Electronic Supplementary Information

Heteroleptic Cu(I) complexes bearing methoxycarbonyl-imidoylindazole and POP ligands - An experimental and theoretical study of their photophysical properties

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Experimental Section

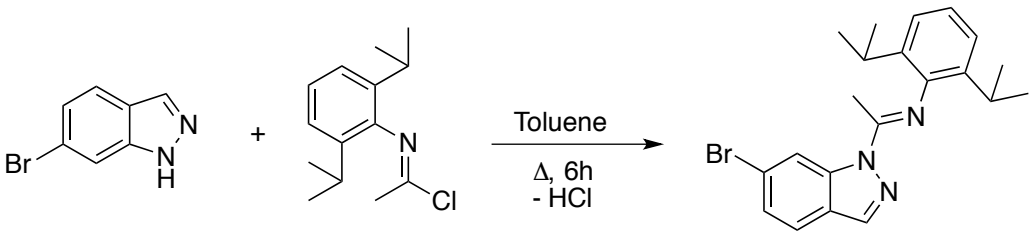
X-Ray diffraction data sets for the compounds **C1**, **C2** and **L4** were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**) and graphics XP (Bruker AXS Inc., **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound **C1** one PF_6 anion is disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For complex **C2** one disordered toluene molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE[1] was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule.

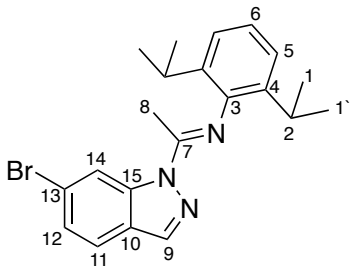
[1] A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13

Synthesis and Characterization of Compounds.

(*E*)-1-(6-bromo-1*H*-indazol-1-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine (Ligand precursor)



N-(2,6-diisopropylphenyl)acetimidoyl chloride[2] (500 mg, 2.10 mmol) was added dropwise to a solution of 6-bromo-1H-indazole (414 mg, 2.10 mmol) in anhydrous toluene. The mixture was refluxed for 6 h with vigorous stirring. The yellow solution was evaporated in vacuum to dryness. Crude product was purified via silica gel chromatography (4:1 Petroleum ether / ethyl acetate). Ligand precursor was isolated as a white crystalline material in 87% yield (730 mg, 1.83 mmol).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.92 (s, 1H, H14), 7.91 (s, 1H, H9), 7.41 (d, *J* = 8.5 Hz, 1H, H11), 7.23 (d, *J* = 8.5 Hz, 1H, H12), 7.05 (d, *J* = 6.8 Hz, 2H, H5), 6.98 (t, *J* = 6.8 Hz, 1H, H6), 2.78 (hept, *J* = 6.9 Hz, 2H, H2), 2.28 (s, 3H, H8), 1.04 (d, *J* = 6.9 Hz, 12H, H1-H1').

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 155.0 (C7), 143.4 (C3), 139.7 (C15), 137.2 (C4), 136.6 (C9), 126.9 (C12), 125.1 (C10), 124.0 (C6), 123.3 (C5), 123.1 (C13), 121.7 (C11), 119.3 (C14), 28.4 (C2), 23.6 (C1), 23.0 (C1'), 17.1 (C8).

^{1}H, ^{13}C-GHMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.92 / 139.7, 126.9, 125.1, 123.1 (H14 / C15, C12, C10, C13), 7.91 / 139.7, 123.1 (H9 / C15, C9), 7.41 / 139.7, 136.6, 125.1 (H11 / C15, C9, C10), 7.23 / 125.1, 119.3 (H12 / C10, C14), 7.03 / 143.4, 28.4 (H5 / C3, C2), 6.98

[2] C. Quintero, M. Valderrama, A. Becerra, C. G. Daniliuc and R. S. Rojas, *Org. Biomol. Chem.* 2015, **13**, 6183-6193.

/ 137.2 (H6 / C4), 2.78 / 143.4, 137.2, 123.3, 23.6, 23.0 (H2 / C3, C4, C5, C1, C1'), 2.28 / 155.0 (H8 / C7), 1.04 / 137.2, 28.4 (H1-H1' / C4, C2).

^{1}H, ^{13}C-GHSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.92 / 119.3 (H14 / C14), 7.91 / 136.6 (H9 / C9), 7.41 / 121.7 (H11 / C11), 7.23 / 126.9 (H12 / C12), 7.03 / 123.3 (H5 / C5), 6.98 / 124.0 (H6 / C6), 2.78 / 28.4 (H2 / C2), 2.28 / 17.1 (H8 /C8), 1.04 / 23.6 (H1 / C1), 1.04 / 23.0 (H1' / C1').

GCOSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.41 / 7.23 (H11 / H12), 7.03 / 6.98 (H5 / H6), 2.78 / 1.04 (H2 / H1-H1').

IR (KBr): ν/cm^{-1} = 3059, 2963, 2970, 1722, 1666, 1632, 1610, 1591, 1479, 1460, 1432, 1412, 1383, 1355, 1307, 1279, 1256, 1205, 1193, 1169, 1153, 1123, 1096, 1056, 1037, 1010, 984, 956, 944, 924, 892, 859, 811, 797, 772, 703, 685, 629, 607, 580, 552, 526, 504, 476, 440.

Elemental analysis (%) $C_{21}H_{24}BrN_3$ (M = 398.34 g/mol): Calculated C 63.32, H 6.07, N 10.55; Found C 63.37, H 6.08, N 10.57.

HRMS(ESI): ($C_{21}H_{25}BrN_3$ $[M + H]^+$) Calculated: 398.1232; Found: 398.1216.

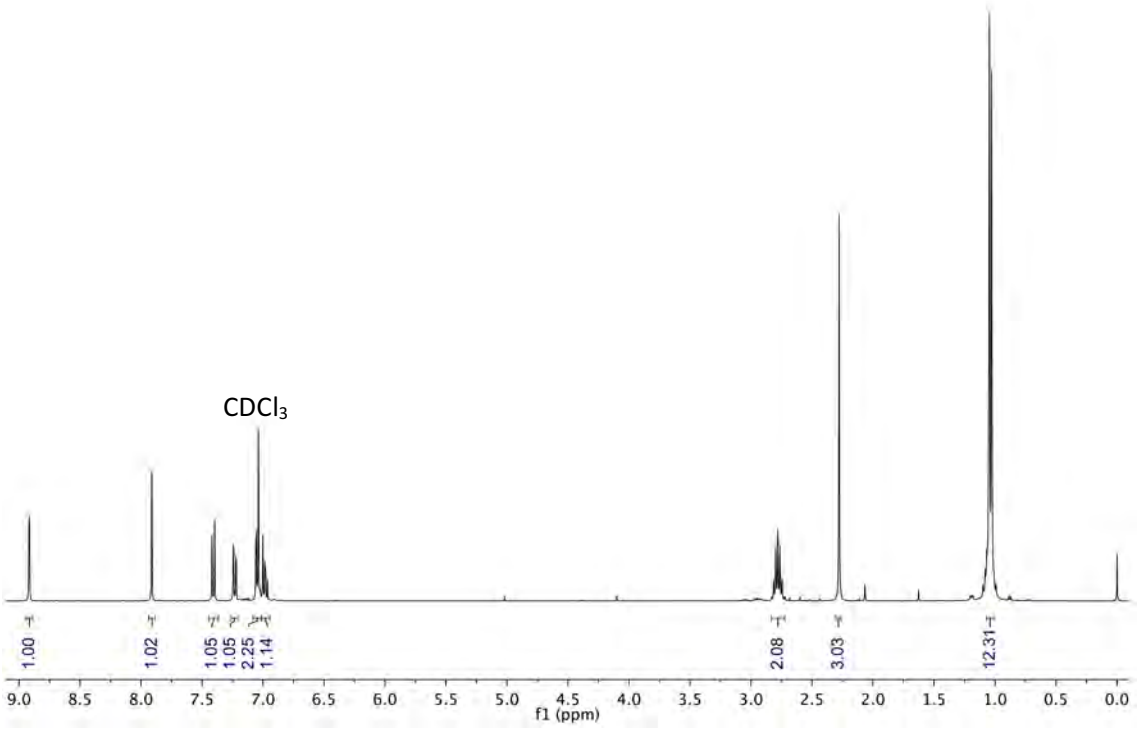


Figure S1. ^{1}HNMR (400 MHz, $CDCl_3$, 298 K).

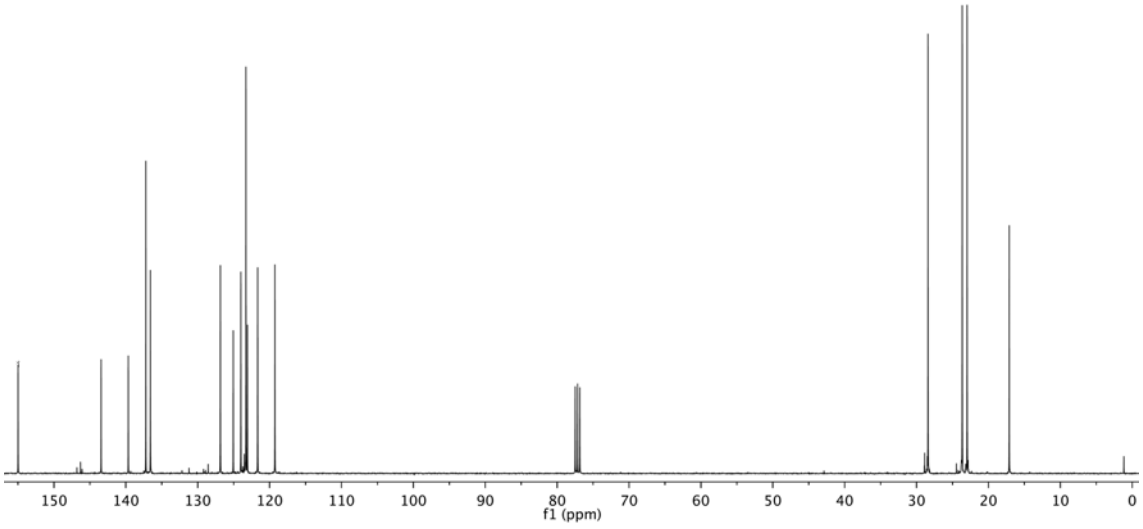
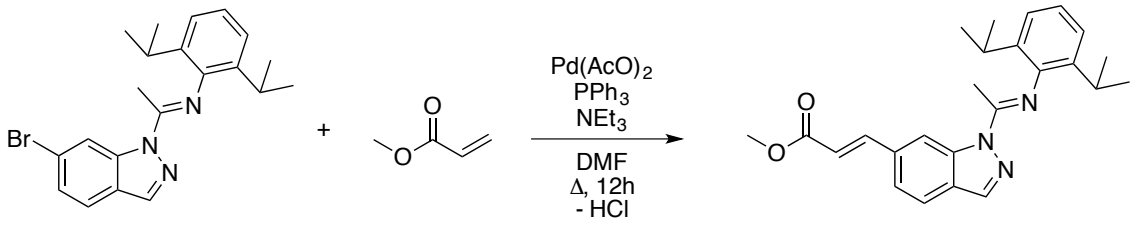
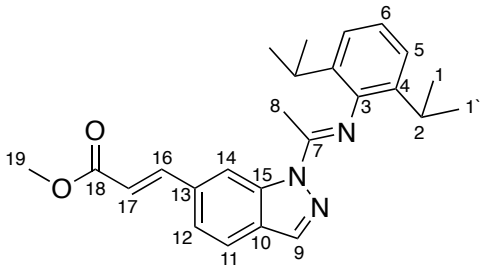


Figure S2. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K).

Methyl (*E*)-3-(1-((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazol-6-yl)acrylate (L4)



A solution of (*E*)-1-(6-bromo-1*H*-indazol-1-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine (ligand precursor) (500 mg, 1.25 mmol), PPh_3 (49 mg, 0.19 mmol), NEt_3 (152 mg, 1.50 mmol), $Pd(AcO)_2$ (21 mg, 0.094 mol) and Methyl acrylate (540 mg, 6.28 mmol) in anhydrous and deoxygenated DMF (50 mL) was heated at 120°C for 12h, in a sealed round flask fitted with Teflon screw cap. The mixture was filtered through celite, washed with CH_2Cl_2, and the filtrate was washed with 40 mL of distilled water. The organic phase was dried with anhydrous Na_2SO_4 and concentrated to dryness. Crude product was purified via silica gel chromatography (4:1 Petroleum ether / ethyl acetate). **L4** was isolated as light yellow crystalline material in 68% yield (344 mg, 0.85 mmol).



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ/ppm = 8.99 (s, 1H, H14), 8.15 (s, 1H, H9), 7.81 (d, *J* = 16 Hz, 1H, H16), 7.79 (d, *J* = 8.3 Hz, 1H, H11), 7.53 (d, *J* = 8.3 Hz, 1H, H12), 7.21 (d, *J* = 7.1 Hz, 2H, H5), 7.14 (t, *J* = 7.1 Hz, 1H, H6), 6.52 (d, *J* = 16 Hz, 1H, H17), 3.80 (s, 3H, H19), 2.92 (hept, *J* = 6.9 Hz, 2H, H2), 2.42 (s, 3H, H8), 1.19 (dd, *J* = 6.9, 3.2 Hz, 12H, H1-H1').

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K): δ/ppm = 167.4 (C18), 155.2 (C7), 145.3 (C16), 143.6 (C3), 139.5 (C15), 137.3 (C4), 136.6 (C9), 134.9 (C13), 127.4 (C10), 124.0 (C6), 123.4 (C5), 122.6 (C12), 121.2 (C11), 119.1 (C17), 117.0 (C14), 51.9 (C19), 28.5 (C2), 23.8 (C1), 23.0 (C1'), 17.2 (C8).

