Supporting information for

High Temperature Ethylene Polymerization Catalyzed by Titanium (IV) Complexes with Tetradentate Aminophenolate Ligands in *cis*-O, N, N Chelating Mode

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1 X-ray diffraction studies

Table S1. Summary of crystallographic data for complexes **2a, 9a, 8d** and **5e**

	2a	**9a**	**8d**	**5e**
Formula	$C_{27}H_{41}Cl_3N_2O_2Ti$	$C_{29}H_{45}Cl_3N_2O_2Ti$	$C_{38}H_{46}Br_4Cl_4N_4O_5Ti_2$	$C_{32}H_{53}ClN_2O_5Ti$
FW	579.85	607.92	1195.96	629.11
T / K	293(2)	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	Pca2(1)	C2/c	P-1	P2(1)/n
a /Å	17.9918(16)	31.567(14)	12.5385(17)	12.595(4)
b / Å	12.0283(11)	12.607(5)	16.754(2)	13.269(4)
c / Å	22.162(2)	24.650(10)	18.355(2)	21.982(7)
α/ °	90	90	99.214(3)	90
β/ °	90	127.231	93.923(3)	104.538(4)
γ/ °	90	90	103.434(3)	90
Volume / Å^3	4796.0(7)	7810(6)	3679.6(8)	3556(2)
Z	4	8	2	4
D_{calc} / Mg m^{-3}	1.186	1.031	1.412	1.175
Abs coeff / mm^{-1}	0.383	0.446	2.581	0.353
F(000)	1824	2560	1588	1352
Crystal size / mm	0.341 × 0.215 × 0.056	0.25 × 0.22 × 0.20	0.311 × 0.145 × 0.056	0.12 × 0.10 × 0.06
2θ range / °	1.69 to 25.50	1.62 to 27.50	1.68 to 25.50	1.70 to 25.01
Reflns collected / unique	27081 / 8516	8551 / 8551	21588 / 13665	14395 / 6253
R(int)	0.1323	0.0000	0.0601	0.0542
Data / restrains / para	8516 / 159 / 501	8551 / 6 / 334	13665 / 5 / 578	6253 / 6 / 379
Goodness-of-fit on F^2	0.960	0.996	0.994	0.954
R_1 [I > 2σ(I)]	0.0782	0.0840	0.0802	0.0671
wR_2 [I > 2σ(I)]	0.1640	0.2359	0.2050	0.1849
Largest diff. peak and hole / e Å^{-3}	0.338 and −0.296	1.547 and −0.632	0.967 and −0.538	0.614 and −0.380

2 ^{1}H NMR and ^{13}C NMR spectra of the titanium and zirconium complexes

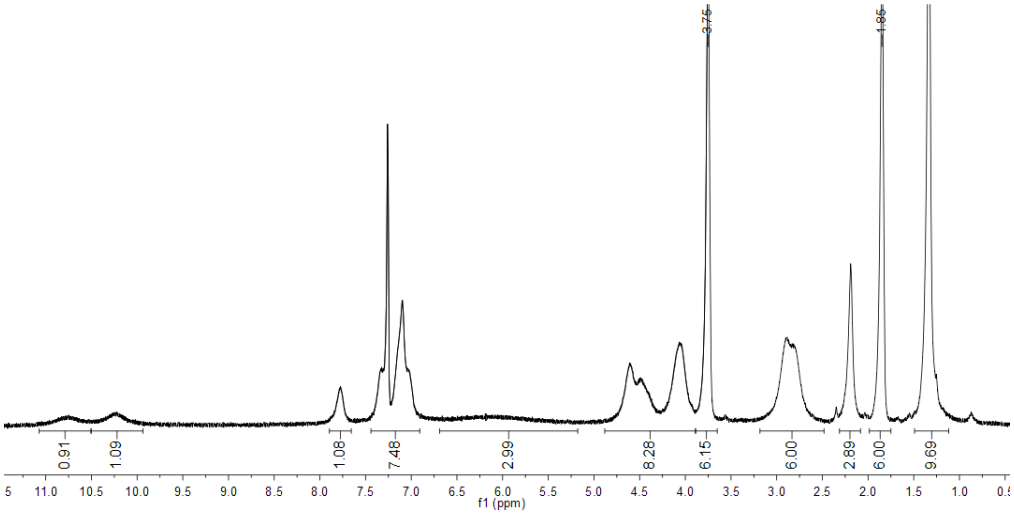

Fig. S1. ^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz).

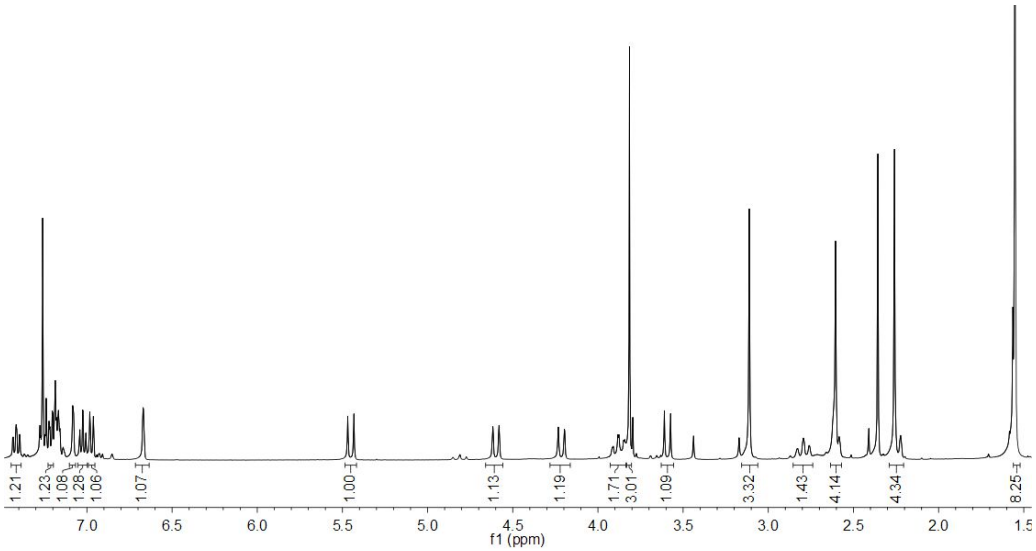

Fig. S2. ^{1}H NMR spectrum of **1a** ($CDCl_3$, 400 MHz).

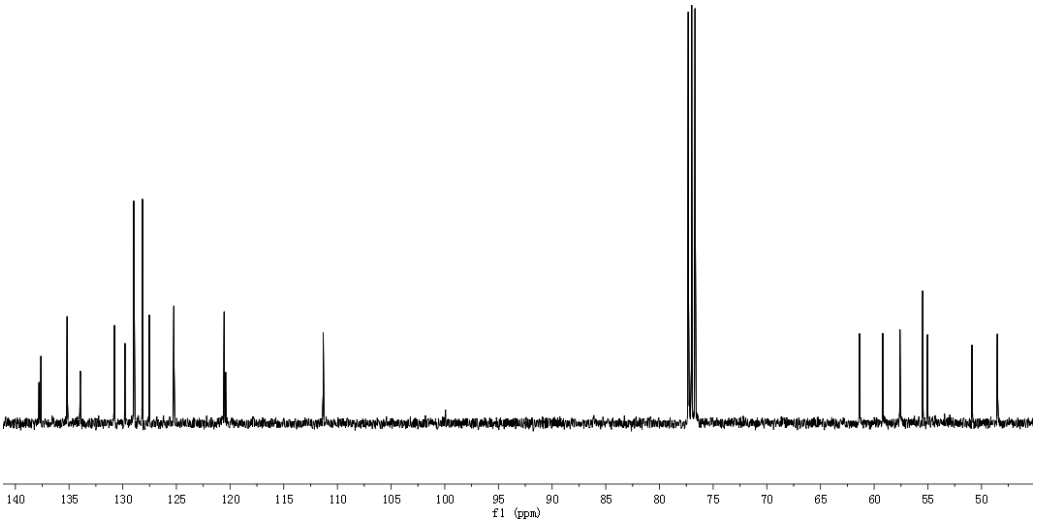

Fig. S3. ^{13}C NMR spectrum of **1a** ($CDCl_3$, 100 MHz).

