*Supporting Information for***Heteroaromatic Thioether – Boronic Acid Cross-Coupling Under Neutral Reaction Conditions**

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GENERAL METHODS

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400MHz (400 MHz ^1H , 100.0 MHz ^{13}C) spectrometer in deuterochloroform (CDCl_3) using chloroform as an internal standard (7.26 ppm ^1H , 77.00 ppm ^{13}C). Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), pent (pentuplet), hex (hextet), hept (heptet), m (multiplet), exch (exchangeable), app (apparent)); coupling constants, J , are reported (Hz); integration is provided. Infrared spectra were recorded on a ASI ReactIR 1000FT-IR spectrometer with a silicone probe. Peaks are reported (cm^{-1}) with the following relative intensities: vs (very strong), s (strong, 67-100%), m (medium, 40-67%), w (weak, 20-40%) and br (broad). GC-MS spectra were recorded on a Shimadzu Gas Chromatograph GC-17A, Mass Spectrometer QP-5000. GC/MS analysis was carried out on a bonded 5% diphenylsiloxane capillary column (30m, 0.25mm id, 0.25 μm df). Elementary analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 plates, 0.25 mm thick with F-254 indicator. Preparative thin-layer chromatography was performed on Merck silica gel 60 plates, 0.50 mm thick with F-254 indicator. Solvents for extraction and chromatography were reagent grade and used as received. Dried solvents (THF, toluene, CH_3CN , benzene, DMA) used as reaction media were purchased from Aldrich and dried over 4Å molecular sieves and titrated for water level prior to use with a Fisher Coulomatic K-F titrator. Et_3N and pyridine were dried over 4Å molecular sieves. All solvents, unless otherwise noted were sparged with nitrogen for several h. All reactions were performed under dry nitrogen in oven- and/or flame-dried glassware.

All boronic acids, 2-(tributylstannyl)pyrazine, and copper thiophene-2-carboxylate were obtained from Frontier Scientific, Inc. 2-Mercaptobenzoxazole was purchased from Acros, 2-(methylthio)pyrazine, 1-phenyl-1*H*-tetrazole-5-thiol, 2-methylthiobenzothiazole, 4-toluenethiol, 2-thio-4-methylpyrimidine hydrochloride, methyl iodide and zinc acetate were purchased from Aldrich. 4,6-Dimethyl-2-mercaptopyridine-3-carbonitrile, ethyl 3-(methylthio)-4-oxo-4,5,6,7-tetrahydrobenzo[*c*]thiophene-1-carboxylate, 2-chloro-3-nitropyridine were purchased from Maybridge Chemical Company Ltd. 2-Chloro-*N,N*-dimethyl-acetamide was purchased from Fluka. Copper methylsalicylate was prepared as described previously.¹

¹ Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2001**, 3, 91-93.

4,6-Dimethyl-2-methylthiopyridine-3-carbonitrile: 4,6-Dimethyl-2-mercaptopyridine-3-carbonitrile (1.64 g, 10.0 mmol) was dissolved in THF (10 mL) and CH_3I (2.00 g, 14.0 mmol) and K_2CO_3 (3.00 g, 22.0 mmol) were added. The suspension was stirred for 18 h under nitrogen at room temperature. The mixture was filtered and volatiles were evaporated under vacuum. The remaining solid was recrystallized from Et_2O : hexanes giving the desired product as white platelets (1.40 g, 78%), m. p.: 84-85 °C [Lit.² 82 °C]; ^1H NMR (CDCl_3 , 400 MHz): δ 6.77 (s, 1H), 2.60 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 92.9, 91.5, 81.8, 49.8, 45.6, 34.9. IR (neat): 2930 (m), 2216 (m), 1583 (s), 1544 (s), 1440 (m), 1355 (s), 1270 (s).

