Electronic Supplementary Information (ESI)

Luminescent monometallic Cu(I) triphenylphosphine complexes based on the methylated 5-trifluoromethyl-3-(2′-pyridyl)-1,2,4-triazole ligands

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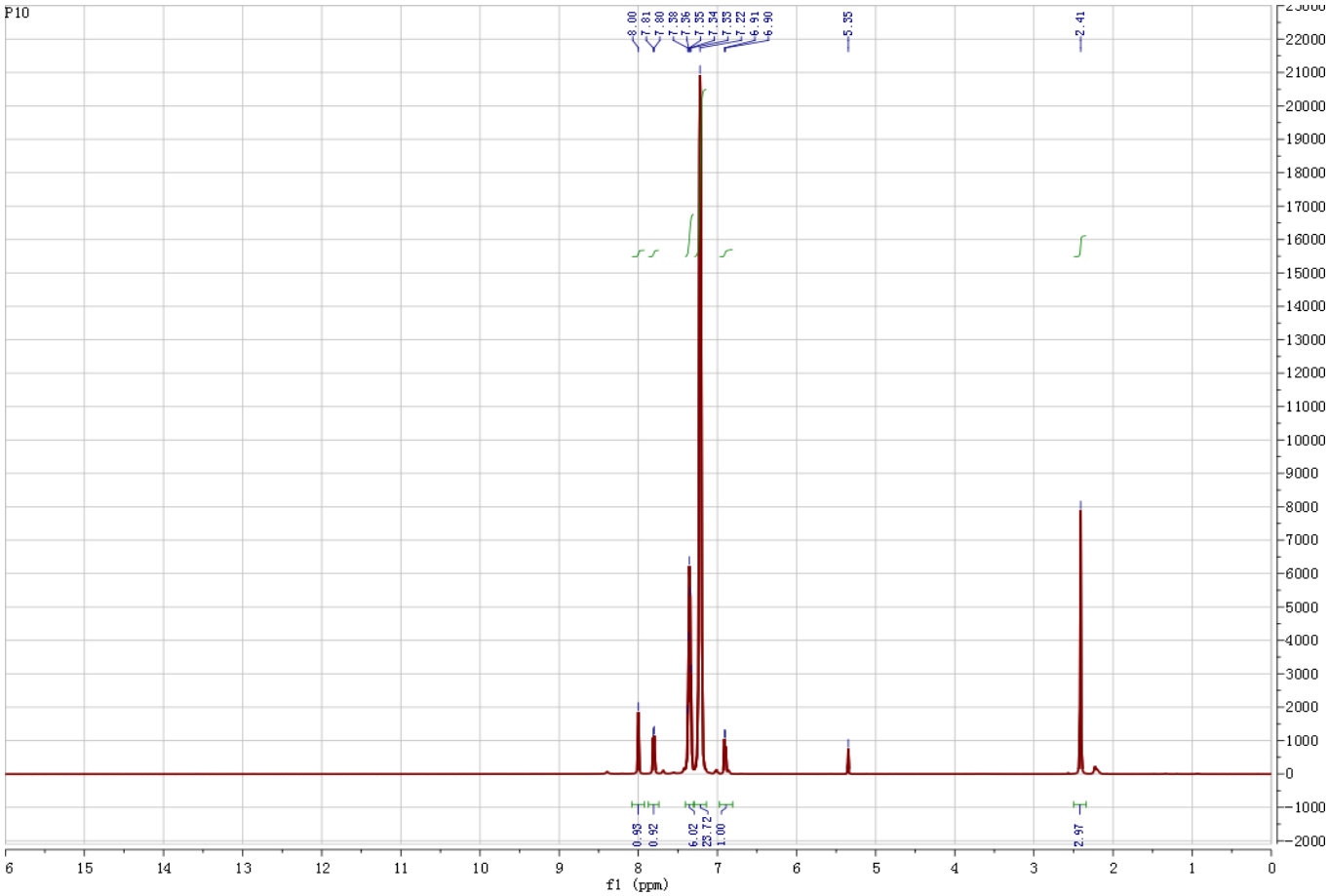


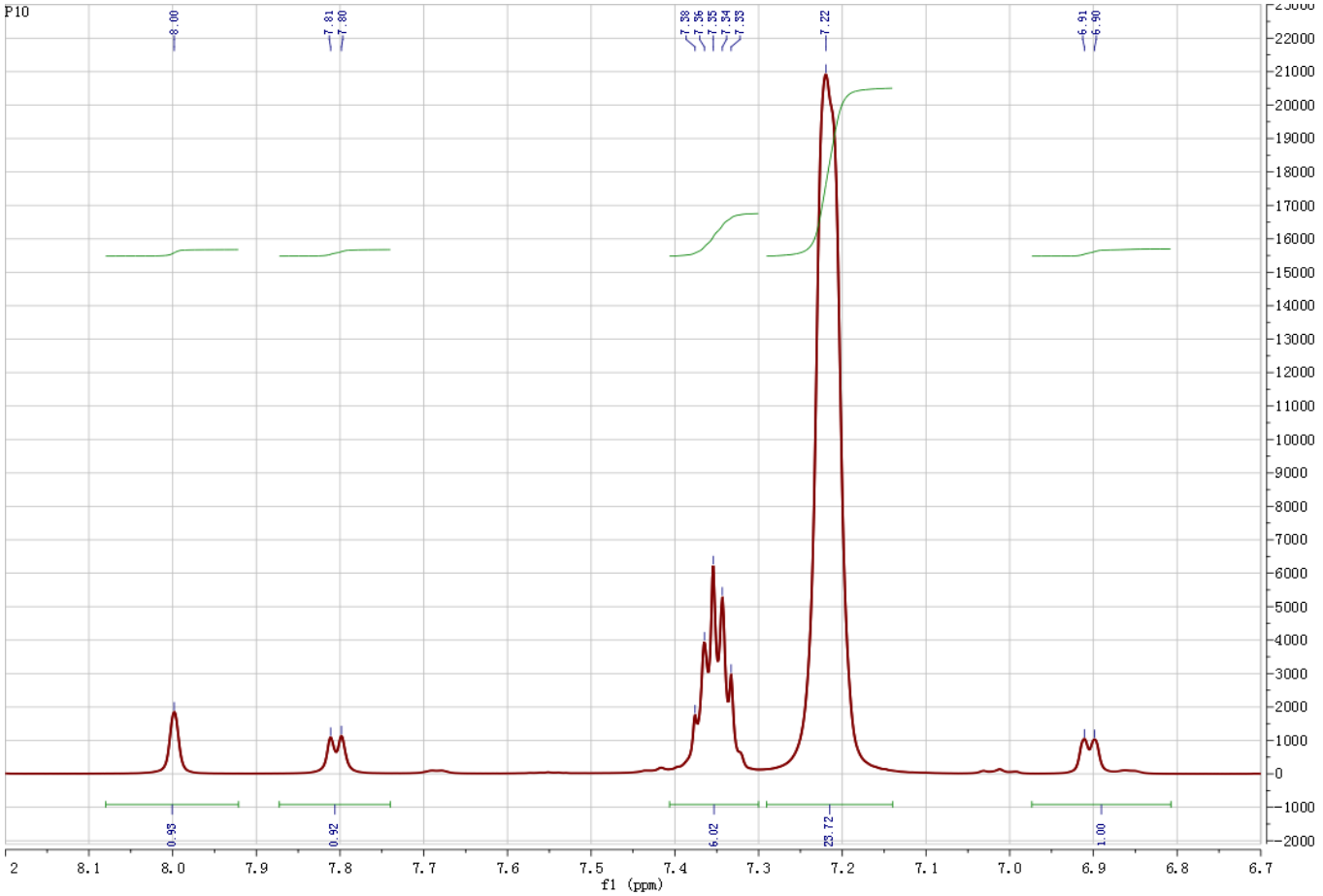


Figure S1 ^{1}H NMR spectra of **1** in CD_2Cl_2.

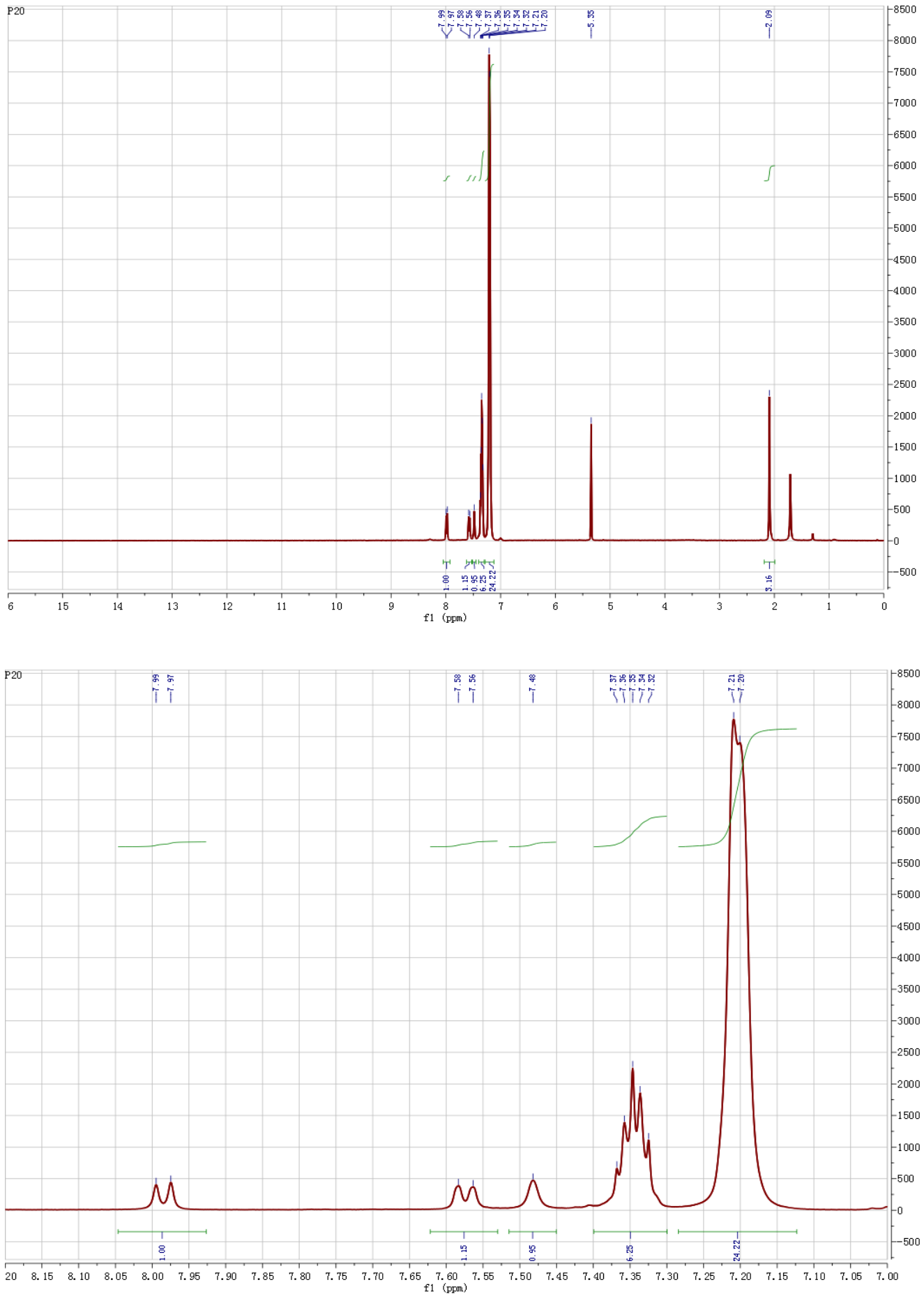


Figure S2 ^{1}H NMR spectra of **2** in CD_2Cl_2.

