Electronic Supplementary Material (ESI) for Dalton Transactions

Isocyanide insertion and cyclization reactions to form indolines using pincer-type complexes of scandium

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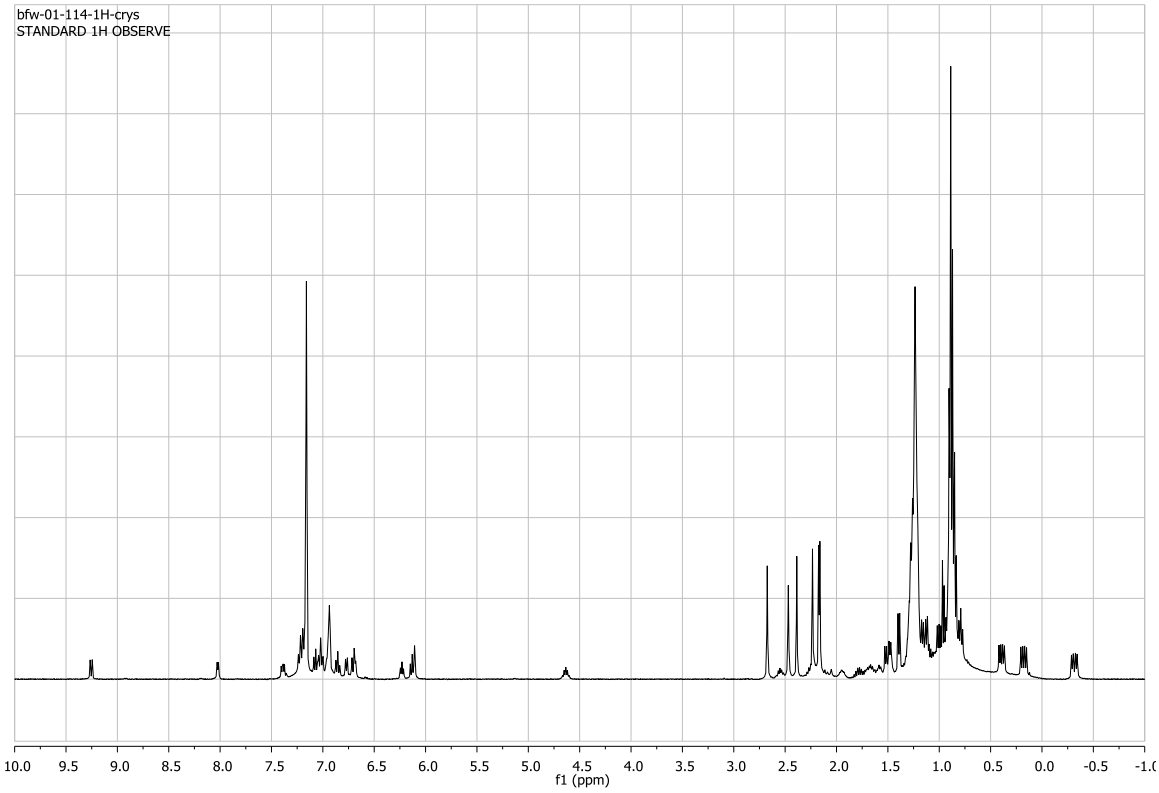
Supporting Information

Alternate Mechanism:

