# SYNTHESIS OF HETEROARENECARBONITRILES BY ELECTROPHILIC CYANATION; REACTION OF METALATED HETEROARENES WITH *p*-TOLUENESULFONYL CYANIDE [1]

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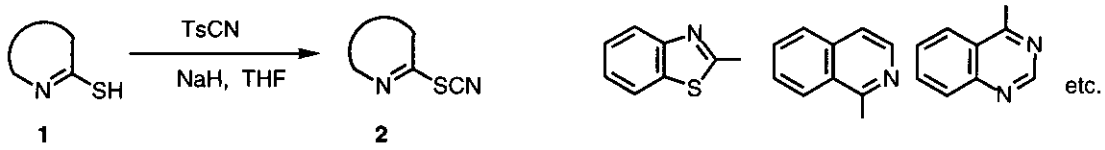
**Abstract**——Several heteroarenecarbonitriles (**5**) were synthesized in moderate yields from heteroarenes (**3**) through metalation, followed by electrophilic cyanation using *p*-toluenesulfonyl cyanide. Similarly, trimethylsilylheteroarenes (**8**) were converted to heteroarenecarbonitriles (**5**) in good yields by treatment with *p*-toluenesulfonyl cyanide.

In the previous paper,[1] we showed that *p*-toluenesulfonyl cyanide (TsCN) is a useful reagent for electrophilic cyanation. Namely, in the presence of base, mercaptoheteroarenes (**1**) reacted with TsCN to give the corresponding thiocyanatoheteroarenes (**2**) in good yields. In this reaction, TsCN provides the cyanogen cation ($CN^+$). To extend the scope of this electrophilic cyanation using TsCN, we applied this method to the



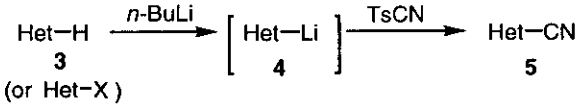

**1** **2**

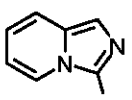
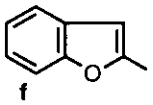
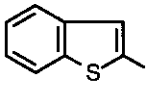
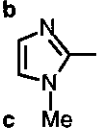
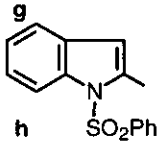
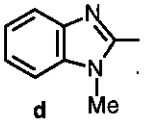
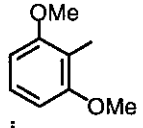
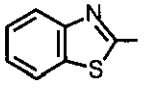
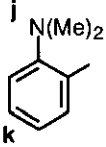
Scheme 1

preparation of heteroarenecarbonitriles (**5**). We anticipated that heteroarenyl carbanions ($Het^-$) would react with TsCN to give the corresponding heteroarenecarbonitriles (**5**). This is a carbon–carbon bond-forming reaction and represents a method for electrophilic introduction of a cyano group into heteroarenes. Many methods for preparing heteroarenecarbonitriles (**5**) have been reported,[2] but there are only a few papers describing electrophilic cyanation.[3] Here we wish to report the results of the reaction of metalated heteroarenes (**4**) with TsCN.

Metalation is a useful method to produce carbanions from organic compounds. Thus, metalloheteroarenes (**4**) should react with TsCN to give the heteroarenecarbonitriles (**5**) by electrophilic cyanation. We examined several kinds of metalloheteroarenes.

It is known that imidazo[1,5-*a*]pyridine (**3a**) is lithiated at the 3-position by treatment with *n*-BuLi.[4] Treatment of imidazo[1,5-*a*]pyridine (**3a**) with *n*-BuLi, followed by dropwise addition of TsCN (Method A) gave imidazo[1,5-*a*]pyridine-3-carbonitrile (**5a**) in 59% yield. However, when the solution of lithiated imidazo[1,5-*a*]pyridine was added dropwise to TsCN (Method B), **5a** was formed in 65% yield. In the preparation of 2-benzofurancarbonitrile (**5f**), only 26% yield was obtained by Method A, and 71% yield by Method B (Scheme 2). The difference may arise because the produced heteroarenecarbonitriles (**5**) can further react with lithioheteroarenes. In the cyanation of benzothiazole (**3e**) by method A, di-2-benzothiazolyl ketone (**7**) was the main product in 61% yield, together with a trace of 2-benzothiazolecarbonitrile (**5e**), as shown in Scheme 3.




