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SUPPORTING INFORMATION

Monodisperse amorphous CuB_{23} alloy short nanotubes: novel efficient catalysts for Heck coupling of inactivated alkyl halides and alkenes

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Summary: 19 Pages; 11 Figures;

Experimental

Reagents

The regents were purchased from Sigma Aldrich or Changzhen High Technology Limited Company (China). Crotononitrile was mixtures of E and Z isomers. Alkenes were deoxygenated via multiple freeze-pump-thaw cycles, purified by vacuum transfer, and stored at -35 °C under an inert atmosphere prior to use. Alkyl iodide were purified by distillation, and stored at -35 °C under an inert atmosphere prior to use. (Trifluoromethyl)benzene, Oxolane, N,N-dimethylformamide and N-methyl-2-pyrrolidonewere dried by passage through a column of neutral alumina under argon and stored in the glovebox prior to use. All other reagents were used as received.

Synthesis and characterization of amorphous CuB_{23} alloy short nanotubes

The self-designed reactor used for the preparation of CuB_{23} short nanotubes via SPP was illustrated in our previous study [1]. The pulsed direct current voltage was 450 V (duty: 50%, frequency: 12 kHz). The electrodes were tungsten wire (diameter: 2 mm) and the gap between the cathode and anode was 1 mm.

In a typical synthesis, 40 mL of 25% $NH_3{\cdot}H_2O$ solution was mixed with 10 mL of copper acetate (0.0085 mol) to form a $Cu(NH_3)_4^{2+}$ complex. Then 32 mL of 1.0 M KBH_4 aqueous solution, and 0.003 M poly(ethylene glycol) was added at 298 K under an argon atmosphere. No significant reaction occurred in the absence of plasma. In contrast, the product was obtained 5 min following application of plasma. The obtained product was washed once with deionized water then thrice with absolute ethanol. The sample was stored in ethanol until use.

For comparison, conventional CuB_{23} sample were prepared via the same method without addition of poly(ethylene glycol). All the commercial catalysts were provided by Changzhen High Technology Limited Company (China).

Characterization of amorphous CuB_{23} alloy short nanotubes

X-ray diffraction (XRD) patterns were obtained using an X′Pert X-ray powder diffractometer equipped with a CuKα radiation source (λ = 0.15406 nm). For compositional analyses, the dry samples were dissolved in boiling aqua fortis using a microwave digestion system. The Cu and B contents in the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Irris, Advantage). The Brunauer–Emmett–Teller (BET) specific surface area of the samples were determined using a N_2 adsorption–desorption technique, in which the samples were degassed at 200 °C for 180 min before the measurements. Scanning transmission electron microscopy (STEM) images and selected-area electron diffraction patterns (SAED) of the samples were taken using a JEOL-2100F microscope. Samples for STEM analysis were prepared by depositing a single drop of diluted nanoparticle dispersion in ethanol on an amorphous, carbon-coated, nickel grid. The surface electronic states of the samples were investigated using X-ray photoelectron spectroscopy (XPS; Perkin–Elmer PHI 5000C ESCA, using AlKα radiation). The samples were fixed in a homemade in situ XPS reactor cell, and after drying under an argon atmosphere, each sample was transferred to the analysis chamber and the XPS spectrum was recorded. All binding energies were referenced to the C1s peak (binding energy of 284.6 eV) of the surface adventitious carbon. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiments were performed with a PHI TRIFT II(USA) equipped with a pulsed liquid metal ion gun. Spectra were acquired in positive ion mode over a mass range of 1–320 Da using a Ga+

primary source with a 100 × 100 mm^2 raster size, 15 kV applied voltage, 600 pA aperture current, and 10-min acquisition time. At least three different spots on each sample were analyzed, and the most representative were presented. Data acquisition and element composition analyses were performed using the Ion-Spec software. The active surface area (S_{Cu}) of the samples was measured by hydrogen chemisorption using a Quantachrome CHEMBET 3000 system, assuming H/Cu(s) = 1 and a surface area of 6.85×10^{-20} m^2 per Cu atom [2].

General Procedure for Alkyl-Heck Reaction

In a glovebox, the alkyl iodide (1.0 equiv), alkene (1.5 equiv), CuB_{23} short nanotubes (0.02 equiv), Na_2CO_3 (2.0 equiv), and NMP (10 mL) with a stirring bar were combined in a sealed tube. After removing the tube from the glovebox, it was heated in an oil bath at 353 K for 12 hours with stirring (800 rpm), and then centrifuged. The solution was separated and the precipitate was washed with ether (5 mL × 3). The solutions were combined and washed with water for three times. The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The product was then yielded by column chromatography on silica gel with hexane/ethyl acetate (20:1) as eluent. The precipitate was further washed sufficiently with ethanol and ether then dried, and the CuB_{23} short nanotubes were recovered for further using.

