Supporting Information

Aluminum Complexes with Bidentate Amido Ligands: Synthesis, Structure and Performance on Ligand-Initiated Ring-Opening Polymerization of *rac*-Lactide

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1. X-ray diffraction data of complexes 2b and 3b.

Table S1. The crystal data and structure refinement for complexes 2b and 3b.

	2b	**3b**
Formula	$C_{23}H_{35}AlN_2$	$C_{22}H_{31}AlN_2$
Formula weight	366.51	350.47
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	P 21/c	P 21 21 21
a (Å)	10.075(3)	7.880(3)
b (Å)	17.439(6)	13.970(5)
c (Å)	13.495(5)	18.482(7)
α (°)	90	90
β (°)	105.666(4)	90
γ (°)	90	90
V (Å^3)	2283.0(13)	2034.5(14)
Z	4	4
Density (g·cm^{-3})	1.066	1.144
Absorp coeff/mm^{-1}	0.097	0.106
F (000)	800	760
Data collected (hkl)	–12<=h<=12, –21<=k<=11, –16<=l<=16	–9<=h<=10, –16<=k<=17, –22<=l<=23
θ range for data collection/◦	1.954 to 26.010	1.827 to 27.010
Max. and min. transmission	1 and 0.753	1 and 0.507
Data/restrains/parameters	4494 / 0 / 239	4339 / 0 / 230
Goodness-of-fit on F^2	0.902	0.936
Final R indices [I > 2σ(I)]	R1 = 0.0453, wR2 = 0.1140	R1 = 0.0389, wR2 = 0.0919
R indices (all data)	R1 = 0.0898, wR2 = 0.1287	R1 = 0.0518, wR2 = 0.0972
Largest diff. peak and hole/e Å^{-3}	0.261 and –0.192	0.163 and –0.166

2. ^{1}H NMR and ^{13}C NMR spectra of proligands 1a-1j and aluminum complexes 2b, 2d, 3a-3j.

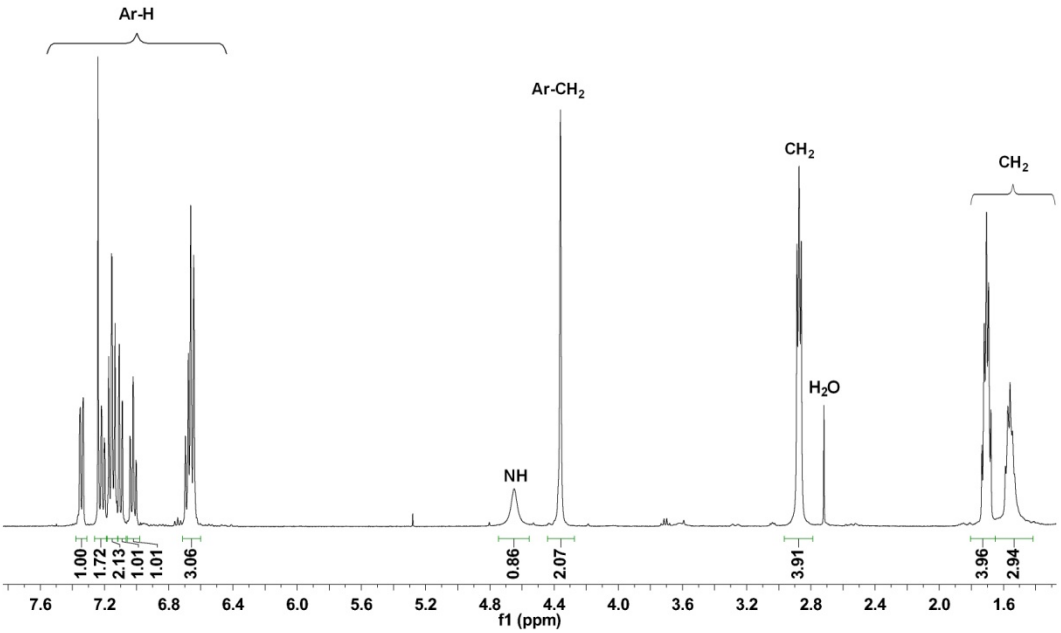

Figure S1. The ^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400 MHz).

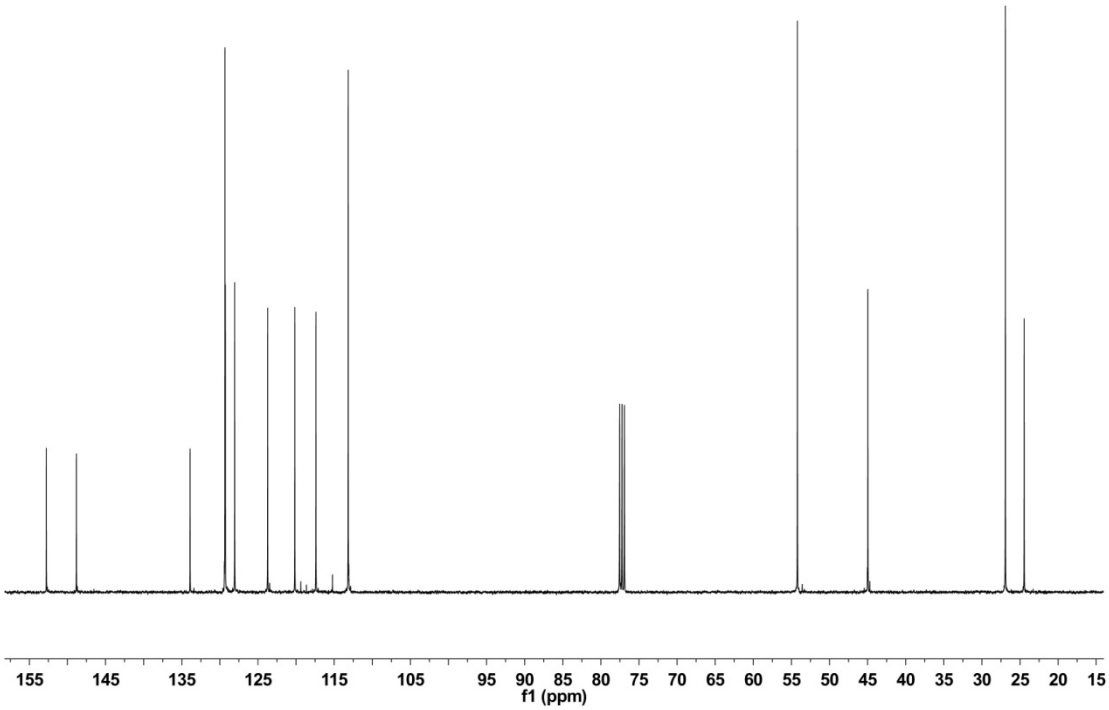

Figure S2. The ^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz).

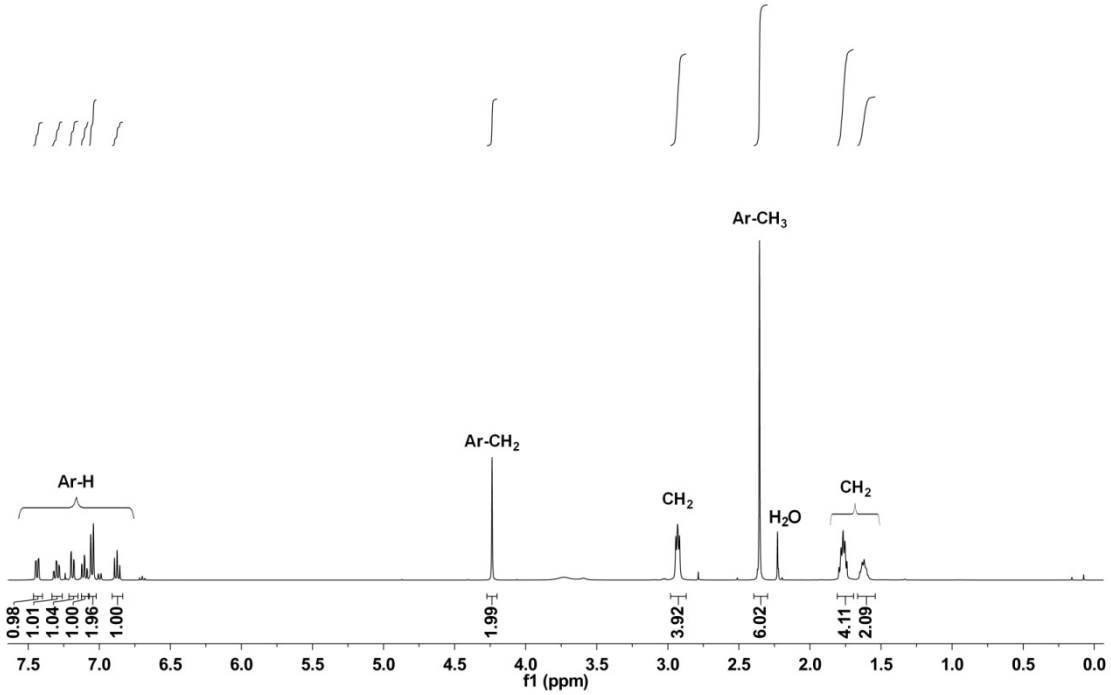

Figure S3. The ^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400 MHz).

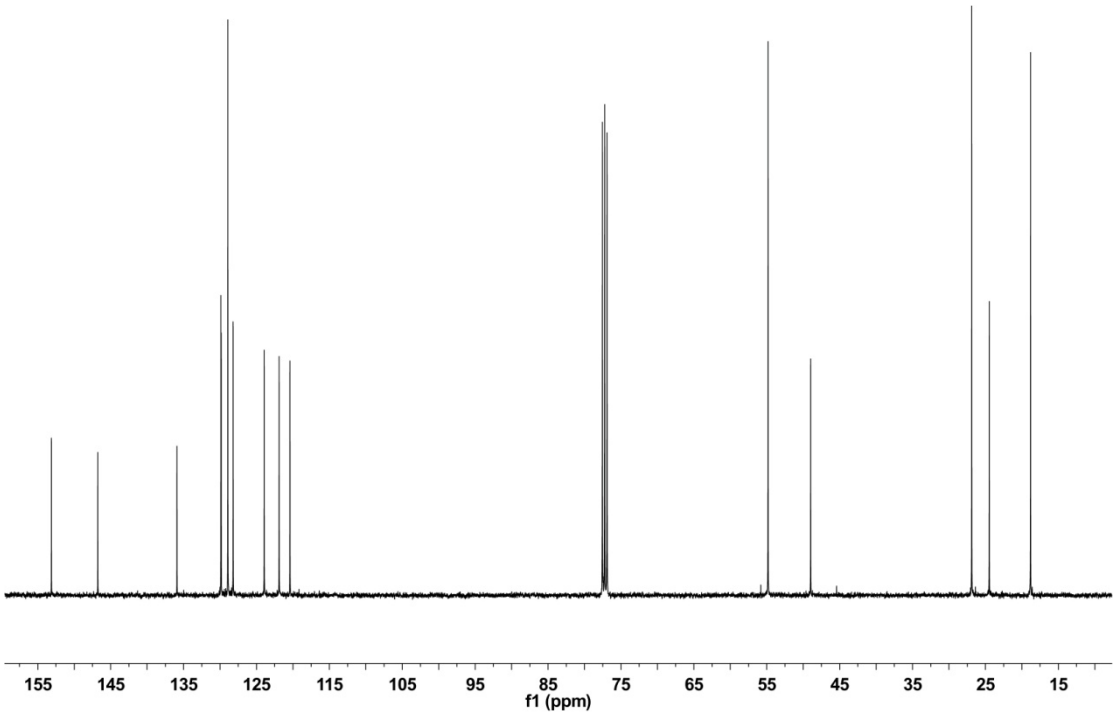

Figure S4. The ^{13}C NMR spectrum of compound **1b** ($CDCl_3$, 100 MHz).

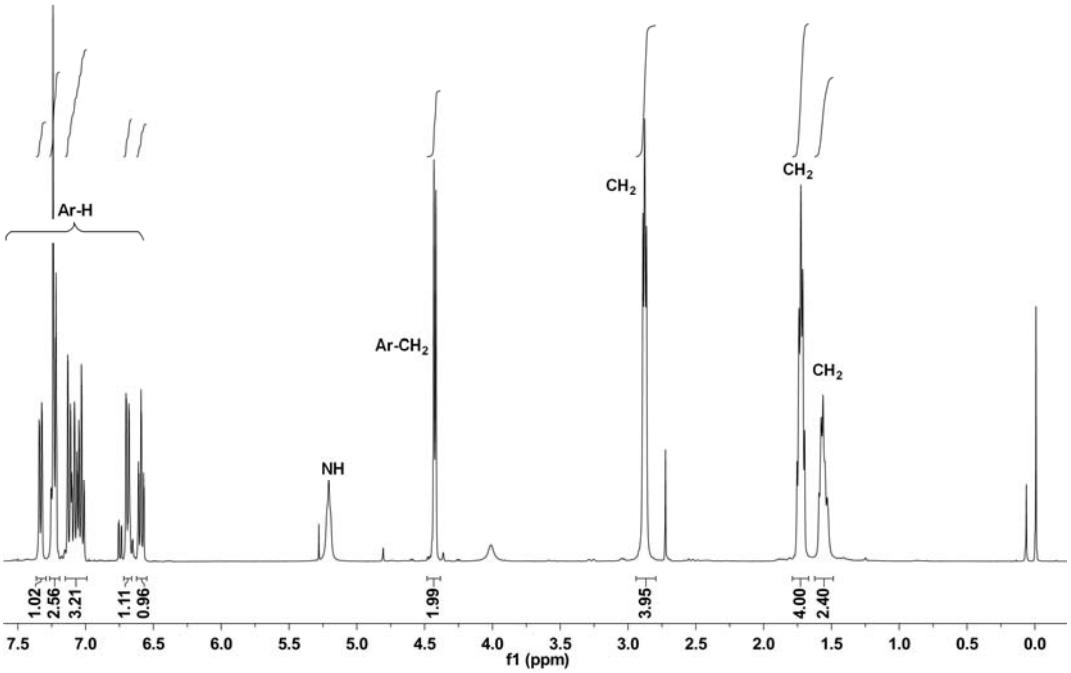

Figure S5. The ^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400 MHz).

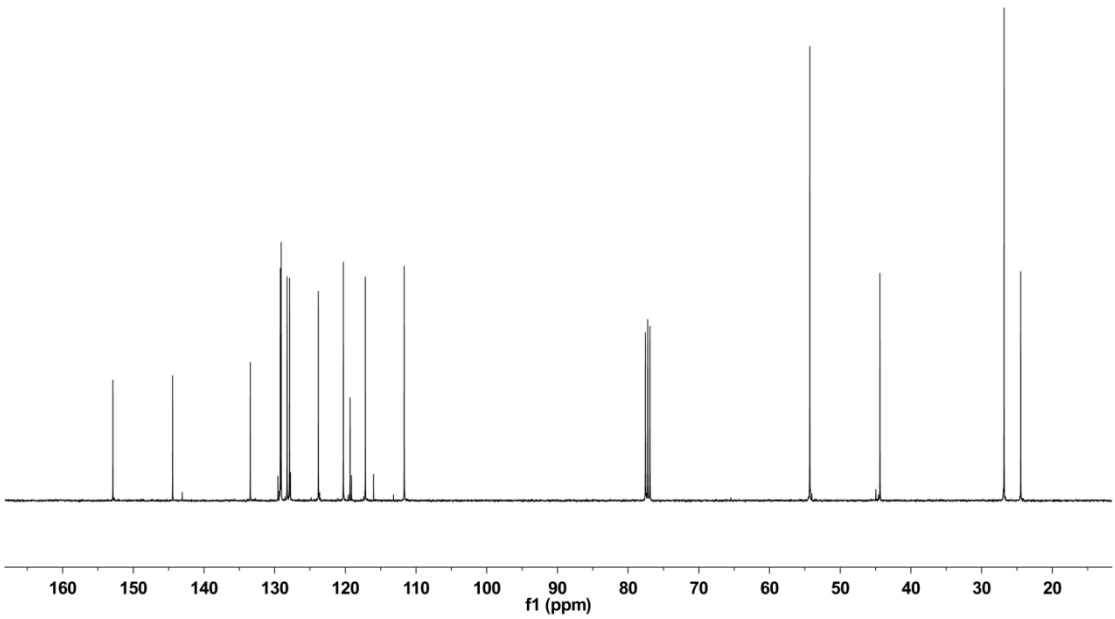

Figure S6. The ^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 100 MHz).

