Supporting Information B

Content

Data of crystallography

Table SI 1. Data of crystal structure determination.

	1	**3'**	**4**	**5**	**7**	**9**
Empirical formula	$C_{33}H_{77}BrGeIrP_3Si_4$	$C_{77}H_{89}BF_{24}GeIrP_3 \cdot (C_6H_4F_2)$	$C_{65}H_{89}BF_{24}IrP_3Si_4Sn \cdot (C_5H_{12})$	$C_{65}H_{92}BF_{24}GeIrNP_3Si_4 \cdot (C_6H_4F_2)$	$C_{65}H_{93}BF_{24}GeIrN_2P_3Si_4$ [+ solvent]	$C_{65}H_{91}BF_{24}GeIrOP_3Si_4$
M [g/mol]	1023.95	1953.12	1925.52	1938.46	1839.32	1825.35
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	2	2	2	2	2	4
a [Å]	9.4185(2)	13.1189(5)	13.2398(2)	14.2316(4)	14.1173(3)	13.5265(3)
b [Å]	19.3630(5)	16.5312(8)	17.9186(3)	16.3160(5)	14.5184(3)	29.1770(6)
c [Å]	13.1703(3)	20.4703(9)	19.4299(3)	20.1185(6)	21.7431(5)	20.9879(4)
α [°]	90	83.579(2)	79.5280(10)	72.480(2)	95.2730(10)	90
β [°]	91.8060(10)	77.942(2)	77.9630(10)	79.550(2)	93.8510(10)	99.1470(10)
γ [°]	90	86.174(2)	87.0490(10)	89.197(2)	96.0900(10)	90
V [Å^3]	2400.68(10)	4309.9(3)	4432.65(12)	4376.9(2)	4399.24(17)	8177.8(3)
D_c [g/cm^3]	1.416	1.505	1.443	1.471	1.389	1.482
μ [mm^{-1}]	4.447	2.045	1.976	2.065	2.048	2.203
F(000)	1040	1968	1940	1956	1856	3680
Crystal size [mm]	0.212 × 0.157 × 0.088	0.308 × 0.173 × 0.146	0.186 × 0.176 × 0.166	0.359 × 0.206 × 0.120	0.370 × 0.150 × 0.088	0.331 × 0.213 × 0.108
θ range [°]	3.516 – 32.077	2.496 – 26.373	2.087 – 27.483	1.916 – 33.765	1.418 – 27.533	1.817 – 26.372
Limiting indices	–14 ≤ h ≤ 14 –28 ≤ k ≤ 27 –19 ≤ l ≤ 19	–16 ≤ h ≤ 16 –20 ≤ k ≤ 20 –25 ≤ l ≤ 25	–16 ≤ h ≤ 17 –23 ≤ k ≤ 22 –25 ≤ l ≤ 25	–22 ≤ h ≤ 22 –25 ≤ k ≤ 25 –31 ≤ l ≤ 31	–18 ≤ h ≤ 18 –18 ≤ k ≤ 18 –28 ≤ l ≤ 28	–16 ≤ h ≤ 16 –36 ≤ k ≤ 36 –26 ≤ l ≤ 26
Reflections collected	46487	68208	70740	176819	97899	182816
Independent reflexes	16308	17584	20160	34481	20087	16666
R_{int}	0.0359	0.0598	0.0409	0.0365	0.0374	0.0515
Completeness [%]	99.6	99.8	99.5	99.7	99.6	99.7
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmission (max., min.)	0.6357, 0.7463	0.572, 0.754	0.6379, 0.7456	0.524, 0.790	0.6749, 0.7456	0.6260, 0.7463
Parameters / restraints	417 / 1	1090 / 367	985 / 371	1190 / 1476	939 / 4	1068 / 1607
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.0249, 0.0503	0.0480, 0.1191	0.0527, 0.1291	0.0382, 0.0881	0.0413, 0.0978	0.0328, 0.0758
$R1$, w$R2$ (all data)	0.0285, 0.0511	0.0626, 0.1269	0.0659, 0.1364	0.0490, 0.0916	0.0532, 0.1027	0.0386, 0.0790
Goof on F^2	1.016	1.053	1.050	1.153	1.048	1.086
Peak / hole [$e \cdot$ Å^{-3}]	1.913, –0.632	2.556, –2.073	2.572, –2.248	2.006, –1.696	1.721, –1.418	3.543, –1.136
CCDC	2208289	2208294	2208298	2208291	2208292	2208301

Table SI 2. Data of crystal structure determination.

	10	**12b**	**13**	**19**	**20**	**21**
Empirical formula	$C_{65}H_{91}BF_{24}IrOP_3Si_4Sn$	$C_{65}H_{90}BBrF_{24}IrP_3Si_4Sn$	$C_{65}H_{91}BF_{24}GeIrP_3Si_4$ [+ solvent]	$C_{42}H_{96}IrP_3Si_4Sn\cdot(C_5H_{12})$	$C_{37}H_{81}IrOP_2Si_4Sn$	$C_{38}H_{81}IrO_2P_2Si_4Sn$
M [g/mol]	1871.42	1934.28	1809.29	1189.54	1027.20	1055.21
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	*Pccn*	$P2_1/c$	$P2_1/c$	$P\bar{1}$	*Pnma*
Z	4	8	8	4	2	4
a [Å]	13.4895(3)	25.6267(5)	14.2730(3)	13.3326(2)	12.0193(3)	25.7861(6)
b [Å]	29.3424(7)	33.9714(6)	32.5399(8)	22.5297(4)	12.6486(3)	18.3283(4)
c [Å]	21.1320(5)	19.4414(4)	37.8100(9)	20.3855(3)	18.8678(4)	10.7792(2)
α [°]	90	90	90	90	86.6680(10)	90
β [°]	99.5010(10)	90	98.9900(10)	95.4370(10)	73.4460(10)	90
γ [°]	90	90	90	90	64.6390(10)	90
V [Å^3]	8249.6(3)	16925.2(6)	17344.8(7)	6095.84(17)	2477.78(10)	5094.42(19)
D_c [g/cm^3]	1.507	1.518	1.386	1.296	1.377	1.376
μ [mm^{-1}]	2.122	2.539	2.075	2.775	3.372	3.284
F(000)	3752	7712	7296	2472	1048	2152
Crystal size [mm]	0.705 × 0.159 × 0.141	0.265 × 0.165 × 0.111	0.287 × 0.173 × 0.147	0.232 × 0.215 × 0.197	0.361 × 0.315 × 0.154	0.242 × 0.240 × 0.144
θ range [°]	1.813 – 33.142	1.966 – 27.507	1.257 – 29.158	3.144 – 27.102	2.982 – 29.608	3.318 – 33.154
Limiting indices	–20 ≤ h ≤ 20 –44 ≤ k ≤ 45 –32 ≤ l ≤ 32	–33 ≤ h ≤ 33 –43 ≤ k ≤ 43 –25 ≤ l ≤ 25	–19 ≤ h ≤ 18 –40 ≤ k ≤ 44 –50 ≤ l ≤ 51	–17 ≤ h ≤ 17 –24 ≤ k ≤ 28 –26 ≤ l ≤ 26	–16 ≤ h ≤ 16 –17 ≤ k ≤ 17 –26 ≤ l ≤ 26	–39 ≤ h ≤ 39 –28 ≤ k ≤ 28 –16 ≤ l ≤ 16
Reflections collected	308659	198543	337314	66512	63641	148848
Independent reflexes	31401	19329	46453	13402	13837	9952
R_{int}	0.0569	0.1063	0.0659	0.0520	0.0389	0.0396
Completeness [%]	99.7	99.7	99.8	99.7	99.5	99.4
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmission (max., min.)	0.5679, 0.7476	0.6700, 0.7456	0.587, 0.750	0.6294, 0.7471	0.5581, 0.7459	0.6905, 0.7465
Parameters / restraints	1111 / 1790	991 / 894	1890 / 711	561 / 3	592 / 9	251 / 0
$R1$, w$R2$ [$I > 2\sigma(I)$]	0.0449, 0.1028	0.0408, 0.0791	0.0660, 0.1255	0.0256, 0.0601	0.0402, 0.0954	0.0250, 0.0514
$R1$, w$R2$ (all data)	0.0527, 0.1084	0.0741, 0.0922	0.1085, 0.1389	0.0306, 0.0626	0.0513, 0.1040	0.0299, 0.0534
Goof on F^2	1.166	1.025	1.117	1.025	1.024	1.106
Peak / hole [$e \cdot$ Å^{-3}]	3.020, –1.649	1.899, –1.440	2.105, –2.635	2.833, –0.966	1.609, –1.425	1.793, –1.715
CCDC	2208295	2208293	2208297	2208299	2208296	2208300

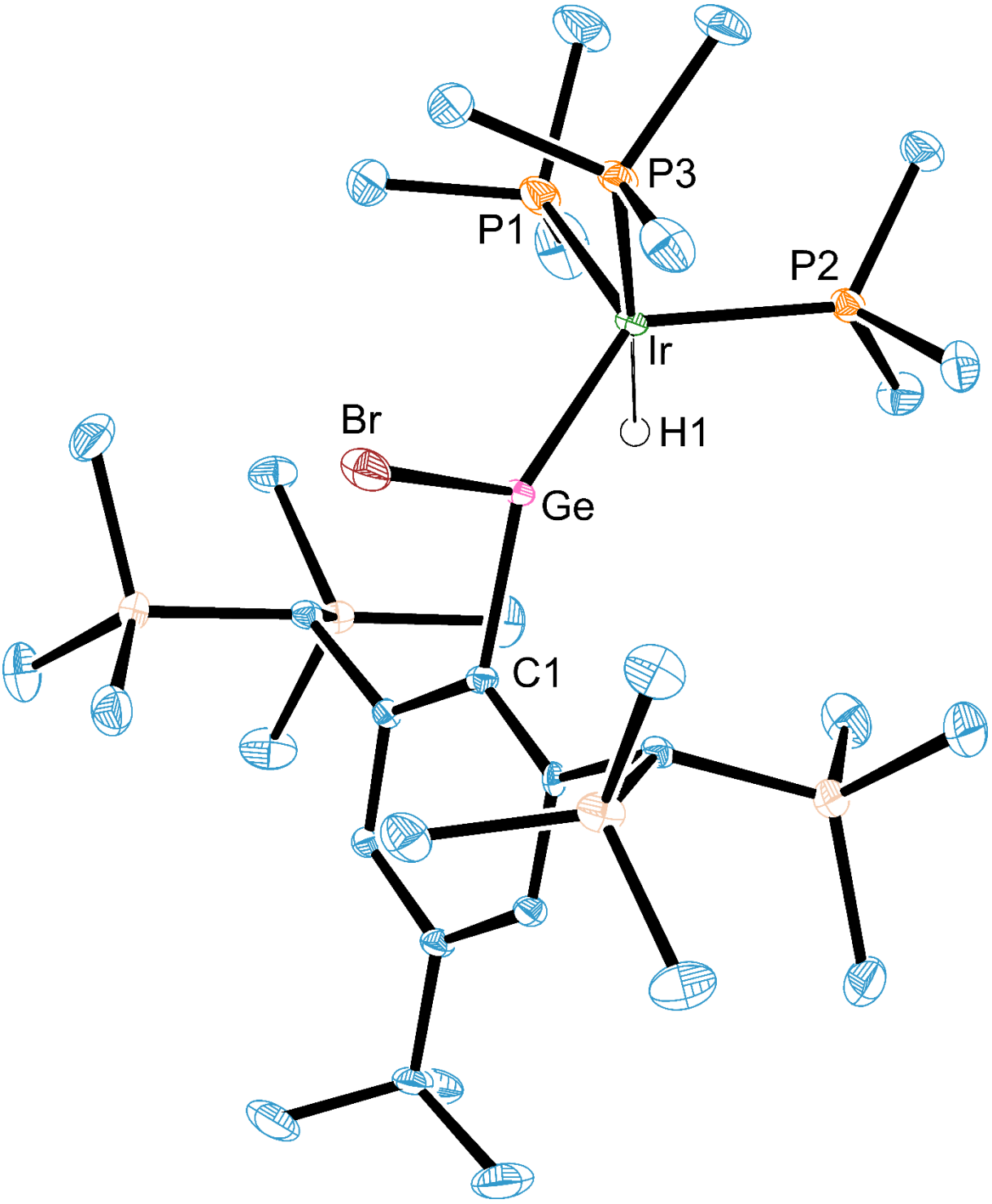


Figure SI 1. ORTEP of the molecular structure of [TbbGeBrIrH(PMe_3)$_3$ (**1**). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms except the Ir-H have been omitted. Selected interatomic distances [Å] and angles [°]: Ge-Br 2.4563(4), Ir-Ge 2.2879(3), Ir-P1 2.2687(10), Ir-P2 2.2791(9), Ir-P3 2.3158(9), Ir-H1 1.63(4), Ir-Ge-C1 140.8(1), Ir-Ge-Br 122.8(1), C1-Ge-Br 96.3(1).

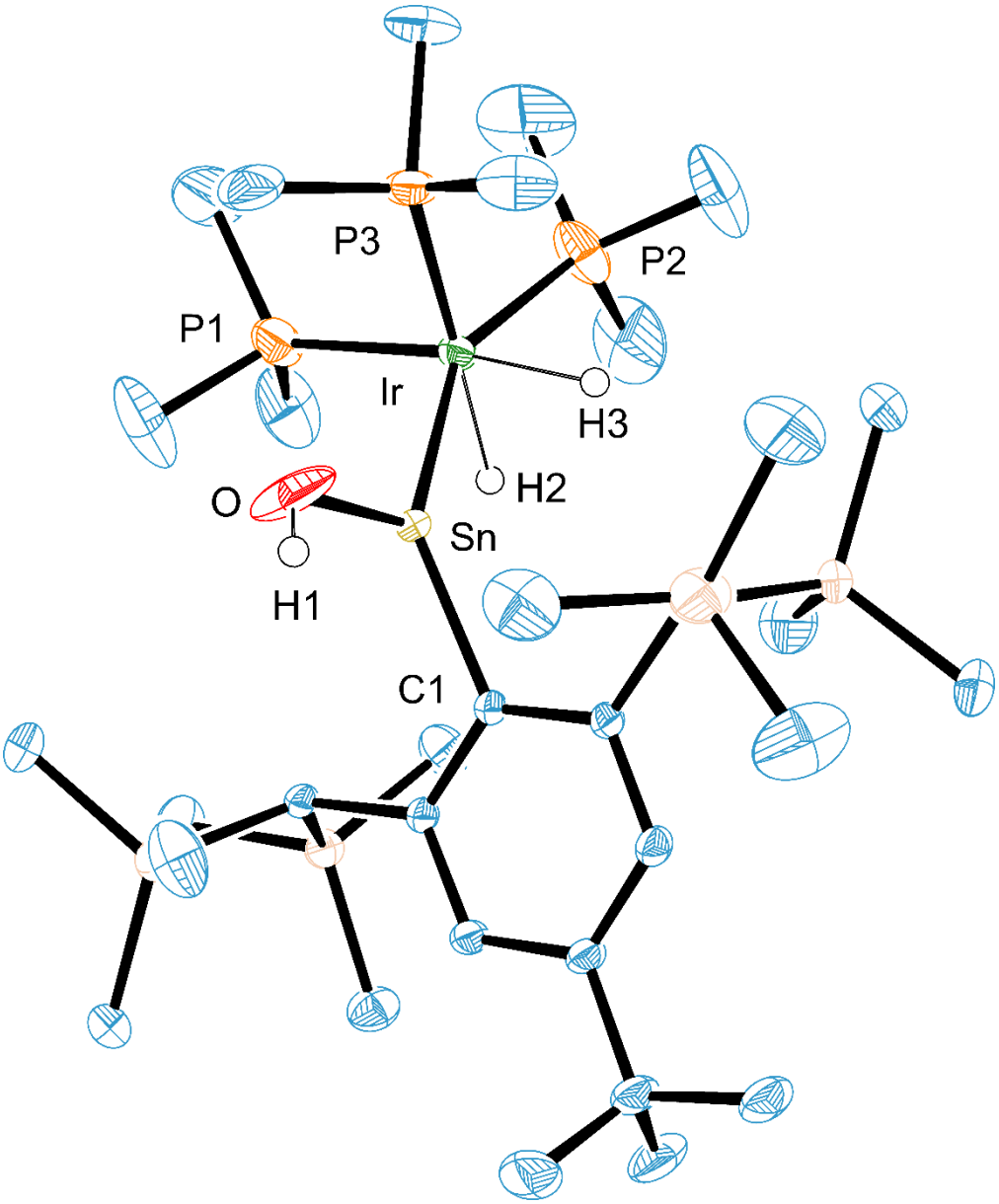


Figure SI 2. ORTEP of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**10**). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms except the Ir-H have been omitted. Selected interatomic distances [Å] and angles [°]: Sn-O 1.995(3), Sn-C1 2.126(2), Sn-Ir 2.5078(4), P1-Ir 2.3389(10), P2-Ir 2.2849(9), P3-Ir 2.3508(9), O-Sn-C1 101.08(10), O-Sn-Ir 118.8(1), C1-Sn-Ir 138.9(1).

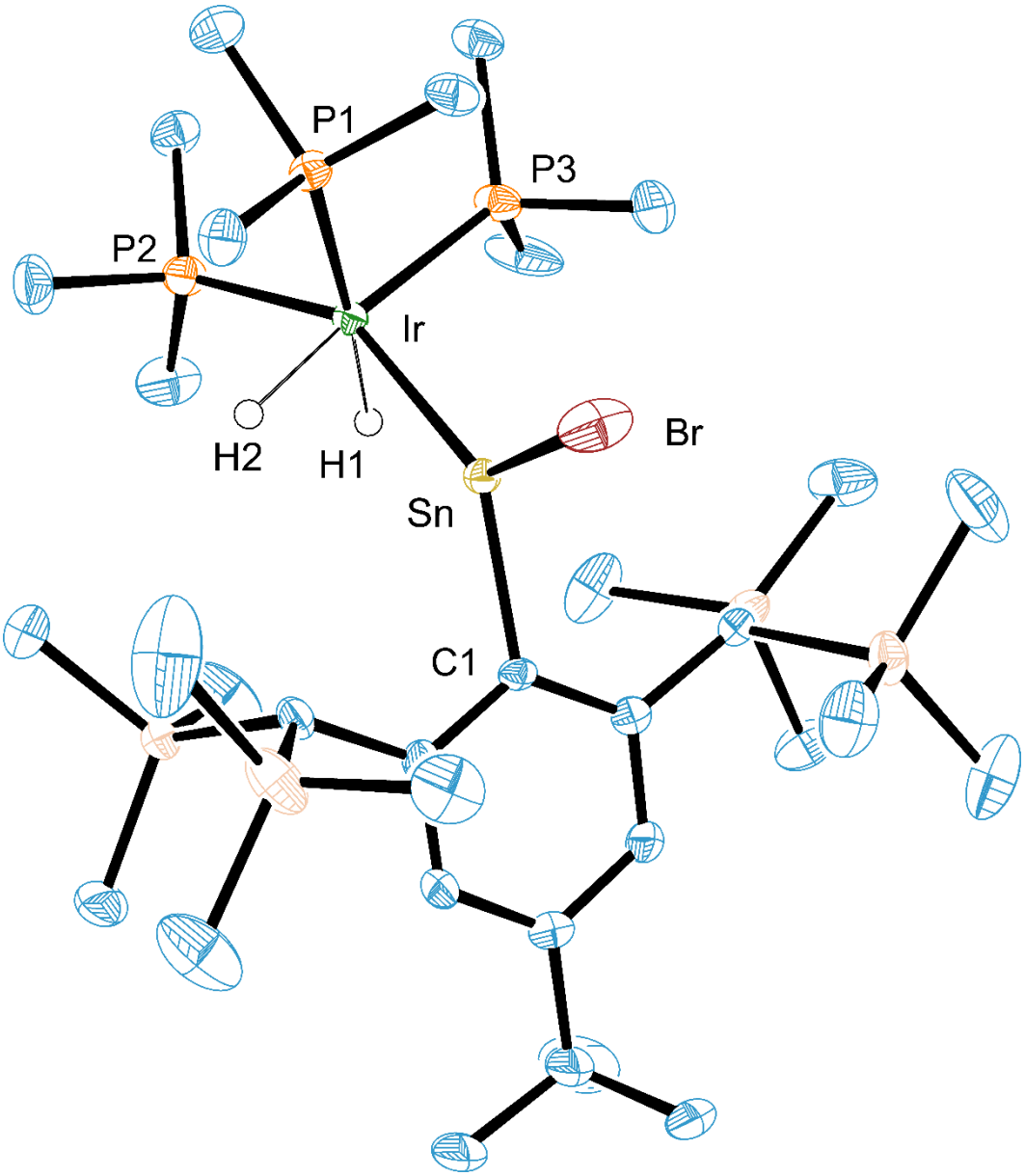
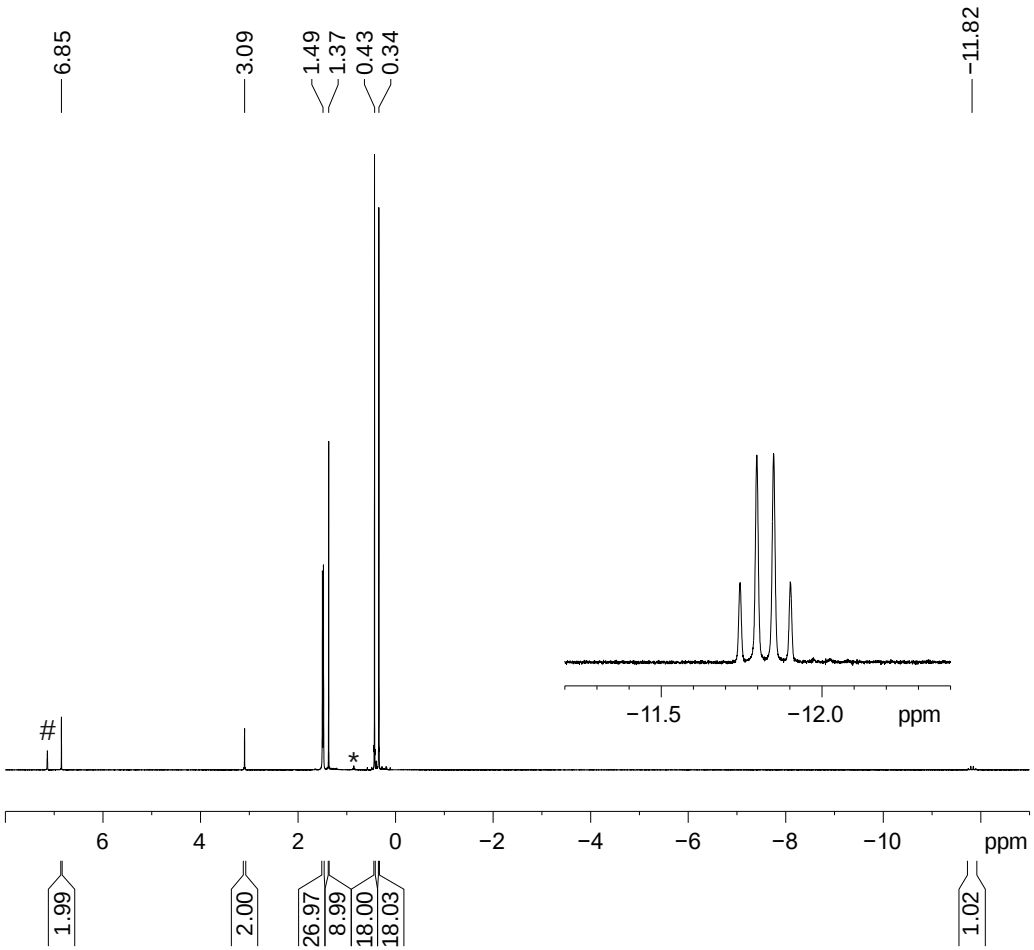


Figure SI 3. ORTEP of [TbbSnBrIrH$_2$(PMe$_3$)$_3$][BAr$^F_4$] (**12b**). Thermal ellipsoids are shown at 50 % probability level. Hydrogen atoms except the Ir-H have been omitted. Selected interatomic distances [Å] and angles [°]: Sn-C1 2.130(4), Sn-Ir 2.5167(3), Sn-Br 2.5387(6), P1-Ir 2.3463(11), P2-Ir 2.2955(12), P3-Ir 2.3351(12), Ir-H1 1.54(6), Ir-H2 1.67(5), C1-Sn-Ir 137.4(1), C1-Sn-Br 99.9(1), Ir-Sn-Br 121.9(1).

NMR spectra of compounds **1**-**21**

NMR Spectra of compound **1**.

^{1}H NMR spectrum of TbbGeBrIrH(PMe_3)$_3$ in benzene-d$_6$ (#) at rt. * *n*-pentane.



Current Data Parameters
NAME JB08K_24112021_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211124
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 12019.230 Hz
FIDRES 0.228259 Hz
AQ 2.1904895 sec
RG 228
DW 41.600 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

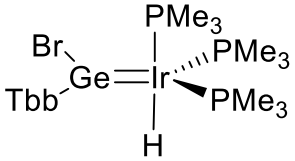
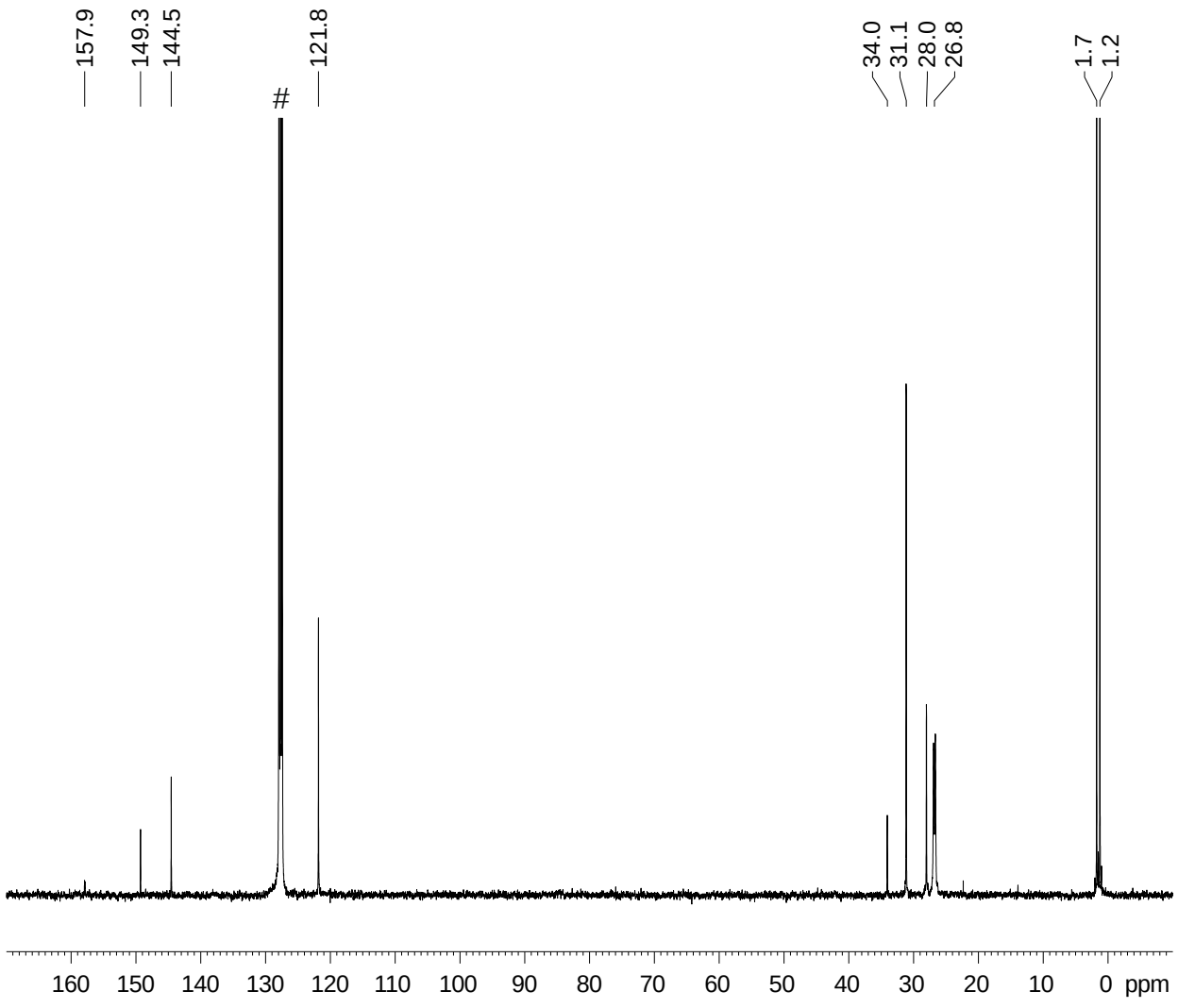


Figure SI 4. ^{1}H NMR spectrum of **1**.

$^{13}C\{^{1}H\}$ NMR spectrum of TbbGeBrIrH(PMe_3)$_3$ in benzene-d_6 (#) at rt.




```
Current Data Parameters
NAME     JB08K_24112021_400N
EXPNO            12
PROCNO            1

F2 - Acquisition Parameters
Date_         20211125
Time              2.09
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          udeft
TD             22218
SOLVENT          C6D6
NS              5734
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG               32800
DW              16.200 usec
DE               6.00 usec
TE              299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1             -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8              1.39 dB
SP13             1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8          0.500
SPOAL13         0.500
SPOFFS8           0 Hz
SPOFFS13          0 Hz

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

F2 - Processing parameters
SI              131072
SF         100.6077400 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
```

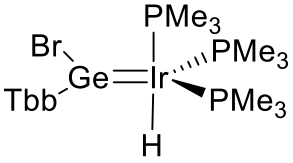
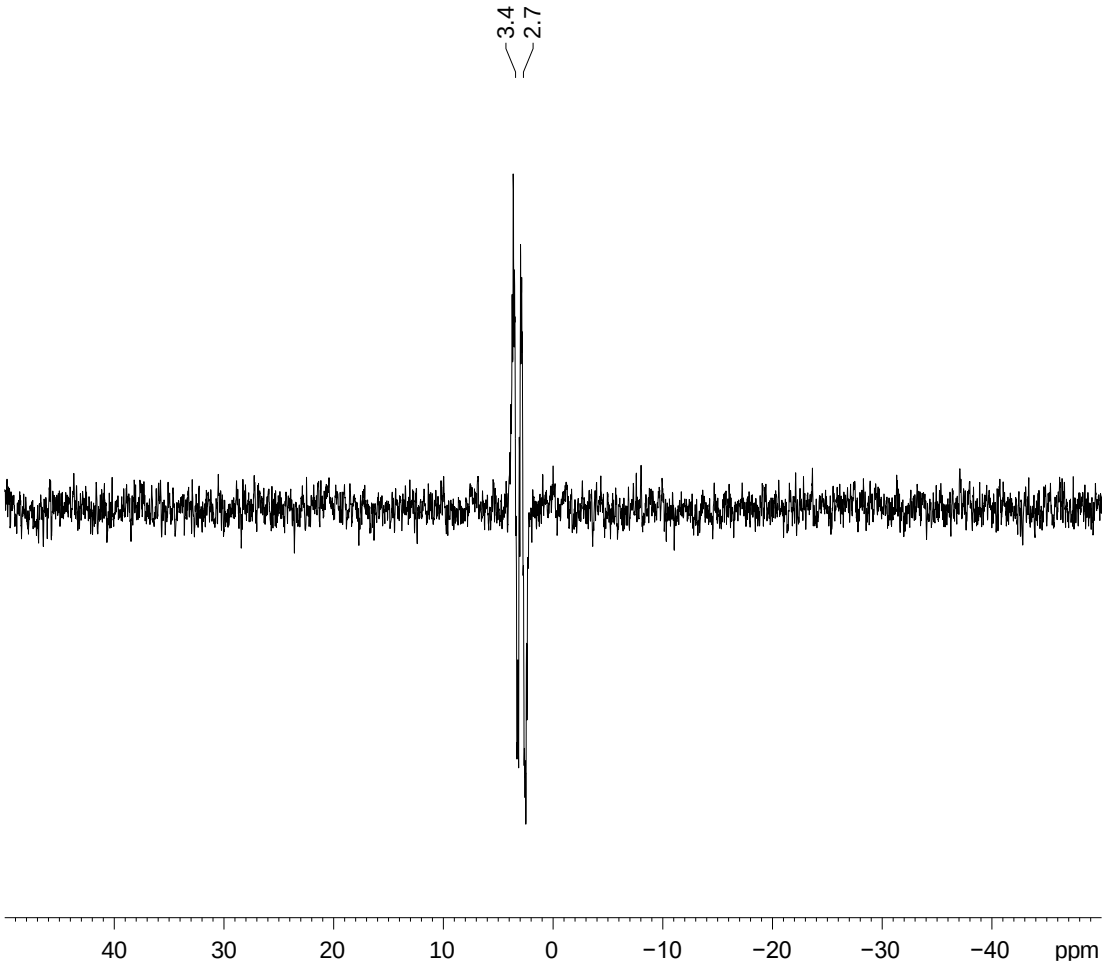


Figure SI 5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1**.

^{29}Si NMR spectrum of Tbb GeBrIrH(PMe$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME JB08K_24112021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211124
Time 14.30 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273411 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

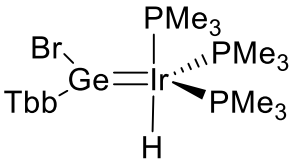
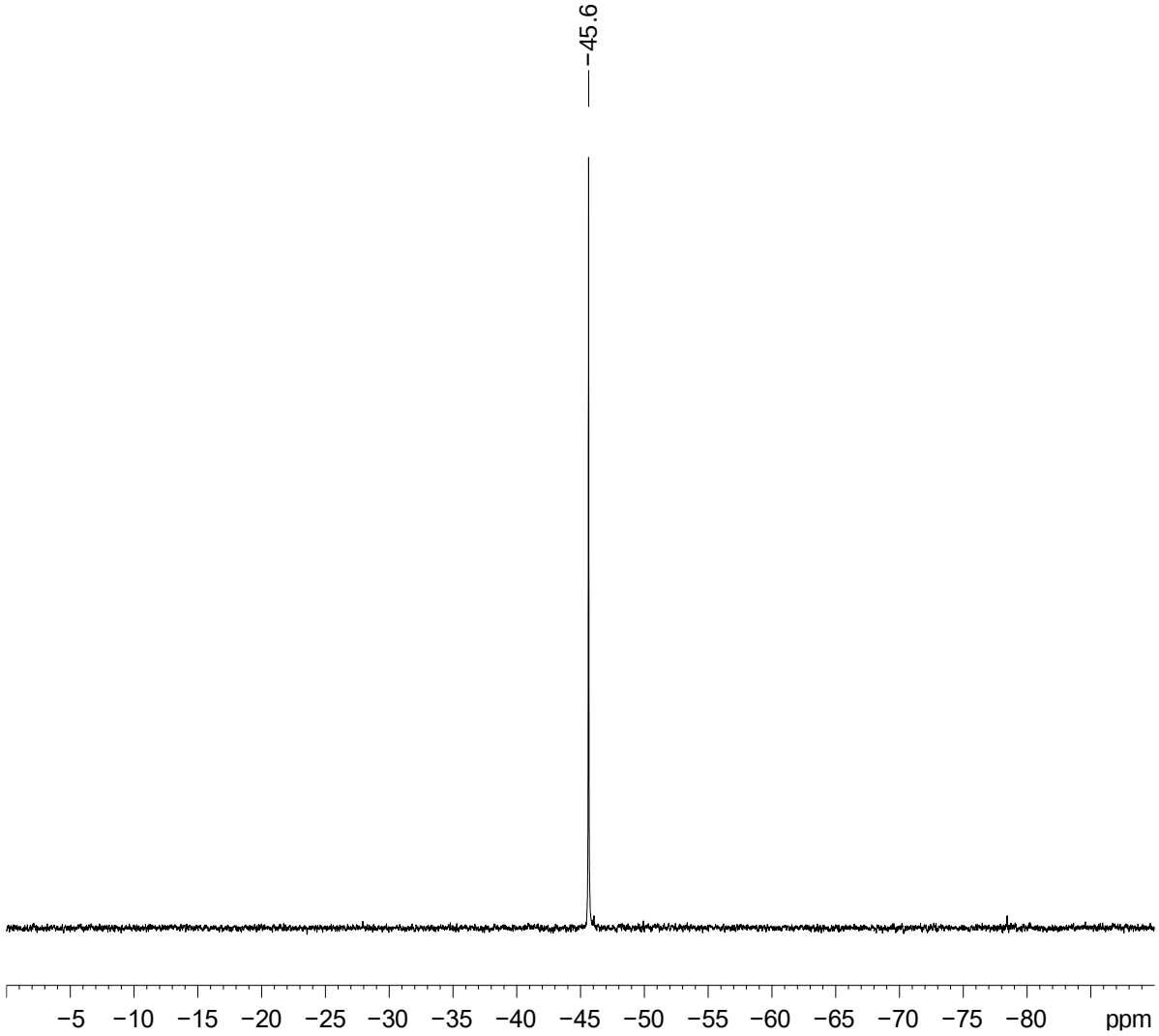


Figure SI 6. ^{29}Si NMR of compound **1**.

$^{31}P\{^{1}H\}$ NMR spectrum of TbbGeBrIrH(PMe_3)$_3$ in benzene-d_6 at rt.



Current Data Parameters
NAME JB08K_24112021_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211124
Time 20.10
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 128
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1053000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

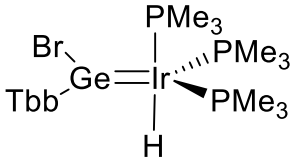
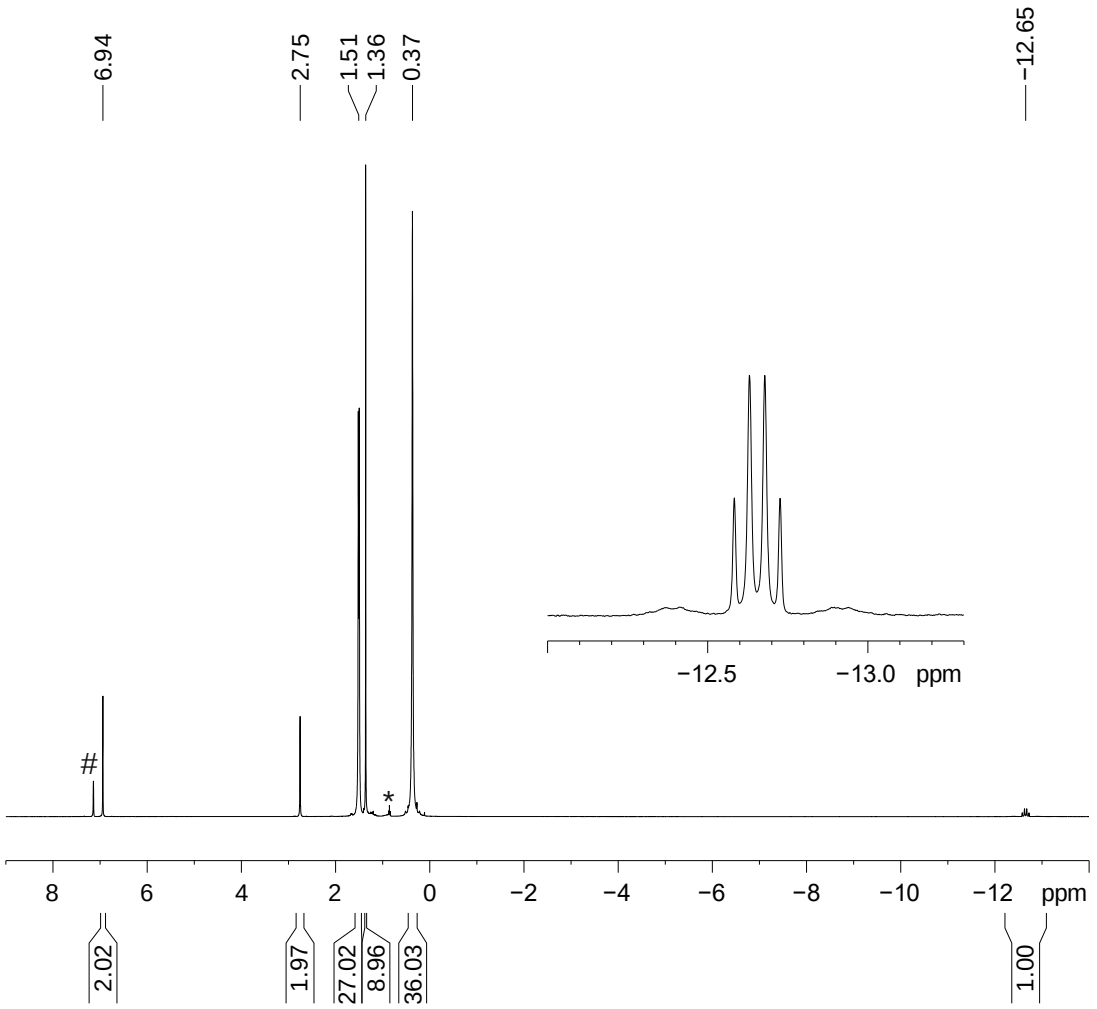


Figure SI 7. $^{31}P\{^{1}H\}$ NMR spectrum of compound **1**.

NMR spectra of compound **2**.

^{1}H NMR spectrum of TbbSnBrIrH(PMe$_3$)$_3$ in benzene-d$_6$ (#) at rt. * *n*-pentane.



Current Data Parameters
NAME MA733_08102021_400
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211008
Time 16.11
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 20000.000 Hz
FIDRES 0.379824 Hz
AQ 1.3164001 sec
RG 161
DW 25.000 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

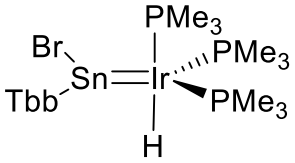
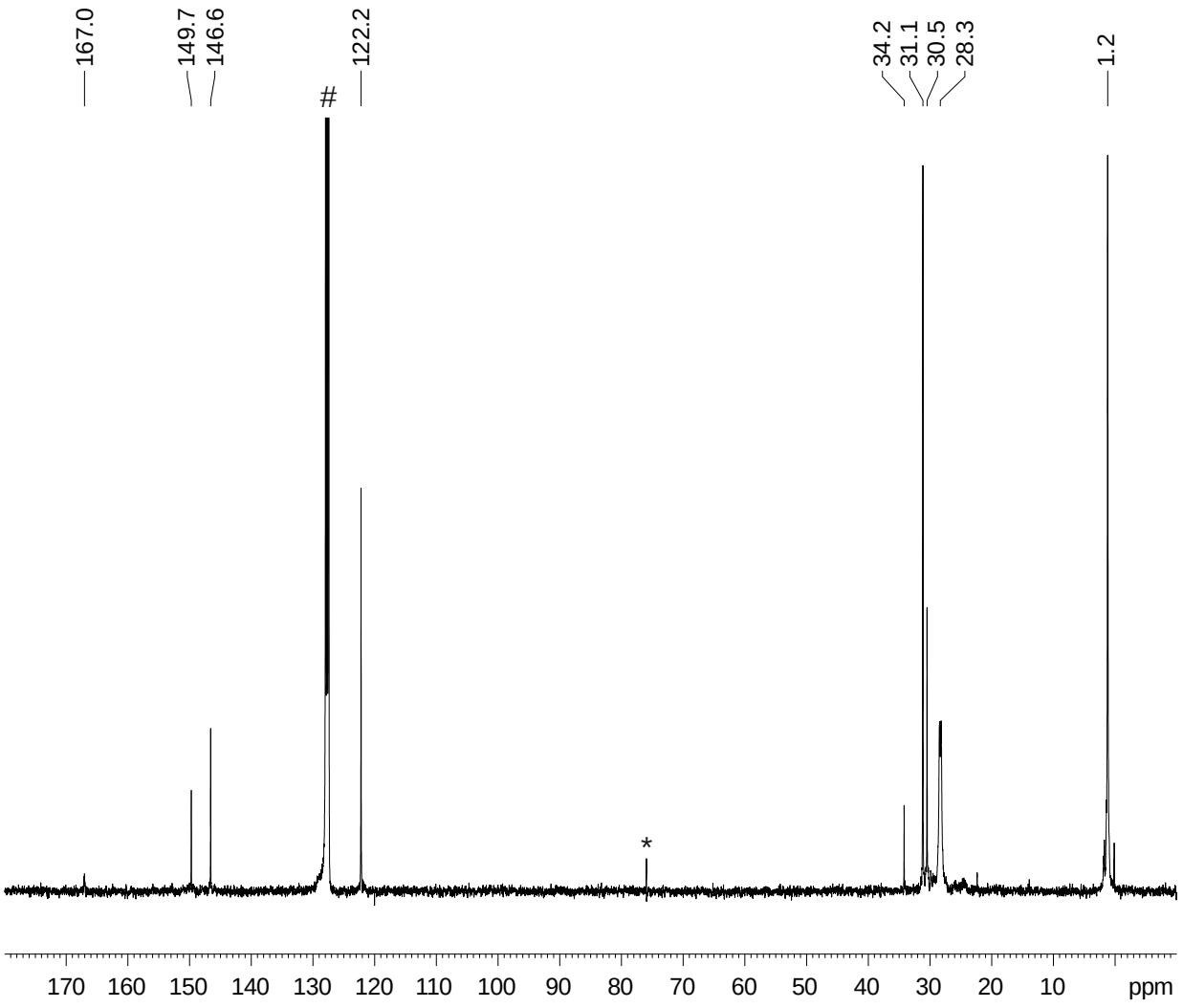
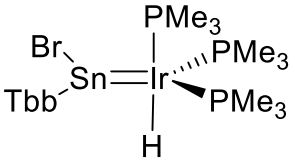


Figure SI 8. ^{1}H NMR spectrum of compound **2**.

$^{13}C\{^{1}H\}$ NMR spectrum of TbbSnBrIrH(PMe_3)$_3$ in benzene-d_6 (#) at rt. * unknown impurity.

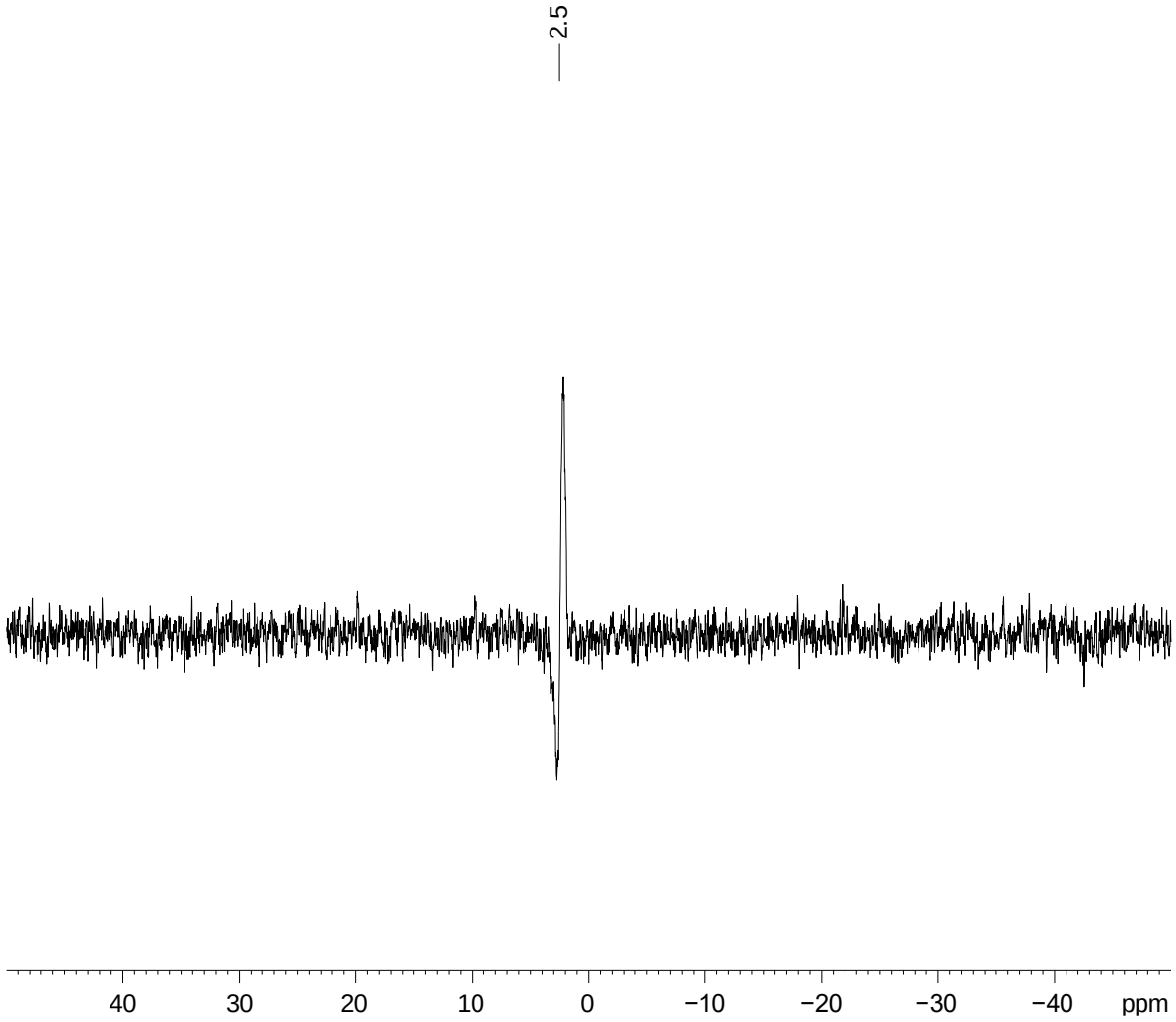





```
Current Data Parameters
NAME     MA722+723K_29102021_400
EXPNO          14
PROCNO          1

F2 - Acquisition Parameters
Date_        20211030
Time             2.20
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          udeft
TD            22218
SOLVENT          C6D6
NS             5734
DS                0
SWH         30864.197 Hz
FIDRES       1.389153 Hz
AQ          0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE             299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             13C
P1             13.50 usec
P13          2000.00 usec
P26           500.00 usec
PL1            -4.16 dB
PL1W       78.55633545 W
SFO1      100.6198135 MHz
SP8            1.39 dB
SP13           1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8          0.500
SPOAL13         0.500
SPOFFS8           0 Hz
SPOFFS13          0 Hz

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

F2 - Processing parameters
SI             131072
SF         100.6077400 MHz
WDW               EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.40
```

Figure SI 9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2**.

^{29}Si NMR spectrum of TbbSnBrIrH(PMe $_3$)$_3$ in benzene-d $_6$ at rt.



Current Data Parameters
NAME MA722+723K_02112021_300N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211102
Time 19.39 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273786 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

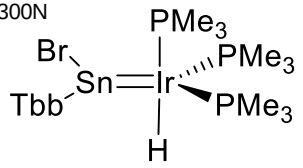
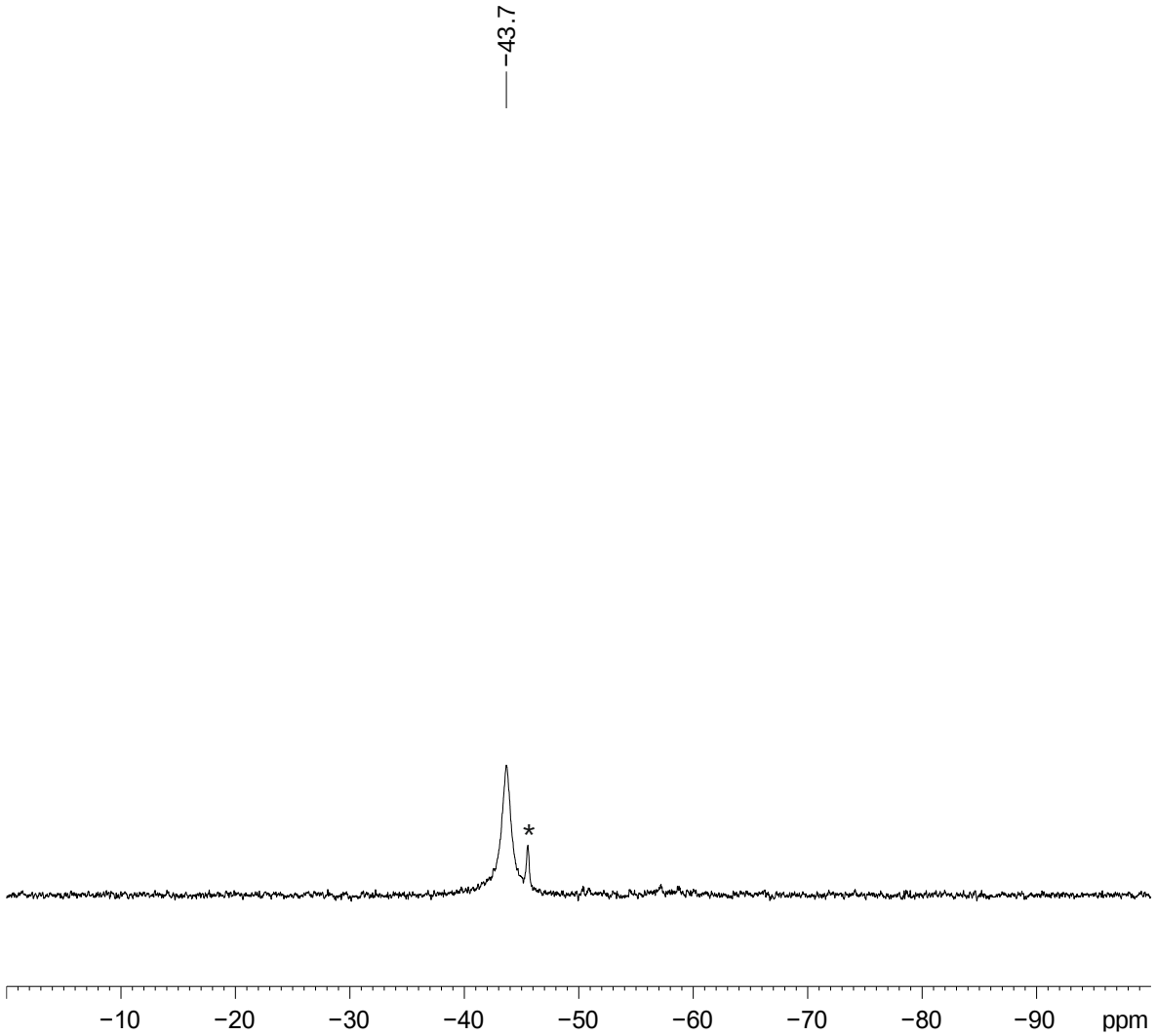


Figure SI 10. ^{29}Si NMR spectrum of compound **2**.

$^{31}P\{^{1}H\}$ NMR spectrum of TbbSnBrIrH(PMe_3)$_3$ in benzene-d_6 at rt. * unknown impurity.




```
Current Data Parameters
NAME     MA722+723_29102021_400N_31P
EXPNO              12
PROCNO              1

F2 − Acquisition Parameters
Date_          20211029
Time              20.13
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD              88150
SOLVENT            C6D6
NS                 384
DS                   0
SWH           65789.477 Hz
FIDRES         0.746336 Hz
AQ            0.6699400 sec
RG                23100
DW                7.600 usec
DE                6.00 usec
TE                299.2 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               31P
P1               11.00 usec
PL1              −3.00 dB
PL1W         45.10684967 W
SFO1        161.9674970 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              131072
SF          161.9674970 MHz
WDW                EM
SSB                 0
LB               7.00 Hz
GB                  0
PC                1.40
```

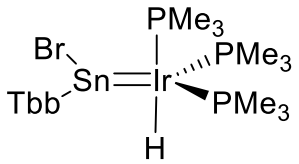
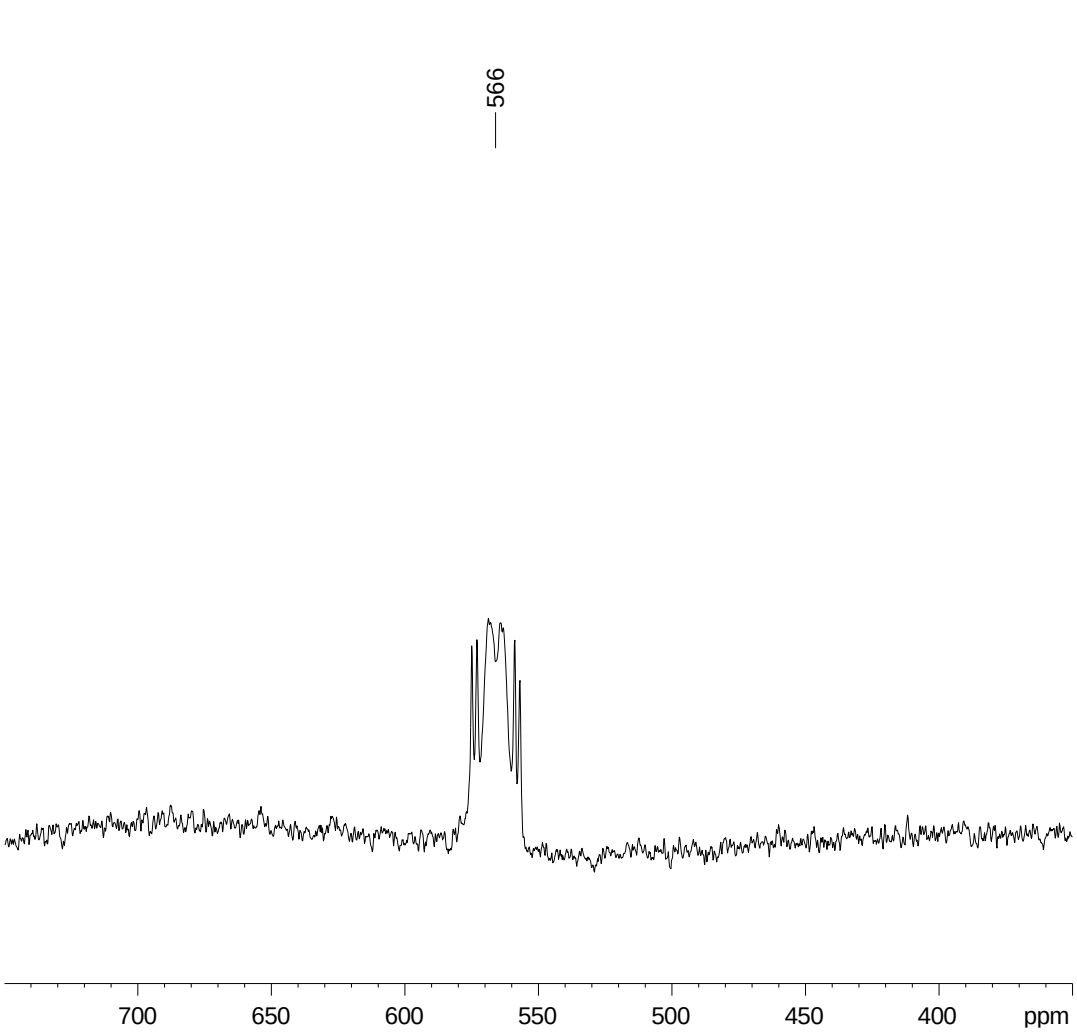


Figure SI 11. $^{31}P\{^{1}H\}$ NMR spectrum of compound **2**.

^{119}Sn NMR spectrum of TbbSnBrIrH(PMe $_3$)$_3$ in benzene-d $_6$ at rt.



Current Data Parameters
NAME MA722+723K_02112021_300N
EXPNO 23
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211102
Time 21.25 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 153600
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.9875260 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

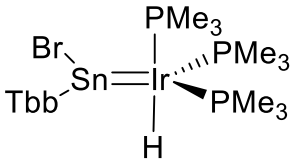
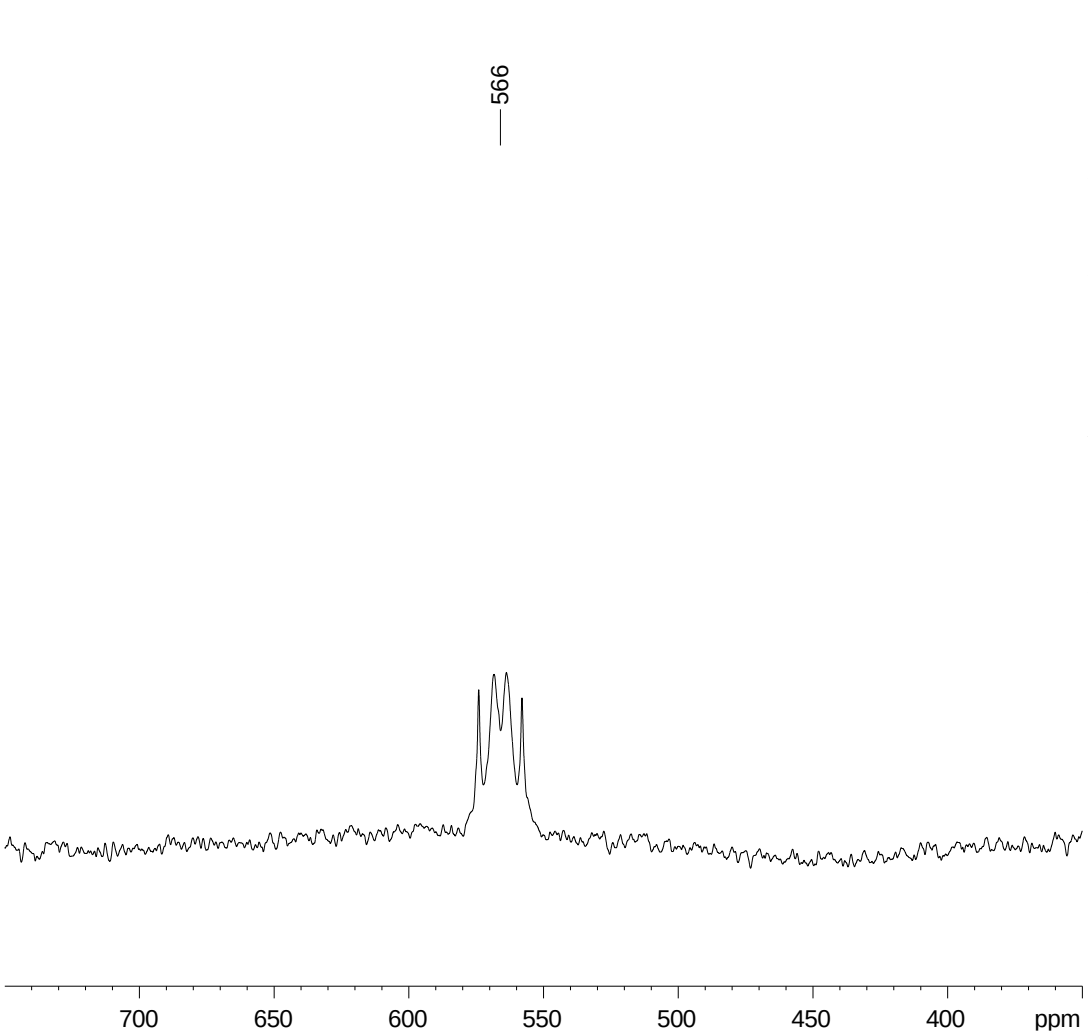


Figure SI 12. ^{119}Sn NMR spectrum of compound **2**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of TbbSnBrIrH(PMe_3)$_3$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA722+723K_02112021_300N
EXPNO 33
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211103
Time 1.53 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 46080
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.9875258 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

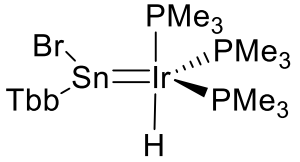
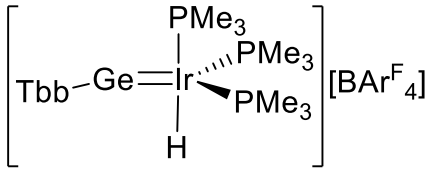
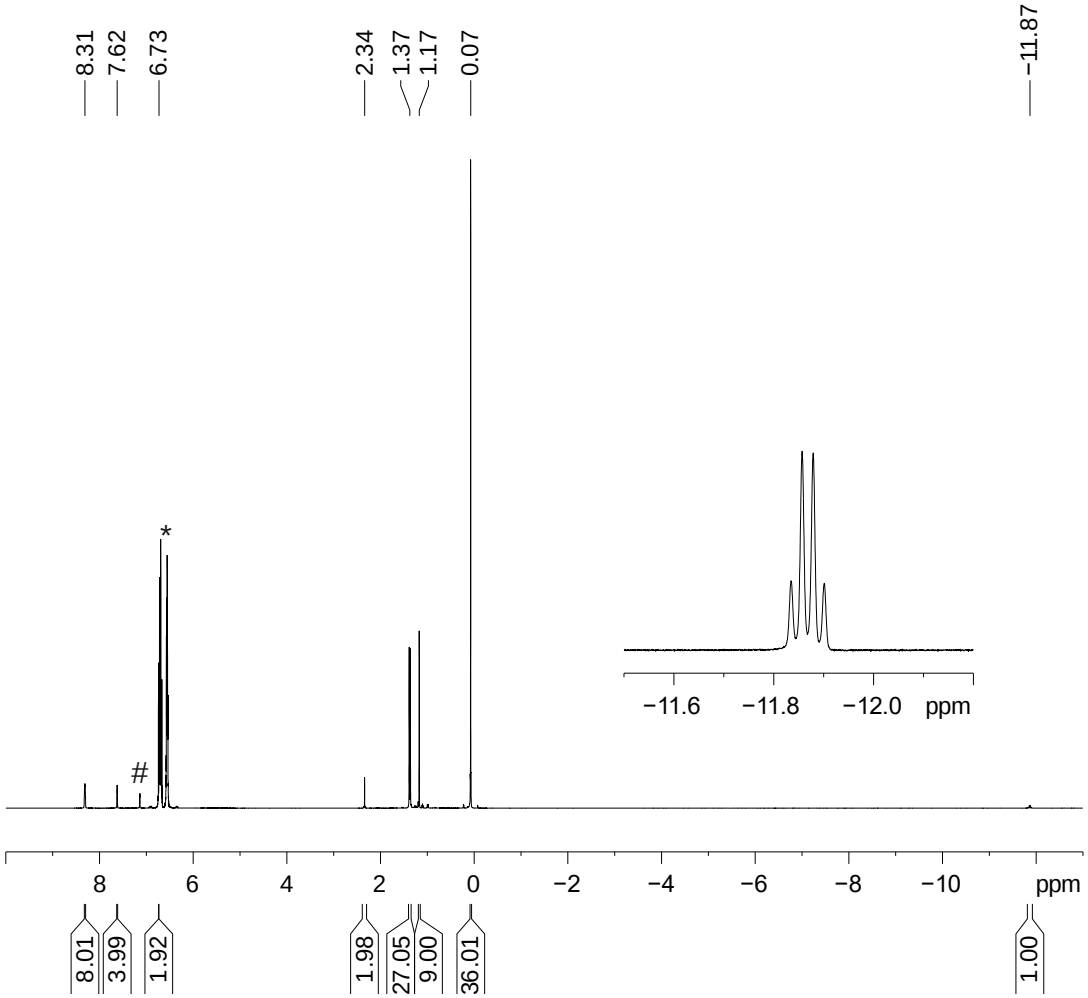


Figure SI 13. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **2**.

NMR spectra of compound **3**.

^{1}H NMR spectrum of [TbbGeIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA744K_03112021_400N
EXPNO 10
PROCNO 1

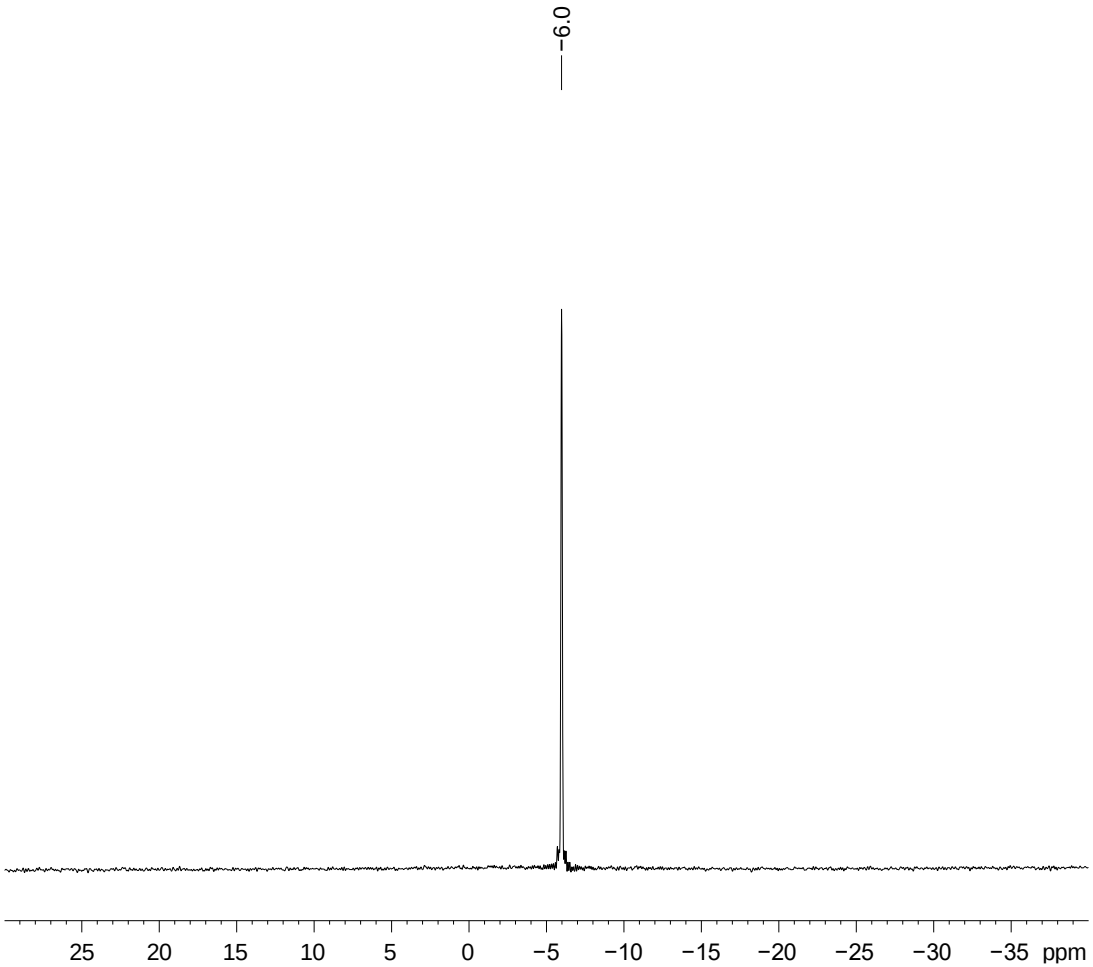
F2 − Acquisition Parameters
Date_ 20211103
Time 20.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 10416.667 Hz
FIDRES 0.197825 Hz
AQ 2.5274880 sec
RG 40.3
DW 48.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 14. ^{1}H NMR spectrum of compound **3**.

^{11}B NMR spectrum of [TbbGeIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA744_13102021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211013
Time 14.30 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

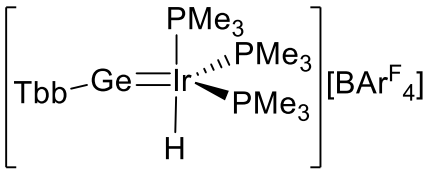
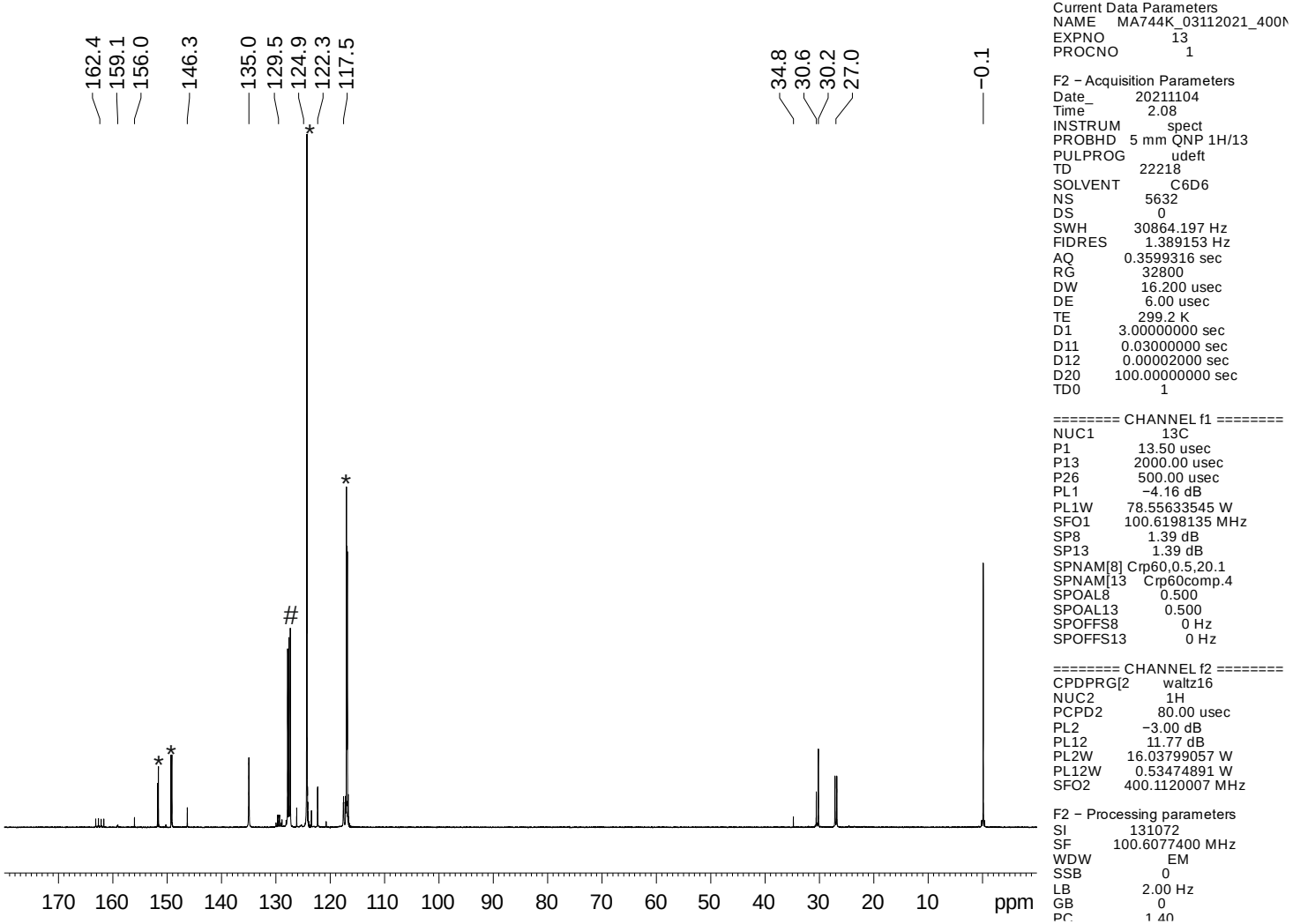


Figure SI 15. ^{11}B NMR spectrum of compound **3**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbGeIrH(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME      MA744K_03112021_400N
EXPNO             13
PROCNO             1

F2 - Acquisition Parameters
Date_          20211104
Time              2.08
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD             22218
SOLVENT           C6D6
NS                5632
DS                   0
SWH           30864.197 Hz
FIDRES         1.389153 Hz
AQ           0.3599316 sec
RG                32800
DW             16.200 usec
DE              6.00 usec
TE              299.2 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20        100.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1             -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8              1.39 dB
SP13             1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

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

F2 - Processing parameters
SI             131072
SF         100.6077400 MHz
WDW                EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
```

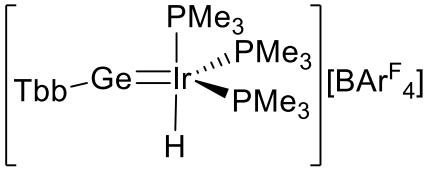
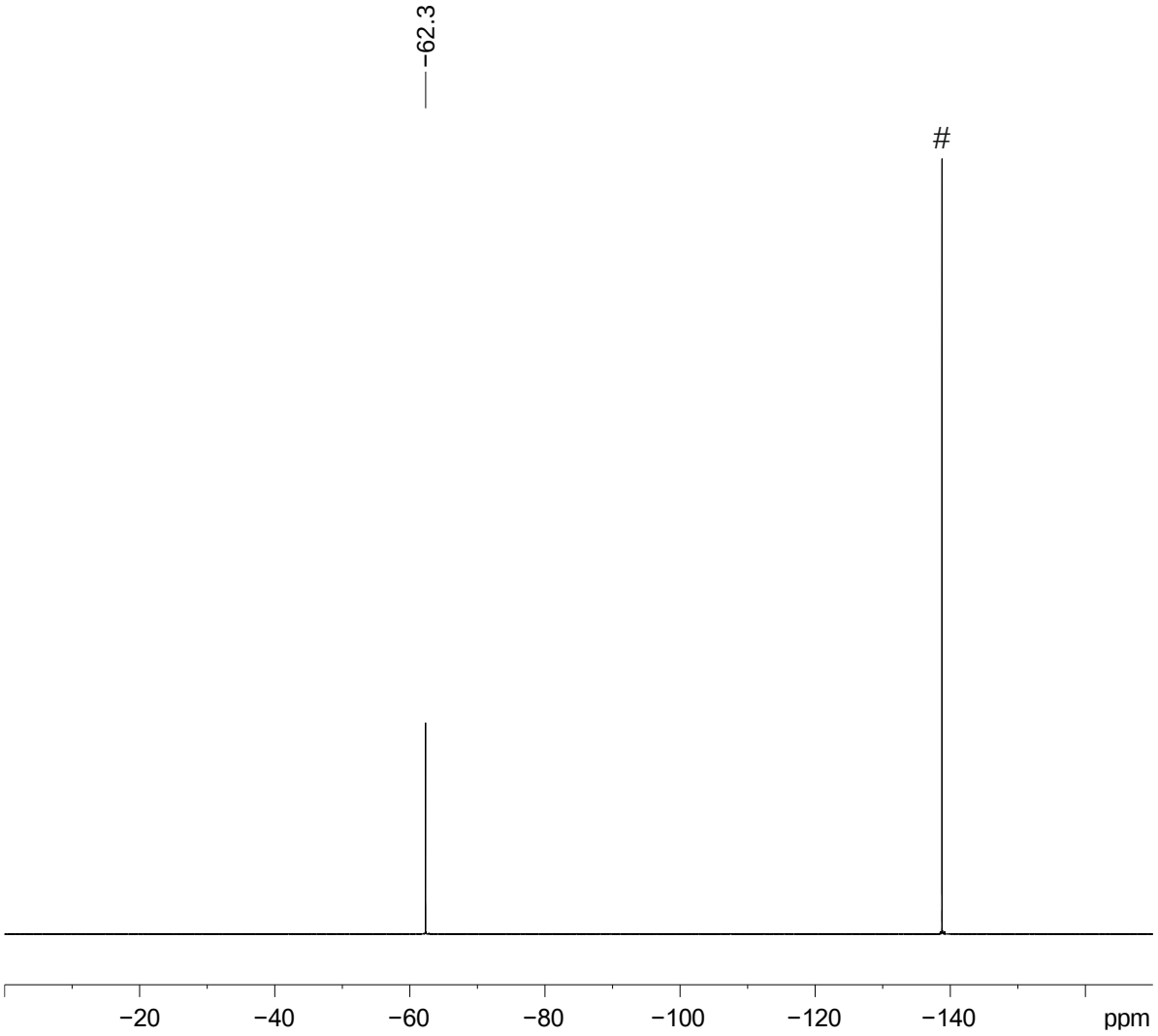


Figure SI 16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3**.

$^{19}F\{^{1}H\}$ NMR spectrum of $[TbbGeIrH(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA744K_03112021_400I
EXPNO 20
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211104
Time 7.42
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn
TD 131072
SOLVENT C6D6
NS 32
DS 0
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6553600 sec
RG 4100
DW 5.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 19F
P1 18.75 usec
PL1 −2.92 dB
PL1W 30.50645256 W
SFO1 376.4306030 MHz

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

F2 − Processing parameters
SI 262144
SF 376.4795470 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

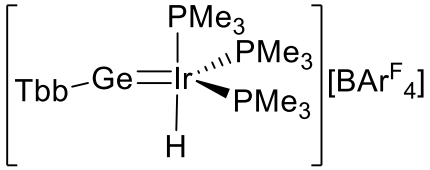
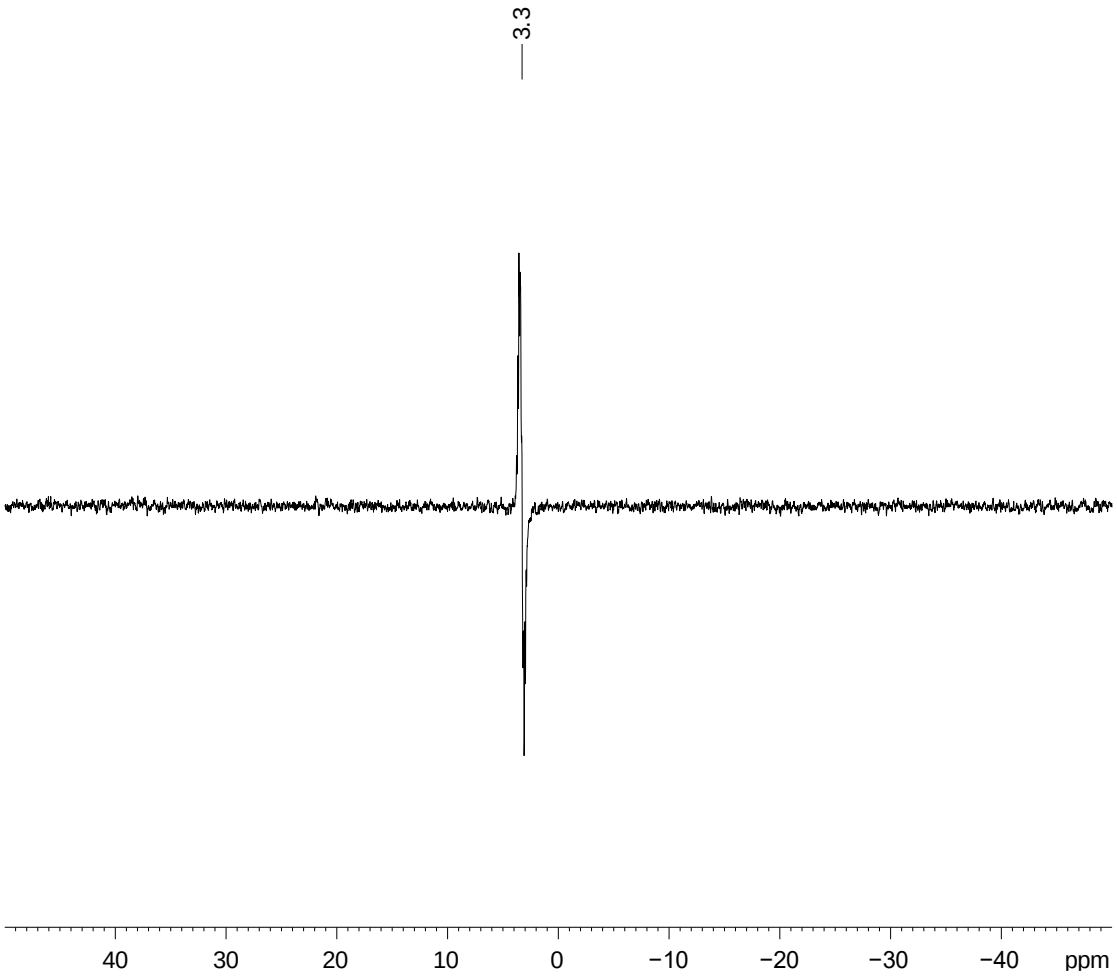


Figure SI 17. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3**.

^{29}Si NMR spectrum of [TbbGeIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA744_13102021_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211013
Time 14.40 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273408 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

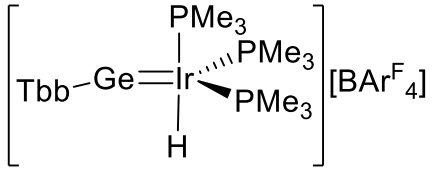
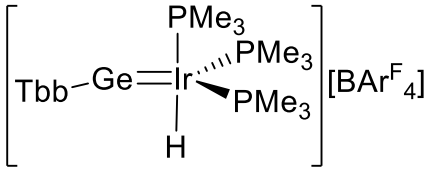
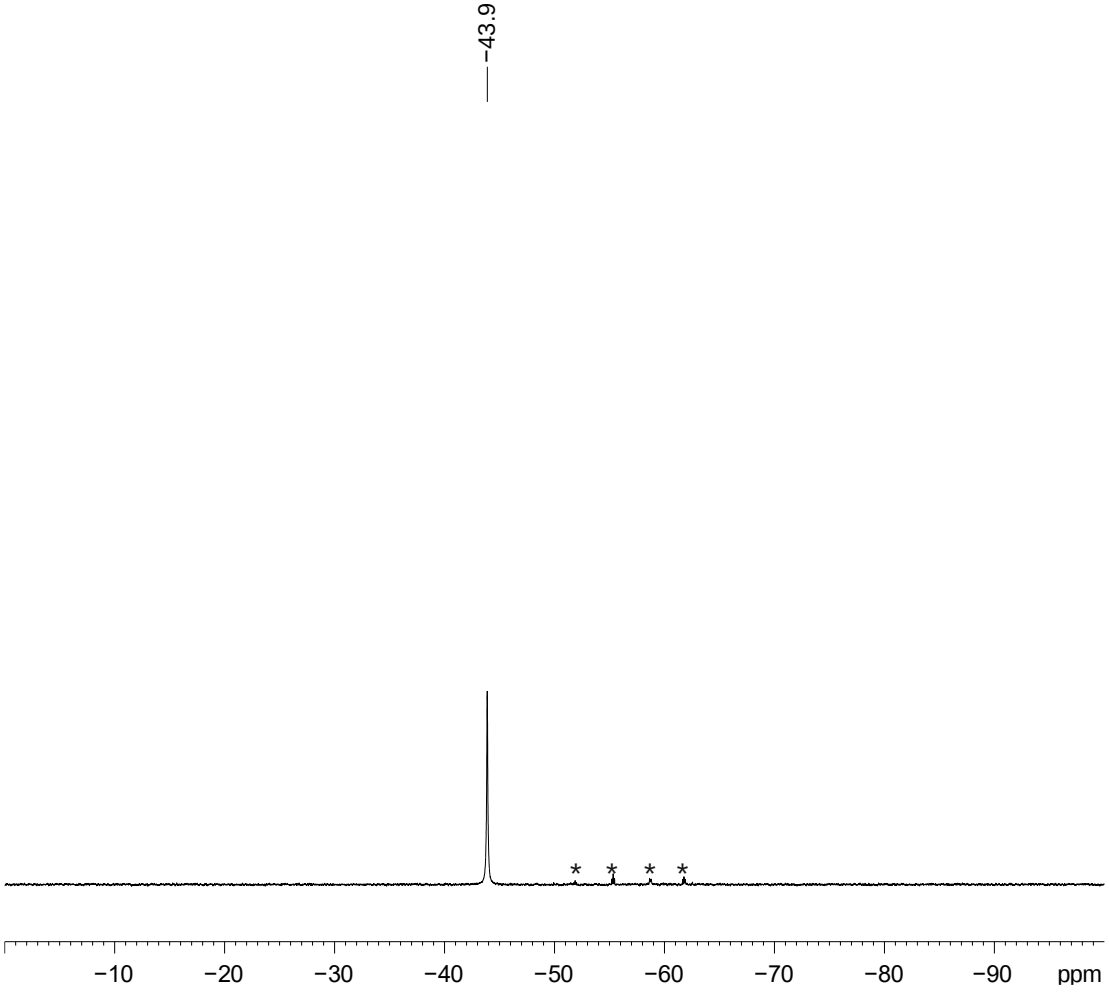


Figure SI 18. ^{29}Si NMR spectrum of compound **3**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbGeIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 and *o*-difluorobenzene at rt.
* unknown impurity and hydrolysis product.



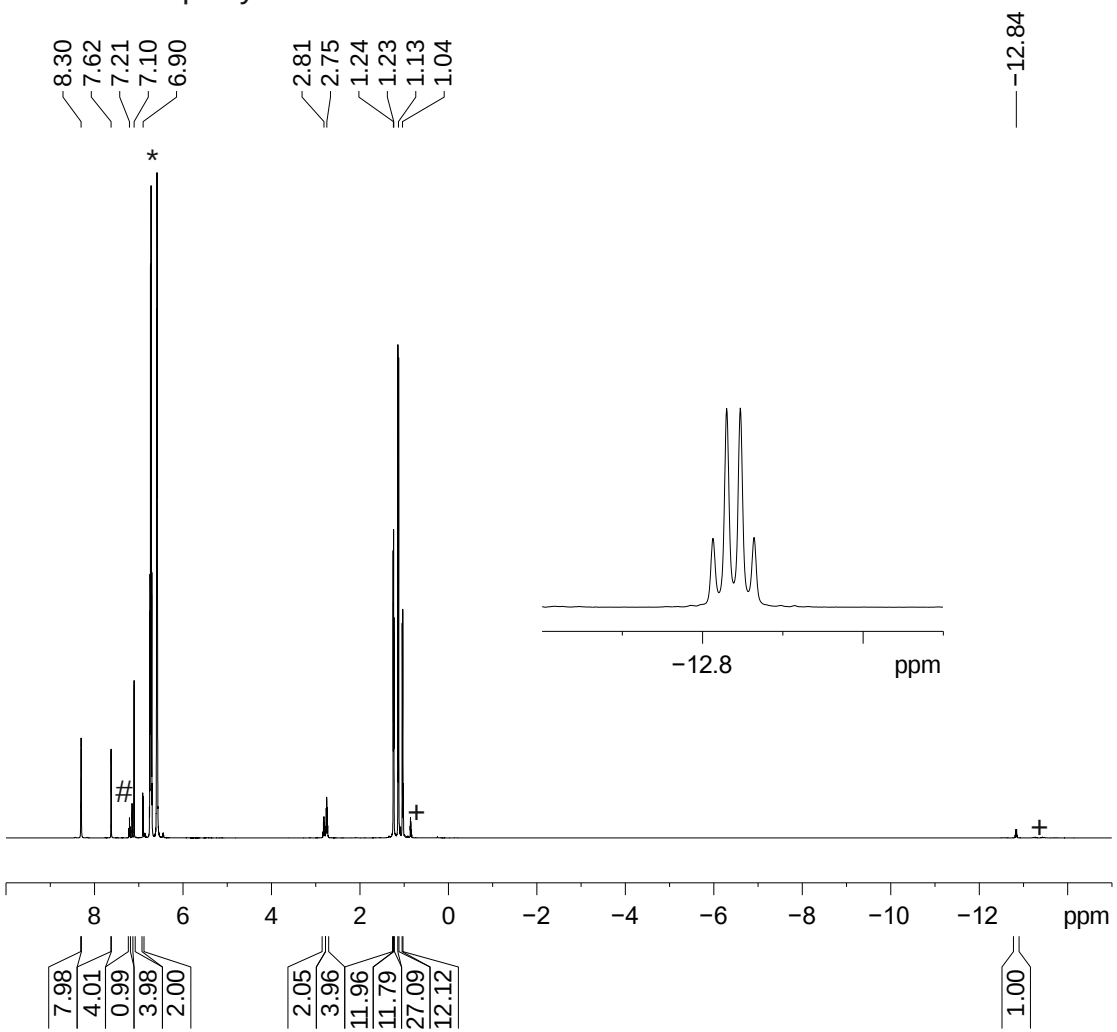



