Supporting Information

Computational design and screening of high-efficient metal dual-atom-modified g-C_3N_4 catalysts for CO_2 photoreduction to C_2 chemicals

Yuming Jin [#a], Shuang Wang [#a], Xiaowa Nie [a*], Chunshan Song [b], and Xinwen Guo[a*]

[a] State Key Laboratory of Fine Chemicals, Frontier Science Center for Smart Materials, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024.

[b] Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, NT, Hong Kong 999077.

*Corresponding Authors:

Xiaowa Nie: niexiaowa@dlut.edu.cn

Xinwen Guo: guoxw@dlut.edu.cn

[#]These authors contributed equally to this work

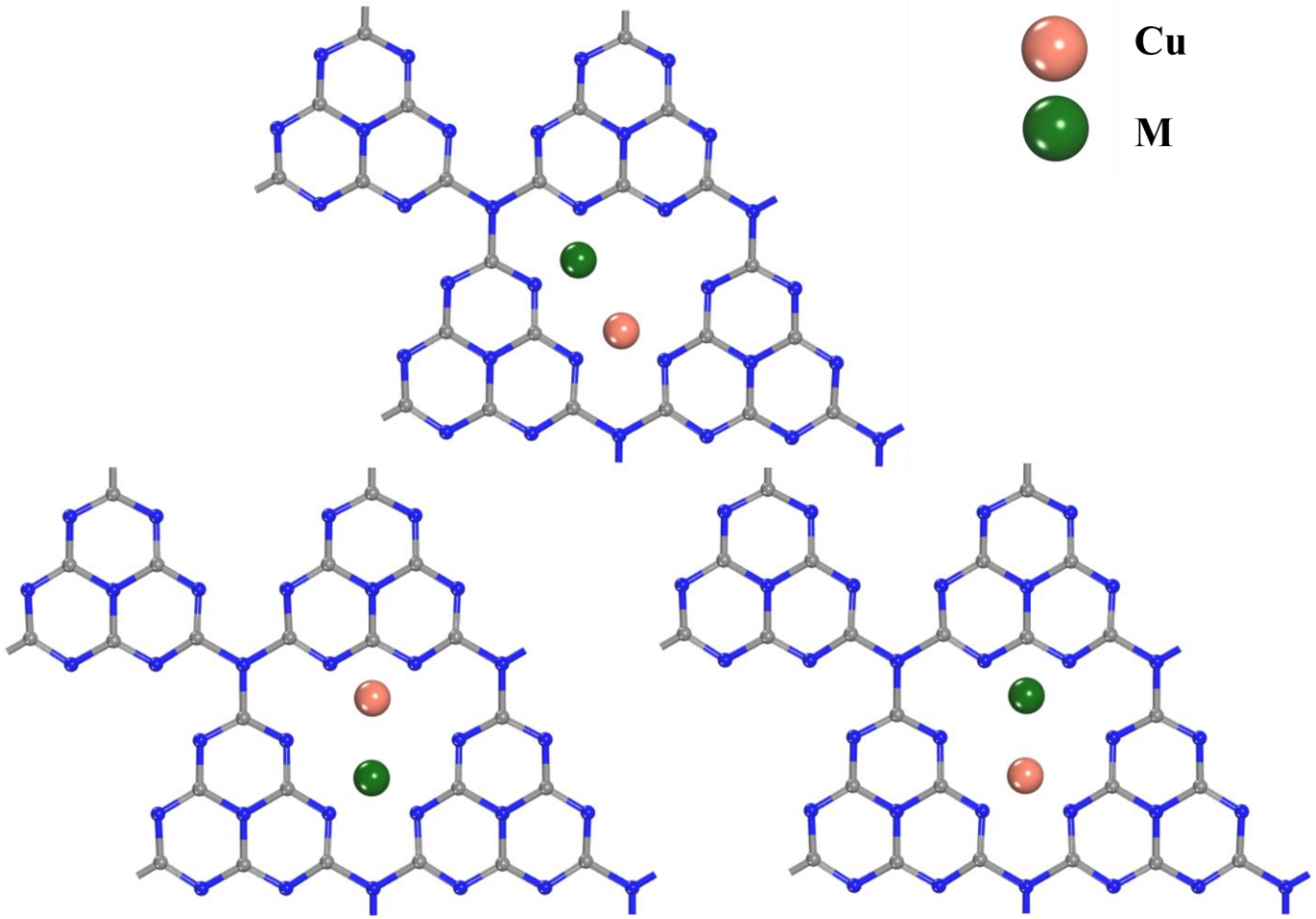


Fig. S1. Different initial structures considered for dual-atom Cu-M being placed into the sixfold cavity of the g-C_3N_4 substrate.

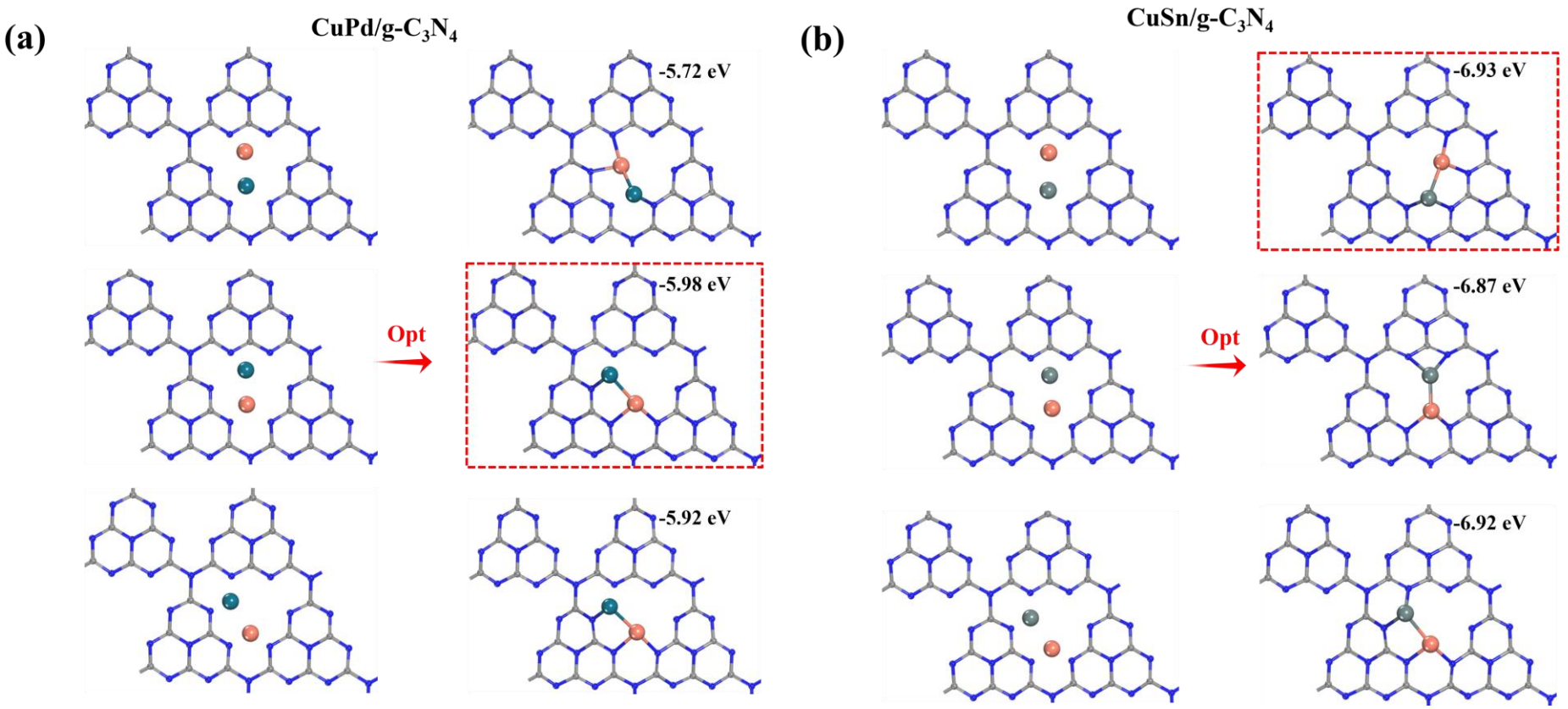


Fig. S2. Stable configuration screening of (a) CuPd/g-C_3N_4 and (b) CuSn/g-C_3N_4 according to structural optimization and binding energy calculation.

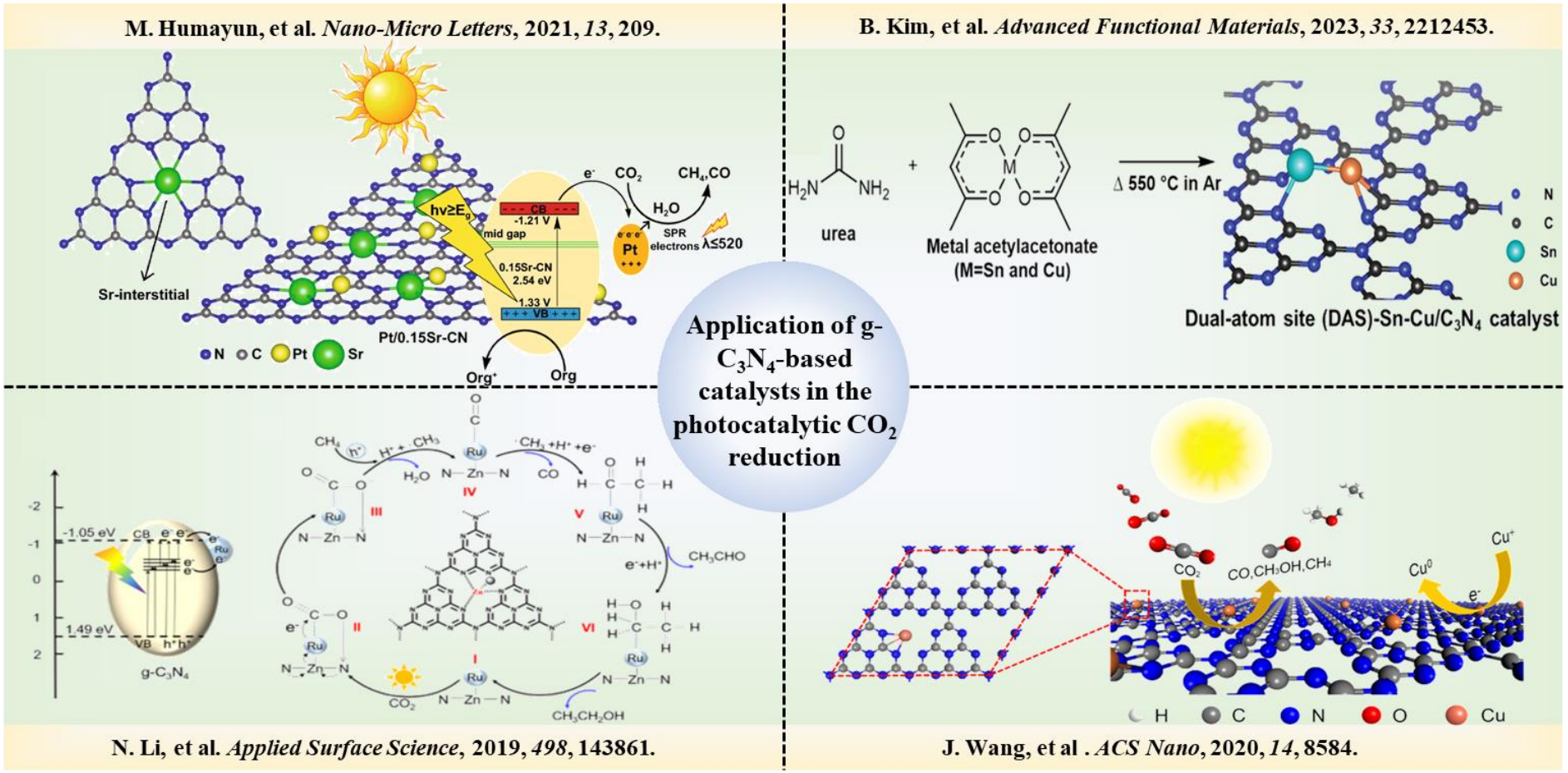


Fig. S3. An overview of metal-modified g-C_3N_4-based catalysts for the photocatalytic CO_2 reduction reported in the literature.

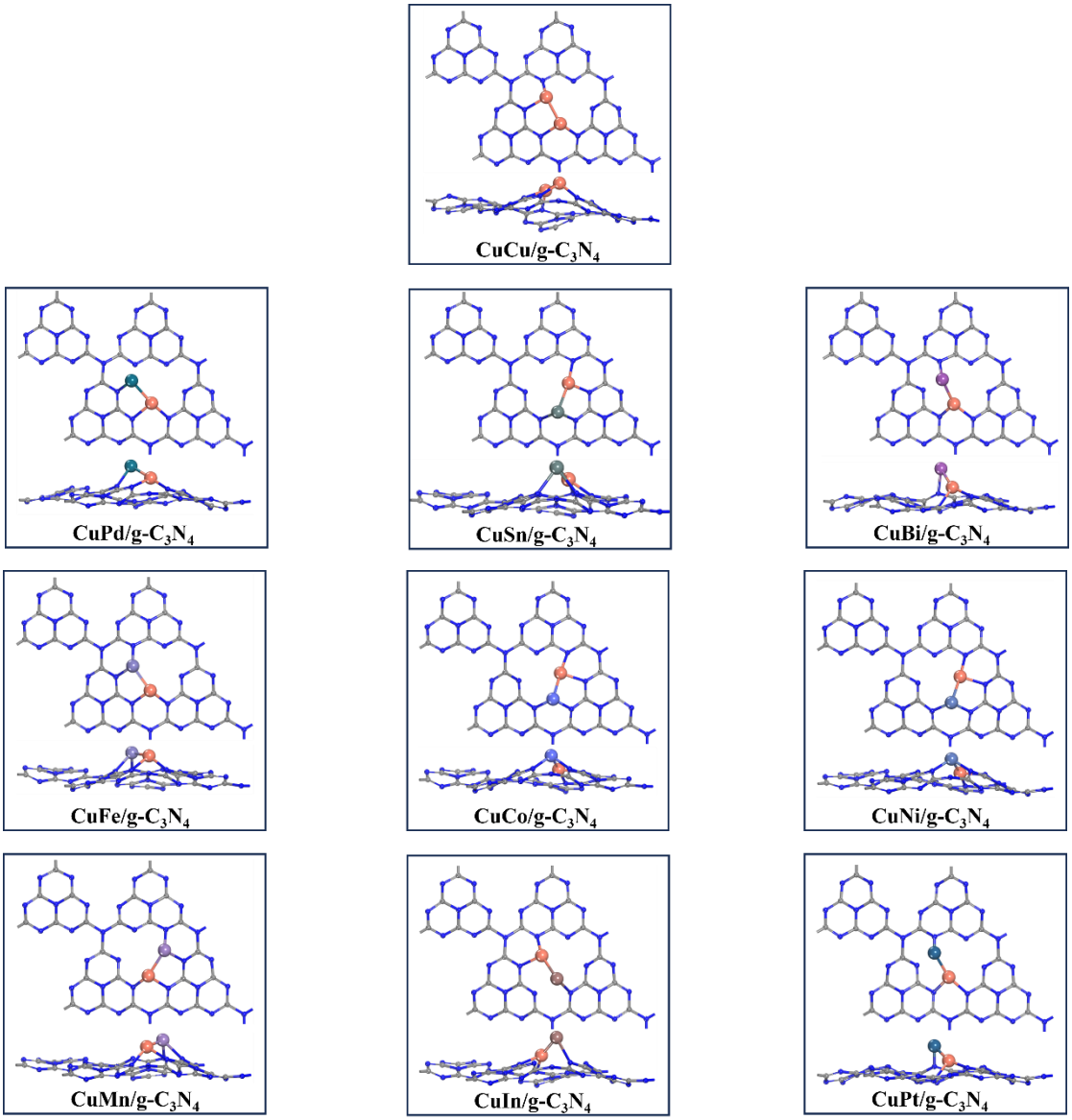


Fig. S4. Optimized configurations of metal dual-atom-modified CuM/g-C_3N_4 (M = Cu, Pd, Sn, Bi, Fe, Co, Ni, Mn, In, and Pt) catalysts.

