

Supplementary Information for

Reactivity and Stability of a Ring-Expanded N-Heterocyclic Carbene Copper(I) Boryl Imidinate

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Experimental	2
Reaction of 1 and H ₂	2
X-ray Crystallography	3
Table 1. Crystal data and structure refinement details	4
<i>In situ</i> reaction monitoring by NMR spectroscopy	5
Figures S1-3: Reaction of compound 1 and H ₂ O	5
Figures S4, S5: Thermolysis of compound 1	6
Figures S6, S7: Reaction of compound 1 and phenyl acetylene	7
Figures S8: Reaction of compound 1 and H ₂	8
NMR Spectra of Compounds 2 and 3	9
Figures S9-S10: NMR spectra of compound 2	9
Figures S11-S12: NMR spectra of compound 3	10
Mass Spectrometry Data	11
Mass spectrum of compound 1 ·H ₂ O	11
Mass spectrum of compound 2	12
Mass spectrum of the reaction of compound 1 and PhCCH	13
IR Spectroscopy Data	11
IR spectrum of compound 3	14
References	15

Experimental

Addition of H₂ to compound 1

In a vial in a glovebox, a solution of (6-Dipp)CuO^tBu (30 mg, 0.055 mmol) in C₆H₆ (0.5 mL) was added to B₂pin₂ (14 mg, 0.055 mmol). Volatiles were removed *in vacuo* precipitating a white powder. The powder was washed with hexane (2 mL) and dried *in vacuo*. The remaining solid was redissolved in C₆H₆ (0.5 mL) was added and then ^tBuNC (12.5 μL, 0.111 mmol) was added forming a yellow solution. Volatiles were removed *in vacuo* precipitating a yellow powder. The solid was re-dissolved into C₆D₆ (0.5 mL) and the reaction mixture was transferred to J. Young's tap NMR tube. The reaction mixture was degassed, and the NMR tube was charged with an atmosphere of H₂. ¹H and ¹¹B NMR spectra were taken confirming no reaction.

X-ray crystallography

The crystals were kept at 150.00(10) K during data collection. Compounds **2** and **3** were collected with a New Xcalibur EosS2 diffractometer with Mo source ($\lambda = 0.71073$).

Compounds **1** and **1·H₂O** were collected on RIGAKU SuperNova with Cu source ($\lambda = 1.54184$). Using Olex2,¹ the structures were solved with the SHELXT² and refined with the ShelXL² refinement package using Least Squares minimisation.

Despite copious recrystallisation efforts, it proved impossible to obtain data that would be of publication standard for the structure of compound **1**. What was achievable, however, was a ball and stick drawing of the molecule (Figure 1(a)). This solution was brokered in space-group *Pca*2₁ (no. 29) with $a = 17.5013(4)$ Å, $b = 10.9111(5)$ Å, $c = 20.7799(4)$ Å. There were 7337 unique data with a respectable R_{int} of 0.0544 and the final R_1 obtained was in the region of 8%. While, at first glance, this seems acceptable for a sample of non-optimal quality, the problems run deeper. Extensive diffuse scattering is evident in the raw frames of data, at relatively low resolutions (2 - 24 Å). Additionally, the ADPs at 30% were anomalously large, another indication of something awry. Multiple integrations in lower symmetries followed by solution/refinement failed to flush out twinning. Lastly, the esds relating to the bond distance in the Figure are evidence for the problems that were present with this sample. As such, we make no deductions whatsoever from these metrics.

One molecule of the copper complex is partnered with one molecule of toluene in the asymmetric unit pertaining to the structure of **1·H₂O**. C15 and C16 in the latter were treated for 50:50 disorder, while the whole of the solvent moiety was modelled to take account of 85:15 disorder. Distance and ADP restraints were employed, on merit, in disordered regions to assist convergence. H1 and H3 were located and refined subject to being 0.90 Å from the relevant parent atoms.

The asymmetric unit comprises half of a molecule in the structure of compound **2**. Atoms Cu1, C2, C16 and N2 are located on a mirror plane, intrinsic to the space-group.

The phenyl ring based on C31 was treated for 50:50 disorder in the structure of compound **3**. Each component was refined as a rigid hexagon with the addition of some ADP restraints.

Table S1. Crystal data and structure refinement details.

Identification code	1	1·H₂O	2	3
Empirical formula	C ₃₉ H ₆₁ BCuN ₃ O ₂	C ₄₆ H ₇₁ BCuN ₃ O ₃	C ₂₉ H ₄₀ CuN ₃	C ₃₆ H ₄₅ CuN ₂
Formula weight	678.25	788.40	494.18	569.28
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	Pca2 ₁	P2 ₁ /n	Pnma	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	17.4988(4)	13.3551(1)	15.5618(4)	13.0160(3)
<i>b</i> / Å	10.9109(4)	19.9750(2)	21.0016(4)	13.4045(3)
<i>c</i> / Å	20.7863(4)	17.1177(2)	8.5339(2)	18.1677(3)
α / °	90	90	90	90
β / °	90	95.775(1)	90	90
γ / °	90	90	90	90
Volume/ Å ³	3968.67(19)	4543.28(8)	2789.07(11)	3169.77(11)
<i>Z</i>	4	4	4	4
<i>r</i> _{calc} / g cm ⁻³	1.135	1.153	1.177	1.193
μ / mm ⁻¹	1.026	0.979	0.803	0.714
<i>F</i> (000)	1464.0	1704.0	1056.0	1216.0
Crystal size/ mm ³	0.242 × 0.147 × 0.135	0.311 × 0.219 × 0.12	0.511 × 0.335 × 0.232	0.46 × 0.425 × 0.315
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)	Mo K α (λ = 0.71073)
2 θ range for data collection/°	8.104 to 147.4	6.82 to 146.454	5.78 to 60.688	6.078 to 60.594
Index ranges	-21 ≤ <i>h</i> ≤ 21, -12 ≤ <i>k</i> ≤ 13, -25 ≤ <i>l</i> ≤ 17	-16 ≤ <i>h</i> ≤ 12, -24 ≤ <i>k</i> ≤ 23, -20 ≤ <i>l</i> ≤ 21	-22 ≤ <i>h</i> ≤ 12, -28 ≤ <i>k</i> ≤ 29, -12 ≤ <i>l</i> ≤ 10	-13 ≤ <i>h</i> ≤ 17, -18 ≤ <i>k</i> ≤ 18, -24 ≤ <i>l</i> ≤ 24
Reflections collected	53017	46145	26374	34594
Independent reflections, <i>R</i> _{int}	6548, 0.0460,	9072, 0.0298	3959, 0.0267	8491, 0.0342
Data/restraints/paramet ers	6548/78/506	9072/245/571	3959/0/161	8491/127/378
Goodness-of-fit on <i>F</i> ²	1.034	1.033	1.030	1.038
Final <i>R</i> 1, <i>wR</i> 2 indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0782, 0.2323	0.0325, 0.0851	0.0333, 0.0841	0.0320, 0.0656
Final <i>R</i> 1, <i>wR</i> 2 indexes [all data]	0.0857, 0.2475	0.0357, 0.0879	0.0403, 0.0880	0.0399, 0.0687
Largest diff. peak/hole / e Å ⁻³	0.64/-0.57	0.28/-0.43	0.37/-0.25	0.35/-0.25
Flack parameter	0.94(8)	-	-	-0.001(4)
CCDC code	n/a	2201279	2201280	2201281

