Electronic Supporting Information

Yb(II) Triple-Decker Complex with μ-Bridging Naphthalene Dianion $[Cp^{Bn5}Yb(DME)]_2(\mu\text{-}\eta^4:\eta^4\text{-}C_{10}H_8)$. Oxidative Substitution of $[C_{10}H_8]^{2-}$ by 1,4-Diphenylbuta-1,3-diene, P_4 and Protonolysis of the Yb-$C_{10}H_8$ Bond by $PhPH_2$

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Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of complex 1.

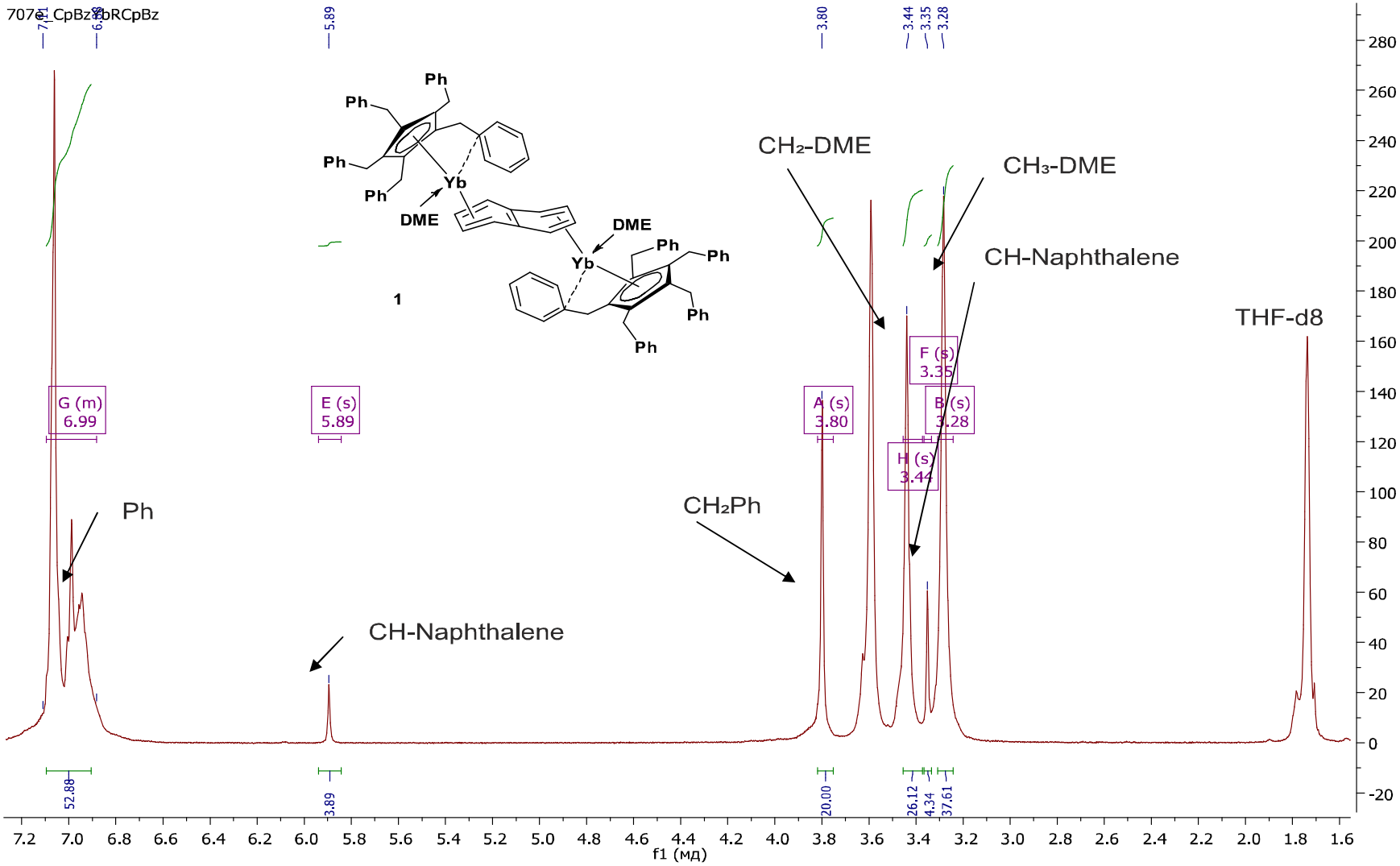

Figure S2. ^{13}C **NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 1.**

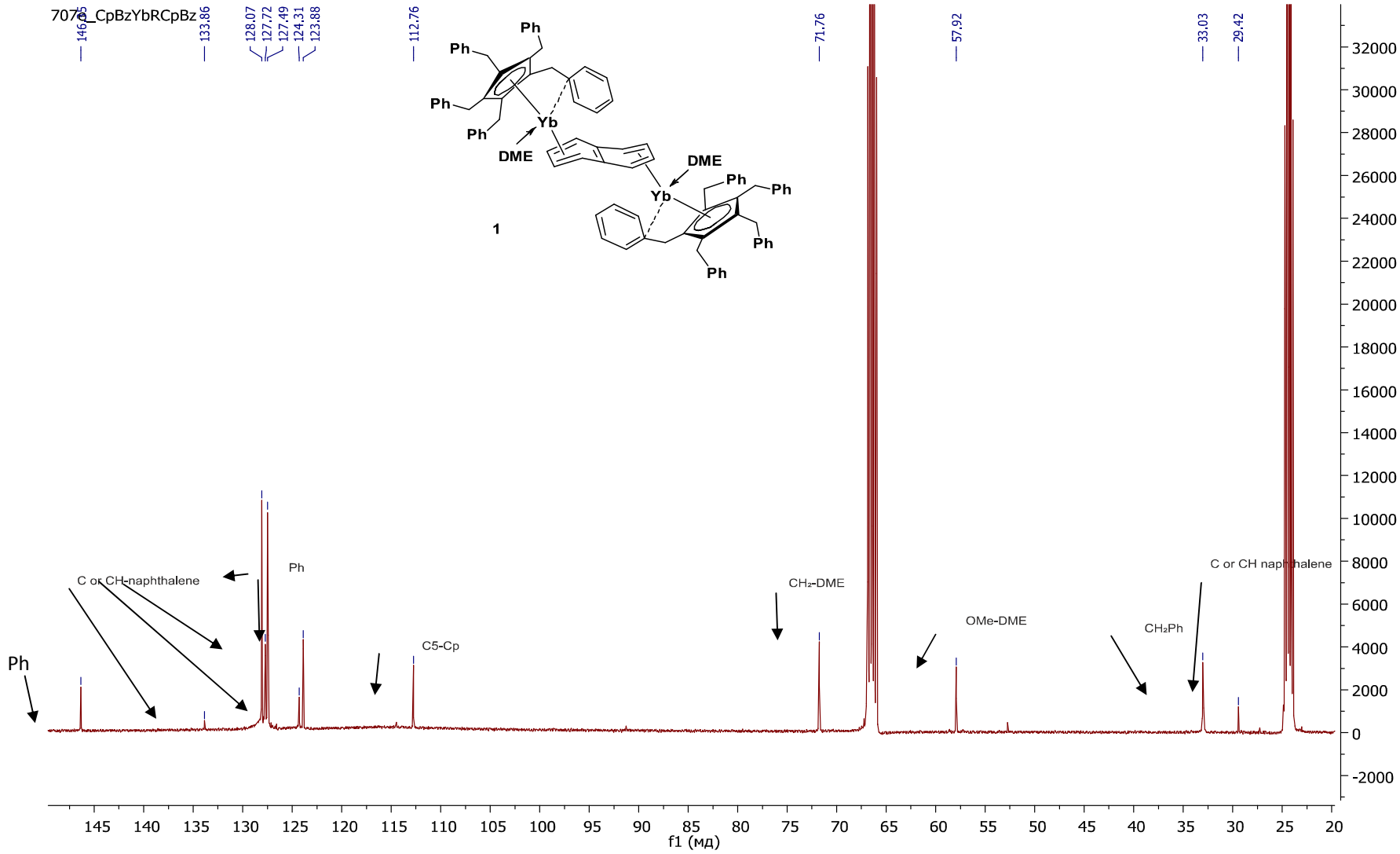

Figure S3. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of complex 4.

