Supporting Information for:

On the mechanochemical synthesis of *C*-scorpionates with an oxime moiety and their application in the copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction

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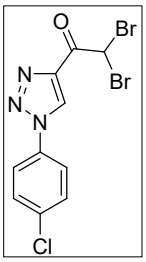
1. Synthesis of oximes



1-(1-*p*-Chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone: A solution of bromine (9 mmol. 0.46 mL) in glacial acetic acid (3 mL) was added dropwise to a solution of 1,2,3-triazolylethanone (4.5 mmol. 1 g) in glacial acetic acid (15 mL). The mixture was heated at 40 ^{o}C for 40 h. After this time. the mixture was allowed to cool to room temperature. The solid in suspension was filtered and washed with ethanol 50% and dried under vacuum. Compound **T2** was obtained as a white solid in 91% yield (4.10 mmol. 1.54 g). mp 174.6-175.0 ^{o}C (from ethyl acetate/hexane); IV (ATR) ν 833. 1012. 1258. 1497. 1527. 1699. 2934 and 3146 cm^{-1}. ^{1}H NMR δ ($CDCl_3$) 7.18 (s. 1H). 7.55-7.59 (m. 2H). 7.72-7.76 (m. 2H). 8.68 (s. 1H); ^{13}C NMR δ ($CDCl_3$) 38.8. 122.1. 125.9. 130.4. 134.5. 136.1. 142.6. 180.1; HRMS (ESI) *m/z*: [M+H^{+}] Calcd. for $C_{10}H_7N_3OBr_2Cl$ 377.8639; found 377.8636.

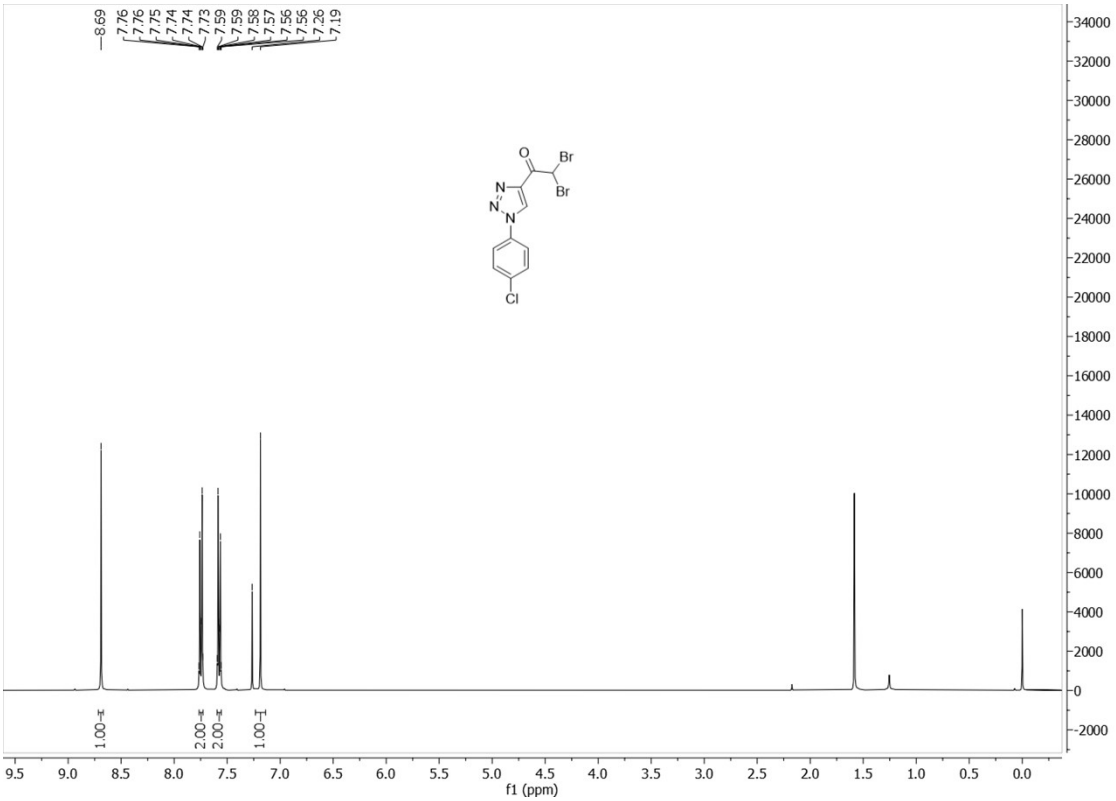


Figure S1. ^{1}H NMR of 1-(1-p-Chlorophenyl-1H-1,2,3-triazol-4-yl)-2,2-dibromoethanone (400 MHz, $CDCl_3$).

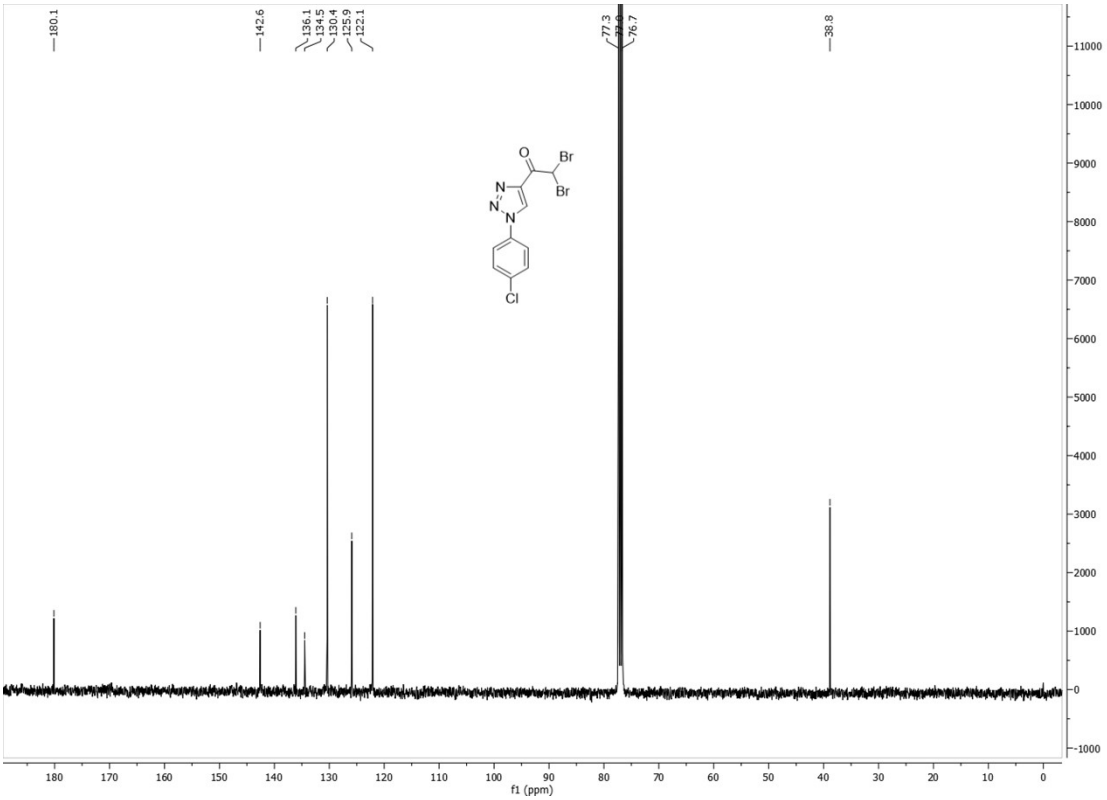
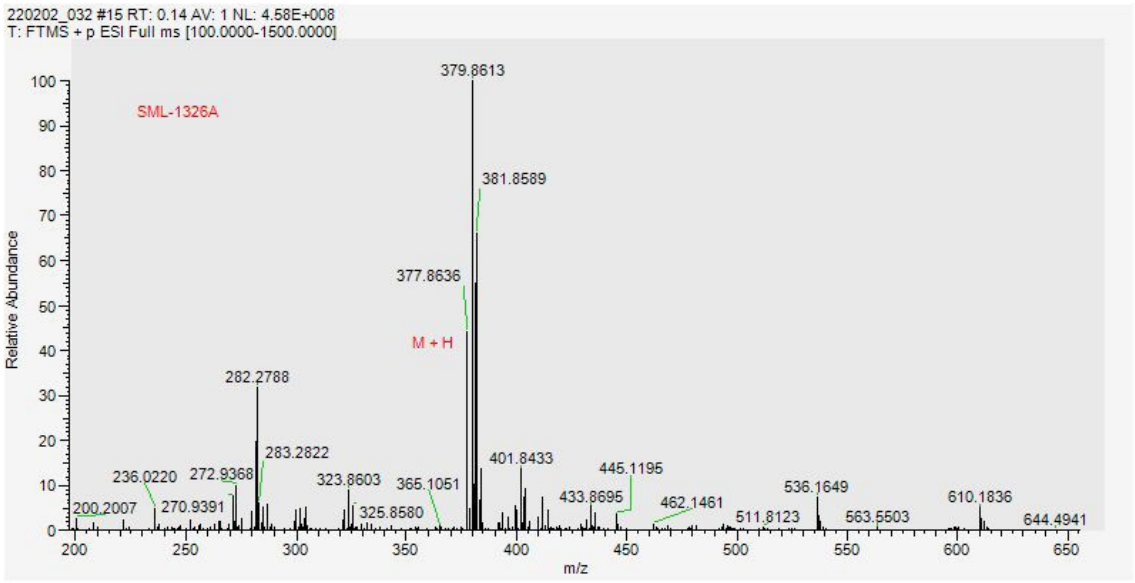


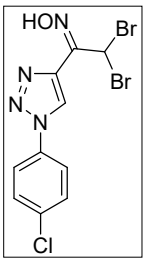
Figure S2. ^{13}C NMR of 1-(1-p-Chlorophenyl-1H-1,2,3-triazol-4-yl)-2,2-dibromoethanone (100 MHz, $CDCl_3$).



Descripción de la muestra: Sólida

Display Formula	S Fit	RDB	Delta [ppm]	Theo. mass	Combined Score
$C_{10}H_7ON_3{}^{79}Br_2{}^{35}Cl$	81,6	7,5	-0,89	377,86389	98,35

Figure S3. High-Resolution Mass Spectrum of 1-(1-p-Chlorophenyl-1H-1,2,3-triazol-4-yl)-2,2-dibromoethanone (ESI-TOF).



1-(1-*p*-Chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone oxime (**4b**): Hydroxylamine hydrochloride (18 mmol. 1.25 g) was added to a solution of 1-(1-*p*-Chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone (3 mmol. 1.13 g) in ethanol (50 mL). The mixture was stirred at room temperature. monitored by TLC until all the 1-(1-*p*-Chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone was consumed (ca. 5 d). The solvents were evaporated. The crude product was triturated with water, filtered, washed with water and dried under vacuum. Oxime **4b** was obtained as a white solid in 81% yield (2.43 mmol. 0.96 g). mp 169.7-171.0 ºC (from ethanol); IR (ATR) ν 718. 826. 972. 1031. 1093. 1253. 1499 and 3249 cm^{-1}; ^{1}H NMR δ (Acetone-d_6) 7.38 (s. 1H). 7.68-7.72 (m. 2H). 8.05-8.09 (m. 2H). 9.35 (s. 1H). 12.00 (s. 1H); ^{13}C NMR δ (Acetone-d_6) 67.6. 122.5. 126.9. 129.9. 134.3. 135.6. 135.8. 145.6; HRMS (ESI-TOF) *m/z*: [M+H^+] Calcd. for $C_{10}H_8N_4OBr_2Cl$ 392.8748; found 392.8736.

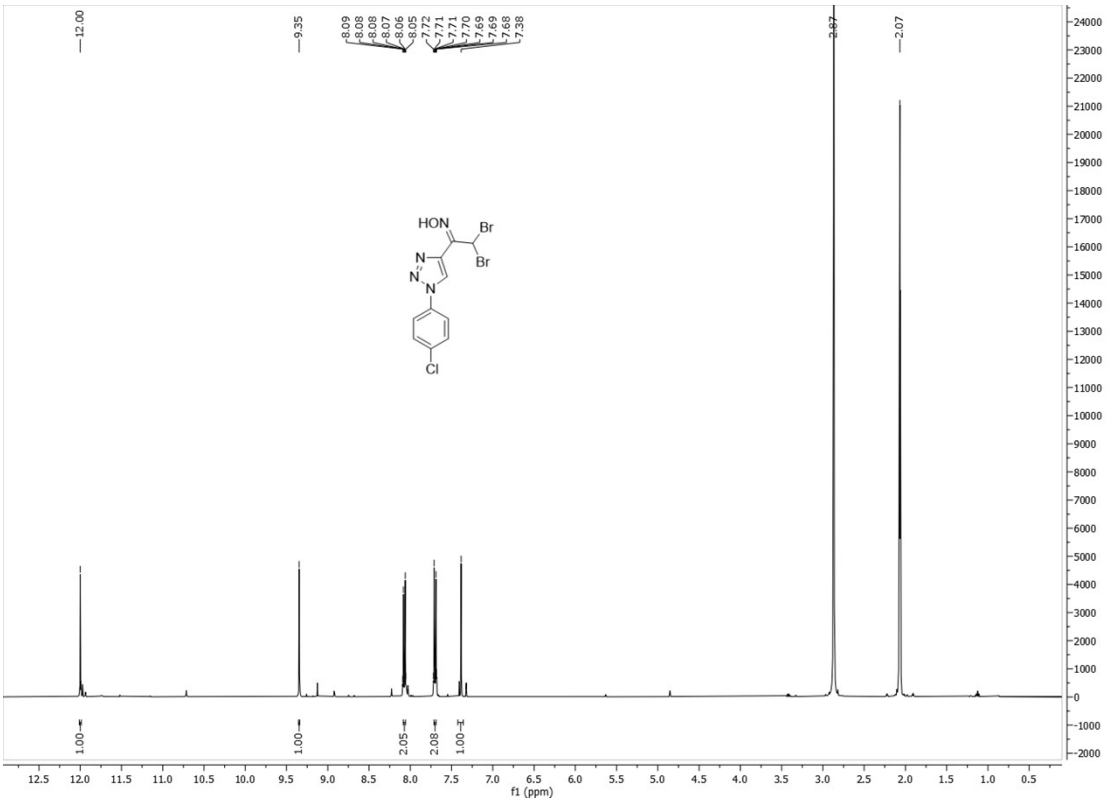


Figure S4. ^{1}H NMR of 11-(1-*p*-chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone oxime (**4b**) (400 MHz, DMSO-d_6).

