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Novel Synthetic Strategy towards the Efficient Synthesis of Substituted Bis(pyrazolyl)(2-pyridyl)methane Ligands

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Dedicated to Professor Dr. Dr. h. c. Karsten Krohn on the occasion of his retirement

Keywords: N ligands / Ligand design / Heteroscorpionate ligands / Structure elucidation

A general one-pot synthesis of new substituted heteroscorpionate ligands is presented. These mixed-functionality ligands were obtained in a catalyzed Peterson rearrangement starting from the substituted pyrazole, thionyl chloride, and an aldehyde. Thus, the synthesis of polyfunctional tridentate ligands is enabled, and they contain, besides the two pyrazole groups, other functionalities relevant for coordination chemistry. Additionally, the steric hindrance is easily defined in the ligands by the substitution of the pyrazole rings. By combination of the versatility in donor function and steric demand, a systematic tuning of the properties of the bis(pyrazolyl)methane ligands is possible. The synthesis and full characterization of 11 bis(pyrazolyl)methane ligands are reported. Two of these were structurally characterized as well.

Introduction

The synthesis of bis(pyrazolyl)methanes and their application in coordination chemistry and bioinorganic and organometallic chemistry have been investigated for decades.[1,2] They convince by their good donor properties, which are tunable by their substitution patterns, and they show biomimetic character as a result of their resemblance to the ubiquitously occurring histidine unit. A great disadvantage is their difficult synthetic access, which limits their general use in comparison to the related poly(pyrazolyl)borates.

Tris(pyrazolyl)methanes can be obtained by reaction of chloroform with pyrazole and Na_2CO_3.[3,4] In contrast to this, bis(pyrazolyl)methanes have to be synthesized by more complicated reactions: The synthesis of the simplest bis(pyrazolyl)methane $H_2C(pz)_2$ was first reported by Trofimenko as a reaction of pyrazole (Hpz) with CH_2Cl_2 in an autoclave at 150 °C.[5] Heteroscorpionate ligands derived from bis(pyrazolyl)methane have been prepared generally by two different methods: The first route starts from the preparation of the *N*,*N*′-methylenebis(pyrazolyl) system and subsequent introduction of the third coordinating moiety at the methylene bridge.[1,2,6,7] The second route involves the reaction of two pyrazolyl rings with a reagent carrying the third coordinating moiety.[1,2,8–14] For example, the reaction of an N,N,O-heteroscorpionate bearing a 2-hydroxyphenyl group occurs through reaction of 1,1′-carbonylbis(pyrazole) with salicylaldehyde.[14]

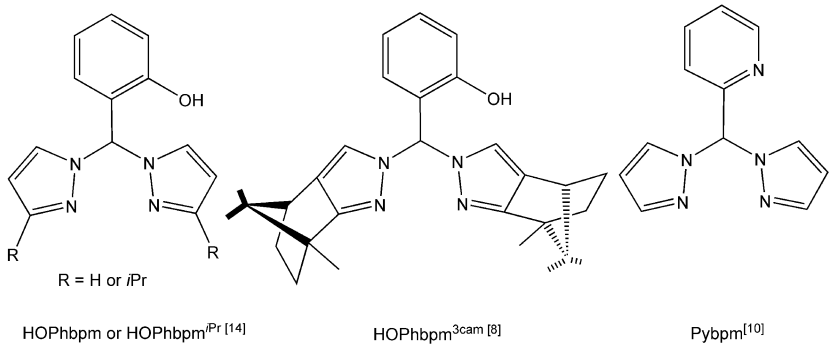

Figure 1. Classical members of the bis(pyrazolyl)methane family.

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In this way, polyfunctional tridentate ligands containing two substituted pyrazolyl groups were synthesized that also incorporate other coordinationally relevant groups like phenols or pyridines (Figure 1). Thiols or carboxylates are also possible.

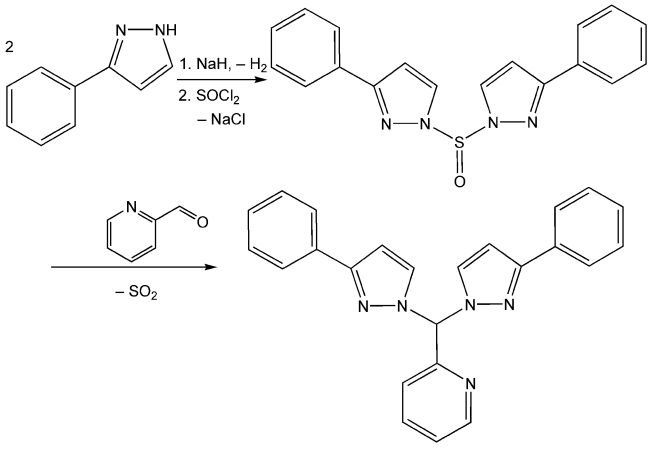
In spite of these intense efforts, an efficient generally applicable route to substituted bis(pyrazolyl)methanes is lacking. Some substituted bis(pyrazolyl)methanes have been reported,[12–14] but the synthetic parameters had to be optimized for each case in a time-consuming process. In this paper, we report on the synthesis and characterization of 11 new bis(pyrazolyl)methane ligands and describe a general and efficient one-pot synthesis for heteroscorpionate ligands with substituted pyrazoles.

Results and Discussion

Ligand Synthesis

The syntheses of heteroscorpionate ligands from bis(pyrazolyl)methanes and phenols or substituted phenols are known,[14–16] but, in these syntheses phosgene is used or the yields are moderate. Carrano et al.[13,14] have also synthesized bis(pyrazolyl)methanes of substituted pyrazoles with phenol as a third ligand, but the synthetic conditions must be varied for each substituted pyrazole or the reaction takes a long time (more than 24 h). Additionally, the aldehyde has to be added in great excess, which has to be removed after the reaction. Burzlaff et al.[8] published in 2009 a synthesis of an enantiopure N,N,O scorpionate ligand with camphorpyrazole and thionyl chloride on the basis of the results originally reported by Reger et al.[12,17] This method is based on a modified Peterson rearrangement during the reaction of aldehydes and 1,1′-sulfinylbis(pyrazole).

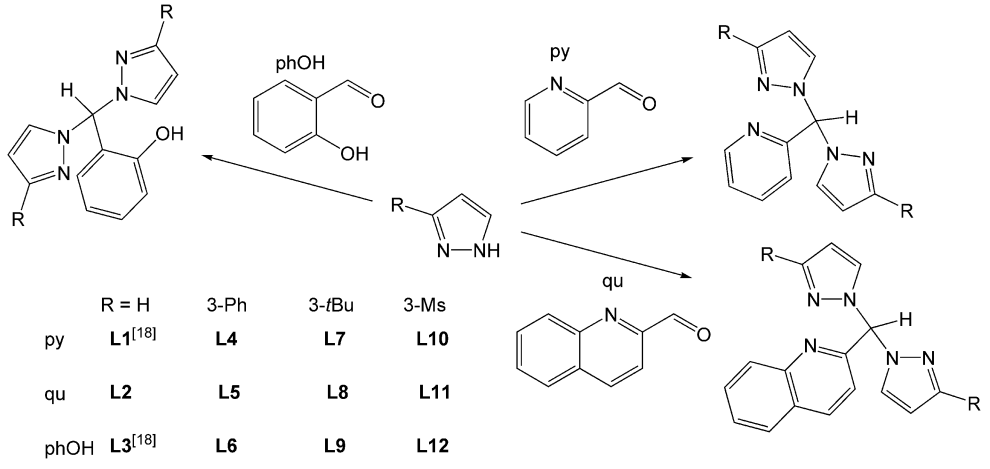
Herein we present a one-pot synthesis of bis(pyrazolyl)-methanes. A general synthetic strategy for bis(pyrazolyl)-methanes with pyridine as the third ligand and substituted pyrazoles is reported for the first time. The ligands were synthesized by following a general procedure that allows the modified Peterson reaction of substituted pyrazoles with an aldehyde to form the desired bis(pyrazolyl)methane ligand. This one-pot synthesis involves the reaction of the pyrazole with NaH and $SOCl_2$ and then with the desired third ligand. At first, the sulfoxide compound is formed in situ. Without any further purification, the sulfoxide compound reacts with the aldehyde to form the desired ligand and SO_2, whereat cobalt(II) chloride acts as catalyst. We have found that the use of thionyl chloride instead of phosgene in this step provides a more efficient route with yields up to 90%. Considering the green aspects of this chemistry, this method is favorable over the use of phosgene. Scheme 1 shows the reaction by using the example of pyridine-2-carbaldehyde and 3-phenylpyrazole (3-Phpz).



Scheme 1. Synthesis of **L4**.

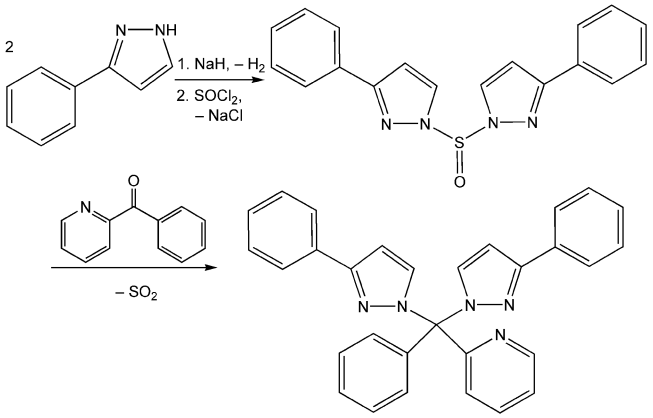
In this report, pyridine-2-carbaldehyde, quinoline-2-carbaldehyde, salicylaldehyde, and benzoyl pyridine are used as the aldehyde component and 3-phenylpyrazole (3-Phpz), 3-*tert*-butylpyrazole (3-*t*Bupz), and 3-mesitylpyrazole (3-Mspz) are used as substituted pyrazoles. The reaction succeeded with all mentioned aldehydes and yielded the following new ligands in good yields (Scheme 2).

