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Supplementary Data

Synthesis of Benzyl Hydrazine Derivatives via Amination of Benzylic C (sp3)–H Bonds with Dialkyl Azodicarboxylates

A. Samzadeh-Kermani

Department of Chemistry, Faculty of Science, University of Zabol, Zabol, Iran

Fax +98-61-335856; E-mail: drsamzadeh@gmail.com; arsamzadeh@uoz.ac.ir

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(B) Reaction of xylene derivatives in the absence of ligand
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(A) Study of possible mechanism

Some additional experiments performed to explore the possible reaction pathway of the present transformation:

1. Firstly, Radical scavenger such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) completely inhibits the model reaction which indicate that the transformation may proceed via a radical intermediate.

![Reaction Scheme 1]

2. In the absence of toluene, only a traces amount of 4 was obtained, which can further support a radical pathway. suggest that styrene radical is not formed in the reaction system. It is worth mentioning that no products arising from the self-coupling of 2a was observed.

![Reaction Scheme 2]

3. Competing Kinetic Isotope Effect (KIE) Experiment: an intermolecular competing kinetic isotope effect (KIE) experiment was carried out.

![NMR Spectra]

$^1$HNMR of the mixture of 3a and 3a'
Note: The value of $k_H/k_D$ was calculated from the $^1$H NMR spectra above which should be the mixture of compound 3a and 3a’ (the KIE scheme). The sum of the integral of 3a and 3a’ at chemical shift 4.97-5.05 was integrated as 2.00 (both 3a and 3a’ keep almost the same multiple bond hydrogens). Compound 3a has 2 hydrogen atoms at chemical shift 4.44, while 3a’ has no H atoms. The amount of 3a could be defined as 0.82 (1.64/2=0.82), on the other hand, the sum of 3a and 3a’ is 2.00 (signal at 4.97-5.05, 2 CH), so the amount of 3a’ is 0.18 (2.00/2-0.82=0.18). As a result, $k_H/k_D = 0.82/0.18 = 4.6$. 
(B) Reaction of xylene derivatives in the absence of ligand

Table 1. Examination of double amination of sp3 C-H with 2a

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>b</td>
<td>4-Me</td>
<td>3b, 85</td>
</tr>
<tr>
<td>2</td>
<td>c</td>
<td>3-Me</td>
<td>3c, 83</td>
</tr>
<tr>
<td>3</td>
<td>d</td>
<td>2-Me</td>
<td>3d, 53</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1 (2.0 mL), 2a (1.0 mmol), Cu₂O (0.10 mmol), Phen (0.06 mmol), DTBP (1.5 mmol), 4 Å MS (300 mg), 110 °C for 28 h, in a sealed tube under an argon atmosphere.

b Reaction conditions: 1 (2.0 mL), 2a (1.0 mmol), Cu₂O (0.10 mmol), DTBP (1.5 mmol), 4 Å MS (300 mg), 110 °C for 28 h, in a sealed tube under an argon atmosphere.

c The digit in parenthesis belong to the double amination product.
(C) Original $^1$H & $^{13}$C-NMR Spectra
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![Chemical Structure](image)

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**Bruker**

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**Parameters**

- **Sample Name**: 3m
- **Solvent**: DMSO-d6
- **Temperature**: 298 K
- **Field Strength**: 600 MHz
- **Frequency**: 270.08 MHz
- **GAIN**: 6.36 dB
- **TE**: 300.0 μs
- **TR**: 3.6 s
- **CP**: 40.490 kHz
- **D1**: 5.60000 MHz

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**NMR Plot Parameters**

- **Chemical Shifts**:
  - 2.00 ppm
  - 3.00 ppm
  - 4.00 ppm
  - 5.00 ppm
  - 6.00 ppm

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**Data**

- **Time**: 32.27
- **INSTAN**: nore
- **PREM**: 8 nm NaCl
- **PEAKS**: 40
- **TE**: 300.0 μs
- **GAIN**: 6.36 dB
- **D1**: 5.60000 MHz

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**Additional Notes**

- **Notes on Analysis**
- **Experimental Conditions**
- **Data Interpretation**