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A Novel Synthesis of 4-Aryl- and 4-Heteroarylpyridines *via* Diethyl(4-pyridyl)borane

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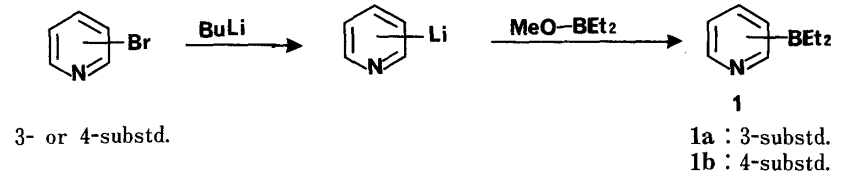
A convenient method for the preparation of 4-aryl- and 4-heteroarylpyridines by the palladium-catalyzed cross-coupling reaction of diethyl(4-pyridyl)borane with aryl and heteroaryl halides is described.

Keywords——diethyl(4-pyridyl)borane; aryl halide; heteroaryl halide; 4-arylpyridine; 4-heteroarylpyridine; terpyridyl; palladium-catalyzed cross-coupling reaction

The current interest in 4-aryl- and 4-heteroarylpyridines is based on their promising pharmacological profile and their versatility as synthetic intermediates.[1] Although syntheses of arylpyridines have been achieved in a variety of ways, the direct arylation of the pyridine nucleus has limited scope, because of restricted utilization of aryl groups, and lack of regioselectivity.[1] Recently, some improved methods for the direct introduction of an aryl group into the pyridine nucleus have been reported, *i.e.*, the regioselective nucleophilic addition of aryl-Grignard or copper reagents at the 2- or 4-position of pyridine, which necessitates the subsequent oxidation of the resulting dihydropyridines,[2] or the transition metal-catalyzed cross-coupling reaction between halopyridines and arylmetallic compounds (Mg, Zn), in which the use of 4-halopyridines is restrictive due to their marked instability.[3] As yet, there is no versatile procedure for the direct preparation of 4-aryl- and 4-heteroarylpyridines.

In our previous reports, the synthetic application of diethyl(3-pyridyl)borane (**1a**) to the regioselective preparation of 3-substituted pyridine derivatives has been described.[4] Herein, we wish to report that the palladium-catalyzed cross-coupling reaction of diethyl(4-pyridyl)borane (**1b**), conveniently prepared from 4-lithiopyridine and diethylmethoxy-



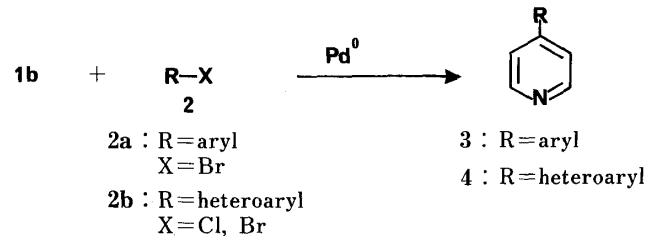
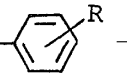


Chart 1

borane,[5] with aryl and heteroaryl halides provides a direct access to 4-aryl- and 4-heteroarylpyridines. The whole reaction sequence is shown in Chart 1.

Diethyl(4-pyridyl)borane (**1b**) (1 eq) was treated with bromobenzene (1.5 eq) in the presence of powdered potassium hydroxide (KOH) (3 eq), tetrabutylammonium bromide (Bu_4NBr) (0.5 eq) and tetrakis(triphenylphosphine)palladium [$Pd(Ph_3P)_4$] (0.05 eq) in tetrahydrofuran (THF) at refluxing temperature under nitrogen atmosphere to give 4-phenylpyridine in 78% yield. Bromobenzenes (**2a**) with various functional groups were also subjected to this reaction to afford 4-arylpyridines (**3**), regioselectively, in good to moderate yields, as

