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Supporting information for

A New Tri-nuclear Cu-carbonate Cluster Utilizing CO₂ as C1-Building Block-Reactive Intermediates, Probable Mechanism, EPR and Magnetic Studies

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Scheme S1. Detailed schematic representation of the reaction pathway.

compound 2 [CCDC 1880852] 3[CCDC 1880853] 4[CCDC 1880854] empirical formula C ₂₄ H ₄ Ol ₂ N ₃ B ₁ F ₄ Cu ₁ C ₁₈ H ₂₄ N ₂ Bo ₂ F ₂ Cu _{0.5} C _{36.33} H ₄₈ N ₄ OF ₈ Cu ₁ P _{1.33} formula weight 591.84 343.57 813.62 crystal size [mm ³] 0.226×0.044×0.022 0.326×0.135×0.045 0.114× 0.107× 0.036 crystal system triclinic trigonal trigonal space group P-1 P3221 R3 a [Å] 7.4731(5) 11.2232(15) 19.4230(19) b [Å] 13.2115(10) 11.2232(15) 19.4230(19) c [Å] 14.9811(11) 27.924(4) 29.434(3) α [°] 86.824(4) 90.00 90.00 β [°] 81.552(4) 90.00 90.00 γ [°] 81.251(4) 120.00 120.00 γ [%] 1.445.20(18) 3046.0(9) 9616(2) Z 2 6 9 9 ρ [g/cm ³] 1.360 1.124 1.264 F(000) 618 1086				
empirical formula C ₂₄ H ₄ OC ₂ N ₃ B ₁ F ₄ Cu ₁ C ₁₈ H ₂₄ N ₂ B _{0.5} F ₂ Cu _{0.5} C ₃₆ .3 ₃ H ₄₈ N ₄ OF ₈ Cu ₁ P _{1.33} formula weight 591.84 343.57 813.62 crystal size [mm ³] 0.226×0.044×0.022 0.326×0.135×0.045 0.114× 0.107× 0.036 crystal system triclinic trigonal trigonal space group P-1 P3221 R3 a [Å] 7.4731(5) 11.2232(15) 19.4230(19) b [Å] 13.2115(10) 11.2232(15) 19.4230(19) c [Å] 14.9811(11) 27.924(4) 29.434(3) α [°] 86.824(4) 90.00 90.00 β [°] 81.552(4) 90.00 90.00 γ [°] 81.251(4) 120.00 120.00 ζ [°] 81.251(4) 120.00 120.00 ζ [°] 1.360 1.124 1.264 [°](cm ³] 1.360 1.124 1.264 [°](om ⁻¹] 0.984 0.583 0.627 [mim ⁻¹] 0.984 0.583 0.627	compound	2 [CCDC 1880852]	3 [CCDC 1880853]	4 [CCDC 1880854]
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crystal size [mm³]0.226×0.044×0.0220.326×0.135×0.0450.114× 0.107× 0.036crystal systemtriclinictrigonaltrigonaltrigonalspace group -1 $P3221$ $R3$ a [Å]1.215(10)11.2232(15)19.4230(19)b [Å]13.2115(10)11.2232(15)19.4230(19)c [Å]14.9811(11)27.924(4)29.434(3)a [°]86.824(4)90.0090.00 α [°]81.552(4)90.0090.00 γ [°]81.52(4)90.00120.00 γ [°]81.52(4)90.0090.00 γ [°]1445.20(18)3046.0(9)916(2) γ [°]13.601.1241264 ρ [g/cm³]1.3601.1243807 ρ [g/cm³]1.3601.8843807 μ [mm ⁻¹]0.9840.5830.627 η [mm ⁻¹]0.9840.5830.6275/0.7456 θ -range [°]0.571/0.74550.6189/0.74560.6255/0.7456 h/k -range9.9.151.27.0621.88-24.9872.789-27.062 h/k -range19.9.162.951.9079(0.0425)2.3382 [0.1113]observed refl. (r_{Pm1} 30697 [0.0595]1.9079 [0.0425]2.3382 [0.1113]observed refl. (r_{Pm1} 3.6371.0971.025atal restarints $r_{param.}$ 0.617/0.4333.579/19/2.1836.937/3.30/488opodness-of-fit (r_{P} 0.0424.01960.0787,0.21630.0812.0.2111atal restarints $r_{param.}$ 0.6019.0.12200.875,0.2253 <t< td=""><td>formula weight</td><td>591.84</td><td>343.57</td><td>813.62</td></t<>	formula weight	591.84	343.57	813.62
