Electronic Supplementary Information for Dalton Transactions

Two-Dimensional Double-Metal Cyanide Complexes: Highly Active Catalysts for the Homopolymerization of Propylene Oxide and Copolymerization of Propylene Oxide and Carbon Dioxide

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Table of contents

X-ray analysis of $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$

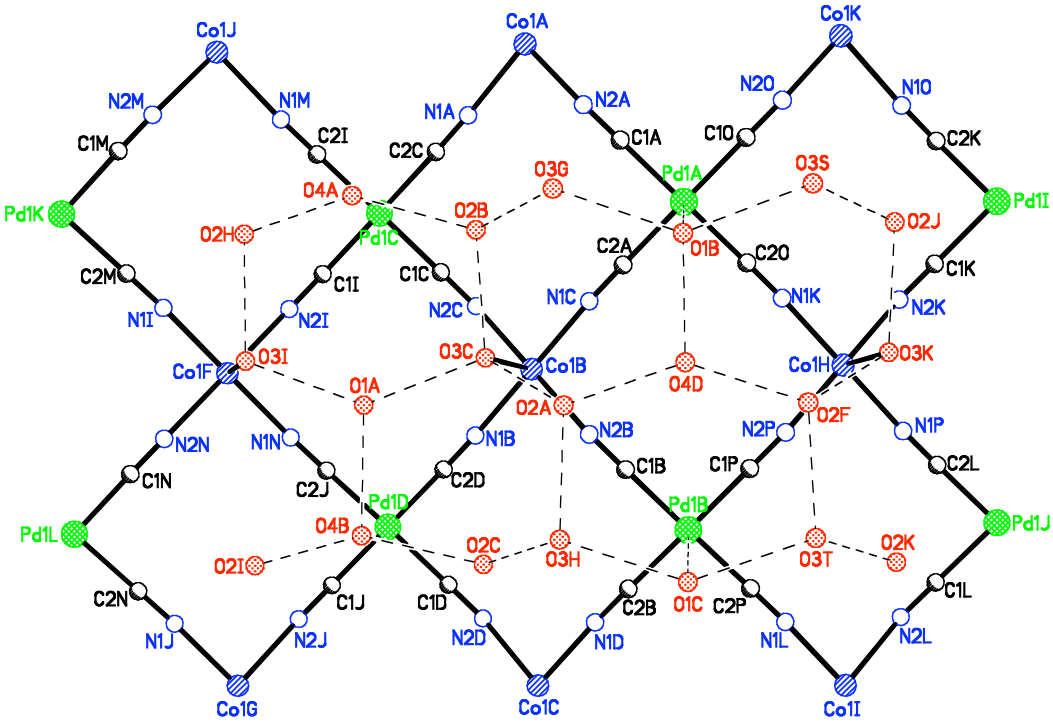

Fig. 1 Top view of the X-ray crystal structure of $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$.

Table 1. Crystal data and structure refinement for $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$.

Identification code	PdCo	
Empirical formula	C2 H6 Co0.50 N2 O3 Pd0.50	
Formula weight	188.75	
Temperature	105(2) K	
Wavelength	0.9360 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 12.041(2) Å	α= 90°
	b = 14.217(3) Å	β= 90°
	c = 7.4030(15) Å	γ = 90°
Volume	1267.3(4) $Å^3$	
Z	8	
Density (calculated)	1.979 Mg/m^3	
Absorption coefficient	2.745 mm^{-1}	
F(000)	740	
Crystal size	0.07 x 0.04 x 0.01 mm^3	
Theta range for data collection	4.09 to 30.09°	
Index ranges	0<=h<=12, 0<=k<=14, 0<=l<=7	
Reflections collected	721	
Independent reflections	721 [R(int) = 0.0000]	
Completeness to theta = 22.38°	84.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	721 / 0 / 79	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1599	
R indices (all data)	R1 = 0.0579, wR2 = 0.1651	
Largest diff. peak and hole	1.608 and -1.543 $e \cdot Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	4353(1)	7500	9907(1)	11(1)
Co(1)	5000	5000	5000	14(1)
O(1)	6867(4)	7500	4263(7)	30(1)
O(2)	1810(2)	5691(2)	5585(5)	23(1)
O(3)	6601(3)	5605(2)	5591(5)	20(1)
O(4)	2479(4)	2500	-499(7)	27(1)
N(1)	5285(3)	4032(3)	7113(5)	19(1)
N(2)	4334(3)	5945(3)	6926(6)	18(1)
C(1)	4292(3)	6517(3)	8010(7)	11(1)
C(2)	4556(4)	6522(3)	11787(7)	15(1)

Table 3. Bond lengths [Å] and angles [°] for $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$.