| Het– | | 5, Yield (%) Method A | Method B | Het– or Ar– | | 5 or 6, Yield (%) Method A | Method B |
|---|---|---|---|---|---|---|---|
|  a | **5a** | 59 | 65 |  f | **5f** | 26 | 71 |
|  b | **5b** | 25 | 50 |  g | **5g** | | 52 |
|  c | **5c** | 40 | 77 |  h | **5h** | 66 | 73 |
|  d | **5d** | 39 | 57 |  j | **6j** | | 57 |
|  e | **5e** | trace | 33 |  k | **6k** | | 24 |

Scheme 2

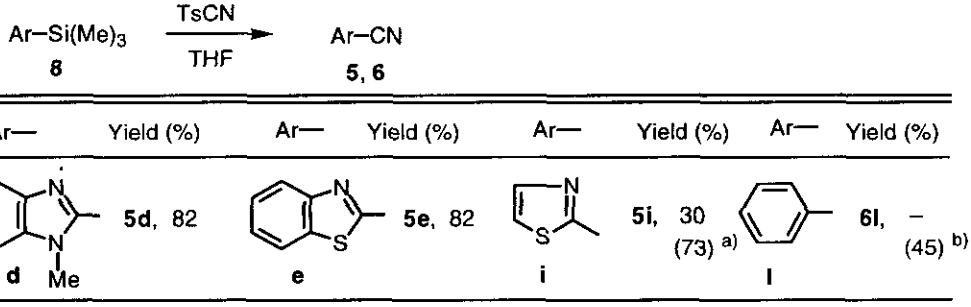
Cyanogen bromide (BrCN) is also used in electrophilic cyanation. In the synthesis of thiocyanatoheteroarenes (**2**), BrCN and TsCN, both gave thiocyanatoheteroarenes in good yields.[1] However, Bolze and Dell reported


3e 61% 7

Scheme 3

that cyanation by treatment of lithioarenes with BrCN does not proceed, namely, treatment of 2-lithio-3-methoxyanisole with BrCN gave 2-bromo-3-methoxyanisole.[5] The expected 3,6-dimethoxybenzonitrile (**6j**) could not be obtained. This result indicates that BrCN affords the bromo cation ($Br^+$) under these conditions. For direct introduction of a cyano group into heteroarenes, we found that TsCN is an effective reagent, presumably because the cyano cation ($CN^+$) is readily formed. TsCN provides a so-called soft cyano cation in comparison with BrCN because of the nature of the binding groups, bromine and sulfone.

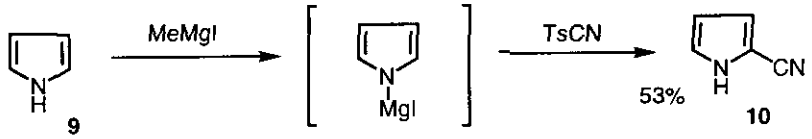
To find a more suitable method for this electrophilic cyanation, we tried other methods to generate the heteroarenyl carbanion. It is known that the carbon–silicon bond of trimethylsilylheteroarenes cleaves easily, resulting in the formation of the heteroarenyl carbanion.[6] This led us to examine the use of trimethylsilylheteroarenes (**8**) as the heteroarenyl carbanion donors. As shown in Scheme 4, we obtained good results in electrophilic cyanation using trimethylsilylheteroarenes compared with that using lithioheteroarenes. However, it seems that the donor effect of the arenyl carbanion of trimethylsilylarenes (**8**) is less than that of lithioarenes (**4**).




a) Obtained by reaction without solvent (THF).
b) Obtained from phenyllithium by Method B

