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## A New Route to 1,5-Disubstituted 4-Arylsulfonylpyrazoles by Lithiation of 1-Methyl-4-Arylsulfonylpyrazoles

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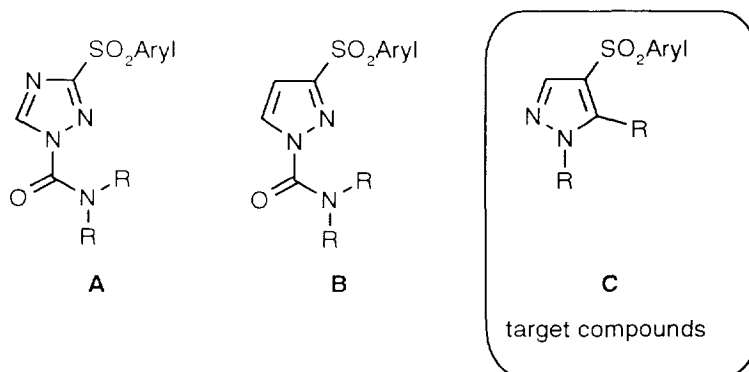
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**Abstract:** The arylsulfonylvinamidinium salts **1** reacted with hydrazine in refluxing ethanol to give rise to 4-arylsulfonylpyrazoles **2** in reasonable yield. Regioselective lithiation of N-methylpyrazoles **3** with LDA followed by treatment with various electrophiles afforded the corresponding 1,5-disubstituted 4-arylsulfonylpyrazoles **5** in good yield.

### INTRODUCTION

The pyrazole ring system appears often in agrochemicals and methods for its synthesis have attracted considerable interest.<sup>1</sup> Depending on the substituents and the substitution pattern there are many pyrazoles with insecticidal,<sup>2</sup> fungicidal<sup>3</sup> and herbicidal<sup>4</sup> activity. Recently, 3-arylsulfonylpyrazoles **B**,<sup>5</sup> which can be regarded as analogues of the similarly substituted triazole herbicides **A**,<sup>6</sup> have been synthesized and disclosed as herbicides. As part of a lead finding program we were interested in the synthesis of substituted 4-arylsulfonylpyrazoles **C** and their evaluation as herbicides (Scheme 1).

Scheme 1: Compounds discussed

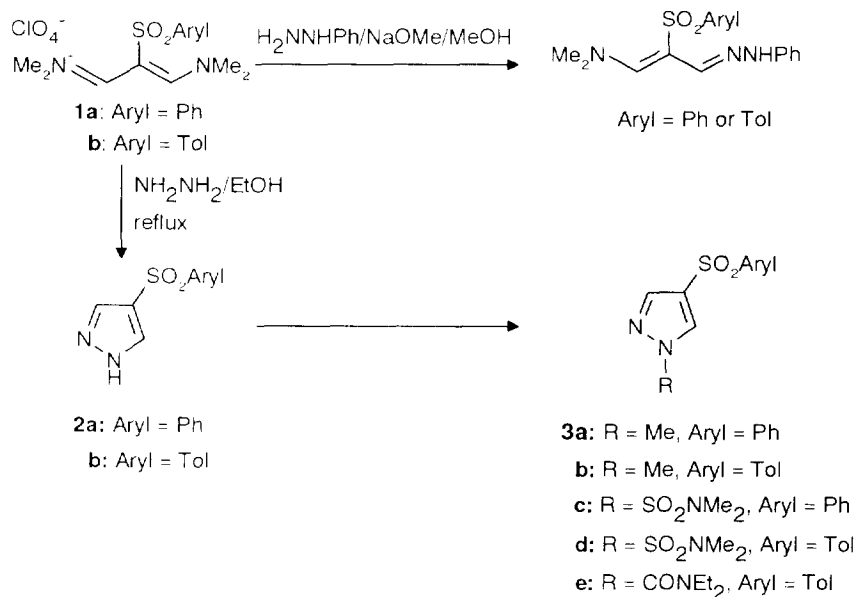


### RESULTS AND DISCUSSION

To the best of our knowledge syntheses of unsubstituted 4-arylsulfonylpyrazoles, which are precursors of N-carbamoyl substituted pyrazoles **C**, have not been described in the literature.<sup>7</sup> Recently, Gupton and coworkers have reported a convenient synthesis of arylsulfonylvinamidinium salts **1a** and **1b** employing a