In situ reaction monitoring by NMR spectroscopy

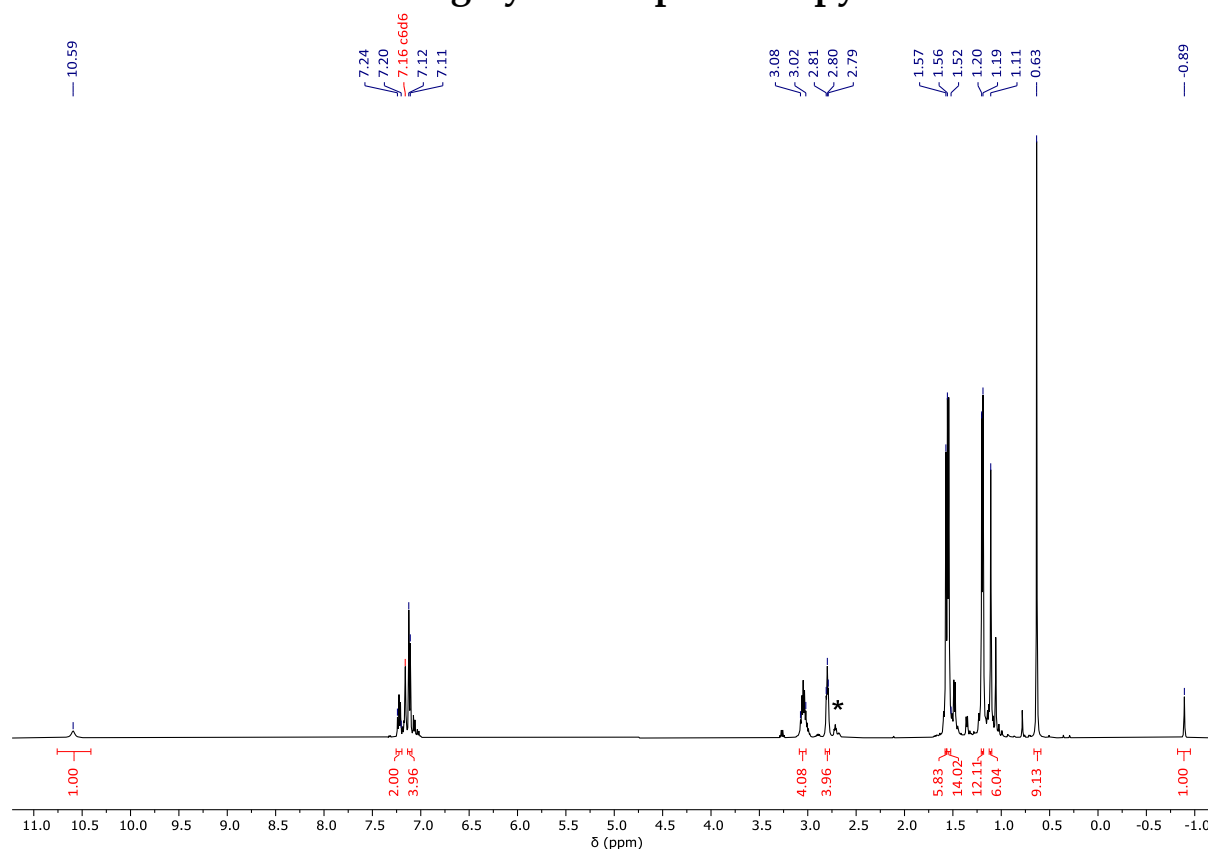


Figure S1. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **1** with H_2O .
 * = Approx. 17 % (6-Dipp)CuOBpin impurity.

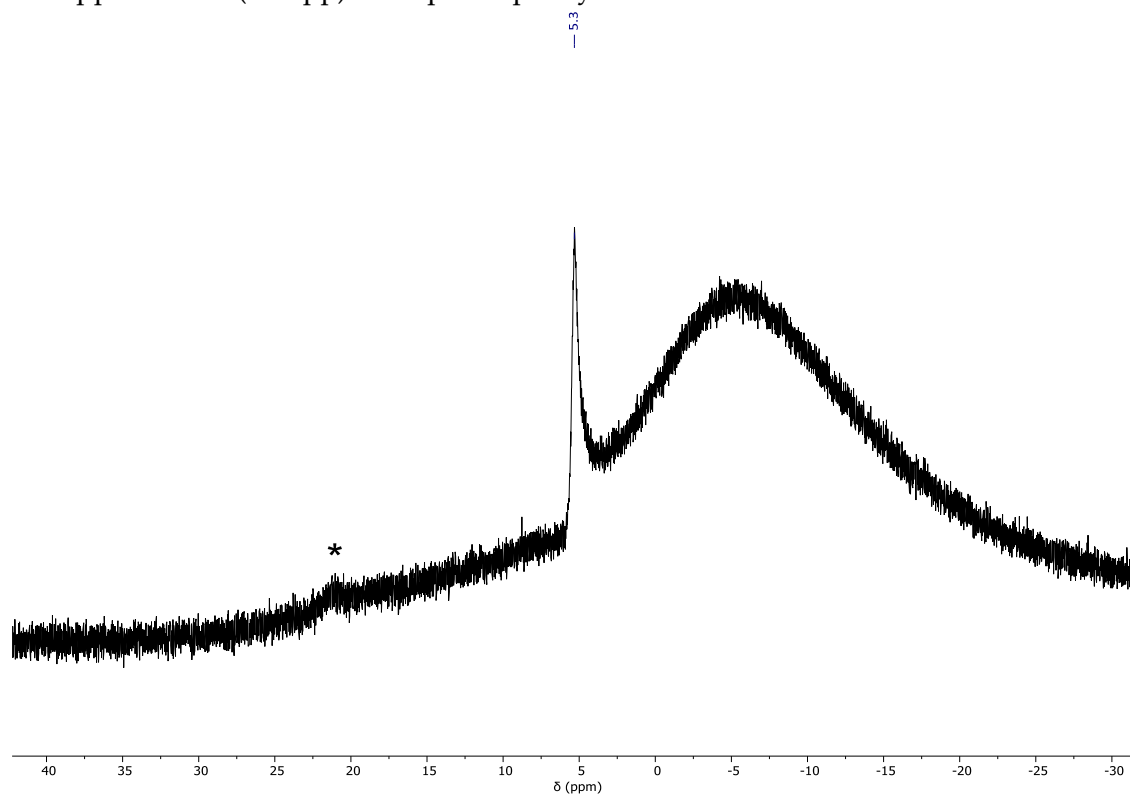


Figure S2. The ^{11}B NMR spectrum (160 MHz, C_6D_6) of the reaction of compound **1** with H_2O .
 * = Approx. 17 % (6-Dipp)CuOBpin impurity.

