Methylation of (1-azolyl)-1,4-dihydroxybenzenes

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Abstract

Nine new compounds have been prepared by methylation of monoazolyl and bisazolyl derivatives of 1,4-dihydroxybenzene. The azolyl substituents at positions 2 or 2,3 are 1-pyrazolyl, 3,5-dimethyl-1-pyrazolyl and 2-methyl-1-imidazolyl. The resulting compounds with one or two methoxy groups have been characterized by ^{1}H and ^{13}C NMR, by IR and by mass spectrometry. In two cases, both dimethoxy derivatives, the *meso* and *d,l* isomers have been identified.

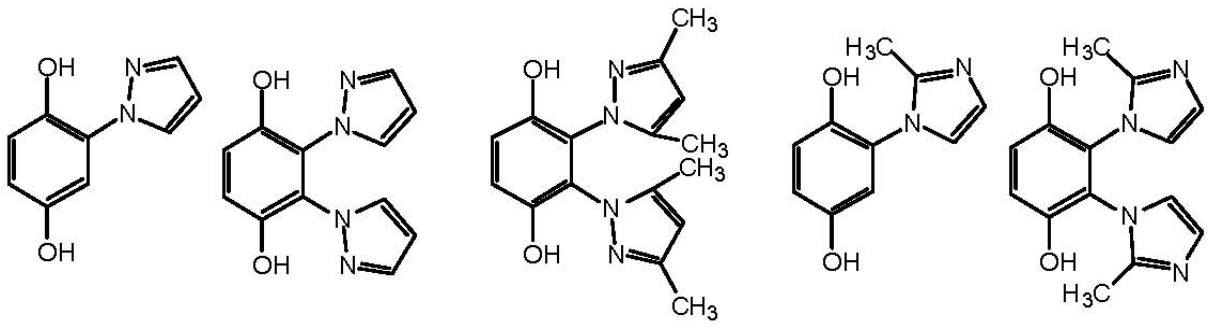
Keywords: Pyrazoles, hydroquinones, ethoxybenzenes, ^{13}C NMR; *meso* and *d,l* isomers

Introduction

During our studies related to the synthesis of *N*-azolyl derivatives of 1,4-dihydroxybenzene (hydroquinone) several cases of hindered rotation of the azolyl residues have been described.[1-3] In order to increase the steric demand of the OH groups, it was decided to transform them into OMe groups and to study the *meso* vs. *d,l* isomerism of the resulting compounds.

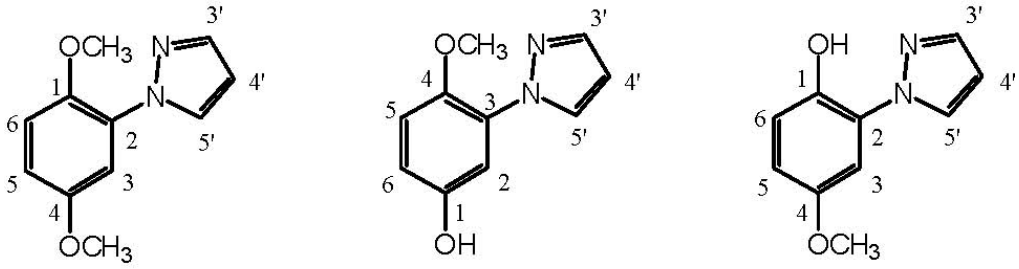
Results and Discussion

The compounds selected were 2-(1-pyrazolyl)-1,4-dihydroxybenzene (**1**), 2,3-bis(1-pyrazolyl)-1,4-dihydroxybenzene (**2**), 2,3-bis(3,5-dimethyl-1-pyrazolyl)-1,4-dihydroxy-benzene (**3**), 2-(2-methyl-1-imidazoly)-1,4-dihydroxybenzene (**4**) and 2,3-bis(2-methyl-1-imidazolyl)-1,4-dihydroxybenzene (**5**).