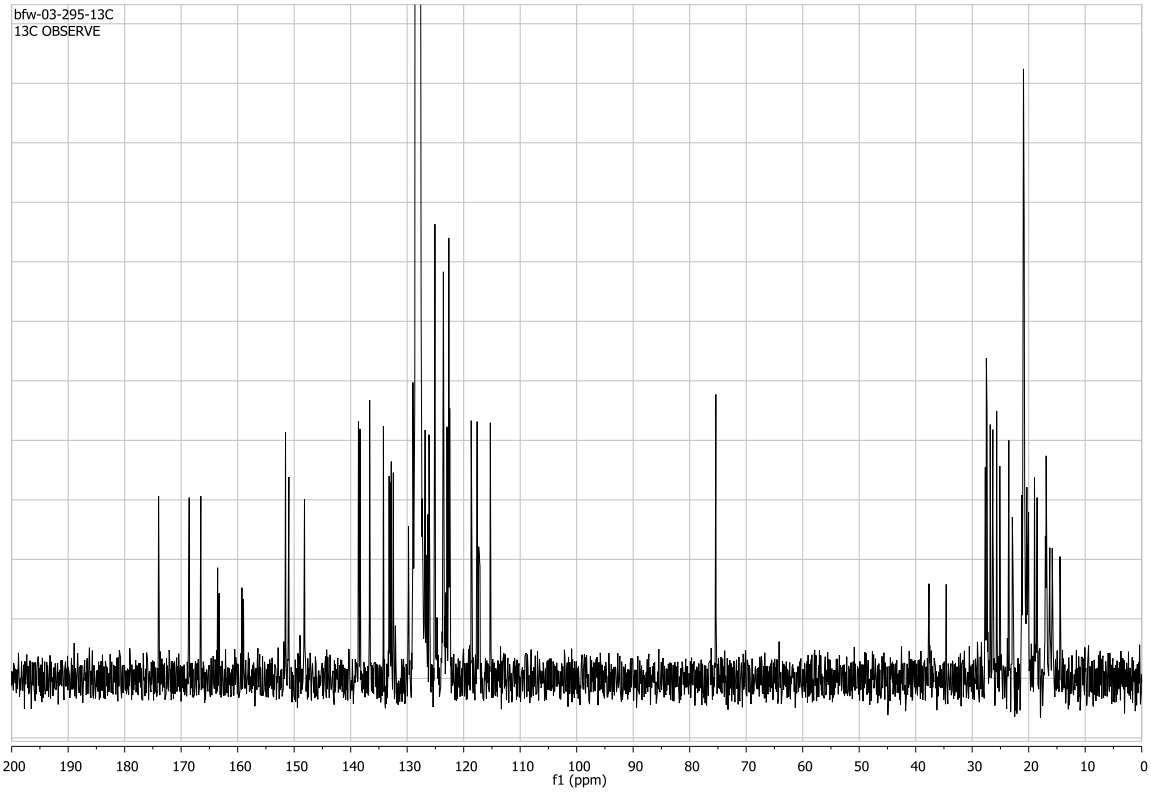
The following mechanism was proposed during the review process, citing similar rectivity in W. J. Evans, JACS, 2011, 3507-3516, and B. Hessen, Chem. Commun., 1995, 145-146 and references 10-12 therein.

While this is a valid mechanism for the formation of **3**, it requires the C-C bond of the DMeP group to be broken or polarized before the addition of the isonitrile. This is not consistent with the lack of methyl migration in **6**, unless a migration back is invoked. We conceed that there may be seperate mechanisms for the formation of each product, but since the products are similar, we will invoke Occam's razor and say that probably both products lie along analagous pathways until proven otherwise.

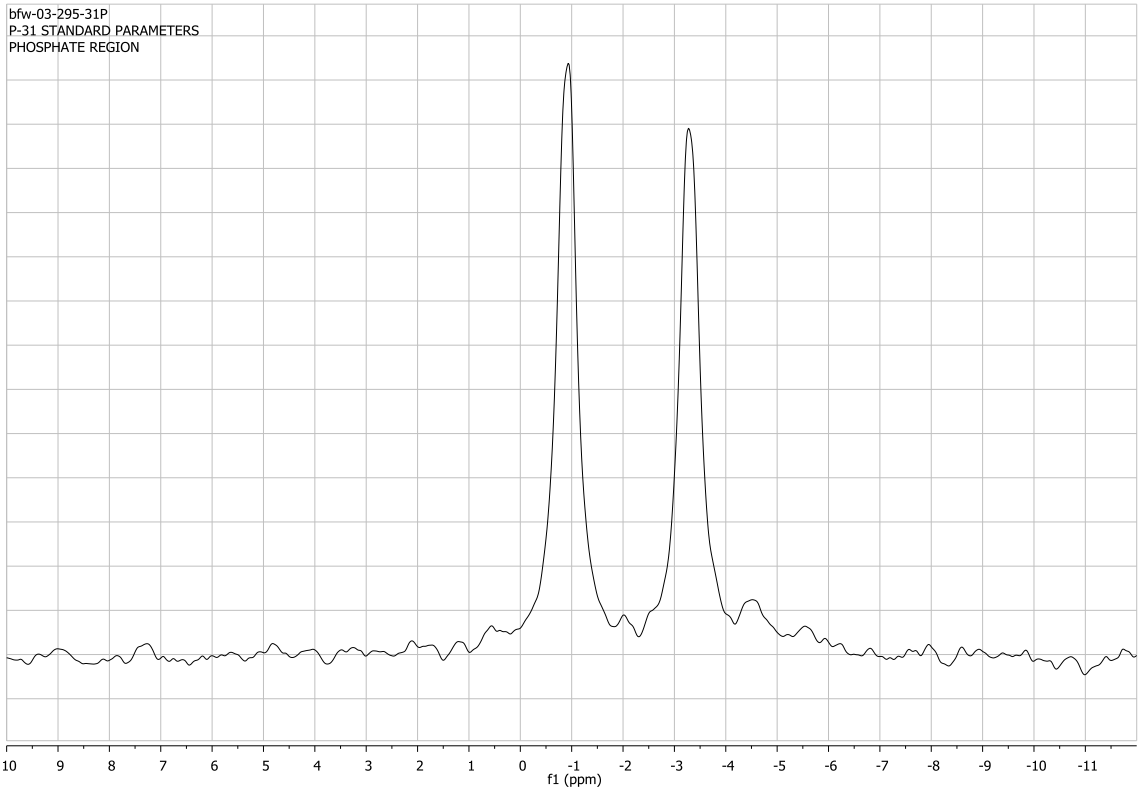
Spectra for Complex 3:



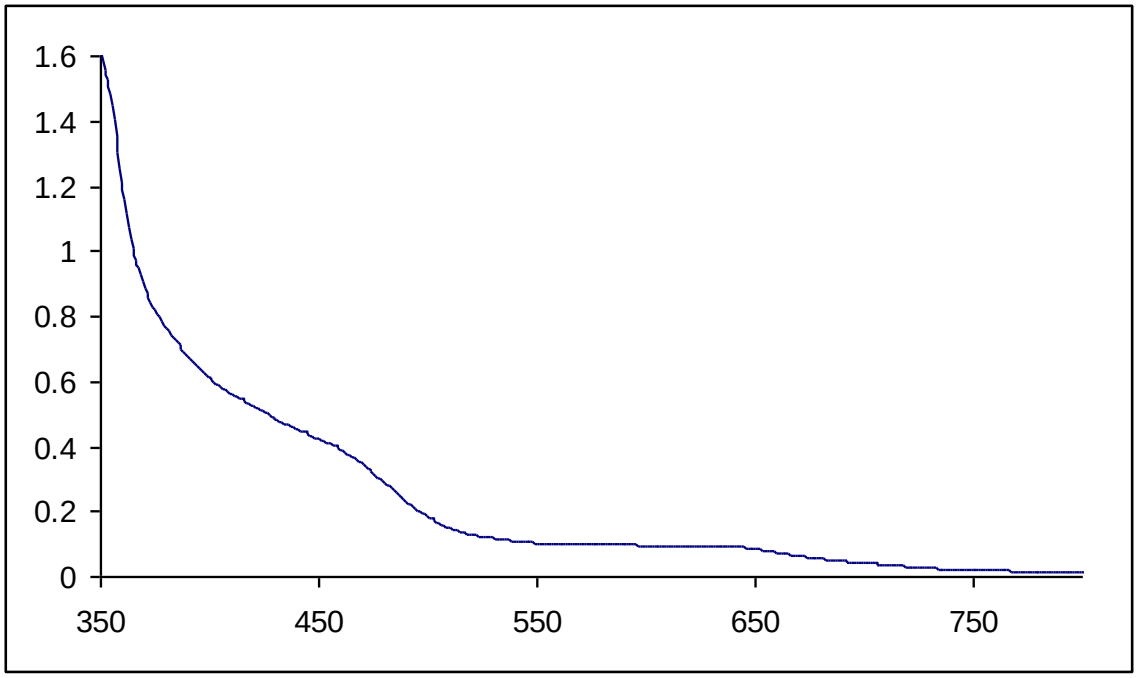
^{1}H NMR Spectrum (25°C)



^{13}C NMR Spectrum (25°C)