Reger et al.[12,19] applied this condensation chemistry to ketones. In our studies, we found that only 3-Phpz of the substituted pyrazoles reacts with the ketone benzoyl pyr-



Scheme 2. Overview of the synthesized ligands.[18]

idine to new ligand **L13** (Scheme 3). Remarkably, the reaction of this ketone with the two other substituted pyrazoles (3-*t*Bupz and 3-Mspz) does not occur because the sterically demanding groups (*tert*-butyl and mesityl) probably hinder the reaction.



Scheme 3. Synthesis of **L13**.

This synthesis protocol allows systematic tuning of the properties of the bis(pyrazolyl)methane ligands. By combining the different substituted pyrazoles with the third ligand (e.g., pyridine, quinoline, thiol, phenol, etc.), a library of bis(pyrazolyl)ligands could be built up. By the thionyl chloride method, a multitude of bis(pyrazolyl)methane ligands with substituted pyrazoles is easily accessible.

NMR Spectroscopy

The chemical shifts of the C_{apical}–H atom are listed in Table 1.[20] In ligands with pyridine as the third coordinating moiety, the peak of the C_{apical}–H atom appears at higher field than in ligands with quinoline as a third coordinating moiety. According to that, the electron density at the C_{apical}–H atom in ligands with pyridine as the third ligand is higher. Surprisingly, the position of the C_{apical}–H signals of the ligands with pyrazolyl and with phenylpyrazolyl as the pyrazolyl moiety is similar. Also, the signals of the ligands with *tert*-butylpyrazolyl and mesitylpyrazolyl are similar. The shifts of the ligands with phenol as the third ligand show no consistent trend. Upon closer inspection of the C_{apical}–H signal of the different substituted pyrazoles, the following trends can be derived: The HC(3-Phpz)$_2$(x) ligands show the C_{apical}–H shift at the lowest field. The signals of the unsubstituted pyrazolyl ligands appear at higher field. The ligands with more demanding substituents like mesityl or *tert*-butyl show the signal at even higher field.

Table 1. ^{1}H NMR spectroscopic shifts of the C_{apical}–H atom in $CDCl_3$.[20]

	δ [ppm]		
	x = py	x = qu	x = phOH
HC(pz)$_2$(x)	7.74	7.90	7.57
HC(3-Phpz)$_2$(x)	7.79	7.97	7.87
HC(3-*t*Bupz)$_2$(x)	7.32	7.50	7.39
HC(3-Mspz)$_2$(x)	7.32	7.45	7.68

Crystal Structure

To discuss the structural features of the diverse ligands, we chose two crystal structures for a closer look: The structure of **L4** exhibits properties typical of heteroscorpionate ligands with pyridine as the third ligand, whereas **L6** has a phenol as the third ligand. Single crystals of **L4** were obtained by slow crystallization of a saturated methanol/acetonitrile solution over a few days and those of **L6** where obtained from a saturated methanol solution. The results of the structure analyses are shown in Figures 2 and 3, and selected bond lengths and angles are collected in Table 2; parameters related to data collection and refinement are listed in Table 3.

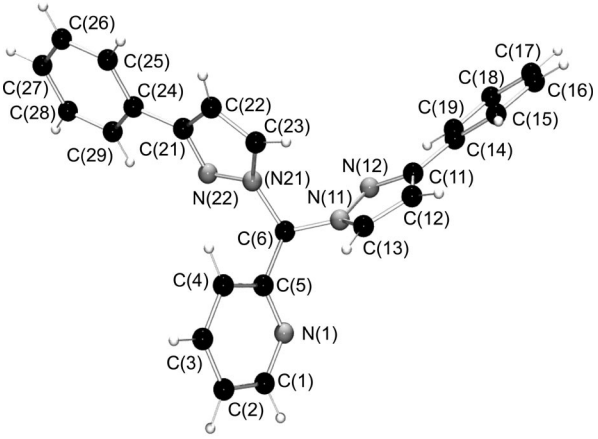


Figure 2. Molecular structure of **L4**.

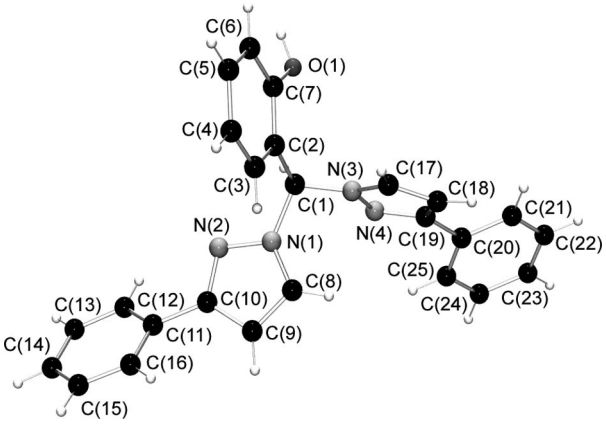


Figure 3. Molecular structure of **L6**.

The characteristic bond lengths and angles of both structures are virtually the same. The selected bond lengths and angles are in good agreement with comparable molecules, for example, the bond lengths and angles of **L4** do not differ significantly from those in bis(indazol-1-yl)pyridin-2′-ylmethane [C_{ap}–N_{pz} 1.444(3)/1.452(3) Å; C_{ap}–C_{arom} 1.524(3) Å; N_{pz}–C_{ap}–C_{arom} 112.3(2)/113.8(2)°; N_{pz}–C_{ap}–N_{pz} 112.2(2)°].[21] Also, the characteristic parameters of **L6** do not differ from those of heteroscorpionate ligands with phenol or substituted phenol as the third ligand: C_{ap}–N_{pz} 1.466/1.467 Å[11] or 1.462(8)/1.463(7) Å[14] or 1.465/

Table 2. Selected bond lengths and angles of the molecules in crystals of **L4** and **L6** and comparison to DFT calculated values.

	L4	DFT[a]	**L6**	DFT[a]
Bond lengths [Å]				
C_{ap}–N_{pz}	1.444(2)	1.454	1.443(5)	1.449
	1.464(2)	1.466	1.467(5)	1.465
N_{pz}–N_{pz}	1.362(2)	1.352	1.360(4)	1.353
	1.361(2)	1.348	1.363(4)	1.349
C_{ap}–C_{arom}	1.513(2)	1.521	1.528(5)	1.528
Bond angles [°]				
N_{pz}–C_{ap}–N_{pz}	108.7(2)	109.7	107.2(3)	110.2
N_{pz}–C_{ap}–C_{arom}	111.8(2)	111.8	112.4(3)	112.7
	112.5(2)	112.6	110.3(4)	111.4
Twist angles [°]				
Phenyl vs. pyrazolyl	11.2	2.5	36.0	0.3
	1.3	0.5	37.4	3.8
Pyrazolyl vs. pyrazolyl	83.6	89.9	88.9	89.3
Third ligand vs. pyrazolyl	86.6	80.3	81.0	84.8
	87.3	88.6	77.3	87.9

[a] Gaussian03, B3LYP/6-31g(d).

Table 3. Crystallographic data for **L4** and **L6**.

	L4	**L6**
Molecular Mass	377.44	392.45
Empirical formula	$C_{24}H_{19}N_5$	$C_{25}H_{20}N_4O$
Molecular Mass	377.44	392.45
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	13.7336(11)	8.8020(10)
b [Å]	5.5628(4)	10.6835(13)
c [Å]	25.362(2)	11.2411(14)
α [°]		75.394(3)
β [°]	104.509(9)	76.988(3)
γ [°]		87.152(3)
V [Å^3]	1875.8(3)	996.2(2)
Z	4	2
$D_{calcd.}$ [g cm^{-3}]	1.337	1.308
$F(000)$	792	412
Temperature [K]	173(1)	120(2)
Θ_{max} [°]	25.50	27.88
Reflections collected	6873	7899
Independent reflections	3491	4724
R_1 [$I \geq 2\sigma(I)$]	0.0348	0.0524
wR_2 (all data)	0.0551	0.1246
Largest diff. peak/hole [e Å^{-3}]	0.160/–0.201	0.238/–0.237

1.461 Å;[13] C_{ap}–C_{arom} 1.518 Å[11] or 1.515(11) Å[14] or 1.514 Å;[13] N_{pz}–C_{ap}–C_{pz} 110.01°[11] or 109.3(5)°[14] or 111.11°;[13] N_{pz}–C_{ap}–C_{arom} 113.21/116.19°[11] or 112.0(5)/114.2(5)°[14] or 111.62/113.53°.[13]

A closer consideration of the twist angles in the crystal structures reveals interesting features: in **L4**, the phenyl rings of the substituted pyrazolyl functions are nearly in plane with the pyrazolyl rings (11.2/1.3°) and thus less twisted against the pyrazolyl rings than in **L6** (36.0/37.4°). The fact that the phenyl and pyrazolyl rings are in plane results from π stacking of the molecules. It is apparent from the unit cell that pairs of molecules orientate one of their phenyl-pyrazolyl units in the opposite direction to each other such that π interactions between the aromatic systems of two of these units can occur (Figure 4). The distance of these planes is calculated to be 3.732 Å. In **L6**, an intermolecular hydrogen-bond interaction between the phenol H atom to the pyrazole N atom of another molecule is present. The distance between the N atom and the H atom is 1.985(11) Å and is in accordance with other N···H hydrogen bonds.[22,23]

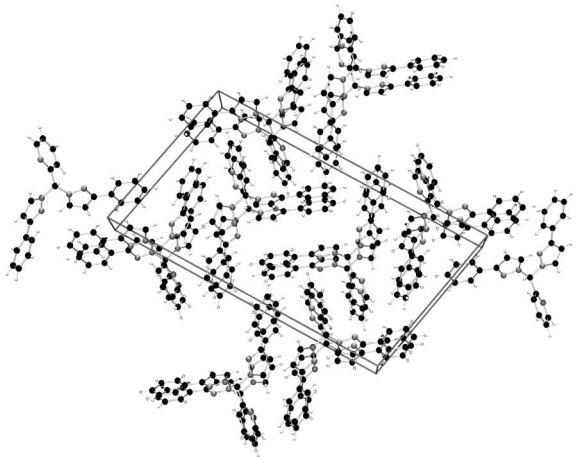


Figure 4. Crystal packing of **L4**.

