Metalated N-Heterocyclic Reagents Prepared by the Frustrated Lewis Pair TMPMgCl·BF₃ and their Addition to Aromatic Aldehydes and Activated Ketones

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Supporting Information
NMR spectra
4-[hydroxy(pyridin-2-yl)methyl]benzonitrile (4a)
(4-chlorophenyl)(pyridin-2-yl)methanol (4b)
(4-bromophenyl)(pyridin-2-yl)methanol (4c)
(3,4-dichlorophenyl)(pyridin-2-yl)methanol (4d)
2,2,2-trifluoro-1-phenyl-1-(pyridin-2-yl)ethanol (4e)
(4-bromophenyl)(quinolin-2-yl)methanol (4f)
1-(4-bromophenyl)-2,2,2-trifluoro-1-(quinolin-2-yl)ethanol (4g)
(4-chlorophenyl)(3-(methylthio)pyrazin-2-yl)methanol (7a)
(4-bromophenyl)(3-(methylthio)pyrazin-2-yl)methanol (7b)
1-(4-bromophenyl)furo[3,4-c]pyridin-3(1H)-one (10a)
(4-bromophenyl)(3-fluoropyridin-4-yl)methanol (10b)
(4-chlorophenyl)(3-chloropyridin-4-yl)methanol (10c)
4-((3,4-dichlorophenyl)(hydroxy)methyl)-N,N-diethylnicotinamide (10d)
Metalated intermediate 9a

'H-NMR expansions of intermediate 9a of the aromatic region (left) and the CH2 signal region (right).
$^{13}$C-NMR expansions of the intermediate 9a of the aromatic region (120-230 ppm, left) and the aliphatic region (0-70 ppm) right).
(3-(ethoxycarbonyl)pyridin-1-ium-1-yl)trifluoroborate (11)

\[ \text{HNMR} \]

\[ \text{B-NMR} \]

X: parts per Million

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Trifluoro(2,2,6,6-tetramethylpiperidin-1-ium-1-yl)borate (12)

**¹H-NMR**

X : parts per Million : ¹H

**¹⁹F-NMR of 12**

X : parts per Million : ¹⁹F

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11B-NMR of 12

13C-NMR of 12

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13C-NMR of 12, expansion