Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Material

Unusual Phosphine Oxidation: New Triazolopyridine-Quinoline Phosphine Oxide Fluorescents Dyes

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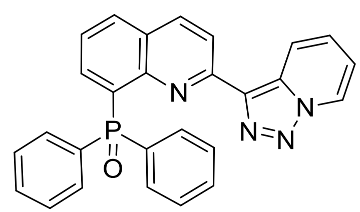
General procedures

Starting materials, if commercially available, were purchased and used as such, provided that suitable checks (melting ranges, refractive indices and gas chromatography) had confirmed the claimed purity. When known compounds had to be prepared by literature procedures, pertinent references are given. Air- and moisture-sensitive materials were stored in Schlenk tubes. They were protected by and handled under argon, in appropriate glassware. Tetrahydrofuran was dried by distillation from sodium after the characteristic blue colour of sodium diphenyl ketyl (benzophenone-sodium “radical-anion”) had been seen to persist. Ethereal or other organic extracts were dried by washing with brine and then by storage over sodium sulfate. Melting points or ranges (m.p.) given were determined on a Kofler heated stage and found to be reproducible after recrystallization, unless stated otherwise (“decomp.”). Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63–210 μm). ^{1}H and (^{1}H decoupled) ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 300 and 101 or 75 MHz, respectively. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (δ = 7.27 ppm). Coupling constants (J) are given in Hz. Coupling patterns are abbreviated as, for example, s (singlet), d (doublet), t (triplet), td (triplet of doublets), m (multiplet), app. s (apparent singlet) and br. (broad). COSY experiments were performed for all compounds. HRMS Electron Impact (EI) or ElectroSpray (ES) determinations were made using a VG Autospec Trio 1000 (Fisons). The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. UV-Vis absorption spectra were recorded on an Agilent 8453 spectroscopy system. The emission spectra were recorded with a PTI MO-5020 spectrofluorimeter in the 300–600 nm range and JASCO FP-6200 spectrofluorimeter at room temperature.. Quantum yield was determined with a Hamamatsu-PHA equipment. Ligand solutions were prepared 10^{-5} M in ethanol-water 98/2 w/w. Metal solutions were prepared with nitrate salts (Mn, Pb, Ag), chloride (Co, Ni, Cd), perchlorate (Zn, Cu) sulfate (Fe(III) Fe(II)NH_4SO_4) in 0,1 to 0,005 M.

2-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)-8-(diphenylphosphoryl)quinoline (8): yellow powder (0.8 g, 89%). Mp 241°C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.06 (d, *J* = 8.9 Hz, 1H), 8.68 (d, *J* = 6.9 Hz, 1H), 8.57 (d, *J* = 8.7 Hz, 1H), 8.29 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.8-7.7 (m, 4H), 7.6-7.3 (m, 9H), 7.02 (dt, *J* = 6.8, 6.8, 0.7 Hz, 1H) ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 152.1 (C), 148.8 (d, *J* = 4.4 Hz, C), 137.3 (d, *J* = 10.5 Hz, CH), 137.0 (d, *J* = 21.0 Hz,C), 136.9 (CH), 133.9 (C) 133.0 (d, *J* = 2.7 Hz, CH), 132.7 (d, *J* = 20.6 Hz, 2C), 132.0 (d, *J* = 9.9 Hz, 4CH), 131.5 (d, *J* = 2.9 Hz, 2CH), 130.8 (d, *J* = 1.4 Hz, C) 128.4 (d, *J* = 12.3 Hz, 4CH), 127.7 (d, *J* = 7.1 Hz, C), 127.1 (CH), 125.0 (d, *J* = 13.7 Hz, CH), 124.7 (CH), 122.6 (CH), 119.9 (CH), 116.3 (CH).^{31}P NMR (161 MHz, $CDCl_3$): δ = 31.0 (PO). MS(EI): m/z(%) **=** 446(10), 418(52), 417(100), 340(19). HRMS ESI-[TOF] for $C_{27}H_{19}N_4OP$: calcd. 446.1296; found 446.1300.



8 (89%)

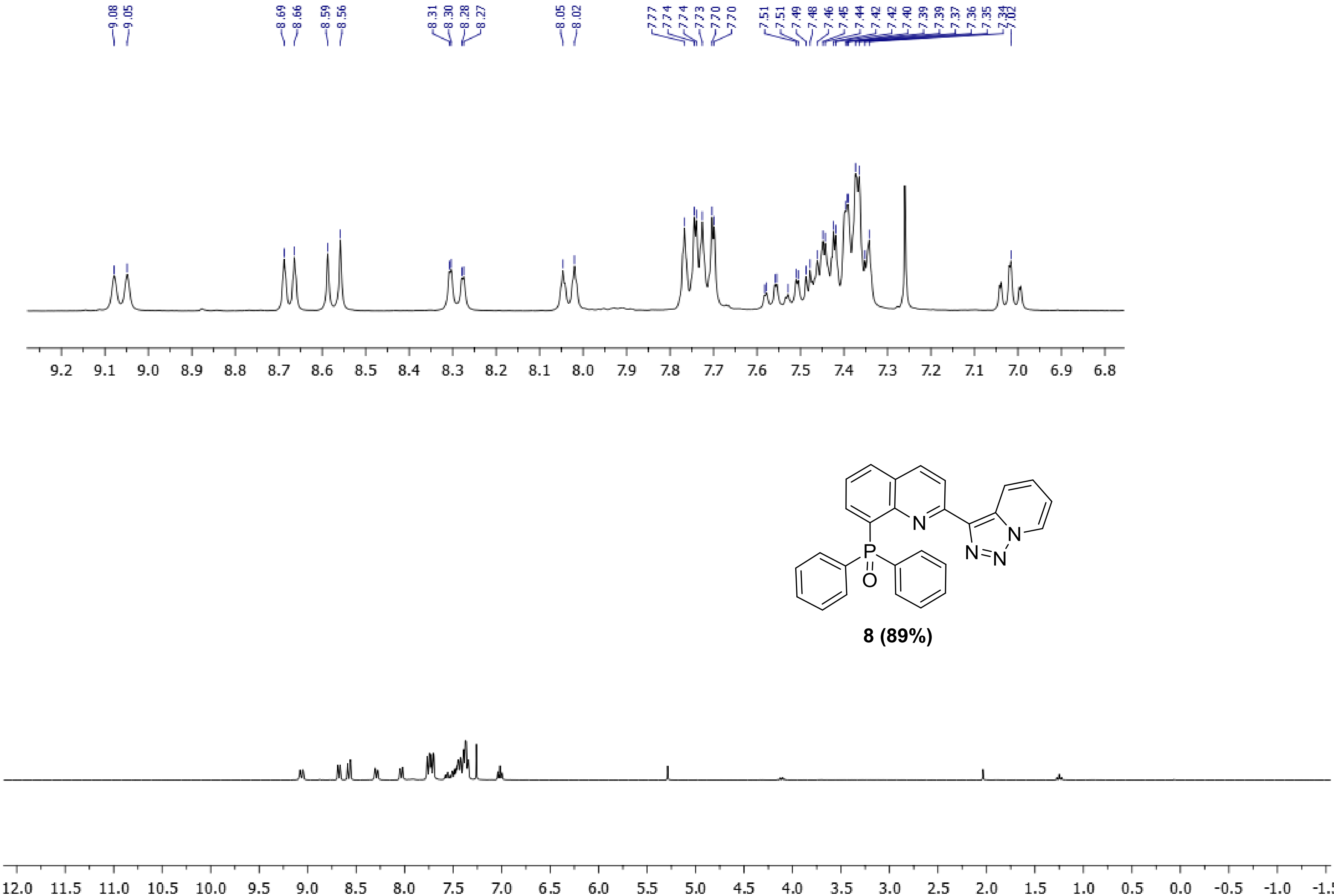


Figure S1: ^{1}H NMR (300 MHz, $CDCl_3$) of **8**:

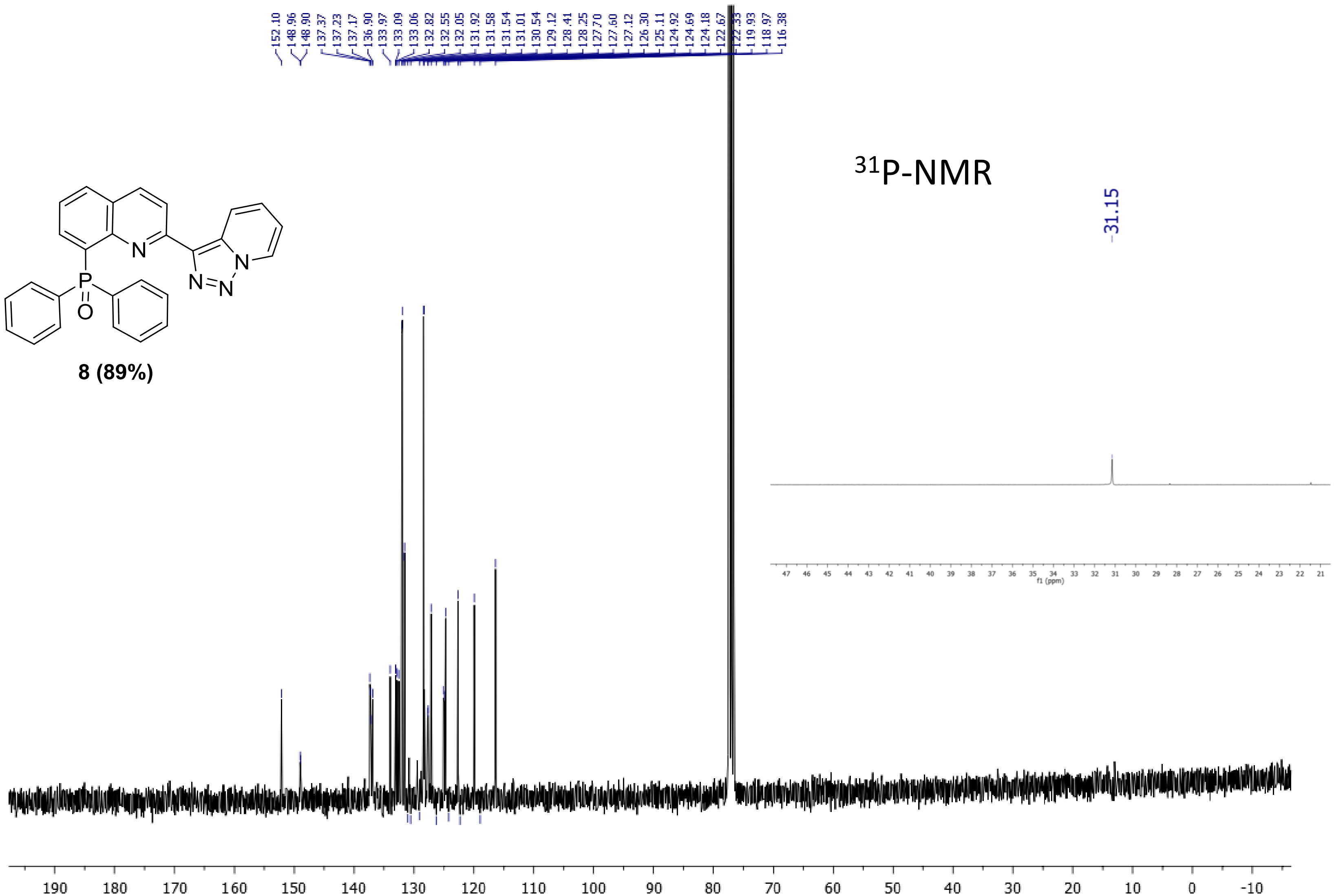
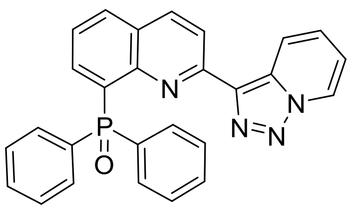


Figure S2: ^{13}C NMR (75.5 MHz, $CDCl_3$) and ^{31}P NMR (161 MHz, $CDCl_3$) of **8**:



8 (89%)

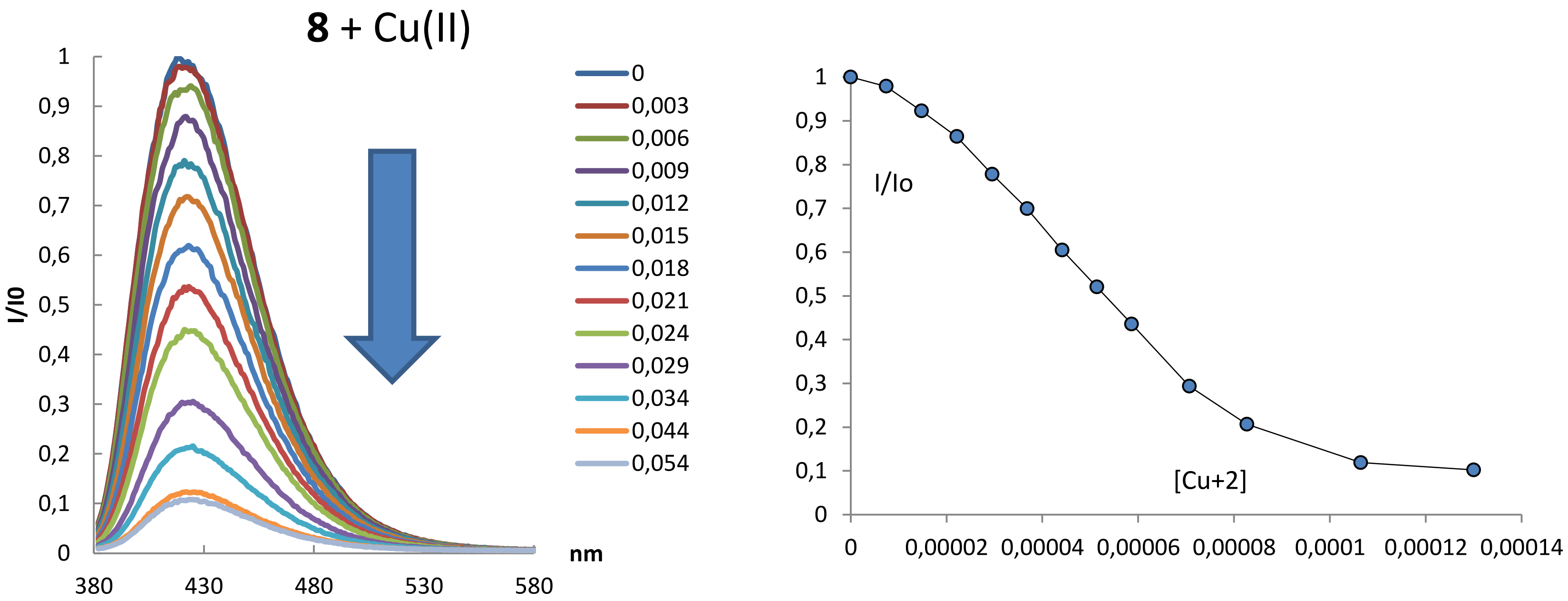
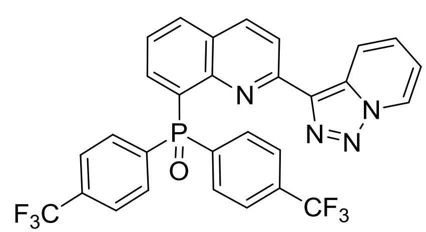
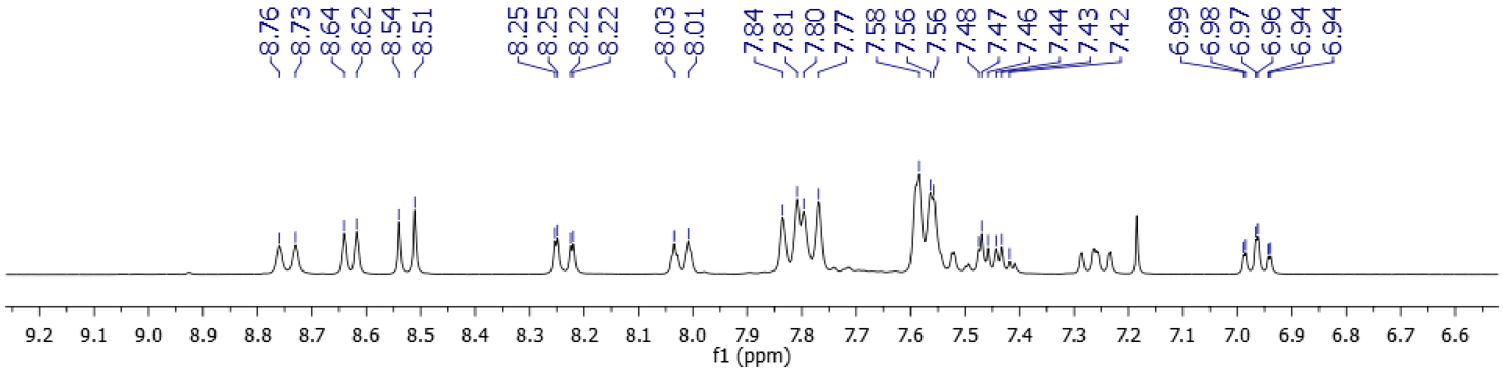


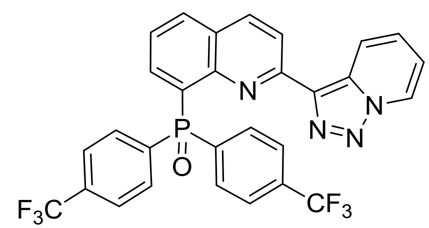
Figure S3: Fluorescence Quenching of **8** upon the addition of copper perchlorate salt

2-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)-8-(bis(4-(trifluoro methyl)phenyl)phosphoryl)quinoline (9): yellow powder (0.5 g, 81%). mp 247 – 250 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.9 Hz, 1H), 8.64 (d, *J* = 7.0 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 11.7 Hz, 2H), 7.80 (d, *J* = 11.8 Hz, 2H), 7.62-7.54 (m, 4H), 7.55-7.41 (m, 2H), 7.27 (dd, *J* = 8.9, 6.8 Hz, 1H), 6.97 (dt, *J* = 6.8, 6.8, 1.1 Hz, 1H).^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 152.6 (C), 148.7 (d, *J* = 4.46 Hz, C), 137.9 (C), 137.3 (d, *J* =10.5 Hz,CH), 137.0 (d, *J* = 1.0 Hz,CH), 136.9 (d, *J* = 30.0 Hz, C),136.5 (C), 133.93 (CH), 133.9 (CH), 133.7 (qd, *J* = 30.4, 30.4 30.4,1.1 Hz,2×C), 132.7 (C), 132.4 (d, *J* = 10.2 Hz,4×CH), 127.7 (d, *J* = 7.4 Hz, 2×C), 127.6 (C), 127.3 (CH), 127.4 (q, J = 280.1 Hz, 2×C),125.4 (dq, *J* = 11.1, 3.7, 3.7, 3.7 Hz, 4×CH), 125.1 (CH), 121.7 (CH), 120.5 (CH), 116.4 (CH).^{31}P NMR (161 MHz, $CDCl_3$): δ = 28.0 (PO). MS (EI): m/z(%) = 582(12), 555(43), 554(100), 553(80), 533,(47), 409(33), 355(50), 338(38).HRMS ESI-[TOF] for $C_{29}H_{17}F_6N_4OP$: calcd. 582.1044; found 582.1048.



