Synthesis and structural characterization of metal complexes with macrocyclic tetracarbene ligands

Fan Fei,[a] Taotao Lu,[a] Xue-Tai Chen,[a*] Zi-Ling Xue[b]

[a]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China. E-mail: xtchen@nju.edu.cn*

[b]*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA.*

Electronic Supplementary Information

Table S1 Summary of Crystallographic Data for **1-3**

Compound	**1**·2DMF	**2**·2DMF	**3**
CCDC No.	1543852	1543853	1543854
Formula	$C_{46}H_{54}N_{10}F_{12}O_2Ag_2P_2$	$C_{48}H_{62}N_{10}F_{18}O_4Ag_3P_3$	$C_{132}H_{144}N_{24}F_{36}Ag_6P_6$
Formula weight	1284.67	1601.60	3576.71
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P\,2_1/c$	$P\,2_1/c$	$F\,ddd$
Crystal size (mm)	0.27×0.21×0.18	0.21×0.18×0.15	0.27×0.21×0.18
a(Å)	13.6857(12)	12.7364(12)	31.573(2)
b(Å)	19.1641(16)	30.092(3)	43.500(2)
c(Å)	20.6310(18)	16.1895(16)	45.318(3)
α(°)	90	90	90
β(°)	105.861(2)	98.396(2)	90
γ(°)	90	90	90
V(Å^3)	5205.0(8)	6138.4(11)	62242(7)
D_{calc} (g/cm^3)	1.641	1.733	1.530
Z	4	4	8
T(K)	296	296	120(2)
Radiation (MoKa)	0.71073	0.71073	0.71073
F (000)	2596	3200	28800
absorpt_coefficient (mm^{-1})	0.905	1.131	0.898
θ range (°)	1.477 to 25.019	1.44 to 25.020	0.915 to 25.019
Data/restr/paras	9177/697/295	10719/791/425	13704/955/576
Reflections collected	28849	41247	114889
Reflns obs. [I >2б(I)]	7323	6298	10279
R_{int}	0.0365	0.1178	0.0571
GOF	1.050	1.098	0.991
R_1/wR_2 [I >2б(I)] [a]	0.0459/0.1300	0.0895 / 0.2204	0.0973/0.2627
R_1/wR_2 (all data)	0.0607 /0.1427	0.1426 / 0.2525	0.1189/0.2792
Larg peak and hole(e/Å^3)	1.005/-0.717	1.656 / -0.966	1.577/-0.908

[a] $R_1 = \Sigma||F_o|-|Fc||/\Sigma|F_o|$; w$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

Table S2 Summary of Crystallographic Data for **6-8**

Compound	**6**	**7**	**8**
CCDC No.	1543855	1543856	1543857
Formula	$C_{40}H_{40}N_8F_{12}NiP_2$	$C_{42}H_{44}N_8F_{12}$ NiP_2	$C_{44}H_{48}N_8F_{12}$ NiP_2
Formula weight	981.45	1009.50	1037.55
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P\ 2_1/n$	P-1	P-1
Crystal size (mm)	0.26×0.22×0.19	0.22×0.11×0.09	0.22×0.11x0.09
a(Å)	16.245(3)	13.072(3)	12.7750(11)
b(Å)	14.013(3)	14.373(3)	14.4409(13)
c(Å)	20.618(4)	15.647(4)	16.4321(14)
α(°)	90.00	71.028(4)	78.288(3)
β(°)	93.493(4)	71.887(4)	71.501(3)
γ(°)	90.00	65.687(4)	63.7750(10)
V(Å^3)	4684.8(16)	2479.5(10)	2571.9(4)
D_{calc} (g/cm^3)	1.392	1.352	1.340
Z	4	2	2
T(K)	296	120	190
Radiation (MoKa)	0.71073	0.71073	0.71073
F (000)	2008	1036	1068
absorpt_coefficient (mm^{-1})	0.568	0.538	0.521
θ range (°)	1.5 to 27.66	2.36 to 27.00	2.60 to 16.96
Data/restr/paras	10790/697/1834	10688/652/771	9027/623/231
Reflections collected	31772	15800	19591
Reflns obs. [I >2б(I)]	5154	5790	4077
R_{int}	0.0874	0.067	0.0856
GOF	1.051	1.069	1.038
R_1/wR_2 [I >2б(I)] [a]	0.0793/0.2048	0.0959 / 0.1897	0.0829/0.2113
R_1/wR_2 (all data)	0.1429/0.2348	0.1617 / 0.2073	0.1678 /0.2590
Larg peak and hole(e/Å^3)	0.571/-0.841	1.236 / -0.716	0.554/-0.584

[a] $R_1 = \Sigma||F_o|-|Fc||/\Sigma|F_o|$; w$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

Table S3 Summary of Crystallographic Data for **9-11**

Compound	**9**	**10**	**11**
CCDC No.	1543858	1543859	1543860
Formula	$C_{40}H_{40}N_8F_{12}PdP_2$	$C_{42}H_{44}N_8F_{12}$ PdP_2	$C_{44}H_{48}N_8F_{12}$ PdP_2
Formula weight	1029.14	1057.19	1085.24
Crystal system	Triclinic	Triclinic	Tetragonal
Space group	*P*-1	*P*-1	$P\,4_32_12$
Crystal size (mm)	0.32×0.30×0.11	0.17×0.15×0.12	0.26×0.23×0.21
a(Å)	12.925(4)	11.4236(19)	20.0846(7)
b(Å)	13.073(4)	13.822(2)	20.0846(7)
c(Å)	16.324(6)	15.218(2)	38.506(2)
α(°)	75.270(7)	90.046(4)	90
β(°)	69.306(7)	96.534(4)	90
γ(°)	66.767(6)	102.324(4)	90
V(Å^3)	2350.0(14)	2331.5(6)	15533.1(14)
D_{calc} (g/cm^3)	1.454	1.506	1.392
Z	2	2	12
T(K)	153	296	153
Radiation (MoKa)	0.71073	0.71073	0.71073
F (000)	1040	1072	6624
absorpt_coefficient (mm^{-1})	0.548	0.555	0.501
θ range (°)	2.314 to 27.00	2.05 to 27.51	2.028 to 25.019
Data/restr/paras	10118/697/1906	10612/586/6	13712/926/208
Reflections collected	14560	19199	112367
Reflns obs. [I >2б(I)]	7036	5615	11378
R_{int}	0.0558	0.1225	0.1059
GOF	1.055	1.057	1.097
R_1/wR_2 [I >2б(I)] [a]	0.0613/0.1422	0.1032 / 0.2004	0.0663/0.1685
R_1/wR_2 (all data)	0.0969/0.1579	0.1858 / 0.2254	0.0802 /0.1758
Larg peak and hole(e/Å^3)	1.566/-0.880	1.792 / -1.108	0.642/-0.593

[a] $R_1 = \Sigma||F_o|-|Fc||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

Table S4 Summary of Crystallographic Data for **12-14**

Compound	**12**	**13**	**14**
CCDC No.	1543861	1543862	1543863
3Formula	$C_{40}H_{40}N_8F_{12}PtP_2$	$C_{42}H_{44}N_8F_{12}$ PtP_2	$C_{44}H_{48}N_8F_{12}$ PtP_2
Formula weight	1117.83	1145.88	1173.93
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
Crystal size (mm)	0.15×0.13×0.10	0.33×0.30×0.28	0.17×0.15×0.12
a(Å)	12.866(2)	13.4115(8)	12.740(2)
b(Å)	12.956(2)	14.8836(8)	14.279(3)
c(Å)	16.280(3)	15.8680(8)	16.577(3)
α(°)	75.394(4)	92.478(2)	78.433(4)
β(°)	69.092(2)	112.811(2)	71.473(4)
γ(°)	67.037(2)	116.6420(10)	64.699(4)
V(Å^3)	2314.0(7)	2517.5(2)	2577.7(8)
D_{calc} (g/cm^3)	1.604	1.512	1.512
Z	2	2	32
T(K)	190(2)	296	293(2)
Radiation (MoKa)	0.71073	0.71073	0.71073
F (000)	1104	1136	1168
absorpt_coefficient (mm^{-1})	3.188	2.932	2.865
θ range (°)	2.324 to 25.019	2.41 to 27.59	2.509 to 25.020
Data/restr/paras	8068/568/186	11545/650/786	9019/623/224
Reflections collected	12226	22124	14523
Reflns obs. [I >2б(I)]	6151	9389	6359
R_{int}	0.0590	0.0479	0.0595
GOF	1.040	1.021	1.077
R_1/wR_2 [I >2б(I)] [a]	0.0631/0.1476	0.0472 / 0.0923	0.0617/0.1610
R_1/wR_2 (all data)	0.0893/0.1567	0.0658 / 0.0968	0.1010 /0.1718
Larg peak and hole(e/Å^3)	1.920/-3.144	1.981 / -1.102	1.626/-1.416

[a] $R_1 = \Sigma||F_o|-|Fc||/\Sigma|F_o|$; w$R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

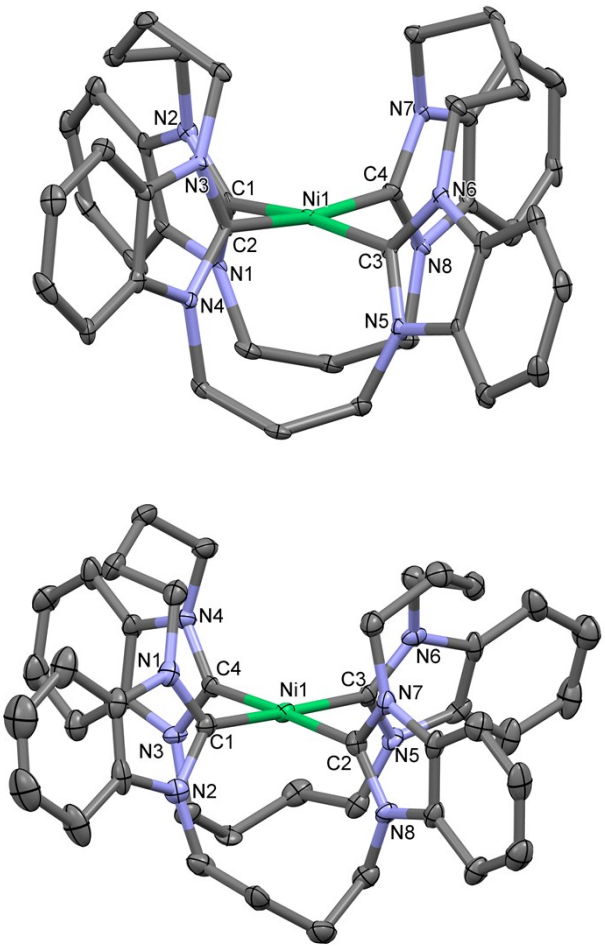

Figure S1 Structures of Ni^{II} complexes **7** (upper) and **8** (bottom) showing 30% probability ellipsoids. The hexafluorophosphate anions and hydrogen atoms are omitted for clarity. Selected bond lengths(Å) and angles(°) of **7**: Ni1-C1 1.946(6), Ni1-C2 1.933(6), Ni1-C3 1.956(6), Ni1-C4 1.954(6), C1-Ni1-C2 94.9(2), C2-Ni1-C3 86.2(2), C3-Ni1-C4 95.8(2), C1-Ni1-C4 84.0(2); **8**: Ni1-C1 1.954(6), Ni1-C2 1.947(7), Ni1-C3 1.941(7), Ni1-C4 1.899(7), C1-Ni1-C2 89.3(3), C2-Ni1-C3 88.1(3), C3-Ni1-C4 90.8(3), C1-Ni1-C4 91.9(3).

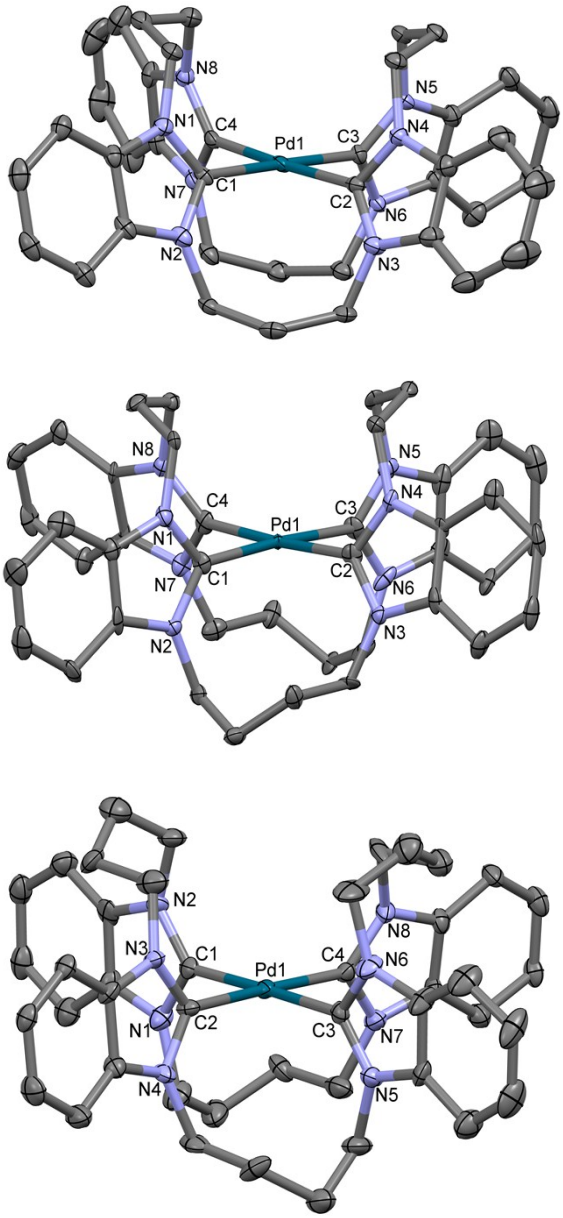

Figure S2 Structures of Pd^{II} complex **9** (upper), **10** (middle) and **11** (bottom) showing 30% probability ellipsoids. The hexafluorophosphate anions and hydrogen atoms are omitted for clarity. Selected bond lengths(Å) and angles(°) of **9**: Pd1-C1 2.044(4), Pd1-C2 2.033(5), Pd1-C3 2.042(4), Pd1-C4 2.025(5), C1-Pd1-C2 92.18(17), C2-Pd1-C3 88.17(17), C3-Pd1-C4 88.60(17), C1-Pd1-C4 91.08(17); **10**: Pd1-C1 2.036(9), Pd1-C2 2.056(9), Pd1-C3 2.056(8), Pd1-C4 2.045(9), C1-Pd1-C2 96.8(3), C2-Pd1-C3 83.7(3), C3-Pd1-C4 95.1(3), C1-Pd1-C4 84.6(3); **11**: Pd1-C1 2.100(10), Pd1-C2 2.029(9), Pd1-C3 2.051(9), Pd1-C4 2.039(9), C1-Pd1-C2 89.3(4), C2-Pd1-C3 89.7(3), C3-Pd1-C4 87.9(3), C1-Pd1-C4 93.2(3).

