Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Material

Introducing intramolecular, interligand arene–alkynyl □-interactions into heteroleptic [Cu(N^N)(P^P)]+ complexes

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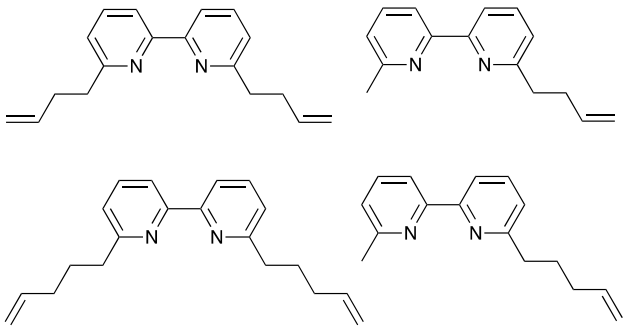

Scheme S1. Structures of previously published N^N ligands 6,6'-bis(but-3-en-1-yl)-2,2'-bipyridine, 6-(but-3-en-1-yl)-6'-methyl-2,2'-bipyridine, 6,6'-bis(pent-4-en-1-yl)-2,2'-bipyridine or 6-(pent-4-en-1-yl)-6'-methyl-2,2'-bipyridine.
Reference: J. Wöhler, M. Meyer, A. Prescimone, E.C. Constable and C.E. Housecroft, *Dalton Trans*., 2022, **51**, 13094.

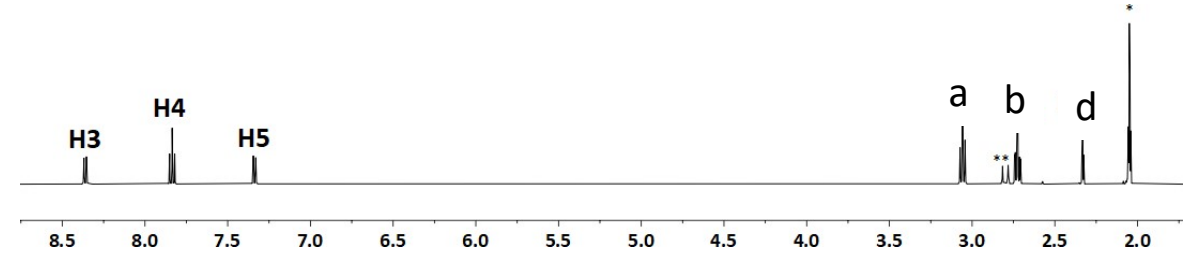

Fig. S1. ^{1}H NMR spectrum of **1**. (500 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = residual acetone-d_5; ** = H_2O and HOD.

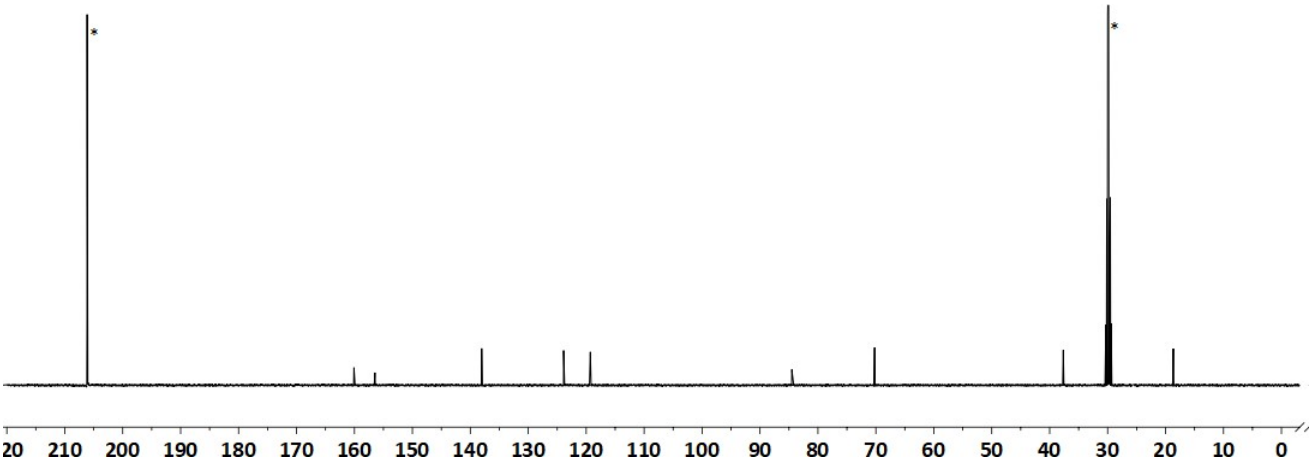

Fig. S2. ^{13}C{^{1}H} NMR spectrum of **1**. (126 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = acetone-d_6.

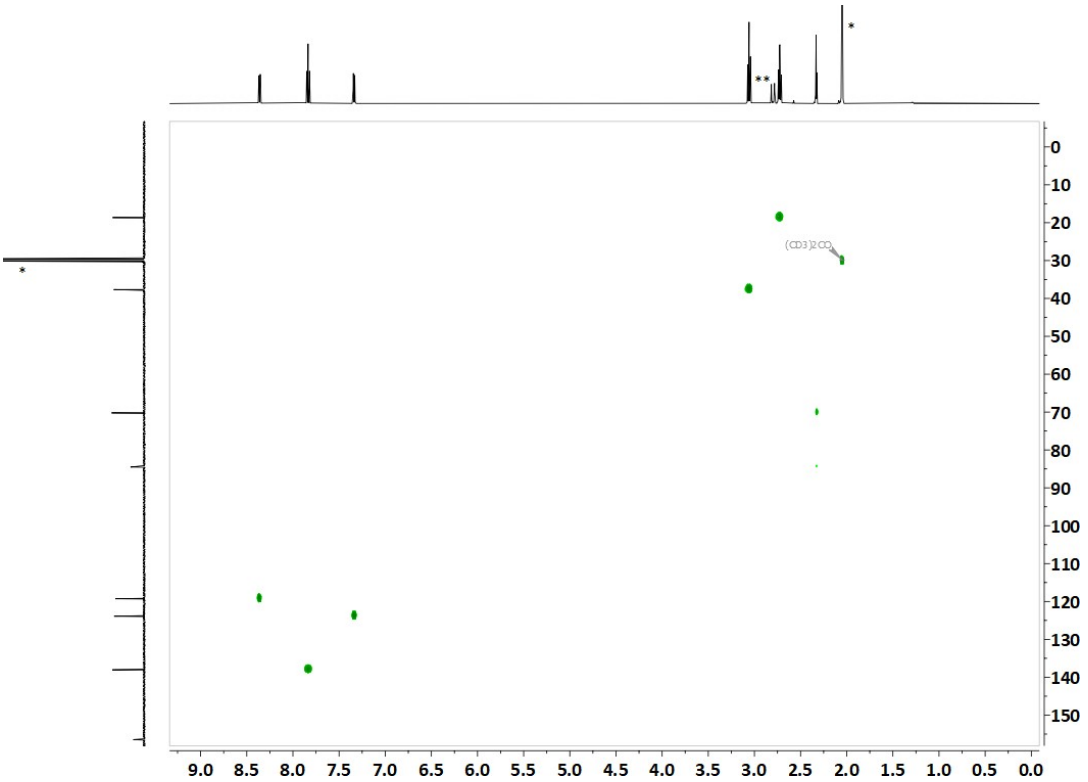

Fig. S3. HMQC spectrum of **1**. (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, 298 K, acetone-d_6). * = acetone-d_6 (in ^{13}C{^{1}H}) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

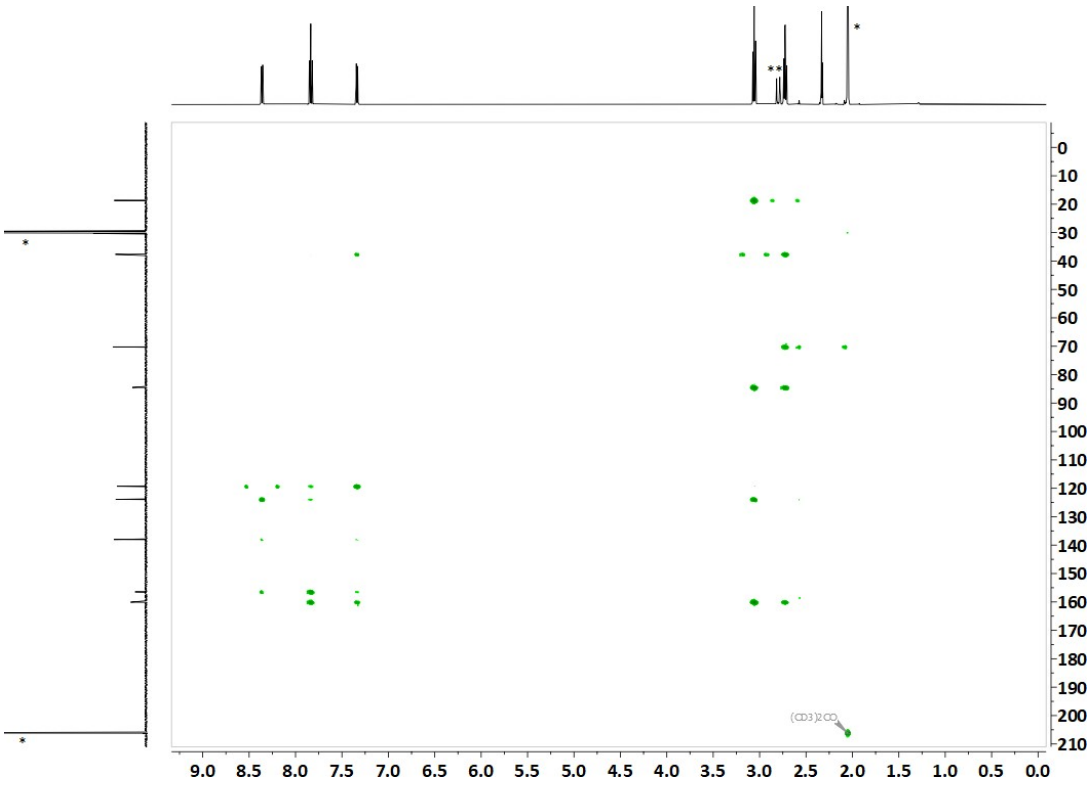

Fig. S4. HMBC spectrum of **1**. (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, 298 K, acetone-d$_6$). * = acetone-d_6 (in ^{13}C{^{1}H}) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

