Palladium-catalyzed cyanation of aryl and heteroaryl iodides with copper(I) cyanide

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The palladium-catalyzed cyanation of aryl and heteroaryl iodides or bromides using copper(I) cyanide as a cyano group source afforded the corresponding aryl and heteroaryl cyanides in good yields.

Introduction

Since the cyano group is a stable and useful functional group, which can be transformed to various other functional groups such as acyl, carboxy, formyl, carbamoyl, *etc*., many synthetic methods for aryl and heteroaryl cyanides have been studied. Among them, the following methods are known as classical methods for the direct introduction of a cyano group to arenes and heteroarenes: the cyanation of aryl and heteroaryl halides with copper(I) cyanide (CuCN), the Reissert–Henze cyanation of π-deficient heteroaromatic *N*-oxides, and the electrophilic cyanation of π-sufficient heteroaromatics.

The cyanation of aryl and heteroaryl halides with CuCN has been used for the synthesis of the corresponding cyanides, and this method can be generally applicable to the iodo and bromo derivatives of arenes and π-sufficient heteroarenes. However, the reaction conditions, *e.g*., heating in DMF or quinoline, are relatively severe. The reaction of α- or γ-halogeno π-deficient heteroarenes affords the products in low yields and is only practically applicable to the β-halogeno derivatives.[1]

Although the Reissert–Henze cyanation of π-deficient heteroarene *N*-oxides[2] generally gives the corresponding cyanides in good yields, and the modification using trimethylsilyl cyanide instead of alkali metal cyanides has been developed, the positions of the cyano group are principally restricted to the α-positions with respect to the *N*-oxide groups.

A few direct electrophilic cyanations of π-sufficient heteroaromatics are also known;[3] for example, the electrophilic substitution reaction of indoles with (ethoxycarbonylimino)-triphenylphosphorane or triphenylphosphine–thiocyanogen gave indole-3-carbonitriles. These reactions are restricted to only proceed at the electrophilically active positions. They are not general or efficient preparative methods of aryl and heteroaryl cyanides.

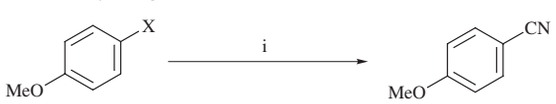
The transition metal-catalyzed cyanation of aryl halides and triflates is a useful modern method to prepare aryl cyanides. In particular, palladium-catalyzed cyanation is known to have generality in synthesis of benzonitrile derivatives, and potassium,[4] sodium,[5] trimethylsilyl,[6] and zinc cyanide[7] as the cyano group source have been used in the cyanation. The reported palladium-catalyzed cyanations were centred on the benzene derivatives, and there is no report on heteroaromatic derivatives except for the halogenopyrazines[4e,f] and 3-bromopyridine.[8]

In order to establish a cyanation method generally applicable to arenes, π-deficient, and π-sufficient heteroarenes and to find a new cyano group source, we studied the palladium-catalyzed cyanation of aryl and heteroaryl halides using CuCN as the cyano group source. Recently, a copper(I) species-catalyzed reaction using sodium cyanide as a cyano group source[8] has been reported and as in connection with our study.

At first, we examined the reaction conditions using 4-methoxyiodobenzene **1a** as the substrate, tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] as the palladium(0) catalyst, which is known to be more stable than tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], and diphenylphosphinoferrocene (DPPF) as the ligand.

As shown in Table 1, a DMF solution of **1a** and CuCN in the presence of $Pd_2(dba)_3$ and DPPF was heated at 120 °C for 2 h (Run 1) to give 4-methoxybenzonitrile **3a** in 80% yield. In order to find milder reaction conditions and an easier isolation oper-

Table 1 Palladium-catalyzed cyanation of 4-methoxyhalogenobenzenes **1a** and **2a** with CuCN



1a: X=I
2a: X=Br

3a

Reagents and conditions: i, CuCN, $Pd_2(dba)_3$, DPPF, 1,4-dioxane, reflux.

