Electronic Supplementary Material (ESI) for Dalton Transactions

Deactivation of Gold(I) Catalysts in the Presence of Thiols and Amines – Characterisation and Catalysis

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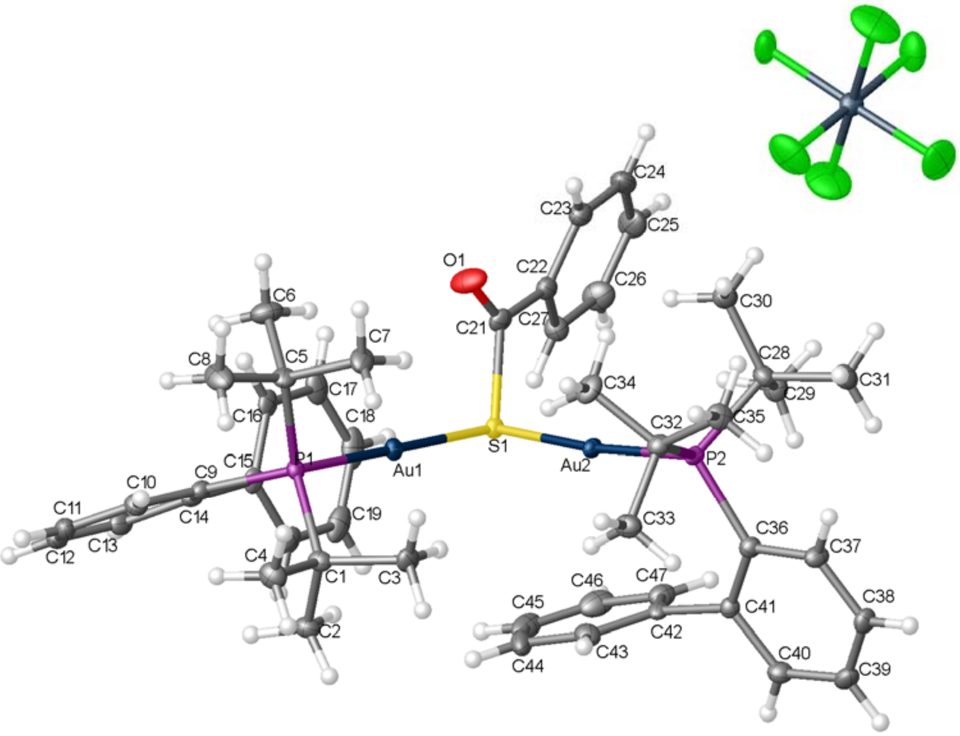
Supporting Information

Compound 6a


O1
C21
C22
C23
C24
C25
C26
C27
C6
C7
C8
C5
C17
C16
C18
C15
P1
C9
C10
C11
C12
C13
C14
Au1
S1
Au2
C19
C4
C1
C3
C2
C34
C32
C35
C30
C28
C29
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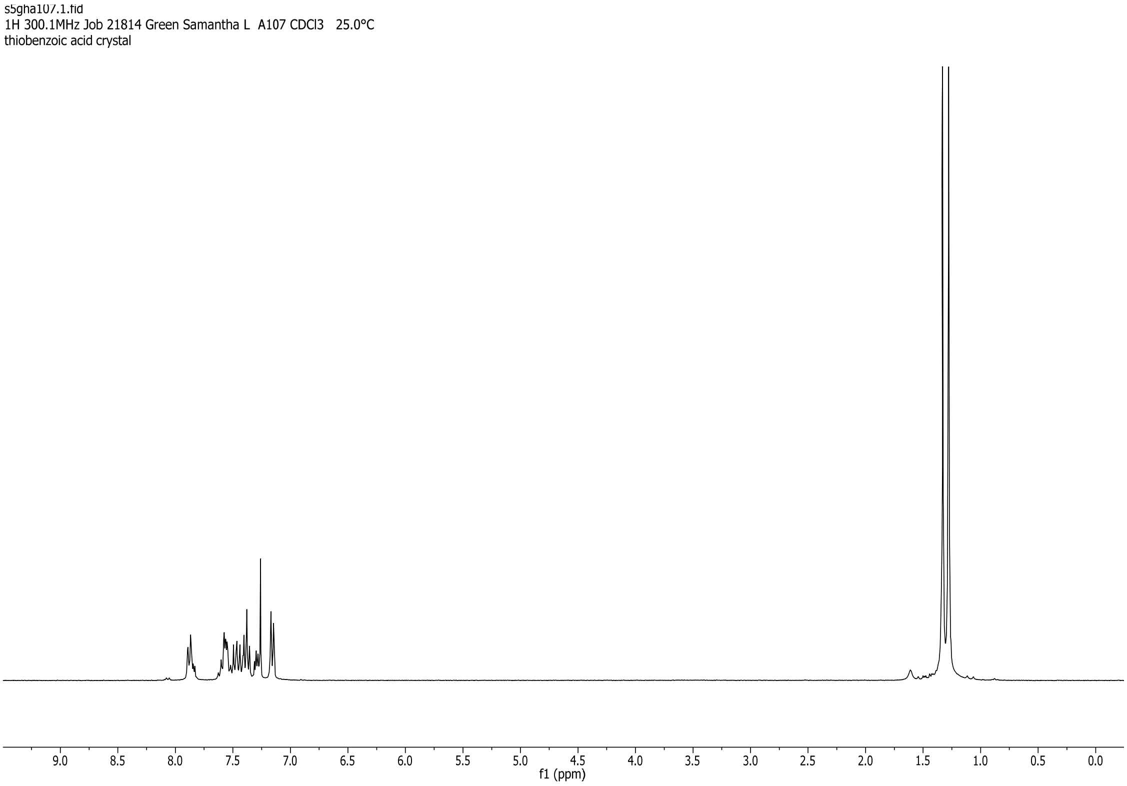
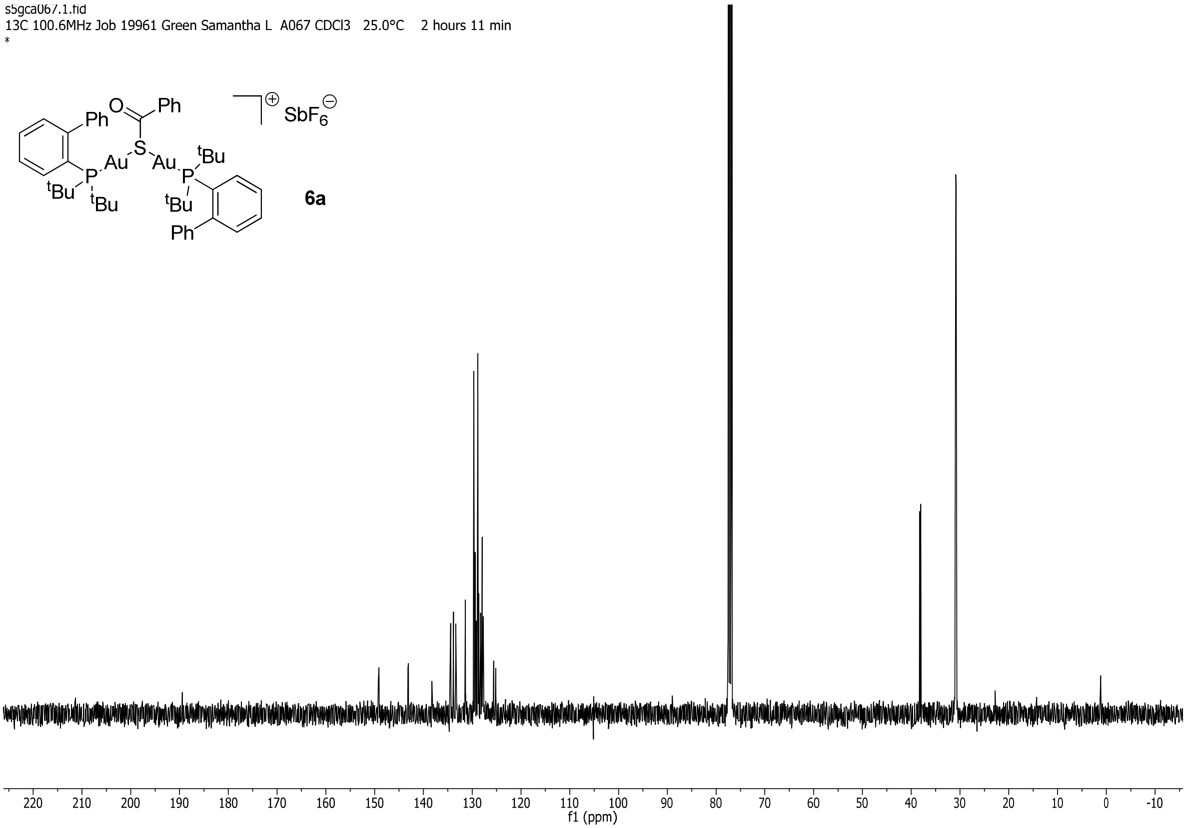
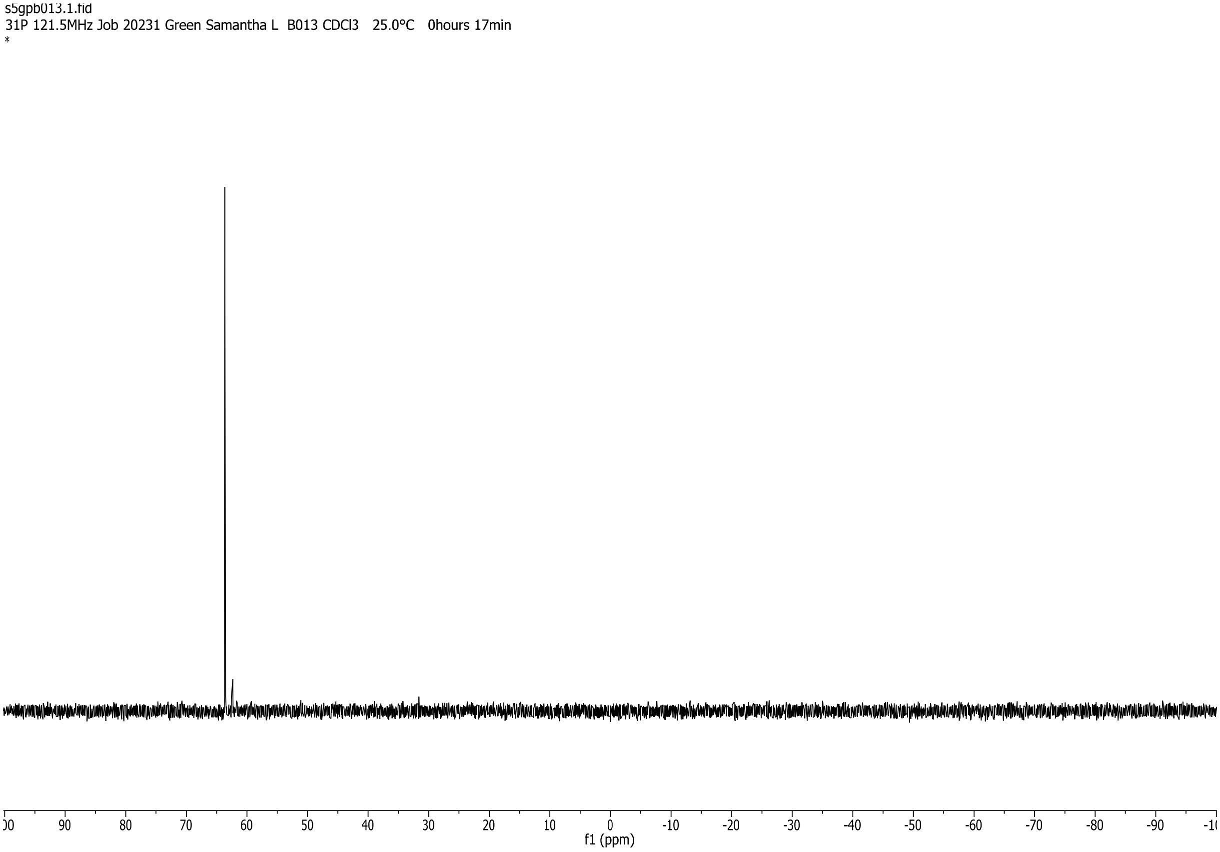
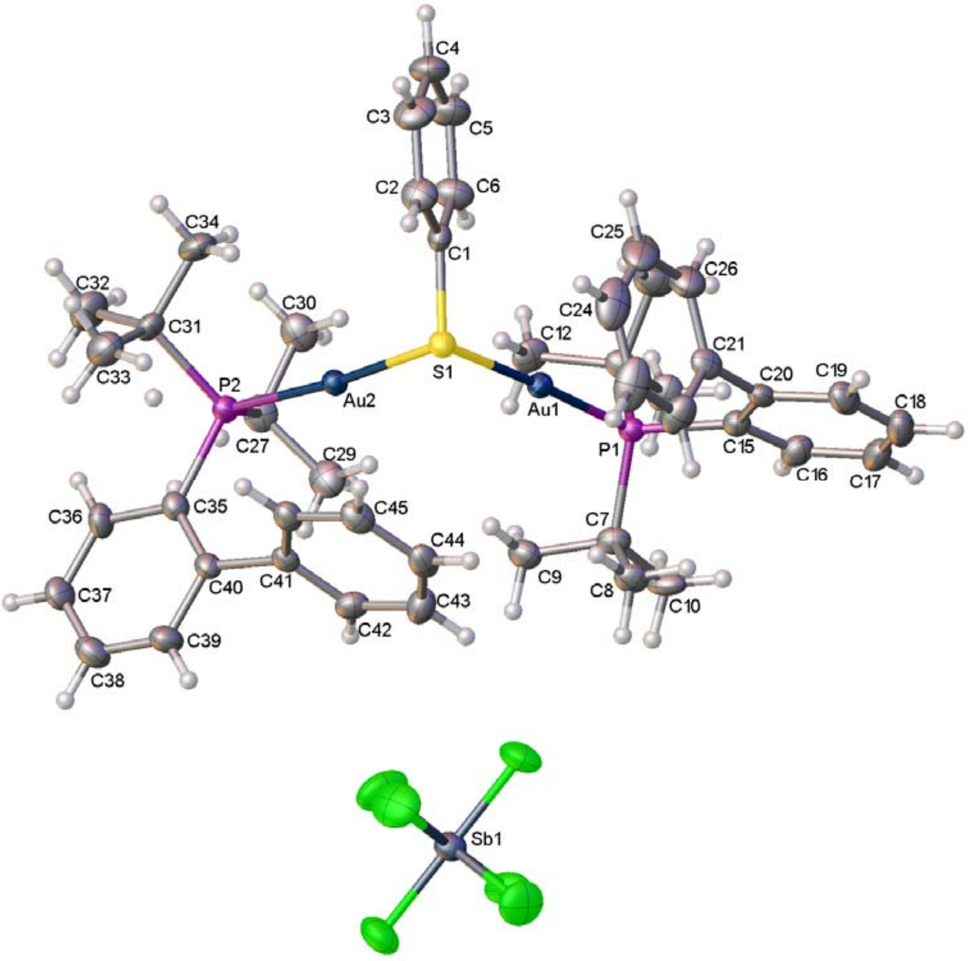
C43
C44
C45
C46
C47