```
Current Data Parameters
NAME      MA744K_03112021_400N
EXPNO             12
PROCNO             1

F2 − Acquisition Parameters
Date_          20211103
Time              20.16
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD             88150
SOLVENT           C6D6
NS                256
DS                  0
SWH           65789.477 Hz
FIDRES         0.746336 Hz
AQ           0.6699400 sec
RG               23100
DW               7.600 usec
DE               6.00 usec
TE               299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              31P
P1              11.00 usec
PL1             −3.00 dB
PL1W        45.10684967 W
SFO1        161.9674970 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              131072
SF          161.9674970 MHz
WDW                EM
SSB                 0
LB               3.00 Hz
GB                  0
PC               1.40
```

Figure SI 19. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3**.

NMR spectra of compound **3'**.

^{1}H NMR spectrum of [Ar*GeIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt. + unknown impurity.



Current Data Parameters
NAME MA920_08062022_600
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220608
Time 12.20 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 32
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 10.98
DW 20.800 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1300000 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.41200066 W

F2 − Processing parameters
SI 65536
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00

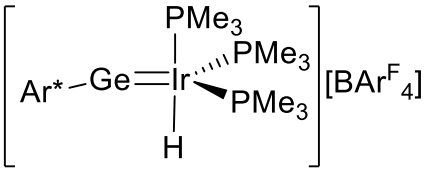
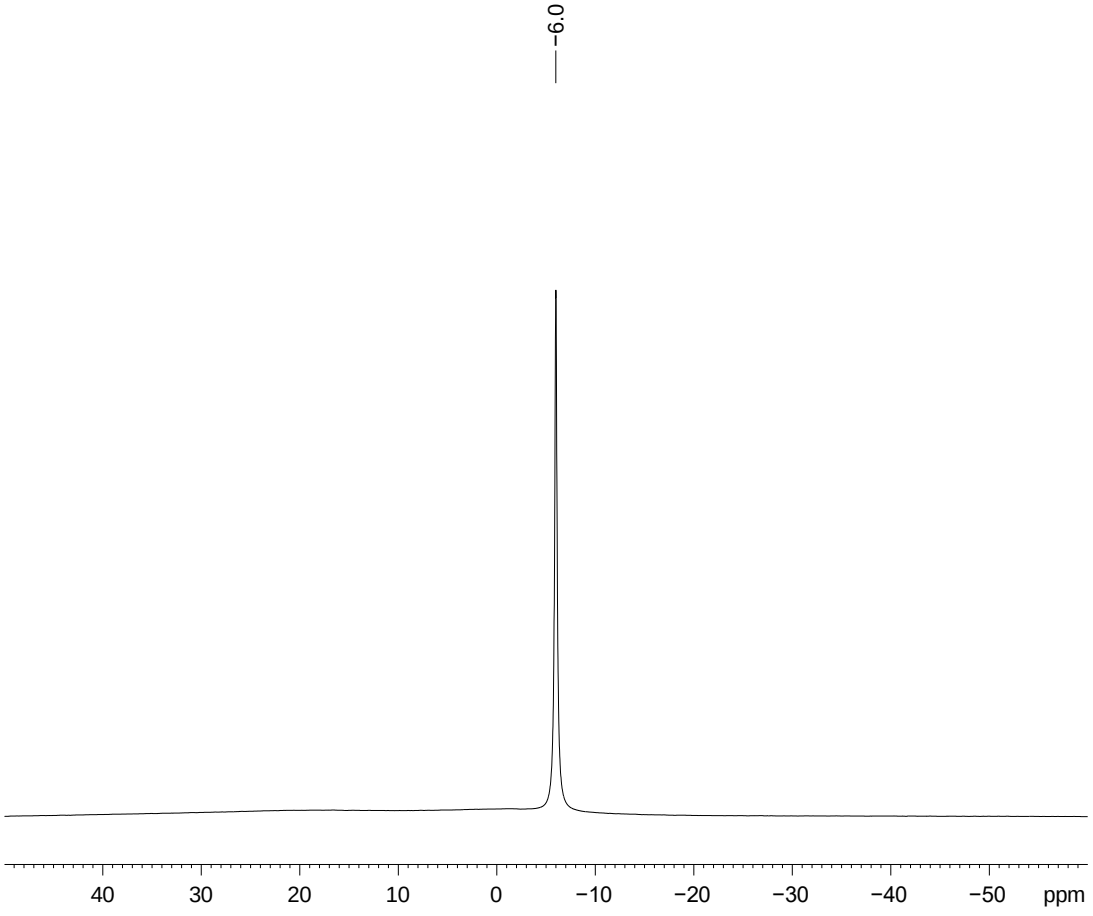


Figure SI 20. ^{1}H NMR spectrum of compound **3'**.

$^{11}B\{^{1}H\}$ NMR spectrum of [Ar*GeIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA920_08062022_600
EXPNO 16
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 1.18 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgbsig
TD 16384
SOLVENT C6D6
NS 2048
DS 4
SWH 38461.539 Hz
FIDRES 4.695012 Hz
AQ 0.2129920 sec
RG 189.6
DW 13.000 usec
DE 18.00 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 192.5455530 MHz
NUC1 11B
P1 19.80 usec
P2 39.60 usec
PLW1 50.00000000 W
SFO2 600.1328206 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 16384
SF 192.5455530 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

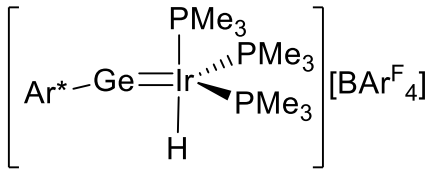
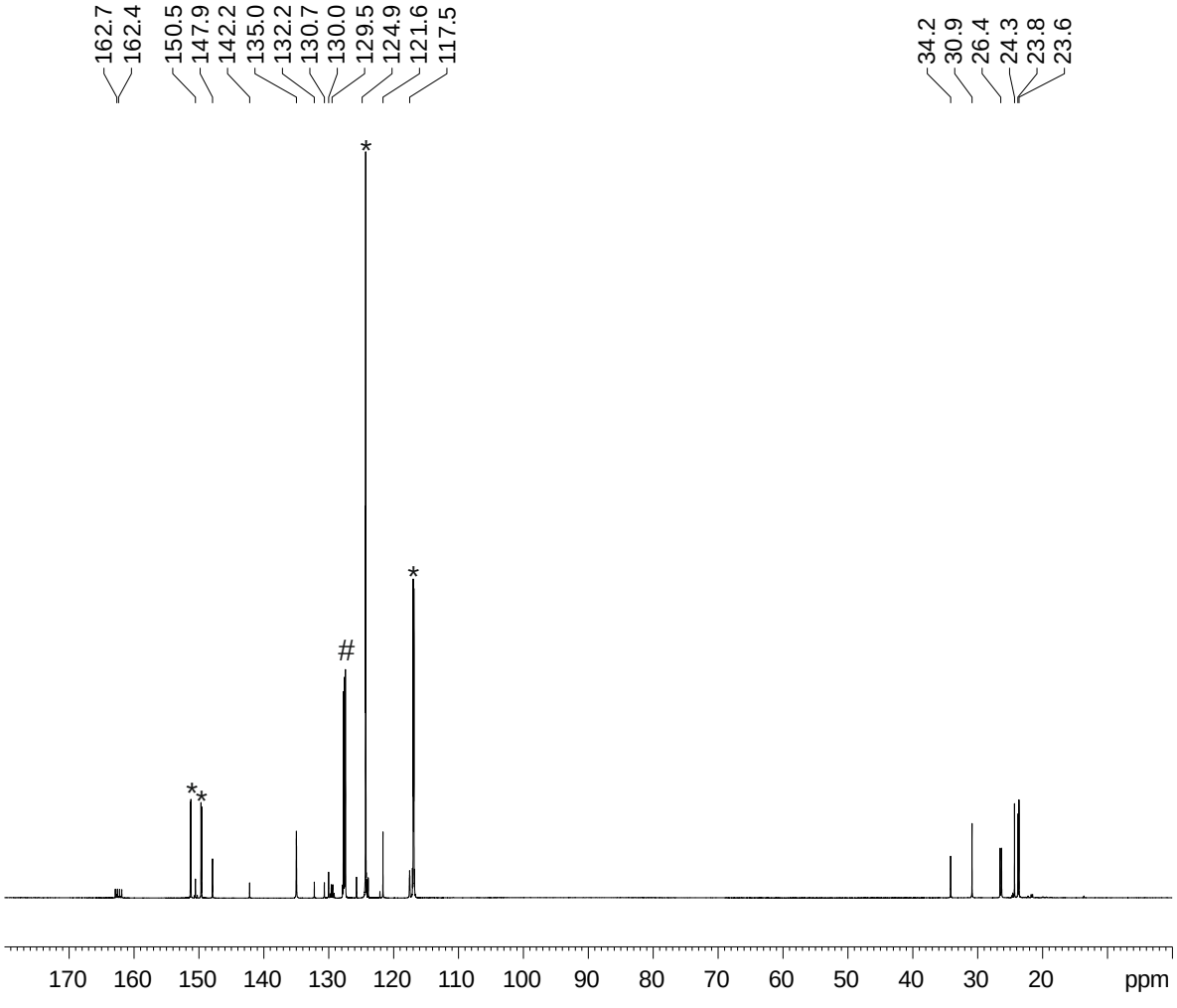


Figure SI 21. ^{11}B NMR spectrum of compound **3'**.

$^{13}C\{^{1}H\}$ NMR spectrum of [Ar*GeIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.



Current Data Parameters
NAME MA920_08062022_60(
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220608
Time 18.42 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG udeft
TD 26082
SOLVENT C6D6
NS 2048
DS 8
SWH 36231.883 Hz
FIDRES 2.778306 Hz
AQ 0.3599316 sec
RG 189.6
DW 13.800 usec
DE 18.00 usec
TE 298.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 20.00000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 57.02700043 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 8.71310043 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 131072
SF 150.9028085 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

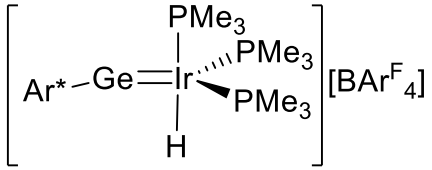
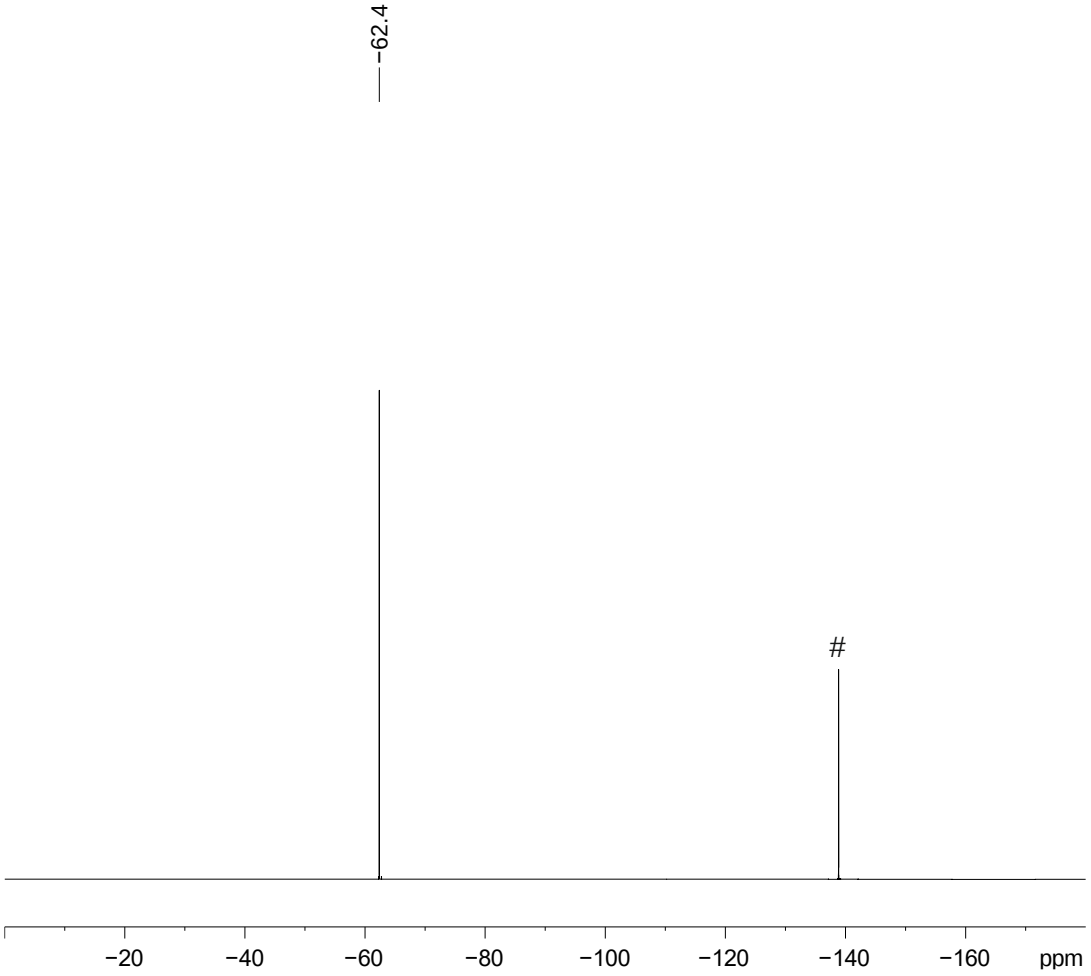


Figure SI 22. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3'**.

$^{19}F\{^{1}H\}$ NMR spectrum of [Ar*GeIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA920_08062022_600
EXPNO 19
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 2.21 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgflqn
TD 131072
SOLVENT C6D6
NS 128
DS 4
SWH 133928.578 Hz
FIDRES 2.043588 Hz
AQ 0.4893355 sec
RG 19.61
DW 3.733 usec
DE 18.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 564.6299196 MHz
NUC1 19F
P1 15.00 usec
PLW1 27.71999931 W

F2 − Processing parameters
SI 65536
SF 564.6863882 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

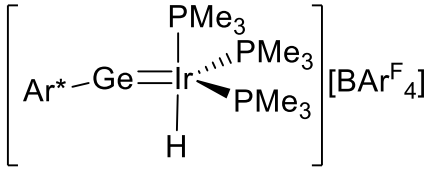
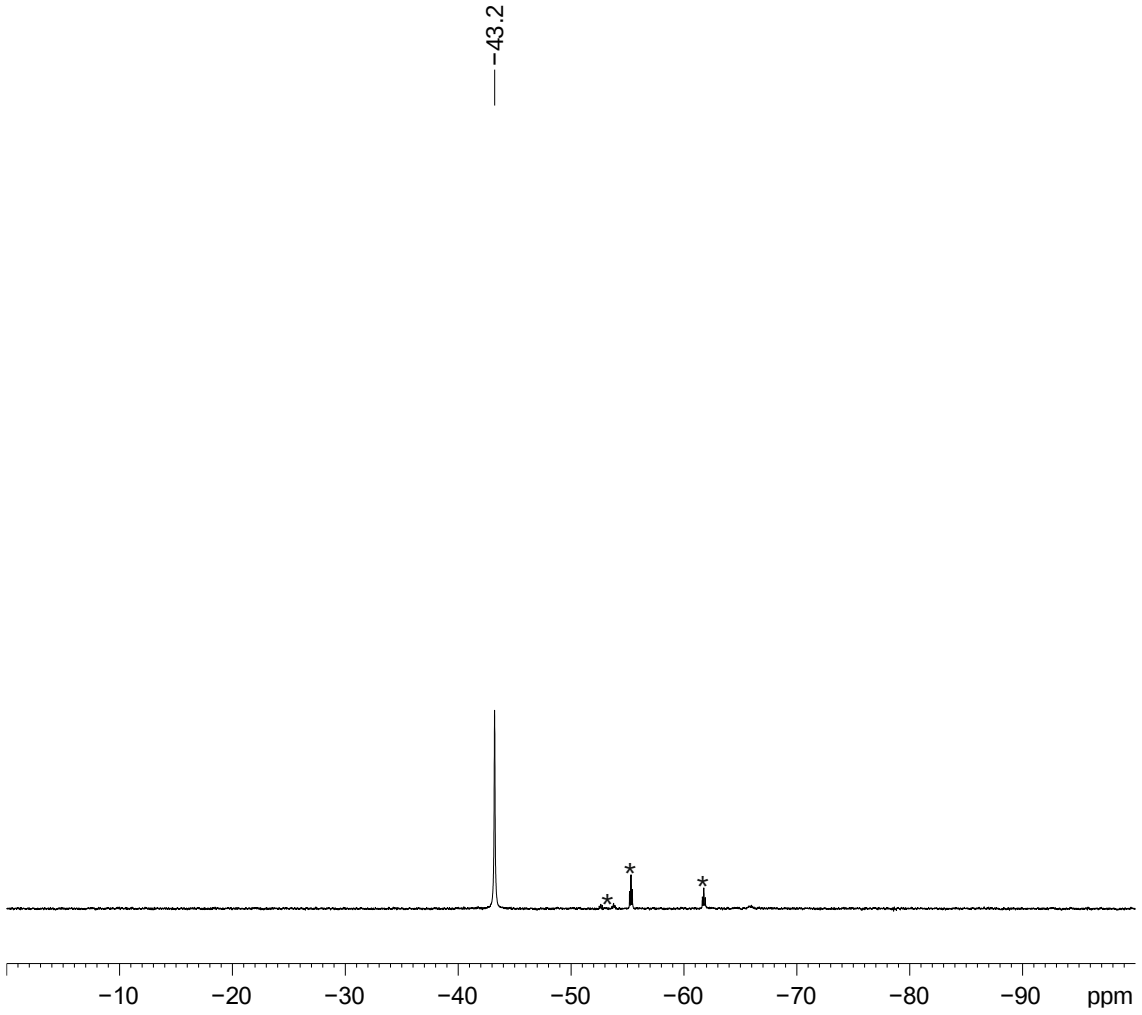


Figure SI 23. $^{19}F\{^{1}H\}$ NMR spectrum of compound **3'**.

$^{31}P\{^{1}H\}$ NMR spectrum of [Ar*GeIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt. * unknown impurity.




```
Current Data Parameters
NAME     MA920_09062022_400
EXPNO            11
PROCNO            1

F2 − Acquisition Parameters
Date_         20220609
Time          15.43
INSTRUM         spect
PROBHD   5 mm X,F/H,F B
PULPROG        zgig30b
TD            88150
SOLVENT          C6D6
NS               64
DS                0
SWH         65789.477 Hz
FIDRES       0.746336 Hz
AQ          0.6699400 sec
RG             23100
DW             7.600 usec
DE             6.00 usec
TE             299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             31P
P1            14.50 usec
PL1           −4.00 dB
PL1W       56.78615952 W
SFO1       161.9674970 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2             1H
PCPD2          90.00 usec
PL2            −1.50 dB
PL12           15.65 dB
PL2W       11.35402870 W
PL12W       0.21885175 W
SFO2       400.1120007 MHz

F2 − Processing parameters
SI            131072
SF         161.9674970 MHz
WDW              EM
SSB               0
LB             3.00 Hz
GB                0
PC             1.40
```

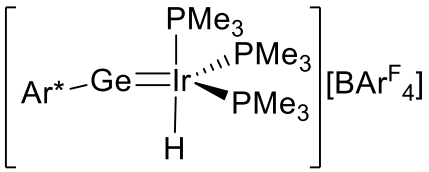
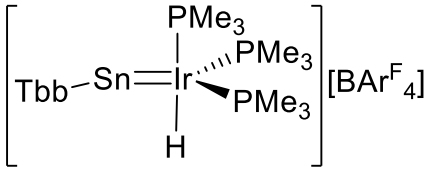
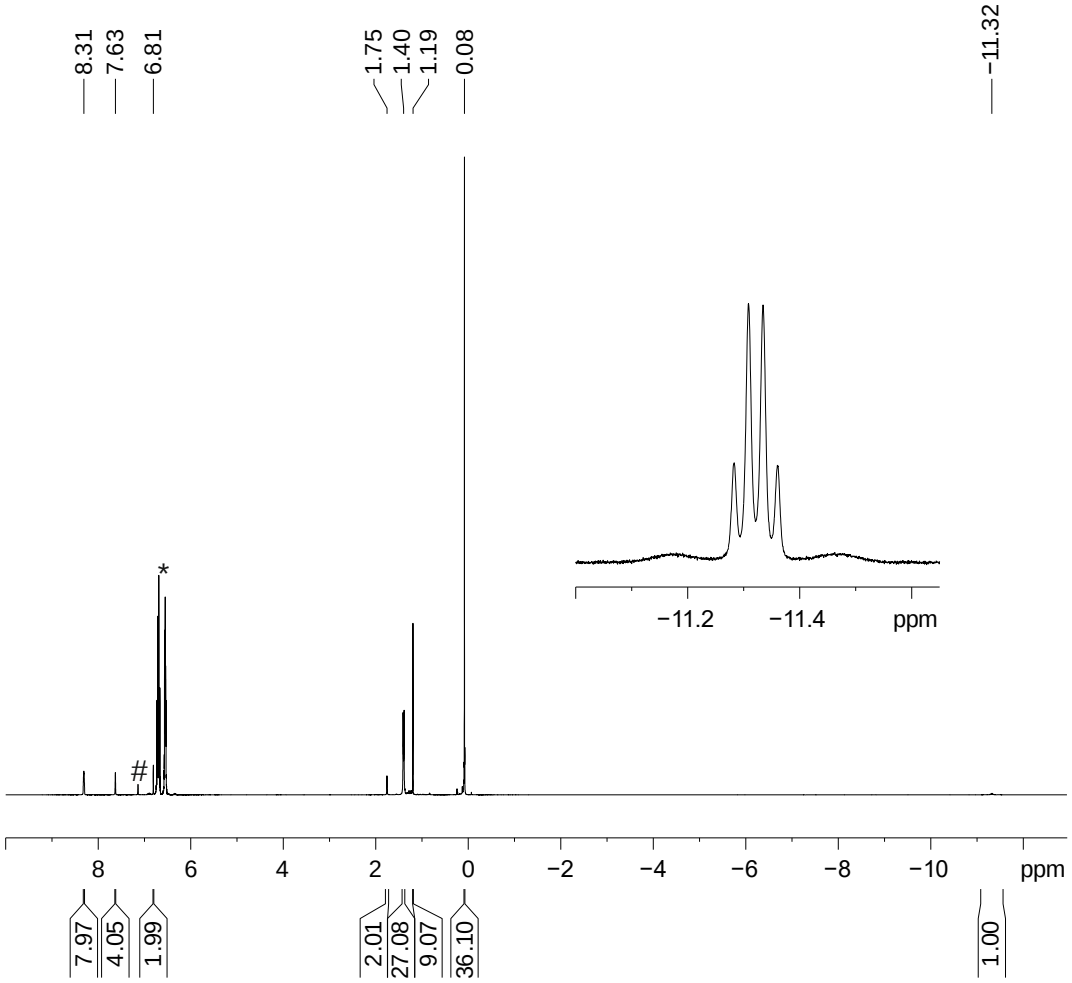


Figure SI 24. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3'**.

NMR spectra of compound **4**.

^{1}H NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA737_13102021_400N
EXPNO 10
PROCNO 1

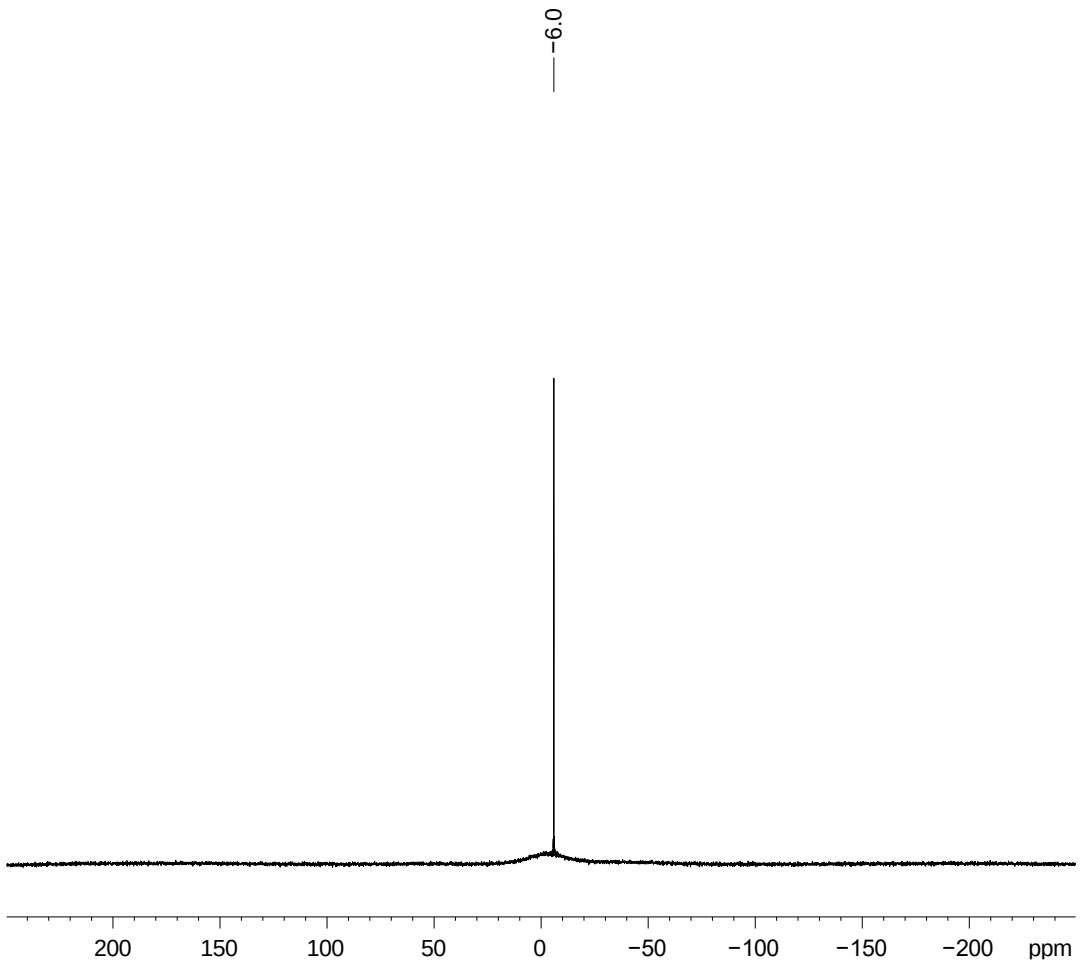
F2 − Acquisition Parameters
Date_ 20211013
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 11160.714 Hz
FIDRES 0.211955 Hz
AQ 2.3589888 sec
RG 40.3
DW 44.800 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1104001 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 25. ^{1}H NMR spectrum of compound **4**.

^{11}B NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA737_12102021_300N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211012
Time 19.13 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

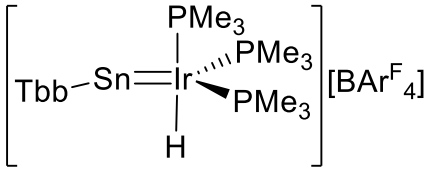
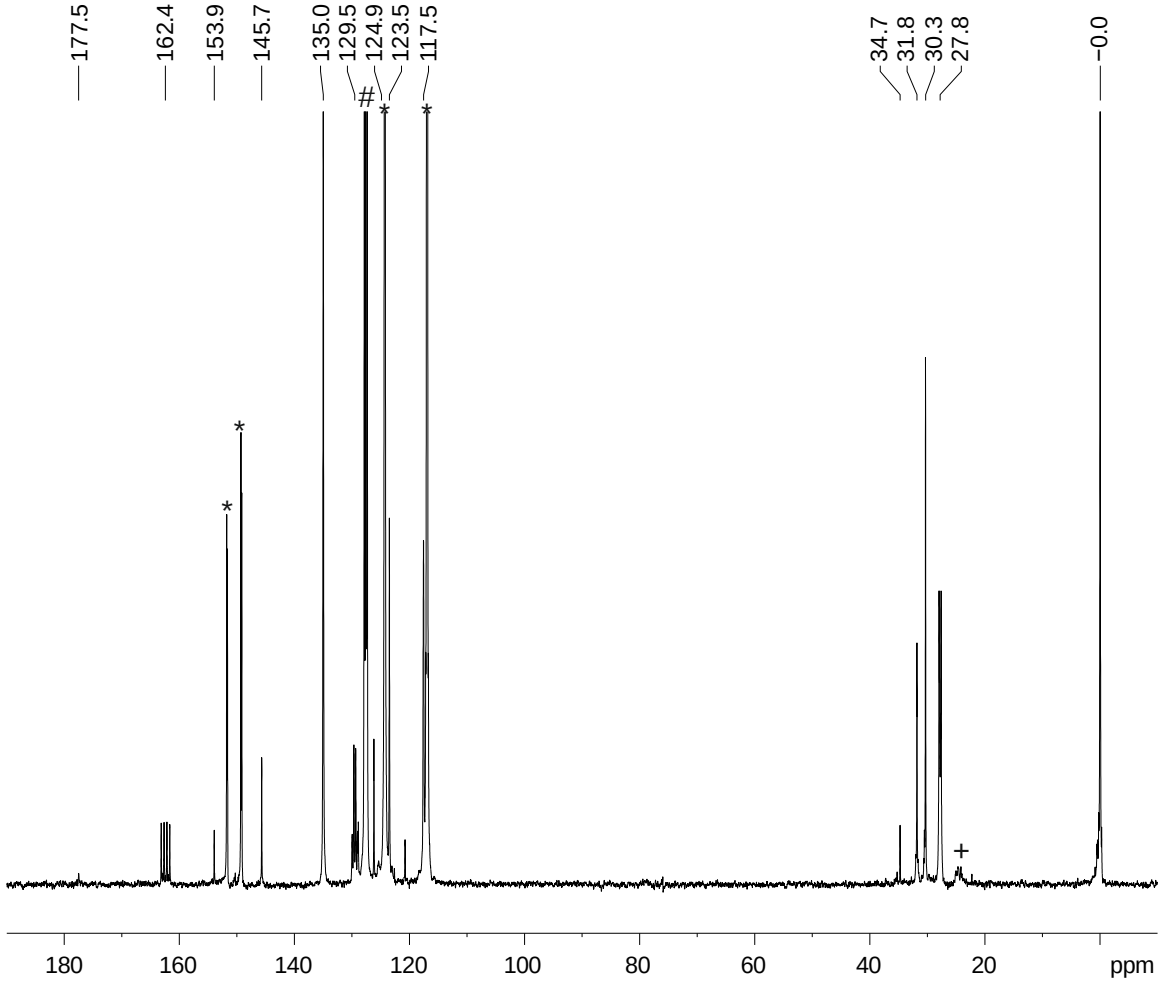


Figure SI 26. ^{11}B NMR spectrum of compound **4**.

$^{13}C\{^{1}H\}$ NMR spectrum of [TbbSnIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.
+ unknown impurity.




```
Current Data Parameters
NAME      MA737_13102021_400N
EXPNO             13
PROCNO             1

F2 - Acquisition Parameters
Date_          20211014
Time              2.16
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD             22218
SOLVENT           C6D6
NS              5734
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE             299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1             -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8              1.39 dB
SP13             1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

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

F2 - Processing parameters
SI              131072
SF         100.6077400 MHz
WDW               EM
SSB                0
LB              5.00 Hz
GB                 0
PC              1.40
```

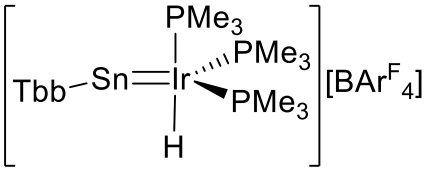
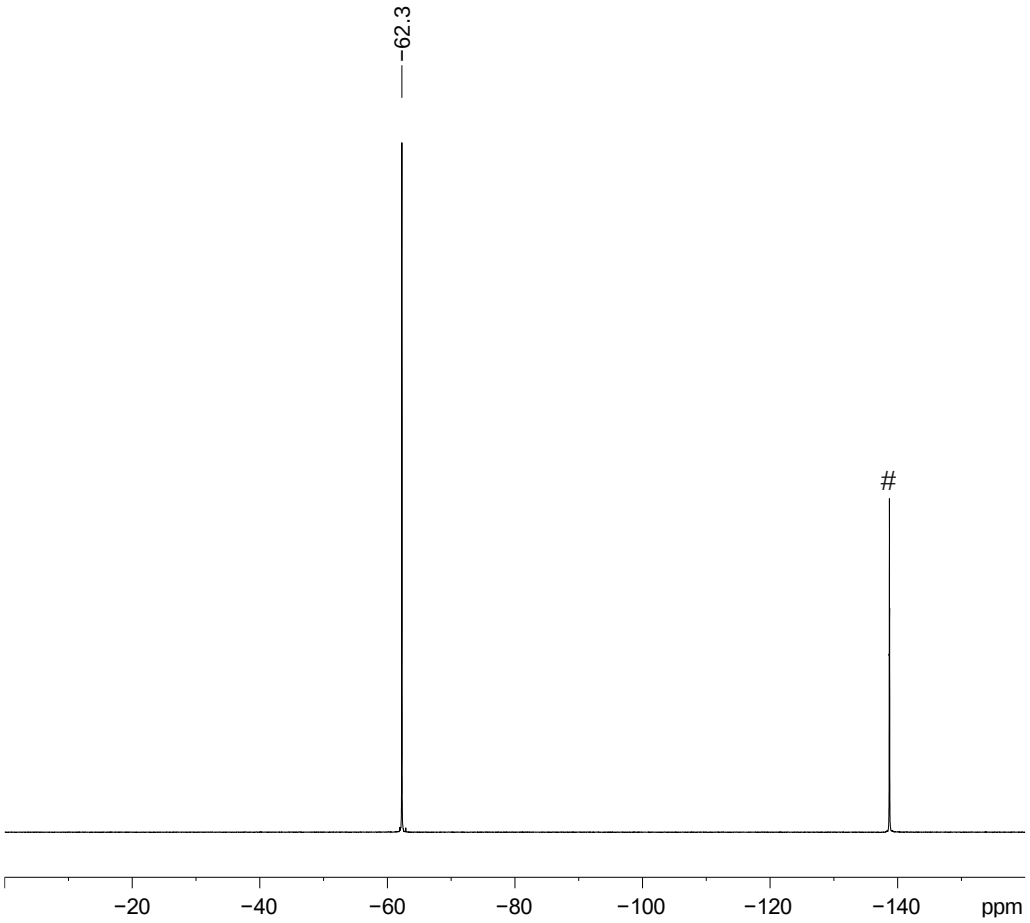


Figure SI 27. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA737_12102021_300N
EXPNO 12
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211012
Time 19.17 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 262144
SOLVENT C6D6
NS 16
DS 4
SWH 66964.289 Hz
FIDRES 0.510897 Hz
AQ 1.9573419 sec
RG 204.67
DW 7.467 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 282.3761148 MHz
NUC1 19F
P1 15.00 usec
P2 30.00 usec
PLW1 6.86250019 W

F2 − Processing parameters
SI 65536
SF 282.4043552 MHz
WDW EM
SSB 0
LB 7.00 Hz
GB 0
PC 1.00

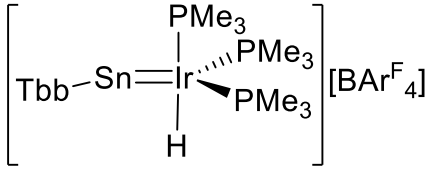
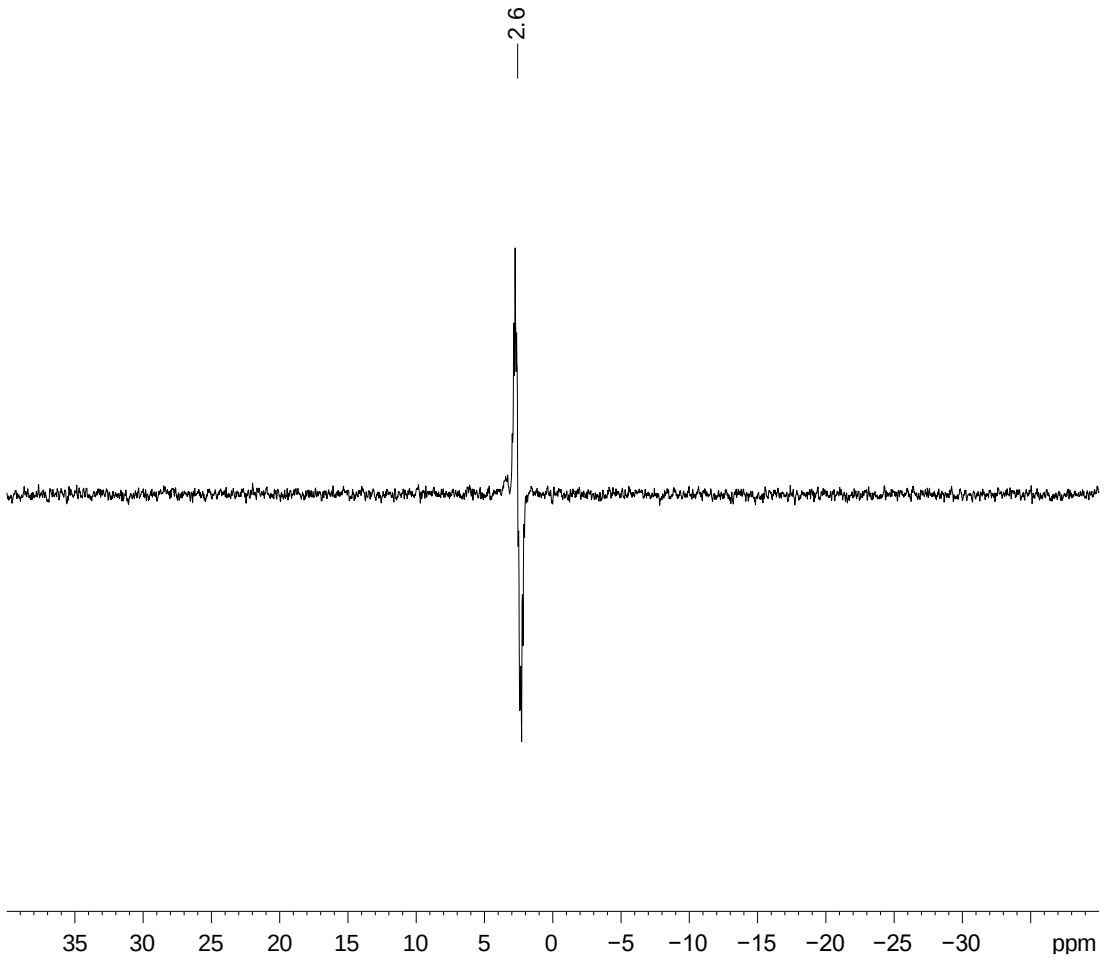


Figure SI 28. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4**.

^{29}Si NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA737_14102021_300N
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211014
Time 19.23 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273676 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

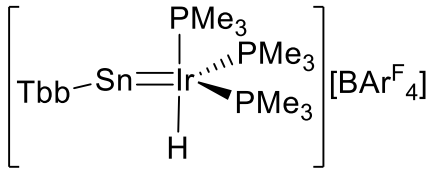
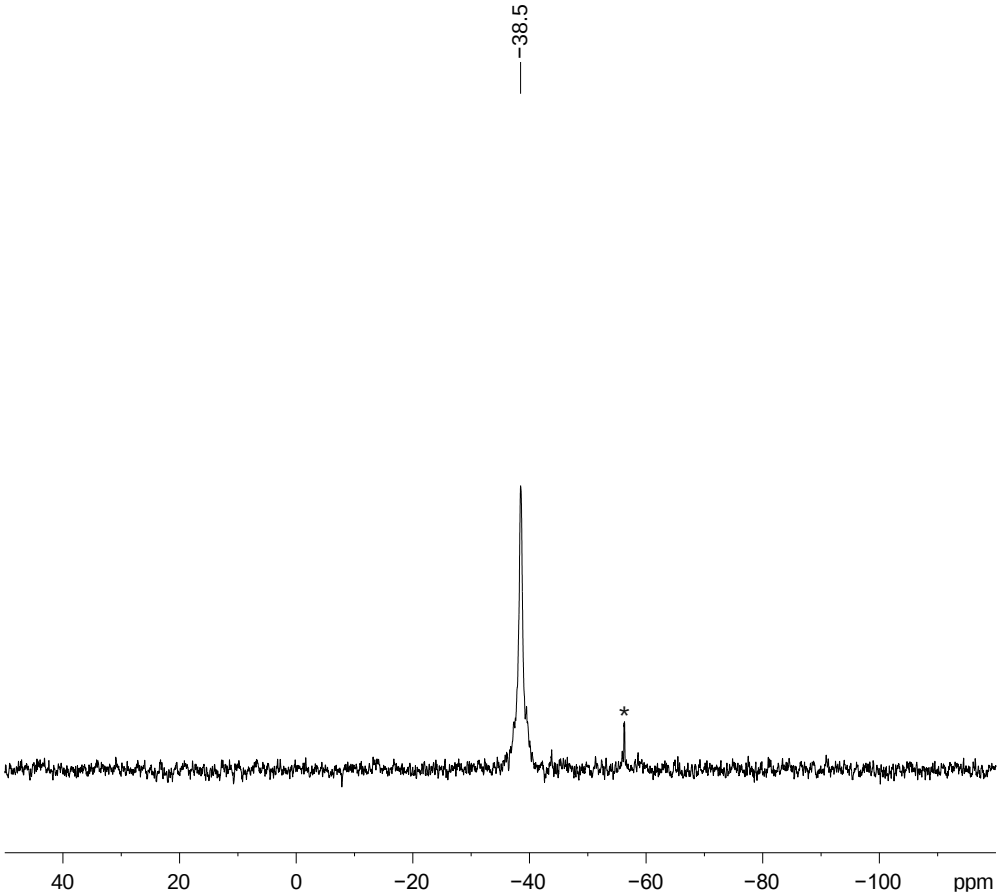


Figure SI 29. ^{29}Si NMR spectrum of compound **4**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbSnIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 and *o*-difluorobenzene at rt. * unknown impurity.



Current Data Parameters
NAME MA737_13102021_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211013
Time 20.09
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 64
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 13.00 Hz
GB 0
PC 1.40

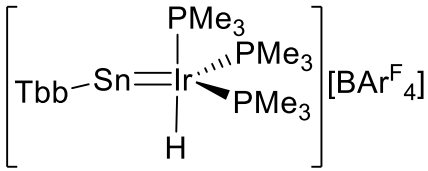
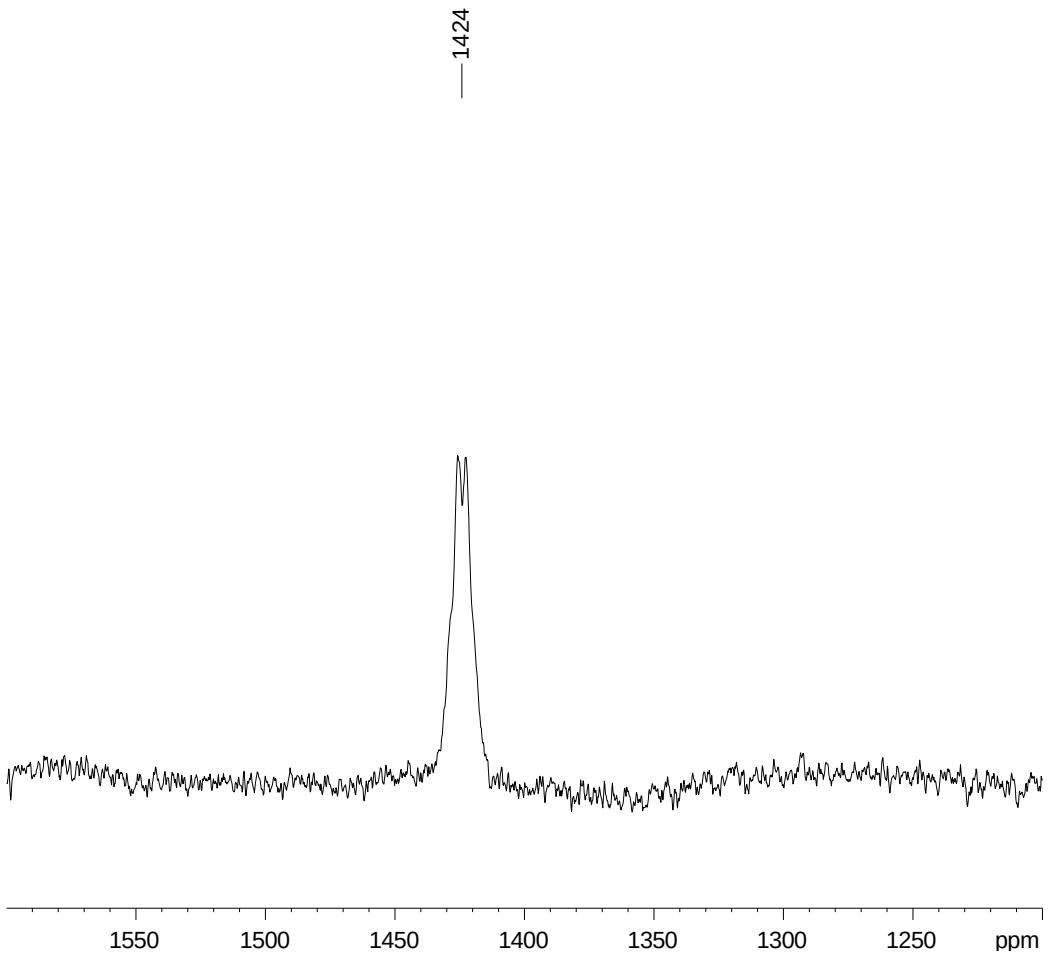


Figure SI 30. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4**.

^{119}Sn NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA737_14102021_300N
EXPNO 23
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211014
Time 21.19 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 184320
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 112.0770620 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

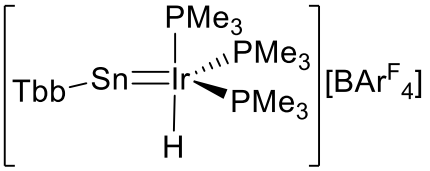
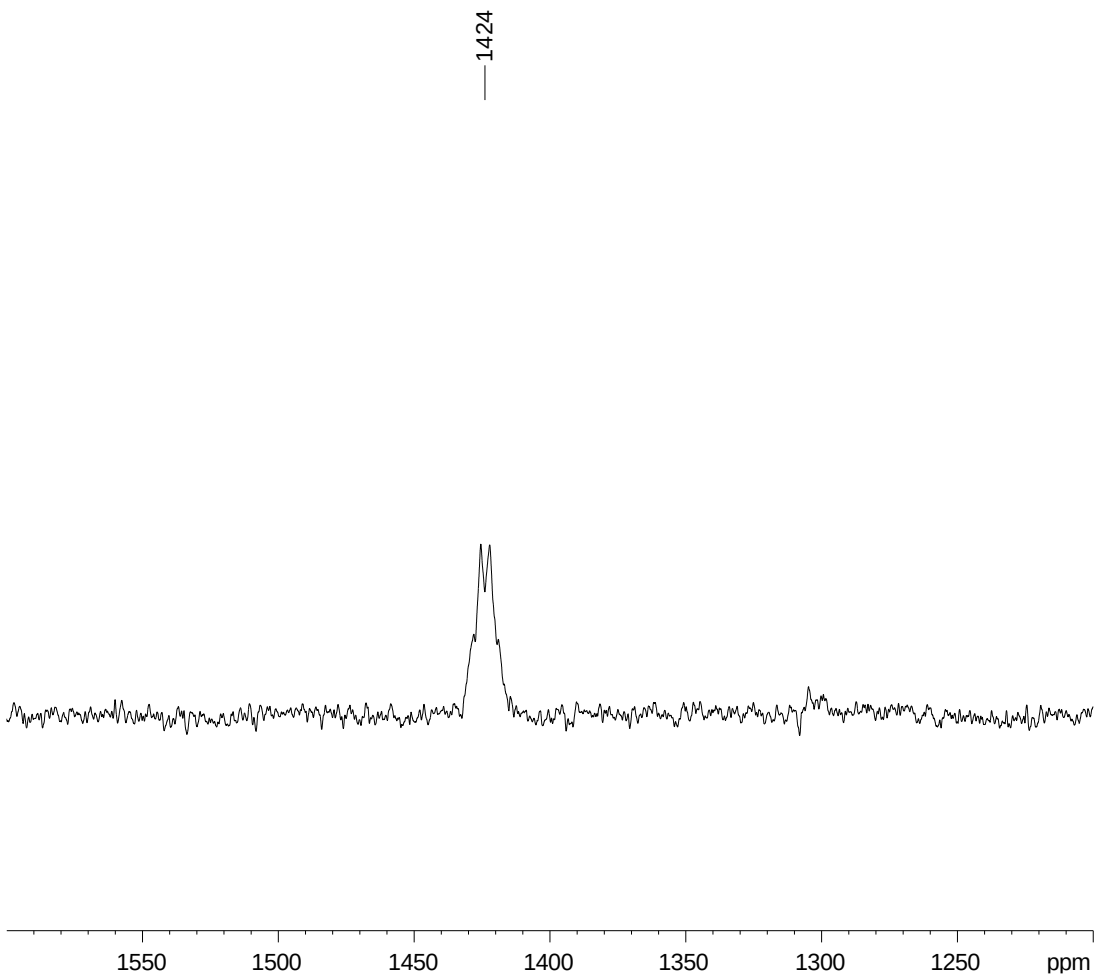


Figure SI 31. ^{119}Sn NMR spectrum of compound **4**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of [TbbSnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA737_14102021_300N
EXPNO 33
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211015
Time 2.34 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 52224
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 112.0770618 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 1.40

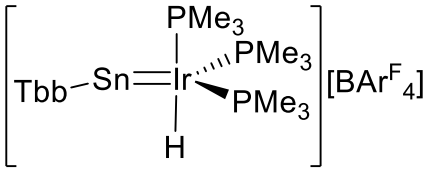


Figure SI 32. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **4**.

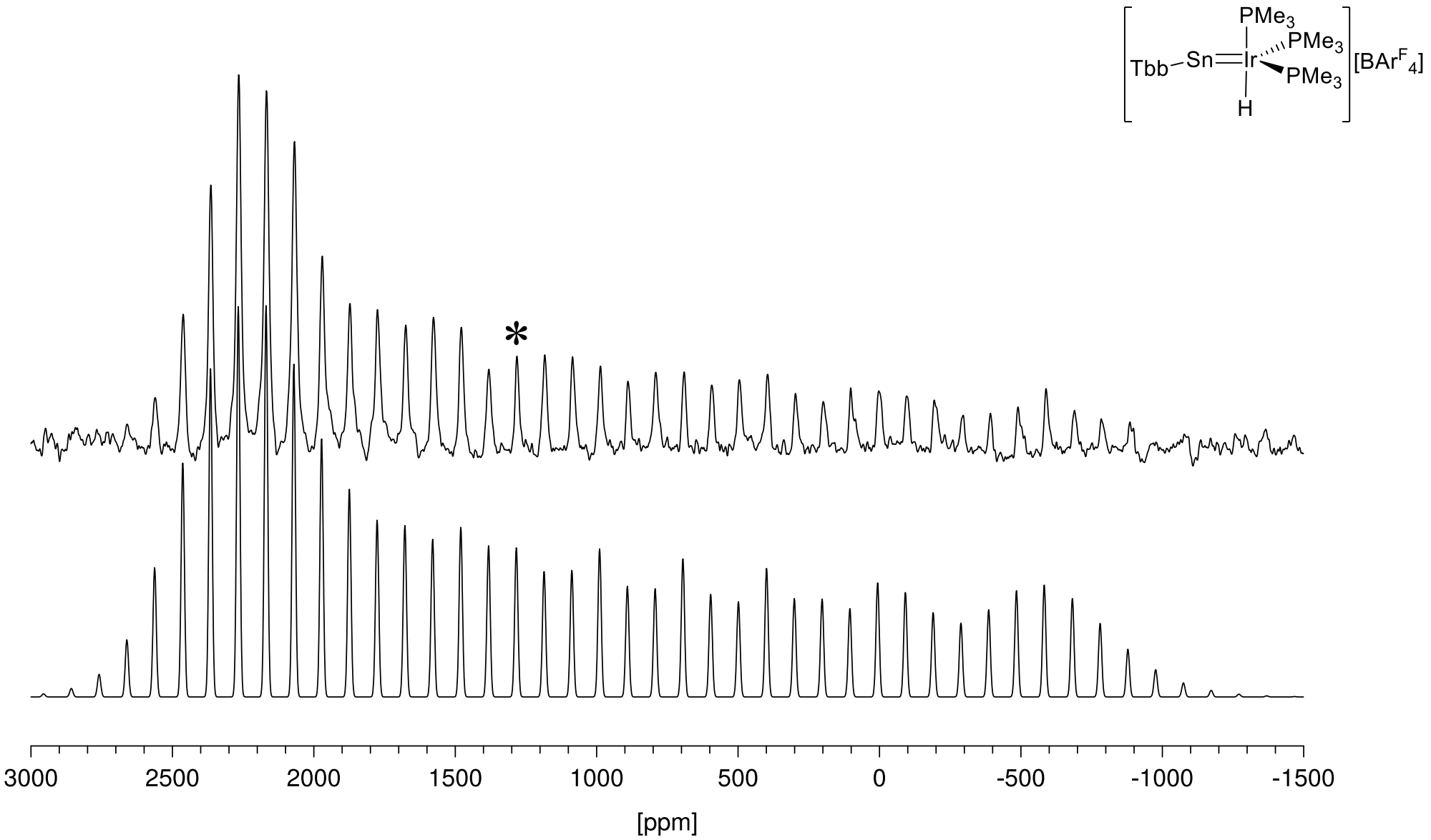
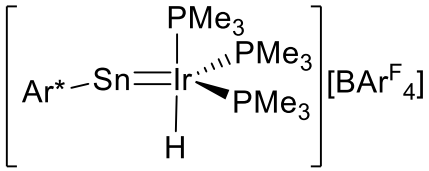


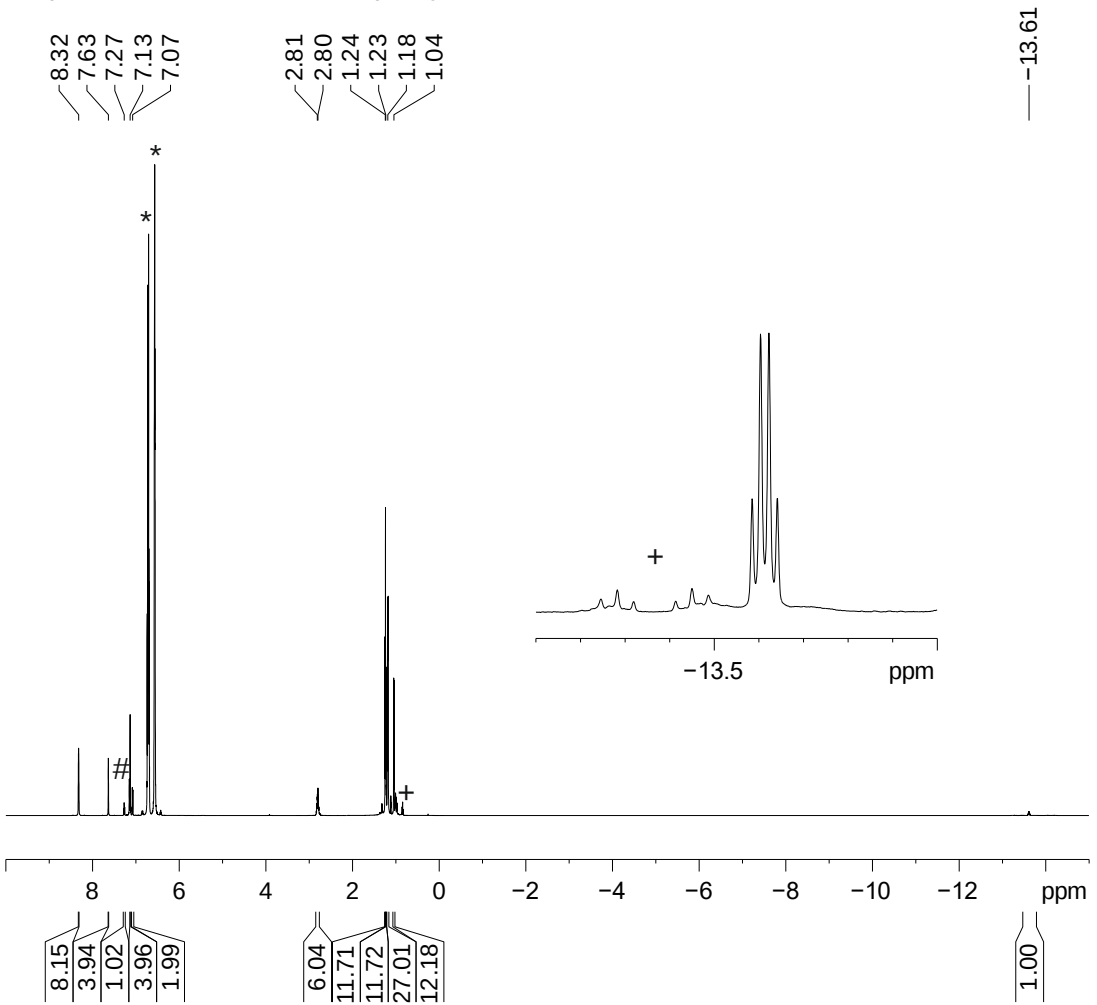
Fig. SI 33. 111.92 MHz ^{119}Sn MAS NMR spectrum of Y obtained at 7.05 T and a spinning rate of 11 kHz. The isotropic peak is marked by an asterisk. 480000 scans, 0.5 s recycle delay, 600 kHz sweep width.

δ_{iso} = 1284 ppm, δ_{11} = 2622 ppm, δ_{22} = 2208 ppm, δ_{33} = -978 ppm, span Ω = 3600 ppm, skew κ = 0.77.

NMR spectra of compound **4'**.

^{1}H NMR spectrum of [Ar*SnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane and unknown impurity.





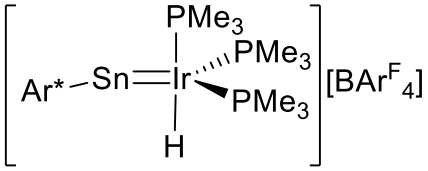
Current Data Parameters
NAME MA885_09062022_600
EXPNO 10
PROCNO 1

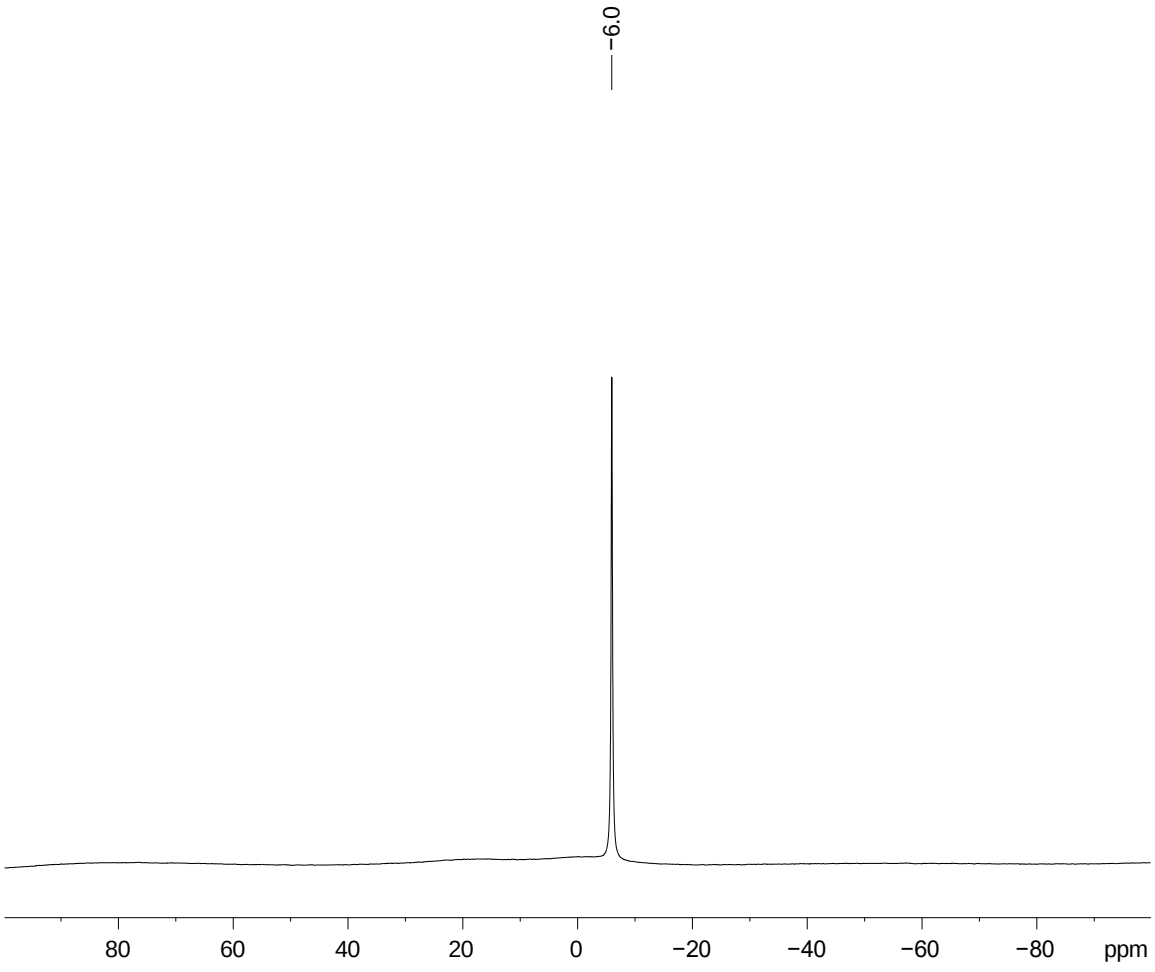
F2 − Acquisition Parameters
Date_ 20220609
Time 9.19 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 64
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 15.53
DW 20.800 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1300000 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.41200066 W

F2 − Processing parameters
SI 65536
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00

Figure SI 34. ^{1}H NMR spectrum of compound **4'**.

$^{11}B\{^{1}H\}$ NMR spectrum of [Ar*SnIrH(PMe_3)$_3$][$B(Ar^F)_4$] in benzene-d_6 and *o*-difluorobenzene at rt.





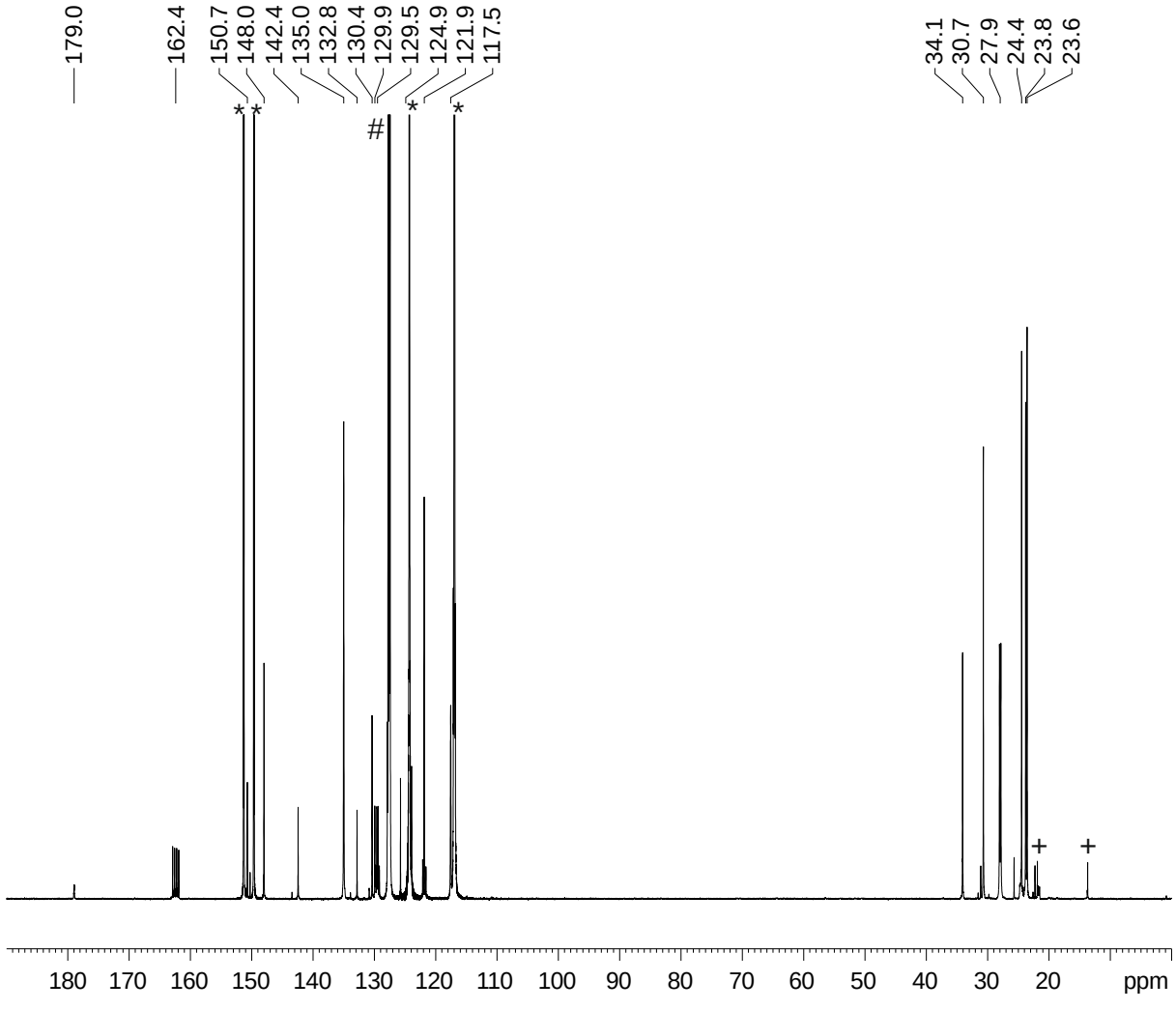
Current Data Parameters
NAME MA885_09062022_600
EXPNO 18
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 16.25 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgbsig
TD 16384
SOLVENT C6D6
NS 1024
DS 4
SWH 38461.539 Hz
FIDRES 4.695012 Hz
AQ 0.2129920 sec
RG 189.6
DW 13.000 usec
DE 18.00 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 192.5455530 MHz
NUC1 11B
P1 19.80 usec
P2 39.60 usec
PLW1 50.00000000 W
SFO2 600.1328206 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 16384
SF 192.5455530 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

Figure SI 35. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4'**.

$^{13}C\{^{1}H\}$ NMR spectrum of [Ar*SnIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane.



Current Data Parameters
NAME MA885_09062022_60(
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 11.44 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG udeft
TD 25902
SOLVENT C6D6
NS 1792
DS 8
SWH 36231.883 Hz
FIDRES 2.797613 Hz
AQ 0.3574476 sec
RG 189.6
DW 13.800 usec
DE 18.00 usec
TE 298.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 20.00000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 57.02700043 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 8.71310043 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 131072
SF 150.9028085 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

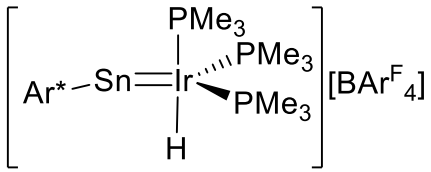
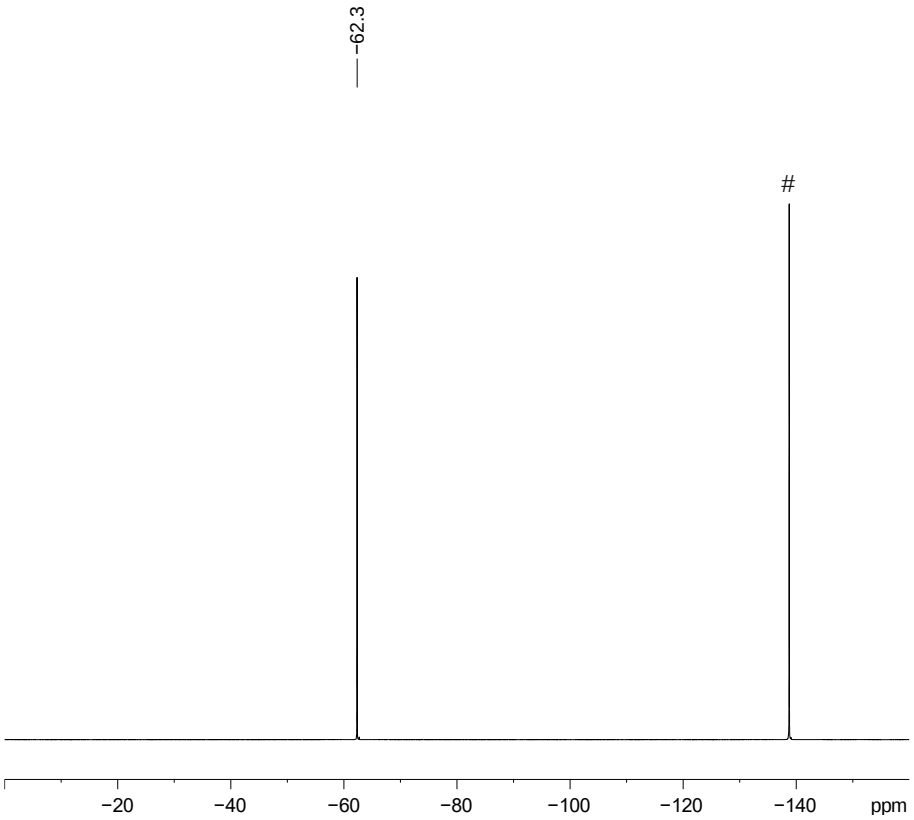


Figure SI 36. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4'**.

$^{19}F\{^{1}H\}$ NMR spectrum of [Ar*SnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA885_09062022_600
EXPNO 16
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 16.09 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgflqn
TD 130892
SOLVENT C6D6
NS 64
DS 4
SWH 133928.578 Hz
FIDRES 2.046398 Hz
AQ 0.4886635 sec
RG 22.25
DW 3.733 usec
DE 18.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 564.6299196 MHz
NUC1 19F
P1 15.00 usec
PLW1 27.71999931 W

F2 − Processing parameters
SI 65536
SF 564.6863882 MHz
WDW EM
SSB 0
LB 7.00 Hz
GB 0
PC 1.00

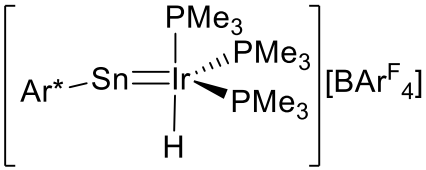
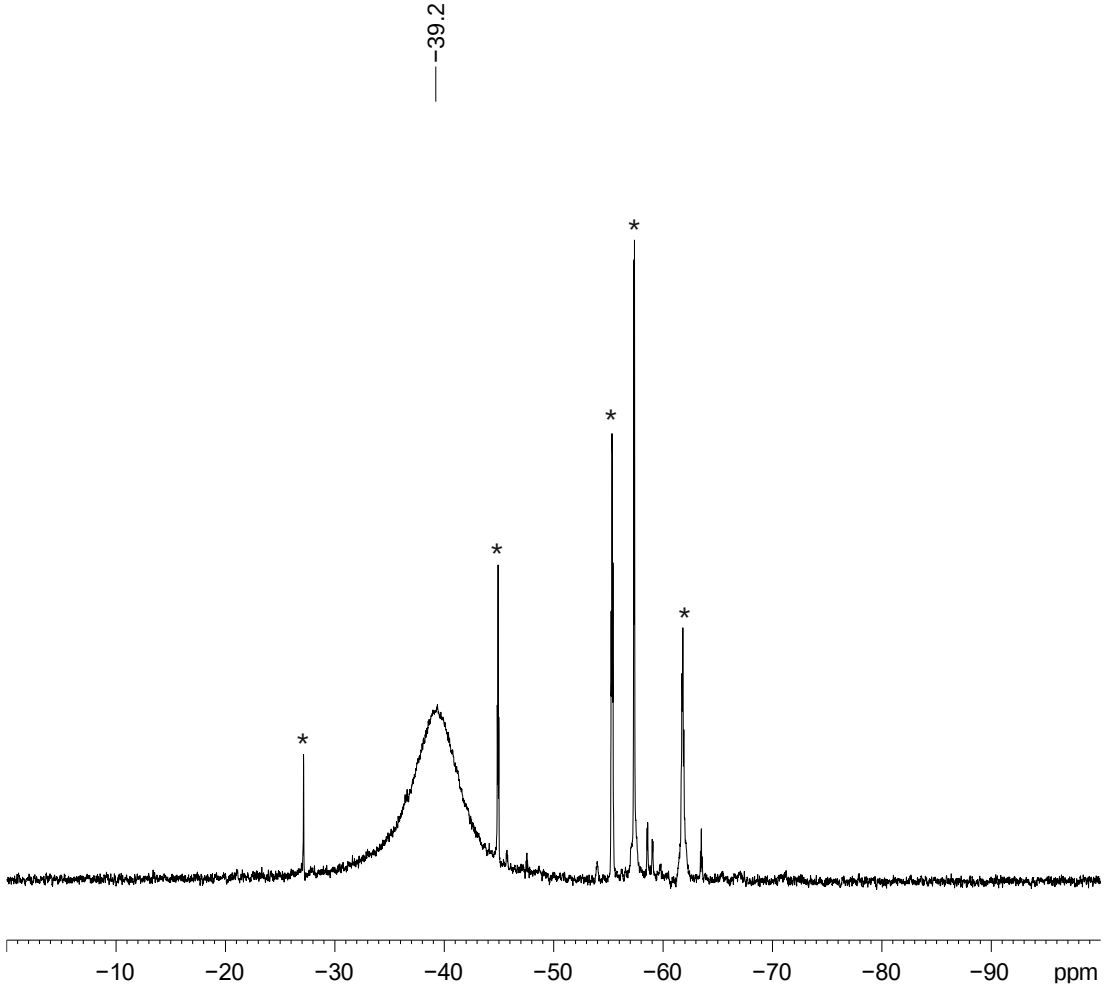


Figure SI 37. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4'**.

$^{31}P\{^{1}H\}$ NMR spectrum of [Ar*SnIrH(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA885_09062022_600
EXPNO 17
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220609
Time 16.16 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 128
DS 4
SWH 96153.844 Hz
FIDRES 2.934382 Hz
AQ 0.3407872 sec
RG 189.6
DW 5.200 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 242.9249301 MHz
NUC1 31P
P1 12.00 usec
PLW1 52.43000031 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W
PLW13 0.34606999 W

F2 − Processing parameters
SI 32768
SF 242.9370770 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

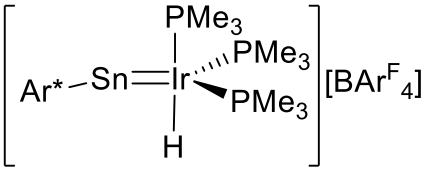
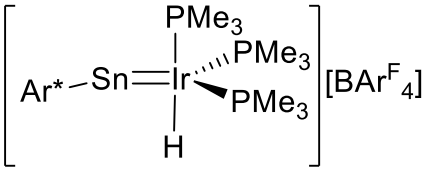
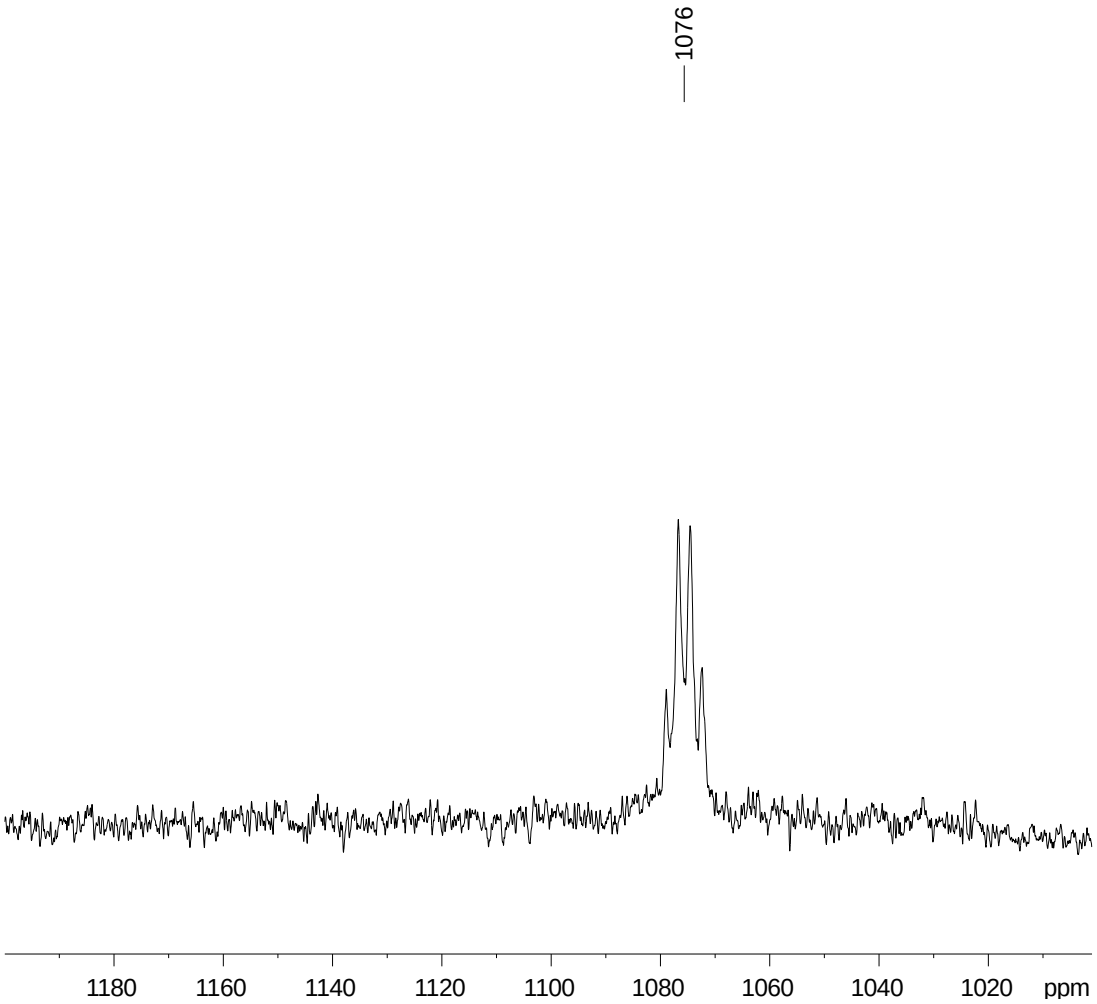


Figure SI 38. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4'**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of [Ar*SnIrH(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 and *o*-difluorobenzene at rt.





Current Data Parameters
NAME MA885_09062022_600
EXPNO 19
PROCNO 1

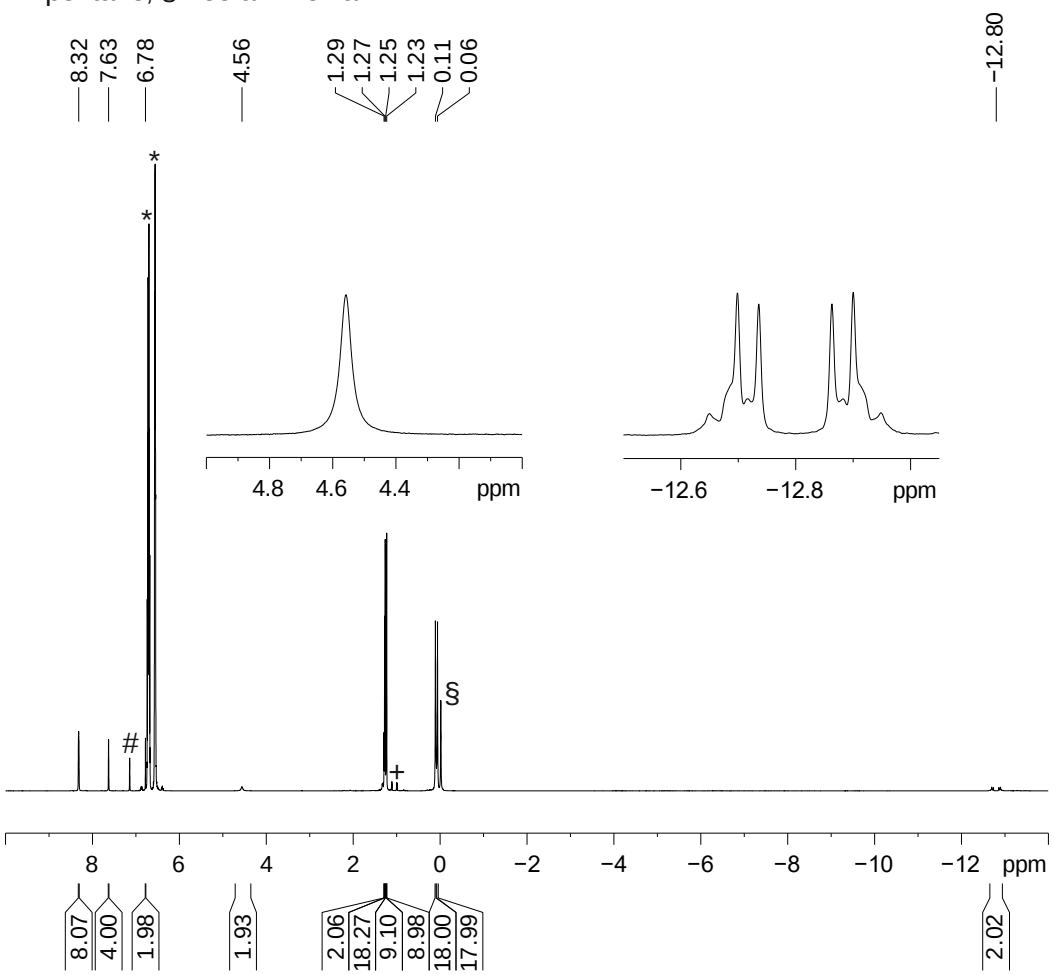
F2 − Acquisition Parameters
Date_ 20220609
Time 17.02 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgig30
TD 65536
SOLVENT C6D6
NS 4096
DS 4
SWH 178571.422 Hz
FIDRES 5.449567 Hz
AQ 0.1835008 sec
RG 189.6
DW 2.800 usec
DE 18.00 usec
TE 298.0 K
D1 0.30000001 sec
D11 0.03000000 sec
TD0 1
SFO1 224.1055786 MHz
NUC1 119Sn
P1 14.23 usec
PLW1 50.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 32768
SF 223.7922698 MHz
WDW EM

Figure SI 39. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **4'**.

NMR spectra of compound **5**.

^{1}H NMR spectrum of [TbbGe(NH_2)IrH_2(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.
+ n-pentane, § free ammonia.



Current Data Parameters
NAME JB12_12112021_500
EXPNO 1
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211112
Time 13.10
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 128
DS 0
SWH 20000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 4
DW 25.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.63 usec
PL1 −0.52 dB
PL1W 24.34997177 W
SFO1 500.1300000 MHz

F2 − Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

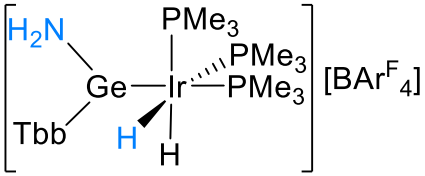
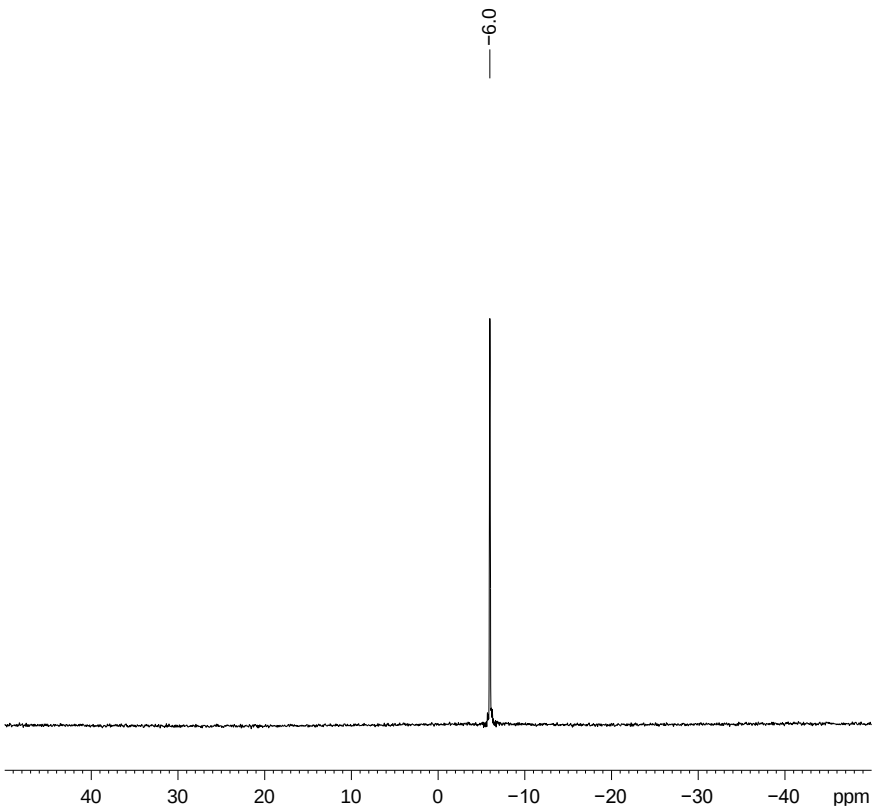


Figure SI 40. ^{1}H NMR spectrum of compound **5**.

^{11}B NMR spectrum of [TbbGe(NH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME JB07+12K_18112021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211118
Time 15.07 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

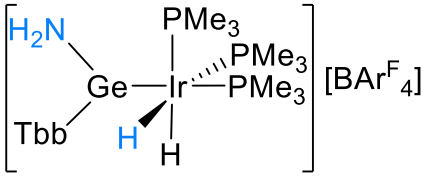
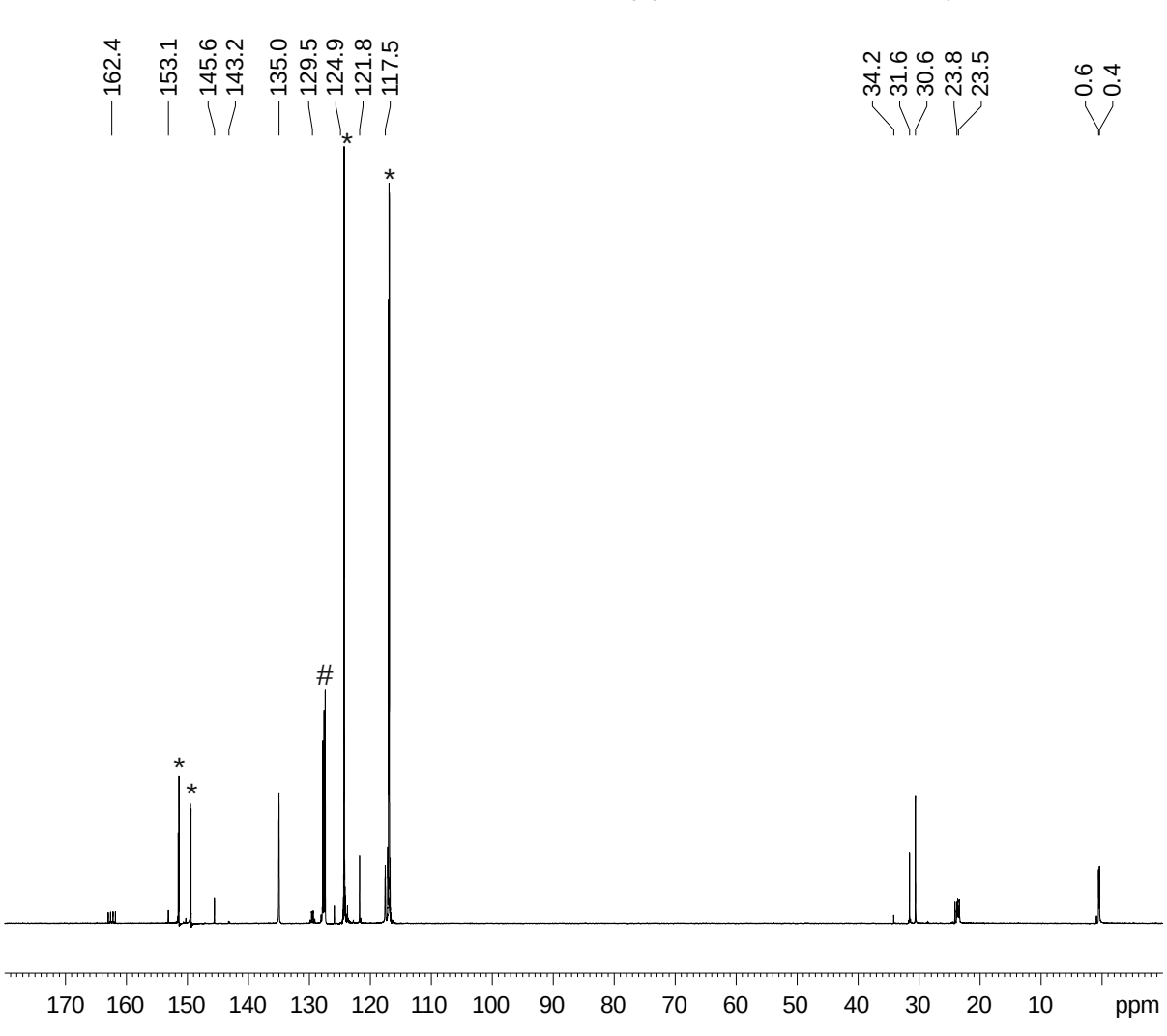


Figure SI 41. ^{11}B{^{1}H} NMR spectrum of compound **5**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbGe(NH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME     JB12_12112021_500
EXPNO              7
PROCNO             1

F2 - Acquisition Parameters
Date_          20211113
Time              8.57
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG           udeft
TD               27268
SOLVENT           C6D6
NS               20480
DS                   0
SWH          37878.789 Hz
FIDRES        1.389130 Hz
AQ           0.3599376 sec
RG               2050
DW             13.200 usec
DE              6.00 usec
TE              299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1               8.32 usec
P13            2000.00 usec
P26             500.00 usec
PL1              0.40 dB
PL1W        76.51497650 W
SFO1       125.7728799 MHz
SP8             10.16 dB
SP13            10.16 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13    Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2          80.00 usec
PL2            -0.52 dB
PL12            15.51 dB
PL2W        24.34997177 W
PL12W        0.60743308 W
SFO2       500.1325006 MHz

F2 - Processing parameters
SI              262144
SF         125.7577890 MHz
WDW                EM
SSB                0
LB              2.00 Hz
GB                 0
PC                 1.40
```

