A chemically-induced, room temperature, single source precursor to CuS (covellite) nanomaterials: Synthesis and reactivity of $[Cu(S_2CNHBz)]_n$

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Electronic supplementary information

Experimental section

Experimental section

All reactions were carried out in air using standard lab reagents.

Synthesis of $[Cu(S_2CNHBz)]_n$ (1)

NaOH (0.97 g, 24 mmol) and $BzNH_2$ (2.57 g, 24 mmol) were dissolved in water (100 ml). To this CS_2 (1.82 g, 24 mmol) was added dropwise with rapid stirring. After ca. 30 min a clear pale-yellow solution resulted. To this was added dropwise with rigorous stirring a solution of $CuSO_4 \cdot 5H_2O$ (2.99 g, 12 mmol) in water (40 ml). A heavy yellow precipitate formed. After complete addition the suspension was stirred for ca. 1 h and then the yellow solid was collected by vacuum filtration, washed with water (ca. 4 x 50 ml), MeOH (ca. 3 x 50 ml), thf (ca. 2 x 40 ml) and dried at ca. 60 ^oC to give a light yellow solid (**1** 2.30 g, 78 %). Slow evaporation of the methanol washing afforded colourless crystals of the $(BzNH)_2C{=}S$ as characterised crystallographically (see ESI) and NMR. Characterising data: **1**: Anal. Calc. for $CuS_2NC_8H_8$: C, 39.10; H, 3.26; N, 5.70. Found: C, 38.76; H, 3.45; N, 5.53. IR (cm^{-1}) 3221 (N-H), 1494 (C-N), 1454, 1428, 1380, 1338, 1305, 1248 (C-S), 1205, 1083, 1041, 1026, 969, 915, 897, 821, 742, 694, 613, 551, 538, 515, 445. ^1H NMR (DMSO-d_6,): δ 4.73 (d, J 4 Hz, 2H, CH_2), 7.27-7.45 (m, 5H, Ph), 10.90 (t, J 4 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 204.3, 136.7, 128.9, 128.4, 128.2, 127.7, 127.3, 127.2, 51.8. μ_{eff}: 0 BM. **$(BzNH)_2C{=}S$**: ^1H NMR (d^6-dmso) δ 7.98 (brs, 2H, NH), 7.35-7.32 (m, 10H, Ph), 4.71 (brs, 4H, CH_2). $^{13}C\{^1H\}$ (d^6-dmso) 183.0, 139.3, 128.3, 127.8, 126.9, 47.1.

Synthesis of $[Cu(\kappa^2\text{-}S_2CNHBz)(PPh_3)_2]$ (2)

To a mixture of **1** (50 mg, 0.24 mmol) and PPh_3 (130 mg, 0.50 mmol) in a large sample vial was added ca. 10 ml of CH_2Cl_2. The solution was manually shaken for ca. 10 min during which time insoluble **1** slowly dispersed to afford a colourless solution. This was filtered under gravity and the filtrate was layered with hexanes. Slow mixing of the solvents, and later slow evaporation of the solvents, led to the deposition of white crystals of **2** (75 mg, 82%). Crystals of **2** suitable for X-ray crystallography were grown by the slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. We also prepared **2** from the reaction of $[Cu(NO_3)(PPh_3)]$ and NaS_2CNHBz. $[Cu(NO_3)(PPh_3)_2]$ (0.13 g, 0.20 mmol) was dissolved in CH_2Cl_2 (20 mL) and to this was added $NaS_2CNH^iBz.3H_2O$ (44.8 mg 0.20 mmol). The pale-yellow solution was stirred at room temperature for ca. 1 h, becoming slightly darker. A small amount of acid was added

(to remove any PPh_3) and the solution was washed with water (5 mL) and dried over $MgSO_4$. After filtration and removal of volatiles under reduced pressure, **2** was isolated (0.11 g, 73%).

Characterising data: **2**: Anal. Calc. for $CuS_2NP_2C_{44}H_{38}.CH_2Cl_2$: C, 64.25; H, 4.76; N, 1.67. Found: C, 64.43; H, 4.85; N, 1,73. ^{1}H NMR ($CDCl_3$) δ 4.75 (d, J 8.0 Hz, 2H, CH_2), 7.26-7.47 (m, 35H, Ph), 7.66 (brs, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 211.0, 137.5, 134.5, 134.3, 133.9, 133.8, 129.3, 129.1, 128.6, 128.4, 128.3, 128.0, 127.4, 51.1. $^{31}P\{^1H\}$ ($CDCl_3$) δ -1.88.

Synthesis of [Cu(κ^2-S_2CNHBz)(κ^2-dppf)] (3)

To a mixture of **1** (0.50 mg, 0.21 mmol) and dppf (125 mg, 0.45 mmol) in a large sample vial was added ca. 10 ml of CH_2Cl_2. The solution was manually shaken for ca. 30 min during which time insoluble **1** slowly dispersed to afford a bright orange solution. This was filtered under gravity and the filtrate layered with methanol. Slow mixing of the solvents led to the deposition of orange **3** (0.28 g, 85%). Characterising data: **3**: Anal. Calc. for $CuS_2NP_2FeC_{42}H_{36}$: C, 63.04; H, 4.50; N, 1.75. Found: C, 63.56; H, 4.61; N, 1.78. ^{1}H NMR ($CDCl_3$) 7.63 (m, 8H, Ph), 7.38 (t, J 4 Hz, 1H, NH), 7.35-7.17 (m, 17H, Ph), 4.65 (d, J 4 Hz, 2H, CH_2), 4.20 (d, J 2 Hz, 4H, C_5H_4), 4.08 (d, J 2 Hz, 4H, C_5H_4), $^{13}C\{^1H\}$ NMR ($CDCl_3$) 211.7, 137.6, 135.1, 135.0, 134.9, 134.2, 134.1, 134.0, 129.6, 128.7, 128.4, 128.3, 128.3, 128.0, 127.5, 74.0 (d, J 6 Hz), 71.5 (d, J 6 Hz), 51.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -16.4.

Decomposition studies

A hot plate was pre-heated to ~105 °C (to ensure the temperature inside the flask was 90 °C). 300 mg of **1** was dispersed in 90 mL of dmso in a 100 mL round bottom flask, which was then placed on the pre-heated hot plate and heated for 3 h. Aliquots of 100 μL were taken at 30 min, 60 min, 120 min, and 180 min, and then diluted in 1.9 mL dmso.

Approximately 300 mg of **1** was dissolved in n-butylamine (ca. 20 ml) to give a dark brown solution. Standing at room temperature for ca. 1 h resulted in the solution slowly decolouring with concomitant generation of CuS as a fine dark green precipitate.

In a sample vial, ca. 50 mg of **1** was suspended in ca. 10 ml of dmso at room temperature. To this was added ca. 3 drops of $BuNH_2$. The yellow suspension slowly dissolved with shaking to give a dark brown solution after ca. 1 h. This solution was left to stand for ca. 1 week resulting in formation of CuS as a fine dark green precipitate

X-ray crystallography

Crystallographic data for **2** was collected by the EPSRC UK National Crystallography Service at the University of Southampton [**S1**]. A Rigaku FRE+ diffractometer (Mo-K_α radiation, 0.71073 Å) was used equipped with HF Varimax confocal mirrors, an AFC12 goniometer, HG Saturn 724+ detector, and an Oxford Cryo-systems low-temperature device.

For **3** and dibenzylthiourea, data was collected on an Oxford Diffraction Xcalibur S single-crystal diffractometer operating at 150(1) K with a Sapphire 3 CCD plate and graphite-monochromated Cu Kα radiation, λ = 1.54184 Å (for **3**) or graphite-monochromated Mo Kα radiation, λ = 0.71073 Å (for dibenzylthiourea).

All datasets were processed using CrysAlisPro [**S2**] and solutions were solved and refined using Olex-2 [**S3**]. Crystallographic data is summarised in Table S1.

S1. S. J. Coles, D. R. Allan, C. M. Beavers, S. J. Teat and S. J. W. Holgate, Leading edge chemical crystallography service provision and its impact on crystallographic data science in the twenty-first century. In: Structure and Bonding, 2020, Berlin, Heidelberg, Springer, 1–72.

S2. CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.

S3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341.

Table S1. Crystallographic data and structure refinement

	2	**3**	**$(BzNH)_2C=S$**
Empirical formula	$C_{44}H_{38}NS_2P_2Cu$	$C_{42}H_{36}N_2S_2P_2CuFe$	$C_{15}H_{16}N_2S$
CCDC number	2378475	2378476	2378477
Formula weight (Å)	770.35	800.17	256.36
Temperature (K)	100(1)	150(2)	296(1)
Crystal system	monoclinic	triclinic	orthorhombic
Space group	I2/a	P-1	Pbca
Unit cell dimensions			
a (Å)	38.4141(11)	11.9613(4)	10.8357(10)
b (Å)	15.0197(4)	16.1413(5)	9.3683(7)
c (Å)	44.0156(12)	18.9872(6)	26.594(2)
α(°)	90	95.408(3)	90
β(°)	116.023(3)	93.201(3)	90
γ (°)	90	92.636(3)	90
Volume (Å^3)	22930.3(12)	3639.2(10)	2699.6(4)
Z	24	4	8
Density (calc.) (g/cm^3)	1.339	1.461	1.261
Absorption coefficient	0.797	6.061	0.223
F(000)	9600	1648	1088
Crystal size (mm)	0.10 × 0.10 × 0.10	0.37 × 0.28 × 0.17	0.30 × 0.25 × 0.20
θ Range for data collection (°)	3.88 to 61.02	6.88 to 144.52	5.95 to 58.56
Index ranges	$-54 \le h \le 54$ $-21 \le k \le 20$ $-62 \le l \le 62$	$-14 \le h \le 9$ $-19 \le k \le 19$ $-18 \le l \le 23$	$-8 \le h \le 13$ $-12 \le k \le 9$ $-34 \le l \le 27$
Reflections collected	178339	26444	9535
Independent reflections	35000	14004	3163
Data / restraints / parameters	35000/0/1351	14004/18/929	3163/0/163
Goodness-of-fit on F^2	0.992	1.047	1.115
Final *R* indices [I>2σ(I)]	R_1 = 0.0538, wR_2 = 0.0983	R_1 = 0.0463 wR_2 = 0.1207	R_1 = 0.0545 wR_2 = 0.1211
R indices (all data)	R_1 = 0.1047, wR_2 = 0.1153	R_1 = 0.0623 wR_2 = 0.1292	R_1 = 0.0713 wR_2 = 0.1300
Largest diff. peak and hole (e.Å^{-3})	0.50/-0.48	0.76/-0.43	0.27/-0.33

