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Bulky and Modular 3,3′-Bipyrazoles as Ligands: Synthesis, Characterization, and Catalytic Activity of Pd Complexes

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In the present study, the properties of a new bidentate *N*,*N*′-chelating ligand class that bears an electron-excessive 3,3′-bipyrazole core have been investigated. The ligands are easily accessible in a three-step procedure by condensation with diethyl oxalate followed by tandem condensation with hydrazine hydrate and finally by aryl- or alkylation exclusively at the *N*-1,1′-pyrazole positions to furnish overall eleven new ligands with different electronic properties. After structural analysis of the ligands, their coordination to palladium, copper, and cobalt has been studied. These ligands coordinate the 2,2′-pyrazolyl nitrogen atoms in a bidentate fashion to the metals to realize complexes with an (**L**)MX_2 motif. We present two crystal structures of Pd and Cu complexes, which to the best of our knowledge represent the first d^8 and d^9 2,2′-bipyrazole compounds coordinated through bidentate complexation. Initial catalytic experiments have been performed with palladium complexes with three bipyrazole ligands of this new class; the palladium-catalyzed copper-free Wacker oxidation of different alkenes showed superior activity compared to 2,2′-bipyridines. We attribute this to a higher redox potential of the 3,3′-bipyrazoles, which are − besides electronic effects − also strongly influenced by steric effects. These might be enforced by the extended ligand backbone, the choice of the wingtip substitution, and the smaller coordination cavity within the N^2,$N^{2'}$ atoms compared to 2,2′-bipyridine ligands.

Introduction

2,2′-Bipyridines are well known and established ligands in addition to being among one of the most explored chelate systems in coordination chemistry.[1] Due to their redox properties and ease of functionalization, they are commonly used as catalysts[2] (i.e., allylic oxidations,[3,4] substitutions,[5–7] cyclopropanations,[8,9] and transfer hydrogenations[10]). Surprisingly, 3,3′-bipyrazoles have been less used and investigated as potential ligands.[11–13] Intrigued by the converse electronic nature of the π-excessive 3,3′-bipyrazoles[14,15] relative to 2,2′-bipyridines, which are π acceptors, we became interested in their coordination properties and catalytic activity by considering the influence of steric as well as electronic effects. Therefore, we designed a new ligand pattern that fulfills the following criteria: (1) short synthesis from readily available starting materials, (2) steric bulkiness with the possibility of introducing different moieties, and (3) a modular ligand system with a sterically and electronically diverse substitution pattern. Furthermore, this ligand system should be preliminarily screened for catalytic activity, thereby enabling further insights into the development of stereoselective transformations. To the best of our knowledge, there is so far no literature about backbone-fused 3,3′-bipyrazoles and their use as potential ligands for metal-complex-catalyzed transformations. Natural (+)-(1*R*,4*R*)-camphor proved to be the building block of choice in the design of our new ligand class, since (+)-camphor fulfills all the above-mentioned criteria and furthermore enabled us to extend this strategy to the majority of bicyclic monoterpenes commonly found in catalyst designs.[2,9,16–19]

Results and Discussion

The bipyrazole ligands **3a**–**k** were readily synthesized in a three-step procedure starting from (+)-camphor (see Scheme 1).

1,3,4,6-Tetraketone **1** was obtained in two tautomeric enol forms as identified by X-ray crystallographic analysis by double Claisen condensation with diethyl oxalate in 93% yield. A third condensation with hydrazine hydrate[20,21] furnished the key intermediate 3,3′-bicamphorpyrazole (bcpz) **2** as an insoluble powder in 91% yield. After several attempts to solubilize **2**, we found that prolonged heating under basic conditions resulted in complete solvation of the 3,3′-bipyrazolate, which in turn provided a useful indicator

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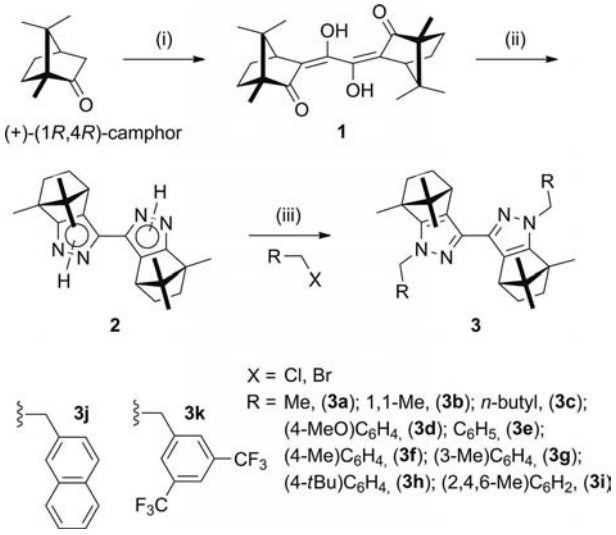


Scheme 1. Synthesis of 3,3′-bipyrazoles **3a**–**k**. i) NaH, THF, 65 °C, 3 d; then 1.0 equiv. $(CO_2Et)_2$, 65 °C, 1 d, 93%. ii) N_2H_5OH, EtOH, 78 °C, 2 d, 91%. iii) NaH, THF, 65 °C, 2 h; then 2.0 equiv. RCH_2X, 65 °C, 4 h (16 h for **3c** and **3i**), 79–98%.

of the reaction progress. Furthermore, dialkylation was achieved exclusively at the pyrazole 1,1′-positions without formation of regioisomeric mixtures, which often hampers synthesis and requires additional separation steps.[22–24] We attribute this to steric congestion and metal complexation of the 2,2′ nitrogen atoms in the center of the ligand under these experimental conditions. It should be emphasized that, due to the here developed and optimized synthetic protocol and crystallizability of the intermediates, the synthesis of the ligands **3a**–**i** was achieved in only three steps without the need of tedious workup procedures or chromatographic separations and with overall excellent yields between 67 and 82%. Single crystals of the free ligands were obtained by slow evaporation of saturated solutions in ethanol and revealed a C_2-symmetric *transoid* structure state with respect to the pyrazole nitrogen atoms, which were obtained for all ligand structures reported here (solid states of **3e**–**j**). The crystal structures of the sterically most demanding ligands mesitylene-3,3′-bicamphorpyrazole **3i** and naphthalene-3,3′-bicamphorpyrazole **3j** are depicted in Figure 1 with an N–C–C–N torsion angle of 172.8(8)° (**3i**) and 165.0(10)° (**3j**), respectively.

The monomeric palladium complexes of all eleven new ligands were obtained by conversion with $[PdCl_2(CH_3CN)_2]$ in acetonitrile at room temperature in good yields (see Scheme 2). To confirm the ability of complex formation of the novel ligands, the monomeric bidentate copper(II) and cobalt(II) complexes of ligands **3h** and **3j** were prepared and **4h**$^{(Cu)}$ crystallized from ethanol-containing solutions. The copper(II) complex of **3h** shows a distorted structure between tetrahedral and square-planar conformation, with an N–Cu–N plane twisted about 51.7° to the Cl–Cu–Cl plane, which is a known phenomena for κ^2-**L**$CuCl_2$ complexes but less pronounced in related κ^2-2,2′-copper(II) compounds[25] and hardly visible in κ^2-2,2′-bipyridine copper(II) complexes[26,27] (see Figure 2). To the best of our knowledge,

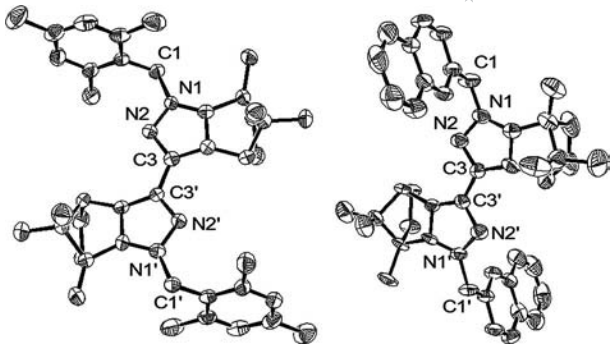
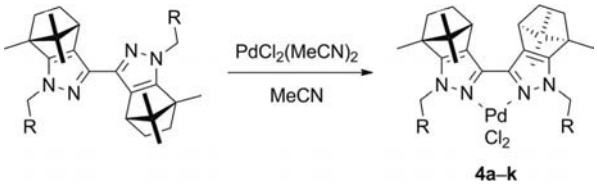


Figure 1. X-ray crystal structure of ligand **3i** (left) and **3j** (right) showing the *transoid* structure. Thermal ellipsoids are plotted at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths [pm] for **3i**: N1–N2 136.6(4), N1′–N2′ 135.8(4), N2–C3 134.3(5), N2′–C3′ 134.8(5); **3j**: N1–N2 139.0(10), N1′–N2′ 135.6(10), N2–C3 136.5(11), N2′–C3′ 136.7(10).

these two crystal structures represent − in addition to d^6 complexes (Ru) − the first examples of d^8 (Pd) and d^9 (Cu) 3,3′-bipyrazole complexes with bidentate coordination of the 2,2′ nitrogen atoms.[11,28] All complexes were characterized by elemental analyses, NMR spectroscopy (except paramagnetic Cu, Co complexes), IR, and FAB-MS.



Scheme 2. Preparation of palladium–(bcpz) complexes **4a**–**k**.

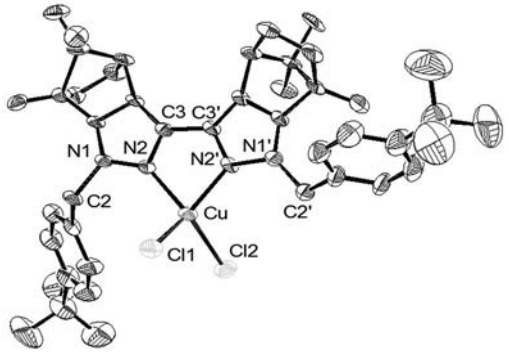


Figure 2. Distorted geometry observed in the copper(II) complex of **3h**. Thermal ellipsoids are plotted at 50% probability level and hydrogen atoms are omitted for clarity.

In contrast to the free ligands, the palladium complexes scarcely crystallize. However, small single crystals of **4h** suitable for X-ray analysis by using synchrotron radiation were obtained by slow diffusion of pentane into a saturated diethyl ether solution. As shown in Figure 3, two molecules of the complex $[Pd\{(bcpz)1,1'\text{-}(p\text{-}tBuC_6H_4)_2\}]$ adopt a cagelike structure with its benzyl wingtips encapsulating one single diethyl ether molecule. The Pd1 atom lies 49.8 pm above the mean bipyrazole plane (Pd1 coordina-

tion plane 20.5° out of bipyrazole plane; for Pd2 41.7 pm and 16.5°, respectively) and the bite angle N–Pd–N is 78.3(1)° for Pd1 and 78.9(1)° for Pd2.

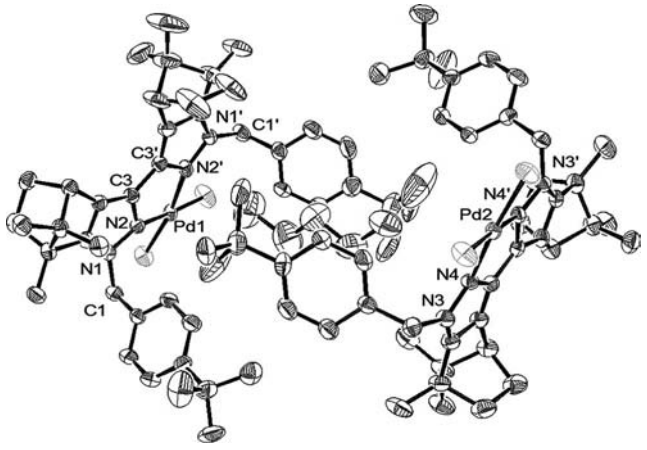


Figure 3. X-ray crystal structure of palladium 3,3′-bipyrazole complex **4h** showing the *cisoid* structure. Thermal ellipsoids are plotted at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths [pm]: Pd1–N2 206.4(3), Pd1–N2′ 207.5(3), N1–N2 136.5(4), N1′–N2′ 137.3(4), N2–C3 133.6(5), N2′–C3′ 136.8(5).