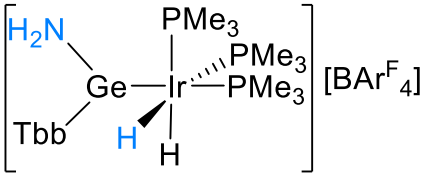
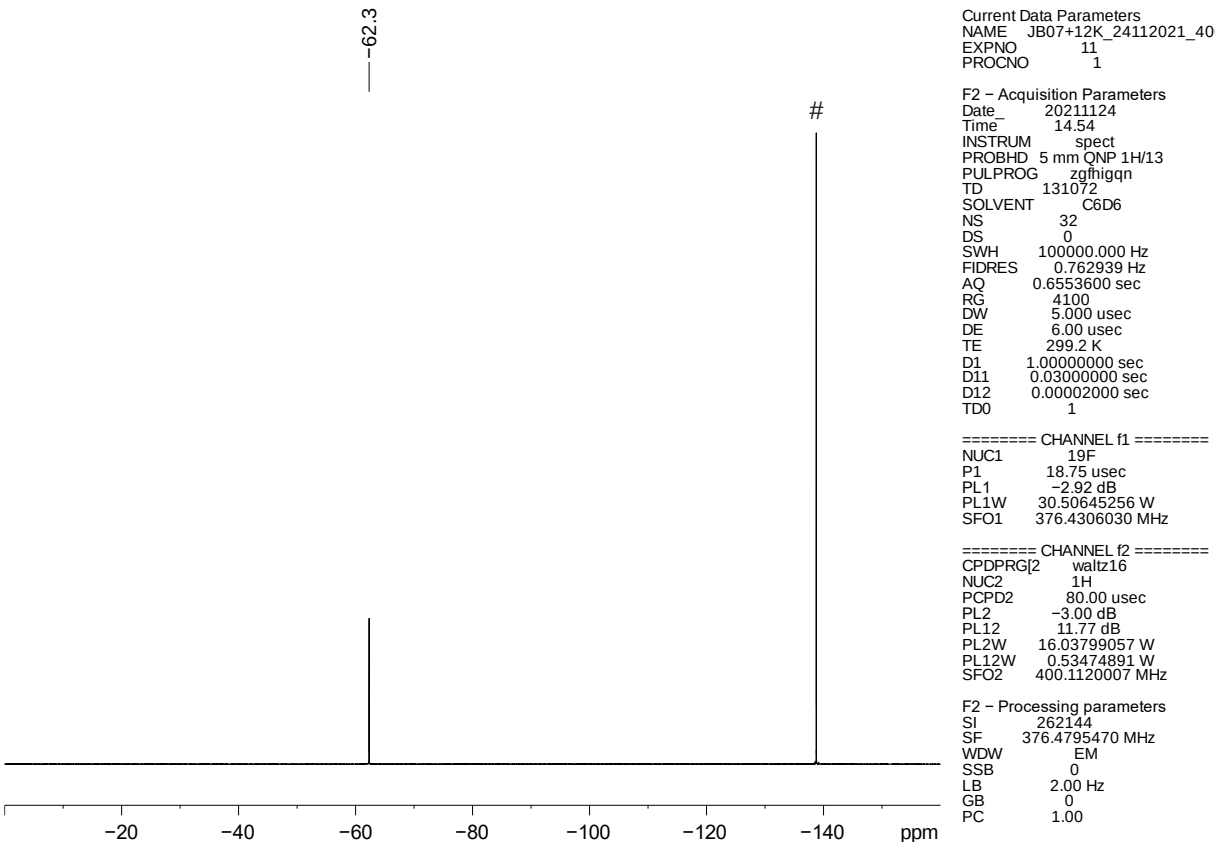


Figure SI 42. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5**.

$^{19}F\{^{1}H\}$ NMR spectrum of $[TbbGe(NH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME     JB07+12K_24112021_40
EXPNO            11
PROCNO            1

F2 − Acquisition Parameters
Date_         20211124
Time             14.54
INSTRUM          spect
PROBHD  5 mm QNP 1H/13
PULPROG        zgfhigqn
TD             131072
SOLVENT            C6D6
NS                 32
DS                  0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ           0.6553600 sec
RG                4100
DW               5.000 usec
DE               6.00 usec
TE               299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              19F
P1              18.75 usec
PL1             −2.92 dB
PL1W        30.50645256 W
SFO1       376.4306030 MHz

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

F2 − Processing parameters
SI            262144
SF         376.4795470 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.00
```

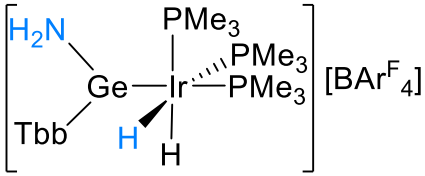
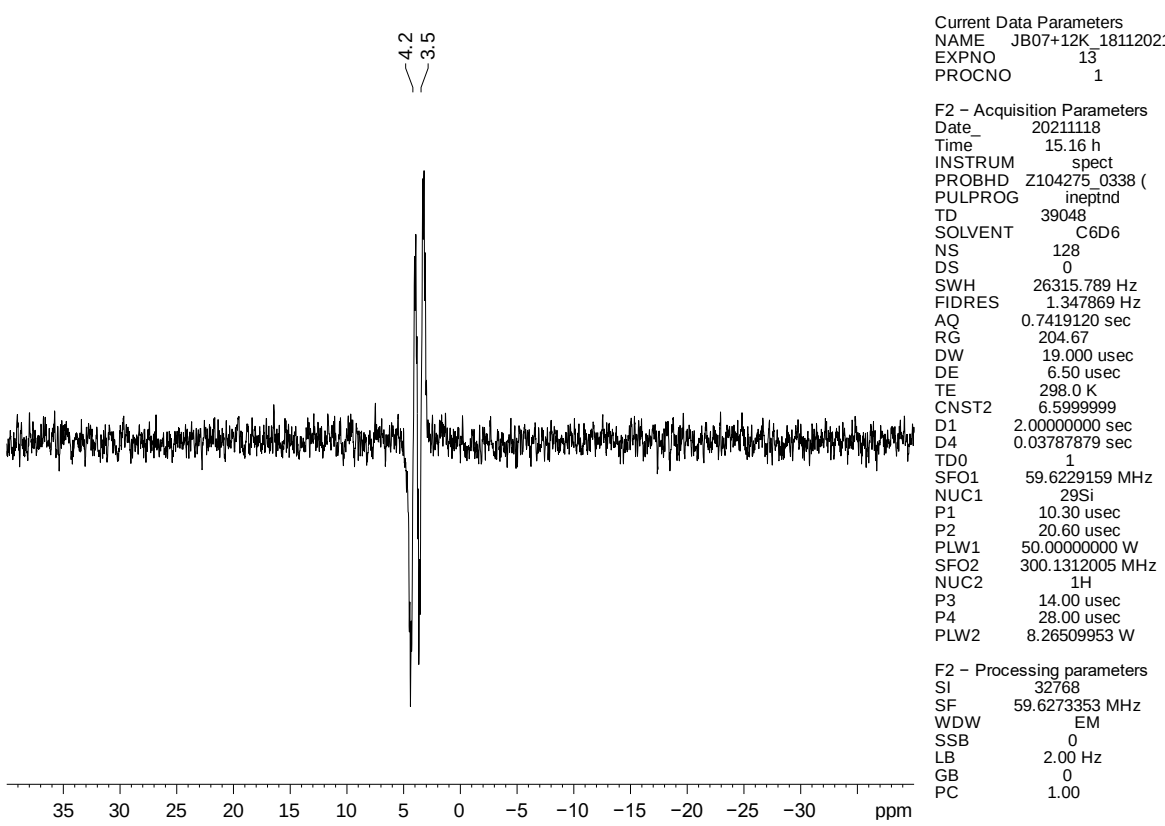


Figure SI 43. $^{19}F\{^{1}H\}$ NMR spectrum of compound **5**.

^{29}Si NMR spectrum of [TbbGe(NH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME JB07+12K_18112021_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211118
Time 15.16 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273353 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

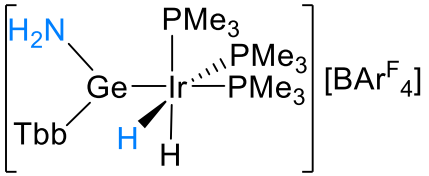
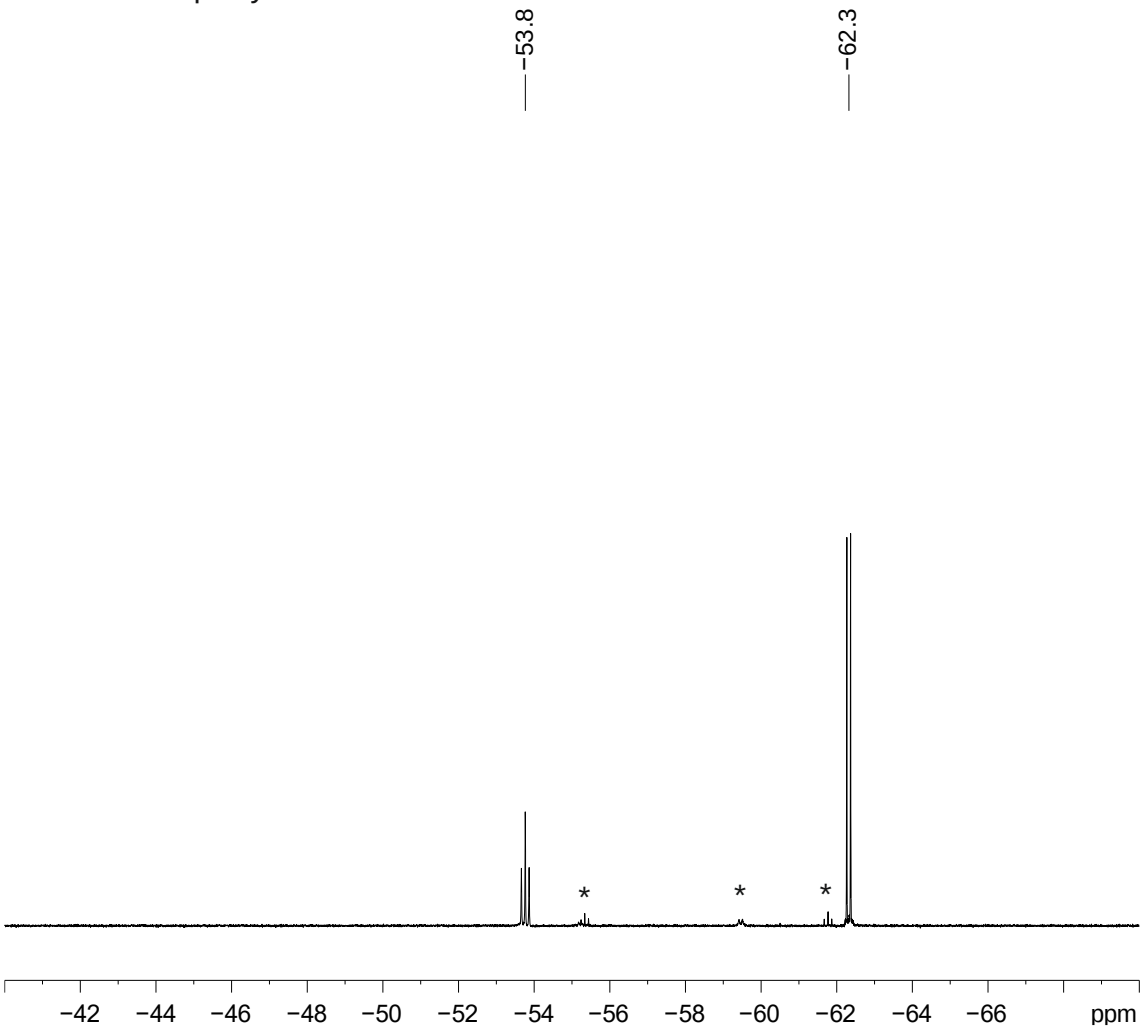


Figure SI 44. ^{29}Si NMR spectrum of compound **5**.

$^{31}P\{^{1}H\}$ NMR spectrum of $[TbbGe(NH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME JB12_12112021_500
EXPNO 2
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211112
Time 13.21
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zgpg30
TD 109230
SOLVENT C6D6
NS 128
DS 0
SWH 81521.742 Hz
FIDRES 0.746331 Hz
AQ 0.6699440 sec
RG 2050
DW 6.133 usec
DE 6.00 usec
TE 299.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 3.00 dB
PL1W 46.07667160 W
SFO1 202.4563352 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 −0.52 dB
PL12 15.51 dB
PL13 19.71 dB
PL2W 24.34997177 W
PL12W 0.60743308 W
PL13W 0.23093967 W
SFO2 500.1260000 MHz

F2 − Processing parameters
SI 131072
SF 202.4563350 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

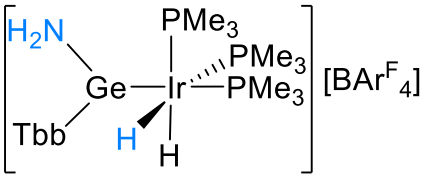
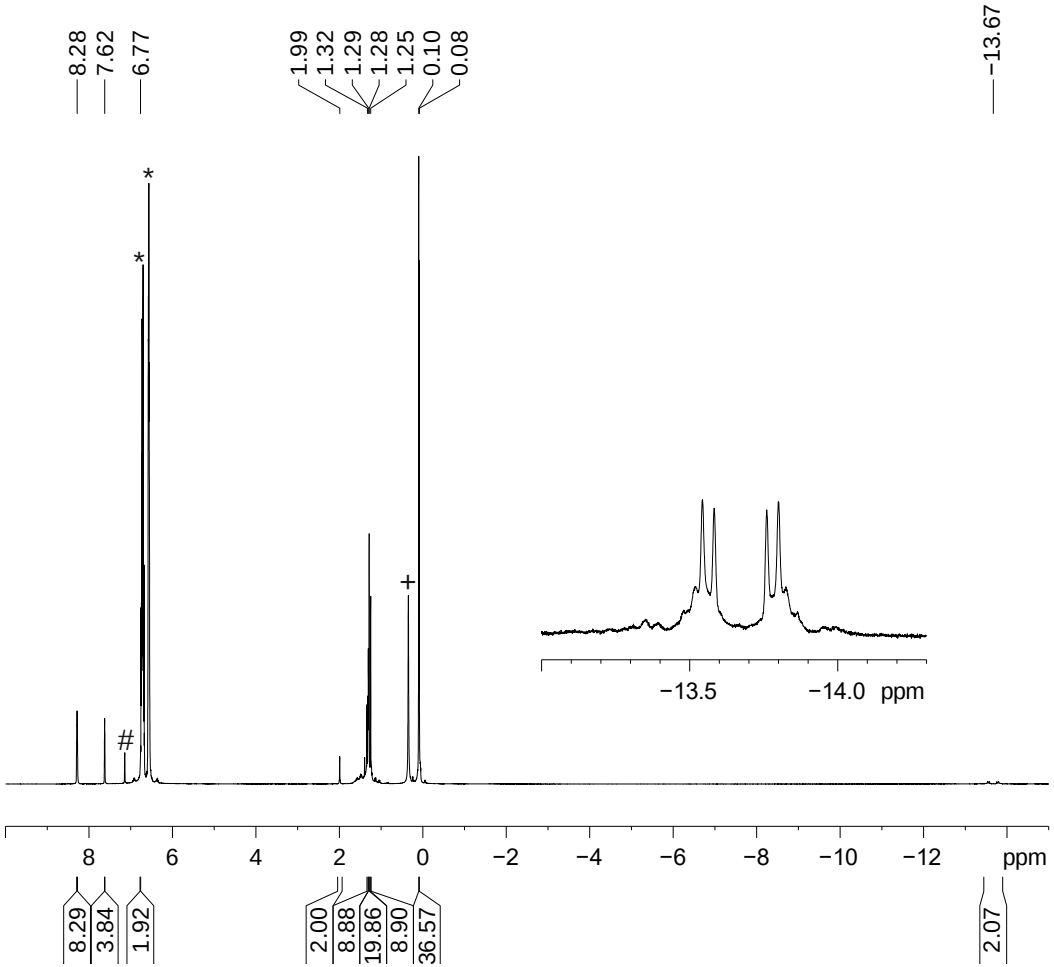


Figure SI 45. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5**.

NMR spectra of compound **6**: **4** in reaction with NH_3.

^1H NMR spectrum of **4** + NH_3 (excess) in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt. + free ammonia.



Current Data Parameters
NAME MA834_10022022_400N
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220210
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 36
DW 31.200 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

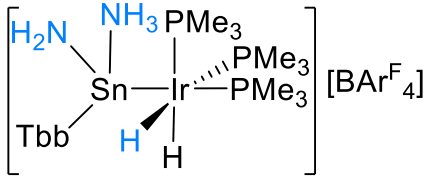
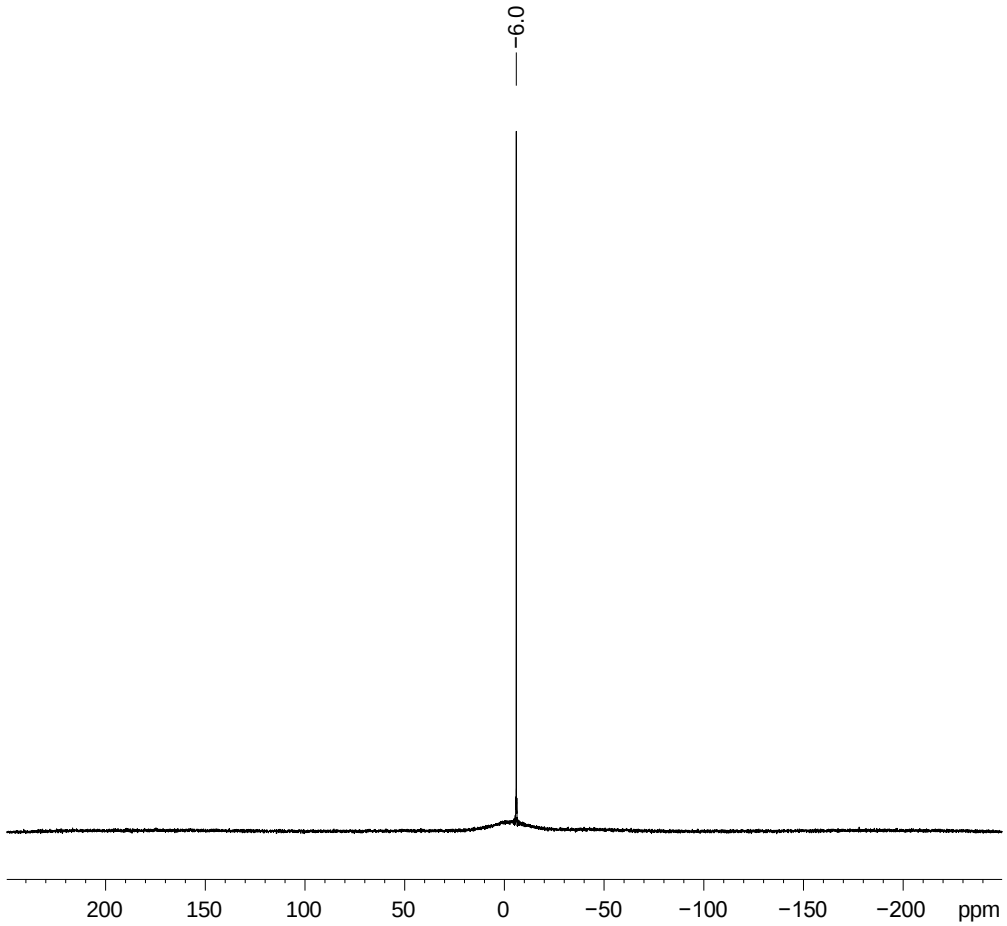


Figure SI 46. ^1H NMR spectrum of compound **6**: **4** in reaction with NH_3.

^{11}B NMR spectrum of **4** + NH_3 (excess) in benzene-d_6 and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA834_11022022_300
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220211
Time 15.58 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

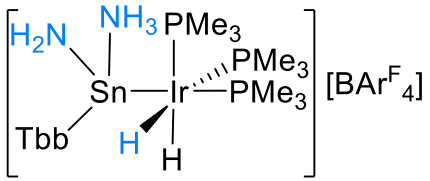
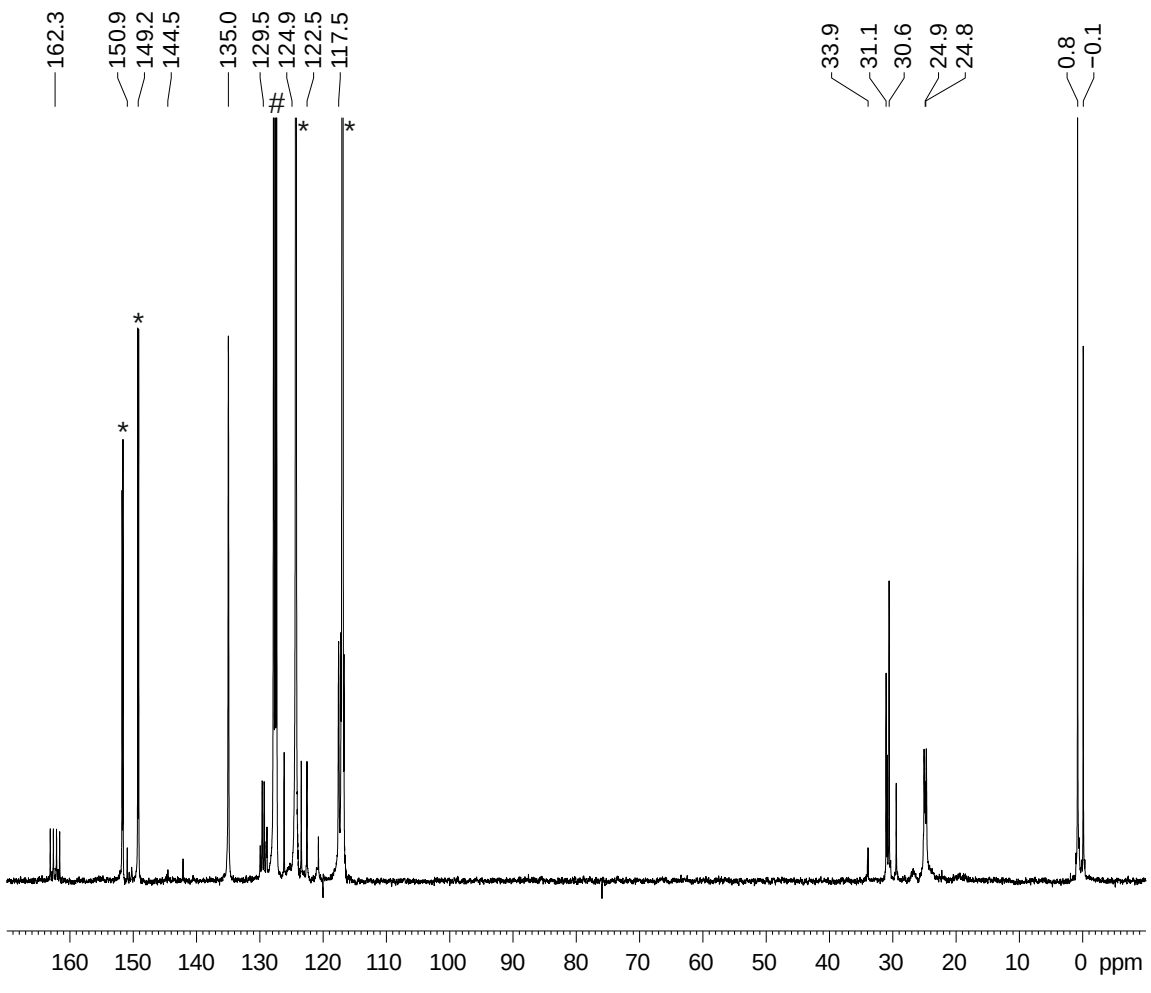


Figure SI 47. ^{11}B NMR spectrum of compound **6**: **4** in reaction with NH_3.

$^{13}C\{^{1}H\}$ NMR spectrum of **4** + NH_3 (excess) in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME      MA834_10022022_400N
EXPNO                  17
PROCNO                  1

F2 − Acquisition Parameters
Date_           20220211
Time               2.44
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD              22218
SOLVENT           C6D6
NS                6144
DS                   0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG               32800
DW              16.200 usec
DE               6.00 usec
TE              299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               13.50 usec
P13             2000.00 usec
P26              500.00 usec
PL1              −4.16 dB
PL1W         78.55633545 W
SFO1        100.6198135 MHz
SP8               1.39 dB
SP13              1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

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

F2 − Processing parameters
SI              131072
SF          100.6077400 MHz
WDW                EM
SSB                 0
LB               3.00 Hz
GB                  0
PC                1.40
```

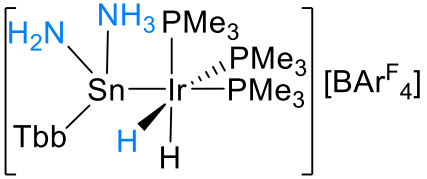
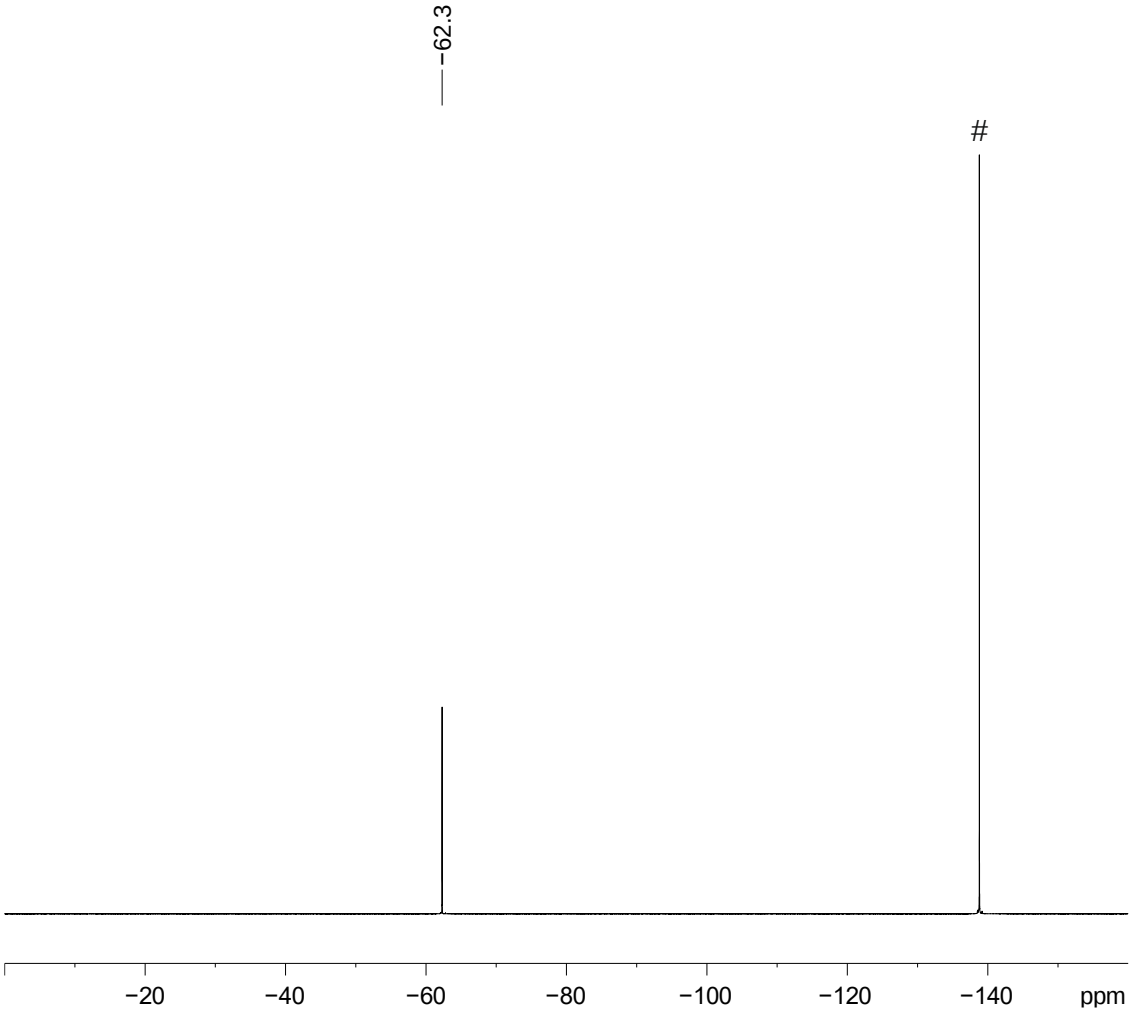


Figure SI 48. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6**: **4** in reaction with NH_3.

$^{19}F\{^{1}H\}$ NMR spectrum of **4** + NH_3 (excess) in benzene-d $_6$ and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA834_10022022_400N
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220210
Time 20.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn
TD 131072
SOLVENT C6D6
NS 32
DS 0
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6553600 sec
RG 4100
DW 5.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 19F
P1 18.75 usec
PL1 −2.92 dB
PL1W 30.50645256 W
SFO1 376.4306030 MHz

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

F2 − Processing parameters
SI 262144
SF 376.4795470 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

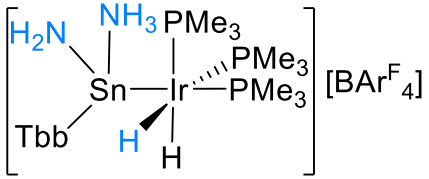
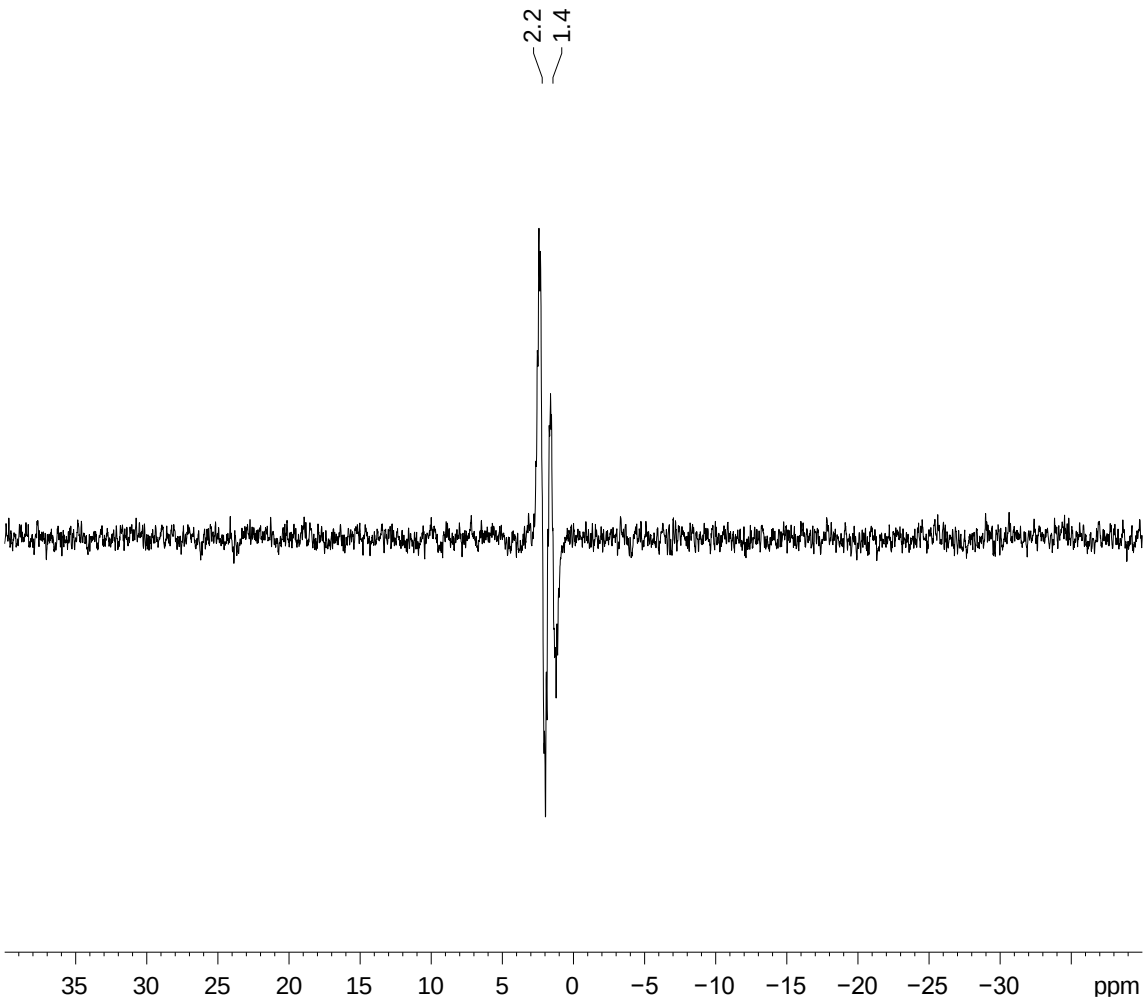


Figure SI 49. $^{19}F\{^{1}H\}$ NMR spectrum of compound **6**: **4** in reaction with NH_3.

^{29}Si NMR spectrum of **4** + NH_3 (excess) in benzene-d $_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA834_11022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220211
Time 16.05 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273749 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

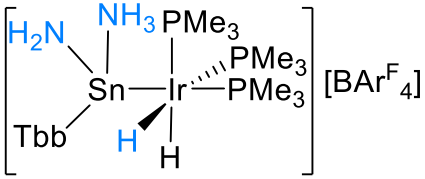
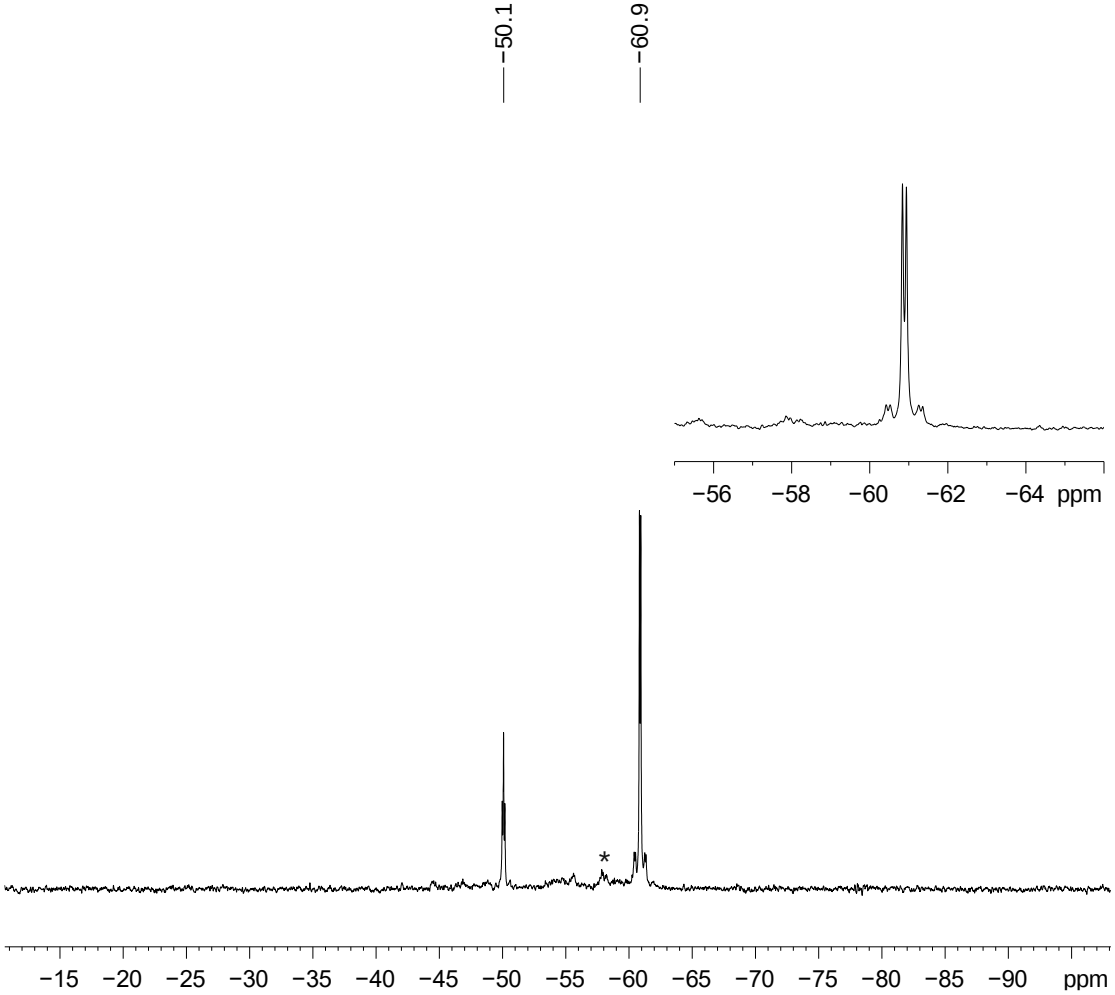


Figure SI 50. ^{29}Si NMR spectrum of compound **6**: **4** in reaction with NH_3.

$^{31}P\{^{1}H\}$ NMR spectrum of **4** + NH_3 (excess) in benzene-d $_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA834_10022022_400N
EXPNO 15
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220210
Time 20.16
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 256
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1060000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 7.00 Hz
GB 0
PC 1.40

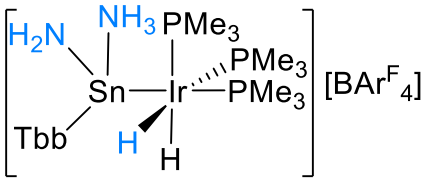
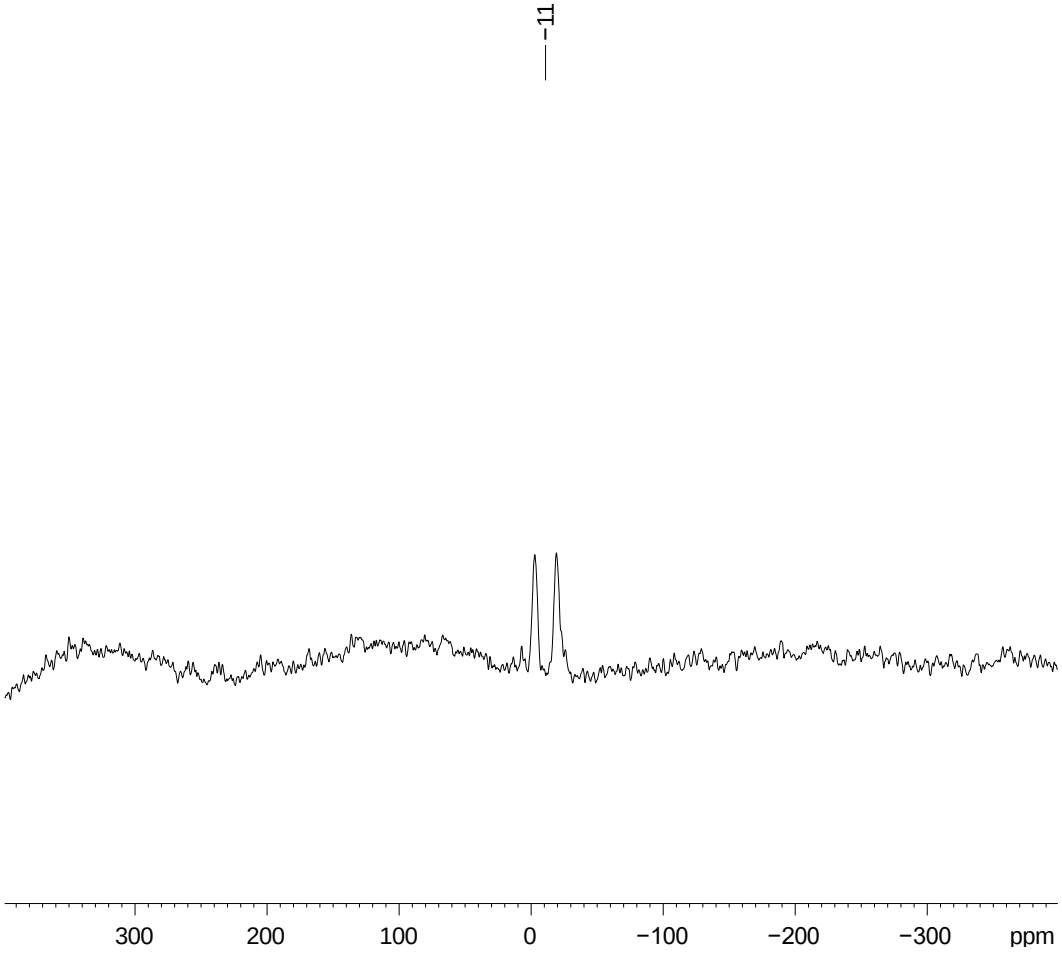


Figure SI 51. $^{31}P\{^{1}H\}$ NMR spectrum of compound **6**: **4** in reaction with NH_3.

^{119}Sn NMR spectrum of **4** + NH_3 (excess) in benzene-d $_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA834_11022022_300N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220212
Time 5.15 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 51200
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.9203740 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 150.00 Hz
GB 0
PC 1.40

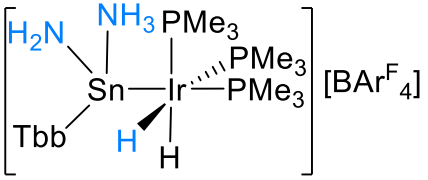
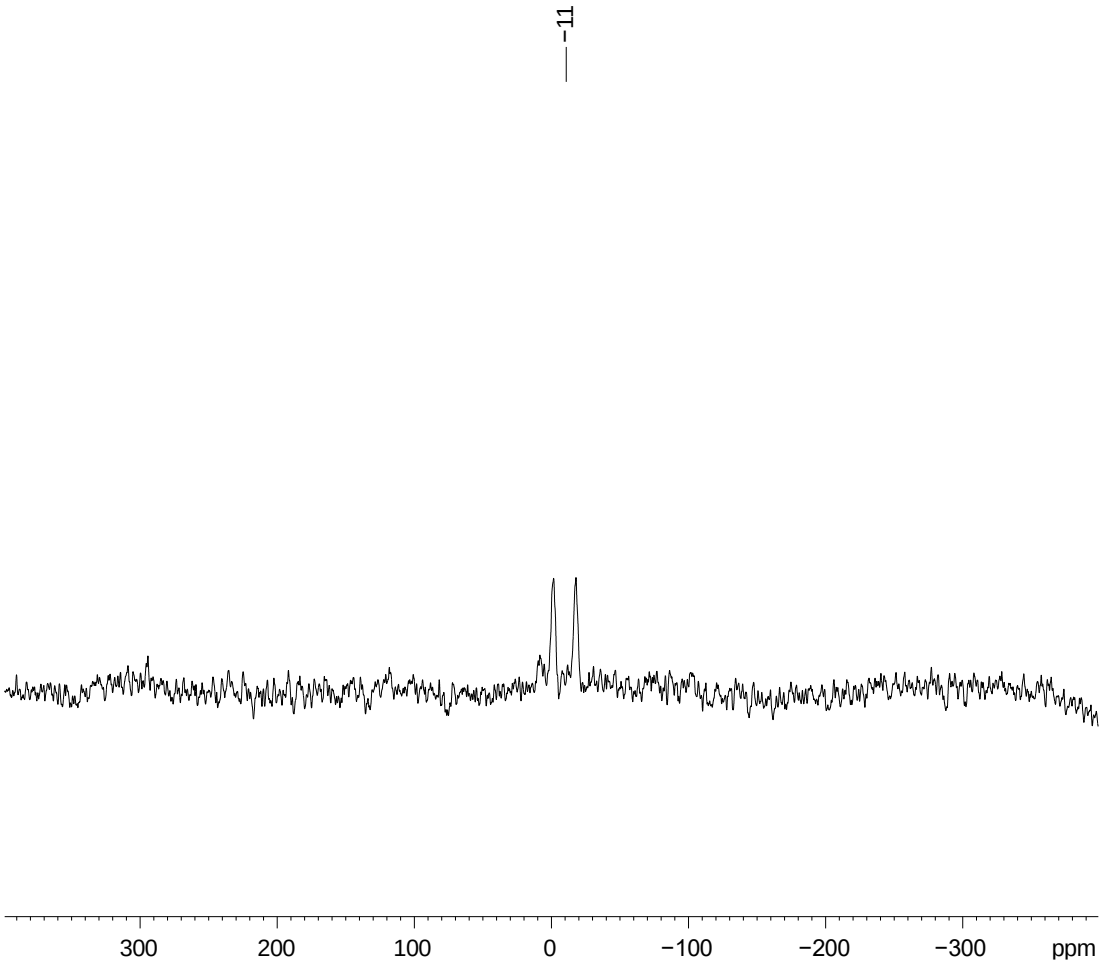


Figure SI 52. ^{119}Sn NMR spectrum of compound **6**: **4** in reaction with NH_3.

$^{119}Sn\{^{1}H\}$ NMR spectrum of **4** + NH_3 (excess) in benzene-d $_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA834_11022022_300N
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220212
Time 9.43 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 15360
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.9203738 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz
WDW EM
SSB 0
LB 100.00 Hz
GB 0
PC 1.40

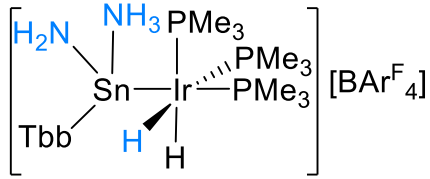
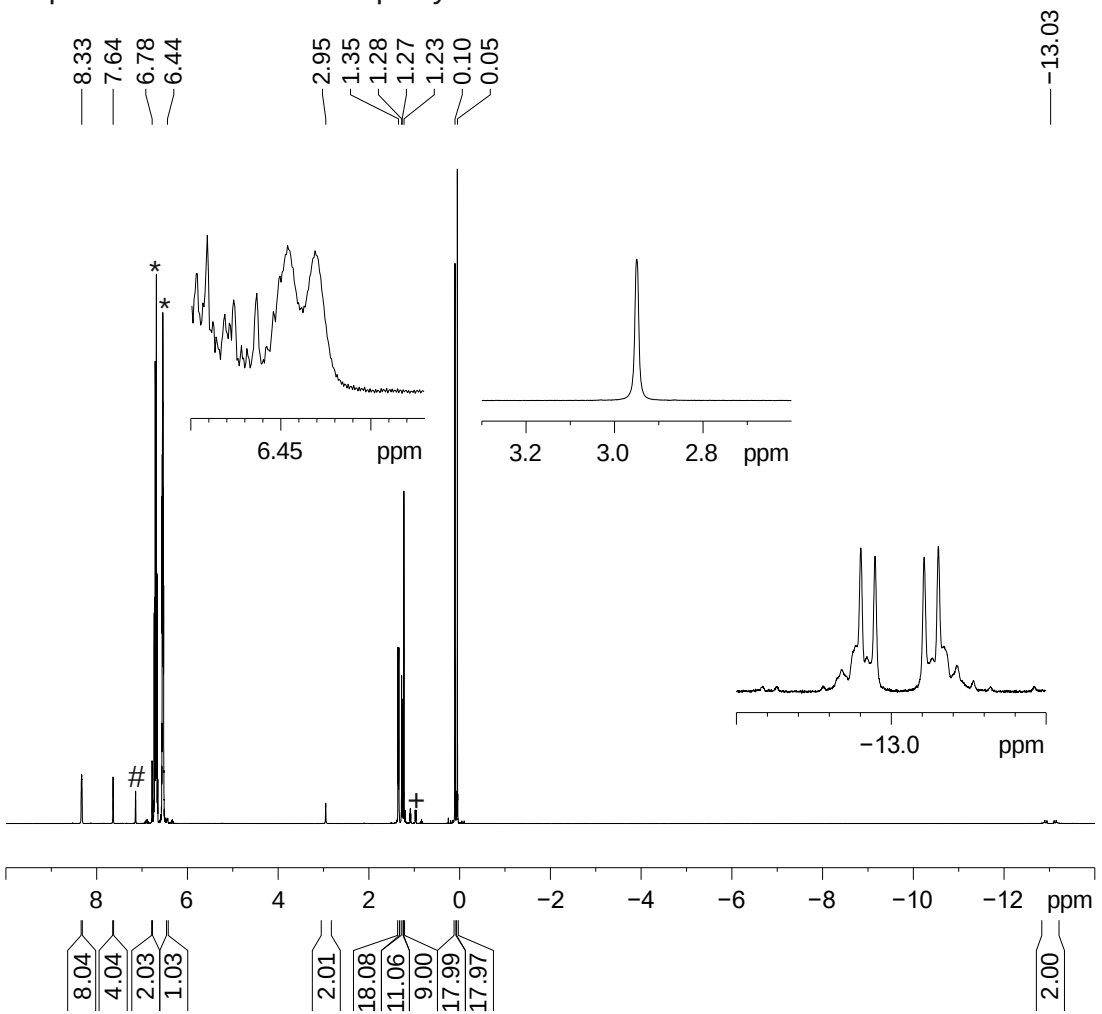


Figure SI 53. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **6**: **4** in reaction with NH_3.

NMR spectra of compound **7**.

^{1}H NMR spectrum of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane and unknown impurity.



Current Data Parameters
NAME MA829_09022022_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220209
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 45.2
DW 31.200 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

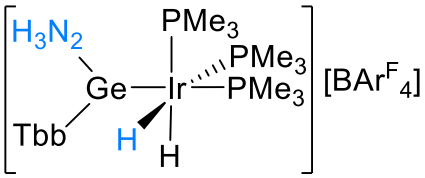
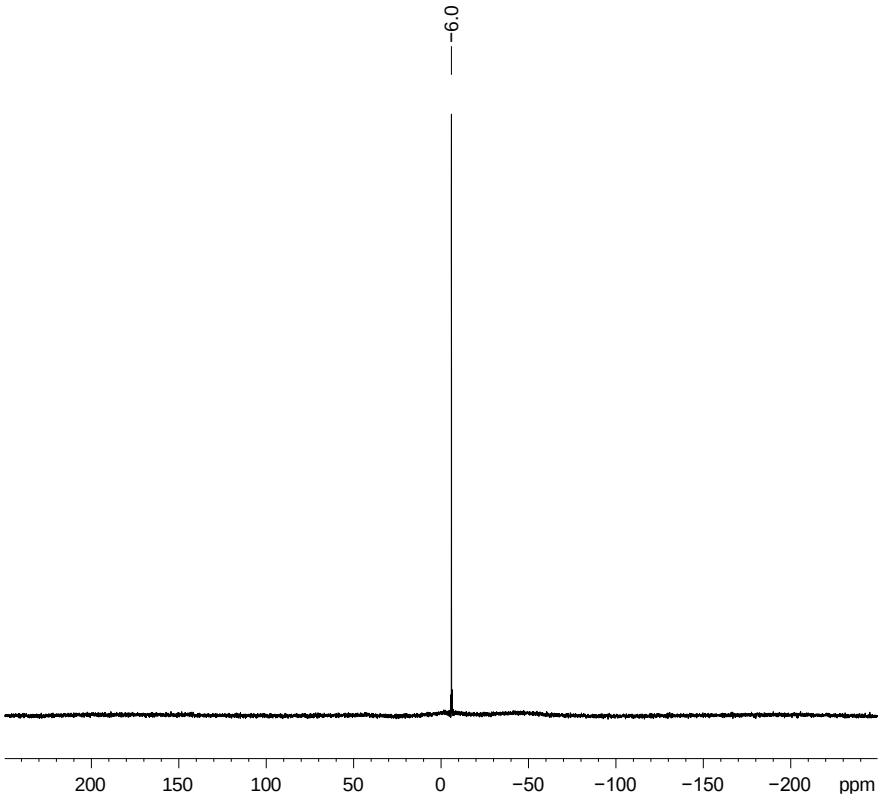


Figure SI 54. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7**.

^{11}B NMR spectrum of $[TbbGe(NHNH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA829_09022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220209
Time 9.01 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

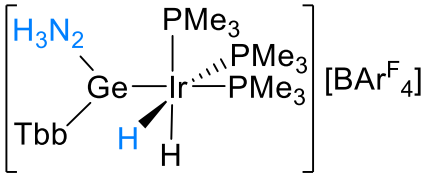
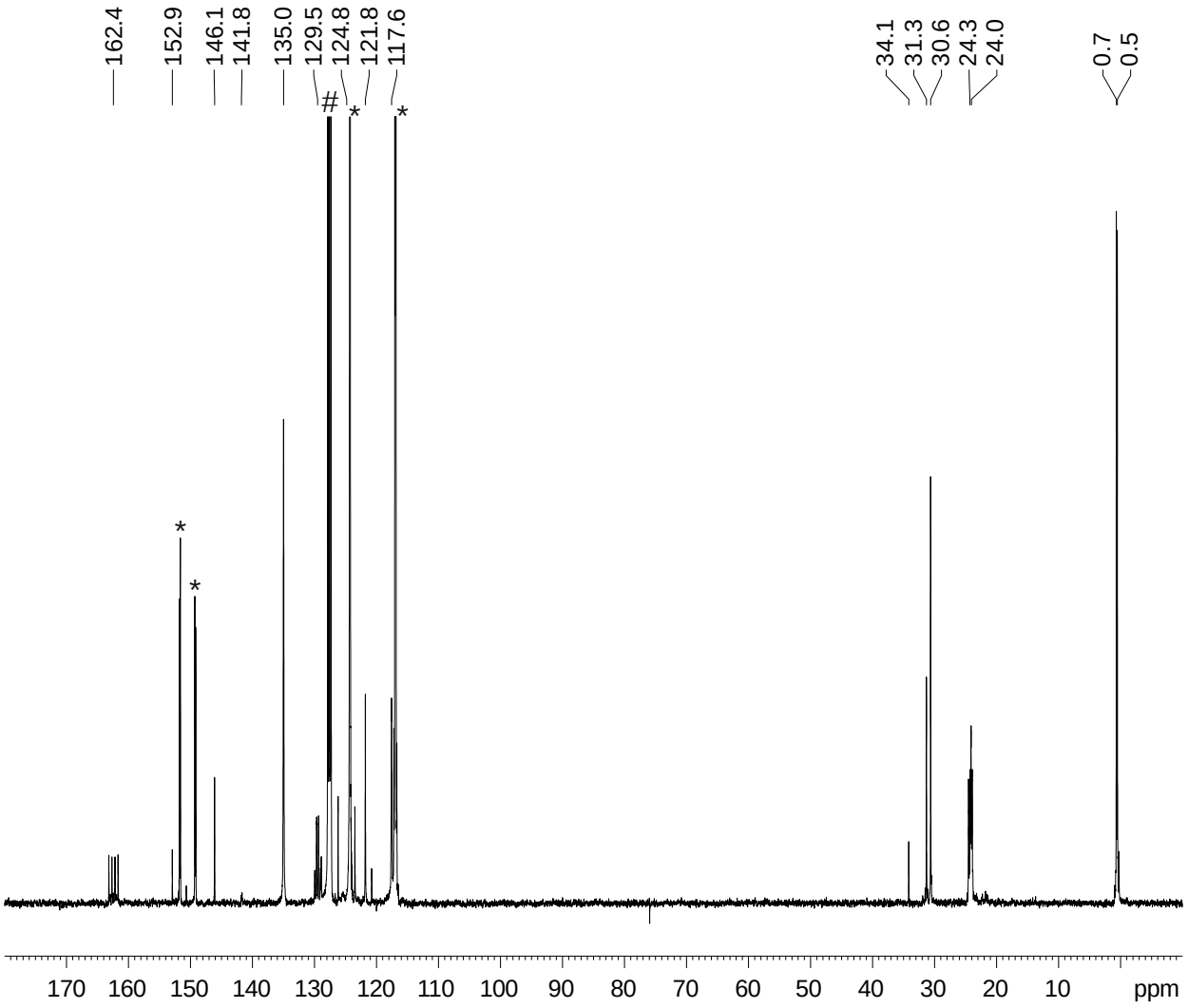


Figure SI 55. ^{11}B NMR spectrum of compound **7**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbGe(NHNH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME      MA829_09022022_400N
EXPNO             13
PROCNO             1

F2 - Acquisition Parameters
Date_          20220210
Time              2.37
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD                22218
SOLVENT           C6D6
NS                6144
DS                0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG                32800
DW               16.200 usec
DE                6.00 usec
TE               299.2 K
D1           3.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D20          100.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1              13C
P1               13.50 usec
P13            2000.00 usec
P26             500.00 usec
PL1              -4.16 dB
PL1W         78.55633545 W
SFO1         100.6198135 MHz
SP8               1.39 dB
SP13              1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8            0.500
SPOAL13           0.500
SPOFFS8             0 Hz
SPOFFS13            0 Hz

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

F2 - Processing parameters
SI              131072
SF           100.6077400 MHz
WDW               EM
SSB               0
LB               2.00 Hz
GB                0
PC               1.40
```

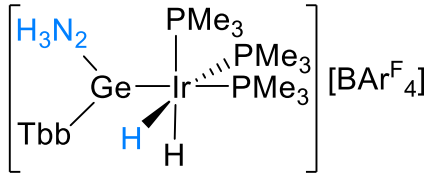
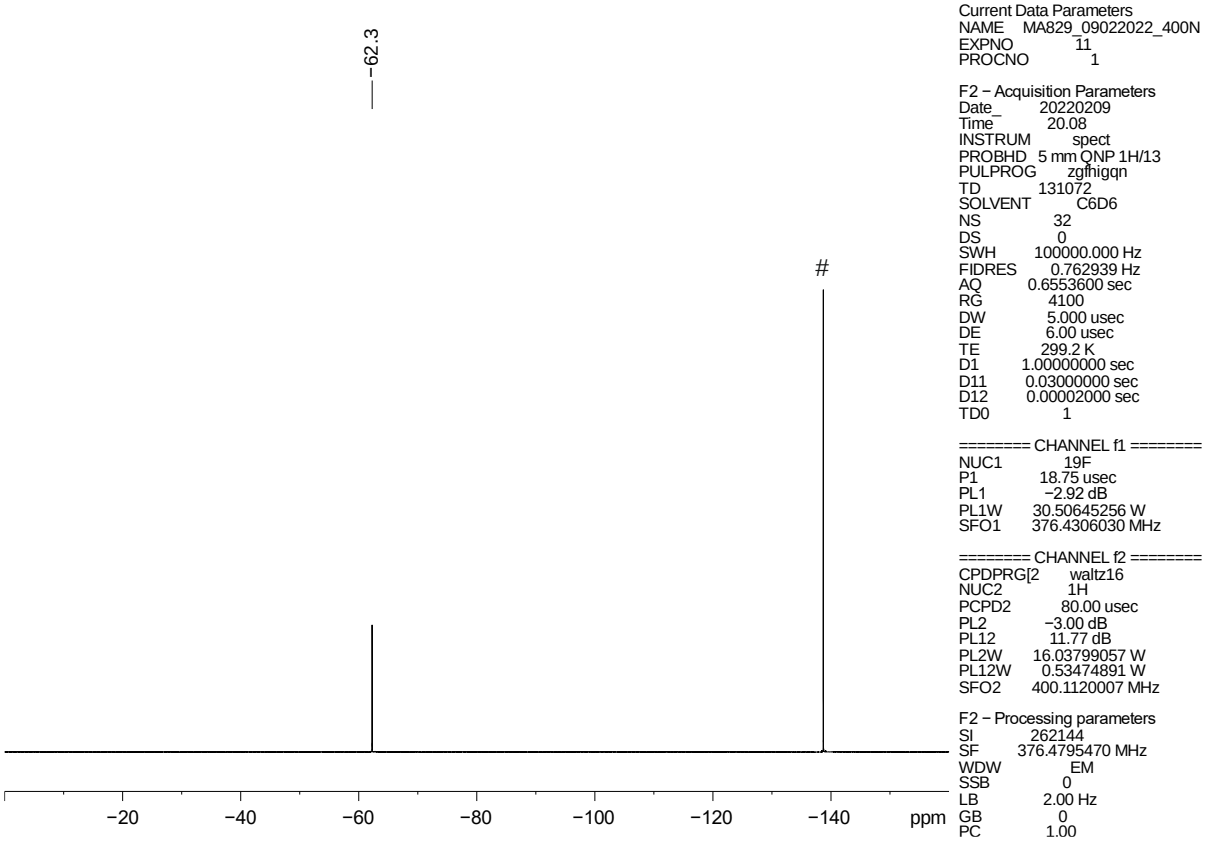


Figure SI 56. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA829_09022022_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220209
Time 20.08
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn
TD 131072
SOLVENT C6D6
NS 32
DS 0
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6553600 sec
RG 4100
DW 5.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 19F
P1 18.75 usec
PL1 −2.92 dB
PL1W 30.50645256 W
SFO1 376.4306030 MHz

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

F2 − Processing parameters
SI 262144
SF 376.4795470 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

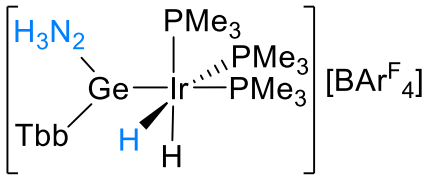
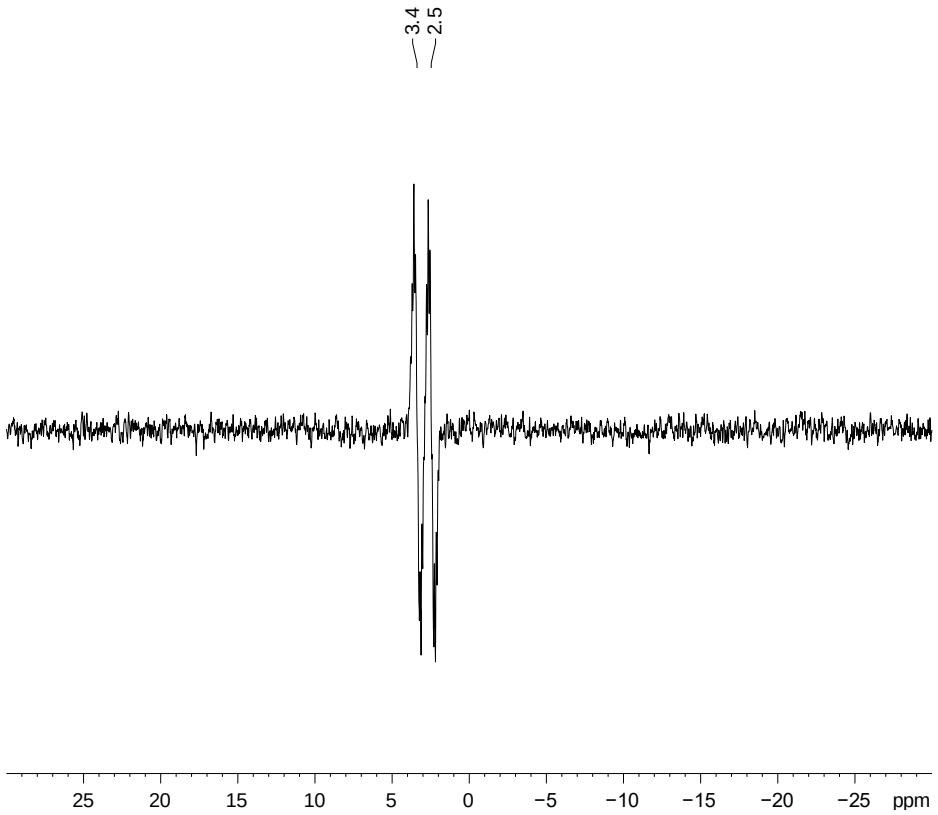


Figure SI 57. $^{19}F\{^{1}H\}$ NMR spectrum of compound **7**.

^{29}Si NMR spectrum of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA829_09022022_300
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220209
Time 9.12 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273860 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

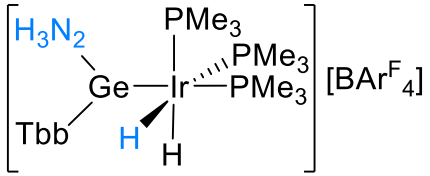
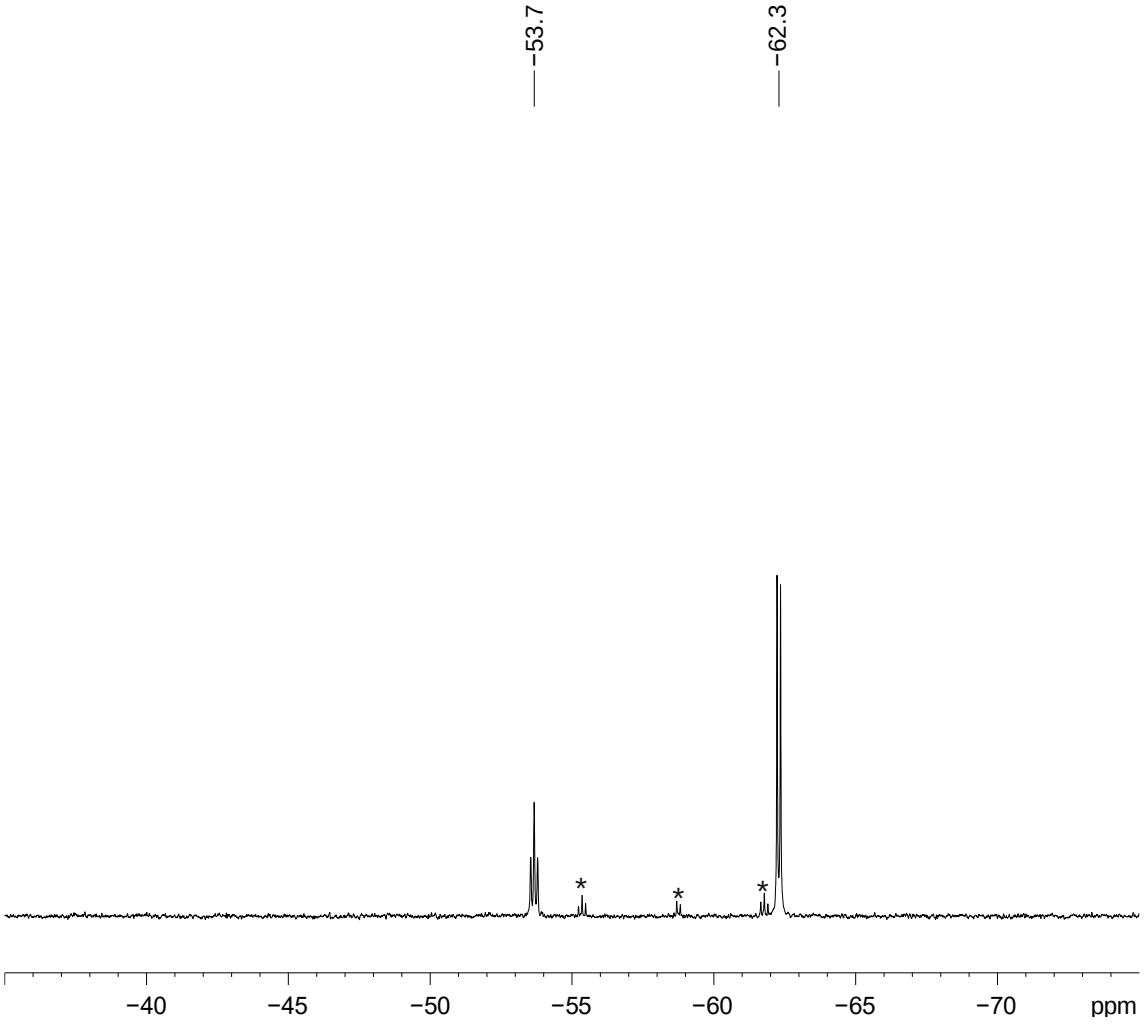


Figure SI 58. ^{29}Si NMR spectrum of compound **7**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbGe(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA829_09022022_400N
EXPNO 12
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220209
Time 20.12
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 128
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1060000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

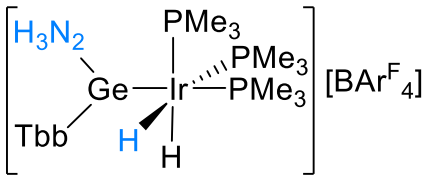
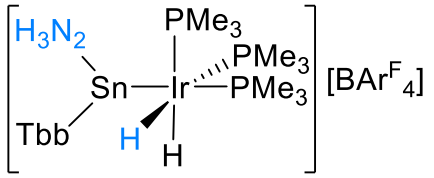
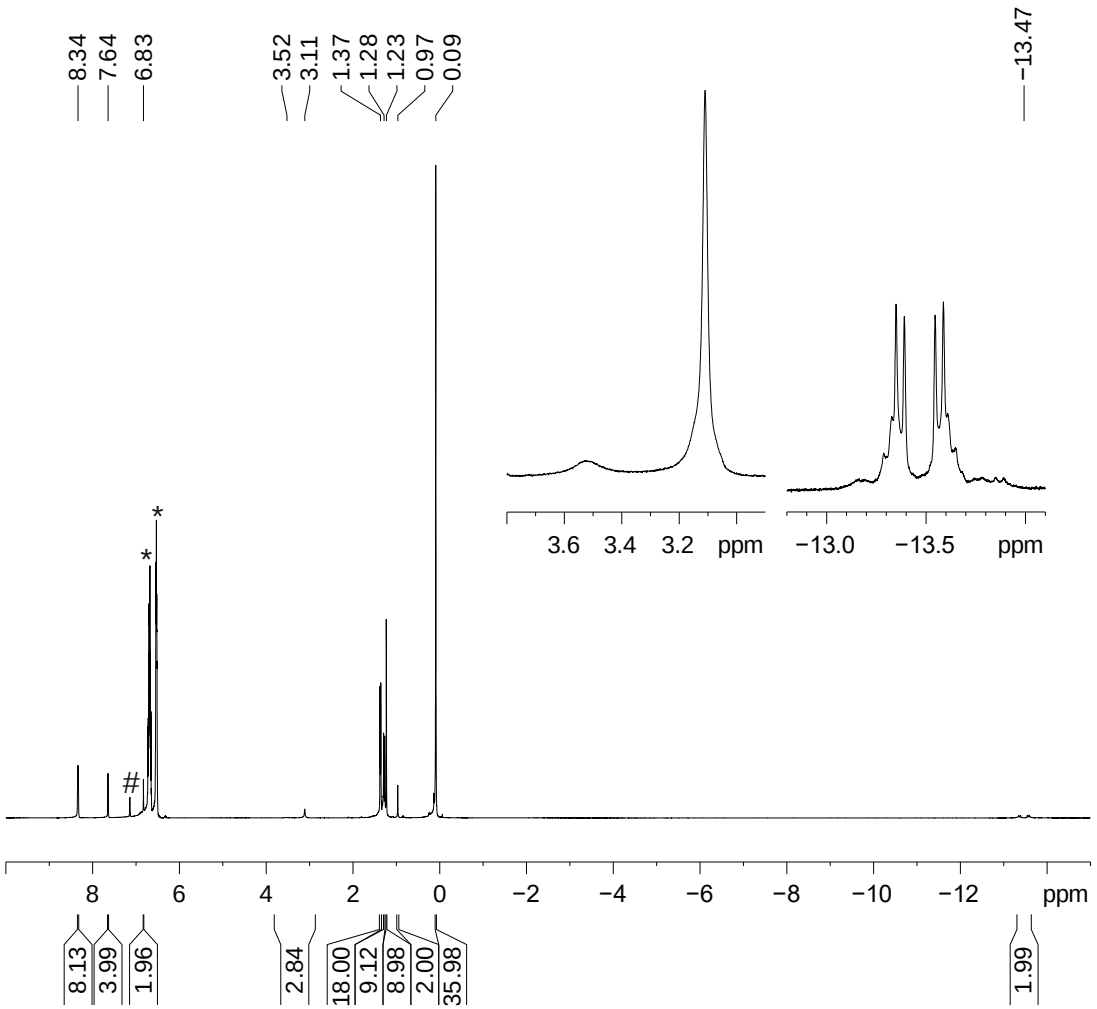


Figure SI 59. $^{31}P\{^{1}H\}$ NMR spectrum of compound **7**.

NMR spectra of compound **8**.

^{1}H NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA843_23022022_400N
EXPNO 10
PROCNO 1

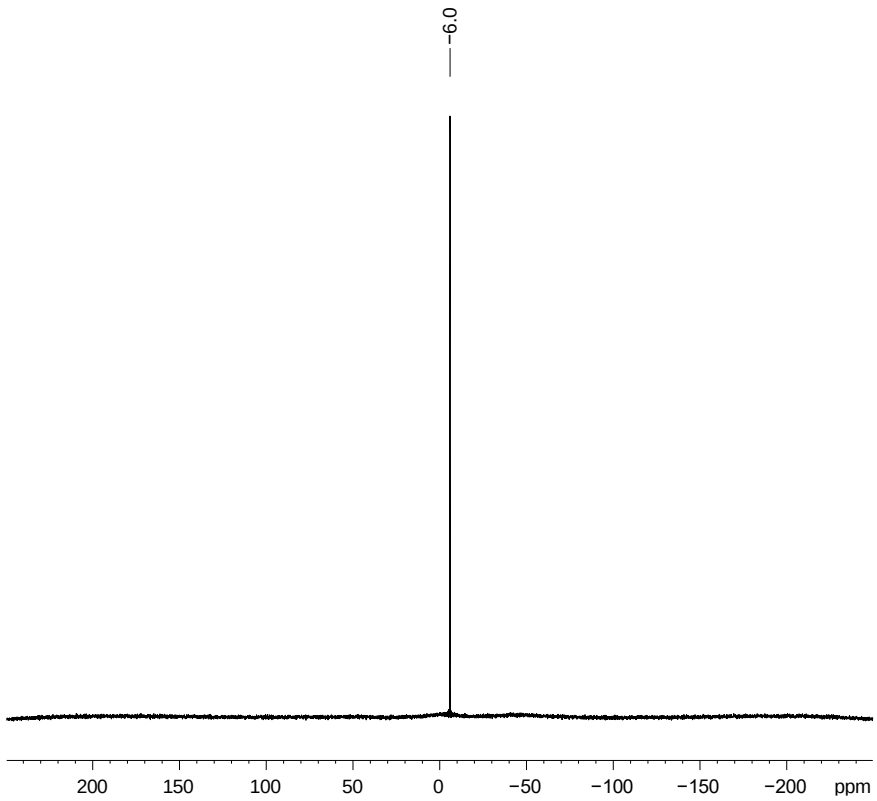
F2 − Acquisition Parameters
Date_ 20220223
Time 16.50
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 128
DS 0
SWH 20000.000 Hz
FIDRES 0.379824 Hz
AQ 1.3164001 sec
RG 45.2
DW 25.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 60. ^{13}C{^{1}H} NMR spectrum of compound **8**.

^{11}B NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA843_24022022_300
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220224
Time 7.43 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

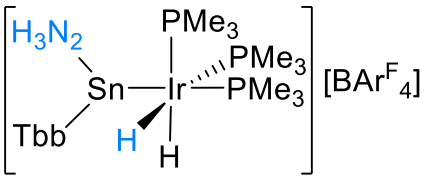
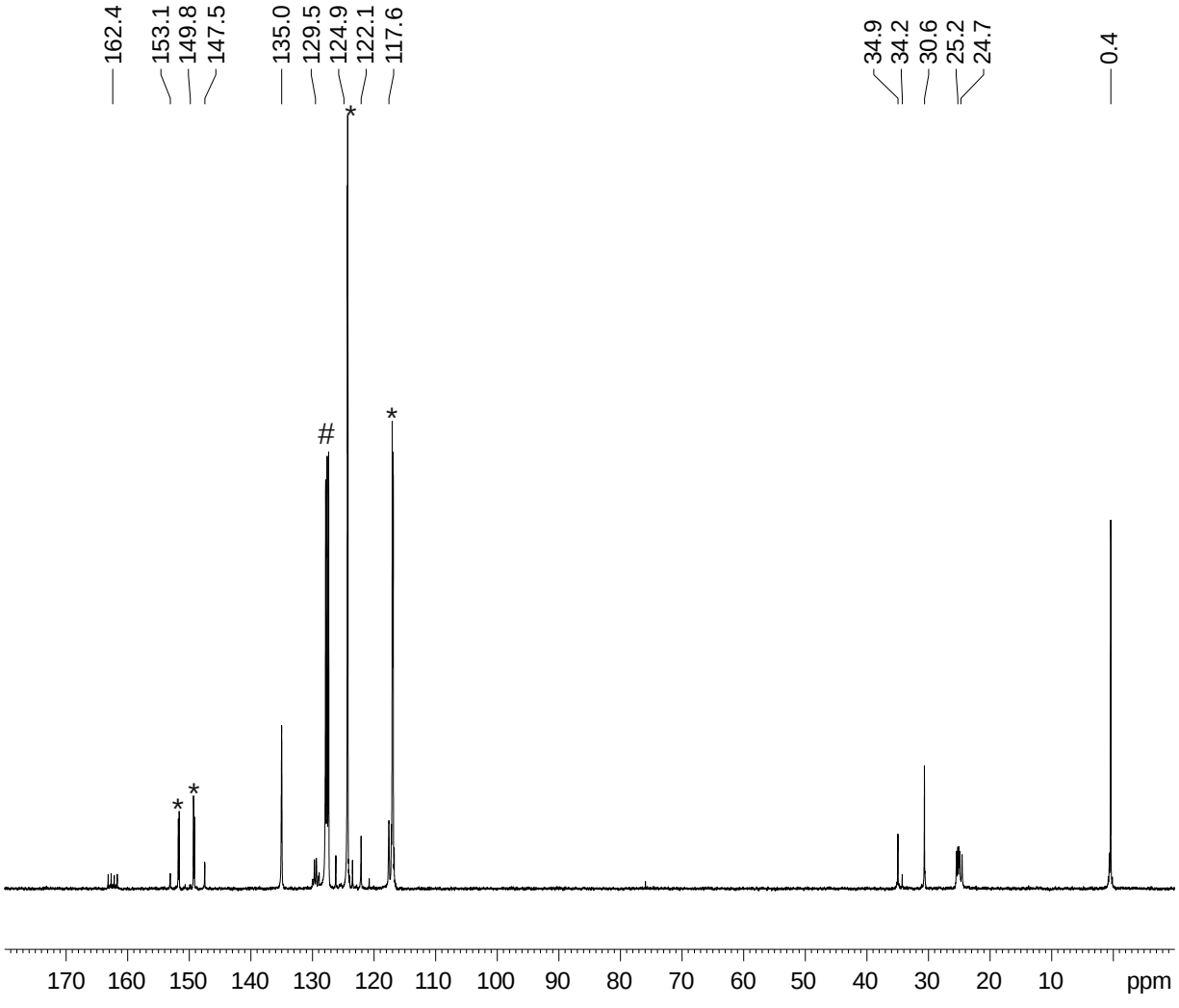
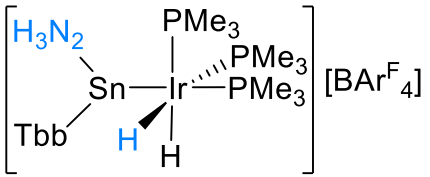


Figure SI 61. ^{11}B NMR spectrum of compound **8**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbSn(NHNH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA843_23022022_400N
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220224
Time 2.50
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG udeft
TD 22218
SOLVENT C6D6
NS 6451
DS 0
SWH 30864.197 Hz
FIDRES 1.389153 Hz
AQ 0.3599316 sec
RG 32800
DW 16.200 usec
DE 6.00 usec
TE 299.2 K
D1 3.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 100.00000000 sec
TD0 1

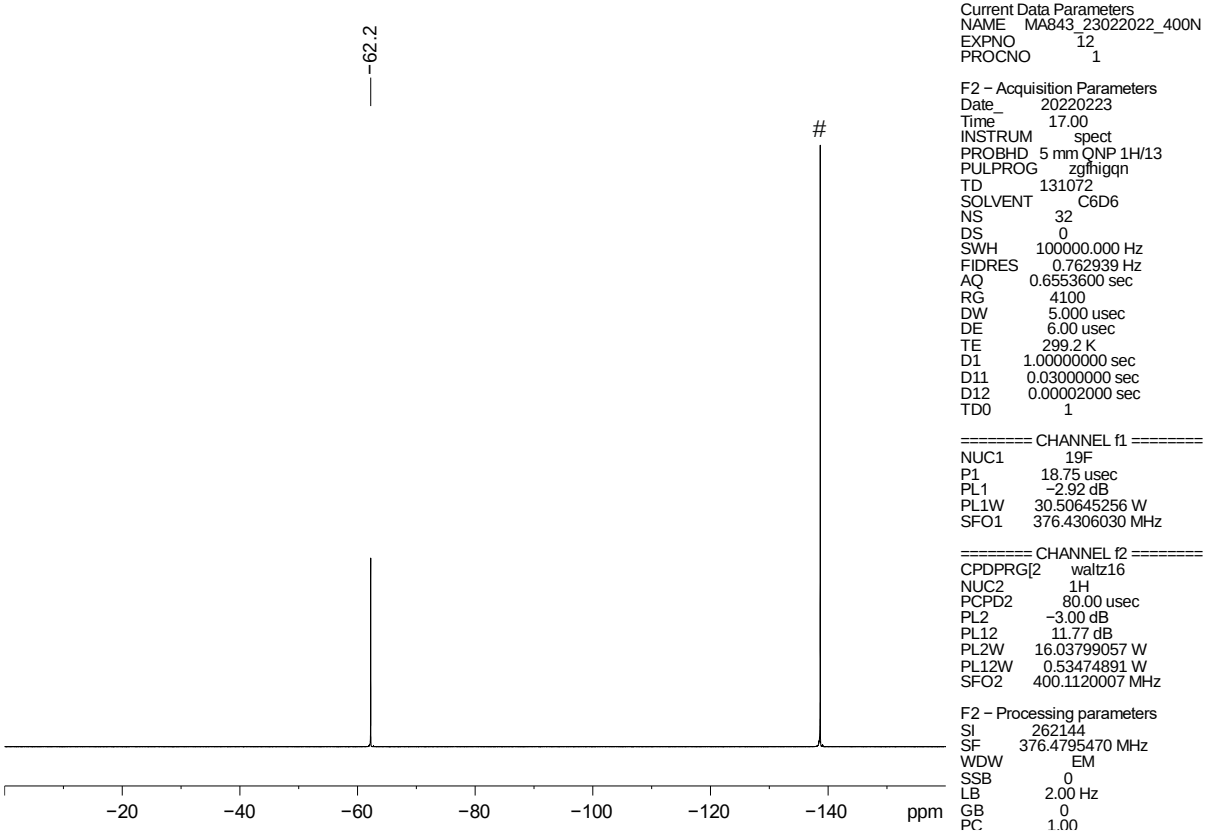
======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
P13 2000.00 usec
P26 500.00 usec
PL1 −4.16 dB
PL1W 78.55633545 W
SFO1 100.6198135 MHz
SP8 1.39 dB
SP13 1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13 Crp60comp.4
SPOAL8 0.500
SPOAL13 0.500
SPOFFS8 0 Hz
SPOFFS13 0 Hz

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

F2 − Processing parameters
SI 131072
SF 100.6077400 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure SI 62. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME    MA843_23022022_400N
EXPNO          12
PROCNO          1

F2 − Acquisition Parameters
Date_       20220223
Time           17.00
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG      zgfhigqn
TD           131072
SOLVENT          C6D6
NS               32
DS                0
SWH       100000.000 Hz
FIDRES      0.762939 Hz
AQ          0.6553600 sec
RG             4100
DW             5.000 usec
DE             6.00 usec
TE             299.2 K
D1         1.00000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             19F
P1             18.75 usec
PL1             −2.92 dB
PL1W       30.50645256 W
SFO1       376.4306030 MHz

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

F2 − Processing parameters
SI            262144
SF       376.4795470 MHz
WDW              EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.00
```

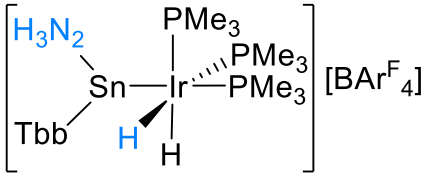
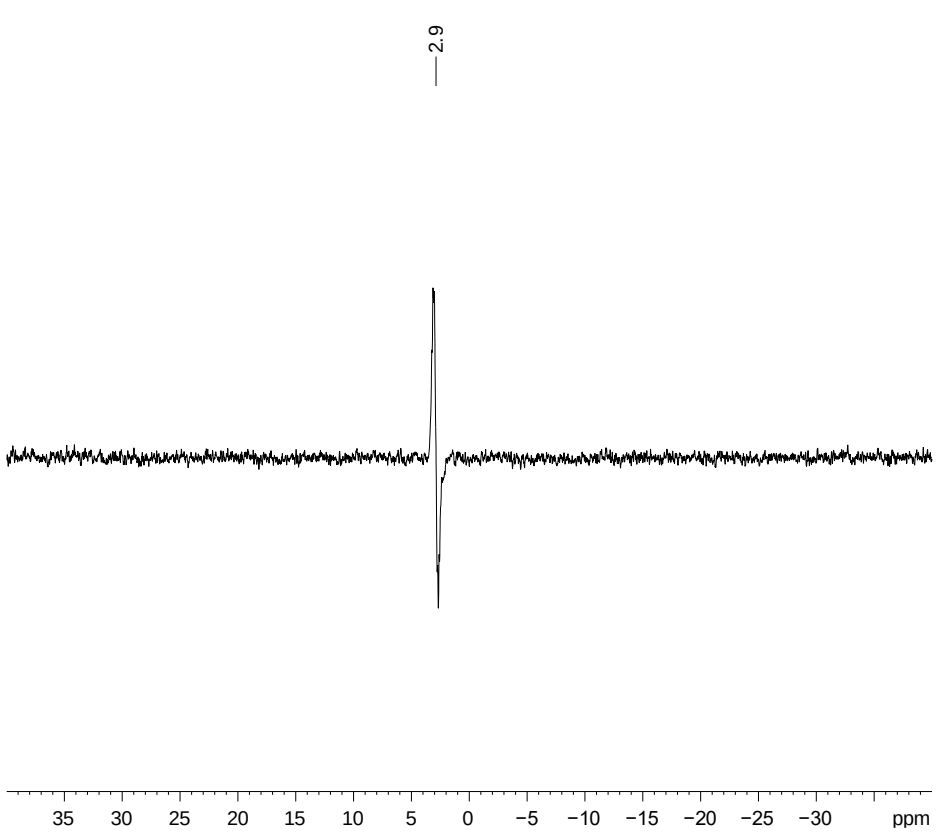


Figure SI 63. $^{19}F\{^{1}H\}$ NMR spectrum of compound **8**.