Pd(1)-C(1)	1.983(5)	C(2)#1-Pd(1)-C(2)	89.1(3)
Pd(1)-C(1)#1	1.983(5)	N(2)-Co(1)-N(2)#2	180.0
Pd(1)-C(2)#1	1.983(5)	N(2)-Co(1)-N(1)#2	91.36(16)
Pd(1)-C(2)	1.983(5)	N(2)#2-Co(1)-N(1)#2	88.64(16)
Co(1)-N(2)	2.117(4)	N(2)-Co(1)-N(1)	88.64(16)
Co(1)-N(2)#2	2.117(4)	N(2)#2-Co(1)-N(1)	91.36(16)
Co(1)-N(1)#2	2.111(4)	N(1)#2-Co(1)-N(1)	180.0
Co(1)-N(1)	2.111(4)	N(2)-Co(1)-O(3)#2	92.94(13)
Co(1)-O(3)#2	2.156(3)	N(2)#2-Co(1)-O(3)#2	87.06(13)
Co(1)-O(3)	2.156(3)	N(1)#2-Co(1)-O(3)#2	87.96(13)
N(1)-C(2)#3	1.149(6)	N(1)-Co(1)-O(3)#2	92.05(13)
N(2)-C(1)	1.143(6)	N(2)-Co(1)-O(3)	87.06(13)
C(2)-N(1)#3	1.149(6)	N(2)#2-Co(1)-O(3)	92.94(13)
Pd(1)-O(1)	3.056(5)	N(1)#2-Co(1)-O(3)	92.05(13)
		N(1)-Co(1)-O(3)	87.95(13)
C(1)-Pd(1)-C(1)#1	89.6(3)	O(3)#2-Co(1)-O(3)	180.0
C(1)-Pd(1)-C(2)#1	175.06(18)	C(2)#3-N(1)-Co(1)	177.3(4)
C(1)#1-Pd(1)-C(2)#1	90.4(2)	C(1)-N(2)-Co(1)	160.2(3)
C(1)-Pd(1)-C(2)	90.4(2)	N(2)-C(1)-Pd(1)	175.3(4)
C(1)#1-Pd(1)-C(2)	175.06(18)	N(1)#3-C(2)-Pd(1)	177.3(4)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z #2 -x+1,-y+1,-z+1 #3 -x+1,-y+1,-z+2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Co(H_2O)_2[Pd(CN)_4] \cdot 4\ H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}\ U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	7(1)	16(1)	11(1)	0	0(1)	0
Co(1)	9(1)	20(1)	12(1)	0(1)	0(1)	0(1)
O(1)	20(3)	41(3)	30(3)	0	-4(3)	0
O(2)	14(2)	30(2)	26(2)	-1(2)	0(2)	2(2)
O(3)	14(2)	26(2)	21(2)	0(2)	-5(2)	-2(2)
O(4)	27(3)	25(3)	29(3)	0	0(3)	0
N(1)	16(2)	19(2)	20(3)	-7(2)	4(2)	0(2)
N(2)	14(2)	14(2)	25(3)	0(2)	-3(2)	-2(2)
C(1)	11(2)	5(3)	17(3)	-2(3)	-3(2)	-5(2)
C(2)	14(2)	9(3)	20(3)	-7(3)	3(2)	4(2)

