Supporting information for:

Wittig-Olefination *via* an Yttrium-Arrested Betaine

Mark R. Crimmin[a,b] and Andrew J. P. White[b]

[a]Dr. Mark R. Crimmin, Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

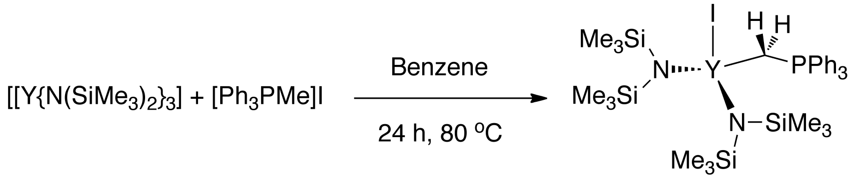
[b]Dr. Andrew J. P. White, Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, United Kingdom

E-mail: m.crimmin@imperial.ac.uk

General Experimental: All manipulations were carried out under standard Schlenk-line of glovebox techniques under an inert atmosphere of dinitrogen. Either a vacuum atmospheres HE-493 model glovebox, operating under an inert atmosphere which was tested by the colourmetric indicator obtained from the reduction of Cp_2TiCl_2 with Zn in diethylether, or a Saffron glovebox equipped with a Belle Technology O_2 operating at <5 ppm O_2 was employed.[1] Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for a minimum of 12 hours at 150 °C prior to use. Elemental analyses were conducted by Stephen Boyer of London Metropolitan University.

NMR spectra were obtained on Bruker 300 or 400 MHz machines, all peaks are referenced against residual solvent and values are quoted in ppm. Data were processed in Topspin or MestReNova.

Materials: C_6D_6 and d^8-toluene were purchased from Sigma-Aldrich and dried over activated 4 Å sieves before.[2] $[Y\{N(SiMe_3)_2\}_3]$ was prepared by salt-metathesis reactions of yttrium trichloride with $[K\{N(SiMe_3)_2\}]$ according to the literature.[3] Phosphonium salts were prepared by reaction of the phosphine with methyl iodide in dry diethyl ether and all remaining compounds were obtained from Sigma-Aldrich and used as received.

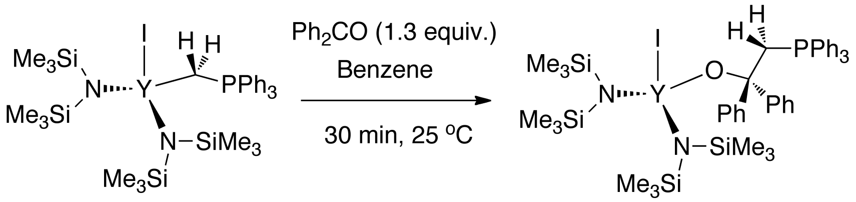


1 - δ ^{31}P = + 30.9

*Synthesis of **1**:* In a glovebox, [Y{N(SiMe$_3$)$_2$}$_3$] (500 mg, 0.88 mmol) and methyltriphenylphosphonium iodide (356 mg, 0.88 mmol) were weighed out separately and transferred to a Schlenk tube. The tube was sealed, removed from the box and benzene (20 mL) added. The mixture was heated to 80 ^{o}C for 20 h. After cooling to room temperature two different workup procedures were applied.

Method A: The mixture was filtered and concentrated to approximately 2.5 mL. n-Hexane (30 mL) was carefully added to this solution to form two layers. Slow diffusion of n-hexane into the concentrated benzene solution over 48 h at room temperature resulted in precipitation of impure unreacted [PhP$_3$Me]I (116 mg). Following filtration, concentration of the mother liquor to 10 mL followed by storage at -18 ^{o}C gave **1** as colourless crystals (334 mg, 0.411 mmol, 47%). **1** was isolated by filtration. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 0.45 (s, 36 H), 1.38 (d, 2H, $^{2}J_{P\text{-}H}$ = 16.0 Hz), 7.03-7.06 (m, 12H), 7.53-7.58 (m, 6H); ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 5.66, 129.37, 129.49, 132.90, 133.09, 133.19 remaining resonances not observed; ^{31}P NMR (162 MHz, C$_6$D$_6$) δ +30.9. Elemental Anal. Calc for C$_{31}$H$_{53}$IN$_2$PSi$_4$Y; C, 45.80; H, 6.57; N, 3.45 found C, 45.67; H, 6.43; N, 3.32.

Method B: The mixture was filtered and the benzene was removed under reduced pressure. n-Hexane (20 mL) was added to the mixture and then removed under reduced pressure to give crude **1** as a glassy crystalline solid (627 mg). Crystals of **1** were obtained by extraction of the crude product into (2 x 30 mL portions) n-hexane and storage at -20 °C (due to the low solubility of the product in the solvent mass recovery of this method exceptionally low ~5%). Although X-ray quality crystals were obtained from this experiment and NMR data proved identical to those provided above, repeated attempts to acquire accurate CHN analysis on this material failed. The details of these experiments are as follows: Elemental Anal. Calc for $C_{31}H_{53}IN_2PSi_4Y$; C, 45.80; H, 6.57; N, 3.45 found attempt 1 C, 39.30; H, 4.74; N, 1.55 attempt 2 39.18; H, 5.23; N, 1.72 attempt 3 C, 39.94; H, 4.64; N, 1.14.



1 - δ ^{31}P = + 30.9

2 - δ ^{31}P = + 16.0

Synthesis of ***2****:* Crude **1** was used directly in this reaction. In a glovebox, **1** (200 mg, 0.25 mmol) and benzophenone (60 mg, 0.32 mmol, 1.3 equiv.) were weighed into a Schlenk-tube. The tube was sealed and removed from the box and attached to a vacuum line. Benzene (10 mL) was added *via* cannula, and the reaction mixture stirred for 30 min. The solvent was removed *in vacuo* and the resulting white solid washed thoroughly with two 20 mL portions of n-hexane. The product was dried under vacuum and **2** was isolated as a white powder (190 mg, 0.19 mmol 76 %). X-ray quality crystals were obtained by slow diffusion of n-hexane into a concentrated benzene solution. ^{1}H NMR (400 MHz, C_6D_6) δ 0.55 (s, 36H), 5.06 (d, 2H, $^{2}J_{P\text{-}H}$ = 11.2 Hz, $-CH_2PPh_3$), 6.78-6.81 (m, 6H, J = 8.0, 8.0 and 4.0 Hz, $-PC_6H_5$), 6.88-6.92 (m, 6H, $-PC_6H_5$), 6.92-6.95 (m, 6H, $-OC(C_6H_5)_2$), 7.13-7.19 (m, 3H, $-PC_6H_5$), 7.55-7.57 (d, 4H, J = 8.4 Hz, $-OC(C_6H_5)_2$); ^{13}C NMR (101 MHz, C_6D_6) δ 5.98, 41.45 (d, $^{1}J_{31P\text{-}13C}$ = 31.4 Hz), 83.50 (dd, $^{2}J_{^{31}P\text{-}^{13}C}$ = 5.6 Hz and $^{2}J_{^{89}Y\text{-}^{13}C}$ = 2.8 Hz) 119.90 (d, $^{1}J_{^{31}P\text{-}^{13}C}$ = 84.8 Hz), 127.37, 127.82, 128.80, 129.71 (d, $J_{^{31}P\text{-}^{13}C}$ = 13.1 Hz), 133.66 (d, $J_{^{31}P\text{-}^{13}C}$ = 10.1 Hz), 134.06 (d, $J_{^{31}P\text{-}^{13}C}$ = 3.0 Hz), 146.36; ^{31}P NMR (162 MHz, C_6D_6) δ +16.0. Elemental Anal. Calc for $C_{44}H_{63}IN_2OPSi_4Y$; C, 53.11; H, 6.38; N, 2.81 found C, 53.28; H, 6.45; N, 2.70.

Synthesis of Ph_3PCH_2:[4] In a glovebox, triphenylmethylphosphonium iodide (2.8 g, 6.86 mmol) and potassium *tert*-butoxide (0.77 g, 6.86 mmol) were weighed into a Schlenk tube. The tube was sealed and removed from the box, diethyl ether (30 mL) was added *via* cannula and the reaction mixture was heated to 35 °C for 48 h. The reaction mixture was allowed to cool to room temperature and the orange solution filtered by cannula. Removal of the solvent gave a yellow crystalline solid (1.38 g, 5.0 mmol, 73%). ^{1}H NMR (300 MHz, C_6D_6) δ 0.81 (d, 2H, $J_{P\text{-}H}$ = 7.8 Hz), 7.00-7.60 (m, 9H), 7.70-7.77 (m, 6H); 13C NMR (101 MHz, C_6D_6) δ -4.73, -3.74, 128.36 (d, $J_{P\text{-}C}$ = 11.4 Hz), 130.55 (d, $J_{P\text{-}C}$ = 2.8 Hz), 132.60 (d, $J_{P\text{-}C}$ = 9.7 Hz), 135.18 (d, $J_{P\text{-}C}$ = 84.3 Hz); ^{31}P NMR (121 MHz, C_6D_6) δ + 22.0.

Synthesis of ***2-Cl:*** Crude **1** was used directly in this reaction. In a glovebox, **1** (100 mg, 0.12 mmol) and 2-chlorobenzophenone (34.5 mg, 0.16 mmol, 1.3 equiv.) were weighed into a Schlenk-tube. The tube was sealed and removed from the box and attached to a vacuum line. Benzene (5 mL) was added *via* cannula, and the reaction mixture stirred for 30 min. The solvent was removed *in vacuo* and the resulting white solid washed thoroughly with a 20 mL portion of hexanes. The product was dried under vacuum and isolated as a white powder (27.0 mg, 0.03 mmol, 21%). ^{1}H NMR (400 MHz, C_6D_6) δ 0.48 (s, 18H), 0.62 (s, 18H), 4.98 (d, 2H, $J_{P\text{-}H}$ = 13.2 Hz), 6.96 (dd, 1H, J = 8.8 and 8.0 Hz), 6.56 (d, 1H, J = 8.0 Hz), 6.66 (dd, 1H, J = 8.8 and 7.6 Hz), 6.90-7.15 (m, 12 H), 7.36-7.38 (m, 6H), 7.55-7.57 (m, 2H), 8.22 (d, 1H, J = 7.6 Hz); ^{13}C NMR (101 MHz, C_6D_6) δ 6.24, 6.52, 38.74 (d, J = 40.4 Hz), 83.31 (dd, J = 5.1 and 5.1 Hz), 119.78 (d, $J_{P\text{-}C}$ = 85.3 Hz) 126.40, 126.87, 128.69, 129.00 129.95 (d, J = 12.6 Hz), 131.15, 131.42, 133.00 134.17 (d, $J_{P\text{-}C}$ = 10.0 Hz), 143.51, 148.92 (d, $J_{P\text{-}C}$ = 8.6 Hz) remaining resonance obscured by C_6D_6; ^{31}P NMR (162 MHz, C_6D_6) δ +19.8.

NMR scale olefination experiments with triphenylphosphine oxide: C_6Me_6 (2.0-7.0 mg) was accurately weighed as an internal standard. In a glovebox, **2** (20.0 mg, 0.02 mmol) was weighed and combined with the pre-weighed standard. The mixture was dissolved in C_6D_6 (0.5 mL) and transferred to a Youngs tap NMR tube. The tube was removed from the box and the ^1H NMR spectrum recorded. The tube was then pumped back in to the box and triphenylphosphine oxide (5.6 mg, 0.02 mmol) was added, again the tube was removed from the box and the reaction monitorred by NMR spectroscopy. The yield was recorded by integration and comparison of alkene resonance of 1,1-diphenylethane (δ = 5.21 ppm) and the methylene resonance of **2** (δ = 5.04 ppm) against the internal standard. Products were assigned by comparison against control samples, synthesised by reaction of [Ph_3PCH_2] with the benzophenone and 2-chlorobenzophenone.

