

Electronic Supplementary Information

Synthesis of new phosphorescent imidoyl-indazol and phosphines mixed ligand Cu(I) complexes - Structural characterization and photophysical properties.

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Experimental Section

All reagents commercially available were used as received from Sigma-Aldrich, unless otherwise specified. NMR spectra were recorded on NMR Bruker AV 400. Chemical shifts are given in parts per million relative to TMS [^1H and ^{13}C , $\delta(\text{SiMe}_4) = 0$] or an external standard [$\delta(\text{BF}_3\text{OEt}_2) = 0$ for ^{11}B NMR, $\delta(\text{CFCl}_3) = 0$ for ^{19}F NMR]. Most NMR assignments were supported by additional 2D experiments. Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer. For Mass spectra were obtained on an HP 5988A spectrometer (Hewlett-Packard, Palo Alto, CA, USA). FT-IR spectra were recorded on a Bruker Vector-22 Spectrophotometer using KBr pellets. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel. Column chromatography was carried out using Merck silica gel 60 (70–230 mesh).

UV-Vis absorption spectra were recorded on a *Jasco V-570* UV/Vis/NIR spectrophotometer. Photoluminescence spectra at 77 K were taken on an *Edinburgh Instrument* spectrofluorimeter equipped with a 900 W Xe arc lamp as excitation source, a photomultiplier tube and an InGaAs detector for the visible and the NIR detection, respectively. Dichloromethane solutions of the complexes were previously degassed with N_2 for approximately 20 min. A cryostat mounted on the spectrofluorimeter was used. KBr pellets containing complexes **1-4** were prepared by grinding the solid sample with solid potassium bromide purchased from Sigma-Aldrich. Poly(methyl methacrylate) (PMMA) films were prepared from CH_2Cl_2 solutions of **1-4** and low molecular weight poly(methyl methacrylate) followed by drop casting onto a glass surface. In both cases the concentration was adjusted depending on the absorption coefficient of the sample. The thickness of the polymeric film was not controlled. Femtosecond time-resolved experiments were performed using a pump-probe setup based on the Spectra-Physics Hurricane Ti:sapphire laser source and the Ultrafast Systems Helios spectrometer. The 400-nm pump pulses were generated with a Spectra Physics SHG. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450-750 nm). Effective time resolution: ca. 300 fs, temporal chirp over the white-light 450-750 nm range: ca. 200 fs, temporal window of the optical delay stage: 0-2000 ps. The time-

resolved spectral data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

The electrochemical characterization of the compounds was conducted in a conventional three-compartment, three-electrode cell using a polycrystalline platinum disk (0.07 cm^2 geometric area) as working electrode at room temperature. The counter electrode was a coiled Pt wire with a surface area at least ten times greater than the working electrode, separated from the electrolytic solution by a sintered glass. Prior to each experiment, the working electrode was polished with alumina slurry (particle size 0.05 to $0.3 \text{ }\mu\text{m}$) to a mirror finish, thoroughly rinsed with deionized water and acetone. Prior to all the experiments, solutions were purged with nitrogen during 15 min and a nitrogen atmosphere was maintained over the solution during the measurements. The supporting electrolyte, Tetrabutylammonium tetrafluoroborate (TBATFB) was dried at 110°C and kept into a dryer until used. A Ag/Ag^+ non-aqueous electrode was used as reference electrode ($10 \text{ mmol}\cdot\text{L}^{-1} \text{ Ag}^+$). Ferrocene ($\text{FeCp}_2^{0/+}$) was used as an internal electrode-potential standard.^[1] All the potentials quoted in this work are referred to a Ag/AgCl electrode. All measurements were performed at a CHI730E potentiostat, using a concentration of 0.1 mol L^{-1} of TBATFB, $1 \cdot 10^{-3} \text{ mol L}^{-1}$ of each compound in dichloromethane.

Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a *Continuum Surelite II* Nd:YAG laser (FWHM = 6-8 ns) with frequency doubled, (532 nm, 330 mJ) or tripled, (355 nm, 160 mJ) option, an *Applied Photophysics* xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted or emitted by the sample was focused onto the entrance slit of a 300 mm focal length *Acton SpectraPro 2300i* triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (*Hamamatsu R3896*). Signals from the photomultiplier (kinetic traces) were processed by means of a *LeCroy 9360* (600 MHz, 5 Gs/s) digital oscilloscope.

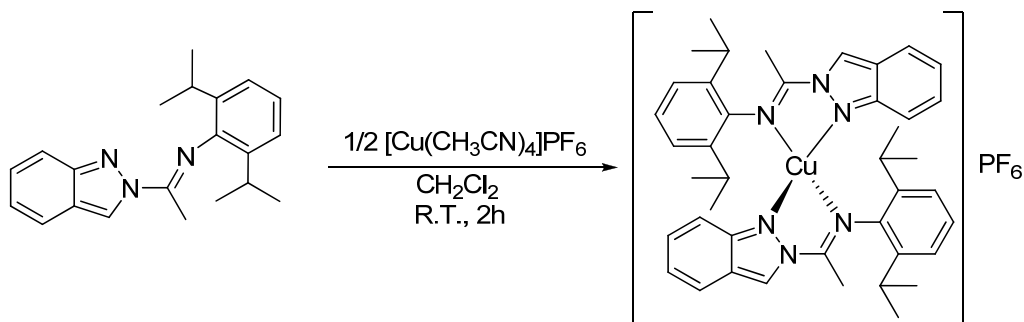
X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, 276, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, A59, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112-122) and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound **1** one disordered over two positions PF_6 anion was found in the asymmetrical unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. In addition a disordered $CHCl_3$ molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek *J. Appl. Cryst.*, 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. For compound **2** one PF_6 anion and two *iPr* groups were found disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. One and a half badly disordered toluene molecules were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

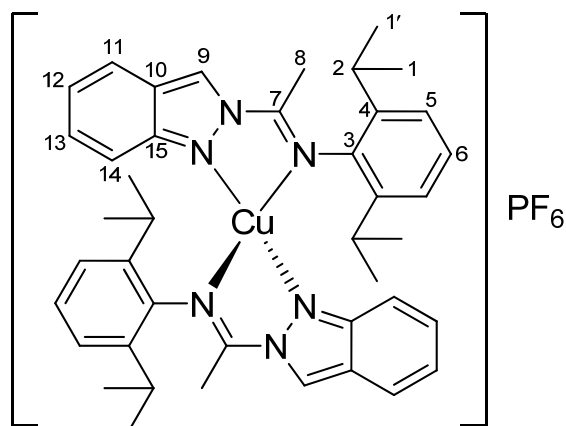
CCDC 1422058 - 1422059 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Synthesis and Characterization of Compounds.

[bis((1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline)Cu(I)]PF₆. (1)



A solution of [Cu(CH₃CN)₄]PF₆ (233 mg, 0.63 mmol) in dichloromethane was added dropwise to a solution of (1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline^[2] (400 mg, 1.25 mmol) in dry dichloromethane. The reaction mixture was stirred for 2 hours at room temperature. Then, the volatiles were removed in vacuum. Crude product was purified by crystallization. Obtaining **7** as a deep red crystalline material in 94% yield (499 mg, 0.59 mmol).



¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = 8.80 (s, 1H, H₉), 7.73 (d, *J* = 8.5 Hz, 1H, H₁₄), 7.22 (t, *J* = 7.3 Hz, 1H, H₁₃), 7.02 (m, 5H, H₅, H₆, H₁₁, H₁₂), 2.79 (broad, 2H, H₂), 2.46 (s, 3H, H₈), 1.00 (d, *J* = 6.7 Hz, 6H, H_{1'}), 0.34 (broad, 6H, H₁).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ/ppm = 157.4 (C₇), 147.6 (C₁₅), 140.9 (C₃), 139.3 (C₄), 131.8 (C₁₃), 127.3 (C₁₂), 125.4 (C₆), 125.1 (C₉), 124.8 (C₅), 124.1 (C₁₀), 122.5 (C₁₄), 116.3 (C₁₁), 28.8 (C₂), 23.5 (C_{1'}), 22.9 (C₁), 16.1 (C₈).

¹H, ¹³C-HMBC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 8.80 / 147.6, 124.1 (H9 / C15, C10), 7.73 / 147.6, 131.8, 124.1 (H14 / C15, C13, C10), 7.22 / 147.6, 124.1 (H13 / C15, C10), 7.02 / 124.1 (H12 / C10), 7.02 / 139.3 (H6 / C4), 7.02 / 140.9, 28.8 (H12 / C3, C2), 2.46 / 157.4 (H8 / C7), 1.00 / 139.3, 28.8 (H1' / C4, C2).

¹H, ¹³C-HSQC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 8.80 / 125.1 (H9 / C9), 7.73 / 122.5 (H14 / C14), 7.22 / 131.8 (H13 / C13), 7.02 / 127.3 (H12 / C12), 7.02 / 125.4 (H6 / C6), 7.02 / 124.8 (H5 / C5), 7.02 / 116.3 (H11 / C11), 2.79 / 28.8 (H2 / C2), 2.46 / 16.1 (H8 / C8), 1.00 / 23.5 (H1' / C1'), 0.34 / 22.9 (H1 / C1).

COSY (400 MHz / 400 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹H) = 7.73 / 7.22 (H14 / H13), 2.79 / 1.00, 0.34 (H2 / H1, H1').