Guided by the idea that the twist between the pyrazolyl rings and the phenyl rings is crucial for intermolecular packing, we performed gas-phase DFT calculations on the structural properties of **L4** and **L6** (Table 2). These calculations reproduce the bond lengths and angles very well, but the predicted twist between the pyrazolyl and the phenyl rings for both ligands is too small. The energy difference between the DFT-optimized structures and the twisted structures found in the solid state is 0.02 kcal/mol for **L4** and 0.33 kcal/mol for **L6**. These energy differences are below the range of the accuracy of DFT calculations at that theoretical level. Hence, the potential energy surface is relatively flat for the twist between the pyrazolyl and phenyl rings such that the twist is highly influenced by packing effects and normally occurring weak intermolecular interactions like H bonds.

Conclusions

In summary, we report on an efficient method for the general synthesis of substituted bis(pyrazolyl)methanes. This method makes use of thionyl chloride instead of phosgene and allows the combination of various substituted pyrazoles with different aldehydes. By connecting different substituted pyrazoles with the third ligand function, a library of bis(pyrazolyl)methane ligands could be built up. This advantageous synthetic protocol enables systematic tuning of the properties of the bis(pyrazolyl)methane ligands and has been optimized towards overall yields in the range of 55–95%. Furthermore, two ligands were structurally characterized and an interesting packing effect was identified.

Experimental Section

Materials and Methods: All manipulations involving air- and moisture-sensitive compounds were carried out by using standard Schlenk techniques. The solvents were purchased from commercial sources. THF was freshly distilled from sodium/potassium and benzophenone prior to use. Sodium hydride (95%, Sigma Aldrich), thionyl chloride (Fluka), pyridine-2-carbaldehyde (99%, Alfa Aesar), quinoline-2-carbaldehyde (97%, Alfa Aesar), salicylaldehyde (99%, Alfa Aesar), benzoyl aldehyde (99%, Alfa Aesar), pyrazole (98%, Alfa Aesar), and anhydrous $CoCl_2$ (98%, Aldrich) were used as purchased. The substituted pyrazoles were synthesized according to published procedures: 3-Phpz,[24] 3-*t*Bupz,[24] and 3-Mspz.[25]

Physical Measurements: NMR spectra were recorded with a Bruker Avance 500 spectrometer. The NMR signals were calibrated to the residual signals of the deuterated solvents ($CDCl_3$ δ_H = 7.26 ppm). These assignments were confirmed by standard Bruker gradient enhanced HMBC, HMQC, SELTOCSY, and INAPT pulse sequences. IR spectra were recorded with a Nicolet P510. Mass spectra in the EI (70 eV) and ESI modes were recorded with a Finnigan MAT 40 and a Finnigan TSQ instrument, respectively. Elemental analyses were recorded with a Perkin–Elmer analyzer Model 2400.

Crystal Structure Analyses: Crystal data for compounds **L4** and **L6** are presented in Tables 2 and 3. Data for **L4** was collected with an Xcalibur S Diffractometer from Oxford Diffraction with graphite-monochromated Mo-K_α radiation. The data collection covered almost the whole sphere of reciprocal space with 8 sets at different κ-angles and 430 frames with ω-rotation (Δ/ω = 1°) at two times 60 s per frame. The crystal-to-detector distance was 4.5 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections showed that there was no indication for any decay. The structure was solved by direct methods with SHELXS97[26] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL97.[27] The hydrogen atoms were placed in geometrically calculated positions using a riding model with U_{iso} constrained 1.2 times U_{eq} for the carrier atom. Atomic scattering factors for neutral atoms and real imaginary were taken from International Tables for X-ray Crystallography.[28] The figure was created by SHELXTL.[29] Data for **L6** was collected with a Bruker-AXS SMART[30] APEX CCD by using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction was performed with SAINT and SADABS.[30] The structure was solved by direct and conventional Fourier methods and all non-hydrogen atoms refined anisotropically with full-matrix least-squares based on F^2 (SHELXTL[30]). Hydrogen atoms were derived from difference Fourier maps and placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C methyl). All methyl groups were allowed to rotate but not to tip.

CCDC-765253 (for **L4**) -762957 (for **L6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Density functional theory (DFT) calculations were performed with the program suite Gaussian 03.[31] The geometries of **L4** and **L6** were optimized (Table 2) by using the B3LYP[32] hybrid DFT functional and the 6-31g(d) basis sets implemented in Gaussian on all atoms. Tight conversion criteria were applied. The starting geometries were generated from the crystal structures. Frequency calculations confirmed the stationary points to be minima. Electronic energies for gas-phase-optimized structures of **L4**, **L6**, and their counterparts with fixed angles were computed by using the B3LYP functional and a 6-311+g(d) basis set.

General Synthesis of Heteroscorpionate Ligands L1–L12: NaH (2.4 g, 100 mmol) was suspended in freshly distilled THF (100 mL) and stirred at 0 °C. The relevant pyrazole (100 mmol) was added gradually to the suspension over 15 min and the stirring was continued at 0 °C until gas evolution stopped (ca. 30 min.). Then, thionyl chloride (3.7 mL, 50 mmol) was added dropwise to this pale-colored solution at 0 °C. After stirring for additional 45 min at 0 °C and then 30 min at room temperature, the desired aldehyde (50 mmol) and a catalytic amount of cobalt(II) chloride were added, and the reaction mixture was heated under vigorous stirring at reflux overnight. During this time period the mixture turned intensely colored and evolution of SO_2 was observed. Some ligands were carefully heated because the mixture can develop foam in great amounts. The reaction mixture was allowed to cool to room temperature before diethyl ether (50 mL) and water (100 mL) were gradually added. The biphasic solution was then stirred for 1 h. The layers were separated, and the aqueous phase was extracted with diethyl ether (3 × 60 mL). The combined organic phase was washed with distilled water, dried with sodium sulfate and filtered. The solvent was then removed in vacuo, and the resulting solid was suspended in hexane. This flask was placed in an ultrasound bath to break up the lumps that had formed, yielding a solid. This solid was collected by filtration, washed efficient with hexane and dried in vacuo.

(2-Pyridinyl)bis(pyrazolyl)methane $(pz)_2(py)CH$ (L1):[18] Following the general synthesis, pyrazole (6.8 g, 100 mmol) and pyridine-2-carbaldehyde (4.8 mL, 50 mmol) were used. The final product was obtained as yellow-orange solid (10.6 g, 95%). M.p. 56 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.34 [t, $J_{H,H}$ = 2.1 Hz, 2 H, 4-H (pz)], 7.05 [d, $J_{H,H}$ = 7.6 Hz, 1 H, 3-H (py)], 7.29 [dd, $J_{H,H}$ = 4.8, 7.6 Hz, 1 H, 5-H (py)], 7.63 [d, $J_{H,H}$ = 1.6 Hz, 2 H, 5-H (pz)], 7.64 [d, $J_{H,H}$ = 2.2 Hz, 2 H, 3-H (pz)], 7.72 [t, $J_{H,H}$ = 7.7 Hz, 1 H, 4-H (py)], 7.74 (s, 1 H, CH), 8.64 [d, $J_{H,H}$ = 1.6, 4.7 Hz, 1 H, 3-H (py)] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 78.5 [$C(pz)_2(py)$], 106.7 [4-C(pz)], 122.2 [3-C(py)], 123.9 [5-C(py)], 129.9 [5-C(pz)], 137.2 [4-C(py)], 140.8 [3-C (pz)], 149.7 [6-C(py)], 154.8 [2-C(py)] ppm. IR (KBr): $\tilde{\nu}$ = 3139 (w), 3110 (w, ν_{CH}), 3054 (vw, ν_{CH}), 3012 (vw, ν_{CH}), 2960 (vw, ν_{CH}), 2717 (vw), 2678 (vw), 2601 (vw), 2547 (vw), 1972 (vw), 1778 (vw), 1731 (vw), 1646 (w), 1589 (m), 1572 (w), 1508 (m), 1477 (w), 1465 (w), 1454 (vw), 1430 (s), 1390 (vs). 1363 (w), 1346 (w), 1321 (m), 1298 (m), 1286 (m), 1261 (w), 1241 (vw), 1216 (w), 1191 (w), 1172 (vw), 1149 (vw), 1085 (s), 1057 (m), 1045 (m), 997 (w), 974 (w), 964 (w), 916 (w), 896 (vw), 873 (m), 840 (w), 813 (m), 804 (m), 786 (s), 773 (s), 752 (vs, ν_{CH}), 734 (m), 678 (w), 647 (m), 620 (w), 608 (w), 493 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 225.1 (40) [$M^+ = C_{12}H_{11}N_5$], 159.1 (18), 158.1 (100) [$C_9H_8N_3^+$], 147.1 (82) [$C_7H_7N_4^+$], 131.1 (38), 118.1 (16), 79.1 (8), 78.1 (29) [$C_5H_4N^+$], 67.1 (5) [$C_3H_3N_2^+$]. $C_{12}H_{11}N_5$ (225.1): calcd. C 63.99, H 4.92, N 31.09; found C 64.03, H 4.96, N 30.90.

