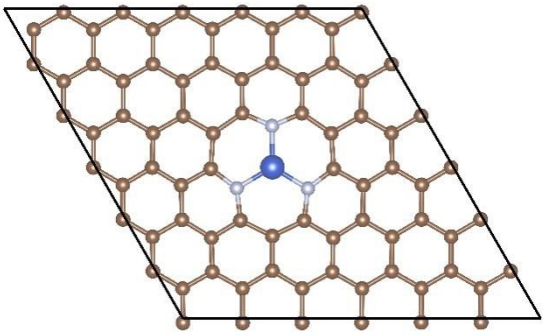
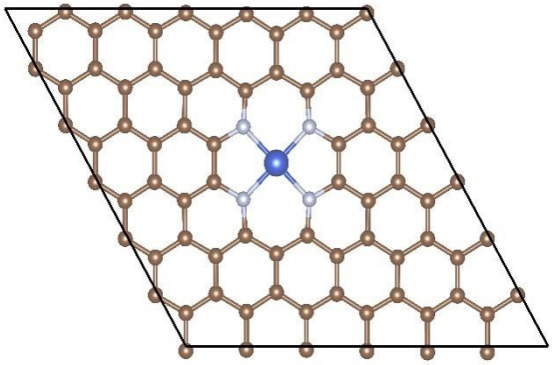
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Supplementary Figures



(a)



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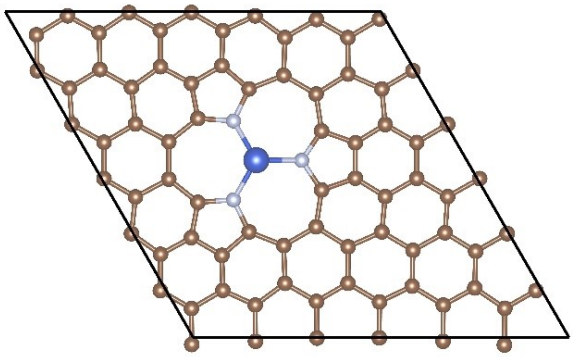
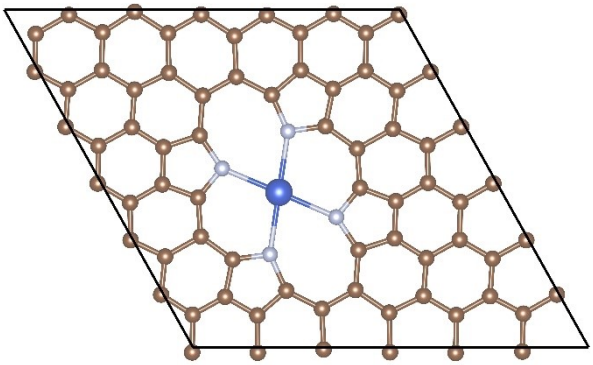


(c)



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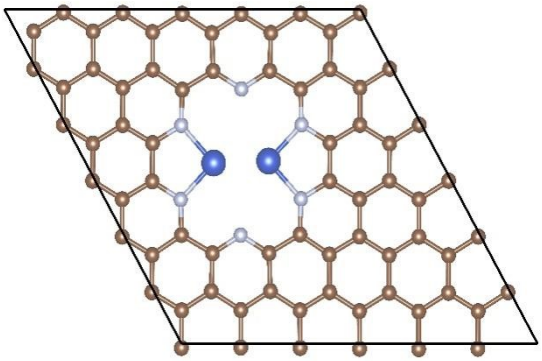
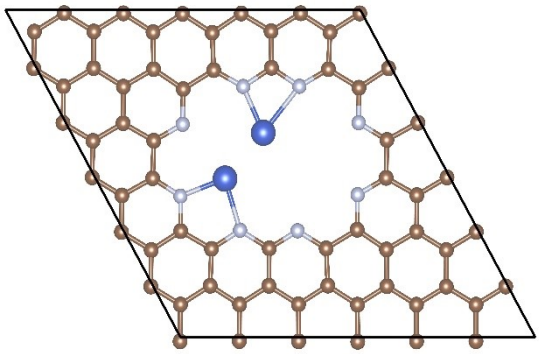
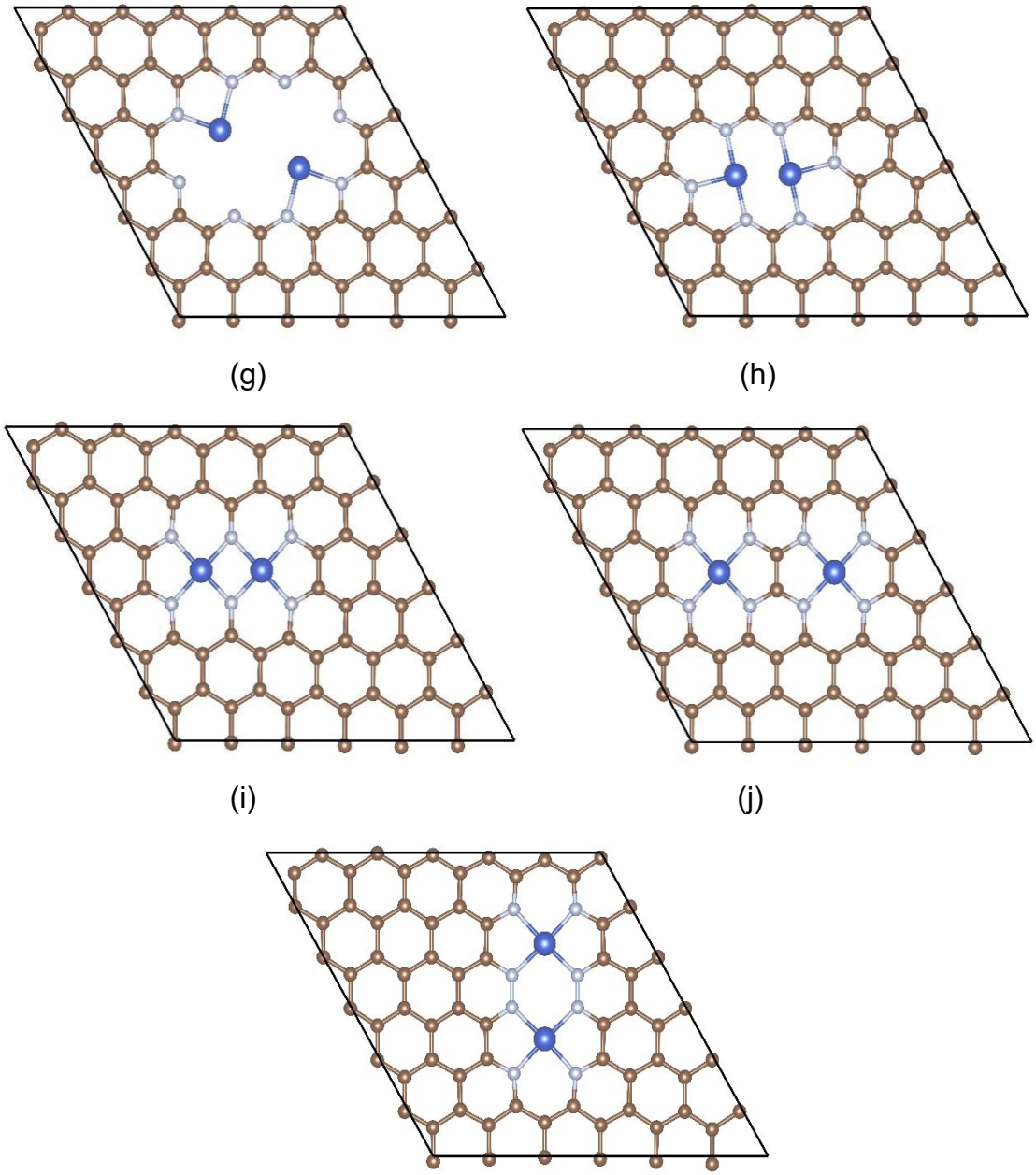


