Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Intramolecular Alkene Hydroaminations Catalyzed by a Bis(thiophosphinic amidate) Zr(IV) Complex

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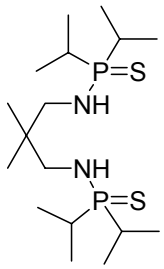
General

Melting points were obtained using a Mel-Temp II apparatus equipped with a digital thermometer and were uncorrected. Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR. Infrared spectra of solids were obtained by standard KBr pellet procedures. ^{1}H NMR spectra were recorded on a Bruker AVANCE DPX-300 (300 MHz) or AVANCE DPX-500 (500 MHz) spectrometer. J. Young NMR tubes were purchased from Aldrich or J. Young Ltd. Chemical shifts were reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: δ 7.27, benzene: δ 7.16, toluene: δ 7.09). ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX-300 (300 MHz) or AVANCE DPX-500 (500 MHz) spectrometer with complete decoupling. Chemical shifts were reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.23). Analytical thin layer chromatography was performed on Polygram® SIL G/UV_{254} 1.25 mm silica gel plates with a fluorescent indicator. Flash chromatography was performed on Merck silica gel 60. Solvents for extraction and flash chromatography were reagent grade.

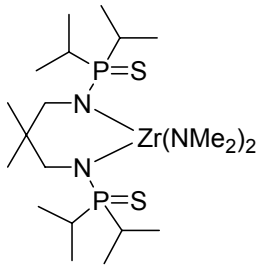
All experiments were carried out under an argon atmosphere. Organozirconium complexes were manipulated under an argon atmosphere in a glove box. Benzene-d_6 and toluene-d_8 were distilled from Na and aminoalkenes were distilled from CaH_2 under an argon atmosphere and stored at -30 °C in a glove box. 2,2-Dimethylpent-4-en-1-amine,[1] 1-methylpent-4-enylamine,[2] pent-4-enylamine,[1] 