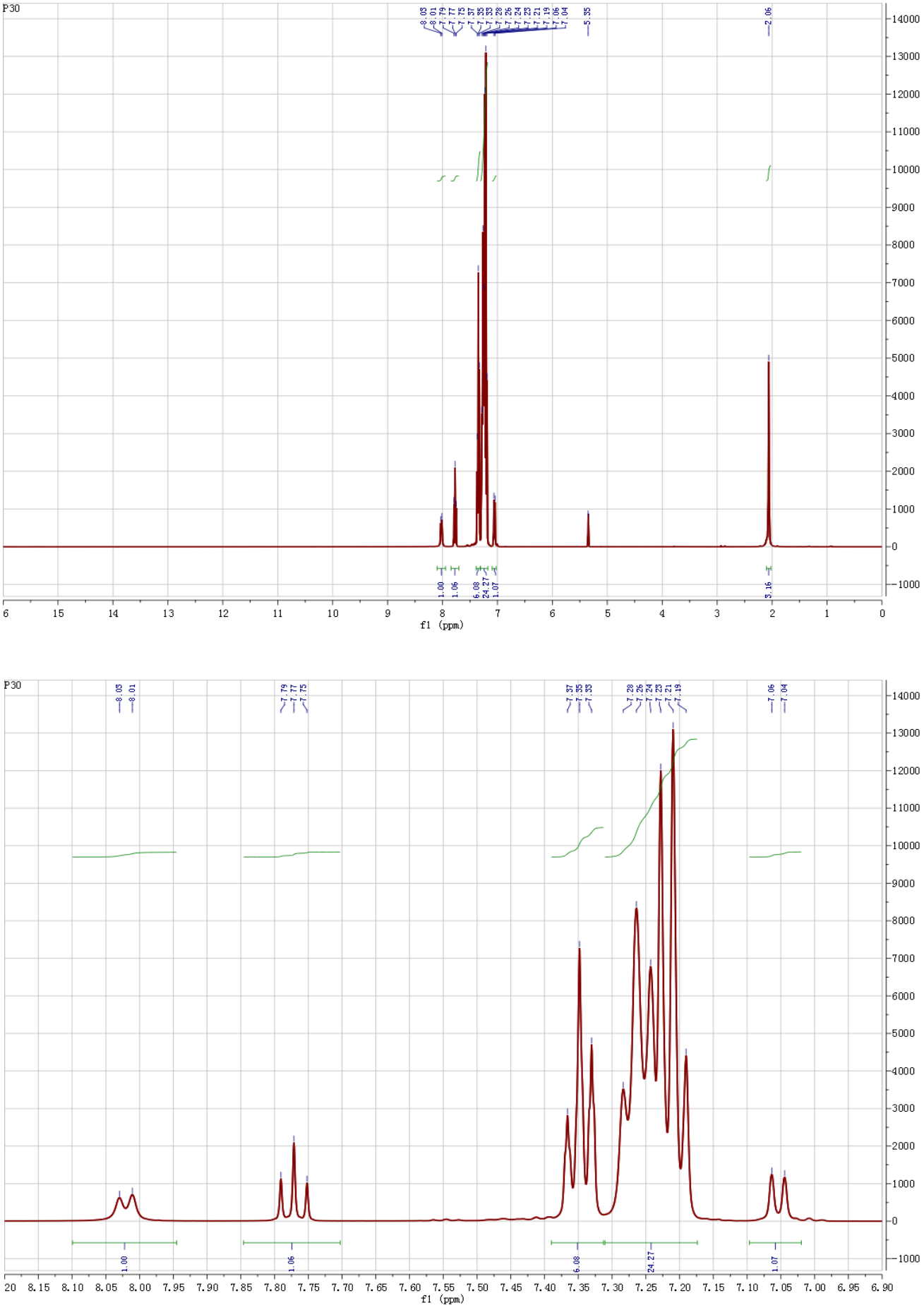


Figure S3 ^{1}H NMR spectra of **3** in CD_2Cl_2.

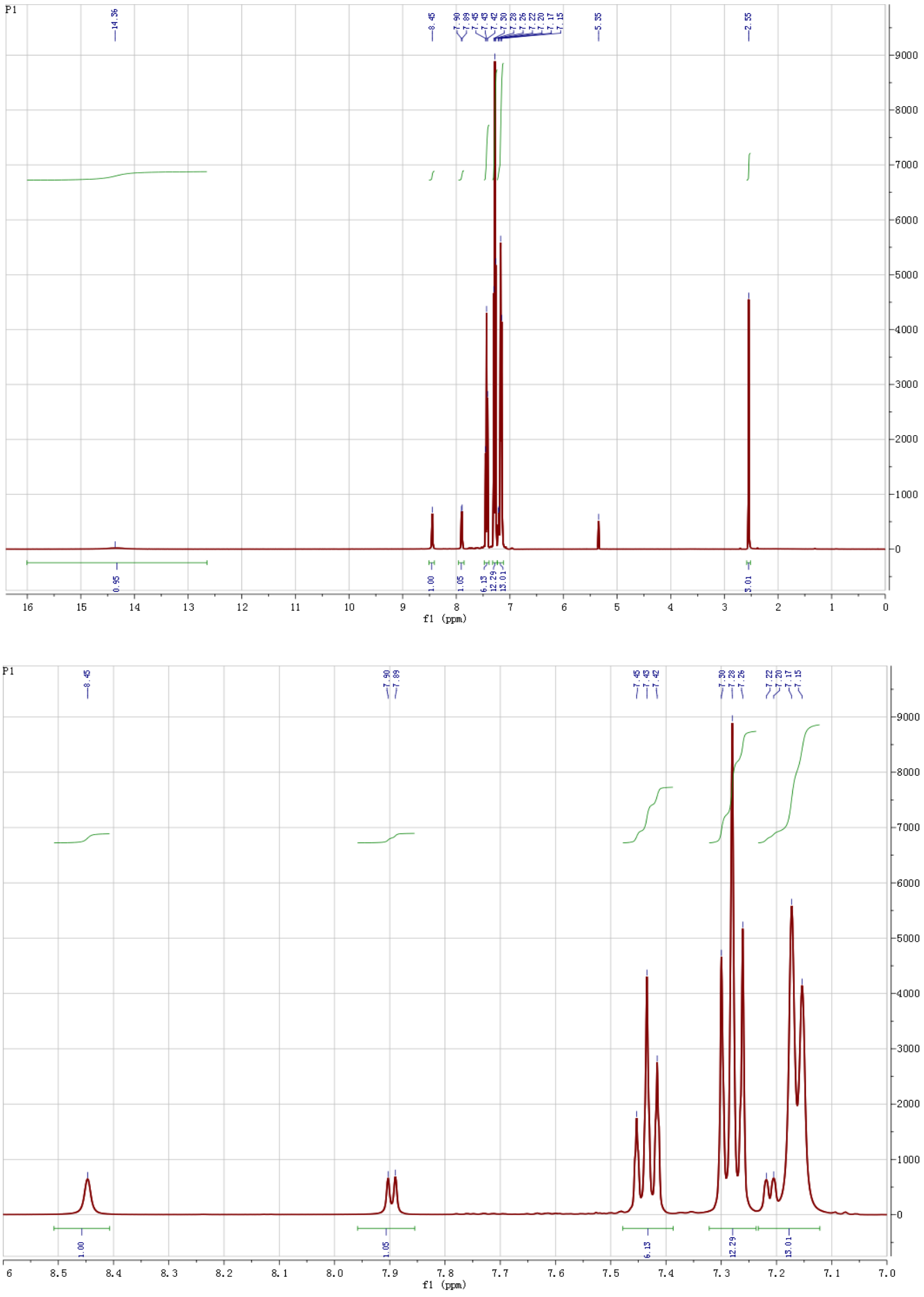


Figure S4 ^{1}H NMR spectra of **4** in CD_2Cl_2.

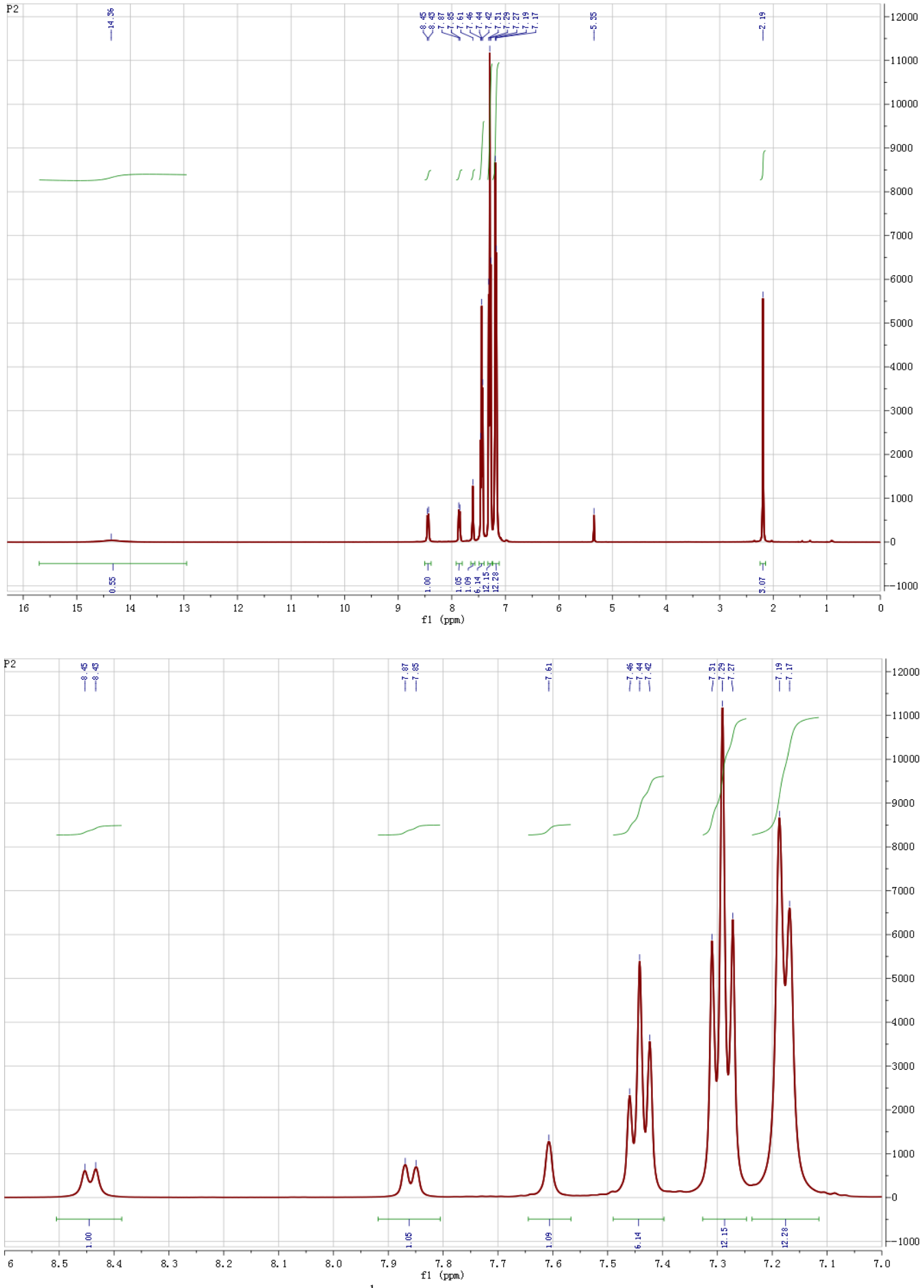


Figure S5 ^{1}H NMR spectra of **5** in CD_2Cl_2.

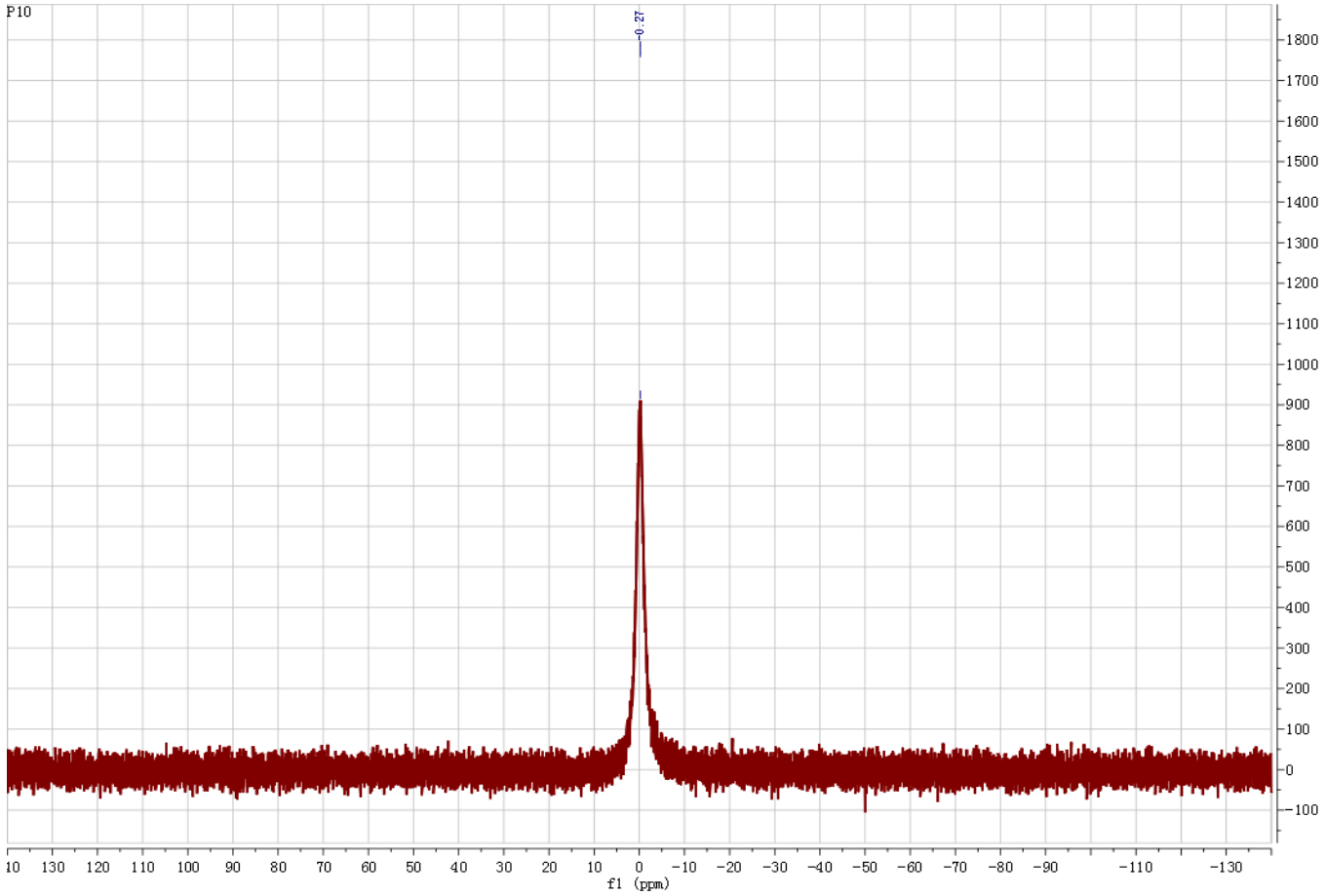


Figure S6 ^{31}P NMR spectrum of **1** in CD_2Cl_2.