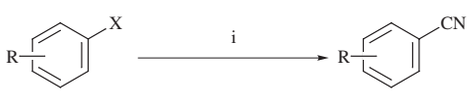
Run	X	Additive	Solvent	Temp. (*T*/°C)	Time (*t*/h)	Yield (%)
1	I	None	DMF	120	2	80
2	I	None	Dioxane	Reflux	1	39
3	I	Et_4NCN	DMF	120	1	85
4	I	Et_4NCN	DMF	100	2	78
5	I	Et_4NCN	Dioxane	Reflux	2	82
6	I	Et_4NCN	THF	Reflux	1	93
7	I	Et_4NCN	MeCN	Reflux	2	87
8	Br	Et_4NCN	DMF	120	4	29
9	Br	Et_4NCN	Dioxane	Reflux	3	91

ation for the products, the reaction in 1,4-dioxane at the reflux temperature (101 °C, Run 2) was examined, but the yield of **3a** decreased to 39%. When the above DMF solution containing tetraethylammonium cyanide (Et_4NCN), which was not an effective cyano group source, as an additive was heated at 100 °C or 120 °C, the yields of **3a** were not significantly changed (Runs 3 and 4). In the reaction containing Et_4NCN in 1,4-dioxane, however, the yield was dramatically improved (Run 5). These reaction conditions were found to be effective for the palladium-catalyzed reaction of 4-methoxybromobenzene **2a** with CuCN (Run 9). Although the reaction mixture containing Et_4NCN in other solvents such as THF and acetonitrile (Run 6 and 7) also gave **3a** in good yields, these solvents were not effective for the reaction of heteroaryl halides such 3-iodo-1-(phenylsulfonyl)indole **4b** as will be described below. Therefore, we selected 1,4-dioxane as the reaction solvent.

For the reaction of the bromo derivative **2a**, similar results were obtained, namely refluxing in 1,4-dioxane for 3 h gave **3a** in 91% yield. Based on these experiments, we decided that refluxing in 1,4-dioxane in the presence of Et_4NCN should be selected as the reaction conditions for the palladium-catalyzed cyanation of aryl halides with CuCN using $Pd_2(dba)_3$ and DPPF.

Next, the reaction conditions were applied to halogenobenzene derivatives having substituents at the 2- or 4-position. As shown in Table 2, the iodo- and bromobenzenes were transformed into the corresponding benzonitriles in 56–94% yields except for 2-nitrobromobenzene, although the reason for the low yield in this case is not clear at present.

Table 2 Palladium-catalyzed cyanation of halogenobenzenes **1a**–**f** and **2a**–**f** with CuCN

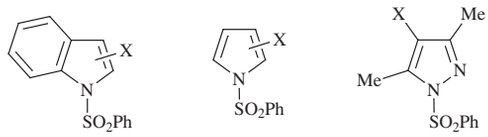


1a-f, **2a-f** **3a-f**

Reagents and conditions: i, CuCN, Et_4NCN, $Pd_2(dba)_3$, DPPF, 1,4-dioxane, reflux.

Compd.	R	X	Time (*t*/h)	Yield (%)
1a	4-OMe	I	2	82
1b	4-CO_2Me	I	1	88
1c	4-NO_2	I	2	65
1d	2-OMe	I	1	94
1e	2-CO_2Me	I	1	88
1f	2-NO_2	I	1	67
2a	4-OMe	Br	3	91
2b	4-CO_2Me	Br	1	89
2c	4-NO_2	Br	3	56
2d	2-OMe	Br	1	76
2e	2-CO_2Me	Br	1	83
2f	2-NO_2	Br	1	23

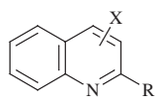
The palladium-catalyzed cyanation using CuCN as a cyano group source was applied to heteroaryl halides. *N*-(Phenylsulfonyl)indoles **4a**,**b**, the pyrrole derivatives **5a**,**b**, and quinoline derivatives **7** and **8a**–**c** were used as representative π-sufficient and π-deficient heteroarenes. The results in Table 3 show that the reaction using heteroaryl iodides **4**–**6**, **8** gave the corresponding nitriles **9**–**12** in good yields without using Et_4NCN as an additive. In the case of 2-bromoquinoline **7**, however, the addition of Et_4NCN to the reaction mixture gave quinoline-2-carbonitrile **12a** in 77% yield.



