

# Supporting Information

## **Aromatic C-H Bond Cleavage by Cu(I) Ate-Complex**

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## General Information

All reactions were run under an inert atmosphere in a glovebox. All glassware was oven dried at 110 °C for more than 1 hour prior to use. N, N-dimethylformamide (DMF) was dried and distilled from calcium (II) hydride. Unless otherwise stated, commercially available reagents were used as received. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C).

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response ( $\sim 10^{10}$  photons detected/sec) with 10% absorption ( $N_2$ ) in the incident ion chamber and 70% absorption (60%  $N_2$  and 40% Ar) in the transmission detector. A Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration and multiple scans were taken to ensure spectrum reproducibility <sup>1</sup>.

Air sensitive solution samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring

fitting to prevent exposure to air and water <sup>2</sup>. For solution samples, the Cu concentration was adjusted to be 0.05 - 0.1 M with a path length of 3.5 mm, which is suitable for transmission measurement. Each solid sample was mixed with boron nitride to a weight ratio of about 2% (Cu) in the glove box. The mixture was grinded well with mortar and pestle, and then 25 mg of the mixture was packed into a solid sample tube with a radius of 2.0 mm. After sealed in a cell holder with Kapton windows, the cell holder was taken out of the glovebox and used for transmission mode measurement.

The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Experimental phase shift and back scattering amplitude were used to fit the EXAFS data. Cu-O phase shift and back scattering amplitude were obtained from reference compounds: Cu<sub>2</sub>O (2 Cu-O at 1.85 Å) <sup>3</sup>. Background removal and normalization procedures were carried out using the Athena software package using standard methods <sup>4</sup>. Standard procedures based on WinXAS 3.2 software were used to extract the extended X-ray absorption fine structure (EXAFS) data <sup>5</sup>. The coordination parameters were obtained by a least square fit in R-space of the nearest neighbor, k<sup>2</sup>-weighted Fourier transform data.

NMR spectra were recorded on a Bruker Avance spectrometer at 298K (500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR). All samples were prepared in a glovebox using DMF (D7) as solvent with the concentration of 0.1M. After the solution was prepared, it was transferred into a NMR tube with J. Young valve and sealed. For the ReactIR kinetic

experiments, all spectra were recorded on a Mettler Toledo React IRTM 15 spectrometer using a diamond comb.