2-(4-Tolylthio)-3-nitropyridine: 2-Chloro-3-nitropyridine (1.58 g, 10.0 mmol) was placed in a flask and dissolved in DMA (5 mL) together with 4-toluenethiol (1.24 g, 10.0 mmol) and NaOH (0.45 g, 11.2 mmol). The reaction mixture was stirred under nitrogen for 24 h at 60 °C, then it was poured into ice where yellow crystals slowly precipitated. The product was recrystallized from acetone : Et_2O : hexanes to give the desired product as yellow crystals (2.11 g, 85%), m. p.: 102-103 °C [Lit.³ 104 °C]; ^1H NMR (CDCl_3 , 400 MHz): δ 8.52- 8.48 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.17 (dd, J = 8.2, 4.6 Hz, 2H), 2.42 (s, 3H). IR (neat): 3076 (w), 2922 (w), 1583 (vs), 1556 (s), 1513 (vs), 1397 (s), 1336 (vs), 1254 (s), 1123 (s), 1069 (m), 1019 (m).

2-Methylthio-4-methylpyrimidine:⁴ 2-Mercapto-4-methylpyrimidine hydrochloride (1.62 g, 10.0 mmol) was placed in a flask and suspended in THF (20 mL). CH_3I (2.00 g, 14.0 mmol) and K_2CO_3 (5.00 g, 36.6 mmol) were added and the suspension was stirred for 24 h at room temperature under a nitrogen atmosphere. The reaction progress was followed by GC/MS. After the reaction was complete, Et_2O (30 mL) was added, the suspension was filtered, and the solid was washed thoroughly with Et_2O (30 mL). Volatiles were evaporated and the product was obtained as a yellowish liquid (1.32 g, 94%); ^1H NMR (CDCl_3 , 400 MHz): δ 8.35 (d, J = 4.8 Hz, 1H), 6.81 (d, J = 4.8 Hz, 1H), 2.55 (s, 3H), 2.44 (s, 3H). IR (neat): 2999 (w), 2930 (w), 1571 (vs), 1544 (s), 1417 (s), 1328 (vs), 1208 (s).

S-[2-(4-Methyl)pyrimidinyl]thioglycolic acid, N,N-dimethylamide: 2-Mercapto-4-methylpyrimidine hydrochloride (1.62 g, 10.0 mmol) was placed in a flask and suspended in THF (20 mL). 2-Chloro-*N,N*-dimethylacetamide (1.30 g, 10.7 mmol) and K_2CO_3 (5.00 g, 36.6 mmol) were added and the suspension was stirred for 24 h. After that Et_2O (30 mL) was added and the suspension was filtered and the solid washed thoroughly with Et_2O (30 mL). Volatiles were evaporated and the resulting solid was recrystallized from Et_2O : hexanes mixtures giving product as yellowish platelets (1.56 g, 74%); m. p.: 60 - 63 °C; ^1H NMR (CDCl_3 , 400 MHz): δ 8.33 (d, J = 5.2 Hz, 1H), 6.81 (d, J = 5.2 Hz, 1H), 4.09 (s, 2H), 3.15 (s, 3H), 2.98 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.6, 168.2, 167.5, 156.7, 116.3, 37.7, 35.9, 33.5, 24.0. IR (neat): 2934 (w), 1644 (vs), 1571 (s), 1417 (m), 1332 (m). Anal. Calcd for $\text{C}_9\text{H}_{13}\text{N}_3\text{OS}$: C, 51.16; H, 6.20; N, 19.89; S, 15.18; Found: C, 51.24; H, 6.15; N, 19.86; S, 15.08.

² Schmidt, U.; Giesselmann, G. *Chem. Ber.*, **1960**, *93*, 1590-1597.

³ Hamed, E. A., El-Bardan, A. A., Saad, E. F., Gohar, G. A., Hassan, G. M., *J. Chem. Soc. Perkin Trans. 2*; **1997**, *11*, 2415-2422.

⁴ Nishiwaki, T. *Tetrahedron*, **1967**, *23*, 2657-2654.

