Electronic Supplementary Material (ESI) for RSC Advances

Pillar[5]arene-based phosphine oxides: novel ionophores for solvent extraction separation of f-block elements from acidic media

Yuyu Fang, Lei Wu, Jiali Liao, Long Chen, Yuanyou Yang, Ning Liu, Lutao He, Shuliang Zou, Wen Feng,* Lihua Yuan*

Institute of Nuclear Science and Technology, Key Laboratory for Radiation Physics and Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China. Fax: +86-28-85418755; Tel: +86-28-85416996; E-mail: lhyuan@scu.edu.cn; wfeng9510@scu.edu.cn.

Supporting Information

Contents

1. General Information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II- 400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). Chemical shifts are reported in δ values in ppm using tetramethlysilane (TMS) and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = double doublet and m = multiplet. High resolution mass (HRMS) data were obtained by WATERS Q-TOF Premier. Solvents for extraction and chromatography were reagent grade. CH_2Cl_2 was distilled from CaH_2. $CDCl_3$ were from Cambridge Isotope Laboratories (CIL). UV- spectra were measured by SHIMADZU UV-2450. Inductive coupled plasma atomic emission spectroscopy (ICP-AES) measurements were made by Thermo Elemental, U.S.A.

2. NMR and ESI-HRMS Spectra

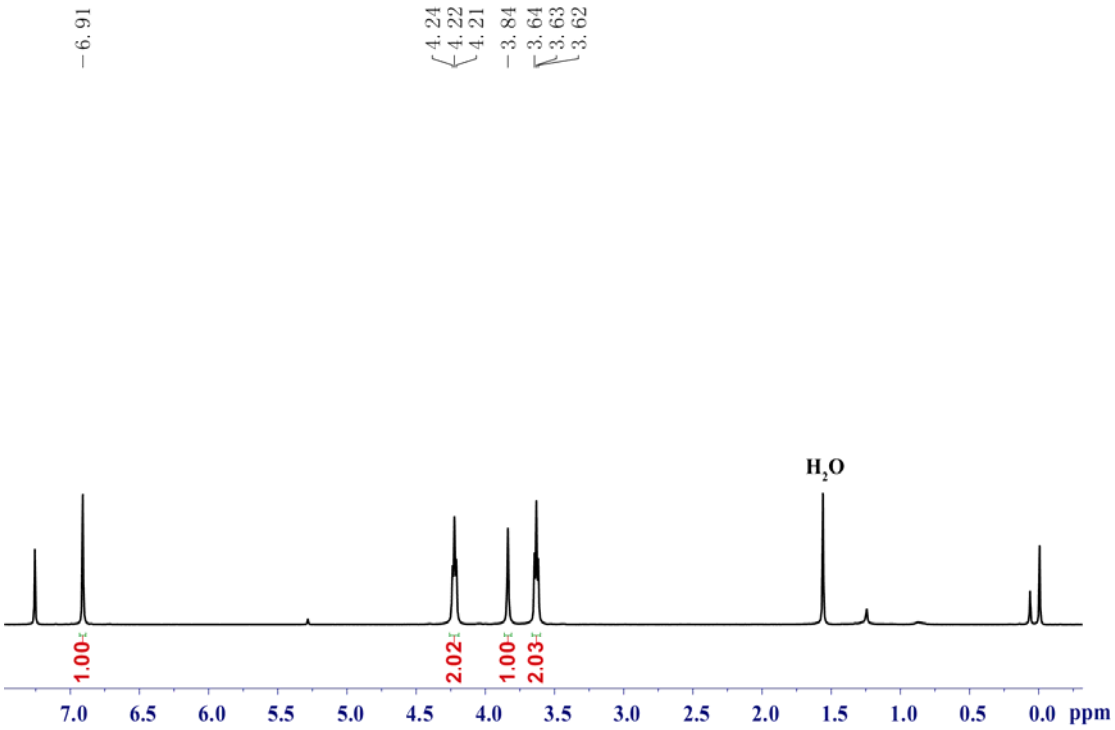

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**.

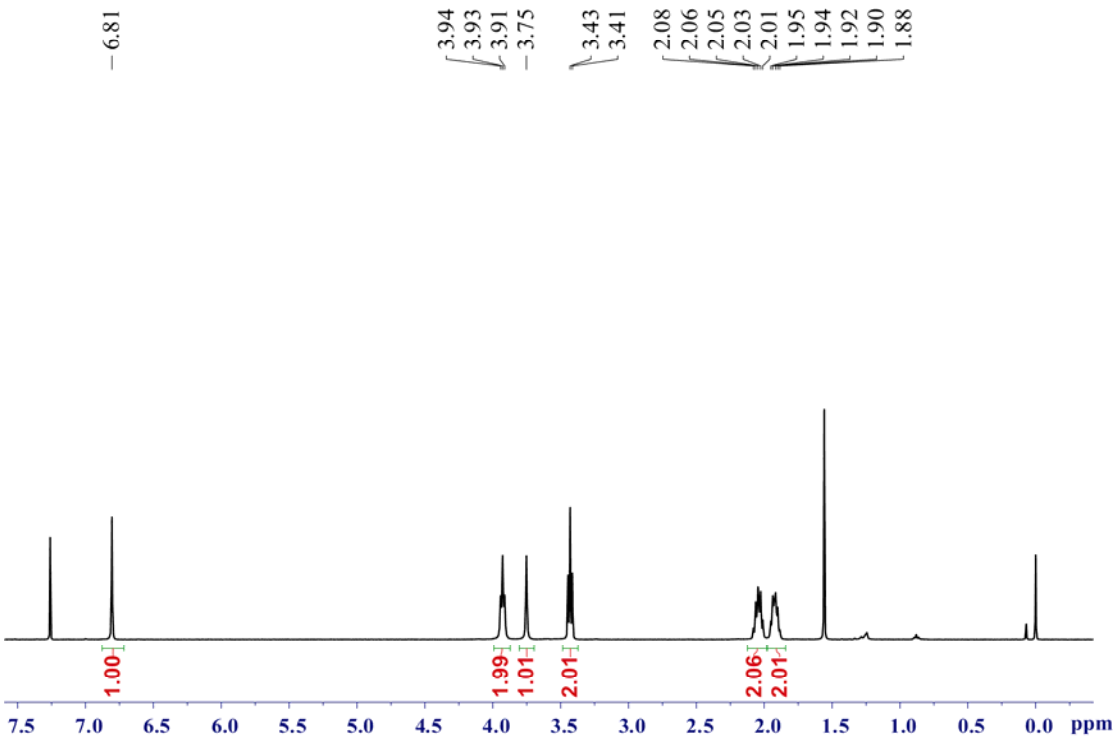

Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**.

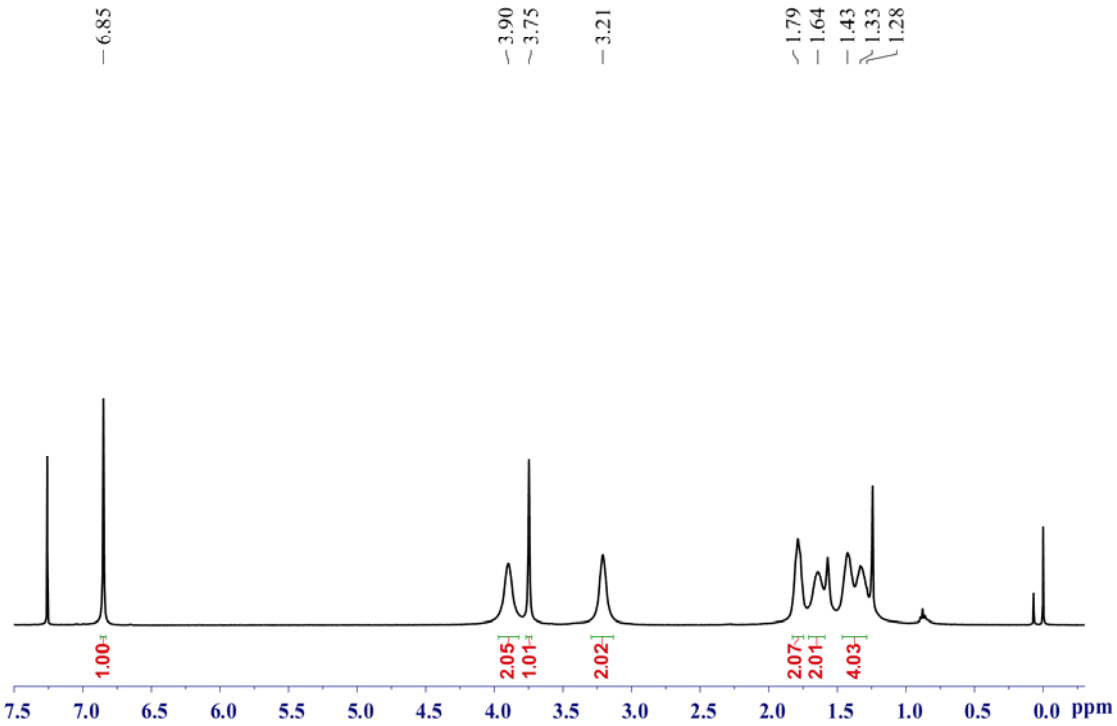

Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c**.

