Electronic Supplementary Information

Synthesis of pillar[n]arenes (n=5,6) with deep eutectic solvent choline chloride·2$FeCl_3$

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1.Experimental section

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used without further purification. 1, 4-dibutyloxybenzene (**3a**), 1, 4-dihexyloxybenzene (**4a**) and 1, 4-dioctyloxybenzene (**5a**) were synthesized according to the papers.[S1]

Measurements. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer at 298K. The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 ppm for ^{13}C). ESI-MS measurement was performed on Thermo Finnigan LCQ advantage at 298K. All MALDI-TOF-MS spectra were recorded with an Axima TOF2 mass spectrometry. EPR spectra were recorded on a Bruker X-band A200 spectrometer. The solution sample was taken out into a small tube and then analyzed by EPR. EPR spectra was recorded at 298K on EPR spectrometer operating at 9.420 GHz. Typical spectrometer parameters were: scan range, 3000 G; center field set, 3361 G; time constant, 163.84 ms; scan time,30.00 s; modulation amplitude 2.0 G; modulation frequency 100 kHz; receiver gain $1.00*10^4$; microwave power, 19.71 mW.

Preparation of deep eutectic solvent. A mixture of the ferric chloride ($FeCl_3$) and choline chloride in a molar ratio of 2:1 was heated to 100°C with gentle stirring until a dark brown clear liquid formed.

The synthesis process of pillar[n]arenes. To the solution of 1,4-diethoxybenzene (**1a**) (1.6620g, 10 mmol) in dichloromethane (150 ml) was added paraformaldehyde (0.9000g, 30 mmol). And then, $[ChCl][FeCl_3]_2$ (0.6970g 1.5 mmol) was added to the solution.After the mixture stirred at 25℃ for 4h, the reaction was quenched by addition of water. The organic phase was separated and washed with saturated aqueous $NaHCO_3$, H_2O, and brine. The crude product was purified by column chromatograph to yield **1b** (CH_2Cl_2/petroleum ether = 3 : 1), **1c** (CH_2Cl_2/petroleum ether = 100 : 1).

2.Characterization data and spectra for 1b.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (s, 1H), 3.83 (q, *J*=6.92 Hz, 2H), 3.77 (s, 1H,), 1.27 (t, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 149.8, 128.4, 115.0, 63.7, 29.8,15.1. HR ESI-MS calcd. for $C_{55}H_{70}O_{10}Na$ $[M+Na]^+$ 913.4867, found 913.4.

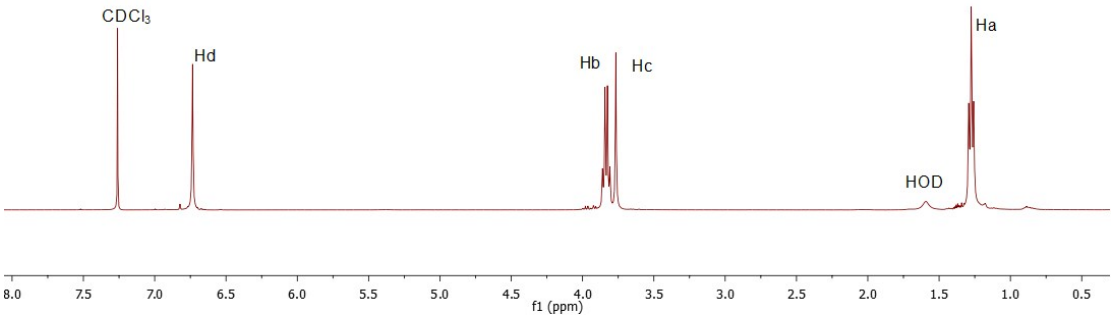

Fig S1 ^{1}H NMR spectrum of **1b** ($CDCl_3$; 400MHz).

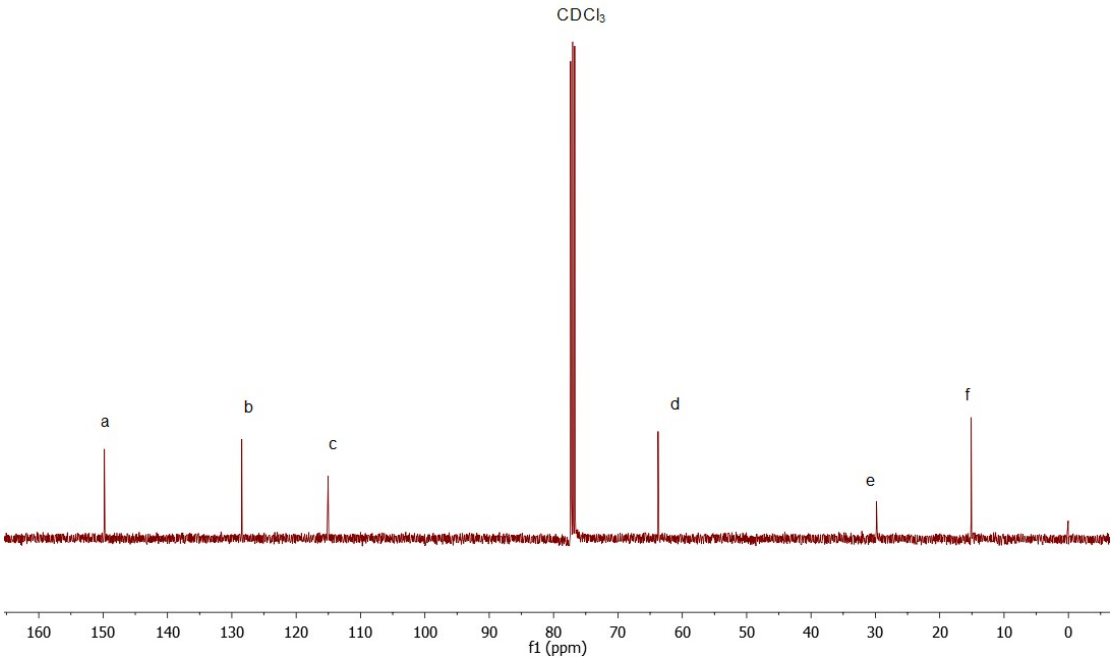

Fig S2 ^{13}C NMR spectrum of **1b** ($CDCl_3$; 100MHz).

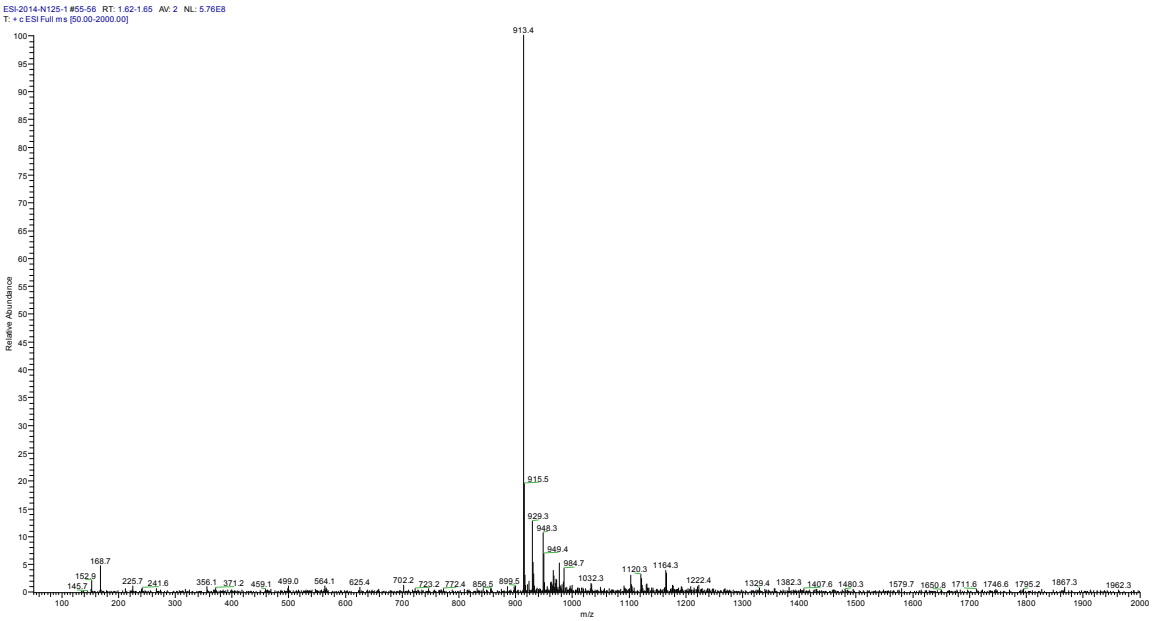

Fig S3 HR ESI-MS of **1b**.

3.Characterization data and spectra for 1c.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (s, 1H), 3.88 – 3.74 (m, 3H), 1.29 (t, J = 5.9 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$):δ 150.4, 127.8, 115.2, 64.0, 30.9, 15.2. HR ESI-MS calcd. for $C_{66}H_{84}O_{12}Na$ $[M+Na]^+$ 1091.5860, found 1091.5.

