Supplementary Information

A novel ratiometric fluorescent and colorimetric sensor based on 1,8–naphthalimide derivative for nanomolar Cu^{2+} sensing: Smartphone and food applications

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Fig S2.	^{13}C–NMR spectrum of the compound **B** in $CDCl_3$–d_6
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Preparation of 4–Bromo–N–butyl–1,8–naphthalimide (B)

Compound **A** (0.32 g, 1.15 mmol) and n–butylamine (0.45 g, 6.55 mmol) was placed in a flask and refluxed for 6h in glacial acetic acid (20.0 mL). After 6 h, the suspension was put into ice–water (200.0 mL) and filtered. The obtained precipitate was washed with H_2O and then recrystallized from CH_3COOH (yield: 79.3%). Mp: 102-104 ^{o}C. ^{1}H–NMR (600 MHz, $CDCl_3$): δ 8.61 (d, J = 7.2 Hz, 1H), 8.50(d, J = 8.4 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 4.17 (t, J = 7.6 Hz, 2H,), 1.76−1.68 (m, 2H), 1.44 (dt, 7.4 J = 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C–NMR (150 MHz, $CDCl_3$): δ 163.66, 133.23, 132.02, 131.22, 131.09, 130.64, 130.20, 129.02, 128.08, 123.16, 122.30, 40.38, 30.16, 20.37, 13.84 [1]

Preparation of 4–hydrazine hydrate N–butyl–1,8–naphtic anhydride (C)

Hydrazine hydrate (2.86 g, 85%, v/v) and **B** (3.0 g, 9.03 mmol) were solved in ethylene glycol mono methyl ether (20 mL) and refluxed for 1 day. Then, 180 mL of ice–H_2O was added into the reaction mixture. The precipitate was filtered and dried in a vacuum to obtain a red precipitate (yield: 80.3%). Mp: 230-232 ^{o}C. ^{1}H–NMR (600 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.57 (d, J = 8.3 Hz, 1H), 8.37 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 4.64 (s, 2H), 3.98 (t, J = 7.3 Hz, 2H), 1.58–1.52 (m, 2H), 1.34–1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C–NMR (150 MHz, $CDCl_3$) δ 164.17, 163.32, 153.60, 134.61, 130.97, 129.70, 128.64, 124.52, 122.15, 118.84, 107.78, 104.41, 39.46, 30.28, 20.30, 14.20 [1].

Preparation of 3'-formyl-4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (D)

Compound **D** was synthesized according to our previous study [2].