TABLE I. Formation of 4-Arylpyridines (**3**) **1b** +  → **3**

2a

R of **2a**	React. time (h)	**3**	Yield[a] of **3** (%)	mp (°C) or bp (°C/mmHg)	Formula	Analysis (%) Calcd (Found)		
						C	H	N
H	3	**3a**	78	mp 75—77 (lit.[9] mp 78)	—		—	
2-Me	3.5	**3b**	70	bp 180/18[c]	$C_{18}H_{14}N_4O_7$[f]	54.27	3.54	14.07
				Picrate mp 163—164[d]		(54.38	3.51	14.05)
4-Me	3.5	**3c**	77	bp 115/1[c]	$C_{18}H_{14}N_4O_7$[f]	54.27	3.54	14.07
				mp 85—87		(54.42	3.49	13.99)
				Picrate mp 193—195[d]				
2-OMe	5	**3d**	70	bp 120/1[c]	$C_{18}H_{14}N_4O_8$[f]	52.18	3.41	13.52
				mp 63—64		(52.05	3.53	13.61)
				Picrate mp 197—199[d]				
4-OMe	3	**3e**	75	bp 115/1[c]	$C_{18}H_{14}N_4O_8$[f]	52.18	3.41	13.52
				mp 95—96		(51.94	3.23	13.28)
				Picrate mp 210—211[d]				
2-NO_2	2.5	**3f**	47	mp 49—50[e]	$C_{17}H_{11}N_5O_9$[f]	47.56	2.58	16.31
				Picrate mp 185—186[d]		(47.63	2.55	16.24)
4-NO_2	2	**3g**	73	mp 109—110[e]	$C_{17}H_{11}N_5O_9$[f]	47.56	2.58	16.31
				Picrate mp 208—209[d]		(47.51	2.58	16.09)
2-Cl	4	**3h**	18	bp 145/18[c]	$C_{17}H_{11}ClN_4O_7$[f]	48.46	2.70	13.20
				Picrate mp 171—173[d]		(48.78	2.50	13.49)
4-Cl	1.5	**3i**	75	bp 130/1[c]	$C_{17}H_{11}ClN_4O_7$[f]	48.46	2.70	13.20
				mp 71—72		(48.19	2.69	13.22)
				Picrate mp 218—220[d]				
2-COOMe	4.5	**3j**	51	bp 175/1[c]	$C_{19}H_{14}N_4O_9$[f]	51.59	3.19	12.67
				Picrate mp 193—194[d]		(51.65	3.03	12.85)
4-COOMe	3.5	**3k**	77	bp 160/1[c]	$C_{19}H_{14}N_4O_9$[f]	51.59	3.19	12.67
				mp 65—66		(51.63	3.01	12.49)
				Picrate mp 196—198[d]				
2-NH_2	12 (4)[b]	**3l**	24 (44)[b]	bp 140/1[c]	$C_{11}H_{10}N_2$	77.62	5.92	16.46
				mp 82—84		(77.59	5.82	16.51)
3-NH_2	12 (3)[b]	**3m**	40 (60)[b]	mp 162—163 (lit.[10] mp 165—166)	—		—	
4-NH_2	12 (3)[b]	**3n**	42 (60)[b]	mp 224—226 (lit.[11] mp 227—228)	—		—	
2-CONHPh	4	**3o**	35	mp 192—193[e]	$C_{18}H_{14}N_2O$	78.81	5.14	10.21
						(79.04	5.19	10.17)
2-OCH_2Ph	4	**3p**	21	Syrup	$C_{24}H_{18}N_4O_8$[f]	58.77	3.70	11.43
				Picrate mp 187—188[d]		(58.85	3.69	11.37)

a) Isolated yield. *b*) Reaction with iodoaniline. *c*) Bath temperature. *d*) Recrystallized from EtOH. *e*) Recrystallized from acetone–hexane. *f*) Picrate.

listed in Table I. Spectral data for the products (**3**) are summarized in Table V. In the cases of the formation of 4-(aminophenyl)pyridines, the yields could be improved by using the corresponding iodoanilines (Table I).

Recently, the preparation of spiro[benzofura-3(2*H*),4′-piperidine] (**6**) *via* 4-(2-hydroxyphenyl)pyridine (**5**), which was derived from *p*-methoxybenzaldehyde *via* an indirect sequence, has been reported.[6] The preparation of **5** could be easily performed by the reaction of **1b** with *o*-benzyloxybromobenzene followed by catalytic hydrogenolysis of the *O*-benzyl group using 10% Pd on charcoal in EtOH. However, the reaction of **1b** with bromobenzenes (**7**) which possess an active methylene or methyl group gave no isolable product. An attempt to obtain **8**, which should be easily transformable to **6**, was unsuccessful (Chart 2).