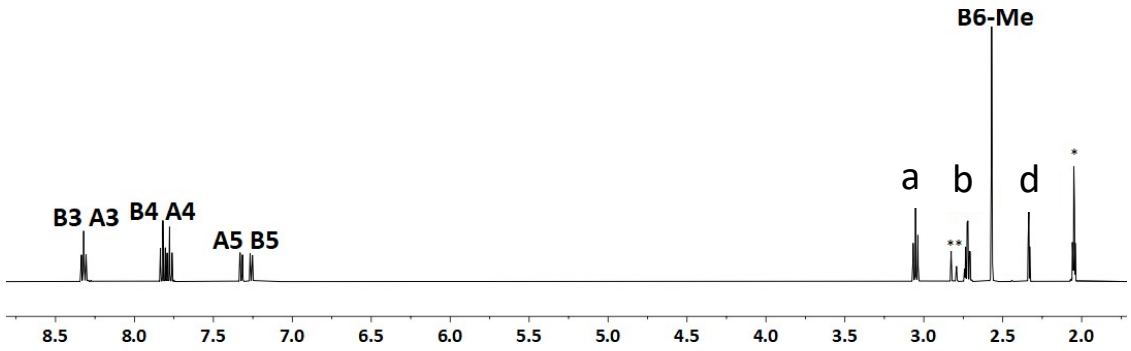

Fig. S5. ^{1}H NMR spectrum of **2**. (500 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = residual acetone-d_5; ** = H_2O and HOD.

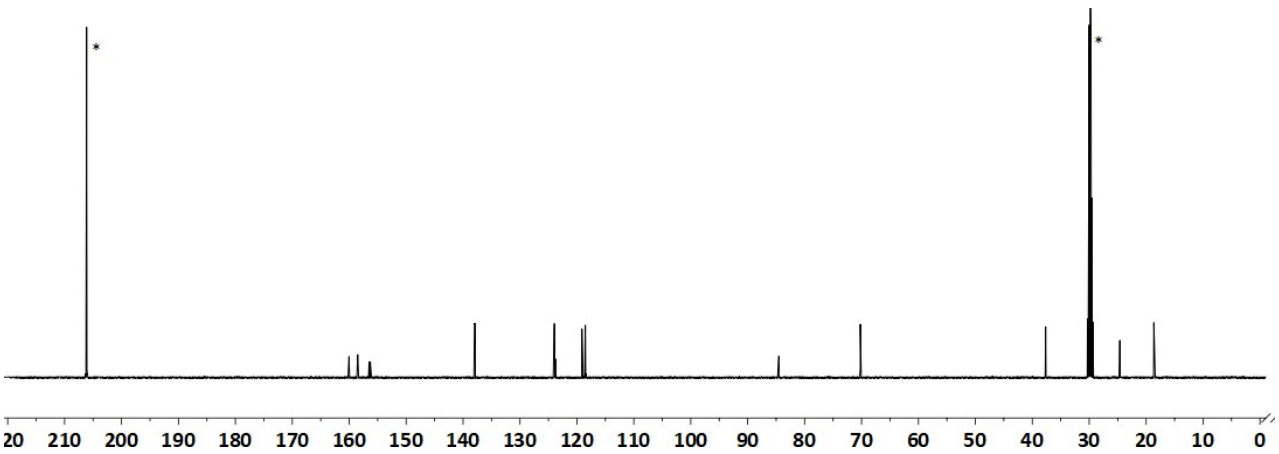

Fig. S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2**. (126 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = acetone-d_6.

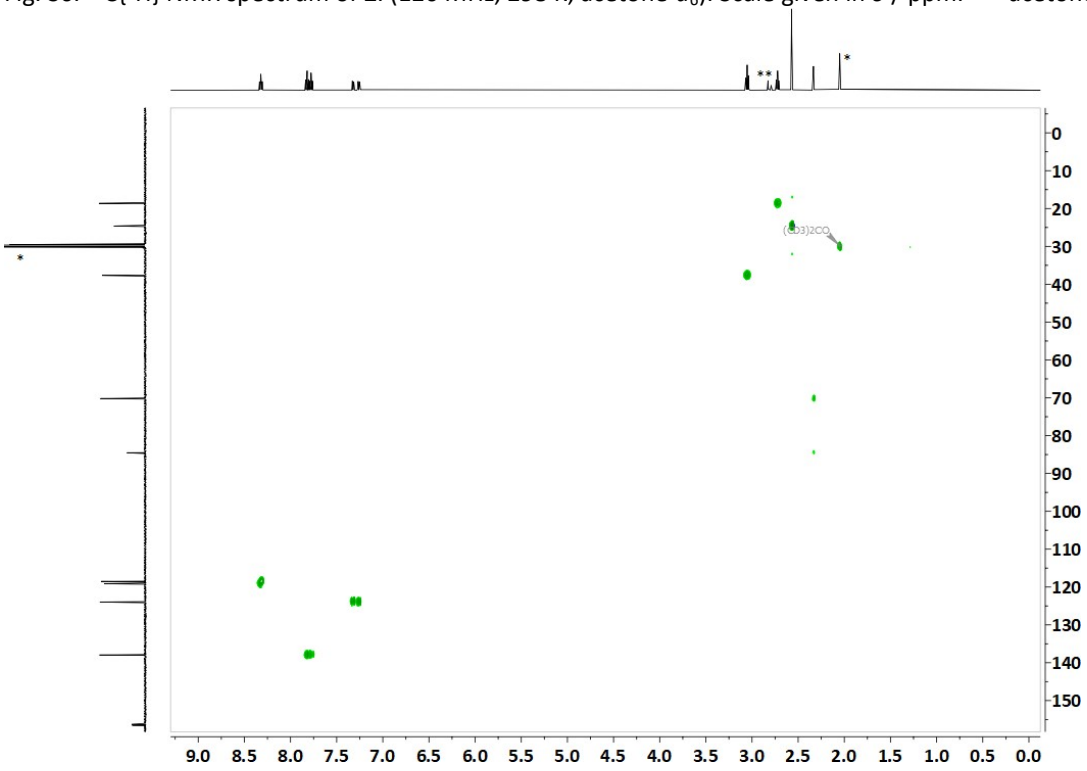

Fig. S7. HMQC spectrum of **2**. (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^{1}H\}$) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

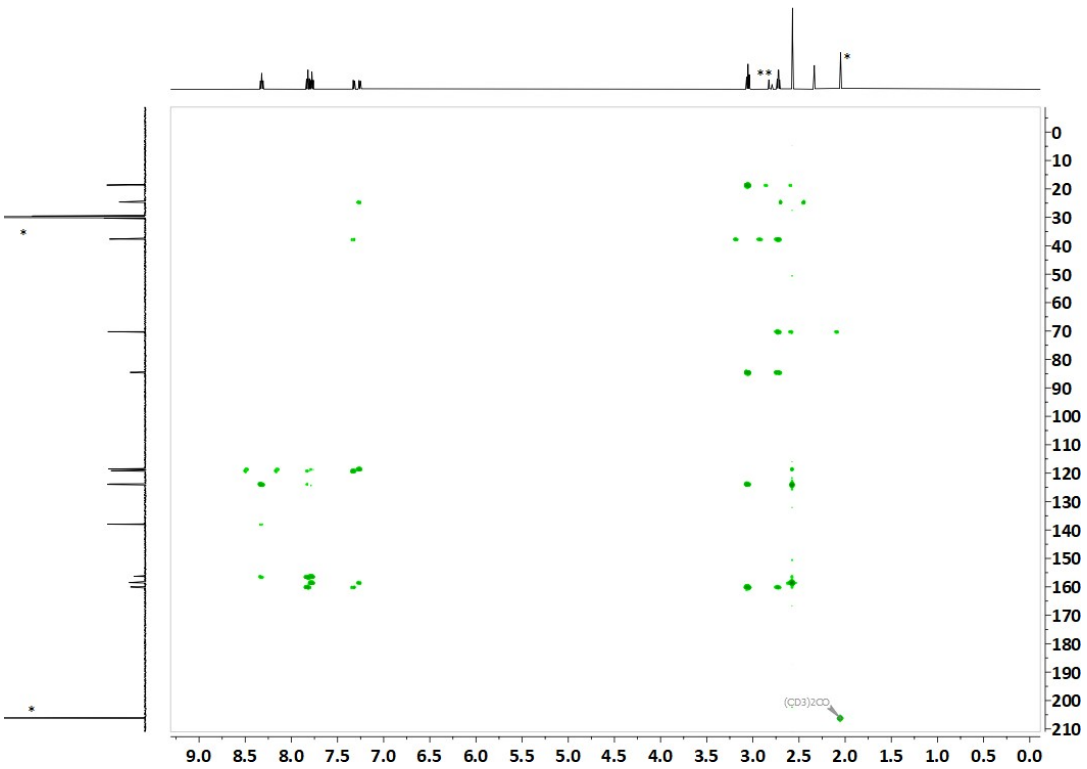

Fig. S8. HMBC spectrum of **2**. (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^{1}H\}$) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