^{29}Si NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA843_24022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220224
Time 7.50 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273797 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

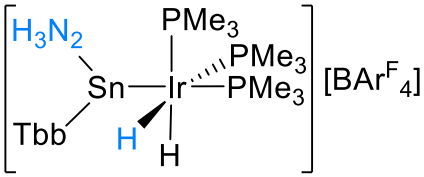
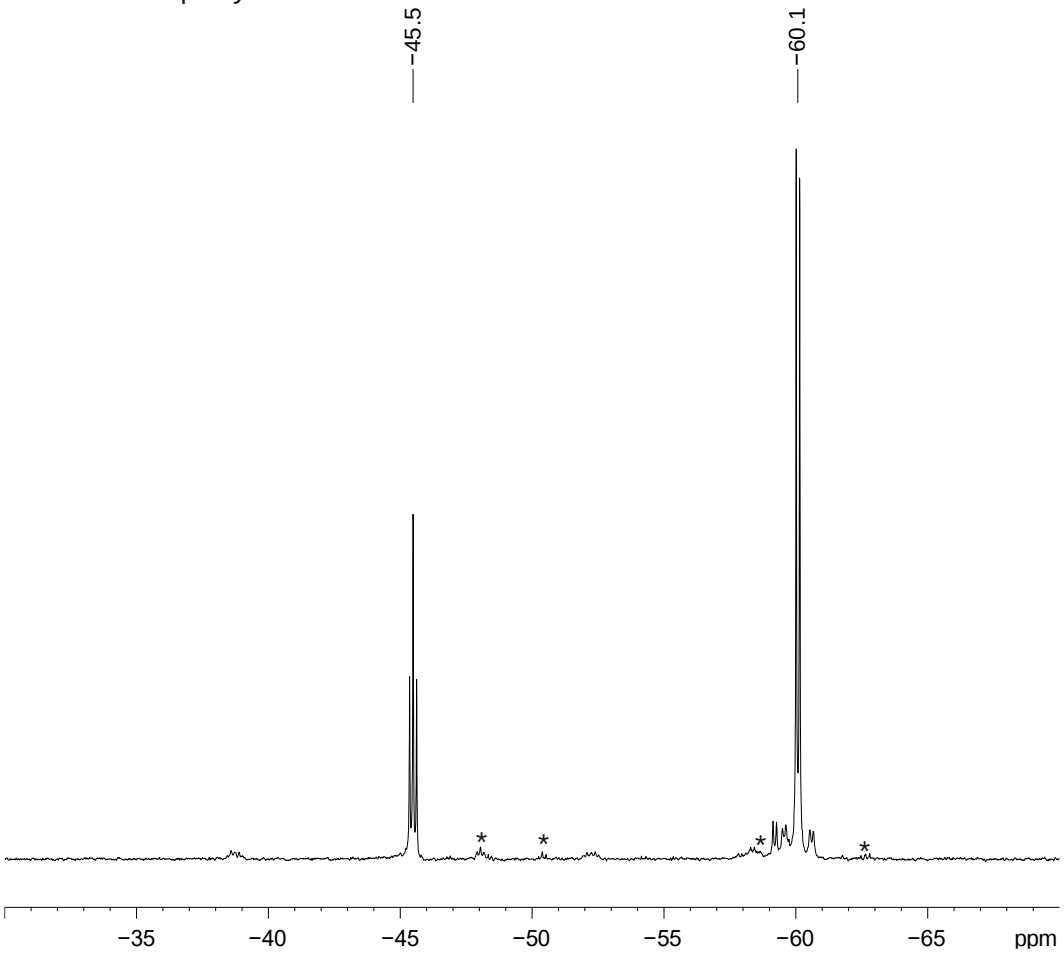


Figure SI 64. ^{29}Si NMR spectrum of compound **8**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA843_24022022_300N
EXPNO 31
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220225
Time 3.30 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 78426
SOLVENT C6D6
NS 256
DS 0
SWH 49019.609 Hz
FIDRES 1.250086 Hz
AQ 0.7999452 sec
RG 204.67
DW 10.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 121.4948510 MHz
NUC1 31P
P0 4.00 usec
P1 12.00 usec
PLW1 11.36400032 W
SFO2 300.1284994 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 121.4948510 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

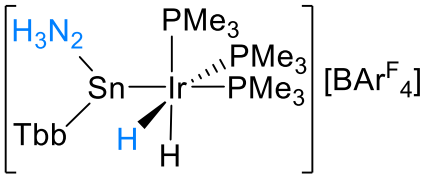
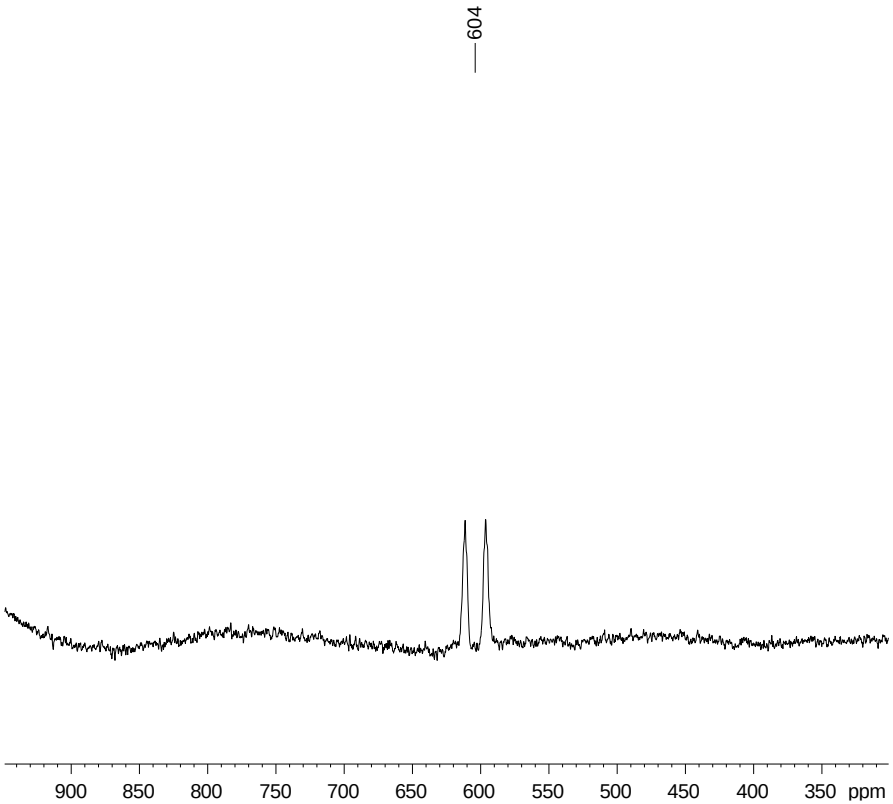


Figure SI 65. $^{31}P\{^{1}H\}$ NMR spectrum of compound **8**.

^{119}Sn NMR spectrum of [TbbSn(NHNH$_2$)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA843_24022022_300N
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220224
Time 20.26 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 168960
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.9819300 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

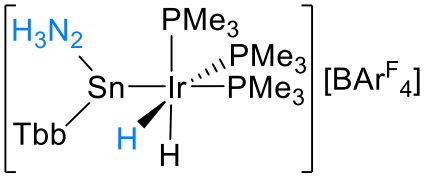
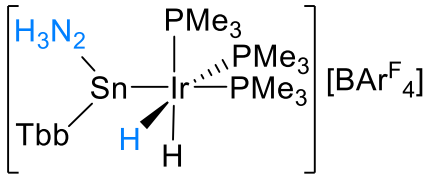
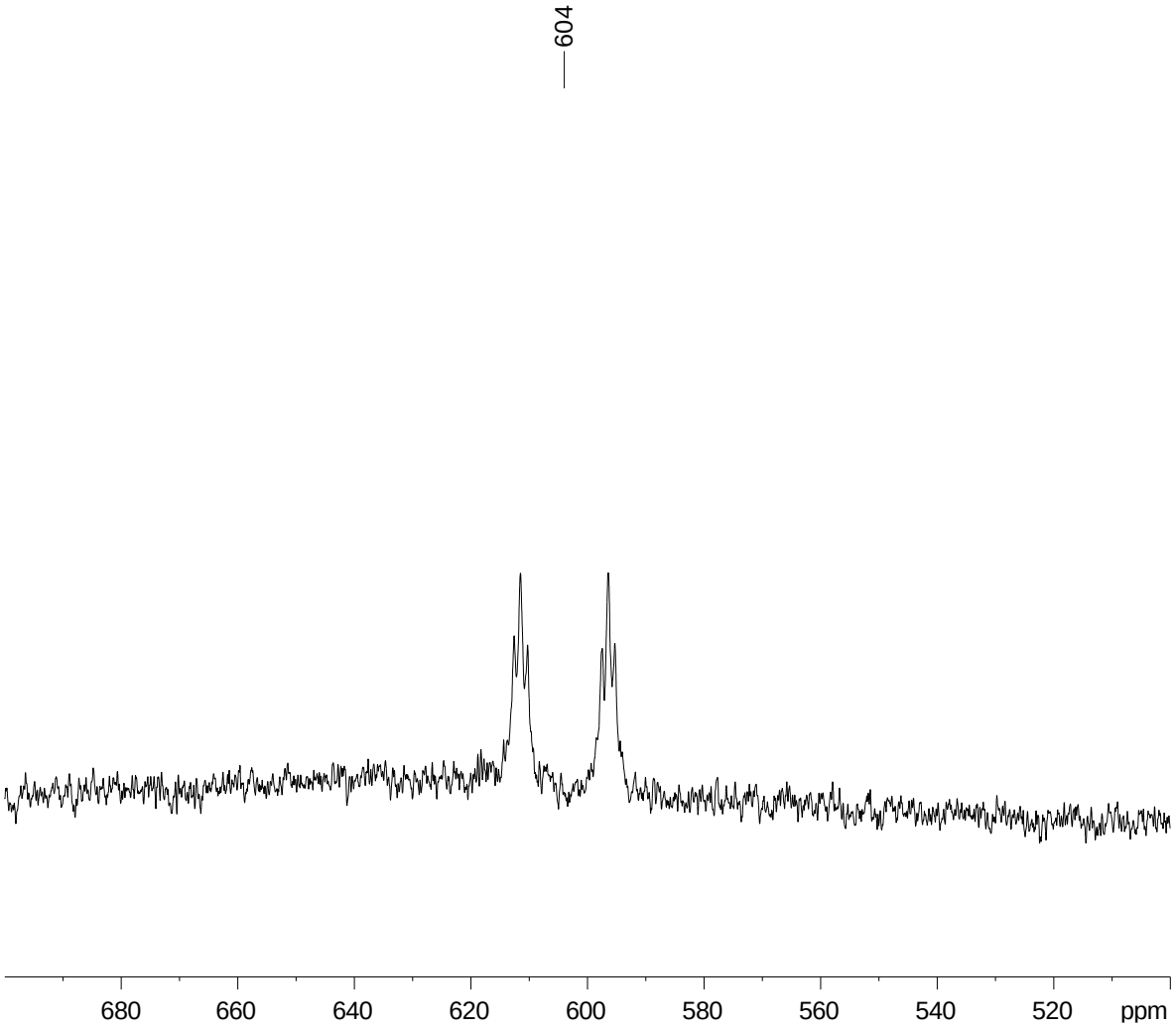


Figure SI 66. ^{119}Sn NMR spectrum of compound **8**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $[TbbSn(NHNH_2)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.





Current Data Parameters
NAME MA843_24022022_300N
EXPNO 24
PROCNO 1

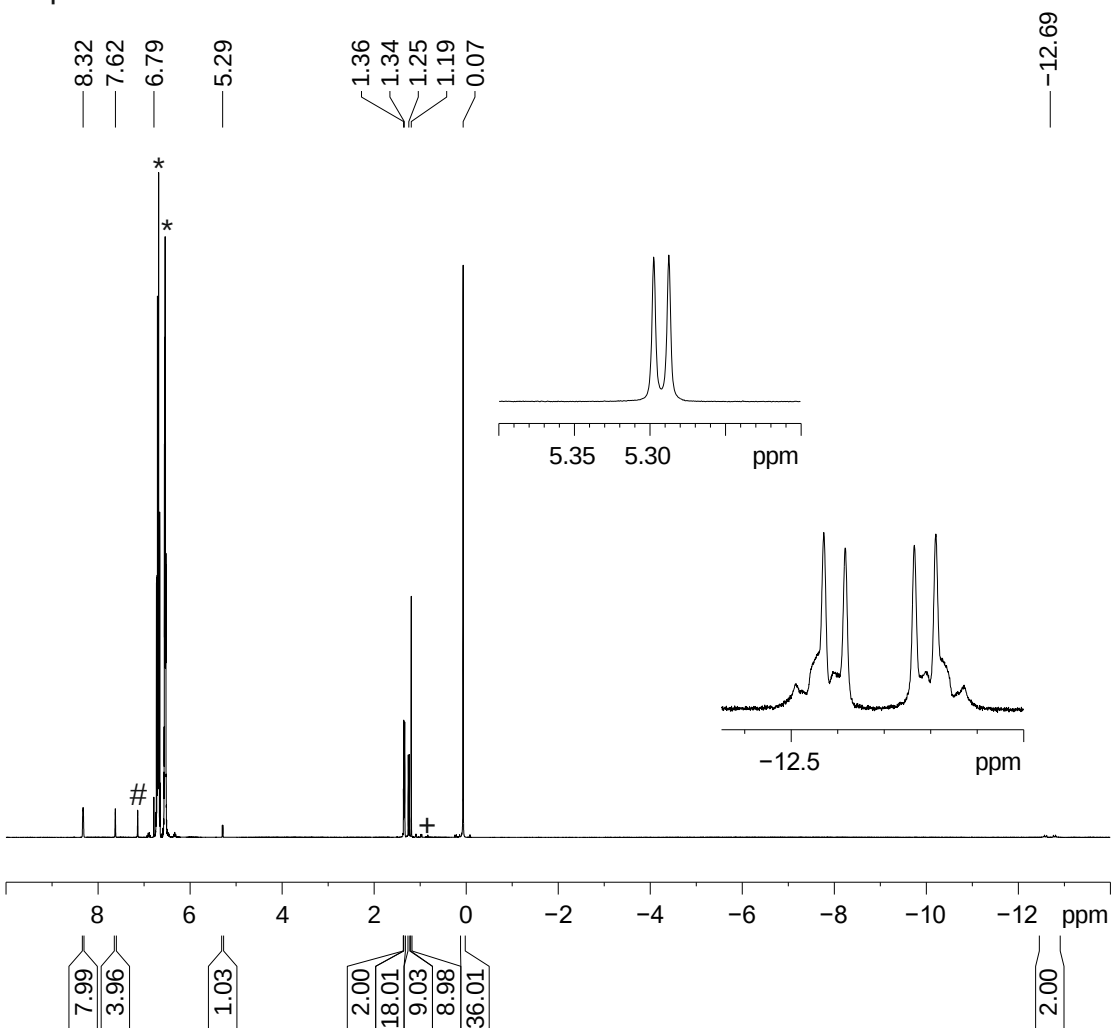
F2 − Acquisition Parameters
Date_ 20220225
Time 0.30 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 51200
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.9819298 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

Figure SI 67. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **8**.

NMR spectra of compound **9**.

^{1}H NMR spectrum of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane.



Current Data Parameters
NAME JB14+15K_19112021_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211119
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 12019.230 Hz
FIDRES 0.228259 Hz
AQ 2.1904895 sec
RG 45.2
DW 41.600 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

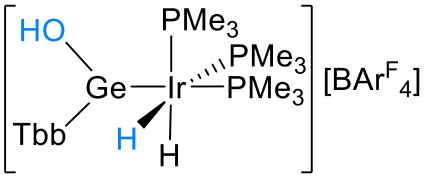
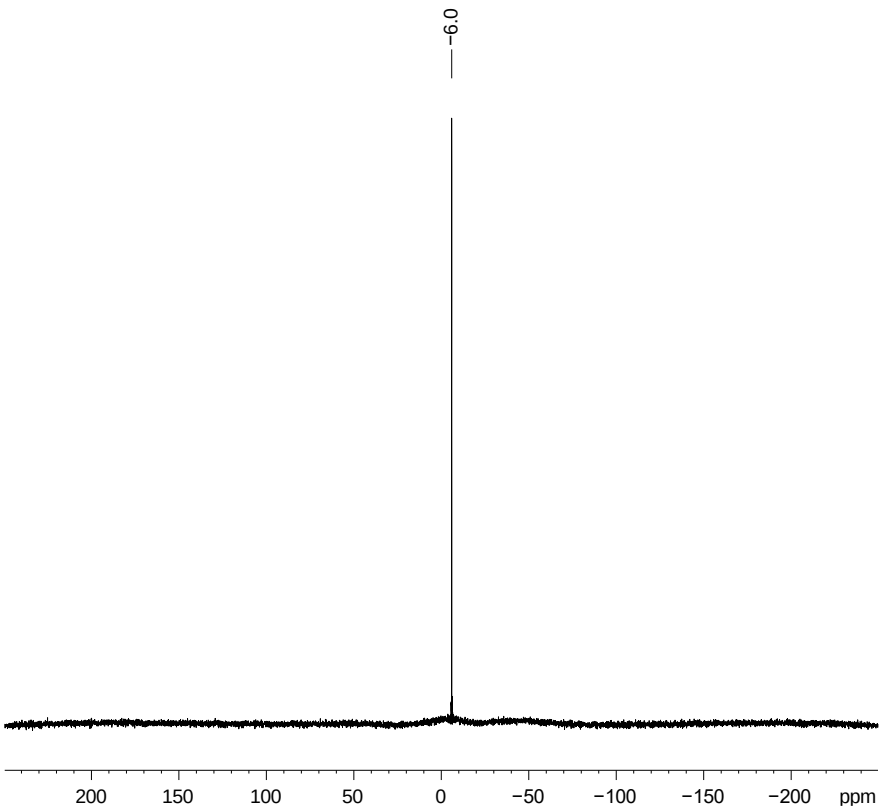


Figure SI 68. ^{1}H NMR spectrum of compound **9**.

^{11}B NMR spectrum of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME JB14+15K_24112021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211124
Time 15.02 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

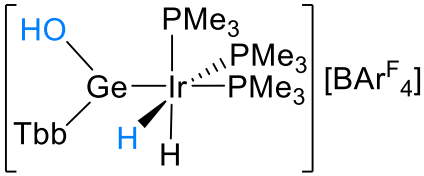
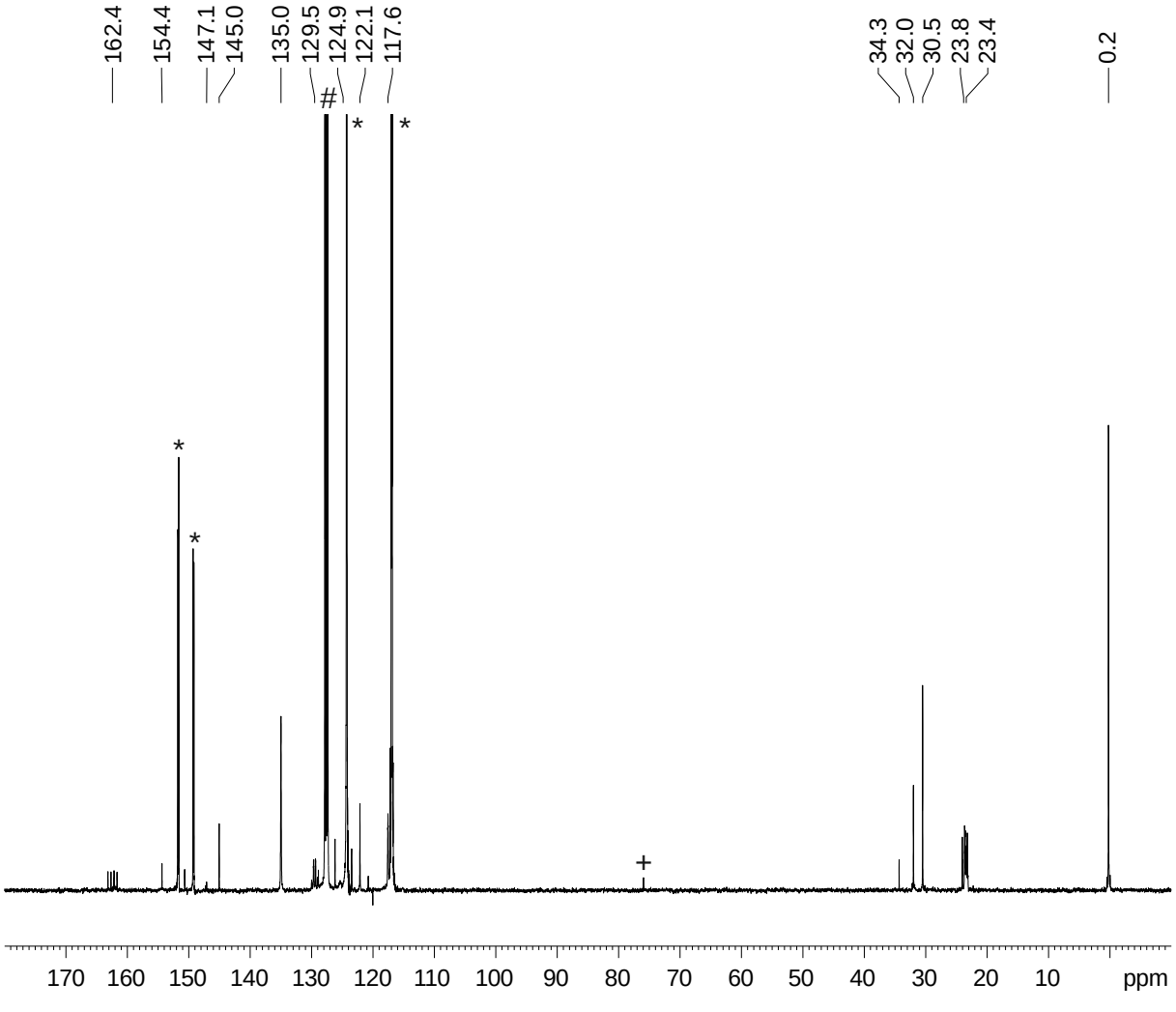


Figure SI 69. ^{11}B NMR spectrum of compound **9**.

$^{13}C\{^{1}H\}$ NMR spectrum of [TbbGe(OH)IrH_2(PMe_3)$_3$][B(Ar^F)$_4$] in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt. + unknown impurity.




```
Current Data Parameters
NAME     JB14+15K_19112021_400N
EXPNO          13
PROCNO          1

F2 - Acquisition Parameters
Date_       20211120
Time            2.14
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG         udeft
TD           22218
SOLVENT         C6D6
NS              5734
DS                 0
SWH        30864.197 Hz
FIDRES      1.389153 Hz
AQ         0.3599316 sec
RG             32800
DW            16.200 usec
DE             6.00 usec
TE            299.2 K
D1         3.00000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
D20      100.00000000 sec
TD0             1

======== CHANNEL f1 ========
NUC1            13C
P1            13.50 usec
P13         2000.00 usec
P26          500.00 usec
PL1           -4.16 dB
PL1W       78.55633545 W
SFO1      100.6198135 MHz
SP8            1.39 dB
SP13           1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8         0.500
SPOAL13        0.500
SPOFFS8          0 Hz
SPOFFS13         0 Hz

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

F2 - Processing parameters
SI           131072
SF        100.6077400 MHz
WDW             EM
SSB             0
LB           2.00 Hz
GB              0
PC           1.40
```

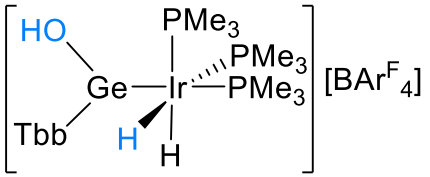
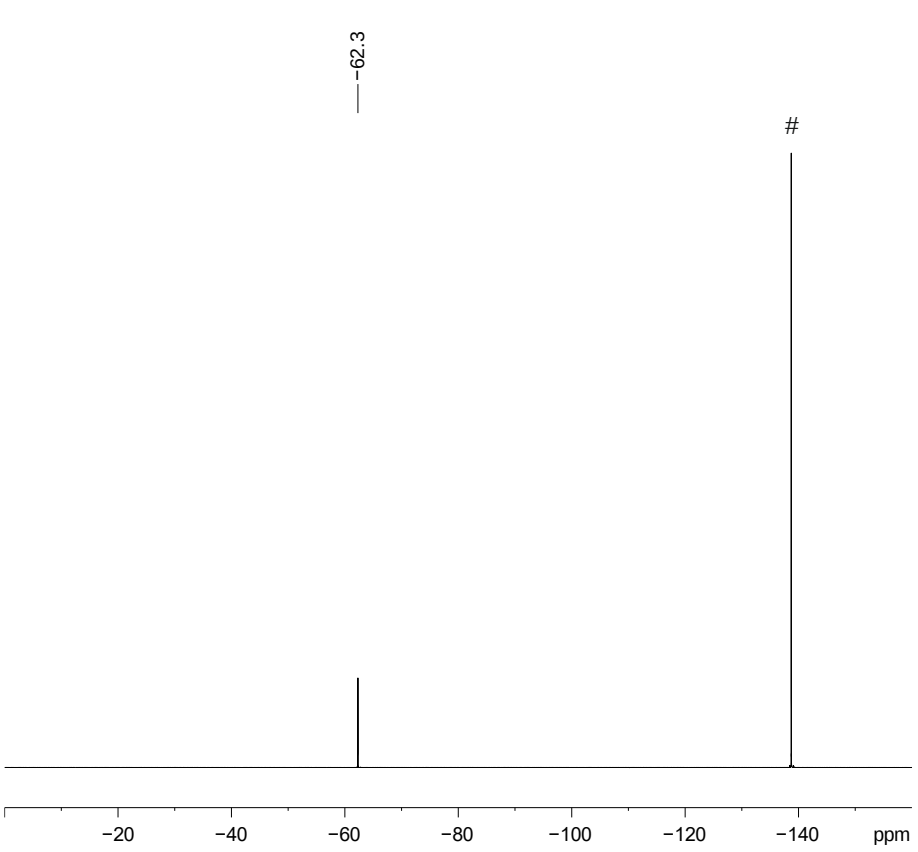


Figure SI 70. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME JB14+15K_19112021_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211119
Time 20.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn
TD 131072
SOLVENT C6D6
NS 32
DS 0
SWH 100000.000 Hz
FIDRES 0.762939 Hz
AQ 0.6553600 sec
RG 4100
DW 5.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 19F
P1 18.75 usec
PL1 −2.92 dB
PL1W 30.50645256 W
SFO1 376.4306030 MHz

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

F2 − Processing parameters
SI 262144
SF 376.4795470 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

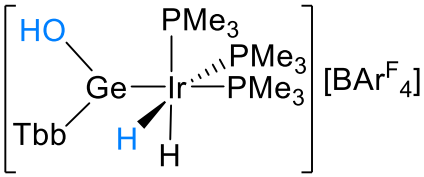
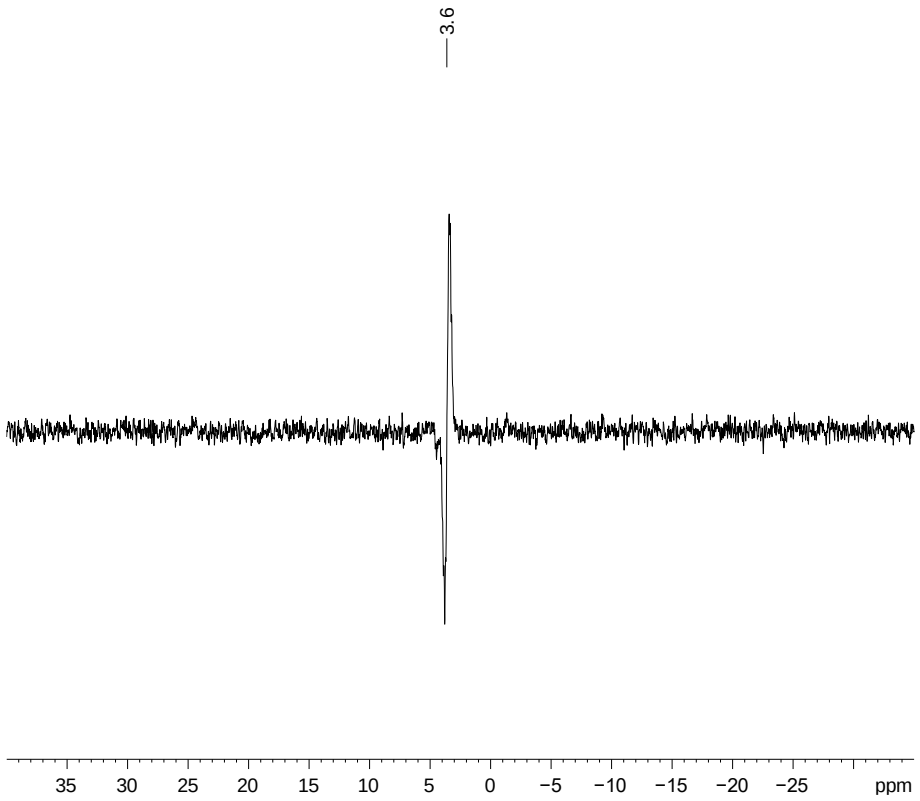


Figure SI 71. $^{19}F\{^{1}H\}$ NMR spectrum of compound **9**.

^{29}Si NMR spectrum of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME JB14+15K_24112021_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211124
Time 15.12 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273537 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

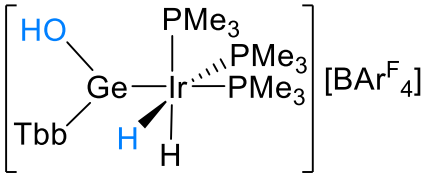
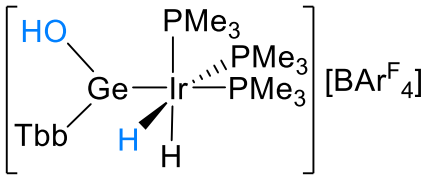
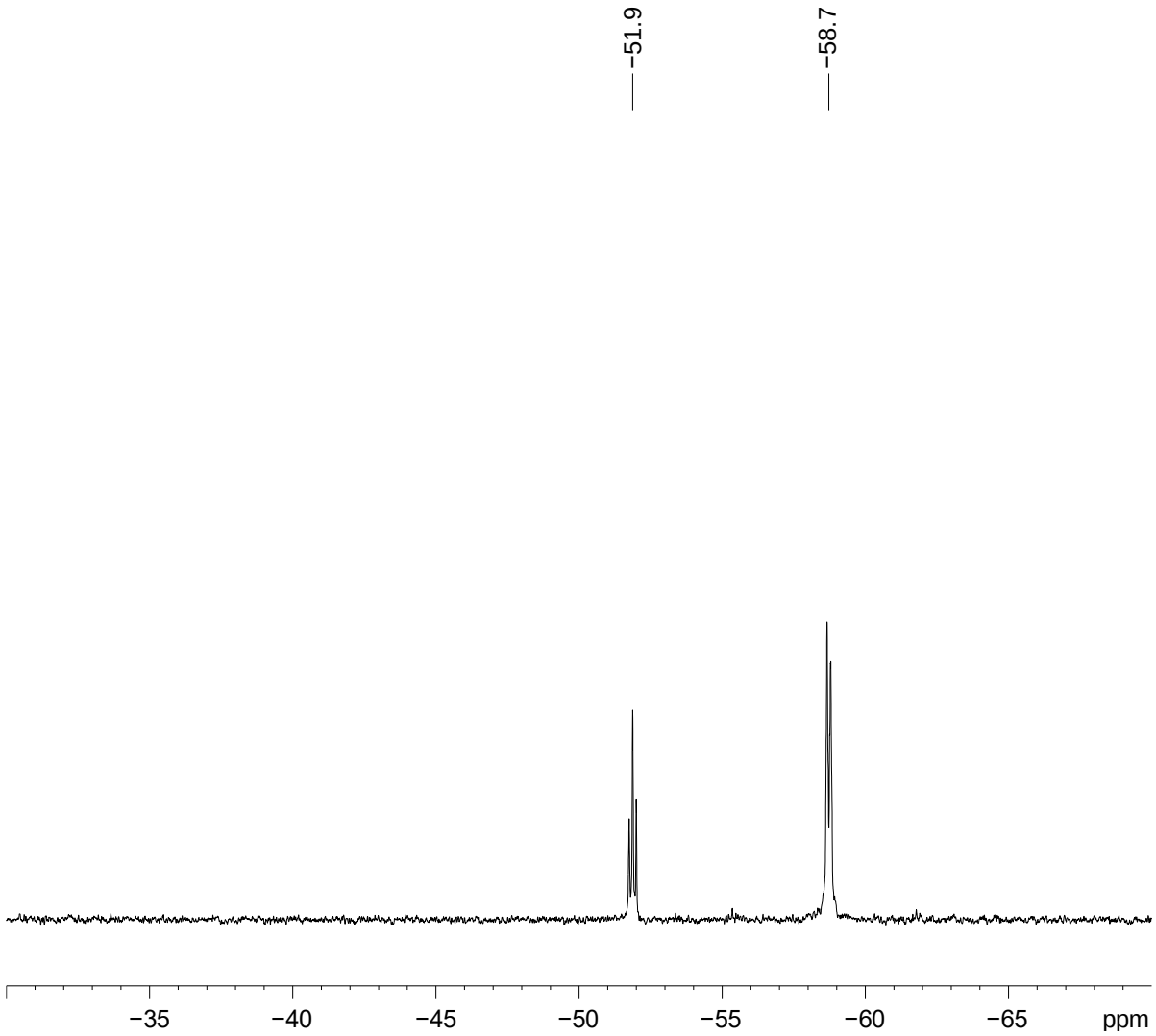


Figure SI 72. ^{29}Si NMR spectrum of compound **9**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbGe(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.





Current Data Parameters
NAME JB14+15K_19112021_400N
EXPNO 12
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211119
Time 20.15
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 256
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 MHz

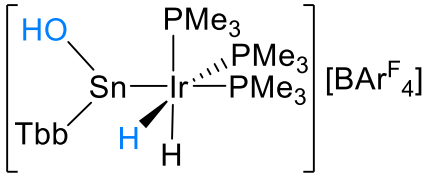
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 −3.00 dB
PL12 11.77 dB
PL13 13.14 dB
PL2W 16.03799057 W
PL12W 0.53474891 W
PL13W 0.39007664 W
SFO2 400.1120007 MHz

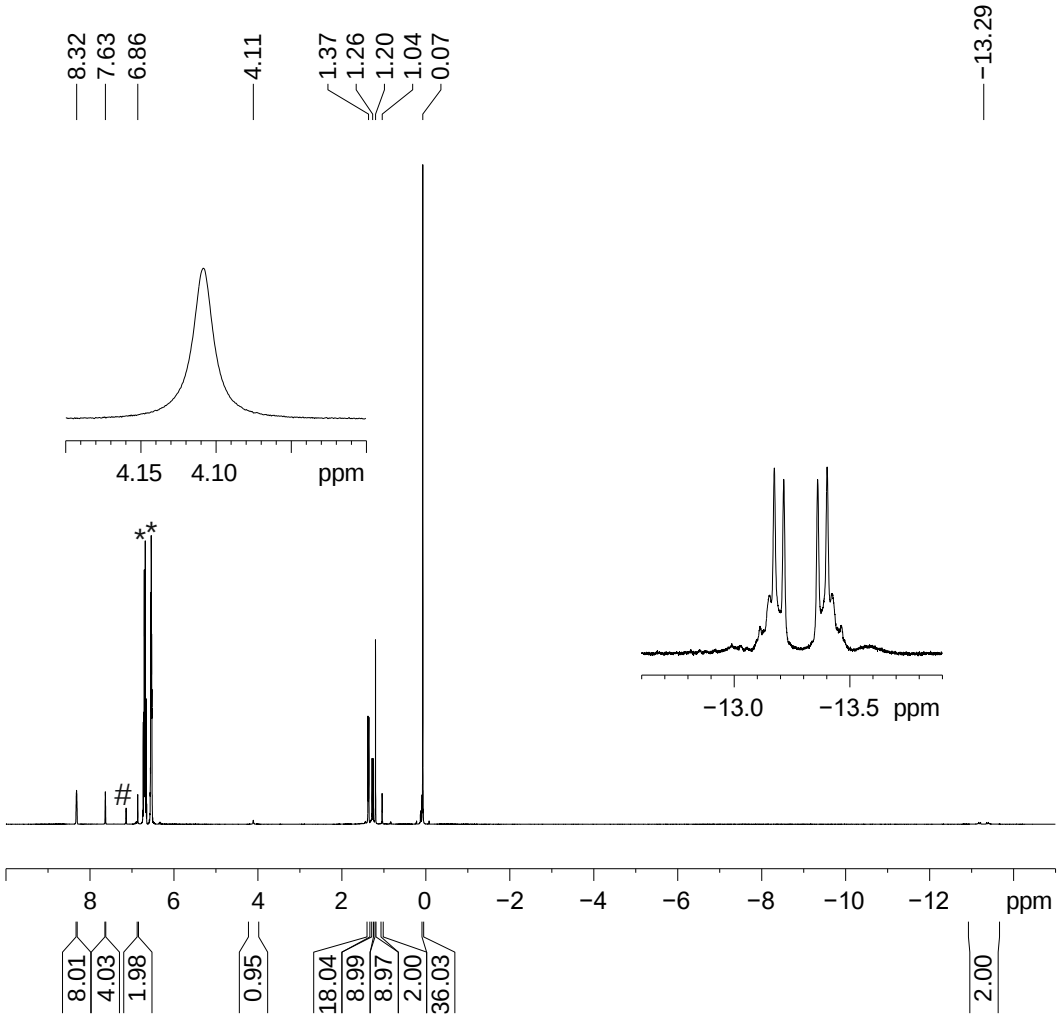
F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

Figure SI 73. $^{31}P\{^{1}H\}$ NMR spectrum of compound **9**.

NMR spectra of compound **10**.

^{1}H NMR spectrum of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA774+775K_03122021_400N
EXPNO 10
PROCNO 1

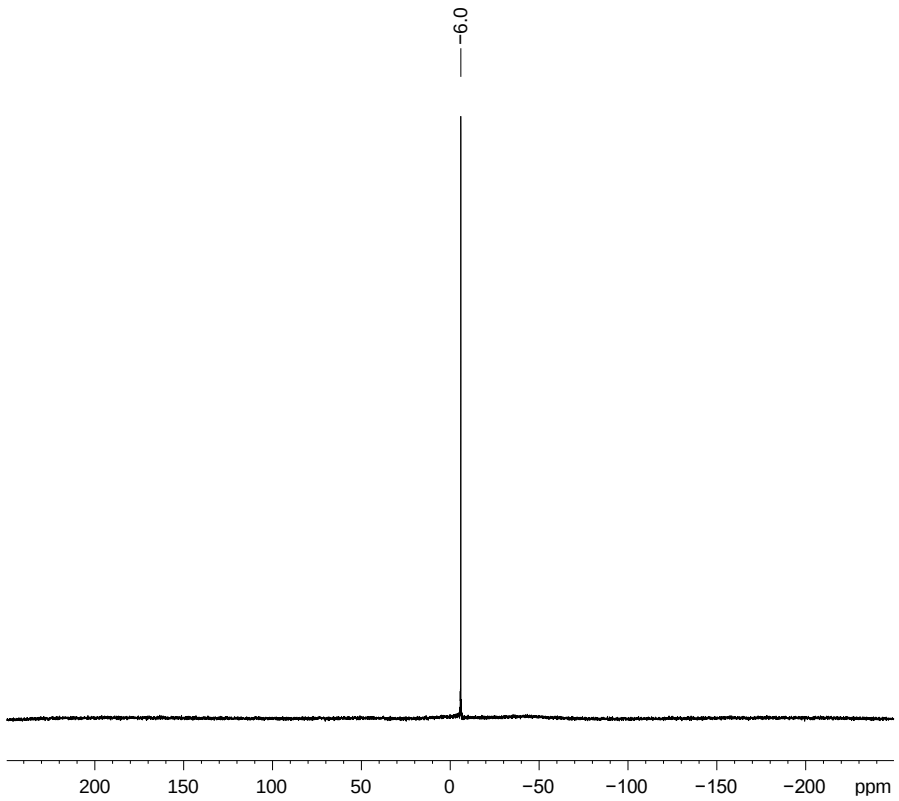
F2 − Acquisition Parameters
Date_ 20211203
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 12019.230 Hz
FIDRES 0.228259 Hz
AQ 2.1904895 sec
RG 45.2
DW 41.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 74. ^{1}H NMR spectrum of compound **10**.

^{11}B NMR spectrum of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA774+775K_07122021_300Sn
EXPNO 30
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211207
Time 13.05 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

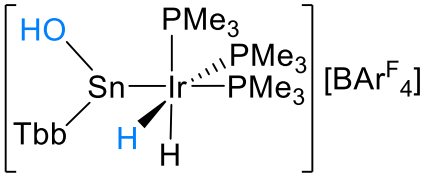
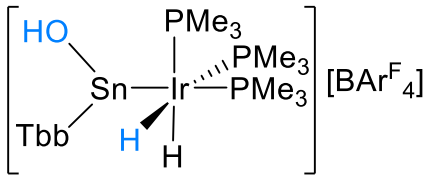
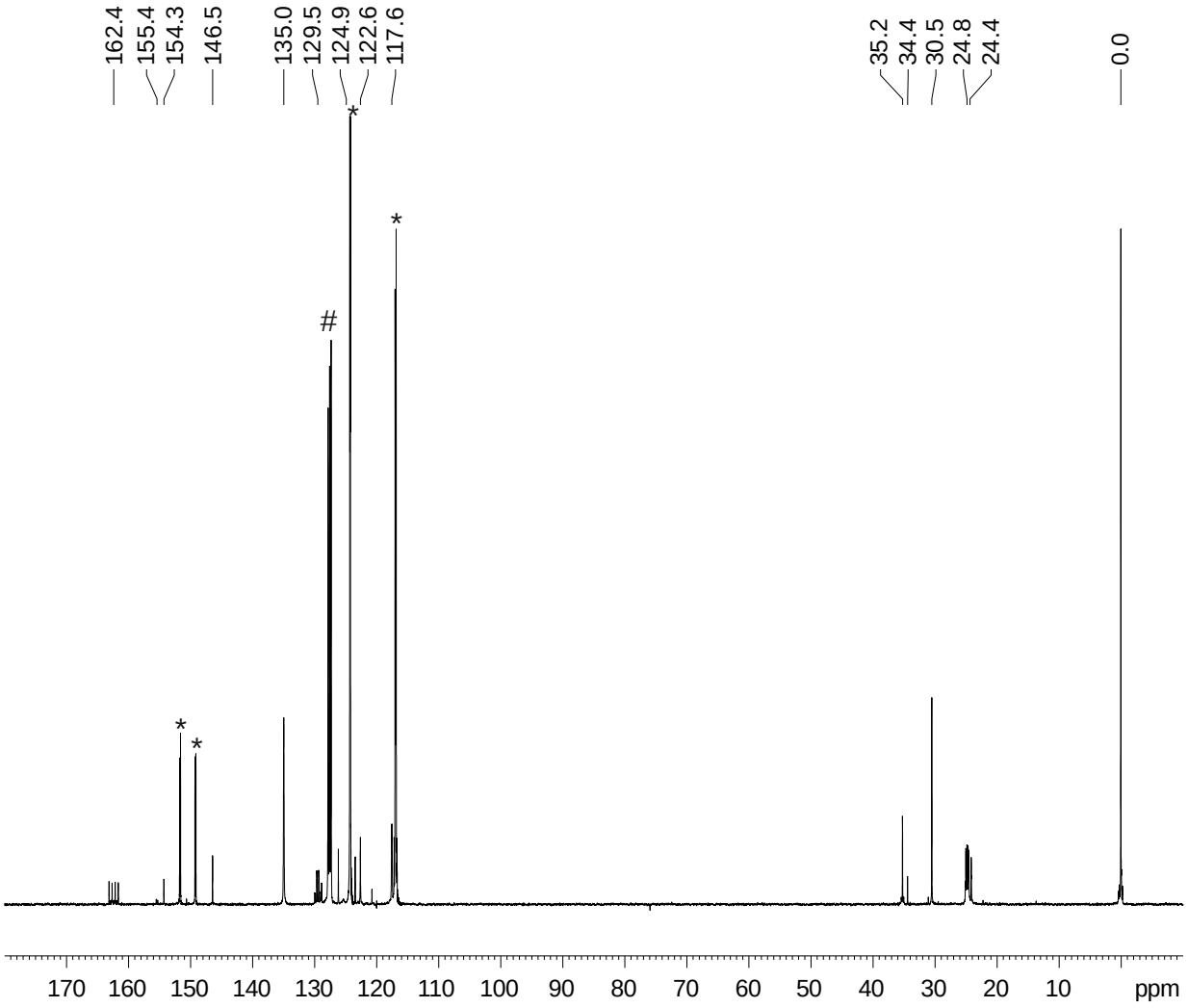


Figure SI 75. ^{11}B NMR spectrum of compound **10**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbSn(OH)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA774+775K_03122021_400
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211204
Time 2.21
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG udeft
TD 22218
SOLVENT C6D6
NS 5837
DS 0
SWH 30864.197 Hz
FIDRES 1.389153 Hz
AQ 0.3599316 sec
RG 32800
DW 16.200 usec
DE 6.00 usec
TE 299.2 K
D1 3.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 100.00000000 sec
TD0 1

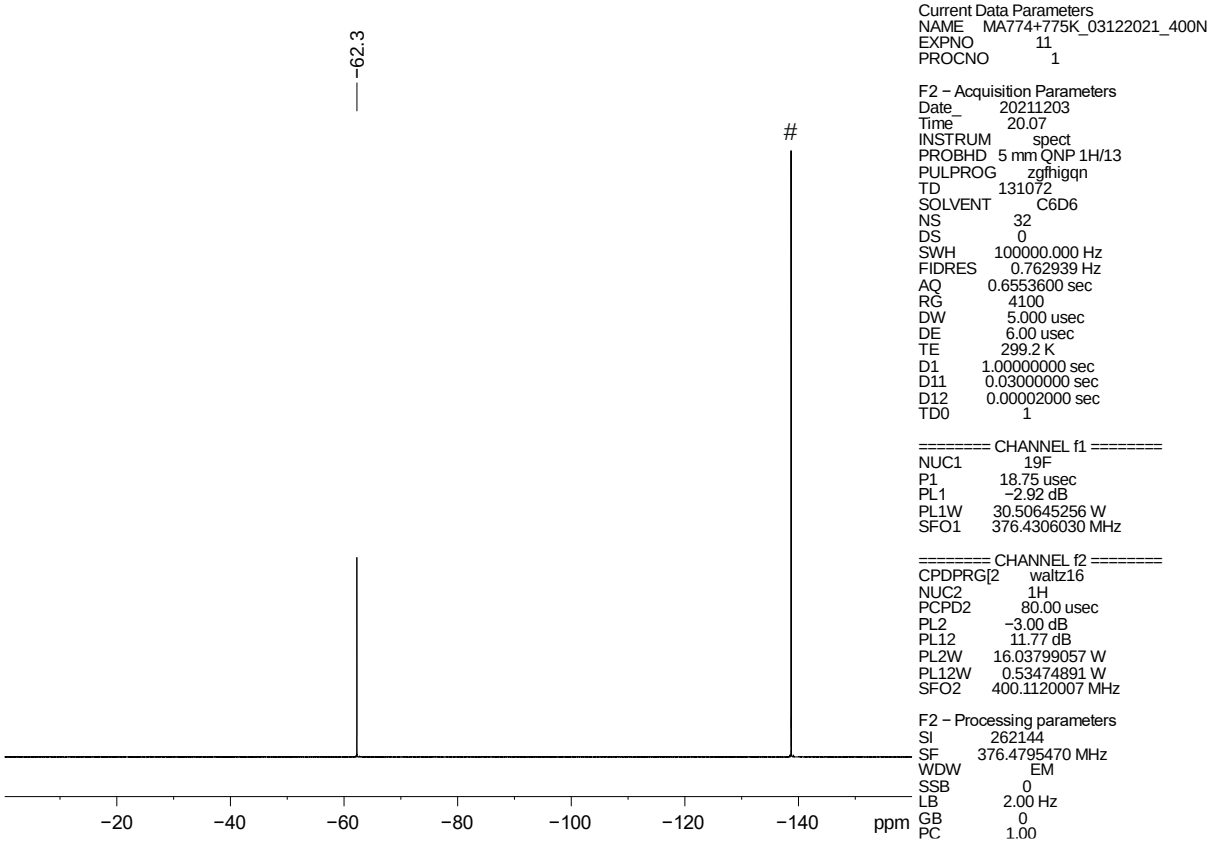
======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
P13 2000.00 usec
P26 500.00 usec
PL1 −4.16 dB
PL1W 78.55633545 W
SFO1 100.6198135 MHz
SP8 1.39 dB
SP13 1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13 Crp60comp.4
SPOAL8 0.500
SPOAL13 0.500
SPOFFS8 0 Hz
SPOFFS13 0 Hz

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

F2 − Processing parameters
SI 131072
SF 100.6077400 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure SI 76. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME    MA774+775K_03122021_400N
EXPNO          11
PROCNO          1

F2 − Acquisition Parameters
Date_       20211203
Time          20.07
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG      zgfhigqn
TD           131072
SOLVENT          C6D6
NS               32
DS                0
SWH       100000.000 Hz
FIDRES      0.762939 Hz
AQ          0.6553600 sec
RG             4100
DW             5.000 usec
DE             6.00 usec
TE             299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             19F
P1             18.75 usec
PL1            −2.92 dB
PL1W       30.50645256 W
SFO1       376.4306030 MHz

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

F2 − Processing parameters
SI            262144
SF       376.4795470 MHz
WDW              EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.00
```

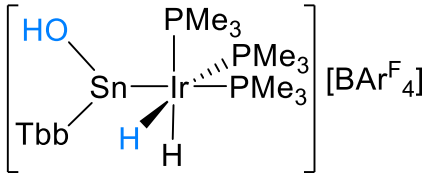
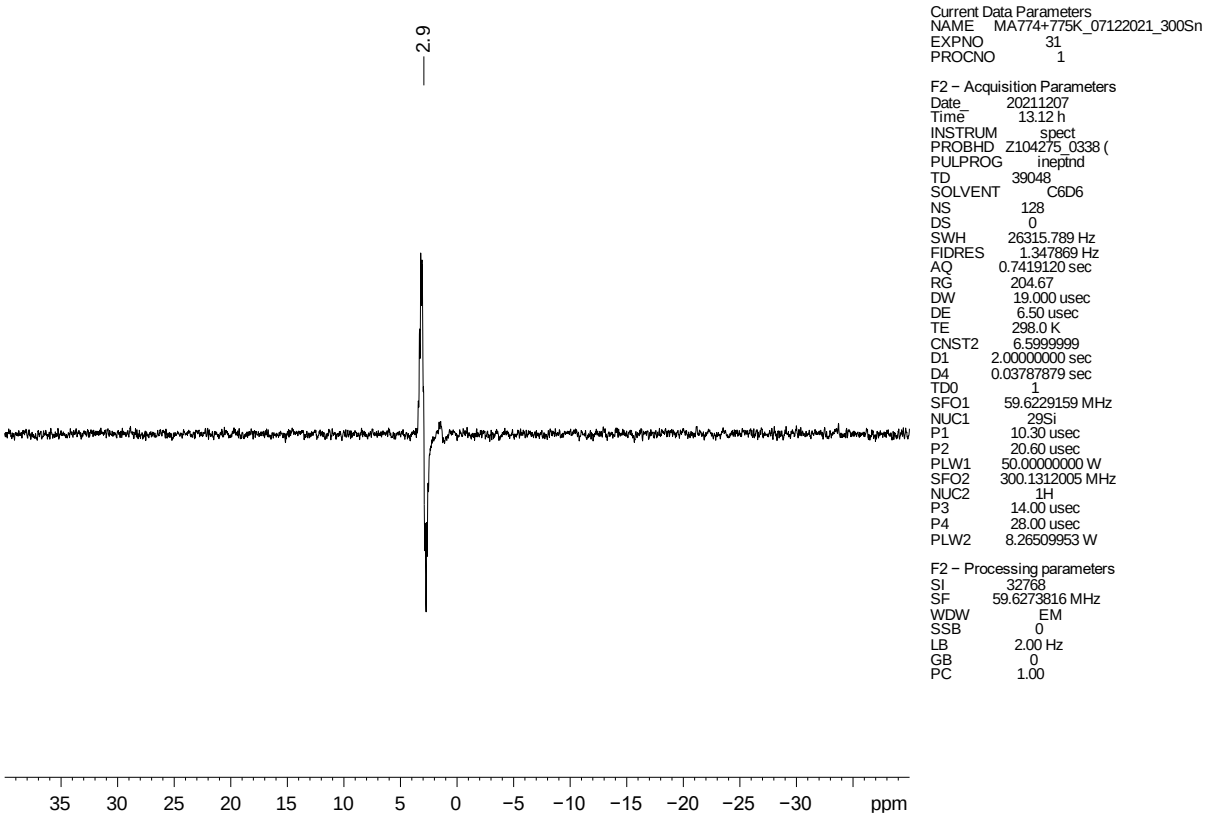


Figure SI 77. $^{19}F\{^{1}H\}$ NMR spectrum of compound **10**.

^{29}Si NMR spectrum of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA774+775K_07122021_300Sn
EXPNO 31
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211207
Time 13.12 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273816 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

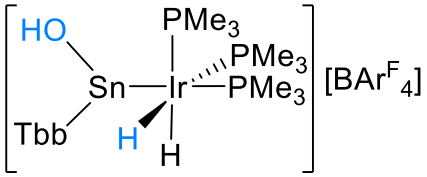
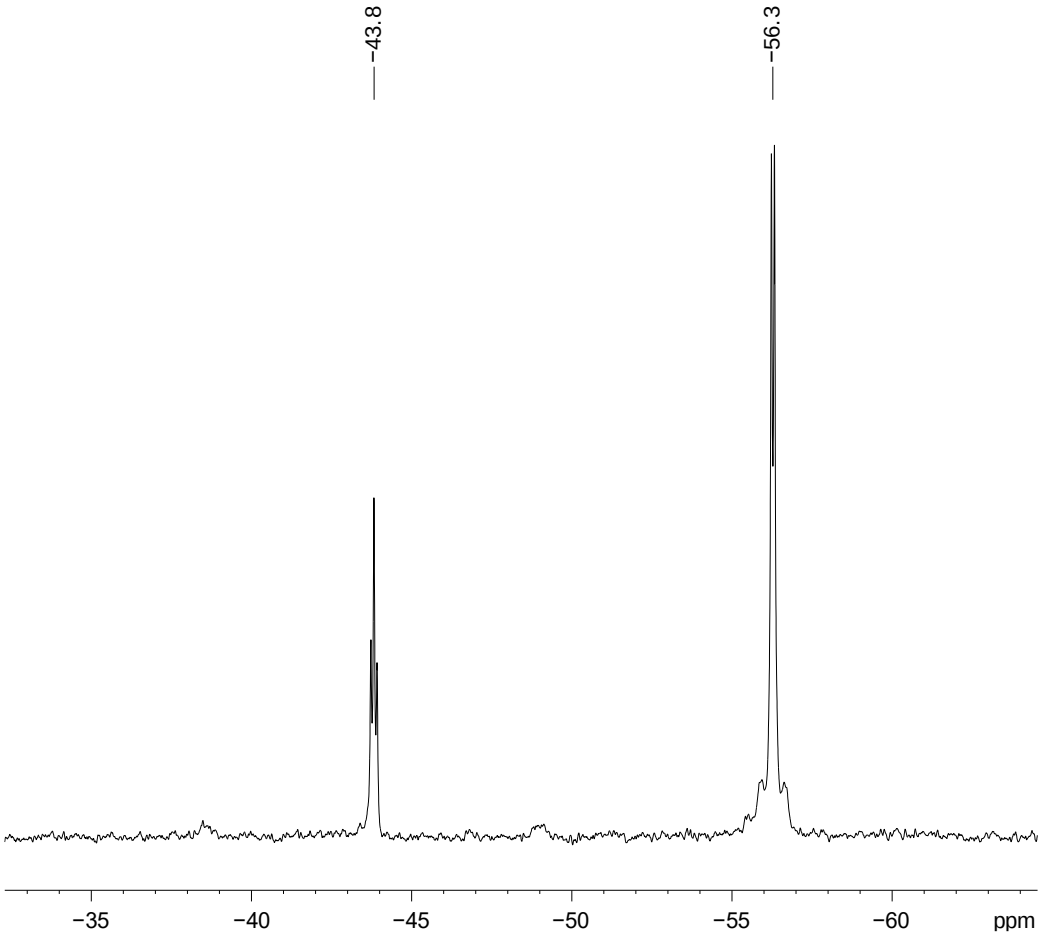


Figure SI 78. ^{29}Si NMR spectrum of compound **10**.

$^{31}P\{^{1}H\}$ NMR spectrum of $[TbbSn(OH)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.




```
Current Data Parameters
NAME     MA774+775K_03122021_400N
EXPNO            12
PROCNO            1

F2 − Acquisition Parameters
Date_         20211203
Time             20.12
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG         zgpg30
TD              88150
SOLVENT           C6D6
NS                128
DS                  0
SWH         65789.477 Hz
FIDRES        0.746336 Hz
AQ          0.6699400 sec
RG              23100
DW              7.600 usec
DE              6.00 usec
TE              299.2 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             31P
P1             11.00 usec
PL1             −3.00 dB
PL1W       45.10684967 W
SFO1       161.9674970 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              131072
SF         161.9674970 MHz
WDW                EM
SSB                0
LB              7.00 Hz
GB                 0
PC              1.40
```

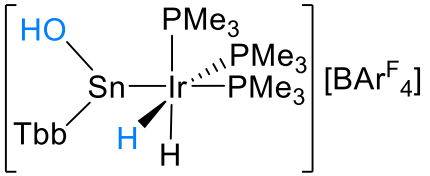
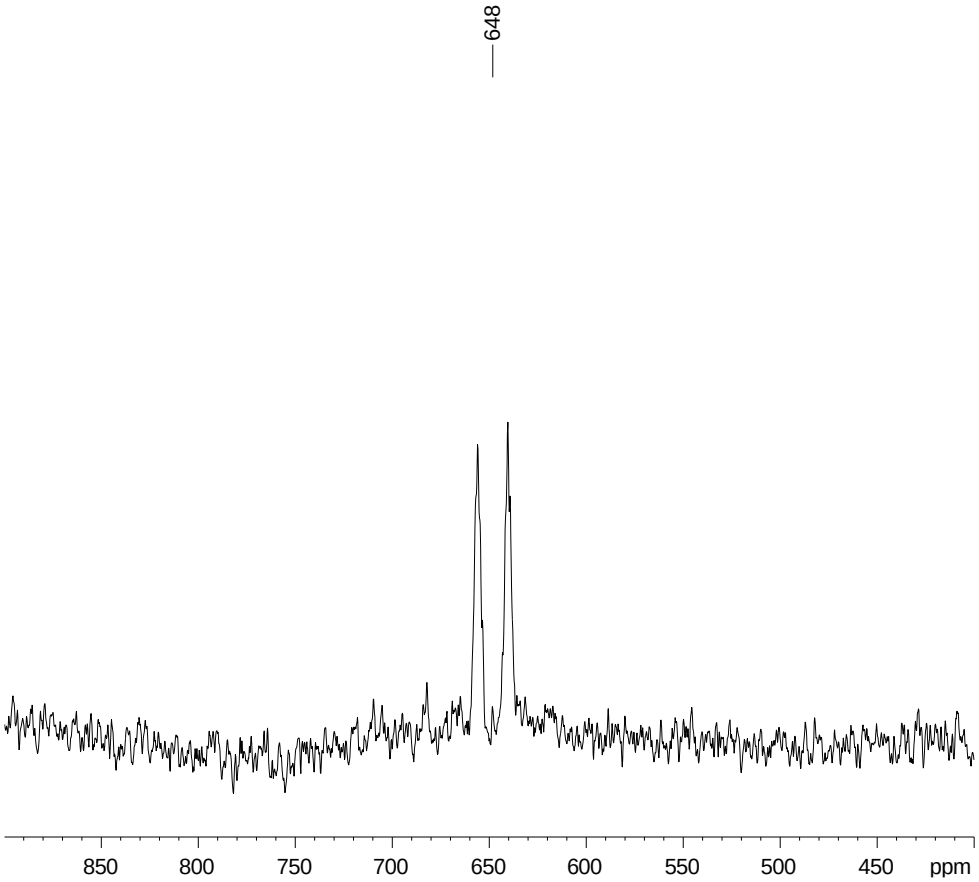


Figure SI 79. $^{31}P\{^{1}H\}$ NMR spectrum of compound **10**.

^{119}Sn NMR spectrum of [TbbSn(OH)IrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA774+775K_07122021_300Sn
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211207
Time 9.40 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 30720
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.9875260 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 1.40

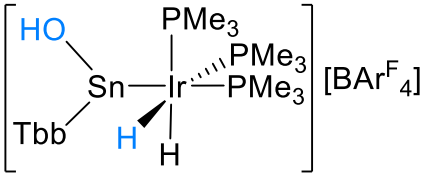
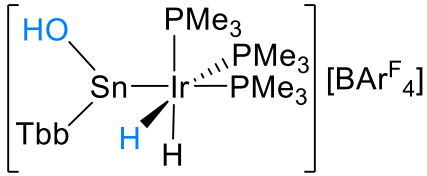
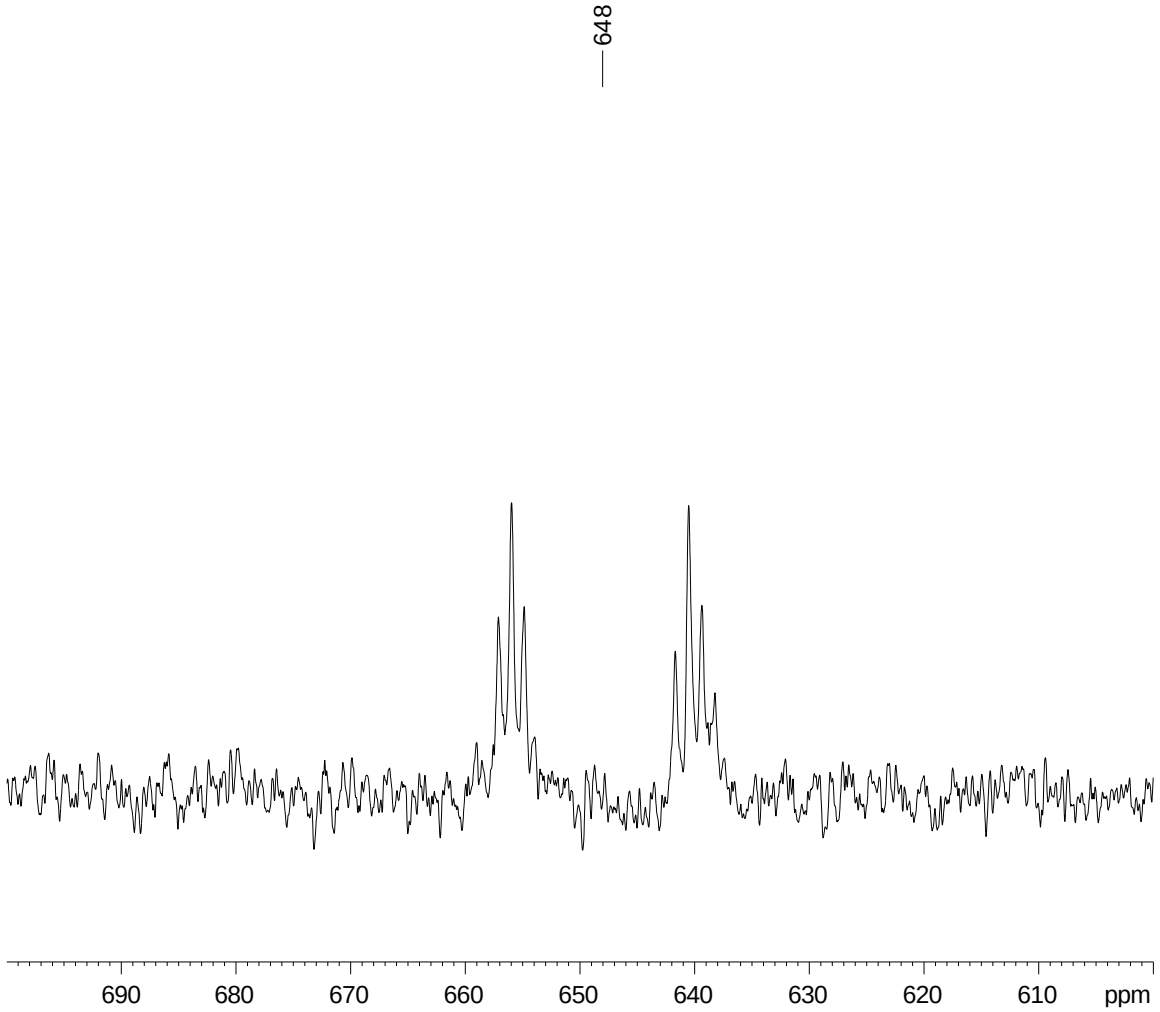


Figure SI 80. ^{119}Sn NMR spectrum of compound **10**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $[TbbSn(OH)IrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.





Current Data Parameters
NAME MA774+775K_07122021_300S
EXPNO 24
PROCNO 1

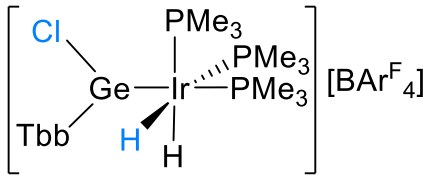
F2 − Acquisition Parameters
Date_ 20211207
Time 9.56 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 9318
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.9875258 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

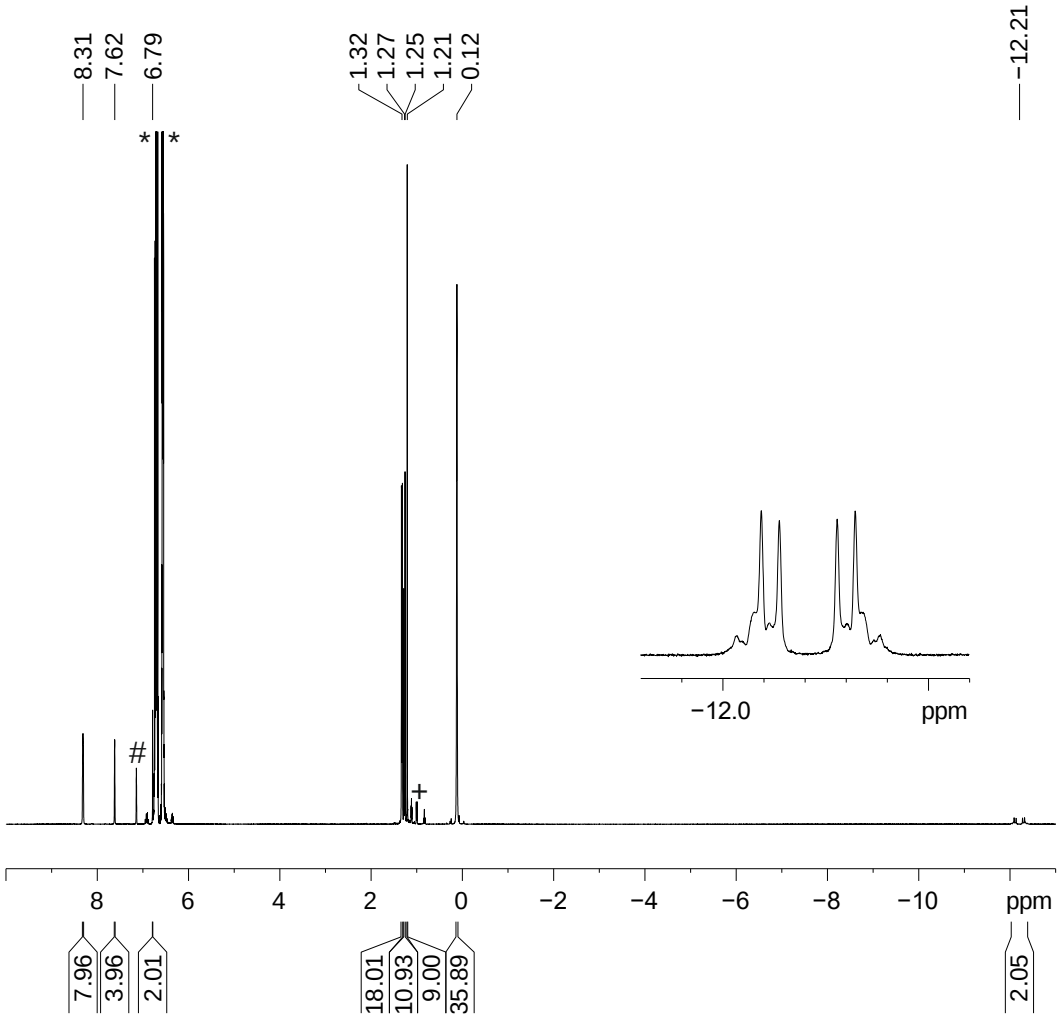
F2 − Processing parameters
SI 65536
SF 111.9203738 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

Figure SI 81. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **10**.

NMR spectra of compound **11a**.

^{1}H NMR spectrum of [TbbGeClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane and unknown impurity.





Current Data Parameters
NAME MA799+839_15022022_400N
EXPNO 12
PROCNO 1

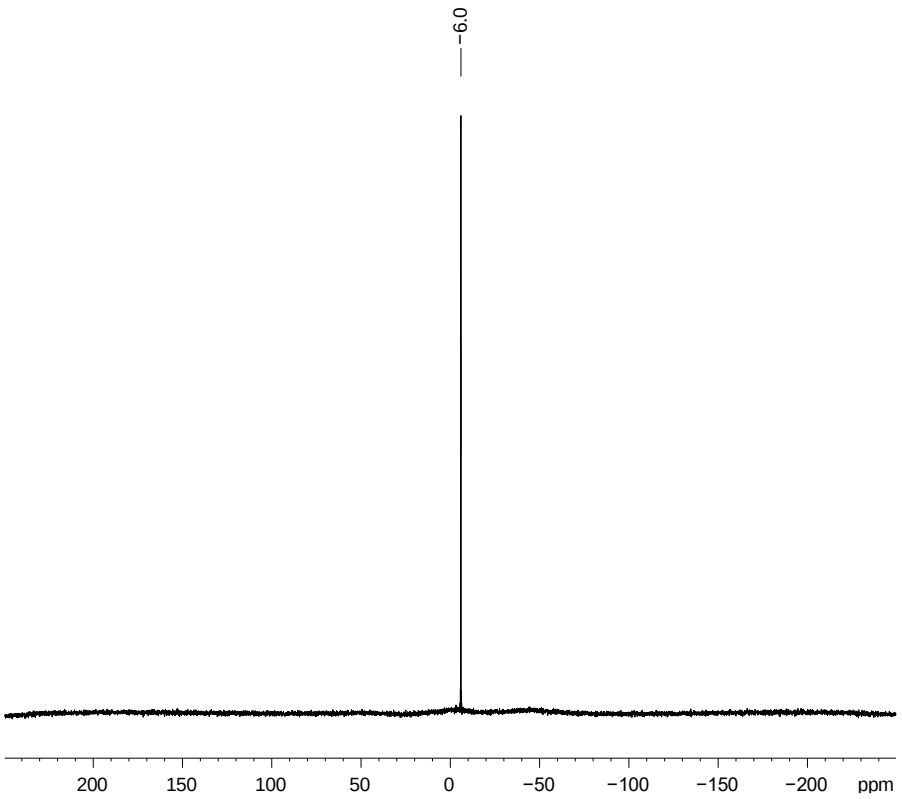
F2 − Acquisition Parameters
Date_ 20220215
Time 20.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 36
DW 31.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 82. ^{1}H NMR spectrum of compound **11a**.

^{11}B NMR spectrum of [TbbGeClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA799+839_16022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220216
Time 9.25 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

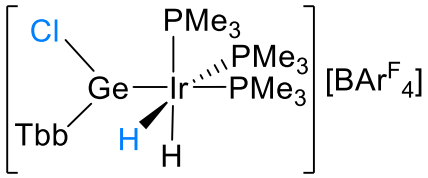
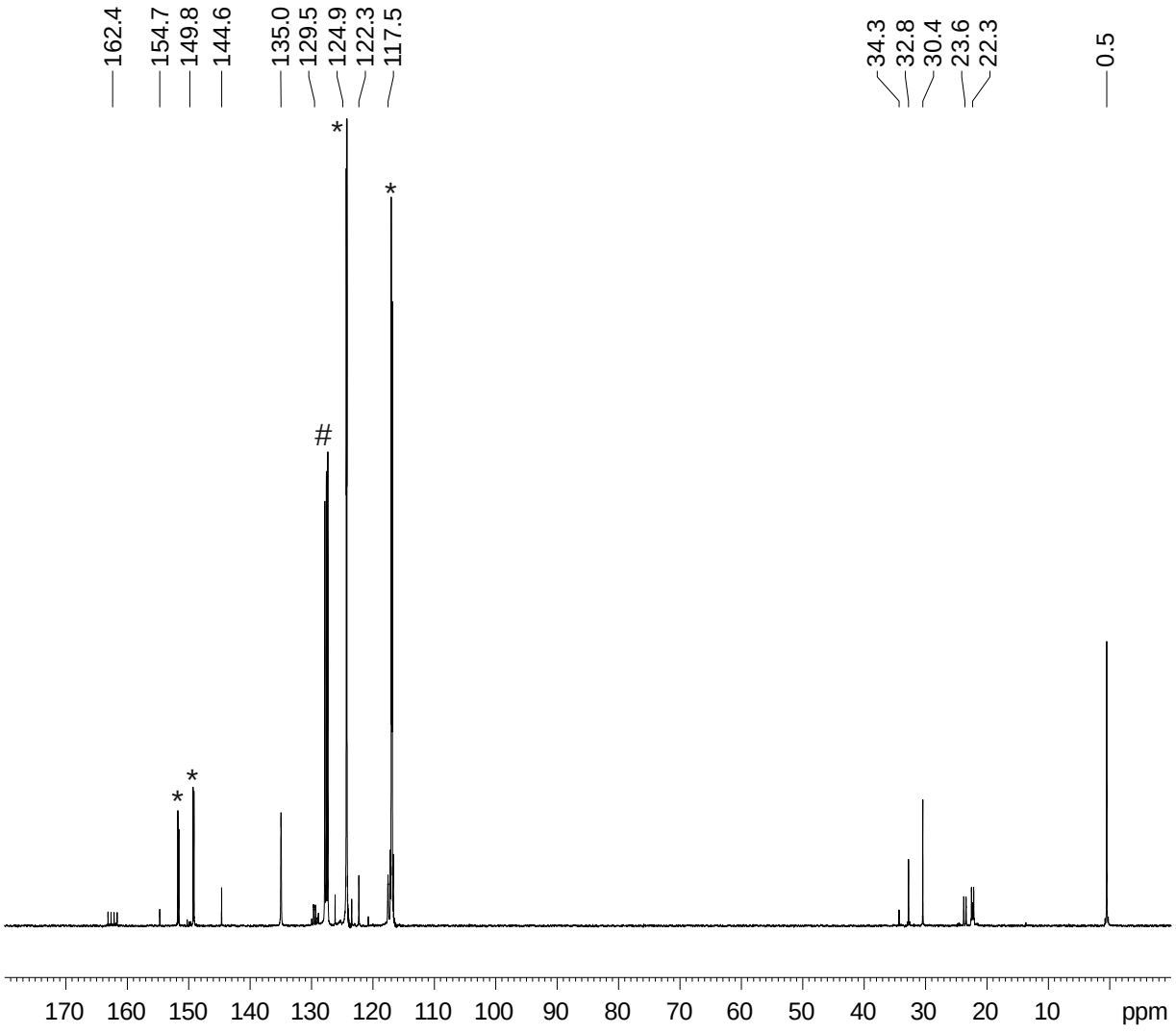


Figure SI 83. ^{11}B NMR spectrum of compound **11a**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbGeClIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME     MA799+839_15022022_400I
EXPNO            13
PROCNO            1

F2 - Acquisition Parameters
Date_         20220216
Time             2.37
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          udeft
TD             22218
SOLVENT           C6D6
NS              6246
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE             299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             13C
P1             13.50 usec
P13          2000.00 usec
P26           500.00 usec
PL1            -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8             1.39 dB
SP13            1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8          0.500
SPOAL13         0.500
SPOFFS8           0 Hz
SPOFFS13          0 Hz

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

F2 - Processing parameters
SI             131072
SF         100.6077400 MHz
WDW              EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.40
```

