Aluminum complexes of the redox-active [ONO] pincer ligand

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Supporting Information

Contents

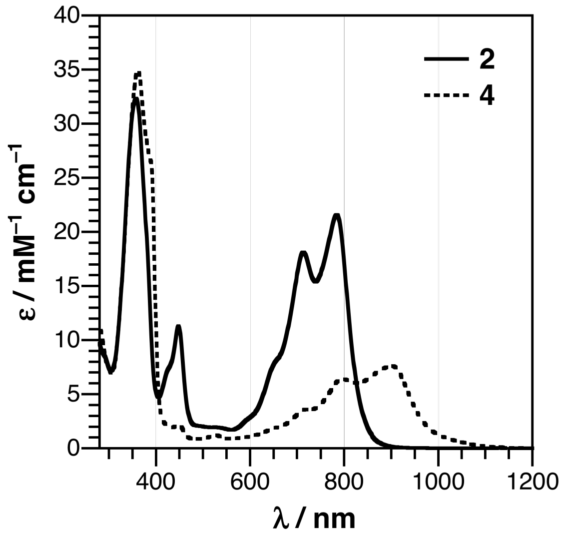
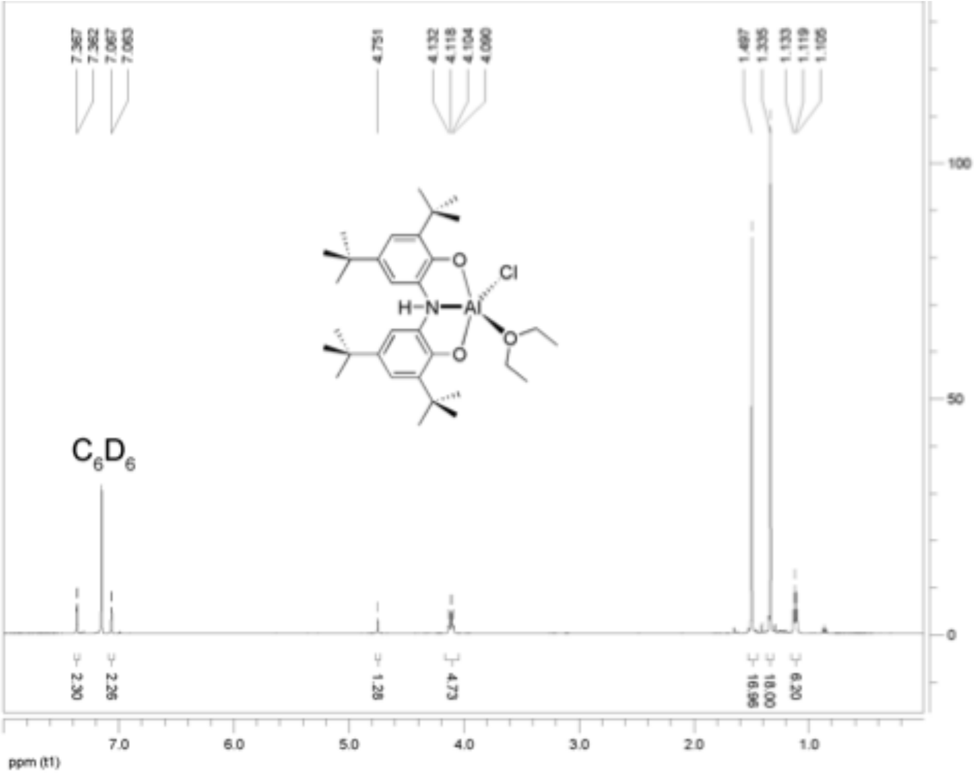


Figure S1. UV-vis-NIR spectra of [ONO^{q}]Al(acacPh$_2$)Cl (**2**) and [ONO^{sq}]Al(acacPh$_2$)(py) (**4**) in C_6H_6 at 298 K.

