

Supplementary Information

Copper(I) complexes with phosphine derived from sparfloxacin. Part I – structures, spectroscopic properties and cytotoxicity.

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Tab. S1 The $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (298 K, CDCl_3 , δ [ppm], J [Hz]) for **POH**, **OPOH**, **dmp**, **1-POH**, **2-POH**, **bq**, **3-POH**, **4-POH**

	PPh₂CH₂OH	OPPh₂CH₂OH	dmp	1-POH	2-POH	bq	3-POH	4-POH
^{31}P	-9.33	30.91		-5.47	-2.85		-3.01	-3.19
H^{Ph}	7.60-7.31	7.96-7.34		7.37-7.15	7.32-7.14		7.32-7.07	7.25-6.89
H¹	4.42 d (8.39)	4.40 s*		4.76 s*	4.61 s*		4.43 s*	4.73 s*
H-OH	1.80 m	6.27 m		not observed	not observed		not observed	not observed
C^{Ph(i)}	135.65 d (12.0)	129.49 d (97.18)		not observed	not observed		132.84 s*	not observed
C^{Ph(o)}	132.91 d (17.6)	131.25 d (9.08)		132.50 s*	132.32 d (12.72)		131.32 d (9.99)	132.47 s*
C^{Ph(m)}	128.39 d (5.6)	128.67 d (11.80)		128.50 d (7.27)	128.56 d (8.17)		128.76 d (11.81)	128.05 d (8.17)
C^{Ph(p)}	128.64 s	132.32 d (1.82)		129.59 s	129.64 s		129.54 s	128.72 s
C¹	62.46 d (13.0)	60.84 d (82.65)		63.10 d (23.63)	62.36 d (20.89)		63.35 s*	63.35 s*
H³			7.42 d (8.16)	7.50 d (8.20)	7.49 d (8.20)			
H⁴			8.04 d (8.16)	8.22 d (8.20)	8.21 d (8.20)	8.26 d (8.80)	8.86 d (8.58)	8.77 s*
H⁵			7.62 s	7.79 s	7.75 s	7.77 ddd (8.4; 6.9; 1.5)	7.59 t (7.44)	7.51 s*
H⁶			7.62 s	7.79 s	7.75 s	7.58 ddd (8.0; 6.9; 1.1)	7.77 t (8.30)	7.60 s*
H⁷			8.04 d (8.16)	8.22 d (8.20)	8.21 d (8.20)	7.88 d (8.20)	7.90 d (8.01)	7.60 s*
H⁸			7.42 d (8.16)	7.50 d (8.20)	7.49 d (8.20)	-	-	-
H⁹						8.33 d (8.41)	8.24 d (8.58)	8.07 s*
H¹⁰						8.87 d (8.80)	8.34 d (8.58)	8.20 s*
H^{15,16}			2.90 s	2.79 s	2.71 s	-	-	-
C¹						156.12 s	156.23 s	151.17 s
C²			159.07 s	159.49 s	158.91 s	-	-	-
C³			123.29 s	124.96 s	124.90 s	147.84 s	147.92 s	146.16 s
C⁴			136.07 s	136.64 s	136.76 s	129.87 s	129.92 s	130.64 s
C⁵			125.22 s	125.40 s	125.43 s	129.53 s	129.50 s	129.43 s
C⁶			125.22 s	125.40 s	125.43 s	126.93 s	126.94 s	not observed
C⁷			136.07 s	136.64 s	136.76 s	127.61 s	127.64 s	127.30 s
C⁸			123.29 s	124.96 s	124.90 s	128.42 s	128.44 s	128.36 s
C⁹			159.07 s	159.49 s	158.91 s	136.73 s	136.74 s	137.93 s
C¹⁰			-	-	-	119.42 s	119.42 s	118.96 s
C^{11,12}			145.03 s	143.09 s	142.78 s			
C^{13,14}			126.58 s	127.08 s	126.97 s			
C^{15,16}			26.64 s	26.77 s	26.27 s			

* signal broadened

Tab. S2 The $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (298 K, CDCl_3 , δ [ppm], J [Hz]) for **POH** and **HSf**, **PSf**, **OPsf**³⁴

	PPh₂CH₂OH	HSf	PSf	OPsf
^{31}P	-9.33	-	-35.88 s	26.48 s
H^{Ph}	7.60-7.11	-	7.65-7.29	7.89-7.41
H¹	4.42 d (7.70)	-	3.93 s*	3.68 d (2.3)
H-OH	1.80 m			
H^{2,6}		3.33 m	3.20 m	3.16 m
H^{3,5}		3.93 m	3.93 m	3.93 m
H^{7,8}		1.10 d (6.3)	0.94 d (5.9)	1.01 d (6.0)
H¹³		6.46 s*	6.46 s*	6.44 s*
H¹⁹		8.63 s	8.62 s	8.57 s
H²¹		3.93 m	3.93 s*	3.89 m
H²²		1.22 m	1.21 m	1.22-1.10
H²²		1.06 m	1.07 m	1.22-1.10
H²³		-	14.54 s*	14.16 s*
C^{Ph(i)}	135.65 d (12.0)	-	133.97 d (24.6)	133.26 d (91.7)
C^{Ph(o)}	132.91 d (17.6)	-	133.48 d (19.4)	131.70 d (1.9)
C^{Ph(m)}	128.39 d (5.6)	-	128.56 d (6.6)	128.48 d (10.9)
C^{Ph(p)}	128.64 s	-	128.66 s	130.96 d (8.5)
C¹	62.46 d (13.0)	-	51.35 s*	50.29 d (75.7)
C^{2,6}		51.22 s	54.50 d (11.4)	55.46 d (3.3)
C^{3,5}		57.77 t (3.6)	57.92 t (4.0)	57.37 t (3.8)
C^{7,8}		19.39 s	17.30 s	17.46 s
C¹¹		134.50 dd (13.6, 10.9)	134.18 dd (13.2, 10.0)	134.26 dd (12.3, 10,1)
C¹²		136.59 dd (237.9, 6.4)	136.55 dd (258.6, 6.2)	136.43 dd (237.8, 6.2)
C¹³		136.15 dd 13.6, 1.8)	136.17 dd (13.5, 1.7)	136.34 dd (13.3, 1.1)
C¹⁴		105.97 d (4.5)	105.31 d (5.2)	105.78 d (5.2)
C¹⁵		128.16 dd (5,9; 2,3)	128.16 dd (6.3, 2.4)	128.08 dd (6.2, 2.4)
C¹⁶		140.00 dd (237.1, 5.5)	139.78 dd (239.1, 5.2)	140.34 dd (237.3, 10,1)
C¹⁷		180.16 s	180.14 s	179.99 s
C¹⁸		106.73 s	106.73 s	106.51 s
C¹⁹		149.37 s	149.38 s	149.25 s
C²¹		40.38 d (14.5)	40.39 dd (14.4; 3.6)	40.34 dd (14.4; 5.0)
C²²		9.06 d (7.3)	9.10 d (8.0)	9.02 d (7.7)
C²³		166.66 s	166.66 s	166.56 s

* signal broadened

Tab. S3 The $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (298 K, CDCl_3 , δ [ppm], J [Hz]) for **PSf**, **dmp**, **1-PSf**, **2-PSf**