(e)

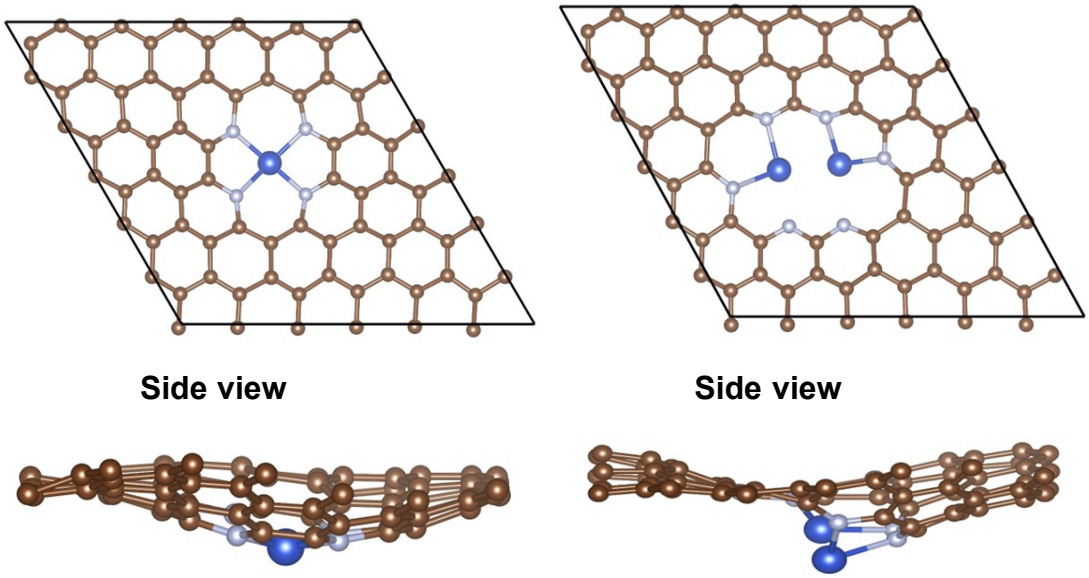


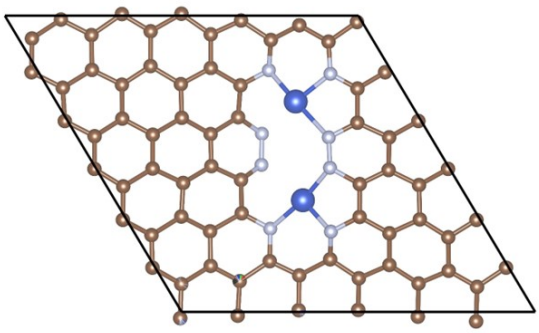
(f)



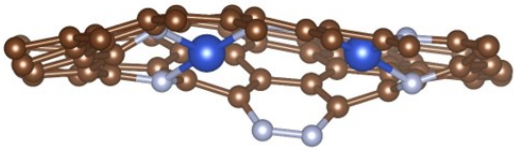
Supplementary Figure 1 Optimized SACs and DACs configurations (brown: C; blue: Cu; gray: N). (a) CuNC-3-pyridine. (b) CuNC-4-pyridine. (c) CuNC-3-pyrrole. (d) CuNC-4-pyrrole. (e) CuCu-NC-2a. (f) CuCu-NC-2b. (g) CuCu-NC-2c. (h) CuCuNC-3. (i) CuCuNC-4a. (j) CuCuNC-4b. (k) CuCuNC-4c (brown: C; blue: Cu; gray: N).

Top view **Top view**


Side view
Side view
(a)
(b)
Top view
Top view
Side view
Side view
(c)
(d)
Top view

