Supporting Information

Low valent lead hydride chemistry: hydroplumbylation of phenylacetylene and 1,1-dimethylallene

Sebastian Weiß, Hartmut Schubert, Lars Wesemann*

Content

Experimental section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or an MBraun Glovebox. Toluene was distilled from potassium, while *n*-hexane was obtained from an MBRAUN solvent purification system. In addition, all solvents were repeatedly degassed by several freeze-pump-thaw cycles and stored in a glovebox. [(Ar*PbH)$_2$] and (Ar*PbBr)$_2$ (Ar* = 2,6-Trip$_2$C$_6$H$_3$, Trip = 2,4,6-triisopropylphenyl) were synthesized following literature procedures.[1, 2] 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 spectra were recorded on a Bruker DRX-250 NMR spectrometer (^{1}H, 250.13 MHz; ^{13}C, 62.90 MHz; ^{207}Pb, 52.29 Hz) equipped with a 5 mm ATM probe head, a Bruker AvanceII+400 NMR spectrometer (^{1}H, 400.11 MHz; ^{13}C, 100.61 MHz) equipped with a 5 mm QNP (quad nucleus probe) head and a Bruker AvanceII+500 NMR-spectrometer (^{1}H, 500.13 MHz; ^{13}C, 125.76 MHz, ^{207}Pb, 104.63 MHz) equipped with a 5 mm ATM probe head and a setup for variable temperature. The chemical shifts are reported in δ values in ppm relative to external SiMe$_4$ (^{1}H, ^{13}C) or PbMe$_4$ (^{207}Pb) using the chemical shift of the solvent ^{2}H resonance frequency and Ξ = 25.145020 % for ^{13}C and Ξ = 20.920599% for ^{207}Pb.[3] The multiplicity of the signals is abbreviated as s = singlet, d = doublet, t = triplet, sept = septet and m = multiplet or unresolved. The proton and carbon signals were assigned by detailed analysis of ^{1}H, ^{13}C{^{1}H}, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC and ^{13}C{^{1}H} DEPT 135 spectra.

Syntheses

Improved synthesis of (Ar*PbH)$_2$

To a solution of (Ar*PbBr)$_2$ (150 mg, 0.0974 mmol, 1.0 eq.) in hexane (6 mL) at –40°C a solution of DIBAL-H (1.0 M in hexane, 195 µL, 0.195 mmol, 2.0 eq.) was added. The solution turns slightly orange. After 16 h at –40°C (Ar*PbH)$_2$ as yellow crystals could be obtained (128 mg, 95%).

Synthesis of Ar*PbCHCHPh (2)

To a solution of (Ar*PbH)$_2$ (50 mg, 0.0362 mmol, 1.0 eq.) in toluene (1 mL) at room temperature phenylacetylene (8.12 µL, 0.0725 mmol, 2.0 eq.) was added. After 30 min the colour of the solution turns deep red. All volatiles were removed under reduced pressure. The residue was solved in hexane (1.5 mL) and filtered. After few days at –40°C red crystals can be obtained (36 mg, 63%).

^{1}H-NMR (500.13 MHz, C$_6$D$_6$): δ (ppm) δ 1.13 (d, 12 H, *p*-CH*Me*$_2$, $^3J_{H,H}$= 7.0 Hz), 1.16 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 7.0 Hz), 1.38 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 6.8 Hz), 2.72 (sept, 2 H, *p*-C*H*Me$_2$, $^3J_{H,H}$= 7.0 Hz), 3.39 (sept, 4 H, *o*-C*H*Me$_2$, $^3J_{H,H}$= 6.8 Hz), 7.02 (m, 1H, p-C$_6$H$_5$), 7.13 (s, 4 H, *m*-C$_6$H$_2$), 7.22 (m, 2H, m-C$_6$H$_5$), 7.42 (m, 2H, o-C$_6$H$_5$), 7.44 (t, 1 H, p-C$_6$H$_{3',}$$^3J_{H,H}$= 7.7 Hz), 7.82 (d, 2 H, m-C$_6$H$_3$, $^3J_{H,H}$= 7.4 Hz), 7.93 (d, 1H, PbCHC*H*, $^3J_{H,H}$= 19.1 Hz), 12.56 (d, 1H, PbC*H*CH, $^3J_{H,H}$= 19.1 Hz); **^{13}C{^{1}H}-NMR** (100.61 MHz, C$_6$D$_6$): δ (ppm) 23.6 (*o*-CH*Me*$_2$), 24.2 (*p*-CH*Me*$_2$), 26.5 (*o*-CH*Me*$_2$), 31.0 (*o*-*C*HMe$_2$), 34.7 (p-*C*HMe$_2$), 121.4 (*m*-C$_6$H$_2$), 125.0 (p-C$_6$H$_3$), 127.1 (o-C$_6$H$_5$), 128.4 (p-C$_6$H$_5$), 128.9 (m-C$_6$H$_5$), 134.8 (i-C$_6$H$_2$), 137.0 (*m*-C$_6$H$_3$), 144.1 (i-C$_6$H$_5$), 146.1 (PbCH*C*H), 146.2 (o-C$_6$H$_3$), 147.5 (*o*-C$_6$H$_2$), 148.9 (*p*-C$_6$H$_2$), 257.7 (*i*-C$_6$H$_3$), 264.5 (Pb*C*HCH); **^{207}Pb-NMR** (52.33 MHz, C$_6$D$_6$): δ (ppm) 6543. **Anal. Calcd.** (%) C$_{44}$H$_{56}$Pb: C, 66.72; H, 7.13. Found: C, 66.15; H, 7.11.