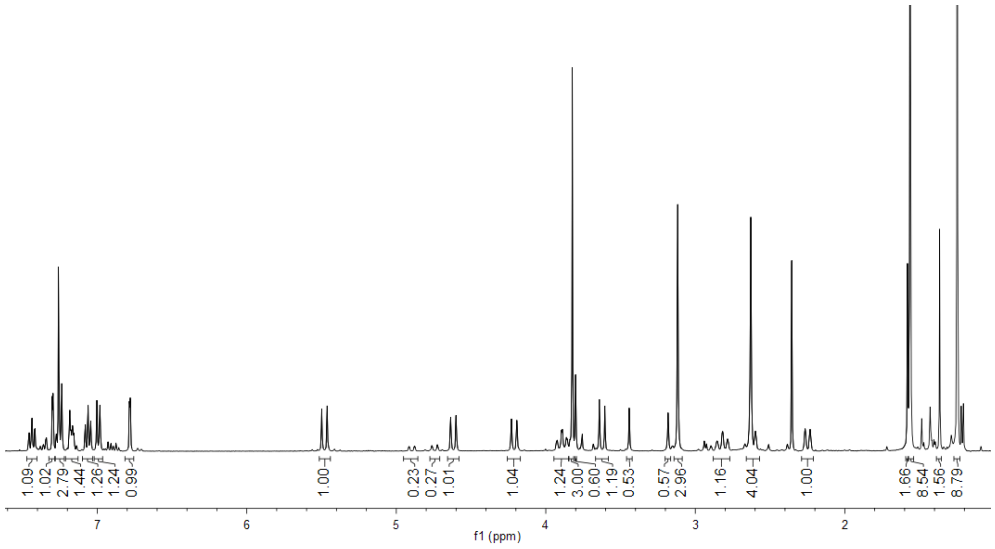

Fig. S4. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 400 MHz).

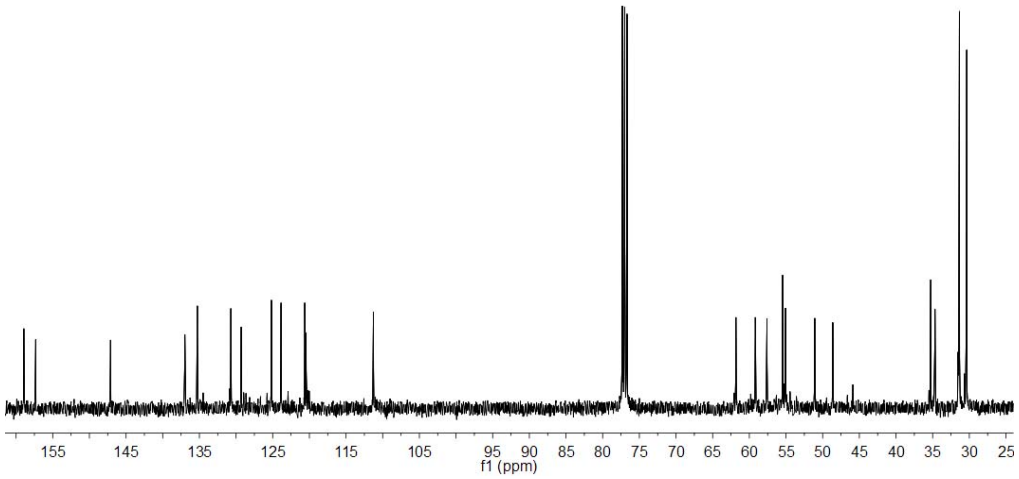

Fig. S5. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 100 MHz).

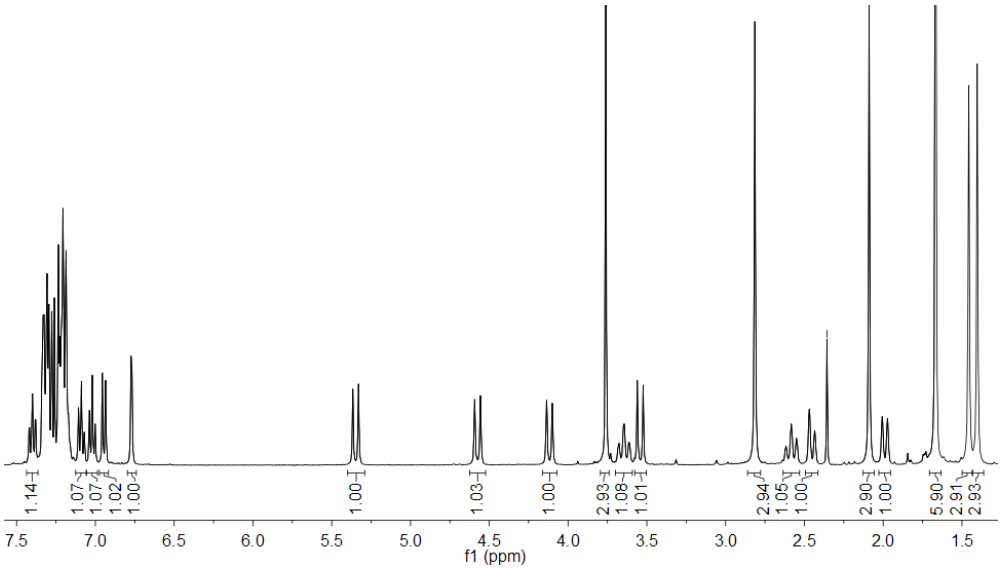

Fig. S6. ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz).

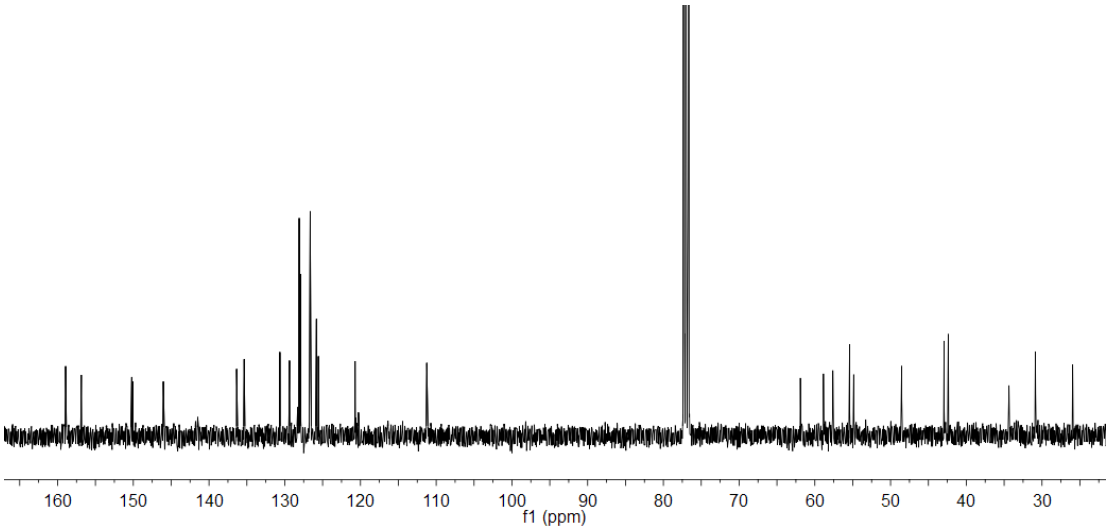

Fig. S7. ^{13}C NMR spectrum of **3a** ($CDCl_3$, 100 MHz).