crystal systemtriclinictrigonaltrigonaltrigonalspace group -1 9221 83 a [Å] $7.4731(5)$ $11.2232(15)$ $19.4230(19)$ b [Å] $13.2115(10)$ $11.2232(15)$ $19.4230(19)$ c [Å] $14.9811(11)$ $27.924(4)$ $29.434(3)$ a [°] $86.824(4)$ 90.00 90.00 $β$ [°] $81.552(4)$ 90.00 90.00 $γ$ [°] $81.52(4)$ 90.00 20.00 $γ$ [°] $81.52(4)$ 3046.09 $916(2)$ $γ$ [°] $1445.20(18)$ 3046.09 $916(2)$ $γ$ [°] $1445.20(18)$ 3046.09 $916(2)$ $γ$ [°] $1445.20(18)$ 124 1264 $γ$ [°] $1445.20(18)$ 124 1264 $γ$ [°] 1360 1124 1264 $ρ$ [g (m^3] $0.572/0.7455$ $0.683/0.7456$ $0.6275/0.7456$ $ρ$ [g (m^{-1}] 0.984 0.583 $0.6275/0.7456$ $ρ$ (mm^{-1}] $0.971/0.7455$ $0.6189/0.7456$ $0.6255/0.7456$ $θ$ (mm^{-1}] $0.967/0.0595$ $10979(0.425)$ $23382[0.1113]$ $nesaure drefl. (r_{emt}]30697(0.059510979(0.425)23382[0.1113]observed refl. (r_{emt}]8177579/19/218937/330/488r_{emt}1.0251.042(1.046)0.0424.01960.0787,0.2163g (r_{emt})1.0251.042(1.046)0.029(0.025)0.057,0.256$	crystal size [mm ³]	0.226×0.044×0.022	0.326×0.135×0.045	0.114× 0.107× 0.036
space groupP-1P3221R3a [Å]7.473(5)11.232(15)9.433(19)b [Å]3.2115(10)11.2232(15)9.4230(19)c [Å]14.9811(1)27.924(4)9.434(3)a [°]8.824(4)9.009.00β [°]8.552(4)9.009.00γ [°]8.155(4)9.009.00γ [°]8.1251(4)12.009.00γ [°]144.50(18)3046.0(9)9616(2)γ [Å]1.3601.249.01ρ [g/cm³]1.3601.243.60ρ [g/cm³]0.9840.5830.627ημmm ⁻¹ 0.9840.6189/0.74560.6255/0.7456θ-range [°]0.751-27.0621.88-24.9872.789-27.062hk/range9.916.11913.412.13.43.3323.423.29.34measured refi.8176850263unique refi. [Am]30670.0595119070.042513.382 (0.1113]observed refi. (>>4222.823786cr(n)godness-oft (F ²)1.0351.0971.025godness-oft (F ²)0.0424.0.10960.0787.0.21630.812.0.2111nu curve (M)0.0424.0.10960.0787.0.21630.159.0.2161	crystal system	triclinic	trigonal	trigonal
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b [Å]13.2115(10)11.2232(15)19.4230(19)c [Å]14.9811(11)27.924(4)29.434(3) α [°]86.824(4)90.0090.00 β [°]81.552(4)90.0090.00 γ [°]81.251(4)120.00120.00 γ [°]1445.20(18)3046.0(9)9616(2) Z 269 ρ [g/cm³]1.3601.1243807 μ [mm ⁻¹]0.9840.5830.627 r_{min} / T_{max} 0.6772/0.74550.6189/0.74560.6255/0.7456 θ -range [°]2.751-27.0622.188-24.9872.789-27.062 hk -range19.16.±19-13.+1213.+1332.33±23.±2329.34measured refl.811768502663unique refl. [R_{mc}]30697 [0.0595]19079 [0.0425]2.382 [0.1113]observed refl. ($l > 2$ 5275283786 $2 \sigma(l)$ 1.0351.0971.025goodness-of-fit (F^2)1.0351.0970.0812,0.2111 $n (range)$ 0.0424,0.10960.0787,0.21630.812,0.2111 $n (range)$ 0.0619,0.12220.0857,0.22530.1592,0.2586	<i>a</i> [Å]	7.4731(5)	11.2232(15)	19.4230(19)
c [Å] 14.9811(1) 27.924(4) 94.3(3) α [°] 86.824(4) 90.00 90.00 β [°] 81.552(4) 90.00 90.00 γ [°] 81.552(4) 20.00 120.00 γ [°] 81.552(4) 20.00 90.00 γ [°] 81.552(4) 3046.0(9) 9616(2) γ [°] 1445.20(18) 3046.0(9) 9616(2) γ [°] 1.360 1.124 1.264 γ [°] 1.360 1.026 1.027 γ [°] 0.6772/0.7455 0.6189/0.7456 0.6257.07456 θ-range [°] 0.751-27.062 2.188-24.987 2.789-27.062 hk/range 1917 6850 263 1.01113 observed refl. [𝑘] 30697 [0.0555] 19079 [0.0425] 2.382 [0.1113] observed refl. [𝑘] 822 1097 [0.1245] 3	b [Å]	13.2115(10)	11.2232(15)	19.4230(19)