Synthesis of Ar*PbC(H)$_2$C(H)C(CH$_3$)$_2$ (3)

To a solution of (Ar*PbH)$_2$ (100 mg, 0.0725 mmol, 1.0 eq.) in toluene (3 mL) at room temperature 1,1-dimethylallene (14.2 µL, 0.145 mmol, 2.0 eq.) was added. Immediately the colour of the solution turns dark brown. All volatiles were removed under reduced pressure. The residue was solved in hexane (1 mL) and filtered. All volatiles were removed under reduced pressure (103 mg, 94%). From a concentrated hexane solution at –40°C red crystals can be obtained (37 mg, 34%).

^{1}H-NMR (298 K, 400.11 MHz, Tol-d$_8$): δ (ppm) 1.13 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 6.8 Hz), 1.25 (d, 12 H, *p*-CH*Me*$_2$, $^3J_{H,H}$= 7.2 Hz), 1.35 (d, 2 H, C(CH$_3$)$_2$C(H)C(*H*)$_2$, $^3J_{H,H}$= 9.4 Hz), 1.40 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 7.2 Hz), 1.49 (br s, 3 H, C(C*H*$_3$)$_2$C(H)C(H)$_2$), 1.93 (br s, 3 H, C(C*H*$_3$)$_2$C(H)C(H)$_2$), 2.83 (sept, 2 H, *p*-C*H*Me$_2$, $^3J_{H,H}$= 6.9 Hz), 3.24 (sept, 4 H, *o*-C*H*Me$_2$, $^3J_{H,H}$= 6.9 Hz), 4.27 (br t, 1 H, C(CH$_3$)$_2$C(*H*)C(H)$_2$, $^3J_{H,H}$= 9.8 Hz), 7.18 (s, 4 H, *m*-C$_6$H$_2$), 7.27 (t, 1 H, p-C$_6$H$_3$′,$^3J_{H,H}$= 7.4 Hz), 7.49 (d, 2 H, m-C$_6$H$_3$, $^3J_{H,H}$= 7.5 Hz); **^{1}H-NMR** (233 K, 500.13 MHz, Tol-d$_8$): δ (ppm) 1.17 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 6.7 Hz), 1.24 (s, 3 H, C(C*H*$_3$)$_2$C(H)C(H)$_2$), 1.27 (d, 12 H, *p*-CH*Me*$_2$, $^3J_{H,H}$= 6.7 Hz), 1.47 (d, 12 H, *o*-CH*Me*$_2$, $^3J_{H,H}$= 6.9 Hz), 1.56 (d, 2 H, C(CH$_3$)$_2$C(H)C(*H*)$_2$, $^3J_{H,H}$= 9.7 Hz), 1.73 (s, 3 H, C(C*H*$_3$)$_2$C(H)C(H)$_2$), 2.81 (sept, 2 H, *p*-C*H*Me$_2$, $^3J_{H,H}$= 6.9 Hz), 3.31 (sept, 4 H, *o*-C*H*Me$_2$, $^3J_{H,H}$= 6.8 Hz), 4.14 (br t, 1 H, C(CH$_3$)$_2$C(*H*)C(H)$_2$, $^3J_{H,H}$= 10.1 Hz), 7.22 (s, 4 H, *m*-C$_6$H$_2$), 7.27 (t, 1 H, p-C$_6$H$_3$′,$^3J_{H,H}$= 7.4 Hz), 7.48 (d, 2 H, m-C$_6$H$_3$, $^3J_{H,H}$= 7.4 Hz); **^{13}C{^{1}H}-NMR** (298 K, 100.61 MHz, Tol-d$_8$): δ (ppm) 23.6 (*o*-CH*Me*$_2$), 24.3 (*p*-CH*Me*$_2$), 24.4 (C(*C*H$_3$)$_2$C(H)C(H)$_2$), 26.2 (*o*-CH*Me*$_2$ + C(*C*H$_3$)$_2$C(H)C(H)$_2$), 30.8 (*o*-*C*HMe$_2$), 34.8 (p-*C*HMe$_2$), 84.8 (C(CH$_3$)$_2$C(H)*C*(H)$_2$), 113.2 (C(CH$_3$)$_2$*C*(H)C(H)$_2$), 121.3 (*m*-C$_6$H$_2$), 124.6 (p-C$_6$H$_3$), 129.5 (*C*(CH$_3$)$_2$C(H)C(H)$_2$), 134.7 (*m*-C$_6$H$_3$), 136.7 (*i*-C$_6$H$_2$), 146.5 (*o*-C$_6$H$_3$), 147.8 (*o*-C$_6$H$_2$), 148.8 (*p*-C$_6$H$_2$), 237.9 (*i*-C$_6$H$_3$); **^{207}Pb-NMR** (298 K, 104.63 MHz, Tol-d$_8$):δ (ppm) 3773 ppm. **Anal. Calcd.** (%) $C_{41}H_{58}Pb$: C, 64.96; H, 7.71. Found: C 64.18, H 7.05.