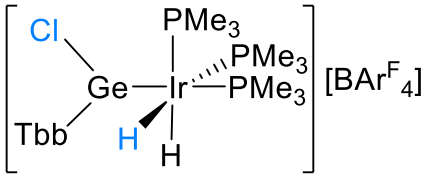
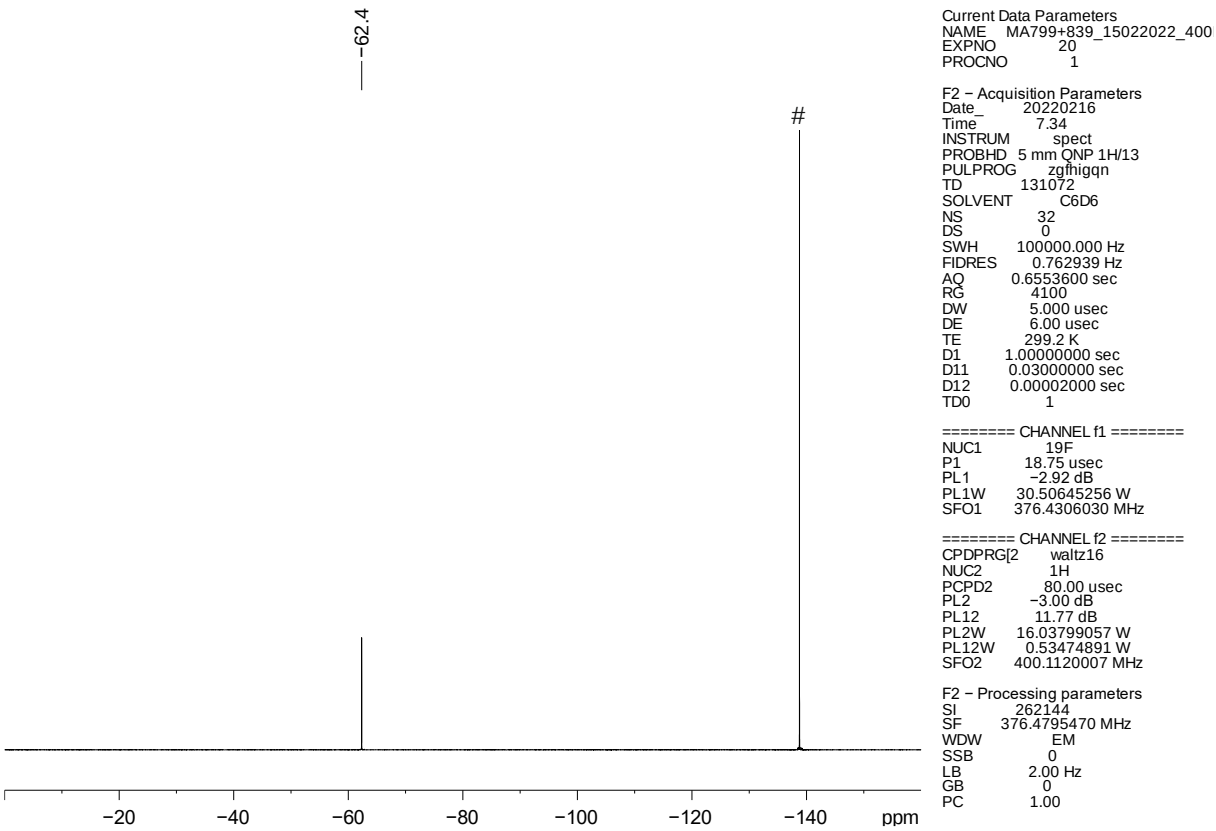


Figure SI 84. $^{13}C\{^{1}H\}$ NMR spectrum of compound **11a**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbGeClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME    MA799+839_15022022_400
EXPNO           20
PROCNO           1

F2 − Acquisition Parameters
Date_       20220216
Time            7.34
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG      zgfhigqn
TD           131072
SOLVENT          C6D6
NS               32
DS                0
SWH       100000.000 Hz
FIDRES      0.762939 Hz
AQ         0.6553600 sec
RG              4100
DW             5.000 usec
DE             6.00 usec
TE            299.2 K
D1         1.00000000 sec
D11        0.03000000 sec
D12        0.00002000 sec
TD0              1

======== CHANNEL f1 ========
NUC1            19F
P1            18.75 usec
PL1           −2.92 dB
PL1W      30.50645256 W
SFO1      376.4306030 MHz

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

F2 − Processing parameters
SI           262144
SF       376.4795470 MHz
WDW              EM
SSB              0
LB            2.00 Hz
GB               0
PC            1.00
```

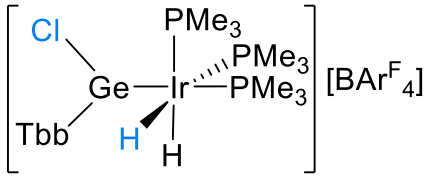
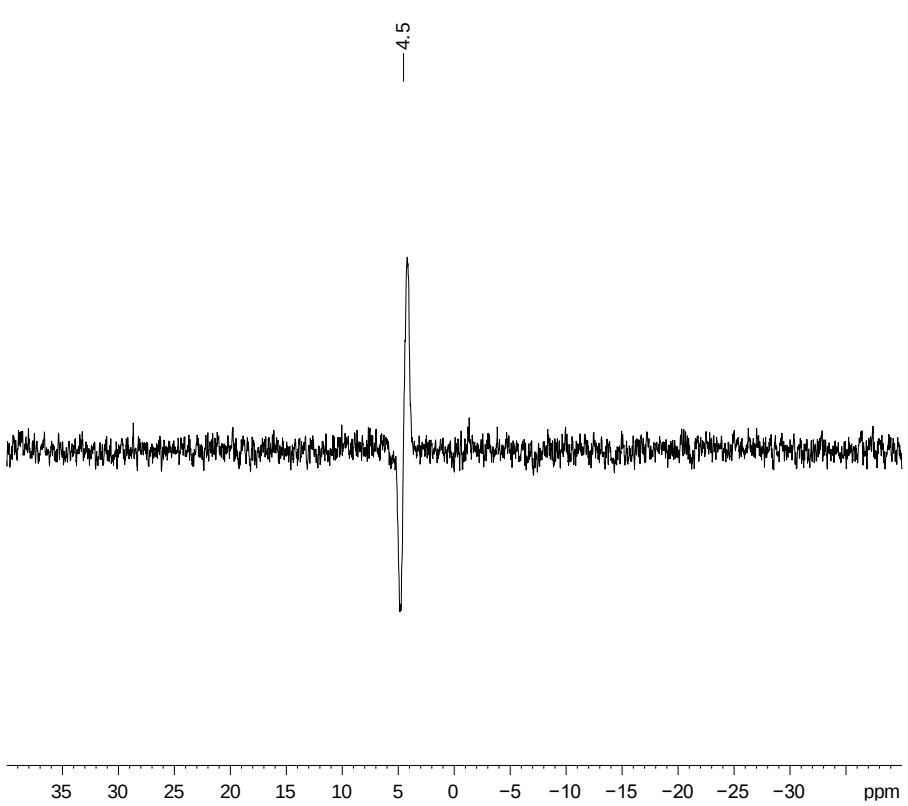


Figure SI 85. $^{19}F\{^{1}H\}$ NMR spectrum of compound **11a**.

^{29}Si NMR spectrum of [TbbGeClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA799+839_16022022_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220216
Time 12.22 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273428 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

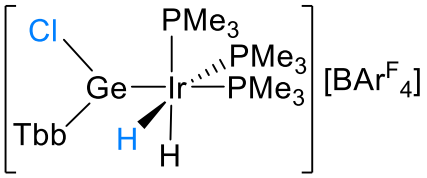
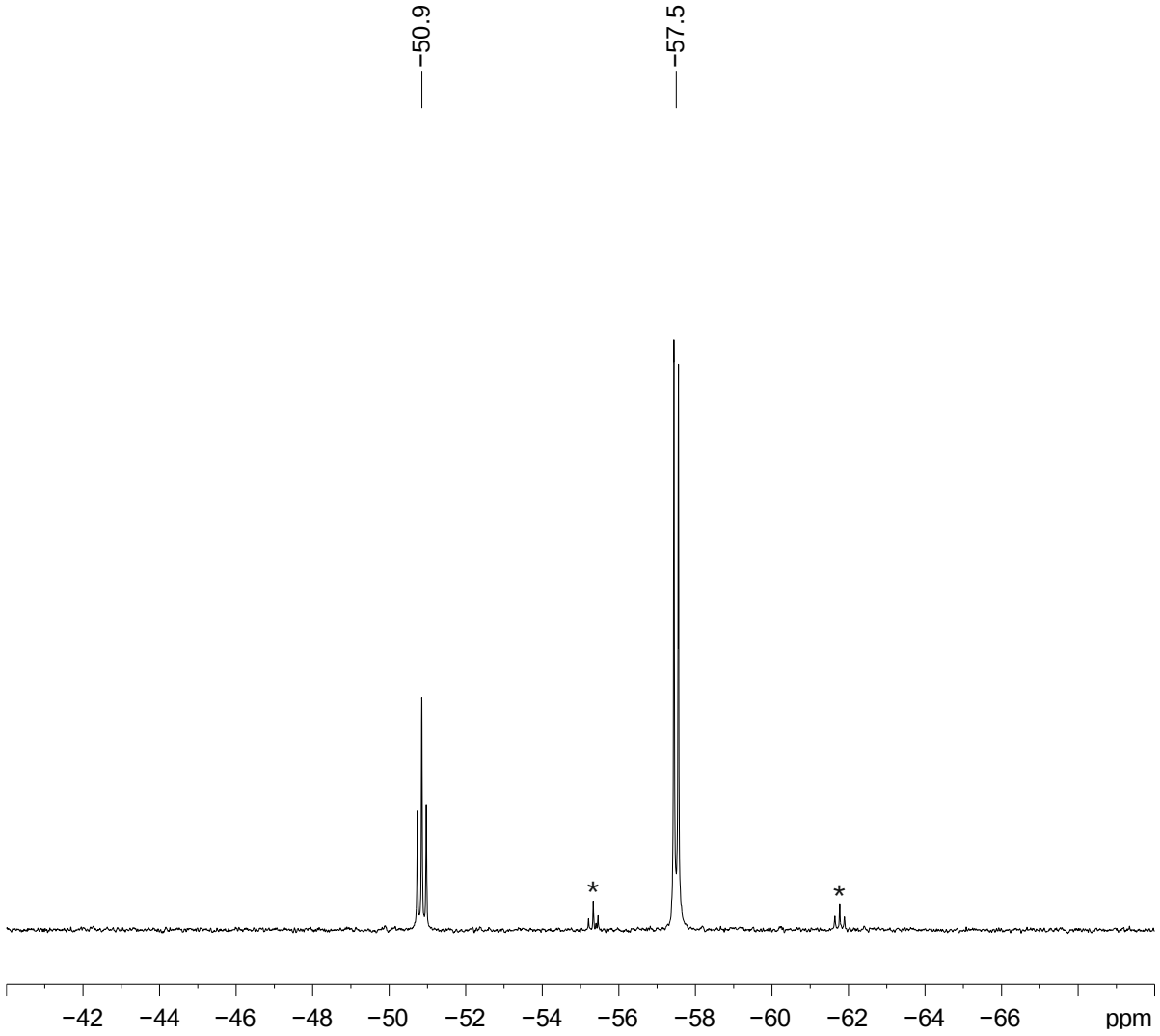


Figure SI 86. ^{29}Si NMR spectrum of compound **11a**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbGeClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA799+839_15022022_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220215
Time 16.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 256
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1080000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

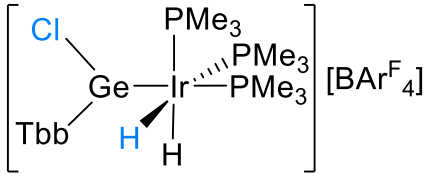
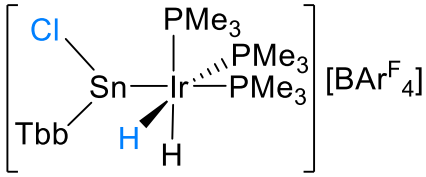
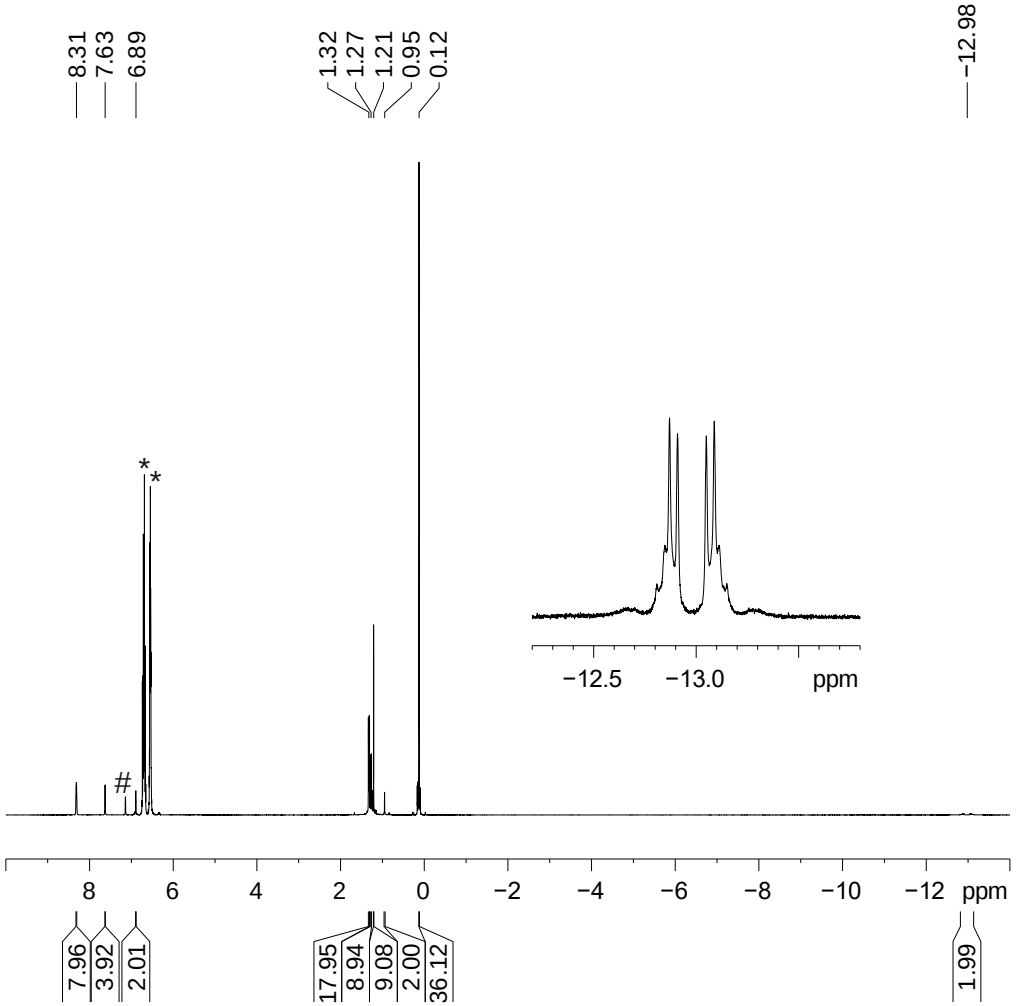


Figure SI 87. $^{31}P\{^{1}H\}$ NMR spectrum of compound **11a**.

NMR spectra of compound **12a**

^{1}H NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt.





Current Data Parameters
NAME MA800+842_21022022_400N
EXPNO 10
PROCNO 1

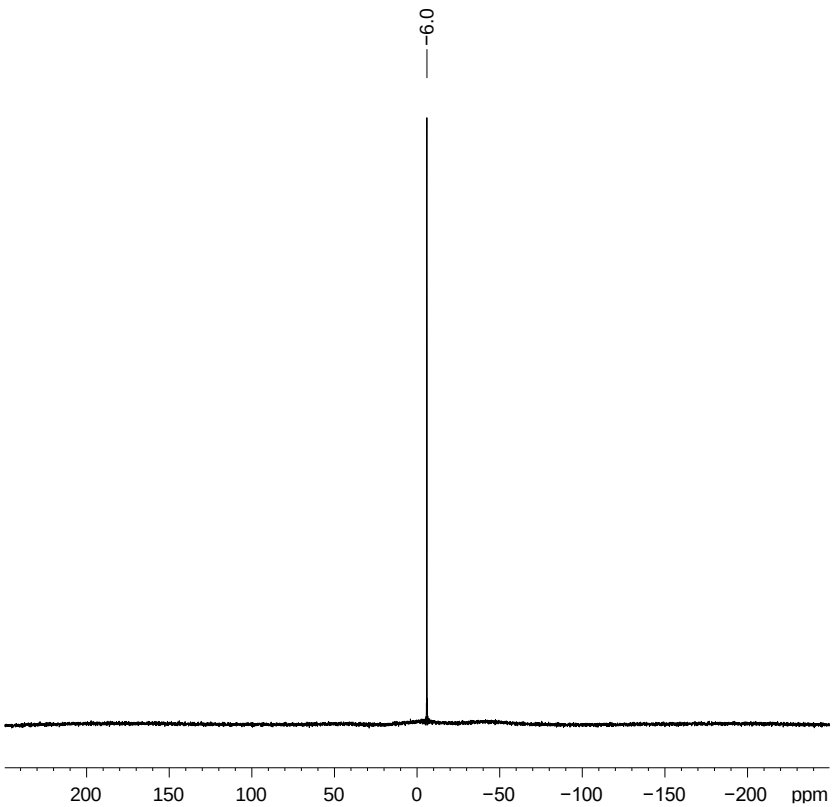
F2 − Acquisition Parameters
Date_ 20220221
Time 16.03
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 45.2
DW 31.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Figure SI 88. ^{1}H NMR spectrum of compound **12a**.

^{11}B NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA800+842_18022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220218
Time 14.47 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

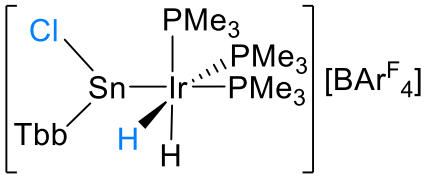
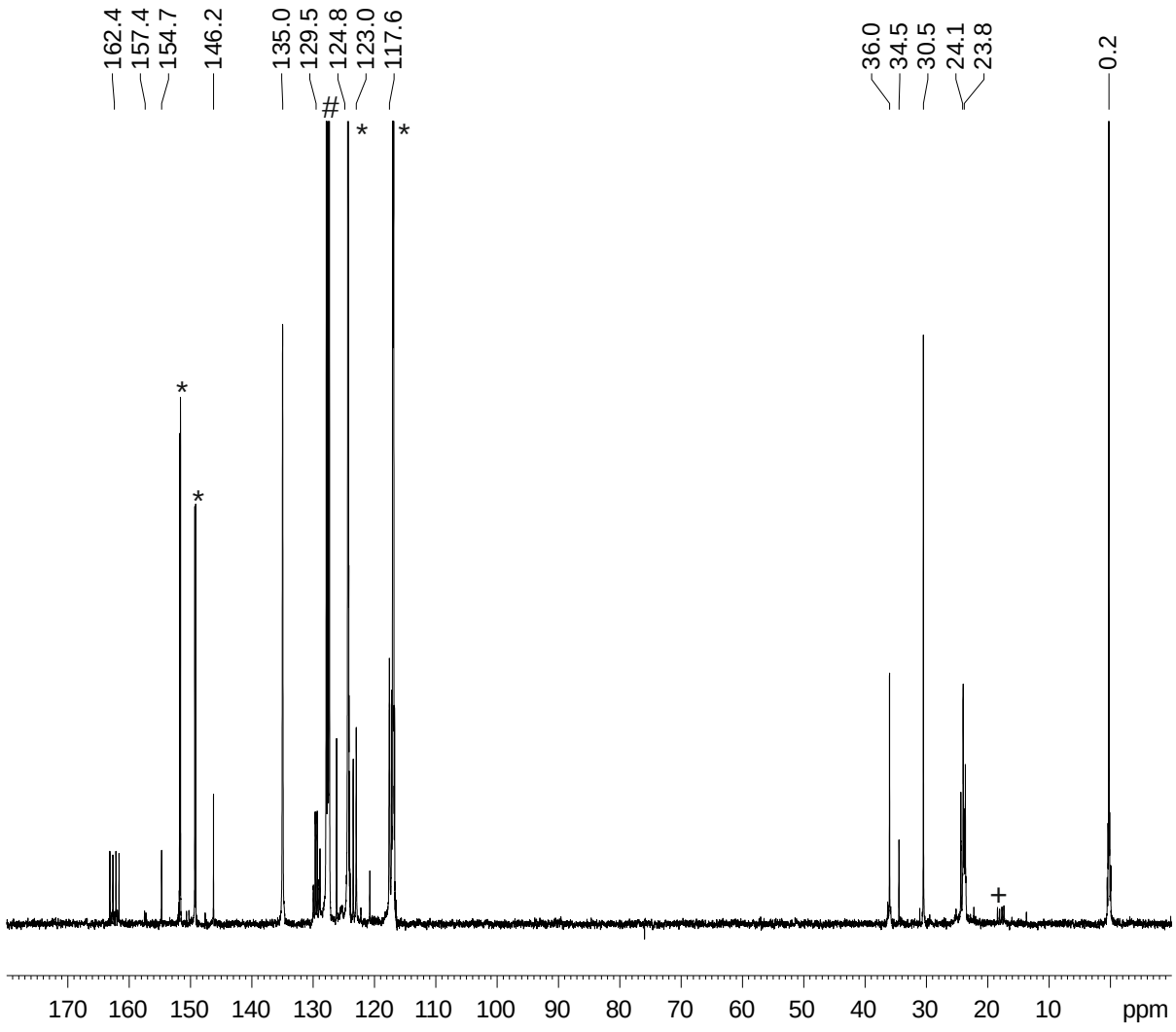


Figure SI 89. ^{11}B NMR spectrum of compound **12a**.

$^{13}C\{^{1}H\}$ NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + unknown impurity.




```
Current Data Parameters
NAME      MA800+842_21022022_400
EXPNO             13
PROCNO             1

F2 - Acquisition Parameters
Date_          20220222
Time              2.52
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD             22218
SOLVENT           C6D6
NS              6554
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE             299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1            -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8             1.39 dB
SP13            1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

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

F2 - Processing parameters
SI              131072
SF         100.6077400 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
```

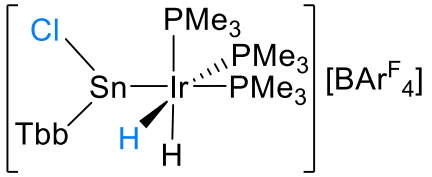
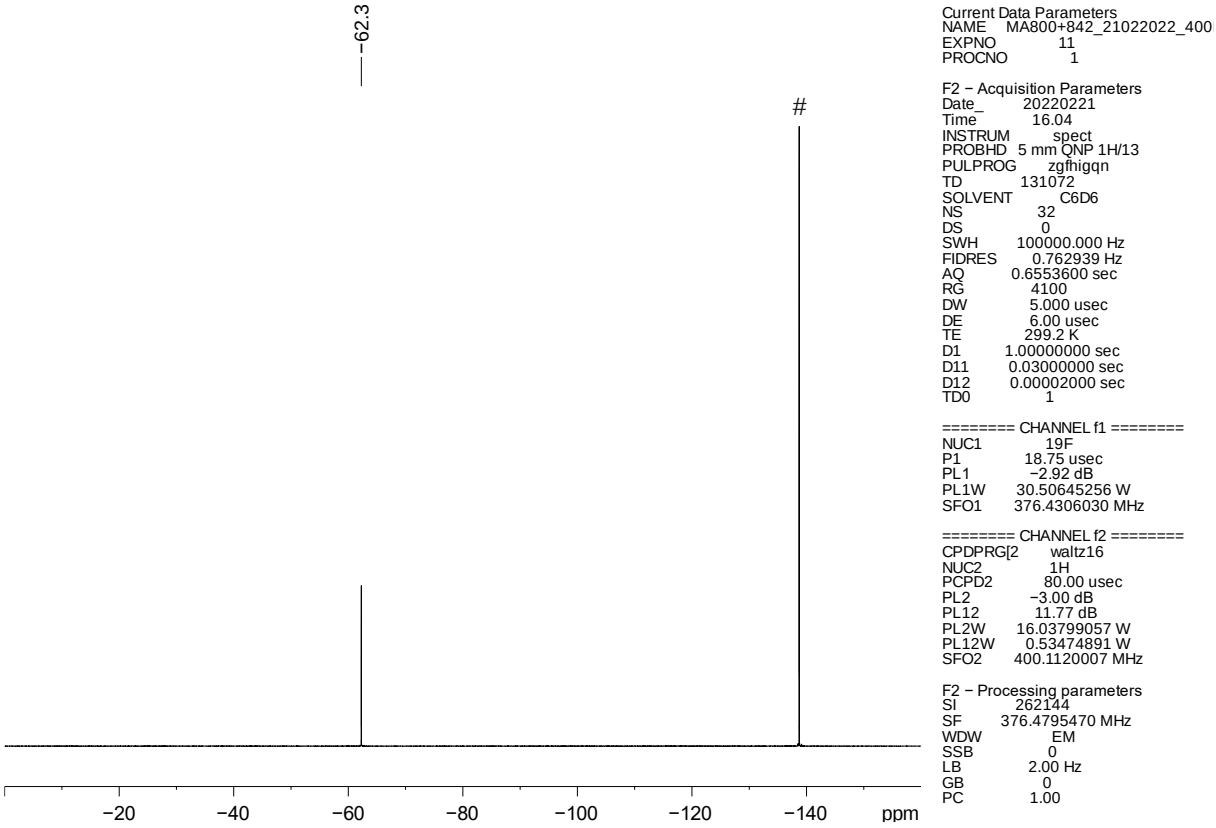


Figure SI 90. $^{13}C\{^{1}H\}$ NMR spectrum of compound **12a**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME     MA800+842_21022022_400
EXPNO            11
PROCNO            1

F2 − Acquisition Parameters
Date_         20220221
Time             16.04
INSTRUM          spect
PROBHD  5 mm QNP 1H/13
PULPROG       zgfhigqn
TD             131072
SOLVENT           C6D6
NS                32
DS                 0
SWH        100000.000 Hz
FIDRES       0.762939 Hz
AQ          0.6553600 sec
RG               4100
DW              5.000 usec
DE              6.00 usec
TE              299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              19F
P1              18.75 usec
PL1             −2.92 dB
PL1W       30.50645256 W
SFO1       376.4306030 MHz

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

F2 − Processing parameters
SI            262144
SF         376.4795470 MHz
WDW               EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.00
```

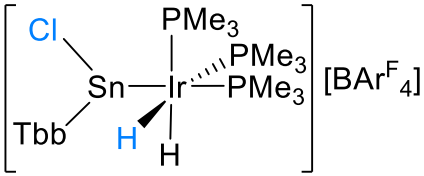
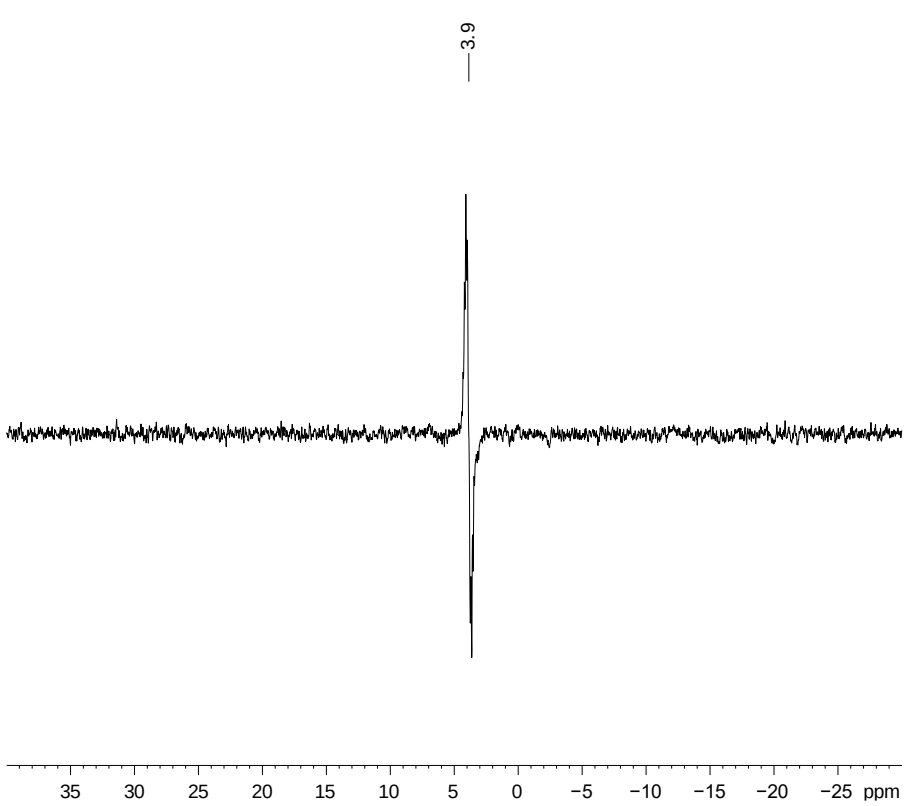


Figure SI 91. $^{19}F\{^{1}H\}$ NMR spectrum of compound **12a**.

^{29}Si NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA800+842_18022022_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220218
Time 14.56 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273625 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

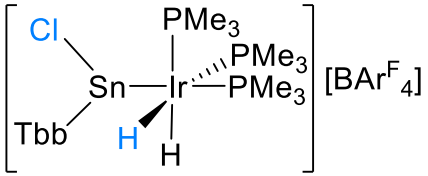
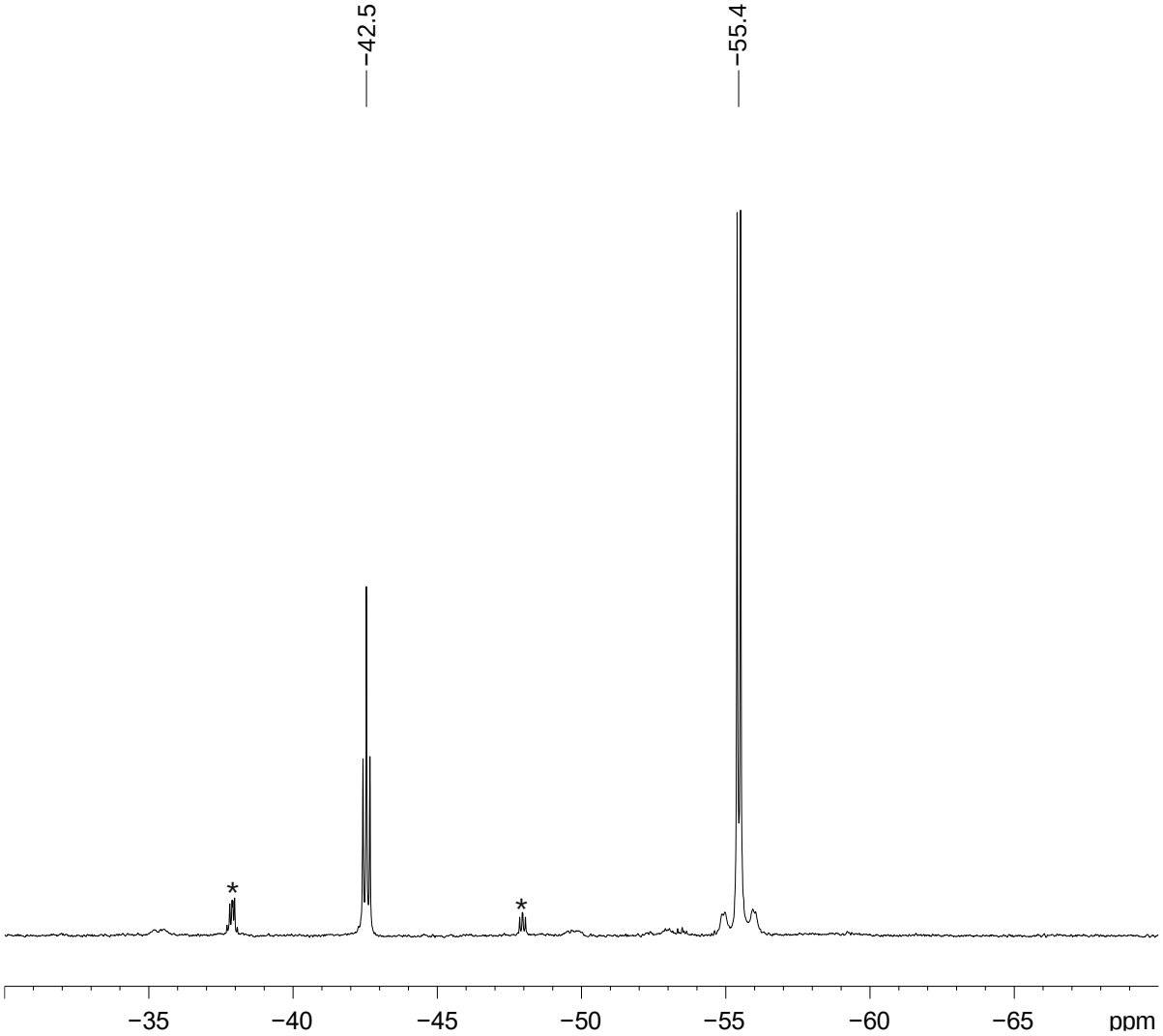


Figure SI 92. ^{29}Si NMR spectrum of compound **12a**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA800+842_22022022_300
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220222
Time 14.49 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 78426
SOLVENT C6D6
NS 256
DS 0
SWH 49019.609 Hz
FIDRES 1.250086 Hz
AQ 0.7999452 sec
RG 204.67
DW 10.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 121.4948510 MHz
NUC1 31P
P0 4.00 usec
P1 12.00 usec
PLW1 11.36400032 W
SFO2 300.1284994 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 121.4948510 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

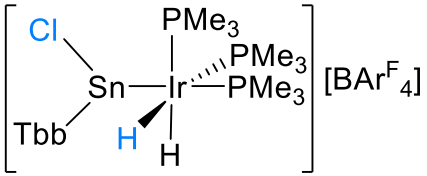
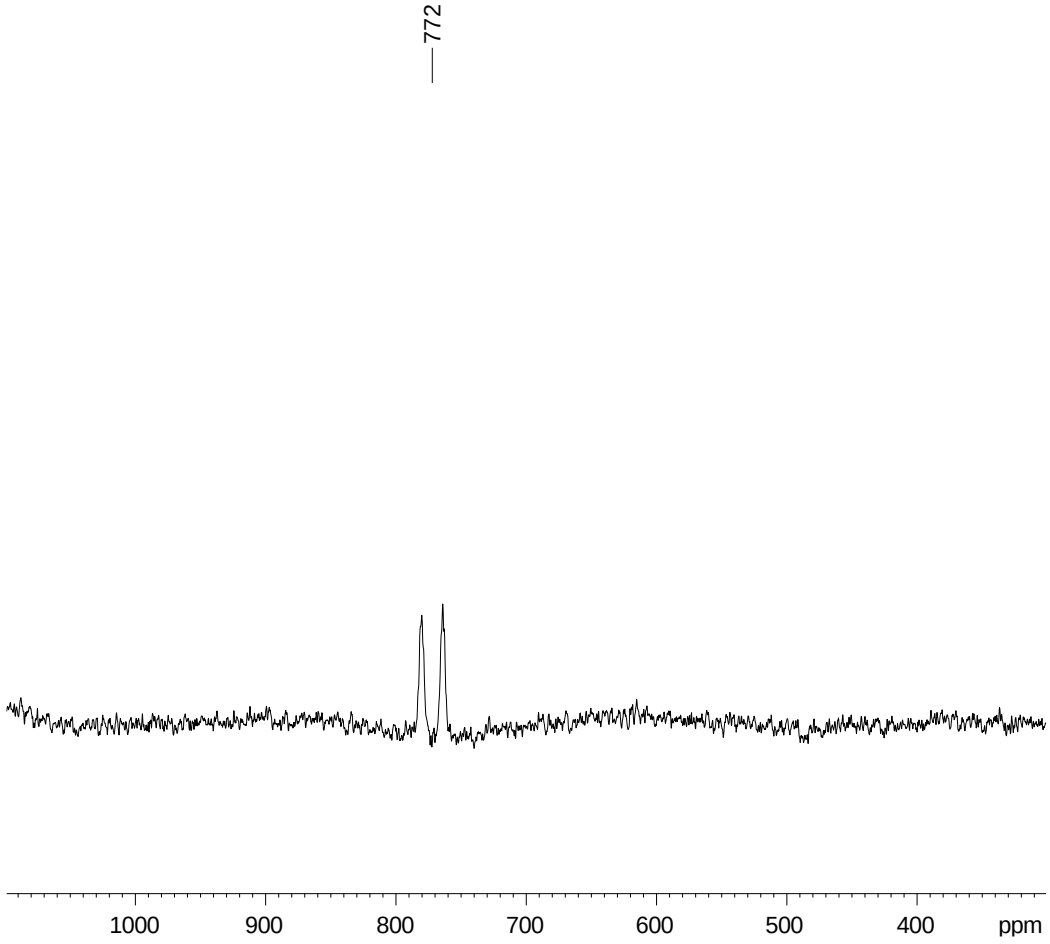


Figure SI 93. $^{31}P\{^{1}H\}$ NMR spectrum of compound **12a**.

^{119}Sn NMR spectrum of [TbbSnClIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA800+842_21022022_300
EXPNO 26
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220221
Time 11.05 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 53248
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.9987180 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 1.40

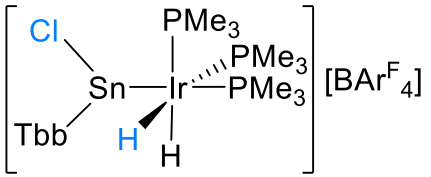
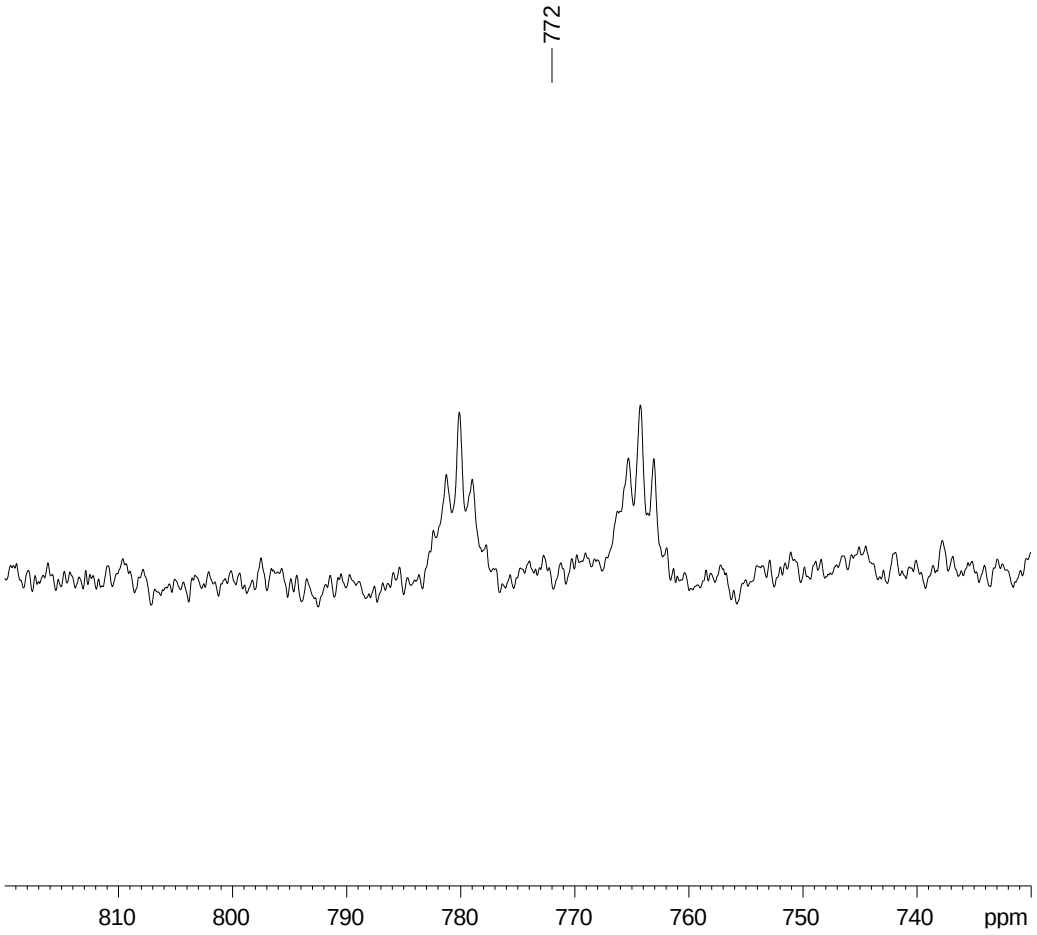


Figure SI 94. ^{119}Sn NMR spectrum of compound **12a**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $[TbbSnClIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA800+842_21022022_300
EXPNO 36
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220221
Time 11.20 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 15770
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.9987178 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

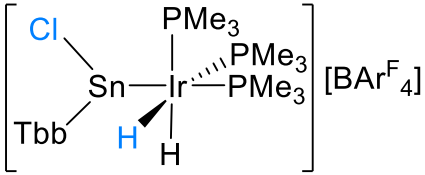
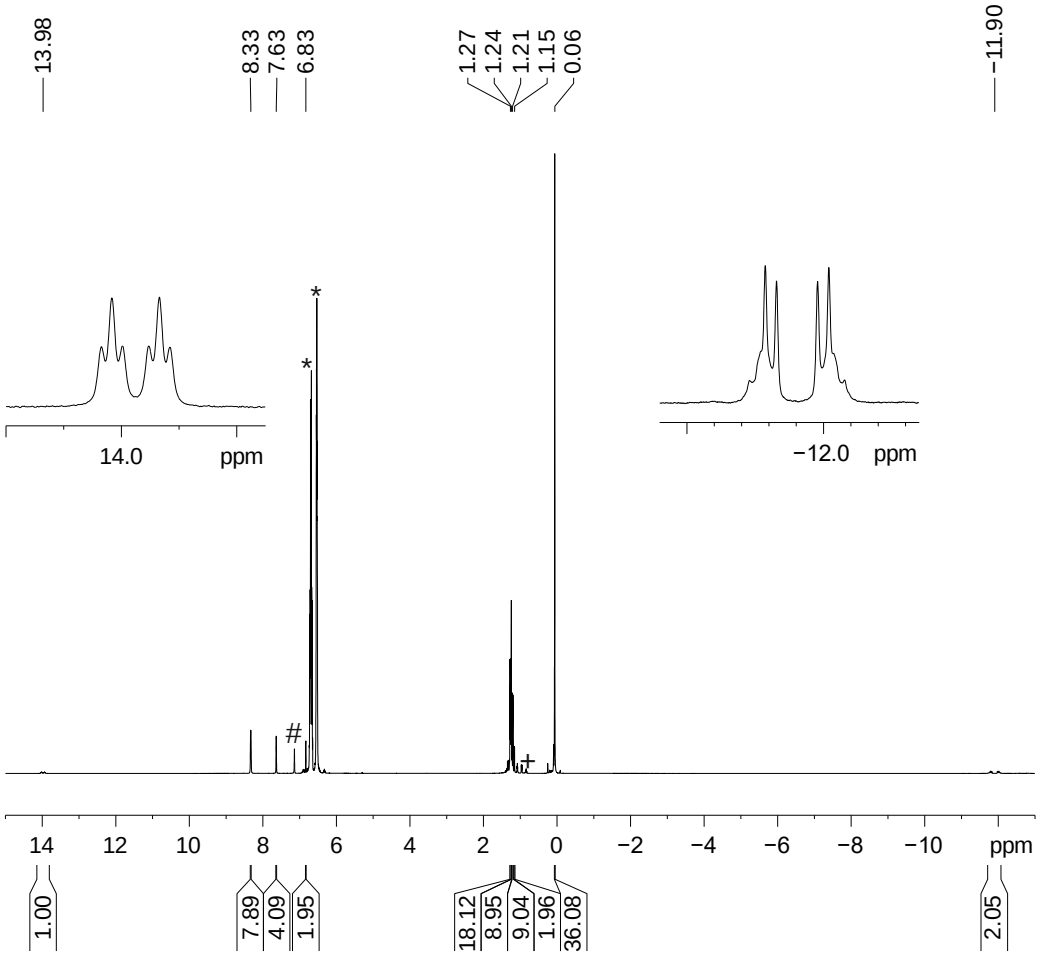
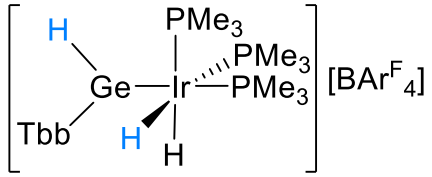


Figure SI 95. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **12a**.

NMR spectra of compound **13**.

^{1}H NMR spectrum of [TbbGeHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + *n*-pentane and unknown impurity.





Current Data Parameters
NAME MA803K_04022022_400N
EXPNO 12
PROCNO 1

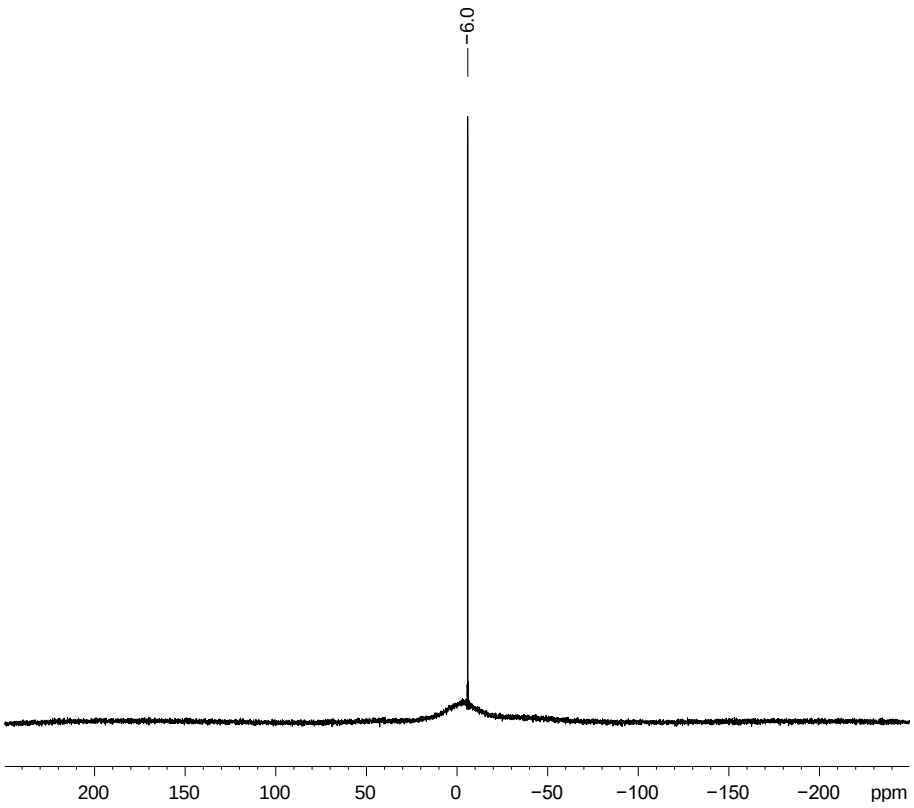
F2 − Acquisition Parameters
Date_ 20220205
Time 7.47
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 128
DS 0
SWH 20000.000 Hz
FIDRES 0.379824 Hz
AQ 1.3164001 sec
RG 45.2
DW 25.000 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 −3.00 dB
PL1W 16.03799057 W
SFO1 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100011 MHz
WDW EM
SSB 0
LB 0.70 Hz
GB 0
PC 1.00

Figure SI 96. ^{1}H NMR spectrum of compound **13**.

^{11}B NMR spectrum of [TbbGeHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA803K_07022022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220207
Time 12.54 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

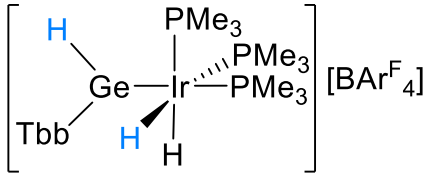
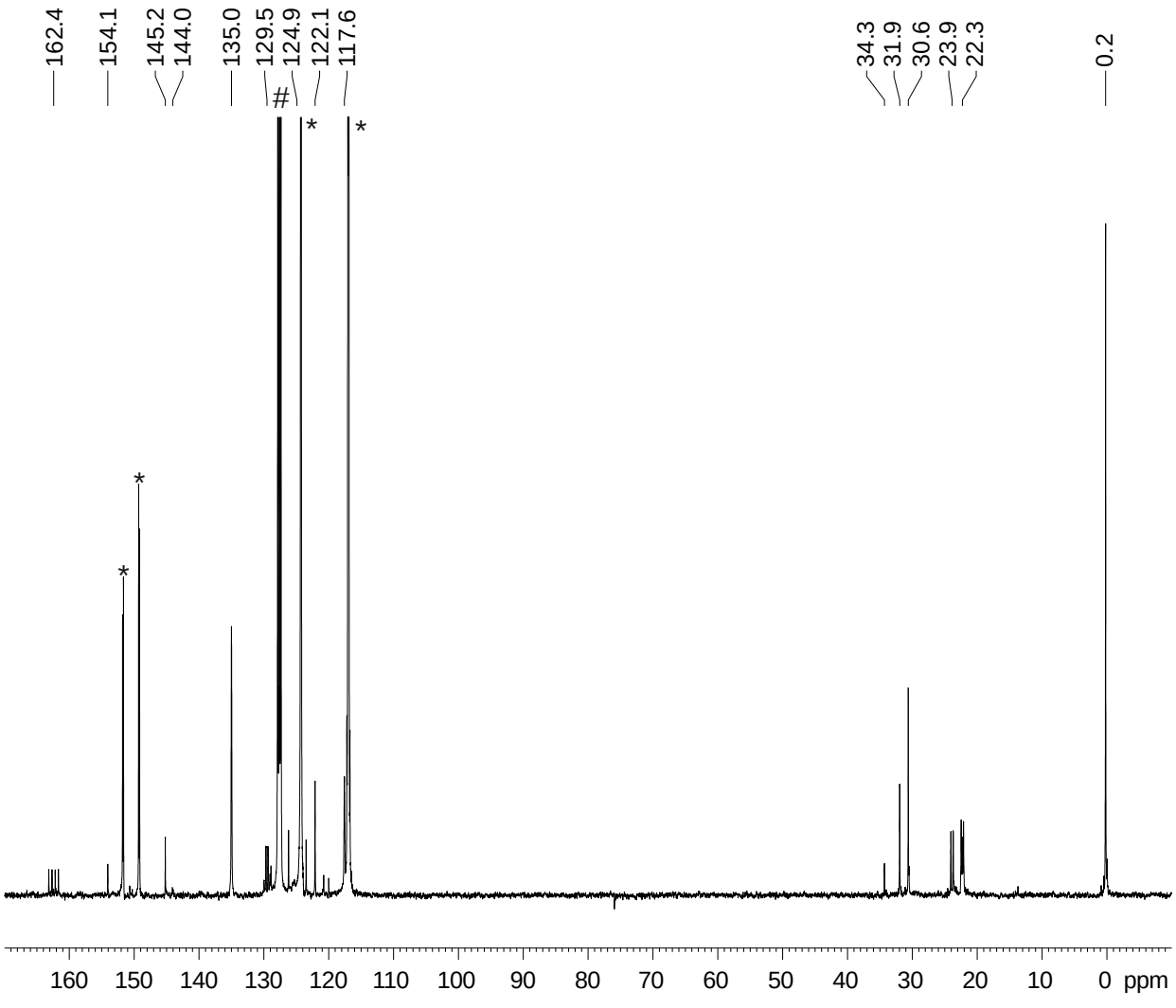


Figure SI 97. ^{11}B NMR spectrum of compound **13**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbGeHIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.




```
Current Data Parameters
NAME      MA803K_04022022_400M
EXPNO             14
PROCNO             1

F2 - Acquisition Parameters
Date_          20220206
Time             12.57
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           udeft
TD             22218
SOLVENT           C6D6
NS              5939
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ           0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE              299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1             -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8             1.39 dB
SP13            1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8          0.500
SPOAL13         0.500
SPOFFS8           0 Hz
SPOFFS13          0 Hz

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

F2 - Processing parameters
SI              131072
SF         100.6077400 MHz
WDW               EM
SSB                0
LB              3.00 Hz
GB                 0
PC              1.40
```

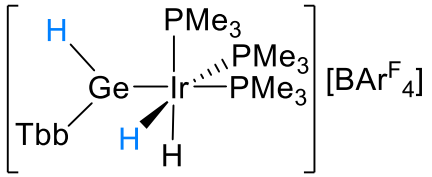
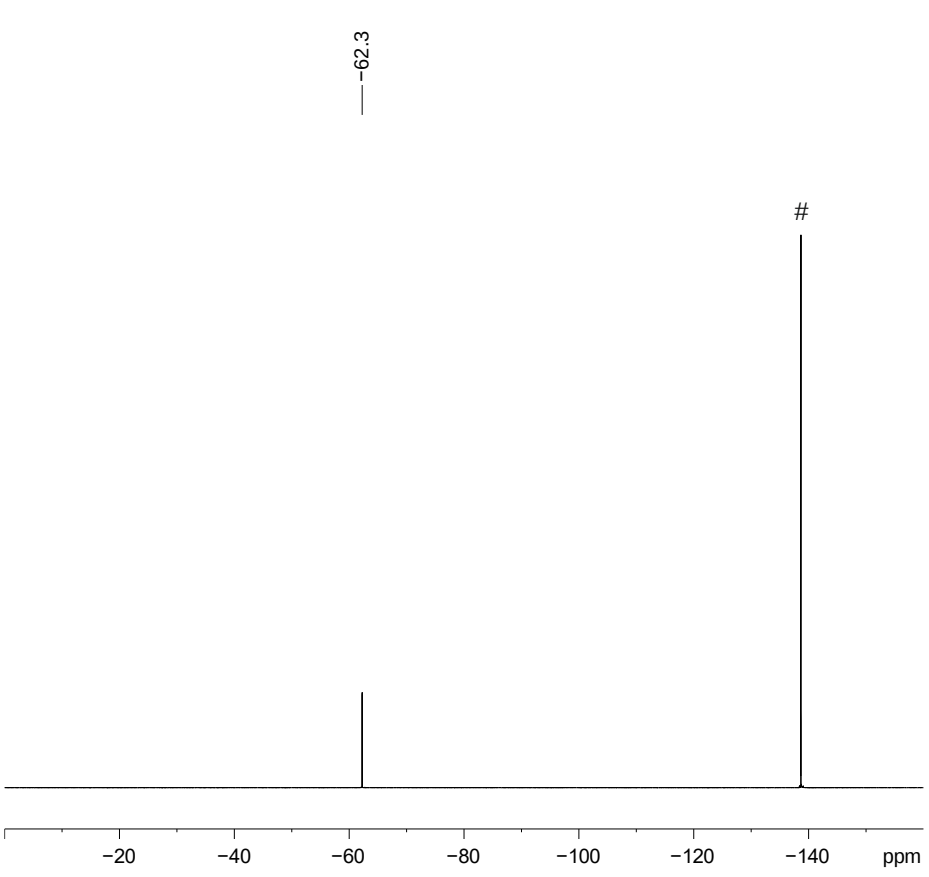


Figure SI 98. $^{13}C\{^{1}H\}$ NMR spectrum of compound **13**.

$^{19}F\{^{1}H\}$ NMR spectrum of [TbbGeHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME    MA803K_04022022_400N
EXPNO           20
PROCNO           1

F2 − Acquisition Parameters
Date_        20220206
Time           18.02
INSTRUM         spect
PROBHD  5 mm QNP 1H/13
PULPROG       zgfhigqn
TD           131072
SOLVENT          C6D6
NS               32
DS                0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ           0.6553600 sec
RG               4100
DW              5.000 usec
DE              6.00 usec
TE              299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0              1

======== CHANNEL f1 ========
NUC1            19F
P1            18.75 usec
PL1           −2.92 dB
PL1W       30.50645256 W
SFO1       376.4306030 MHz

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

F2 − Processing parameters
SI            262144
SF         376.4795470 MHz
WDW              EM
SSB              0
LB            2.00 Hz
GB               0
PC            1.00
```

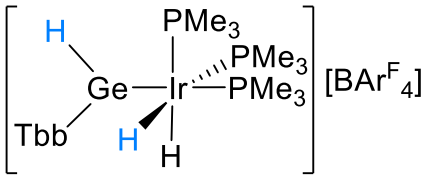
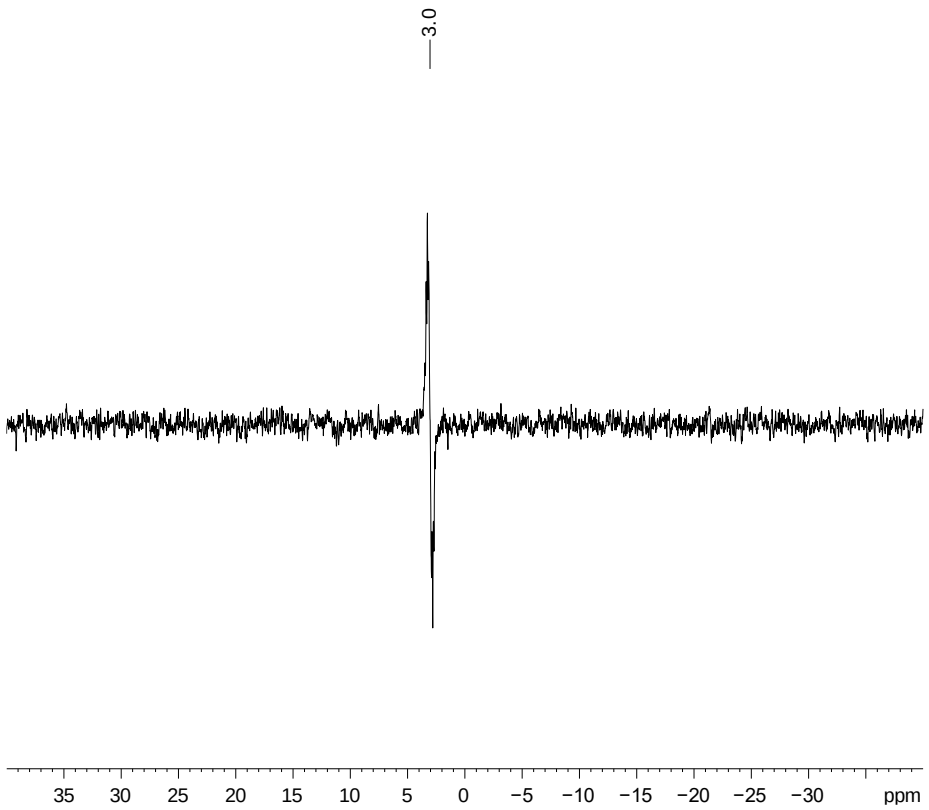


Figure SI 99. $^{19}F\{^{1}H\}$ NMR spectrum of compound **13**.

^{29}Si NMR spectrum of [TbbGeHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA803K_07022022_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220207
Time 13.03 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273648 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

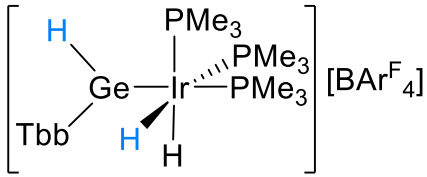
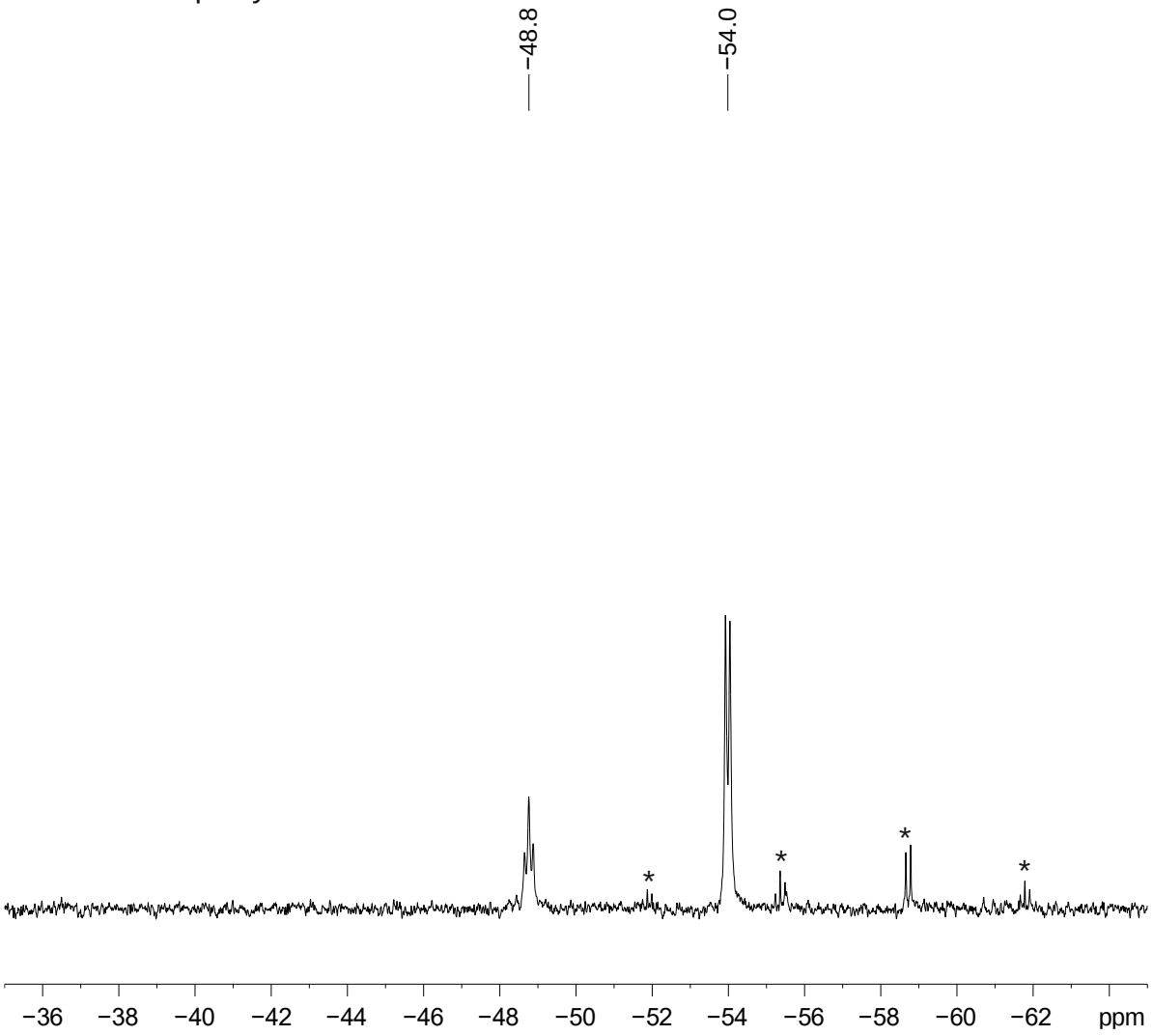


Figure SI 100. ^{29}Si NMR spectrum of compound **13**.

$^{31}P\{^{1}H\}$ NMR spectrum of [TbbGeHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.
* unknown impurity.



Current Data Parameters
NAME MA803K_04022022_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220204
Time 15.02
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 128
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1060000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

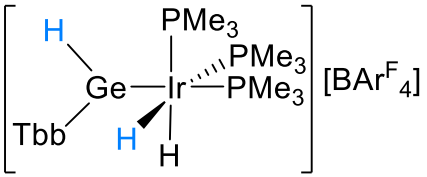
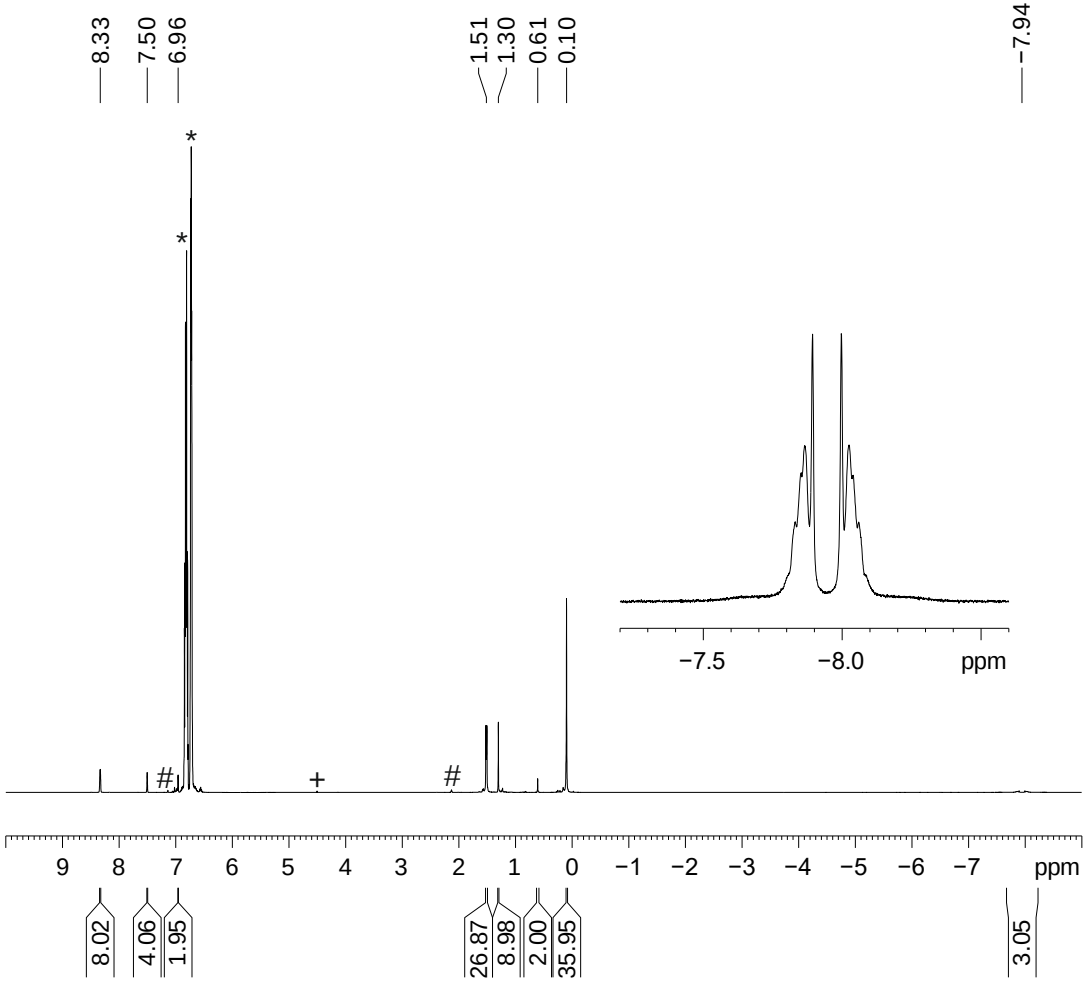


Figure SI 101. $^{31}P\{^{1}H\}$ NMR spectrum of compound **13**.

NMR spectra of compound **14**.

^{1}H NMR spectrum of [TbbSnIrH$_3$(PMe$_3$)$_3$][B(Ar^F)$_4$] in toluene-d$_8$ (#) and *o*-difluorobenzene (*) at −30 °C. + H_2.



Current Data Parameters
NAME MA873_07032022_500
EXPNO 1
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220307
Time 10.38
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zg30
TD 65536
SOLVENT Tol
NS 64
DS 0
SWH 25000.000 Hz
FIDRES 0.381470 Hz
AQ 1.3107200 sec
RG 4
DW 20.000 usec
DE 6.00 usec
TE 243.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.30 usec
PL1 −0.52 dB
PL1W 24.34997177 W
SFO1 500.1300000 MHz

F2 − Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

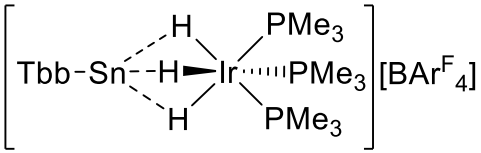
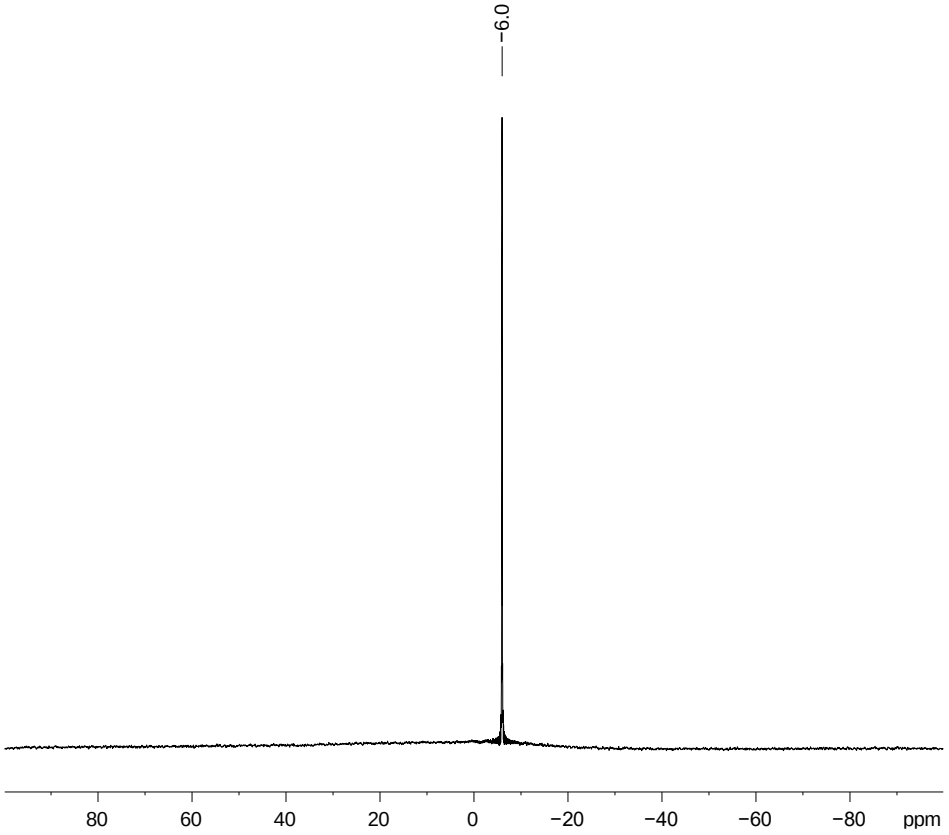


Figure SI 102. ^{1}H NMR spectrum of compound **14**.

$^{11}B\{^{1}H\}$ NMR spectrum of $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ in toluene-d_8 and *o*-difluorobenzene at −30 °C.




```
Current Data Parameters
NAME     MA873_07032022_500
EXPNO                 5
PROCNO                1

F2 − Acquisition Parameters
Date_          20220307
Time              14.17
INSTRUM           spect
PROBHD  5 mm TBO BB−1H
PULPROG          zgigbs
TD                4096
SOLVENT            Tol
NS                 310
DS                   0
SWH           32051.281 Hz
FIDRES         7.825020 Hz
AQ           0.0638976 sec
RG                1030
DW               15.600 usec
DE                6.00 usec
TE               243.3 K
D1          0.10000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               11B
P1               11.80 usec
P2               23.60 usec
PL1                0 dB
PL1W        88.92077637 W
SFO1       160.4615795 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              −0.52 dB
PL12              15.06 dB
PL2W        24.34997177 W
PL12W        0.67374945 W
SFO2       500.1320005 MHz

F2 − Processing parameters
SI                32768
SF         160.4615790 MHz
WDW                EM
SSB                 0
LB              10.00 Hz
GB                  0
PC                1.40
```

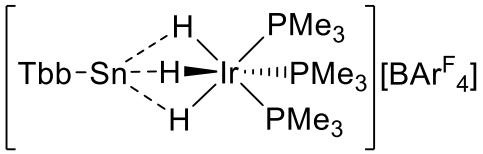
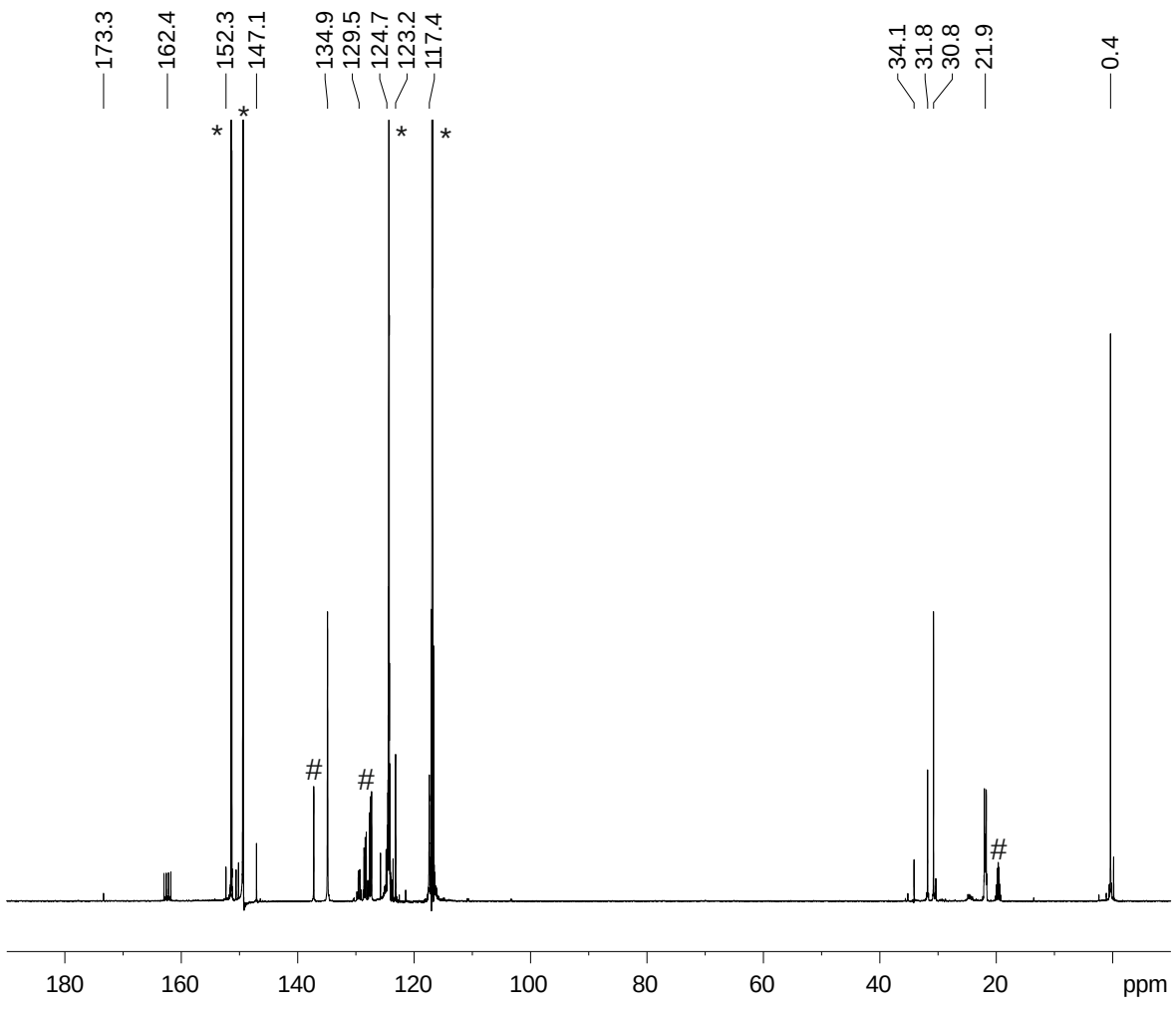


Figure SI 103. ^{11}B NMR spectrum of compound **14**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ in toluene-d_8 (#) and *o*-difluorobenzene (*) at −30 °C.