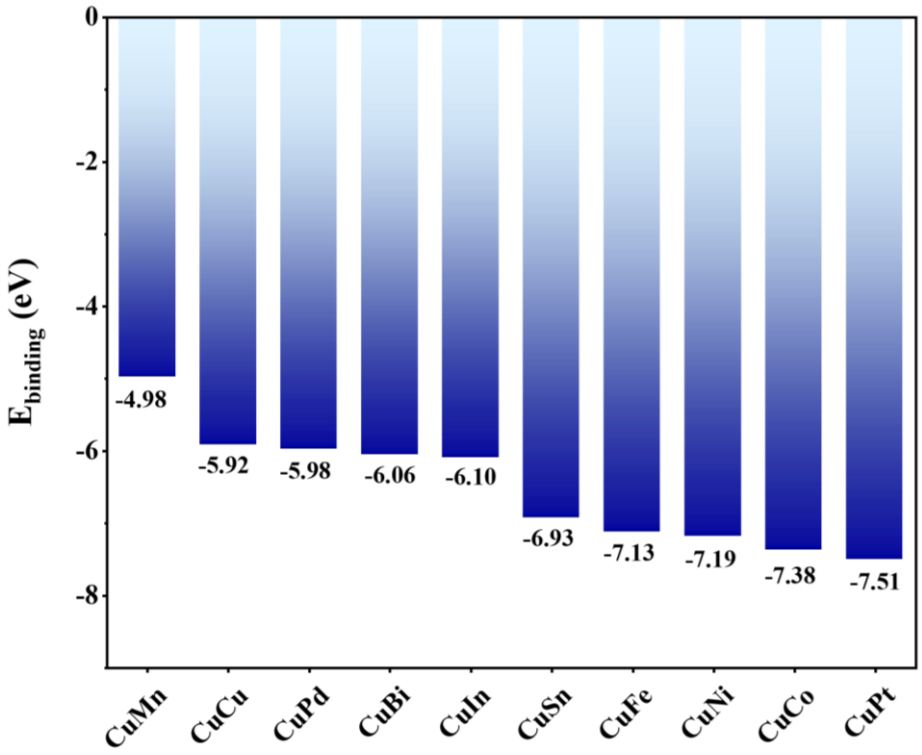


Fig. S5. Binding energies of metal dual-atom assembles CuM (M = Cu, Pd, Sn, Bi, Fe, Co, Ni, Mn, In, and Pt) over the g-C_3N_4 support.

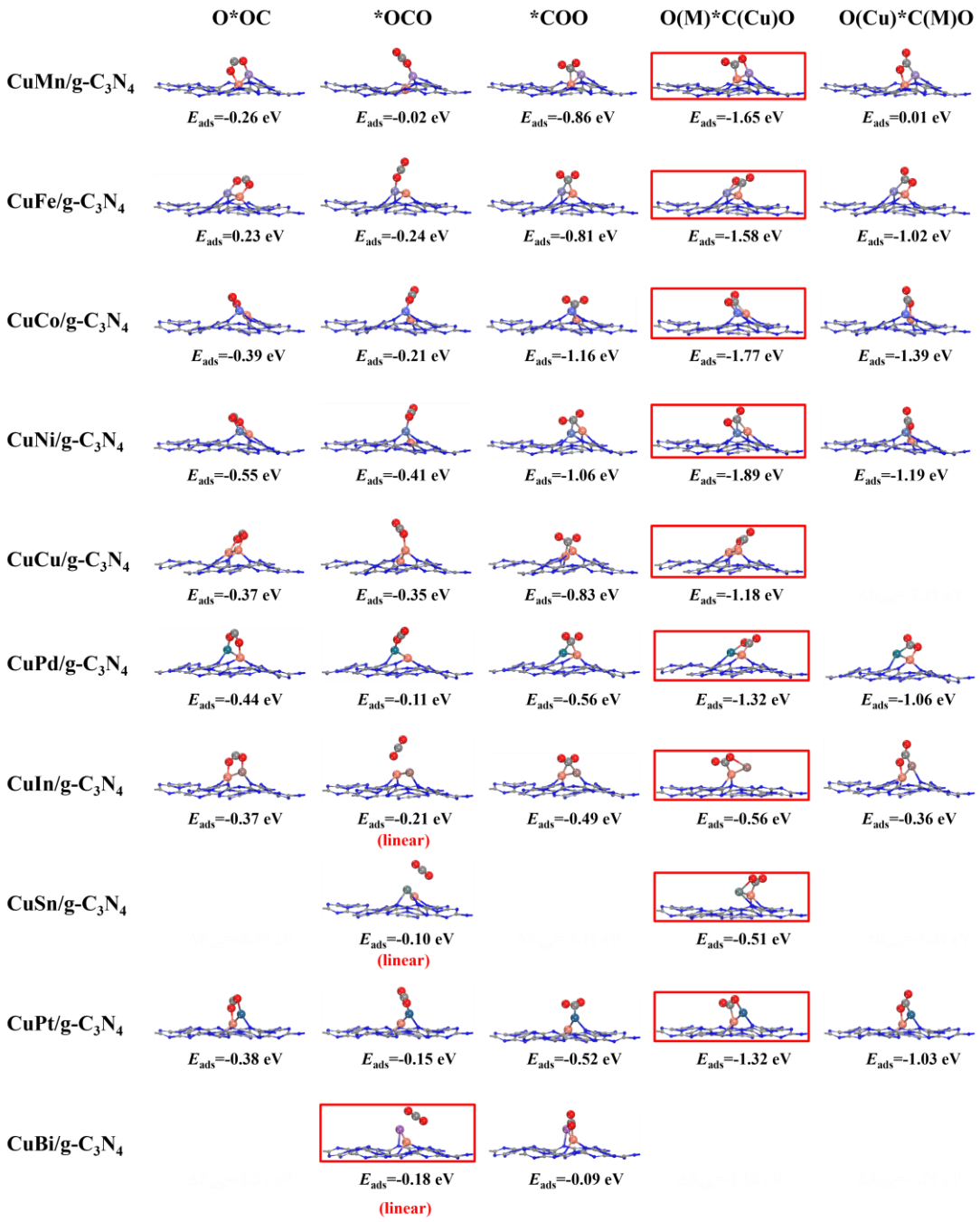


Fig. S6. The stable adsorption configurations of CO_2 and the adsorption energies of CO_2 on the CuM/g-C_3N_4 (M = Cu, Pd, Sn, Bi, Fe, Co, Ni, Mn, In, and Pt) catalysts.

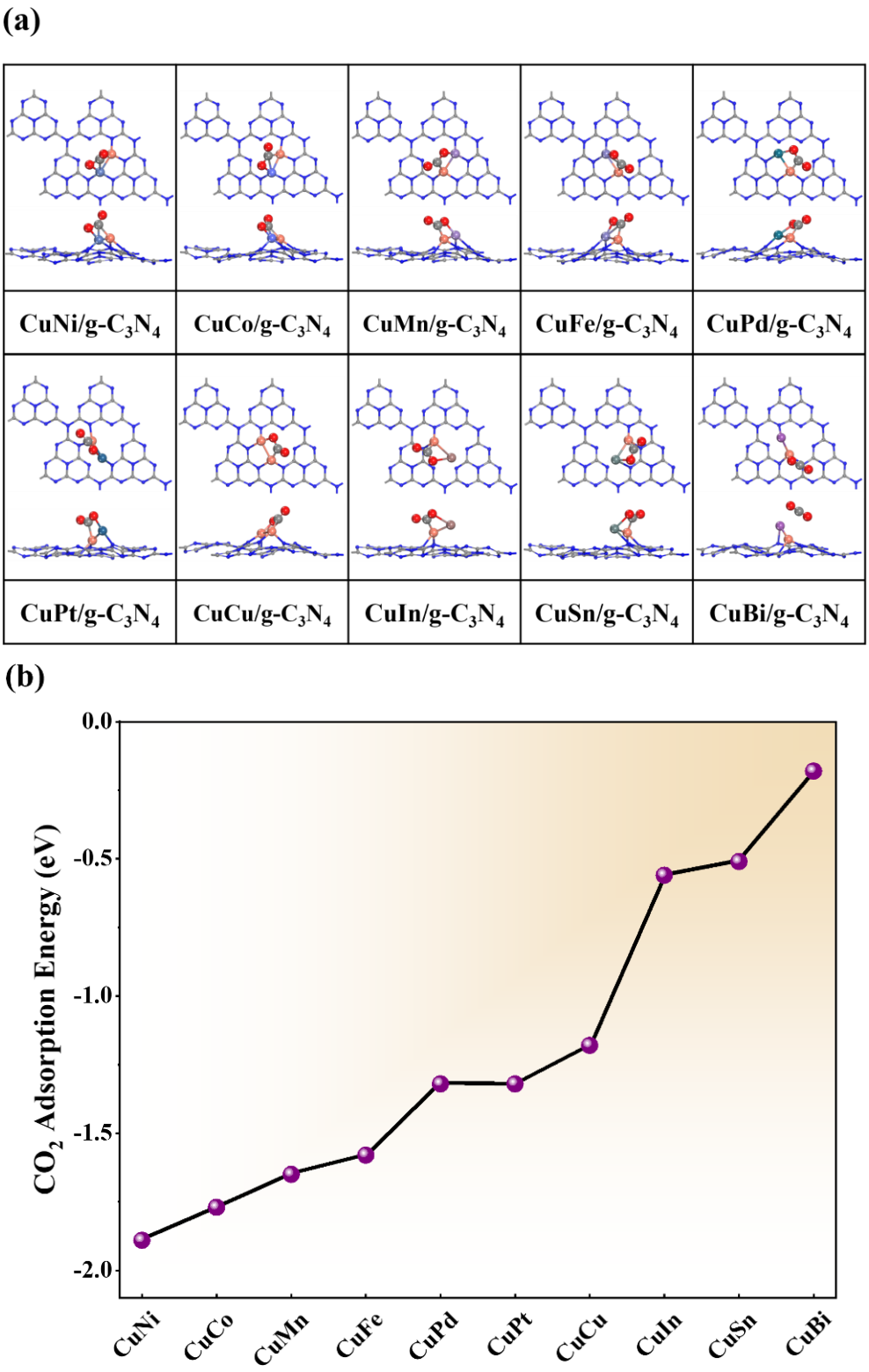


Fig. S7. (a) The most stable CO_2 adsorption structures on the CuM/g-C_3N_4 (M = Mn, Fe, Co, Ni, Cu, Pd, In, Sn, Pt, and Bi) catalysts. (b)The adsorption energies of CO_2 on the CuM/g-C_3N_4 (M = Mn, Fe, Co, Ni, Cu, Pd, In, Sn, Pt, and Bi) catalysts.

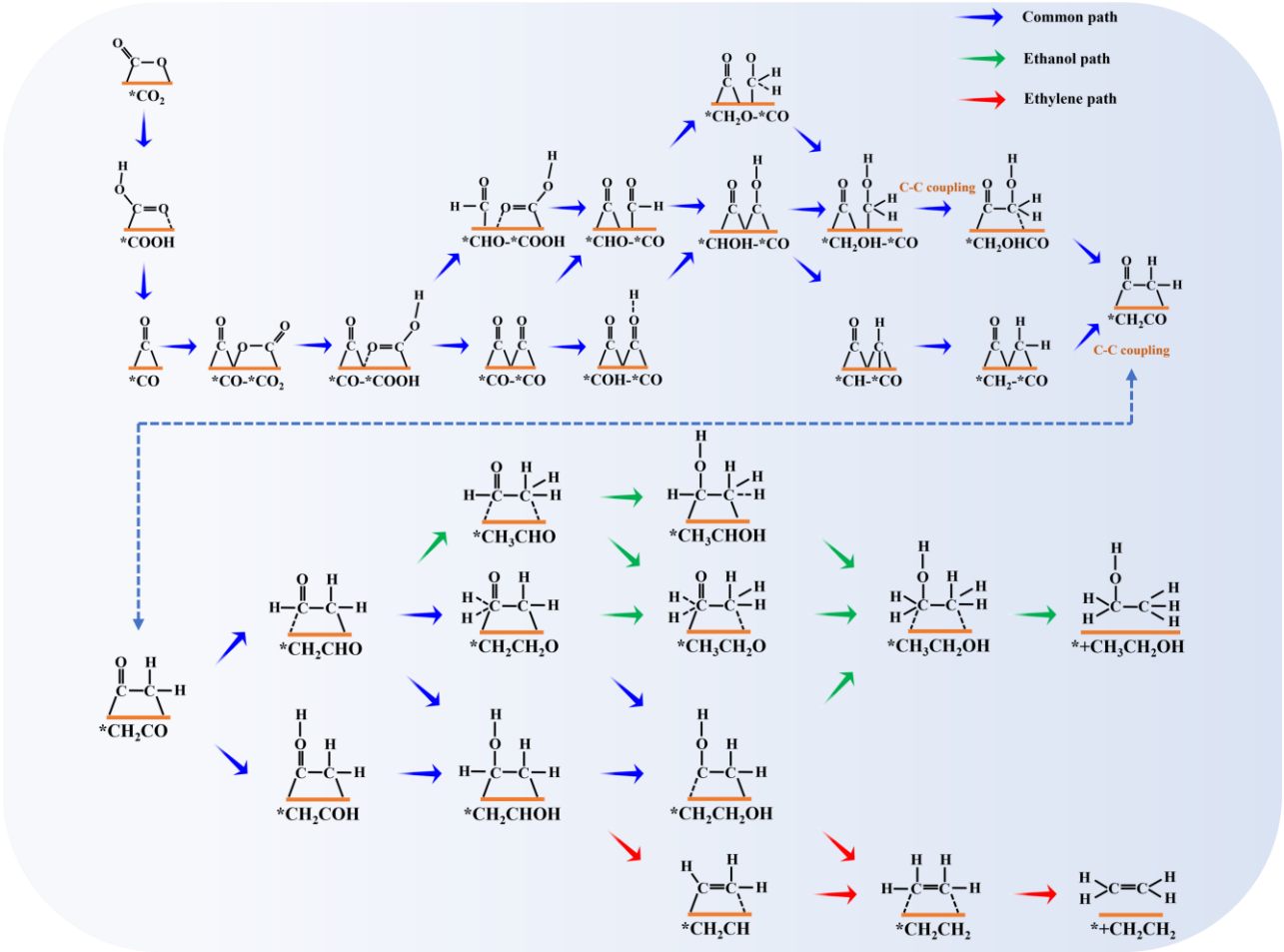
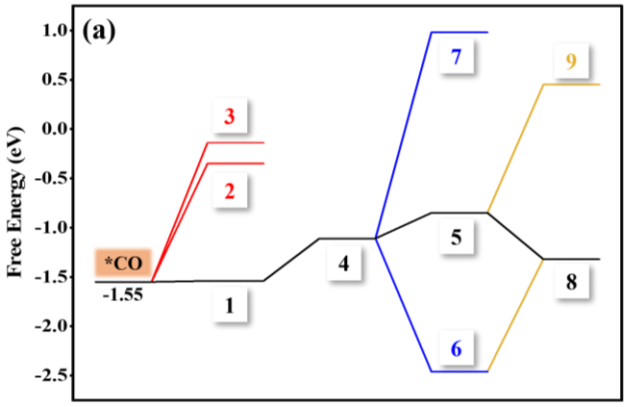
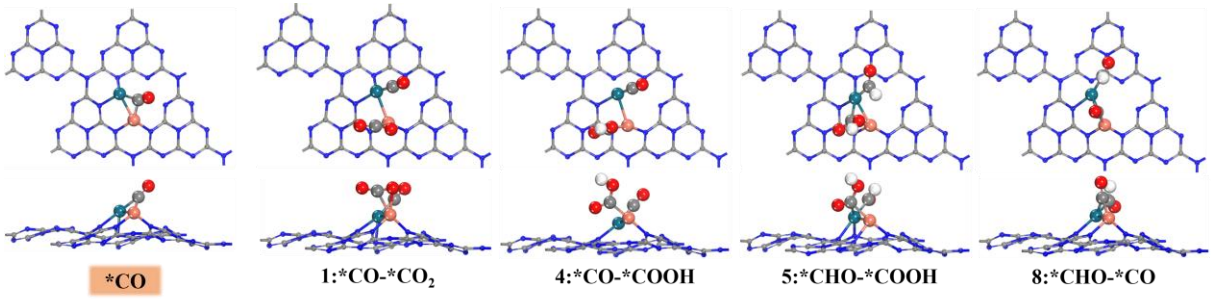
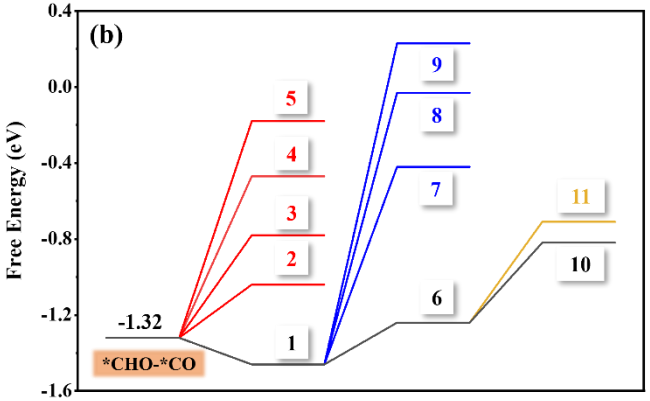


Fig. S8. Possible reaction pathways considered for the reduction of CO_2 to C_2 (C_2H_5OH and C_2H_4) products on the CuM/g-C_3N_4 (M = Mn, Fe, Co, Ni, Cu, Pd, In, Sn, Pt, and Bi) catalysts.