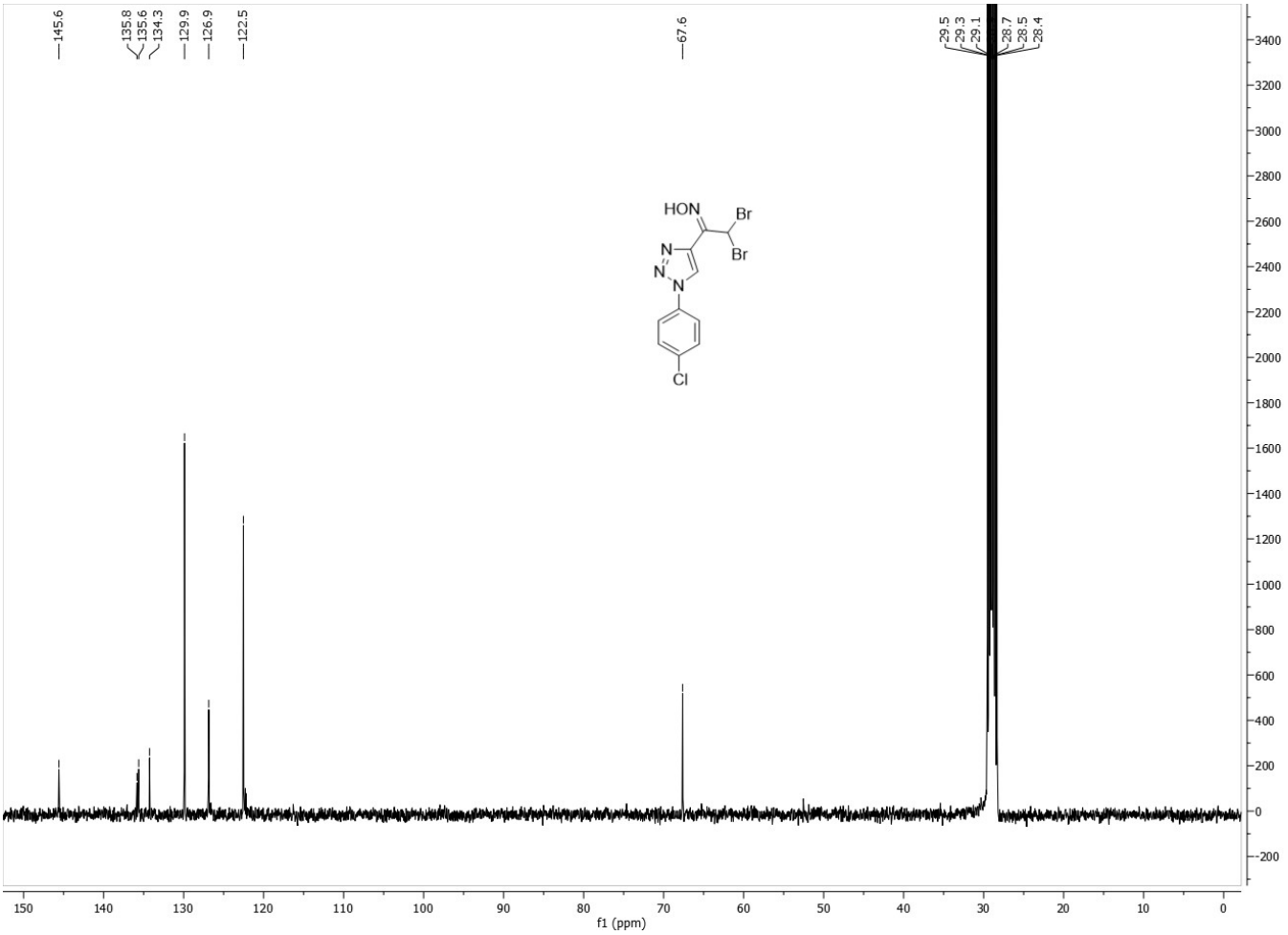
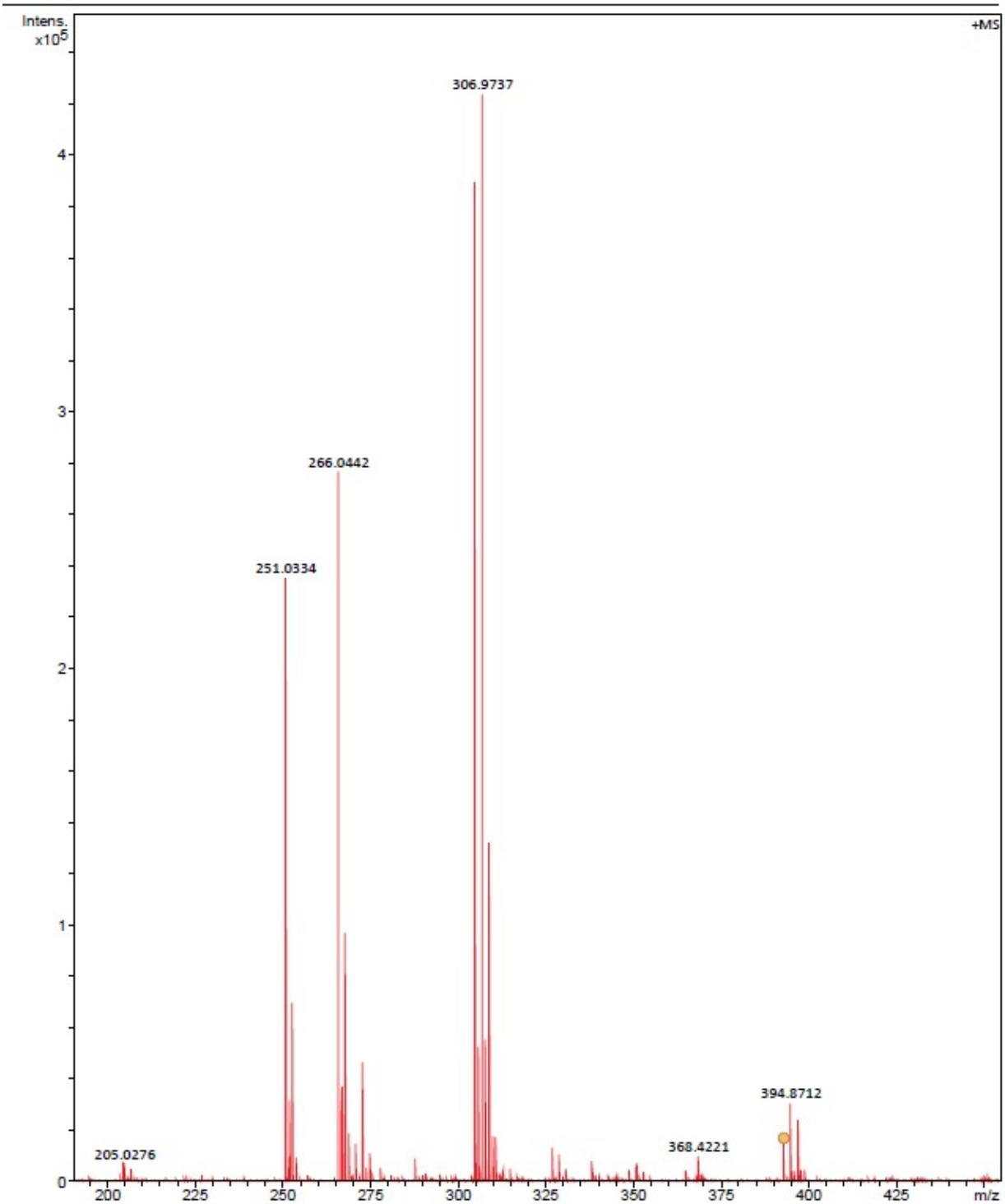


Figure S5. ^{13}C NMR of 1-(1-*p*-chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone oxime (**4b**) (100 MHz, DMSO-d_6).

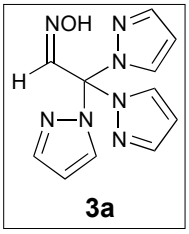


Mass Spectrum Molecular Formula Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
392.8736	1	C10H8Br2ClN4O	392.8748	2.9	45.1	1	100.00	7.5	even	ok

Figure S6. High-Resolution Mass Spectrum of 1-(1-*p*-chlorophenyl-1*H*-1,2,3-triazol-4-yl)-2,2-dibromoethanone oxime (**4b**) (ESI-TOF).

2. Synthesis of C-scorpionates



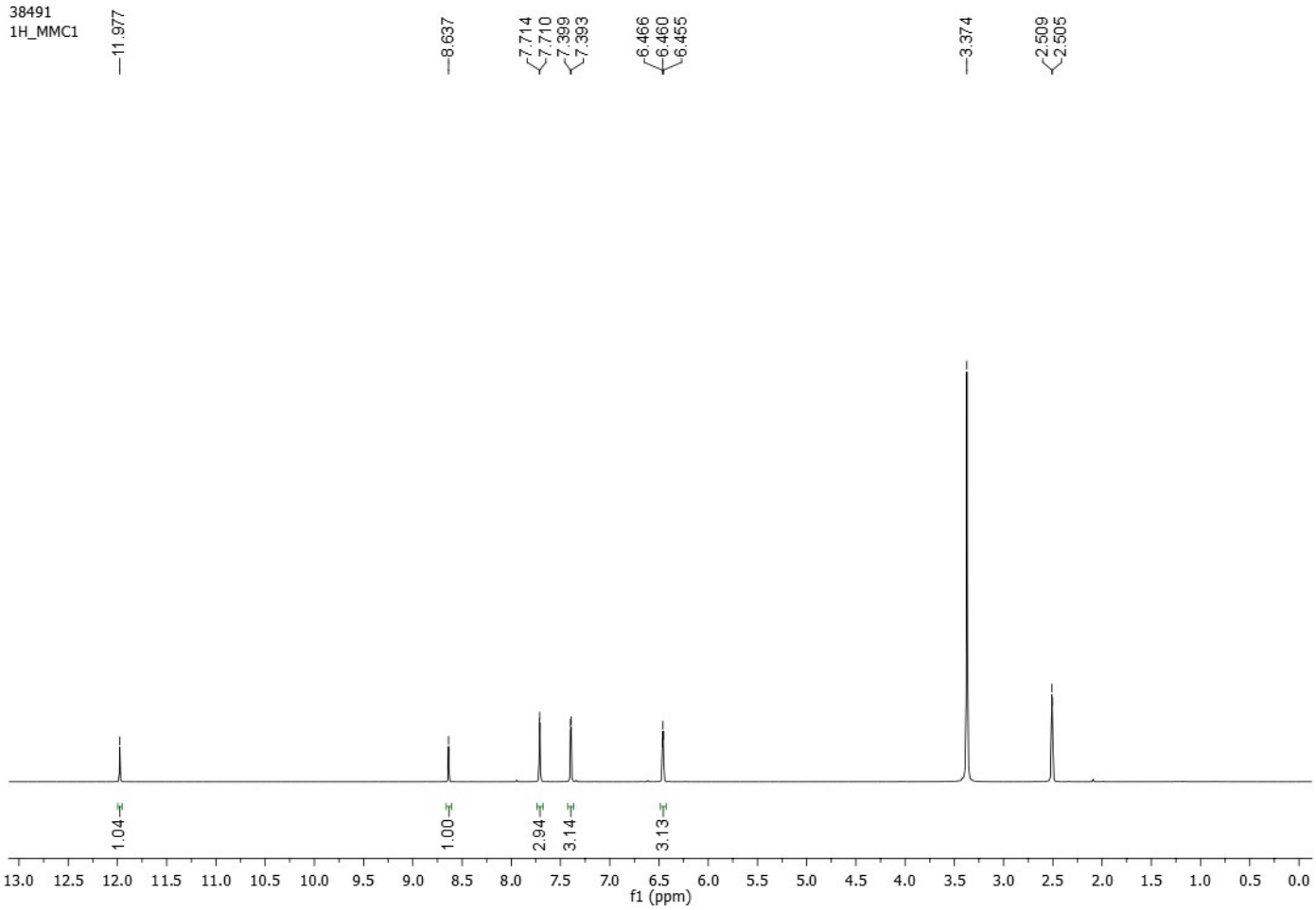


Figure S7 ^{1}H-NMR of compound **3a** (400 MHz, DMSO-d_6).

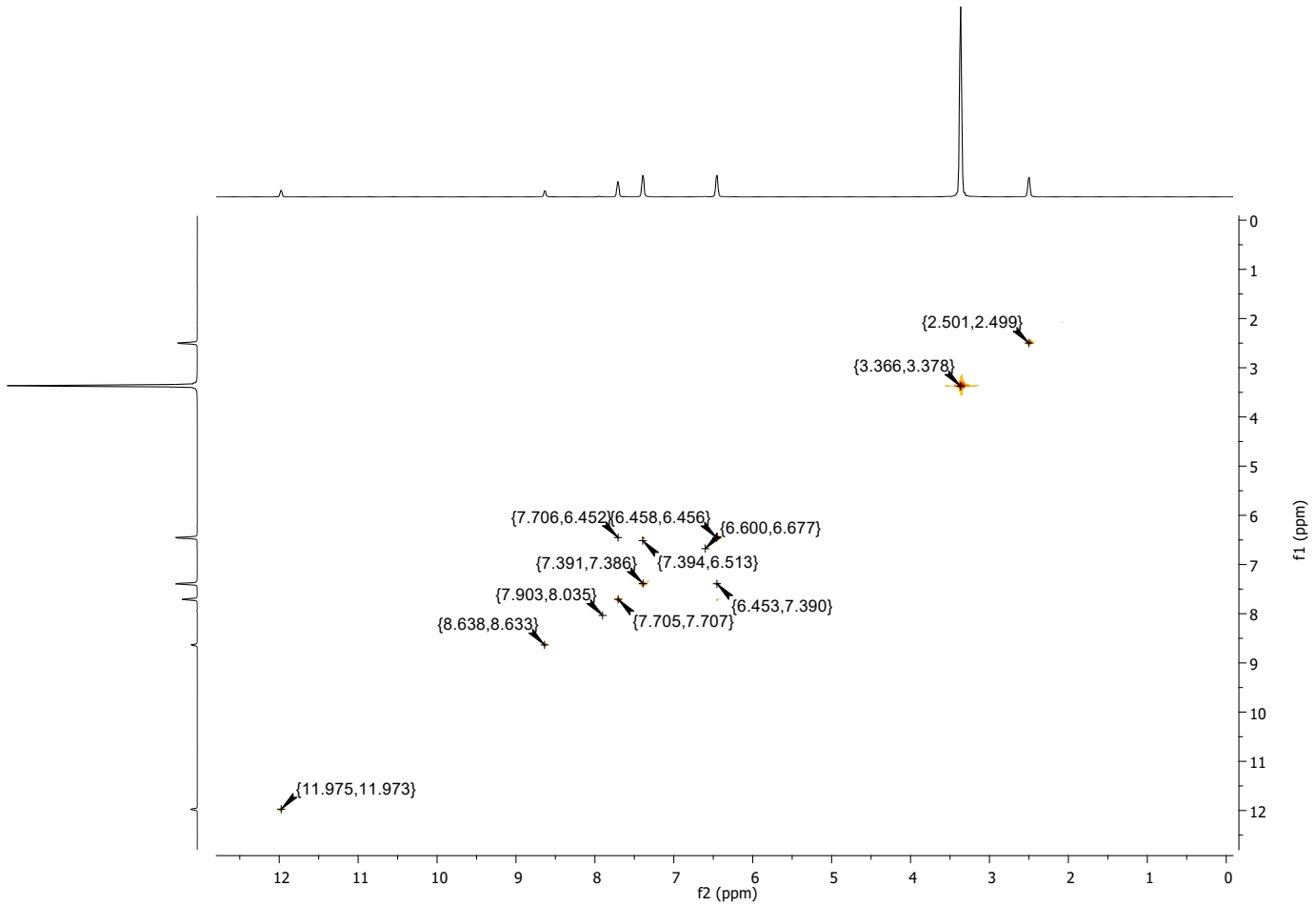
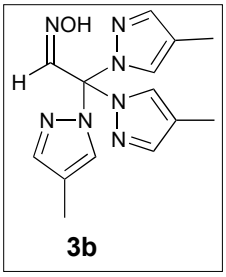


Figure S8. NOESY Spectrum



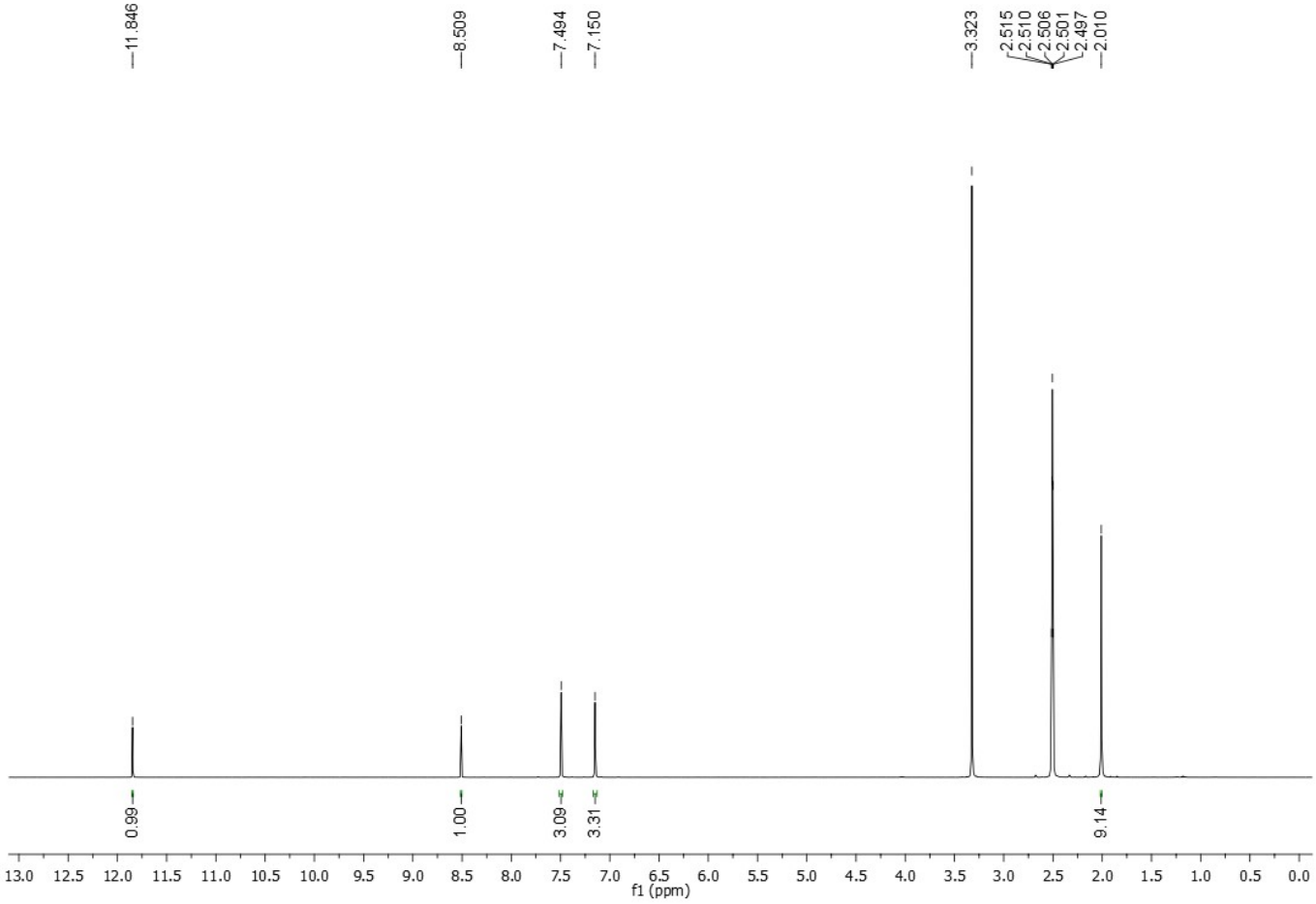


Figure S9 ^{1}H-NMR of compound **3b** (400 MHz, DMSO-d_6).

