A Scandium Complex Bearing Both Methylidene and Phosphinidene Ligands: Synthesis, Structure and Reactivity

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Supporting Information

Contents

Table S1 Crystallographic data and refinement parameters for complexes **2**–**7**

	2·0.5hexane	**3**	**4**·2toluene
formula	$C_{74}H_{108}N_4PSc_2$	$C_{53}H_{77}N_2P_2Sc_2$	$C_{87}H_{117}N_4O_4PSc_2$
formula Mass	1174.53	849.07	1403.74
color	red	red	purple
cryst system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a, Å	25.123(3)	12.026(5)	14.822(3)
b, Å	13.2323(13)	19.759(8)	15.645(4)
c, Å	24.521(2)	20.811(8)	18.949(4)
α, deg	90.00	90.00	113.854(4)
β, deg	115.889(2)	91.412(7)	92.660(4)
γ, deg	90.00	90.00	99.346(4)
V, Å^3	7333.5(12)	4943(3)	3934.8(16)
Z	4	4	2
D_{calcd}, (mg/m^3)	1.064	1.141	1.185
F(000)	2548	1840	1512
T(K)	140(2)	140(2)	140(2)
θ range, deg	1.664 to 26.00	2.21 to 21.10	2.20 to 22.06
no. of reflns measured	51453	25118	27189
no. of independent reflns	14370	8649	14618
no. of obsd reflns ($I > 2\sigma(I)$)	10398	3312	6797
No. of params	755	541	871
final R_1, wR ($I > 2\sigma(I)$)	0.0643, 0.1651	0.0893, 0.2086	0.0752, 0.1847
goodness of fit on F^2	1.095	0.941	0.948
$\Delta\rho_{max, min}$, eÅ^{-3}	2.696, -1.063	0.575, -0.577	1.064, -0.583

	5	**6**·toluene	**7**
formula	$C_{72}H_{101}N_4PS_2Sc_2$	$C_{85}H_{114}N_5PSc_2$	$C_{76}H_{110}N_5PSc_2$
formula Mass	1207.58	1326.70	1214.58
color	red	red	red
cryst system	Orthorhombic	Monoclinic	Triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a, Å	14.3427(19)	14.0110(11)	13.267(2)
b, Å	20.817(3)	25.2574(18)	15.031(2)
c, Å	24.445(3)	21.3220(16)	23.008(5)
α, deg	90.00	90.00	103.167(4)
β, deg	90.00	94.025(2)	97.861(4)
γ, deg	90.00	90.00	110.238(3)
V, Å^3	7298.6(17)	7526.8(10)	4073.5(12)
Z	4	4	2
D_{calcd}, (mg/m^3)	1.099	1.171	0.990
F(000)	2600	2864	1316
T(K)	140(2)	140(2)	140(2)
θ range, deg	2.19 to 20.59	2.17 to 28.51	2.20 to 28.83
no. of reflns measured	73836	76027	27891
no. of independent reflns	22451	23217	15154
no. of obsd reflns ($I > 2\sigma(I)$)	12331	12698	8387
No. of params	754	863	784
final R_1, *wR* (I > 2σ(I))	0.0670, 0.1227	0.0626, 0.1385	0.0791, 0.2060
goodness of fit on F^2	1.094	1.004	1.084
$\Delta\rho_{max, min}$, eÅ^{-3}	0.455, -0.512	0.730, -0.640	1.530, -0.519

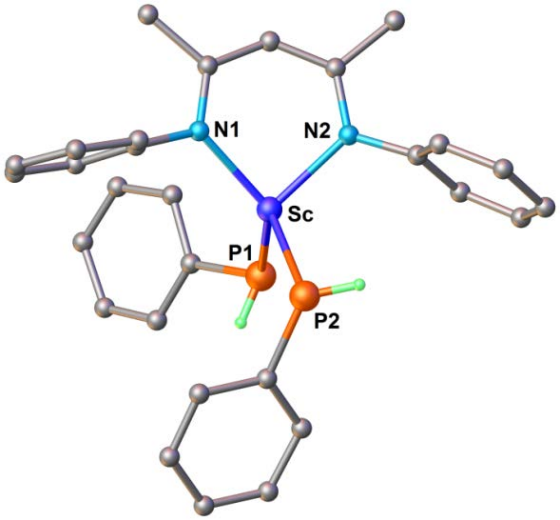
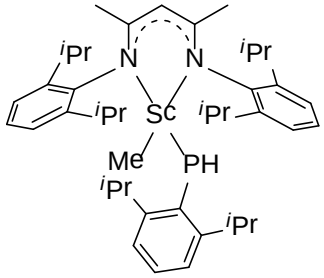


Figure. S1 Molecular structure of complex **3** (ball and stick representation). DIPP isopropyl groups and hydrogen atoms (except the phosphido hydrogen atoms) were omitted for clarity. Selected bond distances [Å] and angles [°]: Sc−P1 2.570(3), Sc−P2 2.609(3), Sc−N2 2.102(6), Sc−N1 2.114(5), N2−Sc−N1 89.4(2), P1−Sc−P2 108.74(8).



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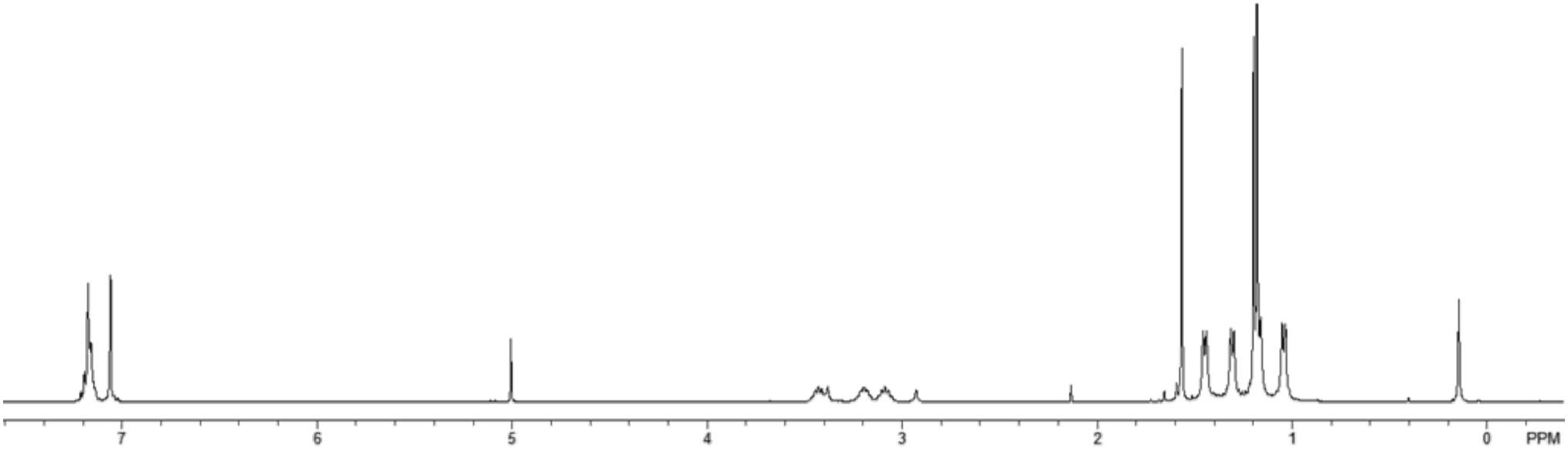


Figure S2. ^{1}H NMR spectrum of **1** (400 MHz, C_6D_6, 25 ^{o}C).