For the structural determination of the Heck reaction products, ^1H NMR spectra were determined on a Bruker AV spectrometer (^1H NMR at 200, 300 or 400 MHz and ^{13}C NMR at 125 MHz) with solvent resonance as the internal standard (^1H NMR: $CDCl_3$ at 7.28 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass (now Waters Corporation, 34 Maple Street, Milford, MA 01757) Quattro-II, Triple Quadrupole Mass Spectrometer, with a Zspray nano-Electrospray source design, in combination with a NanoMate (Advion, 19 Brown Road, Ithaca, NY 14850) chip based electrospray sample introduction system and nozzle, or using an Agilent 6850 series gas chromatography system equipped with an Agilent 5973N mass selective detector. Thin layer chromatography (TLC) was performed on SiliaPlate 250µm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), aqueous basic potassium permanganate solution, or ethanolic acidic p-anisaldehyde solution followed by heating.

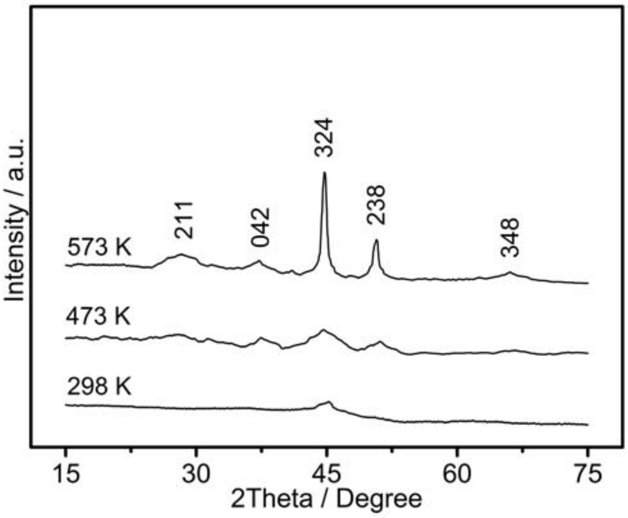


Fig.S1 XRD patterns of CuB_{23} short nanotubes treated at different temperatures in Ar atmosphere for 2 h.

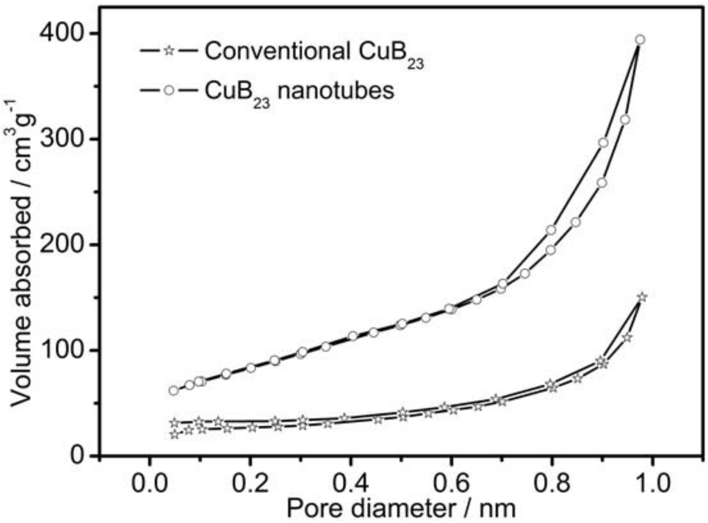


Fig.S2 N_2 adsorption–desorption plots of the samples.