The complex stability in solution, integrity of the *cisoid* structure, and the feasibility of rotating the wingtips are the prerequisite for any application as a catalytic system in homogeneous catalysis. Therefore solutions of the palladium(II) complexes **4d**–**k** were studied by temperature-dependent ^{1}H NMR spectroscopy. The two protons of each wingtip methylene group at C1 and C1′ of the free ligands show a characteristic singlet between δ = 5.0 and 5.6 ppm for arylated structures, as expected for two sets of enantiotopic protons, whereas complexation with Pd^{II} results in a distinct pattern for the *cisoid* structure. Splitting of the methylene signals with a downfield shift to δ = 5.8 and 6.3 ppm is generally observed for the two sets of diastereotopic protons of arylated bcpz compounds including geminal $^2J_{C,H}$ couplings (δ = 13.8–14.1 ppm for alkyl; δ = 15.6–16.7 ppm for benzylic protons). This is observed for the proton spectra of *N*,*N*′-alkylated ligands **3a**–**c** as well, which undergo downfield shifts between δ = 4.3 and 6.0 ppm combined with more complex splitting patterns (see Figure 4).

Variable-temperature (VT) proton NMR spectra of **4h**–**j** in 1,1,2,2-[D_2]tetrachloroethane between 243 and 363 K did not indicate the presence of further conformations in solution. The starting spectra remained unchanged, thus proving complex stability over a broad temperature range. To investigate the influence of solvent, the CD spectra of **4h** were recorded in various solvents. The CD spectra show two strong absorptions with a maximum positive Cotton effect at 266–271 nm and a negative Cotton effect at 225–227 nm in both THF and CH_2Cl_2 solutions, which are larger than in the free ligand. The zero crossings in the CD spectra are in satisfactory agreement with the maximum absorptions of the complexes, as can be seen in the UV spectra. By contrast, in CH_3CN a more disordered random conformation seems to dominate. Surprisingly, evaluation of the CD spectra of the Pd^{II} complexes revealed a reverse solution behavior exclusively for the 3,5-trifluorobenzyl-substituted complex **4k**, with a pronounced broad positive Cotton effect between 275 and 283 nm (see the Supporting Information).

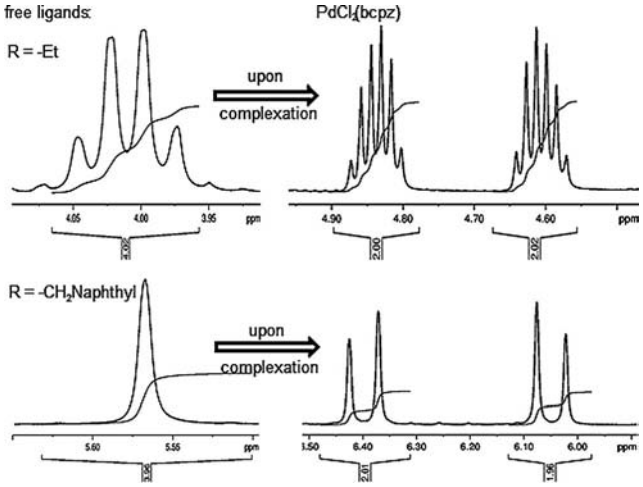


Figure 4. Distinctive ^{1}H NMR spectroscopic pattern of **3a** and **3j** showing splitting of wingtip methylene signals into a set of two diastereotopic protons upon complexation to afford **4a** and **4j** (recorded after 16 h).

With these ligands and complexes in hand, their catalytic potential was screened in the copper-free catalytic oxidation of terminal alkenes.[29–31] Compound **4h** was arbitrarily chosen as the model complex for preliminary catalytic screening.[32] For comparison, [$PdCl_2$(3,3′-bpy)][33] (3,3′-bpy = 3,3′-bipyrazole) was synthesized and tested in parallel as a benchmark under the same reaction conditions. After optimizing reaction conditions, the oxidations of alkenes with molecular oxygen showed overall good conversions to the corresponding ketones (72–87%; see Table 1). These results are noteworthy, even though prolonged reaction times were required, since no or very low conversions were observed using molecular oxygen combined with [$PdCl_2$(3,3′-bpy)] (**5**) as catalyst. Much shorter reaction times of 17 h were obtained with benzoquinone (BQ) as the internal oxidant with overall conversions of 89–99%. To evaluate the performance of the catalysts with respect to their substitution pattern, a test set of three catalysts (**4h**–**k**) as representatives for *N*,*N*′-arylated Pd(bcpz) compounds was chosen. The most electron-deficient 3,5-bis(trifluoromethyl)-substituted complex **4k** showed only low conversions of 1-octene and vinylcyclohexane, whereas catalysts **4h** (*p*-*tert*-butylbenzyl-substituted) and **4i** (mesitylene substituted) were much more active. With **4i**, yields of 83–99% of the corresponding ketones were obtained. We explain this by the higher redox potential of the 3,3-bipyrazoles, which are in addition to electronic effects also strongly influenced by steric effects, which may be enforced by the ligand backbone. While still maintaining the structure, framework, and coordination cavity, higher reactivities and conversions with increasing electronic-donating properties of arylsubstituted

bcpz-type catalysts in the range of mesitylene > *p*-*tert*-butylbenzyl >> 3,5-bis(trifluoromethyl)benzyl were observed. No conversion was achieved using the corresponding palladium(II) acetates of **4h** and **5** as catalysts.[34] Secondary alcohols as starting materials were not oxidized.[35,36] From our experimental experiences, we can exclude formation of Pd black, and all catalysts showed activity even after two cycles, which underlines the stability and recyclability of the catalysts investigated here.

Table 1. Summarized results of the copper-free Wacker oxidation of alkenes using Pd complexes **4h**, **4i**, **4k**, and **5**[a].

	Substrate	Cat.	Ox.[c]	Yield [%][b] aldehyde	ketone	Conv. [%][b]
1	1-octene	**5**	O_2	–	35	36
		4h	O_2	–	80	94[c]
2	4-methylstyrene	**5**	O_2	25	1	34
		4h	O_2	33	27	87
3	vinylcyclohexane	**5**	O_2	–	3	5
		4h	O_2	–	67	72
4	1-octene	**5**	BQ	–	2	2
		4k	BQ	–	19	19
		4h	BQ	<1	99	>99
		4i	BQ	2	97	>99
5	vinylcyclohexane	**5**	BQ	–	3	3
		4k	BQ	–	6	6
		4h	BQ	–	61	62
		4i	BQ	–	83	83

[a] Reaction conditions: catalyst (5 mol-%), alkene (0.90 mM), O_2 (1 atm) or benzoquinone (3.00 equiv.) and *n*-undecane (10.0 μL) as internal standard in a dimethylacetamide (DMA)/water mixture (6:1) at 70 °C stirred for 17 h in a cap sealed vial (3 d with O_2). [b] Reactions were monitored and yields determined by GC and GC–MS analysis using a 25 m HP-5MS column and He as the inert carrier gas. [c] 11% of 1-octene isomers detected.

Conclusion

In summary, we have described a novel class (bcpz) of a sterically bulky ligand system, which features a rigid, bulky backbone yet still maintains flexibility and diversity through different substitution patterns (wingtips), thus allowing electronic and steric tuning of the ligands. Since redox potentials of transition-metal complexes are strongly influenced by steric effects, which may be enforced by the ligand backbone, the constant ligand sphere combined with variable and tunable substituents and the smaller cavity of 3,3′-bipyrazoles compared to the widely used 2,2′-bipyridines may help in developing new catalysts. The corresponding Cu^{II}, Co^{II}, and a series of Pd^{II} complexes were prepared and their conformational behavior was studied with regard to substitution in the solid, as well as in solution state using X-ray, CD, and VT ^1H NMR spectroscopic analyses. To the best of our knowledge, these complexes of **3h** represent the first examples of d^8 (Pd) and d^9 (Cu) 3,3′-bipyrazole complexes that coordinate through bidentate complexation. Initial catalytic investigations revealed that these palladium complexes showed higher activities with increasing electron donating properties induced by appropriate wingtip substitution [–CH_2R: Mes > *p*-*t*BuBn >> 3,5-$(CF_3)_2$Bn] in the copper-free Wacker oxidation of terminal alkenes. Furthermore, preliminary results in our laboratories showed excellent yields and selectivities in the Pd^{II}-catalyzed isomerization of allylbenzenes, which will be reported in due course. Therefore, it can be envisaged that our short and high-yielding synthetic protocol, combined with the versatility of the system, which allows a systematic screening of steric as well as electronic effects, will give rise to a number of new types of fused and even optional chiral 3,3′-bipyrazoles in the near future. Further experiments on the formation of tetradentate, bimetallic bcpz–metal complexes and their application in catalysis are underway.

Experimental Section

General Remarks: All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma–Aldrich or VWR and were used without further purification unless otherwise noted. Dichloromethane was freshly distilled from calcium hydride under an argon atmosphere; THF was freshly distilled from sodium under argon atmosphere. Deuterated solvents were purchased from Euriso-Top. Acetonitrile was dried by a MB SPS-800 with the aid of drying columns. Handling of air- and moisture-sensitive materials was carried out in flame-dried flasks under an atmosphere of argon using Schlenk techniques. NMR spectra were recorded with Bruker Avance 500, Bruker Avance 300, and Bruker ARX-250 spectrometers at room temp. Chemical shifts (in ppm) were referenced to residual solvent protons.[37] GC and GC–MS measurements were performed with a Thermo PolarisQ Trace GC–MS equipped with split injector (250 °C), free induction decay (FID; 250 °C), and a quadrupole ion-trap MS (Thermo, San Jose, CA). MS spectra were recorded with a Finnigan MAT TSQ 700 or a JEOL JMS-700 spectrometer. IR spectra were recorded with a Bruker Vector 22 FTIR. Elemental analyses were performed by the analytical laboratories of the chemical institute of the University of Heidelberg. Melting points were determined with a Büchi melting-point apparatus and temperatures were uncorrected. Crystal-structure analysis was accomplished with Bruker Smart CCD and Bruker APEX diffractometers.

