Supporting information

Oxidation of di-/tri-substituted phenols

In a typical experimental procedure, 50 mg of CSASBA-15(0.2) was placed in the reactor with 10 mmol of TMP-OH and 15 mL of MeCN solvent. The mixture was stirred constantly while the temperature was slowly raised to 353 K. After reaching 353 K, 40 mmol of HP was carefully added to the reaction mixture through a septum and the mixture was continuously refluxed for 60 min under atmospheric pressure. After completion of the reaction, the products were collected through the recovery of CSASBA-15(0.2). To find the best catalyst, various mesostructured Cu(II)-salicylaldimine functionalized silica catalysts were used for the oxidation of TMP-OH under similar reaction conditions. Various reaction parameters, i.e. the time, temperature, and stoichiometric ratio of the reactants (TMP-OH to HP ratios), were studied to determine the optimal reaction conditions for W-CSASBA-15(0.2). The oxidation of TMP-OH was also performed with different oxidants, i.e. HP, TBHP, UHP, and molecular oxygen (O_2). In the production of TMB=O, pseudocumene was used instead of TMP-OH. To identify the best solvent for CSASBA-15(0.2) reactions, various solvents, i.e. MeCN, MeOH, AC=O, MeCOOH and ethanol, were used for the selective synthesis of TMB=O.

From the resulting mixture using diethyl ether, the organic products were extracted after completion of the reaction, cooled to room temperature, and compared with authentic samples by gas chromatography (GC; Chromosorb WHP 80/100) using a flame ionization detector. The products were further confirmed using a combined GC-mass spectrometry system (GC-MS; Hewlett G1800A).

Furthermore, using various mesostructured Cu(II)-salicylaldimine functionalized silica catalysts, i.e. CSASBA-15(0.2), W-CSASBA-15(0.2), and recyclable CSASBA-15(0.2), liquid-phase oxidations of di-/tri-substituted phenols were performed in a vigorously stirred thermostated glass-vessel reactor at a specific temperature for a specific period of time in the presence of HP as a green oxidizing agent. After completion of the reaction, the organic products were extracted from the resulting mixture using non-chlorinated solvents (diethylether/ethylacetate/hexane). All the crude products were compared with authentic samples by GC and confirmed via GC-MS. The C–C coupling products in the reaction mixture were identified by ^{1}H NMR spectroscopy after separating the used catalyst. The spectral data for the C–C coupling products are as follows:

(i) HMBP-OH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 6.71 (s, 2H, aromatic H_6).

(ii) TTDPQ. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 4 H), 1.36 (s, 36 H)

(iii) TIPDPQ. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 4 H), 3.02 (septet, J = 7.2 Hz, 4 H), 1.2 (d, J = 7.2 Hz, 24 H)

(iv) TMDPQ. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 4 H), 2.15 (s, 12 H)

(v) TMoDPQ. ^{1}H NMR (400 MHz, *d*-DMSO): δ 8.3 (s, 4 H), 3.71 (s, 12 H).

For liquid-phase oxidations of di-/tri-substituted phenols, the recyclable mesoporous CSASBA-15 catalysts, i.e. CSASBA-15(0.2) and CSASBA-15(0.1), were reused (50 mg of catalyst) to determine their catalytic stabilities. The W-CSASBA-15(0.2) catalyst (50 mg of catalyst) was used in these reactions to determine its catalytic activity. After completion of each catalytic reaction, the catalyst was filtered and analyzed by ICP-AES to determine the percentage of copper, and the conversions of phenols and selectivities for DSBQs were calculated using standard formulas after GC and GC-MS analyses.

Table S1: Physicochemical characterization of Cu(II)-salicylaldiamine functionalized mesoporous silica catalysts