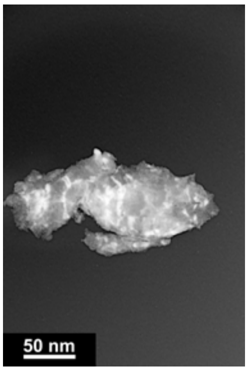
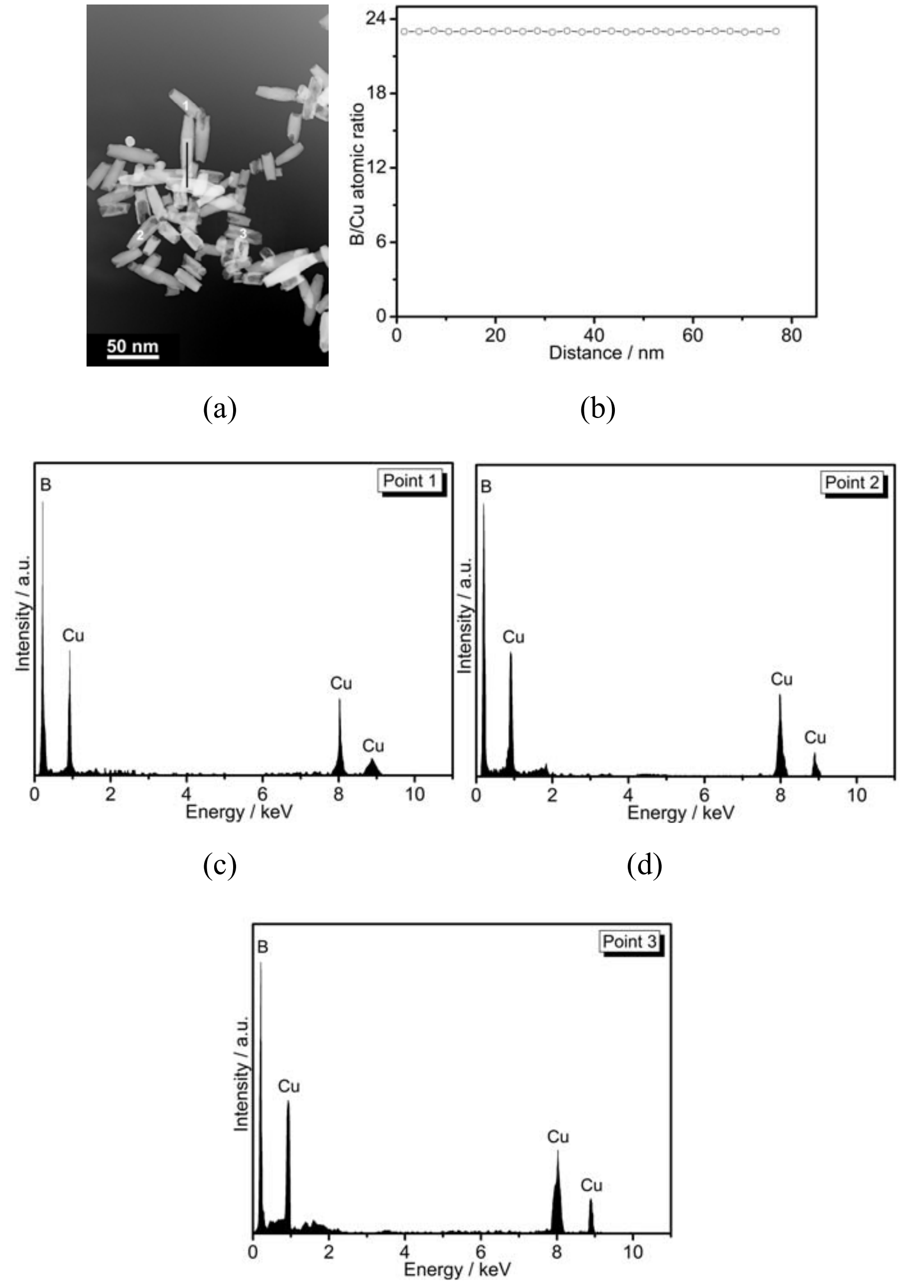


Fig.S3 The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of conventional CuB_{23}.

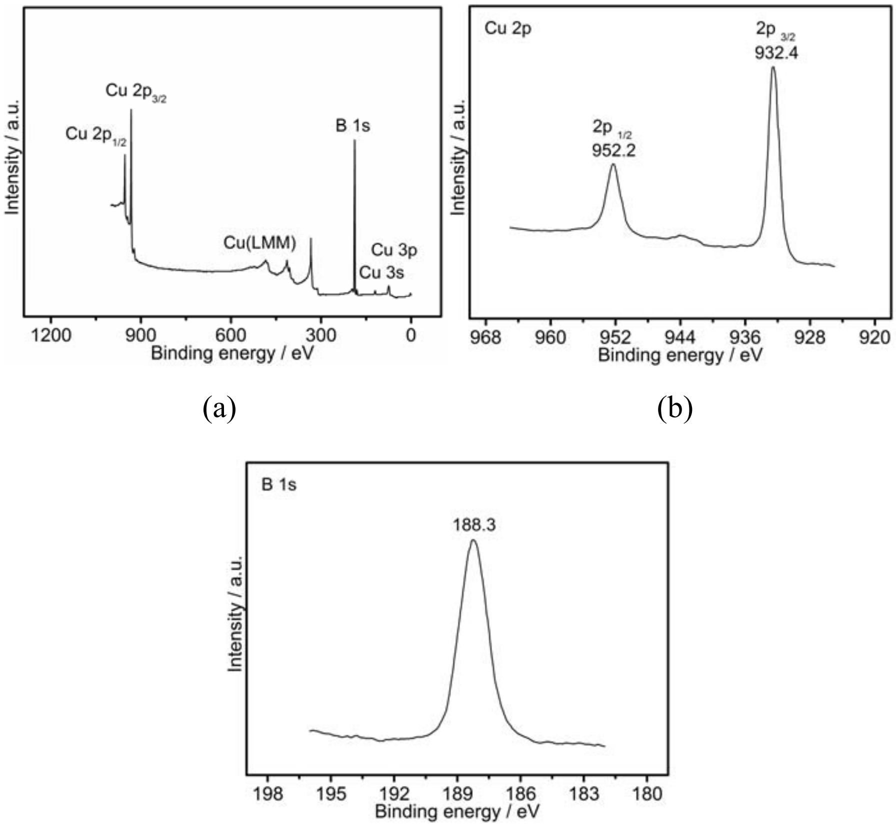


(a) (b)

(c) (d)

(e)

Fig.S4 (a) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (b) B/Cu atomic ratio recorded along the black cross-sectional compositional line shown in (a); (c) - (e) the Energy-dispersive X-ray spectroscopy (EDS) at points 1-3 in (a) of the as-prepared CuB_{23} short nanotubes.



