

Synthesis of Chiral Bicyclic Guanidinium Salts using Di(imidazole-1-yl)methanimine

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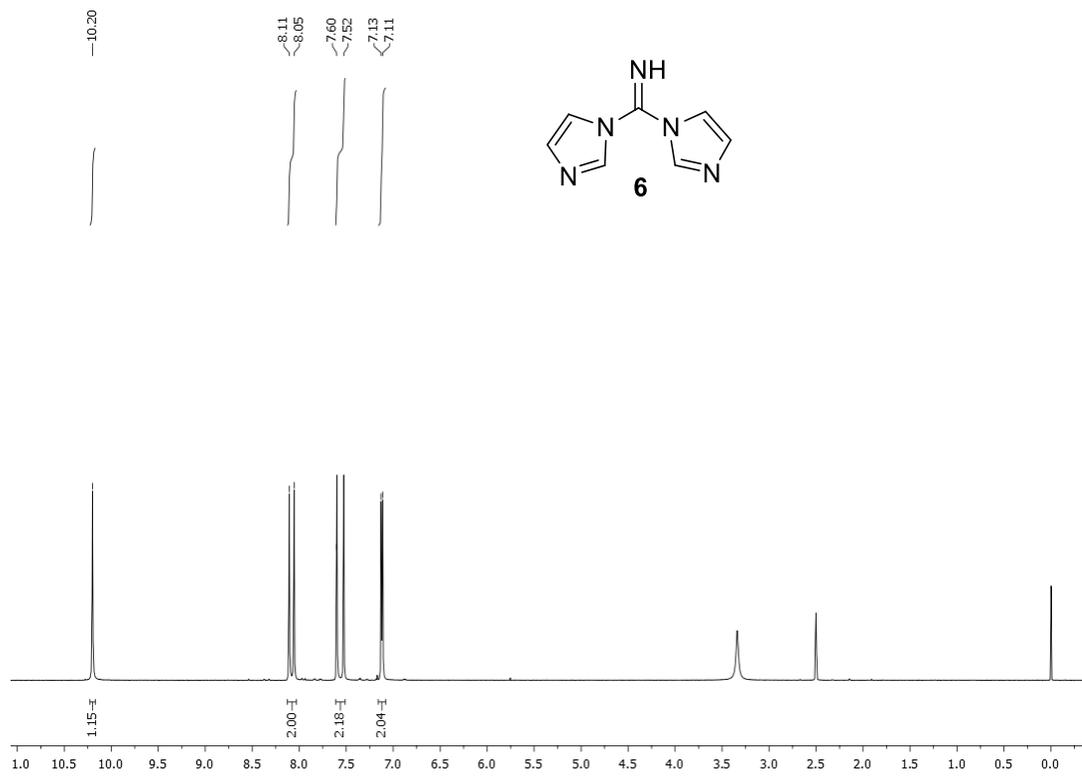
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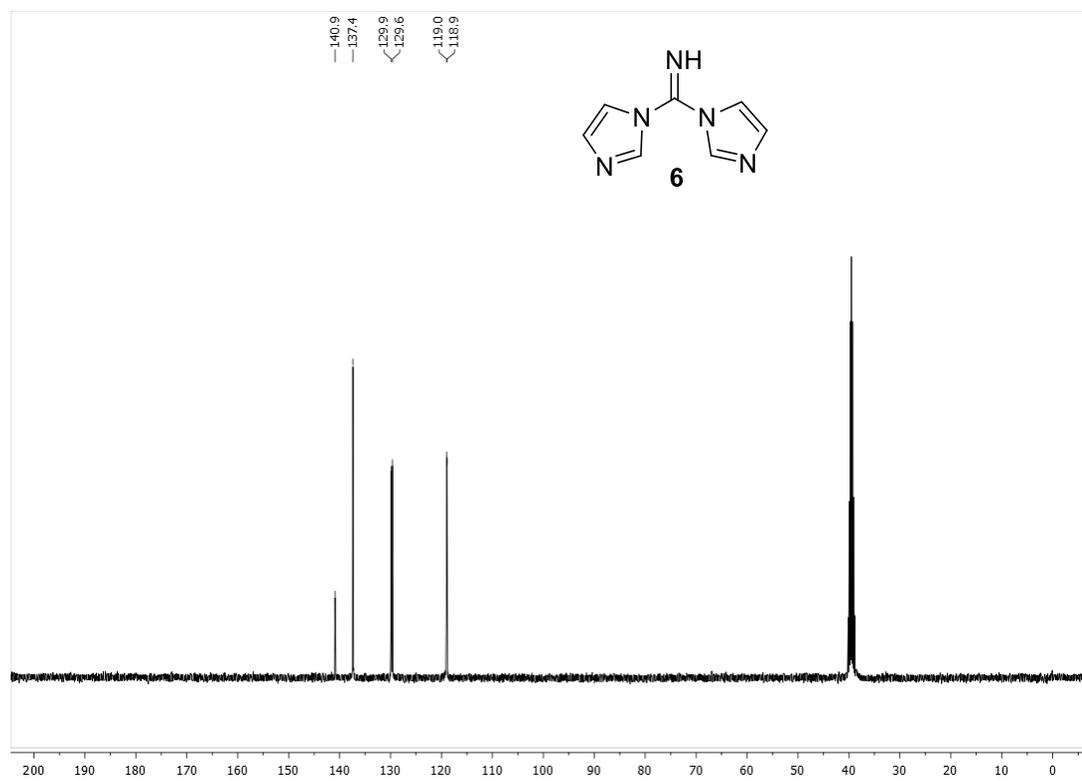
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1. Copies of ^1H and ^{13}C NMR Spectra

^1H NMR (400 MHz, $\text{DMSO-}d_6$)

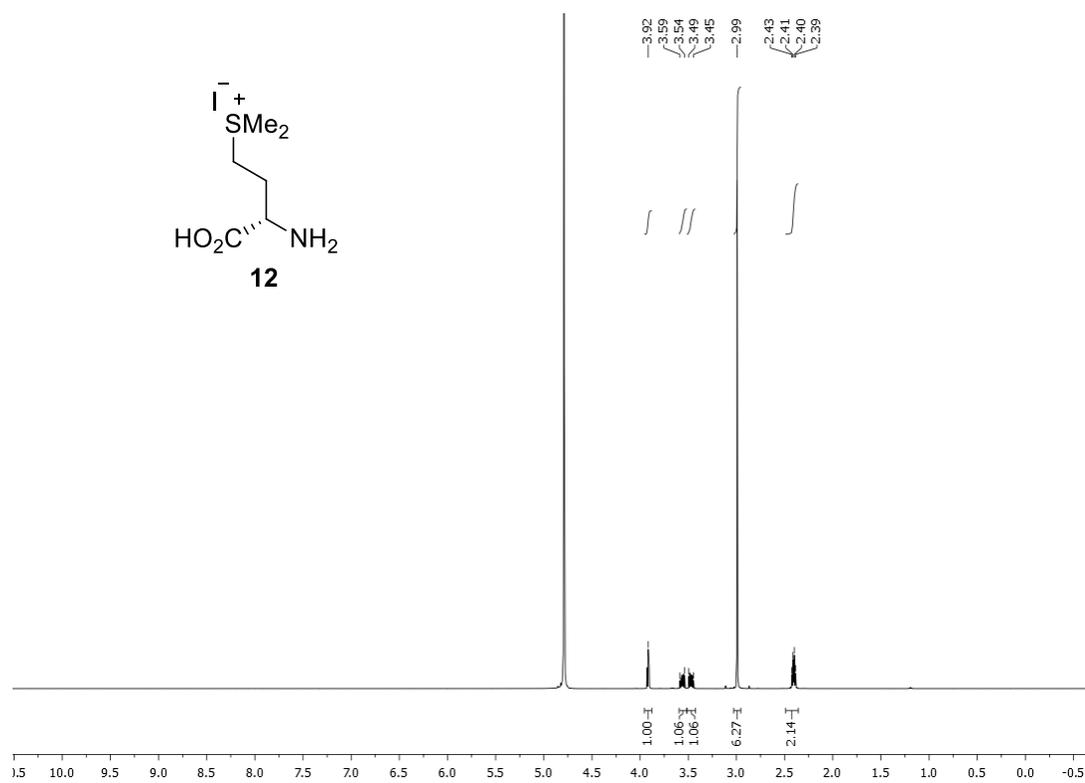


^{13}C NMR (101 MHz, $\text{DMSO-}d_6$)

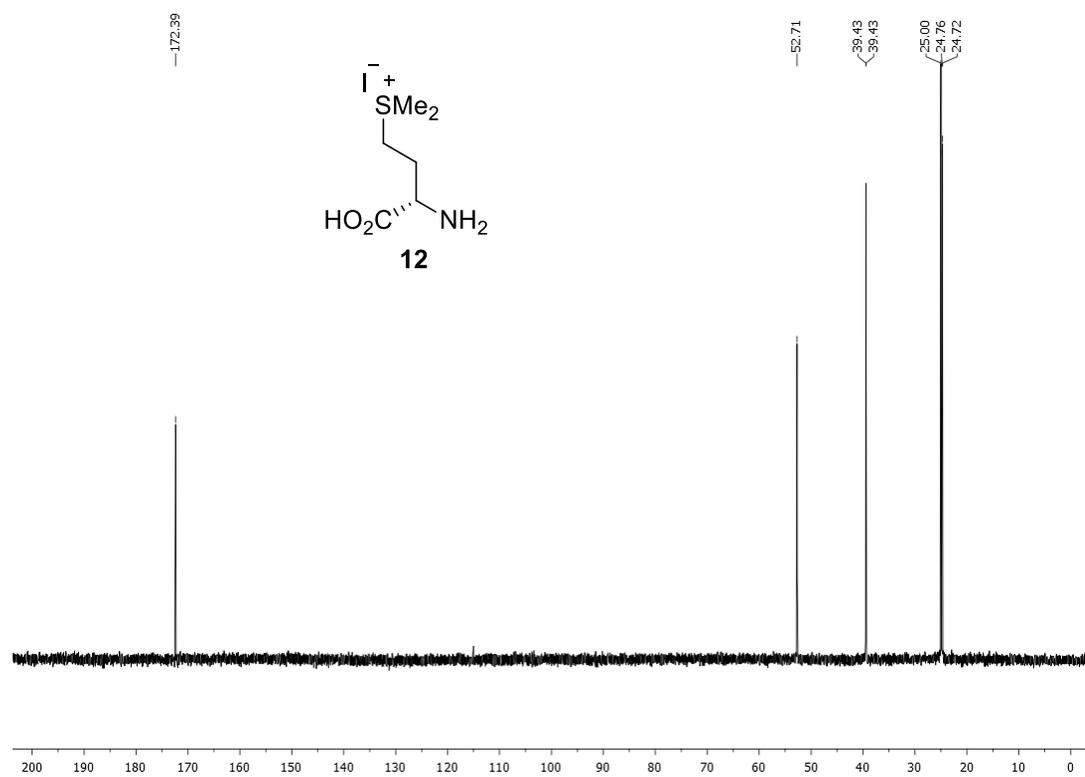


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^1H NMR (600 MHz, D_2O)