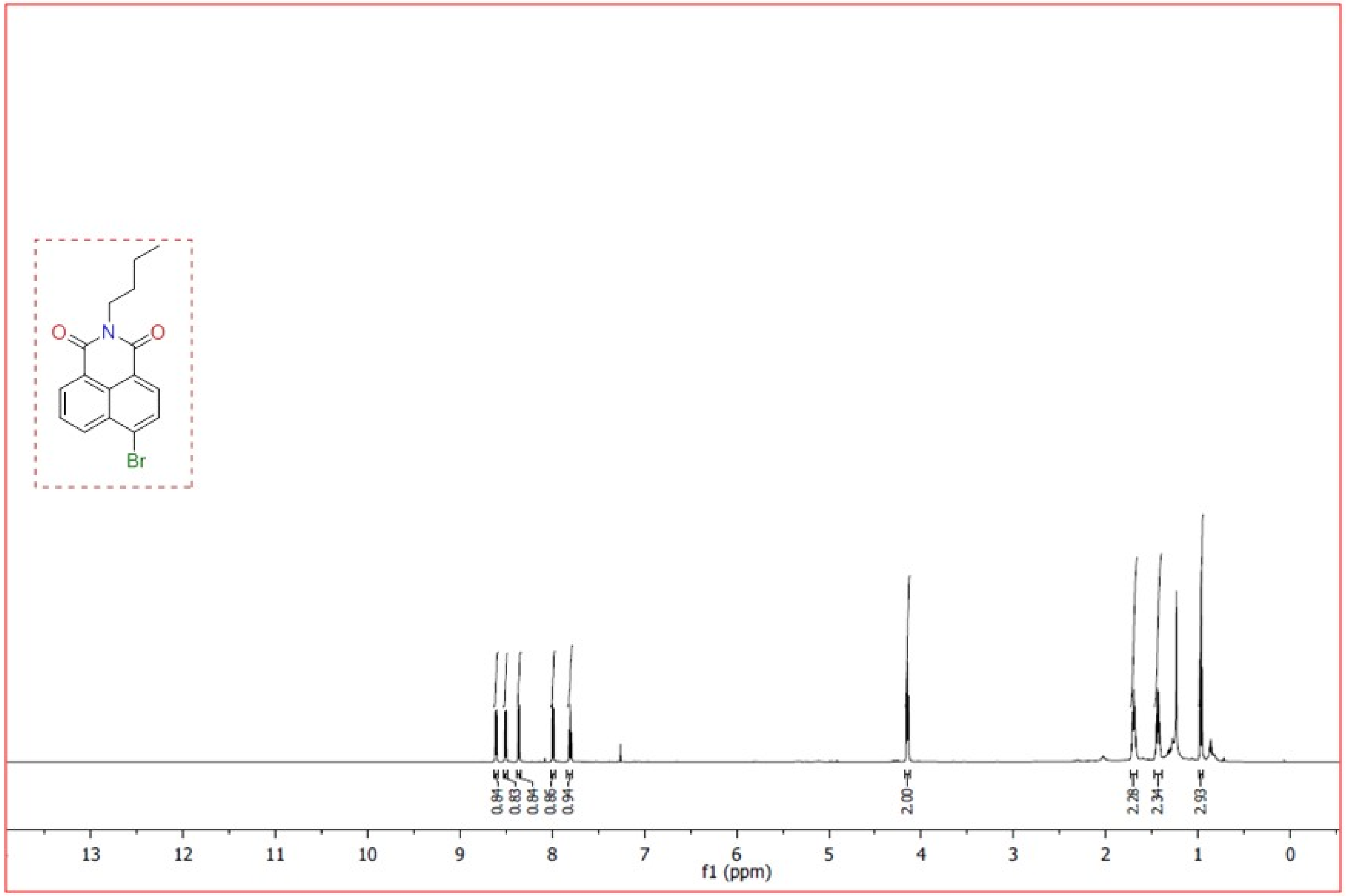


Fig S1. ^{1}H–NMR spectrum of the compound **B** in $CDCl_3$–d_6

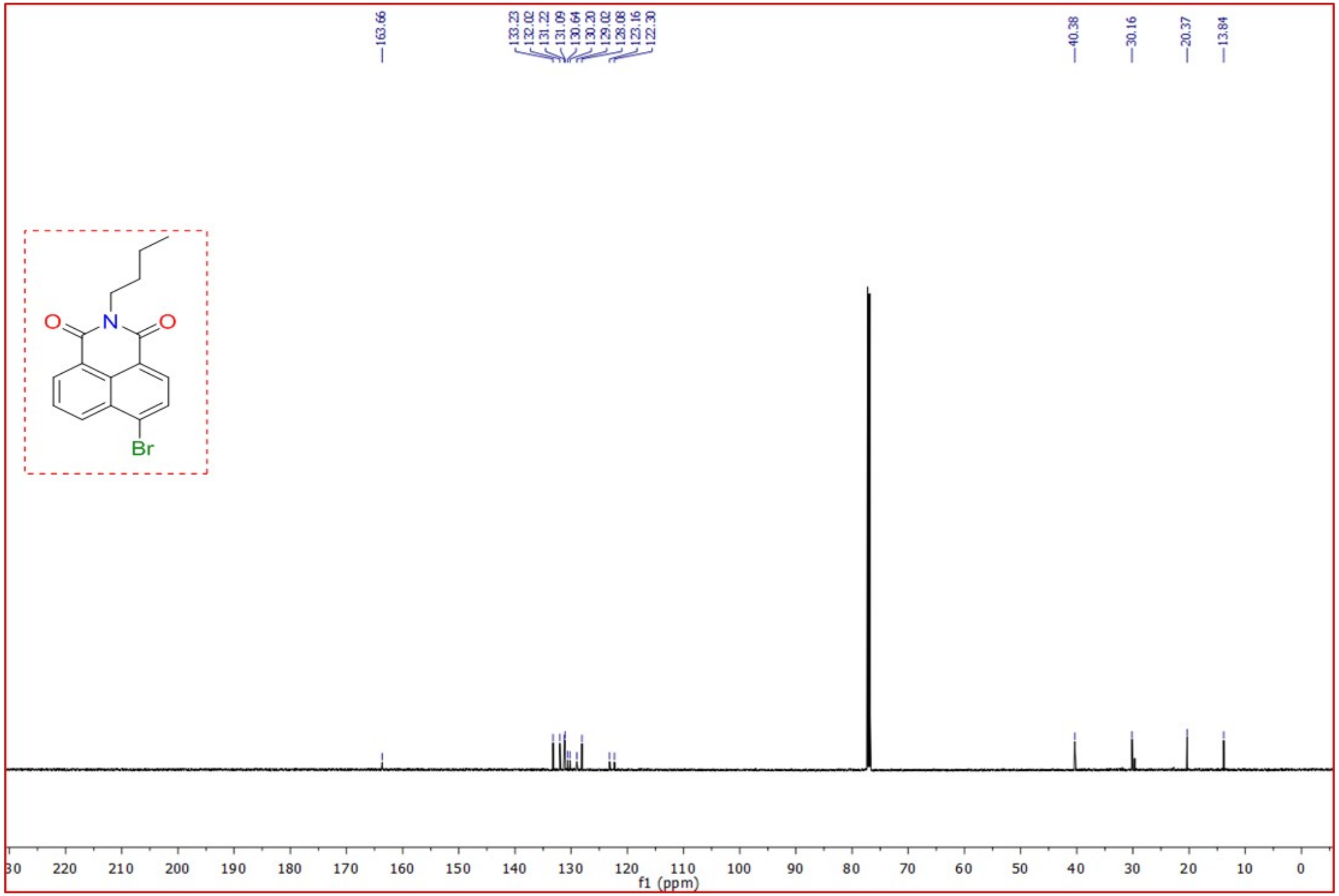


Fig S2. ^{13}C–NMR spectrum of the compound **B** in $CDCl_3$–d_6

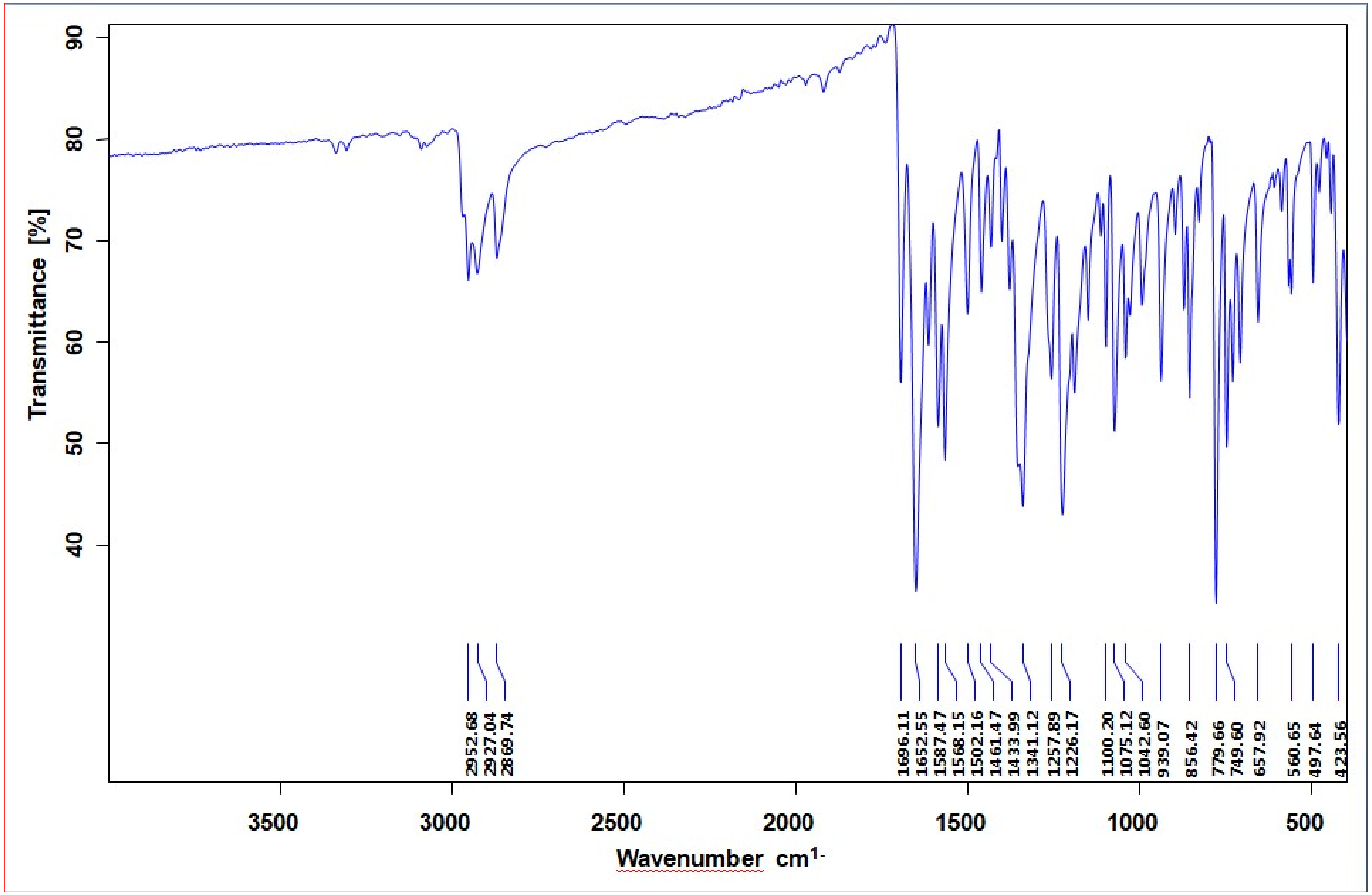


Fig S3. FT-IR spectrum of the compound **B**

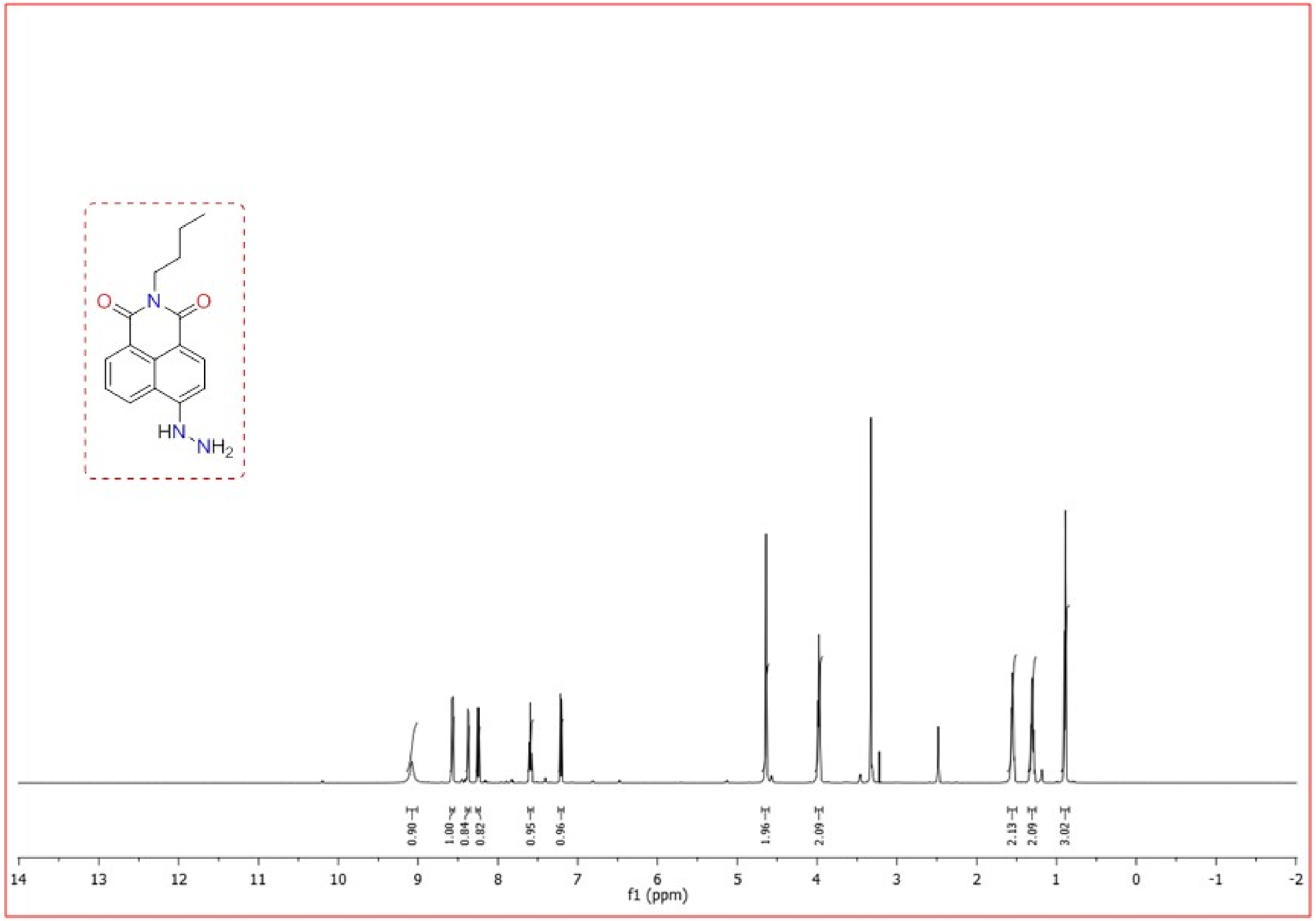


Fig S4. ^{1}H–NMR spectrum of the compound **C** in DMSO–d_6

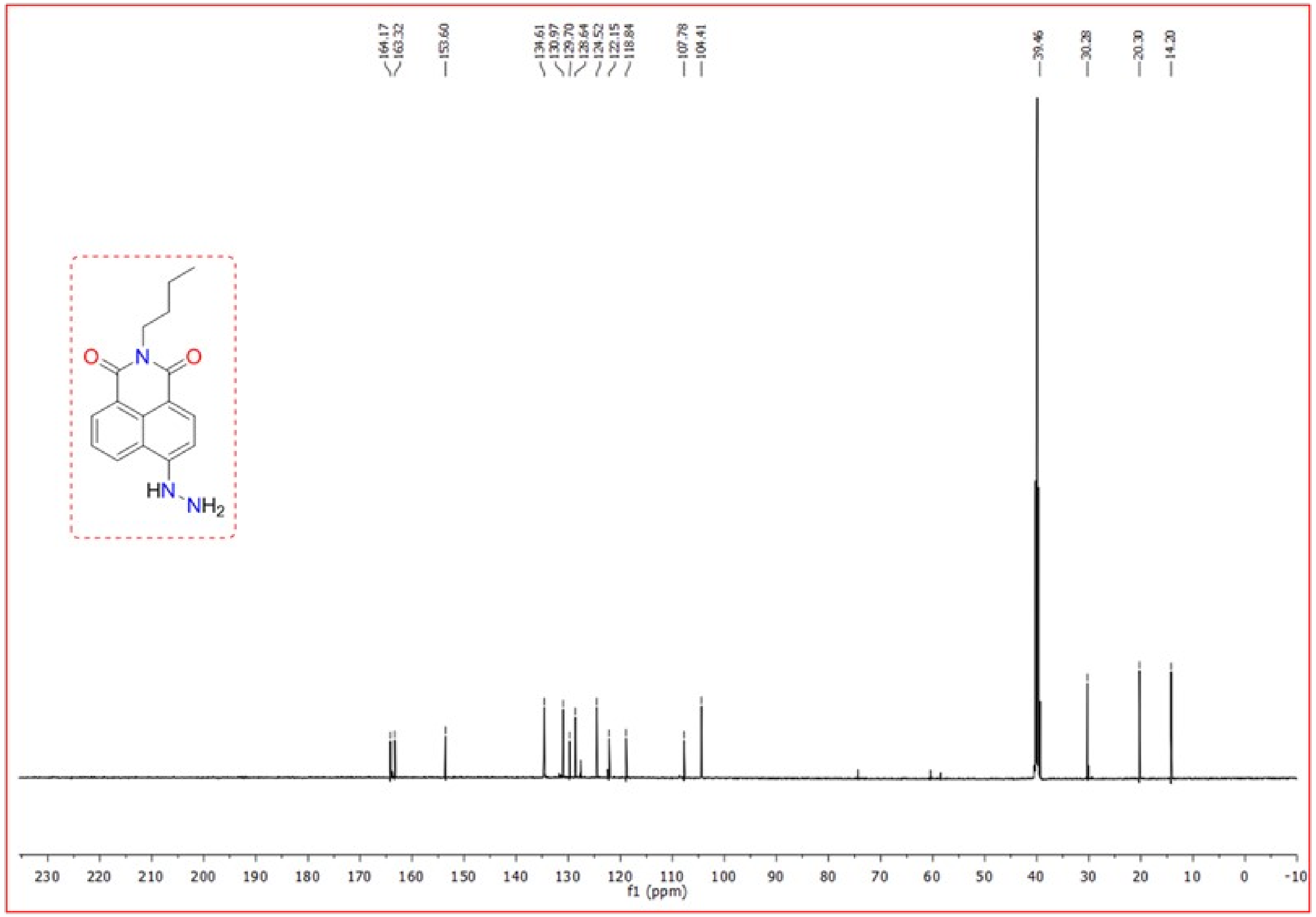


