Supplementary Materials

Table S1. Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_{30}H_{56}Cu_3N_6O_{34}$
Formula weight	1235.42
Temperature/K	173
Crystal system	monoclinic
Space group	Pn
a/Å	13.4261(9)
b/Å	7.4630(6)
c/Å	24.3637(18)
α/°	90
β/°	91.187(6)
γ/°	90
Volume/Å^3	2440.7(3)
Z	2
ϱ_{calc}g/cm^3	1.681
μ/mm^1	1.405
F(000)	1274.0
Crystal size/mm^3	0.2 × 0.16 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.45 to 59.804
Index ranges	-14 ≤ h ≤ 18, -9 ≤ k ≤ 10, -31 ≤ l ≤ 33
Reflections collected	10249
Independent reflections	7431 [R_{int} = 0.0722, R_{sigma} = 0.1494]
Data/restraints/parameters	7431/8/690
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0874, wR_2 = 0.1830
Final R indexes [all data]	R_1 = 0.1381, wR_2 = 0.2256
Largest diff. peak/hole / e Å^{-3}	1.39/-0.91
Flack Parameter	0.13(3)

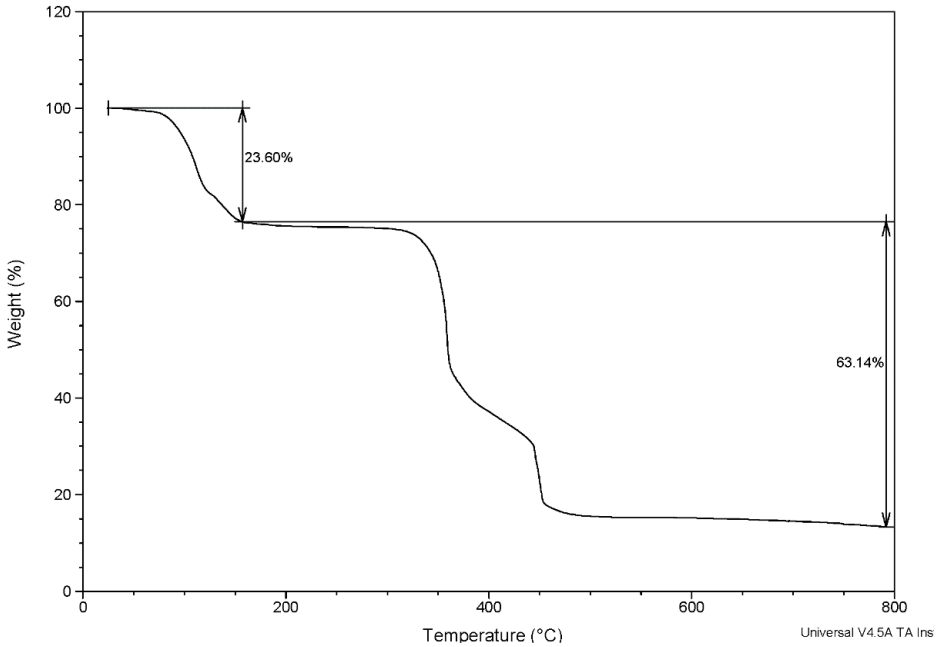

Figure S1. TGA graph for compound **1**.

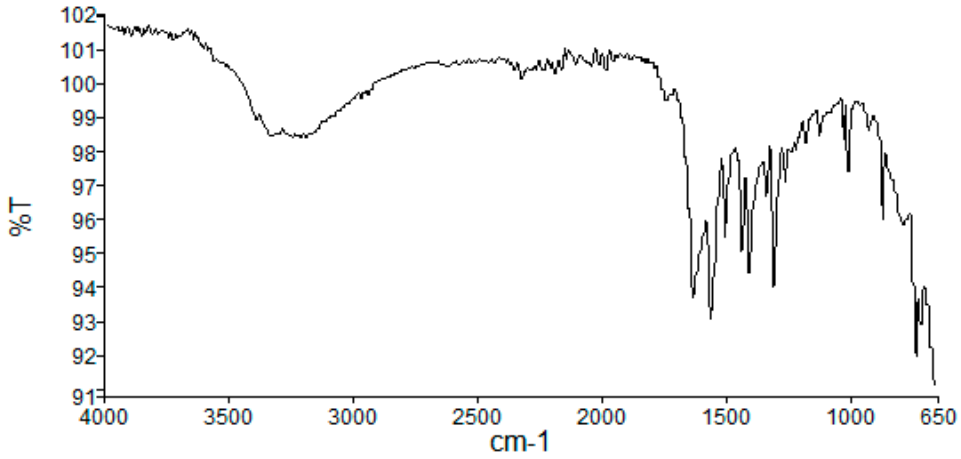

Figure S2. The IR spectrum of compound **1**.