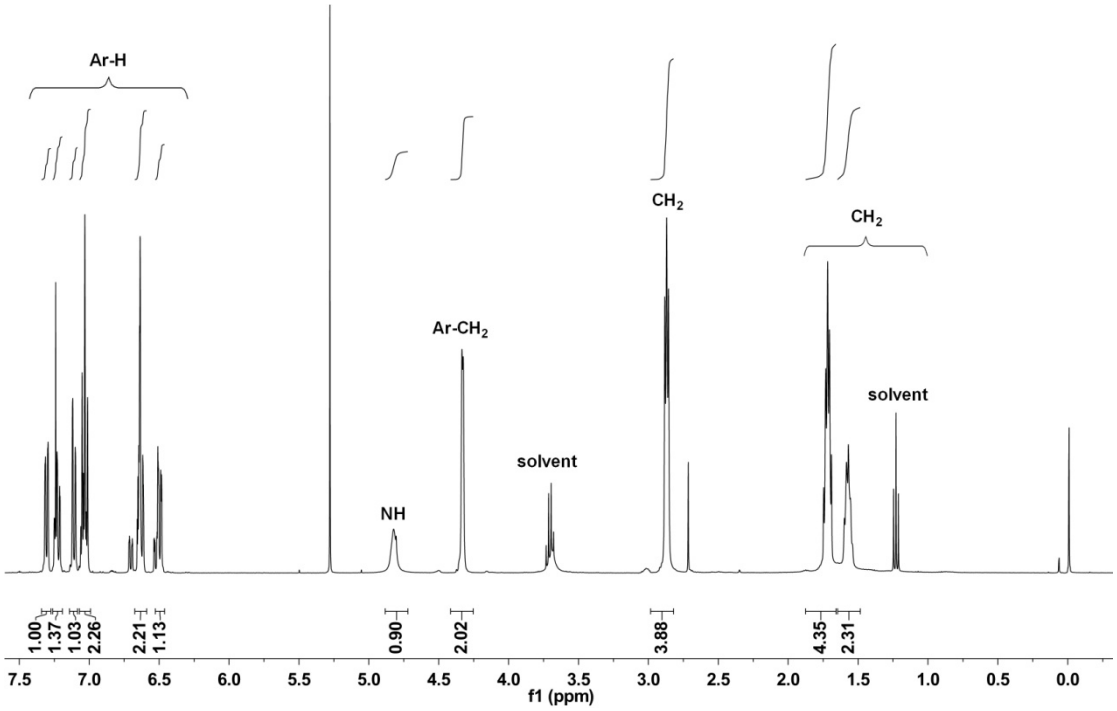

Figure S7. The ^{1}H NMR spectrum of compound **1d** ($CDCl_3$, 400 MHz).

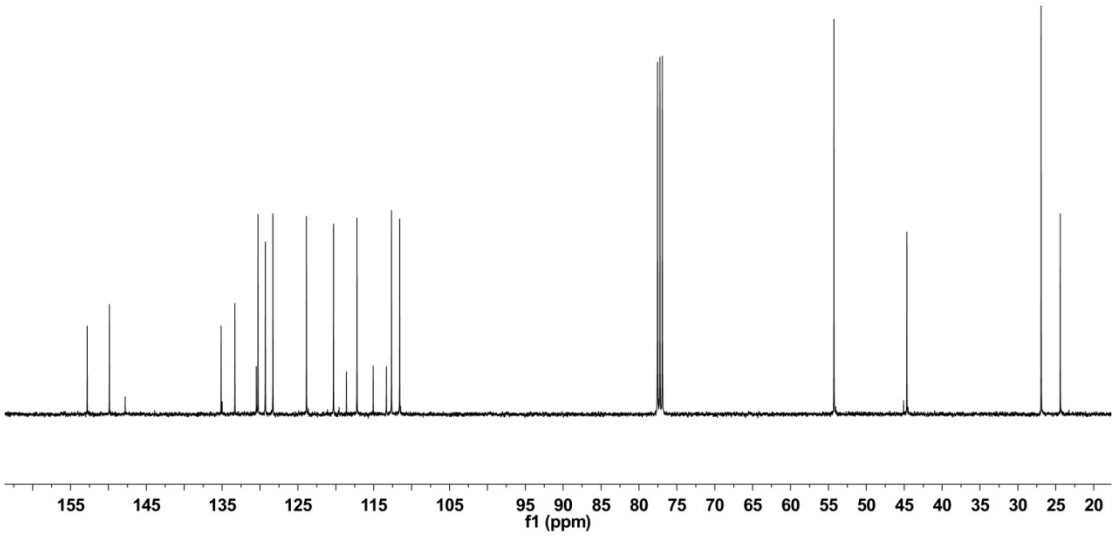

Figure S8. The ^{13}C NMR spectrum of compound **1d** ($CDCl_3$, 100 MHz).

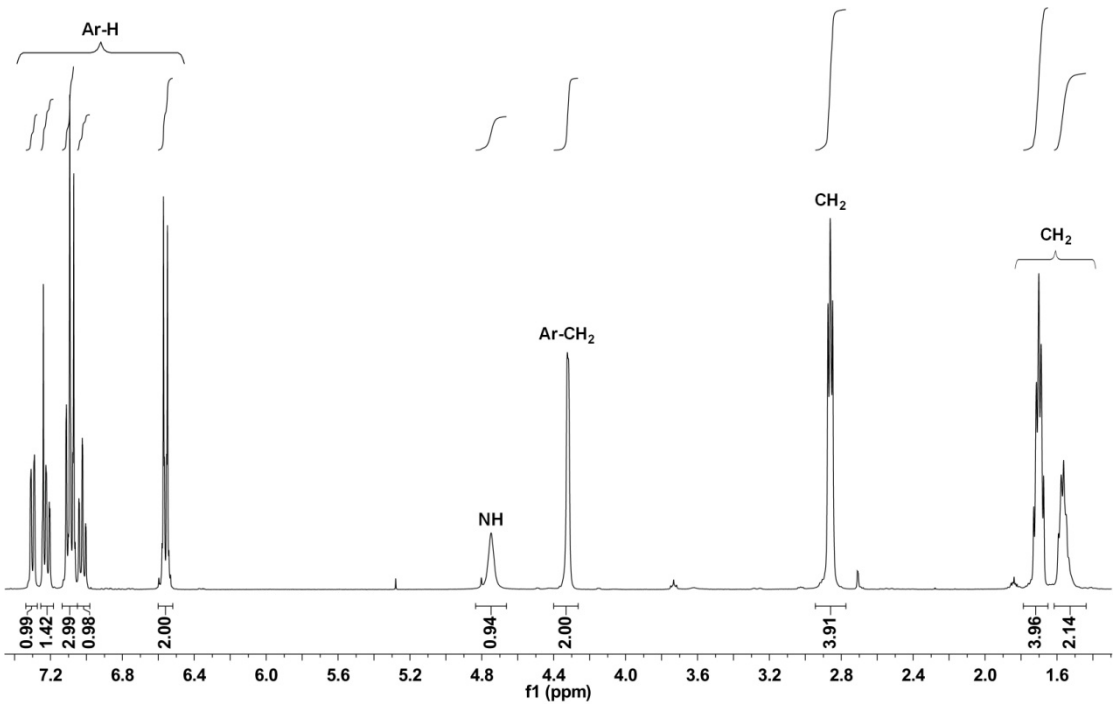

Figure S9. The ^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 400 MHz).

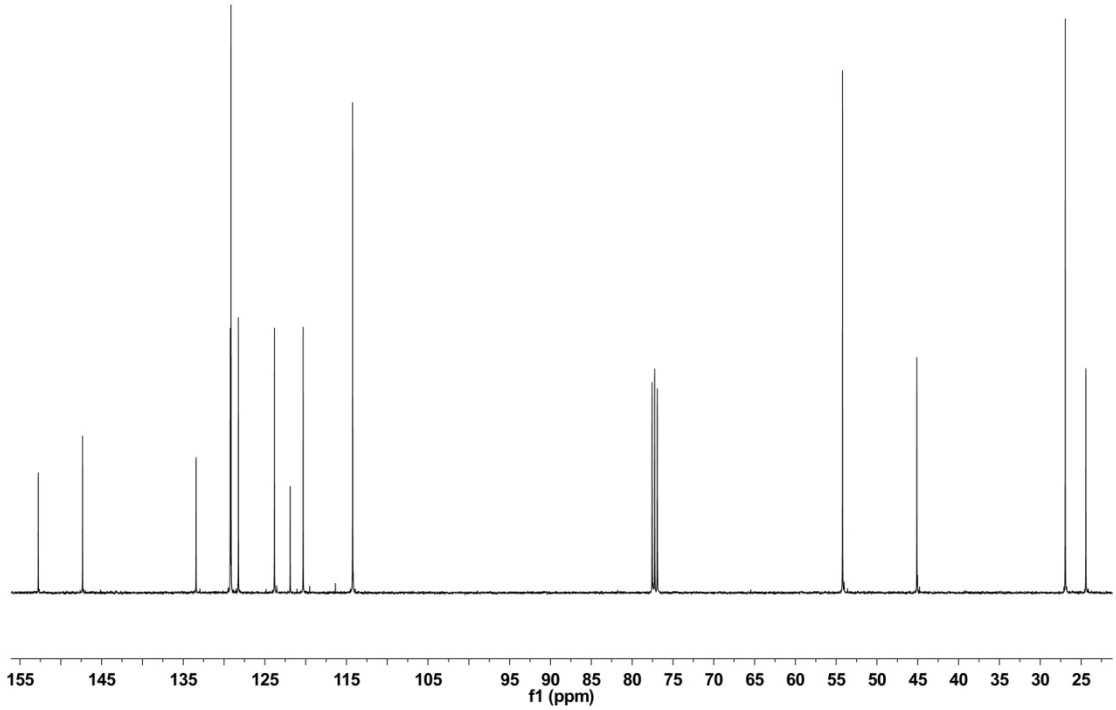

Figure S10. The ^{13}C NMR spectrum of compound **1e** ($CDCl_3$, 100 MHz).

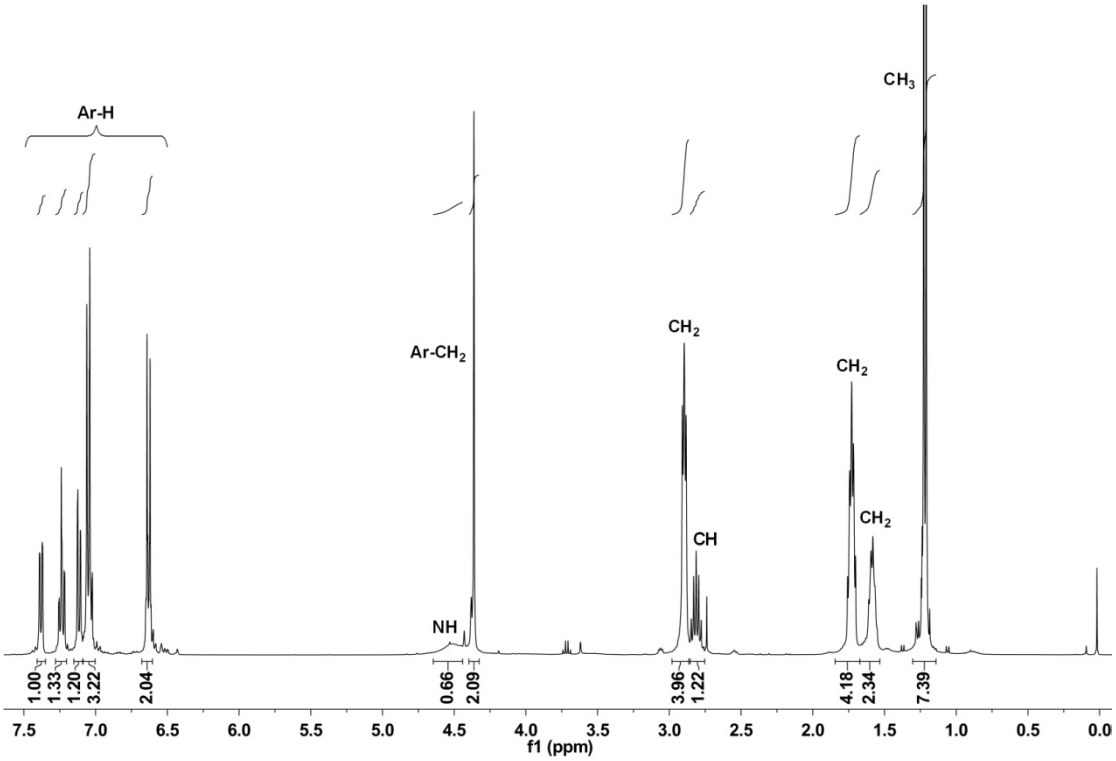

Figure S11. The ^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 400 MHz).

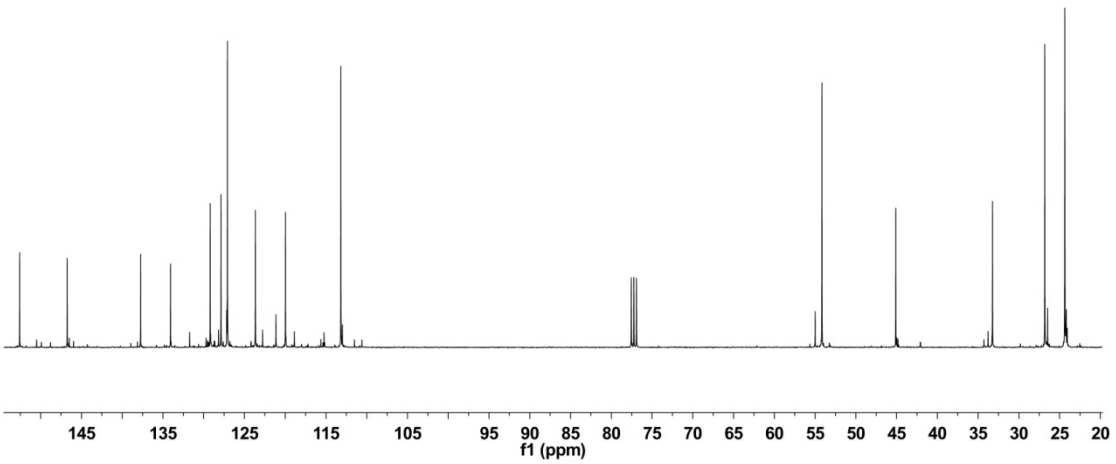

Figure S12. The ^{13}C NMR spectrum of compound **1f** ($CDCl_3$, 100 MHz).