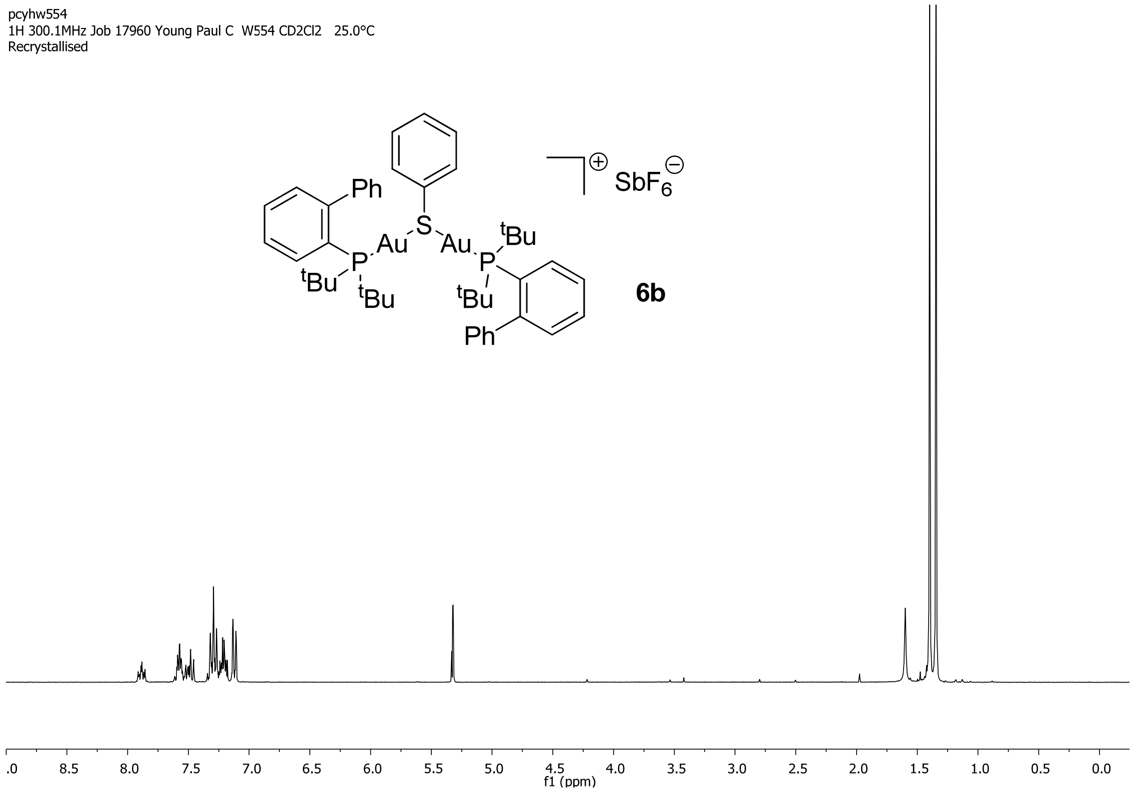

s5gha107.1.fid
1H 300.1MHz Job 21814 Green Samantha L A107 CDCl3 25.0°C
thiobenzoic acid crystal
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

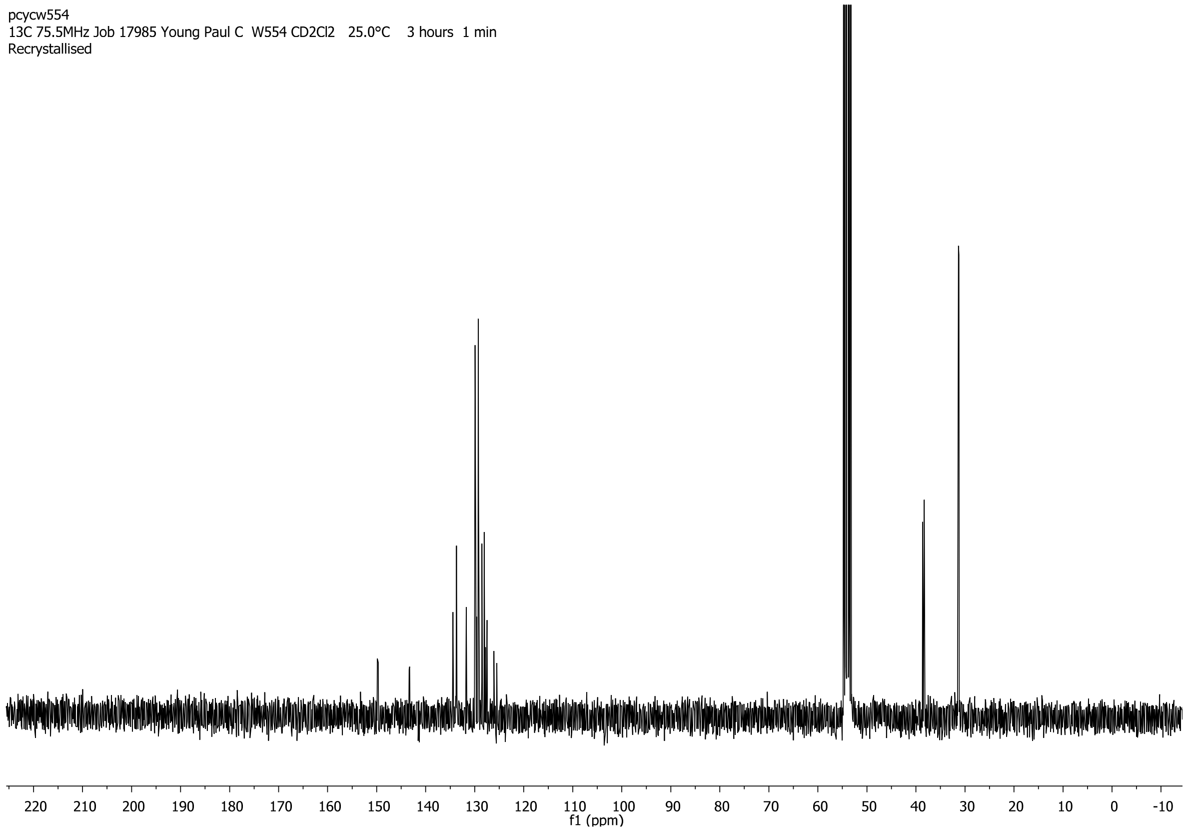

s5gca067.1.fid
13C 100.6MHz Job 19961 Green Samantha L A067 CDCl3 25.0°C 2 hours 11 min
*
Ph
O
Ph
S
Au
Au
P
P
tBu
tBu
tBu
tBu
Ph
SbF6
6a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

