Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic supplementary data to accompany

Copper(I) and silver(I) complexes of 9,9-dimethyl-4,5-bis(di-*tert*-butylphosphino)xanthene: photophysical properties and structural rigidity under pressure

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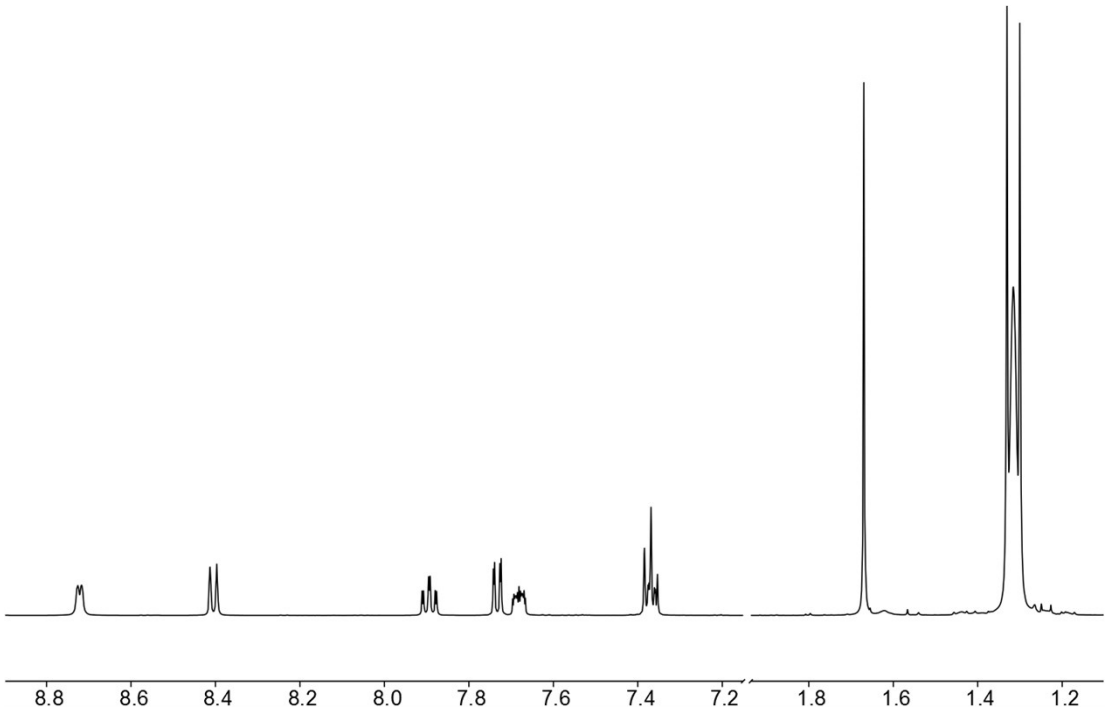

Fig. S1: ^{1}H NMR spectrum (cutout) of [Cu(*t*Bu-xantphos)(bpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz.

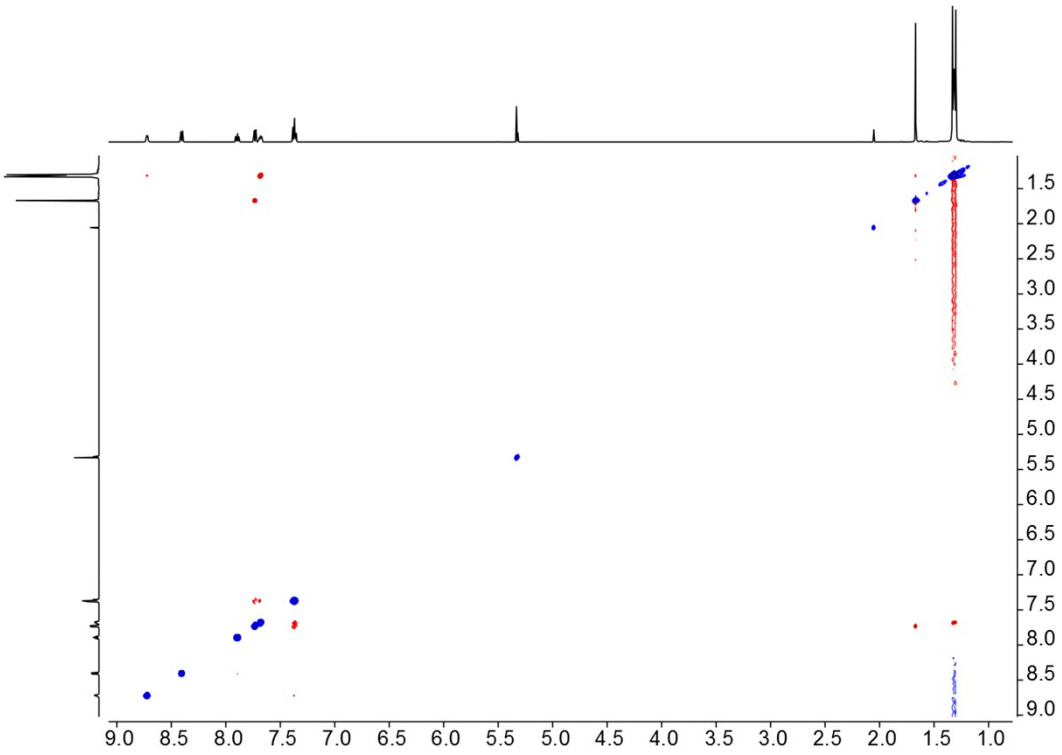

Fig. S2: NOESY spectrum of [Cu(*t*Bu-xantphos)(bpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz. The NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.31 ppm and the H^{A6} signal at δ 8.72 ppm is clearly visible.