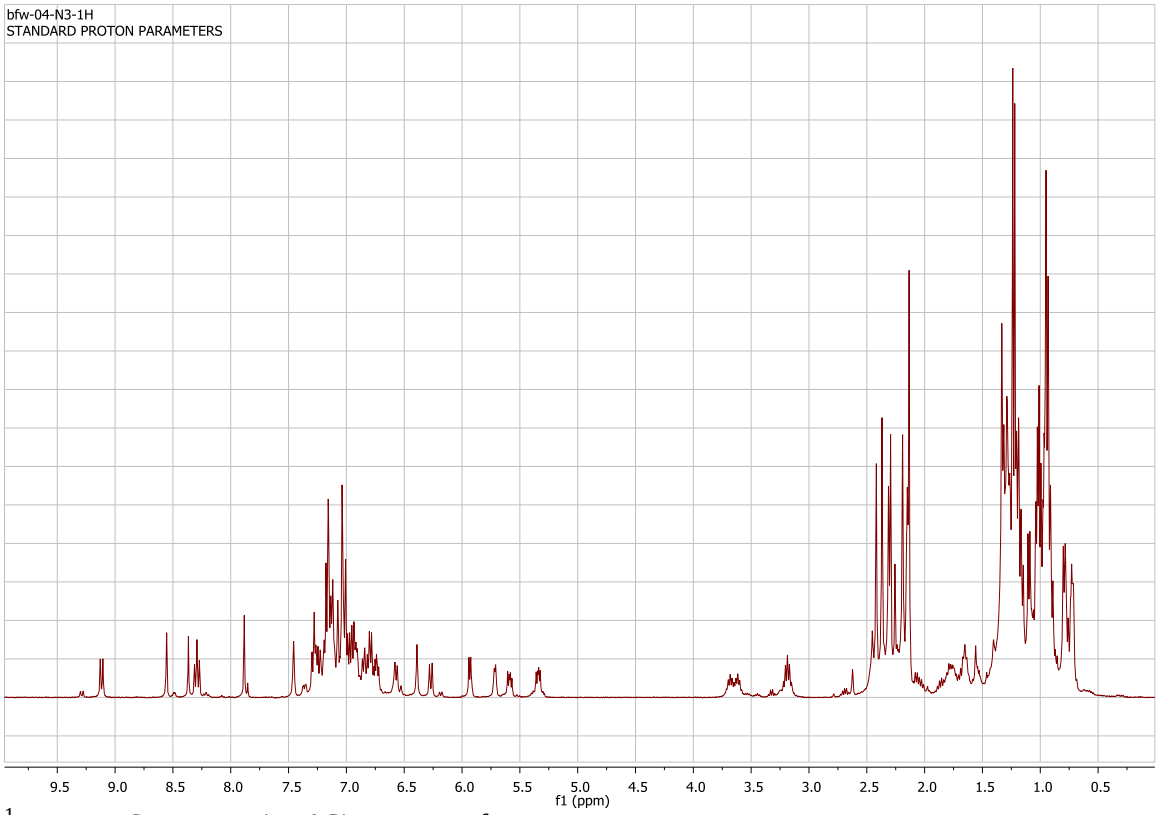


^{31}P NMR Spectrum (25°C)