## Figures and Tables

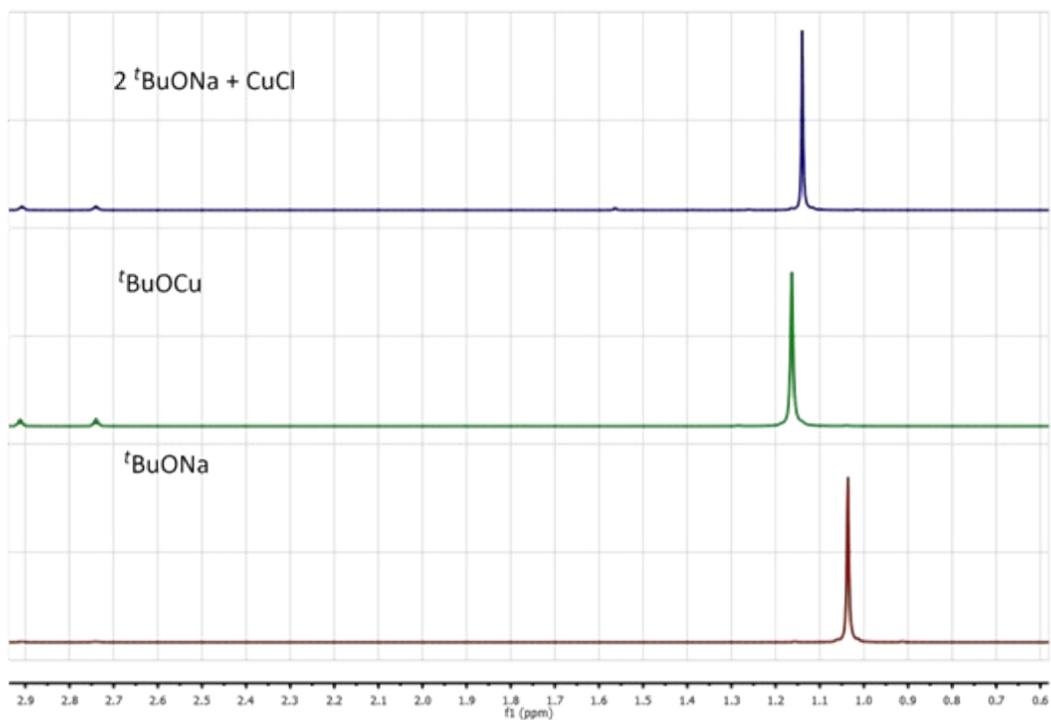


Figure S1.  $^1\text{H}$  NMR spectra of  $^t\text{BuONa}$ ,  $^t\text{BuOCu}$  and  $[\text{Cu}(\text{O}^t\text{Bu})_2]\text{Na}$

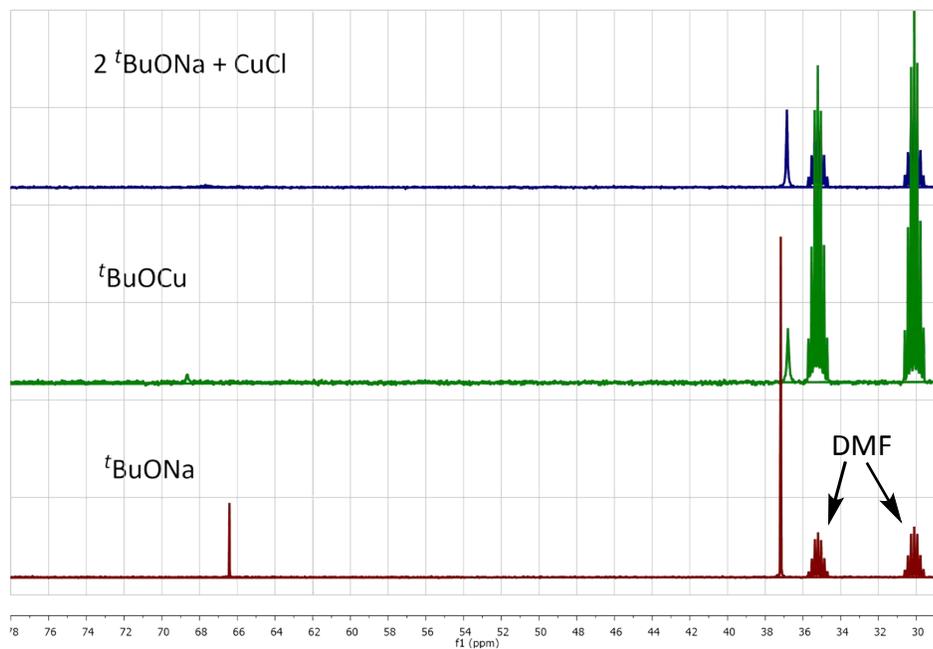


Figure S2.  $^{13}\text{C}$  NMR spectra of  $^t\text{BuONa}$ ,  $^t\text{BuOCu}$  and  $[\text{Cu}(\text{O}^t\text{Bu})_2]\text{Na}$