(2-Quinolinyl)bis(pyrazolyl)methane $(pz)_2(qu)CH$ (L2): Following the general synthesis, pyrazole (6.8 g, 100 mmol) and quinoline-2-carbaldehyde (7.9 g, 50 mmol) were used. The final product was obtained as a dark-orange solid (11.7 g, 85%). M.p. 78 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.36 [t, $J_{H,H}$ = 2.2 Hz, 2 H, 4-H (pz)], 7.29 [d, $J_{H,H}$ = 7.5 Hz, 1 H, 3-H (qu)], 7.56 [t, $J_{H,H}$ = 7.4 Hz, 1 H, 7-H(qu)], 7.64 [d, $J_{H,H}$ = 1.8 Hz, 2 H, 3-H (pz)], 7.70 [d, $J_{H,H}$ = 2.5 Hz, 1 H, 5-H (pz)], 7.72 [m, 1 H, 8-H(qu)], 7.82 [d, $J_{H,H}$ = 8.2 Hz, 1 H, 6-H(qu)], 7.90 (s, 1 H, CH), 8.07 [d, $J_{H,H}$ = 7.6 Hz, 1 H, 9-H(qu)], 8.19 [d, $J_{H,H}$ = 8.5 Hz, 1 H, 4-H(qu)] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 79.1 [$C(pz)_2(qu)$], 106.6

[4-C(pz)], 119.5 [3-C(qu)], 127.4 [7-C(qu)], 127.5 [6-C(qu)], 127.8 [5-C(qu)], 129.7 [9-C(qu)], 130.0 [8-C(qu)], 130.1 [5C(pz)], 137.4 [4-C(qu)], 140.9 [3-C(pz)], 147.5 [10-C(qu)], 154.5 [2-C(qu)] ppm. IR (KBr): $\tilde{\nu}$ = 3131 (w), 3114 (w, ν_{CH}), 3068 (vw, ν_{CH}), 3019 (vw, ν_{CH}), 2992 (vw, ν_{CH}), 2655 (vw), 2362 (vw), 2138 (vw), 1978 (vw), 1949 (vw), 1864 (vw), 1833 (vw), 1737 (vw), 1712 (vw), 1617 (w, ν_{CN}), 1589 (m, ν_{CN}), 1560 (vw), 1538 (vw), 1504 (s), 1459 (vw), 1438 (w), 1428 (m), 1394 (s), 1374 (m), 1347 (m), 1329 (vw), 1314 (m), 1305 (s), 1299 (s), 1260 (w), 1213 (m), 1189 (w), 1170 (w), 1155 (vw), 1139 (vw), 1122 (w), 1108 (vw), 1087 (s), 1059 (m), 1049 (m), 1014 (vw), 991 (vw), 973 (m), 961 (w), 954 (w), 920 (w), 902 (m), 880 (w), 856 (w), 846 (w), 819 (s, ν_{CH}), 797 (s), 792 (s), 781 (s), 769 (vs, ν_{CH}), 745 (s), 666 (w), 651 (w), 626 (m), 619 (m), 585 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 275.1 (66) [$M^+ = C_{16}H_{13}N_5^+$], 274.1 (14) [$M^+ - H$], 209.1 (22), 208.1 (100), [$M^+ - C_3H_3N_2$], 207.1 (16), 181.1 (39), 168.1 (8), 154.1 (7), 147.1 (44) [$C_7H_7N_4^+$], 129.1 (24), 128.1 (22) [$C_9H_6N^+$], 101.1 (7), 77.0 (7), 67.0 (3) [$C_3H_3N_2^+$]. $C_{16}H_{13}N_5$ (275.1): calcd. C 69.80, H 4.76, N 25.44; found C 69.43, H 4.87, N 25.37.

(2-Hydroxyphenyl)bis(pyrazolyl)methane (pz)$_2$(phOH)CH (L3):[18] Following the general synthesis, pyrazole (6.8 g, 100 mmol) and salicylaldehyde (5.3 mL, 50 mmol) were used. The final product was obtained as yellow-orange solid (22.1 g, 91%). M.p. 140 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 6.32 [t, $J_{H,H}$ = 2.6 Hz, 2 H, 4-H (pz)], 6.89 [t, $J_{H,H}$ = 7.5 Hz, 1 H, 4-H (phOH)], 6.98 [d, $J_{H,H}$ = 8.5 Hz, 1 H, 6-H (phOH)], 7.11 [d, $J_{H,H}$ = 7.5 Hz, 1 H, 3-H (phOH)], 7.28 [t, $J_{H,H}$ = 8.5 Hz, 3 H, 5-H (phOH)], 7.56 [d, $J_{H,H}$ = 1.4 Hz, 2 H, 3-H (pz)], 7.67 [d, $J_{H,H}$ = 2.6 Hz, 2 H, 2-H (pz)], 7.99 (s, 1 H, CH), 9.65 [br., 1 H (phOH)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 74.3 [C(pz)$_2$(phOH)], 105.5 [4-C (pz)], 116.4 [6-C (phOH)], 119.6 [4-C (phOH)], 122.7 [3-C (phOH)], 129.0 [3-C (phOH)], 129.6 [5-C(pz)], 130.7 [5-C(phOH)], 139.8 [3-C (pz)], 154.9 [1-C (phOH)] ppm. IR (KBr): $\tilde{\nu}$ = 3145 (vw, $\nu_{CH_{arom}}$), 3126 (vw, $\nu_{CH_{arom}}$), 3110 (vw, $\nu_{CH_{arom}}$), 3097 (vw, $\nu_{CH_{arom}}$), 2958 (vw, $\nu_{CH_{aliph}}$), 2865 (vw, $\nu_{CH_{aliph}}$), 2721 (w), 2695 (w), 2591 (w), 2460 (w), 1608 (m), 1506 (m), 1461 (vs), 1434 (w), 1401 (s), 1367 (w), 1349 (m), 1320 (m), 1307 (s), 1295 (s), 1267 (m), 1243 (w), 1233 (w), 1223 (w), 1201 (w), 1180 (w), 1159 (vw), 1104 (w), 1087 (s), 1056 (s), 1044 (m), 979 (w), 963 (vw), 916 (vw), 873 (s), 866 (m), 813 (w), 798 (m), 776 (m), 759 (vs), 751 (vs), 661 (vw), 653 (vw), 626 (m), 607 (vw), 548 (vw), 538 (vw), 466 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 240.1 (13) [$M^+ = C_{13}H_{12}N_4O^+$], 173.1 (18) [$M^+ - C_3H_3N_2$], 172.1 (100), 171.1 (6), 167.1 (6), 146.1 (6) [$C_7H_6N_4^+$], 145.1 (62), 144.1 (19), 143.1 (5), 119.1 (9), 118.1 (12), 117.1 (6), 105.1 (5), 92.1 (5) [$C_5H_5O^+$], 91.1 (7), 90.1 (3), 77.1 (8), 68.1 (11) [$C_3H_4N_2^+$]. $C_{13}H_{12}N_4O$ (240.1): calcd. C 64.99, H 5.03, N 23.32; found C 64.59, H 5.08, N 23.27.

(2-Pyridinyl)bis(3-phenylpyrazolyl)methane (3-Phpz)$_2$(py)CH (L4): Following the general synthesis, 3-phenylpyrazole (14.4 g, 100 mmol) and pyridine-2-carbaldehyde (4.8 mL, 50 mmol) were used. The final product was obtained as pale-brown solid (12.7 g, 74%). M.p. 160 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 6.83 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 4-H (3-Phpz)], 7.32 [t, $J_{H,H}$ = 7.4 Hz, 2 H, *p*-H (3-Phpz)], 7.39 [m, 4 H, *o*-H (3-Phpz)], 7.42 [m, 5 H, 3-H (py)], 7.45 [dd, $J_{H,H}$ = 4.5, 7.4 Hz, 1 H, 5-H (py)], 7.87 [d, $J_{H,H}$ = 8.6 Hz, 4 H, *o*-H (3-Phpz)], 7.90 [t, $J_{H,H}$ = 7.8 Hz, 1 H, 4-H (py)], 7.96 (s, 1 H, CH), 7.99 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 5-H (3-Phpz)], 8.65 [dd, $J_{H,H}$ = 1.7, 4.6 Hz, 1 H, 6-H (py)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 78.8 [C(3-Phpz)$_2$(py)], 103.5 [4-C (3-Phpz)], 122.4 [3-C (py)], 124.0 [5-C (py)], 125.5 [*o*-C(3-Phpz)], 127.7 [*p*-C(3-Phpz)], 128.5 [*m*-C(3-Phpz)], 131.8 [5-C (3-Phpz)], 133.3 [C_{ph} (3-Phpz)], 137.2 [4-C (py)], 149.4 [6-C (py)], 152.0 [C_{pz} (3-Phpz)], 155.1 [2-C (py)] ppm. IR (KBr): $\tilde{\nu}$ = 3149 (vw, $\nu_{CH_{arom}}$), 3089 (vw, $\nu_{CH_{arom}}$), 3058 (w, $\nu_{CH_{arom}}$), 3031 (vw, $\nu_{CH_{arom}}$), 2923 (vw, $\nu_{CH_{aliph}}$), 1953 (vw), 1889 (vw), 1810 (vw), 1772 (vw), 1754 (vw), 1700 (vw), 1652 (vw), 1585 (w), 1560 (vw), 1529 (vw), 1498 (m), 1455 (m), 1432 (w), 1382 (vw), 1355 (w), 1323 (vw), 1301 (vw), 1270 (vw), 1205 (m), 1151 (vw), 1099 (w), 1074 (m), 1049 (m), 1026 (vw), 1011 (vw), 993 (vw), 948 (vw), 937 (vw), 916 (vw), 898 (vw), 869 (w), 750 (vs), 694 (vs), 657 (vw), 619 (vw), 505 (vw), 468 (vw), 444 (vw), 428 (vw), 416 (vw), 408 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 377.1 (3) [$M^+ = C_{24}H_{19}N_5^+$], 279.2 (5), 235.1 (11), 234.1 (16) [$M^+ - C_9H_7N_2$], 167.1 (10), 157.1 (5), 145.1 (9) [$C_7H_5N_4^+$], 144.1 (100), 143.1 (119) [$C_9H_7N_2^+$], 118.1 (39), 117.1 (10), 116.1 (4), 115.1 (14), 113.1 (3), 105.1 (6), 104.1 (3), 92.0 (2), 91.0 (3), 90.0 (7), 89.0 (7), 78.0 (3), [$C_5H_4N^+$], 77.0 (14), 71.1 (5), 70.1 (4), 69.1 (2). $C_{24}H_{19}N_5$ (377.1): calcd. C 76.37, H 5.07, N 18.55; found C 76.07, H 5.00, N 18.17.