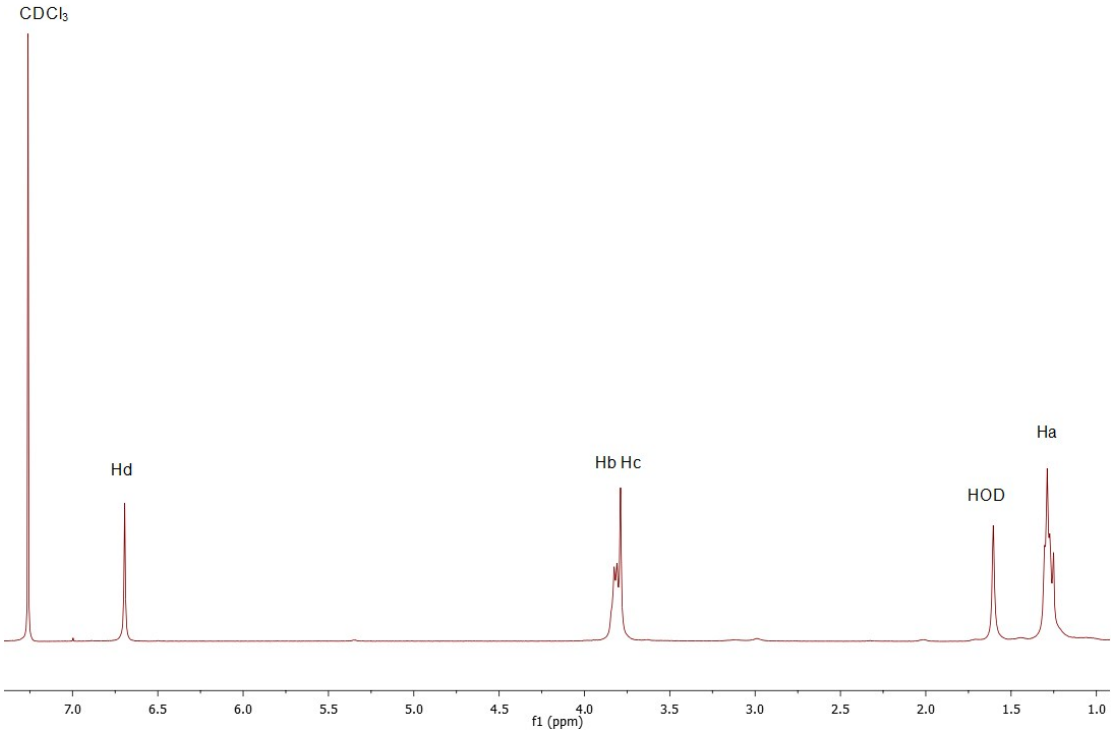

Fig S4 ^{1}H NMR spectrum of **1c** ($CDCl_3$; 400MHz).

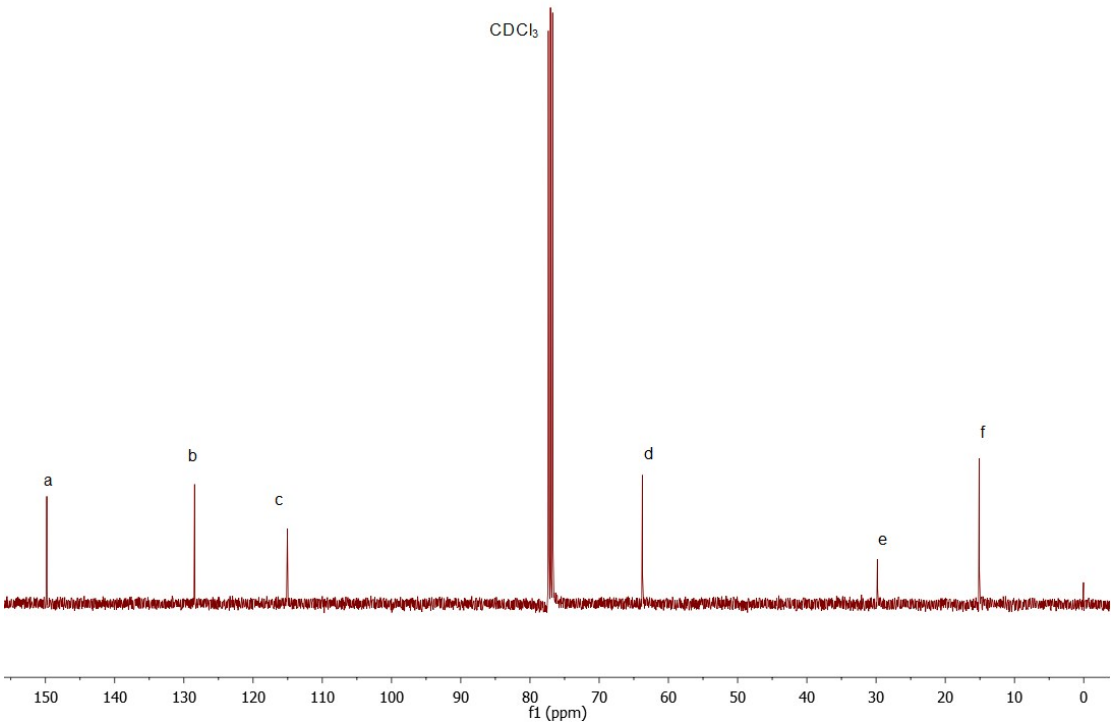

Fig S5 ^{13}C NMR spectrum of **1c** ($CDCl_3$; 100MHz).

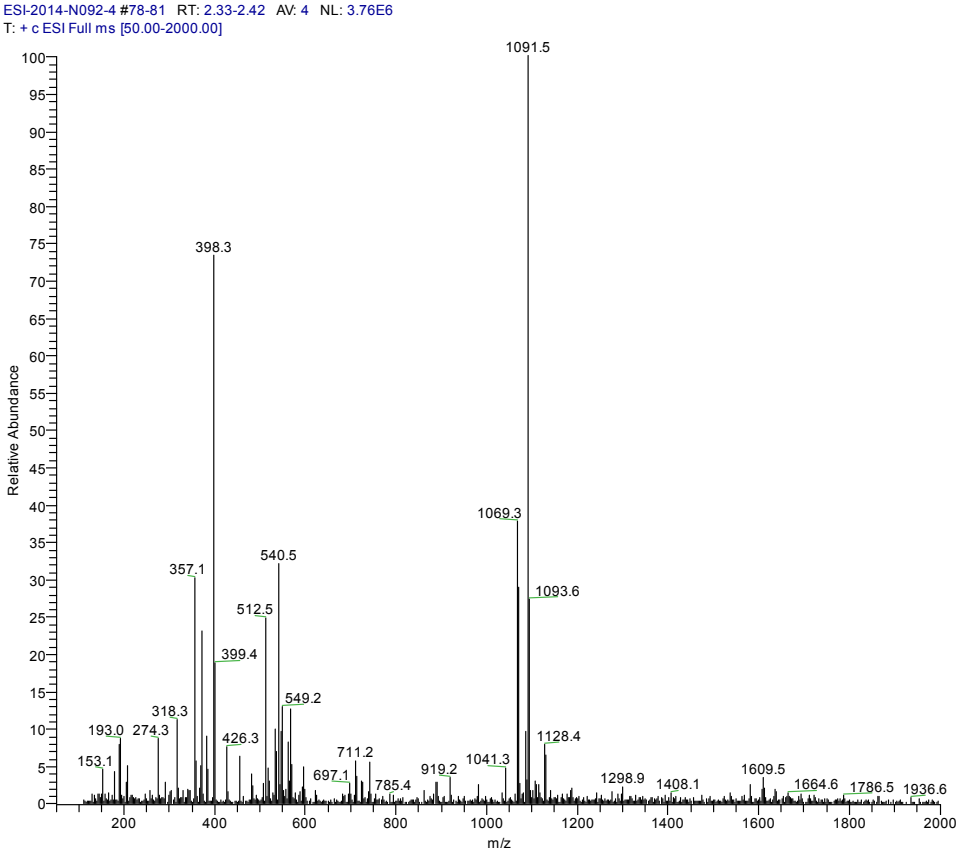

Fig S6 HR ESI-MS of **1c**.

4.Characterization data and spectra for 2b.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (s, 1H), 3.77 (s, 1H), 3.65 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 128.3, 114.2, 55.9, 29.8. HR ESI-MS calcd. for $C_{45}H_{50}O_{10}Na$ $[M+Na]^+$ 773.3032, found 773.3.

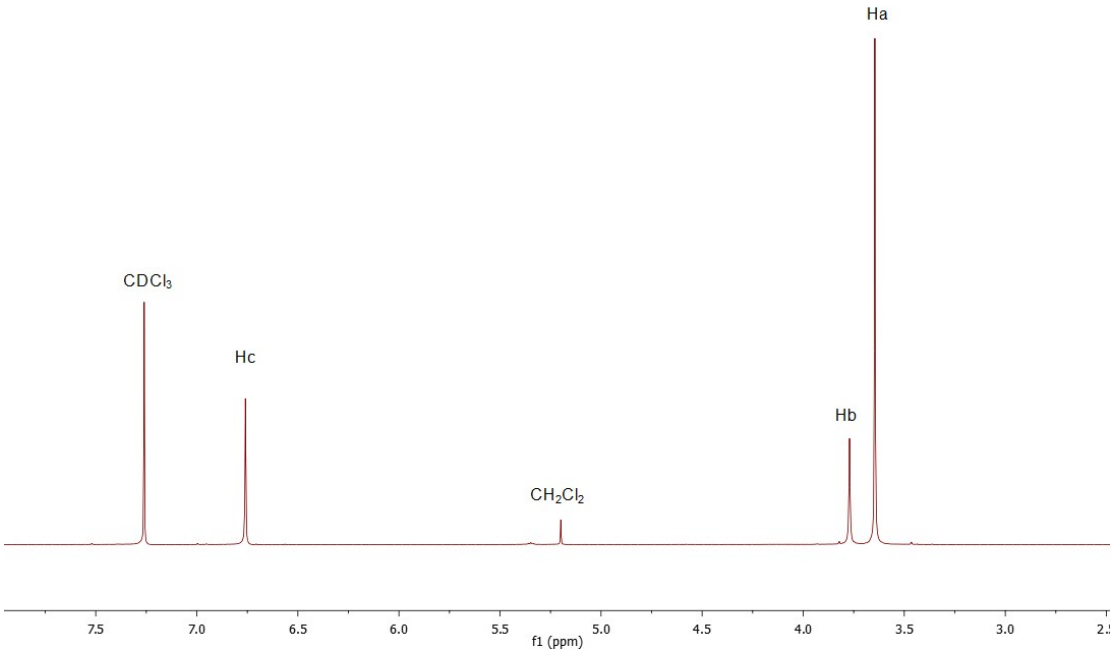

Fig S7 ^{1}H NMR spectrum of **2b** ($CDCl_3$; 400MHz).