2,2-dimethyl-5-phenylpent-4-en-1-amine,[3] 2,2-dimethylhex-5-en-1-amine,[1] and *N*-methyl-pent-4-en-1-amine[4] were prepared according to reported procedures.

Synthesis of *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (3)[5]



To a solution of 2,2-dimethylpropane-1,3-diamine (0.25 g, 2.5 mmol) and *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) in dichloromethane (5 mL) was added dropwise chlorodiisopropylphosphine (0.8 mL, 5.0 mmol) dissolved in dichloromethane (3 mL) with stirring at 0 °C. The reaction mixture was allowed to warm to ambient temperature and it was stirred overnight. Sulfur (0.17 g, 5.25 mmol) was then added in small portions to the resulting mixture. The reaction mixture was stirred for 2 h at room temperature, then it was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the desired product **3** (0.71 g, 72%), using 20% ethyl acetate in *n*-hexane for elution (R_f = 0.23 (I_2)). Recrystallization from methylcyclohexane gave the title compound (0.67 g, 68%) as a white solid (mp = 143-144 °C). ^{1}H NMR (C_6D_6, 500 MHz): δ 2.95 (t, *J* = 8.0 Hz, 4H, C*H*$_2$), 2.67 (q, *J* = 8.0 Hz, 2H, N*H*), 2.10 (septet, *J* = 7.0 Hz, 4H, C*H*), 1.11 (d, *J* = 7.0 Hz, 6H, CHC*H*$_3$), 1.07 (t, *J* = 5.75 Hz, 12H, CHC*H*$_3$), 1.03 (d, *J* = 7.0 Hz, 6H, CHC*H*$_3$), 0.82 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 125 MHz): δ 47.38, 31.07, 30.58, 24.10, 17.01, 16.69. ^{31}P NMR (C_6D_6, 121 MHz): δ 89.54. IR (KBr): 3324.3, 3207.0, 2974.0, 1446.5, 1073.8, 829.8, 708.4 cm^{-1}. HRMS (EI): exact mass calcd for $[C_{17}H_{40}N_2P_2S_2]^+$ 398.2108, found 398.2097

Zr(IV) bis(thiophosphinic amidate) complex (1)