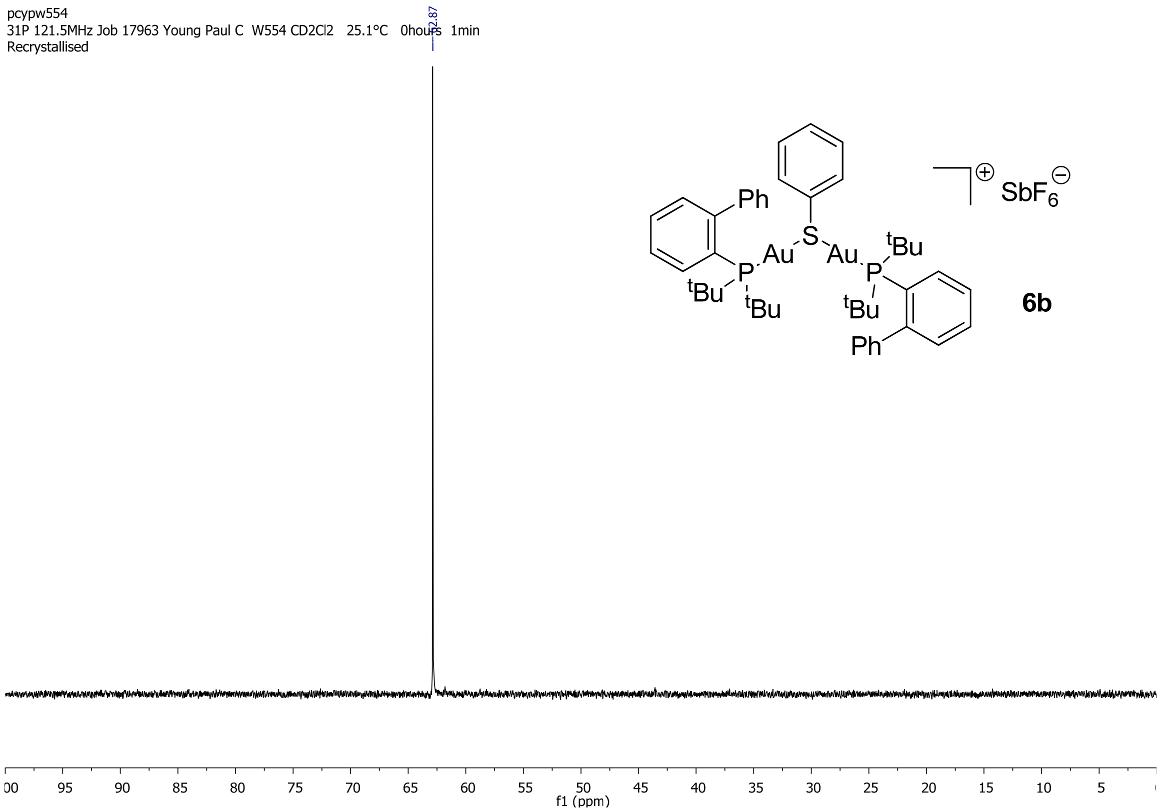

s5gpb013.1.fid
31P 121.5MHz Job 20231 Green Samantha L B013 CDCl3 25.0°C 0hours 17min
*
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

Compound 6b


C4
C3
C5
C2
C6
C34
C1
C25
C26
C32
C30
C24
C31
C12
C21
S1
C20
C19
C33
P2
Au2
Au1
C18
C27
P1
C15
C29
C16
C17
C36
C35
C45
C7
C44
C37
C40
C41
C9
C8
C43
C10
C42
C39
C38
Sb1

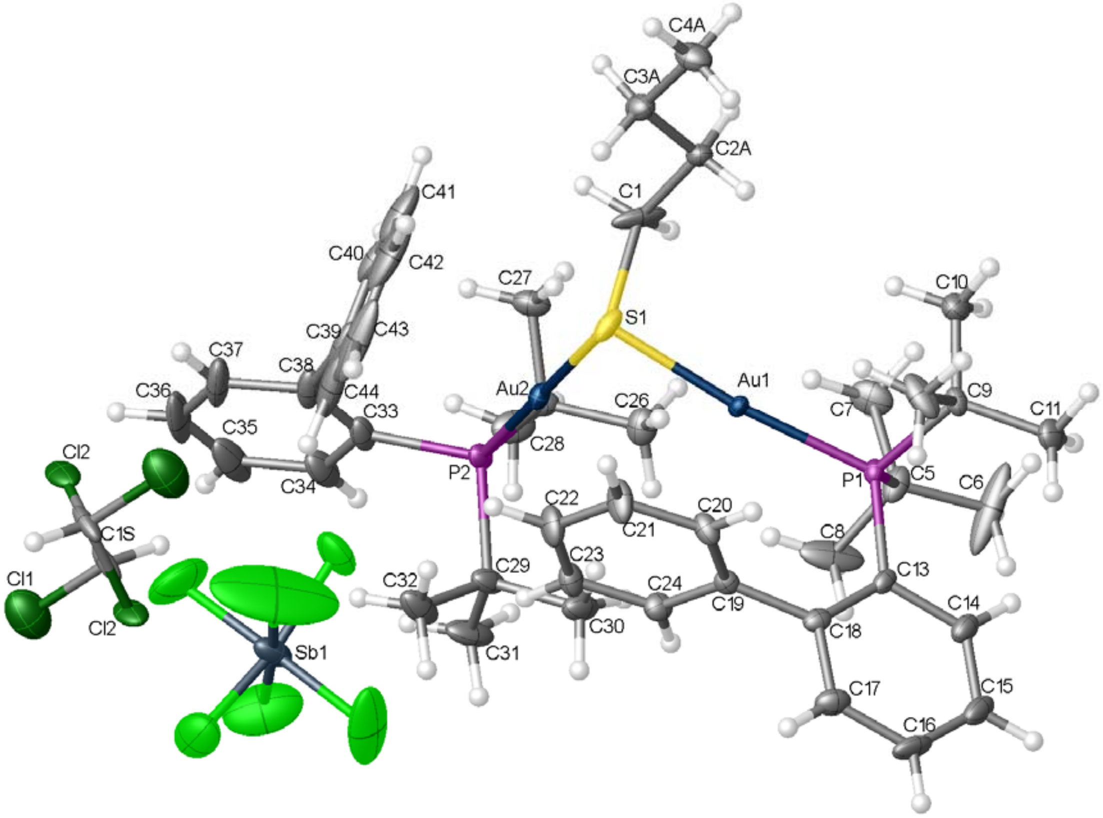

pcyhw554
1H 300.1MHz Job 17960 Young Paul C W554 CD2Cl2 25.0°C
Recystallised
Ph
S
Au
Au
P
P
tBu
tBu
tBu
tBu
Ph
SbF6
6b
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pcycw554
13C 75.5MHz Job 17985 Young Paul C W554 CD2Cl2 25.0°C 3 hours 1 min
Recystallised
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


pcypw554
31P 121.5MHz Job 17963 Young Paul C W554 CD2Cl2   25.1°C   0hours 1min
Recrystallised
62.87
Ph
Au
S
Au
P
P
tBu
tBu
tBu
tBu
Ph
SbF6
00
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