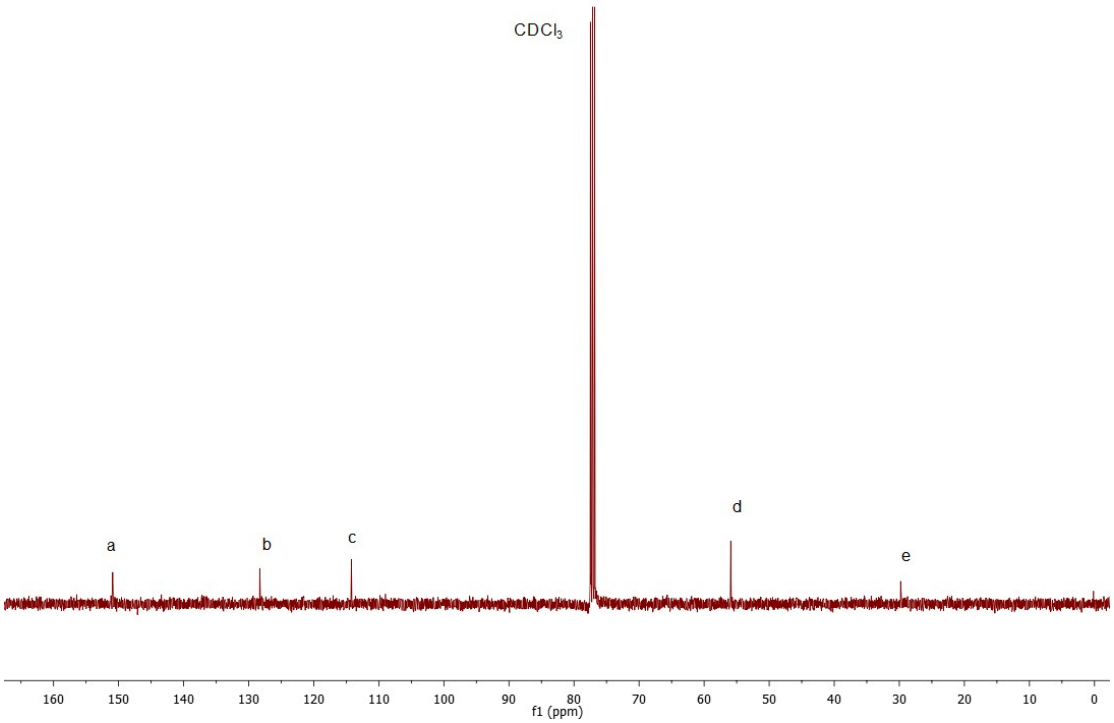

Fig S8 ^{13}C NMR spectrum of **2b** ($CDCl_3$; 100MHz).

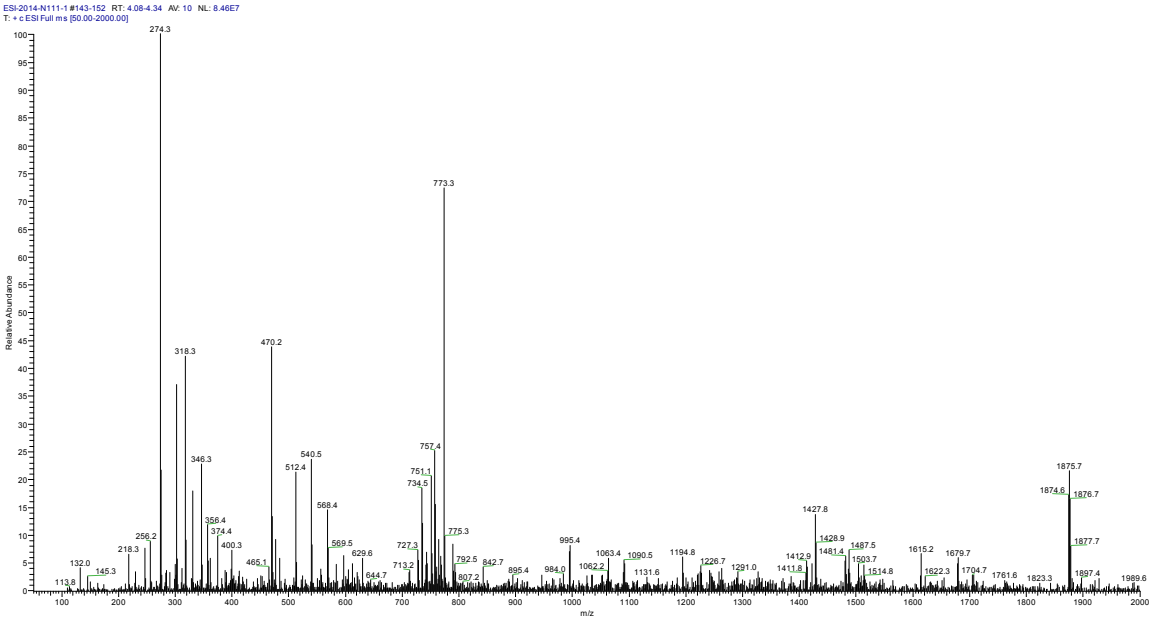

Fig S9 HR ESI-MS of **2b**.

5.Characterization data and spectra for 3b.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 1H), 1.82 – 1.70 (m, 2H), 1.57 – 1.46 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 128.1, 114.5, 67.9, 32.1, 29.3, 19.5, 14.0. HR ESI-MS calcd. for $C_{45}H_{50}O_{10}Na$ $[M+Na]^+$ 1193.7997, found 1193.7.

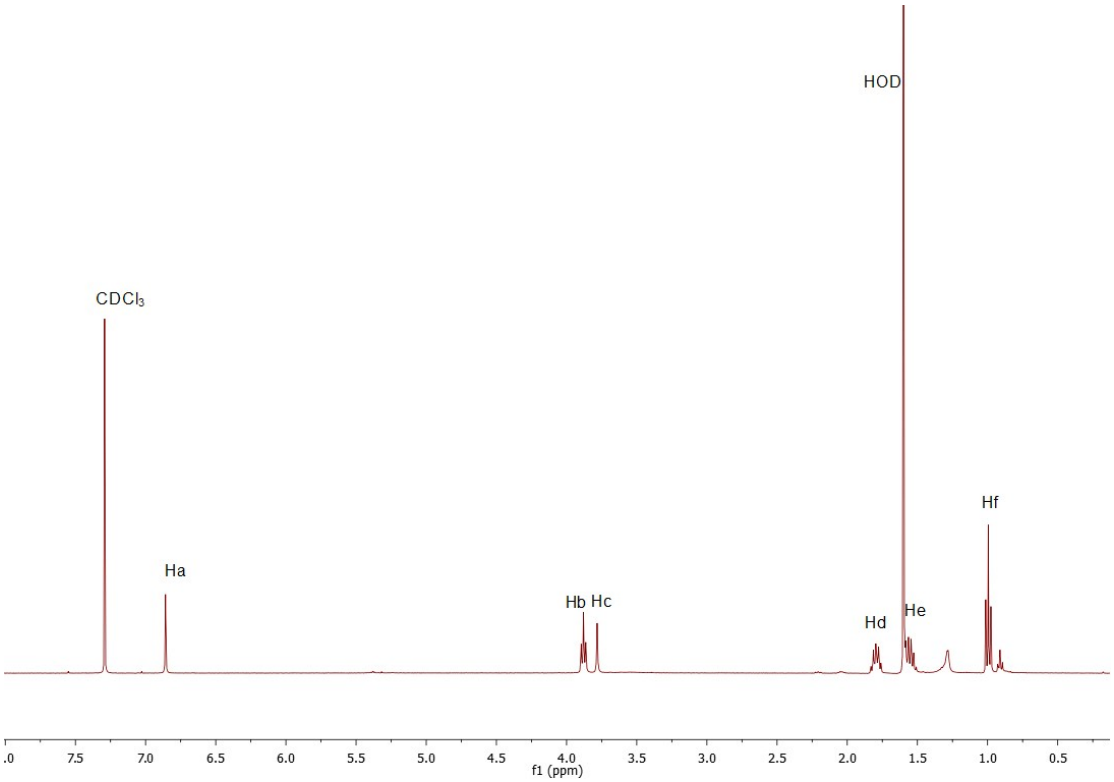

Fig S10 ^{1}H NMR spectrum of **3b** ($CDCl_3$; 400MHz).