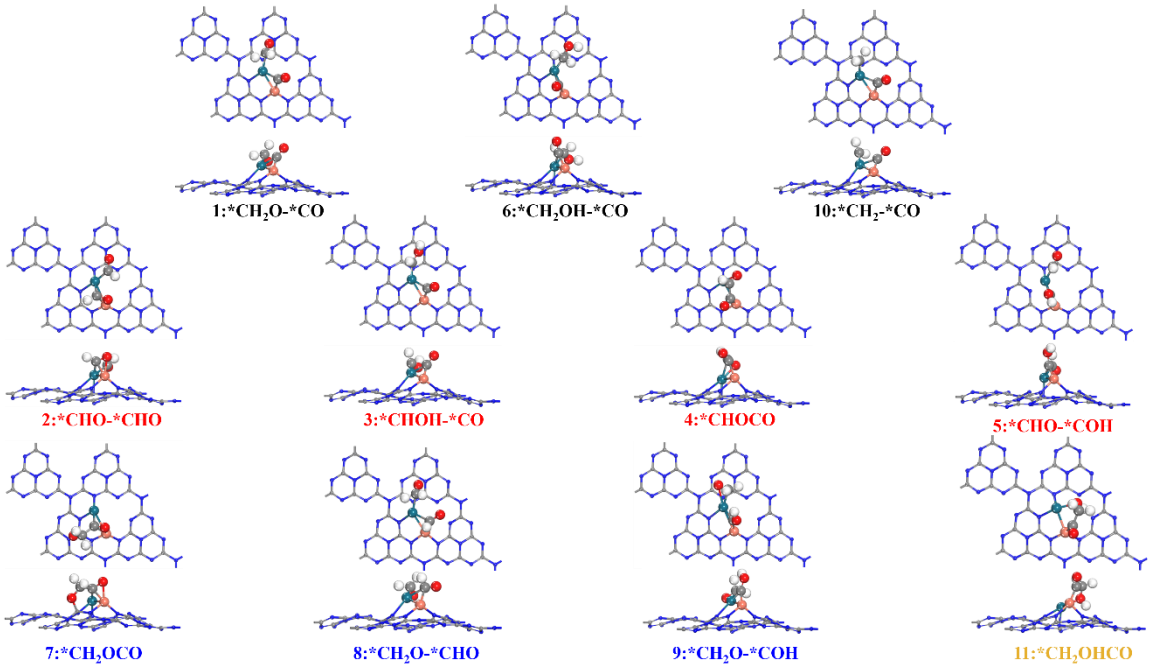


Optimal pathway	Other possible pathway
1 *CO-*CO_2: -1.54	2 *CHO: -0.35
4 *CO-*COOH: -1.11	3 *COH: -0.14
5 *CHO-*COOH: -0.85	6 *CO-*CO: -2.46
8 *CHO-*CO: -1.32	7 *COH-*COOH: 0.98
	9 *CHOH-*COOH: 0.45





Optimal pathway		Other possible pathway			
1	*CH_2O-*CO: -1.46	2	*CHO-*CHO: -1.04	7	*CH_2OCO: -0.42
6	*CH_2OH-*CO: -1.24	3	*CHOH-*CO: -0.78	8	*CH_2O-*CHO: -0.03
10	*CH_2-*CO: -0.82	4	*CHOCO: -0.47	9	*CH_2O-*COH: 0.23
		5	*CHO-*COH: -0.18	11	*CH_2OHCO: -0.71



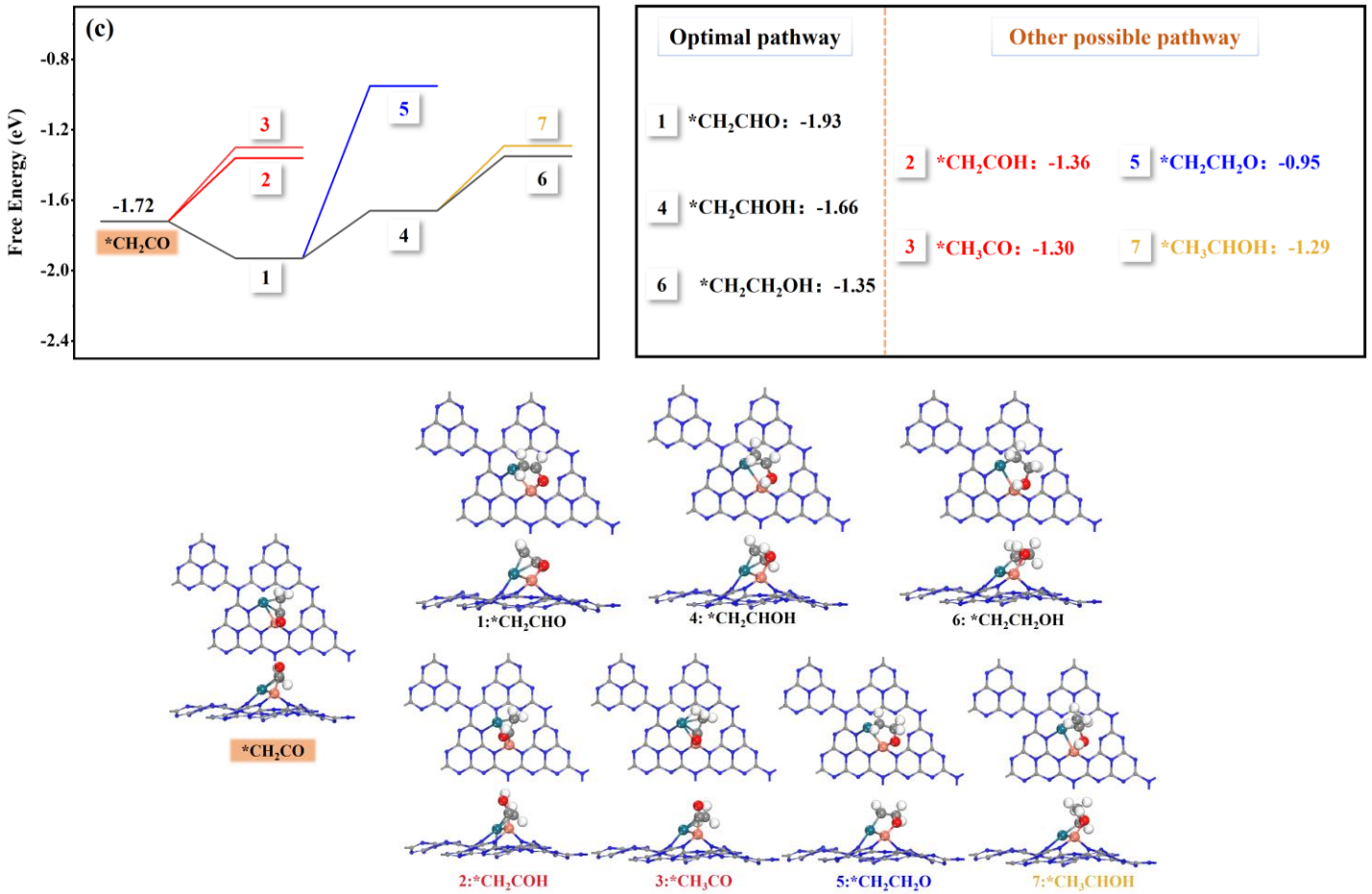
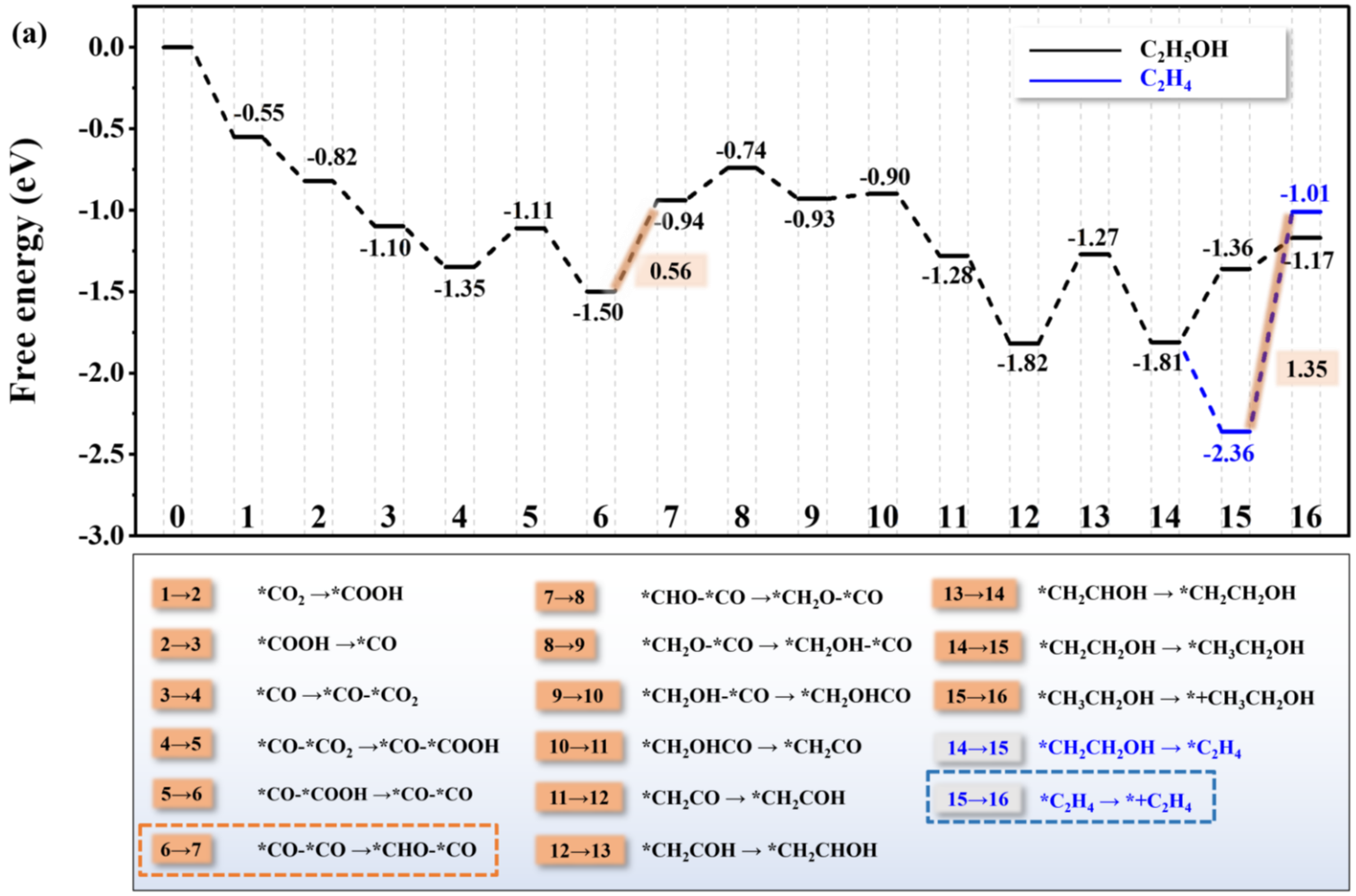


Fig. S9. The calculated Gibbs free energy diagrams of the optimal reaction pathway and other possible pathways for the reduction of CO_2 to C_2 (C_2H_4 and C_2H_5OH) products on CuPd/g-C_3N_4, as well as the optimized structures of all intermediate species.


(a)
Free energy (eV)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
-0.55
-0.82
-1.10
-1.35
-1.11
-1.50
-0.94
0.56
-0.74
-0.93
-0.90
-1.28
-1.82
-1.27
-1.81
-1.36
-2.36
-1.01
-1.17
1.35
C2H5OH
C2H4
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CH2O-*CO
8→9 *CH2O-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2OHCO
10→11 *CH2OHCO → *CH2CO
11→12 *CH2CO → *CH2COH
12→13 *CH2COH → *CH2CHOH
13→14 *CH2CHOH → *CH2CH2OH
14→15 *CH2CH2OH → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

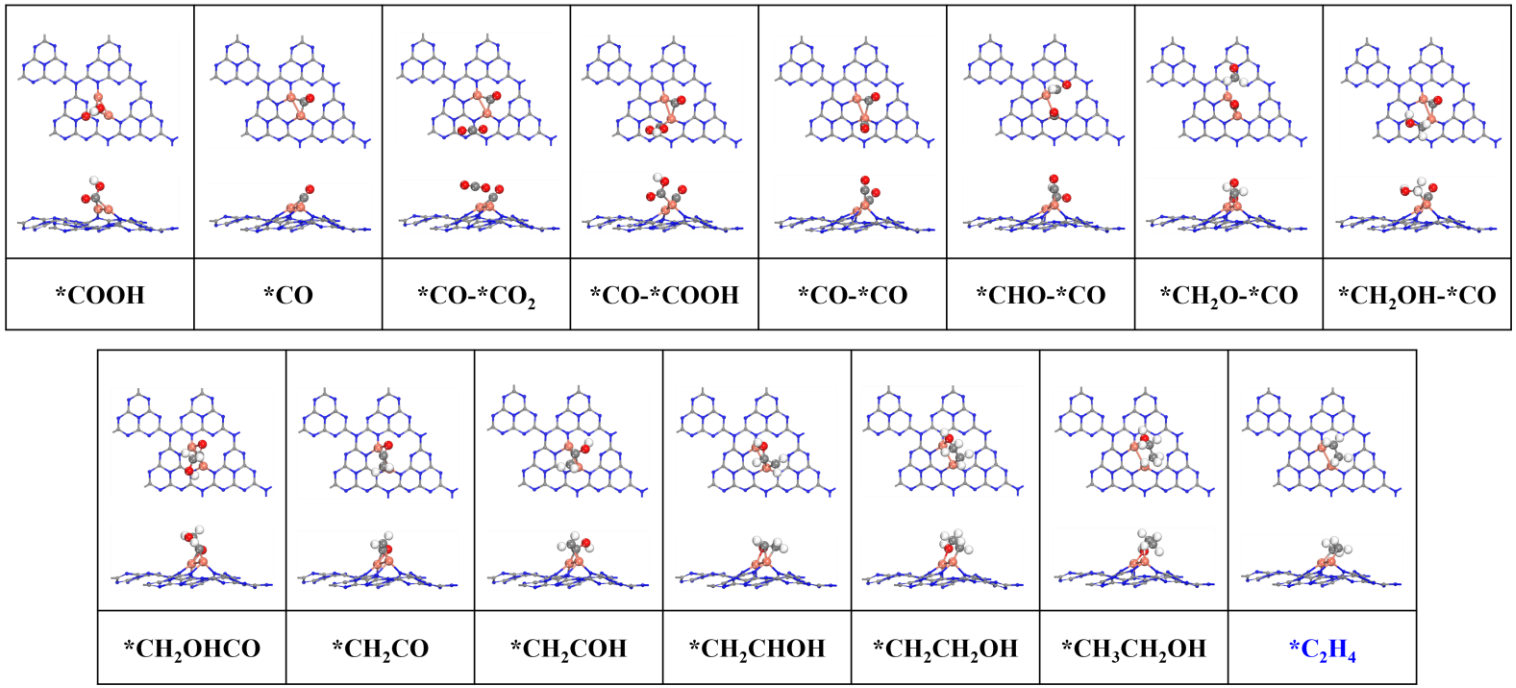
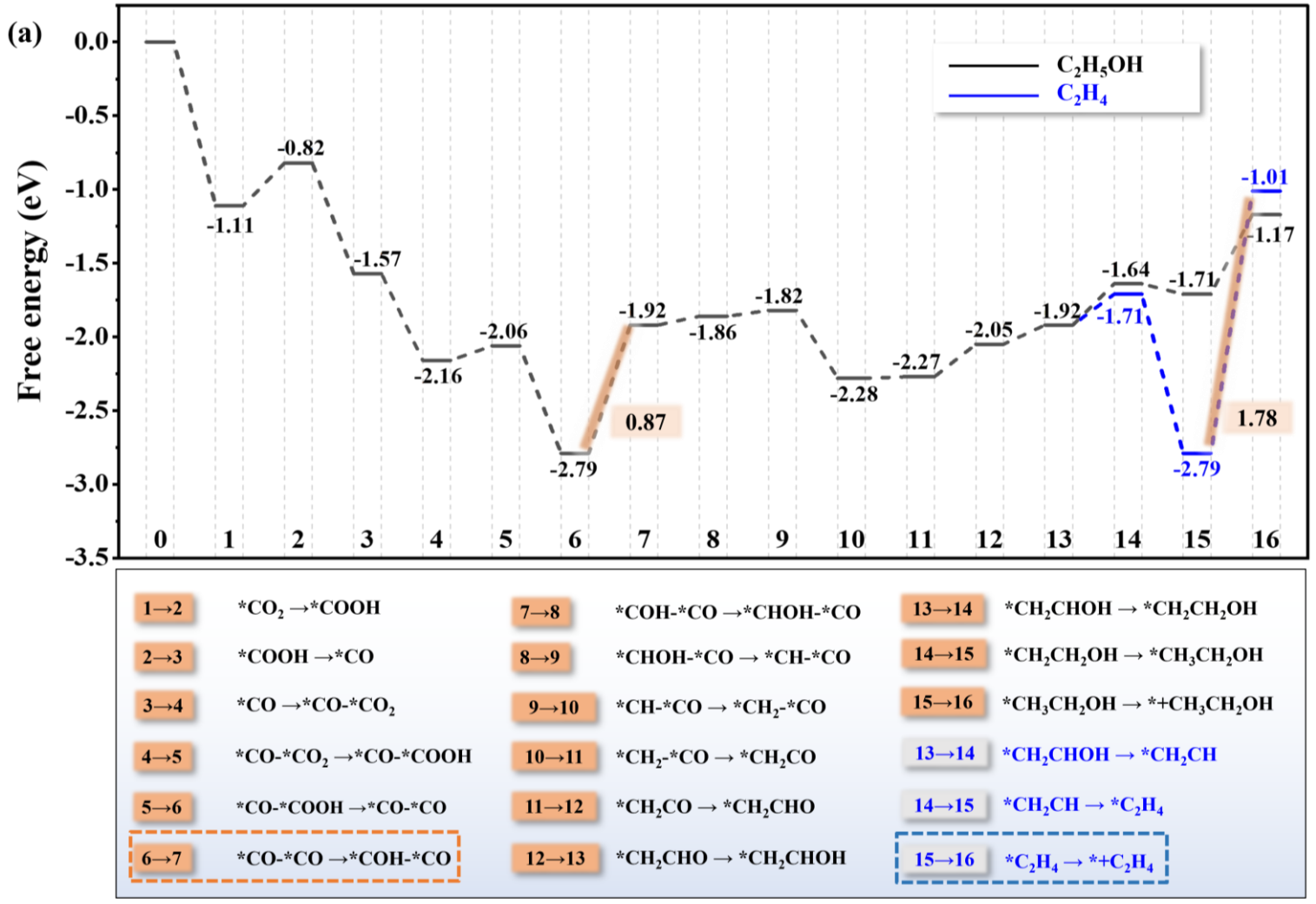


