An environmentally benign multi-component reaction: Regioselective synthesis of fluorinated 2-aminopyridines using diverse properties of nitro group

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X-ray Structure and Data of 4a & 5s

Figure S1. X-Ray crystal structure of 4a; ellipsoids are drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for 4a

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<tr>
<td>Temperature</td>
<td>293(2) K</td>
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<tr>
<td>Wavelength</td>
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<td>Crystal system, space group</td>
<td>Triclinic, P -1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 8.2387(14) Å, alpha = 78.884(2) deg.</td>
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<td></td>
<td>b = 9.1226(15) Å, beta = 77.335(2) deg.</td>
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<tr>
<td></td>
<td>c = 15.647(3) Å, gamma = 63.875(2) deg.</td>
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<td>F(000)</td>
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<td>Crystal size</td>
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<tr>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
<td>0.432 and -0.275eÅ⁻³</td>
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**Figure S2.** X-Ray crystal structure of 5s; ellipsoids are drawn at the 30% probability level.

**Table S2.** Crystal data and structure refinement for 5s

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<tr>
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<td>Wavelength</td>
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<td>Crystal system, space group</td>
<td>Triclinic, P -1</td>
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<td>Unit cell dimensions</td>
<td>a = 8.6308(16) Å, alpha = 78.895(2) deg.</td>
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<td></td>
<td>b = 9.4049(18) Å, beta = 81.887(2) deg.</td>
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<td></td>
<td>c = 13.955(3) Å, gamma = 74.726(2) deg.</td>
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<td>Volume</td>
<td>1067.4(3) Å^3</td>
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<td>Z, Calculated density</td>
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<td>Crystal size</td>
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</tr>
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<td>Limiting indices</td>
<td>-10&lt;=h&lt;=10, -11&lt;=k&lt;=11, -16&lt;=l&lt;=16</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>8534 / 3809 [R(int) = 0.0261]</td>
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<tr>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
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<td>Goodness-of-fit on F^2</td>
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<td>Extinction coefficient</td>
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<td>Largest diff. peak and hole</td>
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Symmetry transformations used to generate equivalent atoms:
Figure S3. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4a
Figure S4. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4a
Figure S5. $^1$H NMR (600 MHz, CDCl$_3$) spectra of compound 4b
Figure S6. $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of compound 4b
Figure S7. $^{19}$F NMR (564 MHz, CDCl$_3$) spectra of compound 4b
Figure S8. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4c
**Figure S9.** $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4c
Figure S10. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4d
Figure S11. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4d
Figure S12. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4e
Figure S13. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4e
Figure S14. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4f
Figure S15. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4f
Figure S16. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4g
Figure S17. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4g
Figure S18. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4h
Figure S19. $^{13}$C NMR (125 MHz, DMSO-$_d_6$) spectra of compound 4h
Figure S20. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4i
Figure S21. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4i
Figure S22. $^1$H NMR (600 MHz, CDCl$_3$) spectra of compound 4j
Figure S23. $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of compound 4j
Figure S24. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4k
Figure S25. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4k
Figure S26. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4l
Figure S27. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4l
Figure S28. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4m
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Figure S32. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4o.
Figure S33. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4o
Figure S34. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 4p
Figure S35. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 4p
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Figure S38. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5a
Figure S39. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5a
Figure S40. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5b
Figure S41. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5b
Figure S42. $^1$H NMR (600 MHz, CDCl$_3$) spectra of compound 5c
Figure S43. $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of compound 5c
Figure S44. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5d
Figure S45. $^{13}$C NMR (125MHz, DMSO-$d_6$) spectra of compound 5d
Figure S46. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5e
Figure S47. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5e
Figure S48. $^1$H NMR (600 MHz, CDCl$_3$) spectra of compound 5f
Figure S49. $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of compound 5f
Figure S50. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 5g
Figure S51. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 5g
Figure S52. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5h
Figure S53. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5h
Figure S54. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5i
Figure S55. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5i
Figure S56. $^1$H NMR (500 MHz, CDCl$_3$) spectra of compound 5j
Figure S57. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 5j
Figure S58. $^1$H NMR (600 MHz, CDCl$_3$) spectra of compound 5k
Figure S59. $^{13}$C NMR (150 MHz, CDCl$_3$) spectra of compound 5k
Figure S60. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5l
Figure S61. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 51
Figure S62. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5m
**Figure S63.** $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5m
Figure S64. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5n
Figure S65. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5n
Figure S66. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5o
Figure S67. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5o
Figure S68. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5p
Figure S69. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5p
Figure S70. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5q
Figure S71. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5q
Figure S72. $^1$H NMR (500 MHz, CDCl₃) spectra of compound 5r
Figure S73. $^{13}$C NMR (125 MHz, CDCl$_3$) spectra of compound 5r
Figure S74. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5s
Figure S75. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5s
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Figure S77. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5t
Figure S78. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5u
Figure S79. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5u
Figure S80. $^1$H NMR (500 MHz, DMSO-$d_6$) spectra of compound 5v
Figure S81. $^{13}$C NMR (125 MHz, DMSO-$d_6$) spectra of compound 5v
Figure S82. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 5w
Figure S83. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 5w
Figure S84. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 5x
Figure S85. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 5x
Figure S86. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 5f'
Figure S87. $^{13}$C NMR (150MHz, DMSO-$d_6$) spectra of compound 5f'
Figure S88. HPLC of the reaction mixture
Figure S89. HRMS of intermediate 11
**Figure S90.** HRMS of intermediate 12/13
Figure S91. HRMS of compound 4h
HRMS of compound 5h

Figure S92. HRMS of compound 5h