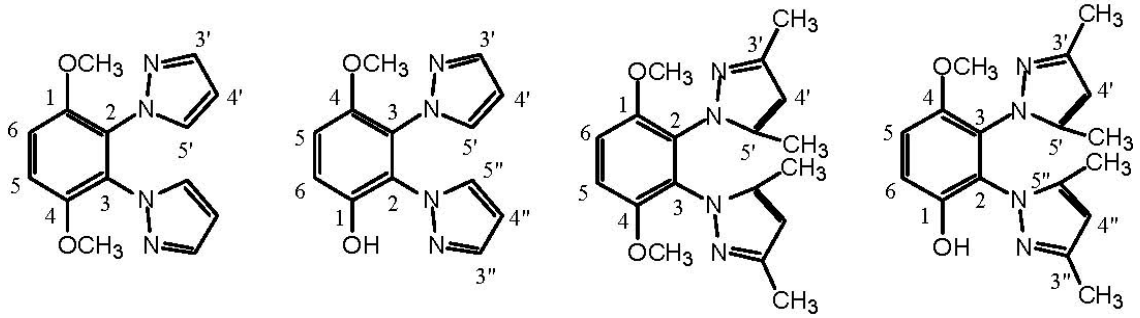
1 2 3 4 5

Amongst the different methods used to methylate phenols,[4] the action of methyl sulfate on the phenoxide anions was selected, in order to avoid the quaternisation of the azoles, particularly the highly reactive imidazoles.[5] Therefore, the reactions were carried out in $NaOH/H_2O$ at reflux. In the case of pyrazole (**1**), three compounds were obtained. The overall yield was 72% and the relative amounts 85% (**6**), 8% (**7**) and 7% (**8**), determined by ^1H NMR on the reaction crude.



6 7 8

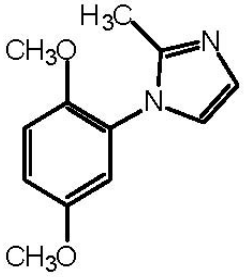
From (**2**) and (**3**) the reaction proceeds with similar overall yields (near 70%) but, due to the symmetry, only two compounds were isolated in each case: 77% (**9**), 23% (**10**) and 80% (**11**), 20% (**12**).



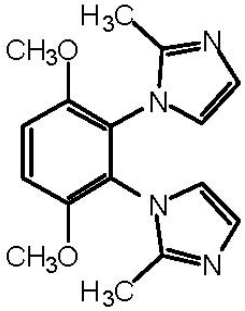
9 10 11 12

In the case of imidazoles (**4**) and (**5**) the results were not satisfactory, only 10% of (**13**) and 5% of (**14**) were obtained. Alternative procedures such as different phase transfer methods,

diazomethane, etc. did not provide the desired products in better yields.



13



14

^{1}H and ^{13}C NMR spectroscopies

Compounds (**6**)-(**14**) were identified by NMR (Tables 1, 2 and Scheme 1), mass spectrometry, IR and microanalysis.

The assignments of Tables 1 and 2 were based on those of the starting materials (1) - (5)[1] and on general data on azoles.[6] One notable observation is the signal of the proton adjacent to the pyrazolyl substituent in compounds (1),[1] (6), (7) and (8). When the pyrazole ring is *ortho* to one OH, the signal appears at 6.92 ppm (1, 8) while when it is *ortho* to a methoxy group (6, 7) it appears at 7.37-7.38 ppm; the other substituent (*meta* to the pyrazole) does not affect the chemical shift. This is certainly related to the conformation of the pyrazolyl residue: planar in the case of the OH (O-H···N intramolecular hydrogen bond) and non planar in the case of the OMe substituent.

Table 1. ^{1}H NMR spectra (δ, ppm, J, Hz) of pyrazoles (6)-(12) in $CDCl_3$

Comp	H-2	H-3	H-5	H-6	H-3'	H-4'	H-5'
6	----	7.37					
	6.83	6.97	7.70	6.42	8.10	…	----
	J_{35}=3.0	J_{56}=9.0	----	$J_{3'4'}$=1.7	$J_{4'5'}$=2.4	$J_{3'5'}$=0.5	
7	7.38----						
	6.89	6.75	7.73	6.43	8.01	….	J_{25}=2.9
	J_{56}=8.9	$J_{3'4'}$=1.8	$J_{4'5'}$=2.4				
8	----	6.92	6.76	7.03	7.73	6.50	7.97
J_{36}=2.8	J_{56}=8.9	$J_{3'4'}$=1.7	$J_{4'5'}$=2.3	$J_{3'5'}$=0.4			
9	----	----	7.09	7.09	7.56	6.21	7.30
$J_{3'4'}$=1.8	$J_{4'5'}$=2.5	$J_{3'5'}$=0.5					
10	----	----	7.19	6.94	7.78	6.41	6.57
J_{56}=9.2	$J_{3'4'}$=1.8	$J_{4'5'}$=2.3					
11	----	----	7.05	7.05	----	5.72	----
7.07	7.07	5.76	----				
12	----	----	6.97	6.93	----	5.72	----
J_{56}=9.2							