2,2-Bipyridinepalladium(II) chloride (**5**) was synthesized starting from $[PdCl_2(MeCN)_2]$[39] according to a literature procedure.[40]

Bis{(1*R*,4*S*)-7,7-dimethyl-3-oxobicyclo[2.2.1]heptan-2-ylidene}-glyoxal (1): This compound was prepared using a modified procedure of the reported one.[38] Sodium hydride (0.87 g, 0.036 mol) was slowly added to a solution of (+)-camphor (5.00 g, 0.033 mol) in anhydrous THF (150 mL). The suspension was stirred under reflux heating (75 °C) for 3 d until the mixture turned into a yellow, clear solution. The solution was allowed to cool down to room temperature and half of the volume of diethyl oxalate (2.4 g, 0.016 mol) dissolved in anhydrous THF (100 mL) was added dropwise. After 2 h, the remaining diethyl oxalate solution was added dropwise and the orange solution was stirred under reflux for one day. The red solution was cooled to room temperature, and the solvent was evaporated under reduced pressure. Dichloromethane (200 mL) was added and the suspension was extracted three times with water (200 mL). The aqueous layer was acidified with aqueous 1 N hydrochloric acid and extracted with diethyl ether until the aqueous layer remained almost colorless. The organic layers were combined, washed with brine, dried with sodium sulfate, and the solvent removed under reduced pressure to obtain an orange powder. Purification by washings with a small amount of acetone and drying under high vacuum yielded **1** as a bright yellow powder

(5.47 g, 0.015 mmol, 93%); m.p. 178–186 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.84 [s, 6 H, 2× (–CH_3)], 0.93 [s, 6 H, 2× (–CH_3)], 0.99 [s, 6 H, 2× (–CH_2CCH_3)], 1.40–1.51 [m, 4 H, 2× (–CCH_2–)], 1.69–1.79 [m, 2 H, 2× (–$CHCH_2$–)], 2.01–2.10 [m, 2 H, 2× (–$CHCH_2$–)], 3.28 [d, J = 4.0 Hz, 2 H, 2× (–CH)], 11.83 [br. s, 2 H, 2× (–OH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 8.7, 18.6, 20.6, 27.1, 30.5, 48.5, 48.9, 57.9, 120.6, 155.3, 214.7 ppm. MS (EI): m/z (%) = 151 (15), 179 (100) $[C_{11}H_{15}O_2]^+$, 247 (94), 330 (54), 358 (34) $[M]^+$. HRMS (EI): m/z calcd. for $C_{22}H_{30}O_4$: 358.2144; found 358.2158. IR (KBr): $\tilde{\nu}$ = 3442, 2960, 2871, 1661, 1579, 1456, 1390, 1376, 1337, 1269, 1225, 1179, 1155, 1146, 1106, 1069, 1027, 826, 815 cm^{-1}. $C_{22}H_{30}O_4$ (358.48): calcd. C 73.71, H 8.44; found C 73.22, H 8.40.

7,7′,8,8,8′,8′-Hexamethyl-4,4′,5,5′,6,6′,7,7′-octahydro-1*H*,1′*H*-3,3′-bi-4,7-methanoindazole (2): Hydrazinium hydroxide (9.5 mL g^{-1}, 9.22 g, 0.184 mol) was added to a boiling solution of **1** (3.50 g, 9.76 mmol) in absolute ethanol (200 mL) at once through a short reflux condenser. After heating at reflux for two days, the precipitate was collected by hot filtration. The filtrate was concentrated under reduced pressure at 70 °C, and the formed precipitates were successively collected. Washings with ethyl acetate and drying under high vacuum yielded pure **2** (3.13 g, 8.93 mmol, 91%) as a fluffy, insoluble white powder; m.p. > 250 °C. MS (EI): m/z (%) = 55 (15), 77 (16), 67 (22), 121 (23), 133 (31), 159 (35), 176 (20) $[C_{11}H_{16}N_2]^+$, 177 (69), 187 (19), 220 (19), 307 (32) [M – (3× CH_3)]$^+$, 350 (17) $[M]^+$. HRMS (EI): m/z calcd. for $C_{22}H_{30}N_4$: 350.2470; found 350.2442. IR (KBr): $\tilde{\nu}$ = 3428, 3262, 2957, 2871, 1632, 1473, 1453, 1418, 1388, 1375, 1367, 1270, 1237, 1180, 1170, 1129, 1083, 969, 950 cm^{-1}. $C_{22}H_{30}N_4$ (350.51): calcd. C 75.39, H 8.63, N 15.98; found C 75.18, H 8.88, N 15.77.

General Procedure for Alkylation and Arylation of Bicamphorpyrazole 2. Syntheses of 3a–k: Compound **2** (1.00 equiv.) and NaH (2.30 equiv.) were suspended in anhydrous THF (10–50 mM, referenced to **2**), stirred for 30 min at room temperature, and heated at reflux for 2 h until they turned into a clear colorless solution. The solution was then cooled to room temperature and the appropriate amount of arylhalogenide (2.05 equiv.) was added. The solution was stirred at room temperature for 30 min and heated at reflux for 4–16 h. The precipitate was filtered off, and the solvent was evaporated under reduced pressure. The residue was taken up in CH_2Cl_2 and washed with water and brine. The organic phase was separated, dried with Na_2SO_4, and the solvent was evaporated under reduced pressure to yield the corresponding arylated compounds as analytically pure solids. In the case of alkylation, alkylhalogenides (2.20 equiv.) were added. Standard workup procedure and drying at elevated temperatures under high vacuum yielded pure alkylated compounds. Whenever necessary, the compounds were washed with small amounts of pentane.

1,1′-Diethyl-7,7′,8,8,8′,8′-hexamethyl-4,4′,5,5′,6,6′,7,7′-octahydro-1*H*,1′*H*-3,3′-bi-4,7-methanoindazole (3a): Compound **3a** was prepared following the standard procedure using **2** (150 mg, 0.427 mmol), sodium hydride (25 mg, 1.024 mmol), and ethyl bromide (116 μL, 0.938 mmol) in anhydrous THF (80 mL). The solution was heated at reflux for 16 h. Extensive drying at elevated temperature under high vacuum yielded pure **3a** (229 mg, 0.542 mmol, 97%) as a yellowish powder; m.p. 132–148 °C. ^{1}H NMR (300.13 MHz, CD_3CN): δ = 0.73 [s, 6 H, 2× (–CH_3)], 0.93 [s, 6 H, 2× (–CH_3)], 1.02–1.10 [m, 2 H, 2× (–CCH_2–)], 1.16–1.20 [m, 2 H, 2× (–CCH_2–)], 1.24 [t, J = 7.2 Hz, 6 H, 2× (–CH_2CH_3)], 1.34 [s, 6 H, 2× (–CH_2CCH_3)], 1.82–1.90 [m, 2 H, 2× (–$CHCH_2$–)], 2.08–2.17 [m, 2 H, 2× (–$CHCH_2$–)], 2.90 [d, J = 3.9 Hz, 2 H, 2× (–CCH)], 4.01 [q, J = 7.2 Hz, 4 H, 2× (–CH_2CH_3)] ppm. ^{13}C NMR (75.46 MHz, CD_3CN): δ = 11.9, 17.7, 20.2, 21.1, 28.7, 34.7, 46.1, 49.5, 53.7, 63.9, 127.3, 138.9, 155.4 ppm. MS (EI): m/z (%) = 73 (26), 133 (14), 355 (13), 377 (75), 406 (14), 420 (33) [M – (*n*-pentyl)]$^+$, 434 (11) [M – (*n*-butyl)]$^+$, 447 (73) [M – (3× CH_3)]$^+$, 420 (9) [M – (ethyl)]$^+$, 475 (9) [M – (CH_3)]$^+$, 490 (62) $[M]^+$. HRMS (EI): m/z calcd. for $C_{32}H_{50}N_4$: 490.4035; found 490.4018. IR (KBr): $\tilde{\nu}$ = 3428, 2957, 2870, 1632, 1504, 1451, 1386, 1378, 1365, 1352, 1310, 1282, 1247, 1133, 1107, 1082, 1060, 1049, 1029 cm^{-1}.

1,1′-Diisopropyl Derivative 3b: Compound **3b** was prepared following the standard procedure using **2** (200 mg, 0.571 mmol), sodium hydride (33 mg, 1.376 mmol), and isopropyl bromide (215 μL, 2.29 mmol) in anhydrous THF (90 mL). After 2 h at reflux temperature, additional isopropyl bromide (215 μL) was added. Extensive drying at elevated temperature under high vacuum yielded pure **3b** (236 mg, 0.542 mmol, 95%) as a yellowish powder; m.p. 155–162 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, TMS): δ = 0.74–0.68 [m, 2 H, 2× (–$CHCH_2$–)], 0.78 [s, 6 H, 2× (–CH_3)], 0.91 [s, 6 H, 2× (–CH_3)], 1.02–1.10 [m, 2 H, 2× (–$CHCH_2$–)], 1.36 [s, 6 H, 2× (–CH_2CCH_3)], 1.50 [d, J = 6.9 Hz, 6 H, 2× (–$NCHCH_3$)], 1.53 [d, J = 6.9 Hz, 6 H, 2× (–$NCHCH_3$)], 1.90–1.73 [m, 2 H, 2× (–$CHCH_2$–)], 2.02–2.15 [m, 2 H, 2× (–$CHCH_2$–)], 2.85 [d, J = 5.0 Hz, 2 H, 2× (–CCH)], 4.47 [q, J = 6.8 Hz, 2 H, 2× (–CH_2CH_3)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 12.5, 19.9, 20.6, 23.2, 23.4, 27.6, 34.1, 48.4, 51.9, 52.8, 62.4, 126.5, 137.7, 152.7 ppm. MS (EI): m/z (%) = 307 (11), 349 (60) [M – (2× *i*Pr)]$^+$, 355 (9), 377 (8), 391 (55) [M – (*i*Pr)]$^+$, 405 (8), 419 (20) [M – (CH_3)]$^+$, 434 (58) [M$^+$]. HRMS (EI): m/z calcd. for $C_{28}H_{42}N_4$: 434.3409; found 434.3405. IR (KBr): $\tilde{\nu}$ = 3394, 2954, 2869, 1627, 1474, 1452, 1386, 1373, 1366, 1269, 1250, 1234, 1082, 1058, 1020, 971, 954, 915 cm^{-1}.

1,1′-Dipentyl Derivative 3c: Compound **3** was prepared following the standard procedure using **2** (150 mg, 0.427 mmol), sodium hydride (25 mg, 1.024 mmol), and *n*-pentyl bromide (116 μL, 0.938 mmol) in anhydrous THF (80 mL). The solution was heated at reflux for 16 h. Extensive drying at elevated temperature under high vacuum yielded pure **3c** (229 mg, 0.542 mmol, 97%) as a yellowish, insoluble powder; m.p. > 250 °C. MS (EI): m/z (%) = 73 (26), 133 (14), 355 (13), 377 (75), 406 (14), 420 (33) [M – (*n*-pentyl)]$^+$, 434 (11) [M – (*n*-butyl)]$^+$, 447 (73) [M – (3× CH_3)]$^+$, 420 (9) [M – (ethyl)]$^+$, 475 (9) [M – (CH_3)]$^+$, 490 (62) $[M]^+$. HRMS (EI): m/z calcd. for $C_{32}H_{50}N_4$: 490.4035; found 490.4018. IR (KBr): $\tilde{\nu}$ = 3431, 2956, 2871, 1627, 1511, 1454, 1387, 1375, 1366, 1286, 1277, 1260, 1135, 1109, 1084, 1058, 1043, 1015, 1000 cm^{-1}.

1,1′-Bis(4-methoxybenzyl) Derivative 3d: Compound **3d** was prepared following the standard procedure using **2** (300 mg, 0.856 mmol), sodium hydride (45 mg, 1.883 mmol), and 4-methoxybenzyl chloride (246 μL, 1.75 mmol) in anhydrous THF (100 mL). The solution was heated at reflux for 4 h. After crystallization out of ethanol and washings with acetone, **3d** (398 mg, 0.676 mmol, 79%) was obtained as a yellowish powder; m.p. 151–154 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.78 [s, 6 H, 2× (–CH_3)], 0.87 [s, 6 H, 2× (–CH_3)], 1.07–1.09 [m, 2 H, 2× (–CCH_2–)], 1.10 [s, 6 H, 2× (–CH_2CCH_3)], 1.18–1.23 [m, 4 H, 2× (–CCH_2–)], 1.65–1.70 [m, 2 H, 2× (–$CHCH_2$–)], 2.06–2.08 [m, 2 H, 2× (–$CHCH_2$–)], 2.92 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 3.73 [s, 6 H, 2× (–OCH_3)], 5.32 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, –NCH_2–), 5.36 (d, $^2J_{H,H}$ = 16.0 Hz, 2 H, –NCH_2–), 6.68 [s, 2 H, 2× (ArH)], 6.73–6.77 [m, 4 H, 2× 2(ArH)], 7.17–7.20 [m, 2 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.3, 19.6, 20.4, 27.3, 33.4, 48.4, 52.4, 54.0, 55.2, 62.6, 112.0, 13.0, 119.1, 127.2, 129.3, 138.2, 140.2, 154.0, 159.7 ppm. MS (EI): m/z (%) = 121 (44) $[C_8H_9O]^+$, 469 (94) [M – (methoxybenzyl)]$^+$, 483 (17) [M –

$(C_8H_9O)]^+$, 547 (48), 575 (7) [M – $(CH_3)]^+$, 590 (100) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{38}H_{46}O_2N_4$: 590.3621; found 590.3585. IR (KBr): $\tilde{\nu}$ = 3436, 2955, 2871, 1602, 1587, 1491, 1455, 1437, 1387, 1365, 1348, 1281, 1261, 1147, 1117, 1085, 1045, 999 cm^{-1}.