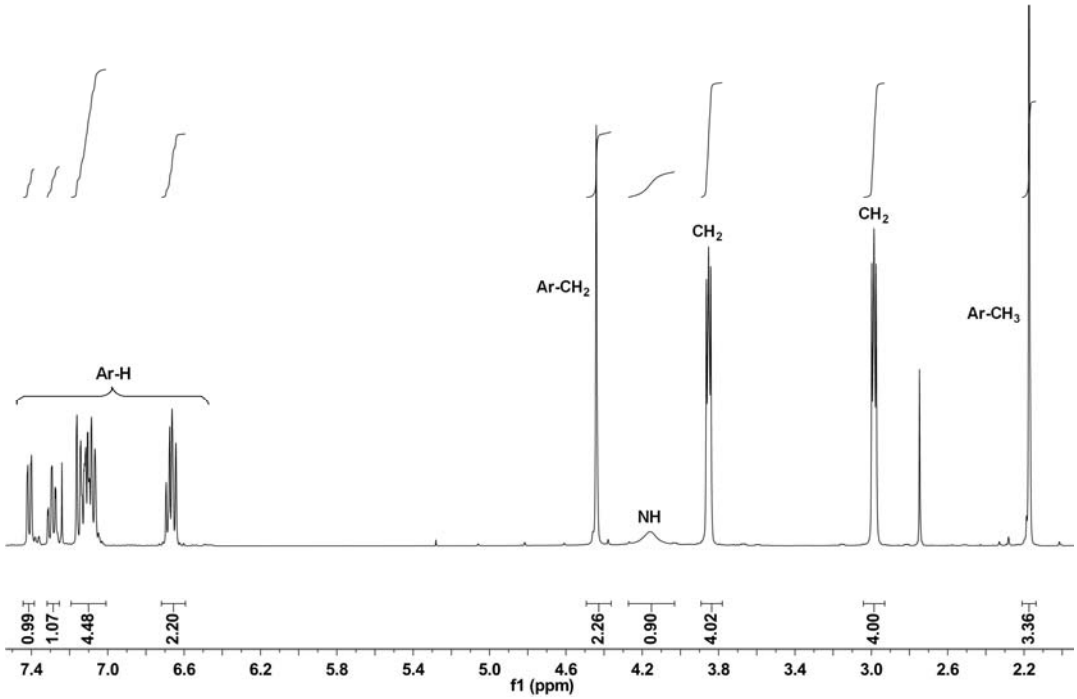

Figure S13. The ^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400 MHz).

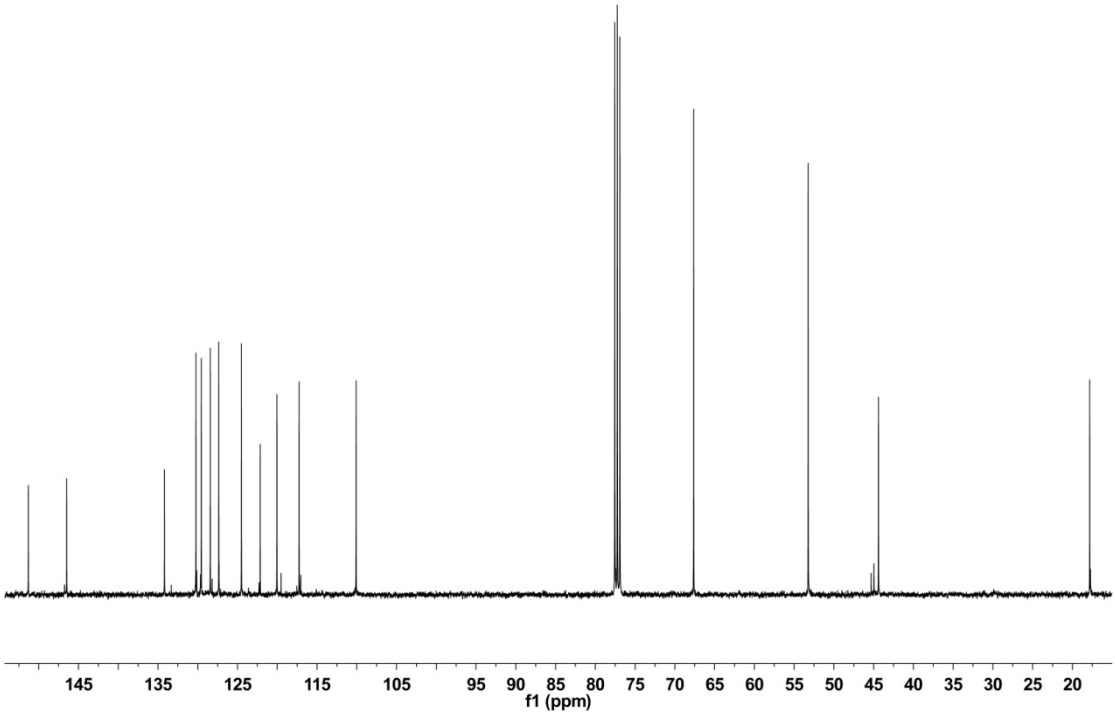

Figure S14. The ^{13}C NMR spectrum of compound **1g** ($CDCl_3$, 100 MHz).

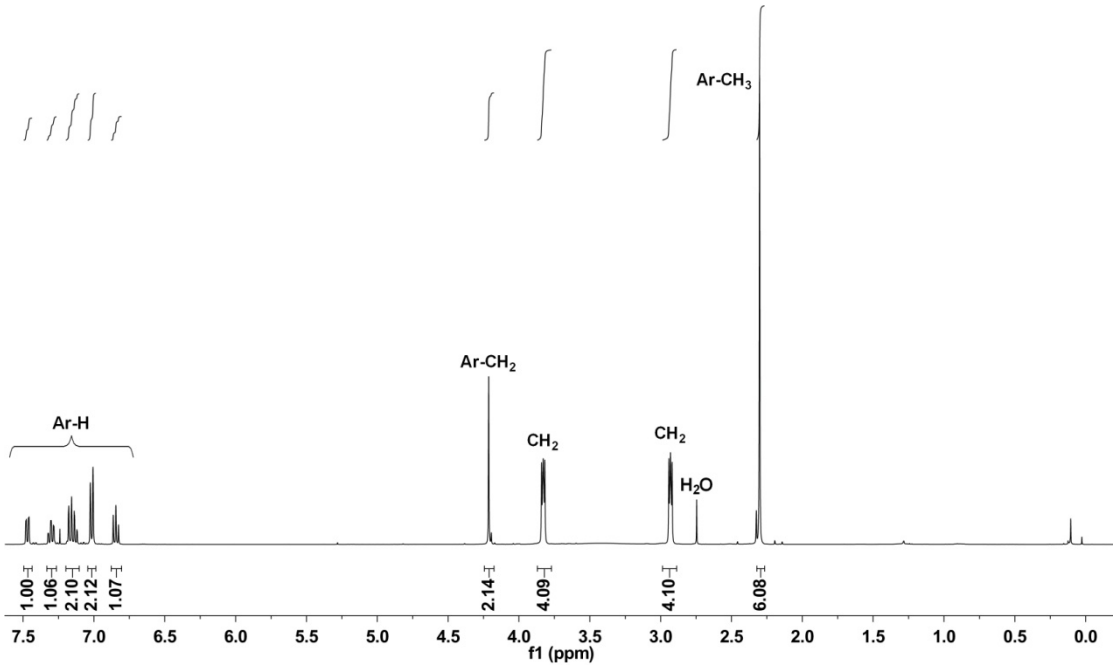

Figure S15. The ^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 400 MHz).

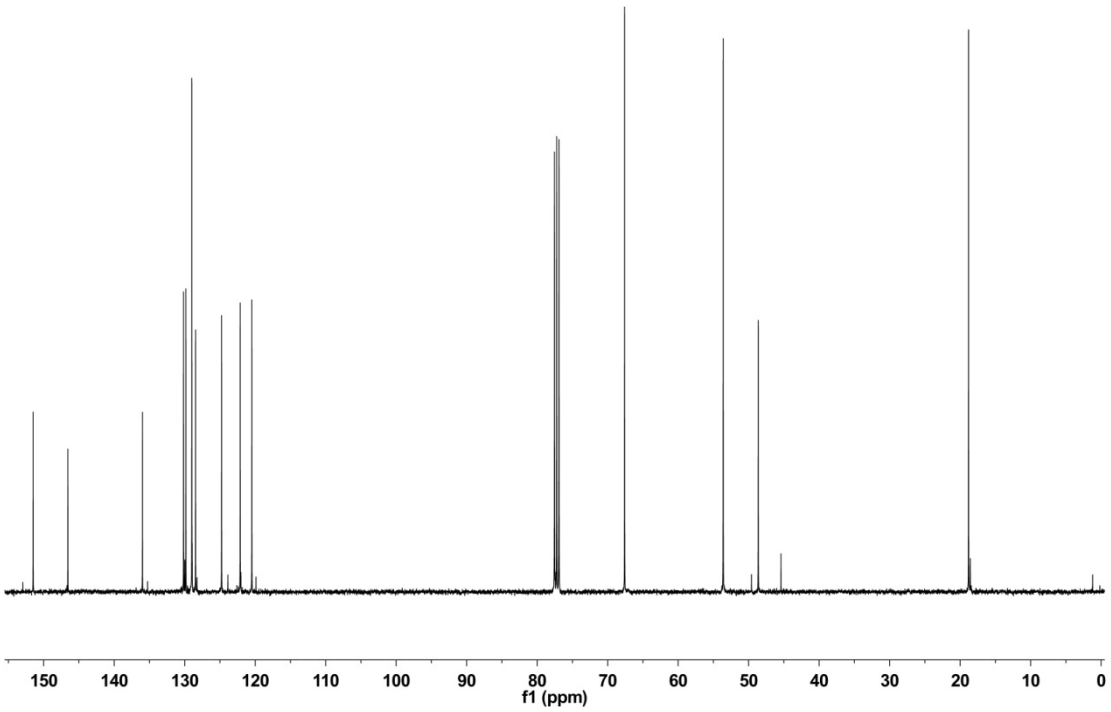

Figure S16. The ^{13}C NMR spectrum of compound **1h** ($CDCl_3$, 100 MHz).

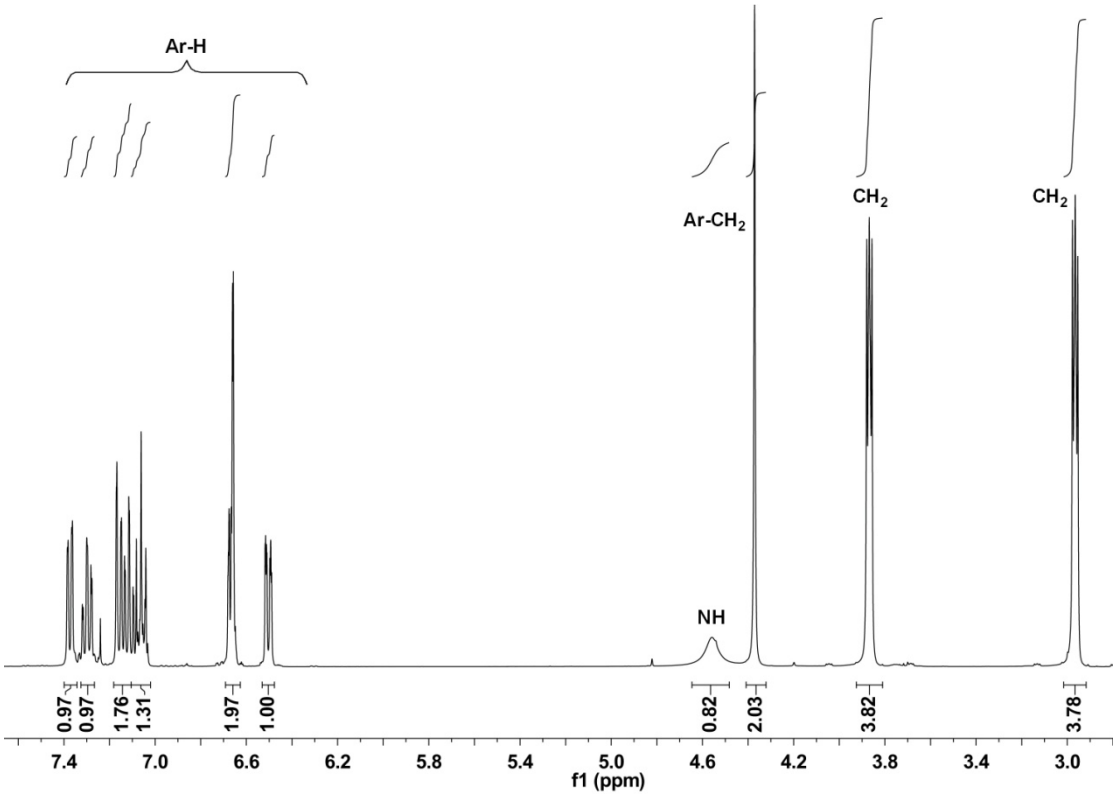

Figure S17. The ^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 400 MHz).

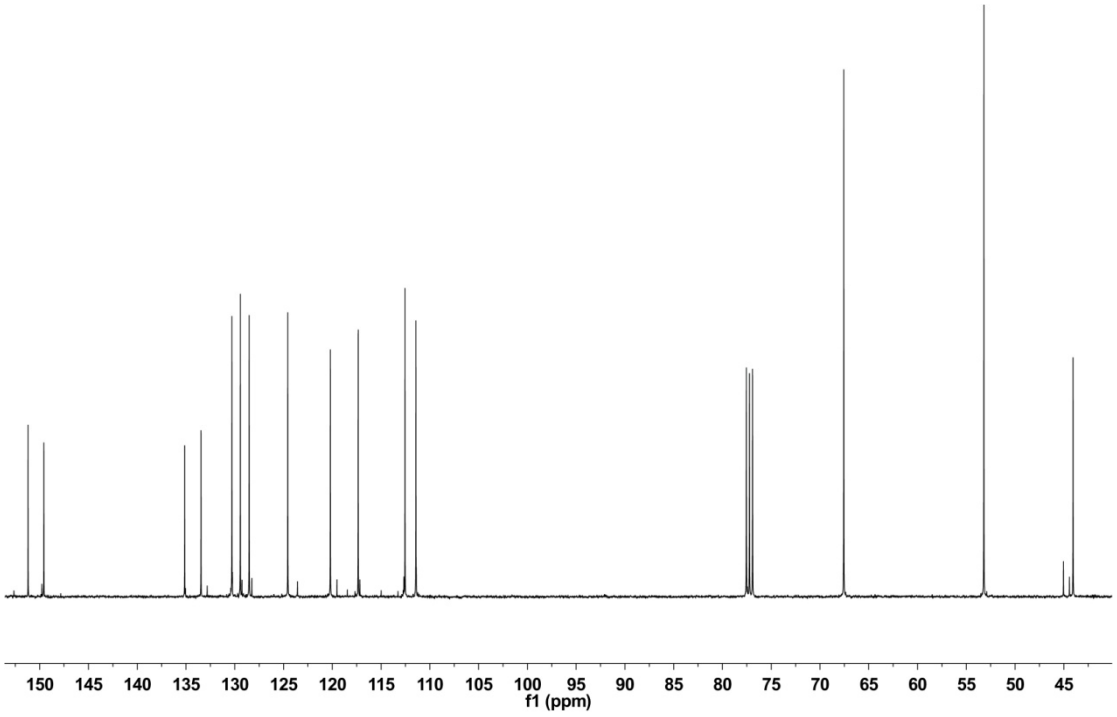

Figure S18. The ^{13}C NMR spectrum of compound **1i** ($CDCl_3$, 100 MHz).