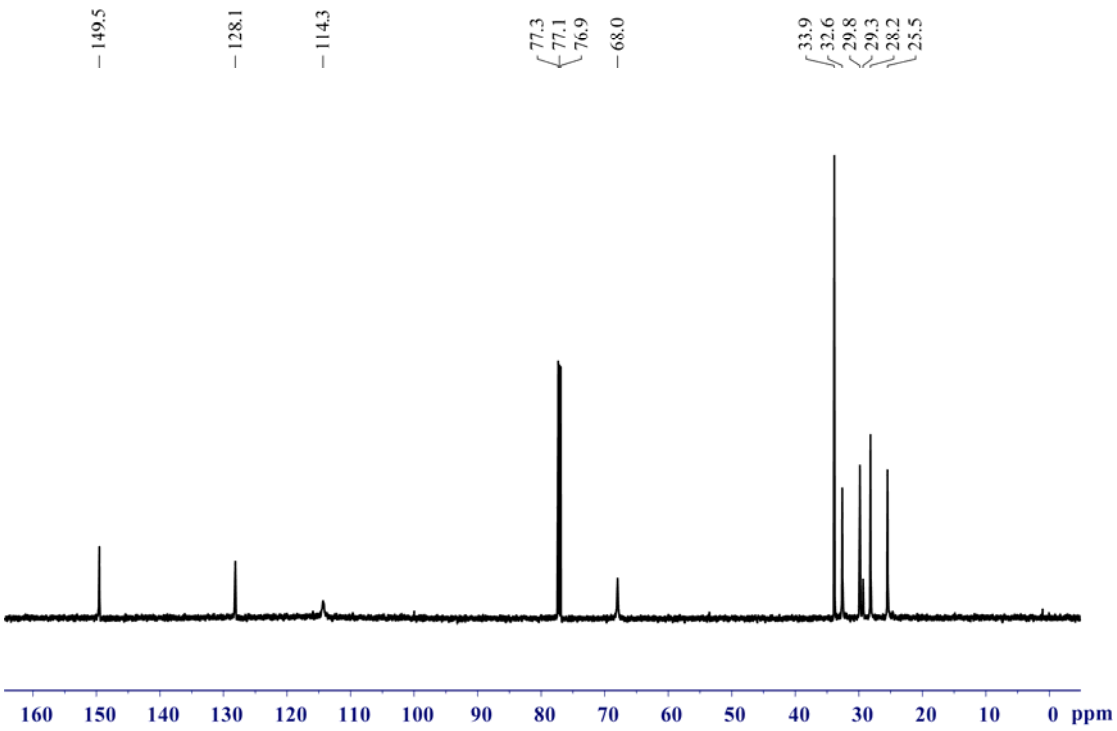

Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4c**.

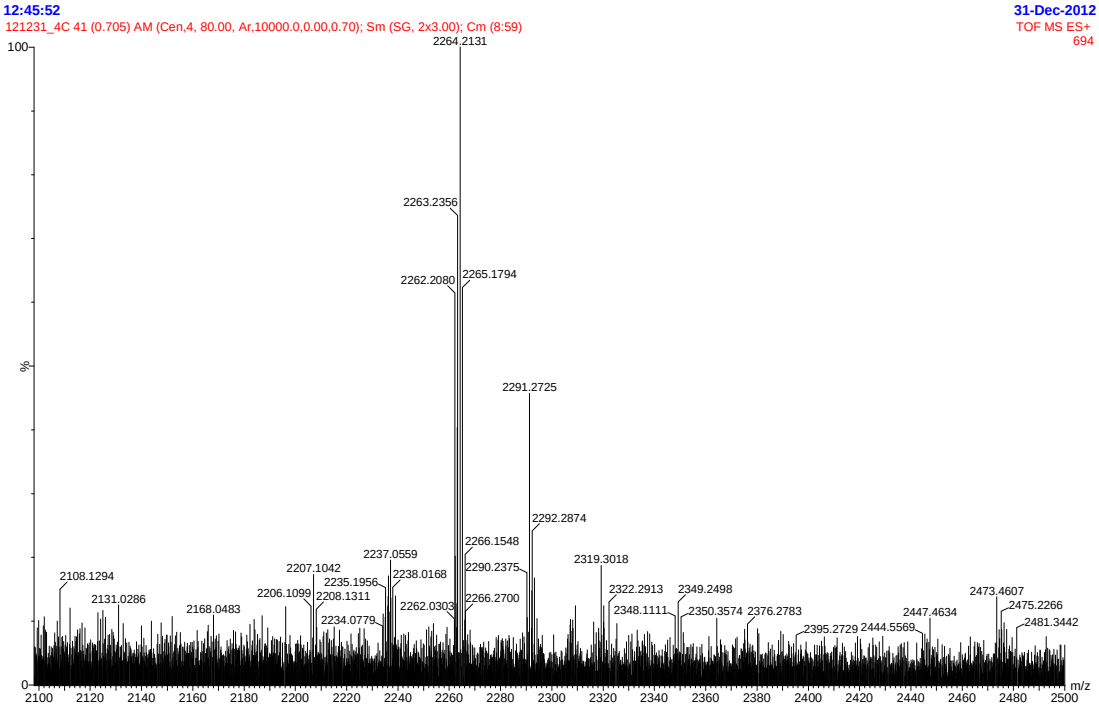

Figure S5. ESI-HRMS spectrum of **4c**.