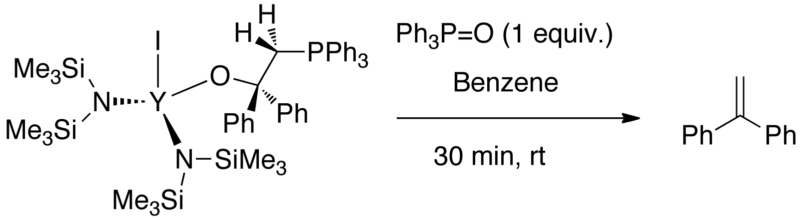


Table S1. Duplicate runs of the reaction of **2** with Ph_3PO

Run	Time / h	NMR Yield / %
1	0.5	88
2	0.5	87
3	0.5	90

Cross-over NMR scale olefination experiments: C_6Me_6 (2.0-7.0 mg) was accurately weighed as an internal standard. In a glovebox, **2** (20.0 mg, 0.02 mmol) or **2-Cl** (20.0 mg, 0.02 mmol) was weighed and combined with the pre-weighed standard. The mixture was dissolved in d^8-toluene (0.5 mL) and transferred to a Youngs tap NMR tube. The tube was removed from the box and the ^1H NMR spectrum recorded. The tube was then pumped back in to the box and 20 equivalents the appropriate ketone (see Table S2) was added. The tube was removed from the box, heated to 80 °C and the reaction monitorred by NMR (both in probe and out of probe). The yield was recorded by integration and comparison of alkene resonance of either 1,1-diphenylethene ($\delta = 5.21$ ppm) or 2-chloro-1,1-diphenylethene (5.16 and 5.71 ppm) and the methylene resonance of **2** (5.04 ppm) or **2-Cl** (5.00 ppm) against the internal standard.

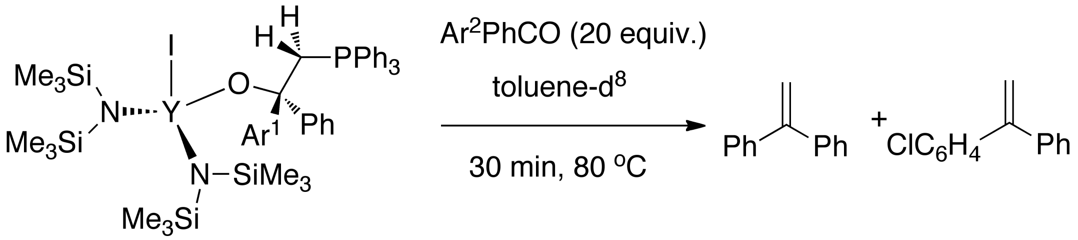


Table S2. Duplicate runs of the reaction of **2** and **2-Cl** with ketones

Entry	Complex	Ar^1	Ar^2	Time / h	NMR Yield / %
1	**2**	Ph	Ph	0.5	83 : 0
2	**2-Cl**	2-ClC_6H_4	Ph	0.5	74 : 14
3	**2**	Ph	2-ClC_6H_4	0.5	24 : 62

Figure S1: ^{1}H NMR data for the reaction of [Y{N(SiMe$_3$)$_2$}$_3$] with Ph$_3$PMeI to form **1**

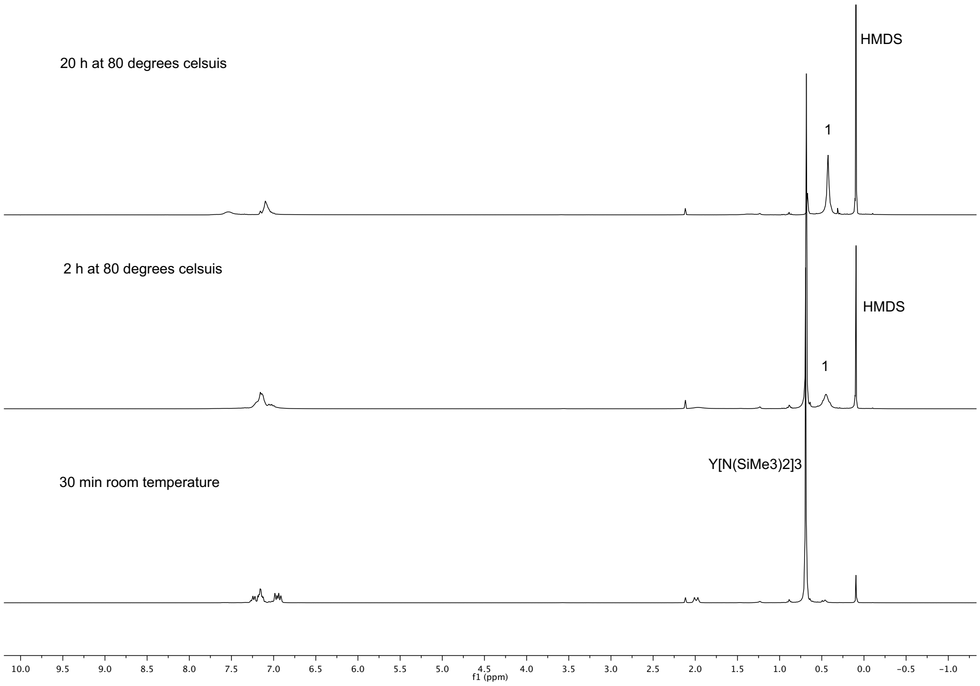


Figure S2: ^{31}P NMR data for the reaction of [Y{N(SiMe$_3$)$_2$}$_3$] with Ph$_3$PMeI to form **1**

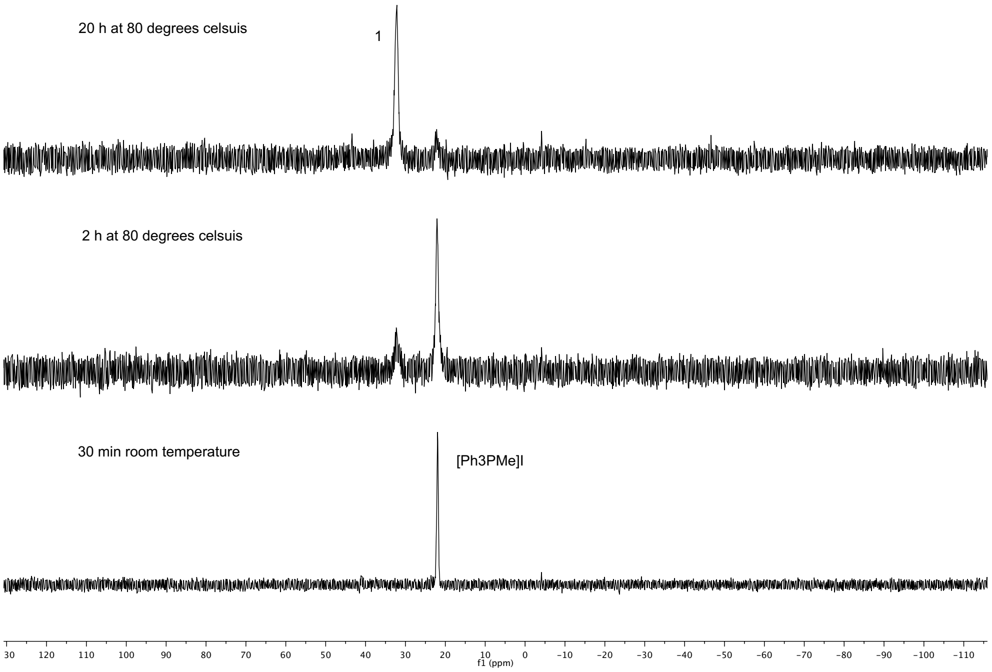


Figure S3: Truncated ^{1}H NMR data (δ 1.5-6.2 ppm) for the reaction of **2** with excess 2-chlorobenzophenone (top) 10 minutes at 25 °C, (bottom) 30 minutes at 80 °C

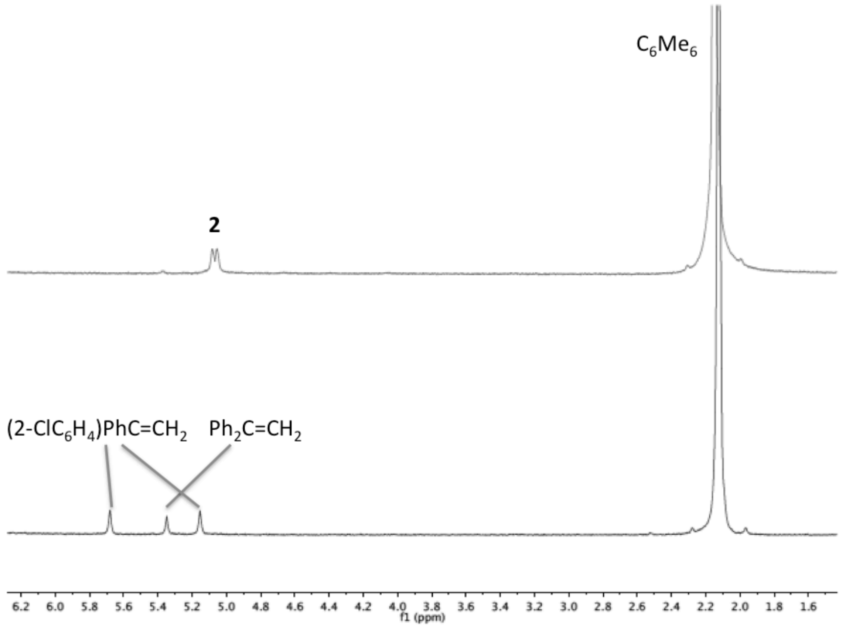


Figure S4: Truncated ^{1}H NMR data (δ 1.5-6.2 ppm) for the reaction of **2-Cl** with excess benzophenone (top) 10 minutes at 25 °C, (bottom) 30 minutes at 80 °C

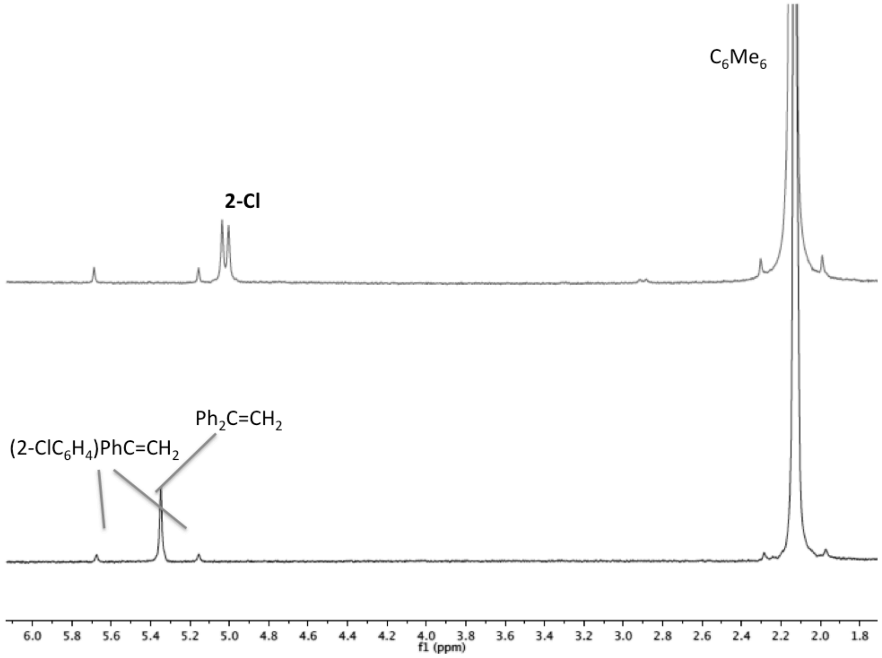


Figure S5: ORTEP representation of **1**. Thermal ellipsoids at 30% probability. H-atoms omitted for clarity. Selected bond angles (^{o}) and bond lengths (Å), Y-C(1) 2.460(6), P-C(1) 1.728(6), Y-N(1) 2.207(5), Y-N(2) 2.244(5), Y-I 3.0161(8), Y-C(1)-P 138.8(3).