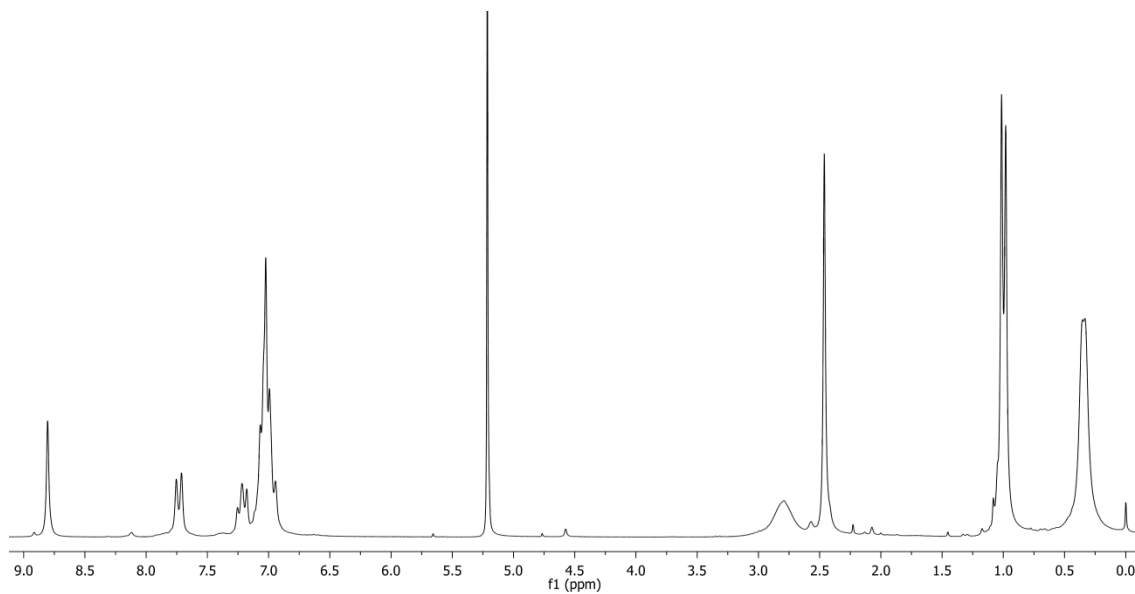
¹⁹F NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = -72.6 (d, $J^{F-P} = 710\text{Hz}$).

³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ/ppm = -144.3 (hept, $J^{P-F} = 710\text{Hz}$, PF₆).

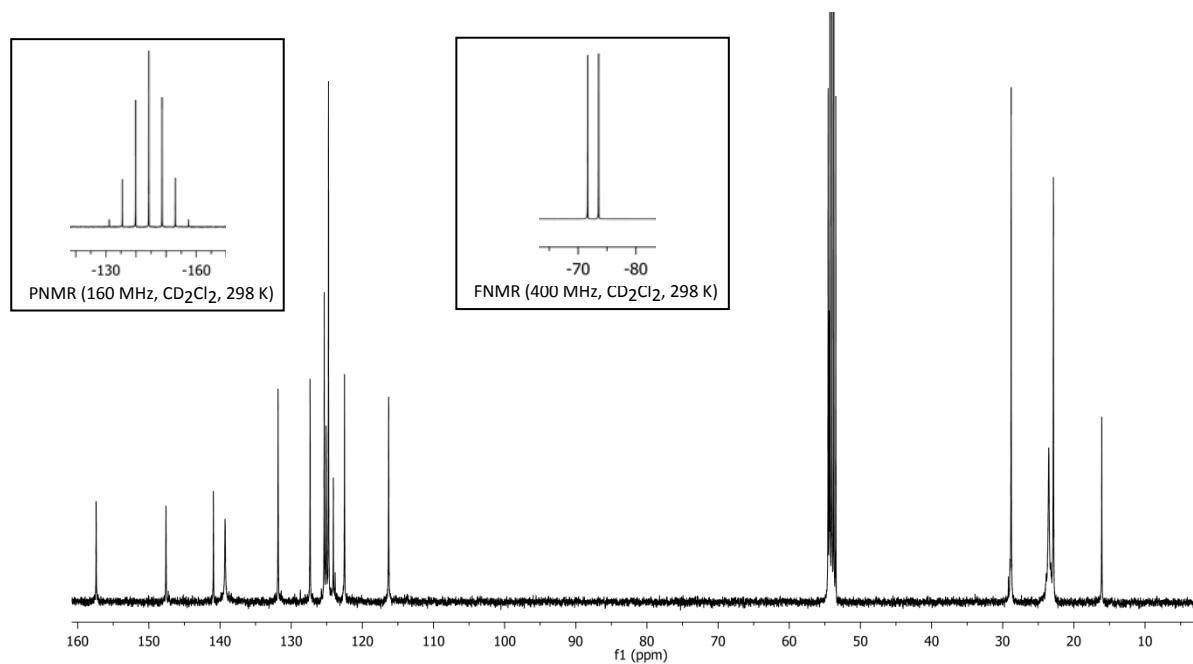
IR (KBr): ν/cm⁻¹ = 3147, 3065, 2964, 2927, 2868, 1643, 1625, 1589, 1523, 1462, 1441, 1409, 1385, 1363, 1325, 1306, 1256, 1220, 1189, 1152, 1134, 1091, 1059, 1041, 1002, 987, 967, 936, 916, 841, 795, 755, 737, 713, 629.

Elemental analysis (%) C₄₂H₅₀CuF₆N₆P (M = 847.40 g/mol): calculated C 59.53, H 5.95, N 9.92; found C 59.32, H 6.57, N 10.18.

HRMS-ESI: (C₄₂H₅₀CuN₆ [M]⁺) Calc: 701.3393 ; Found: 701.3356.

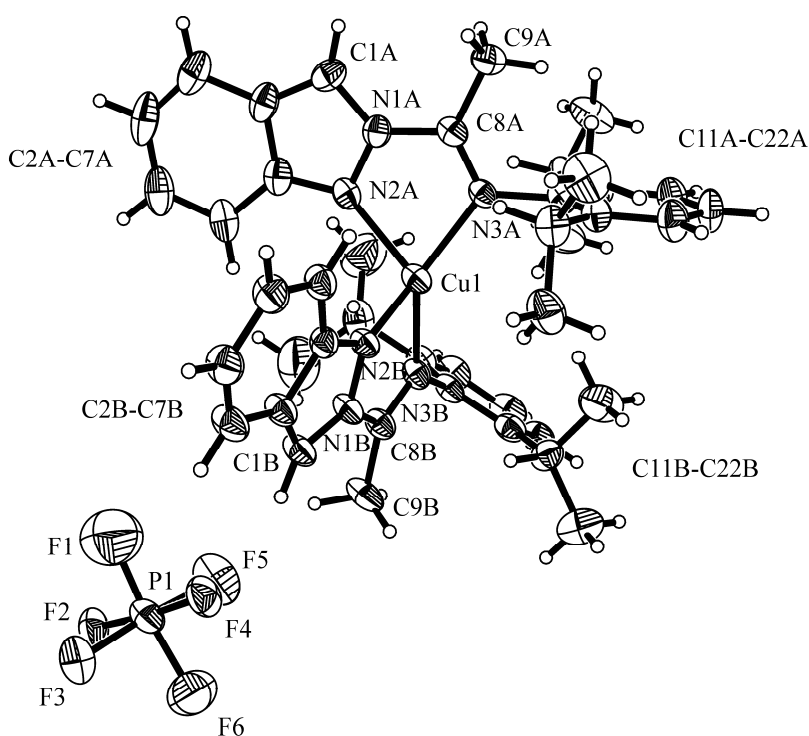


^1H NMR (400 MHz, CD_2Cl_2 , 298 K)



$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K)

X-ray crystal structure analysis of 1: formula $C_{42}H_{50}CuN_6F_6P$, $M = 847.39$, red crystal, $0.13 \times 0.10 \times 0.03$ mm, $a = 32.1326(6)$, $b = 12.6582(2)$, $c = 22.0163(5)$ Å, $\beta = 98.758(1)^\circ$, $V = 8850.5(3)$ Å³, $\rho_{\text{calc}} = 1.272$ gcm⁻³, $\mu = 0.590$ mm⁻¹, empirical absorption correction ($0.927 \leq T \leq 0.982$), $Z = 8$, monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 25706 reflections collected ($\pm h, \pm k, \pm l$), 7654 independent ($R_{\text{int}} = 0.056$) and 5457 observed reflections [$I > 2\sigma(I)$], 579 refined parameters, $R = 0.082$, $wR^2 = 0.227$, max. (min.) residual electron density 0.67 (-0.37) e.Å⁻³, the hydrogen atoms were calculated and refined as riding atoms.



Selected structural parameters for complex 1.

