Supplementary Information

Syntheses, Characterization, and Structural studies of Copper(I) complexes containing 1,1′-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) and their Application in Palladium-Catalyzed Sonogashira Coupling of Aryl halides

Manoj Trivedi[a*], Gurmeet Singh[a], Abhinav Kumar[b] and Nigam P. Rath[c*]

[a*]Department of Chemistry, University of Delhi, Delhi-110007, India

[b]Department of Chemistry, Faculty of Science, University of Lucknow, Lucknow-226 007, India

[c*]Department of Chemistry & Biochemistry and Centre for Nanoscience, University of Missouri-St. Louis, One University Boulevard, St. Louis, MO 63121-4499, USA

E-mail address: manojtri@gmail.com (M.T.); rathn@umsl.edu(NPR).

Corresponding author. Tel.: + 91 9811730475 (MT); (314) 516-5333 (NPR).

Table 1. Crystallographic data for **1**, **2** and **3**.

	1	**2**	**3**
Empirical Formula	$C_{52}H_{88}Cl_4Cu_4Fe_2P_4$	$C_{78}H_{132}Br_6Cu_6Fe_3P_6$	$C_{52}H_{88}I_4P_4Cu_4Fe_2$
FW	1344.76	2283.90	1710.56
crystal system	Orthorhombic	Triclinic	Orthorhombic
space group	Fddd	*P*-1	Pca21
a, Å	16.4372(15)	15.0968(8)	20.4931(18)
b, Å	25.568(3)	17.6712(10)	11.2070(9)
c, Å	30.217(3)	19.1629(11)	26.943(4)
α, deg	90.00	68.193(3)	90.00
β, deg	90.00	69.974(2)	90.00
γ, deg	90.00	82.735(2)	90.00
V, Å^3	12699(2)	4459.4(4)	6188.0(12)
Z	8	2	4
d_{calc}, g cm^{-3}	1.407	1.701	1.836
μ, mm^{-1}	2.060	4.709	3.938
T, K	100(2)	100(2)	293(2)
R_1 all	0.0924	0.0842	0.1615
R_1 [I > 2σ(I)]	0.0483	0.0450	0.1492
wR_2	0.1570	0.0963	0.3658
wR_2 [I > 2σ(I)]	0.1172	0.0837	0.3531
GoF	1.145	1.014	1.451

Table 2. Selected bond lengths (Å), and Bond angles (°) for **1**, **2**, and **3**.

1		2		3	
Cu(1)-P(1)	2.1950(17)	Br(1)-Cu(1)	2.4064(8)	I(1)-Cu(2)	2.574(5)
Cu(1)-Cl(1)$^{\#1}$	2.4315(17)	Br(1)-Cu(2)	2.4763(7)	I(1)-Cu(4)	2.738(5)
Cu(1)-Cl(1)	2.3747(16)	Br(2)-Cu(1)	2.3884(8)	I(1)-Cu(1)	2.801(5)
Cu(1)-Cl(1)$^{\#2}$	2.5269(16)	Br(2)-Cu(3)	2.4759(8)	I(4)-Cu(3)	2.538(5)
Cu(1)-Cu(1)$^{\#3}$	2.9369(16)	Br(3)-Cu(3)	2.4308(7)	I(4)-Cu(4)	2.648(5)
Cl(1)-Cu(1)$^{\#1}$	2.4315(17)	Br(3)-Cu(2)	2.4311(7)	I(2)-Cu(2)	2.555(5)
Cl(1)-Cu(1)$^{\#2}$	2.5270(16)	Br(4)-Cu(4)	2.4592(8)	I(2)-Cu(1)	2.659(5)
P(1)-C(1)	1.821(6)	Br(4)-Cu(5)	2.4740(8)	I(3)-Cu(3)	2.567(5)
P(1)-C(6)	1.917(7)	Br(5)-Cu(6)	2.4232(7)	I(3)-Cu(1)	2.756(5)
P(1)-C(10)	1.885(7)	Br(5)-Cu(5)	2.6883(8)	I(3)-Cu(4)	2.854(5)
P(1)-Cu(1)-Cl(1)	132.25(7)	Br(5)-Cu(4)	2.6900(9)	Cu(2)-P(2)	2.203(10)
P(1)-Cu(1)-Cl(1)$^{\#1}$	115.35(7)	Br(6)-Cu(6)	2.4413(8)	Cu(2)-Cu(1)	2.731(6)
Cl(1)$^{\#1}$-Cu(1)-Cl(1)	94.05(6)	Br(6)-Cu(5)	2.5669(8)	Cu(3)-P(3)	2.229(10)
P(1)-Cu(1)-Cl(1)$^{\#2}$	116.84(6)	Br(6)-Cu(4)	2.7471(8)	Cu(3)-Cu(4)	2.733(6)
Cl(1)-Cu(1)-Cl(1)$^{\#2}$	87.06(6)	Cu(1)-P(1)	2.1998(13)	Cu(4)-P(4)	2.232(10)
Cl(1)$^{\#1}$-Cu(1)-Cl(1)$^{\#2}$	105.70(5)	Cu(1)-Cu(2)	2.9789(8)	Cu(1)-P(1)	2.273(9)
P(1)-Cu(1)-Cu(1)$^{\#3}$	125.43(5)	Cu(2)-P(2)	2.2134(12)	P(2)-C(29)	1.97(3)
Cl(1)-Cu(1)-Cu(1)$^{\#3}$	102.10(4)	Cu(2)-Cu(3)	2.8597(8)	P(2)-C(33)	1.82(3)
Cl(1)$^{\#1}$-Cu(1)-Cu(1)$^{\#3}$	55.20(4)	Cu(3)-P(3)	2.2048(13)	P(1)-C(21)	1.91(4)
Cl(1)$^{\#2}$-Cu(1)-Cu(1)$^{\#3}$	52.19(4)	Cu(4)-P(4)	2.2216(13)	P(1)-C(25)	1.94(3)
Cu(1)-Cl(1)-Cu(1)$^{\#1}$	84.76(5)	Cu(4)-Cu(5)	2.6980(8)	P(4)-C(49)	1.91(4)
Cu(1)-Cl(1)-Cu(1)$^{\#2}$	88.57(5)	Cu(5)-P(5)	2.2088(12)	P(4)-C(45)	1.96(3)
Cu(1)$^{\#1}$-Cl(1)-Cu(1)$^{\#2}$	72.61(5)	Cu(5)-Cu(6)	2.8962(8)	P(3)-C(37)	1.79(3)
		Cu(6)-P(6)	2.2059(13)	P(3)-C(41)	1.91(2)
		P(1)-C(19)	1.877(5)	Cu(2)-I(1)-Cu(4)	125.80(16)
		P(1)-C(23)	1.888(5)	Cu(2)-I(1)-Cu(1)	60.90(14)
		P(2)-C(11)	1.883(5)	Cu(4)-I(1)-Cu(1)	89.84(16)

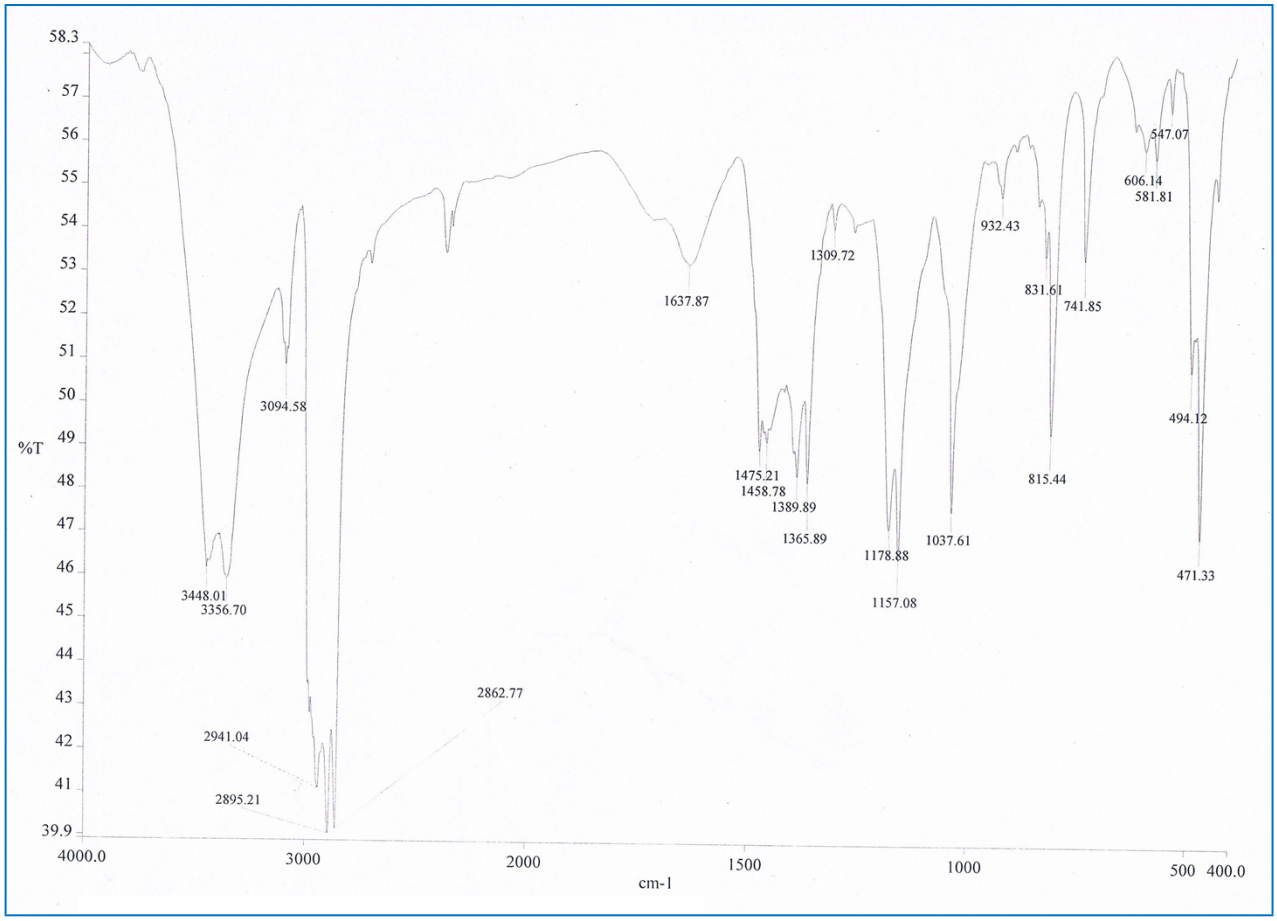
P(3)-C(37)	1.878(5)	Cu(3)-I(4)-Cu(4)	63.56(15)
P(3)-C(41)	1.900(5)	Cu(2)-I(2)-Cu(1)	63.14(15)
P(4)-C(49)	1.887(5)	Cu(3)-I(3)-Cu(1)	125.92(17)
P(4)-C(45)	1.902(5)	Cu(3)-I(3)-Cu(4)	60.27(14)
P(5)-C(63)	1.885(5)	Cu(1)-I(3)-Cu(4)	88.41(15)
P(5)-C(67)	1.902(4)	P(2)-Cu(2)-I(2)	126.2(3)
P(6)-C(71)	1.888(5)	P(2)-Cu(2)-I(1)	121.1(3)
P(6)-C(75)	1.897(5)	I(2)-Cu(2)-I(1)	112.12(18)
P(2)-C(15)	1.898(4)	P(2)-Cu(2)-Cu(1)	140.2(3)
Cu(1)-Br(1)-Cu(2)	75.18(2)	I(2)-Cu(2)-Cu(1)	60.28(14)
Cu(1)-Br(2)-Cu(3)	86.57(3)	I(1)-Cu(2)-Cu(1)	63.66(14)
Cu(3)-Br(3)-Cu(2)	72.06(2)	P(3)-Cu(3)-I(4)	124.5(3)
Cu(4)-Br(4)-Cu(5)	66.31(2)	P(3)-Cu(3)-I(3)	122.6(3)
Cu(6)-Br(5)-Cu(5)	68.80(2)	I(4)-Cu(3)-I(3)	112.65(19)
Cu(6)-Br(5)-Cu(4)	86.30(3)	P(3)-Cu(3)-Cu(4)	140.6(3)
Cu(5)-Br(5)-Cu(4)	60.22(2)	I(4)-Cu(3)-Cu(4)	60.18(14)
Cu(6)-Br(6)-Cu(5)	70.61(2)	I(3)-Cu(3)-Cu(4)	65.07(14)
Cu(6)-Br(6)-Cu(4)	84.69(3)	P(4)-Cu(4)-I(4)	119.5(3)
Cu(5)-Br(6)-Cu(4)	60.91(2)	P(4)-Cu(4)-I(1)	119.1(3)
P(1)-Cu(1)-Br(2)	124.71(4)	I(4)-Cu(4)-I(1)	99.59(16)
P(1)-Cu(1)-Br(1)	128.83(4)	P(4)-Cu(4)-Cu(3)	115.9(3)
Br(2)-Cu(1)-Br(1)	106.06(3)	I(4)-Cu(4)-Cu(3)	56.26(13)
Br(2)-Cu(1)-Cu(2)	67.64(2)	Cu(3)-Cu(4)-I(1)	124.55(18)
Br(1)-Cu(1)-Cu(2)	53.48(2)	P(4)-Cu(4)-I(3)	121.4(3)
P(2)-Cu(2)-Br(3)	121.51(4)	I(4)-Cu(4)-I(3)	101.03(15)
P(2)-Cu(2)-Br(1)	119.23(4)	I(1)-Cu(4)-I(3)	90.50(14)
Br(3)-Cu(2)-Br(1)	109.63(3)	Cu(3)-Cu(4)-I(3)	54.66(13)
P(2)-Cu(2)-Cu(3)	170.85(4)	P(1)-Cu(1)-I(2)	118.8(3)
Br(3)-Cu(2)-Cu(3)	53.967(19)	P(1)-Cu(1)-I(3)	119.9(3)
Br(1)-Cu(2)-Cu(3)	69.39(2)	P(1)-Cu(1)-I(1)	120.6(3)

Br(1)-Cu(2)-Cu(1)	51.346(19)	I(3)-Cu(1)-I(1)	91.26(14)
Cu(3)-Cu(2)-Cu(1)	69.65(2)	Cu(2)-Cu(1)-I(3)	124.55(19)
P(3)-Cu(3)-Br(3)	127.09(4)		
P(3)-Cu(3)-Br(2)	129.12(4)		
Br(3)-Cu(3)-Br(2)	98.73(3)		
P(3)-Cu(3)-Cu(2)	154.45(4)		
Br(3)-Cu(3)-Cu(2)	53.977(19)		
Br(2)-Cu(3)-Cu(2)	68.70(2)		
P(4)-Cu(4)-Br(4)	121.59(4)		
P(4)-Cu(4)-Br(5)	124.34(4)		
Br(4)-Cu(4)-Br(5)	97.72(3)		
P(4)-Cu(4)-Cu(5)	175.57(5)		
Br(4)-Cu(4)-Cu(5)	57.11(2)		
Br(5)-Cu(4)-Cu(5)	59.86(2)		
P(4)-Cu(4)-Br(6)	121.15(4)		
Br(4)-Cu(4)-Br(6)	98.10(3)		
Br(5)-Cu(4)-Br(6)	85.75(2)		
Cu(5)-Cu(4)-Br(6)	56.24(2)		
P(5)-Cu(5)-Br(4)	113.56(4)		
P(5)-Cu(5)-Br(6)	124.58(4)		
Br(4)-Cu(5)-Br(6)	102.68(3)		
P(5)-Cu(5)-Br(5)	123.64(4)		
Br(4)-Cu(5)-Br(5)	97.40(3)		
Br(6)-Cu(5)-Br(5)	89.47(2)		
P(5)-Cu(5)-Cu(4)	169.99(4)		
Br(4)-Cu(5)-Cu(4)	56.58(2)		
Br(6)-Cu(5)-Cu(4)	62.84(2)		
Br(4)-Cu(5)-Br(5)	97.40(3)		
Br(6)-Cu(5)-Br(5)	89.47(2)		
Br(6)-Cu(5)-Cu(6)	52.67(2)		