Comp	H-3"	H-4"	H-5"	OH	OCH_3	3-CH_3	5-CH_3
6	----	----	----	----	3.81	----	----
3.81							
7	----	----	----	8.26	3.77	----	----
8	----	----	----	10.85	3.81	----	----
9	----	----	----	----	3.78	----	----
10	7.70	6.21	7.35	10.02	3.77	----	----
$J_{3"4"}$=1.8	$J_{4"5"}$=2.4	$J_{3"5"}$=0.5					
11	----	5.72	----	----	3.76	2.11	2.09
5.76	3.74	2.15	2.15				
12	----	5.68	----	N.o.	3.71	2.19	2.00
2.05	1.98						

N.o. Not observed.

Table 2. ^{13}C NMR spectra (δ, ppm, J, Hz) of compounds (**6**) - (**12**) in $CDCl_3$

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	OCH_3
6	144.6	129.7	109.7	153.6	112.9	113.5	56.2
	^1J=162.1		^1J=162.0	^1J=159.8	^1J=144.5		
	^3J=5.4	^2J=0.8	55.4				
	^3J=5.9	^1J=143.7					
7	150.7	112.6	129.4	144.8	114.1	115.0	56.6
	^1J=160.8		^1J=159.5	^1J=161.9	^1J=144.3		
	^3J=4.9	^3J=4.9					
8	143.3	124.8	104.4	152.6	112.7	119.6	56.0
	^1J=157.5		^1J=161.8	^1J=144.7			
	^3J=5.4	^3J=7.0 (OH)					
9	149.2	127.9	127.9	149.2	112.8	112.8	56.5
	^1J=162.2		^1J=144.7				
10	144.5	121.8	124.1	149.2	111.6	118.9	56.7
	^2J=3.3	^3J=7.1	^3J=8.2	^1J=162.7	^1J=163.6	^1J=144.6	
	^3J=10.2	^2J=1.4					
11	150.1	128.2	128.2	150.1	112.5	112.5	56.2
	^1J=161.5		^1J=144.5				
	150.1	128.2	128.2	150.1	112.8	112.8	56.6
12	149.7	126.0	126.2	149.5	113.7	118.7	56.6
	^1J=160.9	^1J=163.0	^1J=144.3				

Comp.	C-3'	C-4'	C-5'	C-3"	C-4"	C-5"	3-CH_3	5-CH_3
6	139.6	106.0	131.3	----	----	----	----	----
	^1J=185.4	^1J=177.0	^1J=191.2					
	^2J=5.7	^2J=10.2[a]	^2J=9.5					
	^3J=8.4	^2J=8.5[b]	^3J=4.5					
7	140.0	106.4	132.1	----	----	----	----	----
	^1J=186.1	^1J=178.0	^1J=191.3					
	^2J=6.0	^2J=9.5[a]	^2J=9.2					
	^3J=8.2	^2J=9.5[b]	^3J=4.5					
8	139.1	106.8	126.8	----	----	----	----	----
	^1J=188.3	^1J=179.2	^1J=188.7					