Vilsmeier-Haack reaction of the corresponding arylsulfonyl acetic acid with a mixture of dimethylformamide and phosphorus oxychloride.<sup>8</sup> Condensation of these salts with guanidine carbonate proceeded in the anticipated way giving rise to 5-arylsulfonyl-2-aminopyrimidines.<sup>8</sup> On the other hand, however, the vinamidinium salts **1a** and **1b** showed, upon treatment with phenylhydrazine, unusual behavior affording only the open chain phenylhydrazones and not the expected pyrazoles.<sup>8</sup> Since it is well documented that vinamidinium salts react with hydrazines to form pyrazoles,<sup>9</sup> we investigated the condensation of **1a** and **1b** with hydrazine itself, and found out that reaction of **1a** and **1b** with hydrazine in refluxing ethanol proceeded in the expected fashion giving rise to the 4-arylsulfonylpyrazoles **2a** and **2b** in reasonable yields (Scheme 2). Subsequent N-methylation was achieved with dimethyl sulfate in methanolic sodium methoxide yielding pyrazoles **3a** and **3b**. N-Methylpyrazole **3b** has previously been prepared by Padwa and coworkers and the physical data are in good agreement.<sup>10</sup> Furthermore, base-facilitated reaction of pyrazoles **2a** and **2b** with N,N-dimethylsulfonyl chloride gave the N,N -dimethylsulfonylpyrazoles **3c** and **3d**. By analogy with the herbicidal 3-arylsulfonylpyrazoles B we synthesized the N,N-diethylcarbamoylpyrazole **3e**, which unfortunately, when applied to different plants in a greenhouse test, exhibited not the expected herbicidal activity.

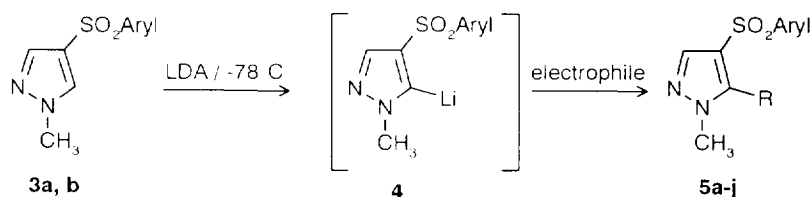
**Scheme 2:** Synthesis of 4-Arylsulfonylpyrazoles **2** and **3**



It is well established that N-substituted pyrazoles are regioselectively lithiated in the 5-position. Subsequent treatment with electrophiles then furnishes 1,5-disubstituted pyrazoles.<sup>11</sup> This methodology has recently found a useful application in the synthesis of 1,3-disubstituted (or 1,3,4-trisubstituted) pyrazole-5-sulfonamide derivatives.<sup>12</sup> With this in mind we investigated the lithiation of 4-arylsulfonylpyrazoles **3a** and **3b** with lithium diisopropylamide followed by reaction with a broad range of electrophiles. When pyrazoles **3a** and **3b** were treated with lithium diisopropylamide, they underwent, as expected, deprotonation

selectively at the 5-position furnishing the corresponding 4-arylsulfonyl-5-lithiopyrazoles **4**. Treatment of the 5-lithiopyrazoles with various electrophiles then gave rise to the N-methyl-4,5-disubstituted pyrazoles **5a-5j** (Scheme 3). Thus, it was possible to introduce for example the carboxaldehyde group (**5c**, **5h**), arylthio moieties (**5d**, **5i**) or the methyl group (**5a**, **5f**). Furthermore, we also succeeded in introducing the tributylstannyl rest using this lithiation procedure. The 1,5-dimethylpyrazole **5f** has previously been prepared by Padwa and coworkers but the physical data are not in agreement.<sup>10</sup> The Padwa group has synthesized the 4-arylsulphonyl-dimethylpyrazole by a 1,3-dipolar cycloaddition reaction of p-tolyl-2-(trimethylsilyl)ethynyl sulfone with 2-diazopropane, followed by treatment of the cycloadduct with methyl iodide in the presence of aluminum chloride (van Alphen-Huettel rearrangement) and subsequent desilylation with tetrabutylammonium fluoride. The pyrazole proton of this synthesized compound (m.p. 99-100°C) has a chemical shift of 7.69 ppm, whereas the proton of our synthesized pyrazole **5f** (m. p. 117-118°C) appears at 7.80 ppm. Based upon literature precedence and the NMR shifts we think it unlikely that we obtained the 3-lithiopyrazoles and assume that the Padwa synthesis gave rise to the 1,3-dimethylpyrazole and not the suspected 1,5-dimethylpyrazole.