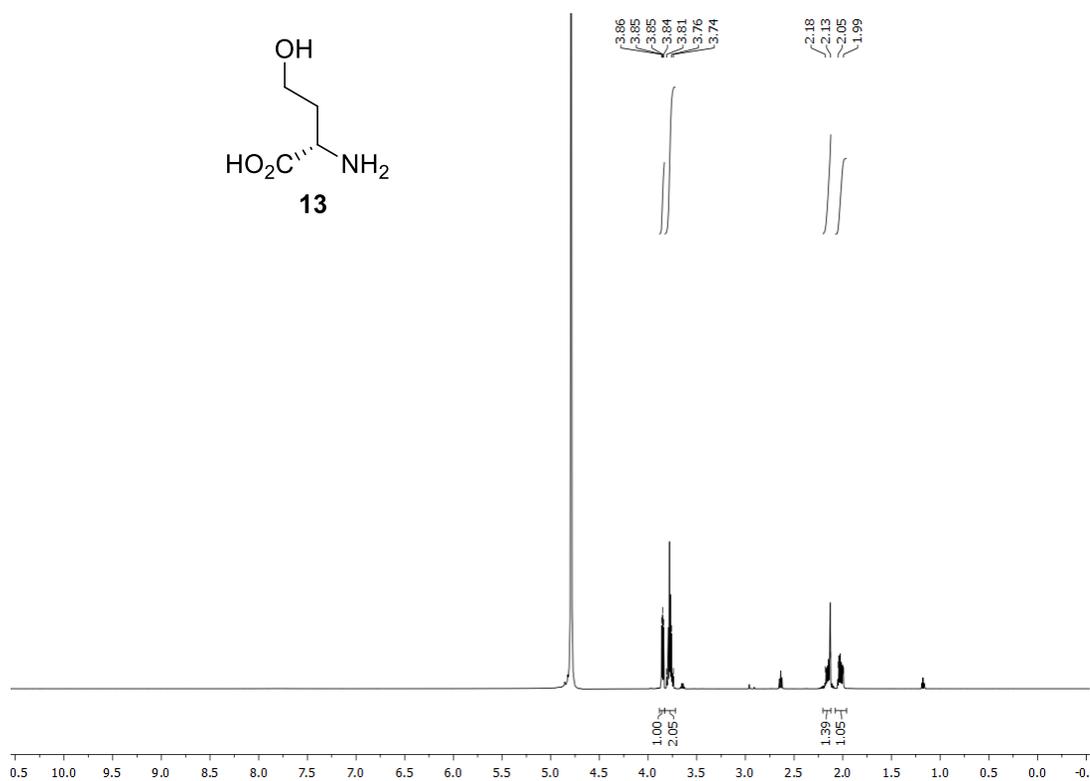


^{13}C NMR (151 MHz, D_2O)

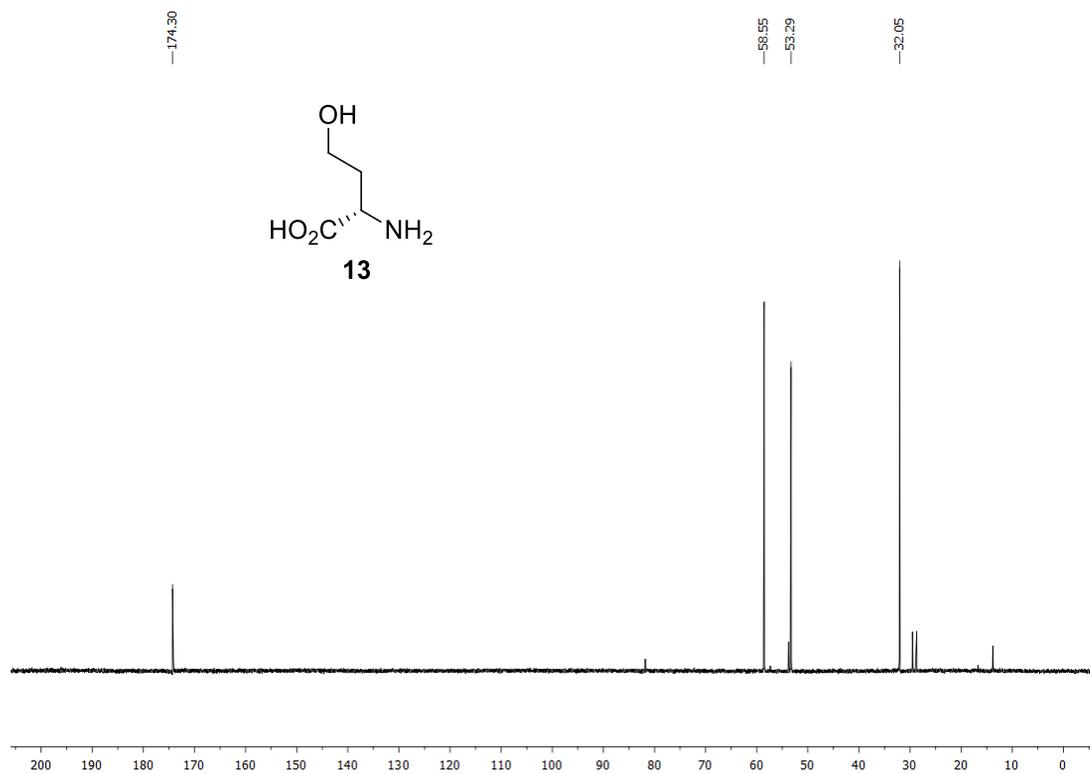


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^1H NMR (600 MHz, D_2O)

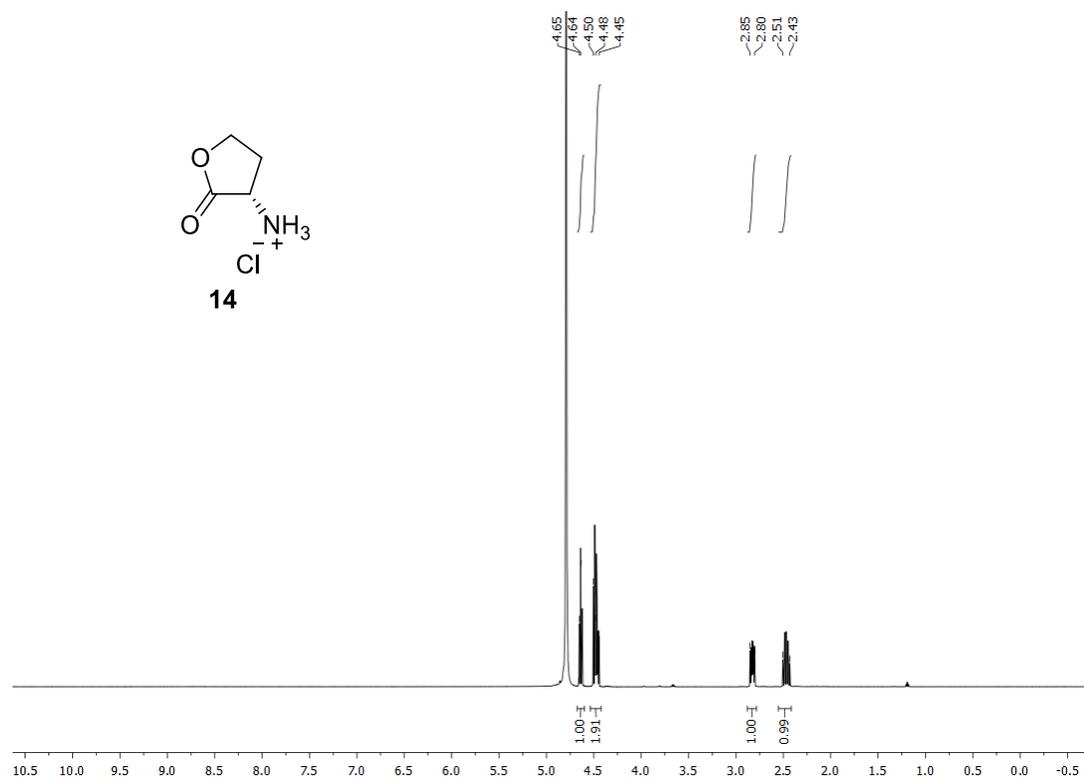


^{13}C NMR (151 MHz, D_2O)

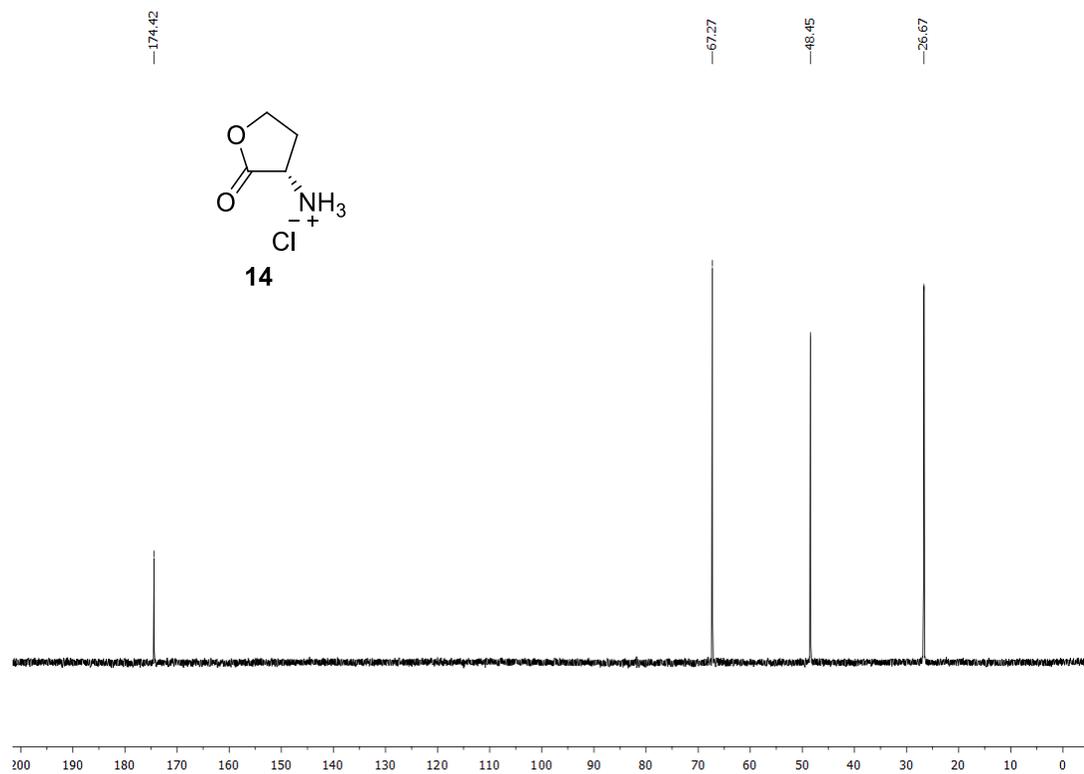


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^1H NMR (600 MHz, D_2O)