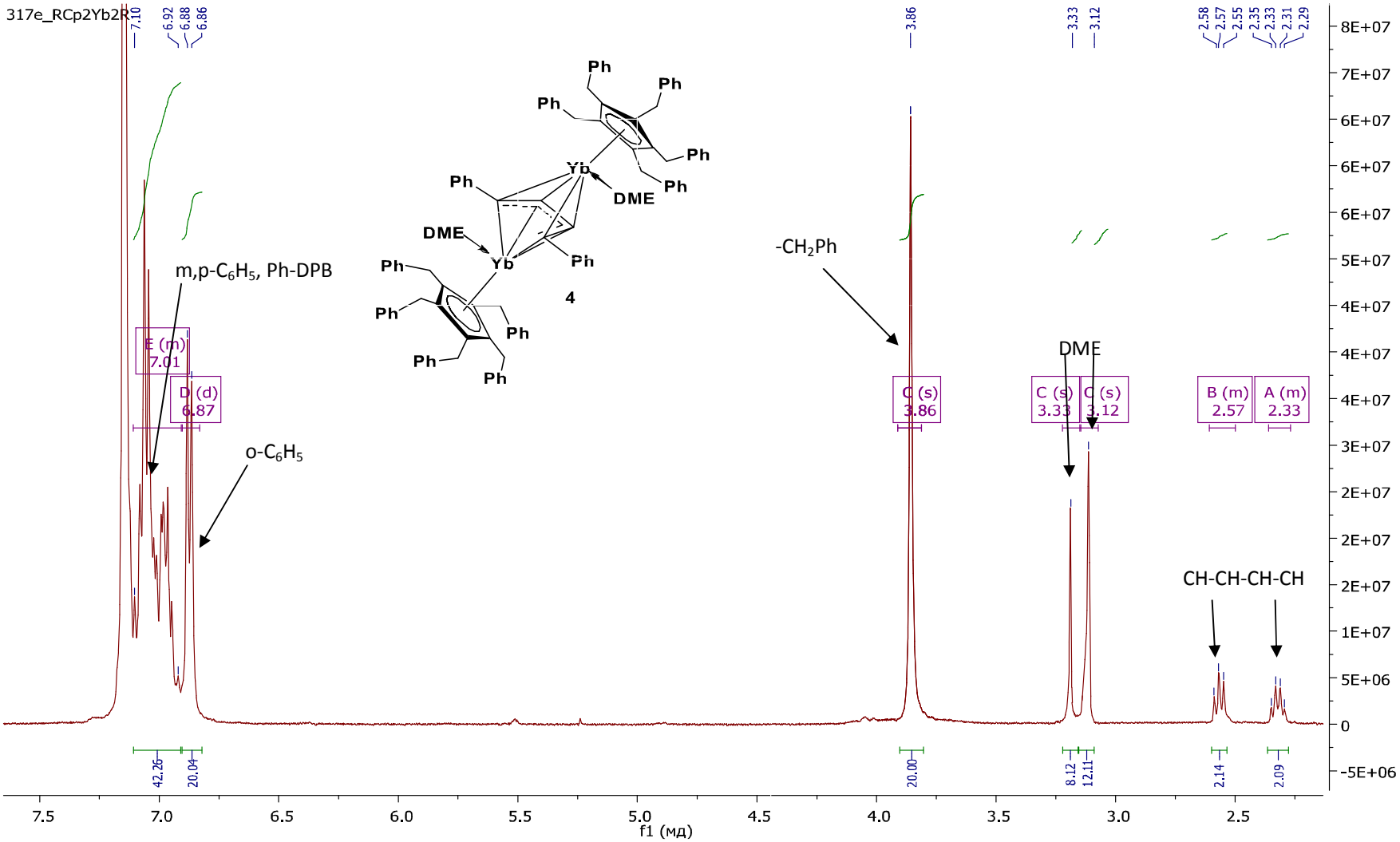

Figure S4. ^{13}C NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 4.

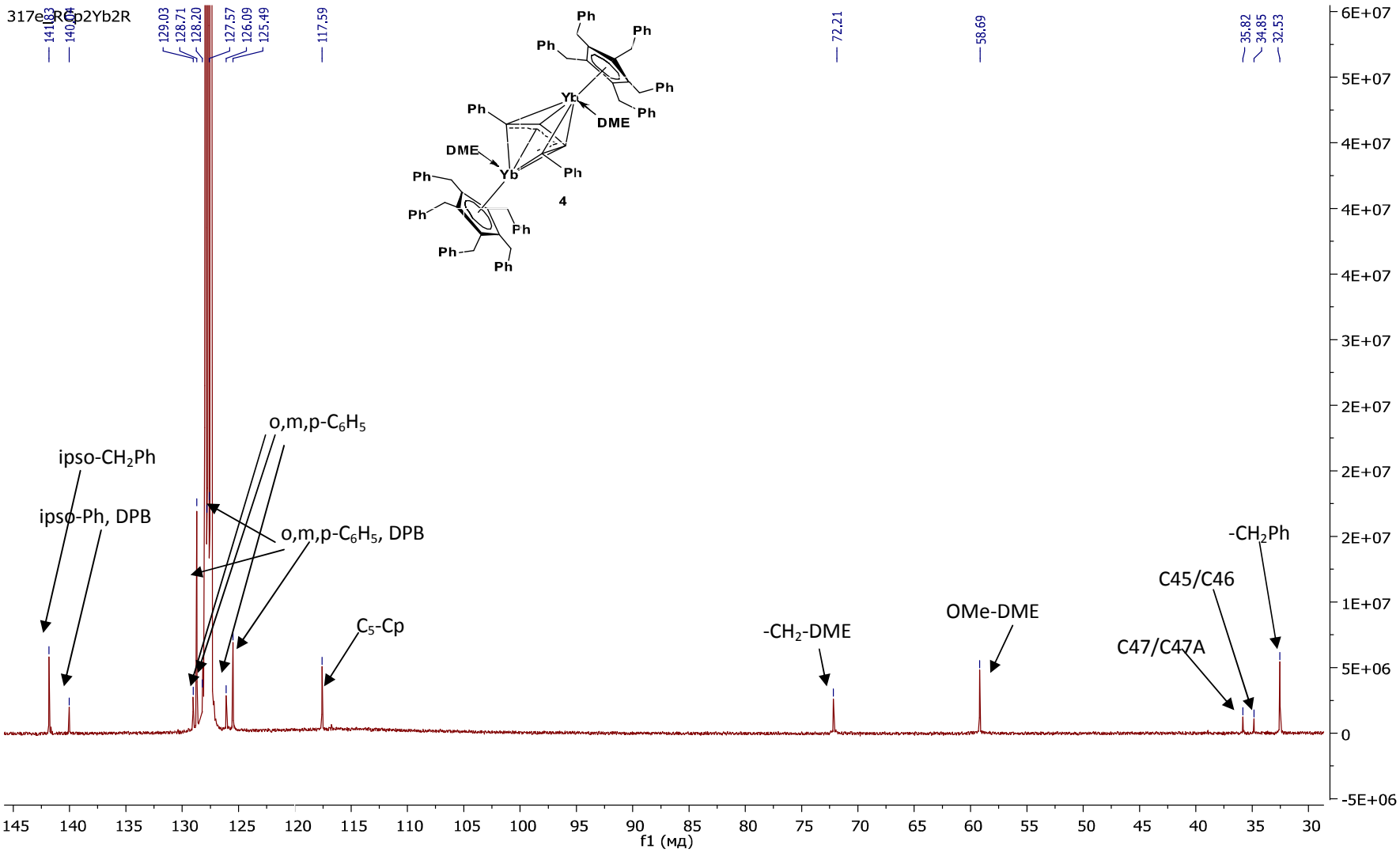

Figure S5. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of complex 6.