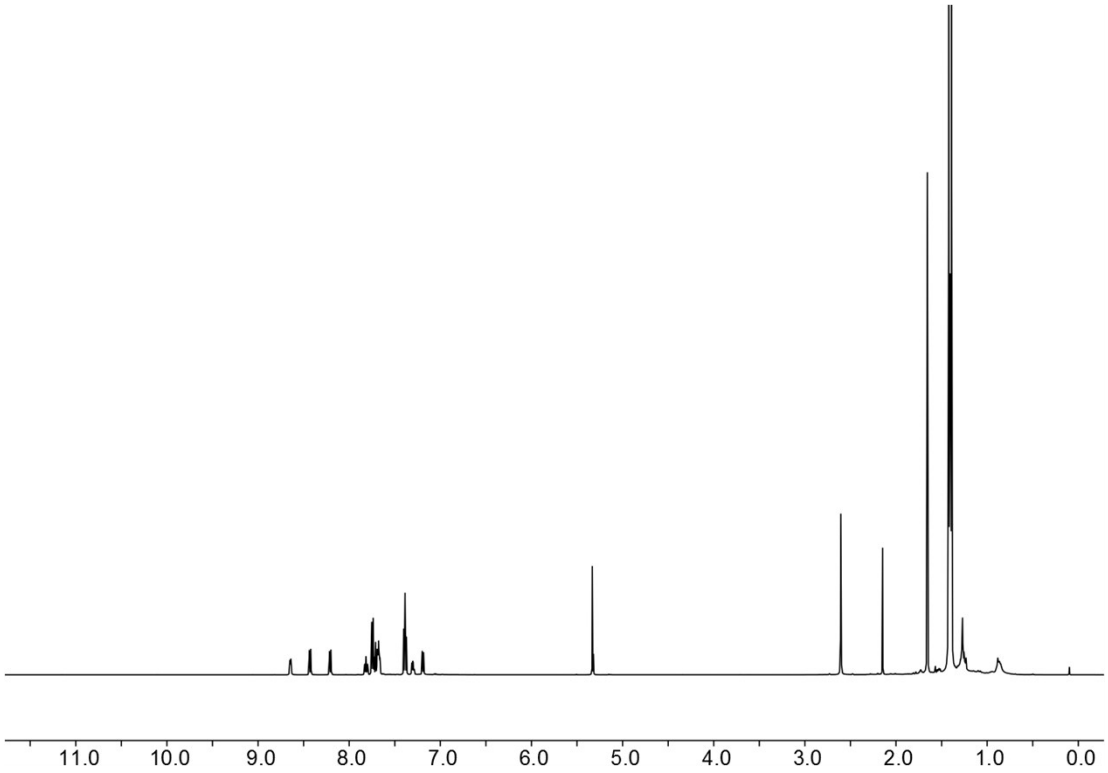

Fig. S3: ^{1}H NMR spectrum of [Cu(*t*Bu-xantphos)(6-Mebpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz.

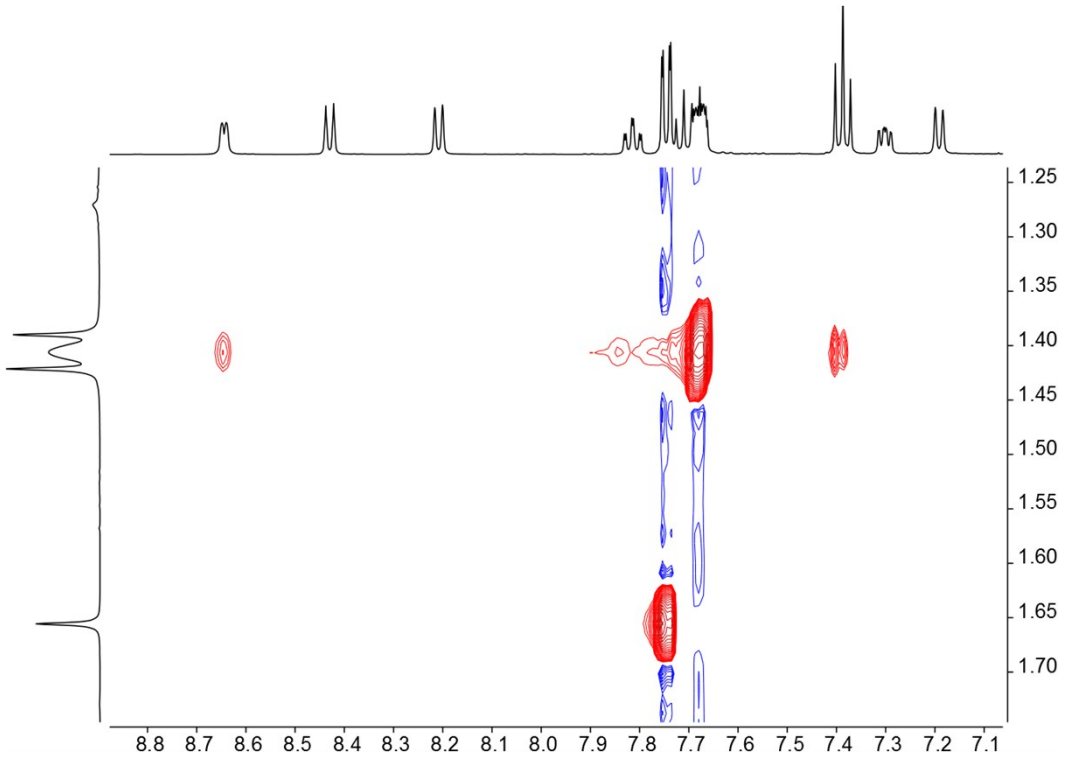

Fig. S4: NOESY spectrum (cutout) of [Cu(*t*Bu-xantphos)(6-Mebpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz. The NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.40 ppm and the H^{A6} signal at δ 8.64 ppm is clearly visible.