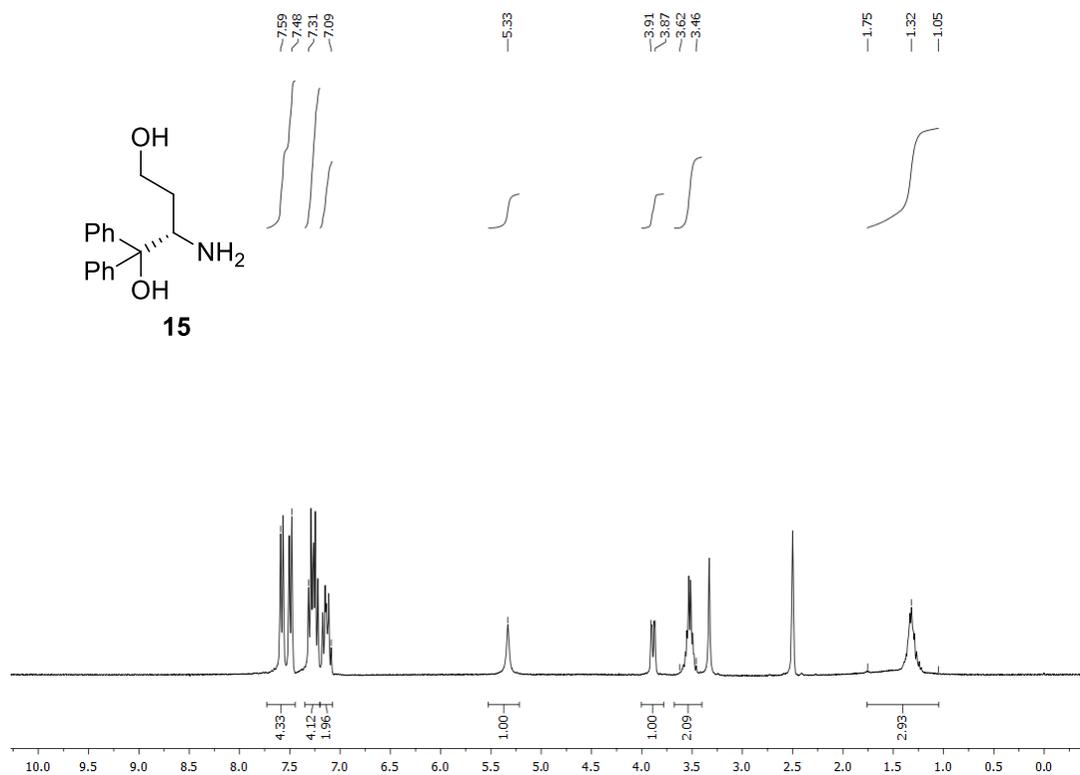


^{13}C NMR (151 MHz, D_2O)

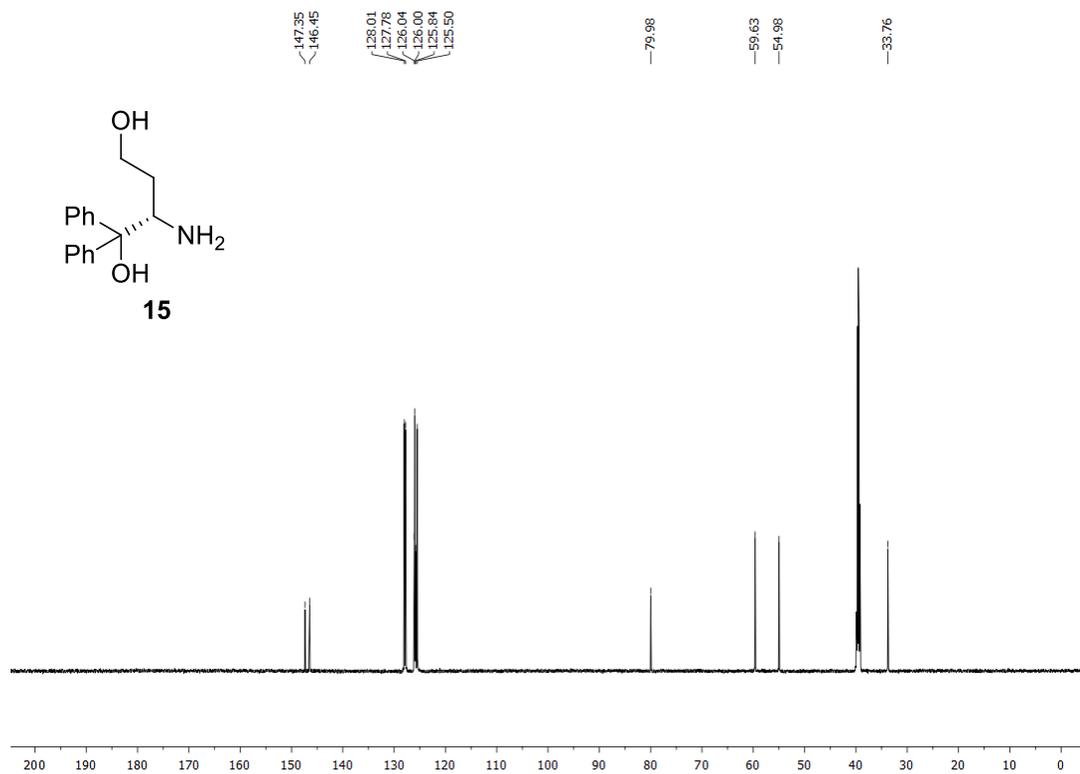


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^1H NMR (300 MHz, $\text{DMSO-}d_6$)

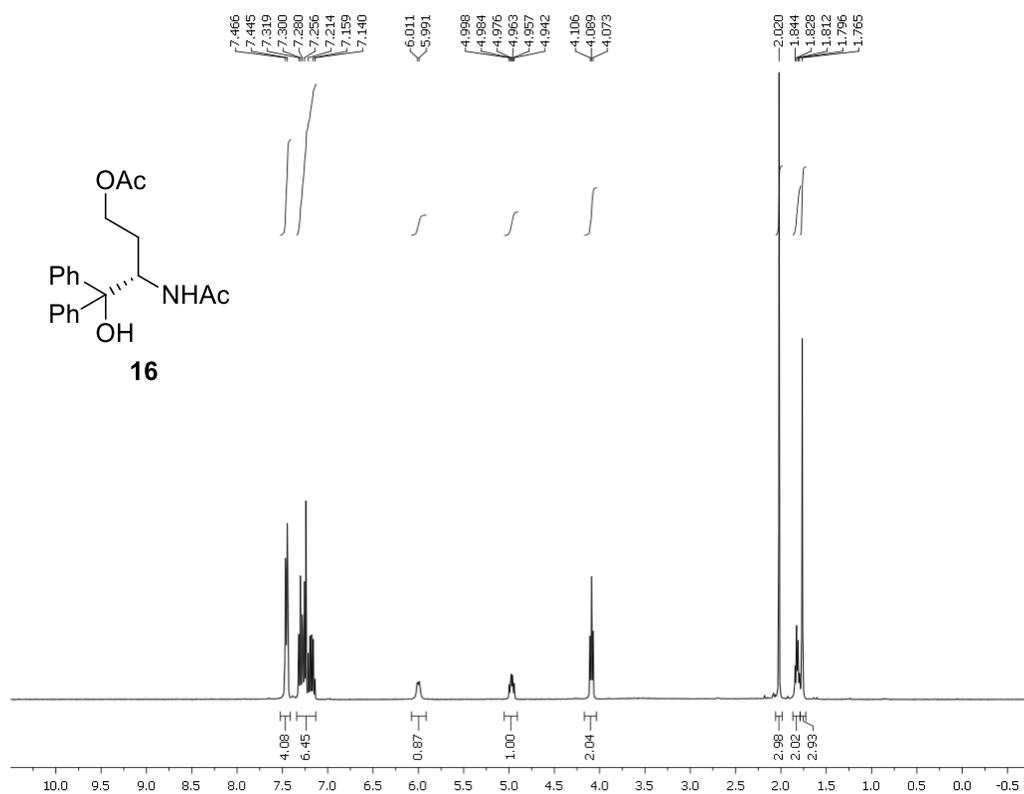


^{13}C NMR (151 MHz, $\text{DMSO-}d_6$)