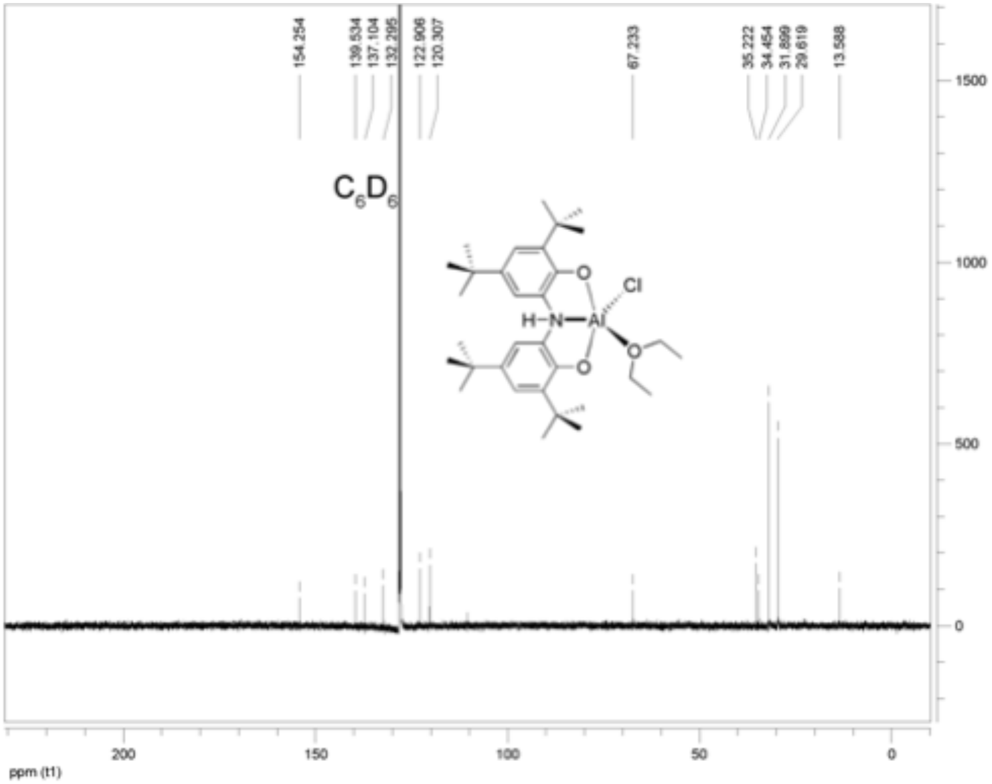
Supplemental ^{1}H and ^{13}C{^{1}H} NMR Spectra of Diamagnetic Compounds

NMR spectra were collected with Bruker Avance 500 MHz spectrometers (^{1}H 500 MHz, ^{13}C 128 MHz) in either C_6D_6 or CD_3CN solvents that were degassed by several freeze-pump-thaw cycles, dried with sodium benzophenone ketyl radical or CaH_2, respectively, and vacuum-distilled before use. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual ^{1}H and ^{13}C impurities in the solvent (7.15 and 128.02 for C_6D_6; 1.94 and 1.24 for CD_3CN, respectively). NMR spectra were measured at 298 K and chemical shifts are reported by using the standard δ notation in parts per million.

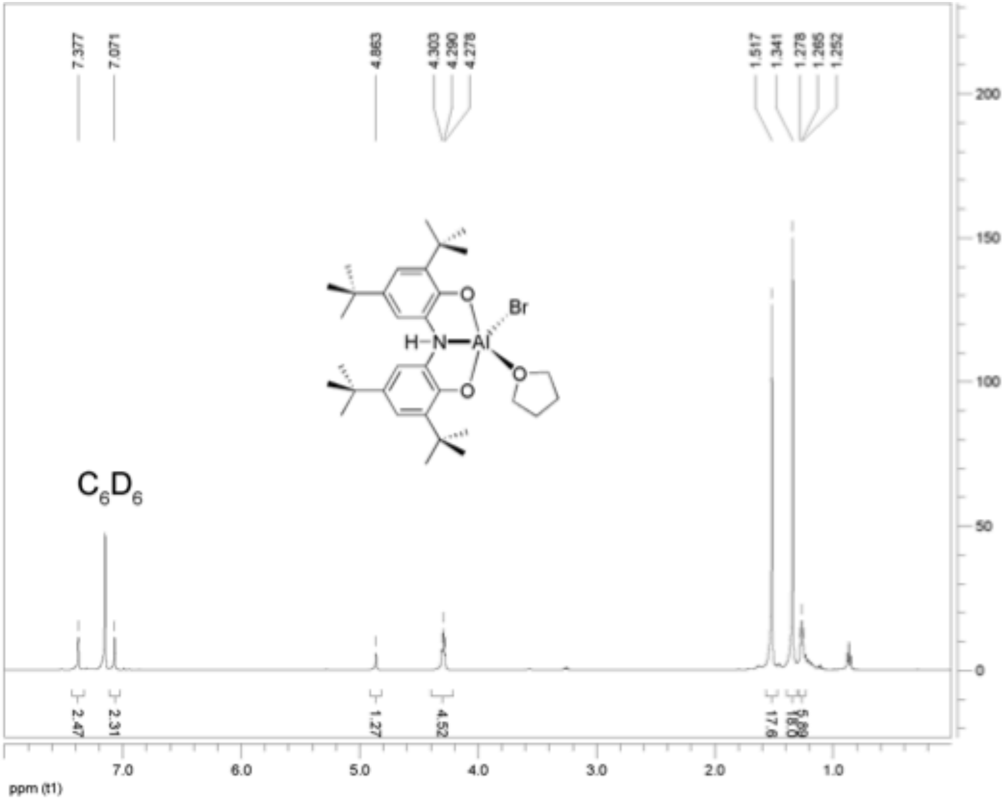
[ONHO^{cat}]HAlCl(OEt$_2$) (1a): ^{1}H NMR (C_6D_6):