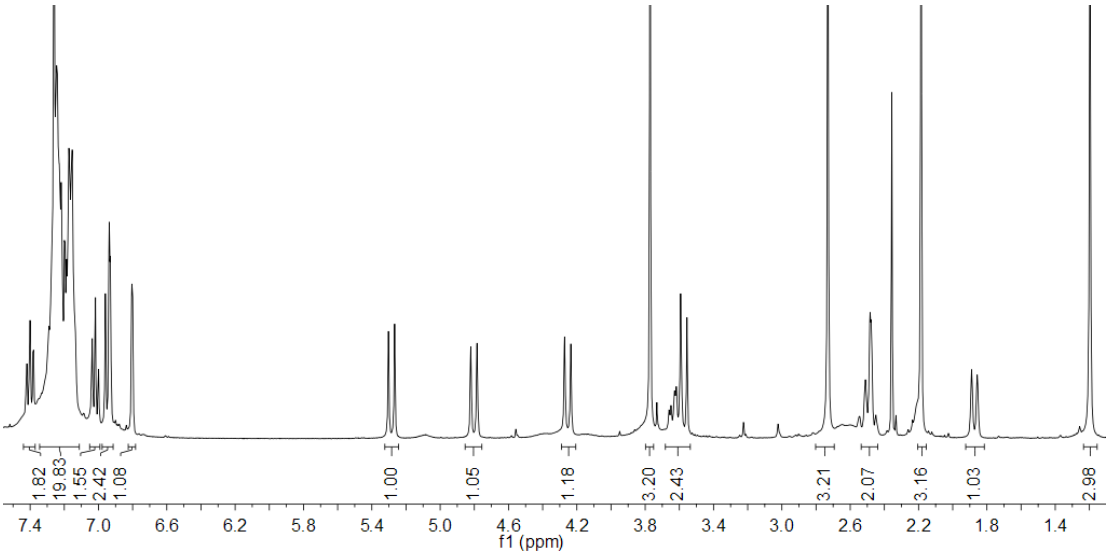

Fig. S8. ^{1}H NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

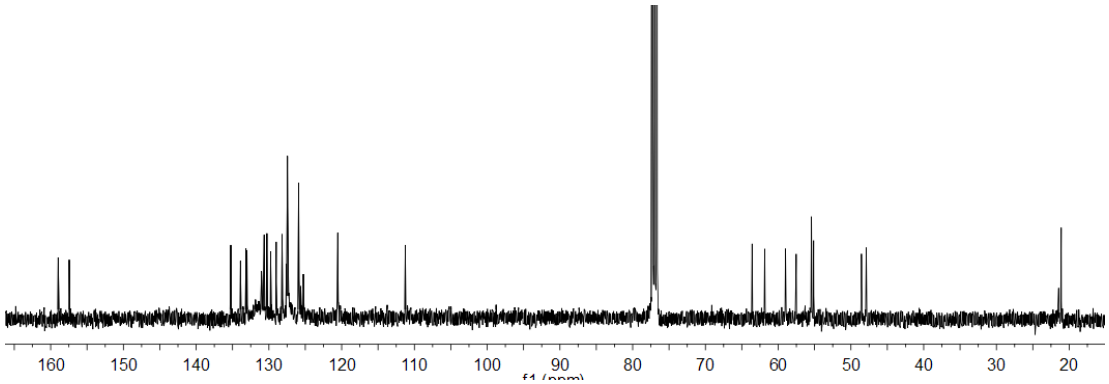

Fig. S9. ^{13}C NMR spectrum of **4a** ($CDCl_3$, 100 MHz).

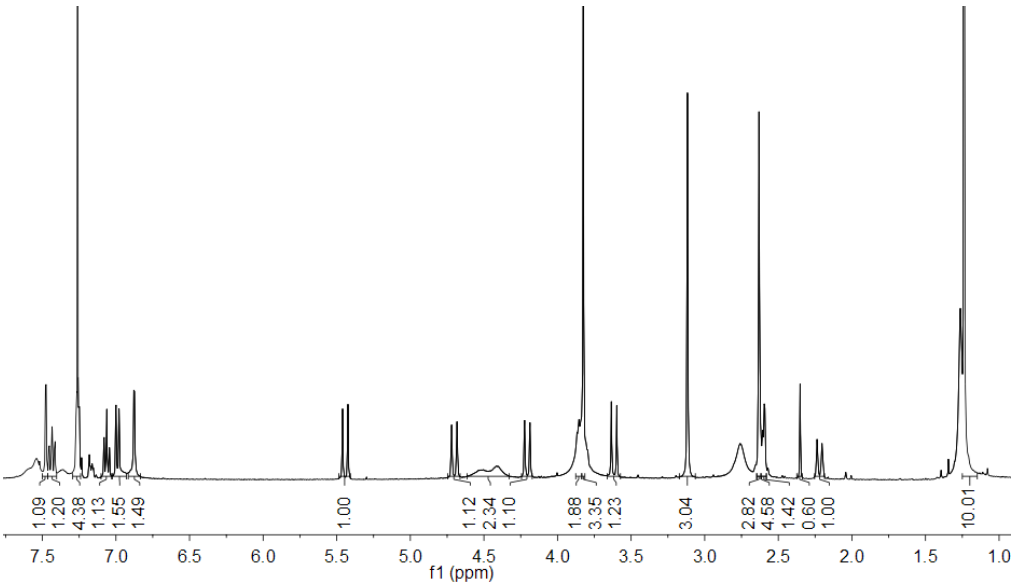

Fig. S10. ^{1}H NMR spectrum of **6a** ($CDCl_3$, 400 MHz).

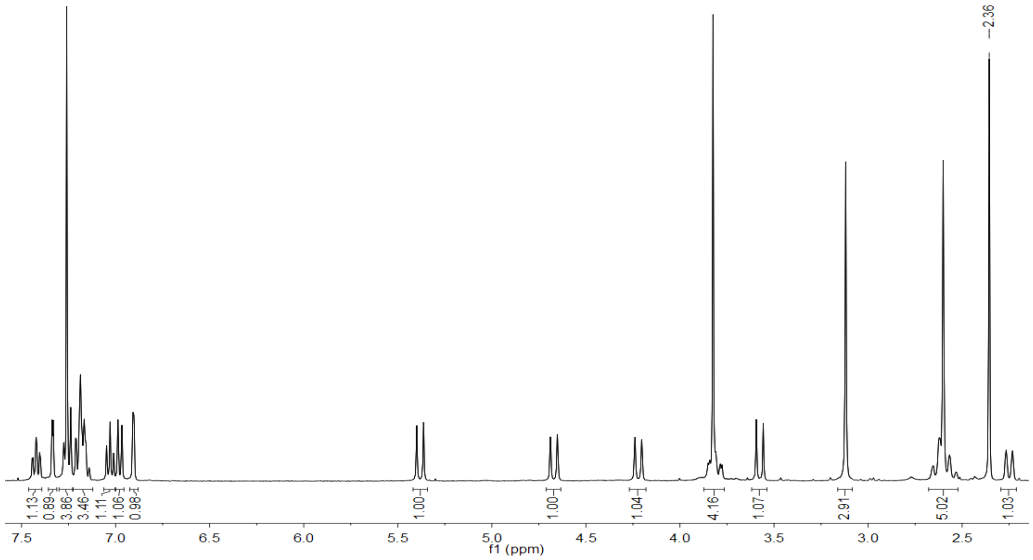

Fig. S11. ^{1}H NMR spectrum of **7a** ($CDCl_3$, 400 MHz).

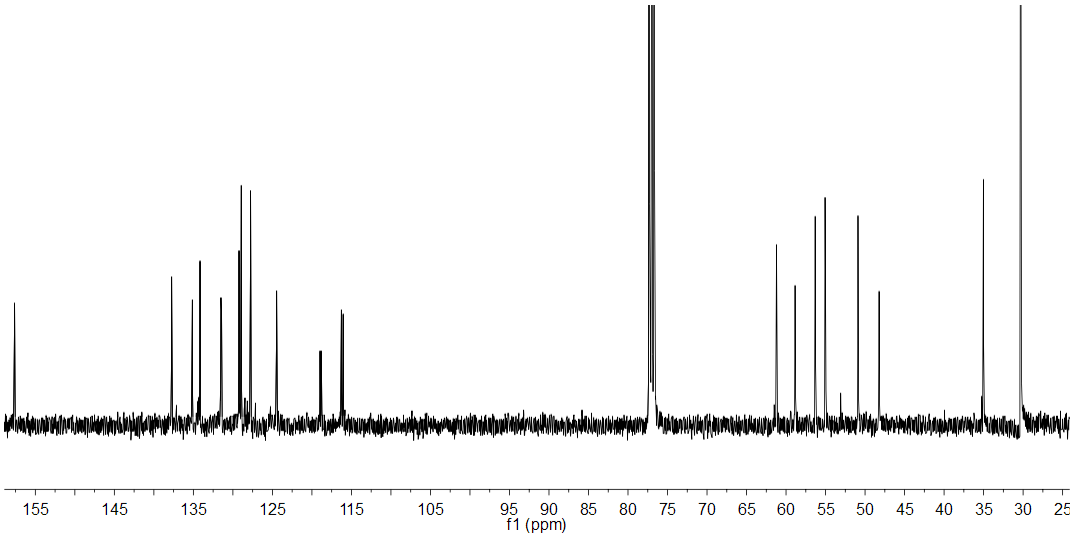

Fig. S12. ^{13}C NMR spectrum of **7a** ($CDCl_3$, 100 MHz).