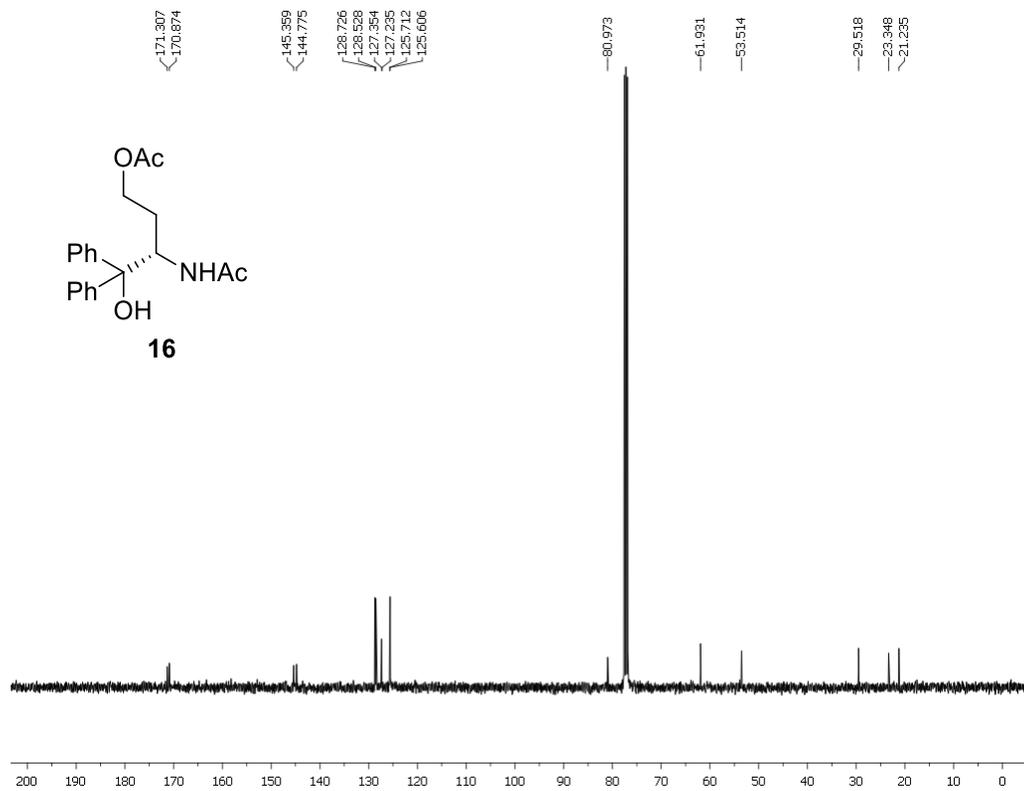


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^1H NMR (400 MHz, CDCl_3)

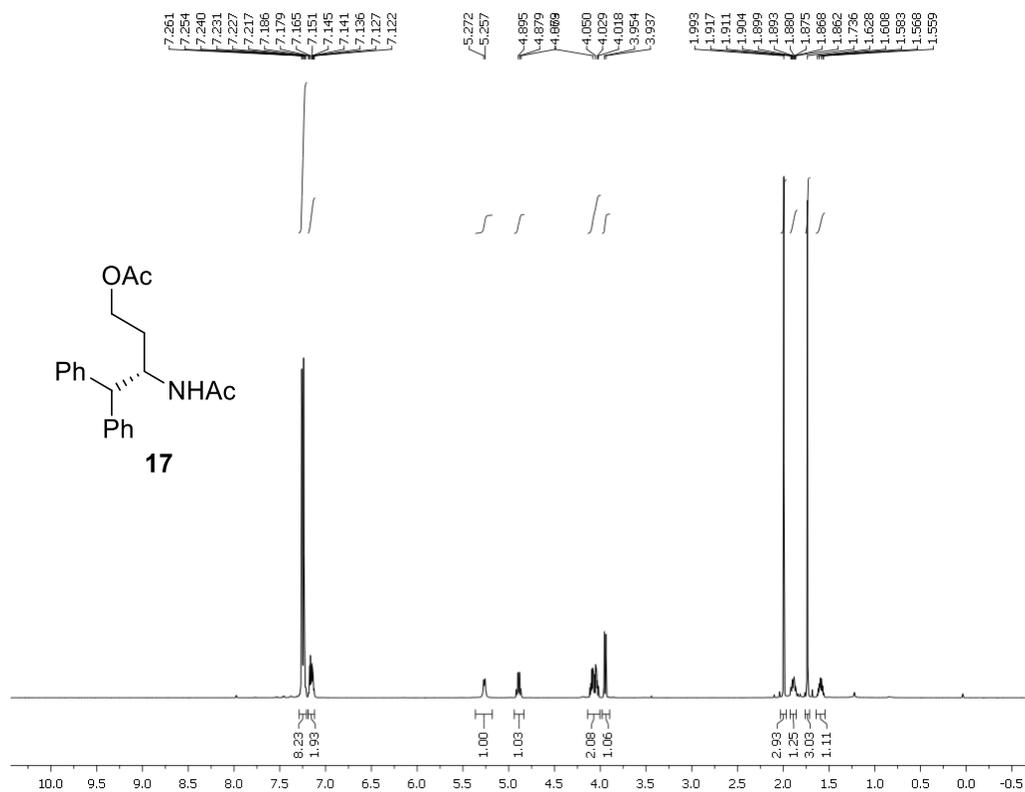


^{13}C NMR (101 MHz, CDCl_3)

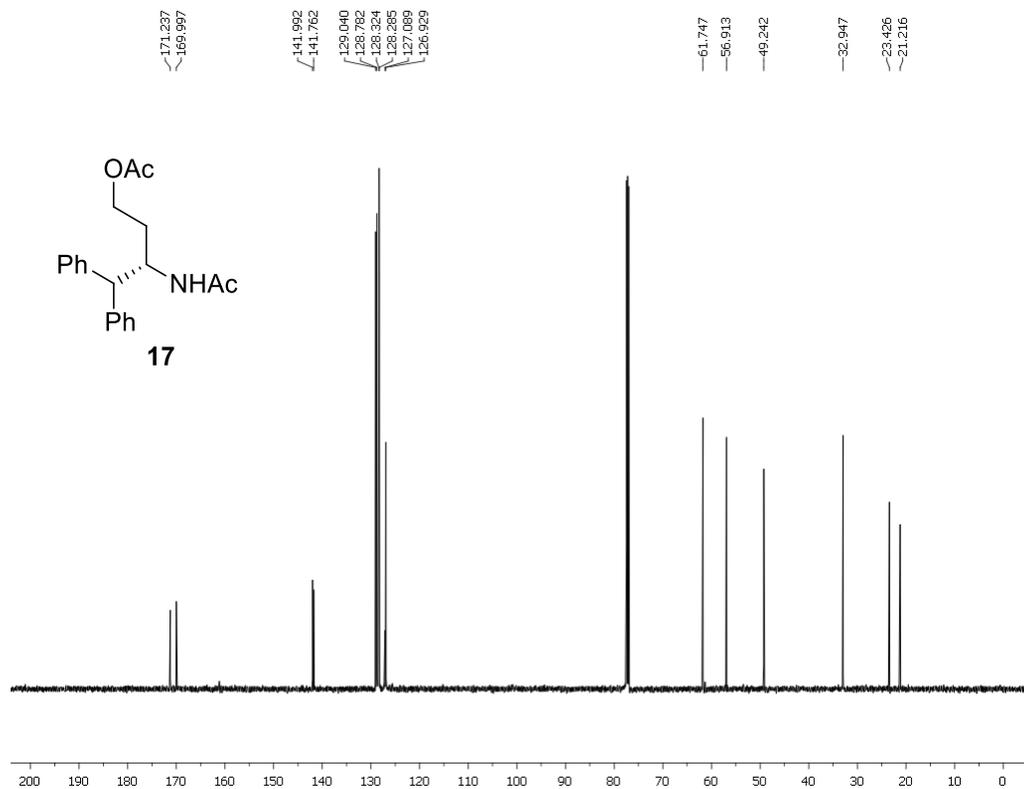


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^1H NMR (600 MHz, CDCl_3)