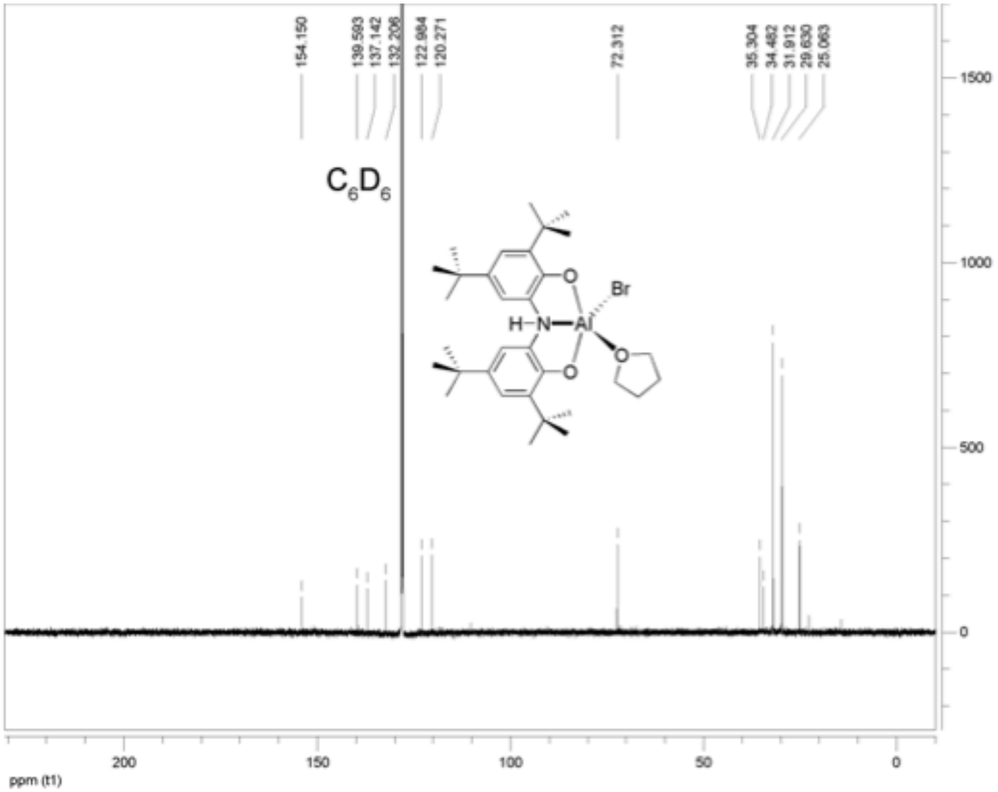
^{13}C{^{1}H} NMR (C_6D_6):