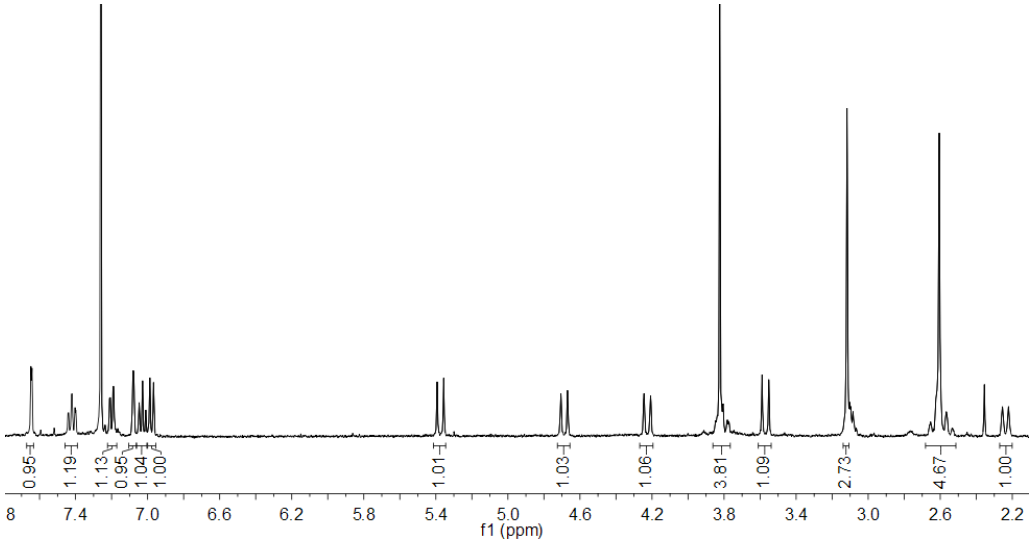

Fig. S13. ^{1}H NMR spectrum of **8a** ($CDCl_3$, 400 MHz).

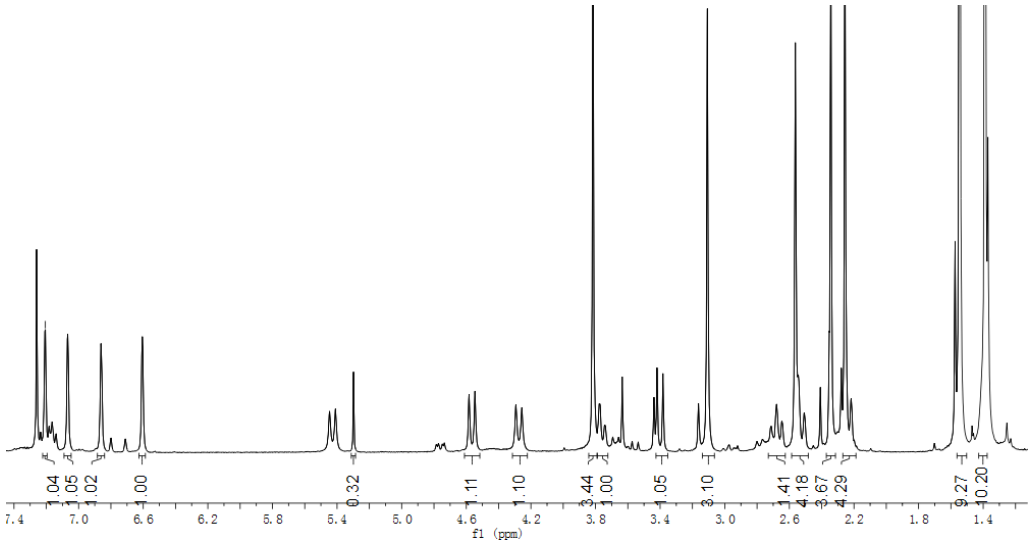

Fig. S14. ^{1}H NMR spectrum of **9a** ($CDCl_3$, 400 MHz).

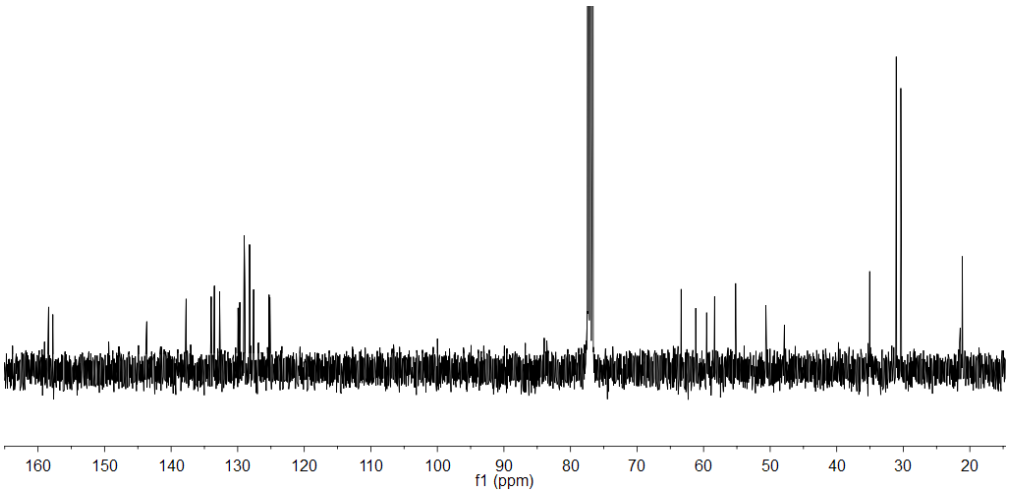

Fig. S15. ^{13}C NMR spectrum of **9a** ($CDCl_3$, 100 MHz).

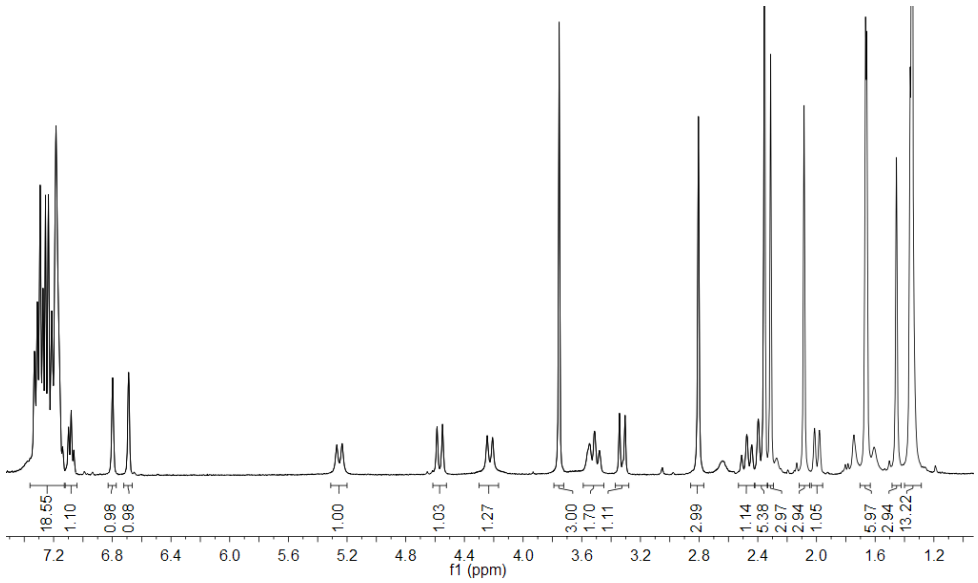

Fig. S16. ^{1}H NMR spectrum of **10a** ($CDCl_3$, 400 MHz).