Crystal structure analyses

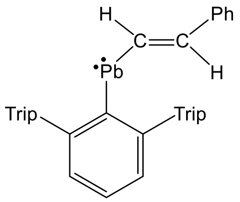
X-ray crystal structure analysis: X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite monochromated Mo Kα radiation or a Bruker APEX II Duo diffractometer with a Mo IµS microfocus tube. The programs used were Bruker´s APEX2 v2011.8-0 including SAINT for data reduction and SHELXS for structure solution and SADABS for multiscan absorption correction, as well as WinGX suite of programs v1.70.01 including SHELXL for structure refinement.[4-7]

Table S1. Crystal structure refinement table of compounds **2**, **3**

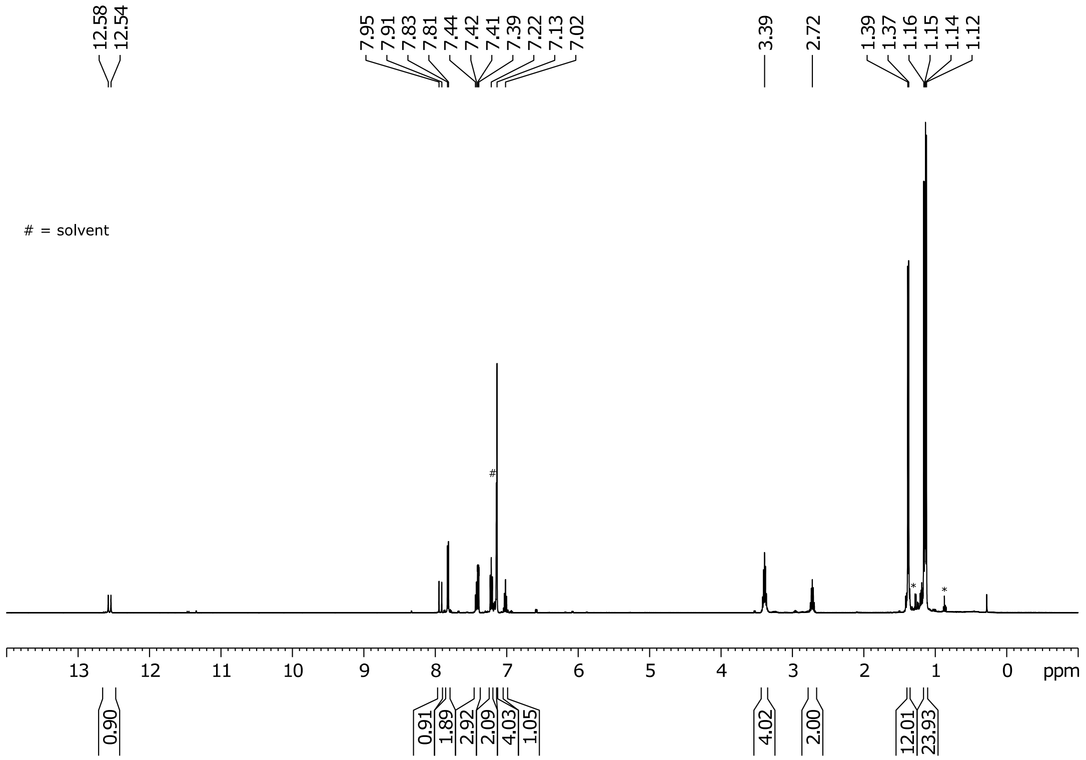
	2	**3**
empirical formula	$C_{44}H_{56}Pb$	$C_{41}H_{58}Pb$
M [g/mol]	792.07	758.06
λ [Å]	0.71073	0.71073
T [K]	100(2)	100(2)
crystal system	triclinic	triclinic
space group	P -1	P -1
Z	2	4
a [Å]	10.7640(2)	14.0970(3)
b [Å]	13.1364(2)	16.7228(4)
c [Å]	14.7038(3)	17.7335(4)
α [°]	87.2140(10)	104.0660(10)
β [°]	89.7630(10)	102.0580(10)
γ [°]	66.5670(10)	108.9560(10)
V [Å^3]	1905.13(6)	3641.57(15)
D_c [g/cm^3]	1.381	1.383
μ [mm^{-1}]	4.455	4.658
F(000)	804	1544
crystal size [mm]	0.218x0.201x0.163	0.17x0.13x0.10
θ range [°]	1.692 – 27.139	1.247 – 27.932
limiting indices	–13≤h≥13	–18≤h≥18
	–16≤k≥16	–21≤k≥22
	–18≤l≥18	–23≤l≥23
reflections collected	36187	99884
independent reflections	8401	17385
R_{int}	0.0335	0.0339
completeness	99.7	99.5
absorption correction	numerical	multi-scan
max., min. transmisson	0.85, 0.71	0.75, 0.57
parameter/restraints	418/0	852/55
$R1$, w$R2$ $[I > 2\sigma(I)]$	0.0231, 0.0484	0.0389, 0.0984
$R1$, w$R2$ (all data)	0.0293, 0.0497	0.0551, 0.1072
Goof on F^2	1.116	1.067
peak / hole $[e \cdot \text{Å}^{-3}]$	1.427, –1.525	3.193, –1.418
CCDC	1940176	1940175