Fig S5. ^{13}C–NMR spectrum of the compound **C** in DMSO–d_6

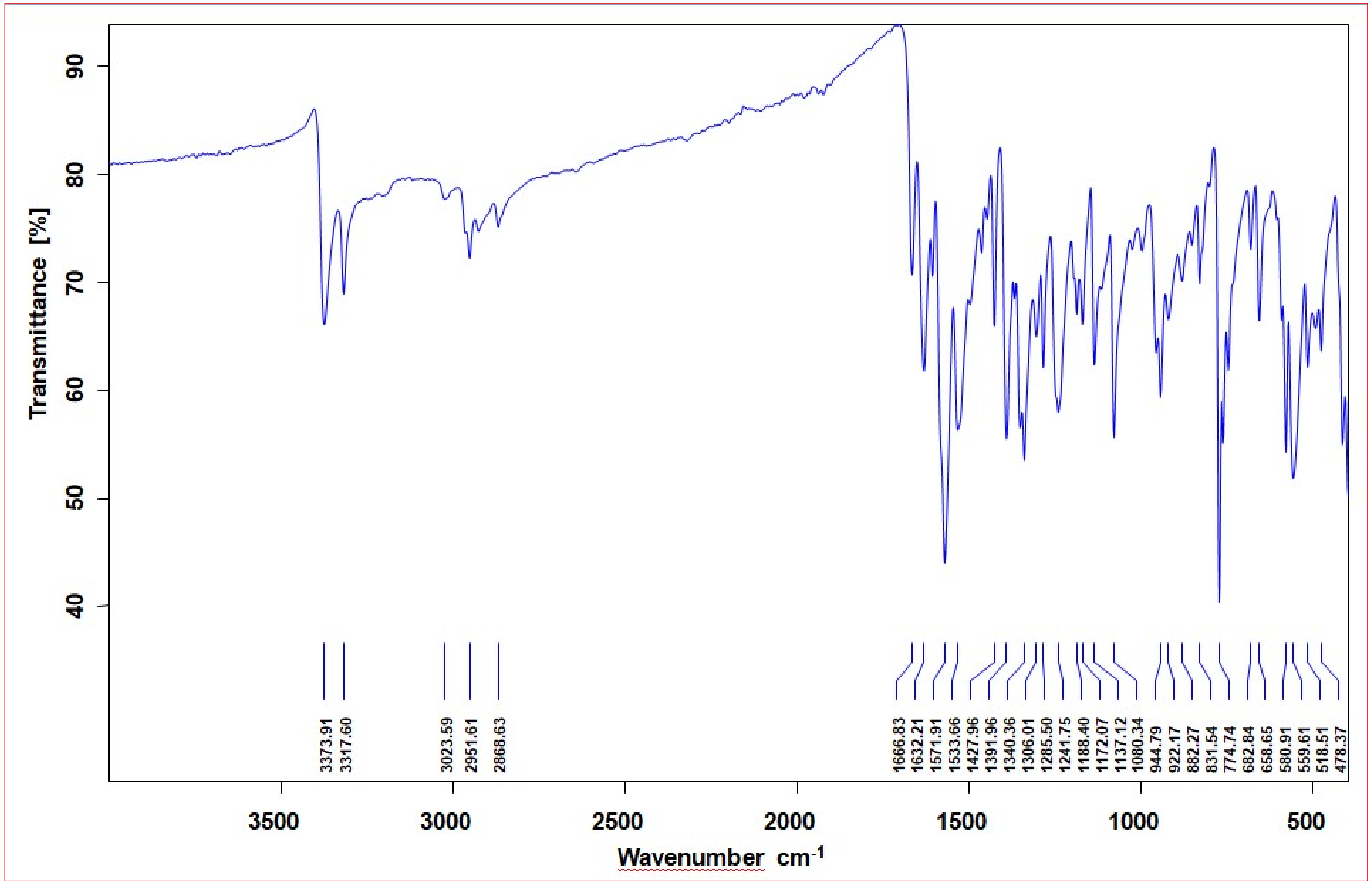


Fig S6. FT-IR spectrum of the compound **C**

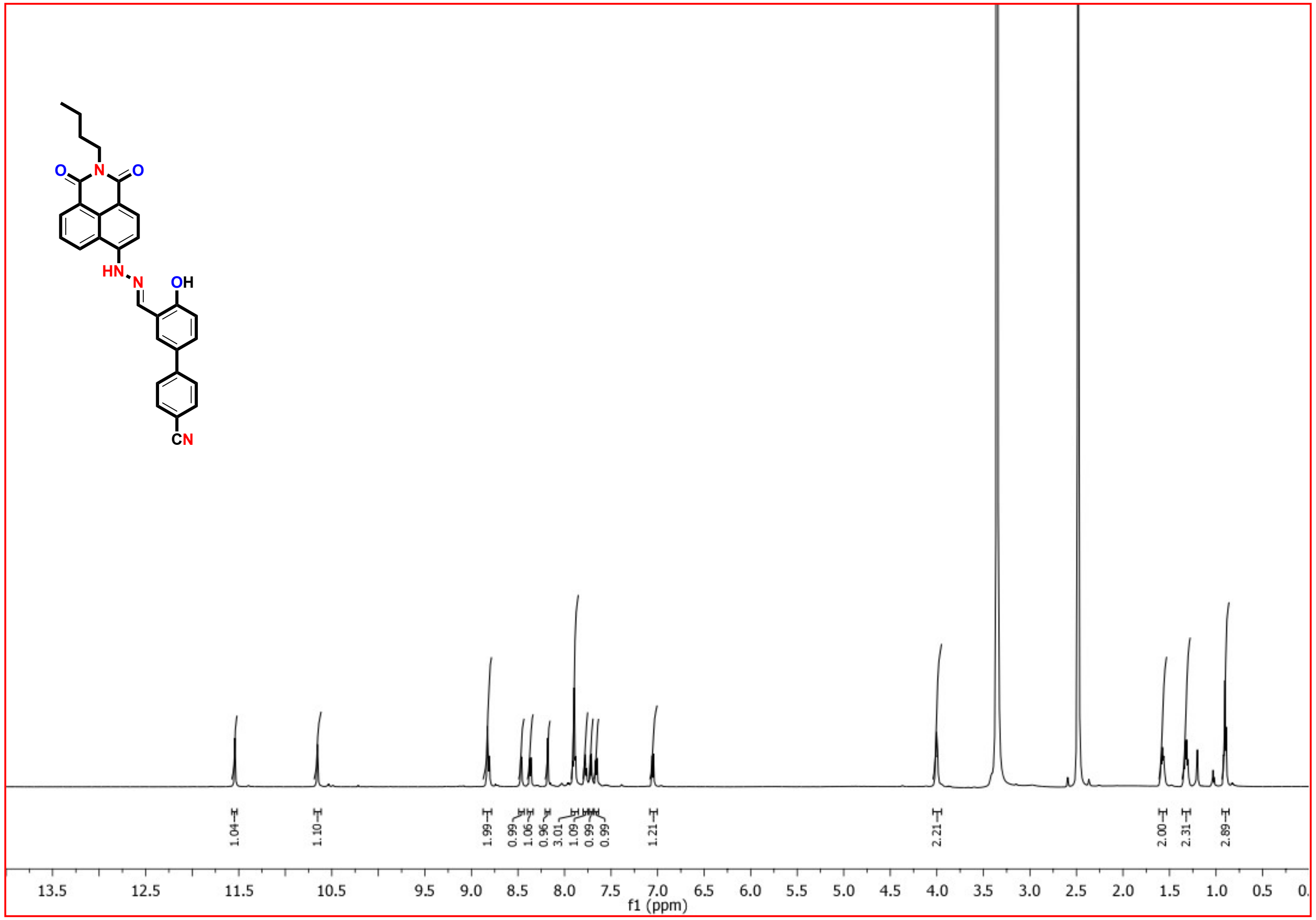


Fig S7. ^{1}H–NMR spectrum of the **BUDIN** in DMSO–d_6

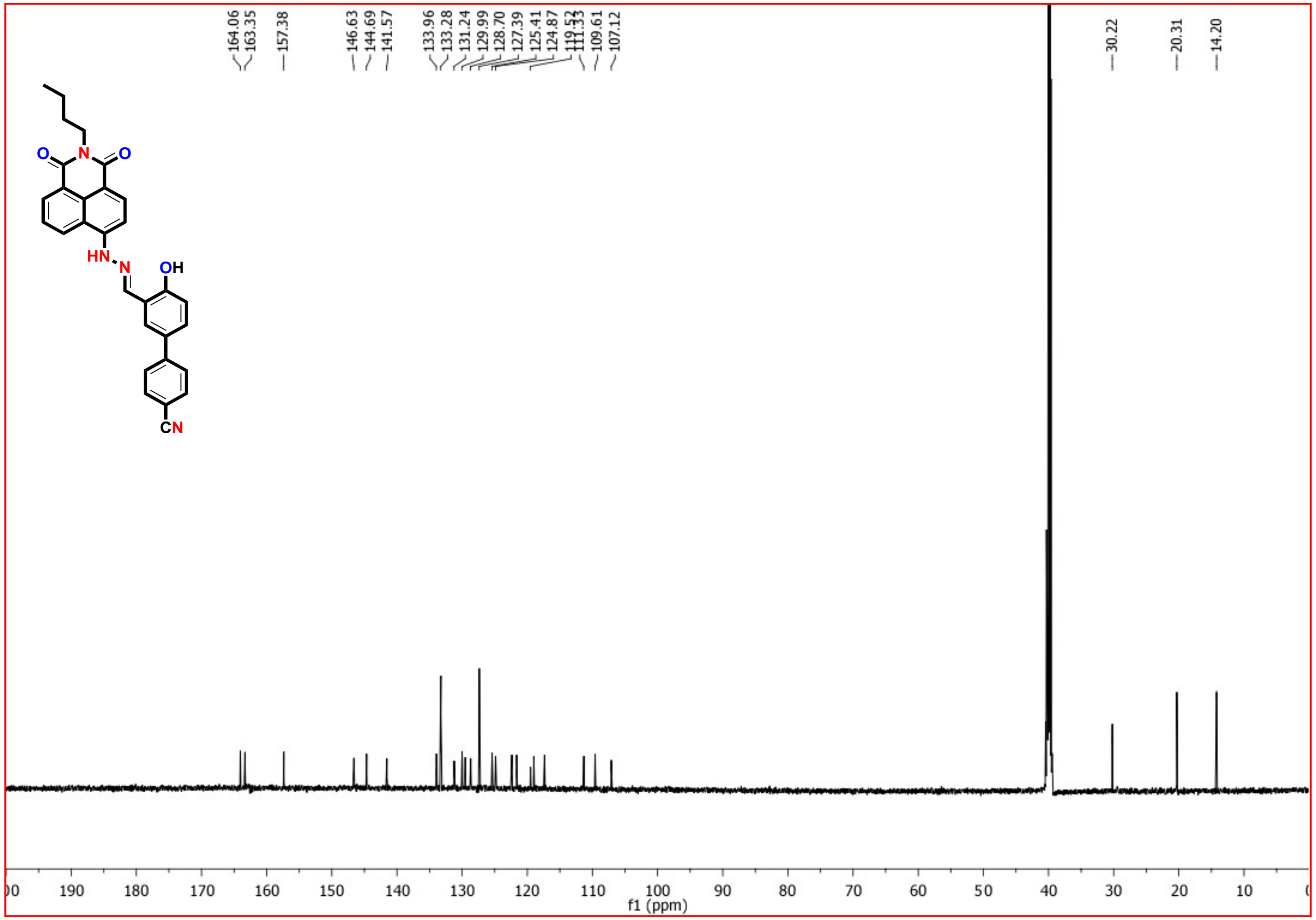


Fig S8. ^{13}C–NMR spectrum of the **BUDIN** in DMSO–d_6

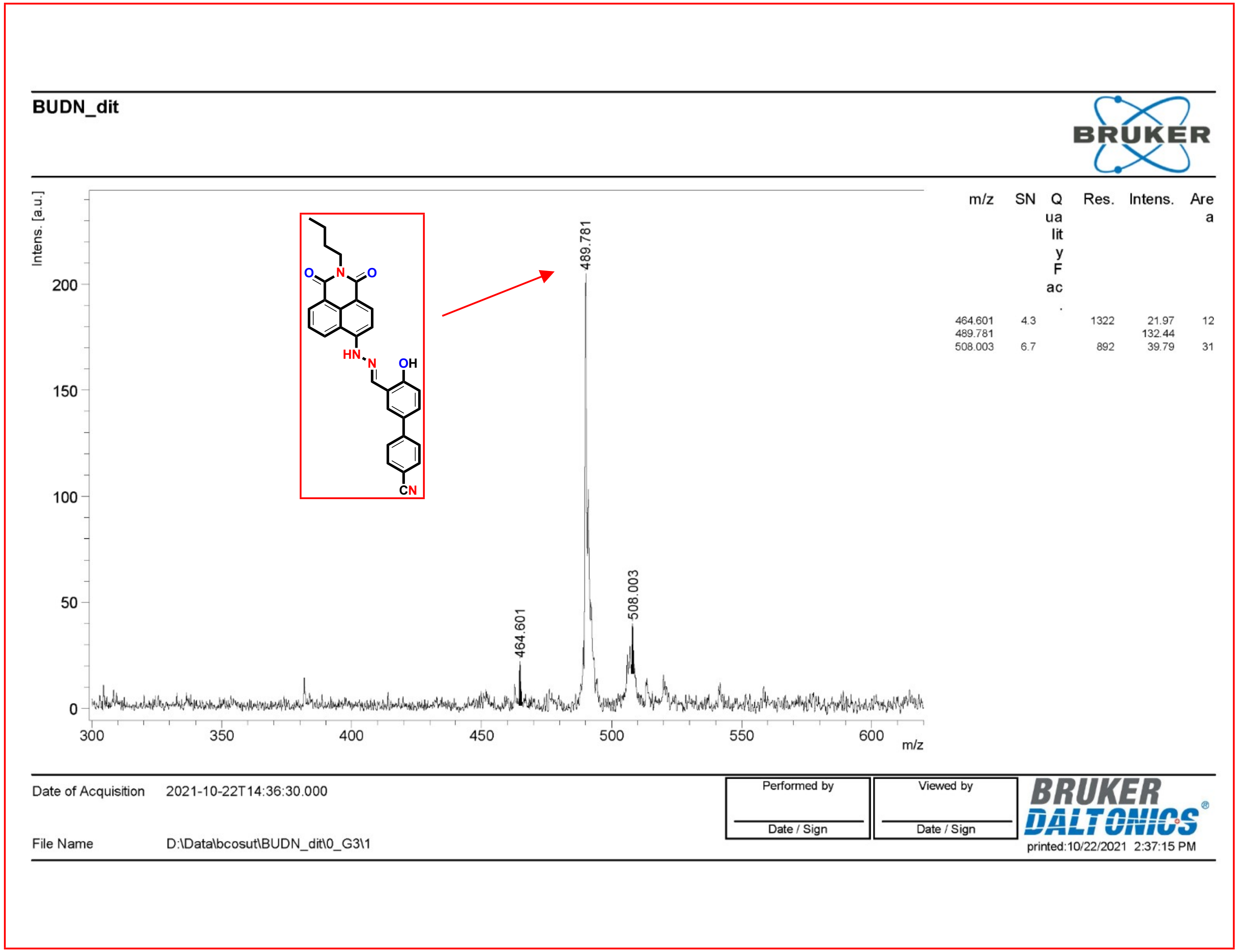


Fig S9. MALDI TOF MS spectrum of the **BUDIN**

