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Supporting Information

Demystifying the mechanism of NMP ligands in promoting Cu-catalyzed acetylene hydrochlorination: Insights from density functional theory study

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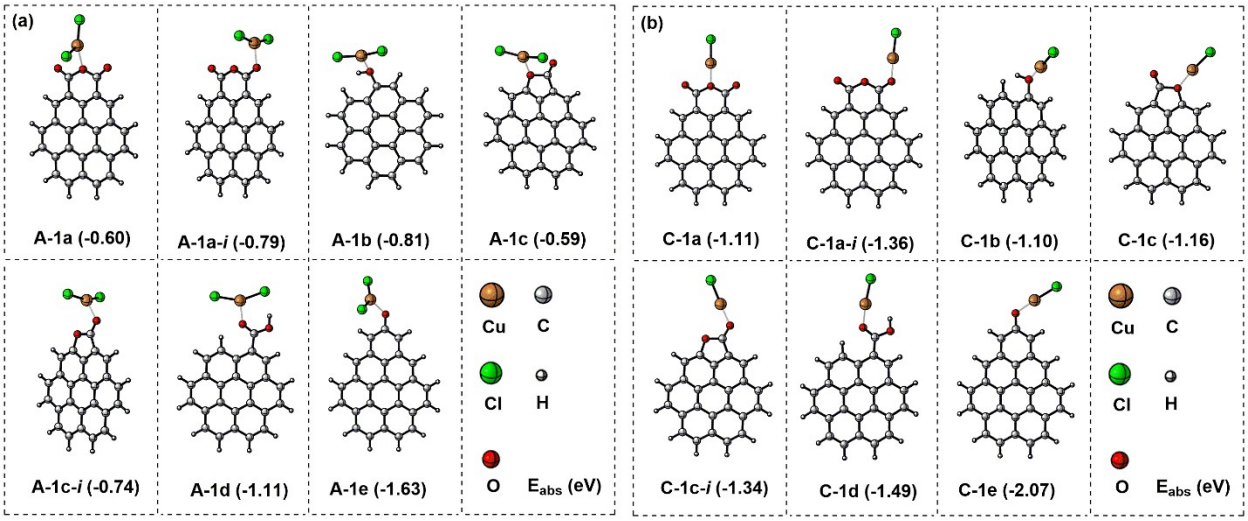

Fig. S1 Optimized geometries of **A-1n** Cu(II)/AC and **C-1n** Cu(I)/AC.