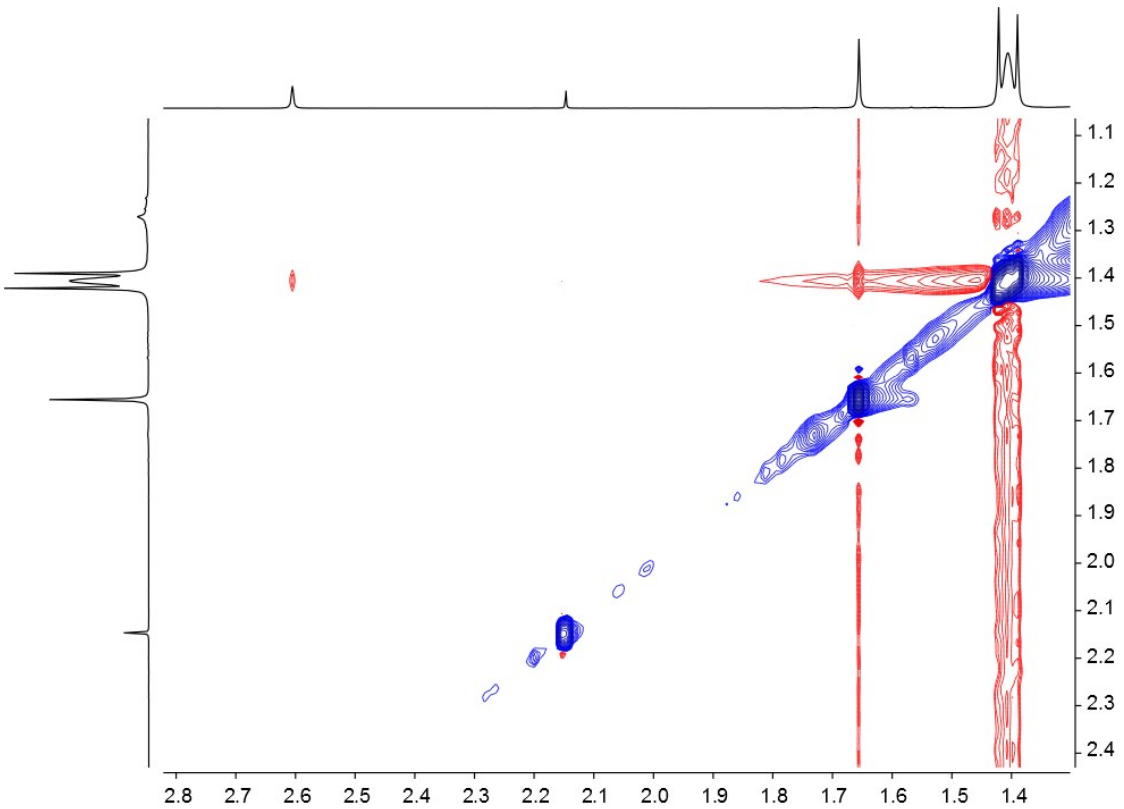

Fig. S5: NOESY spectrum (cutout) of [Cu(*t*Bu-xantphos)(6-Mebpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz. The NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.40 ppm and the Me signal of 6-Mebpy at δ 2.61 ppm is clearly visible.

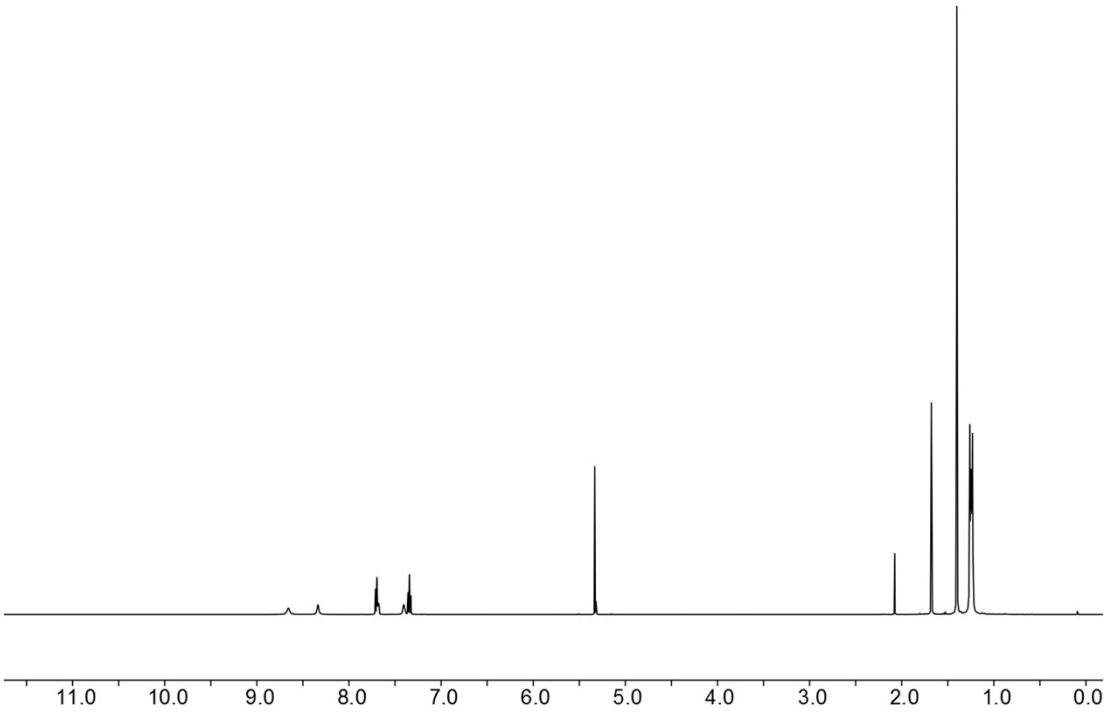

Fig. S6: ^{1}H NMR spectrum of [Cu(*t*Bu-xantphos)(4,4'-*t*Bu$_2$bpy)][PF$_6$] in CD_2Cl_2 at 298 K, 500 MHz.