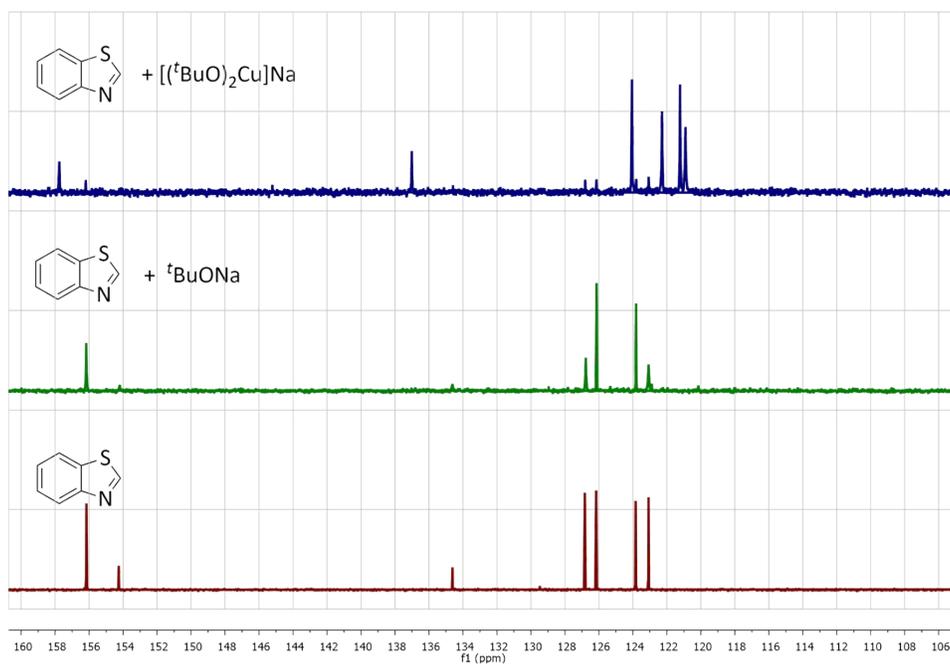


Figure S3.  $^{13}\text{C}$  NMR spectra of ArH,  $^t\text{BuOCu}+\text{ArH}$  and  $[\text{ArCu}(\text{O}^t\text{Bu})]\text{Na}$

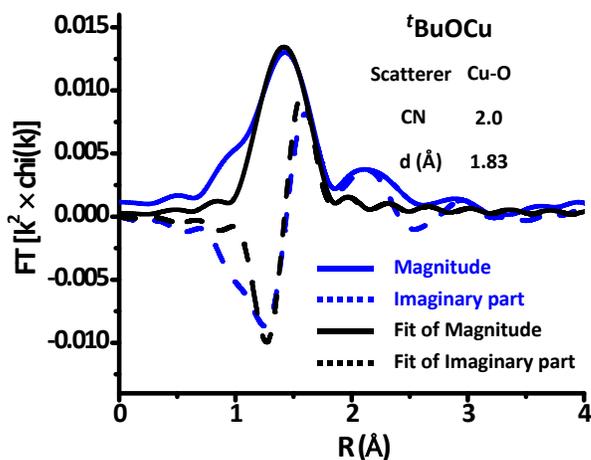
**Table S1. Summary of the Edge Energy and Oxidation States**

Sample	Edge Energy (eV)	Pre-edge Energy (eV)	Oxidation State
Cu foil	8979.0	N.A.	0
Cu <sub>2</sub> O (solid)	8980.2	N.A.	+ 1
CuCl (solid)	8981.9	N.A.	+ 1
CuI (solid)	8981.7	N.A.	+ 1
<sup>t</sup> BuOCu (solid)	8980.5	N.A.	+ 1
<sup>t</sup> BuOCu (DMF solution)	8980.9	N.A.	+ 1
CuCl <sub>2</sub> (solid)	8984.8	8978.0	+ 2
CuCl <sub>2</sub> (DMF solution)	8984.1	8977.2	+ 2
Cu(acac) <sub>2</sub> (solid)	8984.0	8978.0	+ 2
Cu(acac) <sub>2</sub> (DMF solution)	8984.0	8978.0	+ 2
[Cu(O <sup>t</sup> Bu) <sub>2</sub> ]Na (in DMF)	8980.9	N.A.	+ 1
[ArCu(O <sup>t</sup> Bu)]Na (in DMF)	8980.2	N.A.	+ 1

**Table S2. Summary of the EXAFS fitting results**

Sample	Absorber-Scatterer Pair	Coordination Number	Bond Distance (Å)	$\Delta \sigma$	$\Delta E_0$ (eV)	Comments
Cu foil	Cu-Cu	12	2.55	N.A.	N.A.	Single Crystal Data
Cu <sub>2</sub> O (solid)	Cu-O	2	1.85	N.A.	N.A.	
CuCl (solid)	Cu-Cl	4	2.34	N.A.	N.A.	
<sup>t</sup> BuOCu (solid)	Cu-O	2	1.85	N.A.	N.A.	
CuCl <sub>2</sub> (solid)	Cu-Cl	4	2.26	N.A.	N.A.	
<sup>t</sup> BuOCu (solid)	Cu-O	2.0	1.83	0.001	-1.74	EXAFS fitting results
[Cu(O <sup>t</sup> Bu) <sub>2</sub> ]Na (DMF solution)	Cu-O	2.2	1.83	0.001	2.91	
[ArCuO <sup>t</sup> Bu]Na (DMF solution)	Cu-O/C	2.0	1.83	0.001	0.65	

$\Delta \sigma$ : relative Debye-Waller factor to experimental standard.