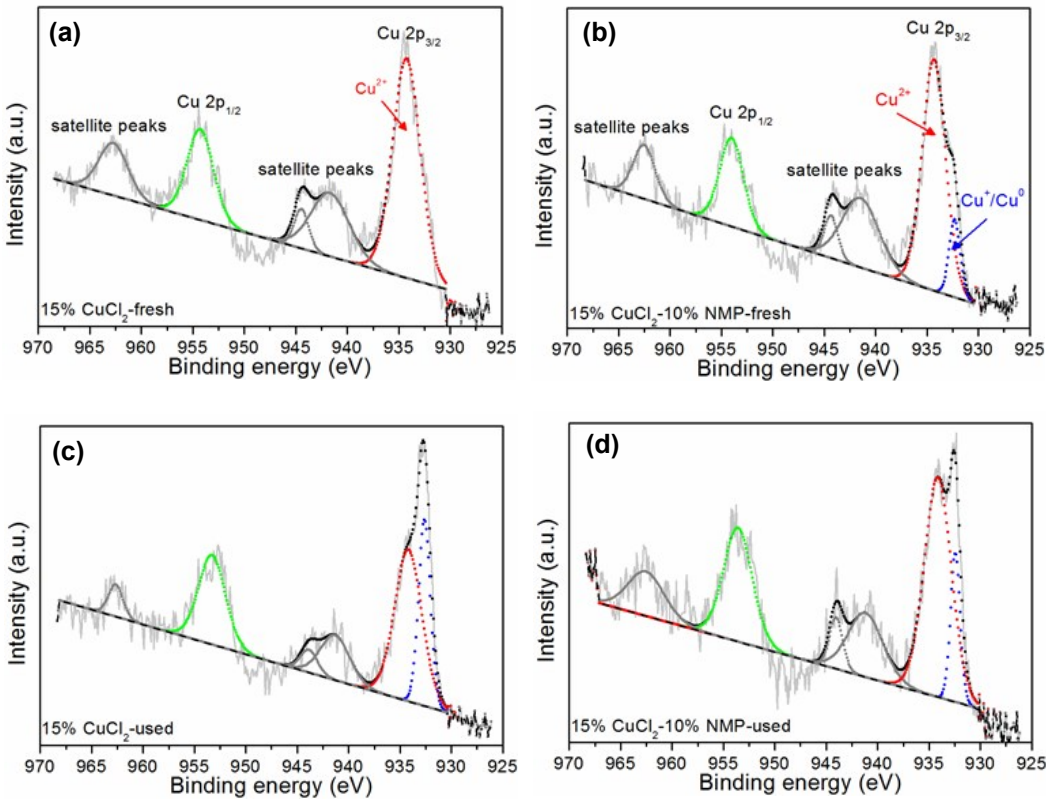

Fig. S2 Copper 2p XPS spectra of fresh catalysts (a) $CuCl_2$/AC and (b) $CuCl_2$-NMP/AC; used catalysts (c) $CuCl_2$/AC and (d) $CuCl_2$-NMP/AC.

Table 1 Surface Cu Components of Catalysts (XPS Cu 2p)

Catalyst	$Area_{Cu^{2+}}$ (%)	$Area_{Cu^{+}/Cu^{0}}$ (%)
15%$CuCl_2$-fresh	90.48	9.52
15%$CuCl_2$-10%NMP-fresh	86.35	13.65
15%$CuCl_2$-used	65.37	34.63
15%$CuCl_2$-10%NMP-used	80.71	19.29

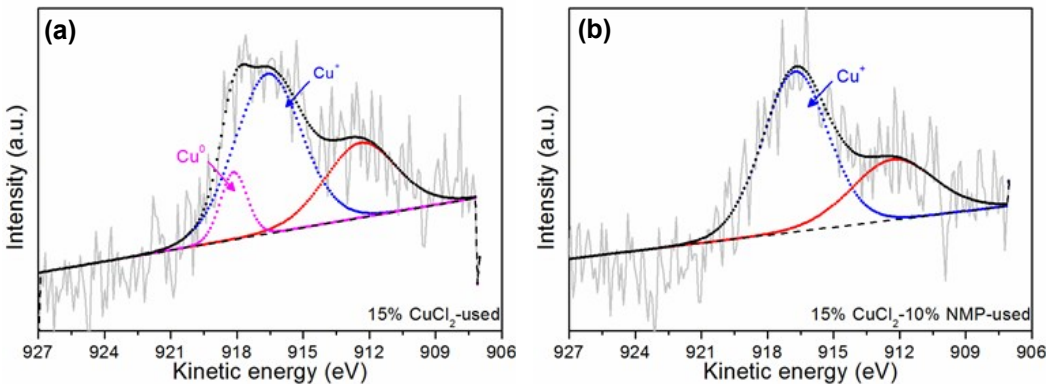

Fig. S3 Cu LMM Auger spectra of used catalysts (a) $CuCl_2$/AC and (b) $CuCl_2$-NMP/AC.

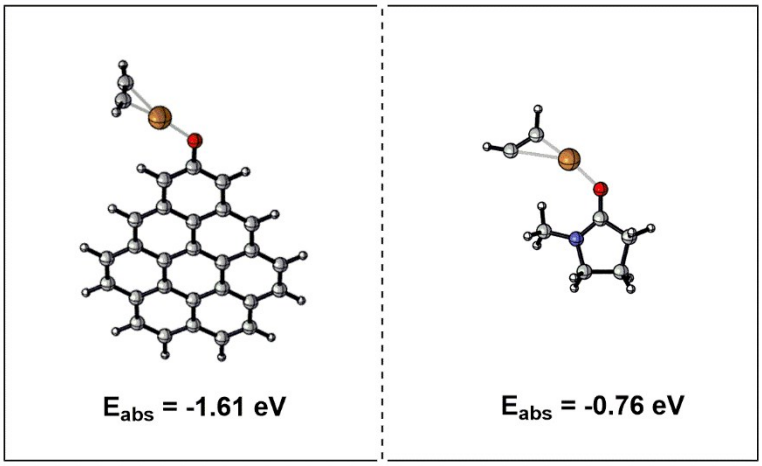

Fig. S4 Adsorption configurations and energies of C_2H_2 and HCl on Cu^0 complexes.

