Supporting Information

Cationic palladium(II)-catalyzed dehydrative nucleophilic substitutions of benzhydryl alcohols with electron-deficient benzenethiols in water

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A mixture of 2-mercaptobenzoic acid 1a (77 mg, 0.5 mmol), PdCl₂(MeCN)₂ (6.7 mg, 0.025 mmol), and benzhydrol 2a (110 mg, 0.6 mmol) in H₂O (2 mL) was heated at 80 °C for 16 h in a sealed tube under air. After the reaction mixture was cooled, p-nitroanisole (77 mg, 0.5 mmol, internal standard) was added to the reaction mixture, which was extracted with AcOEt. The organic layer was washed with brine, and concentrated in vacuo. The residue was analyzed by ¹H-NMR spectroscopy.

Conversion yield was calculated by integration.

<table>
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<tr>
<th>Signal δ</th>
<th>desired 3a</th>
<th>p-nitroanisole internal standard</th>
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<tr>
<td>5.97 (methin-¹H)</td>
<td>8.21 (Ar-¹H)</td>
<td></td>
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<tr>
<td>0.63 (1H)</td>
<td>2.00 (2H)</td>
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<tr>
<td>65% from 1a</td>
<td>77 mg (0.5 mmol)</td>
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</table>
Hammett study (A)

A mixture of 4-mercaptobezoic acid 1 (154 mg, 1 mmol), Pd(OAc)$_2$ (11 mg, 0.05 mmol), benzhydrol 2a (184 mg, 1 mmol), and benzhydryl alcohols 2X (1 mmol) in H$_2$O (4 mL) was heated at 80 °C in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over MgSO$_4$ and concentrated in vacuo. The residue was analyzed by $^1$H-NMR spectroscopy.

<table>
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<th>log($k_r/k_i$)</th>
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<tr>
<td>Me</td>
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<td>0.96</td>
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<td>diF</td>
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<td>-0.09</td>
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<tr>
<td>H</td>
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<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>0.114</td>
<td>-0.57</td>
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</table>

$\log(k_{r}/k_{i}) = \log(25.74/95.15) = -0.57$
Hammett study (B)

A mixture of 5-substituted thiosalicylic acid 1X (0.25 mmol), 1a (34.0 mg, 0.25 mmol), PdCl₂(MeCN)₂ (4.1 mg, 0.016 mmol), and benzhydrol 2a (45.9 mg, 0.25 mmol) in H₂O (1 mL) was heated at 120 °C in a sealed tube under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. The residue was analyzed by ¹H-NMR spectroscopy.

<table>
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<tr>
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<th>σ⁺</th>
<th>log(kᵣ/kᵣ₀)</th>
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Scale-up experiment

A mixture of 2-mercaptobenzoic acid 1a (1.54 g, 10 mmol), PdCl$_2$(MeCN)$_2$ (129.8 mg, 0.5 mmol), and benzhydrol 2a (2.20 g, 12 mmol) in H$_2$O (40 mL) was heated at 95 °C for 16 h under air. After cooling, the reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over MgSO$_4$ and concentrated in vacuo. The residue was recrystallized from hexane/AcOEt to give desired product 3a (2.31 g, 72%).
S9
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O₂N

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