

Supporting Information

“Heavy Group 15 Element Compounds of a Sterically Demanding Bis(iminophosphorane)methanide and Methandiide.”

Christian P. Sindlinger[§], Andreas Stasch[§], Lars Wesemann[§]

[§]Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

[§]School of Chemistry, Monash University, PO Box 23, Melbourne, VIC 3800, Australia

Experimental Details

General Information

All manipulations were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox. THF, diethylether and benzene were distilled from sodium/benzophenone, toluene from sodium and hexane from potassium. Pentane was obtained from an MBRAUN solvent purification system. Benzene-*d*₆ was distilled from sodium and stored over potassium, THF-*d*₈ was distilled from LiAlD₄ and stored under exclusion of light.

An insoluble impurity of BiOCl (up to 15%) was removed from BiCl₃ (Aldrich, >98%) by leaching of BiCl₃ with THF and removal of the solvent under reduced pressure (0.001 mbar) for 2 days. 2,6-Diisopropylaniline (dippNH₂) (Aldrich, 90%, tech. grade) was distilled under reduced pressure prior to use. 2,6-Diisopropylphenylazide^[1] and bis(2,6-diisopropylphenyliminophosphorane)methane^[2] were synthesized according to literature procedures. All other compounds were purchased commercially (Aldrich) and used without further purification.

Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL analyzer.

NMR spectroscopy

NMR spectra were recorded with either a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (¹H), 101.25 MHz (³¹P), a Bruker Avancell+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (¹H), 100.62 (¹³C) and 161.97 MHz (³¹P) or a Bruker AVII+ 500 NMR spectrometer with a 5 mm ATM probe head and operating at 500.13 (¹H), 125.76 (¹³C), 202.5 MHz (³¹P). Chemical shifts are reported in δ values in ppm and referenced on the solvent ²H resonance frequency. The proton and carbon signals were assigned where possible via a detailed analysis of ¹H, ¹³C, ¹³C-UDEFT, ¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹³C HMBC and ¹H-¹⁵N HSQC NMR spectra.

Crystallography

X-ray data for [{C(Ph₂PNdipp)(Ph₂PNHdipp)}BiCl₂], [{C(Ph₂PNdipp)(Ph₂PNHdipp)}SbI₂] [{C(Ph₂PNdipp)₂}BiCl] were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated Mo K α radiation and data for K[HC(Ph₂PNdipp)₂] was collected with a Gemini Ultra Ruby/Xcalibur diffractometer with graphite-monochromated Mo K α radiation. The programs used were Bruker's APEX2 v2011.8-0, including SADABS for absorption correction and SAINT for structure solution, as well as the WinGX suite of programs version 1.70.01, including SHELXS for structure solution and SHELXL for structure refinement.^[3-6] For refinement details see the attached .cif-files.

Synthesis

Li[HC(Ph₂PNDipp)] (1a): Obtained from a modified procedure reported in the literature.^[7] To a solution of H₂C(PPh₂Ndipp)₂ (**1**) (3.00 g, 4.08 mmol, 1 eq) in toluene (35 mL) a solution of *n*-BuLi (2.7 mL, 1.6M in hexane, 4.32 mmol, 1.06 eq) was added dropwise over a period of 10 min at room temperature and the mixture was stirred overnight. The volume was reduced in vacuo to approx. 10 mL and hexane (15 mL) was added. The suspension was stirred for 30 min and the colorless precipitate was collected by filtration, washed with hexane (10 mL), and dried under reduced pressure to obtain **1a** (2.41 g, 3.25 mmol, 80%) as a colorless to pale yellow solid. Spectroscopic data were identical to those reported in the literature.^[7]

Li₂[C(Ph₂PNDipp)] (1b)^[8]: Reaction and was performed similar to previously described procedures.^[9] To a solution of H₂C(PPh₂Ndipp)₂ (**1**) in benzene (approx. 20 mL per g) 2 eq of *n*-BuLi were added at room temperature and stirred for 2 days. A colorless precipitate was isolated by filtration, washed with benzene and dried under reduced pressure to give **1b** (35-45%). Spectroscopic data are found to be similar to those reported for the previously described TMEDA^[7] adducts. ¹H (500.13 MHz, *d*₈-THF, rt) δ 7.59 (br, 8H, *o*-CH_{ar}(Ph)), 7.06 (br, 12H, *m/p*-CH_{ar}(Ph)), 6.70 (d, 4H, *m*-H_{dipp}, ³J_{H-H} = 7.51 Hz), 6.53 (t, 2H, *p*-H_{dipp}, ³J_{H-H} = 7.53 Hz), 3.87 (br sept., 4H, CHMe₂), 1.10-0.10 (br s, 24H, CHMe₂). ¹H (500.13 MHz, *d*₈-THF, -40°C) δ 7.57 (br, 8H, *o*-CH_{ar}(Ph)), 7.10 (br, 12H, *m/p*-CH_{ar}(Ph)), 6.68 (d, 4H, *m*-H_{dipp}, ³J_{H-H} = 7.51 Hz), 6.52 (t, 2H, *p*-H_{dipp}, ³J_{H-H} = 7.53 Hz), 3.93 (br sept., 4H, ³J_{H-H} = 6.50 Hz CHMe₂), 1.02 (br d, 12H, ³J_{H-H} = 6.42Hz, CHMe₂), 0.41 (br d, 12H, ³J_{H-H} = 6.42Hz, CHMe₂). ³¹P{¹H} (202.5 MHz, *d*₈-THF, rt) δ 7.55 (s).

K[HC(Ph₂PNDipp)] (1c): To a mixture of H₂C(PPh₂Ndipp)₂ (**1**) (2.00 g, 2.72 mmol, 1 eq) and K[N(SiMe₃)₂] (0.86 g, 2.87 mmol, 1.06 eq) toluene (35 mL) was added and the suspension was stirred overnight. The resulting orange solution was reduced in volume to approx. 10 mL and hexane (60 mL) was added. A colorless precipitate was collected by filtration, washed with hexane (5 mL) and redissolved in a minimum of hot toluene. After a few days at 0°C a crop of colorless to pale brown crystals were isolated by filtration and dried under reduced pressure to give a first crop of donor-solvent free **1c** (0.70 g, 0.91 mmol, 33%). Upon further concentration of the supernatant mother liquor and analogous isolation of crystals an overall yield of up to 75% can be obtained. Spectroscopic data were identical to those reported in the literature (except for co crystallizing THF molecules).^[10] Few colorless crystals suitable for X-ray diffraction of the solvent free compound crystallized from hexane extracts of reaction solutions in a fridge over a period of several days. ¹H (400.11 MHz, C₆D₆, rt) δ 8.02-7.92 (m, 8H, *o*-CH_{ar}(Ph)), 7.18-6.90 (m, 18H, CH_{ar}), 3.91 (sept., 4H, ³J_{H-H} = 6.85 Hz, CHMe₂), 2.17 (t, 1H, ²J_{P-H} = 3.02 Hz, PCHP), 1.15 (d, 24H, ³J_{H-H} = 6.85 Hz, CHMe₂). ³¹P{¹H} (161.97 MHz, C₆D₆) δ 3.80 (s).