^{1}H, ^{13}C-GHMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.99 / 145.3, 139.5, 127.4, 122.6 (H14 / C16, C15, C10, C12), 8.15 / 139.5, 127.4 (H9 / C15, C10), 7.81 / 167.4, 122.6, 119.1, 117.0 (H16 / C18, C12, C17, C14), 7.79 / 139.5, 134.9 (H11 / C15, C13), 7.53 / 145.3, 127.4, 117.0 (H12 / C16, C10, C14), 7.21 / 143.6, 28.5 (H5 / C3, C2), 7.14 / 137.3 (H6 / C4), 6.52 / 167.4, 134.9

(H17 / C18, C13), 3.80 / 167.4 (H19 / C18), 2.92 / 143.6, 137.3, 123.4, 23.8, 23.0 (H2 / C3, C4, C5, C1, C1'), 2.42 / 155.2 (H8 / C7), 1.19 / 137.3, 28.5, 23.8 (H1' / C4, C2, C1), 1.19 / 137.3, 28.5, 23.0 (H1 / C4, C2, C1').

^{1}H, ^{13}C-GHSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{13}C) = 8.99 / 117.0 (H14 / C14), 8.15 / 136.6 (H9 / C9), 7.81 / 145.3 (H16 / C16), 7.79 / 121.2 (H11 / C11), 7.53 / 122.6 (H12 / C12), 7.21 / 123.4 (H5 / C5), 7.14 / 124.0 (H6 / C6), 6.52 / 119.1 (H17 / C17), 3.80 / 51.9 (H19 / C19), 2.92 / 28.5 (H2 / C2), 2.42 / 17.2 (H8 /C8), 1.19 / 23.8 (H1 / C1), 1.19 / 23.0 (H1' / C1').

GCOSY (400 MHz / 400 MHz, $CDCl_3$, 298 K): δ (^{1}H) / δ (^{1}H) = 7.81 / 6.52 (H16 / H17), 7.79 / 7.53 (H11 / H12), 7.21 / 7.14 (H5 / H6), 2.92 / 1.19 (H2 / H1-H1').

IR (KBr): ν/cm^{-1} = 3110, 3071, 2960, 2864, 1661, 1606, 1571, 1526, 1491, 1459, 1415, 1378, 1344, 1325, 1301, 1255, 1242, 1192, 1135, 1122, 1096, 1055, 1032, 949, 936, 906, 876, 857, 820, 808, 770, 739, 727, 692, 656, 622, 595, 536, 524, 430.

Elemental analysis (%) $C_{25}H_{29}N_3O_2$ (M = 403.52 g/mol): Calculated C 74.41, H 7.24, N 10.41; Found C 74.67, H 7.25, N 10.59.

HRMS(ESI): ($C_{25}H_{30}N_3O_2$ [M + H]) Calculated: 404.2338; Found: 404.2327.

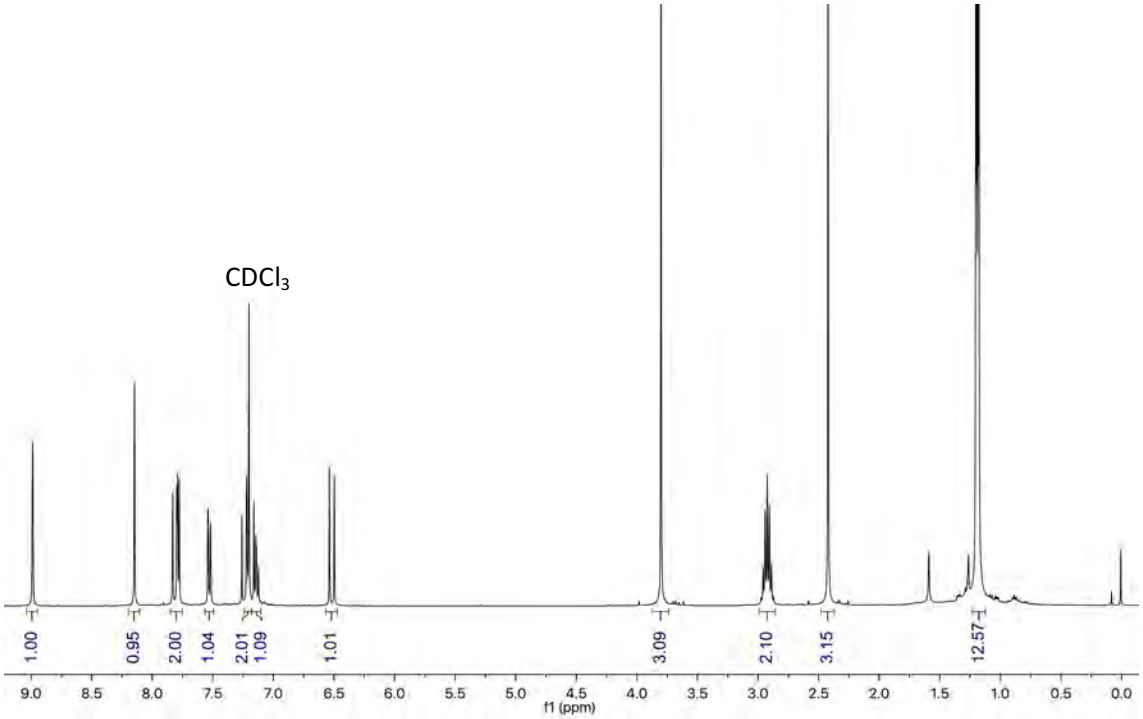


Figure S3. ^{1}HNMR (400 MHz, $CDCl_3$, 298 K).

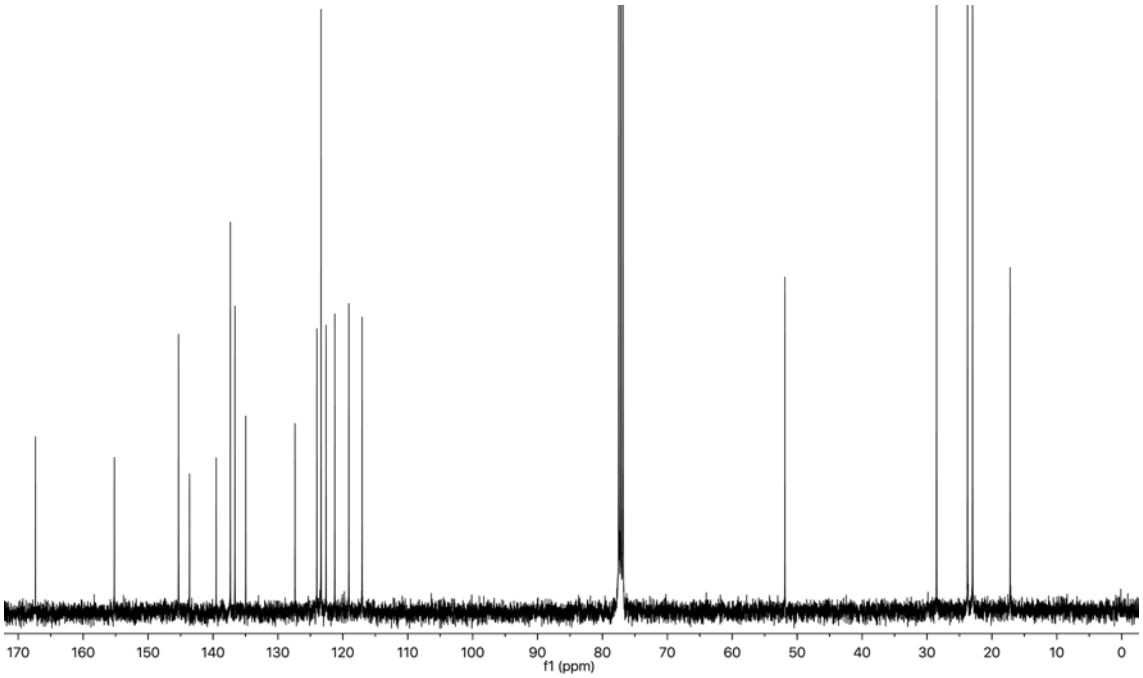


Figure S4. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K).

X-ray crystal structure of **L4**:

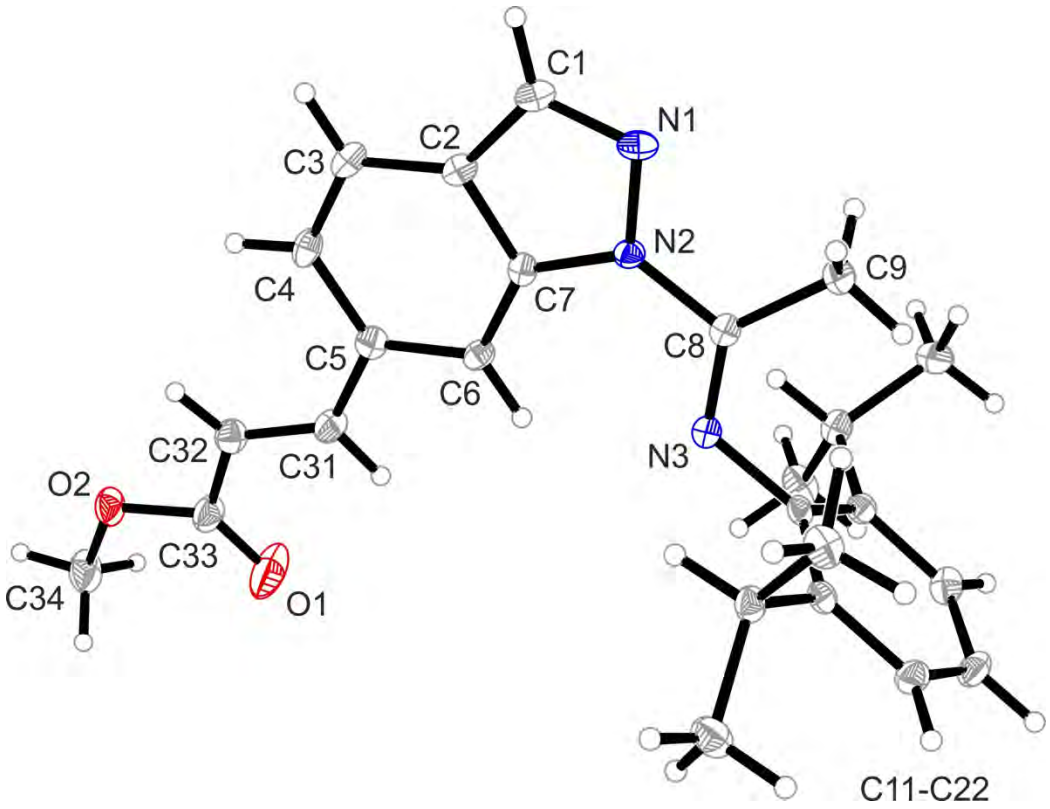
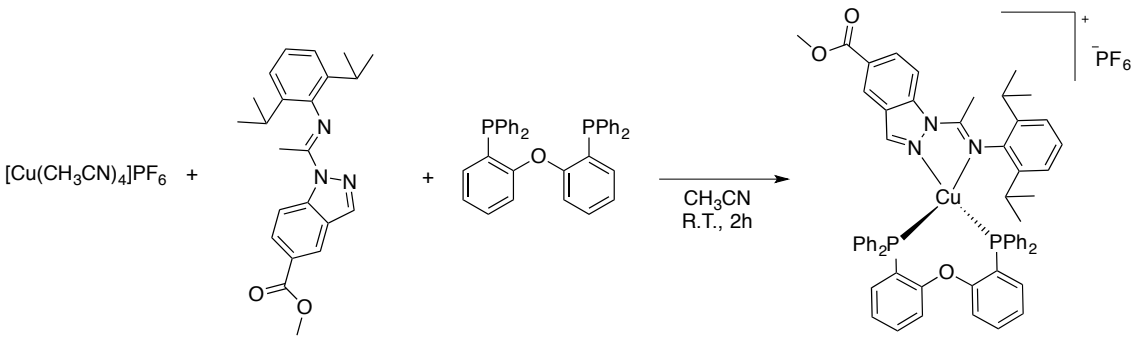


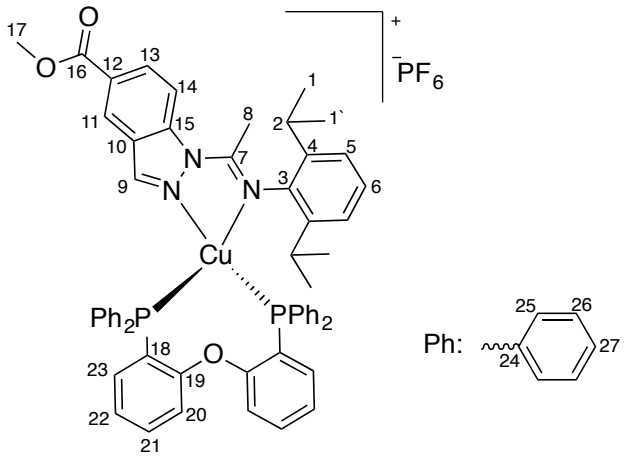
Figure S5. Molecular structure of **L4**. Thermals ellipsoids are shown with 50% probability.

X-ray crystal structure analysis of L4: A colorless needle-like specimen of $C_{25}H_{29}N_3O_2$, approximate dimensions 0.067 mm x 0.084 mm x 0.351 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 752 frames were collected. The total exposure time was 7.31 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 29705 reflections to a maximum θ angle of 26.43° (0.80 Å resolution), of which 4423 were independent (average redundancy 6.716, completeness = 99.5%, R_{int} = 5.55%, R_{sig} = 3.10%) and 3535 (79.92%) were greater than $2\sigma(F^2)$. The final cell constants of a = 20.0322(7) Å, b = 5.8421(2) Å, c = 19.3439(7) Å, β = 107.8170(10)°, volume = 2155.24(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 9542 reflections above 20 σ(I) with 5.124° < 2θ < 52.85°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.946. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{25}H_{29}N_3O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 277 variables converged at R1 = 4.20%, for the observed data and wR2 = 10.86% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.347 $e^-/Å^3$ and the largest hole was -0.324 $e^-/Å^3$ with an RMS deviation of 0.049 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.244 g/cm^3 and F(000), 864 e^-.