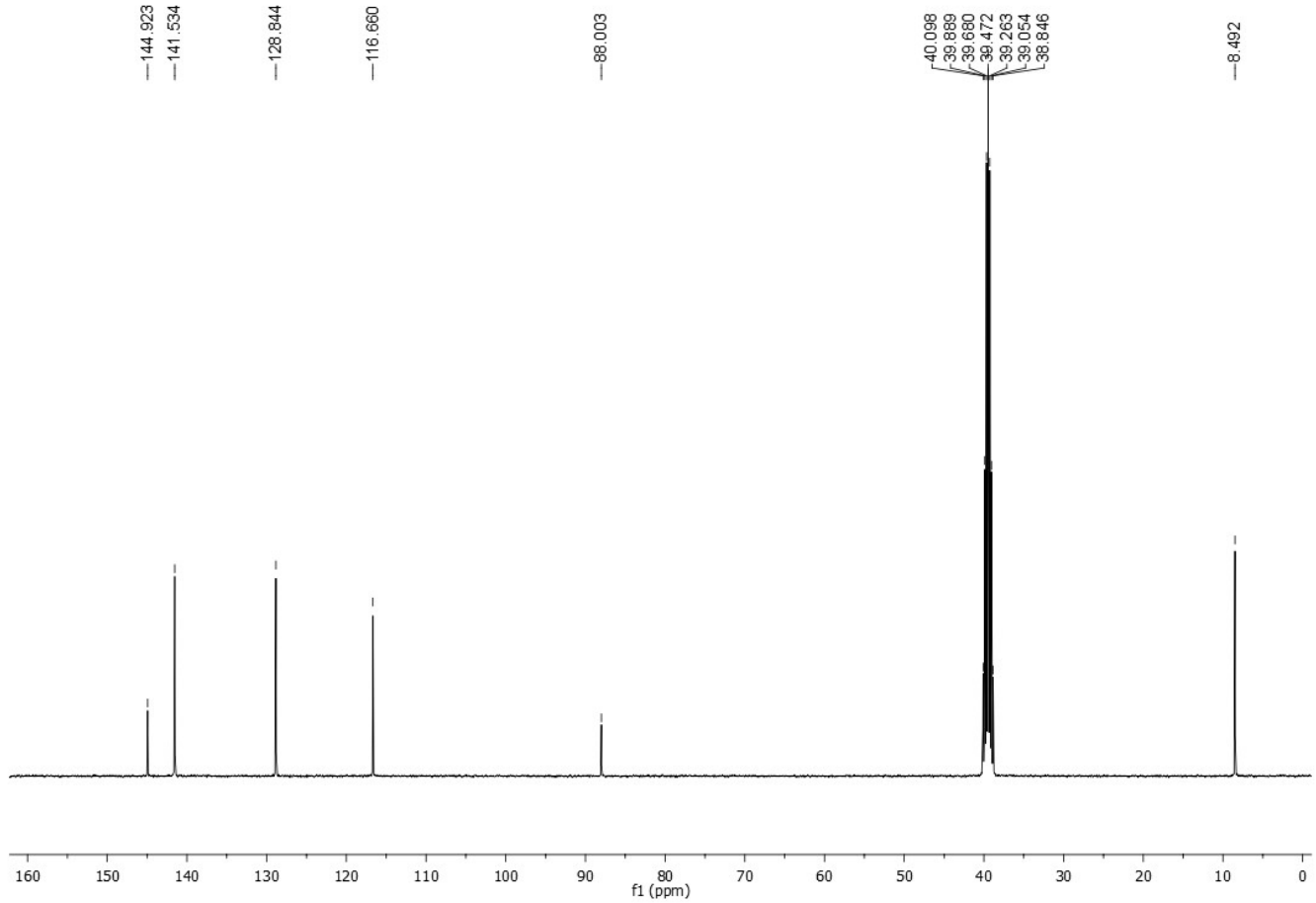


Figure S10 ^{13}C-NMR of compound **3b**. (100 MHz, DMSO-d_6).

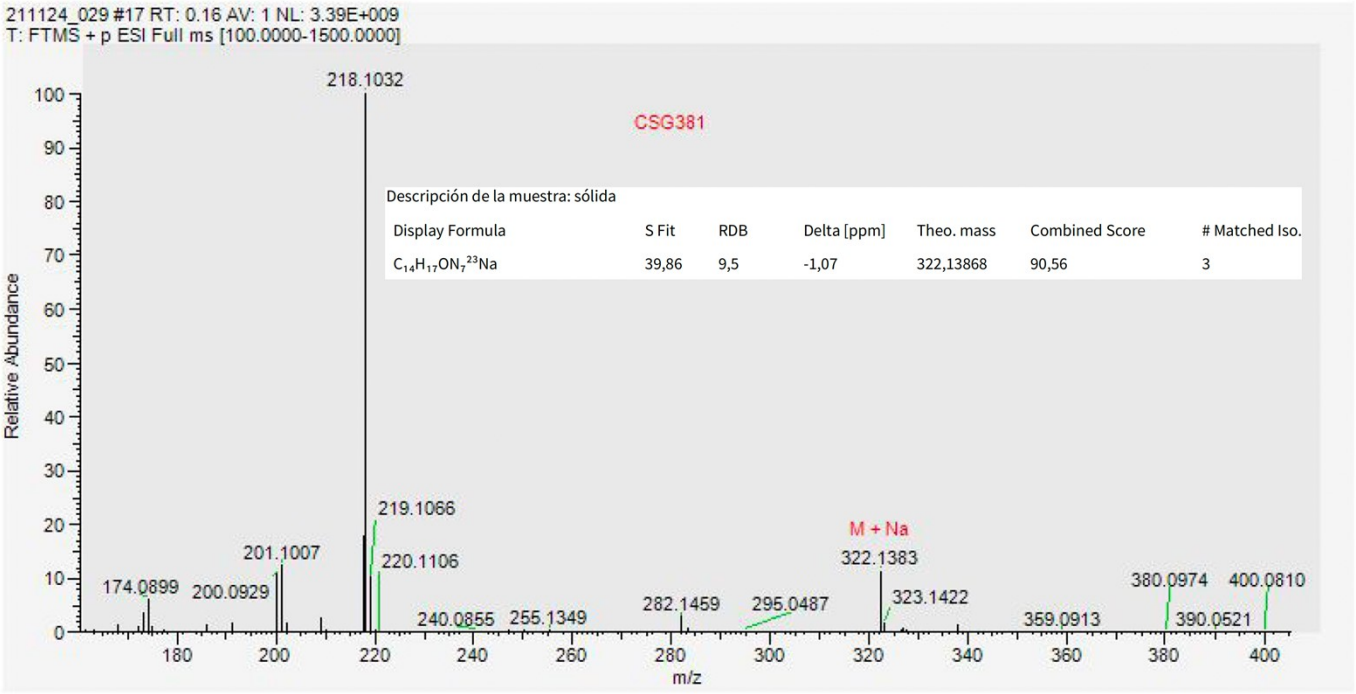
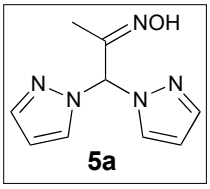


Figure S11 HRMS spectrum of compound **3b**.



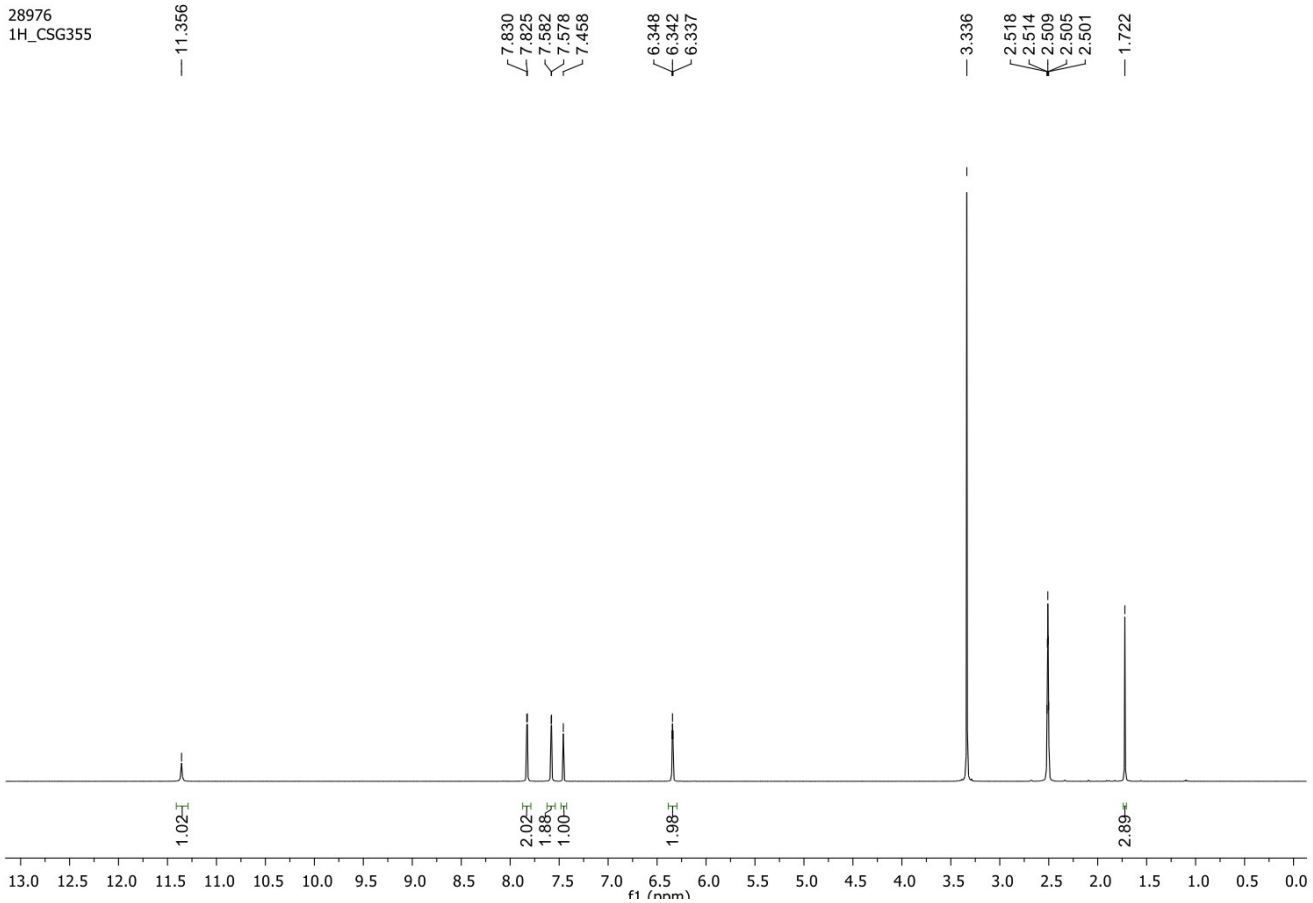
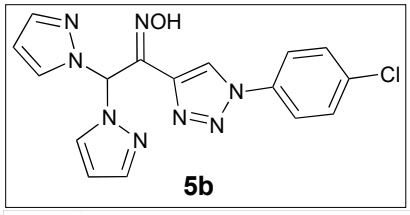


Figure S12 ^{1}H-NMR of compound **5a** (400 MHz, DMSO-d_6).



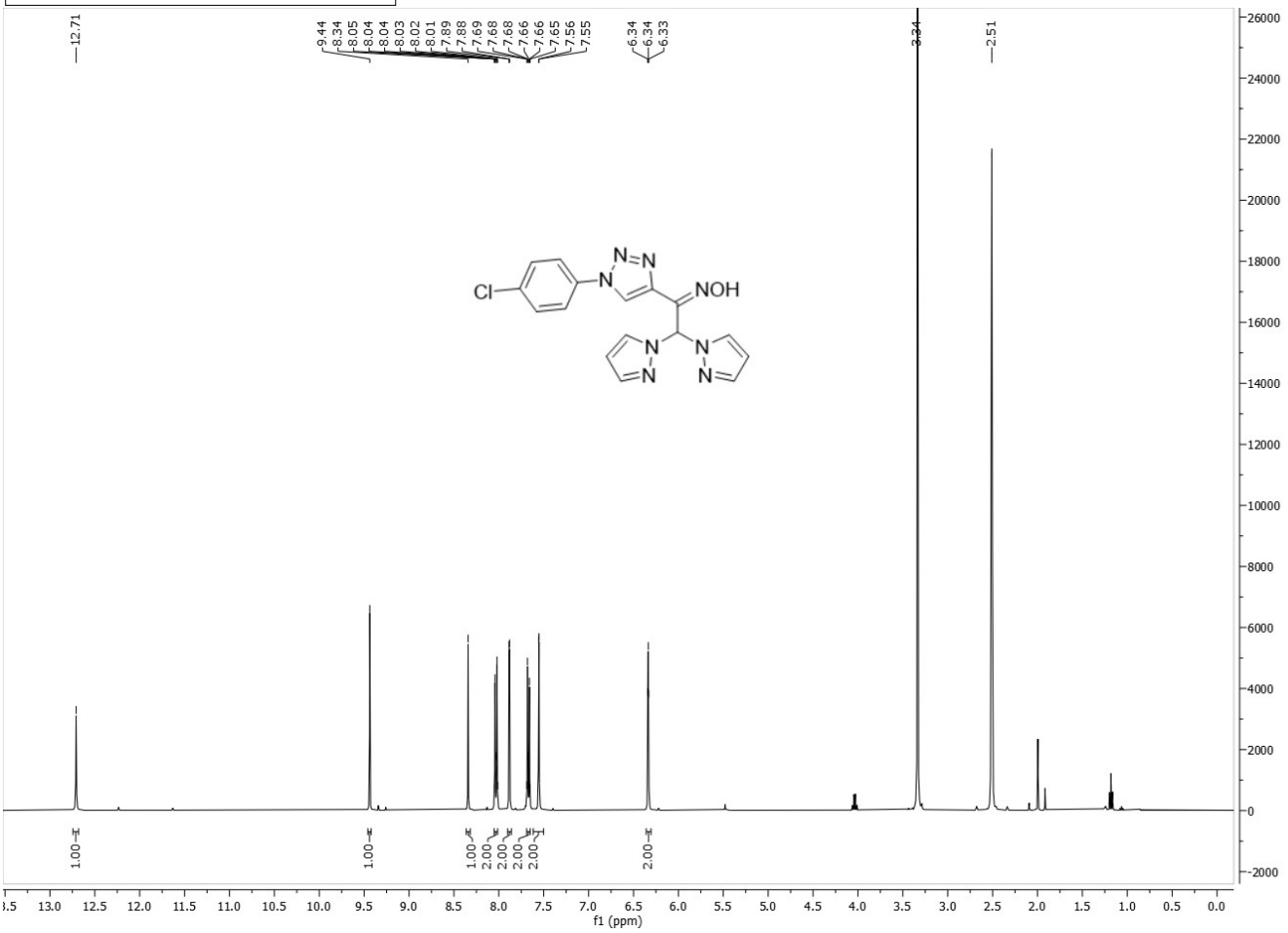


Figure S13 ^{1}H-NMR of compound **5b** (400 MHz, DMSO-d_6).