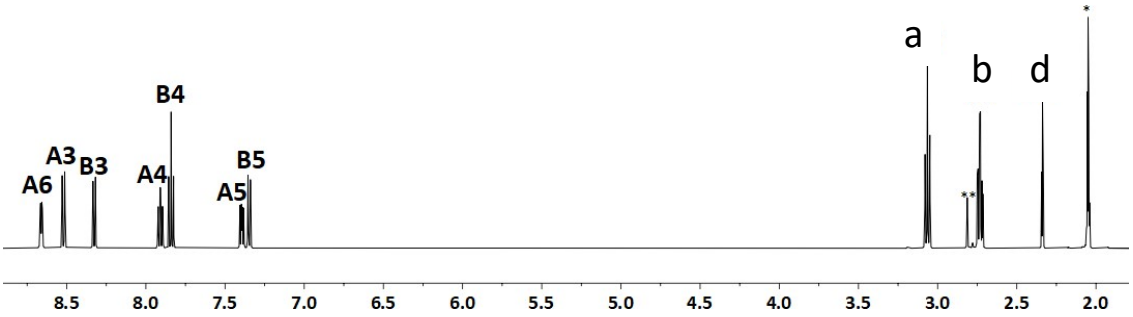

Fig. S9. ^{1}H NMR spectrum of **3**. (500 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = residual acetone-d_5; ** = H_2O and HOD.

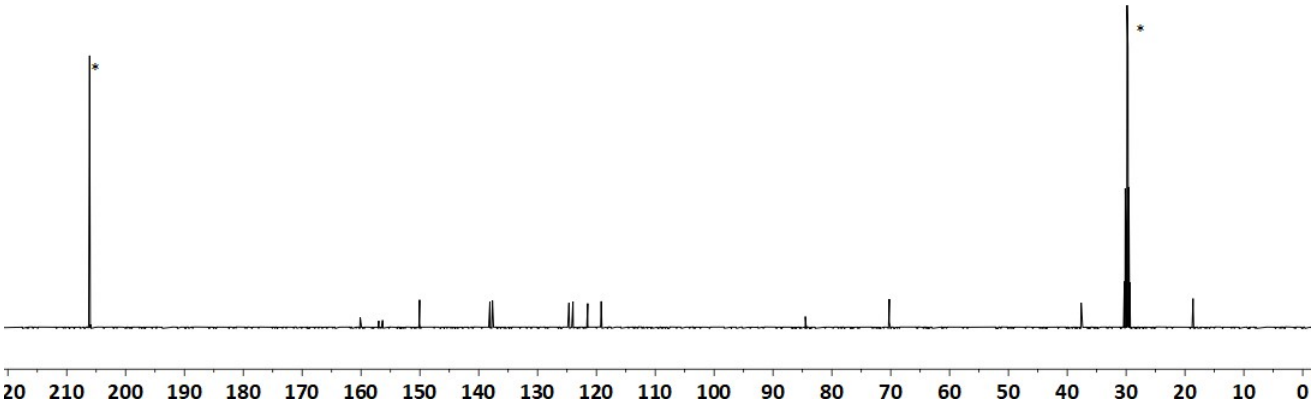

Fig. S10. ^{13}C{^{1}H} NMR spectrum of **3**. (126 MHz, 298 K, acetone-d_6). Scale given in δ / ppm. * = acetone-d_6.

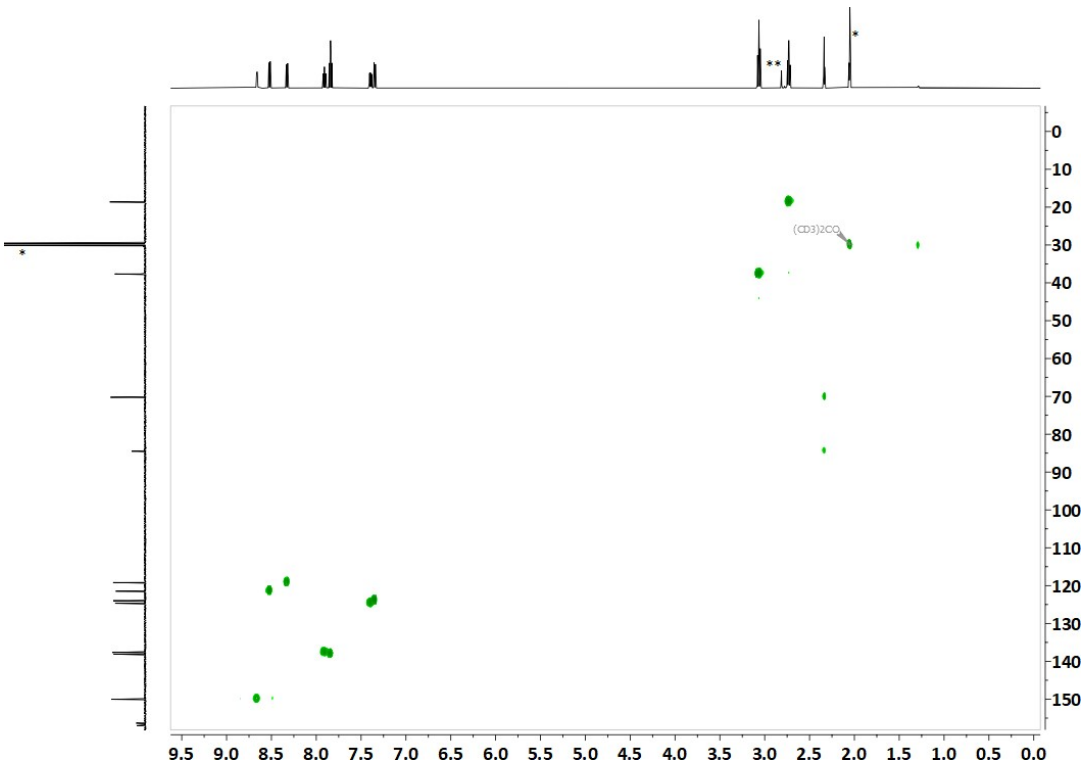

Fig. S11. HMQC spectrum of **3**. (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, 298 K, acetone-d_6). * = acetone-d_6 (in ^{13}C{^{1}H}) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

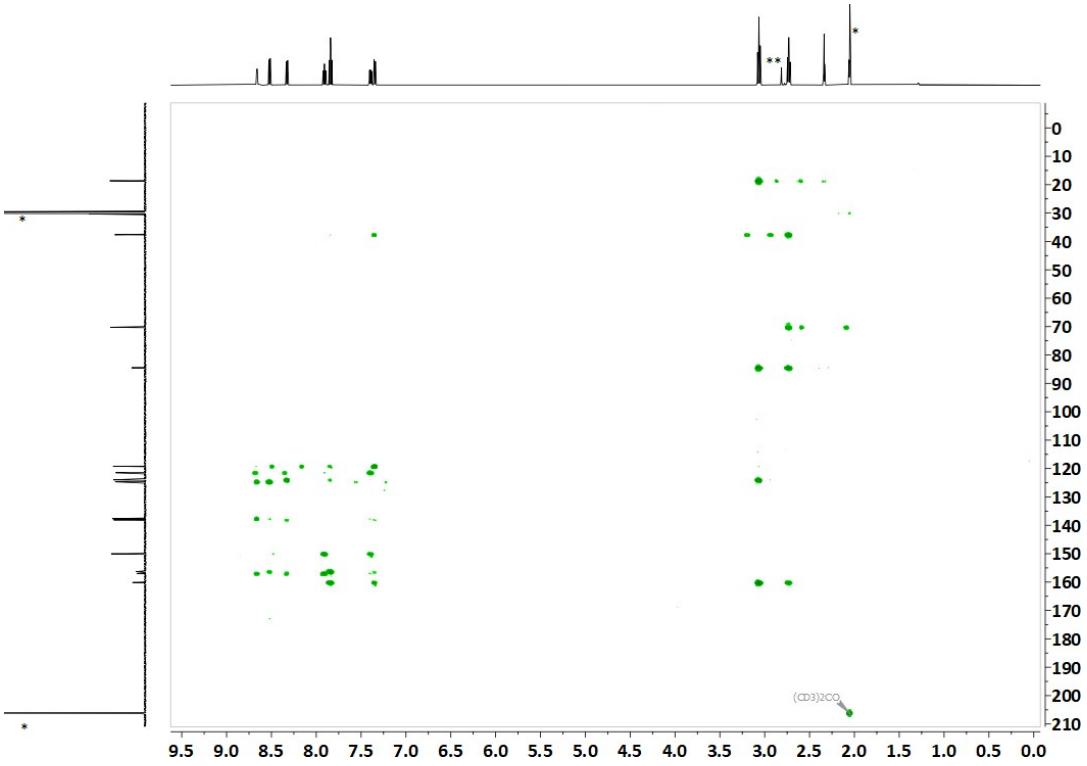

Fig. S12. HMBC spectrum of **3**. (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, 298 K, acetone-d_6). * = acetone-d_6 (in ^{13}C{^{1}H}) or residual acetone-d_5 (in ^{1}H); ** = H_2O.