α [°]86.824(4)90.0090.00 β [°]81.552(4)90.0090.00 γ [°]81.251(4)120.00120.00 γ [°]1445.20(18)3046.0(9)9616(2) z 269 p [g/cm ³]1.3601.1241.264 $f(00)$ 6180.863607 μ [mm ⁻¹]0.9840.5830.627 r_{min} / r_{max} 0.6772/0.74550.6189/0.74560.6255/0.7456 θ -range [°]2.751-27.0622.188-24.9872.789-27.062 h/r -range19.16, ±19-13.412, -13.413, -32.3323.2, ±2.3, -29.34measured refl.811768502663unique refl. [R_{int}]30697 [0.0595]19079 [0.0425]2.3382 [0.1113]observed refl. ($h > 2$ 63.77/149 / 433579 / 19 / 2186937/330/488 $go odness-of-fit (f^2)1.0351.0971.025R_i, wR_2 (h \ge 2 m)0.0424,0.10960.787,0.21630.812,0.2111R_i, wR_2 (h \ge 2 m)0.619,0.12220.857,0.22530.1592,0.2586$	<i>c</i> [Å]	14.9811(11)	27.924(4)	29.434(3)
β [°]81.552(4)90.0090.00 γ (°]81.251(4)120.00120.00 γ (°]1445.20(18)3046.09)9616(2) Z 269 ρ [g/cm ³]1.3601.1241.264 ρ (g/cm ³]0.880.8870.627 μ [mm ⁻¹]0.9840.5830.627 τ_{min} / τ_{max} 0.6772/0.74550.6189/0.74560.6255/0.7456 θ -range [°]2.751-27.0622.188-24.9872.789-27.062 hk -range9.916, ±19-13 ±12, -13 ±13, -32 33±23, ±23, ±23 ±42measured refl.811768502663unique refl. [R_{int}]30697 [0.0595]19079 [0.0425]2382 [0.1113]observed refl. ($l > 2$ 482232283786 $\sigma(n)$ 579 / 19 / 218637/ 330 / 488 ρ range.1.0351.0971.025 g sodness-of-fit (f^2]1.0351.0970.812, 0.2111 r_1 , wR_2 ($r_1 > 2\sigma(n)$)0.619, 0.12200.6857, 0.22530.5159, 0.2586	α [°]	86.824(4)	90.00	90.00
γ [°]81.251(4)120.00120.00ν [ų]1445.20(18)3046.0(9)9616(2)Z269ρ [g/cm³]1.3601.1241.264ρ [g/cm³]6180.8630.627μ [mm-1]0.9840.5830.6275/0.7456θ-range [°]0.572/0.74550.6189/0.74560.6255/0.7456θ-range [°]2.751-27.0621.188-24.9872.789-27.062measured refl.811768502633unique refl. [Kım]30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. (/>482232283786cr(/)517/149/433579/19/2186937/330/488goodness-of-fit (f²)1.0351.0971.025goodness-of-fit (f²)0.0424.0.10960.787,0.21630.812,0.2111ki, wR2 (ki ldata)0.619,0.12200.857,0.22530.1592,0.2586	β[°]	81.552(4)	90.00	90.00
V [ų] 1445.20(18) 3046.0(9) 9616(2) Z 2 6 9 p [g/cm³] 1.360 1.124 1.264 p (000) 618 086 3807 µ [mm⁻¹] 0.984 0.583 0.627 0.717 0.6772/0.7455 0.6189/0.7456 0.6255/0.7456 0-range [°] 0.6772/0.7455 0.6189/0.7456 0.6255/0.7456 0-range [°] 2.751-27.062 2.188-24.987 2.789-27.062 hk/-range 19, ±16, ±19 -13 ±12, ±13 ±13, ±32 ±33 253, ±23, ±23, ±23, ±23, ±23, ±23, ±23, ±2	γ [°]	81.251(4)	120.00	120.00
Z 2 6 9 ρ [g/cm³] 1.360 1.24 1.264 ρ (00) 618 086 3807 μ [mm-1] 0.984 0.583 0.627 Tmin / Tmax 0.6772/0.7455 0.6189/0.7456 0.6255/0.7456 θ-range [°] 0.751-27.062 2.188-24.987 2.789-27.062 hk-range 9.9±16.±19 -13 ±12.±13.±13.±32.33 ±23.±23.±29.34 measured refl. 8117 6850 2663 unique refl. [R _{int}] 30697 [0.0595] 19079 [0.0425] 2382 [0.1113] observed refl. (r)> 242.2 3228 3786 ordta / restraints / 6317 / 149 / 433 579 / 19 / 218 6937/ 330 / 488 goodness-of-fit (F ²) 1.035 1.097 1.025 r1, wR2 (r) > co(r) 0.0424,0.1096 0.0787,0.2163 0.812,0.2111 r1, wR2 (al data) 0.0519,0.1222 0.857,0.2253 0.1592,0.2586	<i>V</i> [ų]	1445.20(18)	3046.0(9)	9616(2)