[((methyl (*E*)-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazole-5-carboxylate)((Oxydi-2,1-phenylene)bis(diphenyl phosphine))Cu(I)]PF_6. (C1)



A solution of methyl (*E*)-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazole-5-carboxylate[1] (100 mg, 0.26 mmol) in acetonitrile was added dropwise to a solution of $[Cu(CH_3CN)_4]PF_6$ (99 mg, 0.26 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of (Oxydi-2,1-phenylene)bis(diphenyl phosphine) (143 mg, 0.26 mmol) was added in CH_2Cl_2 and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH_2Cl_2 / Hexane mixture at -20°C, obtaining **C1** as a bright yellow powder in 90% yield (245 mg, 0.24 mmol).



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 8.48 (d, *J* = 8.5 Hz, 1H, H13), 8.45 (s, 1H, H11), 8.20 (br, 1H, H14), 7.83 (br, 1H, H9), 7.42-6.86 (m, 25H, H22-23, H25-27), 7.38 (t, *J* = 7.7 Hz, 1H, H6), 7.19 (d, *J* = 7.7 Hz, 2H, H5), 6.94 (br, 2H, H20), 6.64 (br, 2H, H21), 3.98 (s, 3H, H17), 2.77 (br, 5H, H2, H8), 0.75 (br, 6H, H1'), 0.52 (br, 6H, H1).

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 166.1 (C16), 158.0 (C19), 157.5 (C7), 141.6 (C3), 141.1 (C15), 140.2 (C4, C9), 134.8 (C21), 133.1, 132.7 (C13), 132.2, 131.1, 131.0, 129.5, 129.3,

128.7, 128.0, 127.5 (C6), 127.2, 125.7 (C20), 125.6 (C11), 125.2 (C5), 113.8 (C14), 53.0 (C17), 28.8 (C2), 24.7 (C1'), 23.2 (C1), 19.7 (C8).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.48 / 125.6 (H13 / C11), 8.45 / 166.1, 141.1, 132.7 (H11 / C16, C15, C13), 7.38 / 140.2, 125.2 (H6 / C4, C5), 7.19 / 141.6, 127.5, 28.8 (H5 / C3, C6, C2), 6.64 / 158 (H21 / C19), 3.98 / 166.1 (H17 / C16), 2.77 / 157.5 (H8 / C7), 2.77 / 141.6, 125.2, 24.7, 23.2 (H2 / C3, C5, C1', C1), 0.75 / 140.2, 28.8 (H1' / C4, C2), 0.52 / 140.2, 28.8 (H1 / C4, C2).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.48 / 132.7 (H13 / C13), 8.45 / 125.6 (H11 / C11), 8.20 / 113.8 (H14 / C14), 7.38 / 127.5 (H6 / C6), 7.19 / 125.2 (H5 / C5), 6.94 / 125.7 (H20 / C20), 6.64 / 134.8 (H21 / C21), 3.98 / 53.0 (H17 / C17), 2.77 / 19.7 (H8 / C8), 2.77 / 28.8 (H2 / C2), 0.75 / 24.7 (H1' / C1'), 0.52 / 23.2 (H1 / C1).

COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{1}H) = 8.48 / 8.20 (H13 / H14), 7.38 / 7.19 (H6 / H5), 6.94 / 6.64 (H20 / H21), 2.77 / 0.75, 0.52 (H2 / H1', H1).

^{19}F NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = -73.2 (d, J^{F-P} = 710 Hz).

^{31}P{1H} NMR (160 MHz, CD_2Cl_2, 298 K): δ/ppm = -10.7 (s, POP), -144.4 (hept, J^{P-F} = 710 Hz, PF_6).

IR (KBr): ν/cm^{-1} = 3058, 2962, 1724, 1619, 1589, 1574, 1520, 1461, 1436, 1389, 1370, 1354, 1323, 1295, 1262, 1227, 1096, 1071, 1028, 999, 914, 841, 802, 746, 695, 557, 509, 489.

Elemental analysis (%) $C_{59}H_{55}CuF_6N_3O_3P_3$ (M = 1124.56 g/mol): Calculated C 63.02, H 4.93, N 3.74; Found C 63.22, H 4.94, N 3.75.

HRMS(ESI): ($C_{59}H_{55}CuN_3O_3P_2$ $[M]^+$) Calculated: 978.3015; Found: 978.2974.

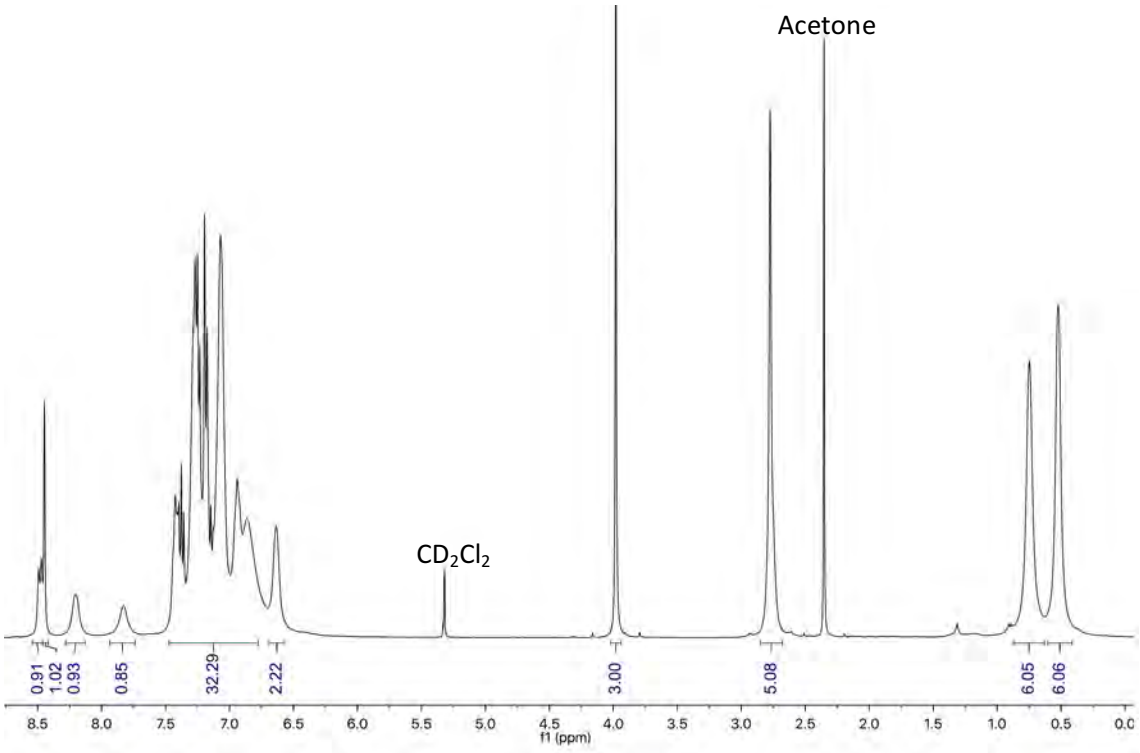


Figure S6. ^{1}HNMR (400 MHz, CD_2Cl_2, 298 K).

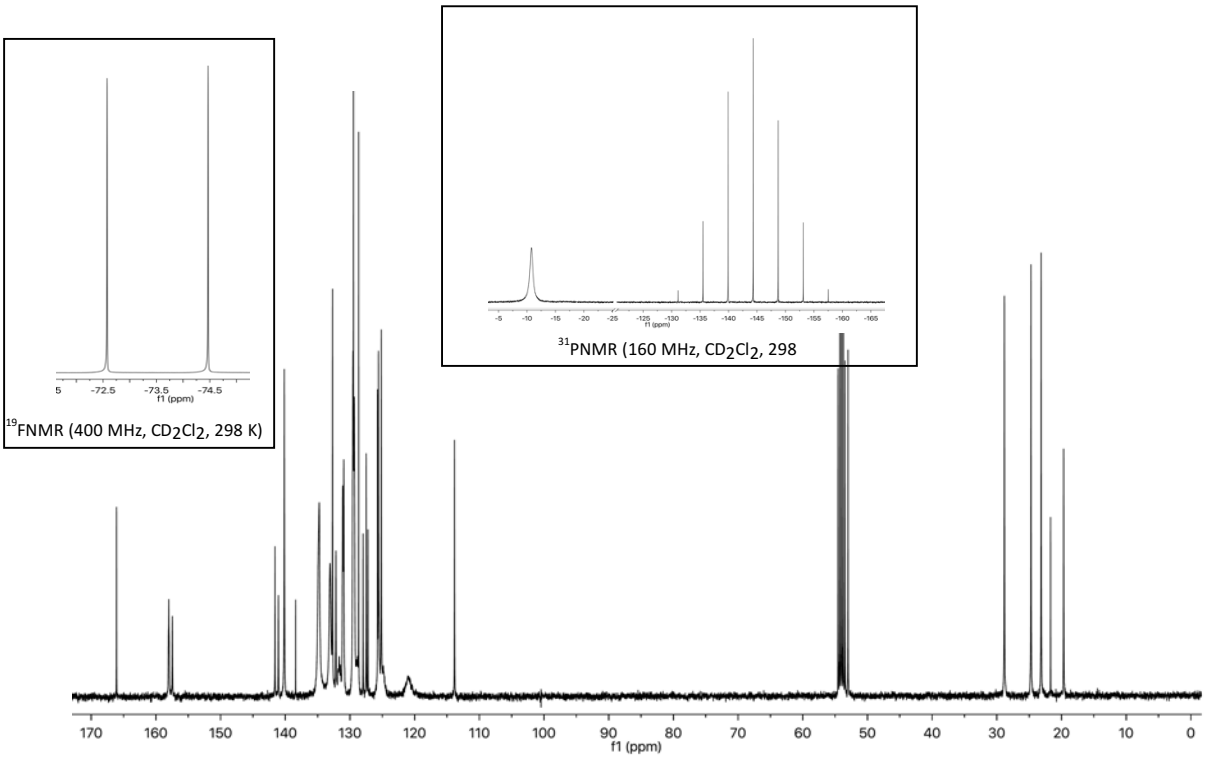


Figure S7. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR.

X-ray crystal structure of C1:

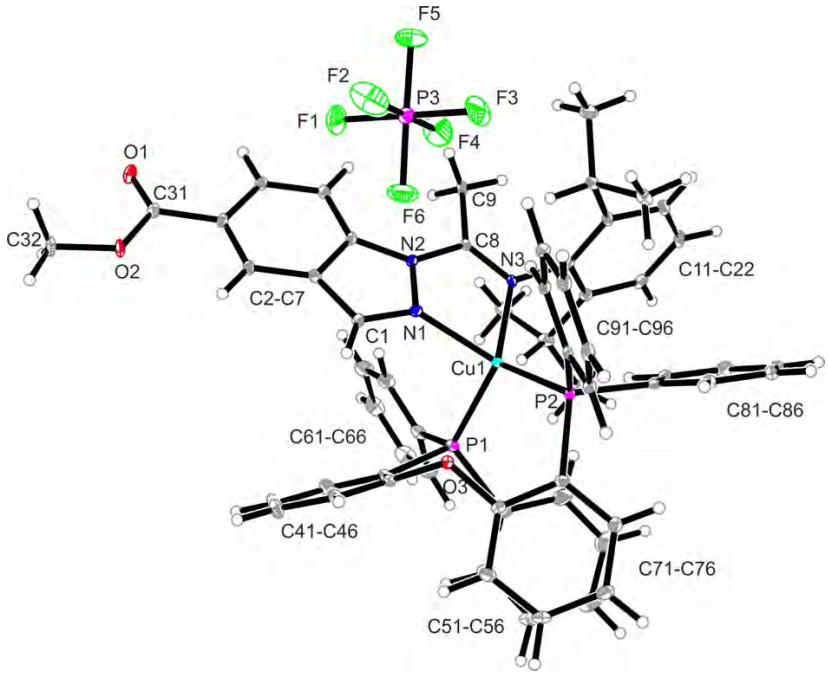
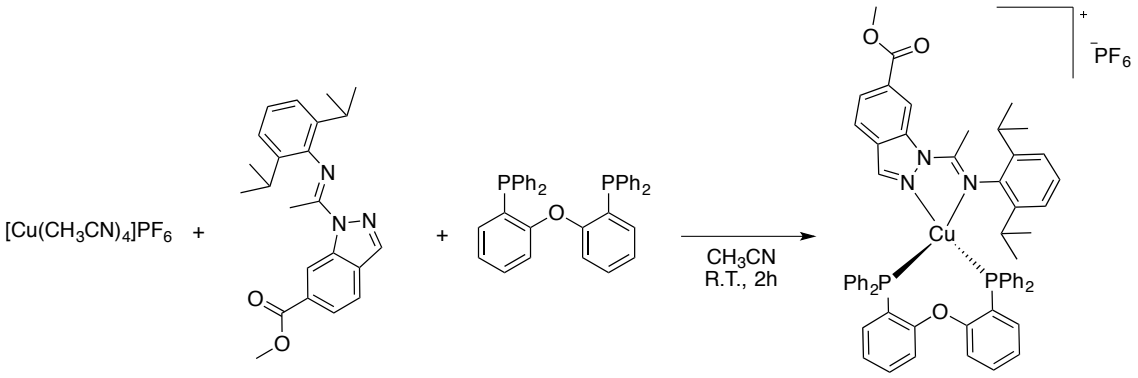


Figure S8. Molecular structure of **C1**. Thermals ellipsoids are shown with 30% probability.