Fig. S10. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuCu/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C2H5OH
C2H4
-1.11
-0.82
-1.57
-2.16
-2.06
-2.79
-1.92
-1.86
-1.82
-2.28
-2.27
-2.05
-1.92
-1.64
-1.71
-1.71
-2.79
-1.01
-1.17
0.87
1.78
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*COH-*CO
7→8 *COH-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH-*CO
9→10 *CH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH2CHOH
13→14 *CH2CHOH → *CH2CH2OH
14→15 *CH2CH2OH → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
13→14 *CH2CHOH → *CH2CH
14→15 *CH2CH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

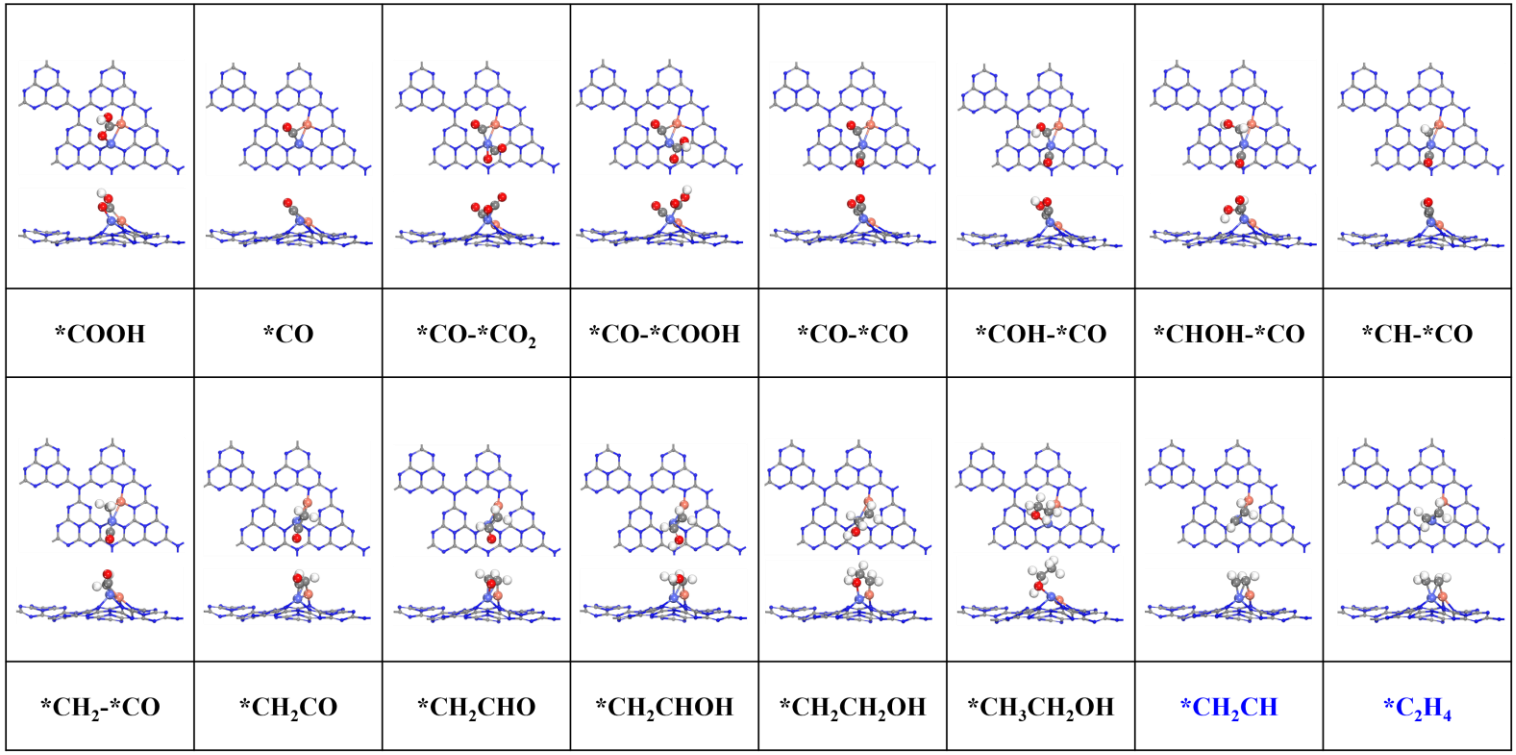
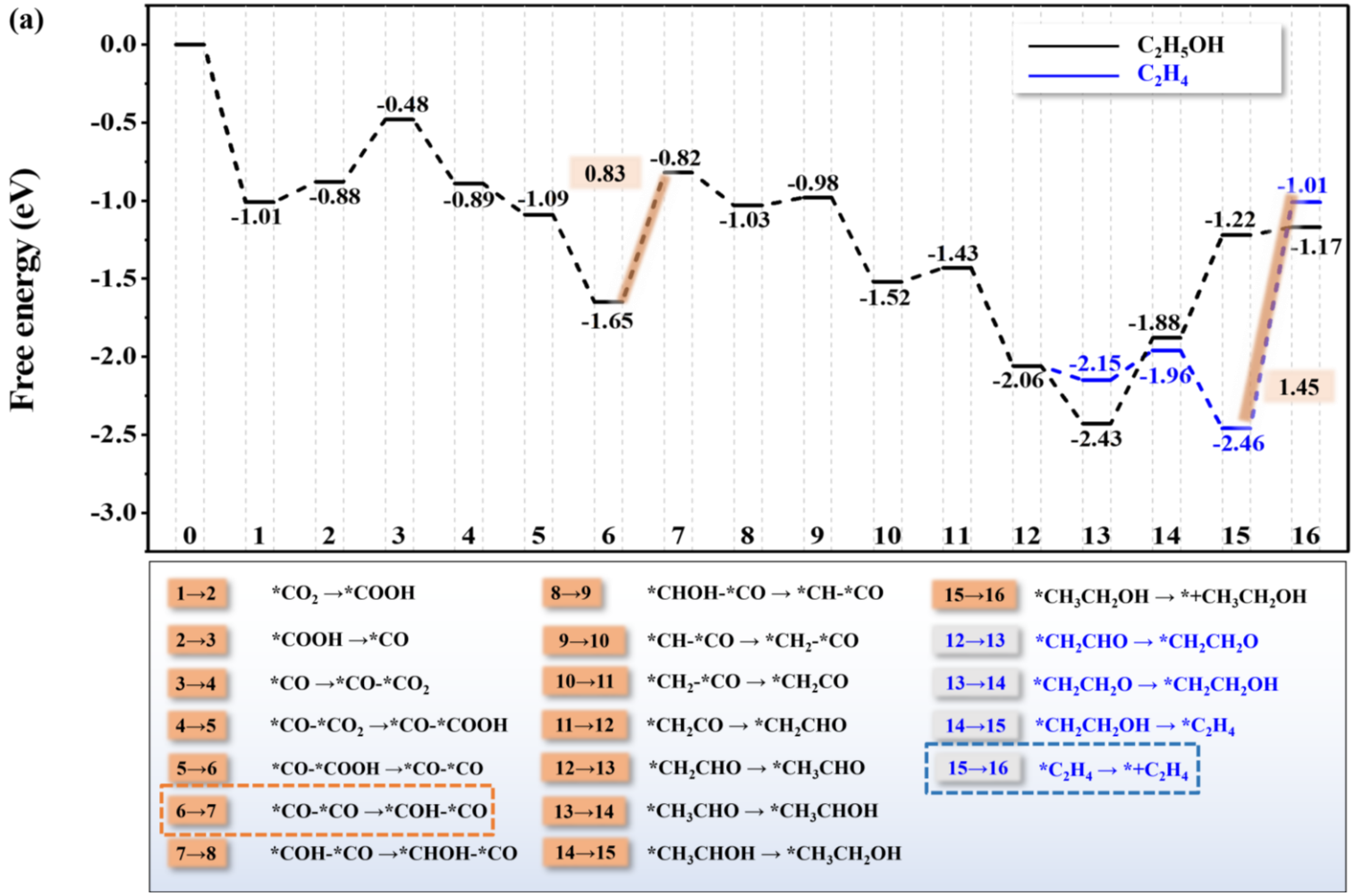


Fig. S11. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuCo/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
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-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C2H5OH
C2H4
-1.01
-0.88
-0.48
-0.89
-1.09
-1.65
0.83
-0.82
-1.03
-0.98
-1.52
-1.43
-2.06
-2.15
-2.43
-1.88
-1.96
-2.46
-1.22
-1.01
-1.17
1.45
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*COH-*CO
7→8 *COH-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH-*CO
9→10 *CH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH3CHO
13→14 *CH3CHO → *CH3CHOH
14→15 *CH3CHOH → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
12→13 *CH2CHO → *CH2CH2O
13→14 *CH2CH2O → *CH2CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

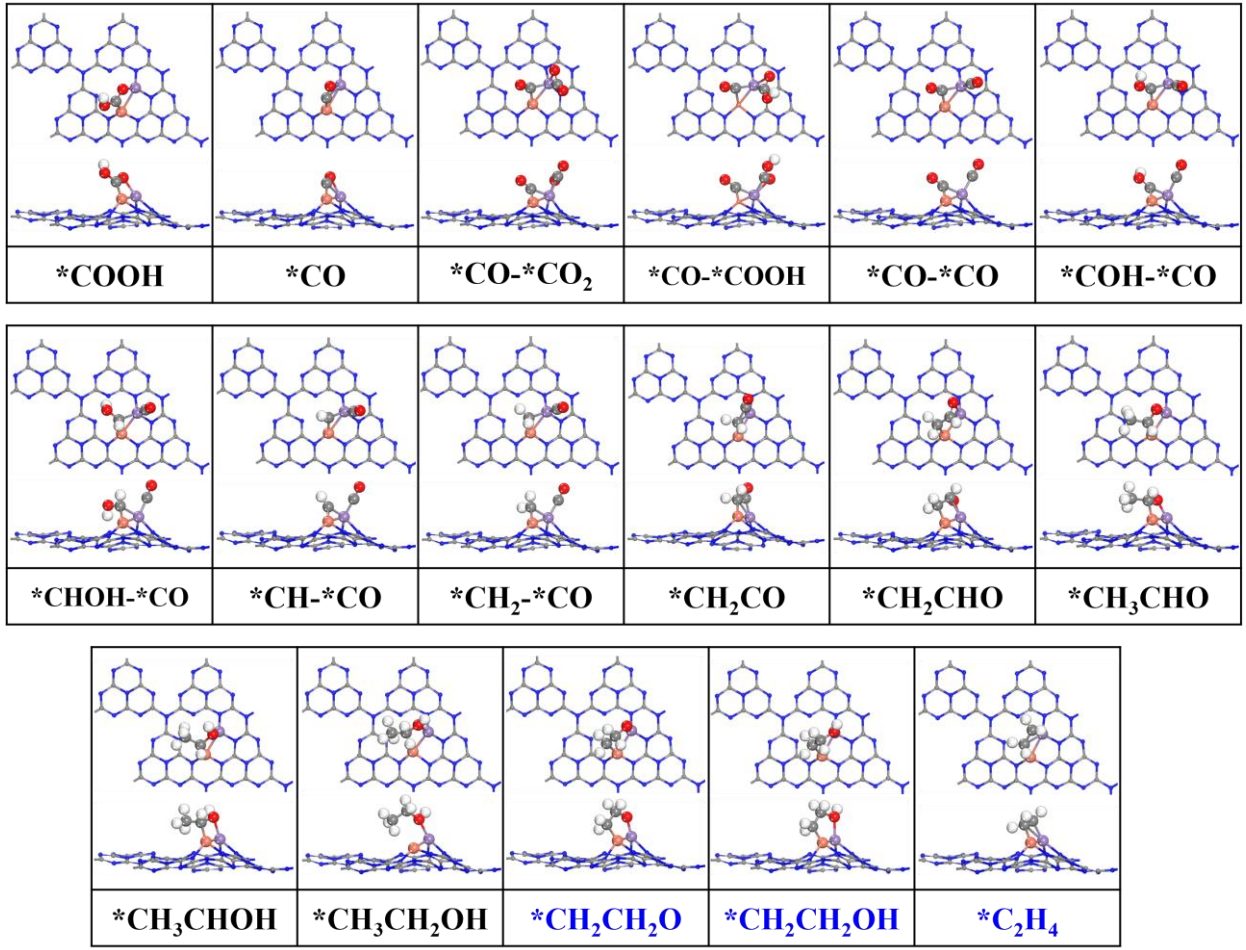
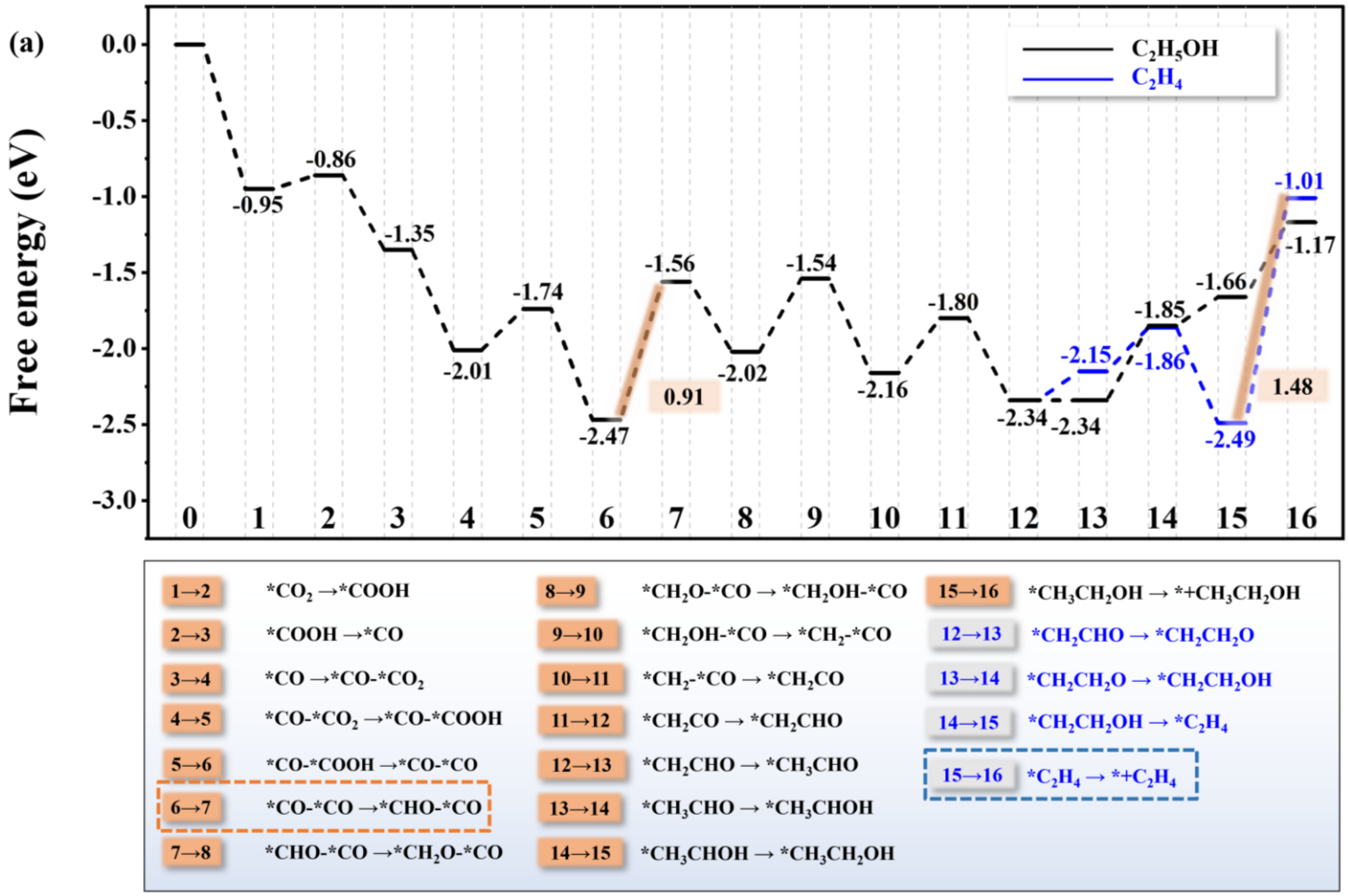