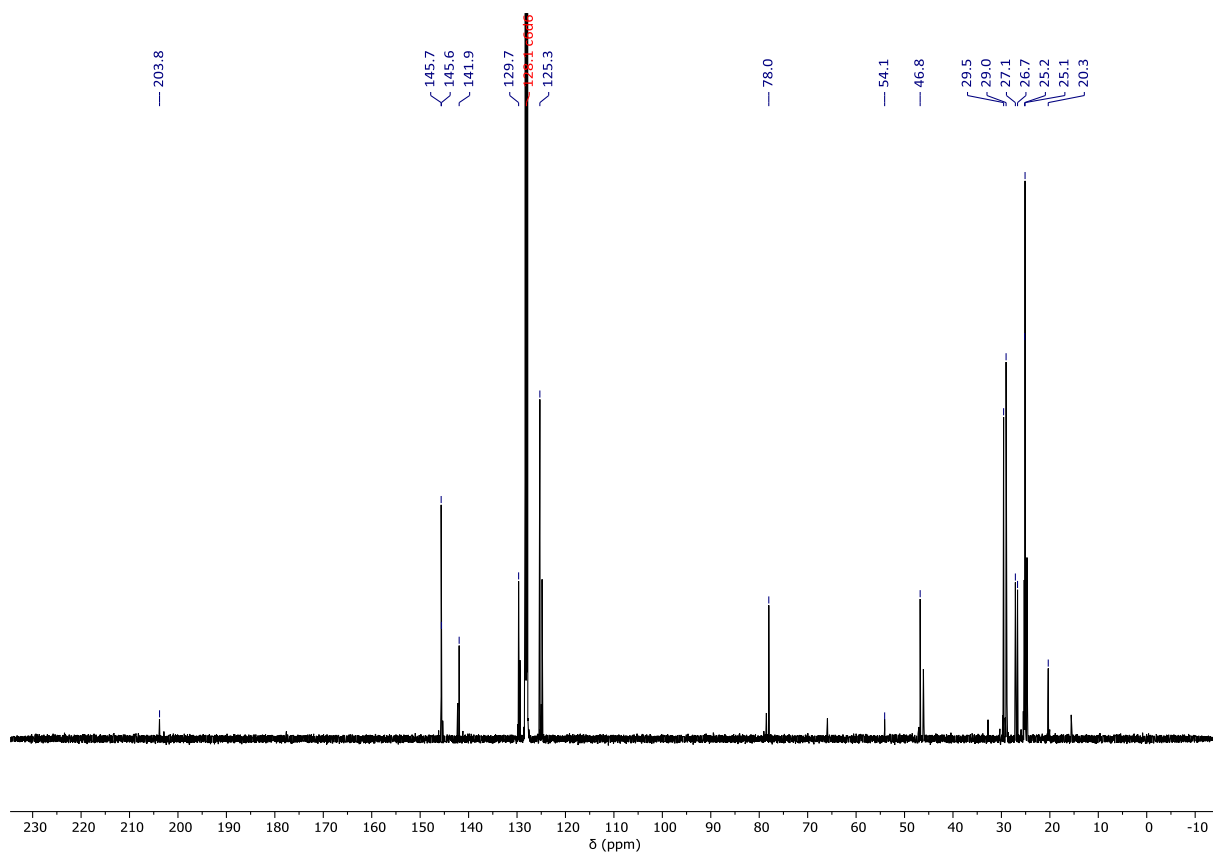


Figure S3. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, C_6D_6) of the reaction of compound **1** with H_2O . Approx. 17 % (6-Dipp)CuOBpin impurity.

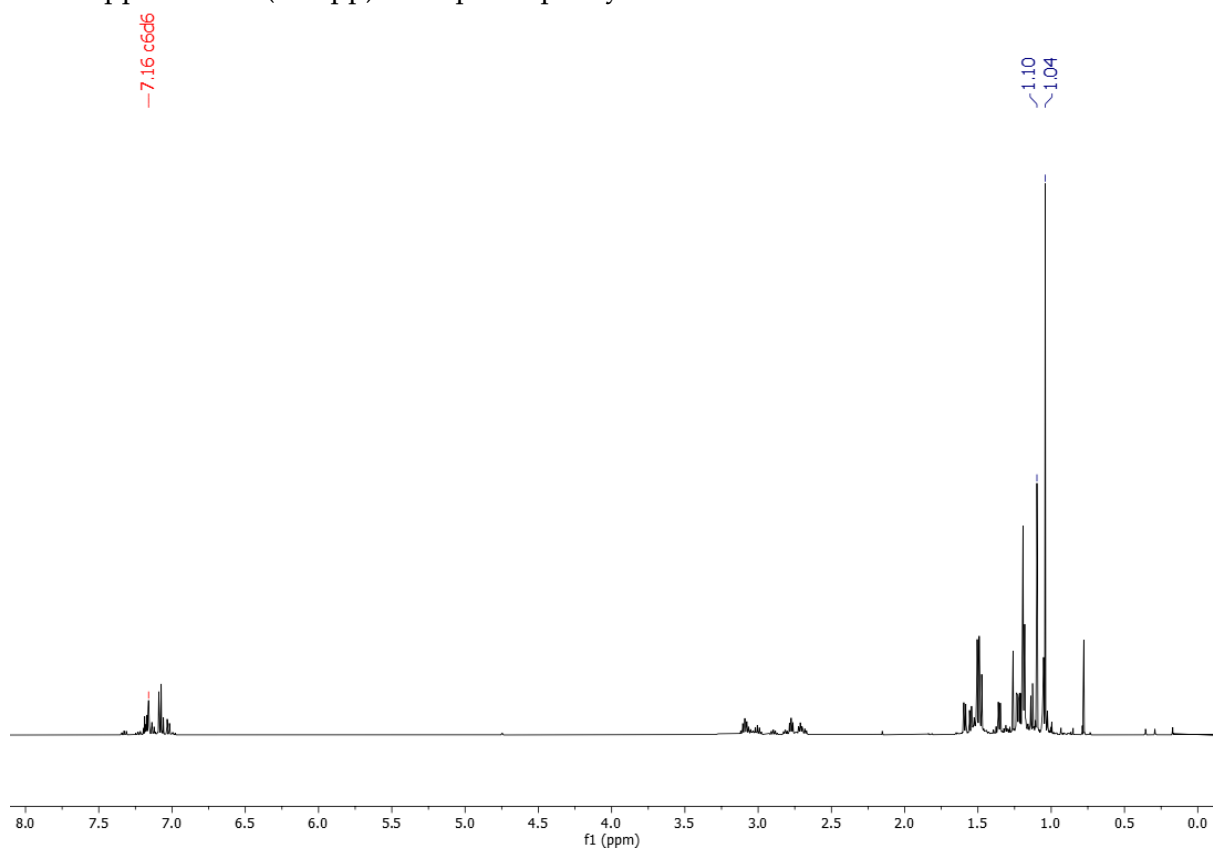


Figure S4. The ^1H NMR spectrum (500 MHz, C_6D_6) of the thermolysis of compound **1**.