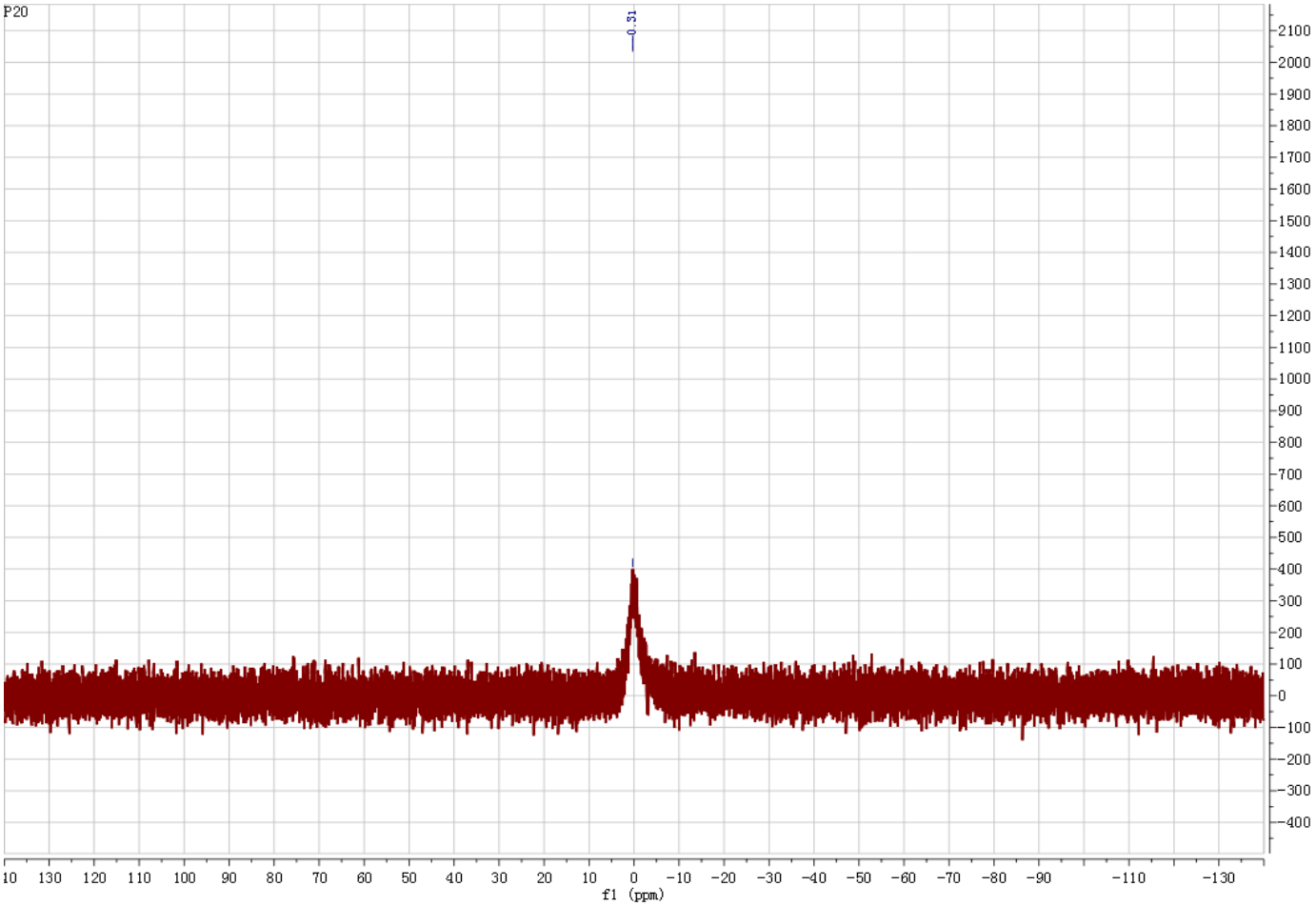


Figure S7 ^{31}P NMR spectrum of **2** in CD_2Cl_2.

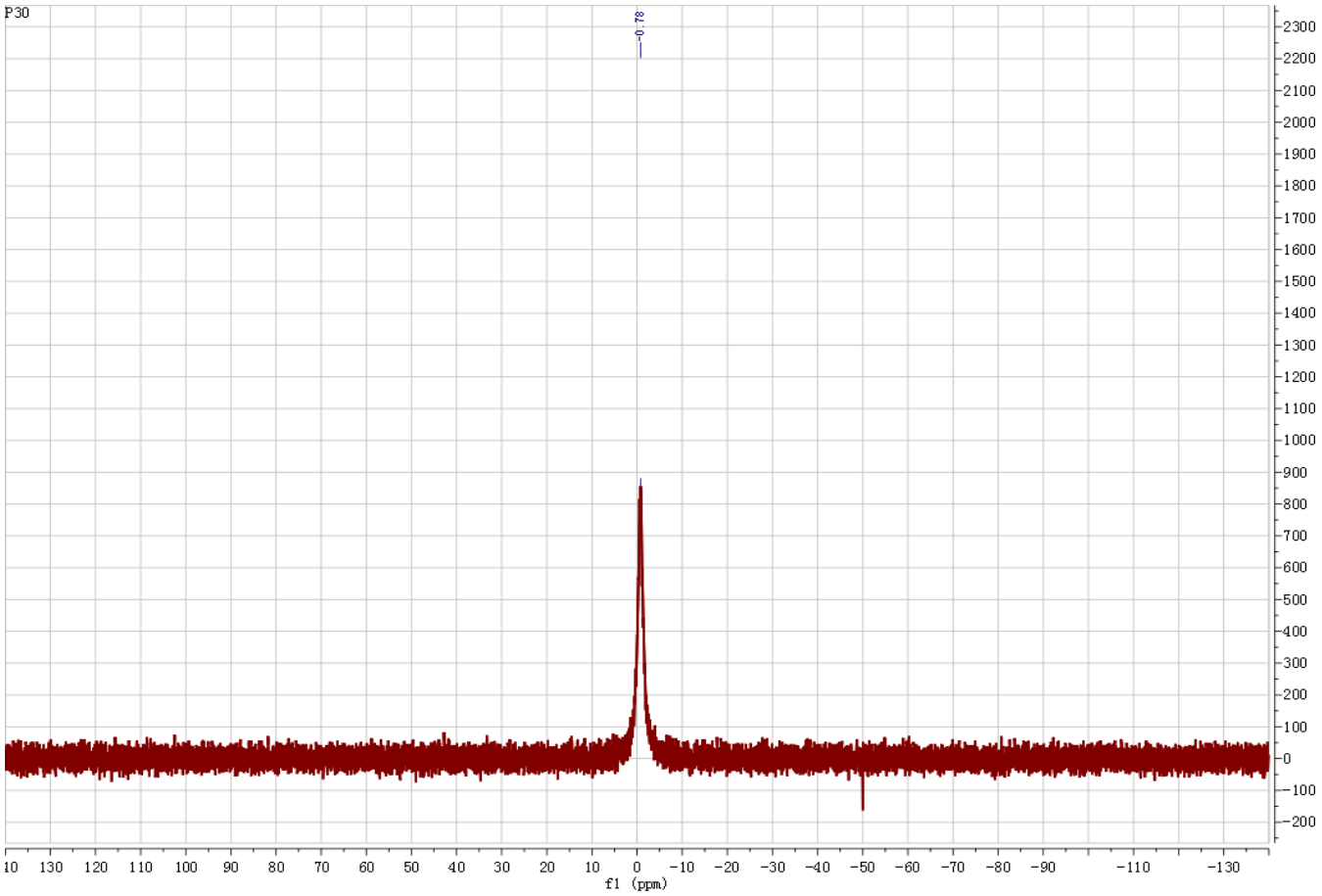


Figure S8 ^{31}P NMR spectrum of **3** in CD_2Cl_2.

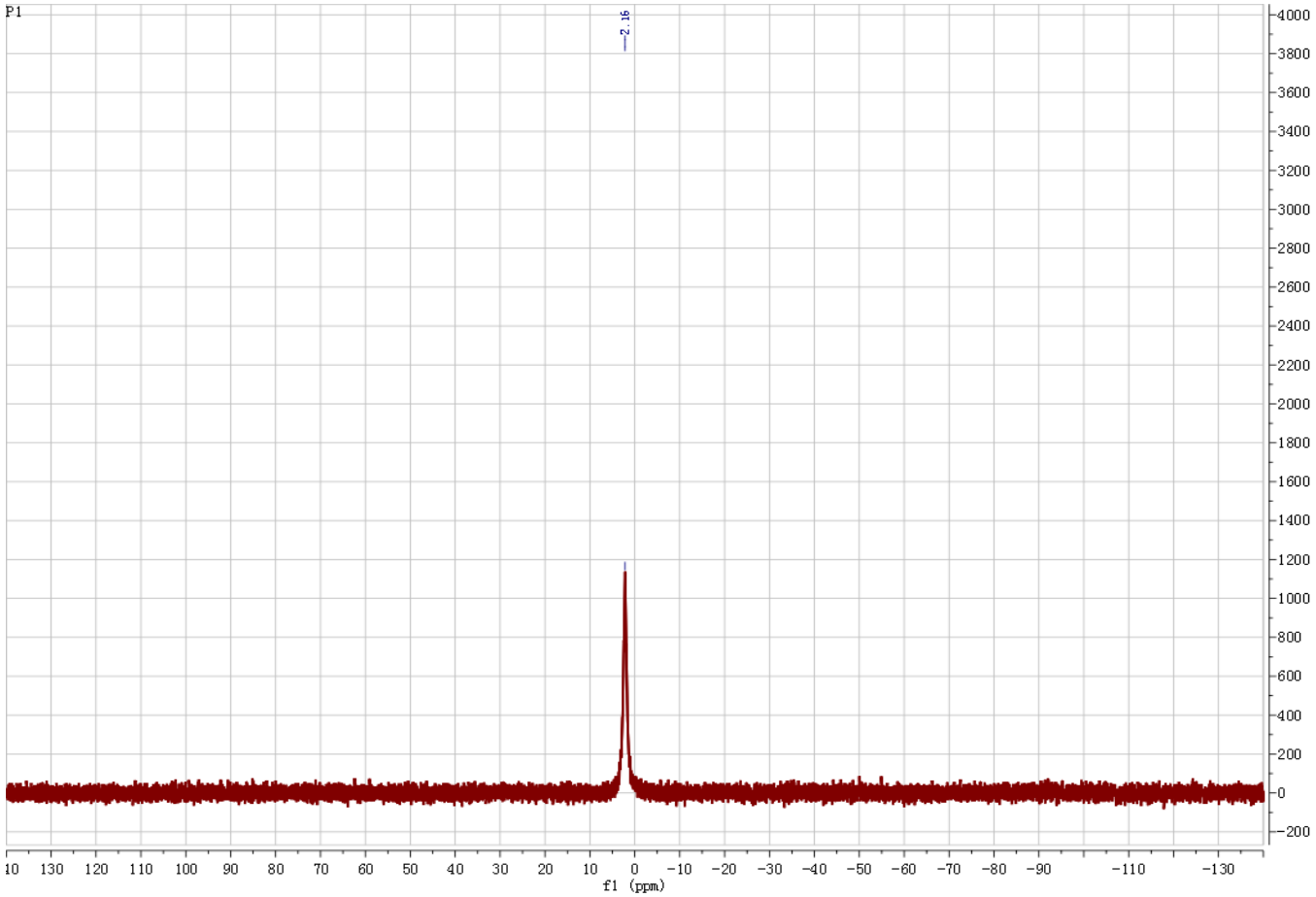


Figure S9 ^{31}P NMR spectrum of **4** in CD_2Cl_2.