Fig. S12. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuMn/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
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-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C2H5OH
C2H4
-0.95
-0.86
-1.35
-2.01
-1.74
-2.47
-1.56
-2.02
-1.54
-2.16
-1.80
-2.34
-2.34
-2.15
-1.86
-1.85
-2.49
-1.66
-1.01
-1.17
0.91
1.48
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CH2O-*CO
8→9 *CH2O-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH3CHO
13→14 *CH3CHO → *CH3CHOH
14→15 *CH3CHOH → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
12→13 *CH2CHO → *CH2CH2O
13→14 *CH2CH2O → *CH2CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

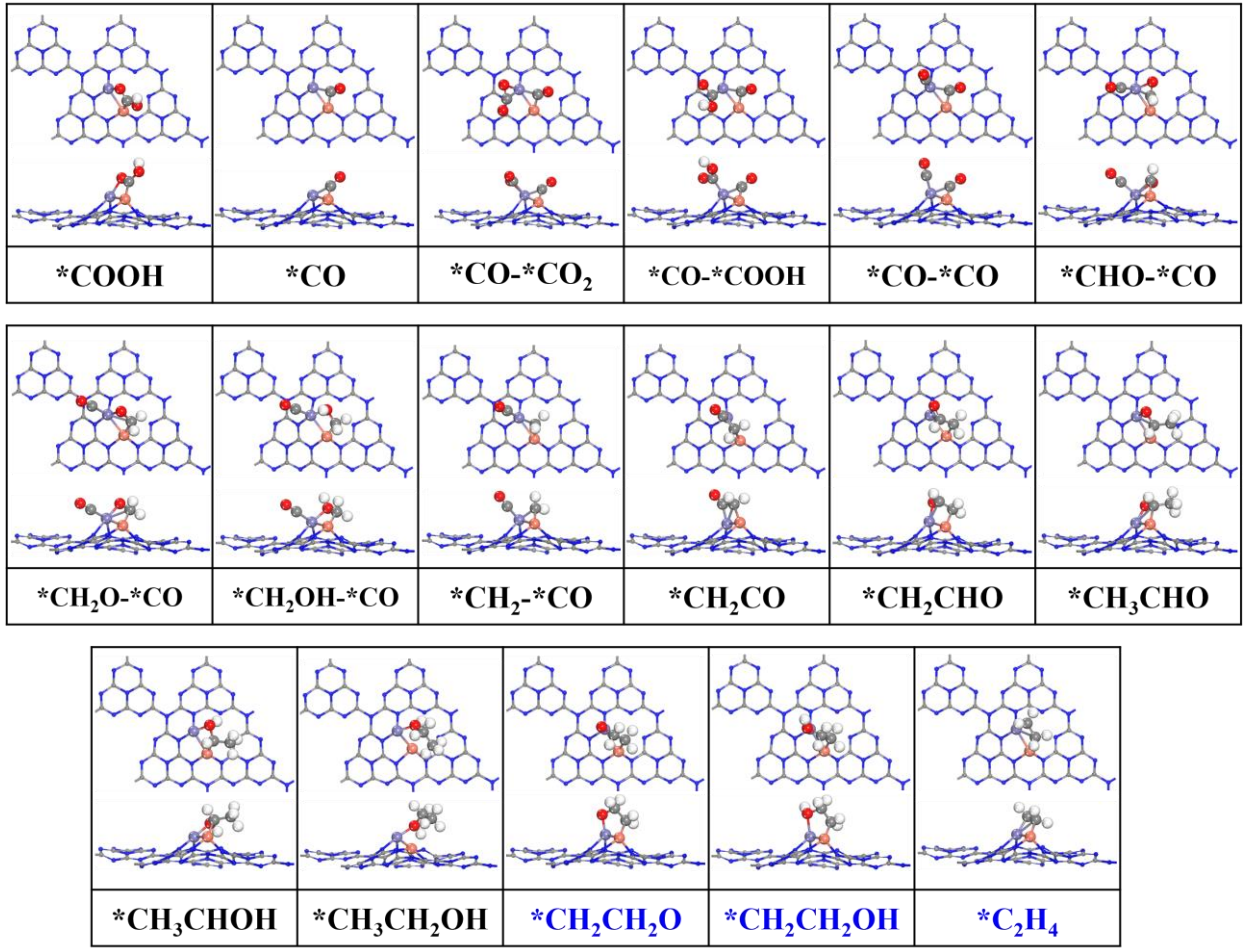
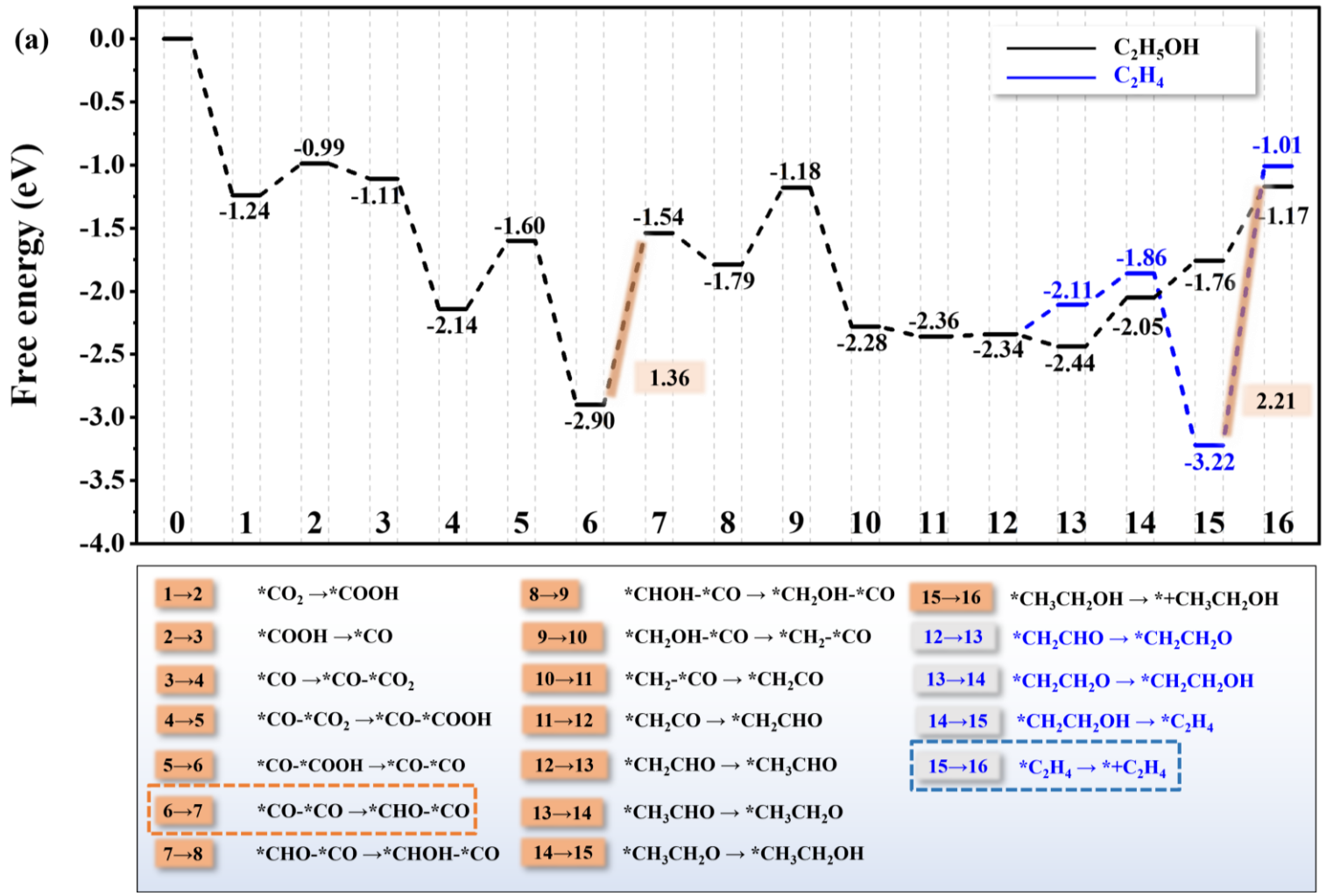


Fig. S13. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuFe/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C2H5OH
C2H4
-1.24
-0.99
-1.11
-2.14
-1.60
-2.90
1.36
-1.54
-1.79
-1.18
-2.28
-2.36
-2.34
-2.11
-2.44
-1.86
-2.05
-1.76
-3.22
2.21
-1.01
-1.17
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH3CHO
13→14 *CH3CHO → *CH3CH2O
14→15 *CH3CH2O → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
12→13 *CH2CHO → *CH2CH2O
13→14 *CH2CH2O → *CH2CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

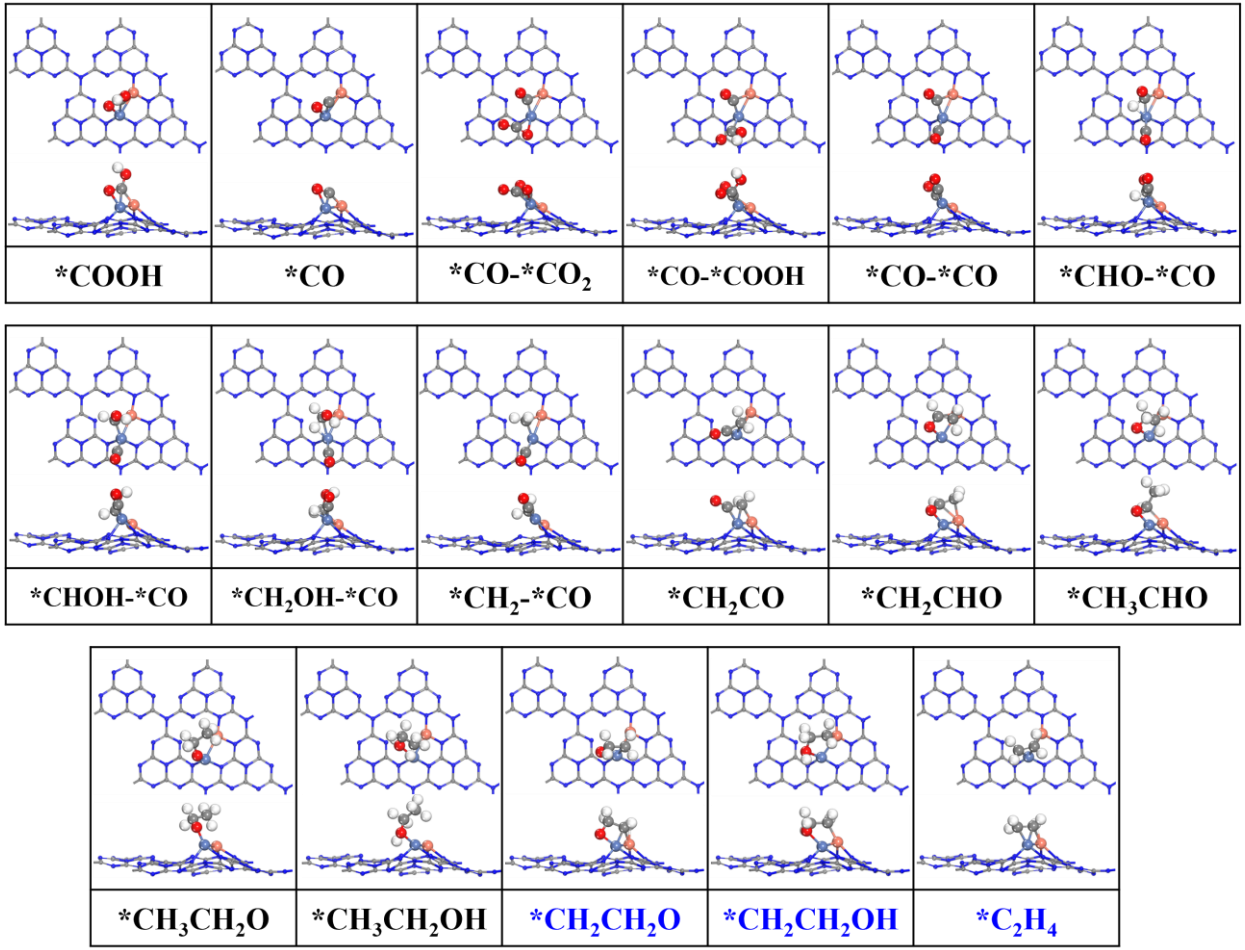
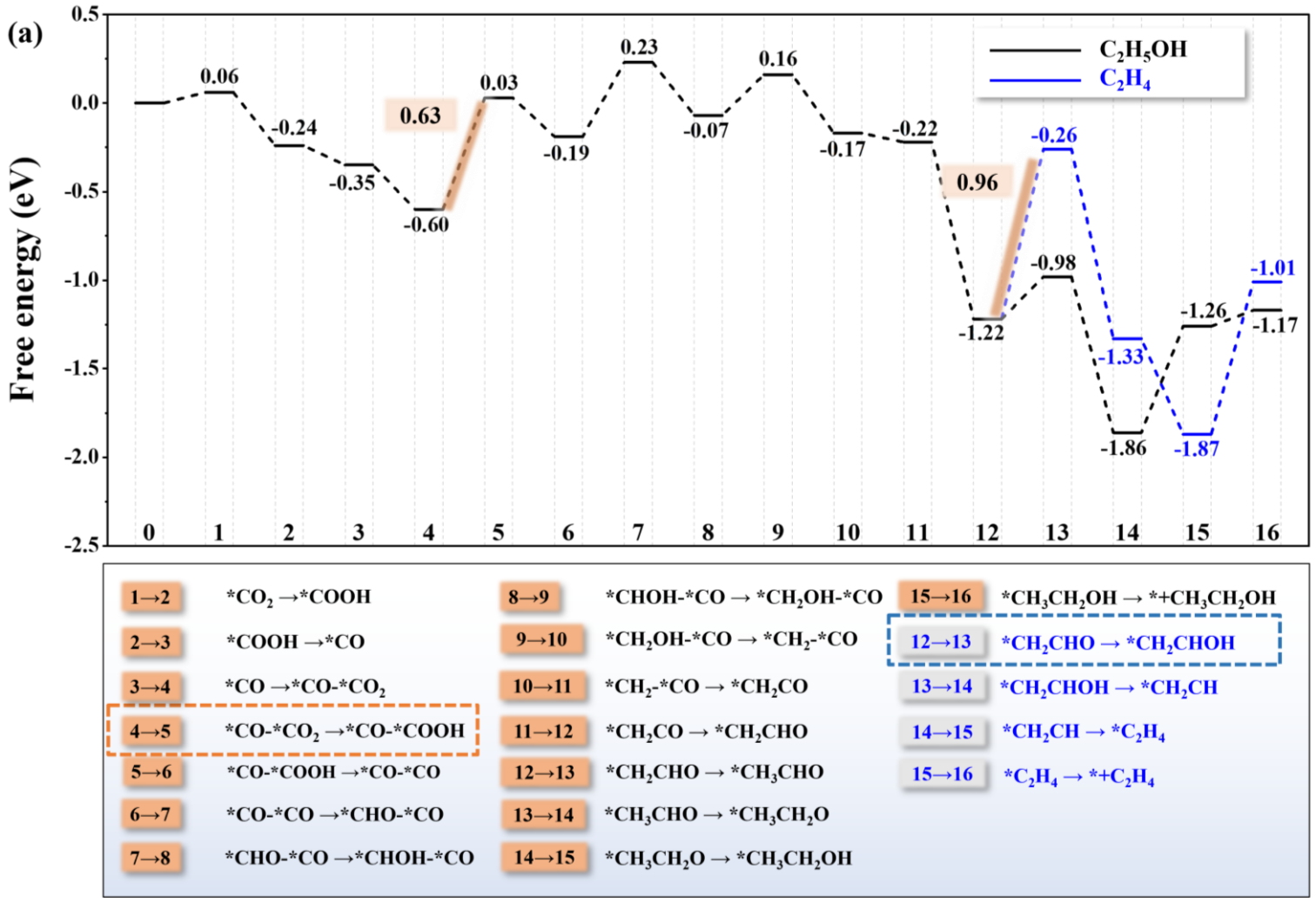


Fig. S14. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuNi/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0.06
-0.24
-0.35
-0.60
0.63
0.03
-0.19
0.23
-0.07
0.16
-0.17
-0.22
0.96
-1.22
-0.98
-0.26
-1.33
-1.86
-1.26
-1.87
-1.01
-1.17
C2H5OH
C2H4
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH3CHO
13→14 *CH3CHO → *CH3CH2O
14→15 *CH3CH2O → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
12→13 *CH2CHO → *CH2CHOH
13→14 *CH2CHOH → *CH2CH
14→15 *CH2CH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