Molecular structure of 2

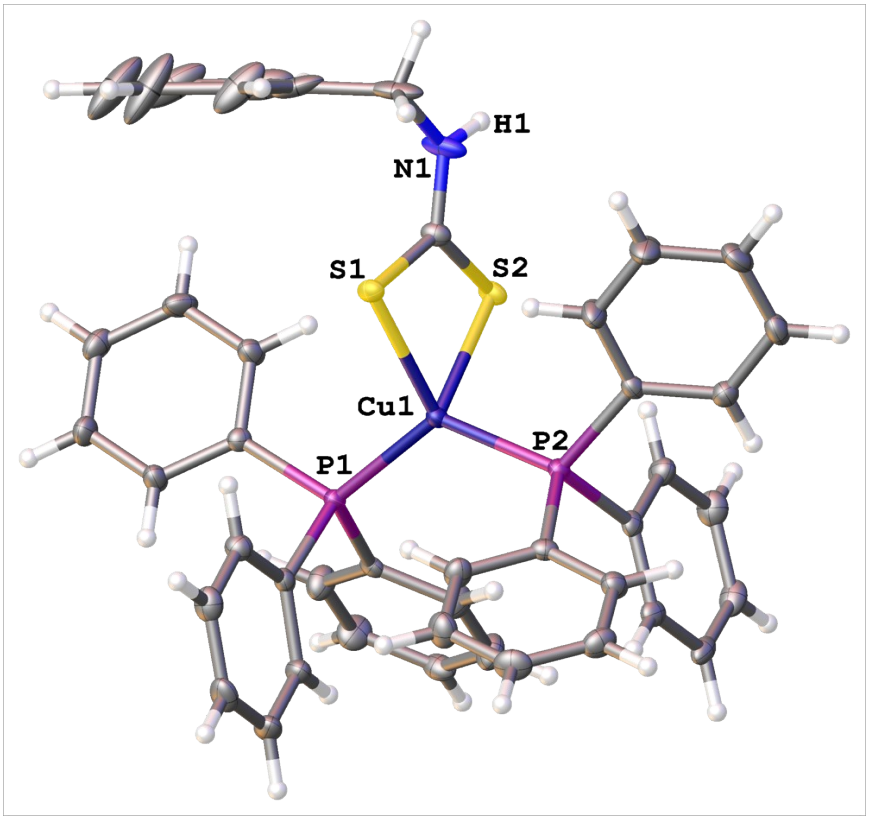


Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	S1	2.3911(6)	C60	C61	1.391(3)
Cu1	S2	2.4146(6)	C61	C62	1.381(3)
Cu1	P1	2.2428(6)	C62	C63	1.389(3)
Cu1	P2	2.2497(6)	C63	C64	1.380(3)
S1	C1	1.703(2)	C65	C66	1.389(3)
S2	C1	1.729(2)	C65	C70	1.392(3)
P1	C9	1.827(2)	C66	C67	1.393(3)
P1	C15	1.822(2)	C67	C68	1.383(3)
P1	C21	1.830(2)	C68	C69	1.376(3)
P2	C27	1.829(2)	C69	C70	1.388(3)
P2	C33	1.829(2)	C71	C72	1.386(3)
P2	C39	1.834(2)	C71	C76	1.397(3)
N1	C1	1.325(3)	C72	C73	1.393(3)
N1	C2	1.461(3)	C73	C74	1.381(3)
C2	C3	1.516(4)	C74	C75	1.383(4)
C3	C4	1.379(4)	C75	C76	1.391(3)
C3	C8	1.383(4)	C77	C78	1.400(3)
C4	C5	1.387(4)	C77	C82	1.387(3)
C5	C6	1.388(4)	C78	C79	1.394(3)
C6	C7	1.386(5)	C79	C80	1.384(3)
C7	C8	1.381(4)	C80	C81	1.381(3)

Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C9	C10	1.391(3)	C81	C82	1.388(3)
C9	C14	1.387(3)	C83	C84	1.394(3)
C10	C11	1.382(3)	C83	C88	1.398(3)
C11	C12	1.377(4)	C84	C85	1.395(3)
C12	C13	1.388(3)	C85	C86	1.377(3)
C13	C14	1.396(3)	C86	C87	1.385(3)
C15	C16	1.394(3)	C87	C88	1.382(3)
C15	C20	1.400(3)	Cu3	S5	2.4219(6)
C16	C17	1.395(3)	Cu3	S6	2.3841(6)
C17	C18	1.385(3)	Cu3	P5	2.2522(6)
C18	C19	1.384(3)	Cu3	P6	2.2543(6)
C19	C20	1.382(3)	S5	C89	1.731(2)
C21	C22	1.390(3)	S6	C89	1.707(2)
C21	C26	1.399(3)	P5	C97	1.832(2)
C22	C23	1.393(3)	P5	C103	1.820(2)
C23	C24	1.384(3)	P5	C109	1.833(2)
C24	C25	1.393(3)	P6	C115	1.826(2)
C25	C26	1.386(3)	P6	C121	1.829(2)
C27	C28	1.398(3)	P6	C127	1.837(2)
C27	C32	1.394(3)	N3	C89	1.324(3)
C28	C29	1.390(3)	N3	C90	1.461(3)
C29	C30	1.378(3)	C90	C91	1.518(3)
C30	C31	1.386(3)	C91	C92	1.378(3)
C31	C32	1.393(3)	C91	C96	1.385(3)
C33	C34	1.391(3)	C92	C93	1.390(3)
C33	C38	1.397(3)	C93	C94	1.383(4)
C34	C35	1.383(3)	C94	C95	1.376(4)
C35	C36	1.387(3)	C95	C96	1.391(4)
C36	C37	1.383(3)	C97	C98	1.402(3)
C37	C38	1.392(3)	C97	C102	1.393(3)
C39	C40	1.398(3)	C98	C99	1.384(3)
C39	C44	1.388(3)	C99	C100	1.384(3)
C40	C41	1.385(3)	C100	C101	1.385(3)
C41	C42	1.389(3)	C101	C102	1.387(3)
C42	C43	1.384(3)	C103	C104	1.400(3)
C43	C44	1.394(3)	C103	C108	1.397(3)
Cu2	S3	2.4004(6)	C104	C105	1.384(3)
Cu2	S4	2.4124(6)	C105	C106	1.385(3)
Cu2	P3	2.2382(6)	C106	C107	1.383(3)
Cu2	P4	2.2490(6)	C107	C108	1.387(3)
S3	C45	1.709(2)	C109	C110	1.394(3)
S4	C45	1.726(2)	C109	C114	1.393(3)
P3	C53	1.833(2)	C110	C111	1.382(3)

Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P3	C59	1.828(2)	C111	C112	1.393(3)
P3	C65	1.824(2)	C112	C113	1.377(3)
P4	C71	1.825(2)	C113	C114	1.391(3)
P4	C77	1.830(2)	C115	C116	1.389(3)
P4	C83	1.831(2)	C115	C120	1.403(3)
N2	C45	1.325(3)	C116	C117	1.394(3)
N2	C46	1.455(3)	C117	C118	1.385(3)
C46	C47	1.520(3)	C118	C119	1.380(3)
C47	C48	1.394(3)	C119	C120	1.389(3)
C47	C52	1.359(4)	C121	C122	1.392(3)
C48	C49	1.390(4)	C121	C126	1.393(3)
C49	C50	1.368(5)	C122	C123	1.395(3)
C50	C51	1.377(4)	C123	C124	1.379(3)
C51	C52	1.393(4)	C124	C125	1.382(3)
C53	C54	1.399(3)	C125	C126	1.386(3)
C53	C58	1.387(3)	C127	C128	1.396(3)
C54	C55	1.385(3)	C127	C132	1.396(3)
C55	C56	1.385(4)	C128	C129	1.388(3)
C56	C57	1.383(3)	C129	C130	1.384(3)
C57	C58	1.393(3)	C130	C131	1.394(3)
C59	C60	1.395(3)	C131	C132	1.386(3)
C59	C64	1.402(3)			