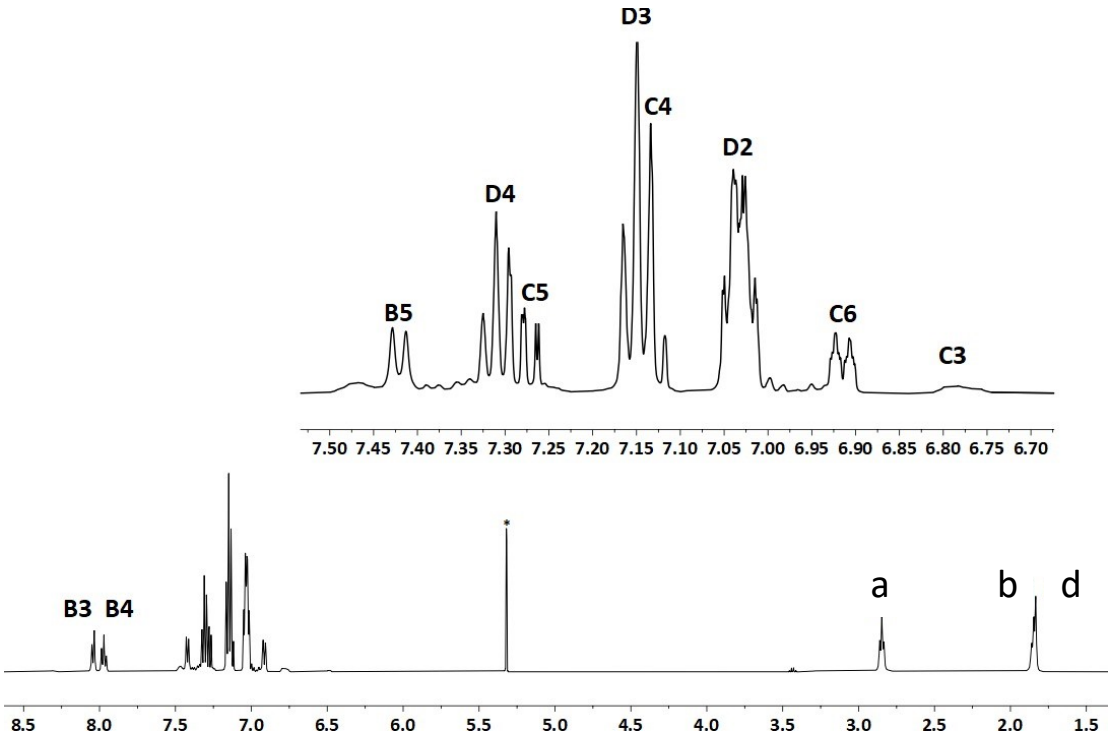

Fig. S13. ^{1}H NMR spectrum (500 MHz, 298 K, CD_2Cl_2) of [Cu(POP)(**1**)][PF_6]. Scale given in δ / ppm. * = residual $CHDCl_2$.

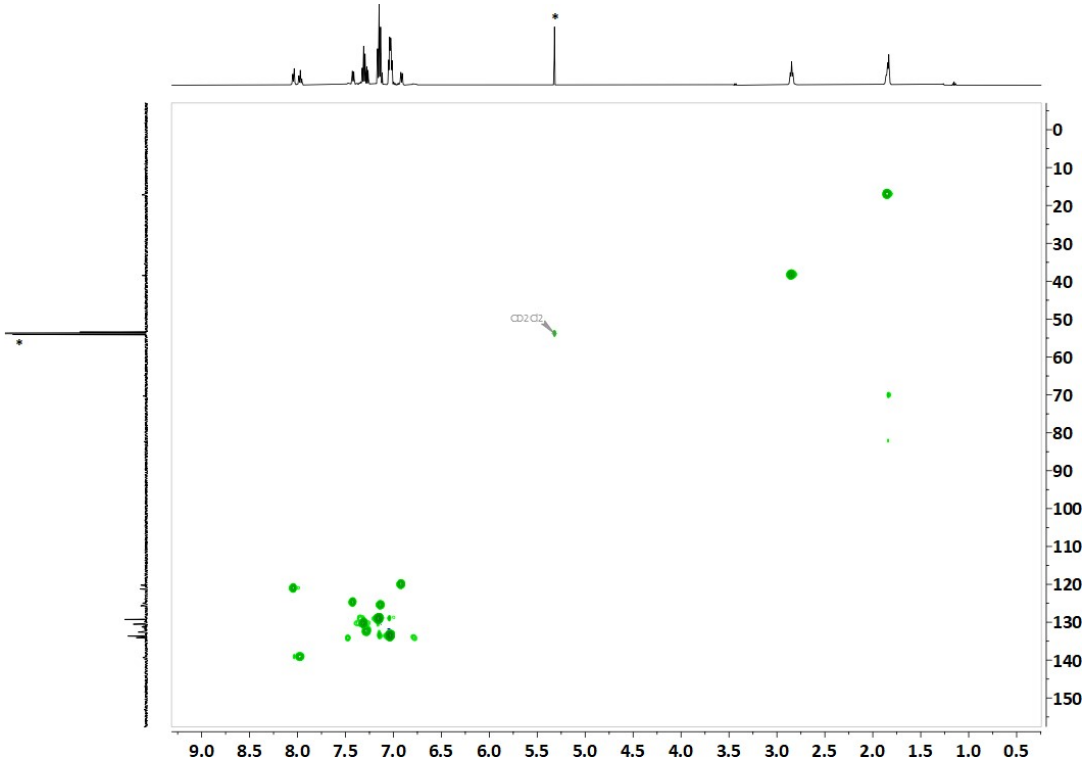

Fig. S14. HMQC spectrum of [Cu(POP)(**1**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, CD_2Cl_2). * = CD_2Cl_2 (in $^{13}C\{^1H\}$) or residual $CHDCl_2$ (in ^{1}H).

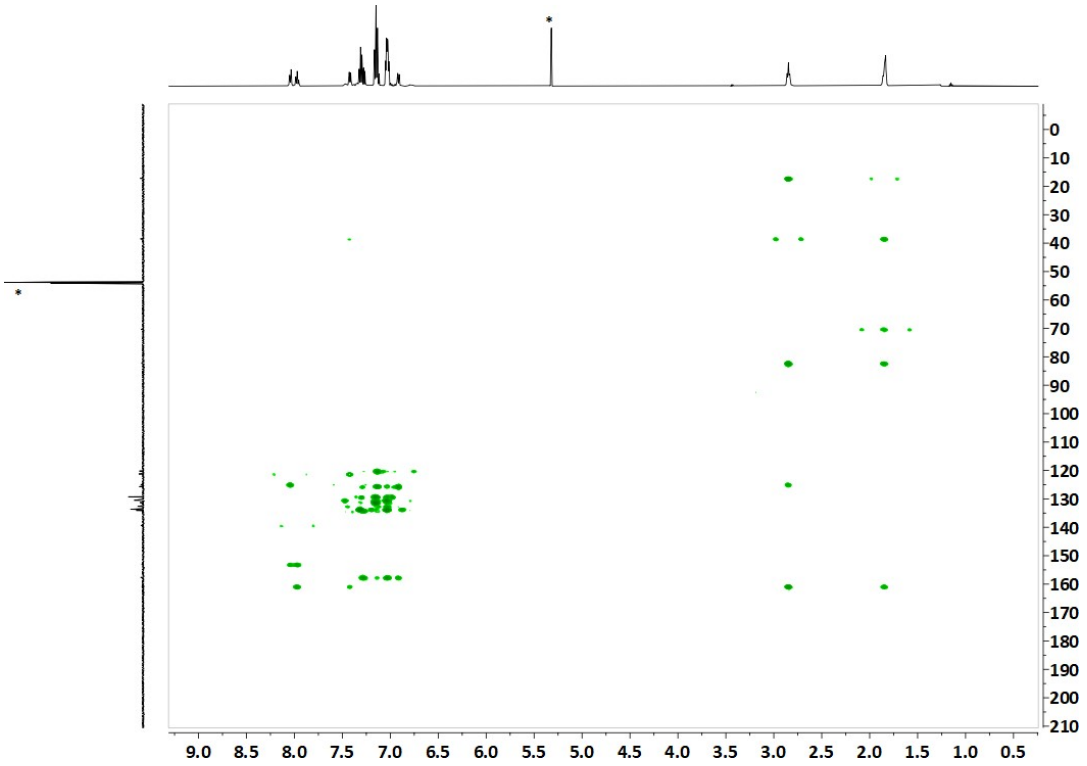

Fig. S15. HMBC spectrum of [Cu(POP)(**1**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, CD_2Cl_2). * = CD_2Cl_2 (in $^{13}C\{^1H\}$) or residual $CHDCl_2$ (in ^{1}H).

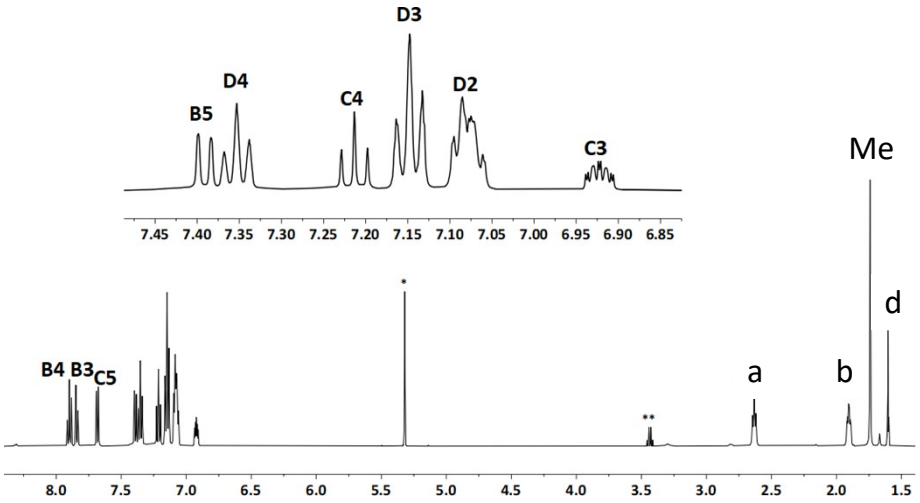

Fig. S16. ^{1}H NMR spectrum (500 MHz, 298 K, CD_2Cl_2) of [Cu(xantphos)(**1**)][PF_6]. Scale given in δ / ppm. * = residual $CHDCl_2$.