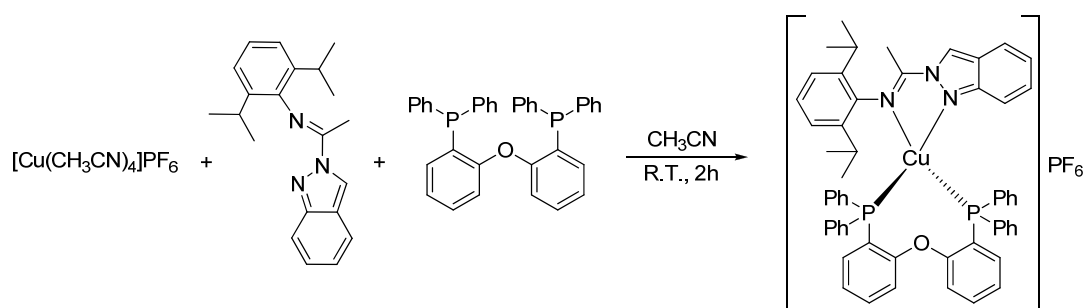
Distances (Å)	
Cu1-N3A	2.055(4)
Cu1-N2A	2.038(4)
Cu1-N3B	2.021(4)
Cu1-N2B	2.080(5)
Bond angles (deg)	
N3A-Cu1-N2A	79.1(2)
N3B-Cu1-N2B	78.8(2)

N3A-Cu1-N2B	128.0(2)
N3A-Cu1-N3B	140.4(2)
N3B-Cu1-N2A	127.2(2)
N2A-Cu1-N2B	103.7(2)

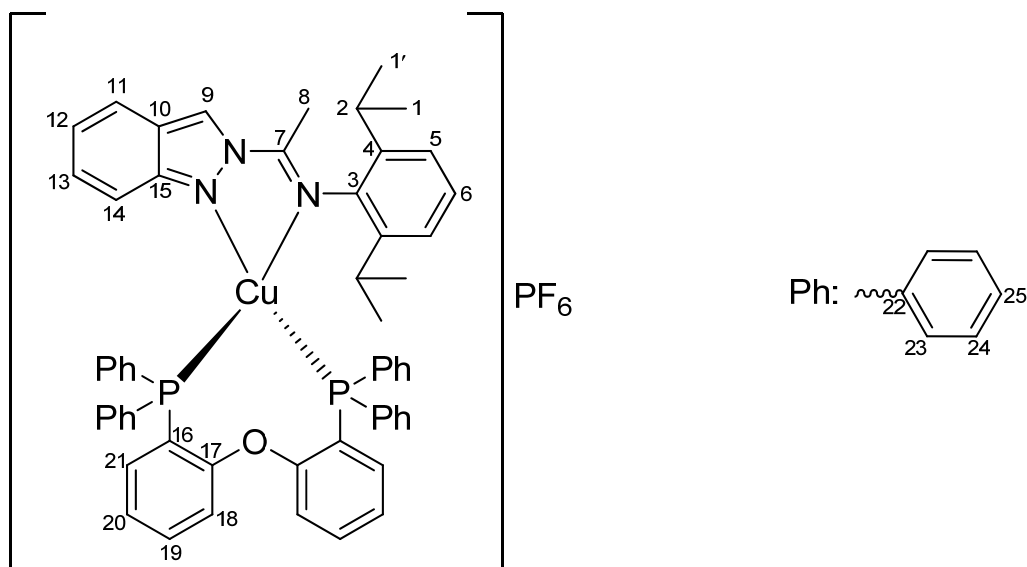
Dihedral angles (deg)

N1B-N2B-Cu1-N2A	112.1(3)
N1B-N2B-Cu1-N3A	-161.0(3)
N3B-C8B-N1B-N2B	-7.5(6)
C9B-C8B-N1B-N2B	171.3(5)
C9B-C8B-N3B-C11B	-4.0(8)

[[((1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline)((Oxydi-2,1-phenylene)bis(diphenyl phosphine))Cu(I)]PF₆. (2**)**



A solution of (1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline^[1] (50 mg, 0.16 mmol) in acetonitrile was added dropwise to a solution of [Cu(CH₃CN)₄]PF₆ (58 mg, 0.16 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) (POP) (84 mg, 0.16 mmol) was added in acetonitrile and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH₂Cl₂ / Hexane mixture at -20°C, obtaining **2** as a yellow crystalline material in 98% yield (163 mg, 0.15 mmol).



¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = 9.06 (s, 1H, H9), 7.84 (d, *J* = 8.6Hz, 1H, H14), 7.39 (t, *J* = 7.5Hz, 1H, H6), 7.27 (m, 8H, H24), 7.14 (d, *J* = 7.8Hz, 2H, H5), 7.11 (m, 2H, H21), 7.05 (m, 9H, H13, H23), 6.88 (t, *J* = 7.2Hz, 1H, H12), 6.81 (m, 3H, H11, H20), 6.70 (broad, 4H, H25), 6.47 (broad, 2H, H19), 2.59 (hept, *J* = 6.5Hz, 2H, H2), 2.54 (s, 3H, H8), 0.62 (d, *J* = 6.1Hz, 6H, H1'), 0.49 (d, *J* = 6.1Hz, 6H, H1).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ/ppm = 158.0 (t, *J*^{C-P} = 5.7Hz, C17), 157.3 (C7), 149.4 (C15), 142.1 (C3), 139.6 (C4), 135.1 (t, *J*^{C-P} = 8.5Hz, C23), 134.5 (C19), 133.0 (t, *J*^{C-P} = 7.9Hz, C25), 132.3 (C21), 131.7 (C22), 131.1 (C6), 130.8 (C12), 129.6 (t, *J*^{C-P} = 4.8Hz, C24), 126.2 (C9), 125.4 (C13), 125.3 (C20), 125.1 (C5), 124.5 (C10), 122.2 (C14), 117.1 (C11), 28.9 (C2), 24.6 (C1'), 22.9 (C1), 17.9 (C8).

¹H, ¹³C-HMBC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 9.06 / 149.4, 124.5 (H9 / C15, C10), 7.84 / 149.4, 130.8, 124.5 (H14 / C15, C12, C13), 7.39 / 139.6, 125.1 (H6 / C4, C5), 7.27 / 131.7 (H24 / C22), 7.14 / 142.1, 28.9 (H5 / C3, C2), 7.11 / 158.0, 134.5 (H21 / C17, C19), 7.05 / 117.1 (H13 / C11), 6.88 / 122.2 (H12 / C14), 6.47 / 158.0, 132.3 (H19 / C17, C21), 2.59 / 139.6, 125.1, 24.6, 22.9 (H2 / C4, C5, C1', C1), 2.54 / 157.3 (H8 / C7), 0.62 / 139.6, 28.9 (H1' / C4, C2), 0.49 / 139.6, 28.9 (H1 / C4, C2).

¹H, ¹³C-HSQC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 9.06 / 126.2 (H9 / C9), 7.84 / 122.2 (H14 / C14), 7.39 / 131.1 (H6 / C6), 7.27 / 129.6 (H24 / C24), 7.14 / 125.1 (H5 / C5), 7.11 / 132.3 (H21 / C21), 7.05 / 135.1 (H23 / C23), 7.05 / 125.4 (H13 / C13), 6.88 / 130.8 (H12 / C12), 6.81 / 125.3 (H20 / C20), 6.81 / 117.1 (H11 / C11), 6.70 / 133.0 (H25 / C25), 6.47 / 134.5 (H19 / C19), 2.59 / 28.9 (H2 / C2), 2.54 / 17.9 (H8 / C8), 0.62 / 24.6 (H1' / C1'), 0.49 / 22.9 (H1 / C1).

COSY (400 MHz / 400 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹H) = 7.39 / 7.14 (H6 / H5), 7.27 / 7.05, 6.70 (H24 / H23, H25), 7.11 / 6.81 (H21 / H20), 6.88 / 6.81 (H12 / H11), 6.81 / 6.47 (H20 / H19).

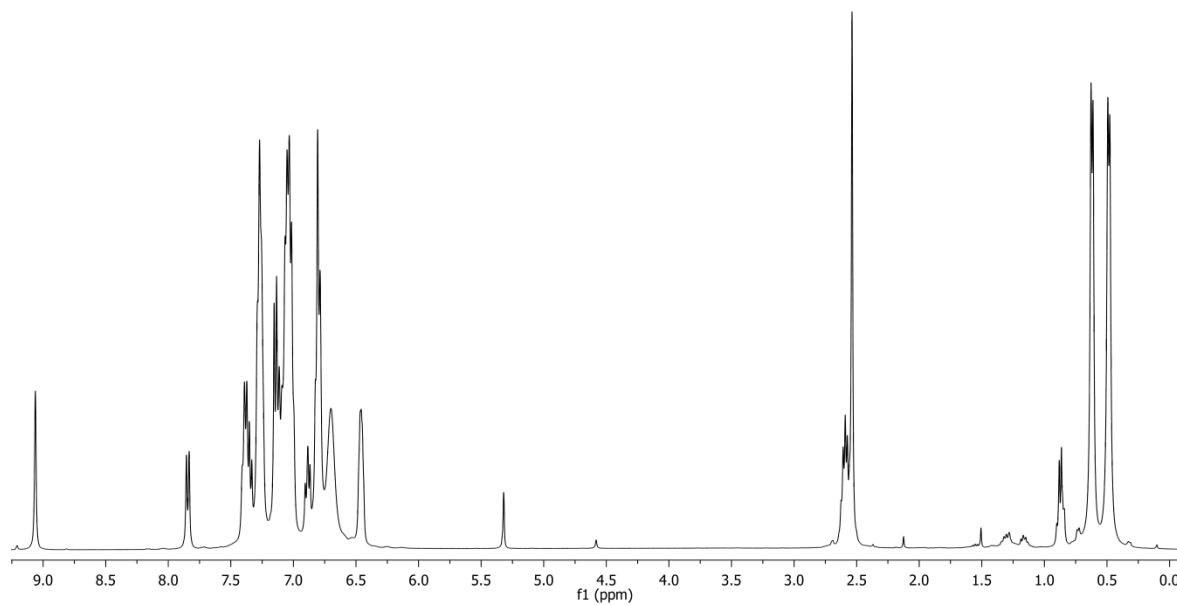
¹⁹F NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = -72.9 (d, *J*^{F-P} = 710Hz).

³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ/ppm = -12.0 (s, POP), -144.3 (hept, *J*^{P-F} = 710Hz, PF₆).