4a: X=2-I
4b: X=3-I
9a: X=2-CN
9b: X=3-CN

5a: X=2-I
5b: X=3-I
10a: X=2-CN
10b: X=3-CN

6: X=I
11: X=CN



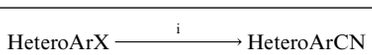
7 : X=2-Br, R=H
8a: X=2-I, R=H
8b: X=3-I, R=H
8c: X=4-I, R=Me

12a: X=2-CN, R=H
12b: X=3-CN, R=H
12c: X=4-CN, R=Me

Since the reaction of halogenoaromatics, especially iodo- or bromoaromatics, with CuCN is known as a classical method for the synthesis of aromatic nitriles as already described above, we finally examined the reaction of the halogenoaromatics used in this study with CuCN in order to confirm that our method is a palladium-catalyzed reaction. Namely, the reaction of aryl bromides or iodides with CuCN in DMF at 120 °C or in 1,4-dioxane at reflux in the presence or absence of Et_4NCN gave the corresponding nitriles in zero or low yields and the starting halogenoaromatics were recovered in high amounts in almost all reactions (Table 4).

The cyanation reaction described in this paper is considered to proceed as follows. An arylpalladium halide which forms by oxidative addition reaction of an aryl halide with a palladium(0) species transforms to an arylpalladium cyanide by ligand exchange reaction with CuCN. The arylpalladium cyanide gives an aryl cyanide by reductive elimination reaction.

Table 3 Palladium-catalyzed cyanation of halogenoheteroaromatics **4**–**8** with CuCN



4–**8** **9**–**12**

Reagents and conditions: i, CuCN, $Pd_2(dba)_3$, DPPF, 1,4-dioxane, reflux.

HeteroArX	Additive	Time (*t*/h)	Yield (%)
2-Iodo-1-(phenylsulfonyl)indole **4a**	None	3	94
3-Iodo-1-(phenylsulfonyl)indole **4b**	None	4	99
2-Iodo-1-(phenylsulfonyl)pyrrole **5a**	None	1	97
3-Iodo-1-(phenylsulfonyl)pyrrole **5b**	None	1	69
4-Iodo-3,5-dimethyl-1-(phenylsulfonyl)pyrazole **6**	None	1	90
2-Bromoquinoline **7**	None	18	42
2-Bromoquinoline **7**	Et_4NCN	1	77
2-Iodoquinoline **8a**	None	1	90
3-Iodoquinoline **8b**	None	1	91
4-Iodo-2-methylquinoline **8c**	None	1	96

Table 4 Reaction of aryl and heteroaryl halides with CuCN

$$ArX \xrightarrow[\text{additive, solvent temp.}]{CuCN} ArCN$$

Reagents and conditions: i, CuCN, 1,4-dioxane, reflux.

Compd.	Additive	Solvent	Temp. (*T*/°C)	Time (*t*/h)	Yield (%)[a]
1a	Et_4NCN	DMF	120	18	39 (20)
1b	Et_4NCN	Dioxane	Reflux	12	(96)
1c	Et_4NCN	Dioxane	Reflux	12	trace (84)
1d	Et_4NCN	Dioxane	Reflux	12	31 (67)
1e	Et_4NCN	Dioxane	Reflux	12	trace (98)
1f	Et_4NCN	Dioxane	Reflux	12	29 (25)
2a	Et_4NCN	DMF	120	40	1 (53)
2a	Et_4NCN	Dioxane	Reflux	12	(58)
4a	None	Dioxane	Reflux	12	(45)
4b	None	Dioxane	Reflux	12	(98)
5a	None	Dioxane	Reflux	12	(96)
5b	None	Dioxane	Reflux	12	(100)
8a	None	Dioxane	Reflux	20	(81)
8b	Et_4NCN	Dioxane	Reflux	12	(99)
8c	None	Dioxane	Reflux	12	(88)

[a] Figure in parentheses are recoveries of the starting halogenoaromatics.

Conclusions

The palladium-catalyzed cyanation of aryl and heteroaryl halides using CuCN as the cyano group source is a general preparative method for aromatic nitriles together with the reported palladium-catalyzed reactions[4–8] using various inorganic and organic cyanides.

Experimental

All mps (Yazawa micro melting point BY-2) and bps are uncorrected. IR spectra were taken on a JASCO IR-810 spectrophotometer. ^{1}H NMR spectra were recorded on Varian Gemini 2000 (300 MHz) and Hitachi R-300 (300 MHz) spectrometers. Chemical shifts are expressed in δ (ppm) values with tetramethylsilane (TMS) as an internal reference, and coupling constants (*J*) are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on JMS-DX303 and JMS-AX500 instruments.