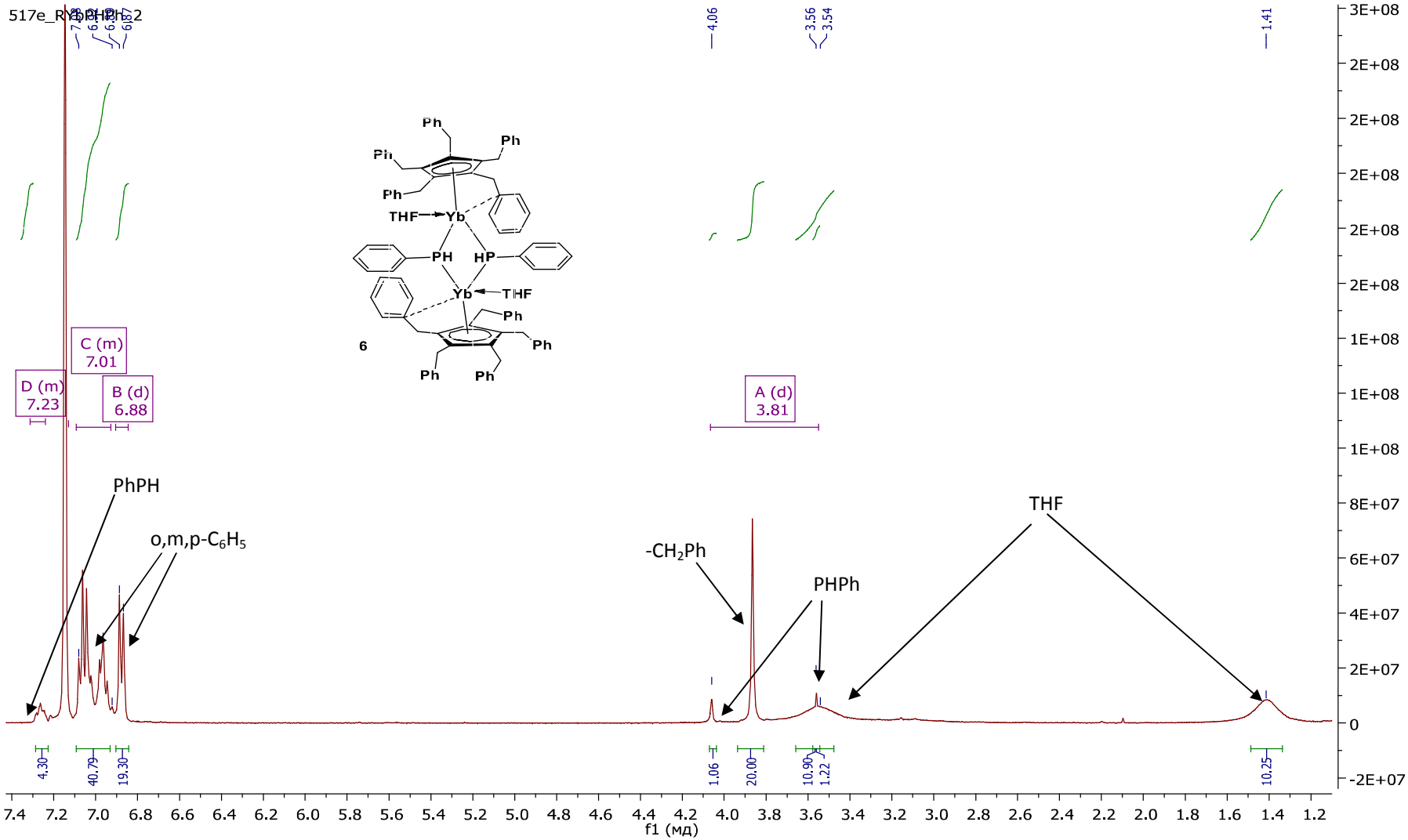

Figure S6. ^{13}C NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 6.

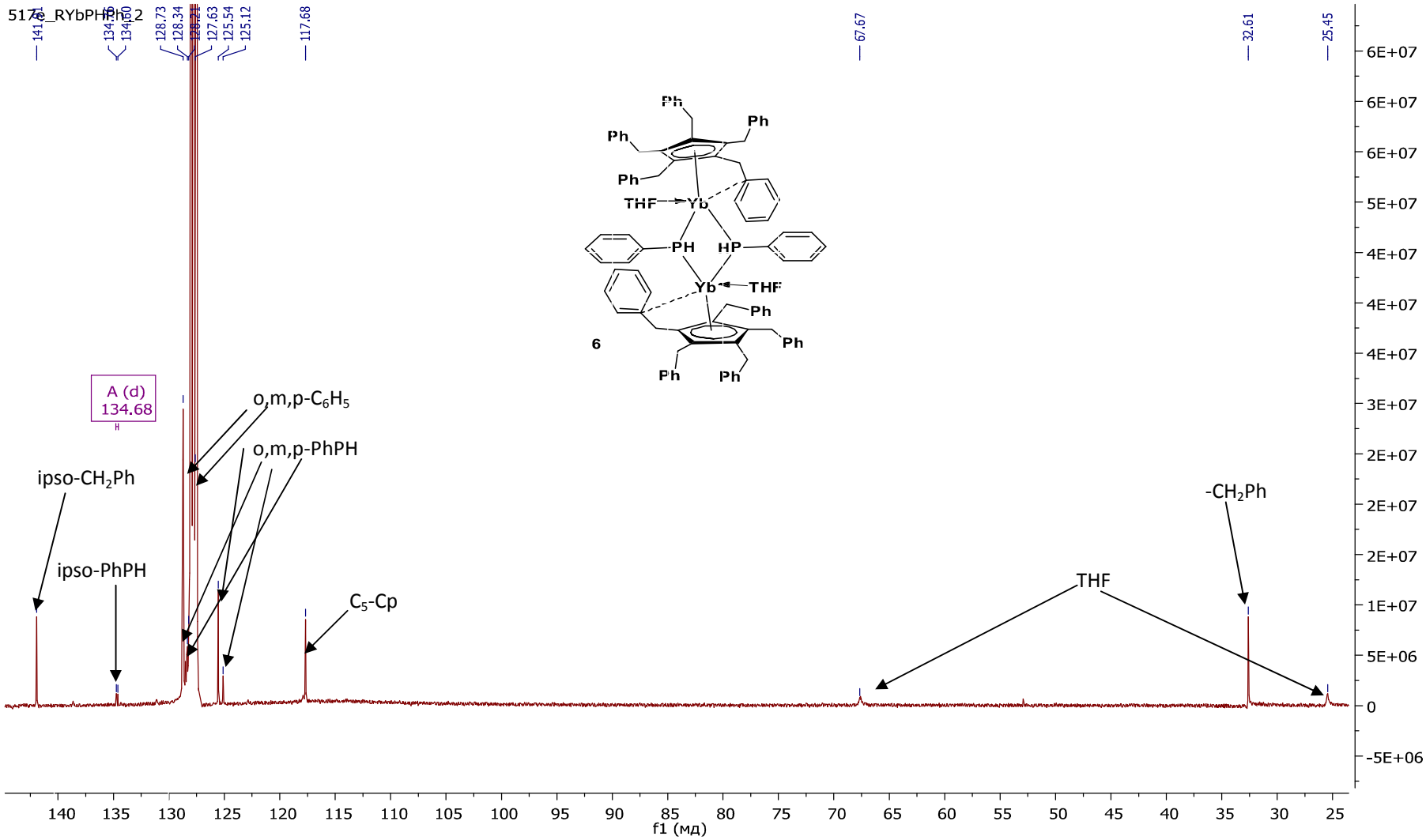

Figure S7. ^{31}P NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 6.

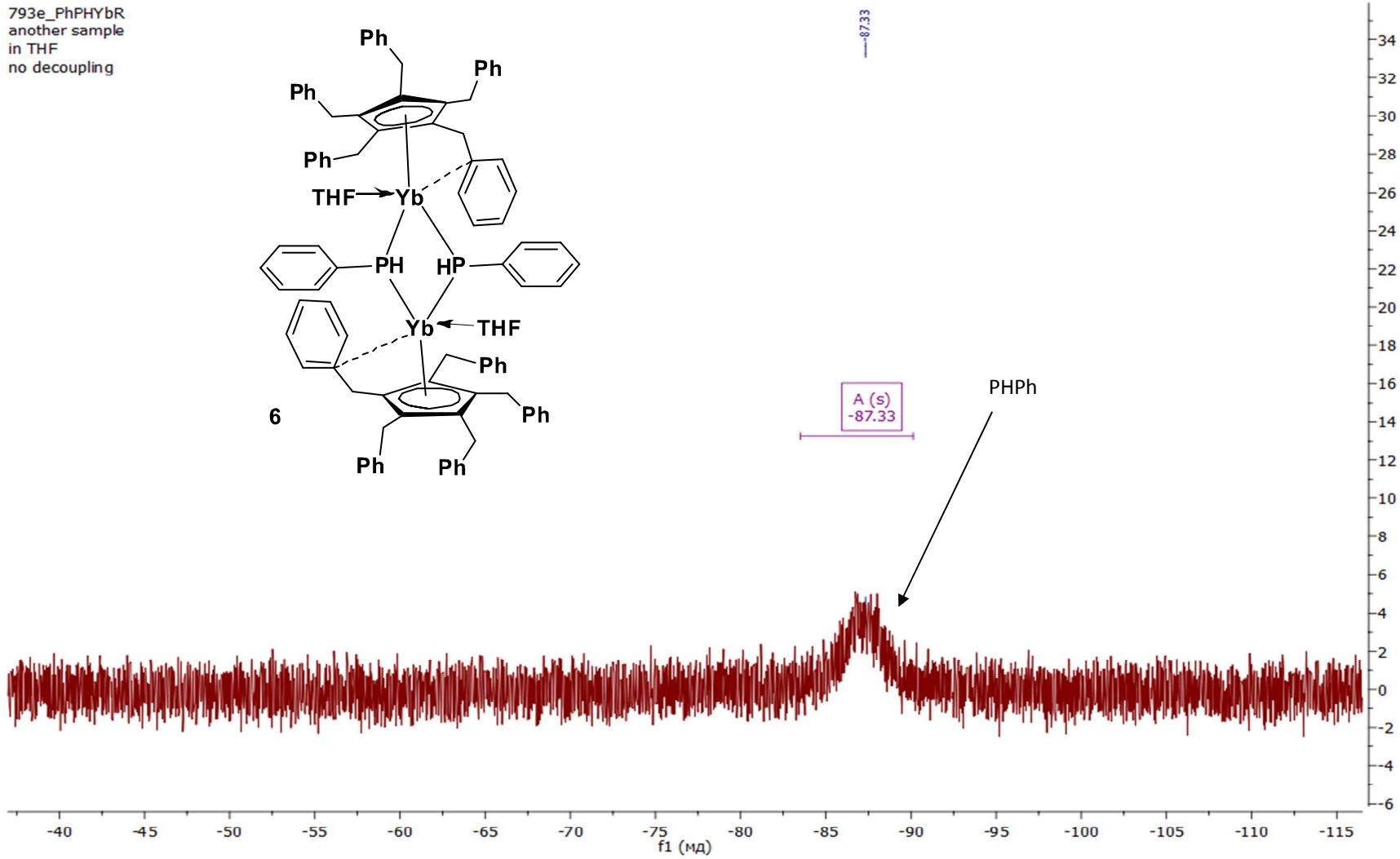

Figure S8. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of complex 5.