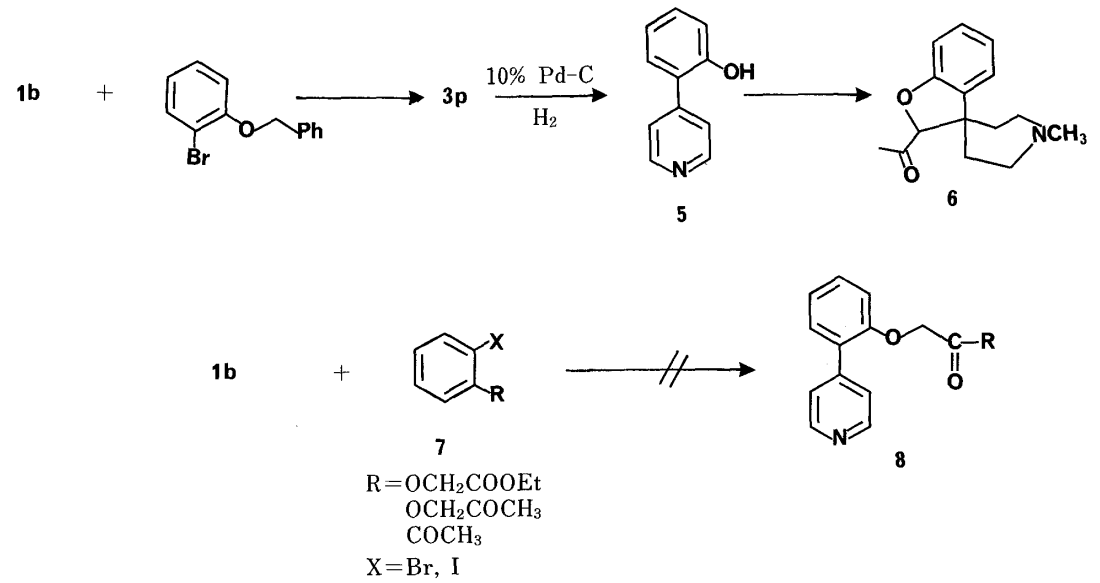


Chart 2

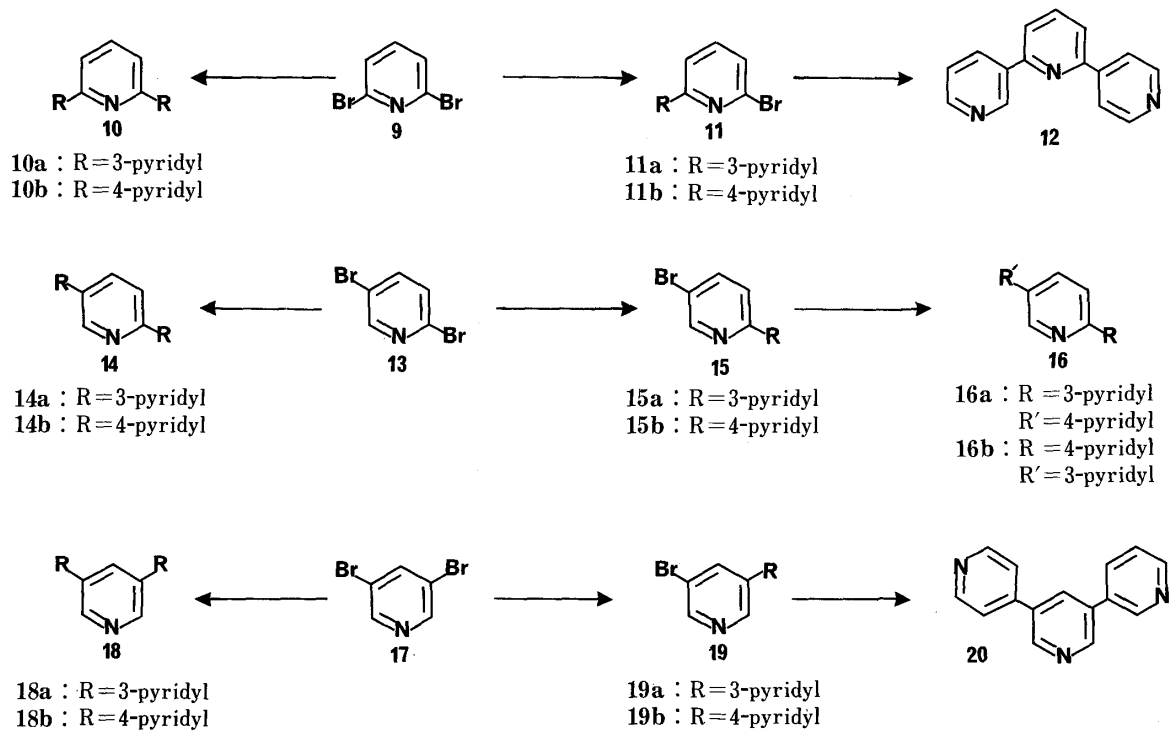
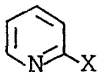
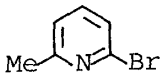
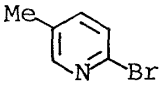
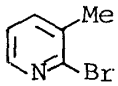
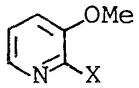
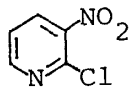
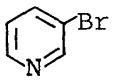
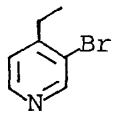
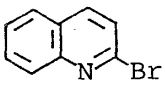
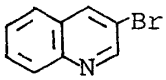
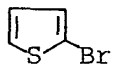
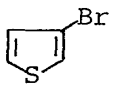
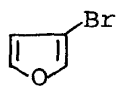
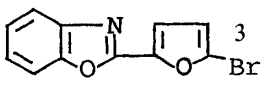
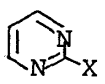