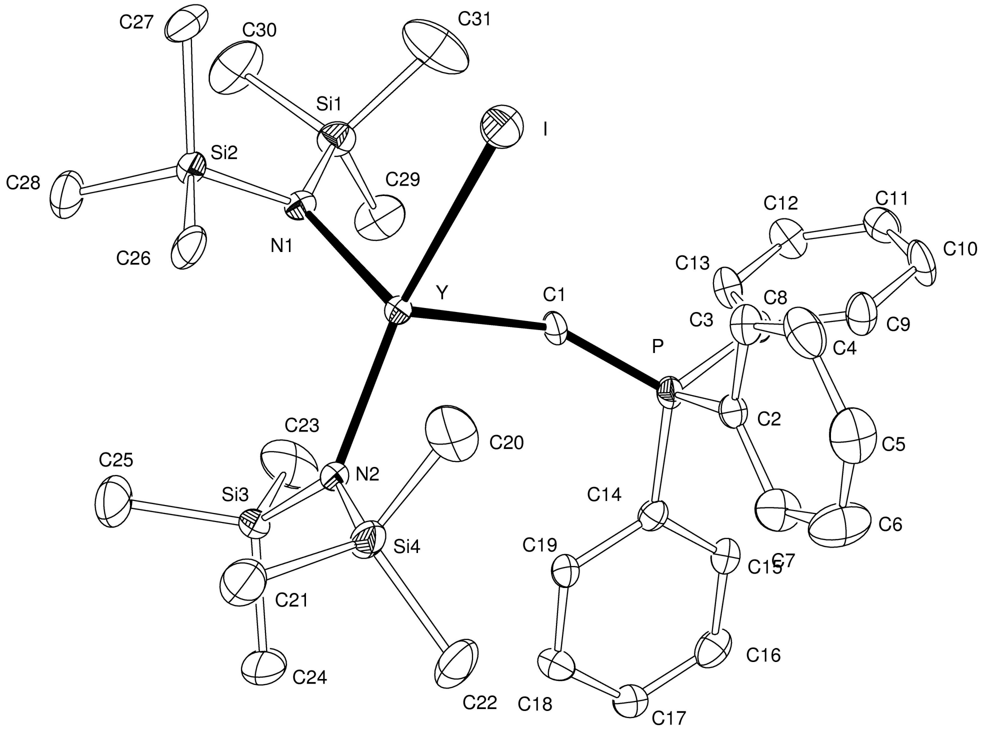
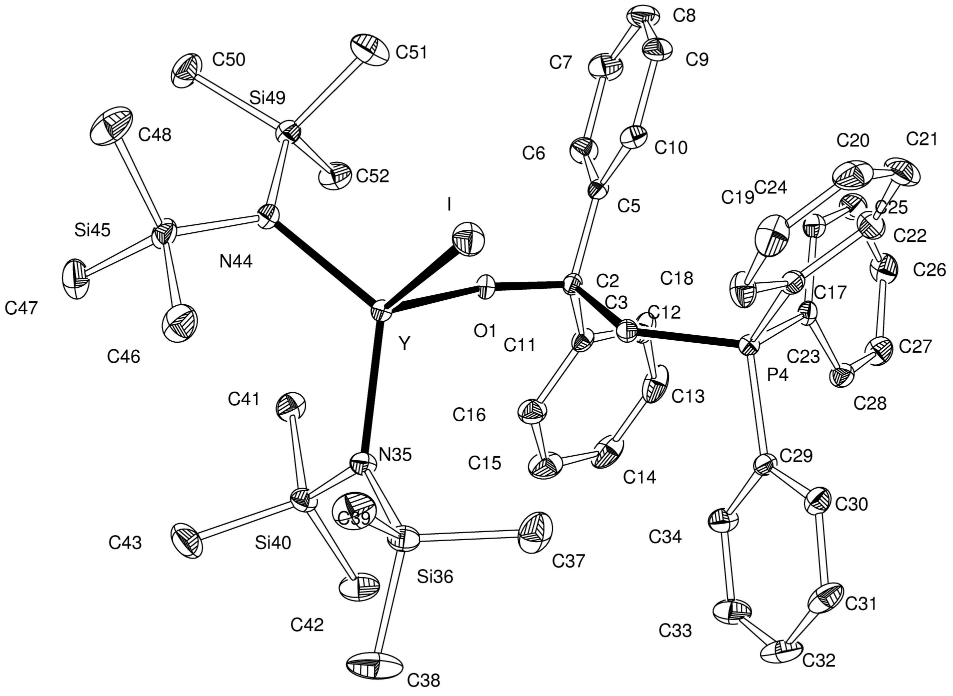


Figure S6: ORTEP representation of **2**. Thermal ellipsoids at 30% probability. H-atoms omitted for clarity. Selected bond angles (^{o}) and bond lengths (Å), Y-O(1) 2.0717(13), Y-N(44) 2.2399(15), Y-N(35), 2.2620(15), O(1)-C(2) 1.401(2), C(2)-C(3) 1.529(2), C(3)-P(4) 1.8315(17), Y-O(1)-C(2) 155.24(11).



References

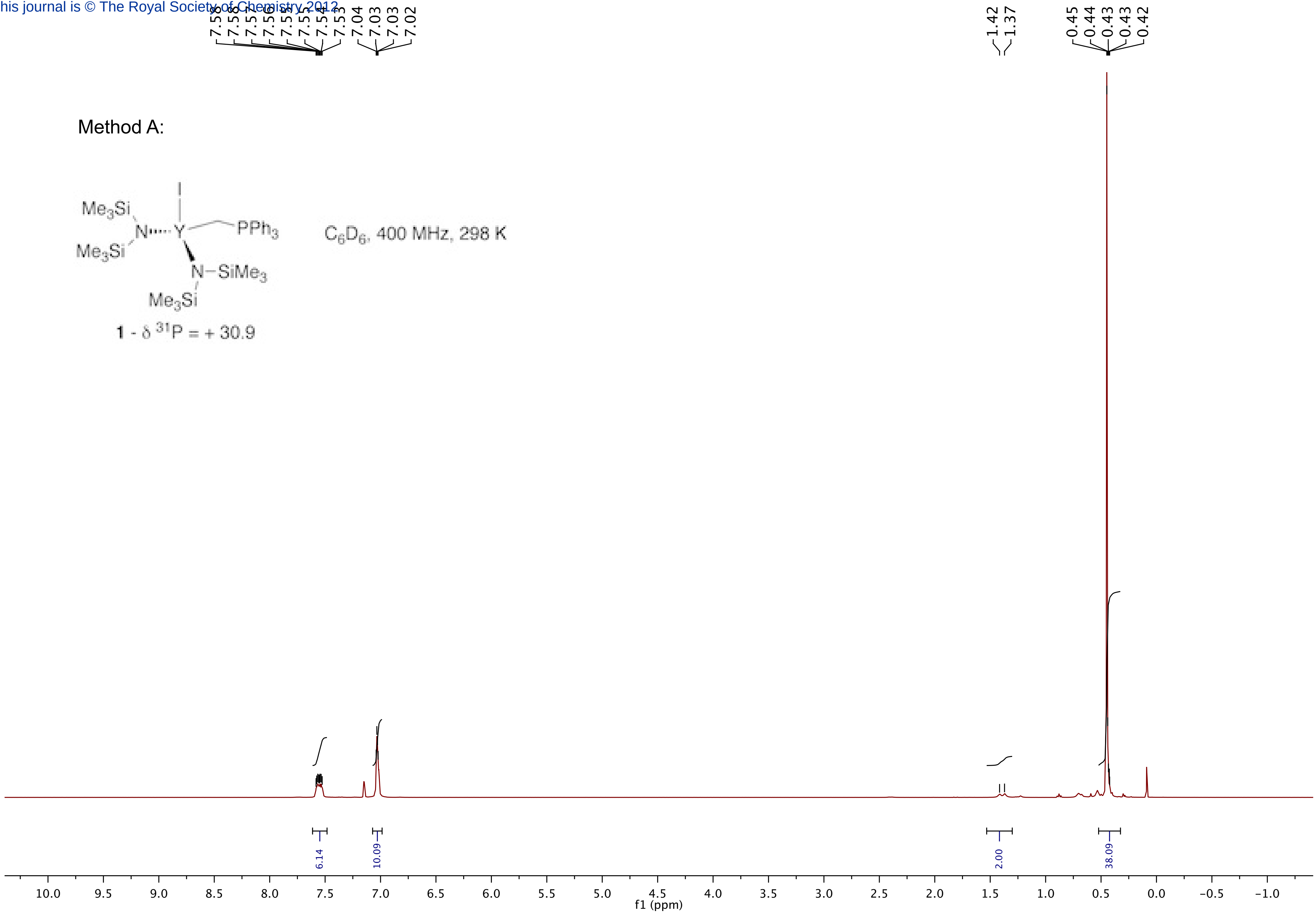
(1) S. J. N. Burgmayer *J. Chem. Ed.* 1998, **75**, 460.

(2) D. B. G. Williams and M. Lawton *J. Org. Chem.* 2010, **75**, 8351

(3) D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J. Chem. Soc., Dalton Trans.* 1973, 1021.

(4) M. Ludwiczak, M. Majchrzak, D. Marciniec, M. Kubicki, *J. Organomet. Chem.* 2011, **696**, 1456.

Method A:



1 - δ ^{31}P = + 30.9

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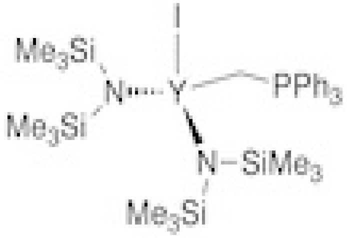
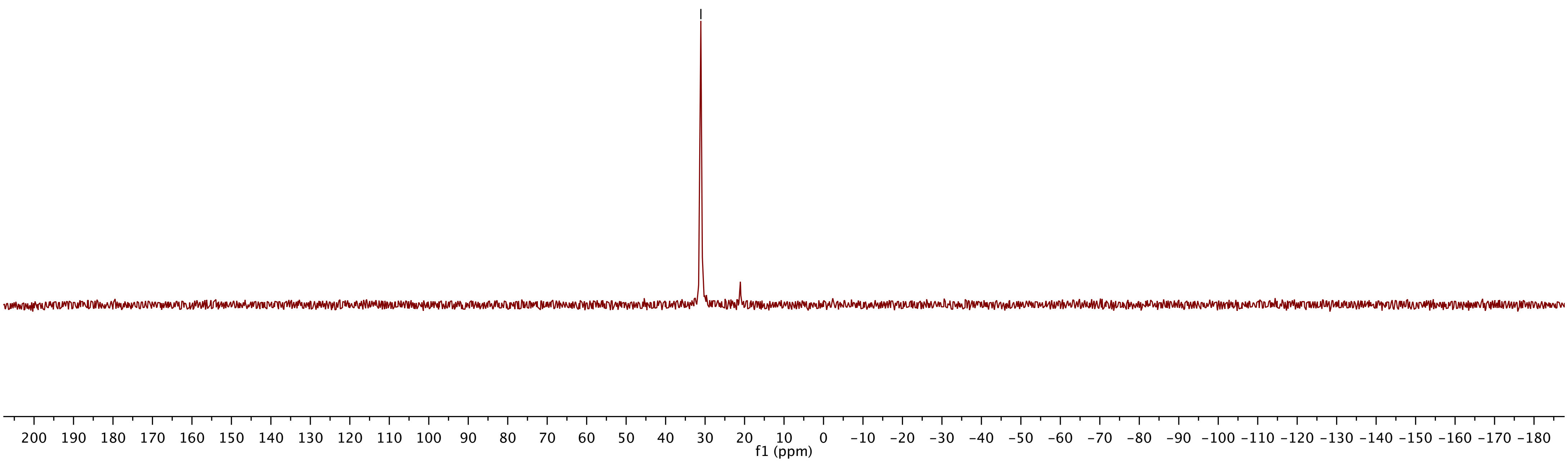
Method A:



$\mathbf{1}$ - δ ^{31}P = + 30.9

C_6D_6, 162 MHz, 298 K



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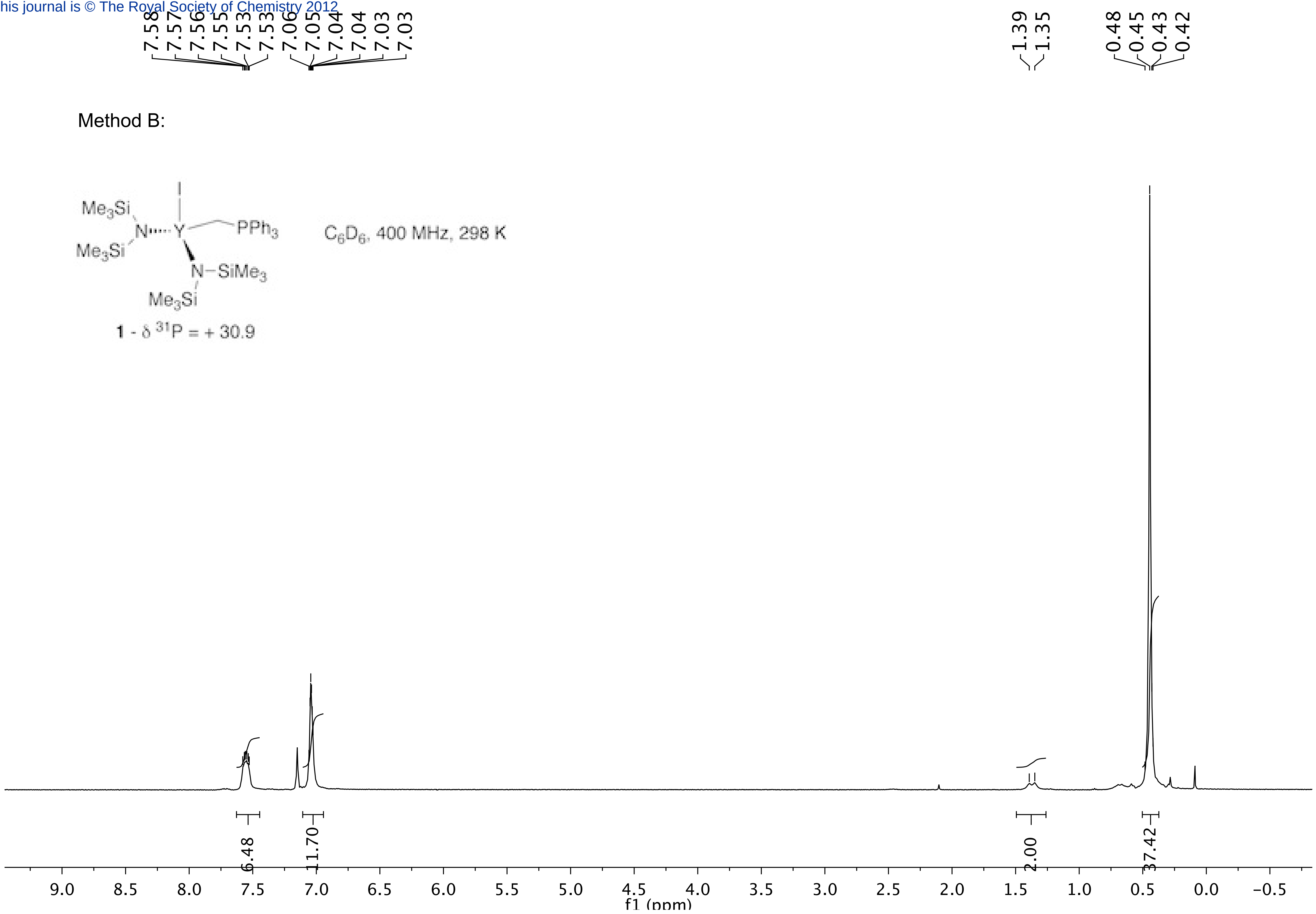
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0.43
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Me3Si
N
Y
PPh3
Me3Si
N–SiMe3
Me3Si
I
1 - δ 31P = + 30.9
C6D6, 400 MHz, 298 K
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2.00
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
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1.5
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0.0
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f1 (ppm)

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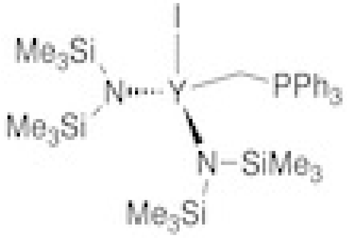
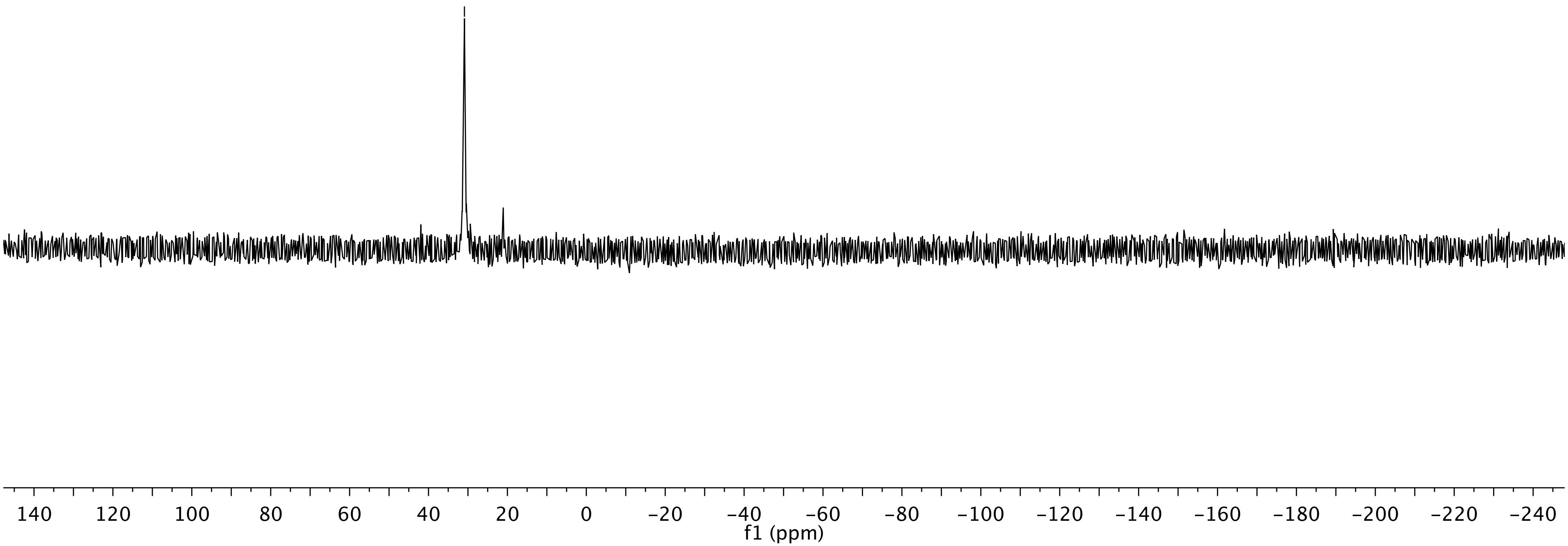
Method B:



1 - δ ^{31}P = + 30.9

C_6D_6, 162 MHz, 298 K



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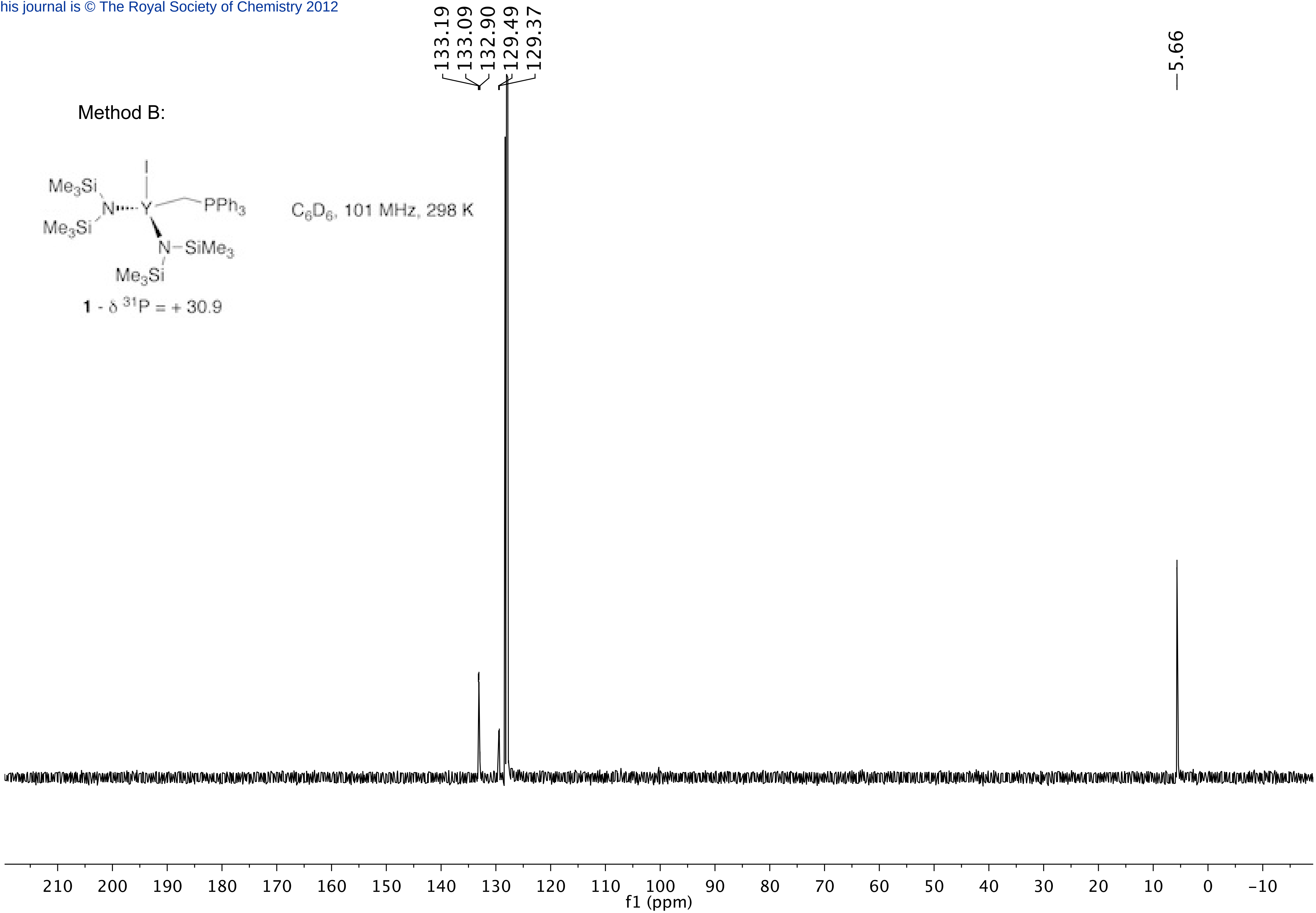