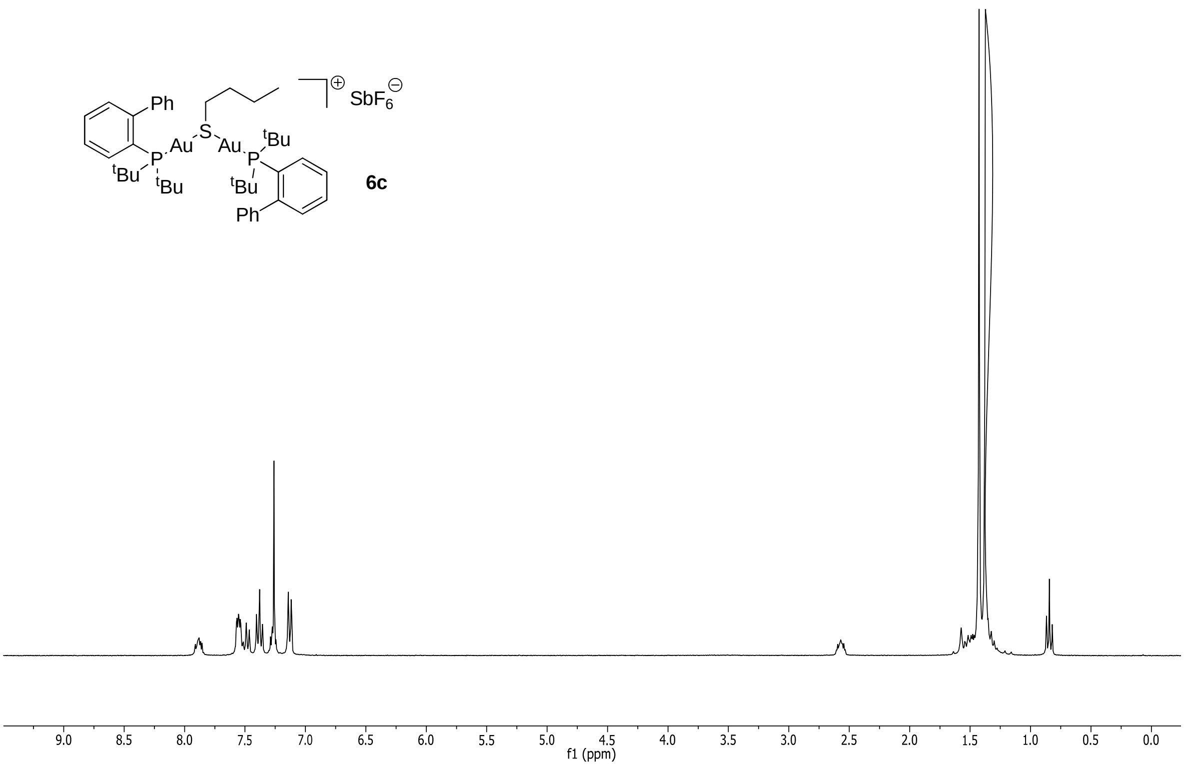
6b

Compound 6c

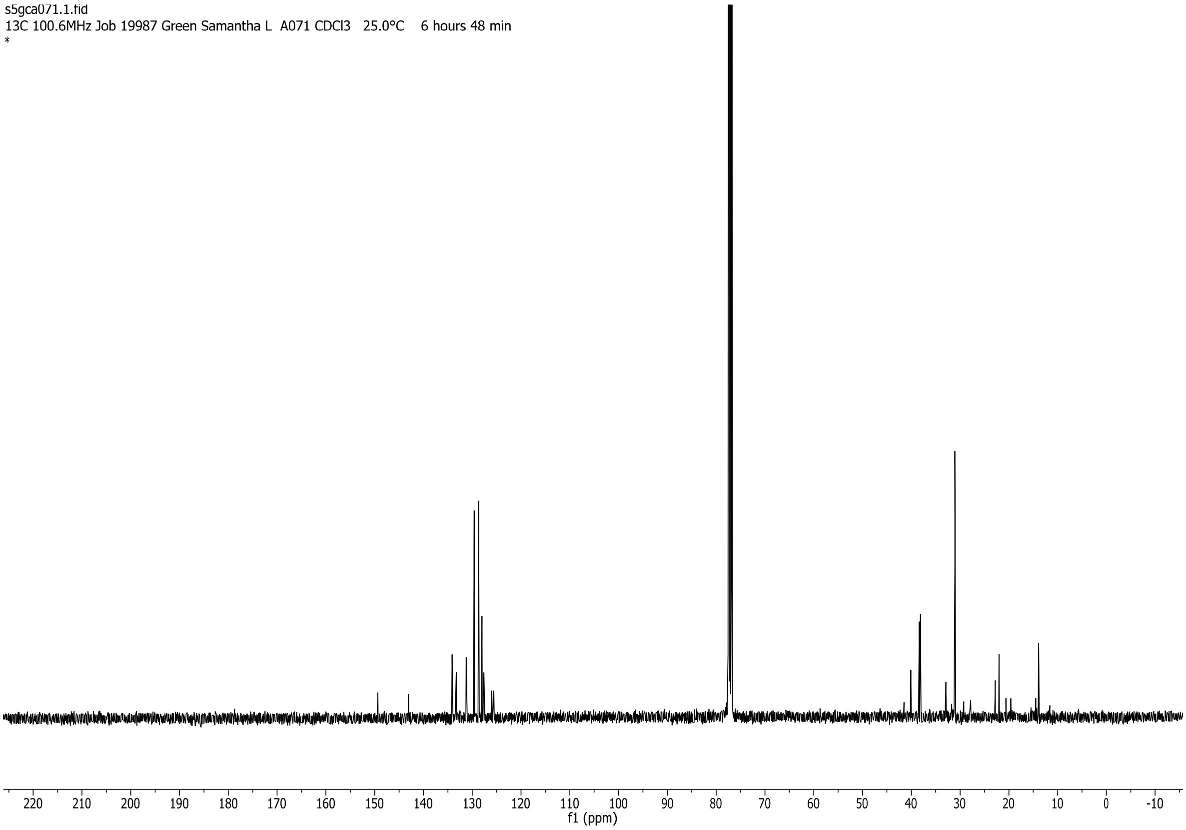


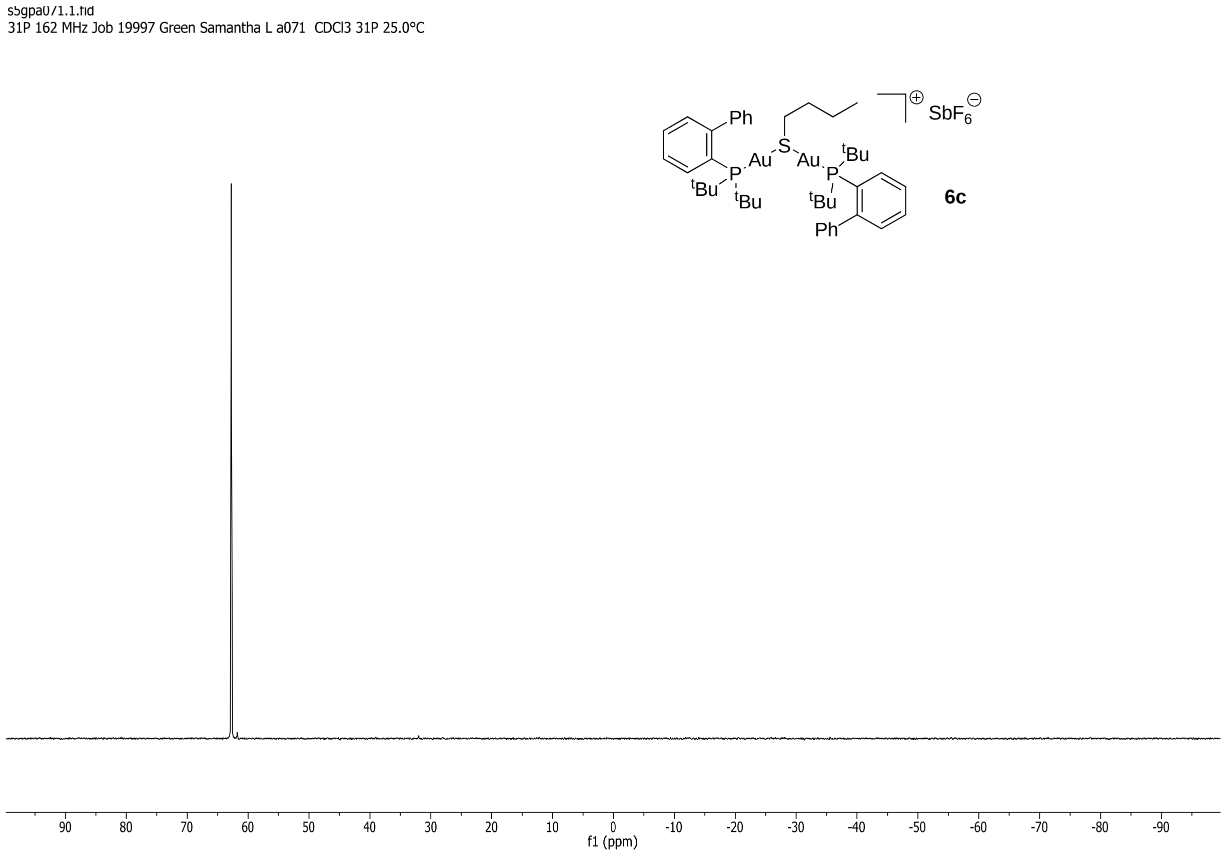
Only major components of disordered butyl chain, SbF_6 and $CHCl_3$ solvent are shown above. The butyl chain is disordered over two positions with relative occupancies of 0.514(8) and 0.486(2). Same distance restraints were applied to C-C distances The $CHCl_3$ solvent is disordered over a centre of inversion and the unique atomic positions have occupancies of 0.5 (C, H) 0.75 (Cl1) and 0.400(11) (Cl2) and 0.350(11) (Cl2a). Same distance restraints were applied to appropriate C-Cl distances [Cl1-C1S, C1S-Cl2, C1S-Cl2_$1, where $1 is the symmetry operation -X,-Y,2-Z]. Two F_6 components were modelled the major component F1a-F6a refined to an occupancy of 0.555(15) and the minor (F1b-F6b) to 0.445(15). Sb-F distances were restrained to be the same (SADI 0.02) and F-F distances within each component were restrained to be the same with twice the standard deviation of the Sb-F distance (SADI 0.04).

s5ghb107.1.fid
1H 300.1MHz Job 21815 Green Samantha L B107 CDCl3 24.9°C
butyl mercaptan

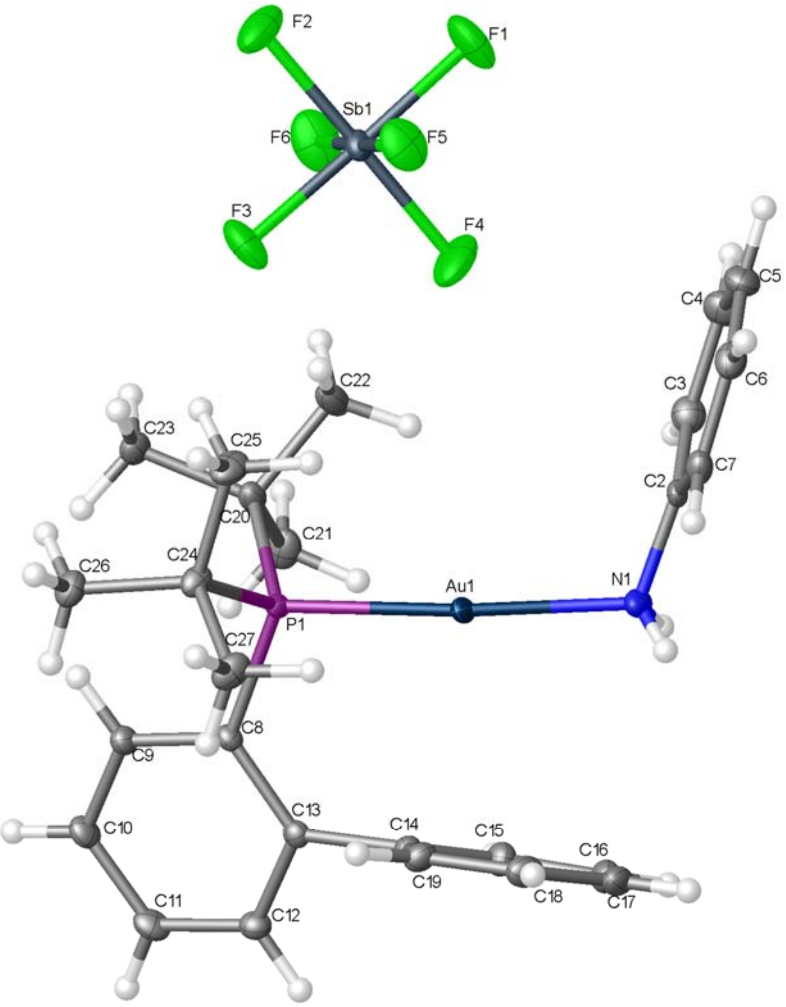


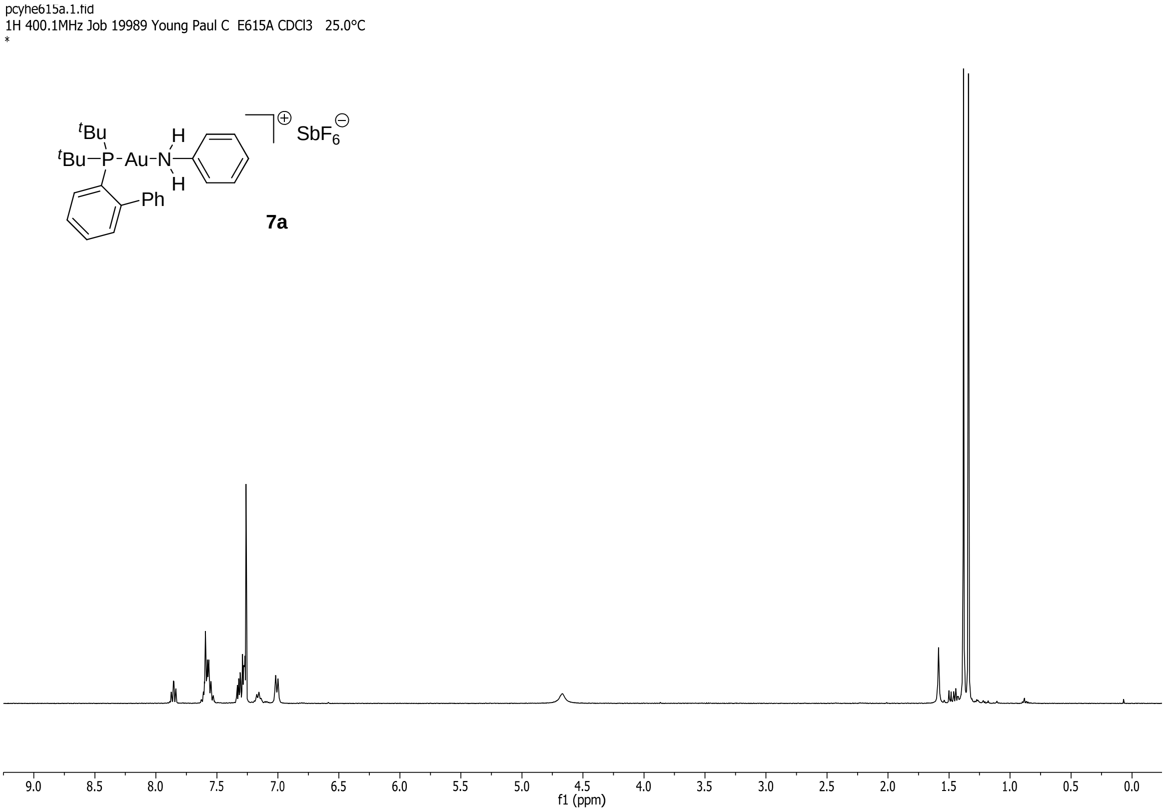
s5gca071.1.fid
13C 100.6MHz Job 19987 Green Samantha L A071 CDCl3 25.0°C 6 hours 48 min
*