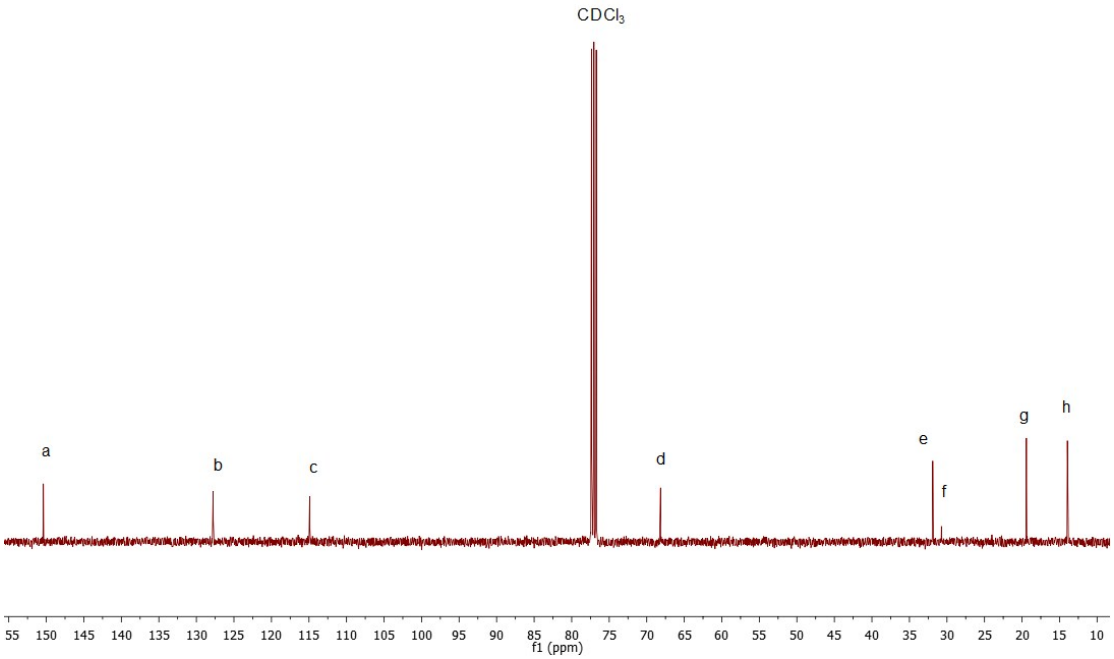

Fig S11 ^{13}C NMR spectrum of **3b** ($CDCl_3$; 100MHz).

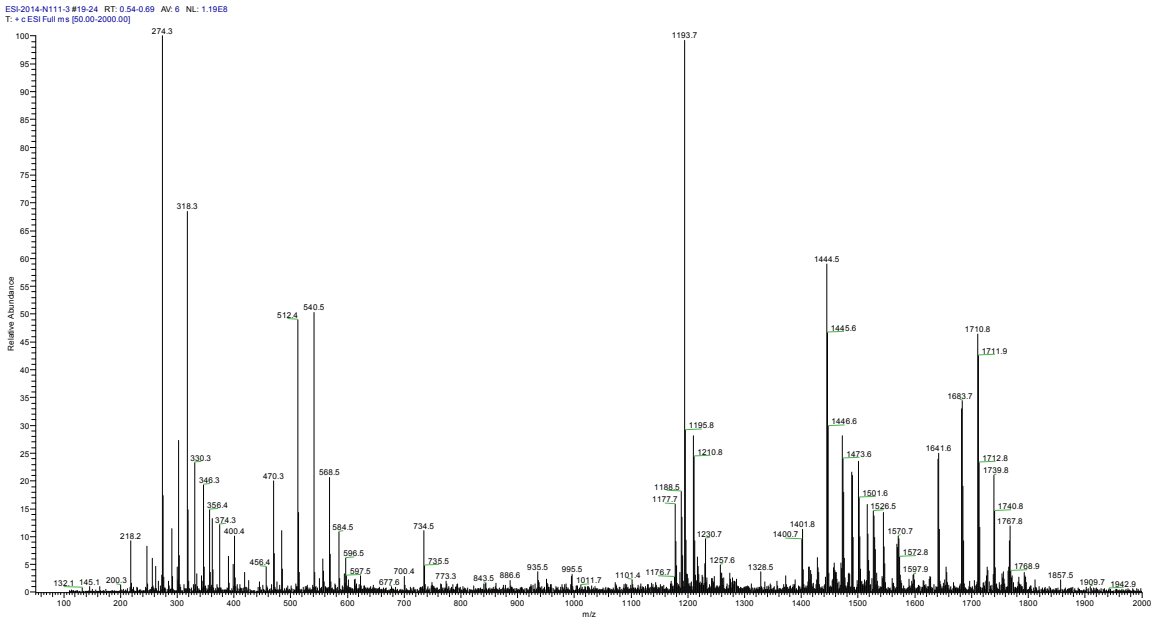

Fig S12 HR ESI-MS of **3b**.

6.Characterization data and spectra for 3c.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 3.78 (s, 1H), 3.75 (t, *J* = 6.5 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.43 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.5, 127.8, 115.0, 32.0, 30.9, 19.5, 14.0.HR ESI-MS calcd. for $C_{90}H_{132}O_{10}Na$ $[M+Na]^+$ 1427.9616, found 1427.8.

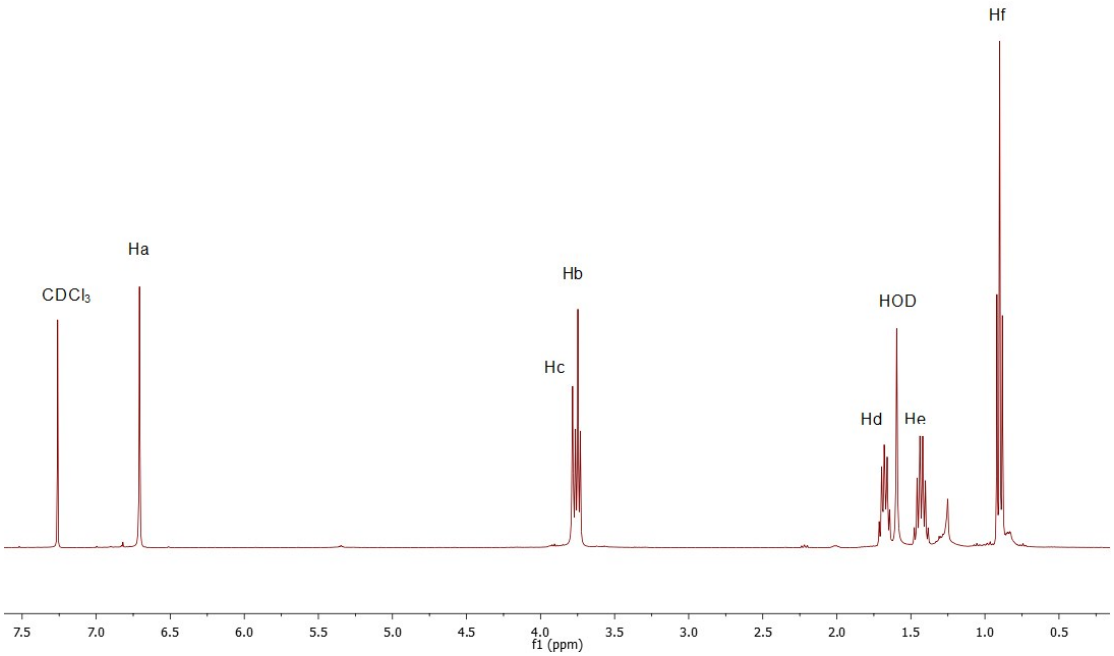

Fig S13 ^{1}H NMR spectrum of **3c** ($CDCl_3$; 400MHz).

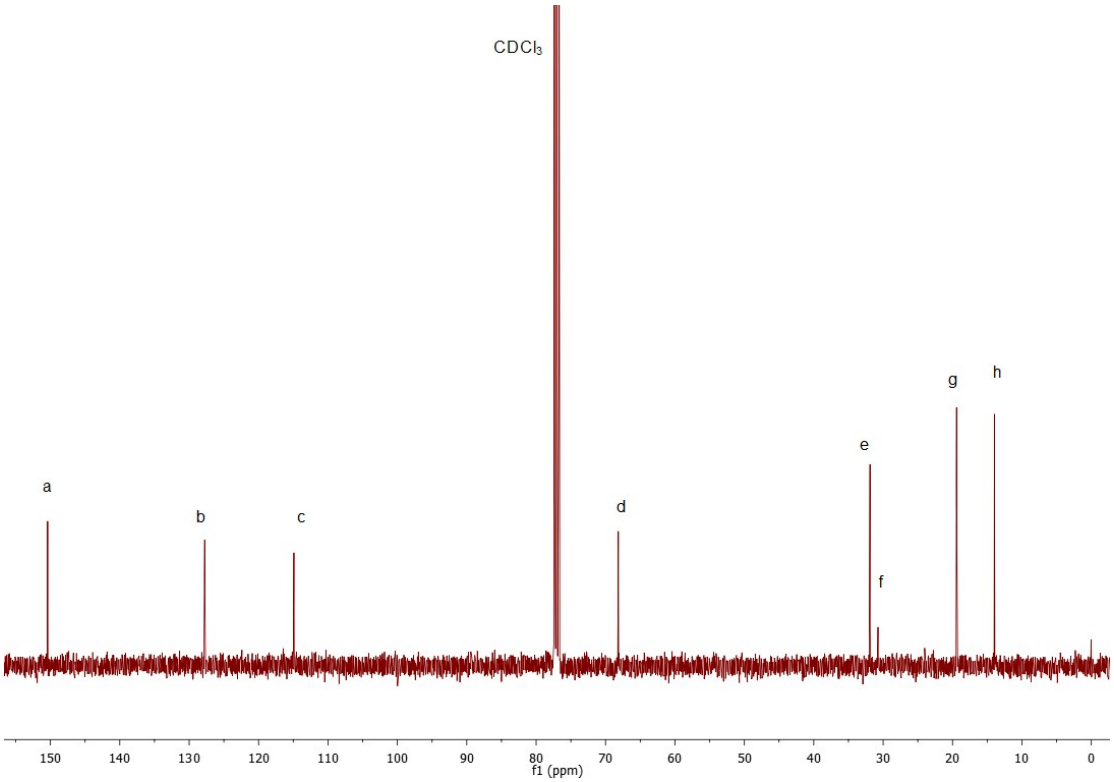

Fig S14 ^{13}C NMR spectrum of **3c** ($CDCl_3$; 100MHz).