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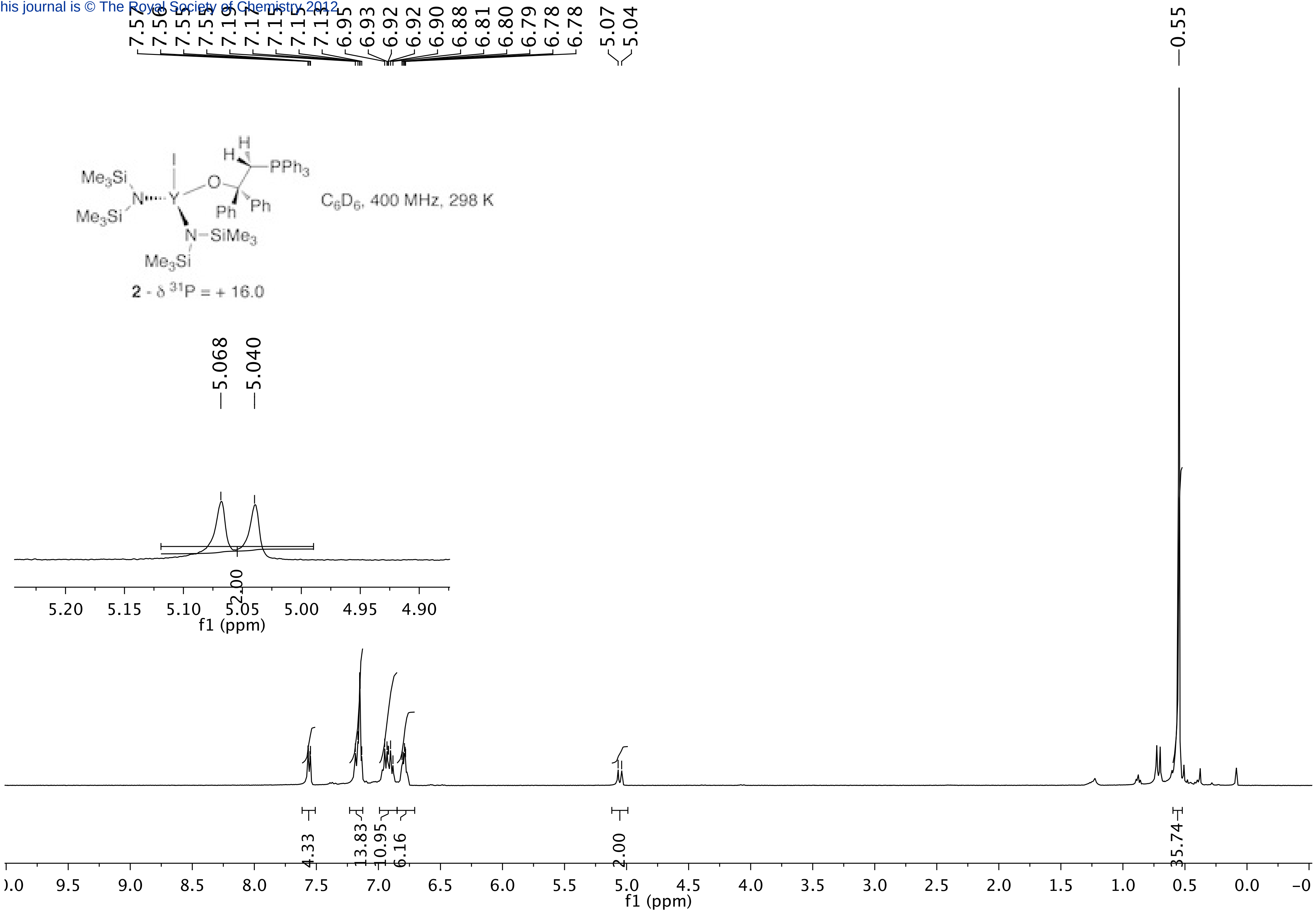
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6.81
6.80
6.79
6.78
6.78
5.07
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Me3Si
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Y
I
O
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Ph
Ph
N–SiMe3
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C6D6, 400 MHz, 298 K
2 - δ 31P = + 16.0
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5.15
5.10
5.05
5.00
4.95
4.90
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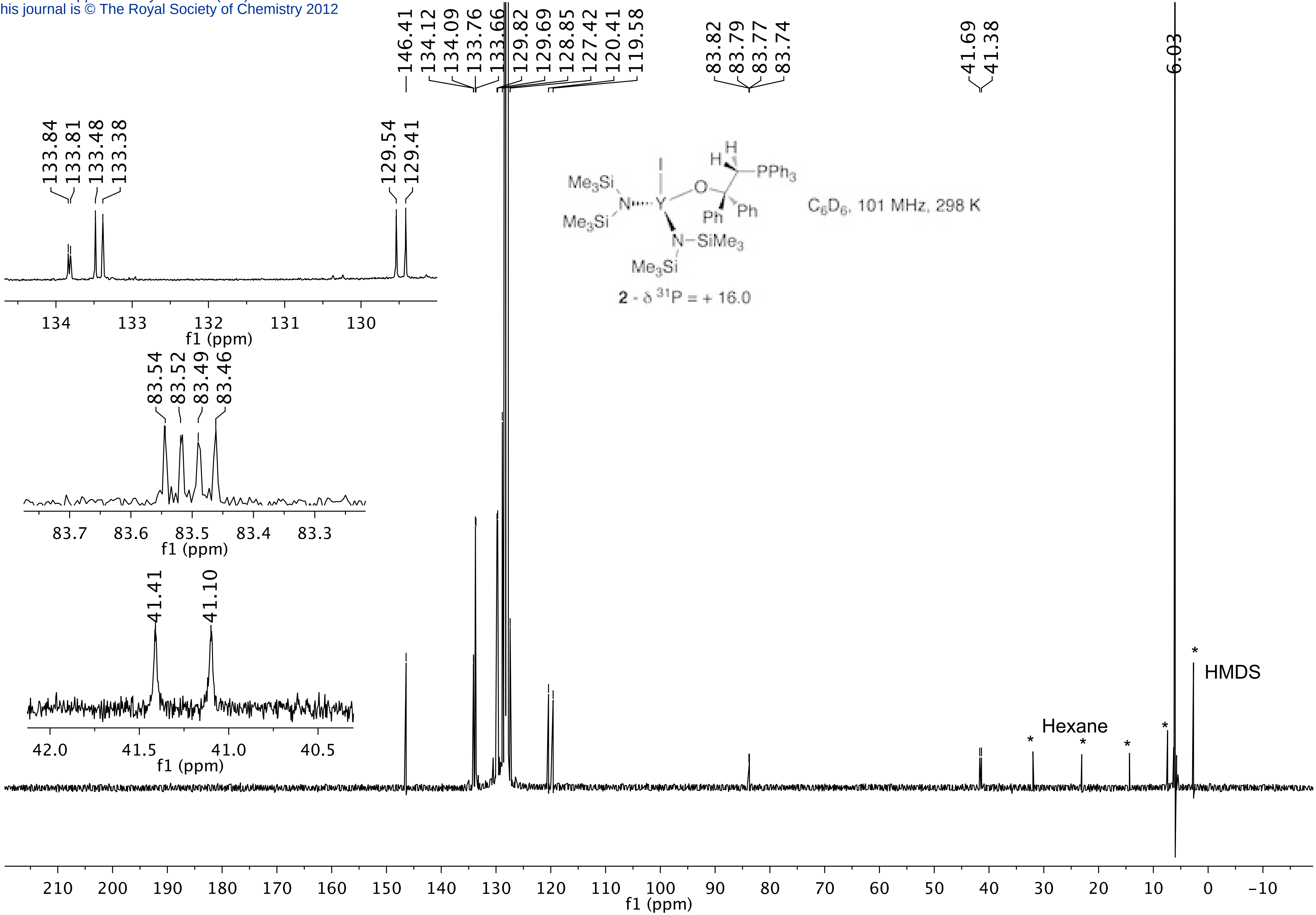
f1 (ppm)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129.54
129.41
134
133
132
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f1 (ppm)
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83.4
83.3
f1 (ppm)