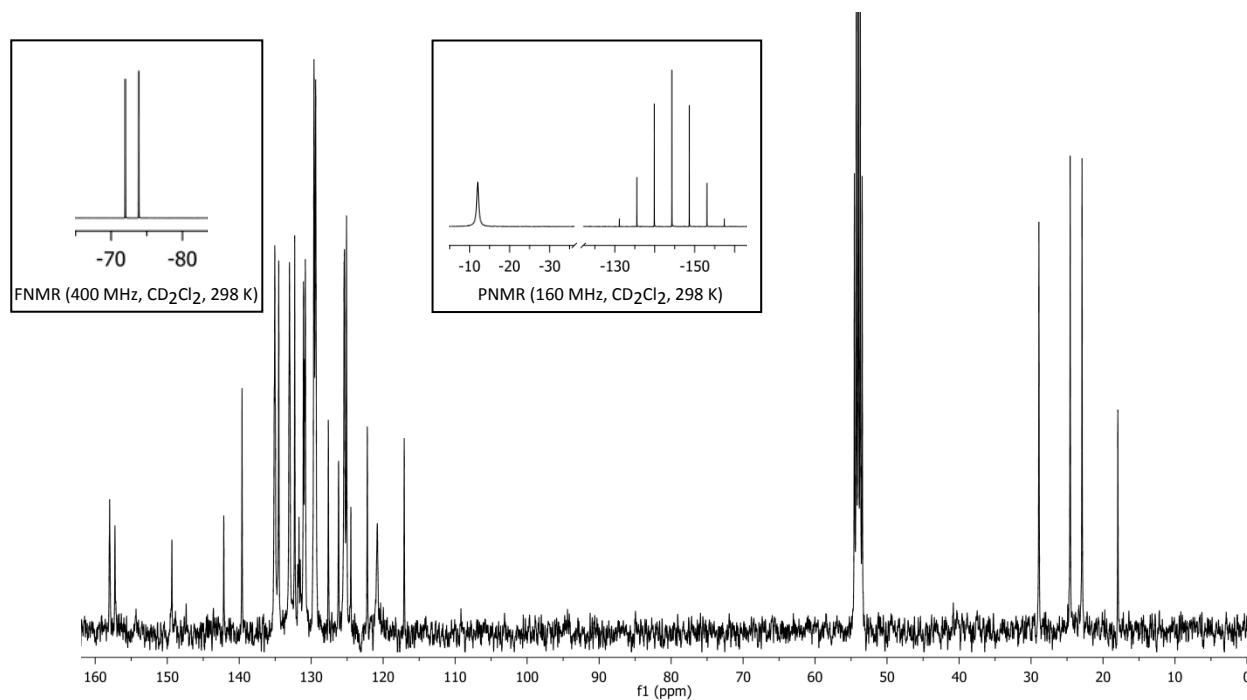
IR (KBr): ν/cm⁻¹ = 3144, 3057, 2963, 2928, 2870, 1678, 1645, 1626, 1588, 1566, 1523, 1480, 1463, 1436, 1406, 1385, 1305, 1260, 1219, 1184, 1161, 1131, 1095, 1071, 1028, 1000, 966, 914, 842, 801, 746, 696, 632.

Elemental analysis (%) $C_{57}H_{53}CuF_6N_3OP_3$ ($M = 1066.51$ g/mol): calculated C 64.19, H 5.01, N 3.94;
found C 63.93, H 5.42, N 4.44.

HRMS-ESI: ($C_{57}H_{53}CuN_3OP_2$ $[M]^+$) Calc: 920.2960 ; Found: 920.2916.

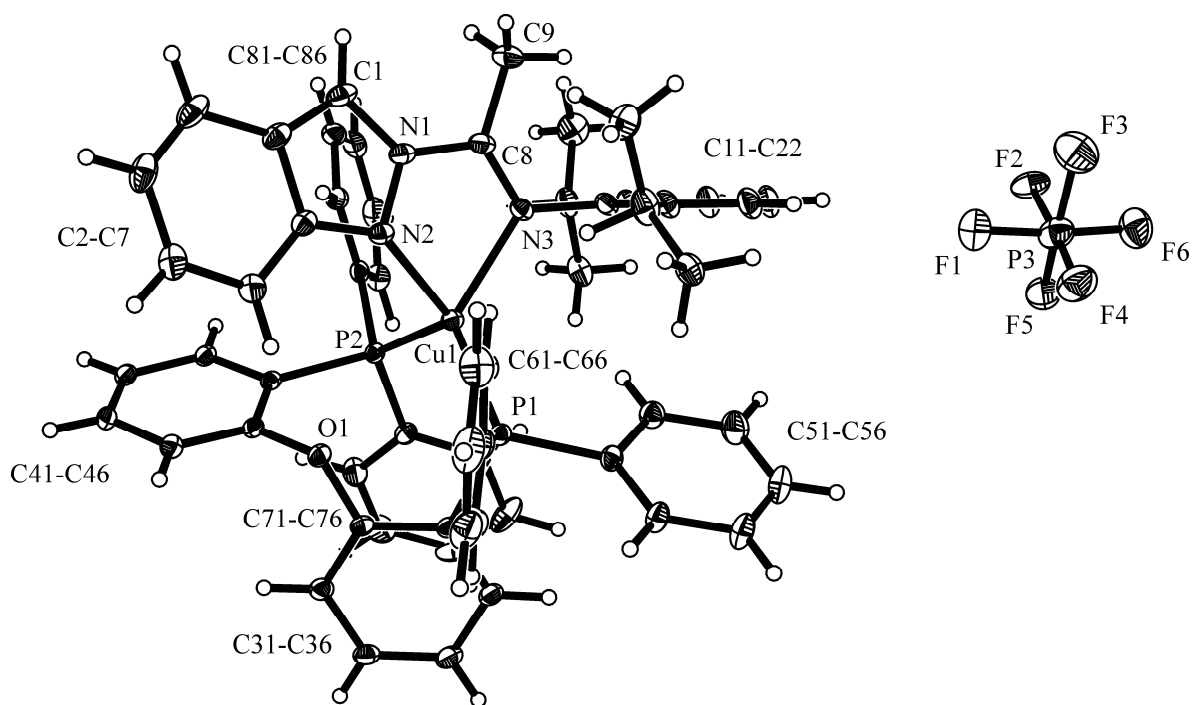


1H NMR (400 MHz, CD_2Cl_2 , 298 K)



$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2 , 298 K)

X-ray crystal structure analysis of 2: formula $C_{57}H_{53}CuF_6N_3OP_3$, $M = 1066.47$, colourless crystal, $0.25 \times 0.20 \times 0.10$ mm, $a = 11.8896(2)$, $b = 15.4611(3)$, $c = 16.7590(4)$ Å, $\alpha = 96.010(1)$, $\beta = 93.695(1)$, $\gamma = 92.264(1)^\circ$, $V = 3054.1(1)$ Å³, $\rho_{\text{calc}} = 1.160$ gcm⁻³, $\mu = 0.491$ mm⁻¹, empirical absorption correction ($0.887 \leq T \leq 0.952$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 28126 reflections collected ($\pm h, \pm k, \pm l$), 10548 independent ($R_{\text{int}} = 0.047$) and 8936 observed reflections [$I > 2\sigma(I)$], 743 refined parameters, $R = 0.064$, $wR^2 = 0.168$, max. (min.) residual electron density 0.43 (-0.40) e.Å⁻³, hydrogen atoms were calculated and refined as riding atoms.

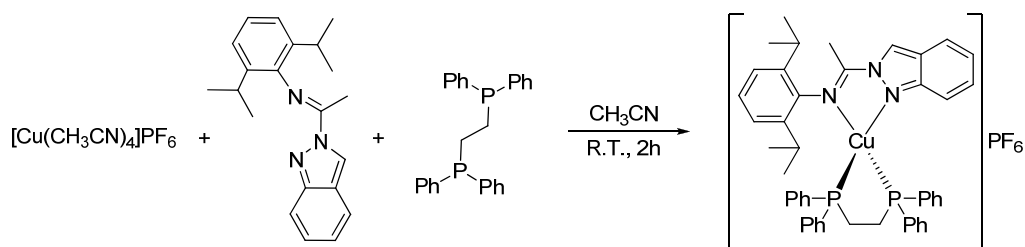


Selected structural parameters for complex 2.

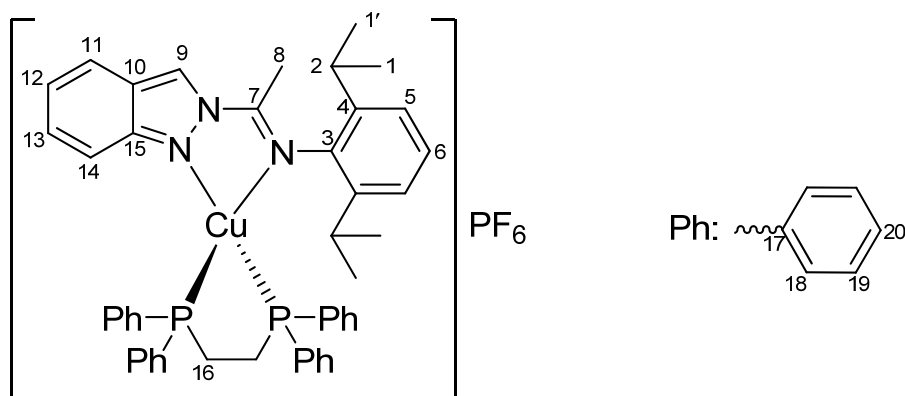
Distances (Å)	
Cu1-N2	2.073(6)
Cu1-N3	2.121(6)
Cu1-P1	2.226(2)
Cu1-P2	2.287(2)
Bond angles (deg)	
N2-Cu1-N3	77.0(2)
P1-Cu1-P2	111.1(1)
P1-Cu1-N2	118.4(2)
P1-Cu1-N3	123.4(2)
P2-Cu1-N2	105.4(2)

P2-Cu1-N3	116.0(2)
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Dihedral angles (deg)	
N1-N2-Cu1-P1	141.7(4)
N1-N2-Cu1-P2	-93.3(4)
N3-C8-N1-N2	10.3(9)
C9-C8-N1-N2	-168.8(7)
C9-C8-N3-C11	12.5(11)
<hr/>	

**(((1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline)((1,2-bis(diphenylphosphino)ethane))
Cu(I)]PF₆. (3)**



A solution of (1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline^[1] (50 mg, 0.16 mmol) in acetonitrile was added dropwise to a solution of [Cu(CH₃CN)₄]PF₆ (58 mg, 0.16 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of 1,2-bis(diphenylphosphino)ethane (PP) (62 mg, 0.16 mmol) was added in acetonitrile and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using CH₂Cl₂ / Hexane mixture and cold, resulting **3** as a dark yellow solid in 95% yield (137 mg, 0.14 mmol).



¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = 9.06 (s, 1H, H9), 7.97 (d, *J* = 8.1Hz, 1H, H14), 7.46 (m, 4H, H20), 7.38 (m, 1H, H6), 7.33 (m, 1H, H13), 7.28 (m, 2H, H5), 7.23 (m, 8H, H19), 7.15 (m, 9H, H11, H18), 2.81 (m, 2H, H2), 2.71 (s, 3H, H8), 2.31 (s, 4H, H16), 1.16 (d, *J* = 6.2Hz, 6H, H1'), 0.80 (d, *J* = 6.2Hz, 6H, H1).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K): $\delta/\text{ppm} = 160.3$ (C7), 149.8 (C15), 140.2 (C3), 139.0 (C4), 134.6 (C13), 133.1 (t, $J^{C-P} = 7.5\text{Hz}$, C18), 132.4 (C20), 130.2 (t, $J^{C-P} = 5.1\text{Hz}$, C19), 129.3 (t, $J^{C-P} = 23\text{Hz}$, C17), 128.9 (C9), 128.3 (C6), 125.2 (C5), 124.4 (C10), 123.7 (C14), 115.7 (C11), 29.4 (C2), 24.7 (t, $J^{C-P} = 16.2\text{Hz}$, C16), 23.7 (C1), 23.4 (C1'), 15.8 (C8).

^1H , ^{13}C -HMBC (400 MHz / 100 MHz, CD_2Cl_2 , 298 K): $\delta(^1\text{H}) / \delta(^{13}\text{C}) = 9.06 / 149.8$, 124.4 (H9 / C15, C10), 7.97 / 149.8, 134.6 (H14 / C15, C13), 7.46 / 133.1 (H20 / C18), 7.38 / 139.0 (H6 / C4), 7.28 / 140.2, 29.4 (H5 / C3, C2), 7.15 / 132.4 (H18 / C20), 2.81 / 23.7, 23.4 (H2 / C1, C1'), 2.71 / 160.3 (H8 / C7), 1.16 / 139.0, 29.4 (H1' / C4, C2), 0.80 / 139.0, 29.4 (H1 / C4, C2).

^1H , ^{13}C -HSQC (400 MHz / 100 MHz, CD_2Cl_2 , 298 K): $\delta(^1\text{H}) / \delta(^{13}\text{C}) = 9.06 / 128.9$ (H9 / C9), 7.97 / 123.7 (H14 / C14), 7.46 / 132.4 (H20 / C20), 7.38 / 128.3 (H6 / C6), 7.33 / 134.6 (H13 / C13), 7.28 / 125.2 (H5 / C5), 7.23 / 130.2 (H19 / C19), 7.15 / 130.2 (H18 / C18), 7.15 / 115.7 (H11 / C11), 2.81 / 29.4 (H2 / C2), 2.71 / 15.8 (H8 / C8), 2.31 / 24.7 (H16 / C16), 1.16 / 23.4 (H1' / C1'), 0.80 / 23.7 (H1 / C1).

COSY (400 MHz / 400 MHz, CD_2Cl_2 , 298 K): $\delta(^1\text{H}) / \delta(^1\text{H}) = 7.97 / 7.33$ (H14 / H13), 7.46 / 7.23 (H20 / H19), 7.23 / 7.15 (H19 / H18), 2.81 / 1.16, 0.80 (H2 / H1', H1).

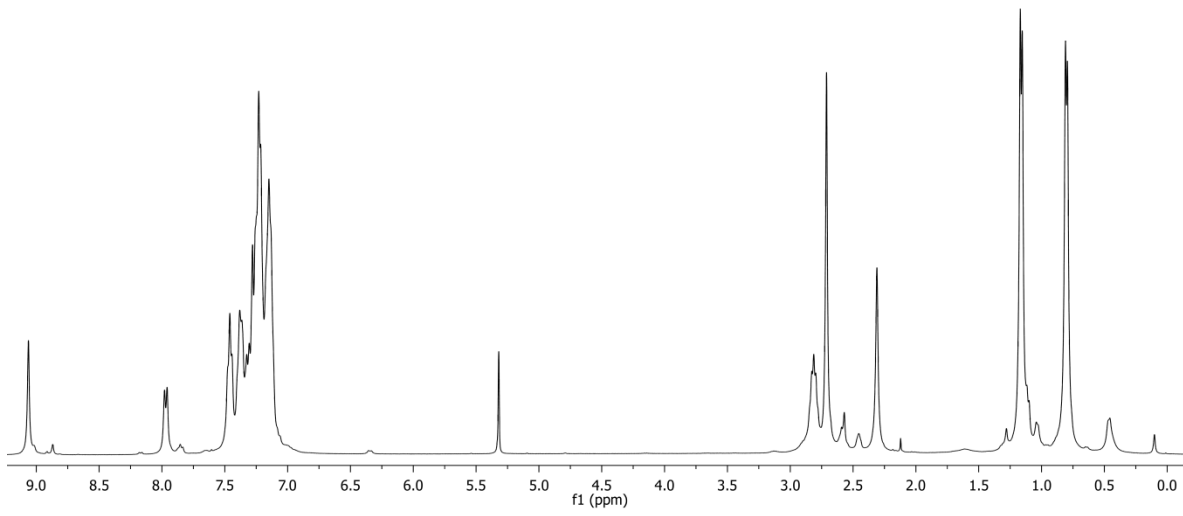
^{19}F NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta/\text{ppm} = -72.7$ (d, $J^{F-P} = 710\text{Hz}$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, CD_2Cl_2 , 298 K): $\delta/\text{ppm} = 7.4$ (s, PP), -144.4 (hept, $J^{P-F} = 710\text{Hz}$, PF_6).

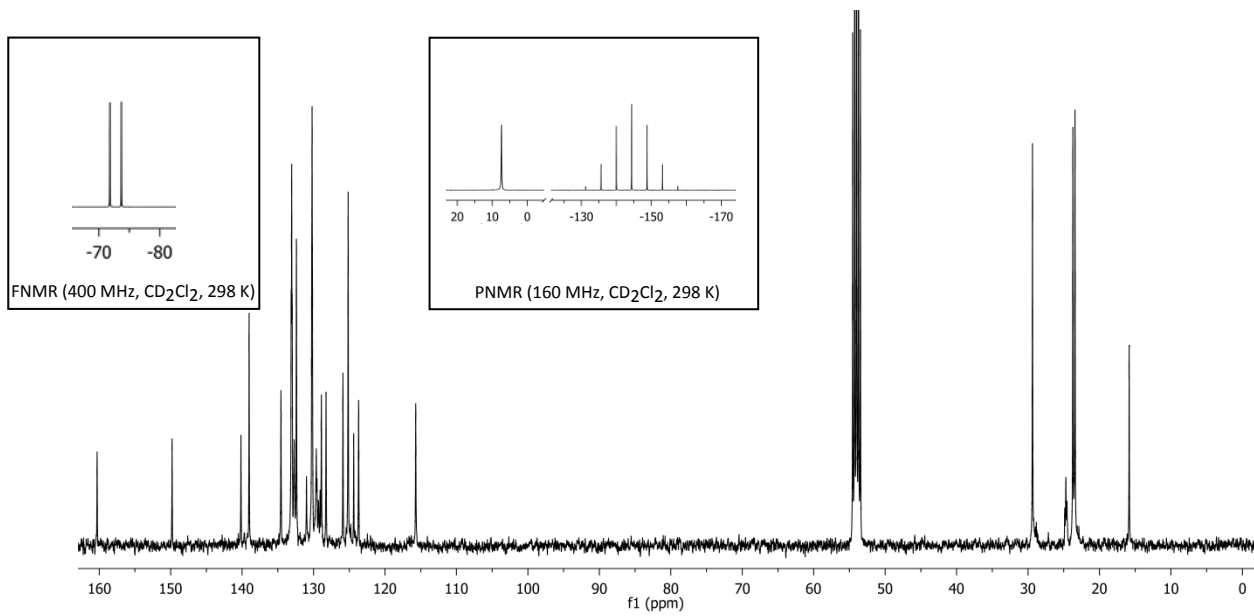
IR (KBr): $\nu/\text{cm}^{-1} = 3148$, 3060, 2963, 2970, 1654, 1632, 1587, 1527, 1466, 1437, 1411, 1383, 1311, 1256, 1222, 1189, 1152, 1133, 1095, 1003, 974, 917, 840, 756, 741, 695, 626.

Elemental analysis (%) $\text{C}_{47}\text{H}_{49}\text{CuF}_6\text{N}_3\text{P}_3$ (M = 926.37 g/mol): calculated C 60.94, H 5.33, N 4.54; found C 60.30, H 4.85, N 5.02.

HRMS-ESI: ($\text{C}_{47}\text{H}_{49}\text{CuN}_3\text{P}_2$ $[\text{M}]^+$) Calc: 780.2698 ; Found: 780.2669.