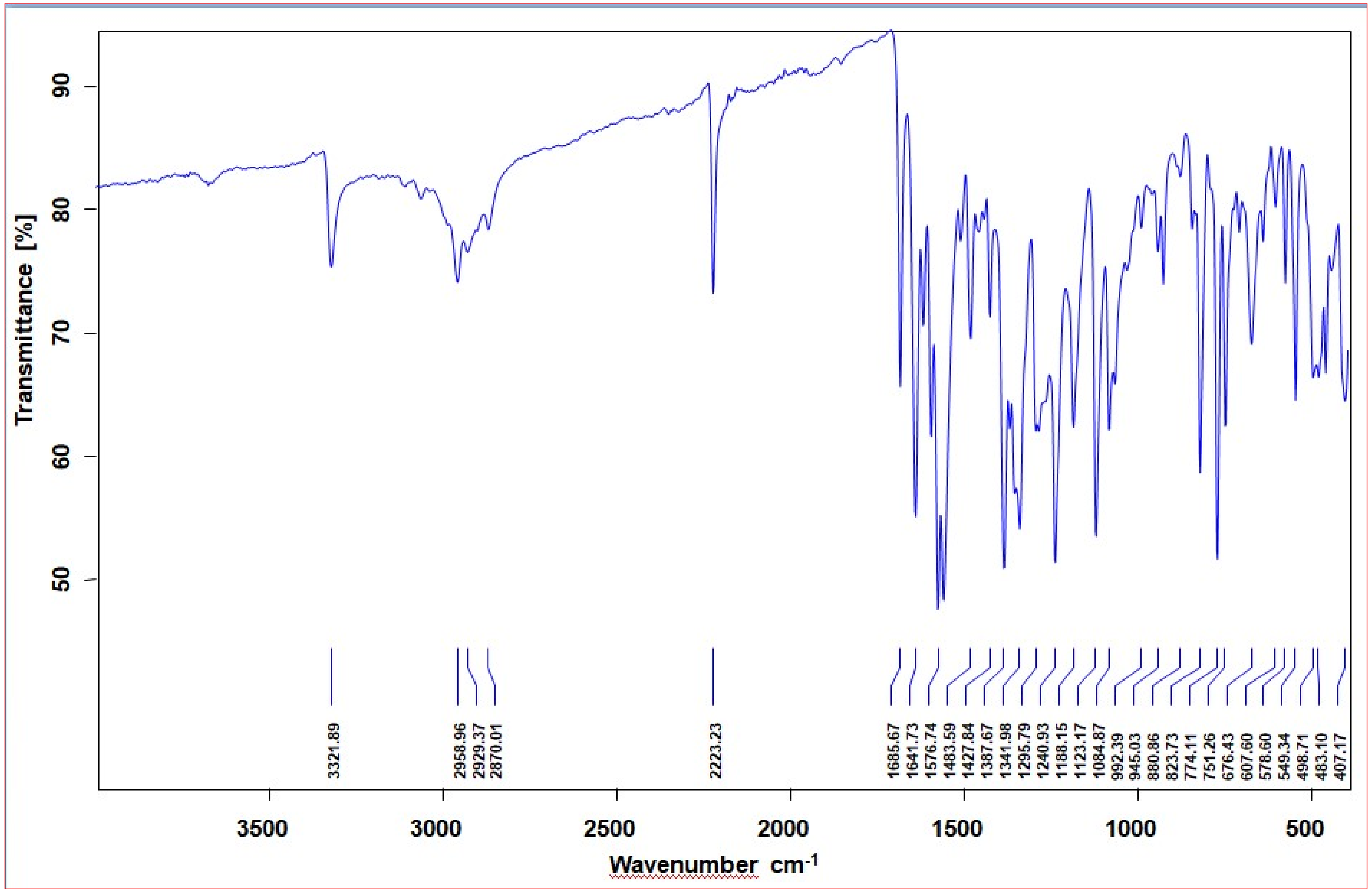


Fig S10. FT-IR spectrum of the **BUDIN**

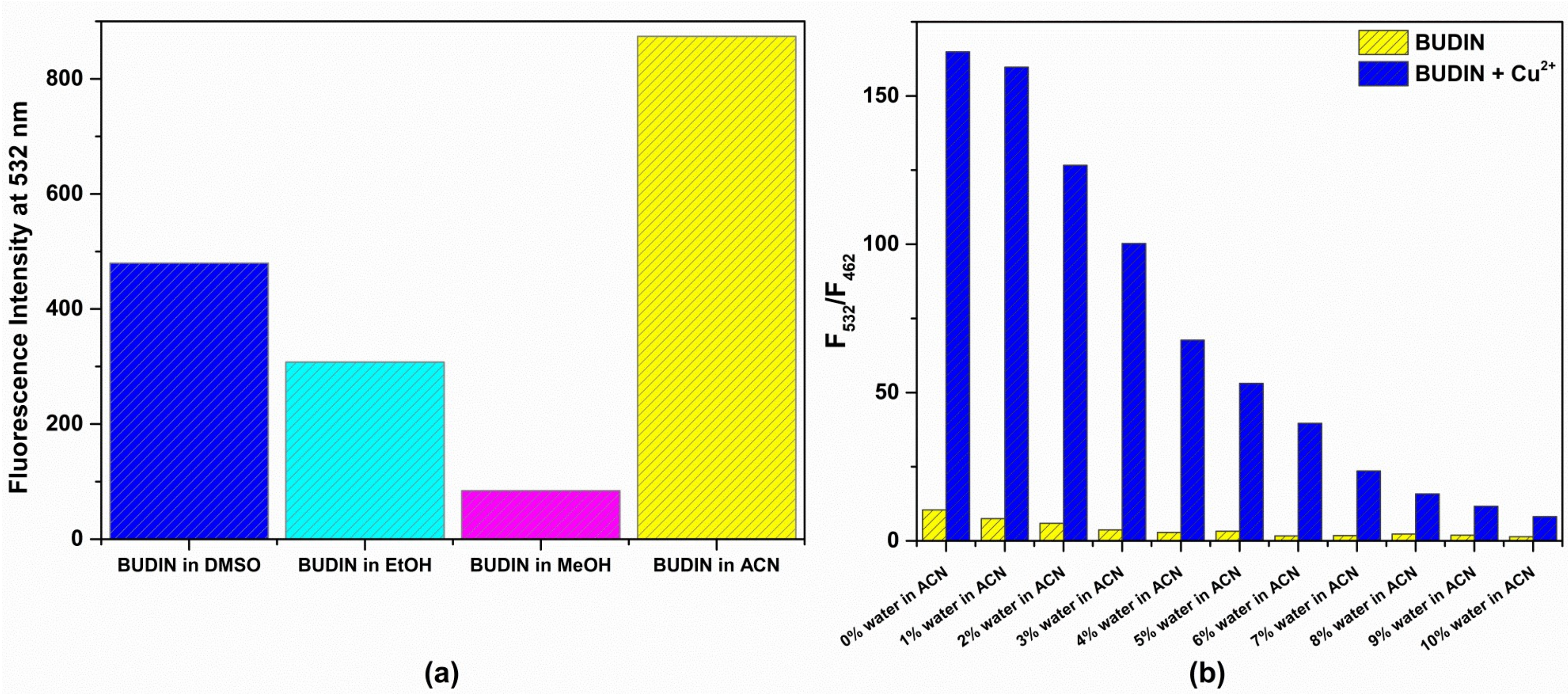


Fig S11. The emission spectra of the **BUDIN**, **BUDIN**–Cu^{2+} **(A)** in different solvents and **(B)** ACN–H_2O binary mixture study in different ratios for the **BUDIN** in the presence and absence of Cu^{2+}

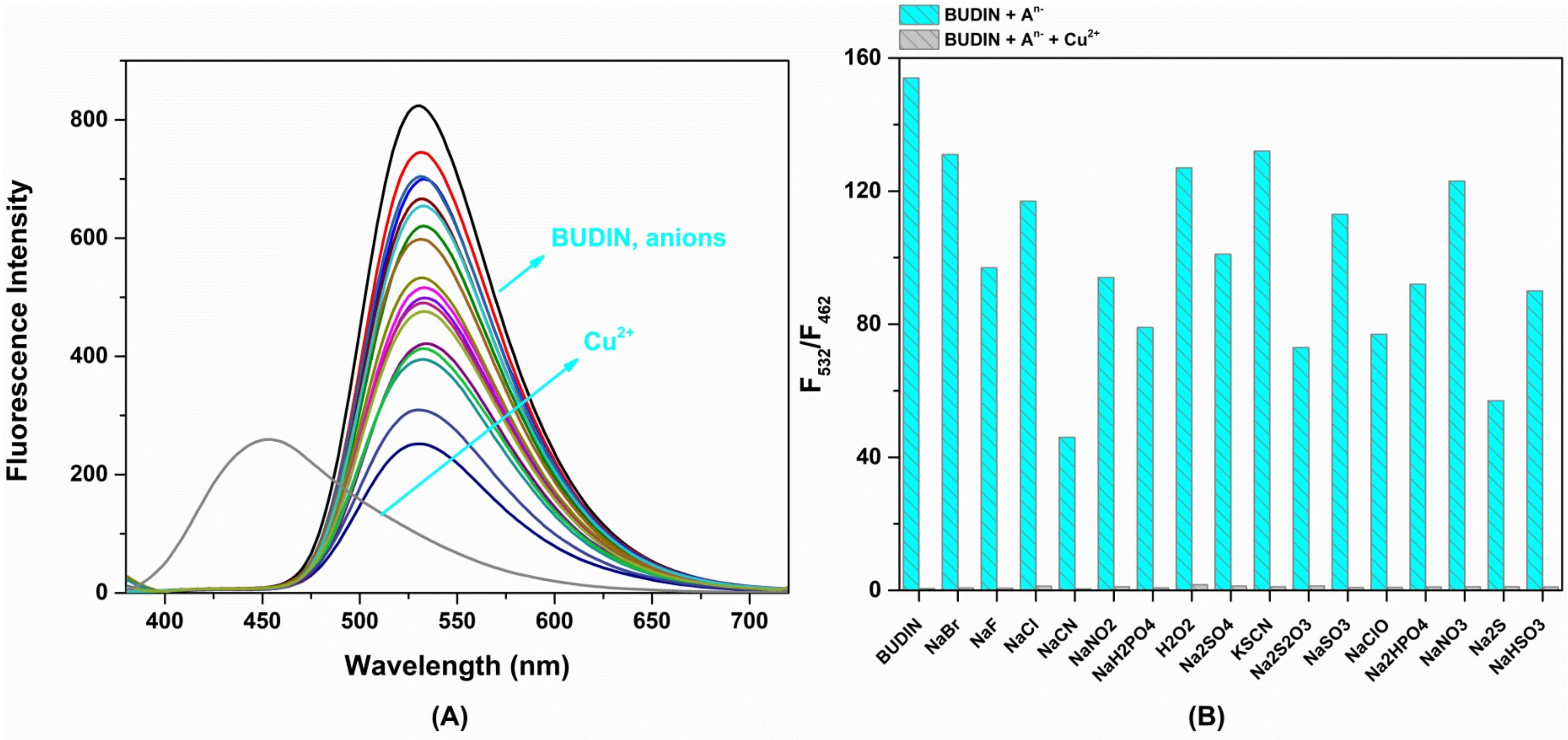


Fig S12. **(A)** Change in emission of **BUDIN** (50 μM) upon the