Double *Heck* Cross-Coupling Reactions of Dibrominated Pyridines

by **Asad Ali**[a]), **Munawar Hussain**[a]), **Imran Malik**[a]), **Alexander Villinger**[a]), **Christine Fischer**[b]), and **Peter Langer***[a])[b])

[a]) Institut für Chemie, Universität Rostock, Albert-Einstein-Strasse 3a, D-18059 Rostock (fax: +49-381-498-6412; e-mail: peter.langer@uni-rostock.de)

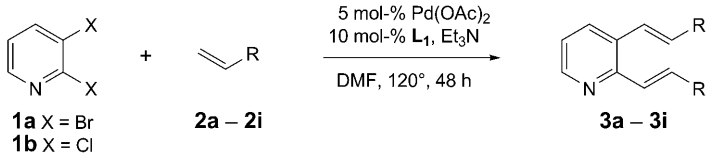
[b]) Leibniz Institut für Katalyse and der Universität Rostock e.V., Albert-Einstein-Strasse 29a, D-18059 Rostock

Double *Heck* cross-coupling reactions of 2,3- and 3,5-dibromopyridine with various alkenes afforded the corresponding novel di(alkenyl)pyridines. The *Heck* reaction of 2,5-dibromopyridine unexpectedly afforded 5,5′-di(alkenyl)-2,2′-bipyridines by palladium-catalyzed dimerization to give 5,5′-dibromo-2,2′-bipyridine and subsequent twofold *Heck* reaction.

Introduction. – In recent years, site-selective reactions of polyhalogenated heterocycles have been intensively studied [1][2]. Cross-coupling reactions of 2,5-dibromopyridine include aminations [3], and *Stille* [4], *Suzuki* [5], *Negishi* [6], *Sonogashira* [7], and *Kumada* couplings [8]. In all cases, the first reaction occured at the more electron-deficient position C(2). In most studies, single coupling reactions were carried out. Recently, *Handy et al.* reported the first double *Suzuki* couplings of 2,5- and 2,3-dibromopyridine, and of several other heterocycles [9a]. *Cid* and co-workers also reported interesting work in this field [9b,c]. Single *Heck* coupling reactions of 2-chloro- and 2-bromopyridine have been studied in recent years [10]. Here, we report double *Heck* reactions of 2,3-, 2,4-, and 3,5-dibromopyridine [10f].

Results and Discussion. – The *Heck* reaction of 2,3-dibromopyridine (**1a**) with acrylates **2a**–**2e** afforded the 2,3-di(alkenyl)pyridines **3a**–**3e** (*Table 1*). The reaction of **1a** with styrenes **2f**–**2i** gave products **3f** and **3h**–**3i** (**3g** could not be isolated due to decomposition during the reaction). All products were isolated in 60–84% yield and contain exclusively (*E*)-configured C=C bonds. The reaction of **2f** and **2i** with 2,3-dichloropyridine (**1b**) instead of **1a** afforded **3f** and **3i**, respectively, albeit, in only poor yields. The reaction conditions were thoroughly optimized for the synthesis of **3c** and **3f** (*Fig. 1*, *Table 2*). The best yields were obtained when the reactions were carried out with **1a**, $Pd(OAc)_2$ (5 mol-%), and the biaryl-monophosphine ligands SPhos (**L_1**, for **3a**–**3g** and **3i**) or XPhos (**L_2**, for **3h**) (10 mol-%) which were both recently developed by *Billingsley* and *Buchwald* (*Fig. 1*) [11]. The use of tris(cyclohexyl)phosphane (**L_4**) gave slightly lower yields. Employing $Pd(Ph_3P)_4$ resulted in considerably lower yields. Et_3N was used as the base in all reactions. The application of other bases (K_2CO_3) did not lead to an increase of the yield. The reactions were carried out in DMF at 120°. A relatively long reaction time (48 h) was necessary to achieve a complete conversion. Recently, *Li* and *Wang* reported [12] that triethanolamine (**L_3**) represents an efficient

Table 1. *Synthesis of 2,3-Di(alkenyl)pyridines* **3a**–**3i**



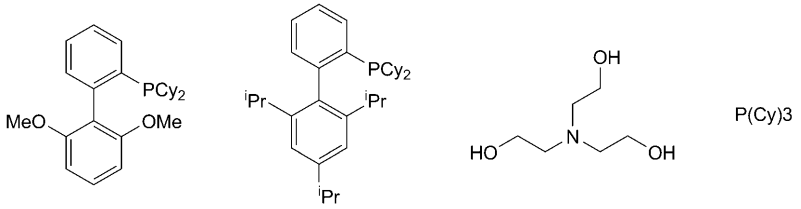
1a X = Br
1b X = Cl

2a – **2i**

3a – **3i**

X of **1**	R of **2** and **3**	**2**, **3**	Yield of **3** [%][a])
Br	CO_2Me	**a**	63
Br	CO_2Et	**b**	71
Br	$CO_2{}^iBu$	**c**	82
Br	$CO_2{}^tBu$	**d**	84
Br	CO_2R[b])	**e**	60
Br	Ph	**f**	72
Cl	Ph	**f**	11
Br	4-^{t}BuO–C_6H_4	**g**	0[c])
Br	4-MeO–C_6H_4	**h**	79[d])
Br	4-Me–C_6H_4	**i**	65
Cl	4-Me–C_6H_4	**i**	9

[a]) Yields of isolated products. [b]) R = $Me(CH_2)_3CH(Et)CH_2$. [c]) Decomposition. [d]) Ligand $\mathbf{L_2}$ was used.