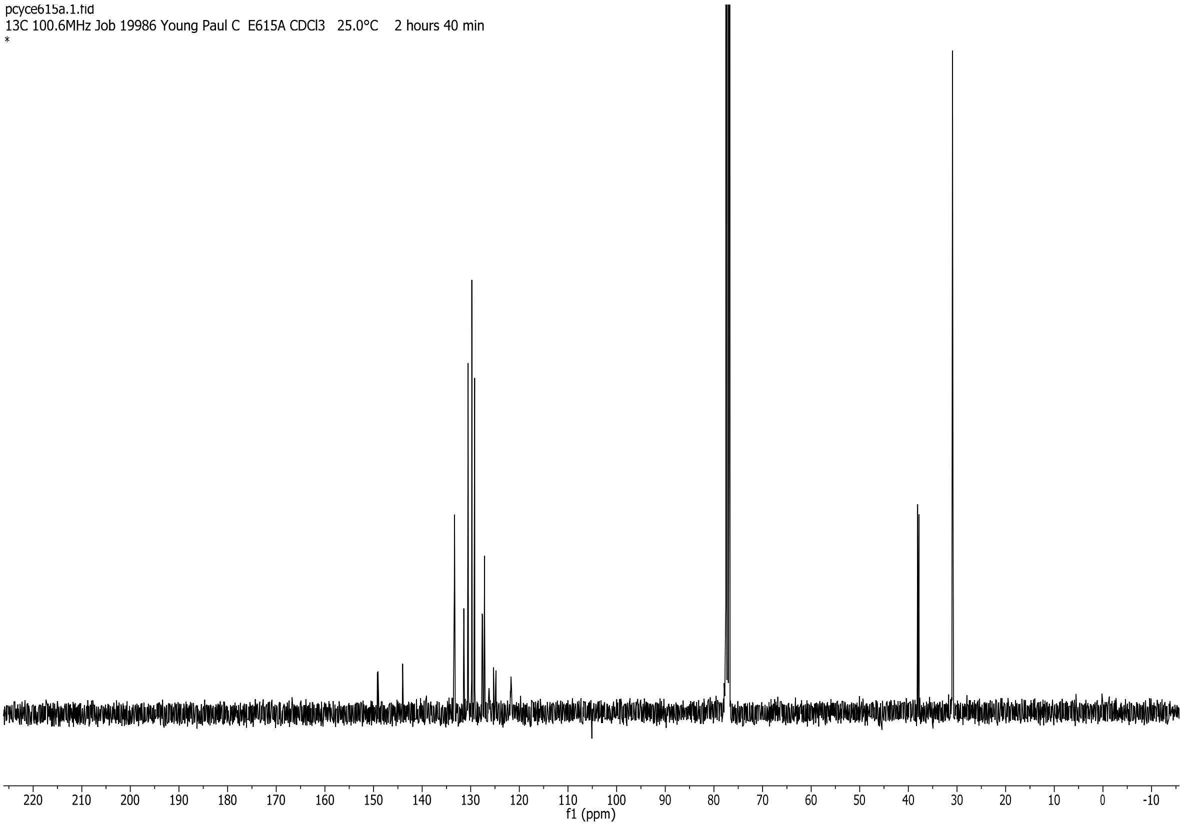


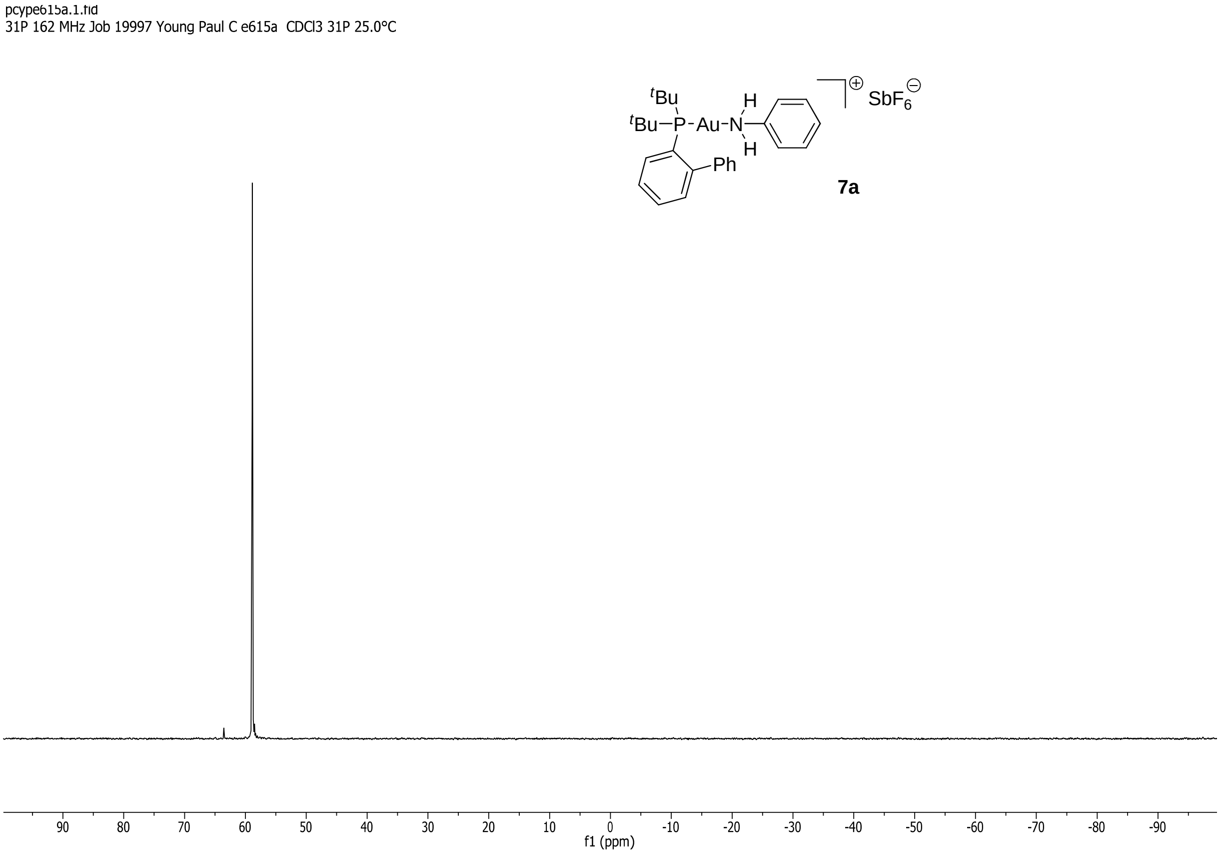

s5gpa071.1.fid
31P 162 MHz Job 19997 Green Samantha L a071 CDCl3 31P 25.0°C
Ph
Au
S
Au
P
P
tBu
tBu
tBu
tBu
Ph
SbF6
6c
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

Compound 7a


F2
F1
Sb1
F6
F5
F3
F4
C5
C4
C6
C3
C22
C23
C25
C7
C2
C20
C21
C26
C24
Au1
N1
P1
C27
C8
C9
C13
C10
C14
C15
C16
C19
C18
C17
C11
C12

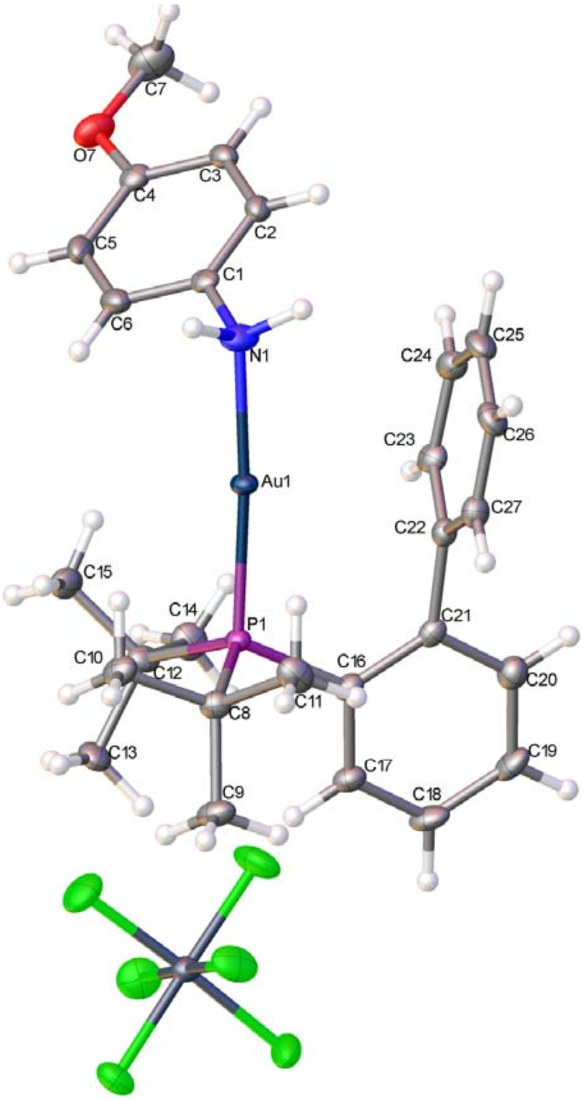

pcyhe615a.1.fid
1H 400.1MHz Job 19989 Young Paul C E615A CDCl3 25.0°C
*
tBu
tBu–P–Au–N
H
H
Ph
SbF6
7a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

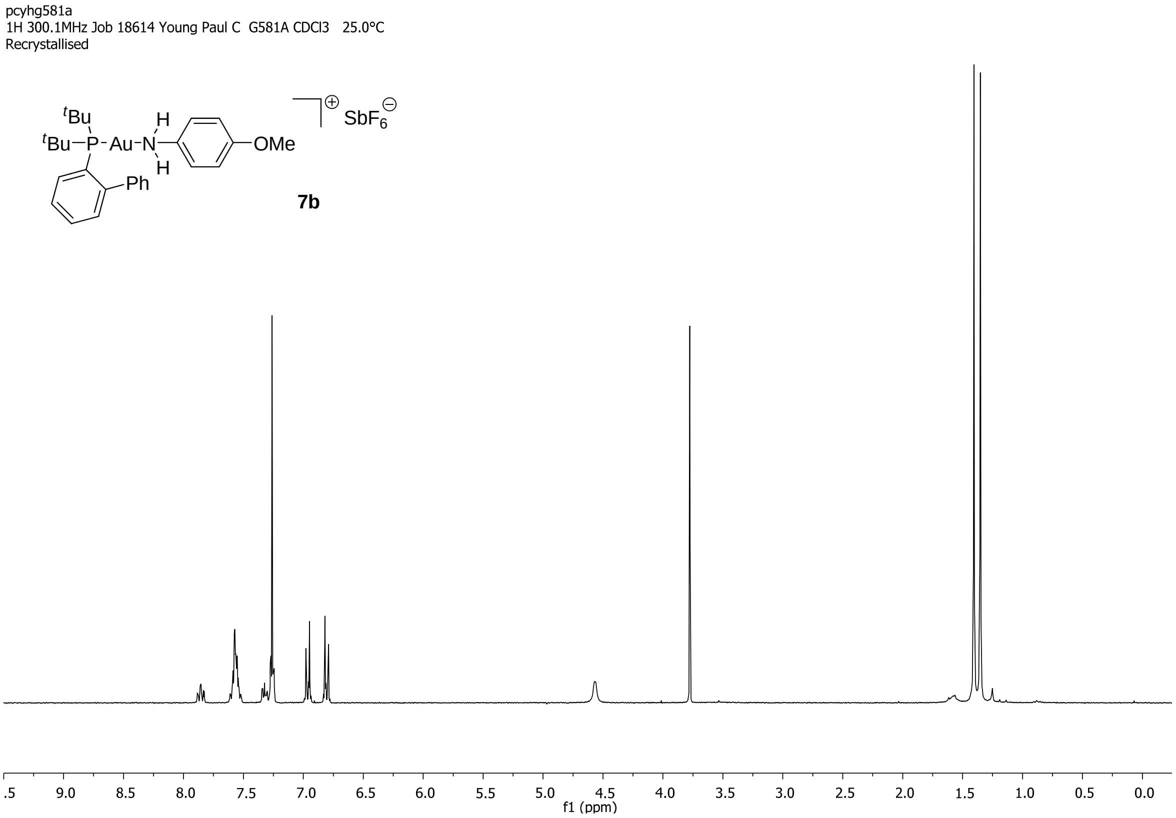

pcyce615a.1.fid
13C 100.6MHz Job 19986 Young Paul C E615A CDCl3 25.0°C 2 hours 40 min
*
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