(a)

(b)

(c)

Fig.S5 (a) Overall; (b) Cu 2p$_{3/2}$ and (c) B 1s XPS spectra of the as-prepared CuB$_{23}$ short nanotubes.

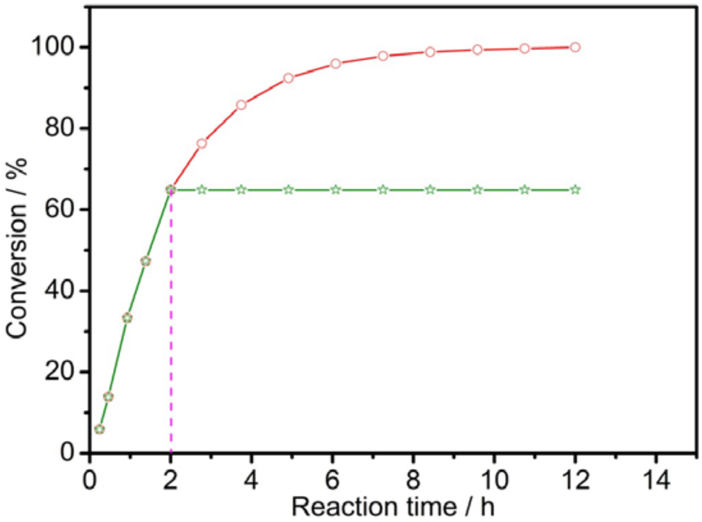


Fig.S6 Residual activity after filtration for Heck coupling reaction between cyclohexyl iodide and methyl acrylate over CuB_{23} nanotubes after 2 h reaction (☆) versus standard catalyst run (○). Reaction conditions: a catalyst containing 0.01 mmol CuB_{23} short nanotubes, cyclohexyl iodide (5.0 mmol), methyl acrylate (7.5 mmol), Na_2CO_3 (10.0 mmol), NMP (10 mL), T = 353 K, t = 12 h, stirring rate = 800 rpm.

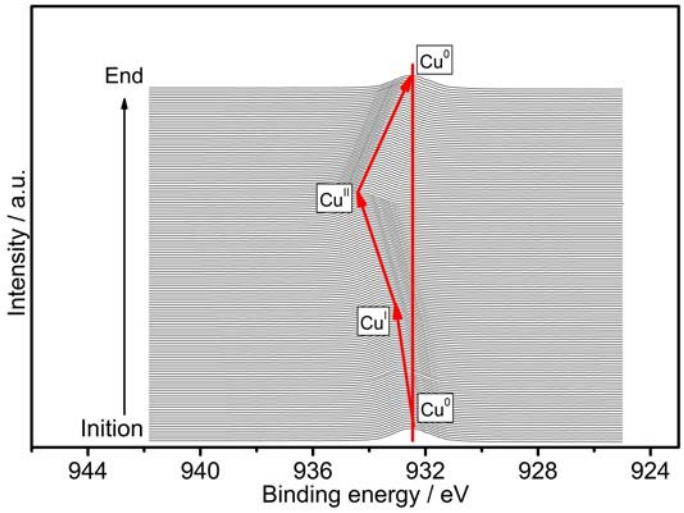


Fig.S7 The typical in-situ Cu $2p_{3/2}$ XPS spectra of CuB_{23} short nanotubes during the reaction.