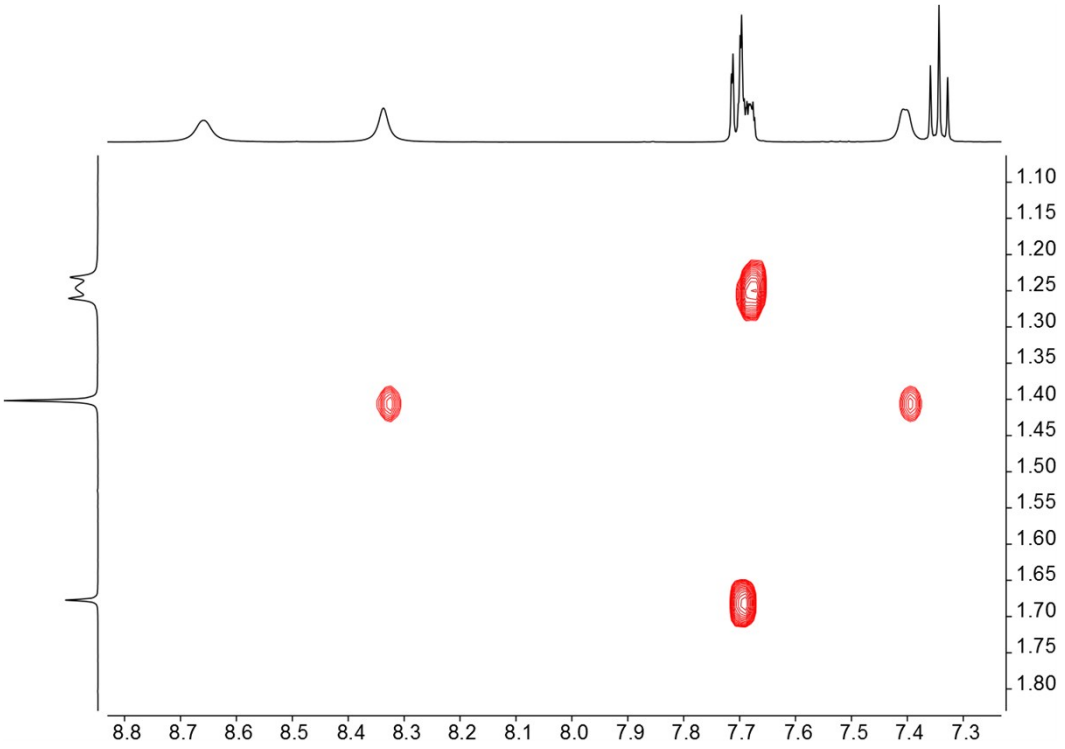

Fig. S7: NOESY spectrum (cutout) of [Cu(*t*Bu-xantphos)(4,4'-*t*Bu$_2$bpy)][PF$_6$] in CD_2Cl_2 at 298 K, 500 MHz. The NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.25 ppm and the H^{A6} signal at δ 8.66 ppm is clearly visible.

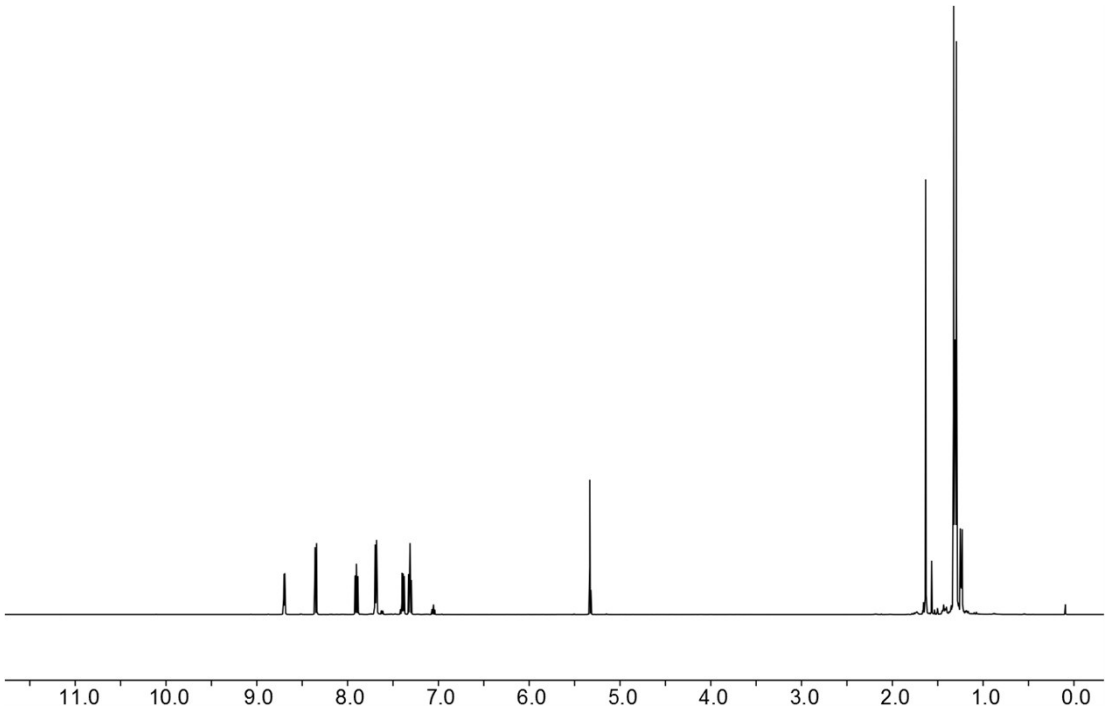

Fig. S8: ^{1}H NMR spectrum of [Ag(*t*Bu-xantphos)(bpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz.