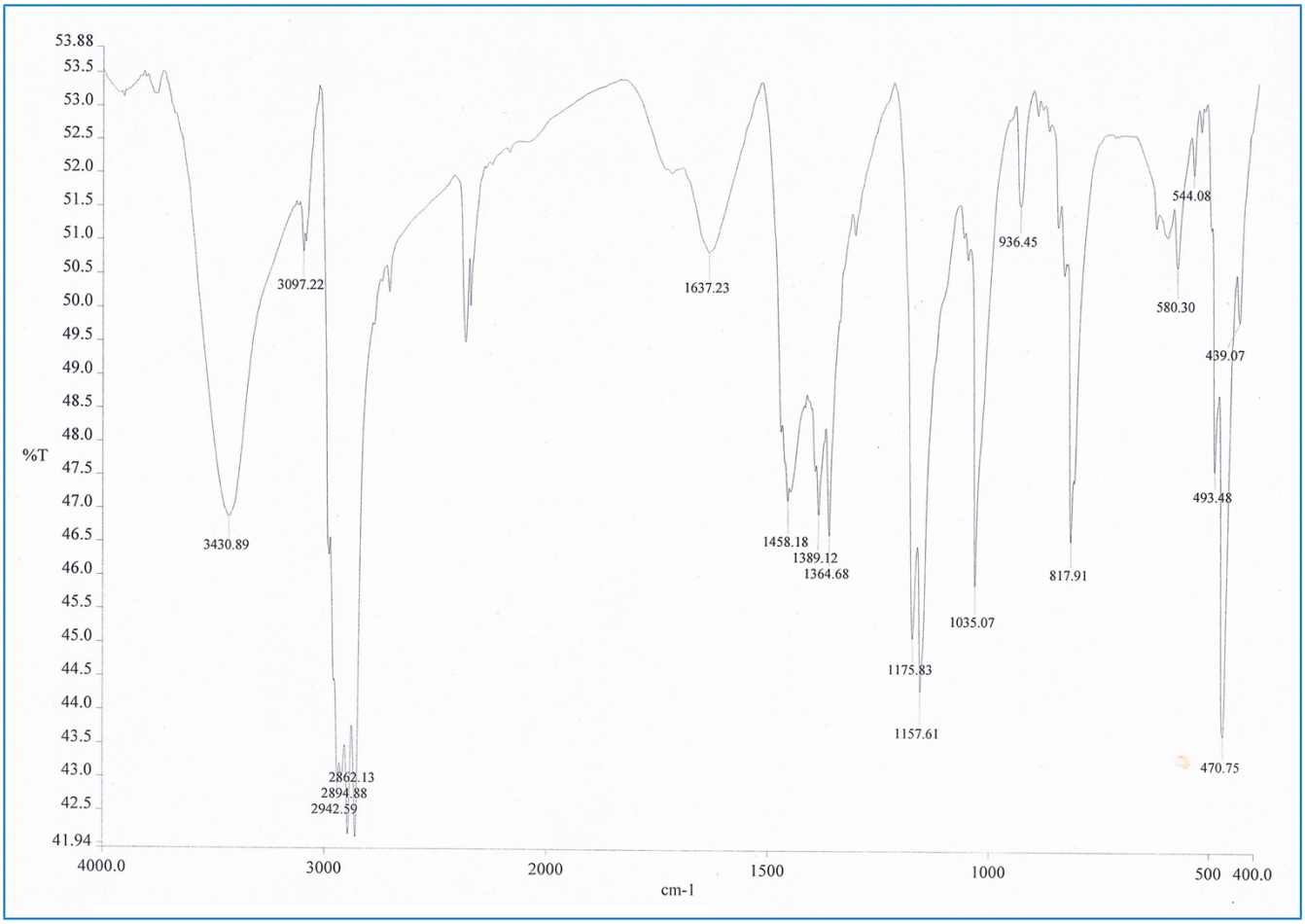
Br(5)-Cu(5)-Cu(6)	51.267(19)
Cu(4)-Cu(5)-Cu(6)	77.43(2)
Br(6)-Cu(5)-Cu(6)	52.67(2)
P(6)-Cu(6)-Br(5)	128.84(4)
P(6)-Cu(6)-Br(6)	131.86(4)
Br(5)-Cu(6)-Br(6)	99.03(3)
C(6)-P(1)-Cu(1)	105.82(14)
C(1)-P(2)-Cu(2)	115.93(14)
C(32)-P(3)-Cu(3)	110.17(14)
C(19)-P(1)-Cu(1)	113.32(15)
C(23)-P(1)-Cu(1)	115.34(16)
C(11)-P(2)-Cu(2)	108.93(15)
C(15)-P(2)-Cu(2)	112.57(14)
C(37)-P(3)-Cu(3)	112.86(16)
C(41)-P(3)-Cu(3)	113.21(15)
C(27)-P(4)-Cu(4)	108.62(14)
C(49)-P(4)-Cu(4)	114.45(16)
C(45)-P(4)-Cu(4)	112.01(14)
C(53)-P(5)-Cu(5)	116.34(14)
C(58)-P(6)-Cu(6)	106.50(14)
C(67)-P(5)-Cu(5)	110.52(15)
C(63)-P(5)-Cu(5)	110.60(16)
C(71)-P(6)-Cu(6)	113.80(15)
C(75)-P(6)-Cu(6)	115.55(15)

Table 3. Hydrogen bonds for the complexes **1-3** [Å and °].

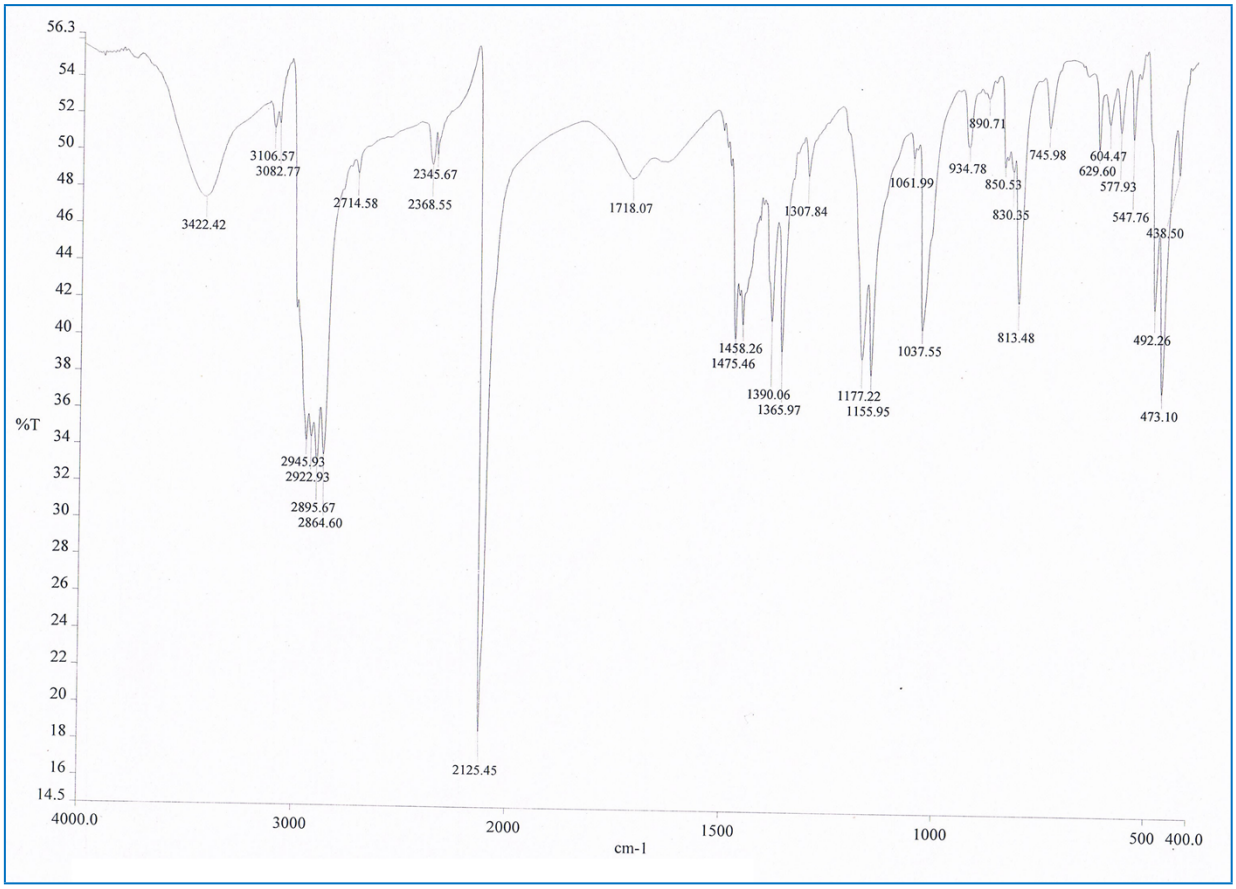
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Complex-1				
C(2)-H(2)···Cl(1)	0.95	2.74	3.622	154
Symmetry transformations used to generate equivalent atoms: x,1/4-y,1/4-z				
Complex-2				
C(7)-H(7)···Br(1)	0.95	3.14	3.985(4)	149.6
C(13)-H(13C)···Br(1)	0.98	3.08	4.009(4)	158.6
C(16)-H(16C)···Br(3)	0.98	3.04	3.965(5)	158.5
C(21)-H(21A)···Br(2)	0.98	2.93	3.875(4)	161.3
C(22)-H(22C)···Br(4)$^{\#1}$	0.98	3.05	3.720(5)	126.9
C(28)-H(28)···Br(4)	0.95	2.95	3.815(4)	152.6
C(40)-H(40C)···Br(2)	0.98	3.14	4.082(5)	161.9
C(44)-H(44A)···Br(1)	0.98	2.90	3.809(5)	153.9
C(47)-H(47A)···Br(4)	0.98	3.08	3.808(5)	132.4
C(69)-H(69A)···Br(4)	0.98	2.90	3.828(5)	157.6
C(72)-H(72C)···Br(3)$^{\#2}$	0.98	3.07	3.824(4)	134.9
C(74)-H(74A)···Br(3)$^{\#2}$	0.98	3.09	3.744(5)	125.1
C(77)-H(77C)···Br(3)$^{\#2}$	0.98	3.05	3.964(5)	155.9
Symmetry transformations used to generate equivalent atoms: $^{\#1}$-x,-y+1,-z+1, $^{\#}$2 -x+1,-y+2,-z				
Complex-3				
C(43)-H(43C)···I(4)	0.96	3.03	3.83(4)	142



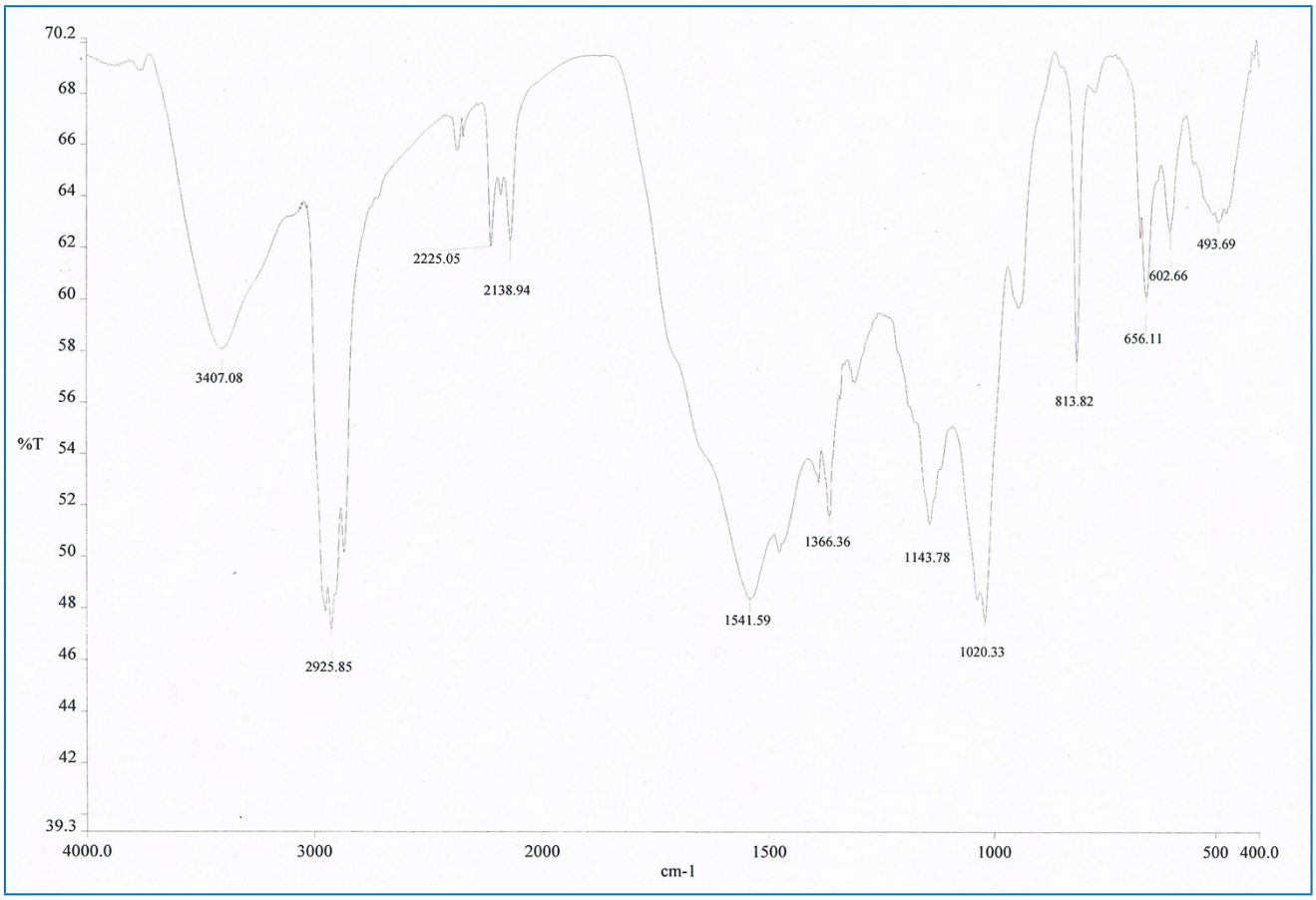
F-1. Infrared spectrum of **1.**



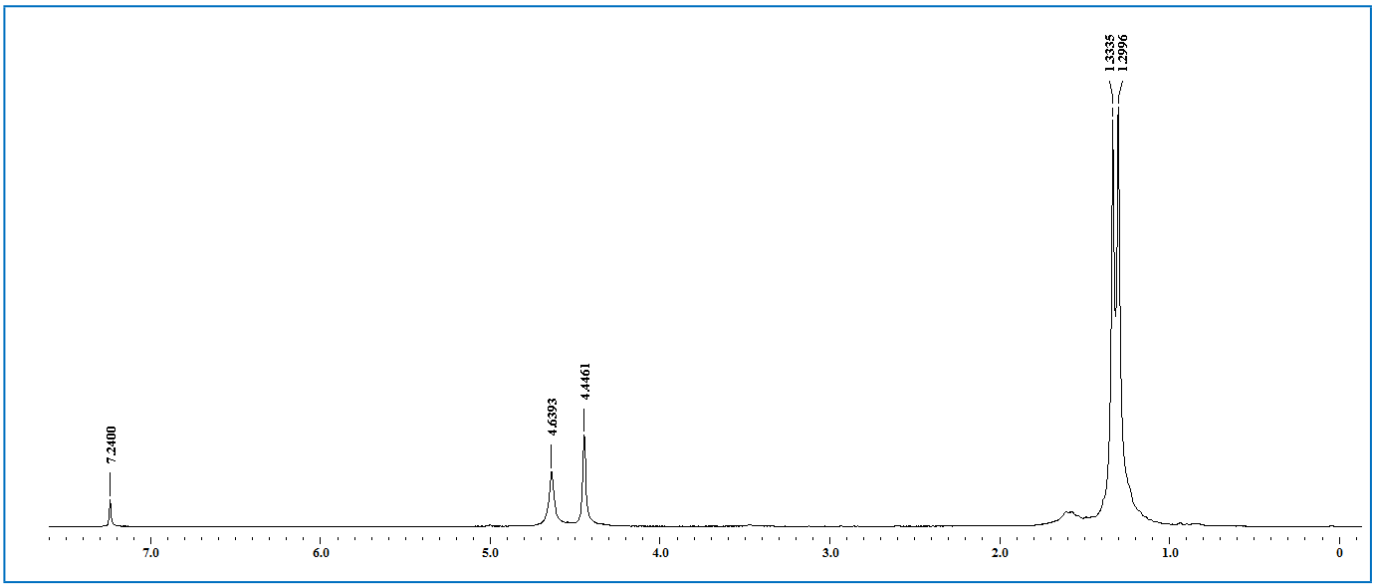
F-2. Infrared spectrum spectrum of **3**.



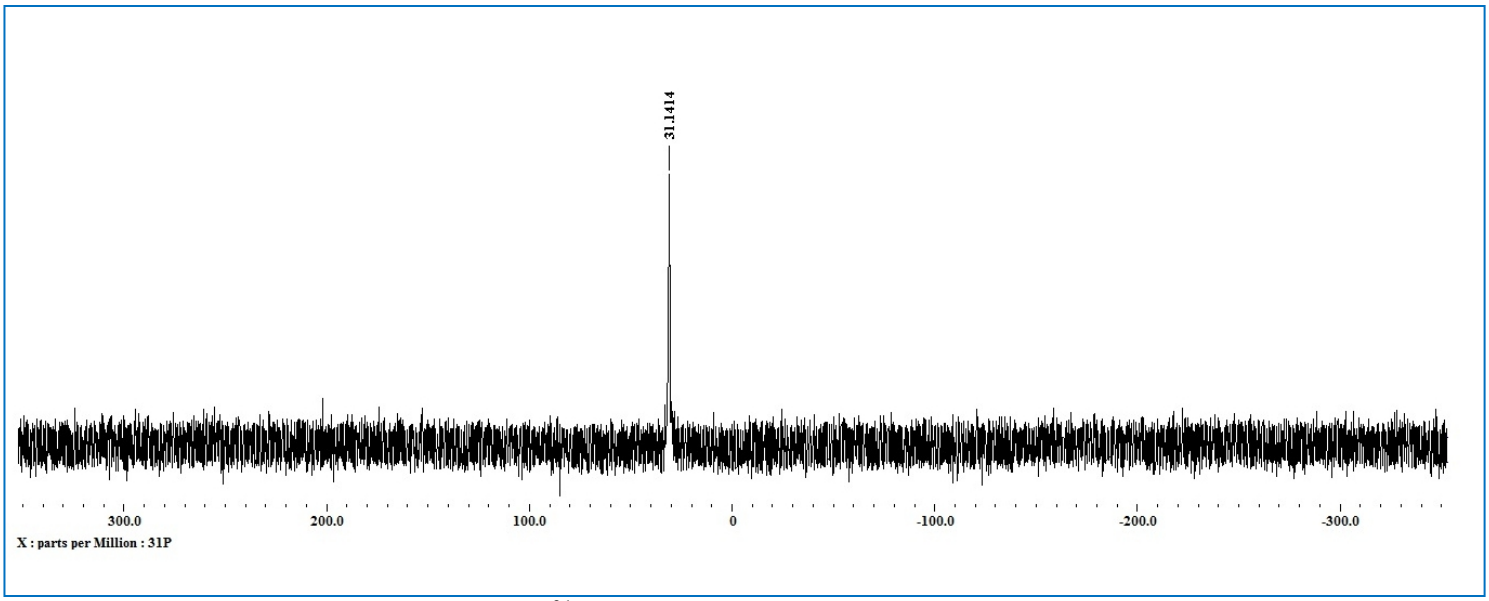
F-3. Infrared spectrum of **2**.