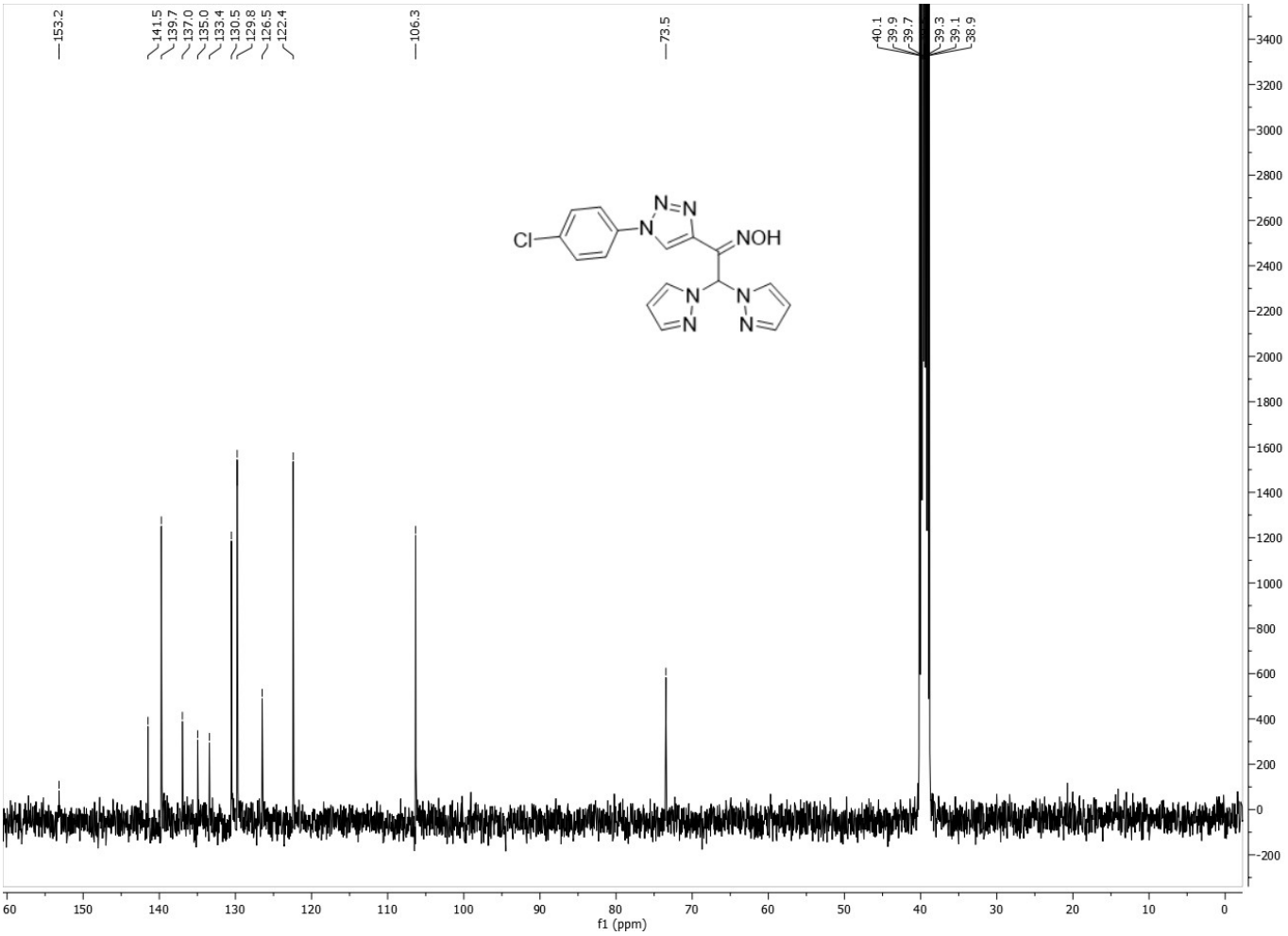
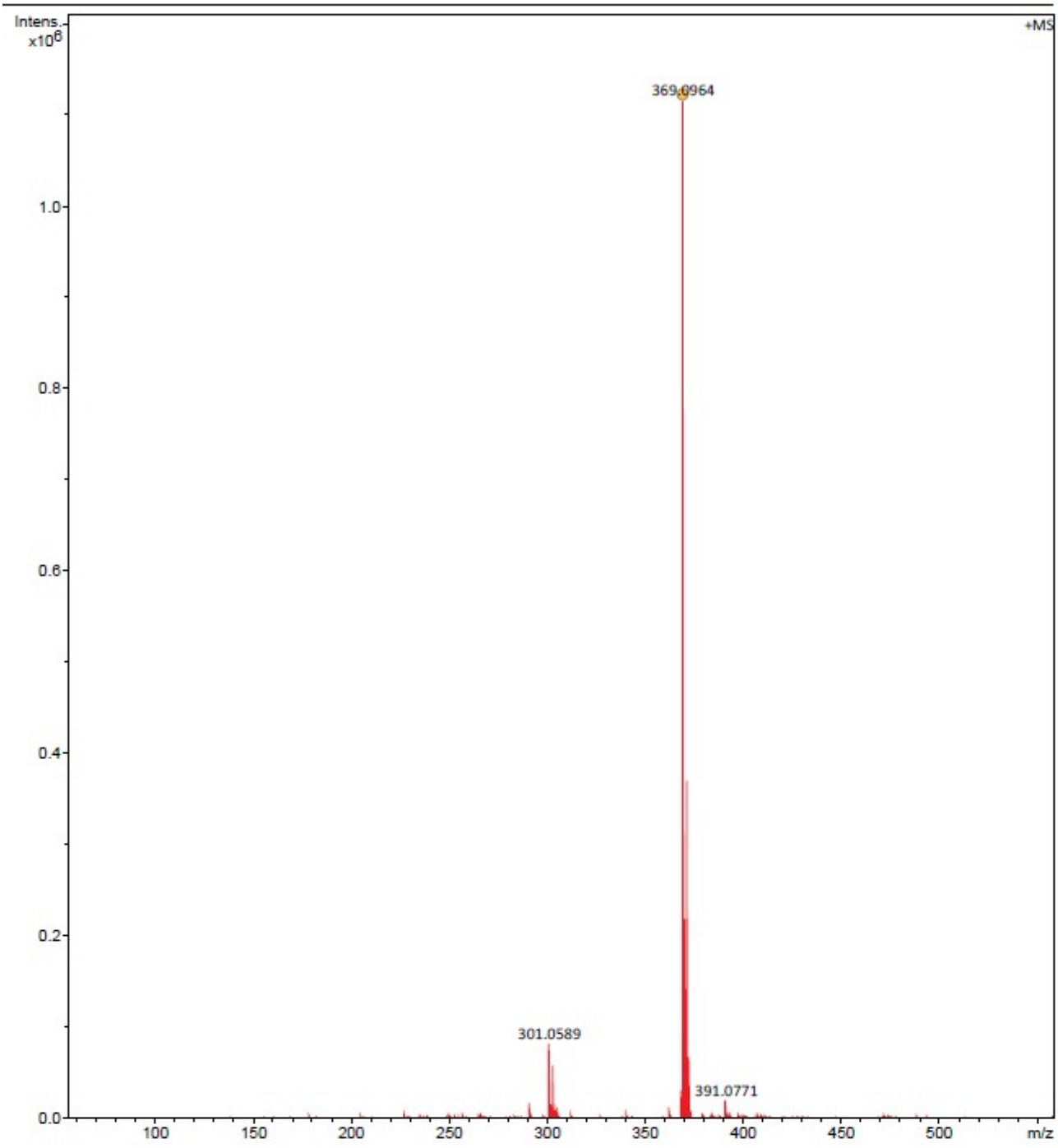


Figure S14 ^{13}C-NMR of compound **5b** (100 MHz, DMSO-d_6).

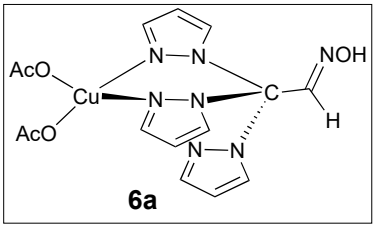


Mass Spectrum Molecular Formula Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
369.0964	1	C16H14ClN8O	369.0974	2.6	7.5	1	100.00	13.5	even	ok

Figure S15 HRMS spectrum of compound **5b**.

3. Copper *C*-Scorpionates



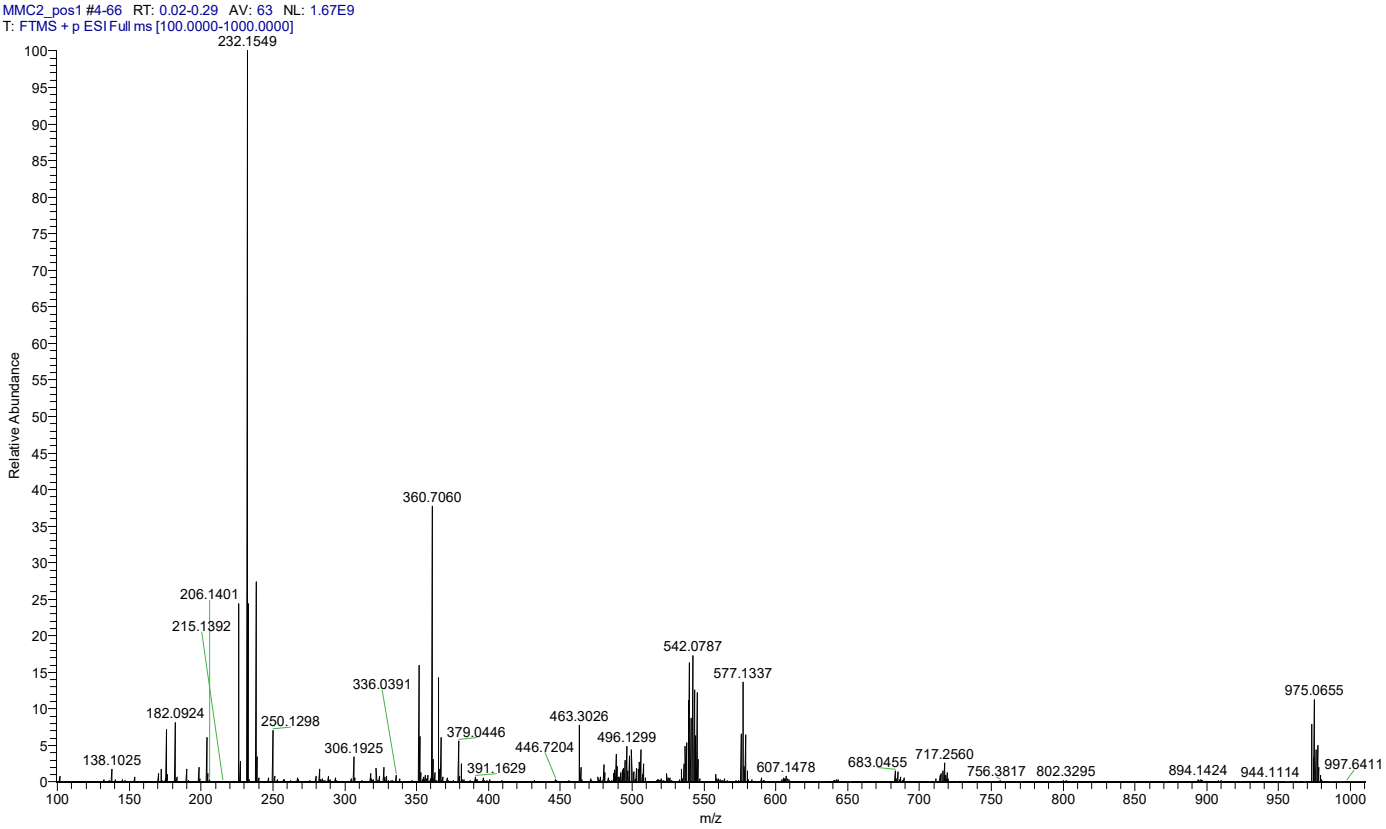
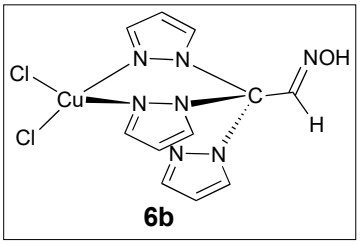
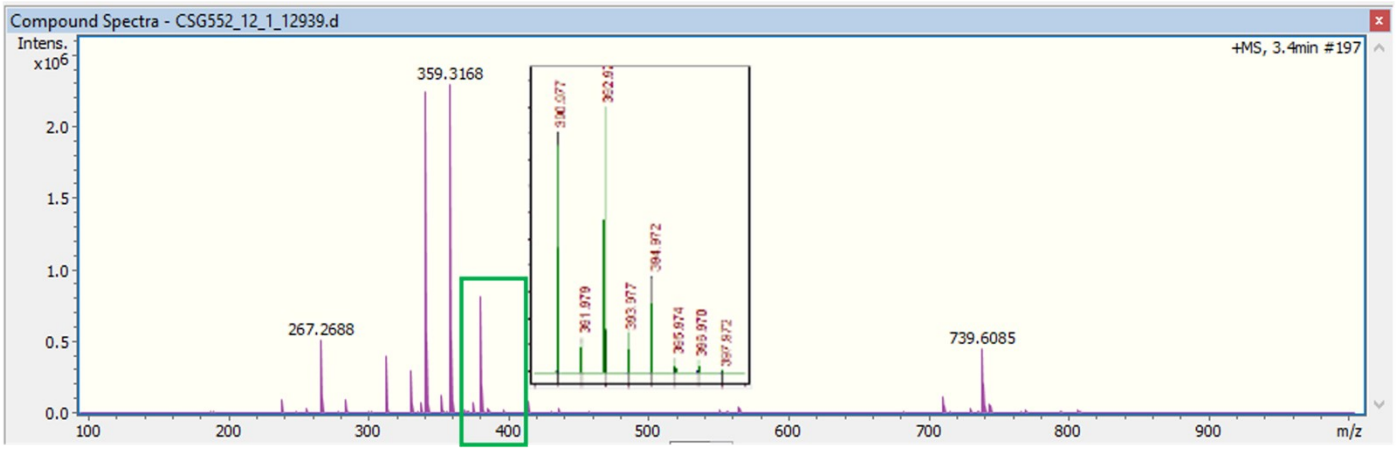


Figure S16 HRMS spectrum of compound **6a.**



6b

HRMS of **6b** obtained in solution



HRMS of **6b** obtained via mechanochemistry

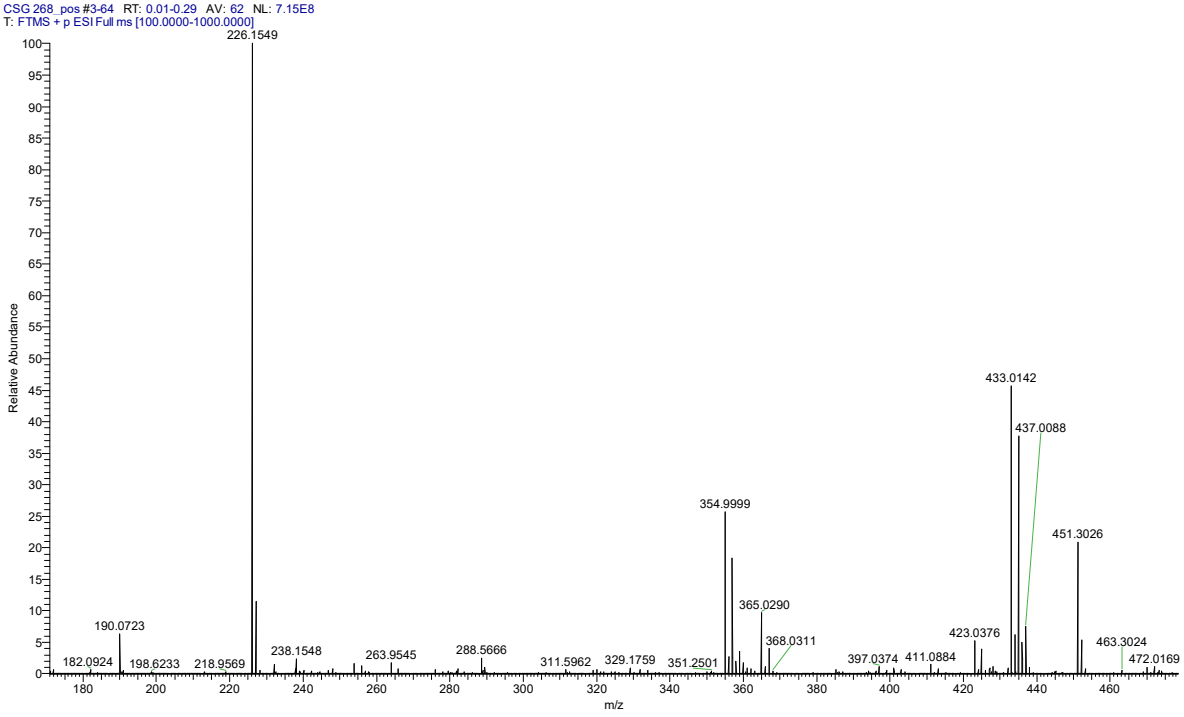


Figure S17. HRMS spectrum of compound **6b.**

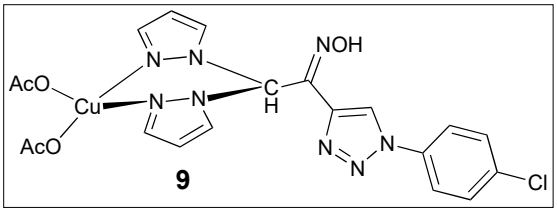
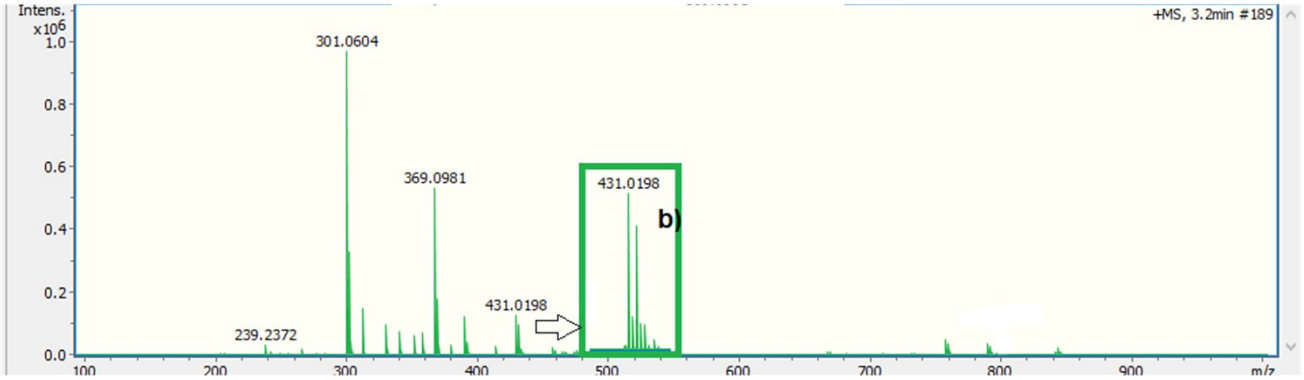


Figure S18. HRMS spectrum of compound **9**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score
431.0198	1	$C_{16}H_{13}ClCuN_8O$	431.0191	-1.6	5.5	1	100.00

4. Infrared and Raman characterization

Table S1. Experimental and calculated bands (B3LYP/6-311++G(d.p). (scale factor 0.977) from the infrared and Raman spectra of 2,2,2-tris(1*H*-pyrazol-1-yl)acetaldehyde oxime (**3a**) (frequencies in cm^{-1}) with the proposed vibration.