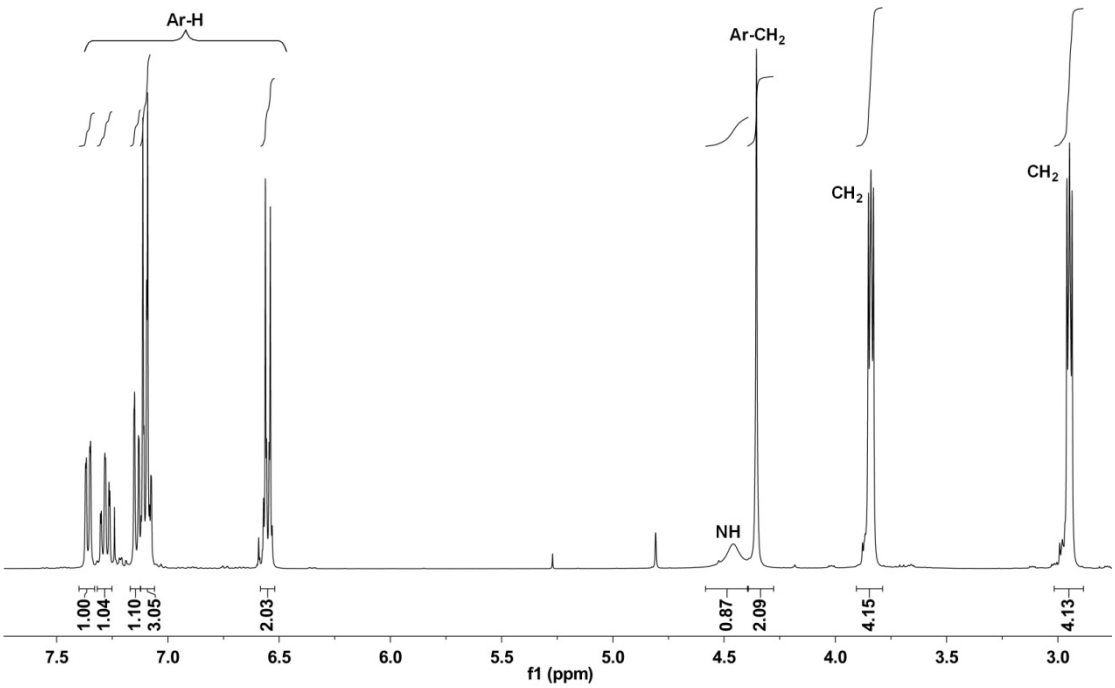

Figure S19. The ^{1}H NMR spectrum of compound **1j** ($CDCl_3$, 400 MHz).

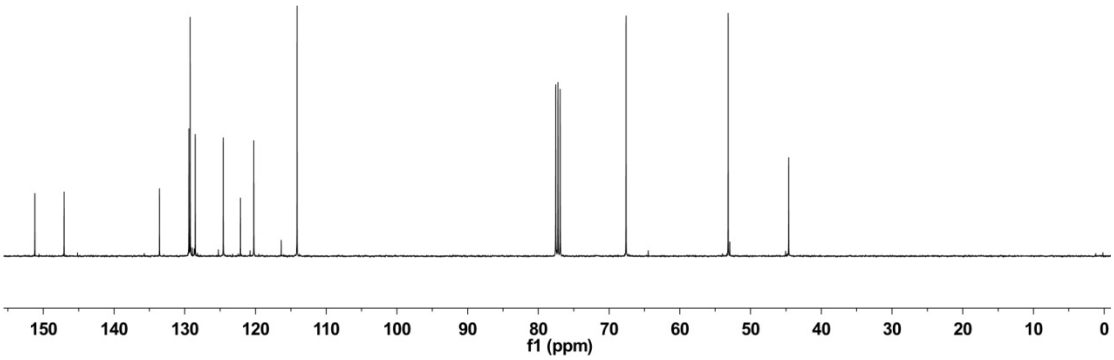

Figure S20. The ^{13}C NMR spectrum of compound **1j** ($CDCl_3$, 100 MHz).

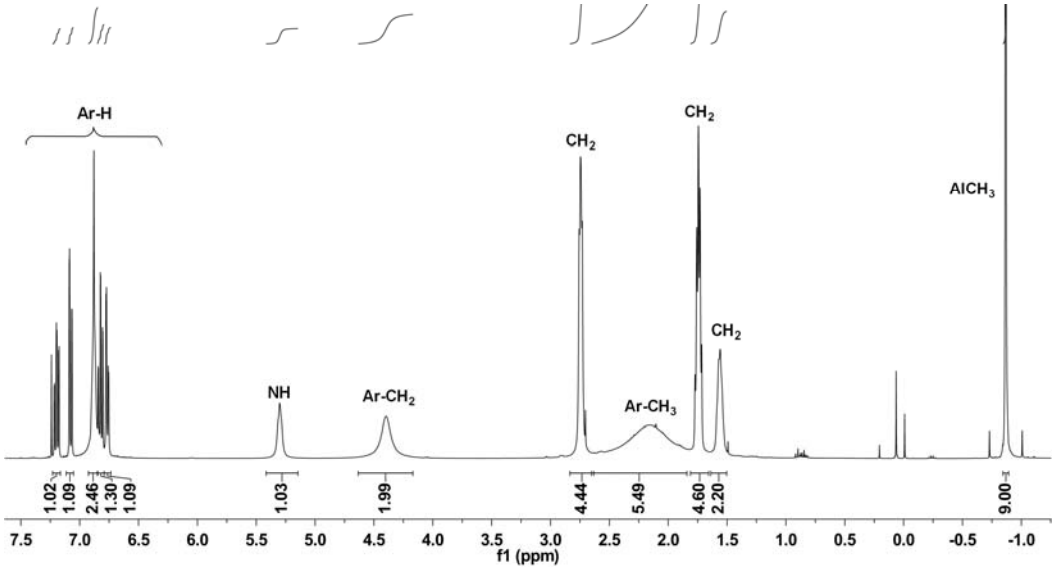

Figure S21. The ^{1}H NMR spectrum of adduct **2b** ($CDCl_3$, 400 MHz).

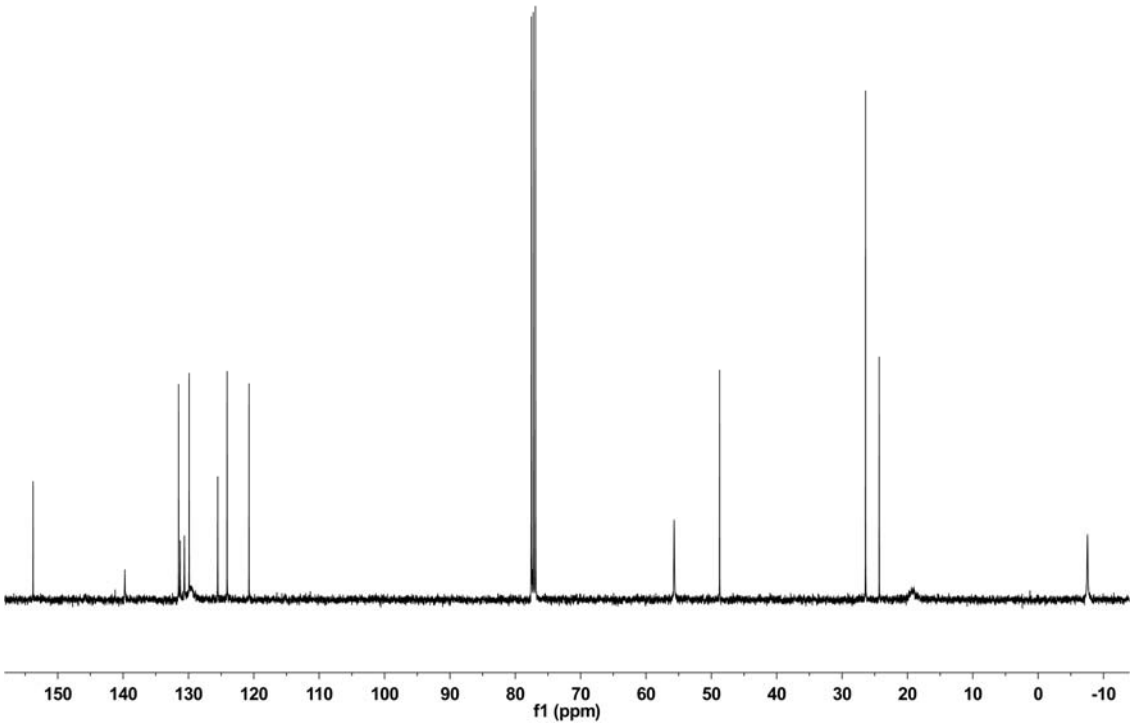

Figure S22. The ^{13}C NMR spectrum of complex **2b** ($CDCl_3$, 100 MHz).

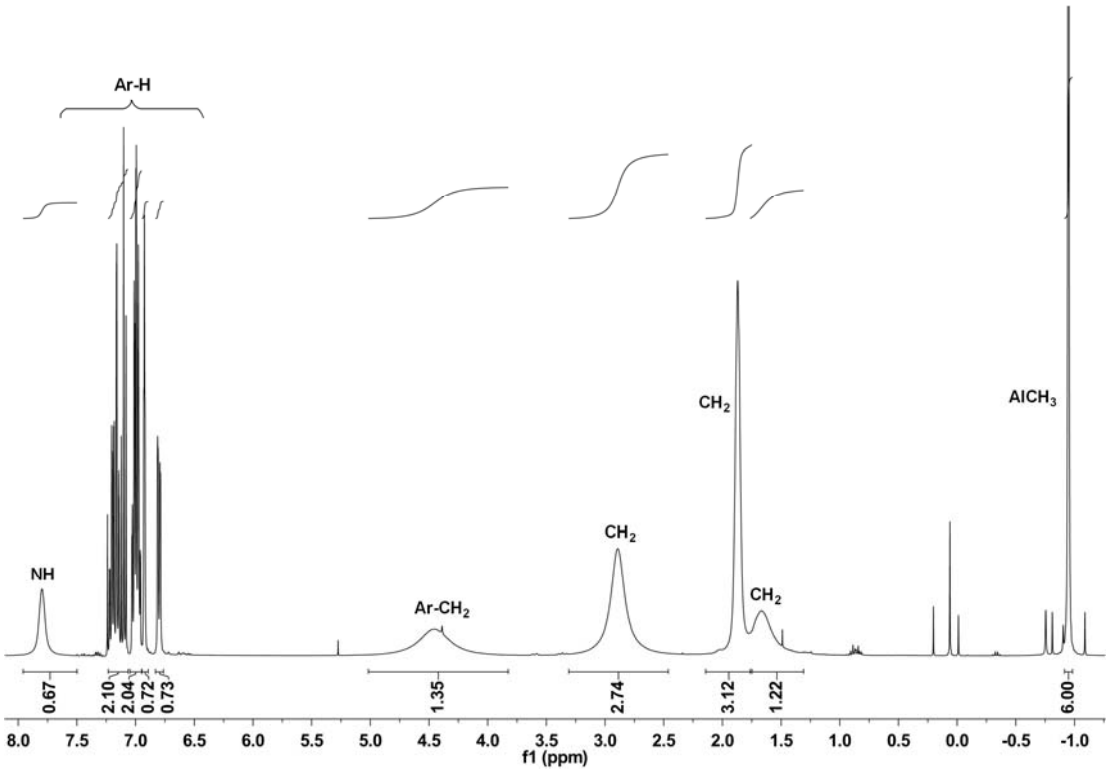

Figure S23. The ^{1}H NMR spectrum of adduct **2d** ($CDCl_3$, 400 MHz).

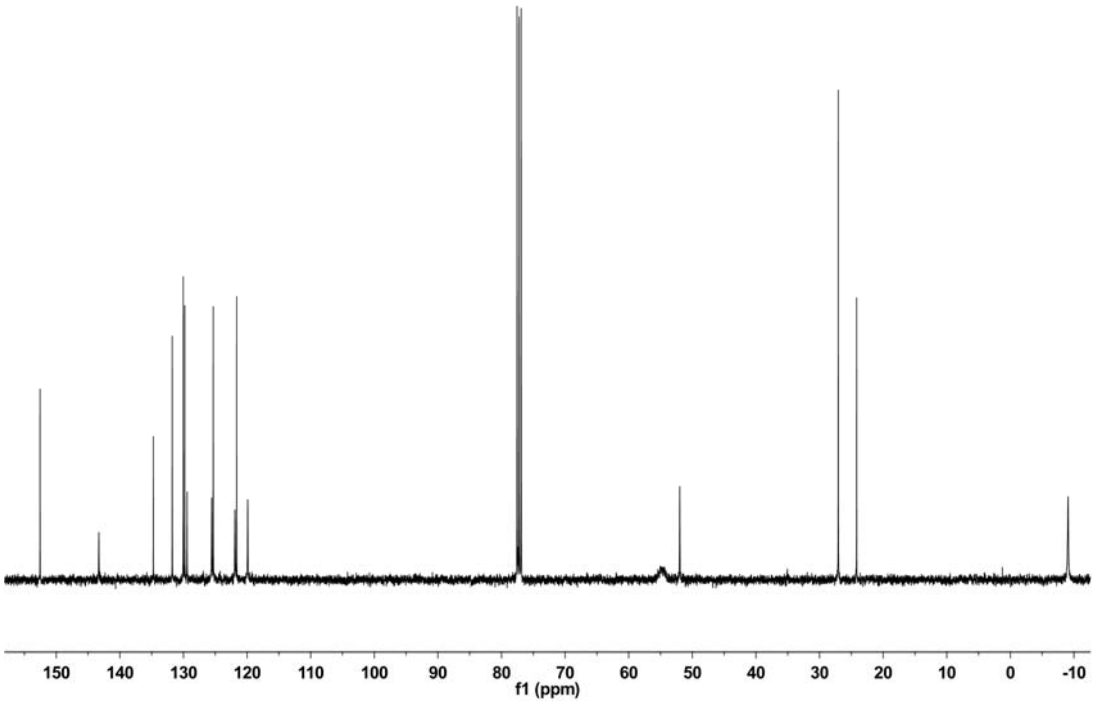

Figure S24. The ^{13}C NMR spectrum of complex **2d** ($CDCl_3$, 100 MHz).

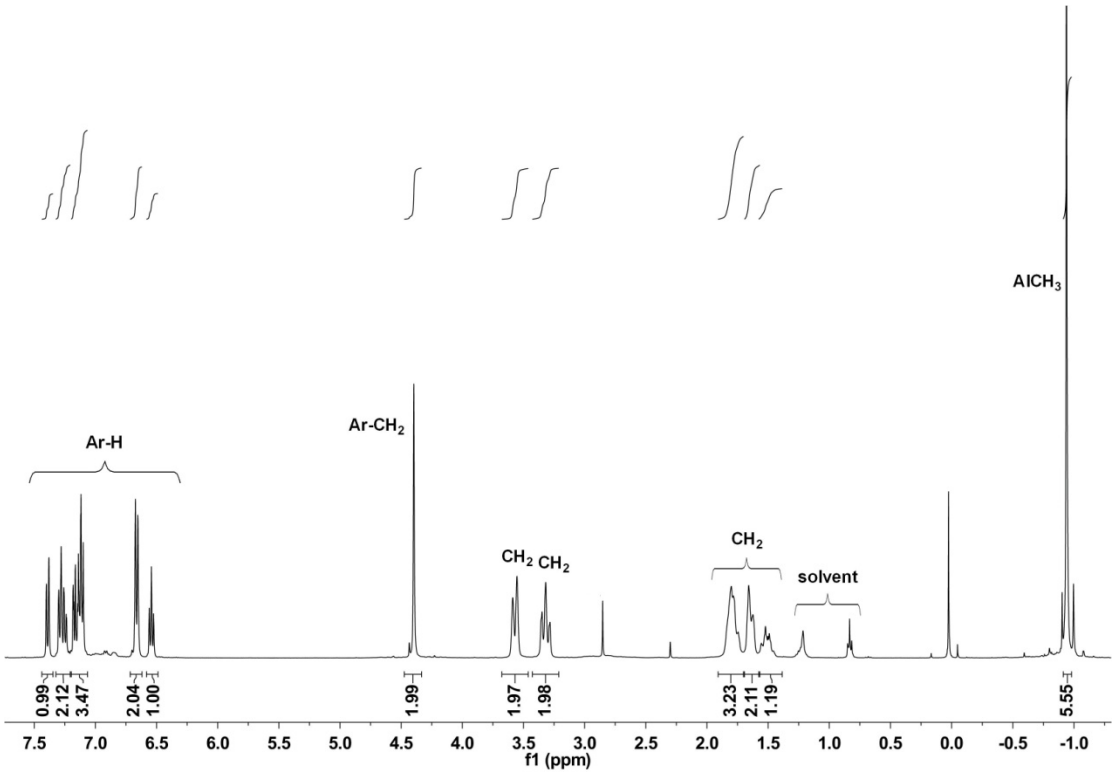

Figure S25. The ^{1}H NMR spectrum of complex **3a** ($CDCl_3$, 400 MHz).