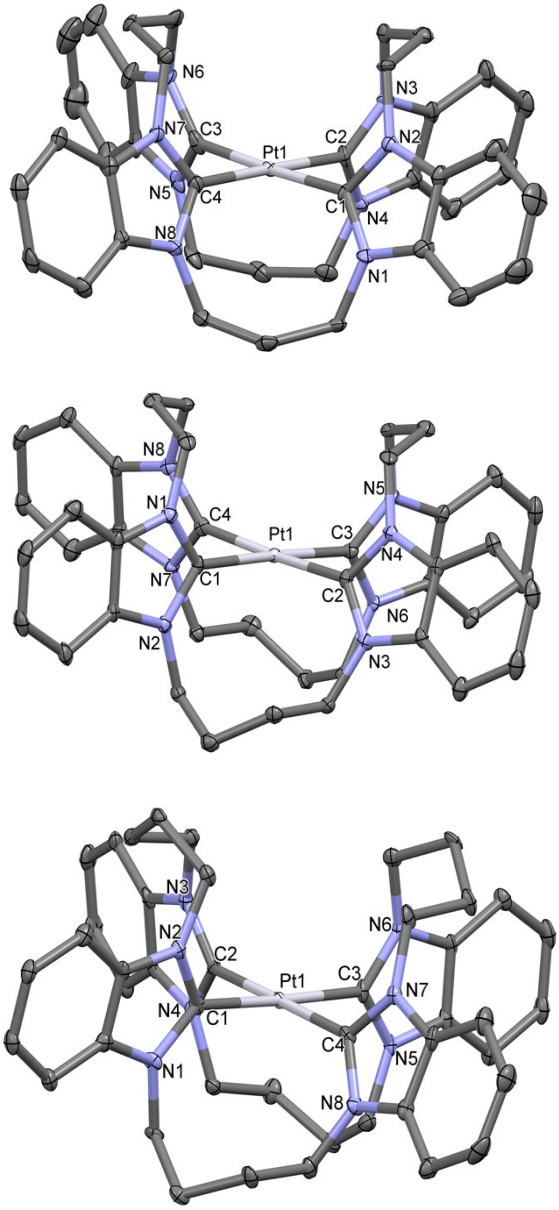

Figure S3 Structures of Pt^{II} complex **12** (upper), **13** (middle) and **14** (bottom) showing 30% probability ellipsoids. The hexafluorophosphate anions and hydrogen atoms are omitted for clarity. Selected bond lengths(Å) and angles(°) of **12**: Pt1-C1 2.017(9), Pt1-C2 2.036(10), Pt1-C3 2.019(8), Pt1-C4 2.041(10), C1-Pt1-C2 89.7(4), C2-Pt1-C3 86.9(4), C3-Pt1-C4 92.1(4), C1-Pt1-C4 91.4(4); **13**: Pt1-C1 2.050(5), Pt1-C2 2.035(5), Pt1-C3 2.041(5), Pt1-C4 2.034(5), C1-Pt1-C2 95.09(19), C2-Pt1-C3 84.30(19), C3-Pt1-C4 96.42(19), C1-Pt1-C4 84.35(19); **14**: Pt1-C1 2.060(9), Pt1-C2 2.081(10), Pt1-C3 2.061(9), Pt1-C4 2.075(10), C1-Pt1-C2 88.4(4), C2-Pt1-C3 89.8(4), C3-Pt1-C4 90.7(4), C1-Pt1-C4 91.1(3).

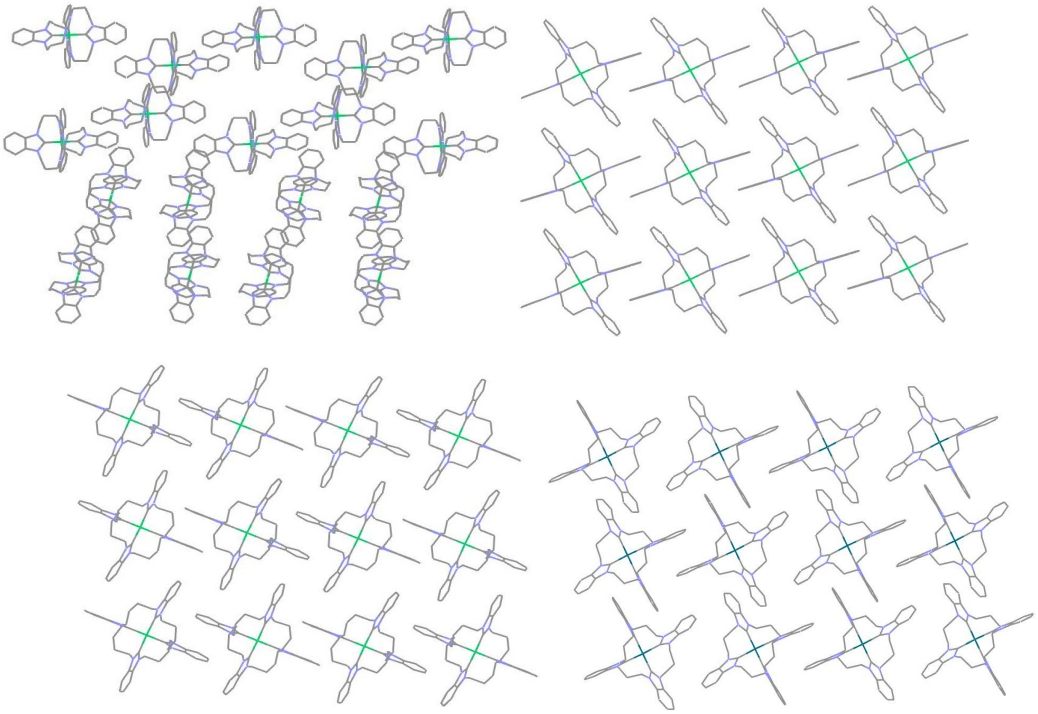

Figure S4 Crystal packing in **6** (top-left), **7** (top-right), **8** (bottom-left), **9** (bottom-right).

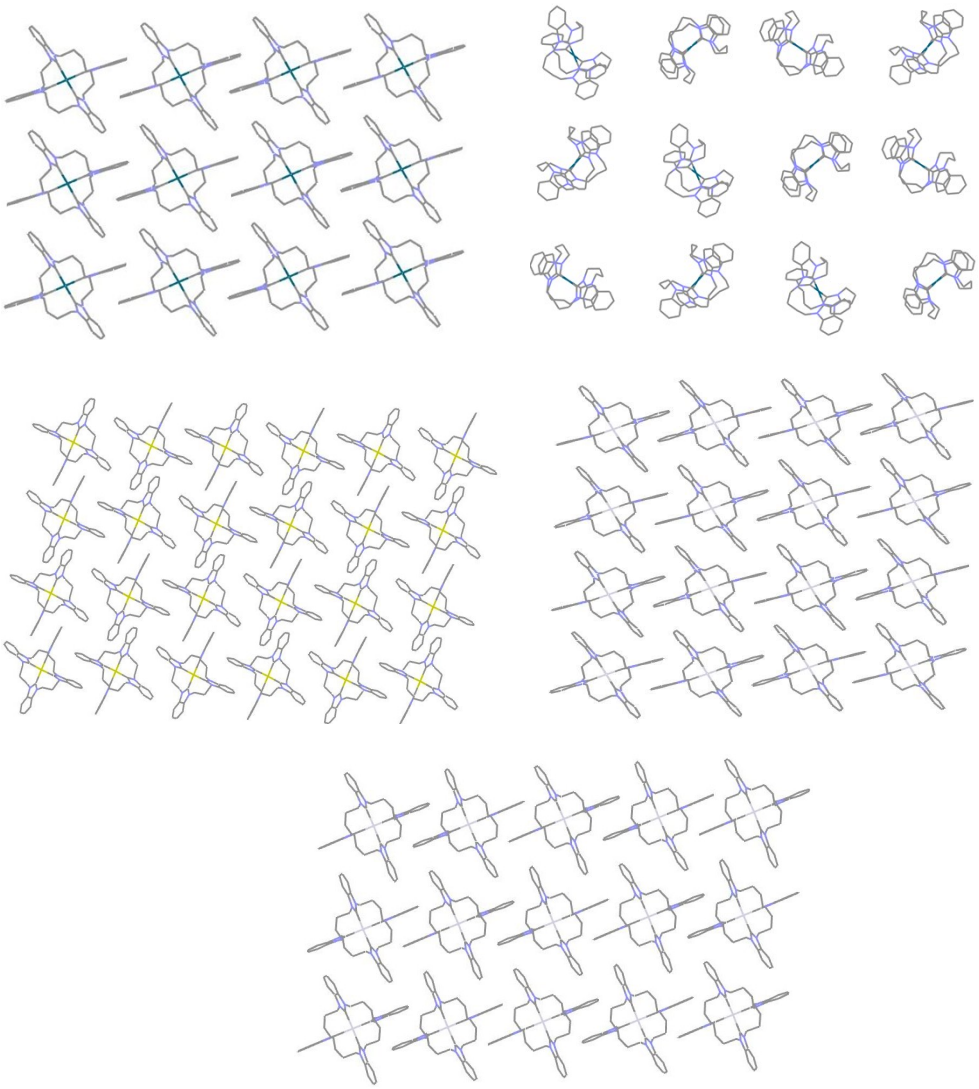

Figure S5 Crystal packing in **10** (top-left), **11** (top-right), **12** (middle-left), **13** (middle-right) and **14** (bottom).

Table S5 π-π stacking interaction distances of **6-14**

	Centroid to centroid [Å]	Face to face [Å]
6	3.589	3.477
7	3.607	3.372
8	3.989	3.464
9	3.761	3.414
10	3.712	3.470
11	null	null
12	3.759	3.418
13	3.617	3.386
14	4.151	3.485

Quantum yields determination

The emission quantum yield (Φ) of $Au_2L^1(PF_6)_2$ (**4**) was determined by respecting to the quantum yield of a reference (Φ_R) using the following equation:[1,2]

$$\Phi = \Phi_R \cdot I/I_R \cdot n^2/n_R^2$$

I is the absorption factor ($f = 1 - 10^{-A}$, where A = absorbance of the solution) vs. integrated emission intensity for **4**. I_R is the absorption factor ($f_R = 1 - 10^{-A_R}$, where A_R = absorbance of the reference solution) vs. integrated emission intensity for the reference solution, n is the refractive index of the solution and n_R is the refractive index of the reference solution. Φ_R is the reported quantum yield of the reference fluorophore.

Quinine sulfate in 0.1 M H_2SO_4 was used as reference solution with $\Phi_R = 0.577$ (T = 22 °C).[1,3] Measurements were performed with excitation wavelengths, λ_{ex} = 345 nm.