IR		Raman		Approximate description
Exp	Calc	Exp	Calc	
3289	3468	3271	3436	vOH
3148	3214	3144	3214	vCH
3130	3202	3133	3186	vCH
3126	3183	3128	3183	vCH
3117	3164	3117	3164	vCH
3111	3160	3113	3160	vCH
3105	3102	3103	3102	vCH
1654/1637	1696	1633	1684	vC=N
1518/1509	1517	1518	1516	vCN(ring)
1423	1441	1507	1477	δOH
1417	1418	1419	1416	vCC(ring)
1384	1384	1386	1391	vCC(ring)
1318	1321	1327	1327	vbreathing ring
1269	1289	1266	1284	δCH
1245	1244	1249	1243	vCN
1227	1227	1228	1227	vCN

1213	1218	1211	1207	δCH (ring)
1200	1195	1202	1198	δCH (ring)
1125	1116	1125	1117	δCH (ring)
1098/1085	1087	1096/1083	1086	δCH (ring)
1055	1072	1052	1073	δCH (ring)
1045	1041	1043	1041	δCH (ring)
1015	1025	1007	1023	δCH (ring)
-	-	982	977	νCN (ring)
960	962	959	963	δCH (ring)
949	939	945	940	νbreathing ring
916	921	914	921	γCH
905	913	905	913	δCC (ring)
862	888	861	864	γCH (ring)
853	859	-	-	δCN
844	844	849	844	γCH (ring)
773/758	747	-	-	γOH
747	745	-	-	γOH
714	739	742	741	γCH (ring)
-	-	702	681	γOH
662	658	659	658	γCN (ring)
N.I.	-	654	653	γCN (ring)
N.I.	-	610	609	γCN (ring)
N.I.	-	603	606	γCN (ring)
N.I.	-	416	414	δCC=N
N.I.	-	406	406	γCC=N
N.I.	-	387	373	δC=NO
N.I.	-	361	366	δCN (ring)
N.I.	-	355	352	νbreathing CN (rings)
N.I.	-	283	278	γCN (ring)
N.I.	-	268	276	γCN (ring)
N.I.	-	258	258	γCN (ring)
N.I.	-	159	182	δCC=N
N.I.	-	117	114	γCN (ring)
N.I.	-	92	97	γCN (ring)
N.I.	-	65	64	γCN (ring)

Abbreviations: ν. elongation; δ. in-plane flexion; γ. out-of-plane flexion; N.I. not investigated.

Table S2. Experimental and calculated bands (B3LYP/6-311++G(d.p). (scale factor 0.977) from the infrared and Raman spectra of **6a** complex (frequencies in cm^{-1}) with the proposed vibration.

IR		Raman		Approximate description
Exp	Calc	Exp	Calc	
1684	1680	1691	1680	νC=N
1560	1602	1573	1602	νC=O
1519	1522	1520	1522	νCC(ring)
1436	1436	1435	1436	$sc CH_3$
1418	1417	1417	1423	νCC(ring)
1388	1389	1387	1389	δOH
	1364		1364	$rock CH_3$

1321	1329	1338	1329	rockCH_3
-	-	1315	1315	vCN(ring)
1263	1267	1278	1267	δOH
1245	1247	1245	1247	δCH
1201	1211	1210	1211	vbreathing ring
1151	1196	1149	1196	δCH (ring)
1118	1117	1119	1117	vbreathing ring
1098	1098	1097	1098	δCH (ring)
1083	1090	1083	1090	δCH (ring)
1045	1047	1046	1047	δCH (ring)
993	998	993	998	γCH_3
961	962	959	962	γCH
914	916	915	913	vbreathing ring
874	864	849	864	γCH (ring)
776	753	772	753	γCH (ring)
N.I.	-	655	659	δOCO
N.I.	-	603	607	γOCC
N.I.	-	414	424	δCCO
N.I.	-	365	377	δC=NO
N.I.	-	288	299	vCu-OAc
N.I.	-	257	259	γCN (ring)
N.I.	-	223	241	γCN (ring)
N.I.	-	205	215	γOCC
N.I.	-	160	166	δCN
N.I.	-	154	154	vCu-OAc
N.I.	-	63	70	γCN (ring)

Abbreviations: v. elongation; δ. in-plane flexion; γ. out-of-plane flexion; N.I. not investigated.

Table S3. Experimental and calculated bands (B3LYP/6-311++G(d.p). (scale factor 0.977) from the infrared and Raman spectra of **6b** complex (frequencies in cm^{-1}) with the proposed vibration.

IR		Raman		Approximate description
Exp	Calc	Exp	Calc	
1636	1679	1637	1679	vCN
1519	1521	1518	1527	vCC (ring)
1459	1430	1434	1423	vCN (ring)
1438	1415	1428	1409	vCC (ring)
1407	1399	1404	1399	δOH
1381	1387	1382	1387	vCN (ring)
1329	1334	1337	1334	vbreathing ring
1321	1321	1318	1321	vbreathing ring
1305	1318	1301	1318	vCN (ring)
1275	1269	1274	1269	δOH
1244	1247	1245	1247	δCH
1206	1231	1218	1231	vCN (ring)
1195	1207	1193	1207	δCH (ring)
-	-	1136	1118	δCH (ring)
1110	1098	1110	1098	δCH (ring)
1106	1093	1104	1093	δCH (ring)

1080/1072	1067	1076/1067	1067	δCH (ring)
1048	1051	1046	1051	δCH (ring)
1028	1038	1021	1038	δCH (ring)
1003	1013	1000	1013	νNO
988	952	985	952	γCH
948	940	945	940	δCNN (ring)
920	914	917	914	δCCC (ring)
869	861	871	861	γCH (ring)
858	856	853	850	γCH (ring)
762	749	762	749	γCH (ring)
745	736	742	736	δCC=N
N.I.	-	647	648	γCN (ring)
N.I.	-	635	637	γCN (ring)
N.I.	-	594	597	γCN (ring)
N.I.	-	565	482	δOH
N.I.	-	425/407	422	γCCN
N.I.	-	392	394	δCC=N
N.I.	-	372	384	δC=NO
N.I.	-	325	324	νCuCl
N.I.	-	288/275	262	γCN (ring)
N.I.	-	228	234	γCN (ring)
N.I.	-	212	210	γCNO
N.I.	-	187	189	γCN (ring)
N.I.	-	178	163	γCN (ring)
N.I.	-	159	160	δCuCl
N.I.	-	114	123	δCuCl
N.I.	-	102	96	γCN (ring)
N.I.	-	79	81	γCN (ring)
N.I.	-	61	66	γCN (ring)

Abbreviations: ν. elongation; δ. in-plane flexion; γ. out-of-plane flexion; N.I. not investigated.

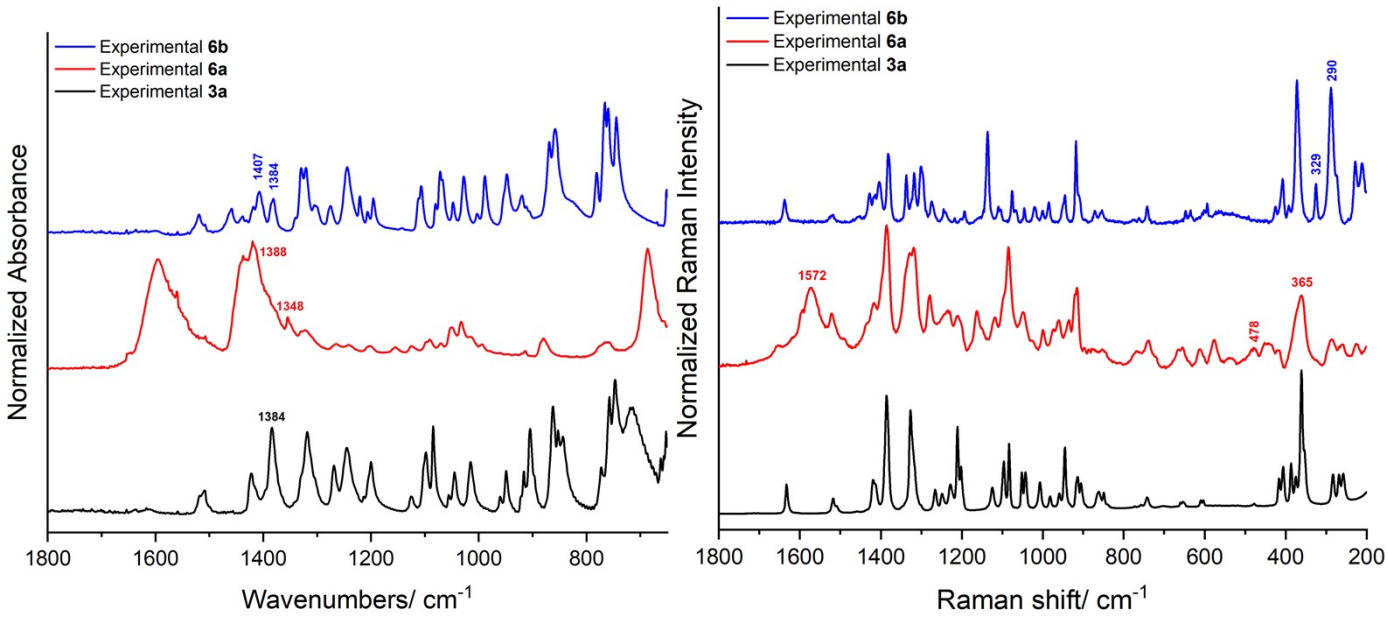


Figure S19. Comparison between the IR (left) and Raman (right) experimental spectra of the (*E*)-2,2,2-tris(1*H*-pyrazol-1-yl)acetaldehyde oxime **3a** and the complexes **6a** and **6b**. obtained in solution.

5. Characterization of the CuAAC products

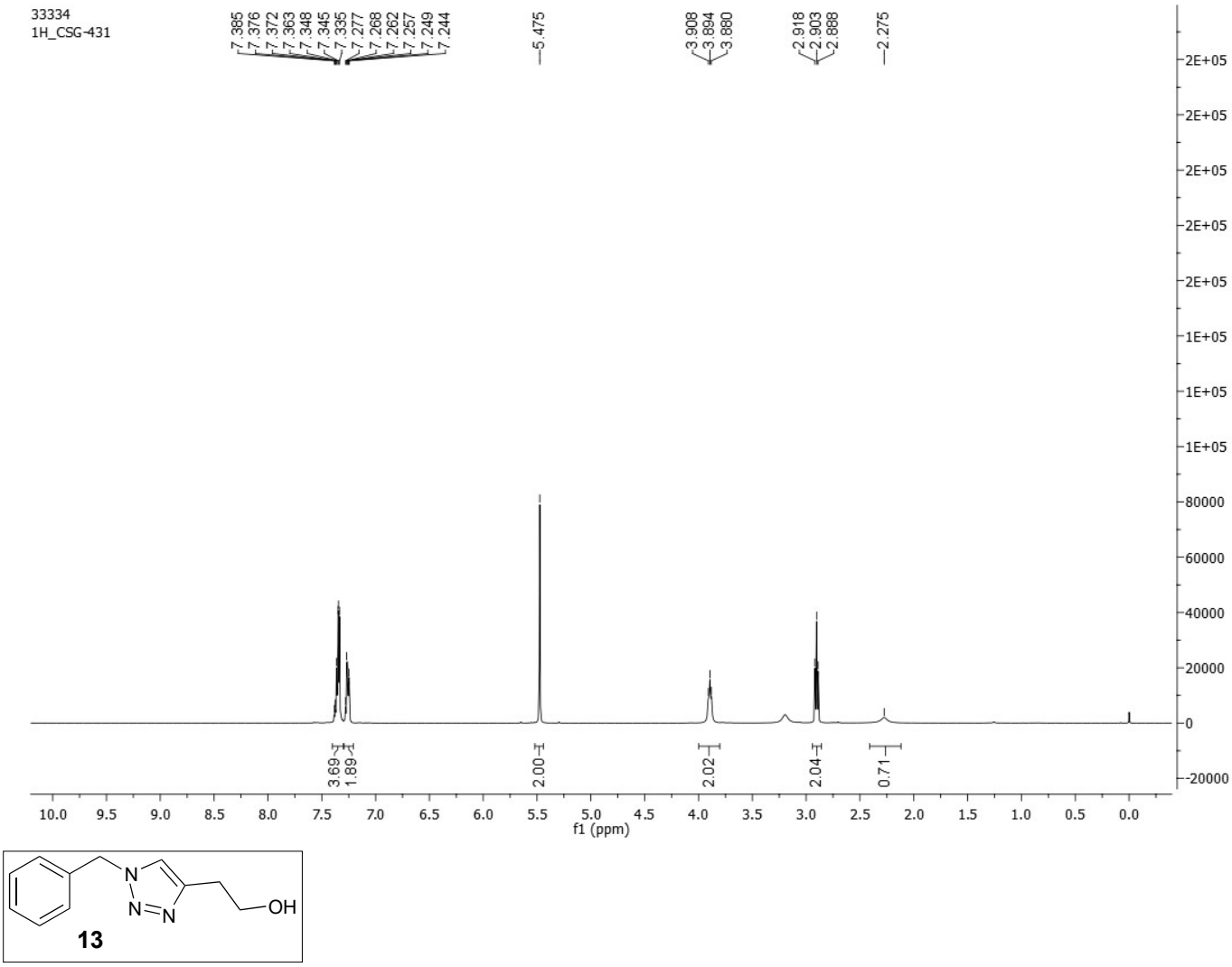
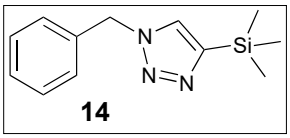


Figure S20. ^{1}H-NMR of compound **13** (400 MHz, $CDCl_3$).