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f1 (ppm)
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Ph
N–SiMe3
Me3Si
2 - δ 31P = + 16.0
C6D6, 101 MHz, 298 K
Hexane
HMDS
*
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200
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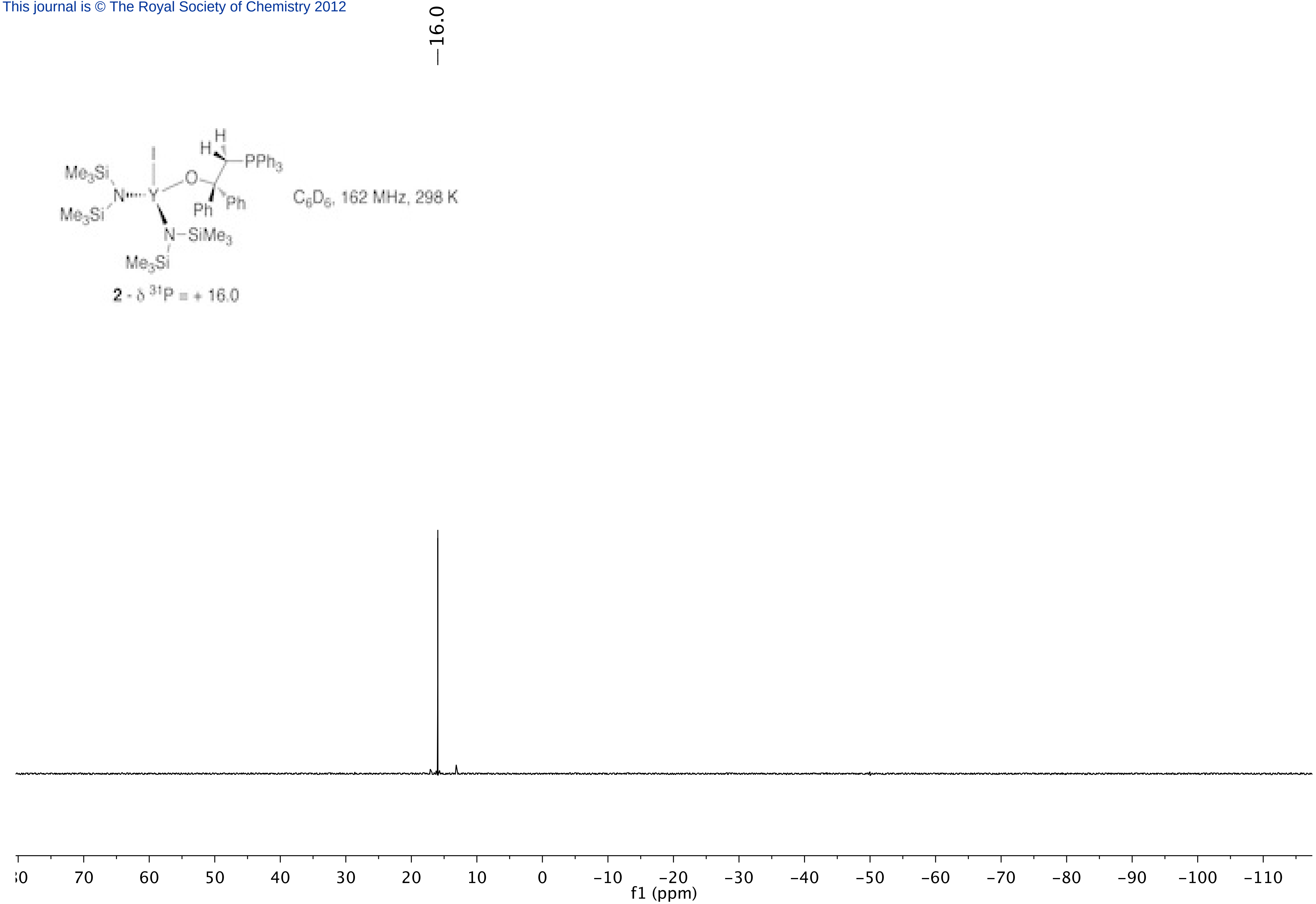
f1 (ppm)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N–SiMe3
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2 - δ 31P = + 16.0
C6D6, 162 MHz, 298 K
70
60
50
40
30
20
10
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−60
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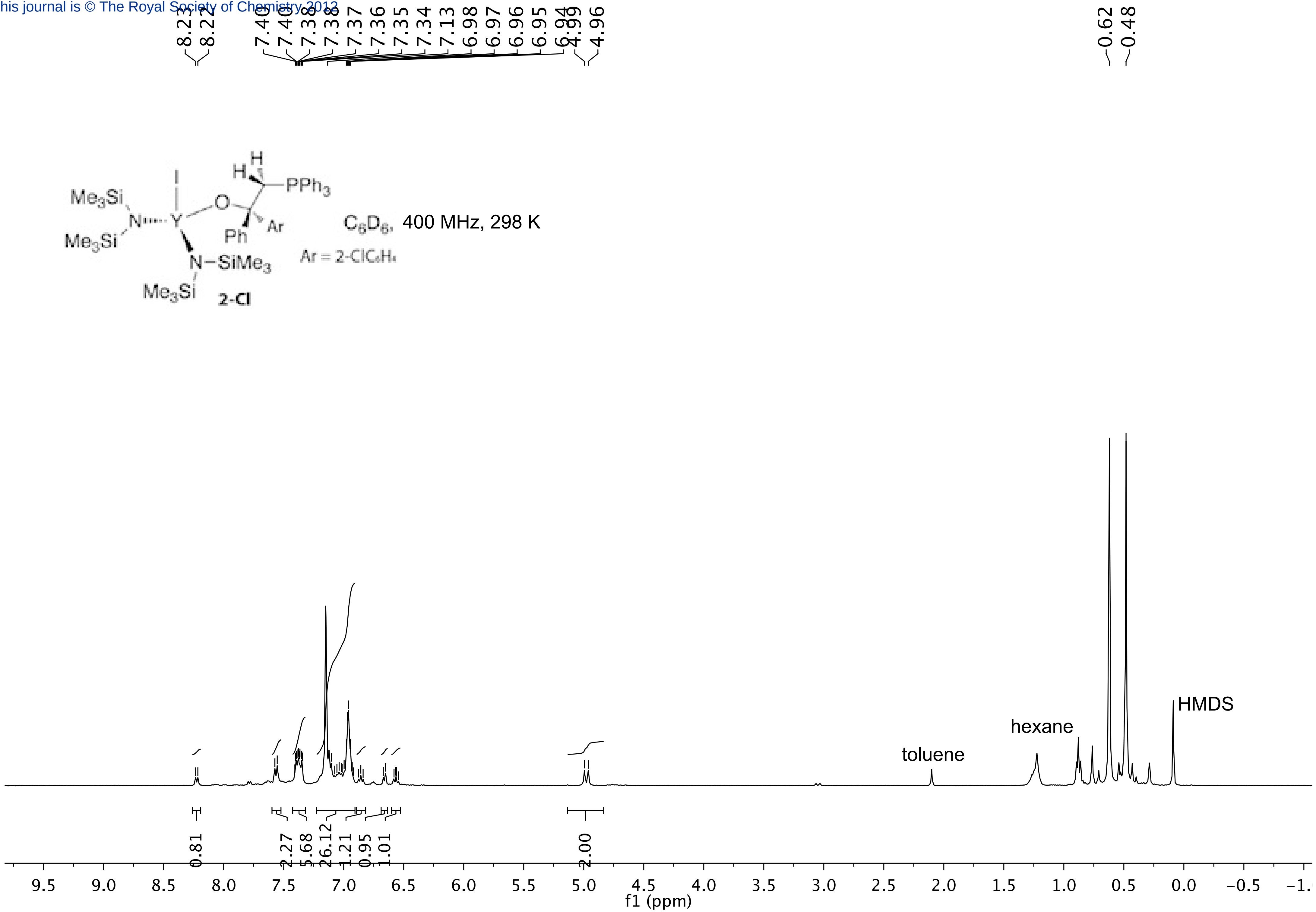
f1 (ppm)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6.96
6.95
6.94
4.99
4.96
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0.48
Me3Si
N
Y
I
O
H
H
PPh3
Ar
Ph