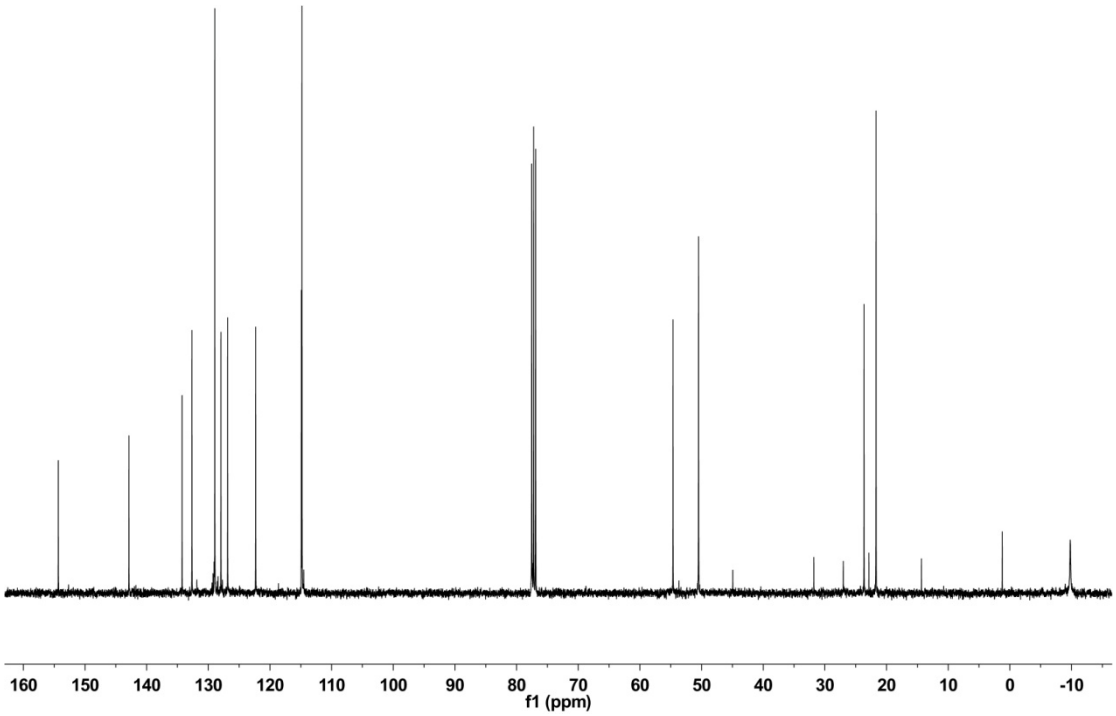

Figure S26. The ^{13}C NMR spectrum of complex **3a** ($CDCl_3$, 100 MHz).

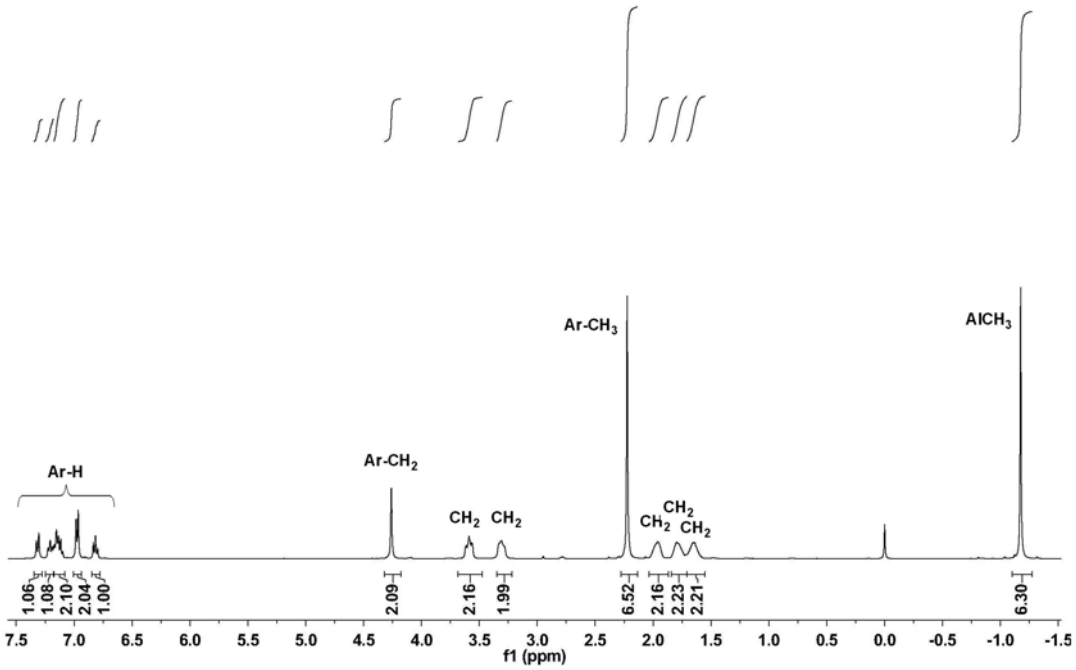

Figure S27. The ^{1}H NMR spectrum of complex **3b** ($CDCl_3$, 400 MHz).

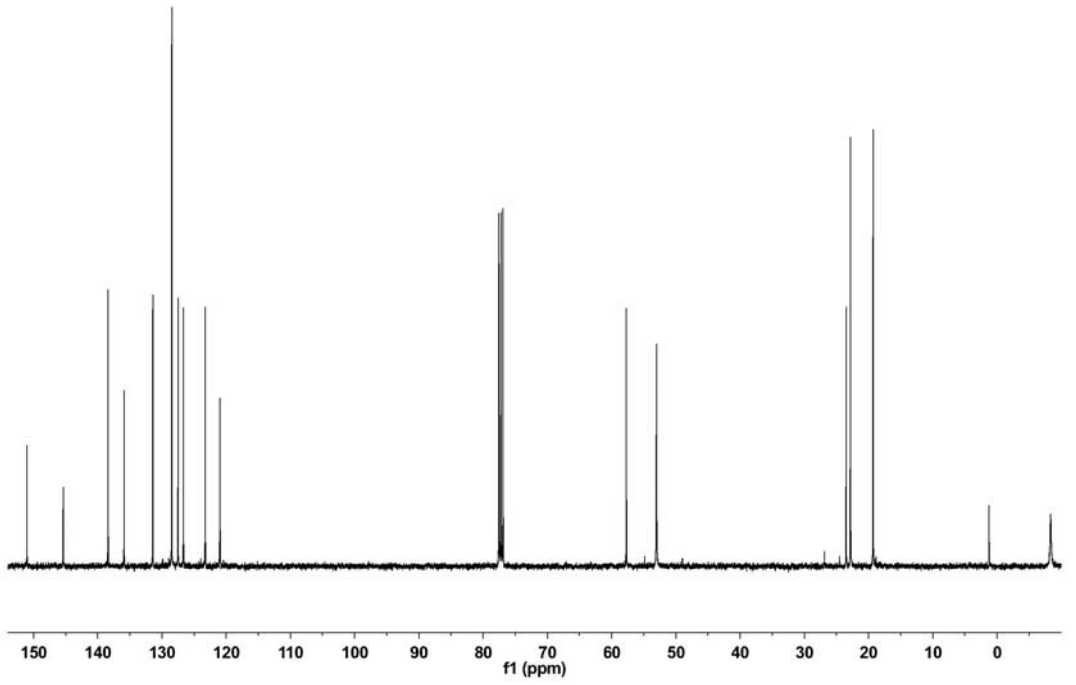

Figure S28. The ^{13}C NMR spectrum of complex **3b** ($CDCl_3$, 100 MHz).

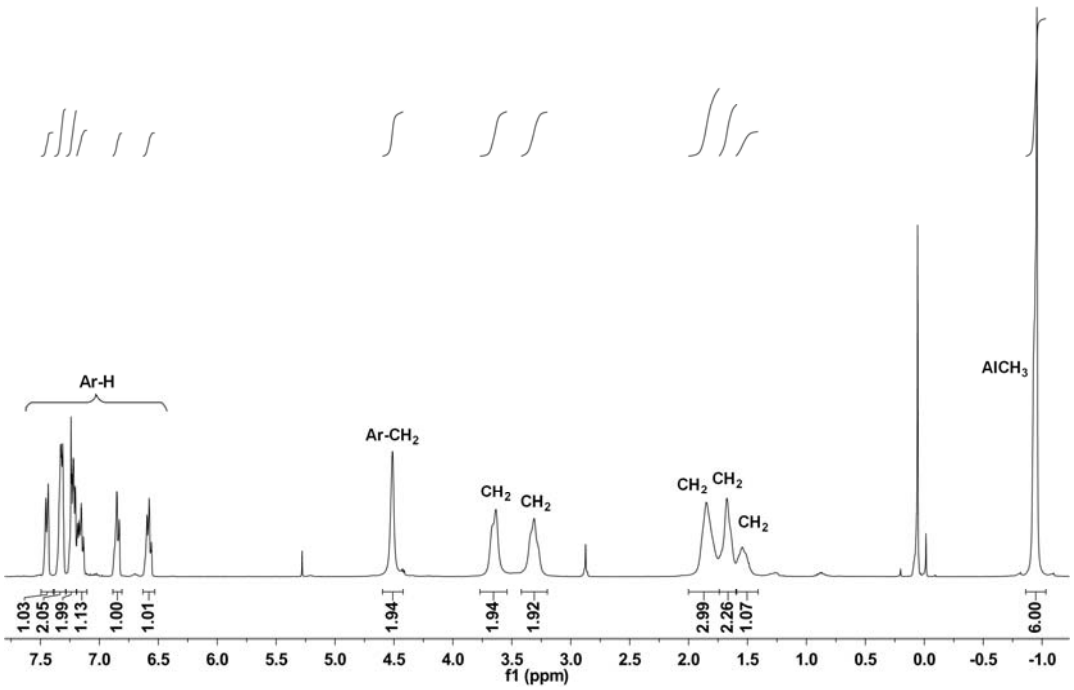

Figure S29. The ^{1}H NMR spectrum of complex **3c** ($CDCl_3$, 400 MHz).

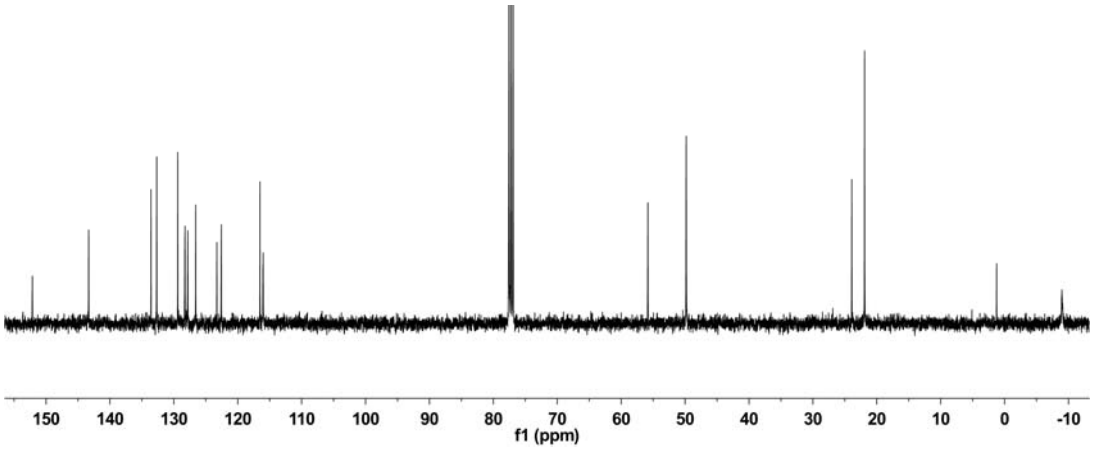

Figure S30. The ^{13}C NMR spectrum of complex **3c** ($CDCl_3$, 100 MHz).

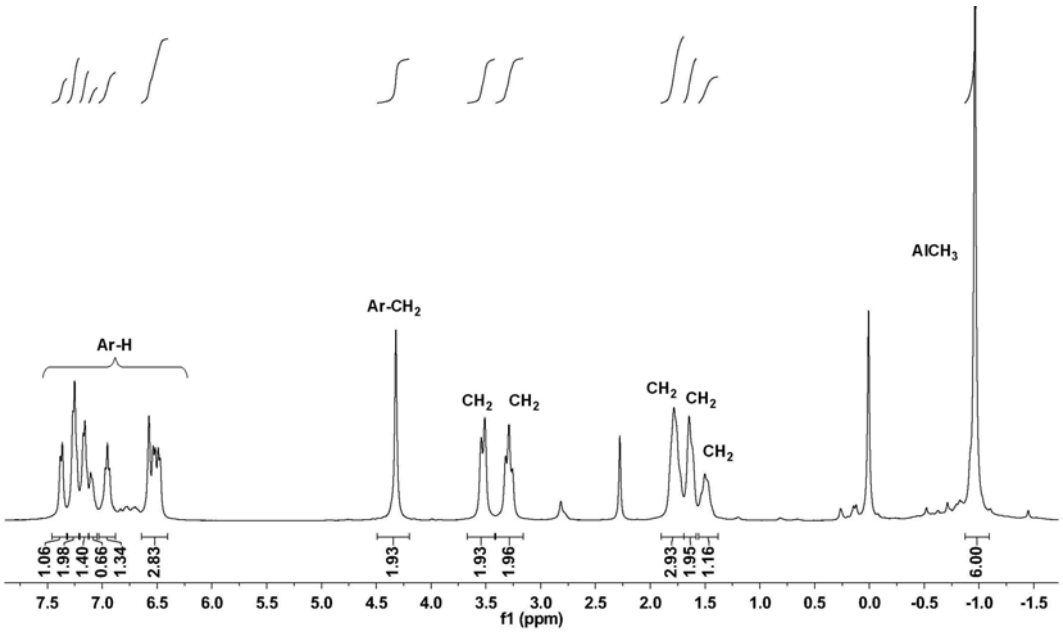

Figure S31. The ^{1}H NMR spectrum of complex **3d** ($CDCl_3$, 400 MHz).