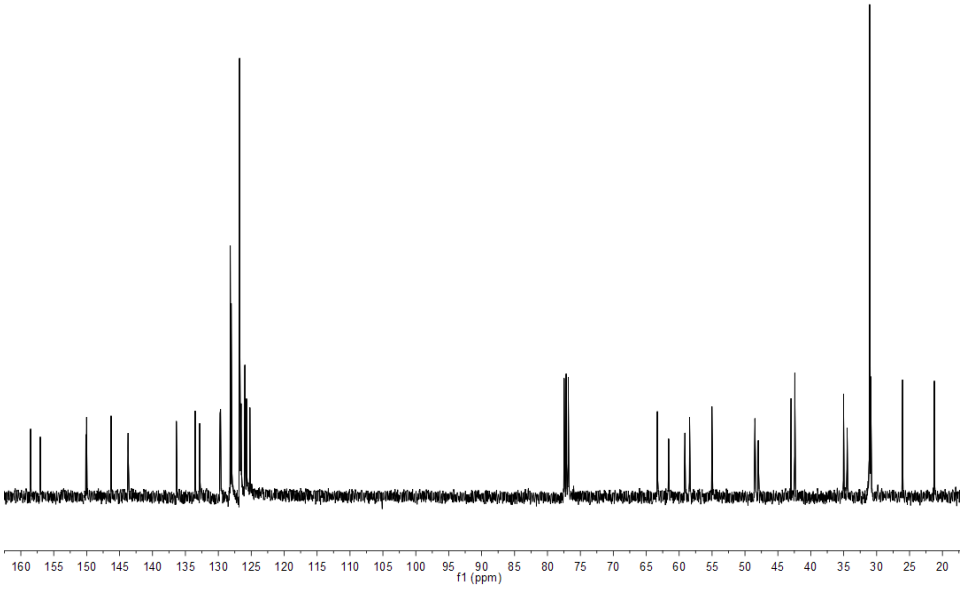

Fig. S17. ^{13}C NMR spectrum of **10a** ($CDCl_3$, 100 MHz).

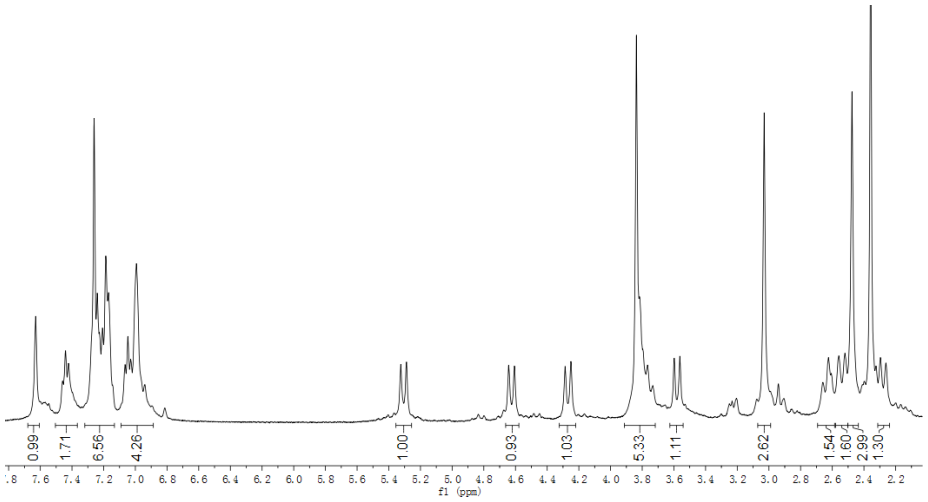

Fig. S18. ^{1}H NMR spectrum of **8b** ($CDCl_3$, 400 MHz).

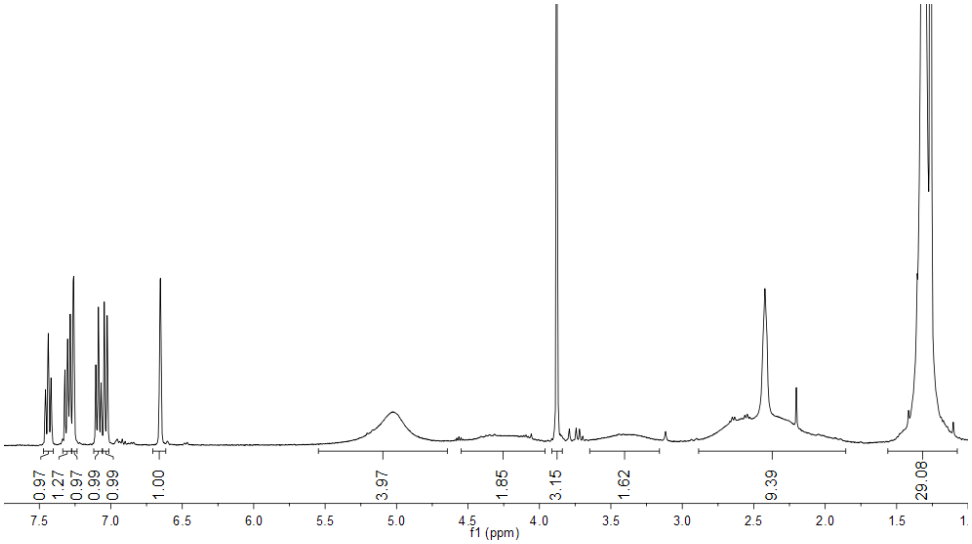

Fig. S19. ^{1}H NMR spectrum of **5e** ($CDCl_3$, 400 MHz).

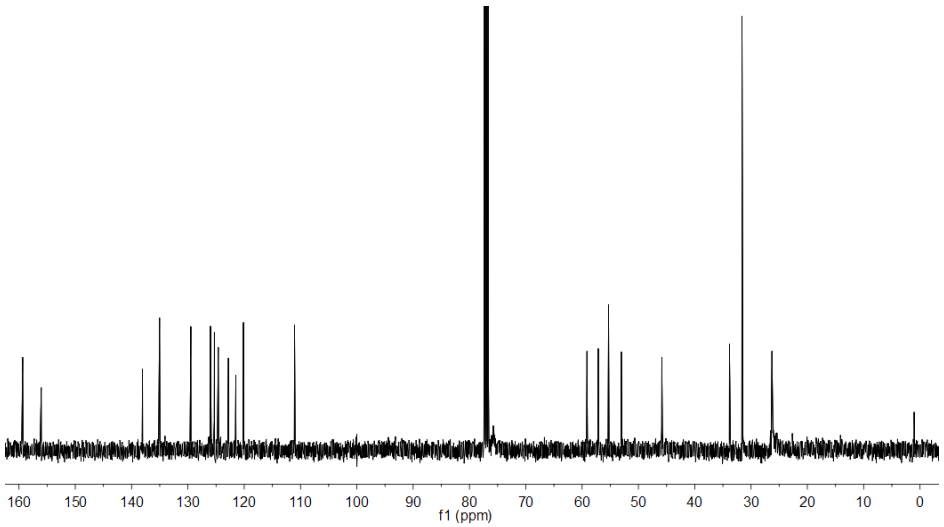

Fig. S20. ^{13}C NMR spectrum of **5e** ($CDCl_3$, 100 MHz).

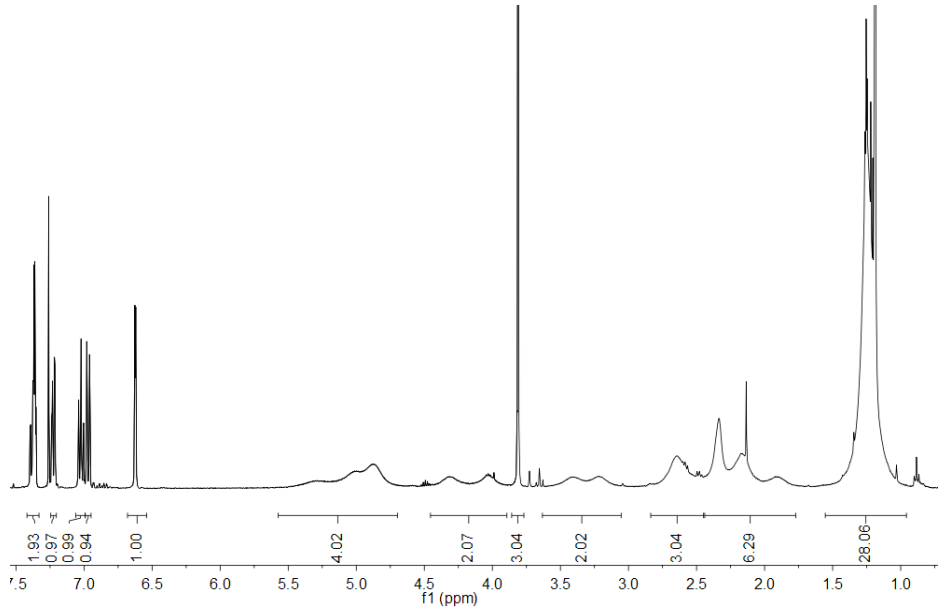

Fig. S21. ^{1}H NMR spectrum of **6e** ($CDCl_3$, 400 MHz).