S-(2-Benzoxazolyl)thioglycolamide: 2-Mercaptobenzoxazole (3.02 g, 20.00 mmol) was placed in a flask and dissolved in THF (40 mL). 2-Chloroacetamide (2.00 g, 2.14 mmol) and K_2CO_3 (6.00 g, 44.00 mmol) were added and the suspension was stirred for 24 h at room temperature under nitrogen. After that the reaction mixture was filtered and the solution was treated with Et_2O and hexanes to precipitate a light tan solid. This was further recrystallized from ethanol giving the desired product as off-white crystals (2.83 g, 68%). M.p.: 159-162 °C. [Lit.⁵ 162-164 °C]; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60 (dm, J = 7.2 Hz, 1H), 7.47 (dm, J = 7.4 Hz, 1H), 7.33-7.26 (m, 2H), 5.63 (bs, 1H), 3.91 (s, 3H), 1.64 (bs, 1H). IR (neat): 3366 (m), 3219 (w), 1675 (s), 1633 (vs), 1490 (s), 1455 (s), 1397 (m), 1235 (w).

S-(5-(1-Phenyl-1H-tetrazolyl)thioglycolic acid, N,N-dimethylamide: 1-Phenyl-1H-tetrazole-5-thiol (1.78 g, 10.0 mmol) was placed in a flask and dissolved in THF (20 mL). 2-Chloro-N,N-dimethylacetamide (1.30 g, 10.7 mmol) and K_2CO_3 (3.00 g, 22.0 mmol) were added. The suspension was stirred at room temperature for 24 h under nitrogen. After that the reaction mixture was filtered and the solute was treated with Et_2O and hexanes precipitating a white solid. The solid was recrystallized from acetone : Et_2O : hexanes (1 : 1 : 3) giving the desired product as white crystals (2.03 g, 77%). M.p: 180-190 °C (decomp.). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.62 - 7.63 (m, 5H), 4.48 (s, 2H), 3.16 (s, 3H), 3.00 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.1, 153.9, 133.5, 130.2, 129.7, 123.7, 38.3, 37.6, 35.9. IR (neat): 2934 (w), 1648 (vs), 1502 (m), 1401 (m). Anal. Calcd for $C_{11}H_{13}N_5OS \cdot H_2O$: C, 46.96; H, 5.37; N, 24.89; S, 11.40; Found: C, 48.07; H, 5.06; N, 25.23; S, 11.55. We were unable to obtain a satisfactory combustion analysis on this compound; in its place we provide photocopies of the corresponding ^1H , ^{13}C NMR and IR spectra.

2-Bromopyrazine:⁶ 2-Tri-*n*-butylstannylpyrazine (0.18 g, 0.50 mmol) was dissolved in CH_2Cl_2 (10 mL) and bromine (0.55 mL of 1M solution in CCl_4) was added dropwise via syringe over 20 minutes. The reaction mixture was then diluted with CH_2Cl_2 and extracted several times with aqueous potassium fluoride. The resulting solution was then dried and passed through a plug of silica gel. Volatiles were then evaporated at atmospheric pressure. The remaining oily product (0.052 g, 65%) was used in the following experiment without further purification. The oil was placed in the Schlenk tube together with copper(I) thiophene-2-carboxylate (0.115 g, 0.60 mmol), 3-methoxyphenylboronic acid (0.076 g, 0.50 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.005 g, 1%) and tris(2-furyl)phosphine (0.01 g, 8%), the reaction vessel was flushed with argon and THF (6 mL) was added via syringe. The reaction mixture was stirred under argon at 50 °C for 18 hours and was followed by TLC and GC/MS. After that time the reaction mixture was dissolved in ether (15 mL) and washed with 10% aqueous NH_4OH (3 x 10 mL) giving only starting material with no trace of desired product.

Typical Procedure for Cross-Coupling Without $Zn(OAc)_2$: Thioether (0.50 mmol), boronic acid (0.55 mmol), copper(I) thiophene-2-carboxylate (0.65 mmol or 0.5 mmol [see below]) and Pd catalyst (4%) were placed in a reaction vessel, and after flushing with argon THF was added. The reaction mixture was stirred at 50 °C for 18 h. Et_2O (20 mL) was then added and the mixture was thoroughly washed with aqueous NH_4OH (10%). The ether layer was dried over $MgSO_4$ and, after volatiles were evaporated, the residues were subjected to preparative plate silica chromatography using polarity

⁵ Brown, D. J., et al., *Aust. J. Chem.*, **1978**, *31*, 447-450.