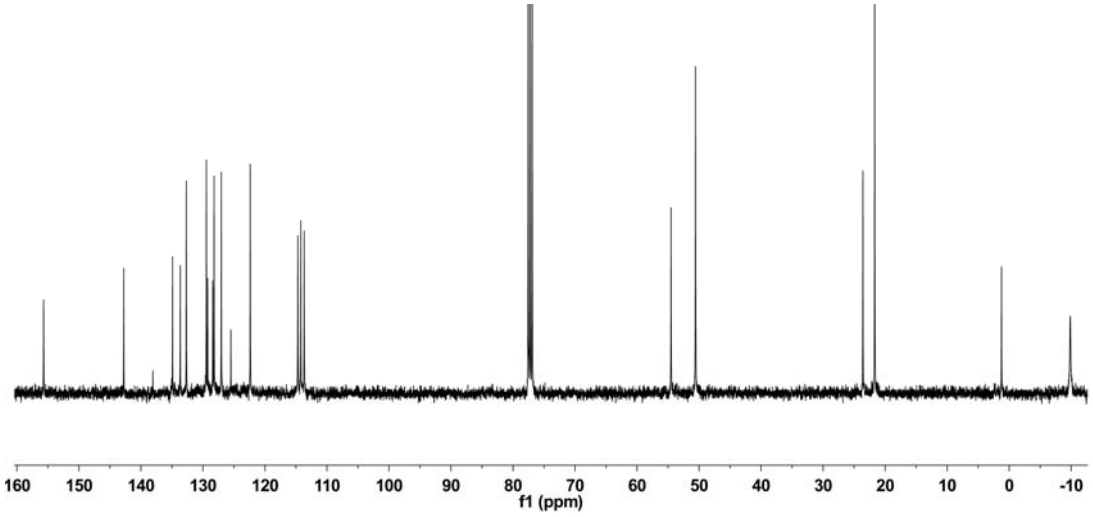

Figure S32. The ^{13}C NMR spectrum of complex **3d** ($CDCl_3$, 100 MHz).

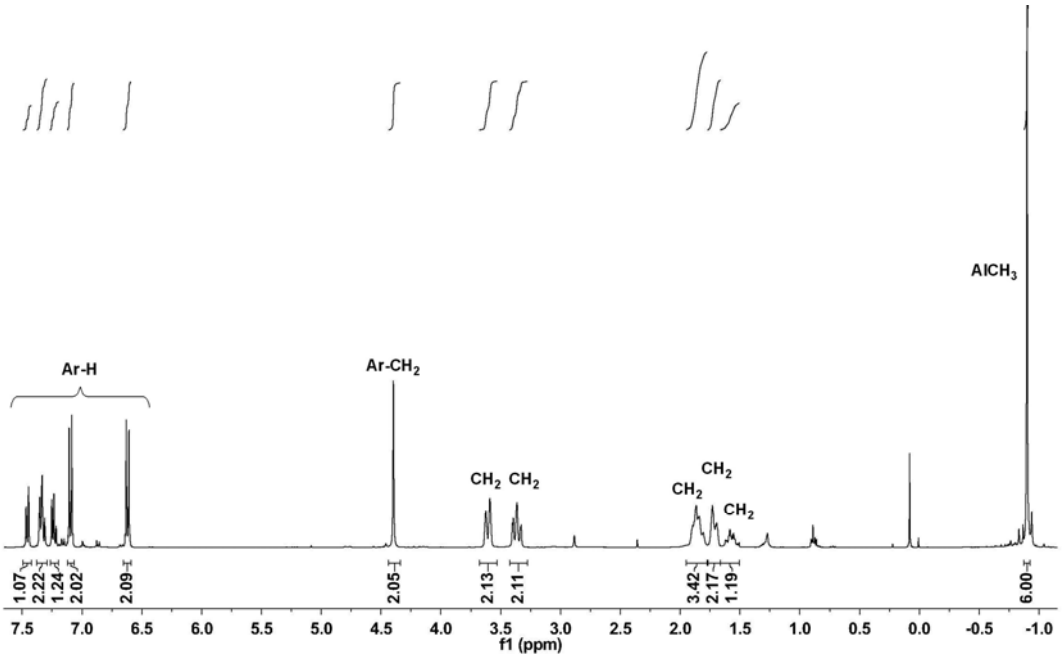

Figure S33. The ^{1}H NMR spectrum of complex **3e** ($CDCl_3$, 400 MHz)

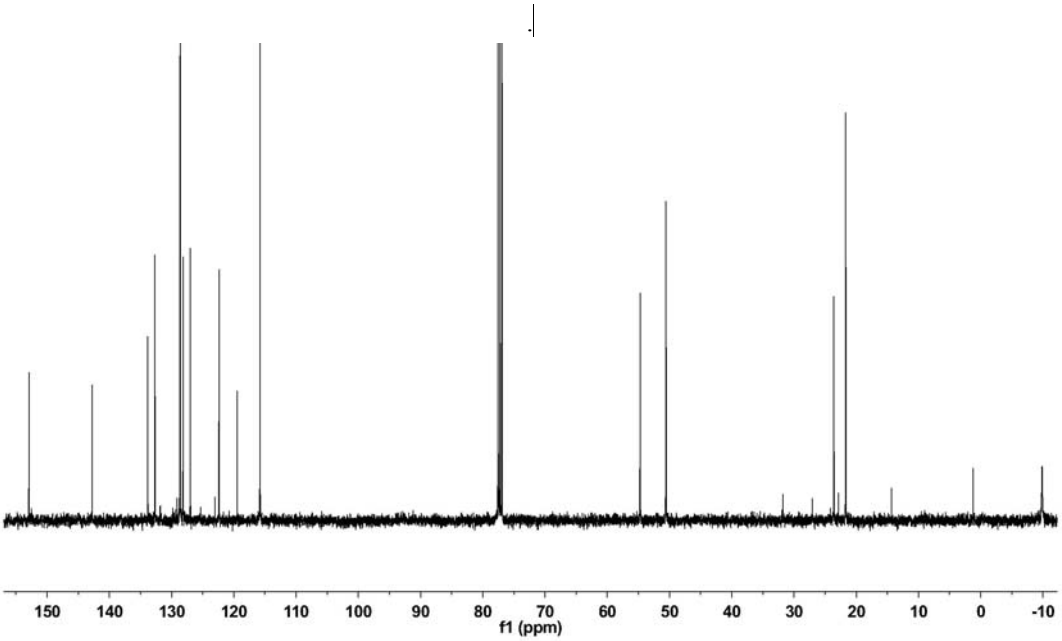

Figure S34. The ^{13}C NMR spectrum of complex **3e** ($CDCl_3$, 100 MHz).

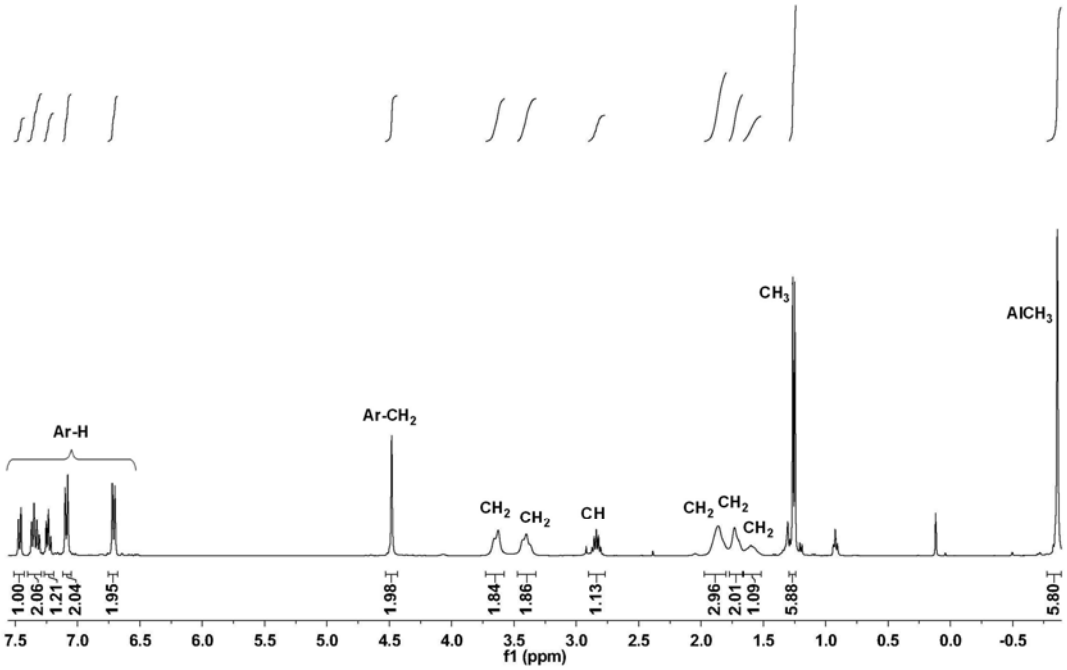

Figure S35. The ^{1}H NMR spectrum of complex **3f** ($CDCl_3$, 400 MHz).

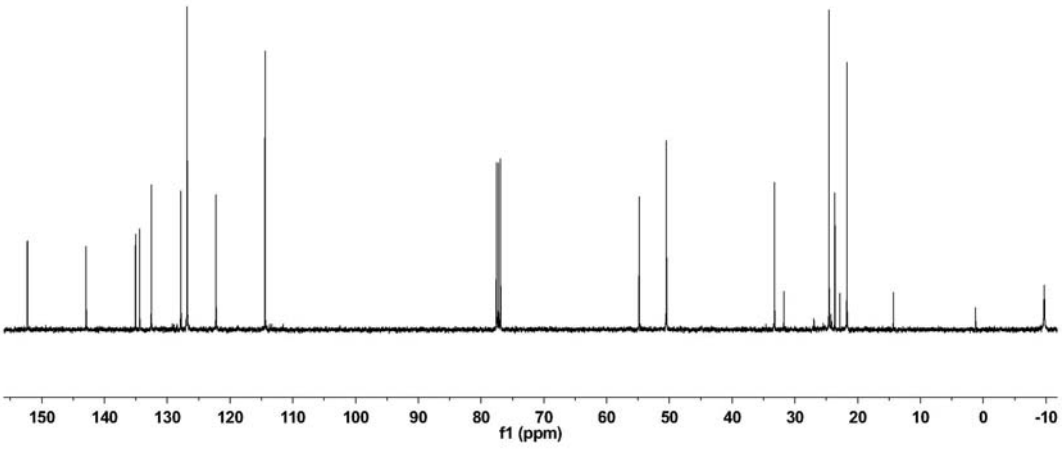

Figure S36. The ^{13}C NMR spectrum of complex **3f** ($CDCl_3$, 100 MHz).

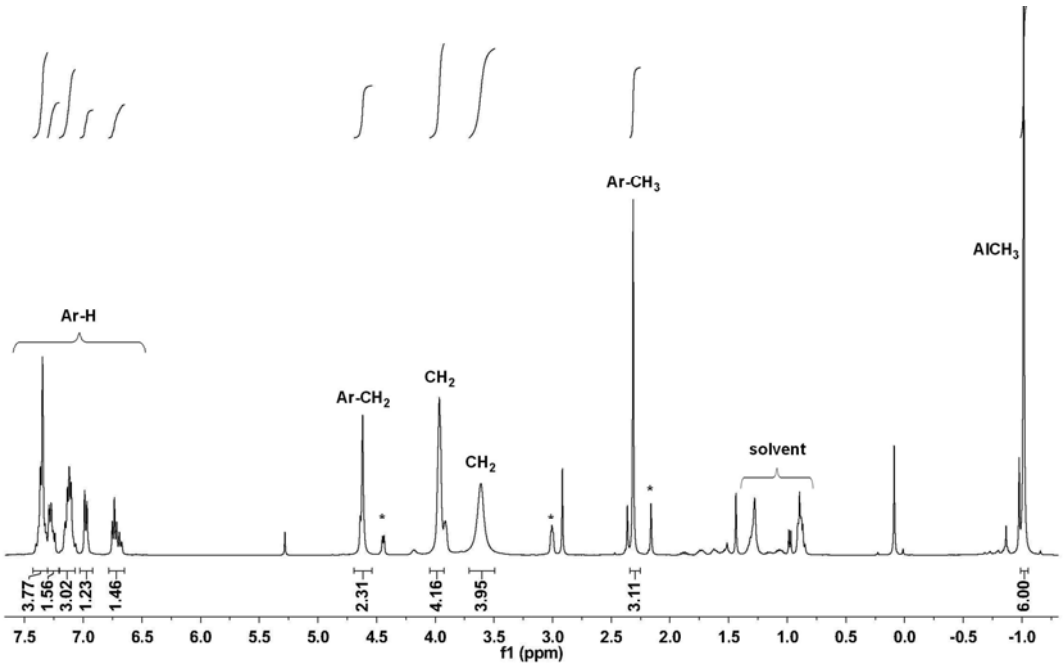

Figure S37. ^{1}H NMR spectrum of complex **3g** ($CDCl_3$, 400 MHz). * The free ligand formed during the course of measurement.

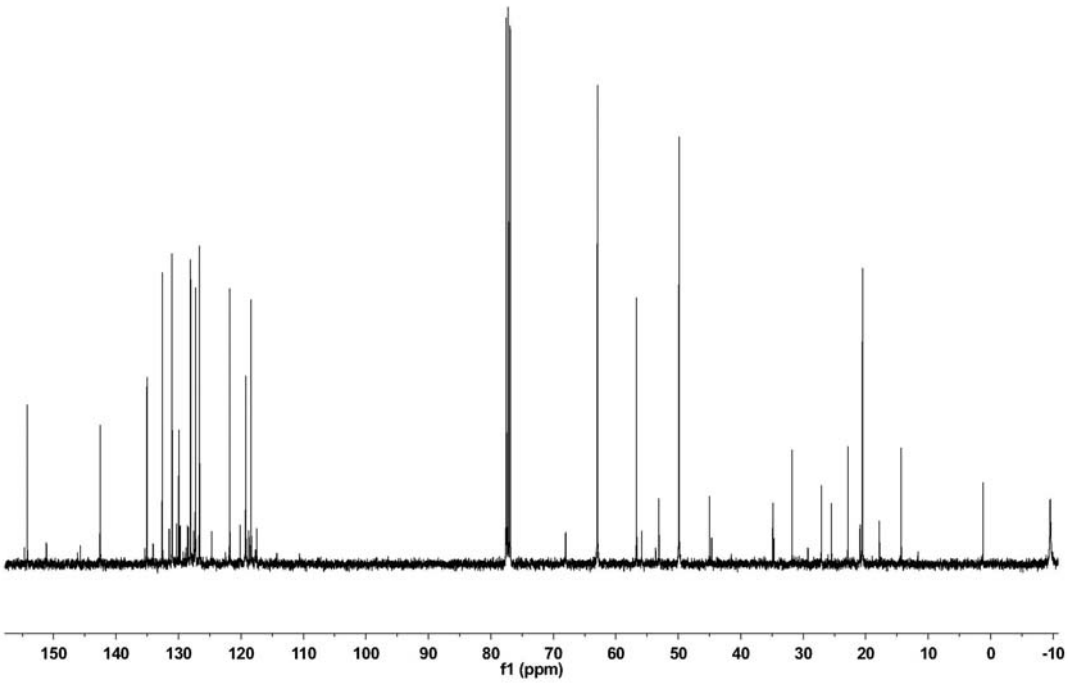

Figure S38. The ^{13}C NMR spectrum of complex **3g** ($CDCl_3$, 100 MHz).