(2-Quinolinyl)bis(3-phenylpyrazolyl)methane (3-Phpz)$_2$(qu)CH (L5): Following the general synthesis, 3-phenylpyrazole (14.4 g, 100 mmol) and quinoline-2-carbaldehyde (7.9 g, 50 mmol) were used. The final product was obtained as a brown solid (15.7 g, 73%). M.p. 122 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 6.83 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-Phpz)], 7.29 [t, $J_{H,H}$ = 7.3 Hz, 2 H, *p*-H (3-Phpz)], 7.36 [t, $J_{H,H}$ = 7.5 Hz, 4 H, *m*-H (3-Phpz)], 7.53 [d, $J_{H,H}$ = 8.7 Hz, 1 H, 3-H (qu)], 7.61 [t, $J_{H,H}$ = 7.6 Hz, 1 H, 7-H(qu)], 7.77 [t, $J_{H,H}$ = 7.5 Hz, 1 H, 8-H(qu)], 7.84 [d, $J_{H,H}$ = 7.3 Hz, 4 H, *o*-H (3-Phpz)], 7.97 [m, 1 H, 6H(qu)], 8.02 [d, $J_{H,H}$ = 8.5 Hz, 1 H, 9-H(qu)], 8.07 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 5-H (3-Phpz)], 8.13 (s, 1 H, CH), 8.40 [d, $J_{H,H}$ = 8.4 Hz, 1 H, 4-H(qu)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 80.0 [C(3-Phpz)$_2$(qu)], 104.5 [4-C (3-Phpz)], 120.7 [3-C (qu)], 126.4 [*o*-C(3-Phpz)], 128.2 [7-C(qu)], 128.6 [*p*-C(3-Phpz)], 128.7 [6-C(qu)], 128.7 [5-C(qu)], 129.3 [*m*-C(3-Phpz)], 130.2 [9-C(qu)], 130.9 [8-C(qu)], 132.9 [5-C (3-Phpz)], 134.2 [C_{ph} (3-Phpz)], 138.2 [4-C(qu)], 148.2 [10-C(qu)], 153.0 [C_{pz} (3-Phpz)], 156.0 [2-C (py)] ppm. IR (KBr): $\tilde{\nu}$ = 3106 (vw, $\nu_{CH_{arom}}$), 3058 (vw, $\nu_{CH_{arom}}$), 3001 (vw, $\nu_{CH_{arom}}$), 2956 (vw, $\nu_{CH_{aliph}}$), 2925 (vw, $\nu_{CH_{aliph}}$), 1955 (vw), 1617 (vw), 1594 (w), 1563 (vw), 1527 (vw), 1500 (vs), 1455 (s), 1428 (vw), 1415 (vw), 1400 (vw), 1378 (vw), 1355 (w), 1340 (vw), 1326 (vw), 1303 (w), 1281 (vw), 1236 (m), 1213 (w), 1176 (vw), 1151 (vw), 1141 (vw), 1118 (vw), 1099 (vw), 1074 (m), 1049 (w), 1027 (vw), 1015 (vw), 998 (vw), 946 (vw), 906 (w), 872 (vw), 852 (vw), 808 (s), 790 (w), 781 (w), 752 (vs), 694 (vs), 667 (vw), 619 (vw), 557 (vw), 522 (vw), 480 (vw), 418 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 427.3 (60) [$M^+ = C_{28}H_{21}N_5^+$], 377.2 (4), 300.3 (3), 299.2 (9) [$M^+ - C_9H_6N$], 288.2 (3), 286.3 (12), 285.2 (82), 284.2 (100) [$M^+ - C_9H_7N_2$], 283.2 (7), 282.2 (4), 281.2 (3), 270.2 (6), 248.2 (10), 247.2 (3), 242.2 (6), 245.2 (9), 244.2 (3), 217.2 (4), 216.2 (2), 182.1 (3), 181.7 (7), 180.1 (2), 167.1 (5), 157.2 (25), 156.1 (5) [$C_{10}H_8N_2^+$], 155.1 (6), 154.1 (4), 144.1 (55), 143.1 (8) [$C_9H_7N_2^+$], 142.1 (7), 130.1 (6), 129.1 (15), 128.1 (39) [$C_9H_6N^+$], 127.1 (4), 119.1 (6), 118.1 (2), 117.1 (6), 116.1 (6), 115.1 (15), 106.1 (3), 105.1 (21), 104.1 (3), 103.1 (6), 102.1 (5), 101.1 (5), 91.1 (3), 90.1 (4), 89.1 (6), 77.1 (25) [$C_6H_5^+$]. $C_{28}H_{21}N_5$ (427.1): calcd. C 78.67, H 4.95, N 16.38; found C 78.47, H 5.00, N 16.07.

(2-Hydroxyphenyl)bis(3-phenylpyrazolyl)methane (3-Phpz)$_2$(phOH)-CH (L6): Following the general synthesis, 3-phenylpyrazole (14.4 g, 100 mmol) and salicylaldehyde (5.3 mL, 50 mmol) were used. The final product was obtained as pale-brown solid (15.1 g, 77%). M.p. 130 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 6.76 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-Phpz)], 6.91 [t, $J_{H,H}$ = 7.4 Hz, 1 H, 4-H (phOH)], 7.01 [dd, $J_{H,H}$ = 1.0, 8.3 Hz, 1 H, 6-H (phOH)], 7.25 [dd, $J_{H,H}$ = 1.5, 8.0 Hz, 1 H, 3-H (phOH)], 7.28 [m, 2 H, *p*-H (3-Phpz)], 7.32 [m, 1 H, 5-H (phOH)], 7.37 [t, $J_{H,H}$ = 7.4 Hz, 4 H, *m*-H (3-Phpz)], 7.77 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 5-H (3-Phpz)], 7.83 [d, $J_{H,H}$ = 8.3 Hz, 4 H, *o*-H (3-Phpz)], 8.04 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 74.6 [C(3-Phpz)$_2$(phOH)], 102.9

[4-C (3-Phpz)], 116.4 [6-C (phOH)], 119.8 [4-C (phOH)], 122.5 [2-C (phOH)], 125.4 [*o*-C(3-Phpz)], 127.7 [*p*-C(3-Phpz)], 128.5 [*m*-C(3-Phpz)], 128.9 [3-C (phOH)], 130.9 [5-C (phOH)], 131.3 [5-C (3-Phpz)], 133.3 [C_{ph} (3-Phpz)], 151.9 [C_{pz} (3-Phpz)], 154.8 [1-C (phOH)] ppm. IR (KBr): $\tilde{\nu}$ = 3131 (vw, $\nu_{CH_{arom}}$), 3106 (vw, $\nu_{CH_{arom}}$), 3064 (vw, $\nu_{CH_{arom}}$), 3029 (vw, $\nu_{CH_{arom}}$), 2960 (vw, $\nu_{CH_{aliph}}$), 2924 (vw, $\nu_{CH_{aliph}}$), 2877 (vw, $\nu_{CH_{aliph}}$), 2832 (vw, $\nu_{CH_{aliph}}$), 2732 (vw), 2605 (vw), 2474 (vw), 1961 (vw), 1886 (vw), 1810 (vw), 1758 (vw), 1704 (vw), 1644 (vw), 1606 (w), 1554 (vw), 1529 (w), 1496 (s), 1463 (s), 1409 (vw), 1398 (w), 1384 (w), 1359 (vw), 1326 (m), 1307 (vw), 1295 (m), 1280 (vw), 1261 (m), 1238 (m), 1213 (m), 1176 (vw), 1160 (vw), 1124 (w), 1097 (m), 1083 (s), 1074 (s), 1056 (s), 1049 (s), 997 (w), 950 (w), 912 (vw), 873 (m), 852 (vw), 813 (w), 788 (m), 775 (m), 759 (vs), 754 (vs), 700 (m), 692 (m), 638 (w), 620 (vw), 549 (vw), 530 (vw), 520 (vw), 476 (vw), 447 (vw), 418 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 392.2 (3) [$M^+ = C_{25}H_{20}N_4O^+$], 250.1 (1), 249.1 (6) [$M^+ - C_9H_7N_2$], 248.1 (26), 247.1 (2), 146.1 (2), 145.1 (28), 144.1 (100) [$C_9H_8N_2^+$], 143.1 (20), 142.1 (1), 118.1 (4), 117.1 (17), 116.1 (8), 115.1 (25), 114.1 (2), 93.1 (19) [$C_6H_5O^+$], 92.1 (2), 91.1 (2), 90.1 (13), 89.1 (11), 88.1 (2), 78.1 (3), 77.1 (20), 76.1 (3). $C_{25}H_{20}N_4O$ (392.1): calcd. C 76.51, H 5.14, N 14.28; found C 76.07, H 5.06, N 14.28.

(2-Pyridinyl)bis(3-*tert*-pyrazolyl)methane (3-*t*Bupz)$_2$(py)CH (L7): Following the general synthesis, 3-*tert*-butylpyrazole (12.4 g, 100 mmol) and pyridine-2-carbaldehyde (4.8 mL, 50 mmol) were used. The final product was obtained as a red waxy solid (10.2 g, 60%). ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 1.26 [s, 18 H, CH_3 (3-*t*Bupz)], 6.22 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-*t*Bupz)], 7.08 [d, $J_{H,H}$ = 7.9 Hz, 1 H, 3-H(py)], 7.32 [t, $J_{H,H}$ = 6.6 Hz, 1 H, 5-H (py)], 7.62 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 5-H (3-*t*Bupz)], 7.66 (s, 1 H, CH), 7.77 [t, $J_{H,H}$ = 7.8 Hz, 1 H, 4-H(py)], 8.56 [d, $J_{H,H}$ = 4.5 Hz, 1 H, 6-H (py)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 30.8 (CH_3, 3-*t*Bupz), 32.6 (C, 3-*t*Bupz), 79.3 [C(3-*t*Bupz)$_2$(py)], 103.2 [4-C (3-*t*Bupz)], 122.8 [3-C (py)], 124.4 [5-C(py)], 130.8 [5-C (3-*t*Bupz)], 137.7 [4-C (py)], 150.0 [6-C (py)], 156.7 [2-C (py)], 162.9 [C_{pz} (3-*t*Bupz)] ppm. IR (KBr) $\tilde{\nu}$ = 3132 (vw, $\nu_{CH_{arom}}$), 3056 (vw, $\nu_{CH_{arom}}$), 2964 (m, $\nu_{CH_{aliph}}$), 2902 (vw, $\nu_{CH_{aliph}}$), 2865 (vw, $\nu_{CH_{aliph}}$), 2821 (vw, $\nu_{CH_{aliph}}$), 1714 (vw), 1650 (vw), 1590 (w), 1574 (vw), 1521 (m), 1463 (w), 1436 (w), 1404 (vw), 1385 (vw), 1361 (m), 1328 (w), 1309 (vw), 1247 (s), 1207 (w), 1187 (vw), 1159 (w), 1095 (vw), 1054 (s), 1026 (vw), 1015 (vw), 993 (w), 979 (vw), 927 (vw), 895 (vw), 869 (w), 854 (vw), 844 (vw), 828 (vw), 808 (m), 786 (w), 758 (vs), 725 (w), 700 (vw), 669 (w), 652 (vw), 624 (vw), 612 (vw), 592 (vw), 501 (vw), 489 (vw), 443 (vw), 401 (w) cm^{-1}. MS (EI): *m*/*z* (%) = 337.3 (33) [$M^+ = C_{20}H_{27}N_5^+$], 259.3 (25) [$M^+ - C_5H_4N$], 215.2 (22), 214.2 (100) [$M^+ - C_7H_{11}N_2$], 200.2 (8), 199.2 (2), 198.2 (3), 158.1 (7), 124.1 (16) [$C_7H_{12}N_2^+$], 118.1 (7), 109.1 (75), 106.1 (5), 93.1 (2), 92.1 (5), 81.1 (12), 78.1 (12) [$C_5H_4N^+$], 69.1 (12), 57.1 (11) [$C_4H_9^+$]. $C_{20}H_{27}N_5$ (337.3): calcd. C 71.18, H 8.06, N 20.75; found C 71.08, H 8.01, N 20.71.