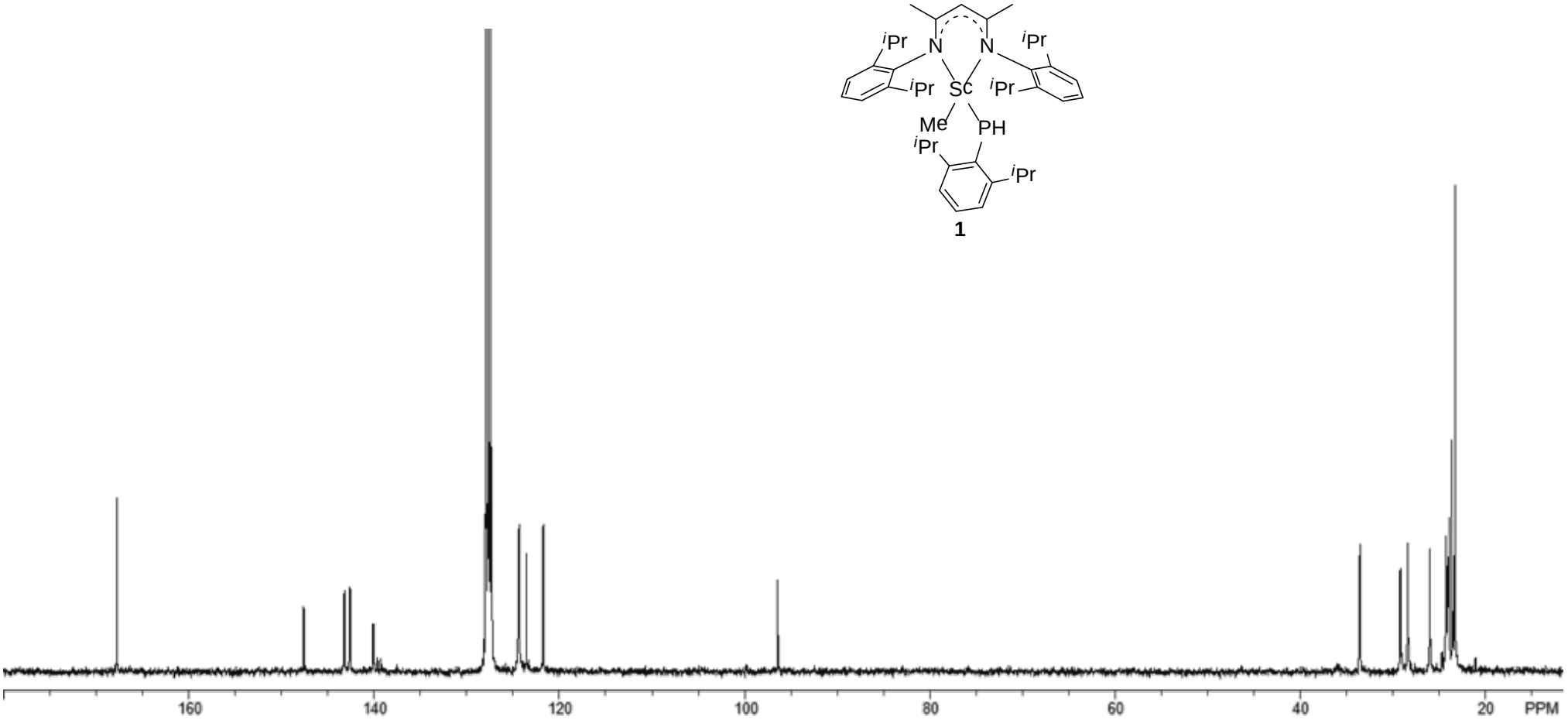
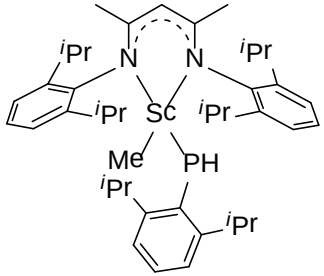


Figure S3. ^{13}C NMR spectrum of **1** (100 MHz, C_6D_6, 25 ^{o}C).



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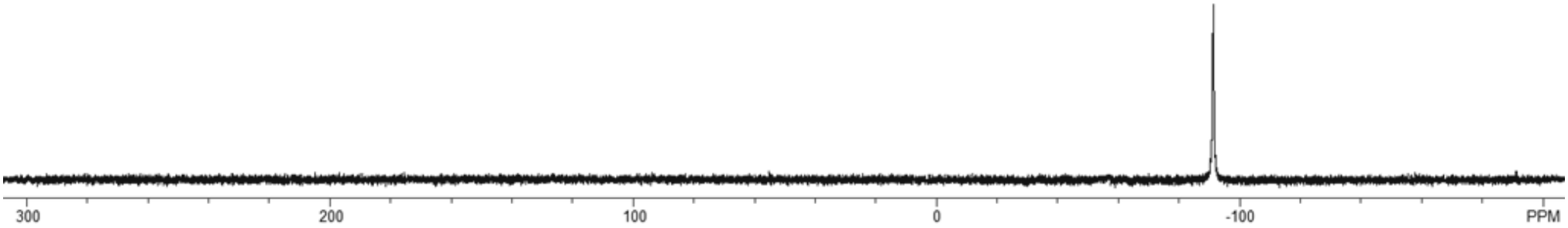


Figure S4. ^{31}P NMR spectrum of **1** (162 MHz, C_6D_6, 25 ^{o}C).

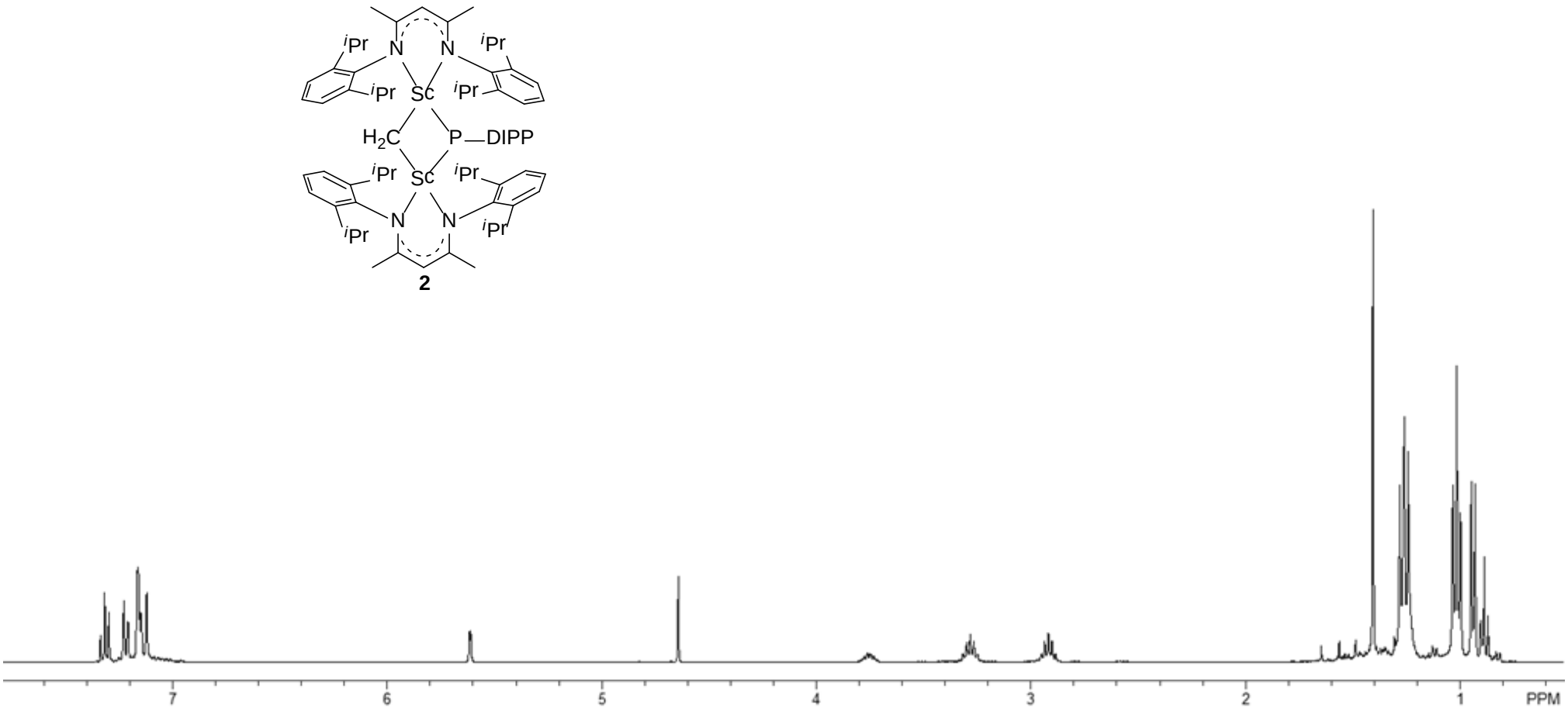


Figure S5. ^{1}H NMR spectrum of **2** (400 MHz, C_6D_6, 25 ^{o}C).