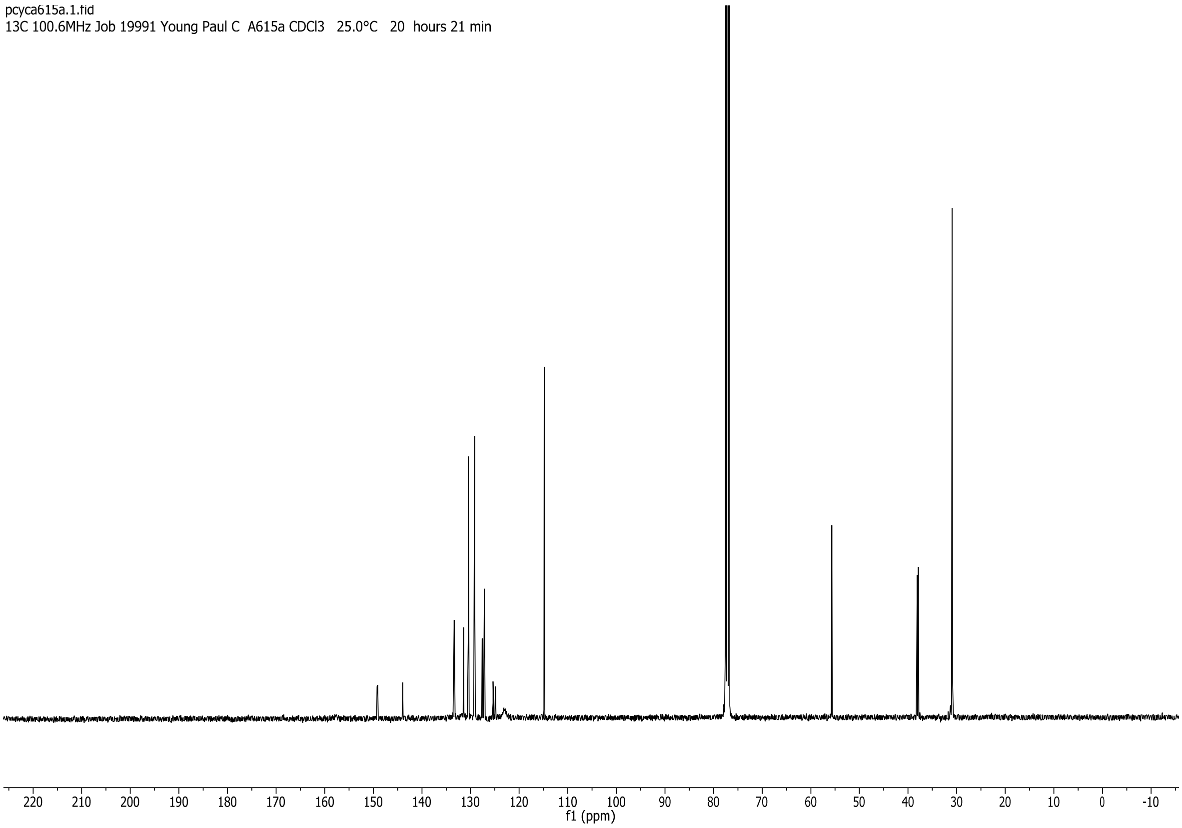

pcype615a.1.fid
31P 162 MHz Job 19997 Young Paul C e615a CDCl3 31P 25.0°C
tBu
tBu
P
Au
N
H
H
Ph
SbF6
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

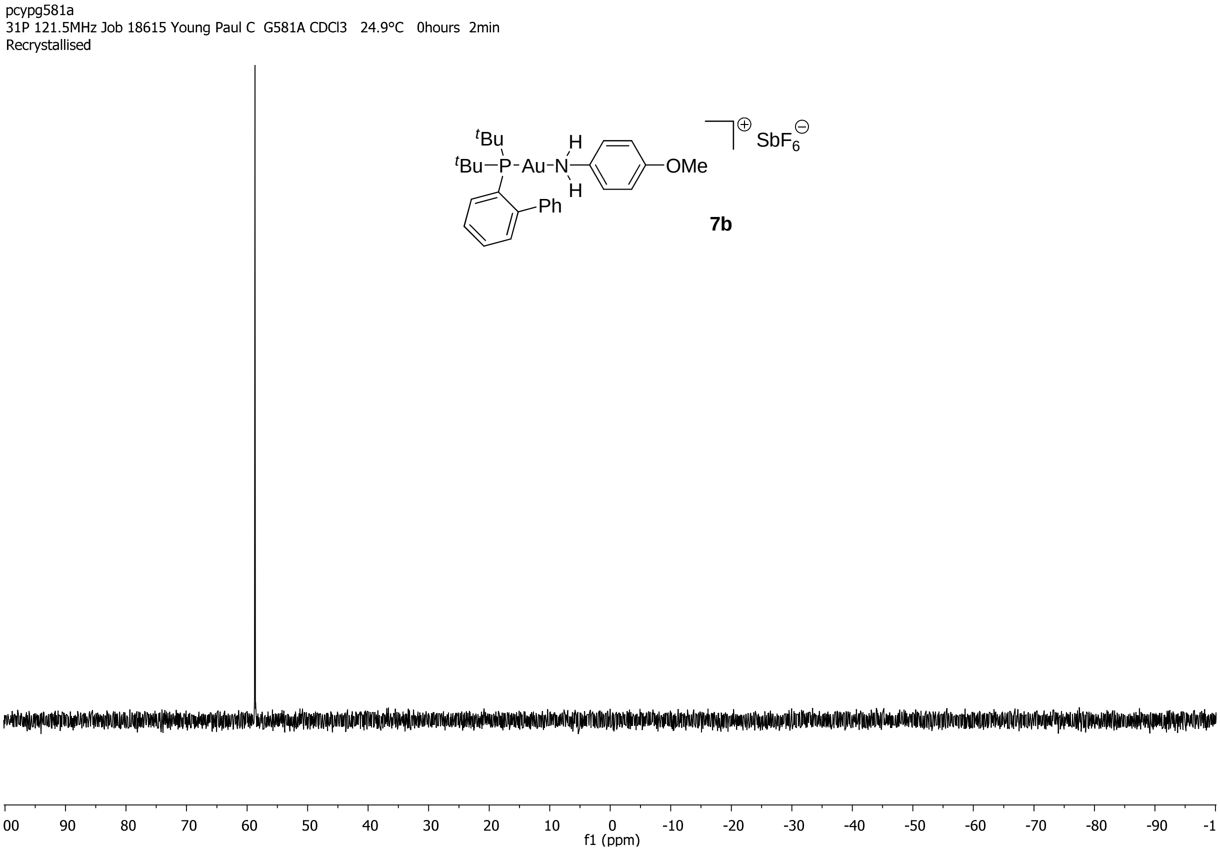
7a

Compound 7b

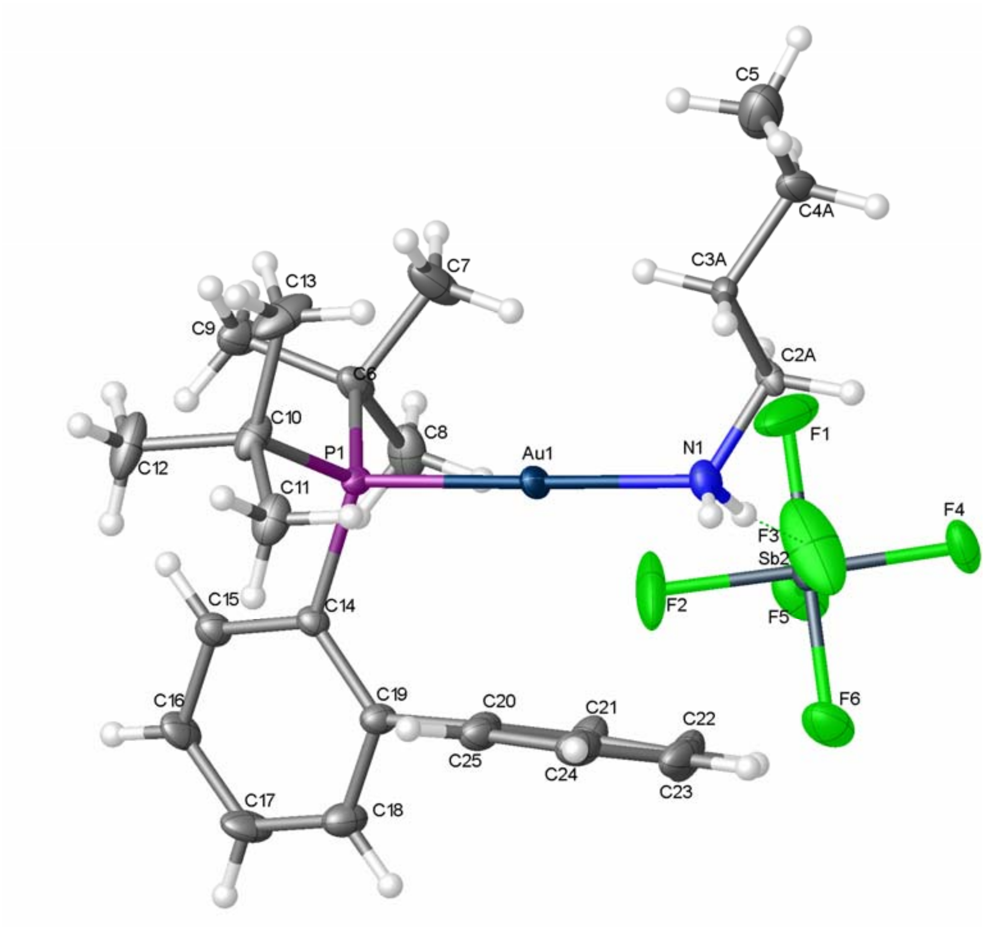

C7
O7
C3
C4
C2
C5
C1
C6
N1
C25
C24
C26
C23
Au1
C27
C22
C15
C14
P1
C21
C10
C12
C16
C20
C11
C8
C13
C19
C17
C18
C9


pcyhg581a
1H 300.1MHz Job 18614 Young Paul C G581A CDCl3 25.0°C
Recrystallised
^{t}Bu
^{t}Bu–P–Au–N
H
H
OMe
Ph
SbF_6^-
+
7b
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