X-ray structure of [SbI₂{C(Ph₂PNDipp)(Ph₂PNHdipp)}] (**3**):

Obtained from toluene solutions of **3** that were layered with hexanes.

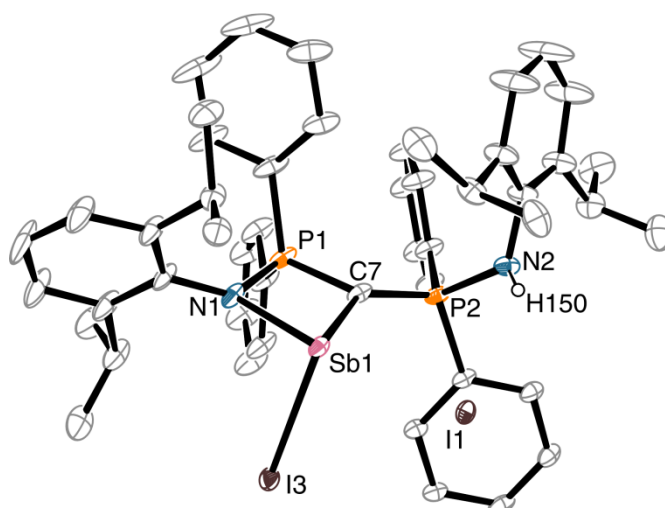


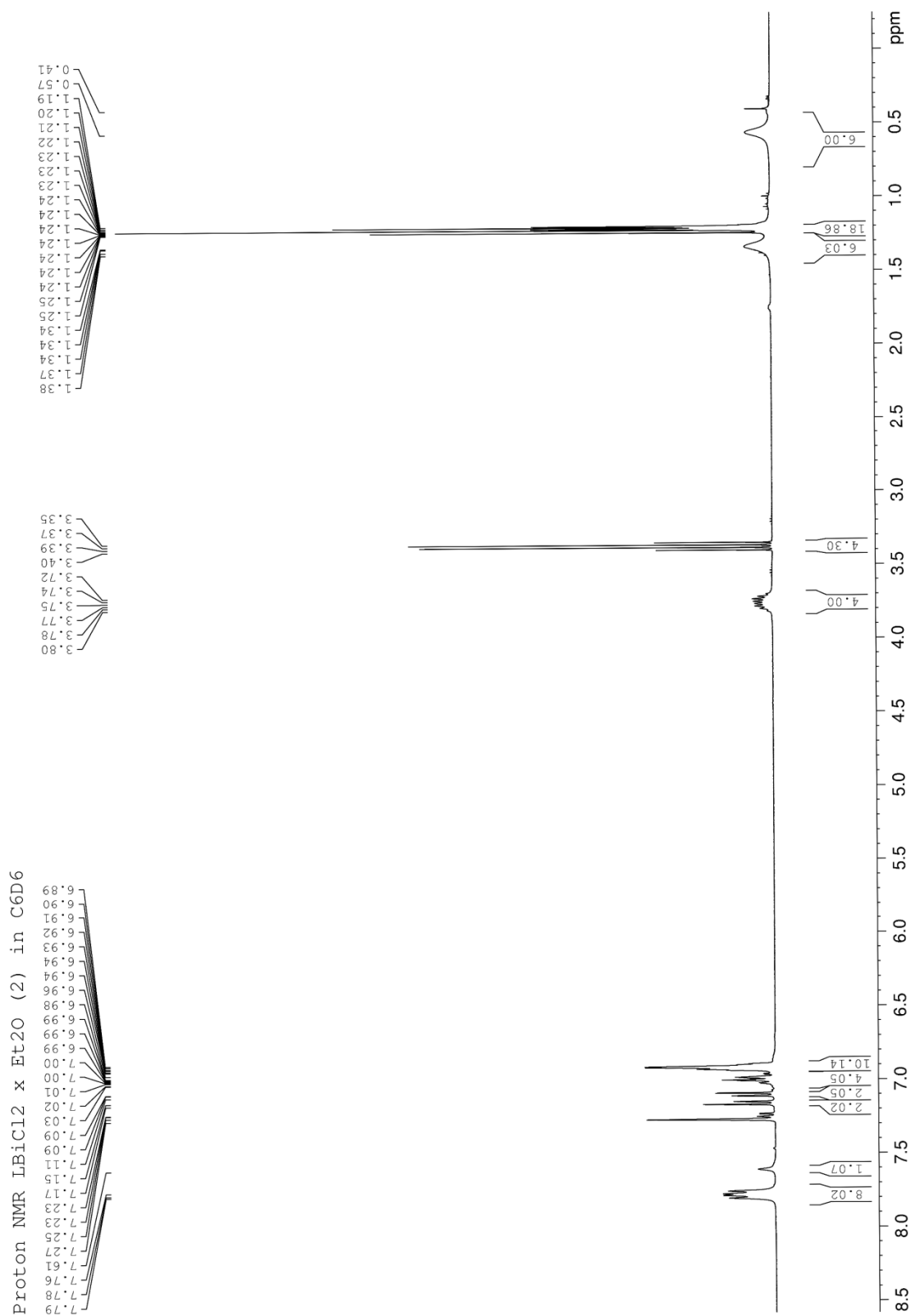
Figure 1SI. ORTEP plot of the molecular structure of **3** · toluene. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms (except H150) and a disordered lattice toluene molecule have been omitted for clarity. Hydrogen atom H150 was located in the Fourier map. Selected bond lengths [Å] are given: C(7)–P(2) 1.709(5), C(7)–P(1) 1.730(4), P(1)–N(1) 1.628(5), P(2)–N(2) 1.680(4), C(7)–Sb(1) 2.137(5), N(1)–Sb(1) 2.206(3), P(1)–Sb(1) 2.9961(8), Sb(1)–I(3) 2.8176(4), Sb(1)–I(1) 3.0463(4), I(1)–H(150) 2.97(5).