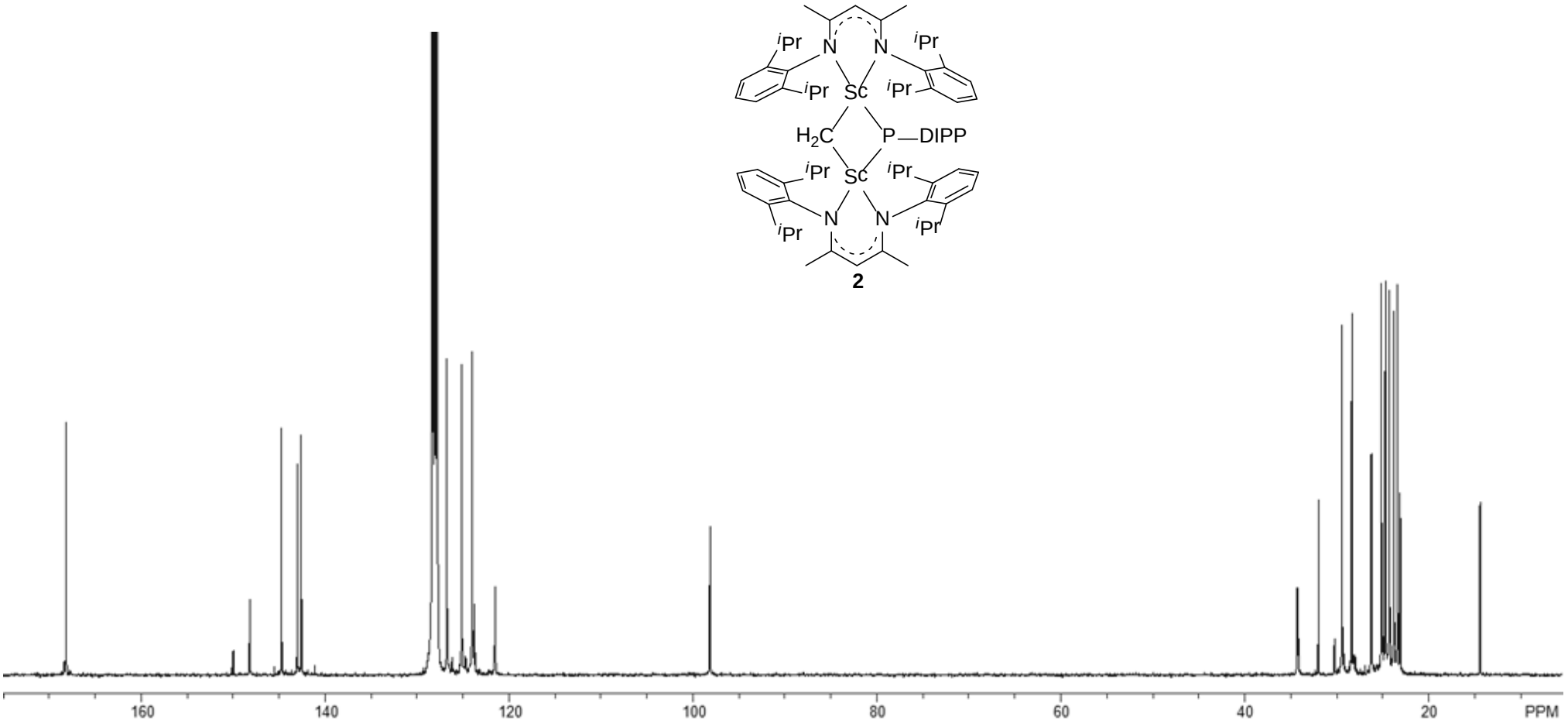
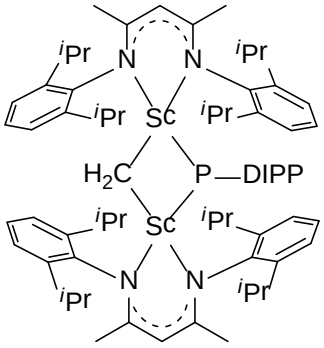


Figure S6. ^{13}C NMR spectrum of **2** (100 MHz, C_6D_6, 25 ^{o}C).



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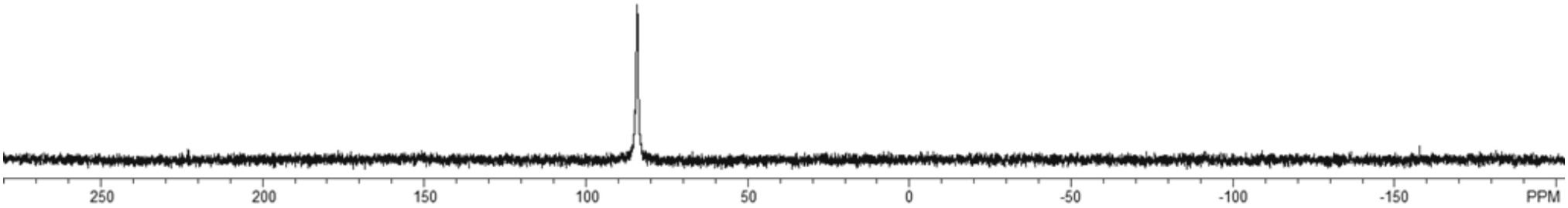


Figure S7. ^{31}P NMR spectrum of **2** (162 MHz, C_6D_6, 25 ^{o}C).

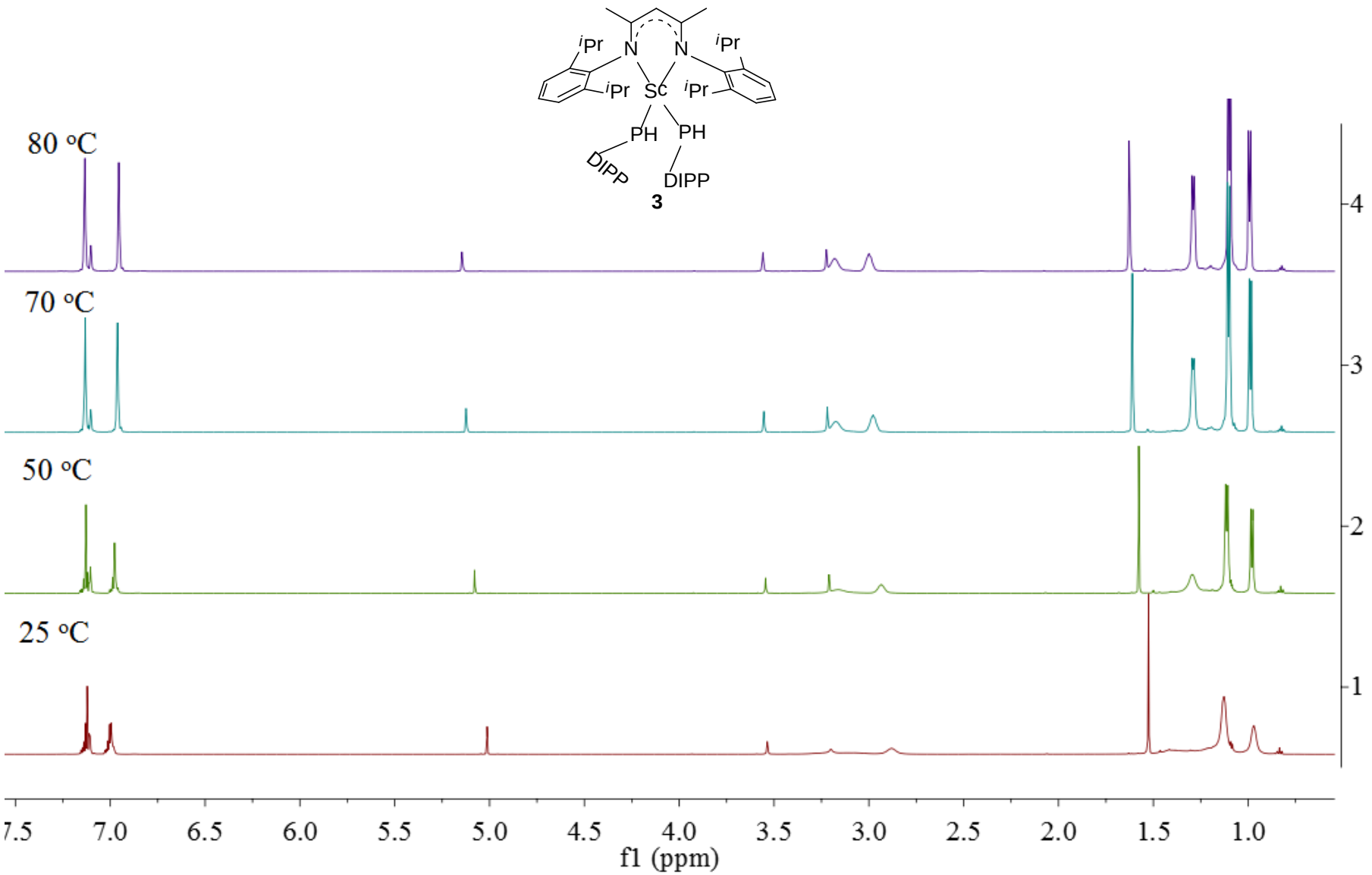


Figure S8. VT ^{1}H -NMR spectra of **3** (600 MHz, C_6D_6).