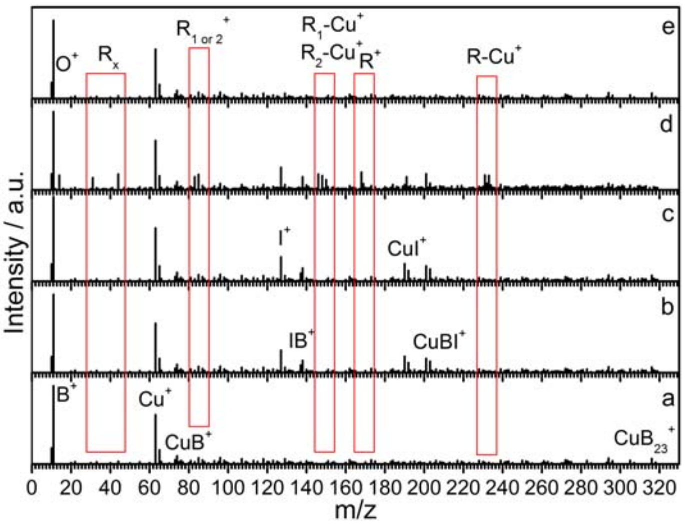
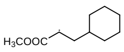
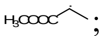
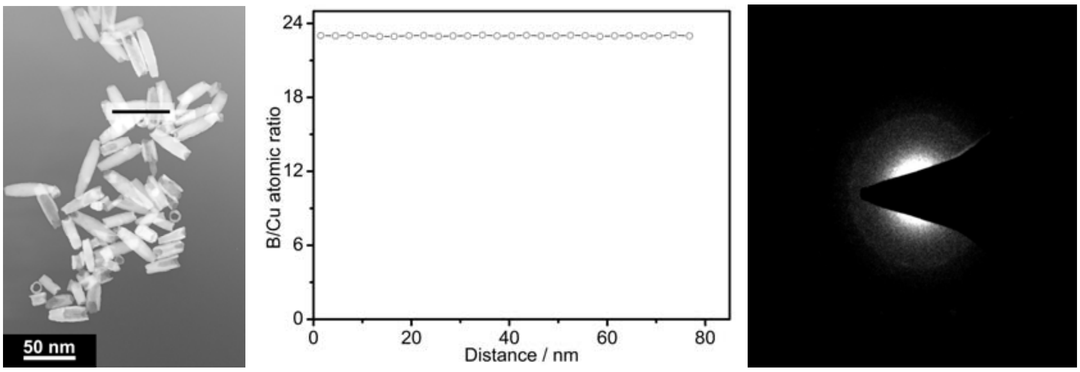
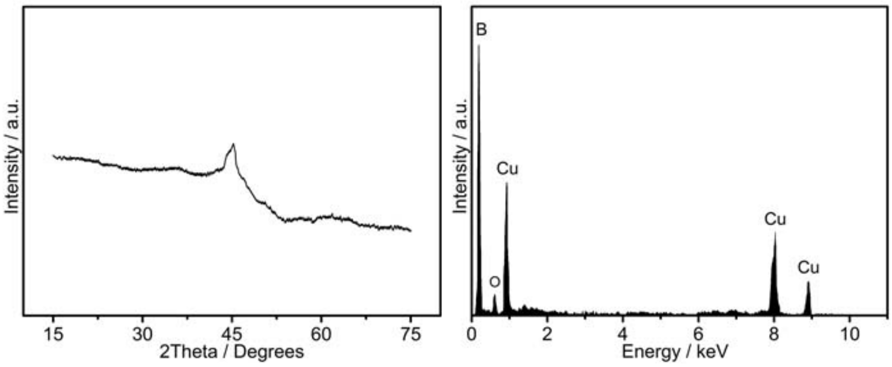


Fig.S8 ToF-SIMS spectra of CuB_{23} short nanotubes separated from the reaction system at different stages: (a) fresh CuB_{23} short nanotubes; (b) after reaction for 30 min with Na_2CO_3; (c) after reaction for 30 min without Na_2CO_3; (d) after reaction for 12 h without Na_2CO_3; (e) after reaction for 12 h with Na_2CO_3. (R= ; R_1= ; R_2= ; R_X = other fragment ions originated from R_1, R_2 or R).



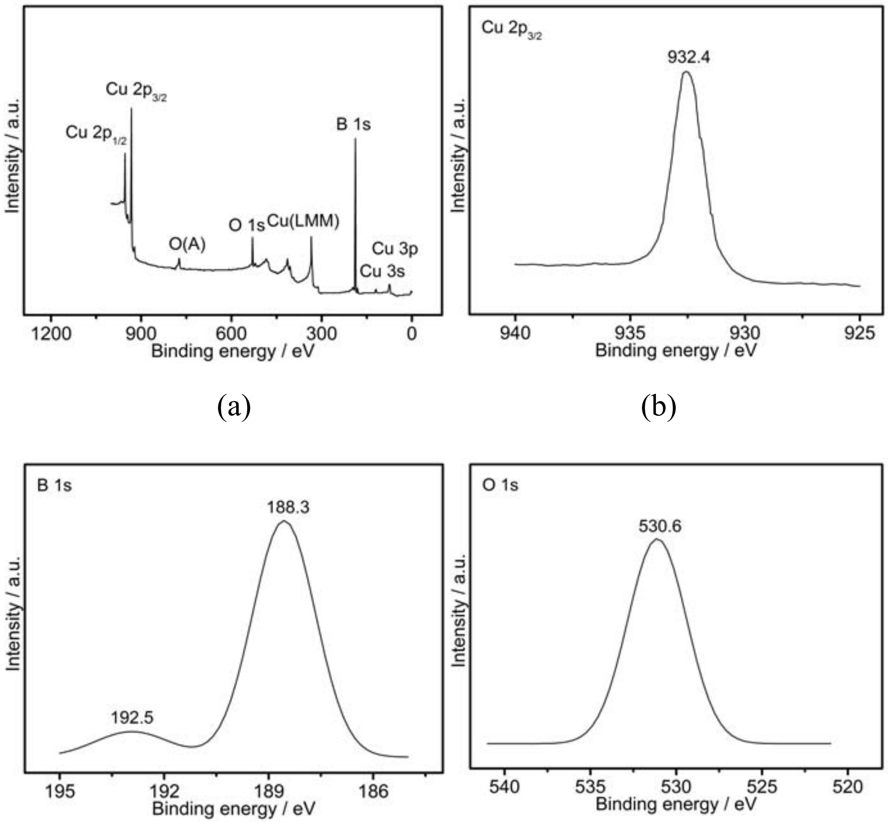
(a) (b) (c)

Fig.S9 (a)The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (b) B/Cu atomic ratio recorded along the black cross-sectional compositional line shown in (a); (c) SAED pattern of CuB_{23} short nanotubes after 10 cycles.