1,1′-Dibenzyl Derivative 3e: Compound **3e** was prepared following the standard procedure using **2** (700 mg, 1.997 mmol), sodium hydride (115 mg, 4.792 mmol), and benzyl bromide (484 μL, 4.093 mmol) in anhydrous THF (110 mL). The solution was heated at reflux for 4 h. Compound **3e** (1.002 g, 1.888 mmol, 94%) was obtained as a yellowish powder; m.p. 151–161 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.76 [s, 6 H, 2× (–CH_3)], 0.86 [s, 6 H, 2× (–CH_3)], 1.07 [s, 6 H, 2× (–CH_2CCH_3)], 1.18–1.23 [m, 4 H, 2× (–CCH_2–)], 1.63–1.68 [m, 2 H, 2× (–$CHCH_2$–)], 2.02–2.07 [m, 2 H, 2× (–$CHCH_2$–)], 2.91 [d, J = 4.0 Hz, 2 H, 2× (–CCH)], 5.35 (d, $^2J_{H,H}$ = 16.0 Hz, 2 H, –NCH_2), 5.39 (d, $^2J_{H,H}$ = 16.0 Hz, 2 H, –NCH_2), 7.13–7.22 [m, 10 H, 2×5(ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.4, 19.8, 20.6, 27.5, 33.6, 48.6, 52.6, 54.2, 62.8, 126.9, 127.4, 128.5, 138.3, 138.8, 154.2 ppm. MS (EI): *m*/*z* (%) = 91 (95) $[C_7H_7]^+$, 439 (77) [M – (benzyl)]$^+$, 453 (14) [M – $(C_6H_5)]^+$, 487 (86) [M – $(3\times CH_3)]^+$, 515 (8) [M – $(CH_3)]^+$, 530 (100) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{36}H_{42}N_4$: 530.3409; found 530.3420. IR (KBr): $\tilde{\nu}$ = 3430, 2955, 2870, 1496, 1473, 1454, 1421, 1386, 1376, 1364, 1308, 1279, 1244, 1118, 1086, 1047, 1029, 999 cm^{-1}.

1,1′-Bis(4-methylbenzyl) Derivative 3f: Compound **3f** was prepared following the standard procedure using **2** (440 mg, 1.255 mmol), sodium hydride (72 mg, 3.014 mmol), and 4-methylbenzyl bromide (476 mg, 2.573 mmol) in anhydrous THF (100 mL). The solution was heated at reflux for 4 h. Compound **3f** (690 mg, 1.235 mmol, 98%) was obtained as a yellowish powder; m.p. 71–92 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, TMS): δ = 0.77 [s, 6 H, 2× (–CH_3)], 0.86 [s, 6 H, 2× (–CH_3)], 1.09 [s, 6 H, 2× (–CH_2CCH_3)], 1.16–1.31 [m, 4 H, 2× (–CCH_2–)], 1.61–1.70 [m, 2 H, 2× (–$CHCH_2$–)], 2.00–2.10 [m, 2 H, 2× (–$CHCH_2$–)], 2.30 (s, 6 H, $ArCH_3$), 2.91 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.30 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, –NCH_2–), 5.36 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, NCH_2–), 7.03–7.09 [m, 8 H, 4×2(ArH)] ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, TMS): δ = 11.4, 19.8, 20.6, 21.2, 27.5, 33.5, 48.6, 52.5, 54.0, 62.7, 126.8, 127.3, 129.1, 135.7, 136.9, 138.2, 154.0 ppm. MS (EI): *m*/*z* (%) = 105 (100) $[C_8H_9]^+$, 453 (90) [M – (*p*-xylenyl)]$^+$, 467 (14) [M – $(C_7H_7)]^+$, 515 (18) [M – $(3\times CH_3)]^+$, 543 (3) [M – $(CH_3)]^+$, 558 (65) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{38}H_{46}N_4$: 558.3722; found 558.3704. IR (KBr): $\tilde{\nu}$ = 3433, 2956, 2868 1515, 1472, 1453, 1422, 1386, 1375, 1364, 1352, 1309, 1298, 1280, 1118, 1085, 1046, 1020, 998 cm^{-1}.

1,1′-Bis(3-methylbenzyl) Derivative 3g: Compound **3g** was prepared following the standard procedure using **2** (500 mg, 1.427 mmol), sodium hydride (82 mg, 3.424 mmol), and 3-methylbenzyl bromide (541 mg, 2.923 mmol) in anhydrous THF (100 mL). The solution was heated at reflux for 4 h. Compound **3g** (730 g, 1.306 mmol, 92%) was obtained as a yellowish powder; m.p. 132–140 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, TMS): δ = 0.78 [s, 6 H, 2× (–CH_3)], 0.87 [s, 6 H, 2× (–CH_3)], 1.07 [s, 6 H, 2× (–CH_2CCH_3)], 1.09–1.26 [m, 4 H, 2× (–CCH_2–)], 1.63–1.71 [m, 2 H, 2× (–$CHCH_2$–)], 2.01–2.11 [m, 2 H, 2× (–$CHCH_2$–)], 2.28 (s, 6 H, $ArCH_3$), 2.92 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.34 [s, 4 H, 2× (–NCH_2–)], 6.92–7.16 [m, 8 H, 2×4(ArH)] ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, TMS): δ = 11.4, 19.8, 20.6, 21.5, 27.5, 33.6, 48.6, 52.6, 54.2, 62.8, 124.0, 127.4, 127.6, 128.1, 128.4, 138.1, 138.2, 138.6, 154.1 ppm. MS (EI): *m*/*z* (%) = 105 (92) $[C_8H_9]^+$, 453 (100) [M – (*m*-xylenyl)]$^+$, 467 (14) [M – $(C_7H_7)]^+$, 515 (19) [M – $(3\times CH_3)]^+$, 543 (4) [M – $(CH_3)]^+$, 558 (94) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{38}H_{46}N_4$: 558.3722; found 558.3690. IR (KBr): $\tilde{\nu}$ = 3435, 2952, 2869, 1609, 1504, 1493, 1455, 1435, 1424, 1386, 1374, 1365, 1347, 1275, 1117, 1081, 1045 cm^{-1}.

1,1′-Bis(4-*tert*-butylbenzyl) Derivative 3h: Compound **3h** was prepared following the standard procedure using **2** (500 mg, 1.427 mmol), sodium hydride (82 mg, 3.424 mmol), and 4-*tert*-butylbenzyl bromide (534 μL, 2.906 mmol) in anhydrous THF (100 mL). The solution was heated at reflux for 4 h. Compound **3h** (887 mg, 1.380 mmol, 97%) was obtained as a yellowish powder; m.p. 214–226 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, TMS): δ = 0.78 [s, 6 H, 2× (–CH_3)], 0.87 [s, 6 H, 2× (–CH_3)], 1.12 [s, 6 H, 2× (–CH_2CCH_3)], 1.17–1.30 [m, 22 H, 2× –*t*Bu, 2× (–CCH_2–)], 1.63–1.71 [m, 2 H, 2× (–$CHCH_2$–)], 2.00–2.10 [m, 2 H, 2× (–$CHCH_2$–)], 2.91 [d, J = 3.1 Hz, 2 H, 2× (–CCH)], 5.28 (d, $^2J_{H,H}$ = 15.7 Hz, 2 H, –NCH_2–), 5.36 (d, $^2J_{H,H}$ = 15.8 Hz, 2 H, –NCH_2–), 7.08–7.11 [m, 4 H, 2×2(ArH)], 7.27–7.29 [m, 4 H, 2×2(ArH)] ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, TMS): δ = 11.5, 19.8, 20.6, 27.5, 31.5, 33.6, 34.6, 48.5, 52.6, 53.9, 62.7, 125.3, 126.7, 127.2, 135.6, 138.3, 150.2, 154.1 ppm. MS (EI): *m*/*z* (%) = 147 (78) $[C_{11}H_{15}]^+$, 495 (100) [M – $(C_{11}H_{15})]^+$, 509 (13) [M – $(C_{10}H_{13})]^+$, 599 (19) [M – $(3\times CH_3)]^+$, 627 (5) [M – $(CH_3)]^+$, 643 (91) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{44}H_{58}N_4$: 642.4661; found 642.4662. IR (KBr): $\tilde{\nu}$ = 3455, 2952, 2869, 1609, 1504, 1493, 1455, 1435, 1424, 1386, 1374, 1365, 1347, 1275, 1117, 1081, 1045 cm^{-1}.

1,1′-Bis(2,4,6-trimethylbenzyl) Derivative 3i: Compound **3i** was prepared following the standard procedure using **2** (244 mg, 0.695 mmol), sodium hydride (40 mg, 1.667 mmol), and 2,4,6-trimethylbenzyl chloride (240 mg, 1.423 mmol) in anhydrous THF (50 mL). The solution was heated at reflux for 16 h. Compound **3i** (398 mg, 0.647 mmol, 93%) was obtained as a yellowish foam; m.p. 153–179 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.78 [s, 6 H, 2× (CH_3)], 0.85 [s, 6 H, 2× (–CH_3)], 0.96 [s, 6 H, 2× (–CH_2CCH_3)], 1.06–1.16 [m, 4 H, 2× (–CCH_2–)], 1.60–1.65 [m, 2 H, 2× (–$CHCH_2$–)], 1.98–2.03 [m, 2 H, 2× (–$CHCH_2$–)], 2.27 [s, 6 H, 2× ($ArCH_3$)], 2.29 [s, 12 H, 4× ($ArCH_3$)], 2.88 [d, J = 3.5 Hz, 2 H, 2× (–CCH)], 5.32 [s, 4 H, 2× (–NCH_2–)], 6.85 [s, 4 H, 4× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.5, 19.9, 20.6, 21.1, 27.4, 33.6, 48.2, 49.3, 53.3, 62.4, 127.1, 129.4, 130.6, 137.4, 138.1, 153.7 ppm. MS (EI): *m*/*z* (%) = 133 (100) $[C_{10}H_{13}]^+$, 481 (86) [M – $(C_{10}H_{13})]^+$, 495 (22) [M – (mesityl)]$^+$, 571 (24) [M – $(3\times CH_3)]^+$, 599 (5) [M – $(CH_3)]^+$, 614 (71) $[M]^+$. HRMS (EI): *m*/*z* calcd. for $C_{42}H_{54}N_4$: 614.4348; found 614.4359. IR (KBr): $\tilde{\nu}$ = 3442, 2956, 2869, 1614, 1487, 1463, 1425, 1386, 1375, 1365, 1284, 1261, 1237, 1118, 1080, 1050, 1032, 997 cm^{-1}.

Crystal Data for 3i: $C_{42}H_{54}N_4$, M_r = 614.89, 0.39×0.23×0.06 mm^3, triclinic, space group $P1$, a = 8.8223(13) Å, b = 10.7579(16) Å, c = 11.2401(17) Å, α = 109.734(3)°, β = 109.934(4)°, γ = 99.710(4)°, V = 894.1(2) $Å^3$, Z = 1, $\rho_{calcd.}$ = 1.14 $g\,cm^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 200(2) K, θ range = 2.1–26.4°; reflections measured 8286, independent 3645, R_{int} = 0.026. Final R indices [$I>2\sigma(I)$]: R_1 = 0.057, wR_2 = 0.126.