In an argon-filled glove box, $Zr(NMe_2)_4$ (20 μL, 0.02 mmol, 1.0 M solution in benzene-d_6 or toluene-d_8) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (7.97 mg, 0.02 mmol) in C_6D_6 (0.4 mL) or toluene-d_8 (0.4 mL) were introduced sequentially into a J. Young NMR tube. The reaction mixture was stirred at 25 °C for 10 min until ligand attachment was judged completed by the disappearance of the $Zr(NMe_2)_4$ resonance in the ^{1}H NMR spectrum with concomitant production of Me_2NH. ^{1}H NMR (C_6D_6, 500 MHz): δ 3.11 (s, 12H, $Zr[N(CH_3)_2])_2$), 2.69 (d, *J* = 10.0 Hz, 4H, CH_2), 1.99 (septet, *J* = 7.25 Hz, 4H, C*H*), 1.16 (d, *J* = 7.0 Hz, 6H, $CHCH_3$), 1.13(dd, *J* = 7.0 Hz, *J* = 1.5 Hz, 12H, $CHCH_3$), 1.09 (d, *J* = 7.0 Hz, 6H, $CHCH_3$), 0.89 (s, 6H, $C(CH_3)_2$). ^{13}C NMR (C_6D_6, 125 MHz): δ 57.87, 44.10, 