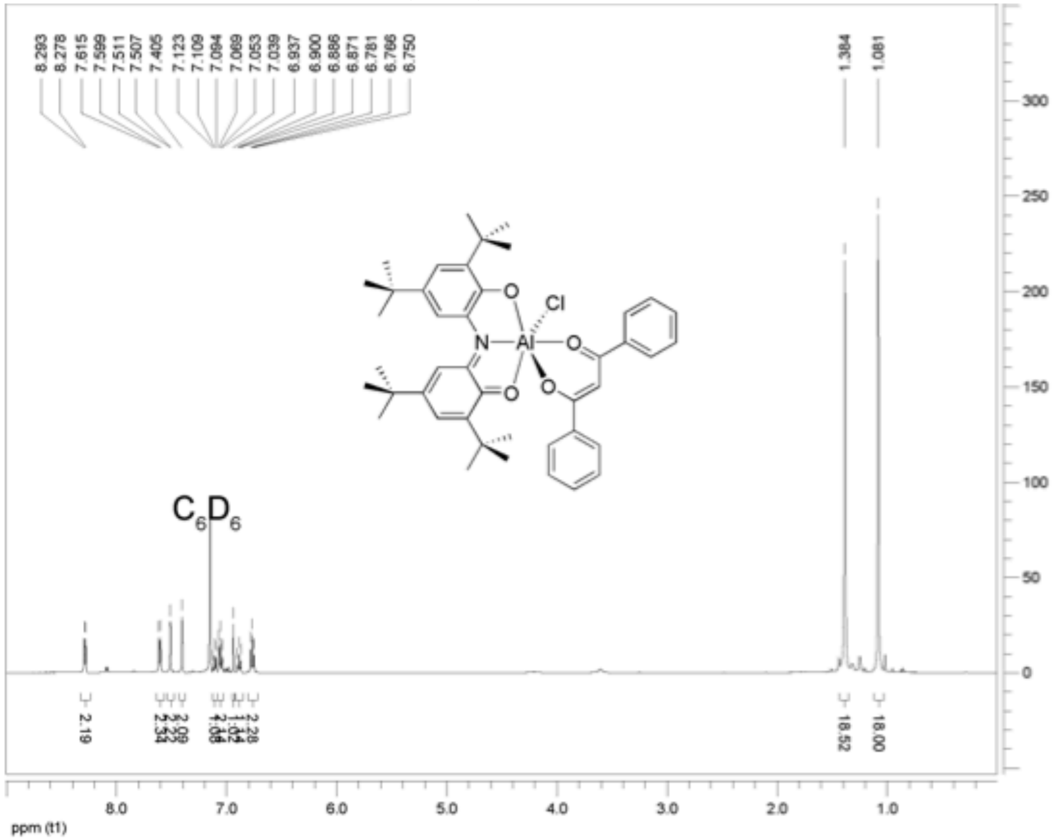
[ONHO^{cat}]AlBr(THF) (1b): ^{1}H NMR (C_6D_6):



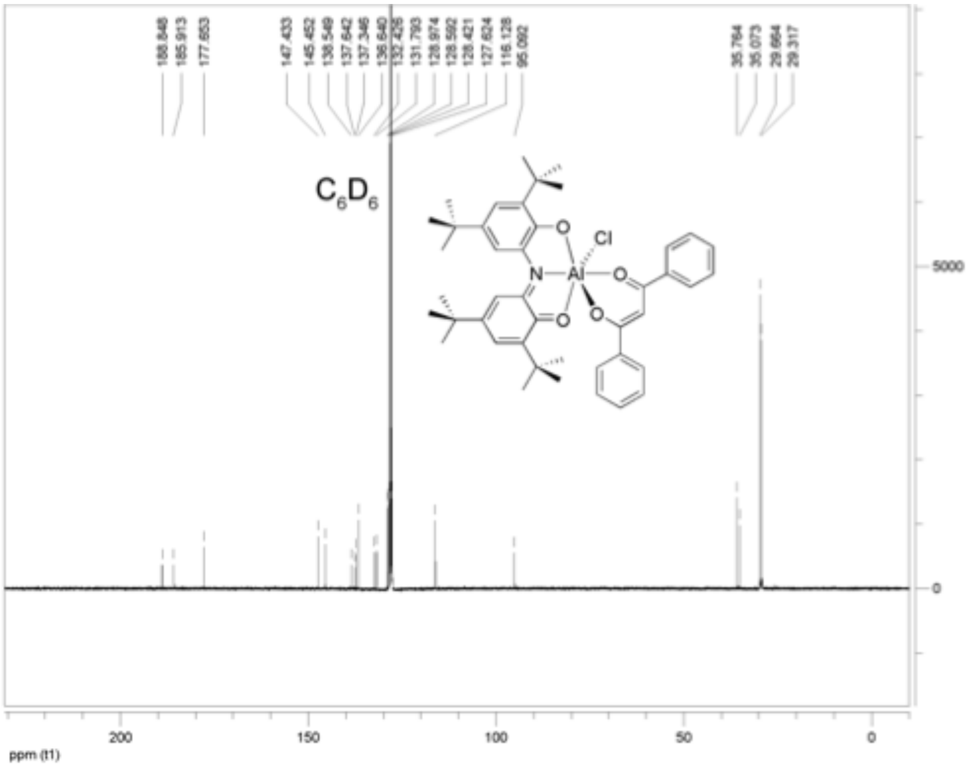
^{13}C{^{1}H} NMR (C_6D_6):