L1 SPhos
Cy = Cyclohexyl

L2 XPhos

L3

L4

Fig. 1. *Ligands Used in This Study*

Table 2. *Optimization of the Syntheses of 2,3-Di(alkenyl)pyridines* **3c** *and* **3f**

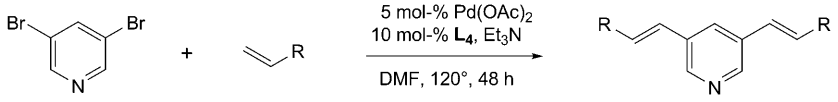
Conditions	**3c** [%][a])	**3f** [%][a])
$Pd(Ph_3P)_4$ (5 mol-%), Et_3N, DMF, 120°, 48 h	38	49
$Pd(OAc)_2$ (5 mol-%), Cy_3P (10 mol-%), Et_3N, DMF, 120°, 48 h	72	63
$Pd(OAc)_2$ (5 mol-%), $\mathbf{L_1}$ (10 mol-%), Et_3N, DMF, 120°, 48 h	82	72
$Pd(OAc)_2$ (5 mol-%), $\mathbf{L_2}$ (10 mol-%), Et_3N, DMF, 120°, 48 h	80	69
$Pd(OAc)_2$ (5 mol-%), $(HOCH_2CH_2)_3N$ (3 ml), 120°, 48 h	2	10

[a]) Yields of isolated products.

and reusable combined base, ligand, and solvent for *Heck* reactions. However, only traces of the product could be isolated when these conditions were applied. The synthesis of 2,3-di(alkenyl)pyridines has, to the best of our knowledge, not been previously reported.

The double *Heck* reaction of 3,5-dibromopyridine (**4**) with acrylates **2a**–**2d**, **2f**, and **2i**–**2k**, using $Pd(OAc)_2$ and $\mathbf{L_4}$, afforded the 3,5-di(alkenyl)pyridines **5a**–**5h** in 69–84% yield (*Table 3*). Similar yields were obtained by using ligands $\mathbf{L_4}$ and $\mathbf{L_1}$. Therefore, the cheaper ligand $\mathbf{L_4}$ was employed. The synthesis of **5c** and **5g** by *Heck* reactions has been previously reported by *Santelli* and co-workers [10f]. The structure of **5g** was independently confirmed by X-ray crystal structure analysis (*Fig. 2*)[1]).

Table 3. *Synthesis of 3,5-Di(alkenyl)pyridines* **5a**–**5h**



4 **2a – 2d, 2f, 2i – 2k** **5a – 5h**

2	**5**	R	Yield of **5** [%][a])
a	**a**	CO_2Me	69
b	**b**	CO_2Et	71
j	**c**	CO_2Bu	82
c	**d**	$CO_2{}^iBu$	84
k	**e**	CO_2Hex	77
d	**f**	$CO_2{}^tBu$	81
f	**g**	Ph	72
i	**h**	4-Me–C_6H_4	76

[a]) Yields of isolated products.

The *Heck* reaction of 2,5-dibromopyridine (**6**) with acrylates **2c**–**2e** and **2i**–**2k** unexpectedly afforded the 5,5′-di(alkenyl)-2,2′-bipyridines **7a**–**7f** in 60–84% yield (*Table 4*). The best yields were obtained with $Pd(OAc)_2$ and $\mathbf{L_2}$. The synthesis of 2,5-di(alkenyl)pyridines by double *Heck* reaction was not possible under various conditions (different catalysts and temperatures). The formation of **7a**–**7f** can be explained by Pd-catalyzed dimerization to give 5,5′-dibromo-2,2′-bipyridine and subsequent twofold *Heck* reaction. The Pd-catalyzed dimerization seems to be faster than the *Heck* reaction. The formation of 2,2′-bipyridines as side-products in *Heck* reactions of 2-bromopyridine [10] and in *Suzuki–Miyaura* reactions of 2,4-dibromopyridine have been previously reported. The structure of **7d** was independently confirmed by X-ray crystal structure analysis (*Fig. 3*).

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[1]) CCDC-779693 and -779694 contain crystallographic data for **7d** and **5g**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

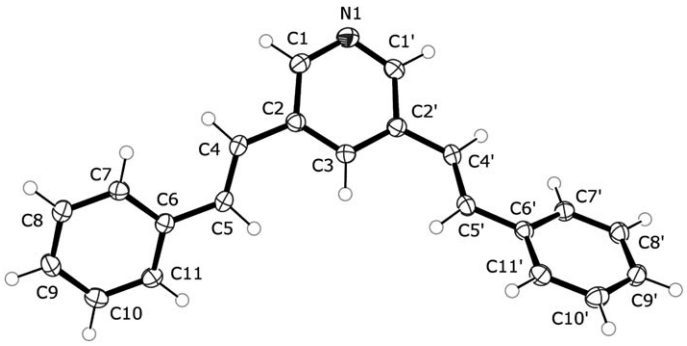
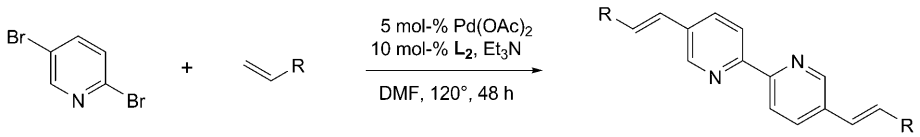


Fig. 2. *ORTEP Plot of* **5g**

Table 4. *Synthesis of Bipyridines* **7a**–**7f**



6 **2c – 2e** **2i – 2k** **7a – 7f**

2	**7**	R	Yield of **7** [%][a])
j	**a**	CO_2Bu	83
k	**b**	CO_2Hex	71
e	**c**	CO_2R[b])	82
d	**d**	$CO_2{}^tBu$	84
c	**e**	$CO_2{}^iBu$	77
i	**f**	4-Me–C_6H_4	60

[a]) Yield of isolated products. [b]) R = $Me(CH_2)_3CH(Et)CH_2$.

In conclusion, we have reported the first double *Heck* cross-coupling reactions of 2,3- and 3,5-dibromopyridine with various alkenes. These reactions afforded the corresponding di(alkenyl)pyridines. The *Heck* reaction of 2,5-dibromopyridine gave 5,5′-di(alkenyl)-2,2′-bipyridines by Pd-catalyzed dimerization and subsequent twofold *Heck* reaction of 5,5′-dibromo-2,2′-bipyridine thus formed.

Experimental Part

General. All cyclization reactions were carried out in pressure tubes under Ar. M.p.: Microheating table *HMK 67/1825 Kuestner* (*Büchi* apparatus); uncorrected. Anal. TLC: *60A* silica-gel plates (SiO_2; 0.20 mm). Flash column chromatography (FC): *60A* SiO_2 (60–200 mesh). IR Spectra: *Nicolet 380* FT-IR spectrometer, KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AVANCE 300 II* and *Bruker AVANCE 250 II* spectrometer in $CDCl_3$; δ in ppm rel. to solvent as internal standard (δ(H) 7.26 and δ(C) 77.0 ppm), *J* in Hz. EI-MS and HR-EI-MS: *Finnigan MAT 95-XP* mass spectrometer at 70 eV; in *m*/*z*.