General procedure for the palladium-catalyzed cyanation of halogenoarenes and halogenoheteroarenes with CuCN

A mixture of a halogenoarene or a halogenoheteroarene (1.0 mmol), CuCN (4.0 mmol), $Pd_2(dba)_3$ (0.04 mmol), DPPF (0.16 mmol), and anhydrous 1,4-dioxane (5 mL) in the presence of (Procedure A) or in the absence of Et_4NCN (1.0 mmol) (Procedure B) was refluxed, for the time shown in Tables 2–4, under argon atmosphere. The reaction mixture was diluted with AcOEt and filtered through a Celite® pad. The filtrate was washed with saturated aq. $NaHCO_3$ (50 mL × 3), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using hexane–AcOEt (10 : 1 for **3a**–**d**, **10a**, and **12b**; 7 : 1 for **3e**, **9a**,**b**, **12a**, and **12c**; 5 : 1 for **10b** and **11**, 3 : 1 for **3f**) as eluent.

4-Methoxybenzonitrile 3a. According to the General Procedure A, the reaction using 4-bromoanisole **2a** (187 mg, 1.0 mmol) gave **3a** (120 mg, 91%). The crude product was recrystallized from hexane–AcOEt to give colorless needles, mp 56–57 °C (lit.,[9] 58 °C); ν_{max}(KBr)/cm^{-1} 2210; δ_H 3.87 (3H, s), 6.96 (2H, d, *J* 8.24), 7.60 (2H, d, *J* 8.24); *m*/*z* 133 (M$^+$, 100%) (Found: M$^+$, 133.0537. C_8H_7NO requires *M*, 133.0527).

Methyl 4-cyanobenzoate 3b. According to the General Procedure A, the reaction using methyl 4-bromobenzoate **2b** (108 mg, 0.5 mmol) gave **3b** (71.6 mg, 89%). The crude product was recrystallized from hexane–acetone to give colorless needles, mp 66–67 °C (lit.,[9] 68 °C); ν_{max}(KBr)/cm^{-1} 1720, and 2250; δ_H 3.97 (3H, s), 7.75 (2H, d, *J* 8.24), 8.15 (2H, d, *J* 8.24); *m*/*z* 161 (M$^+$, 34%), and 130 (100) (Found: M$^+$, 161.0522. $C_9H_7NO_2$ requires *M*, 161.0476).

4-Nitrobenzonitrile 3c. According to the General Procedure A, the reaction using 4-iodonitrobenzene **1c** (249 mg, 1.0 mmol) gave **3c** (95.8 mg, 65%). The crude product was recrystallized from hexane–AcOEt to give colorless plates, mp 148–150 °C (lit.,[9] 148 °C); ν_{max}(KBr)/cm^{-1} 1350, 1520, and 2225; δ_H 7.89 (2H, d, *J* 8.52), 8.37 (2H, d, *J* 8.52); *m*/*z* 148 (M$^+$, 69%), and 102 (100) (Found: M$^+$, 148.0273. $C_7H_4N_2O_2$ requires *M*, 148.0272).

2-Methoxybenzonitrile 3d. According to the General Procedure A, the reaction using 2-iodoanisole **1d** (117 mg, 0.5 mmol) gave **3d** (62.5 mg, 94%) as a colorless liquid; bp 70 °C/3 mmHg (lit.,[9] 135 °C/12 mmHg); ν_{max} (neat)/cm^{-1} 2225; δ_H 3.94 (3H, s), 6.97–6.99 (2H, m), 7.52–7.59 (2H, m); *m*/*z* 133 (M$^+$, 100%) (Found: M$^+$, 133.0538. C_8H_7NO requires *M*, 133.0527).

Methyl 2-cyanobenzoate 3e. According to the General Procedure A, the reaction using methyl 2-iodobenzoate **1e** (262 mg, 1.0 mmol) gave **3e** (142 mg, 88%). The crude product was recrystallized from hexane–acetone to give colorless prisms, mp 47–49 °C (Found: C, 67.38; H, 4.38; N, 8.82. $C_9H_7NO_2$ requires C, 67.08; H, 4.38; N, 8.69%); ν_{max}(KBr)/cm^{-1} 1720, and 2225; δ_H 4.01 (3H, s), 7.66–7.70 (2H, m), 7.81–7.84 (1H, m), 8.14–8.17 (1H, m); *m*/*z* 161 (M$^+$, 30%), and 130 (100) (Found: M$^+$, 161.0516. $C_9H_7NO_2$ requires *M*, 161.0476).

