min. The reaction mixture was diluted with saturated $NaHCO_3$ (aq) and extracted with EtOAc (30 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated, and the crude material was purified with

column chromatography on silca gel (heptane:EtOAc) to give compounds **8a**−**h**.

(3*R*)-6-Bromo-7-naphthalen-1-ylmethyl-5-oxo-8-phenyl-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic Acid Methyl Ester (8b). Compound **8b** (30 mg, 66%) was isolated as a colorless foam: $[\alpha]_D$ −102 (*c* 0.5, $CHCl_3$). IR λ 1749, 1649, 1469, 1216. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.85 (m, 1H), 7.69−7.74 (m, 2H), 7.32−7.48 (m, 3H), 7.14−7.20 (m, 2H), 7.02−7.12 (m, 3H), 6.94−7.00 (m, 1H), 5.77 (dd, J = 8.6, 2.6 Hz,1H), 4.25−4.38 (m, 2H), 3.89 (s, 3H), 3.72 (dd, J = 11.8, 8.6 Hz, 1H), 3.49 (dd, J = 11.8, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 157.8, 152.3, 146.3, 136.3, 133.7, 132.7, 131.7, 129.9, 129.3, 128.8, 128.8, 128.8, 128.6, 127.2, 126.1, 125.7, 125.6, 124.6, 122.9, 117.1, 114.7, 65.1, 53.7, 37.4, 31.9. HRMS (ES^+) calcd [M + H^+] for $C_{26}H_{20}BrNO_3S$ 506.0426, obsd 506.0423

General Procedure for the Preparation of 6-Hydro-8-aryl Bicyclic 2-Pyridones 9a−d. A mixture of 6-bromo-8-aryl bicyclic 2-pyridone **8b**, **8d**, **8f**, or **8h** (0.1 mmol), 10% Pd/C (20 mg), and ammonium formate (1 mmol) in MeOH (3 mL) was heated to reflux for 3 h. The reaction mixture was diluted with water and extracted with EtOAc (30 mL). The organic phase was filtered through celte, dried (Na_2SO_4), filtered, and concentrated. The crude material was purified with column chromatography on silca gel (heptane:EtOAc) to give compounds **9a**−**d**.

(3*R*)-8-(4-Methoxyphenyl)-7-naphthalen-1-ylmethyl-5-oxo-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic Acid Methyl Ester (9b). Compound **9b** (39 mg, 91%) was isolated as a colorless foam: $[\alpha]_D$ −94 (*c* 0.5, MeCN). IR λ 1751, 1653, 1485. ^{1}H NMR (400 MHz, d_3-MeCN) δ 7.86−7.91 (m, 1H), 7.78−7.82 (m, 1H), 7.67−7.71 (m, 1H), 7.40−7.50 (m, 3H), 7.20−7.30 (m, 3H), 6.92−6.97 (m, 2H), 5.55−5.57 (m, 1H), 5.48 (dd, J = 9.0, 2.6 Hz, 1H), 4.01 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 3.73 (dd, J = 12, 9.0 Hz, 1H), 3.41 (dd, J = 12, 2.6 Hz, 1H). ^{13}C NMR (100 MHz, d_3-MeCN) δ 169.9, 161.6, 160.6, 155.9, 149.2, 135.6, 134.8, 132.6, 132.4 (broad), 132.3 (broad), 129.6 (2C), 128.6, 128.3, 127.1, 126.8, 126.6, 124.8, 115.8, 115.3 (broad), 115.0 (broad), 114.9, 64.5, 56.0, 53.6, 37.2, 32.1. HRMS (ES^+) calcd [M + H^+] for $C_{27}H_{23}NO_4S$ 458.1426, obsd 458.1424.

(3*R*)-6-(1*H*-Indol-5-yl)-7-methyl-5-oxo-8-phenyl-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic Acid Methyl Ester (10). A mixture of (3*R*)-6-bromo-7-methyl-5-oxo-8-phenyl-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyridine-3-carboxylic acid methyl ester (**8a**) (20 mg, 0.053 mmol), PEPPSI-iPr (1.8 mg, 0.0026 mmol), indole-5-boronic acid (13 mg, 0.08 mmol), and KF (6 mg, 0.11 mmol) in dry MeOH (1 mL, dried over 3 Å MS) was heated in the microwave oven at 120 °C for 10 min. The reaction mixture was diluted with water and pH was set to 8 with saturated $NaHCO_3$, the water phase was extracted with EtOAc (50 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The crude product was purified with column chromatography on silica gel (heptane:EtOAc 20:80). The title compound was isolated as a colorless foam (16 mg, 72% yield): $[\alpha]_D$ −92 (*c* 0.5, $CHCl_3$). IR λ 3233, 1750, 1627, 1491, 1215. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.07 (br s, 1H), 7.43−7.50 (m, 2H), 7.29−7.42 (m, 6H), 6.92 (dd, J = 8.3, 1.7 Hz, 1H), 6.39−6.43 (m, 1H), 5.6 (dd, J = 9.1, 2.8 Hz, 1H), 3.84 (dd, J = 12.0, 9.1, 1H), 3.74 (s,3H), 3.48 (dd, J = 12.0, 2.8, 1H), 1.75 (s, 1H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 168.9, 159.9, 146.8, 144.3, 137.5, 134.9, 129.9 (2C), 128.8 (2C), 127.9, 127.4, 127.1, 126.4, 125.4, 123.6, 121.8, 115.1, 110.7, 101.1, 63.9, 52.8, 30.5, 19.4. HRMS (ES^+) calcd [M + H^+] for $C_{24}H_{20}N_2O_3S$ 417.1273, obsd 417.1271

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Supporting Information Available: Experimental procedures and spectroscopic data, and copies of ^{1}H and ^{13}C NMR for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.