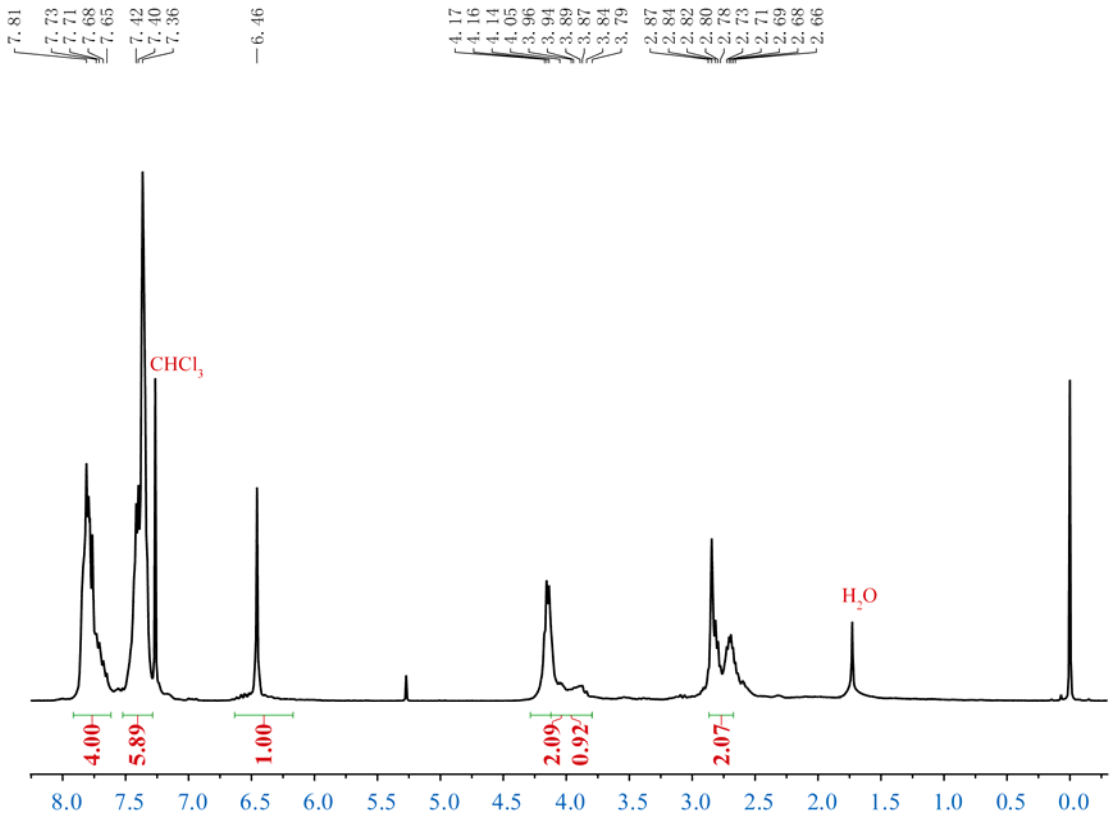

Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1a**.

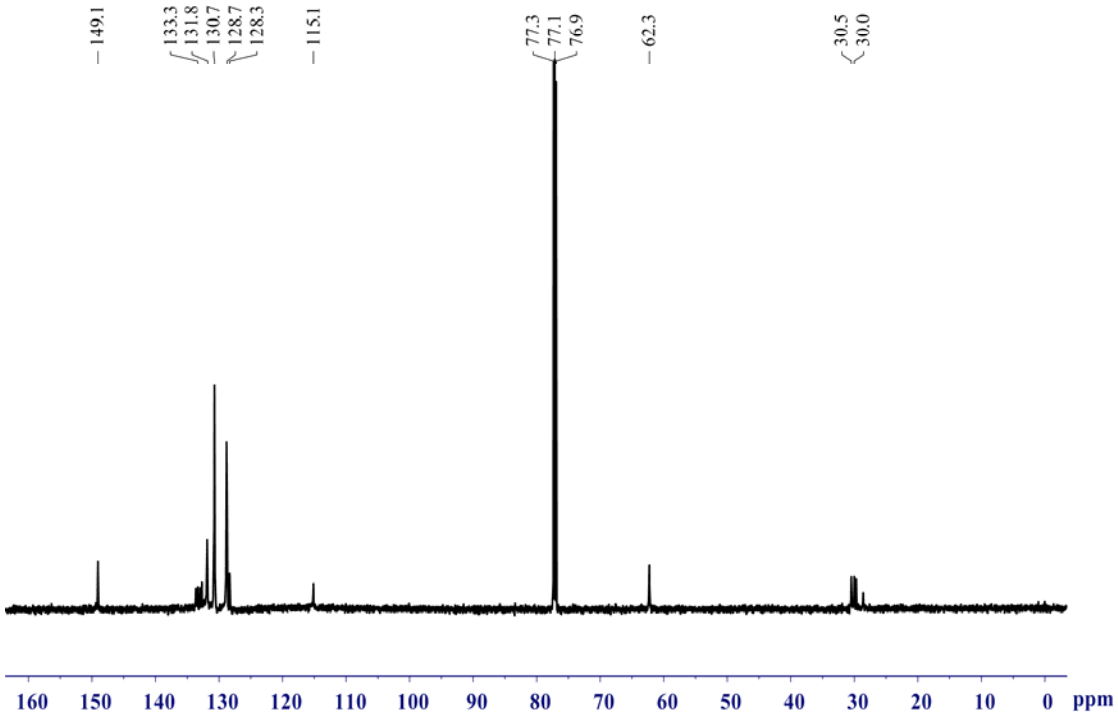

Figure S7. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1a**.

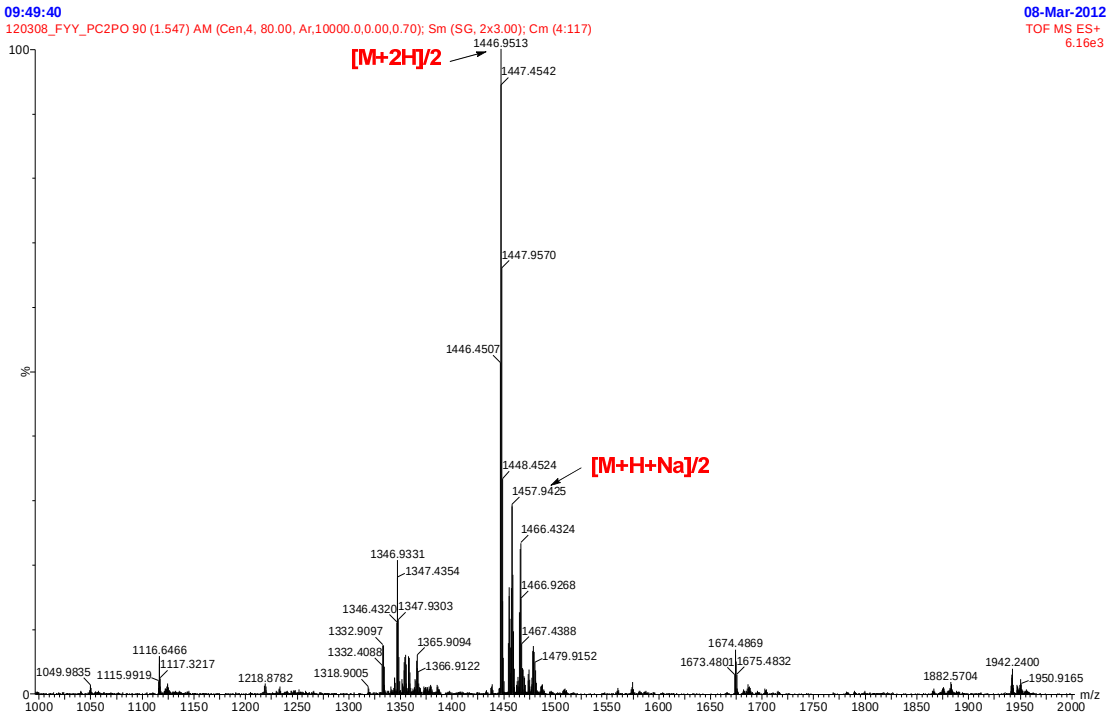

Figure S8. ESI-HRMS spectrum of **1a**.