1,1′-Bis[(naphthalene-2-yl)methyl] Derivative 3j: Compound **3j** was prepared following the standard procedure using **2** (300 mg, 0.856 mmol), sodium hydride (49 mg, 2.043 mmol), and 2-(bromomethyl)naphthalene (382 mg, 1.728 mmol) in anhydrous THF (80 mL). The solution was heated at reflux for 4 h. Compound **3j** (519 mg, 0.823 mmol, 96%) was obtained as a white powder; m.p. 200–223 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, TMS): δ = 0.81 [s, 6 H, 2× (–CH_3)], 0.86 [s, 6 H, 2× (–CH_3)], 1.08 [s, 6 H, 2× (–CH_2CCH_3)], 1.10–1.30 [m, 4 H, 2× (–CCH_2–)], 1.61–1.70 [m, 2 H, 2× (–$CHCH_2$–)], 2.03–2.13 [m, 2 H, 2× (–$CHCH_2$–)], 2.96 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 5.57 [s, 4 H, 2× (–NCH_2–

)], 7.31–7.35 [m, 2 H, 2× (ArH)], 7.42–7.47 [m, 4 H, 2×2(ArH)], 7.59 [s, 2 H, 2× (ArH)], 7.75–7.82 [m, 6 H, 2×3(ArH)] ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$, TMS): δ = 11.5, 19.8, 20.6, 27.5, 33.6, 48.6, 52.6, 54.4, 62.8, 125.1, 125.4, 125.9, 126.2, 127.6, 127.8, 128.0, 128.3, 132.9, 133.4, 136.3, 138.4, 154.3 ppm. MS (EI): *m/z* (%) = 141 (100) $[C_{11}H_9]^+$, 489 (71) $[M - (C_{11}H_9)]^+$, 503 (8) [M – (2-naphthyl)]$^+$, 587 (8) $[M - 3\times(CH_3)]^+$, 615 (2) $[M - (CH_3)]^+$, 630 (44) $[M]^+$. HRMS (EI): *m/z* calcd. for $C_{44}H_{46}N_4$: 630.3722; found 630.3679. IR (KBr): $\tilde{\nu}$ = 3425, 2956, 2870, 1509, 1453, 1438, 1419, 1387, 1376, 1366, 1278, 1261, 1117, 1085, 1046, 1019, 999, 810 cm^{-1}.

Crystal Data for 3j: $C_{44}H_{46}N_4$, M_r = 630.85, 0.27×0.18×0.06 mm^3, triclinic, space group *P*1, *a* = 7.275984 Å, *b* = 11.44737(7) Å, *c* = 12.4101(7) Å, α = 116.572(1)°, β = 99.604(2)°, γ = 93.301(2)°, *V* = 901.19(9) Å^3, *Z* = 1, $\rho_{calcd.}$ = 1.16 g cm^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), *T* = 200(2) K, θ range = 1.9–21.7°; reflections measured 5207, independent 2098, R_{int} = 0.075. Final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.072, wR_2 = 0.167.

1,1′-Bis[3,5-bis(trifluoromethyl)benzyl] Derivative 3k: Compound **3k** was prepared following the standard procedure using **2** (300 mg, 0.856 mmol), sodium hydride (45 mg, 1.88 mmol), and 3,5-bis(trifluoromethyl)benzyl chloride (322 μL, 1.75 mmol) in anhydrous THF (90 mL). The solution was heated at reflux for 4 h. After crystallization out of diethyl ether and washings with pentane, **3k** (289 mg, 0.360 mmol, 42%) was obtained as a white powder; m.p. 155–158 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.80 [s, 6 H, 2× (–CH_3)], 0.90 [s, 6 H, 2× (–CH_3)], 1.08–1.25 [m, 8 H, 2× –CH_2CCH_3, 2× (–CCH_2–)], 1.19–1.25 [m, 2 H, 2× (–CCH_2–)], 1.75–1.80 [m, 2 H, 2× (–$CHCH_2$–)], 2.08–2.14 [m, 2 H, 2× (–$CHCH_2$–)], 3.00 [br. s, 2 H, 2× (–CCH)], 5.46 (d, $^2J_{H,H}$ = 16.5 Hz, 2 H, –NCH_2–), 5.52 (d, $^2J_{H,H}$ = 16.3 Hz, 2 H, –NCH_2–), 7.58 [s, 4 H, 4× (ArH)], 7.77 [s, 2 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.28, 19.5, 20.1, 27.1, 33.6, 48.4, 52.6, 53.0, 62.9, 121.5, 122.0, 124.2, 126.9, 128,1. 131.9, 140.9, 154.7 ppm. MS (EI): *m/z* (%) = 227 (11) $[C_9H_5F_6]^+$, 575 (23) [M – {3,5-bis(trifluormethyl)benzyl}]$^+$, 589 (4) $[M - (C_9H_5F_6)]^+$, 759 (100), 787 (7) $[M - (CH_3)]^+$, 803 (24) $[M]^+$. HRMS (EI): *m/z* calcd. for $C_{40}H_{38}F_{12}N_4$: 802.2905; found 802.2914. IR (KBr): $\tilde{\nu}$ = 3447, 2964, 2874, 1624, 1505, 1464, 1437, 1381, 1348, 1323, 1277, 1245, 1178, 1134, 1084, 1045, 906, 888 cm^{-1}.

General Procedure for the Preparation of bcpz–Palladium(II) Chloride Complexes 4a–k: $[Pd(MeCN)_2Cl_2]$ (1.00 equiv.) was added to a solution of the corresponding bipyrazole ligand **3** (1.00 equiv.) in anhydrous CH_2Cl_2, and the solution was stirred for 16 h at room temperature. The solvent was evaporated under reduced pressure, and the product was taken up in a small amount of chloroform and filtered though a short plug of silica. Evaporation and drying under high vacuum yielded the corresponding Pd(bcpz) complexes as deep orange to red microcrystalline solids.

Pd Complex 4a: Compound **4a** was prepared following the standard procedure using **3a** (94 mg, 0.231 mmol) and bis(acetonitrile)-dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4** (132 mg, 0.226 mmol, 98%) as an ochre-red powder; m.p. 147–158 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 4.84 [dddd, *J* = 7.1 Hz, *J* = 7.0 Hz, *J* = 7.0 Hz, $^2J_{H,H}$ = 14.1 Hz, 2 H, 2× (–NCH_2–)], 4.61 [dddd, *J* = 7.1 Hz, *J* = 7.0 Hz, *J* = 7.0 Hz, $^2J_{H,H}$ = 14.1 Hz, 2 H, 2× (–NCH_2–)], 2.86 [d, *J* = 3.4 Hz, 2 H, 2× (–CCH)], 2.11–2.16 [m, 2 H, 2× (–$CHCH_2$–)], 1.87–1.92 [m, 2 H, 2× (–$CHCH_2$–)], 1.41 [dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 6 H, 2× (–CH_2CCH_3)], 1.35 [s, 6 H, 2× (–CH_2CH_3)], 1.26–1.31 [m, 2 H, 2× (–CCH_2–)], 1.12–1.17 [m, 2 H, 2× (–CCH_2–)], 0.96 [s, 6 H, 2× (–CCH_3)], 0.76 [s, 6 H, 2× (–CCH_3)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.2, 17.5, 19.4, 20.4, 27.1, 33.6, 45.5, 47.9, 54.0, 63.2, 124.5, 138.6, 158.3 ppm. MS (FAB): *m/z* (%) = 511 (100) [M – (HCl), – $(Cl^-)]^+$, 546 (8) [M – $(Cl^-)]^+$, 953 (51) [M + (**L**), –$(Cl^-)]^+$, 1129 (13) [2× M – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{26}H_{37}N_4{}^{106}Pd^+$ [M – (HCl), – $(Cl^-)]^+$: 511.2053; found 511.2042. IR (KBr): $\tilde{\nu}$ = 3443, 2964, 2872, 1635, 1559, 1508, 1466, 1390, 1380, 1306, 1287, 1276, 1247, 1206, 1182, 1137, 1100, 1082, 1063, 1015 cm^{-1}. $C_{26}H_{38}Cl_2N_4Pd$·1/5$CHCl_3$: calcd. C 51.37, H 6.28, N 9.13, Cl 15.44, Pd 17.38; found C 51.25, H 6.46, N 9.28.

Pd Complex 4b: Compound **4b** was prepared following the standard procedure using **3b** (101 mg, 0.231 mmol) and bis(acetonitrile)dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4b** (134 mg, 0.219 mmol, 95%) as an ochre-red powder; m.p. 170–179 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.77 [s, 6 H, 2× (–CCH_3)], 0.96 [s, 6 H, 2× (–CCH_3)], 1.10–1.15 [m, 2 H, 2× (–CCH_2–)], 1.27–1.33 [m, 2 H, 2× (–CCH_2–)], 1.40–1.47 {m, 18 H, 2×[–$CH_2C(CH_3)_2$], 2× –(CH_2CCH_3)}, 1.83–1.90 [m, 2 H, 2× (–$CHCH_2$–)], 2.11–2.16 [m, 2 H, 2× (–$CHCH_2$–)], 2.87 [d, *J* = 3.7 Hz, 2 H, 2× (–CCH)], 5.84 [q, *J* = 6.9 Hz, 2 H, 2× (–NC*H*–)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 15.0, 19.8, 20.5, 22.5, 23.1, 27.0, 47.4, 54.4, 55.5, 62.9, 126.8, 137.8, 157.6 ppm. MS (FAB): *m/z* (%) = 539 (25) [M – (HCl), – $(Cl^-)]^+$, 1010 (14) [M + (**L**), –$(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{28}H_{41}N_4{}^{106}Pd^+$ [M – (HCl), – $(Cl^-)]^+$: 539.2377; found 539.2407. IR (KBr): $\tilde{\nu}$ = 3444, 2966, 2872, 1628, 1559, 1438, 1389, 1369, 1331, 1288, 1277, 1259, 1207, 1181, 1136, 1104, 1083, 1049, 998 cm^{-1}. $C_{28}H_{42}Cl_2N_4Pd$·1/3$CHCl_3$: calcd. C 50.96, H 6.38, N 8.34; found C 50.93, H 6.47, N 8.55.

Pd Complex 4c: Compound **4c** was prepared following the standard procedure using **3c** (114 mg, 0.231 mmol) and bis(acetonitrile)-dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4c** (134 mg, 0.211 mmol, 91%) as an ochre red powder; m.p. 149–154 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.76 [s, 6 H, 2× (–CCH_3)], 0.89 [t, *J* = 7.4 Hz, 6 H, 2× (–CH_2CH_3)], 0.96 [s, 6 H, 2× (–CCH_3)], 1.13–1.17 [m, 2 H, 2× (–*CH*CH–)], 1.26–1.37 [m, 16 H, 2× (–$CHCH_2CH_2$–), 2× (–$CHCH_2CH_2$–), 2× (–CH_2CCH_3)], 1.78–1.89 [m, 4 H, 2× (–$CH_2CH_2CH_3$)], 2.00 (s, 2 H, –CH_2CH_2–), 2.11–2.16 [m, 2 H, 2× (–CH_2CH_2–)], 2.85 [d, *J* = 3.8 Hz, 2 H, 2× (–CCH)], 4.52 (ddd, *J* = 9.4 Hz, *J* = 6.0 Hz, $^2J_{H,H}$ = 13.8 Hz, 2 H, –NCH_2–), 4.73 (ddd, *J* = 9.4 Hz, *J* = 6.3 Hz, $^2J_{H,H}$ = 14.0 Hz, 2 H –NCH_2–) ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.3, 14.2, 19.4, 20.4, 22.5, 27.1, 28.8, 32.0, 33.6, 47.9, 50.4, 54.0, 63.2, 124.3, 138.6, 158.4 ppm. MS (FAB): *m/z* (%) = 595 (84) [M – (HCl), – $(Cl^-)]^+$, 631 (4) [M – $(Cl^-)]^+$, 1121 (1) [M + (**L**), –$(Cl^-)]^+$, 1297 (7) [2× M – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{32}H_{49}N_4{}^{106}Pd^+$ [M – (HCl), – $(Cl^-)]^+$: 595.2992; found 595.2990. IR (KBr): $\tilde{\nu}$ = 3445, 2959, 2931, 2871, 1627, 1465, 1390, 1378, 1307, 1287, 1276, 1247, 1206, 1184, 1137, 1105, 1086, 1067, 1015, 1000 cm^{-1}. $C_{32}H_{50}Cl_2N_4Pd$·5/6$CHCl_3$: calcd. C 51.38, H 6.68, N 7.63; found C 51.42, H 6.62, N 7.72.