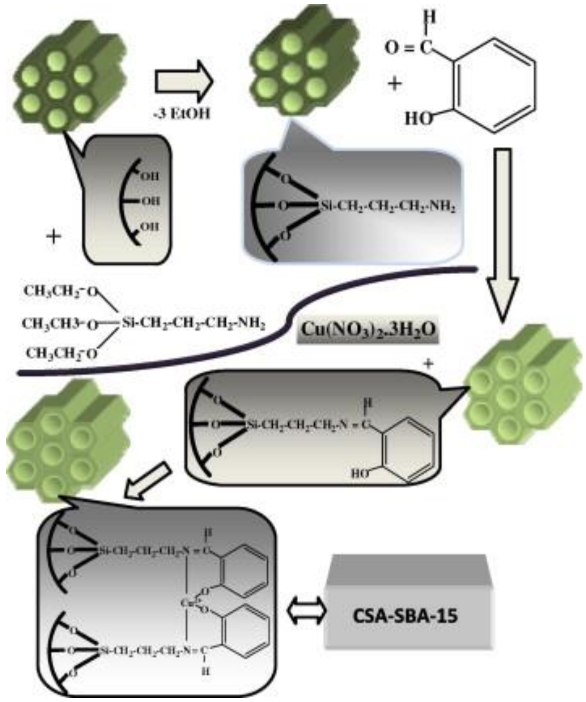
sample	Cu [a] (wt.%)	d_{100} (Å)	a_o (Å)	A_{BET} (m^2/g)	d_p (Å)	V_p (cm^3/g)	$t_w = a_o$-d_p (Å)
SBA-15	-	102.4	118.2	908	87.4	1.07	30.8
APTES-SBA-15	-	106.3	122.8	620	80.2	0.87	42.6
CSASBA-15(0.2)	0.198	113.2	130.6	540	78.8	0.75	51.8
CSASBA-15(0.1)	0.097	108.5	125.3	590	79.5	0.81	45.8
CSASBA-15(0.2) [b]	0.197	111.9	129.2	555	78.9	0.76	50.3
CSASBA-15(0.1) [b]	0.096	106.8	123.3	600	79.4	0.80	43.9
W-CSASBA-15(0.2) [c]	0.197	111.8	129.1	560	78.9	0.76	50.2
CSAMCM-41(0.2)	0.192	36.5	42.1	610	20.0	0.50	22.1
MCM-41	-	35.90	41.45	1179	29.3	0.67	12.1

$a_{0,}$ unit cell parameter; A_{BET}, specific surface area; d_p, pore diameter; V_p, pore volume; pore wall thickness (t_w) = unit cell parameter (a_0) – pore diameter (d_p)

[a] The results are determined by ICP-AES

[b] The results were obtained in 3rd run

[c] The catalyst was washed before using in catalytic oxidation



Scheme S1: Preparation of CSASBA-15 using organic modifying reagents, copper nitrate trihydrate and pure SBA-15

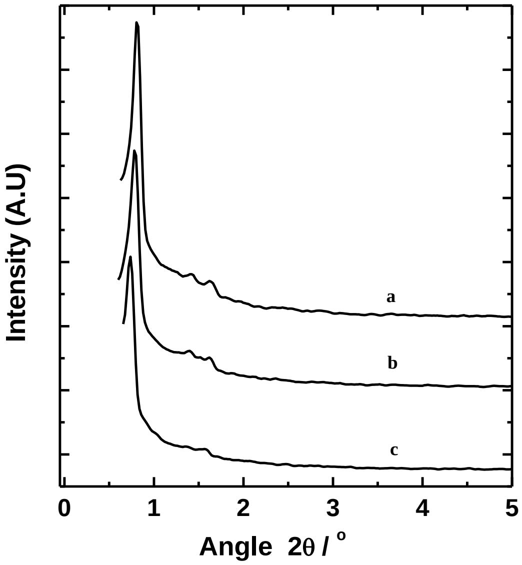


Figure S1: XRD powder patterns of (a) calcined SiSBA-15, (b) APTES-SBA-15, and (c) CSASBA-15(0.2)

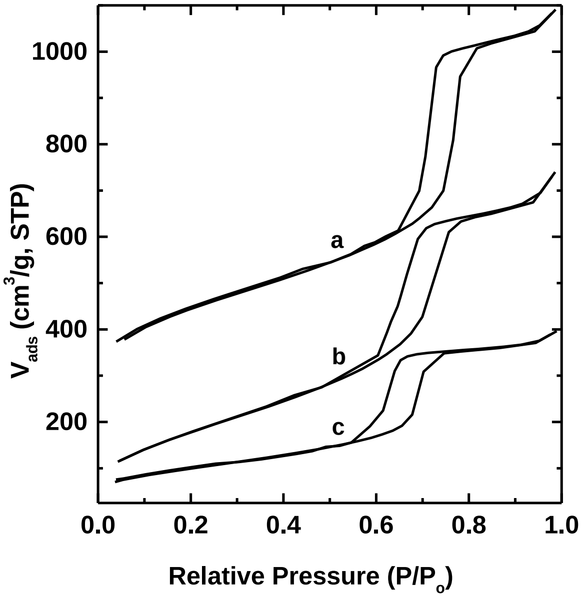


Figure S2: N_2 adsorption isotherms of (a) calcined SiSBA-15, (b) APTES-SBA-15, and (c) CSASBA-15(0.2)