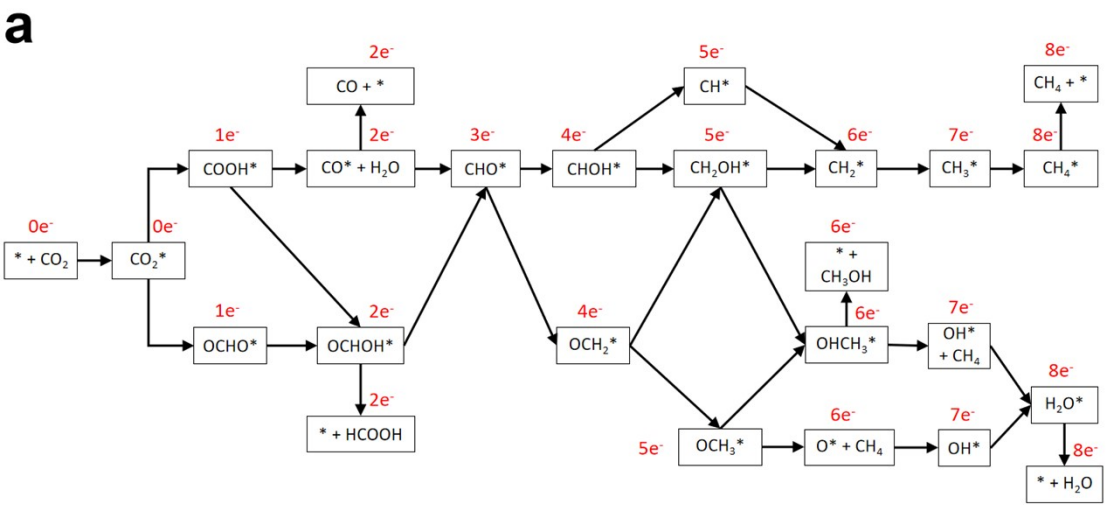


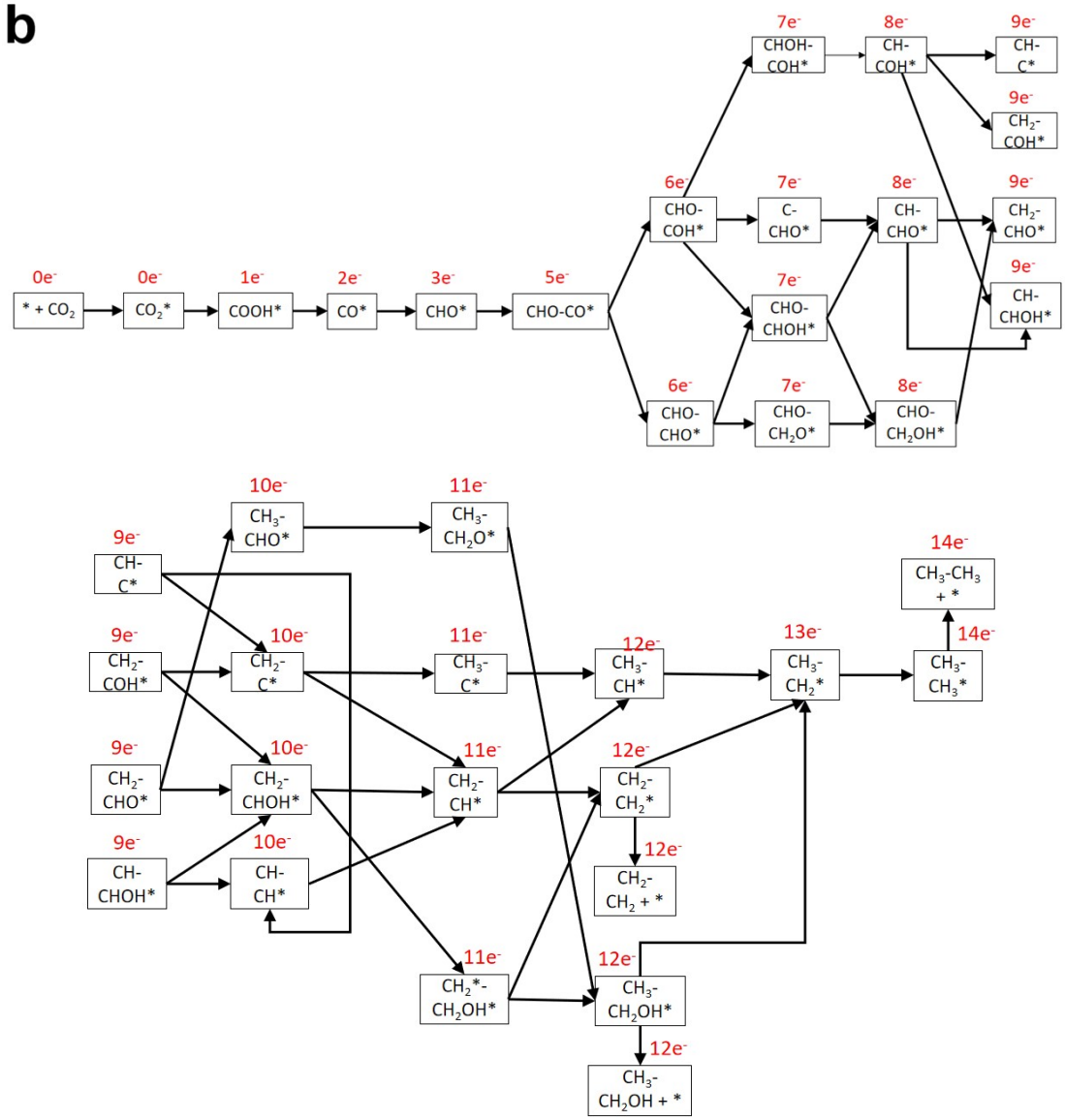
Side view



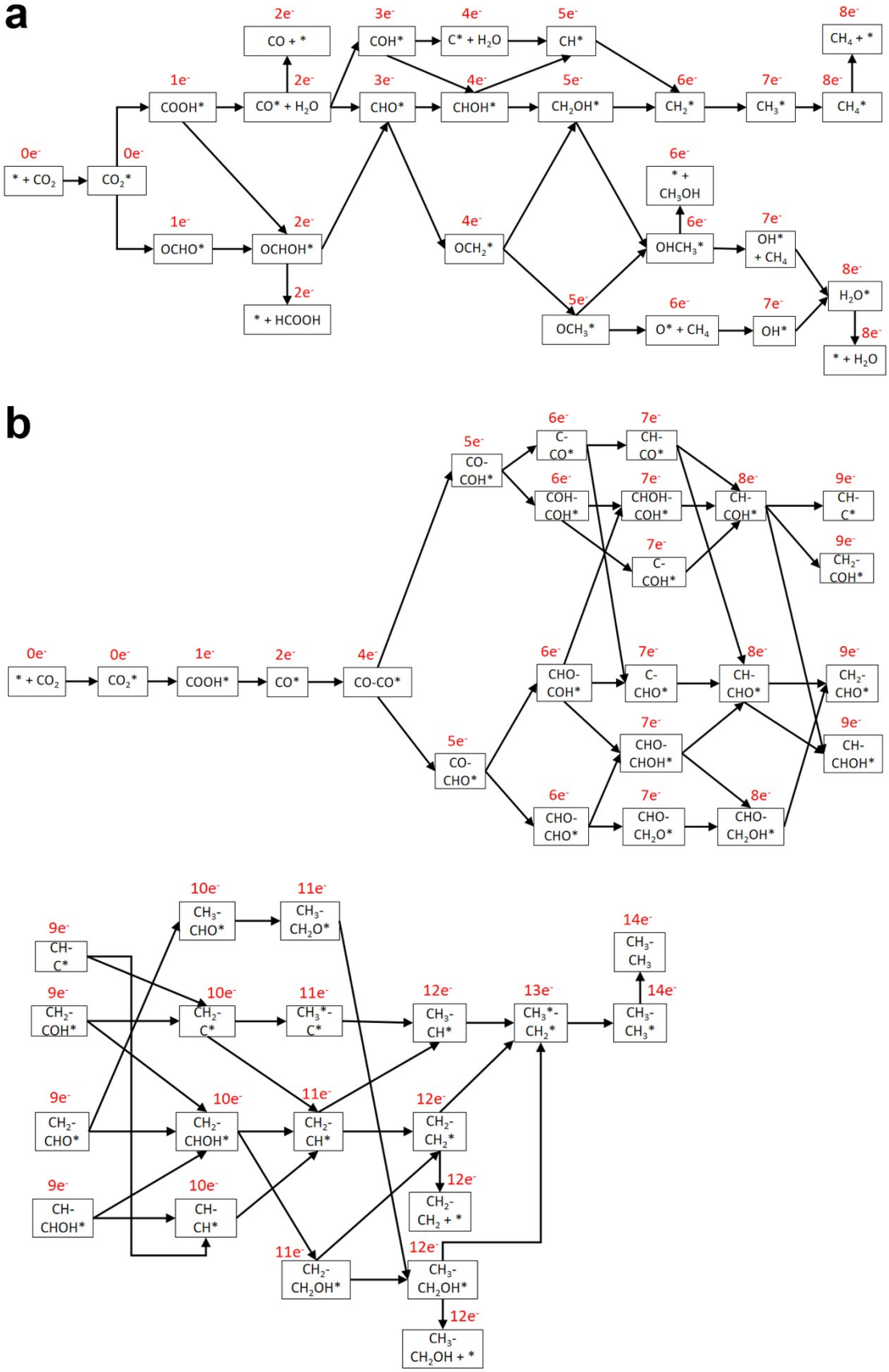
(e)