**Scheme 3:** Lithiation of Pyrazoles **3** and Synthesis of Pyrazoles **5**

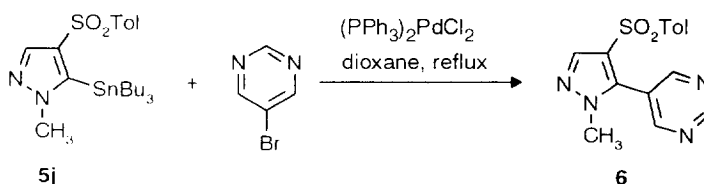


5	Ar	Electrophile	R	Isol. Yields (%)
a	Ph	MeI	Me	71
b	Ph	PhCHO	CH(OH)Ph	30
c	Ph	Me <sub>2</sub> NCHO	CHO	72
d	Ph	MesSSMes	SMes	45
e	Ph	Bu <sub>3</sub> SnCl	SnBu <sub>3</sub>	75
f	Tol	MeI	Me	66
g	Tol	PhCHO	CH(OH)Ph	48
h	Tol	Me <sub>2</sub> NCHO	CHO	49
i	Tol	PhSPh	SPh	61
j	Tol	Bu <sub>3</sub> SnCl	SnBu <sub>3</sub>	76

Pyrazoles **5e** and **5j** represent an interesting class of compounds since they have two functional groups which can be used for further transformations. In addition to the versatile 4-arylsulphonyl moiety, the tributylstannyl group should, for example, facilitate C-C bond formation reactions using the Kumada -

Negishi cross coupling reaction.<sup>13</sup> We have therefore examined the application and usefulness of stannylpyrazole **5j** as a reactant in a Stille-type Kumada-Negishi reaction.<sup>14</sup> Treatment of **5j** with 5-bromopyrimidine in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in refluxing dioxane afforded pyrazolepyrimidine **6** in good yield (Scheme 4). However, reaction of **5j** with 2,3-bischloriodobenzene under the same conditions gave only starting material.

**Scheme 4:** Kumada - Negishi Reaction of Stannylpyrazole **5j**



In summary, we have developed a new and efficient route for the synthesis of 1,5-disubstituted-4-arylsulphonylpyrazoles, which can then be further elaborated if desired.

## EXPERIMENTAL SECTION

*General:* Melting points are not corrected. Preparative column chromatography was performed on silica gel S, 0.063-0.200mm (Riedel-deHaen). <sup>1</sup>H NMR spectra were obtained at 100 or 300 MHz, and chemical shifts are reported relative to TMS. Microanalysis of all new compounds were carried out in our analytical laboratory.

**4-(Phenylsulfonyl)pyrazole (2a):** A mixture of 17.1g (46.6mmol) of 2-(phenylsulfonyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium perchlorate **1a**<sup>8</sup> and 34.2ml of hydrazine hydrate in 170ml of ethanol was refluxed for 8h, cooled to room temperature and allowed to stand overnight. The reaction mixture was poured into 250ml of saturated aqueous ammonium chloride solution and extracted with dichloromethane. The organic phase was dried over sodium sulfate and then concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with 7:3 heptane-ethyl acetate to give 4.1g (42% yield) **2a** as a solid: m.p. 156-158°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 7.90 (s, 2H); 7.90 (m, 2H); 7.55 (m, 3H). Anal. calcd. for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S (208.3): C51.9; H3.9; N13.5. Found: C51.3; H3.9; N13.3.

**4-(Tolylsulfonyl)pyrazole (2b):** This compound was prepared as described for **2a** starting from 2-(tolylsulfonyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium perchlorate **1b**.<sup>8</sup> The crude product can either be purified by chromatography (7:3 heptane-ethyl acetate) or dissolved in methanol and subsequently precipitated with water to give 5.3g (51% yield) **2b** as a solid: m.p. 111-112°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 7.95 (s, 2H); 7.80 (d, 2H); 7.26 (d, 2H); 2.40 (s, 3H). Anal. calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S (222.3): C54.0; H4.5; N12.6. Found: C54.6; H4.8; N12.4.