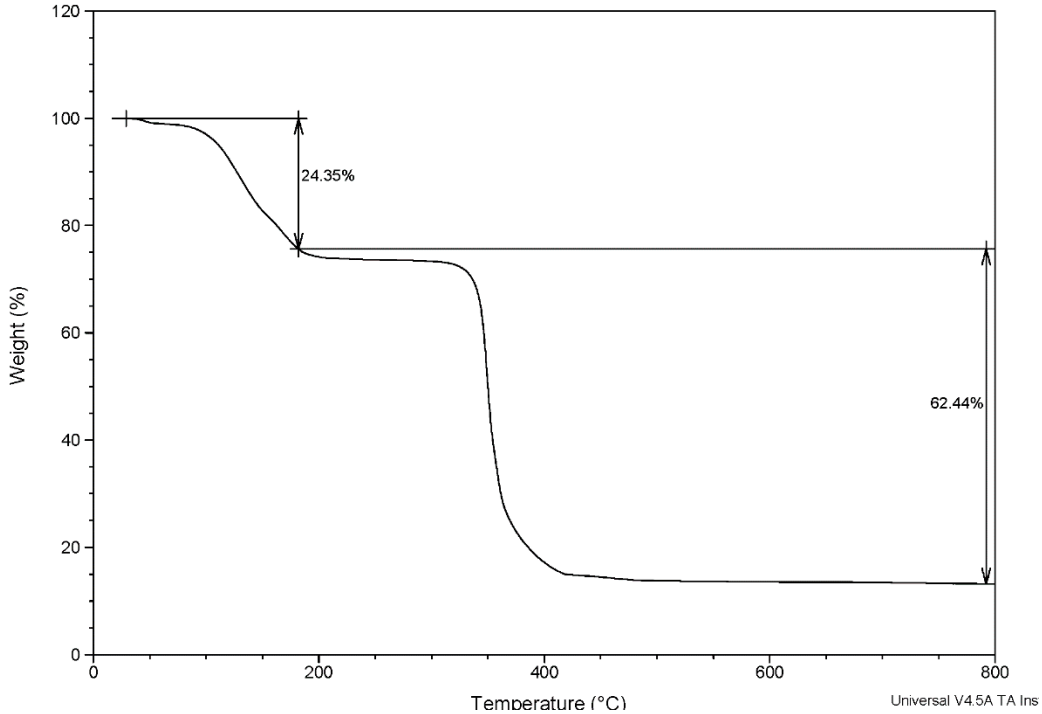

Figure S3. TGA graph for the recycled catalyst.

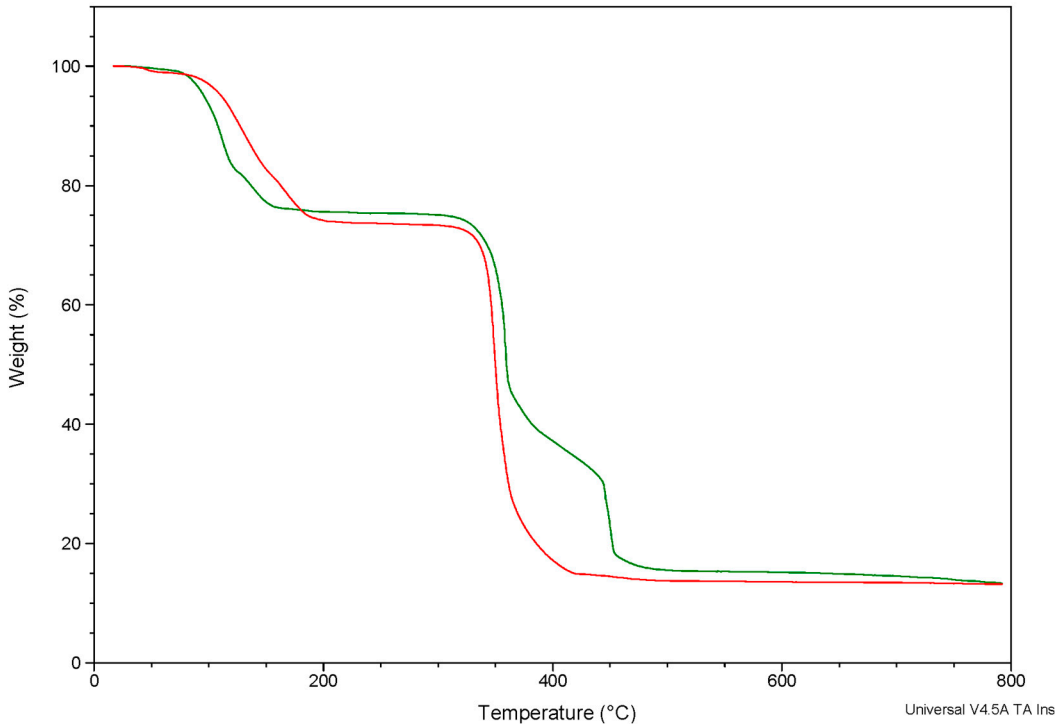

Figure S4. TGA overlay of **1** (green) and the recycled catalyst (red).