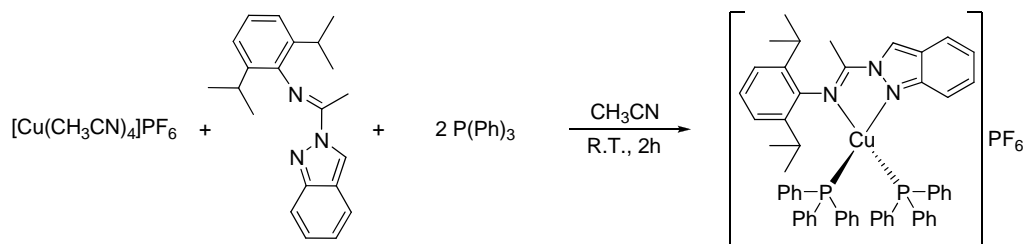


^1H NMR (400 MHz, CD_2Cl_2 , 298 K)

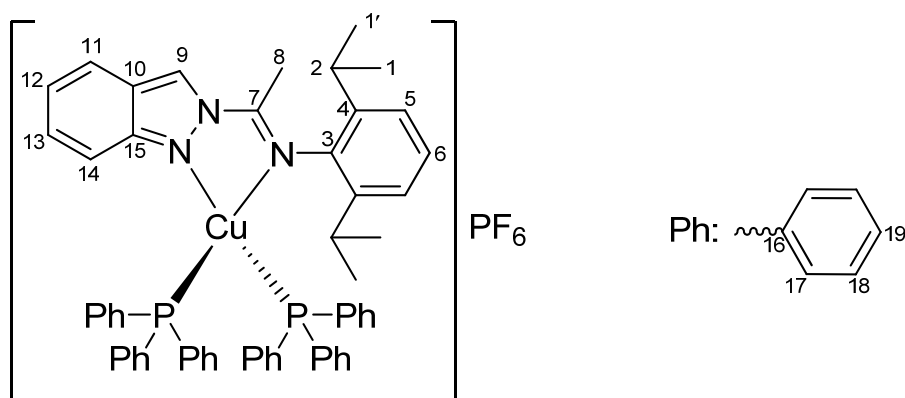


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K)

[((1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline)(bis(triphenylphosphine))Cu(I)]PF₆. (4)



A solution of (1-(2*H*-indazol-2-yl)ethylidene)-2,6-diisopropylaniline^[1] (50 mg, 0.16 mmol) in acetonitrile was added dropwise to a solution of [Cu(CH₃CN)₄]PF₆ (58 mg, 0.16 mmol) in acetonitrile. The reaction mixture was stirred for 30 minutes at room temperature. Then, a solution of triphenylphosphine (PPh₃) (82 mg, 0.31 mmol) was added in acetonitrile and was stirred for 90 minutes at room temperature. The volatiles were removed in vacuum. Crude product was purified by crystallization using cold tetrahydrofuran, obtaining **4** as a dark yellow solid in 92% yield (151 mg, 0.14 mmol).



¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = 9.22 (s, 1H, H₉), 7.94 (d, *J* = 8.4Hz, 1H, H₁₄), 7.42 (m, 1H, H₆), 7.39 (t, *J* = 7.0Hz, 4H, H₁₉), 7.24 (d, *J* = 7.8Hz, 2H, H₅), 7.18 (m, 1H, H₁₃), 7.15 (t, *J* = 7.8Hz, 8H, H₁₈), 7.08 (t, *J* = 7.6Hz, 1H, H₁₂), 6.90 (t, *J* = 9.1Hz, 8H, H₁₇), 6.72 (d, *J* = 8.8Hz, 1H, H₁₁), 2.68 (s, 3H, H₈), 2.53 (hept, *J* = 6.7Hz, 2H, H₂), 0.72 (d, *J* = 6.7Hz, 6H, H_{1'}), 0.37 (d, *J* = 6.7Hz, 6H, H₁).

¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 298 K): δ/ppm = 158.0 (C7), 149.4 (C15), 141.6 (C3), 140.2 (C4), 134.1 (d, $J^{C-P} = 14.8\text{Hz}$, C17), 132.2 (d, $J^{C-P} = 31.5\text{Hz}$, C16), 131.9 (C13), 131.1 (C19), 129.5 (d, $J^{C-P} = 9.4\text{Hz}$, C18), 127.9 (C6), 127.4 (C9), 125.4 (C12), 125.3 (C5), 124.4 (C10), 122.8 (C14), 116.3 (C11), 29.1 (C2), 24.5 (C1'), 23.2 (C1), 18.1 (C8).

¹H, ¹³C-HMBC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 9.22 / 149.4, 124.4 (H9 / C15, C10), 7.94 / 149.4, 131.9, 124.4 (H14 / C15, C13, C10), 7.42 / 140.2 (H6 / C4), 7.39 / 134.1 (H19 / C17), 7.24 / 141.6, 29.1 (H5 / C3, C2), 7.15 / 132.2 (H18 / C16), 6.90 / 131.1 (H17 / C19), 6.72 / 125.4 (H11 / C12), 2.68 / 158.0 (H8 / C7), 2.53 / 140.2, 125.3, 24.5, 23.2 (H2 / C4, C5, C1', C1), 0.72 / 140.2, 29.1, 23.2 (H1' / C4, C2, C1), 0.37 / 140.2, 29.1, 24.5 (H1 / C4, C2, C1').

¹H, ¹³C-HSQC (400 MHz / 100 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹³C) = 9.22 / 127.4 (H9 / C9), 7.94 / 122.8 (H14 / C14), 7.42 / 127.9 (H6 / C6), 7.39 / 131.1 (H19 / C19), 7.24 / 125.3 (H5 / C5), 7.18 / 131.9 (H13 / C13), 7.15 / 129.5 (H18 / C18), 7.08 / 125.4 (H12 / C12), 6.90 / 134.1 (H17 / C17), 6.72 / 116.3 (H11 / C11), 2.68 / 18.1 (H8 / C8), 2.53 / 29.1 (H2 / C2), 0.72 / 24.5 (H1' / C1'), 0.37 / 23.2 (H1 / C1).

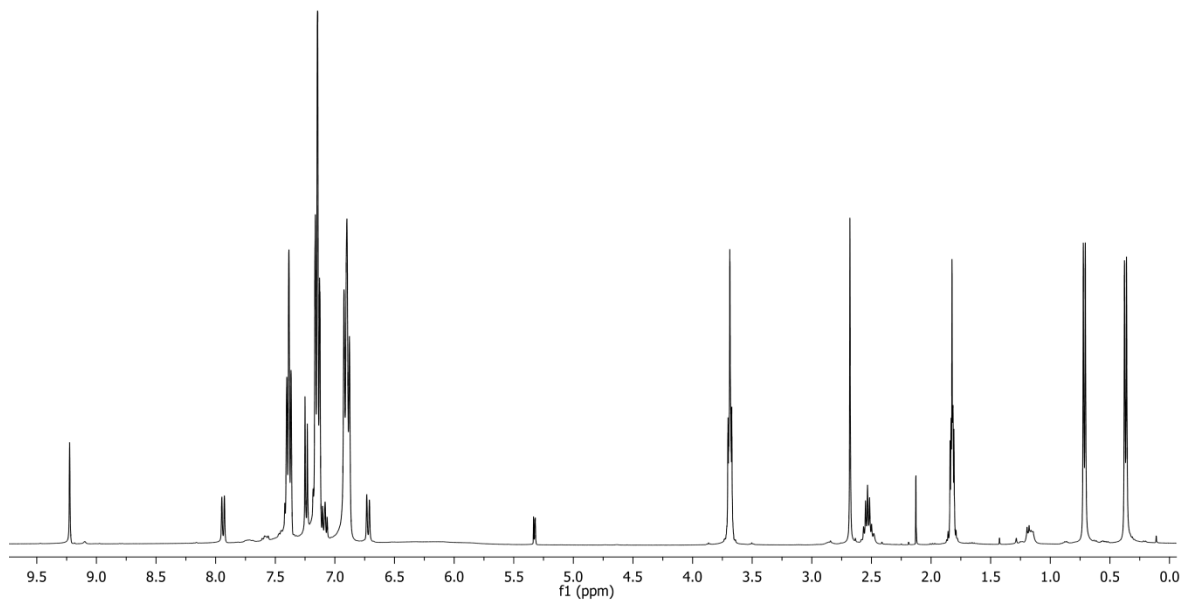
COSY (400 MHz / 400 MHz, CD₂Cl₂, 298 K): δ (¹H) / δ (¹H) = 7.94 / 7.18 (H14 / H13), 7.39 / 7.15 (H19 / H18), 7.42 / 7.24 (H6 / H5), 7.15 / 6.90 (H18 / H17), 7.08 / 6.72 (H12 / H11), 2.53 / 0.72, 0.37 (H2 / H1', H1).

¹⁹F NMR (400 MHz, CD₂Cl₂, 298 K): δ/ppm = -72.8 (d, $J^{F-P} = 710\text{Hz}$).