Chart 3

TABLE II. Formation of 4-Heteroarylpyridines (**4**) **1b**+**2b** ⟶ **4**

2b	React. time (h)	**4**	Yield[c] of **4** (%)	mp (°C) or bp (°C/mmHg)	Formula	Analysis (%) Calcd (Found)		
						C	H	N
	5[a] (3)[b]	**4a**	42[a] (79)[b]	bp 120/1[e] mp 60—62 (lit.[12] mp 61.5)	—		—	
	5	**4b**	75	bp 130/1[e] Picrate mp 242—244[f]	$C_{11}H_{10}N_2+1/10\,H_2O$	76.80 (77.11	5.97 6.01	16.28 16.18)
	3	**4c**	68	bp 130/1[e] mp 69—70	$C_{11}H_{10}N_2$	77.62 (77.78	5.92 5.88	16.46 16.57)
	15	**4d**	33	bp 125/1[e] Picrate mp 175—176[f]	$C_{11}H_{10}N_2+1/5\,H_2O$	76.01 (76.07	6.03 6.02	16.12 16.16)
	12[a] (3)[b]	**4e**	—[a,d] (32)[b]	mp 92—93[g]	$C_{11}H_{10}N_2O$	70.95 (71.02	5.41 5.40	15.05 14.99)
	20	**4f**	25	mp 104—105[h] Picrate mp 183—185[f]	$C_{16}H_{10}N_6O_9$[i]	44.66 (44.89	2.34 2.41	19.53 19.35)
	5	**4g**	64	bp 130/1[e] mp 63—65 (lit.[13] mp 61—62)	—		—	
	8	**4h**	40	bp 140/1[e]	$C_{12}H_{12}N_2$	78.23 (78.24	6.57 6.66	15.21 15.02)
	2	**4i**	74	mp 94—95 (lit.[14] mp 96)	—		—	
	4	**4j**	70	mp 121—123 (lit.[15] mp 124—125)	—		—	
	4	**4k**	66	mp 90—92 (lit.[16] mp 92.5—93.5)	—		—	
	5.5	**4l**	67	mp 136—138 (lit.[16] mp 138.5—139)	—		—	
	5.5	**4m**	54	Unstable solid[j,17]	—		—	
	3	**4n**	62	Unstable solid[k]	—		—	
	5[a] (2)[b]	**4o**	20[a] (50)[b]	bp 90/1[e] mp 81—82 (lit.[18] mp 79—81)	—		—	

a) X=Cl. *b*) X=Br. *c*) Isolated yield. *d*) No isolable product was obtained. *e*) Bath temperature. *f*) Recrystallized from EtOH. *g*) Recrystallized from Et_2O–hexane. *h*) Recrystallized from AcOEt–hexane. *i*) Picrate. *j*) High-resolution MS *m/e*: Calcd for C_9H_7NO: 147.05272. Found: 147.05142. *k*) High-resolution MS *m/e*: Calcd for $C_{16}H_{10}N_2O_2$: 262.0742. Found: 262.0733.

TABLE III. Bromopyridylpyridines (**11**, **15**, **19**)

Compd.	Yield[a] (%)	mp (°C) or bp (°C/mmHg)	Formula	Analysis (%) Calcd (Found)		
				C	H	N
11a	67	bp 150/1[b]	$C_{10}H_7BrN_2$	51.10	3.00	11.92
		mp 73—74		(51.10	2.85	12.11)
11b	57	mp 110—111[c]	$C_{10}H_7BrN_2$	51.10	3.00	11.92
				(51.34	2.83	11.98)
15a	70	bp 150/1[b]	$C_{10}H_7BrN_2$	51.10	3.00	11.92
		mp 75—77		(51.23	2.93	11.85)
15b	65	mp 120—121	$C_{10}H_7BrN_2$	51.10	3.00	11.92
				(51.23	2.97	11.90)
19a	62	bp 130/1[b]	$C_{10}H_7BrN_2$	51.10	3.00	11.92
				(51.26	2.87	11.97)
19b	51	mp 149—150[d]	$C_{10}H_7BrN_2$	51.10	3.00	11.92
				(51.14	2.93	11.85)

a) Isolated yield based on **1**. *b*) Bath temperature. *c*) Recrystallized from acetone–hexane. *d*) Recrystallized from acetone–Et_2O.