Pd Complex 4d: Compound **4d** was prepared following the standard procedure using **3d** (114 mg, 0.193 mmol) and bis(acetonitrile)dichloropalladium(II) (50 mg, 0.193 mmol) in anhydrous acetonitrile (10 mL) to yield **4d** (145 mg, 0.189 mmol, 97%) as a deep orange powder; m.p. 218–222 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.74 [s, 6 H, 2× (–CCH_3)], 0.92 [s, 6 H, 2× (–CCH_3)], 1.06–1.15 [m, 4 H, 2× (–CH_2CH_2–), 2× (–CH_2CH_2–)], 1.23 [s, 6 H, 2× (–CH_2CCH_3)], 1.72–1.76 [m, 2 H, 2× (–CH_2CH_2–)], 2.08–2.13 [m, 2 H, 2× (–CH_2CH_2–)], 2.87 [d, *J* = 3.7 Hz, 2 H, 2× (–CCH)], 5.83 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H,

–NCH_2–), 6.18 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, –NCH_2–), 6.78–6.87 [m, 4 H, 2× 2(ArH)], 6.86–6.87 [m, 2 H, 2× (ArH)], 7.20–7.23 [m, 2 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.1, 19.2, 20.3, 26.8, 32.7, 47.7, 53.3, 54.0, 55.3, 63.2, 112.8, 113.3, 119.3, 125.5, 129.6, 138.3, 139.0, 159.5, 159.7 ppm. MS (FAB): *m/z* (%) = 695 (96) [M – (HCl), – (Cl^-)]$^+$, 733 (24) [M – (Cl^-)]$^+$, 1323 (19) [M + (**L**), – (Cl^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{38}H_{46}{}^{35}ClN_4O_2{}^{108}Pd^+$ [M]$^+$: 733.2347; found 733.2348. IR (KBr): $\tilde{\nu}$ = 3427, 2962, 2874, 1602, 1586, 1491, 1456, 1437, 1390, 1369, 1349, 1305, 1284, 1261, 1148, 1123, 1103, 1046, 1017 cm^{-1}. $C_{38}H_{46}Cl_2N_4O_2Pd\cdot 1/11CHCl_3$: calcd. C 57.93, H 5.88, N 7.07; found C 57.43, H 6.06, N 6.84.

Pd Complex 4e: Compound **4e** was prepared following the standard procedure using **3e** (123 mg, 0.231 mmol) and bis(acetonitrile) dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4e** (158 mg, 0.223 mmol, 96%) as a deep orange powder; m.p. 164–170 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.72 [s, 6 H, 2× (–CCH_3)], 0.90 [s, 6 H, 2× (–CCH_3)], 1.00–1.14 [m, 4 H, 2× (–CH_2CH_2–)], 2× (–CH_2CH_2–)], 1.19 [s, 6 H, 2× (–CH_2CCH_3)], 1.68–1.73 [m, 2 H, 2× (–CH_2CH_2–)], 2.06–2.12 [m, 2 H, 2× (–CH_2CH_2–)], 2.86 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.85 (d, $^2J_{H,H}$ = 15.8 Hz, 2 H, –NCH_2–), 6.23 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, –NCH_2–), 7.23–7.32 [m, 10 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.2, 19.4, 20.4, 26.9, 32.8, 47.9, 53.6, 54.2, 63.4, 125.7, 127.3, 127.9, 128.7, 137.1, 139.1, 159.7 ppm. MS (FAB): *m/z* (%) = 635 (82) [M – (HCl), – (Cl^-)]$^+$, 671 (26) [M – (Cl^-)]$^+$, 1203 (4) [M + (**L**), – (Cl^-)]$^+$, 1381 (6) [2× M – (Cl^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{36}H_{42}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 671.2143; found 699.2164. IR (KBr): $\tilde{\nu}$ = 3442, 2962, 2871, 1626, 1606, 1497, 1454, 1391, 1379, 1369, 1315, 1287, 1276, 1247, 1182, 1124, 1103 cm^{-1}. $C_{36}H_{42}Cl_2N_4Pd\cdot 1/11CHCl_3$: calcd. C 60.22, H 5.89, N 7.78; found C 60.17, H 6.06, N 7.87.

Pd Complex 4f: Compound **4f** was prepared following the standard procedure using **3f** (129 mg, 0.231 mmol) and bis(acetonitrile) dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4f** (166 mg, 0.226 mmol, 98%) as a deep orange powder; m.p. 151–160 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.72 [s, 6 H, 2× (–CCH_3)], 0.90 [s, 6 H, 2× (–CCH_3)], 1.02–1.11 [m, 4 H, 2× (–CH_2CH_2–)], 1.22 [s, 6 H, 2× (–CH_2CCH_3)], 1.69–1.74 [m, 2 H, 2× (–CH_2CH_2–)], 2.06–2.11 [m, 2 H, 2× (–CH_2CH_2–)], 2.31 [s, 6 H, 2× ($ArCH_3$)], 2.85 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 5.77 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, –NCH_2–), 6.18 (d, $^2J_{H,H}$ = 15.5 Hz, 2 H, –NCH_2–), 7.11 [d, J = 8.0 Hz, 4 H, 2× (ArH)], 7.18 [d, J = 8.0 Hz, 4 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.3, 19.4, 20.4, 21.3, 26.9, 32.8, 47.9, 53.4, 54.1, 63.3, 125.6, 127.3, 129.4, 134.0, 137.6, 139.1, 159.5 ppm. MS (FAB): *m/z* (%) = 663 (91) [M – (HCl), – (Cl^-)]$^+$, 699 (30) [M – (Cl^-)]$^+$, 1258 (19) [M + (**L**), – (Cl^-)]$^+$, 1438 (6) [2× M – (Cl^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{38}H_{46}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 699.2457; found 699.2419. IR (KBr): $\tilde{\nu}$ = 3432, 2963, 2872, 1617, 1516, 1457, 1390, 1369, 1316, 1287, 1276, 1248, 1205, 1184, 1124, 1103, 1072, 1050, 1018 cm^{-1}. $C_{38}H_{46}Cl_2N_4Pd\cdot 1/8CHCl_3$: calcd. C 60.83, H 6.19, N 7.44; found C 60.89, H 6.37, N 7.30.

Pd Complex 4g: Compound **4g** was prepared following the standard procedure using **3g** (129 mg, 0.231 mmol) and bis(acetonitrile)dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4g** (166 mg, 0.224 mmol, 97%) as a deep orange powder; m.p. 143–147 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.73 [s, 6 H, 2× (–CCH_3)], 0.91 [s, 6 H, 2× (–CCH_3)], 1.04–1.14 [m, 4 H, 2× (–CH_2CH_2–)], 1.19 [s, 6 H, 2× (–CH_2CCH_3)], 1.70–1.75 [m, 2 H, 2× (–CH_2CH_2–)], 2.08–2.13 [m, 2 H, 2× (–CH_2CH_2–)], 2.31 [s, 6 H, 2× ($ArCH_3$)], 2.87 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 5.84 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, –NCH_2–), 6.16 (d, $^2J_{H,H}$ = 15.9 Hz, 2 H, –NCH_2–), 7.01–7.06 [m, 6 H, 2× (3ArH)], 7.17–7.20 [m, 2 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.2, 19.4, 20.4, 21.6, 26.9, 32.8, 47.9, 53.5, 54.1, 63.3, 124.2, 125.6, 127.8, 128.6, 128.7, 137.0, 138.3, 139.1, 159.6 ppm. MS (FAB): *m/z* (%) = 663 (25) [M – (HCl), – (Cl^-)]$^+$, 699 (30) [M – (Cl^-)]$^+$, 1259 (2) [M + (**L**), –(Cl^-)]$^+$, 1439 (3) [2× M – (Cl^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{38}H_{46}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 699.2457; found 699.2478. IR (KBr): $\tilde{\nu}$ = 3453, 2963, 2871, 1609, 1490, 1456, 1390, 1378, 1369, 1348, 1306, 1287, 1276, 1248, 1184, 1123, 1104, 1092 cm^{-1}. $C_{38}H_{46}Cl_2N_4Pd\cdot 1/8CHCl_3$: calcd. C 60.83, H 6.18, N 7.44; found C 60.69, H 6.36, N 7.41.

Pd Complex 4h: Compound **4h** was prepared following the standard procedure using **3h** (149 mg, 0.231 mmol) and bis(acetonitrile)dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4h** (187 mg, 0.224 mmol, 97%) as a deep orange powder; m.p. 203–205 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.74 [s, 6 H, 2× (–CCH_3)], 0.92 [s, 6 H, 2× (–CCH_3)], 1.05–1.14 [m, 4 H, 2× (–CH_2CH_2–)], 1.24 [s, 6 H, 2× (–CH_2CCH_3)], 1.29 {s, 18 H, 2×[–$C(CH_3)_3$]}, 1.72–1.76 [m, 2 H, 2× (–CH_2CH_2–)], 2.08–2.13 [m, 2 H, 2× (–CH_2CH_2–)], 2.87 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 5.81 (d, $^2J_{H,H}$ = 15.8 Hz, 2 H –NCH_2–), 6.18 (d, $^2J_{H,H}$ = 15.8 Hz, 2 H, –NCH_2–), 7.19 [d, J = 8.3 Hz, 4 H, 2× (ArH)], 7.32 [d, J = 8.4 Hz, 4 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.1, 19.2, 20.3, 26.8, 32.7, 34.5, 47.8, 53.0, 54.0, 63.2, 125.4, 126.9, 133.7, 139.0, 150.7, 159.4 ppm. MS (FAB): *m/z* (%) = 747 (45) [M – (HCl), – (Cl^-)]$^+$, 783 (19) [M – (Cl^-)]$^+$, 1427 (3) [M + (**L**), –(Cl^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{58}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 783.3398; found 783.3434. IR (KBr): $\tilde{\nu}$ = 3445, 2961, 2871, 1622, 1514, 1458, 1415, 1391, 1367, 1316, 1276, 1247, 1205, 1193, 1125, 1050, 1019, 1001 cm^{-1}. $C_{44}H_{58}Cl_2N_4Pd\cdot 1/9CHCl_3$: calcd. C 63.45, H 7.01, N 6.71; found C 63.47, H 7.19, N 6.82.

Crystal Data for 4h: $C_{38}H_{46}Cl_2N_4Pd$, M_r = 736.09, 0.15 × 0.14 × 0.01 mm^3, monoclinic, space group $P2_1$, a = 16.196(5) Å, b = 10.248(3) Å, c = 21.795(7) Å, α = 90°, β = 96.143(4)°, γ = 90°, V = 3596.6(19) Å^3, Z = 4, $\rho_{calcd.}$ = 1.36 g cm^{-3}, Mo-K_α radiation (synchrotron, λ = 0.80000 Å), T = 150 K, θ range = 1.86–31.57°; reflections measured 97835, independent 15609, R_{int} = 0.040. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.027, wR_2 = 0.057.