```
Current Data Parameters
NAME     MA873_07032022_500
EXPNO              9
PROCNO             1

F2 - Acquisition Parameters
Date_          20220308
Time              2.55
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG           udeft
TD             27268
SOLVENT             Tol
NS             25600
DS                 0
SWH          40760.871 Hz
FIDRES        1.494824 Hz
AQ           0.3344875 sec
RG              2050
DW             12.267 usec
DE              6.00 usec
TE             273.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1               8.32 usec
P13           2000.00 usec
P26            500.00 usec
PL1              0.40 dB
PL1W        76.51497650 W
SFO1       125.7728799 MHz
SP8             10.16 dB
SP13            10.16 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8           0.500
SPOAL13          0.500
SPOFFS8            0 Hz
SPOFFS13           0 Hz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2              1H
PCPD2           80.00 usec
PL2            -0.52 dB
PL12            15.06 dB
PL2W        24.34997177 W
PL12W        0.67374945 W
SFO2       500.1325006 MHz

F2 - Processing parameters
SI              262144
SF         125.7577890 MHz
WDW                EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
```

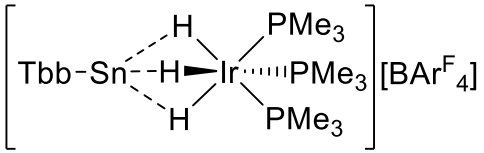
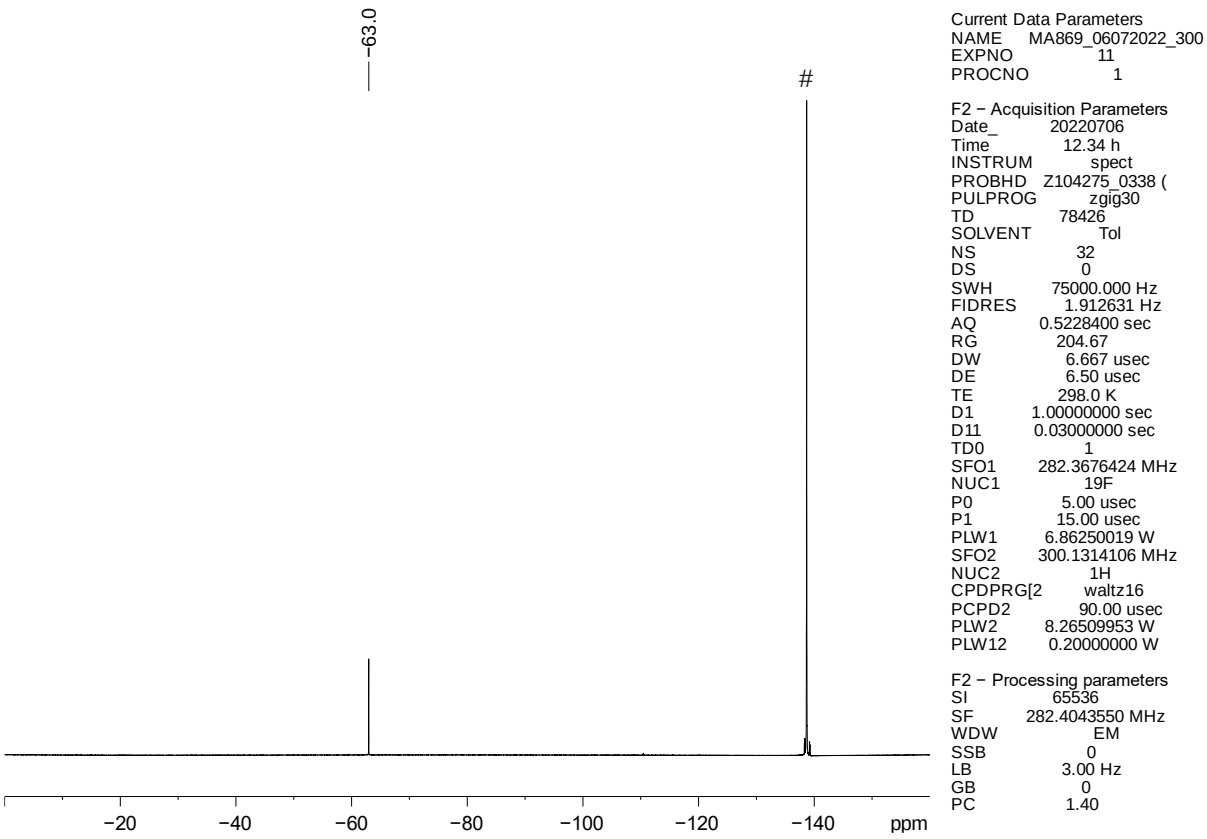


Figure SI 104. $^{13}C\{^{1}H\}$ NMR spectrum of compound **14**.

$^{19}F\{^{1}H\}$ NMR spectrum of $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ in toluene-d_8 and *o*-difluorobenzene (#) at rt.



Current Data Parameters
NAME MA869_06072022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220706
Time 12.34 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 78426
SOLVENT Tol
NS 32
DS 0
SWH 75000.000 Hz
FIDRES 1.912631 Hz
AQ 0.5228400 sec
RG 204.67
DW 6.667 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 282.3676424 MHz
NUC1 19F
P0 5.00 usec
P1 15.00 usec
PLW1 6.86250019 W
SFO2 300.1314106 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 282.4043550 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

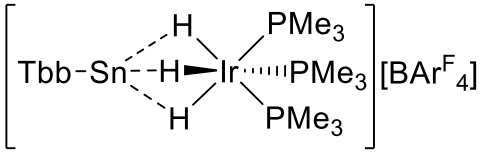
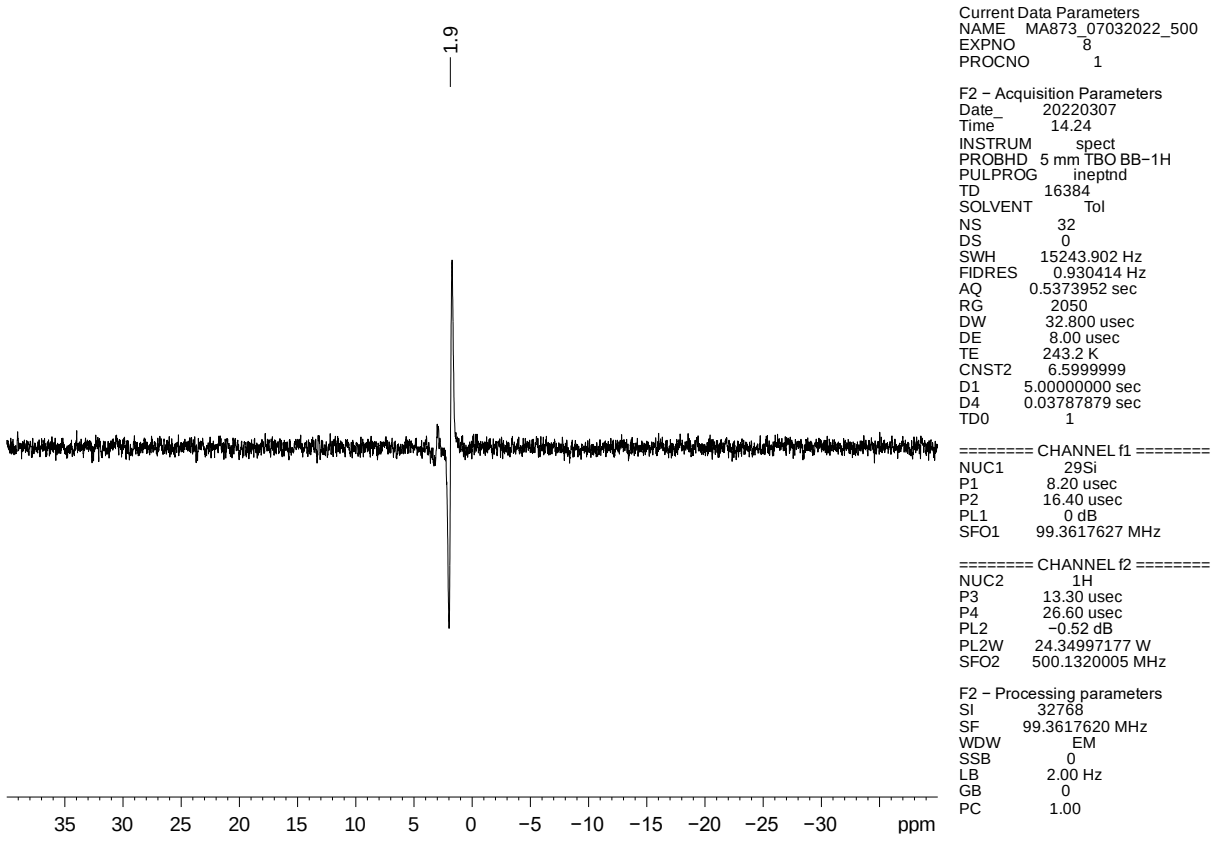


Figure SI 105. $^{19}F\{^{1}H\}$ NMR spectrum of compound **14**.

^{29}Si NMR spectrum of [TbbSnIrH$_3$(PMe$_3$)$_3$][B(Ar^F)$_4$] in toluene-d$_8$ and *o*-difluorobenzene at −30 °C.



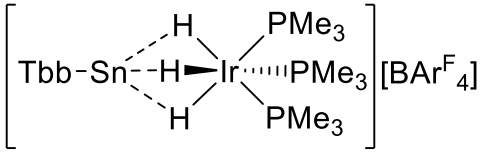
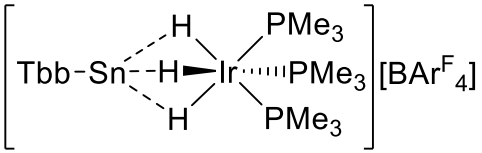
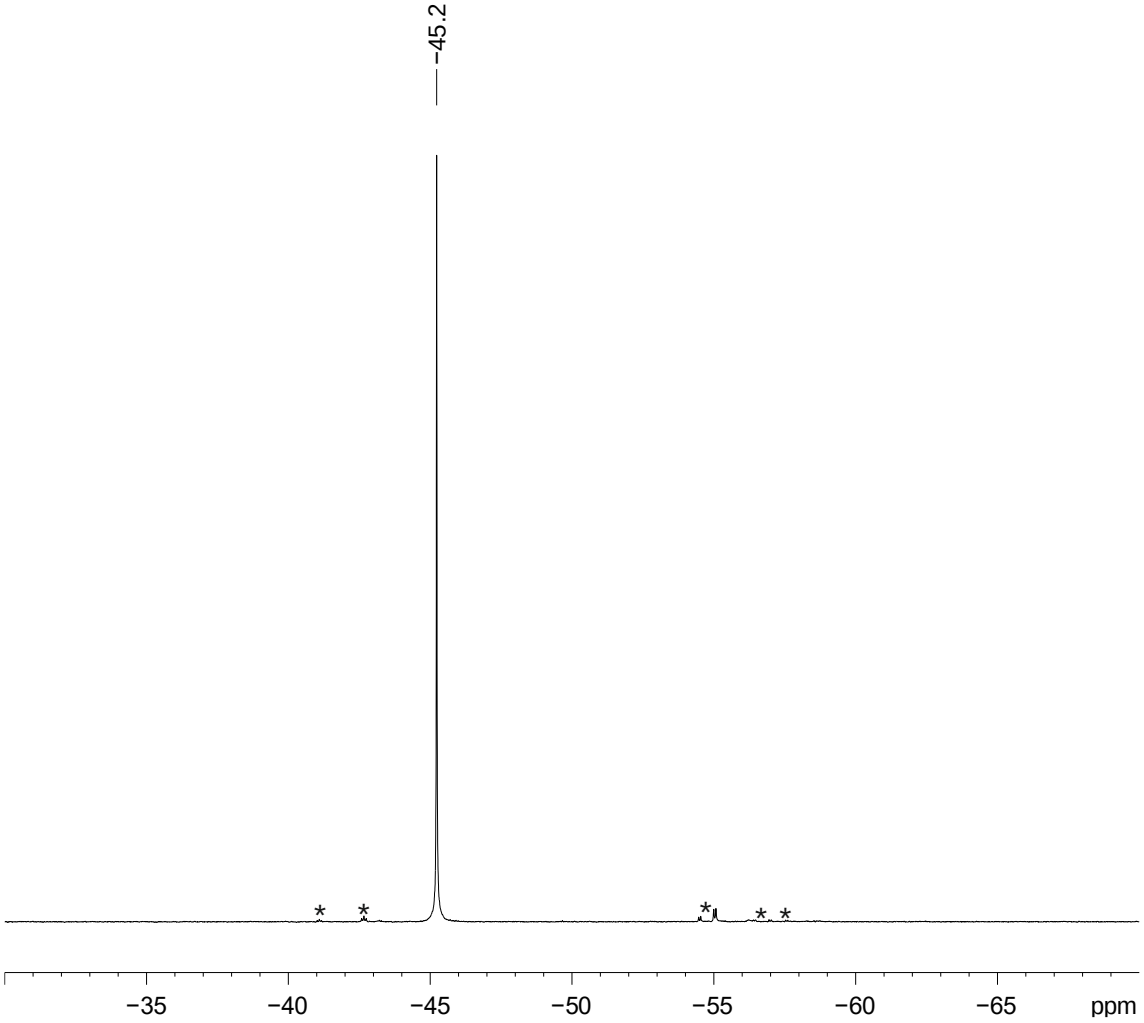


Figure SI 106. ^{29}Si NMR spectrum of compound **14**.

$^{31}P\{^{1}H\}$ NMR spectrum of $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ in toluene-d_8 and *o*-difluorobenzene at −30 °C.
* unknown impurity.





Current Data Parameters
NAME MA873_07032022_500
EXPNO 4
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220307
Time 14.11
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zgpg30
TD 109230
SOLVENT Tol
NS 81
DS 0
SWH 81521.742 Hz
FIDRES 0.746331 Hz
AQ 0.6699440 sec
RG 2050
DW 6.133 usec
DE 6.00 usec
TE 243.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

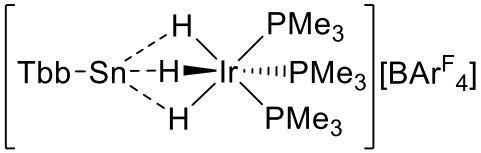
======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 3.00 dB
PL1W 46.07667160 W
SFO1 202.4563352 MHz

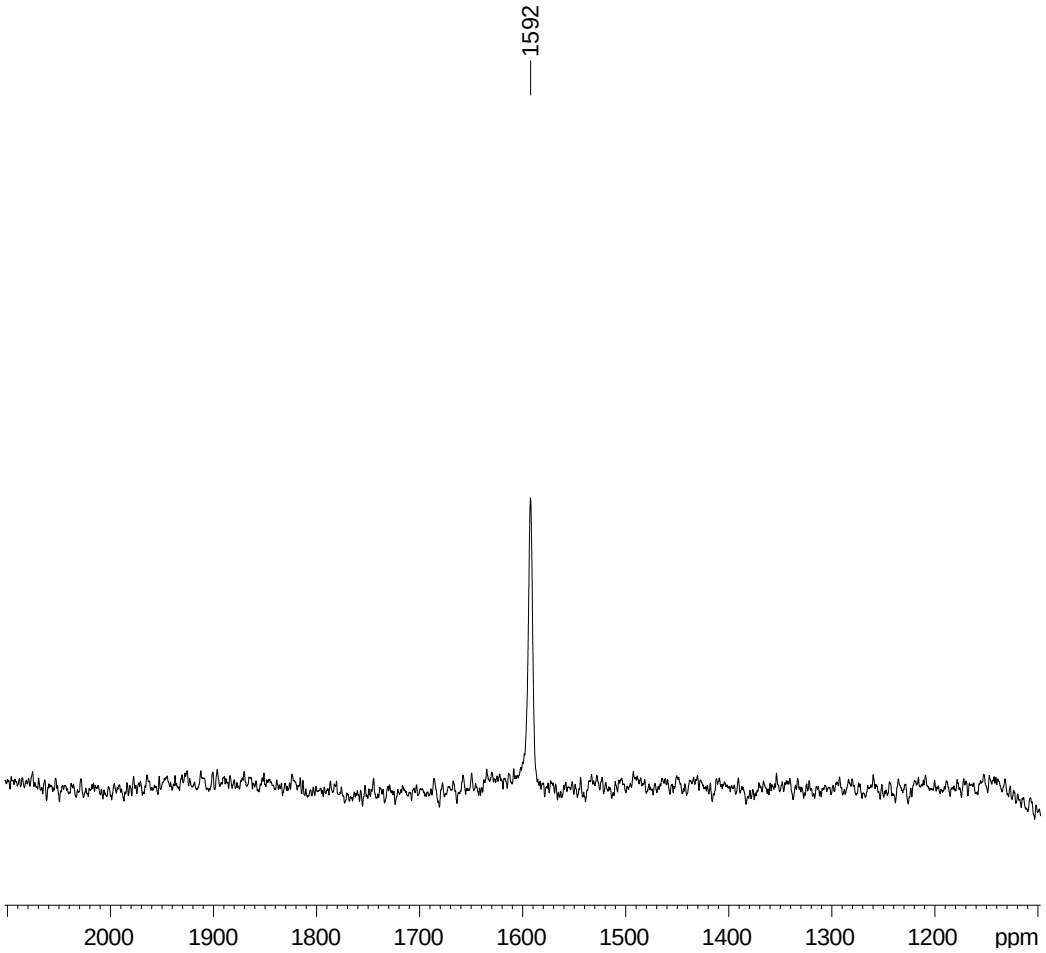
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 −0.52 dB
PL12 15.06 dB
PL13 19.71 dB
PL2W 24.34997177 W
PL12W 0.67374945 W
PL13W 0.23093967 W
SFO2 500.1274993 MHz

F2 − Processing parameters
SI 131072
SF 202.4563350 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

Figure SI 107. $^{31}P\{^{1}H\}$ NMR spectrum of compound **14**.

^{119}Sn NMR spectrum of [TbbSnIrH$_3$(PMe$_3$)$_3$][B(Ar^F)$_4$] in toluene-d$_8$ and *o*-difluorobenzene at −30 °C.





Current Data Parameters
NAME MA873_07032022_500
EXPNO 3
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220307
Time 11.36
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zg30
TD 65536
SOLVENT Tol
NS 21668
DS 0
SWH 187500.000 Hz
FIDRES 2.861023 Hz
AQ 0.1747627 sec
RG 2050
DW 2.667 usec
DE 6.00 usec
TE 243.2 K
D1 0.20000000 sec
TD0 1

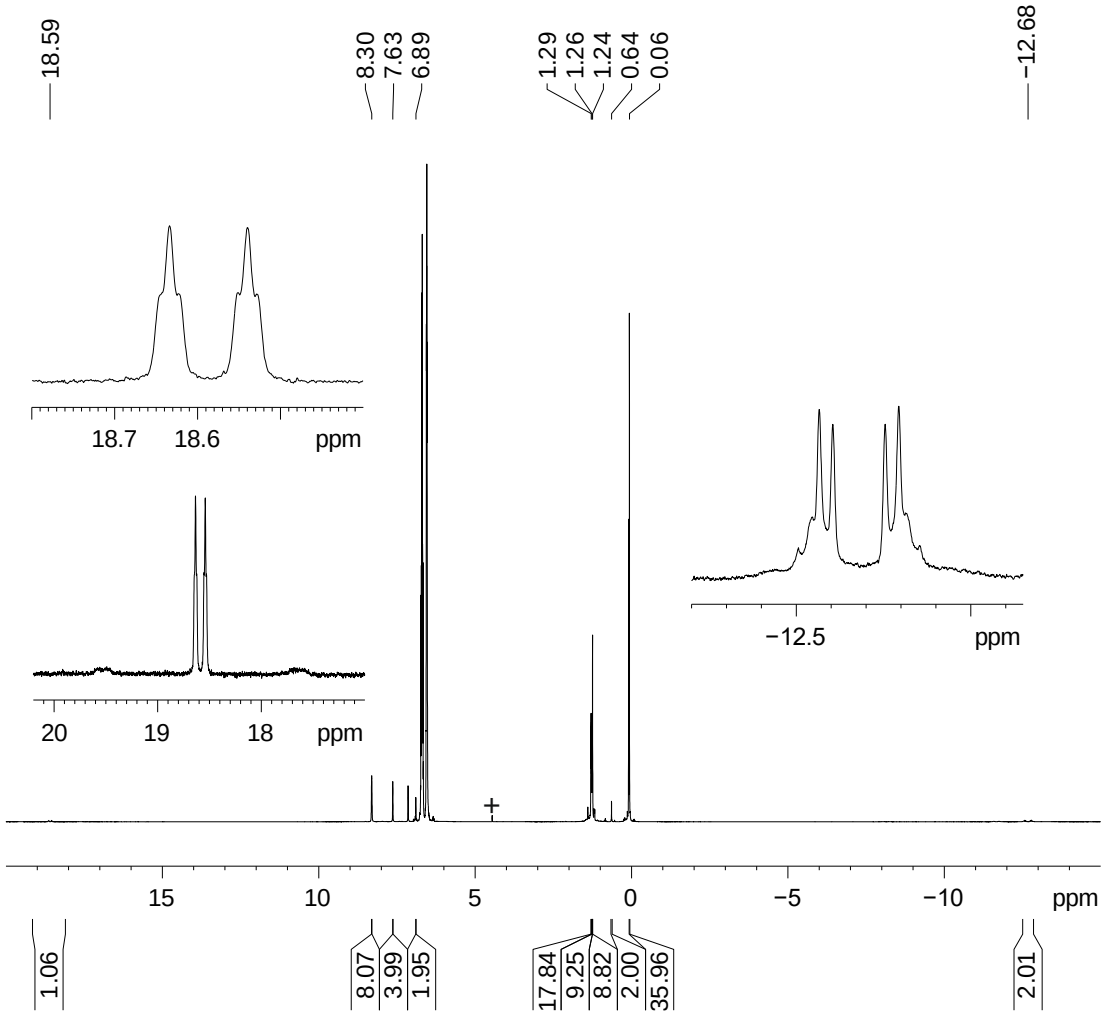
======== CHANNEL f1 ========
NUC1 119Sn
P1 15.50 usec
PL1 3.00 dB
PL1W 45.32131577 W
SFO1 186.8000406 MHz

F2 − Processing parameters
SI 131072
SF 186.5016380 MHz
WDW EM
SSB 0
LB 200.00 Hz
GB 0
PC 1.40

Figure SI 108. ^{119}Sn NMR spectrum of compound **14**.

NMR spectra of compound **15**.

^{1}H NMR spectrum of [TbbSnHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ (#) and *o*-difluorobenzene (*) at rt. + H$_2$.



Current Data Parameters
NAME MA840_21022022_400
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220221
Time 10.54
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 20000.000 Hz
FIDRES 0.379824 Hz
AQ 1.3164001 sec
RG 45.2
DW 25.000 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.00

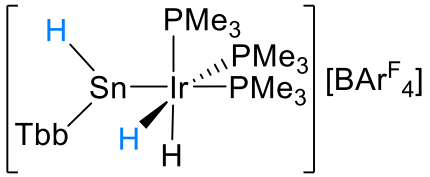
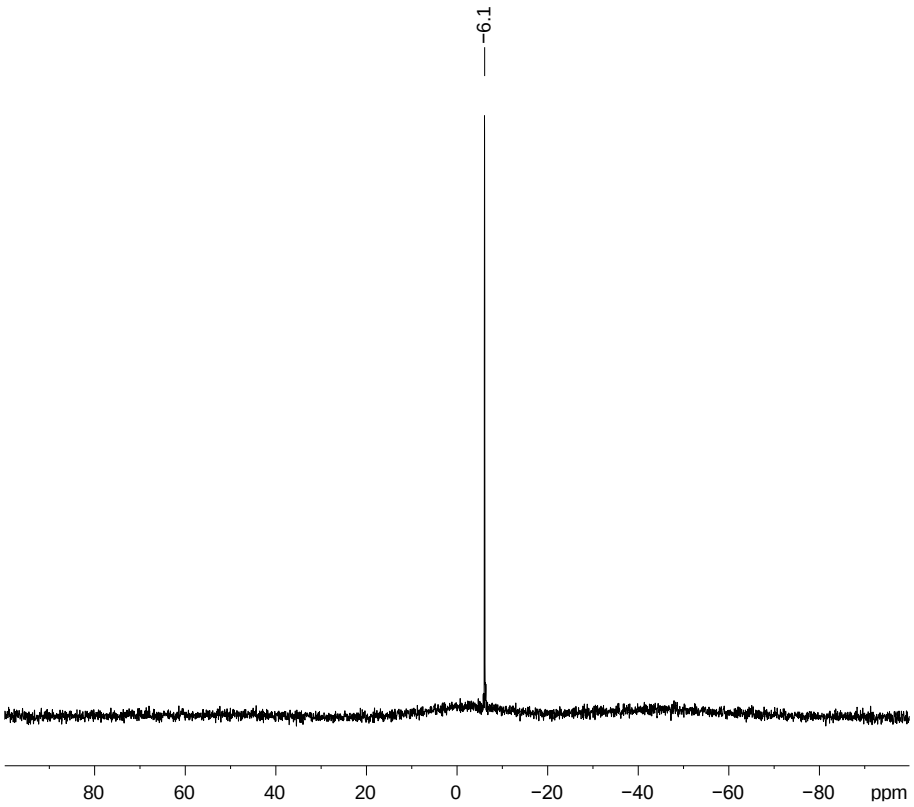


Figure SI 109. ^{1}H NMR spectrum of compound **15**.

^{11}B NMR spectrum of [TbbSnHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA840W_02032022_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220302
Time 14.44 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgbs
TD 8192
SOLVENT C6D6
NS 1024
DS 0
SWH 48076.922 Hz
FIDRES 11.737530 Hz
AQ 0.0851968 sec
RG 204.67
DW 10.400 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
TD0 1
SFO1 96.2936312 MHz
NUC1 11B
P1 5.75 usec
P2 11.50 usec
PLW1 70.00000000 W

F2 − Processing parameters
SI 32768
SF 96.2936312 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

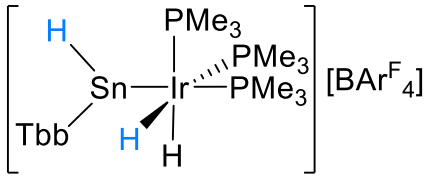
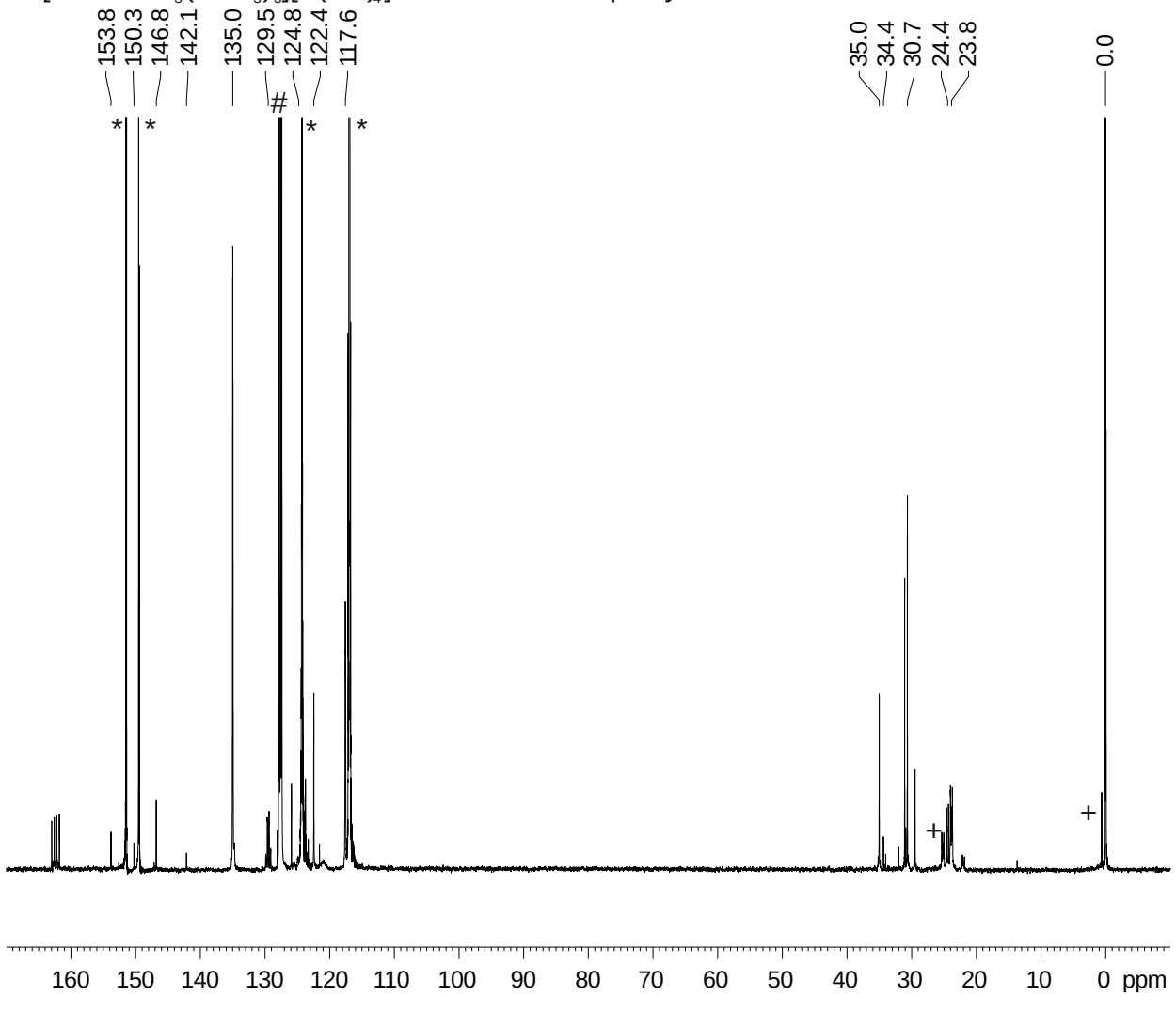


Figure SI 110. ^{11}B NMR spectrum of compound **15**.

$^{13}C\{^{1}H\}$ NMR spectrum of $[TbbSnHIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 (#) and *o*-difluorobenzene (*) at rt.
+ $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ and unknown impurity.



Current Data Parameters
NAME MA840_28022022_500
EXPNO 6
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220301
Time 8.38
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG udeft
TD 27268
SOLVENT C6D6
NS 20480
DS 0
SWH 37878.789 Hz
FIDRES 1.389130 Hz
AQ 0.3599376 sec
RG 2050
DW 13.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 100.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.32 usec
P13 2000.00 usec
P26 500.00 usec
PL1 0.40 dB
PL1W 76.51497650 W
SFO1 125.7728799 MHz
SP8 10.16 dB
SP13 10.16 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13 Crp60comp.4
SPOAL8 0.500
SPOAL13 0.500
SPOFFS8 0 Hz
SPOFFS13 0 Hz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 −0.52 dB
PL12 15.06 dB
PL2W 24.34997177 W
PL12W 0.67374945 W
SFO2 500.1325006 MHz

F2 − Processing parameters
SI 262144
SF 125.7577890 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

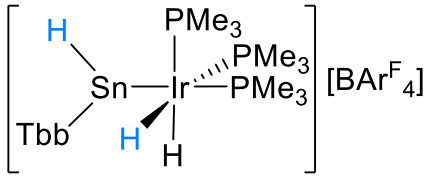
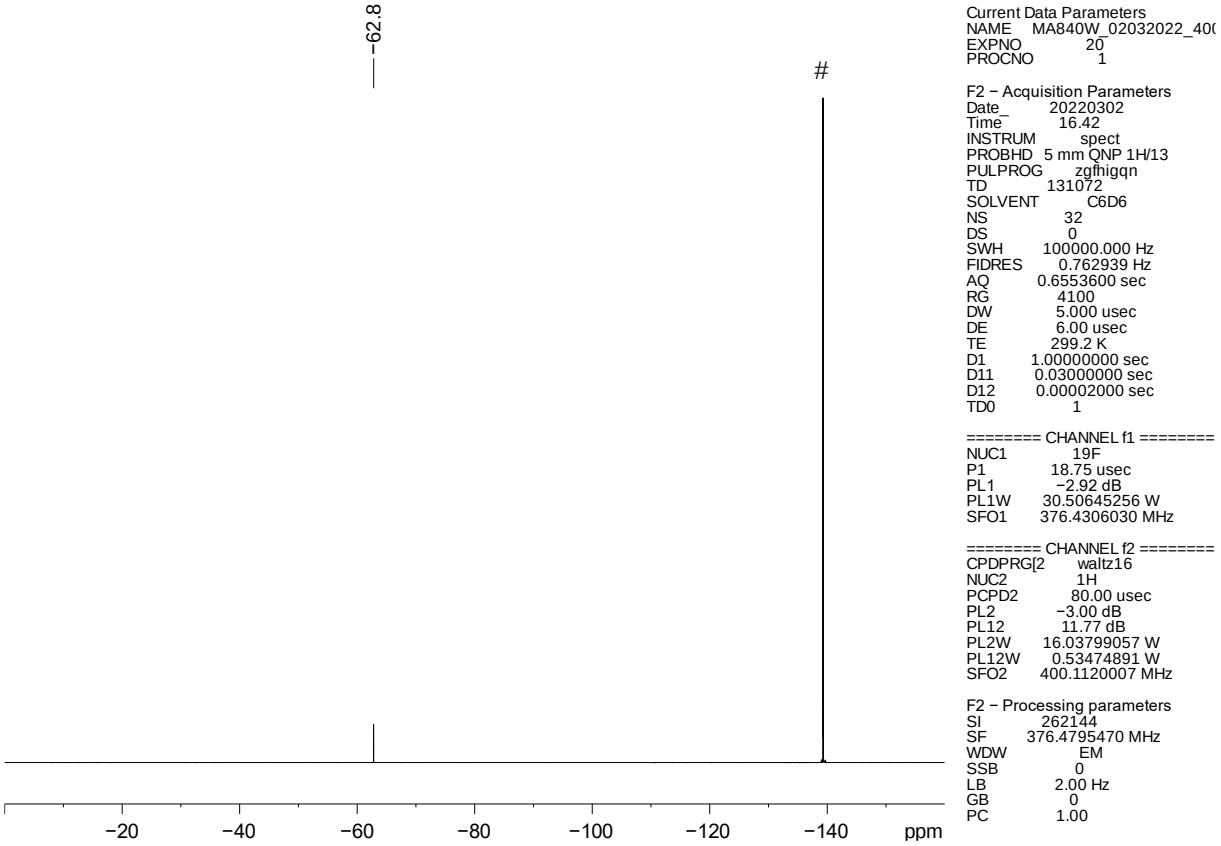


Figure SI 111. $^{13}C\{^{1}H\}$ NMR spectrum of compound **15**.

$^{19}F\{^{1}H\}$ NMR spectrum of $[TbbSnHIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene (#) at rt.




```
Current Data Parameters
NAME     MA840W_02032022_40(
EXPNO            20
PROCNO            1

F2 − Acquisition Parameters
Date_         20220302
Time             16.42
INSTRUM          spect
PROBHD  5 mm QNP 1H/13
PULPROG       zgfhigqn
TD             131072
SOLVENT            C6D6
NS                 32
DS                  0
SWH          100000.000 Hz
FIDRES         0.762939 Hz
AQ           0.6553600 sec
RG                4100
DW               5.000 usec
DE               6.00 usec
TE               299.2 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              19F
P1              18.75 usec
PL1             −2.92 dB
PL1W        30.50645256 W
SFO1        376.4306030 MHz

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

F2 − Processing parameters
SI              262144
SF          376.4795470 MHz
WDW                EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.00
```

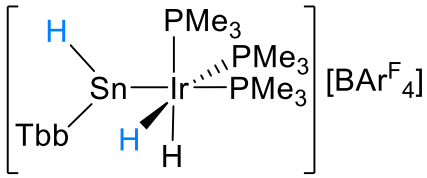
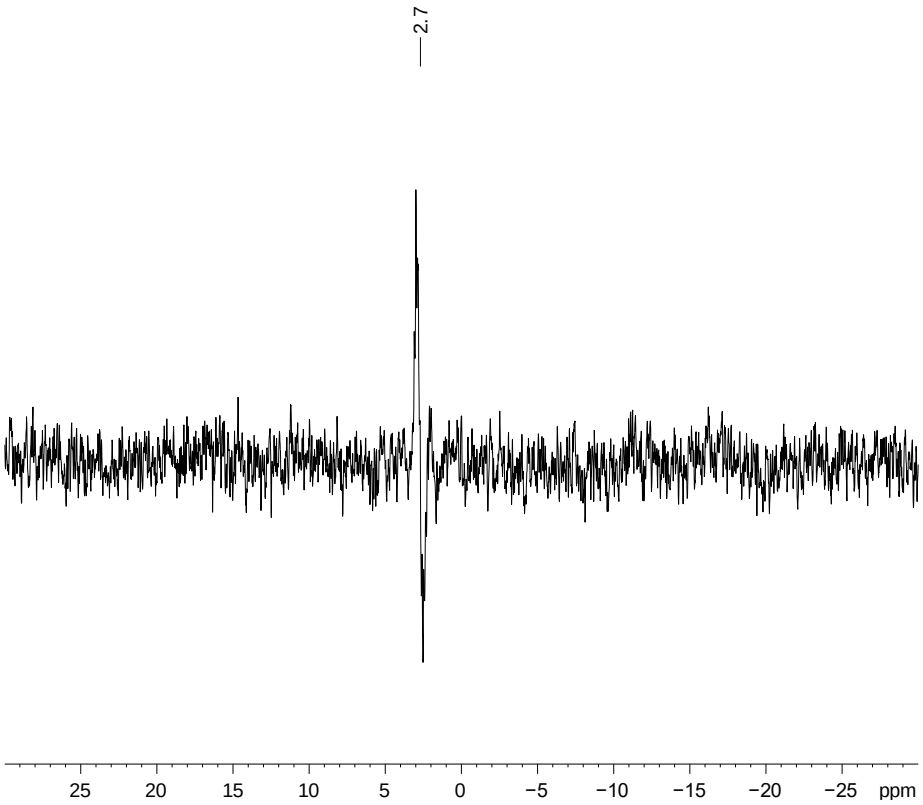


Figure SI 112. $^{19}F\{^{1}H\}$ NMR spectrum of compound **15**.

^{29}Si NMR spectrum of [TbbSnHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA840W_02032022_300
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220302
Time 14.53 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273823 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

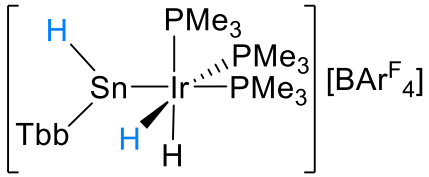
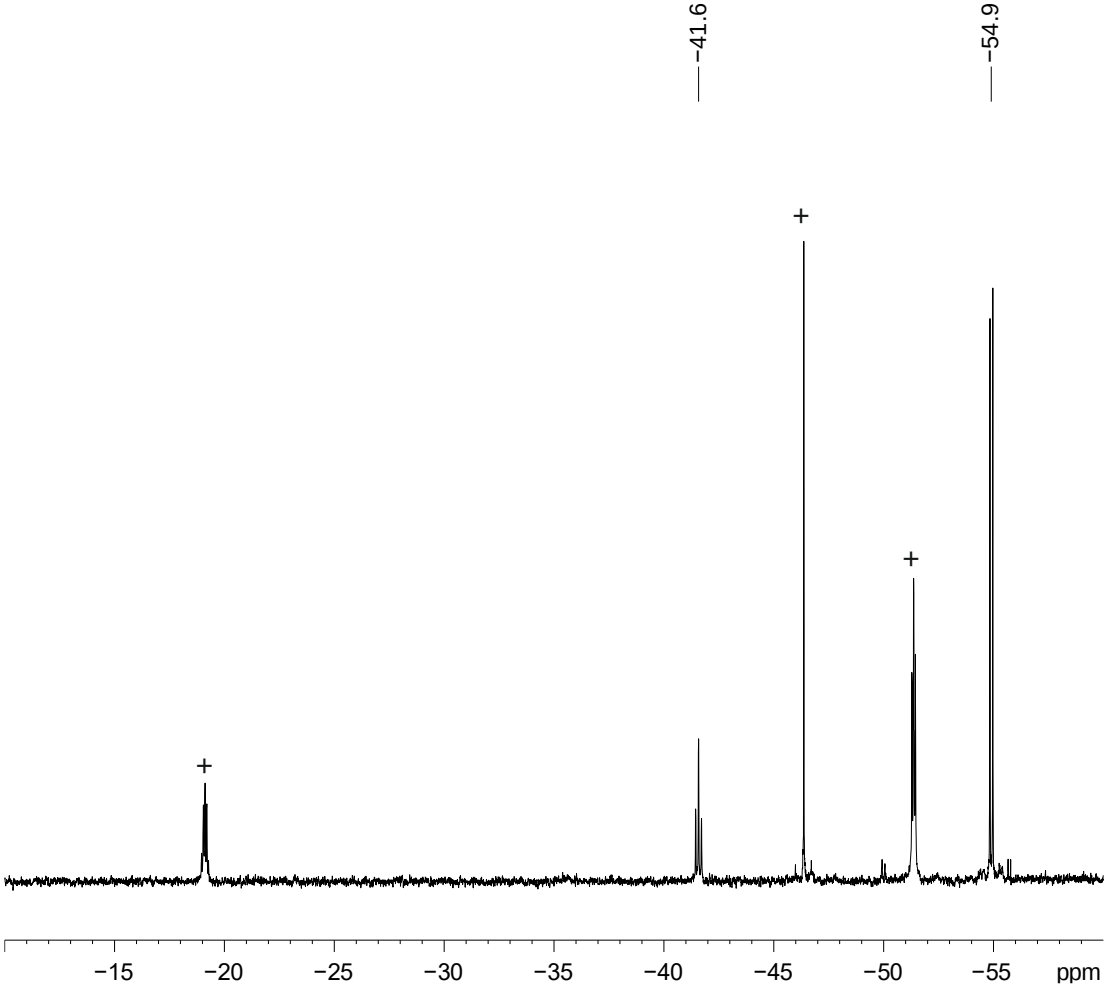


Figure SI 113. ^{29}Si NMR spectrum of compound **15**.

$^{31}P\{^{1}H\}$ NMR spectrum of $[TbbSnHIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.
* $[TbbSnIrH_3(PMe_3)_3][B(Ar^F)_4]$ and unknown impurity.



Current Data Parameters
NAME MA840W_03032022_300
EXPNO 20
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220303
Time 15.51 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 78426
SOLVENT C6D6
NS 256
DS 0
SWH 49019.609 Hz
FIDRES 1.250086 Hz
AQ 0.7999452 sec
RG 204.67
DW 10.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 121.4948510 MHz
NUC1 31P
P0 4.00 usec
P1 12.00 usec
PLW1 11.36400032 W
SFO2 300.1281992 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 121.4948510 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

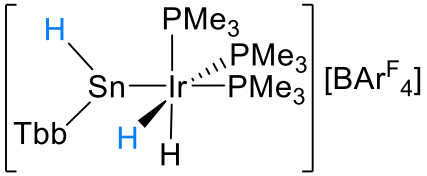
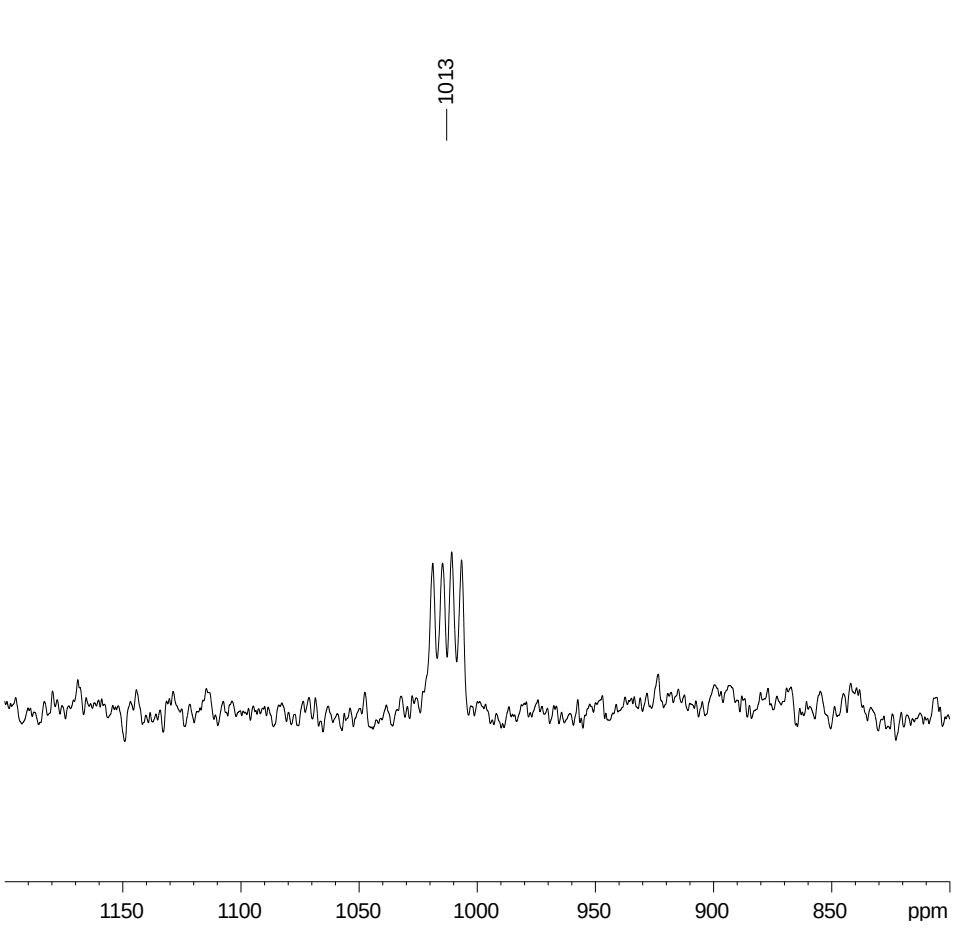


Figure SI 114. $^{31}P\{^{1}H\}$ NMR spectrum of compound **15**.

^{119}Sn NMR spectrum of [TbbSnHIrH$_2$(PMe$_3$)$_3$][B(Ar^F)$_4$] in benzene-d$_6$ and *o*-difluorobenzene at rt.



Current Data Parameters
NAME MA840_25022022_500
EXPNO 4
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220225
Time 13.44
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 100000
DS 0
SWH 150000.000 Hz
FIDRES 2.288818 Hz
AQ 0.2184533 sec
RG 2050
DW 3.333 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 119Sn
P1 15.50 usec
PL1 3.00 dB
PL1W 45.32131577 W
SFO1 186.6694895 MHz

F2 − Processing parameters
SI 131072
SF 186.5016380 MHz
WDW EM
SSB 0
LB 200.00 Hz
GB 0
PC 1.40

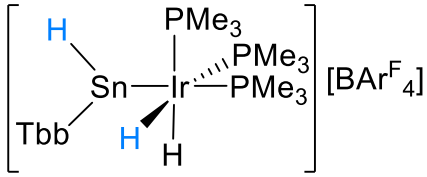
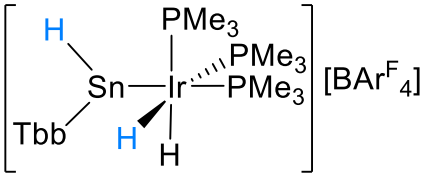
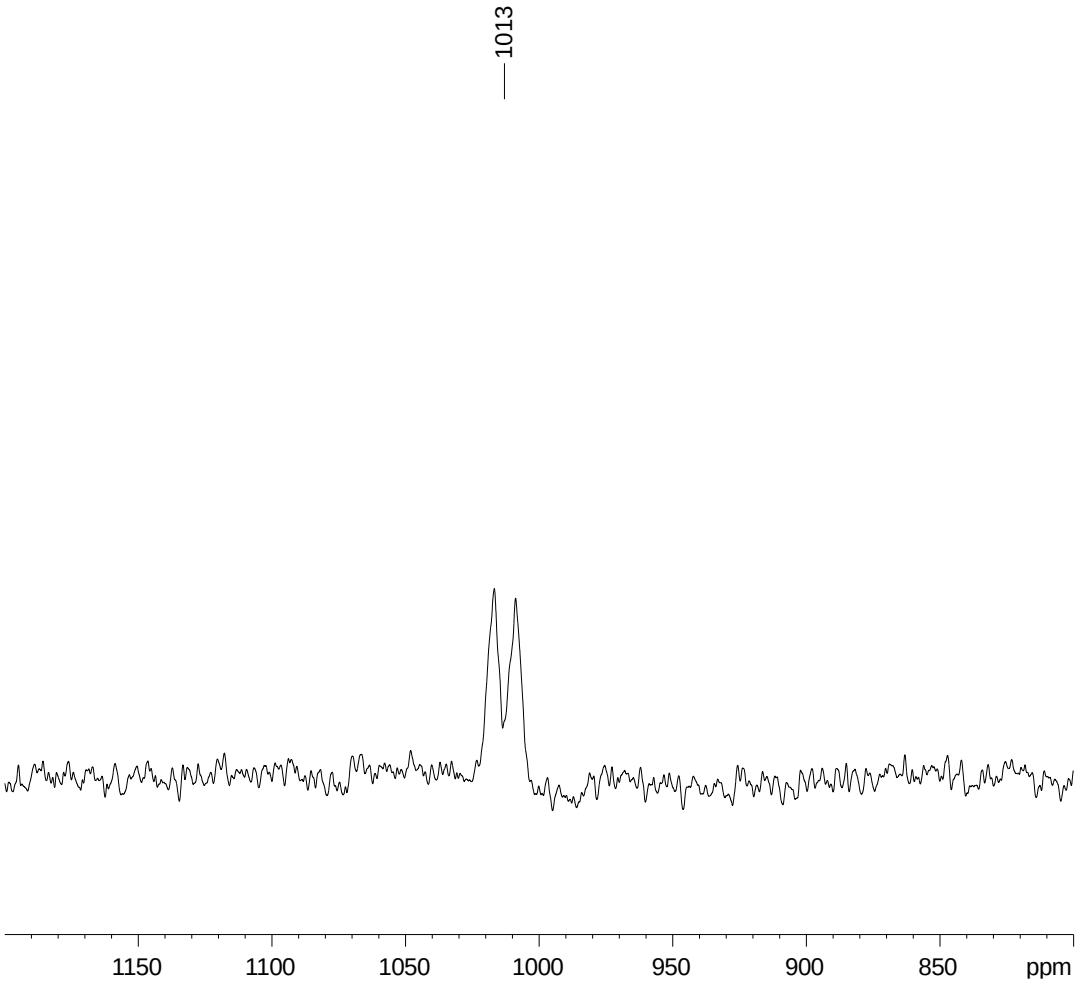


Figure SI 115. ^{119}Sn NMR spectrum of compound **15**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $[TbbSnHIrH_2(PMe_3)_3][B(Ar^F)_4]$ in benzene-d_6 and *o*-difluorobenzene at rt.





Current Data Parameters
NAME MA840_25022022_500
EXPNO 5
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220226
Time 14.49
INSTRUM spect
PROBHD 5 mm TBO BB−1H
PULPROG zgig30
TD 65536
SOLVENT C6D6
NS 100000
DS 0
SWH 150000.000 Hz
FIDRES 2.288818 Hz
AQ 0.2184533 sec
RG 2050
DW 3.333 usec
DE 6.00 usec
TE 299.2 K
D1 0.20000000 sec
D11 0.03000000 sec
TD0 1

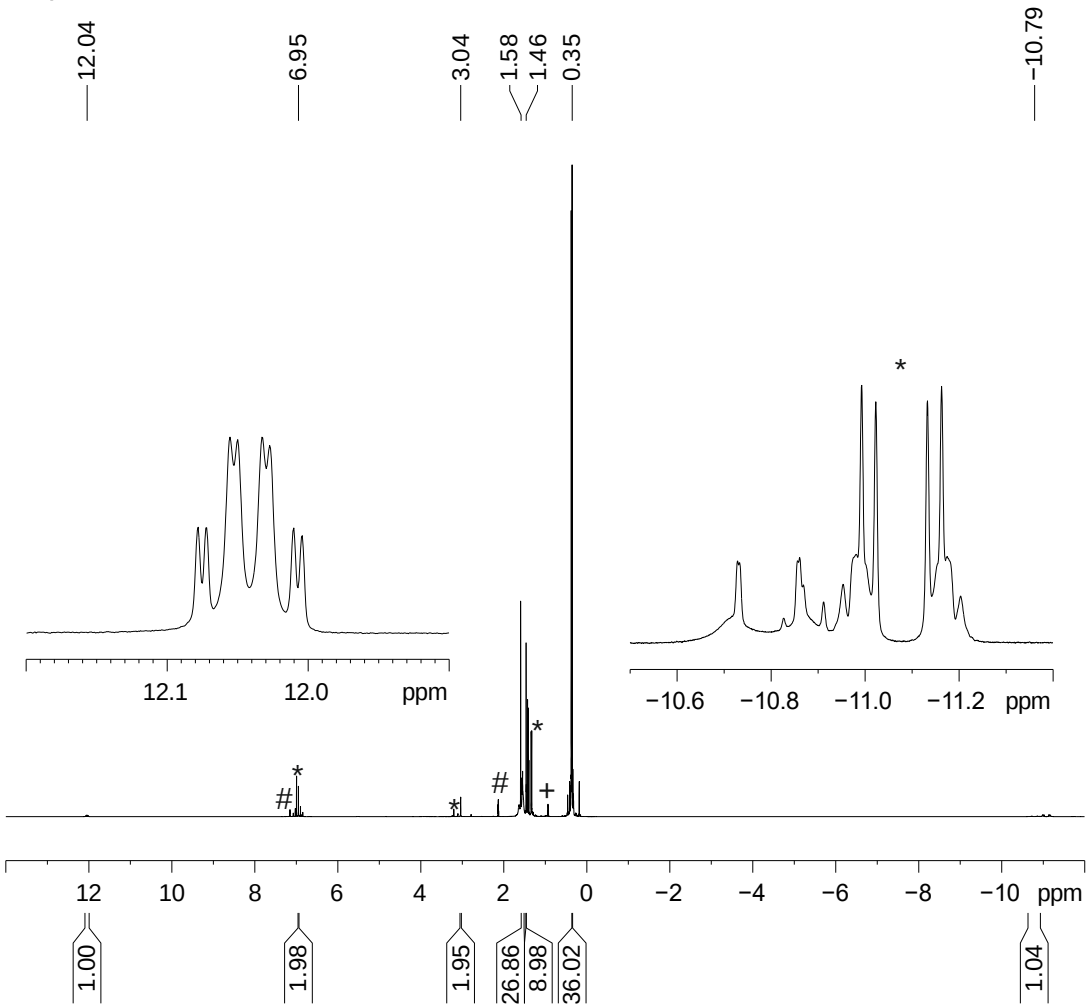
======== CHANNEL f1 ========
NUC1 119Sn
P1 15.50 usec
PL1 3.00 dB
PL1W 45.32131577 W
SFO1 186.6694895 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 −0.52 dB
PL12 15.06 dB
PL2W 24.34997177 W

Figure SI 116. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **15**.

NMR spectra of compound **16**.

^{1}H NMR spectrum of TbbGeHIrH(PMe_3)$_3$ in toluene-d_8 (#) at 0 °C. * TbbGeIrH$_2$(PMe_3)$_3$ and unknown impurity. + *n*-pentane.



Current Data Parameters
NAME MA937_21042022_600
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220421
Time 8.19 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zg30
TD 65536
SOLVENT Tol
NS 32
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 17.08
DW 20.800 usec
DE 10.00 usec
TE 273.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1300000 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.41200066 W

F2 − Processing parameters
SI 65536
SF 600.1299990 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

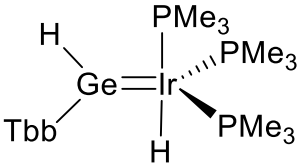
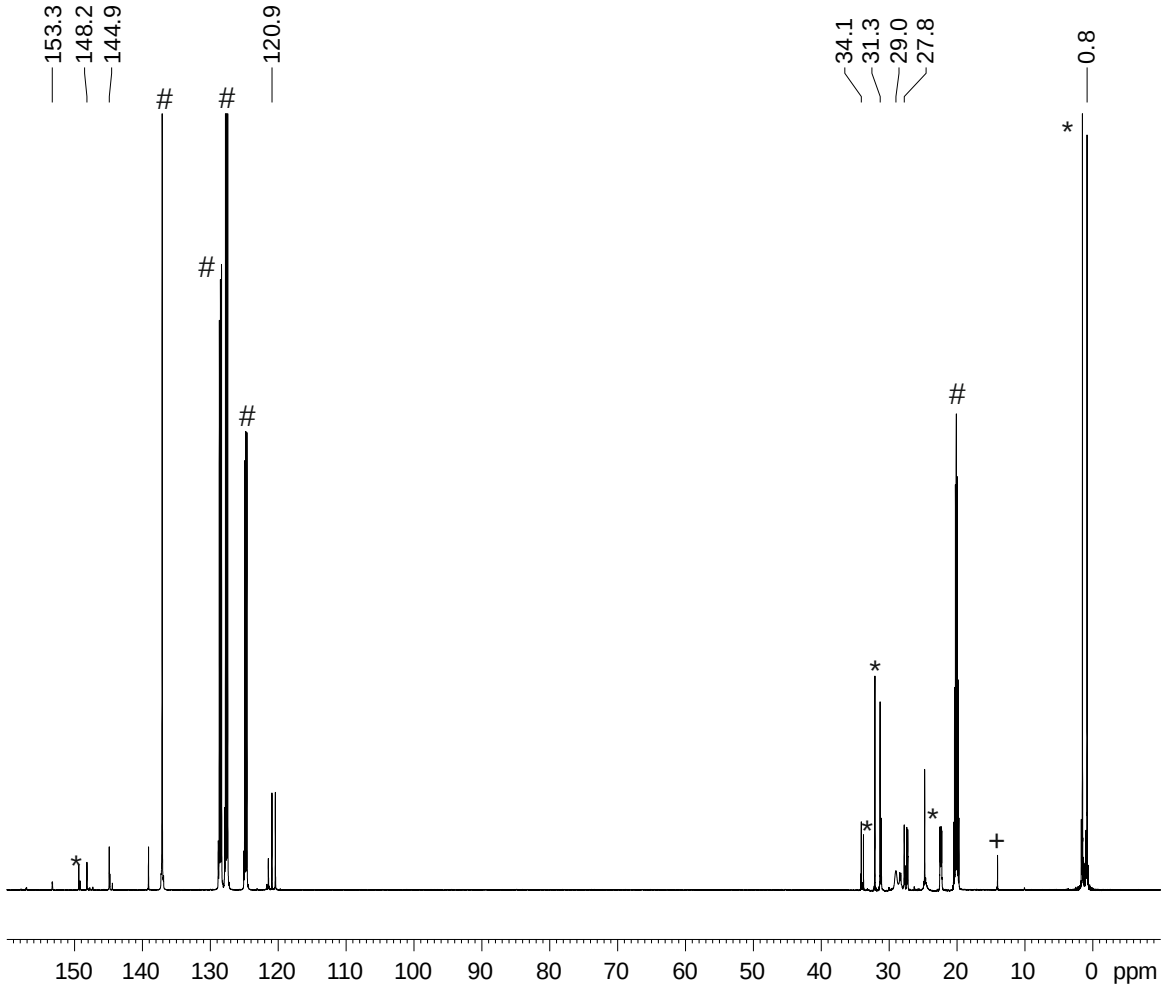


Figure SI 117. ^{1}H NMR spectrum of compound **16**.

$^{13}C\{^{1}H\}$ NMR spectrum of TbbGeHIrH$(PMe_3)_3$ in toluene-d_8 (#) at 0 °C. * TbbGeIrH$_2(PMe_3)_3$ and unknown impurity. + *n*-pentane.



Current Data Parameters
NAME MA937_21042022_600
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220421
Time 11.04 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG udeft
TD 25902
SOLVENT Tol
NS 2048
DS 8
SWH 36231.883 Hz
FIDRES 2.797613 Hz
AQ 0.3574476 sec
RG 189.6
DW 13.800 usec
DE 18.00 usec
TE 273.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 20.00000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 57.02700043 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 8.71310043 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 131072
SF 150.9028169 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

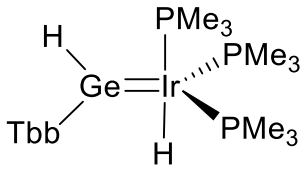
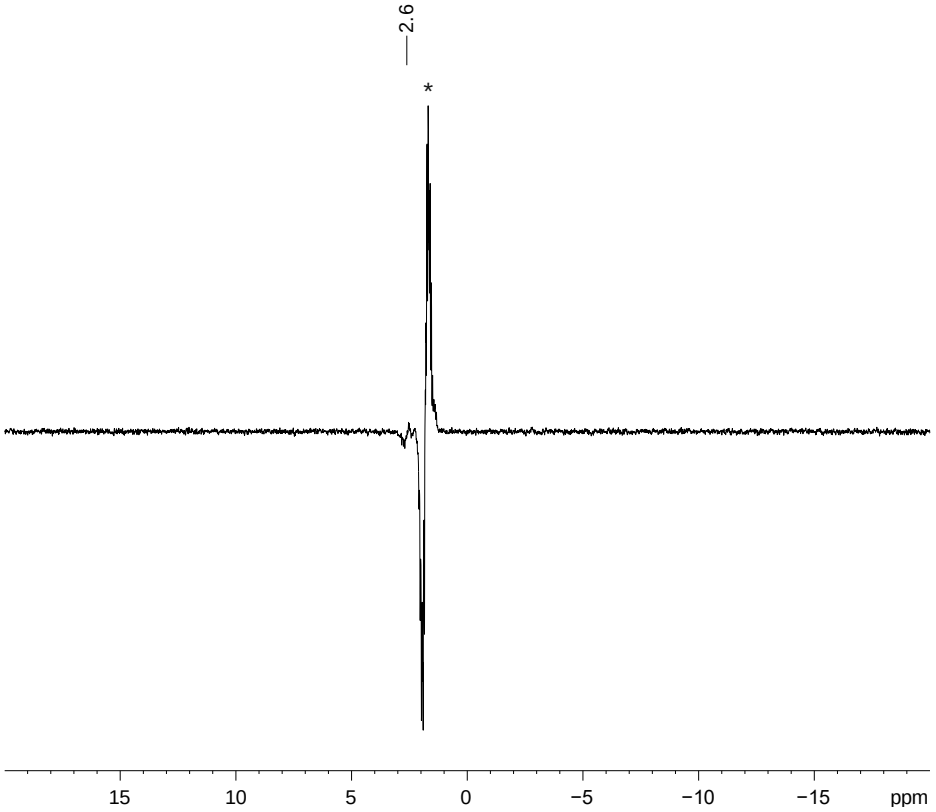


Figure SI 118. $^{13}C\{^{1}H\}$ NMR spectrum of compound **16**.

^{29}Si NMR spectrum of TbbGeHIrH(PMe$_3$)$_3$ in toluene-d$_8$ at 0 °C. * TbbGeIrH$_2$(PMe$_3$)$_3$.



Current Data Parameters
NAME MA937_21042022_600
EXPNO 17
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220421
Time 15.13 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG ineptnd
TD 16384
SOLVENT Tol
NS 128
DS 16
SWH 19132.652 Hz
FIDRES 2.335529 Hz
AQ 0.4281685 sec
RG 189.6
DW 26.133 usec
DE 18.00 usec
TE 273.0 K
CNST2 8.0000000
D1 2.00000000 sec
D4 0.03125000 sec
TD0 1
SFO1 119.2289493 MHz
NUC1 29Si
P1 14.50 usec
P2 29.00 usec
PLW1 50.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
P3 12.00 usec
P4 24.00 usec
PLW2 23.41200066 W

F2 − Processing parameters
SI 32768
SF 119.2289493 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

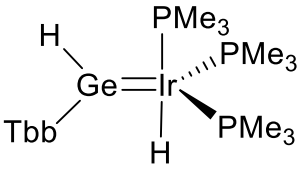
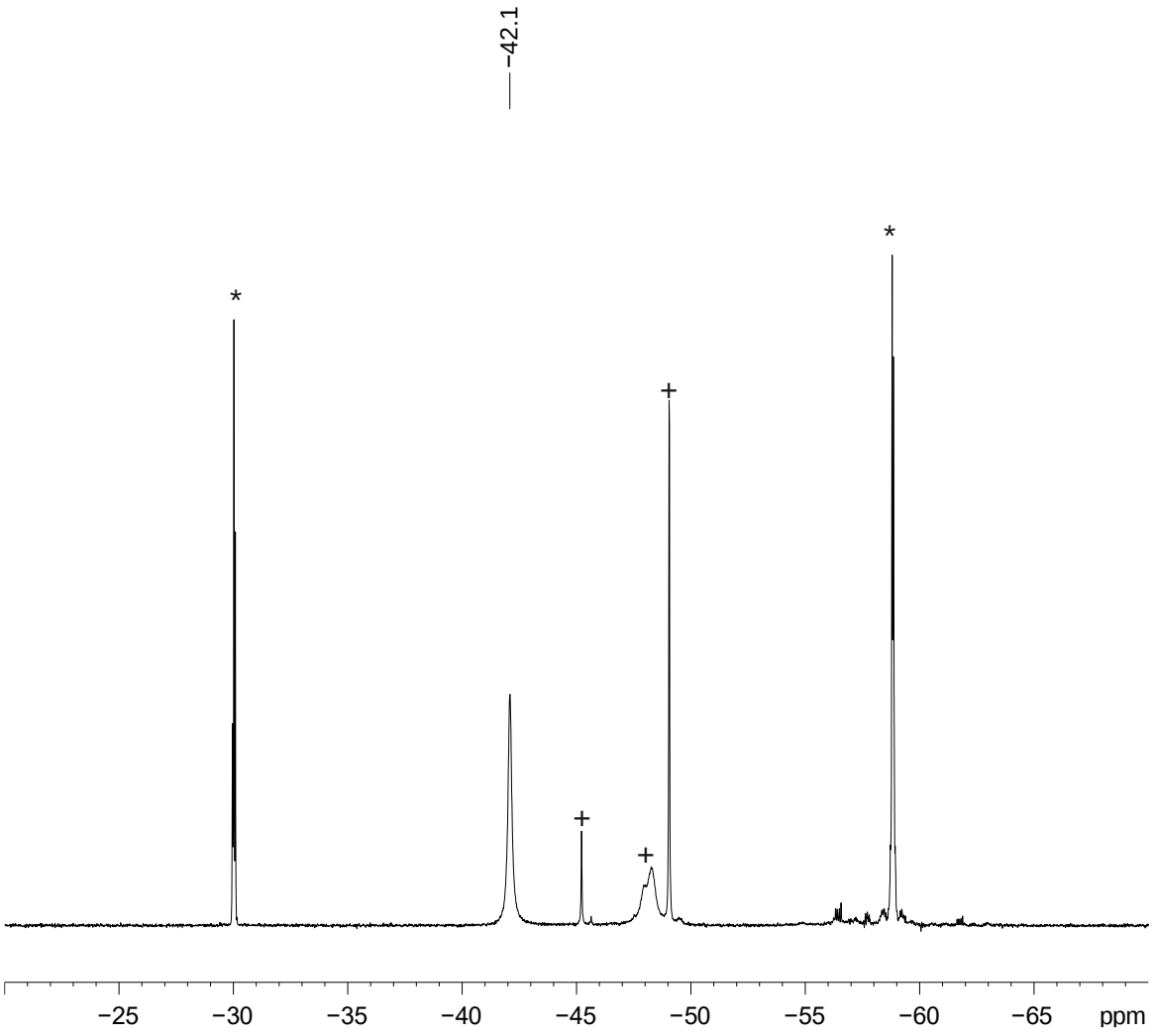


Figure SI 119. ^{29}Si NMR spectrum of compound **16**.

$^{31}P\{^{1}H\}$ NMR spectrum of TbbGeHIrH$(PMe_3)_3$ in toluene-d_8 at 0 °C. * TbbGeIrH$_2(PMe_3)_3$. + unknown impurity.



Current Data Parameters
NAME MA937_21042022_600
EXPNO 16
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220421
Time 15.05 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgpg30
TD 65536
SOLVENT Tol
NS 64
DS 4
SWH 96153.844 Hz
FIDRES 2.934382 Hz
AQ 0.3407872 sec
RG 189.6
DW 5.200 usec
DE 18.00 usec
TE 273.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 242.9249301 MHz
NUC1 31P
P1 12.00 usec
PLW1 52.43000031 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W
PLW13 0.34606999 W

F2 − Processing parameters
SI 32768
SF 242.9370770 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

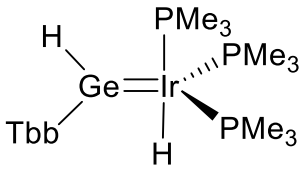
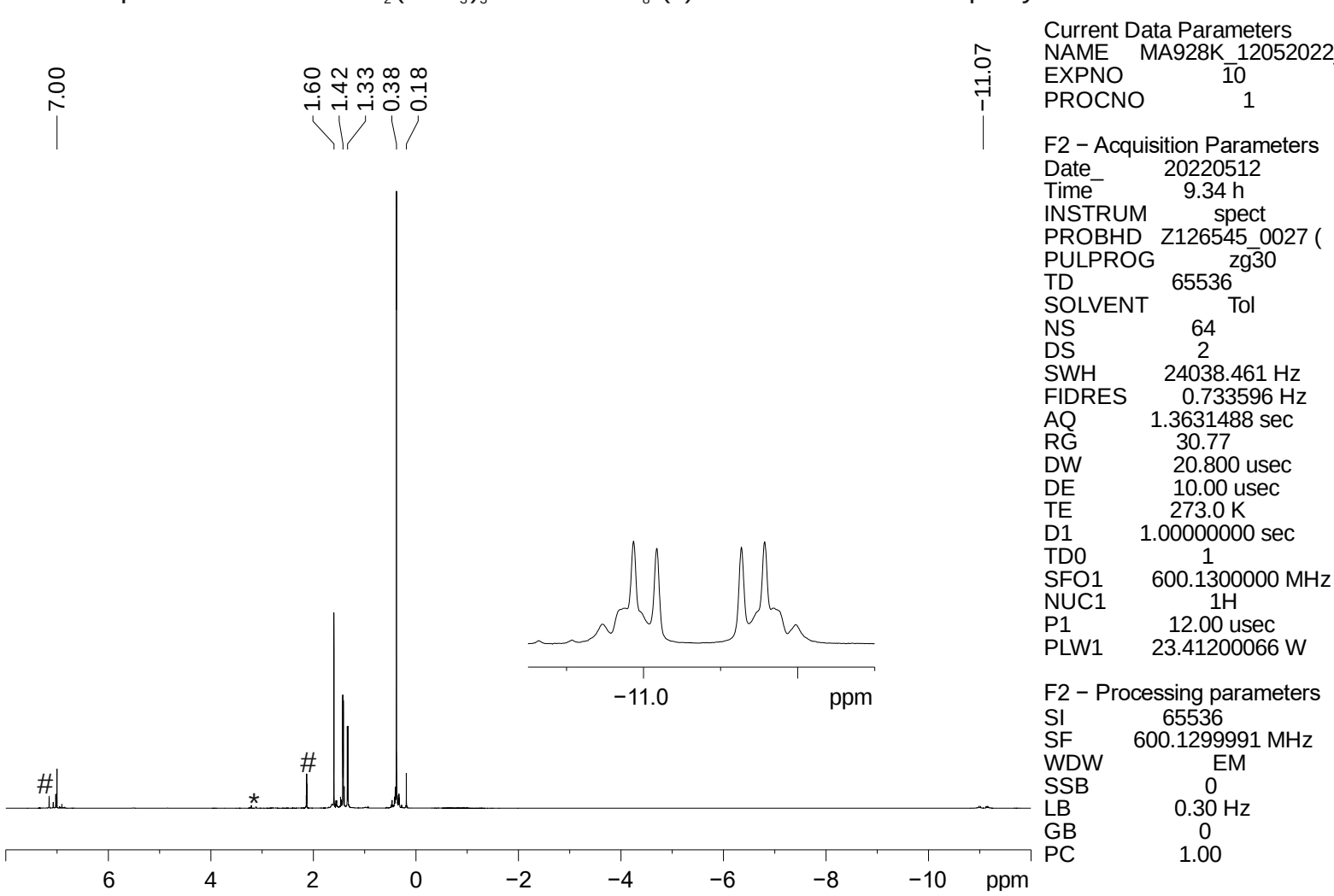


Figure SI 120. $^{31}P\{^{1}H\}$ NMR spectrum of compound **16**.

NMR spectra of compound **17**.

^{1}H NMR spectrum of TbbGeIrH$_2$(PMe$_3$)$_3$ in toluene-d$_8$ (#) at 0 °C. * unknown impurity.



Current Data Parameters
NAME MA928K_12052022_600
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220512
Time 9.34 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zg30
TD 65536
SOLVENT Tol
NS 64
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 30.77
DW 20.800 usec
DE 10.00 usec
TE 273.0 K
D1 1.00000000 sec
TD0 1
SFO1 600.1300000 MHz
NUC1 1H
P1 12.00 usec
PLW1 23.41200066 W

F2 − Processing parameters
SI 65536
SF 600.1299991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

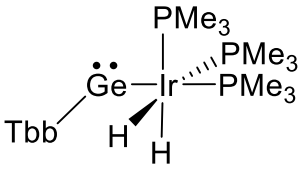
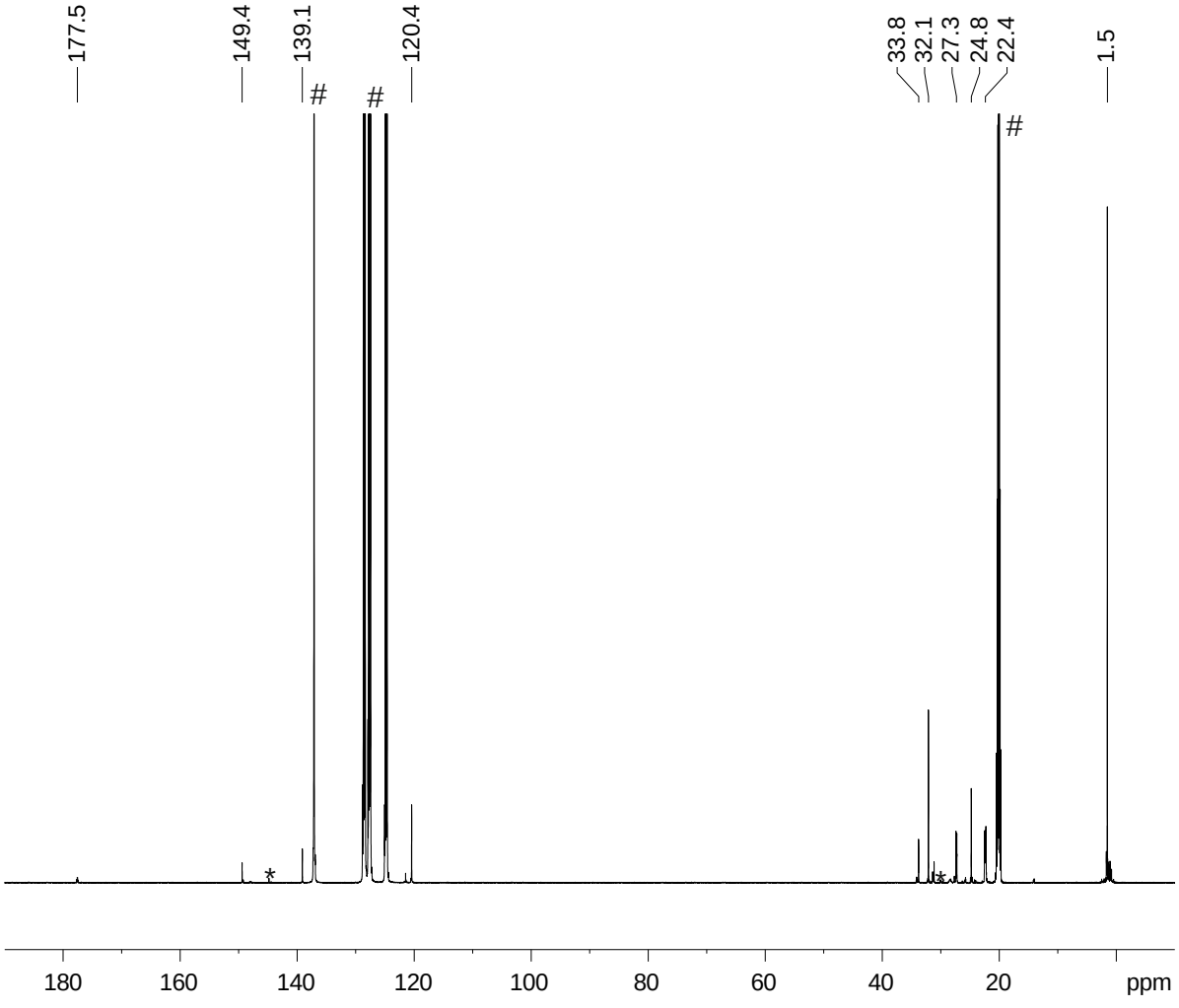


Figure SI 121. ^{1}H NMR spectrum of compound **17**.

$^{13}C\{^{1}H\}$ NMR spectrum of $TbbGeIrH_2(PMe_3)_3$ in toluene-d_8 (#) at 0 °C. * unknown impurity.



Current Data Parameters
NAME MA928K_12052022_60(
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220512
Time 17.42 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG udeft
TD 25902
SOLVENT Tol
NS 6144
DS 8
SWH 36231.883 Hz
FIDRES 2.797613 Hz
AQ 0.3574476 sec
RG 189.6
DW 13.800 usec
DE 18.00 usec
TE 273.0 K
D1 4.00000000 sec
D12 0.00002000 sec
D20 20.00000000 sec
TD0 1
SFO1 150.9178988 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
P26 500.00 usec
PLW1 57.02700043 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 8.71310043 W
SPNAM[8] Crp60,0.5,20.1
SPOAL8 0.500
SPOFFS8 0 Hz
SPW8 8.71310043 W
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W

F2 − Processing parameters
SI 131072
SF 150.9028166 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

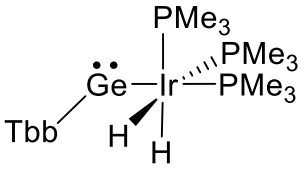
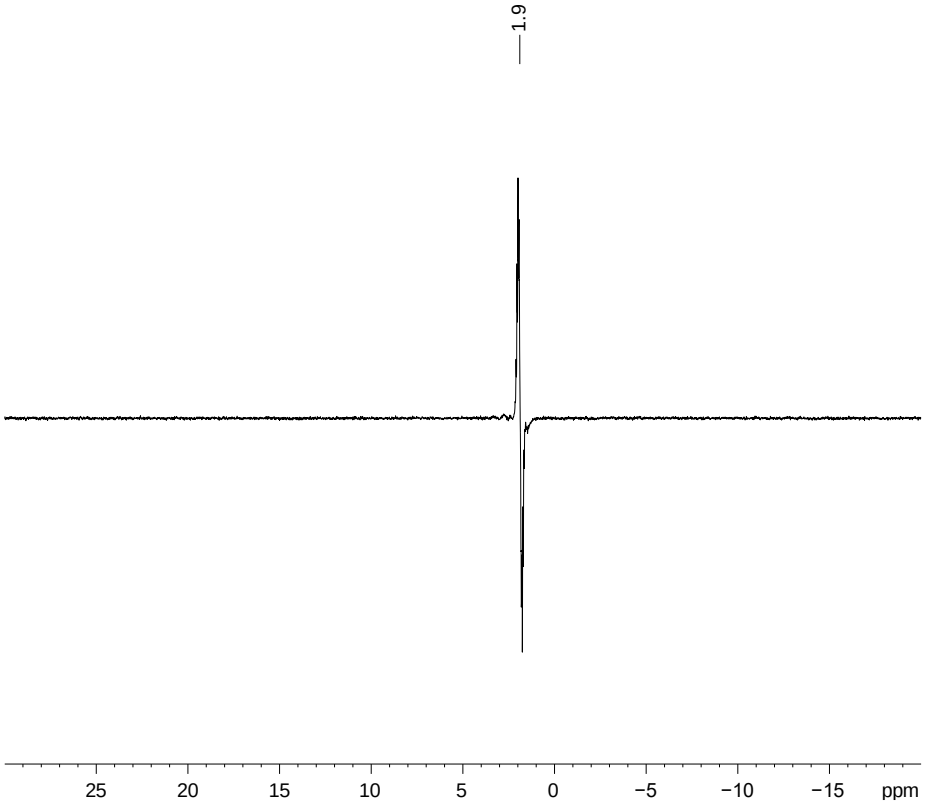


Figure SI 122. $^{13}C\{^{1}H\}$ NMR spectrum of compound **17**.

^{29}Si NMR spectrum of TbbGeIrH$_2$(PMe$_3$)$_3$ in toluene-d$_8$ at 0 °C.



Current Data Parameters
NAME MA928K_12052022_600
EXPNO 17
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220513
Time 7.03 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG ineptnd
TD 16384
SOLVENT Tol
NS 1024
DS 16
SWH 19132.652 Hz
FIDRES 2.335529 Hz
AQ 0.4281685 sec
RG 189.6
DW 26.133 usec
DE 18.00 usec
TE 273.0 K
CNST2 8.0000000
D1 2.00000000 sec
D4 0.03125000 sec
TD0 1
SFO1 119.2289493 MHz
NUC1 29Si
P1 14.50 usec
P2 29.00 usec
PLW1 50.00000000 W
SFO2 600.1324005 MHz
NUC2 1H
P3 12.00 usec
P4 24.00 usec
PLW2 23.41200066 W

F2 − Processing parameters
SI 32768
SF 119.2289493 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

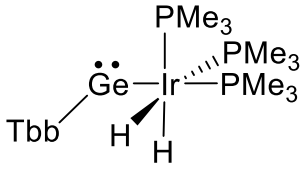
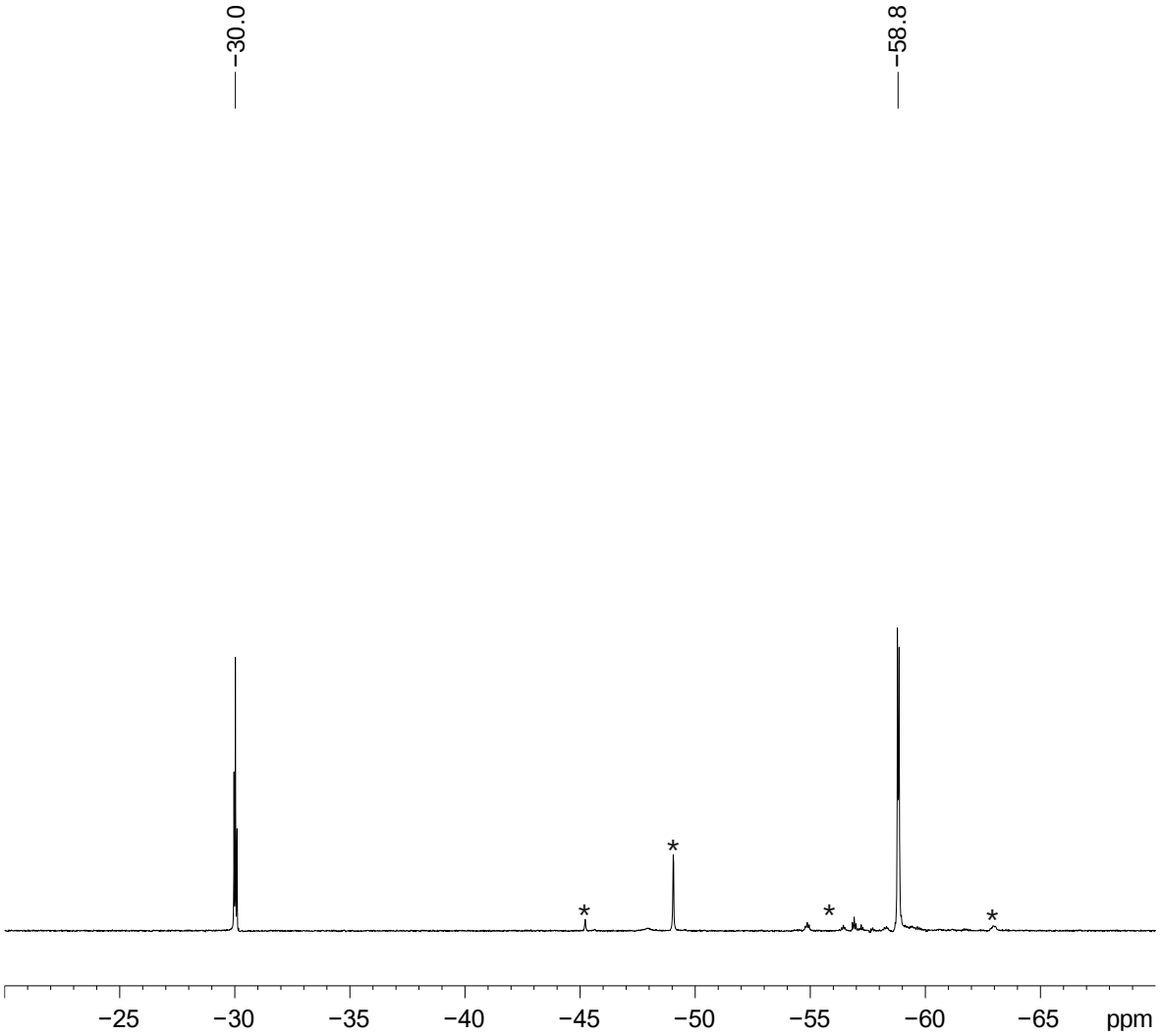


Figure SI 123. ^{29}Si NMR spectrum of compound **17**.

$^{31}P\{^{1}H\}$ NMR spectrum of TbbGeIrH$_2$(PMe$_3$)$_3$ in toluene-d$_8$ at 0 °C. * unknown impurity.



Current Data Parameters
NAME MA928K_12052022_600
EXPNO 16
PROCNO 1

F2 − Acquisition Parameters
Date_ 20220513
Time 6.17 h
INSTRUM spect
PROBHD Z126545_0027 (
PULPROG zgpg30
TD 65536
SOLVENT Tol
NS 256
DS 4
SWH 96153.844 Hz
FIDRES 2.934382 Hz
AQ 0.3407872 sec
RG 189.6
DW 5.200 usec
DE 18.00 usec
TE 273.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 242.9249301 MHz
NUC1 31P
P1 12.00 usec
PLW1 52.43000031 W
SFO2 600.1300000 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 70.00 usec
PLW2 23.41200066 W
PLW12 0.68803000 W
PLW13 0.34606999 W

F2 − Processing parameters
SI 32768
SF 242.9370770 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

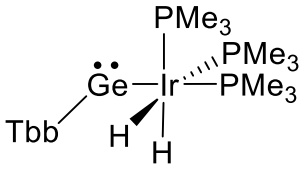
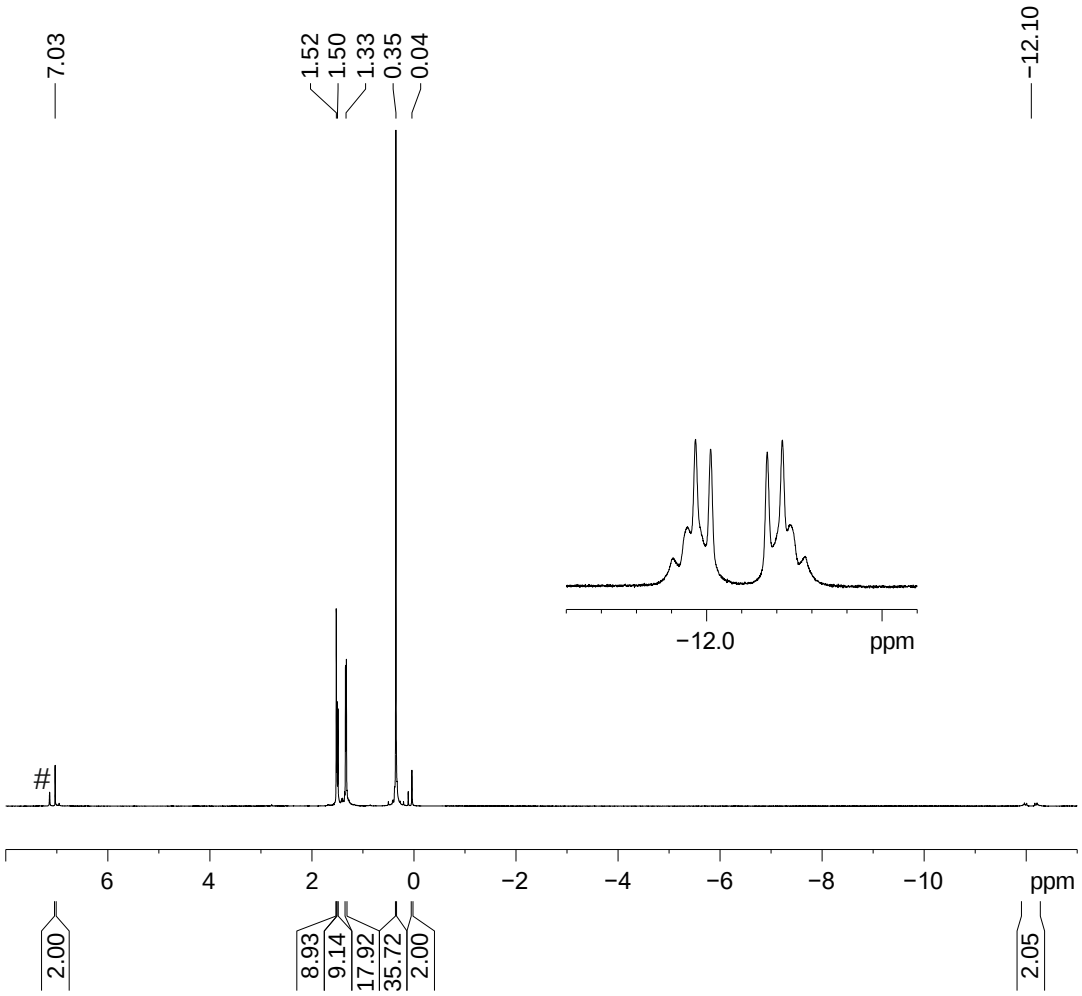


Figure SI 124. $^{31}P\{^{1}H\}$ NMR spectrum of compound **17**.

NMR spectra of compound **18**.

^{1}H NMR spectrum of TbbSnIrH$_2$(PMe$_3$)$_3$ in benzene-d$_6$ (#) at rt.



Current Data Parameters
NAME MA728K_20122021_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211220
Time 16.00
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 12019.230 Hz
FIDRES 0.228259 Hz
AQ 2.1904895 sec
RG 144
DW 41.600 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

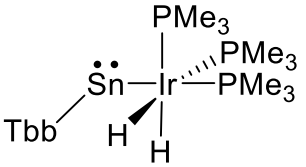
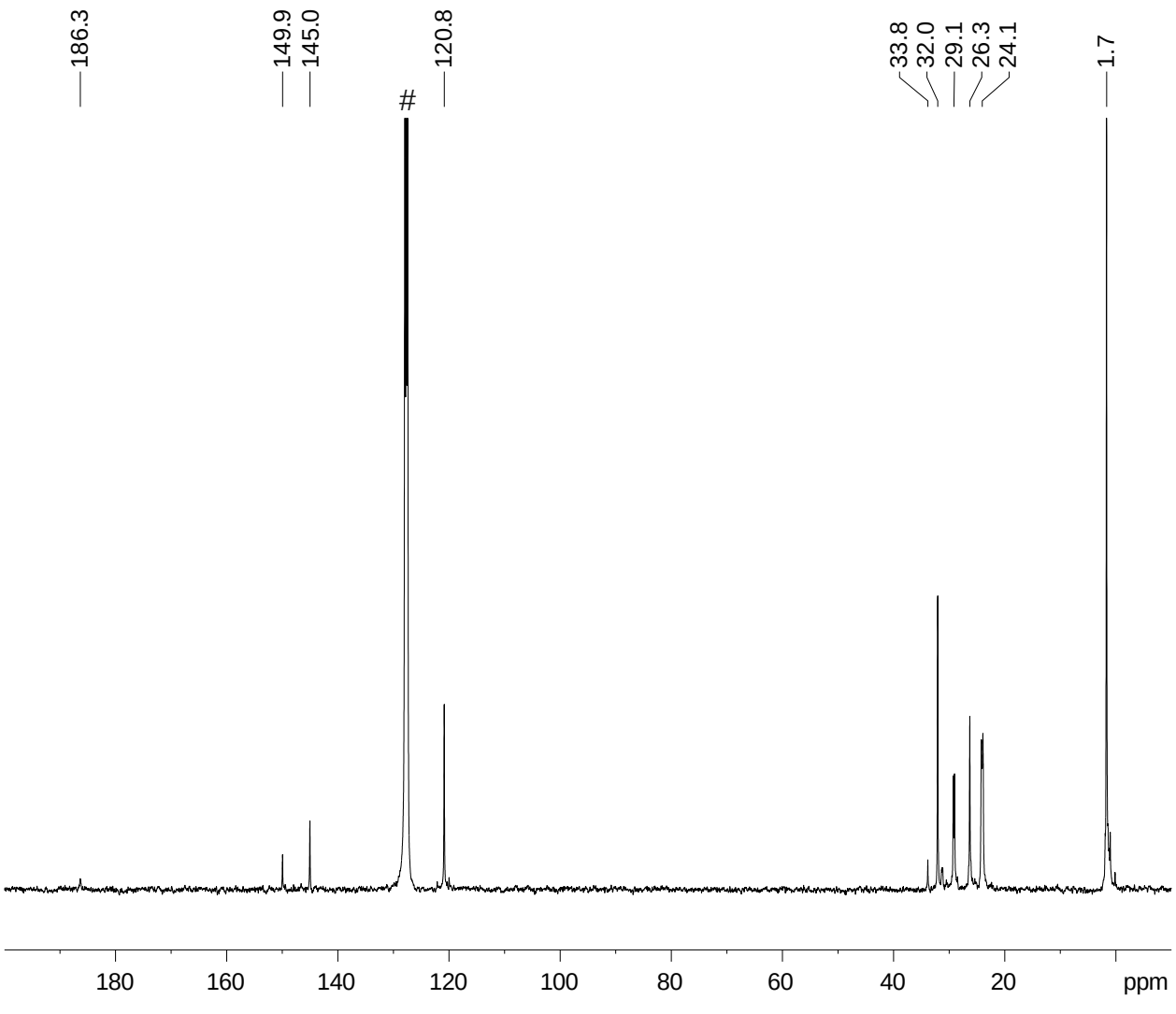


Figure SI 125. ^{1}H NMR spectrum of compound **18**.

$^{13}C\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(PMe_3)_3$ in benzene-d_6 (#) at rt.



Current Data Parameters
NAME MA728K_20122021_400
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211221
Time 2.13
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG udeft
TD 22218
SOLVENT C6D6
NS 5837
DS 0
SWH 30864.197 Hz
FIDRES 1.389153 Hz
AQ 0.3599316 sec
RG 32800
DW 16.200 usec
DE 6.00 usec
TE 299.2 K
D1 3.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 100.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
P13 2000.00 usec
P26 500.00 usec
PL1 −4.16 dB
PL1W 78.55633545 W
SFO1 100.6198135 MHz
SP8 1.39 dB
SP13 1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13 Crp60comp.4
SPOAL8 0.500
SPOAL13 0.500
SPOFFS8 0 Hz
SPOFFS13 0 Hz

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

F2 − Processing parameters
SI 131072
SF 100.6077400 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

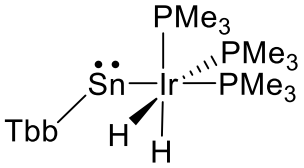
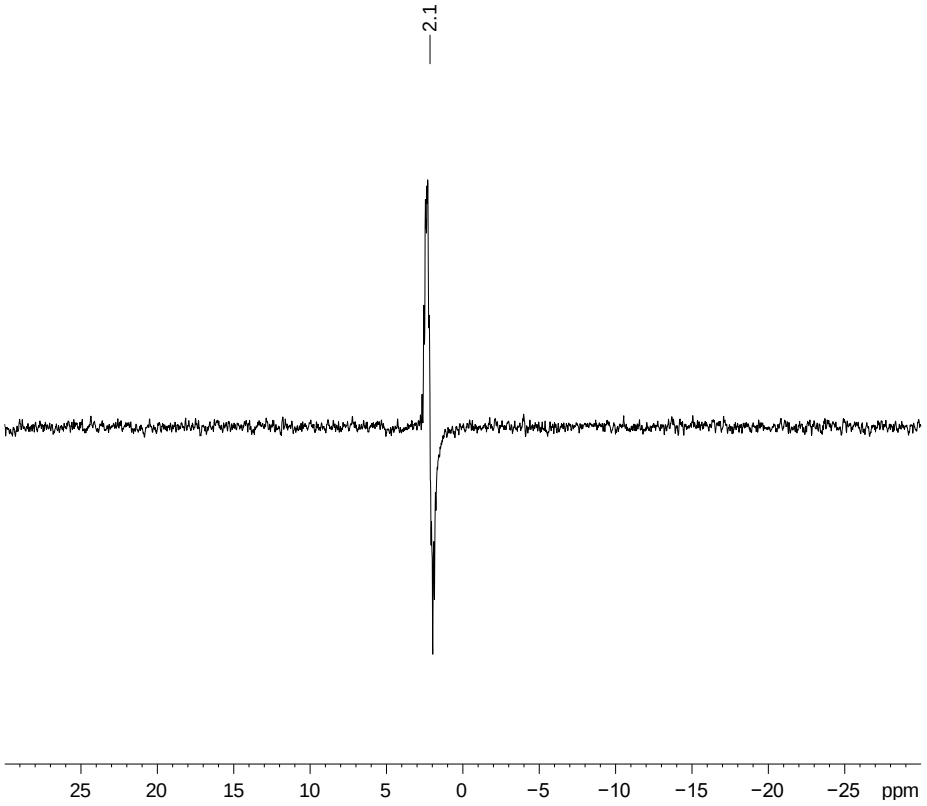


Figure SI 126. $^{13}C\{^{1}H\}$ NMR spectrum of compound **18**.

^{29}Si NMR spectrum of TbbSnIrH$_2$(PMe$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA728K_21122021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211221
Time 11.55 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273582 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

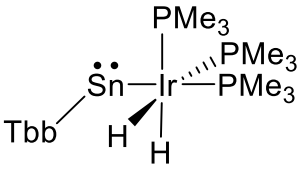
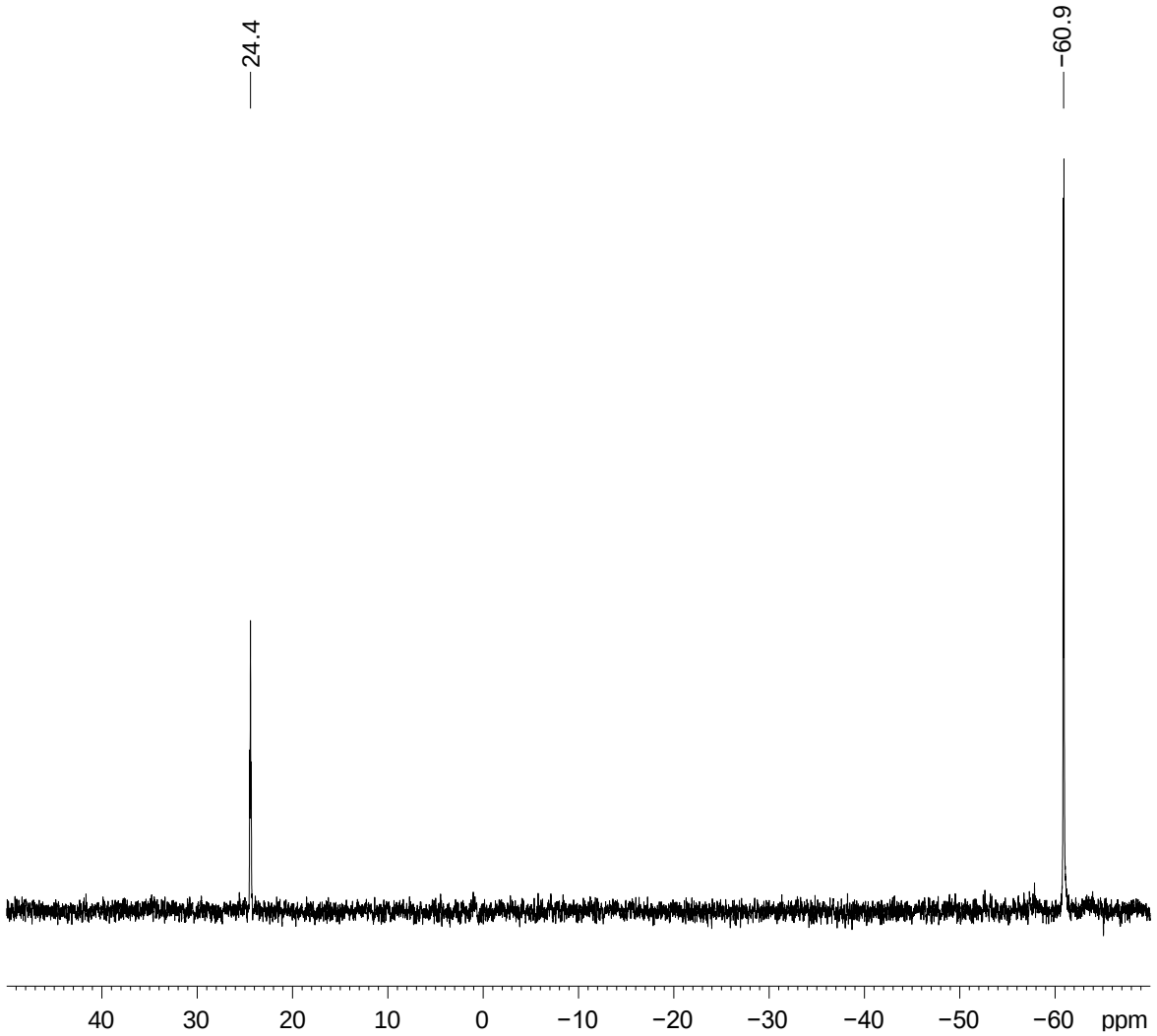


Figure SI 127. ^{29}Si NMR spectrum of compound **18**.

$^{31}P\{^{1}H\}$ NMR spectrum of TbbSnIrH$_2$(PMe$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA728K_20122021_400N
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211220
Time 20.07
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 128
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1060000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

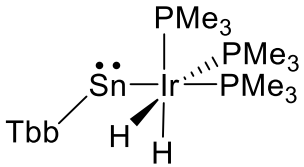
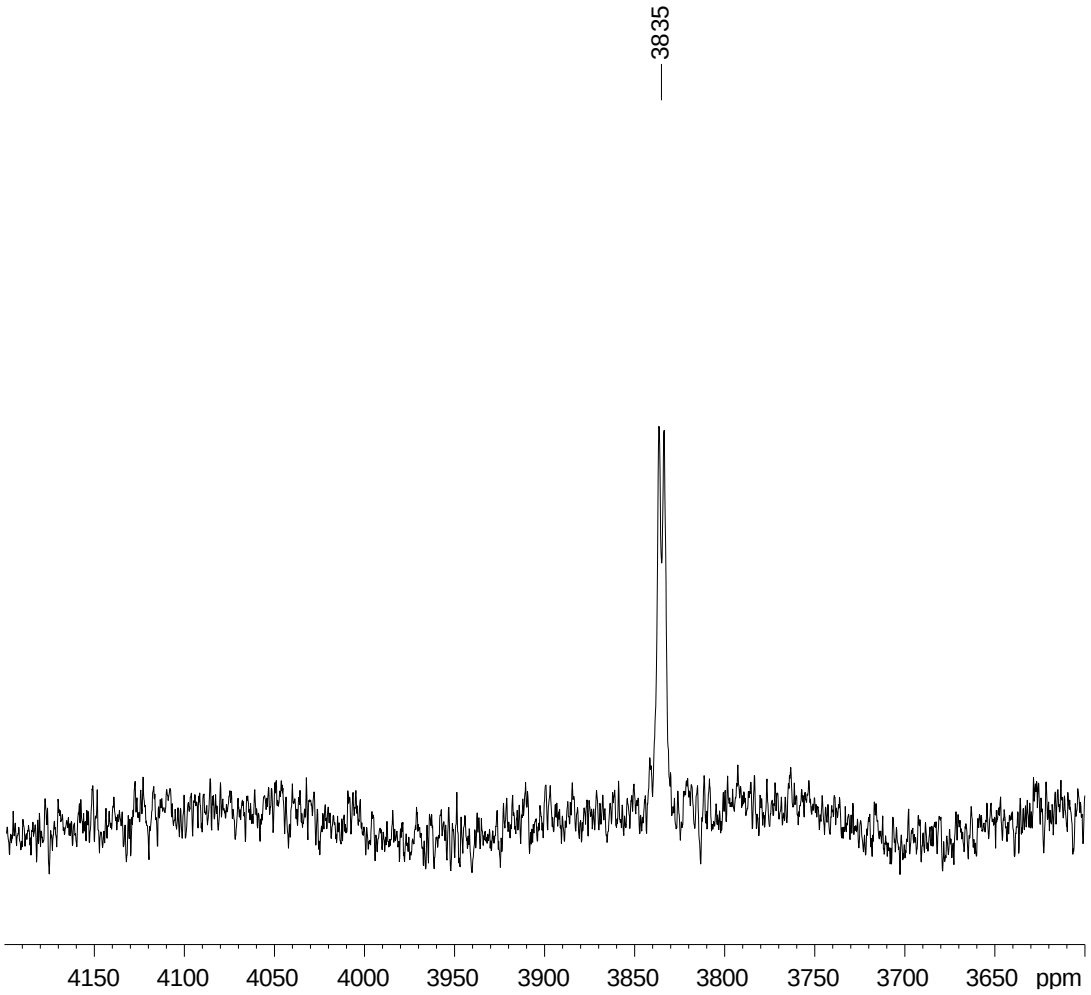


Figure SI 128. $^{31}P\{^{1}H\}$ NMR spectrum of compound **18**.

^{119}Sn NMR spectrum of TbbSnIrH$_2$(PMe$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA728_06102021_300
EXPNO 12
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211006
Time 16.34 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 14336
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 112.3456700 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

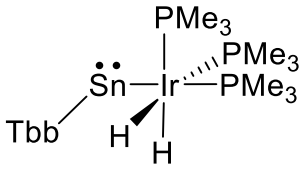
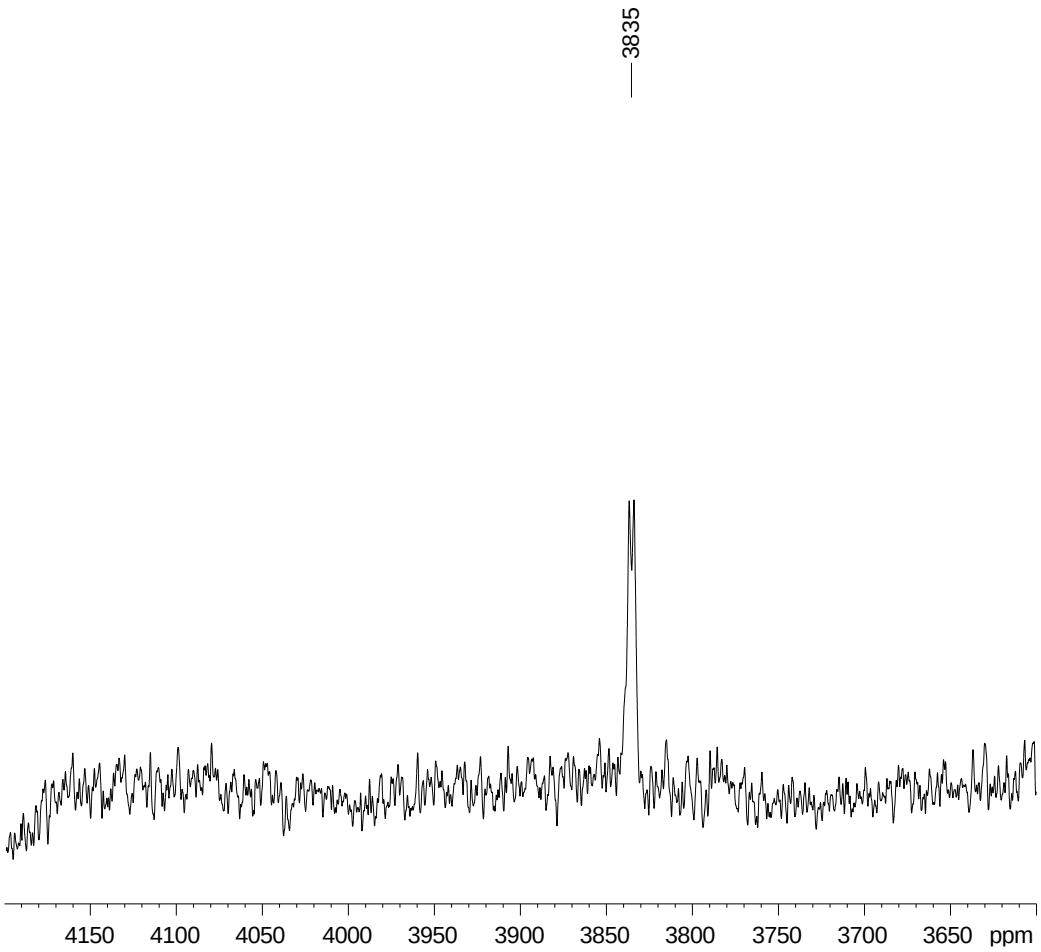


Figure SI 129. ^{119}Sn NMR spectrum of compound **18**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of TbbSnIrH$_2$(PMe$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA728_07102021_300
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211007
Time 12.58 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 4096
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 112.3456698 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

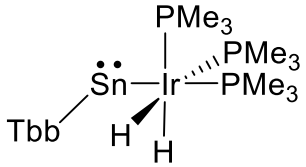
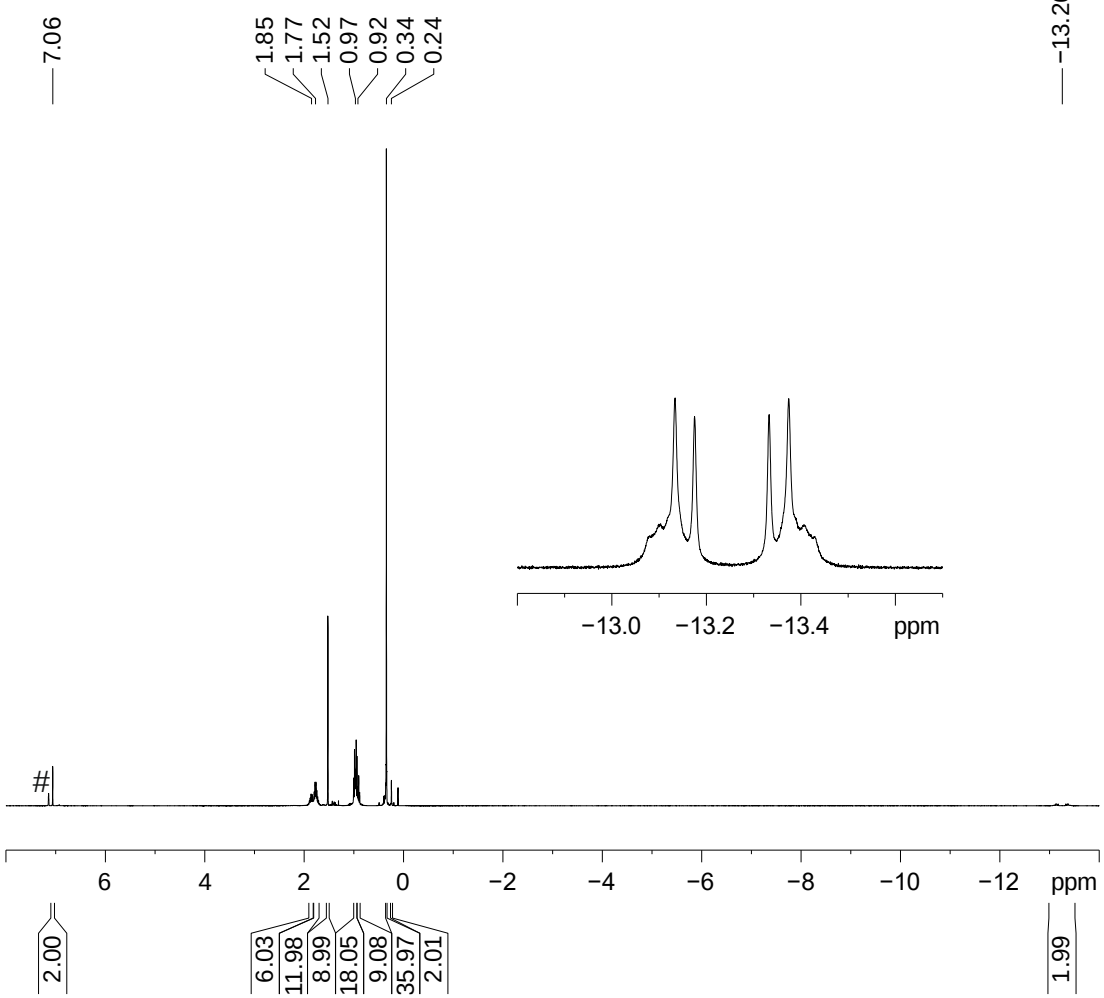


Figure SI 130. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **18**.

NMR spectra of compound **19**.

^{1}H NMR spectrum of TbbSnIrH$_2$(PEt$_3$)$_3$ in benzene-d$_6$ (#) at rt.



Current Data Parameters
NAME MA676K_10092021_400
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210910
Time 10.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 32
DS 0
SWH 10000.000 Hz
FIDRES 0.189912 Hz
AQ 2.6328001 sec
RG 114
DW 50.000 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 400.1089997 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

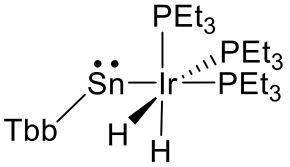
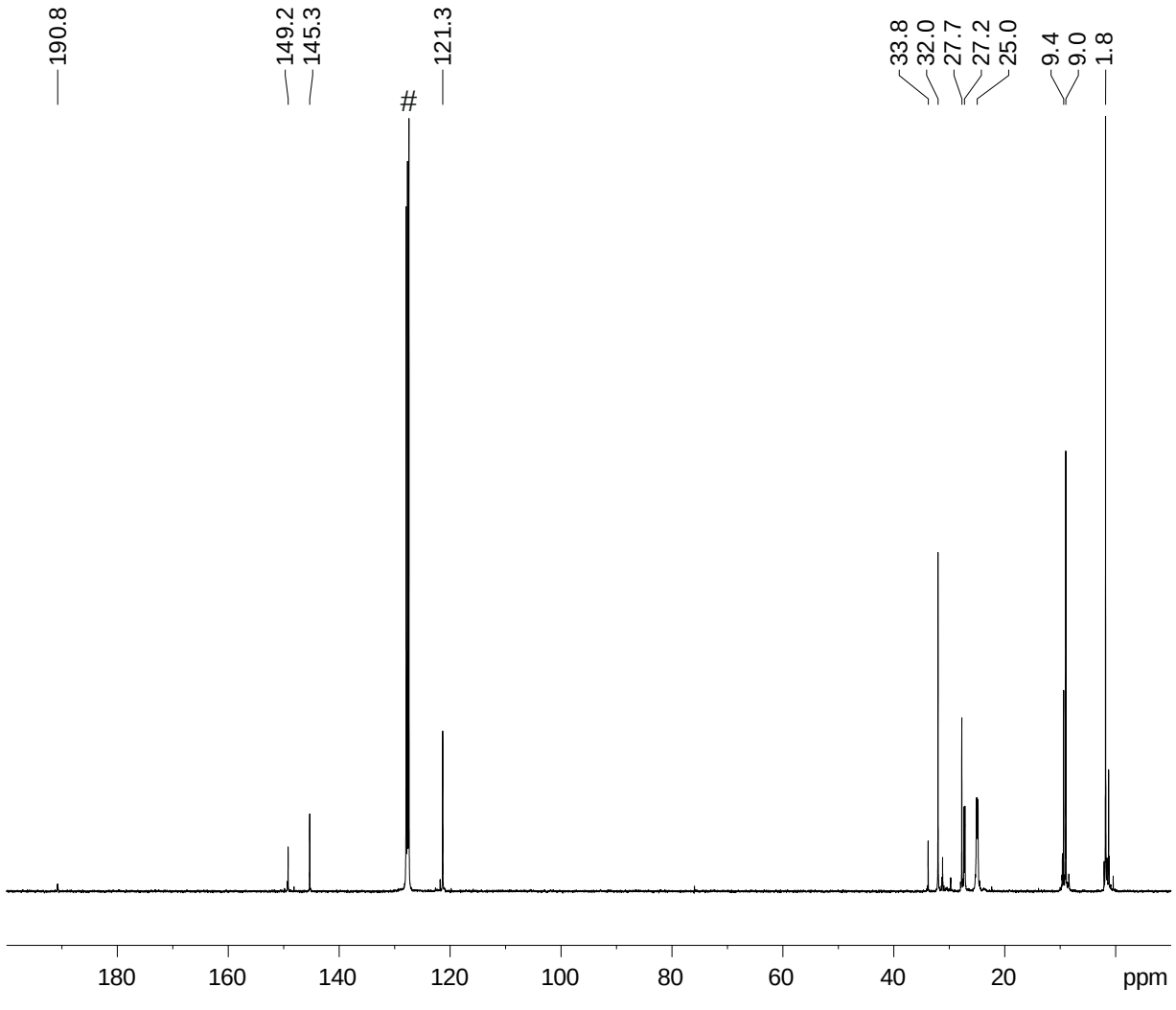


Figure SI 131. ^{1}H NMR spectrum of compound **19**.

$^{13}C\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(PEt_3)_3$ in benzene-d_6 (#) at rt.