(2-Quinolinyl)bis(3-*tert*-pyrazolyl)methane (3-*t*Bupz)$_2$(qu)CH (L8): Following the general synthesis, 3-*tert*-butylpyrazole (12.4 g, 100 mmol) and quinoline-2-carbaldehyde (7.9 g, 50 mmol) were used. The final product was obtained as a dark-red waxy solid (11.2 g, 59%). ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 1.26 [s, 18 H, CH_3 (3-*t*Bupz)], 6.25 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-*t*Bupz)], 7.30 [d, $J_{H,H}$ = 8.6 Hz, 1 H, 3-C (qu)], 7.58 [t, $J_{H,H}$ = 7.6 Hz, 1 H, 7-H (qu)], 7.71 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 5-H (3-*t*Bupz)], 7.73 [t, $J_{H,H}$ = 6.6 Hz, 1 H, 8-H (qu)], 7.84 (s, 1 H, CH), 7.91 [d, $J_{H,H}$ = 8.1 Hz, 1 H, 6-H (qu)], 7.99 [d, $J_{H,H}$ = 8.4 Hz, 1 H, 9-H (qu)], 8.31 [d, $J_{H,H}$ = 8.6 Hz, 1 H, 4-H (qu)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 30.8 (CH_3, 3-*t*Bupz), 32.7 (C, 3-*t*Bupz), 79.8 [C(3-*t*Bupz)$_2$(qu)], 103.7 [4-C (3-*t*Bupz)], 120.6 [3-C (qu)], 128.0 [7-C (qu)], 128.6 [6-C (qu)], 128.6 [5-C (qu)], 130.1 [9-C (qu)], 130.7 [8-C (qu)], 131.1 [5-C (3-*t*Bupz)], 137.8 [4-C (qu)], 148.1 [10-C (qu)], 156.9 [2-C (qu)], 163.3 [C_{pz} (3-*t*Bupz)] ppm. IR (KBr) $\tilde{\nu}$ = 3136 (vw, $\nu_{CH_{arom}}$), 3112 (vw, $\nu_{CH_{arom}}$), 3062 (vw, $\nu_{CH_{arom}}$), 3043 (vw, $\nu_{CH_{arom}}$), 3004 (vw, $\nu_{CH_{arom}}$), 2962 (m, $\nu_{CH_{aliph}}$), 2925 (vw, $\nu_{CH_{aliph}}$), 2900 (vw, $\nu_{CH_{aliph}}$), 2859 (vw, $\nu_{CH_{aliph}}$), 2751 (vw), 1716 (w), 1617 (w), 1596 (m), 1560 (vw), 1521 (s), 1506 (m), 1481 (w), 1459 (m), 1428 (vw), 1400 (vw), 1361 (s), 1321 (vw), 1307 (vw), 1247 (vs), 1220 (w), 1157 (w), 1118 (vw), 1052 (s), 1025 (vw), 1014 (w), 997 (vw), 981 (vw), 954 (vw), 906 (m), 873 (vw), 804 (vs), 781 (vs), 761 (vs), 725 (m), 698 (vw), 669 (vw), 620 (w), 599 (vw), 586 (vw), 555 (vw), 522 (vw), 478 (w), 443 (vw), 418 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 387.2 (15) [$M^+ = C_{24}H_{29}N_5^+$], 279.1 (15), 265.1 (20), 264.1 (65) [$M^+ - C_7H_{11}N_2$], 259.1 (10) [$M^+ - C_9H_6N$], 255.1 (7), 250.1 (9), 248.1 (4), 208.1 (14), 168.1 (7), 167.1 (13), 157.1 (5), 156.1 (4), 137.1 (10), 129.1 (26) [$C_9H_7N^+$], 128.1 (32) [$C_9H_6N^+$], 127.1 (3), 125.1 (5), 124.1 (23) [$C_7H_{12}N_2^+$], 113.1 (3), 110.1 (7), 109.1 (100), 102.1 (5), 101.1 (7), 82.1 (4), 81.1 (20), 77.1 (5), 75.1 (3), 71.1 (6), 70.1 (5), 69.1 (24), 68.1 (2), 63.1 (7), 57.1 (20) [$C_4H_9^+$]. $C_{24}H_{29}N_5$ (387.2): calcd. C 74.38, H 7.54, N 18.07; found C 74.17, H 7.38, N 17.67.

(2-Hydroxyphenyl)bis(3-*tert*-pyrazolyl)methane (3-*t*Bupz)$_2$(phOH)-CH (L9): Following the general synthesis, 3-*tert*-butylpyrazole (12.4 g, 100 mmol) and salicylaldehyde (5.3 mL, 50 mmol) were used. The final product was obtained as an orange solid (9.6 g, 55%). M.p. 85 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 1.26 [s, 18 H, CH_3 (3-*t*Bupz)], 6.20 [d, $J_{H,H}$ = 2.3 Hz, 2 H, 4-H (3-*t*Bupz)], 6.89 [t, $J_{H,H}$ = 7.6 Hz, 1 H, 4-H (phOH)], 6.98 [dd, $J_{H,H}$ = 1.0, 8.2 Hz, 1 H, 6-H (phOH)], 7.18 [dd, $J_{H,H}$ = 1.4, 7.6 Hz, 1 H, 3-H (phOH)], 7.30 [t, $J_{H,H}$ = 8.1 Hz, 1 H, 5-H (phOH)], 7.57 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 5-H (3-*t*Bupz)], 7.73 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 29.8 (C, 3-*t*Bupz), 31.8 (CH_3, 3-*t*Bupz), 75.8 [C(3-*t*Bupz)$_2$(phOH)], 101.9 [4-C (3-*t*Bupz)], 117.6 [6-C (phOH)], 119.5 [4-C (phOH)], 122.8 [2-C (phOH)], 129.9 [3-C (phOH)], 130.1 [5-C (3-*t*Bupz)], 130.9 [5-C (phOH)], 155.4 [1-C (phOH)], 162.2 [C_{pz} (3-*t*Bupz)] ppm. IR (KBr) $\tilde{\nu}$ = 3130 (vw, $\nu_{CH_{arom}}$), 3072 (vw, $\nu_{CH_{arom}}$), 2960 (s, $\nu_{CH_{aliph}}$), 2902 (w, $\nu_{CH_{aliph}}$), 2867 (w, $\nu_{CH_{aliph}}$), 2773 (vw), 2715 (vw), 2597 (vw), 2466 (vw), 1716 (vw), 1606 (s), 1583 (w), 1558 (vw), 1521 (s), 1482 (m), 1459 (vs), 1421 (vw), 1401 (vw), 1361 (s), 1339 (w), 1322 (w), 1297 (m), 1251 (s), 1245 (vs), 1207 (m), 1174 (vw), 1157 (m), 1099 (m), 1054 (vs), 1025 (w), 1013 (w), 995 (w), 977 (vw), 933 (vw), 896 (m), 873 (m), 883 (vw), 811 (m), 794 (m), 754 (vs), 723 (s), 669 (vw), 647 (w), 637 (vw), 615 (vw), 609 (vw), 590 (vw), 545 (w), 497 (vw), 478 (vw), 441 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 352.2 (80) [$M^+ = C_{21}H_{28}N_4O^+$], 259.2 (7) [$M^+ - C_6H_5O$], 230.2 (22), 229.2 (91) [$M^+ - C_7H_{11}N_2$], 214.2 (22), 213.3 (88), 199.2 (4), 186.1 (32), 173.1 (12), 172.1 (28) [$C_{10}H_8N_2O^+$], 171.1 (91), 146.1 (52), 145.1 (98) [$C_7H_5N_4^+$], 144.1 (11), 133.1 (5), 132.1 (12), 124.1 (24), 123.1 (2) [$C_7H_{11}N_2^+$], 121.1 (4), 120.1 (14), 110.1 (10), 109.1 (89), 95.1 (12), 94.1 (5), 93.1 (7) [$C_6H_5O^+$], 92.1 (10), 91.1 (9), 81.1 (25), 80.1 (5), 79.1 (9), 78.1 (5), 77.1 (19), 69.1 (25), 57.1 (53) [$C_4H_9^+$]. $C_{21}H_{28}N_4O$ (352.1): calcd. C 71.56, H 8.01, N 15.90; found C 70.47, H 7.88, N 15.57.