Scheme 4

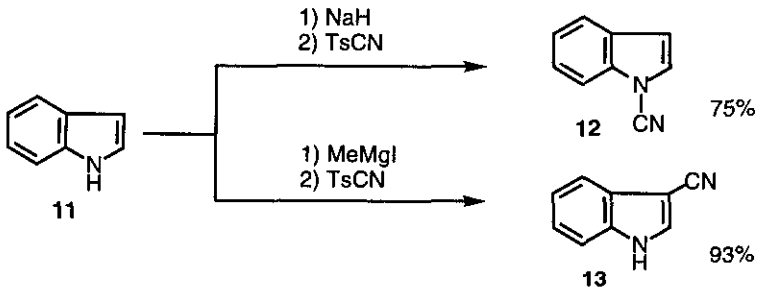
Grignard reagents also provide carbanions. Treatment of the pyrrole (**9**) with methylmagnesium iodide followed by reaction with TsCN furnished 2-pyrrolecarbonitrile (**10**) in 53% yield. We have applied this




9 10

Scheme 5

electrophilic cyanation to regioselective synthesis of indolecarbonitriles,[7] and have already shown that 1-benzenesulfonylindole (**3h**) affords 1-benzenesulfonyl-2-indolecarbonitrile (**5h**) *via* lithiation. Treatment of indole with sodium hydride followed by cyanation with TsCN gave 1-indolecarbonitrile (**12**). 3-Indolecarbonitrile (**13**) was obtained by forming indolylmagnesium iodide, followed by cyanation with TsCN. Appropriate metalations can thus be used to obtain regioselective cyanation of indoles (**11**).




Scheme 6

In conclusion, electrophilic cyanation of heteroarenes (**3**) using TsCN can be achieved through metalation. By this procedure, several heteroarenecarbonitriles (**5**) were synthesized from metalated heteroarenes, such as lithioheteroarenes (**4**), heteroarenylmagnesium halide, and trimethylsilylheteroarenes (**8**).

## EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a JASCO A-102 diffraction grating IR spectrophotometer. $^1$H-NMR spectra were measured at 60 MHz on a JEOL PMX60SI NMR spectrometer, and at 270 MHz on a JEOL JNM-GSX270 FT-NMR spectrometer. Chemical shifts are quoted in parts per million (ppm) with tetramethylsilane as an internal standard, and coupling constants ($J$) are given in Hz.

**Synthesis of Imidazo[1,5-*a*]pyridine-2-carbonitriles; A Typical Procedure.**

**Method A.** A solution of *n*-BuLi in *n*-hexane (1.63 mol/L, 1.8 mL, 3.0 mmol) was slowly added to a solution of imidazo[1,5-*a*]pyridine (3.0 mmol) in 6 mL of THF with stirring at –78 °C under an argon atmosphere and the solution was further stirred for 30 min at –78 °C. A solution of TsCN (815 mg, 4.5 mmol) in 4 mL of THF was added dropwise to the resulting solution at –78 °C and the solution was further stirred for 30 min. The cooling bath was removed and the reaction mixture was further stirred for 2 h, then poured into ice-$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane, benzene, and $CH_2Cl_2$.

**Method B.** A solution of *n*-BuLi in *n*-hexane (1.63 mol/L, 1.8 mL, 3.0 mmol) was slowly added to a solution of imidazo[1,5-*a*]pyridine (3.0 mmol) in 6 mL of THF with stirring at –78 °C under an argon atmosphere and the solution was further stirred for 30 min at –78 °C. The resulting solution was added dropwise to a solution of TsCN (815 mg, 4.5 mmol) in 4 mL of THF at –78 °C, and the whole was further stirred for 30 min. The cooling bath was removed and the reaction mixture was further stirred for 2 h. The reaction mixture was poured into ice-$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane, benzene, and/or $CH_2Cl_2$.

2-Lithio-1-methylimidazole (**4c**), 2-lithio-1-methylbenzimidazole (**4d**), 2-lithiobenzothiazole (**4e**), and 2-lithio-1-benzenesulfonylindole (**4h**) were prepared similarly.