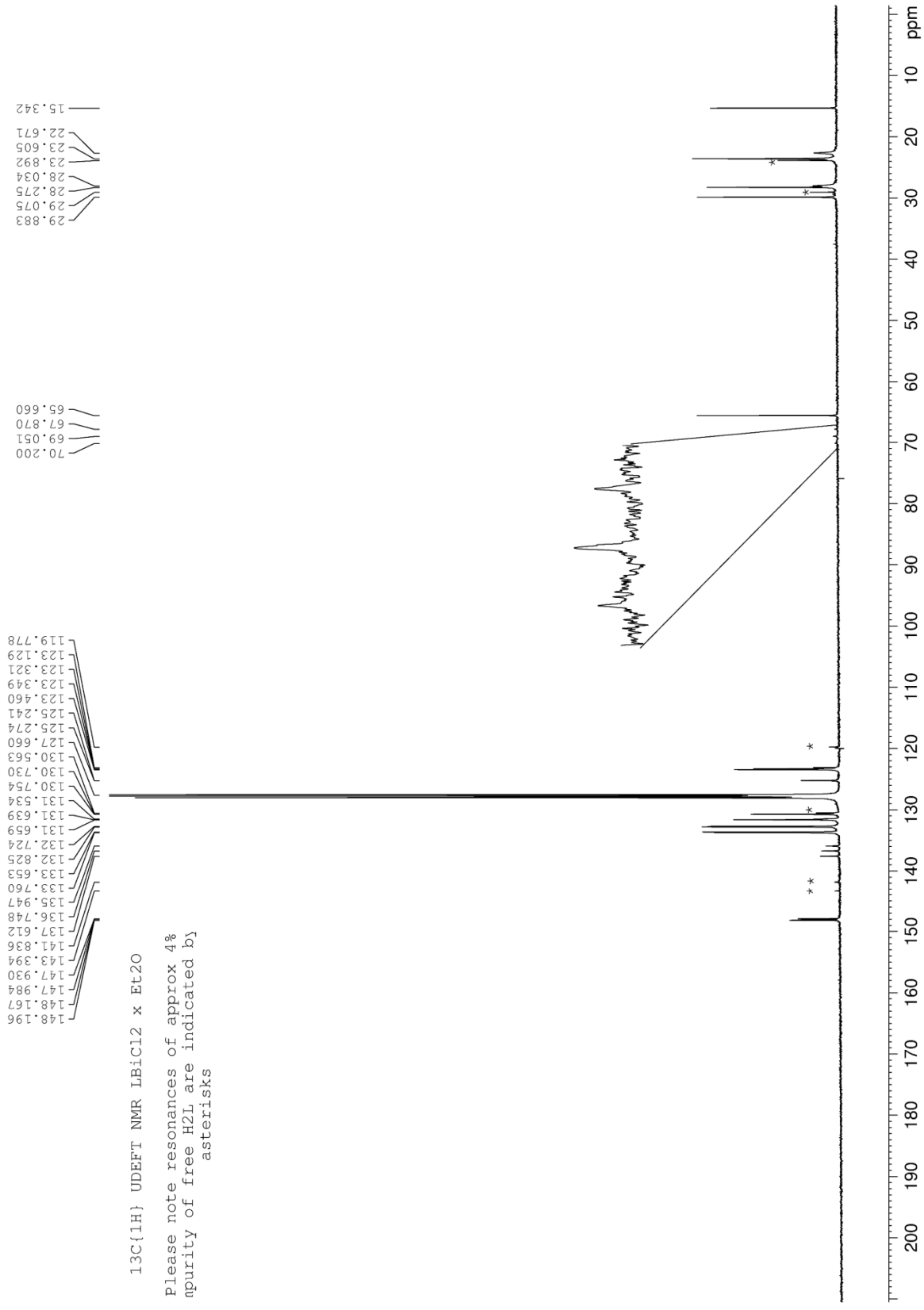
Crystallographic Details

Table 1. Selected crystallographic data for compounds 1c - 4

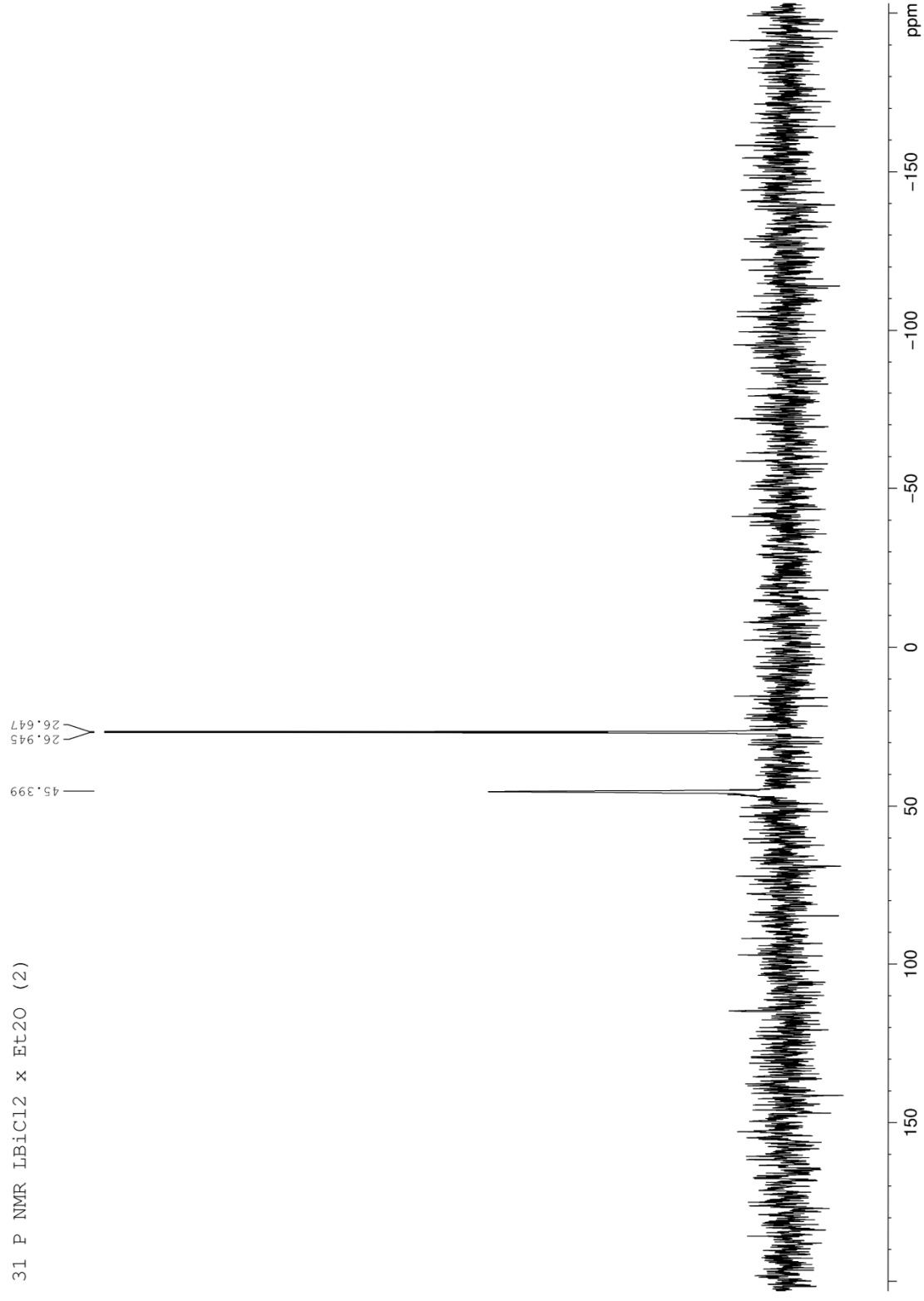
Compound	1c	$2 \times 0.5 \text{ C}_6\text{H}_{14}$	$3 \times \text{C}_7\text{H}_8$	4
CCDC number	969558	969559	969560	969561
Empirical formula	$\text{C}_{49}\text{H}_{55}\text{KN}_2\text{P}_2$	$\text{C}_{52}\text{H}_{62}\text{BiCl}_2\text{N}_2\text{P}_2$	$\text{C}_{56}\text{H}_{63}\text{I}_2\text{N}_2\text{P}_2\text{Sb}$	$\text{C}_{49}\text{H}_{54}\text{BiClIN}_2\text{P}_2$
Formula weight	772.99	1056.86	1201.57	977.31
T [K]	123(2)	100(2)	120(2)	100(2)
Λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	Cc
a [Å]	9.5310(6)	12.0435(5)	20.9028(9)	25.5790(9)
b [Å]	42.837(2)	17.7779(8)	12.7619(6)	8.9542(3)
c [Å]	10.6511(7)	23.3800(10)	40.6061(18)	20.3594(8)
α [°]	90	90	90	90
β [°]	101.489(6)	104.4740(10)	97.8920(10)	110.692(2)
γ [°]	90	90	90	90
V [Å ³]	4261.5(4)	4847.0(4)	10729.5(8)	4362.3(3)
Z	4	4	8	4
ρ [Mg m ⁻³]	1.205	1.448	1.488	1.488
μ [mm ⁻¹]	0.235	3.850	1.761	4.212