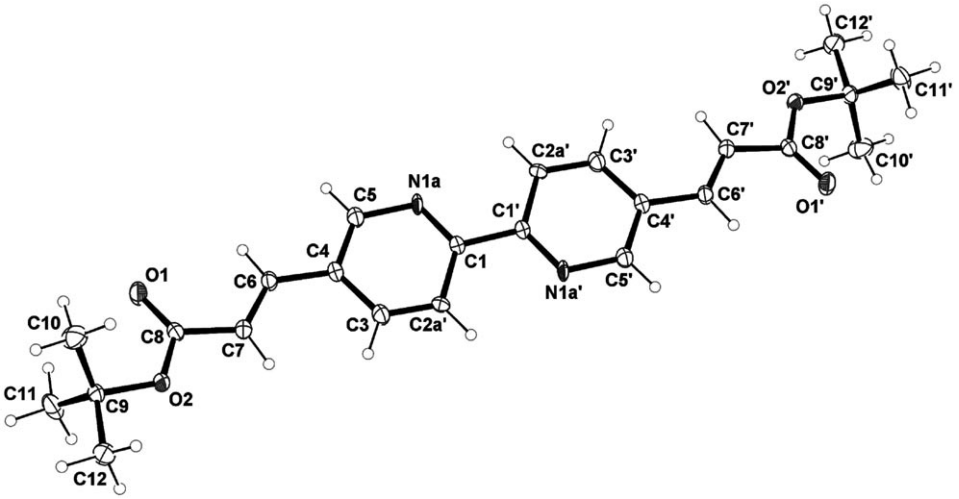


Fig. 3. *ORTEP Plot of* **7d**

General Procedure for Double Heck *Cross-Coupling Reactions.* In a pressure tube (glass bomb), a suspension of $Pd(OAc)_2$ (12 mg, 0.05 mmol, 2.5 mol-% per Br) and dicyclohexyl(2′,4′,6′-triisopropyl-1,1′-biphenyl-2-yl)phosphane (**L_2**; 47 mg, 0.10 mmol) or the same amount of another indicated ligand in DMF (5 ml) was purged with Ar and stirred at 20° to give a yellowish or brownish transparent soln. To the stirred soln. were added the *2,3-* or *3,5-* or *2,5-dibromopyridine* (**1a** or **4** or **6**, resp. 237 mg, 1,0 mmol), Et_3N (1.1 ml, 8.0 mmol), and the acrylate or styrene (1.25 equiv. per Br). The mixture was stirred at 120° for 48 h. The soln. was cooled to 20°, poured into H_2O and CH_2Cl_2 (25 ml each), and the org. and the aq. layer were separated. The latter was extracted with CH_2Cl_2 (3 × 25 ml). The combined org. layers were washed with H_2O (3 × 20 ml), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by FC on SiO_2 (heptanes/AcOEt): compounds **3**, **5**, or **7**.

*Dimethyl 3,3′-Pyridine-2,3-diylbis[(*E*)-prop-2-enoate]* (**3a**). Light yellow oil (175 mg, 71%). IR: 2955*w*, 2929*w*, 2852*w*, 1722*s*, 1709*s*, 1634*m*, 1580*w*, 1555*w*, 1434*s*, 1361*w*, 1300*w*, 1275*w*, 1194*w*, 1161*s*, 1086*s*, 1064*s*, 1010*s*, 990*w*, 970*m*, 932*m*, 870*m*, 778*m*, 732*m*, 720*m*, 702*m*, 605*m*, 582*m*, 568*m*, 544*w*. ^{1}H-NMR (300 MHz): 3.76 (*s*, MeO); 3.77 (*s*, MeO); 6.34 (*d*, *J* = 15.2, CH); 7.01 (*d*, *J* = 15.6, CH); 7.22–7.26 (*m*, 1 arom. H); 7.77 (*dd*, *J* = 1.5, 8.2, 1 arom. H); 7.93 (*d*, *J* = 15.4, CH); 8.00 (*d*, *J* = 15.4, CH); 8.56 (*dd*, *J* = 1.7, 4.6, 1 arom. H). ^{13}C-NMR (62.9 MHz): 51.8, 51.9 (MeO); 123.0, 124.3, 124.6 (CH); 130.1 (C); 134.9, 138.6, 139.2, 150.7 (CH); 150.9, 166.2, 167.0 (C). GC/EI-MS: 247 (2, M^+), 216 (19), 188 (100), 156 (28), 144 (24), 78 (6). HR-EI-MS: 247.08462 (M^+, $C_{13}H_{13}NO_4^+$; calc. 247.08446).

*Diethyl 3,3′-Pyridine-2,3-diylbis[(*E*)-prop-2-enoate]* (**3b**). White solid (195 mg, 71%). M.p. 145–147°. IR: 1705*s*, 1631*s*, 1580*w*, 1552*w*, 1473*w*, 1446*w*, 1423*m*, 1364*m*, 1295*s*, 1228*m*, 1661*s*, 1112*w*, 1065*w*, 1027*s*, 971*s*, 892*s*, 872*s*, 808*s*, 782*s*, 722*m*, 709*m*, 602*m*, 580*m*, 546*m*. ^{1}H-NMR (300 MHz): 1.26 (*t*, *J* = 7.1, Me); 1.27 (*t*, *J* = 7.1, Me); 4.19 (*q*, *J* = 7.1, 14.3, CH_2O); 4.22 (*q*, *J* = 7.1, 14.3, CH_2O); 6.30 (*d*, *J* = 15.2, CH); 6.99 (*d*, *J* = 15.2, CH); 7.20–7.25 (*m*, 1 arom. H); 7.76 (*dd*, *J* = 1.4, 8.1, 1 arom. H); 7.89–7.99 (*m*, 2 arom. H); 8.53 (*dd*, *J* = 1.6, 4.6, 1 arom. H). ^{13}C-NMR (75 MHz): 14.2 (2 Me); 60.7, 60.8 (CH_2O); 123.5, 124.3, 125.1 (CH); 130.1 (C); 134.9, 138.4, 150.7 (CH); 150.8 (C); 165.8, 166.5 (C=O). GC/EI-MS: 275 (3, M^+), 246 (2), 230 (30), 202 (100), 174 (48), 156 (33), 130 (71), 77 (9). HR-EI-MS: 275.11549 (M^+, $C_{15}H_{17}NO_4^+$; calc. 275.11576).