TABLE IV. Terpyridyls (**10**, **12**, **14**, **16**, **18**, **20**)

Compd.	Yield[a] (%)	mp (°C)	Formula	Analysis (%) Calcd (Found)		
				C	H	N
10a	60[b]	80—81	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.13	4.77	18.13)
10b	50[b]	134—136	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.26	4.57	17.86)
12	60[c]	105—106	$C_{15}H_{11}N_3$	77.23	4.75	18.02
	65[d]			(77.33	4.91	17.93)
14a	56[b]	130—131	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.28	4.65	18.16)
14b	47[b]	195—197	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.10	4.74	17.85)
16a	57[d]	141—142	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.34	4.62	17.85)
16b	63[b]	119—120	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.35	4.69	18.21)
18a	60[d]	159—160	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(77.02	4.75	18.01)
18b	52[c]	177—178	$C_{15}H_{11}N_3$	77.23	4.75	18.02
				(76.98	4.71	17.98)
20	55[c]	143—145	$C_{15}H_{11}N_3$	77.23	4.75	18.02
	60[d]			(77.38	4.83	18.01)

a) Isolated yield. *b*) Yield based on dibromopyridine. *c*) Yield based on **1b**. *d*) Yield based on **1a**.

Next, reaction of heteroaryl halides (**2b**) with **1b** under the same conditions was found to be a convenient route to 4-heteroarylpyridines (**4**) (Table II); spectral data for **4** are summarized in Table VI.

Further application of this methodology to an efficient preparation of terpyridyls by the reaction of **1** with dibromopyridines was investigated. Upon treatment of **1b** (2.1 eq) with 2,6-

dibromopyridine (**9**) (1 eq) in the presence of $Pd(Ph_3P)_4$ (0.05 eq), powdered KOH (6 eq) and Bu_4NBr (0.5 eq) in THF under a nitrogen atmosphere, 4,2′;6′,4″-terpyridyl (**10b**) was obtained in 50% yield. Likewise, the reaction of **1a** (2.1 eq) and **9** (1 eq) under the same conditions led to the production of 3,2′;6′,3″-terpyridyl (**10a**) in 60% yield. On the other hand, 1 eq of **1** was allowed to react with 2.1 eq of **9** in the presence of powdered KOH (3 eq), Bu_4NBr (0.5 eq) and $Pd(Ph_3P)_4$ (0.05 eq) in THF under a nitrogen atmosphere to give (6-bromopyridyl)pyridines (**11a**, 67% yield from **1a**: **11b**, 57% yield from **1b**), as shown in Chart 3.

Preparation of other terpyridyls (**14**, **16**, **18**, **20**) could also be attained by the same treatment of the corresponding dibromopyridines (**13**, **17**) with **1** (Chart 3). These results are listed in Tables III and IV. Spectral data for bromopyridylpyridines and terpyridyls are summarized in Tables VII and VIII, respectively.

In summary, the present procedure for the preparation of 4-aryl- and 4-heteroarylpyridines provides an attractive alternative to the known methods in terms of simplicity,

TABLE V. Spectral Data for 4-Arylpyridines (**3**)

3	IR cm^{-1}	^1H-NMR ($CDCl_3$) δ	MS *m/e* (M^+)
3a	1588, 1504, 1484[a]	7.20—7.80 (m, 7H), 8.55 (d, 2H, J=6 Hz)	155
3b	1598, 1541, 1481, 1411[b]	2.25 (s, 3H), 7.05—7.30 (m, 6H), 8.58 (d, 2H, J=5 Hz)	169
3c	1618, 1600, 1540[a]	2.38 (s, 3H), 7.20 (d, 2H, J=6 Hz), 7.35—7.55 (m, 4H), 8.55 (d, 2H, J=5 Hz)	169
3d	1608, 1592[a]	3.75 (s, 3H), 6.80—7.10 (m, 2H), 7.15—7.50 (m, 4H), 8.50 (d, 2H, J=6 Hz)	185
3e	1608, 1596[a]	3.82 (s, 3H), 6.95 (d, 2H, J=8 Hz), 7.39 (d, 2H, J=5 Hz), 7.53 (d, 2H, J=8 Hz), 8.53 (d, 2H, J=5 Hz)	185
3f	1596, 1580, 1526[a]	7.20 (d, 2H, J=5 Hz), 7.30—7.70 (m, 3H), 7.95 (dd, 1H, J=2, 6 Hz), 8.65 (d, 2H, J=5 Hz)	200
3g	1606, 1594, 1554, 1516[a]	7.49 (d, 2H, J=5 Hz), 7.73 (d, 2H, J=8 Hz), 8.30 (d, 2H, J=8 Hz), 8.70 (d, 2H, J=5 Hz)	200
3h	1606, 1592, 1570, 1542[c]	7.15—7.25 (m, 7H), 8.55 (d, 2H, J=6 Hz)	189
3i	1600, 1540, 1502, 1482[a]	7.30—7.70 (m, 6H), 8.00 (d, 2H, J=5 Hz)	189
3j	1728, 1598[b]	3.60 (s, 3H), 7.10—7.55 (m, 5H), 7.80—7.95 (m, 1H), 8.55 (d, 2H, J=5 Hz)	213
3k	1720, 1602[b]	3.90 (s, 3H), 7.46 (d, 2H, J=5 Hz), 7.63 (d, 2H, J=8 Hz), 8.10 (d, 2H, J=8 Hz), 8.63 (d, 2H, J=5 Hz)	213
3l	3356, 3216, 1640, 1612, 1596[a]	3.80 (br s, 2H), 6.60—6.85 (m, 2H), 6.95—7.15 (m, 2H), 7.30 (d, 2H, J=6 Hz), 8.55 (d, 2H, J=6 Hz)	170
3m	3388, 3304, 1600, 1546[a]	4.60 (br s, 2H), 6.55—7.25 (m, 4H), 7.45 (d, 2H, J=5 Hz), 8.50 (d, 2H, J=5 Hz)	170
3n	3452, 3320, 1640, 1588[a]	2.50 (br s, 2H), 6.65 (d, 2H, J=8 Hz), 7.30—7.60 (m, 4H), 8.40 (d, 2H, J=5 Hz)	170
3o	3452, 1676[b]	7.10—7.90 (m, 11H), 8.29 (d, 1H, J=8 Hz), 8.65 (d, 2H, J=6 Hz)	274
3p	1602, 1544, 1504[c]	5.03 (s, 2H), 6.90—7.55 (d, 1H, J=8 Hz), 8.55 (d, 2H, J=5 Hz)	261