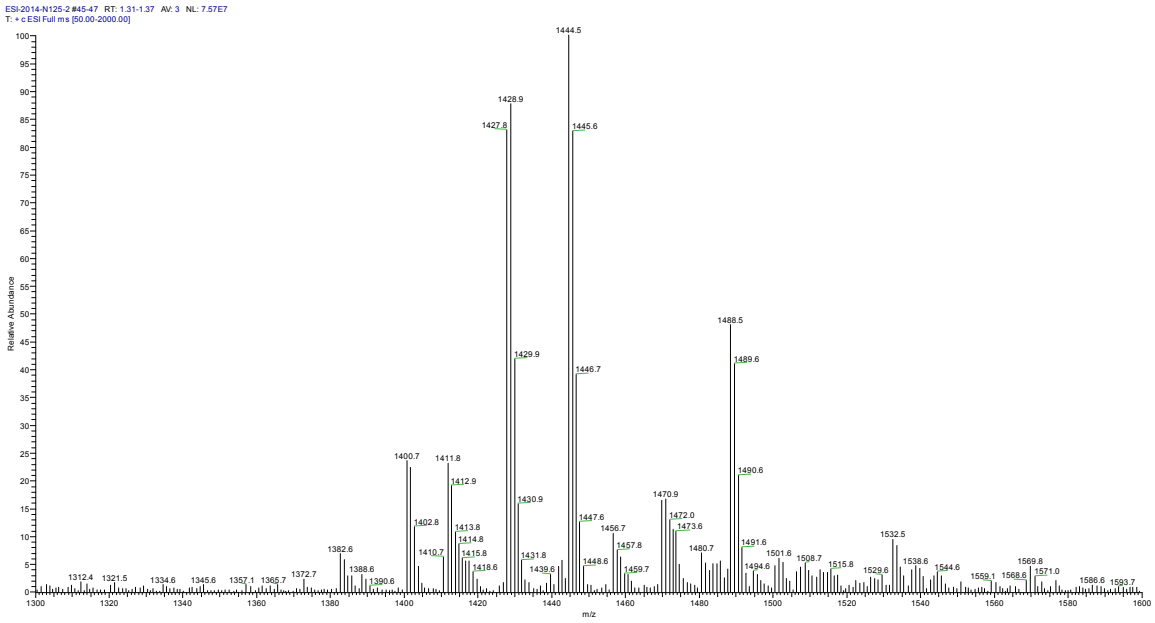

Fig S15 HR ESI-MS of **3c**.

7.Characterization data and spectra for 4b.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 1H), 3.84 (t, J = 5.7 Hz, 2H), 3.75 (s, 1H), 1.88 – 1.74 (m, 2H), 1.52 (m, 2H), 1.41 – 1.27 (m, 4H), 0.97 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.9, 128.2, 114.9, 68.4, 31.9, 30.0, 29.4, 26.2, 22.7, 14.2. HR ESI-MS calcd. for $C_{95}H_{150}O_{10}Na$ $[M+Na]^+$ 1474.1127, found 1474.0.

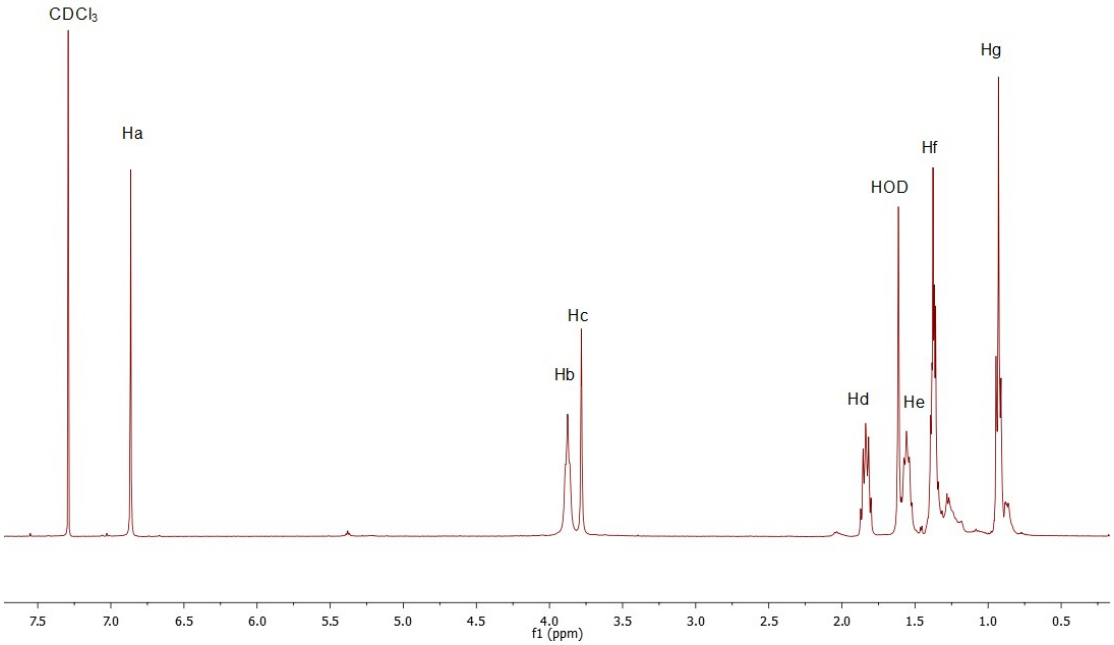

Fig S16 ^{1}H NMR spectrum of **4b** ($CDCl_3$; 400MHz).

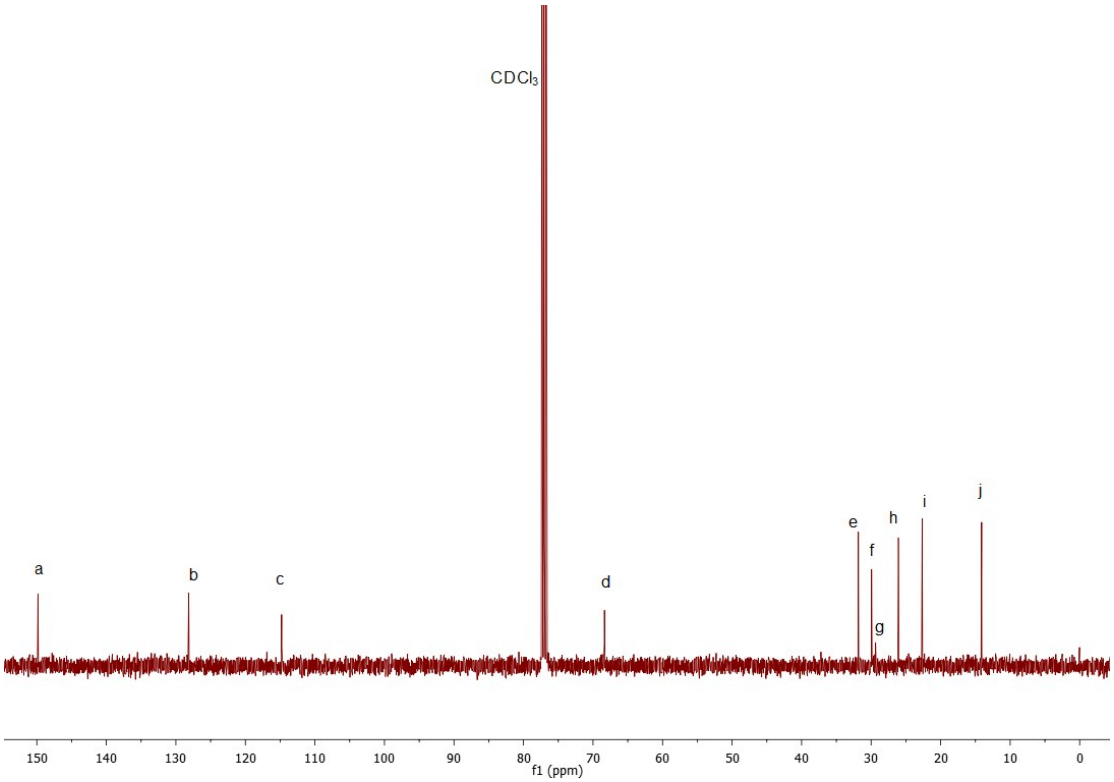

Fig S17 ^{13}C NMR spectrum of **4b** ($CDCl_3$; 100MHz).