9 (81%)





9 (81%)

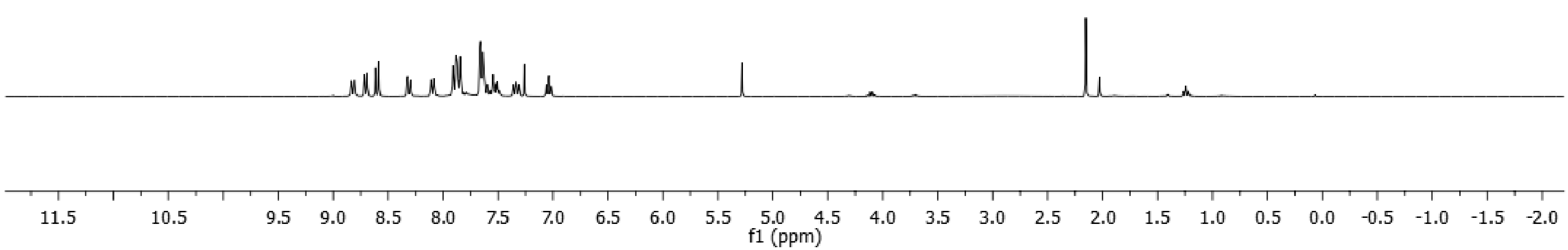


Figure S4: ^{1}H NMR (300 MHz, $CDCl_3$) of **9**:

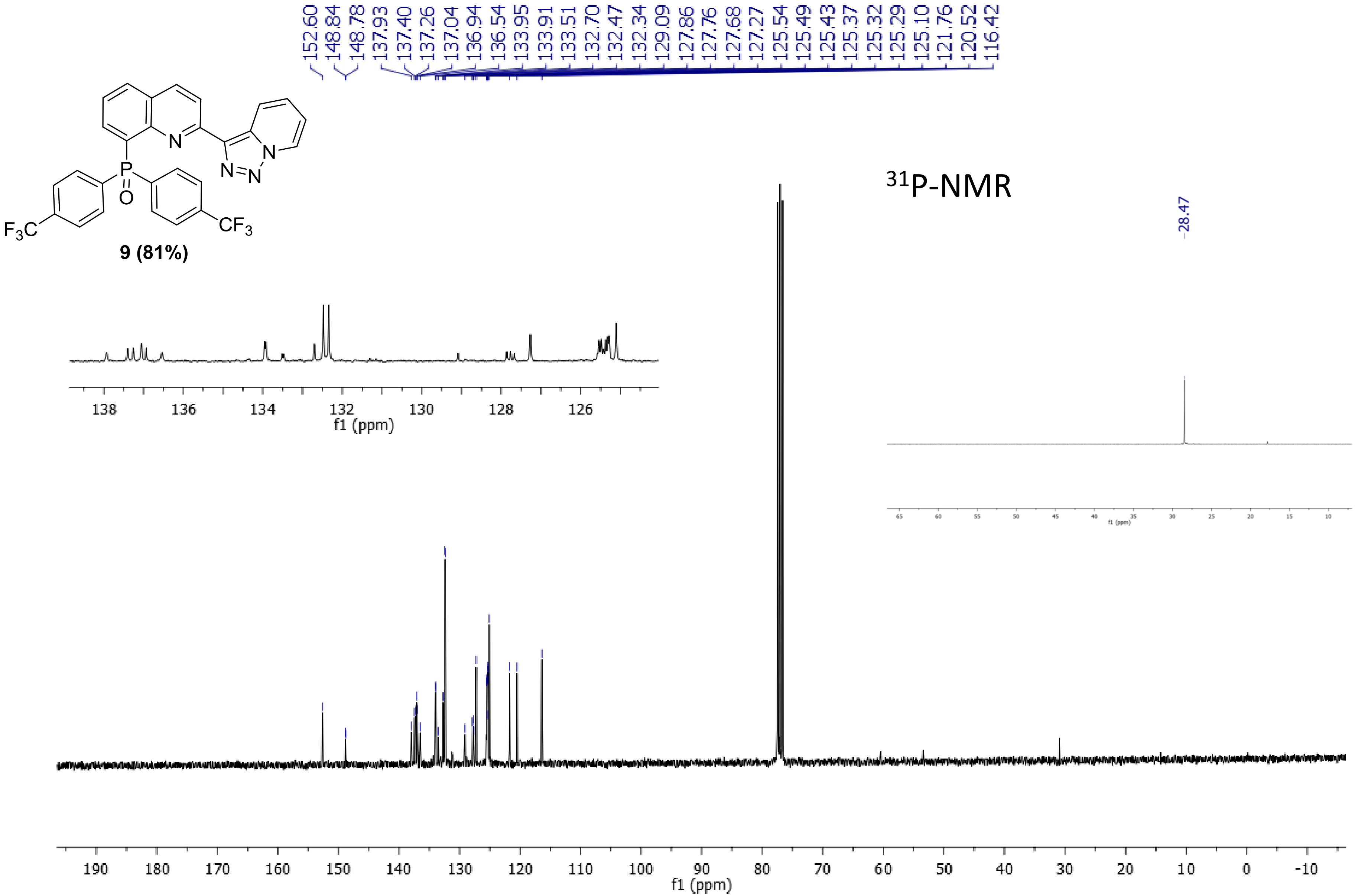
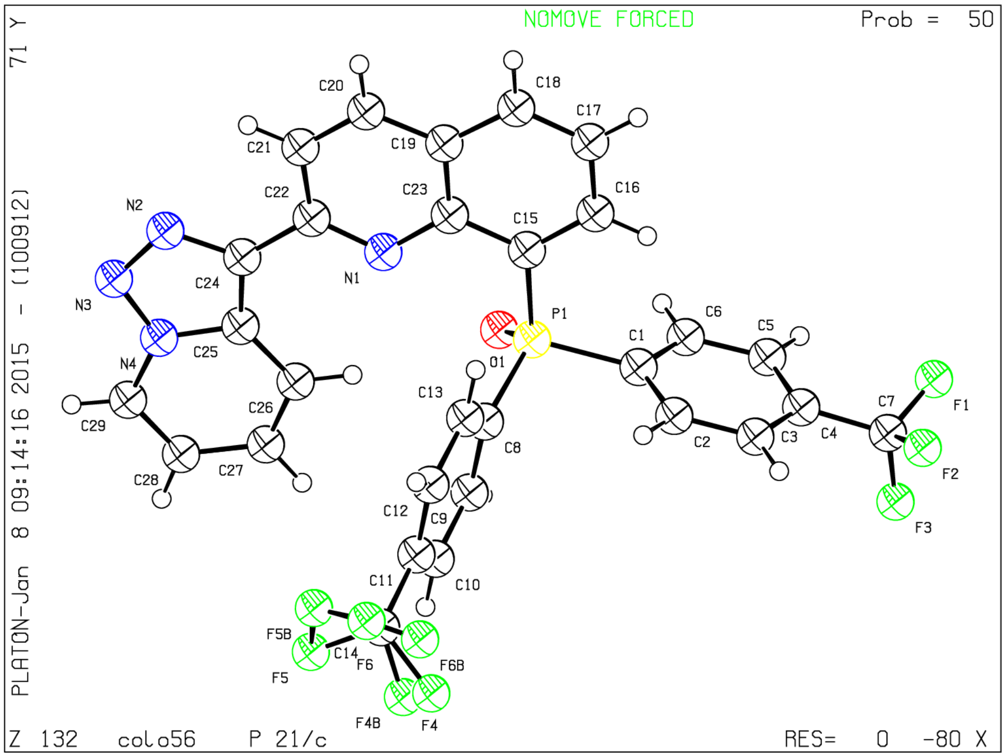


Figure S5: ^{13}C NMR (75.5 MHz, $CDCl_3$) and ^{31}P NMR (161 MHz, $CDCl_3$) of **9**:

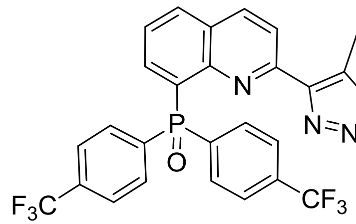


Monoclinic, P21/c
a = 7.6938 (2) Å
b = 12.9560 (2) Å
c = 26.6662 (7) Å
β = 99.140 (1)°
V = 2624.36 Å3

Figure S6: X-ray analysis of **9,** Small rotation caused disorder is observed for one of the CF_3 groups due to group rotation, in the paper this has been removed for clarity.