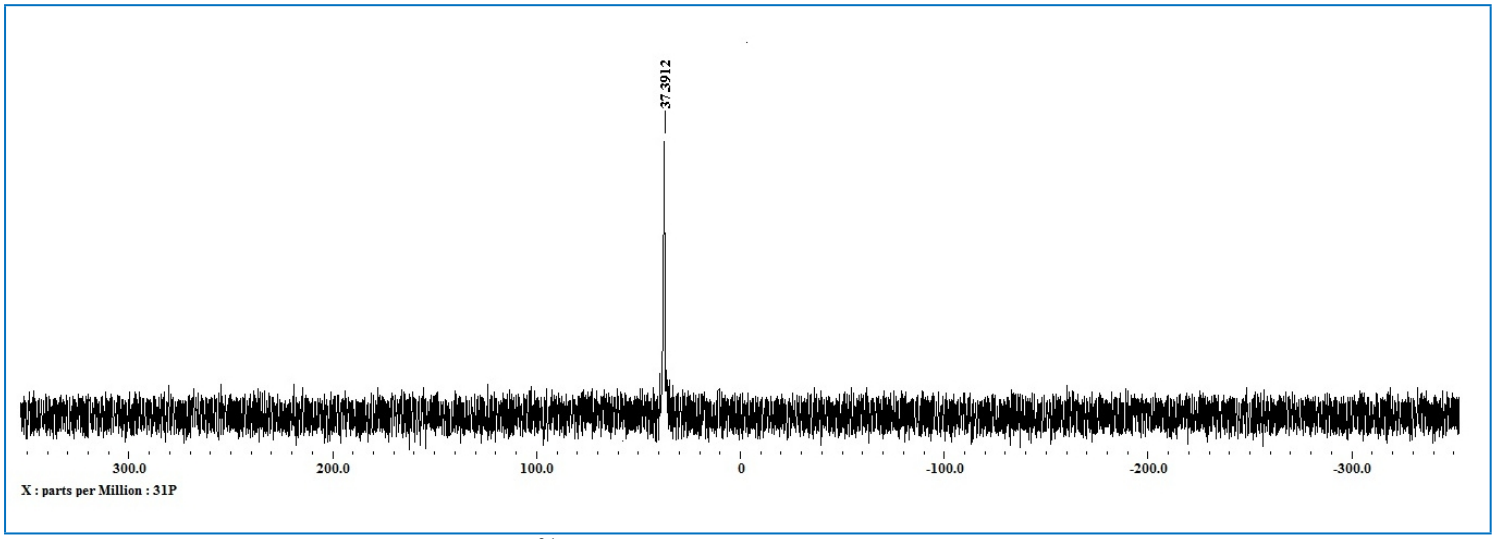
F-4. Infrared spectrum of **4**.



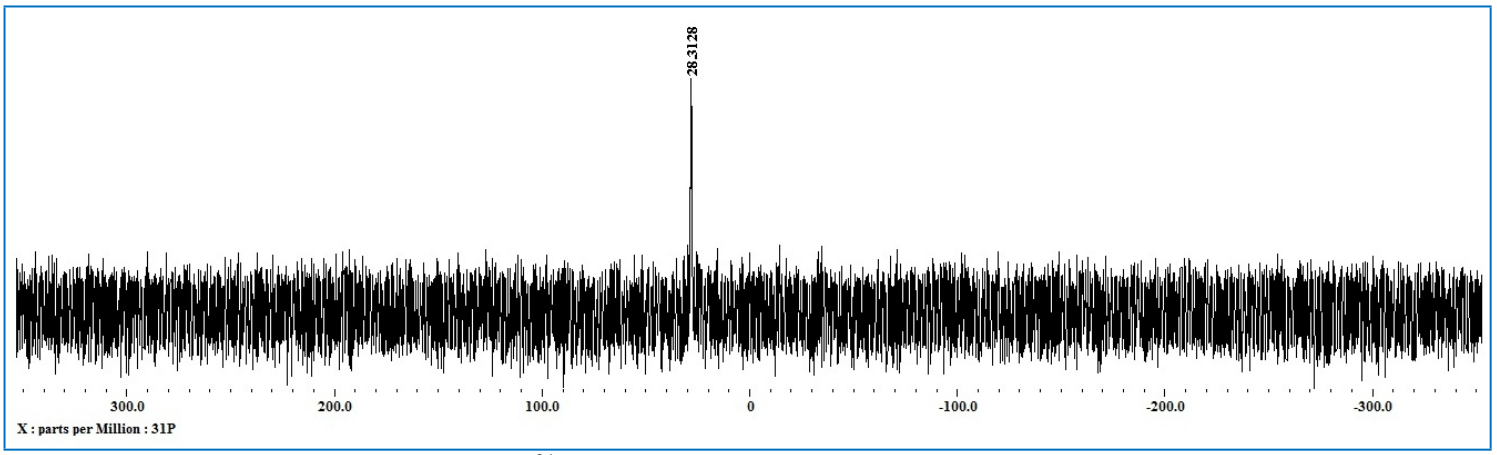
F-5. ^{1}H NMR spectrum of **1** in $CDCl_3$**.**



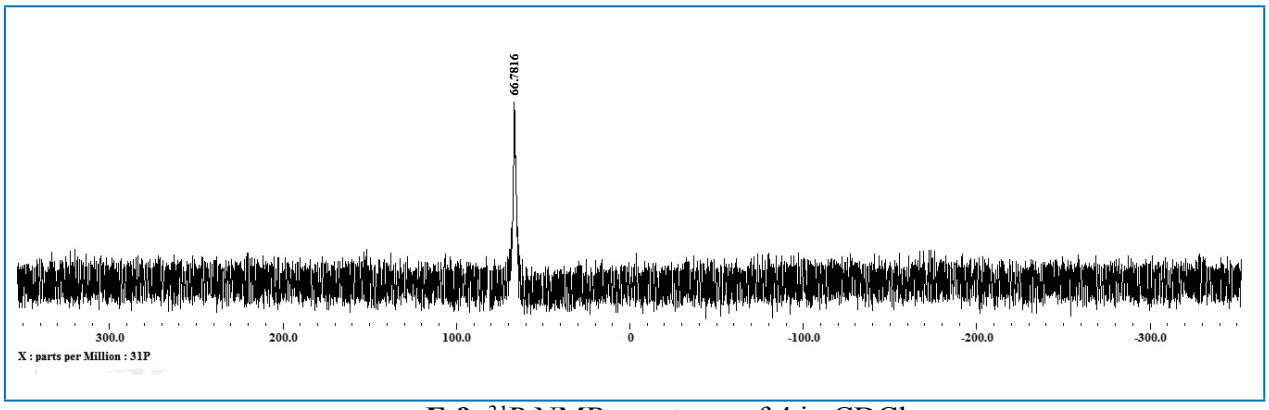
F-6. ^{31}P NMR spectrum of **1** in $CDCl_3$.



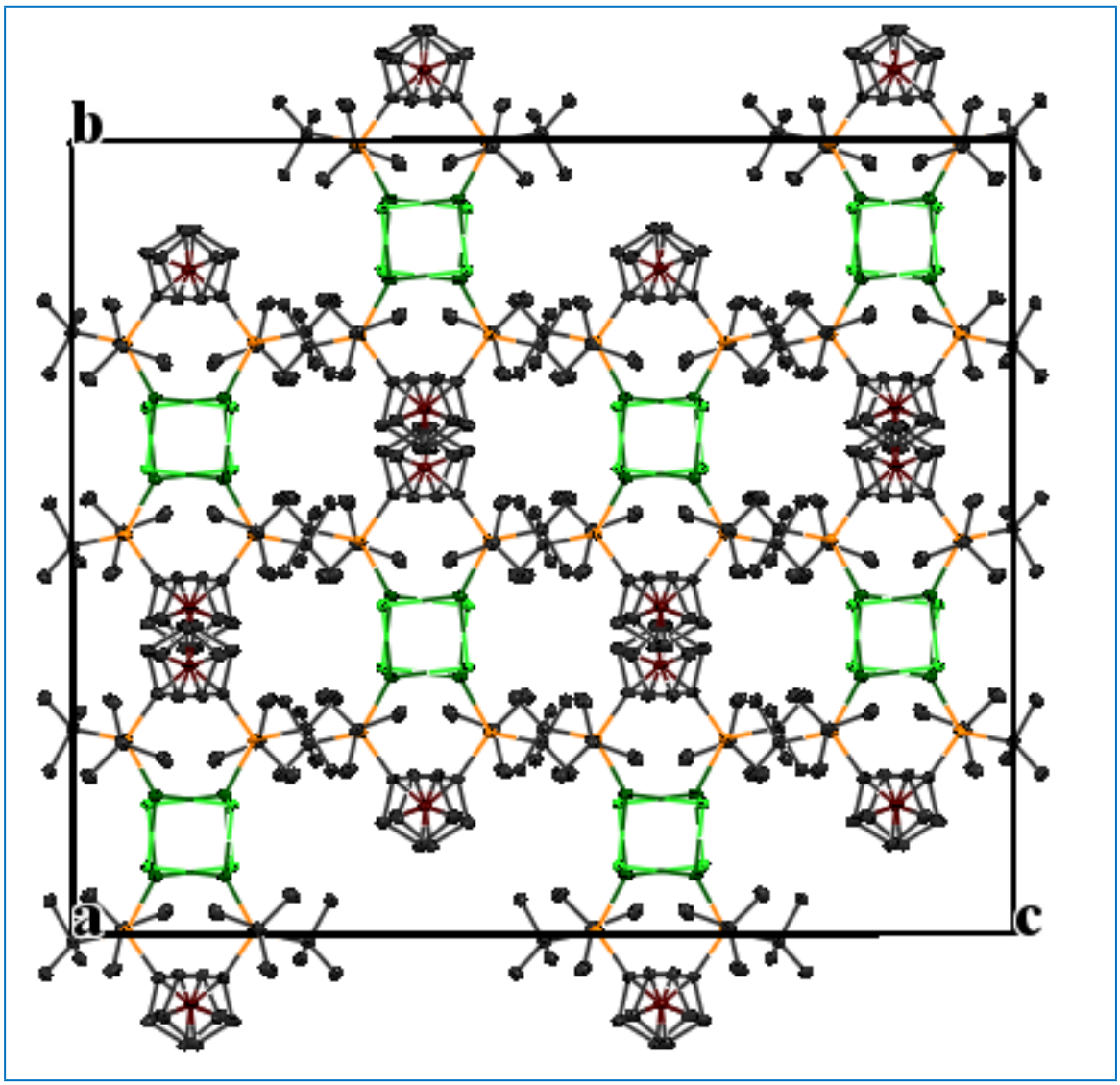
F-7. ^{31}P NMR spectrum of **2** in $CDCl_3$.



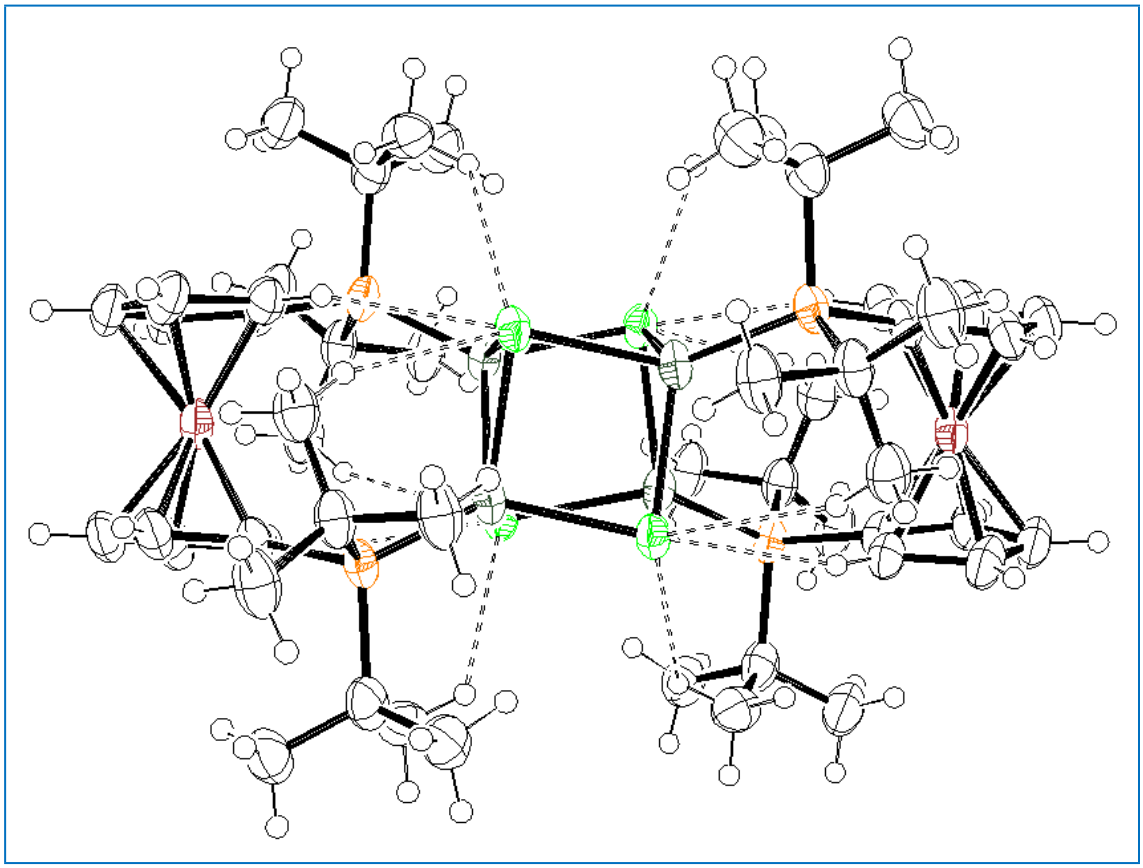
F-8. ^{31}P NMR spectrum of **3** in $CDCl_3$.



F-9. ^{31}P NMR spectrum of **4** in $CDCl_3$.


b
a
c

F-10. Crystal packing diagram of **1**, viewed along the *a* axis.



F-11. Ortep diagram of **1** showing C-H···Cl hydrogen bond interactions in the crystal lattice.