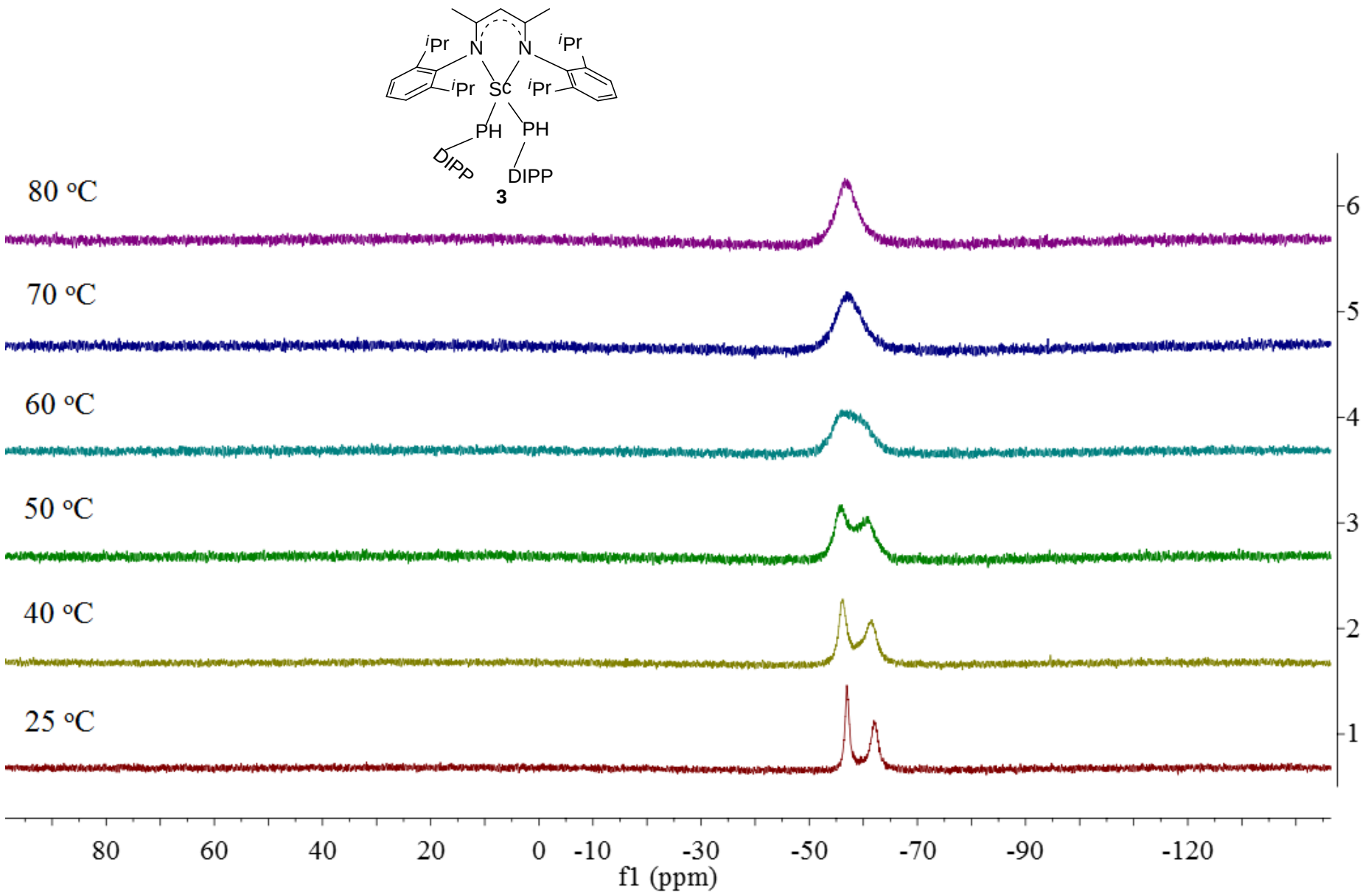
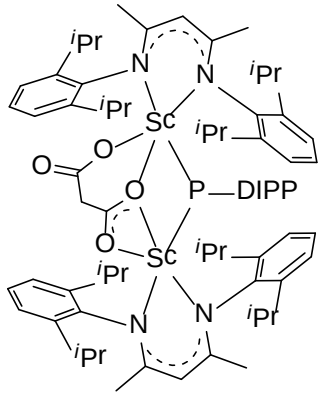


Figure S9. VT ^{31}P NMR spectra of **3** (243 MHz, C_6D_6).



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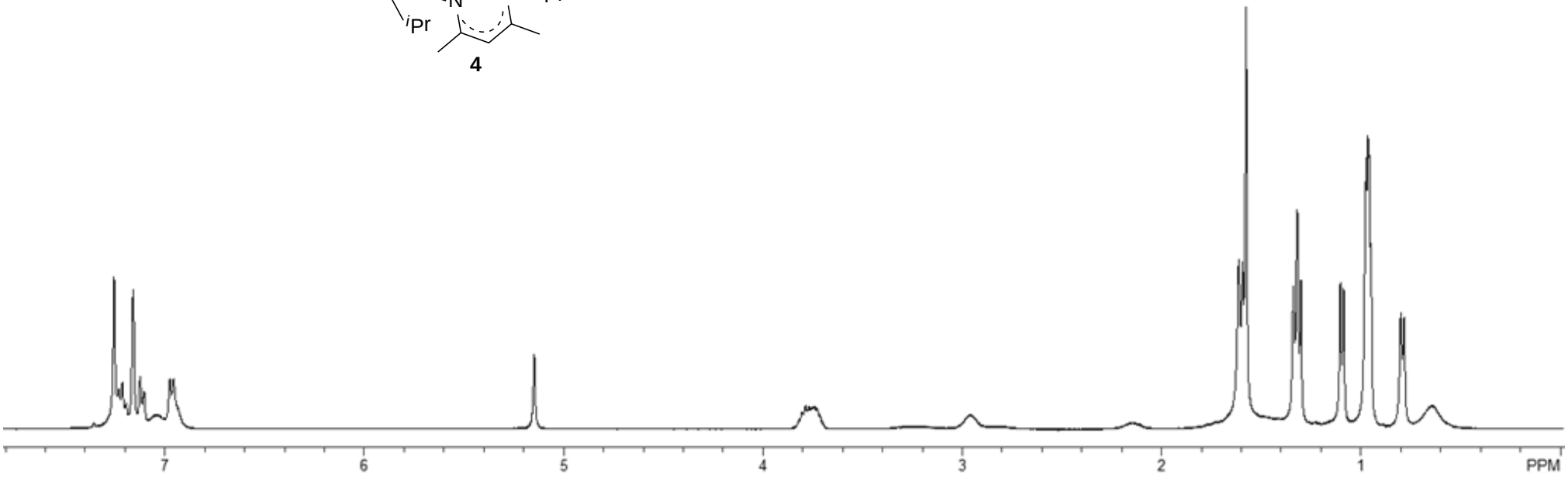
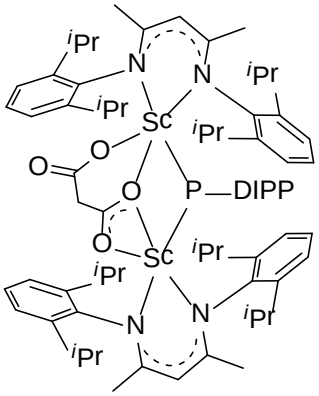


Figure S10. ^{1}H NMR spectrum of **4** (400 MHz, C_6D_6, 25 ^{o}C).



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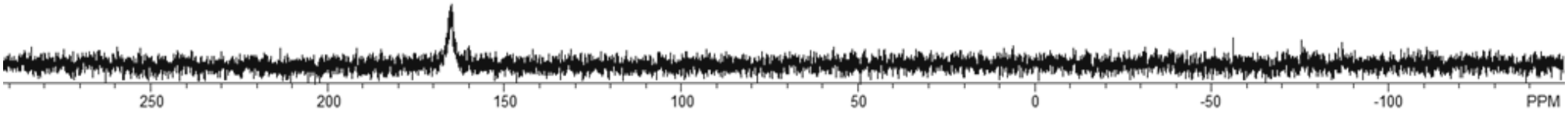
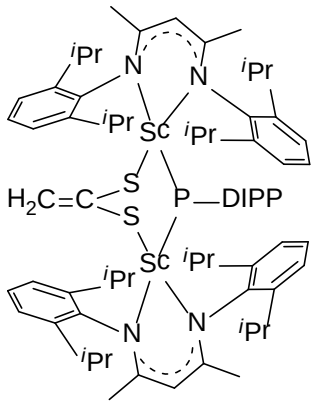


Figure S11. ^{31}P NMR spectrum of **4** (162 MHz, C_6D_6, 25 ^{o}C).



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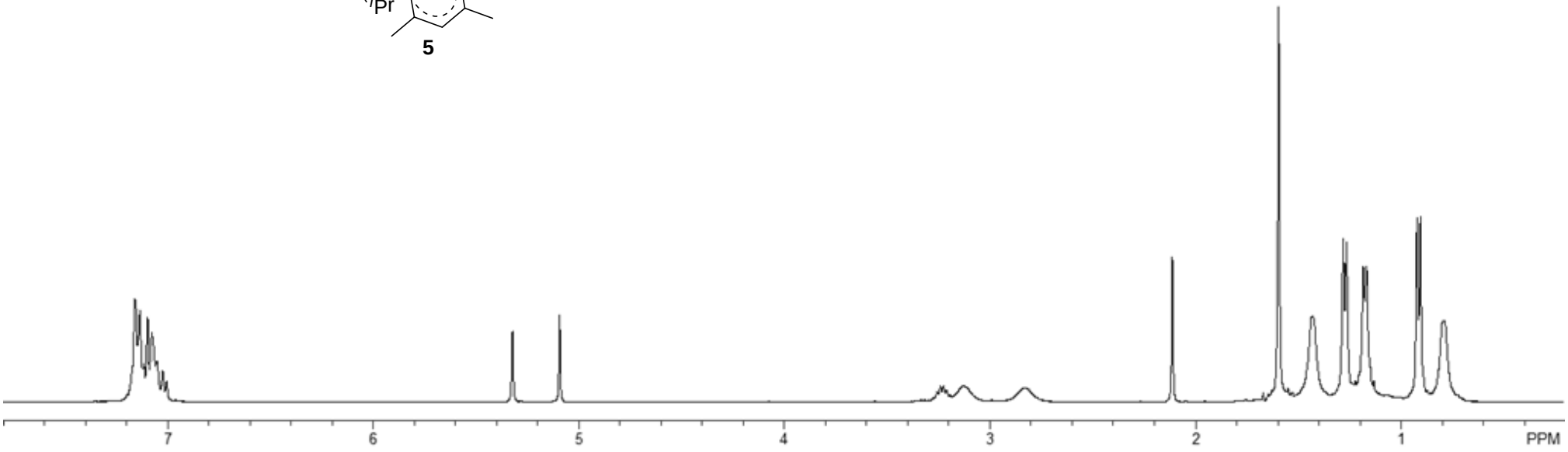


Figure S12. ^{1}H NMR spectrum of **5** (400 MHz, C_6D_6, 25 ^{o}C).