Supplementary Figure 2 Structures of (a) CuNC-4-pyridine, (b) CuCuNC-3, (c) CuCuNC-4a, (d) CuCuNC-4b and (e) CuCuNC-4c after 300K AIMD simulations for 10 ps (brown: C; blue: Cu; gray: N).

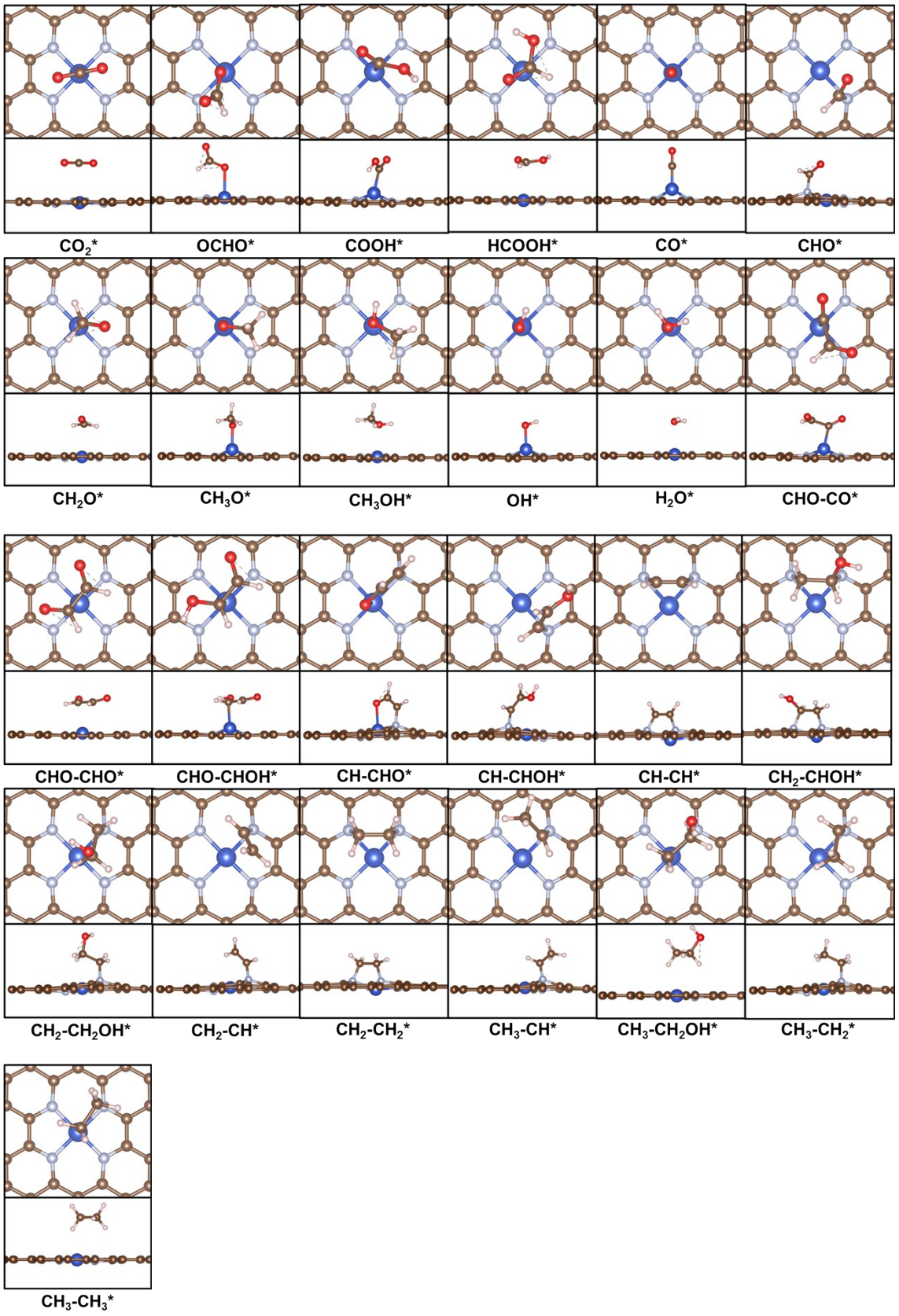




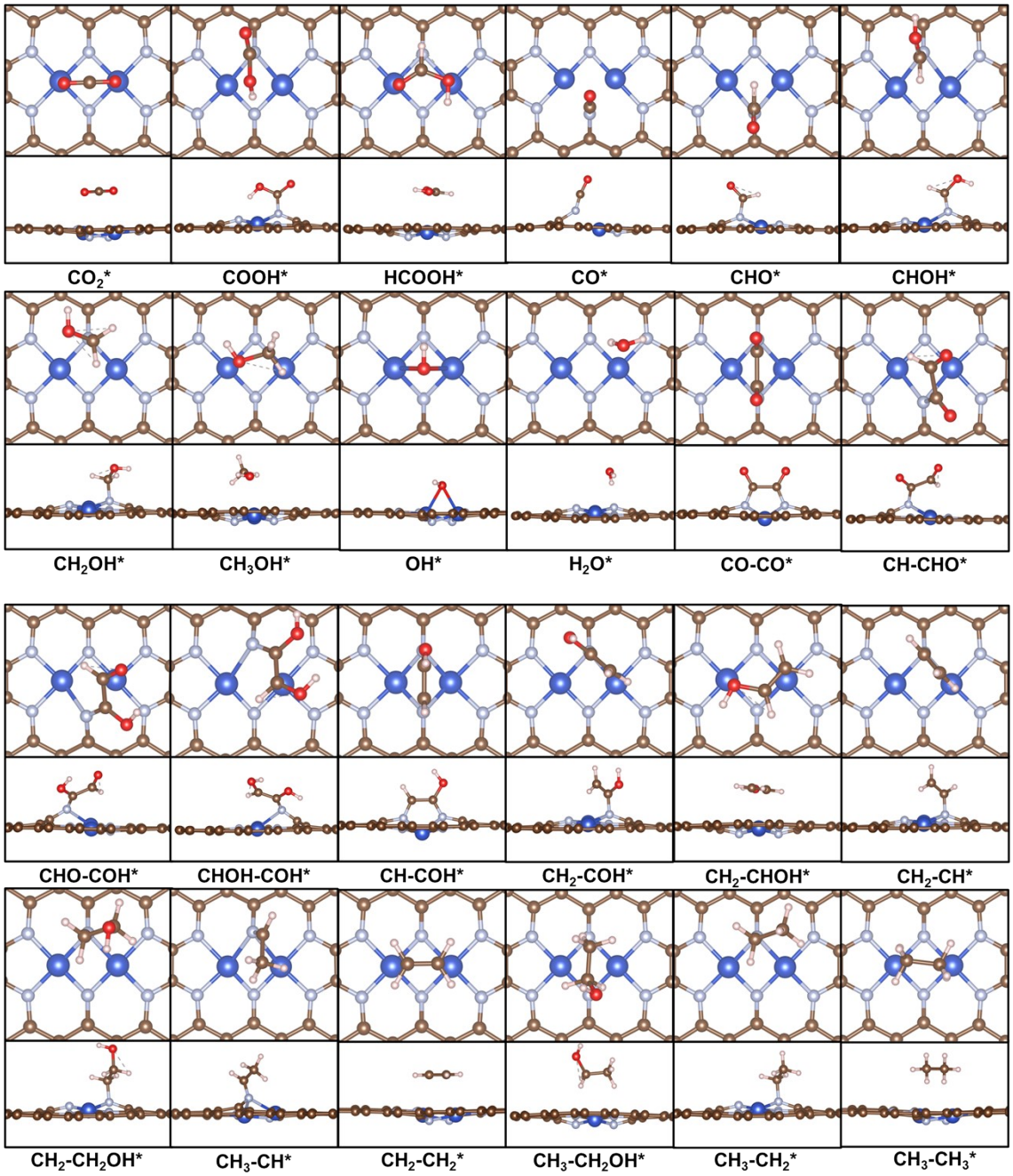
Supplementary Figure 3 Possible pathways for CO_2 electroreduction to (a) C_1 and (b) C_2 products on CuNC-4-pyridine. "*" means the catalyst. More details on elementary steps are listed in Table S2. The numbers in the graph represent the number of electrons transferred.


a
0e⁻
* + CO2
0e⁻
CO2*
1e⁻
COOH*
2e⁻
CO + *
2e⁻
CO* + H2O
3e⁻
COH*
4e⁻
C* + H2O
5e⁻
CH*
3e⁻
CHO*
4e⁻
CHOH*
5e⁻
CH2OH*
6e⁻
CH2*
7e⁻
CH3*
8e⁻
CH4*
8e⁻
CH4 + *
1e⁻
OCHO*
2e⁻
OCHOH*
2e⁻
* + HCOOH
4e⁻
OCH2*
5e⁻
OCH3*
6e⁻
* + CH3OH
6e⁻
OHCH3*
7e⁻
OH* + CH4
6e⁻
O* + CH4
7e⁻
OH*
8e⁻
H2O*
8e⁻
* + H2O
b
0e⁻
* + CO2
0e⁻
CO2*
1e⁻