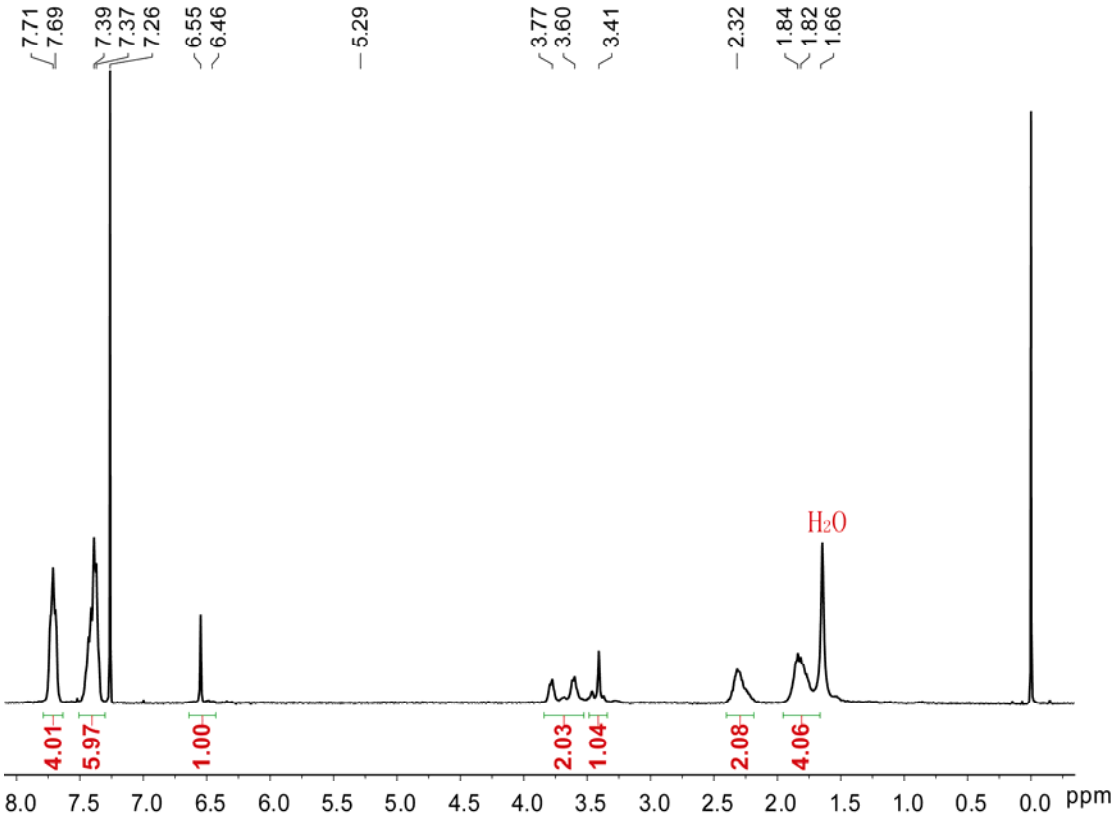

Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1b**.

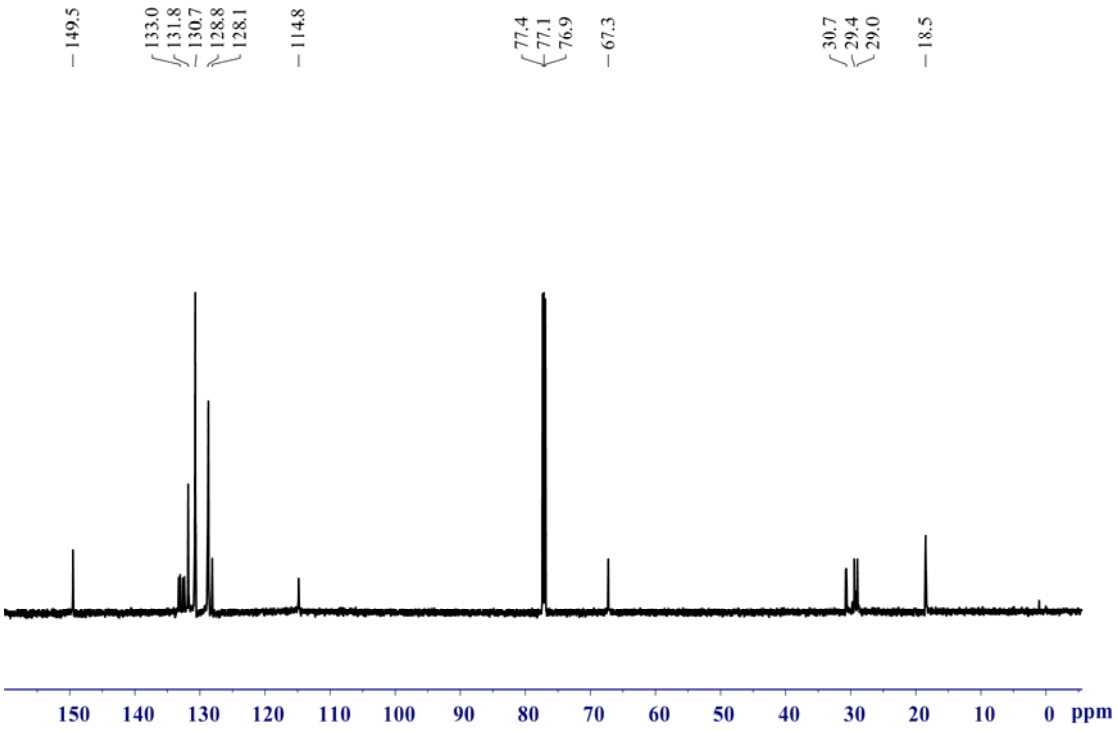

Figure 10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1b**.

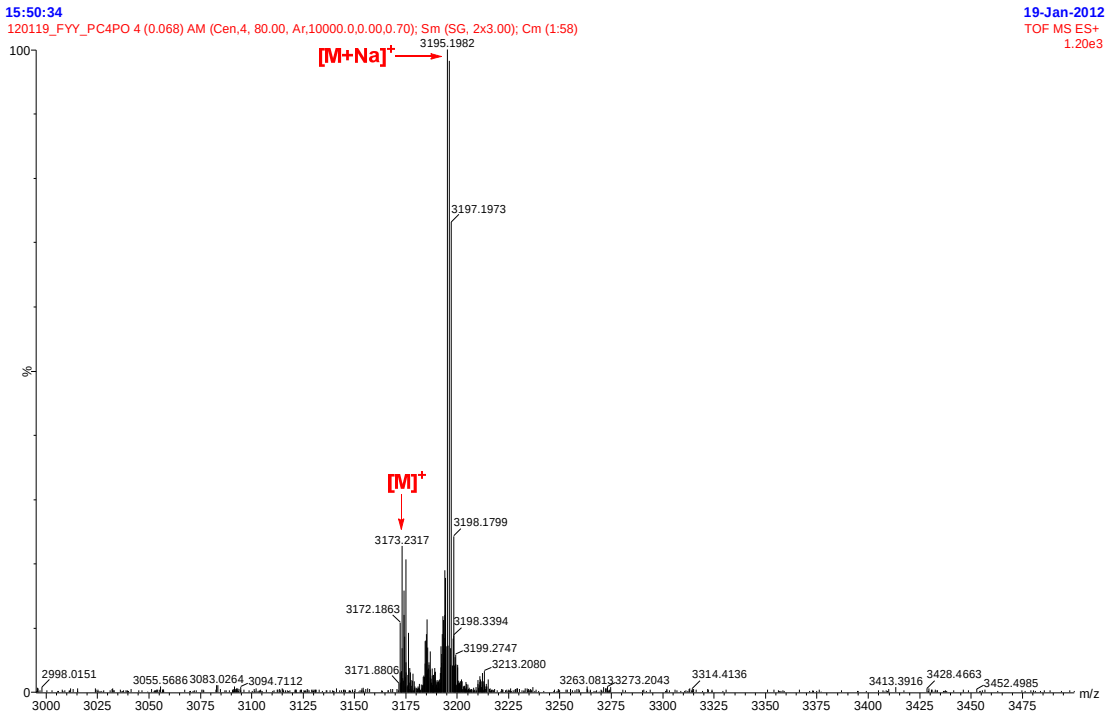

Figure S11. ESI-HRMS spectrum of **1b**.