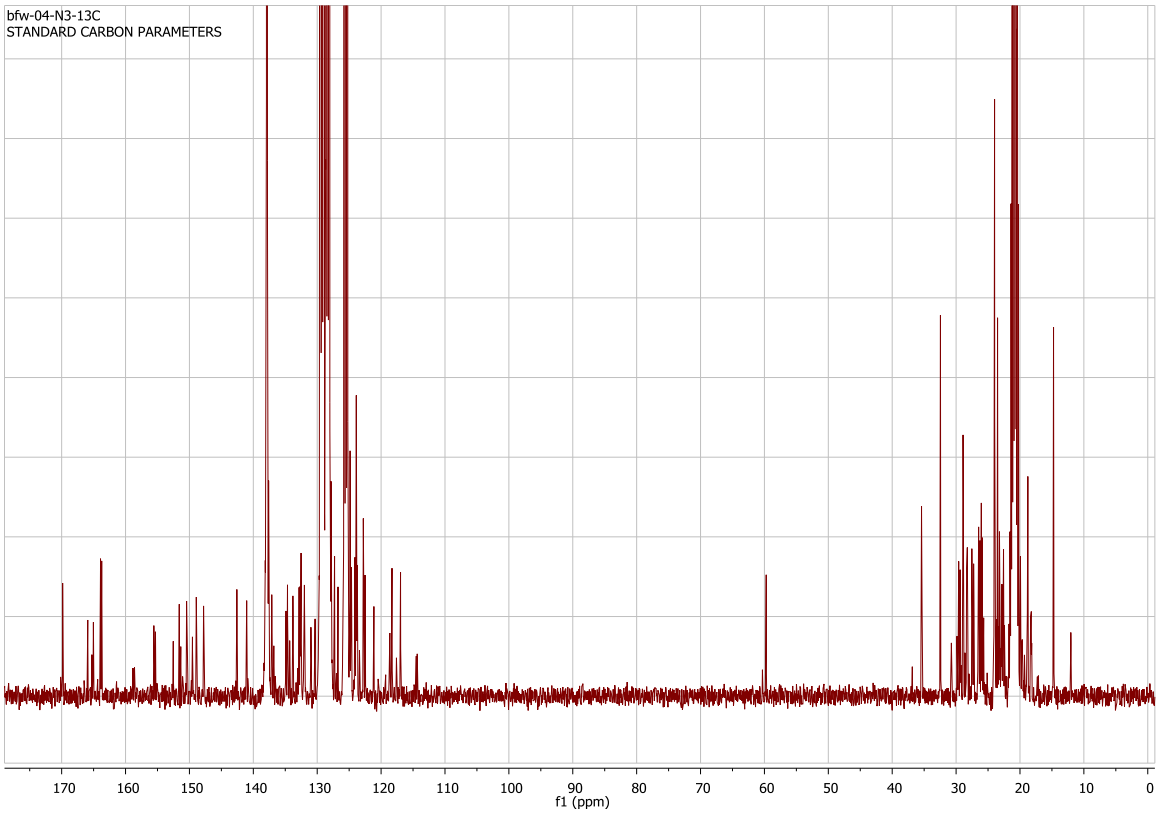


UV-Vis Spectrum (25 °C, pentane)

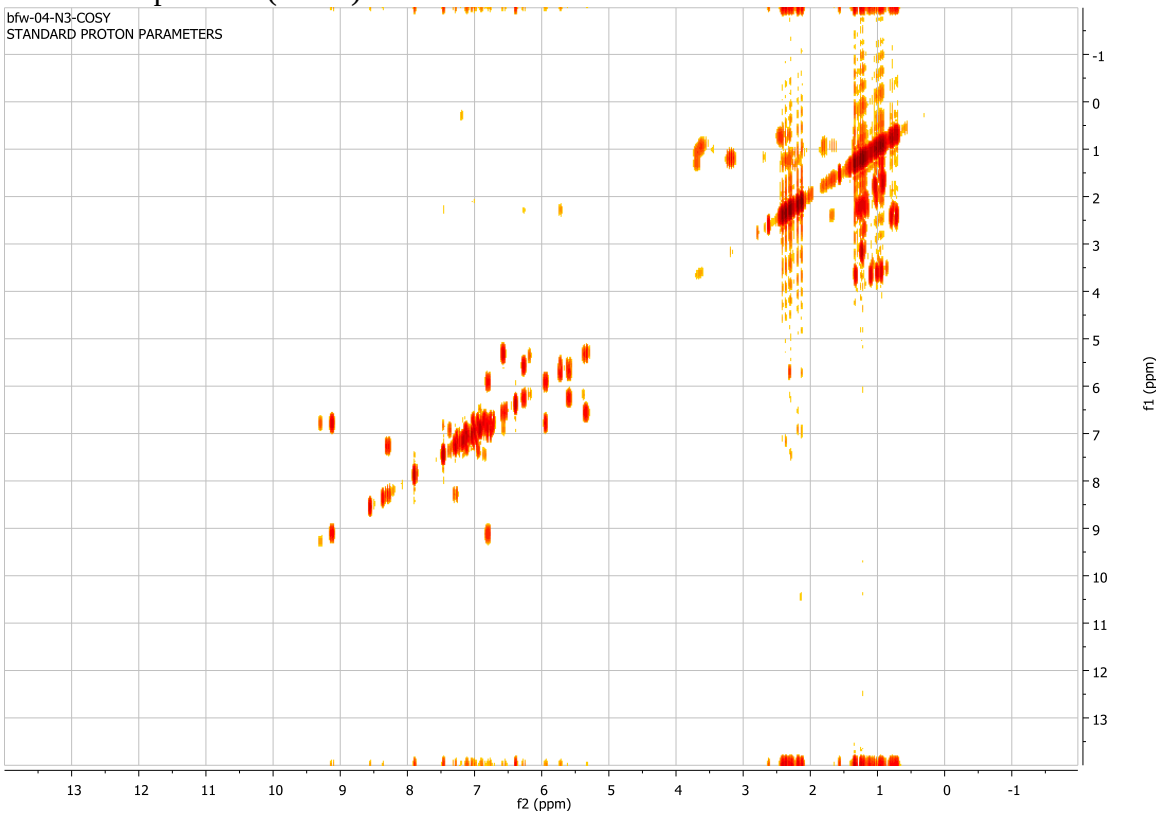
Spectra for Complex 6.