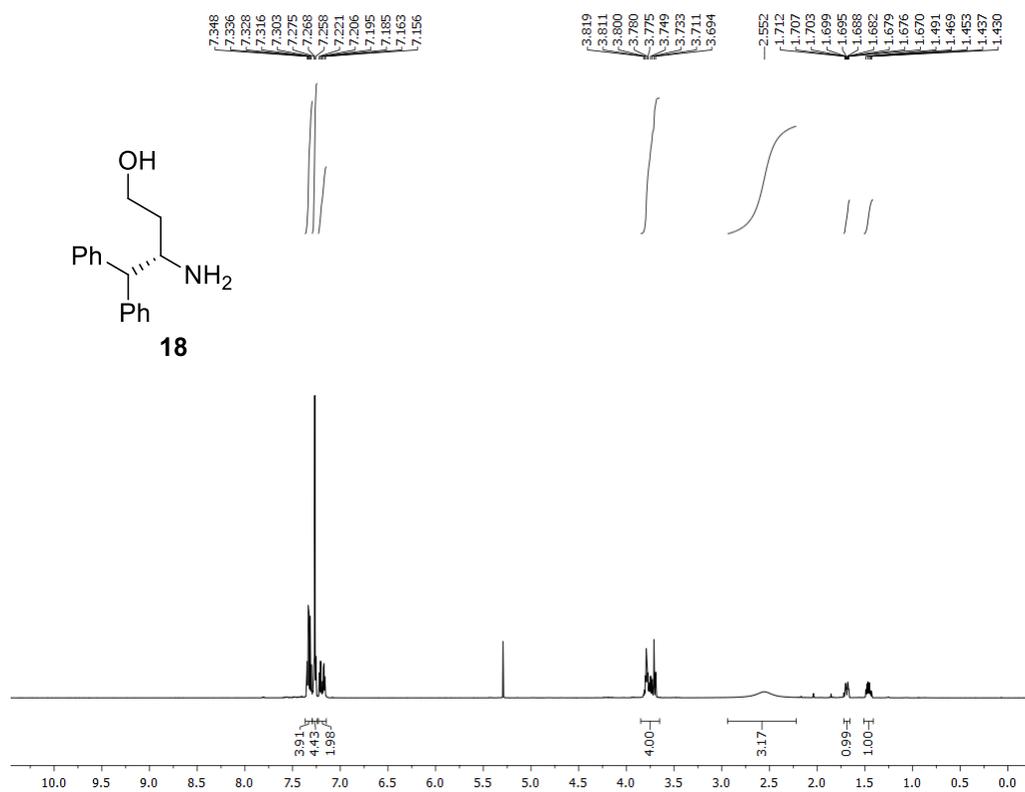


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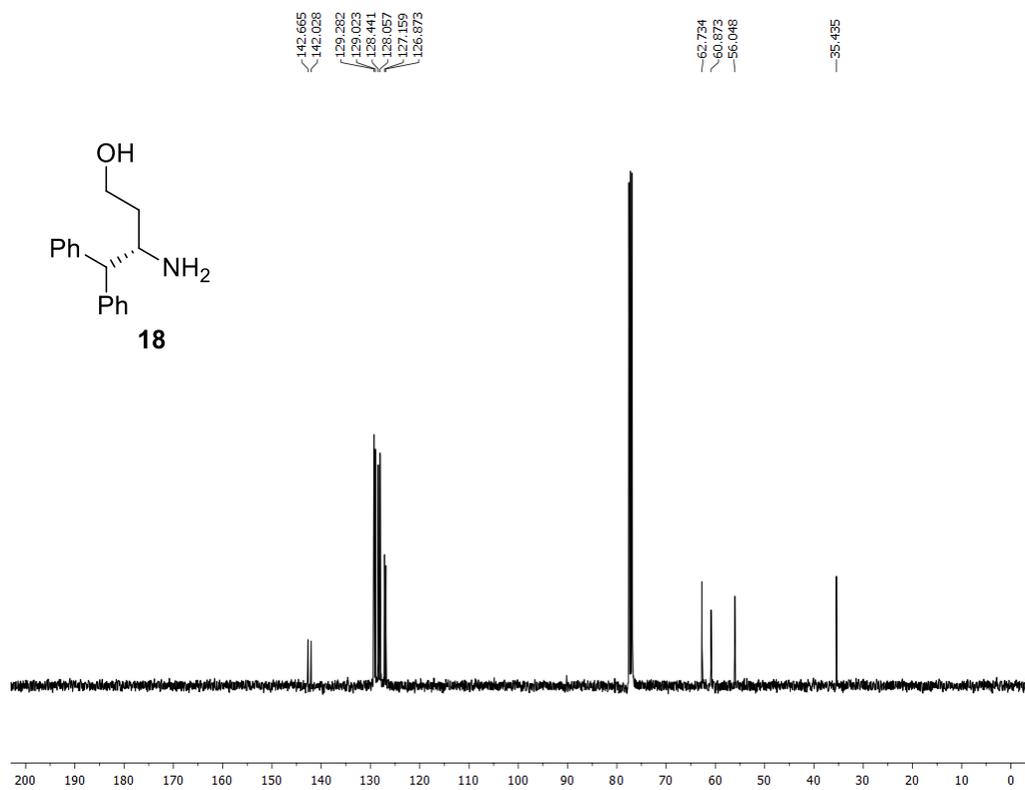


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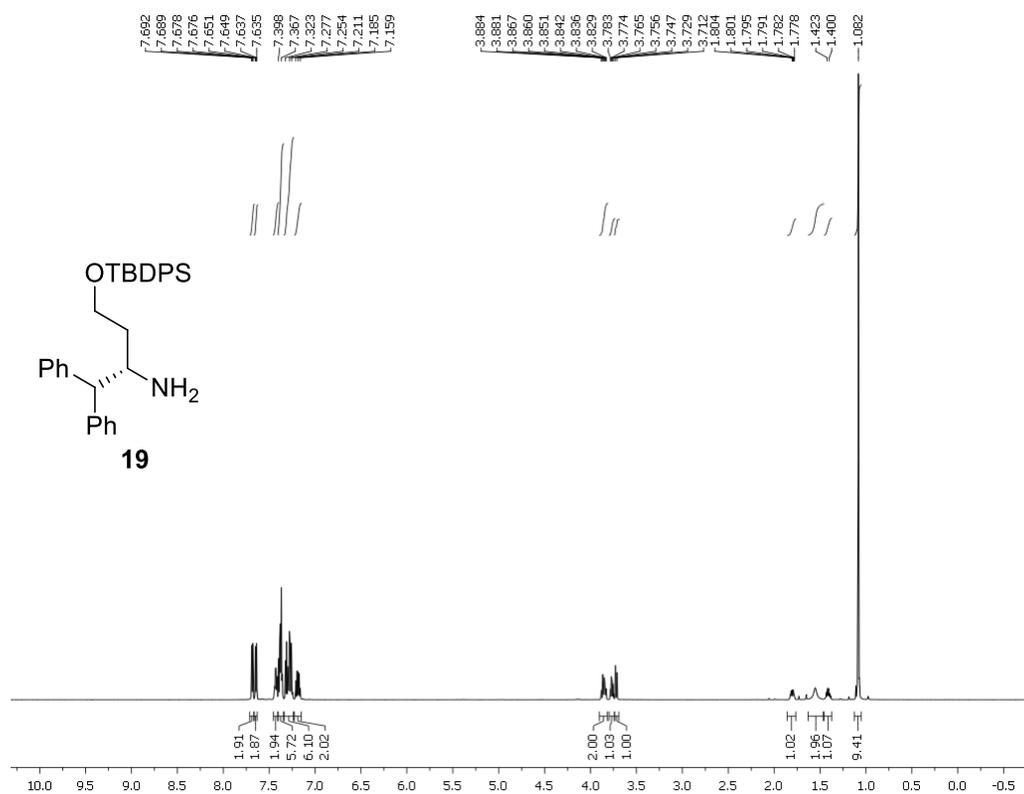


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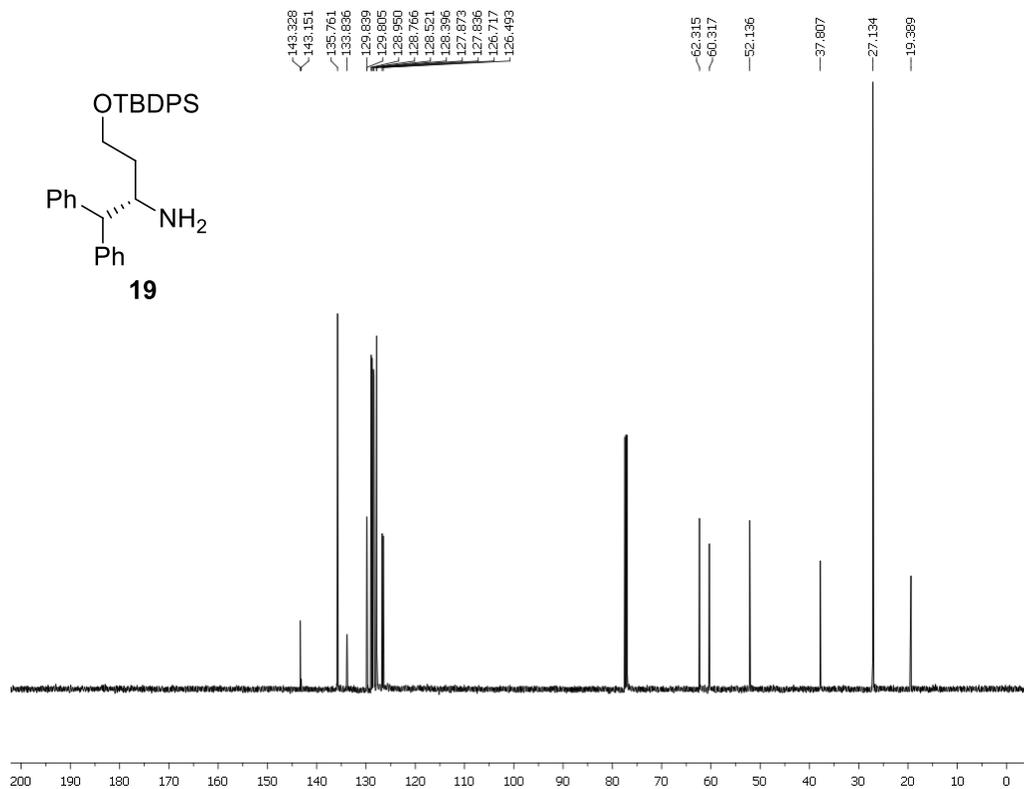


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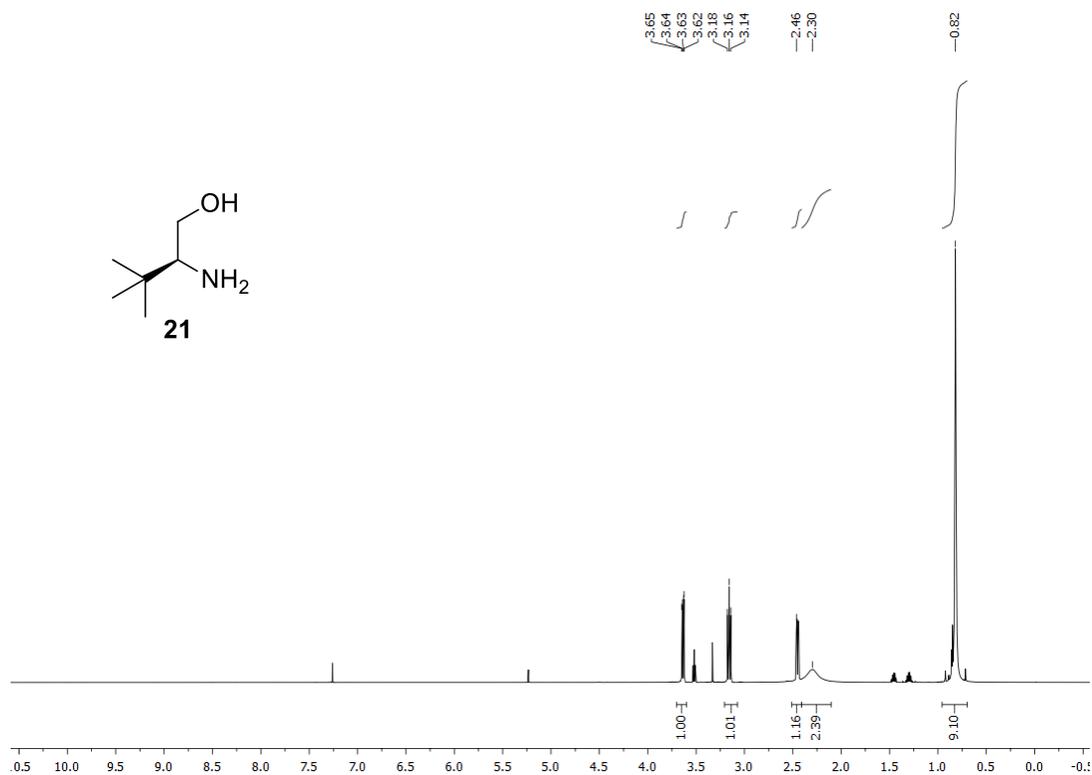