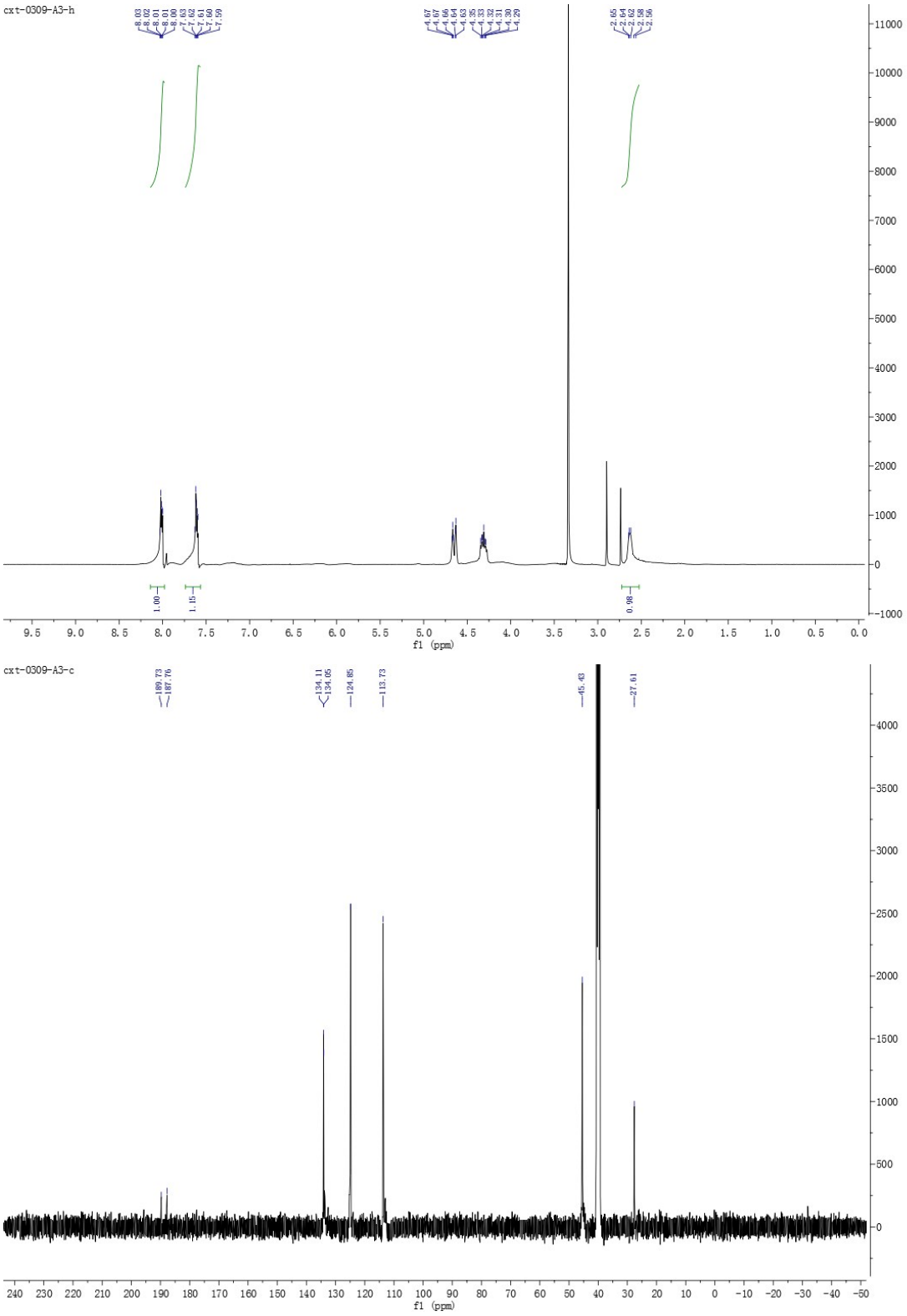

Figure S6 ^{1}H NMR and ^{13}C NMR of **1**

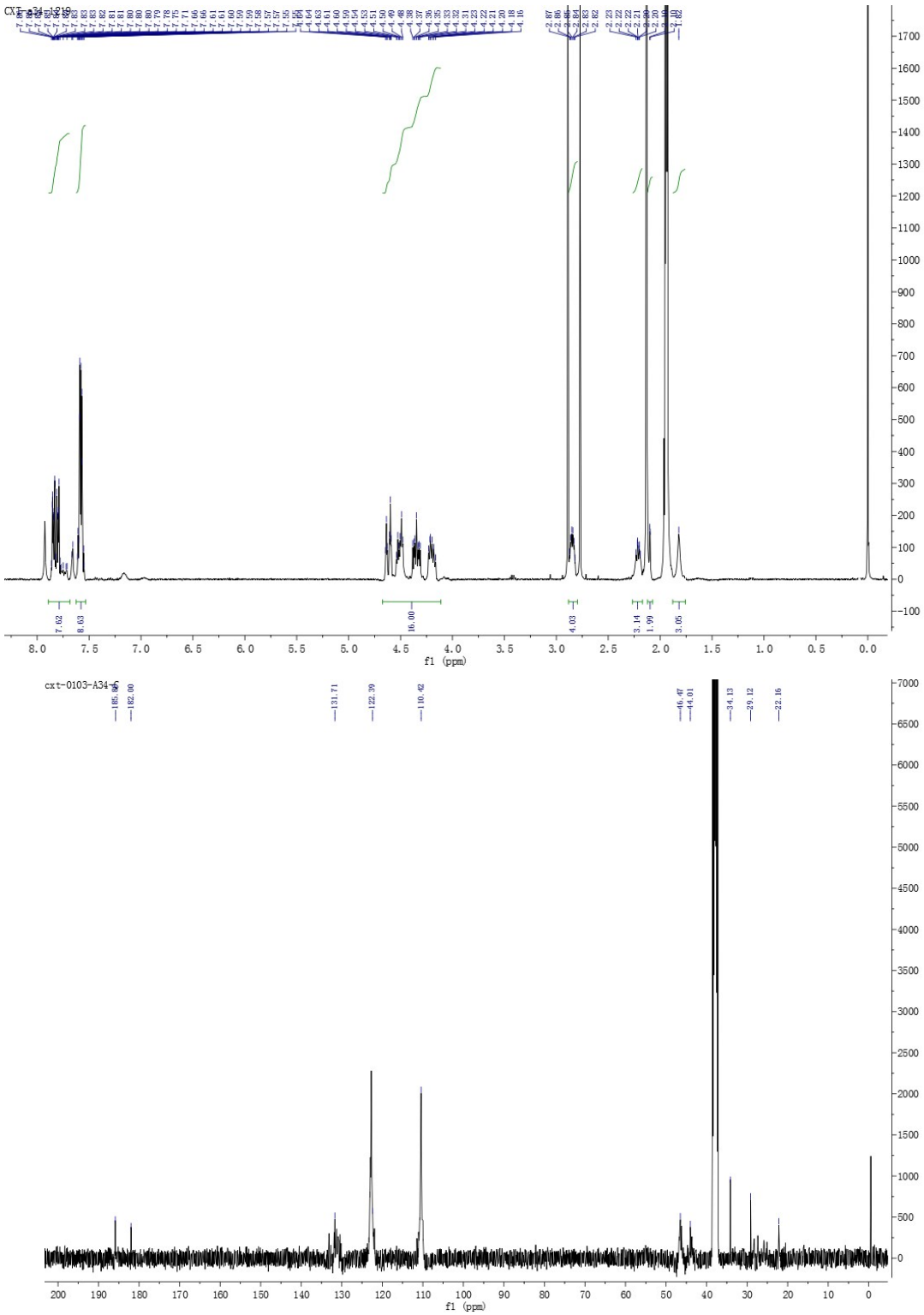

Figure S7 ^{1}H NMR and ^{13}C NMR of **2**

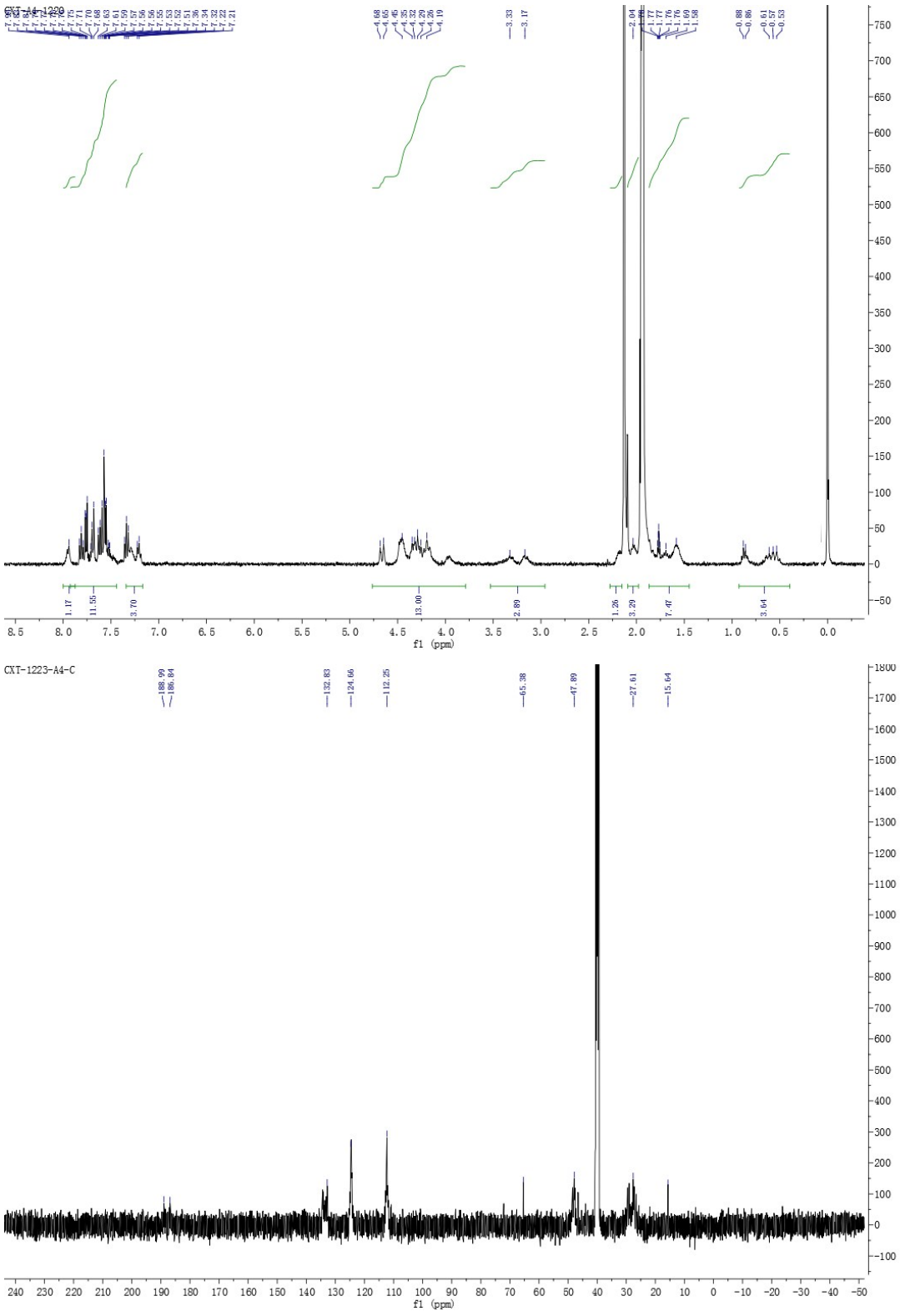

Figure S8 ^{1}H NMR and ^{13}C NMR of **3**

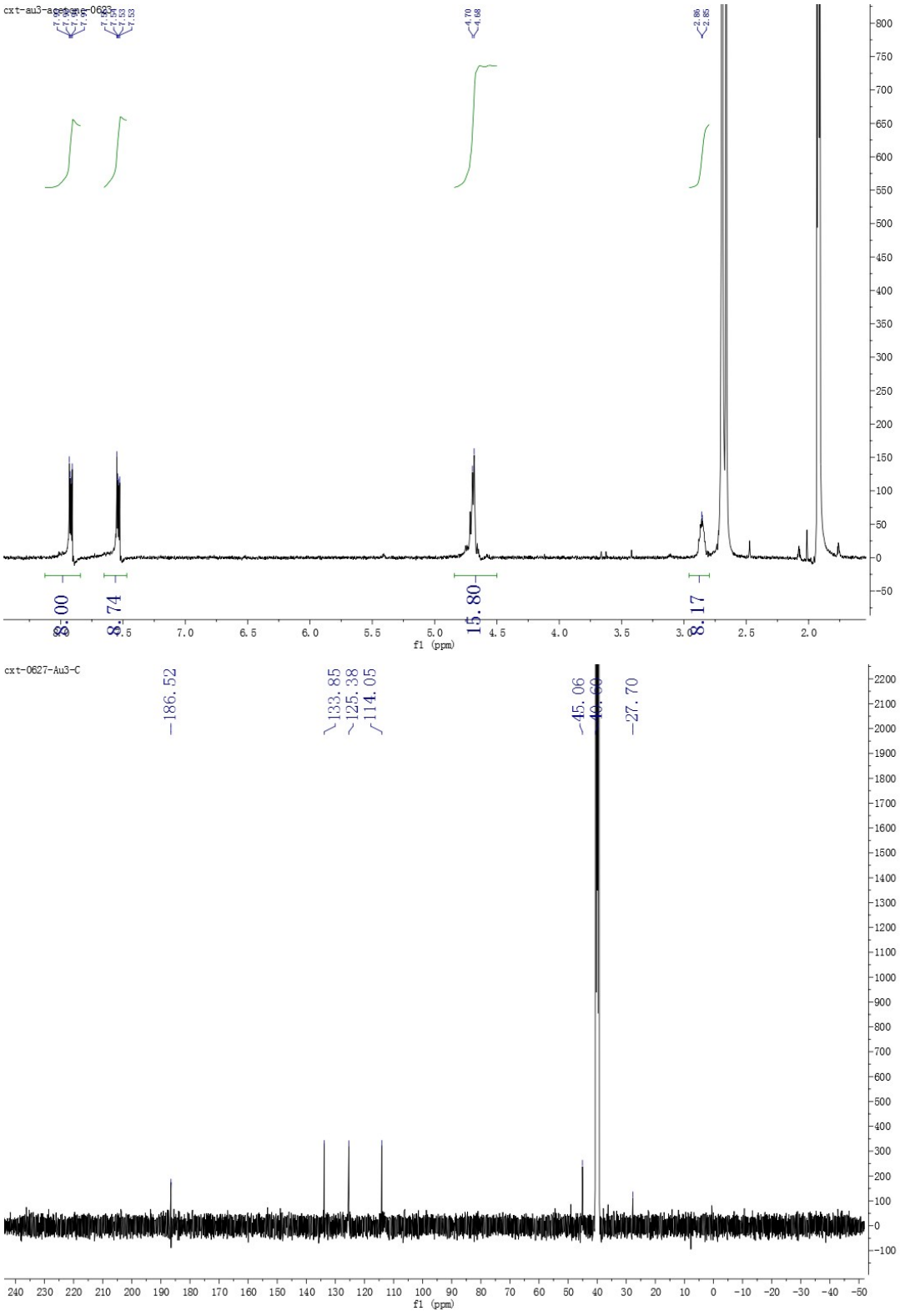

Figure S9 ^{1}H NMR and ^{13}C NMR of **4**

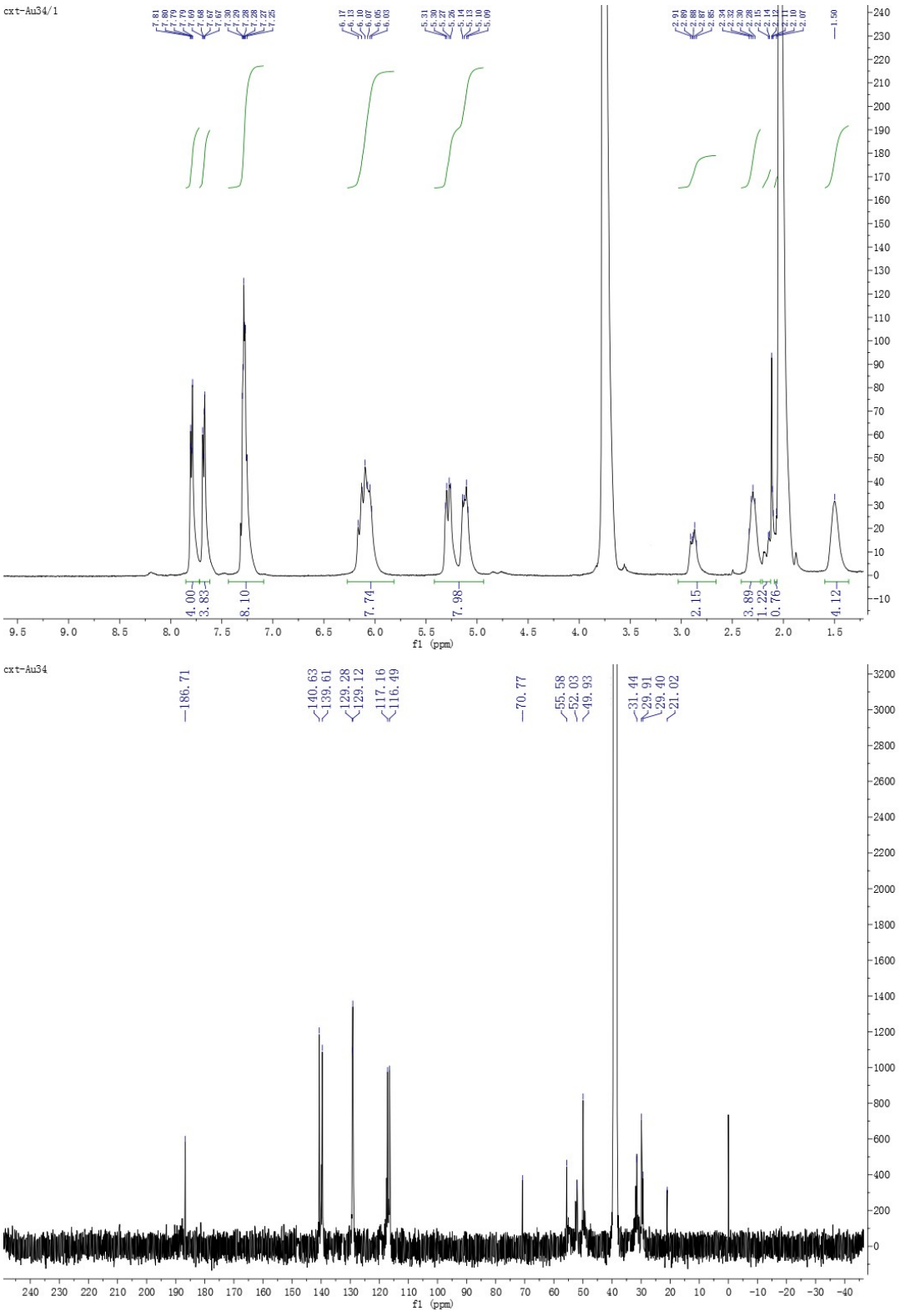