$F(000)$	1648	2140	4800	1968
Crystal size [mm ³]	0.25×0.15×0.10	0.19×0.23×0.26	0.13×0.26×0.34	0.15×0.23×0.31
Theta range [°]	2.01 to 25.00	1.75 to 27.25	1.01 to 26.93	1.70 to 28.73
Index ranges	$-10 \leq h \leq 11$	$-15 \leq h \leq 13$	$-25 \leq h \leq 26$	$-34 \leq h \leq 34$
	$-50 \leq k \leq 33$	$-22 \leq k \leq 21$	$-16 \leq h \leq 15$	$-12 \leq k \leq 12$
	$-11 \leq l \leq 12$	$-29 \leq l \leq 29$	$-51 \leq h \leq 51$	$-27 \leq l \leq 27$
Refl. collected	15270	40518	46516	57252
Indep. refl. / [R(int)]	7493 / 0.0653	10784 / 0.0532	11479 / 0.0236	10971 / 0.0184
Completeness to theta max	99.7%	99.3%	98.6%	99.7%
Data/restraints/parameter	7493/0/495	10784/0/545	11479/22/546	10971/2/504
Goof	1.067	1.032	1.286	1.030
Final R indices [$I > 2\sigma(I)$]				
$R1 / wR2$	0.0647 / 0.1329	0.0278 / 0.0706	0.0396 / 0.0932	0.0131 / 0.0311
R indices (all data)				
$R1 / wR2$	0.1058 / 0.1523	0.0409 / 0.0747	0.0494 / 0.1032	0.0139 / 0.0313
Largest diff. peak and hole [eÅ ⁻³]	0.549 and -0.337	2.331 and -1.336	1.390 and -1.132	0.638 and -0.389