N–SiMe3
Me3Si
2-Cl
C6D6, 400 MHz, 298 K
Ar = 2-ClC6H4
toluene
hexane
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0.81
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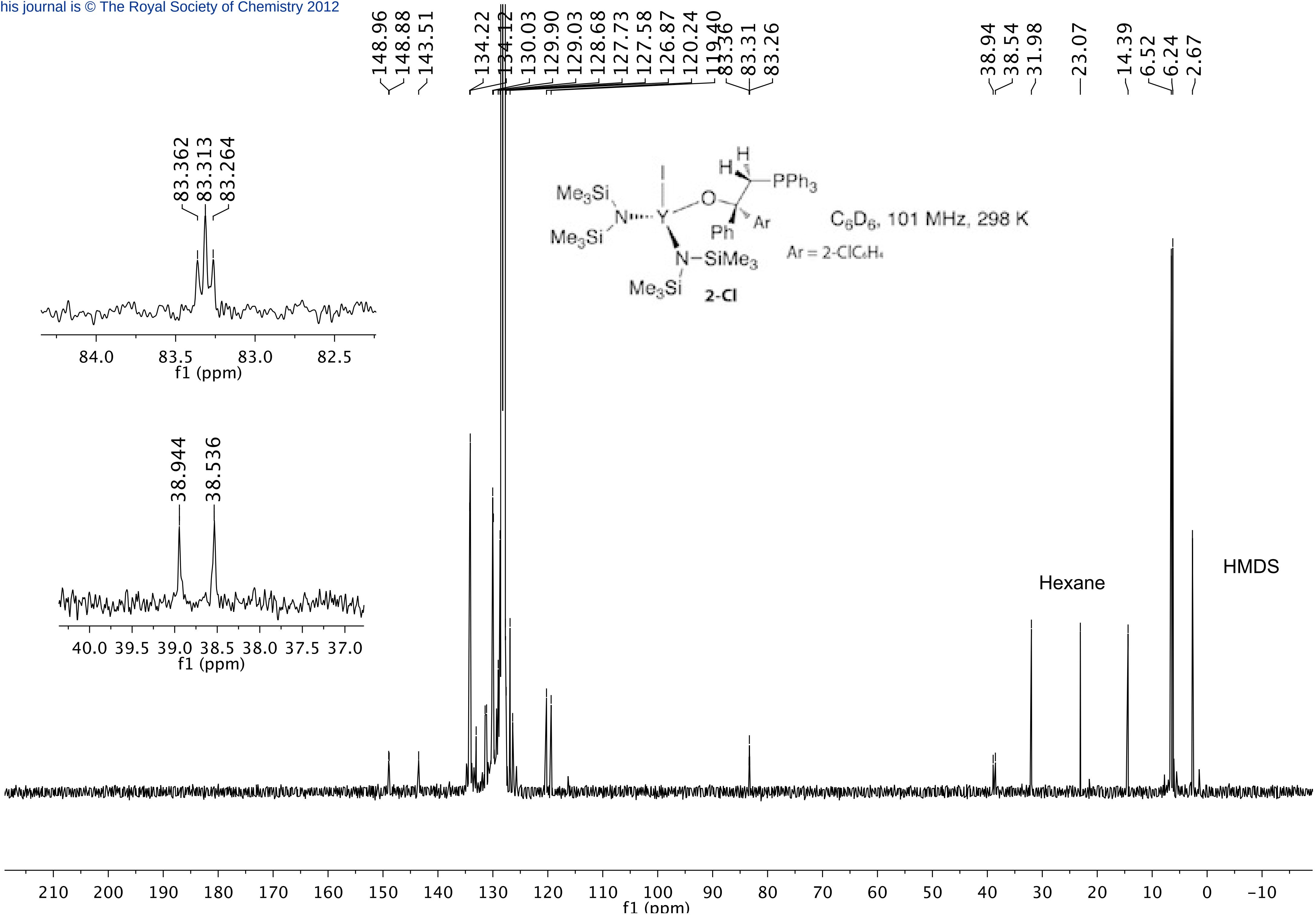
f1 (ppm)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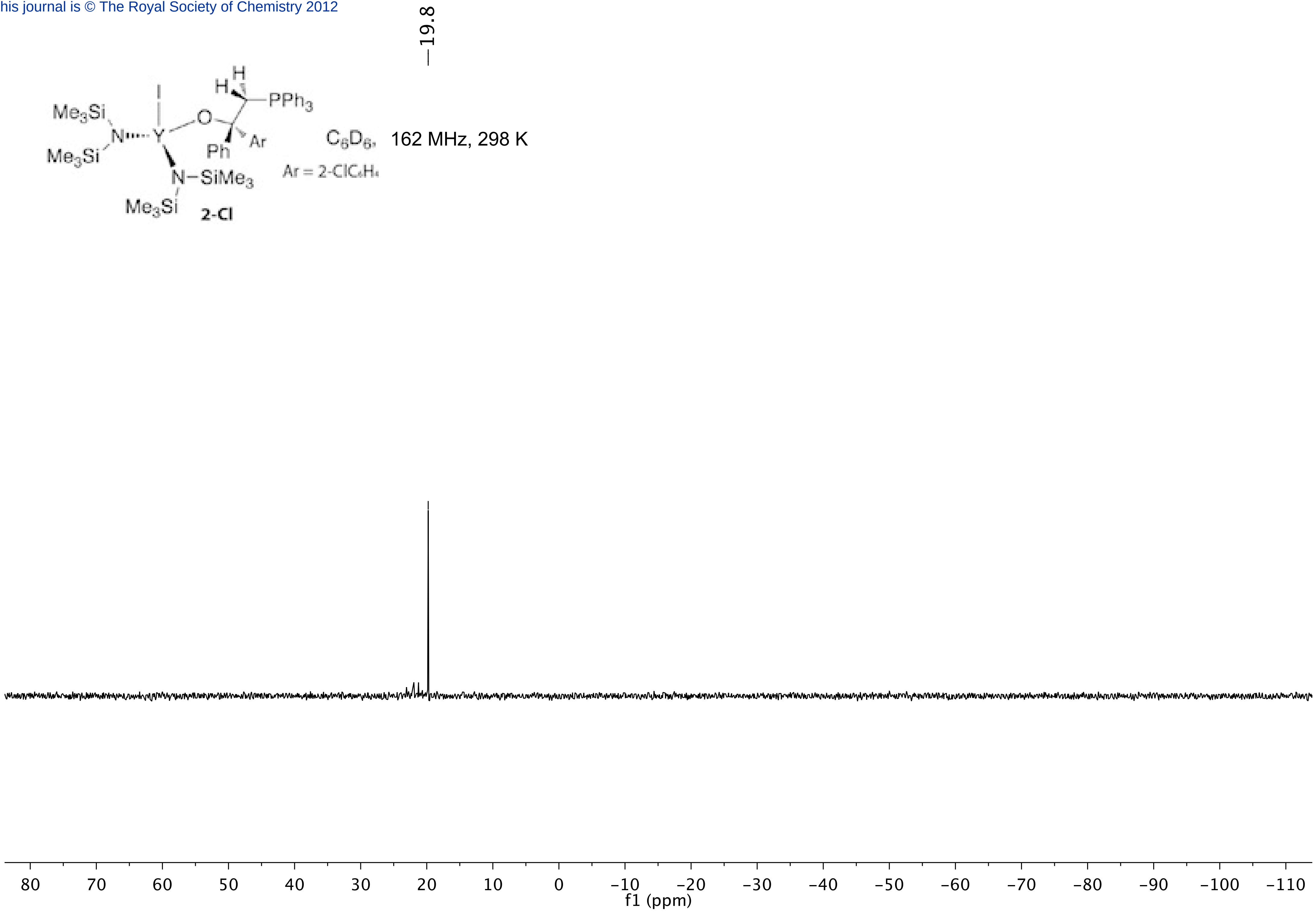
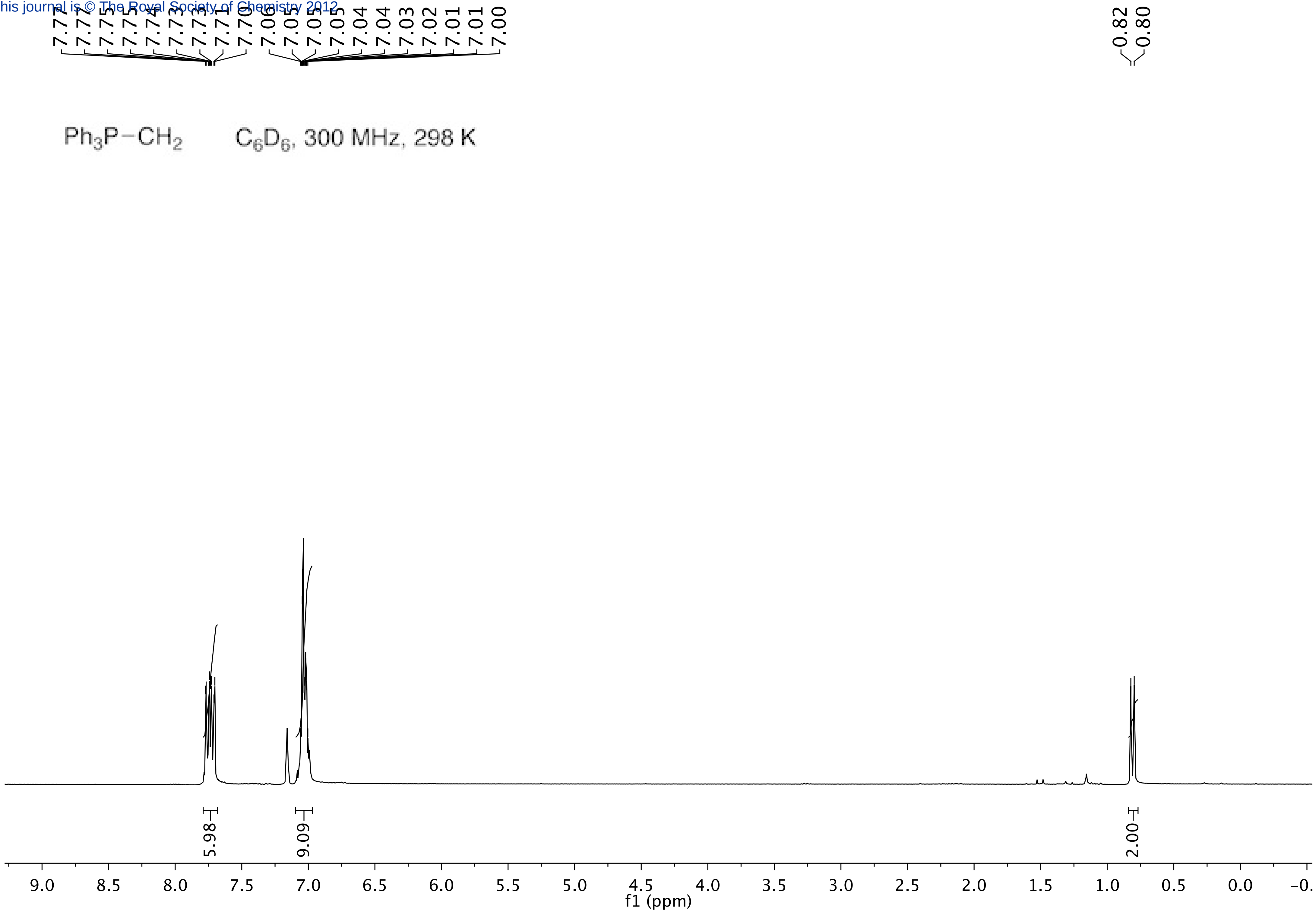
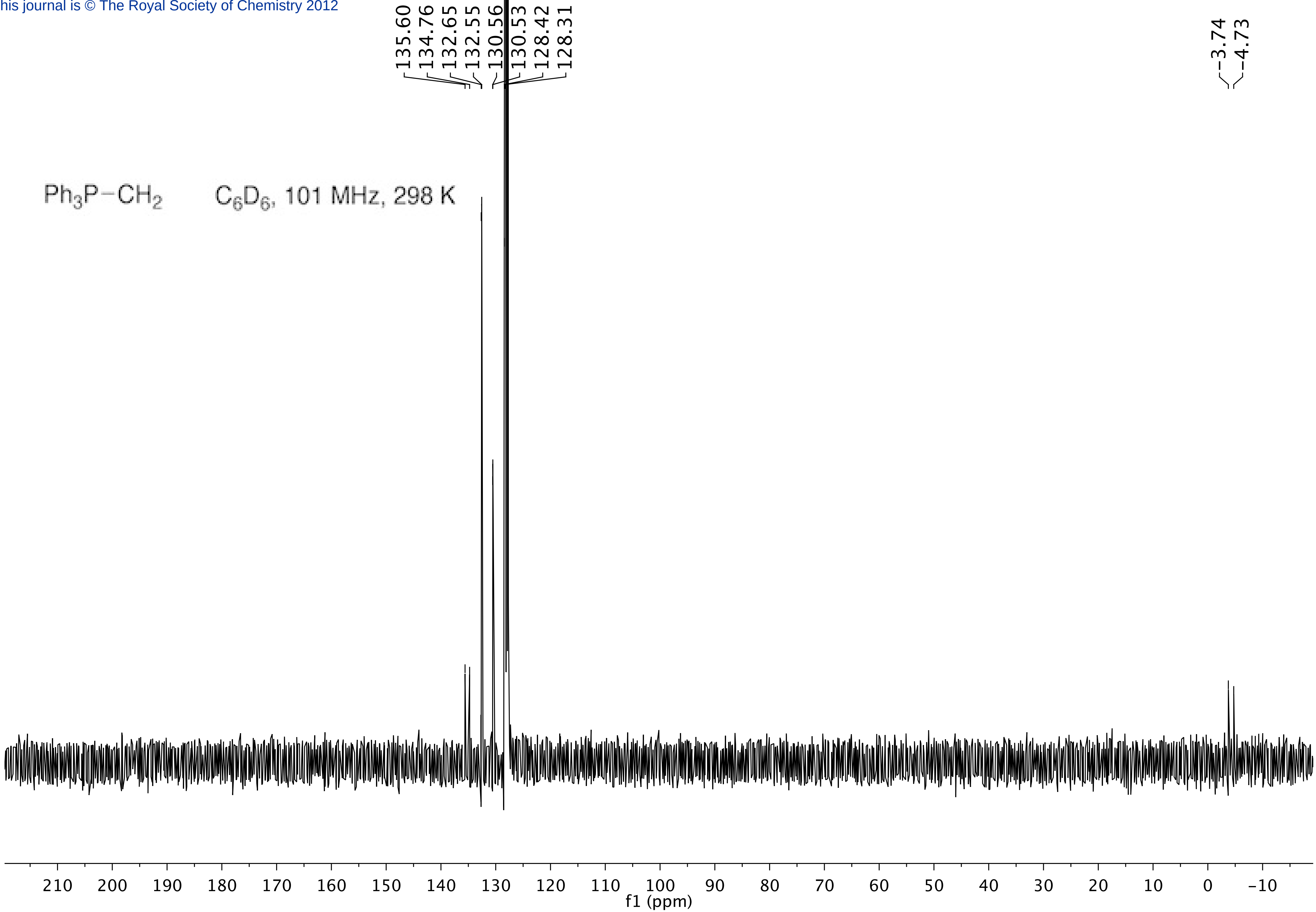
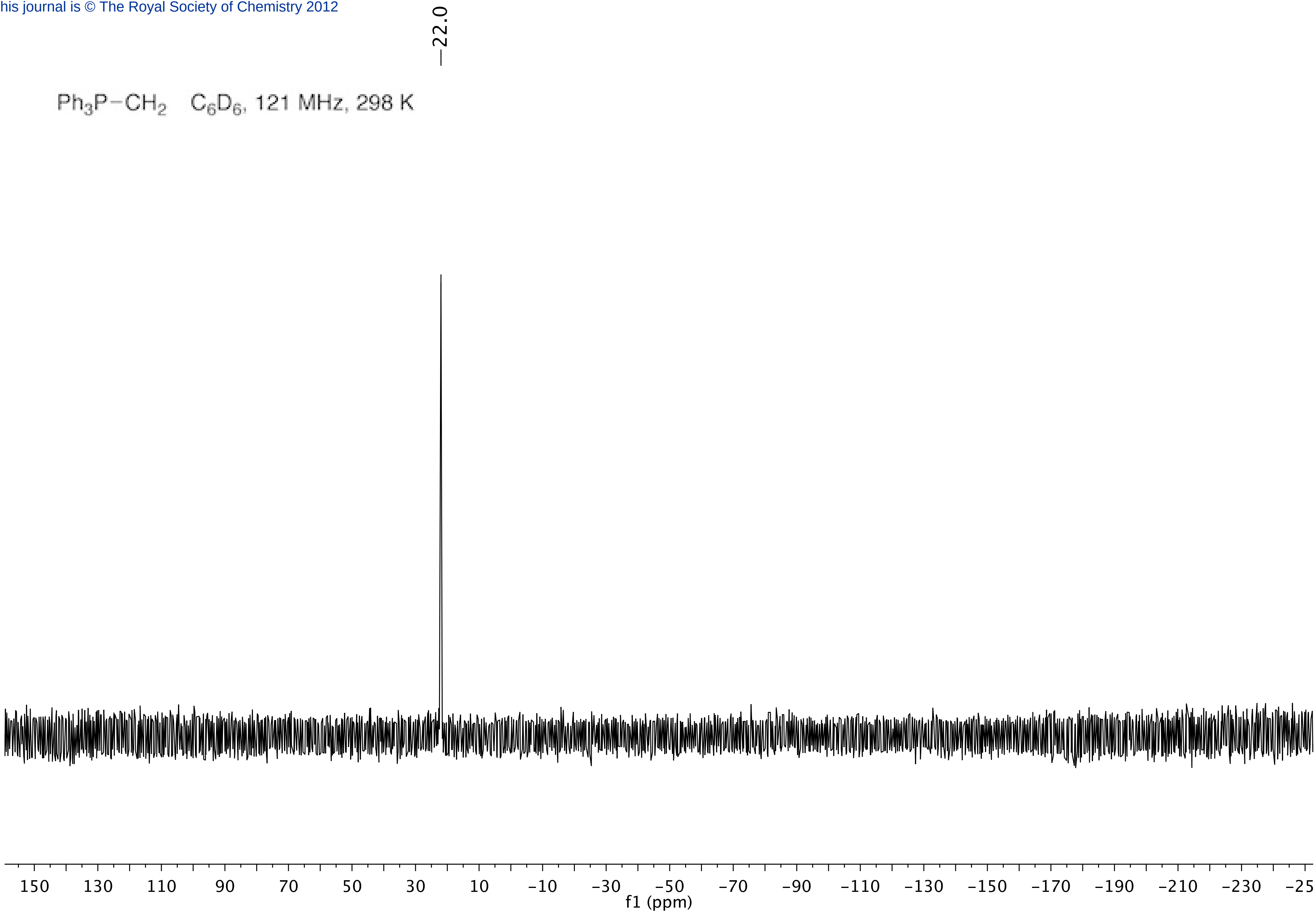
134.22
134.12
130.03
129.90
129.03
128.68
127.73
127.58
126.87
120.24
119.40
83.36
83.31
83.26
38.94
38.54
31.98
23.07
14.39
6.52
6.24
2.67
83.362
83.313
83.264
84.0
83.5
83.0
82.5
f1 (ppm)
38.944
38.536
40.0 39.5 39.0 38.5 38.0 37.5 37.0
f1 (ppm)
Me3Si
Me3Si
N
Y
I
O
H
H
PPh3
Ph
Ar
N–SiMe3
Me3Si
2-Cl
C6D6, 101 MHz, 298 K
Ar = 2-ClC6H4
Hexane
HMDS
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)