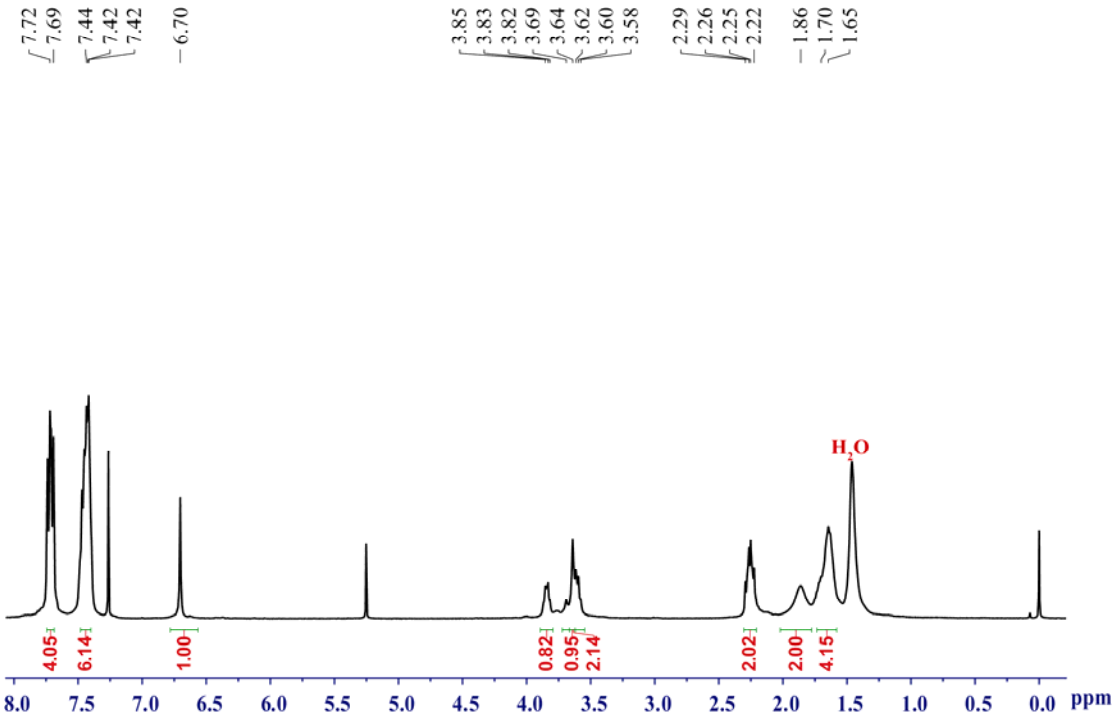

Figure S12 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1c**.

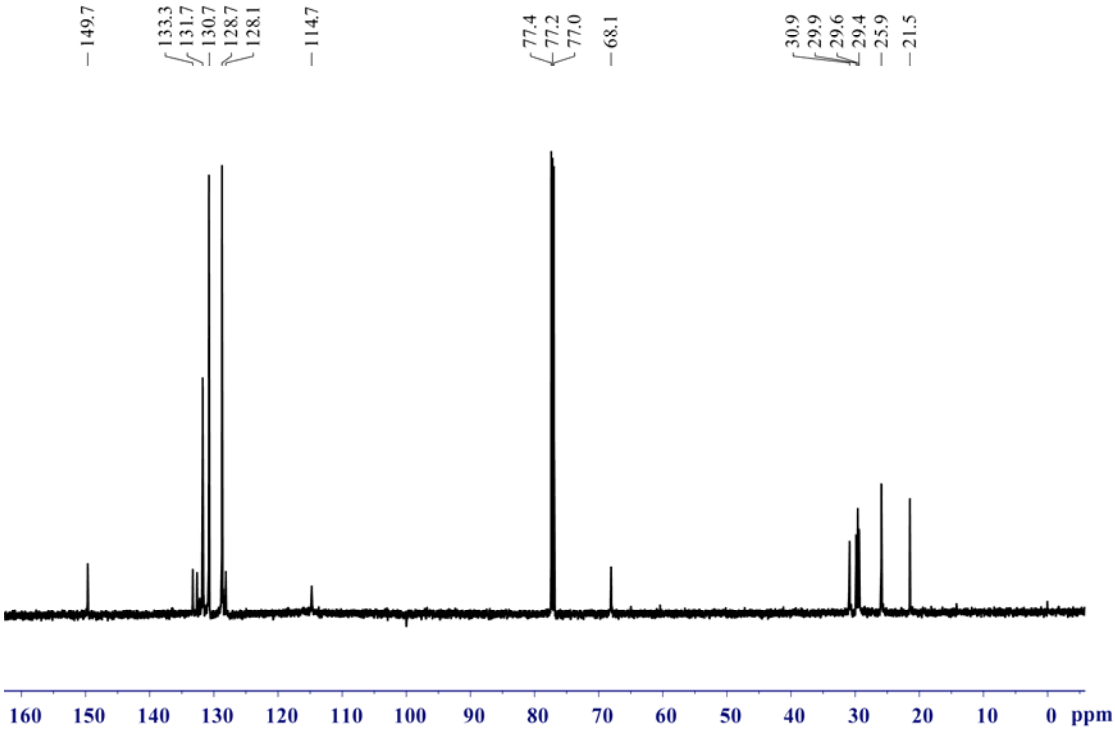

Figure S13 ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1c**.

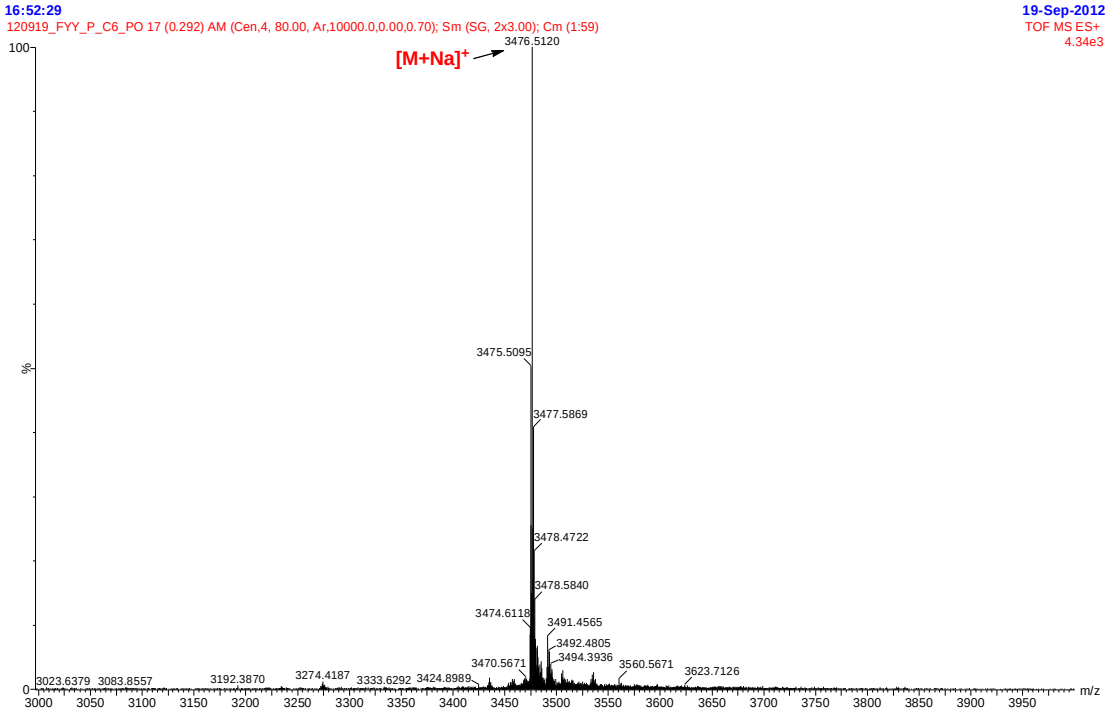

Figure S14. ESI-HRMS spectrum of **1c**.

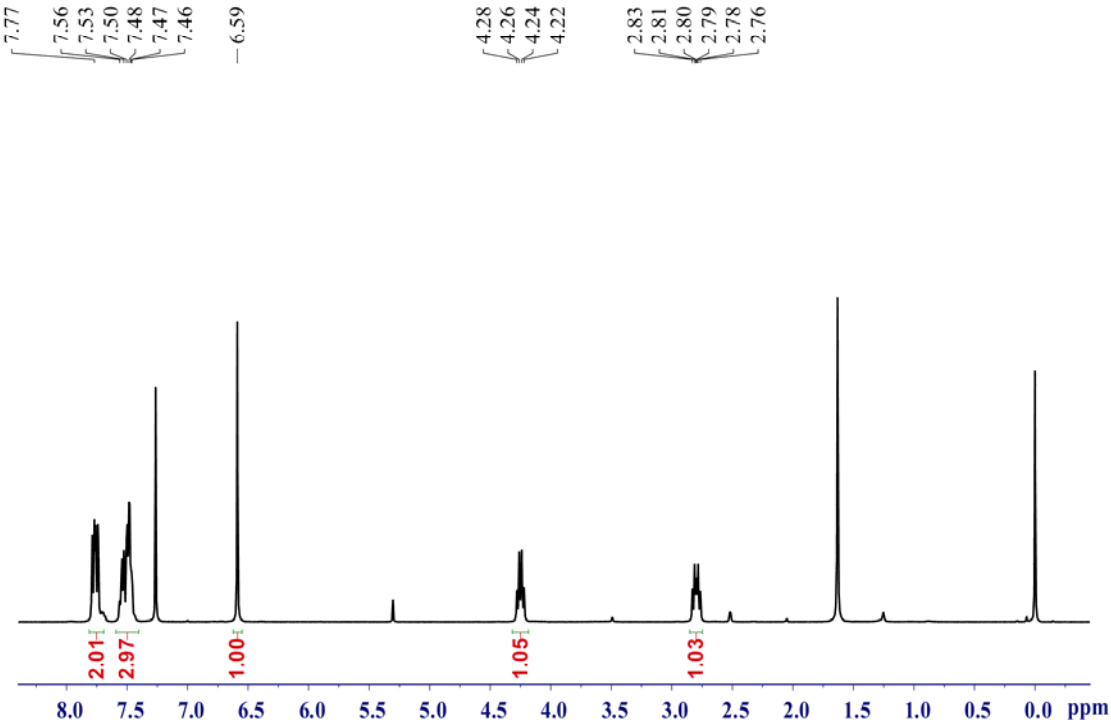

Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**.