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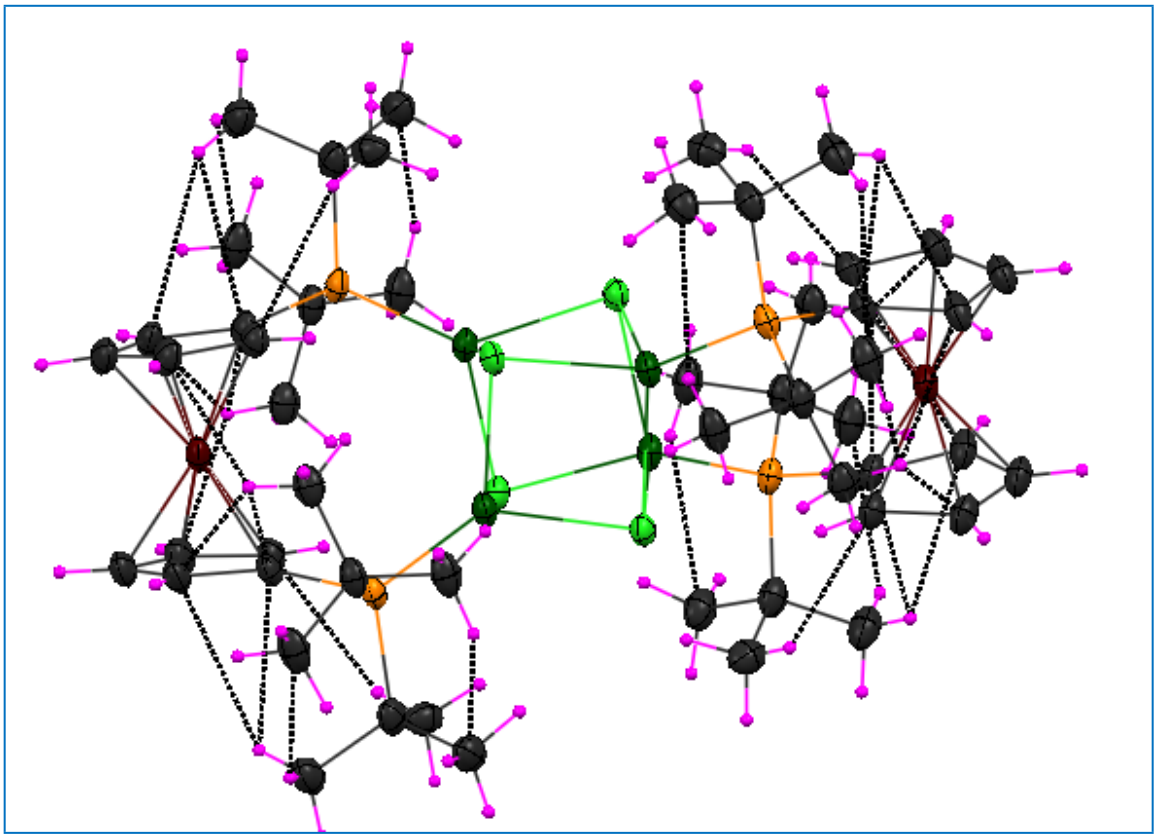
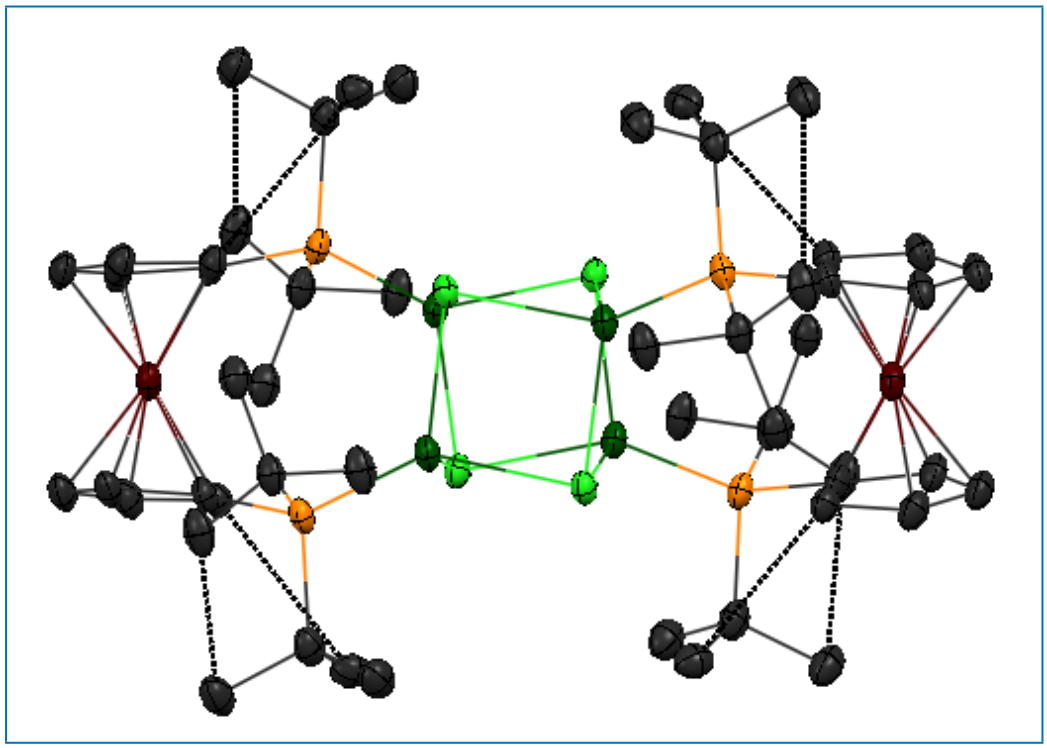
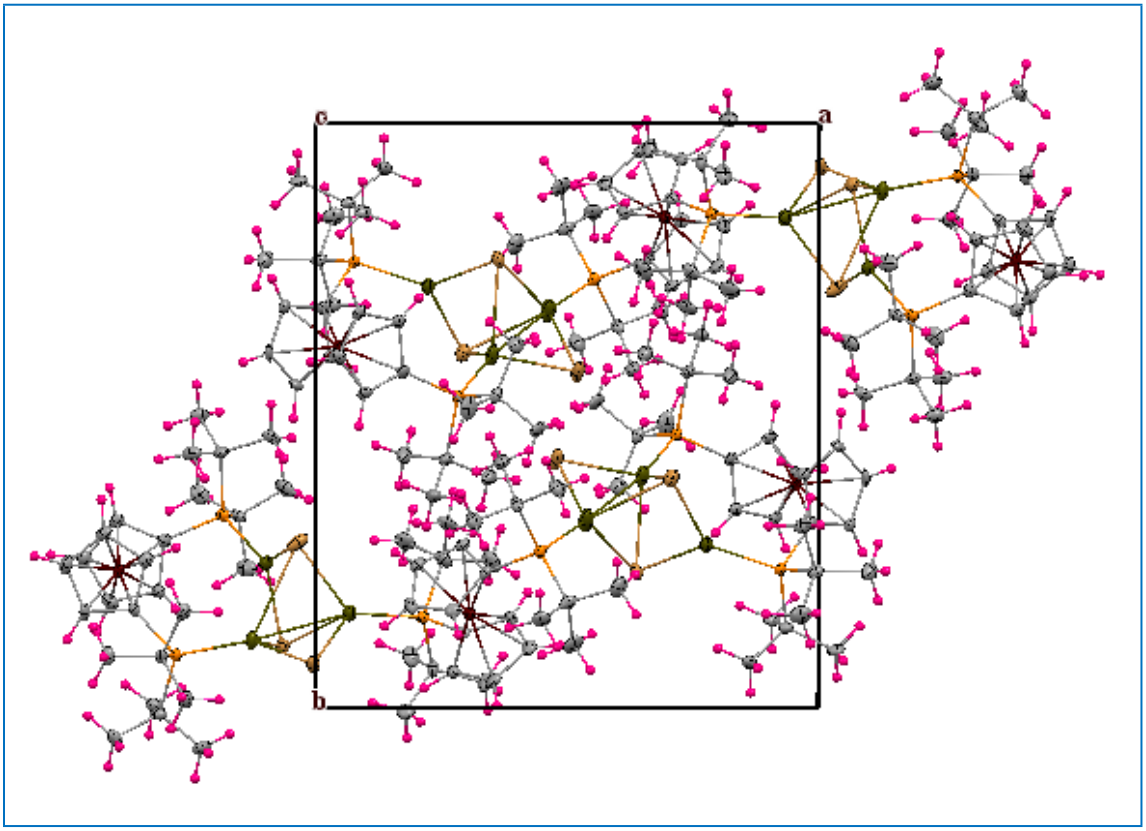


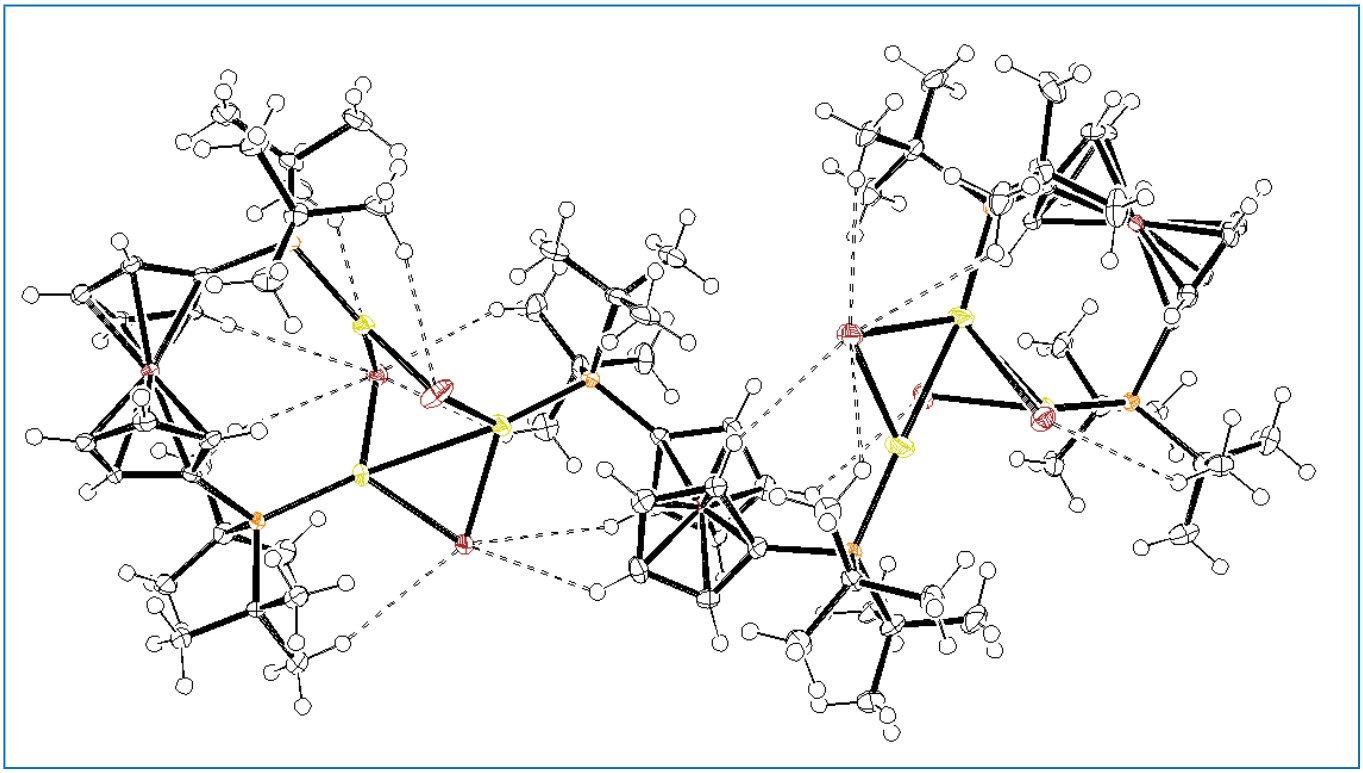
F-12. C-H···π interactions in **1**.



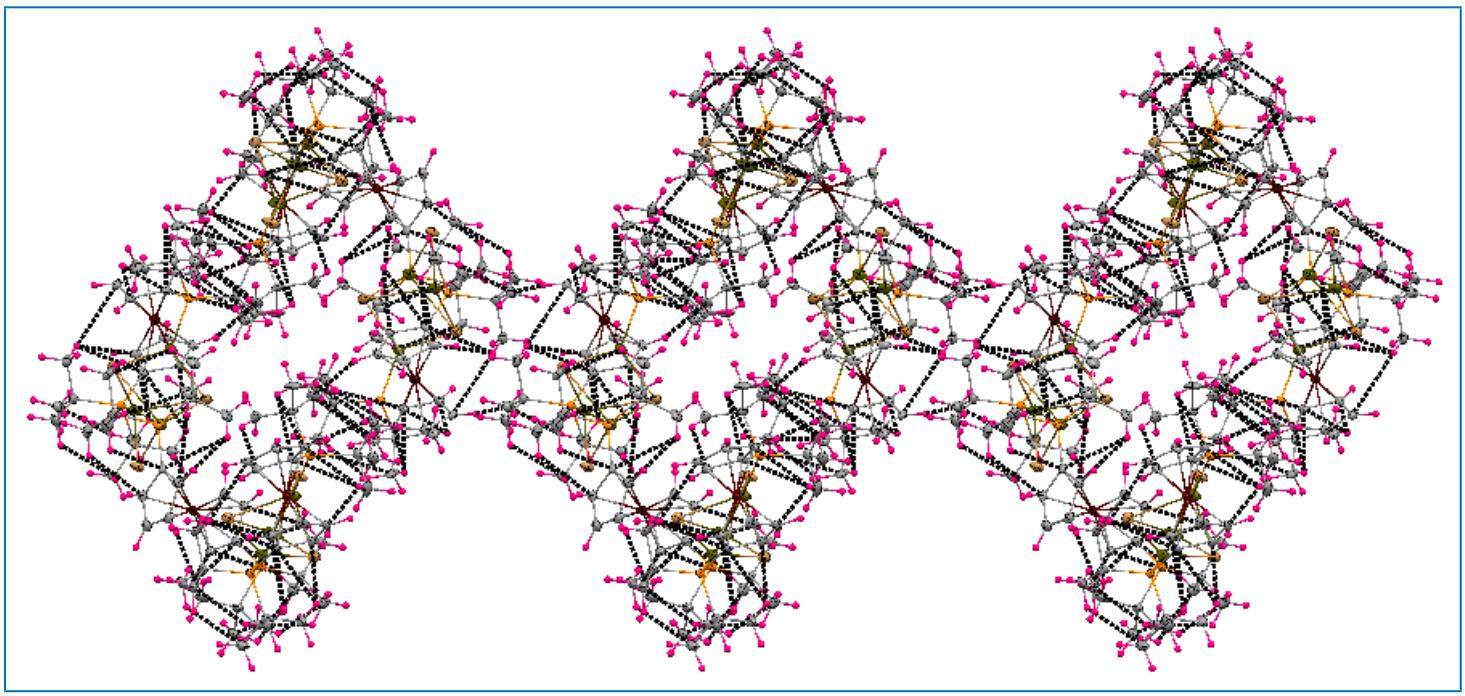
F-13. π ···π interactions in **1**.



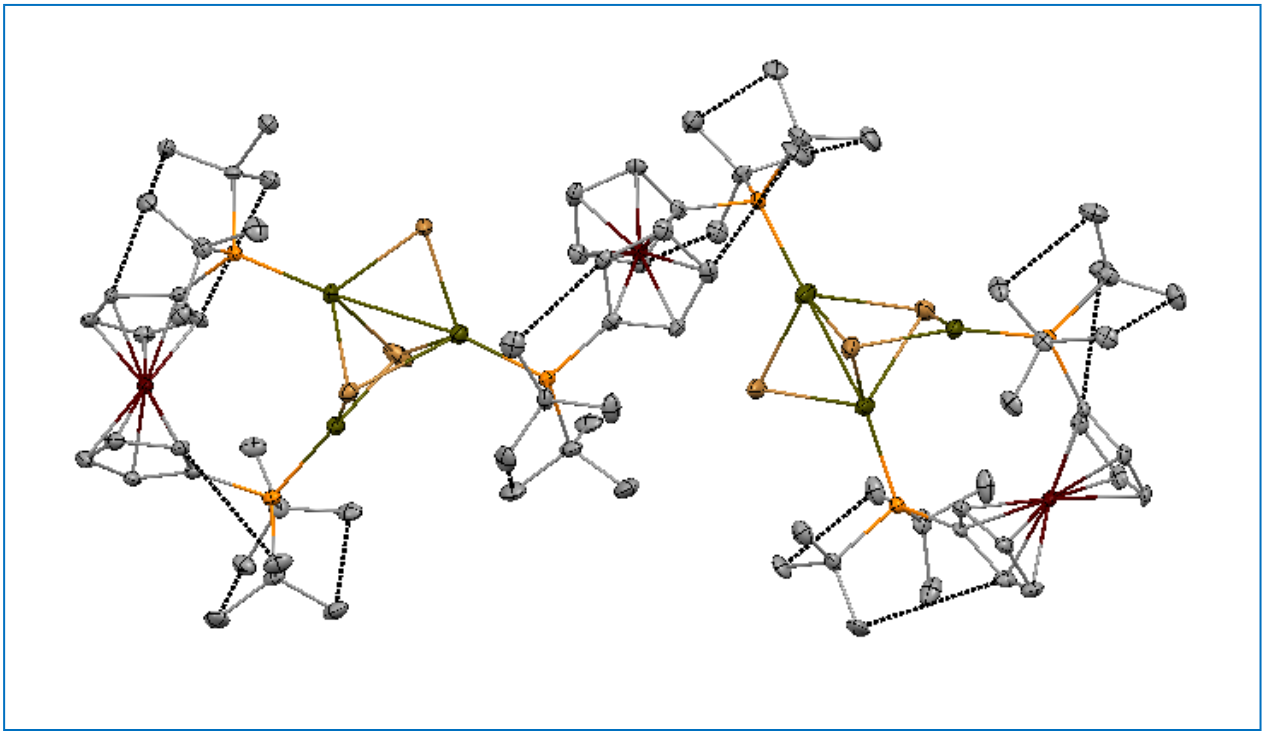
F-14. Crystal packing diagram of **2**, viewed along the *c* axis.



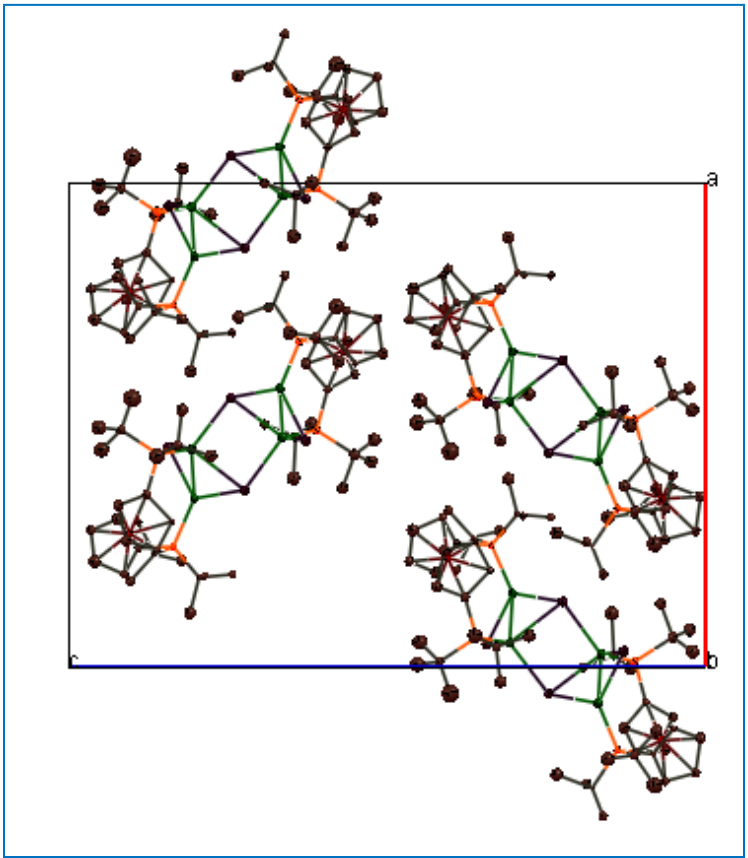
F-15. Ortep diagram of **2** showing C-H···Br hydrogen bond interactions in the crystal lattice.



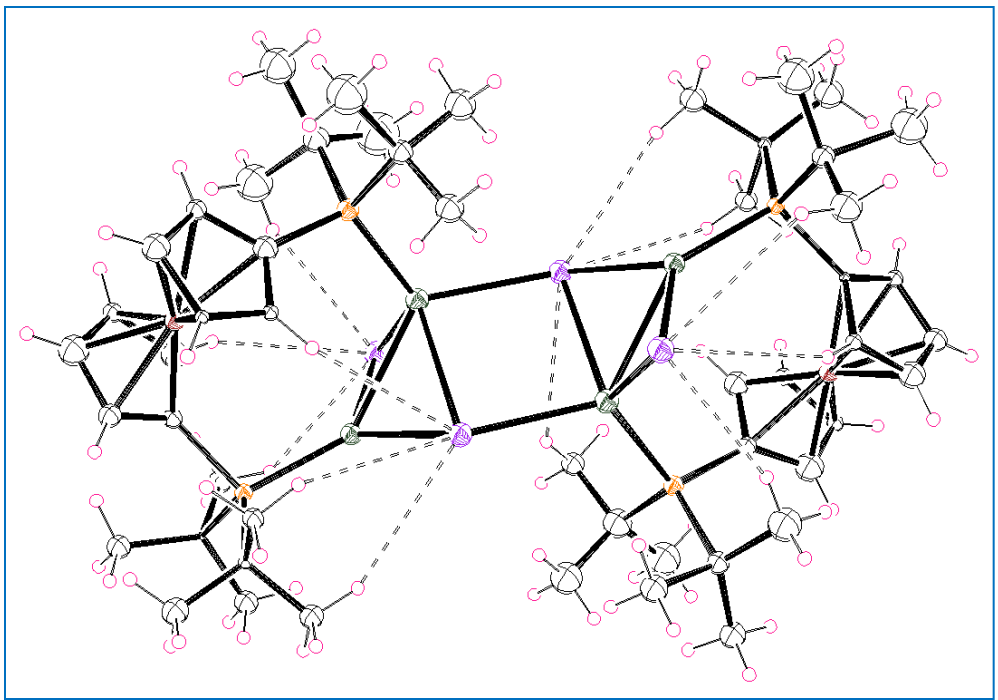
F-16. C-H···π interactions in **3**.