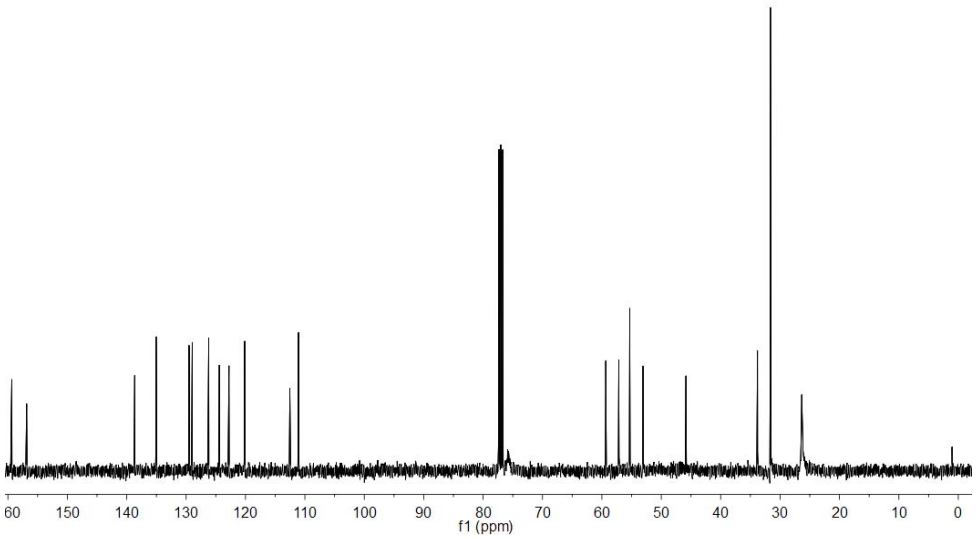

Fig. S22. ^{13}C NMR spectrum of **6e** ($CDCl_3$, 100 MHz).

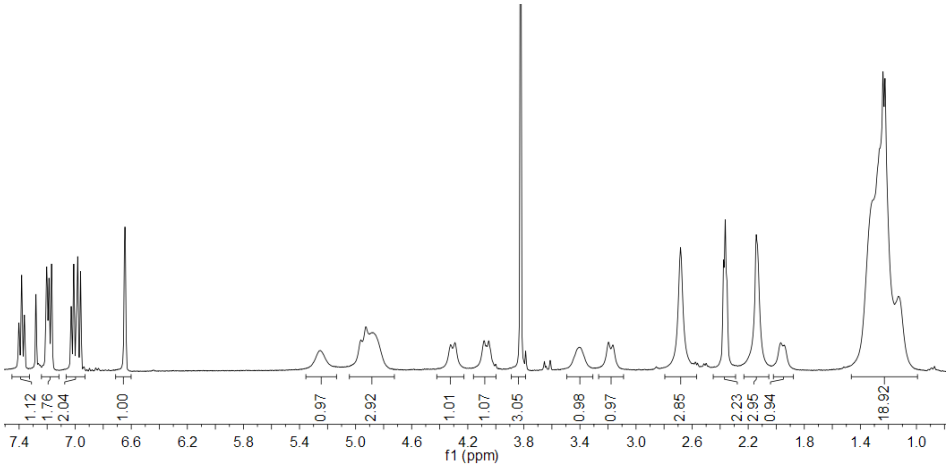

Fig. S23. ^{1}H NMR spectrum of **7e** ($CDCl_3$, 400 MHz).

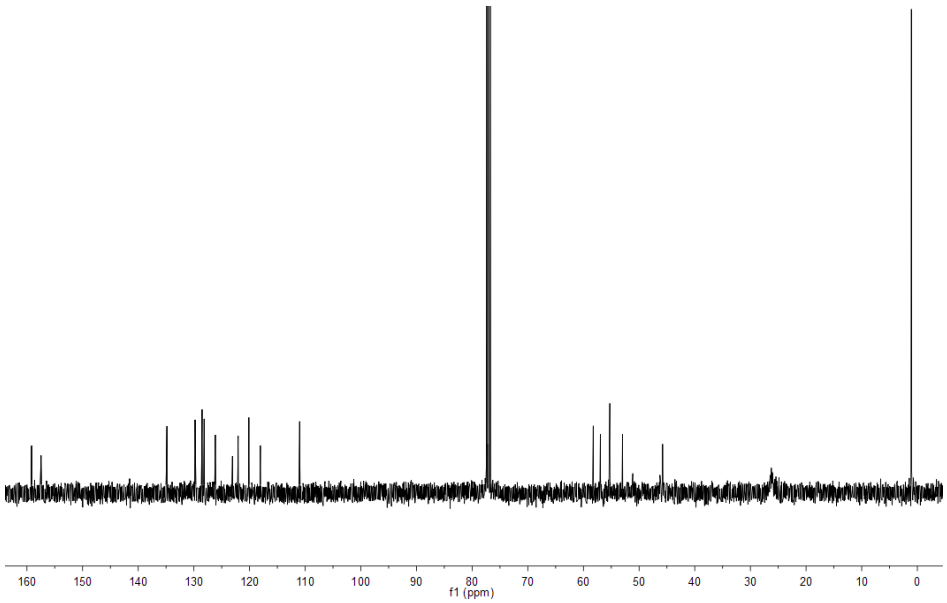

Fig. S24. ^{13}C NMR spectrum of **7e** ($CDCl_3$, 100 MHz).

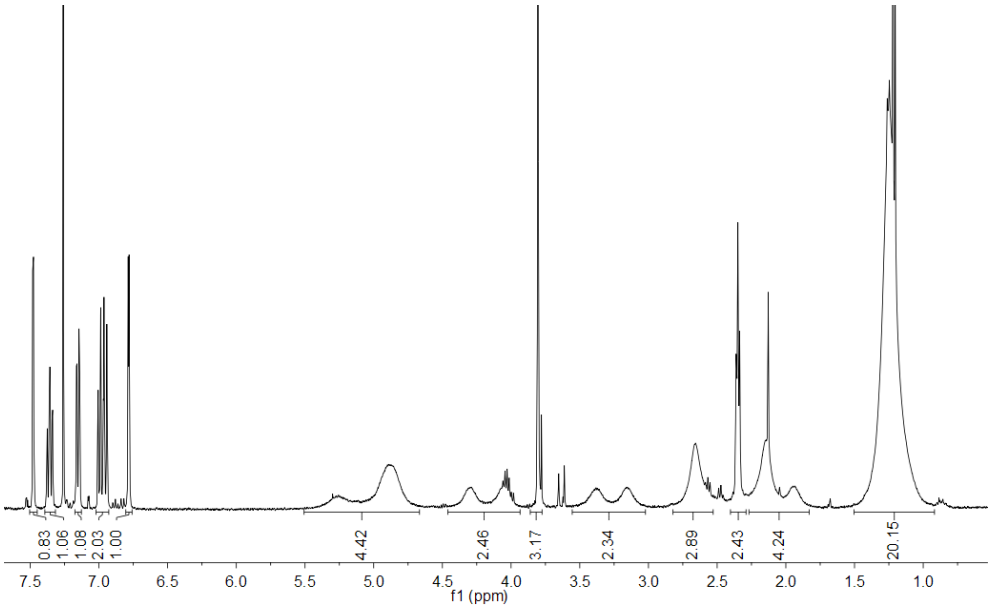

Fig. S25. ^{1}H NMR spectrum of **8e** ($CDCl_3$, 400 MHz).