The lithiation of other heteroarenes was carried out according to the reported procedures; 3-lithiopyridine (**4b**),[8] 2-lithiobenzofuran (**4f**),[9] 2-lithiobenzothiophene (**4g**),[10] 2-lithio-3-methoxyanisole,[8] and 2-lithio-*N*,*N*-dimethylaniline.[11]

Imidazo[1,5-*a*]pyridine-3-carbonitrile (**5a**): The fraction eluted with *n*-hexane–benzene (1:1) gave **5a**. Colorless needles (*n*-hexane–benzene), mp 123–124 °C. *Anal.* Calcd for $C_8H_5N_3$: C, 67.13; H, 3.52; N, 29.35. Found: C, 67.12; H, 3.23; N, 29.16. IR (KBr) $cm^{-1}$: 2218 (CN). $^1$H-NMR ($CDCl_3$) δ: 8.25 (1H, d, $J$ = 5.8, $C^5$-H), 7.78–6.78 (3H, m, $C^{6-8}$-H), 7.57 (1H, s, $C^1$-H).

3-Pyridinecarbonitrile (**5b**): The fraction eluted with $CH_2Cl_2$ gave **5b**.

1-Methyl-2-imidazolecarbonitrile (**5c**): Colorless oil ( lit.,[12] 65–70 °C/0.4 mm). IR (neat) $cm^{-1}$: 2232 (CN). MS (m/z): 107 ($M^+$).

1-Methyl-2-benzimidazolecarbonitrile (**5d**): The fraction eluted with *n*-hexane–benzene (1:1) gave **5d**. Colorless needles (benzene), mp 177–178 °C. *Anal.* Calcd for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.71; H, 4.34; N, 27.05. IR (KBr) $cm^{-1}$: 2234 (CN). $^1$H-NMR ($CDCl_3$) δ: 7.85 (1H, d, $J$ = 8.1, $C^4$-H), 7.53–7.39 (3H, m, $C^{5-7}$-H), 4.01 (3H, s, Me). MS (m/z): 157 ($M^+$).

2-Benzothiazolecarbonitrile (**5e**): The fraction eluted with *n*-hexane–$CH_2Cl_2$ (2:1) gave **5e**. Colorless needles (*n*-hexane-benzene), mp 82 °C. *Anal.* Calcd for $C_8H_4N_2S$: C, 59.98; H, 2.52; N, 17.49. Found: C, 59.79; H, 2.21; N, 17.67. IR (KBr) $cm^{-1}$: 2224 (CN). $^1$H-NMR ($CDCl_3$) δ: 8.40–7.85 (2H, m, $C^4$ and $C^7$-H), 7.80–7.40 (2H, m, $C^5$ and $C^6$-H). MS (m/z): 160 ($M^+$).

2-Benzofurancarbonitrile (**5f**): The fraction eluted with *n*-hexane–$CH_2Cl_2$ (2:1) gave **5f**. Colorless needles (*n*-hexane–AcOEt), mp 36 °C (lit.,[13] 36 °C). IR (neat) $cm^{-1}$: 2228 (CN). $^1$H-NMR ($CDCl_3$) δ: 7.77–7.15 (5H, m, $C^{3-7}$-H). MS (m/z): 143 ($M^+$).

2-Benzothiophenecarbonitrile (**5g**): Colorless oil. IR (KBr) $cm^{-1}$: 2214 (CN). $^1$H-NMR ($CDCl_3$) δ: 7.90–7.84 (3H, m, $C^2$, $C^4$ and $C^7$-H), 7.56–7.45 (2H, m, $C^5$ and $C^6$-H). MS (m/z): 159 ($M^+$).

1-Benzenesulfonyl-2-indolecarbonitrile (**5h**): The fraction eluted with *n*-hexane–$CH_2Cl_2$ (1:2) gave **5h**.