NMR spectra of poly(PO-*co*-PC) and PPO

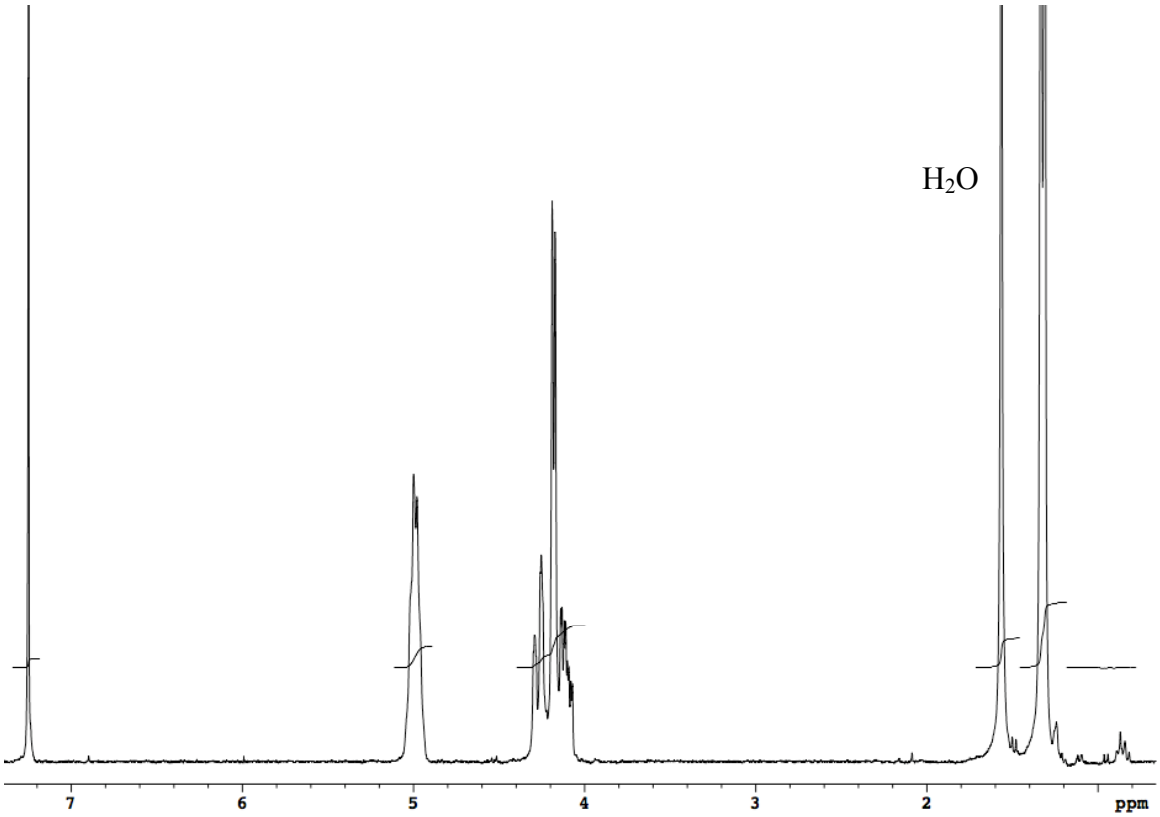

Fig. 2 Full ^{1}H NMR spectrum (300 MHz, $CDCl_3$) from Fig. 3A in the text (reference PPC, f_{CO_2} = 1.0). See references 5(*h*) and 22 in the text for polymer synthesis details.

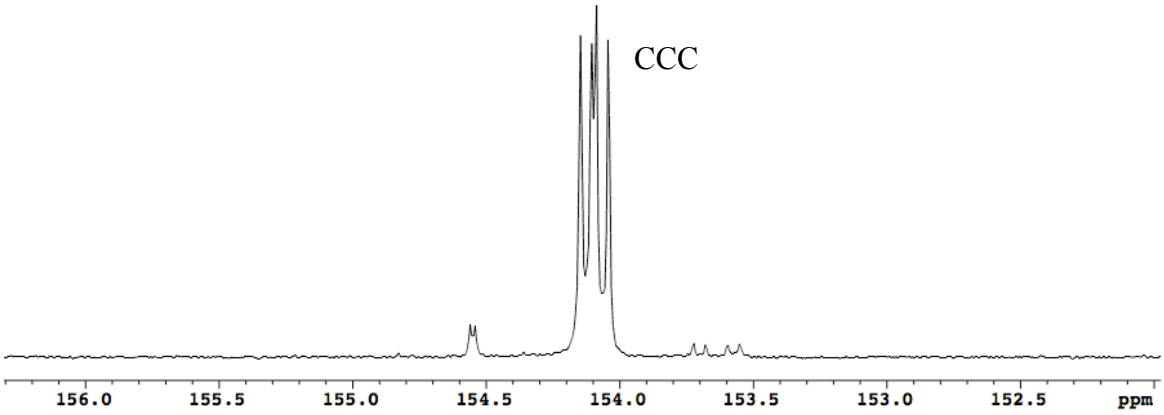

Fig. 3 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of reference PPC used in Fig. 3A of the text (f_{CO_2} = 1.0). CCC = Carbonate-Carbonate-Carbonate. See references 5(*h*) and 22 in the text for polymer synthesis details.