**Figure S4. EXAFS fitting results of <sup>t</sup>BuOCu**

( $k^2$ -weighted, FT:  $2.54 < k < 11.36 \text{ \AA}^{-1}$  and fitting range:  $1.05 < R < 1.75 \text{ \AA}$ ; CN: coordination number; d: bond distance)

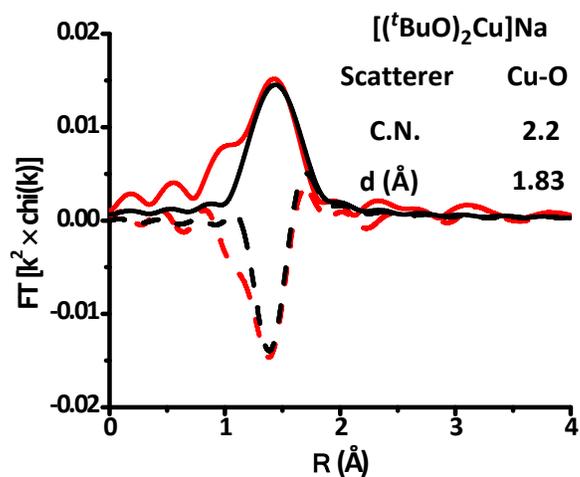


Figure S5. EXAFS fitting results of  $[(t\text{BuO})_2\text{Cu}]\text{Na}$

( $k^2$ -weighted, FT: 2.51 – 11.55  $\text{\AA}^{-1}$ , fitting range: 1.20 – 1.82  $\text{\AA}$ ; CN: coordination number; d: bond distance)

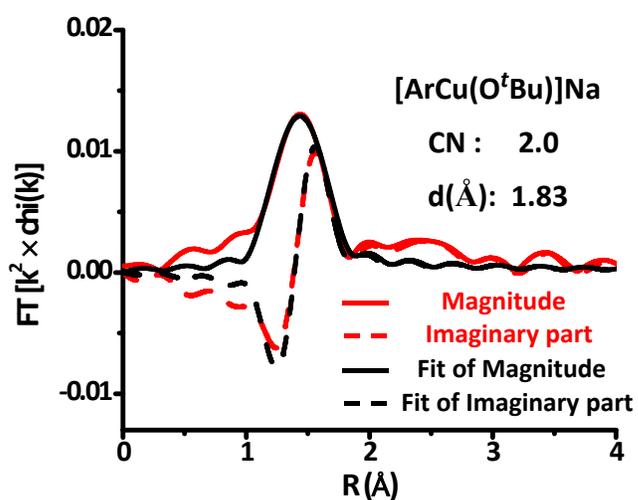
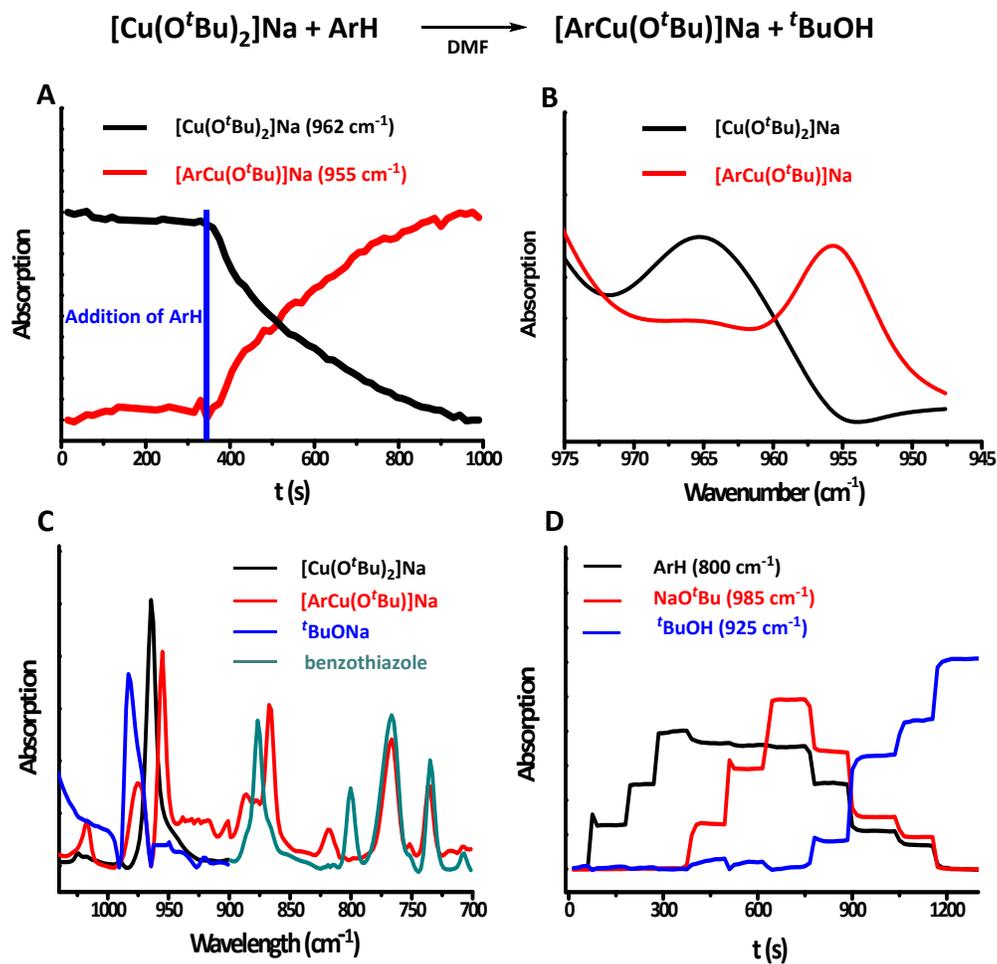