a) KBr. *b*) $CHCl_3$. *c*) Neat.

generality and yield.

Experimental

All melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. Infrared (IR) (absorption) spectra were recorded with a Hitachi 270-30 spectrometer. Nuclear magnetic resonance (NMR) spectra were determined with a Hitachi R-40 or a JEOL FX-90Q spectrometer. Chemical shifts are reported relative to internal tetramethylsilane and given in δ-values. Coupling constants are reported in hertz and splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra (MS) were recorded on a JEOL JMS-QH100 or a JEOL JMS-D300 spectrometer.

Column chromatography and flash chromatography were performed on silica gel 70—230 and 230—400 mesh ASTM obtained from Merck, respectively. THF and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl before use.

Diethyl(3-pyridyl)borane (**1a**) was prepared by the procedure previously reported.[5,7]

Diethyl(4-pyridyl)borane (1b)——An ethereal solution (30 ml) of 4-bromopyridine (5.02 g, 32 mmol) was added dropwise to an ethereal solution (100 ml) of BuLi (1.6 M solution in hexane, 20 ml) at -40 °C under a nitrogen

TABLE VI. Spectral Data for 4-Heteroarylpyridines (**4**)

4	IR cm^{-1}	^{1}H-NMR ($CDCl_3$) δ	MS m/e (M^+)
4a	1588, 1552[a]	7.20—7.36 (m, 1H), 7.80—7.90 (m, 4H), 8.65 (d, 2H, J=5 Hz)	156
4b	1596, 1574, 1554[b]	2.60 (s, 3H), 7.10 (dd, 1H, J=2, 6 Hz), 7.40—7.90 (m, 4H), 8.60 (d, 2H, J=5 Hz)	170
4c	1602, 1565, 1552[c]	2.36 (s, 3H), 7.55—8.00 (m, 4H), 8.50—8.85 (m, 3H)	170
4d	1604, 1574, 1546[b]	2.35 (s, 3H), 7.10—7.28 (m, 1H), 7.30—7.70 (m, 3H), 8.46 (dd, 1H, J=1, 5 Hz), 8.63 (d, 2H, J=5 Hz)	170
4e	1596, 1582[d]	3.90 (s, 3H), 7.20—7.40 (m, 2H), 7.85 (d, 2H, J=5 Hz), 8.25—8.50 (m, 1H), 8.65 (d, 2H, J=5 Hz)	186
4f	1594, 1565, 1550, 1522[d]	7.35—7.60 (m, 3H), 8.20 (dd, 1H, J=1, 9 Hz), 8.65 (d, 2H, J=5 Hz), 8.82 (d, 1H, J=4 Hz)	201
4g	1598, 1578, 1474, 1426[b]	7.20—7.55 (m, 3H), 7.70—8.00 (m, 1H), 8.55—8.70 (m, 3H), 8.80 (d, 1H, J=2 Hz)	156
4h	1602[b]	1.00—1.50 (m, 3H), 2.20—2.80 (m, 2H), 7.15—7.35 (m, 3H), 8.35 (d, 1H, J=5 Hz), 8.55 (d, 1H, J=5 Hz), 8.73 (d, 2H, J=5 Hz)	184
4i	1596[a]	7.35—7.90 (m, 4H), 8.00—8.40 (m, 4H), 8.75 (d, 2H, J=6 Hz)	206
4j	1598[d]	7.55 (d, 2H, J=5 Hz), 7.65—8.55 (m, 3H), 8.65 (d, 2H, J=5 Hz), 9.08 (d, 1H, J=3 Hz)	206
4k	1598, 1550, 1528, 1490[d]	7.00—7.25 (m, 1H), 7.30—7.55 (m, 4H), 8.52 (d, 1H, J=5 Hz)	161
4l	1594, 1554, 1528, 1494[d]	7.30—7.50 (m, 4H), 7.53—7.70 (m, 1H), 8.55 (d, 2H, J=5 Hz)	161
4m	1610, 1436[c]	6.69 (s, 1H), 7.30 (d, 2H, J=6 Hz), 7.43 (s, 1H), 7.80 (s, 1H), 8.50 (d, 2H, J=5 Hz)	145
4n	1634, 1620, 1592[d]	6.96 (d, 1H, J=3 Hz), 7.20—7.80 (m, 7H), 8.60 (d, 2H, J=5 Hz)	262
4o	1600, 1560, 1548[d]	7.20—7.40 (m, 1H), 8.33 (d, 2H, J=6 Hz), 8.65—8.90 (m, 4H)	157