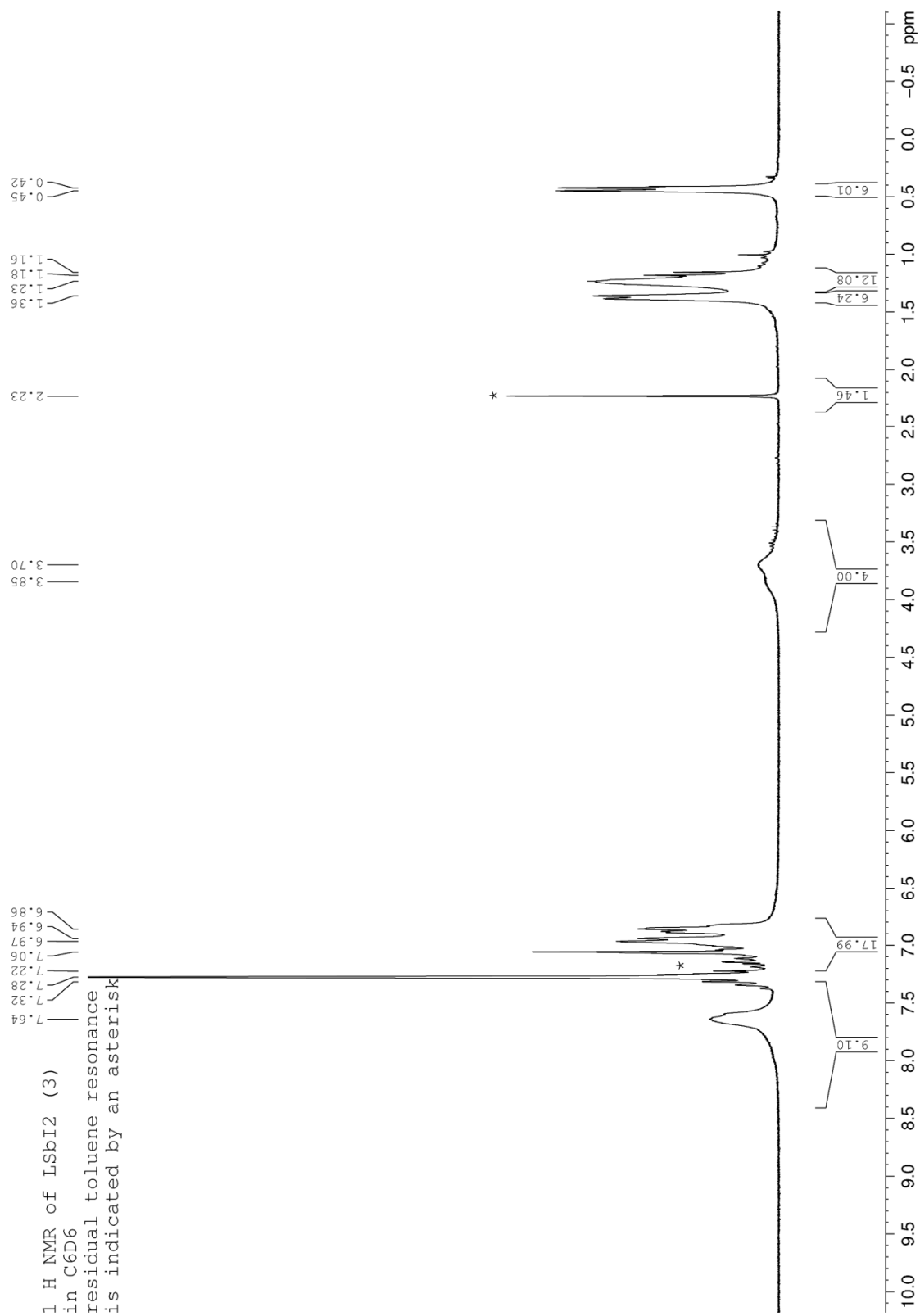
NMR Spectra

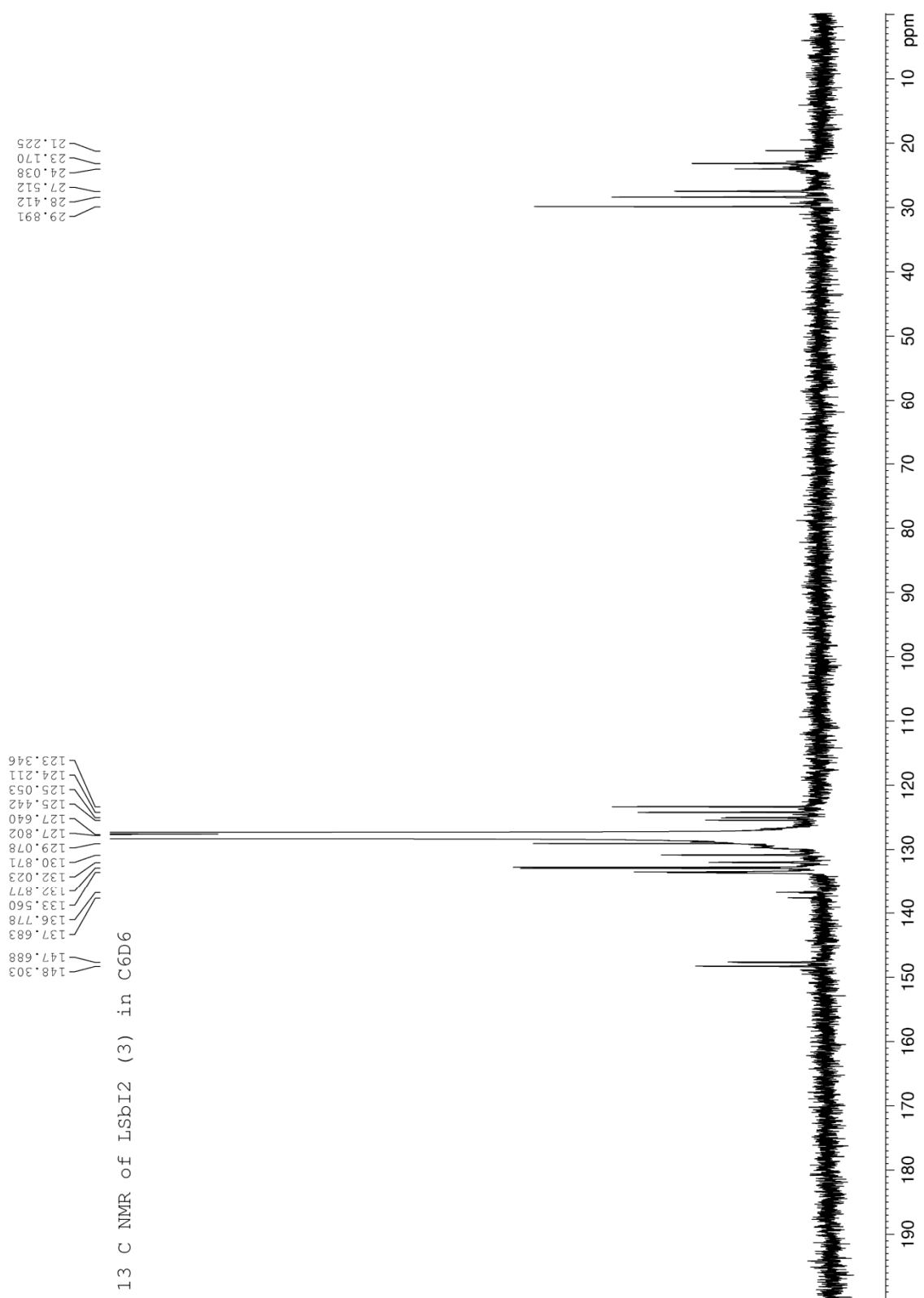




31 P NMR LBiCl2 x Et2O (2)



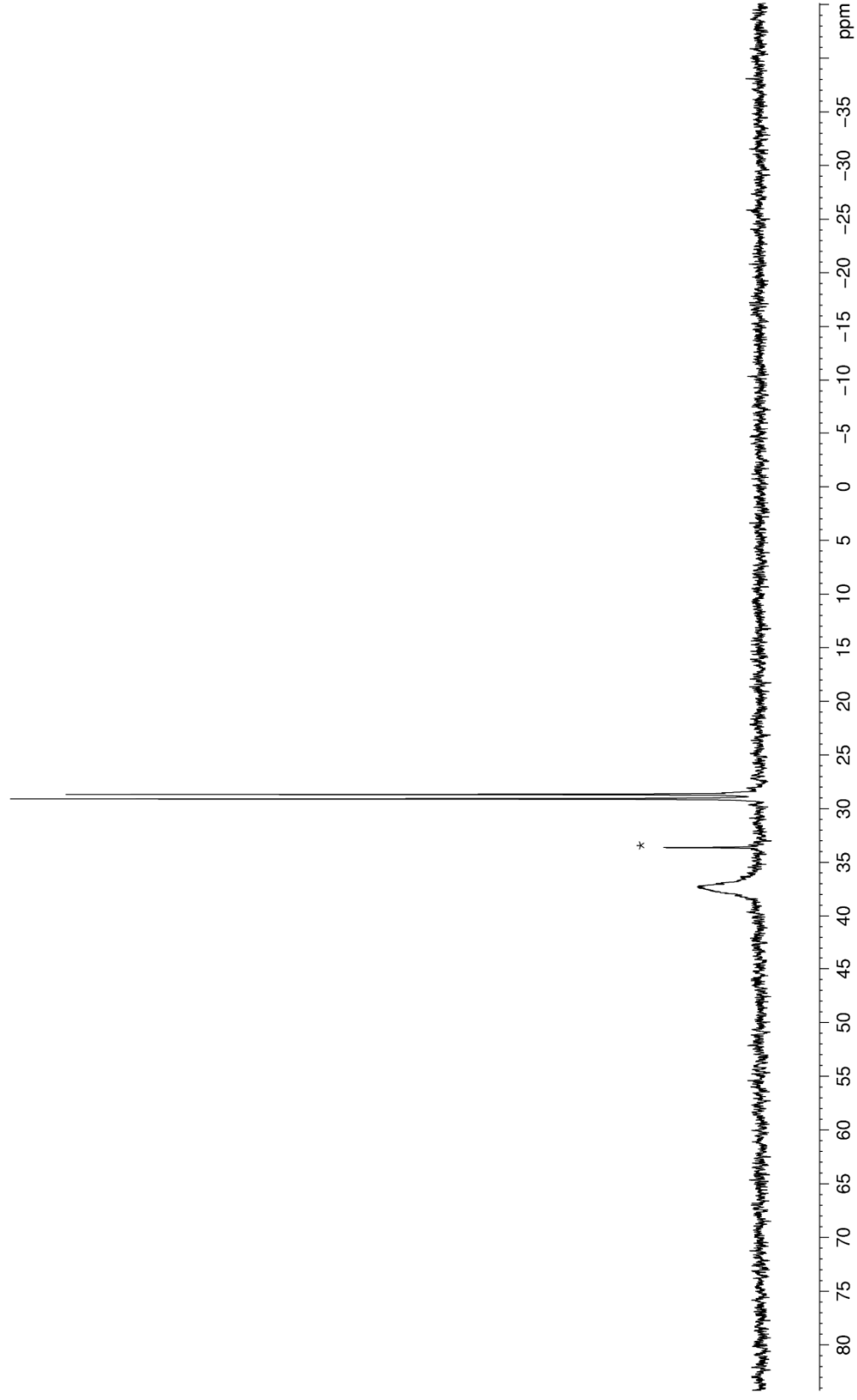