Figure S10 ^{1}H NMR and ^{13}C NMR of **5**

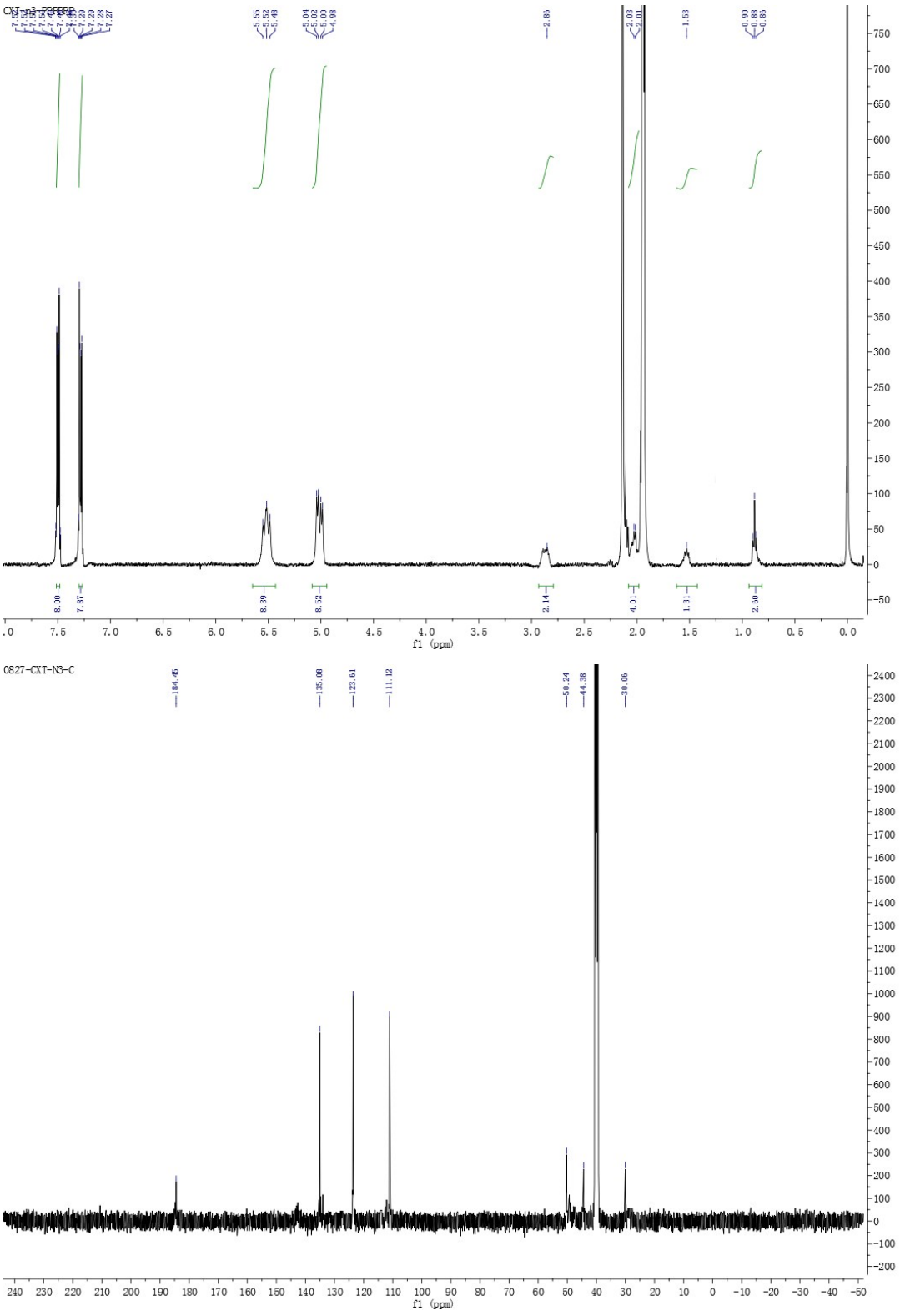

Figure S11 ^{1}H NMR and ^{13}C NMR of **6**

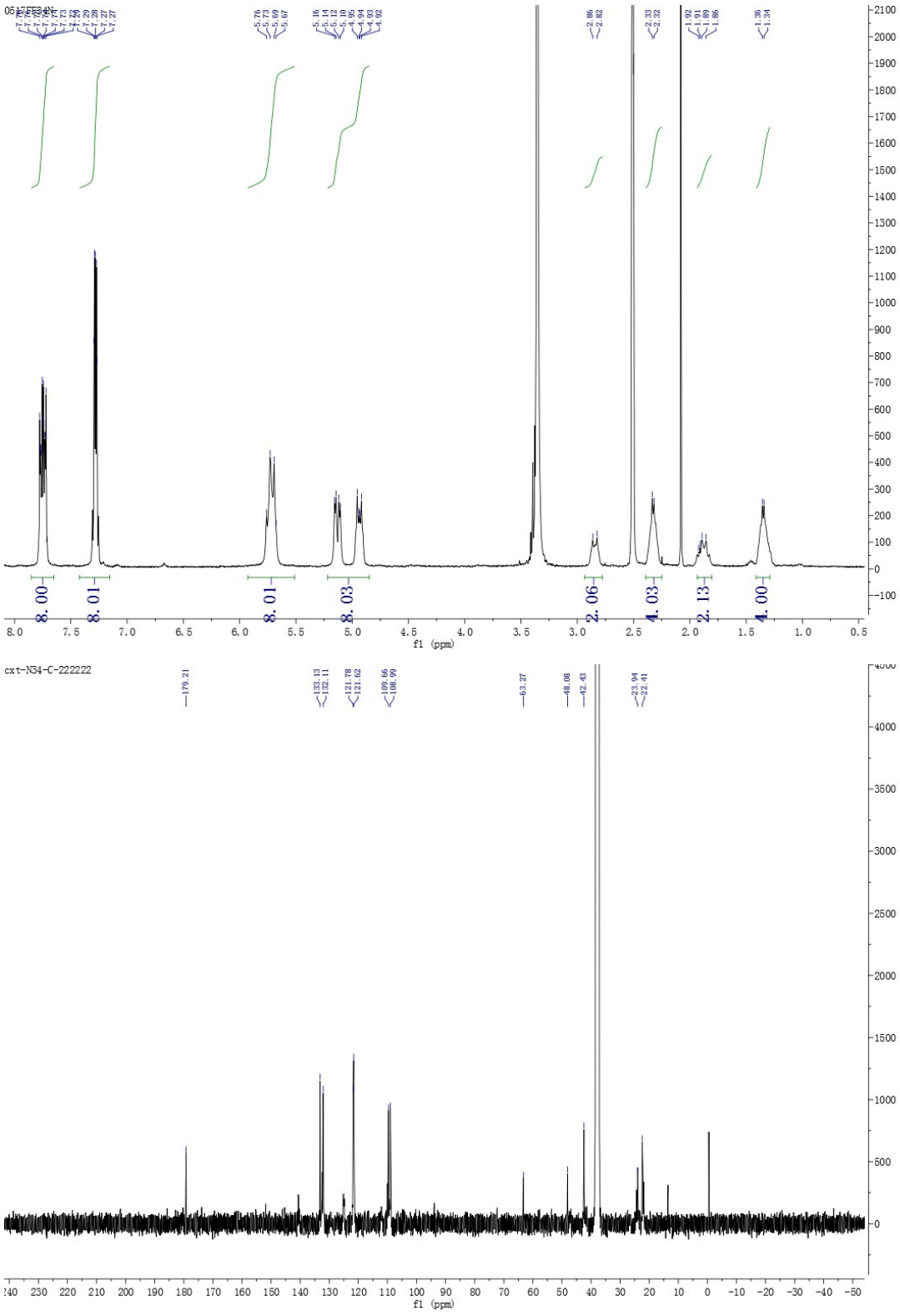

Figure S12 ^{1}H NMR and ^{13}C NMR of **7**

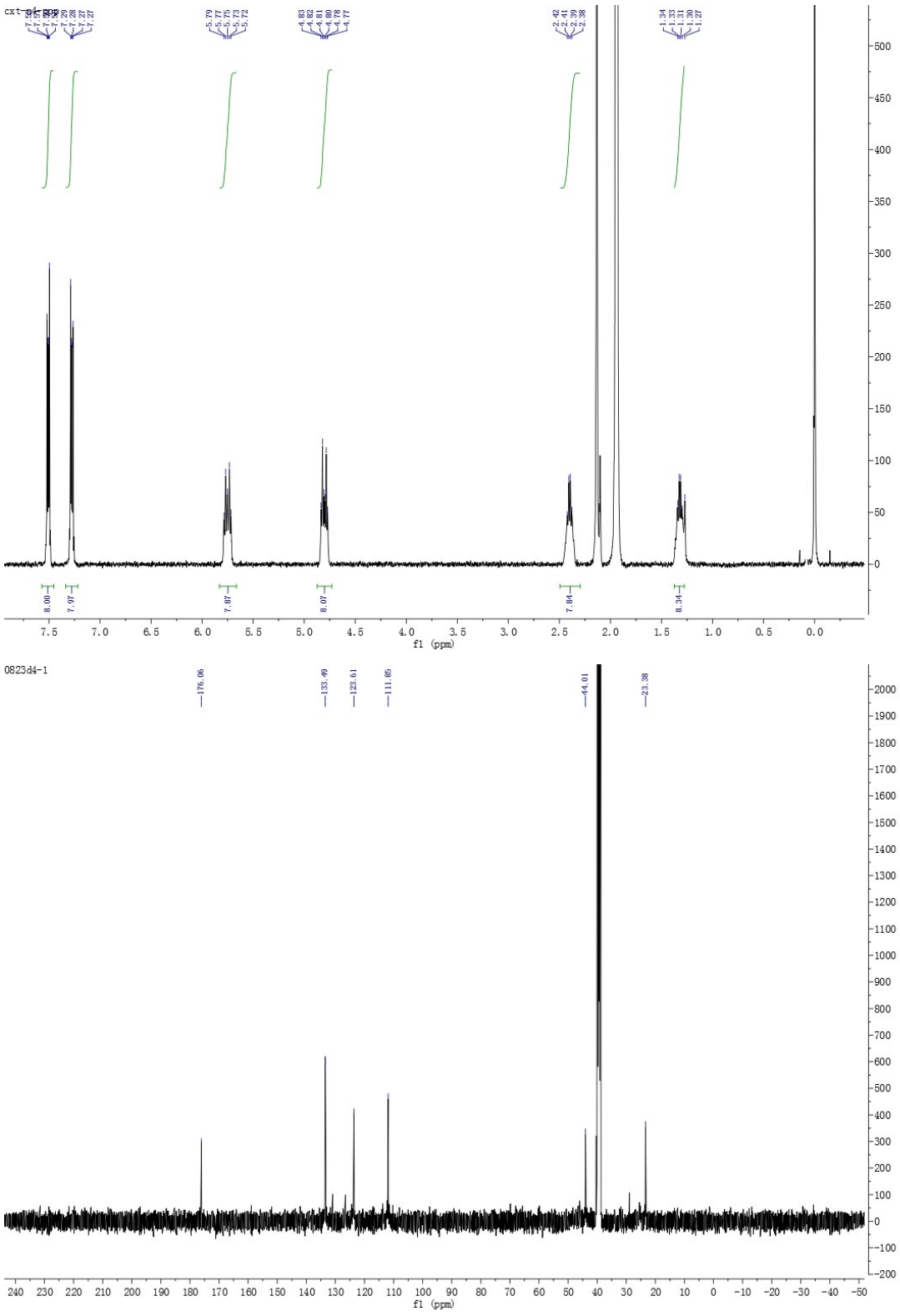

Figure S13 ^{1}H NMR and ^{13}C NMR of **8**

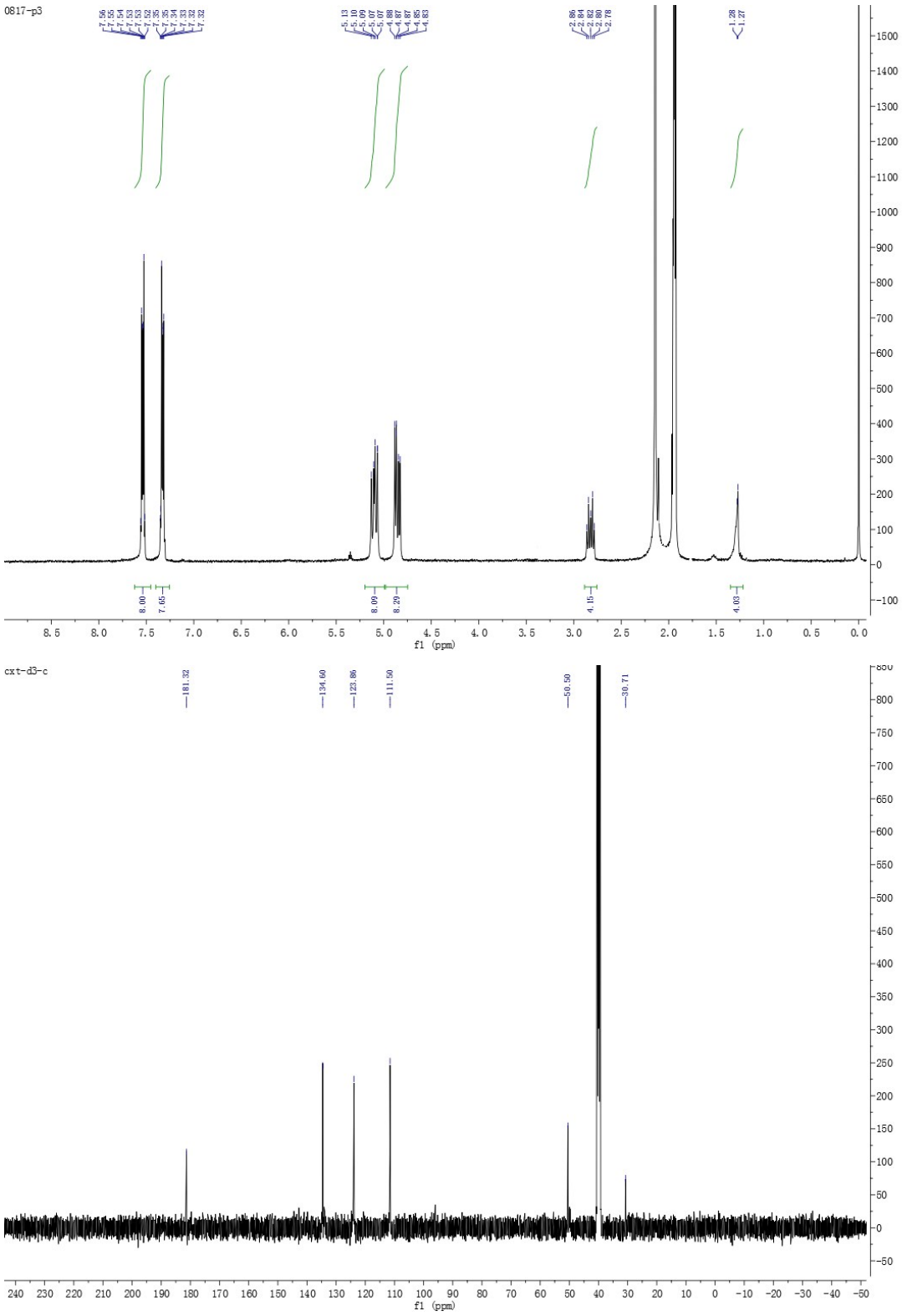