Pd Complex 4h$^{(OAc)}$: Compound **4h$^{(OAc)}$** was prepared following the standard procedure using **3h** (100 mg, 0.156 mmol) and palladium(II) acetate (35 mg, 0.156 mmol) in anhydrous dichloromethane (12 mL) to yield **4h$^{(OAc)}$** (129 mg, 0.149 mmol, 96%) as a white powder. Decomp. > 170 °C. ^{1}H NMR (399.89 MHz, CD_2Cl_2): δ = 0.75 [s, 6 H, 2× (–CCH_3)], 0.90 [s, 6 H, 2× (–CCH_3)], 1.08 [s, 6 H, 2× (–CH_2CCH_3)], 1.12–1.20 [m, 4 H, 2× (–CH_2CH_2–)], 1.30 {s, 18 H, 2×[–$C(CH_3)_3$]}, 1.49 [s, 6 H, 2× (–OAc)], 1.69–1.75 [m, 2 H, 2× (–CH_2CH_2–)], 2.07–2.14 [m, 2 H, 2× (–CH_2CH_2–)], 2.92 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.35 (d, $^2J_{H,H}$ = 16.1 Hz, 2 H –NCH_2–), 5.47 (d, $^2J_{H,H}$ = 16.2 Hz, 2 H, –NCH_2–), 7.06 [d, J = 8.3 Hz, 4 H, 2× (ArH)], 7.37 [d, J = 8.3 Hz, 4 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.0, 19.3, 20.4, 22.7, 27.0, 31.5, 32.9, 34.7, 47.9, 52.5, 53.9, 63.1, 125.7, 126.3, 133.4, 138.0, 150.8, 158.3, 179.1 ppm. MS (FAB): *m/z* (%) = 747 (100) [M – (HOAc), – (OAc^-)]$^+$, 1391 (15) [M + (**L**), –2× (OAc^-)]$^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{57}N_4{}^{106}Pd^+$ [M]$^+$: 747.3634; found 747.3631. IR (KBr): $\tilde{\nu}$ = 3432, 2961, 2871, 1638, 1581, 1515, 1458, 1414, 1391, 1367, 1288, 1262, 1206, 1184, 1128, 1108, 1017 cm^{-1}. $C_{48}H_{64}N_4O_4Pd\cdot 1/9CHCl_3$: calcd. C 66.46, H 7.44, N 6.46; found C 65.41, H 7.47, N 6.39.

Pd Complex 4h$^{(OAc)}$: Compound **4h**$^{(OAc)}$ was prepared following the standard procedure using **3h** (100 mg, 0.156 mmol) and palladium(II) acetate (35 mg, 0.156 mmol) in anhydrous dichloromethane (12 mL) to yield **4h**$^{(OAc)}$ (129 mg, 0.149 mmol, 96%) as a white powder. Decomp. > 170 °C. ^{1}H NMR (399.89 MHz, CD_2Cl_2): δ = 0.75 [s, 6 H, 2× (–CCH$_3$)], 0.90 [s, 6 H, 2× (–CCH$_3$)], 1.08 [s, 6 H, 2× (–CH$_2$CC*H*$_3$)], 1.12–1.20 [m, 4 H, 2× (–CH$_2$C*H*$_2$–)], 1.30 {s, 18 H, 2×[–C(CH$_3$)$_3$]}, 1.49 [s, 6 H, 2× (–OAc)], 1.69–1.75 [m, 2 H, 2× (–C*H*$_2$CH$_2$–)], 2.07–2.14 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 2.92 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.35 (d, $^2J_{H,H}$ = 16.1 Hz, 2 H –NCH$_2$–), 5.47 (d, $^2J_{H,H}$ = 16.2 Hz, 2 H, –NCH$_2$–), 7.06 [d, J = 8.3 Hz, 4 H, 2× (ArH)], 7.37 [d, J = 8.3 Hz, 4 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 11.0, 19.3, 20.4, 22.7, 27.0, 31.5, 32.9, 34.7, 47.9, 52.5, 53.9, 63.1, 125.7, 126.3, 133.4, 138.0, 150.8, 158.3, 179.1 ppm. MS (FAB): *m*/*z* (%) 747 (100) [M – (HOAc), – (OAc$^-$)]$^+$, 1391 (15) [M + (**L**), –2× (OAc$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{57}N_4{}^{106}Pd^+$ [M]$^+$: 747.3634; found 747.3631. IR (KBr): $\tilde{\nu}$ = 3432, 2961, 2871, 1638, 1581, 1515, 1458, 1414, 1391, 1367, 1288, 1262, 1206, 1184, 1128, 1108, 1017 cm^{-1}. $C_{48}H_{64}N_4O_4Pd\cdot 1/9CHCl_3$: calcd. C 66.46, H 7.44, N 6.46; found C 65.41, H 7.47, N 6.39.

Pd Complex 4i: Compound **4i** was prepared following the standard procedure using **3i** (142 mg, 0.231 mmol) and bis(acetonitrile)-dichloropalladium(II) (60 mg, 0.231 mmol) in anhydrous acetonitrile (10 mL) to yield **4i** (173 mg, 0.218 mmol, 95%) as an ochre red powder; m.p. 162–172 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.60 [s, 6 H, 2× (–CCH$_3$)], 0.68 [s, 6 H, 2× (–CCH$_3$)], 0.81 [s, 6 H, 2× (–CH$_2$CC*H*$_3$)], 0.85–0.91 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 1.05–1.10 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 1.47–1.52 [m, 2 H, 2× (–C*H*$_2$CH$_2$–)], 2.02–2.07 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 2.10 [s, 12 H, 2× (ArCH$_3$)], 2.24 [s, 6 H, 2× (ArCH$_3$)], 2.81 [d, J = 3.6 Hz, 2 H, 2× (–CCH)], 5.74 (d, $^2J_{H,H}$ = 16.6 Hz, 2 H, –NCH$_2$–), 6.35 (d, $^2J_{H,H}$ = 16.6 Hz, 2 H, –NCH$_2$–), 6.78 [s, 4 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 10.5, 19.5, 20.4, 20.5, 21.0, 27.2, 32.2, 47.7, 51.8, 55.3, 63.1, 126.7, 130.0, 137.3, 137.7, 137.8, 159.0 ppm. MS (FAB): *m*/*z* (%) = 719 (59) [M – (HCl), – (Cl$^-$)]$^+$, 754 (5) [M – (Cl$^-$)]$^+$, 1371 (6) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{42}H_{54}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 755.3084; found 755.3137. IR (KBr): $\tilde{\nu}$ = 3447, 2960, 2874, 1613, 1483, 1457, 1423, 1390, 1379, 1323, 1288, 1277, 1261, 1246, 1182, 1125, 1099, 1031, 1016, 850 cm^{-1}. $C_{42}H_{54}Cl_2N_4Pd\cdot 1/4CHCl_3$: calcd. C 61.11, H 6.58, N 6.73; found C 61.01, H 6.66, N 6.85.

Pd Complex 4j: Compound **4j** was prepared following the standard procedure using **3j** (150 mg, 0.238 mmol) and bis(acetonitrile)-dichloropalladium(II) (62 mg, 0.238 mmol) in anhydrous acetonitrile (10 mL) to yield **4j** (173 mg, 0.225 mmol, 95%) as a deep orange powder; m.p. 158–170 °C. ^{1}H NMR (500.13 MHz, CD_2Cl_2, TMS): δ = 0.78 [s, 6 H, 2× (–CCH$_3$)], 0.91 [s, 6 H, 2× (–CCH$_3$)], 1.03–1.19 [m, 4 H, 2× (–CH$_2$C*H*$_2$–)], 1.21 [s, 6 H, 2× (–CH$_2$CC*H*$_3$)], 1.69–1.77 [m, 2 H, 2× (–C*H*$_2$CH$_2$–)], 2.07–2.17 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 2.96 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 6.05 (d, $^2J_{H,H}$ = 16.2 Hz, 2 H, –NCH$_2$–), 6.40 (d, $^2J_{H,H}$ = 16.2 Hz, 2 H, –NCH$_2$–), 7.41–7.52 [m, 6 H, 2× (ArH)], 7.62 [s, 2 H, 2× (ArH)], 7.81–7.87 [m, 7 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, CD_2Cl_2, TMS): δ = 11.4, 19.5, 20.6, 27.2, 33.3, 48.5, 63.8, 125.3, 126.0, 126.4, 126.7, 126.9, 128.2, 128.4, 129.0, 133.4, 133.8, 135.4, 139.7, 160.4 ppm. MS (FAB): *m*/*z* (%) = 735 (63) [M – (HCl), – (Cl$^-$)]$^+$, 771 (8) [M – (Cl$^-$)]$^+$, 1402 (4) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{46}{}^{35}ClN_4{}^{106}Pd^+$ [M]$^+$: 771.2459; found 771.2455. IR (KBr): $\tilde{\nu}$ = 3446, 3115, 2963, 2872, 1654, 1634, 1602, 1509, 1457, 1424, 1390, 1378, 1370, 1329, 1286, 1275, 1248, 1124 cm^{-1}. $C_{28}H_{42}Cl_2N_4Pd\cdot 1/8CHCl_3$: calcd. C 64.25, H 5.64, N 6.79; found C 64.06, H 5.74, N 6.87.

Pd Complex 4k: Compound **4k** was prepared following the standard procedure using **3k** (102 mg, 0.127 mmol) and bis(acetonitrile)dichloropalladium(II) (33 mg, 0.127 mmol) in anhydrous acetonitrile (10 mL) to yield **4k** (120 mg, 0.122 mmol, 96%) as a yellow powder; m.p. 145–148 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, TMS): δ = 0.78 [s, 6 H, 2× (–CCH$_3$)], 0.96 [s, 6 H, 2× (–CCH$_3$)], 1.14 [s, 6 H, 2× (–CH$_2$CC*H*$_3$)], 1.16–1.25 [m, 4 H, 2× (–CH$_2$C*H*$_2$–), 2× (–C*H*$_2$CH$_2$–)], 1.84–1.89 [m, 2 H, 2× (–C*H*$_2$CH$_2$–)], 2.17–2.23 [m, 2 H, 2× (–CH$_2$C*H*$_2$–)], 2.97 [d, J = 3.7 Hz, 2 H, 2× (–CCH)], 6.10 (d, $^2J_{H,H}$ = 16.7 Hz, 2 H, –NCH$_2$–), 6.32 (d, $^2J_{H,H}$ = 16.7 Hz, 2 H, –NCH$_2$–), 7.52 (s, 4 H, 4× (ArH), 7.80 [s, 2 H, 2× (ArH)] ppm. ^{13}C NMR (125.75 MHz, $CDCl_3$, TMS): δ = 10.9, 19.1, 20.0, 26.7, 33.0, 47.9, 52.5, 54.1, 63.6, 119.7, 121.7, 124.1, 126.3, 126.5, 132.1, 132.0, 139.3, 140.0, 159.9 ppm. MS (FAB): *m*/*z* (%) = 907 (100) [M – (HCl), – (Cl$^-$)]$^+$, 945 (26) [M – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{40}H_{38}{}^{35}ClF_{12}N_4{}^{108}Pd^+$ [M]$^+$: 945.1632; found 945.1594. IR (KBr): $\tilde{\nu}$ = 3446, 2965, 2026, 1973, 1624, 1457, 1382, 1351, 1280, 1175, 1136, 1017, 907, 845 cm^{-1}. $C_{36}H_{42}Cl_2N_4Pd\cdot 1/13CHCl_3$: calcd. C 48.63, H 3.88, N 5.66; found C 48.39, H 4.02, N 5.54.