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Cu1	S2	75.778(19)	C60	C59	P3	124.97(17)
P1	Cu1	S1	110.98(2)	C60	C59	C64	118.3(2)
P1	Cu1	S2	115.03(2)	C64	C59	P3	116.59(16)
P1	Cu1	P2	125.64(2)	C61	C60	C59	120.2(2)
P2	Cu1	S1	114.91(2)	C62	C61	C60	120.7(2)
P2	Cu1	S2	103.27(2)	C61	C62	C63	119.6(2)
C1	S1	Cu1	83.06(7)	C64	C63	C62	119.9(2)
C1	S2	Cu1	81.84(7)	C63	C64	C59	121.2(2)
C9	P1	Cu1	117.11(7)	C66	C65	P3	118.52(16)
C9	P1	C21	103.74(10)	C66	C65	C70	118.9(2)
C15	P1	Cu1	115.89(7)	C70	C65	P3	122.57(17)
C15	P1	C9	104.05(10)	C65	C66	C67	120.3(2)
C15	P1	C21	103.07(9)	C68	C67	C66	120.0(2)
C21	P1	Cu1	111.37(8)	C69	C68	C67	120.1(2)
C27	P2	Cu1	118.18(7)	C68	C69	C70	120.0(2)
C27	P2	C33	102.69(10)	C69	C70	C65	120.6(2)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C27	P2	C39	105.49(10)	C72	C71	P4	122.19(17)
C33	P2	Cu1	116.54(7)	C72	C71	C76	118.7(2)
C33	P2	C39	101.89(9)	C76	C71	P4	118.90(18)
C39	P2	Cu1	110.30(8)	C71	C72	C73	120.9(2)
C1	N1	C2	123.85(19)	C74	C73	C72	119.8(2)
S1	C1	S2	118.67(12)	C73	C74	C75	120.1(2)
N1	C1	S1	122.09(17)	C74	C75	C76	120.0(2)
N1	C1	S2	119.25(16)	C75	C76	C71	120.5(2)
N1	C2	C3	112.9(2)	C78	C77	P4	122.37(16)
C4	C3	C2	121.9(3)	C82	C77	P4	118.35(16)
C4	C3	C8	118.7(3)	C82	C77	C78	119.3(2)
C8	C3	C2	119.3(3)	C79	C78	C77	120.0(2)
C3	C4	C5	121.1(3)	C80	C79	C78	119.9(2)
C4	C5	C6	119.9(3)	C81	C80	C79	120.3(2)
C7	C6	C5	118.9(3)	C80	C81	C82	120.0(2)
C8	C7	C6	120.6(3)	C77	C82	C81	120.5(2)
C7	C8	C3	120.7(3)	C84	C83	P4	125.08(17)
C10	C9	P1	118.03(18)	C84	C83	C88	118.8(2)
C14	C9	P1	123.53(16)	C88	C83	P4	116.05(16)
C14	C9	C10	118.4(2)	C83	C84	C85	119.9(2)
C11	C10	C9	120.9(2)	C86	C85	C84	120.6(2)
C12	C11	C10	120.6(2)	C85	C86	C87	119.8(2)
C11	C12	C13	119.5(2)	C88	C87	C86	120.1(2)
C12	C13	C14	119.8(2)	C87	C88	C83	120.7(2)
C9	C14	C13	120.8(2)	S6	Cu3	S5	75.685(19)
C16	C15	P1	118.36(16)	P5	Cu3	S5	112.95(2)
C16	C15	C20	119.1(2)	P5	Cu3	S6	113.07(2)
C20	C15	P1	122.55(16)	P5	Cu3	P6	124.11(2)
C15	C16	C17	119.8(2)	P6	Cu3	S5	106.31(2)
C18	C17	C16	120.5(2)	P6	Cu3	S6	114.06(2)
C19	C18	C17	119.8(2)	C89	S5	Cu3	82.20(7)
C20	C19	C18	120.2(2)	C89	S6	Cu3	83.83(7)
C19	C20	C15	120.6(2)	C97	P5	Cu3	116.82(7)
C22	C21	P1	123.17(16)	C97	P5	C109	104.59(10)
C22	C21	C26	119.1(2)	C103	P5	Cu3	112.03(8)
C26	C21	P1	117.31(16)	C103	P5	C97	100.91(9)
C21	C22	C23	120.1(2)	C103	P5	C109	105.44(10)
C24	C23	C22	120.7(2)	C109	P5	Cu3	115.47(7)
C23	C24	C25	119.4(2)	C115	P6	Cu3	110.59(8)
C26	C25	C24	120.1(2)	C115	P6	C121	104.85(10)
C25	C26	C21	120.6(2)	C115	P6	C127	103.46(10)
C28	C27	P2	117.93(17)	C121	P6	Cu3	117.81(7)
C32	C27	P2	123.71(16)	C121	P6	C127	99.80(10)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C32	C27	C28	118.3(2)	C127	P6	Cu3	118.50(7)
C29	C28	C27	120.4(2)	C89	N3	C90	125.05(18)
C30	C29	C28	120.4(2)	S6	C89	S5	118.08(12)
C29	C30	C31	120.3(2)	N3	C89	S5	118.88(15)
C30	C31	C32	119.3(2)	N3	C89	S6	123.03(15)
C31	C32	C27	121.3(2)	N3	C90	C91	114.21(19)
C34	C33	P2	117.48(16)	C92	C91	C90	122.3(2)
C34	C33	C38	118.8(2)	C92	C91	C96	118.8(2)
C38	C33	P2	123.74(17)	C96	C91	C90	118.8(2)
C35	C34	C33	120.6(2)	C91	C92	C93	121.2(2)
C34	C35	C36	120.4(2)	C94	C93	C92	119.6(3)
C37	C36	C35	119.7(2)	C95	C94	C93	119.7(3)
C36	C37	C38	120.0(2)	C94	C95	C96	120.4(2)
C37	C38	C33	120.4(2)	C91	C96	C95	120.3(3)
C40	C39	P2	116.58(16)	C98	C97	P5	122.28(16)
C44	C39	P2	124.53(17)	C102	C97	P5	118.44(16)
C44	C39	C40	118.6(2)	C102	C97	C98	119.26(19)
C41	C40	C39	120.8(2)	C99	C98	C97	120.2(2)
C40	C41	C42	120.2(2)	C100	C99	C98	120.2(2)
C43	C42	C41	119.4(2)	C99	C100	C101	119.8(2)
C42	C43	C44	120.4(2)	C100	C101	C102	120.7(2)
C39	C44	C43	120.5(2)	C101	C102	C97	119.8(2)
S3	Cu2	S4	75.676(19)	C104	C103	P5	116.59(16)
P3	Cu2	S3	114.58(2)	C108	C103	P5	125.00(16)
P3	Cu2	S4	112.87(2)	C108	C103	C104	118.0(2)
P3	Cu2	P4	123.76(2)	C105	C104	C103	121.3(2)
P4	Cu2	S3	111.83(2)	C104	C105	C106	120.0(2)
P4	Cu2	S4	107.83(2)	C107	C106	C105	119.5(2)
C45	S3	Cu2	82.35(7)	C106	C107	C108	120.8(2)
C45	S4	Cu2	81.67(7)	C107	C108	C103	120.5(2)
C53	P3	Cu2	114.88(7)	C110	C109	P5	123.76(16)
C59	P3	Cu2	113.42(8)	C114	C109	P5	117.31(16)
C59	P3	C53	104.51(10)	C114	C109	C110	118.9(2)
C65	P3	Cu2	115.77(7)	C111	C110	C109	120.6(2)
C65	P3	C53	104.39(11)	C110	C111	C112	119.9(2)
C65	P3	C59	102.43(9)	C113	C112	C111	120.0(2)
C71	P4	Cu2	115.71(7)	C112	C113	C114	120.2(2)
C71	P4	C77	103.38(10)	C113	C114	C109	120.3(2)
C71	P4	C83	105.40(10)	C116	C115	P6	123.60(17)
C77	P4	Cu2	116.97(7)	C116	C115	C120	118.3(2)
C77	P4	C83	101.90(9)	C120	C115	P6	117.88(16)
C83	P4	Cu2	111.92(8)	C115	C116	C117	120.6(2)
C45	N2	C46	124.83(18)	C118	C117	C116	120.2(2)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S3	C45	S4	118.52(12)	C119	C118	C117	120.0(2)
N2	C45	S3	122.35(16)	C118	C119	C120	119.8(2)
N2	C45	S4	119.10(15)	C119	C120	C115	121.0(2)
N2	C46	C47	114.0(2)	C122	C121	P6	119.07(17)
C48	C47	C46	117.8(2)	C122	C121	C126	118.6(2)
C52	C47	C46	122.9(2)	C126	C121	P6	122.24(16)
C52	C47	C48	119.3(2)	C121	C122	C123	120.7(2)
C49	C48	C47	119.4(3)	C124	C123	C122	120.0(2)
C50	C49	C48	120.7(3)	C123	C124	C125	119.8(2)
C49	C50	C51	119.9(3)	C124	C125	C126	120.6(2)
C50	C51	C52	119.4(3)	C125	C126	C121	120.4(2)
C47	C52	C51	121.3(3)	C128	C127	P6	123.38(17)
C54	C53	P3	118.84(18)	C132	C127	P6	117.38(16)
C58	C53	P3	122.34(18)	C132	C127	C128	119.1(2)
C58	C53	C54	118.6(2)	C129	C128	C127	120.0(2)
C55	C54	C53	120.7(2)	C130	C129	C128	120.9(2)
C56	C55	C54	120.2(2)	C129	C130	C131	119.3(2)
C57	C56	C55	119.8(2)	C132	C131	C130	120.3(2)
C56	C57	C58	120.1(3)	C131	C132	C127	120.5(2)
C53	C58	C57	120.7(2)				

Molecular structure of 3

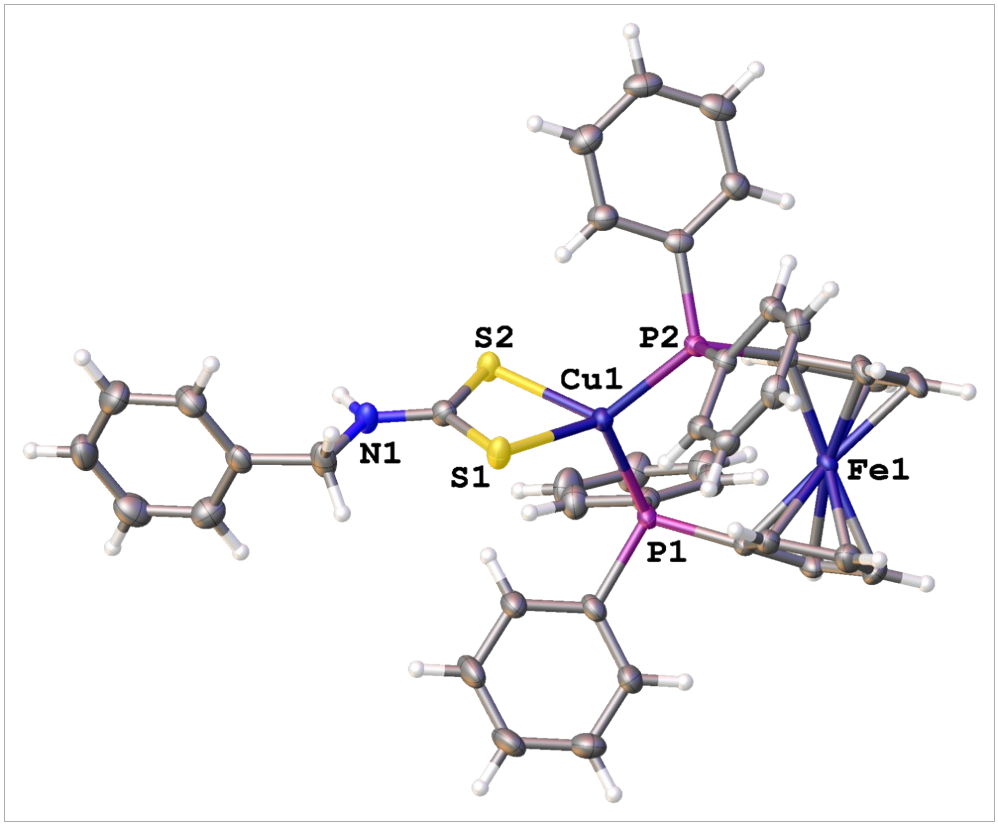


Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	S1	2.4011(9)	Cu02	P4	2.2438(9)
Cu1	S2	2.4113(9)	Fe2	C43	2.033(3)
Cu1	P1	2.2712(8)	Fe2	C44	2.039(3)
Cu1	P2	2.2360(8)	Fe2	C45	2.056(3)
Fe1	C1	2.035(3)	Fe2	C46	2.056(3)
Fe1	C2	2.066(3)	Fe2	C47	2.030(3)
Fe1	C3	2.061(3)	Fe2	C48	2.045(3)
Fe1	C4	2.054(4)	Fe2	C49	2.034(3)
Fe1	C5	2.030(3)	Fe2	C50	2.045(3)
Fe1	C6	2.050(3)	Fe2	C51	2.059(3)
Fe1	C7	2.034(3)	Fe2	C52	2.039(3)
Fe1	C8	2.056(3)	S3	C77	1.708(3)
Fe1	C9	2.057(3)	S4	C77	1.713(3)
Fe1	C10	2.049(3)	P3	C43	1.806(3)
S1	C35	1.705(3)	P3	C53	1.836(3)
S2	C35	1.718(3)	P3	C59	1.834(3)
P1	C1	1.804(3)	P4	C48	1.811(3)
P1	C23	1.832(3)	P4	C65	1.831(3)
P1	C29	1.840(3)	P4	C71	1.835(3)
P2	C6	1.814(3)	N2	C77	1.338(4)

Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P2	C11	1.832(3)	N2	C78	1.447(4)
P2	C17	1.831(3)	C43	C44	1.430(4)
N1	C35	1.337(4)	C43	C47	1.429(5)
N1	C36	1.462(4)	C44	C45	1.412(5)
C1	C2	1.432(4)	C45	C46	1.414(5)
C1	C5	1.444(5)	C46	C47	1.435(5)
C2	C3	1.418(5)	C48	C49	1.433(5)
C3	C4	1.406(6)	C48	C52	1.440(5)
C4	C5	1.424(5)	C49	C50	1.422(5)
C6	C7	1.437(5)	C50	C51	1.423(6)
C6	C10	1.437(4)	C51	C52	1.419(5)
C7	C8	1.421(5)	C53	C54	1.391(5)
C8	C9	1.418(6)	C53	C58	1.397(5)
C9	C10	1.429(5)	C54	C55	1.394(5)
C11	C12	1.402(5)	C55	C56	1.391(6)
C11	C16	1.394(4)	C56	C57	1.368(6)
C12	C13	1.385(5)	C57	C58	1.388(5)
C13	C14	1.382(5)	C59	C60	1.395(5)
C14	C15	1.388(6)	C59	C64	1.377(5)
C15	C16	1.398(5)	C60	C61	1.379(5)
C17	C18	1.398(4)	C61	C62	1.379(6)
C17	C22	1.397(4)	C62	C63	1.373(6)
C18	C19	1.387(5)	C63	C64	1.402(5)
C19	C20	1.399(5)	C65	C66	1.387(5)
C20	C21	1.381(5)	C65	C70	1.392(5)
C21	C22	1.390(5)	C66	C67	1.400(5)
C23	C24	1.391(5)	C67	C68	1.367(7)
C23	C28	1.391(5)	C68	C69	1.376(7)
C24	C25	1.398(6)	C69	C70	1.395(5)
C25	C26	1.384(6)	C71	C72	1.400(4)
C26	C27	1.365(5)	C71	C76	1.395(4)
C27	C28	1.392(5)	C72	C73	1.390(5)
C29	C30	1.383(5)	C73	C74	1.385(5)
C29	C34	1.397(5)	C74	C75	1.393(5)
C30	C31	1.397(5)	C75	C76	1.392(5)
C31	C32	1.386(6)	C78	C79	1.507(5)
C32	C33	1.387(6)	C79	C80	1.449(15)
C33	C34	1.400(5)	C79	C84	1.30(2)
C36	C37	1.509(5)	C79	C85	1.32(2)
C37	C38	1.386(5)	C79	C89	1.49(2)
C37	C42	1.391(5)	C80	C81	1.423(19)
C38	C39	1.384(6)	C81	C82	1.379(16)
C39	C40	1.390(6)	C82	C83	1.32(2)

Table 4 Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C40	C41	1.392(6)	C83	C84	1.37(2)
C41	C42	1.363(6)	C85	C86	1.37(3)
Cu02	S3	2.4358(9)	C86	C87	1.44(2)
Cu02	S4	2.3805(9)	C87	C88	1.30(3)
Cu02	P3	2.2609(9)	C88	C89	1.37(3)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Cu1	S2	75.51(3)	P4	Cu02	S4	117.45(4)
P1	Cu1	S1	115.42(3)	P4	Cu02	P3	110.42(3)
P1	Cu1	S2	108.54(3)	C43	Fe2	C44	41.14(12)
P2	Cu1	S1	116.69(3)	C43	Fe2	C45	68.73(13)
P2	Cu1	S2	122.72(3)	C43	Fe2	C46	68.87(13)
P2	Cu1	P1	113.05(3)	C43	Fe2	C48	113.52(12)
C1	Fe1	C2	40.87(12)	C43	Fe2	C49	142.52(13)
C1	Fe1	C3	68.65(13)	C43	Fe2	C50	176.69(14)
C1	Fe1	C4	69.22(13)	C43	Fe2	C51	137.78(15)
C1	Fe1	C6	115.11(12)	C43	Fe2	C52	111.96(14)
C1	Fe1	C8	171.04(15)	C44	Fe2	C45	40.36(14)
C1	Fe1	C9	132.19(15)	C44	Fe2	C46	68.06(15)
C1	Fe1	C10	108.65(14)	C44	Fe2	C48	143.78(14)
C3	Fe1	C2	40.21(15)	C44	Fe2	C50	135.56(14)
C4	Fe1	C2	67.82(15)	C44	Fe2	C51	110.92(14)
C4	Fe1	C3	39.97(16)	C44	Fe2	C52	114.20(14)
C4	Fe1	C8	115.23(16)	C45	Fe2	C51	112.25(15)
C4	Fe1	C9	148.42(16)	C46	Fe2	C45	40.23(15)
C5	Fe1	C1	41.62(13)	C46	Fe2	C51	140.37(15)
C5	Fe1	C2	68.55(14)	C47	Fe2	C43	41.19(13)
C5	Fe1	C3	68.10(14)	C47	Fe2	C44	68.98(14)
C5	Fe1	C4	40.81(13)	C47	Fe2	C45	68.73(14)
C5	Fe1	C6	106.49(13)	C47	Fe2	C46	41.12(13)
C5	Fe1	C7	113.75(14)	C47	Fe2	C48	110.17(13)
C5	Fe1	C8	146.63(16)	C47	Fe2	C49	111.81(14)
C5	Fe1	C9	170.64(15)	C47	Fe2	C50	140.53(16)
C5	Fe1	C10	130.48(13)	C47	Fe2	C51	178.47(15)
C6	Fe1	C2	149.48(14)	C47	Fe2	C52	138.02(14)
C6	Fe1	C3	167.86(15)	C48	Fe2	C45	175.52(15)
C6	Fe1	C4	129.02(14)	C48	Fe2	C46	136.21(14)
C6	Fe1	C8	68.82(13)	C48	Fe2	C50	69.13(14)
C6	Fe1	C9	68.61(13)	C48	Fe2	C51	68.95(13)
C7	Fe1	C1	147.34(13)	C49	Fe2	C44	174.93(14)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	Fe1	C2	169.18(14)	C49	Fe2	C45	134.81(15)
C7	Fe1	C3	129.71(15)	C49	Fe2	C46	109.02(15)
C7	Fe1	C4	106.55(15)	C49	Fe2	C48	41.12(14)
C7	Fe1	C6	41.20(13)	C49	Fe2	C50	40.79(14)
C7	Fe1	C8	40.66(13)	C49	Fe2	C51	68.43(15)
C7	Fe1	C9	68.27(15)	C49	Fe2	C52	68.82(15)
C7	Fe1	C10	68.96(15)	C50	Fe2	C45	108.78(14)
C8	Fe1	C2	132.13(14)	C50	Fe2	C46	110.79(16)
C8	Fe1	C3	109.30(15)	C50	Fe2	C51	40.58(17)
C8	Fe1	C9	40.33(16)	C52	Fe2	C45	142.24(15)
C9	Fe1	C2	111.30(14)	C52	Fe2	C46	177.48(14)
C9	Fe1	C3	118.27(15)	C52	Fe2	C48	41.29(13)
C10	Fe1	C2	118.28(15)	C52	Fe2	C50	68.53(16)
C10	Fe1	C3	150.53(15)	C52	Fe2	C51	40.52(15)
C10	Fe1	C4	168.80(15)	C77	S3	Cu02	82.34(12)
C10	Fe1	C6	41.03(13)	C77	S4	Cu02	83.95(12)
C10	Fe1	C8	68.55(16)	C43	P3	Cu02	115.46(10)
C10	Fe1	C9	40.73(15)	C43	P3	C53	103.20(15)
C35	S1	Cu1	82.78(11)	C43	P3	C59	102.72(15)
C35	S2	Cu1	82.23(11)	C53	P3	Cu02	112.03(11)
C1	P1	Cu1	112.74(10)	C59	P3	Cu02	117.54(11)
C1	P1	C23	106.68(15)	C59	P3	C53	104.25(15)
C1	P1	C29	102.56(15)	C48	P4	Cu02	116.08(10)
C23	P1	Cu1	115.90(11)	C48	P4	C65	102.17(16)
C23	P1	C29	103.78(15)	C48	P4	C71	101.37(15)
C29	P1	Cu1	113.90(11)	C65	P4	Cu02	118.13(12)
C6	P2	Cu1	112.90(10)	C65	P4	C71	101.91(14)
C6	P2	C11	104.81(14)	C71	P4	Cu02	114.75(11)
C6	P2	C17	101.85(15)	C77	N2	C78	125.2(3)
C11	P2	Cu1	116.41(11)	P3	C43	Fe2	121.87(15)
C17	P2	Cu1	117.93(10)	C44	C43	Fe2	69.65(17)
C17	P2	C11	100.96(14)	C44	C43	P3	129.9(3)
C35	N1	C36	123.7(3)	C47	C43	Fe2	69.29(17)
P1	C1	Fe1	120.34(16)	C47	C43	P3	122.5(2)
C2	C1	Fe1	70.73(17)	C47	C43	C44	107.4(3)
C2	C1	P1	134.5(3)	C43	C44	Fe2	69.21(17)
C2	C1	C5	106.7(3)	C45	C44	Fe2	70.47(19)
C5	C1	Fe1	69.03(17)	C45	C44	C43	108.5(3)
C5	C1	P1	118.6(2)	C44	C45	Fe2	69.17(18)
C1	C2	Fe1	68.40(17)	C44	C45	C46	108.3(3)
C3	C2	Fe1	69.70(19)	C46	C45	Fe2	69.88(19)
C3	C2	C1	108.2(3)	C45	C46	Fe2	69.9(2)
C2	C3	Fe1	70.09(19)	C45	C46	C47	108.1(3)