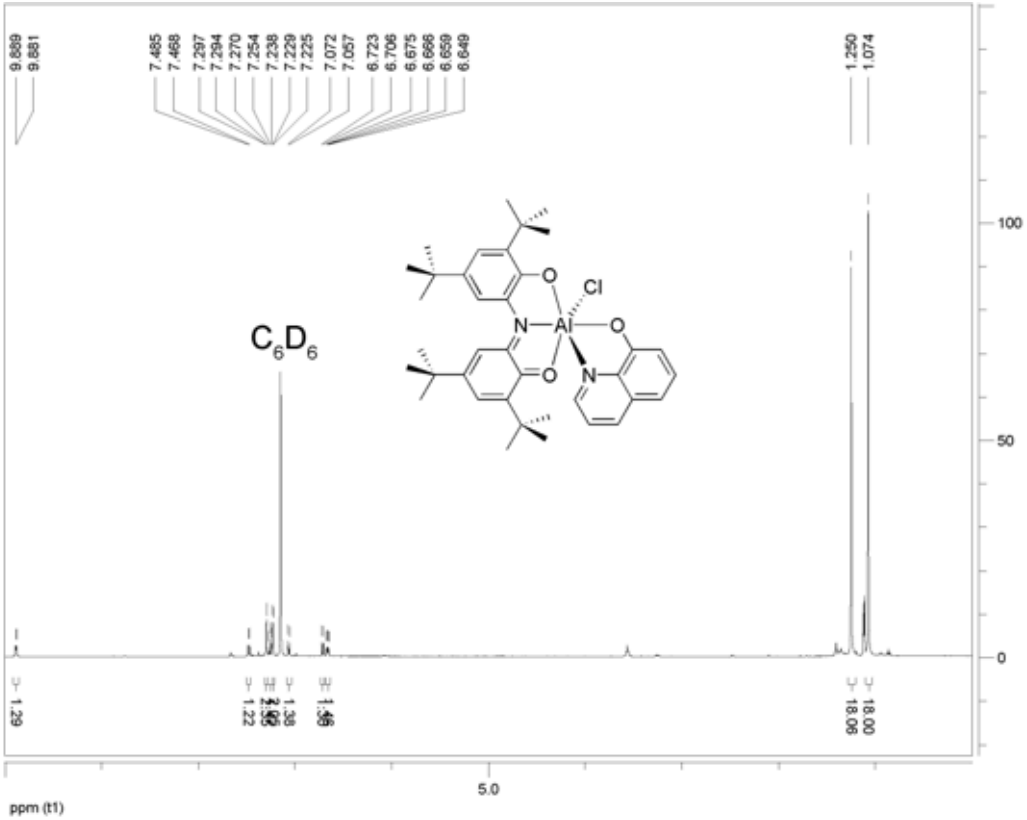
[ONO^q]Al(acacPh$_2$)Cl (2): ^{1}H NMR (C_6D_6):