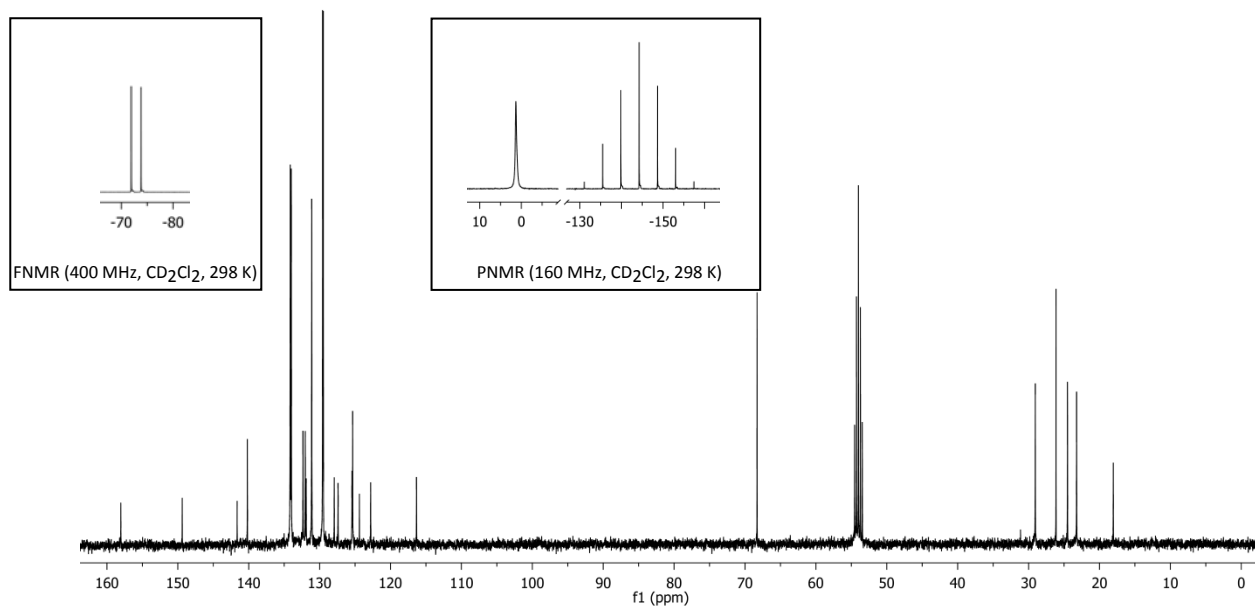
³¹P{¹H} NMR (160 MHz, CD₂Cl₂, 298 K): δ/ppm = 1.3 (s, PPh₃), -144.3 (hept, $J^{P-F} = 710\text{Hz}$, PF₆).

IR (KBr): ν/cm⁻¹ = 3145, 3054, 2970, 2929, 2867, 1648, 1629, 1586, 1524, 1480, 1461, 1436, 1410, 1386, 1365, 1307, 1255, 1221, 1184, 1133, 1094, 1064, 1027, 1000, 968, 841, 797, 749, 697, 669.

Elemental analysis (%) C₅₇H₅₅CuF₆N₃P₃ (M = 1052.52 g/mol): calculated C 65.04, H 5.27, N 3.99; found C 64.52, H 6.39, N 4.04.



^1H NMR (400 MHz, CD_2Cl_2 , 298 K)



$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 298 K)

DFT calculations

Table S1. Optimized geometrical parameters of complexes **1-4** obtained from DFT calculations at the B3LYP/6-31G(d,p)/LANL2DZ level of theory.

	<i>Experimental</i>		<i>DFT-calculations</i>		
	1	1	2	3	4
	Bond distance (Å)				
Cu1-N1A	2.06	2.14	2.40	2.21	2.50
Cu1-N3A	2.04	2.10	2.11	2.12	2.11
Cu1-N1B	2.02	2.10	-	-	-
Cu1-N3B	2.08	2.14	-	-	-
Cu1-P1			2.43	2.38	2.40
Cu1-P2			2.41	2.47	2.42
	Bond angles (deg)				
N1A-Cu1-N3A	79.15	77.46	73.18	76.11	71.30
N1B-Cu1-N3B	78.77	77.46	-	-	-
N1A-Cu1- N3B	128.03	131.57	-	-	-
N1A-Cu1-N1B	140.35	132.00	-	-	-
N1B-Cu1-N3A	127.18	131.55	-	-	-
N3A-Cu1-N3B	103.76	113.44	-	-	-
P1-Cu1-P2			114.74	88.65	119.83
P1-Cu1-N1a			116.49	126.30	117.59
P1-Cu1-N3a			118.85	125.40	110.96
P2-Cu1-N1a			117.75	127.77	111.71
P2-Cu1-N3a			109.34	117.23	115.94

Transient absorption spectroscopy

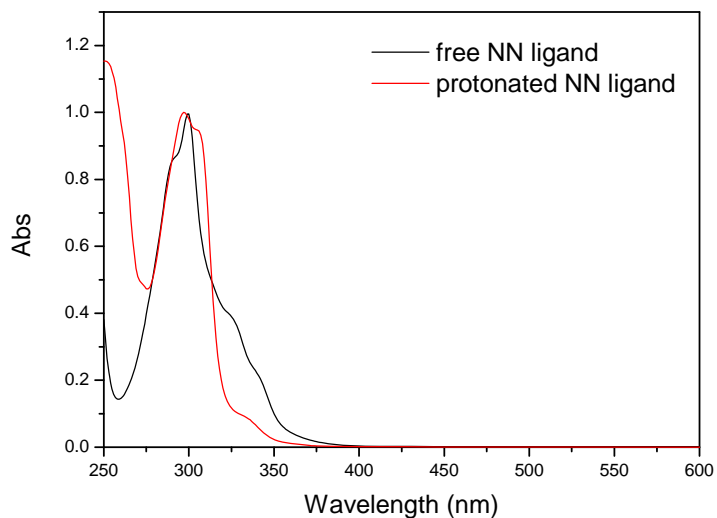


Figure S1. Electronic absorption spectra of the free (black trace) and protonated (red trace) NN ligand in CH_2Cl_2 .

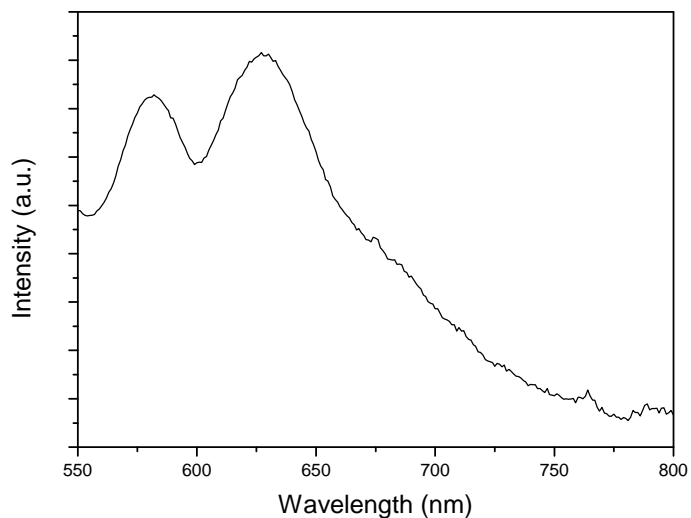


Figure S2. Emission spectrum of the protonated NN ligand at 77 K in a 4/1 ethanol/methanol glassy matrix (protonation has been performed upon addition of few droplets of trifluoroacetic acid before cooling to 77 K).

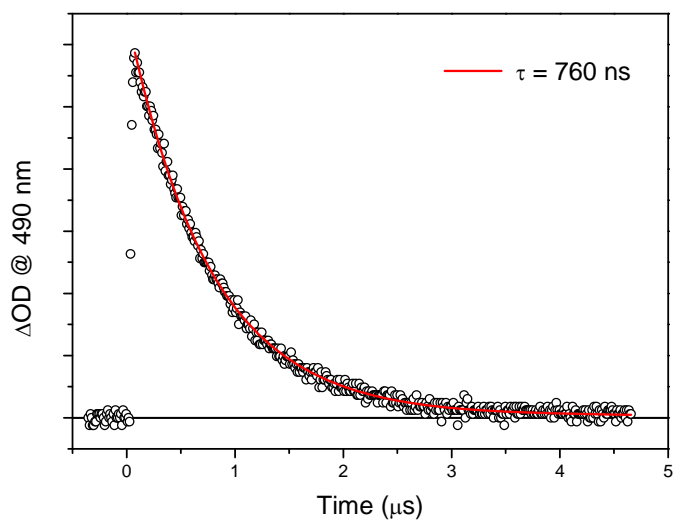


Figure S3. Kinetic analysis at 490 nm of the transient decay of **2** under air-equilibrated conditions, obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) with related single-exponential fitting.

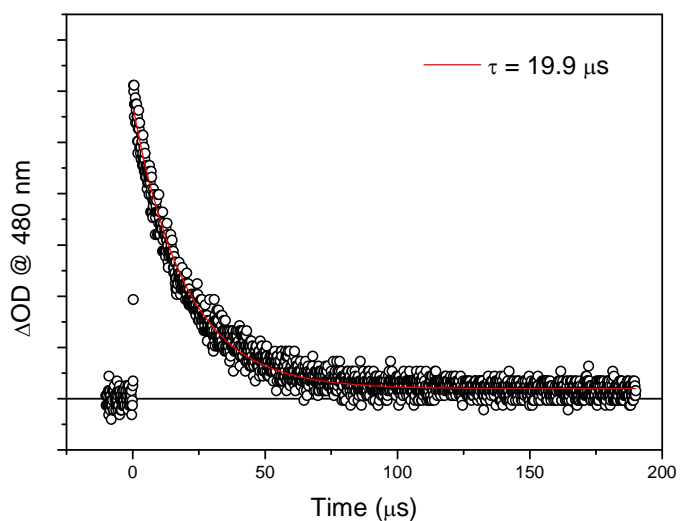


Figure S4. Kinetic analysis at 480 nm of the transient decay of **2** in degassed CH_2Cl_2 (5 freeze-pump-thaw cycles) obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) with related single-exponential fitting.

