Supporting Information

Observation by NMR of cationic Wheland-like intermediates in the deiodination of protected 1-iodonapthalene-2,4-diamines in acidic media

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In the Supplementary Information, the numbering of the positions on the naphthalene rings follows strict IUPAC numbering.
Reactions monitored by NMR.

In a typical reaction, 11 (14.0 mg, 0.29 mmol) was dissolved in a mixture of CDCl₃ (0.15 mL) and trifluoroacetic acid (CF₃CO₂D or CF₃CO₂H) (0.45 mL) at 0°C. Following brief agitation of the sample with a vortex mixer to ensure dissolution and homogeneity of the sample, it was transferred to the NMR spectrometer, with the probe pre-cooled to 0°C. Following locking and shimming, data could be collected, typically within 3-4 minutes of mixing the sample. Where samples were monitored for extended times (days / weeks), the samples were stored in a laboratory which was regulated to 20 ± 1°C.

15: ¹H NMR (CDCl₃/CF₃CO₂H), 500.13 MHz, 273 K) δ 7.93-8.01 (2 H, m, 6,7-H₂), 8.05 (1 H, d, J 8.0 Hz, 5-H), 8.11 (1 H, s, 3-H), 8.42 (1 H, d, J 8.5 Hz, 8-H); ¹³C NMR (CDCl₃/ CF₃CO₂H, 125.77 MHz, 293 K) δ 101.44 (1-C), 116.90 (3-C), 120.96 (5-C), 126.61 (4a-C), 127.75 (4-C), 129.38 (2-C), 131.81 (6-C), 132.34 (7-C), 134.72 (8-C), 135.96 (8a-C).

Figure 1. ¹H NMR spectrum of 15 at 0°C, showing small amounts of 11 (*) formed.
16. $^1$H NMR (CDCl$_3$/CF$_3$CO$_2$H, 500.13 MHz, 293 K) δ 6.05 (1 H, s, 3-H), 6.51 (1 H, s, 1-H), 7.58 (1 H, t, $J$ 7.8 Hz, 6-H), 7.70 (1 H, t, $J$ 7.8 Hz, 7-H), 7.75 (1 H, d, $J$ 7.8 Hz, 8-H), 7.84 (1 H, d, $J$ 8.0 Hz, 5-H); $^{13}$C NMR (CDCl$_3$/CF$_3$CO$_2$H, 125.77 MHz, 293 K) δ 9.79 (1-C), 91.49 (3-C), 121.68 (4a-C), 124.16 (5-C), 129.93 (6-C), 131.48 (8-C), 135.01 (7-C), 141.25 (8a-C), 164.30 (4-C), 173.50 (2-C).

Figure 2. $^1$H NMR spectrum of 16 at 20°C, showing small residual amounts of 10 (*).
Figure 3. HSQC NMR spectrum of 16 at 20°C, showing the peak for CHI at δ 6.50 (1H) and δ 9.54 (13C).

Figure 4. 1H NMR spectrum of 17 with traces of 18 (*), following reaction of 11 with CF₃CO₂D / CDCl₃ at 0°C.
20. $^1$H NMR (CDCl$_3$/CF$_3$CO$_2$H, 500.13 MHz, 293 K) $\delta$ 7.88-7.99 (2 H, m, 6,7-H$_2$), 8.05 (1 H, s, 2-H), 8.10 (1 H, d, $J$ 8.2 Hz, 8-H), 8.14 (1 H, d, $J$ 7.7 Hz, 5-H), 8.28 (1 H, s, 1-H); $^{13}$C NMR (CDCl$_3$/CF$_3$CO$_2$H, 125.77 MHz, 293 K) $\delta$ 116.62 (2-C), 120.05 (8-C), 125.19 (3-C), 126.05 (4-C), 126.73 (4a-C), 129.87 (5-C), 130.57 (6-C), 131.27 (7-C), 134.29 (1-C), 134.33 (3-C).
Figure 6. $^1$H NMR spectrum of 20 and 21 (**) shortly after dissolution of 9 in CDCl$_3$/CF$_3$CO$_2$D at 0°C.

Figure 7. Expansion of Figure 6 to show aromatic region in more detail.
Figure 8. HSQC NMR spectrum of 20 and 21 showing CH$_2$ of the Wheland-type species at δ 4.13 (1H) and δ 33.27 (13C).