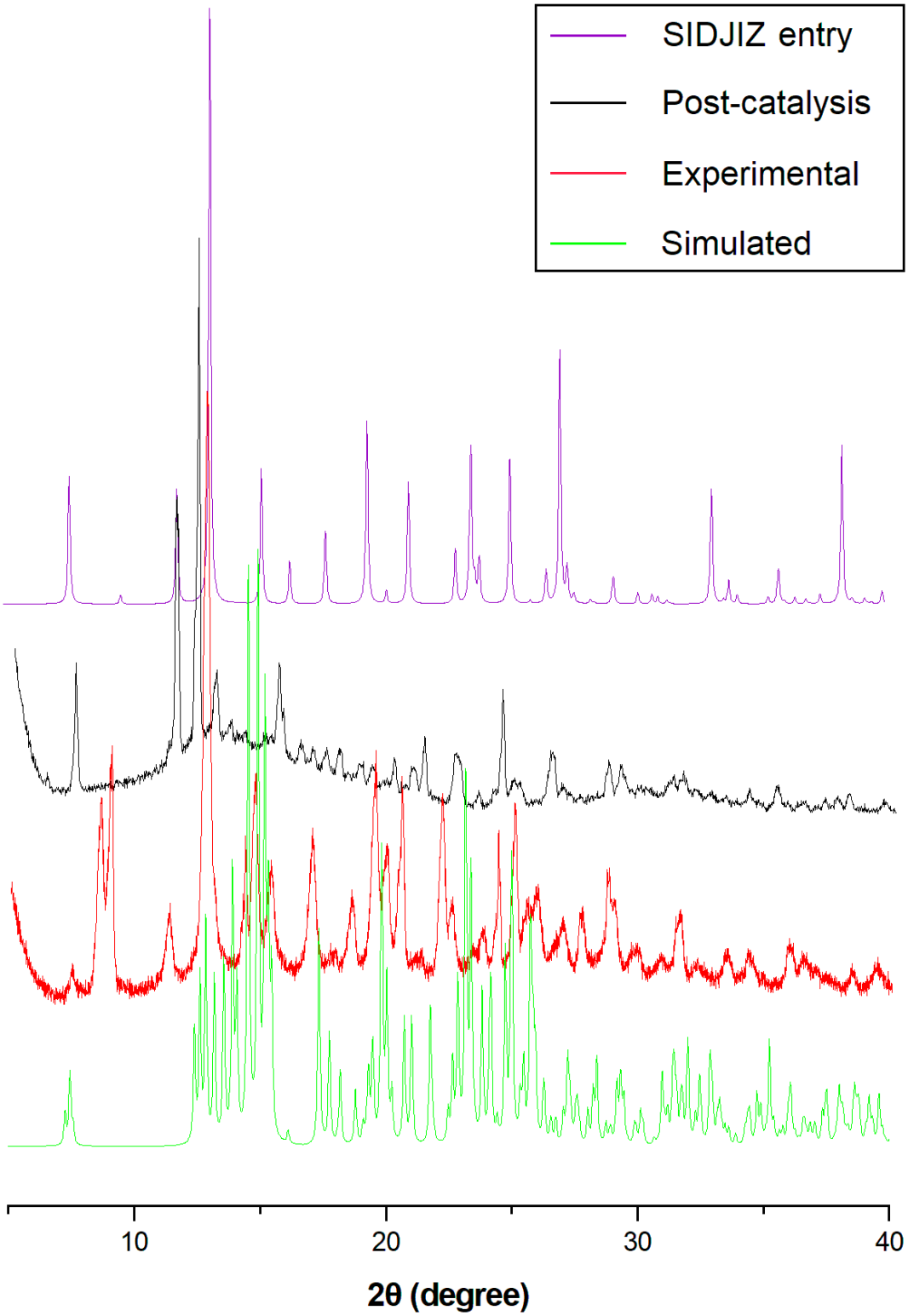

Figure S5. PXRD overlay of **1** (green) as is synthesised (red) and postcatalysis. (black) The simulated pattern of the compound with refcode SIDJIZ (mauve) composed of the same ligand is included for comparison.