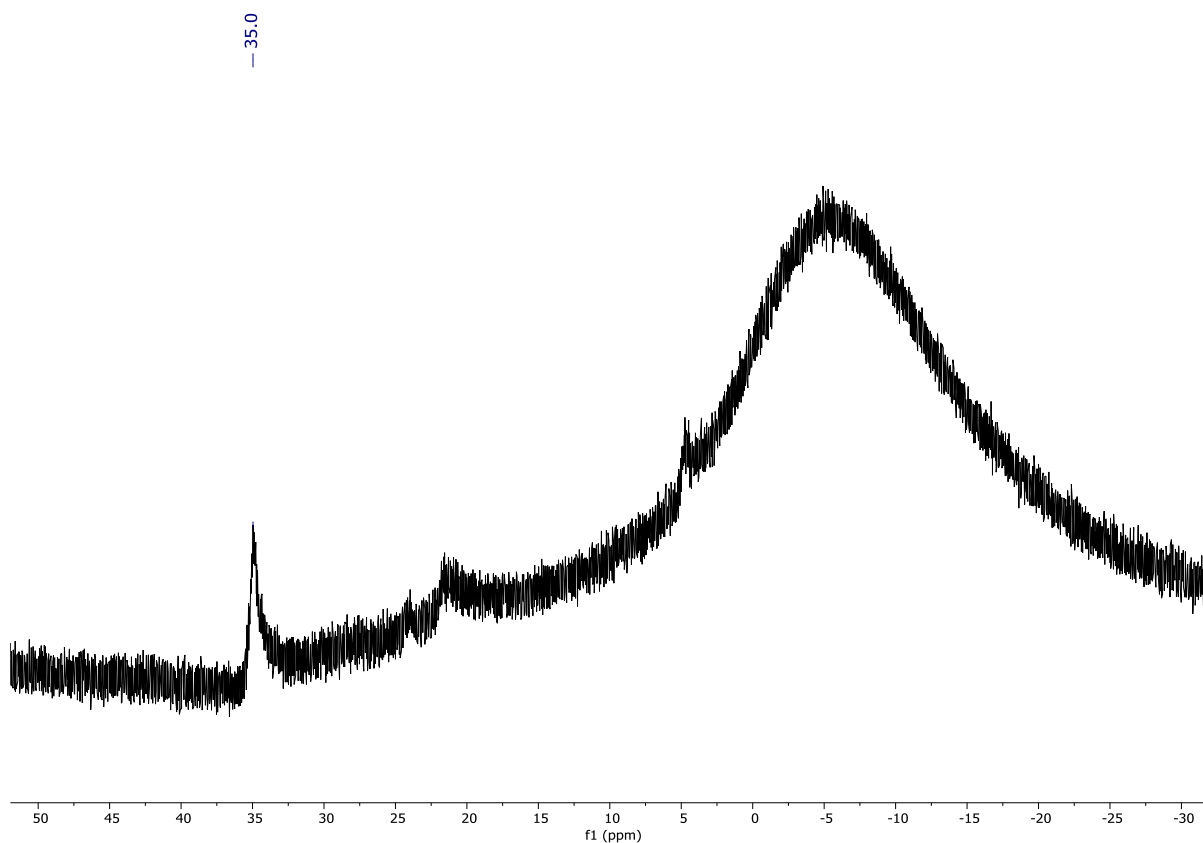


Figure S5. The ^{11}B NMR spectrum (160 MHz, C_6D_6) of the thermolysis of compound **1**.

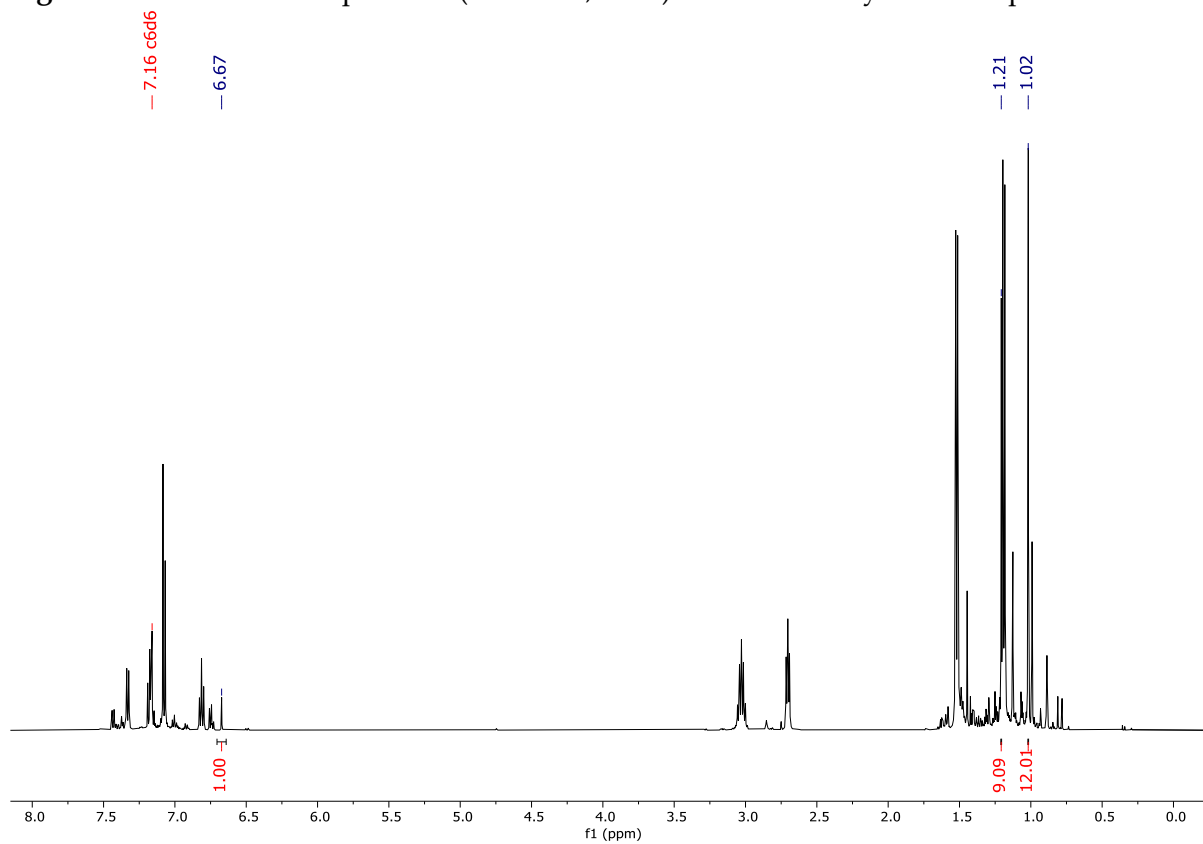


Figure S6. The ^1H NMR spectrum (500 MHz, C_6D_6) of the reaction of compound **1** with phenyl acetylene.