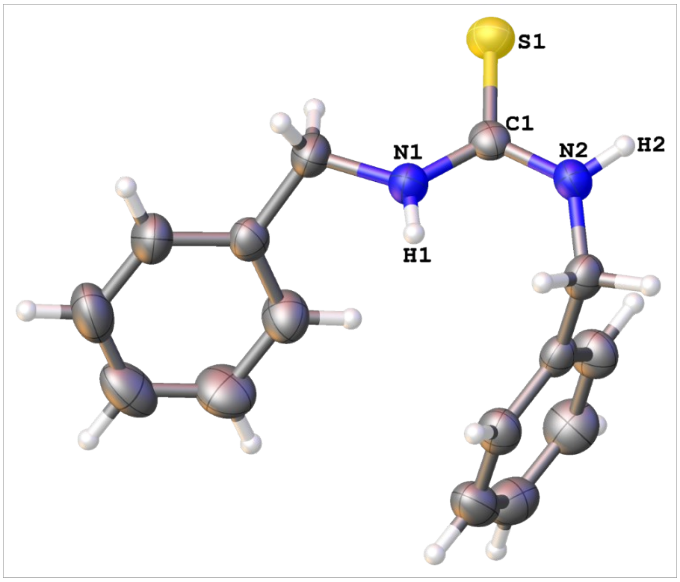
Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C3	Fe1	69.7(2)	C47	C46	Fe2	68.48(19)
C4	C3	C2	108.9(3)	C43	C47	Fe2	69.52(18)
C3	C4	Fe1	70.3(2)	C43	C47	C46	107.7(3)
C3	C4	C5	108.1(3)	C46	C47	Fe2	70.40(19)
C5	C4	Fe1	68.72(19)	P4	C48	Fe2	124.61(15)
C1	C5	Fe1	69.35(18)	C49	C48	Fe2	69.05(18)
C4	C5	Fe1	70.47(19)	C49	C48	P4	128.8(3)
C4	C5	C1	108.1(3)	C49	C48	C52	106.5(3)
P2	C6	Fe1	121.57(15)	C52	C48	Fe2	69.14(18)
C7	C6	Fe1	68.82(18)	C52	C48	P4	124.6(3)
C7	C6	P2	130.2(3)	C48	C49	Fe2	69.84(18)
C10	C6	Fe1	69.46(18)	C50	C49	Fe2	70.02(19)
C10	C6	P2	122.3(3)	C50	C49	C48	108.8(3)
C10	C6	C7	107.1(3)	C49	C50	Fe2	69.19(18)
C6	C7	Fe1	69.98(17)	C49	C50	C51	108.0(3)
C8	C7	Fe1	70.50(19)	C51	C50	Fe2	70.23(19)
C8	C7	C6	108.5(3)	C50	C51	Fe2	69.2(2)
C7	C8	Fe1	68.84(18)	C52	C51	Fe2	68.99(19)
C9	C8	Fe1	69.88(19)	C52	C51	C50	108.0(3)
C9	C8	C7	107.9(3)	C48	C52	Fe2	69.57(19)
C8	C9	Fe1	69.8(2)	C51	C52	Fe2	70.5(2)
C8	C9	C10	108.6(3)	C51	C52	C48	108.7(3)
C10	C9	Fe1	69.34(19)	C54	C53	P3	118.1(3)
C6	C10	Fe1	69.51(18)	C54	C53	C58	119.1(3)
C9	C10	Fe1	69.9(2)	C58	C53	P3	122.8(3)
C9	C10	C6	107.8(3)	C53	C54	C55	120.5(3)
C12	C11	P2	116.7(2)	C56	C55	C54	119.4(4)
C16	C11	P2	123.9(3)	C57	C56	C55	120.4(4)
C16	C11	C12	119.3(3)	C56	C57	C58	120.5(4)
C13	C12	C11	120.3(3)	C57	C58	C53	120.0(3)
C14	C13	C12	120.3(4)	C60	C59	P3	116.4(3)
C13	C14	C15	120.1(3)	C64	C59	P3	124.0(3)
C14	C15	C16	120.1(3)	C64	C59	C60	119.5(3)
C11	C16	C15	119.8(3)	C61	C60	C59	119.9(4)
C18	C17	P2	119.9(2)	C62	C61	C60	120.8(4)
C22	C17	P2	121.2(2)	C63	C62	C61	119.6(3)
C22	C17	C18	119.0(3)	C62	C63	C64	120.3(4)
C19	C18	C17	120.7(3)	C59	C64	C63	119.9(4)
C18	C19	C20	119.8(3)	C66	C65	P4	117.0(3)
C21	C20	C19	119.6(3)	C66	C65	C70	119.4(3)
C20	C21	C22	120.7(3)	C70	C65	P4	123.5(3)
C21	C22	C17	120.1(3)	C65	C66	C67	120.0(4)
C24	C23	P1	116.8(3)	C68	C67	C66	119.8(4)

Table 5 Bond Angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	C23	C28	118.7(3)	C67	C68	C69	121.1(4)
C28	C23	P1	124.4(3)	C68	C69	C70	119.6(4)
C23	C24	C25	120.6(4)	C65	C70	C69	120.1(4)
C26	C25	C24	119.4(4)	C72	C71	P4	119.3(2)
C27	C26	C25	120.6(4)	C76	C71	P4	121.4(2)
C26	C27	C28	120.2(4)	C76	C71	C72	119.3(3)
C23	C28	C27	120.4(3)	C73	C72	C71	120.3(3)
C30	C29	P1	122.4(3)	C74	C73	C72	120.1(3)
C30	C29	C34	119.4(3)	C73	C74	C75	120.2(3)
C34	C29	P1	118.1(3)	C76	C75	C74	119.8(3)
C29	C30	C31	120.5(3)	C75	C76	C71	120.3(3)
C32	C31	C30	120.2(4)	S3	C77	S4	118.23(19)
C31	C32	C33	119.7(3)	N2	C77	S3	119.8(3)
C32	C33	C34	120.2(4)	N2	C77	S4	121.9(3)
C29	C34	C33	120.0(3)	N2	C78	C79	113.2(3)
S1	C35	S2	118.81(19)	C80	C79	C78	109.7(8)
N1	C35	S1	121.5(2)	C84	C79	C78	128.4(10)
N1	C35	S2	119.7(3)	C84	C79	C80	121.6(10)
N1	C36	C37	109.3(3)	C85	C79	C78	129.2(9)
C38	C37	C36	120.2(3)	C85	C79	C89	113.3(12)
C38	C37	C42	118.8(3)	C89	C79	C78	116.6(10)
C42	C37	C36	121.0(3)	C81	C80	C79	116.7(9)
C39	C38	C37	120.7(3)	C82	C81	C80	116.8(11)
C38	C39	C40	119.9(4)	C83	C82	C81	123.4(12)
C39	C40	C41	119.1(4)	C82	C83	C84	120.8(14)
C42	C41	C40	120.7(4)	C79	C84	C83	120.3(16)
C41	C42	C37	120.8(4)	C79	C85	C86	126.4(13)
S4	Cu02	S3	75.11(3)	C85	C86	C87	117.5(17)
P3	Cu02	S3	108.46(3)	C88	C87	C86	119.6(17)
P3	Cu02	S4	118.22(4)	C87	C88	C89	122.4(16)
P4	Cu02	S3	123.43(3)	C88	C89	C79	120.5(17)

Molecular structure of BzNHC(S)NHBz



Bond Lengths for $(BzNH)_2C=S$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.6983(19)	C6	C7	1.371(4)
N1	C1	1.335(2)	C7	C8	1.385(3)
N1	C2	1.455(2)	C9	C10	1.507(3)
N2	C1	1.334(2)	C10	C11	1.377(3)
N2	C9	1.459(2)	C10	C15	1.381(3)
C2	C3	1.504(3)	C11	C12	1.383(3)
C3	C4	1.378(3)	C12	C13	1.369(3)
C3	C8	1.373(3)	C13	C14	1.374(3)
C4	C5	1.377(3)	C14	C15	1.379(3)
C5	C6	1.360(4)			

Bond Angles for $(BzNH)_2C=S$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	125.58(16)	C6	C7	C8	120.7(2)
C1	N2	C9	125.46(16)	C3	C8	C7	120.5(2)
N1	C1	S1	123.04(14)	N2	C9	C10	113.06(16)
N2	C1	S1	119.91(14)	C11	C10	C9	120.99(17)
N2	C1	N1	117.05(16)	C11	C10	C15	118.39(18)
N1	C2	C3	112.63(16)	C15	C10	C9	120.62(17)
C4	C3	C2	119.33(18)	C10	C11	C12	121.45(19)
C8	C3	C2	122.49(18)	C13	C12	C11	119.3(2)
C8	C3	C4	118.16(19)	C12	C13	C14	120.2(2)
C5	C4	C3	121.1(2)	C13	C14	C15	120.2(2)
C6	C5	C4	120.6(2)	C14	C15	C10	120.5(2)
C5	C6	C7	119.0(2)				