^{1}H NMR of product propargylamines

1-(1-cyclohexyl-3-phenylprop-2-ynyl)pyrrolidine (Table 3, Entry 1):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.34 – 7.26 (m, 3H), 3.37 (d, *J* = 8.4 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.69 – 2.64 (m, 2H), 2.15 – 2.07 (m, 1H), 2.00 – 1.95 (m, 1H), 1.84 – 1.77 (m, 6H), 1.73 – 1.66 (m, 1H), 1.65 – 1.54 (m, 1H), 1.34 – 1.06 (m, 5H).

1-(1-cyclohexyl-3-phenylprop-2-ynyl)piperidine (Table 3, Entry 2):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.33 – 7.28 (m, 3H), 3.14 (d, *J* = 9.9 Hz, 1H), 2.69 – 2.64 (m, 2H), 2.47 – 2.41 (m, 2H), 2.18 – 2.04 (m, 2H), 1.84 – 1.76 (m, 2H), 1.75 – 1.54 (m, 6H), 1.50 – 1.44 (m, 2H), 1.35 – 1.17 (m, 3H), 1.10 – 0.92 (m, 2H).

1-[1-Cyclohexyl-3-(4-methylphenyl)-2-propynyl]hexamethylamine (Table 3, Entry 3):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.31 – 7.26 (m, 3H), 3.17 (d, *J* = 10.1 Hz, 1H), 2.85 – 2.78 (m, 2H), 2.62 – 2.55 (m, 2H), 2.20 – 2.08 (m, 2H), 1.81 – 1.75 (m, 2H), 1.72 – 1.62 (m, 8H), 1.56 – 1.48 (m, 1H), 1.37 – 1.17 (m, 3H), 1.06 – 0.88 (m, 2H).

4-(1-cyclohexyl-3-phenylprop-2-ynyl)morpholine (Table 3, Entry 4):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.33 – 7.27 (m, 3H), 3.81 – 3.69 (m, 4H), 3.15 (d, *J* = 9.8 Hz, 1H), 2.75 – 2.68 (m, 2H), 2.57 – 2.49 (m, 2H), 2.16 – 2.02 (m, 2H), 1.83 – 1.58 (m, 4H), 1.36 – 0.94 (m, 5H).

1-cyclohexyl-N,N-diethyl-3-phenylprop-2-yn-1-amine (Table 3, Entry 5):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.31 – 7.26 (m, 3H), 3.31 (d, J = 9.9 Hz, 1H), 2.72 – 2.64 (m, 2H), 2.48 – 2.40 (m, 2H), 2.15 – 2.07 (m, 2H), 1.82 – 1.65 (m, 4H), 1.29 – 1.12 (m, 4H), 1.07 (t, J = 7.2 Hz, 6H), 0.94 – 0.85 (m, 1H).

N-(1-cyclohexyl-3-phenylprop-2-yn-1-yl)-N-methylaniline (Table 3, Entry 6):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 3H), 7.32 – 7.23 (m, 4H), 6.92 – 6.86 (m, 2H), 6.81 – 6.73 (m, 1H), 4.36 (d, J = 9.6 Hz, 1H), 2.93 (s, 3H), 2.22 – 2.14 (m, 1H), 1.95 – 1.67 (m, 7H), 1.21 – 0.95 (m, 3H).

1-(1,3-diphenylprop-2-ynyl)pyrrolidine (Table 3, Entry 7):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.54 – 7.46 (m, 2H), 7.41 – 7.27 (m, 6H), 4.95 (s, 1H), 2.78 – 2.70 (m, 4H), 1.86 – 1.78 (m, 4H).

1-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)pyrrolidine (Table 3, Entry 8):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H), 7.33 – 7.30 (m, 3H), 7.19 – 7.16 (m, 2H), 4.84 (s, 1H), 2.71 – 2.67 (m, 4H), 2.36 (s, 3H), 1.83 – 1.77 (m, 4H).

1-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Table 3, Entry 9):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 4H), 7.35 – 7.28 (m, 3H), 6.93 – 6.87 (m, 2H), 4.83 (s, 1H), 3.82 (s, 3H), 2.70 – 2.66 (m, 4H), 1.82 – 1.79 (m, 4H).

1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl)pyrrolidine (Table 3, Entry 10):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.56 (m, 2H), 7.52 – 7.38 (m, 4H), 7.35 – 7.33 (m, 3H), 4.99 (s, 1H), 2.81 – 2.70 (m, 4H), 1.87 – 1.78 (m, 4H).

1-(1-cyclohexylhept-2-yn-1-yl)pyrrolidine (Table 3, Entry 11):

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.08 (d, J = 8.2 Hz, 1H), 2.67 – 2.52 (m, 4H), 2.23 (td, J = 6.9, 2.1 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.90 – 1.83 (m, 2H), 1.79 – 1.71 (m, 2H), 1.70 – 1.63 (m, 2H), 1.54 – 1.01 (m, 11H), 0.92 (t, J = 7.2 Hz, 3H).