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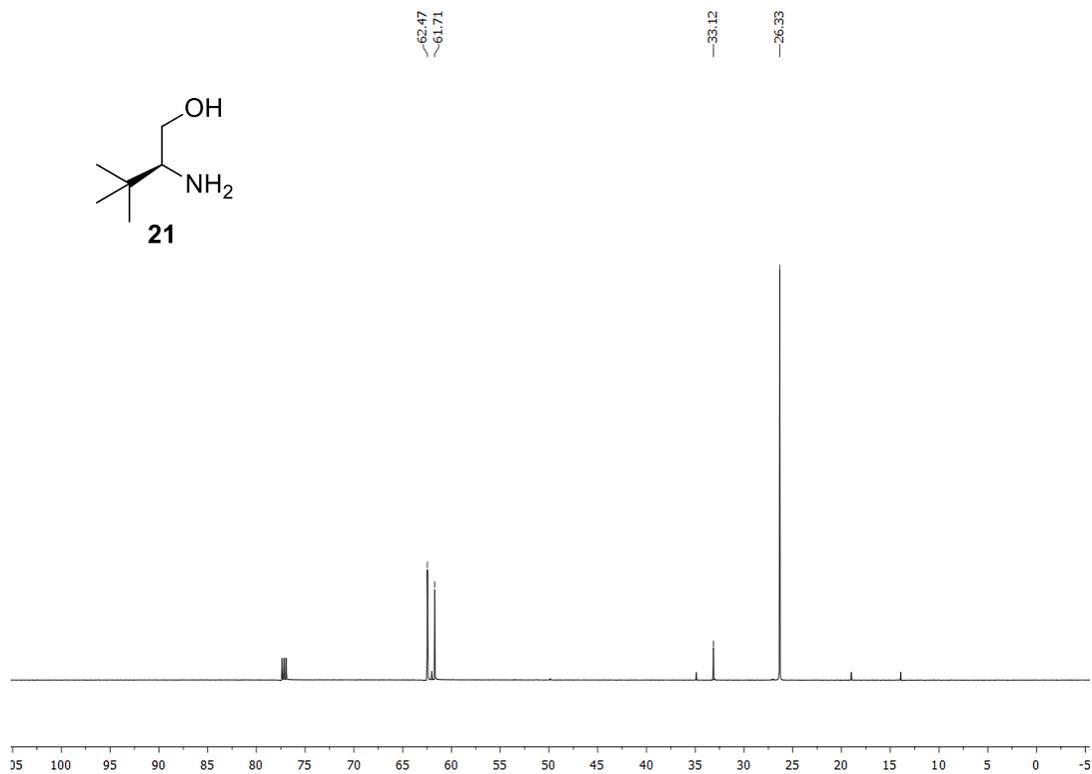


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^1H NMR (600 MHz, CDCl_3)

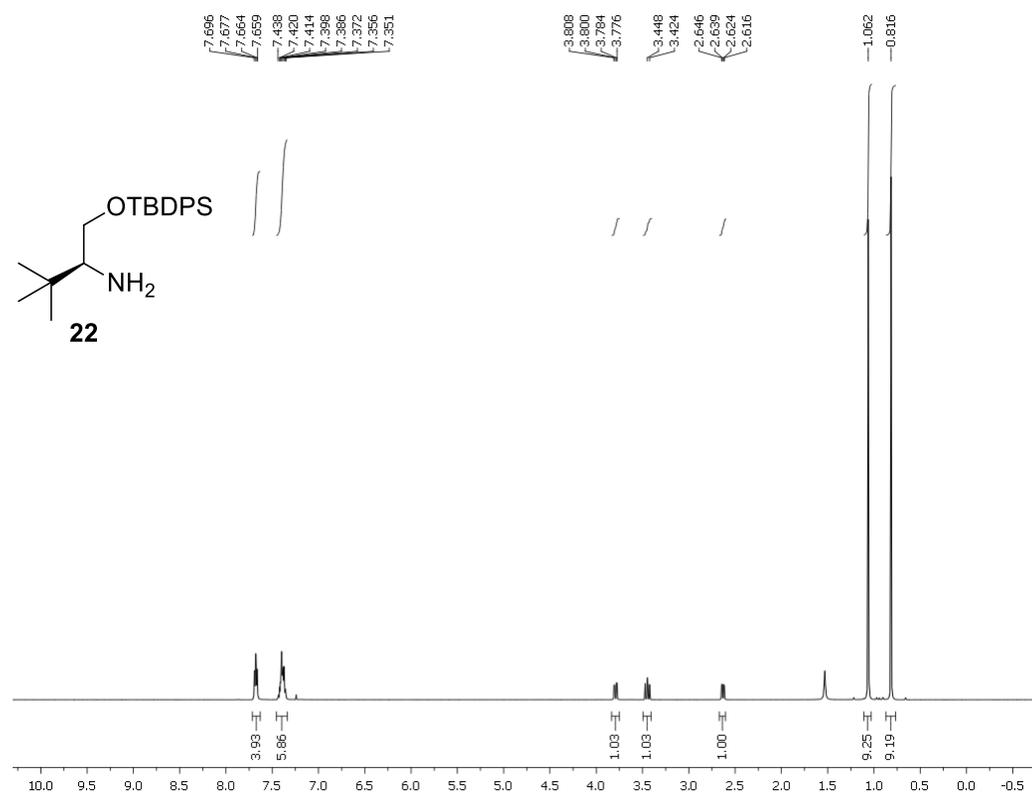


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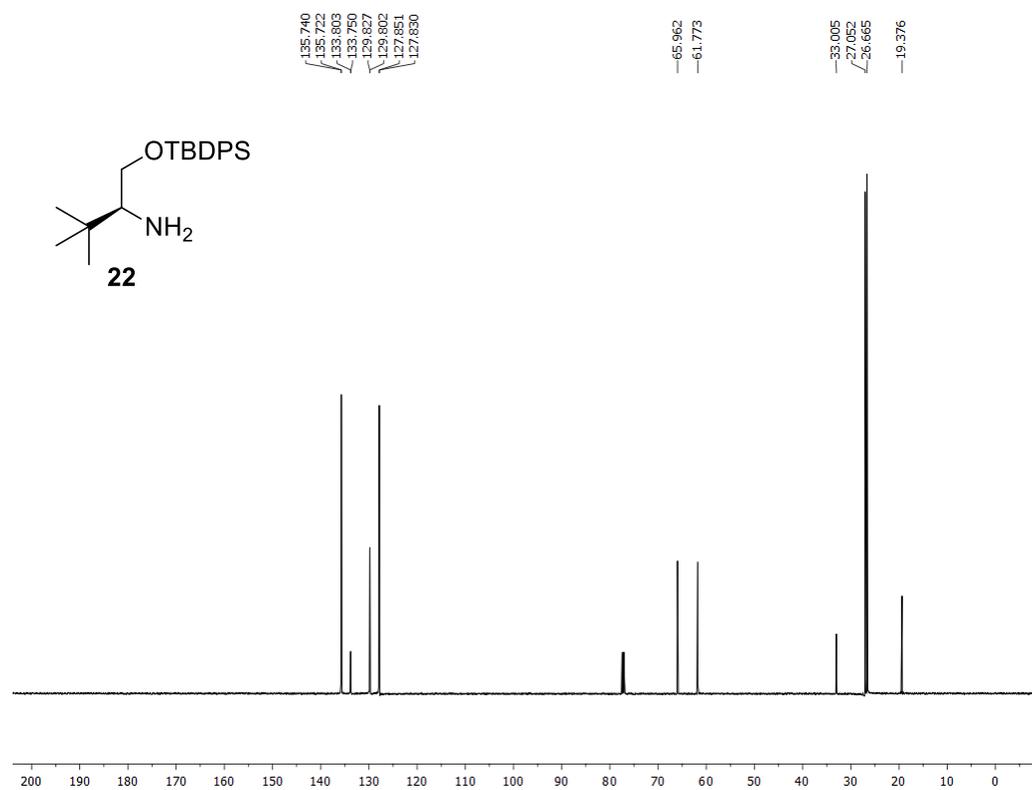


Supporting information

^1H NMR (400 MHz, CDCl_3)