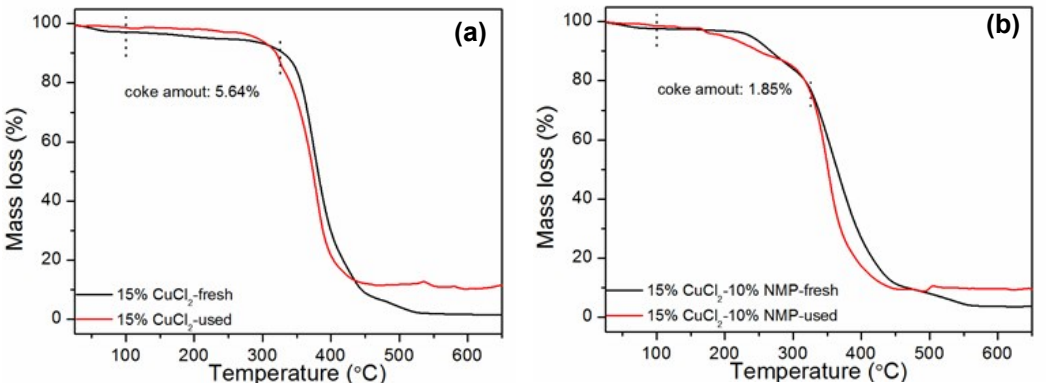

Fig. S5 TGA curves of fresh and used catalysts (a) $CuCl_2$/AC and (b) $CuCl_2$-NMP/AC.