a) Nujol. *b*) Neat. *c*) $CHCl_3$. *d*) KBr.

TABLE VII. Spectral Data for Bromopyridylpyridines (**11**, **15**, **19**)[a]

Compd.	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ
11a	1574, 1546, 1482	7.20—7.80 (m, 4H), 8.10—8.40 (m, 1H), 8.50—8.70 (m, 1H), 9.15 (s, 1H)
11b	1598, 1578, 1544, 1498	7.30—7.90 (m, 5H), 8.65 (d, 2H, J=5 Hz)
15a	1590, 1580, 1568, 1550	7.20—7.45 (m, 1H), 7.50—7.70 (m, 1H), 7.73—7.98 (m, 1H), 8.13—8.40 (m, 1H), 8.50—8.80 (m, 2H), 9.10 (s, 1H)
15b	1600, 1574, 1565, 1542	7.40—8.00 (m, 4H), 8.60—8.80 (m, 3H)
19a	1580, 1552, 1484, 1434	7.25—7.55 (m, 1H), 7.70—7.90 (m, 1H), 7.90—8.15 (m, 1H), 8.55—8.85 (m, 4H)
19b	1608, 1598, 1580, 1560, 1536, 1438	7.40—7.60 (m, 3H), 7.95—8.15 (m, 1H), 8.60—8.90 (m, 4H)

a) Mass spectra of all compounds showed satisfactory molecular ion peaks (M^+) at *m/e* 234 and 236.

TABLE VIII. Spectral Data for Terpyridyls (**10**, **12**, **14**, **16**, **18**, **20**)[a]

Compd.	IR (KBr) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ
10a	1620, 1596, 1580, 1560	7.20—7.50 (m, 2H), 7.60—7.90 (m, 3H), 8.25—8.46 (m, 2H), 8.57 (dd, 2H, J=1, 5 Hz), 9.22 (d, 2H, J=2 Hz)
10b	1596, 1554	7.80—8.05 (m, 7H), 8.65 (d, 4H, J=5 Hz)
12	1596, 1580, 1566, 1546	7.20—7.63 (m, 1H), 7.73—8.20 (m, 5H), 8.53—8.96 (m, 5H)
14a	1592, 1574	7.20—7.60 (m, 2H), 7.70—8.10 (m, 3H), 8.20—8.50 (m, 1H), 8.50—8.75 (m, 2H), 8.75—9.00 (m, 2H), 9.20 (s, 1H)
14b	1600, 1574, 1554	7.40—7.70 (m, 2H), 7.70—8.20 (m, 4H), 8.56—8.85 (m, 4H), 8.95 (s, 1H)
16a	1600, 1590	7.26—7.66 (m, 3H), 7.70—8.10 (m, 2H), 8.15—8.46 (m, 1H), 8.53—8.83 (m, 3H), 8.92 (s, 1H), 9.19 (s, 1H)
16b	1590, 1564, 1550, 1490	7.20—7.63 (m, 1H), 7.73—8.20 (m, 5H), 8.53—8.96 (m, 5H)
18a	1568, 1482, 1438, 1400	7.30—7.50 (m, 2H), 7.80—8.10 (m, 3H), 8.60—8.75 (m, 2H), 8.80—9.00 (m, 4H)
18b	1606, 1596, 1552, 1446	7.40—7.60 (m, 4H), 7.95—8.20 (m, 1H), 8.50—9.00 (m, 6H)
20	1638, 1632, 1598, 1560, 1552, 1486	7.30—7.70 (m, 3H), 7.80—8.20 (m, 2H), 8.50—9.00 (m, 6H)

a) Mass spectra of all compounds showed satisfactory molecular ion peaks (M^+) at *m/e* 233.