(2-Pyridinyl)bis(3-mesitylpyrazolyl)methane (3-Mspz)$_2$(py)CH (L10): Following the general synthesis, 3-mesitylpyrazole (18.6 g, 100 mmol) and pyridine-2-carbaldehyde (4.8 mL, 50 mmol) were used. The final product was obtained as a yellow solid (16.8 g, 73%). M.p. 128 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.05 [s, 12 H, CH_3, (3-Mspz)], 2.33 [s, 6 H, CH_3, (3-Mspz)], 6.18 [d, $J_{H,H}$ = 1.6 Hz, 2 H, 4-H (3-Mspz)], 6.90 [s, 4 H, *m*-H (3-Mspz)], 7.13 [m, 1 H, 3-H (py)], 7.24 [m, 1 H, 5-H (py)], 7.32 (s, 1 H, CH), 7.52 [d, $J_{H,H}$ = 1.7 Hz, 2 H, 3-H (3-Mspz)], 7.55 [m, 1 H, 4-H (py)], 8.27 [d, $J_{H,H}$ = 4.4 Hz, 1 H, 6-H (py)] ppm. ^{13}C NMR (125 MHz,

$CDCl_3$, 25 °C): δ = 20.6 [$C_{CH_3,o}$ (3-Mspz)], 21.4 [$C_{CH_3,p}$ (3-Mspz)], 75.2 [C(3-Mspz)$_2$(phOH)], 106.1 [4-C (3-Mspz)], 123.7 [3-C (py)], 125.4 [5-C (py)], 128.5 [*m*-C (3-Mspz)], 128.6 [C_{Ms} (3-Mspz)], 136.0 [5-C (3-Mspz)], 136.3 [4-C (py)], 138.4 [*o*-C (3-Mspz)], 140.2 [*p*-C (3-Mspz)], 144.6 [C_{pz} (3-Mspz)], 148.4 [6-C (py)], 156.4 [6-C (py)] ppm. IR (KBr) $\tilde{\nu}$ = 3163 (m, $\nu_{CH_{arom}}$), 3123 (w, $\nu_{CH_{arom}}$), 3071 (vw, $\nu_{CH_{arom}}$), 3034 (vw, $\nu_{CH_{arom}}$), 2949 (w, $\nu_{CH_{aliph}}$), 2919 (w, $\nu_{CH_{aliph}}$), 2854 (vw, $\nu_{CH_{aliph}}$), 2825 (vw, $\nu_{CH_{aliph}}$), 2794 (vw), 2737 (vw), 2597 (vw), 2708 (vw), 1735 (vw), 1717 (vw), 1702 (vw), 1686 (vw), 1654 (vw), 1637 (vw), 1613 (m), 1590 (w), 1573 (w), 1544 (m), 1509 (vw), 1455 (s), 1438 (m), 1384 (m), 1356 (vw), 1335 (m), 1315 (m), 1288 (w), 1231 (w), 1199 (vs), 1168 (vw), 1151 (vw), 1100 (w), 1077 (w), 1046 (m), 1030 (w), 1015 (w), 996 (vw), 980 (vw), 964 (vw), 938 (w), 921 (w), 874 (m), 852 (vs), 826 (m), 813 (m), 795 (m), 768 (vs), 743 (m), 732 (m), 707 (vw), 673 (vw), 663 (vw), 649 (vw), 615 (w), 600 (vw), 578 (w), 500 (vw), 470 (w), 447 (vw), 407 (vw) cm^{-1}. MS (ESI): *m*/*z* (%) = 462.3 (22) [$M^+ = C_{30}H_{31}N_5^+$ + H], 277.2 (18), 276.2 (100) [$C_{18}H_{18}N_3^+$], 187.2 (15) [$C_{12}H_{13}N_2^+$ + 2H]. $C_{30}H_{31}N_5$ (461.6): calcd. C 78.06, H 6.77, N 15.17; found C 77.92, H 6.63, N 15.05.

(2-Quinolinyl)bis(3-mesitylpyrazolyl)methane (3-Mspz)$_2$(qu)CH (L11): Following the general synthesis, 3-mesitylpyrazole (18.6 g, 100 mmol) and quinoline-2-carbaldehyde (7.9 g, 50 mmol) were used. The final product was obtained as an orange solid (17.8 g, 70%). M.p. 122 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.13 [s, 12 H, CH_3, (3-Mspz)], 2.30 [s, 6 H, CH_3, (3-Mspz)], 6.31 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-Mspz)], 6.90 [s, 4 H, *m*-H (3-Mspz)], 7.18 [d, $J_{H,H}$ = 8.5 Hz, 1 H, 3-H (qu)], 7.45 (s, 1 H, CH), 7.51 [t, $J_{H,H}$ = 7.5 Hz, 1 H, 7-H (qu)], 7.65 [t, $J_{H,H}$ = 7.4 Hz, 1 H, 8-H (qu)], 7.78 [m, 1 H, 6-H (qu)], 7.96 [m, 1 H, 9-H (qu)], 7.97 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 5-H (3-Mspz)], 8.14 [d, $J_{H,H}$ = 8.5 Hz, 1 H, 4-H (qu)] ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.4 [$C_{CH_3,o}$ (3-Mspz)], 21.1 [$C_{CH_3,p}$ (3-Mspz)], 75.9 [C(3-Mspz)$_2$(phOH)], 107.7 [4-C (3-Mspz)], 118.6 [3-C(qu)], 126.9 [7-C (qu)], 127.5 [6-C (qu)], 127.6 [5-C (qu)], 128.0 [*m*-C (3-Mspz)], 129.5 [5-C (3-Mspz)], 129.6 [8-C(qu)], 129.7 [9-C(qu)], 130.7 [C_{Ms} (3-Mspz)], 136.9 [4-C(qu)], 137.6 [*o*-C (3-Mspz)], 138.7 [*p*-C (3-Mspz)], 147.5 [10-C(qu)], 151.0 [C_{pz} (3-Mspz)], 156.3 [2-C (qu)] ppm. IR (KBr) $\tilde{\nu}$ = 3162 (w, $\nu_{CH_{arom}}$), 3119 (vw, $\nu_{CH_{arom}}$), 3064 (vw, $\nu_{CH_{arom}}$), 3032 (vw, $\nu_{CH_{arom}}$), 2950 (w, $\nu_{CH_{aliph}}$), 2918 (w, $\nu_{CH_{aliph}}$), 2854 (vw, $\nu_{CH_{aliph}}$), 2731 (vw), 1735 (vw), 1718 (vw), 1700 (vw), 1685 (vw), 1613 (s), 1595 (m), 1576 (w), 1560 (w), 1544 (w), 1528 (vw), 1505 (m), 1488 (m), 1452 (m), 1429 (m), 1384 (m), 1333 (m), 1304 (m), 1263 (vw), 1234 (m), 1223 (w), 1199 (m), 1167 (vw), 1151 (vw), 1140 (vw), 1115 (vw), 1100 (vw), 1079 (w), 1043 (m), 1013 (w), 982 (vw), 964 (vw), 925 (vw), 907 (w), 876 (vw), 852 (s), 811 (vs), 797 (s), 776 (vs), 744 (m), 708 (vw), 660 (vw), 632 (vw), 618 (w), 578 (vw), 557 (vw), 523 (vw), 512 (vw), 501 (vw), 478 (vw), 446 (vw), 421 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 511.3 (11) [$M^+ = C_{34}H_{33}N_5^+$], 444.1 (10), 328.2 (5), 327.2 (29), 326.2 (19) [$M^+ - C_{12}H_{13}N_2$], 325.2 (5), 314.1 (7), 241.1 (9), 240.1 (65), 239.1 (21), 199.2 (12), 198.2 (10) [$C_{13}H_{14}N_2^+$], 197.1 (46), 196.2 (8), 187.2 (17), 186.1 (100), 185.1 (43) [$C_{12}H_{13}N_2^+$], 184.1 (10), 183.1 (20), 182.1 (9), 181.1 (16), 171.1 (19), 170.1 (14) [$C_{11}H_{10}N_2^+$], 169.1 (30), 168.1 (18), 167.1 (10), 159.1 (36), 258.1 (74), 157.1 (19), 156.1 (26), 155.1 (25) [$C_{10}H_7N_2^+$], 154.1 (16), 153.1 (9), 145.1 (13) [$C_7H_5N_4^+$], 144.1 (60), 143.1 (81), 142.1 (37), 141.1 (29) [$C_{10}H_7N^+$], 140.1 (10), 131.1 (19), 130.1 (19), 129.1 (52), 128.1 (78) [$C_9H_6N^+$], 127.1 (14), 119.0 (36) [$C_9H_{11}^+$], 117.1 (12), 116.1 (18), 115.1 (45), 113.1 (11), 111.2 (14), 109.2 (10), 103.1 (10), 102.1 (10), 101.1 (14), 99.2 (13), 98.1 (33), 97.1 (21), 95.1 (15), 91.1 (35), 85.2 (28), 84.1 (10), 83.1 (20), 81.1 (17), 79.1 (11) [$C_4H_3N^+$], 77.1 (19), 71.1 (41), 70.1 (17), 69.1 (30), 67.0 (14) [$C_3H_3N_2^+$]. $C_{34}H_{33}N_5$ (511.3): calcd. C 79.71, H 6.50, N 13.69; found C 79.47, H 6.75, N 13.51.