Figure 9. ^1H NMR spectrum of 22 and 23 (*) shortly after dissolution of 4 in CDCl$_3$/CF$_3$CO$_2$D at 0°C.
**Figure 10.** Expansion of Figure 9 to show aromatic region.

**Figure 11.** $^1$H NMR spectrum of 22 and 23 (*) 48 h after dissolution of 9 in CDCl₃/CF₃CO₂D.
Figure 12. $^1$H expansion of Figure 11 to show aromatic region. Note the diminished intensity of the singlets at δ 8.28 and δ 8.05 due to exchange of H with D at 1-H and 3-H in 22.

21: $^1$H NMR (CDCl$_3$/CF$_3$CO$_2$H, 500.13 MHz, 293 K) δ 4.13 (2 H, s, 4-H$_2$), 6.01 (1 H, s, 2-H), 7.55 (1 H, d, J 7.9 Hz, 5-H), 7.61 (1 H, t, J 7.5 Hz, 7-H), 7.74 (1 H, t, J 7.5 Hz, 6-H), 7.87 (1 H, d, J 7.9 Hz, 8-H); $^{13}$C NMR (CDCl$_3$/CF$_3$CO$_2$H, 125.77 MHz, 293 K) δ 33.27 (4-C), 93.58 (2-C), 123.02 (8a-C), 123.22 (8-C), 128.85 (7-C), 129.29 (5-C), 134.31 (6-C), 136.52 (4a-C), 165.73 (1-C), 171.87 (3-C).

27: $^1$H (500.13 MHz, CDCl$_3$/CF$_3$CO$_2$H, 273 K) δ 7.84 (1 H, t, J 7.5 Hz, 6-H), 7.88 (1 H, t, J 7.5 Hz, 1H, 7-H), 7.97 (1 H, d, J 8.2 Hz, 5-H), 8.44 (1 H, d, J 8.6 Hz, 8-H), 8.57 (1 H, s, 3-H); $^{13}$C NMR (125.77 MHz, CDCl$_3$/CF$_3$CO$_2$H, 273 K) δ 99.94 (1-C), 116.65 (q, J 108.8 Hz, CF$_3$), 116.71 (3-C), 120.59 (5-C), 125.48 (4a-C), 126.84 (4-C), 130.40 (6-C), 131.40 (7-C), 133.71 (2-C), 134.58 (8-C), 135.68 (8a-C), 158.24 (q, J 40.3 Hz, C=O).
Figure 13. $^1$H NMR spectrum of 27 in CDCl$_3$/CF$_3$CO$_2$D.

Figure 14. $^1$H NMR spectrum of 29 in CDCl$_3$/CF$_3$CO$_2$D.
29. $^1$H (500.13 MHz, CDCl$_3$/CF$_3$CO$_2$H, 273 K) $\delta$ 7.75-7.81 (2 H, m, 6,7-H$_2$), 7.95 (1 H, m, 8-H), 8.04 (1 H, m, 5-H), 8.18 (1 H, d, $J$ 1.9 Hz, 2-H), 8.29 (1 H, s, 4-H), 9.31 (NH); $^{13}$C NMR (125.77 MHz, CDCl$_3$/CF$_3$CO$_2$H, 273 K) $\delta$ 116.10 (q, $J$ 103.7 Hz, CF$_3$), 116.48 (2-C), 119.63 (8-C), 123.08 (4-C), 125.15 (8a-C), 125.91 (1-C), 129.74 (6-C), 129.79 (5-C), 129.80 (7-C), 131.52 (3-C), 134.81 (4a-C), 157.58 (q, $J$ 39.1 Hz, C=O).

![Figure 15](image-url)

Figure 15. $^1$H NMR spectrum of 29 and 30 (*) 48 h after dissolution of 26 in CDCl$_3$/CF$_3$CO$_2$D.
Spectra of synthesised compounds

Figure 16. $^1$H NMR spectrum of 7 in (CD$_3$)$_2$SO.
Figure 17. $^{13}$C NMR spectrum of 7 in (CD$_3$)$_2$SO.

Figure 18. HSQC NMR spectrum of 7 in (CD$_3$)$_2$SO.
Figure 19. HMBC NMR spectrum of 7 in (CD$_3$)$_2$SO.