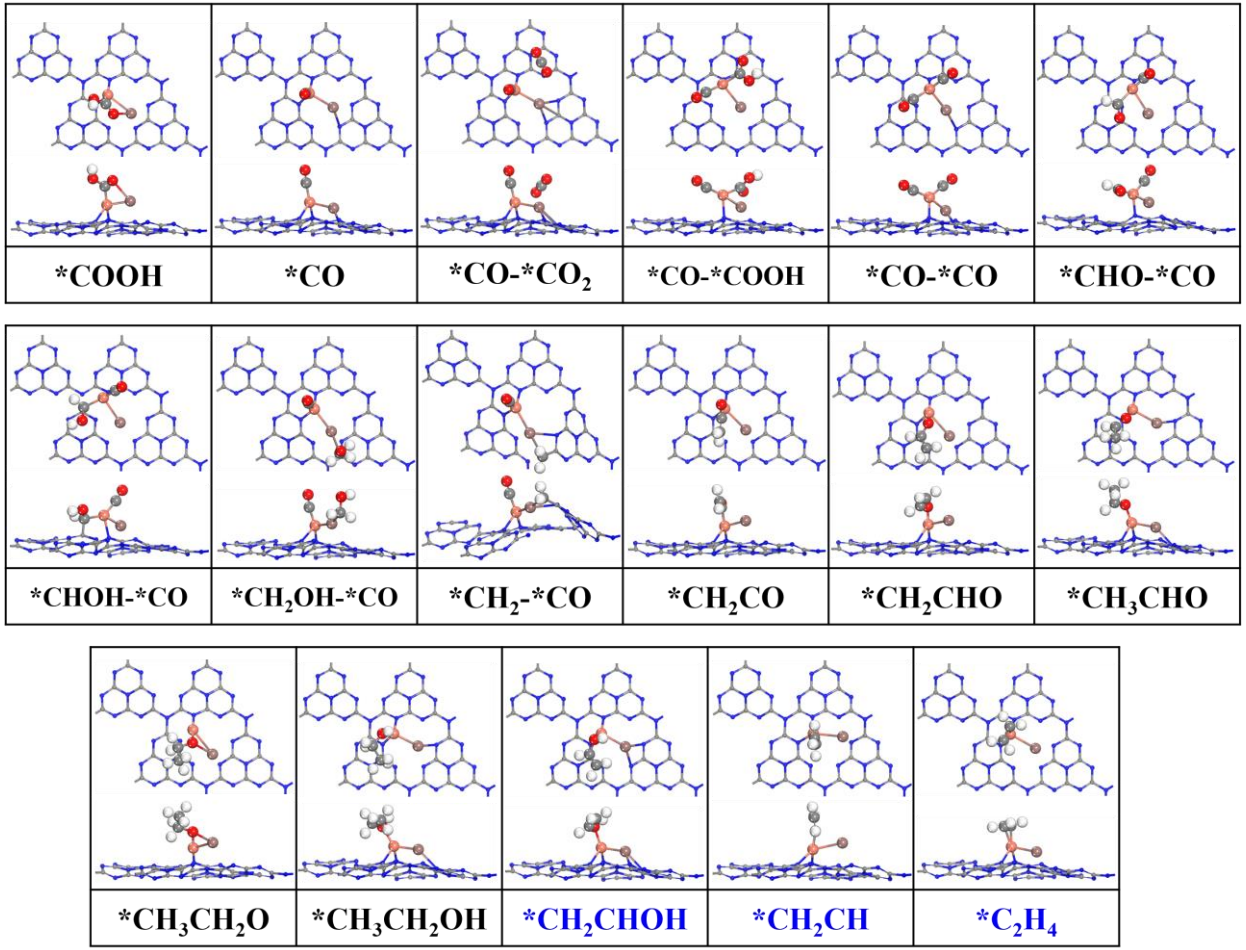
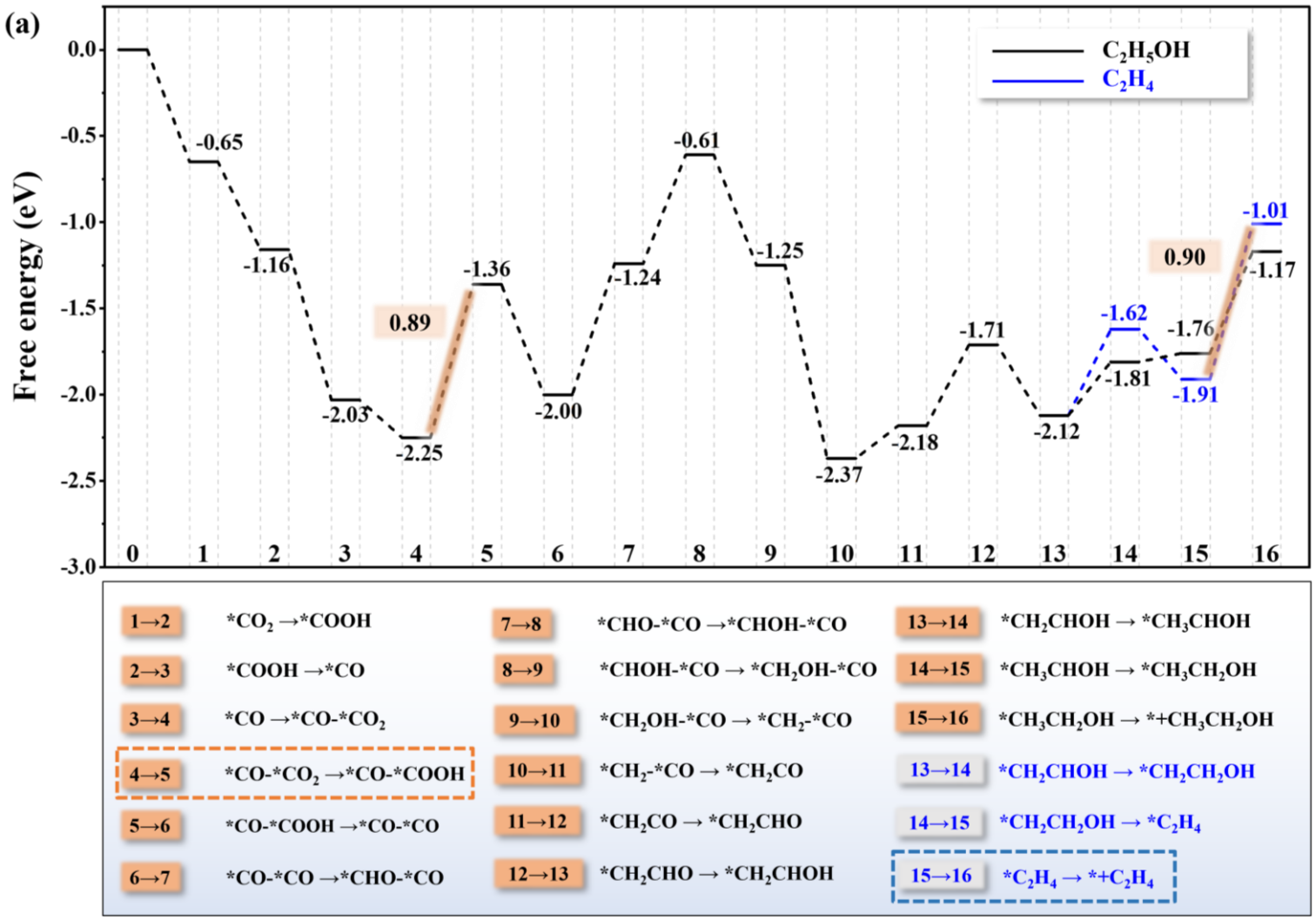


Fig. S15. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuIn/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
C2H5OH
C2H4
-0.65
-1.16
-2.03
-2.25
-1.36
-2.00
-1.24
-0.61
-1.25
-2.37
-2.18
-1.71
-2.12
-1.62
-1.81
-1.76
-1.91
-1.01
-1.17
0.89
0.90
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH2CHOH
13→14 *CH2CHOH → *CH3CHOH
14→15 *CH3CHOH → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
13→14 *CH2CHOH → *CH2CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

(b)

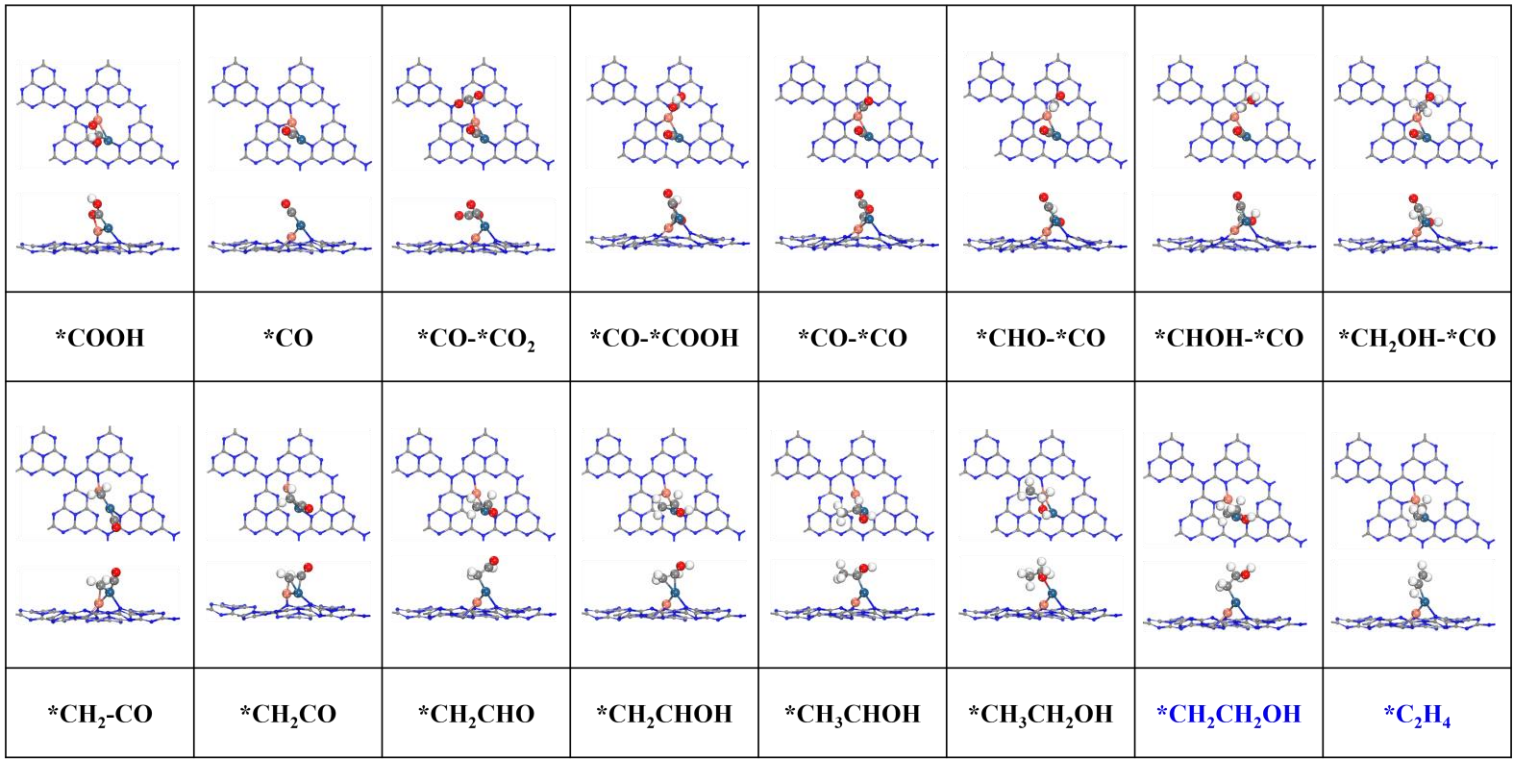
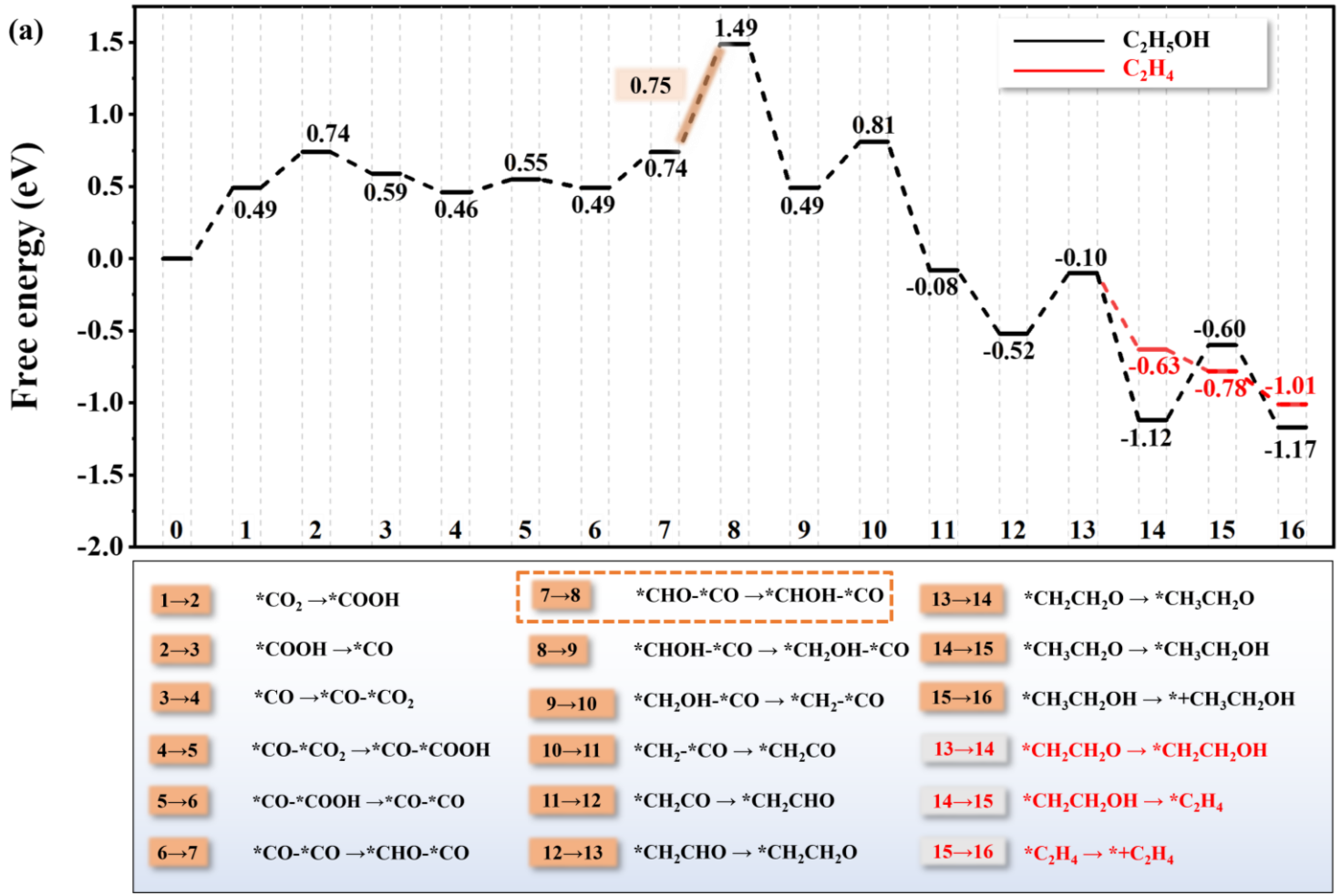


Fig. S16. (a) The calculated Gibbs free energy diagram of the optimal pathway for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on CuPt/g-C_3N_4. (b) The optimized structures of all intermediate species.