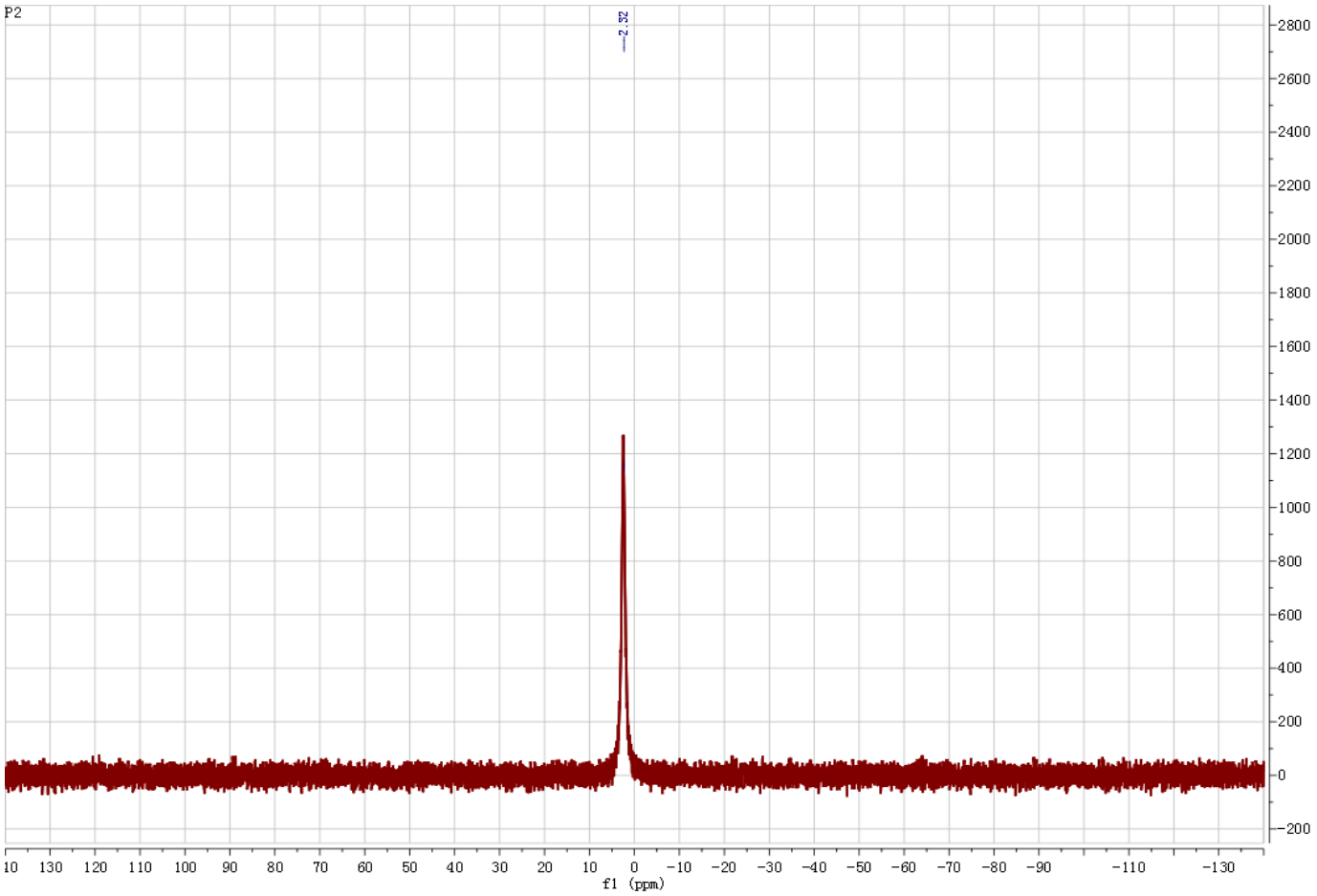
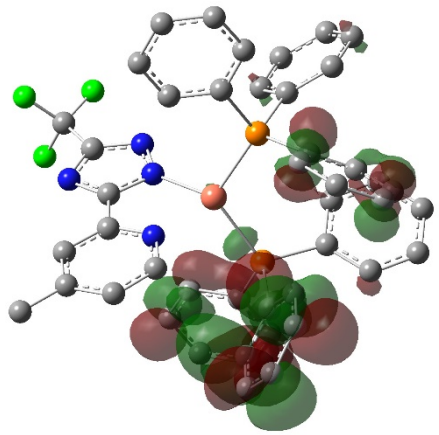
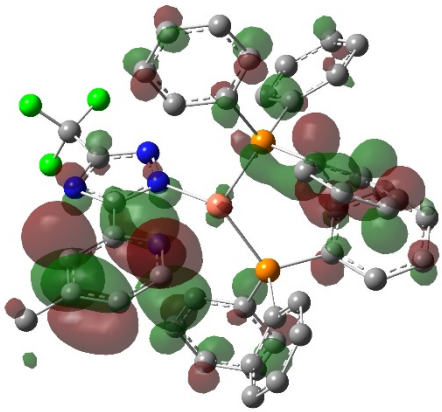
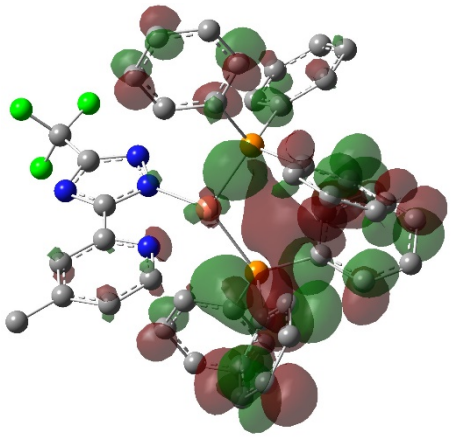
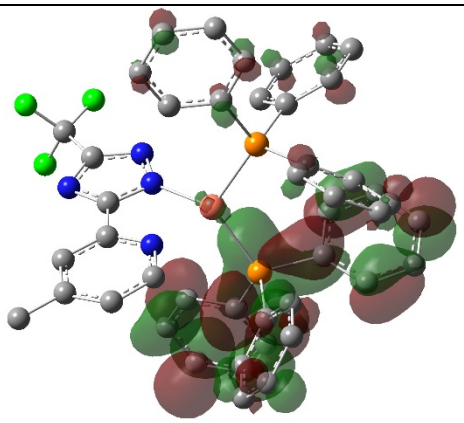
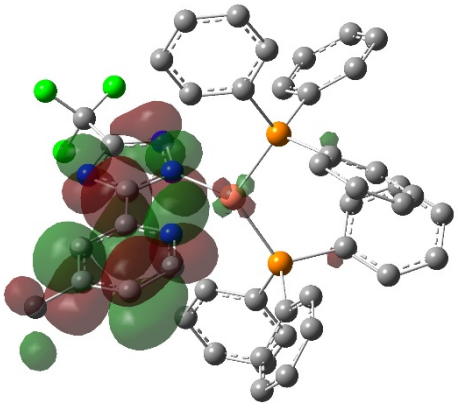
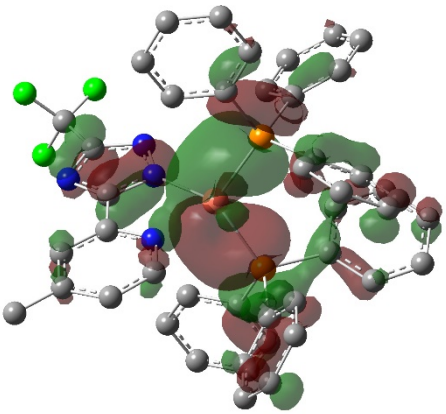


Figure S10 ^{31}P NMR spectrum of **5** in CD_2Cl_2.

Table S1 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) and the absorption transitions for complex **1** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
		Cu (s/p/d)	PPh_3	*p*-mpftz
LUMO+8	-0.28	8.56 (2/97/1)	89.85	1.59
LUMO+5	-0.53	9.69 (6/91/3)	41.71	48.59
LUMO+3	-0.72	4.86 (15/74/11)	91.07	4.08
LUMO+2	-0.76	6.81 (44/53/4)	91.74	1.46
LUMO	-1.16	6.29 (11/76/13)	11.13	82.58
HOMO	-5.85	29.44 (0/22/78)	59.05	11.51
HOMO-1	-6.34	38.92 (7/16/77)	35.12	25.95
HOMO-2	-6.53	33.18 (7/10/83)	14.95	51.87
HOMO-3	-6.59	21.69 (3/19/78)	13.04	65.26

state	*E*/nm (eV)	O.S.	transition	assignment
S_1	333 (3.72)	0.1159	HOMO→LUMO (90%)	^{1}LLCT/^{1}MLCT/^{1}IL
S_2	309 (4.01)	0.0277	HOMO-1→LUMO (53%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-2→LUMO (26%)	
S_6	294 (4.22)	0.0444	HOMO-2→LUMO (37%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-1→LUMO (31%)	
			HOMO-3→LUMO (10%)	
S_{10}	278 (4.47)	0.1184	HOMO-3→LUMO (47%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO→LUMO+5 (24%)	
			HOMO-2→LUMO (15%)	
S_{15}	264 (4.70)	0.1119	HOMO→LUMO+8 (64%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-1→LUMO+2 (21%)	

	
LUMO+8	LUMO+5
	
LUMO+3	LUMO+2
	
LUMO	HOMO

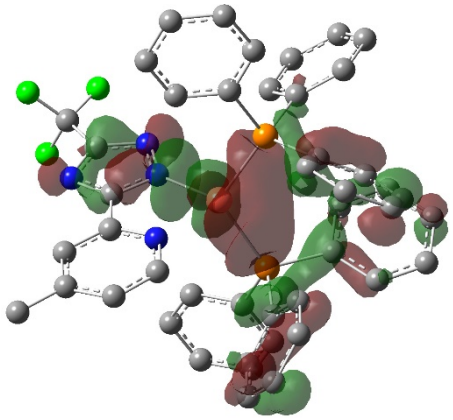
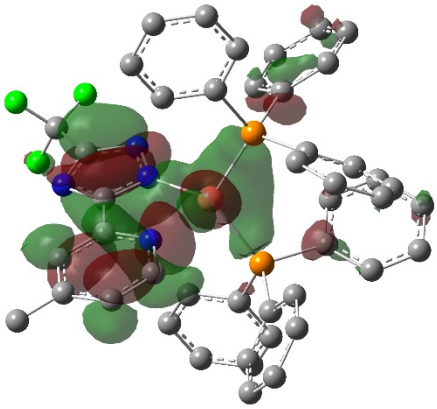
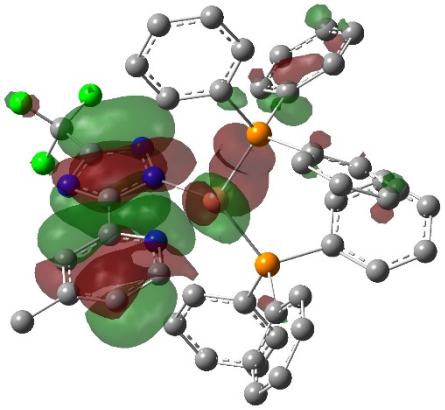
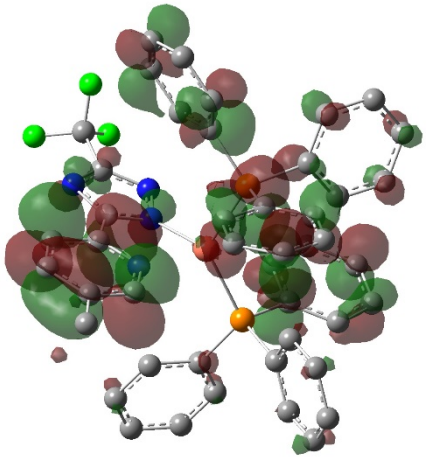
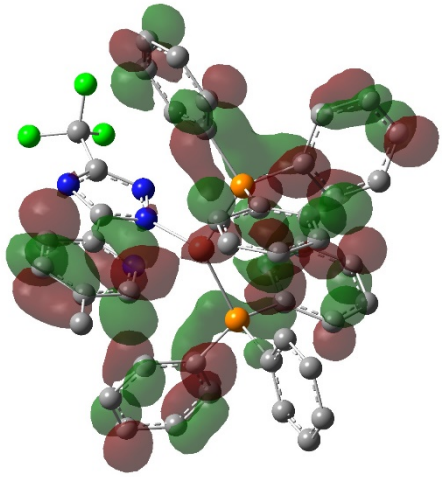
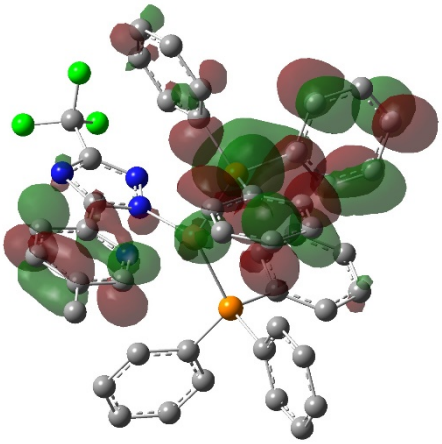
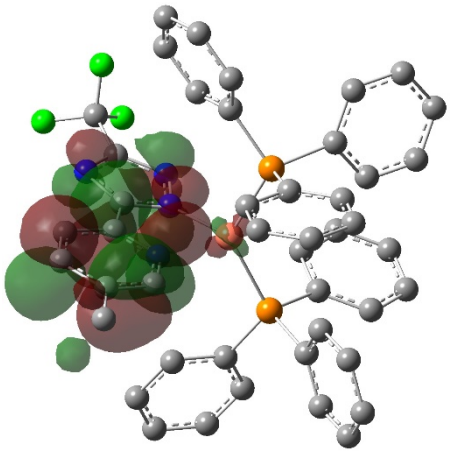
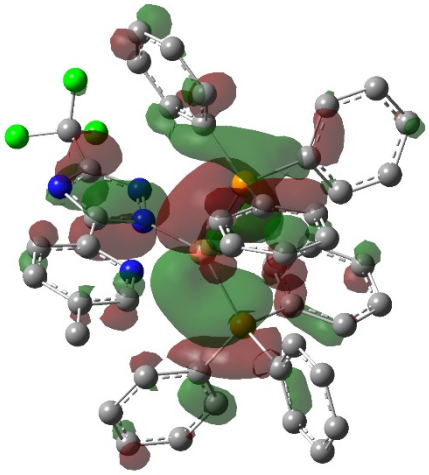
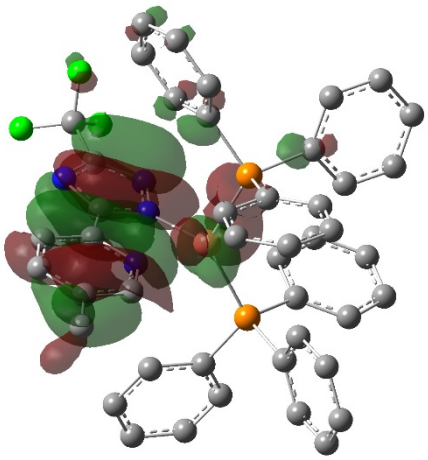
	
HOMO-1	HOMO-2
	
HOMO-3	

Figure S11 Plots of the frontier molecular orbitals involved in the absorption transitions for complex **1** in CH_2Cl_2 media by TDDFT method at the M06 level (isovalue = 0.025). The red and green parts represent different phases, respectively. For clarity, the hydrogen atoms are omitted.