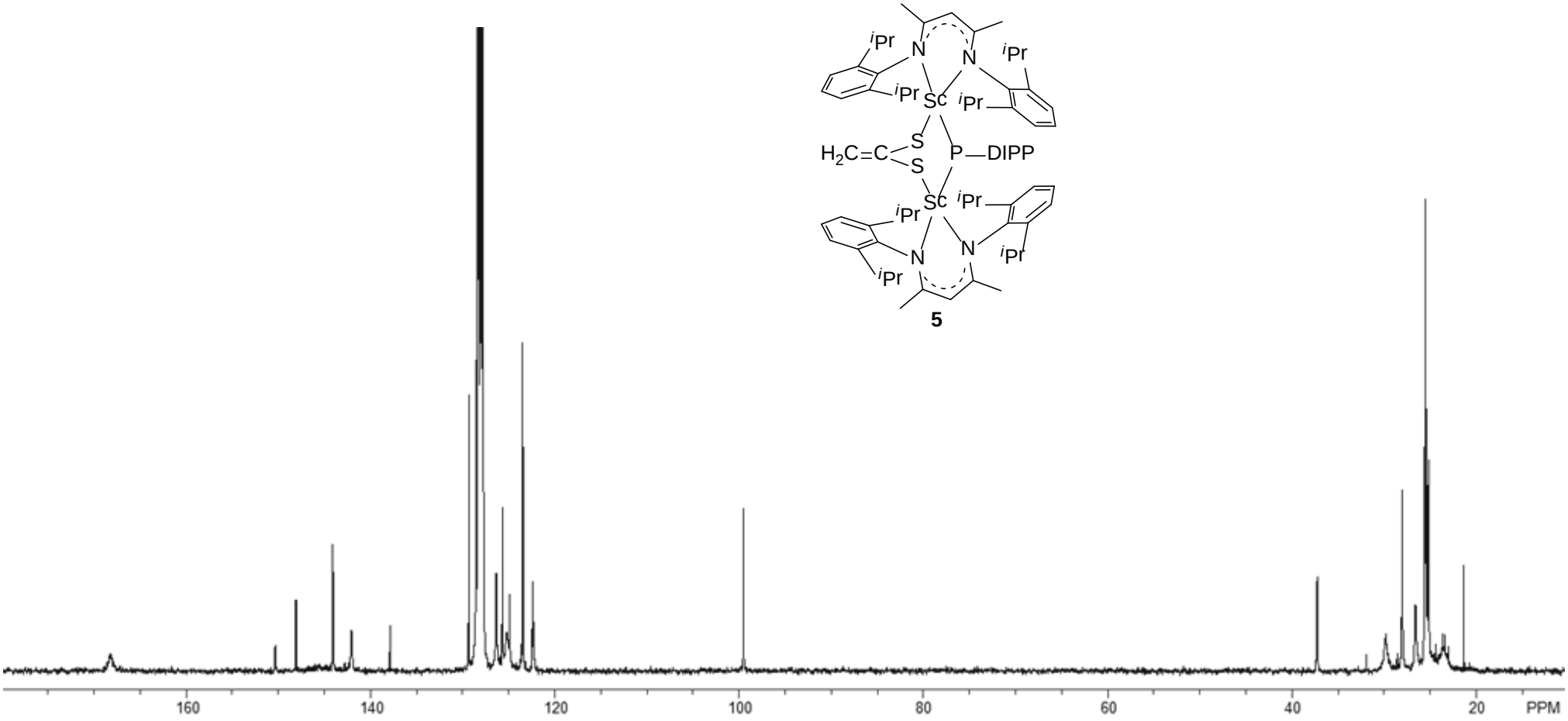
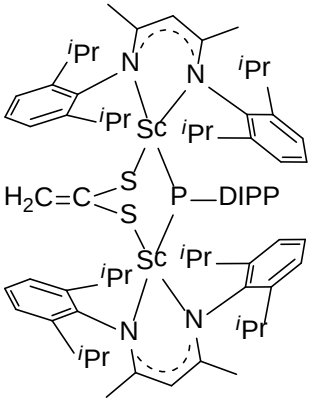


Figure S13. ^{13}C NMR spectrum of **5** (100 MHz, C_6D_6, 25 ^{o}C).



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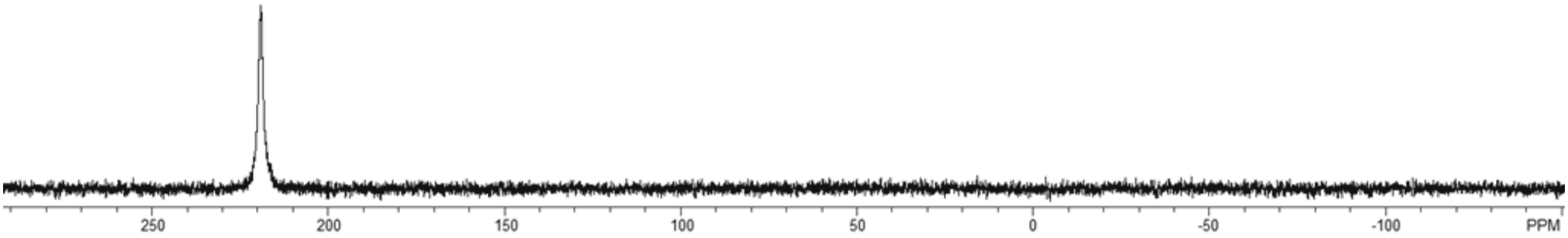
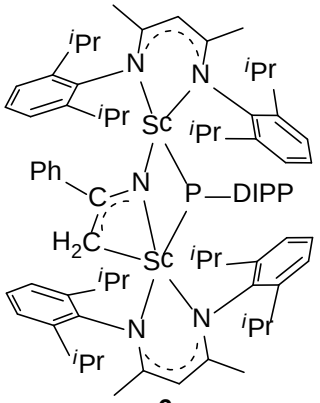


Figure S14. ^{31}P NMR spectrum of **5** (162 MHz, C_6D_6, 25 ^{o}C).



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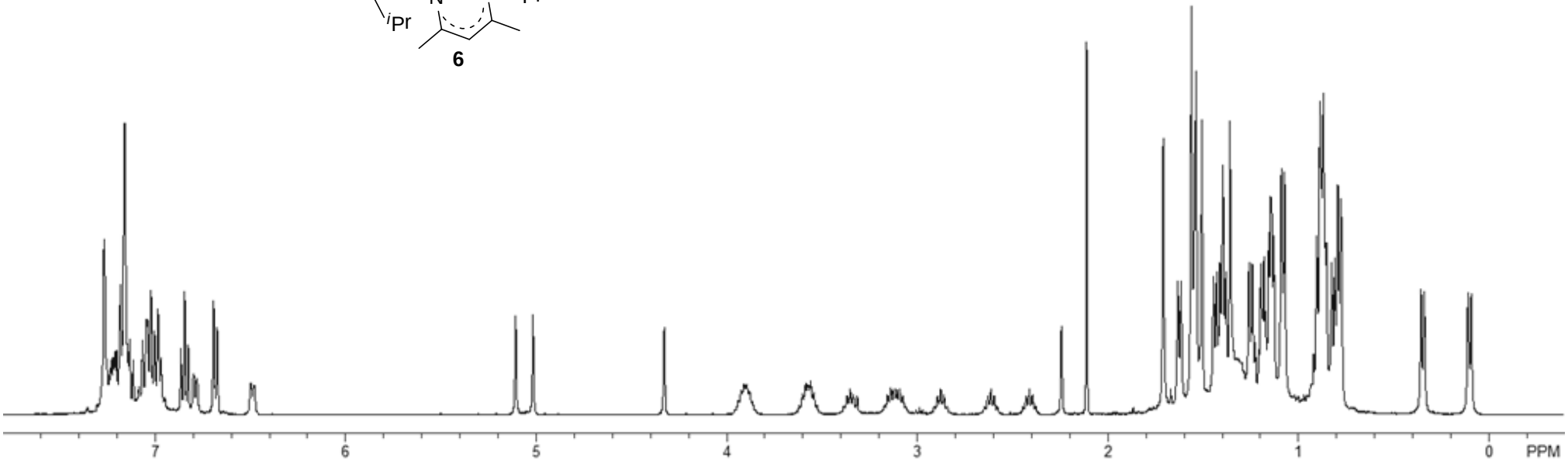
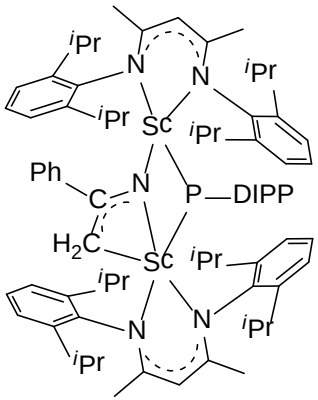


Figure S15. ^{1}H NMR spectrum of **6** (400 MHz, C_6D_6, 25 ^{o}C).