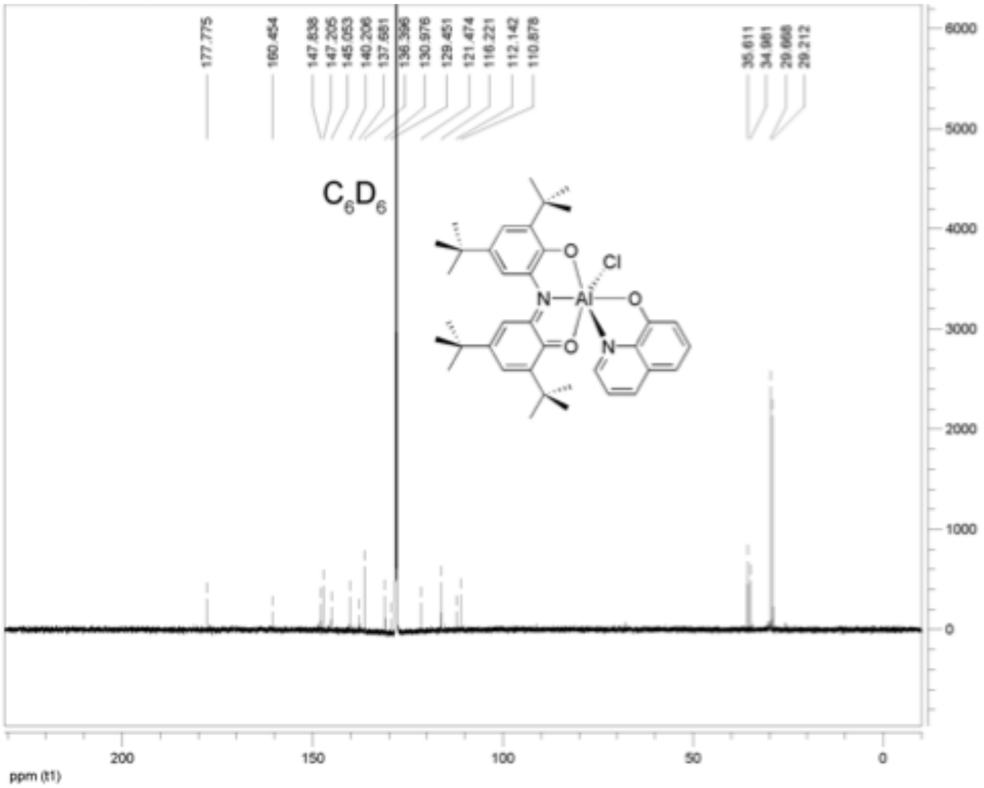
$^{13}C\{^1H\}$ NMR (C_6D_6):



[ONO^q]Al(quinO)Cl (3): ^{1}H NMR (C_6D_6):



^{13}C{^{1}H} NMR (C_6D_6):



Crystallographic Refinement Details

[ONHO^{cat}]AlBr(THF) (**1b**): A hemisphere of data was collected on a colorless plate of approximate dimensions 0.57 × 0.17 × 0.10 mm using a 25 sec/frame scan time. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

[ONO^q]Al(acacPh$_2$)Cl (**2**): A hemisphere of data was collected on a black prism of dimensions 0.38 × 0.20 × 0.19 mm using a 45 sec/frame scan time. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

[ONO]Al(o-$O_2C_6Cl_4$)(py) (**6**): A hemisphere of diffraction data was collected on a black block of dimensions 0.20 × 0.12 × 0.10 mm using a 60 sec/frame scan time. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. There was a pocket of disordered solvent that was positioned across an inversion center. Although diethyl-ether molecules could be seen in this disorder, modeling them using standard modeling procedures was not very stable. Additionally, the largest Q-peak was directly on the inversion center too far from another atom to be included in reasonable disorder modeling. Thus, the program SQUEEZE[1] by Spek et. a. in the PLATON[2] software suite was used to calculate the electron count in this solvent pocket at 69 electrons. This corresponds roughly to 1.5 diethyl-ether molecules, resulting in a total of 3 disordered ether molecules per unit cell, consistent with the disorder observed in the structure during initial refinement.

[ONO]Al(o-$O_2C_{16}H_8$)(py) (**8**): A hemisphere of diffraction data was collected on a black plate of dimensions 0.27 × 0.18 × 0.06 mm using a 35 sec/frame scan time. The diffraction

symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. One of the two THF molecules was disordered over two positions with a freely-refined occupancy of 65:35, and was modeled using standard distance restraints.

References

1. P. Van Der Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A46**, 194-201.
2. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.