```
Current Data Parameters
NAME     MA685K_22092021_400N
EXPNO            23
PROCNO            1

F2 - Acquisition Parameters
Date_         20210923
Time              2.23
INSTRUM          spect
PROBHD   5 mm QNP 1H/13
PULPROG          udeft
TD             22218
SOLVENT          C6D6
NS              5837
DS                 0
SWH          30864.197 Hz
FIDRES        1.389153 Hz
AQ          0.3599316 sec
RG              32800
DW             16.200 usec
DE              6.00 usec
TE             299.2 K
D1          3.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1              13.50 usec
P13           2000.00 usec
P26            500.00 usec
PL1             -4.16 dB
PL1W        78.55633545 W
SFO1       100.6198135 MHz
SP8             1.39 dB
SP13            1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8          0.500
SPOAL13         0.500
SPOFFS8           0 Hz
SPOFFS13          0 Hz

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

F2 - Processing parameters
SI             131072
SF         100.6077400 MHz
WDW               EM
SSB                0
LB              2.00 Hz
GB                 0
PC              1.40
```

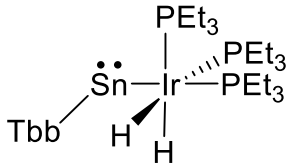
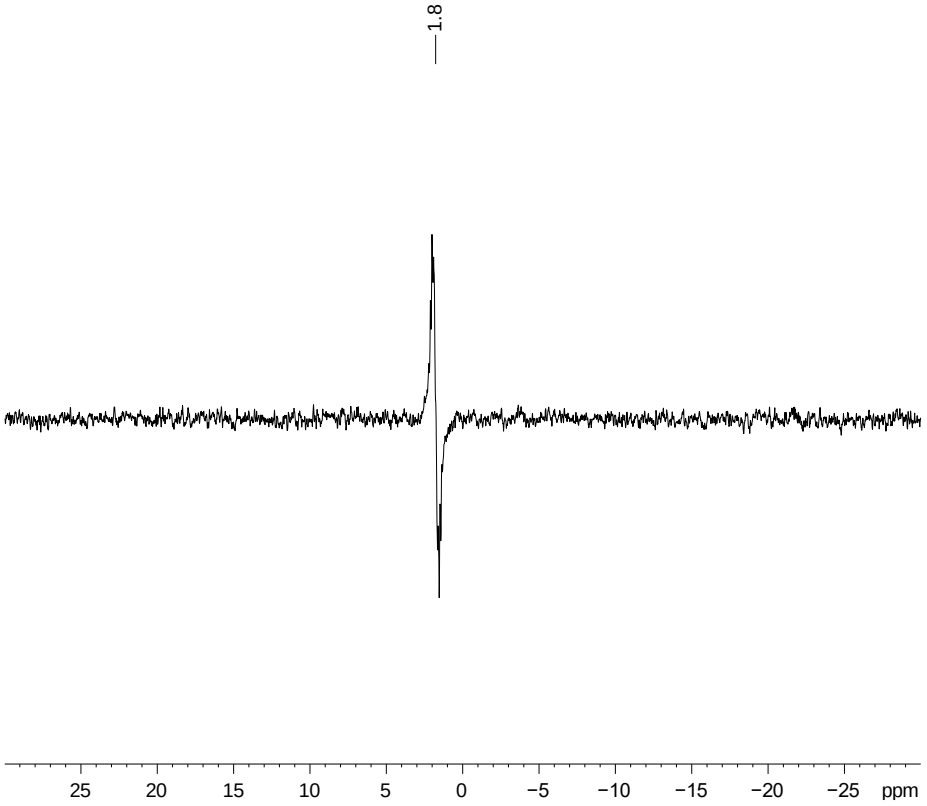


Figure SI 132. $^{13}C\{^{1}H\}$ NMR spectrum of compound **19**.

^{29}Si NMR spectrum of TbbSnIrH$_2$(PEt$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA674_20082021_300N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210820
Time 12.02 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273862 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

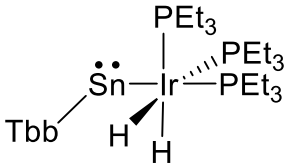
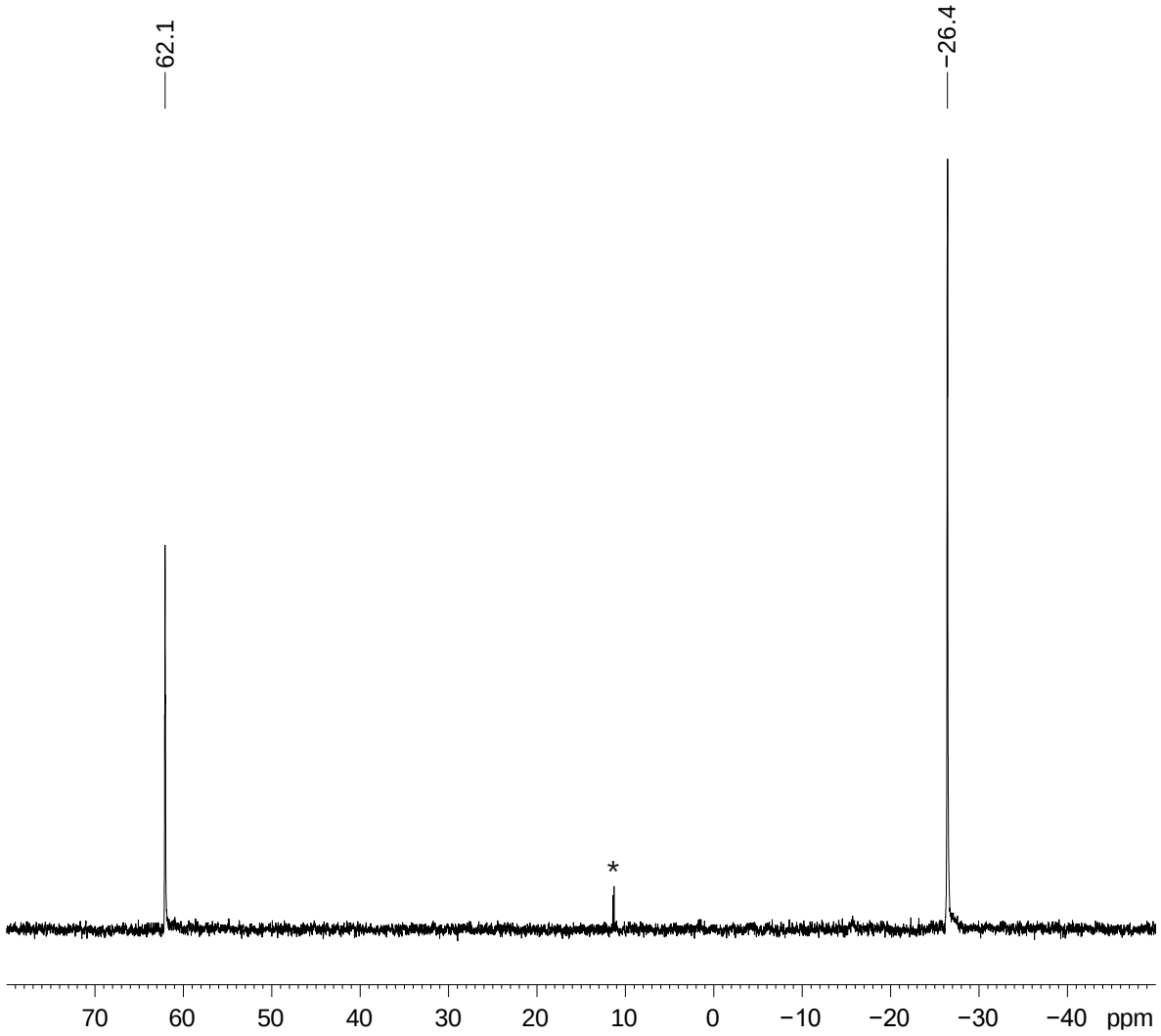


Figure SI 133. ^{29}Si NMR spectrum of compound **19**.

$^{31}P\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(PEt_3)_3$ in benzene-d_6 at rt. * unknown impurity.



Current Data Parameters
NAME MA676K_10092021_400
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210910
Time 10.30
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 128
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

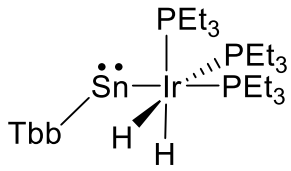
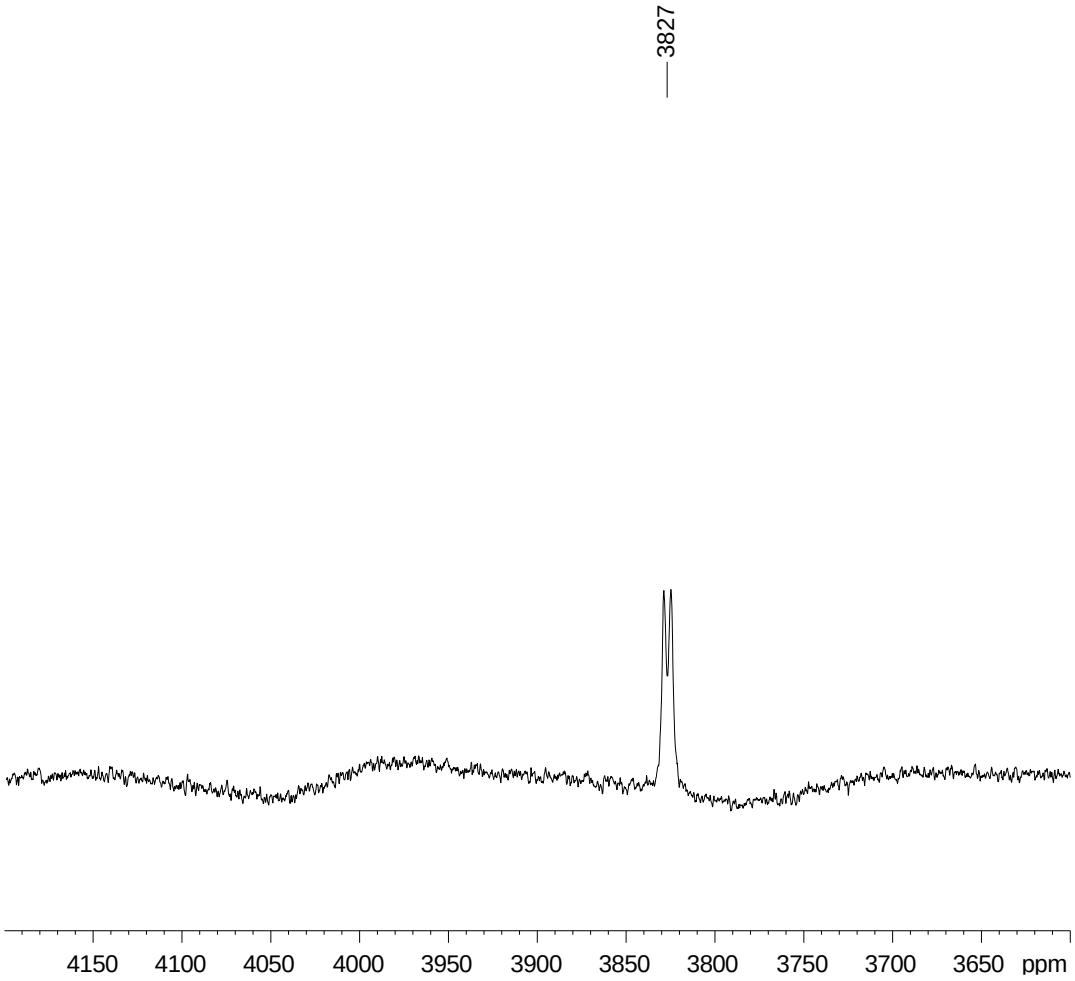


Figure SI 134. $^{31}P\{^{1}H\}$ NMR spectrum of compound **19**.

^{119}Sn NMR spectrum of TbbSnIrH$_2$(PEt$_3$)$_3$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA674_20082021_300N
EXPNO 23
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210820
Time 20.49 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 184320
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 112.3456700 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40

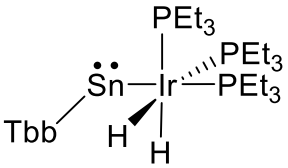
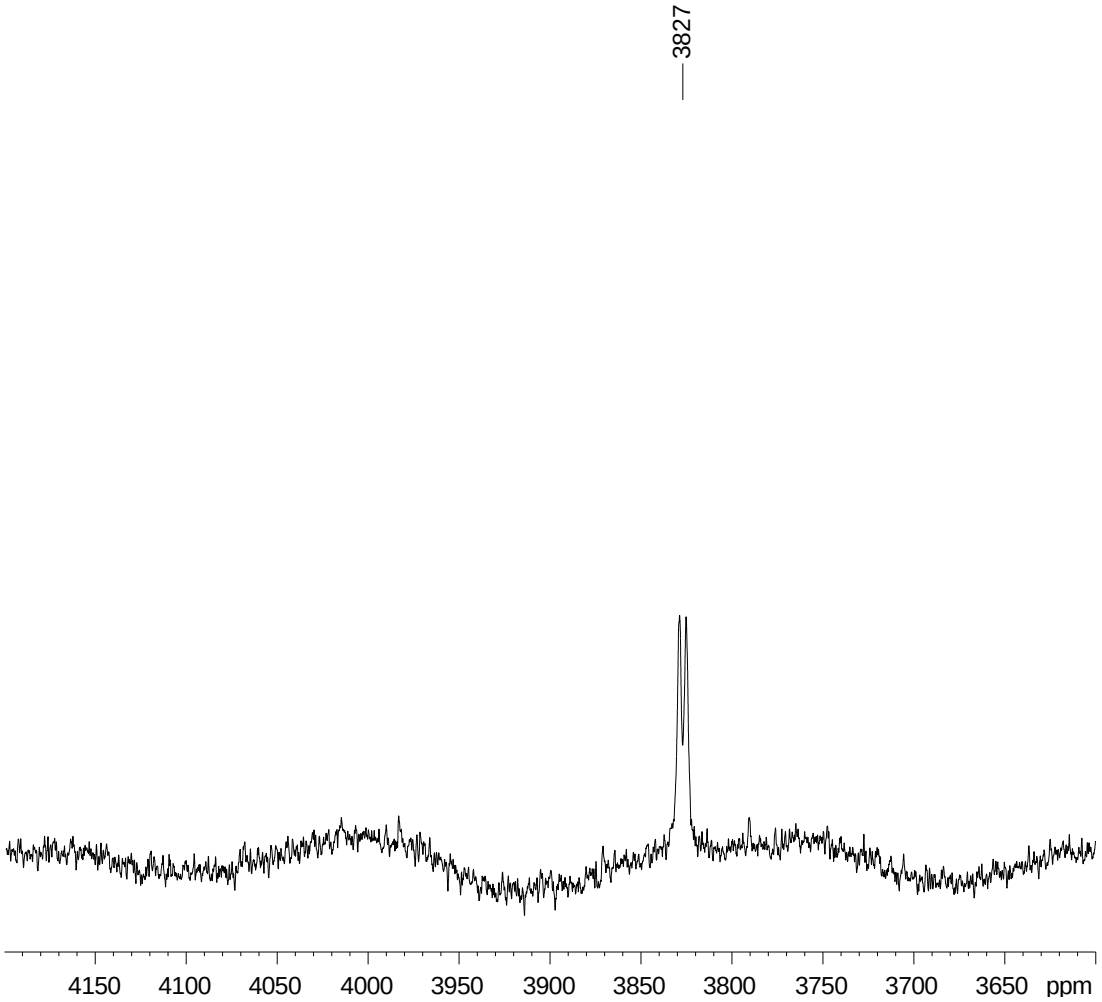


Figure SI 135. ^{119}Sn NMR spectrum of compound **19**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(PEt_3)_3$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA674_20082021_300N
EXPNO 33
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210821
Time 2.11 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 55296
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 112.3456698 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

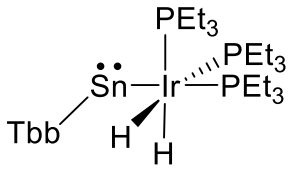
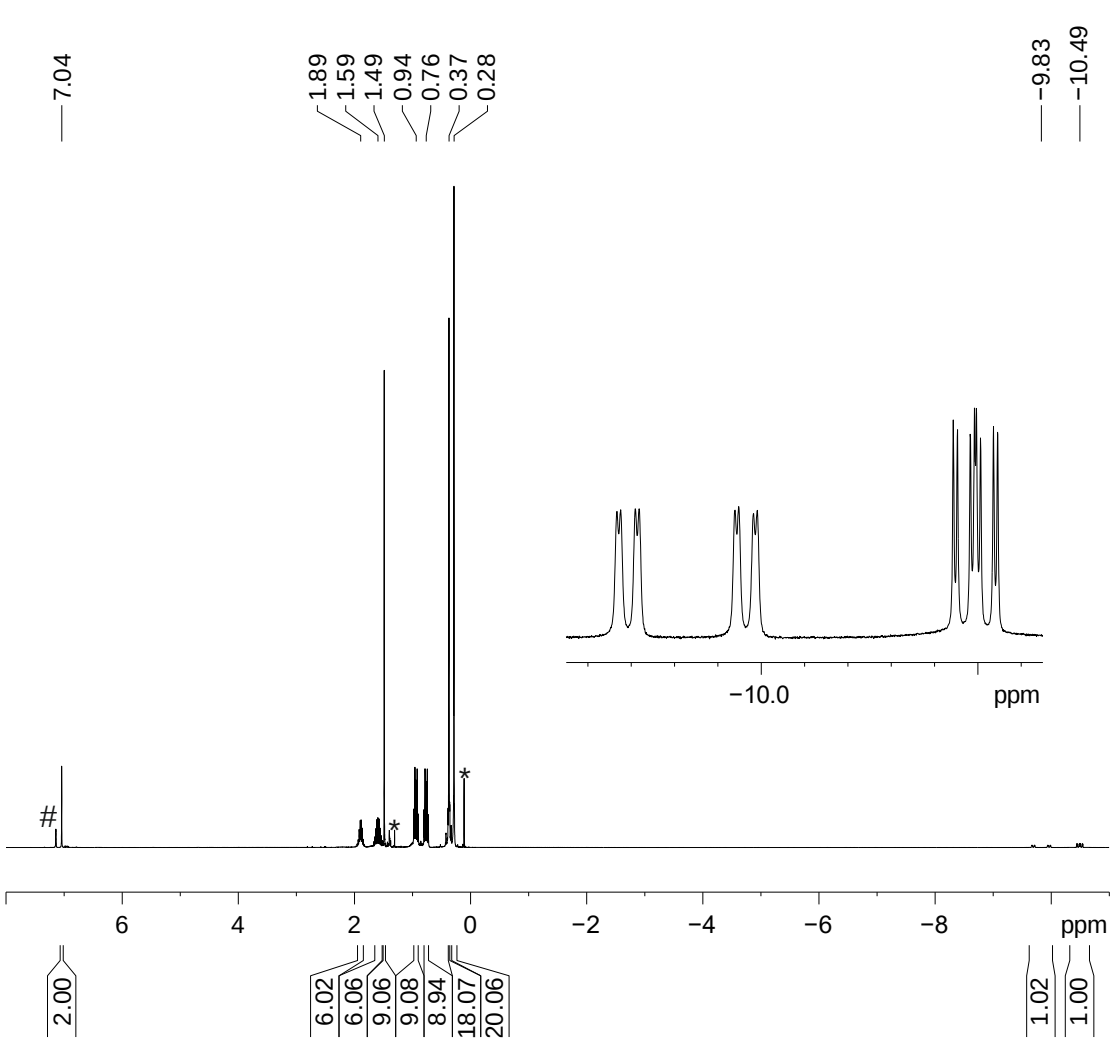


Figure SI 136. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **19**.

NMR spectra of compound **20**.

^{1}H NMR spectrum of TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ in benzene-d$_6$ (#) at rt. * unknown impurity.



Current Data Parameters
NAME MA695_15092021_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210915
Time 14.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 64
DS 0
SWH 16025.641 Hz
FIDRES 0.304346 Hz
AQ 1.6428672 sec
RG 128
DW 31.200 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 400.1100000 MHz

F2 − Processing parameters
SI 65536
SF 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

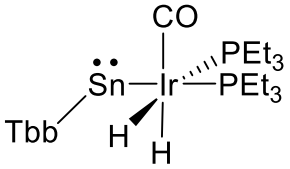
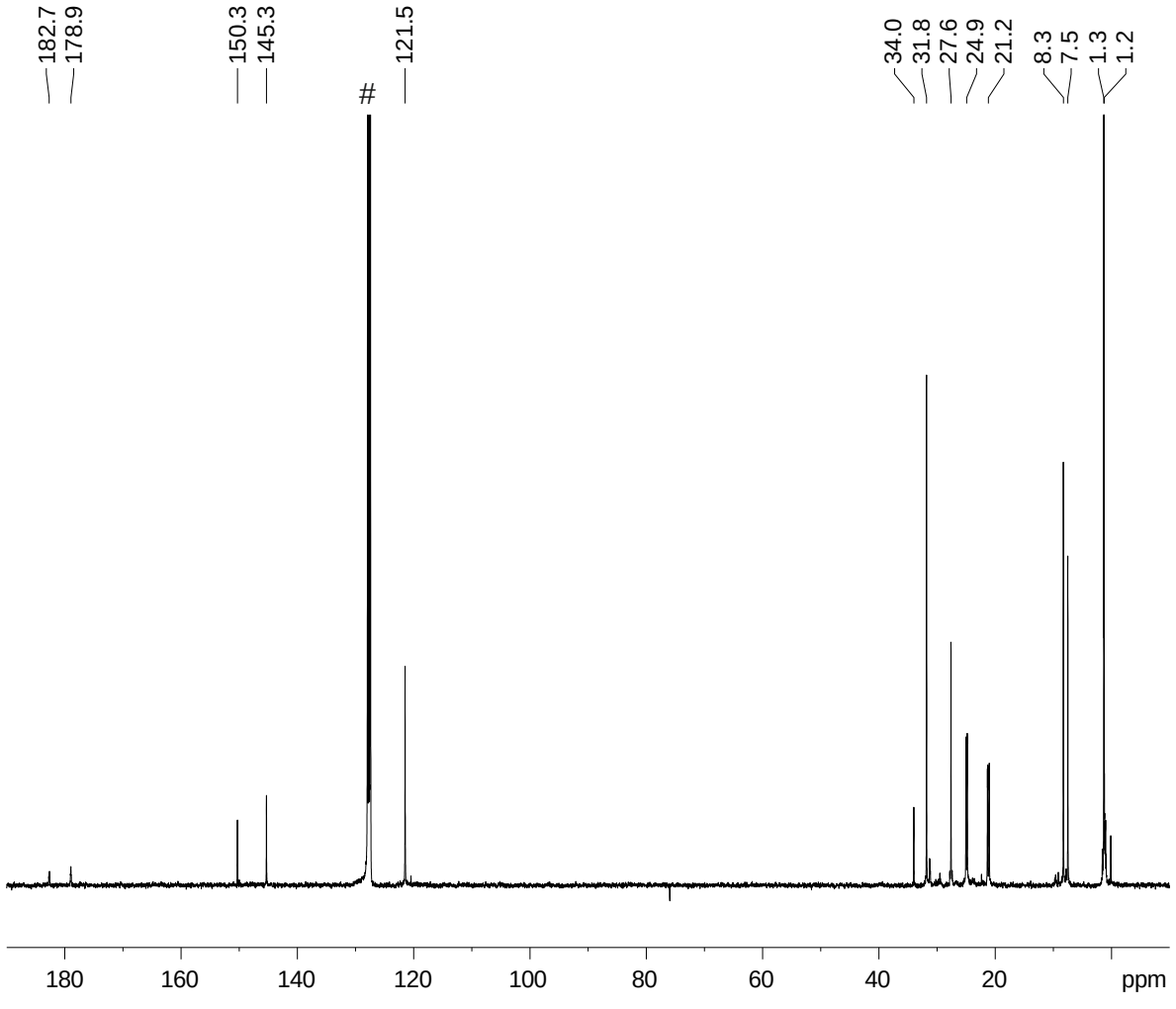


Figure SI 137. ^{1}H NMR spectrum of compound **20**.

$^{13}C\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(CO)(PEt_3)_2$ in benzene-d_6 (#) at rt.



Current Data Parameters
NAME MA695_15092021_400N
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210916
Time 2.14
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG udeft
TD 22218
SOLVENT C6D6
NS 5734
DS 0
SWH 30864.197 Hz
FIDRES 1.389153 Hz
AQ 0.3599316 sec
RG 32800
DW 16.200 usec
DE 6.00 usec
TE 299.2 K
D1 3.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D20 100.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 13.50 usec
P13 2000.00 usec
P26 500.00 usec
PL1 −4.16 dB
PL1W 78.55633545 W
SFO1 100.6198135 MHz
SP8 1.39 dB
SP13 1.39 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13 Crp60comp.4
SPOAL8 0.500
SPOAL13 0.500
SPOFFS8 0 Hz
SPOFFS13 0 Hz

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

F2 − Processing parameters
SI 131072
SF 100.6077400 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

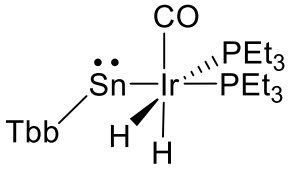
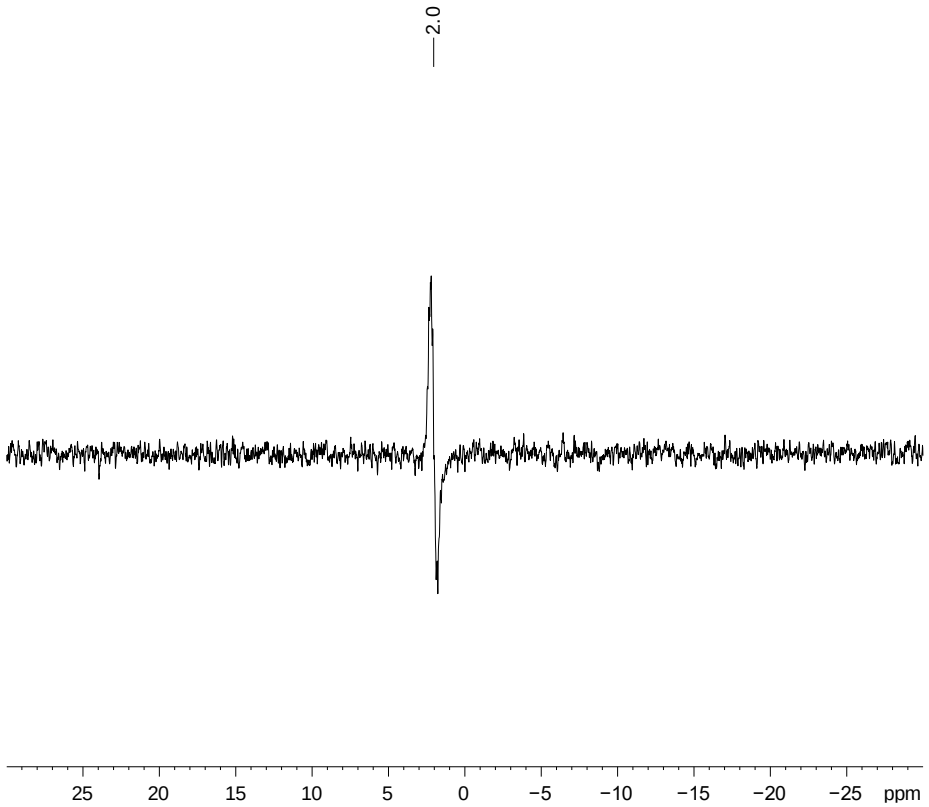


Figure SI 138. $^{13}C\{^{1}H\}$ NMR spectrum of compound **20**.

^{29}Si NMR spectrum of TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA694K_08112021_300
EXPNO 14
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211108
Time 15.12 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 128
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273701 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

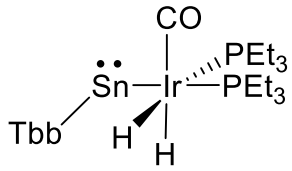
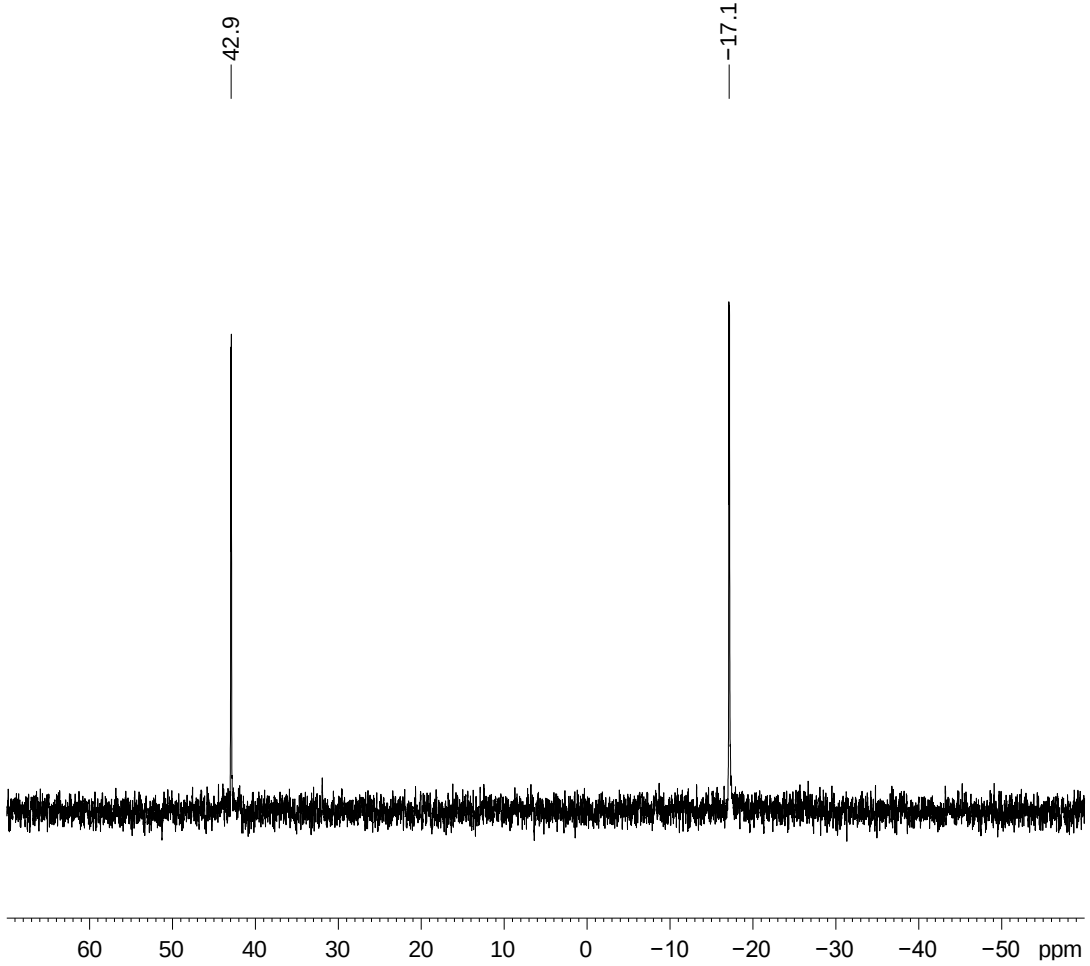


Figure SI 139. ^{29}Si NMR spectrum of compound **20**.

$^{31}P\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(CO)(PEt_3)_2$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA694K_08112021_400
EXPNO 21
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211108
Time 15.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 256
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 400.1060000 MHz

F2 − Processing parameters
SI 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

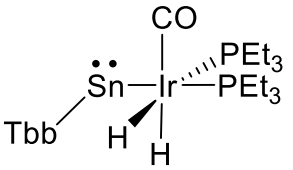
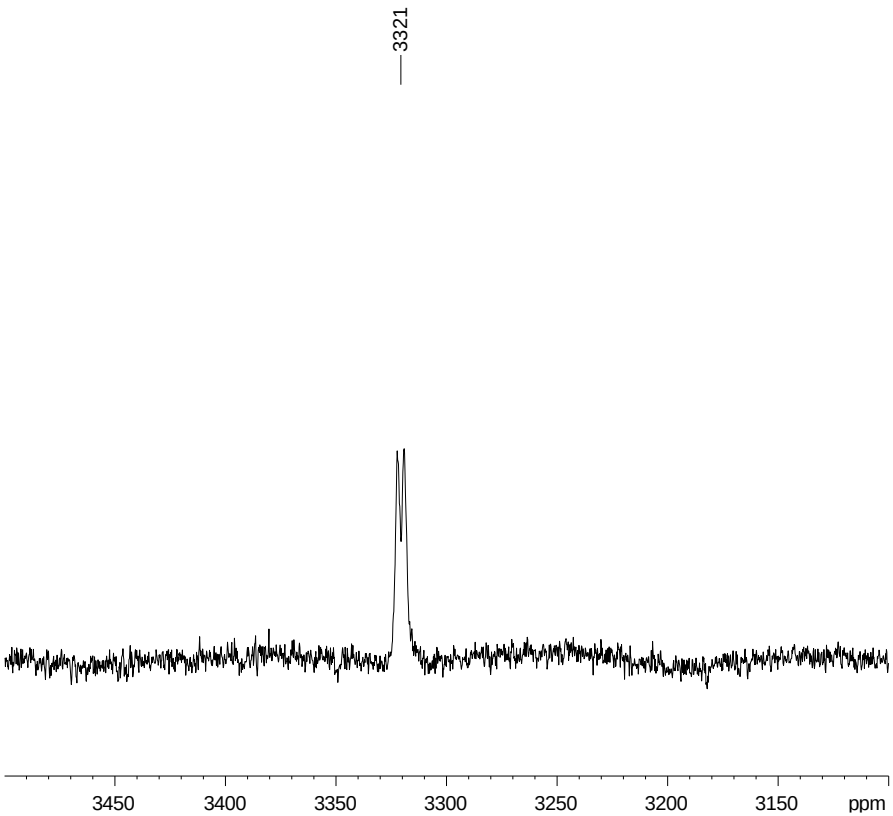


Figure SI 140. $^{31}P\{^{1}H\}$ NMR spectrum of compound **20**.

^{119}Sn NMR spectrum of TbbSnIrH$_2$(CO)(PEt$_3$)$_2$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA692_09092021_300N
EXPNO 23
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210909
Time 21.02 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 168960
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 112.2897100 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

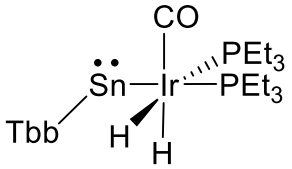
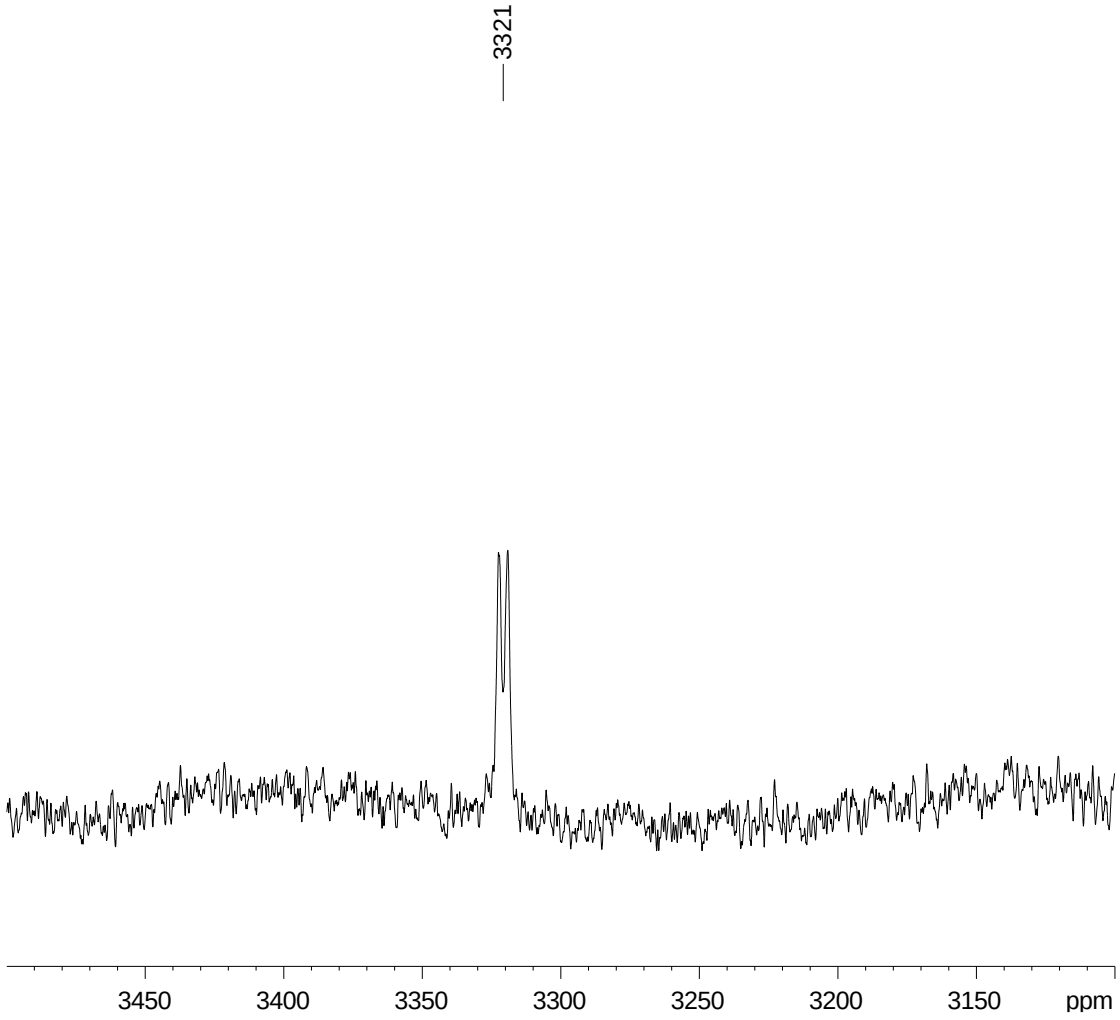


Figure SI 141. ^{119}Sn NMR spectrum of compound **20**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $TbbSnIrH_2(CO)(PEt_3)_2$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA692_09092021_300N
EXPNO 33
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210910
Time 1.47 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 46080
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 112.2897098 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

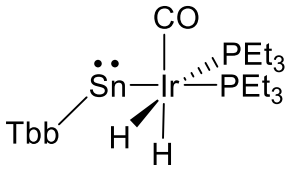
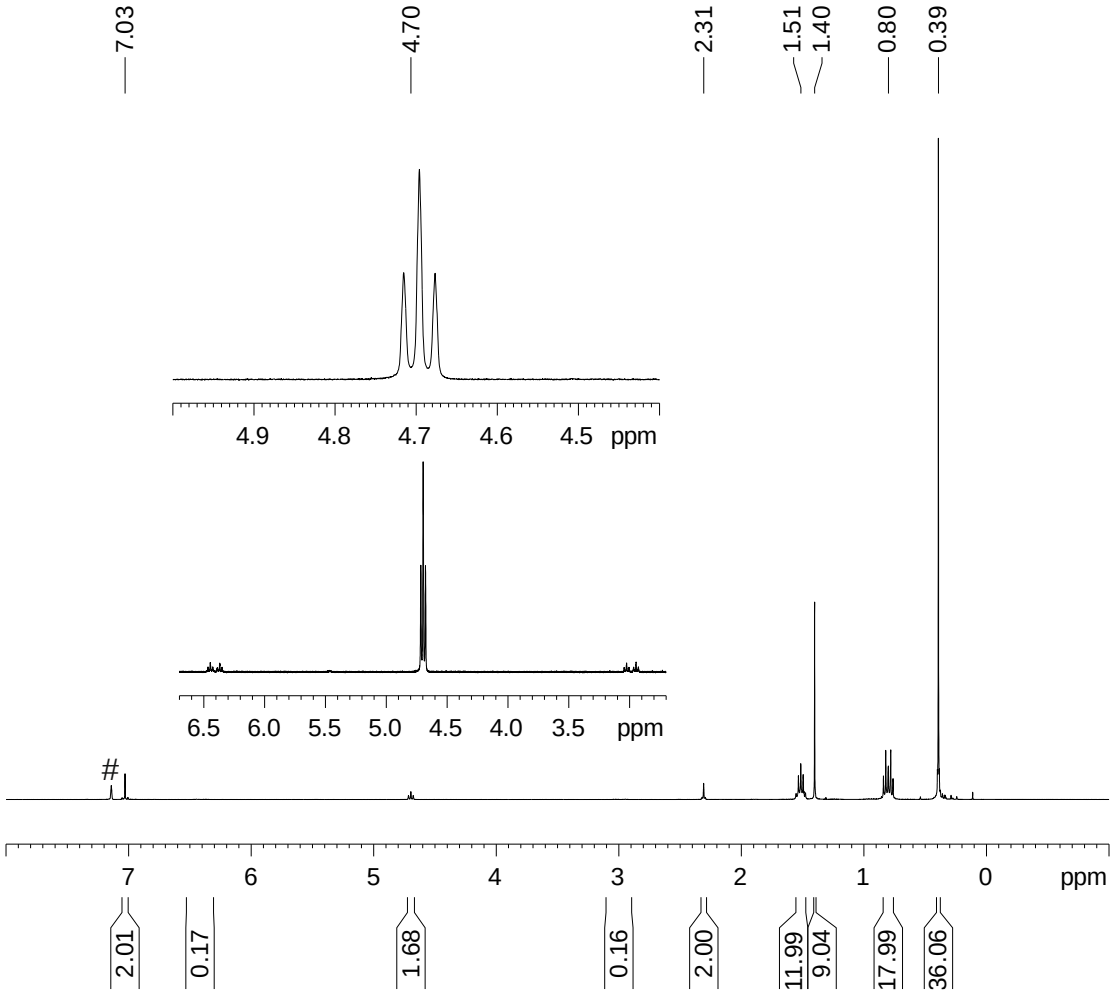


Figure SI 142. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **20**.

NMR spectra of compound **21**.

^{1}H NMR spectrum of TbbSnH$_2$Ir(CO)$_2$(PEt$_3$)$_2$ in benzene-d$_6$ (#) at rt.



Current Data Parameters
NAME MA696K_07102021_400N
EXPNO 10
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211007
Time 20.05
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 52656
SOLVENT C6D6
NS 32
DS 0
SWH 8305.647 Hz
FIDRES 0.157734 Hz
AQ 3.1698911 sec
RG 181
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 400.1100000 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

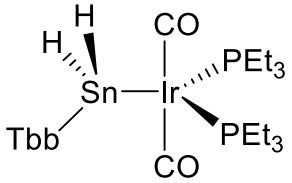
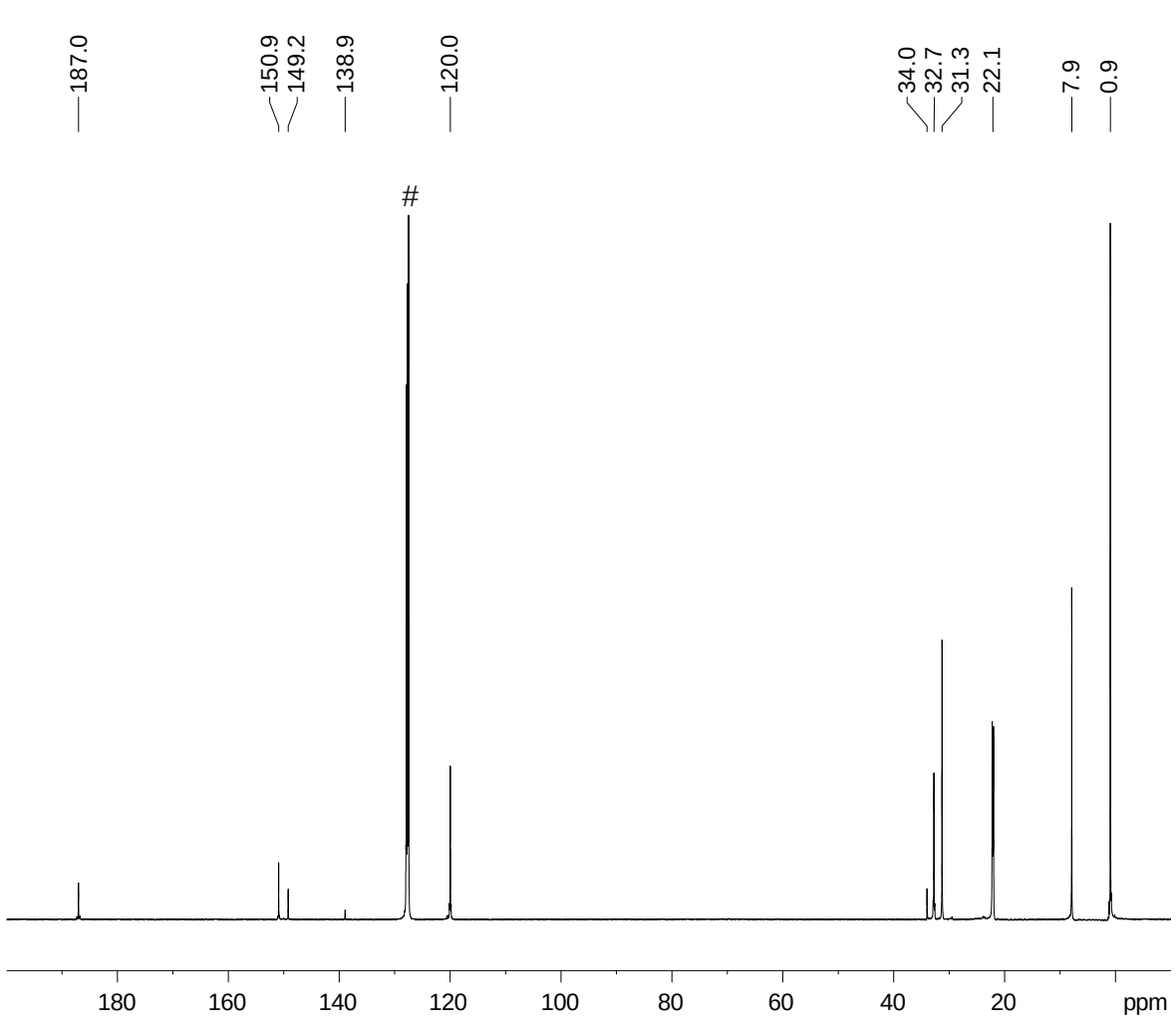


Figure SI 143. ^{1}H NMR spectrum of compound **21**.

$^{13}C\{^{1}H\}$ NMR spectrum of $TbbSnH_2Ir(CO)_2(PEt_3)_2$ in benzene-d_6 (#) at rt.




```
Current Data Parameters
NAME     MA696K_06102021_500
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_          20211007
Time              9.29
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG           udeft
TD             27268
SOLVENT           C6D6
NS               40960
DS                   0
SWH           37878.789 Hz
FIDRES         1.389130 Hz
AQ           0.3599376 sec
RG                2050
DW              13.200 usec
DE               6.00 usec
TE               299.1 K
D1          1.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec
D20       100.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                8.32 usec
P13              2000.00 usec
P26               500.00 usec
PL1                0.40 dB
PL1W         76.51497650 W
SFO1        125.7728799 MHz
SP8               10.16 dB
SP13              10.16 dB
SPNAM[8] Crp60,0.5,20.1
SPNAM[13   Crp60comp.4
SPOAL8             0.500
SPOAL13            0.500
SPOFFS8              0 Hz
SPOFFS13             0 Hz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2               1H
PCPD2            80.00 usec
PL2             -0.52 dB
PL12             15.51 dB
PL2W         24.34997177 W
PL12W         0.60743308 W
SFO2        500.1325006 MHz