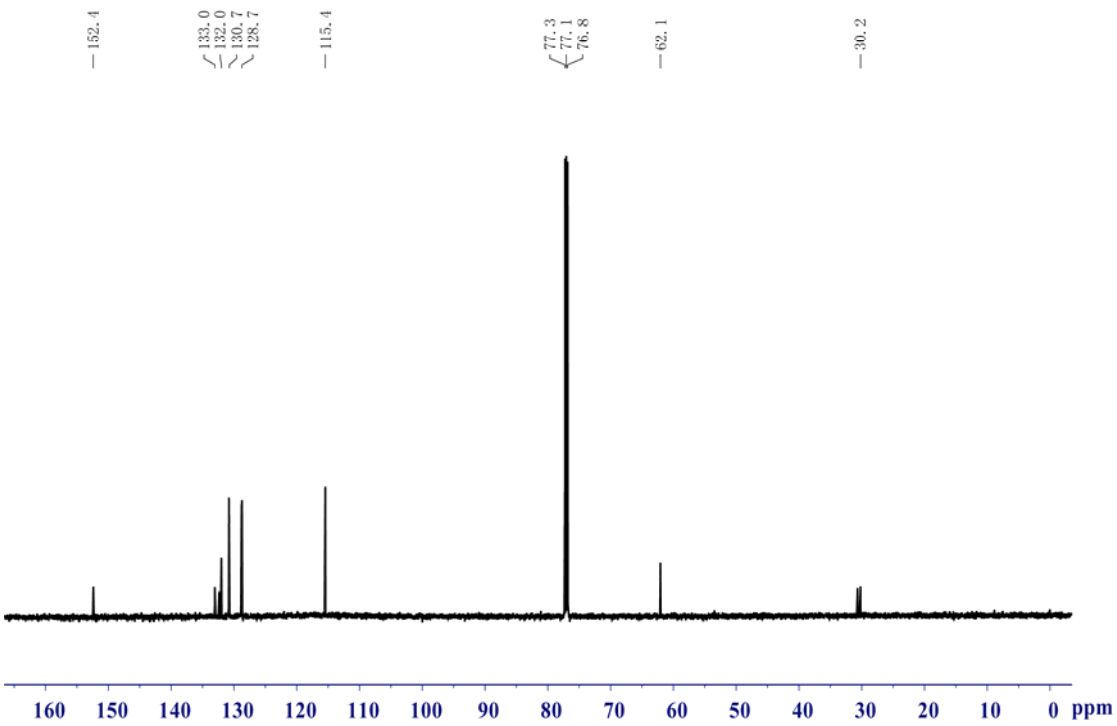

Figure S16 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2a**.

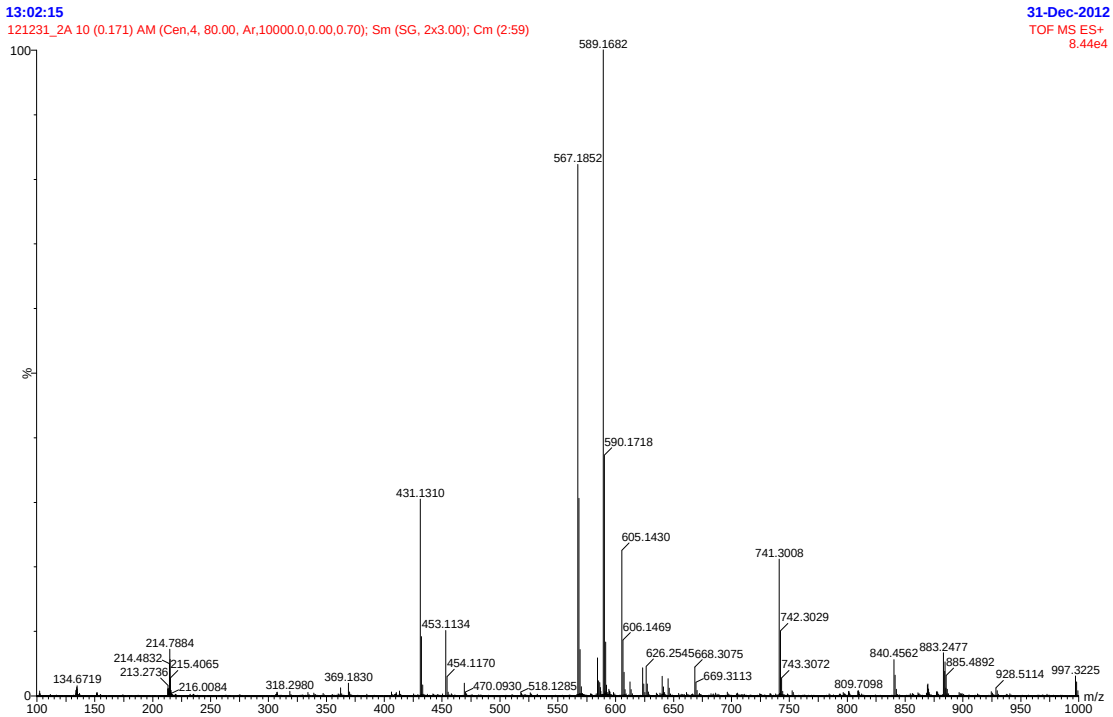

Figure S17. ESI-HRMS spectrum of **2a**.

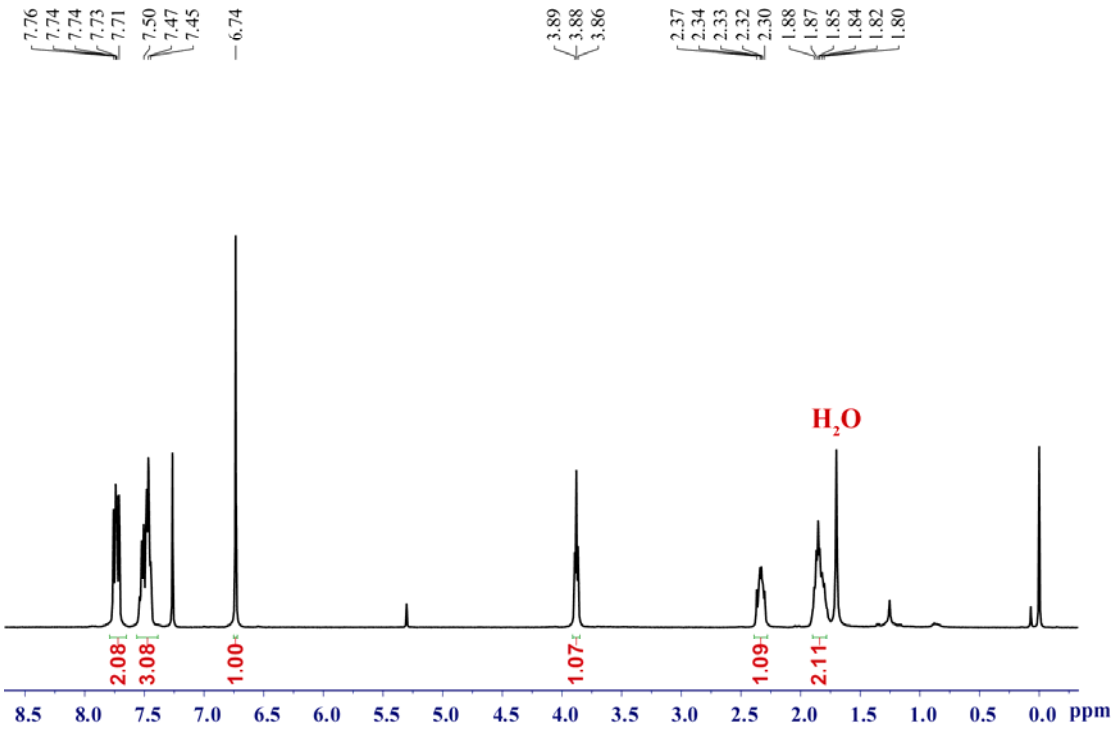

Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**.