Table S1. Fractional atomic coordinates for **9**

	x	y	z			x	y	z
C1	−0.0058 (4)	−0.2662 (3)	−0.42751 (12)		**H20**	0.4656	−0.2390	−0.1640
C2	0.1009 (5)	−0.2444 (3)	−0.46330 (15)		**C21**	0.3891 (5)	−0.3835 (3)	−0.18381 (14)
H2	0.2177	−0.2705	−0.4590		**H21**	0.4355	−0.4145	−0.1522
C3	0.0388 (6)	−0.1847 (3)	−0.50539 (15)		**C22**	0.3016 (4)	−0.4445 (3)	−0.22445 (13)
H3	0.1119	−0.1714	−0.5302		**C23**	0.2509 (4)	−0.3014 (2)	−0.27638 (12)
C4	−0.1286 (6)	−0.1448 (3)	−0.51124 (15)		**C24**	0.2798 (4)	−0.5554 (3)	−0.21779 (13)
C5	−0.2357 (5)	−0.1637 (3)	−0.47542 (16)		**C25**	0.2002 (4)	−0.6274 (3)	−0.25239 (13)
H5	−0.3504	−0.1346	−0.4794		**C26**	0.1046 (5)	−0.6300 (3)	−0.30245 (14)
C6	−0.1765 (5)	−0.2251 (3)	−0.43362 (15)		**H26**	0.0783	−0.5680	−0.3212
H6	−0.2510	−0.2393	−0.4093		**C27**	0.0516 (6)	−0.7226 (3)	−0.32297 (16)
C7	−0.1978 (7)	−0.0842 (3)	−0.55808 (17)		**H27**	−0.0101	−0.7255	−0.3568
C8	0.2306 (4)	−0.4299 (2)	−0.39192 (12)		**C28**	0.0866 (5)	−0.8157 (3)	−0.29495 (16)
C9	0.1696 (4)	−0.5145 (3)	−0.42211 (14)		**H28**	0.0490	−0.8798	−0.3103
H9	0.0467	−0.5267	−0.4305		**C29**	0.1731 (5)	−0.8137 (3)	−0.24658 (16)
C10	0.2869 (5)	−0.5805 (3)	−0.43988 (15)		**H29**	0.1938	−0.8751	−0.2271
H10	0.2451	−0.6379	−0.4605		**F1**	−0.3153 (7)	−0.0148 (3)	−0.55100 (15)
C11	0.4663 (4)	−0.5623 (3)	−0.42739 (13)		**F2**	−0.0708 (6)	−0.0327 (3)	−0.57639 (15)
C12	0.5289 (4)	−0.4797 (3)	−0.39722 (14)		**F3**	−0.2661 (5)	−0.1435 (2)	−0.59596 (11)
H12	0.6521	−0.4686	−0.3885		**F4**	0.5519 (11)	−0.6385 (5)	−0.5000 (3)
C13	0.4105 (4)	−0.4127 (3)	−0.37959 (13)		**F5**	0.5756 (8)	−0.7325 (5)	−0.4334 (2)
H13	0.4528	−0.3551	−0.3591		**F6**	0.7557 (9)	−0.6116 (5)	−0.4362 (3)
C14	0.5910 (5)	−0.6334 (3)	−0.44764 (16)		**N1**	0.2380 (3)	−0.4057 (2)	−0.26957 (10)
C15	0.1753 (4)	−0.2599 (2)	−0.32426 (12)		**N2**	0.3493 (4)	−0.6048 (3)	−0.17440 (12)
C16	0.1823 (5)	−0.1547 (3)	−0.33195 (14)		**N3**	0.3208 (5)	−0.7044 (3)	−0.17901 (13)
H16	0.1310	−0.1266	−0.3638		**N4**	0.2297 (4)	−0.7196 (2)	−0.22684 (12)
C17	0.2642 (5)	−0.0882 (3)	−0.29345 (15)		**O1**	−0.0854 (3)	−0.40489 (18)	−0.35758 (9)
H17	0.2679	−0.0160	−0.2995		**P1**	0.06508 (10)	−0.34648 (6)	−0.37219 (3)
C18	0.3384 (5)	−0.1273 (3)	−0.24731 (15)		**F4B**	0.5330 (11)	−0.6760 (5)	−0.4914 (3)
H18	0.3936	−0.0821	−0.2216		**F5B**	0.7153 (9)	−0.6669 (5)	−0.4106 (3)
C19	0.3336 (4)	−0.2346 (3)	−0.23756 (13)		**F6B**	0.7227 (9)	−0.5742 (5)	−0.4662 (3)
C20	0.4056 (5)	−0.2804 (3)	−0.19071 (14)					



9 (81%)

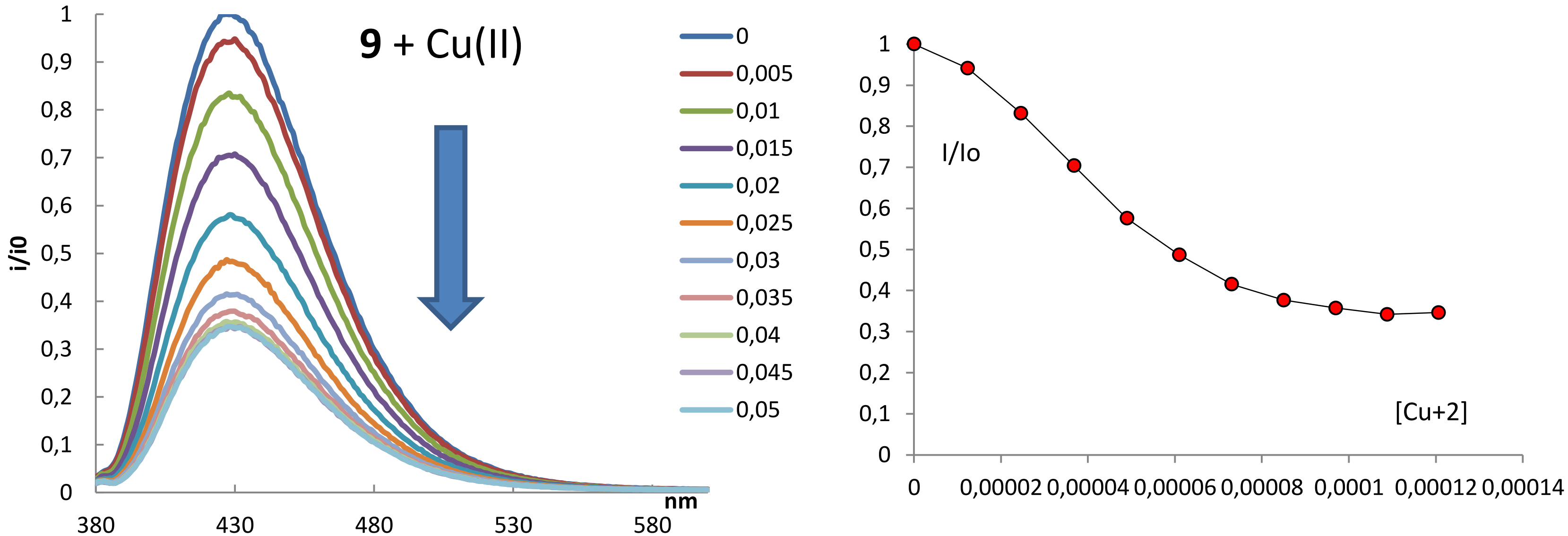
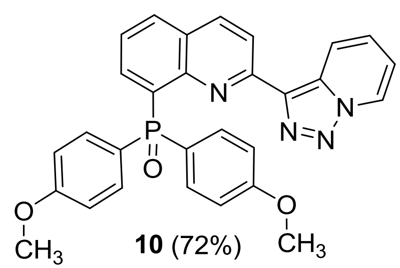


Figure S7: Fluorescence Quenching of **9** upon the addition of copper perchlorate salt

2-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)-8-(bis(4-methoxy phenyl)phosphoryl)quinoline (10): Pale colourless needles (0.4 g, 72%). mp 260 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.11 (d, *J* = 8.9 Hz, 1H), 8.67 (d, *J* = 7.0 Hz, 1H), 8.54 (d, *J* = 8.7 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69-7.58 (m, 4H), 7.59-7.49 (m, 1H), 7.43 (dt, *J* = 7.7, 7.4, 2.3 Hz, 1H), 7.35 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.00 (t, *J* = 6.8, 6.8 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.0 Hz, 4H), 3.75 (s, 6H).^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.0 (d, *J* = 2.8 Hz,2×C), 152.1 (C), 150.0 (d, *J* = 4.4 Hz. C), 137.4 (C), 137.2 (d, *J* = 10.5 Hz, CH), 136.7 (CH), 133.8 (d, *J* = 11.3 Hz, 4×CH), 132.8 (d, *J* = 2.6 Hz,CH), 131.8 (C), 130.4 (C), 127.6 (d, *J* = 7.0 Hz, 2×C), 127.1 (CH), 125.7 (C), 125.0 (d, *J* = 13.7 Hz, CH), 124.7 (CH), 124.2 (C), 122.8 (CH), 119.7 (CH), 116.4 (CH),113.9 (d, *J* = 13.4 Hz,4×C), 55.2 (s,2C)^{31}P NMR (161 MHz, $CDCl_3$): δ = 30.6 (PO). MS (EI): m/z(%) = 506(12), 478(37), 477(100), 462(22). HRMS ESI-[TOF] for $C_{29}H_{23}N_4O_3P$: calcd. 506.1508; found 506.1504.