F-17. π ···π interactions in **3**.



F-18. Crystal packing diagram of **2**, viewed along the *b* axis.



F-19. Ortep diagram of **2** showing C-H···I hydrogen bond interactions in the crystal lattice.

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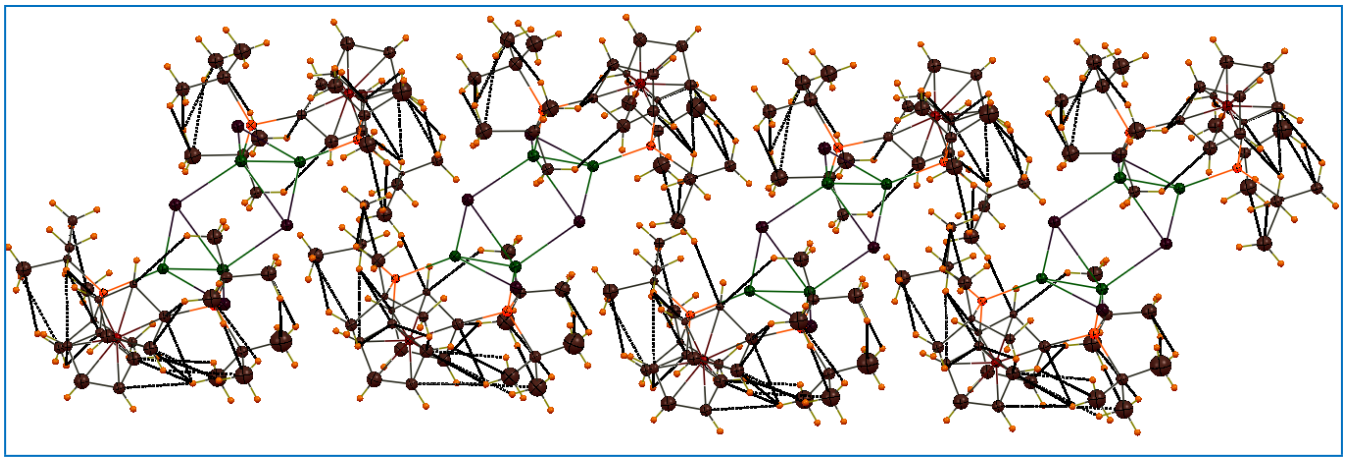
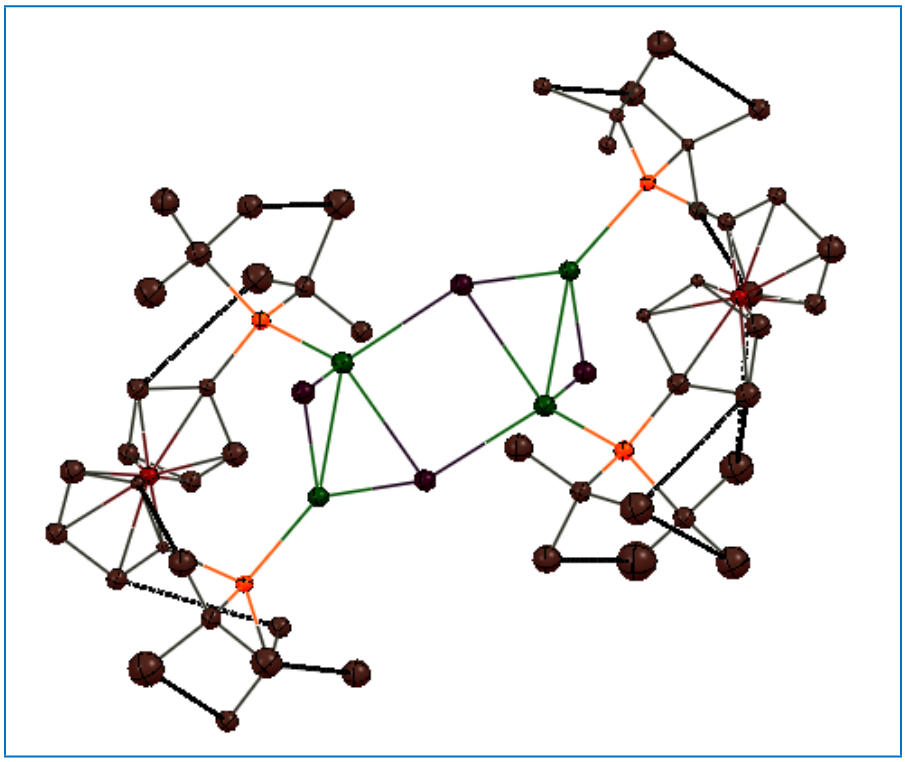
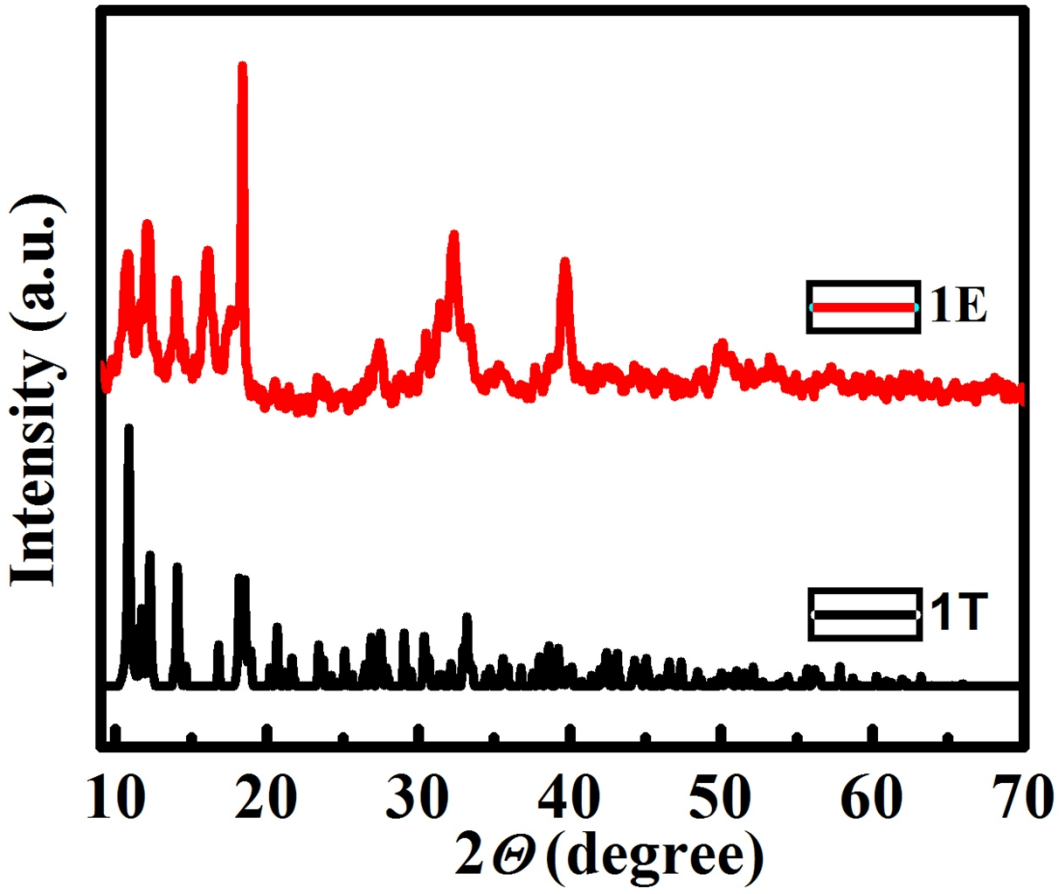


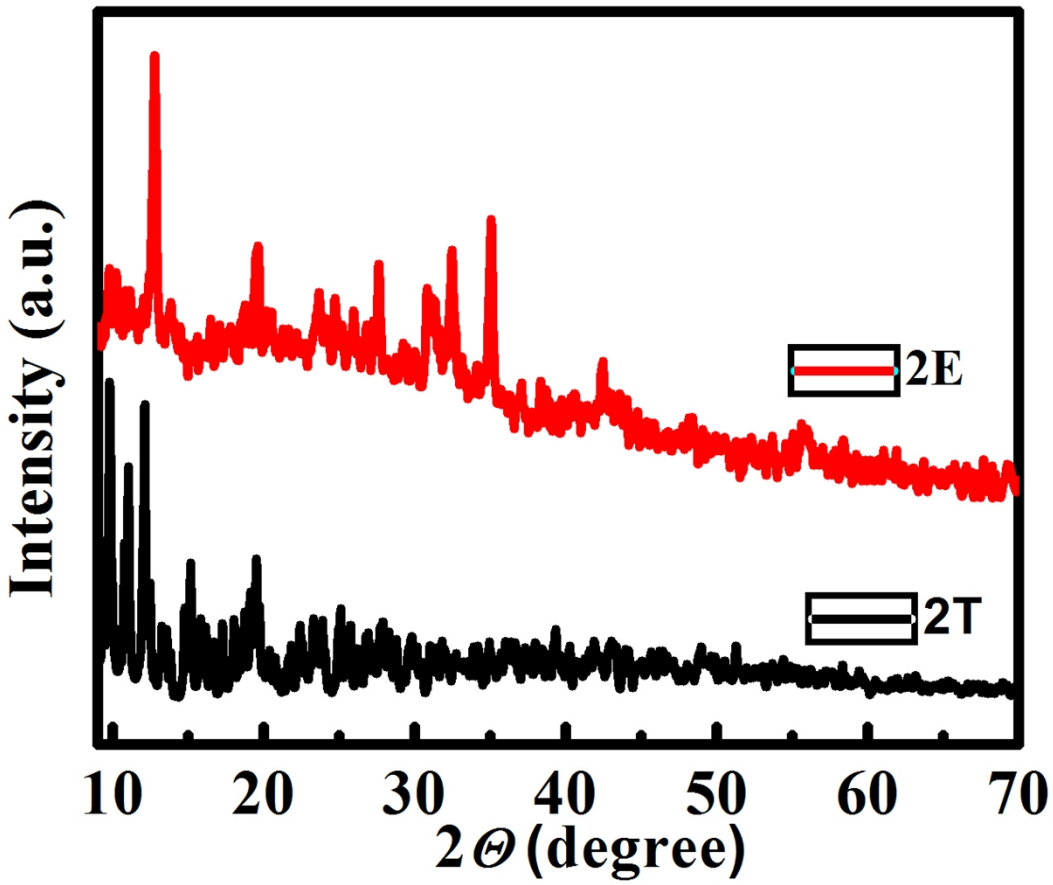
F-20. C-H···π interactions in **2**.



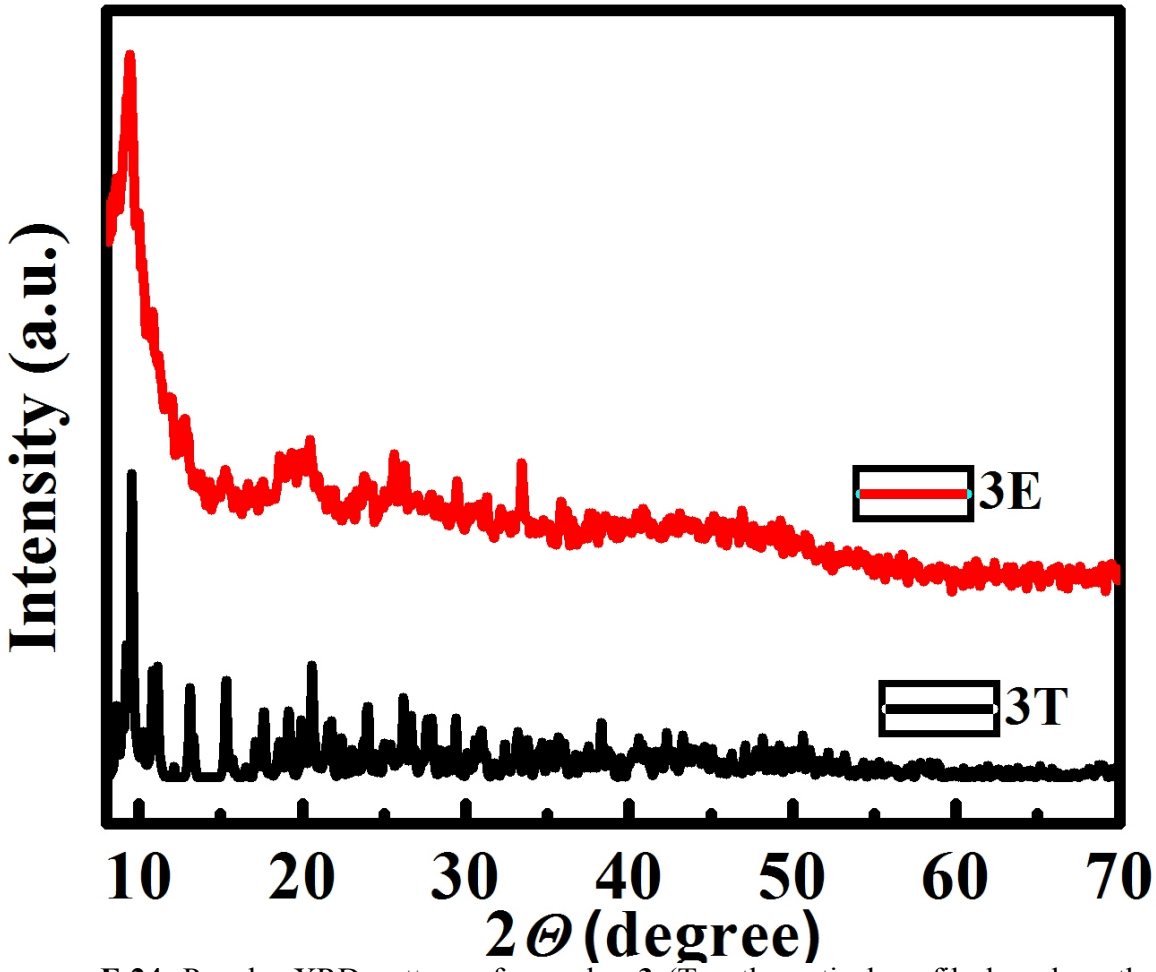
F-21. π ···π interactions in **2**.



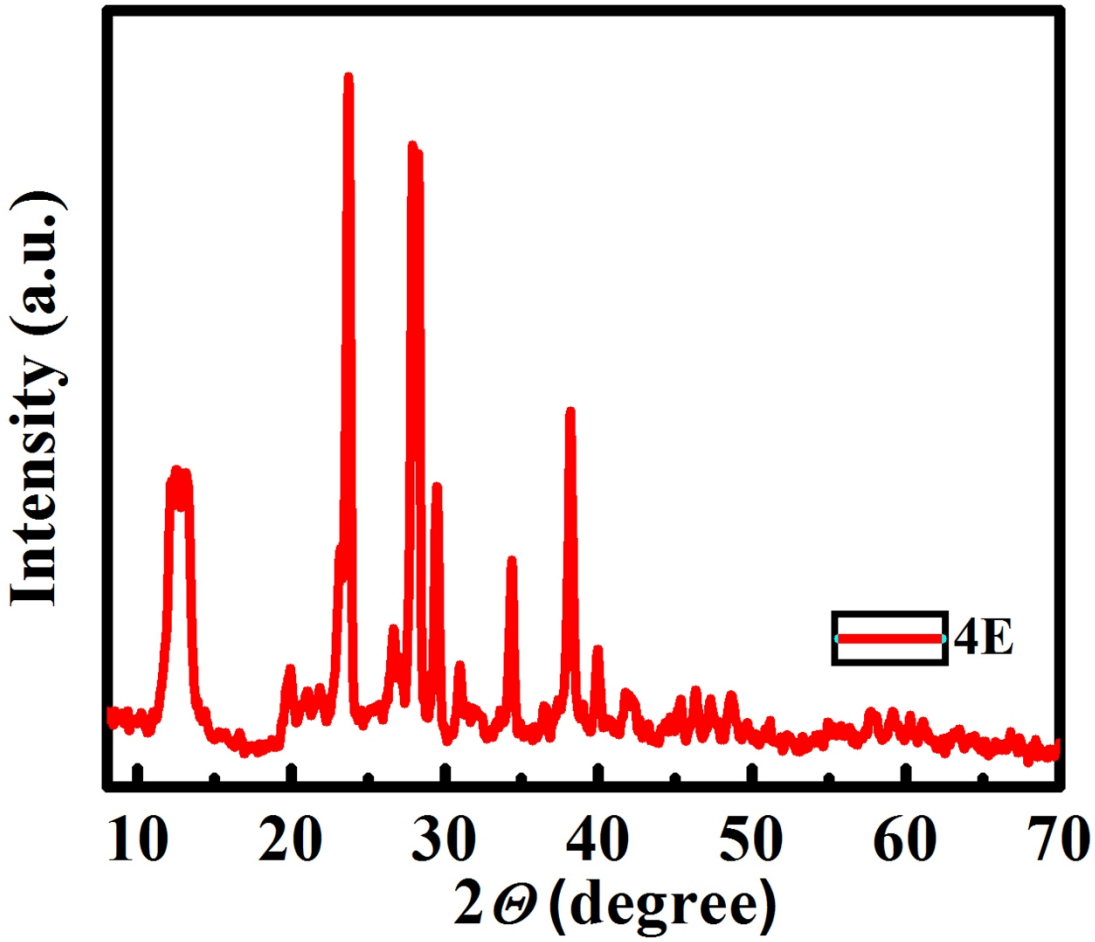
F-22. Powder XRD pattern of complex **1** (T = theoretical profile based on the structures determined by single-crystal XRD; E = experimental data).