**1-Methyl-4-(phenylsulfonyl)pyrazole (3a):** To a solution of 16.83g (81.2mmol) of 4-(phenylsulfonyl)pyrazole **2a** and 4.38g (81.2mmol) of sodium methoxide in 60ml of methanol, was

added dropwise 7.7ml (81.2mmol) of dimethyl sulfate. The reaction mixture was refluxed for 20h, cooled to room temperature, poured into 120ml of water and extracted with dichloromethane. The organic phase was dried over sodium sulfate and then concentrated in vacuo. The resulting crude product was recrystallized from heptane-ethyl acetate to give 13g (72% yield) **3a** as a solid: m.p. 100-102°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 7.95 (m, 2H); 7.84 (s, 1H), 7.79 (s, 1H); 7.55 (m, 3H); 3.92 (s, 3H). Anal. calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S (222.28): C54.6; H4.5; N12.6. Found: C54.3; H4.9; N12.5.

**1-Methyl-4-(tolylsulfonyl)pyrazole (3b):**<sup>10</sup> This compound was prepared using the method employed for **3a**. 7.6g (34mmol) of 4-(tolylsulfonyl)pyrazole **2b** afforded, after recrystallization of the crude product from heptane-ethyl acetate, 6.5g (80% yield) **3b** as a solid: m.p. 125-127°C (lit.<sup>10</sup> m.p. 126-127°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 7.80 (d, 2H); 7.80 (s, 1H); 7.76 (s, 1H); 7.30 (d, 2H); 3.88 (s, 3H); 2.40 (s, 3H). Anal. calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>S (236.29): C55.9; H5.1; N11.9. Found: C55.2; H4.4; N11.6.

**1-(N,N-Dimethylamino)sulfonyl-4-(phenylsulfonyl)pyrazole (3c):** To a solution of 7.3g (35mmol) of 4-(phenylsulfonyl)pyrazole **2a** in 50ml of THF was added 1.1g (36mmol) of sodium hydride (80% suspension in mineral oil). After stirring for 30min 6.5g (42.5mmol) of dimethylsulphamoyl chloride was added dropwise. The reaction mixture was stirred under reflux for 6h, cooled to room temperature, poured into water and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and then concentrated in vacuo. The resulting crude product was purified by chromatography on silica gel eluting with 1:1 heptane-ethyl acetate to give 5.7g (52% yield) **3c** as a solid: m.p. 86-88°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100MHz) δ 8.41 (d, 1H, J<1Hz), 8.00 (d, 1H, J<1Hz), 8.02 (m, 2H), 7.60 (m, 3H). Anal. calcd. for C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub> (315.36): C41.90; H4.2; N13.3. Found: C42.1; H4.3; N13.5.

**1-(N,N-Dimethylamino)sulfonyl-4-(tolylsulfonyl)pyrazole (3d):** To a solution of 15g (67.5mmol) of 4-(tolylsulfonyl)pyrazole **2b** and 15.1g (135mmol) of 1,4-diazabicyclo[2.2.2]octane in 165ml of acetonitrile was added 12.55g (87.4mmol) of N,N-dimethylsulphamoyl chloride. The reaction mixture was stirred at room temperature for 8h, allowed to stand overnight, poured into water and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and then concentrated in vacuo. The resulting crude product was purified by chromatography on silica gel eluting with 1:1 heptane-ethyl acetate to afford 14.8g (66% yield) **3d** as a solid: m.p. 110-112°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 8.35 (d, 1H, J<1Hz), 7.93 (d, 1H, J<1Hz), 7.84 (d, 2H), 7.35 (d, 2H), 3.00 (s, 6H), 2.45 (s, 3H). Anal. calcd. for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub> (329.3): C43.8; H4.6; N12.8. Found: C43.7; H5.0; N13.1.

**1-(N,N-Diethylamino)carbonyl-4-(tolylsulfonyl)pyrazole (3e):** To a solution of 1.0g (4.4mmol) of 4-(tolylsulfonyl)pyrazole **2b** and 1g (8.9mmol) of 1,4-diazabicyclo[2.2.2]octane was added 0.78g (5.7mmol) of diethylcarbamoyl chloride. The reaction mixture was stirred at room temperature for several hours, poured into water and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and then evaporated in vacuo to give 1.3g (92% yield) **3e** as a solid: m.p. 88-90°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 8.50 (d, 1H, J<1Hz), 7.85 (d, 1H, J<1), 7.82 (d, 2H), 7.34 (d, 2H), 3.55 (q, 4H), 2.40 (s, 3H), 1.25 (t, 6H). Anal. calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>S (321.4): C56.0; H6.00; N13.1. Found: C56.6; H6.2; N12.7.