29.08, 28.67, 26.43, 17.68, 16.69. ^{31}P NMR (C_6D_6, 121 MHz): δ 75.10. Anal. Calcd for $C_{21}H_{50}N_4P_2S_2Zr$: C, 43.79; H, 8.75; N, 9.73. Found: C, 43.74; H, 8.73; N, 9.69.

Typical procedure for intramolecular hydroaminations of aminoalkenes using NPS·Zr(NMe$_2$)$_2$ complexes

In an argon-filled glove box, Zr(NMe$_2$)$_4$ (20 μL, 0.02 mmol, 1.0 M solution in benzene-d$_6$ or toluene-d$_8$) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (7.97 mg, 0.02 mmol) in C_6D_6 (0.4 mL) or toluene-d$_8$ (0.4 mL) were introduced sequentially into a J. Young NMR tube. The reaction mixture was stirred at 25 °C for 10 min until ligand attachment was judged completed by the disappearance of the Zr(NMe$_2$)$_4$ resonance in the ^{1}H NMR spectrum with concomitant production of Me_2NH. The appropriate aminoalkene (0.40 mmol) and *p*-xylene (4.9 μL, 0.04 mmol) were added to the resulting solution and then the reaction mixture was subsequently heated at 120 °C or 150 °C in an oil bath to achieve hydroamination.

References

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2. (a) A. C. Cope and W. D. Burrows, *J. Org. Chem.,* 1965, **30**, 2163; (b) W. R. Browman, R. V. Davies, G. S. Sohal and R. B. Timan, *J. Chem. Soc. Perkin Trans. 1.,* 1997, **2**, 155.
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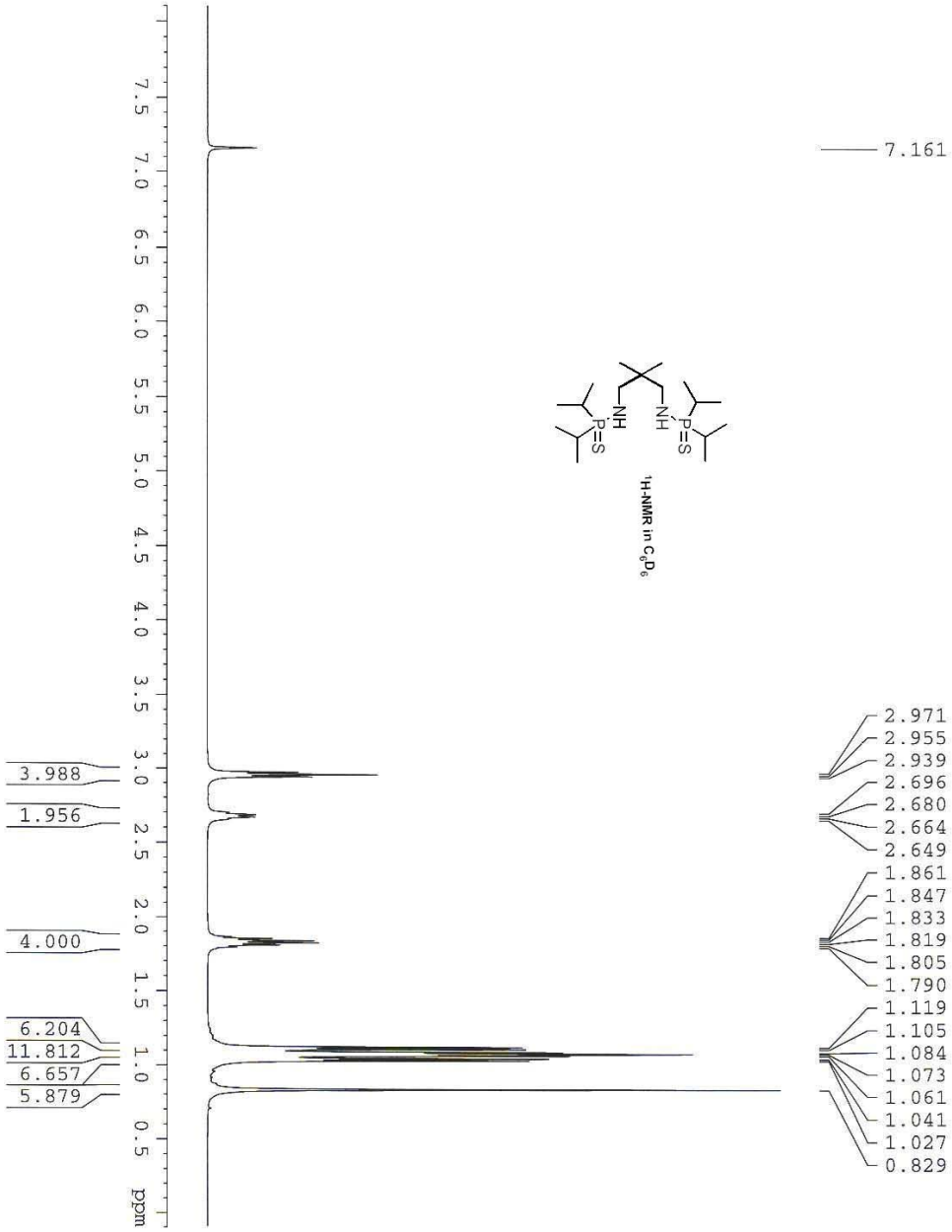
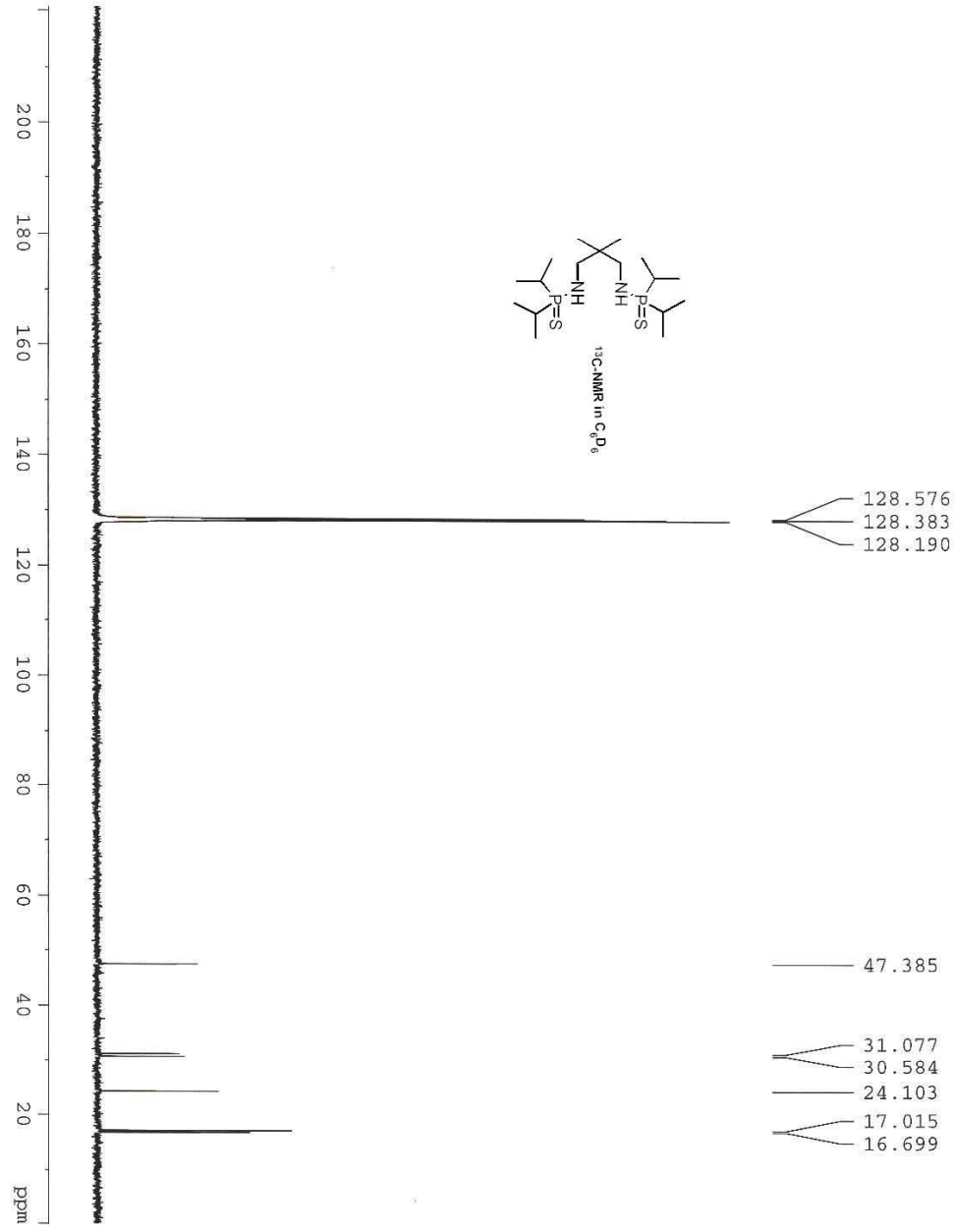
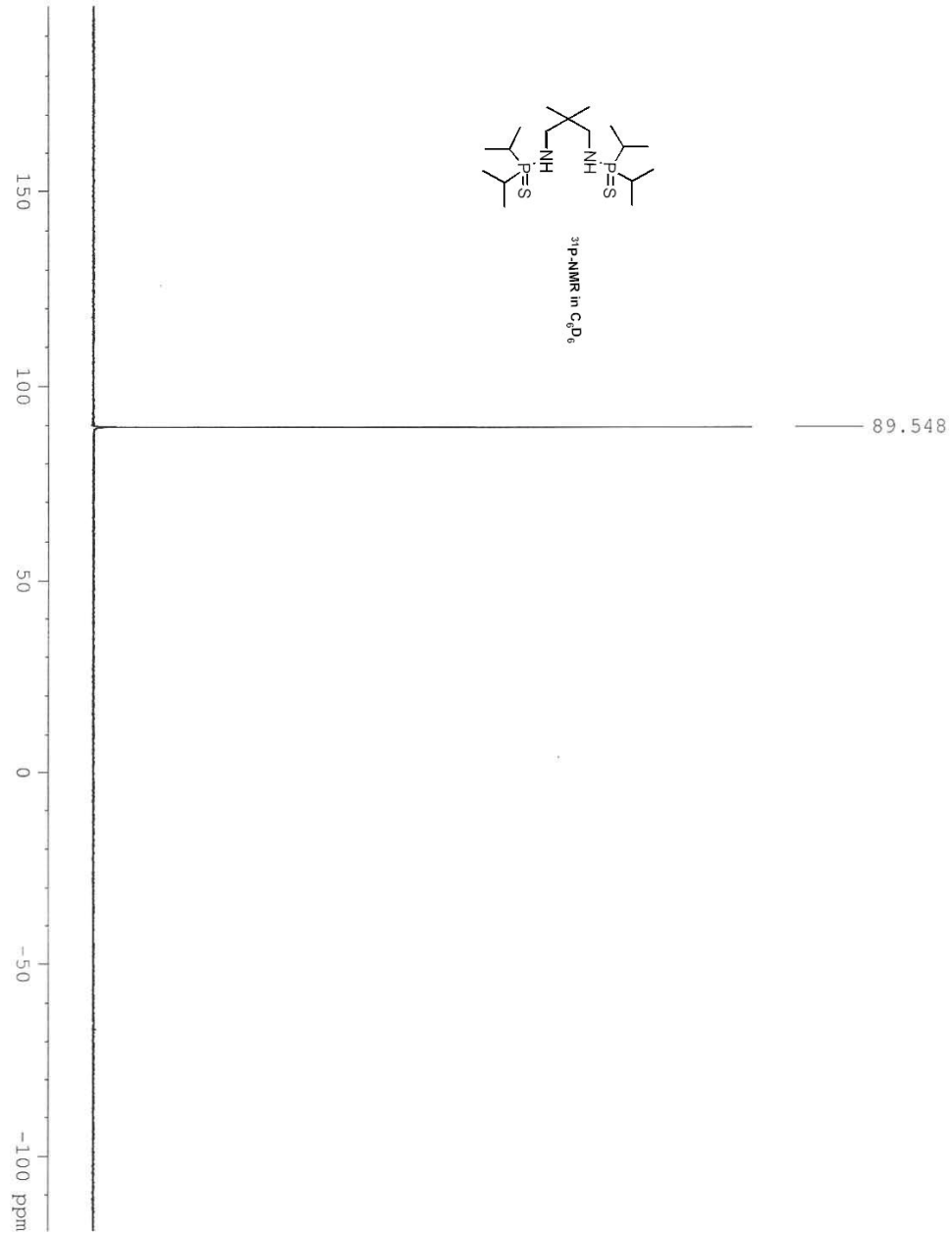
5. Y. K. Kim, T. Livinghouse and Y. Horino, *J. Am. Chem. Soc.,* 2003, **125**, 9560.



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P=S
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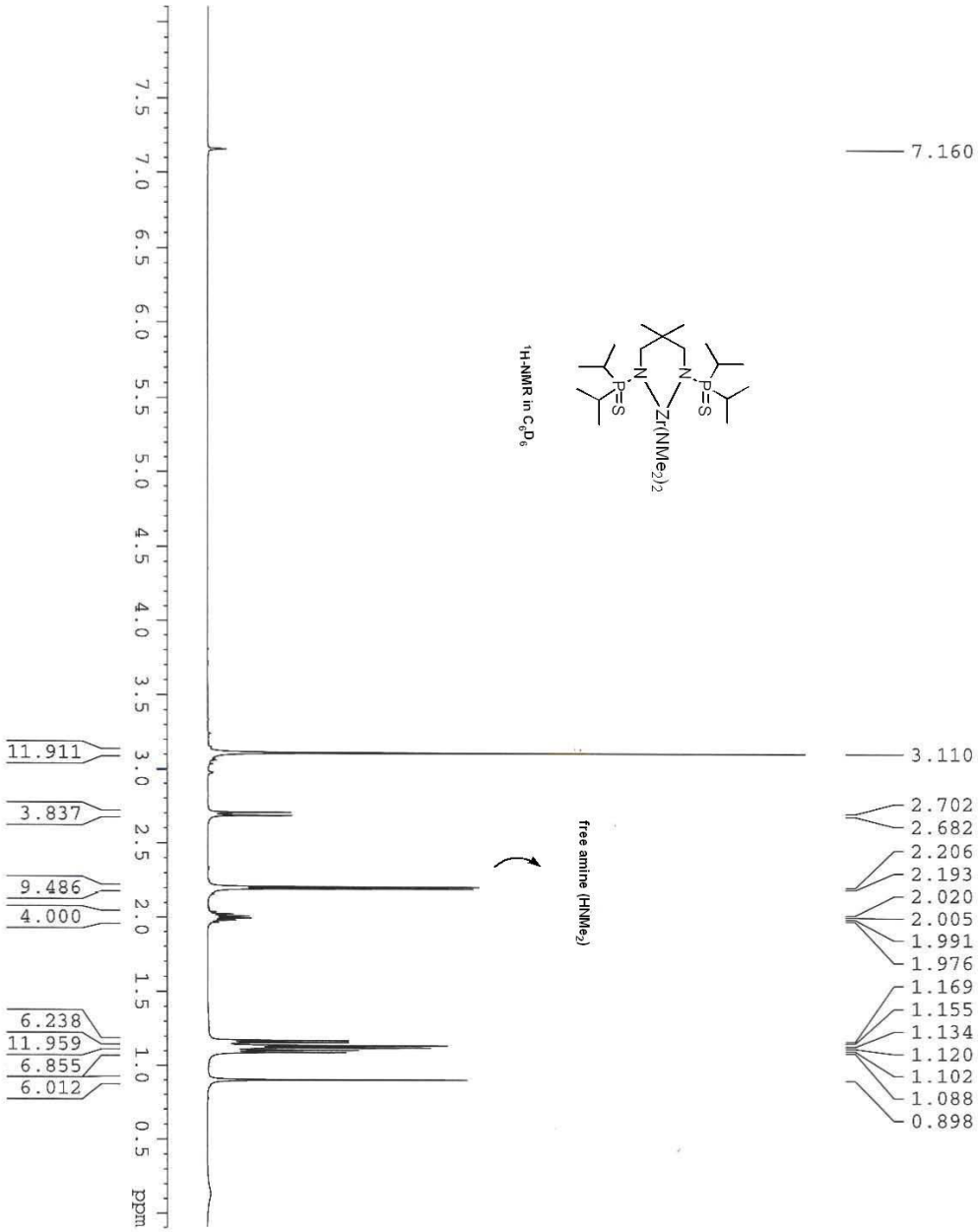
