Enantioselective Alkylation of 2-Alkyl Pyridines Controlled by Organolithium Aggregation

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Supplementary Information II
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**1o**

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**1p**
### Parameter | Value
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1 Title | JIG-2-056-13C
2 Origin | Varian
3 Instrument | inova
4 Solvent | cdcl3
5 Temperature | 35.0
6 Number of Scans | 80
7 Relaxation Delay | 1.00000
8 Spectrometer Frequency | 125.70
9 Nucleus | 13C

![Chemical Structure](image1)

### Parameter | Value
--- | ---
1 Title | JIG-3-116-1H
2 Origin | Varian
3 Instrument | inova
4 Solvent | cdcl3
5 Temperature | 25.0
6 Number of Scans | 8
7 Relaxation Delay | 4.80000
8 Spectrometer Frequency | 599.64
9 Nucleus | 1H

![Chemical Structure](image2)
Parameter | Value
--- | ---
1 Title | JG-2-026-1H
2 Origin | Varian
3 Instrument | Inova
4 Solvent | dcdl3
5 Temperature | 25.0
6 Number of Scans | 4
7 Relaxation Delay | 4.8000
8 Spectrometer Frequency | 499.85
9 Nucleus | 1H

Parameter | Value
--- | ---
1 Title | JG-2-026-13C
2 Origin | Varian
3 Instrument | Inova
4 Solvent | dcdl3
5 Temperature | 25.0
6 Number of Scans | 196
7 Relaxation Delay | 1.0000
8 Spectrometer Frequency | 126.70
9 Nucleus | 13C
**Parameter** | **Value**
---|---
1 Title | S02-174_1H
2 Origin | Varian
3 Instrument | inova
4 Solvent | cdc15
5 Temperature | 30.0
6 Number of Scans | 4
7 Relaxation Delay | 30.0000
8 Spectrometer Frequency | 499.86
9 Nucleus | 1H

![NMR Spectrum](image1)

**Parameter** | **Value**
---|---
1 Title | S02-174_13C
2 Origin | Varian
3 Instrument | inova
4 Solvent | cdc13
5 Temperature | 30.0
6 Number of Scans | 252
7 Relaxation Delay | 1.0000
8 Spectrometer Frequency | 126.70
9 Nucleus | 13C

![NMR Spectrum](image2)
Parameter | Value
--- | ---
1 Title | SG2-165R
2 Origin | Varian
3 Instrument | Inova
4 Solvent | CDCl3
5 Temperature | 30.0
6 Number of Scans | 4
7 Relaxation Delay | 30.0000
8 Spectrometer Frequency | 499.85
9 Nucleus | 1H
### Parameters

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### Chemical Structures

**4a**

![Chemical Structure 4a](image1)

**4b**

![Chemical Structure 4b](image2)
**S50**

**Parameter** | **Value**
--- | ---
1 Title | JG-2-250-13C
2 Origin | Varian
3 Instrument | vnmrs
4 Solvent | cdcl3
5 Temperature | 20.0
6 Number of Scans | 144
7 Relaxation Delay | 1.0000
8 Spectrometer | 100.53
9 Nucleus | 13C

![Diagram of molecule 4d](image)

**Parameter** | **Value**
--- | ---
1 Title | JG-3-016-1H
2 Origin | Varian
3 Instrument | inova
4 Solvent | cdcl3
5 Temperature | 25.0
6 Number of Scans | 8
7 Relaxation Delay | 4.8000
8 Spectrometer Frequency | 599.84
9 Nucleus | 1H

![Diagram of molecule 5](image)
**S1**

**Parameter** | **Value**  
--- | ---
1 Title | JG-S1_13C  
2 Origin | Varian  
3 Instrument | Inova  
4 Solvent | cdc13  
5 Temperature | 23.0  
6 Number of Scans | 368  
7 Relaxation Delay | 1.00000  
8 Spectrometer Frequency | 125.70  
9 Nucleus | 13C

**S1**

**Parameter** | **Value**  
--- | ---
1 Title | JG-2-293-1H  
2 Origin | Varian  
3 Instrument | Inova  
4 Solvent | cdc13  
5 Temperature | 25.0  
6 Number of Scans | 8  
7 Relaxation Delay | 4.80000  
8 Spectrometer Frequency | 499.85  
9 Nucleus | 1H
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![Chemical structure](image)

**S6**
Copies of NMR spectra for aggregate (2-Py)(CH₂CH₂OMe)CHLi•(R)-Li¹DA•HMPA 1r.

1D NMR [³¹P, ⁶Li] Spectroscopic Studies

Figure S2-1. ³¹P NMR spectra (202.404 MHz, toluene-d₈) of 0.10 M 1r-Li prepared from (R)-¹DA with 2.0 equiv [⁶Li]n-BuLi, 1.0 equiv 1r, and 0.75 equiv HMPA recorded at −80 °C after aging at 0 °C for 40 mins: (A) with broad-band ⁶Li decoupling; (B) fully coupled. δ 24.88 (t, ²J_P-Li =3.50), 23.61 (t, ²J_P-Li = 4.51).
Figure S2-2. $^{31}$P NMR spectra (202.404 MHz, toluene-$d_8$) of 0.10 M 1r-Li prepared from (R)-1DA with 2.0 equiv [6Li]n-BuLi, 1.0 equiv 1r, and 0.75 equiv HMPA recorded at –80 °C after aging at 0 °C for 40 mins: (A) with single frequency $^6$Li decoupling 20 Hz off resonance from the $^6$Li doublet at 2.48 ppm; (B) with single frequency $^6$Li decoupling of the $^6$Li doublet at 2.48 ppm.
Figure S2-3. $^6$Li NMR spectra (73.578 MHz, toluene-$d_8$) of 0.10 M 1r-Li prepared from (R)-$^1$DA with 2.0 equiv $[^6]$Li-$n$-BuLi, 1.0 equiv 1r, and 0.75 equiv HMPA recorded at –80 °C after aging at 0 °C for 40 mins: (A) with broad-band $^{31}$P decoupling; (B) fully coupled. δ 2.47 (d, $^2J_{Li-P}$ = 3.50), 1.64 (s).
Figure S2-4. $^6$Li NMR spectra (73.578 MHz, toluene-$d_8$) of 0.10 M $\text{1r-Li}$ prepared from ($R$)-$^1$DA with 2.0 equiv $[^6\text{Li}]n$-BuLi, 1.0 equiv $\text{1r}$, and 0.75 equiv HMPA recorded at $-80 \, ^\circ\text{C}$ after aging at 0 $^\circ\text{C}$ for 40 mins: (A) off-resonance decoupling; (B) on-resonance decoupling of the $^{31}\text{P}$ triplet at 23.61 ppm; (C) on-resonance decoupling of the $^{31}\text{P}$ triplet at 24.9 ppm.
Figure S2-5. $^1$H NMR spectrum (499.76 MHz, toluene-$d_8$) at –80 °C of a sample containing 1r-Li.