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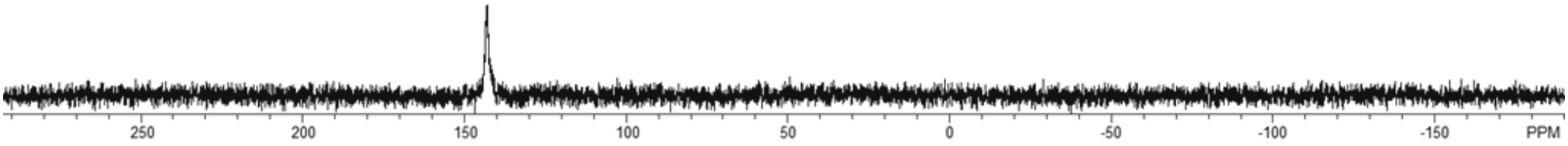
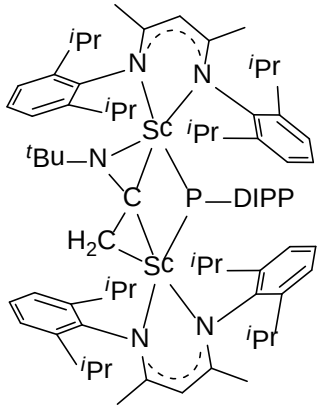


Figure S16. ^{31}P NMR spectrum of **6** (162 MHz, C_6D_6, 25 ^{o}C).



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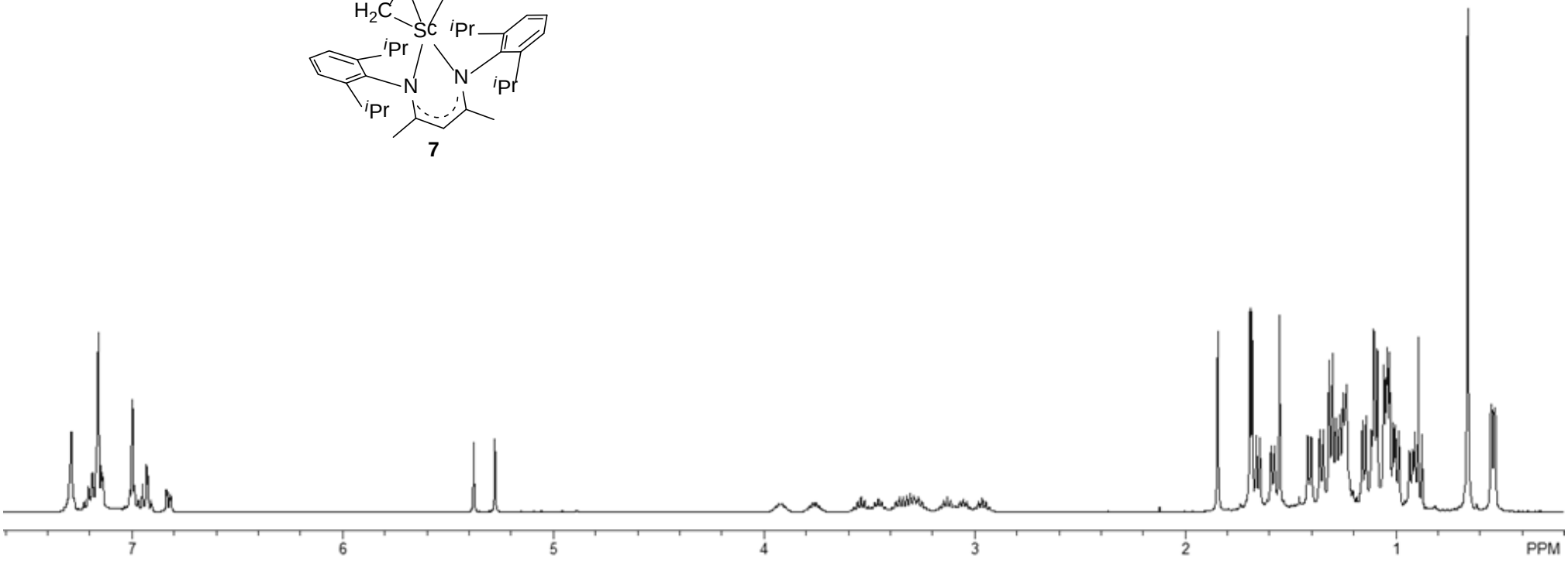

Figure S17. ^{1}H NMR spectrum of **7** (400 MHz, C_6D_6, 25 ^{o}C).

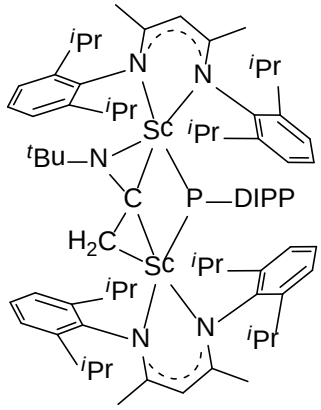

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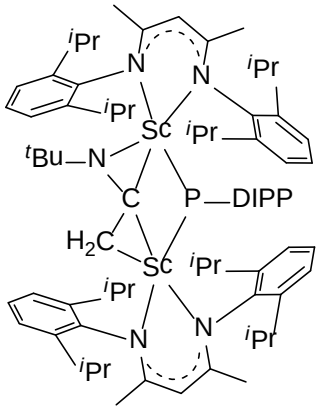
Figure S18. ^{13}C NMR spectrum of **7** (100 MHz, C_6D_6, 25 ^{o}C).



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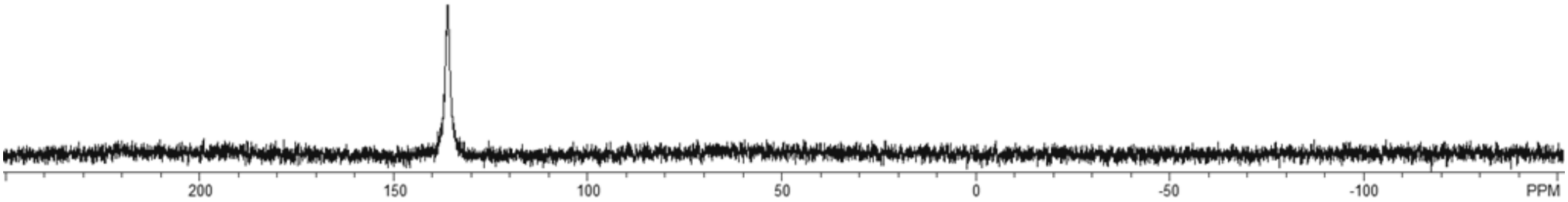

Figure S19. ^{31}P NMR spectrum of **7** (162 MHz, C_6D_6, 25 ^{o}C).