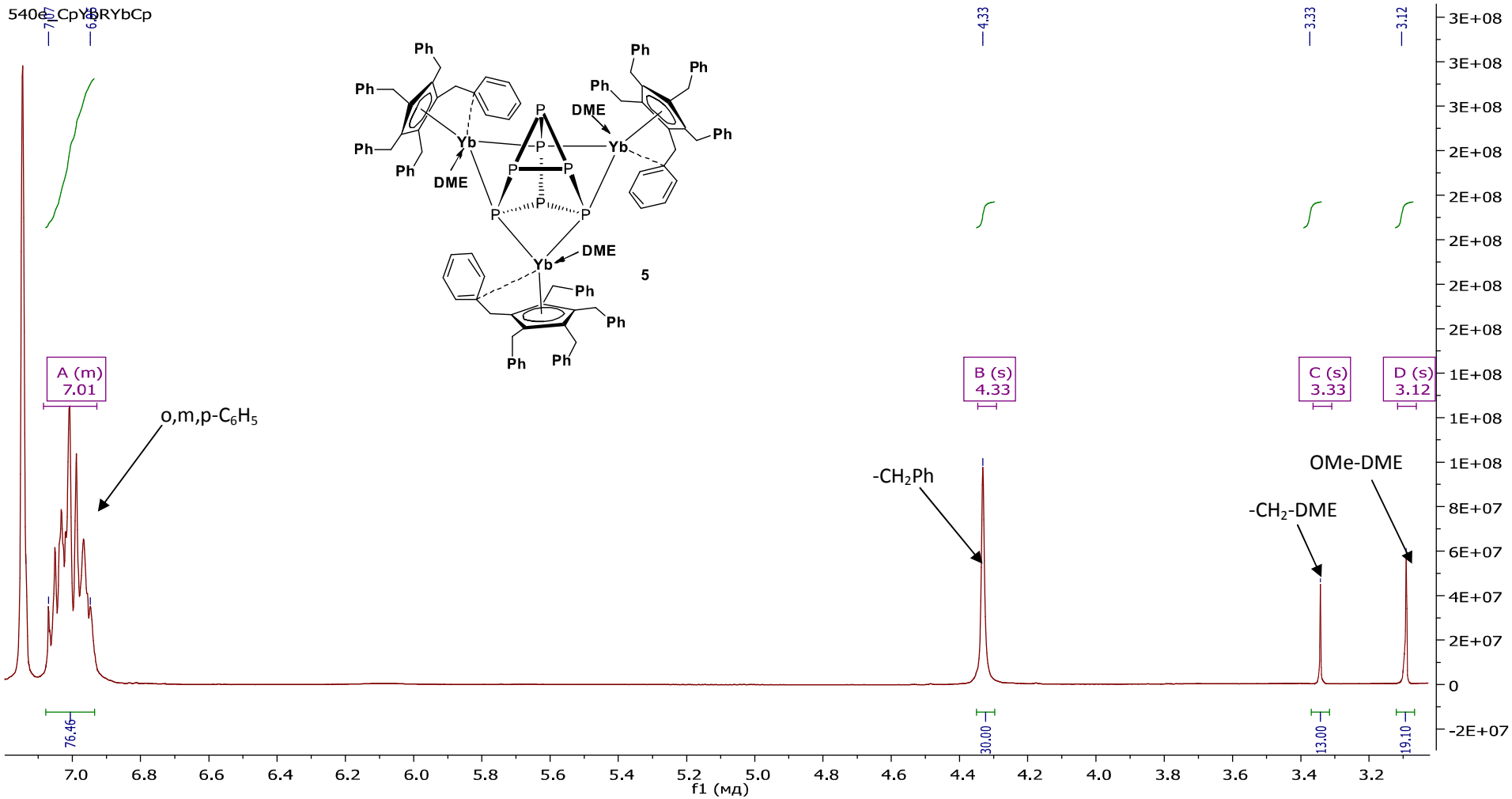

Figure S9. ^{13}C NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 5.

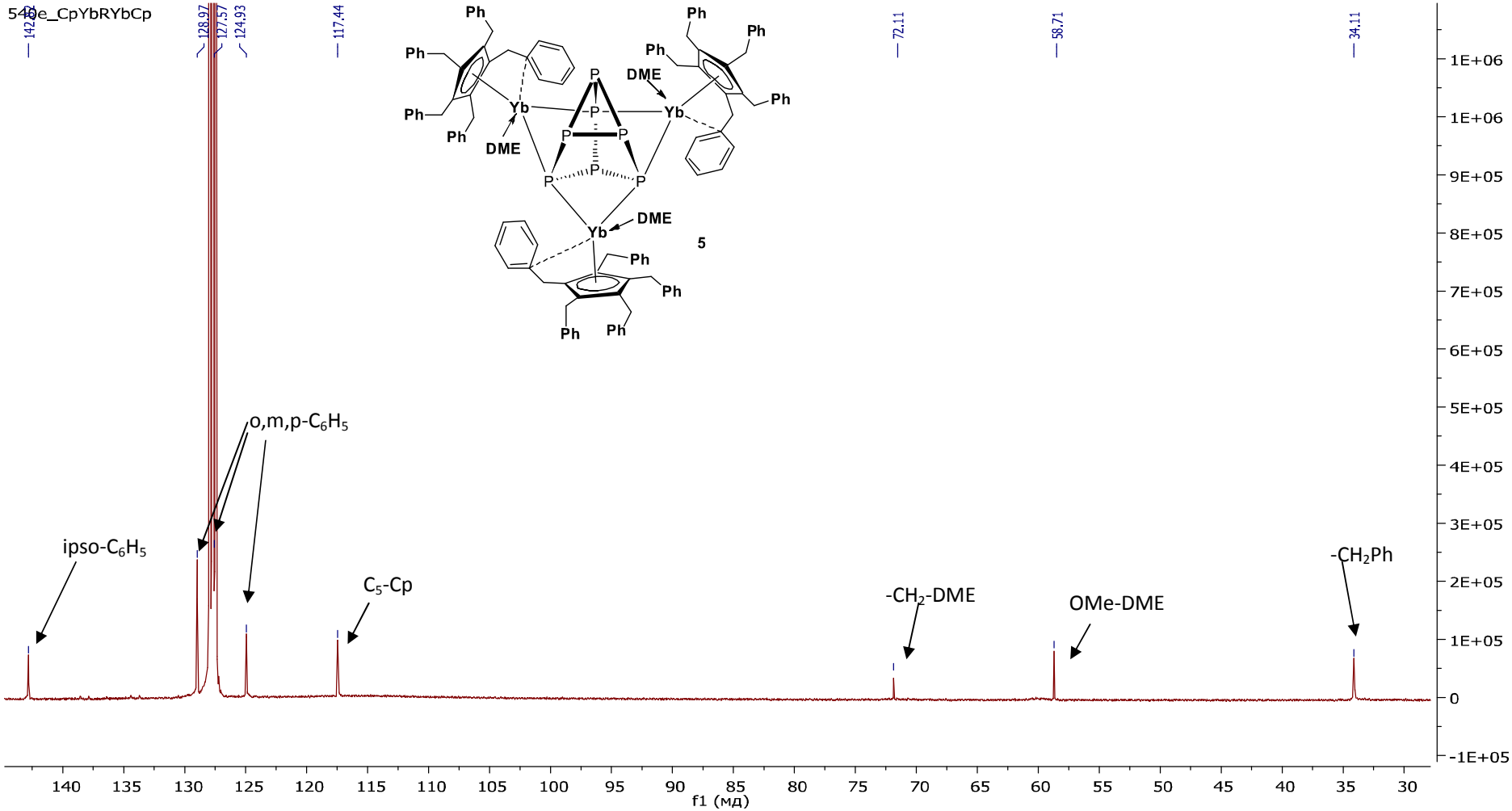

Figure S10. ^{31}P NMR spectrum (100 MHz, C_7D_8, 293 K) of complex 5.