Table S2 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) and the absorption transitions for complex **2** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
		Cu (s/p/d)	PPh_3	*m*-mpftz
LUMO+5	-0.55	15.85 (4/95/1)	51.95	32.19
LUMO+4	-0.66	3.93 (31/68/1)	73.95	22.11
LUMO+2	-0.78	5.74 (35/58/7)	81.52	12.73
LUMO	-1.20	6.43 (3/85/12)	8.66	84.91
HOMO	-6.03	26.18 (0/19/81)	60.88	12.95
HOMO-2	-6.48	20.08 (6/15/79)	12.42	67.50
HOMO-3	-6.52	35.63 (3/10/87)	9.71	54.66

state	E/nm (eV)	O.S.	transition	assignment
S_1	320 (3.87)	0.0853	HOMO→LUMO (86%)	^{1}LLCT/^{1}MLCT/^{1}IL
S_6	286 (4.34)	0.2226	HOMO-2→LUMO (42%)	^{1}IL/^{1}MLCT
			HOMO-3→LUMO (20%)	
			HOMO→LUMO+2 (20%)	
S_{22}	254 (4.88)	0.1349	HOMO-3→LUMO+2 (23%)	^{1}LLCT/^{1}MLCT/^{1}IL
			HOMO-2→LUMO+4 (19%)	
			HOMO-2→LUMO+2 (10%)	

	
LUMO+5	LUMO+4
	
LUMO+2	LUMO
	
HOMO	HOMO-2

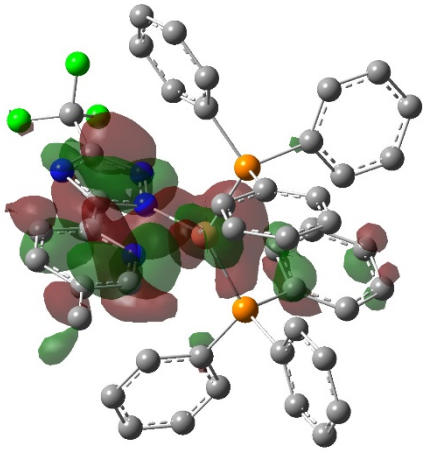
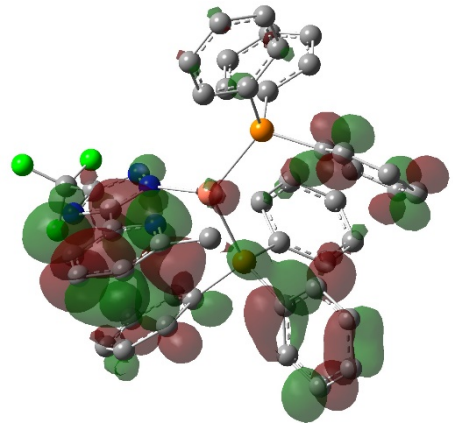
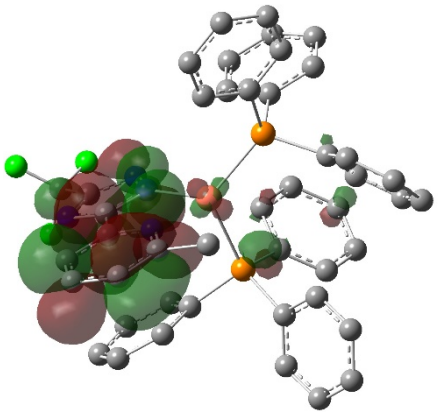
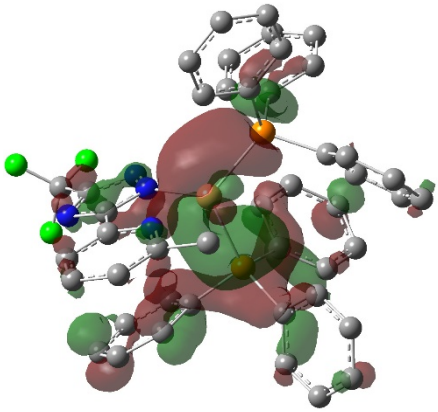
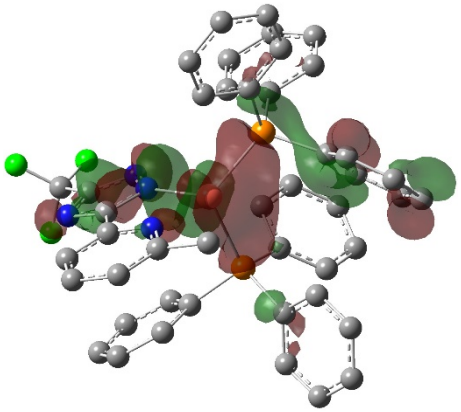
	
HOMO-3	

Figure S12 Plots of the frontier molecular orbitals involved in the absorption transitions for complex **2** in CH_2Cl_2 media by TDDFT method at the M06 level (isovalue = 0.025). The red and green parts represent different phases, respectively. For clarity, the hydrogen atoms are omitted.

Table S3 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) and the absorption transitions for complex **3** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
		Cu (s/p/d)	PPh_3	*o*-mpftz
LUMO+3	-0.59	4.63 (5/91/4)	46.04	49.33
LUMO	-1.18	6.00 (2/83/15)	14.58	79.42
HOMO	-5.79	27.37 (0/23/77)	64.96	7.67
HOMO-1	-6.28	42.73 (5/16/79)	27.22	30.04
HOMO-2	-6.43	10.96 (11/15/74)	10.00	79.04
HOMO-3	-6.61	39.14 (5/14/81)	25.34	35.52

state	E/nm (eV)	O.S.	transition	assignment
S_1	339 (3.65)	0.1249	HOMO→LUMO (96%)	^{1}LLCT/^{1}MLCT/^{1}IL
S_5	296 (4.19)	0.0737	HOMO-2→LUMO (62%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-1→LUMO (10%)	
S_8	286 (4.34)	0.1118	HOMO-3→LUMO (47%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-2→LUMO (22%)	
			HOMO→LUMO+3 (13%)	

	
LUMO+3	LUMO
	
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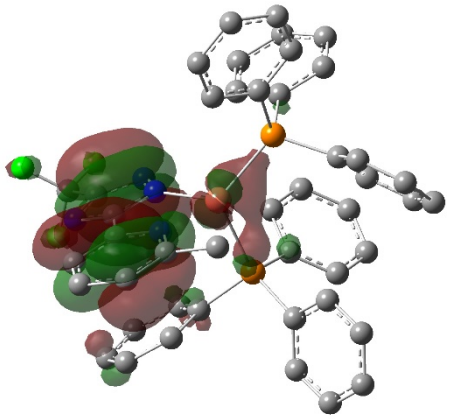
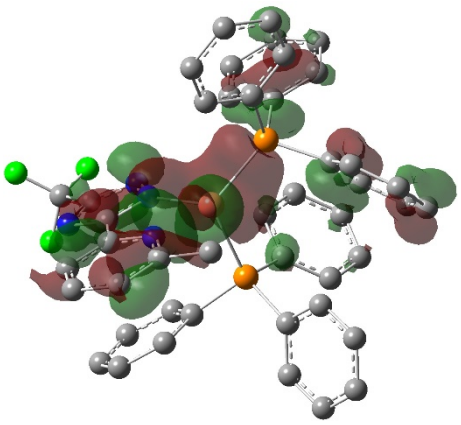
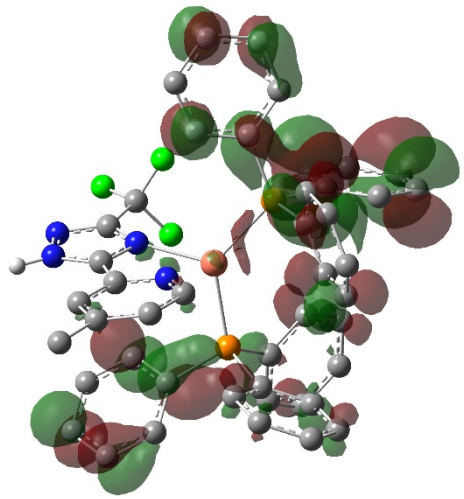
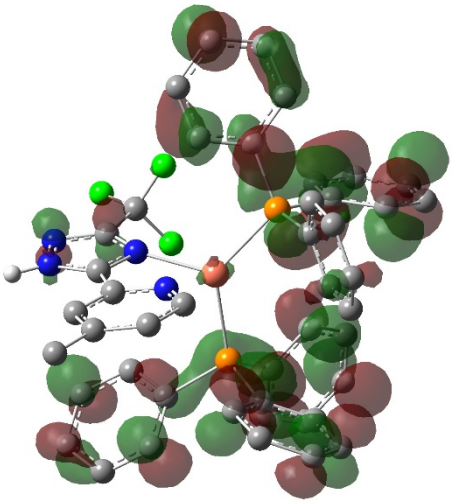
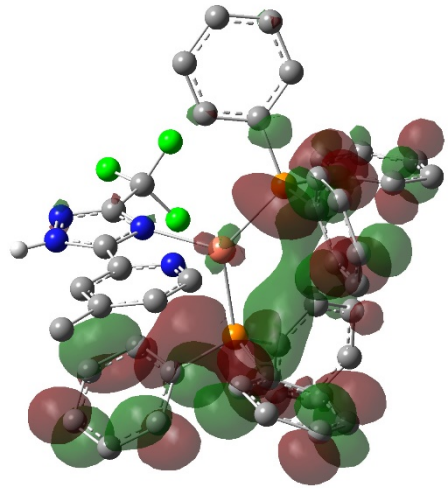
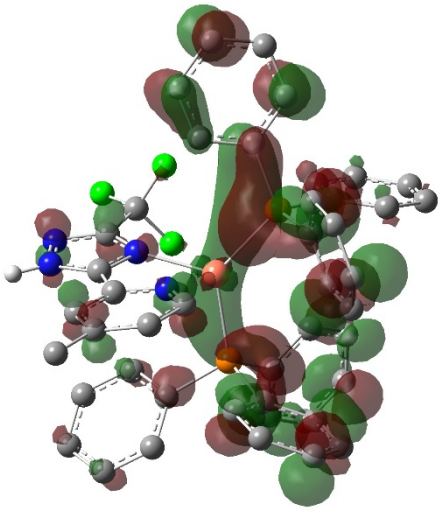
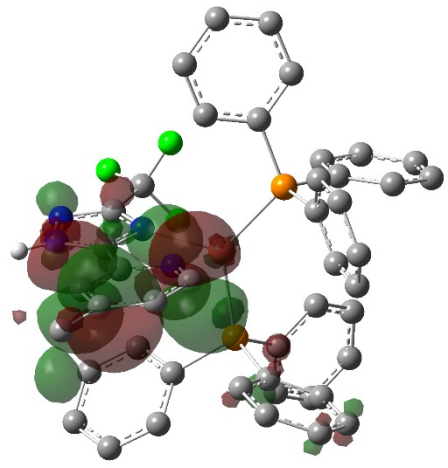
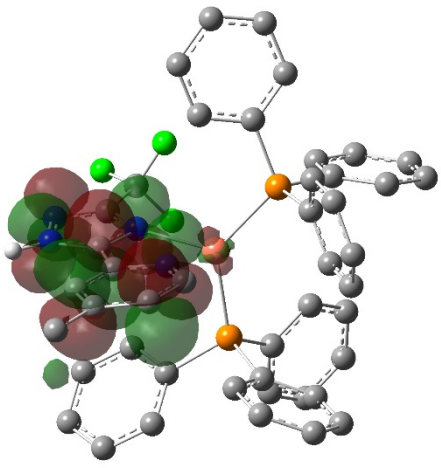
	
HOMO-2	HOMO-3

Figure S13 Plots of the frontier molecular orbitals involved in the absorption transitions for complex **3** in CH_2Cl_2 media by TDDFT method at the M06 level (isovalue = 0.025). The red and green parts represent different phases, respectively. For clarity, the hydrogen atoms are omitted.