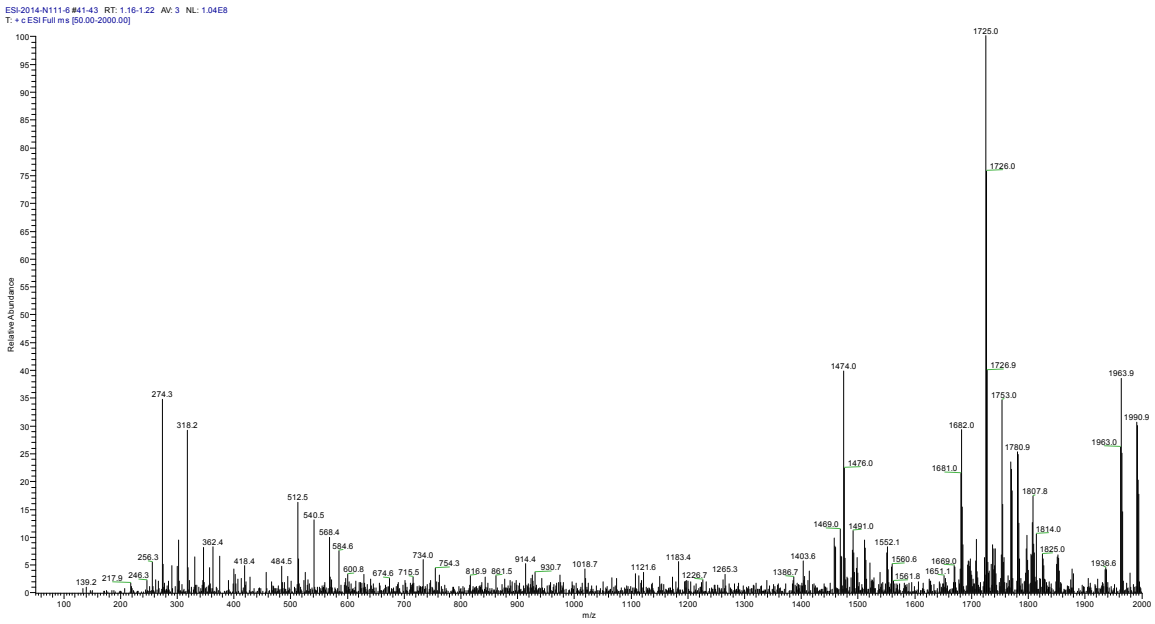

Fig S18 HR ESI-MS of **4b**.

8.Characterization data and spectra for 4c.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (s, 1H), 3.81 – 3.72 (m, 3H), 1.80 – 1.63 (m, 2H), 1.51 – 1.36 (m, 2H), 1.28 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 127.6, 114.9, 68.4, 31.8, 29.8, 29.5, 26.0, 22.7, 14.1. HR ESI-MS calcd. for $C_{114}H_{180}O_{12}Na$ $[M+Na]^+$ 1764.3373, found 1764.1.

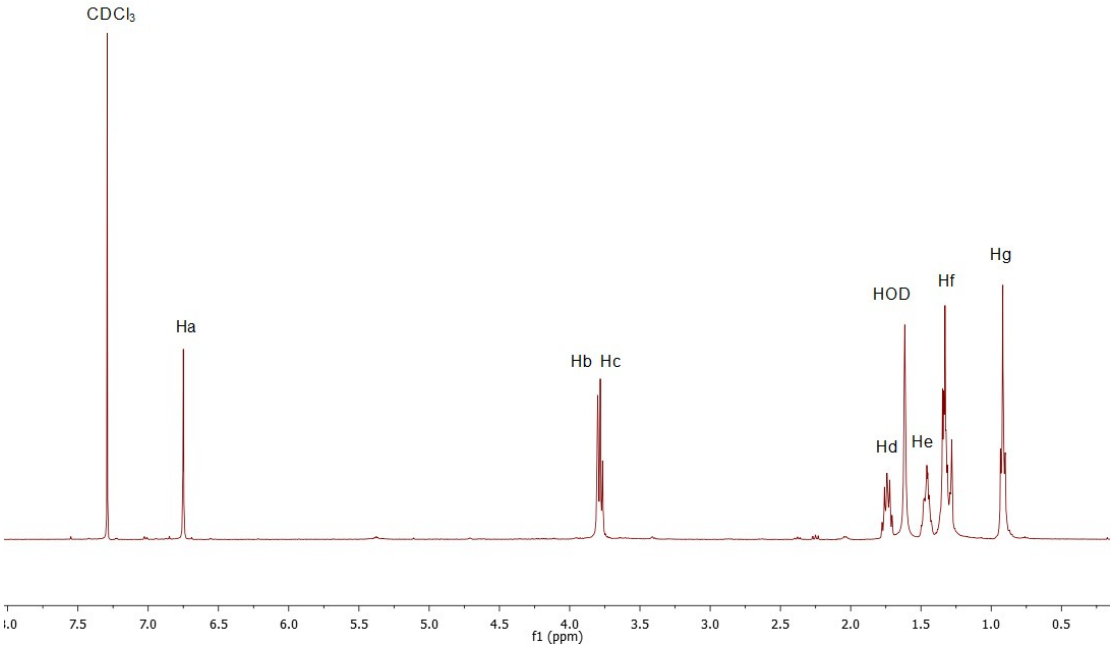

Fig S19 ^{1}H NMR spectrum of **4c** ($CDCl_3$; 400MHz).

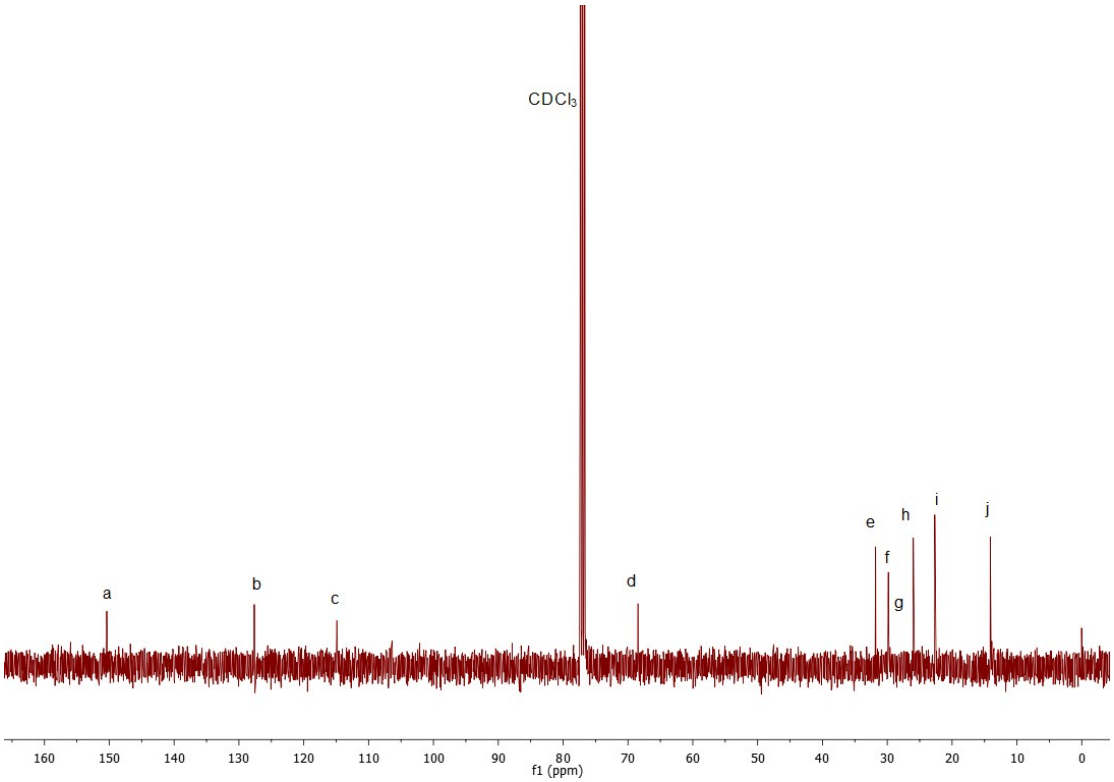

Fig S20 ^{13}C NMR spectrum of **4c** ($CDCl_3$; 100MHz).

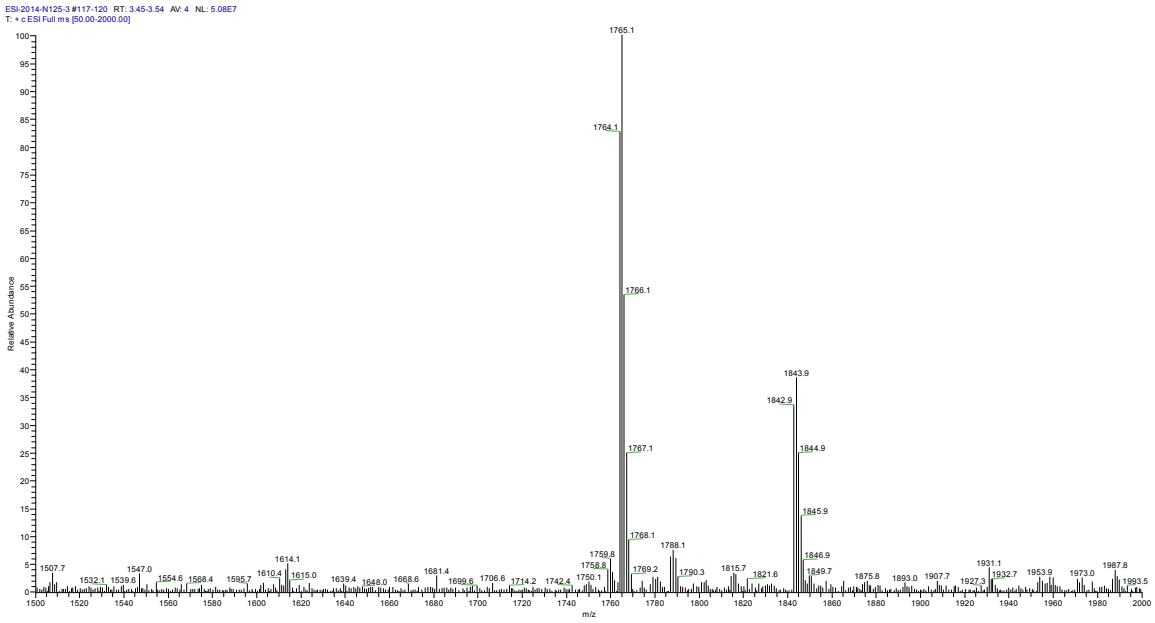

Fig S21 HR ESI-MS of **4c**.