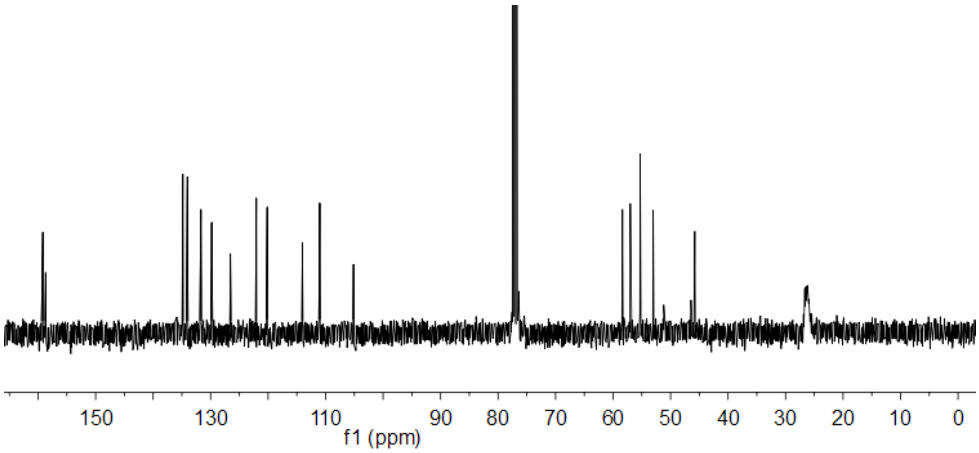

Fig. S26. ^{13}C NMR spectrum of **8e** ($CDCl_3$, 100 MHz).

3 Variable temperature ^{1}H NMR spectra of complex 2a

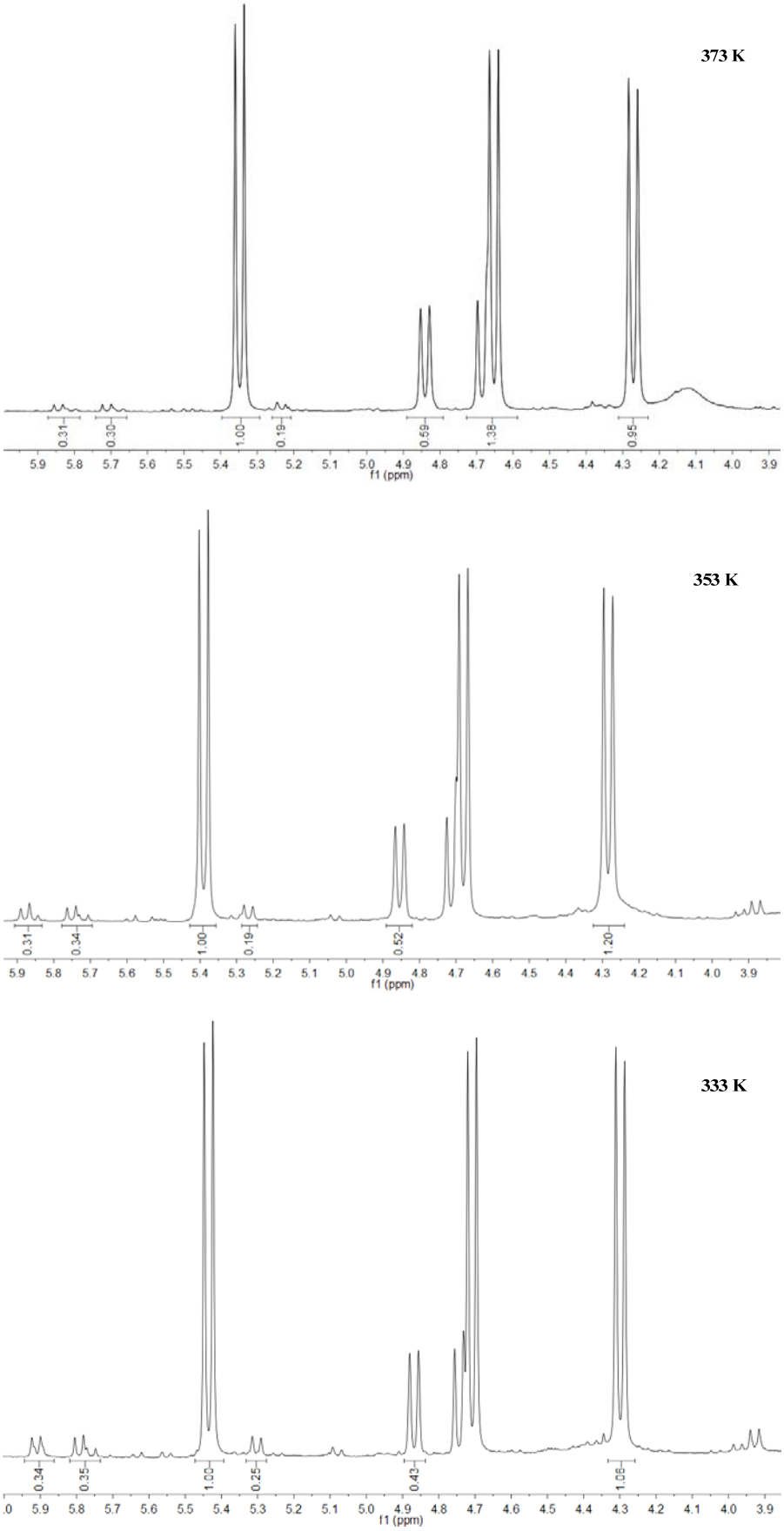

Fig. S27. Variable-temperature ^{1}H NMR spectra of **2a** in toluene-d_8 (partial).

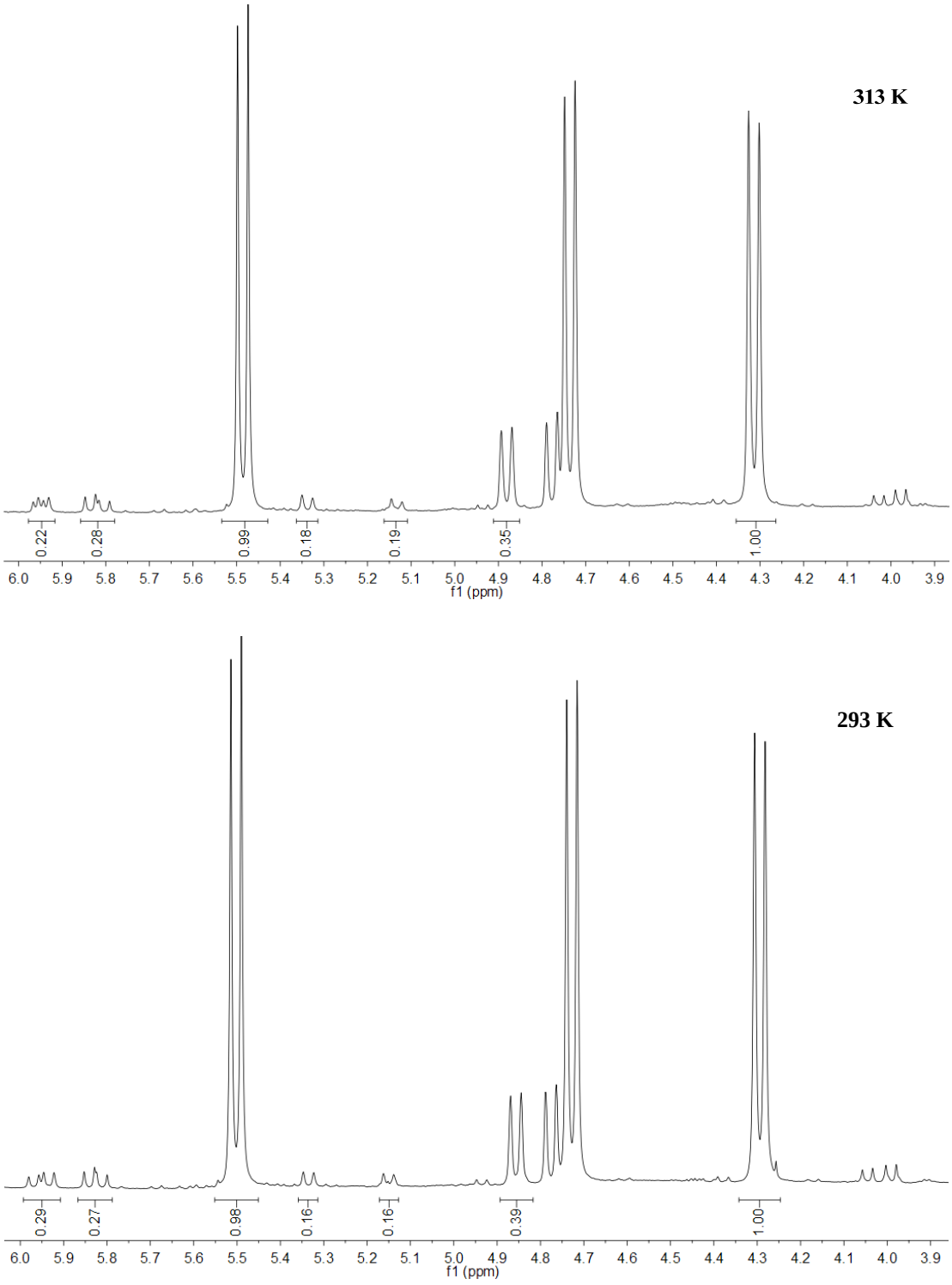

Fig. S28. Variable-temperature ^{1}H NMR spectra of **2a** in toluene-d_8 (partial)