^2J=6.0 ^2J=9.8[a] ^2J=9.2

^3J=8.2 ^2J=8.1[b] ^3J=4.6

9 140.1 105.6 131.9 ---- ---- ---- ---- ----

^1J=185.7 ^1J=177.4 ^1J=189.6

^2J=5.7 ^2J=10.4[a] ^2J=9.2

^3J=8.4 ^2J=8.8[b] ^3J=4.6

10 139.9 107.0 132.1 141.0 107.1 130.8 ---- ----

^1J=187.8 ^1J=179.6 ^1J=189.2 ^1J=186.4 ^1J=178.0 ^1J=192.6

^2J=5.9 ^2J=9.8[a] ^2J=9.1 ^2J=5.8 ^2J=10.4[a] ^2J=9.4

^3J=8.3 ^2J=8.1[b] ^3J=4.6 ^3J=8.3 ^2J=8.7[b] ^3J=4.6

11 148.5 104.1 142.3 148.5 104.1 142.4 13.3 10.9

^2J=6.1 ^1J=172.4 ^2J=7.3 ^1J=126.9 ^1J=128.6

^2J=6.1[c] ^3J=3.3[c] ^2J=7.3[c]

^3J=3.3[c]

148.6 103.9 140.4 148.6 103.9 140.4 13.3 10.8

12 147.2 105.3 143.6 148.6 104.5 142.3 13.4 11.0

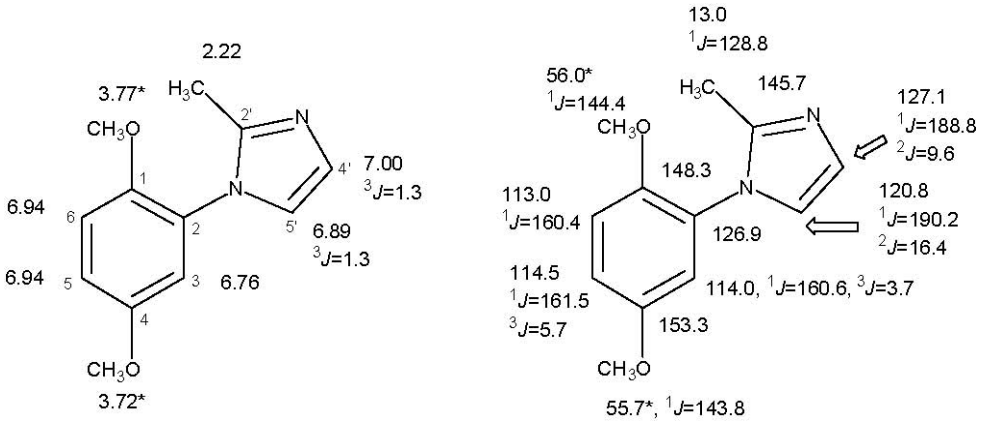
^1J=172.3 ^1J=172.3 ^1J=127.0 ^1J=129.2

13.2 10.9

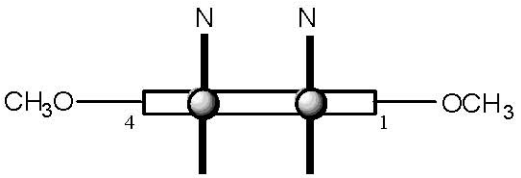
^1J=127.4 ^1J=128.3

[a] With H3'; [b] With H5'; [c] With a C-CH_3 group.

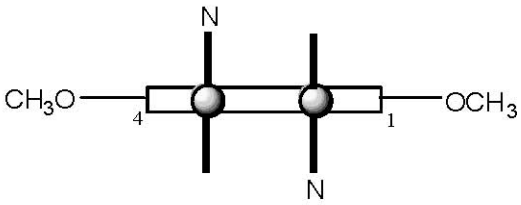
The spectral data corresponding to the monoimidazole derivative **13** are reported in Scheme 1:



Scheme 1. ^{1}H and ^{13}C NMR data of compound (**13**) in $CDCl_3$



meso

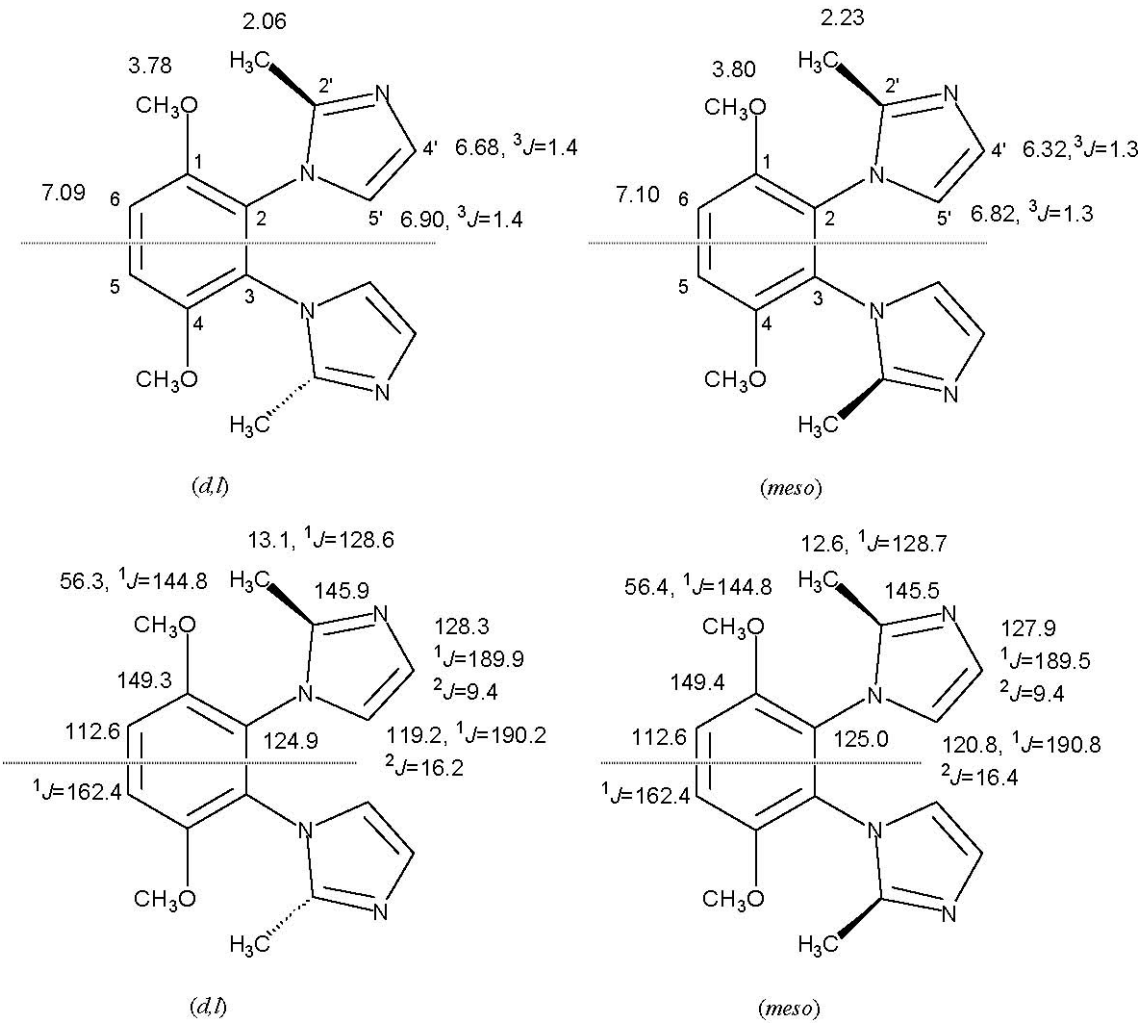


d,l

***Meso* vs. *d,l* isomerism**

In the pyrazole series, the only compound that shows two isomers at room temperature is **11**. Since **12** presents only one series of signals, it can be concluded that two methoxy groups are necessary to hinder the rotation of the 3,5-dimethylpyrazolyl residues. In Tables 1 and 2, the most abundant isomer is reported first (only on this one the coupling constants have been measured) and the less abundant in a second row. The ratio, determined by ^{1}H NMR, is 92:8. According to our previous work, the most abundant should be the *d,l*. The proportions do not change with time, either the barrier is too high or 92:8 is the equilibrium mixture.

In the imidazole series, compound **14** presents also the *meso*/*d,l* isomerism, but here the mixture isolated by column chromatography is 63:37 (by ^{1}H NMR) and after 15 min the proportions are 47:53, after 2 days no variation is observed. The ^{13}C NMR spectrum of the first mixture has been recorded and the differences in intensity used to assign the signals (Scheme 2). Here again, the most abundant isomer corresponds to the *d,l*. If the $CDCl_3$ solution in evaporated, the residue dissolved again in $CDCl_3$ and the ^{1}H NMR spectrum recorded immediately, the *d,l* isomer is very largely predominant. Therefore, in the solid state only this isomer should be present.