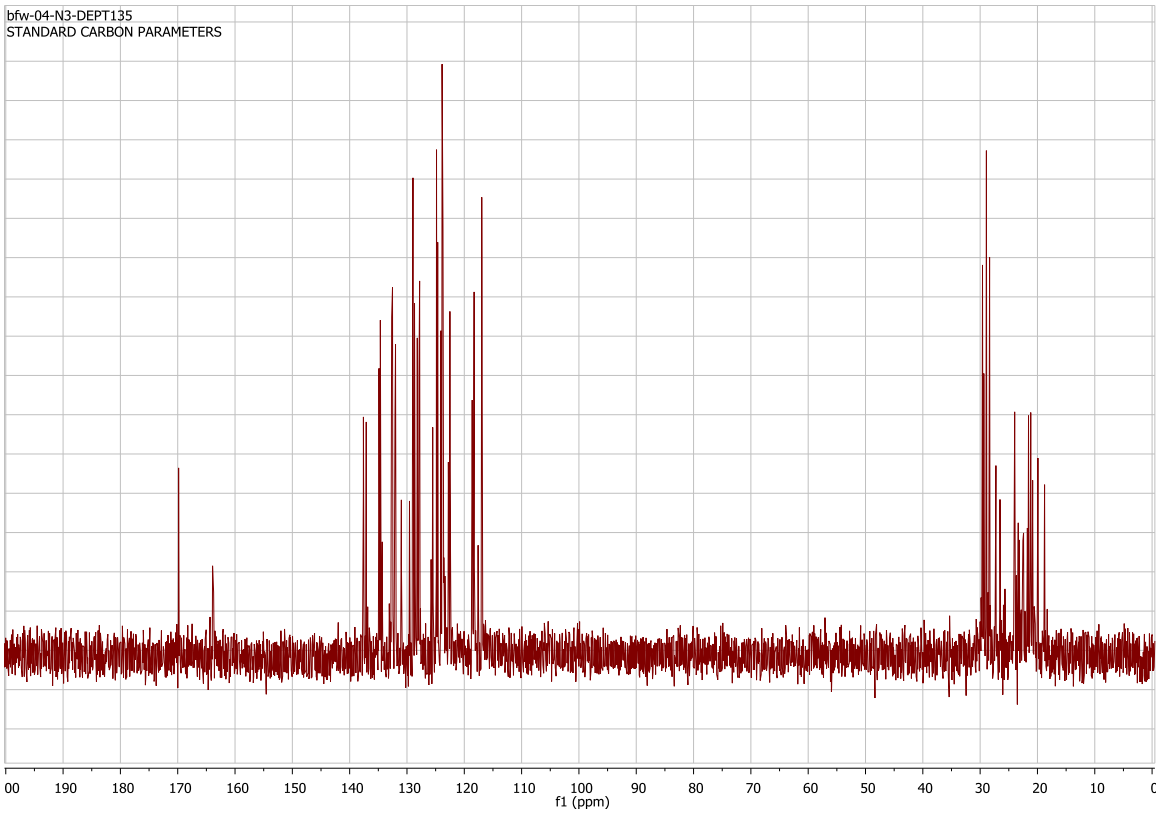
^{1}H NMR Spectrum (25 °C). Traces of PNPH.