NMR spectroscopy

NMR spectra of compound **2**



^{1}H-NMR of Ar*PbCHCHPh in C_6D_6 at RT



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TD                65536
SOLVENT            C6D6
NS                   64
DS                    0
SWH        10330.578 Hz
FIDRES      0.157632 Hz
AQ        3.1719425 sec
RG                    4
DW           48.400 usec
DE             6.00 usec
TE              299.2 K
D1       1.00000000 sec
TD0                   1

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NUC1                 1H
P1           12.75 usec
PL1            -0.52 dB
PL1W     24.34997177 W
SFO1    500.1325007 MHz

F2 - Processing parameters
SI                65536
SF      500.1300000 MHz
WDW                  EM
SSB     0
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PC                 1.00
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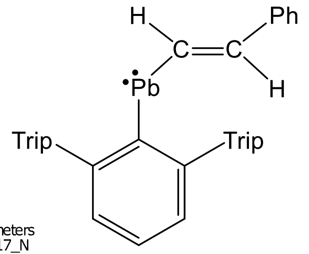
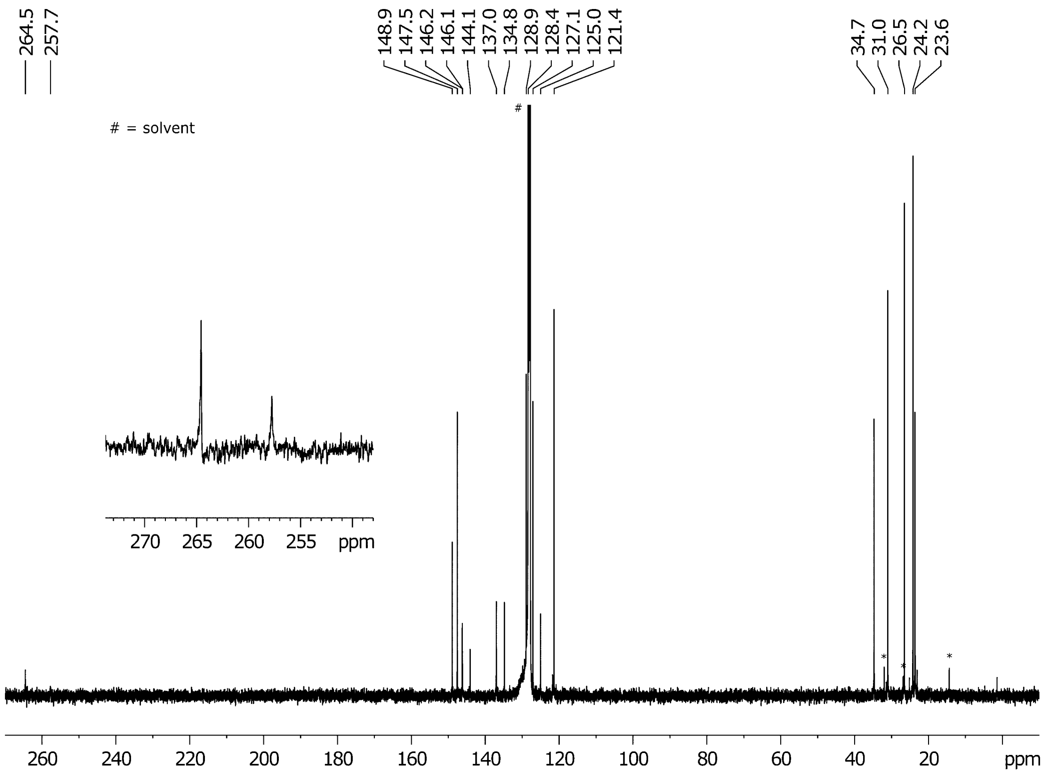
Figure S1. ^{1}H NMR spectrum of compound **2**. (* hexane)



^{13}C-NMR of Ar*PbCHCHPh in C_6D_6 at RT



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PULPROG        zgpg30
TD              53700
SOLVENT          C6D6
NS              15500
DS                  0
SWH         30864.197 Hz
FIDRES       0.574752 Hz
AQ          0.8699400 sec
RG              32800
DW             16.200 usec
DE               6.00 usec
TE              299.2 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
PL1             -4.16 dB
PL1W      78.55633545 W
SFO1      100.6198135 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2           80.00 usec
PL2             -3.00 dB
PL12            11.77 dB
PL13            13.14 dB
PL2W      16.03799057 W
PL12W      0.53474891 W
PL13W      0.39007664 W
SFO2      400.1120007 MHz