4 Variable temperature ^{1}H NMR spectra of complex 5e

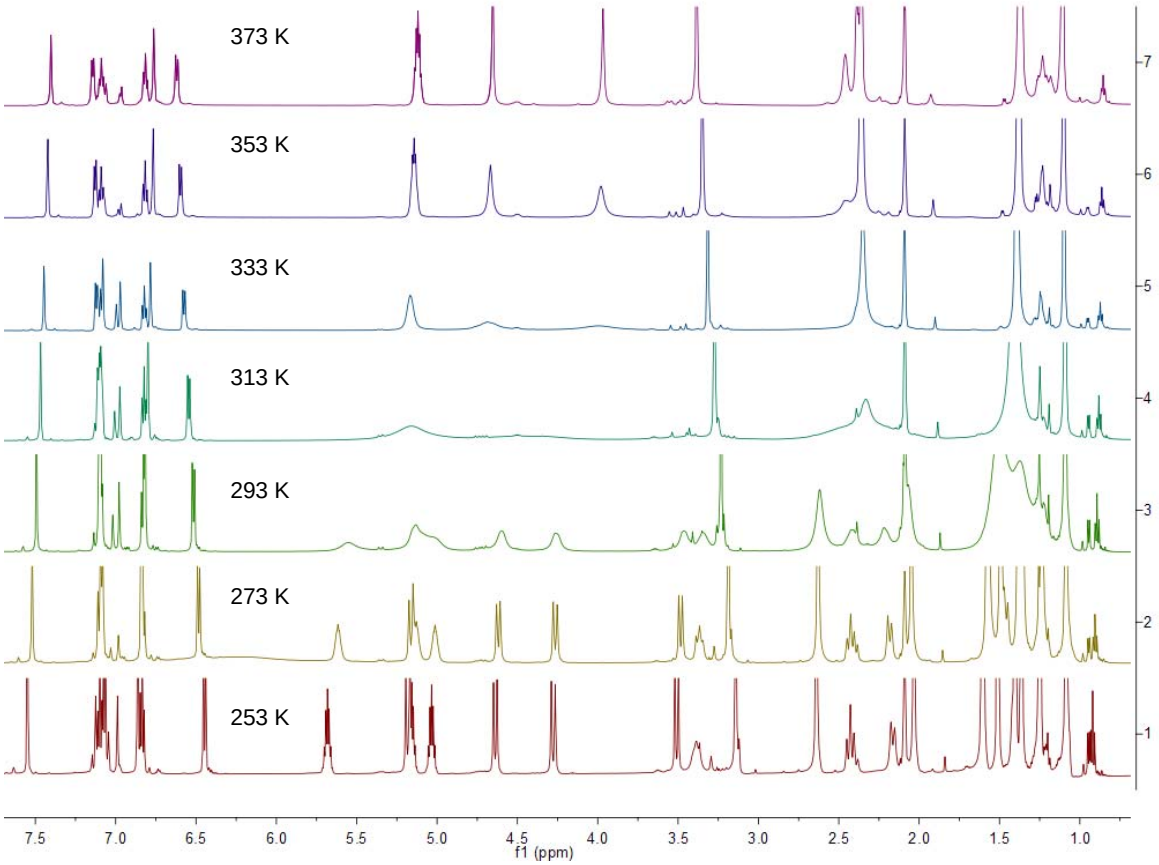

Fig. S29. Variable-temperature ^{1}H NMR spectra of **5e** in toluene-d_8

5 Ethylene polymerization catalyzed by titanium and zirconium complexes.

Table S2. The influence of polymerization temperature on the ethylene polymerization catalyzed by complexes **1a-4a**, **7a**, **9a-10a** and **8b**. [a]

Entry	Cat.	Temp (°C)	Al/Ti	PE (mg)	Activity (kg/(mol-M·h))	M_η [b] (10^4 g/mol)	T_m [c] (°C)
1	**1a**	30	1000	13	78	--	--
2	**1a**	50	1000	16	96	--	--
3	**1a**	80	1000	30	180	*	--
4	**2a**	30	1000	34	204	--	--
5	**2a**	50	1000	52	312	--	--
6	**2a**	80	1000	61	366	*	133.4
7	**3a**	30	1000	45	330	*	--
8	**3a**	50	1000	50	300	*	--
9	**3a**	80	1000	59	354	*	--
10	**4a**	30	1000	11	66	*	--
11	**4a**	50	1000	33	198	*	--
12	**4a**	80	1000	45	270	38.48	--
13	**7a**	30	1000	87	522	*	134.4
14	**7a**	50	1000	98	588	*	133.6
15	**7a**	80	1000	119	714	58.43	133.8
16	**9a**	30	1000	trace	--	--	--
17	**9a**	50	1000	trace	--	--	--
18	**9a**	80	1000	24	144	--	--
19	**10a**	30	1000	trace	--	--	--
20	**10a**	50	1000	trace	--	--	--
21	**10a**	80	1000	20	120	--	--
22	**8b**	30	1000	41	246	*	133.6
23	**8b**	50	1000	87	522	*	133.7
24	**8b**	80	1000	113	678	55.05	134.8

[a] Conditions: toluene as solvent, [Cat.] = 0.04 μmol/mL, V_{total} = 25 mL, MMAO as cocatalyst, 1 MPa of ethylene, 10 min; [b] Intrinsic viscosity was determined in decahydronaphthalene at 135 °C by Ubbelohde viscosimeter technique, and the viscosity average molecular weights were calculated using the relation:[96] $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$, in unit of 10^4 g/mol; * insoluble. [c] Determined by DSC at a heating rate of 10 °C min^{-1}.

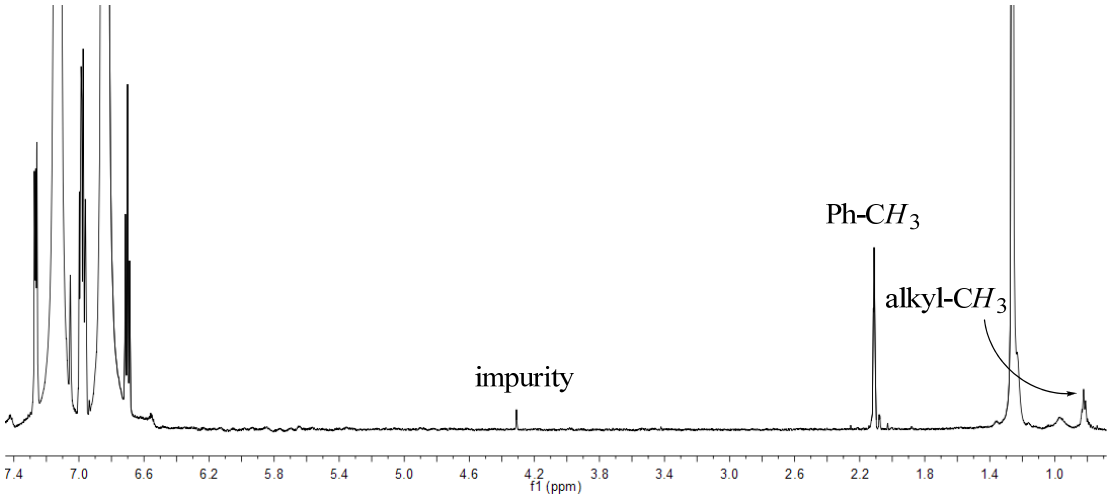

Fig. S29. ^{1}HNMR spectrum of polymer obatined by complex **8a** (entry 17, 400 MHz, *o*-$C_6H_4Cl_2$: C_6D_6 = 4 : 1, 100 °C).