Colorless needles (*n*-hexane), mp 126–128 °C. *Anal.* Calcd for $C_{15}H_{10}N_2O_2S$: C, 63.82; H, 3.57; N, 9.92. Found: C, 63.78; H, 3.28; N, 9.72. IR (KBr) $cm^{-1}$: 2220 (CN). $^1$H-NMR ($CDCl_3$) δ: 8.31–7.80 (3H, m, $C^3$, $C^4$ and $C^7$-H), 7.70–7.20 (7H, m, $C^5$, $C^6$-H and Ph).

2,6-Dimethoxybenzonitrile (**6j**): Colorless needles (*n*-hexane–acetone), mp 118 °C (lit.,[14] 118 °C). IR (KBr) $cm^{-1}$: 2214 (CN). $^1$H-NMR ($CDCl_3$) δ: 7.44 (1H, t, $J$ = 8.4, $C^4$-H), 6.56 (2H, d, $J$ = 8.4, $C^3$ and $C^5$-H).

2-Dimethylaminobenzonitrile (**6k**): Colorless oil (lit.,[15] bp 58–65 °C/0.6 mm). IR (neat) $cm^{-1}$: 2210 (CN).

**Reaction of 2-Lithiobenzothiazole with TsCN.** A solution of *n*-BuLi in *n*-hexane (1.63 mol/L, 1.8 mL, 3.0 mmol) was slowly added to a solution of benzothiazole (405 mg, 3.0 mmol) in 6 mL of ether with stirring at –78 °C under an argon atmosphere and the solution was further stirred for 5 min. A solution of TsCN (815 mg, 4.5 mmol) in 4 mL of ether was added dropwise to the resulting solution at –78 °C and stirring was continued for 30 min. The cooling bath was removed and the reaction mixture was further stirred for 2 h, then poured into ice-$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with *n*-hexane–$CH_2Cl_2$ gave di-2-benzothiazolyl ketone (**7**). Orange needles (*n*-hexane–acetone), mp 182–183 °C (lit.,[16] 184 °C). IR (KBr) $cm^{-1}$: 1657 (CO). $^1$H-NMR ($CDCl_3$) δ: 8.38 (2H, d, $J$ = 6.8, $C^4$ and $C^{4'}$-H or $C^5$ and $C^{5'}$-H ), 8.06 (2H, d, $J$ = 6.8, $C^4$ and $C^{4'}$-H or $C^5$ and $C^{5'}$-H ), 7.67–7.57 (4H, m, $C^{6–7}$ and $C^{6'–7'}$-H). $^{13}$C-NMR ($CDCl_3$) δ: 176.5 (CO), 162.2, 153.3, 137.9, 128.4, 127.4, 126.3, 122.2. MS (m/z): 296 ($M^+$).

**Synthesis of Heteroarenecarbonitriles (5) by Reaction of Trimethylsilylheteroarenes (8) with TsCN.**

**1-Methyl-2-benzimidazolecarbonitrile (5d).** A solution of 1-methyl-2-trimethylsilylbenzimidazole (**8d**, 2.10 g, 10.3 mmol) and TsCN (1.86 g, 10.3 mmol) in THF (20 mL) was refluxed for 5 h under an argon atmosphere. The reaction mixture was poured into ice–$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with $CH_2Cl_2$ gave **5d** in 82% yield (1.33 g).

**2-Benzothiazolecarbonitrile (5e).** A solution of 2-trimethylsilylbenzothiazole (**8e**, 400 mg, 1.9 mmol) and TsCN (350 mg, 1.9 mmol) in THF (10 mL) was refluxed for 5 h under an argon atmosphere. The reaction mixture was poured into ice–$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with *n*-hexane–$CH_2Cl_2$ (1:1) gave **5e** in 82% yield (250 mg).

**2-Thiazolecarbonitrile (5i).** A mixture of 2-trimethylsilylthiazole (**8i**, 296 mg, 1.9 mmol) and TsCN (342 mg, 1.9 mmol) was heated at 70 °C for 5 h under an argon atmosphere. The reaction mixture was poured into ice–$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and

concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with $CH_2Cl_2$ gave **5i** in 73% yield (153 mg). Colorless oil (lit.,[17] bp 98 °C/24 mm). IR (neat) $cm^{-1}$: 2228 (CN). $^1$H-NMR ($CDCl_3$) δ: 8.10 (1H, d, $J$ = 2.7, $C^4$-H), 7.80 (1H, d, $J$ = 2.7, $C^5$-H). MS (m/z): 110 ($M^+$).