10 (72%)

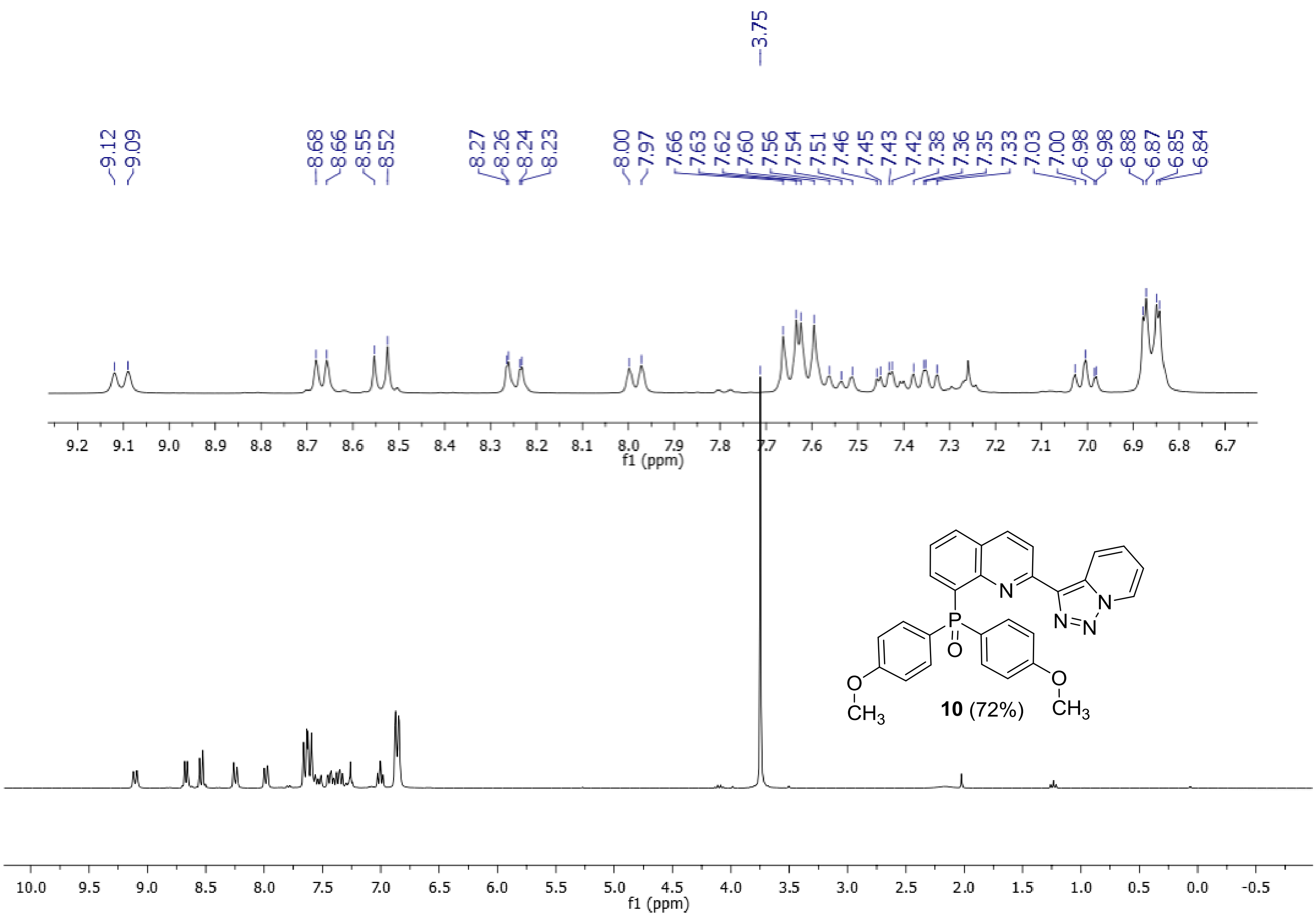


Figure S8: ^{1}H NMR (300 MHz, $CDCl_3$) of **10**:

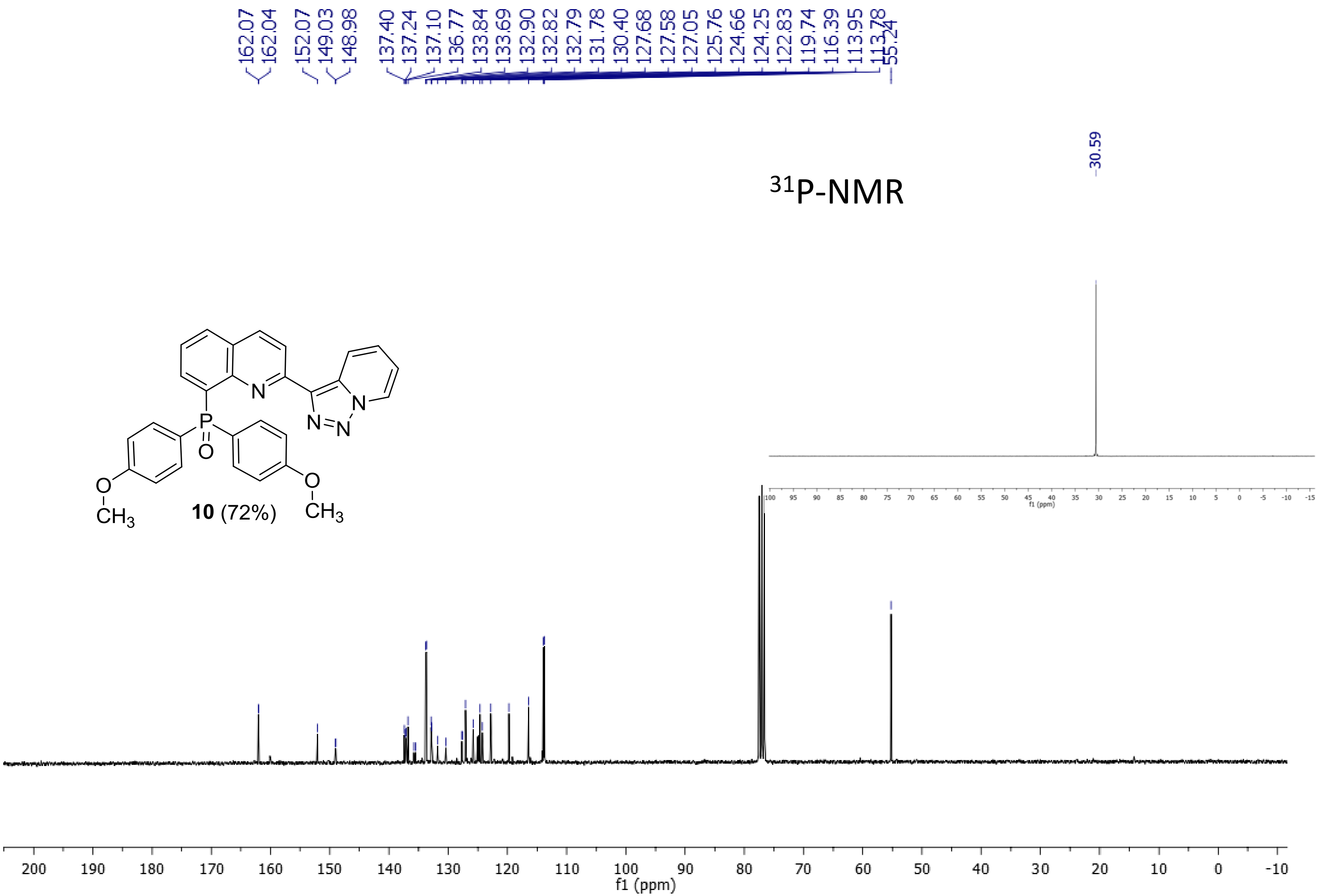
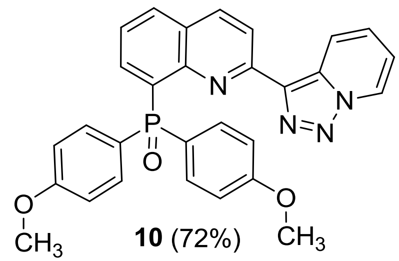
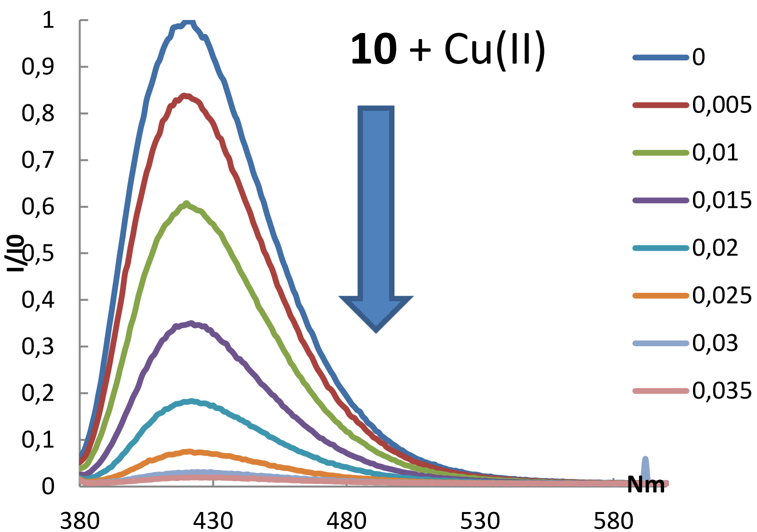


Figure S9: ^{13}C NMR (75.5 MHz, $CDCl_3$) and ^{31}P NMR (161 MHz, $CDCl_3$) of **10**:





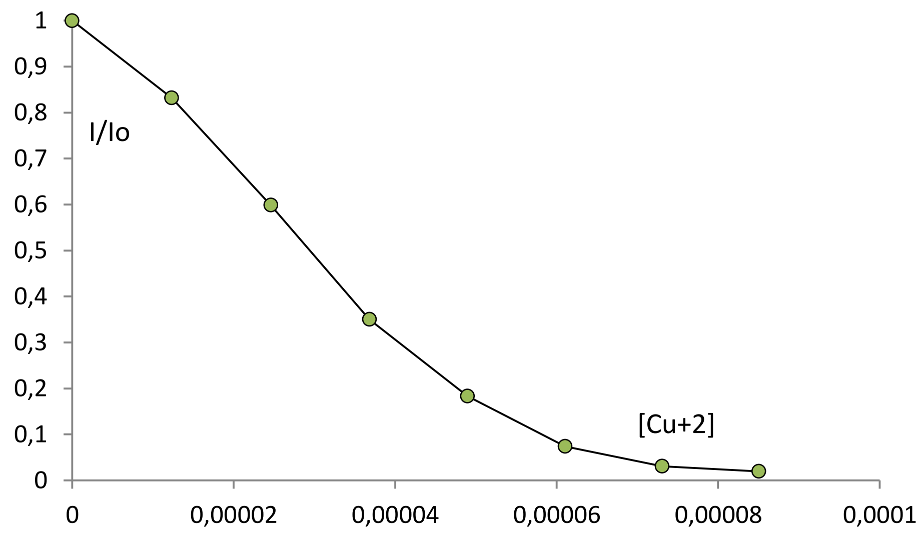
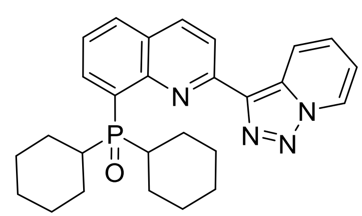


Figure S10: Fluorescence Quenching of **10** upon the addition of copper perchlorate salt

2-([1,2,3]triazolo[1,5-*a*]pyridin-3-yl)-8-(dicyclohexylphosphoryl) quinoline (11): Pale yellow needles (0.3 g, 59%). mp 235 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.88 (app d, *J* = 7.2 Hz, 2H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.46 (dd, *J* = 11.8, 6.8 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.4, 7.4 Hz, 1H), 7.51 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.17 (t, *J* = 6.8, 6.8 Hz, 1H), 2.9-2.7 (m, 2H), 2.4-2.2 (m, 2H), 1.9-0.8 (m, 18H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 151.7 (C), 147.6 (C), 137.9 7 (d, *J* = 5.6 Hz, CH), 137.7 (d, *J* = 2.2 Hz, CH), 137.6 (d, *J* = 20.1 Hz, C), 137.5 (C), 131.9 (d, *J* = 1.5 Hz, CH), 131.8 (C), 127.3 (d, *J* = 7.2 Hz, C), 126.8 (d, *J* = 0.8 Hz, CH), 125.9 (CH), 125.7 (d, *J* = 10.2 Hz, CH), 119.9 (CH), 119.9 (CH), 116.1 (CH), 38.2 (d, *J* = 67.1 Hz, 2×CH), 26.7 (d, *J* = 3.5 Hz, 2×CH_2), 26.6 (2×CH_2), 26.0 (d, *J* = 3.6 Hz, 2×CH_2), 25.7 (4×CH_2). ^{31}P NMR (161 MHz, $CDCl_3$): δ = 48.1 (PO). MS (EI): m/z(%) = 458(39), 430(47), 376(31), 348(30), 347(30), 301(22), 267(100) 266(30),265(45), 219(36),218(29).HRMS ESI-[TOF] for $C_{29}H_{31}N_4OP$: calcd. 458.2235; found 458.2229.



11 (59%)

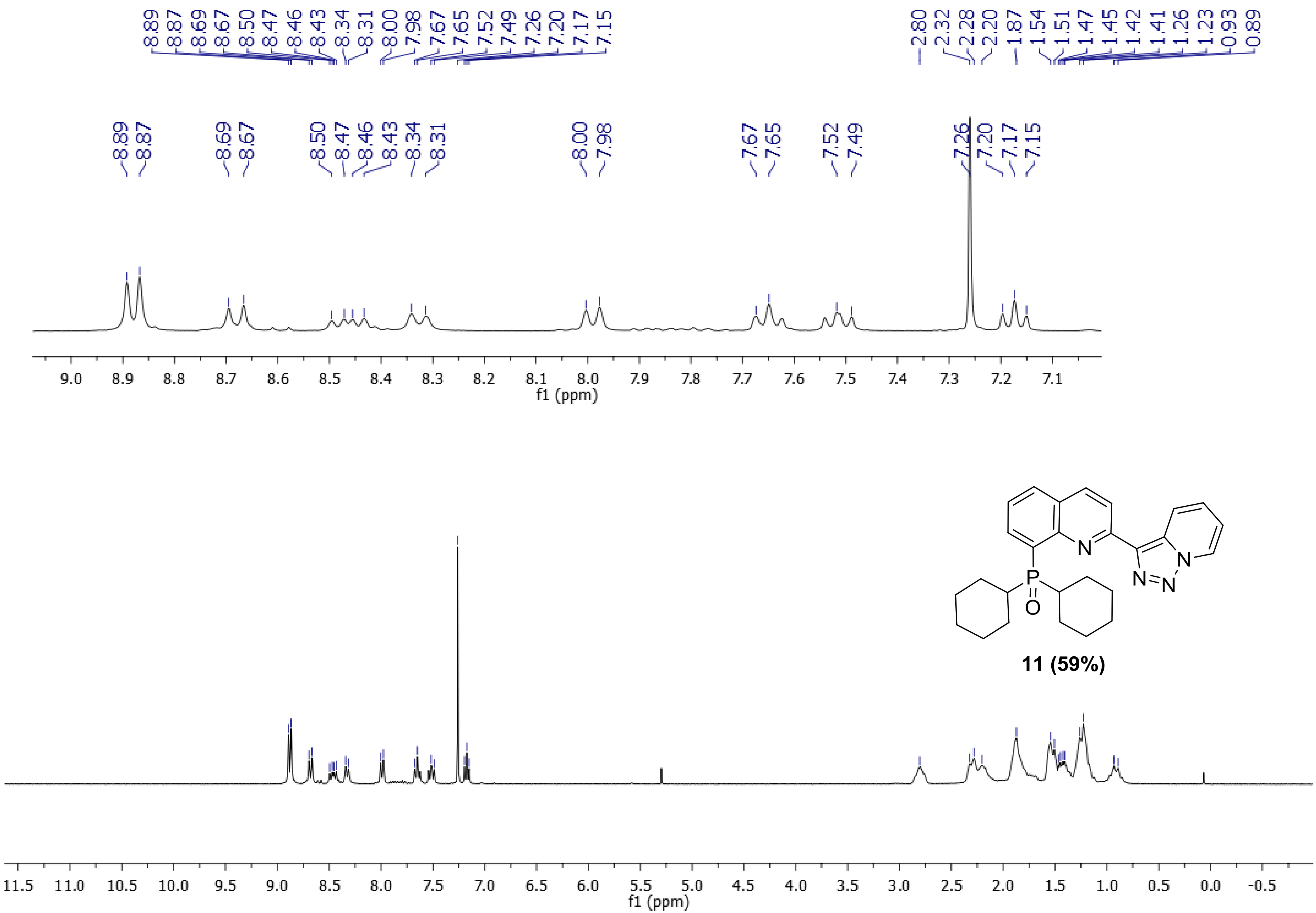


Figure S11: ^{1}H NMR (300 MHz, $CDCl_3$) of **11**:

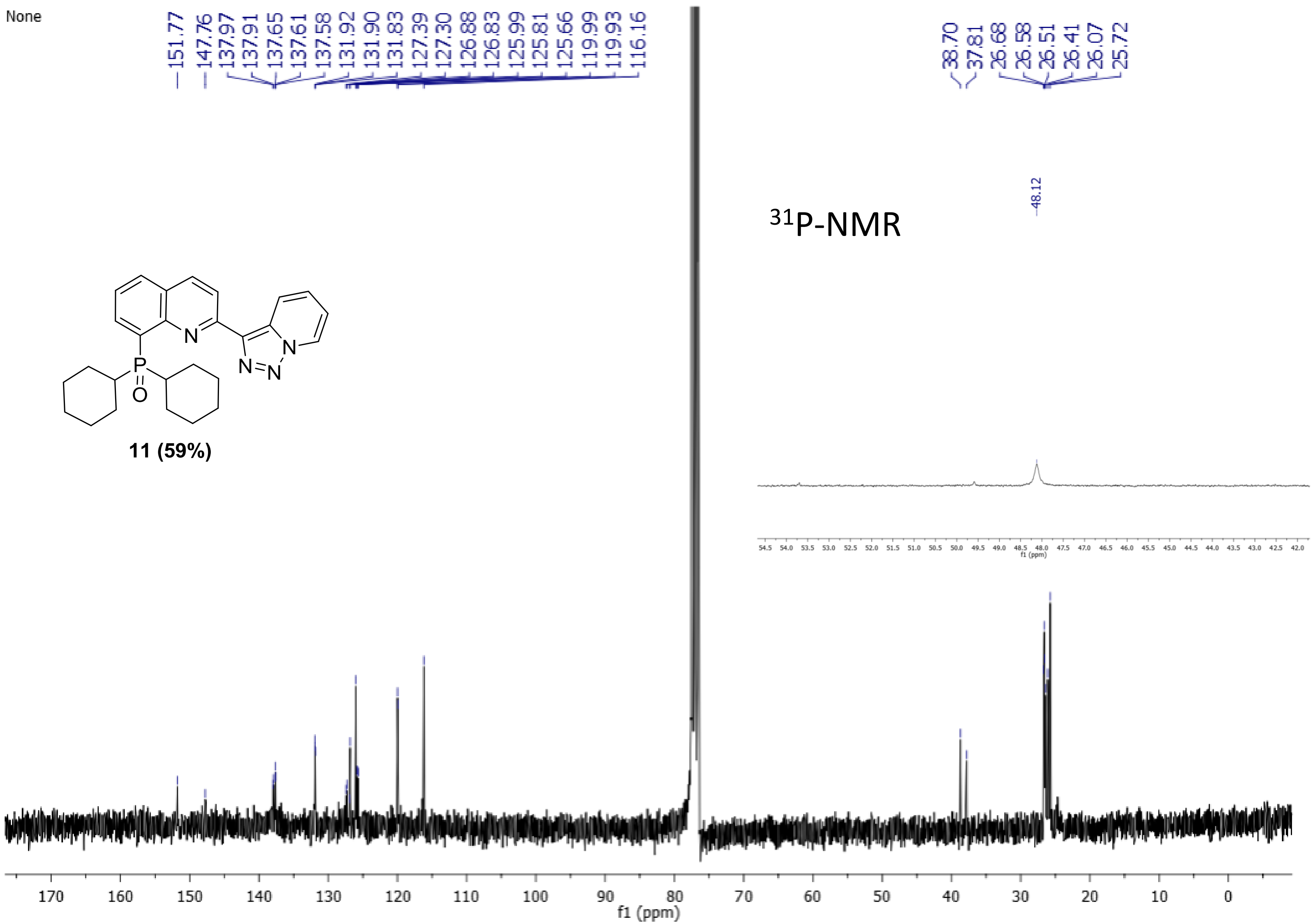
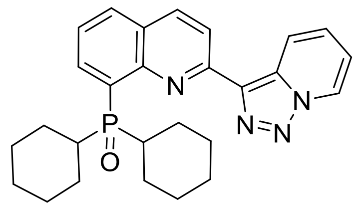
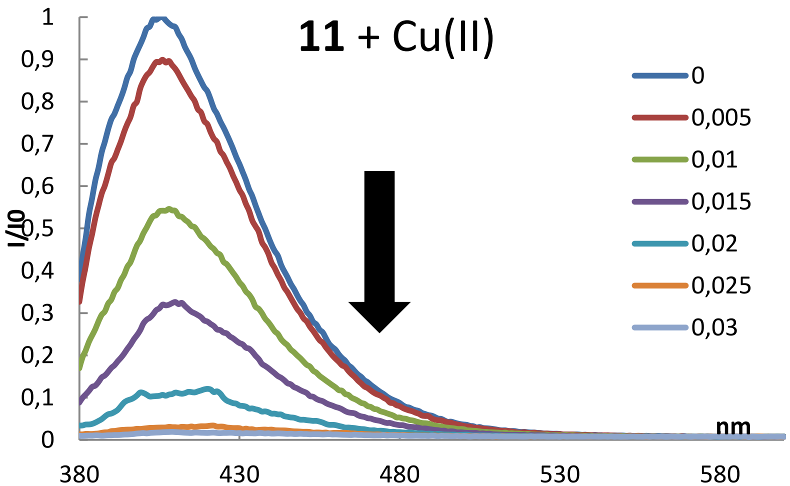


Figure S12: ^{13}C NMR (75.5 MHz, $CDCl_3$) and ^{31}P NMR (161 MHz, $CDCl_3$) of **11**:



11 (59%)



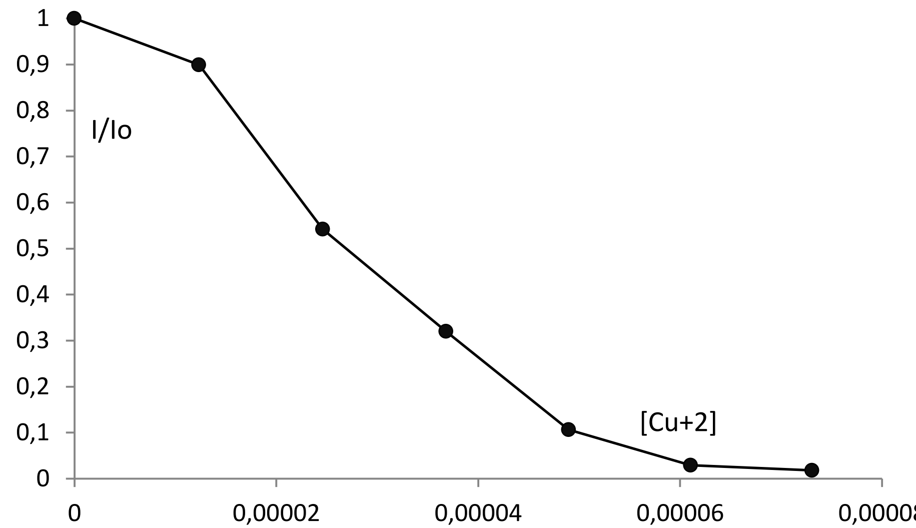
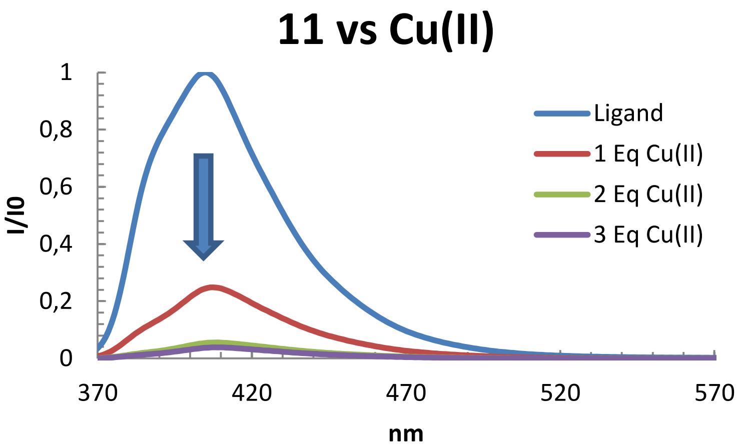


Figure S13: Fluorescence Quenching of **11** upon the addition of copper perchlorate salt



[**11**] = 0,0000298 M

V_{11}: 3 mL

[Cu(II)] = 0,005 M

NH_3 aq 30%

Figure S14: Copper test

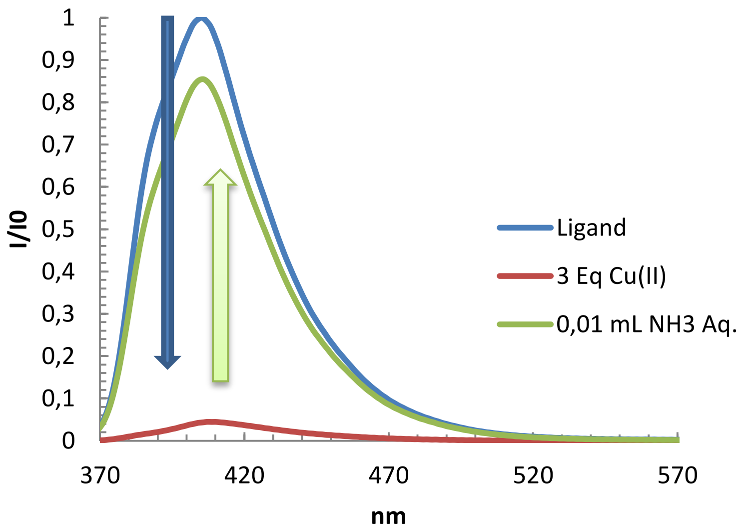


Figure S15: Copper test ammonia displcemnt.