⁶ Tobias, S., Schmitt, P., Guenther, H., *Chem. Ber.*, **1982**, *115*, 2015-2021

gradient solvents as the eluent. Thus the plate was eluted first with hexanes. Due to the polar nature of some target molecules they were replaced with more polar system based on ether acetone mixture and elution of the plate continued until the product separated from the baseline.

1,4-Dimethoxy-2-(3-cyano-4,6-dimethyl)pyridylbenzene: Yield 76%, white crystals [m.p.: 105 - 108 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 7.01 (s, 1H), 6.96 - 6.93 (m, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 2.62 (s, 3H), 2.55 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 161.6, 159.4, 153.6, 151.0, 150.8, 127.8, 122.6, 116.5, 116.4, 115.8, 112.5, 108.7, 55.9, 55.7, 24.8, 20.4. IR (neat): 2941 (w), 2837 (w), 2223 (m), 1586 (s), 1502 (s), 1455 (m), 1274 (m), 1224 (s), 1046 (m). Anal. Calcd for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44; Found: C, 71.55; H, 6.05; N, 10.38.

4-[2-(3-Cyano-4,6-dimethyl)pyridyl]benzoic acid, methyl ester: Yield 72%, white crystals [m.p.: 131 - 133 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 8.17 (app d, *J* = 8.4 Hz, 2H), 7.93 (app d, *J* = 8.8 Hz, 2H), 7.15 (s, 1H), 3.95 (s, 3H), 2.64 (s, 3H), 2.59 (app s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 166.6, 161.9, 160.1, 152.5, 141.9, 131.1, 129.8, 129.0, 123.2, 116.6, 105.9, 52.3, 24.9, 20.1. IR (neat): 3003 (w), 2957 (w), 2930 (w), 2219 (m), 1718 (vs), 1590 (s), 1440 (s), 1293 (vs), 1112 (s). Anal. Calcd for C₁₆H₁₄N₂O₂: C, 72.16; H, 5.30; N, 10.52; Found: C, 72.00; H, 5.47; N, 10.3.

2-(3,4-Methylenedioxyphenyl)-3-nitropyridine: Yield 87%, yellow crystals [m.p.: 99-101 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 8.80 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.08 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.39 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.08 - 7.04 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ 152.0, 151.9, 149.1, 148.1, 146.1, 132.1, 129.9, 122.5, 122.0, 108.5, 101.5. IR (neat): 3076 (w), 2903 (w), 1590 (m), 1525 (vs), 1505 (s), 1455 (vs), 1355 (s), 1239 (vs), 1038 (s). Anal. Calcd for C₁₂H₈N₂O₄: C, 59.02; H, 3.30; N, 11.47; Found: C, 58.93; H, 3.32; N, 11.39.

2-(3,4-Methylenedioxyphenyl)-4-methylpyrimidine: Yield 86%, off white crystals [m.p.: 145 - 147 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 8.56 (d, *J* = 5.2, 1H), 8.04 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.92 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 4.8 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H), 2.53 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.0, 163.7, 156.6, 149.7, 147.9, 132.2, 122.8, 118.0, 108.3, 108.1, 101.3, 24.3. IR (neat): 2910 (w), 1579 (s), 1502 (m), 1436 (vs), 1351 (s), 1251 (s), 1038 (s). Anal. Calcd for C₁₂H₁₀N₂O₂: C, 67.28; H, 4.71; N, 13.08; Found: C, 67.21; H, 4.75; N, 13.00.

2-(3-Nitrophenyl)-4-methylpyrimidine: Yield 74%, yellowish crystals [m.p.: 98 - 99 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 9.32 (t, *J* = 1.8 Hz, 1H), 8.80 (dt, *J* = 7.2, 1.4 Hz, 1H), 8.69 (d, *J* = 5.2 Hz, 1H), 8.32 (dq, *J* = 8.4, 1.2 Hz, 1H), 7.65 (t, *J* = 8 Hz, 1H), 7.15 (d, *J* = 4.8 Hz, 1H), 2.63 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.8, 162.1, 157.0, 148.7, 139.7, 133.9, 130.3, 129.4, 125.0, 123.3, 122.1, 119.6, 24.4. IR (neat): 3115 (w), 3096 (w), 1590 (m), 1525 (vs), 1432 (m), 1359 (s). Anal. Calcd for C₁₁H₉N₃O₂: C, 61.39; H, 4.22; N, 19.53; Found: C, 61.26; H, 4.18; N, 19.32.