(a) (b)

Fig.S10 (a) XRD pattern and (b) EDAX spectrum of CuB_{23} short nanotubes after 10 cycles.



(a) (b)

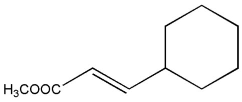
(c) (d)

Fig.S11 (a) Overall XPS; (b) Cu $2p_{3/2}$; (c) B 1s and (d) O 1s XPS spectra of CuB_{23} short nanotubes after 10 cycles.

Analytical data for Heck-coupling products

In Table 1

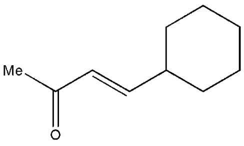
Methyl (E)-3-cyclohexylprop-2-enoate: [3]



Orange oil; ^1H NMR (300 MHz, $CDCl_3$) δ 6.91 (dd, J = 6.8, 15.9 Hz, 1 H), 5.76 (dd, J=2.8, 15.9 Hz, 1 H), 3.72 (s, 3 H), 2.15-0.87 (m, 11 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 154.3, 118.2, 51.1, 40.1, 31.4, 25.6, 25.4; HRMS calculated for $[C_{10}H_{16}O_2+H]^+$ = 169.24, found = 169.23.

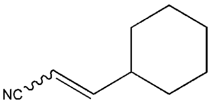
In Table 2 – entries 1-5:

***(E)*-4-Cyclohexylbut-3-en-2-one**: [4]

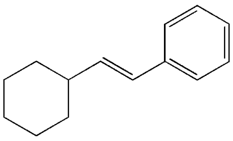


Pale yellow oil. ^1H NMR (300 MHz, CD_2Cl_2) δ 6.71 (dd, J = 16.1, 6.8 Hz, 1 H), 5.98 (dd, J = 16.3, 1.2 Hz, 1 H), 2.20 (s, 3H, CH_3), 2.18-2.11 (m, 1H), 1.79-1.11 (m, 10 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ=199.0, 153.5, 129.1, 41.0, 32.2, 26.9, 26.3, 26.1; HRMS calculated for $[C_{10}H_{16}O+H]^+$ =153.24, found 153.26.

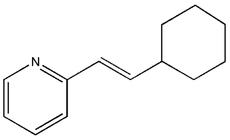
(E/Z)-3-cyclohexylacrylonitrile: [5]



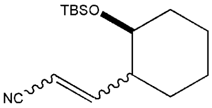
Yellow oil. ^1H NMR (400 MHz, $CDCl_3$, E/Z signals) δ 6.69 - 5.28 (dd, *J* = 6.7, 16.5，16.6 Hz, 2 H), 5.22 (d, *J* = 11.0 Hz, 1 H), 2.71 - 2.58 (m, 1 H), 1.84 - 1.66 (m, 7 H), 1.47 - 1.07 (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.2, 118.0, 116.2, 97.5, 97.2, 41.5, 41.1, 31.8, 31.2, 25.7, 25.6, 25.5, 25.1; HRMS calculated for $[C_9H_{13}N+H]^+$ =136.22, found = 136.13.

(*E*)-(2-cyclohexylvinyl)benzene: [6] 

Yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.40-7.23 (m, 5H), 6.39 (d, J = 12.0 Hz, 1 H), 5.55-5.46 (m, 1 H), 2.59-2.44 (m, 1 H), 1.40-1.14 (m, 10 H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.4, 128.6, 127.4, 126.9, 126.1, 41.3, 33.1, 29.8, 26.3, 26.2. HRMS calculated for $[C_{14}H_{18}]^+$ = 186.30, found = 186.28.