Figure S1 ^{1}H NMR spectrum of **1**

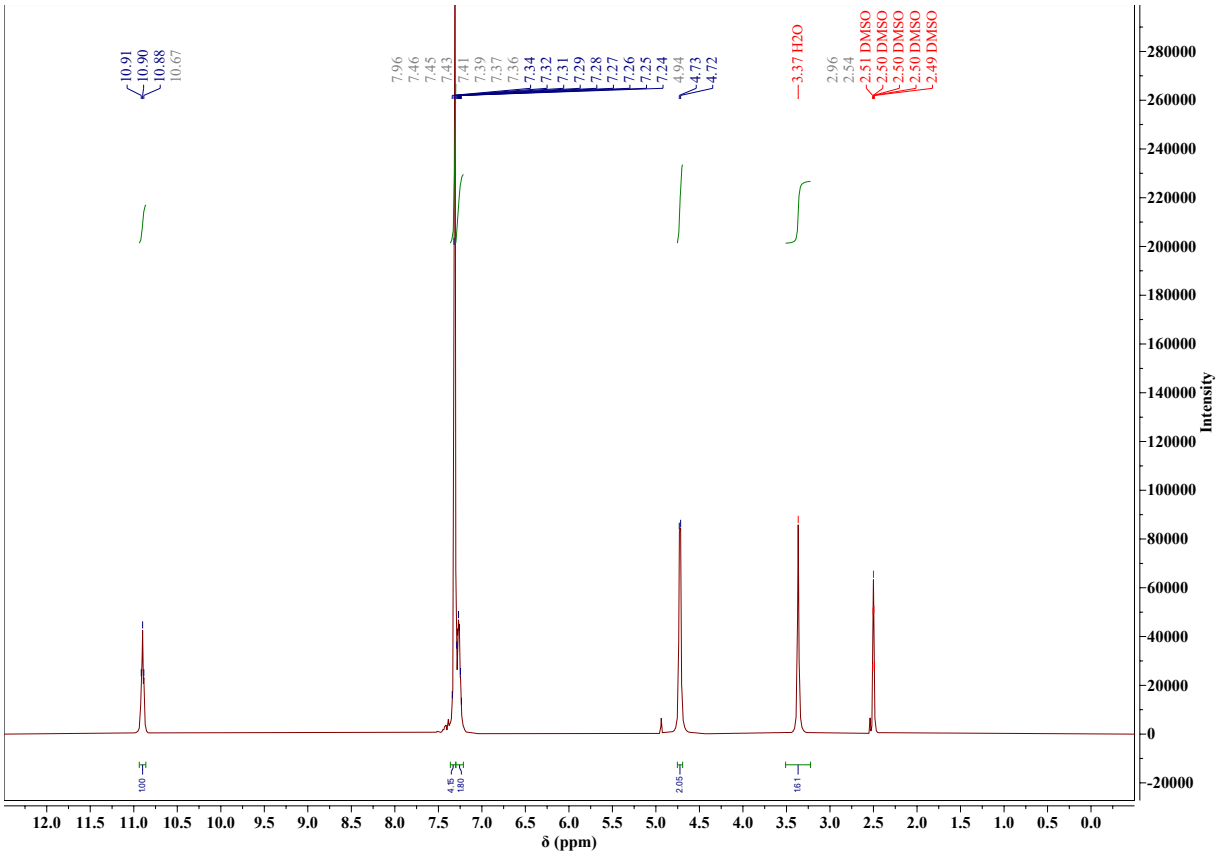


Figure S2 ^{13}C{^{1}H} NMR spectrum of **1**

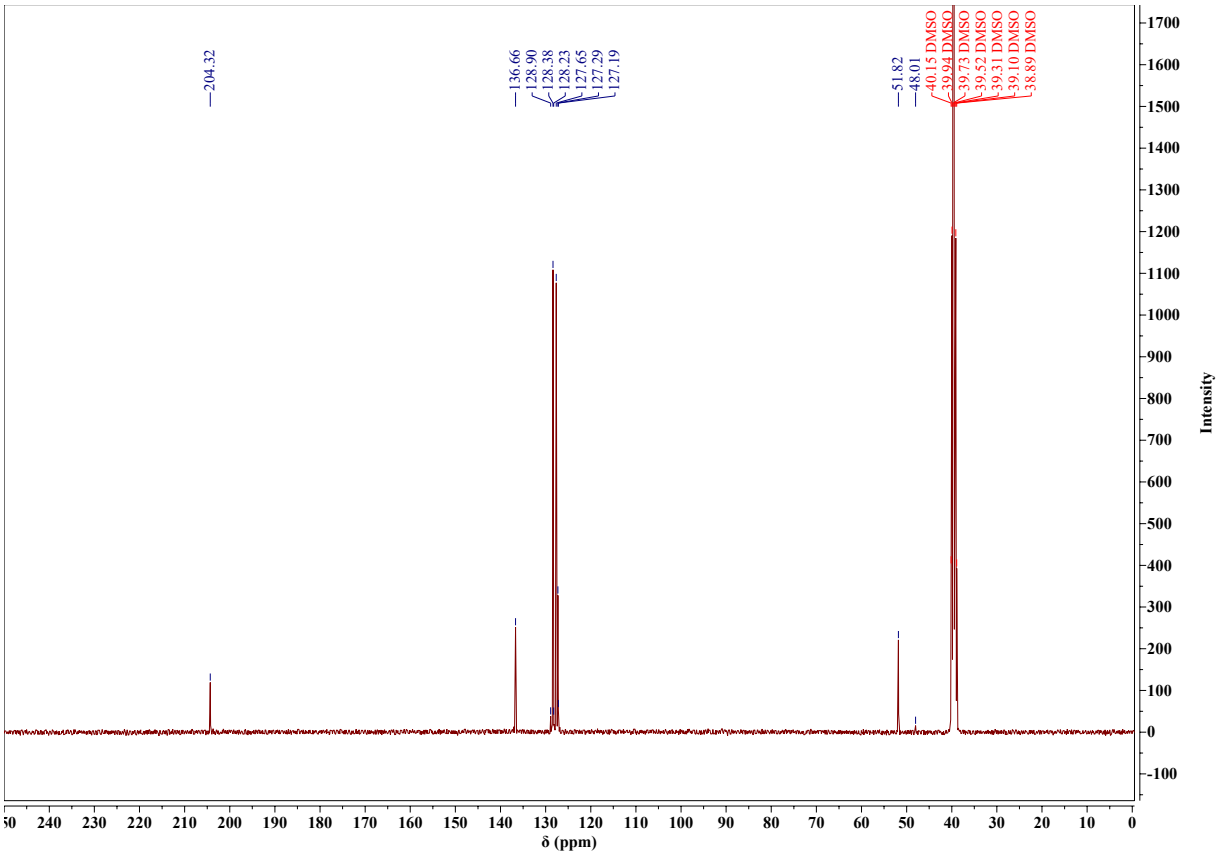


Figure S3 ^{1}H NMR spectrum of $(BzNH)_2C=S$

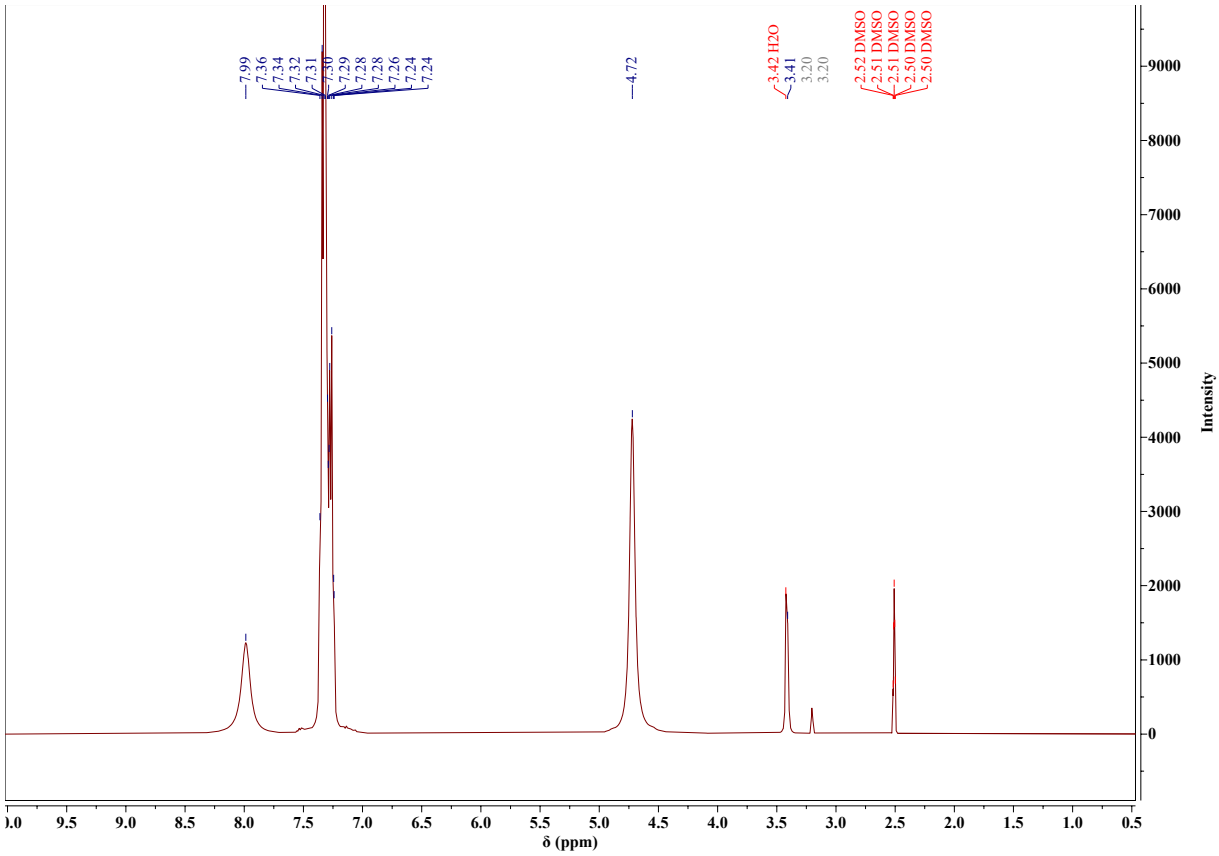


Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of $(BzNH)_2C=S$