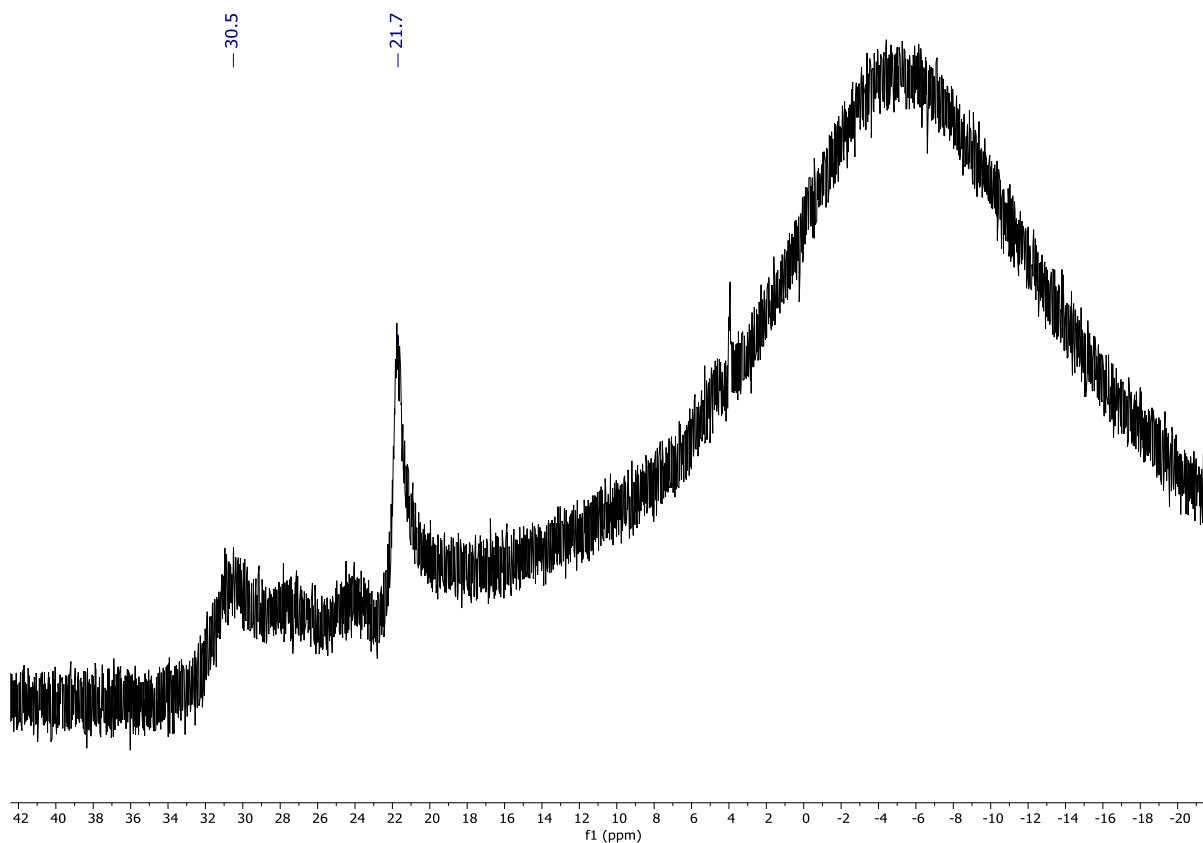


Figure S7. The ^{11}B NMR spectrum (160 MHz, C_6D_6) of the reaction of compound **1** with phenyl acetylene.

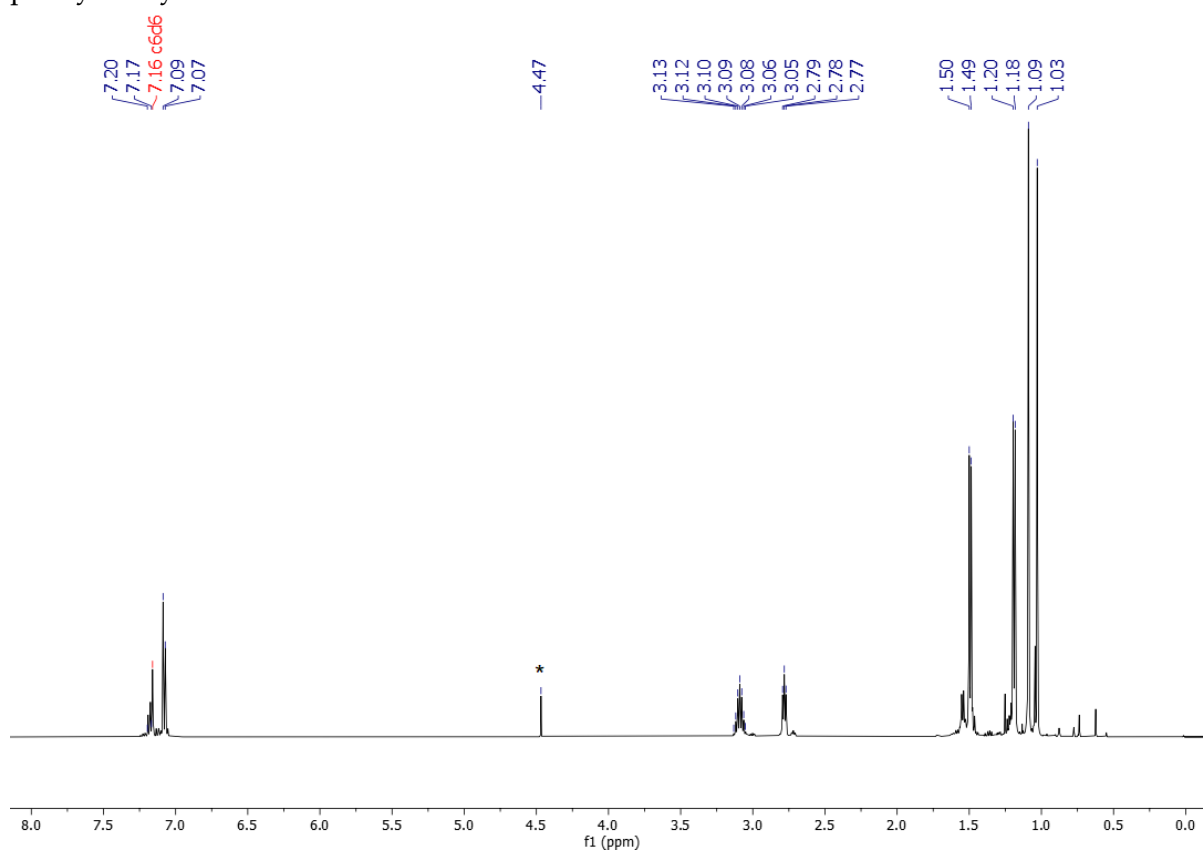


Figure S8. The ^1H NMR spectrum (500 MHz, C_6D_6) of compound **1** with H_2 present in solution showing no reaction. * = Hydrogen.

NMR spectra of compounds 2 and 3

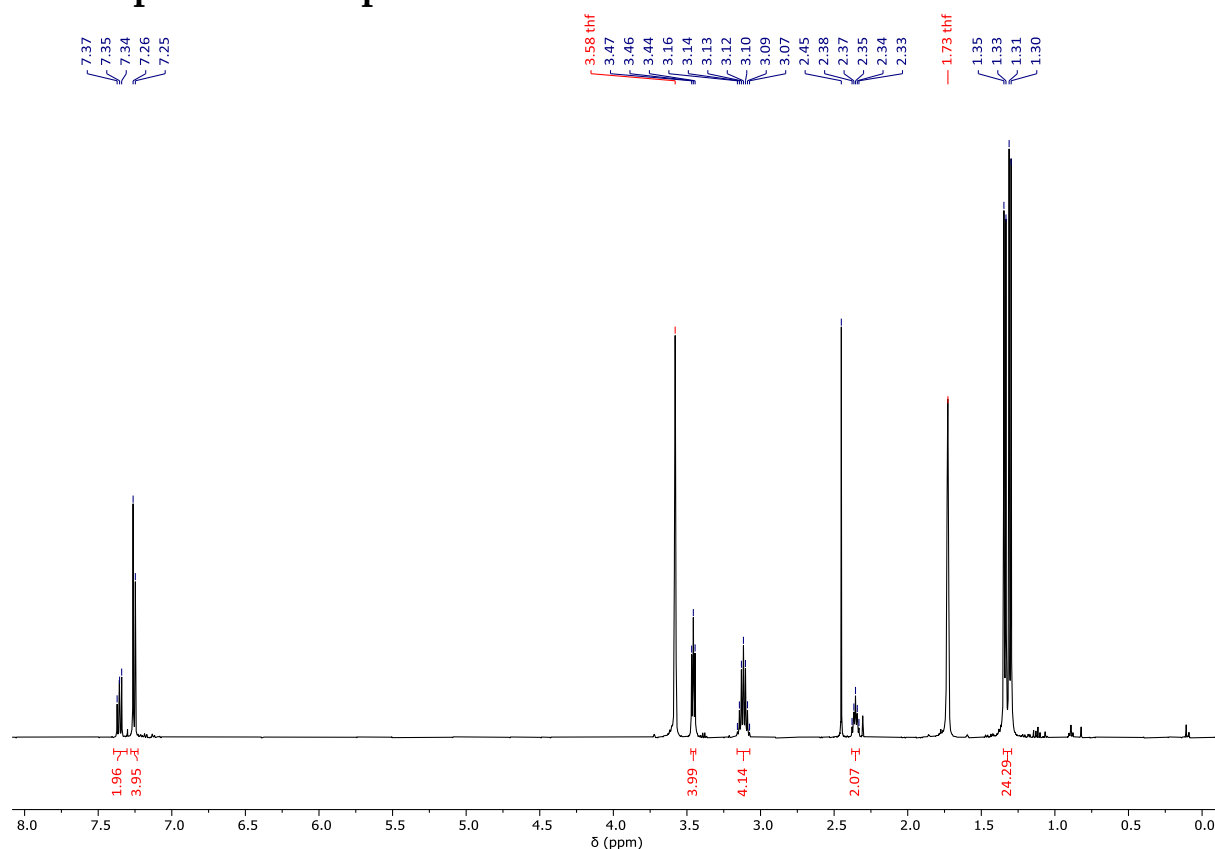


Figure S9. The ¹H NMR spectrum (500 MHz, *d*₈-THF) of compound 2.