*Bis(2-methylpropyl) 3,3′-Pyridine-2,3-diylbis[(*E*)-prop-2-enoate]* (**3c**). Light-yellow semisolid (271 mg, 82%). IR: 2960*m*, 2874*m*, 1712*s*, 1635*m*, 1469*m*, 1424*m*, 1376*m*, 1369*m*, 1305*s*, 1292*s*, 1276*s*, 1256*s*, 1158*s*, 1010*s*, 973*s*, 802*m*, 780*m*, 702*m*, 606*m*, 590*m*. ^{1}H-NMR (300 MHz): 0.89 (*d*, *J* = 6.8, 2 Me); 0.93 (*d*, *J* = 6.7, 2 Me); 1.90–2.00 (*m*, 2 H); 3.93 (*d*, *J* = 6.7, CH_2); 3.96 (*d*, *J* = 6.7, CH_2); 6.33 (*d*, *J* = 15.6,

1 H); 7.01 (*d*, *J* = 15.9, 1 H); 7.20–7.25 (*m*, 1 arom. H); 7.80 (*dd*, *J* = 1.5, 8.0, arom. H); 7.95 (*d*, *J* = 15.2, H); 8.00 (*d*, *J* = 15.8, H); 8.55 (*dd*, *J* = 1.6, 4.5, arom. H). ^{13}C-NMR (75 MHz): 19.0, 19.1 (Me); 27.8 (CH); 70.8, 71.0 (CH_2O); 123.5, 124.3, 125.2 (CH); 130.1 (C); 135.0, 138.4, 139.0, 150.6 (CH); 150.8, 165.1, 165.8 (C). GC/EI-MS: 331 (2, M^+), 258 (46), 230 (100), 202 (29), 174 (81), 156 (19), 129 (38). HR-EI-MS: 331.17745 (M^+, $C_{19}H_{25}NO_4^+$; calc. 331.17836).

*Di(*tert*-butyl) 3,3′-Pyridine-2,3-diylbis[(*E*)-prop-2-enoate]* (**3d**). Light-yellow solid (278 mg, 84%). M.p. 137–138°. IR: 3004*w*, 2978*w*, 2930*w*, 2871*w*, 1698*s*, 1634*w*, 1578*w*, 1552*w*, 1471*w*, 1456*w*, 1422*m*, 1392*m*, 1365*m*, 1392*m*, 1365*s*, 1309*s*, 1254*s*, 1138*s*, 1086*w*, 1062*w*, 1039*w*, 971*s*, 922*m*, 889*m*, 845*m*, 805*m*, 763*m*, 731*m*, 598*m*, 538*m*. ^{1}H-NMR (300 MHz): 1.43 (*s*, 3 Me); 1.44 (*s*, 3 Me); 6.22 (*d*, *J* = 15.2, CH); 6.90 (*d*, *J* = 15.9, CH); 7.17–7.22 (*m*, 1 arom. H); 7.73 (*dd*, *J* = 1.7, 8.0, 1 arom. H); 7.84 (*d*, *J* = 15.2, CH); 7.86 (*d*, *J* = 15.8, CH); 8.50 (*dd*, *J* = 1.7, 4.6, 1 arom. H). ^{13}C-NMR (62.9 MHz): 28.0 (3 Me); 28.1 (3 Me); 80.7, 81.0 (C); 124.0, 125.3, 127.0 (CH); 130.1 (C); 134.9, 137.6, 138.0, 150.4 (CH); 150.9 (CH); 164.9, 165.7 (C=O). GC/EI-MS: 331 (1, M^+), 275 (1), 230 (23), 202 (39), 174 (99), 130 (100), 102 (10), 57 (91). HR-EI-MS: 331.17840 (M^+, $C_{19}H_{25}NO_4^+$; calc. 331.17836).

*Bis(2-ethylhexyl) 3,3′-Pyridine-2,3-diylbis[(*E*)-prop-2-enoate]* (**3e**). Light-yellow oil (265 mg, 60%). IR: 2957*m*, 2927*m*, 2872*m*, 2869*m*, 1713*s*, 1636*w*, 1580*w*, 1554*w*, 1460*w*, 1425*w*, 1380*w*, 1296*m*, 1260*m*, 1220*w*, 1204 *w*, 1163*s*, 1085*w*, 1063*w*, 1027*w*, 1014*w*, 974*m*, 918*w*, 869*w*, 801*w*, 780*m*, 729*w*, 703*w*, 606*w*. ^{1}H-NMR (300 MHz): 0.82–0.87 (*m*, 4 Me); 1.27–1.31 (*m*, 6 CH_2); 1.28–1.31 (*m*, 2 CH_2); 1.33–1.60 (*m*, 2 CH); 4.06–4.09 (*m*, 2 CH_2O); 6.31 (*d*, *J* = 15.2, CH); 7.01 (*d*, *J* = 15.2, CH); 7.20–7.25 (*m*, 1 arom. H); 7.78 (*dd*, *J* = 1.5, 8.0, 1 arom. H); 7.92 (*d*, *J* = 15.2, CH); 7.97 (*d*, *J* = 15.2, CH); 8.55 (*dd*, *J* = 1.8, 4.5, 1 arom. H). ^{13}C-NMR (62.9 MHz): 10.9, 11.0, 14.0 (Me); 22.9, 23.8 28.9, 30.4 (CH_2); 38.7, 38.8 (CH); 67.1, 67.4 (CH_2O); 123.6, 124.2, 125.2 (CH); 138.3 (C); 135.0, 138.4, 138.9, 150.6 (CH); 150.9 (C); 165.9, 166.6 (C=O). GC/EI-MS: 443 (2, M^+), 398 (4), 332 (42), 286 (100), 202 (48), 70 (16), 57 (29). HR-EI-MS: 443.30301 (M^+, $C_{27}H_{41}NO_4^+$; calc. 443.30356).