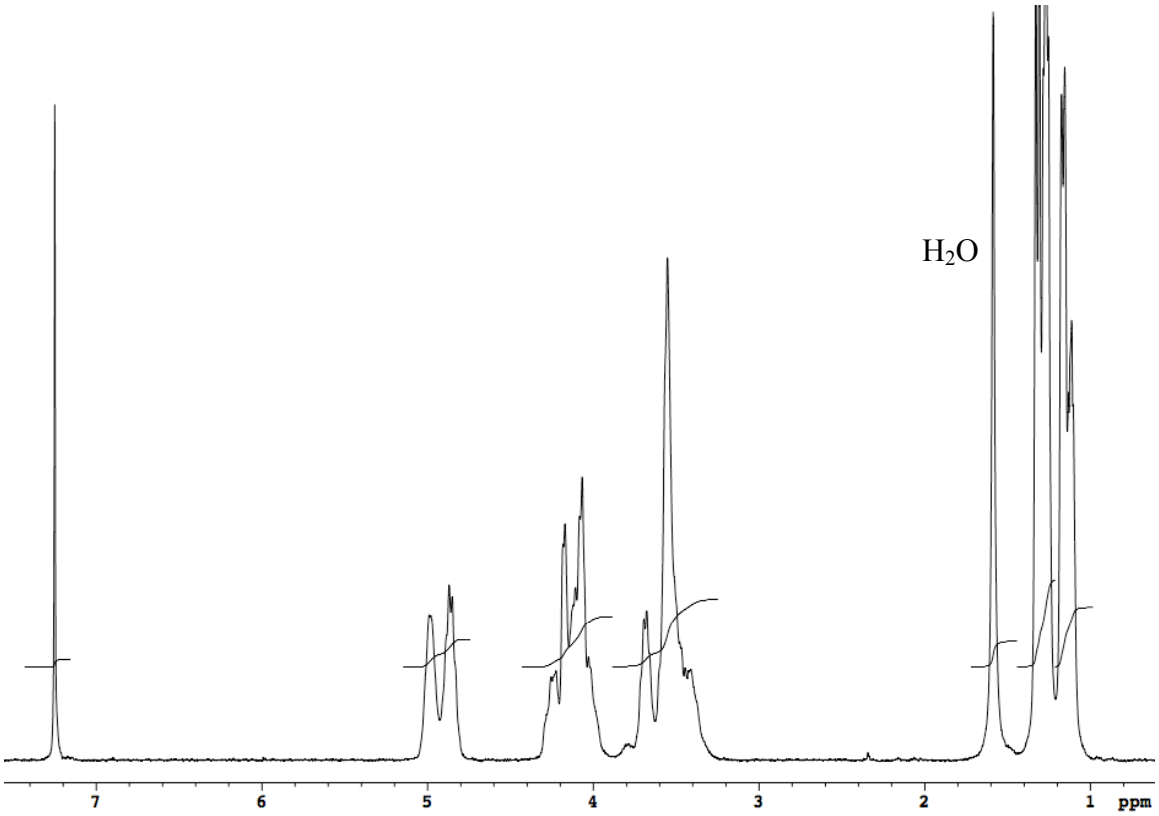

Fig. 4 Full ^{1}H NMR spectrum (300 MHz, $CDCl_3$) from Fig. 3B in the text (Table 1, entry 7, f_{CO_2} = 0.56).