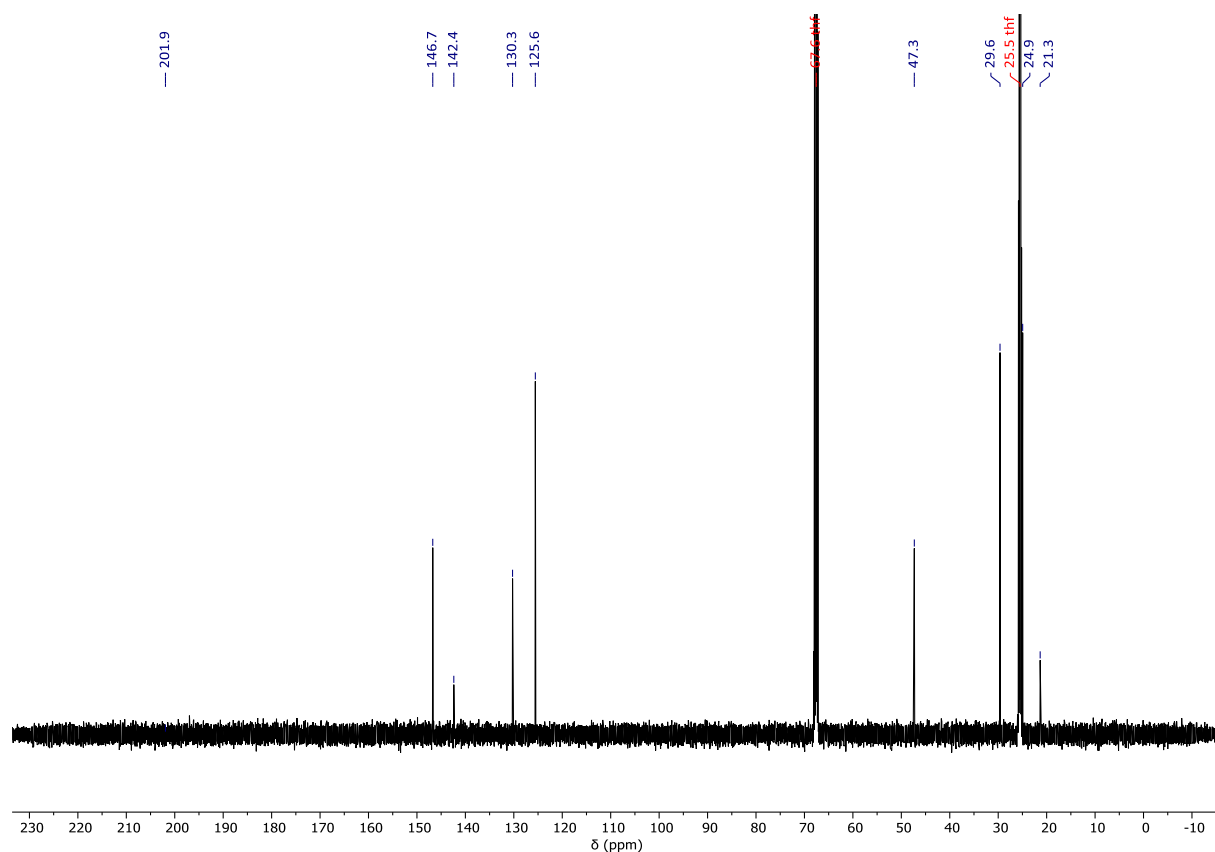


Figure S10. The ¹³C{¹H} NMR spectrum (126 MHz, *d*₈-THF) of compound 2.

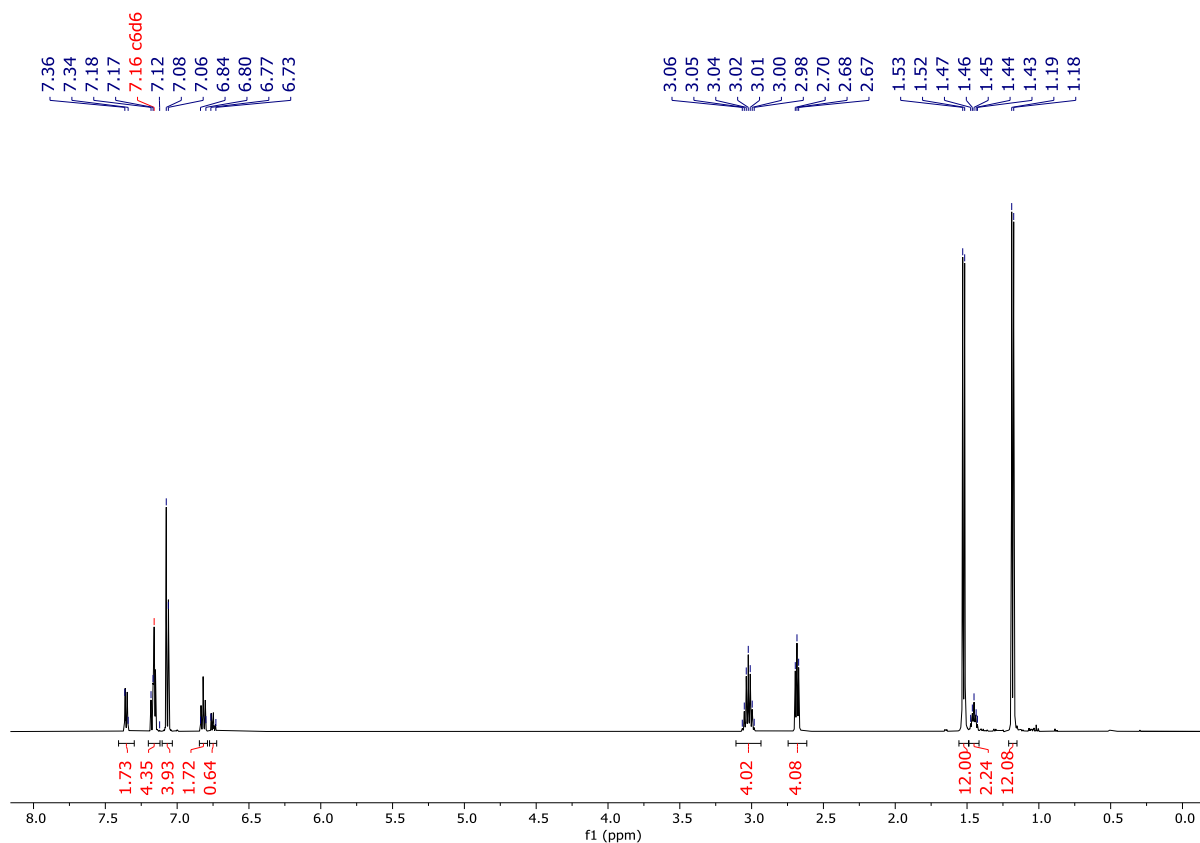


Figure S11. The ¹H NMR spectrum (500 MHz, C₆D₆) of compound **3**.