	PSf	dmp	1-PSf	2-PSf
^{31}P	-35.88 s		-11.93 s*; -28.42s*	-8.76s*; -31.32s*
H^{Ph}	7.65-7.29		7.87-7.15	7.49-7.18
H^1	3.93 s*		3.92 d (5.05)	3.92 d (6.68)
$\text{H}^{2,6}$	3.20 m		3.08 m	3.01 m
$\text{H}^{3,5}$	3.93 m		3.36 d (13.61)	3.33 d (12.02)
$\text{H}^{7,8}$	0.94 d (5.9)		0.91 d (6.22)	0.88 d (6.29)
H^{13}	6.46 s*		6.49 s*	6.47 s*
H^{19}	8.62 s		8.65 s	8.62 s
H^{21}	3.93 s*		3.92 m	3.93 m
H^{22}	1.21 m		1.23 m	1.23 m
H^{22}	1.07 m		1.12 d (6.22)	1.11 d (6.29)
H^{23}	14.54 s*		14.53 s*	14.61 s*
$\text{C}^{\text{Ph(i)}}$	133.97 d (24.6)		133.37 d (15.44)	133.21 d (17.26)
$\text{C}^{\text{Ph(o)}}$	133.48 d (19.4)		132.71 d (12.71)	132.36 d (12.71)
$\text{C}^{\text{Ph(m)}}$	128.56 d (6.6)		128.48 d (9.08)	128.59 d (8.17)
$\text{C}^{\text{Ph(p)}}$	128.66 s		129.52 s	129.65 s
C^1	51.35 s*		51.22 s*	51.25 s*
$\text{C}^{2,6}$	54.50 d (11.4)		54.19 d (7.27)	54.32 d (9.08)
$\text{C}^{3,5}$	57.92 t (4.0)		57.59 s*	57.47 t (3.63)
$\text{C}^{7,8}$	17.30 s		19.21 s	19.26 s
C^{11}	134.18 dd (13.2. 10.0)		not observed	not observed
C^{12}	136.55 dd (258.6. 6.2)		136.55 dd (237.5. 5.9)	136.15 dd (237.5. 5.9)
C^{13}	136.17 dd (13.5. 1.7)		134.48 dd (10.9. 1.8)	134.39 dd (10.45. 4.09)
C^{14}	105.31 d (5.2)		105.97 d (5.45)	106.01 d (5.45)
C^{15}	128.16 dd (6.3. 2.4)		128.13 dd (5.9. 2.27)	128.16 dd (5.91. 2.27)
C^{16}	139.78 dd (239.1. 5.2)		139.98 dd (237.0. 5.45)	138.27 dd (236.3. 5.9)
C^{17}	180.14 s		180.13 s	180.15 s
C^{18}	106.73 s		106.71 s	106.75 s
C^{19}	149.38 s		149.32 s	149.35 s
C^{21}	40.39 dd (14.4; 3.6)		40.37 d (14.53)	40.41 dd (14.53. 5.45)
C^{22}	9.10 d (8.0)		9.03 d (8.17)	9.05 dd (7.72. 2.27)
C^{23}	166.66 s		166.61 s	166.63 s
$\text{H}^{3,8}$		7.42 d (8.16)	7.55 d (8.16)	7.50 d (8.39)
$\text{H}^{4,7}$		8.04 d (8.16)	8.25 d (8.16)	8.19 d (8.20)
$\text{H}^{5,6}$		7.62 s	7.83 s	7.74 s
$\text{H}^{15,16}$		2.90 s	2.81 s	2.76 s
$\text{C}^{2,9}$		159.07 s	159.46 s	158.99 s
$\text{C}^{3,8}$		123.29 s	124.93 s	124.92 s
$\text{C}^{4,7}$		136.07 s	136.56 s	136.61 s
$\text{C}^{5,6}$		125.22 s	125.37 s	125.40 s
$\text{C}^{11,12}$		145.03 s	143.07 s	142.90 s
$\text{C}^{13,14}$		126.58 s	127.06 s	126.97 s
$\text{C}^{15,16}$		26.64 s	26.75 s	26.27 s

* signal broadened

Tab. S4 $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra (298 K, CDCl_3 , δ [ppm], J [Hz]) for **PSf**, **bq**, **3-PSf**, **4-PSf**

	PSf	bq	3-PSf	4-PSf
^{31}P	-35.88 s		-10.48s*, 35.12s*	-7.43s*, -28.69s*
H^{Ph}	7.65-7.29		7.36-6.93	7.33-7.01
H^1	3.93 s*		3.92 d (3.43)	3.92 s*
$\text{H}^{2,6}$	3.20 m		3.09 m	3.08 m
$\text{H}^{3,5}$	3.93 m		3.33 d (12.02)	3.33 d (11.06)
$\text{H}^{7,8}$	0.94 d (5.9)		0.81 d (5.72)	0.85 d (6.1)
H^{13}	6.46 s*		6.46 s*	6.47 s*
H^{19}	8.62 s		8.63 s	8.61 s
H^{21}	3.93 s*		3.92 m	3.92 m
H^{22}	1.21 m		1.21 m	1.22 m
H^{22}	1.07 m		1.11 d (6.29)	1.11 d (6.29)
H^{23}	14.54 s*		14.60 s*	14.69 s*
$\text{C}^{\text{Ph(i)}}$	133.97 d (24.6)		not observed	133.22 d (16.35)
$\text{C}^{\text{Ph(o)}}$	133.48 d (19.4)		133.51 d (18.17)	132.50 d (13.63)
$\text{C}^{\text{Ph(m)}}$	128.56 d (6.6)		128.55 d (7.27)	128.47 d (9.08)
$\text{C}^{\text{Ph(p)}}$	128.66 s		128.38 s	128.60 s
C^1	51.35 s*		51.24 s*	51.25 s*
$\text{C}^{2,6}$	54.50 d (11.4)		54.53 d (9.99)	54.47 d (4.54)
$\text{C}^{3,5}$	57.92 t (4.0)		57.71 s*	57.76 t (3.18)
$\text{C}^{7,8}$	17.30 s		19.34 s	19.39 s
C^{11}	134.18 dd (13.2, 10.0)		not observed	not observed
C^{12}	136.55 dd (258.6, 6.2)		136.59 dd (237.5, 5.9)	136.02 dd (237.0, 5.4)
C^{13}	136.17 dd (13.5, 1.7)		134.48 dd (13.63, 10.9)	not observed
C^{14}	105.31 d (5.2)		106.01 d (5.45)	106.71 s*
C^{15}	128.16 dd (6.3, 2.4)		128.16 dd (5.9, 2.27)	128.16 dd (6.36, 2.73)
C^{16}	139.78 dd (239.1, 5.2)		140.01 dd (236.6, 5.0)	139.35 dd (236.5, 5.9)
C^{17}	180.14 s		180.16 s*	180.23 s
C^{18}	106.73 s		106.76 s	106.79 s
C^{19}	149.38 s		149.39 s	149.42 s
C^{21}	40.39 dd (14.4; 3.6)		40.32 d (14.53)	40.39 dd (14.53, 0.91)
C^{22}	9.10 d (8.0)		9.07 d (7.27)	9.08 d (8.17)
C^{23}	166.66 s		166.66 s	166.72 s
H^4		8.26 d (8.80)	8.92 s*	8.65 s*
H^5		7.77 ddd (8.4; 6.9; 1.5)	7.57 m	7.50 m
H^6		7.58 ddd (8.0; 6.9; 1.1)	7.49 m	7.44 m
H^7		7.88 d (8.20)	7.49 m	7.44 m
H^9		8.33 d (8.41)	7.89 s*	7.62 s*
H^{10}		8.87 d (8.80)	8.15 s*	8.12 s*
C^1		156.12 s	not observed	not observed
C^3		147.84 s	146.13 s	146.51 s
C^4		129.87 s	131.02 s	130.70 s
C^5		129.53 s	130.59 s	130.10 s
C^6		126.93 s	128.70 s	127.44 s
C^7		127.61 s	129.51 s	129.16 s
C^8		128.42 s	129.66 s	129.56 s
C^9		136.73 s	137.34 s	136.98 s
C^{10}		119.42 s	119.36 s	118.89 s