F2 - Processing parameters
SI              262144
SF         125.7577890 MHz
WDW                EM
SSB                 0
LB               4.00 Hz
GB                  0
PC                1.40
```

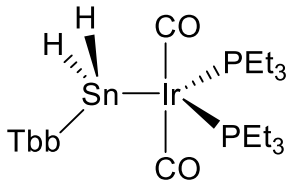
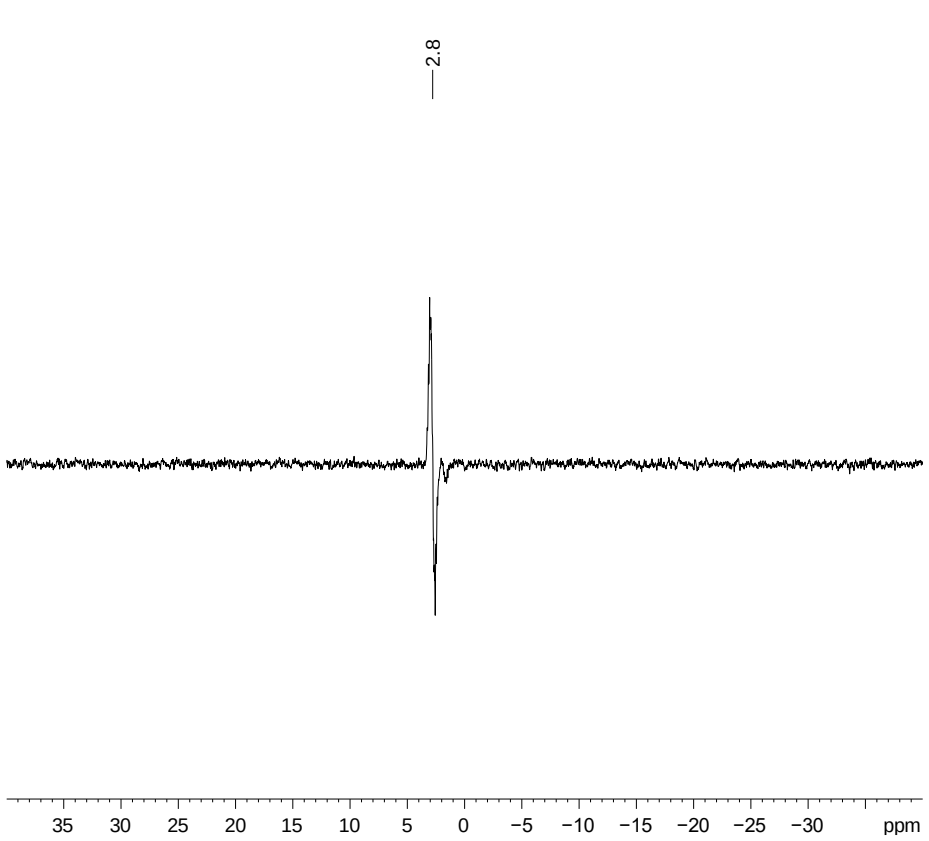


Figure SI 144. $^{13}C\{^{1}H\}$ NMR spectrum of compound **21**.

^{29}Si NMR spectrum of TbbSnH$_2$Ir(CO)$_2$(PEt$_3$)$_2$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA692_13092021_300N
EXPNO 31
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210914
Time 4.20 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG ineptnd
TD 39048
SOLVENT C6D6
NS 256
DS 0
SWH 26315.789 Hz
FIDRES 1.347869 Hz
AQ 0.7419120 sec
RG 204.67
DW 19.000 usec
DE 6.50 usec
TE 298.0 K
CNST2 6.5999999
D1 2.00000000 sec
D4 0.03787879 sec
TD0 1
SFO1 59.6229159 MHz
NUC1 29Si
P1 10.30 usec
P2 20.60 usec
PLW1 50.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
P3 14.00 usec
P4 28.00 usec
PLW2 8.26509953 W

F2 − Processing parameters
SI 32768
SF 59.6273533 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

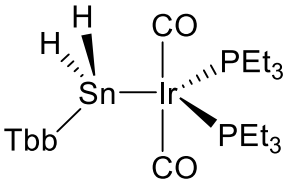
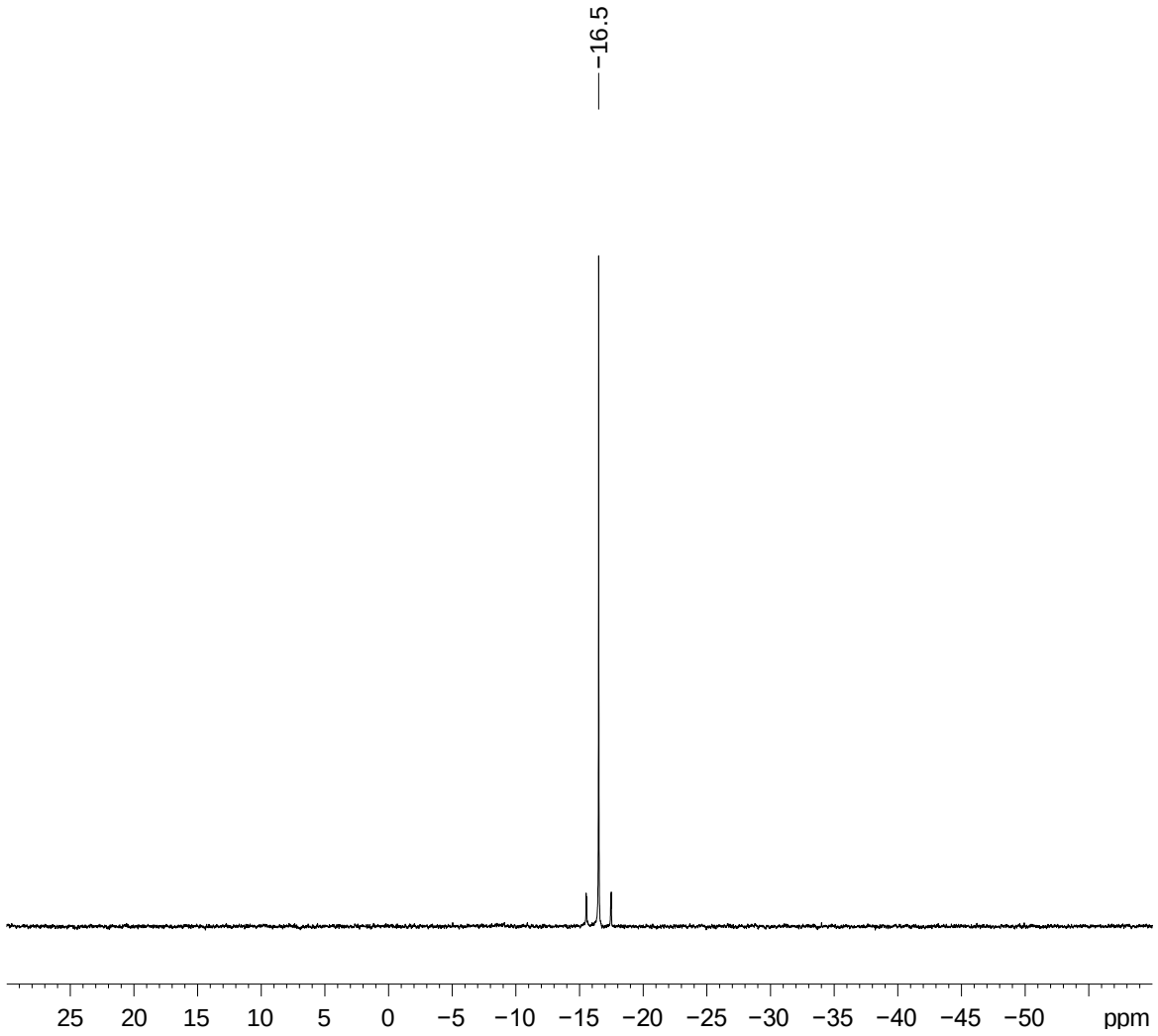


Figure SI 145. ^{29}Si NMR spectrum of compound **21**.

$^{31}P\{^{1}H\}$ NMR spectrum of $TbbSnH_2Ir(CO)_2(PEt_3)_2$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA696K_07102021_400N
EXPNO 11
PROCNO 1

F2 − Acquisition Parameters
Date_ 20211007
Time 20.13
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 88150
SOLVENT C6D6
NS 256
DS 0
SWH 65789.477 Hz
FIDRES 0.746336 Hz
AQ 0.6699400 sec
RG 23100
DW 7.600 usec
DE 6.00 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 11.00 usec
PL1 −3.00 dB
PL1W 45.10684967 W
SFO1 161.9674970 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 131072
SF 161.9674970 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

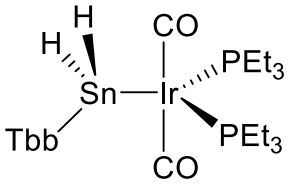
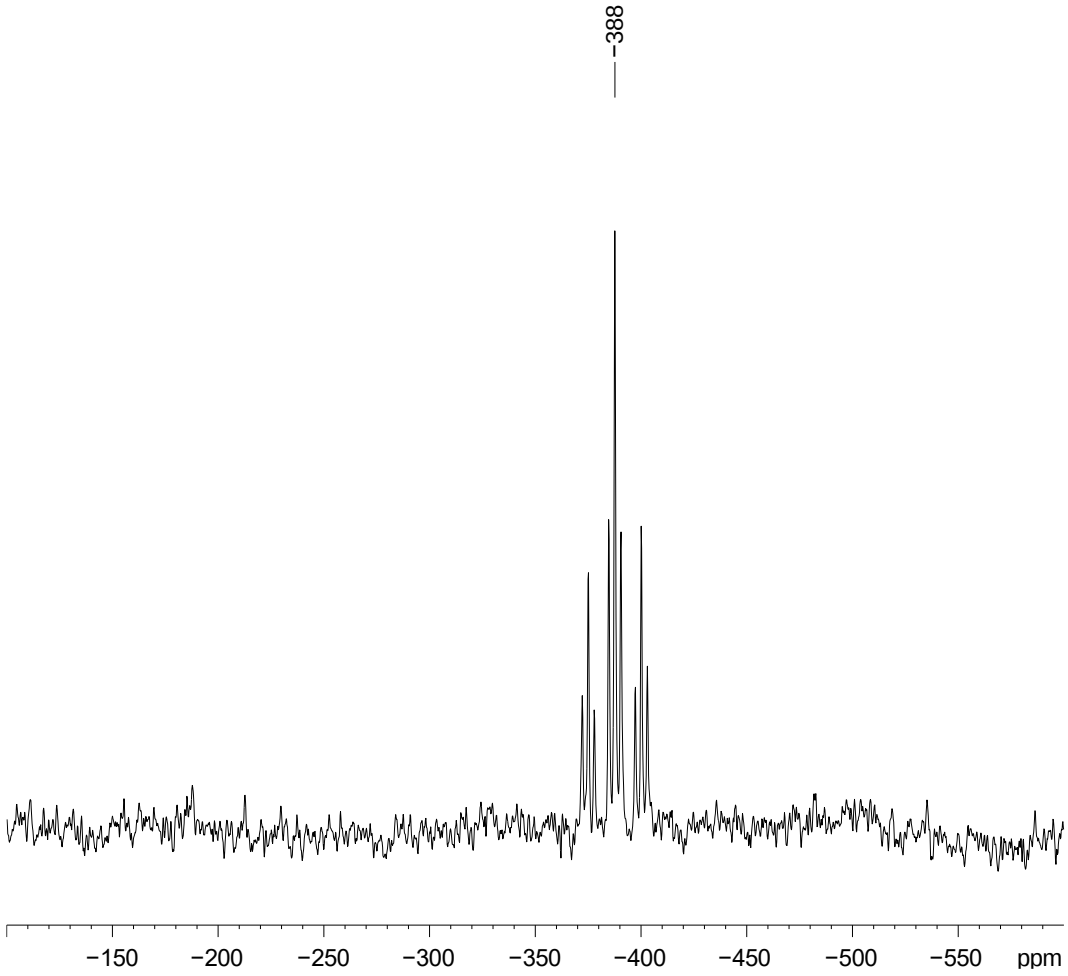


Figure SI 146. $^{31}P\{^{1}H\}$ NMR spectrum of compound **21**.

^{119}Sn NMR spectrum of TbbSnH$_2$Ir(CO)$_2$(PEt$_3$)$_2$ in benzene-d$_6$ at rt.



Current Data Parameters
NAME MA692_13092021_300N
EXPNO 13
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210913
Time 20.33 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zg30
TD 8918
SOLVENT C6D6
NS 153600
DS 1
SWH 89285.711 Hz
FIDRES 20.023708 Hz
AQ 0.0499408 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.02000000 sec
TD0 1
SFO1 111.8756060 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W

F2 − Processing parameters
SI 4096
SF 111.9203740 MHz
WDW EM
SSB 0
LB 70.00 Hz
GB 0
PC 1.40

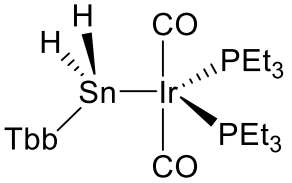
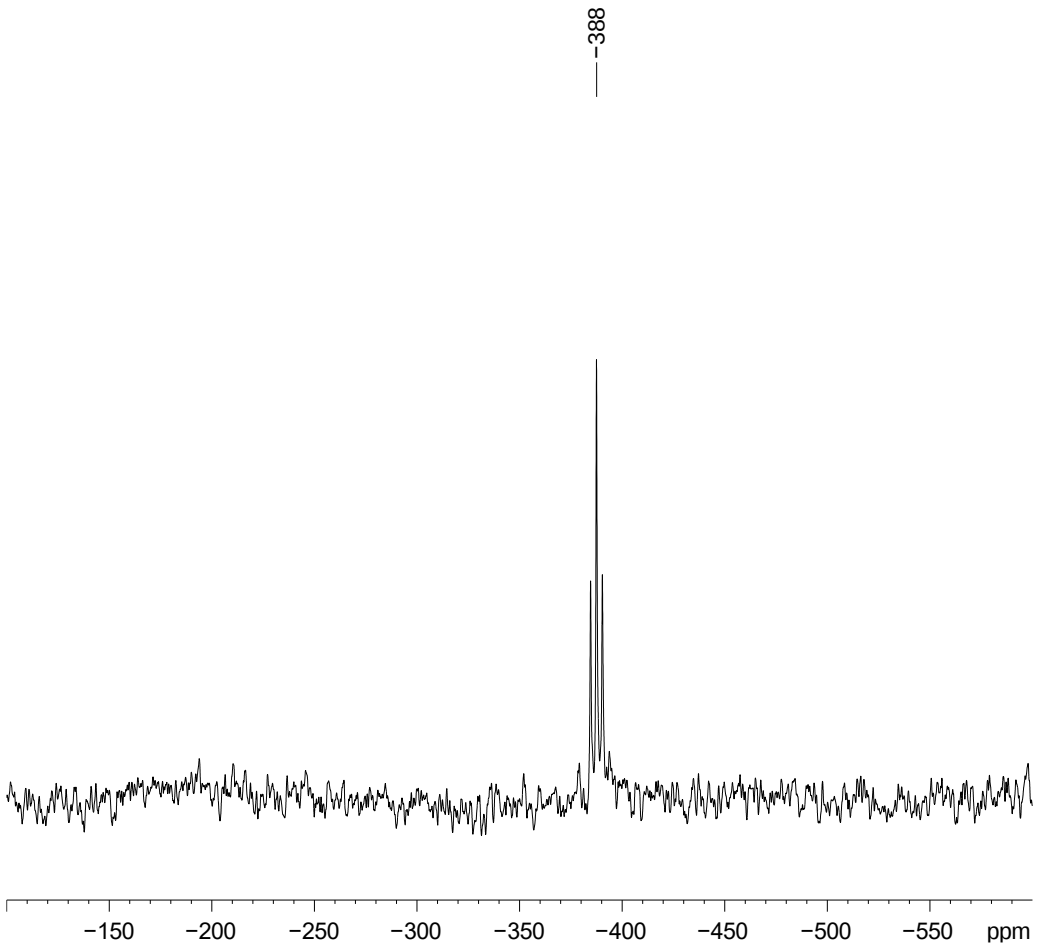


Figure SI 147. ^{119}Sn NMR spectrum of compound **21**.

$^{119}Sn\{^{1}H\}$ NMR spectrum of $TbbSnH_2Ir(CO)_2(PEt_3)_2$ in benzene-d_6 at rt.



Current Data Parameters
NAME MA692_13092021_300N
EXPNO 23
PROCNO 1

F2 − Acquisition Parameters
Date_ 20210914
Time 1.01 h
INSTRUM spect
PROBHD Z104275_0338 (
PULPROG zgig30
TD 39186
SOLVENT C6D6
NS 46080
DS 4
SWH 89285.711 Hz
FIDRES 4.557021 Hz
AQ 0.2194416 sec
RG 204.67
DW 5.600 usec
DE 6.50 usec
TE 298.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TD0 1
SFO1 111.8756058 MHz
NUC1 119Sn
P0 4.03 usec
P1 12.10 usec
PLW1 12.00000000 W
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 8.26509953 W
PLW12 0.20000000 W

F2 − Processing parameters
SI 65536
SF 111.9203738 MHz

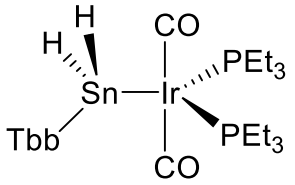
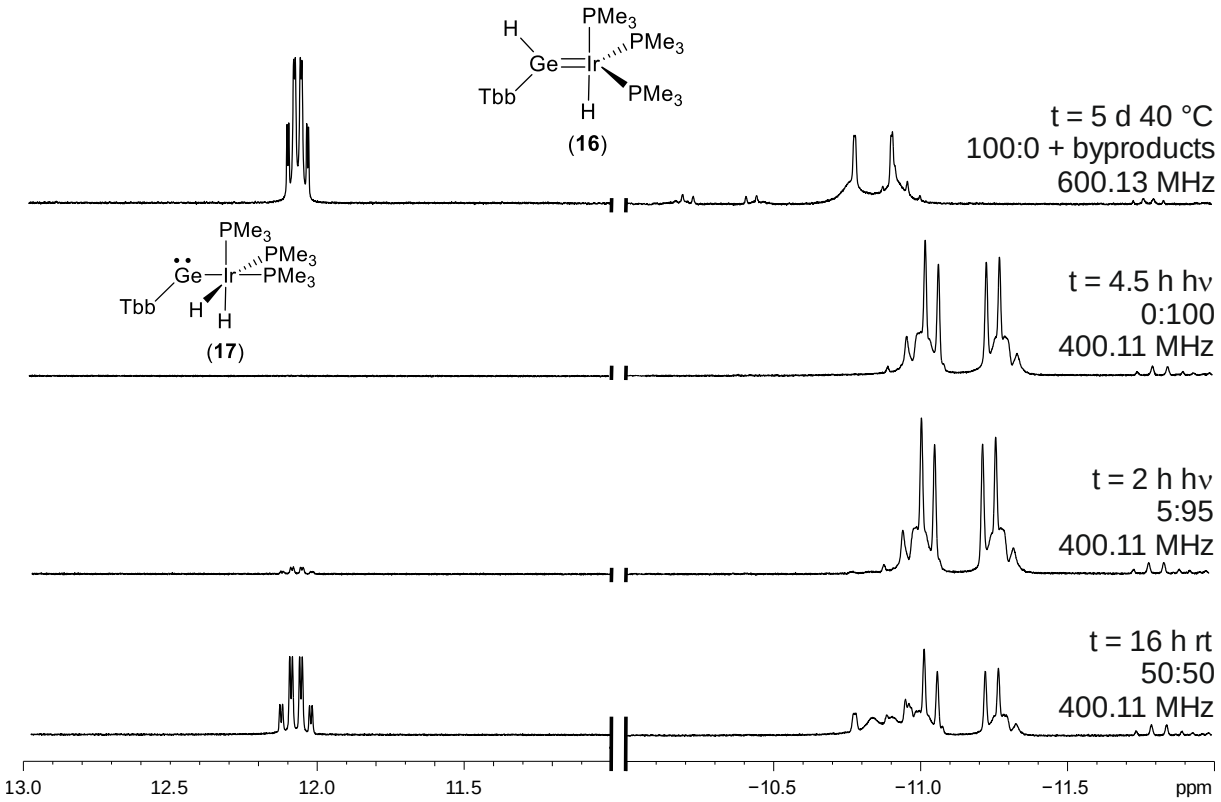
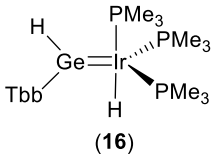


Figure SI 148. $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **21**.

1,2-H shift between **16** and **17**.





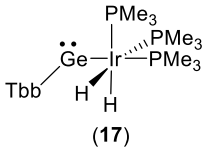
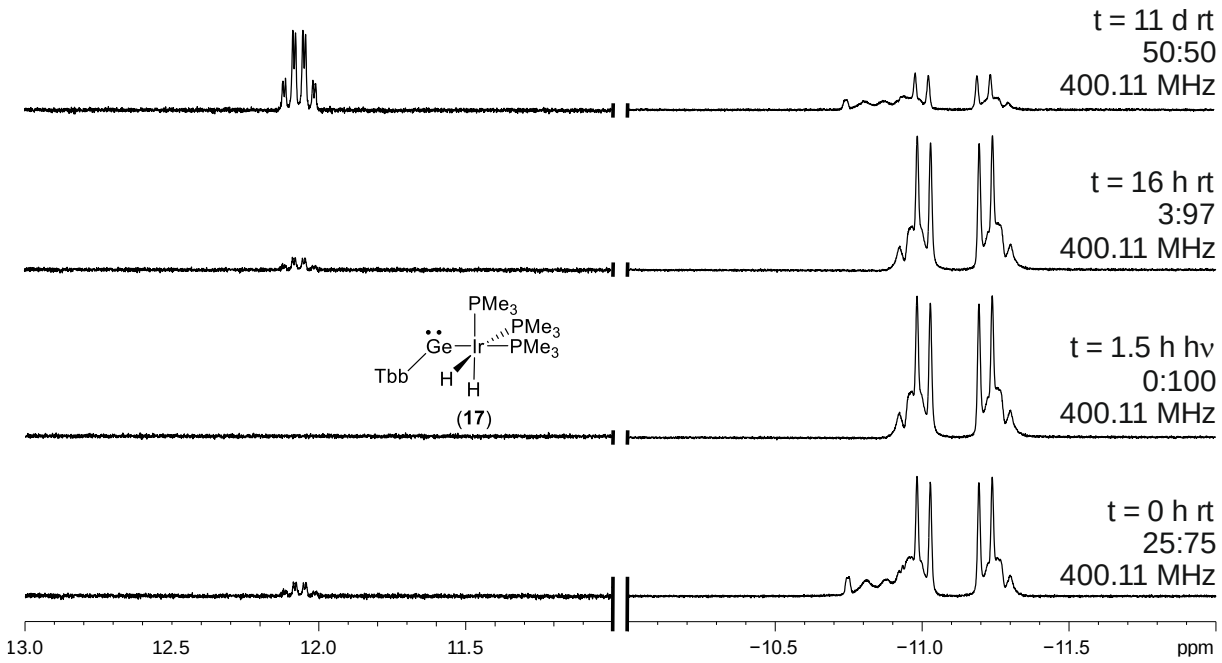
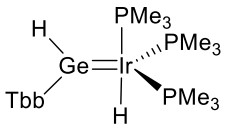
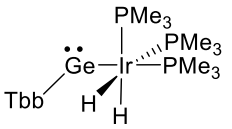


Figure SI 149. Series of ^{1}H NMR spectra:
t=16 h, rt, 50:50 mixture between **16** and **17**, 16 h after syntheses;
t = 4.5 h, hν, **17**;
t = 5 d, 40°C, **16**.





(**16**)



(**17**)

Figure SI 150. Series of ^{1}H NMR spectra:
t = 0 h, mixture between **16** and **17** directly after syntheses;
t = 1.5 h hv, **17**;
t = 11d, rt, mixture **16** and **17**.

Ligand induced transfer from **20** to **21**.

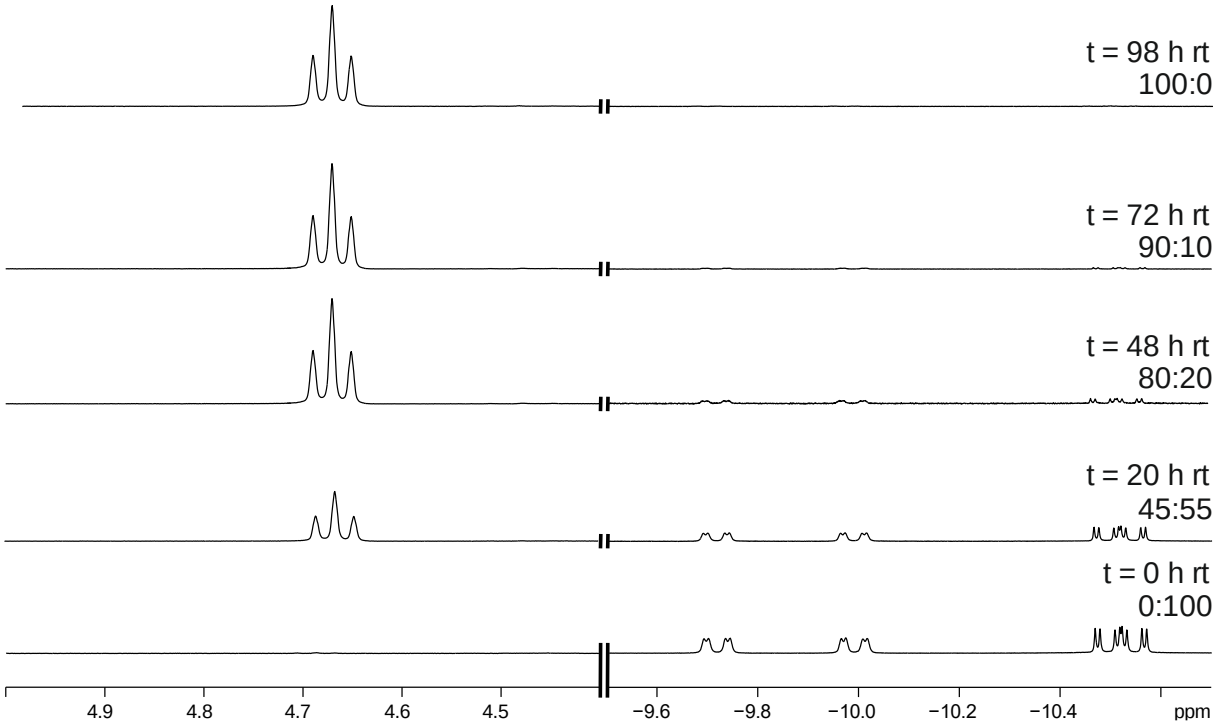
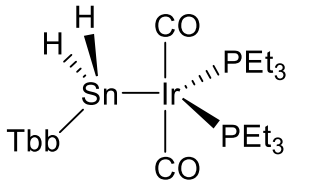
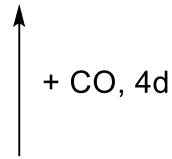
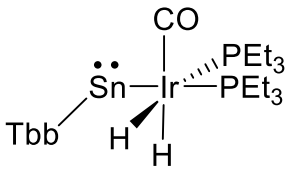


Figure SI 151. Series of ^{1}H NMR spectra for the transfer of compound **20** (t=0), to **21** (t = 98h, rt).



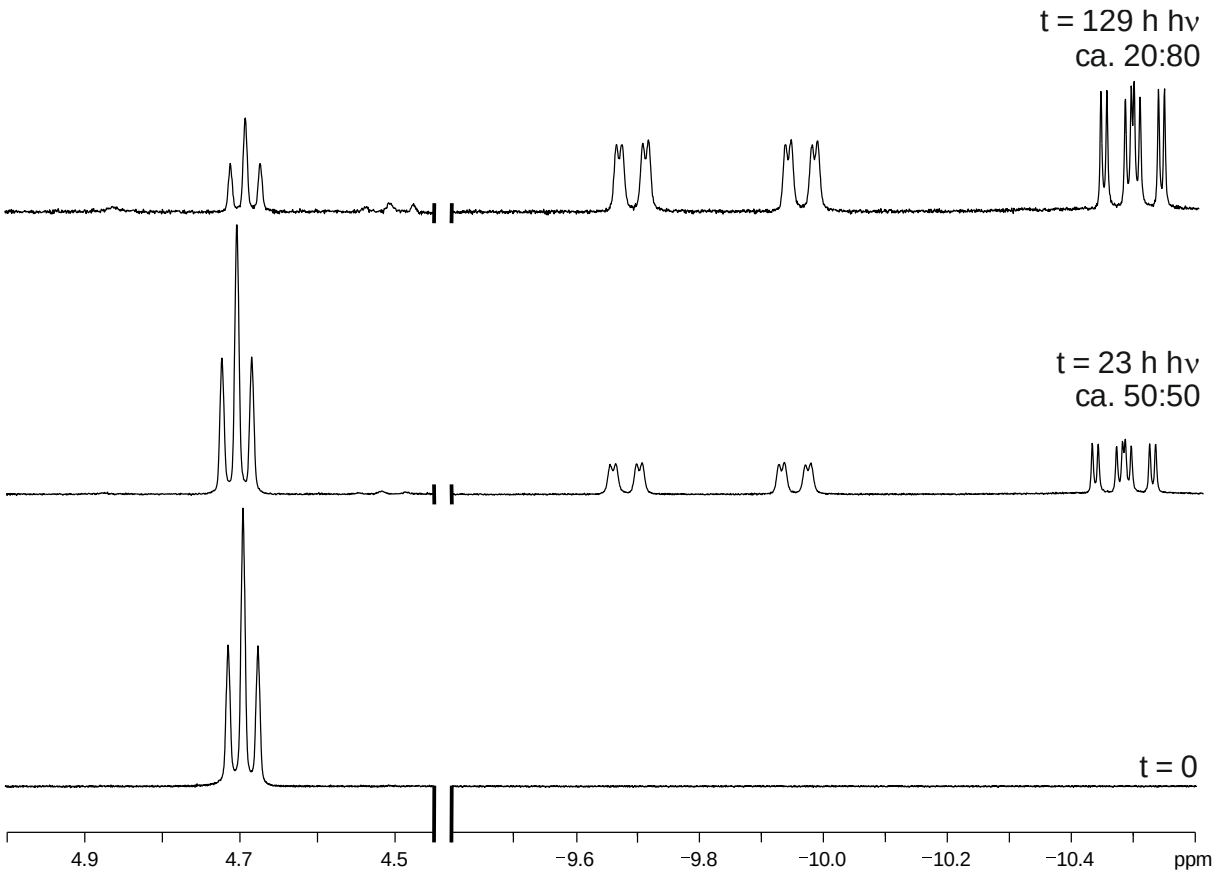
(**21**)





(**20**)

Photochemical ligand induced transfer from **21** to **20**.



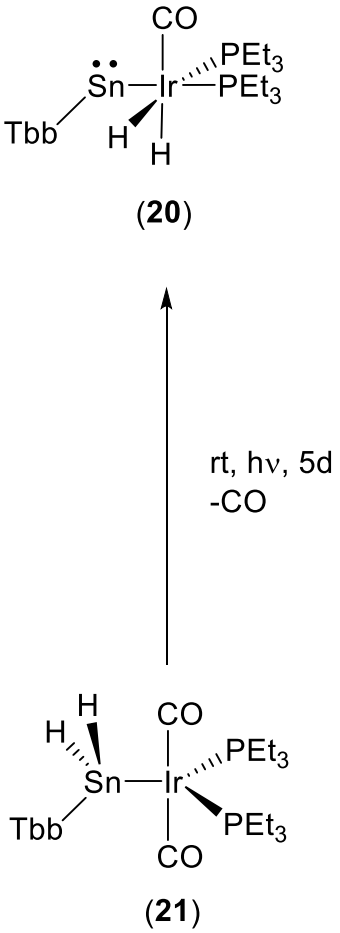


Figure SI 152. Series of ^{1}H NMR spectra for the transfer of **21** (t=0), to a mixture between **20** and **21** (t = 129h, hν).

Variable temperature $^{31}P\{^{1}H\}$ and ^{1}H NMR studies of **1**

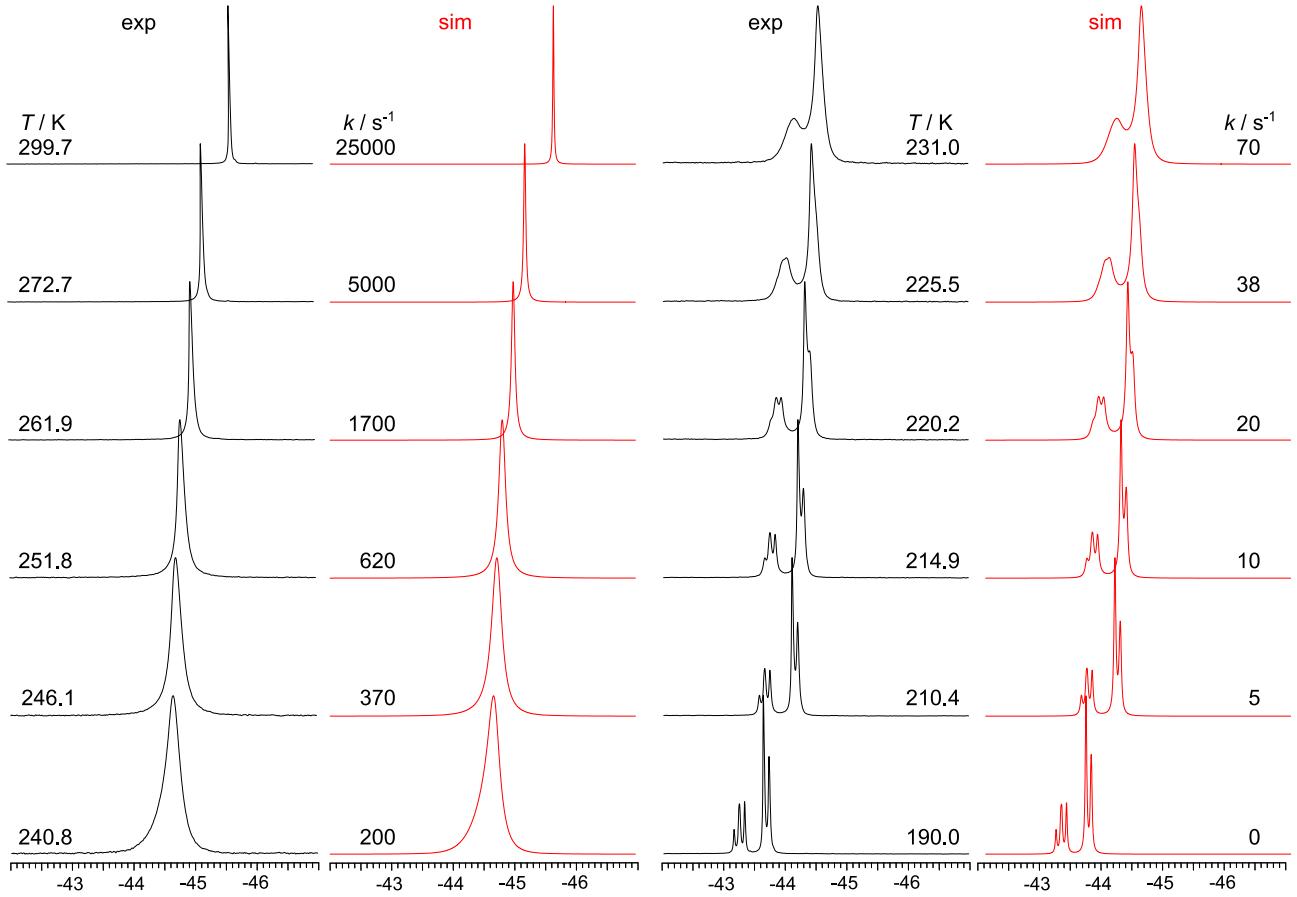


Figure SI 153. Experimental (black) and simulated (red) variable temperature 202.46 MHz $^{31}P\{^{1}H\}$ NMR spectra of **1** in toluene-d_8. Details of the AB_2 spin system simulations are listed in Table SX.

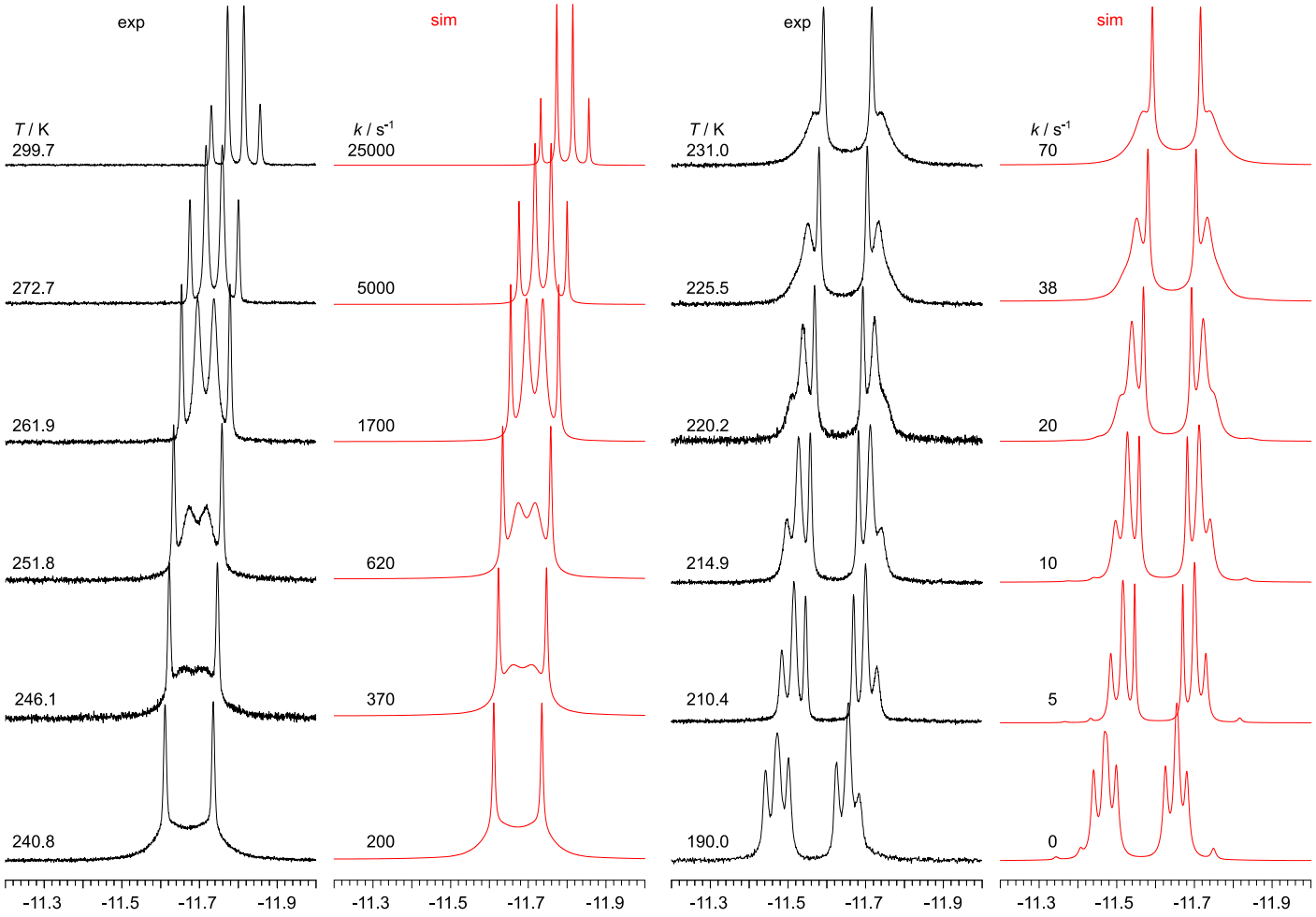


Figure SI 154. Experimental (black) and simulated (red) variable temperature 500.13 MHz ^{1}H NMR spectra of **1** in toluene-d_8. Details of the AB_2X spin system simulations are listed in Table SX.

Table SI 3. Parameters used in the simulation of variable temperature $^{31}P\{^{1}H\}$ (AB_2 spin system) and ^{1}H (AB_2X spin system) NMR spectra of **1**.

	^{31}P		^{1}H				
T / K	δ(A) / ppm	δ(B) / ppm	X	$^{2}J_{AB}$ / Hz	$^{2}J_{AX}$ / Hz	$^{2}J_{BX}$ / Hz	k / s^{-1}
190.05	-43.25	-43.68	-11.56	-17.5	94.9	-15.9	0
210.36	-43.67	-44.16	-11.61	-18.1	94.6	-16.4	5
214.92	-43.75	-44.26	-11.62				10
220.16	-43.85	-44.37	-11.63				20
225.47	-43.95	-44.48	-11.64				38
231.04	-44.06	-44.59	-11.65				70
240.79	-44.23	-44.79	-11.67				200
246.07	-44.32	-44.90	-11.69				370
251.81	-44.42	-45.01	-11.70				620
261.93	-44.59	-45.20	-11.72				1700
272.66	-44.76	-45.40	-11.74				5000
299.68	-45.19	-45.89	-11.79	-18.1	94.6	-16.4	25000

Arrhenius activation energy: 11.962(.185) kcal/mole

log(frequency factor): 13.181(.160)

Eyring activation enthalpy: 11.454(.191) kcal/mole

activation entropy: 0.082(.756) eu

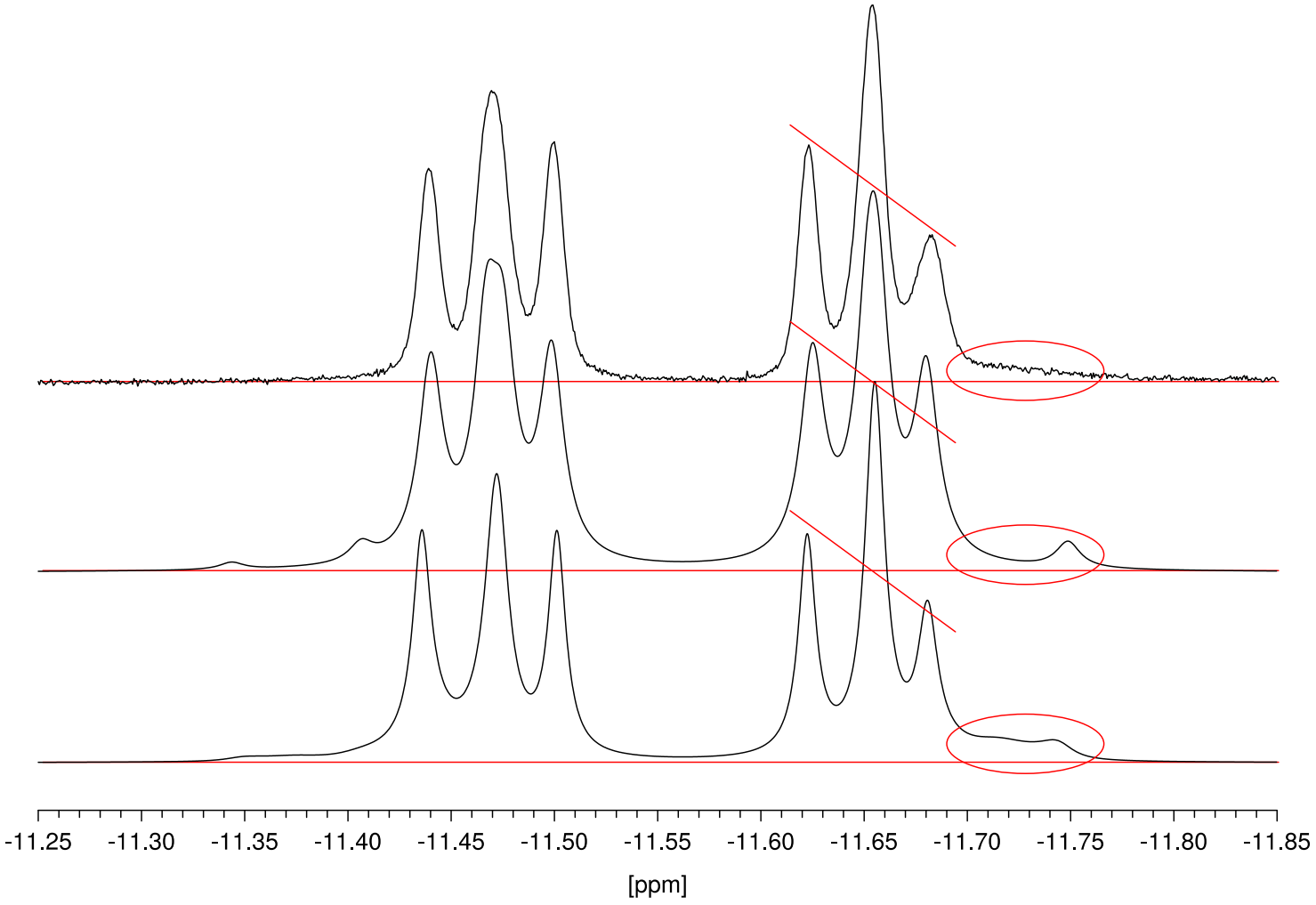


Figure SI 155. Experimental (top) and simulated 500.13 MHz ^{1}H NMR spectra of **1** in toluene-d_8. Middle trace: AB2 spin system without chemical exchange between phosphines. Part of the asymmetry of the experimental spectrum is reproduced, but differences in the indicated features exist. Bottom trace: an ABC spin system with exchange between B and C can reproduce the features better. Presumably hindered rotation of the Tbb substituent plays a role rather than phosphine exchange.

IR-Spectroscopy

IR spectra were recorded in KBr with a Bruker Vertex 70 spectrometer. IR-spectra of compounds **1**,**2**,**7**-**12**, **18**-**21** are presented. Compounds **3**,**4**,**5** are too sensitive and show with the extensively dried KBr spontaneous decolorization upon mixing. Compounds 13-17 mixtures?,

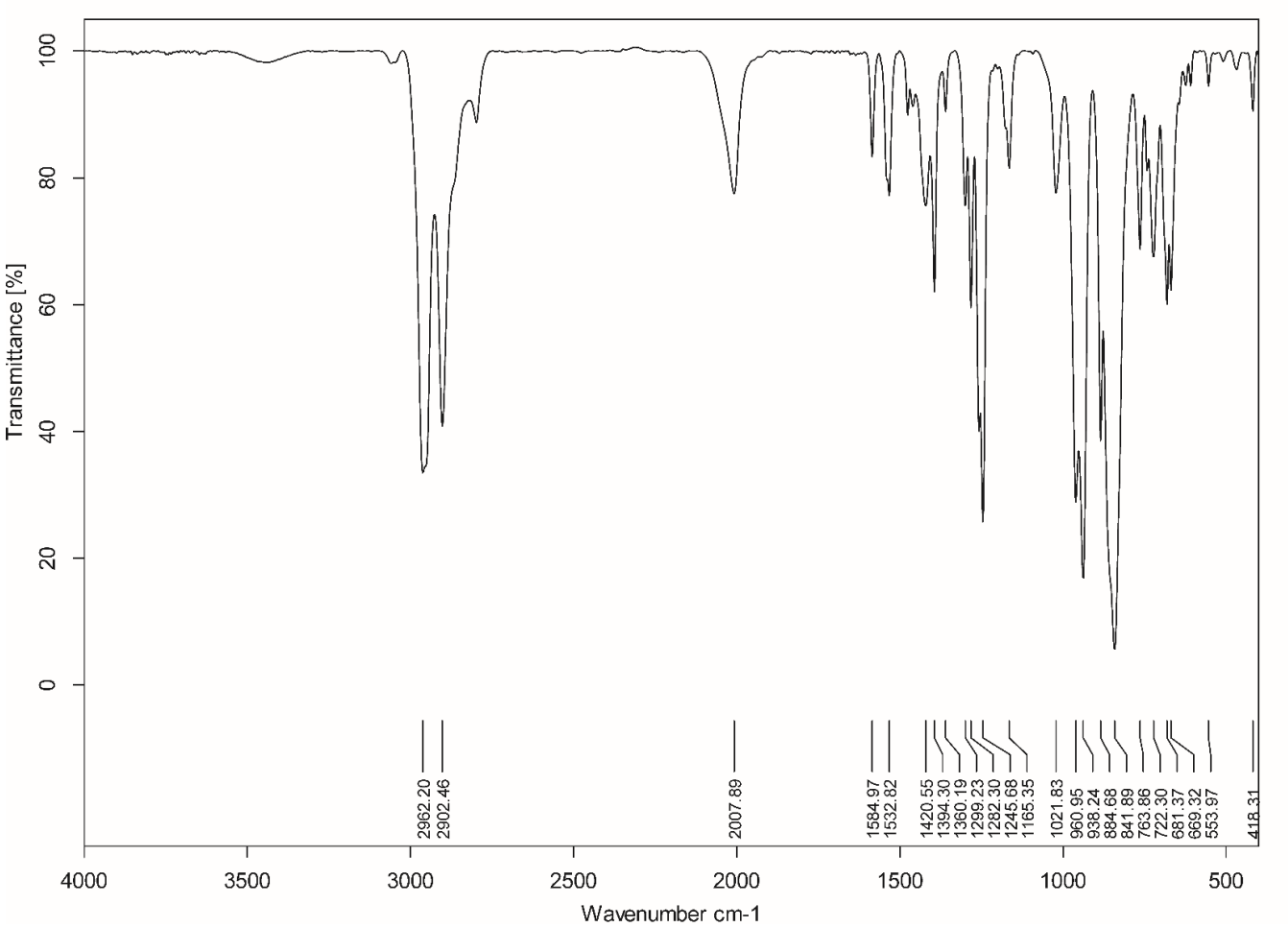


Figure SI 156. IR spectrum of compound **1**.

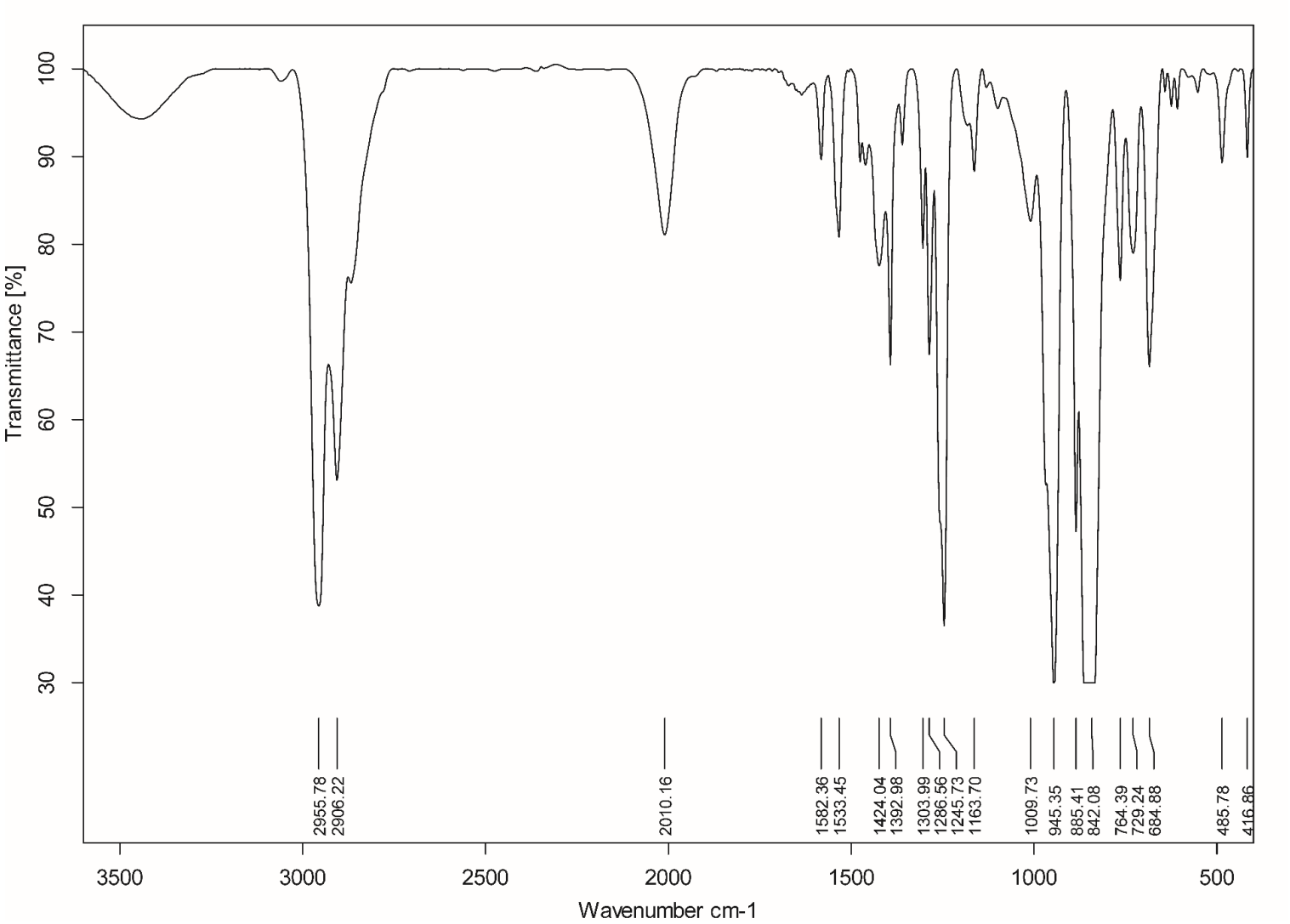


Figure SI 157. IR spectrum of compound **2**.

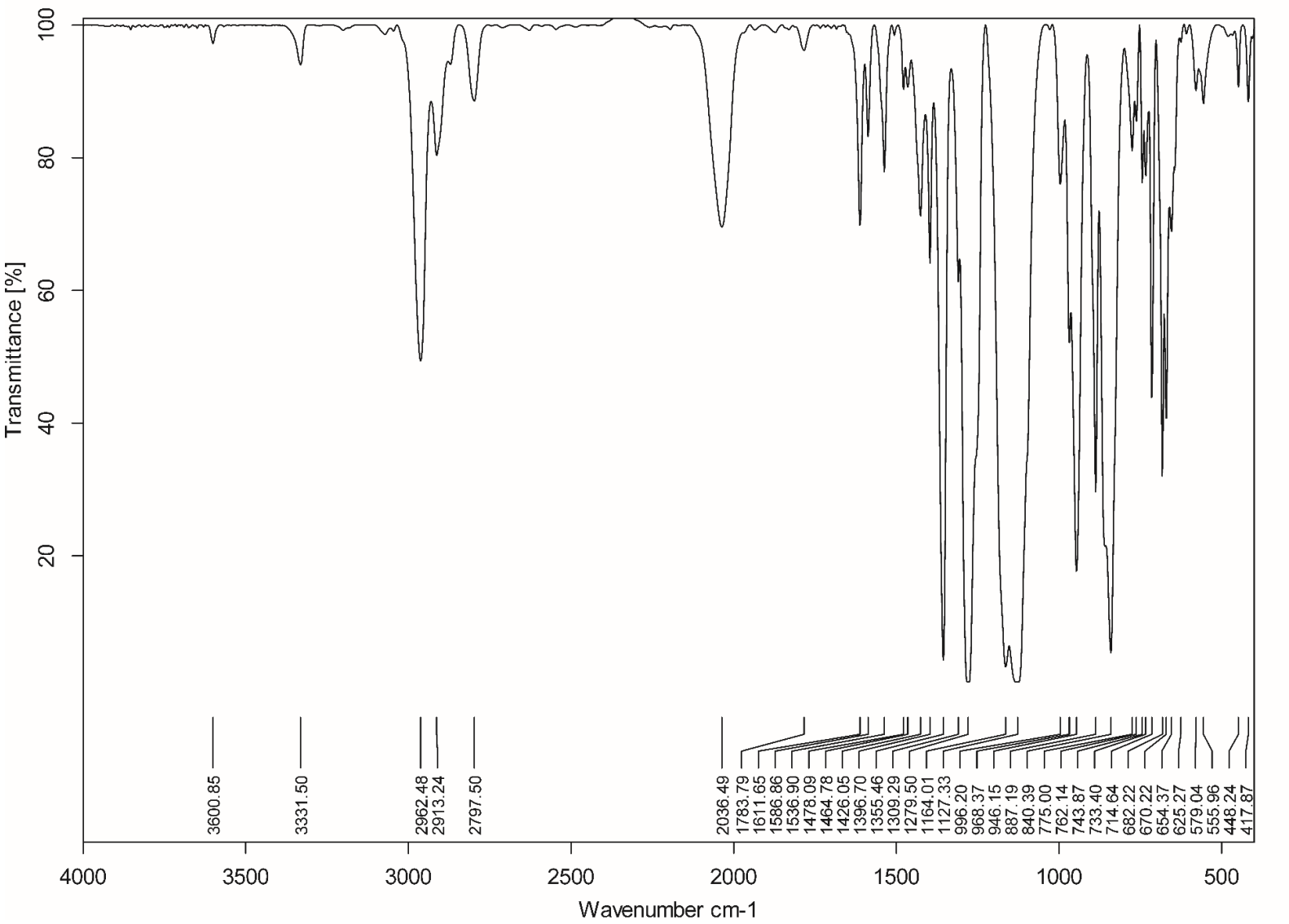


Figure SI 158. IR spectrum of compound **7**.

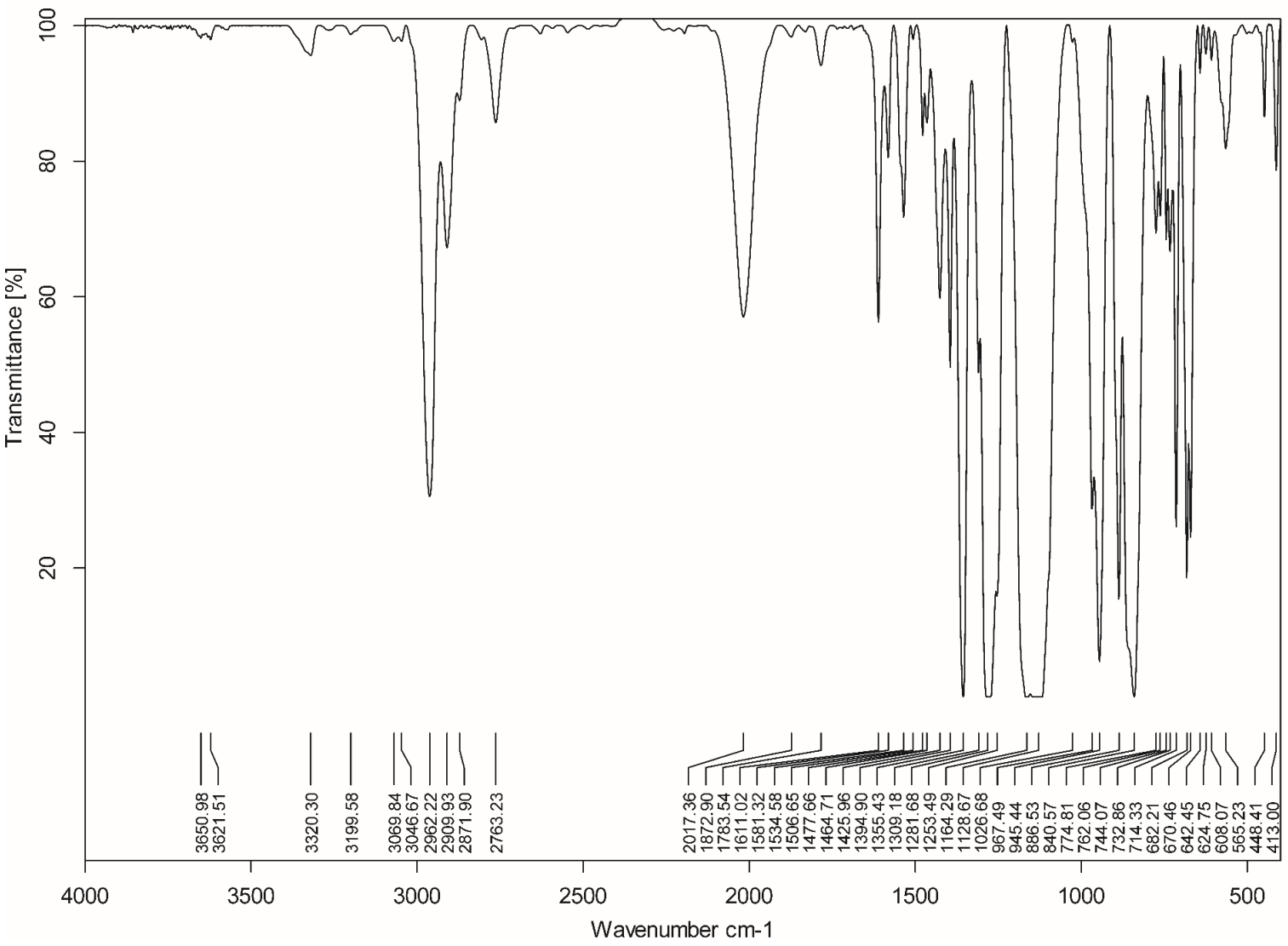


Figure SI 159. IR spectrum of compound **8**.

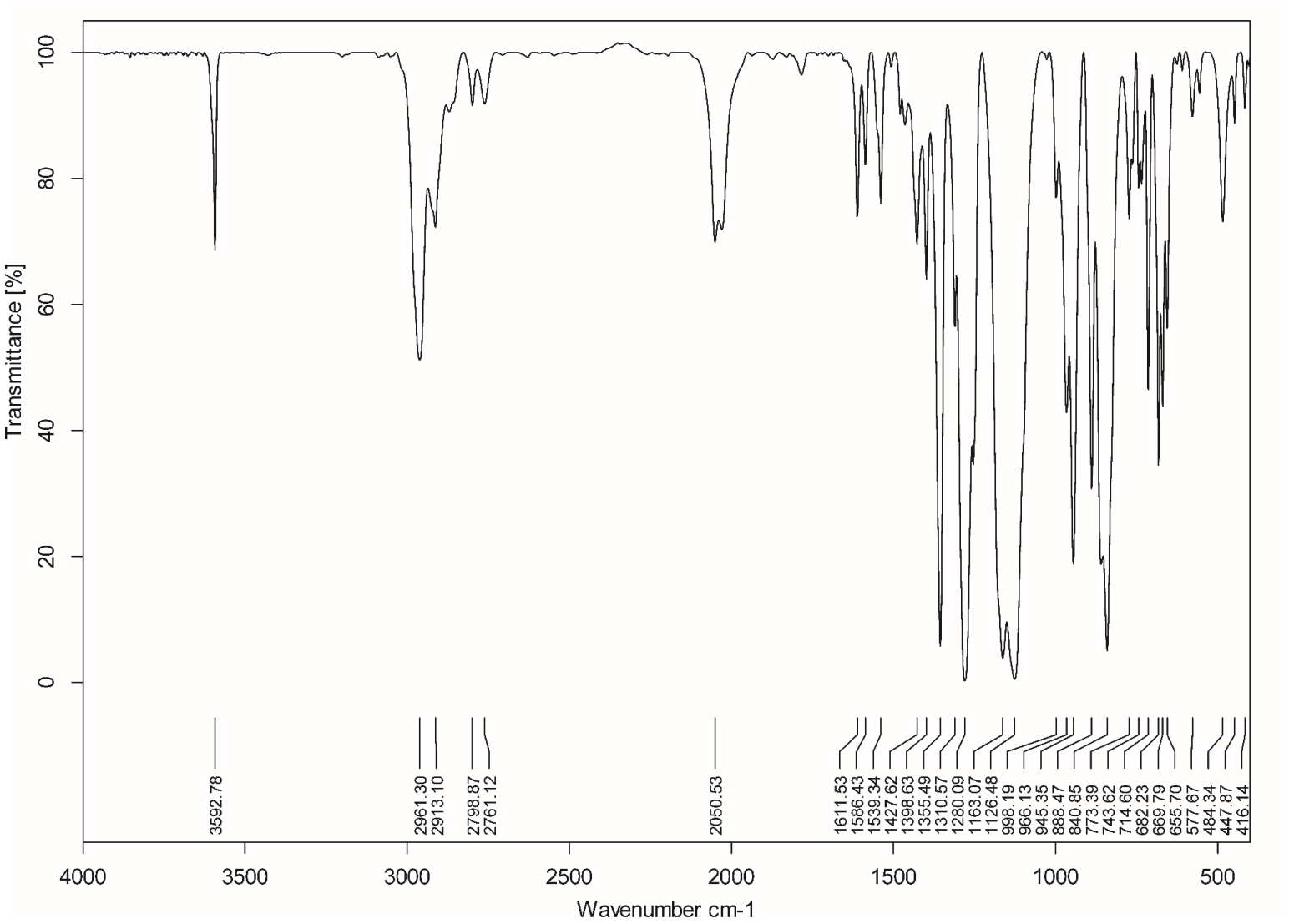


Figure SI 160. IR spectrum of compound **9**.

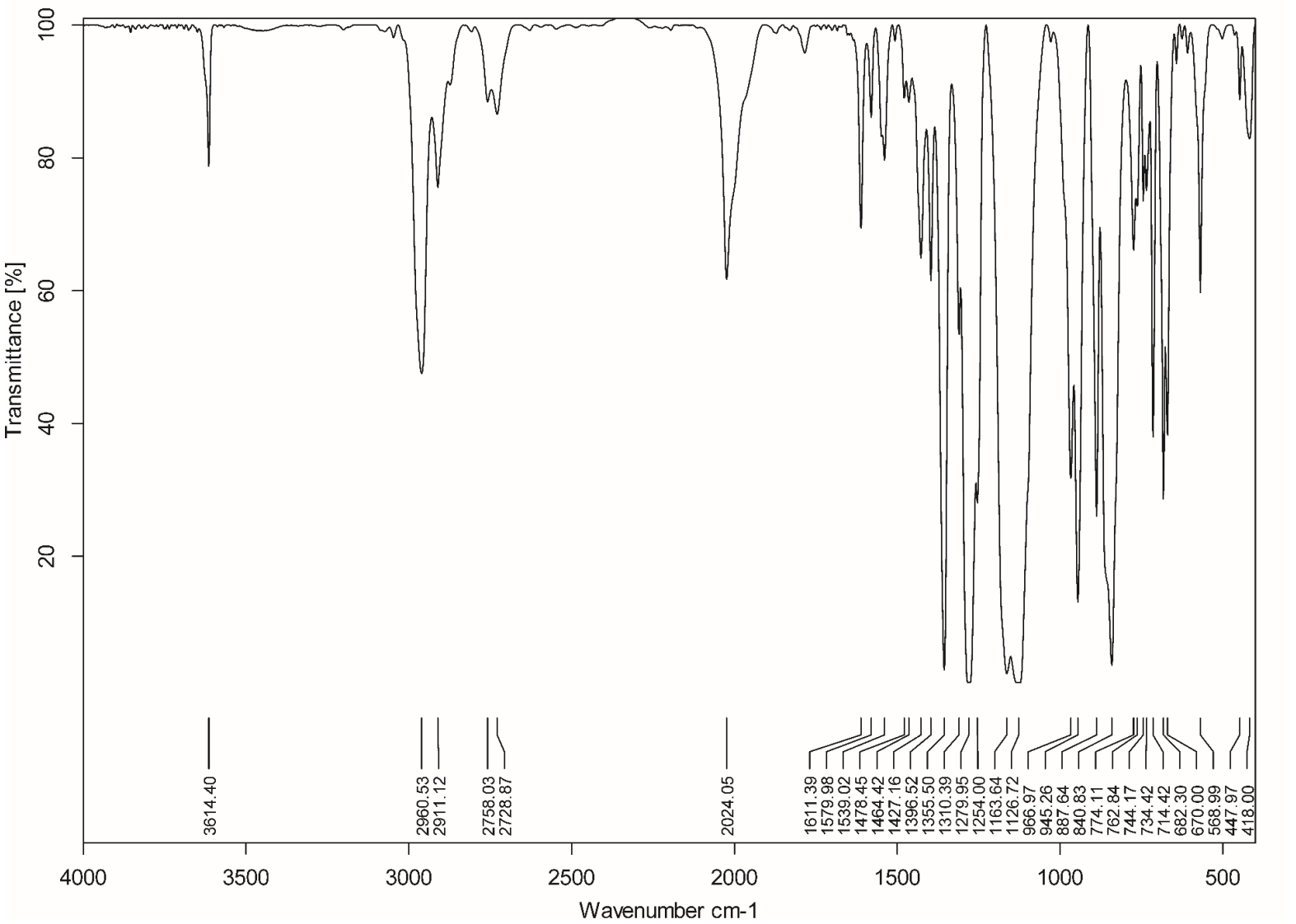


Figure SI 161. IR spectrum of compound **10**.

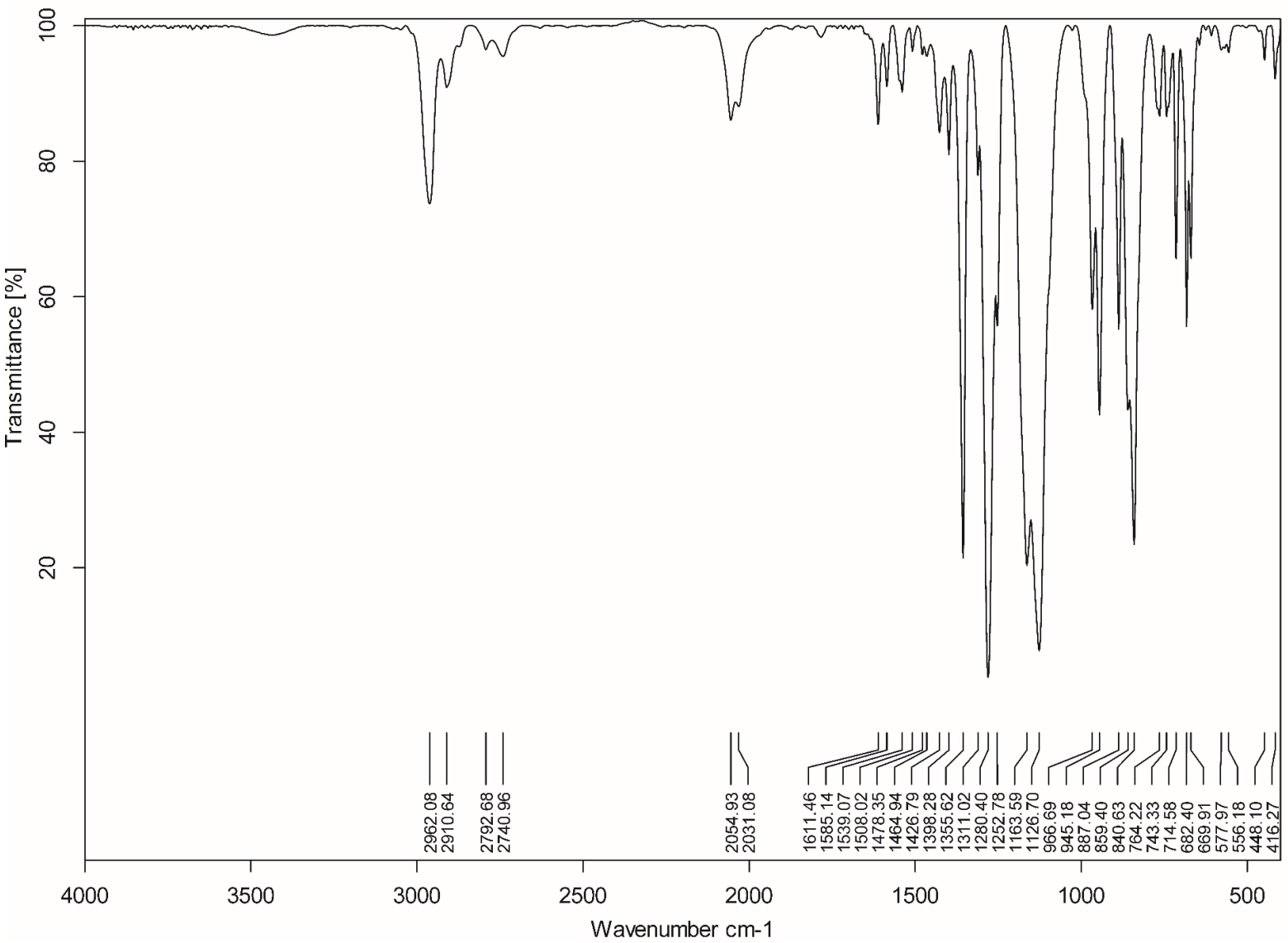


Figure SI 162. IR spectrum of compound **11**.

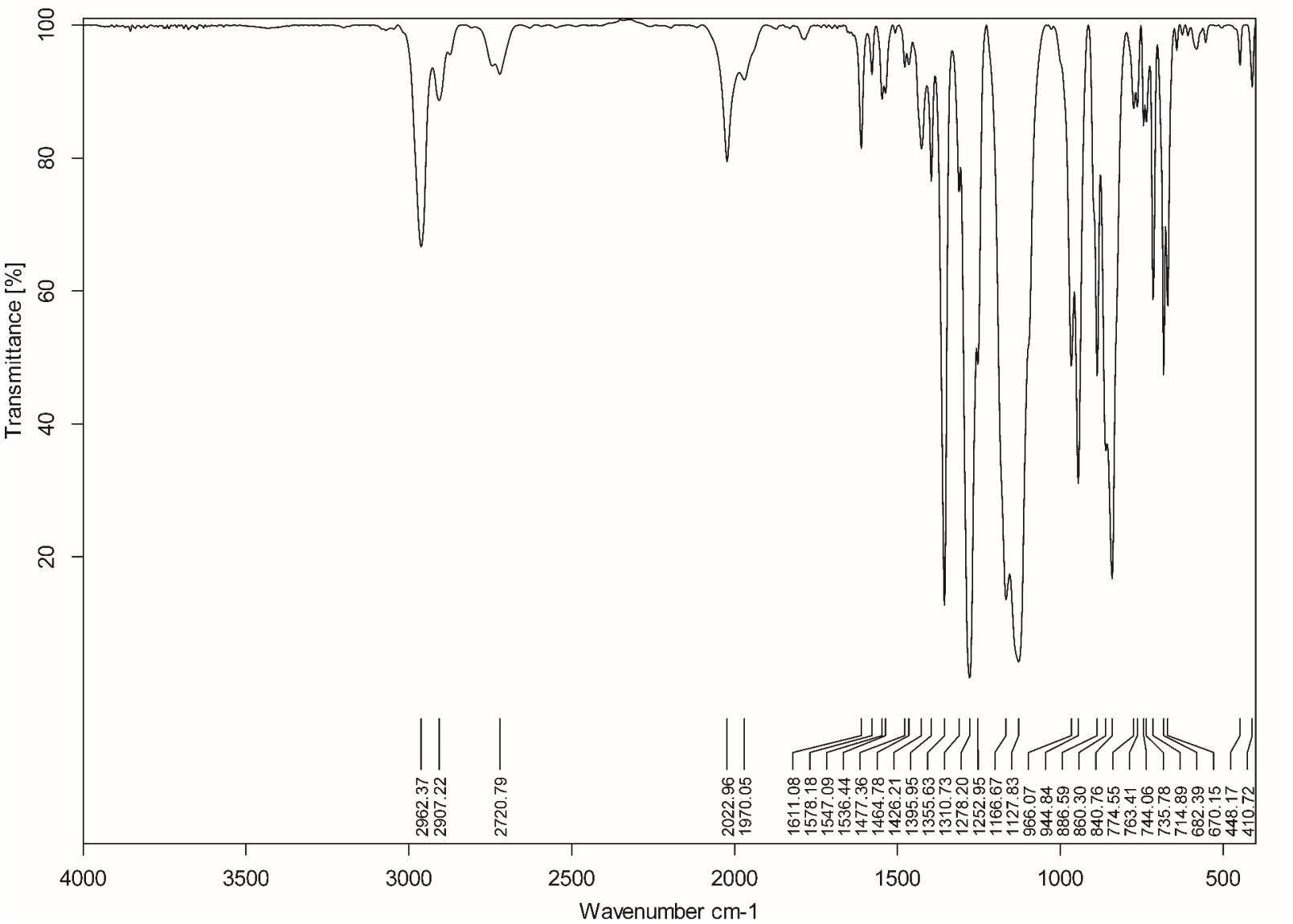


Figure SI 163. IR spectrum of compound **12**.

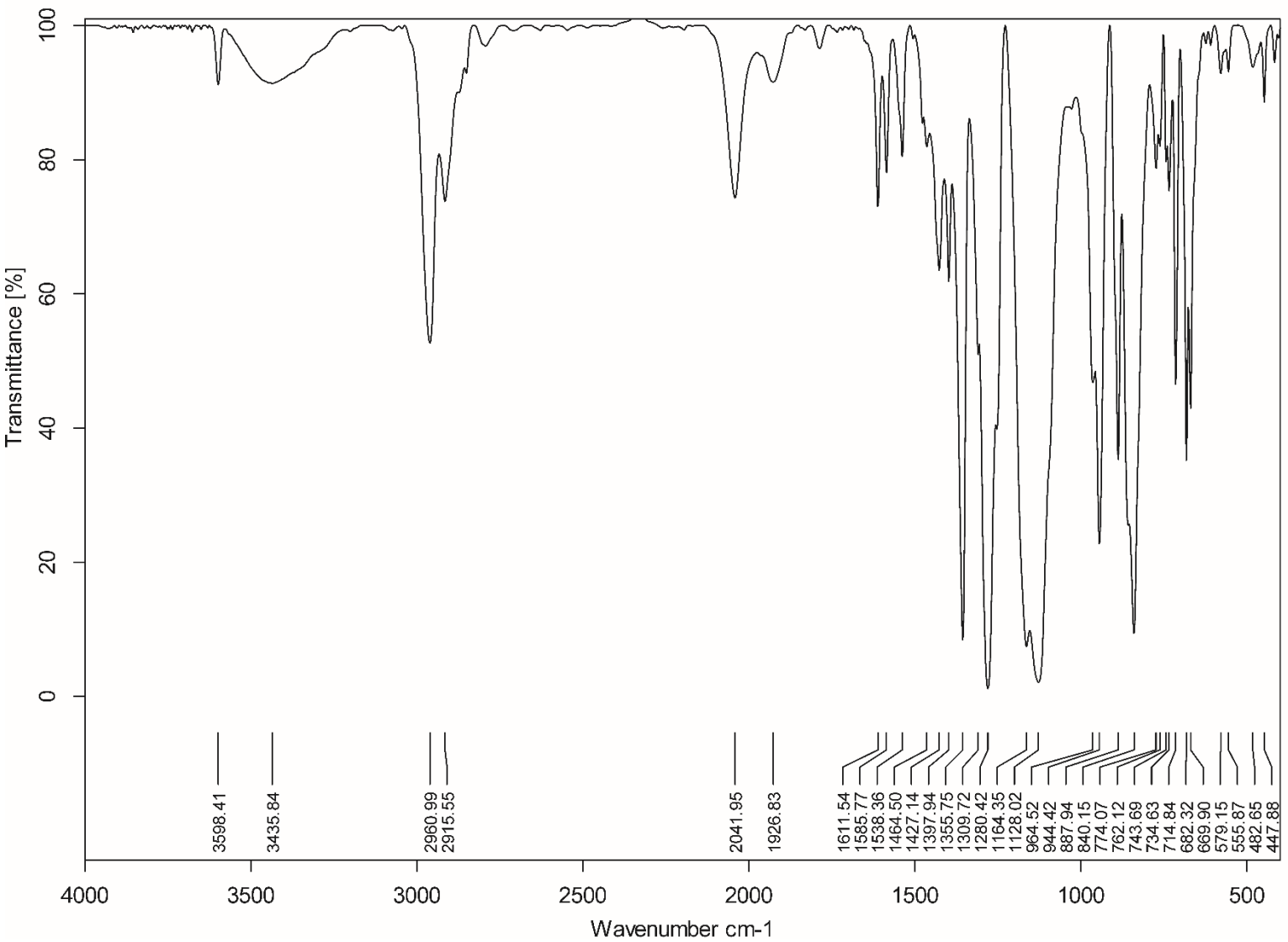


Figure SI 164. IR spectrum of compound **13**.

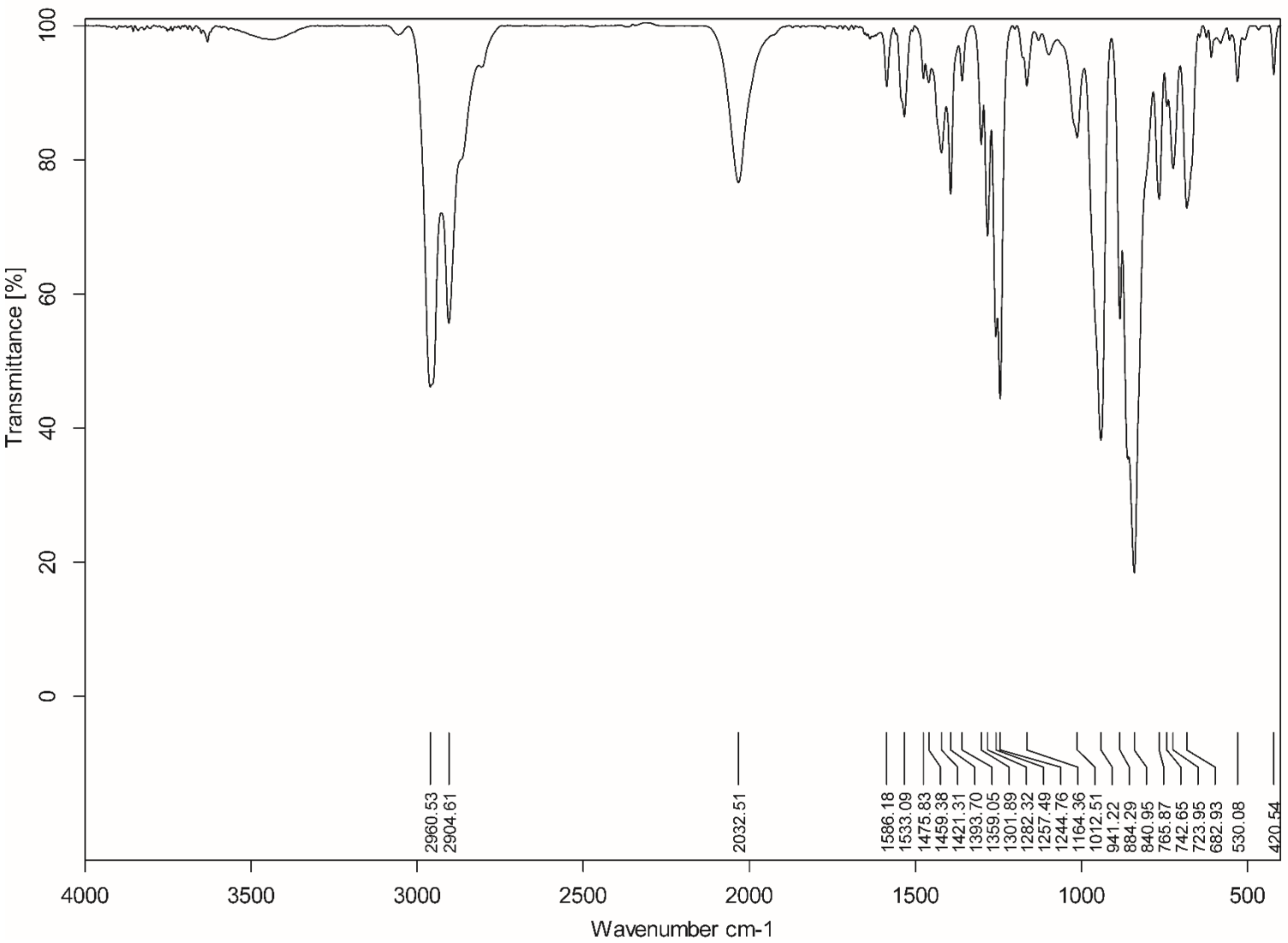


Figure SI 165. IR spectrum of compound **17**.

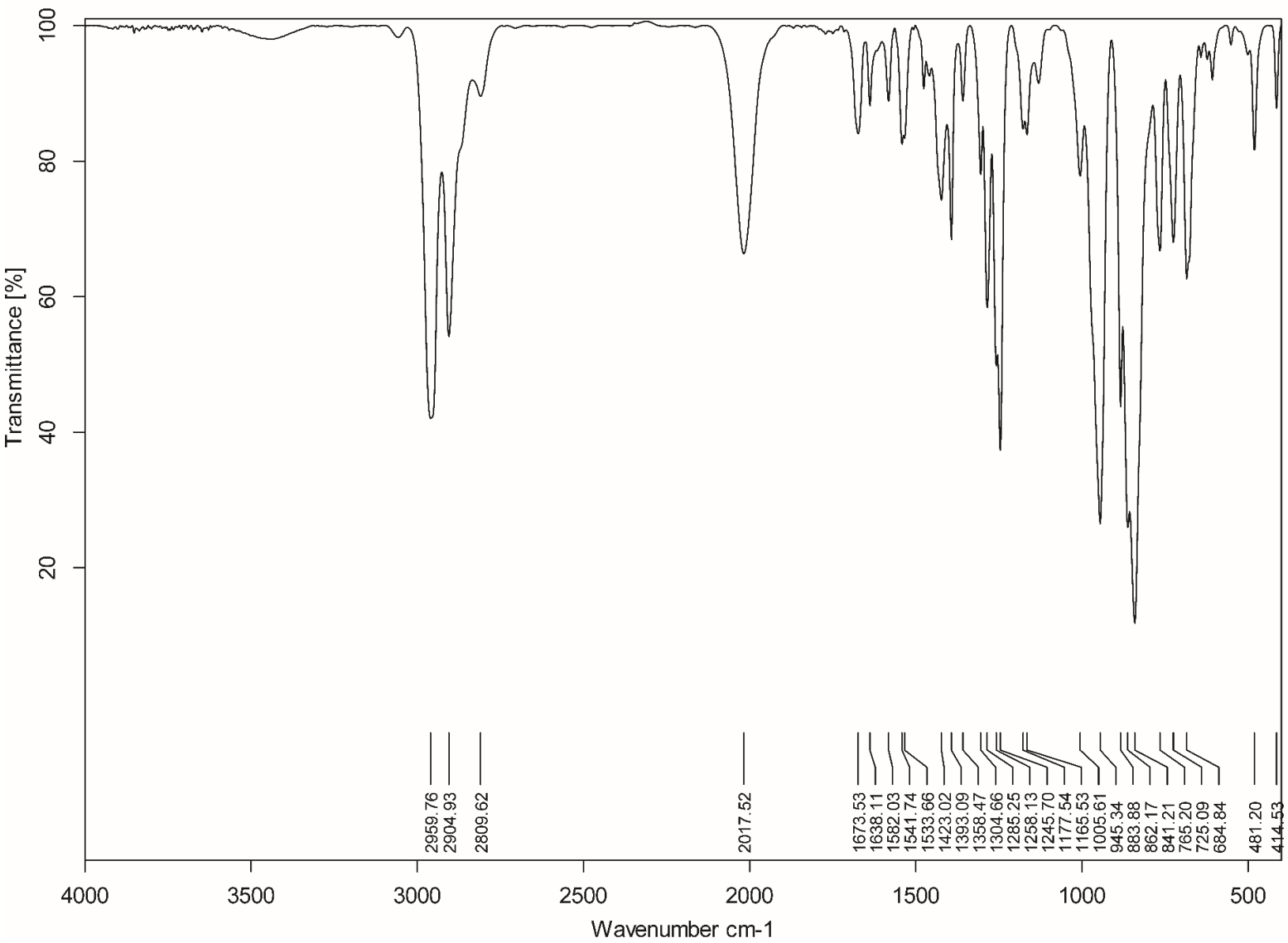


Figure SI 166. IR spectrum of compound **18**.

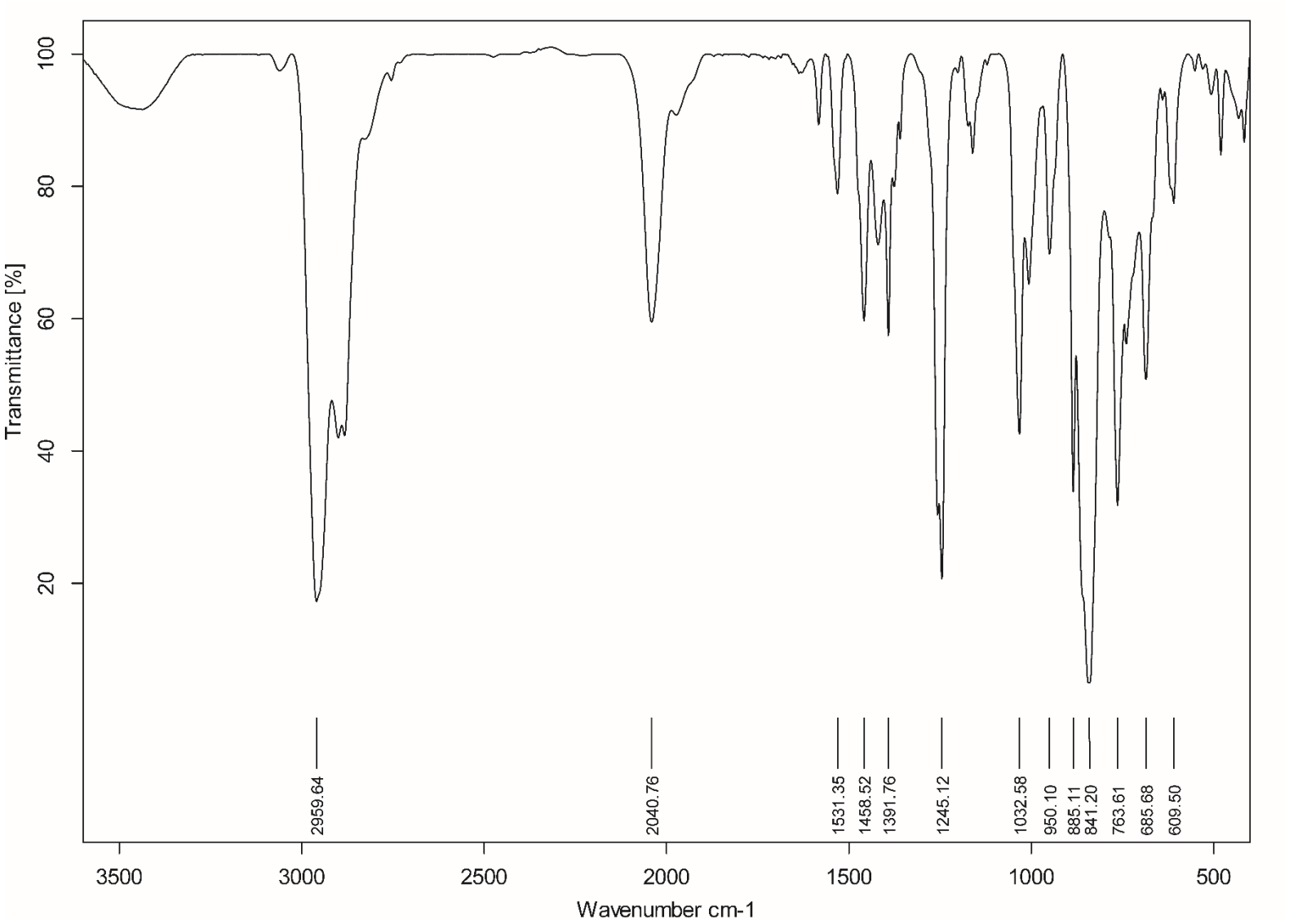


Figure SI 167. IR spectrum of compound **19**.

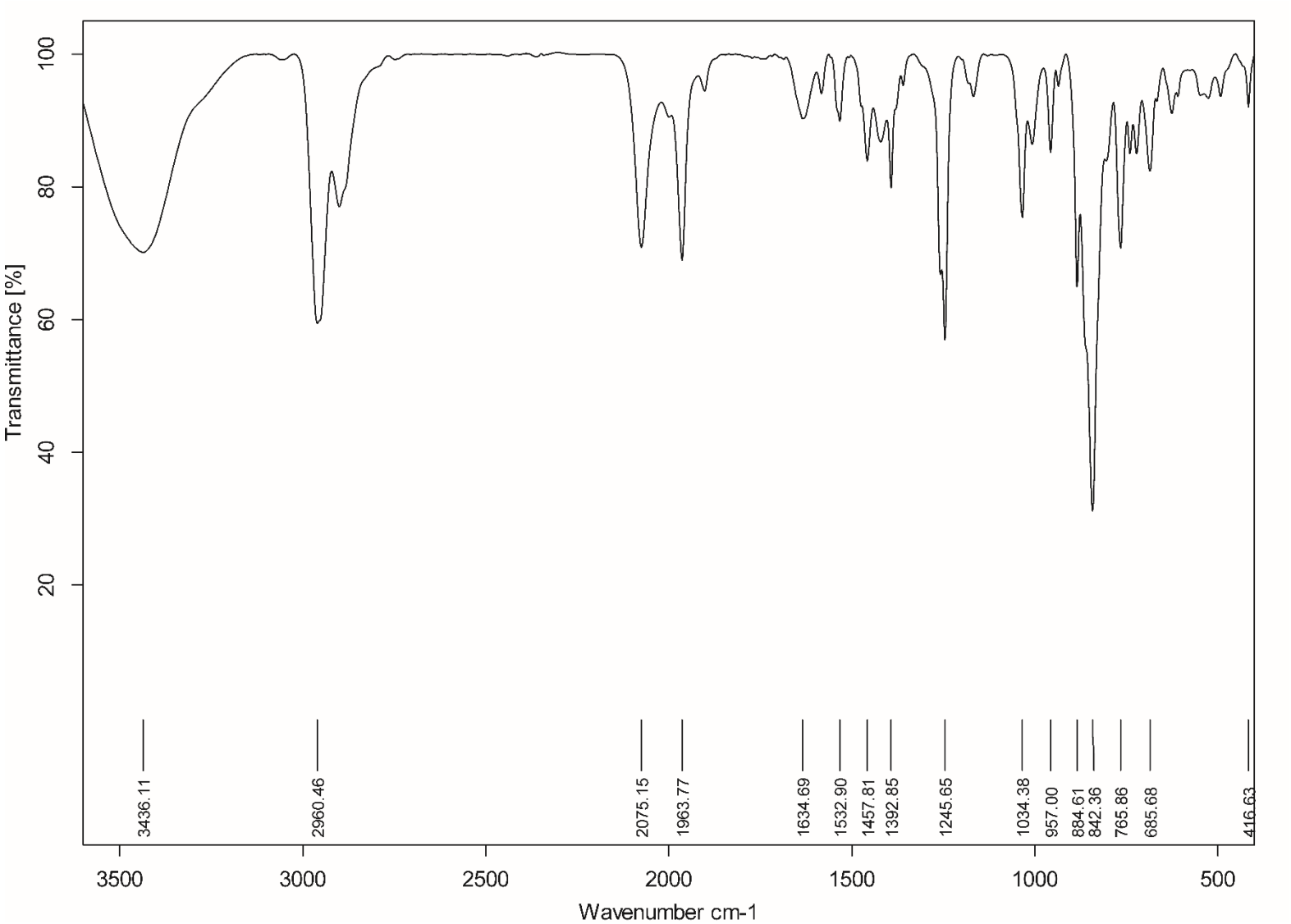


Figure SI 168. IR spectrum of compound **20**.

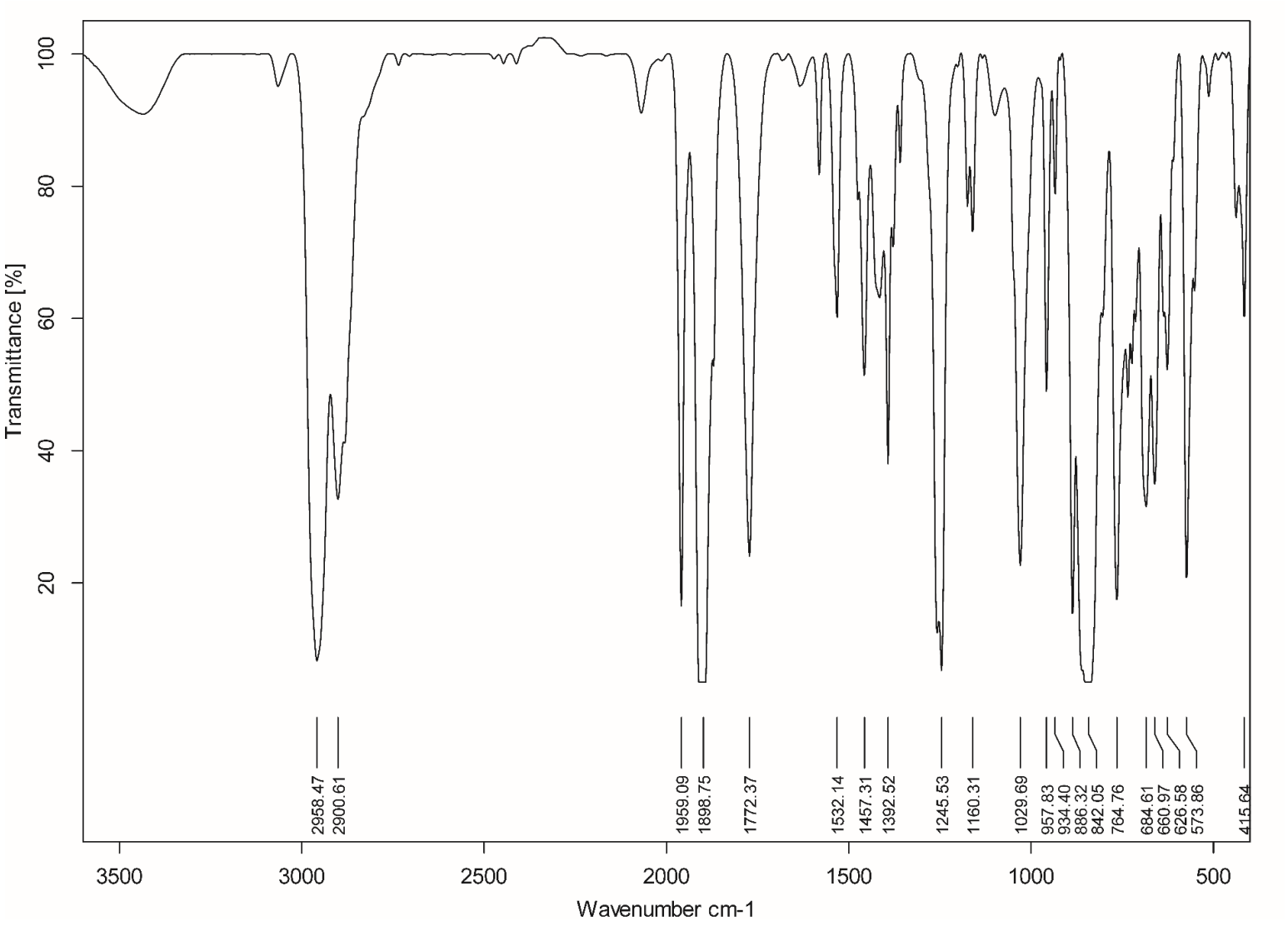


Figure SI 169. IR spectrum of compound **21**.