Table S4 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) and the absorption transitions for complex **4** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
		Cu (s/p/d)	PPh_3	*p*-mpftzH
LUMO+6	-0.86	18.58 (57/42/1)	78.21	3.21
LUMO+5	-0.91	7.65 (7/91/2)	87.94	4.42
LUMO+3	-1.05	5.04 (3/84/12)	91.36	3.60
LUMO+2	-1.13	9.73 (46/50/4)	83.17	7.10
LUMO+1	-1.45	7.31 (8/88/4)	15.90	76.79
LUMO	-2.37	1.25 (22/38/40)	4.59	94.17
HOMO	-6.52	25.35 (0/46/54)	71.97	2.68
HOMO-1	-6.80	34.87 (30/12/58)	55.97	9.16

state	E/nm (eV)	O.S.	transition	assignment
S_1	379 (3.27)	0.0320	HOMO→LUMO (98%)	^{1}LLCT/^{1}MLCT
S_2	357 (3.47)	0.0139	HOMO-1→LUMO (94%)	^{1}LLCT/^{1}MLCT
S_4	294 (4.22)	0.0220	HOMO→LUMO+1 (94%)	^{1}LLCT/^{1}MLCT/^{1}IL
S_9	276 (4.50)	0.1124	HOMO→LUMO+3 (60%)	^{1}IL/^{1}MLCT
S_{15}	266 (4.65)	0.1342	HOMO→LUMO+5 (65%)	^{1}IL/^{1}MLCT
			HOMO-1→LUMO+3 (19%)	
S_{18}	264 (4.69)	0.1346	HOMO→LUMO+6 (59%)	^{1}IL/^{1}MLCT
			HOMO-1→LUMO+2 (19%)	

	
LUMO+6	LUMO+5
	
LUMO+3	LUMO+2
	
LUMO+1	LUMO

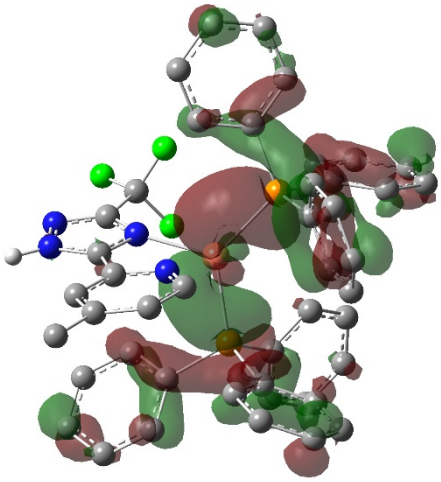
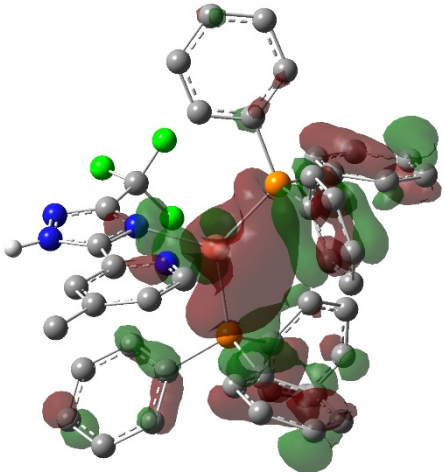
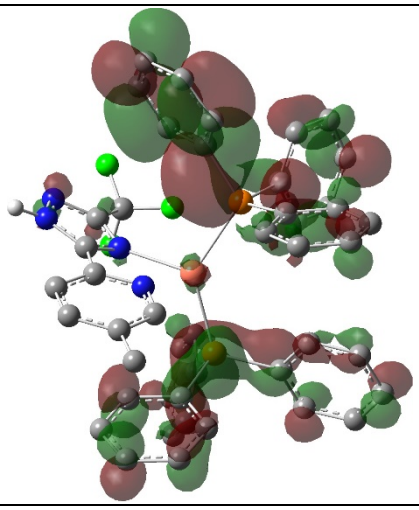
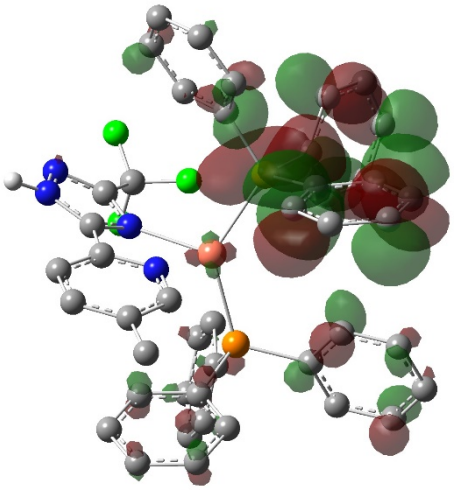
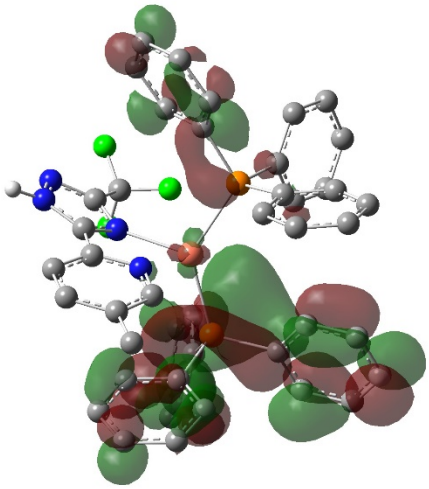
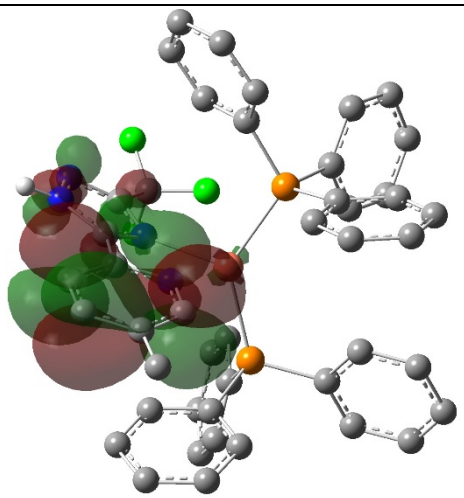
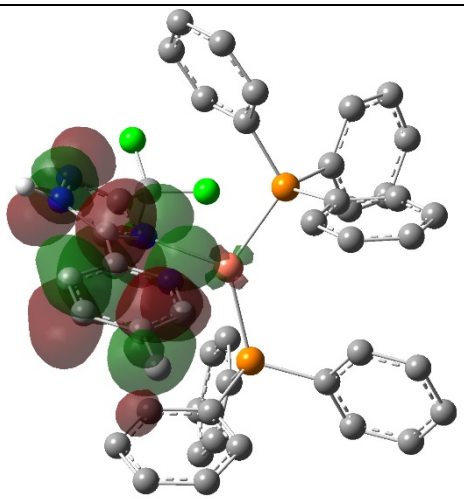
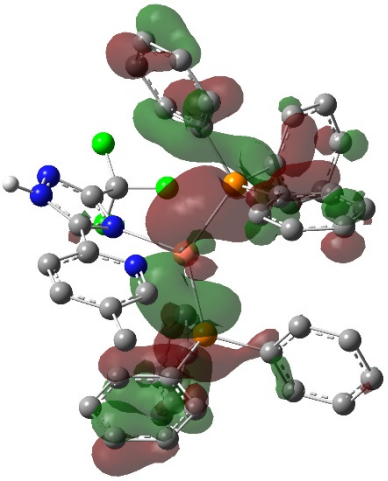
	
HOMO	HOMO-1

Figure S14 Plots of the frontier molecular orbitals involved in the absorption transitions for complex **4** in CH_2Cl_2 media by TDDFT method at the M06 level (isovalue = 0.025). The red and green parts represent different phases, respectively. For clarity, the hydrogen atoms except for the ones bonded to N atoms are omitted.

Table S5 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) and the absorption transitions for complex **5** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
		Cu (s/p/d)	PPh_3	*m*-mpftzH
LUMO+5	-0.90	1.73 (2/78/19)	93.52	4.75
LUMO+3	-1.10	9.16 (4/93/3)	87.67	3.17
LUMO+2	-1.14	5.66 (21/70/9)	92.67	1.67
LUMO+1	-1.44	7.14 (17/79/4)	9.38	83.48
LUMO	-2.26	1.37 (3/57/39)	4.00	94.62
HOMO	-6.53	23.79 (1/38/61)	73.76	2.45
HOMO-1	-6.84	37.00 (27/15/58)	52.85	10.16

state	E/nm (eV)	O.S.	transition	assignment
S_1	366 (3.39)	0.0424	HOMO→LUMO (98%)	^{1}LLCT/^{1}MLCT
S_2	348 (3.57)	0.0064	HOMO-1→LUMO (90%)	^{1}LLCT/^{1}MLCT/^{1}IL
S_5	281 (4.41)	0.0878	HOMO→LUMO+2 (61%)	^{1}IL/^{1}MLCT/^{1}LLCT
			HOMO-1→LUMO+1 (24%)	
S_6	279 (4.44)	0.0656	HOMO-1→LUMO+1 (54%)	^{1}LLCT/^{1}MLCT/^{1}IL
			HOMO→LUMO+2 (16%)	
			HOMO→LUMO+3 (14%)	
S_{13}	266 (4.66)	0.2406	HOMO→LUMO+5 (63%)	^{1}IL/^{1}MLCT
			HOMO-1→LUMO+2 (12%)	

	
LUMO+5	LUMO+3
	
LUMO+2	LUMO+1
	
LUMO	HOMO

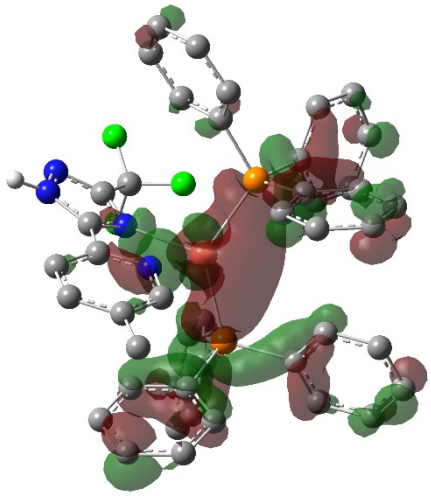
	
HOMO-1	

Figure S15 Plots of the frontier molecular orbitals involved in the absorption transitions for complex **5** in CH_2Cl_2 media by TDDFT method at the M06 level (isovalue = 0.025). The red and green parts represent different phases, respectively. For clarity, the hydrogen atoms except for the ones bonded to N atoms are omitted.

Table S6 Partial molecular orbital compositions (%) by SCPA approach (C-squared population analysis proposed by Ros and Schuit) in the lowest triplet state for complexes **1**–**5**, respectively, in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

orbital	energy (eV)	MO contribution (%)		
1		Cu (s/p/d)	PPh_3	*p*-mpftz
LUMO	-1.55	4.59 (5/72/23)	7.27	88.14
HOMO	-5.83	26.47 (0/21/79)	54.62	18.90
HOMO-1	-6.15	7.69 (4/35/61)	10.71	81.59
2		Cu (s/p/d)	PPh_3	*m*-mpftz
LUMO	-1.55	4.96 (9/71/20)	7.09	87.96
HOMO	-5.92	13.99 (1/11/88)	30.39	55.63
HOMO-1	-6.10	17.44 (1/33/66)	42.34	40.22
HOMO-3	-6.47	47.68 (3/10/88)	10.68	41.65
3		Cu (s/p/d)	PPh_3	*o*-mpftz
LUMO	-1.56	4.87 (8/69/23)	8.68	86.46
HOMO	-5.86	24.73 (0/22/77)	58.59	16.68
4		Cu (s/p/d)	PPh_3	*p*-mpftzH
LUMO	-2.31	2.25 (5/33/62)	4.85	92.89
HOMO	-5.78	22.21 (0/26/74)	70.39	7.40
HOMO-1	-6.76	28.56 (29/22/50)	62.73	8.71
HOMO-2	-7.20	57.35 (1/7/93)	16.10	26.56
HOMO-14	-7.97	34.65 (1/0/99)	39.20	26.14
5		Cu (s/p/d)	PPh_3	*m*-mpftzH
LUMO	-2.44	3.06 (3/45/52)	4.37	92.56
HOMO	-5.89	27.90 (0/16/84)	59.53	12.57

Table S7 The emission transitions for complexes **1**–**5** in CH_2Cl_2 media calculated by TDDFT method at the M06 level.

complex	state	*E*/nm (eV)	O.S.	transition	assignment
1	T_1	515 (2.41)	0.0000	HOMO→LUMO (74%) HOMO-1→LUMO (13%)	^{3}LLCT/^{3}MLCT/^{3}IL
2	T_1	535 (2.32)	0.0000	HOMO-1→LUMO (39%) HOMO→LUMO (36%) HOMO-3→LUMO (14%)	^{3}IL/^{3}LLCT/^{3}MLCT
3	T_1	518 (2.40)	0.0000	HOMO→LUMO (81%)	^{3}LLCT/^{3}MLCT/^{3}IL
4	T_1	567 (2.19)	0.0000	HOMO-1→LUMO (52%) HOMO-2→LUMO (18%) HOMO-14→LUMO (14%)	^{3}LLCT/^{3}MLCT/^{3}IL
5	T_1	576 (2.15)	0.0000	HOMO→LUMO (94%)	^{3}LLCT/^{3}MLCT/^{3}IL

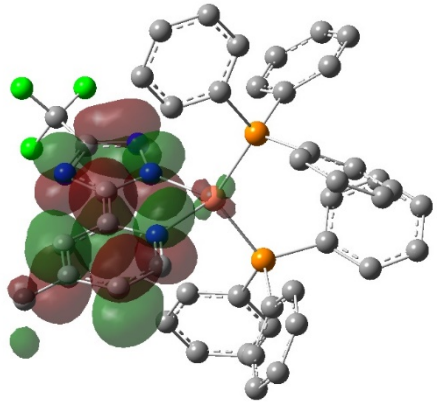
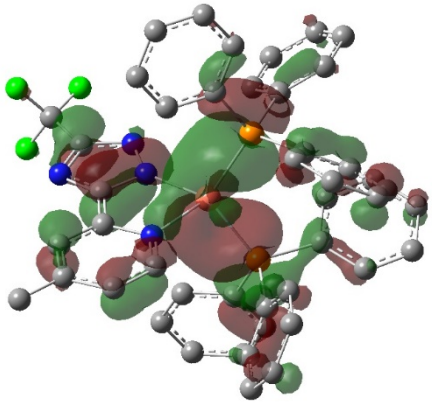
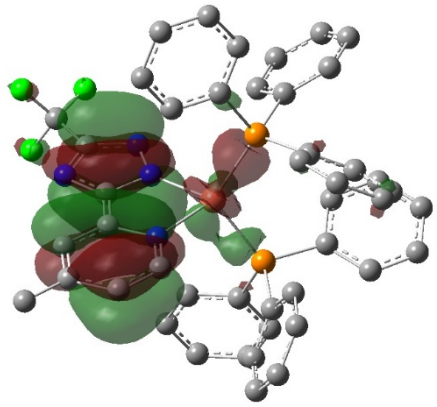
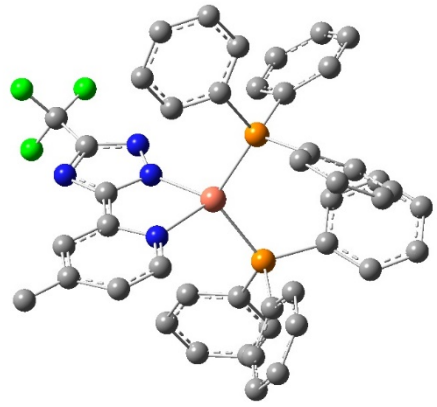
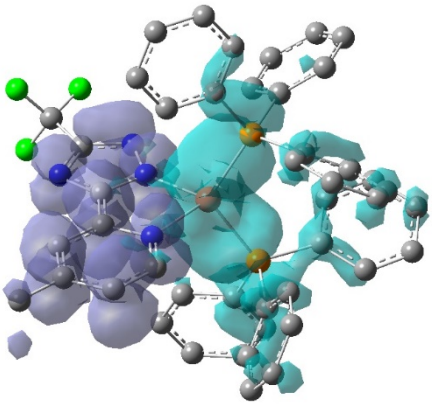
	
LUMO	HOMO
	
HOMO-1	
	
Optimized structure	CDD

Figure S16 The optimized structure, plots of frontier molecular orbitals (isovalue = 0.025) involved in the emission transitions, and the charge density difference (CDD) map (isovalue = 0.0006) between lowest-energy triplet state T_1 and the ground state S_0 for complex **1** in CH_2Cl_2 media calculated by TDDFT method at the M06 level. The red and green parts represent different phases. And the purple and blue parts display the electron accumulation and depletion region, respectively. For clarity, the hydrogen atoms are omitted.