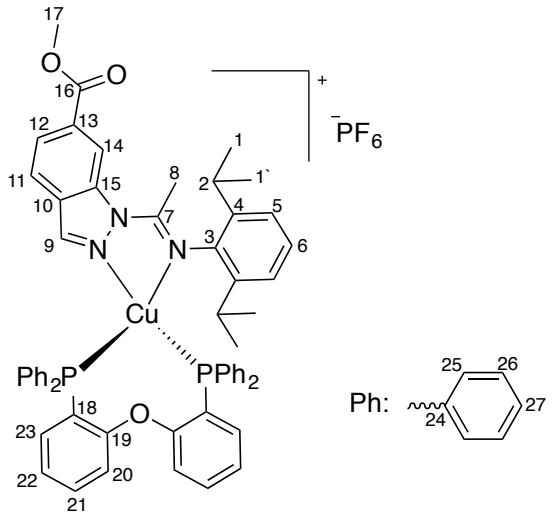
X-ray crystal structure analysis of C1: A yellow plate-like specimen of $C_{59}H_{55}CuN_3O_3P_2 \cdot PF_6 \cdot 1.5$ x C_7H_8, approximate dimensions 0.040 mm x 0.120 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1458 frames were collected. The total exposure time was 20.25 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 120445 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 24972 were independent (average redundancy 4.823, completeness = 99.8%, R_{int} = 3.62%, R_{sig} = 3.20%) and 20810 (83.33%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.2137(5) Å, b = 19.5244(9) Å, c = 28.7399(13) Å, α = 98.2350(10)°, β = 99.2170(10)°, γ = 93.8360(10)°, volume = 6121.0(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 9019 reflections above 20 σ(I) with 4.438° < 2θ < 55.12°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.951. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9150 and 0.9800. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 4 for the formula unit, $C_{59}H_{55}CuN_3O_3P_2 \cdot PF_6 \cdot 1.5$ x C_7H_8. The final anisotropic full-matrix least-squares refinement on F^2 with 1610 variables converged at R1 = 4.22%, for the observed data and wR2 = 9.86% for all data. The goodness-of-fit was 1.036. The largest peak in the final

difference electron density synthesis was 1.039 $e^-/Å^3$ and the largest hole was -0.499 $e^-/Å^3$ with an RMS deviation of 0.064 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.370 g/cm^3 and F(000), 2628 e^-.

[((methyl (*E*)-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazole-6-carboxylate)((Oxydi-2,1-phenylene)bis(diphenyl phosphine))Cu(I)]PF_6. (C2)



A solution of methyl (*E*)-1-(1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazole-6-carboxylate[1] (100 mg, 0.26 mmol) in acetonitrile was added dropwise to a solution of $[Cu(CH_3CN)_4]PF_6$ (99 mg, 0.26 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of (Oxydi-2,1-phenylene)bis(diphenyl phosphine) (143 mg, 0.26 mmol) was added in CH_2Cl_2 and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH_2Cl_2 / Hexane mixture at -20°C, obtaining **C2** as yellow powder in 93% yield (253 mg, 0.25 mmol).



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 8.66 (br, 1H, H14), 8.13 (d, *J* = 8.4 Hz, 1H, H12), 7.80 (d, *J* = 8.4 Hz, 1H, H11), 7.76 (br, 1H, H9), 7.39-6.81 (m, 25H, H22-23, H25-27), 7.35 (t, *J* = 7.7 Hz, 1H, H6), 7.15 (d, *J* = 7.7 Hz, 2H, H5), 6.91 (br, 2H, H20), 6.58 (br, 2H, H21), 4.02 (s, 3H, H17), 2.75 (s, 3H, H8), 2.70 (br, 2H, H2), 0.70 (br, 6H, H1'), 0.48 (br, 6H, H1).

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 166.4 (C16), 158.1 (C19), 157.0 (C7), 141.6 (C3), 140.2 (C4), 139.3 (C9), 138.8 (C15), 134.9 (C21), 133.1, 132.7, 131.2, 131.0, 129.9 (C10), 129.6, 129.4, 128.7, 127.6 (C6), 126.1 (C12), 125.6 (C20), 125.3 (C5), 123.7 (C11), 114.9 (C14), 53.5 (C17), 28.9 (C2), 24.8 (C1'), 23.1 (C1), 19.9 (C8).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.13 / 166.4, 129.9, 114.9 (H12 / C16, C10, C14), 7.80 / 139.3, 138.8, 129.9 (H11 / C9, C15, C10), 7.35 / 140.2, 125.3 (H6 / C4, C5), 7.15 / 141.6, 28.9 (H5 / C3, C2), 4.02 / 166.4 (H17 / C16), 2.75 / 157.0 (H8 / C7), 2.70 / 141.6, 125.3, 24.8, 23.1 (H2 / C3, C5, C1', C1), 0.48 / 140.2, 28.9, 24.8 (H1 / C4, C2, C1').

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.66 / 114.9 (H14 / C14), 8.13 / 126.1 (H12 / C12), 7.80 / 123.7 (H11 / C11), 7.76 / 139.3 (H9 / C9), 7.35 / 127.6 (H6 / C6), 7.15 / 125.3 (H5 / C5), 6.91 / 125.6 (H20 / C20), 6.58 / 134.9 (H21 / C21), 4.02 / 53.5 (H17 / C17), 2.70 / 28.9 (H2 / C2), 2.75 / 19.9 (H8 / C8), 0.70 / 24.8 (H1' / C1'), 0.48 / 23.1 (H1 / C1).

COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{1}H) = 8.13 / 7.80 (H12 / H11), 6.91 / 6.58 (H20 / H21), 2.70 / 0.70, 0.48 (H2 / H1', H1).

^{19}F NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = -73.6 (d, J^{F-P} = 710 Hz).

$^{31}P\{1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ/ppm = -10.7 (s, POP), -144.5 (hept, J^{P-F} = 710 Hz, PF_6).

IR (KBr): ν/cm^{-1} = 3059, 2961, 2920, 1721, 1655, 1624, 1578, 1542, 1508, 1460, 1436, 1412, 1356, 1306, 1260, 1218, 1096, 1071, 976, 841, 802, 746, 696, 558, 510.

Elemental analysis (%) $C_{59}H_{55}CuF_6N_3O_3P_3$ (M = 1124.56 g/mol): Calculated C 63.02, H 4.93, N 3.74; Found C 63.18, H 4.94, N 3.74.

HRMS(ESI): ($C_{59}H_{55}CuN_3O_3P_2$ $[M]^+$) Calculated: 978.3015; Found: 978.2977.

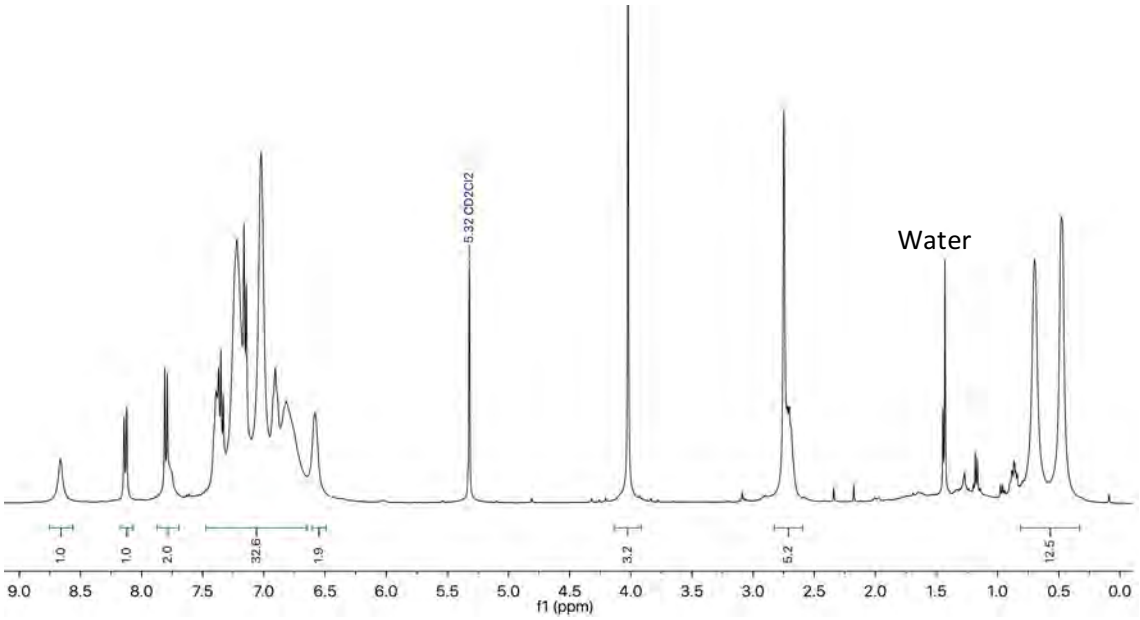


Figure S9. ^{1}HNMR (400 MHz, CD_2Cl_2, 298 K).

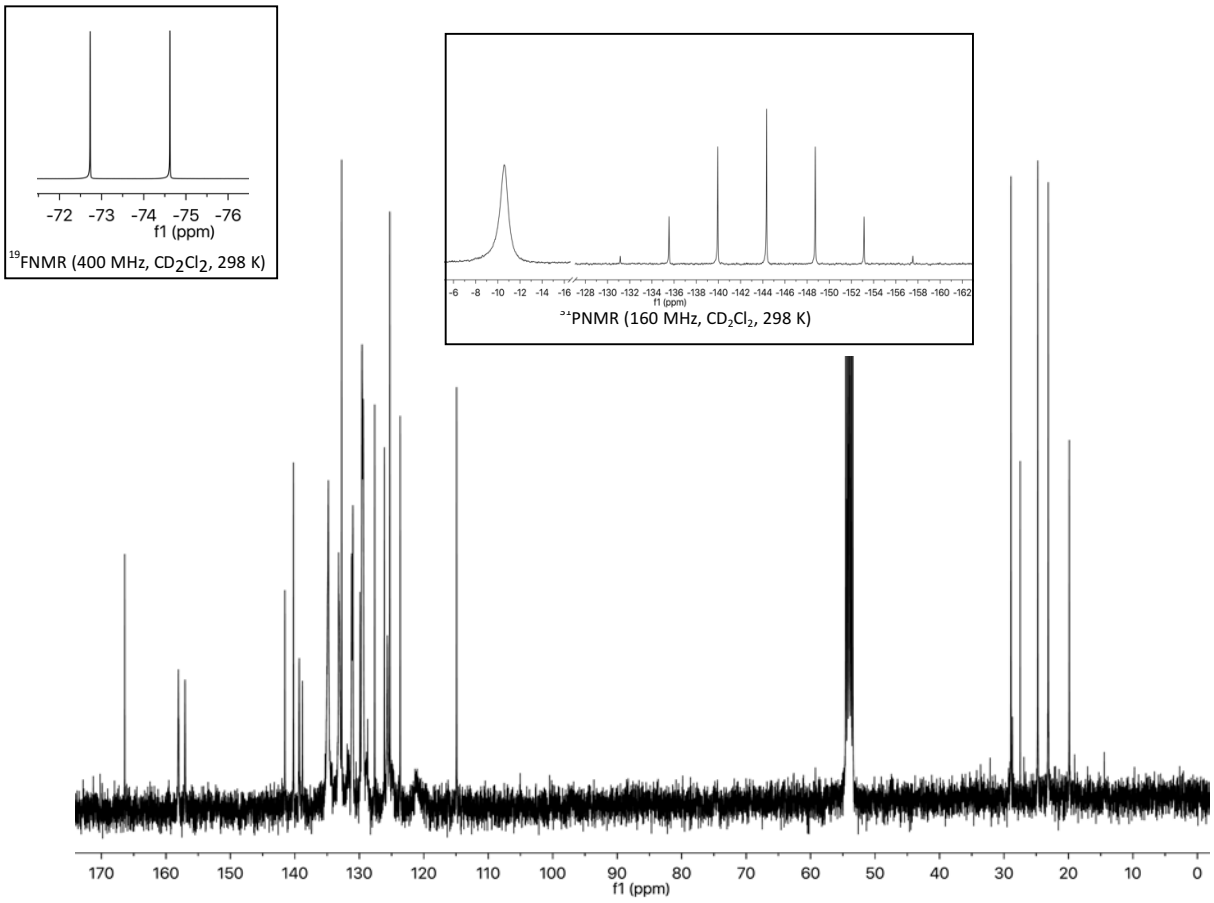


Figure S10. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR.