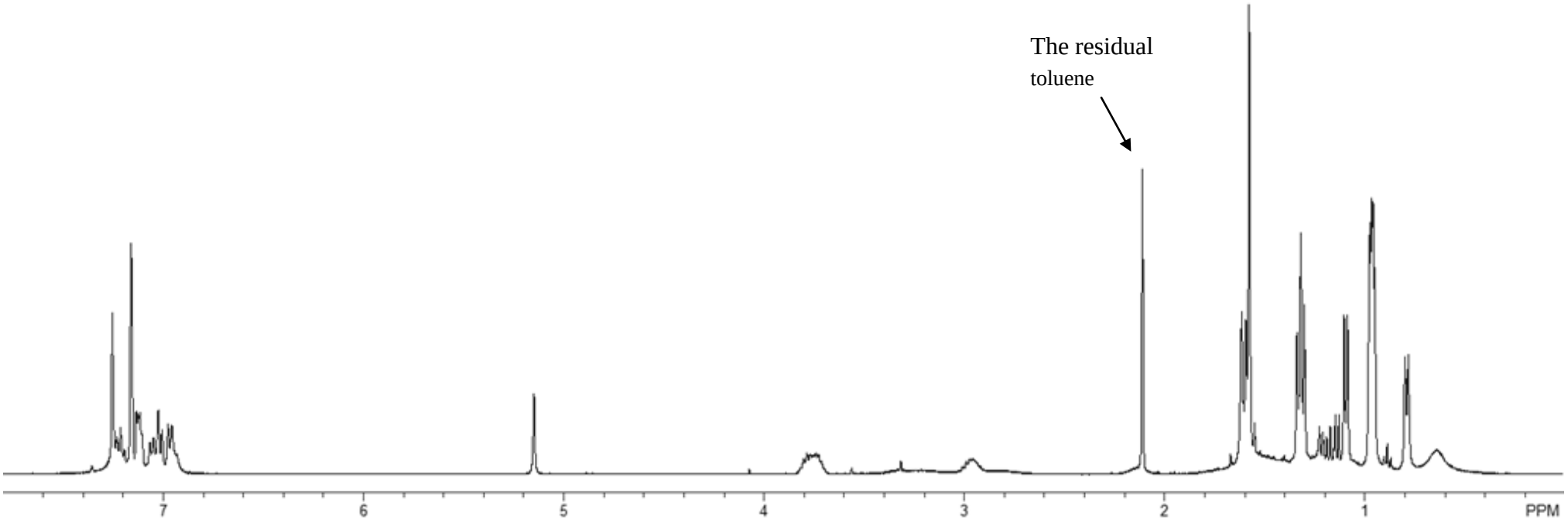

Figure S20. ^{1}H NMR spectrum of the crude product of the reaction of **2** with 3 equiv of CO_2 after the volatiles from the reaction solution were removed (400 MHz, C_6D_6, 25 ^{o}C).

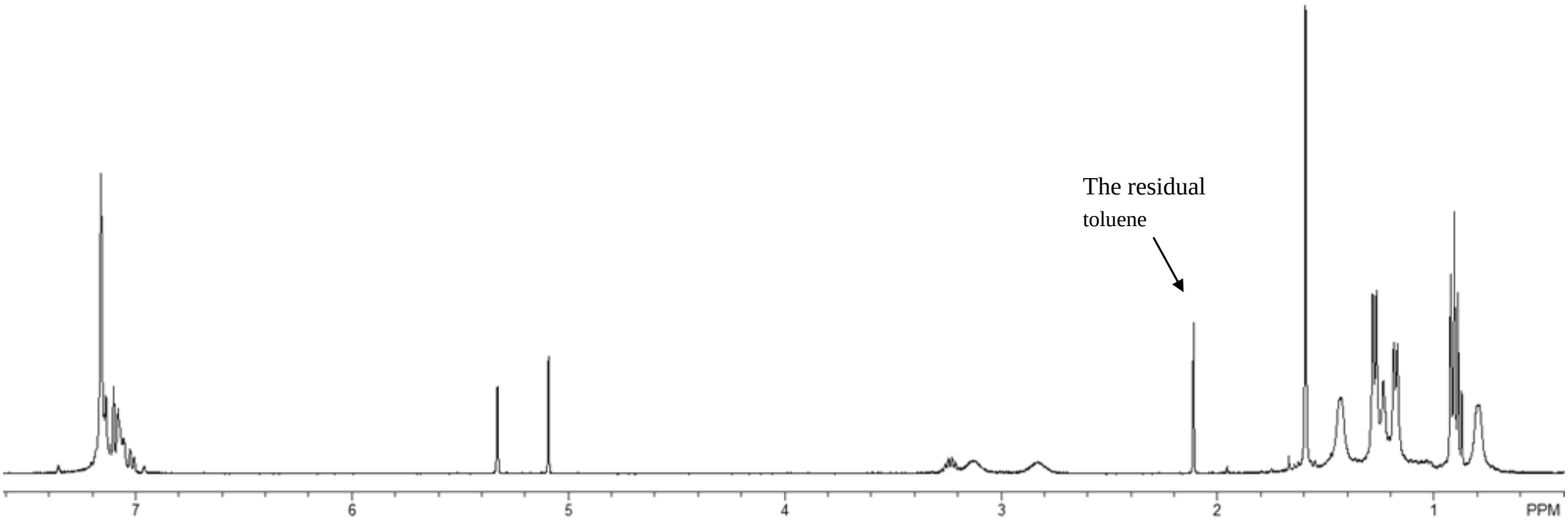

Figure S21. ^{1}H NMR spectrum of the crude product of the reaction of **2** with 2 equiv of CS_2 after the volatiles from the reaction solution were removed (400 MHz, C_6D_6, 25 ^{o}C). The signals at 0.89 and 1.24 ppm belong to hexane, C_6D_6 used for this sample was contaminated by hexane.

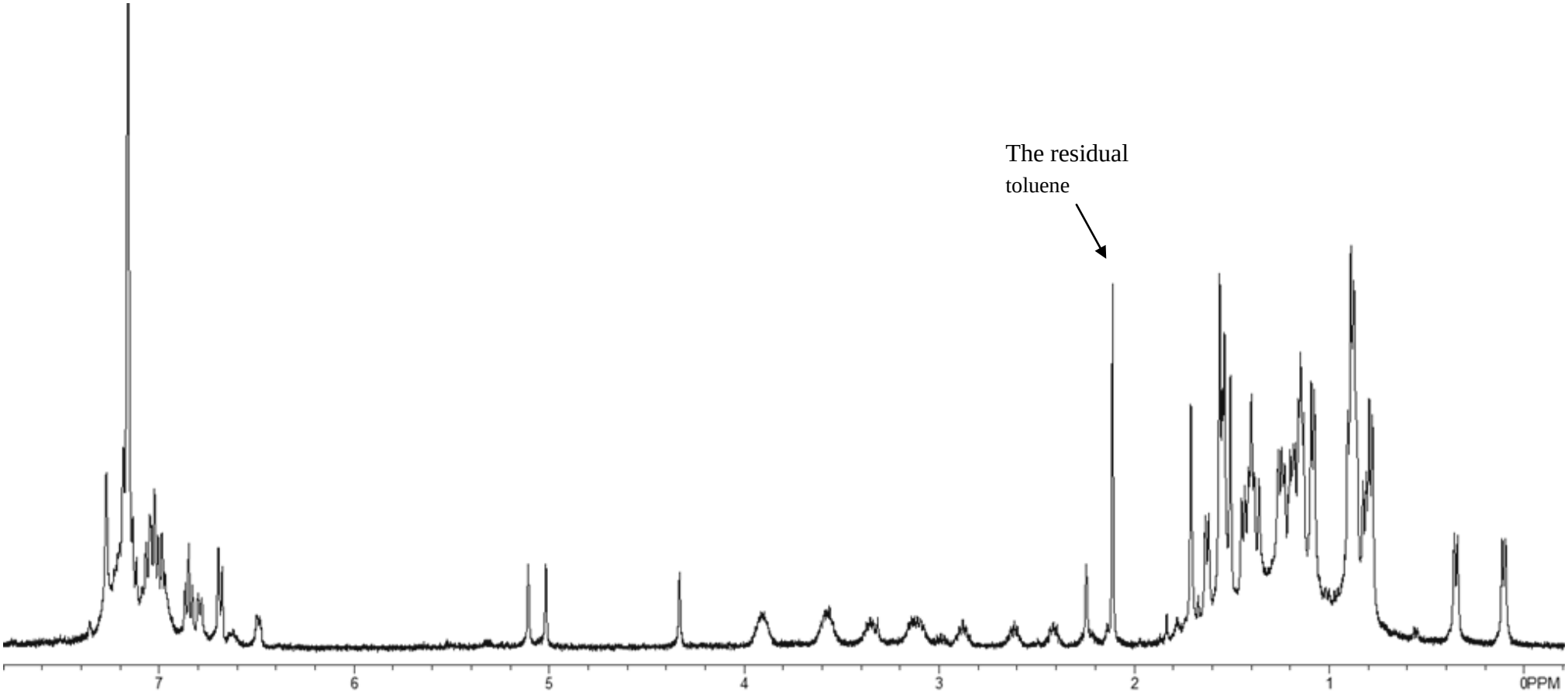

Figure S22. ^{1}H NMR spectrum of the crude product of the reaction of **2** with 1 equiv of PhCN after the volatiles from the reaction solution were removed (400 MHz, C_6D_6, 25 ^{o}C).