2-Methoxy-5-[2-(4-methyl)pyrimidyl]pyridine: Yield 71%, off white crystals [m.p.: 53 - 55 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 9.22 (d, *J* = 2.4 Hz, 1H), 8.59 - 8.55 (m, 2H), 7.00 (d, *J* = 5.2 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 2.54 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 167.2, 165.5, 162.8, 156.7, 147.9, 138.3, 127.1, 118.4, 110.4, 53.7, 24.3. IR (neat): 2949 (w), 1606 (s), 1579 (s), 1556 (s), 1498 (s), 1444 (s), 1282 (s), 1023 (m). Anal. Calcd for C₁₁H₁₁N₃O: C, 65.66; H, 5.51; N, 20.88; Found: C, 65.57; H, 5.48; N, 20.82.

3-(2-Benzothiazolyl)benzaldehyde: Yield 67%, white crystals [m.p.: 87 - 90 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 10.12 (s, 1H), 8.56 (t, *J* = 2.0 Hz, 1H), 8.35 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.00 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 191.5, 166.3, 153.9, 137.0, 135.1, 134.6, 132.9, 131.3, 129.8, 128.9, 126.6, 125.7, 123.5, 121.7. IR (neat): 1698 (s, C=O). Anal. Calcd for C₁₄H₉NOS: C, 70.27; H, 3.79; N, 5.85; S, 13.40; Found: C, 70.23; H, 3.79; N, 5.87, S, 13.28.

1,4-Dimethoxy-2-(2-benzoxazolyl)benzene: Yield 74%, white solid [m.p.: 48 - 50 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 7.83 - 7.81 (m, 1H), 7.68 (d, *J* = 2.8 Hz, 1H), 7.61 - 7.58 (m, 1H), 7.37 - 7.32 (m, 2H), 7.08 - 7.01 (m, 2H), 3.98 (s, 3H), 3.87 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 161.4, 153.4, 152.8, 150.3, 142.0, 125.0, 124.3, 120.2, 119.0, 116.4, 115.2, 113.7, 110.5, 56.8, 55.9. IR (neat): 2945 (w), 2837 (w), 1610 (w), 1586 (m), 1552 (s), 1455 (s), 1247 (s), 1042 (s). Anal. Calcd for C₁₅H₁₃NO₃: C, 70.58; H, 5.13; N, 5.49; Found: C, 70.51; H, 5.15; N, 5.52.

Ethyl 3-(4-methoxycarbonylphenyl)-4-oxo-4,5,6,7-tetrahydrobenzo[c]thiophene-1-carboxylate: Yield 82%, off white crystals [m.p.: 111 - 113 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 8.06 (app d, *J* = 8.4 Hz, 2H), 7.60 (app d, *J* = 8.4 Hz, 2H), 4.36 (q, *J* = 5.2 Hz, 2H), 3.93 (s, 3H), 3.30 (t, *J* = 6.0 Hz, 1H), 3.19 (t, *J* = 6.2 Hz, 1H), 2.59 - 2.53 (m, 2H), 2.13 - 2.053 (m, 2H), 1.38 (app t, *J* = 7.2 Hz, 3H). Anal. Calcd for C₁₉H₁₈O₅S: C, 63.67; H, 5.06; S, 8.95; Found: C, 63.66; H, 5.09; S, 8.97.

1-[5-(Phenyl-1H-tetrazolyl)]-3-methoxybenzene: Yield 65%, off white crystals [m.p.: 94 - 95 °C]; ¹H NMR (CDCl₃, 400 MHz): δ 7.55 - 7.53 (m, 3H), 7.41 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.28 (t, *J* = 8.00 Hz, 1H), 7.14 (app s, 1H), 7.06 - 7.00 (m, 2H), 3.73 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.7, 153.4, 134.5, 130.4, 130.0, 129.8, 125.3, 124.5, 1221.1, 117.6, 113.8, 55.3. IR (neat): 3069 (w), 2941 (w), 1714 (w), 1594 (s), 1502 (s), 1478 (s), 1440 (m), 1243 (m). Anal. Calcd for C₁₄H₁₂N₄O: C, 66.65; H, 4.79; N, 22.21; Found: C, 66.53; H, 4.76; N, 22.11.