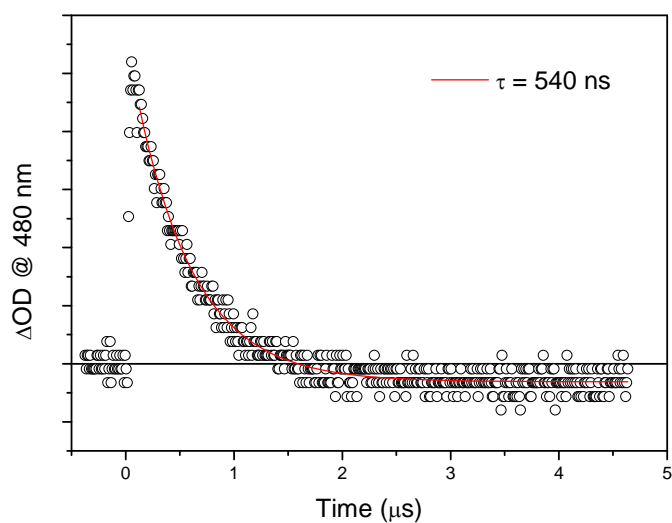


Figure S5. Kinetic trace at 480 nm of the transient decay of **3** in CH_2Cl_2 under air-equilibrated conditions obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) with related single-exponential fitting.

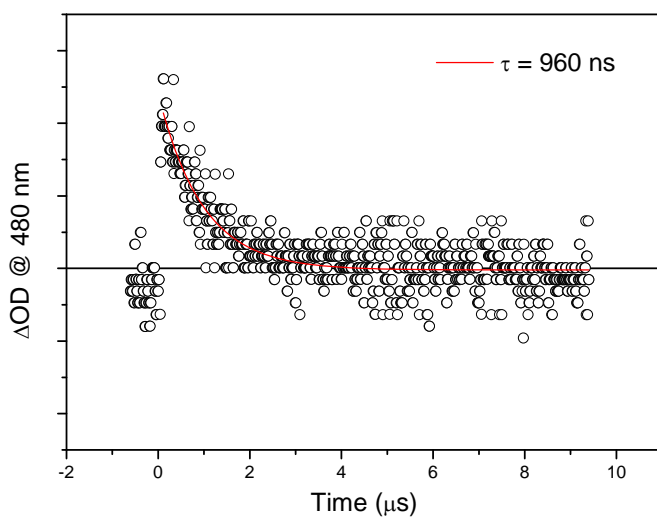


Figure S6. Kinetic analysis at 480 nm of the transient decay of **3** ($3 \times 10^{-5} \text{ M}$) in degassed CH_2Cl_2 obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) with related single-exponential fitting.

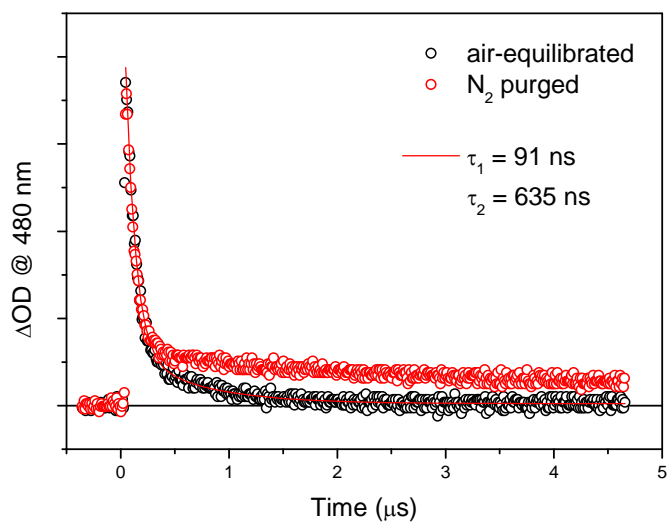


Figure S7. Kinetic analysis at 480 nm of the transient decay of **4** in CH_2Cl_2 (with related bi-exponential fitting) obtained under air-equilibrated conditions (black trace) and after 10-min purging with N_2 (excitation at 355 nm, FWHM = 6-8 ns).

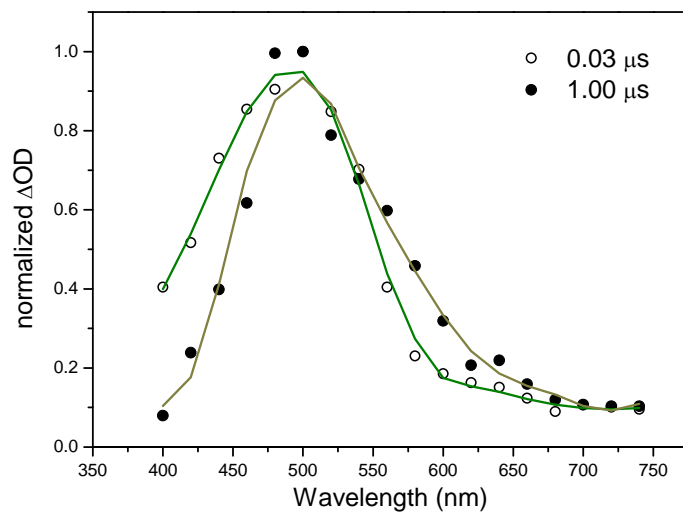


Figure S8. Normalized transient absorption spectra of complex **4** in CH_2Cl_2 obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) at 30 ns time delay (empty dots) and at 1 μs time delay (full dots).

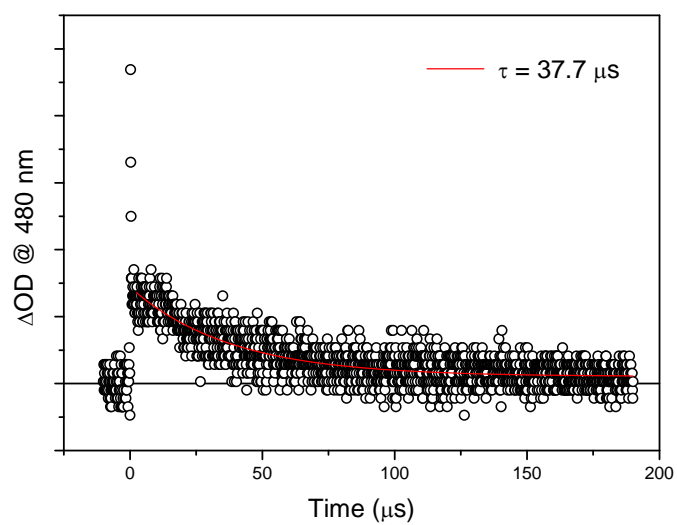


Figure S9. Kinetic analysis at 480 nm of the transient decay of **4** in degassed CH_2Cl_2 (5 freeze-pump-thaw cycles) obtained by laser flash photolysis (excitation at 355 nm, FWHM = 6-8 ns) with related single-exponential fitting.

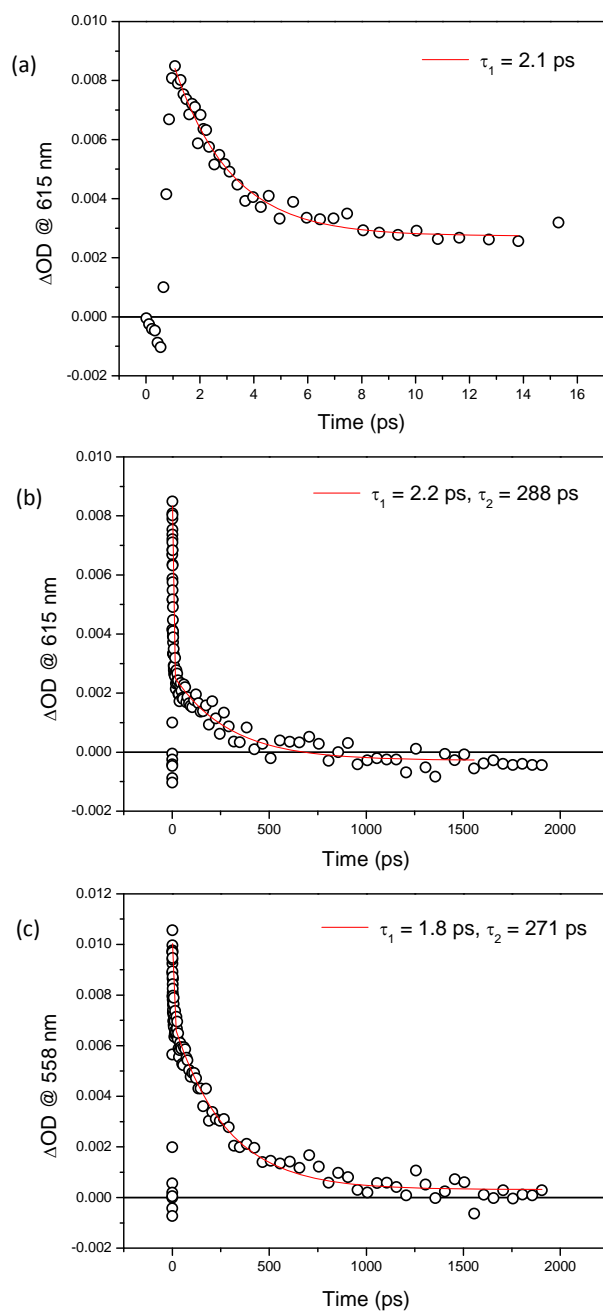


Figure S10. Kinetic analysis of the transient decay of **1** in CH_2Cl_2 obtained by ultrafast spectroscopy (excitation at 400 nm) with related exponential fitting at (a) 615 nm (detail of 0-16 ps), (b) 615 nm (full window), and (c) 558 nm (full window).

[1] G. Gritzner, J. Kuta, *J. In Pure and Applied Chemistry*, 1984, **56**, 461.

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