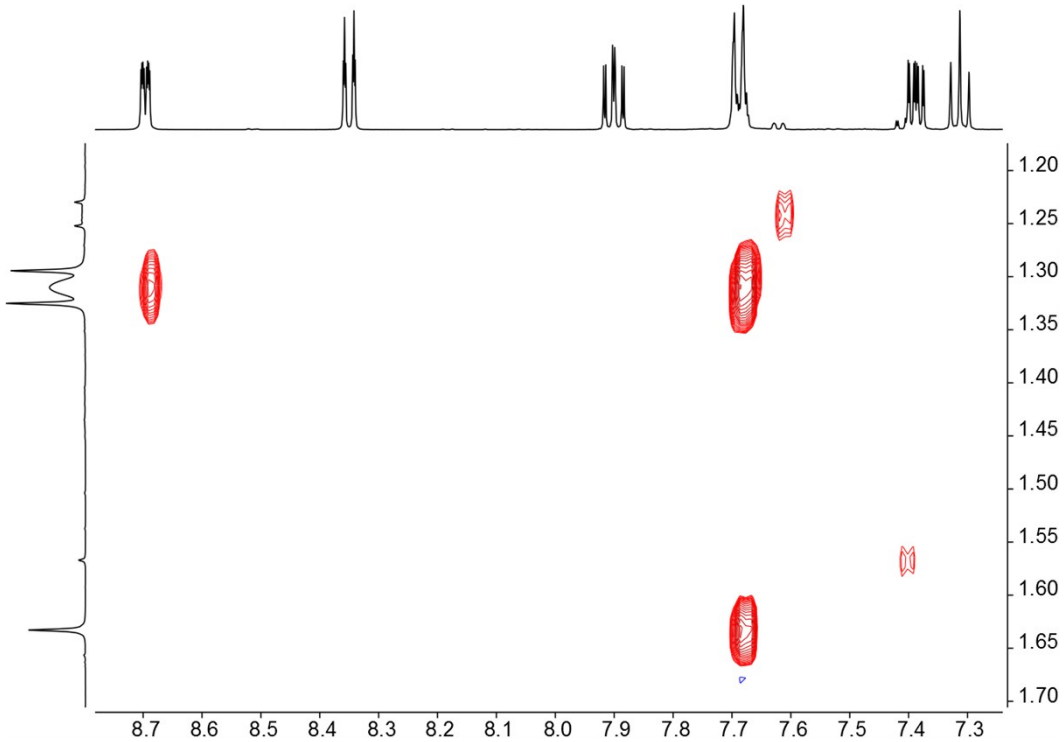

Fig. S9: NOESY spectrum (cutout) of [Ag(*t*Bu-xantphos)(bpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz. The NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.31 ppm and the H^{A6} signal at δ 8.70 ppm is clearly visible.

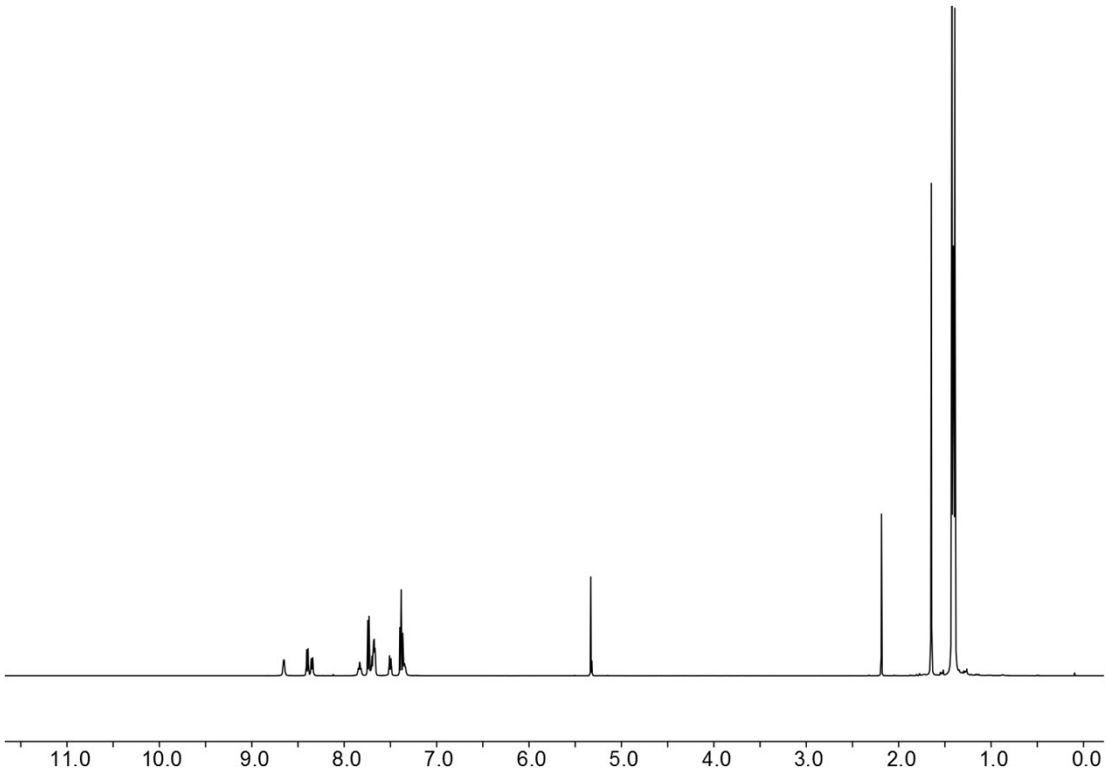

Fig. S10: ^{1}H NMR spectra of the residue of the attempted preparation of [Cu(*t*Bu-xantphos)(6-Brbpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz.