Scheme 2. ^{1}H and ^{13}C NMR data of compound **14**

Experimental Section

General Procedures. Melting points were determined in a microscope hot stage apparatus and are uncorrected. Column chromatography was performed on silicagel Merck 60 (70-230 mesh) using the appropriate eluent. The R_f values were measured on tlc aluminium sheets of silica gel 60 F254 (layer thickness 0.2 mm) with the solvent indicated in each case. Mass spectra were obtained with a Shimadzu QP-5000 spectrometer at 60 eV using the EI mode. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra in solution were obtained using a Bruker DRX-400 instrument. Chemical shifts (δ) in ppm are referred to Me4Si. All spectra were recorded at 300 K.

In a three-necked round bottomed flask provided with a reflux condenser and magnetic stirring were placed 10.33 mmol of NaOH in 2.5 mL of water and 4.13 mmol of the corresponding 1,4-dihydroxybenzene. Then, 8.26 mmol of dimethyl sulfate were added and the reaction warmed up to 70 °C during 1 h. If a precipitate appears it was filtered off. The solution was cooled down and extracted with CH_2Cl_2 (3 x 20 mL) and the organic lawyer was dried over anhydrous sodium sulfate. The solvent is evaporated under reduced pressure and the residue (eventually together with the precipitate) is chromatographed using as eluent that indicated in each particular case. In some reactions, when the aqueous phase is neutralized with diluted acetic acid, a precipitate appears that corresponds to monomethylation products.

Methylation of 2-(1-pyrazolyl)-1,4-dihydroxybenzene (1). The relative amounts of (**6**), (**7**) and (**8**) were determined by ^{1}H NMR. For the chromatographic separations a mixture of CH_2Cl_2/EtOH 98:2 was used as eluent.

2-(1-Pyrazolyl)-1,4-dimethoxybenzene (6). Relative amount 85%, bp. 120-5 °C/0.1 mm Hg. R_f = 0.83 (CH_2Cl_2/EtOH 98:2). IR (Nujol, ν cm^{-1}) 1615, 1595, 1515, 1500, 1465, 1435, 1400, 1390, 1335, 1325, 1310, 1275, 1265, 1235, 1210, 1180, 1145, 1105, 1090, 1050, 1035, 945, 920, 860, 800, 755, 745, 685, 655, 620. MS (m/z, %) 205 ($M^{+\cdot}$+1, 13), 204 ($M^{+\cdot}$, 100), 203 ($M^{+\cdot}$-1, 23), 189 (33), 176 (38), 175 (52), 174 (12), 173 (17), 163 (10), 145 (14), 144 (11), 135 (10), 119 (14), 93 (17), 92 (16), 91 (21), 79 (41), 78 (15), 69 (25), 68 (13), 67 (19), 66 (13), 65 (34), 63 (25), 62 (10), 54 (25), 53 (50), 52 (45), 51 (58), 50 (23). Anal. Calc. for $C_{11}H_{12}N_2O_2$: C 64.69, H 5.92, N 13.72. Found C 64.57, H 6.04, N 13.88 %.

3-(1-Pyrazolyl)-1-hydroxy-4-methoxybenzene (7). Relative amount 8%, mp. 140-2 °C. R_f = 0.50 (CH_2Cl_2/EtOH 98:2). IR (KBr, ν cm^{-1}) 2930, 2810, 2675, 1620, 1505, 1460, 1430, 1405, 1355, 1340, 1290, 1265, 1225, 1200, 1190, 1145, 1110, 1060, 1050, 1030, 980, 920, 890, 855, 825, 770, 760, 730, 630. MS (m/z, %) 191 ($M^{+\cdot}$+1, 19), 190 ($M^{+\cdot}$, 100), 189 ($M^{+\cdot}$-1, 26), 162 (38), 161 (68), 160 (16), 148 (87), 146 (37), 145 (15), 134 (15), 133 (12), 131 (14), 120 (14), 118 (13), 117 (16), 93 (20), 92 (18), 91 (10), 80 (14), 79 (19), 68 (13), 67 (15), 66 (19), 65 (46), 63 (12), 55 (14), 54 (16), 53 (39), 52 (46), 51 (31), 50 (12). Anal. Calc. for $C_{10}H_{10}N_2O_2$: C 63.14, H 5.29, N 14.72. Found C 63.21, H 5.34, N 14.66 %.