* signal broadened

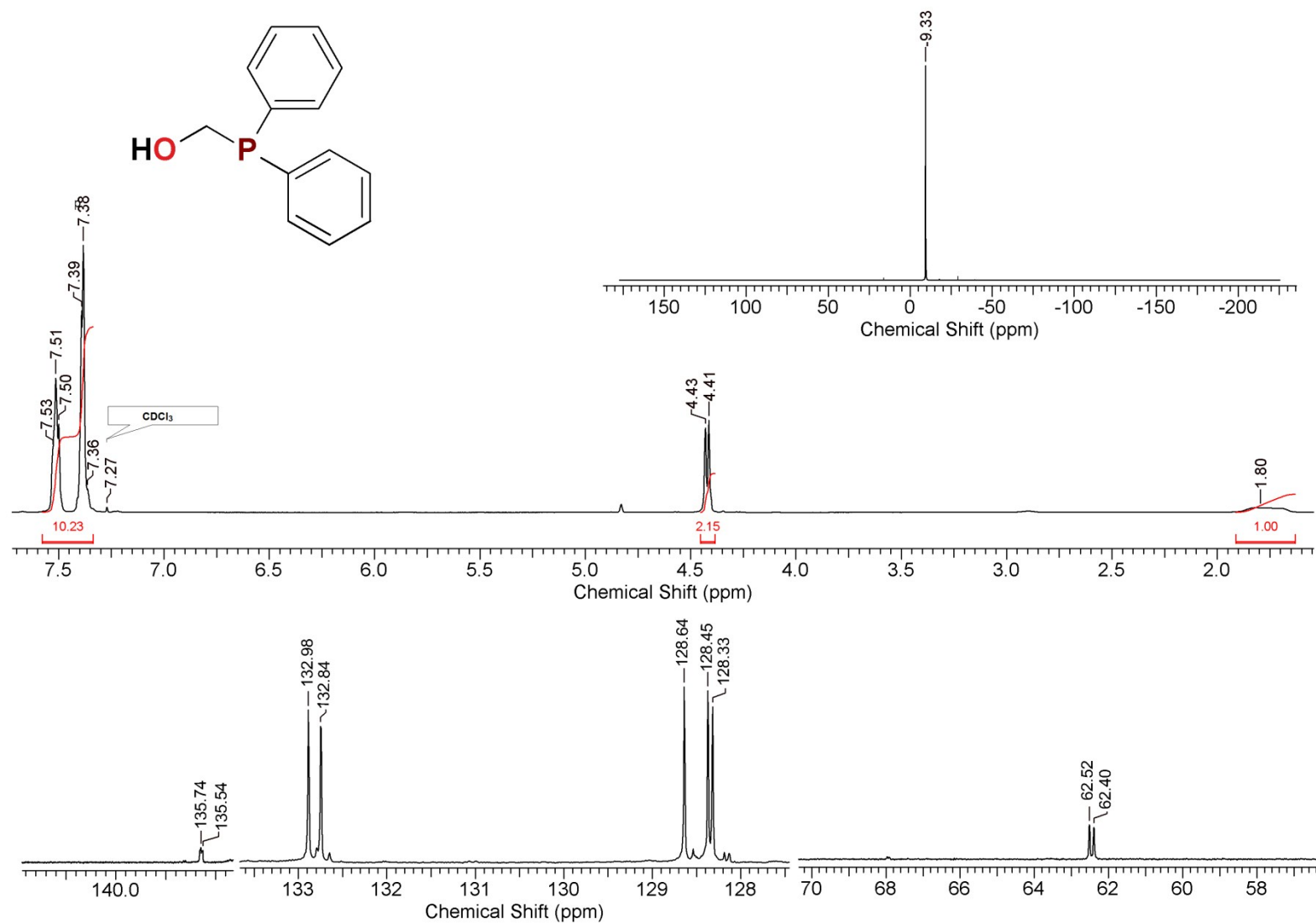


Fig S1 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **POH** (298 K, CDCl_3)

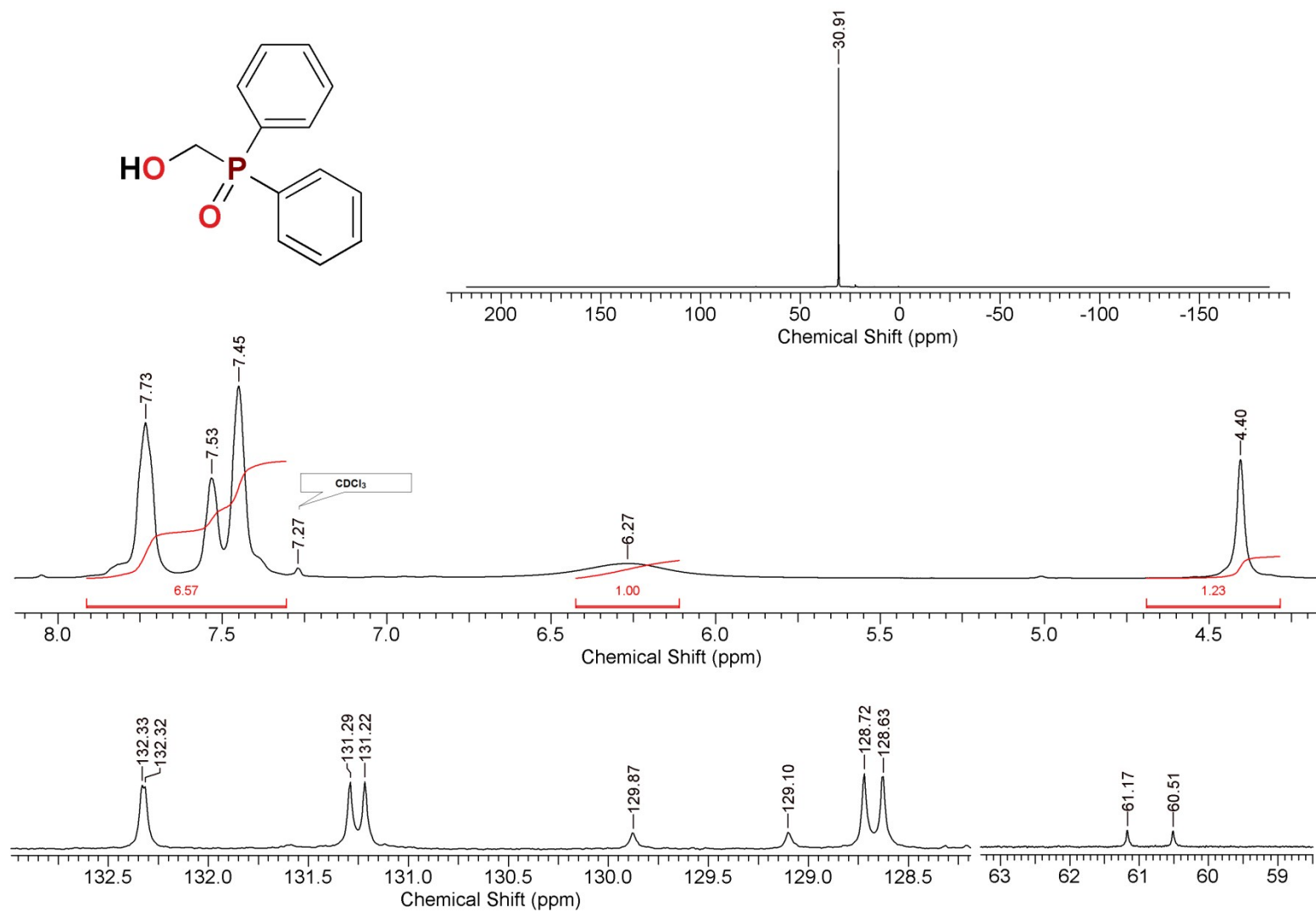


Fig S2 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **OPOH** (298 K, CDCl_3)

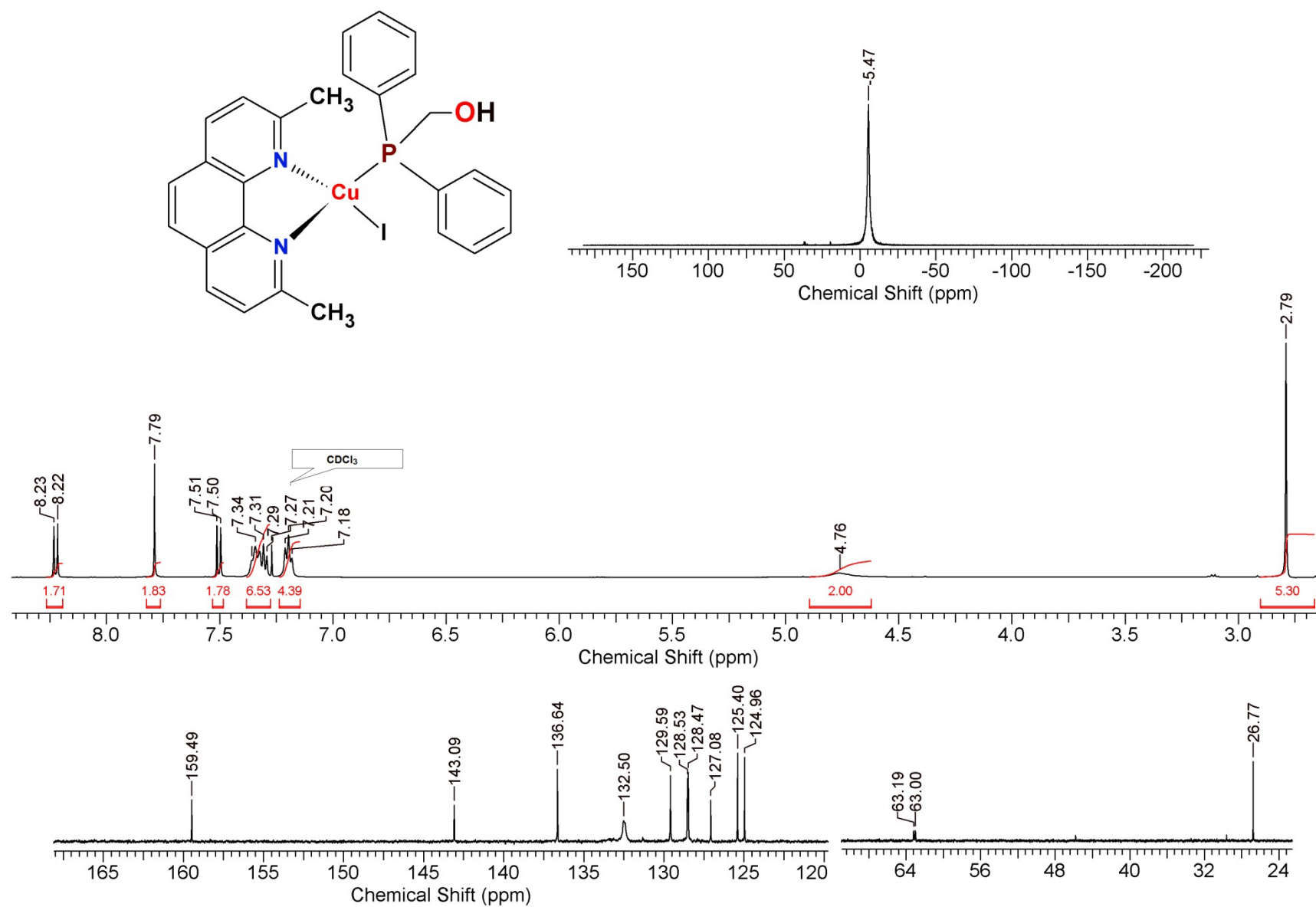


Fig S3 ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra for **1-POH** (298 K, CDCl₃)