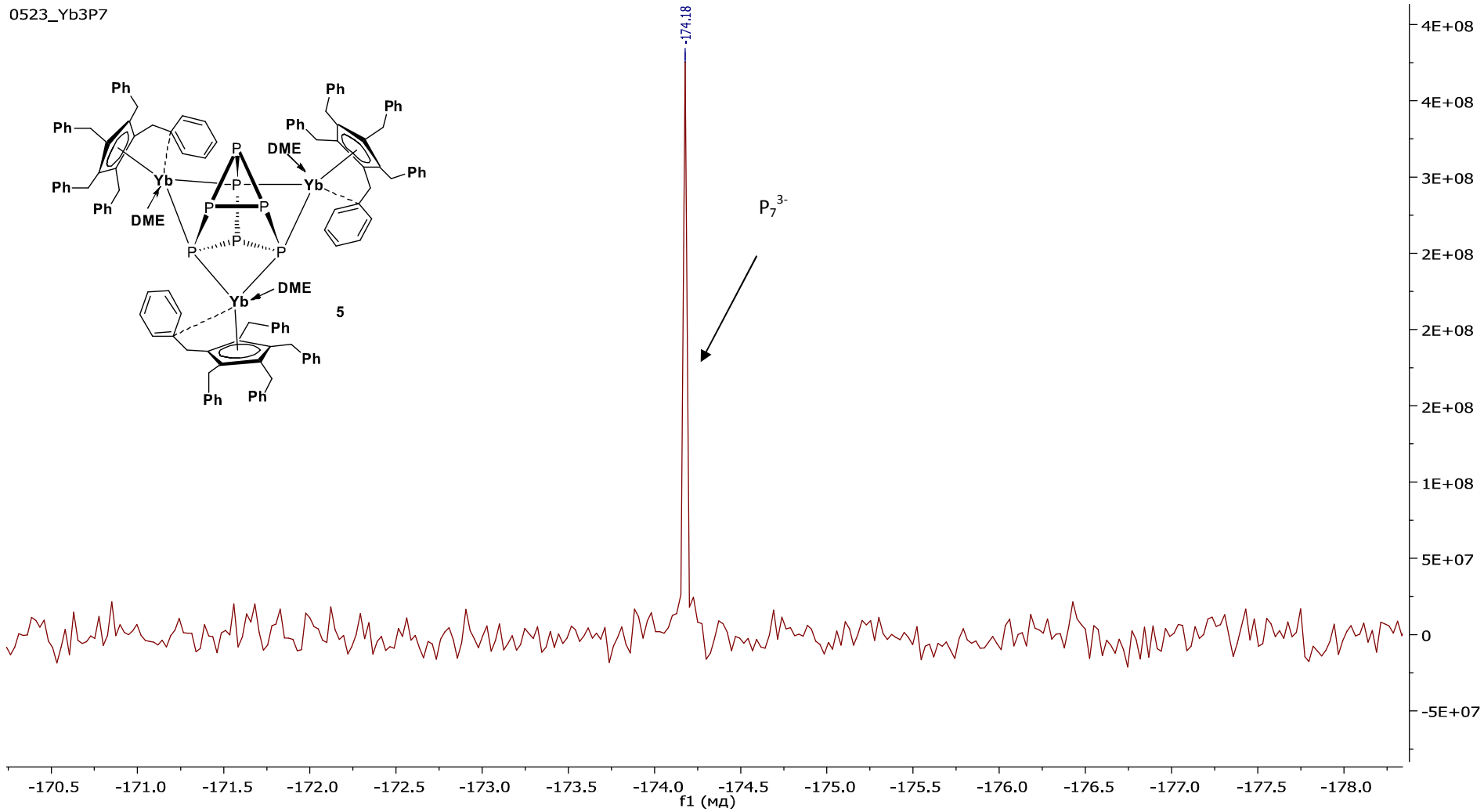

Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6, 293 K) of complex 7.

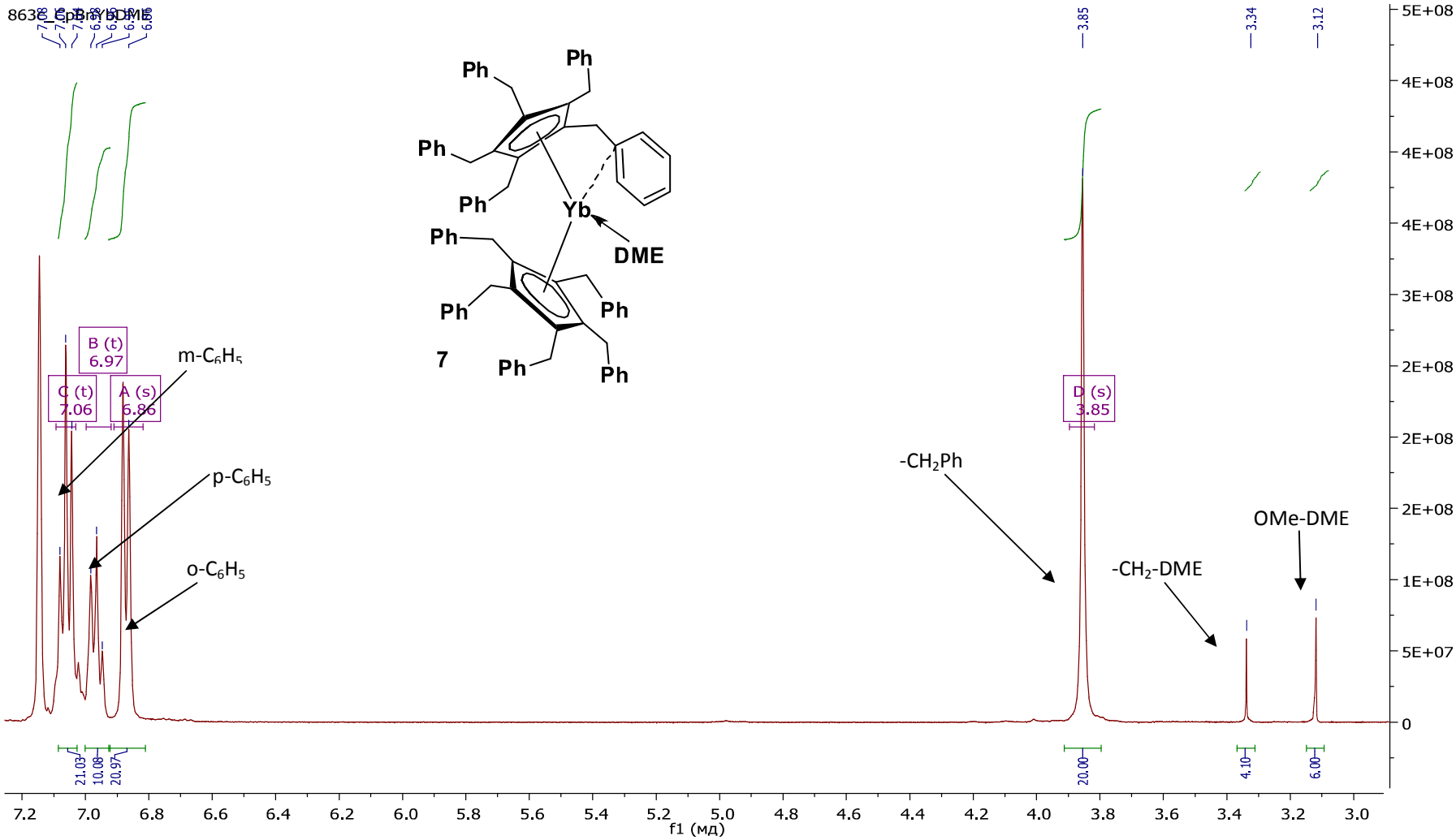

Figure S12. ^{13}C NMR spectrum (100 MHz, C_6D_6, 293 K) of complex 7.