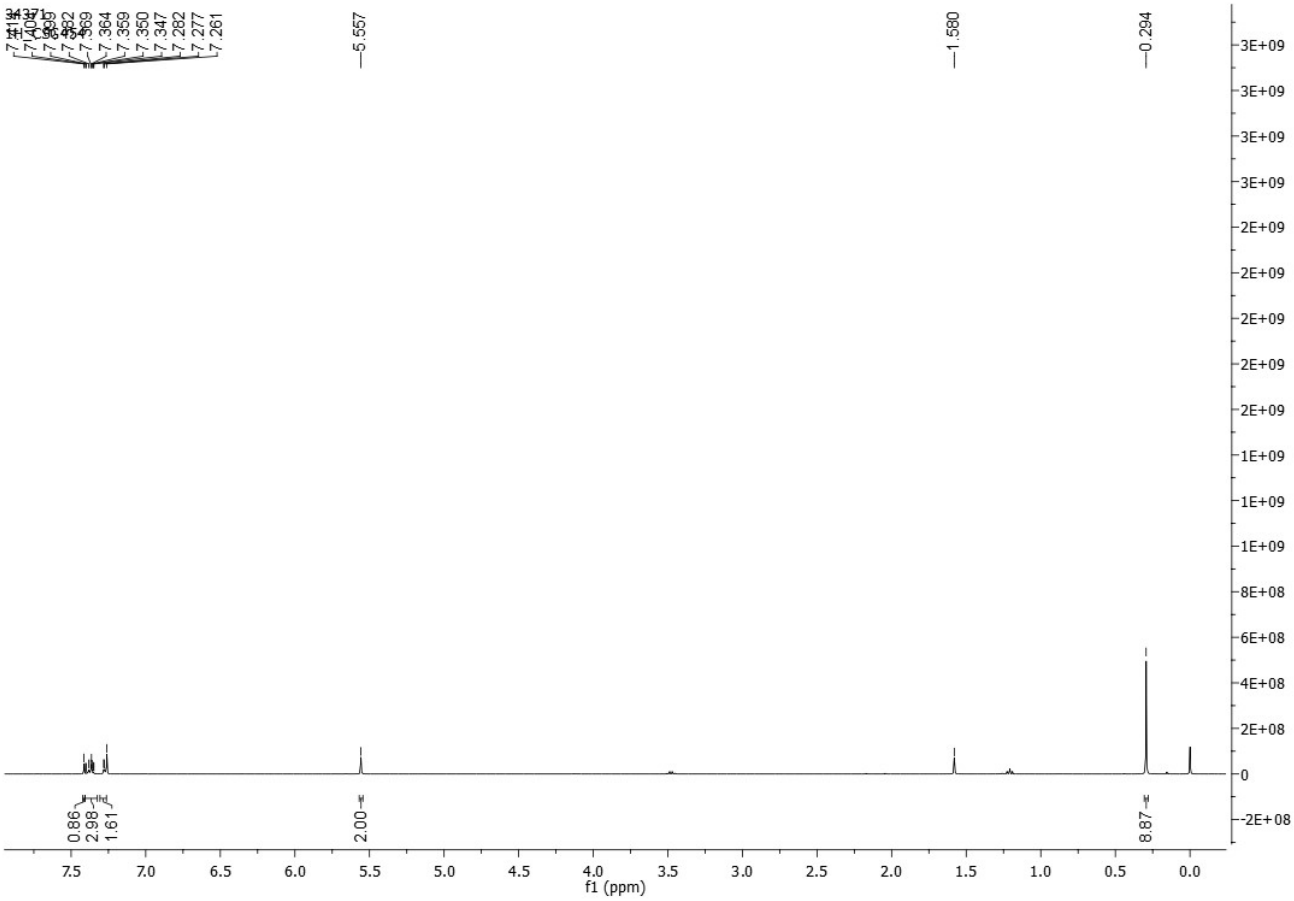
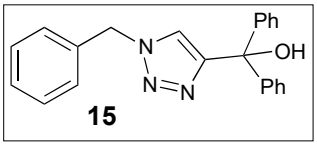


Figure S21. ^{1}H-NMR of compound **14** (400 MHz, $CDCl_3$).



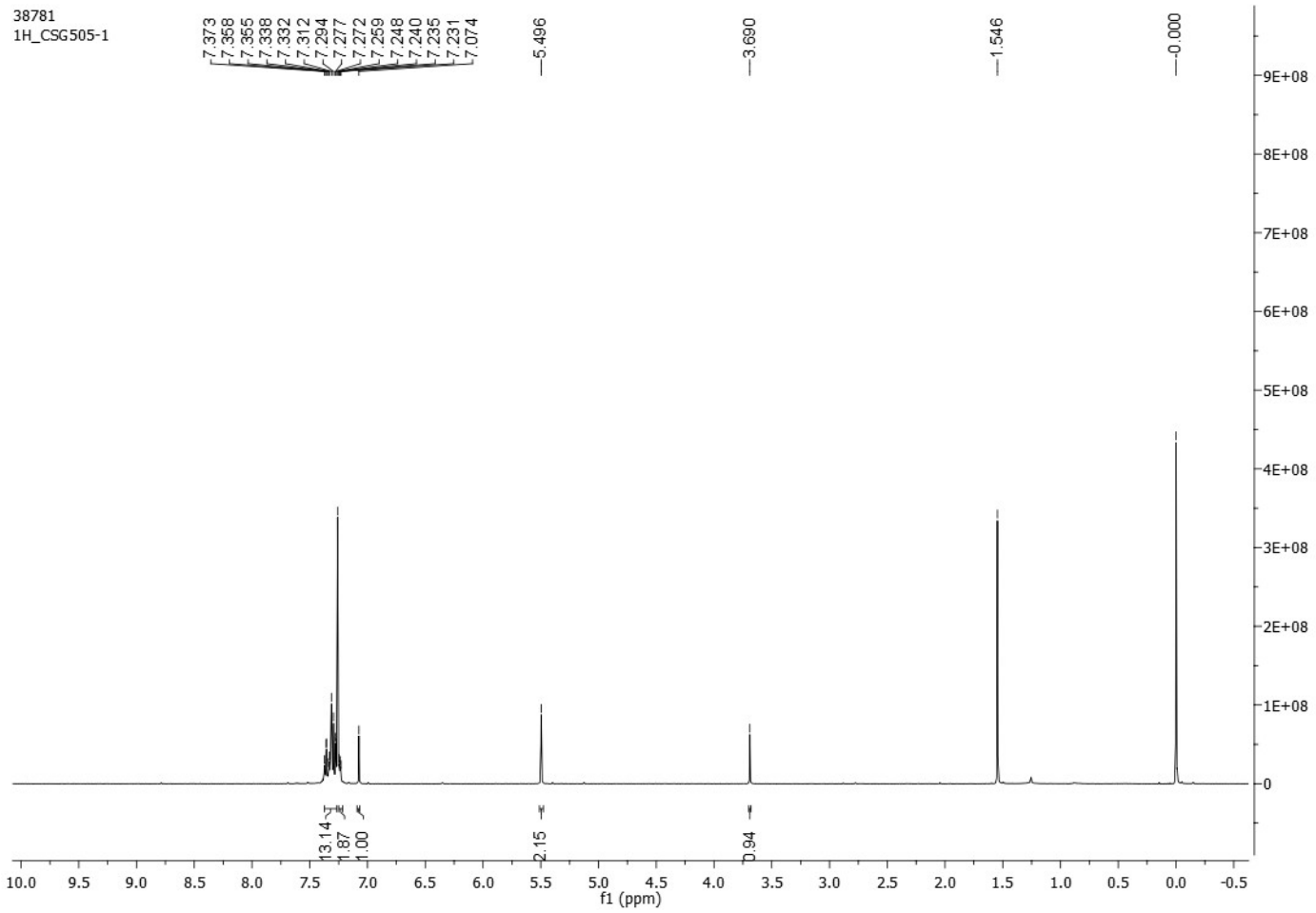
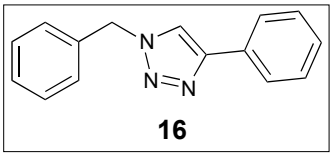


Figure S22. ^{1}H-NMR of compound **15** (400 MHz, $CDCl_3$).



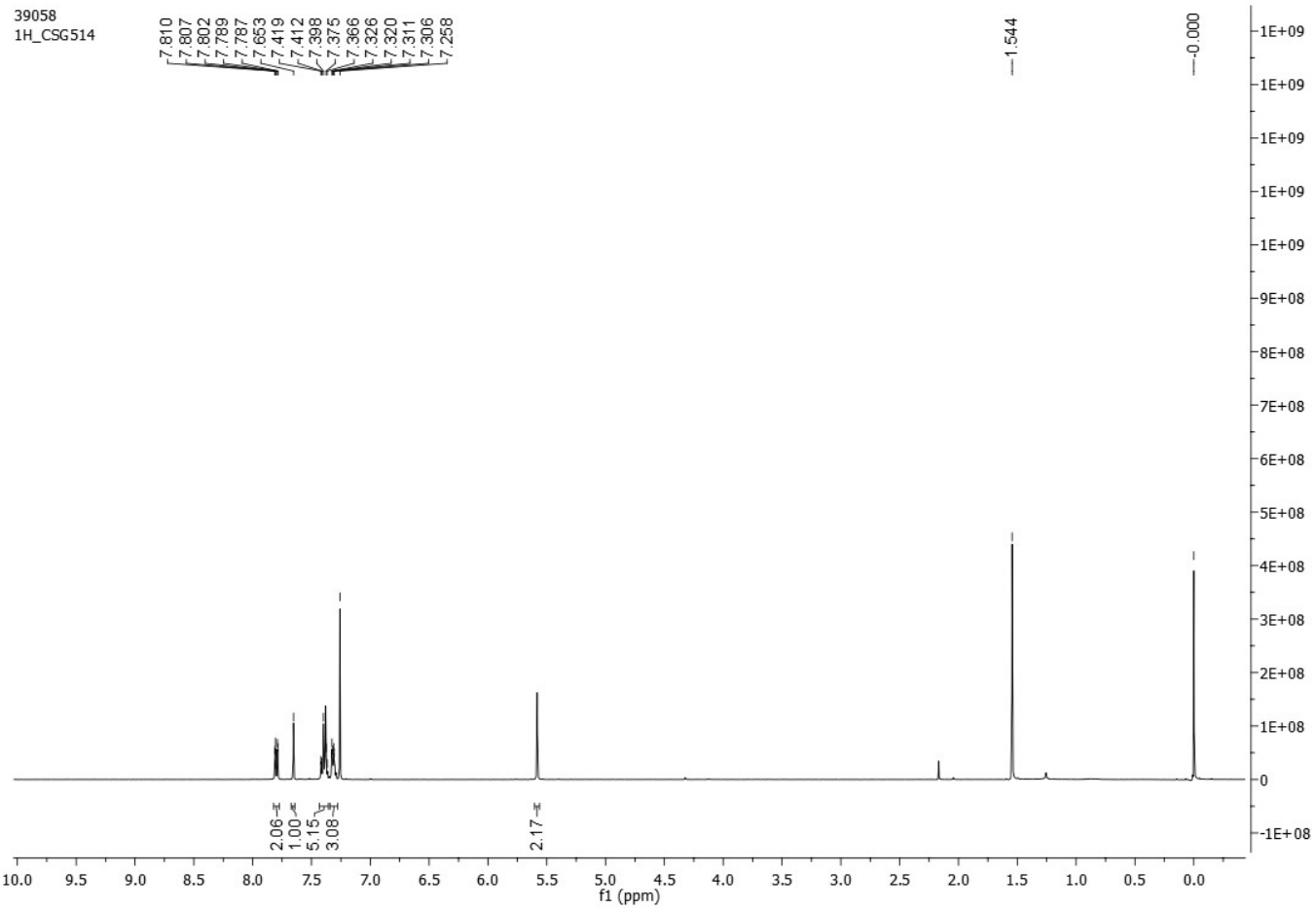
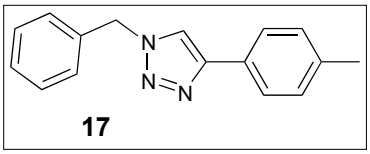


Figure S23. ^{1}H-NMR of compound **16** (400 MHz, $CDCl_3$).



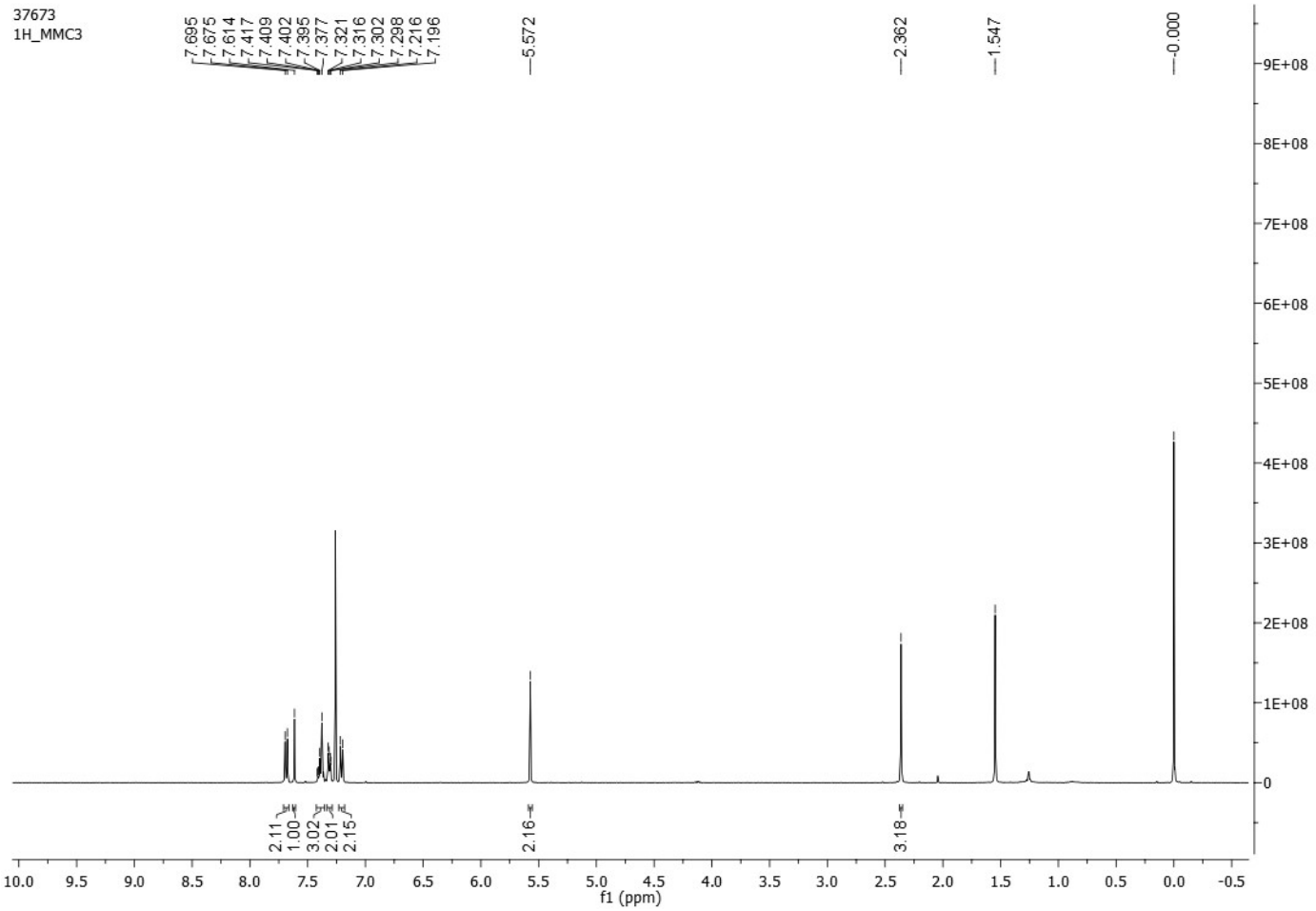
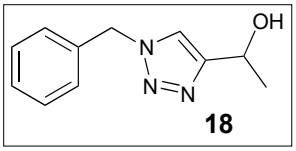


Figure S24. ^{1}H-NMR of compound **17** (400 MHz, $CDCl_3$).



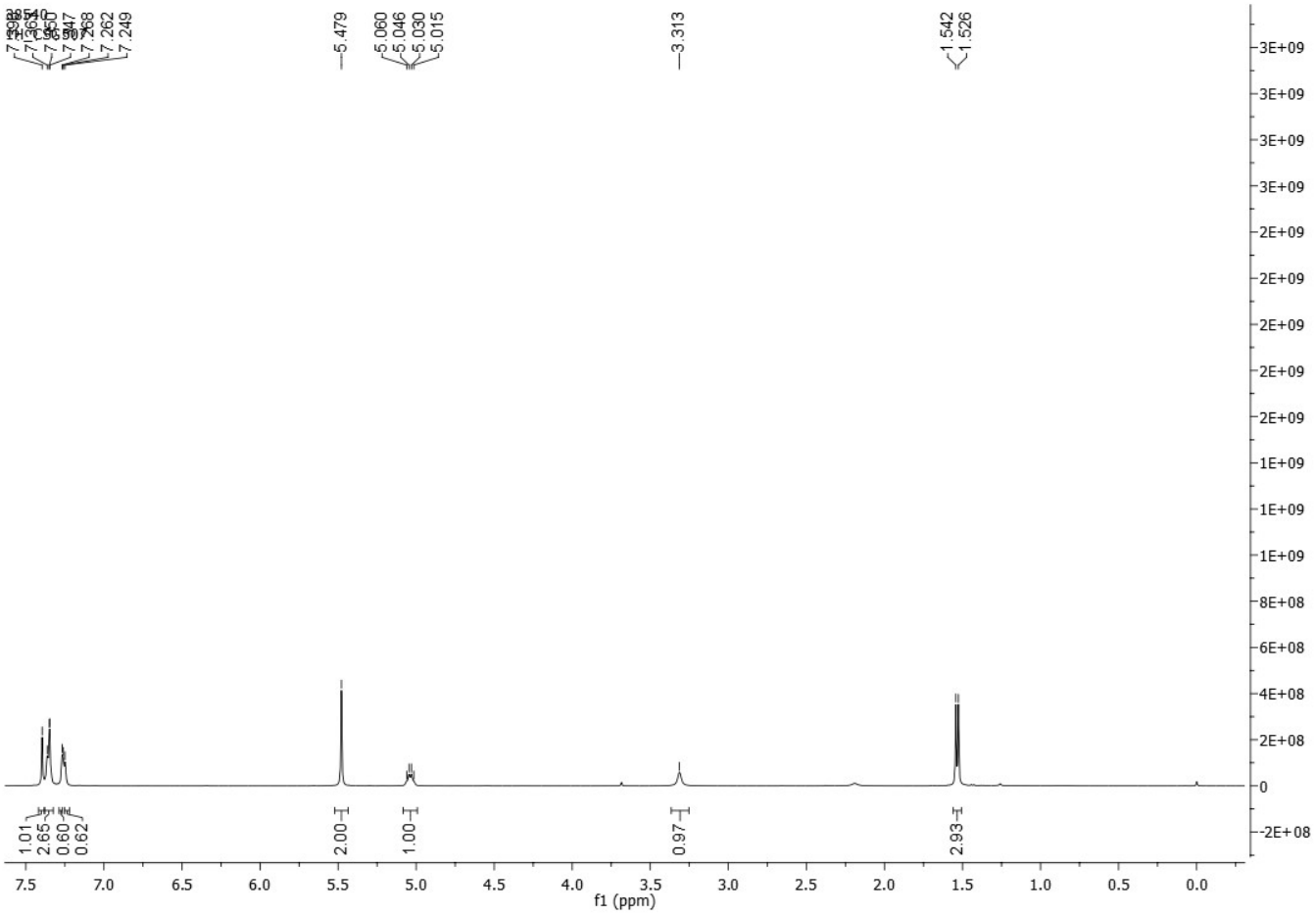


Figure S25. ^{1}H-NMR of compound **18** (400 MHz, $CDCl_3$).