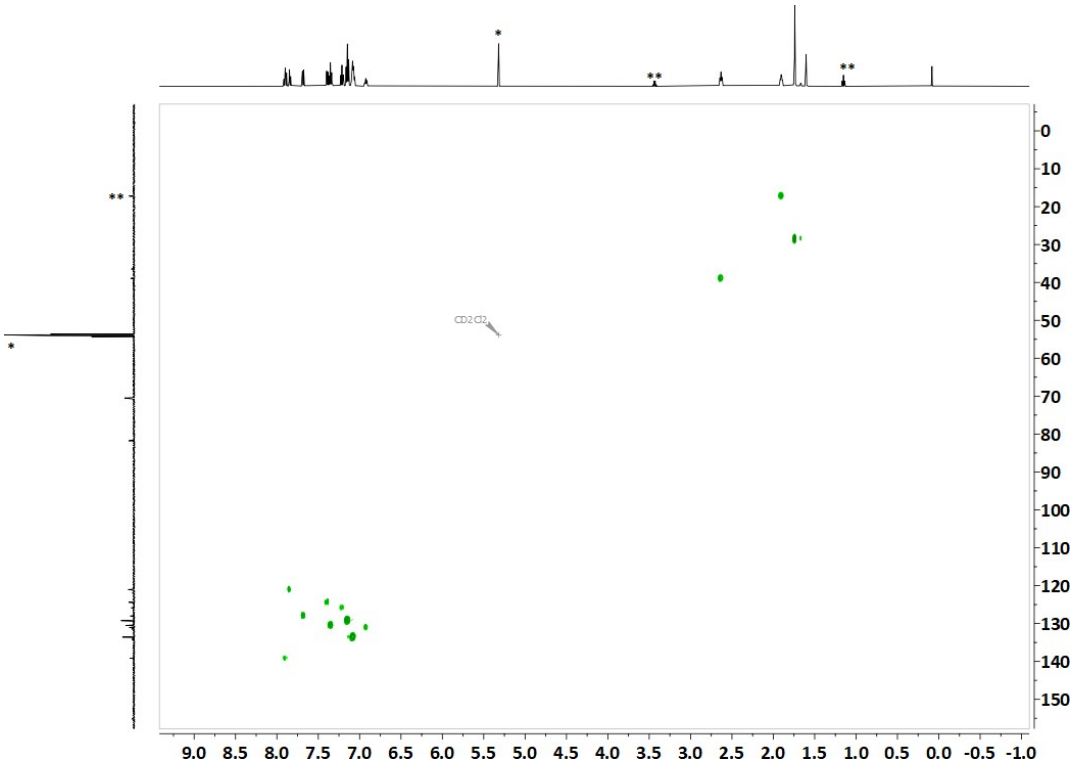

Fig. S17. HMQC spectrum of [Cu(xantphos)(**1**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^{1}H\}$, 298 K, CD_2Cl_2). * = CD_2Cl_2 (in $^{13}C\{^{1}H\}$) or residual $CHDCl_2$ (in ^{1}H).

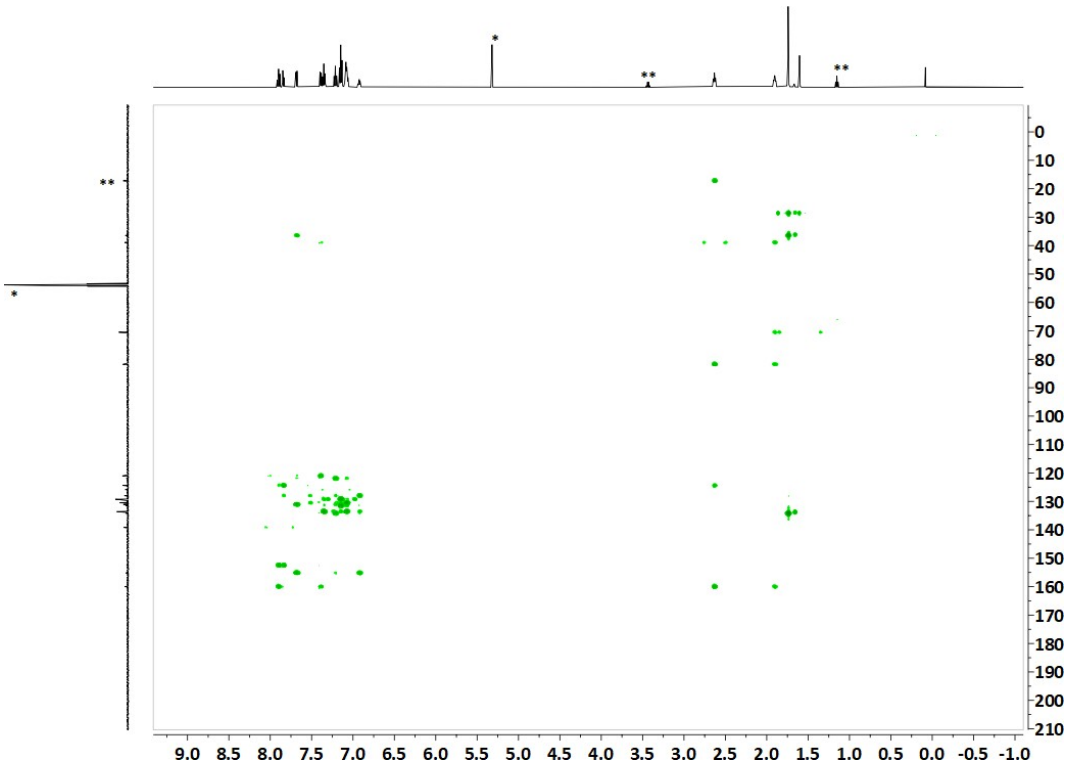

Fig. S18. HMBC spectrum of [Cu(xantphos)(**1**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, CD_2Cl_2). * = CD_2Cl_2 (in $^{13}C\{^1H\}$) or residual $CHDCl_2$ (in ^{1}H).

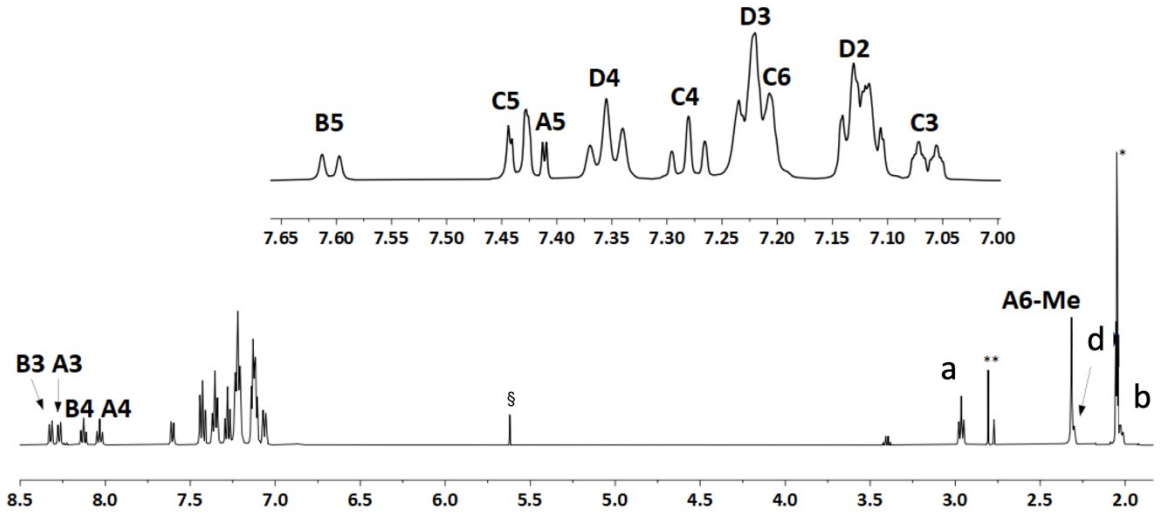

Fig. S19. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**2**)][PF_6]. Scale given in δ / ppm. * = acetone-d_5. ** = H_2O and HOD. § = CH_2Cl_2.