X-ray crystal structure of C2:

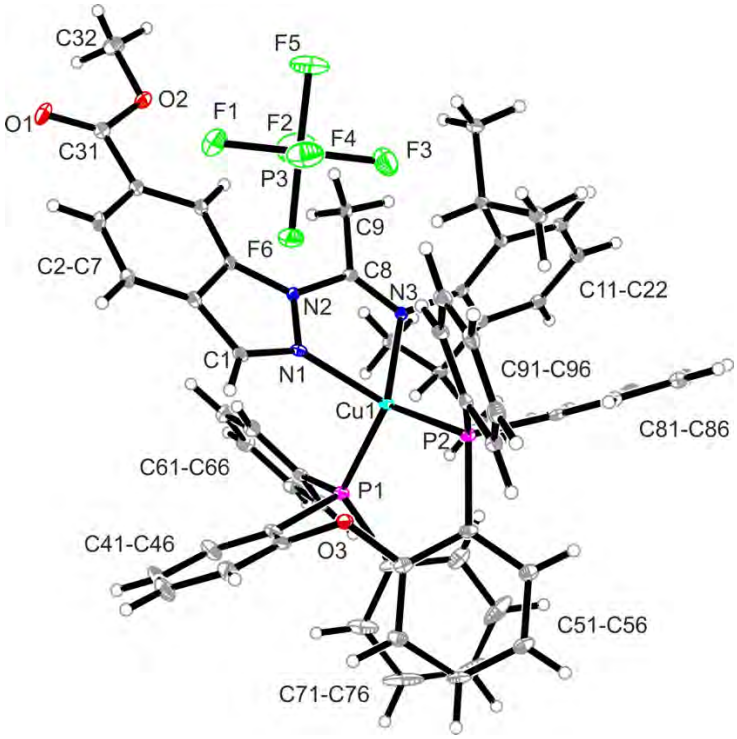
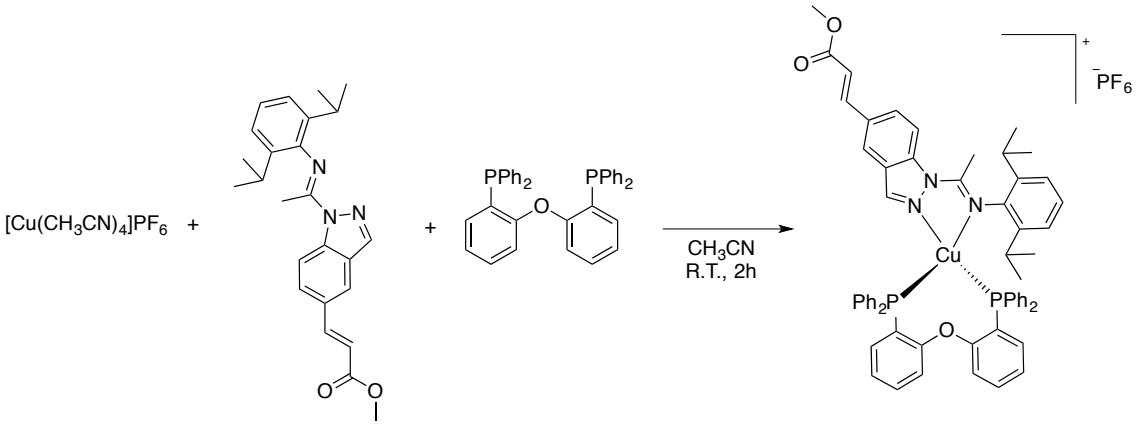


Figure S11. Molecular structure of **C2**. Thermals ellipsoids are shown with 30% probability.

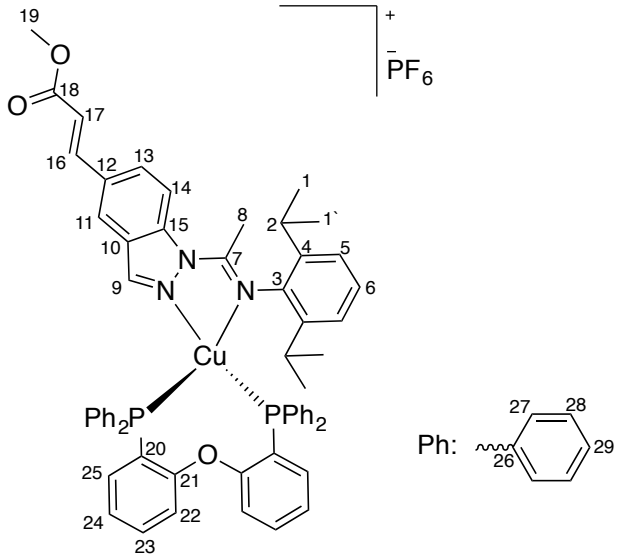
X-ray crystal structure analysis of C2: A yellow plate-like specimen of $C_{59}H_{55}CuN_3O_3P_2 \cdot PF_6$, approximate dimensions 0.045 mm x 0.159 mm x 0.211 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 689 frames were collected. The total exposure time was 5.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 10321 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 10321 were independent (average redundancy 1.000, completeness = 99.8%, R_{int} = 6.88%, R_{sig} = 4.33%) and 8112 (78.60%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.0944(4) Å, b = 15.3062(5) Å, c = 15.7640(5) Å, α = 95.3340(10)°, β = 91.6650(10)°, γ = 103.357(2)°, volume = 2823.14(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 9385 reflections above 20 σ(I) with 4.730° < 2θ < 54.87°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.940. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8950 and 0.9760. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{59}H_{55}CuN_3O_3P_2 \cdot PF_6$. The final anisotropic full-matrix least-squares

refinement on F^2 with 682 variables converged at R1 = 3.77%, for the observed data and wR2 = 9.25% for all data. The goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was 0.418 $e^-/Å^3$ and the largest hole was -0.444 $e^-/Å^3$ with an RMS deviation of 0.062 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.323 g/cm^3 and F(000), 1164 e^-.

[((methyl (*E*)-3-(1-((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazol-5-yl)acrylate)((Oxydi-2,1-phenylene)bis(diphenyl phosphine))Cu(I)]PF_6. (C3)



A solution of methyl (*E*)-3-(1-((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazol-5-yl)acrylate[2] (100 mg, 0.25 mmol) in acetonitrile was added dropwise to a solution of $[Cu(CH_3CN)_4]PF_6$ (92 mg, 0.25 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of (Oxydi-2,1-phenylene)bis(diphenyl phosphine) (133 mg, 0.25 mmol) was added in CH_2Cl_2 and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH_2Cl_2 / Hexane mixture at -20°C, obtaining **C3** as a bright yellow powder in 87% yield (248 mg, 0.22 mmol).



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 8.04 (br, 1H, H14), 8.01 (br, 1H, H11), 7.82 (s, 1H, H13), 7.79 (d, *J* = 16 Hz, 1H, H16), 7.70 (br, 1H, H9), 7.40-6.82 (m, 25H, H24-25, H27-29), 7.34 (t, *J* = 7.8 Hz, 1H, H6), 7.14 (d, *J* = 7.8 Hz, 2H, H5), 6.91 (br, 2H, H22), 6.58 (br, 2H, H23), 6.58 (d, *J* = 16 Hz, 1H, H17), 3.81 (s, 3H, H19), 2.69 (br, 5H, H2, H8), 0.69 (br, 6H, H1'), 0.47 (br, 6H, H1).

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 167.2 (C18), 158.1 (C21), 157.2 (C7), 142.9 (C16), 141.6 (C3), 140.2 (C4), 139.8 (C9), 139.6 (C15), 134.9 (C23), 133.1, 132.6 (C12), 131.2, 131.0, 130.7 (C11), 129.5, 129.4, 128.7, 127.9, 127.5 (C6), 125.8, 125.6 (C22), 125.2 (C5), 123.4 (C13), 120.4 (C17), 114.2 (C14), 52.3 (C19), 28.9 (C2), 24.8 (C1'), 23.2 (C1), 19.7 (C8).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.04 / 123.4 (H14 / C13), 8.01 / 142.9, 139.6, 123.4 (H11 / C16, C15, C13), 7.82 / 142.9, 139.6 130.7 (H13 / C16, C15, C11), 7.79 / 167.2, 130.7, 120.4 (H16 / C18, C11, C17), 7.34 / 140.2, 125.2 (H6 / C4, C5), 7.14 / 141.6, 127.5, 28.9 (H5 / C3, C6, C2), 6.58 / 158.1 (H23 / C21), 6.58 / 167.2, 142.9, 132.6 (H17 / C18, C16, C12), 3.81 / 167.2 (H19 / C18), 2.69 / 157.2 (H8 / C7), 2.69 / 141.6, 125.2, 24.8, 23.2 (H8 / C3, C5, C1', C1), 0.69 / 140.2, 28.9, 23.2 (H1' / C4, C2, C1), 0.47 / 140.2, 28.9, 24.8 (H1 / C4, C2, C1').

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.04 / 114.2 (H14 / C14), 8.01 / 130.7 (H11 / C11), 7.82 / 123.4 (H13 / C13), 7.79 / 142.9 (H16 / C16), 7.70 / 139.8 (H9 / C9), 7.34 / 127.5 (H6 / C6), 7.14 / 125.2 (H5 / C5), 6.91 / 125.6 (H22 / C22), 6.58 / 134.9 (H23 / C23), 6.58 / 120.4 (H17 / C17), 3.81 / 52.3 (H19 / C19), 2.69 / 28.9 (H2 / C2), 2.69 / 19.7 (H8 / C8), 0.69 / 24.8 (H1' / C1'), 0.47 / 23.2 (H1 / C1).

COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{1}H) = 8.04 / 7.82 (H14 / H13), 7.79 / 6.58 (H16 / H17), 7.34 / 7.14 (H6 / H5), 6.91 / 6.58 (H22 / H23), 2.69 / 0.69, 0.47 (H2 / H1', H1).

^{19}F NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = -73.5 (d, J^{F-P} = 711 Hz).

$^{31}P\{1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ/ppm = -10.8 (s, POP), -144.5 (hept, J^{P-F} = 711 Hz, PF_6).

IR (KBr): ν/cm^{-1} = 3058, 2961, 1718, 1619, 1589, 1570, 1510, 1461, 1436, 1390, 1370, 1307, 1260, 1218, 1096, 1070, 1029, 914, 841, 746, 695, 557, 509.

Elemental analysis (%) $C_{61}H_{57}CuF_6N_3O_3P_3$ (M = 1150.60 g/mol): Calculated C 63.68, H 4.99, N 3.65; Found C 63.88, H 5.01, N 3.66.

HRMS(ESI): ($C_{61}H_{57}CuN_3O_3P_2$ $[M]^+$) Calculated: 1004.3171; Found: 1004.3146.

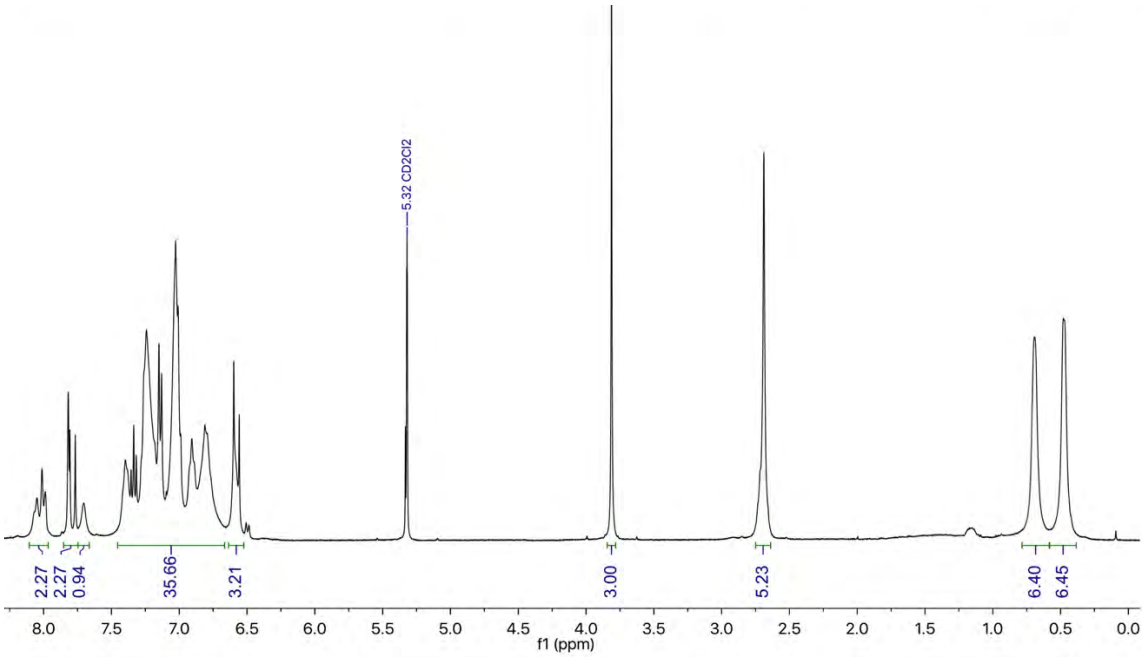


Figure S12. ^{1}HNMR (400 MHz, CD_2Cl_2, 298 K).