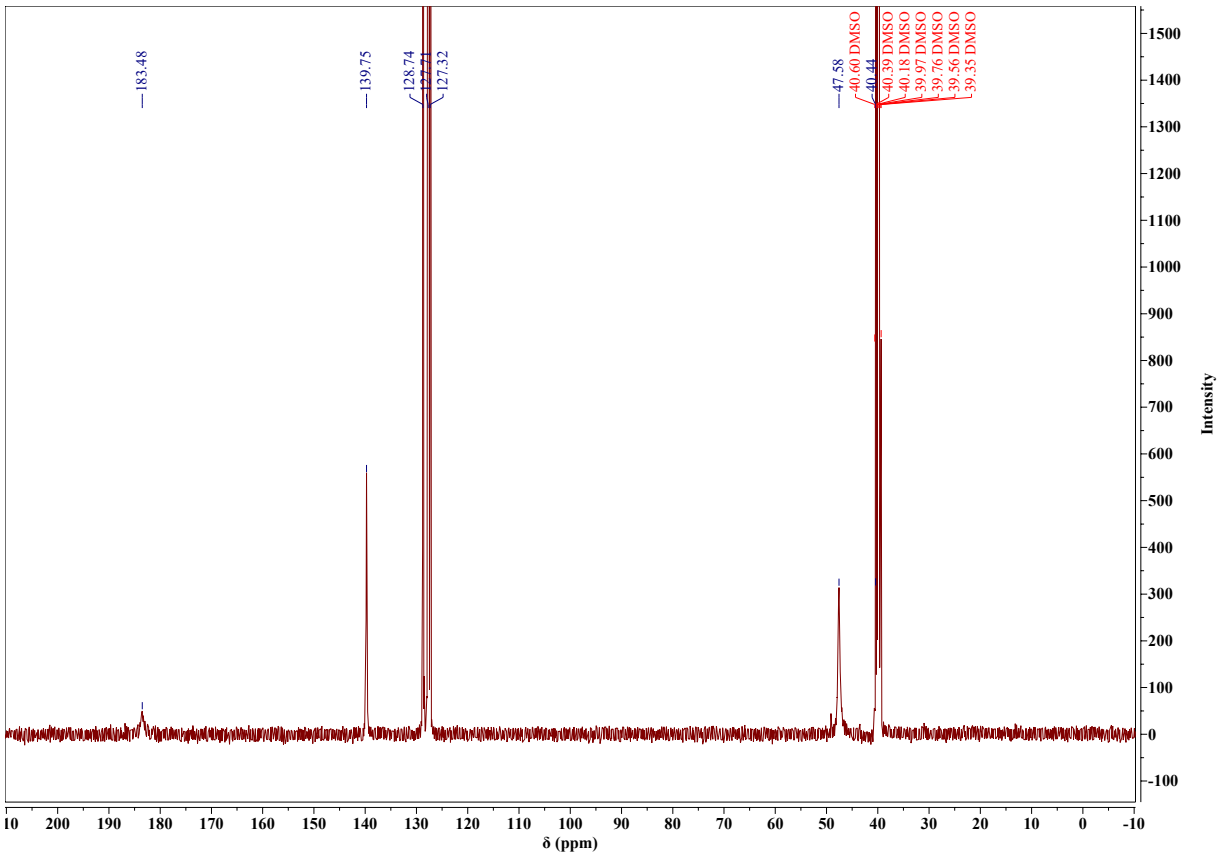


Figure S5 ^{1}H NMR spectrum of **2**

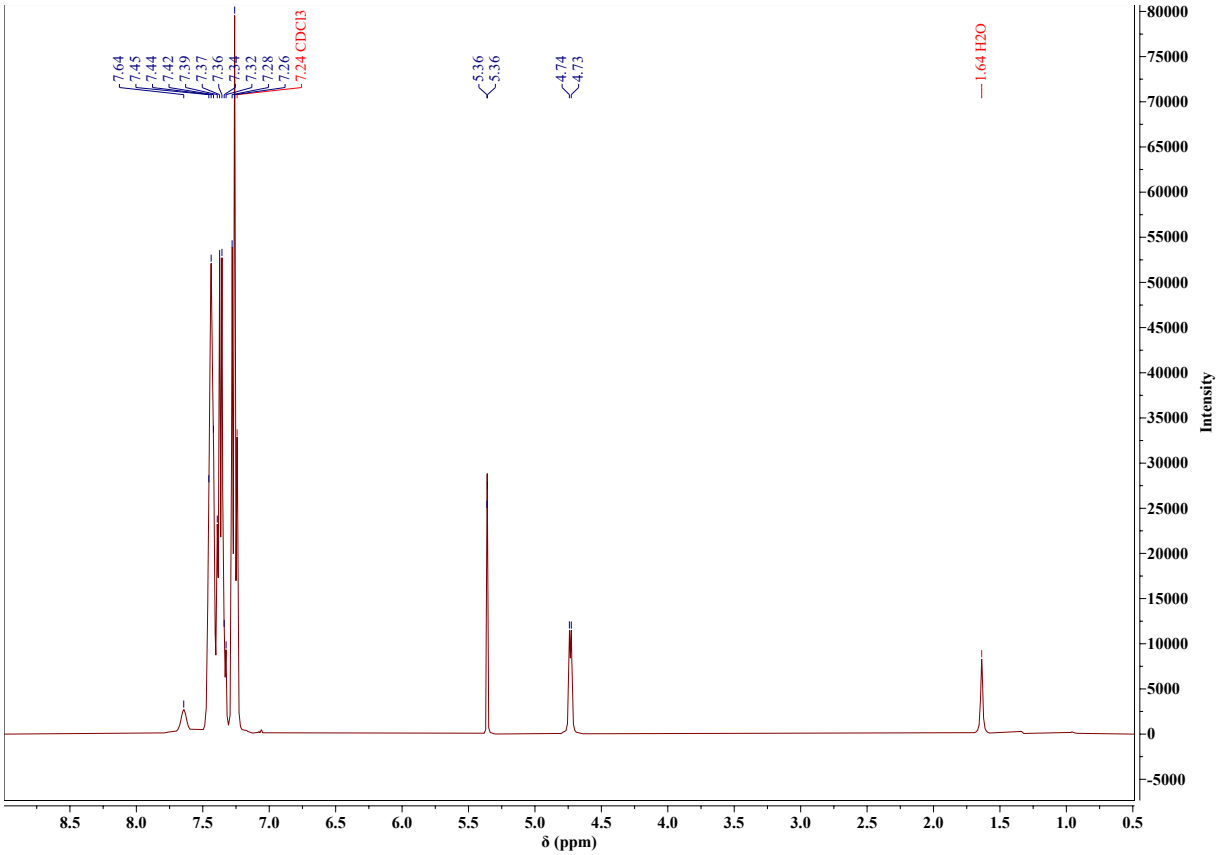


Figure S6 ^{13}C{^{1}H} NMR spectrum of **2**

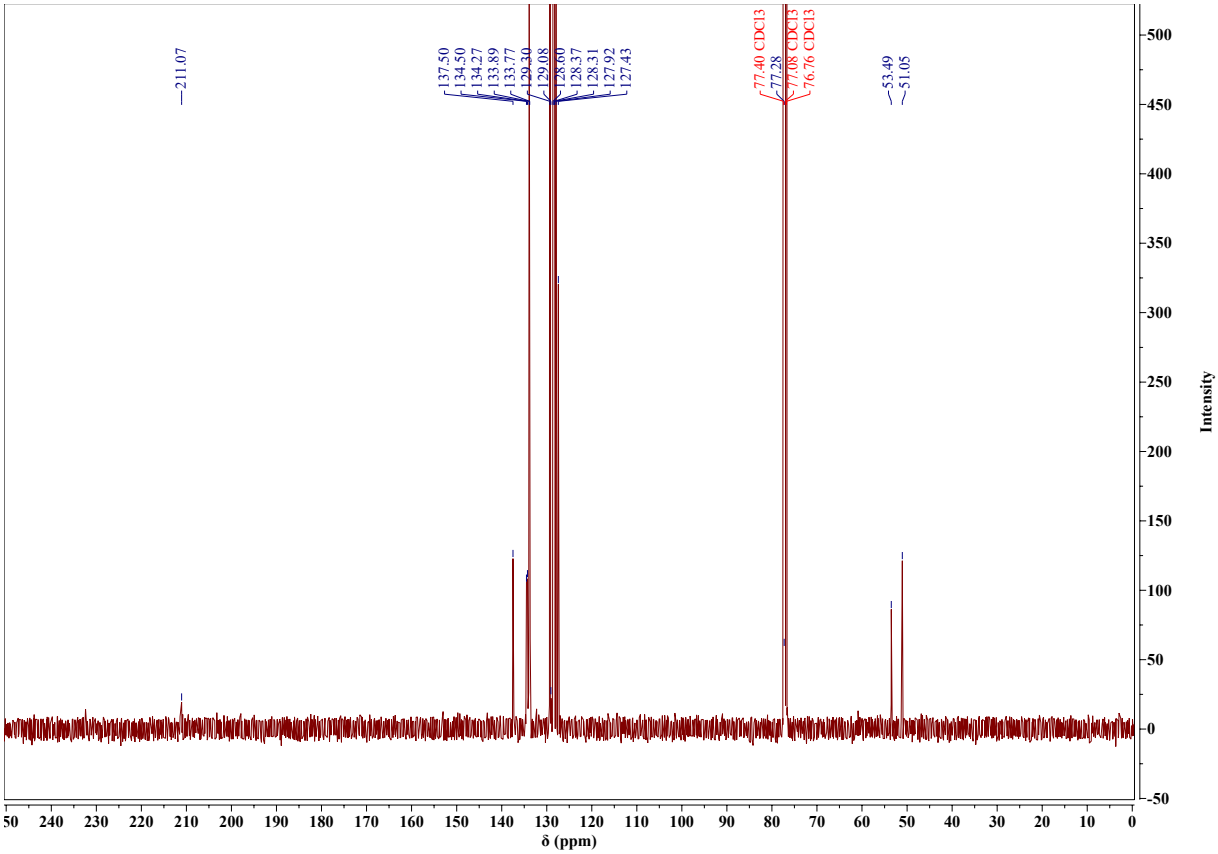


Figure S7 $^{31}P\{^{1}H\}$ NMR spectrum of **2**

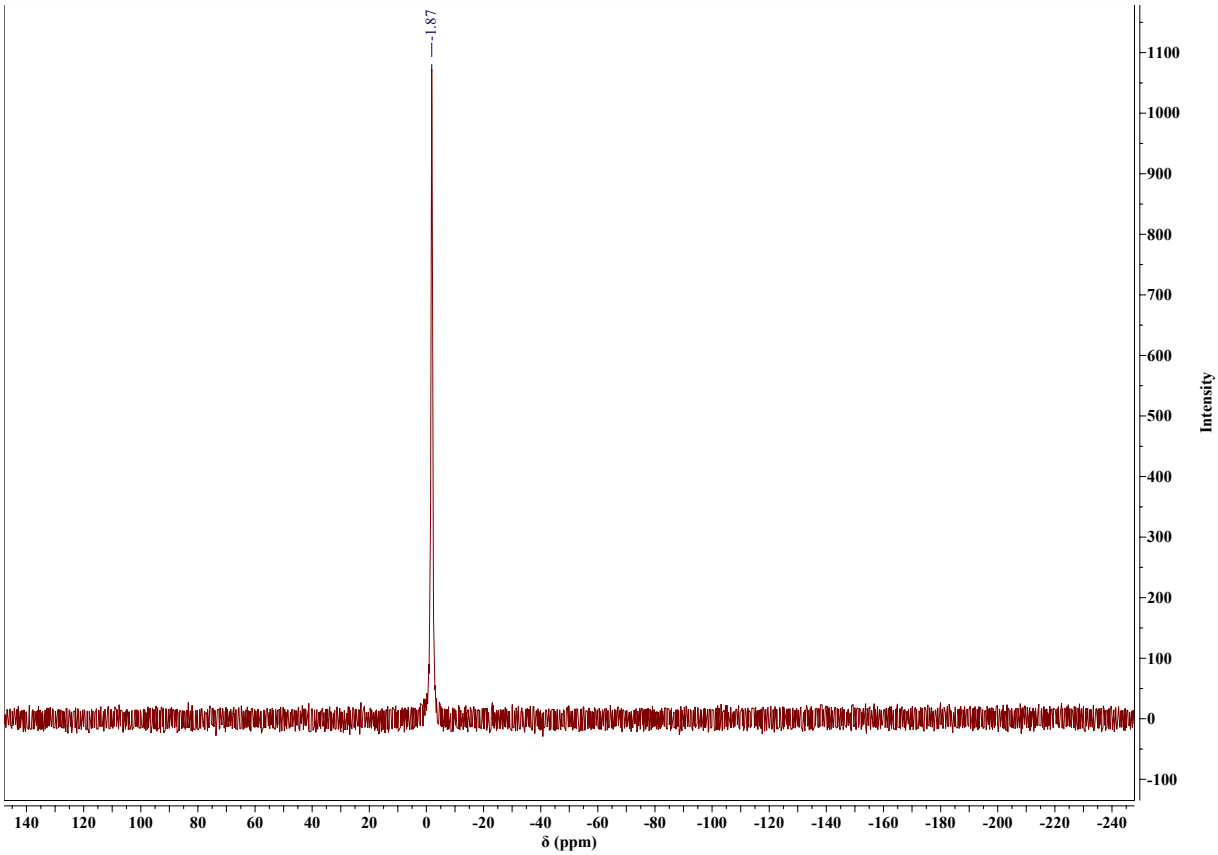