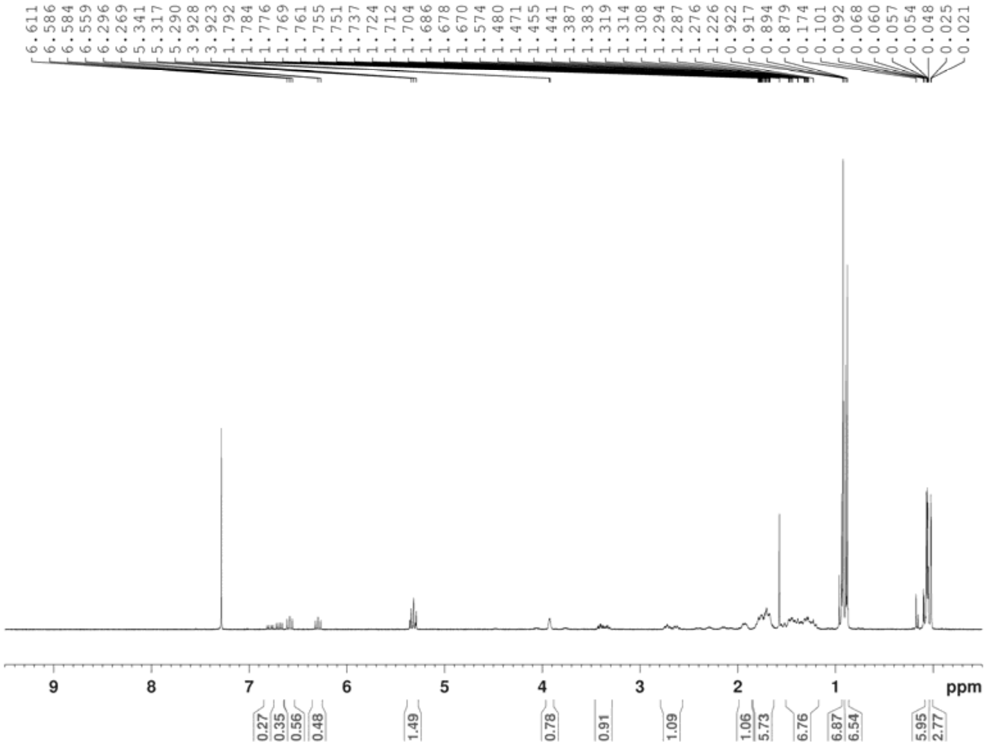
(E)-2-(2-cyclohexylvinyl)pyridiner: [5] 

Pale yellow oil. ^{1}H NMR (300 MHz, CDCl3) δ 8.55 (d, *J* = 4.6 Hz, 1 H), 7.61 (dt, *J* = 1.7, 7.7 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 7.12 - 7.07 (m, 1 H), 6.72 (dd, *J* = 7.0, 15.8 Hz, 1 H), 6.46 (dd, *J* = 1.1, 15.8 Hz, 1 H), 2.27 - 2.16 (m, 1 H), 1.90 - 1.16 (m, 10 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.4, 149.4, 141.4, 136.4, 127.4, 121.5, 121.1, 40.9, 32.6, 26.1, 26.0; HRMS calculated for $[C_{13}H_{17}N+H]^+$ = 188.29, found = 188.30.

(E/Z)-3-(2-((tert-butyldimethylsilyl)oxy)cyclohexyl)acrylonitrile: [5] 

Yellow oil (1:2 E:Z, 1:1 dr). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.79 - 6.69 (dd, *J* = 7.3，8.1, 16.4，16.6 Hz, 1 H), 6.59-6.30 (dd, *J* = 10.0, 11.0 Hz, 1 H)，5.36 - 5.28 (m, 2 H), 3.94-3.30 (m, 2 H), 2.76 - 2.58 (m, 1 H), 1.97 - 1.89 (m, 1 H), 1.83 - 1.62 (m, 6 H), 1.53 -1.18 (m, 6 H), 0.93 - 0.86 (m, 13 H), 0.11 - 0.01 (m, 9 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.0, 158.9, 158.6, 158.2, 117.9, 117.7, 116.4, 116.3, 99.7, 99.6, 99.2, 98.0 ,74.0, 73.9, 69.6, 69.5, 50.2, 49.5, 46.6, 45.8, 35.7, 35.2, 33.2, 32.9, 30. 5, 30.0, 29.7, 29.6, 26.2, 25.9, 25.8, 25.7, 25.2, 24.7, 24.6, 24.5, 24.4, 24.2, 19.8, 18.2,18.1, 18.0, 17.9, -3.9, -4.1, -4.4,

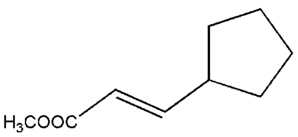
-4.5, -4.6, -4.7, -4.9, -5.0; HRMS calculated for $[C_{15}H_{27}NOSi+H]^+$ = 266.46, found = 266.50.



^{1}H NMR of (E/Z)-3-(2-((tert-butyldimethylsilyl)oxy)cyclohexyl)acrylonitrile

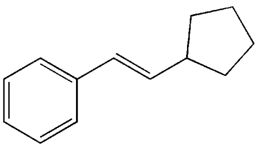
In Table 3 – entries 1-8:

Methyl (E)-3-cyclopentylprop-2-enoate: [7]



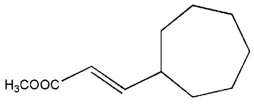
Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.95 (d, J=16 Hz, 1H); 5.72 (dd, J=16, 7.6 Hz, 1H); 1.31 -1.94 (m, 8H), 2.49 -2.68 (m, 1 H), 3.72 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.2, 154.7, 118.3, 56.9, 46.1, 43.8, 32.2, 24.9; HRMS calculated for $[C_9H_{14}O_2+H]^+$: 155.21, found: 155.07.