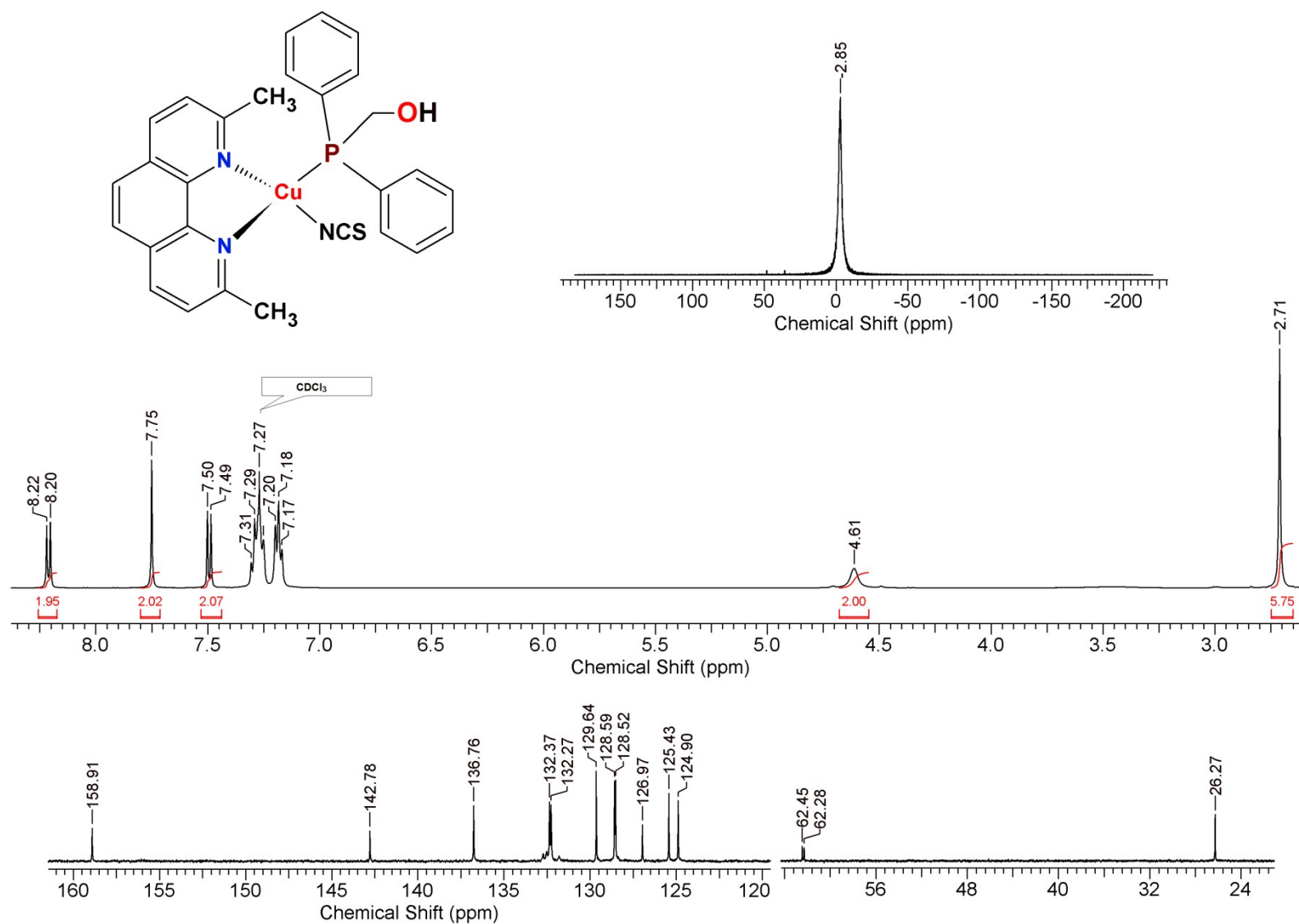


Fig S4 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **2-POH** (298 K, CDCl_3)

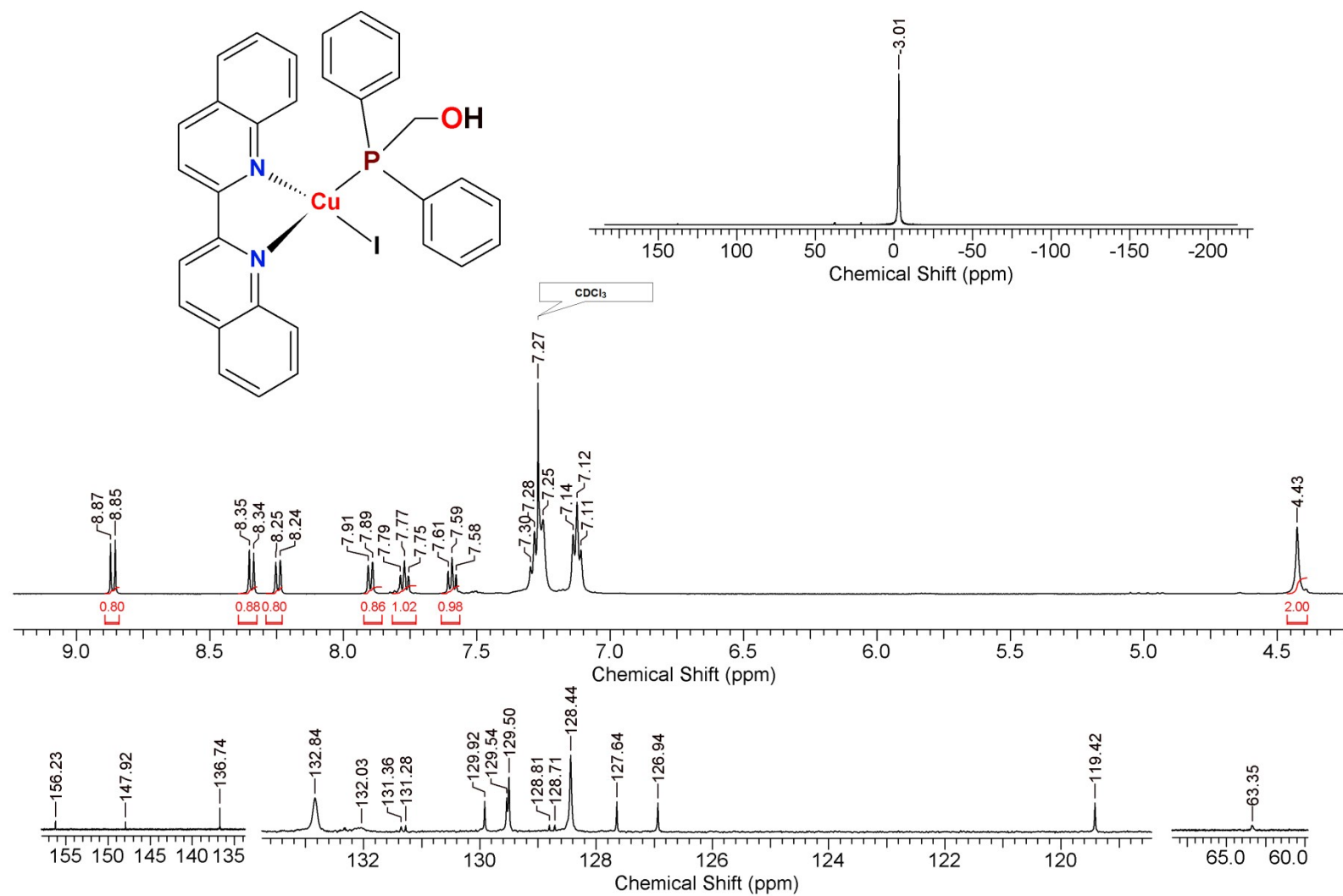


Fig S5 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **3-POH** (298 K, CDCl_3)