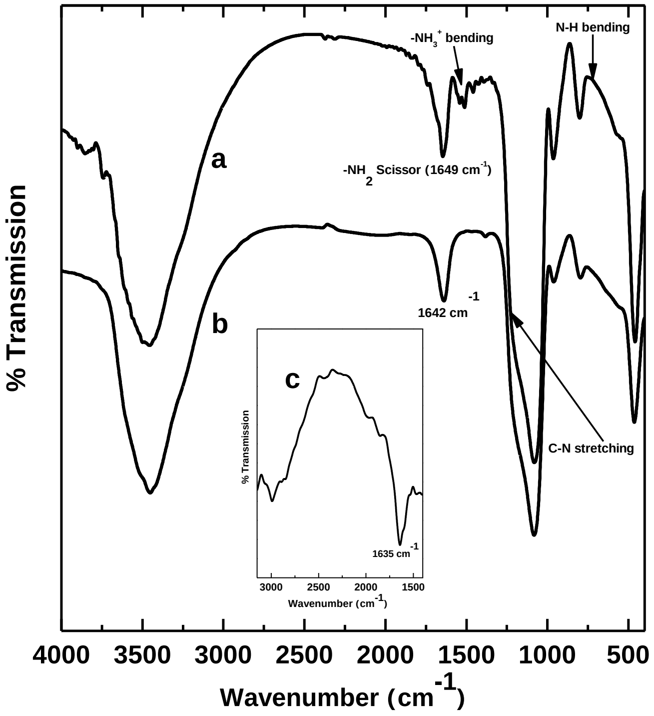


Figure S3: FTIR spectra of (a) APTES-SBA-15, (b) calcined SiSBA-15, and (c) CSASBA-15(0.2)

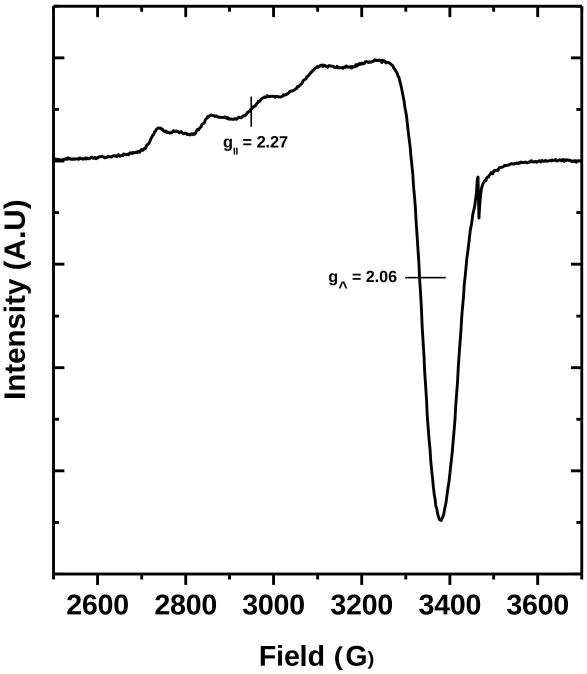


Figure S4: ESR spectrum of CSASBA-15(0.2)

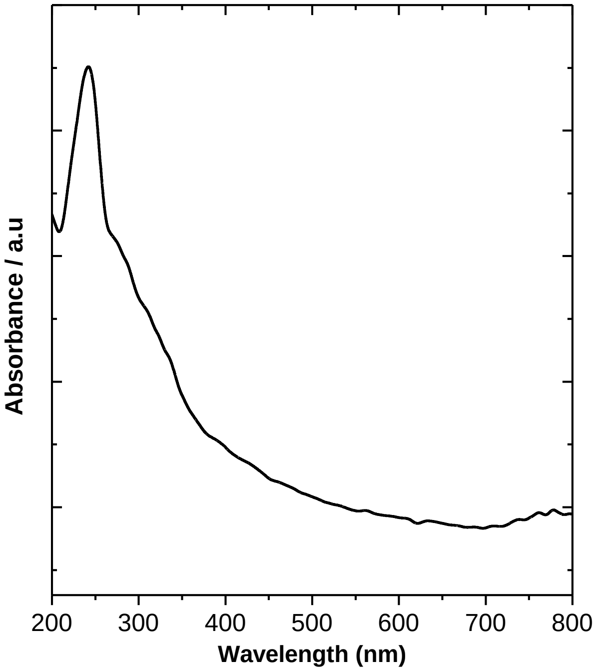


Figure 5S : UV vis DRS spectrum of CSASBA-15(0.2)