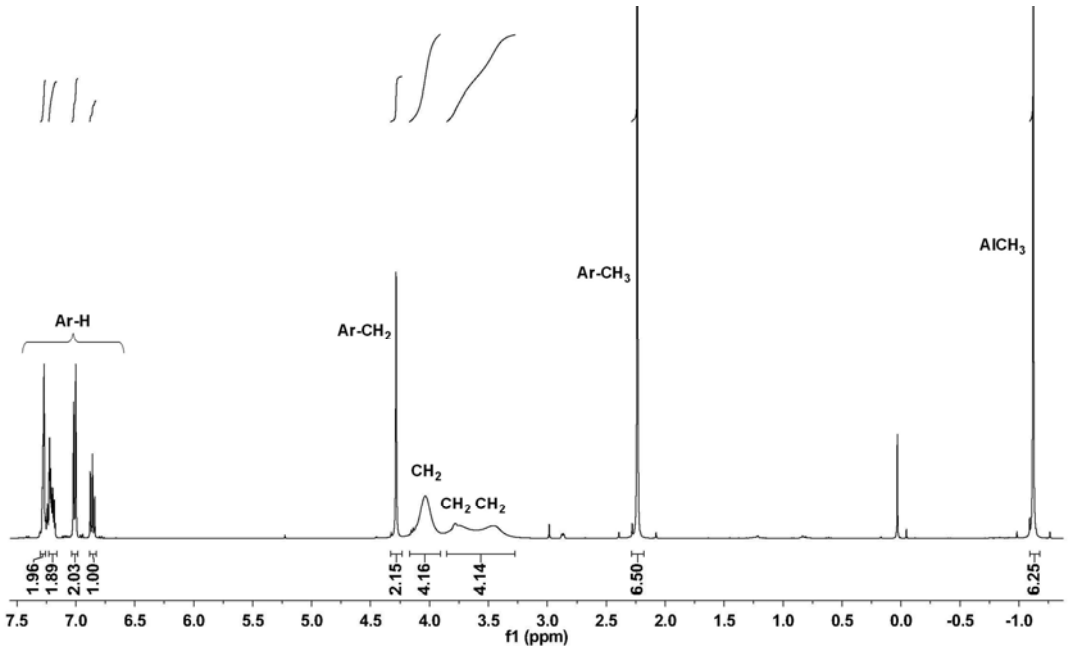

Figure S39. The ^{1}H NMR spectrum of complex **3h** ($CDCl_3$, 400 MHz).

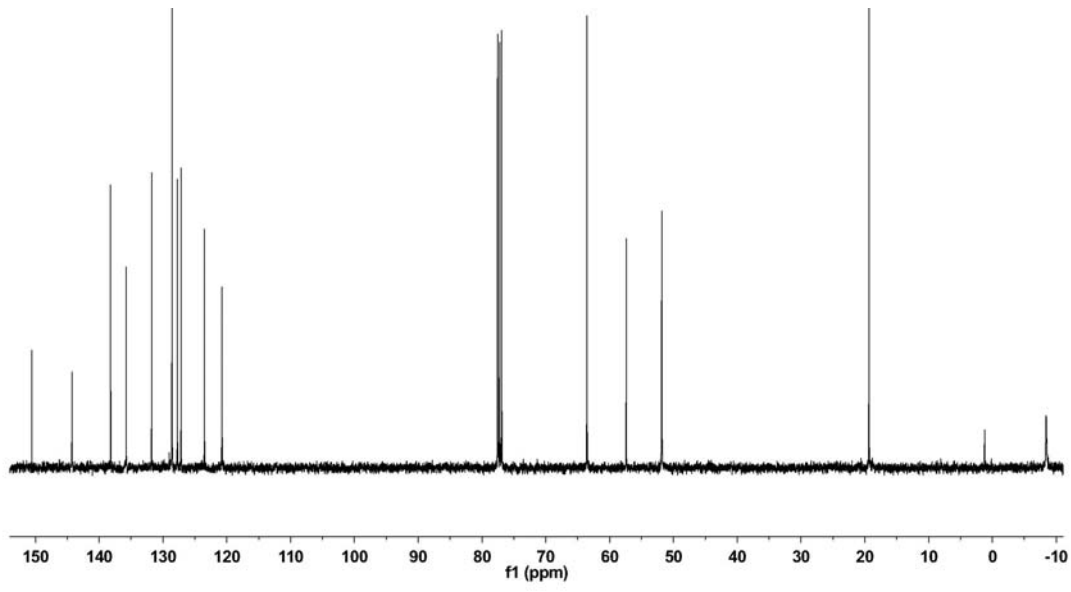

Figure S40. The ^{13}C NMR spectrum of complex **3h** ($CDCl_3$, 100 MHz).

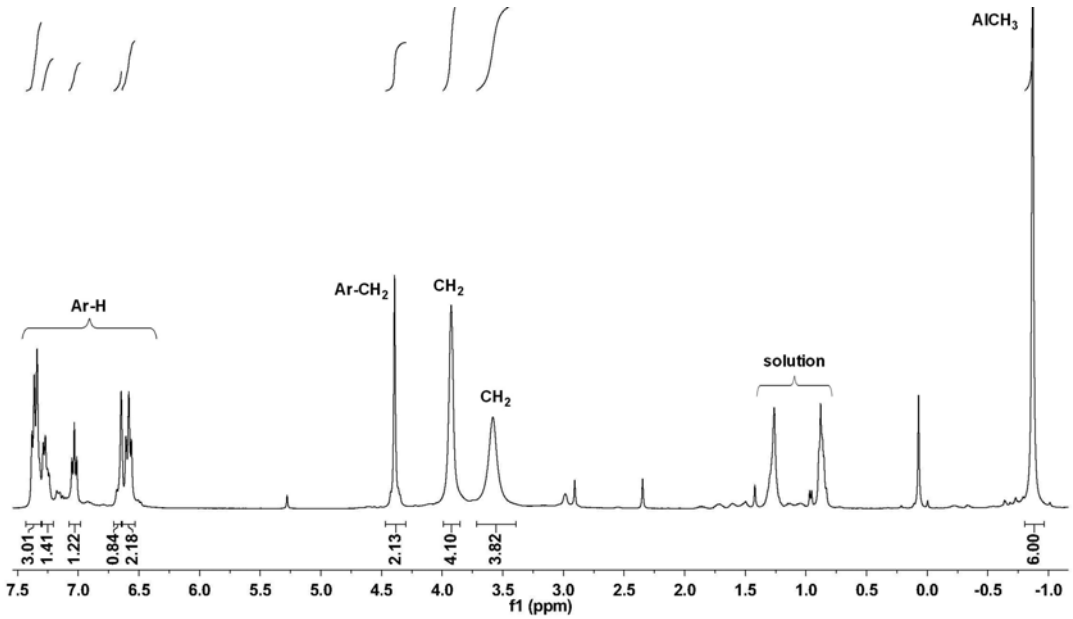

Figure S41. The ^{1}H NMR spectrum of complex **3i** ($CDCl_3$, 400 MHz).

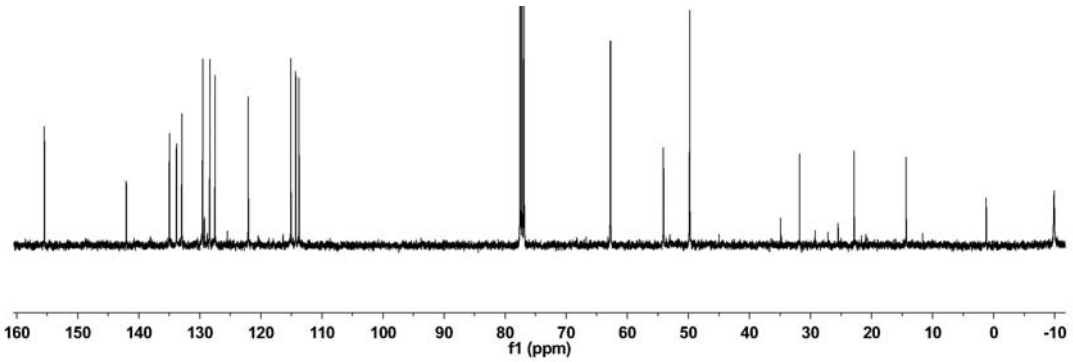

Figure S42. The ^{13}C NMR spectrum of complex **3i** ($CDCl_3$, 100 MHz).

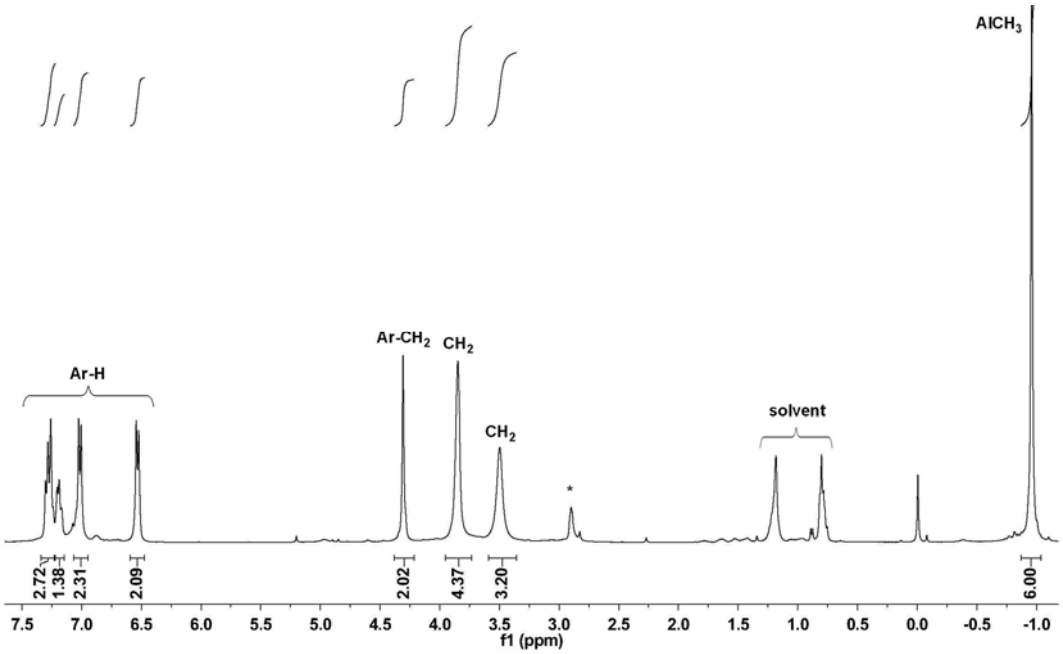

Figure S43. The ^{1}H NMR spectrum of complex **3j** ($CDCl_3$, 400 MHz). * The free ligand formed during the course of measurement.

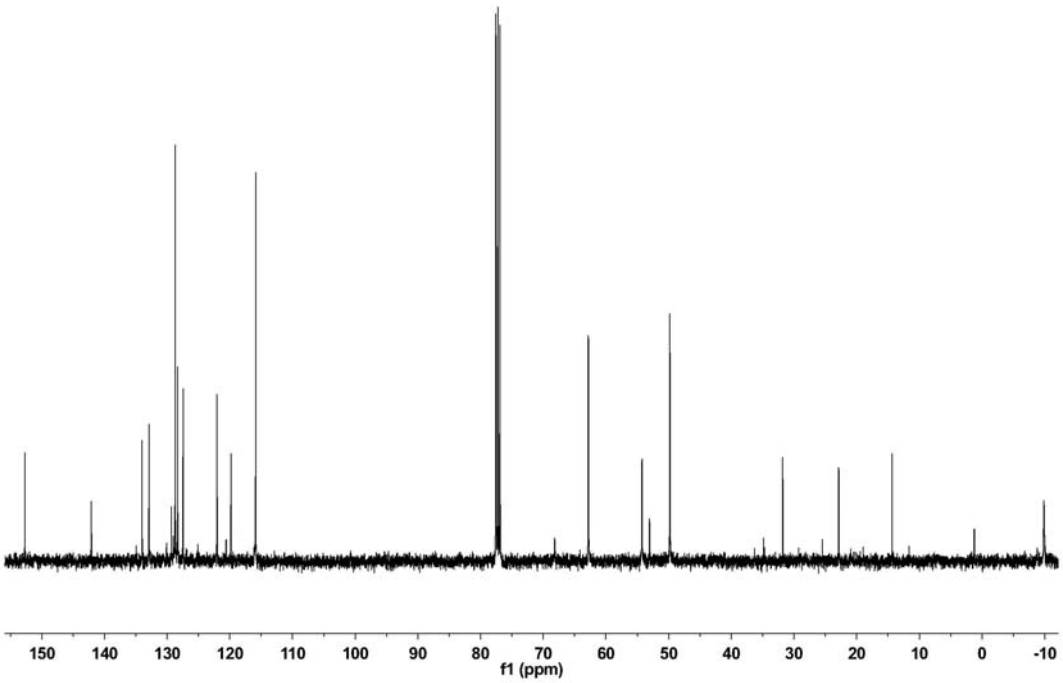

Figure S44. The ^{13}C NMR spectrum of complex **3j** ($CDCl_3$, 100 MHz).

3. Representative GPC traces of the obtained PLA samples

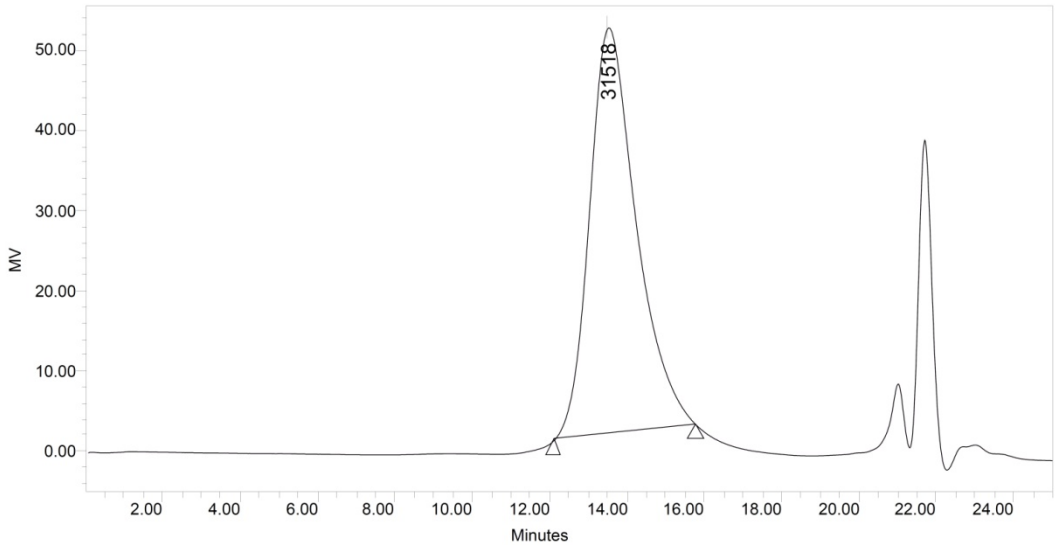

Figure S45. GPC trace of isolated PLA prepared via ROP of *rac*-lactide by **3f**. Conditions: 100 equiv. of *rac*-lactide, 65 °C, toluene, 91% conversion, 18 h.

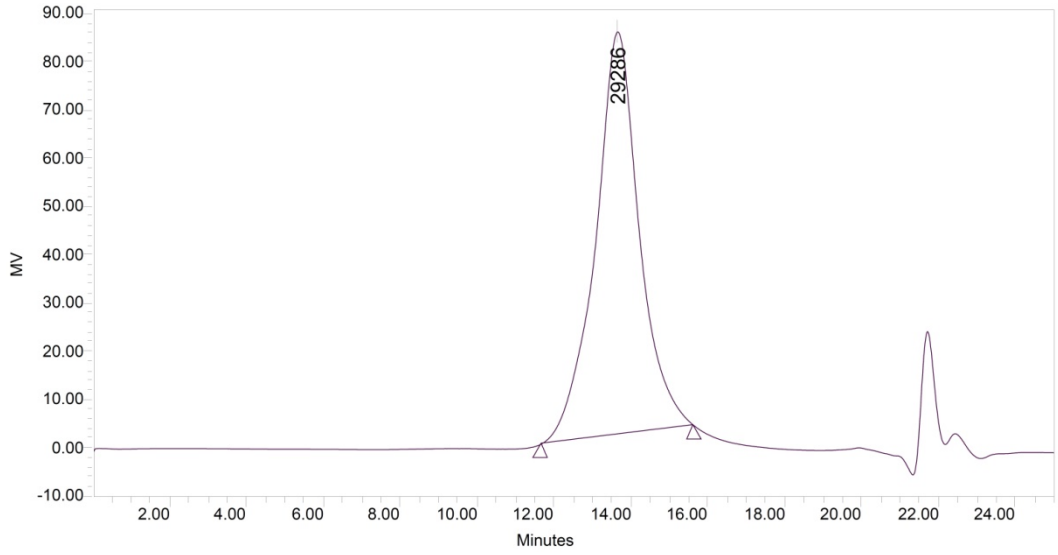

Figure S46. GPC trace of isolated PLA prepared via ROP of *rac*-lactide by **3c**. Conditions: 100 equiv. of *rac*-lactide, 65 °C, toluene, 92% conversion, 20 h.