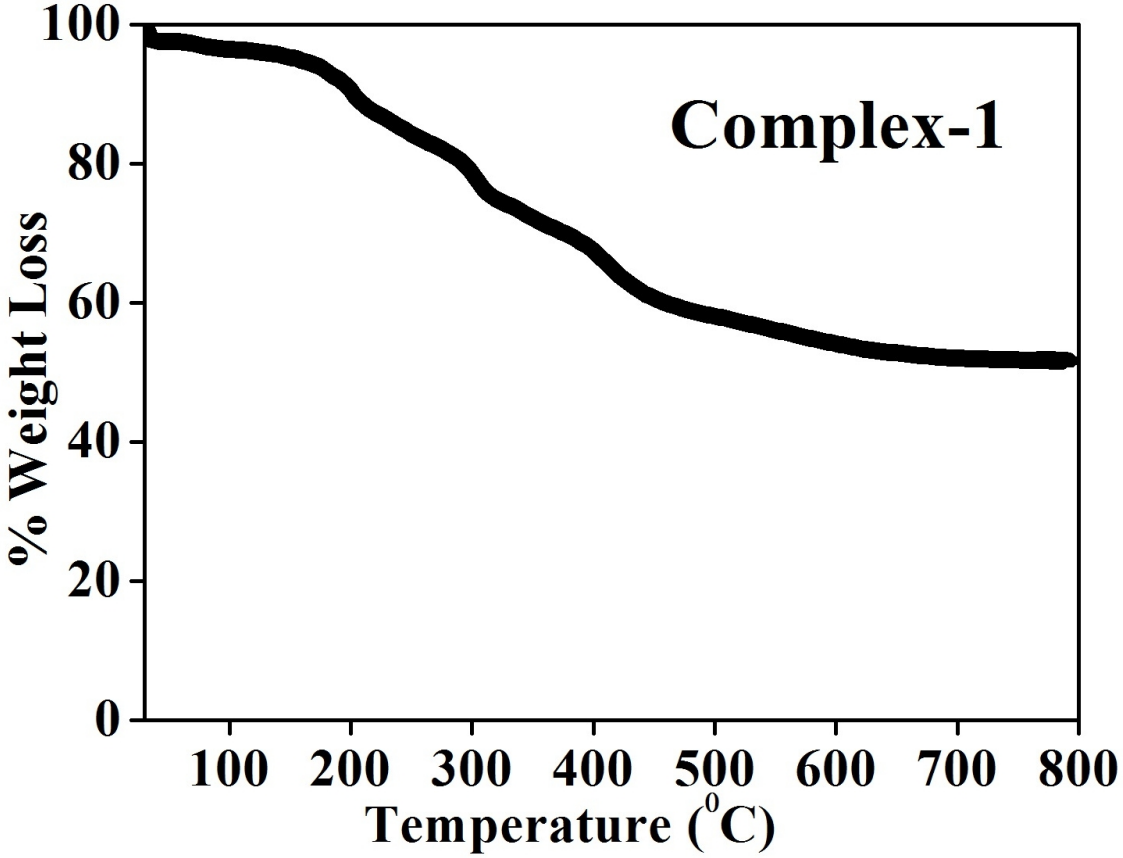
F-23. Powder XRD pattern of complex **2** (T = theoretical profile based on the structures determined by single-crystal XRD; E = experimental data).



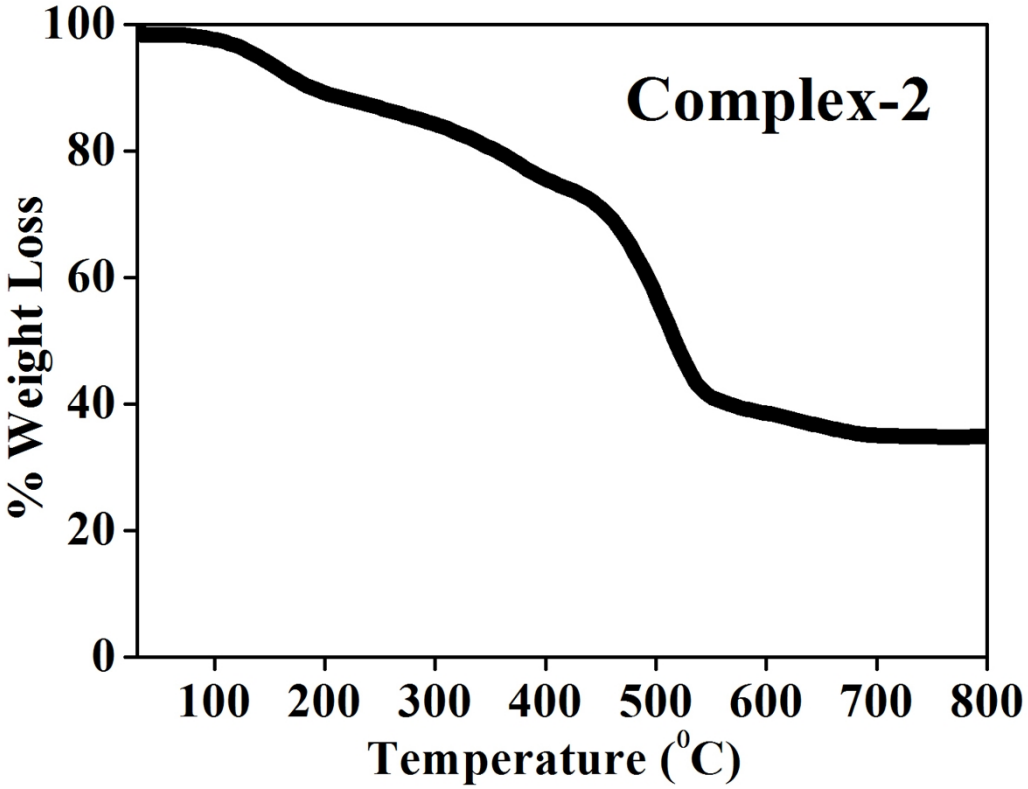
F-24. Powder XRD pattern of complex **3** (T = theoretical profile based on the structures determined by single-crystal XRD; E = experimental data).



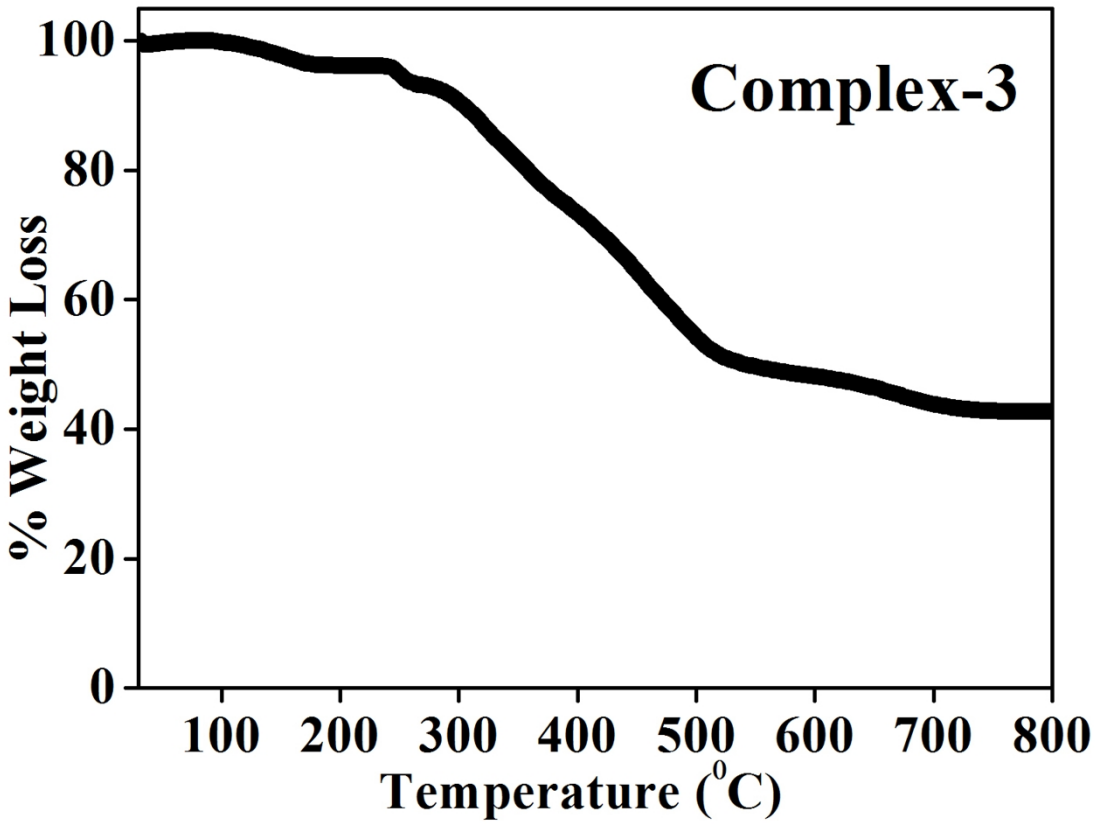
F-25. Powder XRD pattern of complex **4** (E = experimental data).



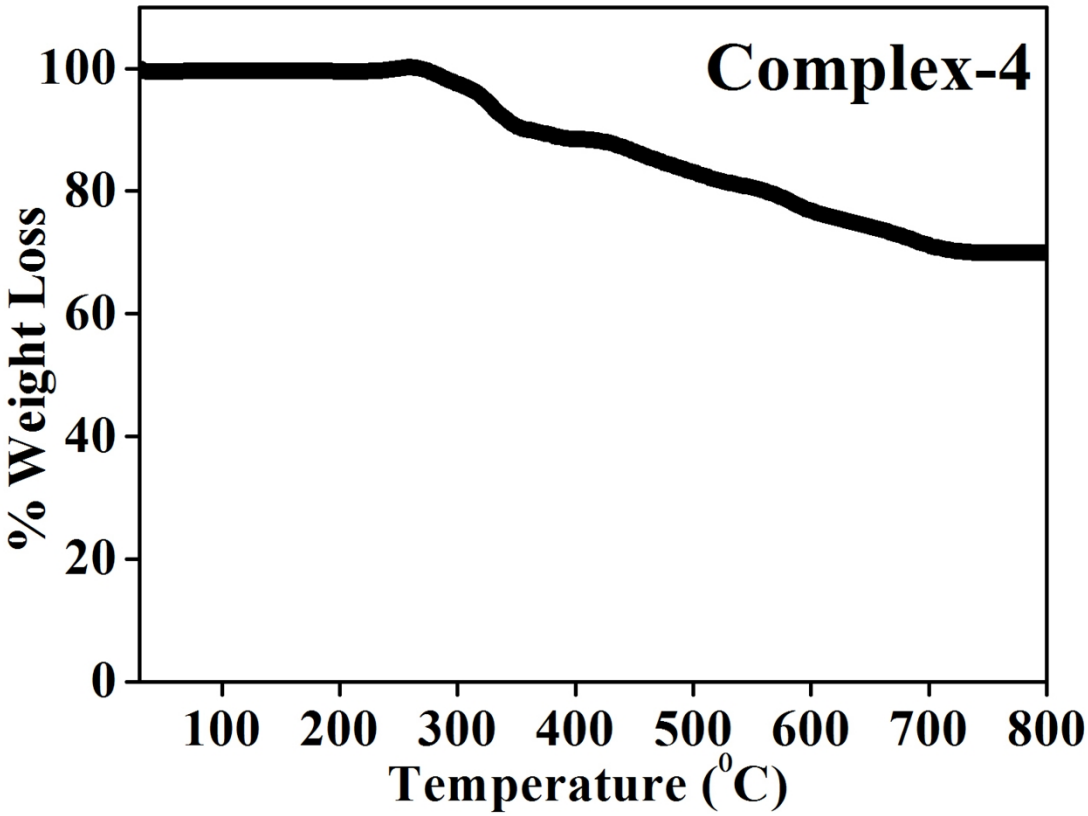
F-26. TGA curve for complex **1** in air.



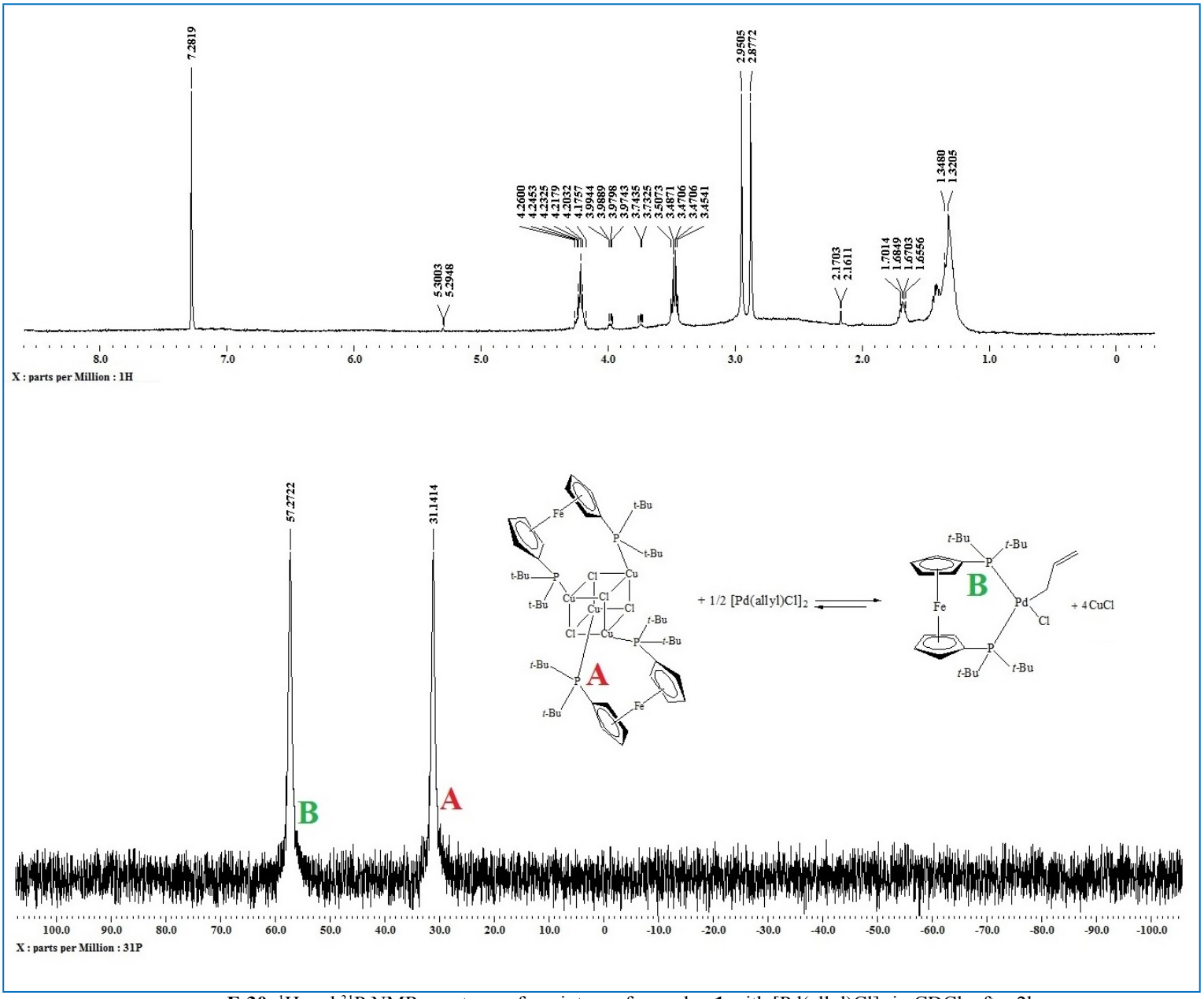
F-27. TGA curve for complex **2** in air.



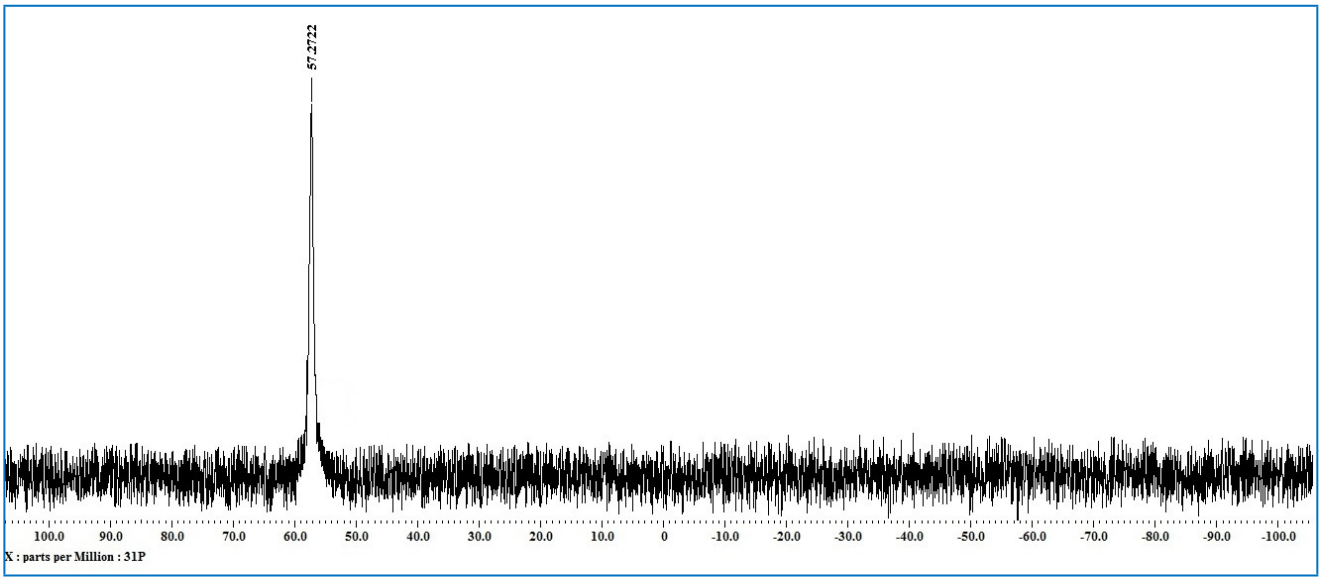
F-28. TGA curve for complex **3** in air.