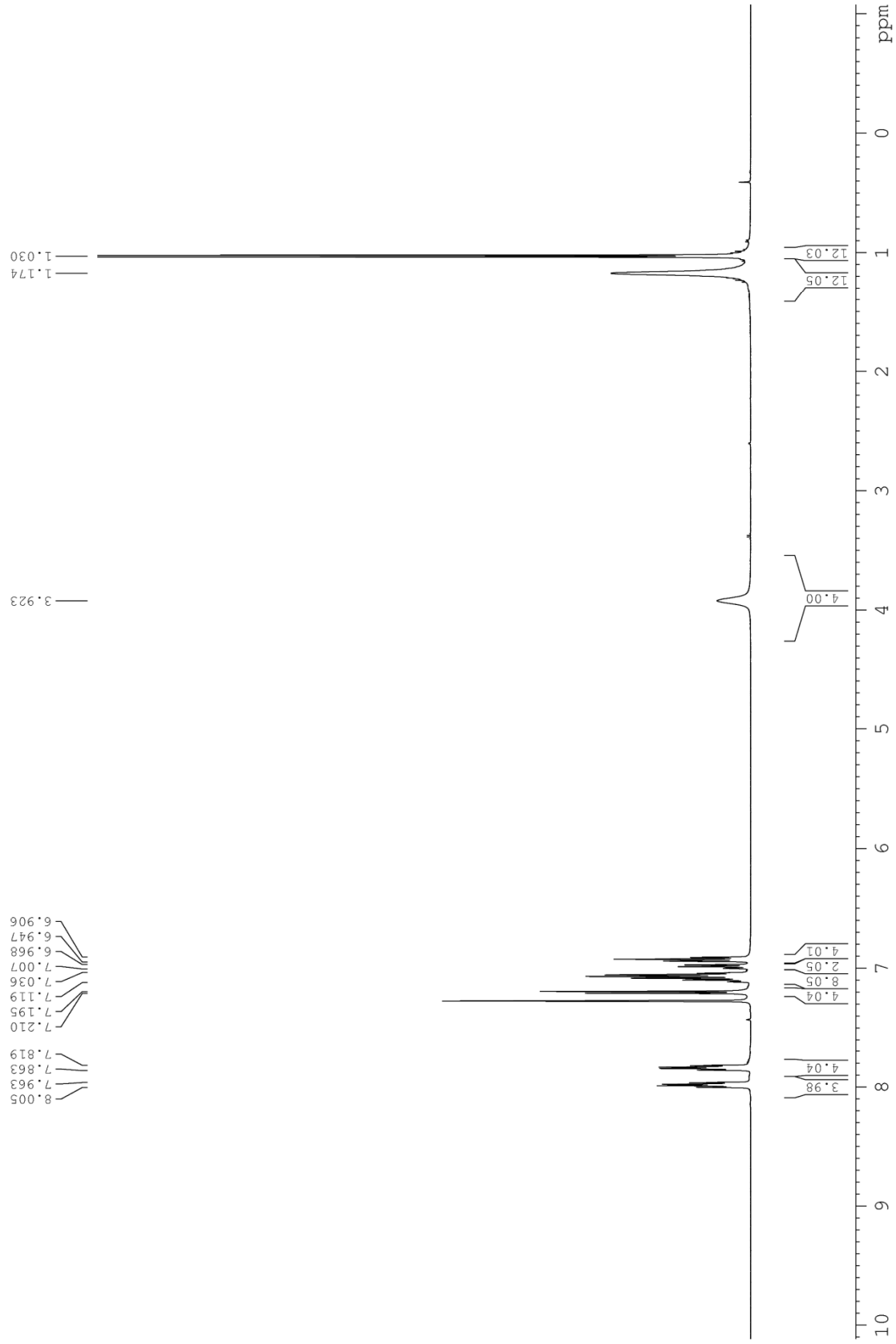
³¹P NMR of L2SbI₂ (3) in C₆D₆

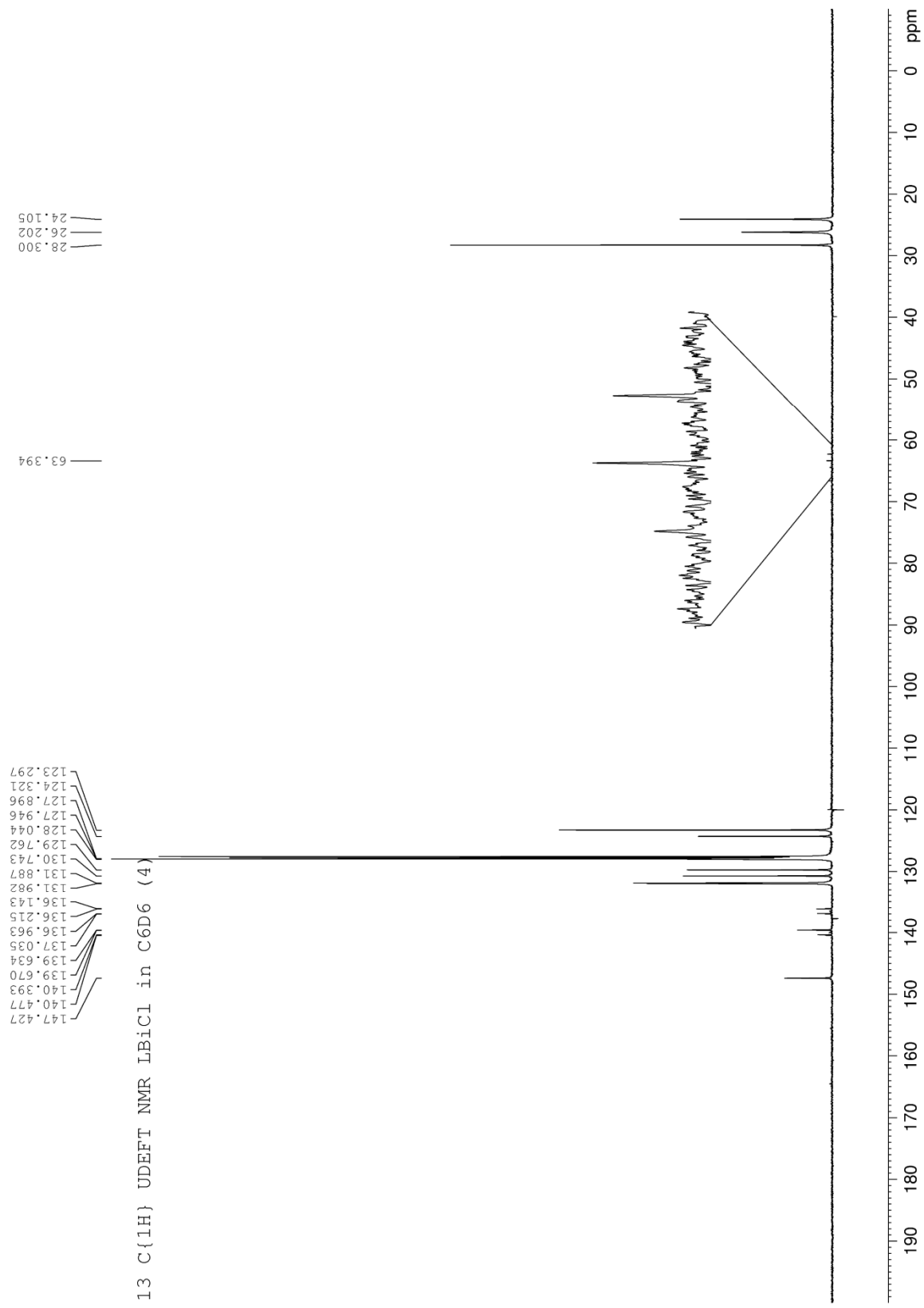
An impurity is indicated by an asterisk

28.692