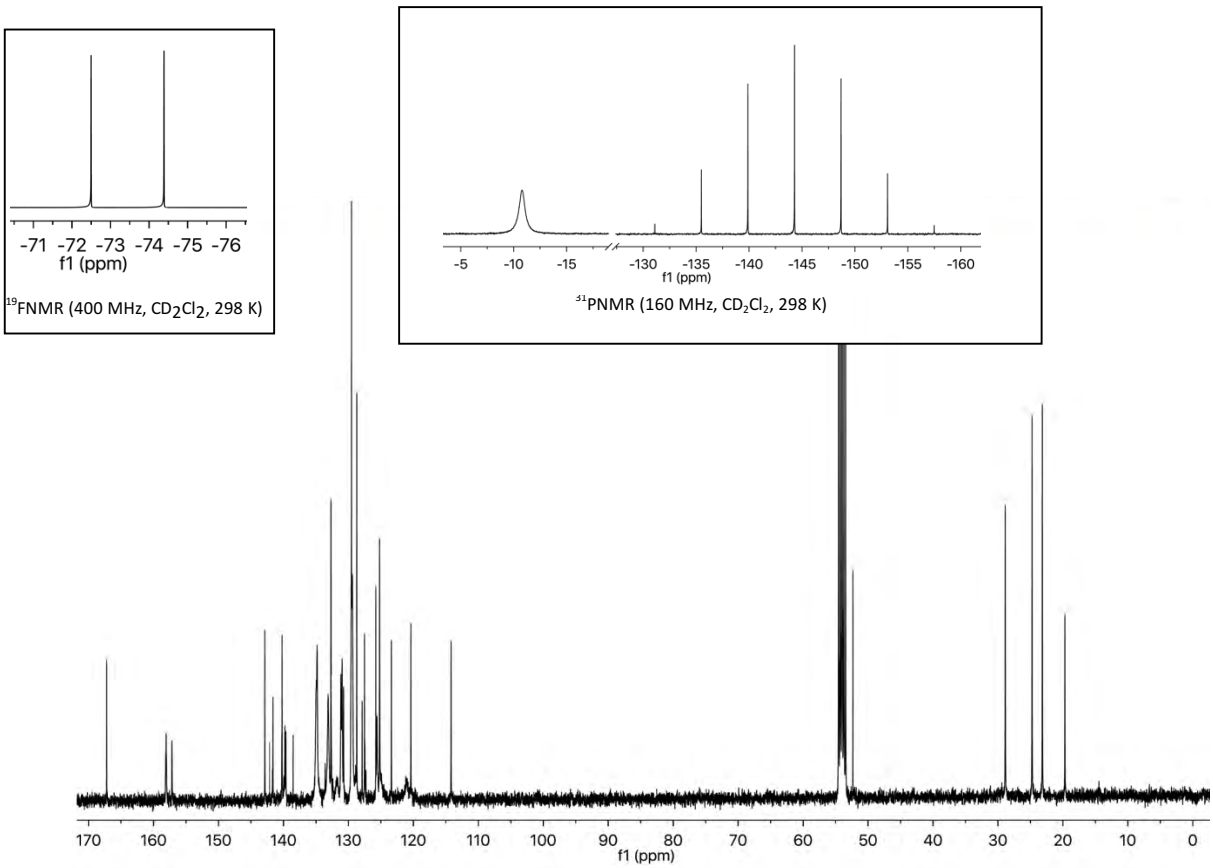
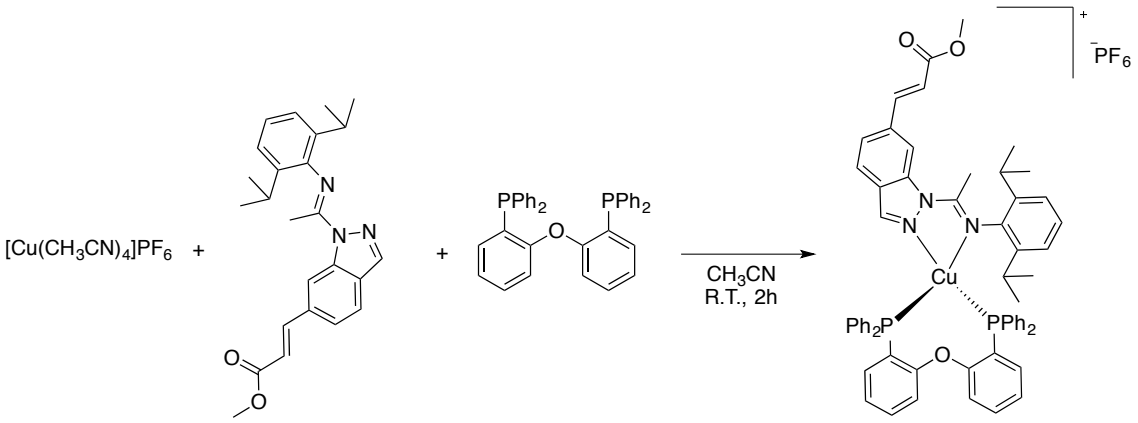
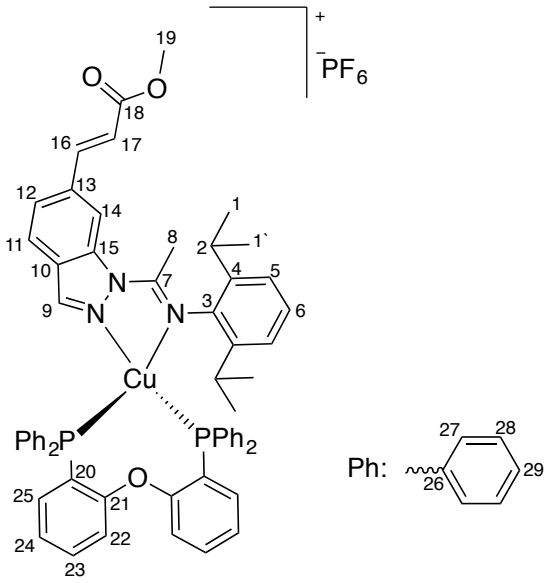


Figure S13. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR.

[((methyl (*E*)-3-(1-((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazol-6-yl)acrylate)((Oxydi-2,1-phenylene)bis(diphenyl phosphine))Cu(I)]PF_6. (C4)



A solution of methyl (*E*)-3-(1-((*E*)-1-((2,6-diisopropylphenyl)imino)ethyl)-1*H*-indazol-6-yl)acrylate (**L4**) (100 mg, 0.25 mmol) in acetonitrile was added dropwise to a solution of $[Cu(CH_3CN)_4]PF_6$ (92 mg, 0.25 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of (Oxydi-2,1-phenylene)bis(diphenyl phosphine) (133 mg, 0.25 mmol) was added in CH_2Cl_2 and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH_2Cl_2 / Hexane mixture at -20°C, obtaining **C4** as a bright yellow powder in 91% yield (259 mg, 0.23 mmol).



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = 8.09 (br, 1H, H14), 7.94 (d, *J* = 16 Hz, 1H, H16), 7.73 (d, *J* = 8.5 Hz, 1H, H11), 7.68 (br, 1H, H9), 7.57 (d, *J* = 8.5 Hz, 1H, H12), 7.42-6.84 (m, 25H, H24-

25, H27-29), 7.32 (m, 1H, H6), 7.16 (m, 1H, H5), 6.91 (br, 2H, H22), 6.72 (d, *J* = 16 Hz, 1H, H17), 6.61 (br, 2H, H23), 3.84 (br, 3H, H19), 2.74 (m, 5H, H8, H2), 0.73 (br, 6H, H1), 0.51 (br, 6H, H1').

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K): δ/ppm = 167.0 (C18), 158.1 (C21), 157.2 (C7), 143.6 (C16), 141.8 (C3), 140.3 (C4), 139.6 (C15), 139.4 (C9), 134.8 (C23), 133.2, 132.6, 131.1, 129.5, 129.3, 128.7, 128.1 (C10), 127.5 (C6), 125.8 (C13), 125.6 (C22), 125.2 (C12), 125.1 (C5), 123.9 (C11), 122.2 (C17), 113.1 (C14), 52.3 (C19), 28.8 (C2), 24.7 (C1), 23.2 (C1'), 19.7 (C8).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.09 / 143.6, 125.8 (H14 / C16, C13), 7.94 / 167.0, 122.2, 113.1 (H16 / C18, C17, C14), 7.73 / 139.6, 128.7 (H11 / C15, C10), 7.57 / 143.6, 128.7, 113.1 (H12 / C16, C10, C14), 7.32 / 140.3, 125.1 (H6 / C4, C5), 7.16 / 141.8, 28.8 (H5 / C3, C2), 6.72 / 167.0, 125.8 (H17 / C18, C13), 6.61 / 158.1 (H23 / C21), 3.84 / 167.0 (H19 / C18), 2.74 / 157.2 (H8 / C7), 2.74 / 141.8, 140.3, 125.1, 24.7, 23.2 (H2 / C3, C4, C5, C1, C1'), 0.73 / 140.3, 28.8, 23.2 (H1 / C4, C2, C1'), 0.51 / 140.3, 28.8, 24.7 (H1' / C4, C2, C1).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{13}C) = 8.09 / 113.1 (H14 / C14), 7.94 / 143.6 (H16 / C16), 7.73 / 123.9 (H11 / C11), 7.68 / 139.4 (H9 / C9), 7.57 / 125.2 (H12 / C12), 7.32 / 127.5 (H6 / C6), 7.16 / 125.1 (H5 / C5), 6.91 / 125.6 (H22 / C22), 6.72 / 122.2 (H17 / C17), 6.61 / 134.8 (H23 / C23), 3.84 / 52.3 (H19 / C19), 2.74 / 28.8 (H2 / C2), 2.74 / 19.7 (H8 / C8), 0.73 / 24.7 (H1 / C1), 0.51 / 23.2 (H1' / C1').

COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K): δ (^{1}H) / δ (^{1}H) = 7.94 / 6.72 (H16 / H17), 7.73 / 7.57 (H11 / H12), 7.32 / 7.16 (H6 / H5), 6.91 / 6.61 (H22 / H23), 2.74 / 0.73, 0.51 (H2 / H1, H1').

^{19}F NMR (400 MHz, CD_2Cl_2, 298 K): δ/ppm = -73.1 (d, J^{F-P} = 711 Hz).

$^{31}P\{1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ/ppm = -10.8 (s, POP), -144.4 (hept, J^{P-F} = 711 Hz, PF_6).

IR (KBr): ν/cm^{-1} = 3058, 2962, 1719, 1619, 1575, 1480, 1461, 1436, 1416, 1389, 1370, 1416, 1389, 1308, 1260, 1212, 1095, 1070, 1035, 999, 950, 916, 840, 802, 746, 695, 625, 557, 509, 489.

Elemental analysis (%) $C_{61}H_{57}CuF_6N_3O_3P_3$ (M = 1150.60 g/mol): Calculated C 63.68, H 4.99, N 3.65; Found C 63.83, H 5.00, N 3.66.

HRMS(ESI): ($C_{61}H_{57}CuN_3O_3P_2$ $[M]^+$) Calculated: 1004.3171; Found: 1004.3117.

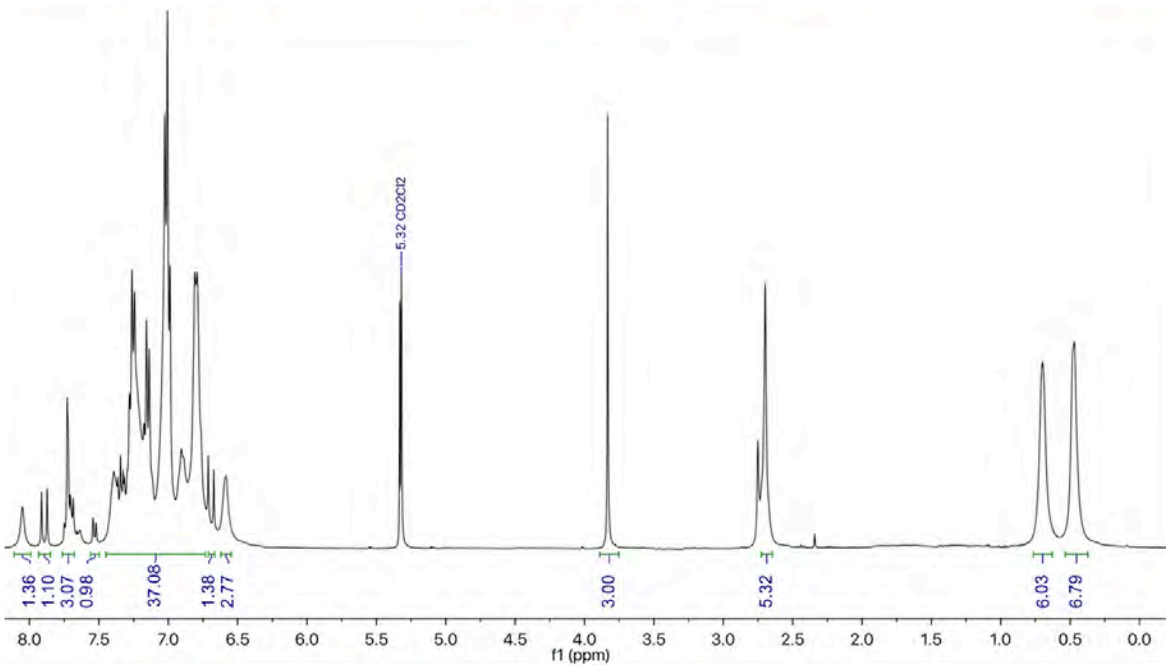


Figure S14. ^{1}HNMR (400 MHz, CD_2Cl_2, 298 K).

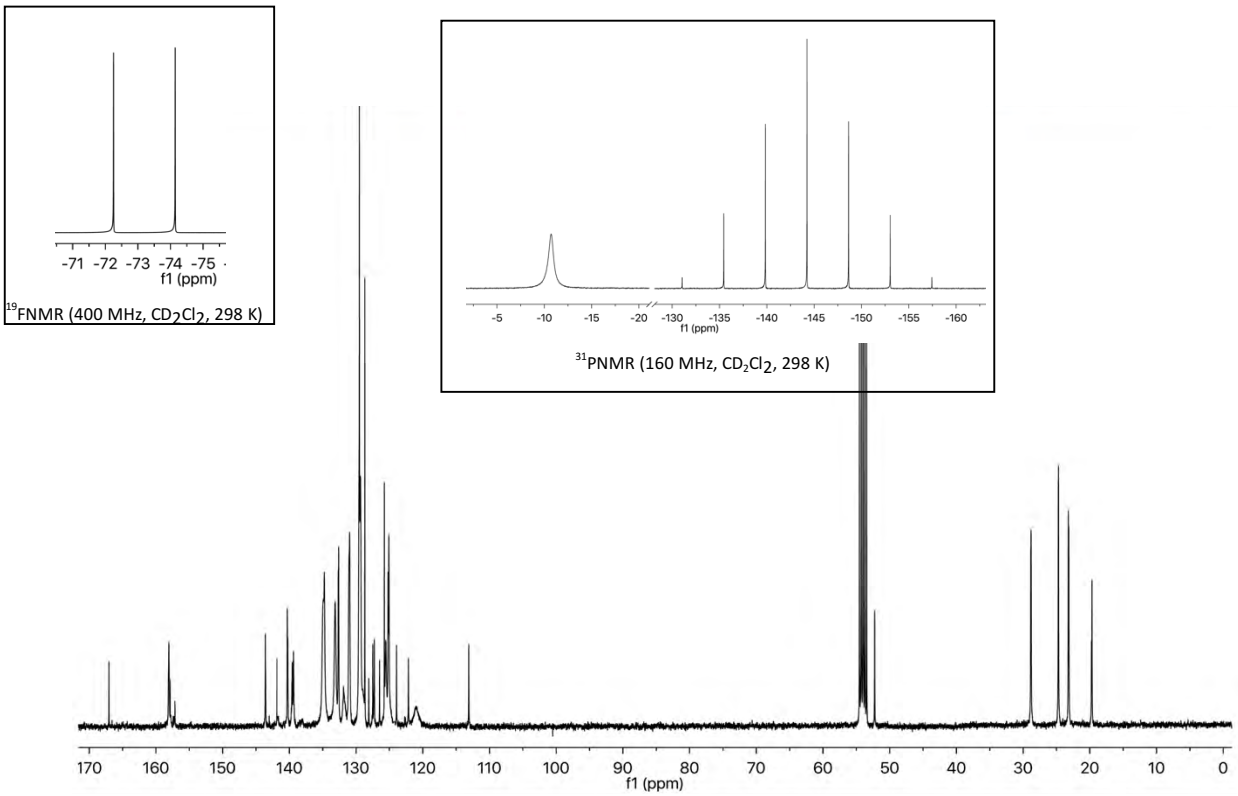


Figure S15. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 298 K) and inserts of ^{19}FNMR y ^{19}PNMR.