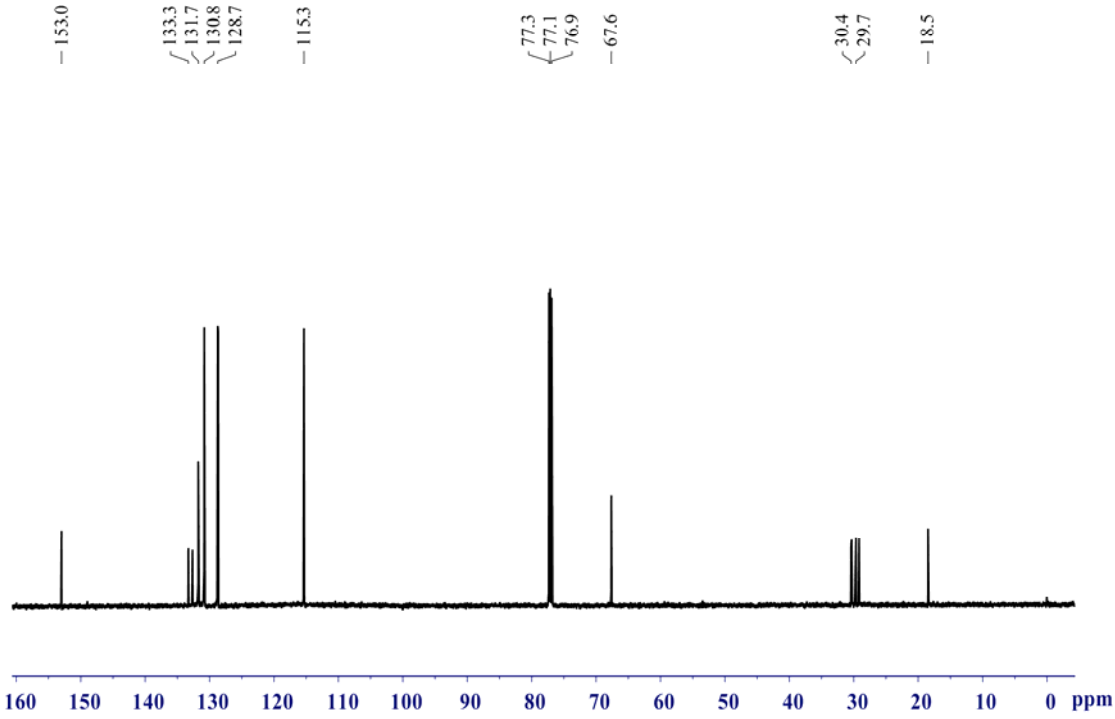

Figure S19 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2b**.

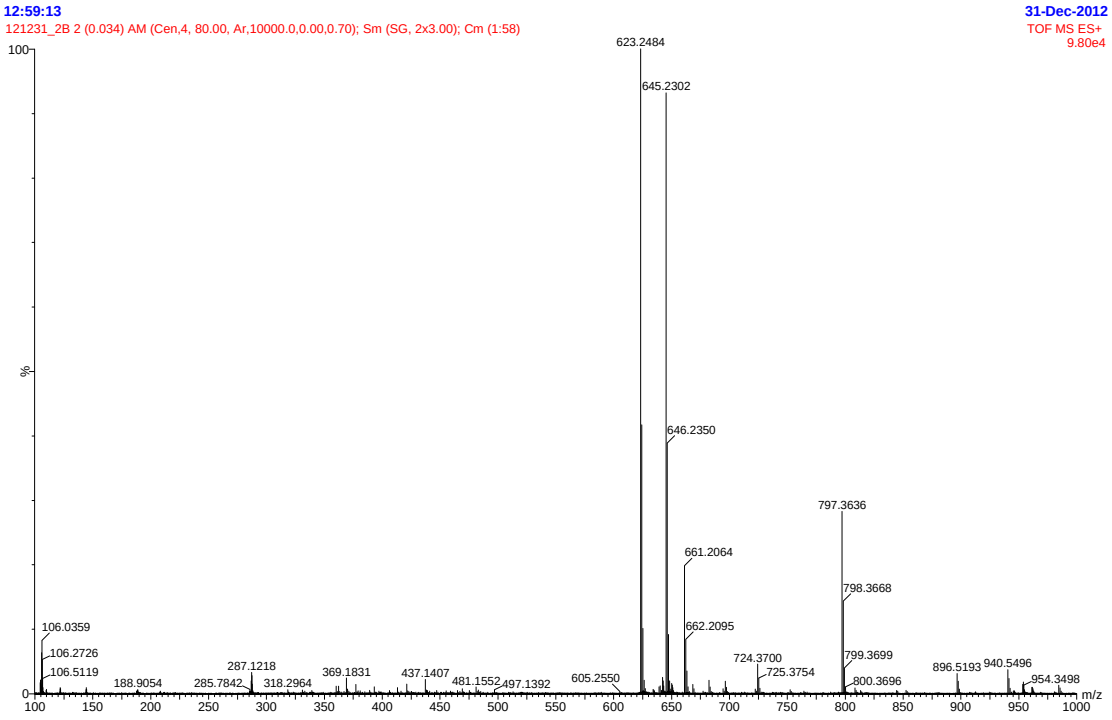

Figure S20. ESI-HRMS spectrum of **2b**.