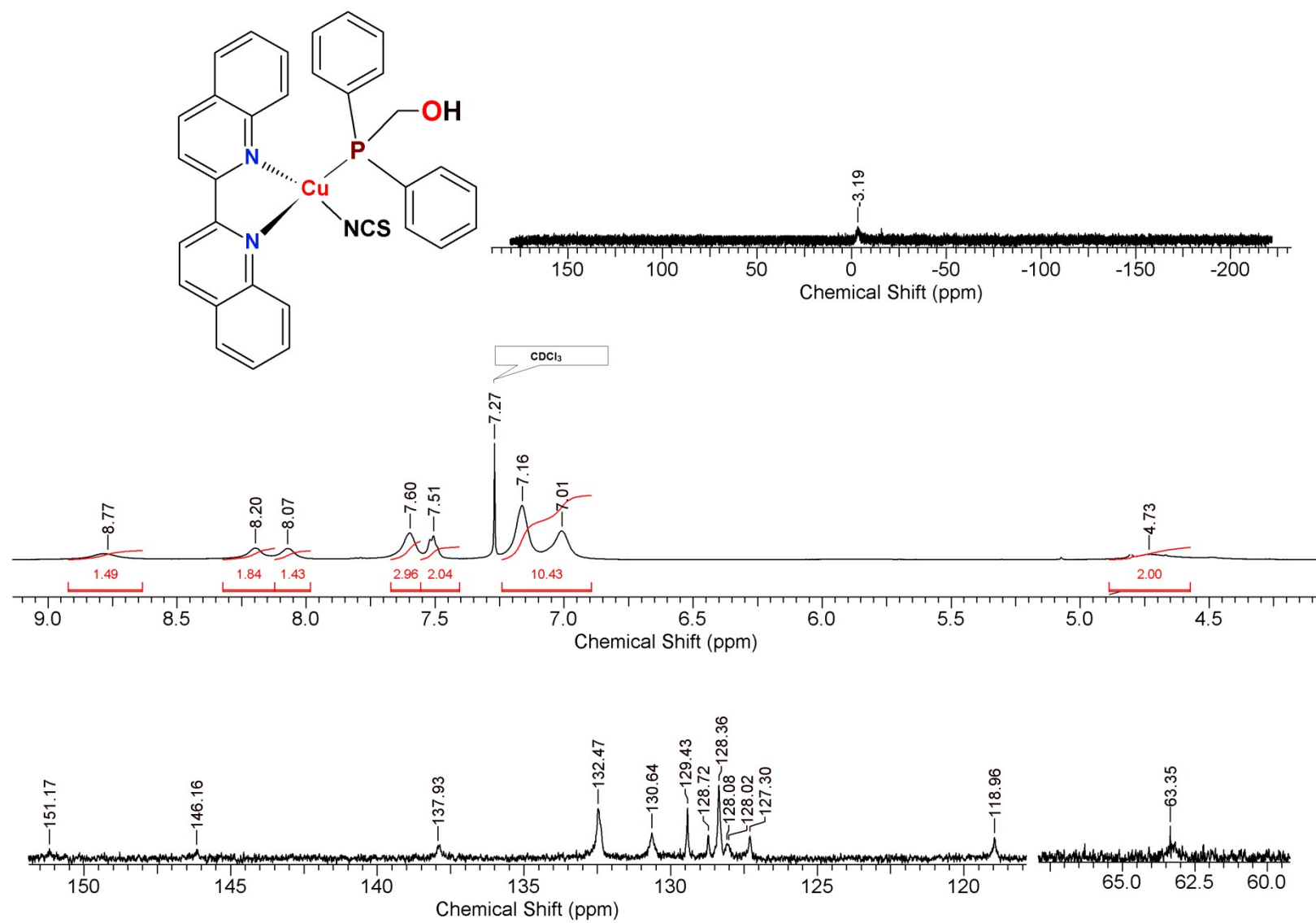


Fig S6 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **4-POH** (298 K, CDCl_3)

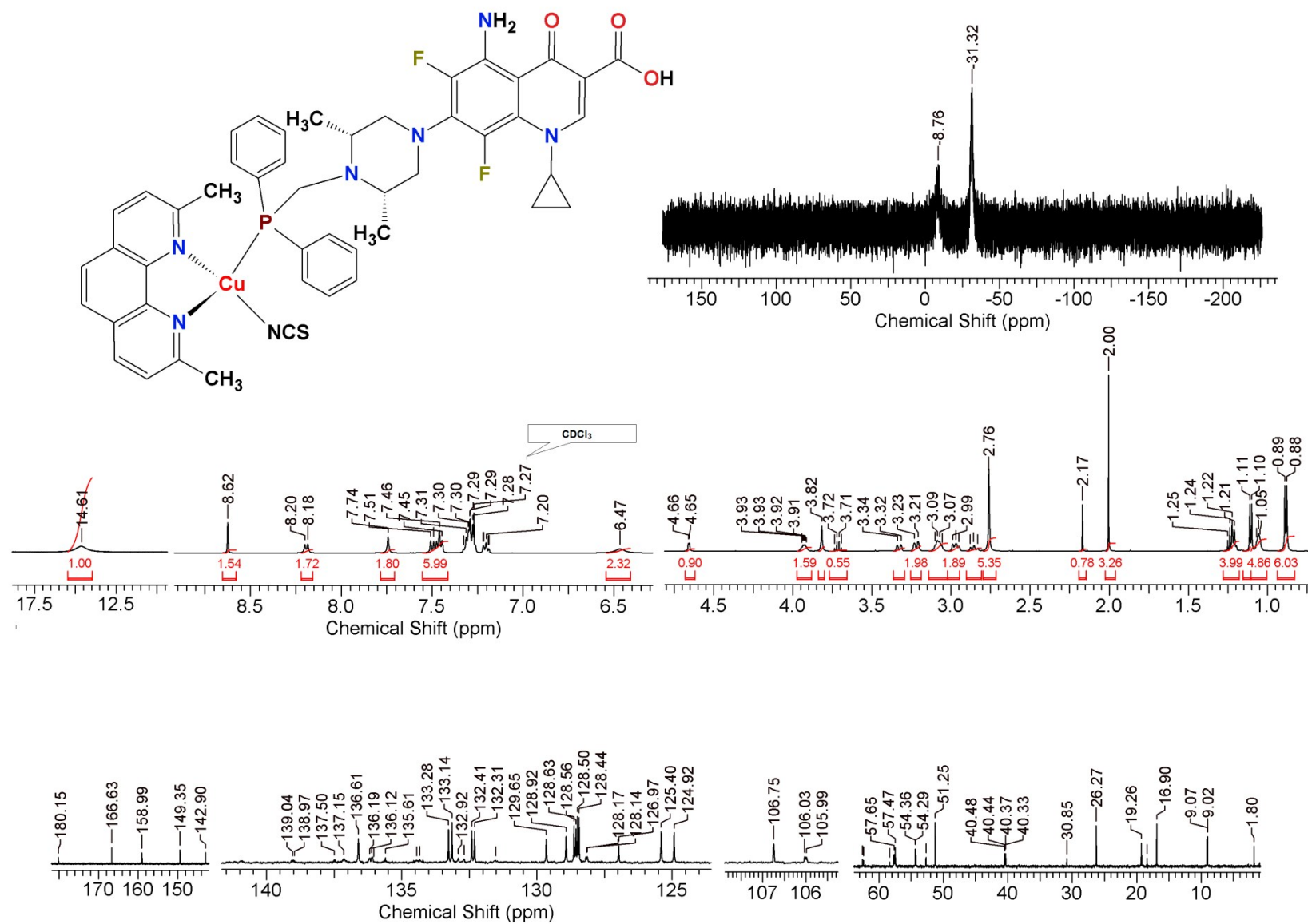


Fig S8 ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra for **2-PSf** (298 K, CDCl₃)