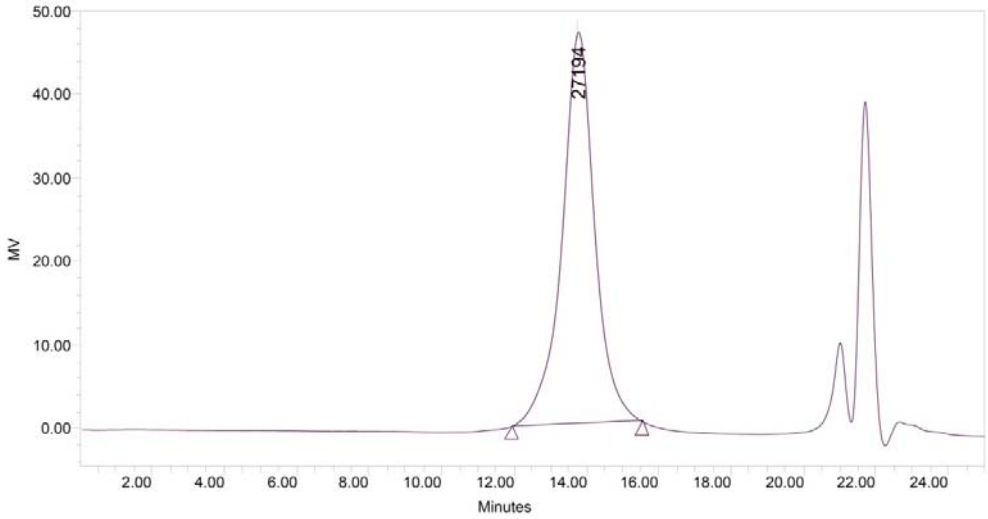

Figure S47. GPC trace of isolated PLA prepared via ROP of *rac*-lactide by **3e**. Conditions: 100 equiv. of *rac*-lactide, 65 °C, toluene, 88% conversion, 15 h.

4. NMR studies of *rac*-LA oligomerization initiated by complex 3f

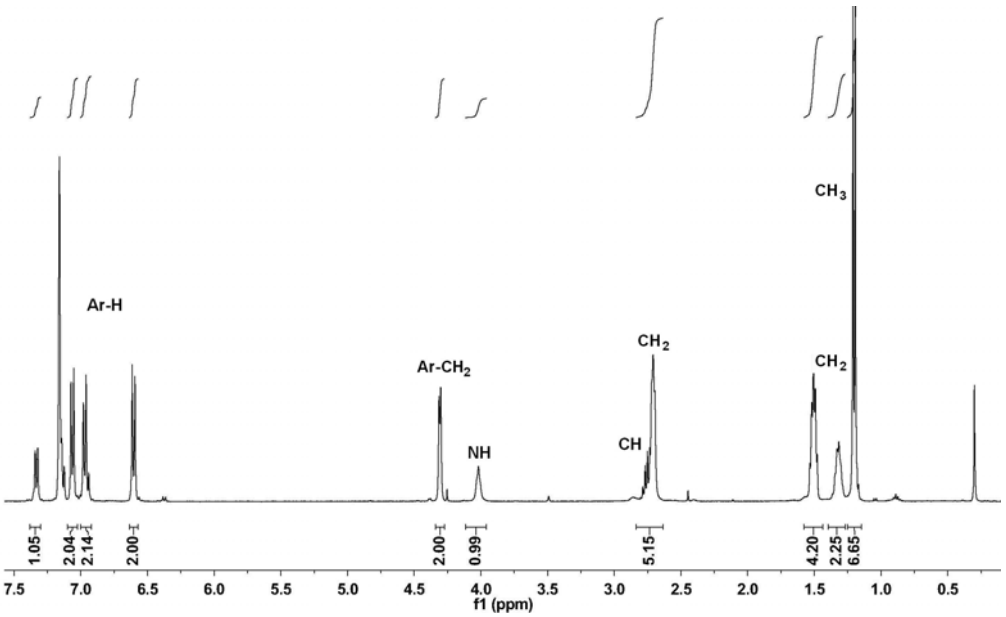

Figure S48. The ^{1}H NMR spetrum of the ligand **1f** in C_6D_6 (400 MHz).

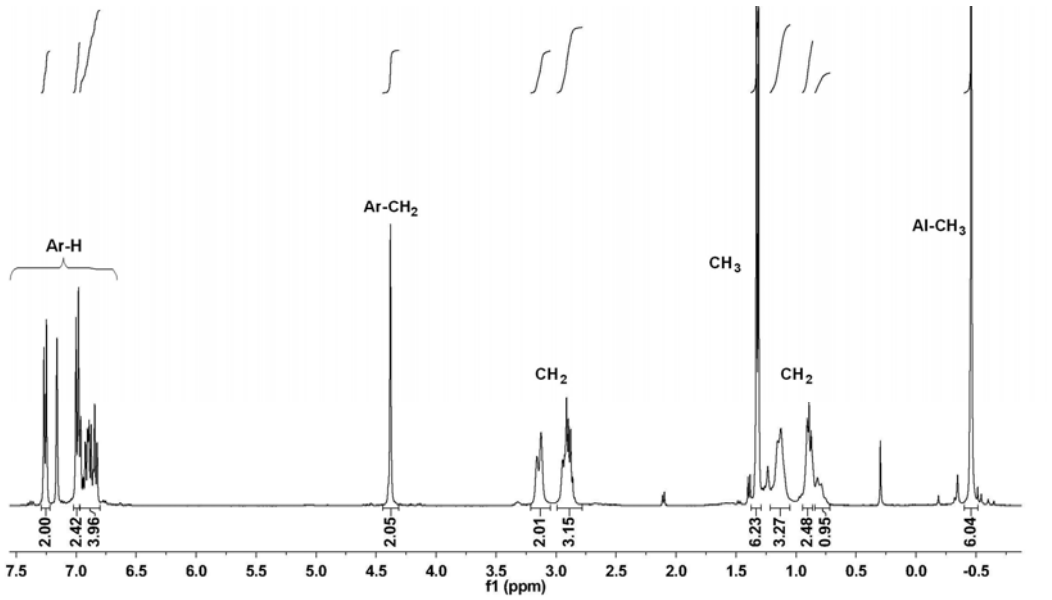

Figure S49. The ^{1}H NMR spetrum of the complex **3f** in C_6D_6 (400 MHz).

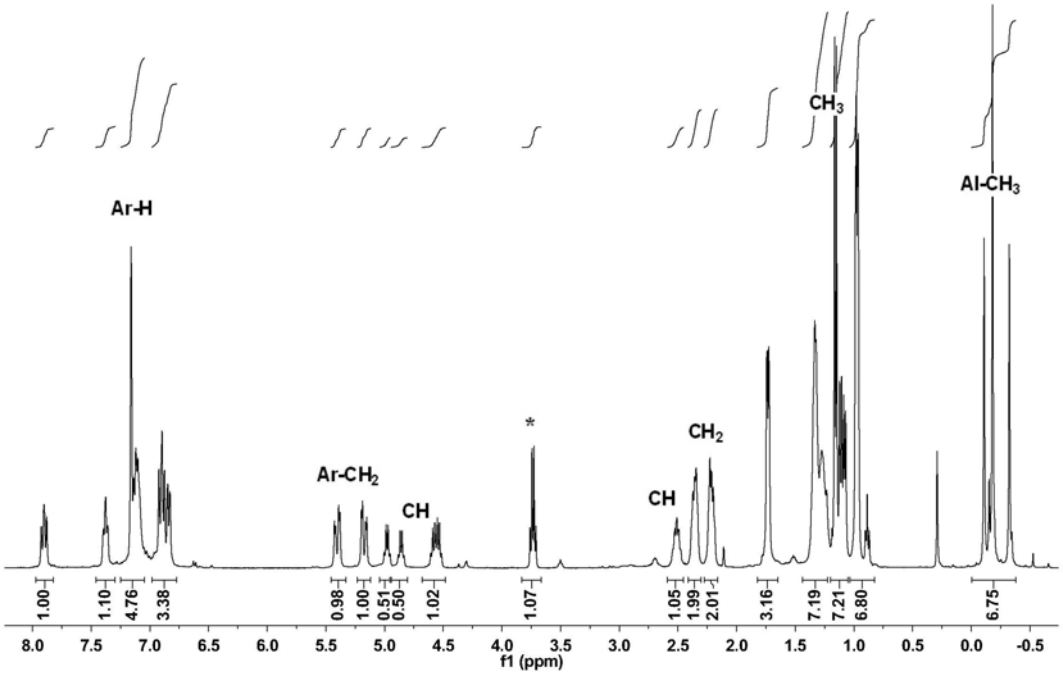

Figure S50. The ^{1}H NMR spetrum of the mixture of the complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1 : 1.5) at room temperature (C_6D_6, 400 MHz; * free lactide monomer).

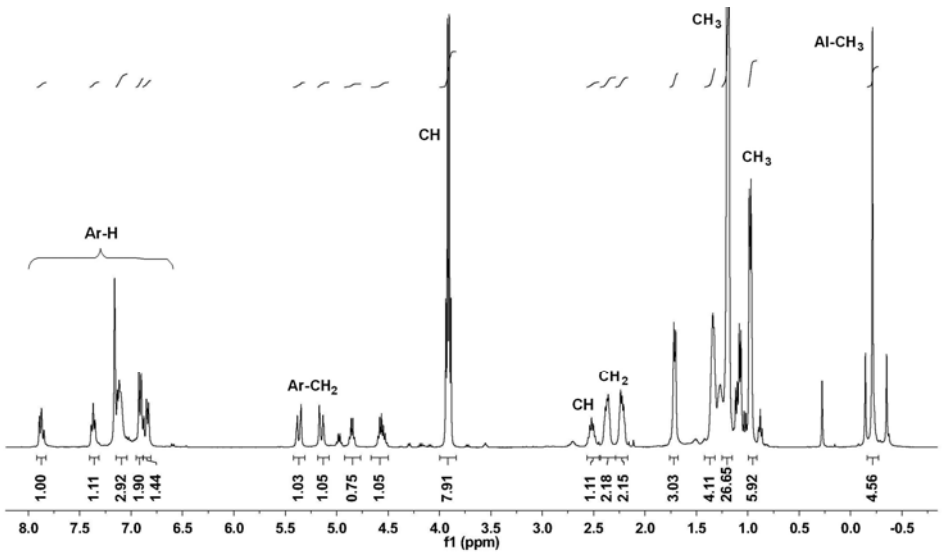

Figure S51. The ^{1}H NMR spetrum of the mixture of the complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1:5) at room temperature (C_6D_6, 400 MHz).

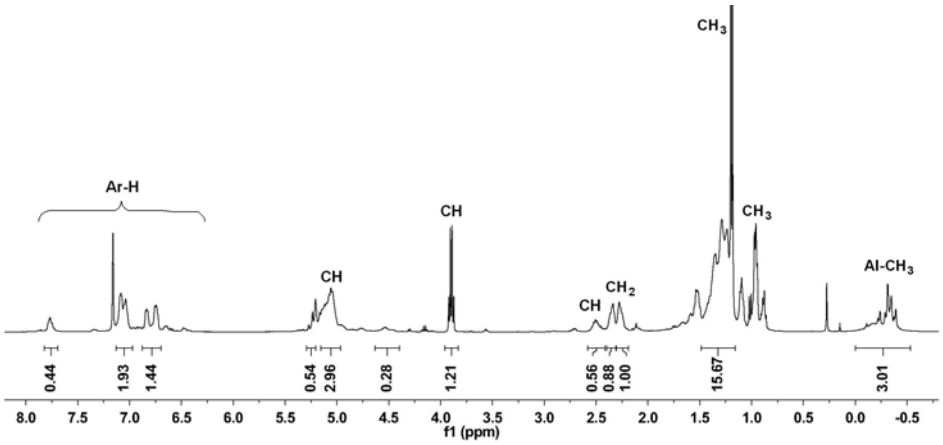

Figure S52. The ^{1}H NMR spetrum of the mixture of the complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1:5) at 65 ^{o}C after 50 min (C_6D_6, 400 MHz).

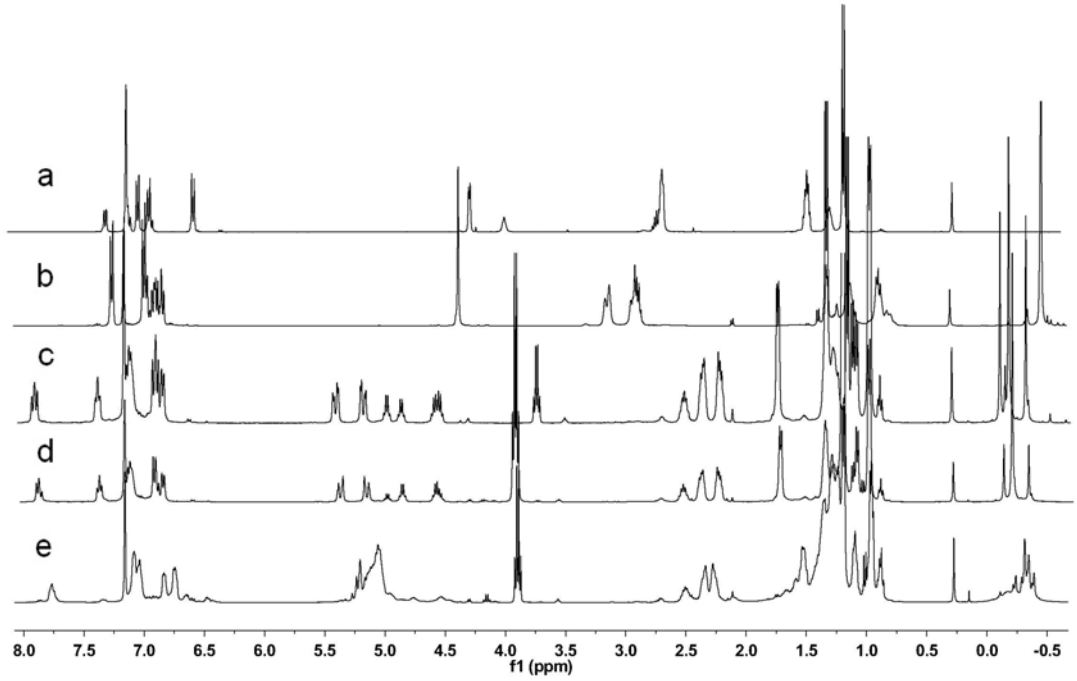

Figure S53. The comparison of ^{1}H NMR spetra of **(a)** ligand **1f**; **(b)** complex **3f**; **(c)** the reaction mixture of complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1:1.5) at room temperature; (**d**): the reaction mixture of complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1:5) at room temperature; (e) the reaction mixture of the complex **3f** and *rac*-LA ([**3f**]: [*rac*-LA] = 1:5) at 65 ^{o}C after 50 min (C_6D_6, 400 MHz).