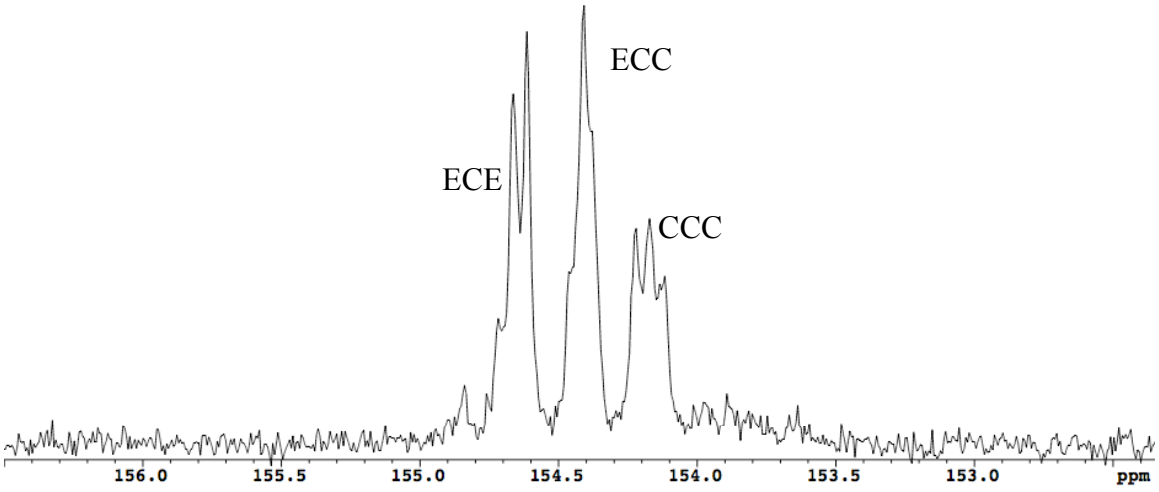

Fig. 5 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of poly(PO-*co*-PC) produced in Table 1, entry 7 of the text (f_{CO_2} = 0.56). ECC = Ether-Carbonate-Carbonate, ECE = Ether-Carbonate-Ether.