atmosphere and the whole was stirred for 20 min. Then, the mixture was cooled to −70 °C, and diethylmethoxyborane [prepared from triethylborane (1 M solution in hexane, 70 ml) and methanol (2.24 g) in the presence of diethylborylpivalate (0.5 ml)][8] was added dropwise. The mixture was gradually warmed to room temperature, and stirred overnight. The whole was diluted with AcOEt (100 ml), washed with brine (70 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with benzene as an eluent to give 3.29 g (70%) of **1b**, which was used for the subsequent reactions without further purification. An analytical sample was recrystallized from acetone; mp above 300 °C. IR ν_{max}^{KBr} cm^{-1}: 2948, 2908, 2872, 1670, 1492, 1453, 1422. NMR ($CDCl_3$) δ: 0.40—1.05 (m, 10H), 6.96 (d, 2H, J=6 Hz), 7.68 (d, 2H, J=6 Hz). High-resolution MS *m/e*: Calcd for $C_9H_{14}BN$: 147.1218. Found: 147.1210.

General Procedure for the Preparation of 3 and 4——A mixture of **1b** (294 mg, 2 mmol), halide (**2**) (3 mmol), powdered KOH (636 mg, 6 mmol), Bu_4NBr (322 mg, 1 mmol) and $Pd(Ph_3P)_4$ (115 mg, 0.1 mmol) in THF (10 ml) was

refluxed under a nitrogen atmosphere. The mixture was diluted with AcOEt (50 ml), washed with brine (40 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography with hexane–AcOEt (2 : 1) (for **3**), hexane–AcOEt (1 : 2) (for **4c–n**), or hexane–AcOEt (1 : 10) (for **4a—j, 4o**).

4-(2-Hydroxyphenyl)pyridine (5)——A mixture of **3p** (100 mg) and 10% Pd on charcoal (10 mg) in EtOH (10 ml) was stirred at room temperature under atmospheric pressure of hydrogen. After hydrogen uptake had ceased, the catalyst and the solvent were removed to leave a crystalline material, which was successively washed with acetone to give **5** (51 mg, 80%); mp 213—215 °C [sublimed at 180 °C (18 mmHg)] (lit.[6] mp 216—217 °C). IR ν_{max}^{KBr} cm^{-1}: 3044, 2948, 2868, 2588, 1606, 1546. NMR (DMSO-d_6) δ: 6.93—7.06 (m, 2H), 7.10—7.43 (m, 2H), 7.45—7.65 (m, 2H), 8.50 (d, 2H, J=5 Hz), 9.76 (s, 1H). MS m/e: 171 (M^+).

Preparation of Bromopyridylpyridines (11, 15, 19): 4-(6-Bromo-2-pyridyl)pyridine (11b)——A mixture of 2,6-dibromopyridine (**9**) (2.96 g, 12.6 mmol), **1b** (882 mg, 6 mmol), powdered KOH (936 mg, 18 mmol), Bu_4NBr (966 mg, 3 mmol) and $Pd(Ph_3P)_4$ (346 mg, 0.3 mmol) in THF (20 ml) was refluxed for 3 h under a nitrogen atmosphere. The mixture was diluted with AcOEt (80 ml), washed with brine (50 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography with AcOEt–hexane (1 : 1) to give 800 mg (57%) of **11b**. Compounds **11a**, **15**, **19** were prepared in a manner similar to that described for **11b**.

Preparation of Terpyridyls (10, 14, 18): 4,2′;6′,4″-Terpyridyl (10b)——A mixture of 2,6-dibromopyridine (**9**) (705 mg, 3 mmol), **1b** (926 mg, 6.3 mmol), powdered KOH (936 mg, 18 mmol), Bu_4NBr (483 mg, 1.5 mmol) and $Pd(Ph_3P)_4$ (173 mg, 0.15 mmol) in THF (20 ml) was refluxed for 4 h under a nitrogen atmosphere. The mixture was diluted with AcOEt (80 ml), washed with brine (50 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography eluted with AcOEt–EtOH (20 : 1) to give 349 mg (50%) of **10b**. Other terpyridyls (**10a**, **14**, **18**) were prepared in a similar manner.

Preparation of Terpyridyls (12, 16, 20): 3,2′;6′,4″-Terpyridyl (12) from 11a——A mixture of **11a** (702 mg, 3 mmol), **1b** (294 mg, 2 mmol), powdered KOH (312 mg, 6 mmol), Bu_4NBr (322 mg, 1 mmol) and $Pd(Ph_3P)_4$ (115 mg, 0.1 mmol) in THF (15 ml) was refluxed under a nitrogen atmosphere. The mixture was diluted with AcOEt (80 ml), washed with brine (40 ml), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash chromatography with AcOEt–EtOH (20 : 1) as an eluent to give 419 mg (60%) of **12**. Compounds **12** from **11b**, **16**, **20** were prepared in a similar manner.

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