(2-Hydroxyphenyl)bis(3-mesitylpyrazolyl)methane (3-Mspz)$_2$(phOH)-CH (L12): Following the general synthesis, 3-mesitylpyrazole (18.6 g, 100 mmol) and salicylaldehyde (5.3 mL, 50 mmol) were used. The final product was obtained as a white solid (18.1 g, 76%). M.p. 135 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.07 [s, 12 H, CH_3, (3-Mspz)], 2.33 [s, 6 H, CH_3, (3-Mspz)], 6.20 [d, $J_{H,H}$ = 2.3 Hz, 2 H, 4-H (3-Mspz)], 6.89 [d, $J_{H,H}$ = 7.9 Hz, 1 H, 6-H (phOH)], 6.92 [s, 4 H, *m*-H (3-Mspz)], 6.96 [d, $J_{H,H}$ = 7.5 Hz, 1 H, 4-H (phOH)], 7.28 [t, $J_{H,H}$ = 7.8 Hz, 1 H, 5-H (phOH)], 7.34 [d, $J_{H,H}$ = 7.4 Hz, 1 H, 3-H (phOH)], 7.68 (s, 1 H, CH), 7.82 [d, $J_{H,H}$ = 2.4 Hz, 2 H, 5-H (3-Mspz)], 9.91 (br., 1 H, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.4 [$C_{CH_3,o}$ (3-Mspz)], 21.1 [$C_{CH_3,p}$ (3-Mspz)], 78.1 [C(3-Mspz)$_2$(phOH)], 107.2 [4-C (3-Mspz)], 119.9 [6-C (phOH)], 121.1 [2-C (phOH)], 128.0 [4-C (phOH)], 128.1 [*m*-C (3-Mspz)], 130.0 [C_{Ms} (3-Mspz)], 130.9 [3-C (phOH)], 131.0 [5-C (3-Mspz)], 131.8 [5-C (phOH)], 137.4 [*o*-C (3-Mspz)], 137.8 [*p*-C (3-Mspz)], 152.0 [C_{pz} (3-Mspz)], 155.7 [1-C (phOH)] ppm. IR (KBr): $\tilde{\nu}$ = 3154 (w, $\nu_{CH_{arom}}$), 3119 (vw, $\nu_{CH_{arom}}$), 3032 (vw, $\nu_{CH_{arom}}$), 3012 (vw, $\nu_{CH_{arom}}$), 2949 (w, $\nu_{CH_{aliph}}$), 2919 (w, $\nu_{CH_{aliph}}$), 2855 (vw, $\nu_{CH_{aliph}}$), 2825 (vw, $\nu_{CH_{aliph}}$), 2728 (w), 2597 (vw), 2468 (vw), 2381 (vw), 2346 (vw), 2304 (vw), 2281 (vw), 2100 (vw), 1959 (vw), 1923 (vw), 1883 (vw), 1802 (vw), 1762 (vw), 1734 (vw), 1717 (vw), 1702 (vw), 1685 (vw), 1654 (vw), 1612 (vs), 1602 (vs), 1575 (w), 1542 (w), 1526 (m), 1503 (m), 1488 (s), 1459 (vs), 1375 (m), 1330 (w), 1315 (s), 1289 (vw), 1266 (m), 1234 (s), 1203 (s), 1168 (w), 1155 (w), 1101 (s), 1085 (m), 1049 (vs), 1029 (s), 996 (w), 983 (vw), 964 (w), 932 (m), 875 (s), 851 (vs), 815 (m), 799 (m), 790 (m), 762 (vs), 743 (s), 721 (m), 655 (vw), 640 (m), 626 (vw), 615 (vw), 601 (vw), 577 (w), 547 (w), 535 (vw), 502 (vw), 470 (w), 452 (vw), 437 (vw), 421 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 476.2 (11) [$M^+ = C_{31}H_{32}N_4O^+$], 387.2 (5), 290. 1 (6) [$M^+ - C_{12}H_{14}N_2$], 264.1 (23), 208.1 (4), 197.1 (84), 187.1 (34), 186.1 (100), 185.1 (45) [$C_{12}H_{13}N_2^+$], 171.1 (37) [$C_{10}H_7N_2O^+$], 170.1 (13), 169.1 (12), 168.1 (12), 159.1 (50), 158.1 (84), 157.1 (13), 156.1 (9), 155.1 (7), 154.1 (8), 145.1 (10) [$C_7H_5N_4^+$], 144.1 (76), 143.1 (25), 142.1 (20), 141.1 (21), 131.1 (6), 130.1 (8), 129.1 (13), 128.1 (20), 127.1 (8), 122.1 (30), 121.1 (29), 115.1 (29), 104.1 (5), 103.1 (6), 93.1 (14) [$C_6H_5O^+$], 91.1 (16), 77.1 (14), 76.1 (8), 66.1 (4) [$C_3H_2N_2^+$], 65.1 (15). $C_{31}H_{32}N_4O$ (476.2): calcd. C 78.12, H 6.77, N 11.76; found C 77.87, H 6.71, N 11.92.

(2-Pyridinyl)(phenyl)[bis(3-phenylpyrazolyl)]methane (3-Phpz)$_2$(py)-(ph)C (L13): NaH (2.4 g, 100 mmol) was suspended in freshly distilled THF (100 mL) and stirred at 0 °C. 3-Phenylpyrazole (14.4 g, 100 mmol) was added gradually to the suspension over 15 min and the stirring was continued at 0 °C until gas evolution stopped (ca. 30 min.). Then, thionyl chloride (3.7 mL, 50 mmol) was added dropwise to this pale-brown solution at 0 °C. After stirring for an additional 45 min at 0 °C and then 30 min at room temperature, benzoyl pyridine (4.6 g, 25 mmol) and a catalytic amount of cobalt(II) chloride were added, and the reaction mixture was heated under vigorous stirring at reflux overnight. During this time period the mixture turned intensely blue pink and evolution of SO_2 was observed. The reaction mixture was allowed to cool to room temperature before diethyl ether (50 mL) and water (100 mL) were gradually added. The biphasic solution was then stirred for 1 hour. The layers were separated, and the aqueous phase was extracted with diethyl ether (3 × 60 mL). The combined organic phase was washed with distilled water, dried with sodium sulfate and filtered. The solvent was then removed in vacuo, and the residual substituted pyrazole was removed by distillation under vacuum (135 °C, 0.9 Torr). The crude product was suspended in hexane, and the flask was placed in an ultrasound bath to break up the lumps that had formed, yielding a solid. This solid was collected by filtration and dried in vacuo. A brown solid (8.7 g, 77%) resulted as the final

product. M.p. 122 °C. ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C): δ = 6.79 [d, $J_{H,H}$ = 2.5 Hz, 2 H, 4-H (3-Phpz)], 7.27 [t, $J_{H,H}$ = 7.3 Hz, 2 H, *p*-H (3-Phpz)], 7.33–7.35 [m, 6 H, *m*-H (3-Phpz) and *o*-H (ph)], 7.37 [m, 1 H, *o*-H (ph)], 7.41 [m, 2 H, *m*-H (ph)], 7.42 [m, 1 H, 3-H (py)], 7.43 [m, 1 H, 5-H (py)], 7.60 [d, $J_{H,H}$ = 2.6 Hz, 2 H, 5-H (3-Phpz)], 7.77 [d, $J_{H,H}$ = 8.0 Hz, 2 H, *o*-H (3-Phpz)], 7.87 [t, $J_{H,H}$ = 7.8 Hz, 1 H, 4-H (py)], 8.62 [dd, $J_{H,H}$ = 1.9, 4.7 Hz, 1 H, 6-H (py)] ppm. ^{13}C NMR (125 MHz, [D$_6$]acetone, 25 °C): δ = 87.7 [C(3-Phpz)$_2$(py)(ph)], 102.6 [4-C (3-Phpz)], 123.6 [3-C (py)], 124.6 [5-C (py)], 125.6 [*o*-C(3-Phpz)], 127.5 [*p*-C(3-Phpz)], 127.7 [*m*-C(ph)], 128.4 [*m*-C(3-Phpz)], 128.7 [*o*-C(ph)], 129.5 [*p*-C(ph)], 133.4 [C$_{ph}$ (3-Phpz)], 134.0 [5-C (3-Phpz)], 136.6 [4-C (py)], 140.0 [C(ph)], 148.2 [6-C (py)], 151.6 [C$_{pz}$ (3-Phpz)], 158.5 [2-C (py)] ppm. IR (KBr): $\tilde{\nu}$ = 3149 (vw, $\nu_{CH_{arom}}$), 3099 (vw, $\nu_{CH_{arom}}$), 3058 (vw, $\nu_{CH_{arom}}$), 3031 (vw, $\nu_{CH_{arom}}$), 2923 (vw, $\nu_{CH_{aliph}}$), 1953 (vw), 1889 (vw), 1810 (vw), 1772 (vw), 1754 (vw), 1700 (vw), 1652 (vw), 1585 (w), 1560 (vw), 1529 (w), 1498 (m), 1455 (m), 1432 (w), 1382 (vw), 1355 (w), 1323 (vw), 1301 (vw), 1270 (vw), 1205 (m), 1154 (vw), 1099 (w), 1074 (m), 1049 (m), 1026 (vw), 1011 (vw), 993 (vw), 948 (vw), 937 (vw), 916 (vw), 898 (vw), 869 (w), 750 (vs), 694 (vs), 657 (vw), 619 (vw), 505 (vw), 468 (vw), 444 (vw), 428 (vw), 416 (vw), 408 (vw) cm^{-1}. MS (EI): *m*/*z* (%) = 453.1 (82) [M$^+$ = C$_{30}$H$_{23}$N$_5^+$], 376.1 (7) [M$^+$ – C$_6$H$_5$], 375.1 (11) [M$^+$ – C$_5$H$_4$N], 334.1 (6), 333.1 (7), 312.1 (33), 311.1 (95) [M$^+$ – C$_{12}$H$_{10}$], 310.1 (100) [M$^+$ – C$_9$H$_7$N$_2$], 309.1 (58), 308.1 (21), 285.1 (7), 284.1 (14), 283.1 (7), 282.1 (8), 281.1 (10), 234.1 (11), 233.1 (17) [M$^+$ – C$_{15}$H$_{12}$N$_2$], 232.2 (11) [M$^+$ – C$_{14}$H$_{11}$N$_3$], 231.1 (6), 207.1 (15), 206.1 (17), 205.1 (34), 204.1 (6), 181.1 (15), 180.1 (19), 179.1 (9), 169.1 (7), 168.1 (72), 167.1 (91) [M$^+$ – C$_{18}$H$_{14}$N$_4$], 166.1 (19), 155.1 (9) [C$_{10}$H$_7$N$_2^+$], 144.1 (57) [C$_7$H$_4$N$_4^+$], 128.1 (15), 117.1 (8), 116.1 (6), 115.1 (31), 105.1 (5), 104.1 (13), 103.1 (20), 102.1 (6), 89.1 (11), 78.1 (20) [C$_5$H$_4$N$^+$], 77.1 (48) [C$_6$H$_5^+$]. C$_{30}$H$_{23}$N$_5$ (453.1): calcd. C 79.45, H 5.11, N 15.44; found C 79.27, H 4.96, N 15.28.

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