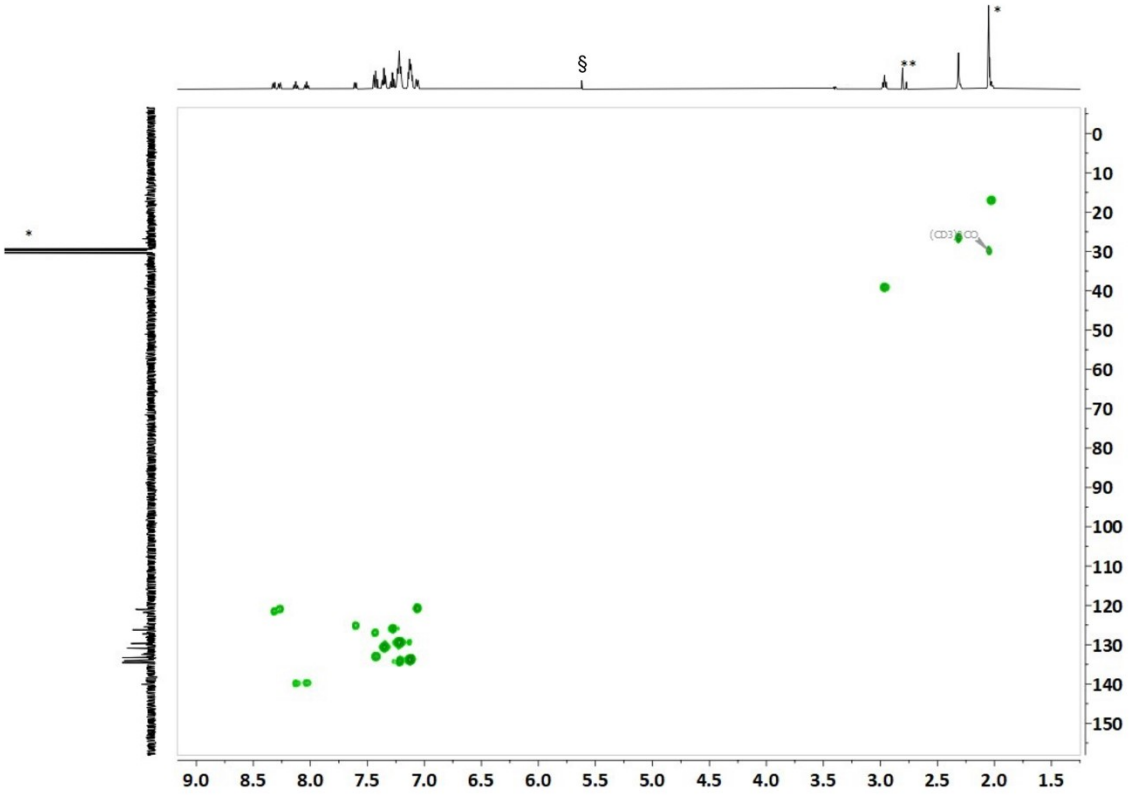

Fig. S20. HMQC spectrum of [Cu(POP)(**2**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2.

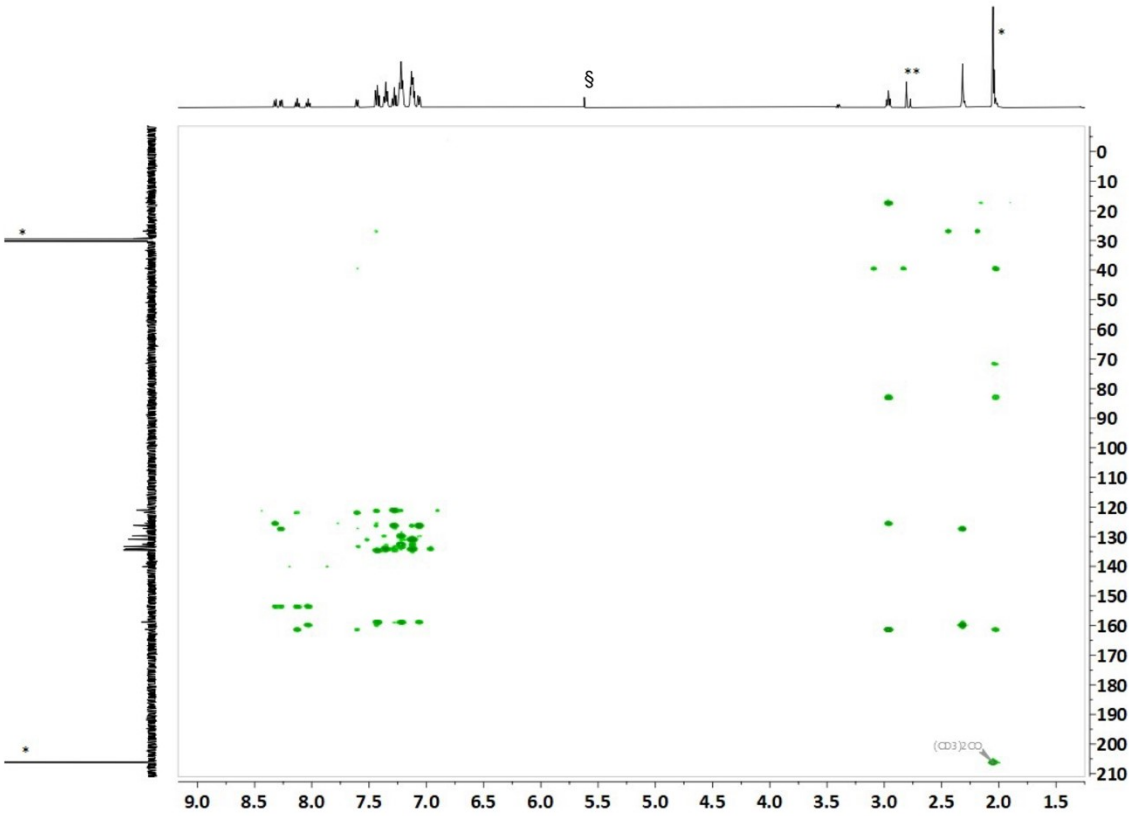

Fig. S21. HMBC spectrum of [Cu(POP)(**2**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2.

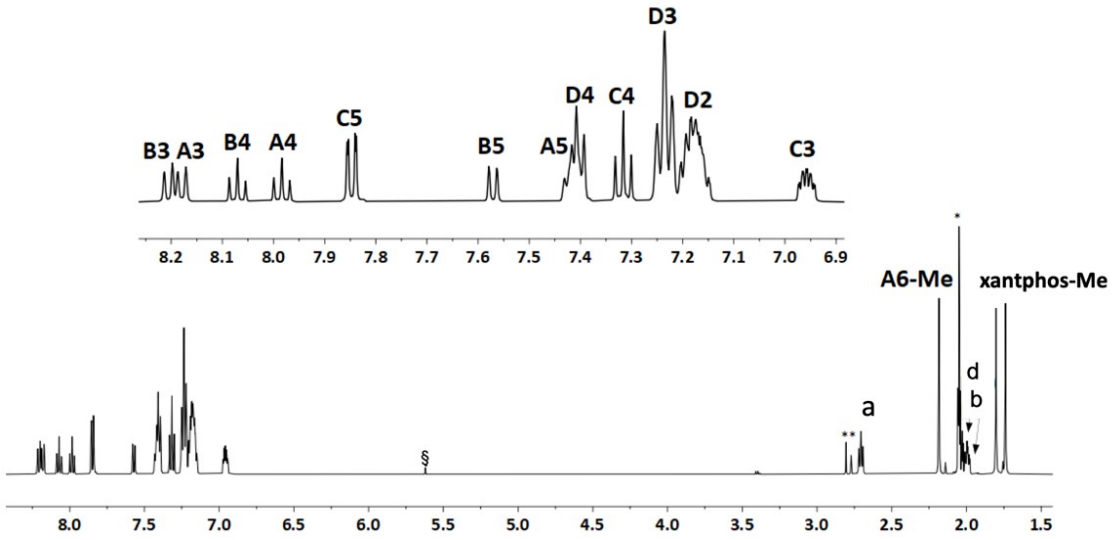

Fig. S22. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6 of [Cu(xantphos)(**2**)][PF_6]. Scale given in δ / ppm. * = acetone-d_5. ** = H_2O and HOD. § = CH_2Cl_2.

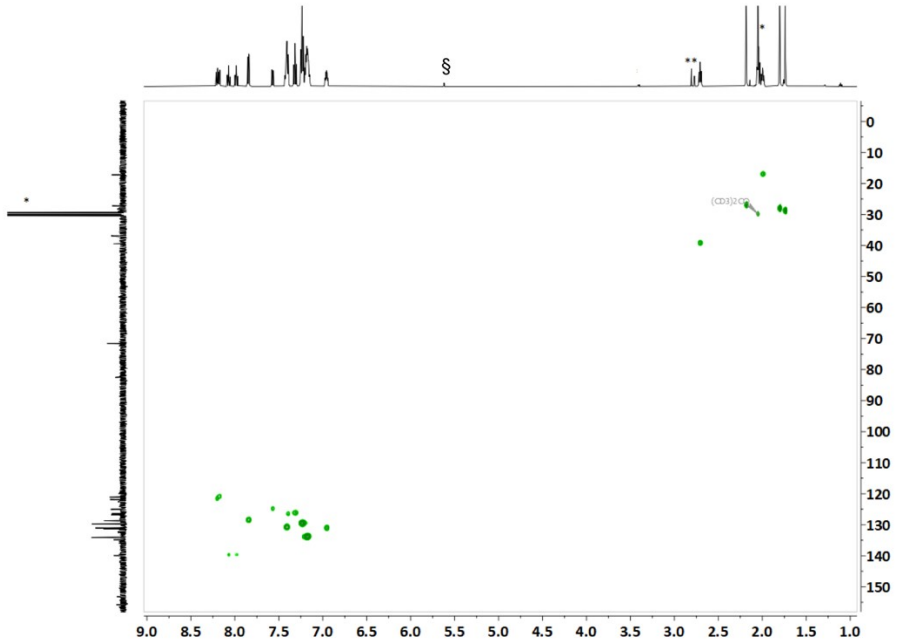

Fig. S23. HMQC spectrum of [Cu(xantphos)(**2**)][PF_6]. (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, 298 K, acetone-d_6). * = acetone-d_6 (in ^{13}C{^{1}H}) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2.