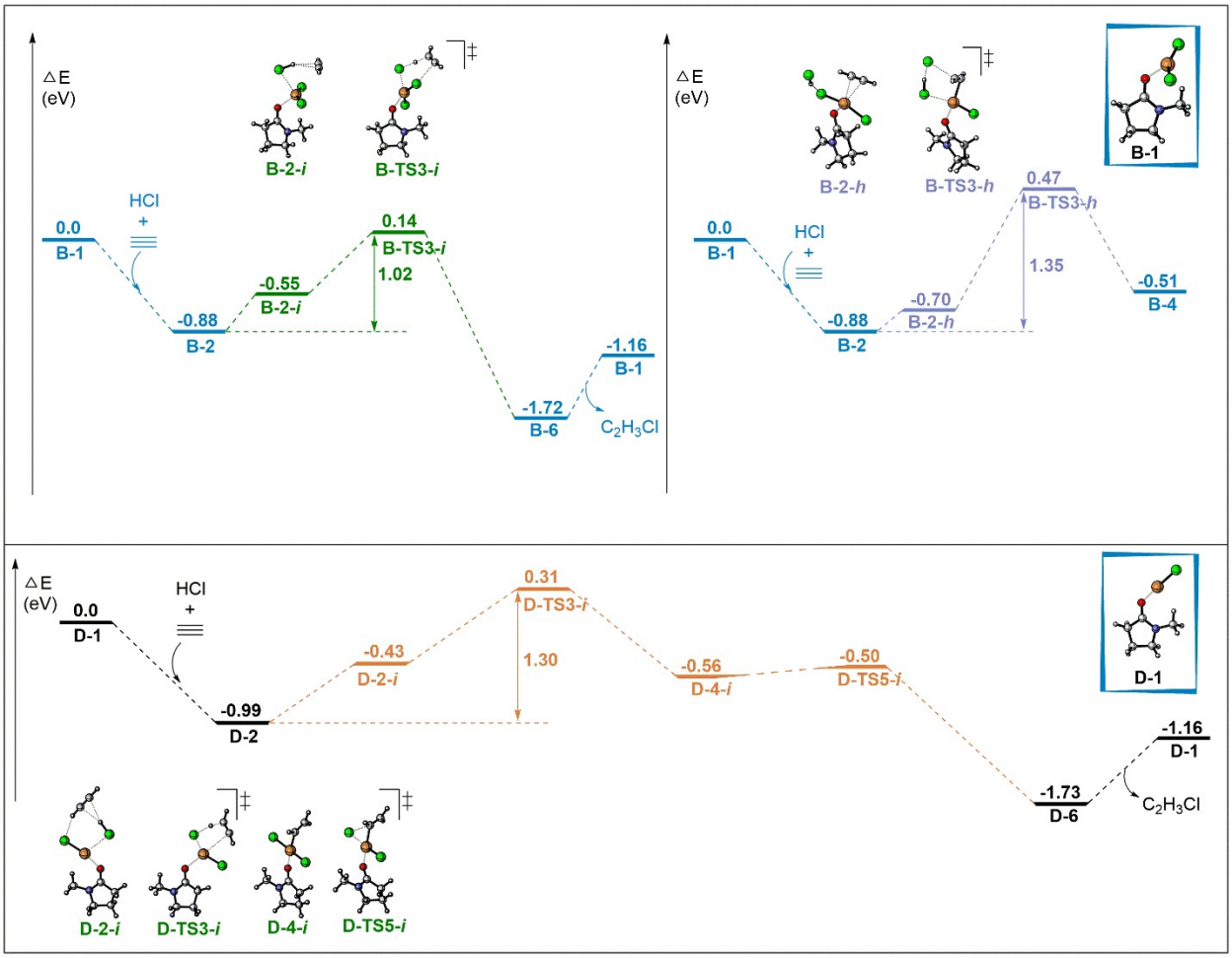

Fig. S6 Energy profiles of acetylene hydrochlorination of HCl and C_2H_2 with the Cu-NMP/AC catalyst along other possible pathways.

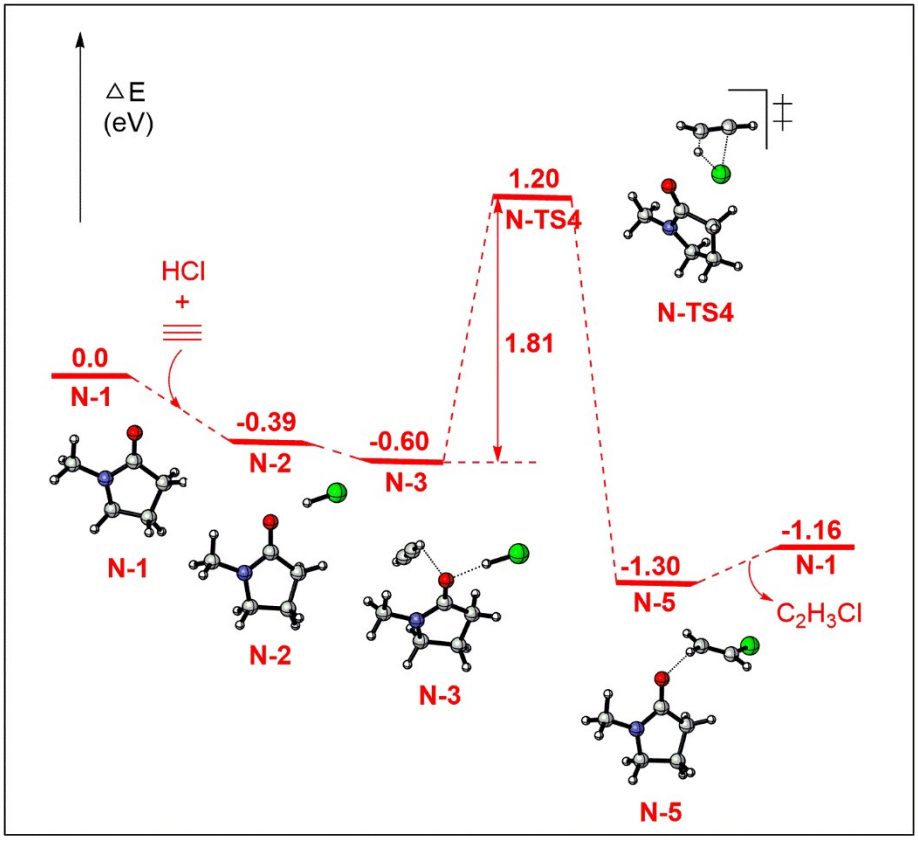

Fig. S7 Energy profile of acetylene hydrochlorination of HCl and C_2H_2 with the NMP catalyst.