F2 - Processing parameters
SI              65536
SF        100.6077008 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
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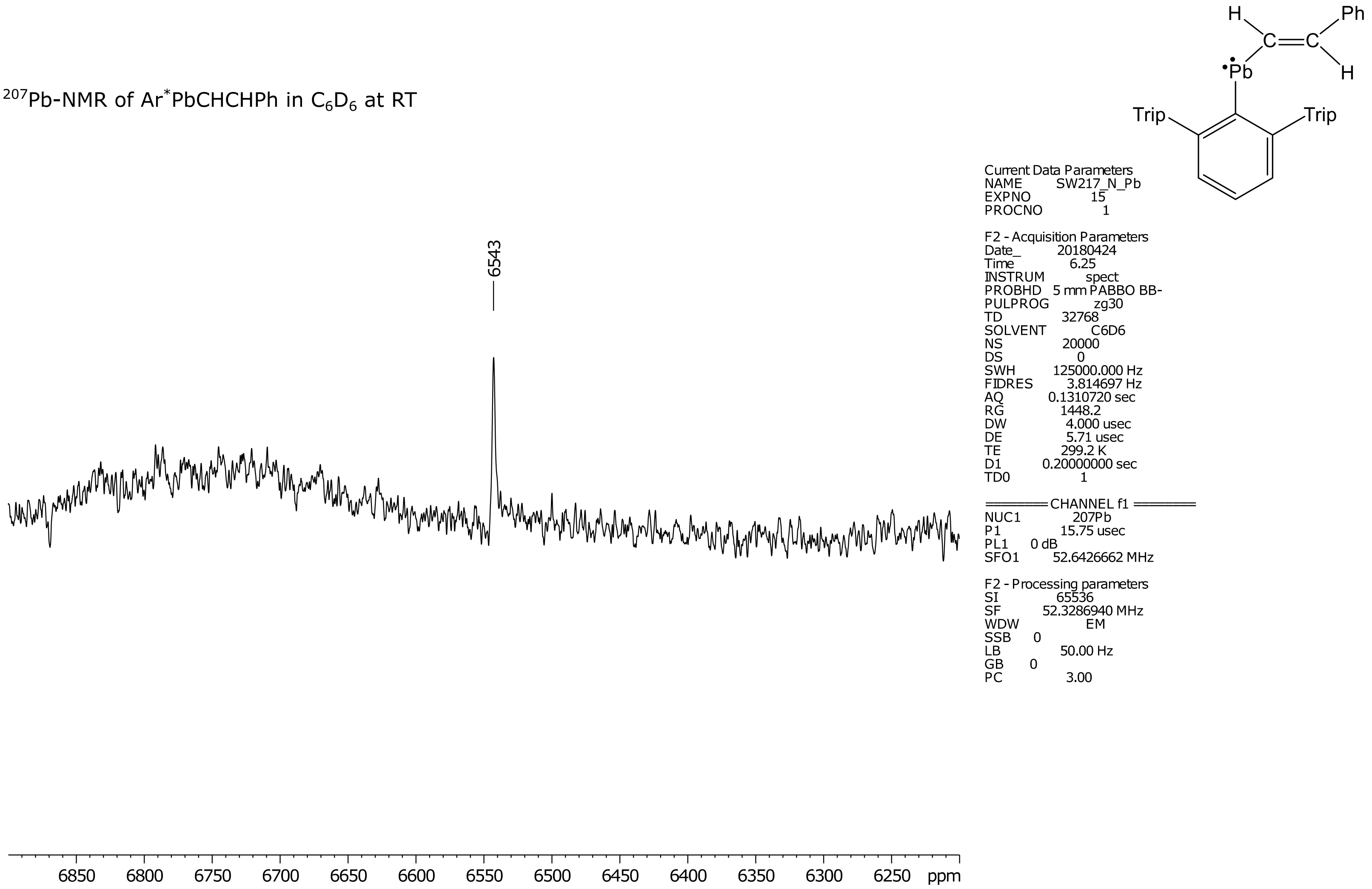
Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2**. (* hexane)

^{207}Pb-NMR of Ar*PbCHCHPh in C_6D_6 at RT



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TD              32768
SOLVENT          C6D6
NS              20000
DS                  0
SWH       125000.000 Hz
FIDRES      3.814697 Hz
AQ         0.1310720 sec
RG             1448.2
DW              4.000 usec
DE               5.71 usec
TE              299.2 K
D1         0.20000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1            207Pb
P1              15.75 usec
PL1      0 dB
SFO1       52.6426662 MHz