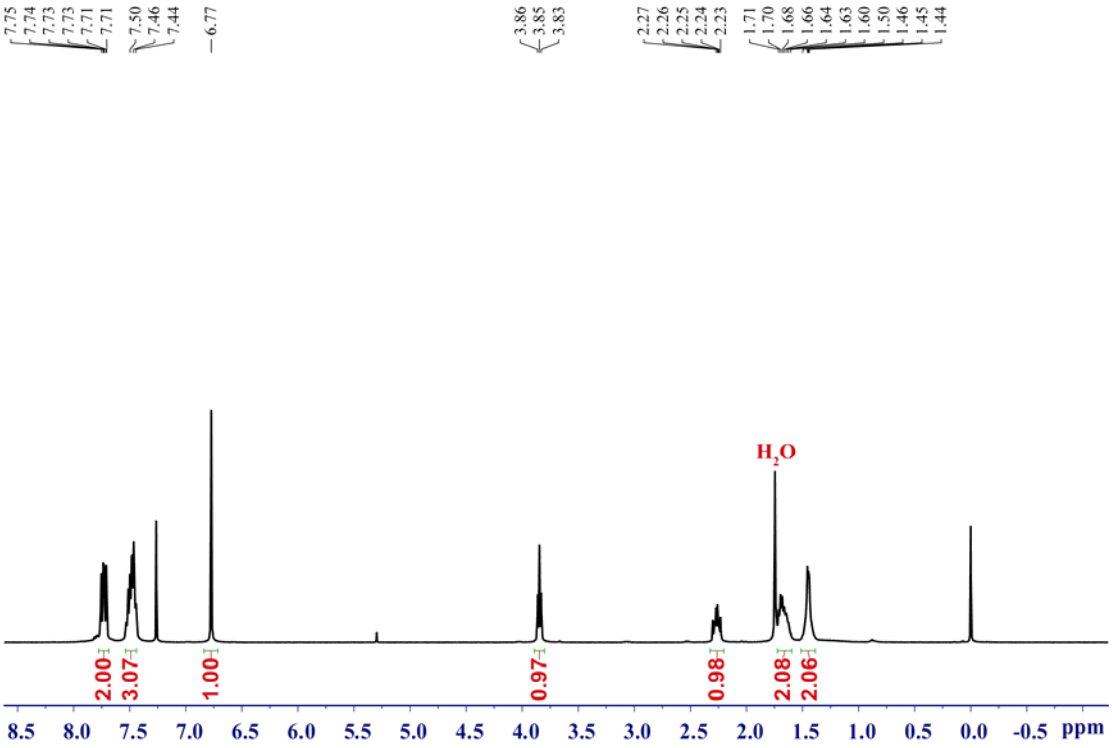

Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

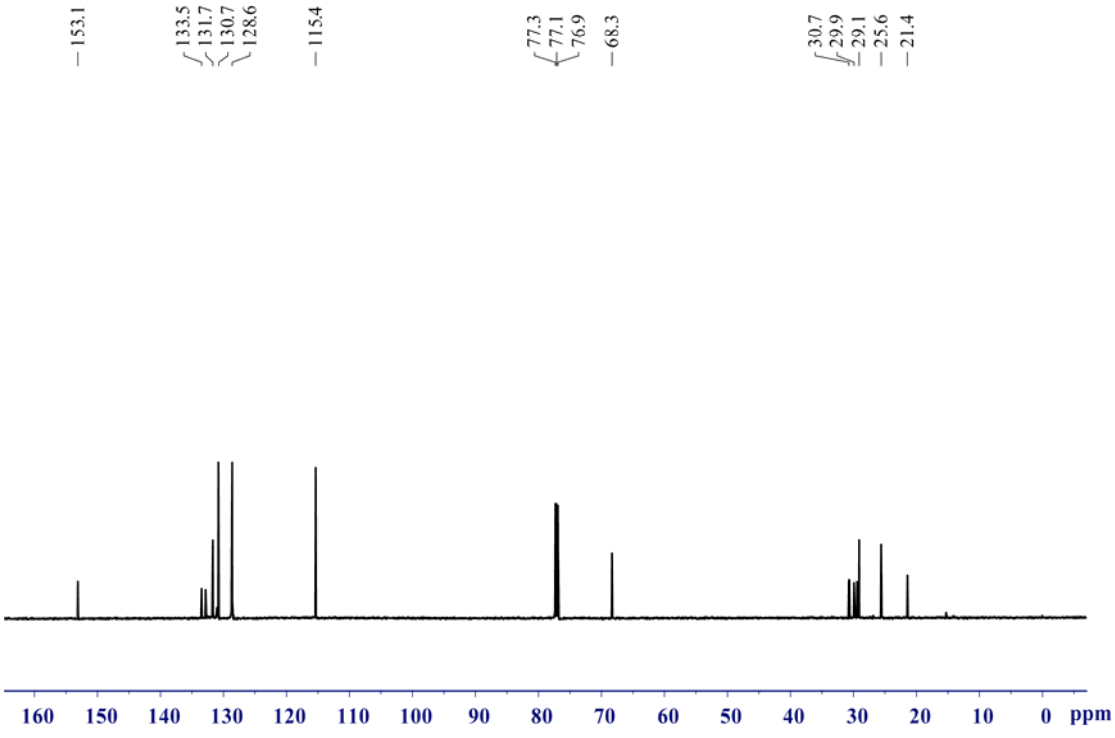

Figure S22 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

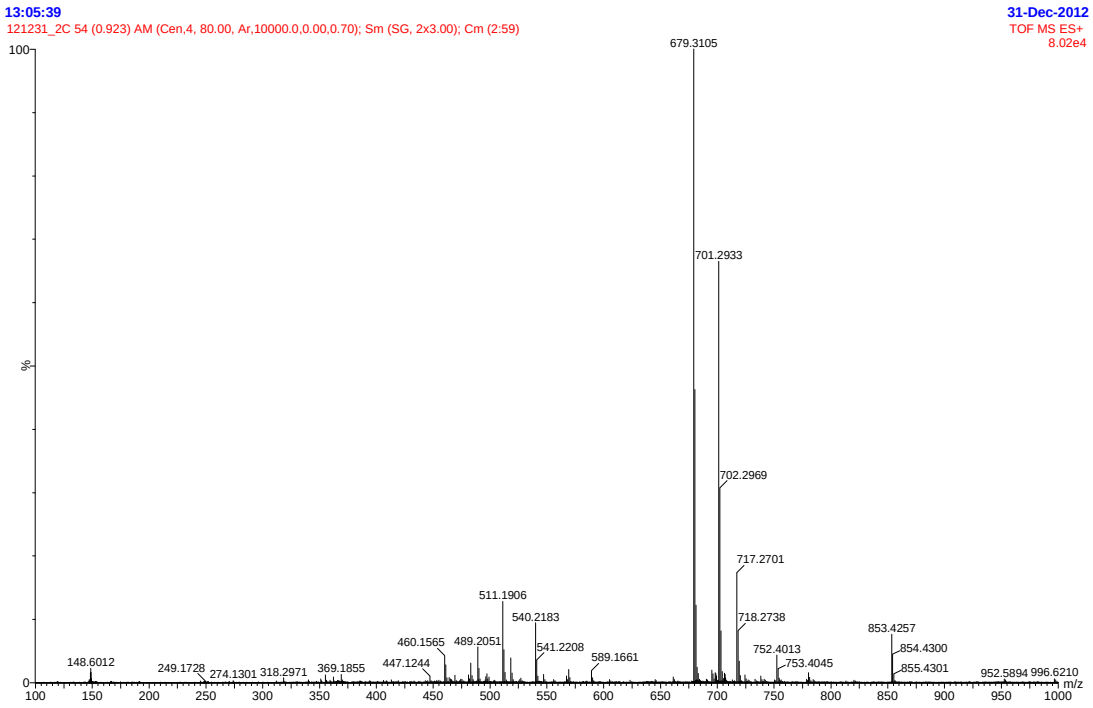

Figure S23. ESI-HRMS spectrum of **2c**.

3. The Extraction of Lanthanides and Actinides

Table S1 Separation factors (SF) of f-element cations for **1** and **2a** (1.0×10^{-3} M) from 1 M HNO_3 aqueous solution into dichloromethane (T = 20 ± 1°C).

Cations	**1a**		**1b**		**1c**		**2a**
	D_{Th}/D_M	D_U/D_M	D_{Th}/D_M	D_U/D_M	D_{Th}/D_M	D_U/D_M	D_{Th}/D_M
La^{3+}	1.02	4.15	6.78	109	12.2	70.7	0.32
Ce^{3+}	1.14	4.65	3.83	61.6	12.0	69.5	0.31
Pr^{3+}	1.08	4.38	4.14	66.5	11.7	67.8	0.30
Nd^{3+}	1.45	5.91	3.31	53.1	11.2	65.3	0.32
Sm^{3+}	1.44	5.85	3.68	59.2	9.76	56.7	0.34
Eu^{3+}	1.47	5.98	3.38	54.3	11.4	66.1	0.32
Gd^{3+}	1.34	5.46	4.44	71.3	11.1	64.5	0.36
Yb^{3+}	1.57	6.43	3.96	63.6	16.3	94.5	0.38
Lu^{3+}	1.38	5.60	4.74	76.2	14.5	84	0.41
Th^{4+}	--	4.07	--	16.1	--	5.89	

Table S2 Extraction percentage (%E) and separation factors (SF)of thorium(IV) and uranyl(VI) nitrates from 1 M HNO_3 and various sodium nitrate aqueous solution into dichloromethane containing the ligand **1b** (T = 20 ± 1°C).

Cations	n M $NaNO_3$ + 1 M HNO_3 (n = 0-4)				
	0 M	1 M	2 M	3 M	4 M
Th^{4+}	23.6	28.7	30.7	30.7	30.7
UO_2^{2+}	56.0	64.1	74.0	80.7	83.0
D_U/D_{Th}	4.12	4.44	6.42	9.43	11.0