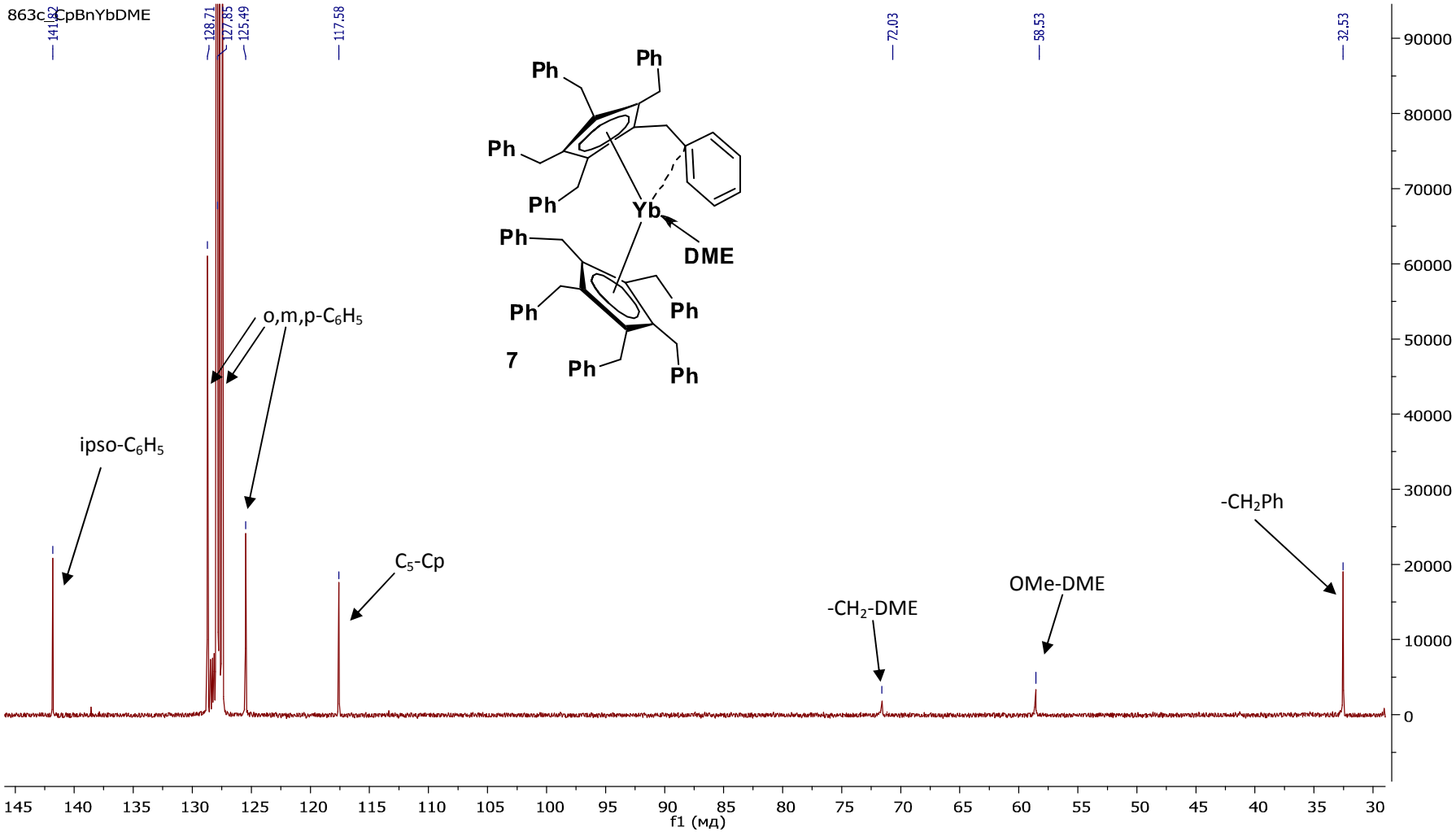

Figure S13. IR spectrum of complex 1 (Nujol, KBr).

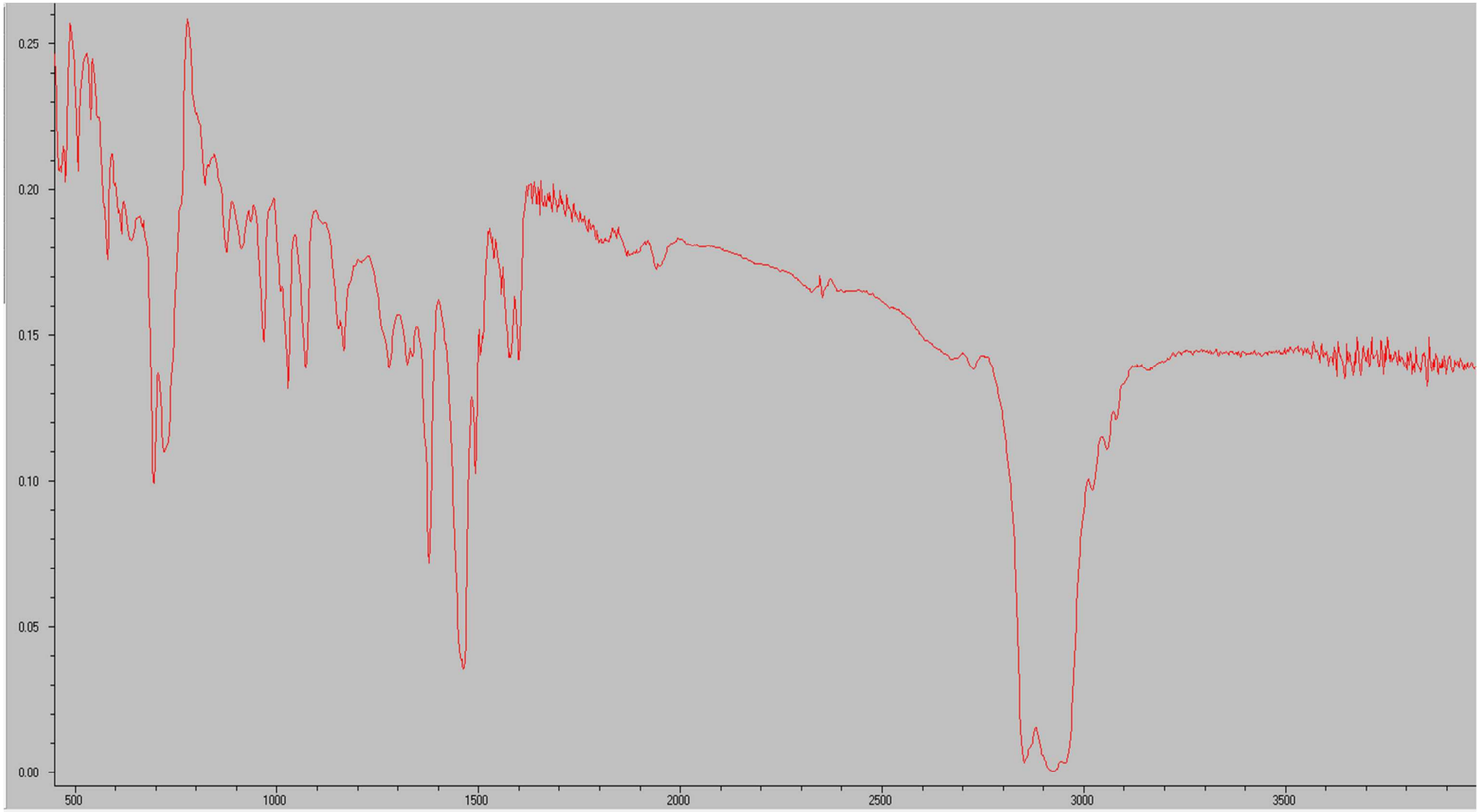

Figure S14. IR spectrum of complex 4 (Nujol, KBr).