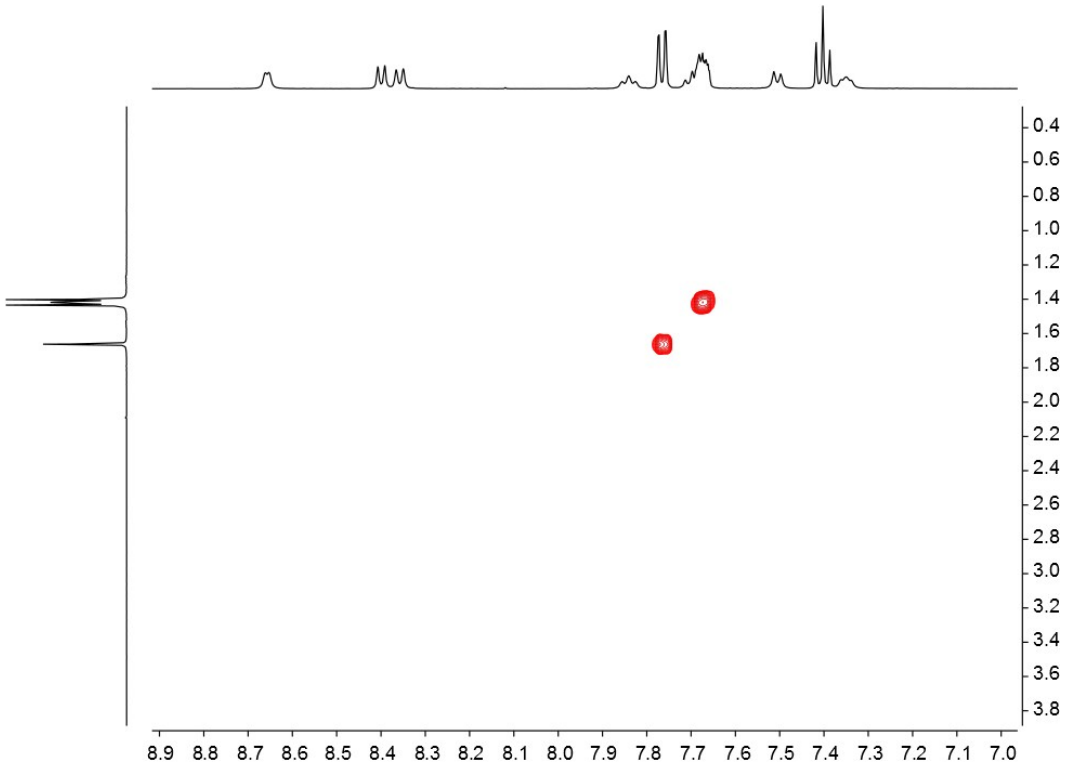

Fig. S11: NOESY spectrum (cutout) of the attempted preparation of [Cu(*t*Bu-xantphos)(6-Brbpy)][PF_6] in CD_2Cl_2 at 298 K, 500 MHz. The absence of a NOESY cross peak between the *t*Bu signal of *t*Bu-xantphos at δ 1.40 ppm and the H^{A6} signal at δ 8.64 ppm is clearly visible.

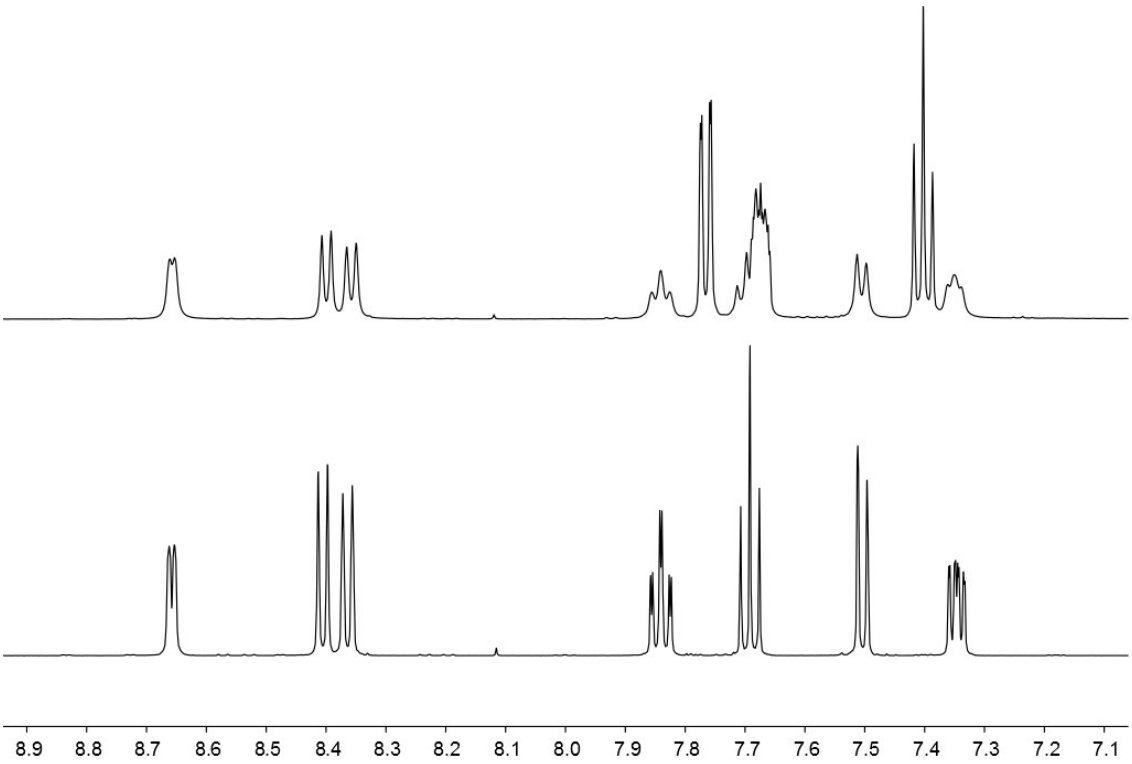

Fig. S12: ^{1}H NMR spectra (cutout) of the residue of the attempted preparation of [Cu(*t*Bu-xantphos)(6-Brbpy)][PF_6] (top) and of free 6-Brbpy (bottom) in CD_2Cl_2 at 298 K, 500 MHz.