F2 - Processing parameters
SI              65536
SF         52.3286940 MHz
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PC               3.00
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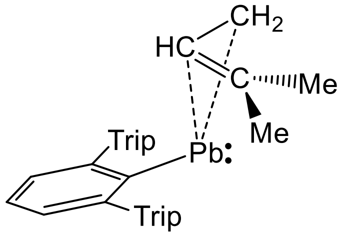
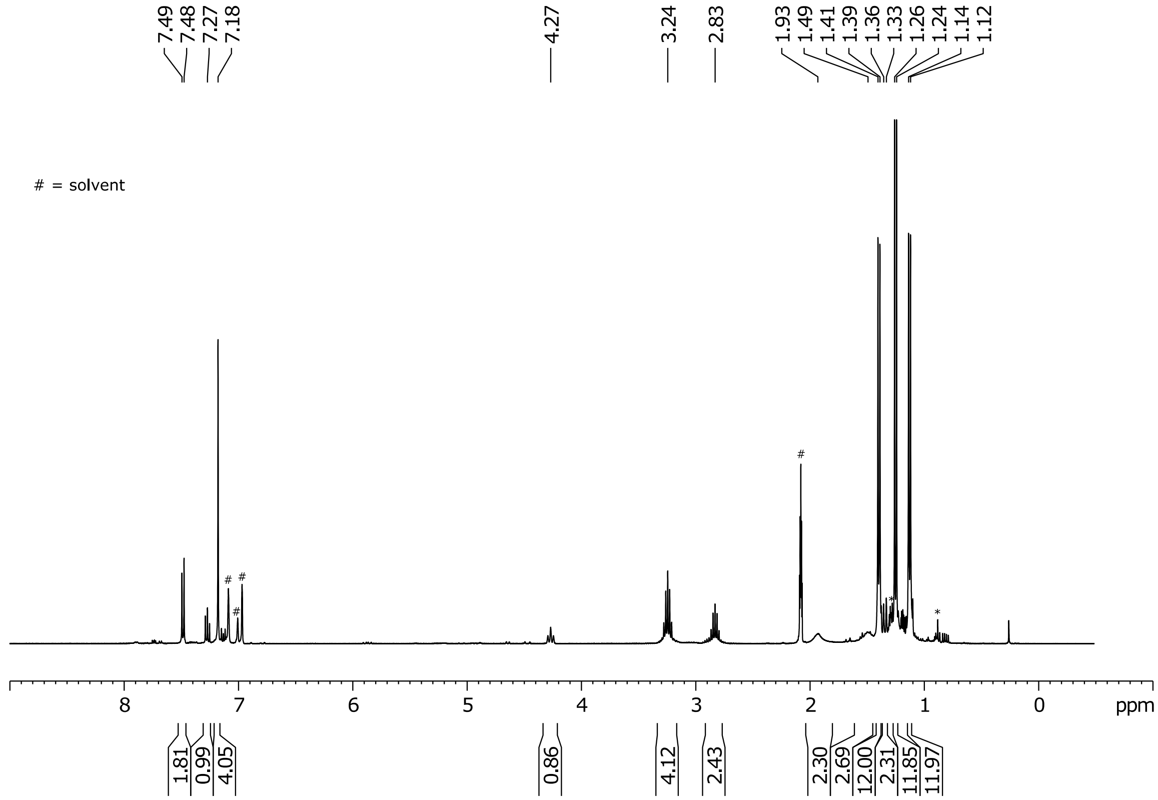
Figure S3. ^{207}Pb NMR spectrum of compound **2**.

NMR spectra of compound **3**



^{1}H-NMR of Ar*PbC(H)$_2$C(H)C(CH$_3$)$_2$ in Tol-d$_8$ at RT



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PULPROG          zg30
TD              52656
SOLVENT           Tol
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DS                  0
SWH       8305.647 Hz
FIDRES    0.157734 Hz
AQ       3.1698911 sec
RG                256
DW         60.200 usec
DE           6.00 usec
TE            299.2 K
D1      1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1          14.60 usec
PL1           -3.00 dB
PL1W     16.03799057 W
SFO1    400.1120007 MHz

F2 - Processing parameters
SI              65536
SF     400.1080428 MHz
WDW                EM
SSB      0
LB       0 Hz
GB       0
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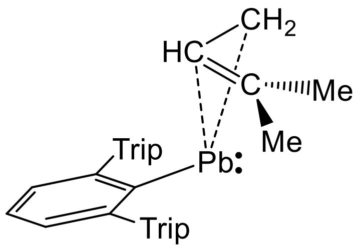
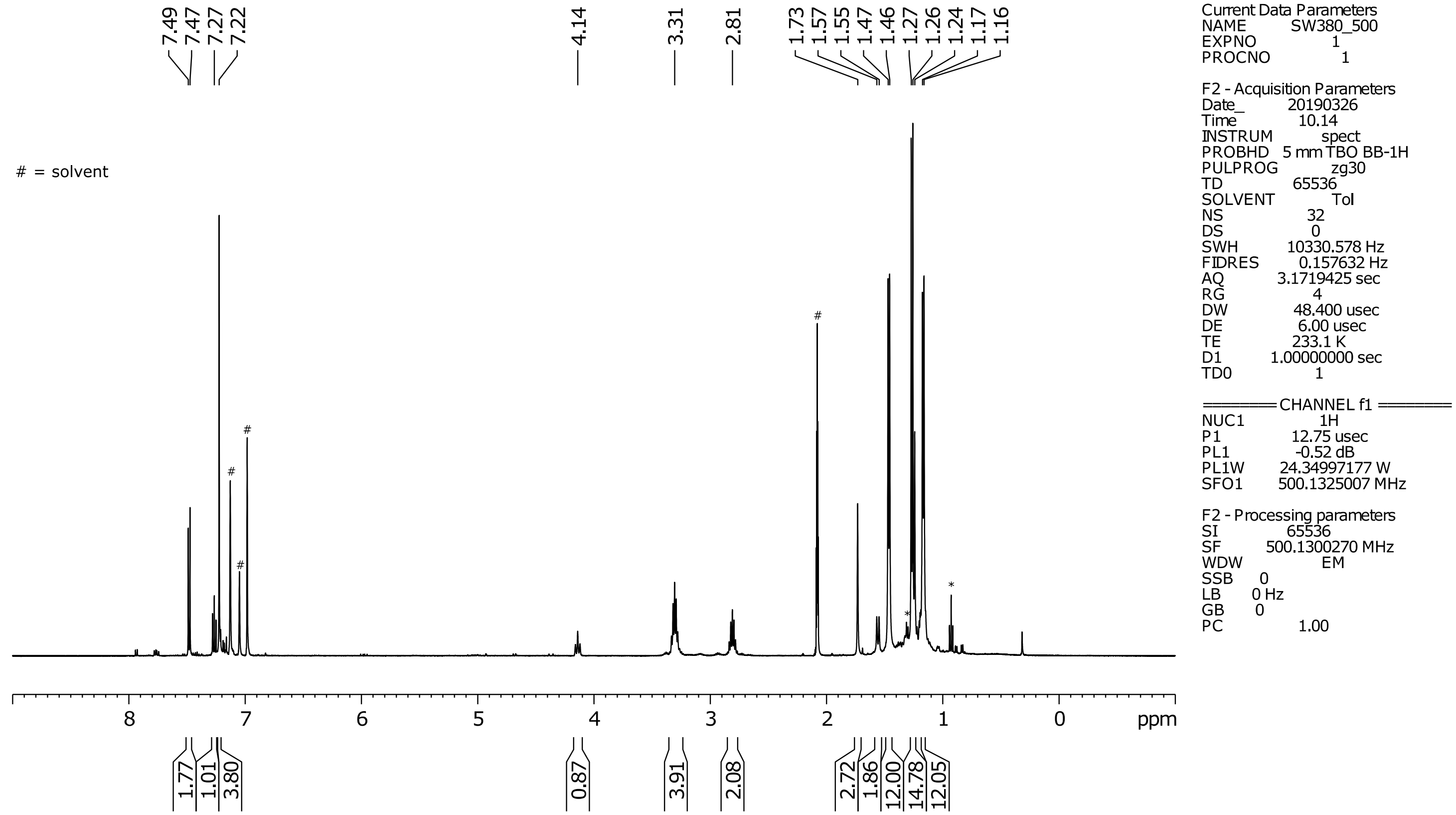
Figure S4. ^{1}H NMR spectrum of compound **3**. (* hexane)