COOH*
2e⁻
CO*
4e⁻
CO-CO*
5e⁻
CO-COH*
5e⁻
CO-CHO*
6e⁻
C-CO*
6e⁻
COH-COH*
7e⁻
CH-CO*
7e⁻
CHOH-COH*
7e⁻
C-COH*
8e⁻
CH-COH*
9e⁻
CH-C*
9e⁻
CH2-COH*
6e⁻
CHO-COH*
7e⁻
C-CHO*
8e⁻
CH-CHO*
9e⁻
CH2-CHO*
7e⁻
CHO-CHOH*
9e⁻
CH-CHOH*
6e⁻
CHO-CHO*
7e⁻
CHO-CH2O*
8e⁻
CHO-CH2OH*
9e⁻
CH-C*
9e⁻
CH2-COH*
9e⁻
CH2-CHO*
9e⁻
CH-CHOH*
9e⁻
CH2-CHOH*
10e⁻
CH3-CHO*
10e⁻
CH2-C*
10e⁻
CH2-CHOH*
10e⁻
CH-CH*
11e⁻
CH3-CH2O*
11e⁻
CH3*-C*
11e⁻
CH2-CH*
11e⁻
CH2-CH2OH*
12e⁻
CH3-CH*
12e⁻
CH2-CH2*
12e⁻
CH2-CH2 + *
12e⁻
CH3-CH2OH*
12e⁻
CH3-CH2OH + *
13e⁻
CH3*-CH2*
14e⁻
CH3-CH3
14e⁻
CH3-CH3*

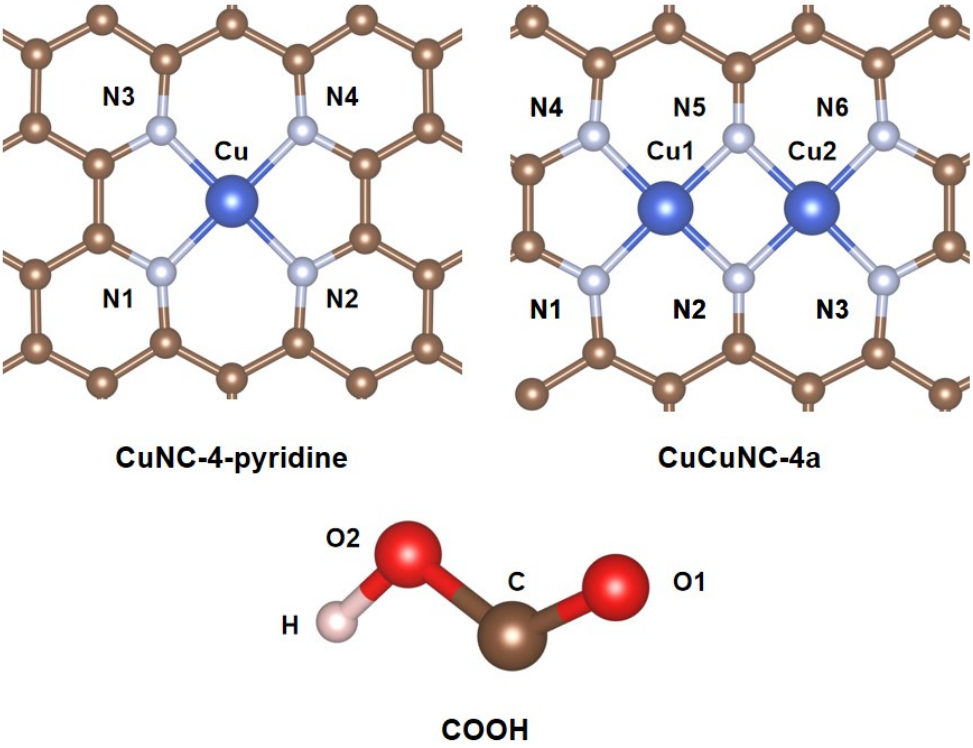
Supplementary Figure 4 Possible pathways for CO_2 electroreduction to (a) C_1 and (b) C_2 products on CuCuNC-4a. "*" means the catalyst. More details on elementary steps are listed in Table S3. The numbers in the graph represent the number of electrons transferred.