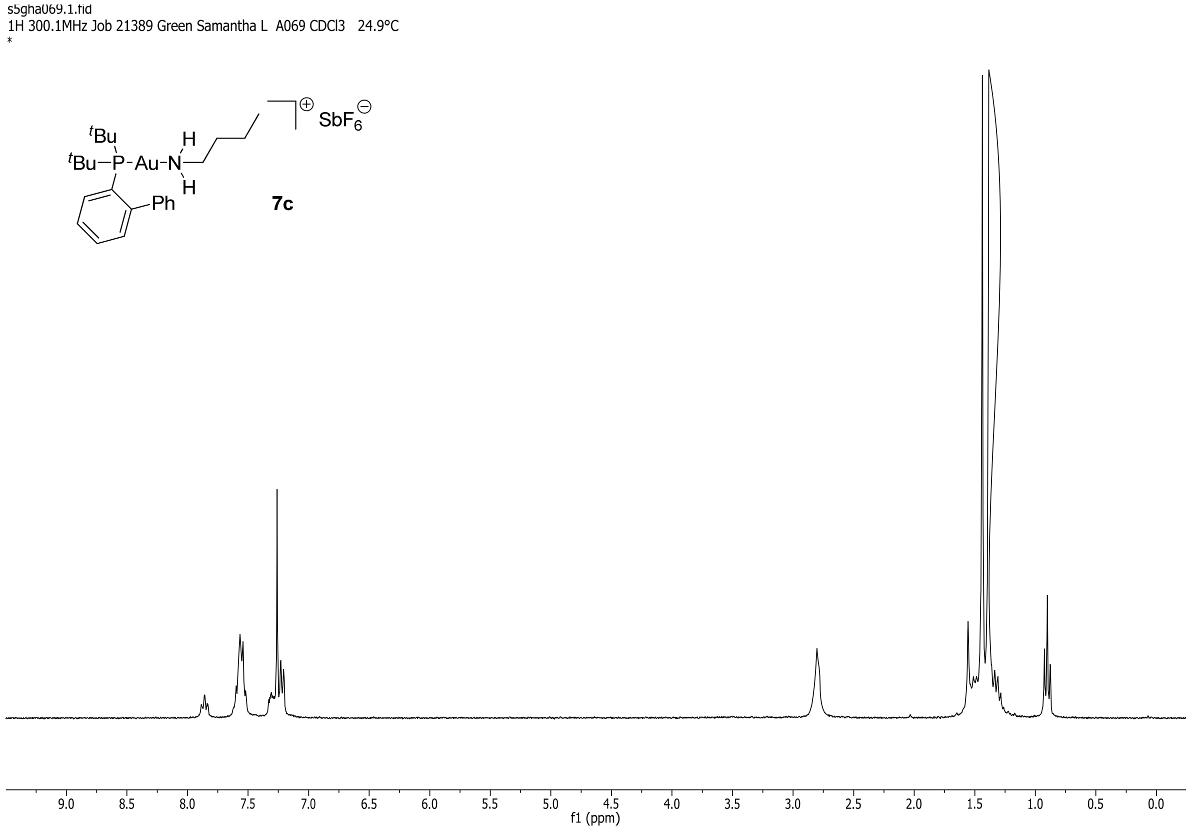

pcyca615a.1.fid
13C 100.6MHz Job 19991 Young Paul C A615a CDCl3 25.0°C 20 hours 21 min
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

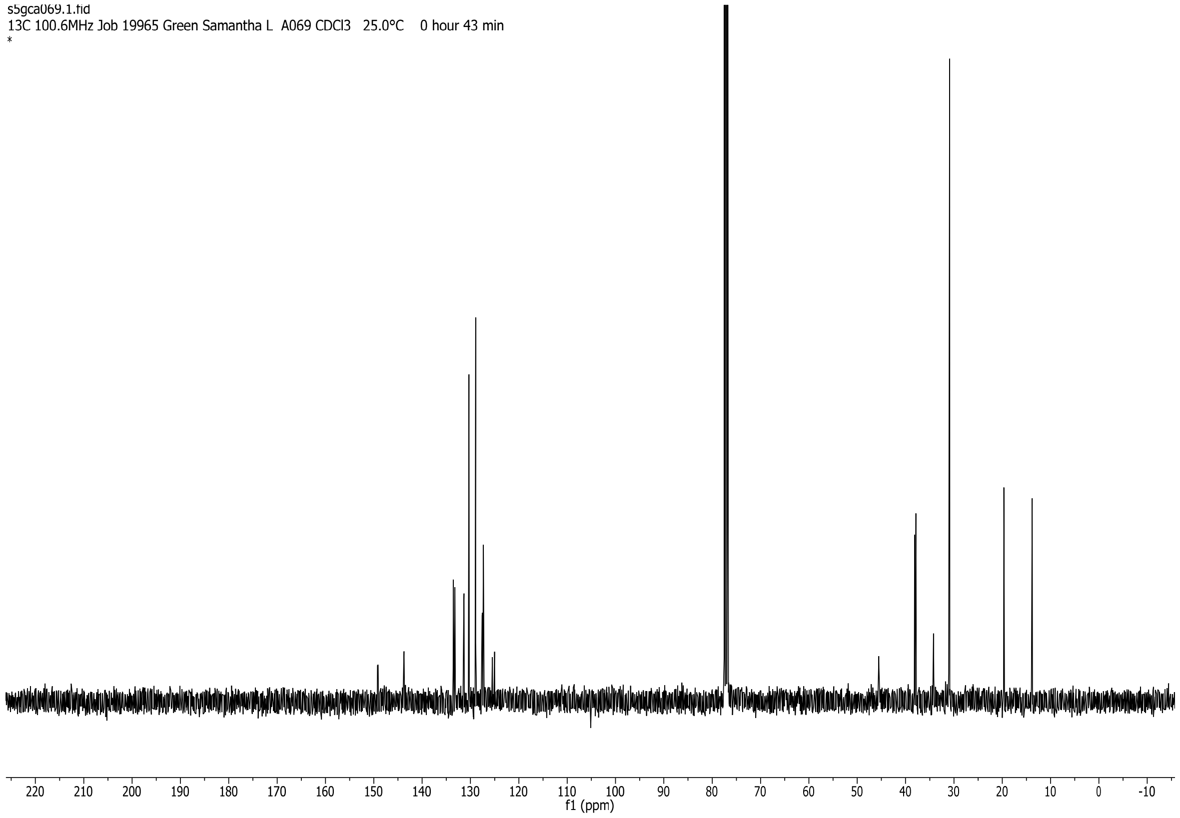

pcypg581a
31P 121.5MHz Job 18615 Young Paul C G581A CDCl3 24.9°C 0hours 2min
Recrystallised
tBu
tBu
P
Au
N
H
H
OMe
Ph
SbF6
7b
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

Compound 7c

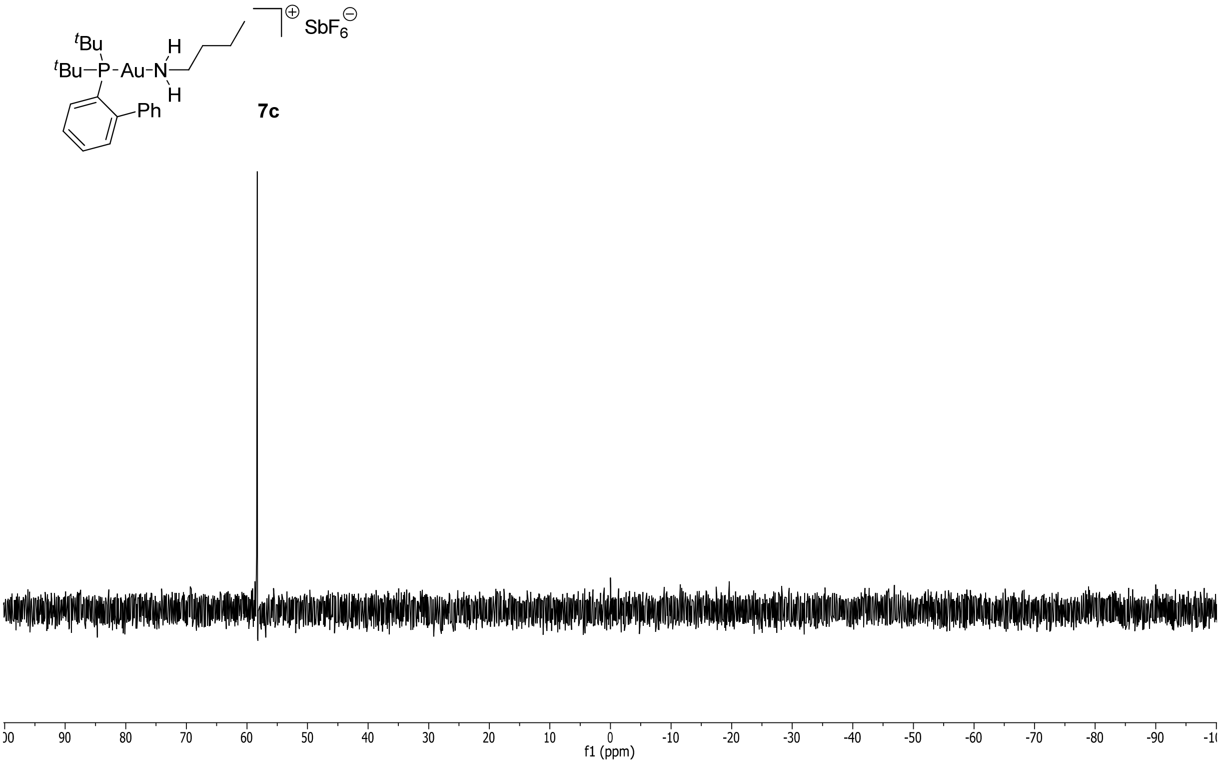


Only one component of the disordered n-butyl chain is shown, the two conformations have occupancies of 0.485(7) labels with suffix A and 0.515(7) for suffix B.


s5gha069.1.fid
1H 300.1MHz Job 21389 Green Samantha L A069 CDCl3 24.9°C
*
tBu
tBu–P–Au–N
H
H
Ph
⊕ SbF6 ⊖
7c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

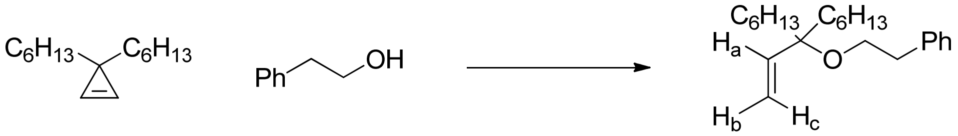

s5gca069.1.fid
13C 100.6MHz Job 19965 Green Samantha L A069 CDCl3 25.0°C 0 hour 43 min
*
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

s5gpc037.1.fid
31P 121.5MHz Job 20351 Green Samantha L C037 CDCl3 25.0°C 0hours 18min
Echavarren cat. + n-butylamine after crystallising