^{1}H-NMR of Ar*PbC(H)$_2$C(H)C(CH$_3$)$_2$ in Tol-d$_8$ at –40°C



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EXPNO 1
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT Tol
NS 32
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 4
DW 48.400 usec
DE 6.00 usec
TE 233.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.75 usec
PL1 -0.52 dB
PL1W 24.34997177 W
SFO1 500.1325007 MHz

F2 - Processing parameters
SI 65536
SF 500.1300270 MHz
WDW EM
SSB 0
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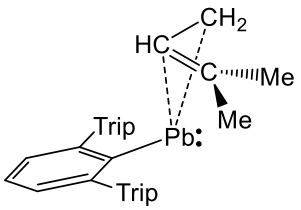
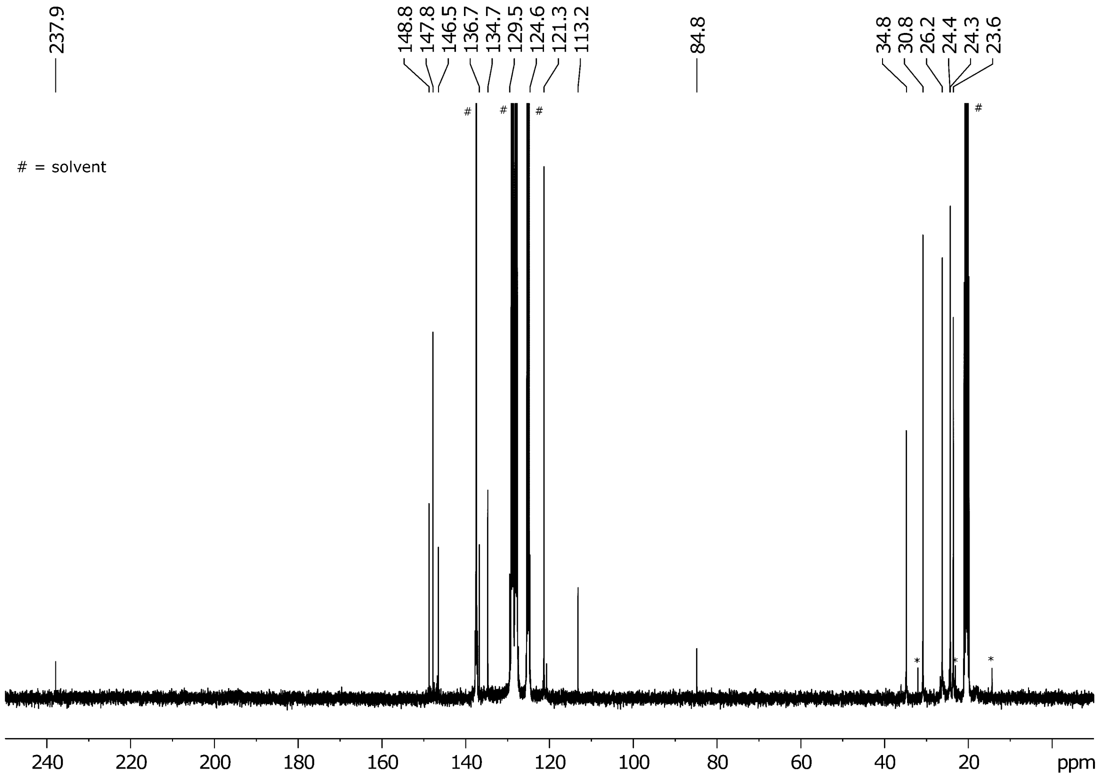
Figure S5. ^{1}H NMR spectrum (–40°C) of compound **3**. (* hexane)