Supplementary Figure 5 Optimized intermediates for CO_2 electroreduction on CuNC-4-pyridine site (brown: C; blue: Cu; gray: N; red: O; white: H).



Supplementary Figure 6 Optimized intermediates for CO_2 electroreduction on CuCuNC-4a site (brown: C; blue: Cu; gray: N; red: O; white: H).



Supplementary Figure 7 Position numbers of C, N, Cu, O and H atoms on CuNC-4-pyridine and CuCuNC-4a and COOH.

Supplementary Tables

Supplementary Table 1 Bader charge transfer of Cu, N, O and H atoms in CuNC-4-pyridine and CuCuNC-4a with and without adsorbed COOH.

Bader charge (|e|)	CuNC-4-pyridine	CuNC-4-pyridine-COOH	CuCuNC-4a	CuCuNC-4a-COOH
Cu1	-0.96	-0.87	-0.97	-0.91
Cu2	-	-	-0.97	-0.92
N1	1.17	1.20	1.18	1.23
N2	1.29	1.21	1.13	1.17
N3	1.30	1.19	1.25	1.25
N4	1.25	1.24	1.27	1.23
N5	-	-	1.17	1.24
N6	-	-	1.21	1.20
C	-	-1.26	-	-1.93
O1	-	1.17	-	1.19
O2	-	1.14	-	1.16
H	-	-0.65	-	-0.62

Supplementary Table 2 Free energies for elementary steps in possible pathways for CO_2 electroreduction to (a) C_1 and (b) C_2 products on CuNC-4-pyridine. "*" means the catalyst.

Step Index	Reaction	Reaction Free Energy
1	$* + CO_2 + H^+ + e^- \rightarrow COOH*$	1.39
2	$COOH* + H^+ + e^- \rightarrow CO* + H_2O$	-0.88
3	$CO* \rightarrow CO + *$	-0.30
4	$CO* + H^+ + e^- \rightarrow CHO*$	0.71
5	$CHO* + H^+ + e^- \rightarrow CHOH*$	0.79
6	$CHOH* + H^+ + e^- \rightarrow CH* + H_2O$	0.26
7	$CHOH* + H^+ + e^- \rightarrow CH_2OH*$	-0.95
8	$CH* + H^+ + e^- \rightarrow CH_2*$	-1.27
9	$CH_2OH* + H^+ + e^- \rightarrow CH_2* + H_2O$	-0.05
10	$CH_2* + H^+ + e^- \rightarrow CH_3*$	-0.95
11	$CH_3* + H^+ + e^- \rightarrow CH_4 + *$	-1.41
12	$* + CO_2 + H^+ + e^- \rightarrow OCHO*$	0.77

13	$OCHO^* + H^+ + e^- \rightarrow HCOOH^*$	-0.23
14	$HCOOH^* \rightarrow HCOOH + *$	-0.20
15	$OCHOH^* + H^+ + e^- \rightarrow CHO^* + H_2O$	0.68
16	$CHO^* + H^+ + e^- \rightarrow CH_2O^*$	-0.68
17	$CH_2O^* + H^+ + e^- \rightarrow CH_3O^*$	0.47
18	$CH_2O^* + H^+ + e^- \rightarrow CH_2OH^*$	0.52
19	$CH_3O^* + H^+ + e^- \rightarrow CH_3OH^*$	-0.98
20	$CH_3OH^* \rightarrow CH_3OH + *$	-0.13
21	$CH_2OH^* + H^+ + e^- \rightarrow CH_3OH^*$	-1.03
22	$CH_3OH^* + H^+ + e^- \rightarrow OH^* + CH_4$	0.14
23	$OH^* + H^+ + e^- \rightarrow H_2O + *$	-1.53
24	$CH_3O^* + H^+ + e^- \rightarrow O^* + CH_4$	1.27
25	$O^* + H^+ + e^- \rightarrow OH^*$	-2.10
26	$COOH^* + H^+ + e^- \rightarrow OCHOH^*$	-0.85
27	$CH_3^* + H^+ + e^- \rightarrow CH_4 *$	-1.40
28	$CH_4^* \rightarrow CH_4 + *$	-0.01
29	$OH^* + H^+ + e^- \rightarrow H_2O^*$	-1.11
30	$H_2O^* \rightarrow H_2O + *$	-0.41
31	$CO^* + CHO^* \rightarrow CO\text{-}CHO^* + *$	-0.30
32	$CHO\text{-}CO^* + H^+ + e^- \rightarrow CHO\text{-}COH^*$	0.70
33	$CHO\text{-}COH^* + H^+ + e^- \rightarrow C\text{-}CHO^* + H_2O$	-1.51
34	$CHO\text{-}COH^* + H^+ + e^- \rightarrow CHO\text{-}CHOH^*$	-1.25
35	$C\text{-}CHO^* + H^+ + e^- \rightarrow CH\text{-}CHO^*$	0.37
36	$CHO\text{-}CHOH^* + H^+ + e^- \rightarrow CH\text{-}CHO^* + H_2O$	0.11
37	$CH\text{-}CHO^* + H^+ + e^- \rightarrow CH_2\text{-}CHO^*$	-1.18
38	$CH\text{-}CHO^* + H^+ + e^- \rightarrow CH\text{-}CHOH^*$	-0.07
39	$CH_2\text{-}CHO + H^+ + e^- \rightarrow CH_3\text{-}CHO^*$	-0.68
40	$CH_2\text{-}CHO + H^+ + e^- \rightarrow CH_2\text{-}CHOH^*$	1.52
41	$CH\text{-}CHOH^* + H^+ + e^- \rightarrow CH_2\text{-}CHOH^*$	0.41
42	$CH\text{-}CHOH^* + H^+ + e^- \rightarrow CH\text{-}CH^* + H_2O$	0.36
43	$CH_3\text{-}CHO^* + H^+ + e^- \rightarrow CH_3\text{-}CH_2O^*$	1.19
44	$CH_3\text{-}CH_2O^* + H^+ + e^- \rightarrow CH_3\text{-}CH_2OH^*$	-1.43