2-(1-Pyrazolyl)-1-hydroxy-4-methoxybenzene (8). Relative amount 7%, mp. 58-60 °C. R_f = 0.88 (CH_2Cl_2/EtOH 98:2). IR (KBr, ν cm^{-1}) 3140, 3130, 2920, 2850, 1610, 1520, 1490, 1470, 1455, 1430, 1345, 1290, 1250, 1235, 1190, 1110, 1070, 1040, 960, 875, 835, 785, 760, 620. MS (m/z, %) 191 ($M^{+\cdot}$+1, 10), 190 ($M^{+\cdot}$, 83), 176 (11), 175 (100), 149 (21), 147 (25), 119 (11), 93 (13), 92 (13), 85 (14), 83 (13), 79 (26), 71 (27), 70 (14), 69 (25), 68 (12), 67 (13), 66 (11), 65 (17), 57 (61), 56 (17), 55 (43), 54 (14), 53 (36), 52 (27), 51 (29). Anal. Calc. for $C_{10}H_{10}N_2O_2$: C 63.14, H 5.29, N 14.72. Found C 63.49, H 5.11, N 14.81 %.

Methylation of 2,3-bis(1-pyrazolyl)-1,4-dihydroxybenzene (2). The precipitate that appears in the course of the reaction corresponds to compound 9. When the aqueous phase is neutralized

with diluted acetic acid, compound 10 precipitates (9/10 ratio: 77/23). The organic phase is purified by column chromatography (eluent: CH_2Cl_2/EtOH 98:2).

2,3-Bis(1-pyrazolyl)-1,4-dimethoxybenzene (9). Mp. 165 °C. R_f = 0.57 (CH_2Cl_2/EtOH 98:2). IR (KBr, ν cm^{-1}) 2920, 2840, 1610, 1510, 1490, 1460, 1440, 1405, 1395, 1380, 1330, 1290, 1270, 1230, 1180, 1160, 1130, 1090, 1080, 1050, 1045, 1035, 995, 915, 890, 880, 835, 815, 795, 750, 705, 650, 635, 620. MS (m/z, %) 271 ($M^{+\cdot}$+1, 33), 270 ($M^{+\cdot}$, 100), 269 ($M^{+\cdot}$-1, 50), 255 (36), 242 (18), 241 (18), 239 (15), 228 (12), 227 (10), 226 (13), 201 (29), 200 (14), 199 (11), 173 (23), 172 (11), 145 (10), 144 (11), 80 (1), 79 (15), 78 (11), 64 (13), 54 (18), 53 (19), 52 (26). Anal. Calc. for $C_{14}H_{14}N_4O_2$: C 62.21, H 5.22, N 20.73. Found C 62.04, H 5.39, N 20.63 %.

2,3-Bis(1-pyrazolyl)-1-hydroxy-4-methoxybenzene (10). Mp. 162-4 °C. R_f = 0.72 (CH_2Cl_2/ EtOH 98:2). IR (KBr, ν cm^{-1}) 3115, 1600, 1490, 1450, 1435, 1400, 1390, 1320, 1270, 1245, 1215, 1190, 1175, 1135, 1095, 1070, 1055, 1045, 1020, 965, 945, 880, 815, 765, 710, 670, 635, 600. MS (m/z, %) 257 ($M^{+\cdot}$+1, 25), 256 ($M^{+\cdot}$, 100), 242 (15), 241 (90), 214 (16), 79 (12), 54 (15), 53 (15), 52 (18). Anal. Calc. for $C_{13}H_{12}N_4O_2$: C 60.93, H 4.72, N 21.86. Found C 60.88, H 5.03, N 21.59 %.

Methylation of 2,3-bis(3,5-dimethyl-1-pyrazolyl)-1,4-dihydroxybenzene (3).

Compound **11** precipitates from the reaction medium and was collected by filtration. The organic extracts were purified by chromatography (eluent: CH_2Cl_2/EtOH 95:5).