Figure S14 ^{1}H NMR and ^{13}C NMR of **9**

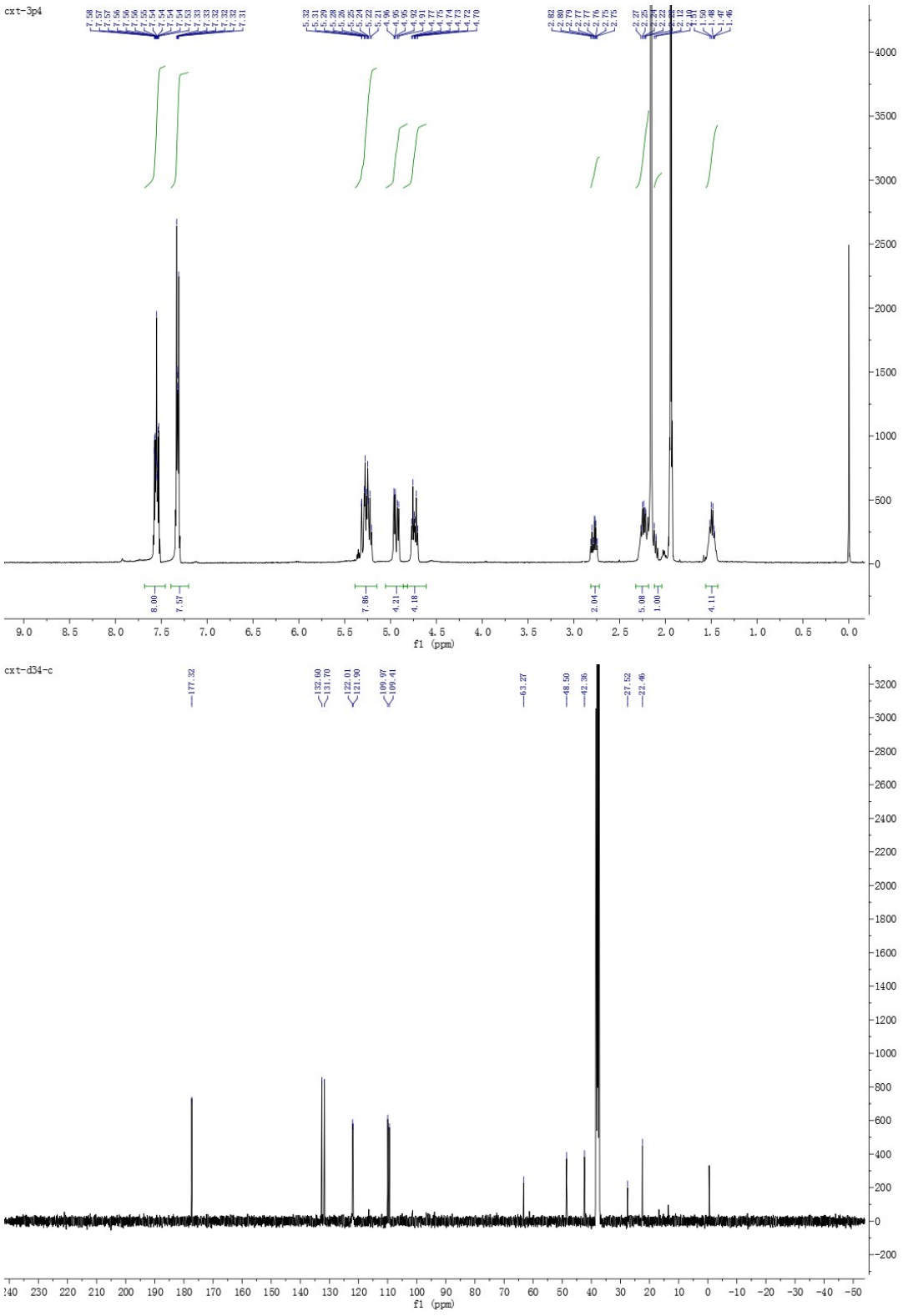

Figure S15 ^{1}H NMR and ^{13}C NMR of **10**

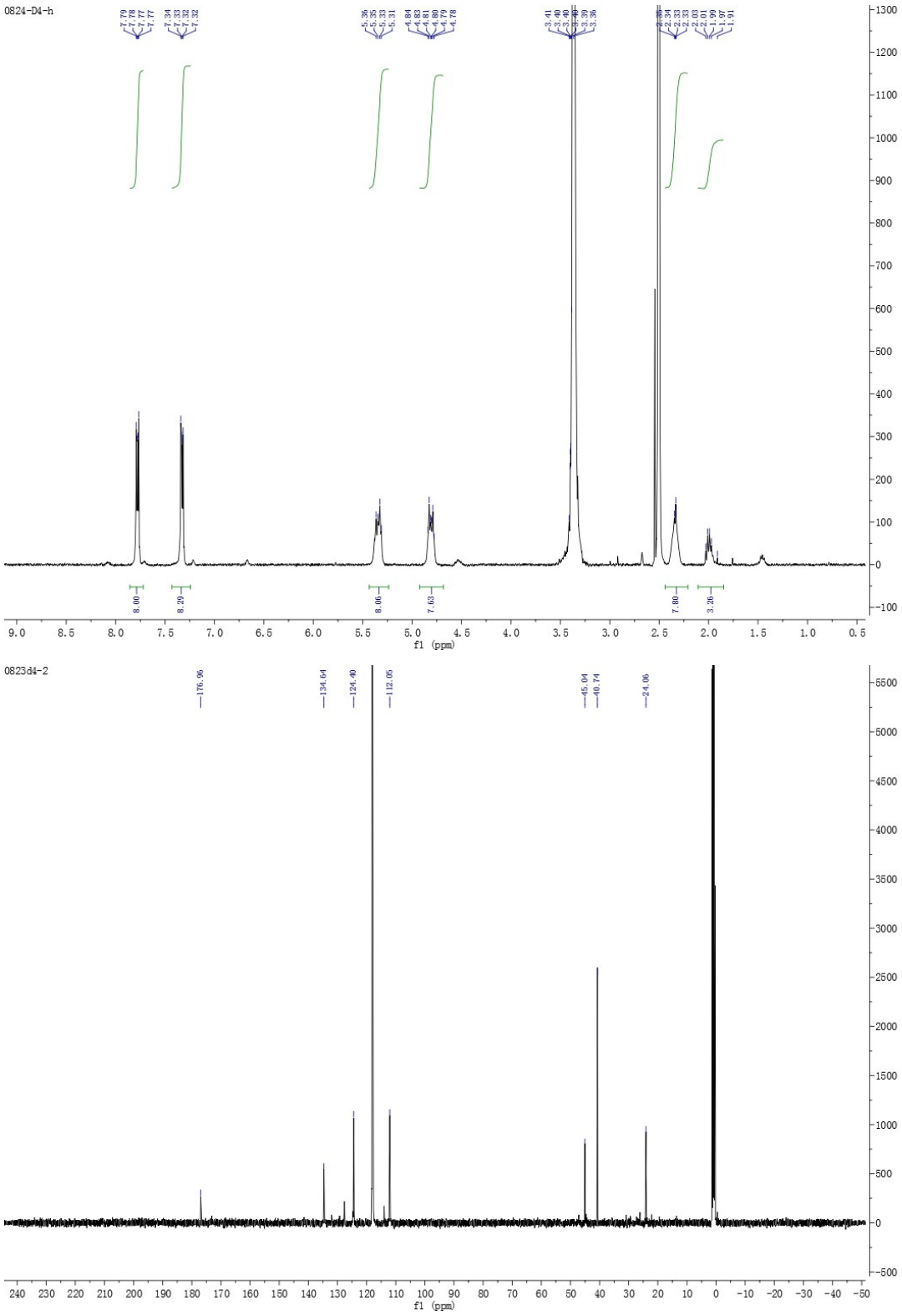

Figure S16 ^{1}H NMR and ^{13}C NMR of **11**

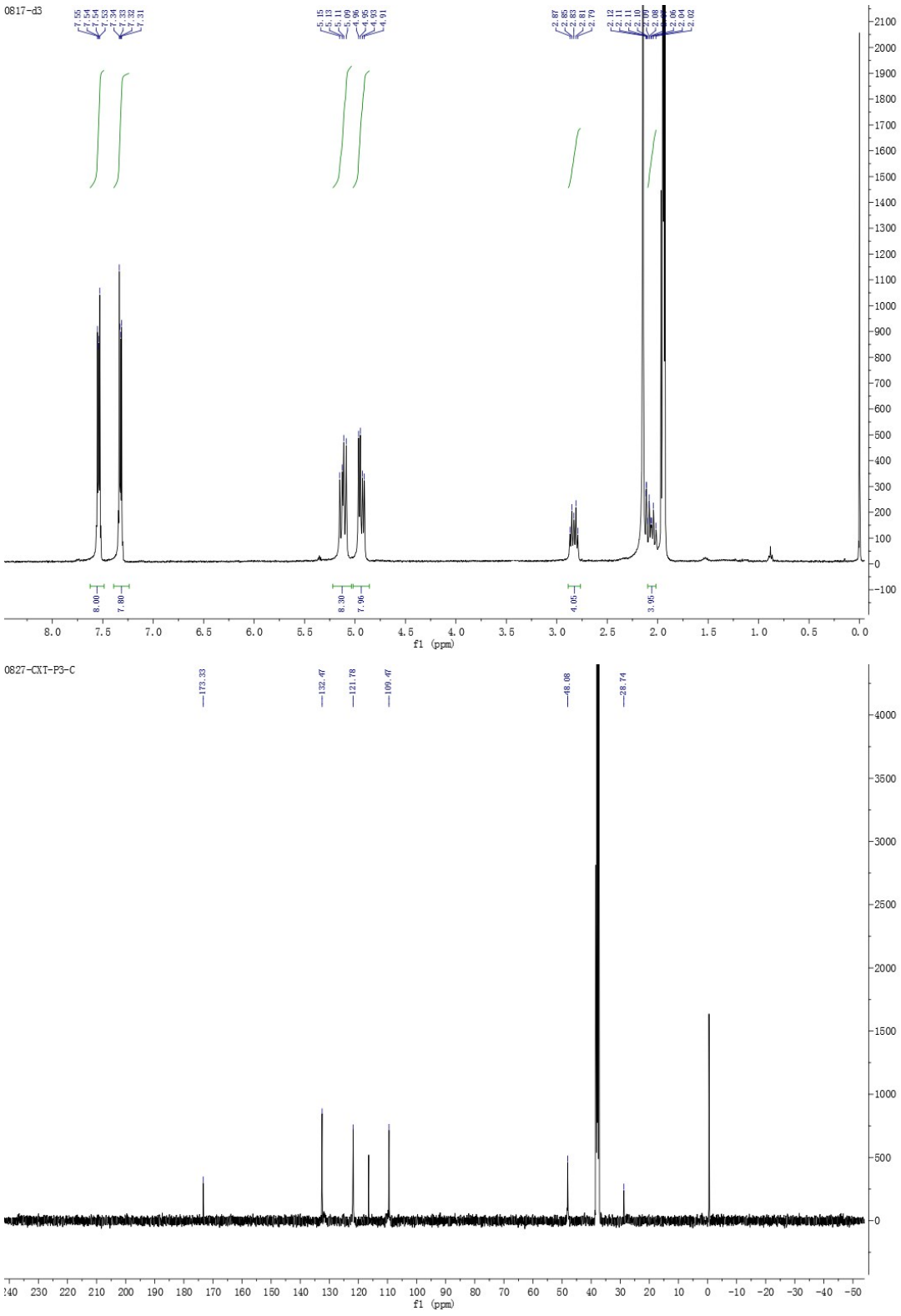

Figure S17 ^{1}H NMR and ^{13}C NMR of **12**

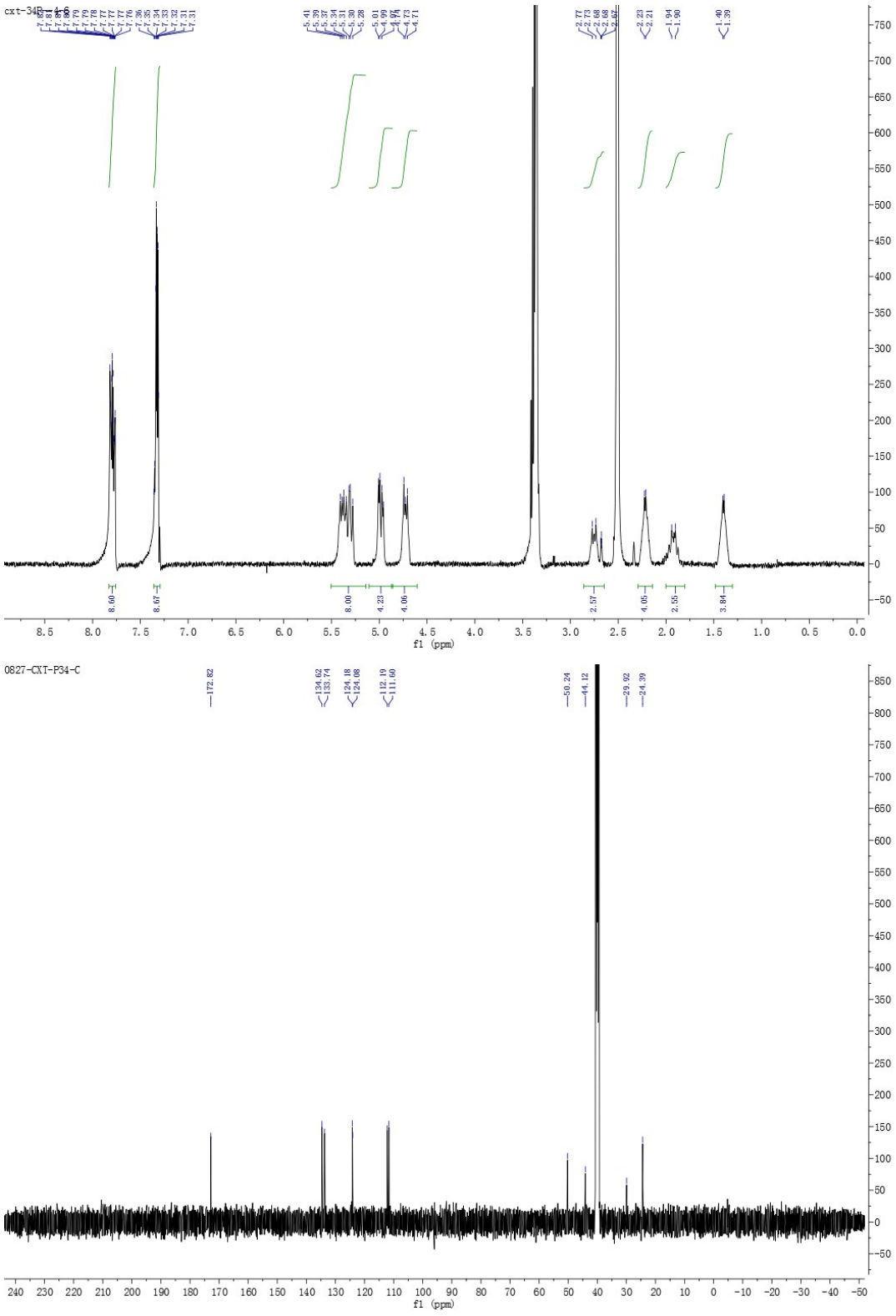