^{13}C-NMR of Ar*PbC(H)$_2$C(H)C(CH$_3$)$_2$ in Tol-d$_8$ at RT



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PROCNO              1

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TD            53700
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NS            15500
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FIDRES    0.574752 Hz
AQ       0.8699400 sec
RG            32800
DW          16.200 usec
DE            6.00 usec
TE           299.2 K
D1     1.00000000 sec
D11    0.03000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1            13C
P1            13.50 usec
PL1           -4.16 dB
PL1W    78.55633545 W
SFO1    100.6198135 MHz

======== CHANNEL f2 ========
CPDPRG[2     waltz16
NUC2              1H
PCPD2         80.00 usec
PL2           -3.00 dB
PL12          11.77 dB
PL13          13.14 dB
PL2W    16.03799057 W
PL12W    0.53474891 W
PL13W    0.39007664 W
SFO2    400.1120007 MHz

F2 - Processing parameters
SI            65536
SF      100.6072070 MHz
WDW              EM
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GB      0
PC             1.40
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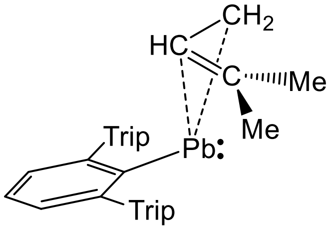
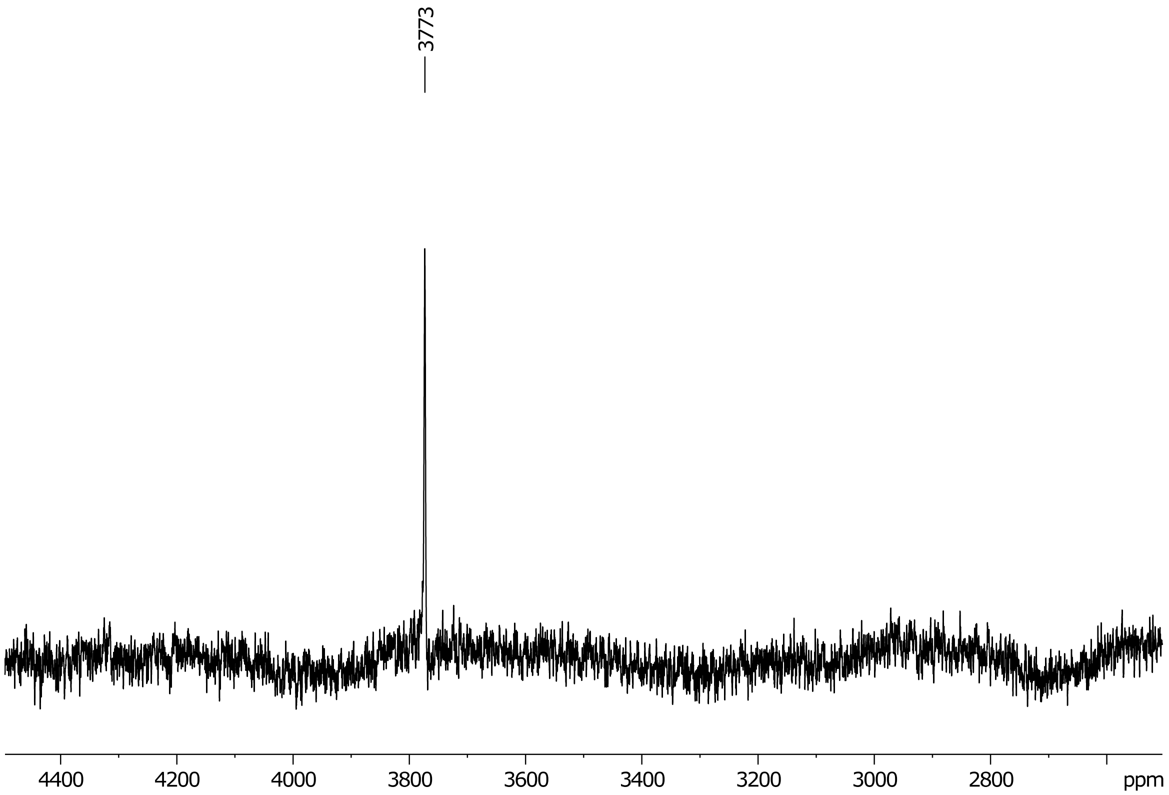
Figure S6. ^{13}C{^{1}H} NMR spectrum of compound **3**. (* hexane)



^{207}Pb-NMR of Ar*PbC(H)$_2$C(H)C(CH$_3$)$_2$ in Tol-d$_8$ at RT



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PROCNO                1

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TD               15608
SOLVENT            Tol
NS               56320
DS                   0
SWH        208333.328 Hz
FIDRES      13.347856 Hz
AQ         0.0374592 sec
RG                2050
DW           2.400 usec
DE           17.40 usec
TE             299.2 K
D1      0.05000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1             207Pb
P1            9.50 usec
PL1     0 dB
SFO1    104.9963977 MHz

F2 - Processing parameters
SI              131072
SF      104.6301920 MHz
WDW                 EM
SSB     0
LB            50.00 Hz
GB      0
PC                1.40
```

Figure S7. ^{207}Pb NMR spectrum of compound **3**.

References

1 J. Schneider, C. P. Sindlinger, K. Eichele, H. Schubert and L. Wesemann, *J. Am. Chem. Soc.*, 2017, **139**, 6542-6545.

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