6. E-Factor and EcoScale Calculation

Table S4. EcoScale Penalty point calculation table

Parameter		Penalty points
1	**Yield**	(100 – %yield)/2
2	**Price of reaction components** (to obtain 10 mmol of end product)	
	Inexpensive (< $10)	0
	Expensive (> $10 and < $50)	3
	Very expensive (> $50)	5
3	**Safety**[a]	
	N (dangerous for environment)	5
	T (toxic)	5
	F (highly flammable)	5
	E (explosive)	10
	F+ (extremely flammable)	10
	T+ (extremely toxic)	10
4	**Technical setup**	
	Common setup	0
	Instruments for controlled addition of chemicals[b]	1
	Unconventional activation technique[c]	2
	Pressure equipment, > 1 atm[d]	3
	Any additional special glassware	1
	(Inert) gas atmosphere	1
	Glove box	3
5	**Temperature/time**	
	Room temperature, < 1 h	0
	Room temperature, < 24 h	1
	Heating, < 1 h	2
	Heating, > 1 h	3
	Cooling to 0 °C	4
	Cooling, < 0 °C	5
6	**Workup and purification**	
	None 0	0
	Cooling to room temperature	0
	Adding solvent	0
	Simple filtration	0
	Removal of solvent with bp < 150 °C	0
	Crystallization and filtration	1
	Removal of solvent with bp > 150 °C	2
	Solid phase extraction	2
	Distillation	3
	Sublimation	3
	Liquid-liquid extraction[e]	3
	Classical Chromatography	10

[a]Based on the hazard warning symbols. [b]Dropping funnel, syringe pump, gas pressure regulator, etc. [c]Microwave irradiation, ultrasound or photochemical activation, etc. [d]$scCO_2$, high pressure hydrogenation equipment, etc. [e]If applicable, the process includes drying of solvent with desiccant and filtration of desiccant.

Table S5. Data for the trichloroacetaldehyde oxime synthesized as described by Brintzinger and Titzmann[1]

SYNTHESIS OF TRICHLRO OXIME

E-FACTOR

grams of REACTANTS

Compound	Mw	density	mol	mL	grams
Cloral hydrat	165,4		2		330,8
hydroxylamir	69,49		1		69,49
CaCl2	147,01		1,49649684		220
water	18	1	11,1111111	200	200

grams of PRODUCT

Product Chloral oxime			
MW		mol product	grams
162,39		0,71	115,2969

E-FACTOR
6,11458851

ECOSCALE

mol to prepare 10 mmol of product	reaction conditions: 1 h 50 ºC	Price (SIGMA-ALDRICH 20	sds INFO
0,02816901	liquid-liquid extraction	50G 34,60 euros	10 highly toxic
0,01408451	evaporation	100G 33,10 Euros	10 highly toxic + 5 environment
0,02107742	remove the excess of chloral through destilation at 1	250G 26,80 euros	toxic 5
0,15649452	Yield 71%		

DETERMIANTION of PRICE of REACTANTS

solids				RESULT		
	mass bottle	Mm (g/mol)	price (euro)	price (euro/n	mmol to pro	Cost to produce 10 mmol pf product
Chloral hydrate	50	165,4	34,6	0,1144568	0,02816901	0,00322414
Hydroxylamine	100	69,49	33,1	0,02300119	0,01408451	0,00032396
CaCl2	250	147,01	26,8	0,01573947	0,02107742	0,00033217

Liquids					RESULT		
	volume bottl	density	mass bottle	Mm (g/mol)	price (euro)	price (euro/mmol)	
Water				18		0	0

	yield	price	Safety	Technical set	Temperature	Workup/Puri	TOTAL
penalty poin	14,5	0	30	0	2	6	52,5

ECOSCALE (100-penalty points)
47,5

Table S6. Data for synthesis of compound **3a** (this work) and the previously described by Pinho e Melo[2].

SYNTHESIS OF TrisPYRAZOL-1-YL OXIME

E-FACTOR

grams of REACTANTS AND SOLVENTS this work

Compound	Mw	density	mmol	mL	grams
oxime	162,4		3,2		0,51968
pyrazole	68,1		10,5		0,71505
Na2CO3	106		16		1,696

grams of REACTANTS AND SOLVENTS Pinho e Melo

Compound	Mw	density	mmol	mL	grams
oxime	162,4		3,5		0,5684
pyrazole	68,1		10,5		0,71505
Na2CO3	106		17,5		1,855
DCM	84,93	1,33	548,098434	35	46,55

grams of PRODUCT

	yield	product Mw	mmol	grams
this work	53	257,3	1,696	0,4363808
Pinho e Melc	87	257,3	2,784	0,7163232

E-FACTOR

this work	5,71599209
Pinho e Melc	68,365965

ECOSCALE

mmol to prepare 10 mmol of product	Price (SIGMA-ALDRICH 2023)	sds INFO	reaction conditions: 1 h 50 ºC
18,82352941			Mechanochemistry (25Hz, 30 min)
61,76470588	5G 20,20€	Highly toxic 10 + Harmful to aquatic life	add ethyl acetate
94,11764706	500G 42,00€	Toxic 5	filtrate
			evaporation
12,57183908			16 h, rt
37,71551724			filtration
62,8591954			evaporation
1968,744375	1L 148,00€	Highly toxic 10	flash chromatography

DETERMINATION of PRICE of REACTANTS

solids				RESULT		
	mass bottle	Mm (g/mol)	price (euro)	price (euro/r	mmol to pro	Cost to produce 10 mmol pf product
oxime						
Pyrazole	5	68,1	20,2	0,275124	61,7647059	16,9929529
Na2CO3	500	106	42	0,008904	94,1176471	0,83802353

Liquids					RESULT		
	volume bottl	density	mass bottle	Mm (g/mol)	price (euro)	price (euro/mmol)	
DCM	1000	1,33	1330	84,93	148	0,00945086	1968,74438 18,6063218

		yield	price	Safety	Technical set	Temperature	Workup/Puri	TOTAL
penalty points	this Work	23,5	3	20	2	0	0	48,5
	Pinho e Melc	6,5	6	30	0	1	10	53,5

ECOSCALE (100-penalty points)

this Work	51,5
Pinho e Melo	46,5

Table S7. Data for the synthesis of **6b (this work)** and the previously described synthesis of tris(pyrazol-1-yl)methane described by Pettinari[3]

SYNTHESIS of Cu COMPLEX

E-FACTOR

grams of REACTANTS AND SOLVENTS this work

Compound	Mw	density	mmol	mL	grams
pro-ligand	257,26		0,1943559		0,05
CuCl2.2H2O	170,48		0,1943559		0,03313379

grams of REACTANTS AND SOLVENTS Pettinari 2002

Compound	Mw	density	mmol	mL	grams
pro-ligand	214,23		0,98025487		0,21
CuCl2.2H2O	170,48		0,49859221		0,085
Methanol	32,04	0,792	741,573034	30	23,76

grams of PRODUCT

	yield	product Mw	mmol	grams
this work	79	391,7	0,15354116	0,06014207
Pettinari 200	43	348,68	0,21439465	0,07475513

E-FACTOR

this work	0,3822901
Pettinari 200	320,783951

ECOSCALE

mmol to prepare 10 mmol of product	Price (SIGMA-ALDRICH 2023)	sds INFO	reaction conditions: 1 h 50 ºC
			Mechanochemistry (25Hz, 30 min)
12,6582278			removed with spatula
12,6582276	100G 65,70€	Highly Toxic 10 and Toxic to aquatic life 5	
45,7219835			12 h, rt, nitrogen atm.
23,255814	100G 65,70€	Highly Toxic 10 and Toxic to aquatic life 5	filtration
34589,1575	1L 77,90€	Acute toxicity 10 highly flammable 10	washed with diethyl ether

DETERMIANTION of PRICE of REACTANTS

solids

	mass bottle	Mm (g/mol)	price (euro)	RESULT price (euro/r	mmol to pro	Cost to produce 10 mmol pf product
pro-ligand						
CuCl2.2H2O	100	170,48	65,7	0,11200536	12,6582276	1,41778934

Liquids

	volume bottl	density	mass bottle	Mm (g/mol)	price (euro)	RESULT price (euro/mmol)		
methanol	1000	0,792	792	32,04	77,9	0,00315141	741,573034	2,337

		yield	price	Safety	Technical set	Temperature	Workup/Puri	TOTAL
penalty poin	this Work	10,5	0	15	2	0	0	27,5
	Pettinari 200	28,5	0	35	1	1	0	65,5

ECOSCALE (100-penalty points)

this Work	72,5
Pettinari 200	34,5

Table S8. Data for synthesis of compound **13 (this work)** and as previously described by Martins.[4]

CuAAC reaction

E-FACTOR

grams of REACTANTS AND SOLVENTS this work

Compound	Mw	density	mmol	mL	grams
Benzyl bromi	171,04		0,436		0,05
3-butinol	70,09		0,4796		0,03361516
Sodium azid	65,01		0,4796		0,0311788
Catalyst	391,7		0,00654		0,00256172

grams of REACTANTS AND SOLVENTS Martins 2018

Compound	Mw	density	mmol	mL	grams
Benzyl bromi	171,04		0,3		0,051312
3-butinol	70,09		0,33		0,0231297
Sodium azid	65,01		0,33		0,0214533
Catalyst	833,94		0,0045		0,00375273
H2O	18	1	41,6666667	0,75	0,75
Methanol	32,04	0,792	18,5393258	0,75	0,594

grams of PRODUCT

	yield	product Mw	mmol	mgrams
this work	78	203,25	0,374088	0,07603339
Pinho e Melc	79	203,25	0,237	0,04817025

E-FACTOR

this work	0,54347563
Martins 2011	28,9696956

ECOSCALE

mmol to prepare 10 mmol of product	Price (SIGMA-ALDRICH 2023)	sds INFO	reaction conditions:
11,6550117	25G 24,30€	Toxicity 5	
12,8205128	5G 55,40€	Toxic 5, flamable 5	mech 3h
12,8205128	10G 26,30€	Hyghly toxic 10, harmful aquatic life 5	cromatography
0,17482517			
			MW(125ºC, 30 min)
			water added, filtered off, washed with petroleum ether and dried in vacuum.
12,6582278			
13,9240506			
13,9240506			
0,18987342			
1758,0872			
782,250036	1L 77,90€	Acute toxicity 10 highly flammable 10	

DETERMINATION of PRICE of REACTANTS

solids

	mass bottle	Mm (g/mol)	price (euro)	RESULT price (euro/mi	mmol to pro	Cost to produce 10 mmol pf product
Benzyl bromide	25	171,04	24,3	0,16625088	11,6550117	1,93765594
3-butinol	5	70,09	55,4	0,7765972	12,8205128	9,95637436
Sodium azide	10	65,01	26,3	0,1709763	12,8205128	2,19200385
Catalyst					0,17482517	

Liquids

	volume bottl	density	mass bottle	Mm (g/mol)	price (euro)	RESULT price (euro/mmol)		
Methanol	1000	0,792	792	32,04	77,9	0,003151409	782,250036	2,46318987

		yield	price	Safety	Technical set	Temperature/	Workup/Puri	TOTAL
penalty poin	this Work	11	0	30	2	1	10	54
	Martins 201	10,5	0	50	2	2	0	64,5

ECOSCALE (100-penalty points)

this Work	46
Pinho e Melc	35,5

7. XRD supplementary material

Table S9. CRYSTAL DATA AND DETAILS OF THE STRUCTURE DETERMINATION
FOR: CSG503B_A P 21/N R = 0.04

CRYSTAL DATA	
FORMULA	C11 H11 N7 O
FORMULA WEIGHT	257.27
CRYSTAL SYSTEM	MONOCLINIC
SPACE GROUP	P21/N (NO. 14)
A. B. C [ANGSTROM]	10.2989(3) 9.5354(3) 12.3745(4)
ALPHA. BETA. GAMMA [DEG]	90 91.395(2) 90
V [ANG**3]	1214.87(7)
Z	4
D(CALC) [G/CM**3]	1.407
MU(MOKA) [/MM]	0.100
F(000)	536
CRYSTAL SIZE [MM]	0.16 X 0.18 X 0.25
DATA COLLECTION	
TEMPERATURE (K)	293
RADIATION [ANGSTROM]	MOKA 0.71073
THETA MIN-MAX [DEG]	3.4. 27.5
DATASET	-13: 13 ; -12: 12 ; -16: 16
TOT.. UNIQ. DATA. R(INT)	114886. 2792. 0.047
OBSERVED DATA [I > 2.0 SIGMA(I)]	2285
REFINEMENT	
NREF. NPAR	2792. 175
R. WR2. S	0.0353. 0.0975. 1.03
W = ^2^(FO^2^)+(0.0422P)^2^+0.3590P] WHERE P=(FO^2^+2FC^2^)/3'	
MAX. AND AV. SHIFT/ERROR	0.00. 0.00
MIN. AND MAX. RESD. DENS. [E/ANG^3]	-0.18. 0.20

Table S10. FINAL COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS OF THE NON-HYDROGEN ATOMS
FOR: CSG503B_A P 21/N R = 0.04

ATOM	X	Y	Z	U(EQ) [ANG^2]
O1	0.54282(10)	0.59101(10)	0.37986(8)	0.0442(3)
N1	0.48687(11)	0.45835(12)	0.38222(8)	0.0399(3)
N2	0.36140(10)	0.24657(11)	0.16577(8)	0.0333(3)
N3	0.29901(12)	0.35381(13)	0.11518(9)	0.0472(4)
N4	0.50228(9)	0.15852(11)	0.30132(8)	0.0331(3)
N5	0.62023(10)	0.17497(13)	0.25636(8)	0.0416(3)
N6	0.29495(10)	0.24362(11)	0.34647(8)	0.0346(3)
N7	0.31050(12)	0.25073(15)	0.45530(9)	0.0518(4)
C1	0.40572(11)	0.26521(13)	0.27736(9)	0.0304(3)
C2	0.46467(12)	0.41014(13)	0.28988(9)	0.0345(3)
C3	0.25410(15)	0.2973(2)	0.02448(11)	0.0554(5)
C4	0.28510(15)	0.1570(2)	0.01622(11)	0.0554(5)
C5	0.35341(14)	0.12596(16)	0.10844(11)	0.0446(4)
C6	0.67504(15)	0.05020(18)	0.26689(12)	0.0522(5)
C7	0.59441(17)	-0.04567(18)	0.31614(14)	0.0587(5)
C8	0.48364(15)	0.02565(16)	0.33627(12)	0.0489(5)
C9	0.19168(15)	0.23615(17)	0.49122(12)	0.0528(5)
C10	0.10096(14)	0.22088(17)	0.40808(13)	0.0518(5)
C11	0.16907(12)	0.22661(15)	0.31600(11)	0.0411(4)

U(EQ) = 1/3 OF THE TRACE OF THE ORTHOGONALIZED U TENSOR

Table S11. HYDROGEN ATOM POSITIONS AND ISOTROPIC DISPLACEMENT PARAMETERS
FOR: CSG503B_A P 21/N R = 0.04

ATOM	X	Y	Z	U(ISO) [ANG^2]
H1	0.5577(17)	0.6139(19)	0.4548(15)	0.0660
H2	0.48416	0.46279	0.22912	0.0410
H3	0.20681	0.34655	-0.02806	0.0660
H4	0.26377	0.09650	-0.04044	0.0670
H5	0.38777	0.03922	0.12820	0.0530
H6	0.75812	0.02917	0.24391	0.0630
H7	0.61243	-0.13910	0.33201	0.0700
H8	0.40948	-0.00975	0.36788	0.0590
H9	0.17141	0.23616	0.56404	0.0630
H10	0.01178	0.20913	0.41408	0.0620
H11	0.13577	0.22013	0.24564	0.0490