Theoretical calculation

Table S1. Properties of the low-lying singlet excited states (S_i) of complexes **C1**-**4**. [a]

Complex	State	λ_{max} [nm] (E [eV])	f	Monoexcitations (CI coeff.; % cont.)	Description of the electronic transition
C1	S_1	372 (3.34)	0.131	H→L (0.89; 80%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
	S_2	353 (3.51)	0.042	H−1→L (0.87; 76%)	Cu(d)+*N,N*(*n*,π)→*N,N*(π^*); ^{1}LC/^{1}MLCT
C2	S_1	398 (3.12)	0.154	H→L (0.94; 88%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
	S_2	374 (3.31)	0.030	H−1→L (0.91; 83%)	Cu(d)+*N,N*(*n*,π)→*N,N*(π^*); ^{1}LC/^{1}MLCT
C3	S_1	371 (3.34)	0.164	H→L+1 (0.76; 57%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
				H→L (-0.50; 25%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
	S_2	353 (3.52)	0.037	H−1→L+1 (0.76; 57%)	Cu(d)+*N,N*(*n*,π)→*N,N*(π^*); ^{1}LC/^{1}MLCT
				H→L (0.42; 18%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
				H−1→L (-0.40; 16%)	Cu(d)+*N,N*(*n*,π)→*N,N*(π^*); ^{1}LC/^{1}MLCT
C4	S_1	407 (3.04)	0.253	H→L (0.95; 91%)	Cu(d)+*P,P*(*n*)→*N,N*(π^*); ^{1}LLCT/^{1}MLCT
	S_2	381 (3.26)	0.031	H−1→L (0.92; 85%)	Cu(d)+*N,N*(*n*,π)→*N,N*(π^*); ^{1}LC/^{1}MLCT

[a] Data were obtained in CH_2Cl_2 at the PBE0/6-31G(d,p)/LANL2DZ level of theory. *E*: transition energies. *f*: oscillator strength. CI coeff.: CI coefficient. % cont: percentage of contribution to the excited state wavefunction. H and L correspond to the HOMO and LUMO, respectively.

Electrochemical properties

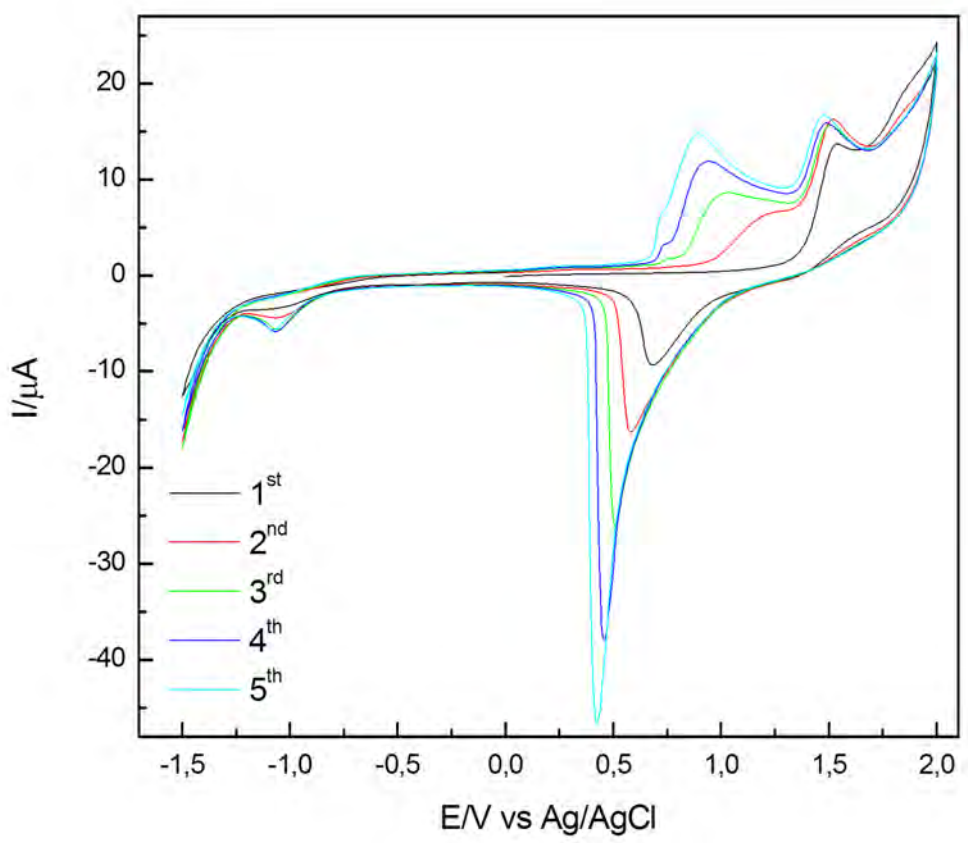


Figure S16. Continuous five cycles between −1.50 and 2.00 V at scan rate of 0.1Vs^{-1}. Pt working electrode, Ag/AgCl reference electrode and wire Pt as counter electrode. Degassed solution of 1mM of **C2**/0.1 M $TBAPF_6/CH_2Cl_2$.

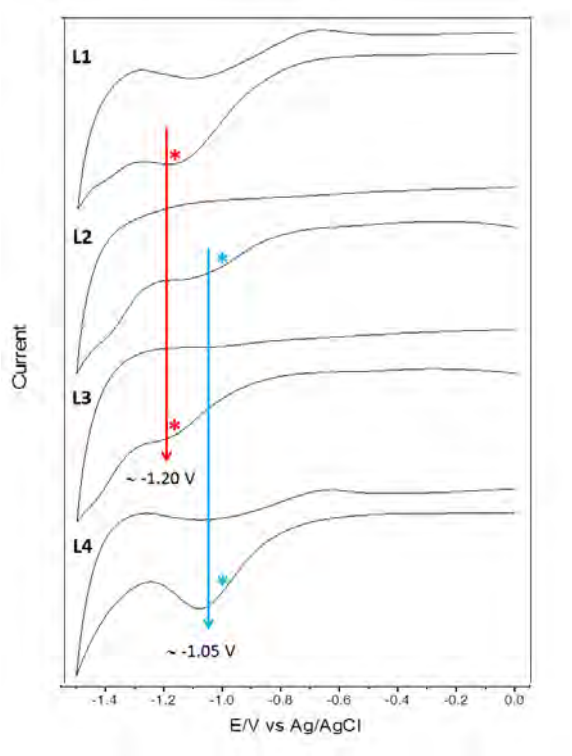


Figure S17. Cyclic voltammetric profiles recorded in anhydrous CH_2Cl_2 solution of L1-L4 (1 mM) with 0.1 M $TBAPF_6$ as supporting electrolyte at a scan rate of 0.1 V /s. Three-electrode cell configuration (Pt disc working electrode, saturated Ag/AgCl reference electrode and a Pt wire counter electrode).

Absorption spectra of ligands L1-4

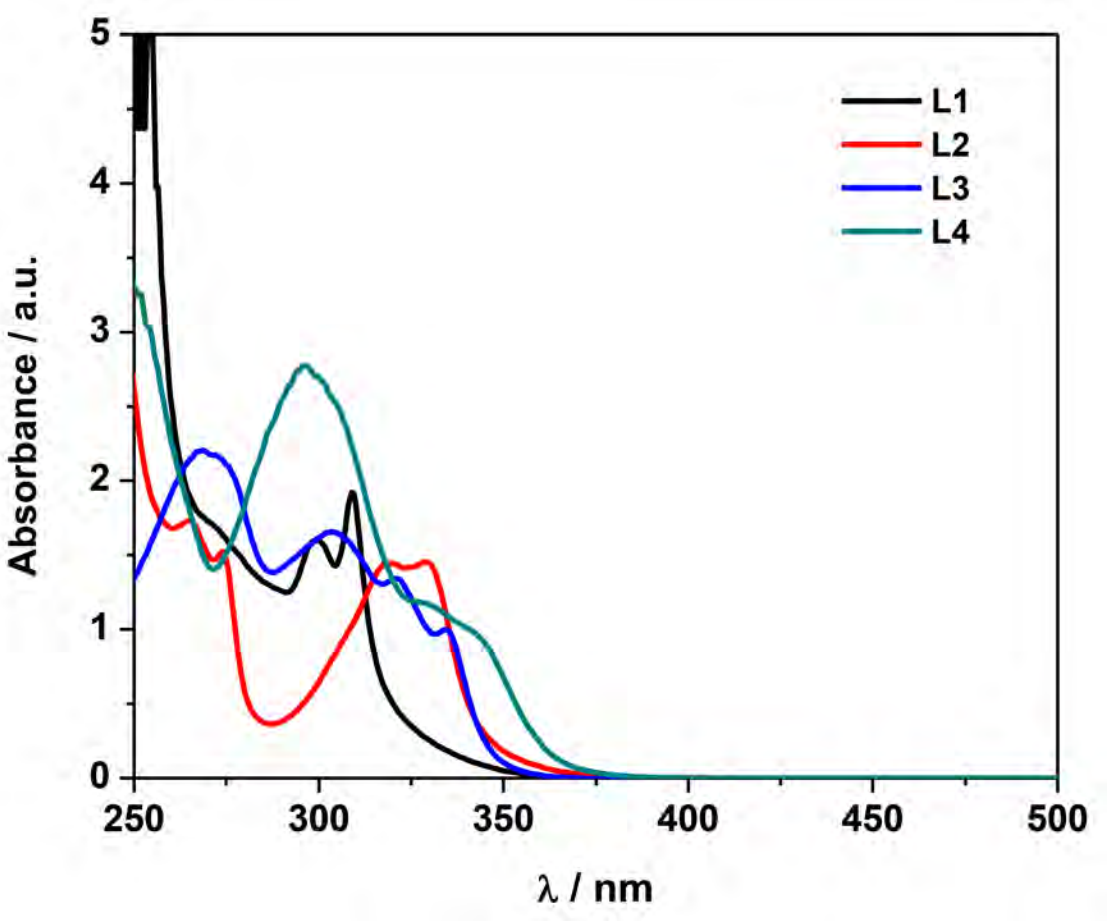


Figure S18. Absorption spectra of ligands **L1**-**4** in CH_2Cl_2 at room temperature.

Phosphorescence spectra of protonated ligands L1-4

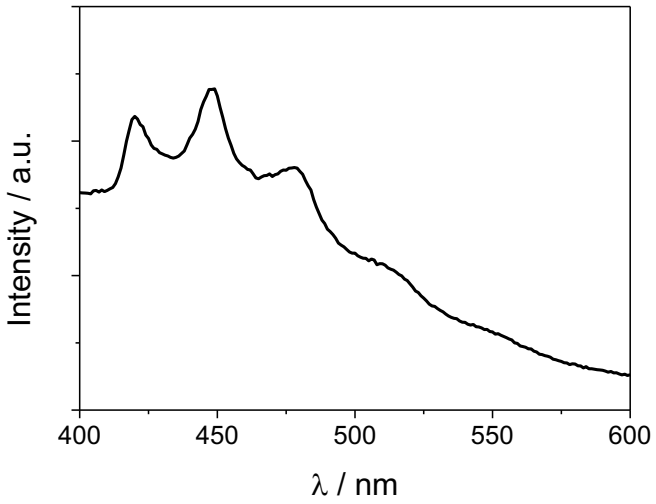


Figure S19. Phosphorescence spectrum of protonated ligand **L1** in glassy matrix at 77 K (4/1 ethanol/methanol, with few droplets of concentrated $HClO_4$).

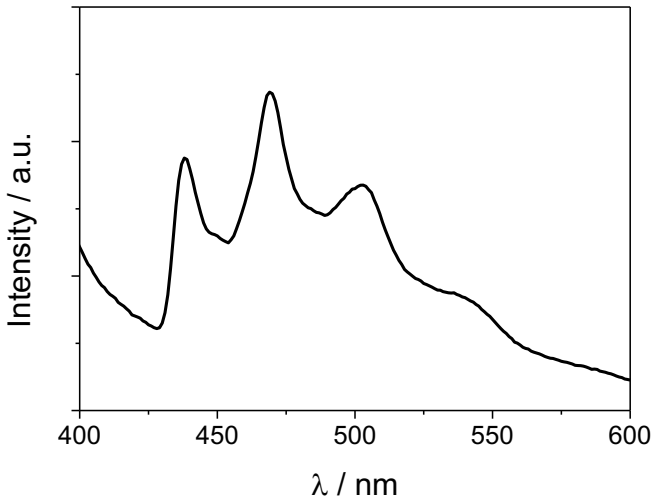


Figure S20. Phosphorescence spectrum of protonated ligand **L2** in glassy matrix at 77 K (4/1 ethanol/methanol, with few droplets of concentrated $HClO_4$).