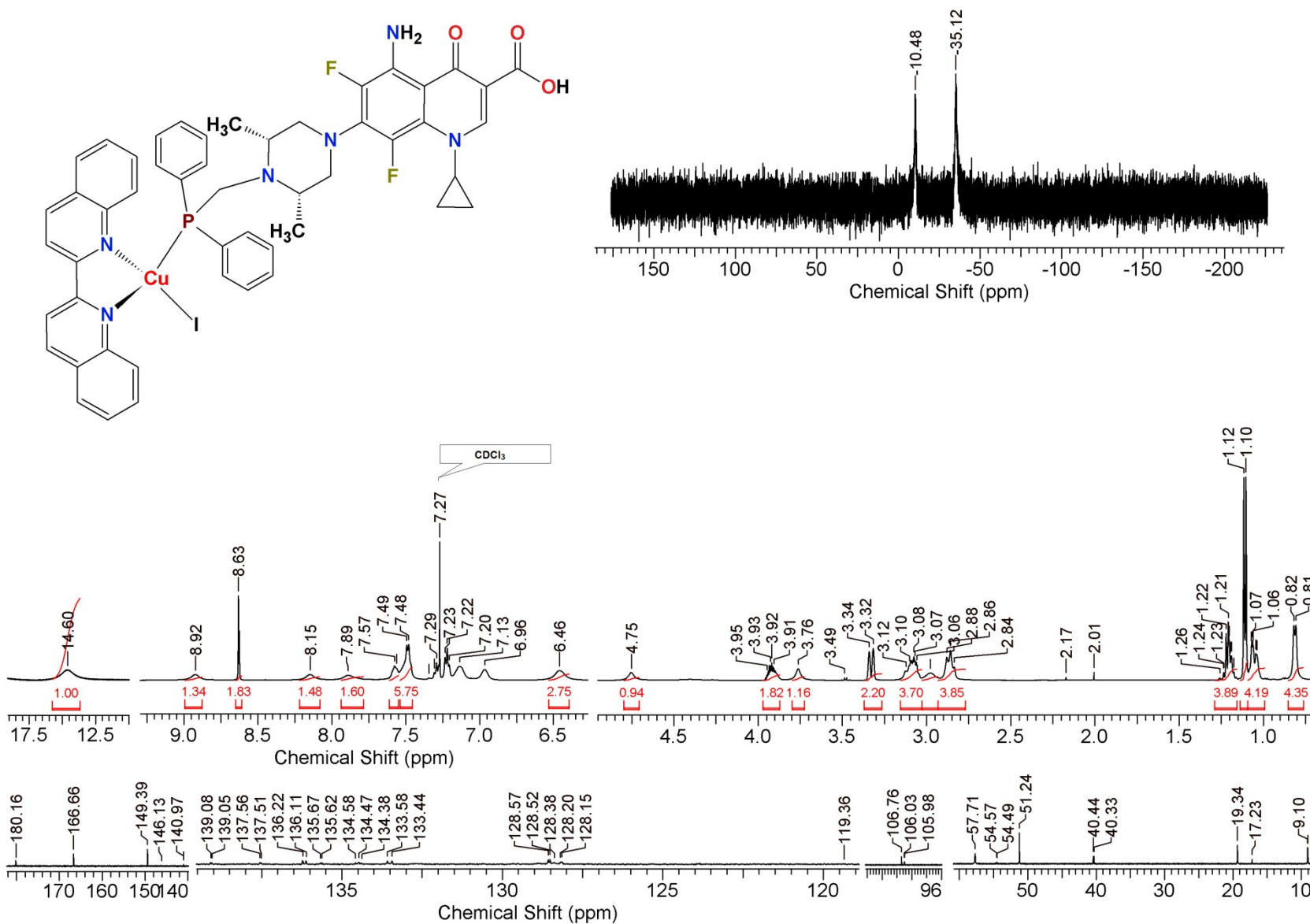


Fig S9 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **3-PSf** (298 K, CDCl_3)

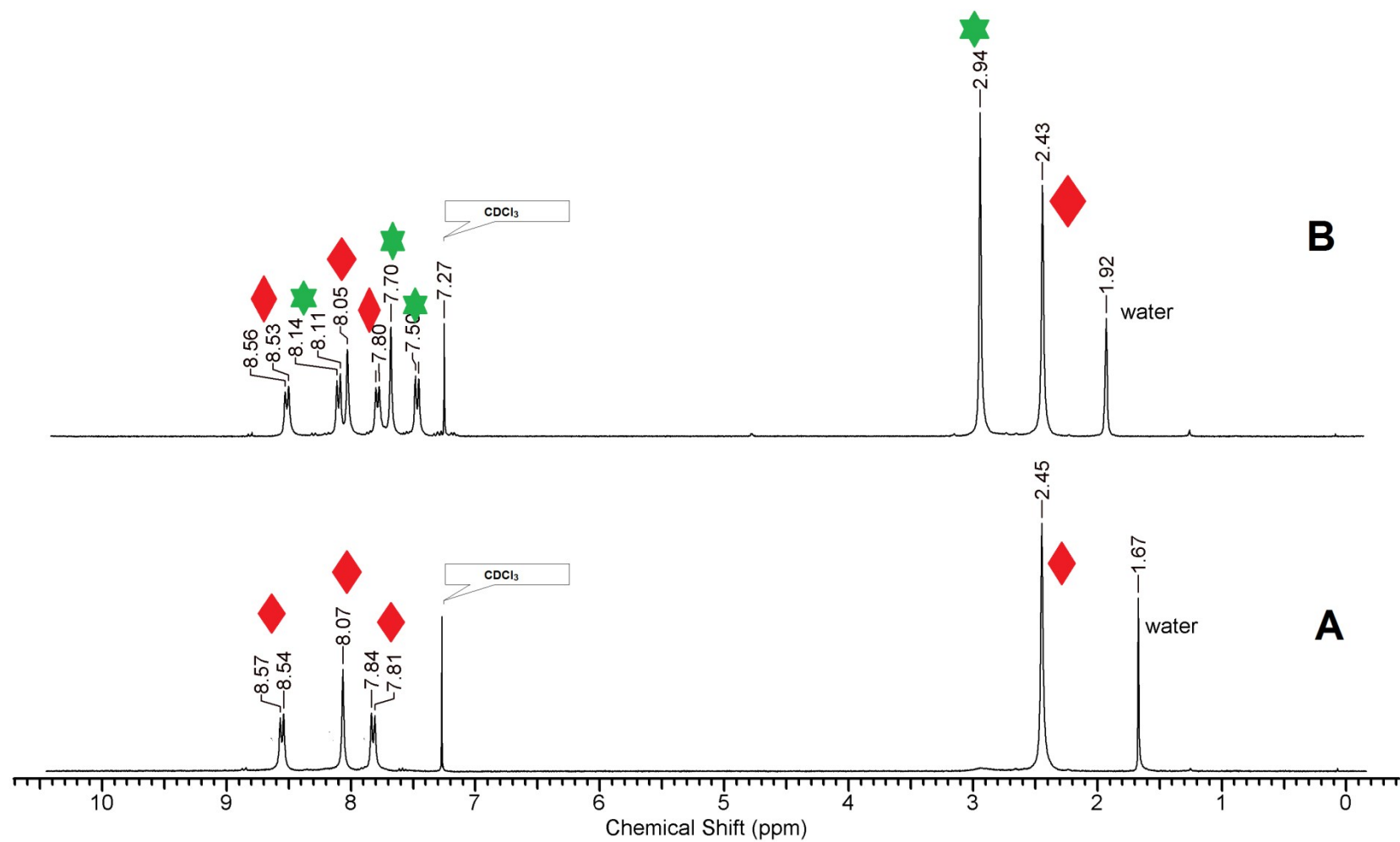


Fig. S11 ^1H NMR spectra of (A) $[\text{Cu}_2\text{I}_2(\text{dmp})_2]$ (B) $[\text{Cu}_2\text{I}_2(\text{dmp})_2] + \text{dmp}$ after 12 h (300 K, CDCl_3);
 ♦ complex, ★ free dmp