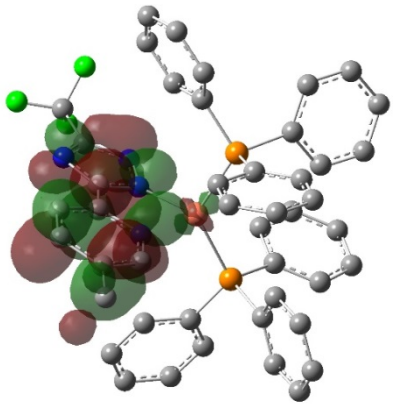
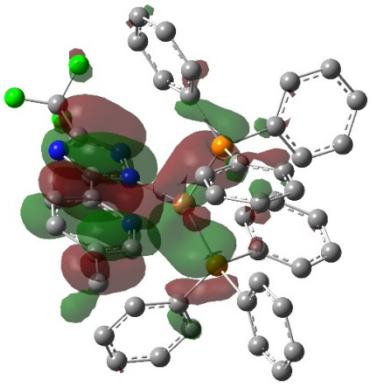
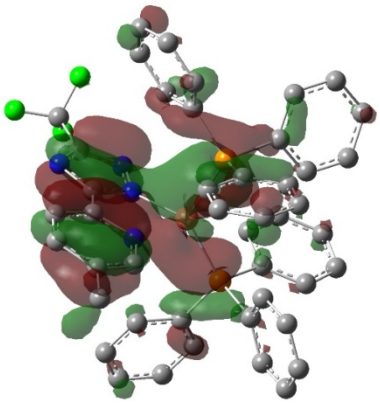
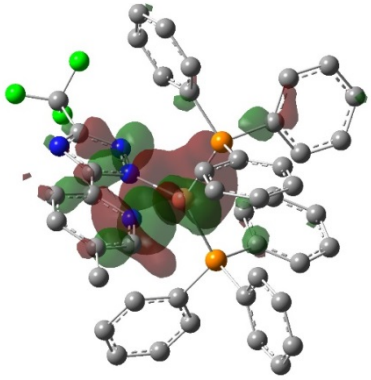
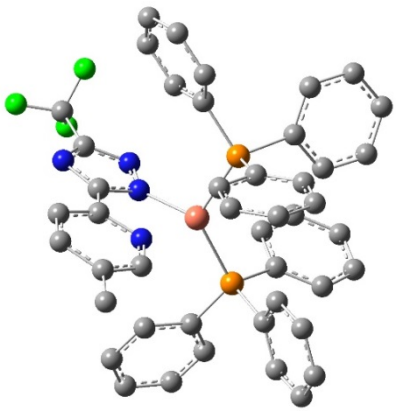
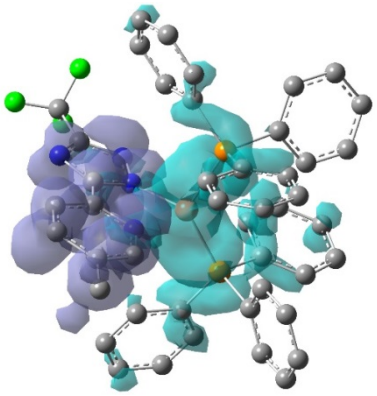
	
LUMO	HOMO
	
HOMO-1	HOMO-3
	
Optimized structure	CDD

Figure S17 The optimized structure, plots of frontier molecular orbitals (isovalue = 0.025) involved in the emission transitions, and the charge density difference (CDD) map (isovalue = 0.0006) between lowest-energy triplet state T_1 and the ground state S_0 for complex **2** in CH_2Cl_2 media calculated by TDDFT method at the M06 level. The red and green parts represent different phases. And the purple and blue parts display the electron accumulation and depletion region, respectively. For clarity, the hydrogen atoms are omitted.

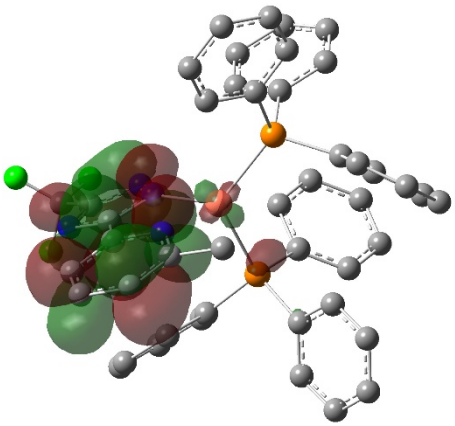
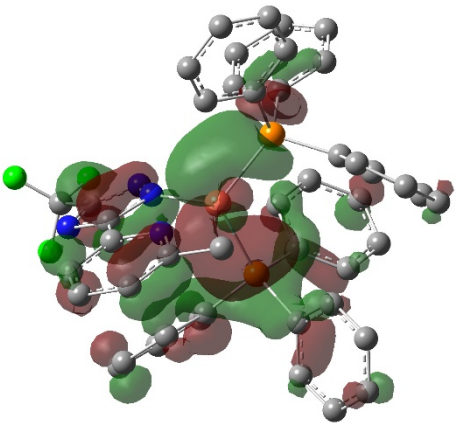
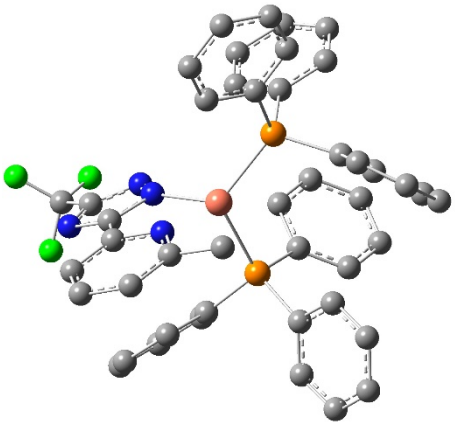
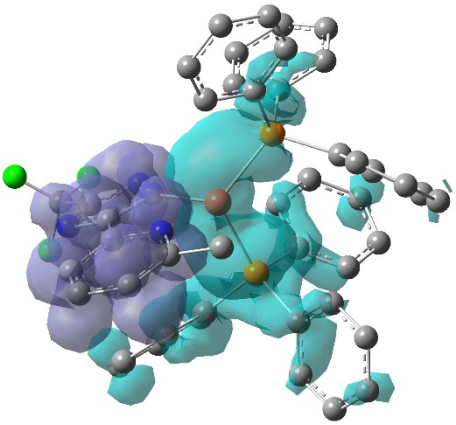
	
LUMO	HOMO
	
Optimized structure	CDD

Figure S18 The optimized structure, plots of frontier molecular orbitals (isovalue = 0.025) involved in the emission transitions, and the charge density difference (CDD) map (isovalue = 0.0006) between lowest-energy triplet state T_1 and the ground state S_0 for complex **3** in CH_2Cl_2 media calculated by TDDFT method at the M06 level. The red and green parts represent different phases. And the purple and blue parts display the electron accumulation and depletion region, respectively. For clarity, the hydrogen atoms are omitted.

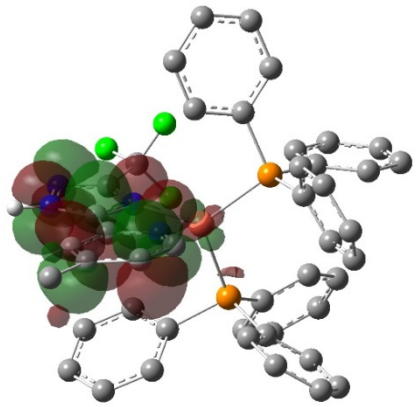
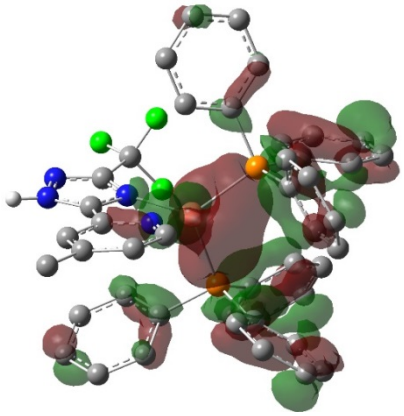
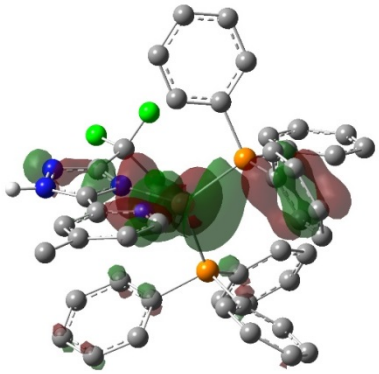
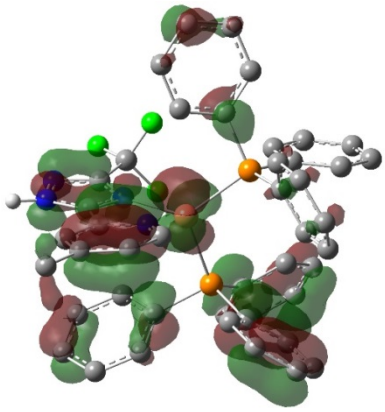
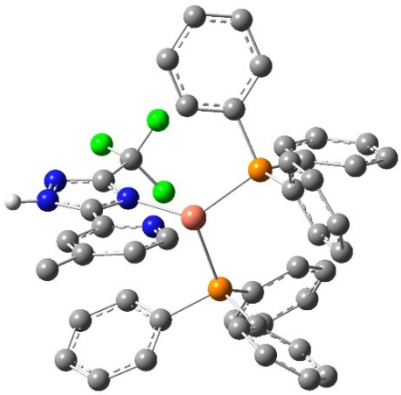
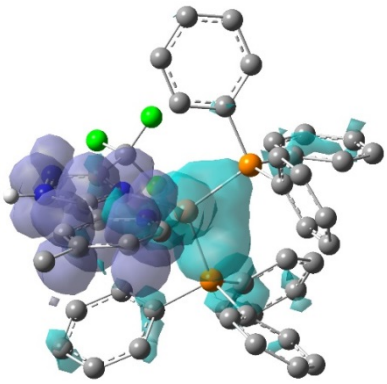
	
LUMO	HOMO-1
	
HOMO-2	HOMO-14
	
Optimized structure	CDD

Figure S19 The optimized structure, plots of frontier molecular orbitals (isovalue = 0.025) involved in the emission transitions, and the charge density difference (CDD) map (isovalue = 0.0006) between lowest-energy triplet state T_1 and the ground state S_0 for complex **4** in CH_2Cl_2 media calculated by TDDFT method at the M06 level. The red and green parts represent different phases. And the purple and blue parts display the electron accumulation and depletion region, respectively. For clarity, the hydrogen atoms except for the ones bonded to N atoms are omitted.