2-Nitrobenzonitrile 3f. According to the General Procedure A, the reaction using 2-iodonitrobenzene **1f** (125 mg, 0.5 mmol) gave **3f** (49.9 mg, 67%). The crude product was recrystallized from hexane–acetone to give colorless needles, mp 109–110 °C (lit.,[9] 108 °C); ν_{max}(KBr)/cm^{-1} 1340, 1540, and 2225; δ_H 7.81–7.87 (2H, m), 7.91–7.96 (1H, m), 8.33–8.39 (1H, m); *m*/*z* 148 (M$^+$, 100%) (Found: M$^+$, 148.0281. $C_7H_4N_2O_2$ requires *M*, 148.0272).

1-(Phenylsulfonyl)indole-2-carbonitrile 9a. According to the General Procedure B, the reaction using 2-iodo-1-(phenylsulfonyl)indole **4a** (383 mg, 1.0 mmol) gave **9a** (266.1 mg, 94%). The crude product was recrystallized from hexane–AcOEt to give colorless prisms, mp 127–128 °C (Found: C, 63.62; H, 3.56; N, 9.93; S, 11.34. $C_{15}H_{10}N_2O_2S$ requires C, 63.82; H, 3.57; N,

9.92; S, 11.36%); ν_{max}(KBr)/cm^{-1} 1170, 1310, and 2225; δ_H 7.36 (2H, t, *J* 6.87), 7.48–7.65 (5H, m), 8.04 (2H, d, *J* 7.42), 8.23 (1H, d, *J* 8.52); *m*/*z* 282 (M^+, 45%), and 77 (100) (Found: M^+, 282.0446. $C_{15}H_{10}N_2O_2S$ requires *M*, 282.0462).

1-(Phenylsulfonyl)indole-3-carbonitrile 9b. According to the General Procedure B, the reaction using 3-iodo-1-(phenylsulfonyl)indole **4b** (383 mg, 1.0 mmol) gave **9b** (278.8 mg, 99%). The crude product was recrystallized from hexane–AcOEt to give colorless prisms, mp 151–152 °C (Found: C, 63.73; H, 3.58; N, 9.99; S, 11.37. $C_{15}H_{10}N_2O_2S$ requires C, 63.82; H, 3.57; N, 9.92; S, 11.36%); ν_{max}(KBr)/cm^{-1} 1170, 1380, and 2227; δ_H 7.37–7.58 (4H, m), 7.60–7.73 (2H, m), 7.95–8.03 (3H, m), 8.12 (1H, s); *m*/*z* 282 (M^+, 37%), and 77 (100) (Found: M^+, 282.0453).

1-(Phenylsulfonyl)pyrrole-2-carbonitrile 10a. According to the General Procedure B, the reaction using 2-iodo-1-(phenylsulfonyl)pyrrole **5a** (117 mg, 0.35 mmol) gave **10a** (78.7 mg, 97%). The crude product was recrystallized from hexane–acetone to give needles, mp 83–85 °C (Found: C, 56.91; H, 3.54; N, 12.06; S, 13.72. $C_{11}H_8N_2O_2S$ requires C, 56.89; H, 3.47; N, 12.06; S, 13.80%); ν_{max}(KBr)/cm^{-1} 1180, 1380, and 2240; δ_H 6.34 (1H, t, *J* 3.30), 6.98 (1H, dd, *J* 1.65, 3.85), 7.50 (1H, dd, *J* 1.65, 3.30), 7.57–7.63 (2H, m), 7.68–7.74 (1H, m), 8.05–8.09 (2H, m); *m*/*z* 232 (M^+, 37%) and 77 (100) (Found: M^+, 232.0322. $C_{11}H_8N_2O_2S$ requires *M*, 232.0306).

1-(Phenylsulfonyl)pyrrole-3-carbonitrile 10b. According to the General Procedure B, the reaction using 3-iodo-1-(phenylsulfonyl)pyrrole **5b** (167 mg, 0.5 mmol) gave **10b** (80.4 mg, 69%). The crude product was recrystallized from hexane–acetone to give plates, mp 89–90 °C (Found: C, 56.93; H, 3.53; N, 12.04; S, 13.82. $C_{11}H_8N_2O_2S$ requires C, 56.89; H, 3.47; N, 12.06; S, 13.80%); ν_{max}(KBr)/cm^{-1} 1180, 1380, and 2240; δ_H 6.51 (1H, dd, *J* 1.65, 3.30), 7.19 (1H, dd, *J* 2.20, 3.30), 7.56–7.62 (2H, m), 7.66 (1H, dd, *J* 1.65, 2.20), 7.68–7.74 (1H, m), 7.91–7.95 (2H, m); *m*/*z* 232 (M^+, 39%), and 77 (100) (Found: M^+, 232.0293).