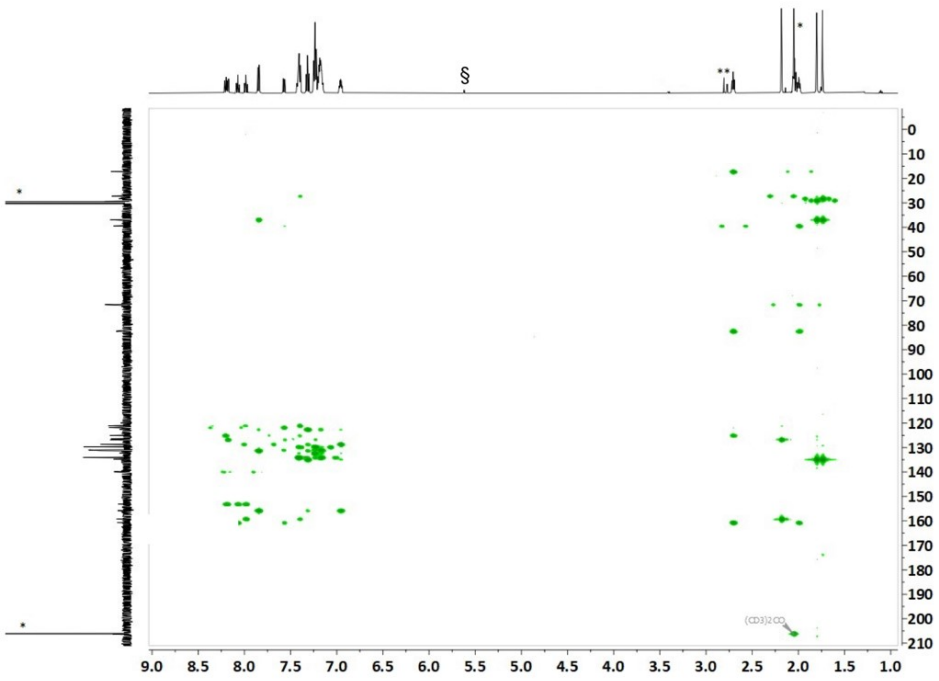

Fig. S24. HMBC spectrum of [Cu(xantphos)(**2**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2.

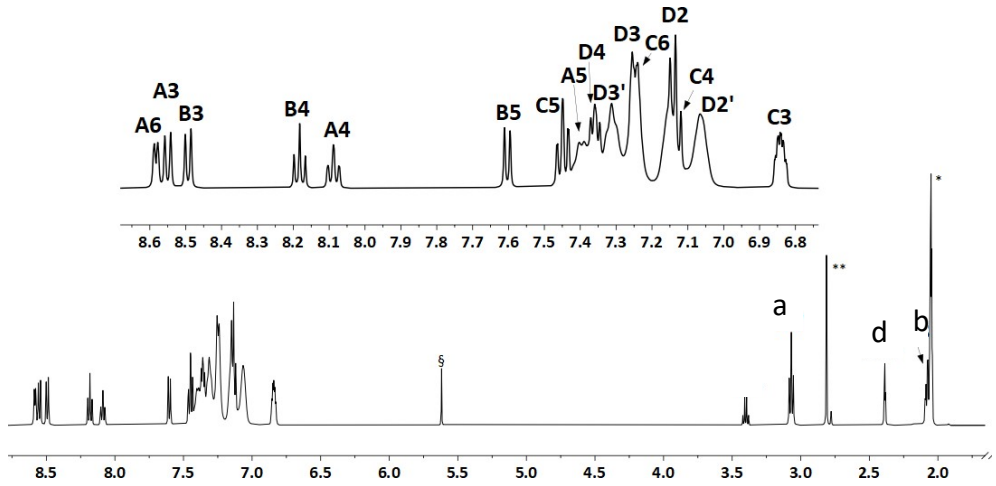

Fig. S25. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**3**)][PF_6]. Scale given in δ / ppm. * residual acetone-d_5. § = CH_2Cl_2. ** = H_2O and HOD. The sample also contains a small amount of Et_2O.

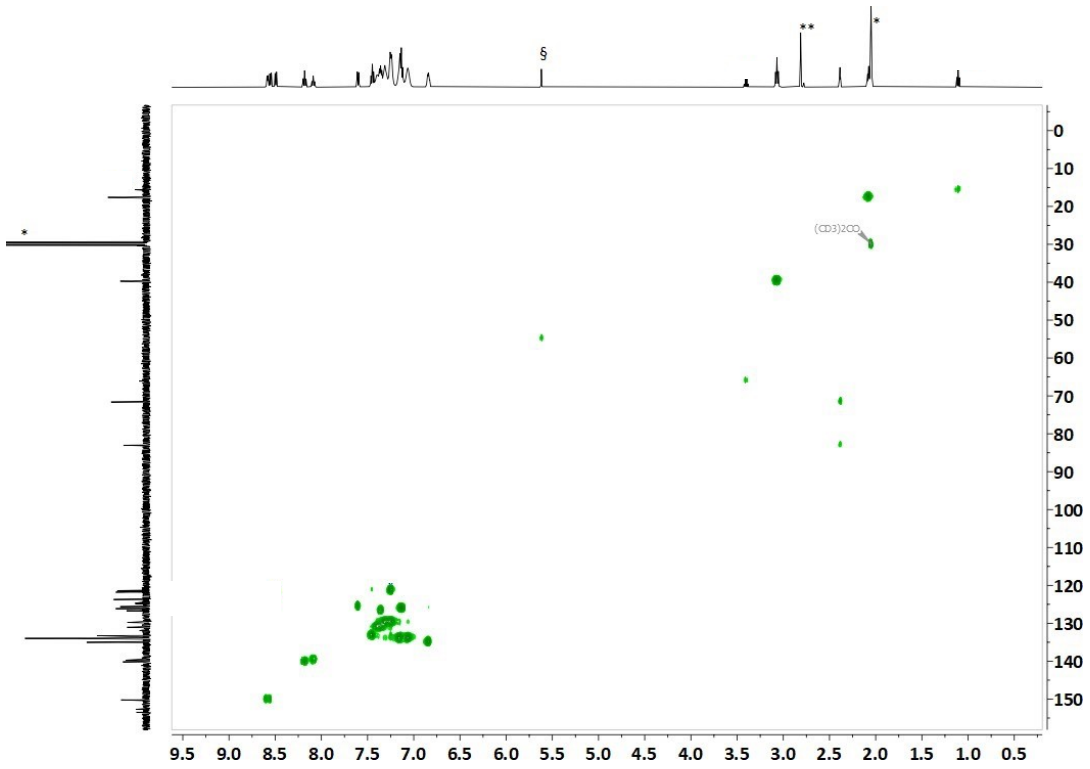

Fig. S26. HMQC spectrum of [Cu(POP)(**3**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2. The sample also contains a small amount of Et_2O.

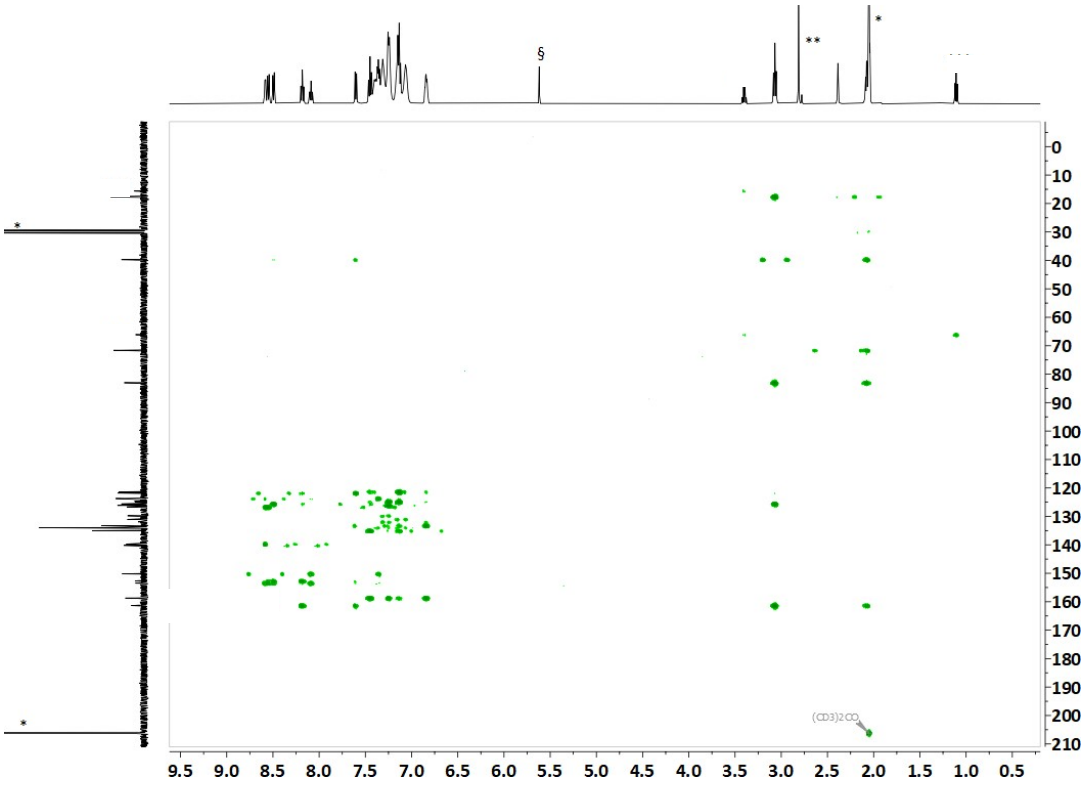

Fig. S27. HMBC spectrum of [Cu(POP)(**3**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O and HOD. § = CH_2Cl_2. The sample also contains a small amount of Et_2O.