Figure S6. EXAFS fitting results of  $[\text{ArCuO}^t\text{Bu}]\text{Na}$

( $k^2$ -weighted, FT: 2.51 – 11.55  $\text{\AA}^{-1}$ , fitting range: 1.08 – 1.86  $\text{\AA}$ ; CN: coordination number; d: bond distance)



**Figure S7.** IR spectra of the reaction of  $[(^t\text{BuO})_2\text{Cu}]\text{Na}$  with ArH.

(A) Reaction kinetics. (B) IR spectra of  $[\text{Cu}(\text{O}^t\text{Bu})_2]\text{Na}$  and  $[\text{ArCu}(\text{O}^t\text{Bu})]\text{Na}$  (specific peaks used to monitor the kinetics). (C) IR spectra of  $[(^t\text{BuO})_2\text{Cu}]\text{Na}$ ,  $[\text{ArCu}(\text{O}^t\text{Bu})]\text{Na}$ ,  ${}^t\text{BuONa}$  and ArH. (D) *Step-wise* reaction of  $[(^t\text{BuO})_2\text{Cu}]\text{Na}$  with ArH.

# Experimental Details

## 1. Reaction of CuCl with <sup>t</sup>BuONa

### 1.1 NMR experiment

**<sup>t</sup>BuONa:** In the glovebox, <sup>t</sup>BuONa (0.1 mmol, 9.6 mg) was dissolved in 0.7 mL DMF (D7). After transferring into the NMR tube with J. Young valve and sealed in the glovebox, the solution was used for NMR data collection.

**<sup>t</sup>BuOCu:** In the glovebox, CuCl (0.1 mmol, 10.0 mg) was mixed with <sup>t</sup>BuONa (0.1 mmol, 9.6 mg) in 0.7 mL DMF (D7). After stirring for 30 minutes, the obtained solution was transferred into the NMR tube with J. Young valve and sealed in the glovebox and then was used for NMR data collection.

**[<sup>t</sup>(BuO)<sub>2</sub>Cu]Na:** In the glovebox, CuCl (0.1 mmol, 10.0 mg) was mixed with <sup>t</sup>BuONa (0.2 mmol, 19.2 mg) in 0.7 mL DMF (D7). After stirring for 30 minutes, the obtained solution was transferred into the NMR tube with J. Young valve and sealed in the glovebox and then was used for NMR data collection.

### 1.2 XAS experiment

**CuCl + 10 <sup>t</sup>BuONa:** In the glovebox, CuCl (0.5 mmol, 49.5 mg) was added into a round bottom flask. <sup>t</sup>BuONa (5 mmol, 480.0 mg) was dissolved in 10 mL dry DMF and was then added to the flask. After stirring for 30 minutes, the solution was transferred to the solution cell and sealed, and then the XAS spectrum was taken.