Figure 20. $^1$H-$^1$H COSY NMR spectrum of 7 in (CD$_3$)$_2$SO.
Figure 21. $^1$H-$^1$H NOESY NMR spectrum of 7 in (CD$_3$)$_2$SO.

Figure 22. $^1$H NMR spectrum of 8 in (CD$_3$)$_2$SO.
Figure 23. $^{13}$C NMR spectrum of 8 in (CD$_3$)$_2$SO.

Figure 24. HSQC NMR spectrum of 8 in (CD$_3$)$_2$SO.
Figure 25. HMBC NMR spectrum of 8 in (CD$_3$)$_2$SO.

Figure 26. $^1$H NMR spectrum of 10 in CDCl$_3$. 
Figure 27. $^{13}$C NMR spectrum of 10 in CDCl$_3$.

Figure 28. HSQC NMR spectrum of 10 in CDCl$_3$. 
Figure 29. HMBC NMR spectrum of 10 in CDCl3.

Figure 30. 1H NMR spectrum of 11 in CDCl3.
Figure 31. Expansion of part of $^1$H NMR spectrum of 11 in CDCl$_3$.

Figure 32. Expansion of part of $^1$H NMR spectrum of 11 in CDCl$_3$. 
Figure 33. $^{13}$C NMR spectrum of 11 in CDCl$_3$.

Figure 34. HSQC NMR spectrum of 11 in CDCl$_3$. 
Figure 35. HMBC NMR spectrum of 11 in CDCl₃.

Figure 36. Expansion of part of HMBC NMR spectrum of 11 in CDCl₃.
Figure 37. $^1$H-$^1$H COSY NMR spectrum of 11 in CDCl$_3$.

Figure 38. $^1$H-$^1$H NOESY NMR spectrum of 11 in CDCl$_3$. 
Figure 39. $^1$H NMR spectrum of 24 in (CD$_3$)$_2$SO.

Figure 40. Expansion of part of $^1$H NMR spectrum of 24 in (CD$_3$)$_2$SO.
Figure 41. $^{13}$C NMR spectrum of 24 in (CD$_3$)$_2$SO.

Figure 42. Expansion of part of $^{13}$C NMR spectrum of 24 in (CD$_3$)$_2$SO.
Figure 43. HSQC NMR spectrum of 24 in (CD$_3$)$_2$SO.

Figure 44. HMBC NMR spectrum of 24 in (CD$_3$)$_2$SO.
Figure 45. Expansion of part of HMBC NMR spectrum of 24 in (CD$_3$)$_2$SO.

Figure 46. 'H-'H NOESY NMR spectrum of 24 in (CD$_3$)$_2$SO.
Figure 47. $^{19}$F NMR spectrum of 24 in (CD$_3$)$_2$SO.

Figure 48. $^1$H NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 49. Expansion of part of $^1$H NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 50. Expansion of part of $^1$H NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 51. $^{13}$C NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 52. Expansion of part of $^{13}$C NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 53. HSQC NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 54. Expansion of part of HSQC NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 55. HMBC NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 56. Expansion of part of HMBC NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 57. $^1$H-$^1$H NOESY NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 58. Expansion of part of $^1$H-$^1$H NOESY NMR spectrum of 25 in (CD$_3$)$_2$SO.
Figure 59. $^{19}$F NMR spectrum of 25 in (CD$_3$)$_2$SO.

Figure 60. $^1$H NMR spectrum of 26 in (CDCl$_3$).
Figure 61. Expansion of part of $^1$H NMR spectrum of 26 in CDCl$_3$.

Figure 62. $^{13}$C NMR spectrum of 26 in CDCl$_3$. 
Figure 63. Expansion of part of $^{13}$C NMR spectrum of 26 in CDCl$_3$.

Figure 64. HSQC NMR spectrum of 26 in CDCl$_3$. 
Figure 65. Expansion of part of HSQC NMR spectrum of 26 in CDCl₃.

Figure 66. HMBC NMR spectrum of 26 in CDCl₃.
**Figure 67.** Expansion of part of HMBC NMR spectrum of 26 in CDCl$_3$.

**Figure 68.** $^{19}$F NMR spectrum of 26 in CDCl$_3$. 