Supporting Information

**C(5) Site-Selective Functionalization of (S)-Cotinine**

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Page 2: $^1$H NMR of crude borylation reaction mixture comprising cotinine 2 and boronate ester 3

Page 3-12: $^1$H and $^{13}$C NMR spectra of compounds 4 and 5a-h.
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cotinine (3).

$^1$H-NMR (400 MHz): $^1$H NMR of the crude borylation reaction mixture arising from Ir-catalysed borylation of ($-$)-cotinine 2 leading to 3. $^1$H NMR of ($-$)-cotinine 2 (starting material and marked by #) is shown for comparison alongside the reaction mixture containing the borylated product 3 with residual 2. The aromatic region shown inside the blue circle has been amplified for clarity. Crude 3 was converted directly, without any purification, to 4, which was then subjected to chromatography.
(–)-5-Bromocotinine (4).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(−)-S-Aminocotinine (5a).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(-)-5-(4-Tolyl)cotinine (5b).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(−)-5-Cyanocotinine (5c).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(-)-5-(E-2-Phenylethenyl)cotinine (5d).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(-)-5-(2-Trimethylsilylethynyl)cotinine (5e).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(-)-S-Ethynylcotinine (5f).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(+)-Methyl cotinine-5-carboxylate (5g).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$
(+)-5-(Cotinin-5-yl)-cotinine (5h).

$^1$H-NMR (500 MHz), $^{13}$C-NMR (125 MHz): CDCl$_3$