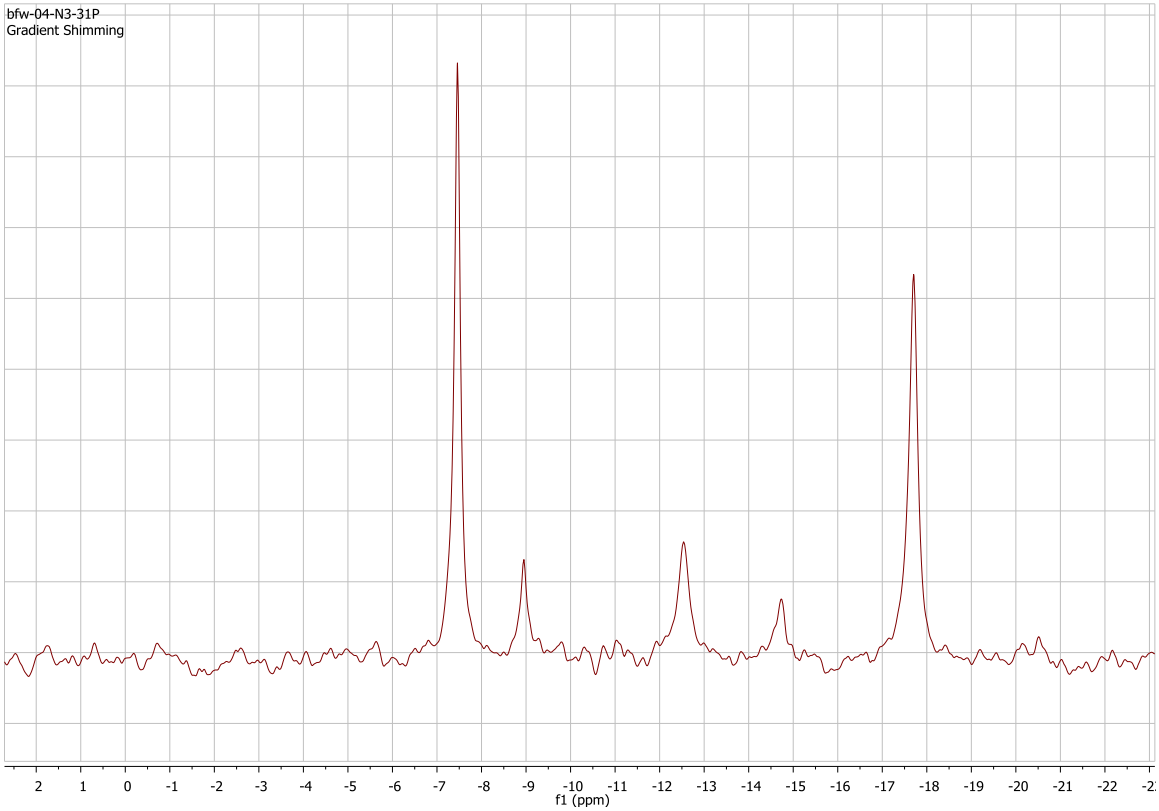
^{13}C NMR Spectrum (25 °C). Traces of PNPH.



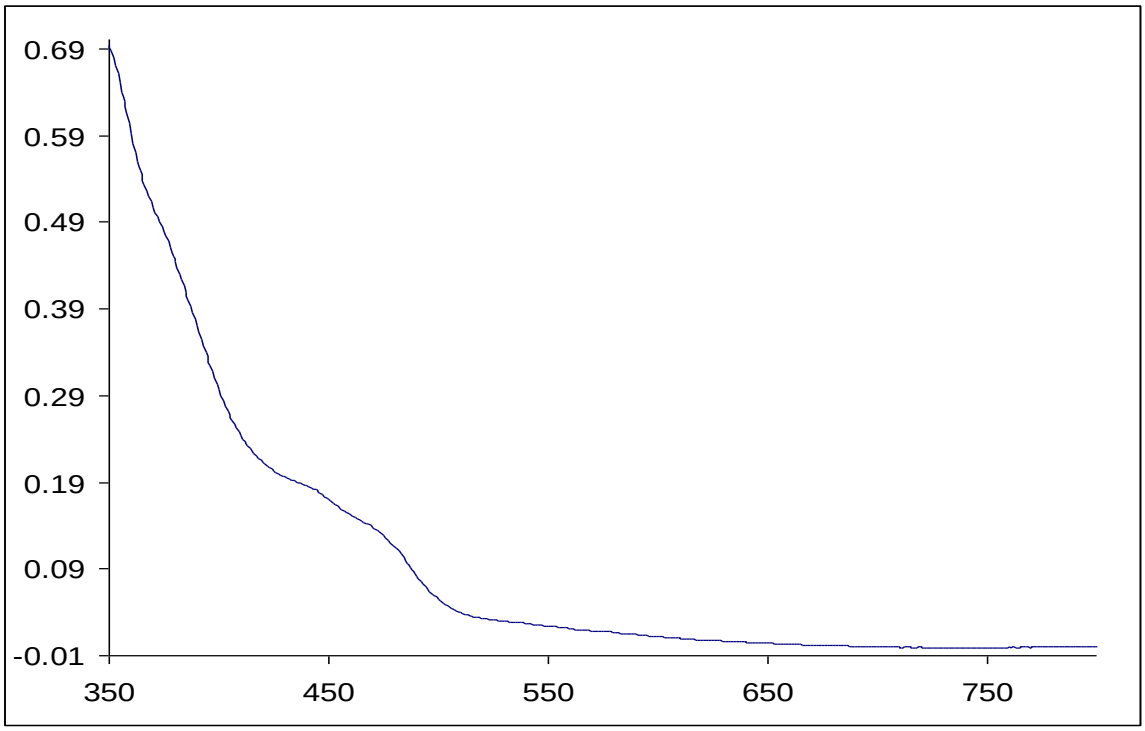
COSY NMR Spectrum (25 °C). Traces of PNPH.