ρ [g/cm³] 1.360 1.124 1.264 F(000) 618 1086 3807 μ [mm ⁻¹] 0.984 0.583 0.627 Tmin / Tmax 0.6772/0.7455 0.6189/0.7456 0.6255/0.7456 θ-range [°] 2.751-27.062 2.188-24.987 2.789-27.062 hk/-range ±9,±16,±19 -13 +12,-13 +13,-32 33 ±23,±23,-29 34 measured refl. 8117 6850 2663 unique refl. [Rint] 30697 [0.0595] 19079 [0.0425] 2382 [0.1113] observed refl. (I > 4822 3228 3786 2\cr\()) - 579 / 19 / 218 6937 / 330 / 488 goodness-of-fit (F ²) 1.035 1.097 1.025 R1, wR2 (I > 2\cr\()) 0.424, 0.1096 0.787, 0.2163 0.812, 0.2111 R1, wR2 (all data) 0.619, 0.1222 0.857, 0.2253 0.1592, 0.2586	Ζ	2	6	9
$F(000)$ 618 1086 3807 μ [mm ⁻¹] 0.984 0.583 0.627 T_{min} / T_{max} $0.6772 / 0.7455$ $0.6189 / 0.7456$ $0.6255 / 0.7456$ θ -range [°] $2.751 - 27.062$ $2.188 - 24.987$ $2.789 - 27.062$ hk /-range $\pm 9, \pm 16, \pm 19$ $-13 \pm 12, -13 \pm 13, -32.33$ $\pm 23, \pm 23, -29.34$ measured refl. 8117 6850 2663 unique refl. [R_{int}] $30697 [0.0595]$ $19079 [0.0425]$ $23382 [0.1113]$ observed refl. ($l > 2$ 4822 3228 3786 $2\sigma(l)$ -1025 -1035 1.097 1.025 goodness-of-fit (F^2) 1.035 1.097 1.025 $R_1, wR2$ ($l data$) $0.0619, 0.1222$ $0.0857, 0.2253$ $0.1592, 0.2586$	ρ [g/cm³]	1.360	1.124	1.264
μ [mm ⁻¹]0.9840.5830.627 T_{min} / T_{max} 0.6772/0.74550.6189/0.74560.6255/0.7456 θ -range [°]2.751-27.0622.188-24.9872.789-27.062 hkl -range $\pm 9, \pm 16, \pm 19$ -13 $\pm 12, -13 \pm 13, -32$ 33 $\pm 23, \pm 23, -29$ 34measured refl.811768502663unique refl. [R_{int}]30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. ($l > 2$ 482232283786 $2\sigma(l)$ δ 3579 / 19 / 2186937/ 330/ 488goodness-of-fit (F^2)1.0351.0971.025 $R1, wR2$ ($l > 2\sigma(l)$)0.0424, 0.10960.0787, 0.21630.0812, 0.2111 $R1, wR2$ (all data)0.0619, 0.12220.0857, 0.22530.1592, 0.2586	F(000)	618	1086	3807
T_{min} / T_{max} 0.6772/ 0.74550.6189/ 0.74560.6255/0.7456 θ -range [°]2.751- 27.0622.188- 24.9872.789- 27.062 hkl -range $\pm 9, \pm 16, \pm 19$ $-13 \pm 12, -13 \pm 13, -32.33$ $\pm 23, \pm 23, -29.34$ measured refl.811768502663unique refl. [R_{int}]30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. ($l > 4822$ 32283786 $2\sigma(l)$ 6317 / 149 / 4333579 / 19 / 2186937/ 330/ 488goodness-of-fit (f^2)1.0351.0971.025 $R1, wR2$ ($l > 2\sigma(l)$)0.0424, 0.10960.0787, 0.21630.0812, 0.2111 $R1, wR2$ (all data)0.0619, 0.12220.0857, 0.22530.1592, 0.2586	μ [mm ⁻¹]	0.984	0.583	0.627
θ -range [°]2.751-27.0622.188-24.9872.789-27.062hkl-range $\pm 9, \pm 16, \pm 19$ $-13 \pm 12, -13 \pm 13, -32.33$ $\pm 23, \pm 23, -29.34$ measured refl.811768502663unique refl. [Rint]30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. (l >482232283786 $2\sigma(l)$ 6317 / 149 / 433579 / 19 / 2186937 / 330 / 488goodness-of-fit (F²)1.0351.0971.025R1, wR2 (l > 2 $\sigma(l)$)0.0424, 0.10960.0787, 0.21630.0812, 0.2111R1, wR2 (all data)0.0619, 0.12220.0857, 0.22530.1592, 0.2586	T _{min} / T _{max}	0.6772/ 0.7455	0.6189/ 0.7456	0.6255/0.7456