45	CH_3-CH_2OH^* → CH_3-CH_2OH + *	0.10
46	CH_2-$CHOH^*$ + H^+ + e^- → CH_2-CH^* + H_2O	-1.50
47	CH_2-$CHOH^*$ + H^+ + e^- → CH_2-CH_2OH^*	-1.04
48	CH-CH^* + H^+ + e^- → CH_2-CH^*	-1.44
49	CH_2-CH^* + H^+ + e^- → CH_2-CH_2^*	0.58
50	CH_2-CH_2^* → CH_2-CH_2 + *	-1.44
51	CH_2-CH_2OH^* + H^+ + e^- → CH_2-CH_2^* + H2O	0.12
52	CH_2-CH_2OH^* + H^+ + e^- → CH_3-CH_2OH^*	-1.41
53	CHO-CO^* + H^+ + e^- → CHO-CHO^*	-0.60
54	CHO-CHO^* + H^+ + e^- → CHO-$CHOH^*$	0.05
55	CHO-CHO^* + H^+ + e^- → CHO-CH_2O^*	0.49
56	CHO-CH_2O^* + H^+ + e^- → CHO-CH_2OH^*	-0.85
57	CHO-$CHOH^*$ + H^+ + e^- → CHO-CH_2OH^*	-0.41
58	CHO-CH_2OH^* + H^+ + e^- → CH_2-CHO^* + H_2O	-0.65
59	CHO-COH^* + H^+ + e^- → CHOH-COH^*	-0.35
60	CHOH-COH^* + H^+ + e^- → CH-COH^* + H_2O	0.37
61	CH-COH^* + H^+ + e^- → CH-C^* + H_2O	-0.44
62	CH-COH^* + H^+ + e^- → CH_2-COH^*	-1.25
63	CH-COH^* + H^+ + e^- → CH-$CHOH^*$	-1.23
64	CH-C^* + H^+ + e^- → CH_2-C^*	-0.72
65	CH_2-COH^* + H^+ + e^- → CH_2-C^* + H_2O	0.08
66	CH_2-COH^* + H^+ + e^- → CH_2-$CHOH^*$	0.43
67	CH-C^* + H^+ + e^- → CH-CH^*	-0.43
68	CH_2-C^* + H^+ + e^- → CH_2-CH^*	-1.44
69	CH_2-C^* + H^+ + e^- → CH_3-C^*	0.08
70	CH_3-C^* + H^+ + e^- → CH_3-CH^*	-0.81
71	CH_3-CH^* + H^+ + e^- → CH_3-CH_2^*	-1.25
72	CH_2-CH^* + H^+ + e^- → CH_3-CH^*	0.43
73	CH_2-CH_2^* + H^+ + e^- → CH_3-CH_2^*	-1.39
74	CH_3-CH_2OH^* + H^+ + e^- → CH_3-CH_2^* + H_2O	0.13
75	CO_2 + * → CO_2^*	0.32
76	CH_3-CH_2^* + H^+ + e^- → CH_3-CH_3^*	-1.30

77	CH_3-CH_3* → CH_3-CH_3 + *	0.26

Supplementary Table 3 Free energies for elementary steps for CO_2 electroreduction to (a) C_1 and (b) C_2 products on CuCuNC-4a. "*" means the catalyst.

Step Index	Reaction	Reaction Free Energy
1	* + CO_2 + H^+ + e^- → COOH*	0.27
2	COOH* + H^+ + e^- → CO* + H_2O	0.22
3	CO* → CO + *	-0.29
4	CO* + H^+ + e^- → CHO*	-0.67
5	CHO* + H^+ + e^- → CHOH*	0.51
6	CHOH* + H^+ + e^- → CH* + H_2O	0.37
7	CHOH* + H^+ + e^- → CH_2OH*	-0.22
8	CH* + H^+ + e^- → CH_2*	-0.67
9	CH_2OH* + H^+ + e^- → CH_2* + H_2O	-0.08
10	CH_2* + H^+ + e^- → CH_3*	-0.92
11	CH_3* + H^+ + e^- → CH_4 + *	-0.48
12	CO* + H^+ + e^- → COH*	1.07
13	COH* + H^+ + e^- → C* + H_2O	-0.63
14	C* + H^+ + e^- → CH*	-0.23
15	COH* + H^+ + e^- → CHOH*	-1.23
16	* + CO_2 + H^+ + e^- → OCHO*	0.54
17	OCHO* + H^+ + e^- → HCOOH*	-0.16
18	HCOOH* → HCOOH + *	-0.03
19	OCHOH* + H^+ + e^- → CHO* + H_2O	-0.55
20	CHO* + H^+ + e^- → CH_2O*	0.64
21	CH_2O* + H^+ + e^- → CH_3O*	0.51
22	CH_2O* + H^+ + e^- → CH_2OH*	-0.34
23	CH_3O* + H^+ + e^- → CH_3OH*	-1.11
24	CH_3OH* → CH_3OH + *	0.05
25	CH_2OH* + H^+ + e^- → CH_3OH*	-0.26
26	CH_3OH* + H^+ + e^- → OH* + CH_4	0.29
27	OH* + H^+ + e^- → H_2O + *	-1.50