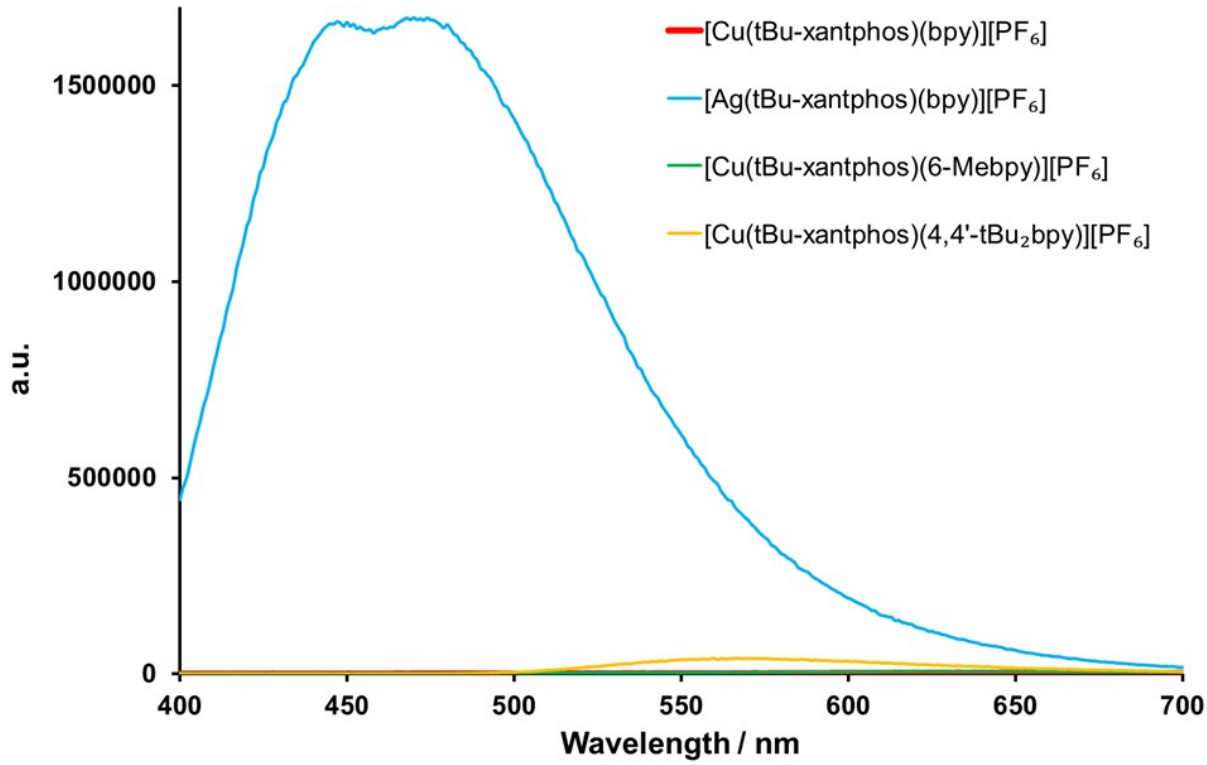

Fig. S13: Emission spectra of the [Cu(*t*Bu-xantphos)(bpy)][PF_6] complexes and [Ag(*t*Bu-xantphos)(bpy)][PF_6] in solid state.

Table S1. Experimental details for ambient and high pressure single crystal X-ray diffraction of [Cu(*t*Bu-xantphos)(bpy)][PF_6]

For all structures: $C_{41}H_{56}CuF_6N_2OP_3$, M_r = 863.36, monoclinic, $P2_1/c$.

Crystal data				
CCDC code	1583820	1583828	1583832	1583834
Temperature (K)	123	293	293	293
Pressure (GPa)	ambient	0.3	0.7	1.2
a, *b*, *c* (Å)	12.2247 (10), 15.0283 (12), 22.5879 (19)	12.187 (8), 15.0361 (10), 22.427 (2)	11.962 (9), 14.7798 (9), 22.070 (2)	11.892 (8), 14.6820 (8), 21.9164 (18)
β (°)	98.452 (3)	98.56 (2)	98.83 (2)	98.94 (2)
V (Å^3)	4104.7 (6)	4064 (3)	3856 (3)	3780 (2)
Z	4	4	4	4
F(000)	1808	1808	1808	1808
Radiation type	Cu *K*α	Synchrotron, λ = 0.48590 Å	Synchrotron, λ = 0.48590 Å	Synchrotron, λ = 0.48590 Å
μ (mm^{-1})	2.38	0.72	0.76	0.77
Crystal size (mm)	0.14 × 0.12 × 0.10	0.05 × 0.05 × 0.04	0.05 × 0.05 × 0.04	0.05 × 0.05 × 0.04
Data collection				
Diffractometer	Bruker Kappa Apex2	Pilatus 300K	Pilatus 300K	Pilatus 300K
Radiation source	Cu *K*α	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19
Monochromator	Graphite	Double crystal Silicon 111	Double crystal Silicon 111	Double crystal Silicon 111
Absorption correction	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *CrysAlis PRO* 1.171.38.41k (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41k (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.41k (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.68, 0.79	0.377, 1.000	0.377, 1.000	0.418, 1.000
No. of measured,	88540, 7254,	16222, 3446,	15253, 2965,	15269, 2899,

independent and observed [$I > 2.0\sigma(I)$] reflections	7132	2263	2091	2007
R_{int}	0.033	0.104	0.100	0.095
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.596	0.625	0.625	0.625
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.034, 1.08	0.076, 0.121, 1.11	0.078, 0.114, 1.18	0.083, 0.129, 1.15
No. of reflections	7062	3442	2963	2899
No. of parameters	655	439	439	439
No. of restraints	0	552	552	552
H-atom treatment	Only H-atom coordinates refined	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.98, -0.49	0.74, -0.67	0.62, -0.67	0.79, -0.67

Crystal data		
CCDC code	1583842	1583844
Temperature (K)	293	293
Pressure (GPa)	2.3	3.3
a, b, c (Å)	11.787 (8), 14.4808 (8), 21.5025 (19)	23.191 (18), 14.3350 (9), 21.247 (2)
β (°)	99.22 (2)	99.44 (3)
V (Å^3)	3623 (3)	6968 (5)
Z	4	8
F(000)	1808	3616
Radiation type	Synchrotron, λ = 0.48590 Å	Synchrotron, λ = 0.48590 Å
μ (mm^{-1})	0.81	0.84
Crystal size (mm)	0.05 × 0.05 × 0.04	0.05 × 0.05 × 0.04
Data collection		
Diffractometer	Pilatus 300K	Pilatus 300K
Radiation source	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19
Monochromator	Double crystal Silicon 111	Double crystal Silicon 111
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.230, 1.000	0.113, 1.000

No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	15236, 2787, 1690	29125, 5365, 2263
R_{int}	0.136	0.202
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.172, 0.432, 1.11	0.127, 0.143, 1.15
No. of reflections	2782	3934
No. of parameters	194	467
No. of restraints	210	484
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.78, -1.57	1.05, -0.96

Computer programs: Apex2 (Bruker AXS, 2006), *CrysAlis PRO* 1.171.38.41k (Rigaku OD, 2015), *SUPERFLIP* (Palatinus & Chapuis, 2007), form ambient pressure structure), form ambient pressure structure, form 3kbar structure, form 12kbar structure, *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).