*2,3-Bis[(*E*)-2-phenylethenyl]pyridine* (**3f**). Light-yellow solid (204 mg, 72%). M.p. 130–132°. IR: 3078*w*, 3055*w*, 3024*w*, 2929*w*, 1732*w*, 1699*w*, 1628*w*, 1597*w*, 5174*w*, 1492*m*, 1448*m*, 1419*m*, 1371*w*, 1323*w*, 1300*w*, 1271*w*, 1240*w*, 1203*w*, 1179*w*, 1162*w*, 1072*w*, 1045*w*, 1027*w*, 958*s*, 915*w*, 847*w*, 770*s*, 744*s*, 687*s*, 543*m*. ^{1}H-NMR (300 MHz): 6.88 (*d*, *J* = 15.2, CH); 7.06 (*dd*, *J* = 7.9, 4.5, 1 arom. H); 7.21–7.31 (*m*, 6 arom. H); 7.36–7.45 (*m*, 4 arom. H); 7.49–7.52 (*m*, 2 arom. H); 7.69–7.74 (*m*, 2 arom. H); 8.44 (*dd*, *J* = 1.8, 4.5, 1 arom. H). ^{13}C-NMR (62.9 MHz): 122.3, 124.2, 124.4, 126.8, 127.3, 128.3, 128.4, 128.7, 128.9 (CH); 131.4 (C); 133.1, 134.4, 134.7 (CH); 137.0, 148.4, 152.5 (C). GC/EI-MS: 283 (100, M^+), 206 (42), 180 (7), 134 (6), 91 (4), 77 (3). HR-EI-MS: 282.12783 ([$M-1$]$^+$, $C_{21}H_{16}N^+$; calc. 282.12827).

*2,3-Bis[(*E*)-2-(4-methoxyphenyl)ethenyl]pyridine* (**3h**). Light-yellow crystalline solid (271 mg, 79%). M.p. 123–124°. IR: 3045*w*, 3000*w*, 2668*w*, 2932*w*, 2836*w*, 1692*w*, 1626*w*, 1600*m*, 1572*m*, 1550*w*, 1508*s*, 1464*m*, 1455*m*, 1439*m*, 1426*m*, 1344*w*, 1332*w*, 1245*s*, 1170*s*, 1023*m*, 967*m*, 936*w*, 856*w*, 818*s*, 791*m*, 775*m*, 715*w*, 688*w*, 612*w*. ^{1}H-NMR (300 MHz): 3.75 (*s*, MeO); 3.76 (*s*, MeO); 6.81–6.88 (*m*, 5 arom. H); 7.03–7.07 (*m*, 1 arom. H); 7.30 (*d*, *J* = 15.7, CH); 7.31 (*d*, *J* = 15.2, CH); 7.39–7.49 (*m*, 4 arom. H); 7.64 (*d*, *J* = 15.2, CH); 7.72 (*dd*, *J* = 1.6, 8.0, 1 arom. H); 8.42 (*dd*, *J* = 1.5, 4.6, 1 arom. H). ^{13}C-NMR (62.9 MHz): 55.3, 55.3 (MeO); 114.1, 114.2, 121.9, 122.1, 122.3, 127.9, 128.6 (CH); 129.3, 130.3 (C); 132.3, 133.9, 134.1, 148.0 (CH); 156.0, 159.7, 159.9 (C). GC/EI-MS: 343 (100, M^+), 236 (72), 222 (9), 121 (31), 77 (2). HR-EI-MS: 343.15642 (M^+, $C_{23}H_{21}NO_2^+$; calc. 343.15723).

*2,3-Bis[(*E*)-2-(4-methylphenyl)ethenyl]pyridine* (**3i**). Light-yellow semi-solid (202 mg, 65%). IR: 3031*w*, 2919*w*, 2853*w*, 2727*w*, 1693*w*, 1626*w*, 1605*w*, 1573*w*, 1550*w*, 1450*w*, 1422*m*, 1324*w*, 1298*w*, 1200*w*, 1182*w*, 1109*w*, 1082*w*, 1039*w*, 1018*w*, 959*s*, 867*w*, 805*s*, 706*w*, 635*w*, 613*w*, 548*w*, 533*m*. ^{1}H-NMR (300 MHz): 2.27 (*s*, Me); 2.28 (*s*, Me); 6.85 (*d*, *J* = 15.2, CH); 7.03–7.14 (*m*, 5 arom. H); 7.32–7.43 (*m*, 6 arom. H); 7.64–7.72 (*m*, 2 arom. H); 8.42 (*dd*, *J* = 1.5, 4.5, 1 arom. H). ^{13}C-NMR (75 MHz): 21.3, 21.4 (Me); 122.0, 123.3, 123.5, 126.6, 127.2, 129.4 (CH); 129.5 (C); 129.6 (CH); 131.5 (C); 132.8, 134.2 (CH); 134.3 (C); 134.5 (CH); 138.2, 138.4 (C); 148.2 (CH); 152.6 (C). GC/EI-MS: 311 (60, M^+), 310 (100), 220 (45), 147 (6), 105 (9). HR-EI-MS: 311.15912 (M^+, $C_{23}H_{21}N^+$; calc. 311.16740).

*Dimethyl 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5a**). White solid (170 mg, 69%). M.p. 156–158°. IR: 2954*m*, 2921*m*, 2851*m*, 1722*s*, 1716*s*, 1642*s*, 1433*m*, 1329*m*, 1316*m*, 1329*m*, 1315*m*, 1292*w*, 1278*w*, 1244*m*, 1189*m*, 1169*s*, 1025*w*, 1014*w*, 999*w*, 977*m*, 854*m*, 785*w*, 738*w*, 727*w*, 704*w*, 688*m*, 600*m*. ^{1}H-NMR (300 MHz): 3.76 (*s*, 2 MeO); 6.46 (*d*, *J* = 16.1, 2 CH); 7.62 (*d*, *J* = 16.1, 2 CH); 7.86 (br. *s*, 1 arom. H); 8.66

(*s*, 2 arom. H). ^{13}C-NMR (62.9 MHz): 60.0 (MeO); 121.1, 132.2 (CH); 132.6 (C); 140.3, 150.3 (CH); 166.4 (C=O). GC/EI-MS: 247 (70, M^+), 232 (64), 216 (100), 200 (30), 184 (72), 156 (46), 128 (31). HR-EI-MS: 247.08498 (M^+, $C_{13}H_{13}NO_4^+$; calc. 247.08446).