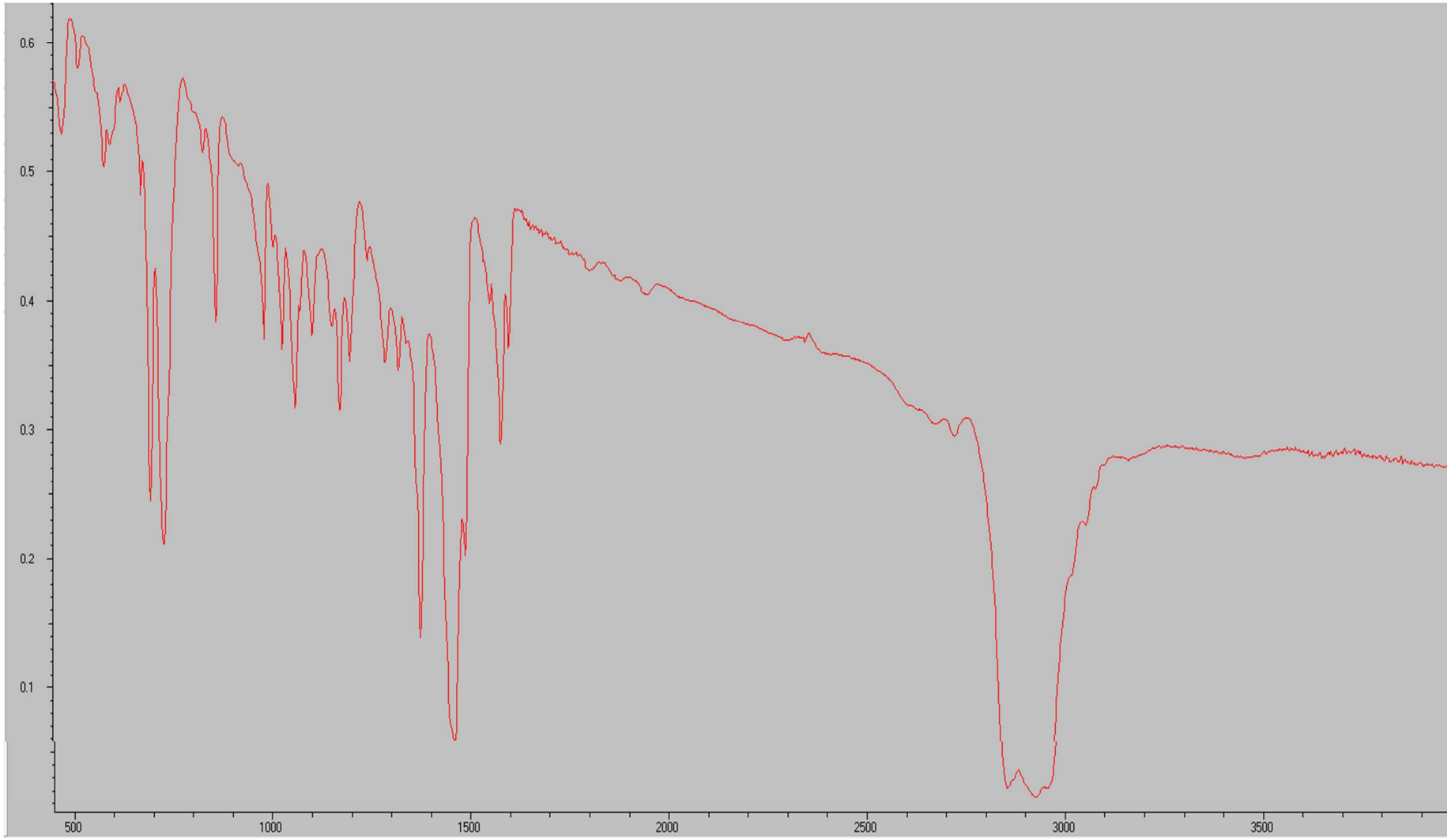

Figure S15. IR spectrum of complex 5 (Nujol, KBr).

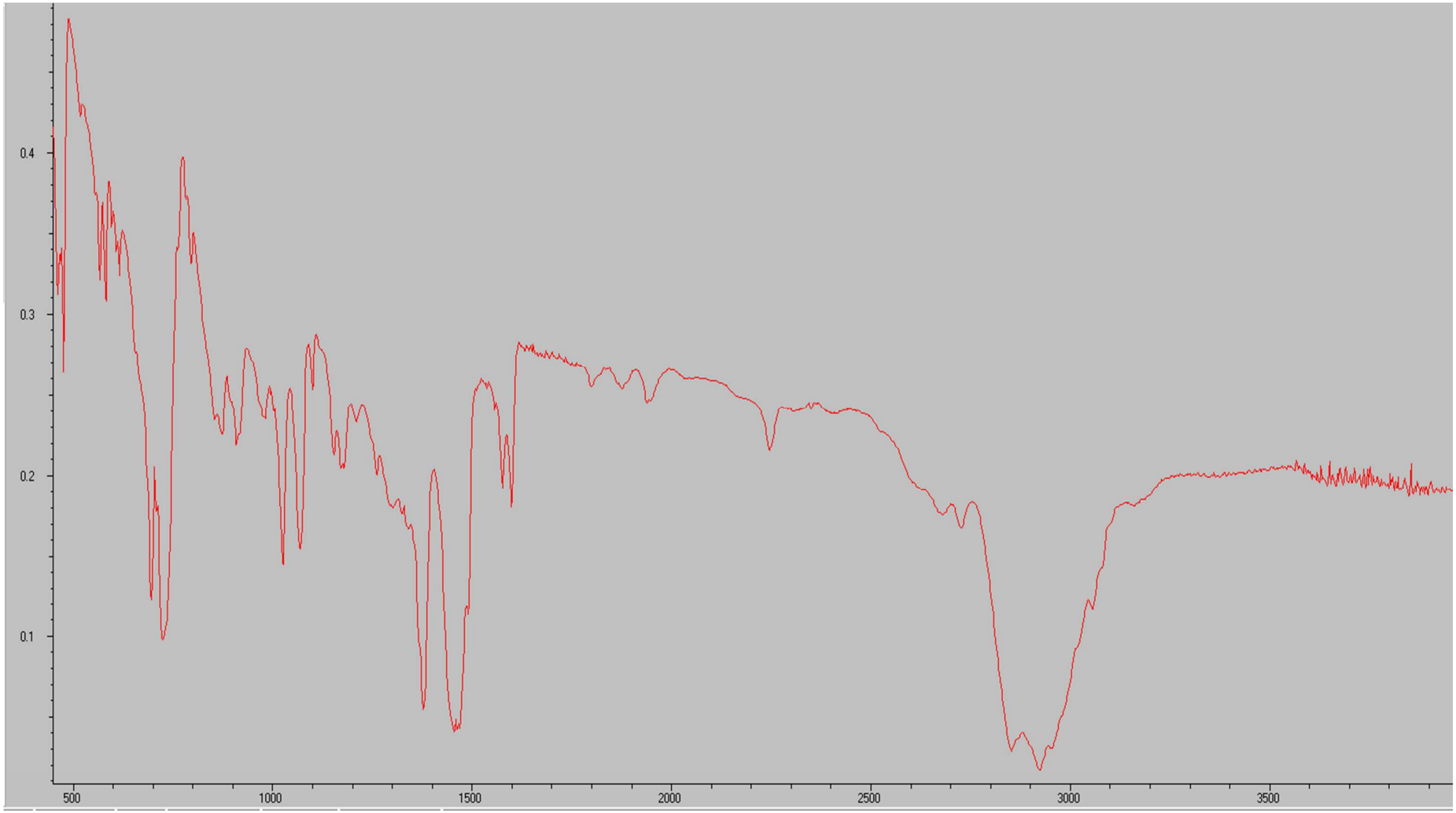

Figure S16. IR spectrum of complex 6 (Nujol, KBr).