9.Characterization data and spectra for 5b.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1H), 3.87 (s, 2H), 3.77 (s, 1H), 1.83 (s, 2H), 1.53 (m, 2H), 1.42 – 1.15 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.82, 128.16, 114.73, 68.31, 31.93, 30.02, 29.74, 29.42, 26.51, 22.78, 14.24. MS (MALDI-TOF) calcd. for $C_{115}H_{190}O_{10}$ $[M]^+$ 1731.4359, found 1731.91.

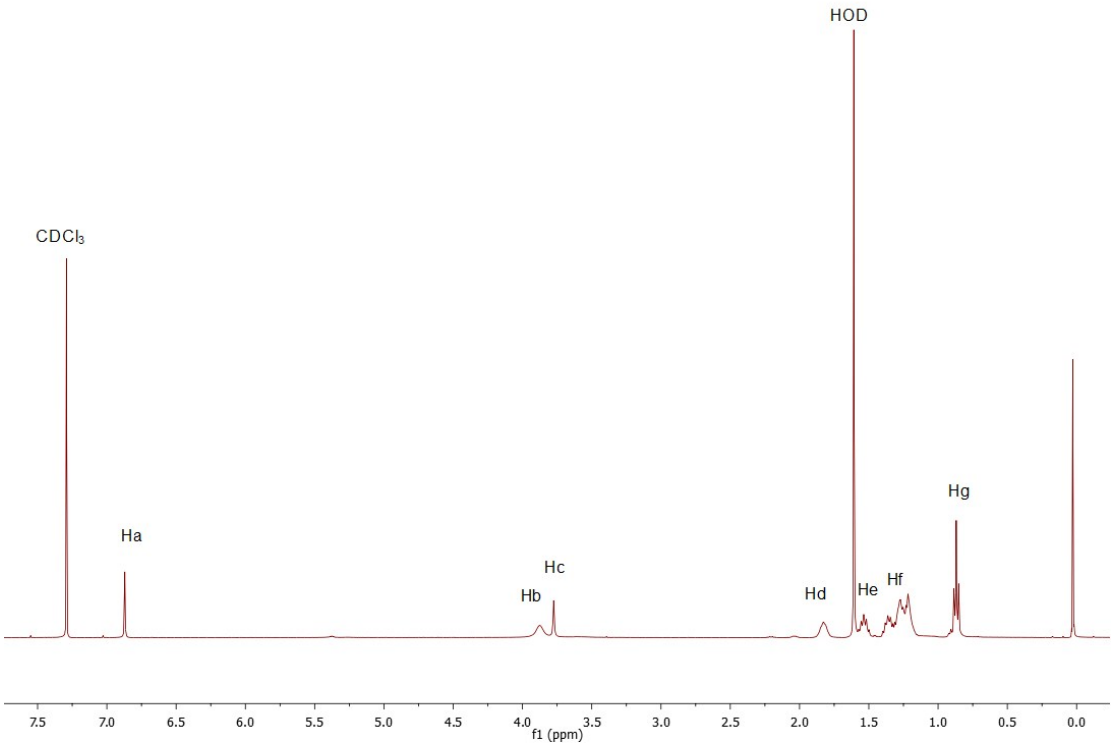

Fig S22 ^{1}H NMR spectrum of **5b** ($CDCl_3$; 400MHz).

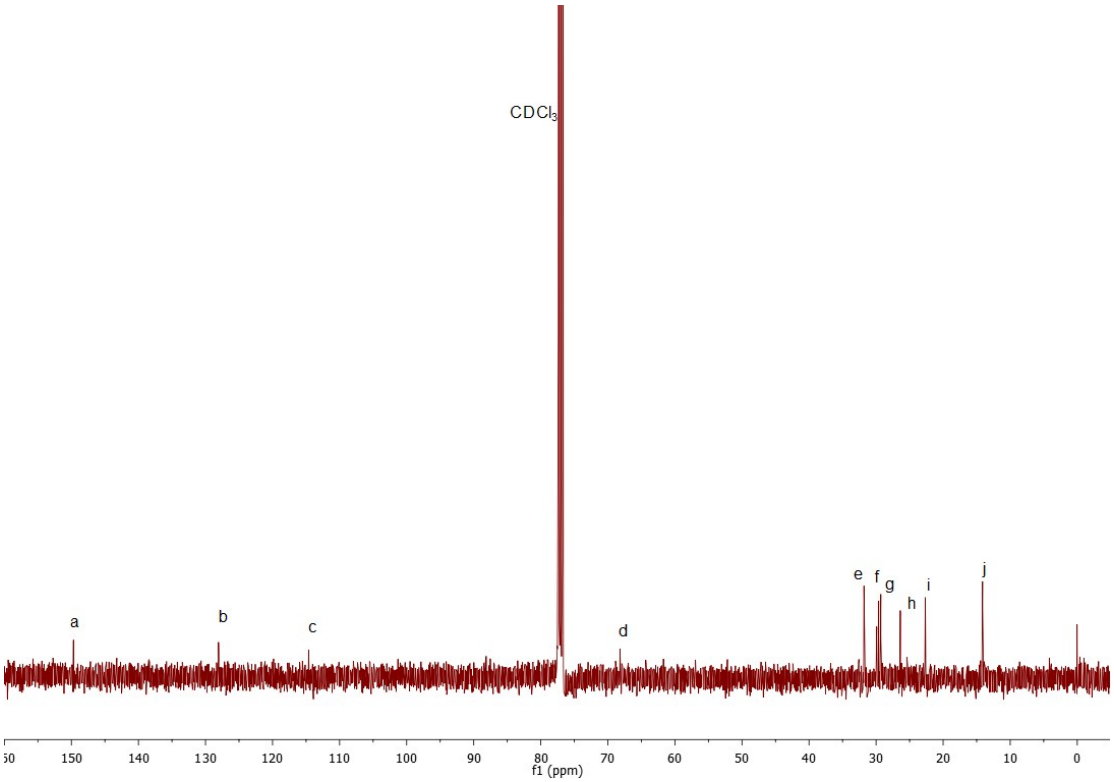

Fig S23 ^{13}C NMR spectrum of **5b** ($CDCl_3$; 100MHz).

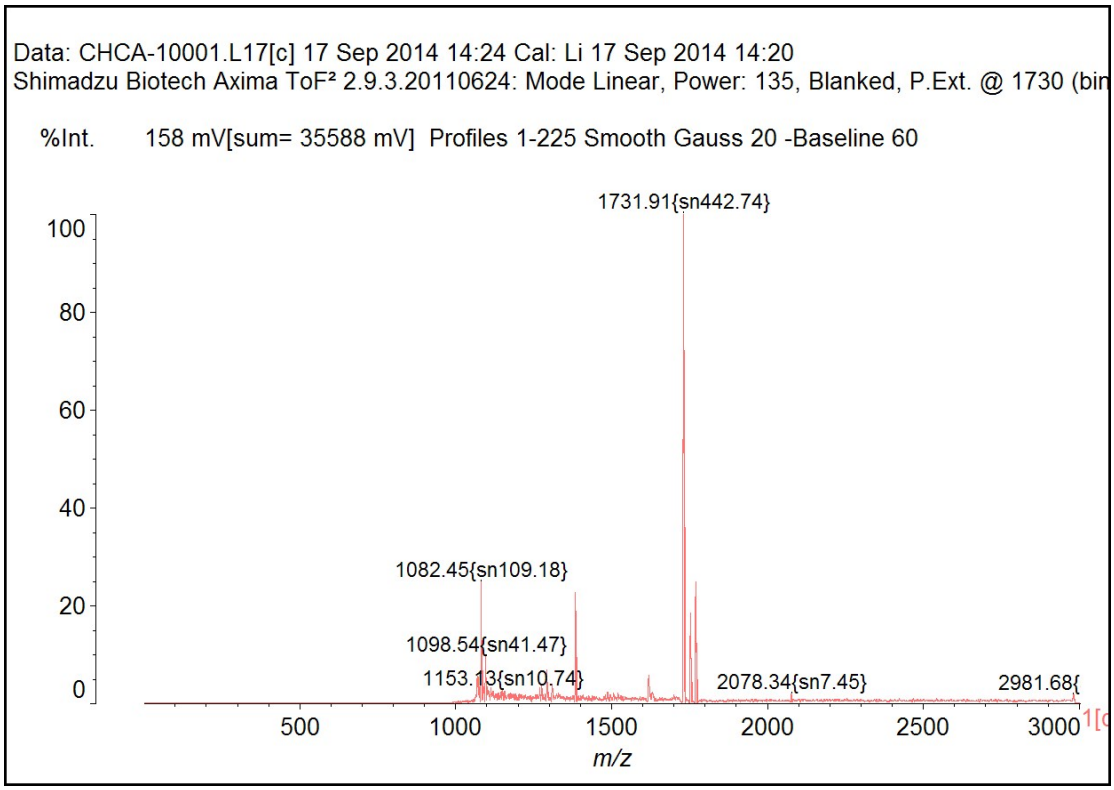

Fig S24 MS (MALDI-TOF) of **5b**.