addition of Cu^{2+} and different anions, and **(B)** the competitive binding ability of **BUDIN** (50 μM) toward Cu^{2+} were observed in the presence of other anions

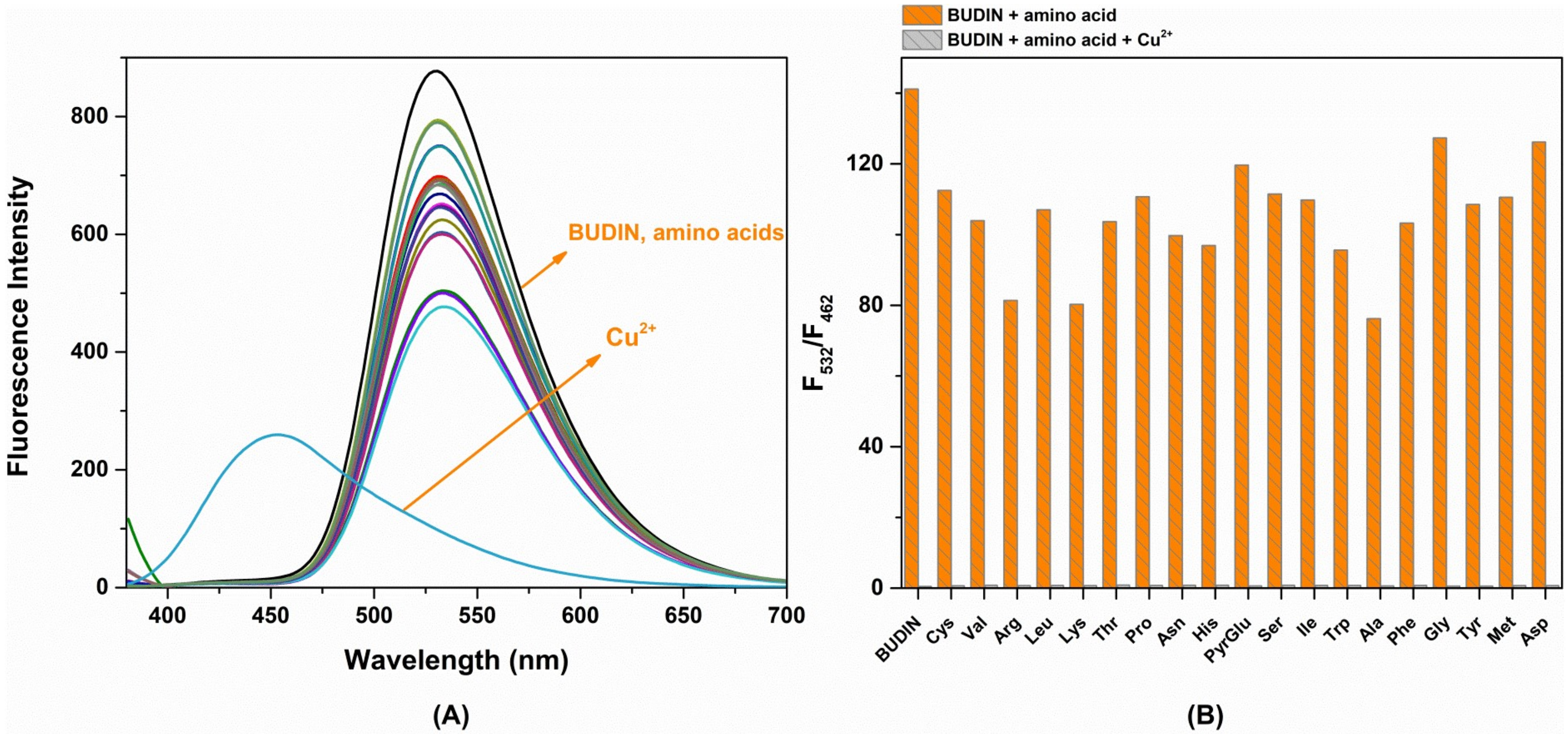


Fig S13. **(A)** Change in emission of **BUDIN** (50 μM) upon the addition of Cu^{2+} and different amino acids, and **(B)** the competitive binding ability of **BUDIN** (50 μM) toward Cu^{2+} were observed in the presence of other amino acids