29.108
33.642
7.295

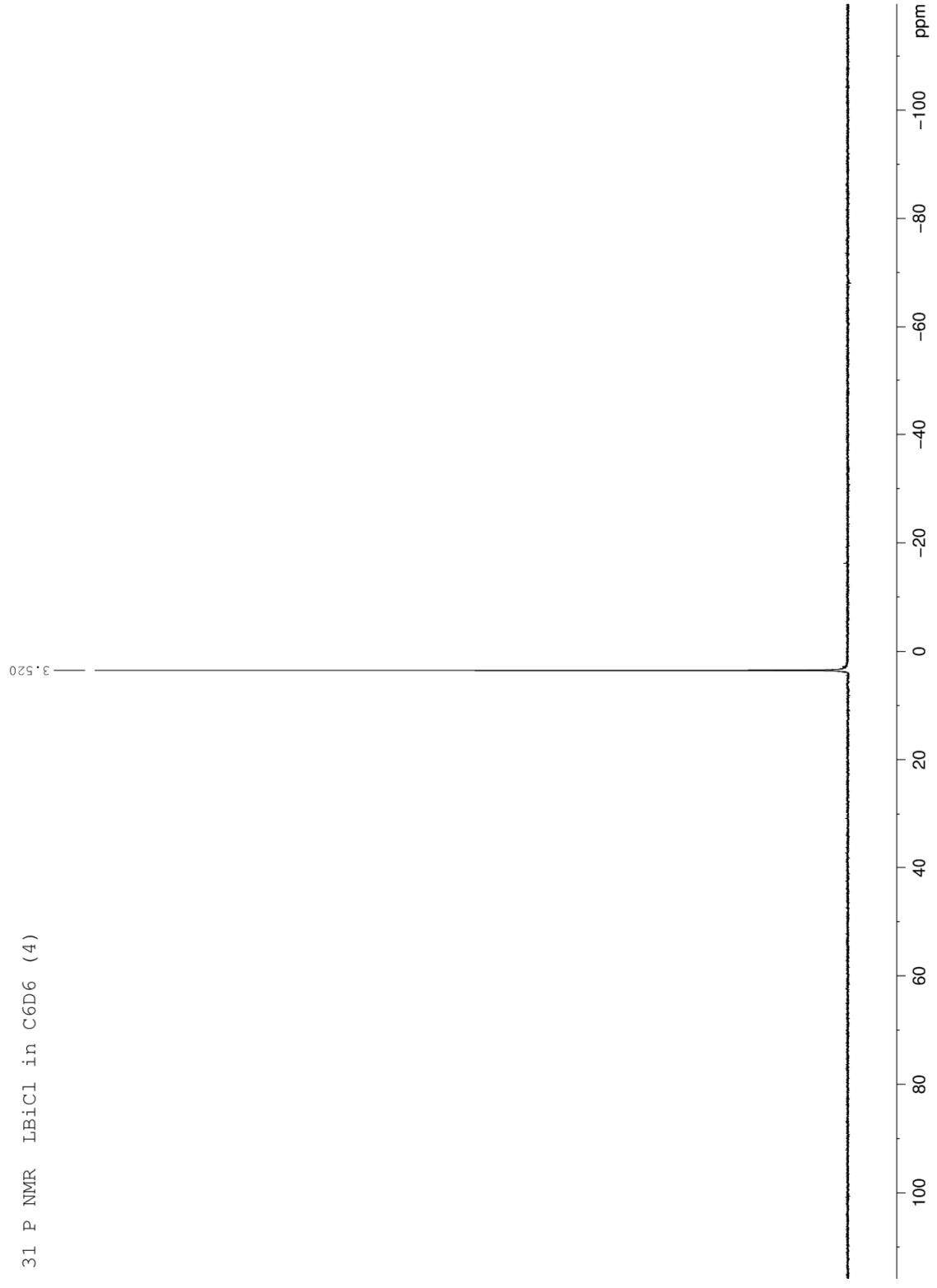


¹H NMR lBiCl in C6D6 (4)

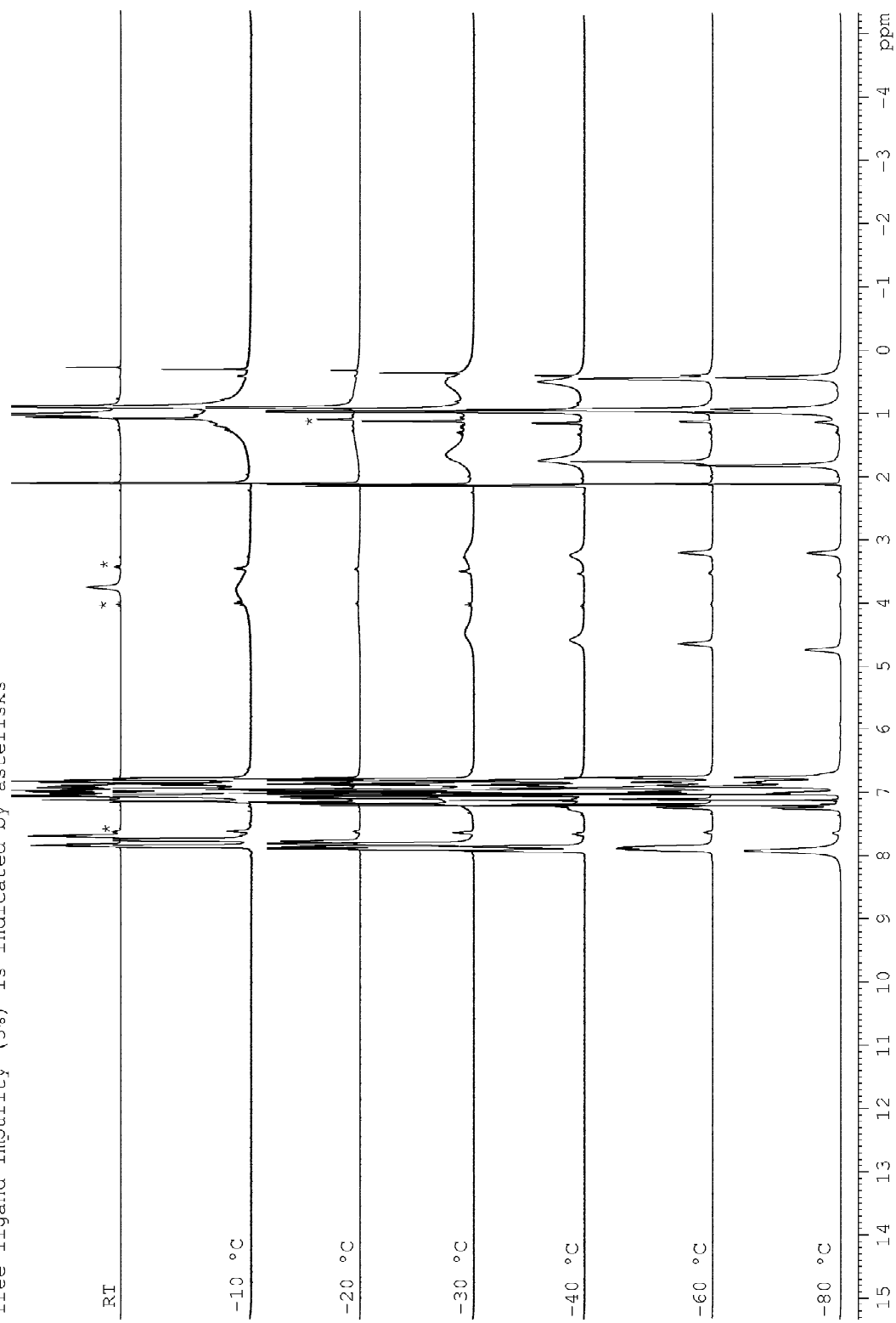




31 P NMR LBiCl in C6D6 (4)



VT Proton NMR on $\text{LiB}(\text{Cl})_4$ in tol-d_8
free ligand impurity (3%) is indicated by asterisks



Literature

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