*Diethyl 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5b**). White solid (195 mg, 71%). M.p. 162–163°. IR: 2982*w*, 2934*w*, 2904*w*, 2874*w*, 1699*s*, 1639*m*, 1592*w*, 1567*w*, 1420*m*, 1368*m*, 1321*m*, 1239*m*, 1167*s*, 1094*m*, 977*s*, 911*w*, 854*s*, 810*w*, 686*m*, 605*w*, 587*w*, 541*w*. ^{1}H-NMR (300 MHz): 1.27 (*t*, *J* = 7.0, 2 Me); 4.22 (*q*, *J* = 7.1, 14.3, 2 CH_2O); 6.48 (*d*, *J* = 16.1, 2 CH); 7.60 (*d*, *J* = 16.1, 2 CH); 7.88 (*s*, 1 arom. H); 8.66 (*s*, 2 arom. H). ^{13}C-NMR (62.9 MHz): 14.2 (Me); 60.9 (CH_2O); 121.5 (CH); 130.5 (C); 132.4, 140.0, 150.2 (CH); 156.9 (C=O). GC/EI-MS: 275 (51, M^+), 246 (61), 230 (100), 200 (44), 184 (42), 128 (14), 51 (7). HR-EI-MS: 275.11571 (M^+, $C_{15}H_{17}NO_4^+$; calc. 275.11576).

*Dibutyl 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5c**). White solid (271 mg, 82%). M.p. 148–149°. IR: 2957*s*, 2933*s*, 2872*s*, 1708*s*, 1638*m*, 1567*w*, 1465*w*, 1448*w*, 1432*w*, 1382*w*, 1355*w*, 1342*w*, 1312*m*, 1285*m*, 1258*m*, 1239*m*, 1168*s*, 1062 *m*, 978*s*, 901*w*, 858*s*, 735*w*, 702*w*, 683*m*, 602*w*, 589*w*. ^{1}H-NMR (300 MHz): 0.89 (*t*, *J* = 7.4, 2 Me); 1.30–1.42 (*m*, 2 CH_2); 1.57–1.67 (*m*, 2 CH_2); 4.15 (*t*, *J* = 6.7, 2 CH_2O); 6.49 (*d*, *J* = 16.1, 2 CH); 7.63 (*d*, *J* = 16.1, 2 CH); 7.89 (*s*, 1 arom. H); 8.66 (*s*, 2 arom. H). ^{13}C-NMR (75 MHz): 13.6 (Me); 19.1, 30.7 (CH_2); 64.8 (CH_2O); 121.4 (CH); 130.4 (C); 132.3, 139.9, 150.3 (CH); 166.0 (C=O). GC/EI-MS: 331 (12, M^+), 258 (100), 230 (22), 202 (53), 184 (35), 156 (22), 128 (17). HR-EI-MS: 331.17819 (M^+, $C_{19}H_{25}NO_4^+$; calc. 331.17836).

*Bis(2-methylpropyl) 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5d**). White solid (278 mg, 84%). M.p. 147–148°. IR: 2956*m*, 2872*m*, 1708*s*, 100*s*, 1638*m*, 1573*w*, 1558*w*, 1470*m*, 1435*m*, 1375*m*, 1312*m*, 1293*m*, 1273*m*, 1256*m*, 1240*m*, 1170*s*, 1020*s*, 980*s*, 858*s*, 799*w*, 732*w*, 706*w*, 682*s*, 590*w*, 552*w*, 534*w*. ^{1}H-NMR (300 MHz): 0.90 (*d*, *J* = 6.8, 4 Me); 1.88–2.00 (*m*, 2 CH); 3.92 (*d*, *J* = 6.7, 2 CH_2O); 6.51 (*d*, *J* = 16.1, 2 CH); 7.60 (*d*, *J* = 16.1, 2 CH); 7.92 (*s*, 1 arom. H); 8.68 (*s*, 2 arom. H). ^{13}C-NMR (75 MHz): 19.0 (Me); 27.8 (CH); 70.9 (CH_2O); 121.4 (CH); 130.6 (C); 132.3, 140.0, 150.3 (CH); 166.0 (C=O). GC/EI-MS: 331 (6, M^+), 276 (27), 258 (100), 220 (61), 202 (30), 184 (20), 156 (13), 56 (10). HR-EI-MS: 331.40611 (M^+, $C_{19}H_{25}NO_4^+$; calc. 331.17836).

*Dihexyl 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5e**). White solid (299 mg, 77%). M.p. 130–132°. IR: 2954*m*, 2927*m*, 2857*m*, 1712*s*, 1644*m*, 1589*w*, 1566*w*, 1464*w*, 1421*w*, 1343*w*, 1316*m*, 1258*s*, 1227*m*, 1166*s*, 1068*m*, 1040*m*, 1023*m*, 993*s*, 980*s*, 903*m*, 866*m*, 857*m*, 794*m*, 613*w*, 603*w*, 545*w*. ^{1}H-NMR (300 MHz): 0.82 (*t*, *J* = 6.8, 2 Me); 1.16–1.35 (*m*, 6 CH_2); 1.58–1.65 (*m*, 2 CH_2); 4.14 (*t*, 2 CH_2O); 6.49 (*d*, *J* = 16.1, 2 CH); 7.59 (*d*, *J* = 16.1, 2 CH); 7.90 (br. *s*, 1 arom. H); 8.65 (*s*, 2 arom. H). ^{13}C-NMR (75 MHz): 13.2 (Me); 21.5, 24.6, 27.6, 30.4 (CH_2); 63.6 (CH_2O); 120.5 (CH); 129.3 (C); 131.3, 139.0, 149.3 (CH); 165.0 (C=O). GC/EI-MS: 387 (8, M^+), 330 (8), 304 (50), 286 (100), 258 (30), 220 (88), 202 (51), 184 (26). HR-EI-MS: 387.240367 (M^+, $C_{23}H_{33}NO_4^+$; calc. 387.24096).