hkl-range $\pm 9, \pm 16, \pm 19$ $-13 \pm 12, -13 \pm 13, -32 = 33$ $\pm 23, \pm 23, -29 = 34$ measured refl. 8117 6850 2663 unique refl. [Rint] $30697 [0.0595]$ $19079 [0.0425]$ $23382 [0.1113]$ observed refl. (l > 4822 3228 3786 $2\sigma(l)$ $6317 / 149 / 433$ $3579 / 19 / 218$ $6937 / 330 / 488$ goodness-of-fit (F ²) 1.035 1.097 1.025 $R1, wR2 (l > 2\sigma(l))$ $0.0424, 0.1096$ $0.0787, 0.2163$ $0.0812, 0.2111$ $R1, wR2 (all data)$ $0.0619, 0.1222$ $0.0857, 0.2253$ $0.1592, 0.2586$	θ -range [°]	2.751- 27.062	2.188- 24.987	2.789– 27.062
measured refl.811768502663unique refl. [R_{int}]30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. ($l > 2$ 482232283786 $2\sigma(l)$) $317 / 149 / 433$ $3579 / 19 / 218$ 6937 / 330 / 488data / restraints / param. $6317 / 149 / 433$ $3579 / 19 / 218$ 6937 / 330 / 488goodness-of-fit (F^2) 1.035 1.097 1.025 $R1, wR2 (l > 2\sigma(l))$ $0.0424, 0.1096$ $0.0787, 0.2163$ $0.0812, 0.2111$ $R1, wR2 (all data)$ $0.0619, 0.1222$ $0.0857, 0.2253$ $0.1592, 0.2586$	hkl-range	±9, ±16, ±19	-13 +12, -13 +13, -32 33	±23, ±23, -29 34
unique refl. $[R_{int}]$ 30697 [0.0595]19079 [0.0425]23382 [0.1113]observed refl. $(l > 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 2 3 3 2 3$	measured refl.	8117	6850	2663
observed refl. (I > $2\sigma(I)$)482232283786data / restraints / param. $6317 / 149 / 433$ $3579 / 19 / 218$ $6937 / 330 / 488$ goodness-of-fit (F²) 1.035 1.097 1.025 R1, wR2 (I > $2\sigma(I)$) $0.0424, 0.1096$ $0.0787, 0.2163$ $0.0812, 0.2111$ R1, wR2 (all data) $0.0619, 0.1222$ $0.0857, 0.2253$ $0.1592, 0.2586$	unique refl. [<i>R</i> _{int}]	30697 [0.0595]	19079 [0.0425]	23382 [0.1113]
data / restraints / param. $6317 / 149 / 433$ $3579 / 19 / 218$ $6937 / 330 / 488$ goodness-of-fit (F^2)1.0351.0971.025 $R1, wR2 (I > 2\sigma(I))$ 0.0424, 0.10960.0787, 0.21630.0812, 0.2111 $R1, wR2 (all data)$ 0.0619, 0.12220.0857, 0.22530.1592, 0.2586	observed refl. (<i>l</i> > 2 σ (<i>l</i>))	4822	3228	3786
goodness-of-fit (F^2)1.0351.0971.025 $R1$, $wR2$ ($I > 2\sigma(I)$)0.0424, 0.10960.0787, 0.21630.0812, 0.2111 $R1$, $wR2$ (all data)0.0619, 0.12220.0857, 0.22530.1592, 0.2586	data / restraints / param.	6317 / 149 / 433	3579 / 19 / 218	6937/ 330/ 488
R1, wR2 ($l > 2\sigma(l)$)0.0424, 0.10960.0787, 0.21630.0812, 0.2111R1, wR2 (all data)0.0619, 0.12220.0857, 0.22530.1592, 0.2586	goodness-of-fit (<i>F</i> ²)	1.035	1.097	1.025
R1, wR2 (all data) 0.0619, 0.1222 0.0857, 0.2253 0.1592, 0.2586	R1, wR2 ($l > 2\sigma(l)$)	0.0424, 0.1096	0.0787, 0.2163	0.0812, 0.2111
	R1, wR2 (all data)	0.0619, 0.1222	0.0857, 0.2253	0.1592, 0.2586
resid. el. dens. [e/A ²] -0.438/ 0.862 -1.14// 1.060 -1.068/ 0.68/	resid. el. dens. [e/ų]	-0.438/ 0.862	-1.147/ 1.060	-1.068/0.687