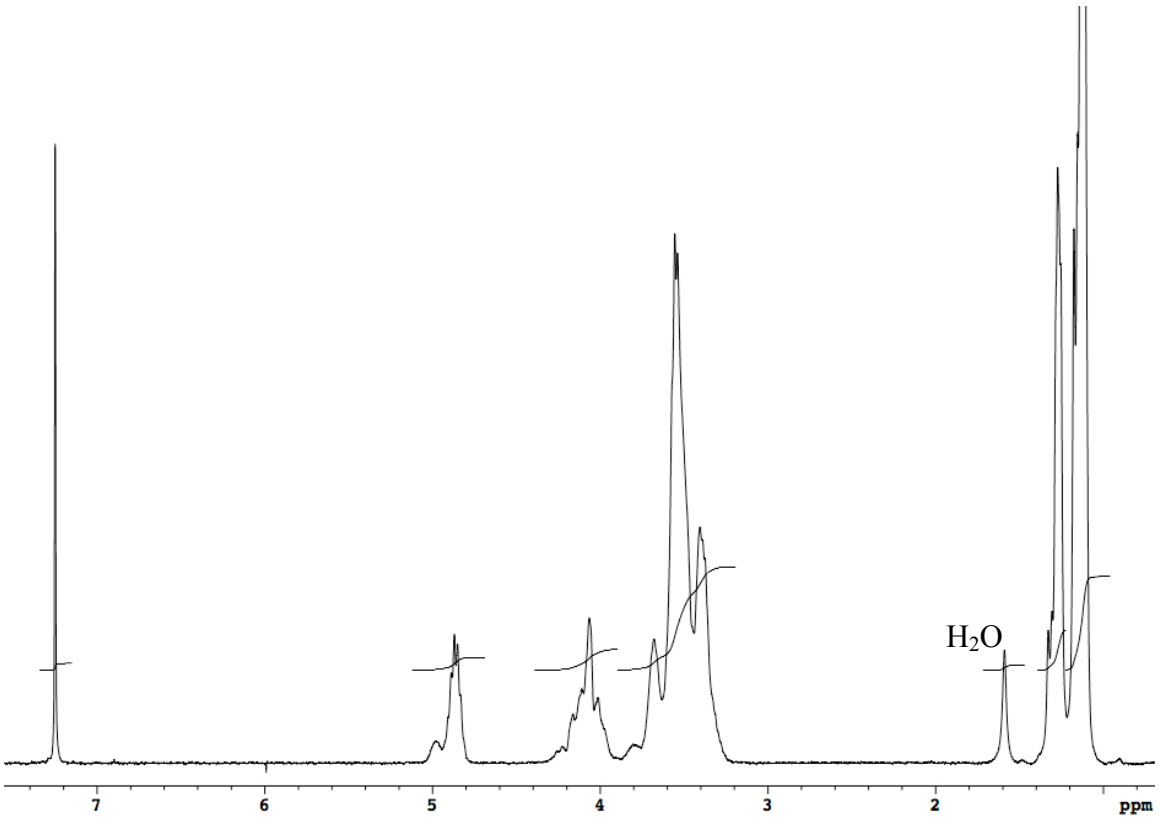

Fig. 6 Full ^{1}H NMR spectrum (300 MHz, $CDCl_3$) from Fig. 3C in the text (Table 1, entry 3, $f_{CO_2} = 0.27$).

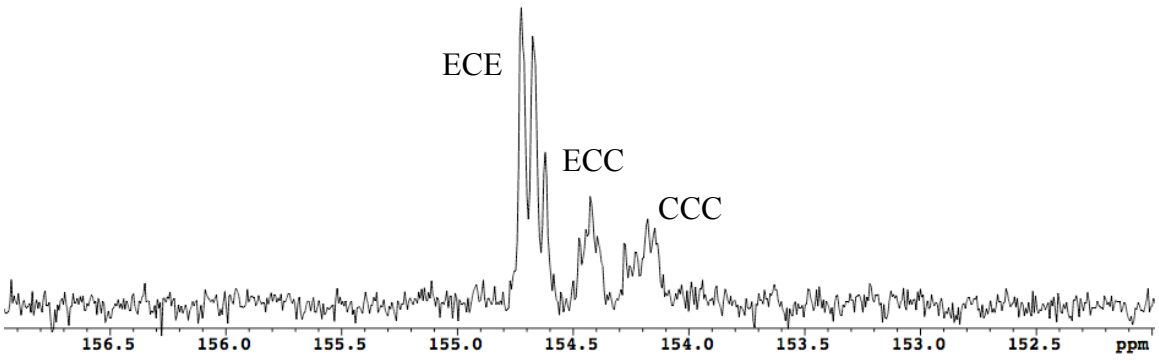

Fig. 7 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of poly(PO-*co*-PC) produced in Table 1, entry 3 of the text ($f_{CO_2} = 0.27$).