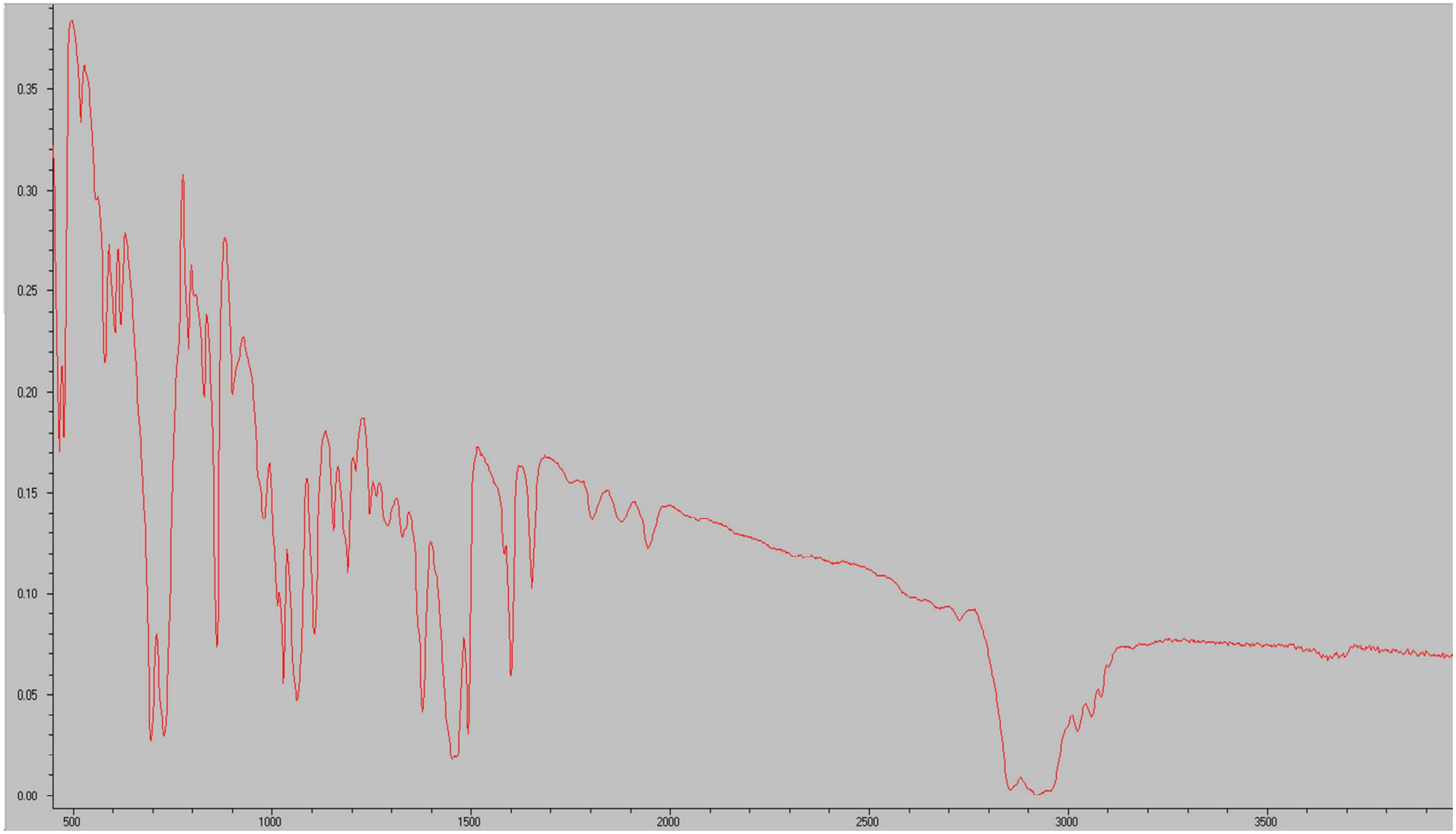

Figure S17. IR spectrum of complex 7 (Nujol, KBr).

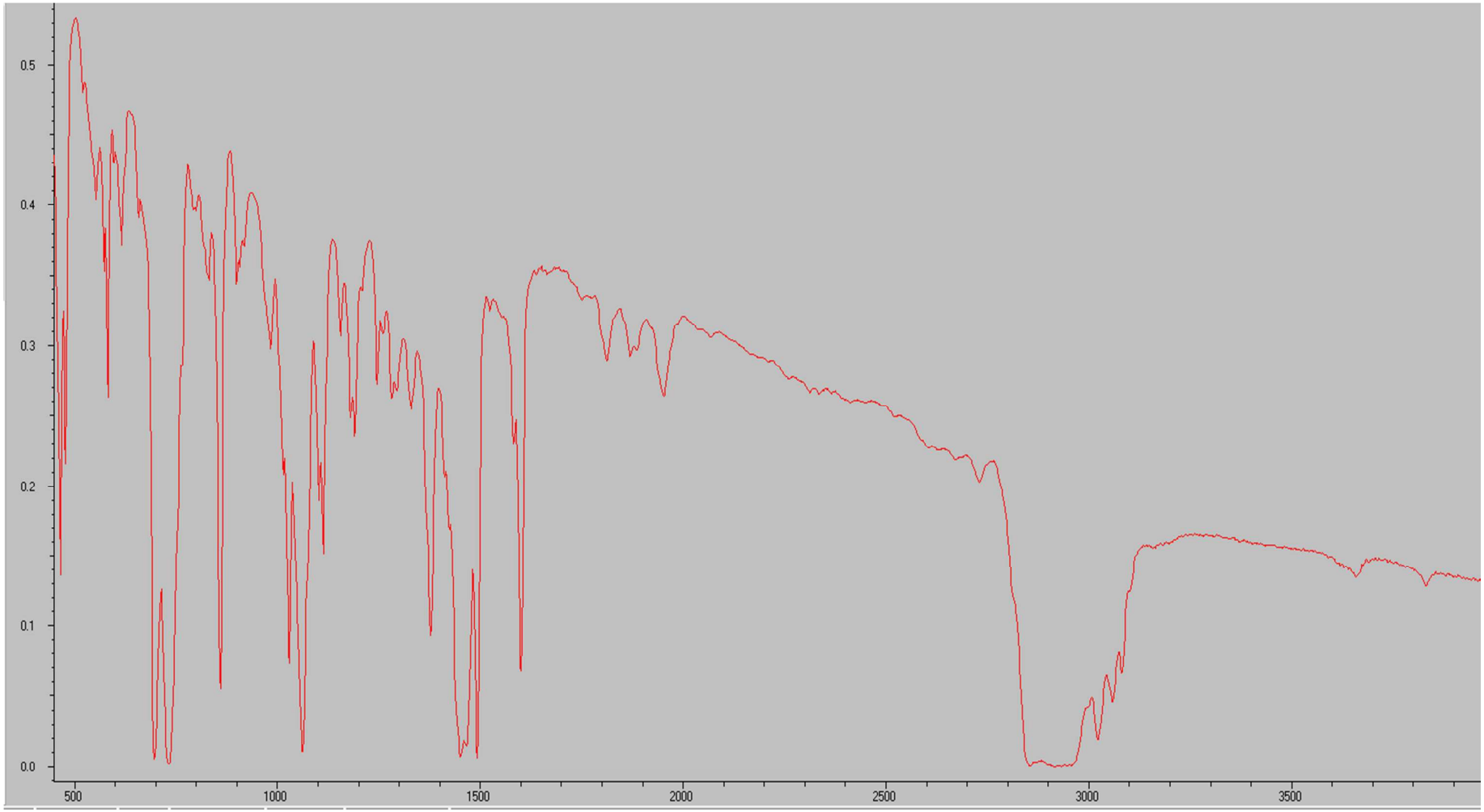

Table S1. Crystallographic data and structural refinement details for 1 and 4–7.

	1	**4**	**5**	**6**	**7**
Formula	$C_{106}H_{118}O_8Yb_2$	$C_{118}H_{118}O_4Yb_2$	$C_{153}H_{159}O_6P_7Yb_3$	$C_{110}H_{118}O_{4.5}P_2Yb_2$	$C_{86}H_{85}O_3Yb$
Mr	1866.08	1946.20	2829.70	1920.06	1339.57
Crystal size	0.94x0.33x0.28	0.2x0.2x0.2	0.5x0.23x0.19	0.21x0.12x0.05	0.33x0.32x0.14
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P-1	P2(1)	P-1	P-1
a, Å	14.3236(6)	10.3061(2)	14.0777(10)	12.4364(15)	10.2669(3)
b, Å	14.5716(7)	15.5010(3)	28.066(2)	13.6603(16)	15.7691(4)
c, Å	21.9673(10)	15.9350(4)	17.2223(12)	14.6156(18)	21.4030(6)
α, °	94.2040(10)	74.539(2)	90	91.919(2)	79.868(1)
β, °	106.4810(10)	83.433(2)	97.3890(10)	113.198(2)	84.444(1)
γ, °	90.4540(10)	77.549(2)	90	98.590(2)	74.315(1)
V, $Å^3$	4382.8(3)	2391.48(9)	6748.0(8)	2244.9(5)	3279.6(2)
Z	2	1	2	1	2
$S\rho_{calc}$, Mg/m^3	1.414	1.351	1.393	1.420	1.356
μ, mm^{-1}	2.179	1.997	2.200	2.161	1.478
F(000)	1916	998	2880	984	1390

θ range for data collections	0.970-26.000	3.081-26.000	1.878-29.149	2.559-25.998	1.358-28.730
Completness to 2θ, °	99.5	99.7	99.9	97.3	99.6
Reflections collected / unique	38085 / 17131	37132 / 9374	73323 / 36134	12881 / 8574	34484 / 16794
GooF	1.053	1.042	0.998	1.035	1.090
R_{int}	0.0236	0.0550	0.0453	0.0383	0.0173
R_1 ($I>2\sigma(I)$)	0.0240	0.0409	0.0459	0.0401	0.0309
wR_2 (all data)	0.0620	0.1032	0.1060	0.0742	0.0785
Largest diff. peak and hole	1.581 / -1.093	1.575 / -0.730	1.345 / -0.810	1.275 / -1.222	1.858 / -0.699

Computational details

The calculations have been carried out with the Gaussian09 software[1] at the DFT level using the hybrid functional B3PW91[2]. Ytterbium atoms were treated with the large-core pseudopotential from the Stuttgart group[3], that includes 4f electrons as part of the core. Oxygen, Carbon and H atoms have been treated with the all electron 6-31G** Pople basis set[4]. The geometry optimization has been performed without any symmetry constraints taking the geometry obtained from X-ray diffraction measurement of the product. Analytical calculations of the vibrational frequencies of the optimized geometry were done to confirm that it's a minimum.

[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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244; K. Burke, J. P. Perdew and W. Yang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, ed. J. F. Dobson, G. Vignale and M. P. Das, Plenum, New York, 1998.

[3] M. Dolg, H. Stoll, A. Savin, A. and H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 173; M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1993, **85**, 441.

[4] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta,* 1978, **28**, 213