Table S1. Crystal data and refinement details for 2, 3 and 4.



Figure S1. 400 MHz NMR spectra of a 0.025M solution of **1** in MeOD. Inset shows magnified spectra of the range 6 ppm to 8.7 ppm.



Figure S2. 400 MHz NMR spectra of a 0.05M solution of $NaBH_4$ in MeOD after purging CO_2 for 3 minutes; the formation of $Na[H_3B(OCHO)]$.^{1, 2}



Figure S3. 400 MHz NMR spectra of the in-situ generated MeOD solution of **3** + remaining excess of Et₃N & NaBH₄. Inset shows magnified spectra of the range 7.2 ppm to 8.9 ppm.



Figure S4. 400 MHz NMR spectra of (a) a 0.05M solution of NaBH₄ in MeOD after purging CO₂ for 3 minutes, (b) insitu generated MeOD solution of **3** + remaining excess of Et₃N & NaBH₄, (c) b + 1atm CO₂ after 24 h and (d) b + 1atm CO₂ after 48 h. The changes in the chemical shift values of the aromatic hydrogens with time are depicted in figure S5.



Figure S5. Magnified depiction of figure 4s of the range 7.2 ppm to 8.8 ppm, showing change over a period of 48 h.



Figure S6. Magnified depiction of figure 4s of the range 1.1 ppm to 3.5 ppm, showing change in the structure over a period of 48 h.^{3, 4}



Figure S7. 100.6 MHz ¹³CNMR spectra of (a) a 0.05M solution of NaBH₄ in MeOD after purging CO₂ for 3 minutes, (b) in-situ generated MeOD solution of **3** + remaining excess of Et₃N & NaBH₄, (c) b + 1atm CO₂ after 24 h and (d) b + 1atm CO₂ after 48 h .^{1, 2, 5-7}



Figure S8. Magnified depiction of figure S7 of the range 95 ppm to 185 ppm, showing change in the structure over a period of 48 h.



Figure S9. Magnified depiction of figure S7 of the range 5 ppm to 65 ppm, showing change in the structure over a period of 48 h.



Figure S10. UV-Vis spectrums of 0.5 mM MeOD solution of **2** (blue trace), **3** + air (after 1 minute, black trace), **3** + air (after 40 minute, brown trace) and **4** (green trace).



Figure S11. EPR spectra of **2** (1.3 mM in MeCN) at different temperatures, 5 K (black), 10 K (red) and 20 K (blue). EPR conditions: microwave power: 200 μ W, microwave frequency 9.287 GHz.



Figure S12. EPR spectra of **4** (1 mM in MeCN) at different temperatures, 5 K (black), 10 K (red) and 20 K (blue). EPR conditions: microwave power: 200 μ W, microwave frequency 9.287 GHz.

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