Figure S8 ^{1}H NMR spectrum of **3**

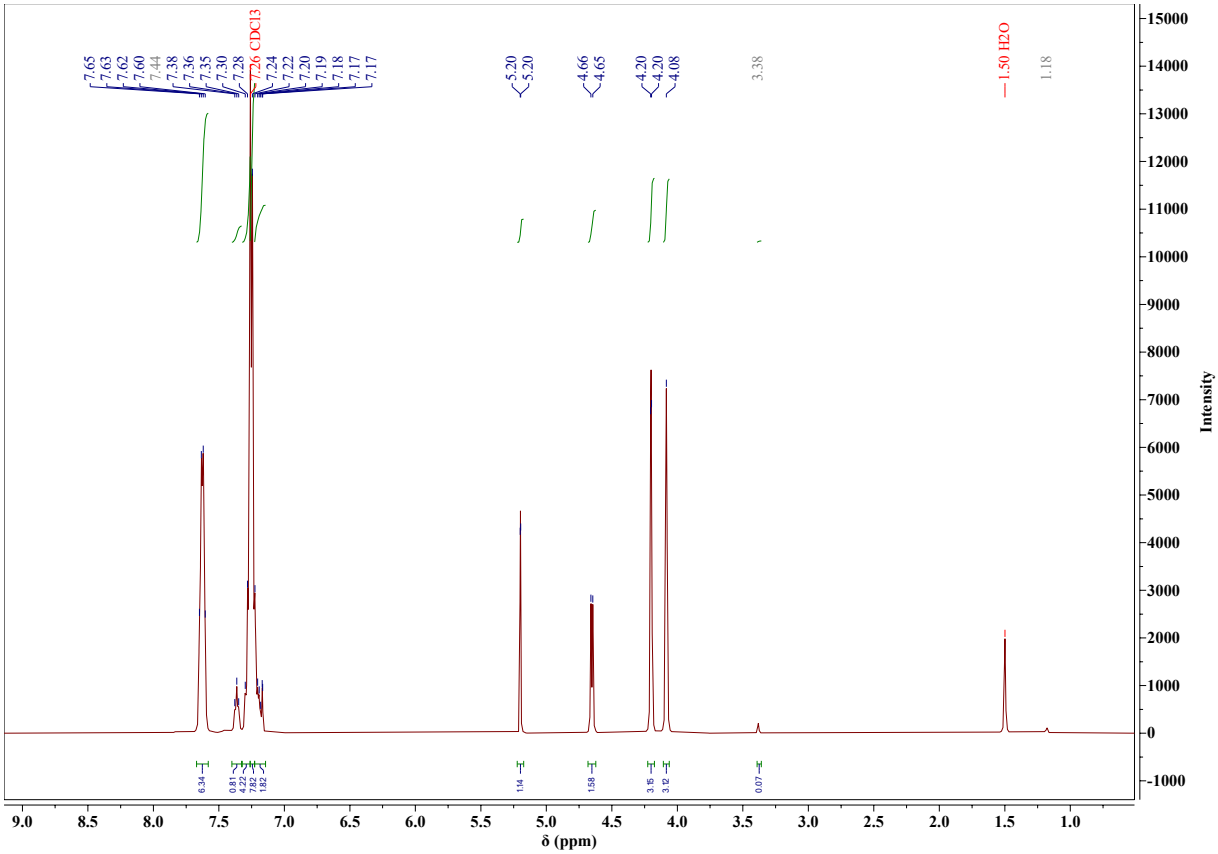


Figure S9 $^{13}C\{^{1}H\}$ NMR spectrum of **3**

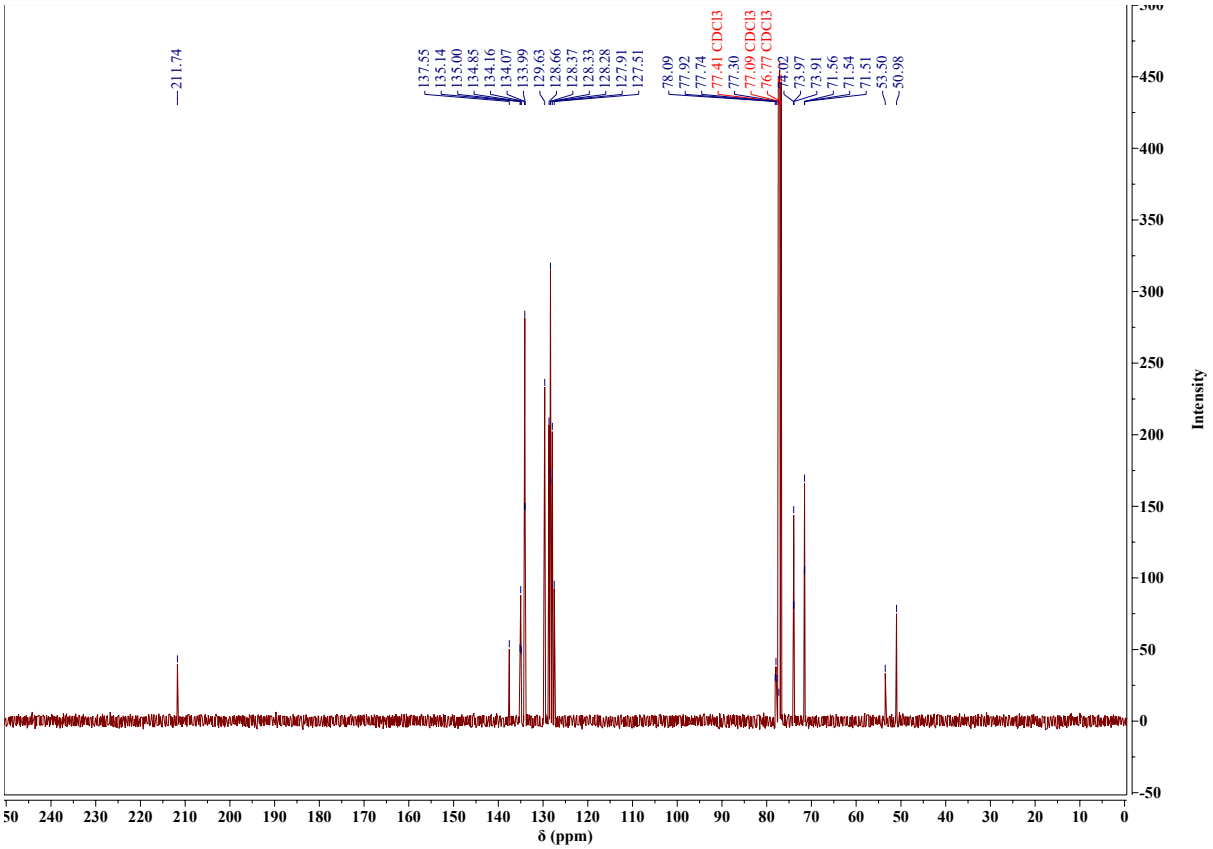


Figure S10 $^{31}P\{^{1}H\}$ NMR spectrum of **3**

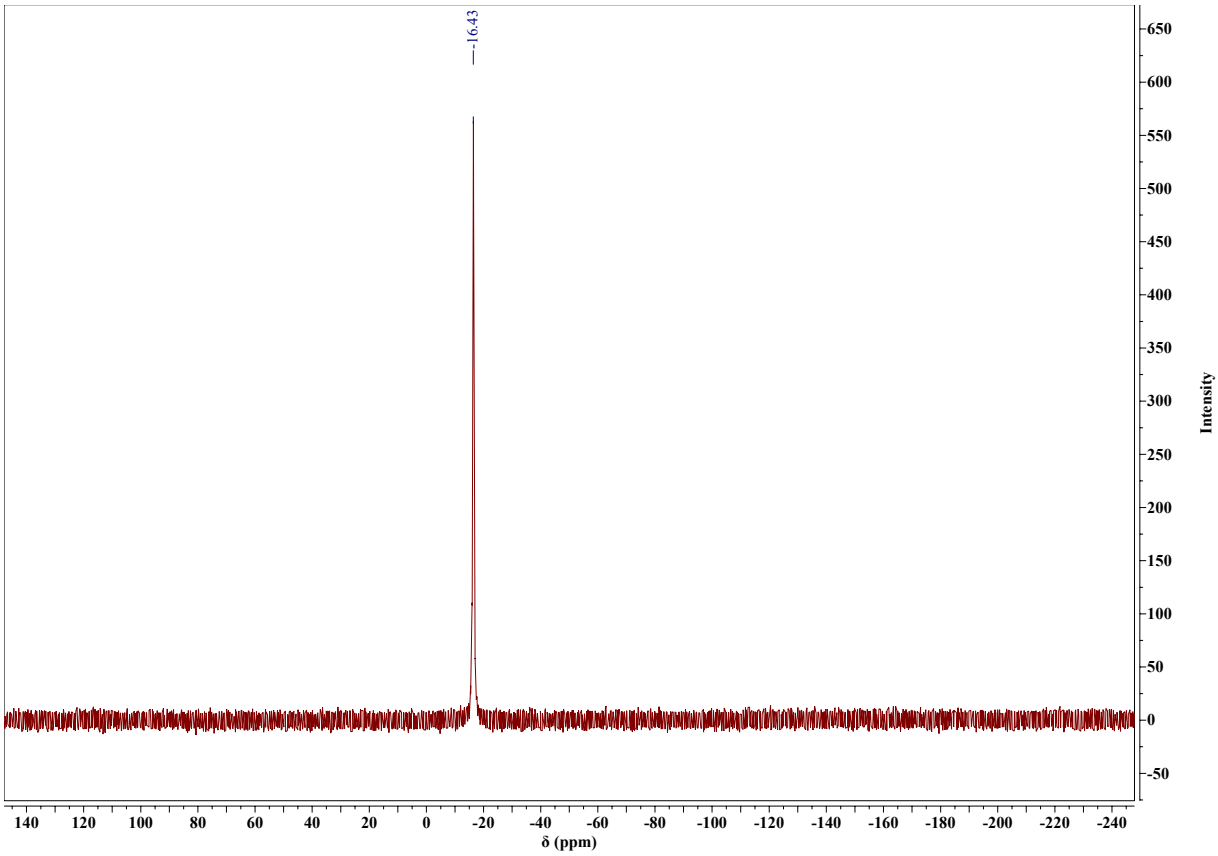


Figure S11 IR spectrum of 1