10.Characterization data and spectra for 5c.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 3.84 – 3.67 (m, 3H), 1.80 – 1.65 (m, 2H), 1.43 (s, 2H), 1.36 – 1.22 (m, 8H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.40, 127.59, 114.89, 68.45, 31.99, 29.93, 29.68, 29.44, 26.40, 22.74, 14.16. MS (MALDI-TOF) calcd. for $C_{115}H_{190}O_{10}$ $[M+H]^+$ 2078.7264, found 2078.64.

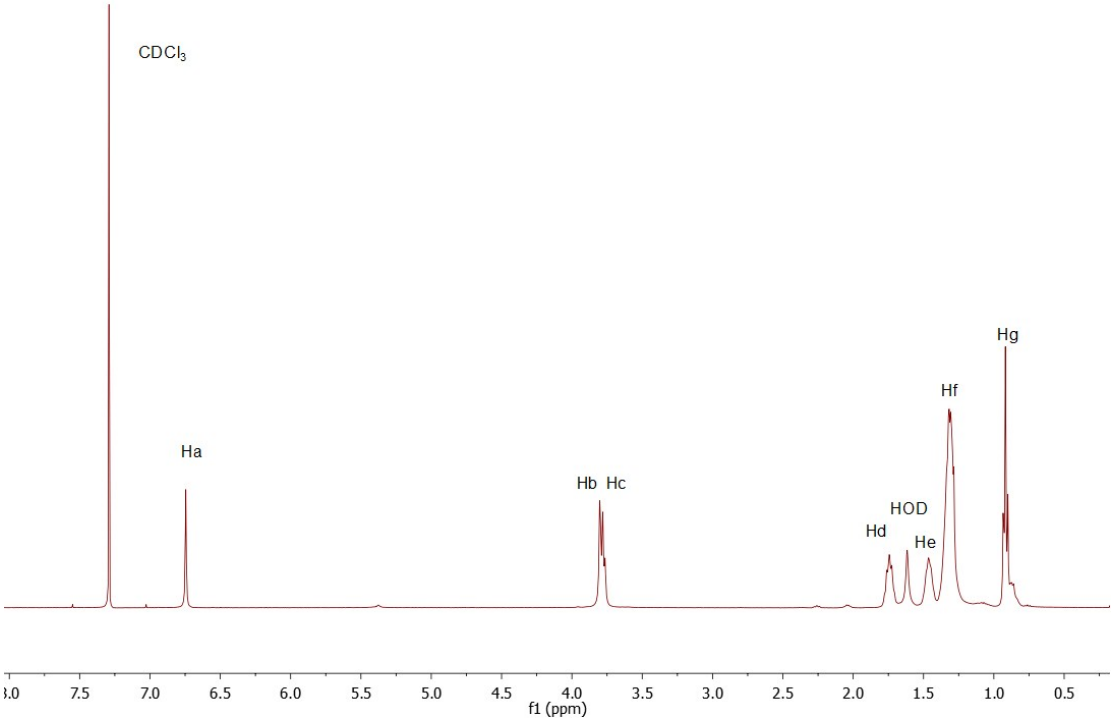

Fig S25 ^{1}H NMR spectrum of **5c** ($CDCl_3$; 400MHz).

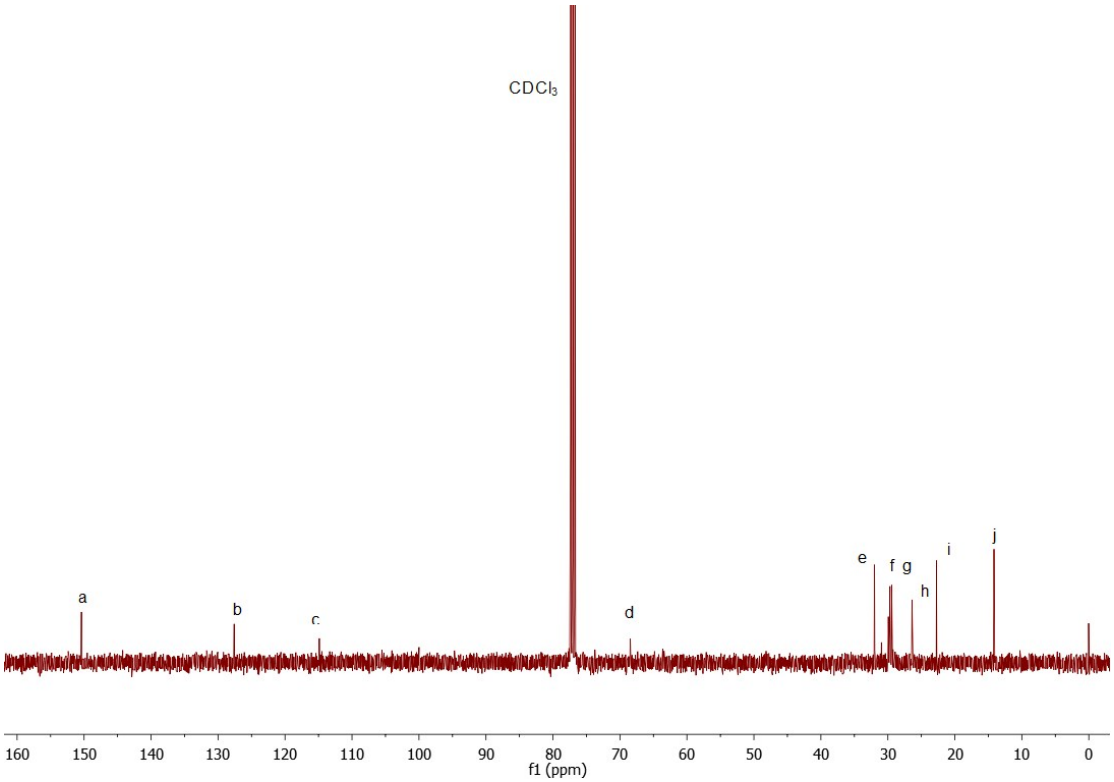

Fig S26 ^{13}C NMR spectrum of **5c** ($CDCl_3$; 100MHz).

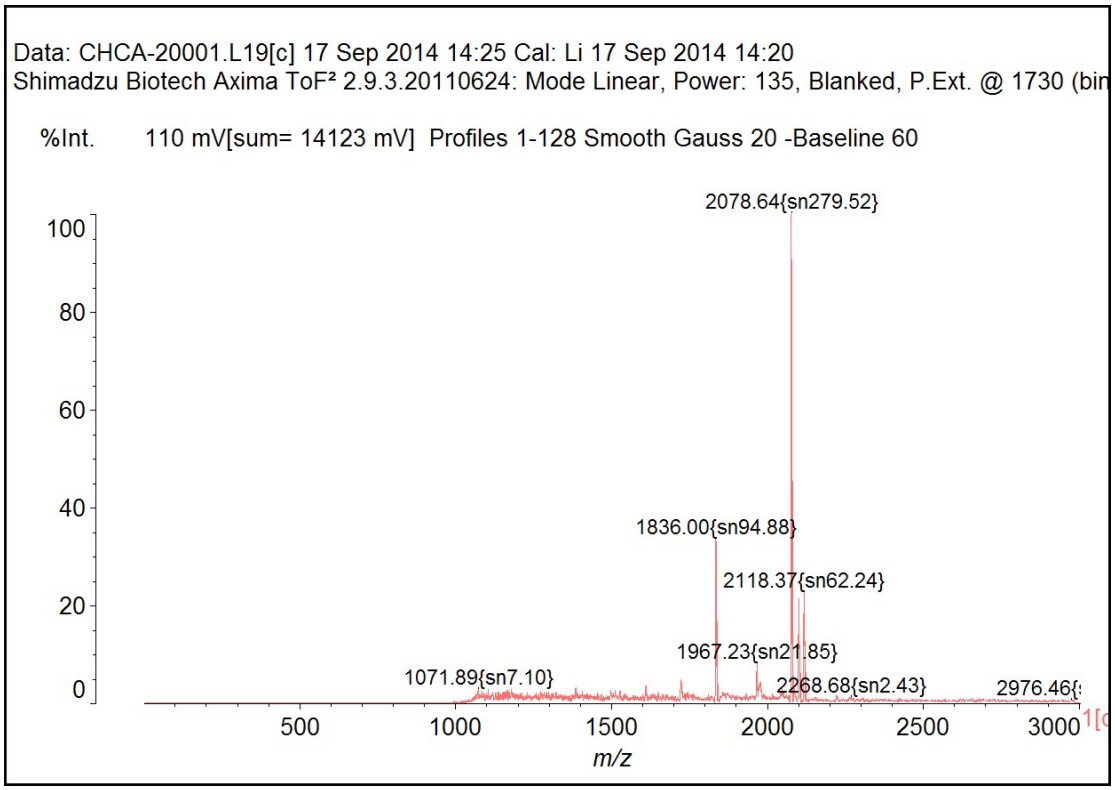

Fig S27 MS (MALDI-TOF) of **5c**.

11.Reference

S1 P. Paduraru, R. Popoff, R. Nair, R. Gries, G. Gries and E. Plettner, J. Comb. Chem. 2008, 10, 123–134.