(a)
Free energy (eV)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0.49
0.74
0.59
0.46
0.55
0.49
0.74
0.75
1.49
0.49
0.81
-0.08
-0.52
-0.10
-0.63
-1.12
-0.60
-0.78
-1.01
-1.17
C2H5OH
C2H4
1→2 *CO2 →*COOH
2→3 *COOH →*CO
3→4 *CO →*CO-*CO2
4→5 *CO-*CO2 →*CO-*COOH
5→6 *CO-*COOH →*CO-*CO
6→7 *CO-*CO →*CHO-*CO
7→8 *CHO-*CO →*CHOH-*CO
8→9 *CHOH-*CO → *CH2OH-*CO
9→10 *CH2OH-*CO → *CH2-*CO
10→11 *CH2-*CO → *CH2CO
11→12 *CH2CO → *CH2CHO
12→13 *CH2CHO → *CH2CH2O
13→14 *CH2CH2O → *CH3CH2O
14→15 *CH3CH2O → *CH3CH2OH
15→16 *CH3CH2OH → *+CH3CH2OH
13→14 *CH2CH2O → *CH2CH2OH
14→15 *CH2CH2OH → *C2H4
15→16 *C2H4 → *+C2H4

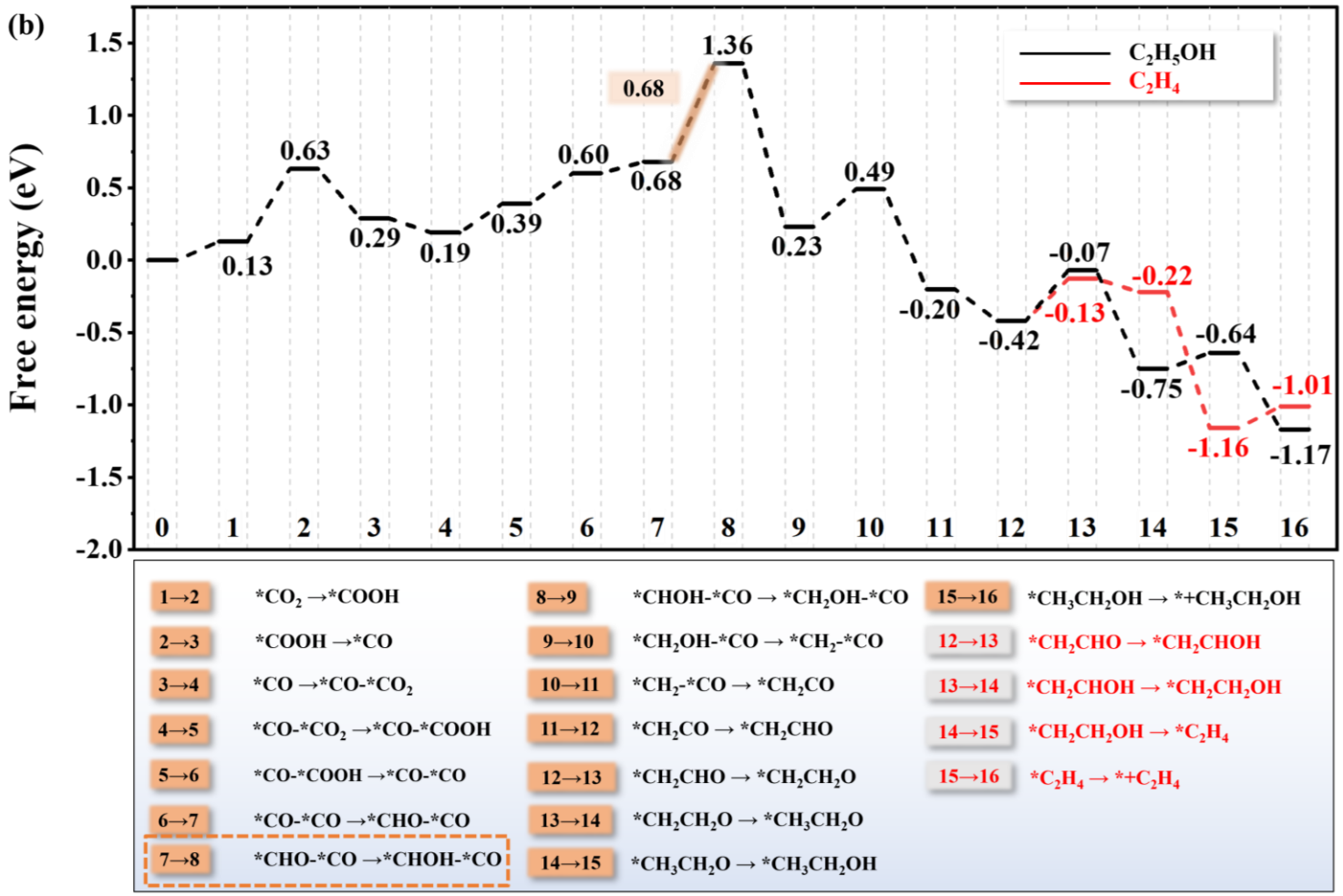


Fig. S17. The calculated Gibbs free energy diagrams of the optimal paths for CO_2 reduction to C_2 (C_2H_5OH and C_2H_4) products on (a) CuBi/g-C_3N_4 and (b) CuSn/g-C_3N_4.

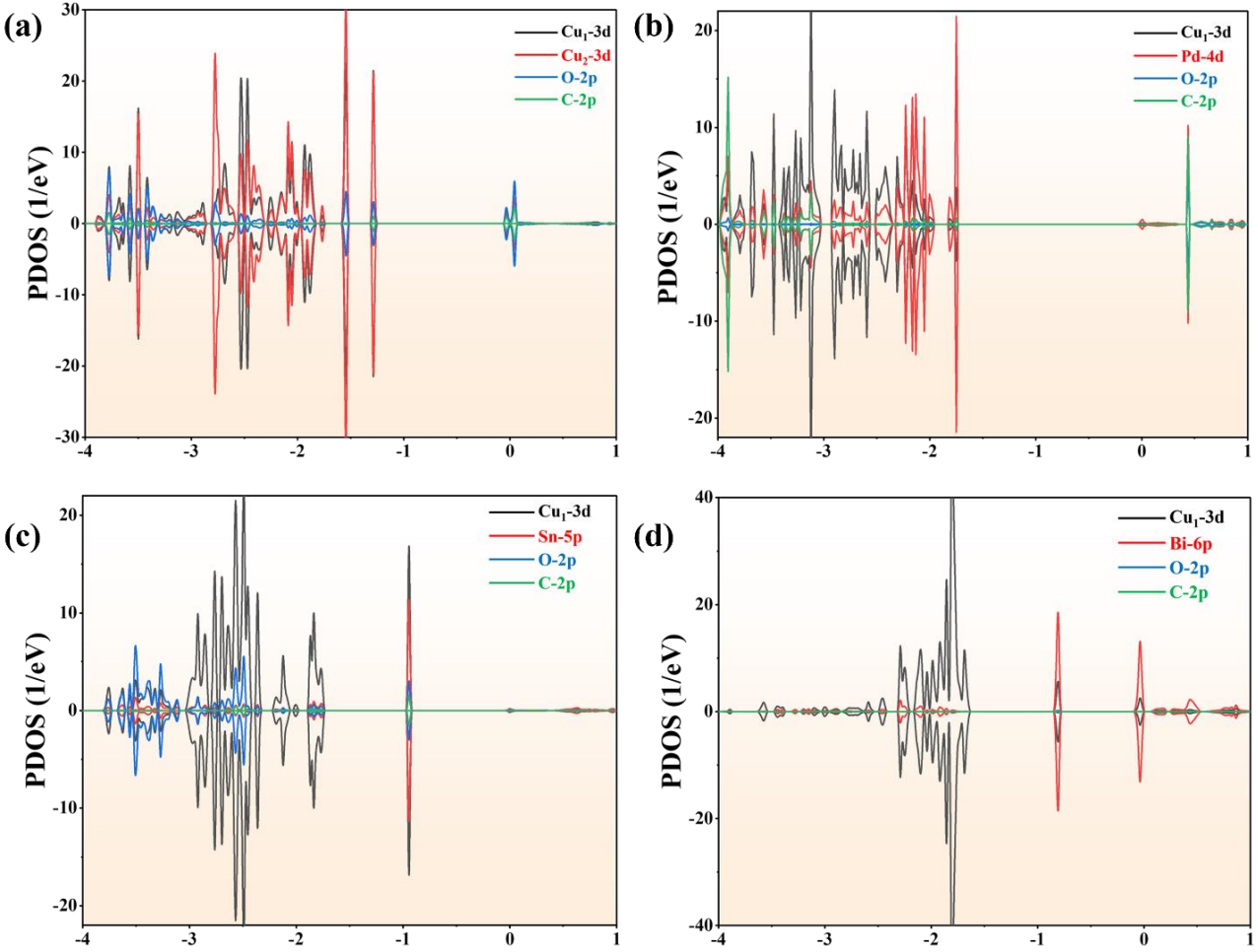


Fig. S18. The calculated projected density of states (PDOS) for CO_2 adsorption on (a) CuCu/g-C_3N_4, (b) CuPd/g-C_3N_4, (c) CuSn/g-C_3N_4, and (d) CuBi/g-C_3N_4.

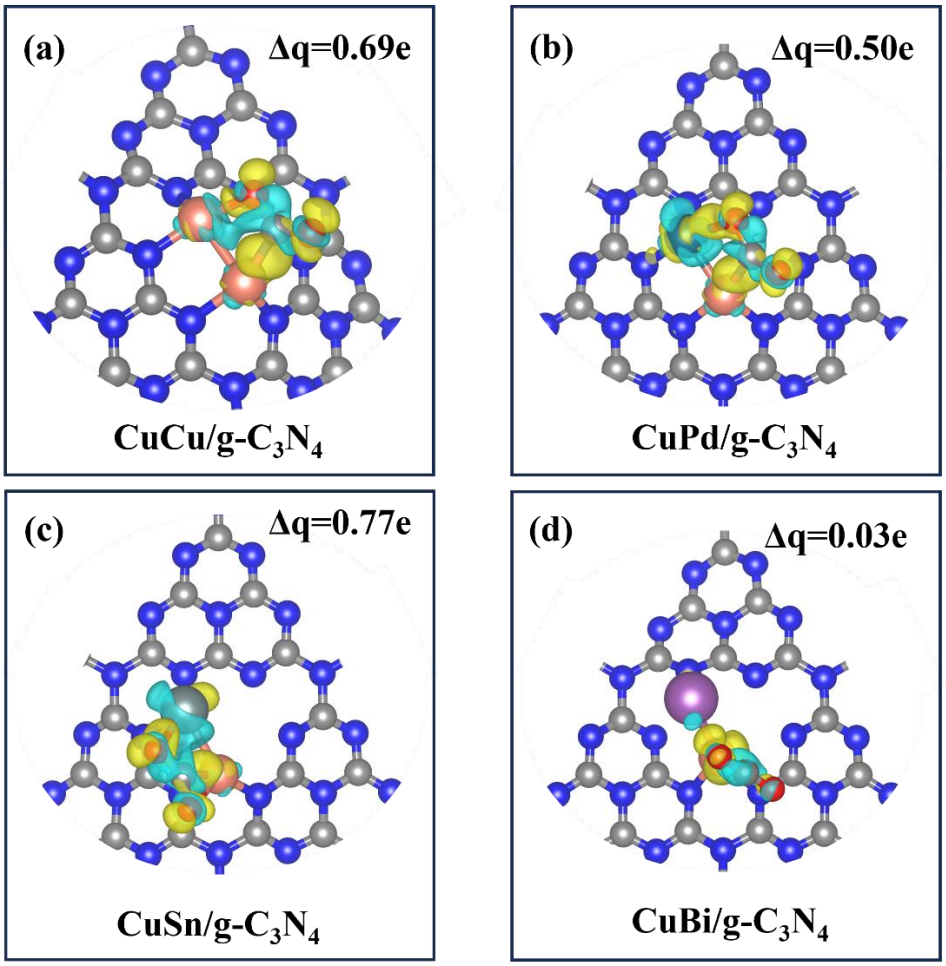


Fig. S19. The calculated differential charge density maps and charge transfer values of CO_2 adsorption on (a) CuCu/g-C_3N_4, (b) CuPd/g-C_3N_4, (c) CuSn/g-C_3N_4, and (d) CuBi/g-C_3N_4.

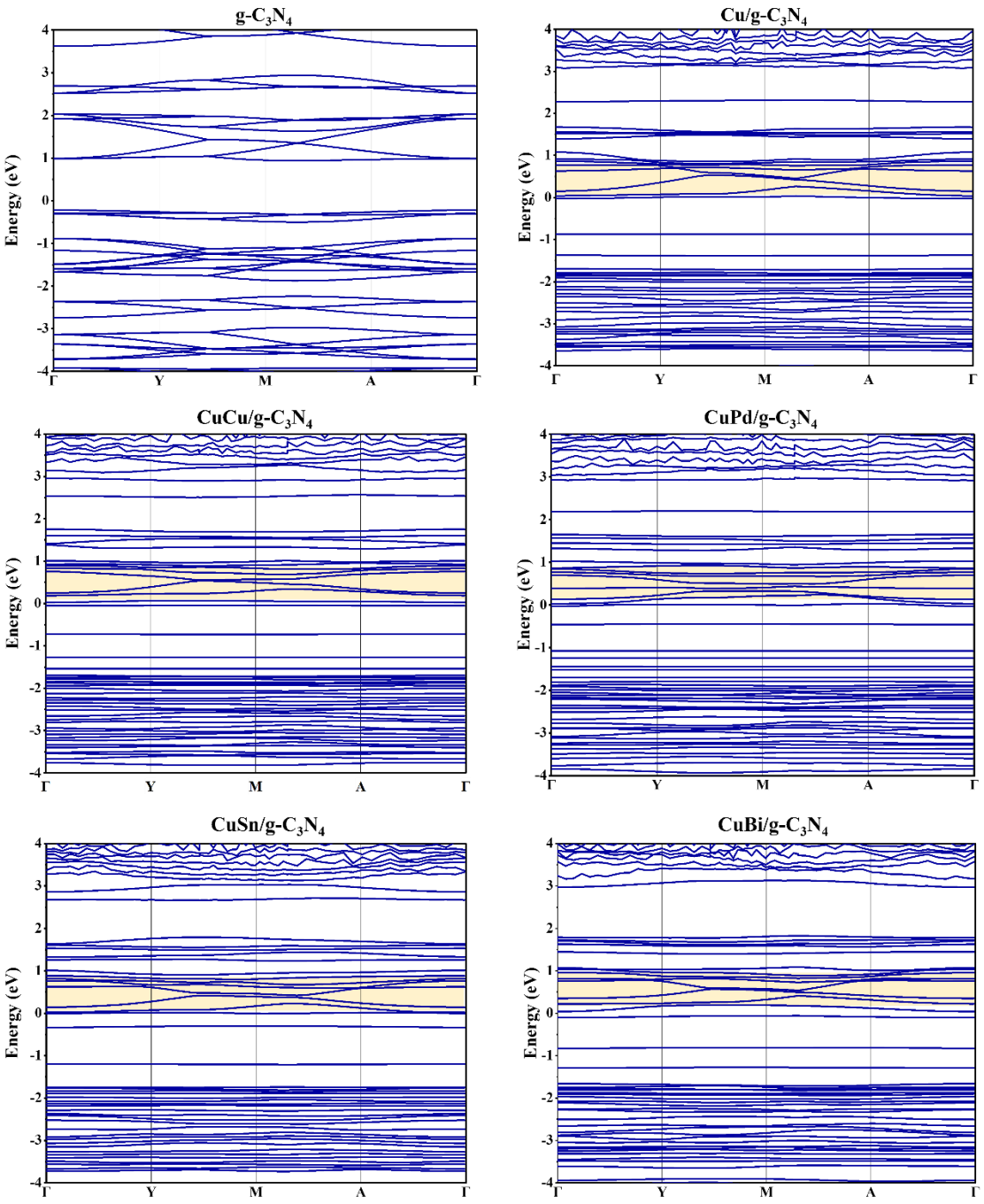


Fig. S20. The calculated energy band structures of g-C_3N_4, Cu/g-C_3N_4, CuCu/g-C_3N_4, CuPd/g-C_3N_4, CuSn/g-C_3N_4, and CuBi/g-C_3N_4.

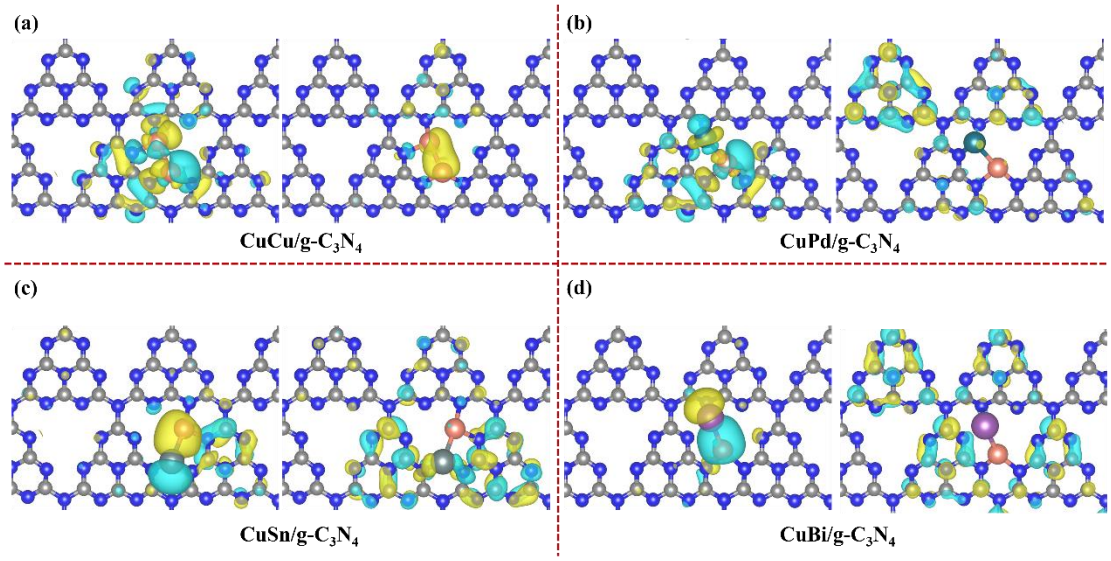


Fig. S21. The calculated valence-band maximum (VBM) (left side) and conduction-band minimum (CBM) (right side) of (a) CuCu/g-C_3N_4, (b) CuPd/g-C_3N_4, (c) CuSn/g-C_3N_4, and (d) CuBi/g-C_3N_4.

Table S1. Adsorption free energies (ΔG_{ads}) of CO_2 molecule on CuM/g-C_3N_4 (M = Cu, Pd, Sn, Bi, Fe, Co, Ni, Mn, In, and Pt) catalysts.