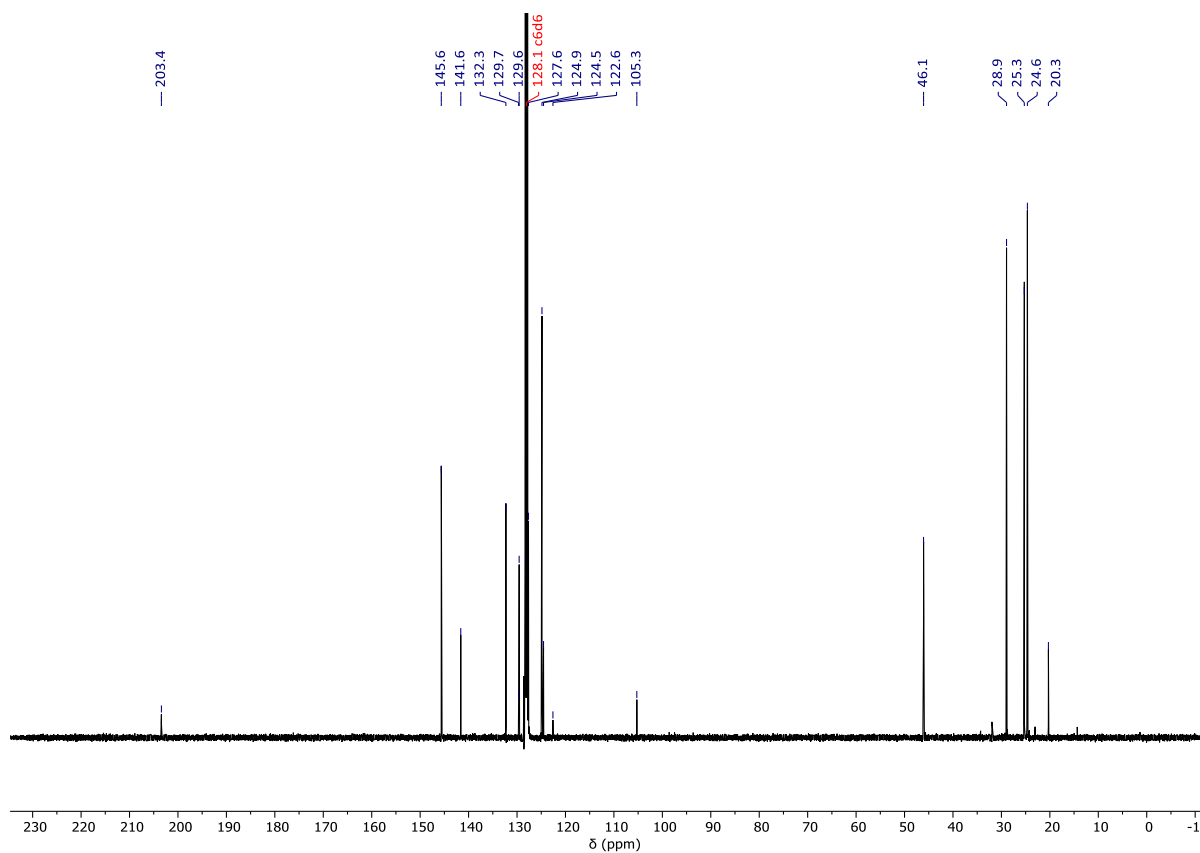


Figure S12. The ¹³C{¹H} NMR spectrum (126 MHz, C₆D₆) of compound **3**.

Mass Spectrometry Data

Compound 1·H₂O, (6-Dipp)CuC(B(OH)(pin)=N(H)'Bu

Walkup MS Report



Data File	RC359_Pos_5mins_MS_28707.d	Sample Name	RC359
Sample Type	Sample	Position	P1-A9
Instrument Name	6545 QToF	User Name	Rex Charman
Acq Method	Pos_5mins_MS.m	Acquired Time	05/07/2022 14:00:45
IRM Calibration Status	Success	DA Method	Pos_5mins_MS.m
Comment			

Sample Group		Info.	
Walkup Sample Description	Toluene wash	Walkup Method	Pos_5mins_C18
Formula	C39H63BCuN3O3	Walkup Method Description	Positive mode ionization using C18 column chromatography
Stream Name	LC 1	Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.0)

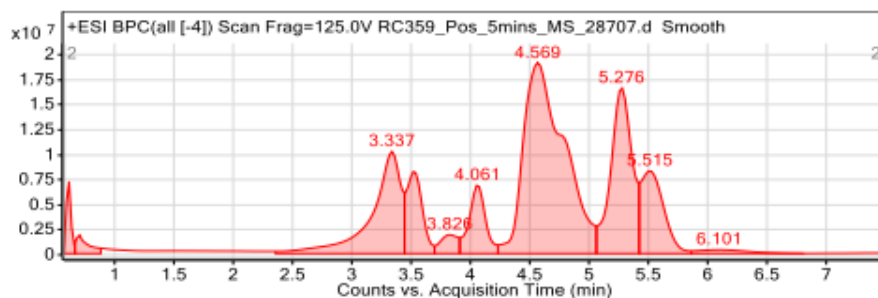


Figure 1: Base peak chromatogram

User Chromatogram Peak List

RT (min)	Area	Area %	Area Sum (%)	Base Peak (m/z)	Width (min)
0.61	20866258	4.57	1.82	233.2244	0.048
0.70	12879699	2.82	1.12	187.1820	0.095
3.34	171967946	37.68	14.97	181.1723	0.230
3.53	75219861	16.48	6.55	187.1826	0.140
3.83	19332143	4.24	1.68	207.1872	0.154
4.06	65365723	14.32	5.69	195.1882	0.138
4.57	456393649	100.00	39.72	405.3358	0.346
5.28	205942044	45.12	17.92	480.4013	0.185
5.52	109866840	24.07	9.56	478.3926	0.202
6.10	11170324	2.45	0.97	233.1490	0.462

Compound Table

Compound Label	RT (min)	Observed mass (m/z)	Neutral observed mass (Da)	Theoretical mass (Da)	Mass error (ppm)	Isotope match score (%)
Cpd 1: C39 H63 B Cu N3 O3	4.14	696.4360	694.4292	694.4295	-0.44	62.10

Mass errors of between -5.00 and 5.00 ppm with isotope match scores above 60% are considered confirmation of molecular formulae

Compound 2, (6-Dipp)CuCN

Walkup MS Report

Data File	6DippCuCN_Pos_5mins_MS_28719.d	Sample Name	6DippCuCN
Sample Type	Sample	Position	P1-A5
Instrument Name	6545 QToF	User Name	Rex Charman
Acq Method	Pos_5mins_MS.m	Acquired Time	7/5/2022 5:19:04 PM
IRM Calibration Status	Success	DA Method	Pos_5mins_MS.m
Comment			

Sample Group		Info.	
Walkup Sample Description		Walkup Method	Pos_5Mins_C18
Formula	C29H40CuN3	Walkup Method Description	Positive mode ionization using C18 column chromatography