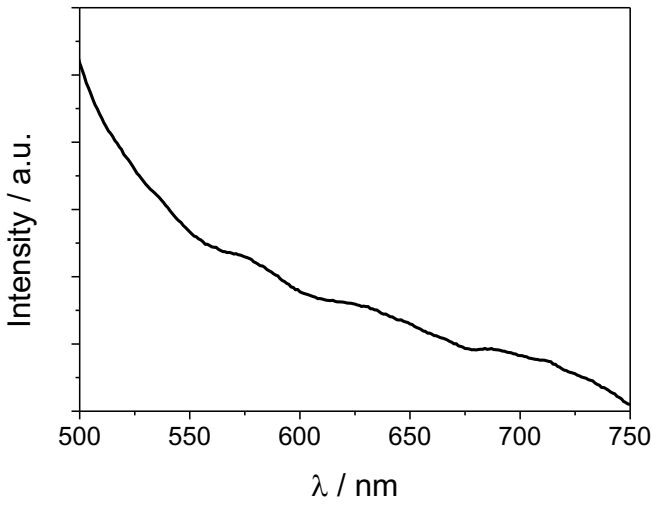


Figure S21. Phosphorescence spectrum of protonated ligand **L3** in glassy matrix at 77 K (4/1 ethanol/methanol, with few droplets of concentrated $HClO_4$). Note that the phosphorescence is herein buried under the intense tail arising from ligand fluorescence.

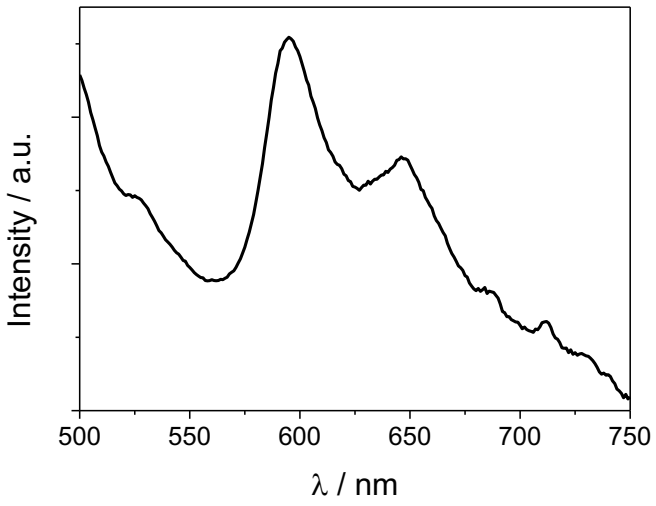


Figure S22. Phosphorescence spectrum of protonated ligand **L4** in glassy matrix at 77 K (4/1 ethanol/methanol, with few droplets of concentrated $HClO_4$). Also in this case, a tail at shorter wavelengths arising from intense ligand fluorescence is clearly discernable.

Variable temperature NMR experiment

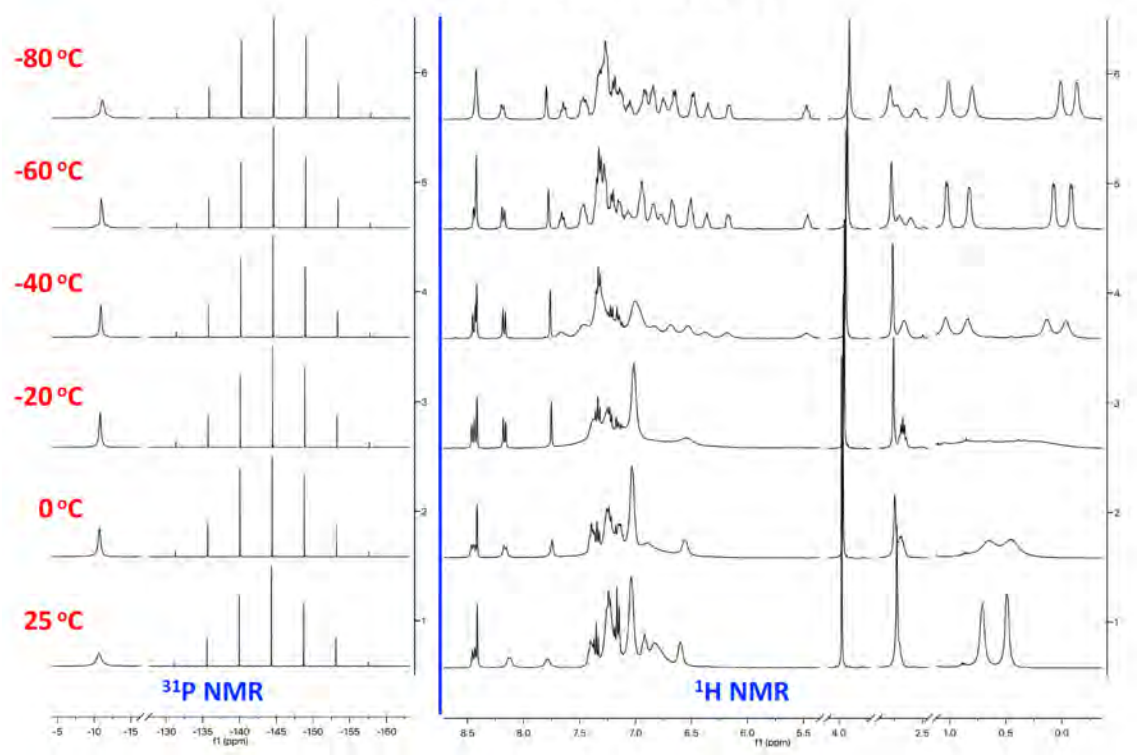


Figure S23. Variable temperature ^{1}H (400 MHz) and ^{31}P (160 MHz) NMR in CD_2Cl_2 of **C1**.

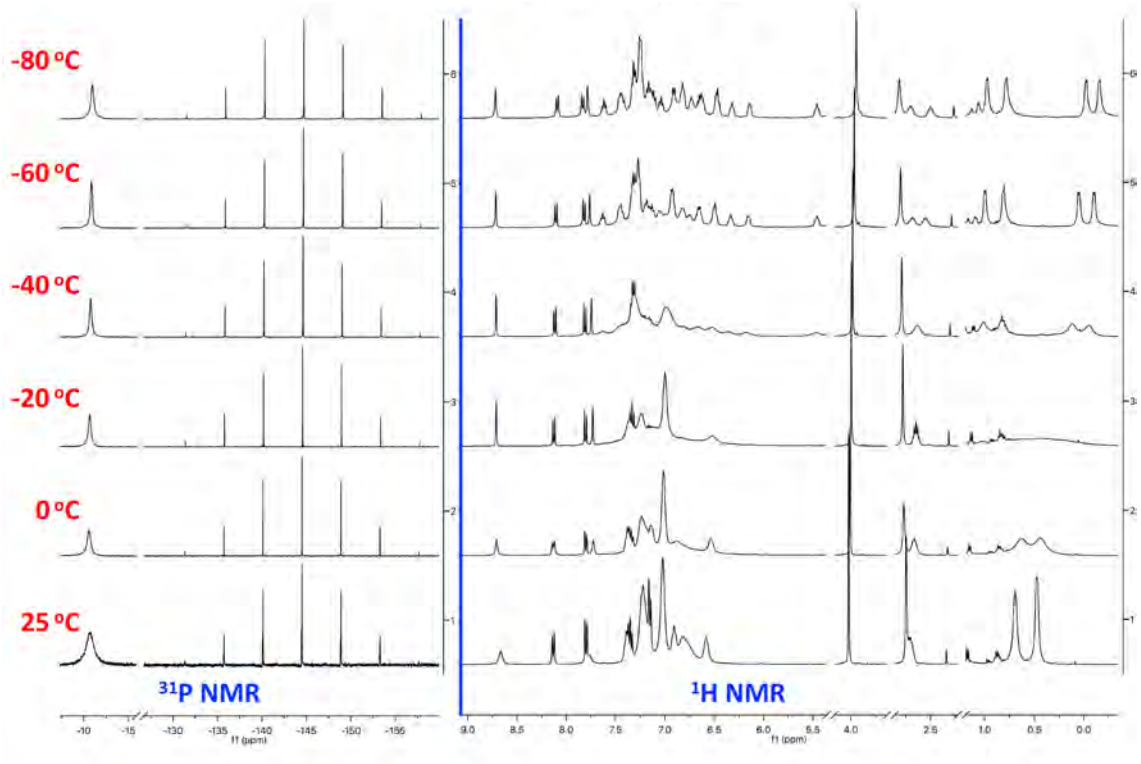


Figure S24. Variable temperature ^{1}H (400 MHz) and ^{31}P (160 MHz) NMR in CD_2Cl_2 of **C2**.

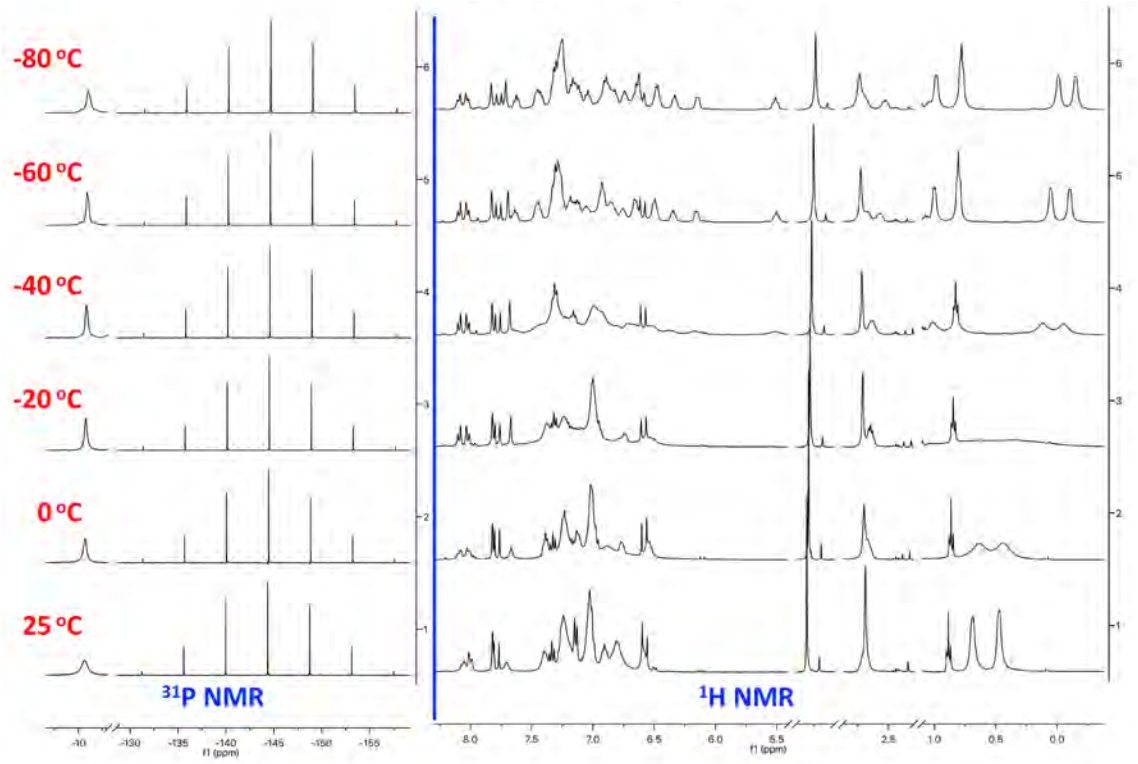


Figure S25. Variable temperature ^{1}H (400 MHz) and ^{31}P (160 MHz) NMR in CD_2Cl_2 of **C3**.

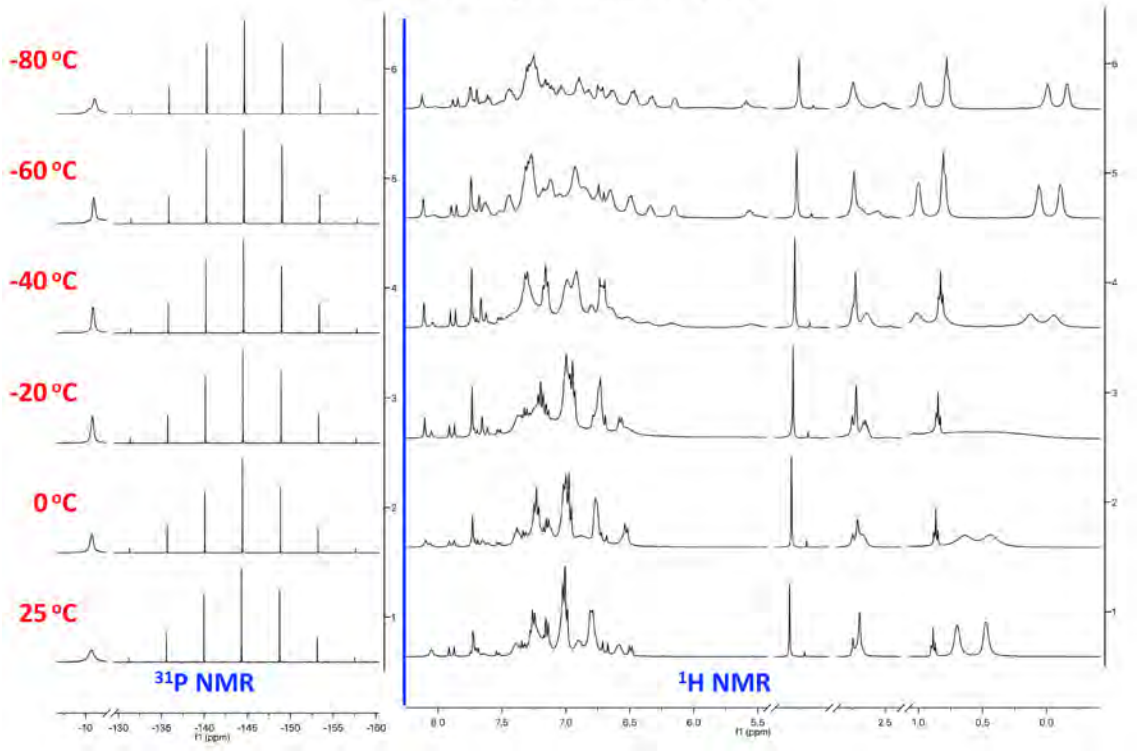


Figure S26. Variable temperature ^{1}H (400 MHz) and ^{31}P (160 MHz) NMR in CD_2Cl_2 of **C4**.