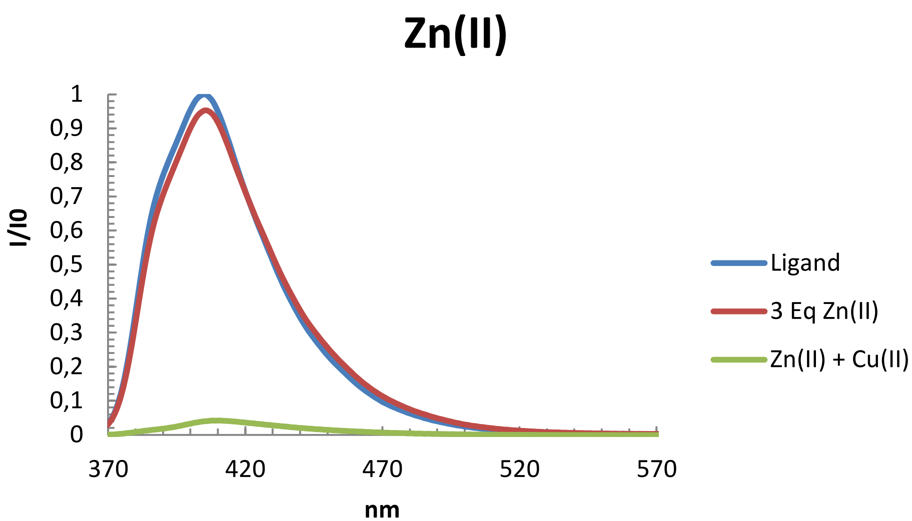


Figure S16: Zn(II) test

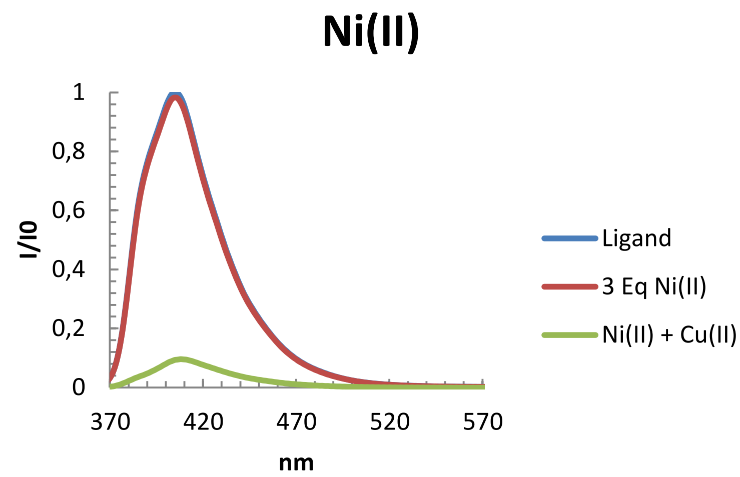


Figure S17: Ni(II) test

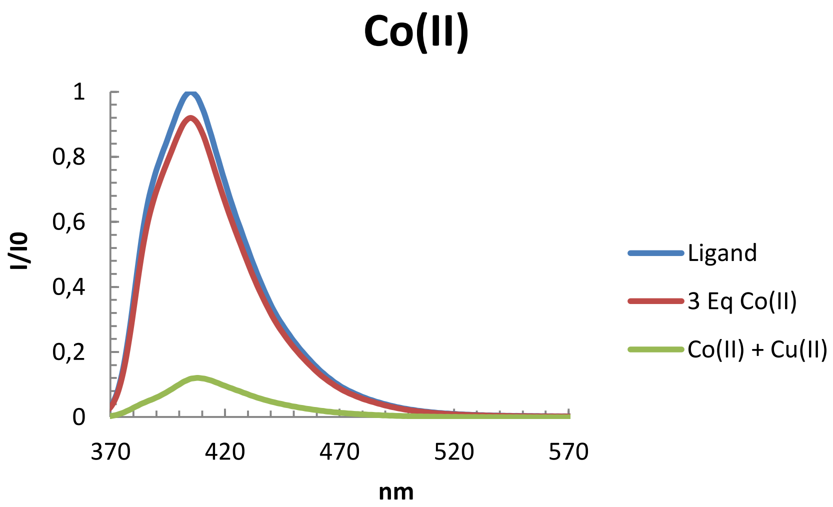


Figure S18: Co(II) test

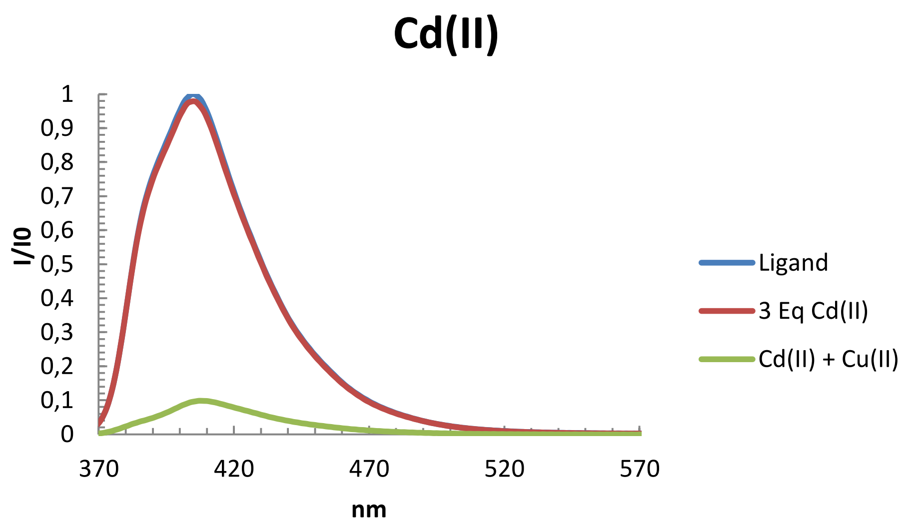


Figure S19: Cd(II) test

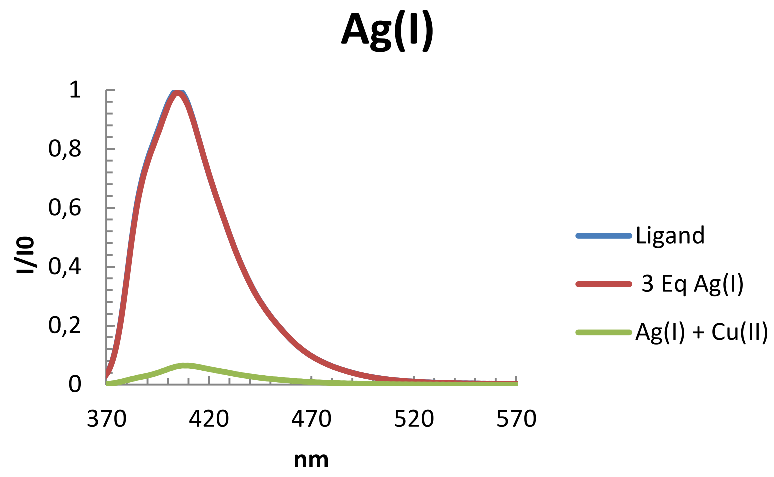


Figure S20: Ag(I) test

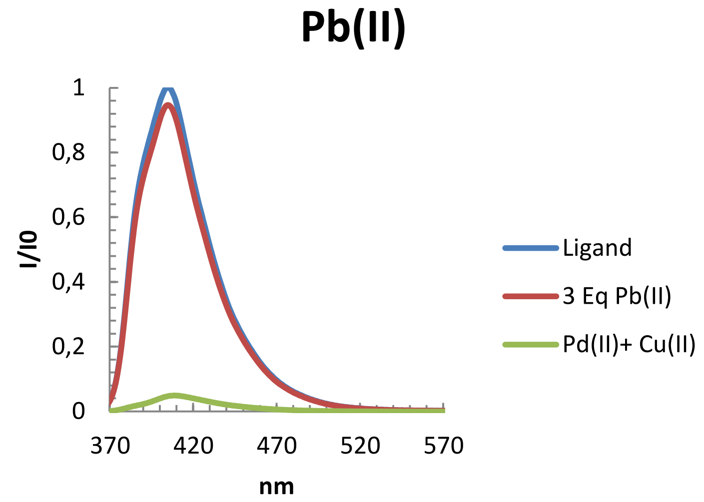


Figure S21: Pb(II) test

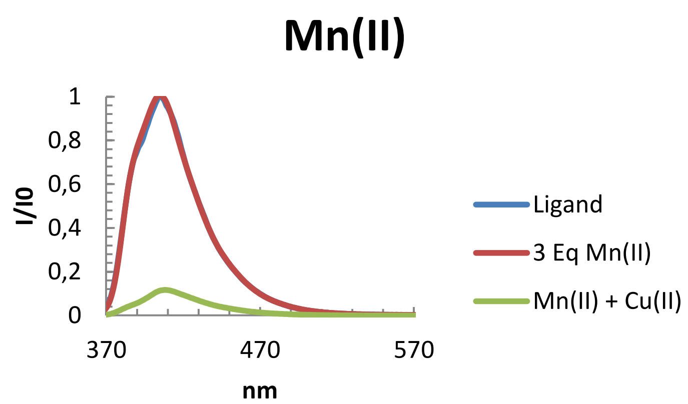


Figure S22: Mn(II) test

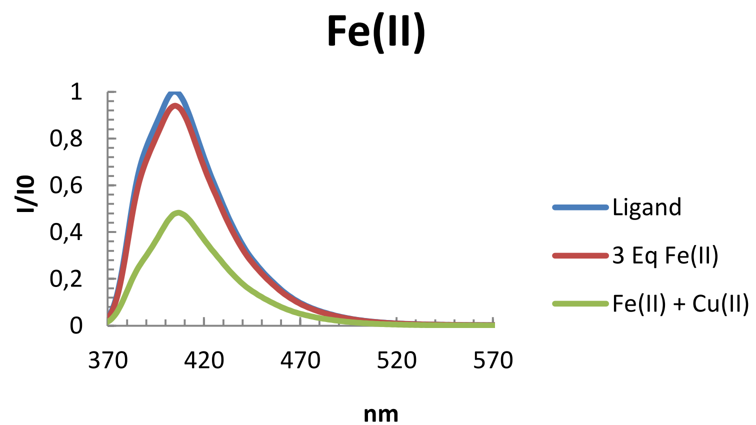
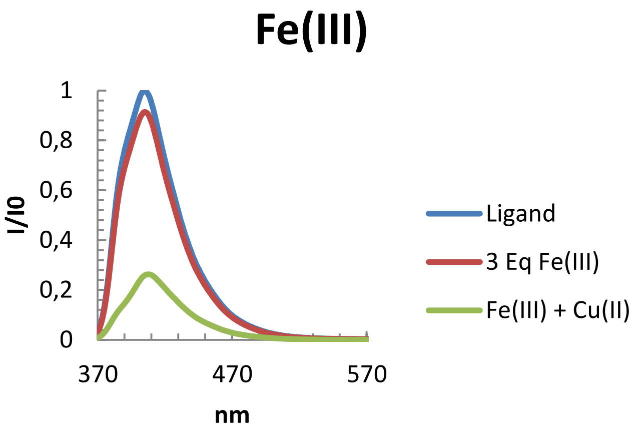


Figure S23: Fe(II) test



			V for 3 Eq	
[Fe(III)]	0,020	M	0,013	mL
[Fe(II)]	0,101	M	0,003	mL
[Co(II)]	0,1118	M	0,002	mL
[Ni(II)]	0,1053	M	0,003	mL
[Mn(II)]	0,099	M	0,003	mL
[Pb(II)]	0,1049	M	0,003	mL
[Cd(II)]	0,0995	M	0,003	mL
[Ag(I)]	0,102	M	0,003	mL
[Cu(II)]	0,005	M	0,054	mL
[Zn(II)]	0,0966	M	0,003	mL

Figure S24: Fe(III) test