	3d	Mn	Fe	Co	Ni	Cu
	O*OC	0.37	0.88	0.24	0.09	0.26
	***OCO**	0.63	0.38	0.41	0.21	0.3
ΔG_{ads}/eV	***COO**	-0.25	-0.18	-0.55	-0.45	-0.22
	O(M)*C(Cu)O	**-1.01**	**-0.95**	**-1.11**	**-1.24**	**-0.55**
	O(Cu)*C(M)O	0.65	-0.41	-0.75	-0.56	/

	4d	Pd	In	Sn
	O*OC	0.19	0.26	/
	***OCO**	0.51	0.45 (linear)	0.54 (linear)
ΔG_{ads}/eV	***COO**	0.09	0.15	/
	O(M)*C(Cu)O	**-0.67**	**0.06**	**0.13**
	O(Cu)*C(M)O	-0.45	0.24	/

	5d	Pt	Bi
	O*OC	0.27	/
	***OCO**	0.47	**0.49 (linear)**
ΔG_{ads}/eV	***COO**	0.13	0.54
	O(M)*C(Cu)O	**-0.65**	/
	O(Cu)*C(M)O	-0.42	/

Table S2. Gibbs free energy change (ΔG) associated with the selectivity-determining step in CO_2 reduction to C_2H_5OH and C_2H_4 products on CuM/g-C_3N_4 (M = Cu, Pd, Sn, Bi, Fe, Co, Ni, Mn, In, and Pt) catalysts.

	CO_2 reduction to C_2H_5OH		CO_2 reduction to C_2H_4	
	Selectivity-determining step	ΔG	Selectivity-determining step	ΔG
CuPd/g-C_3N_4	*CO-*CO_2→*CO-*COOH	0.43	*CH_2CH_2→*+C_2H_4	1.67
CuCu/g-C_3N_4	*CO-*CO→*CHO-*CO	0.56	*CH_2CH_2→*+C_2H_4	1.35
CuIn/g-C_3N_4	*CO-*CO_2→*CO-*COOH	0.63	*CH_2CHO→*CH_2CHOH	0.96
CuSn/g-C_3N_4	*CH_2CHO→*CH_2CH_2O	0.35	*CH_2CHO→*CH_2CHOH	0.29
CuBi/g-C_3N_4	*CH_3CH_2O→*CH_3CH_2OH	0.52	*CH_2CH_2OH→*CH_2CH_2	-0.15
CuMn/g-C_3N_4	*CO-*CO→*COH-*CO	0.83	*CH_2CH_2→*+C_2H_4	1.45
CuCo/g-C_3N_4	*CO-*CO→*COH-*CO	0.87	*CH_2CH_2→*+C_2H_4	1.78
CuPt/g-C_3N_4	*CO-*CO_2→*CO-*COOH	0.89	*CH_2CH_2→*+C_2H_4	0.90
CuFe/g-C_3N_4	*CO-*CO→*CHO-*CO	0.91	*CH_2CH_2→*+C_2H_4	1.48
CuNi/g-C_3N_4	*CO-*CO→*CHO-*CO	1.36	*CH_2CH_2→*+C_2H_4	2.21

Table S3. The zero-point energy (ZPE) values for all adsorbed species involved in CO_2 reduction to C_2 products over the CuM/g-C_3N_4 (M = Mn, Fe, Co, Ni, Cu, Pd, In, Sn, Pt, and Bi) catalysts.

Adsorbate	ZPE	Adsorbate	ZPE
*CO_2	0.29	*CH_2O-*CHO	1.15
*COOH	0.60	*CH_2O*COH	1.24
*CO	0.20	*CH_3O*CO	1.28
*COH	0.49	*CH_2OHCO	1.35
*CHO	0.45	*CH_2*CO	0.82
CO-CO_2	0.50	*CH_2OH*CHO	1.55
*CO-*COOH	0.80	*CH_2CO	0.89
*CO-COOH	0.87	*CH_2*CHO	1.07
*CHO-*COOH	1.10	*CH_2CHO	1.22
*CO-*CO	0.41	*CH_2COH	1.21
*COH-*COOH	1.10	*CH_2CH_2O	1.50
*CHOH-*COOH	1.38	*CH_2CHOH	1.54
*CHO-*CO	0.65	*CH_2CH_2OH	1.87
*COH-*CO	0.71	*CH_3CHO	1.50
*CHOCO	0.69	*CH_2CH_2OH	1.84
*CHO-*CHO	0.94	*CH_3CH_2O	1.86
*CH_2O-*CO	0.93	*CH_3CH_2OH	2.14
*CHOH-*CO	1.00	*CH_2CH	1.11
*CHO-*COH	1.00	*C_2H_4	1.38
*CH_2OCO	1.06		
*CH_2OH-*CO	1.27		

Table S4. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuMn/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
$*+CO_2 \rightarrow *CO_2$	-1.01	$*CH_2\text{-}*CO \rightarrow *CH_2CO$	0.09
$*CO_2 \rightarrow *COOH$	0.13	$*CH_2CO \rightarrow *CH_2CHO$	-0.63
$*COOH \rightarrow *CO$	0.40	$*CH_2CHO \rightarrow *CH_3CHO$	-0.37
$*CO \rightarrow *CO\text{-}*CO_2$	-0.41	$*CH_3CHO \rightarrow *CH_3CHOH$	0.55
$*CO\text{-}*CO_2 \rightarrow *CO\text{-}*COOH$	-0.20	$*CH_3CHOH \rightarrow *CH_3CH_2OH$	0.66
$*CO\text{-}*COOH \rightarrow *CO\text{-}*CO$	-0.56	$*CH_3CH_2OH \rightarrow *+C_2H_5OH$	0.05
$*CO\text{-}*CO \rightarrow *COH\text{-}*CO$	0.83	$*CH_2CHO \rightarrow *CH_2CH_2O$	-0.09
$*COH\text{-}*CO \rightarrow *CHOH\text{-}*CO$	-0.21	$*CH_2CH_2O \rightarrow *CH_2CH_2OH$	0.19
$*CHOH\text{-}*CO \rightarrow *CH\text{-}*CO$	0.05	$*CH_2CH_2OH \rightarrow *C_2H_4$	-0.50
$*CH\text{-}*CO \rightarrow *CH_2\text{-}*CO$	-0.54	$*C_2H_4 \rightarrow *+C_2H_4$	1.45

Table S5. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuFe/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
$*+CO_2 \rightarrow *CO_2$	-0.95	$*CH_2\text{-}*CO \rightarrow *CH_2CO$	0.36
$*CO_2 \rightarrow *COOH$	0.09	$*CH_2CO \rightarrow *CH_2CHO$	-0.54
$*COOH \rightarrow *CO$	-0.49	$*CH_2CHO \rightarrow *CH_3CHO$	0.00
$*CO \rightarrow *CO\text{-}*CO_2$	-0.66	$*CH_3CHO \rightarrow *CH_3CHOH$	0.49
$*CO\text{-}*CO_2 \rightarrow *CO\text{-}*COOH$	0.27	$*CH_3CHOH \rightarrow *CH_3CH_2OH$	0.19
$*CO\text{-}*COOH \rightarrow *CO\text{-}*CO$	-0.73	$*CH_3CH_2OH \rightarrow *+C_2H_5OH$	0.49
$*CO\text{-}*CO \rightarrow *CHO\text{-}*CO$	0.91	$*CH_2CHO \rightarrow *CH_2CH_2O$	0.19
$*CHO\text{-}*CO \rightarrow *CH_2O\text{-}*CO$	-0.46	$*CH_2CH_2O \rightarrow *CH_2CH_2OH$	0.29
$*CH_2O\text{-}*CO \rightarrow *CH_2OH\text{-}*CO$	0.48	$*CH_2CH_2OH \rightarrow *C_2H_4$	-0.63
$*CH_2OH\text{-}*CO \rightarrow *CH_2\text{-}*CO$	-0.62	$*C_2H_4 \rightarrow *+C_2H_4$	1.48

Table S6. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuCo/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	-1.11	*CH_2-*CO→*CH_2CO	0.01
*CO_2→*COOH	0.29	*CH_2CO→*CH_2CHO	0.22
*COOH→*CO	-0.75	*CH_2CHO→*CH_2CHOH	0.13
*CO→*CO-*CO_2	-0.59	*CH_2CHOH→*CH_2CH_2OH	0.28
CO-CO_2→*CO-*COOH	0.10	*CH_2CH_2OH→* CH_3CH_2OH	-0.07
*CO-*COOH→*CO-*CO	-0.73	*CH_3CH_2OH→*+C_2H_5OH	0.54
*CO-*CO→*COH-*CO	0.87	*CH_2CHOH→*CH_2CH	0.21
*COH-*CO→*CHOH-*CO	0.06	*CH_2CH→*C_2H_4	-1.08
*CHOH-*CO→*CH-*CO	0.04	*C_2H_4→*+C_2H_4	1.78
*CH-*CO→*CH_2-*CO	-0.46		

Table S7. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuNi/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	-1.24	*CH_2-*CO→*CH_2CO	-0.08
*CO_2→*COOH	0.25	*CH_2CO→*CH_2CHO	0.02
*COOH→*CO	-0.12	*CH_2CHO→*CH_3CHO	-0.10
*CO→*CO-*CO_2	-1.03	*CH_3CHO→*CH_3CH_2O	0.39
CO-CO_2→*CO-*COOH	0.54	*CH_3CH_2O→*CH_3CH_2OH	0.29
*CO-*COOH→*CO-*CO	-1.30	*CH_3CH_2OH→*+C_2H_5OH	0.59
*CO-*CO→*CHO-*CO	1.36	*CH_2CHO→*CH_2CH_2O	0.23
*CHO-*CO→*CHOH-*CO	-0.25	*CH_2CH_2O→*CH_2CH_2OH	0.25
*CHOH-*CO→*CH_2OH-*CO	0.61	*CH_2CH_2OH→*C_2H_4	-1.36
*CH_2OH-*CO→*CH_2-*CO	-1.10	*C_2H_4→*+C_2H_4	2.21

Table S8. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuCu/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
$*+CO_2 \rightarrow *CO_2$	-0.55	$*CH_2OH\text{-}*CO \rightarrow *CH_2OHCO$	0.03
$*CO_2 \rightarrow *COOH$	-0.27	$*CH_2OHCO \rightarrow *CH_2CO$	-0.38
$*COOH \rightarrow *CO$	-0.28	$*CH_2CO \rightarrow *CH_2COH$	-0.54
$*CO \rightarrow *CO\text{-}*CO_2$	-0.25	$*CH_2COH \rightarrow *CH_2CHOH$	0.55
$*CO\text{-}*CO_2 \rightarrow *CO\text{-}*COOH$	0.24	$*CH_2CHOH \rightarrow *CH_2CH_2OH$	-0.54
$*CO\text{-}*COOH \rightarrow *CO\text{-}*CO$	-0.39	$*CH_2CH_2OH \rightarrow * CH_3CH_2OH$	0.45
$*CO\text{-}*CO \rightarrow *CHO\text{-}*CO$	0.56	$*CH_3CH_2OH \rightarrow *+C_2H_5OH$	0.19
$*CHO\text{-}*CO \rightarrow *CH_2O\text{-}*CO$	0.20	$*CH_2CH_2OH \rightarrow *C_2H_4$	-0.55
$*CH_2O\text{-}*CO \rightarrow *CH_2OH\text{-}*CO$	-0.19	$*C_2H_4 \rightarrow *+C_2H_4$	1.35

Table S9. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuPd/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
$*+CO_2 \rightarrow *CO_2$	-0.67	$*CH_2-*CO \rightarrow *CH_2CO$	-0.90
$*CO_2 \rightarrow *COOH$	0.11	$*CH_2CO \rightarrow *CH_2CHO$	-0.21
$*COOH \rightarrow *CO$	-0.99	$*CH_2CHO \rightarrow *CH_2CHOH$	0.27
$*CO \rightarrow *CO-*CO_2$	0.01	$*CH_2CHOH \rightarrow *CH_2CH_2OH$	0.31
$*CO-*CO_2 \rightarrow *CO-*COOH$	0.43	$*CH_2CH_2OH \rightarrow *CH_3CH_2OH$	-0.24
$*CO-*COOH \rightarrow *CHO-*COOH$	0.26	$*CH_3CH_2OH \rightarrow *+C_2H_5OH$	0.42
$*CHO-*COOH \rightarrow *CHO-*CO$	-0.47	$*CH_2CHOH \rightarrow *CH_2CH$	-0.08
$*CHO-*CO \rightarrow *CH_2O-*CO$	-0.14	$*CH_2CH \rightarrow *C_2H_4$	-0.94
$*CH_2O-*CO \rightarrow *CH_2OH-*CO$	0.22	$*C_2H_4 \rightarrow *+C_2H_4$	1.67
$*CH_2OH-*CO \rightarrow *CH_2-*CO$	0.42		

Table S10. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuIn/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	0.06	*CH_2*CO→*CH_2CO	-0.05
*CO_2→*COOH	-0.3	*CH_2CO→*CH_2CHO	-1.00
*COOH→*CO	-0.11	*CH_2CHO→*CH_3CHO	0.24
*CO→*CO-*CO_2	-0.25	*CH_3CHO→*CH_3CH_2O	-0.88
CO-CO_2→*CO-*COOH	0.63	*CH_3CH_2O→*CH_3CH_2OH	0.60
*CO-*COOH→*CO-*CO	-0.22	*CH_3CH_2OH→*+C_2H_5OH	0.09
*CO-*CO→*CHO-*CO	0.42	*CH_2CHO→*CH_2CHOH	0.96
*CHO-*CO→*CHOH-*CO	-0.30	*CH_2CHOH→*CH_2CH	-1.07
*CHOH-*CO→*CH_2OH-*CO	0.23	*CH_2CH→*C_2H_4	-0.54
*CH_2OH-*CO→*CH_2*CO	-0.33	*C_2H_4→*+C_2H_4	0.86

Table S11. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuSn/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	0.13	*CH_2-*CO→*CH_2CO	-0.69
*CO_2→*COOH	0.5	*CH_2CO→*CH_2CHO	-0.22
*COOH→*CO	-0.34	*CH_2CHO→*CH_2CH_2O	0.35
*CO→*CO-*CO_2	-0.10	*CH_2CH_2O→*CH_3CH_2O	-0.68
CO-CO_2→*CO-*COOH	0.20	*CH_3CH_2O→*CH_3CH_2OH	0.11
*CO-*COOH→*CO-*CO	0.21	*CH_3CH_2OH→*+C_2H_5OH	-0.53
*CO-*CO→*CHO-*CO	0.08	*CH_2CHO→*CH_2CHOH	0.29
*CHO-*CO→*CHOH-*CO	0.68	*CH_2CHOH→*CH_2CH_2OH	-0.09
*CHOH-*CO→*CH_2OH-*CO	-1.13	*CH_2CH_2OH→*C_2H_4	-0.94
*CH_2OH-*CO→*CH_2-*CO	0.26	*C_2H_4→*+C_2H_4	0.15

Table S12. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuPt/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	-0.65	*CH_2-*CO→*CH_2CO	0.19
*CO_2→*COOH	-0.51	*CH_2CO→*CH_2CHO	0.47
*COOH→*CO	-0.87	*CH_2CHO→*CH_2CHOH	-0.41
*CO→*CO-*CO_2	-0.22	*CH_2CHOH→*CH_3CHOH	0.31
CO-CO_2→*CO-*COOH	0.89	*CH_3CHOH→*CH_3CH_2OH	0.05
*CO-*COOH→*CO-*CO	-0.64	*CH_3CH_2OH→*+C_2H_5OH	0.59
*CO-*CO→*CHO-*CO	0.76	*CH_2CHOH→*CH_2CH_2OH	0.50
*CHO-*CO→*CHOH-*CO	0.63	*CH_2CH_2OH→*C_2H_4	-0.29
*CHOH-*CO→*CH_2OH-*CO	-0.64	*C_2H_4→*+C_2H_4	0.90
*CH_2OH-*CO→*CH_2-*CO	-1.12		

Table S13. The Gibbs free energy change of each elementary step corresponding to the optimal energy path on the CuBi/g-C_3N_4 catalyst.

Elementary steps	**Δ*G***	**Elementary steps**	**Δ*G***
+CO_2→CO_2	0.49	*CH_2-*CO→*CH_2CO	-0.89
*CO_2→*COOH	0.25	*CH_2CO→*CH_2CHO	-0.44
*COOH→*CO	-0.15	*CH_2CHO→*CH_2CH_2O	0.42
*CO→*CO-*CO_2	-0.13	*CH_2CH_2O→*CH_3CH_2O	-1.02
CO-CO_2→*CO-*COOH	0.09	*CH_3CH_2O→*CH_3CH_2OH	0.52
*CO-*COOH→*CO-*CO	-0.06	*CH_3CH_2OH→*+C_2H_5OH	-0.57
*CO-*CO→*CHO-*CO	0.25	*CH_2CH_2O→*CH_2CH_2OH	-0.53
*CHO-*CO→*CHOH-*CO	0.75	*CH_2CH_2OH→*C_2H_4	-0.15
*CHOH-*CO→*CH_2OH-*CO	-1.00	*C_2H_4→*+C_2H_4	-0.23
*CH_2OH-*CO→*CH_2-*CO	0.32		