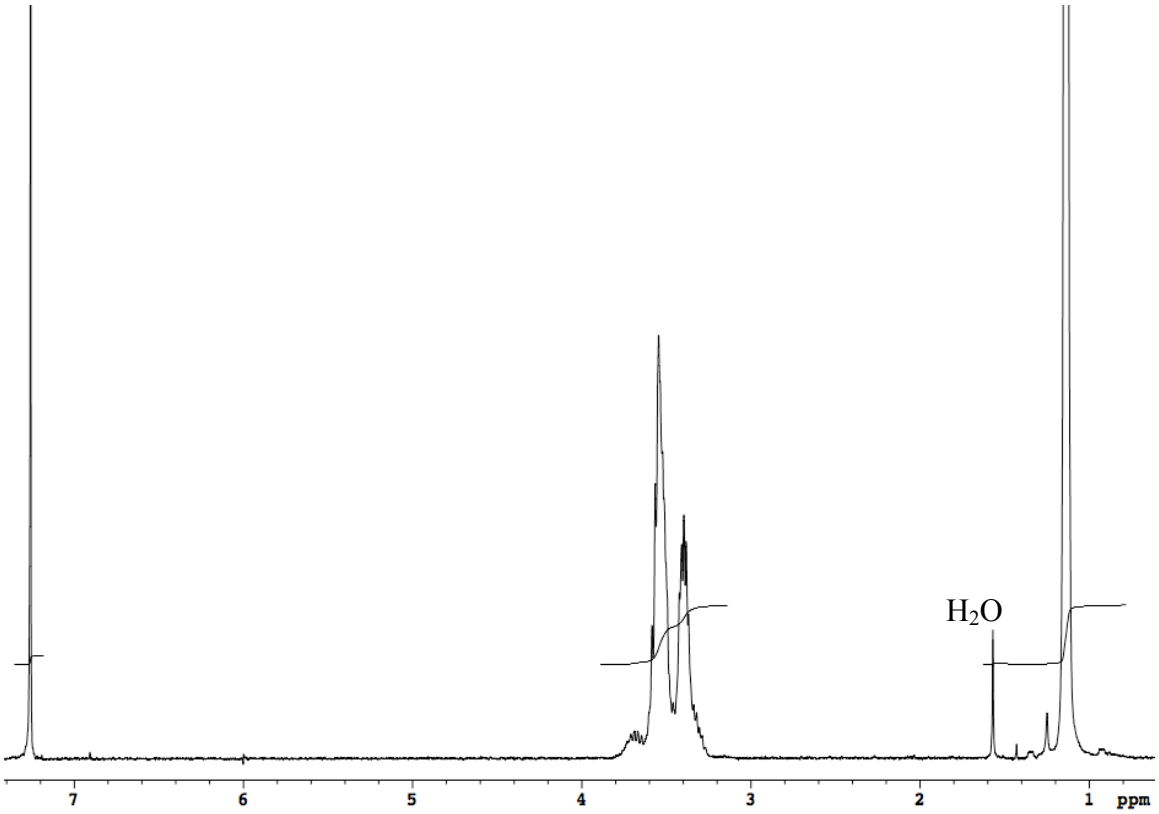

Fig. 8 Full ^{1}H NMR spectrum (300 MHz, $CDCl_3$) from Fig. 3D in the text (Table 1, entry 14, $f_{CO_2} = 0$).

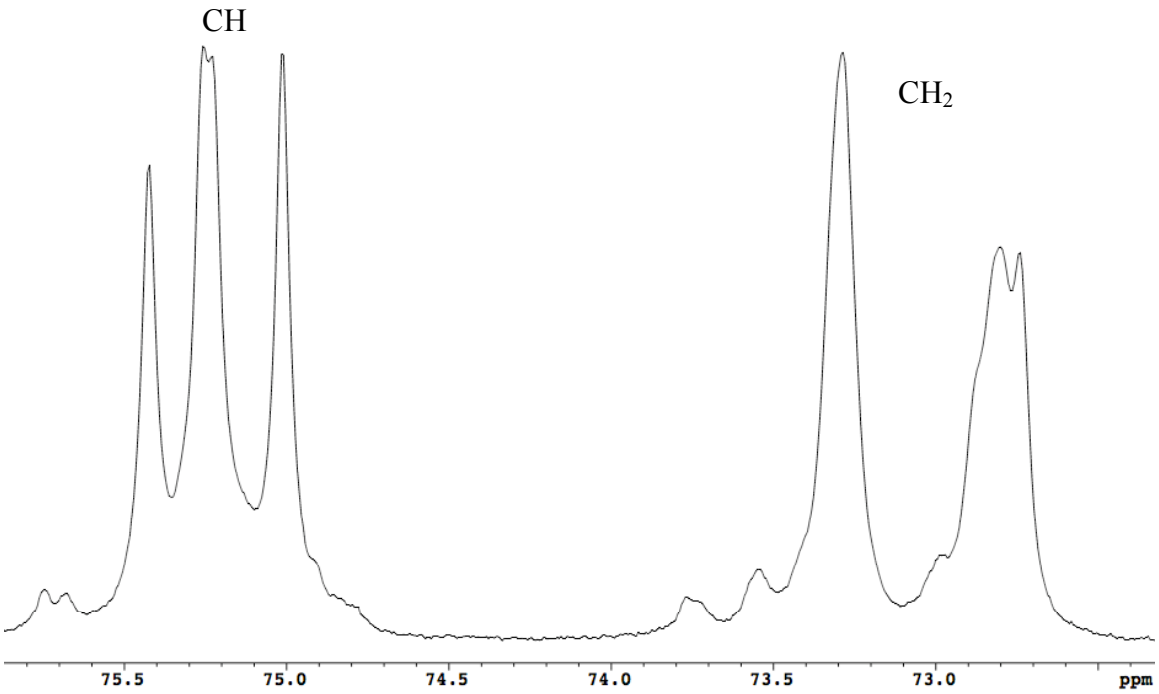

Fig. 9 ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of PPO produced in Table 1, entry 14 of the text ($f_{CO_2} = 0$).