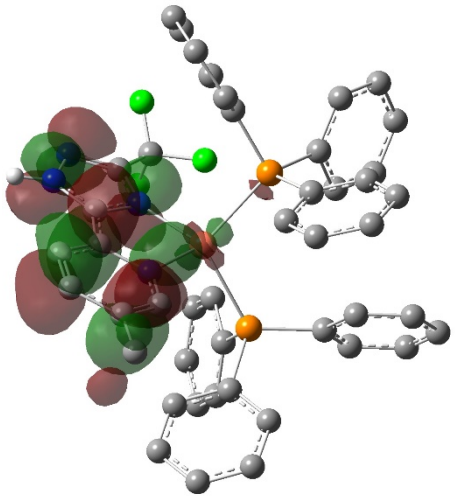
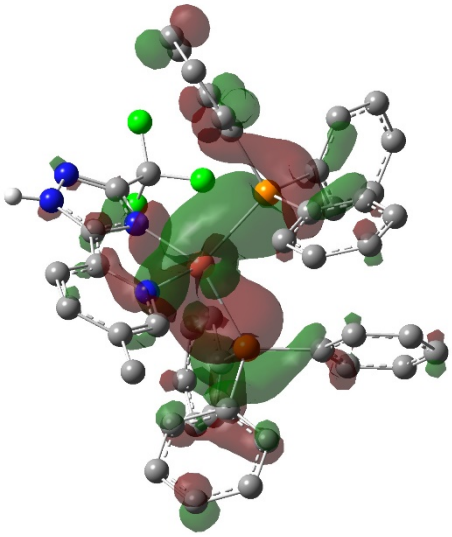
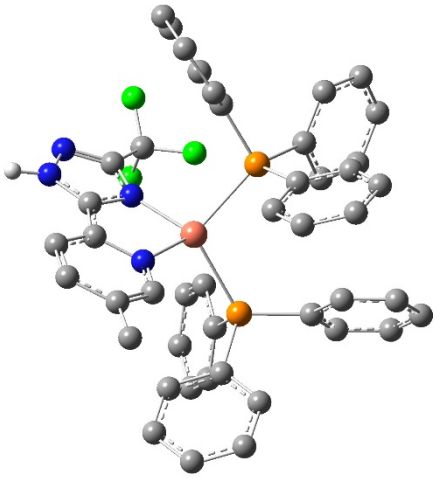
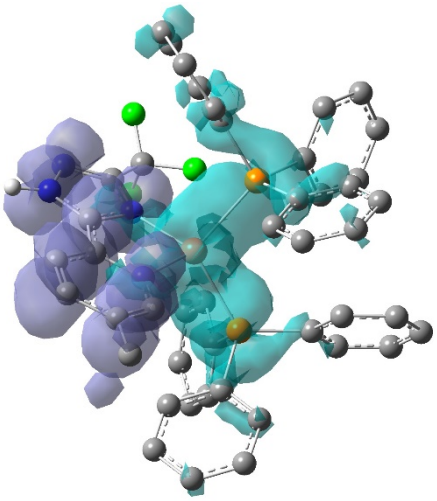
	
LUMO	HOMO
	
Optimized structure	CDD

Figure S20 The optimized structure, plots of frontier molecular orbitals (isovalue = 0.025) involved in the emission transitions, and the charge density difference (CDD) map (isovalue = 0.0006) between lowest-energy triplet state T_1 and the ground state S_0 for complex **5** in CH_2Cl_2 media calculated by TDDFT method at the M06 level. The red and green parts represent different phases. And the purple and blue parts display the electron accumulation and depletion region, respectively. For clarity, the hydrogen atoms except for the ones bonded to N atoms are omitted.

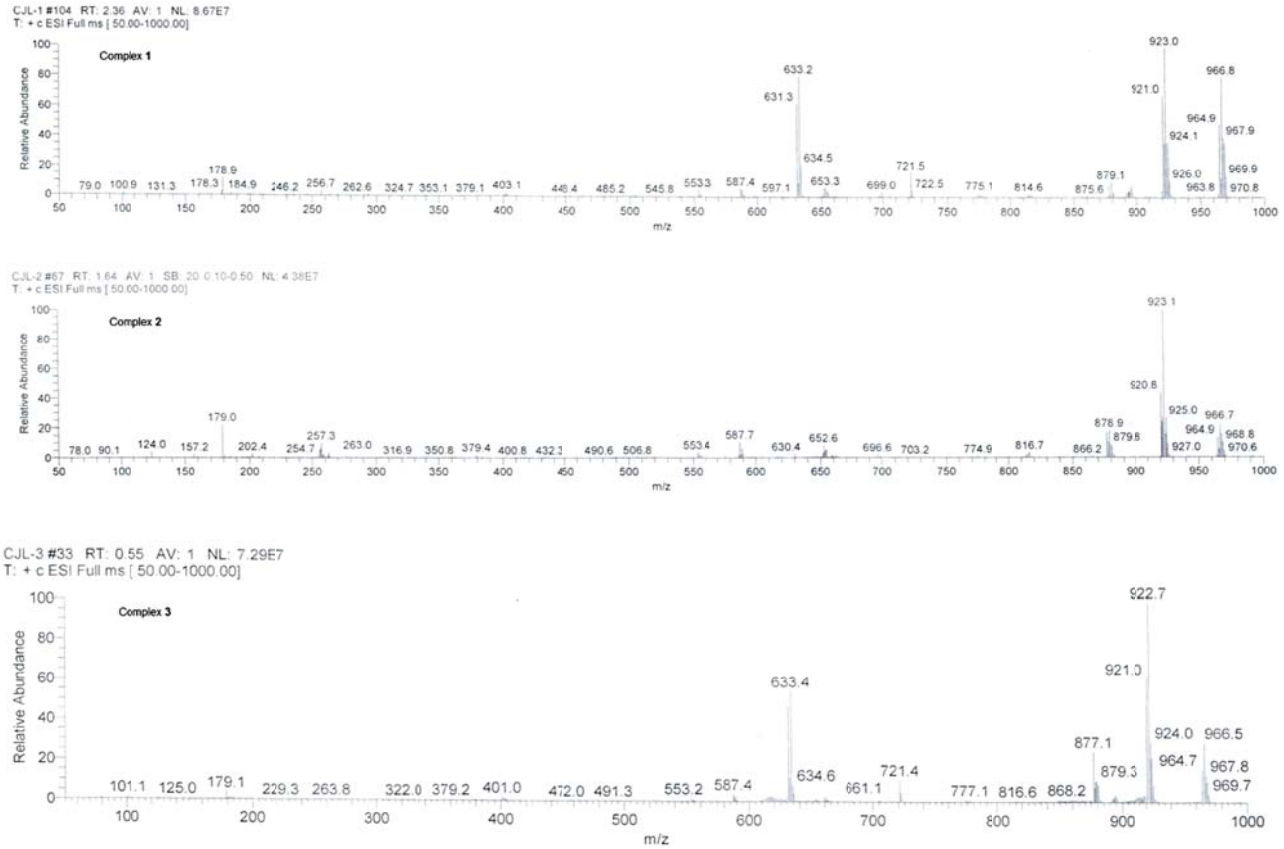


Figure S21 The ESI mass spectra of **1**–**3**.

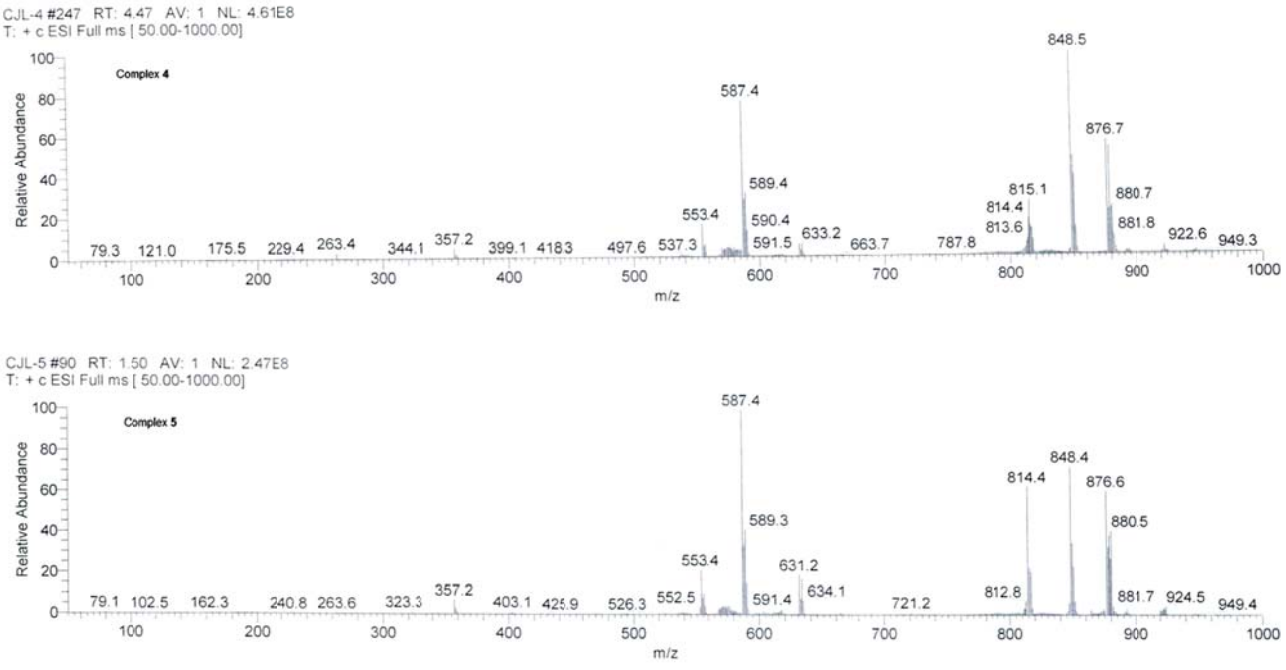
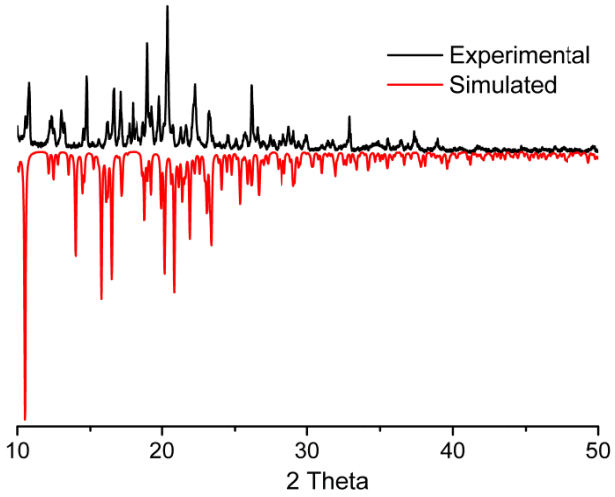
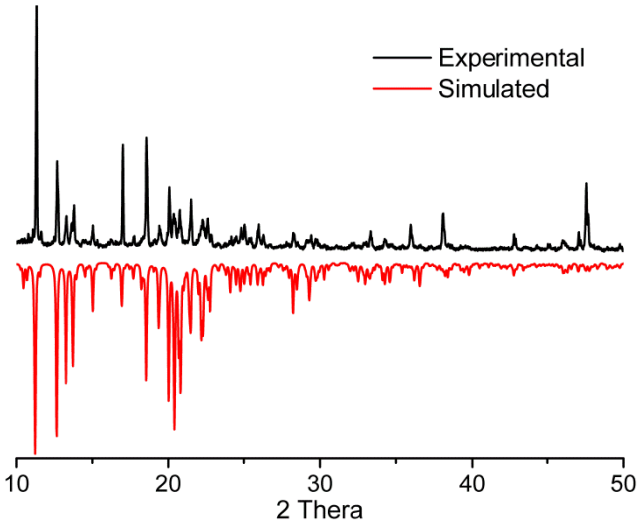


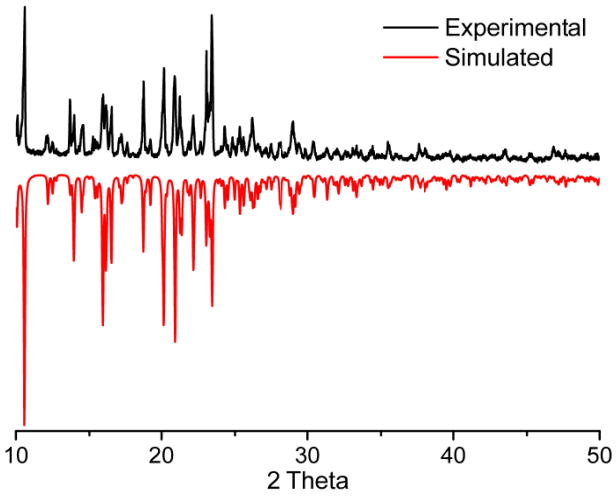
Figure S22 The ESI mass spectra of **4**–**5**.



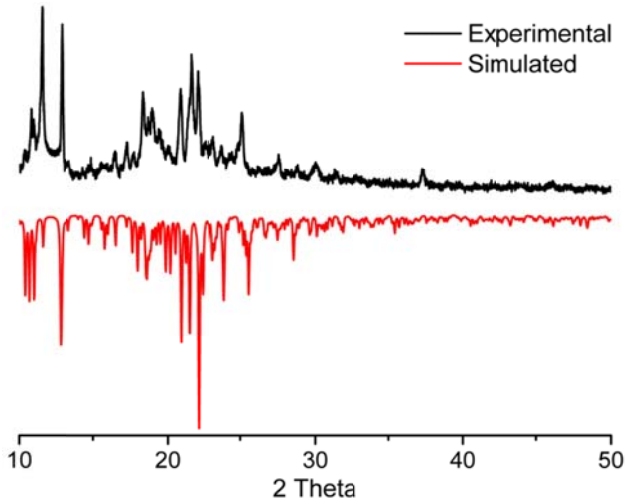
Complex **1**



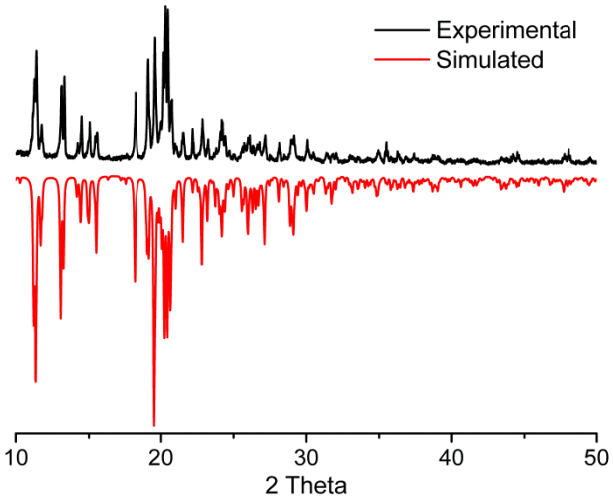
Complex **2**



Complex **3**



Complex **4**



Complex **5**

Figure S23 The PXRD patterns of **1**–**5**.