150
100
50
0
-50
-100 ppm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1.120
1.102
1.088
0.898
11.911
3.837
9.486
4.000
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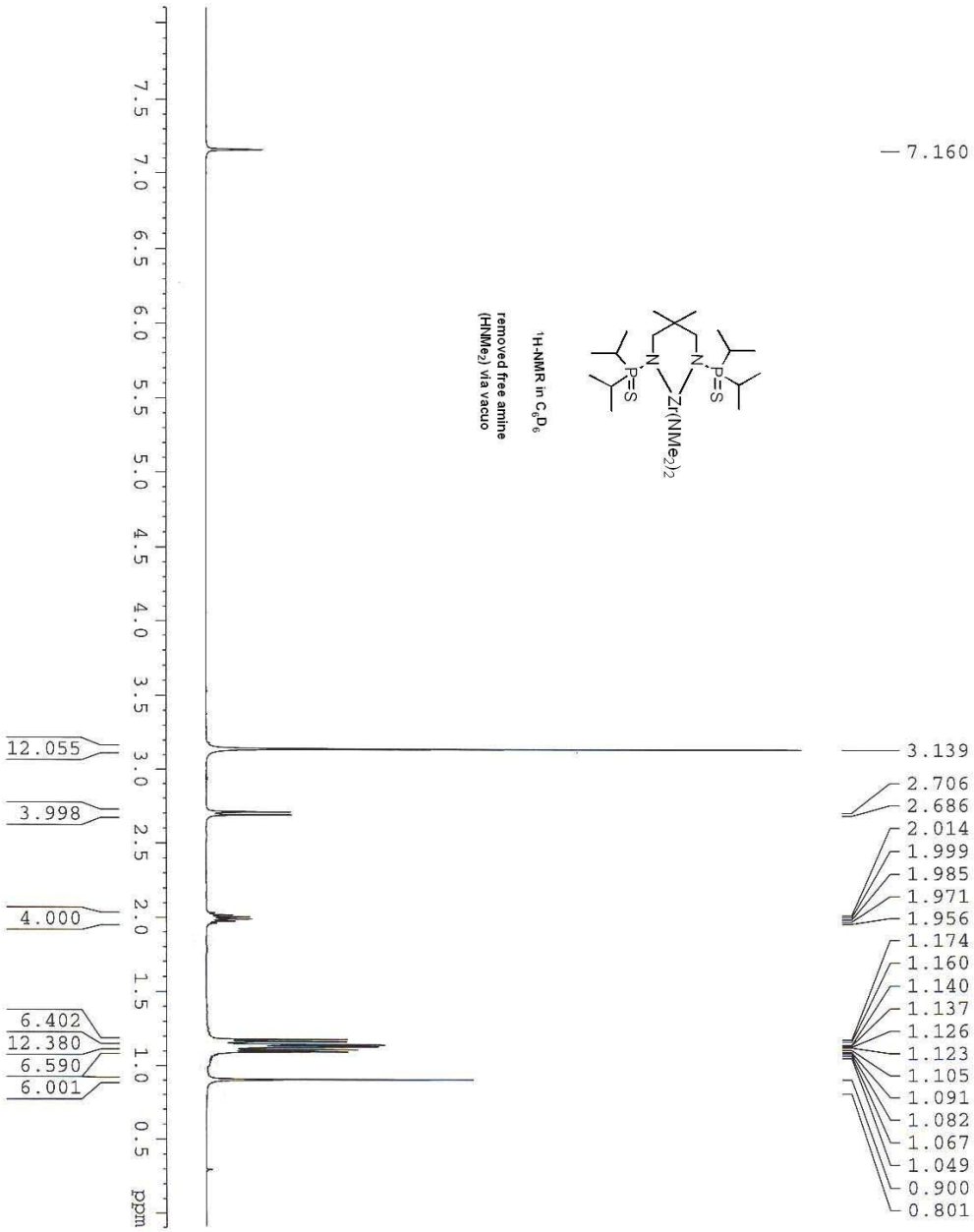
11.959
6.855
6.012
ppm
free amine (HNMe2)
1H-NMR in C6D6
Zr(NMe2)2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3.139
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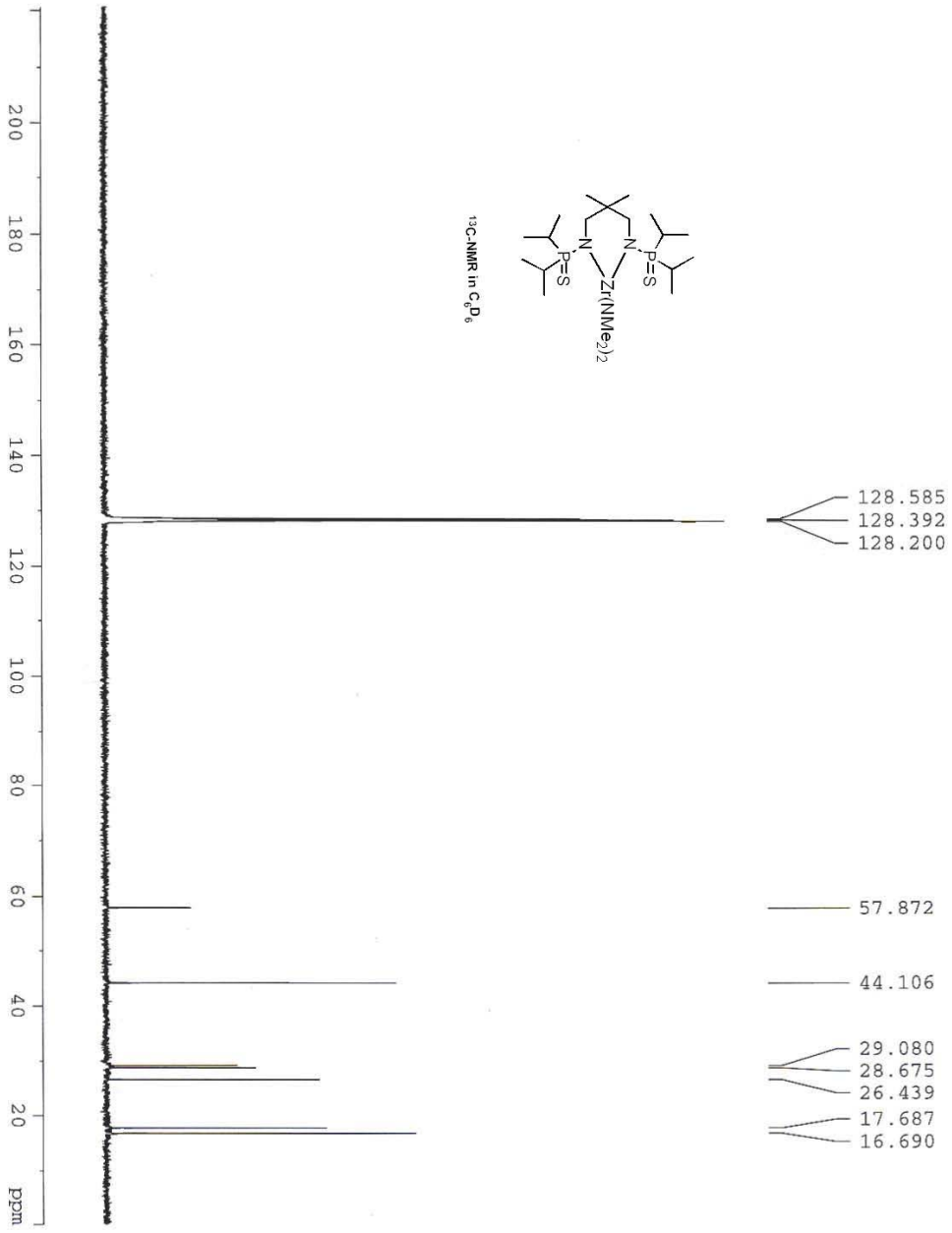
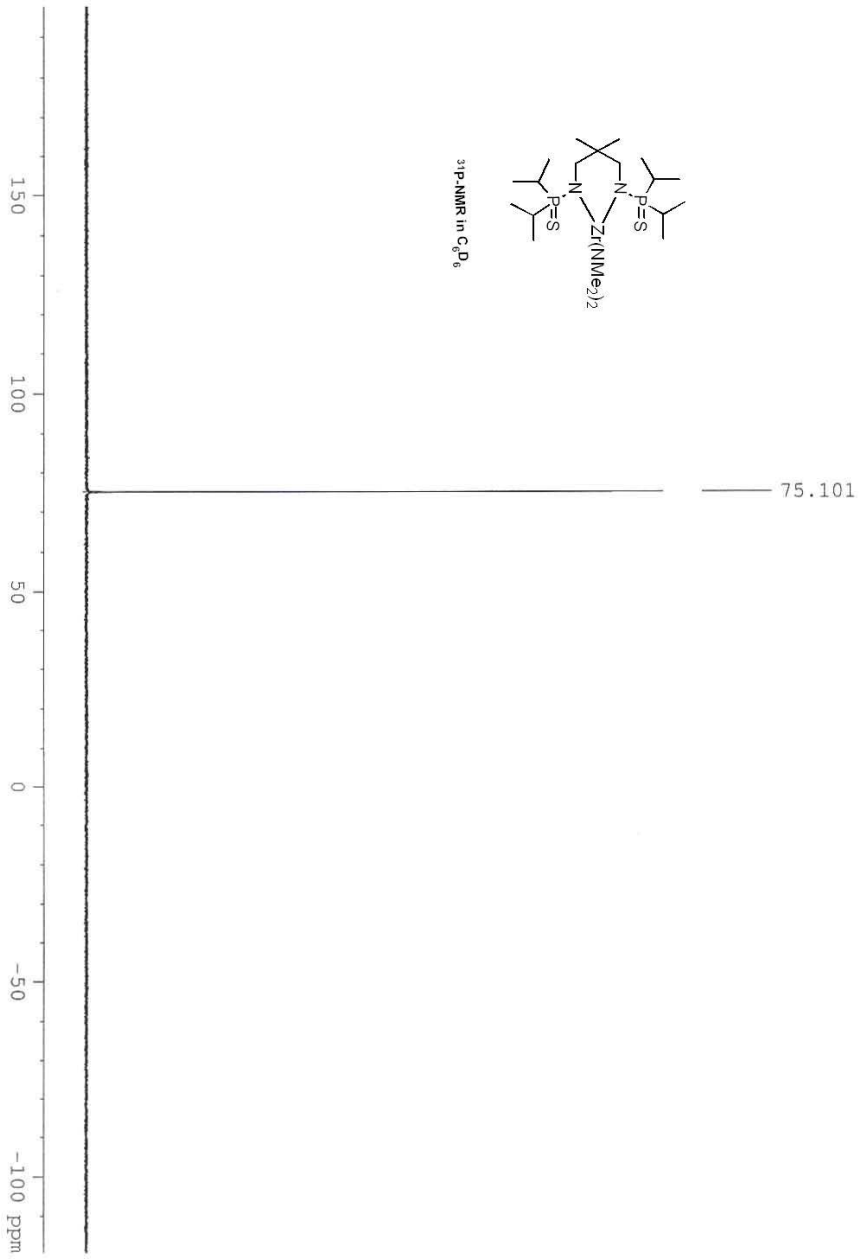
1.137
1.126
1.123
1.105
1.091
1.082
1.067
1.049
0.900
0.801
12.055
3.998
4.000
6.402
12.380
6.590
6.001
ppm
^{1}H-NMR in C_6D_6
removed free amine (HNMe$_2$) via vacuo
Zr(NMe$_2$)$_2$




31P-NMR in C6D6
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N
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P=S
Zr(NMe2)2
75.101
150
100
50
0
-50
-100 ppm