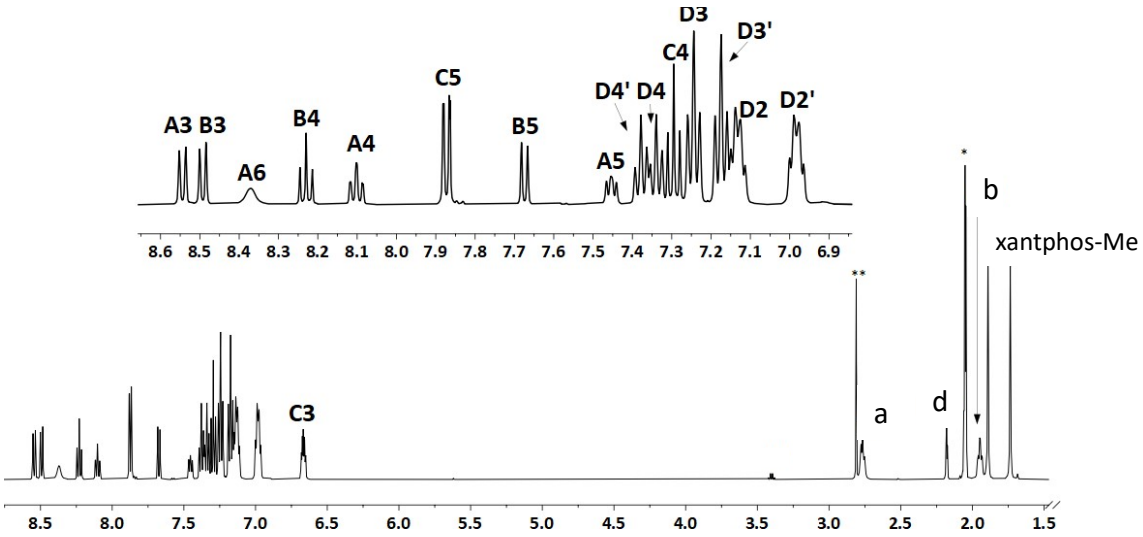

Fig. S28. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(xantphos)(**3**)][PF_6]. Scale given in δ / ppm. * = residual acetone-d_5. ** = H_2O.

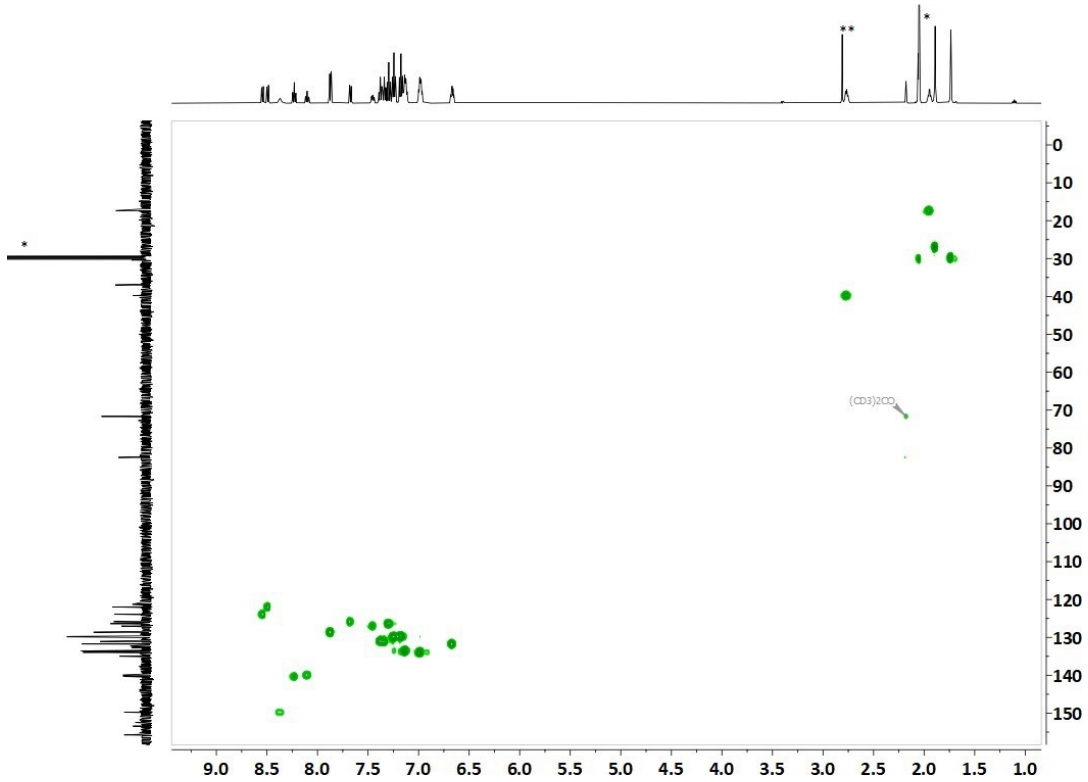

Fig. S29. HMQC spectrum of [Cu(xantphos)(**3**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O.

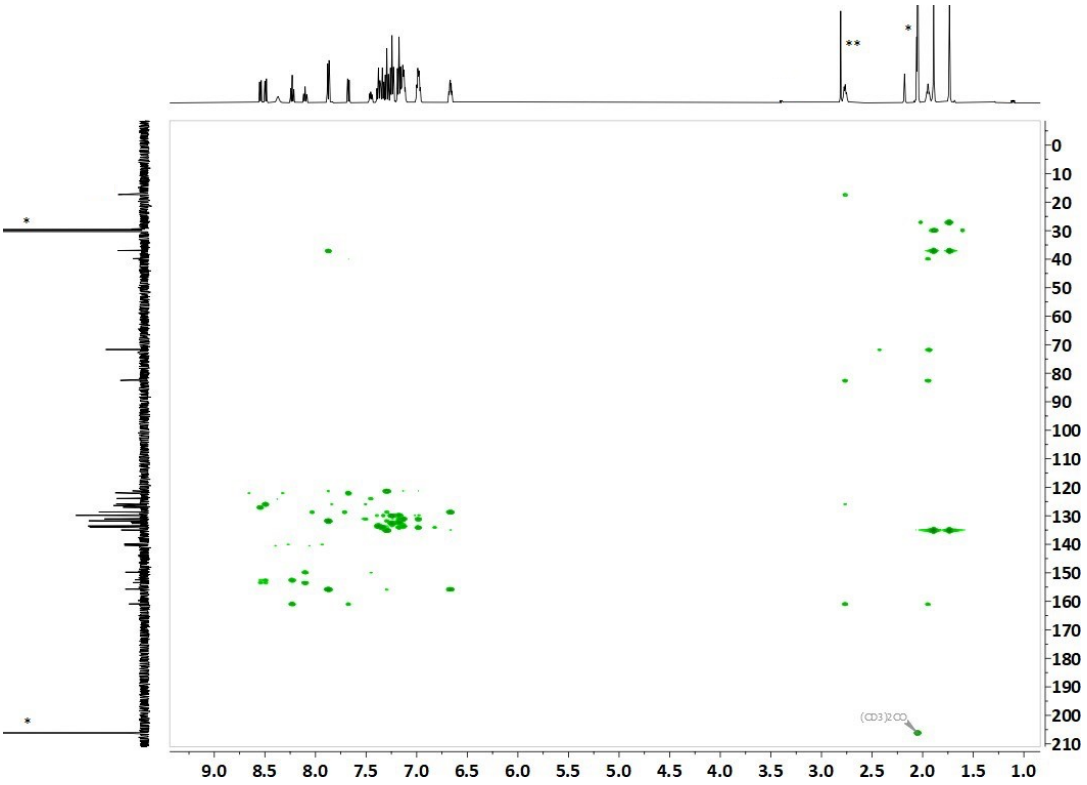

Fig. S30. HMBC spectrum of [Cu(xantphos)(**3**)][PF_6]. (500 MHz ^{1}H, 126 MHz $^{13}C\{^1H\}$, 298 K, acetone-d_6). * = acetone-d_6 (in $^{13}C\{^1H\}$) or residual acetone-d_5 (in ^{1}H). ** = H_2O.

Table S1. Excited state lifetimes from a biexponential fit[a] of the [Cu(N^N)(P^P)][PF_6] complexes as powders.[a]

Complex Cation	τ_1 / μs	A_1	τ_2 / μs	A_2	$<\tau>$ / μs
[Cu(**1**)(POP)][PF_6]	12	0.89	1.6	0.08	11.1
[Cu(**1**)(xantphos)][PF_6]	14	0.87	1.7	0.09	12.8
[Cu(**2**)(POP)][PF_6]	18.7	0.90	0.9	0.05	17.8
[Cu(**2**)(xantphos)][PF_6]	11.3	0.75	2.2	0.19	9.5
[Cu(**3**)(POP)][PF_6]	4.3	0.70	1.7	0.27	3.5
[Cu(**3**)(xantphos)][PF_6]	10.5	0.86	2.2	0.11	9.6

[a] The excited state lifetime $<\tau>$ is calculated from the equation $\sum A_i\tau_i / \sum (A_i)$ where A_i is the pre-exponential factor of the lifetime τ_i.