3,5-Dimethyl-1-(phenylsulfonyl)pyrazole-4-carbonitrile 11. According to the General Procedure B, the reaction using 4-iodo-3,5-dimethy-1-(phenylsulfonyl)pyrazole **6** (362 mg, 1.0 mmol) gave **11** (235.6 mg, 90%). The crude product was recrystallized from hexane–acetone to give colorless needles, mp 106–108 °C (Found: C, 55.19; H, 4.29; N, 16.03; S, 12.26. $C_{12}H_{11}N_3O_2S$ requires C, 55.16; H, 4.24; N, 16.08; S, 12.27%); ν_{max}(KBr)/cm^{-1} 1200, 1400, and 2250; δ_H 2.33 (3H, s), 2.70 (3H, s), 7.58–7.63 (2H, m), 7.70–7.75 (1H, m), 8.01–8.04 (2H, m); *m*/*z* 261 (M^+, 11%), and 77 (100) (Found: M^+, 261.0602. $C_{12}H_{11}N_3O_2S$ requires *M*, 261.0571).

Quinoline-2-carbonitrile 12a. According to the General Procedure B, the reaction using 2-iodoquinoline **8a** (255 mg, 1.0 mmol) gave **12a** (139.5 mg, 90%). The crude product was recrystallized from hexane–AcOEt to give colorless plates, mp 92–94 °C (lit.,[10] 94 °C) (Found: C, 77.91; H, 3.90; N, 18.15. $C_{10}H_6N_2$ requires C, 77.91; H, 3.92; N, 18.17%); ν_{max}(KBr)/cm^{-1} 2250; δ_H 7.69–7.75 (2H, m), 7.86 (1H, dt, *J* 1.37, 6.87), 7.91 (1H, d, *J* 7.97), 8.19 (1H, d, *J* 8.52), 8.32 (1H, d, *J* 8.52); *m*/*z* 154 (M^+, 100%) (Found: M^+, 154.0544. $C_{10}H_6N_2$ requires *M*, 154.0531).

Quinoline-3-carbonitrile 12b. According to the General Procedure B, the reaction using 3-iodoquinoline **8b** (128 mg, 0.5 mmol) gave **12b** (69.9 mg, 91%). The crude product was recrystallized from hexane–acetone to give colorless prisms, mp 105–107 °C (lit.,[10] 109 °C) (Found: C, 77.96; H, 3.99; N, 18.14. $C_{10}H_6N_2$ requires C, 77.91; H, 3.92; N, 18.17%); ν_{max}(KBr)/cm^{-1} 2240; δ_H 7.71 (1H, t, *J* 8.24), 7.88–7.94 (2H, m), 8.19 (1H, d, *J* 9.07), 8.56 (1H, d, *J* 1.92), 9.06 (1H, d, *J* 1.92); *m*/*z* 154 (M^+, 100%) (Found: M^+, 154.0533. $C_{10}H_6N_2$ requires *M*, 154.0531).

2-Methylquinoline-4-carbonitrile 12c. According to the General Procedure B, the reaction using 4-iodo-2-methylquinoline **8c** (135 mg, 0.5 mmol) gave **12c** (81 mg, 96%). The crude product was recrystallized from hexane–acetone to give colorless needles, mp 102–104 °C (Found: C, 78.46; H, 4.72; N, 16.43. $C_{11}H_8N_2$ requires C, 78.55; H, 4.79; N, 16.66%); ν_{max}(KBr)/cm^{-1} 2240; δ_H 2.81 (3H, s), 7.64 (1H, s), 7.70 (1H, dt, *J* 1.37, 8.24), 7.83 (1H, dt, *J* 1.37, 8.24), 8.12 (1H, d, *J* 8.24), 8.16 (1H, d, *J* 8.24); *m*/*z* 168 (M^+, 100%) (Found: M^+, 168.0691. $C_{11}H_8N_2$ requires *M*, 168.0687).

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