2,3-Bis(3,5-dimethyl-1-pyrazolyl)-1,4-dimethoxybenzene (**11**). Mp. 154-5 °C. R_f = 0.81 (CH_2Cl_2/EtOH 95:5). IR (KBr, ν cm^{-1}) 2960, 2920, 2840, 1595, 1555, 1500, 1470, 1440, 1415, 1380, 1360, 1285, 1260, 1180, 1150, 1130, 1085, 1030, 970, 830, 795, 770, 740, 700. MS (m/z, %) 327 ($M^{+\cdot}$+1, 20), 326 ($M^{+\cdot}$, 67), 325 ($M^{+\cdot}$-1, 11), 312 (20), 311 (100), 295 (18), 284 (14), 280 (11). Anal. Calc. for $C_{18}H_{22}N_4O_2$: C 66.24, H 6.79, N 17.17. Found C 66.25, H 6.59, N 17.06 %.

2,3-Bis(3,5-dimethyl-1-pyrazolyl)-1-hydroxy-4-methoxybenzene (12). Mp. 166-7 °C. R_f = 0.68 (CH_2Cl_2/EtOH 95:5). IR (KBr, ν cm^{-1}) 2920, 1555, 1500, 1460, 1445, 1385, 1350, 1290, 1275, 1190, 1140, 1100, 1040, 925, 845, 820, 690, 680, 665. MS (m/z, %) 313 ($M^{+\cdot}$+1, 14), 312 ($M^{+\cdot}$, 73), 298 (19), 297 (100), 84 (13), 82 (11). Anal. Calc. for $C_{17}H_{20}N_4O_2$: C 65.37, H 6.45, N 17.94. Found C 65.12, H 6.52, N 18.04 %.

Methylation of 2-(1-imidazolyl)-1,4-dihydroxybenzene (4). The reaction crude was purified by column chromatography (eluent: CH_2Cl_2/EtOH 90:10), 2-(1-imidazolyl)-1,4-dimethoxybenzene (**13**) was obtained in a 10% yield. Mp. 113-5 °C. R_f = 0.88 (CH_2Cl_2/EtOH 90:10). IR (KBr, ν cm^{-1}) 1585, 1505, 1455, 1435, 1400, 1315, 1300, 1270, 1215, 1180, 1150, 1130, 1085, 1040, 1015, 1000, 875, 815, 795, 740, 725, 690, 670. MS (m/z, %) 219 ($M^{+\cdot}$+1, 22), 218 ($M^{+\cdot}$, 100), 203 (32), 191 (11), 176 (26), 163 (11), 161 (48), 119 (11), 79 (14), 77 (10), 68 (11), 55 (17), 50 (12). Anal. Calc. for $C_{12}H_{14}N_2O_2$: C 66.04, H 6.47, N 12.84. Found C 65.95, H 6.37, N 12.81 %.

Methylation of 2,3-bis(1-imidazolyl)-1,4-dihydroxybenzene (5). The reaction crude was purified by column chromatography (eluent: CH_2Cl_2/EtOH 90:10), 2,3-bis(1-imidazolyl)-1,4-

dimethoxybenzene (**14**) was obtained in a 5 % yield. Mp. 205-8 °C. R_f = 0.59 (CH_2Cl_2/EtOH 90:10). IR (KBr, ν cm^{-1}) 2915, 2850, 1525, 1495, 1460, 1325, 1290, 1265, 1235, 1195, 1180, 1135, 1120, 1075, 1015, 985, 820, 800, 765, 735, 710, 680, 655, 625. MS (m/z, %) 298 ($M^{+\cdot}$, 46), 297 ($M^{+\cdot}$-1, 18), 284 (15), 283 (100), 268 (10), 267 (13), 253 (44), 226 (10), 201 (19), 104 (11), 93 (12), 79 (11), 78 (16), 77 (15), 76 (12), 69 (11), 66 (10), 65 (12), 64 (14), 55 (12), 54 (16), 53 (11), 52 (16). Anal. Calc. for $C_{16}H_{18}N_4O_2$: C 64.41, H 6.08, N 18.78. Found C 64.44, H 6.21, N 18.83 %.

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References and Notes

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