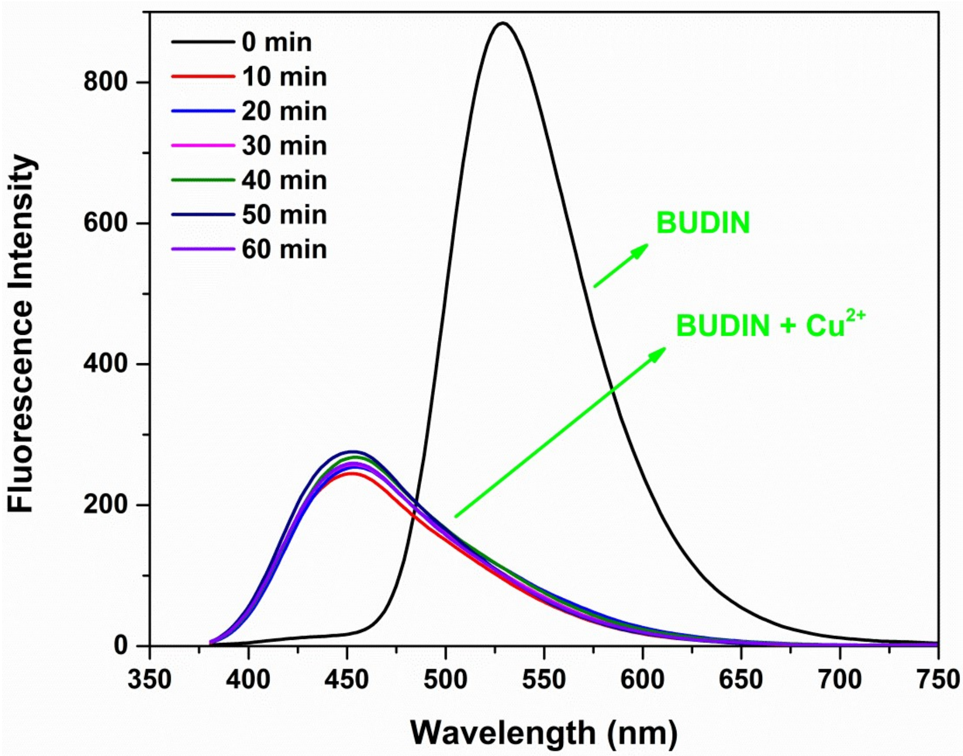


Fig S14. The photo stability of the **BUDIN** and **BUDIN**−Cu^{2+} under the light irradiation

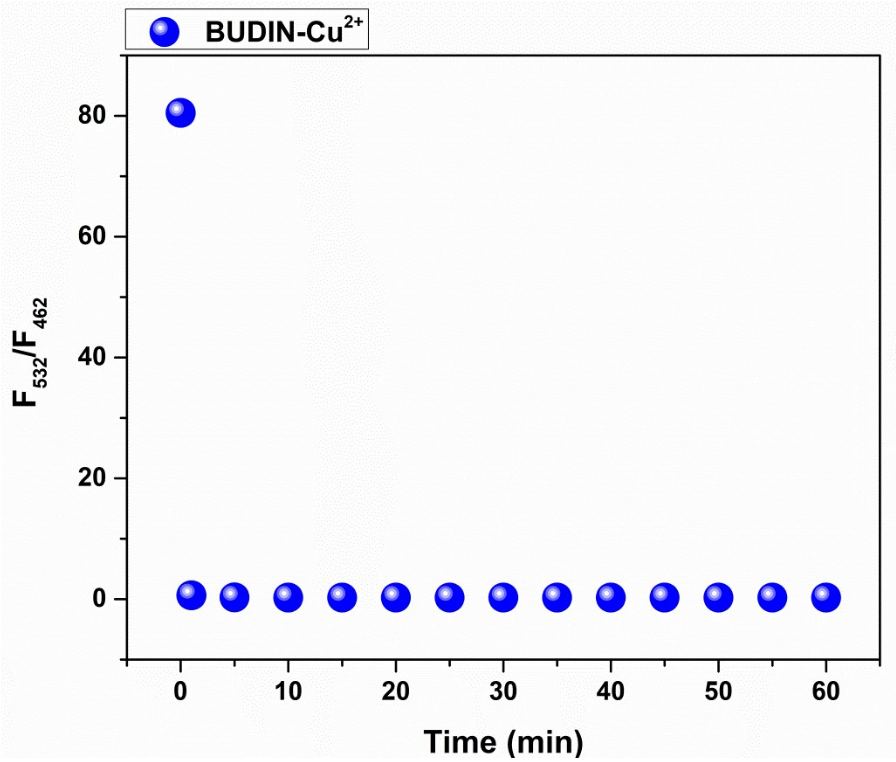


Fig S15. The time stability of the **BUDIN** and **BUDIN**−Cu^{2+}

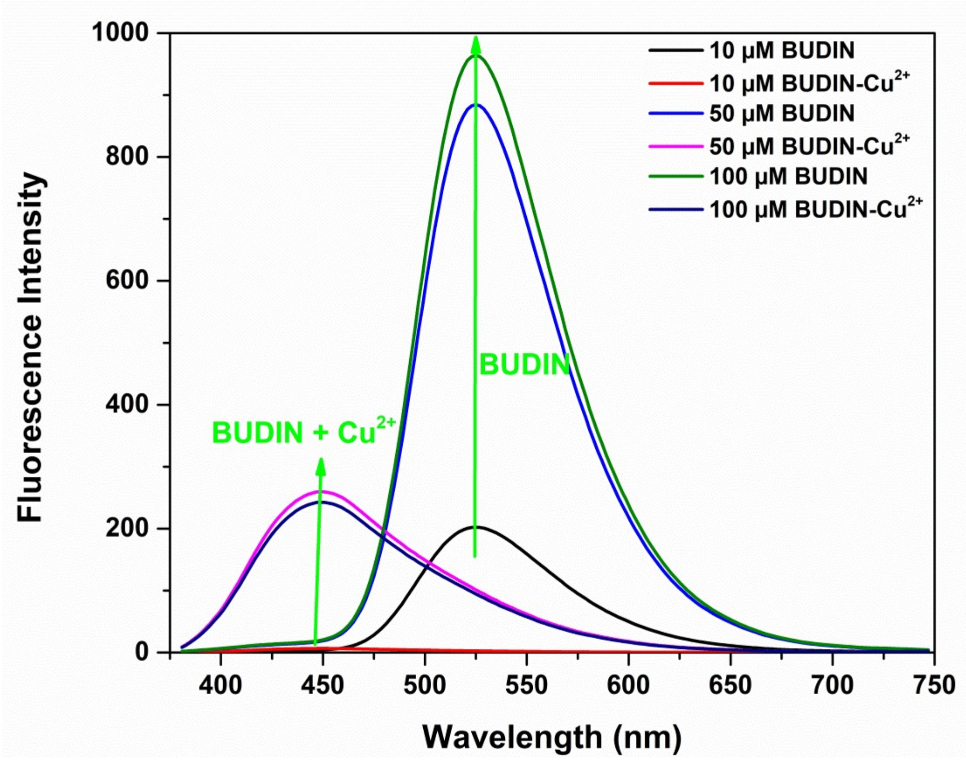
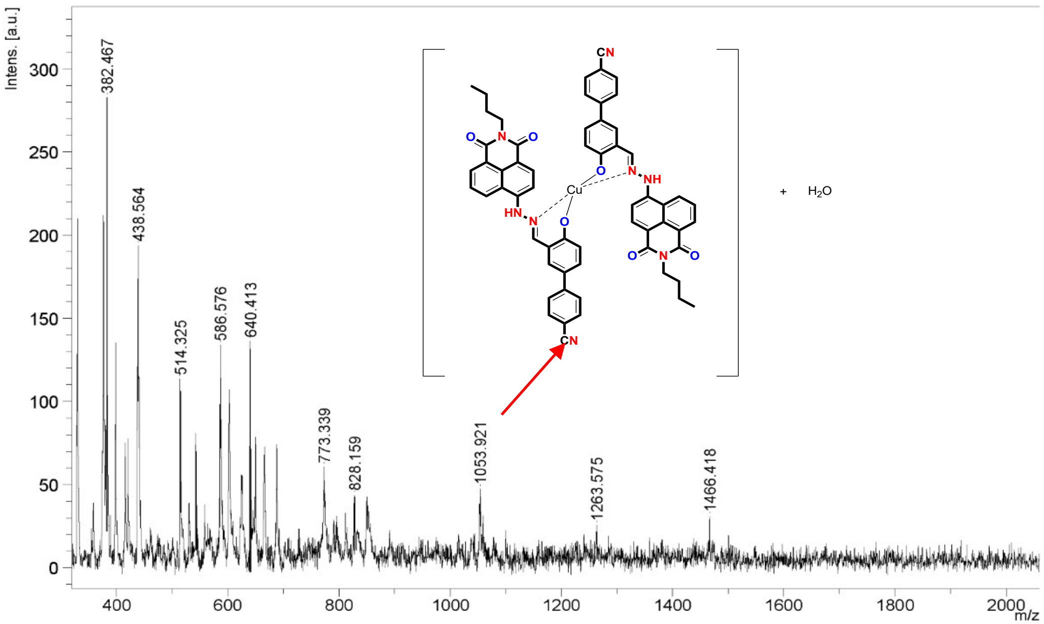


Fig S16. The concentration effect of the **BUDIN** for the detection of Cu^{2+}

budn-cu_iaa



m/z	SN	Quality Fac.	Res.	Intens.	Area
382.467	17.3		594	282.78	234
438.564	11.1		919	193.82	167
514.325	6.4		579	113.55	139
542.450	4.5		834	80.80	89
586.576	6.9		985	133.72	146
640.413	7.5		509	136.21	236
773.339	3.6		1847	59.81	41
827.416	2.5		1396	38.14	28
828.159	2.8		1077	42.95	43
849.895	2.9		1527	41.76	32
1053.921	3.7		1217	47.28	59
1263.575	2.1		1368	25.34	26
1466.418	2.7		2026	30.54	41
1500.605	1.8		2596	19.26	13

Date of Acquisition 2021-10-25T14:47:05.000

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Fig S17. MALDI TOF MS spectrum of the complex of **BUDIN**–Cu^{2+}

