Supporting Information

N-Heterocyclic Carbene-triggered Transition-metal-free Synthesis of 2,3-Disubstituted Benzofuran Derivatives†

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1. General methods

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm\(^{-1}\). \(^1\)H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl\(_3\) (100 MHz, \(^13\)C NMR) or DMSO-\(d_6\) with chemical shift (\(\delta\)) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q II HRMS/MS instrument (Bruker) with the technique of electrospray ionization.

2. General procedure for the preparation of compounds 3a-3s

An oven-dried 10-mL Schlenk tube equipped with a magnetic stir bar was charged with thiazolium salt 4e (16.6 mg, 0.04 mmol), Cs\(_2\)CO\(_3\) (32.5 mg, 0.10 mmol) and \(o\)-quinone methides 2 (0.2 mmol). This tube was closed with a septum, removed from the atmosphere and put under positive \(N_2\) pressure. To this mixture was added freshly distilled 1,4-dioxane (4 mL) and aldehydes 1 (0.22 mmol) with a syringe. The mixture was stirred at room temperature until completion (monitored by TLC). Then the reaction mixture was opened to the atmosphere and \(p\)-toluenesulfonic acid (76 mg, 0.4 mmol) was added in one portion. Once the intermediate ketone was consumed (monitored by TLC), removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silicagel, mixtures of petroleum ether /ethyl acetate, 50:1, v/v).
3. X-ray Structure of compound 3j

The configuration of 3j was determined by the X-ray analysis of its crystal (Figure 1). The crystal was prepared from the solution of 3j in CHCl₃. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1444225.

Figure 1. X-ray crystal structure of 3j
4. NMR Spectra

$^1$H NMR Spectrum of Compound (3a)

$^{13}$C NMR Spectrum of Compound (3a)
$^1$H NMR Spectrum of Compound (3b)

$^{13}$C NMR Spectrum of Compound (3b)
\textbf{H NMR Spectrum of Compound (3c)}

\textbf{\textsuperscript{13}C NMR Spectrum of Compound (3c)}
$^1$H NMR Spectrum of Compound (3d)

$^{13}$C NMR Spectrum of Compound (3d)
$^1$H NMR Spectrum of Compound (3e)

$^{13}$C NMR Spectrum of Compound (3e)
**$^1$H NMR Spectrum of Compound (3f)**

**$^{13}$C NMR Spectrum of Compound (3f)**
$^1$H NMR Spectrum of Compound (3g)

$^{13}$C NMR Spectrum of Compound (3g)
$^1$H NMR Spectrum of Compound (3h)

$^{13}$C NMR Spectrum of Compound (3h)
$^1$H NMR Spectrum of Compound (3i)

$^{13}$C NMR Spectrum of Compound (3i)
$^1$H NMR Spectrum of Compound (3j)

$^{13}$C NMR Spectrum of Compound (3j)
$^1$H NMR Spectrum of Compound (3k)

$^{13}$C NMR Spectrum of Compound (3k)
$^1$H NMR Spectrum of Compound (3l)

$^1$C NMR Spectrum of Compound (3l)
$^1$H NMR Spectrum of Compound (3m)

$^{13}$C NMR Spectrum of Compound (3m)
$^1$H NMR Spectrum of Compound (3n)

$^{13}$C NMR Spectrum of Compound (3n)
$^1$H NMR Spectrum of Compound (3o)

$^{13}$C NMR Spectrum of Compound (3o)
$^1$H NMR Spectrum of Compound (3p)

$^{13}$C NMR Spectrum of Compound (3p)
$^1$H NMR Spectrum of Compound (3q)

$^{13}$C NMR Spectrum of Compound (3q)
$^1$H NMR Spectrum of Compound (3r)

$^{13}$C NMR Spectrum of Compound (3r)
$^1$H NMR Spectrum of Compound (3s)

$^{13}$C NMR Spectrum of Compound (3s)
$^1$H NMR Spectrum of Compound (3t)

$^{13}$C NMR Spectrum of Compound (3t)