28	$CH_3O^* + H^+ + e^- \rightarrow O^* + CH_4$	0.40
29	$O^* + H^+ + e^- \rightarrow OH^*$	-1.22
30	$COOH^* + H^+ + e^- \rightarrow OCHOH^*$	0.10
31	$CH_3^* + H^+ + e^- \rightarrow CH_4 ^*$	-0.63
32	$CH_4^* \rightarrow CH_4 + *$	0.15
33	$OH^* + H^+ + e^- \rightarrow H_2O^*$	-1.27
34	$H_2O^* \rightarrow H_2O + *$	-0.23
35	$2CO^* \rightarrow CO\text{-}CO^* + *$	-1.02
36	$CO\text{-}CO^* + H^+ + e^- \rightarrow CO\text{-}CHO^*$	0.36
37	$CO\text{-}CHO^* + H^+ + e^- \rightarrow CHO\text{-}CHO^*$	0.40
38	$CO\text{-}CHO^* + H^+ + e^- \rightarrow CHO\text{-}COH^*$	0.19
39	$CHO\text{-}COH^* + H^+ + e^- \rightarrow C\text{-}CHO^* + H_2O$	0.67
40	$C\text{-}CHO^* + H^+ + e^- \rightarrow CH\text{-}CHO^*$	-1.53
41	$CHO\text{-}COH^* + H^+ + e^- \rightarrow CHO\text{-}CHOH^*$	0.06
42	$CHO\text{-}CHO^* + H^+ + e^- \rightarrow CHO\text{-}CHOH^*$	-0.15
43	$CHO\text{-}CHO^* + H^+ + e^- \rightarrow CHO\text{-}CH_2O^*$	0.45
44	$CHO\text{-}CH2O^* + H^+ + e^- \rightarrow CHO\text{-}CH_2OH^*$	-0.79
45	$CHO\text{-}CHOH^* + H^+ + e^- \rightarrow CH\text{-}CHO^* + H_2O$	-0.92
46	$CHO\text{-}CHOH^* + H^+ + e^- \rightarrow CHO\text{-}CH_2OH^*$	-0.19
47	$CH\text{-}CHO^* + H^+ + e^- \rightarrow CH_2\text{-}CHO^*$	0.00
48	$CH\text{-}CHO^* + H^+ + e^- \rightarrow CH\text{-}CHOH^*$	0.11
49	$CHO\text{-}CH_2OH^* + H^+ + e^- \rightarrow CH_2\text{-}CHO^* + H_2O$	-0.74
50	$CH_2\text{-}CHO^* + H^+ + e^- \rightarrow CH_2\text{-}CHOH^*$	-0.30
51	$CH\text{-}CHOH^* + H^+ + e^- \rightarrow CH_2\text{-}CHOH^*$	-0.41
52	$CH\text{-}CHOH^* + H^+ + e^- \rightarrow CH\text{-}CH^* + H_2O$	-0.47
53	$CH\text{-}CH^* + H^+ + e^- \rightarrow CH_2\text{-}CH^*$	-0.52
54	$CH_2\text{-}CHOH^* + H^+ + e^- \rightarrow CH_2\text{-}CH^* + H2O$	-0.57
55	$CH_2\text{-}CHOH^* + H^+ + e^- \rightarrow CH_2\text{-}CH_2OH^*$	-0.09
56	$CH_2\text{-}CH^* + H^+ + e^- \rightarrow CH_2\text{-}CH_2^*$	-0.24
57	$CH_2\text{-}CH_2^* \rightarrow CH_2\text{-}CH_2 + *$	0.45
58	$CH_2\text{-}CH_2OH^* + H^+ + e^- \rightarrow CH_2\text{-}CH_2^* + H_2O$	-0.72
59	$CH_2\text{-}CH_2OH^* + H^+ + e^- \rightarrow CH_3\text{-}CH_2OH^*$	-0.46

60	CH_3-$CH_2OH^* \rightarrow CH_3$-$CH_2OH + *$	0.19
61	CO-$COH^* + H^+ + e^- \rightarrow C$-$CO^* + H_2O$	0.50
62	CO-$COH^* + H^+ + e^- \rightarrow COH$-$COH^*$	1.09
63	C-$CO^* + H^+ + e^- \rightarrow CH$-$CO^*$	-0.98
64	C-$CO^* + H^+ + e^- \rightarrow C$-$CHO^*$	0.22
65	CH-$CO^* + H^+ + e^- \rightarrow CH$-$COH^*$	0.61
66	CH-$CO^* + H^+ + e^- \rightarrow CH$-$CHO^*$	-0.33
67	COH-$COH^* + H^+ + e^- \rightarrow CHOH$-$COH^*$	-0.82
68	COH-$COH^* + H^+ + e^- \rightarrow C$-$COH^* + H_2O$	0.04
69	C-$COH^* + H^+ + e^- \rightarrow CH$-$COH^*$	-1.00
70	CHO-$COH^* + H^+ + e^- \rightarrow CHOH$-$COH^*$	-0.82
71	$CHOH$-$COH^* + H^+ + e^- \rightarrow CH$-$COH^* + H_2O$	-0.14
72	CH-$COH + H^+ + e^- \rightarrow CH$-$CHOH$	-0.83
73	CH-$COH + H^+ + e^- \rightarrow CH_2$-$COH$	-0.97
74	CH-$COH + H^+ + e^- \rightarrow CH$-$C^* + H_2O$	-0.27
75	CH-$C^* + H^+ + e^- \rightarrow CH$-$CH^*$	-1.02
76	CH-$C^* + H^+ + e^- \rightarrow CH_2$-$C^*$	-0.53
77	CH_2-$CHO^* + H^+ + e^- \rightarrow CH_3$-$CHO^*$	-0.64
78	CH_2-$COH^* + H^+ + e^- \rightarrow CH_2$-$C^* + H_2O$	0.16
79	CH_2-$COH^* + H^+ + e^- \rightarrow CH_2$-$CHOH^*$	-0.28
80	CH_2-$C^* + H^+ + e^- \rightarrow CH_2$-$CH^*$	-1.01
81	CH_3-$CHO^* + H^+ + e^- \rightarrow CH_3$-$CH_2O^*$	1.07
82	CH_3-$CH_2O^* + H^+ + e^- \rightarrow CH_3$-$CH_2OH^*$	-1.28
83	CH_2-$C^* + H^+ + e^- \rightarrow CH_3$-$C^*$	-0.17
84	CH_3-$C^* + H^+ + e^- \rightarrow CH_3$-$CH^*$	-1.11
85	CH_3-$CH^* + H^+ + e^- \rightarrow CH_3$-$CH_2^*$	-0.47
86	CH_2-$CH^* + H^+ + e^- \rightarrow CH_3$-$CH^*$	-0.27
87	CH_2-$CH_2^* + H^+ + e^- \rightarrow CH_3$-$CH_2^*$	-0.50
88	CH_3-$CH_2OH^* + H^+ + e^- \rightarrow CH_3$-$CH_2^* + H_2O$	-0.77
89	$CO_2 + * \rightarrow CO_2^*$	0.18
90	CH_3-$CH_2^* + H^+ + e^- \rightarrow CH_3$-$CH_3^*$	-0.51
91	CH_3-$CH_3^* \rightarrow CH_3$-$CH_3 + *$	0.47

Supplementary Table 3 Bond center of Cu, N and C atoms in CuNC-4-pyridine and CuCuNC-4a with and without adsorbed COOH.

Bond center (eV)	CuNC-4-pyridine	CuNC-4-pyridine-COOH	CuCuNC-4a	CuCuNC-4a-COOH
Cu1-3d	-3.2	-2.3	-3.1	-3.0
Cu2-3d	-	-	-3.1	-3.1
N1-2p	-3.8	-3.4	-3.9	-3.9
N2-2p	-3.8	-3.5	-2.8	-3.2
N3-2p	-3.8	-3.4	-3.9	-3.9
N4-2p	-3.8	-3.4	-3.9	-3.9
N5-2p	-	-	-2.8	-3.3
N6-2p	-	-	-3.9	-3.9
C-2p	-	-2.5	-	-2.2

Supplementary Table 4 The adsorption energy and ICOHP with COOH adsorbed on CuNC-4-pyridine and CuuCuNC-4a.

System	ΔE_{ads}-COOH (eV)	ICOHP
CuNC-4-pyridine	1.39059411	-2.17368
CuCuNC-4a	0.27265554	-11.04964