*Di(*tert*-butyl) 3,3′-Pyridine-3,5-diylbis[(*E*)-prop-2-enoate]* (**5f**). White solid (268 mg, 81%). M.p. 135–136°. IR: 2974*m*, 2929*m*, 2871*m*, 1698*s*, 1644*m*, 1573*w*, 1454*w*, 1433*w*, 1391*m*, 1365*m*, 1328*m*, 1295*m*, 1279*m*, 1256*m*, 1147*s*, 1040*w*, 1025*w*, 970*s*, 857*m*, 848*m*, 807*w*, 782*w*, 761*w*, 724*w*, 687*m*, 605*w*, 591*w*, 540*w*. ^{1}H-NMR (300 MHz): 1.47 (*s*, 6 Me); 6.41 (*d*, *J* = 16.1, 2 CH); 7.49 (*d*, *J* = 16.1, 2 CH); 7.84 (br. *s*, 1 arom. H); 8.62 (*s*, 2 arom. H). ^{13}C-NMR (62.9 MHz): 28.0 (Me); 81.06 (C–O); 123.3 (CH); 130.5 (C); 132.1, 139.0, 150.1 (CH); 165.2 (C=O). GC/EI-MS: 331 (20, M^+), 275 (20), 258 (88), 220 (99), 202 (60), 173 (33), 57 (100). HR-EI-MS: 331.17831 (M^+, $C_{19}H_{25}NO_4^+$; calc. 331.17836).

*3,5-Bis[(*E*)-2-phenylethenyl]pyridine* (**5g**; see also *Fig. 2*)[1]). White solid (204 mg, 72%). M.p. 115–116°. IR: 3098*w*, 3080*w*, 3052*w*, 3023*w*, 2926*w*, 2850*w*, 1446*m*, 1414*w*, 1340*w*, 1309*w*, 1239*w*, 1230*w*, 1178*w*, 1155*w*, 1107*w*, 1023*w*, 999*w*, 983*w*, 962*s*, 919*w*, 892*w*, 825*w*, 833*w*, 797*w*, 779*w*, 745*s*, 691*s*, 545*m*, 526*m*. ^{1}H-NMR (300 MHz): 6.93 (*d*, *J* = 16.4, 2 CH); 7.08 (*d*, *J* = 16.4, 2 CH); 7.17–7.31 (*m*, 6 arom. H); 7.39–7.44 (*m*, 4 arom. H); 7.78 (*s*, 1 arom. H); 8.51 (*s*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 124.7, 126.8, 128.25, 128.8, 129.4, 131.1 (CH); 133.1, 136.7 (C); 147.2 (CH). GC/EI-MS: 283 (62, M^+), 282 (100), 204 (4), 156 (4), 133 (8). HR-EI-MS: 283.13699 (M^+, $C_{21}H_{17}N^+$; calc. 283.13610).

*3,5-Bis[(*E*)-2-(4-methylphenyl)ethenyl]pyridine* (**5h**). White solid (236 mg, 76%). M.p. 118–119°. IR: 3038*m*, 3020*m*, 2998*m*, 2912*m*, 2854*m*, 2725*m*, 1603*w*, 1583*w*, 1510*w*, 1462*w*, 1434*w*, 1414*w*, 1371*w*, 1327*w*, 1303*w*, 1241*w*, 1212*w*, 1180*w*, 1112*w*, 1041*w*, 1017*w*, 966*s*, 950*m*, 889*w*, 849*m*, 841*m*, 799*s*, 667*w*, 626*w*. ^{1}H-NMR (300 MHz): 2.30 (*s*, 2 Me); 6.93 (*d*, *J* = 16.1, 2 CH); 7.09–7.14 (*m*, 6 H); 7.37 (*d*, *J* = 8.1, 4 arom. H); 7.85 (br. *s*, 1 arom. H); 8.50 (*s*, 2 arom. H). ^{13}C-NMR (75 MHz): 21.3 (Me); 123.6, 126.7, 129.4,

129.6, 131.1 (CH); 133.2, 133.8, 138.3 (C); 146.6 (CH). GC/EI-MS: 311 (72, M^+), 310 (100), 294 (10), 170 (6), 154 (12). HR-EI-MS: 310.15921 ($[M-1]^+$, $C_{23}H_{20}N^+$; calc. 310.15957).

*Dibutyl 3,3′-[2,2′-Bipyridine]-5,5′-diylbis[(*E*)-prop-2-enoate]* (**7a**). White solid (169 mg, 83%). M.p. 225–227°. IR: 3055*w*, 2957*w*, 2933*w*, 2872*w*, 1714*s*, 1635*s*, 1469*s*, 1377*s*, 1303*s*, 1250*m*, 1200*m*, 1168*s*, 1140*s*, 1117*s*, 1056*m*, 1020*m*, 989*m*, 976*m*, 953*m*, 925*m*, 900*m*, 862*m*, 833*s*, 723*m*, 707*m*, 652*m*, 532*m*. ^{1}H-NMR (250 MHz): 0.86 (*t*, *J* = 7.3, 2 Me); 1.33–1.45 (*m*, 2 CH_2); 1.57–1.69 (*m*, 2 CH_2); 4.18 (*t*, *J* = 6.7, 2 CH_2O); 6.45 (*d*, *J* = 15.2, 2 CH); 7.61 (*d*, *J* = 15.2, 2 CH); 7.88 (*dd*, *J* = 2.2, 8.4, 2 arom. H); 8.39 (*d*, *J* = 8.3, 2 arom. H); 8.70 (*d*, *J* = 1.9, 2 arom. H). ^{13}C-NMR (62.9 MHz): 13.6 (Me); 19.2, 29.7 (CH_2); 64.7 (CH_2O); 120.6, 121.3 (CH); 130.5 (C); 135.0, 140.0, 149.4 (CH); 156.4, 166.4 (C). GC/EI-MS: 408 (100, M^+), 363 (24), 336 (65), 279 (70), 178 (11). HR-EI-MS: 408.20450 (M^+, $C_{24}H_{28}N_2O_4^+$; calc. 408.20491).