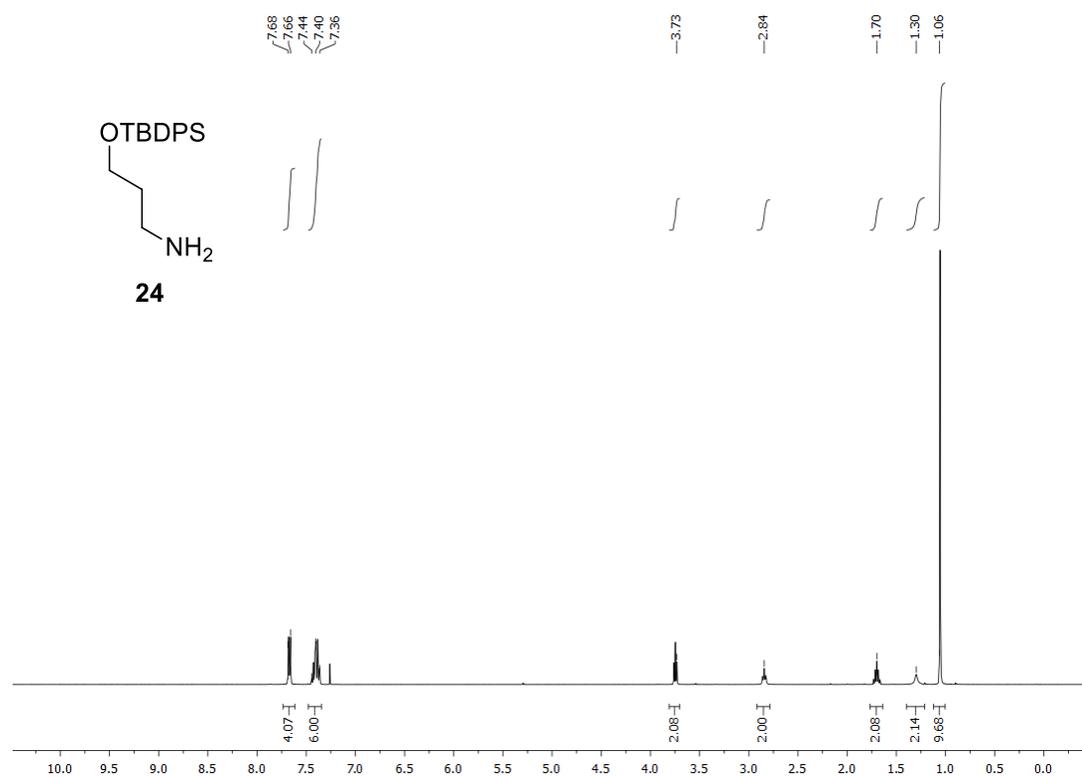


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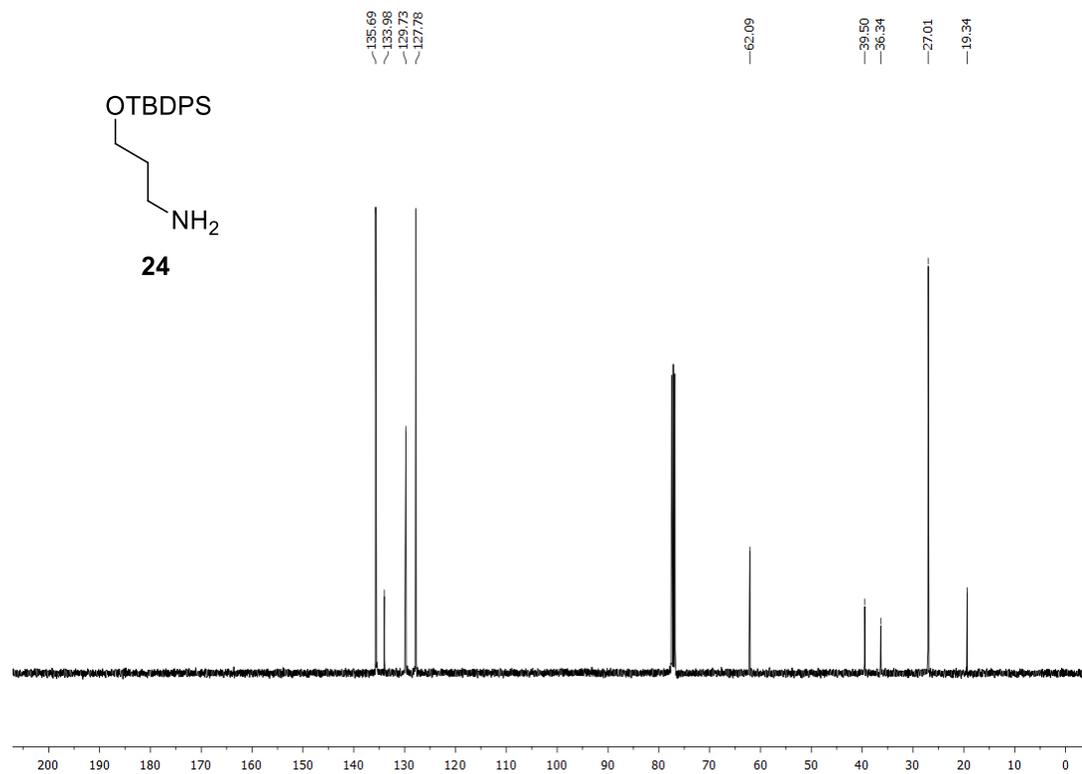


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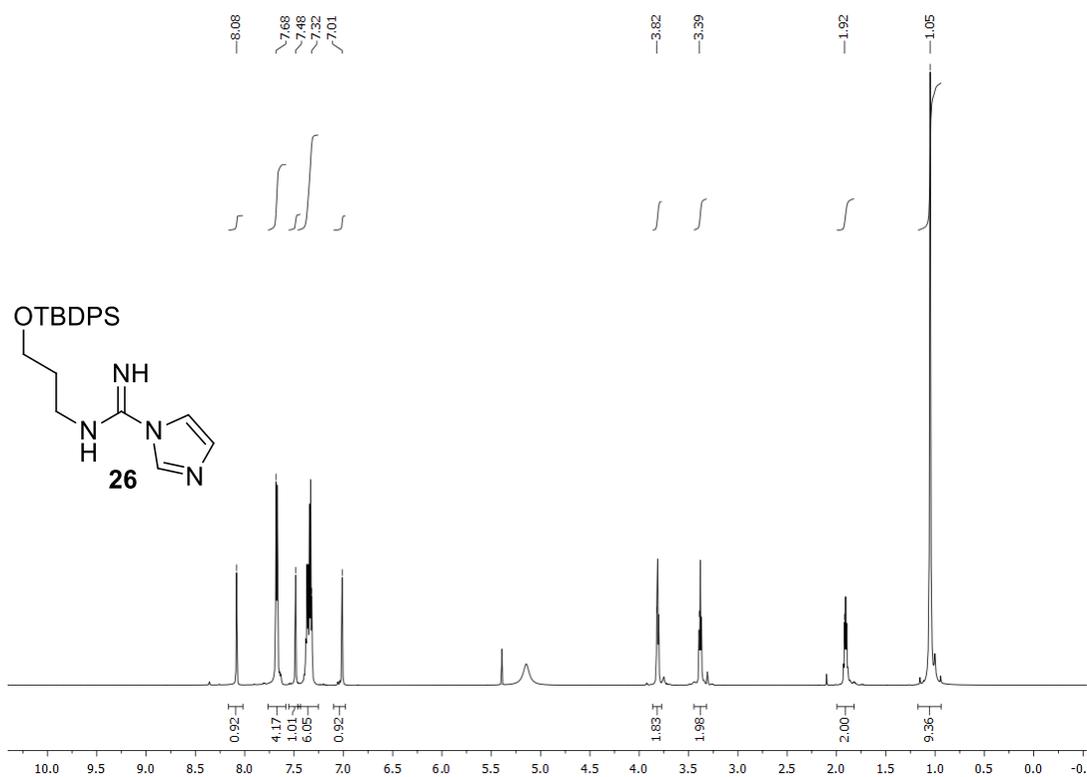


^{13}C NMR (101 MHz, CDCl_3)

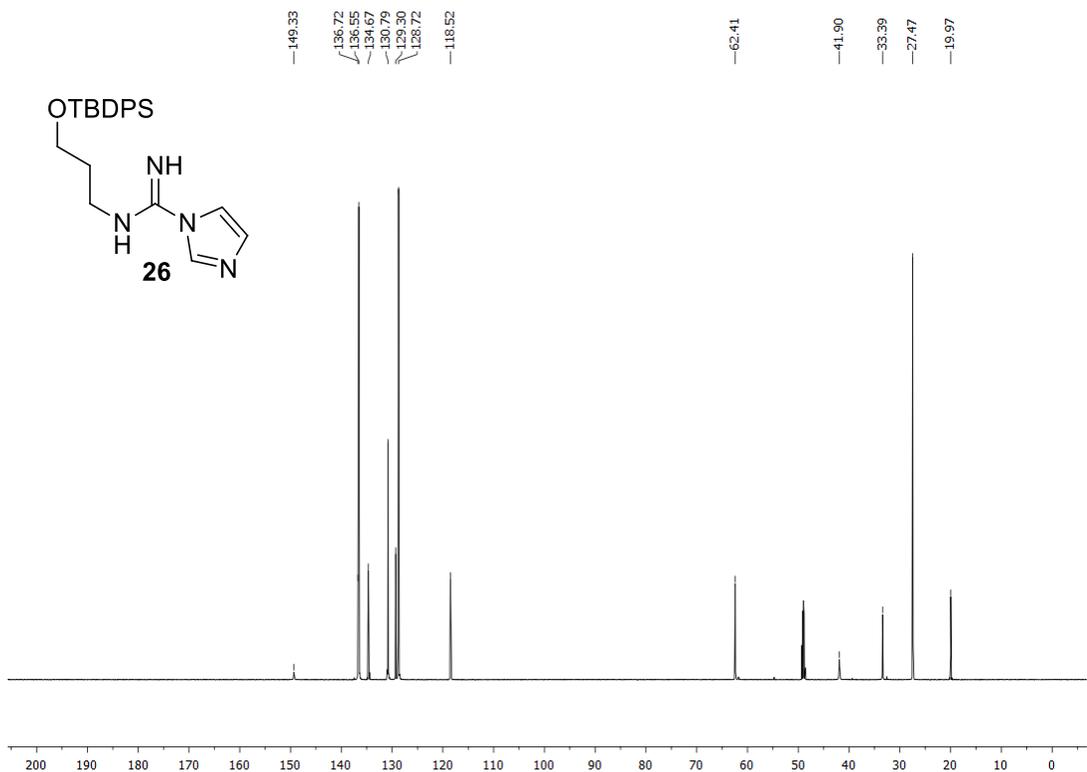


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^1H NMR (600 MHz, CD_3OD)

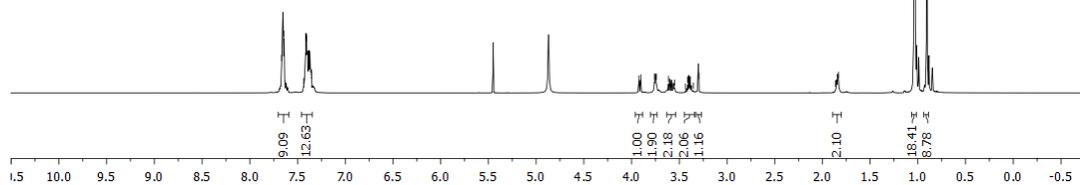
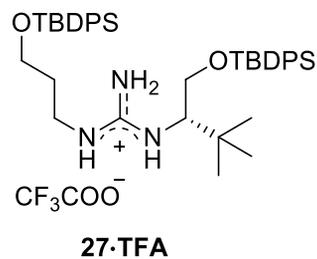
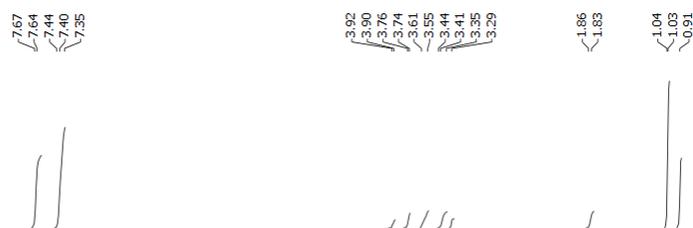


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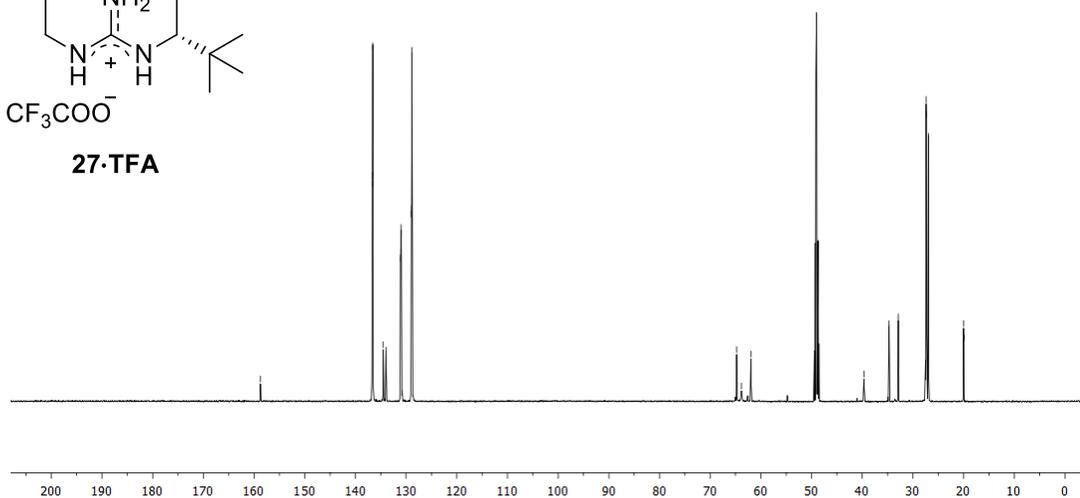
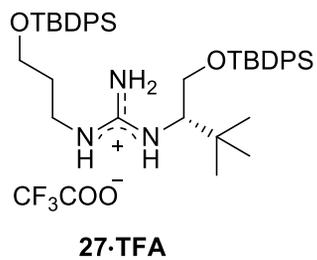