Table 2. Experimental details for ambient and high pressure single crystal X-ray diffraction of [Ag(*t*Bu-xantphos)(bpy)][PF_6]

For all structures: $C_{41}H_{56}AgF_6N_2OP_3$, M_r = 907.68, triclinic, $P\bar{1}$, Z = 2, $F(000)$ = 940.

	SK170_123K	SK170_1	SK170_2	SK170_3
Crystal data				
CCDC code	1583822	1583829	1583833	1583835
Temperature (K)	123	293	293	293
Pressure (GPa)	ambient	1.0	1.7	2.5
a, b, c (Å)	12.3873 (9), 12.5363 (9), 15.3282 (12)	12.0890 (14), 12.3457 (16), 14.6171 (14)	11.9737 (11), 12.2317 (13), 14.4143 (6)	11.8753 (14), 12.1267 (16), 14.2710 (9)
α, β, γ (°)	104.142 (3), 109.108 (2), 103.339 (2)	104.131 (12), 108.001 (11), 104.296 (11)	103.770 (6), 108.026 (6), 104.548 (8)	103.601 (9), 108.062 (8), 104.620 (11)
V (Å^3)	2051.8 (3)	1885.1 (5)	1825.2 (3)	1777.5 (4)
D_x (Mg m^{-3})	1.469	1.599	1.652	1.696
Radiation type	Cu $K\alpha$	Synchrotron, λ =	Synchrotron, λ =	Synchrotron, λ =

		0.48590 Å	0.48590 Å	0.48590 Å
μ (mm^{-1})	5.58	0.73	0.75	0.77
Crystal size (mm)	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06
Data collection				
Diffractometer	Bruker Kappa Apex2	Pilatus 300K	Pilatus 300K	Pilatus 300K
Radiation source	Cu *K*α	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19
Monochromator	Graphite	Double crystal Silicon 111	Double crystal Silicon 111	Double crystal Silicon 111
Scan method	ϕ & ω scans	ω rotation with 0.4 degree frames'_diffrn_detector_area_resol_mean scans	ω rotation with 0.4 degree frames'_diffrn_detector_area_resol_mean scans	ω rotation with 0.4 degree frames'_diffrn_detector_area_resol_mean scans
Absorption correction	Multi-scan *SADABS* (Siemens, 1996)	Multi-scan *CrysAlis PRO* 1.171.38.41k (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.54, 0.72	0.707, 1.000	0.563, 1.000	0.330, 1.000
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	26703, 7397, 7256	7006, 2524, 1990	7820, 2499, 1972	7386, 2415, 1633
R_{int}	0.027	0.050	0.045	0.074
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.610	0.625	0.625	0.625
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.078, 0.90	0.058, 0.086, 0.96	0.059, 0.107, 0.96	0.118, 0.126, 1.17
No. of reflections	7336	2495	2468	2375
No. of parameters	523	439	439	229
No. of restraints	100	544	544	250
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained	H atoms treated by a mixture of independent and constrained	H atoms treated by a mixture of independent and constrained

		refinement	refinement	refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.29, -0.74	0.42, -0.34	0.49, -0.44	1.01, -0.99

Crystal data		
CCDC code	1583843	1583845
Temperature (K)	293	293
Pressure (GPa)	4.0	4.5
a, *b*, *c* (Å)	11.7672 (15), 12.0577 (15), 14.1541 (12)	11.704 (2), 12.033 (2), 14.1045 (16)
α, β, γ (°)	103.490 (11), 108.215 (10), 104.502 (11)	103.362 (15), 108.356 (15), 104.447 (15)
V (Å^3)	1737.6 (4)	1719.0 (6)
D_x (Mg m^{-3})	1.735	1.754
Radiation type	Synchrotron, λ = 0.48590 Å	Synchrotron, λ = 0.48590 Å
μ (mm^{-1})	0.79	0.80
Crystal size (mm)	0.09 × 0.08 × 0.06	0.09 × 0.08 × 0.06
Data collection		
Diffractometer	Pilatus 300K	Pilatus 300K
Radiation source	Diamond Light Source Beamline I19	Diamond Light Source Beamline I19
Monochromator	Double crystal Silicon 111	Double crystal Silicon 111
Scan method	ω rotation with 0.4 degree frames'_diffrn_detector_area_resol _mean scans	ω rotation with 0.4 degree frames'_diffrn_detector_area_resol _mean scans
Absorption correction	Multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET) (compiled Mar 27 2014,17:12:48) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.413, 1.000	0.909, 1.000
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	7233, 2360, 1537	7131, 2347, 1267
R_{int}	0.089	0.082
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.147, 0.238, 0.99	0.142, 0.224, 1.15
No. of reflections	2295	2247

No. of parameters	219	219
No. of restraints	238	238
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.26, -1.02	1.50, -1.54

Computer programs: Apex2 (Bruker AXS, 2006), *CrysAlis PRO* 1.171.38.41k (Rigaku OD, 2015), *SUPERFLIP* (Palatinus & Chapuis, 2007), form ambient pressure structure), form 10kbar structure), form 17kbar structure), form 25kbar structure), *CRYSTALS* (Betteridge *et al.*, 2003), *CAMERON* (Watkin *et al.*, 1996).