**General Procedure for the Synthesis of Pyrazoles 5a-j:** To 9mmol of lithium diisopropylamide [prepared from 0.91g (9mmol) of diisopropylamine in 11ml of THF and 5.6ml of n-butyllithium (1.6 M in hexane)] in 11ml of THF was added 9mmol of 1-methyl-4-(phenylsulfonyl)pyrazole **3a** or 1-methyl-4-(tolylsulfonyl)pyrazole **3b** at -78°C. The mixture was stirred at -78°C for 1h, and then 10mmol of the electrophile was added. After stirring for an additional 1h at -78°C, the reaction

mixture was allowed to come to room temperature and stirred for 2h. Then, the reaction mixture was poured into saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic phase was dried over sodium sulfate and then evaporated in vacuo to give crude product, which was purified either by chromatography or crystallization.

**1,5-Dimethyl-4-(phenylsulfonyl)pyrazole (5a):** 1.42g (10mmol) Iodomethane was added as electrophile. Crystallization from heptane-ethyl acetate afforded 1.5g (71% yield) **5a** as a solid; m.p. 120-122°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.92 (m, 2H), 7.70 (s, 1H), 7.52 (m, 3H); 3.77 (s, 3H); 2.45 (s, 3H). Anal. calcd. for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S (236.3): C55.9; H5.1; N11.9. Found: C55.5; H5.5; N11.6.

**1-Methyl-5-(hydroxy)(phenyl)methyl-4-(phenylsulfonyl)pyrazole (5b):** 1.1g (10mmol) Benzaldehyde was added as electrophile. Crystallization from heptane-ethyl acetate afforded 0.9g (30% yield) **5b** as a solid; m.p. 159-161°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.89 (s, 1H); 7.70 (m, 2H); 7.50 (m, 1H); 7.40 (m, 2H); 7.27 (m, 3H); 7.10 (m, 2H); 6.40 (d, 1H, J=6Hz); 3.96 (d, 1H, J=6Hz); 3.70 (s, 3H). Anal. calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S (326.4): C62.2; H4.9; N8.5. Found: C61.8; H5.1; N8.3.

**1-Methyl-5-carboxaldehyde-4-(phenylsulfonyl)pyrazole (5c):** 0.76g (10.4mmol) Dimethylformamide was added as electrophile. Chromatography on silica gel eluting with 7:3 heptane-ethyl acetate afforded 1.61g (72% yield) **5c** as a solid; m.p. 110-112°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 10.4 (s, 1H); 7.98 (m, 2H); 7.85 (s, 1H); 7.59 (m, 3H); 4.18 (s, 3H). Anal. calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>3</sub>O<sub>3</sub>S (249.3) : C52.8; H4.0; N11.2. Found: C52.6; H 4.1; N10.9.

**1-Methyl-5-mesitylthio-4-(phenylsulfonyl)pyrazole (5d):** 3g (10mmol) Dimesityl disulfide was added as electrophile. Crystallization from heptane-ethyl acetate afforded 1.5g (45% yield) **5d** as a solid; m.p. 174-176°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.98 (s, 1H); 7.94 (m, 2H); 7.50 (m, 3H), 6.81 (s, 2H); 3.30 (s, 3H); 2.23 (s, 3H); 2.00 (s, 6H). Anal. calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> (371.5): C61.3; H5.4; N7.5. Found: C61.4; H5.5; N7.4.

**1-Methyl-5-tributylstannyl-4-(phenylsulfonyl)pyrazole (5e):** 3.3g (10mmol) tributylstannyl chloride was added as electrophile. Chromatography on silica gel eluting with 4:1 heptane-ethyl acetate afforded 3.45g (75% yield) **5e** as a viscous oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.85 (m, 2H); 7.82 (s, 1H); 7.50 (m, 3H); 3.96 (s, 3H); 1.15-1.55 (m, 18H); 0.85 (t, 9H).

**1,5-Dimethyl-4-(tolylsulfonyl)pyrazole (5f):** 1.42g (10mmol) Iodomethane was added as electrophile. Crystallization from heptane-ethyl acetate afforded 1.4g (66% yield) **5f** as a solid; m.p. 117-118°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100 MHz) δ 7.80 (s, 1H); 7.80 (d, 2H); 7.20 (d, 2H); 3.72 (s, 3H); 2.43 (s, 3H); 2.38 (s, 3H). Anal. calcd. for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S (250.3): C57.58; H5.64; N11.19. Found: C57.8; H5.3; N11.1.