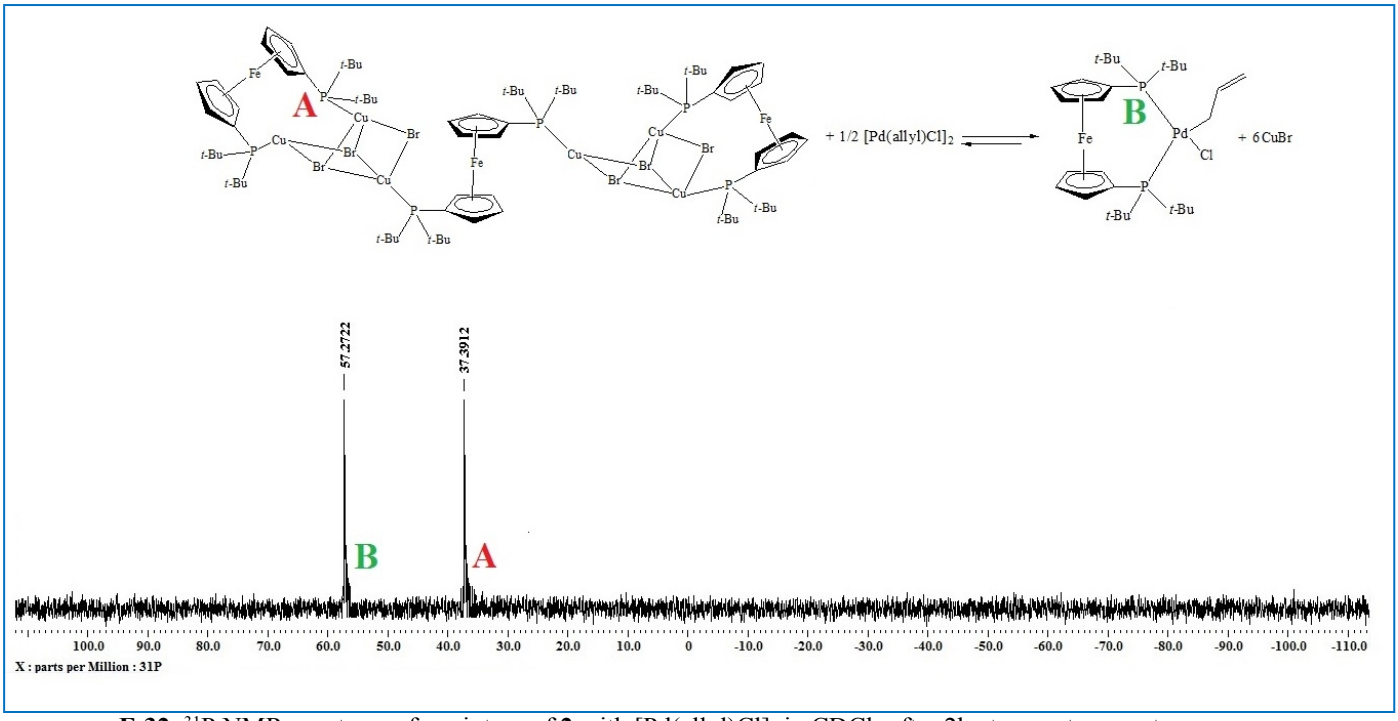
F-29. TGA curve for complex-4 in air.



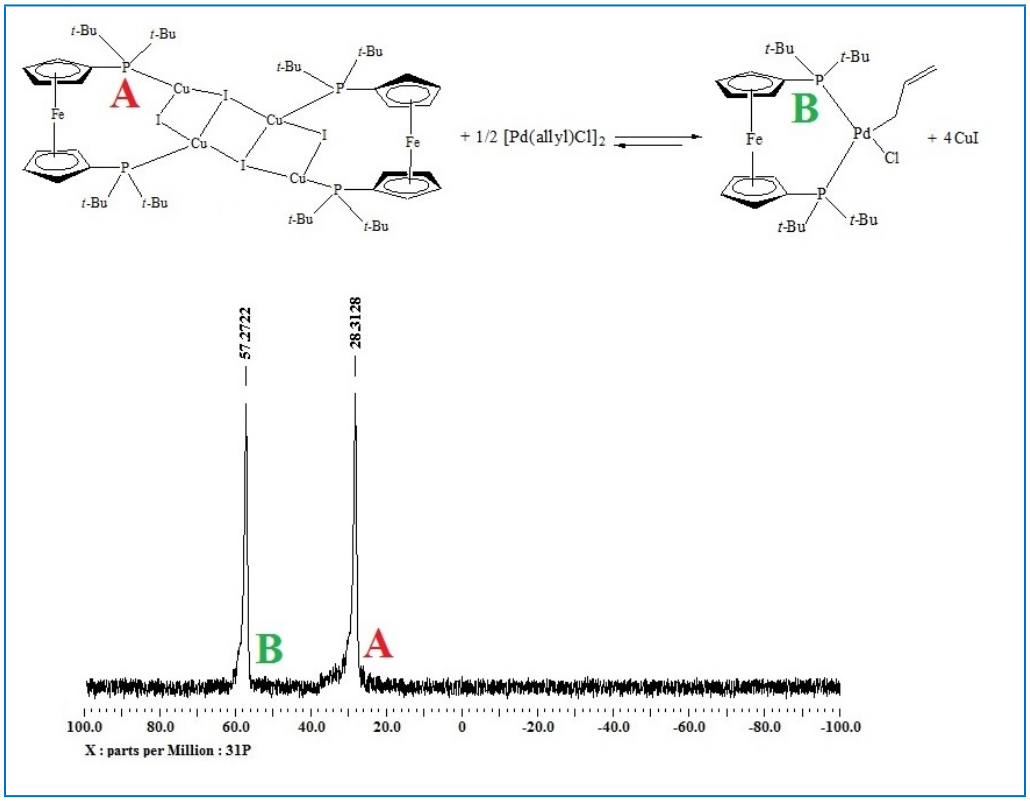
F-30. ^{1}H and ^{31}P NMR spectrum of a mixture of complex **1** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 2h at room temperature.



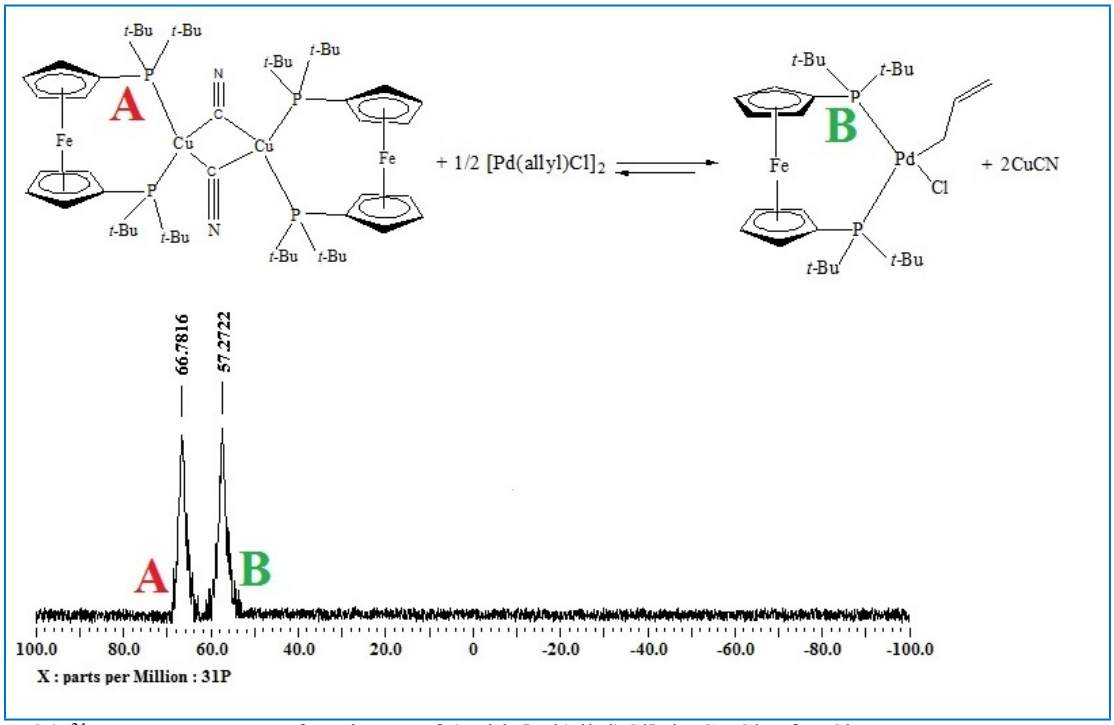
F-31. ^{31}P NMR spectrum of a mixture of **1** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 20h at room temperature: total transfer of the ligand from copper to palladium**.**



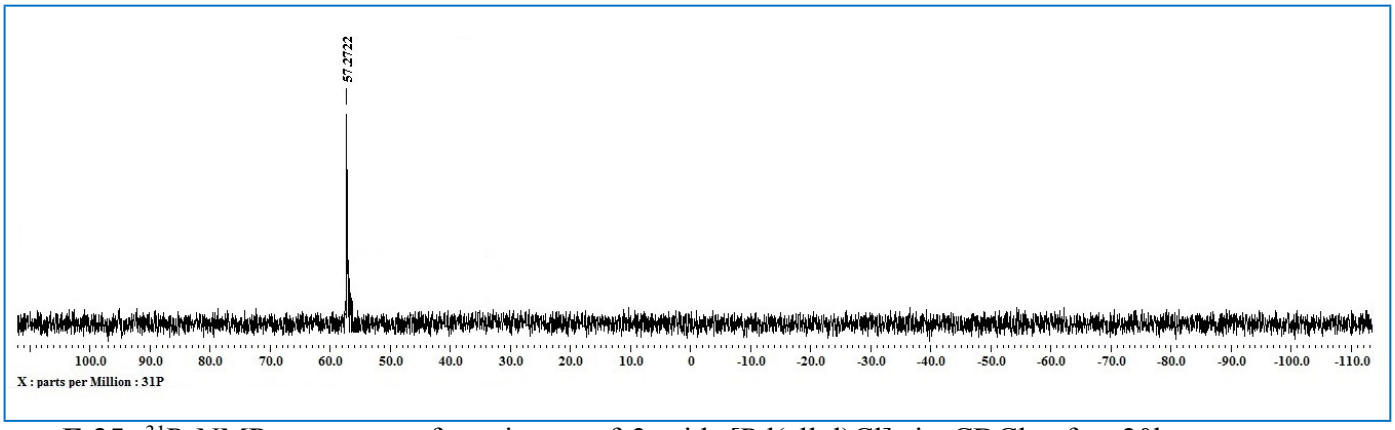
F-32. ^{31}P NMR spectrum of a mixture of **2** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 2h at room temperature**.**



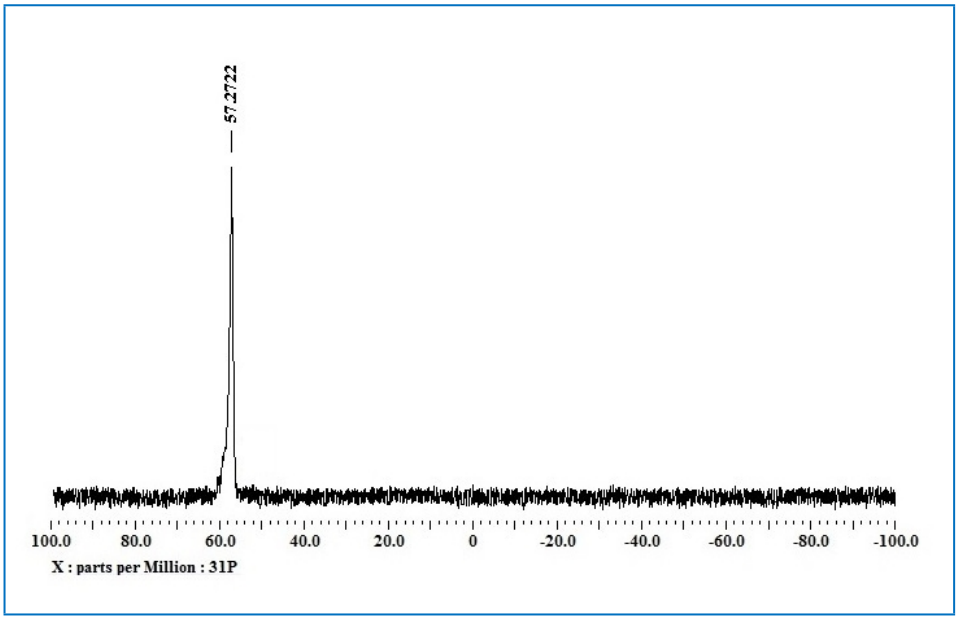
F-33. ^{31}P NMR spectrum of a mixture of **3** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 2h at room temperature**.**



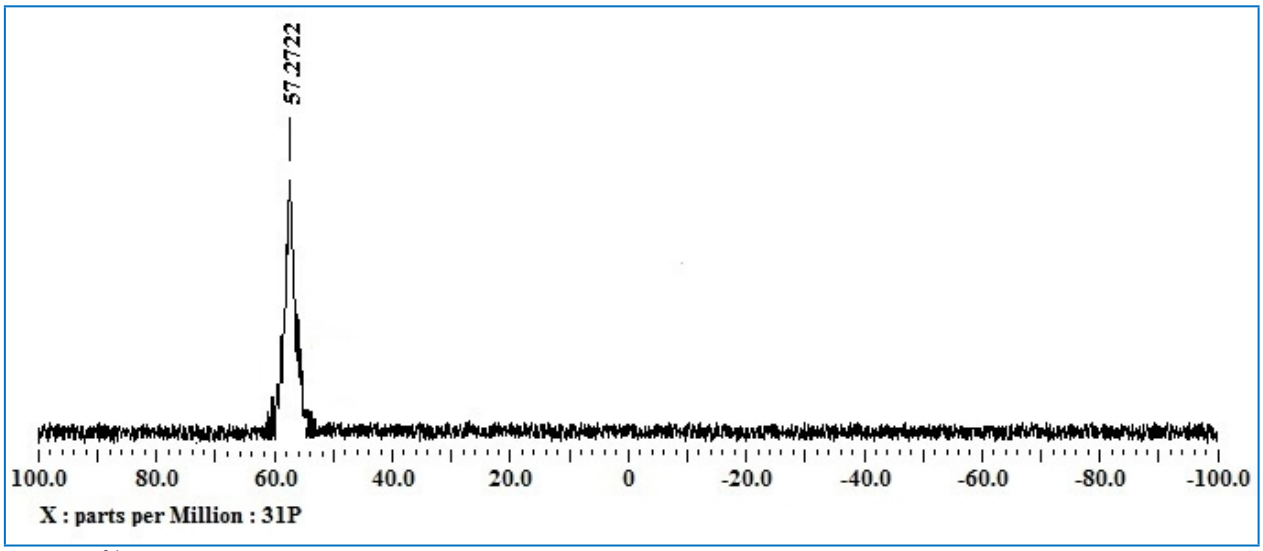
F-34. ^{31}P NMR spectrum of a mixture of **4** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 2h at room temperature**.**



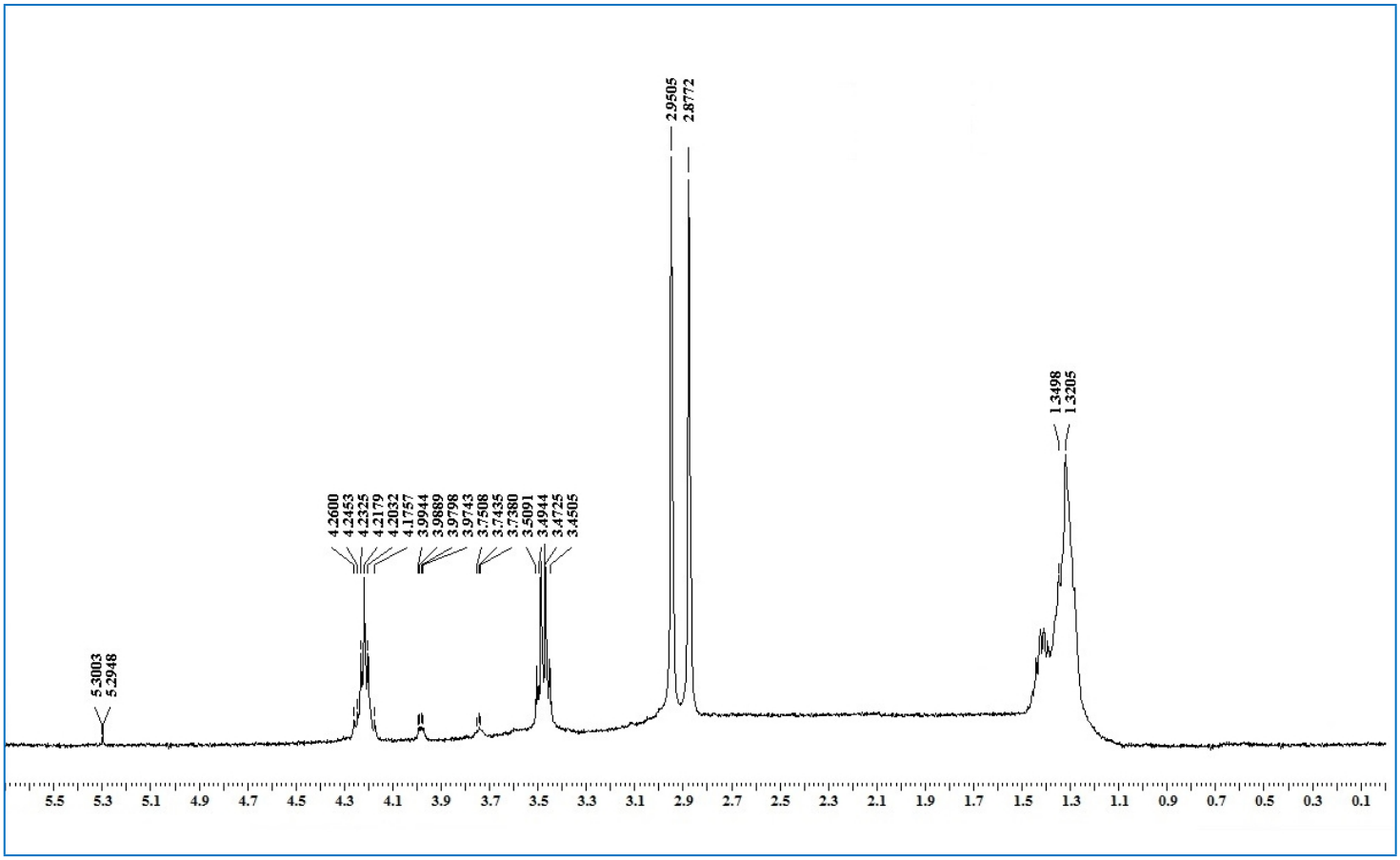
F-35. ^{31}P NMR spectrum of a mixture of **2** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 20h at room temperature: total transfer of the ligand from copper to palladium**.**