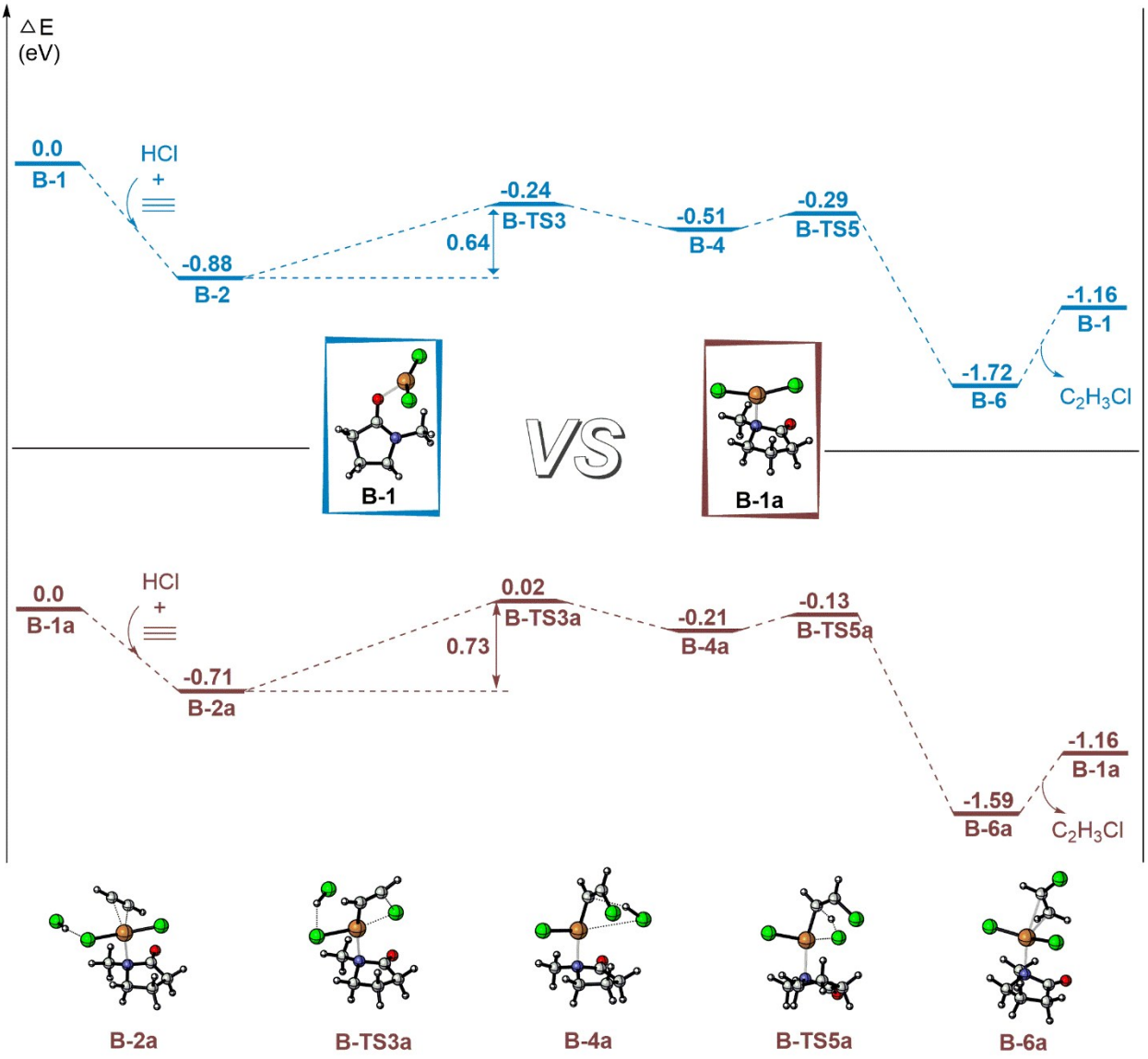

Fig. S8 Energy profile of acetylene hydrochlorination of HCl and C_2H_2 with **B-1** and **B-1a** catalysts.