When above reaction was carried out in THF (10 mL), 2-thiazolecarbonitrile (**5i**) was obtained in 30% yield (62 mg).

**2-Pyrrolecarbonitrile (10).** A solution of methylmagnesium iodide (0.31 mol/L in ether, 9 mL, 2.8 mmol) was added to a solution of pyrrole (**9**, 134 mg, 2.0 mmol) in 6 mL of ether, and the whole was stirred for 30 min at rt. A solution of TsCN (434 mg, 2.4 mmol) in ether (4 mL) was added to the resulting solution and the mixture was further stirred for 2 h at –78 °C, then poured into ice–$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with $CH_2Cl_2$ gave 2-pyrrolecarbonitrile (**10**) in 53% yield (97 mg). Colorless oil.[18] IR (neat) $cm^{-1}$: 2218 (CN). $^1$H-NMR ($CDCl_3$) δ: 9.07 (1H,br s, NH), 6.97 (1H, m, $C^3$-H), 6.87 (1H, m, $C^5$-H), 6.29 (1H, m, $C^4$-H). MS (m/z): 92 ($M^+$).

**1-Indolecarbonitrile (12).** Sodium hydride (NaH, 60% in oil, 144 mg, 3.6 mmol) was added to a solution of indole (**11**, 351 mg, 3.0 mmol) in 10 mL of THF at rt under an argon atmosphere, and the mixture was stirred for 10 min. TsCN (652 mg, 3.6 mmol) was further added to the resulting mixture, and the whole was stirred for 3 h at rt, then poured into ice-$H_2O$, and extracted with AcOEt. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane. The first fraction gave **12**. Colorless oil. IR (neat) $cm^{-1}$: 2242 (CN). $^1$H-NMR ($CDCl_3$) δ: 7.80–7.15 (5H, m, $C^2$ and $C^{4-7}$-H), 6.65 (1H, d, $J$ = 3.8, $C^3$-H). MS (m/z): 142 ($M^+$).

**3-Indolecarbonitrile (13).** A solution of methylmagnesium iodide (0.31 mol/L in ether, 9 mL, 2.8 mmol) was added to a solution of indole (**11**, 234 mg, 2.0 mmol) in 6 mL of ether, and the whole was stirred at rt for 30 min. A solution of TsCN (434 mg, 2.4 mmol) in ether (4 mL) was added to the resulting solution and the mixture was further stirred for 1 h at –50 °C, then poured into ice–$H_2O$ and extracted with $CH_2Cl_2$. The organic layer was washed with $H_2O$, dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on $SiO_2$ with *n*-hexane and $CH_2Cl_2$. The fraction eluted with $CH_2Cl_2$ gave 3-indolecarbonitrile (**13**) in 93% yield (264 mg). Colorless needles (*n*-hexane), mp 178 °C (lit.,[19] 180 °C). *Anal.* Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71. Found: C, 75.85; H, 4.06; N, 19.46. IR (neat) $cm^{-1}$: 2222 (CN). $^1$H-NMR (DMSO-$d_6$) δ: 12.22 (1H, bs, NH), 8.26 (1H, d, $J$ = 2.7, $C^2$-H), 7.65 (1H, d, $J$ = 7.3, $C^7$-H), 7.57 (1H, d, $J$ = 8.4, $C^4$-H),7.32–7.22 (2H, m, $C^5$ and $C^6$-H).

## REFERENCES AND NOTES


1. This paper forms Part II of "Electrophilic Cyanations": Part I; A. Miyashita, I. Nagasaki, Y. Suzuki, K. Iwamoto, and T. Higashino, *Heterocycles*, 1997, **45**, 745.
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Received, 4th March, 1997