DEPT-135 NMR Spectrum (25 °C). Traces of PNPH.



^{31}P NMR Spectrum (25 °C). Traces of PNPH.



UV-Vis Spectrum (25 °C, pentane)

Crystal Structure Collection Data

For 3:

The space group P-1 was determined based on intensity statistics and the lack of systematic absences. The structure was solved using SIR-2004 and refined with SHELXL-97. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for pentane carbon atoms. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0634 and wR2 = 0.2106 (F^2, all data). The remaining electron density is located near the disordered solvent.

For 6:

The space P-1 was determined based on intensity statistics and systematic absences. The structure was solved and refined using SHELXTL. A direct methods solution was calculated, which provided all non-hydrogen atomic positions from the E-map. Full-matrix least squares / non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The pentane solvent molecules were found to be disordered. The C-C bond distances were restrained using SADI commands during refinement. One of the pentane molecules was partially occupied (50%) as well as disordered. The thermal parameters of the carbon atoms in this molecule were restrained with SIMU and DELU commands. The final full matrix least squares refinement converged to R1 = 0.0809 and wR2 = 0.1791 (F^2, all data). The remaining electron densities are located around the disordered pentane molecules. Final full matrix least squares refinement converged to R1 = 0.0612 and wR2 = 0.1696 (F^2, all data). The remaining electron density is located near the disordered pentane.

Table of Crystallographic Parameters

	3	**6**
Molecular formula	$C_{63.50}H_{87}N_5P_2Sc$	$C_{86.5}H_{127}N_6P_2Sc$
Fw	1027.28	1357.84
temp (K)	150(2)	150(2)
cryst system	Triclinic	Triclinic
space group	P-1	P-1
cell constants		
a (Å)	11.8793(8)	14.4984(8)
b (Å)	15.5474(10)	15.6478(9)
c (Å)	18.2839(12)	20.5567(12)
α (deg)	80.909(1)	86.436
β (deg)	78.152(1)	70.6750
γ (deg)	72.501(1)	65.6990
Z	2	2
V (Å^3)	3135.2(4)	3996.1(4)
abs coeff, μ_{calc} (mm^{-1})	0.208	0.179
δ_{calc} (g/cm^3)	1.088	1.128
F(000)	1108	1478
cryst dimens (mm)	0.18 × 0.17 × 0.11	0.20 x 0.20 x 0.15
Radiation	Mo Kα	Mo Kα
h,*k*,*l* ranges colled	-14 <= h <= 14 -18 <= k <= 18 -22 <= l <= 22	-20 <= h <= 20 -20 <= k <= 21 -22 <= l <= 28
θ range (deg)	1.14 to 25.71	1.43 to 29.57
no. of reflens colled	40612	81527
no. of unique reflens	11890	22328
no. of params	678	903
data/param ratio	11890/678	22328/903
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
$R(F)^a$	0.0634	0.0809
$R_w(F^2)^b$	0.2106	0.1791
GOFw^c	1.052	1.175
largest diff peak and hole (e/Å^3)	0.823 and -0.524	0.865 and -0.618

[a] $R = [\sum|\Delta F| / \sum|F_o|]$. [b] $R_w = [\sum w(\Delta F)^2 / \sum wF_o^2]$. [c] Goodness of fit on F^2.