Gradient COSY NMR spectrum

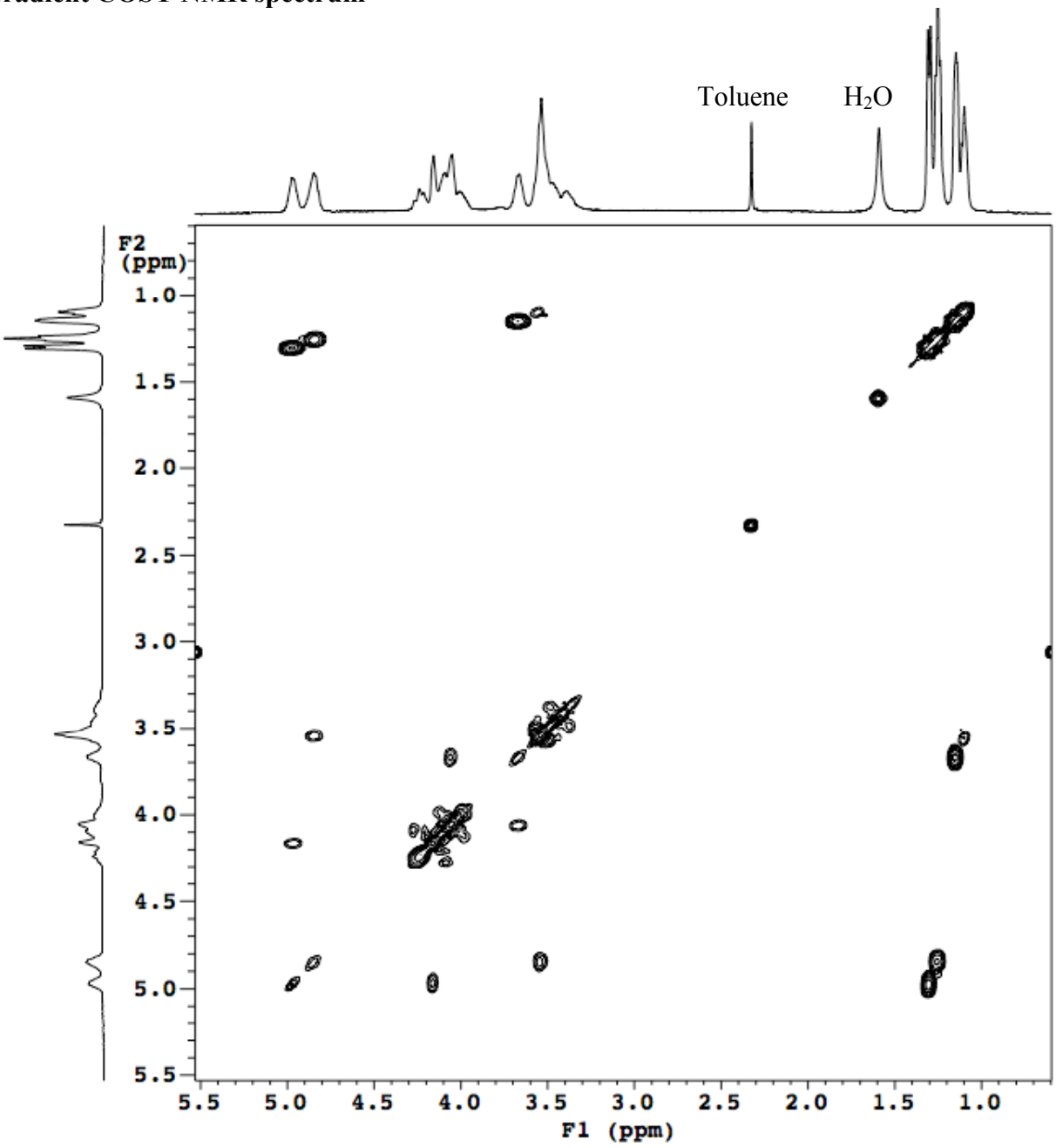

Fig. 10 gCOSY spectrum (400 MHz, $CDCl_3$) of poly(PO-*co*-PC) produced in Table 1, entry 7 of the text (f_{CO_2} = 0.56).