Co Complex 4h$^{(Co)}$: Compound **4h**$^{(Co)}$ was prepared following the standard procedure using **3h** (49.9 mg, 0.078 mmol) and cobalt(II) chloride hexahydrate (18.5 mg, 0.078 mmol) in absolute ethanol (3 mL) to yield **4h**$^{(Co)}$ (54.2 mg, 0.070 mmol, 90%) as a fluffy, pale purple solid; m.p. 170–178 °C. MS (FAB): *m*/*z* (%) = 700 (2) [M – (HCl), – (Cl$^-$)]$^+$, 736 (100) [M – (Cl$^-$)]$^+$, 1378 (11) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{58}{}^{35}ClN_4Co^+$ [M]$^+$: 736.3682; found 736.3704. IR (KBr): $\tilde{\nu}$ = 3434, 2963, 2871, 1619, 1516, 1455, 1427, 1391, 1366, 1337, 1319, 1273, 1248, 1204, 1183, 1129, 1107, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CoN_4\cdot 1/15CHCl_3$: calcd. C 67.75, H 7.49, N 7.17; found C 67.87, H 7.59, N 7.19.

Co Complex 4j$^{(Co)}$: Compound **4j**$^{(Co)}$ was prepared following the standard procedure using **3j** (47.8 mg, 0.076 mmol) and cobalt(II) chloride hexahydrate (18.0 mg, 0.076 mmol) in absolute ethanol (3 mL) to yield **4j**$^{(Co)}$ (53.7 mg, 0.071 mmol, 93%) as a fluffy, pale purple solid; m.p. 145–151 °C. MS (FAB): *m*/*z* (%) = 688 (6) [M – (HCl), – (Cl$^-$)]$^+$, 724 (93) [M – (Cl$^-$)]$^+$, 1354 (1) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{46}{}^{35}ClN_4{}^{63}Co^+$ [M]$^+$: 724.2743; found 724.2808. IR (KBr): $\tilde{\nu}$ = 3434, 3052, 2963, 1689, 1635, 1558, 1542, 1509, 1455, 1372, 1329, 1287, 1274, 1248, 1126, 1103 cm^{-1}. $C_{44}H_{46}Cl_2CoN_4\cdot 1/5CHCl_3$: calcd. C 67.66, H 5.94, N 7.14; found C 67.52, H 6.07, N 7.11.

Cu Complex 4h$^{(Cu)}$: Compound **4h**$^{(Cu)}$ was prepared following the standard procedure using **3h** (50.9 mg, 0.079 mmol) and copper(II) chloride dihydrate (13.5 mg, 0.079 mmol) in absolute ethanol (3 mL) to yield **4h**$^{(Cu)}$ (53.7 mg, 0.071 mmol, 89%) as a fine, red powder; m.p. 174–181 °C. MS (FAB): *m*/*z* (%) = 704 (11) [M – (HCl), – (Cl$^-$)]$^+$, 740 (49) [M – (Cl$^-$)]$^+$, 1382 (9) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{58}{}^{35}ClN_4Cu^+$ [M]$^+$: 740.3646; found 736.3624. IR (KBr): $\tilde{\nu}$ = 3439, 2963, 2872, 1626, 1558, 1542, 1515, 1456, 1391, 1365, 1339, 1319, 1275, 1248, 1183, 1129, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CuN_4\cdot 1/6CHCl_3$: calcd. C 66.53, H 7.35, N 7.03; found C 66.64, H 7.46, N 7.05.

Cu Complex 4j$^{(Cu)}$: Compound **4j**$^{(Cu)}$ was prepared following the standard procedure using **3j** (54.1 mg, 0.086 mmol) and copper(II) chloride dihydrate (14.6 mg, 0.086 mmol) in absolute ethanol (3 mL) to yield **4j**$^{(Cu)}$ (59.5 mg, 0.078 mmol, 91%) as a fine, red powder; m.p. 131–138 °C. MS (FAB): *m*/*z* (%) = 692 (9) [M – (HCl), – (Cl$^-$)]$^+$, 728 (44) [M – (Cl$^-$)]$^+$, 1358 (1) [M + (**L**), – (Cl$^-$)]$^+$. HRMS (FAB): *m*/*z* (%) calcd. for $C_{44}H_{46}{}^{35}ClN_4{}^{63}Cu^+$ [M]$^+$: 728.2707; found 728.2678. IR (KBr): $\tilde{\nu}$ = 3431, 3053, 2963, 2873, 1634, 1510, 1455, 1390, 1370, 1330, 1287, 1275, 1248, 1185,

1126, 1102, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CuN_4 \cdot 1/3CHCl_3$: calcd. C 64.78, H 5.68, N 6.79; found C 64.91, H 5.79, N 6.97.

General Procedure for the Preparation of bcpz Cobalt(II) and Copper(II) Complexes: Cobalt(II) chloride hexahydrate or copper(II) chloride dihydrate (1 equiv.), respectively, were added to a solution of the corresponding bipyrazole ligand (1 equiv.) in absolute ethanol. The solution lightened and became cloudy. After 16 h at room temperature, the solvent was evaporated, and the residue was dissolved in a small amount of chloroform and filtered through a short plug of neutral alumina. The filtrate was evaporated and the product dried under high vacuum to yield the biindazole cobalt(II) complexes as fluffy, pale purple solids and the biindazole copper(II) complexes as red solids, respectively.

Co Complex 4h$^{(Co)}$: Compound **4h**$^{(Co)}$ was prepared following the standard procedure using **3h** (49.9 mg, 0.078 mmol) and cobalt(II) chloride hexahydrate (18.5 mg, 0.078 mmol) in absolute ethanol (3 mL) to yield **4h**$^{(Co)}$ (54.2 mg, 0.070 mmol, 90%) as a fluffy, pale purple solid; m.p. 170–178 °C. MS (FAB): *m/z* (%) = 700 (2) [M – (HCl), – $(Cl^-)]^+$, 736 (100) [M – $(Cl^-)]^+$, 1378 (11) [M + (**L**), – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{58}{}^{35}ClN_4Co^+$ $[M]^+$: 736.3682; found 736.3704. IR (KBr): $\tilde{\nu}$ = 3434, 2963, 2871, 1619, 1516, 1455, 1427, 1391, 1366, 1337, 1319, 1273, 1248, 1204, 1183, 1129, 1107, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CoN_4 \cdot 1/15CHCl$: calcd. C 67.75, H 7.49, N 7.17; found C 67.87, H 7.59, N 7.19.

Co Complex 4j$^{(Co)}$: Compound **4j**$^{(Co)}$ was prepared following the standard procedure using **3j** (47.8 mg, 0.076 mmol) and cobalt(II) chloride hexahydrate (18.0 mg, 0.076 mmol) in absolute ethanol (3 mL) to yield **4j**$^{(Co)}$ (53.7 mg, 0.071 mmol, 93%) as a fluffy, pale purple solid; m.p. 145–151 °C. MS (FAB): *m/z* (%) = 688 (6) [M – (HCl), – $(Cl^-)]^+$, 724 (93) [M – $(Cl^-)]^+$, 1354 (1) [M + (**L**), – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{46}{}^{35}ClN_4{}^{63}Co^+$ $[M]^+$: 724.2743; found 724.2808. IR (KBr): $\tilde{\nu}$ = 3434, 3052, 2963, 1689, 1635, 1558, 1542, 1509, 1455, 1372, 1329, 1287, 1274, 1248, 1126, 1103 cm^{-1}. $C_{44}H_{46}Cl_2CoN_4 \cdot 1/5CHCl$: calcd. C 67.66, H 5.94, N 7.14; found C 67.52, H 6.07, N 7.11.

Cu Complex 4h$^{(Cu)}$: Compound **4h**$^{(Cu)}$ was prepared following the standard procedure using **3h** (50.9 mg, 0.079 mmol) and copper(II) chloride dihydrate (13.5 mg, 0.079 mmol) in absolute ethanol (3 mL) to yield **4h**$^{(Cu)}$ (53.7 mg, 0.071 mmol, 89%) as a fine, red powder; m.p. 174–181 °C. MS (FAB): *m/z* (%) = 704 (11) [M – (HCl), – $(Cl^-)]^+$, 740 (49) [M – $(Cl^-)]^+$, 1382 (9) [M + (**L**), – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{58}{}^{35}ClN_4Cu^+$ $[M]^+$: 740.3646; found 736.3624. IR (KBr): $\tilde{\nu}$ = 3439, 2963, 2872, 1626, 1558, 1542, 1515, 1456, 1391, 1365, 1339, 1319, 1275, 1248, 1183, 1129, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CuN_4 \cdot 1/6CHCl$: calcd. C 66.53, H 7.35, N 7.03; found C 66.64, H 7.46, N 7.05.

Crystal Data for 4h$^{(Cu)}$: $C_{46}H_{58}Cl_2CuN_4$, M_r = 817.40, $0.20 \times 0.18 \times 0.16$ mm^3, triclinic, space group $P1$, a = 11.0049(3) Å, b = 13.1228(3) Å, c = 16.7500(3) Å, α = 103.126(1)°, β = 95.282(1)°, γ = 95.840(1)°, V = 2326.91(9) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.167 g/cm^3, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 200(2) K, θ range = 1.61–21.97°; reflections measured 14388, independent 11090, R_{int} = 0.074. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.10, wR_2 = 0.25.

Cu Complex 4j$^{(Cu)}$: Compound **4j**$^{(Cu)}$ was prepared following the standard procedure using **3j** (54.1 mg, 0.086 mmol) and copper(II) chloride dihydrate (14.6 mg, 0.086 mmol) in absolute ethanol (3 mL) to yield **4j**$^{(Cu)}$ (59.5 mg, 0.078 mmol, 91%) as a fine, red powder; m.p. 131–138 °C. MS (FAB): *m/z* (%) = 692 (9) [M – (HCl), – $(Cl^-)]^+$, 728 (44) [M – $(Cl^-)]^+$, 1358 (1) [M + (**L**), – $(Cl^-)]^+$. HRMS (FAB): *m/z* (%) calcd. for $C_{44}H_{46}{}^{35}ClN_4{}^{63}Cu^+$ $[M]^+$: 728.2707; found 728.2678. IR (KBr): $\tilde{\nu}$ = 3431, 3053, 2963, 2873, 1634, 1510, 1455, 1390, 1370, 1330, 1287, 1275, 1248, 1185, 1126, 1102, 1017 cm^{-1}. $C_{44}H_{58}Cl_2CuN_4 \cdot 1/3CHCl$: calcd. C 64.78, H 5.68, N 6.79; found C 64.91, H 5.79, N 6.97.

General Procedure for the Copper-Free Wacker Oxidation of Terminal Alkenes: The catalyst (5 mol-%) was dissolved in a mixture of DMA (2.5 mL) and water (6:1) in a cap-sealed vial, which was in turn evacuated at –78 °C and refilled with oxygen for three times. The solution was warmed to room temperature and the appropriate alkene (0.89 mM) and of internal standard (undecane) (10 μL) were added. Reaction control samples were taken out of the solution, extracted with diethyl ether, filtered through a short plug of neutral alumina to remove the catalyst, and analyzed by GC and GC–MS (PolarisQ Trace GC–MS, Thermo, San Jose, CA) using a 25 m HP-5MS column (Agilent Technologies, Palo Alto, CA, film thickness 250 nm).

X-ray Crystallography: CCDC-822414 (for **3i**), -832814 (for **3j**), -822413 (for **4h**), and -832815 [for **4h**$^{(Cu)}$] 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.

Supporting Information (see footnote on the first page of this article): NMR spectroscopic data, UV/Vis spectra, CD spectra.

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