Figure S18 ^{1}H NMR and ^{13}C NMR of **13**

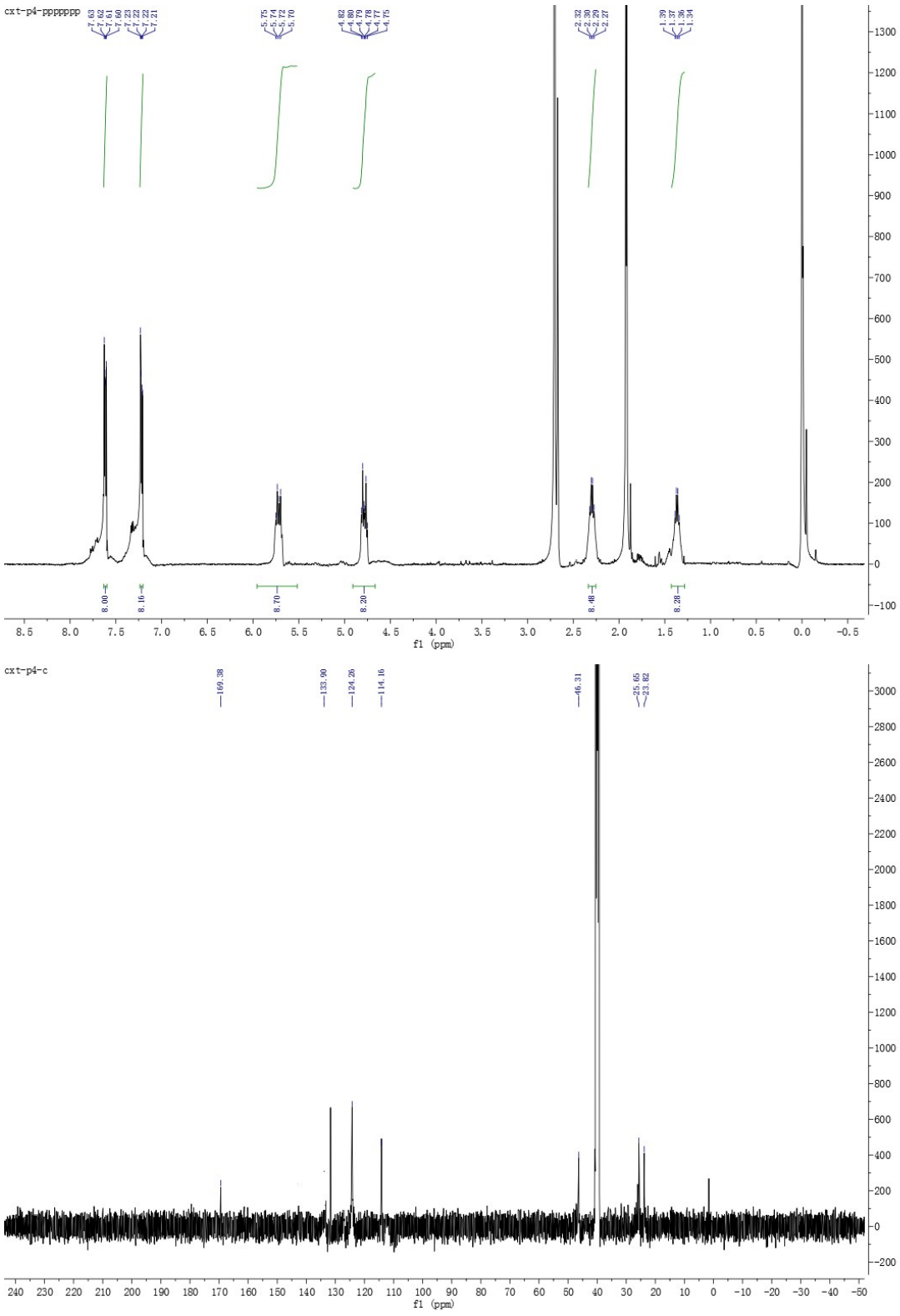

Figure S19 ^{1}H NMR and ^{13}C NMR of **14**

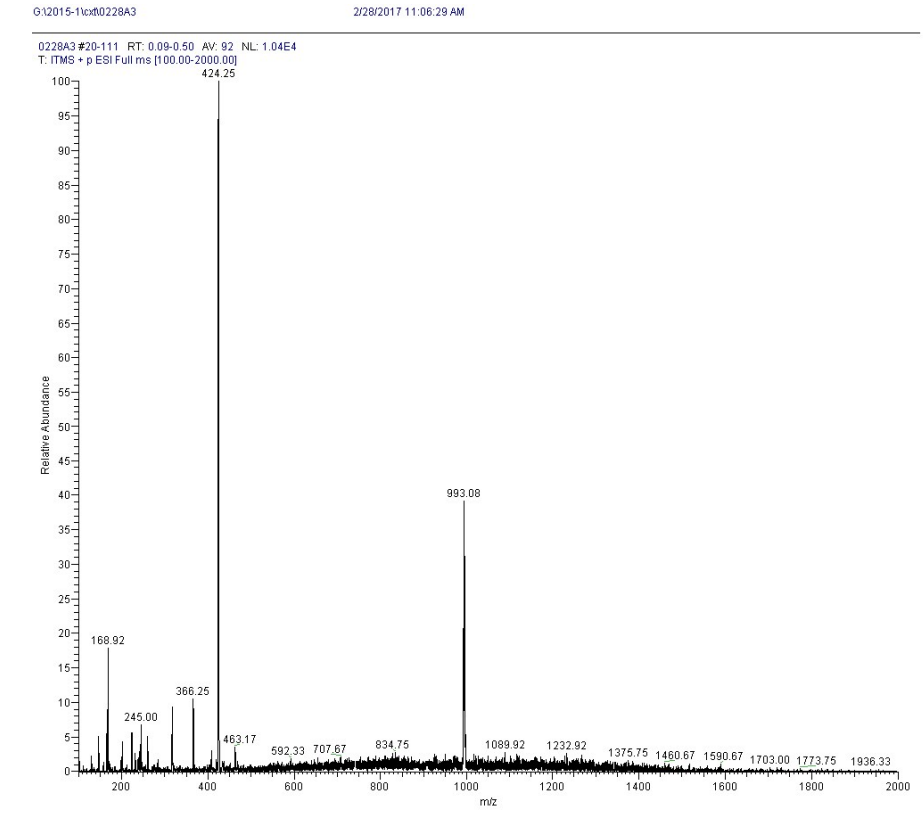

Figure S20 ESI-MS of **1**

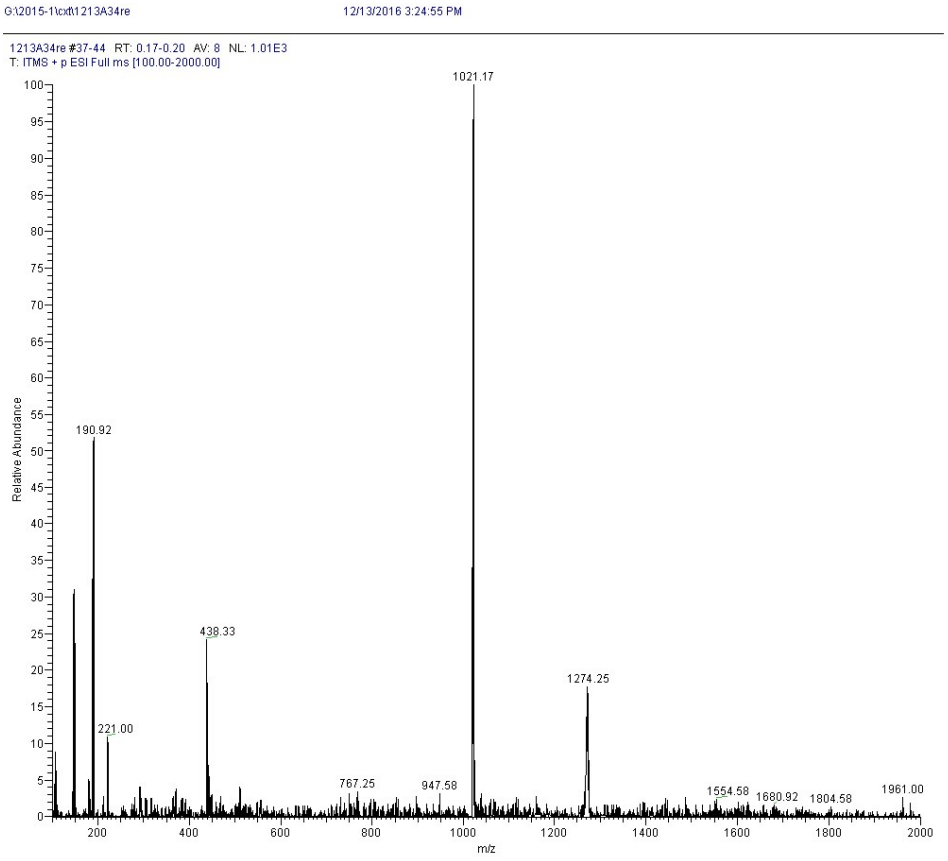

Figure S21 ESI-MS of **2**

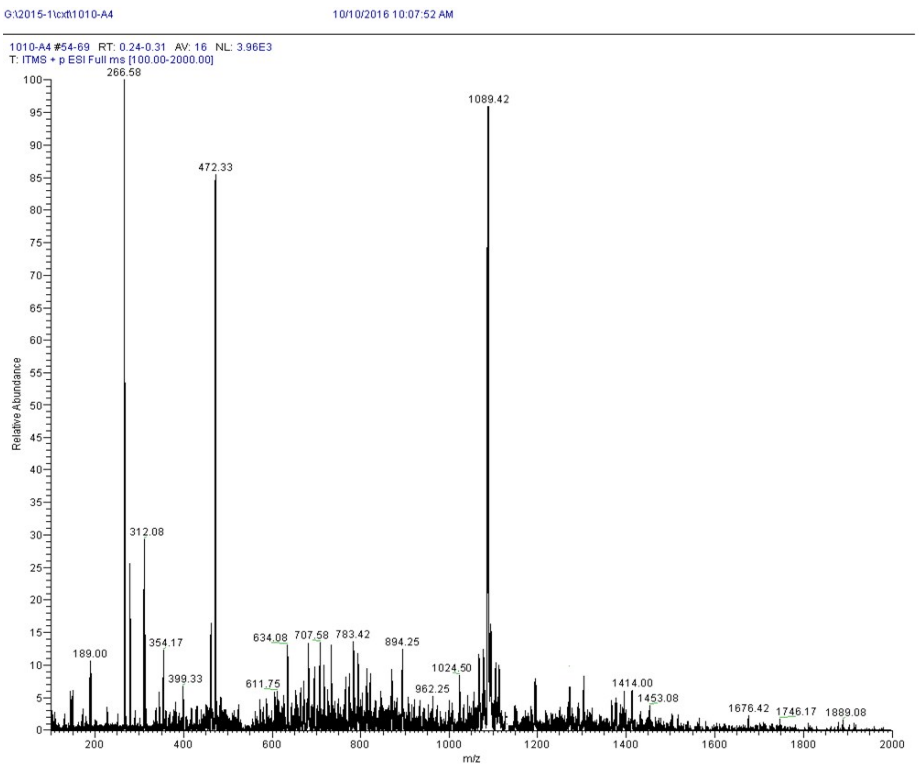

Figure S22 ESI-MS of **3**

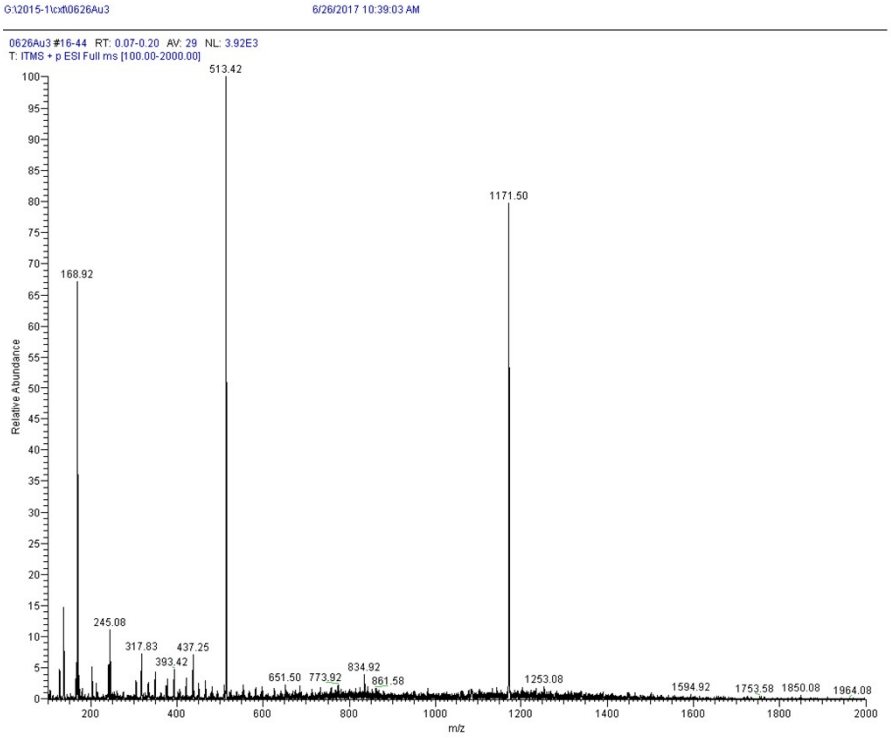