Stream Name	LC 1	Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.0)
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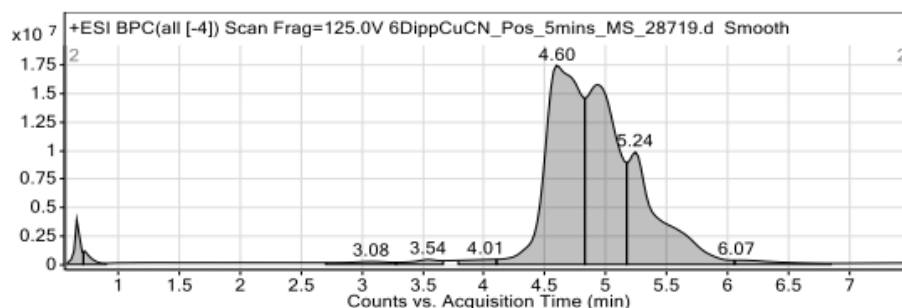


Figure 1: Base peak chromatogram

User Chromatogram Peak List

RT (min)	Area	Area %	Area Sum (%)	Base Peak (m/z)	Width (min)
0.67	12318326	3.47	1.43	144.9848	0.050
0.72	4974868	1.40	0.58	144.9848	0.070
3.08	6669146	1.88	0.78	194.1198	0.380
3.54	6777564	1.91	0.79	130.1608	0.220
4.01	7413934	2.09	0.86	233.1498	0.250
4.60	354888714	100.00	41.30	405.3333	0.270
4.93	274174060	77.26	31.90	962.5116	0.260
5.24	182357500	51.38	21.22	480.4010	0.240
6.07	9796505	2.76	1.14	233.1496	0.450

Compound Table

Compound Label	RT (min)	Observed mass (m/z)	Neutral observed mass (Da)	Theoretical mass (Da)	Mass error (ppm)	Isotope match score (%)
Cpd 1: C29 H40 Cu N3	4.98	516.2423	493.2509	493.2518	-1.86	93.21

Mass errors of between -5.00 and 5.00 ppm with isotope match scores above 60% are considered confirmation of molecular formulae

The reaction of compound 1 with phenyl acetylene, $^1\text{NCH}_2$

Walkup MS Report



Data File	RC358_Pos_LoopInjection_MS_unbiased_28647.d	Sample Name	RC358
Sample Type	Sample	Position	P1-A1
Instrument Name	6545 QToF	User Name	Rex Charman
Acq Method	Pos_LoopInjection_MS_unbiased.m	Acquired Time	01/07/2022 15:17:43
IRM Calibration Status	Success	DA Method	Pos_LoopInjection_MS_unbiased.m
Comment			

Sample Group		Info.	
Walkup Sample Description	6DippCuC(NtBu)BPIn + PhCCH	Walkup Method	Pos_LoopInjection_Unbiased
Formula	C11H22BNO2	Walkup Method Description	Positive mode loop injection with unbiased isotope model
Stream Name	LC 1	Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.0)

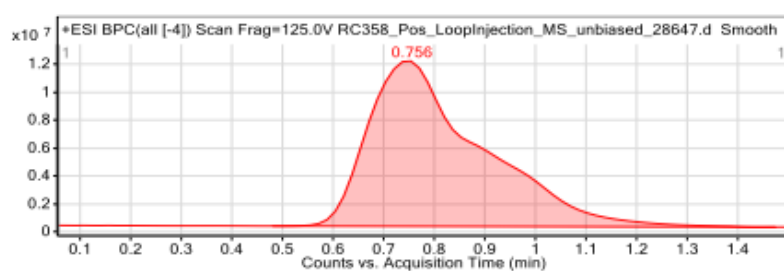


Figure 1: Base peak chromatogram

User Chromatogram Peak List

RT (min)	Area	Area %	Area Sum (%)	Base Peak (m/z)	Width (min)
0.76	183533746	100.00	100.00	188.1433	0.244

Compound Table

Compound Label	RT (min)	Observed mass (m/z)	Neutral observed mass (Da)	Theoretical mass (Da)	Mass error (ppm)	Isotope match score (%)
Cpd 1: C5 H11 N	0.75	86.0962	85.0890	85.0891	-2.26	72.75

Mass errors of between -5.00 and 5.00 ppm with isotope match scores above 60% are considered confirmation of molecular formulae

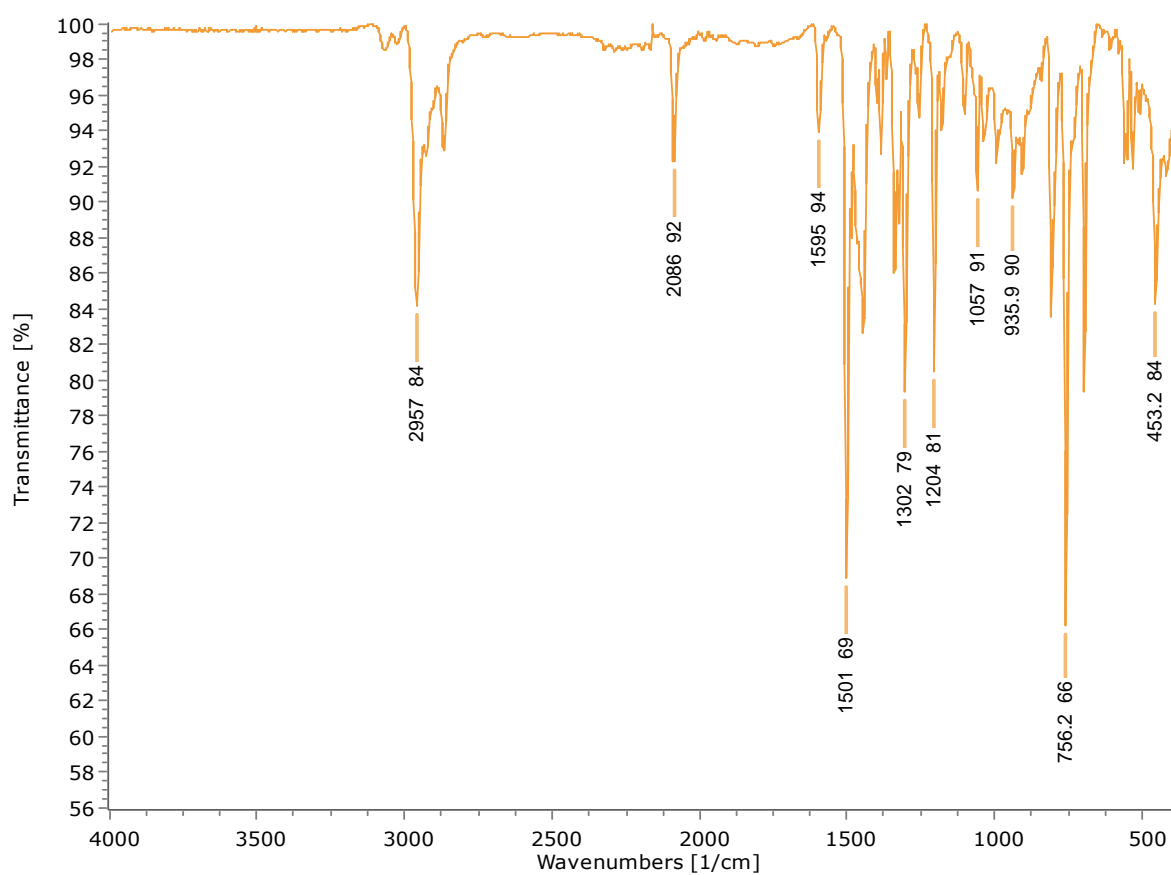


Figure S13 The IR spectrum of compound 3.

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42 (2), 339-341.
2. Sheldrick, G., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A* **2015**, 71 (1), 3-8.