# **Supporting Information**

# Selective Synthesis of Aminoisoquinolines *via* Rh(III)-catalyzed C-H/N-H Bond Functionalization of *N*-Aryl Amidines with Cyclic 2-Diazo-1,3-diketones

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# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3a

# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3b





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3c NH N O 8074 8.048 8.048 7.551 7.551 7.555 7.731 7.737 7.737 7.737 7.158 7.158 < 9.576 < 9.547 2560 2564 2757 2757 2560 2560 $\frac{1.337}{1.312}$ -1.113x lik k M 1,004 2:00<del>1</del> 2:00<del>1</del> 1.04 3.00<del>1</del> 6.00**∓** 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.: fl (ppm) 10.5 — 162.14 — 155.34 $\int 137.08 \\ f 136.32 \\ -132.37 \\ -132.37 \\ -124.93 \\ -124.43 \\ -117.49 \\ -113.49 \\ -113.41 \\ -$ ---- 54.54 --- 48.45 200 190 180 170 160 150 140 130 120 110 100 f1 (ppm) 90 80 70 50 40 30 20 10 0 60

### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3d



<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3e



### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3f



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3g











# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3j





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3k





### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 31





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3m





### H NMR and <sup>13</sup>C NMR Spectra of Compound 3n



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 30





<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3q



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3r

















# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3u





2.195 2.195 2.195 2.195 2.195 2.195 2.131 2.131 2.110







### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3w







### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3x

# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3y





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3z





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3aa





<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3ab





### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3ag







### <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Compound 3ah







# H NMR and <sup>13</sup>C NMR Spectra of Compound 3ai



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm) X-Ray Crystallography structures of Compound 3aa



Figure S1. X-ray crystal structure of 3aa

Crystal data for **3aa**: C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O, Mr = 315.38, Triclinic, a = 10.0296(18) Å, b = 13.277(2) Å, c = 14.687(3) Å,  $\alpha = 64.959(2)^{\circ}$ ,  $\beta = 81.930(2)^{\circ}$ ,  $\gamma = 89.212(2)^{\circ}$ , V = 1752.1(6) Å<sup>3</sup>, T = 293 (2) K, space group P(-1), Z = 4, 6153 reflections collected, 3719 unique (R<sub>int</sub> = 0.0372) which were used in all calculation. The ellipsoid contour probability level in the caption of 30 %.

Crystallographic data for compound **3aa** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1862373.