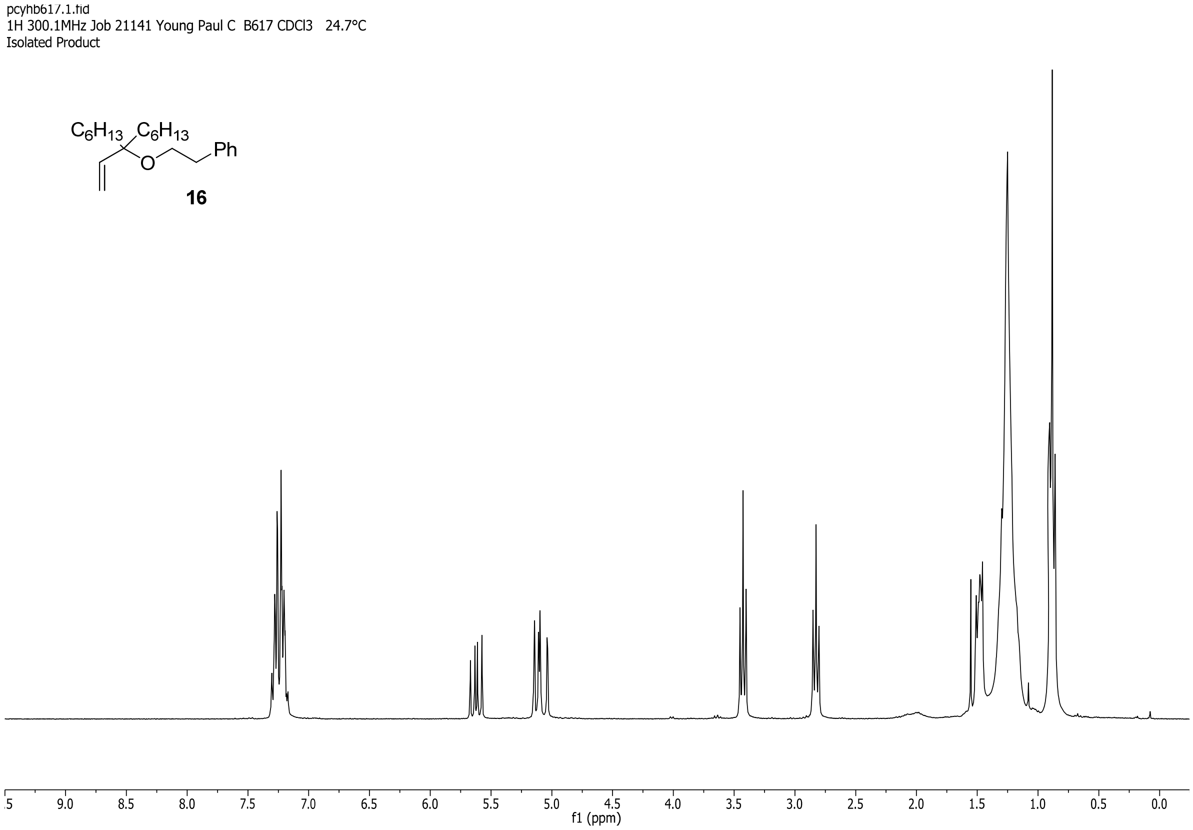
The following procedure was used to synthesis, isolate and characterise pure **16**. Conversions in Table 3 were determined by comparison with pure spectra obtained using this procedure.

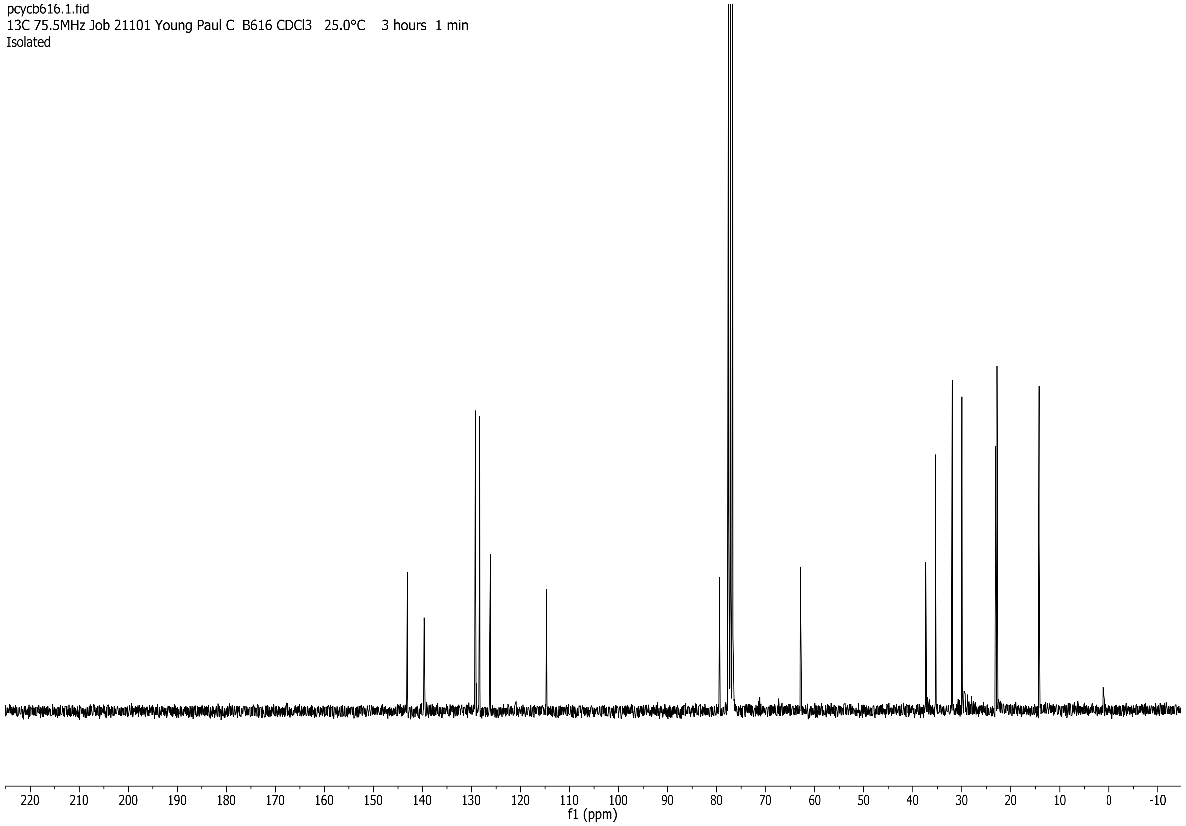
(2-((7-Vinyltridecan-7-yl)oxy)ethyl)benzene 16:



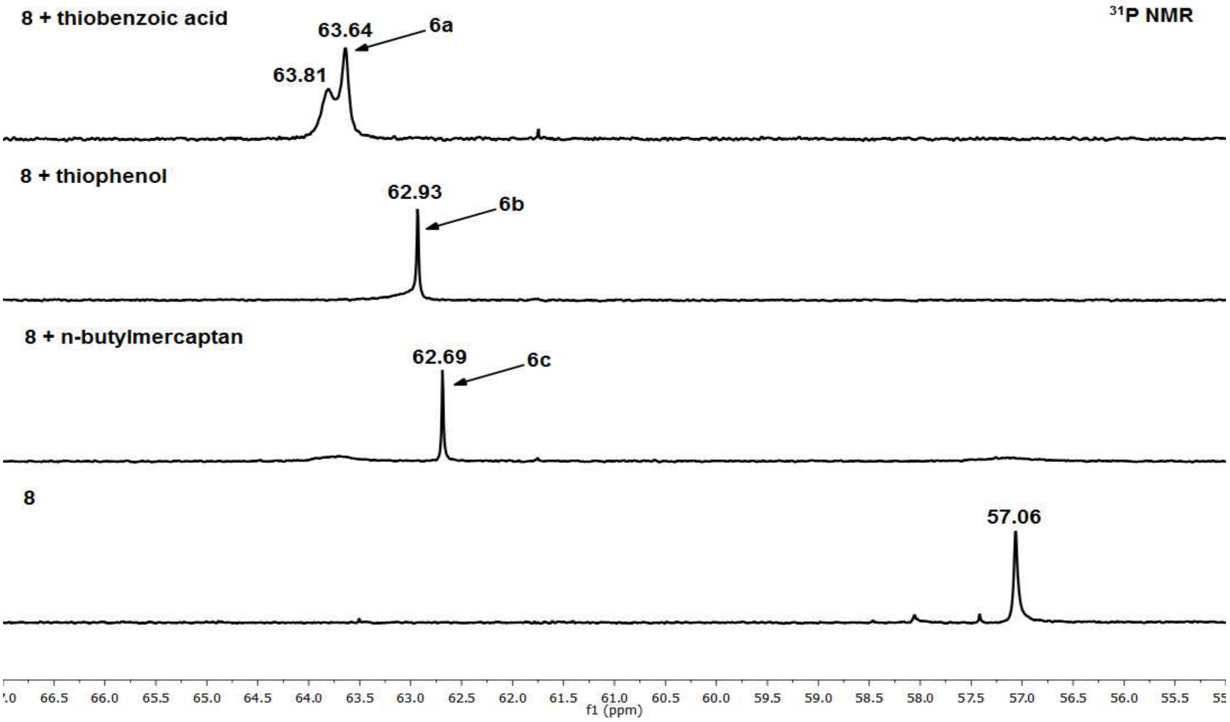
3,3-Dihexylcycloprop-1-ene **11** (14.8 mg, 0.071 mmol) was dissolved in CH_2Cl_2 (0.15 mL) and phenethyl alcohol (52 µL, 52.8 mg, 0.432 mmol) was added *via* Hamilton syringe. Catalyst **8** (2.7 mg, 0.0035 mmol) was added, and the solution was allowed to stir for 15 minutes at 20 °C. The reaction mixture was then filtered through a silica plug (40:1 petroleum ether:diethyl ether) and concentrated under reduced pressure. A ^{1}H NMR was obtained of the crude mixture showing that the tertiary allylic ether was the only product. The product was purified using flash column chromatography (neat petroleum ether → 40:1 petroleum ether:diethyl ether). The desired product **16** was obtained as a colourless oil (19.9 mg, 0.060 mmol, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33 – 7.15 (m, 5H, Ar-H), 5.62 (dd, *J*=17.6, 11.1, 1H, H_a), 5.13 (dd, *J*=11.1, 1.6, 1H, H_b), 5.07 (dd, *J*=17.6, 1.6, 1H, H_c), 3.43 (t, *J*=7.3, 2H, $OC\underline{H_2}CH_2$), 2.83 (t, *J*=7.3, 2H, $CH_2C\underline{H_2}Ph$), 1.54 – 1.09 (m, 20H, alkyl CH_2), 0.88 (t, *J*=6.7, 6H, $CH_2C\underline{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.1 (CH), 139.7 (C), 129.2 (CH), 128.3 (CH), 126.2 (CH), 114.7 (CH_2), 79.4 (C), 62.9 (CH_2), 37.4 (CH_2), 35.4 (CH_2), 32.0 (CH_2), 30.0 (CH_2), 23.1 (CH_2), 22.8 (CH_2), 14.3 (overlapping CH_3); IR ν_{max}/cm^{-1} 2929 s 2857 m (C-H), 1639 w (C=C), 1605 w 1496 m 1455 m (aromatic C=C), 1078 s (C-O-C); HRMS (APCI): *m*/*z* calcd for $C_{23}H_{42}ON$: 348.3261 $[M+NH_4]^+$; found: 348.3259.


pcyhb617.1.fid
1H 300.1MHz Job 21141 Young Paul C B617 CDCl3 24.7°C
Isolated Product
C6H13
C6H13
O
Ph
16
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pcycb616.1.fid
13C 75.5MHz Job 21101 Young Paul C B616 CDCl3 25.0°C 3 hours 1 min
Isolated
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{31}P NMR – 1:1 *S*-nucleophile:**8**



^{1}H NMR – 1:1 *S*-nucleophile:**8**