==========

THE TEMPERATURE FACTOR HAS THE FORM OF EXP(-T) WHERE
T = 8*(PI**2)*U*(SIN(THETA)/LAMBDA)**2 FOR ISOTROPIC ATOMS

Table S12. (AN)ISOTROPIC DISPLACEMENT PARAMETERS
FOR: CSG503B_A P 21/N R = 0.04

ATOM	U(1.1) OR U	U(2.2)	U(3.3)	U(2.3)	U(1.3)	U(1.2)
O1	0.0537(6)	0.0402(5)	0.0385(5)	-0.0042(4)	-0.0044(4)	-0.0140(4)
N1	0.0480(6)	0.0366(6)	0.0348(5)	-0.0020(4)	-0.0034(4)	-0.0073(5)
N2	0.0351(5)	0.0400(6)	0.0246(5)	-0.0020(4)	-0.0041(4)	-0.0012(4)
N3	0.0557(7)	0.0528(7)	0.0325(5)	0.0045(5)	-0.0089(5)	0.0093(6)
N4	0.0316(5)	0.0392(6)	0.0285(5)	0.0029(4)	-0.0014(4)	-0.0010(4)
N5	0.0340(5)	0.0584(7)	0.0325(5)	0.0024(5)	0.0037(4)	0.0036(5)
N6	0.0315(5)	0.0453(6)	0.0271(5)	-0.0040(4)	0.0006(4)	-0.0058(4)
N7	0.0475(7)	0.0808(9)	0.0273(5)	-0.0059(5)	0.0044(5)	-0.0191(6)
C1	0.0298(5)	0.0383(6)	0.0231(5)	-0.0011(4)	-0.0018(4)	-0.0025(5)
C2	0.0364(6)	0.0399(7)	0.0270(5)	0.0005(5)	-0.0010(4)	-0.0048(5)
C3	0.0520(8)	0.0839(12)	0.0297(7)	0.0027(7)	-0.0110(6)	0.0053(8)
C4	0.0524(8)	0.0803(11)	0.0331(7)	-0.0165(7)	-0.0061(6)	-0.0111(8)
C5	0.0497(7)	0.0479(8)	0.0360(7)	-0.0109(6)	-0.0016(5)	-0.0044(6)
C6	0.0464(8)	0.0663(10)	0.0436(7)	-0.0077(7)	-0.0053(6)	0.0183(7)
C7	0.0648(10)	0.0452(8)	0.0652(10)	0.0005(7)	-0.0179(8)	0.0112(7)
C8	0.0502(8)	0.0436(8)	0.0523(8)	0.0114(6)	-0.0085(6)	-0.0079(6)
C9	0.0548(8)	0.0640(10)	0.0405(7)	-0.0089(7)	0.0171(6)	-0.0131(7)
C10	0.0358(7)	0.0585(9)	0.0615(9)	-0.0056(7)	0.0125(6)	-0.0024(6)
C11	0.0316(6)	0.0478(8)	0.0437(7)	-0.0030(6)	-0.0018(5)	-0.0013(5)

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THE TEMPERATURE FACTOR HAS THE FORM OF EXP(-T) WHERE
T = 8*(PI**2)*U*(SIN(THETA)/LAMBDA)**2 FOR ISOTROPIC ATOMS
T = 2*(PI**2)*SUMIJ(H(I)*H(J)*U(I.J)*ASTAR(I)*ASTAR(J)). FOR
ANISOTROPIC ATOMS. ASTAR(I) ARE RECIPROCAL AXIAL LENGTHS AND
H(I) ARE THE REFLECTION INDICES.

Table S13. BOND DISTANCES (ANGSTROM)
FOR: CSG503B_A P 21/N R = 0.04

O1	-N1	1.3906(15)	C3	-C4	1.380(3)
N1	-C2	1.2476(15)	C4	-C5	1.359(2)
O1	-H1	0.961(19)	C6	-C7	1.386(2)
N2	-N3	1.3531(16)	C7	-C8	1.356(2)
N2	-C5	1.3527(18)	C9	-C10	1.381(2)
N2	-C1	1.4547(15)	C10	-C11	1.354(2)
N3	-C3	1.3186(19)	C2	-H2	0.9300
N4	-C1	1.4483(15)	C3	-H3	0.9300
N4	-C8	1.3539(18)	C4	-H4	0.9300
N4	-N5	1.3575(14)	C5	-H5	0.9300
N5	-C6	1.322(2)	C6	-H6	0.9300
N6	-N7	1.3540(15)	C7	-H7	0.9300
N6	-C11	1.3511(16)	C8	-H8	0.9300
N6	-C1	1.4570(15)	C9	-H9	0.9300
N7	-C9	1.319(2)	C10	-H10	0.9300
C1	-C2	1.5159(17)	C11	-H11	0.9300

Table S14. BOND ANGLES (DEGREES)
FOR: CSG503B_A P 21/N R = 0.04

O1	-N1	-C2	112.50(10)	C6	-C7	-C8	105.40(15)
N1	-O1	-H1	104.0(11)	N4	-C8	-C7	106.50(13)
N3	-N2	-C5	112.19(10)	N7	-C9	-C10	112.12(13)
C1	-N2	-C5	127.98(11)	C9	-C10	-C11	105.54(13)
N3	-N2	-C1	118.77(10)	N6	-C11	-C10	106.46(12)
N2	-N3	-C3	103.75(12)	N1	-C2	-H2	120.00
N5	-N4	-C1	116.86(10)	C1	-C2	-H2	120.00
N5	-N4	-C8	111.98(11)	N3	-C3	-H3	124.00
C1	-N4	-C8	128.37(11)	C4	-C3	-H3	124.00
N4	-N5	-C6	103.88(11)	C3	-C4	-H4	127.00
N7	-N6	-C1	120.09(10)	C5	-C4	-H4	127.00
N7	-N6	-C11	111.90(11)	N2	-C5	-H5	127.00
C1	-N6	-C11	127.80(10)	C4	-C5	-H5	127.00
N6	-N7	-C9	103.98(11)	N5	-C6	-H6	124.00
N2	-C1	-N4	107.85(9)	C7	-C6	-H6	124.00
N2	-C1	-C2	108.91(9)	C6	-C7	-H7	127.00
N4	-C1	-N6	108.91(9)	C8	-C7	-H7	127.00
N4	-C1	-C2	110.38(9)	N4	-C8	-H8	127.00
N6	-C1	-C2	112.72(10)	C7	-C8	-H8	127.00
N2	-C1	-N6	107.93(9)	N7	-C9	-H9	124.00
N1	-C2	-C1	119.57(11)	C10	-C9	-H9	124.00
N3	-C3	-C4	112.48(14)	C9	-C10	-H10	127.00
C3	-C4	-C5	105.37(14)	C11	-C10	-H10	127.00
N2	-C5	-C4	106.20(14)	N6	-C11	-H11	127.00
N5	-C6	-C7	112.21(14)	C10	-C11	-H11	127.00

Table S15. TORSION ANGLES (DEGREES)
FOR: CSG503B_A P 21/N R = 0.04

O1	-N1	-C2	-C1	178.99(10)
C1	-N2	-N3	-C3	-170.19(11)
C5	-N2	-N3	-C3	-0.99(15)
N3	-N2	-C1	-N4	-162.11(10)
N3	-N2	-C1	-N6	80.36(13)
N3	-N2	-C1	-C2	-42.32(14)
C5	-N2	-C1	-N4	30.60(16)
C5	-N2	-C1	-N6	-86.92(15)
C5	-N2	-C1	-C2	150.40(12)
N3	-N2	-C5	-C4	1.09(16)
C1	-N2	-C5	-C4	169.07(12)
N2	-N3	-C3	-C4	0.51(16)
C1	-N4	-N5	-C6	-164.22(11)
C8	-N4	-N5	-C6	-1.53(14)
N5	-N4	-C1	-N2	72.87(12)
N5	-N4	-C1	-N6	-170.25(9)
N5	-N4	-C1	-C2	-46.00(13)
C8	-N4	-C1	-N2	-86.54(15)
C8	-N4	-C1	-N6	30.35(16)
C8	-N4	-C1	-C2	154.59(12)
N5	-N4	-C8	-C7	1.71(16)
C1	-N4	-C8	-C7	161.93(13)
N4	-N5	-C6	-C7	0.76(16)
C1	-N6	-N7	-C9	175.86(12)
C11	-N6	-N7	-C9	0.68(16)
N7	-N6	-C1	-N2	177.98(11)
N7	-N6	-C1	-N4	61.15(14)
N7	-N6	-C1	-C2	-61.70(15)

Table S16. TORSION ANGLES (DEGREES) (CONTINUED)
FOR: CSG503B_A P 21/N R = 0.04

C11	-N6	-C1	-N2	-7.68(17)
C11	-N6	-C1	-N4	-124.52(13)
C11	-N6	-C1	-C2	112.63(14)
N7	-N6	-C11	-C10	-0.71(16)
C1	-N6	-C11	-C10	-175.43(12)
N6	-N7	-C9	-C10	-0.39(18)
N2	-C1	-C2	-N1	166.71(11)
N4	-C1	-C2	-N1	-75.07(14)
N6	-C1	-C2	-N1	46.97(15)
N3	-C3	-C4	-C5	0.13(18)
C3	-C4	-C5	-N2	-0.71(16)
N5	-C6	-C7	-C8	0.24(19)
C6	-C7	-C8	-N4	-1.14(17)
N7	-C9	-C10	-C11	0.0(2)
C9	-C10	-C11	-N6	0.43(17)

Table S17. CONTACT DISTANCES(ANGSTROM)
FOR: CSG503B_A P 21/N R = 0.04

O1	.N1_D	3.0045(14)	N6	.N1	2.8727(15)
O1	.N7_D	2.9275(16)	N6	.N3	3.0501(15)
O1	.H2	2.3000	N6	.C10	2.1666(18)
O1	.H11_C	2.6800	N6	.C5	3.2224(17)
O1	.H7_A	2.7400	N6	.C8	2.8503(19)
O1	.H6_B	2.6600	N7	.N4	2.9134(15)
N1	.N4	3.0346(15)	N7	.C2	3.0299(17)
N1	.N6	2.8727(15)	N7	.C8	3.175(2)
N1	.N7	2.8490(17)	N7	.C10	2.2401(19)
N1	.O1_D	3.0045(14)	N7	.N1	2.8490(17)
N1	.N1_D	3.0270(14)	N7	.O1_D	2.9275(16)
N2	.C8	3.2163(18)	C1	.C3	3.4765(18)
N2	.N5	2.9467(15)	C1	.C7	3.571(2)
N2	.C4	2.1682(18)	C1	.C4	3.5854(18)
N2	.C11	2.7559(16)	N1	.H1_D	2.190(18)
N3	.N6	3.0501(15)	C1	.C10	3.5908(19)
N3	.C2	2.7737(16)	C1	.C9	3.4962(19)
N3	.C8_C	3.407(2)	C1	.C6	3.454(2)
N3	.C11	3.0983(18)	C2	.N3	2.7737(16)
N3	.C4	2.244(2)	C2	.C11	3.5331(18)
N4	.C7	2.172(2)	C2	.C11_C	3.5542(19)
N4	.N1	3.0346(15)	C2	.N7	3.0299(17)
N4	.C5	2.8224(17)	N2	.H2	2.5300
N4	.N7	2.9134(15)	N2	.H11	2.5600
N5	.C2	2.7928(17)	C2	.N5	2.7928(17)
N5	.C5	3.2978(18)	C3	.C1	3.4765(18)
N5	.C7	2.248(2)	N3	.H11	2.6800
N5	.N2	2.9467(15)	C3	.C6_H	3.579(2)

Table S18. CONTACT DISTANCES(ANGSTROM) (CONTINUED)
FOR: CSG503B_A P 21/N R = 0.04

N3	.H2	2.5600	C8	.N6	2.8503(19)
N3	.H8_C	2.5200	C8	.N7	3.175(2)
C3	.C5	2.178(2)	C9	.C11	2.177(2)
N4	.H5	2.6700	C9	.C1	3.4962(19)
C4	.N2	2.1682(18)	C10	.C1	3.5908(19)
C4	.C1	3.5854(18)	C10	.N6	2.1666(18)
N4	.H3_E	2.9500	C11	.C5	3.3704(19)
N5	.H3_E	2.8000	C11	.C9	2.177(2)
N5	.H9_F	2.5900	C11	.C2	3.5331(18)
C5	.C3	2.178(2)	C11	.N3	3.0983(18)
C5	.C8	3.237(2)	C11	.C2_I	3.5542(19)
C5	.N4	2.8224(17)	C11	.N2	2.7559(16)
C5	.N5	3.2978(18)	C1	.H8	2.8500
C5	.C11	3.3704(19)	C1	.H11	2.8300
C5	.N6	3.2224(17)	C1	.H5	2.8400
C6	.C1	3.454(2)	C2	.H1	2.960(18)
N6	.H8	2.7000	C3	.H8_C	2.8500
C6	.C3_E	3.579(2)	C3	.H5	3.0800
C6	.C8	2.182(2)	C3	.H10_F	3.0100
C7	.C1	3.571(2)	C4	.H10_F	2.9700
N7	.H7_G	2.9300	C5	.H3	3.0700
C7	.N4	2.172(2)	C5	.H11	2.9800
N7	.H1_D	2.162(18)	C6	.H3_E	2.7300
N7	.H8	2.9000	C6	.H8	3.0900
C8	.C5	3.237(2)	C7	.H3_E	2.9200
C8	.C6	2.182(2)	C8	.H5	2.7400
C8	.N3_I	3.407(2)	C8	.H3_E	3.0700
C8	.N2	3.2163(18)	C8	.H6	3.0700

Table S19. CONTACT DISTANCES(ANGSTROM) (CONTINUED)
FOR: CSG503B_A P 21/N R = 0.04

C9	.H1_D	3.011(18)	H5	.C10_I	3.0700
C9	.H7_G	3.0800	H6	.C8	3.0700
C9	.H11	3.0800	H6	.H7	2.4700
C10	.H5_C	3.0700	H6	.O1_J	2.6600
C11	.H9	3.0700	H7	.O1_K	2.7400
C11	.H2_I	3.0100	H7	.H6	2.4700
H1	.C2	2.960(18)	H7	.H8	2.4800
H1	.N1_D	2.190(19)	H7	.N7_G	2.9300
H1	.N7_D	2.162(18)	H7	.C9_G	3.0800
H1	.C9_D	3.011(18)	H8	.N6	2.7000
H2	.O1	2.3000	H8	.N7	2.9000
H2	.N2	2.5300	H8	.C1	2.8500
H2	.N3	2.5600	H8	.C6	3.0900
H2	.C11_C	3.0100	H8	.H7	2.4800
H3	.C5	3.0700	H8	.N3_I	2.5200
H3	.H4	2.4600	H8	.C3_I	2.8500
H3	.N4_H	2.9500	H9	.C11	3.0700
H3	.N5_H	2.8000	H9	.H10	2.4600
H3	.C6_H	2.7300	H9	.N5_L	2.5900
H3	.C7_H	2.9200	H10	.H9	2.4600
H3	.C8_H	3.0700	H10	.H11	2.4700
H4	.H3	2.4600	H10	.C3_L	3.0100
H4	.H5	2.4800	H10	.C4_L	2.9700
H5	.N4	2.6700	H11	.N2	2.5600
H5	.C1	2.8400	H11	.N3	2.6800
H5	.C3	3.0800	H11	.C1	2.8300
H5	.C8	2.7400	H11	.C5	2.9800
H5	.H4	2.4800	H11	.C9	3.0800

Table S20. CONTACT DISTANCES(ANGSTROM) (CONTINUED)
FOR: CSG503B_A P 21/N R = 0.04

H11 .H10 2.4700 H11 .O1_I 2.6800

Table S21. HYDROGEN BONDS (ANGSTROM. DEG)
FOR: CSG503B_A P 21/N R = 0.04

O1 -- H1 .. N1 0.961(19) 2.190(19) 3.0045(14) 141.7(15) 3_666

O1 -- H1 .. N7 0.961(19) 2.162(18) 2.9275(16) 135.7(14) 3_666

C8 -- H8 .. N3 0.9300 2.5200 3.407(2) 159.00 2_545

C9 -- H9 .. N5 0.9300 2.5900 3.4846(18) 161.00 4_455

TRANSLATION OF SYMMETRY CODE TO EQUIV.POS

A =[1565.00] = [1_565] = X.1+Y.Z
B =[2655.00] = [2_655] = 3/2-X.1/2+Y.1/2-Z
C =[2555.00] = [2_555] = 1/2-X.1/2+Y.1/2-Z
D =[3666.00] = [3_666] = 1-X.1-Y.1-Z
E =[4555.00] = [4_666] = 1/2+X.1/2-Y.1/2+Z
F =[4554.00] = [4_665] = 1/2+X.1/2-Y.-1/2+Z
G =[3656.00] = [3_656] = 1-X.-Y.1-Z
H =[4454.00] = [4_565] = -1/2+X.1/2-Y.-1/2+Z
I =[2545.00] = [2_545] = 1/2-X.-1/2+Y.1/2-Z
J =[2645.00] = [2_645] = 3/2-X.-1/2+Y.1/2-Z
K =[1545.00] = [1_545] = X.-1+Y.Z
L =[4455.00] = [4_566] = -1/2+X.1/2-Y.1/2+Z

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