## 2. Reaction of [(<sup>t</sup>BuO)<sub>2</sub>Cu]Na with ArH

### 2.1 NMR experiment

**Reaction of ArH with 1 eq. of <sup>t</sup>BuONa:** In the glovebox, benzo[*d*]thiazole (ArH, 0.1 mmol, 13.5 mg) was mixed with <sup>t</sup>BuONa (0.1 mmol, 9.6 mg) in 0.7 mL DMF (D<sub>7</sub>). After stirring for 30 minutes, the obtained solution was transferred into a NMR tube with J. Young valve and sealed, and then was used for NMR data collection.

**Reaction of ArH with 1 eq. of [Cu(O<sup>t</sup>Bu)<sub>2</sub>]Na:** In the glovebox, CuCl (0.1 mmol, 9.9 mg) was mixed with <sup>t</sup>BuONa (0.2 mmol, 19.2 mg) in 0.7 mL DMF (D<sub>7</sub>), after stirring for 30 minutes, ArH (0.1 mmol, 13.5 mg) was added. After stirring for another 30 minutes, the obtained solution was transferred into the NMR tube with J. Young valve and sealed, and then was used for NMR data collection.

### 2.2 XAS experiment

In the glovebox, CuCl (0.2 mmol, 19.8 mg) was mixed with <sup>t</sup>BuONa (0.4 mmol, 38.4 mg) in 3 mL DMF, after stirring for 30 minutes, ArH (0.2 mmol, 27.0 mg) was added. After stirring for another 30 minutes, the obtained solution was transferred into the solution cell and sealed with the screw top. The XANES and EXAFS spectra were measured at room temperature.

The XANES spectrum of the new Cu species showed an edge energy of 8980.2 eV which could be assigned as Cu(I). Compared with [Cu(O<sup>t</sup>Bu)<sub>2</sub>]Na, the edge energy of the new species shifted to lower energy by 0.7 eV, which could probably be attributed to coordination of C atom with lower electronegativity than O atom. The XANES spectrum, which is considered as a fingerprint of the coordination environment, is different from

[Cu(O<sup>t</sup>Bu)<sub>2</sub>]Na suggesting the new species observed in the NMR spectrum has a different but similar coordination environment. A relatively intense peak was also observed indicating a 2-coordination environment, which agrees with the R-space fitting results. It is noteworthy that the bond distance of 1.83 Å doesn't necessarily mean both Cu-O and Cu-C bond distances are 1.83 Å, since EXAFS spectra can only give average bond distance.

### 2.3 IR experiment

In a dry three-neck reaction tube, 2.88 g (30 mmol) NaO<sup>t</sup>Bu was added. After evacuation under vacuum and flushed with nitrogen for three times, 20 mL DMF was injected into the tube and the IR measurement was started. After 500 mg (5 mmol) CuCl was added into the solution, the reaction was cooled down to -50°C and 675 mg (5 mmol) ArH was injected. Absorption peak of [Cu (O<sup>t</sup>Bu)<sub>2</sub>]Na at 962 cm<sup>-1</sup> decreased and a peak at 955 cm<sup>-1</sup> was developed (Figure S7 A and B).

*Step-wise reaction:* After evacuation under vacuum and flushed with nitrogen for three times, a three-neck reaction tube was charged with 4 mL DMF. Then IR measurement was started. 135.0 mg (1 mmol) ArH was divided into 3 portions and added into the tube sequentially. The absorption peak of ArH at 800 cm<sup>-1</sup> was observed. 1 minute after addition of ArH, 192.0 mg (2 mmol) NaO<sup>t</sup>Bu was added in three portions. The absorption peak of NaO<sup>t</sup>Bu at 985 cm<sup>-1</sup> was also observed. Then 99.0 mg (1 mmol) CuCl was added in four portions. Both absorption peak of ArH at 800 cm<sup>-1</sup> and NaO<sup>t</sup>Bu at 985 cm<sup>-1</sup> decreased while the CuCl was added in. At the same time, the absorption peak of <sup>t</sup>BuOH at 925 cm<sup>-1</sup> increased (Figure S7 D). According to the IR results, <sup>t</sup>BuONa was unable to

deprotonate ArH, which is consistent with above NMR results. Cu(I)-ate complex  $[\text{Cu}(\text{O}^t\text{Bu})_2]\text{Na}$  plays an important role for C-H activation of ArH. It was also clearly shown that the C-H activation of ArH by  $\text{Cu}(\text{O}^t\text{Bu})_2\text{Na}$  was very fast.

## References

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