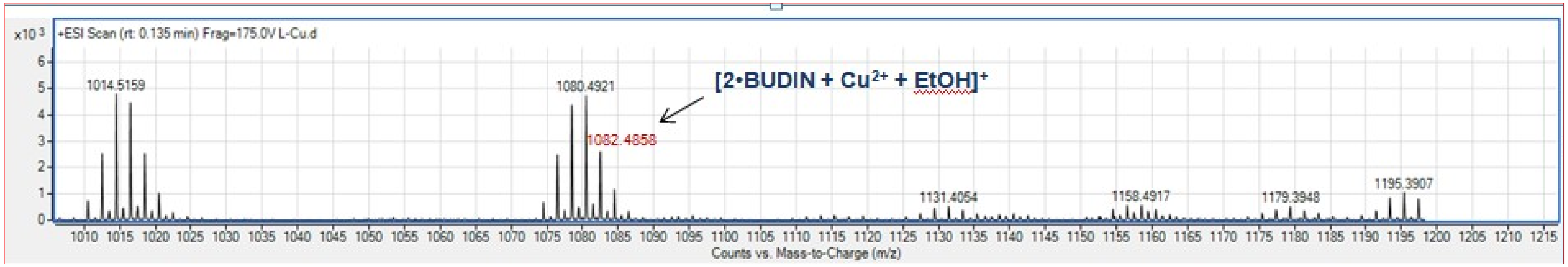


Fig S18. TOF MS spectrum of the complex of **BUDIN**–Cu^{2+}

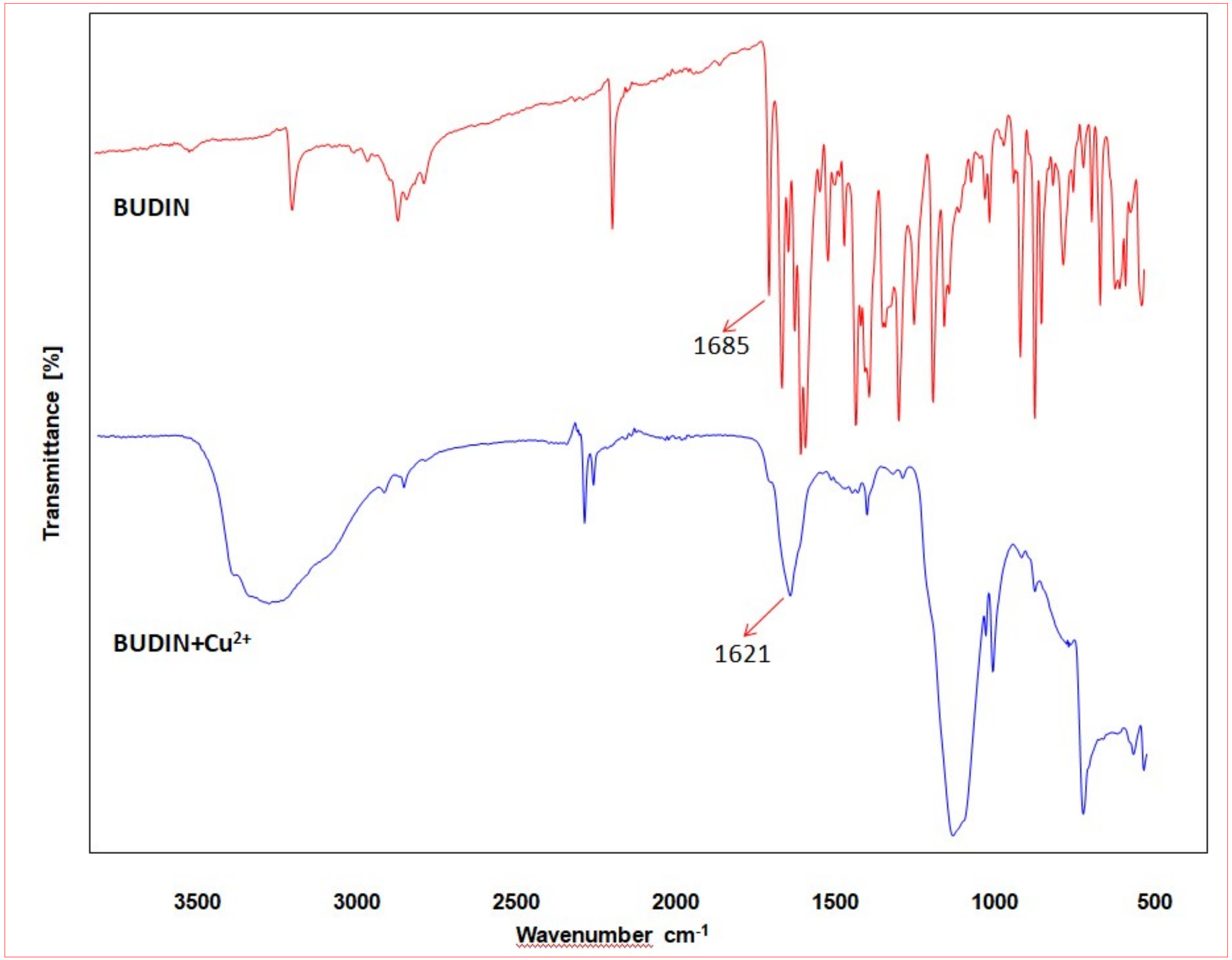
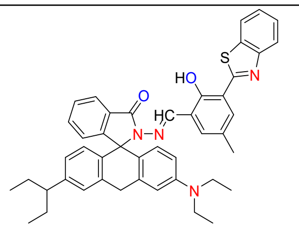
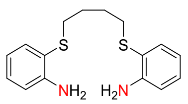
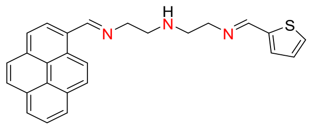
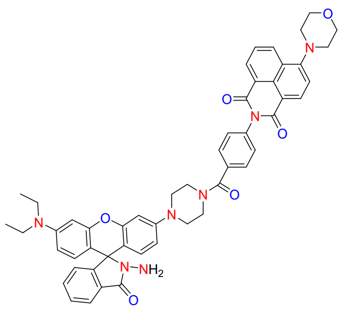
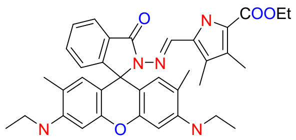
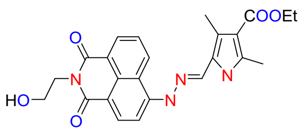
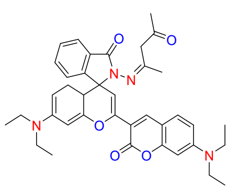


Fig S19. FT-IR spectra of the **BUDIN** and complex of **BUDIN**–Cu^{2+}

Table S1 Comparison of some colorimetric and ratiometric fluorescence sensors for Cu^{2+}

chemical sensor	solvent system	analyte	LOD (M)	application	ref
	HEPES buffer/ACN (v/v=1:1, pH=7.0) colorimetric and ratiometric fluorescence	Cu^{2+} and S^{2-}	6.89×10^{-6} M (for Cu^{2+}) 8.13×10^{-6} (for S^{2-})	-	3
	ACN colorimetric and ratiometric fluorescence	Cu^{2+}	2.29×10^{-6} M	-	4
	H_2O/EtOH (1/1, v/v) ratiometric fluorescence	Cu^{2+}	2×10^{-8} M	yes	5
	H_2O/ACN (9/1, v/v, pH = 7.40) ratiometric fluorescence	Cu^{2+}	18.6×10^{-9} M	yes	6
	EtOH/H_2O (Tris buffered, 10 mM, pH=7.20,2/8,v/v) solution (for Cu^{+2}) EtOH (for Cd^{+2}) colorimetric and ratiometric fluorescence	Cu^{2+} and Cd^{2+}	2.94×10^{-6} M (for Cu^{2+}) 1.13×10^{-6} (for Cd^{2+})	yes	7
	ACN/H_2O (9/1, v:v, pH=7.40) colorimetric and ratiometric fluorescence	Cu^{2+}	10×10^{-6} M	yes	8
	ACN/H_2O (MOPS buffer, 10 mM,pH=7.04, v/v,1/1) ratiometric fluorescent	Cu^{2+}	0.20×10^{-6} M	yes	9

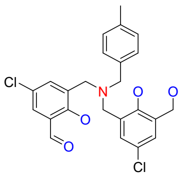
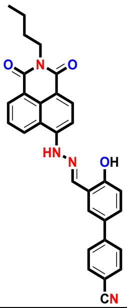
	C_2H_5OH/H_2O (v/v, 9/1) ratiometric fluorescence	Cu^{2+} and Fe^{3+}	0.21×10^{-6} M (for Cu^{2+}) 0.40×10^{-6} M (for Fe^{3+})	yes	10
	ACN/H_2O (97/3, v/v) colorimetric and ratiometric fluorescence	Cu^{2+}	17×10^{-9} M	yes	**this work**

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Table S2. The detection of Cu^{2+} in copper spiked beer and drinking water samples by **BUDIN**

	spiked Cu^{2+} (μmol L^{-1})	found Cu^{2+} (μmol L^{-1})	recovery (%)	RSD (%) (n=3)
beer sample–1	0.00	0.2816 ±0.0061		2.16
	0.10	0.3772 ±0.0085	95.69	2.26
	0.20	0.4856 ±0.0085	102.04	1.76
beer sample–2	0.00	0.2343 ±0.0030		1.28
	0.10	0.3484 ±0.0100	114.10	2.87
	0.20	0.4219 ±0.0100	93.79	2.37
beer sample–3	0.00	0.0969 ±0.0026		2.73
	0.10	0.2059 ±0.0072	108.92	3.50
	0.20	0.2965 ±0.0076	99.78	2.58
drinking water–1	0.00	0.2382 ±0.0064		2.70
	0.10	0.3369 ±0.0100	98.80	2.97
	0.20	0.4301 ±0.0051	95.97	1.19
drinking water–2	0.00	0.1449 ±0.0035		2.42
	0.10	0.2532 ±0.0051	108.31	2.03
	0.20	0.3498 ±0.0036	102.47	1.03
drinking water–3	0.00	0.1650 ±0.0040		2.42
	0.10	0.2724 ±0.0055	107.35	2.02
	0.20	0.3509 ±0.0081	92.94	2.30

Table S3. The detection of Cu^{2+} in copper spiked beer and drinking water samples by **AAS**

	spiked Cu^{2+} (μmol L^{-1})	**found Cu^{2+} (μmol L^{-1})**	**recovery (%)**	**RSD (%) (n=3)**
beer sample–1	0.00	0.2914 ±0.0060		2.05
	0.10	0.3818 ±0.0059	90.37	1.55
	0.20	0.4979 ±0.0066	103.25	1.32
beer sample–2	0.00	0.2430 ±0.0068		2.78
	0.10	0.3457 ±0.0098	102.70	2.82
	0.20	0.4291 ±0.0070	93.02	1.62
beer sample–3	0.00	0.0951 ±0.0037		3.86
	0.10	0.2044 ±0.0045	109.33	2.21
	0.20	0.3010 ±0.0061	102.95	2.02
drinking water–1	0.00	0.2452 ±0.0044		1.80
	0.10	0.3411 ±0.0073	95.87	2.13
	0.20	0.4260 ±0.0069	90.37	1.62
drinking water–2	0.00	0.1474 ±0.0055		3.70
	0.10	0.2474 ±0.0062	99.93	2.51
	0.20	0.3566 ±0.0061	104.58	1.71
drinking water–3	0.00	0.1687 ±0.0055		3.23
	0.10	0.2685 ±0.0070	99.83	2.61
	0.20	0.3604 ±0.0070	95.87	1.94