(2-cyclopentylvinyl)benzene: [8]



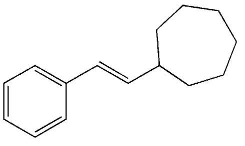
Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.13 - 7.37 (m, 5H), 6.37 (d, J=16 Hz, 1H), 6.20 (dd, J=16, 7.6 Hz, 1H), 2.50 - 2.69 (m, 1 H), 1.30 - 1.93 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 135.8, 128.5, 127.9, 126.8, 126.0, 43.8, 33.2, 25.2; HRMS calculated for $C_{13}H_{16}$: 172.27; found: 172.32.

Methyl (E)-3-cycloheptylprop-2-enoate: [7]



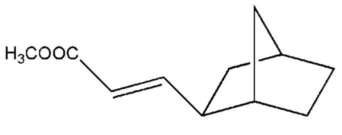
Yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.89 (d, J=15.8 Hz, 1H), 6.19 (dd, J=15.8, 6.6 Hz, 1 H), 3.70 (s, 3 H), 1.33 - 1.88 (m, 12H), 2.21 - 2.37 (m, 1H); ^{13}C NMR (150 MHz, CDCl3): δ 167.23, 154.34, 128.25, 51.18, 43.17, 34.66, 28.33, 26.19; HRMS calculated for $[C_{11}H_{18}O_2+H]^+$: 183.27; found: 183.15.

(E)-(2-cycloheptylvinyl)benzene: [8]



Colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12 - 7.40 (m, 5H), 6.32 (d, J=15.8 Hz, 1 H), 6.19 (dd, J= 6.6,15.8 Hz, 1 H), 2.21 ± 2.37 (m, 1 H), 1.33-1.88 (m, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ138.2, 137.7, 128.5, 126.7, 126.3, 126.0, 43.2, 34.7, 28.3, 26.2; HRMS calculated for $C_{15}H_{20}$: 200.32; found: 200.35.

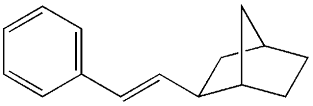
Methyl (E)-3-bicycle[2.2.1]heptylprop-2-enoate: [9]



Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85 (d, *J* = 16.0 Hz，1 H), 6.12 (dd, *J* = 16.0, 8.0 Hz，1 H), 3.70 (s, 3 H), 2.40-2.33 (m，2 H), 2.25-2.22 (m，1 H), 1.70-1.24 (m，8 H);

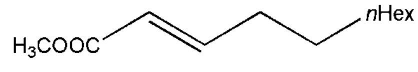
^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 148.3, 128.4, 52.8, 45.4, 42.7, 37.9, 36.6, 35.8, 29.7, 29.0; HRMS calculated for $[C_{12}H_{16}]^+$: 160.26, found: 160.14.

(exo)-2-(styryl)bicycle[2.2.1]heptane: [10]



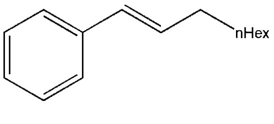
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.34 (m, 4H), 7.30-7.24 (m, 1H), 6.40 (d, *J* = 16.0Hz, 1 H), 6.22 (dd, *J* = 8.0, 16.0Hz, 1 H), 2.40-2.33 (m, 2 H), 2.25-2.22 (m,1 H), 1.70-1.24 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 136.3, 128.4, 127.2, 126.6, 125.9, 45.4, 42.7, 37.9, 36.6, 35.8, 29.7, 29.0; HRMS calculated for $C_{15}H_{18}$: 198.31, found: 198.24.

Methyl (*E*)-Dec-2-enoate: [11]



Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 6.97 (dt, J = 16.0, 7.0 Hz, 1 H), 5.81 (dt, J = 15.7, 1.6 Hz, 1H), 3.72 (s, 3 H), 2.20 (qd, J = 7.15,1.6 Hz, 2 H), 1.45 (m, 2 H), 1.3 (m, 8 H), 0.89 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 167.2, 150.0, 120.8, 51.5, 32.5, 32.0, 29.1, 28.2, 27.9, 22.5, 14.0; HRMS calculated for $[C_{11}H_{20}O_2+H]^+$: 185.29, found: 185.15.

(E)-dec-1-en-1-ylbenzene: [12]



Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.39 (m, 2 H), 7.27-7.34 (m, 2 H), 7.18-7.24 (m, 1 H), 6.40 (d, *J* = 15.8 Hz, 1 H), 6.25 (dt, *J* = 7.2, 15.8 Hz, 1 H), 2.23 (qd, *J* = 1.6, 6.8Hz, 2 H), 1.44-1.53 (m, 2 H), 1.25-1.42 (m, 10 H), 0.91 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0, 131.3, 129.7, 128.5, 126.7, 125.9, 33.1, 31.9, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; HRMS calculated for $C_{16}H_{24}$: 216.37, found 216.29.

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