**1-Methyl-5-(hydroxy)(phenyl)methyl-4-(tolylsulfonyl)pyrazole (5g):** 1.1g (10mmol) Benzaldehyde was added as electrophile. Crystallization from heptane-ethyl acetate afforded 1.4g (48% yield) **5g** as a solid; m.p. 145-146°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 100MHz) δ 7.80 (s, 1H); 7.55 (d, 2H); 7.05-7.35 (m, 5H); 7.20 (d, 2H); 6.40 (d, 2H, J=7Hz); 4.10 (d, 2H J=7Hz); 3.65 (s, 3H); 2.48 (s, 3H). Anal. calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S (342.4): C63.14; H5.30; N8.18. Found: C63.1; H5.3; N8.1.

**1-Methyl-5-carboxaldehyde-4-(tolylsulfonyl)pyrazole (5h):** 0.76g (10.4mmol) Dimethylformamide was added as electrophile. Chromatography on silica gel eluting with 1:1 heptane-ethyl acetate afforded 1.1g (49% yield) **5h** as a solid; m.p. 141-143°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>,

100 MHz)  $\delta$  10.40 (s, 1H); 7.85 (d, 2H); 7.80 (s, 1H); 7.35 (d, 2H); 4.15 (s, 3H); 2.40 (s, 3H). Anal. calcd. for  $C_{12}H_{12}N_2O_3S$  (264.3): C54.53; H4.58; N10.60. Found: C54.2; H4.2; N10.4.

**1-Methyl-5-phenylthio-4-(tolylsulfonyl)pyrazole (5i):** 2.2g (10mmol) Diphenyl disulfide was added as electrophile. Chromatography on silica gel eluting with 1:1 heptane-ethyl acetate afforded 1.8g (61.5% yield) **5i** as a solid: m.p. 105-106°C;  $^1H$  NMR ( $CDCl_3$ , 100MHz)  $\delta$  8.09 (s, 1H); 7.85 (d, 2H); 7.17 (m, 5H); 6.82 (m, 2H); 3.73 (s, 3H); 2.35 (s, 3H). Anal. calcd. for  $C_{17}H_{16}N_2O_2S_2$  (344.40): C59.28; H4.68; N8.13. Found C59.4; H4.5; N8.0.

**1-Methyl-5-tributylstannyl-4-(tolylsulfonyl)pyrazole (5j):** 3.3g (10mmol) Tributylstannyl chloride was added as electrophile. Chromatography on silica gel eluting with 1:1 heptane-ethyl acetate afforded 3.6g (76% yield) **5j** as a viscous oil:  $^1H$  NMR ( $CDCl_3$ , 100MHz)  $\delta$  7.78 (s, 1H); 7.72 (d, 2H); 7.25 (d, 2H); 3.92 (s, 3H); 2.40 (s, 3H); 1.10-1.60 (m, 18H); 0.88 (t, 9H). Anal. calcd. for  $C_{23}H_{38}N_2O_2SSn$  (525.32): C52.59; H7.29; N5.33. Found C52.6; H6.9; N5.8.

**5-[5-(1-Methyl-4-(tolylsulfonyl)pyrazolyl)]pyrimidine (6):** A mixture of 2.5g (4.7mmol) of 1-methyl-5-tributylstannyl-4-(tolylsulfonyl)pyrazole **5j**, 0.75g (4.7mmol) of 5-bromopyrimidine and 0.54g (0.47mmol) of tetrakis(triphenylphosphin)palladium in 70ml of dioxane was refluxed for 30h. After cooling the reaction mixture was filtered and the filtrate concentrated in vacuo. Trituration of the resulting residue with heptane afforded 0.96g (65% yield) **6** as solid: m.p. 165-167<sup>o</sup>mkC;  $^1H$  NMR ( $CDCl_3$ , 300MHz)  $\delta$  9.46 (s, 1H); 8.67 (s, 1H); 8.05 (s, 1H); 7.46 (d, 2H); 7.20 (d, 2H); 3.74 (s, 3H); 2.38 (s, 3H).

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## REFERENCES AND NOTES

Dedicated to Prof. R. R. Schmidt on the occasion of his 60<sup>th</sup> birthday

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