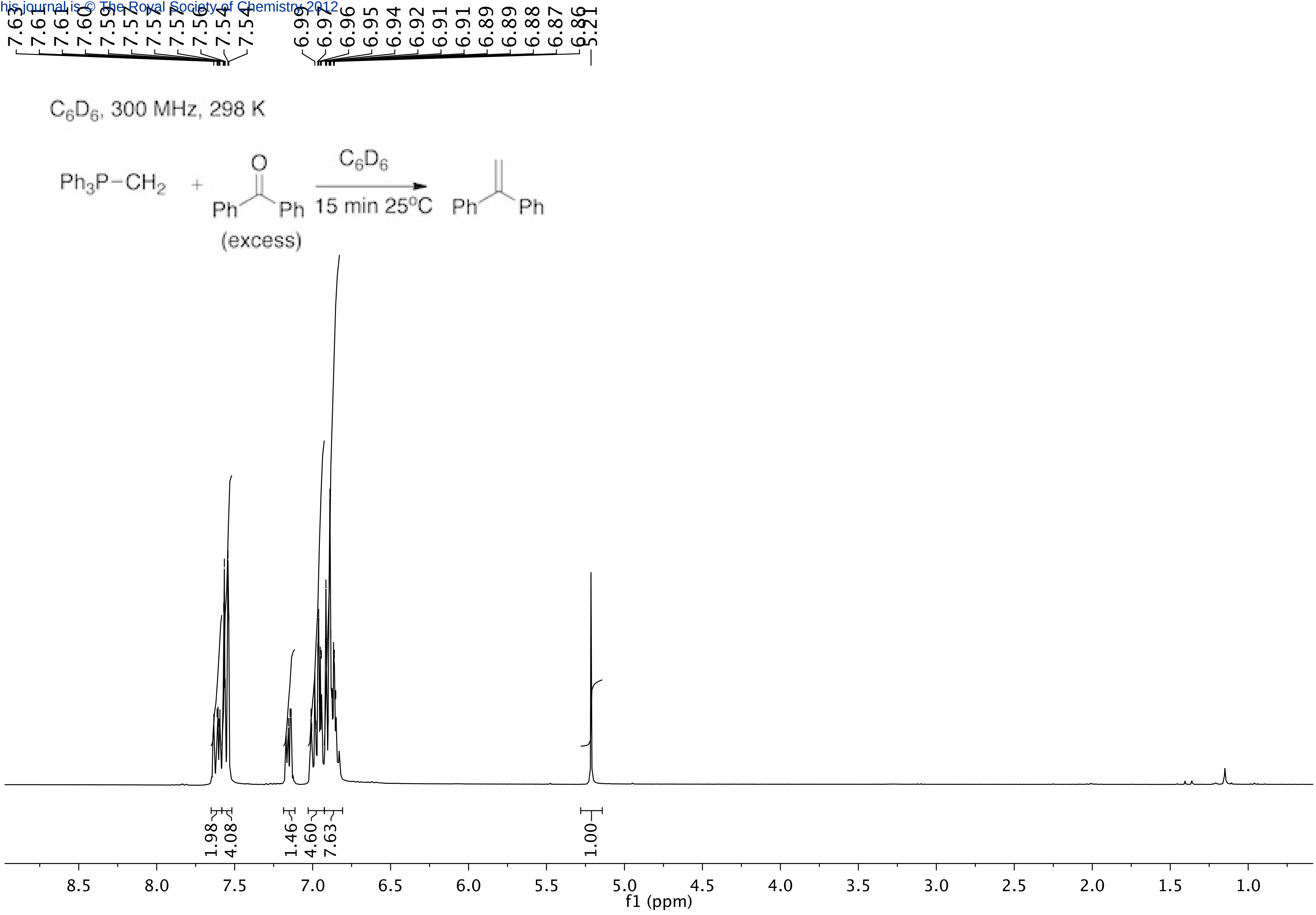


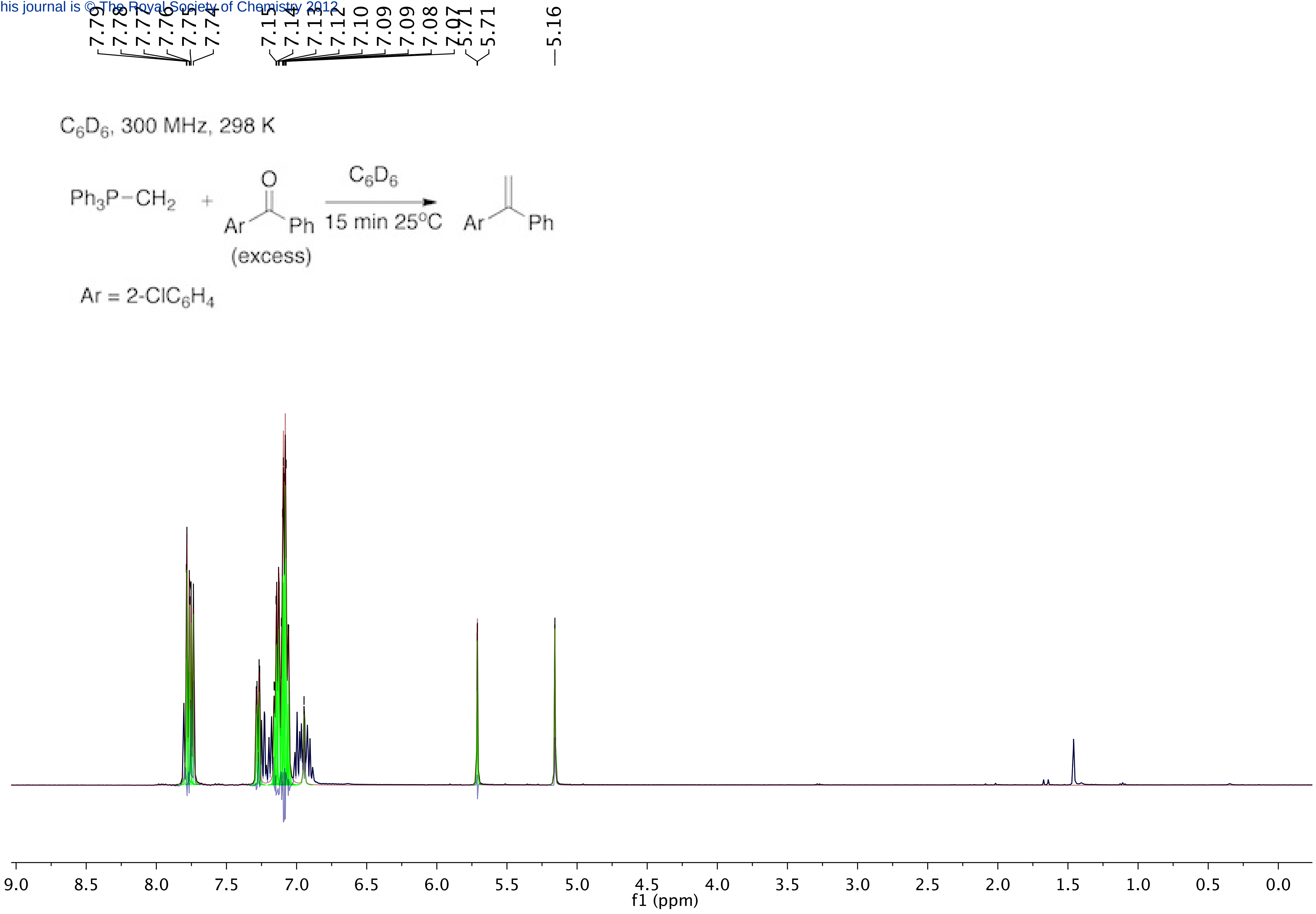
C_6D_6, 162 MHz, 298 K

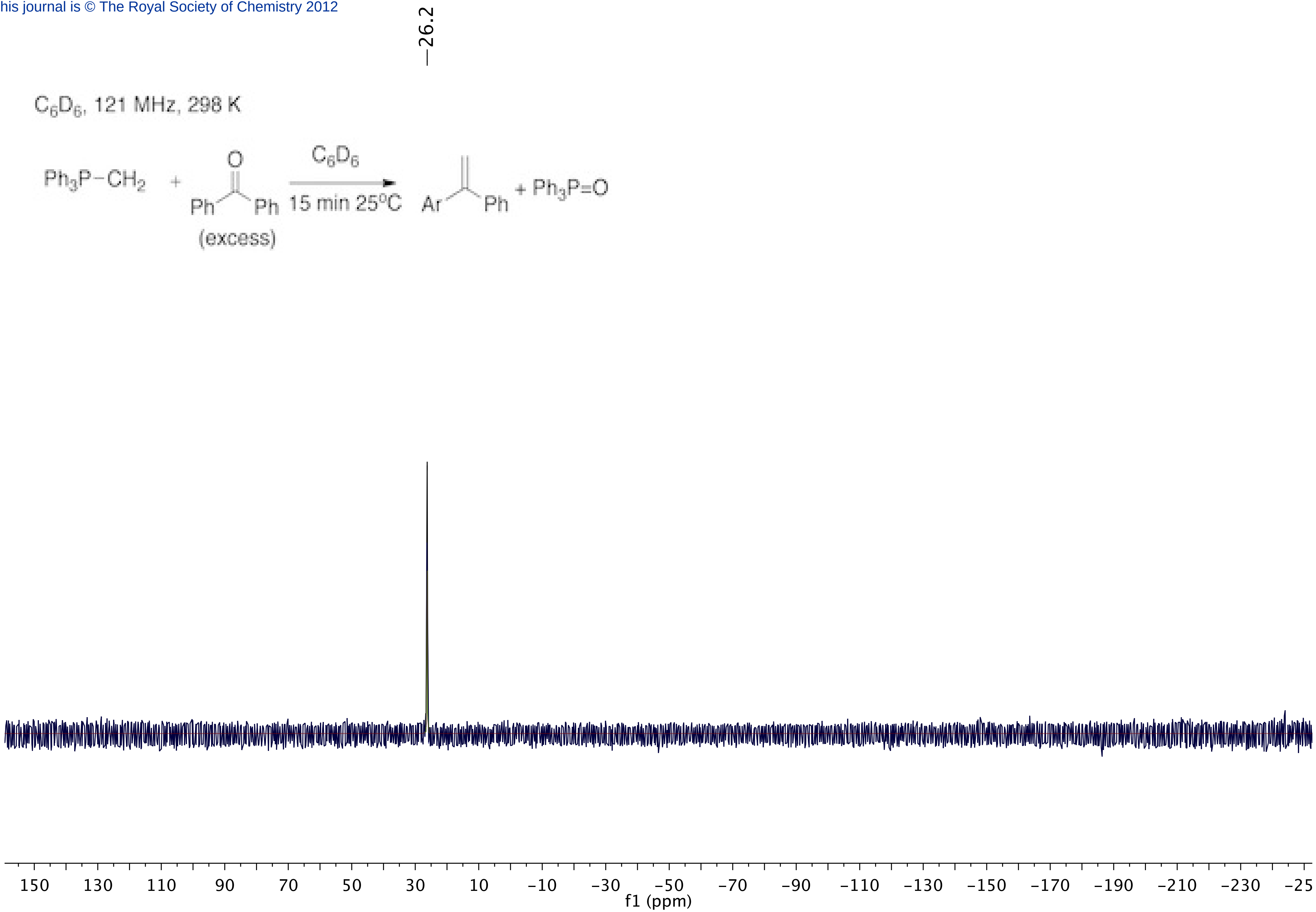

7.77
7.77
7.75
7.75
7.74
7.73
7.73
7.71
7.70
7.06
7.05
7.05
7.05
7.04
7.04
7.03
7.02
7.01
7.01
7.00
0.82
0.80
Ph3P−CH2
C6D6, 300 MHz, 298 K
5.98
9.09
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)


135.60
134.76
132.65
132.55
130.56
130.53
128.42
128.31
-3.74
-4.73
Ph_3P-CH_2
C_6D_6, 101 MHz, 298 K
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)


22.0
$Ph_3P{-}CH_2$ C_6D_6, 121 MHz, 298 K
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−25
f1 (ppm)


7.63
7.61
7.61
7.60
7.59
7.57
7.57
7.56
7.56
7.54
7.54
6.99
6.97
6.96
6.95
6.94
6.92
6.91
6.91
6.89
6.89
6.88
6.87
6.86
5.21
C_6D_6, 300 MHz, 298 K
Ph_3P-CH_2
+
O
Ph
Ph
(excess)
C_6D_6
15 min 25°C
Ph
Ph
1.98
4.08
1.46
4.60
7.63
1.00
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
f1 (ppm)


7.79
7.78
7.77
7.76
7.75
7.74
7.15
7.14
7.13
7.12
7.10
7.09
7.09
7.08
7.07
5.71
5.71
5.16
C6D6, 300 MHz, 298 K
Ph3P−CH2
+
O
Ar
Ph
(excess)
C6D6
15 min 25°C
Ar
Ph
Ar = 2-ClC6H4
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)


26.2
C6D6, 121 MHz, 298 K
Ph3P−CH2
+
O
Ph
Ph
(excess)
C6D6
15 min 25°C
Ar
Ph
+ Ph3P=O
150
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−25
f1 (ppm)