## Supporting Information

## Ligand-Free Pd-Catalyzed Synthesis of 3-Allylbenzofurans by Merging

## Decarboxylative Allylation and Nucleophilic Cyclization

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## Context

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Copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR Spectra for Substrates 5a-5c ..... S63-S68
Copies of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR Spectra for Compound $\mathbf{6 a}$ ..... S69-S70


Figure S1 The ORTEP Drawing of $\mathbf{5 b}$ (The ellipsoid contour 30\% probability levels)
A single crystal 5b was obtained by slowly evaporating $95 \% \mathrm{EtOH}$ solvent at room temperature under the air conditions. Its dimensions of $0.40 \mathrm{~mm} \times 0.13 \mathrm{~mm} \times 0.07 \mathrm{~mm}$ was mounted on a Siemens P1 diffractometer equipped with a graphite mono-chromated $\operatorname{MoKa}(\lambda=0.71073 \AA$ ) radiation at $293(2) \mathrm{K}$. A total of 8438 reflections were collected in the $2.73<\theta<66.03^{\circ}$ range by using an $\omega$ scan mode and 3646 were independent ( $R_{\text {int }}=0.0611$ ), of which 1809 with $I>2 \sigma(I)$ were observed. The calculations were performed with SHELXS-97 and SHELXS-97 programs and corrections for $L p$ factors and absorptions were applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were determined by theoretical calculations. The final cycle of refinement gave $R=0.1172$ and $w R=0.3104$ ( $\mathrm{w}=$ $1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.1389 P)^{2}+5.1948 P\right]$, where $\left.P=\left(F_{\mathrm{o}}{ }^{2}+2 F_{\mathrm{c}}^{2}\right) / 3\right) . S=1.056,(\Delta / \sigma)_{\max }=0.000,(\Delta \rho)_{\min }=$ $0.550 \mathrm{e} / \AA^{3}$ and $(\Delta \rho)_{\max }=-0.254 \mathrm{e} / \AA^{3}$.

The crystal of compound $\mathbf{5 b}$ belongs to Orthorhombic, space group Pbca with $a=4.9482(6)$ Å, $b=26.280(3) \AA, c=26.280(3) \AA, \alpha=\beta=\gamma=90^{\circ}, V=4208.5(8) \AA^{3}, M r=389.47, Z=8, D c=$ $1.229 \mathrm{~g} / \mathrm{cm}^{3}, \mu(\mathrm{Mo} K \alpha)=0.572 \mathrm{~mm}^{-1}, F(000)=1648$, the final $R=0.1172$ and $w R=0.3104$.







$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$



$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$

${ }^{1} \mathrm{H}$ NMR Spectrum of Compound 3c


$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$


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$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$












$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$
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$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$



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| 70 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 |  |  | 60 | 50 | 40 | 30 | 20 | 10 | 0 | -10 |

${ }^{13}$ C NMR Spectrum of Compound 3 g




$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$


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$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$




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${ }^{\mathbf{1}} \mathbf{H}$ NMR Spectrum of Compound 3p



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$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$

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$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$


S41



${ }^{1}$ H NMR Spectrum of Compound 3u




$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$








$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$


S47



$100 \mathrm{MHz} . \mathrm{CDCl}_{3}$



${ }^{1} \mathrm{H}$ NMR Spectrum of Compound $3 \mathbf{x}$

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${ }^{13}$ C NMR Spectrum of Compound 3x


$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$

${ }^{\mathbf{1}} \mathrm{H}$ NMR Spectrum of Compound $3 \mathbf{y}$


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$-2.393$



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$400 \mathrm{MHz} . \mathrm{CDCl}_{3}$















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${ }^{\mathbf{1}} \mathbf{H}$ NMR Spectrum of Compound 5b

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L86.92-



${ }^{13}$ C NMR Spectrum of Compound 6a