Typical Procedure for Cross-Coupling With Zn(OAc)₂: Thioether (0.50 mmol), boronic acid (0.55 mmol), CuTC (0.65 mmol), Zn(OAc)₂ (0.65 mmol) and Pd catalyst (1%) were placed in a reaction vessel, and after flushing with argon THF was added. The reaction mixture was stirred at 50 °C for 18 h. Et₂O (20 mL) was added and the mixture was thoroughly washed with aqueous NH₄OH (10%). The ether layer was dried over MgSO₄ and after volatiles were evaporated, the residues were subjected to preparative silica plate chromatography using polarity gradient solvents as the eluent. Thus the plate was eluted first with hexanes. Due to the polar nature of some target molecules they were replaced with more polar system based on ether acetone mixture and elution of the plate continued until the product separated from the baseline.

3-(2-Benzothiazolyl)pyridine: Yield 53%, off white solid m. p.: 128 - 130 °C. [Lit.⁷ 127 - 128 °C]. ¹H NMR (CDCl₃, 400 MHz): δ 9.30 (d, *J* = 2.00 Hz, 1H), 8.78 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.39 (dt, *J* = 8.8, 1.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.94 (app d, *J* = 8.0 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ 160.6, 149.9, 147.6, 144.6, 131.0, 130.6, 125.7, 122.7, 121.8, 119.8, 119.5, 117.8. IR (neat): 3057 (w), 1586 (m), 1505 (m), 1417 (s).

⁷ Kanaoka, T.; Hamada, T.; Yonemitsu, O. *Chem. Pharm. Bull.*, 1970, 18, 587-590.

1-(2-Pyrazyl)-3,4-(methylenedioxy)benzene: Yield 64%, white crystals [m.p.: 115 – 116 °C]; ^1H NMR (CDCl_3 , 400 MHz): δ 8.94 (d, J = 1.6 Hz, 1H), 8.57 (dd, J = 2.6, 1.4 Hz, 1H), 8.45 (d, J = 2.8 Hz, 1H), 7.54 - 7.52 (m, 2H), 6.93 (d, J = 6.8 Hz, 1H), 6.04 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 152.3, 149.3, 148.6, 143.9, 142.3, 141.7, 130.6, 121.2, 108.7, 107.2, 101.5. IR (neat): 2903 (w), 1610 (w), 1505 (s), 1451 (s), 1262 (m), 1116 (m). Anal. Calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2$: C, 65.99; H, 4.03; N, 13.99; Found: C, 65.71; H, 4.02; N, 13.78.

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tetrazole st.m.

C OBSERVE

expl std13c

SAMPLE date Apr 23 2001 DEC... & VT
 solvent cdc13 dn 399.940 H1
 file exp 42
 ACQUISITION exp 42
 sfrq 100.575 dm -480.0
 tn 0.13 dmm yyy
 at 0.753 dmf w
 np 38400 dseq 9000
 sw 24016.8 dres 1.0
 fb 13000 homo n
 bs 16
 tpwr 60 lb
 pw 9.0 wfile 2.00
 d1 5.000 proc ft
 tof 430.5 fn not used
 nt 10000 math f
 ct 128
 alock n weff react
 gain not used n wexp procplot
 FLAGS wbs testn
 f1 n
 f2 n
 f3 y
 f4 nn
 f5
 f6
 f7
 f8
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 f10
 f11
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Sample_ID:XS2-IV-23a

CDCl3

Pulse Sequence: s2pul

Solvent: cdc13

Ambient temperature

INNOVA-400 "INNOVA400"

PULSE SEQUENCE

Relax: delay 1.000 sec

Pulse 27.0 degrees

Acq. time 2.499 sec

Width 5199.2 Hz

8 repetitions

OBSERVE H1, 399.3389028 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 32768

Total time 0 min, 28 sec

4.478

3.157
3.008

7.623
7.619
7.607
7.602
7.585
7.577
7.562
7.558
7.547
7.542
7.538
7.528
7.260

ppm

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