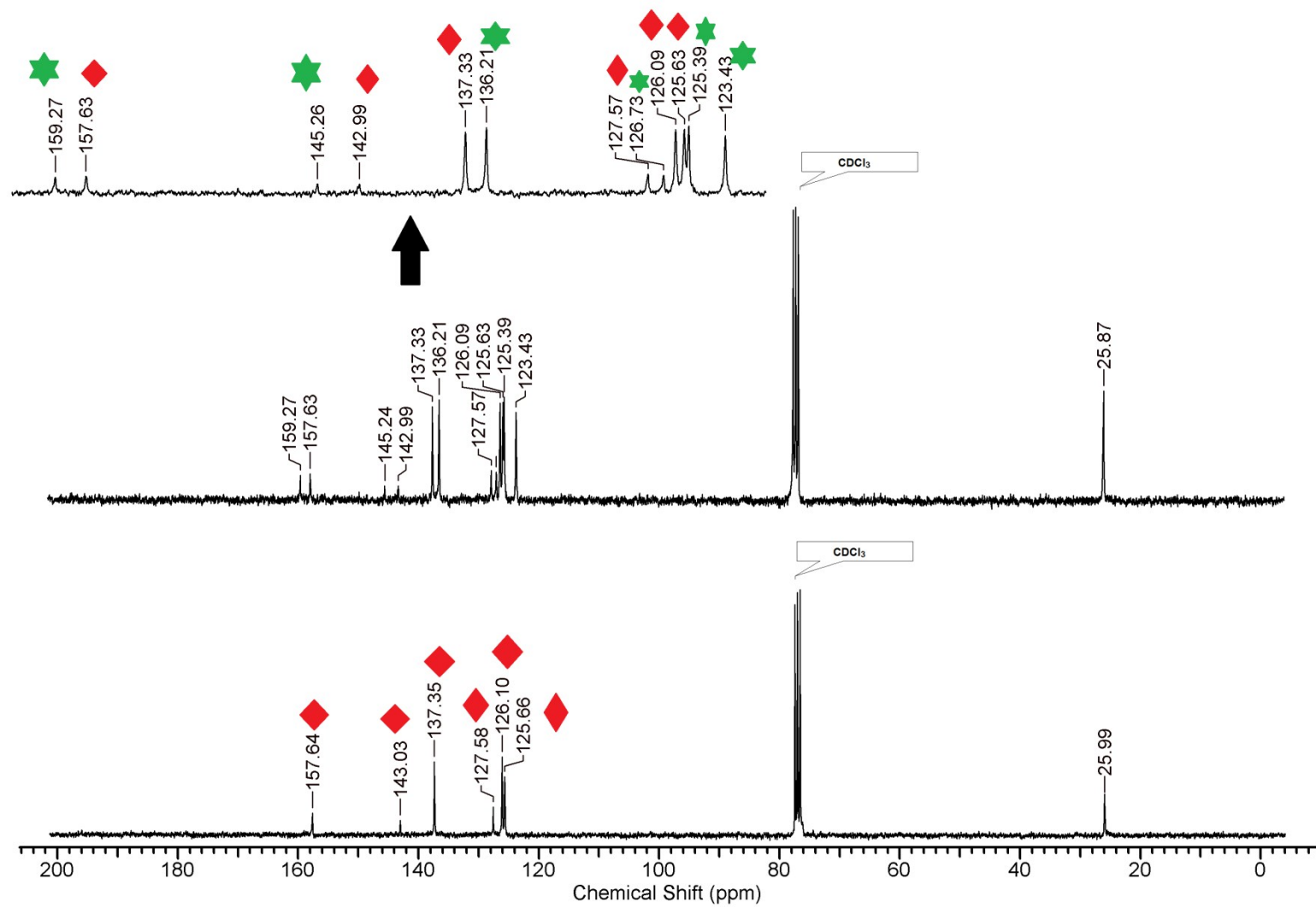


Fig. S12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (A) $[\text{Cu}_2\text{I}_2(\text{dmp})_2]$ (B) $[\text{Cu}_2\text{I}_2(\text{dmp})_2] + \text{dmp}$ after 12 h (300 K, CDCl_3);
 ■ complex, ■ free dmp

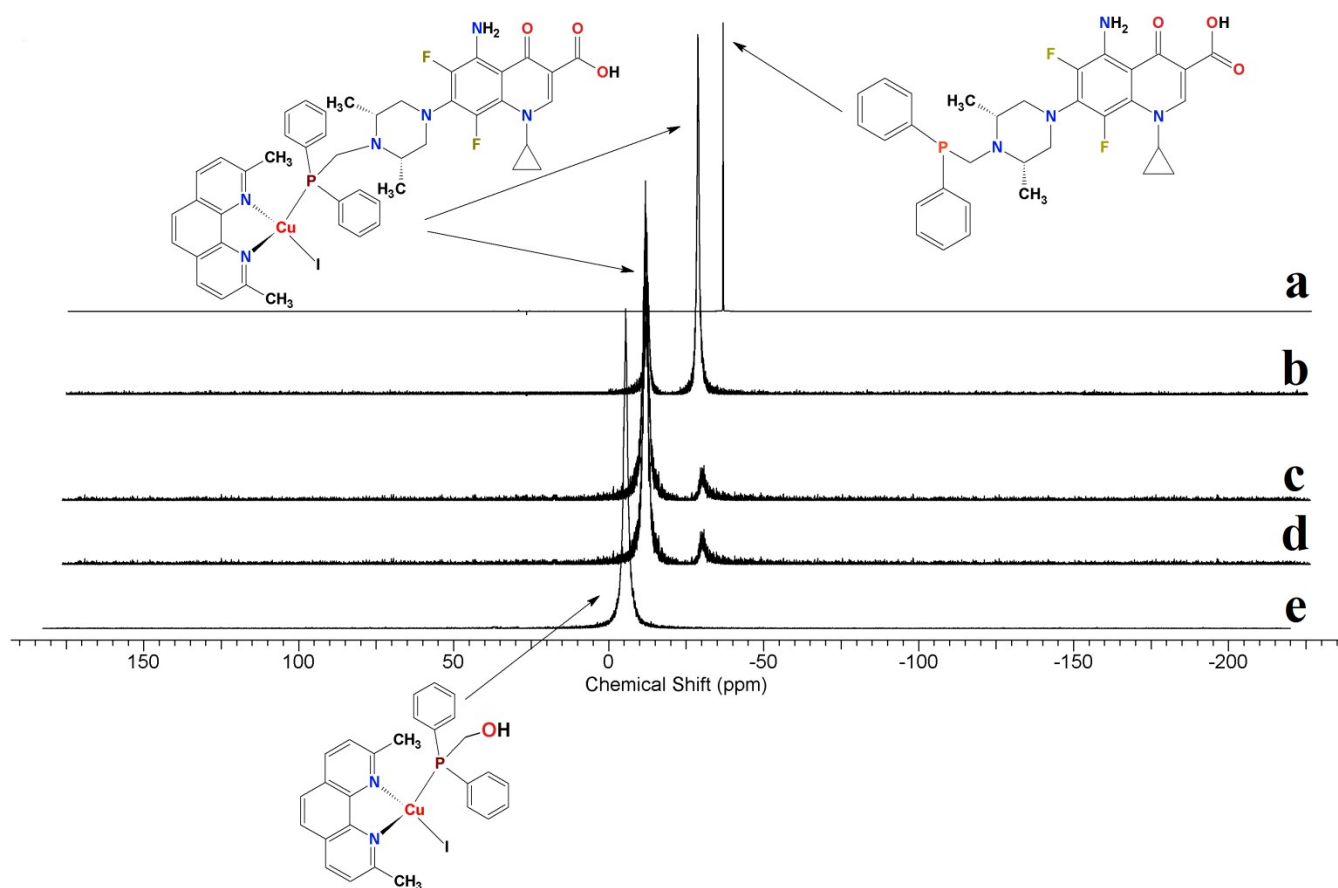


Fig S13 $^{31}\text{P}\{^1\text{H}\}$ power-spectra of **1-PSf** and **1-POH** (298 K, DMSO: H_2O (3:1 V:V)) a) **PSf**, b) **1-PSf + 1.5PSf** c) **1-PSf**, d) **1-PSf** after 72h, e) fresh **1-POH**.

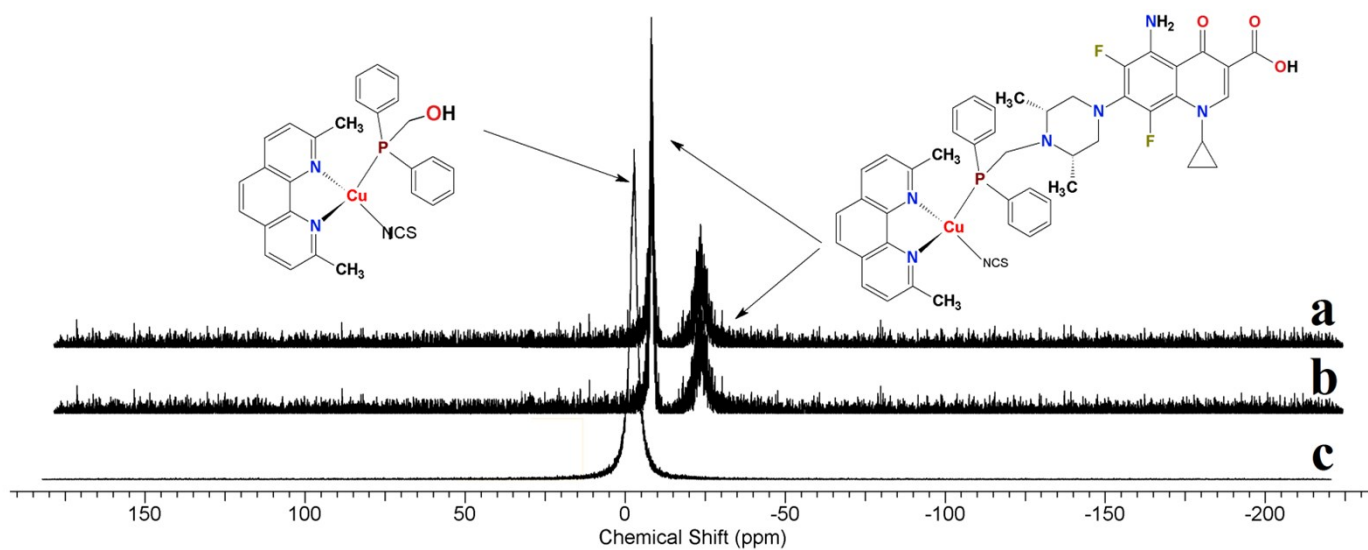


Fig S14 $^{31}\text{P}\{^1\text{H}\}$ power-spectra of **2-PSf** and **2-POH** (298 K, DMSO: H_2O (3:1 V:V)) a) **2-PSf**, b) **2-PSf** after 72h, c) **2-POH**.