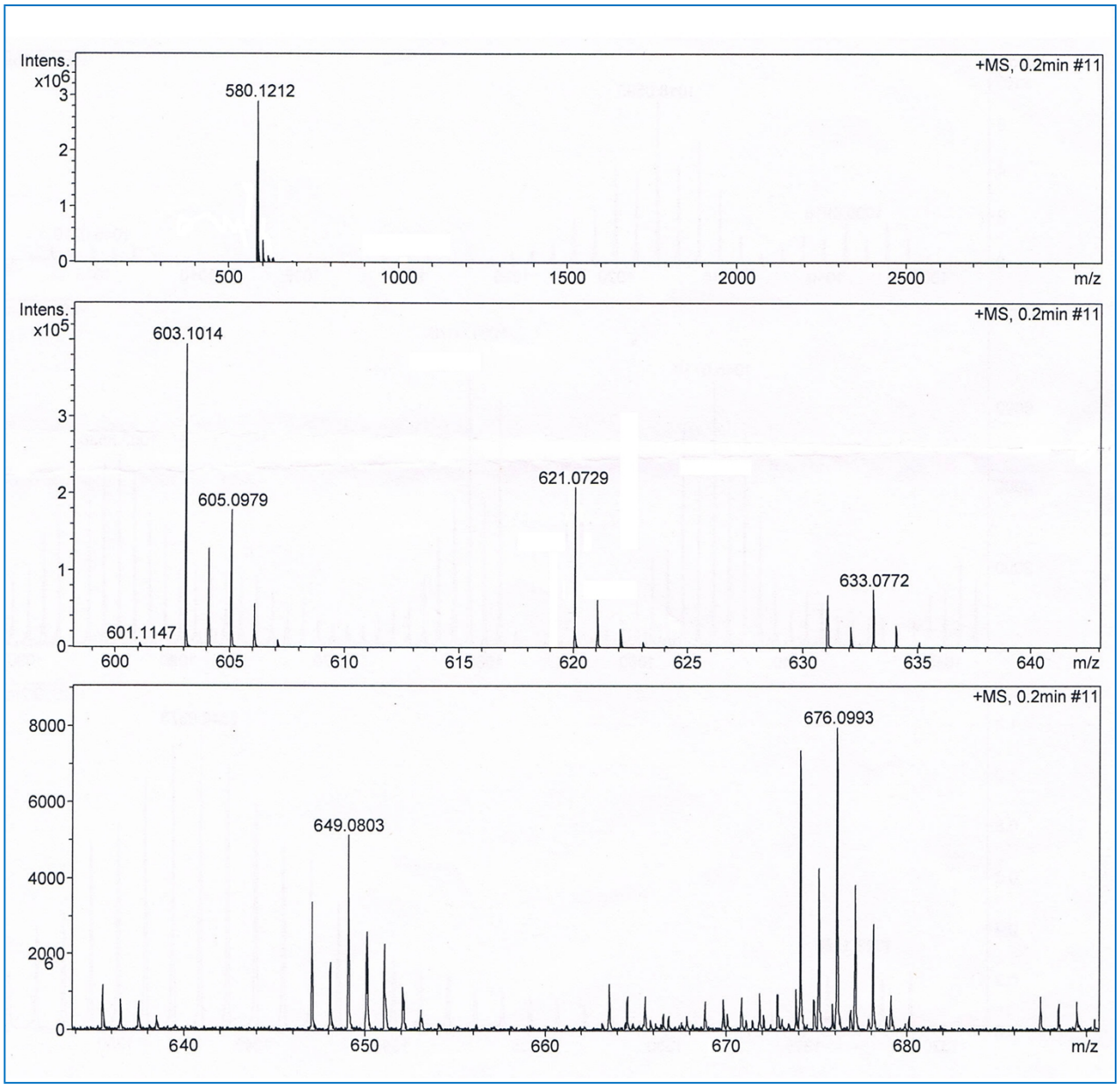
F-36. ^{31}P NMR spectrum of a mixture of **3** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 20h at room temperature: total transfer of the ligand from copper to palladium**.**



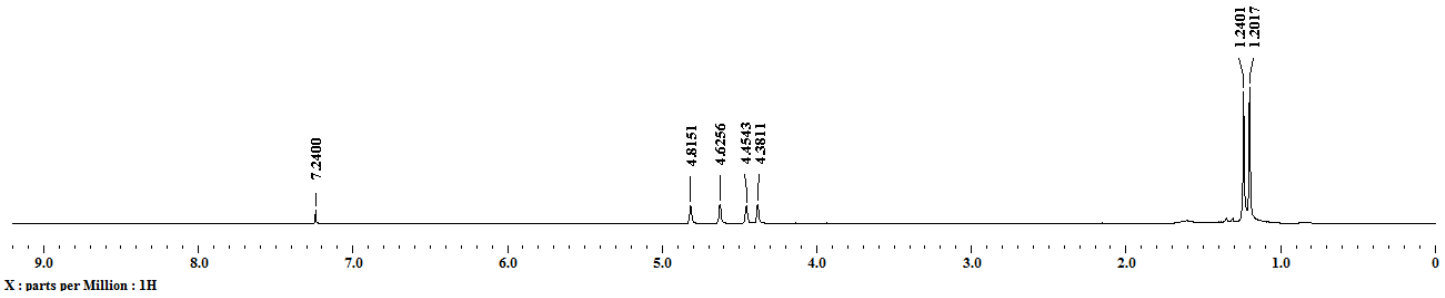
F-37. ^{31}P NMR spectrum of a mixture of **4** with $[Pd(allyl)Cl]_2$ in $CDCl_3$ after 20h at room temperature: total transfer of the ligand from copper to palladium**.**



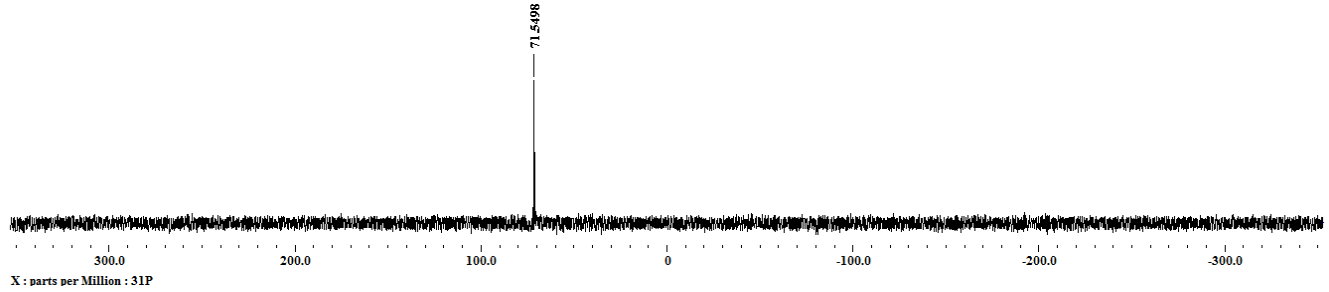
F-38. ^{1}H NMR spectrum of [PdCl(μ_1-C_3H_5)(κ^2-*P,P*-dtbpf)].



F-39. ESI-MS of [PdCl(μ_1-C_3H_5)(κ^2-*P,P*-dtbpf)].

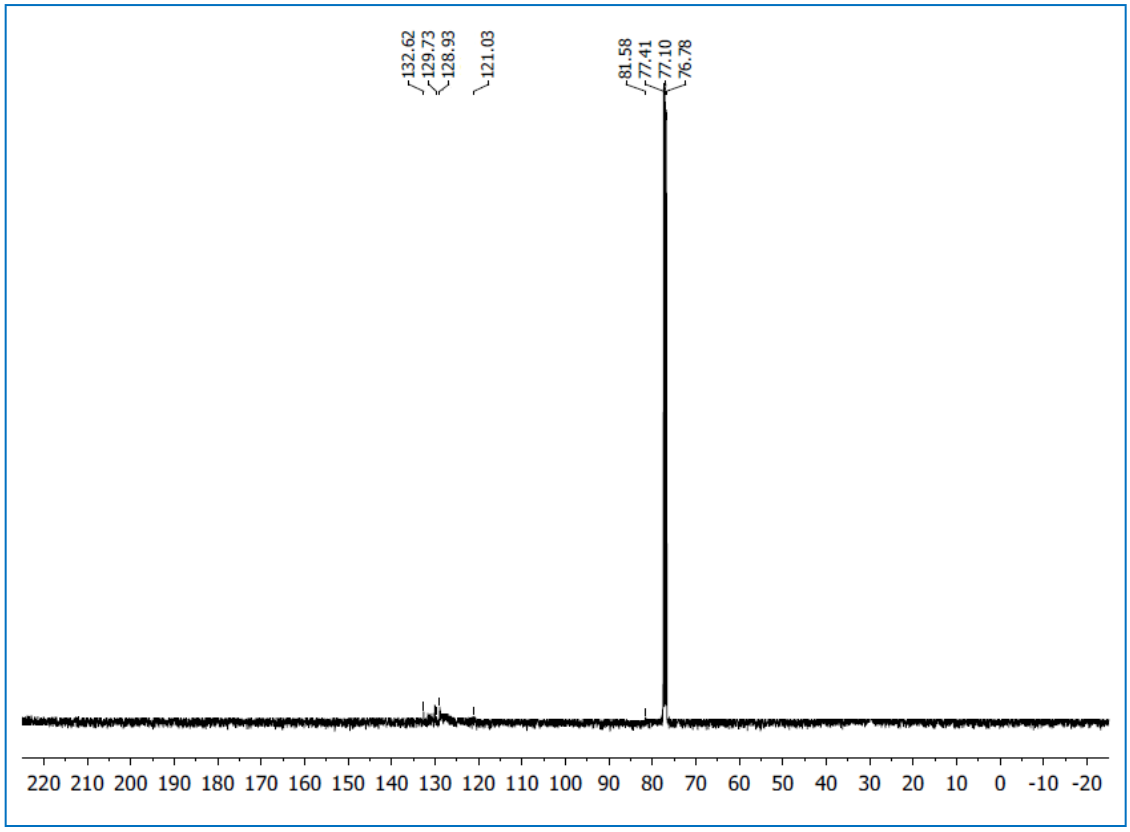


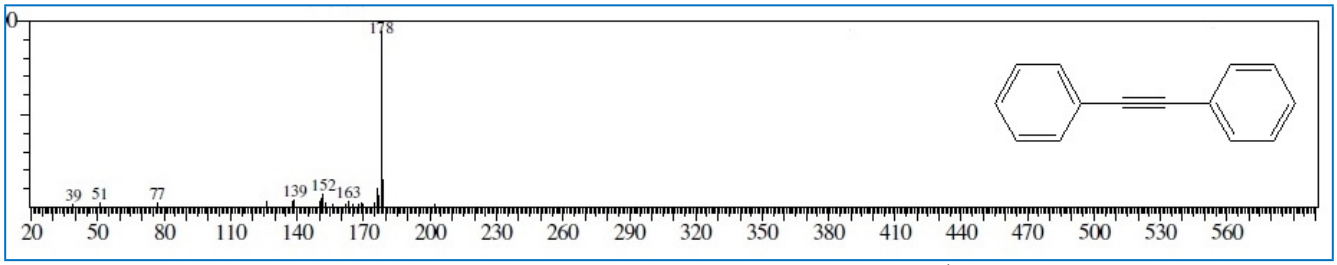
F-40. ^{1}H NMR spectrum of oxidized dtbpf (dtbpf+ H_2O_2) in $CDCl_3$.



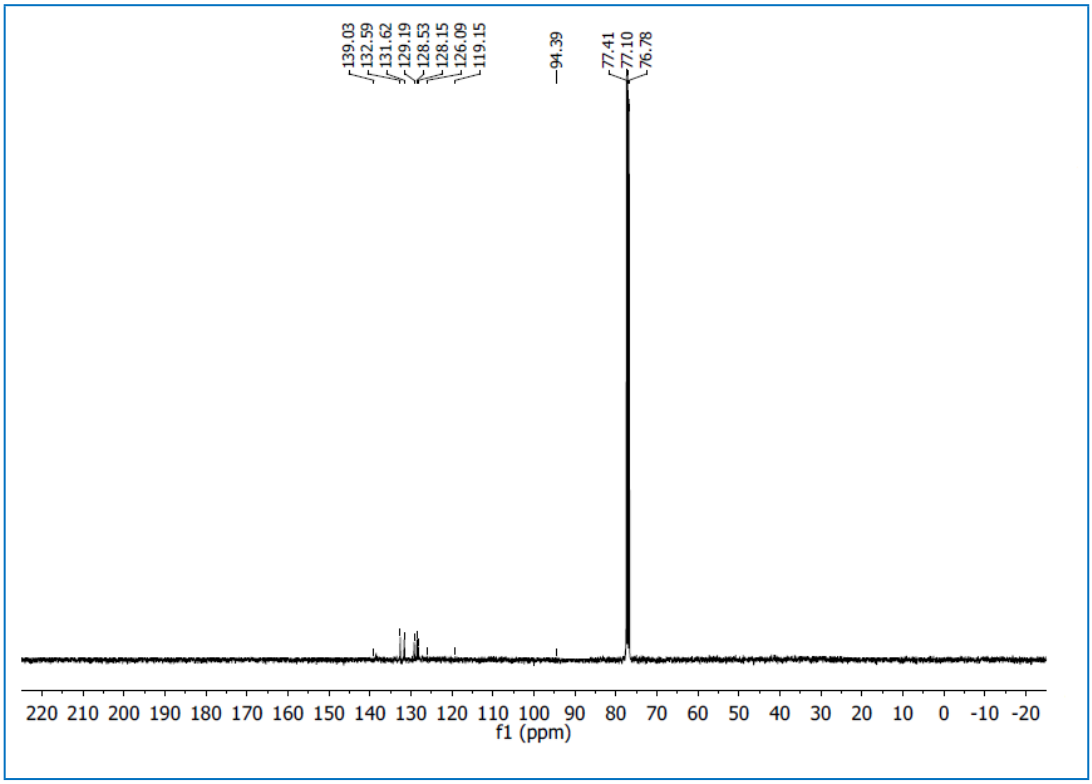
F-41. ^{31}P NMR spectrum of oxidized dtbpf (dtbpf+ H_2O_2) in $CDCl_3$.

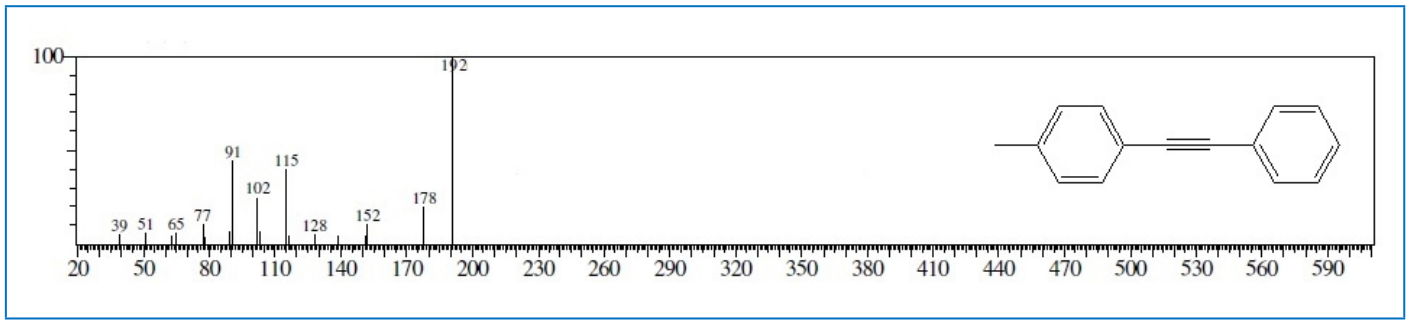
Diphenyl acetylene: White solid, (60-95% yield), mp.: 54-55°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, 4H, J = 7.5 Hz, ArH), δ = 7.50 (m, 6H, ArH) ppm; ^{13}C (400 MHz, $CDCl_3$): δ = 132.62, 129.73, 128.93, 121.03, 81.5 ppm. GCMS *m*/*z*(% rel. inten.) 178 (M^+, 100).[1]





4-methyl-diphenylacetylene: White solid, (58-99% yield), mp.: 52°C ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.62 (s, 3H, -CH_3), δ = 7.40 (m, 4H, ArH), δ = 7.85 (d, 2H, J = 6.4 Hz, ArH), δ = 7.64 (d, 2H, J = 7.5 Hz, ArH), 7.51 (m, 1H, ArH) ppm; ^{13}C (400 MHz, $CDCl_3$): δ =139.03, 132.59, 131.62, 129.19, 128.53, 128.15, 126.09,119.15, 94.39 ppm. GCMS *m*/*z*(% rel. inten.) 192(M^+, 100).[1]





References for Supporting Information:

(1) Modak, A.; Mondal, J.; Bhaumik, A. *Green Chem.* **2012**, *14*, 2840-2855.