*Dihexyl 3,3′-[2,2′-Bipyridine]-5,5′-diylbis[(*E*)-prop-2-enoate]* (**7b**). White solid (329 mg, 71%). M.p. 215–217°. IR: 2952*m*, 2928*m*, 2870*m*, 1714*s*, 1635*s*, 1592*w*,1544*w*, 1468*m*, 1376*m*, 1304*s*, 1273*w*, 1250*w*, 1214*w*, 1199*w*, 1171*s*, 1139*s*, 1067*w*, 1013*w*, 990*m*, 975*m*, 931*w*, 899*w*, 879*w*, 863*w*, 834*m*, 815*w*, 724*m*, 708*m*, 652*m*, 599*w*, 538*w*, 529*w*. ^{1}H-NMR (300 MHz): 0.83 (*t*, *J* = 6.6, 2 Me); 1.17–1.35 (*m*, 6 CH_2); 1.59–1.69 (*m*, 2 CH_2); 4.15 (*t*, *J* = 6.7, 2 CH_2O); 6.49 (*d*, *J* = 15.2, 2 CH); 7.63 (*d*, *J* = 15.2, 2 CH); 7.89 (*d*, *J* = 8.3, 2 arom. H); 8.40 (*d*, *J* = 8.3, 2 arom. H); 8.70 (br. *s*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 13.9 (Me); 22.5, 25.6, 28.6, 31.4 (CH_2); 65.0 (CH_2O); 120.6, 121.3 (CH); 130.5 (C); 135.0, 140.4, 149.3 (CH); 156.3 (C); 166.4 (C=O). GC/EI-MS: 464 (73, M^+), 407 (17), 363 (100), 336 (91), 324 (34), 279 (65), 205 (14), 57 (13). HR-EI-MS: 464.27481 (M^+, $C_{28}H_{36}N_2O_4^+$; calc. 464.26751).

*Bis(2-ethylhexyl) 3,3′-[2,2′-Bipyridine]-5,5′-diylbis[(*E*)-prop-2-enoate]* (**7c**). White solid (213 mg, 82%). M.p. 255–257°. IR: 2957*s*, 2926*s*, 2858*s*, 1709*s*, 1633*s*, 1568*m*, 1468*m*, 1379*m*, 1302*s*, 1254*m*, 1162*s*, 1135*m*, 1050*m*, 1005*w*, 839*m*, 767*w*, 748*w*, 729*w*, 709*w*, 546*w*. ^{1}H-NMR (250 MHz): 0.82–0.90 (*m*, 4 Me); 1.18–1.39 (*m*, 8 CH_2); 1.59–1.69 (*m*, 2 CH); 4.08–4.10 (*m*, 2 CH_2O); 6.51 (*d*, *J* = 15.2, 2 CH); 7.64 (*d*, *J* = 15.2, 2 CH); 7.91 (*dd*, *J* = 2.2, 8.4, 2 arom. H); 8.39 (*d*, *J* = 8.3, 2 arom. H); 8.72 (br. *s*, 2 arom. H). ^{13}C-NMR (62.9 MHz): 11.0, 14.0 (Me); 23.0, 23.8, 28.9, 30.4 (CH_2); 38.8 (CH); 67.2 (CH_2O); 120.6, 121.3 (CH); 130.5 (C); 135.0, 140.4, 149.4 (CH); 156.4 (C); 166.5 (C=O). GC/EI-MS: 520 (21, M^+), 491 (6), 408 (14), 391 (37), 364 (22), 296 (100), 205 (7). HR-EI-MS: 520.33045 (M^+, $C_{32}H_{44}N_2O_4^+$; calc. 520.33011).

*Di(*tert*-butyl) 3,3′-[2,2′-Bipyridine]-5,5′-diylbis[(*E*)-prop-2-enoate]* (**7d**; see also *Fig. 3*)[1]). White solid (342 mg, 84%). M.p. 237–238°. IR: 3006*w*, 2976*w*, 2928*w*, 2855*w*, 1699*s*, 1667*w*, 1634*m*, 1555*w*, 1544*w*, 1468*m*, 1455*m*, 1363*m*, 1315*m*, 1251*m*, 1208*m*, 1146*s*, 1054*m*, 1023*m*, 993*s*, 981*s*, 835*s*, 765*m*, 750*m*, 738*m*, 710*m*, 650*m*, 589*w*. ^{1}H-NMR (300 MHz): 1.47 (*s*, 6 Me); 6.43 (*d*, *J* = 15.2, 2 CH); 7.56 (*d*, *J* = 15.2, 2 CH); 7.89 (*dd*, *J* = 2.2, 8.4, 2 arom. H); 8.39 (*d*, *J* = 8.3, 2 arom. H); 8.71 (*d*, *J* = 2.0, 2 arom. H). ^{13}C-NMR (75.5 MHz): 28.2 (Me); 81.0 (C); 121.3, 122.5 (CH); 130.7 (C); 135.0, 139.3, 149.2 (CH); 156.1 (C); 156.5 (C=O). GC/EI-MS: 408 (24, M^+), 352 (27), 296 (100), 205 (10), 279 (40), 252 (80), 205 (10). HR-EI-MS: 408.20549 (M^+, $C_{24}H_{28}N_2O_4^+$; calc. 408.20491).

*Bis(2-methylpropyl) 3,3′-[2,2′-Bipyridine]-5,5′-diylbis[(*E*)-prop-2-enoate]* (**7e**). White solid (314 mg, 77%). M.p. 231–232°. IR: 2959*m*, 2929*m*, 2873*m*, 1728*s*, 1679*w*, 1641*w*, 1632*w*, 1590*w*, 1462*m*, 1378*m*, 1235*s*, 1169 *s*, 1092*m*, 984*m*, 945*m*, 800*m*, 784*m*, 648*w*. ^{1}H-NMR (300 MHz): 0.93 (*d*, *J* = 6.7, 4 Me); 1.89–1.97 (*m*, 2 CH); 3.94 (*d*, *J* = 6.7, 2 CH_2O); 6.53 (*d*, *J* = 15.2, 2 CH); 7.65 (*d*, *J* = 15.2, 2 CH); 7.91 (*d*, *J* = 2.1, 8.4, 2 arom. H); 8.39 (*d*, *J* = 8.3, 2 arom. H); 8.33 (br. *s*, 2 arom. H). ^{13}C-NMR (62.9 MHz): 18.1 (Me); 26.8 (CH); 69.9 (CH_2O); 119.6, 120.3 (CH); 129.5 (C); 134.0, 139.5, 148.4 (CH); 155.4 (C); 165.4 (C=O). GC/EI-MS: 408 (56, M^+), 352 (17), 296 (100), 205(11), 131 (6). HR-EI-MS: 408.20451 (M^+, $C_{24}H_{28}N_2O_4^+$; calc. 408.20491).

Financial support by the State of Mecklenburg-Vorpommern (*Landesgraduiertenstipendium* for *M. H.*), by the State of Pakistan (HEC scholarships for *M. H.* and *I. M.*), by the *DAAD* (scholarships for *A. A.* and *I. M.*), and by the *Friedrich-Irgard-Harms-Stiftung* (scholarship for *A. A.*) is gratefully acknowledged.

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Received March 18, 2010