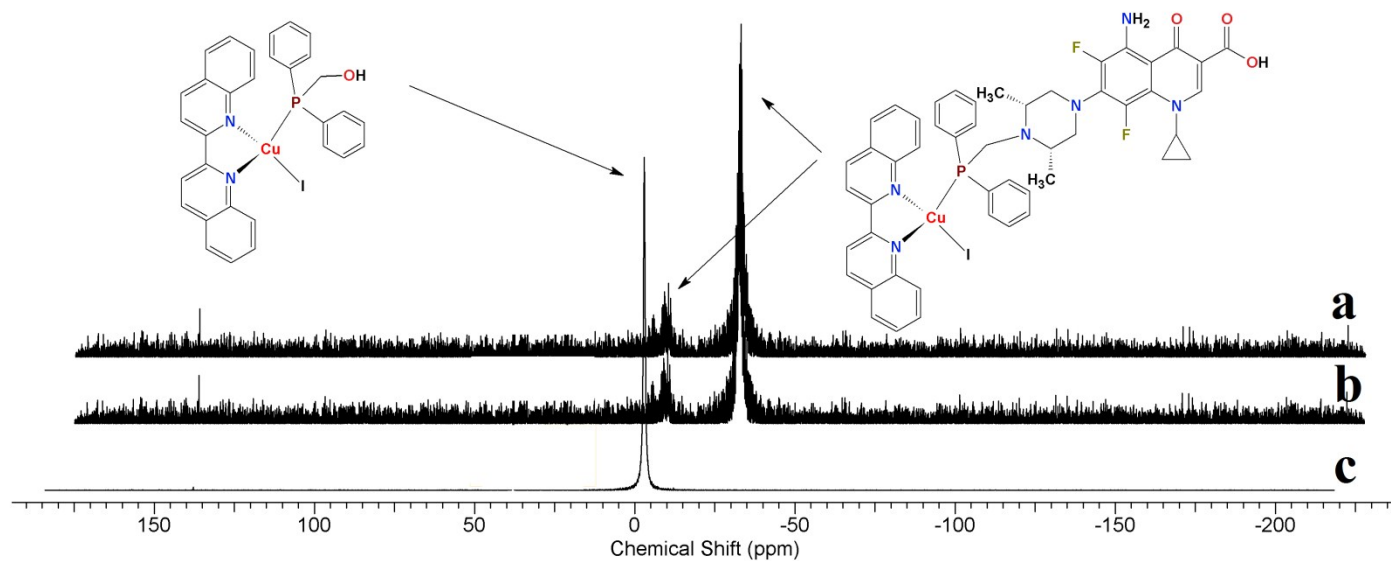


Fig S15 $^{31}\text{P}\{^1\text{H}\}$ power-spectra of **3-PSf** and **3-POH** (298 K, DMSO: H_2O (3:1 V:V)) a) **3-PSf**, b) **3-PSf** after 72h, c) **3-POH**.

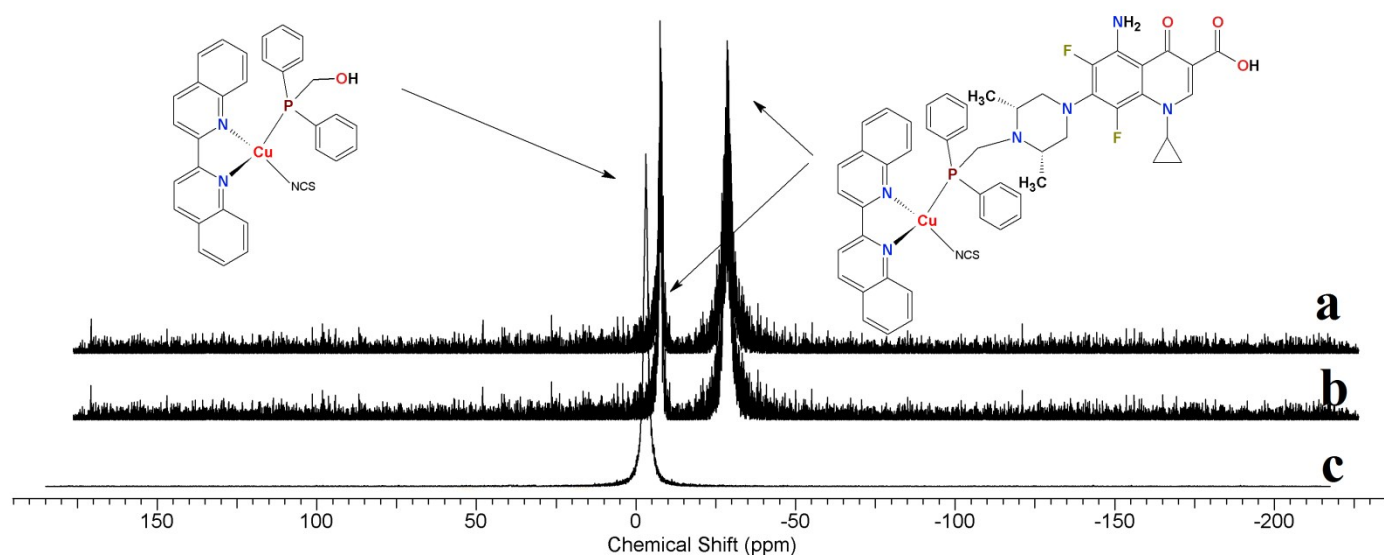


Fig S16 $^{31}\text{P}\{^1\text{H}\}$ power-spectra of **4-PSf** and **4-POH** (298 K, DMSO: H_2O (3:1 V:V)) a) **4-PSf**, b) **4-PSf** after 72h, c) **4-POH**.

Tab. S5 IC₅₀ values [μM] for CT26 and A549 cell lines after 4 and 24 h treatment with the complexes and ligands.

	IC ₅₀ [μM] ± SD			
	4h		24h	
	CT26	A549	CT26	A549
POH	74.47±1.13	73.98±1.25	70.70±5.53	74.36±1.26
OPOH	67.54±1.34	61.34±1.09	59.12±2.56	61.78±1.23
1-POH	30.76±1.12	31.15±6.37	46.86±4.16	26.15±6.33
2-POH	32.49±1.17	41.57±6.32	50.04±4.64	28.84±0.83
3-POH	55.92±3.29	57.32±1.40	60.00±0.56	59.15±2.06
4-POH	63.00±1.65	53.02±0.72	56.70±6.96	57.25±1.96
HSf^[34]	255.20±13.52	273.50±10.63	122.84±4.21	201.53±12.14
PSf^[34]	238.97±16.76	163.23±5.08	264.28±12.07	104.08±3.30
OPSf^[34]	51.03±1.21	74.90±1.43	109.23±8.76	52.72±9.23
1-PSf	7.33±0.06	6.04±0.03	8.29±0.71	7.84±0.16
2-PSf	7.75±0.19	7.02±0.02	7.88±0.58	7.51±0.34
3-PSf	24.52±1.02	24.70±2.50	9.32±0.42	8.25±0.08
4-PSf	42.64±0.73	23.99±1.21	33.79±8.08	9.06±0.47
dmp	64.74±1.28	61.66±1.90	55.97±4.60	58.12±3.99
bq	65.15±2.67	66.30±4.33	58.95±1.93	61.22±3.45
CuI	64.16±3.15	69.95±3.07	58.23±4.56	58.72±6.44
CuNCS	67.92±2.22	70.10±3.21	67.46±1.71	69.02±0.62
cisplatin	269.66±9.67	298.12±13.09	222.45±10.78	241.89±11.98

[34] U. K. Komarnicka, R. Starosta, K. Guz-Regner, G. Bugla-Płoskońska, A. Kyzioł and M. Jeżowska-Bojczuk, J. Mol. Struct. DOI 10.1016/j.molstruc.2015.04.044