Figure S23 ESI-MS of **4**

Figure S24 ESI-MS of **5**

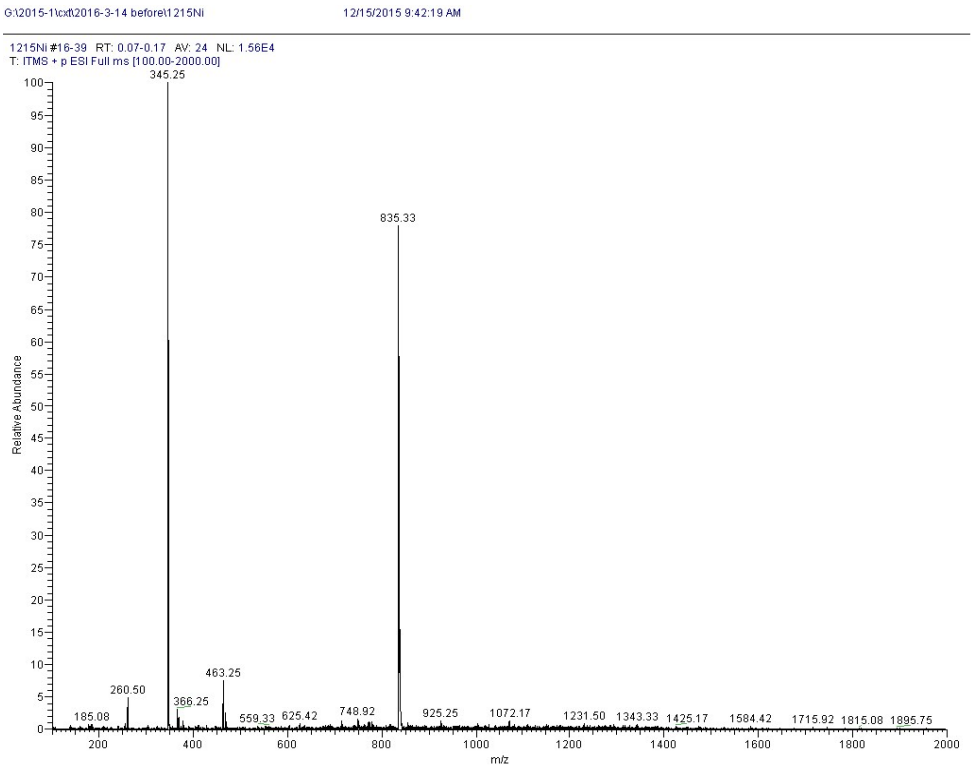

Figure S25 ESI-MS of **6**

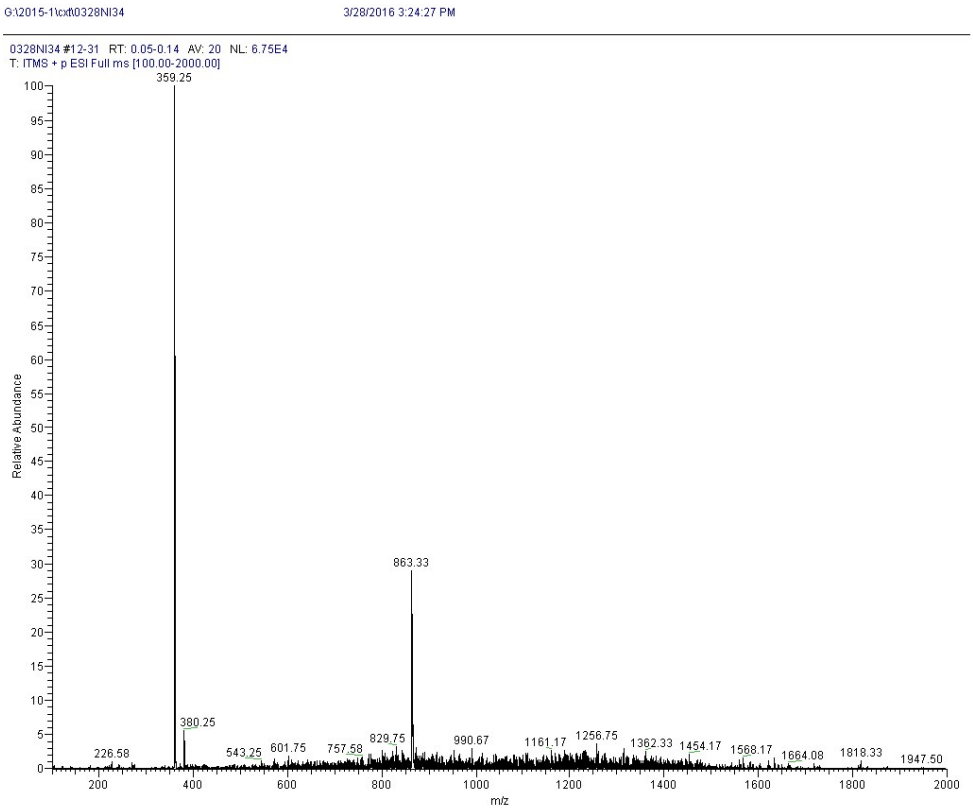

Figure S26 ESI-MS of **7**

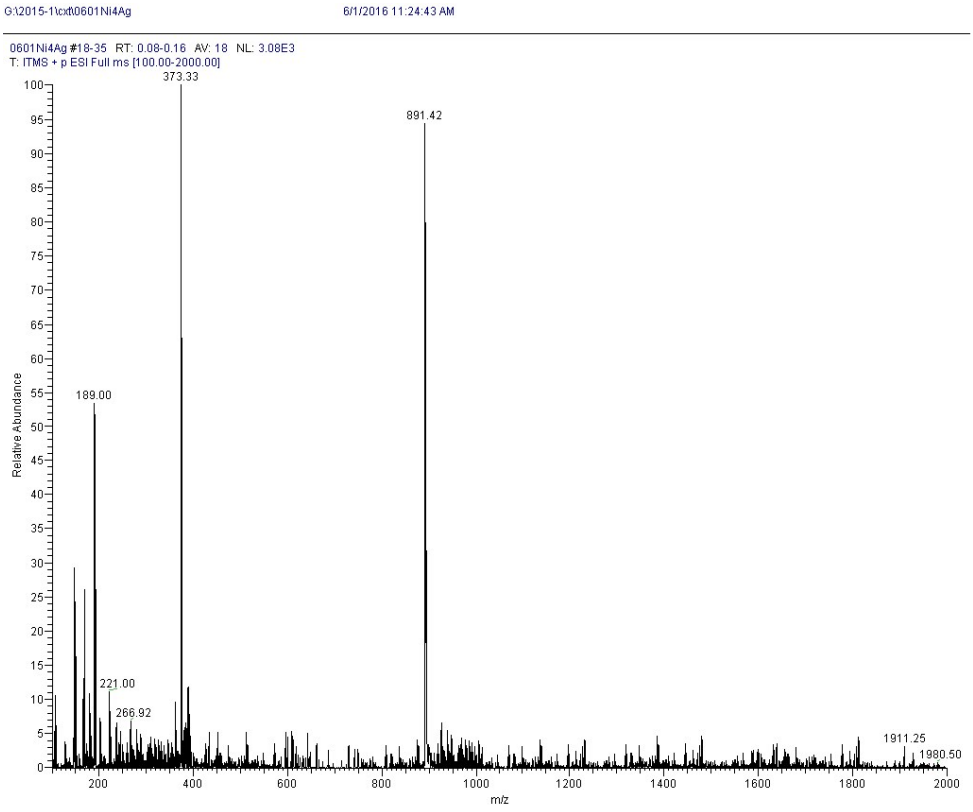

Figure S27 ESI-MS of **8**

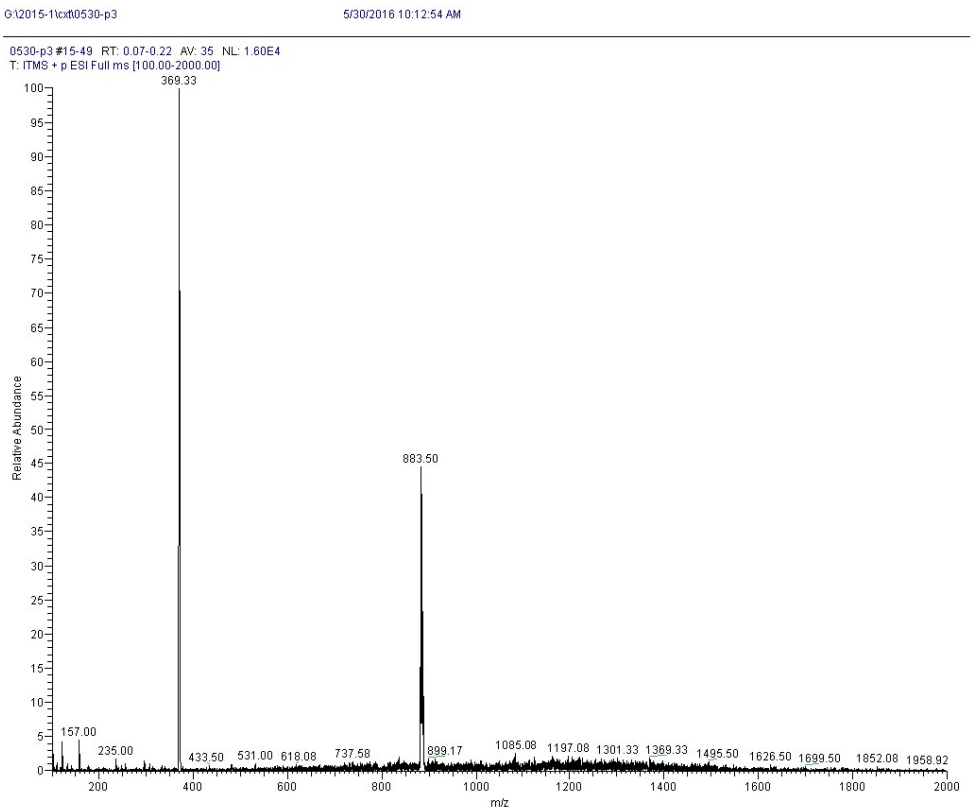

Figure S28 ESI-MS of **9**

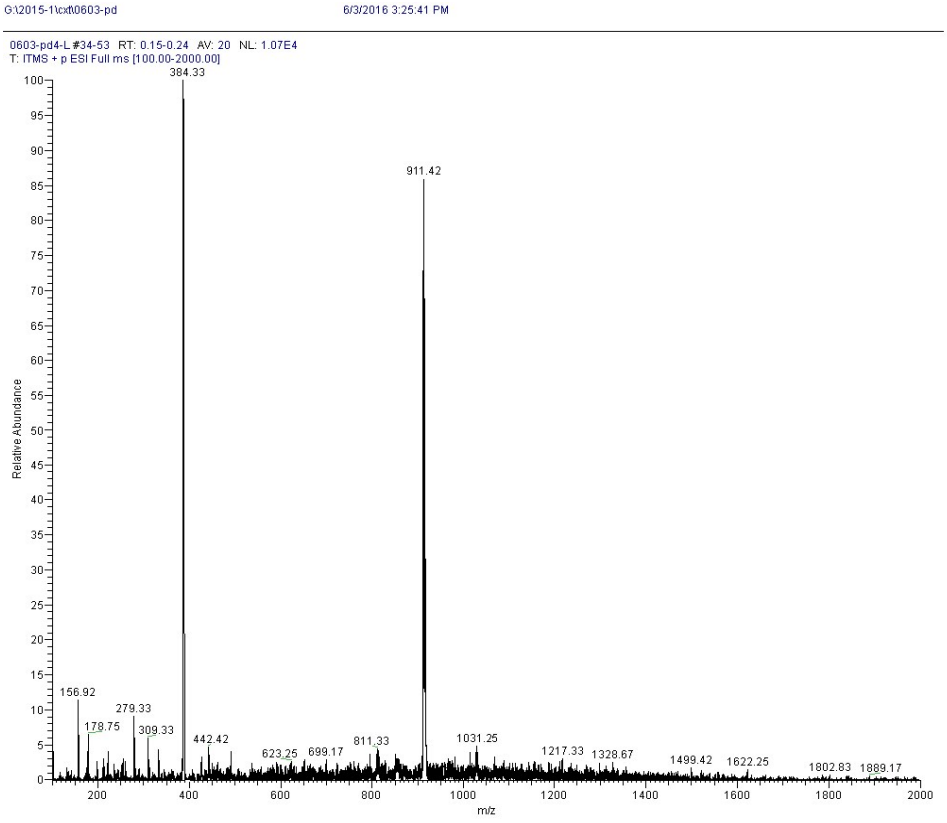