The optimized atomic coordinate values obatined from Gaussian–09 software for BUDIN and BUDIN-Cu^{2+}

BUDIN

C	-3.73694500	2.88498300	0.47247900
C	-2.36685600	3.02453000	0.74751600
C	-1.50688500	1.95106400	0.61362400
C	-1.97699800	0.67828600	0.19151900
C	-3.37574200	0.54694000	-0.11015700
C	-4.23542000	1.66692700	0.04639500
C	-1.72059800	-1.67541800	-0.44577700
C	-3.08047200	-1.77153300	-0.73767700
C	-3.91682500	-0.67960800	-0.57059800
C	-5.35304000	-0.82177100	-0.87681200
N	-6.15093000	0.32296100	-0.71529600
C	-5.68700600	1.55824200	-0.24684100
C	-7.58764100	0.20458200	-1.02060000
C	-8.41793300	-0.21532300	0.19710400
C	-9.91079100	-0.33216400	-0.13480600
C	-10.75817200	-0.74889500	1.07169600
O	-5.84897400	-1.87718200	-1.25825400
O	-6.45849800	2.49915000	-0.09618000
N	0.89983400	0.34031800	0.99686900
C	2.16994600	0.23640300	1.21027400
C	3.22346200	-0.69799200	0.75223800
C	4.49876300	-0.13458000	0.56528600
C	5.61448900	-0.86942400	0.14963500
C	5.44303200	-2.24629000	-0.06978600
C	4.20459500	-2.84377400	0.12833500
C	3.10649700	-2.08738200	0.54378500
O	1.89315400	-2.68582800	0.78721800
C	6.93143900	-0.21698500	-0.04935500
C	7.02336100	1.07801000	-0.58993000
C	8.25475000	1.69428800	-0.77712400
C	9.43731900	1.02105500	-0.42877200
C	9.36147500	-0.27404600	0.11003400
C	8.12386500	-0.87791600	0.29574600
C	10.71084600	1.64946400	-0.62164900
N	11.74508900	2.15893300	-0.77816300
H	-4.42517700	3.71684000	0.58000600
H	-1.97729900	3.98557600	1.07054500
H	-0.45778600	2.06809100	0.84219100
H	-1.08654400	-2.54958400	-0.57266500
H	-3.50808900	-2.70418700	-1.09038000
H	-7.91443500	1.17958600	-1.38583600
H	-7.68001800	-0.53480200	-1.81755300
H	-8.27335400	0.52184600	0.99706200
H	-8.04388500	-1.17863900	0.56678400
H	-10.27358400	0.63067300	-0.52153000
H	-10.04716400	-1.06039700	-0.94680600
H	-11.81900900	-0.82619500	0.80731200
H	-10.66952900	-0.02096100	1.88736800
H	-10.43913200	-1.72337300	1.46118000
H	2.55768300	1.06955600	1.79489000
H	4.61371600	0.92625400	0.77079300
H	6.27557500	-2.85106900	-0.41580600
H	4.08485600	-3.91279800	-0.03829000
H	1.96828400	-3.64239800	0.64088700
H	6.11962300	1.59822600	-0.89259200
H	8.31013900	2.69111600	-1.20252200
H	10.27273400	-0.79321900	0.38897900

H	8.07922100	-1.86765900	0.74019100
C	-1.14743600	-0.48930600	0.02264000
N	0.22673800	-0.54109000	0.23427300
H	0.65214400	-1.45363800	0.07922300

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2 3 2.0 37 1.0
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4 5 1.5 59 1.5
5 6 1.5 9 1.5
6 12 1.0
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11 12 1.0 13 1.0
12 18 2.0
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59 60 1.0
60 61 1.0
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BUDIN-Cu

C	-3.63437500	4.01411000	-0.17389800
C	-2.28268700	3.98439400	-0.56449600
C	-1.39282600	3.11238900	0.03179500
C	-1.81450900	2.22578300	1.05956300
C	-3.18045900	2.30170500	1.49115700
C	-4.07670200	3.19097100	0.84438800
C	-1.44219100	0.58064500	2.84089000
C	-2.76718800	0.70864300	3.27102100
C	-3.64341200	1.53314900	2.58757300
C	-5.05903400	1.60666600	3.03991700
N	-5.90890900	2.45636200	2.32757500
C	-5.50547600	3.27221600	1.26253800
C	-7.32116100	2.54252600	2.76208700
C	-7.54754500	3.63242100	3.81498300
C	-9.01730000	3.71231800	4.24840000
C	-9.26586500	4.79856900	5.29965000
O	-5.46285400	0.94373000	3.98529600
O	-6.29691700	4.01384500	0.70084200
N	0.84110800	1.10806700	0.10433300
C	2.09050300	1.52791100	-0.03563800
C	2.81977500	1.62053200	-1.24184700
C	4.09304300	2.24799400	-1.20644700
C	4.82900300	2.48331800	-2.35518900
C	4.25134800	2.09004500	-3.60396800
C	3.01778200	1.49504400	-3.68789300
C	2.27402400	1.18711300	-2.51057900
O	1.18115600	0.51510900	-2.60838000
C	6.15753400	3.13235500	-2.30976300
C	6.43924000	4.14116800	-1.36986200
C	7.68950500	4.74334400	-1.31746300
C	8.69710900	4.34682800	-2.21303800
C	8.42921900	3.34379400	-3.15922400
C	7.17402200	2.74987000	-3.20465400
C	9.98942000	4.96408800	-2.16126700
N	11.03823400	5.46465700	-2.11623700
H	-4.34240300	4.68942300	-0.64238500
H	-1.93290500	4.65997200	-1.33884400
H	-0.35575500	3.13308900	-0.27496700
H	-0.76723400	-0.08096100	3.37799200
H	-3.13412700	0.15358900	4.12782000
H	-7.91185400	2.74404100	1.86738700
H	-7.58650600	1.56193600	3.15964900
H	-7.23042900	4.59869900	3.40276200
H	-6.91487500	3.42432400	4.68734000
H	-9.64578600	3.90416100	3.36762700
H	-9.33270900	2.73769300	4.64620900
H	-10.32158300	4.83486800	5.58890500
H	-8.99009300	5.78913600	4.91857300
H	-8.67764700	4.61483000	6.20670400
H	2.57776500	1.89782300	0.86705700
H	4.49801700	2.53484300	-0.23972300
H	4.79835300	2.29665600	-4.51912800
H	2.59003800	1.20484300	-4.64150300
H	5.66065500	4.48243700	-0.69433000
H	7.89152000	5.52822700	-0.59617400
H	9.20860400	3.03179900	-3.84639900
H	6.99339400	1.95623500	-3.92324500

C	-0.96271800	1.28723600	1.73802600
N	0.38247900	1.09818100	1.40412400
H	0.90738400	0.49481800	2.03204000
C	3.17113300	-3.20705600	4.32776400
C	1.81759500	-2.82358700	4.38491500
C	1.13035900	-2.49780900	3.23076800
C	1.76486000	-2.54512300	1.96138100
C	3.14044000	-2.93408800	1.91149100
C	3.82294000	-3.26160600	3.11006300
C	1.81162000	-2.32791300	-0.48485400
C	3.16725700	-2.69054600	-0.49847900
C	3.83277500	-2.98997900	0.67573200
C	5.26799800	-3.37568300	0.61785300
N	5.87804700	-3.73227200	1.82565700
C	5.25731300	-3.67341900	3.07869900
C	7.29688000	-4.15163200	1.78363600
C	8.26888800	-2.97993400	1.95480800
C	9.73121100	-3.44336000	1.91813900
C	10.72423900	-2.29019200	2.09260400
O	5.88757400	-3.38694700	-0.43609700
O	5.86511600	-3.94870300	4.10130000
N	-0.85706100	-1.34384400	-0.35902600
C	-2.08810500	-1.78167500	-0.56583000
C	-2.96734300	-1.38357600	-1.60136900
C	-4.18617900	-2.09205000	-1.75149800
C	-5.05576500	-1.84887500	-2.80310600
C	-4.67562900	-0.85887900	-3.76337200
C	-3.49943900	-0.15980000	-3.66683800
C	-2.62227300	-0.35345000	-2.55845300
O	-1.59113500	0.40328300	-2.42710800
C	-6.32482900	-2.59326200	-2.95040600
C	-6.41944900	-3.94641200	-2.57433800
C	-7.61258500	-4.64483400	-2.70366900
C	-8.75091400	-4.00024900	-3.21693600
C	-8.67092800	-2.65098600	-3.59954300
C	-7.47138800	-1.96258800	-3.46900000
C	-9.98474900	-4.71667600	-3.35064400
N	-10.98586500	-5.29904700	-3.45663200
H	3.72142500	-3.46677300	5.22577600
H	1.30972500	-2.78688900	5.34367000
H	0.08506000	-2.21523600	3.31956300
H	1.30320700	-2.13998000	-1.42275000
H	3.70903500	-2.75921600	-1.43577400
H	7.43019300	-4.88060500	2.58431500
H	7.44840000	-4.64021400	0.82016800
H	8.06364900	-2.48076400	2.91038200
H	8.09181300	-2.24769300	1.15626300
H	9.89434400	-4.18951600	2.70796400
H	9.92653100	-3.95542000	0.96573000
H	11.75795600	-2.65083800	2.06508100
H	10.57494600	-1.78005300	3.05184100
H	10.61067000	-1.54396500	1.29677500
H	-2.44543000	-2.57347500	0.09618300
H	-4.44369500	-2.83879200	-1.00520000
H	-5.32725400	-0.67830500	-4.61300700
H	-3.21813800	0.58558400	-4.40290100
H	-5.54000000	-4.46860600	-2.20990700
H	-7.66994900	-5.69097300	-2.42192000
H	-9.55087700	-2.15022300	-3.98930200
H	-7.43549500	-0.91285600	-3.74374200
C	1.11362300	-2.23850600	0.71493400
N	-0.22184000	-1.83072300	0.74553800
H	-0.81790900	-2.14242200	1.50406600

Cu -0.11905900 0.19731400 -1.29234800

1 2 1.5 6 2.0 36 1.0
2 3 2.0 37 1.0
3 4 1.5 38 1.0
4 5 1.5 58 1.5
5 6 1.5 9 1.5
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7 8 1.5 39 1.0 58 1.5
8 9 2.0 40 1.0
9 10 1.0
10 11 1.0 17 2.0
11 12 1.0 13 1.0
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14 15 1.0 43 1.0 44 1.0
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16 47 1.0 48 1.0 49 1.0
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86 87 2.0
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93 117 1.0
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119 120 1.0
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