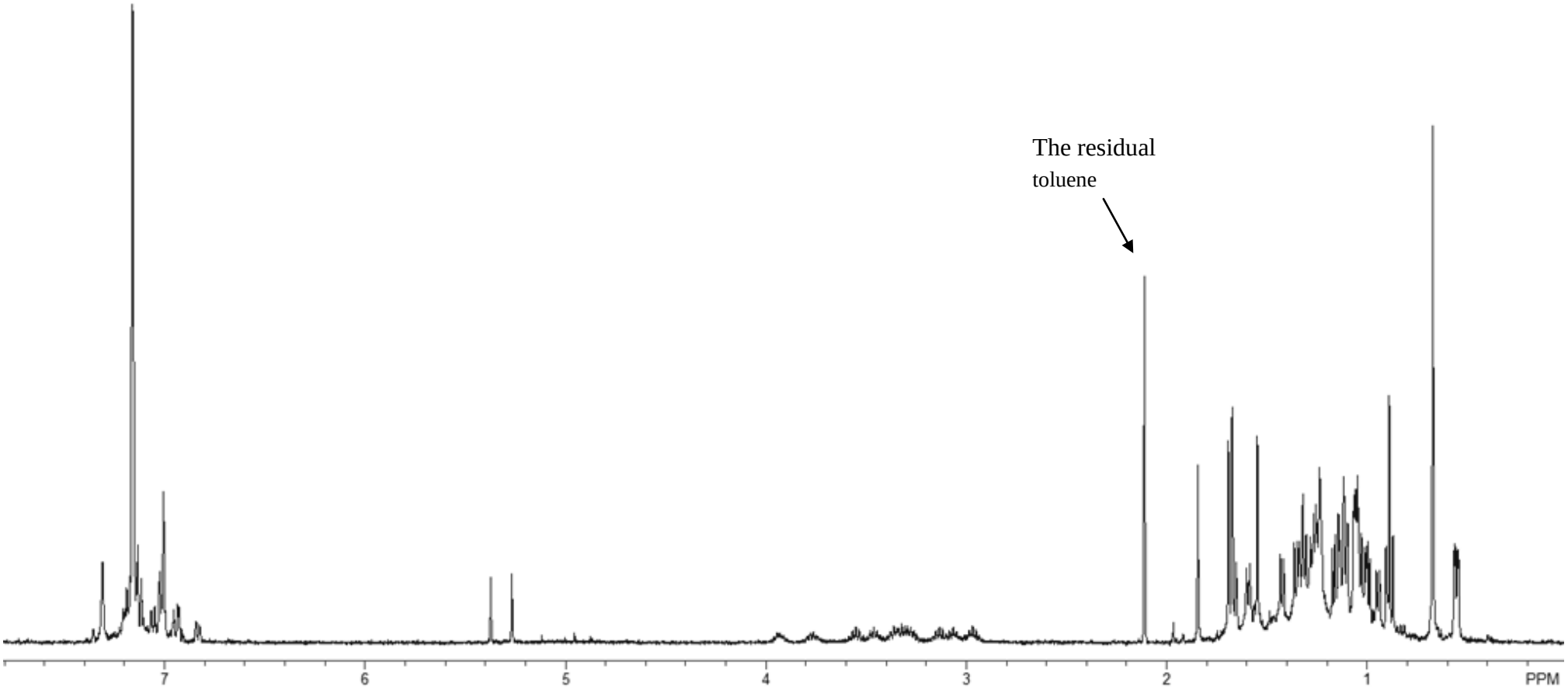

Figure S23. ^{1}H NMR spectrum of the crude product of the reaction of **2** with 1 equiv of ^{t}BuNC after the volatiles from the reaction solution were removed (400 MHz, C_6D_6, 25 ^{o}C).

Computational Data

All calculations were performed using GAUSSIAN09 code.[1] The equilibrium and transition structures were fully optimized at the Becke's 3-parameter hybrid functional[2] combined with the non-local correlation functional provided by Perdew/Wang.[3] Scandium and phosphorous atoms were represented by the relativistic effective core potential SDD, augmented by *f* and *d* polarization functions respectively.[4,5] For the rest atoms the 6-31G(d,p) basis set was used.[6] The natural population analysis (NPA) was performed using Weinhold's methodology.[7]

1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

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5. a) A. Bergner, M. Dolg, W. Kuchle, H. Stoll, H. Preuss, Mol. Phys. **1993**, 80, 1431-1441; b) A. Hollwarth, M. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. **1993**, 208, 237-240.

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7. a) A. E. Reed, L. A. Agrtiss, F. Weinhold, Chem. Rev. **1988**, *88*, 899; b) F. Weinhold, In The Encyclopedia of Computational Chemistry; P. v. R., Schleyer, Ed., John Wiley & Sons: Chichester, pp 1792, **1998**.

Cartesian coordinates of the optimized structure:

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scf done: -3084.751481

Sc	-0.548299	6.735729	14.699366
Sc	-2.680088	7.144002	17.333280
P	-0.256126	7.817988	16.973416
N	0.003662	7.871743	12.880974
N	0.307414	4.943720	13.794192
N	-4.493028	8.342338	17.545326
N	-3.277982	5.993286	19.124169
C	1.543159	8.324961	10.984498
H	0.827656	9.083682	10.667608
H	1.810249	7.704774	10.125883
H	2.453765	8.838205	11.311967
C	1.009865	7.459519	12.108634
C	1.664499	6.211014	12.223645
H	2.513487	6.101201	11.558341
C	1.305681	5.037032	12.900394
C	2.109523	3.804747	12.547244
H	2.716292	3.493493	13.403637
H	2.776153	3.993589	11.704737
H	1.457962	2.962668	12.301365
C	-0.638747	9.124649	12.584577
C	-0.026025	10.359200	12.913209
C	-0.702845	11.542382	12.599056
H	-0.239105	12.493973	12.844763
C	-1.946545	11.529527	11.983098
H	-2.450079	12.462607	11.744202
C	-2.541810	10.313047	11.673424
H	-3.514164	10.304571	11.191410
C	-1.911323	9.099494	11.962064
C	-2.559640	7.793805	11.526316
H	-2.216719	7.007969	12.210075
C	-4.089499	7.816251	11.596321
H	-4.447350	8.153701	12.572708
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H	-1.010170	7.287399	10.059291
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H	1.771591	9.466880	13.631353
C	1.218303	10.990640	15.018483
H	0.786571	11.997859	15.031840
H	2.204690	11.040879	15.491407
H	0.587828	10.336181	15.626106
C	2.305977	11.358740	12.781646
H	2.371992	11.064569	11.729963
H	3.310163	11.305892	13.215917
H	1.998024	12.409651	12.808880
C	-0.191878	3.631992	14.113753
C	-1.230827	3.088561	13.315839
C	-1.735344	1.825579	13.637223
H	-2.524017	1.399035	13.022994
C	-1.248425	1.103742	14.720226
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H	0.157249	1.078401	16.336223
C	0.325636	2.895070	15.203129
C	1.473993	3.392246	16.065557
H	1.837058	4.329675	15.628932
C	1.004192	3.688787	17.493695
H	0.229975	4.461484	17.507376
H	1.838817	4.039927	18.108798
H	0.590423	2.793431	17.967574
C	2.645540	2.397322	16.089458
H	2.370465	1.468815	16.601211
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H	2.981557	2.127722	15.083206
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H	-1.359645	4.811987	12.075806
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C	-5.057820	8.527641	18.749267
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C	-5.127814	8.944715	16.402812
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H	-7.514153	8.232346	14.075852
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C	-5.388440	10.753182	14.816458
H	-5.102618	11.739423	14.461169
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H	-3.440658	10.578353	17.587641
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H	-1.989350	10.305245	15.605106
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H	-1.257314	1.141555	19.998145
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H	-0.285262	3.100071	21.147145
C	-1.624945	4.526714	20.265772
C	-0.974453	5.676530	21.021769
H	-1.575574	6.574713	20.852556
C	0.436780	5.964282	20.492195
H	1.092390	5.099213	20.644843
H	0.877992	6.818035	21.017022
H	0.419330	6.200103	19.425100
C	-0.921841	5.425454	22.537488
H	-1.897414	5.151976	22.950676
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H	-0.223985	4.618202	22.784902
C	-4.478162	3.715411	17.790732
H	-4.444984	4.718822	17.349509
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H	-3.543289	2.714910	16.083234
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H	-6.652604	3.716239	17.942004
H	-5.846890	4.382209	19.369251
C	1.099168	8.636636	17.963067
C	0.812882	9.752631	18.798543
C	1.839935	10.344233	19.540614
H	1.613006	11.191342	20.181620
C	3.146067	9.878876	19.474419
H	3.932032	10.355618	20.054592
C	3.433180	8.795995	18.654689
H	4.454994	8.431687	18.600291
C	2.439302	8.160703	17.903413
C	2.842804	6.991447	17.020803
H	1.946410	6.368718	16.907246
C	3.248957	7.480440	15.623918
H	2.440601	8.056827	15.163089
H	3.491709	6.640948	14.962094
H	4.129332	8.131586	15.682359
C	3.948790	6.113232	17.615369
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H	4.075365	5.210148	17.008447
H	3.714824	5.806862	18.639749
C	-0.591955	10.314009	18.940060
H	-1.118779	10.060723	18.011464
C	-1.336830	9.626700	20.091837
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H	-2.370695	9.982924	20.168011
H	-0.839461	9.821450	21.049515
C	-0.641161	11.836108	19.107282
H	-0.251325	12.160428	20.078927
H	-1.677930	12.185368	19.051494

H	-0.065639	12.346188	18.328506	H	-2.672405	5.242775	15.263935
C	-2.558125	6.339408	15.345572	H	-3.360567	6.826271	14.763006