Figure S29 ESI-MS of **10**

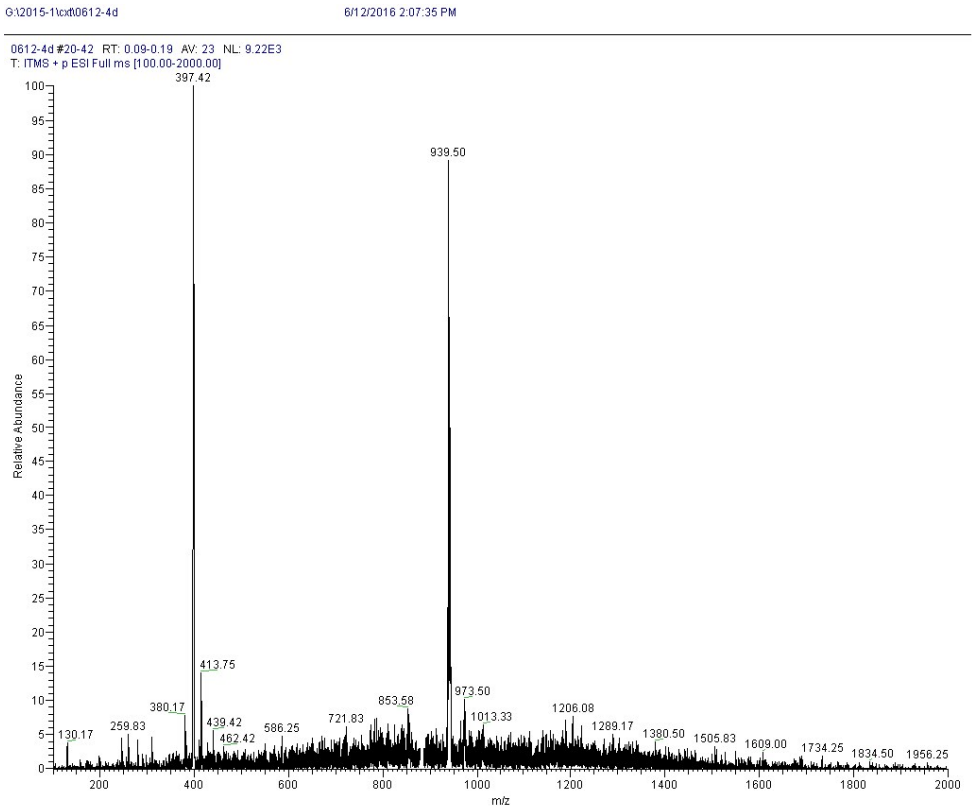

Figure S30 ESI-MS of **11**

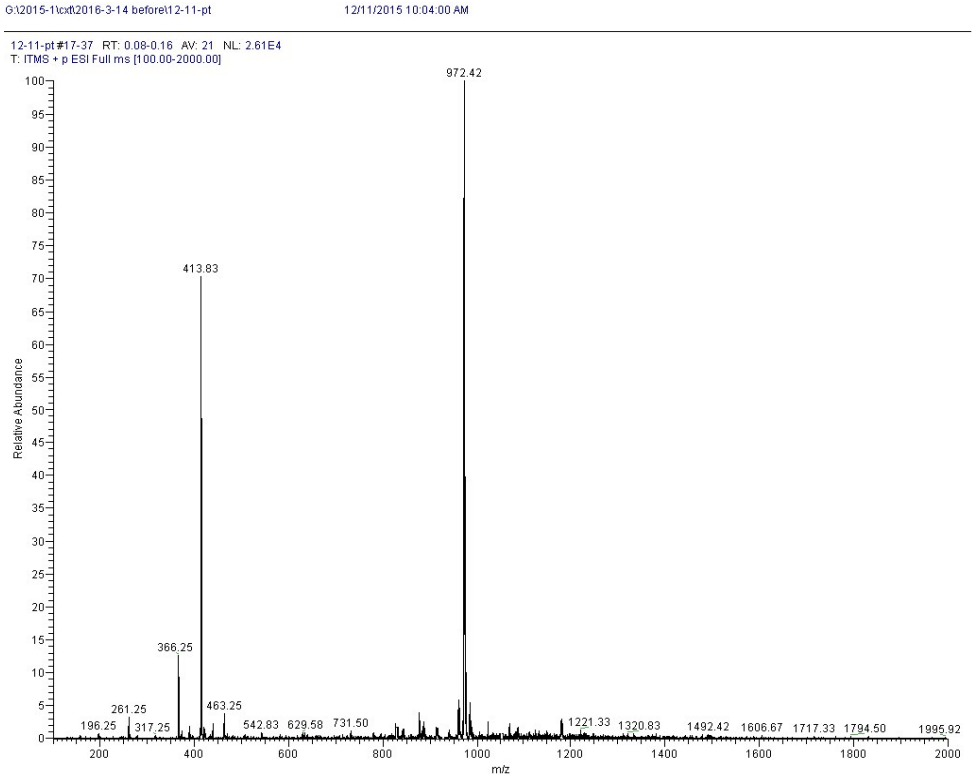

Figure S31 ESI-MS of **12**

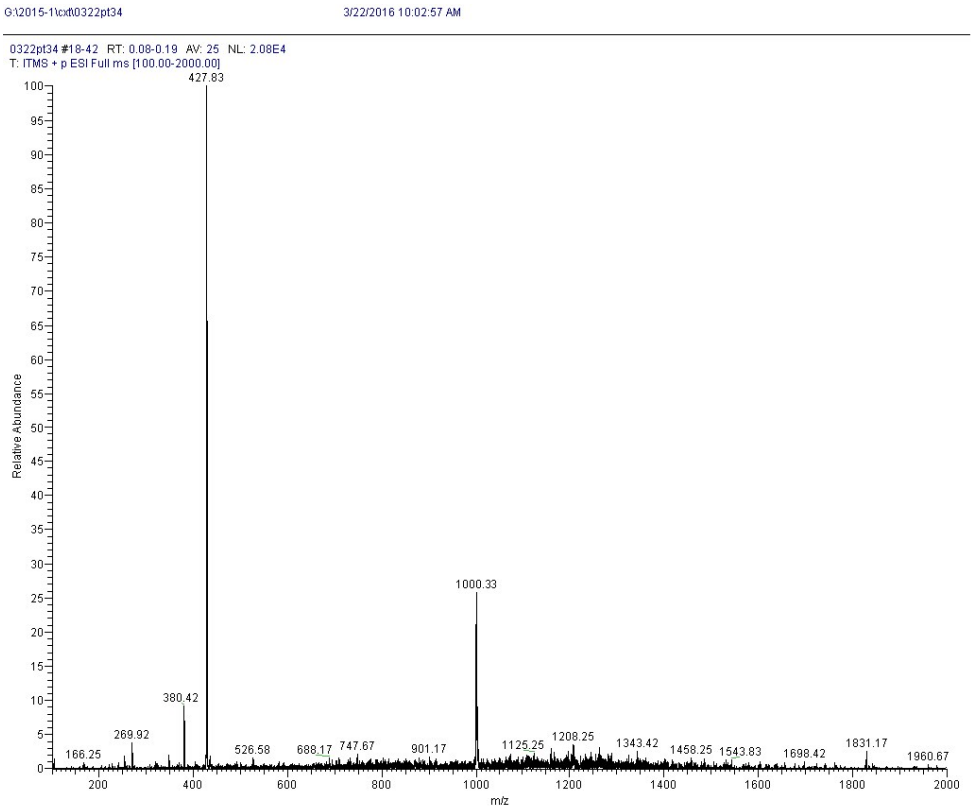

Figure S32 ESI-MS of **13**

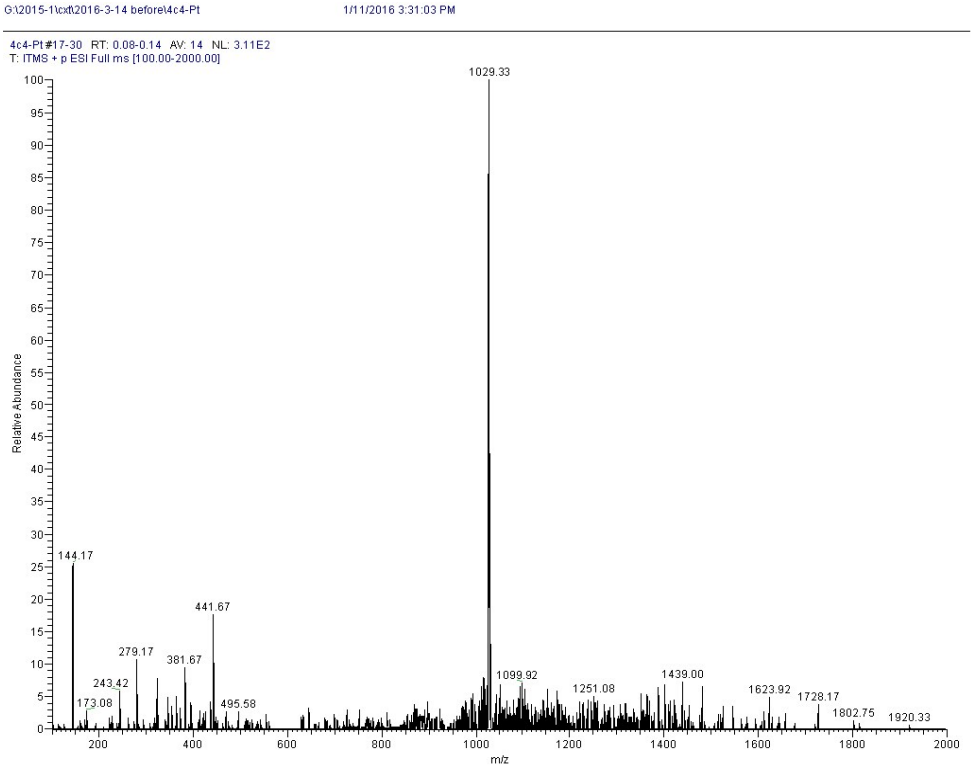

Figure S33 ESI-MS of **14**

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