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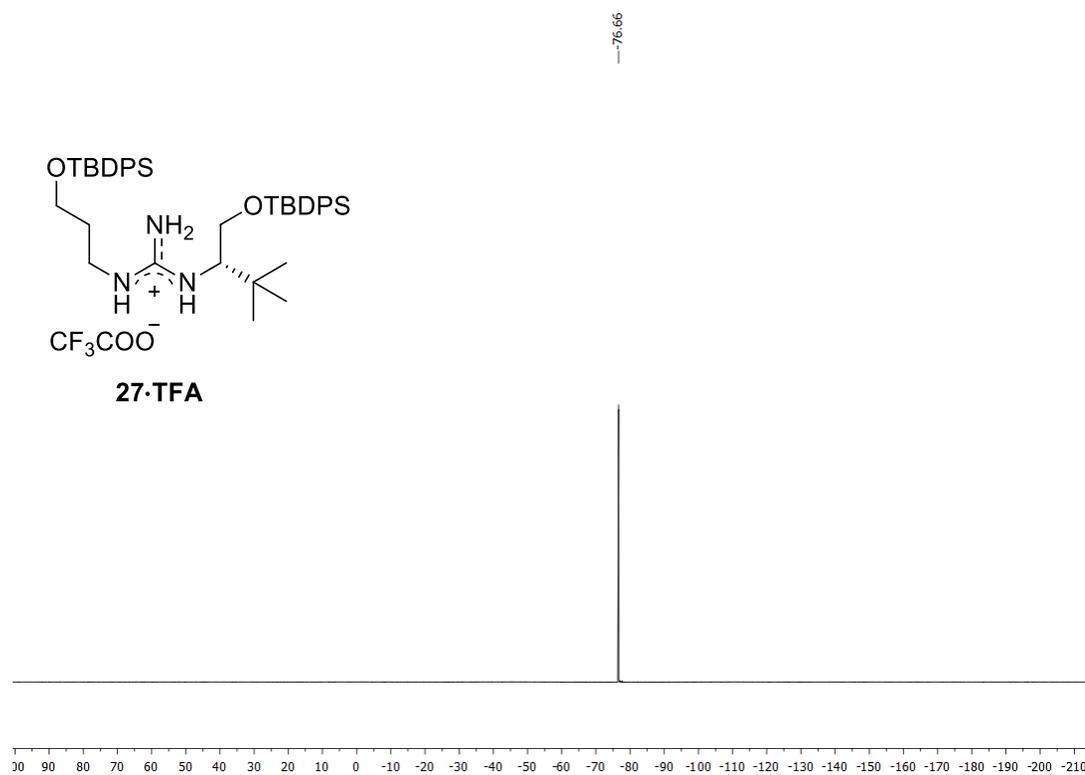


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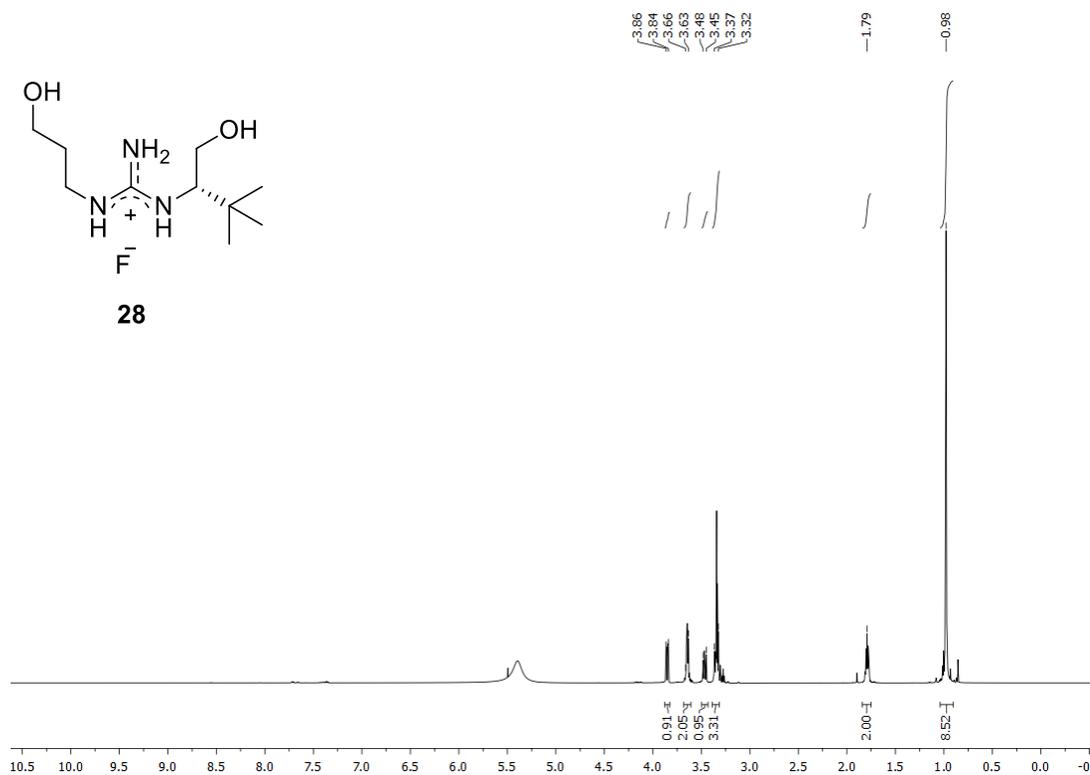
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^{19}F NMR (564 MHz, CD_3OD)

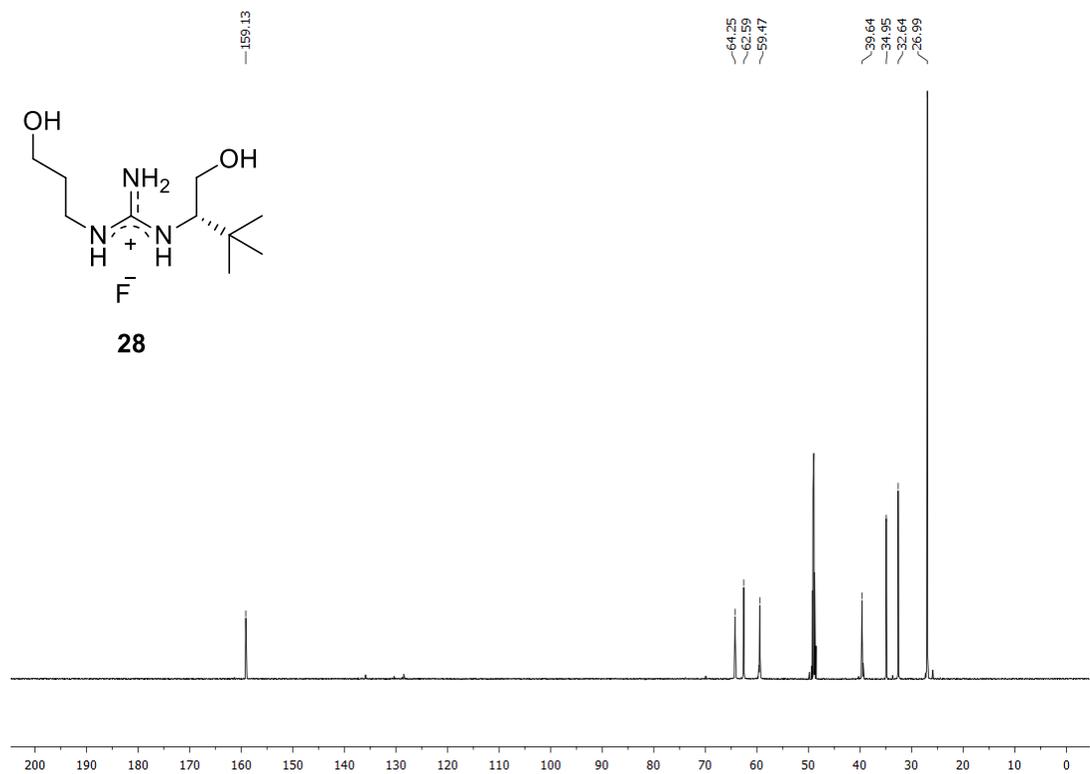


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^1H NMR (600 MHz, CD_3OD)

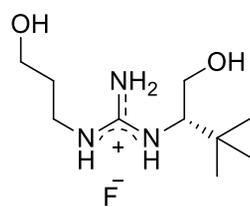


^{13}C NMR (151 MHz, CD_3OD)

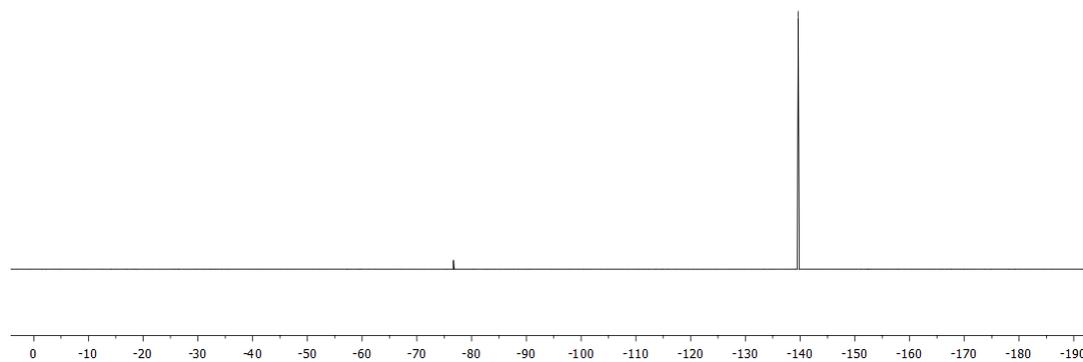


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^{19}F NMR (564 MHz, CD_3OD)

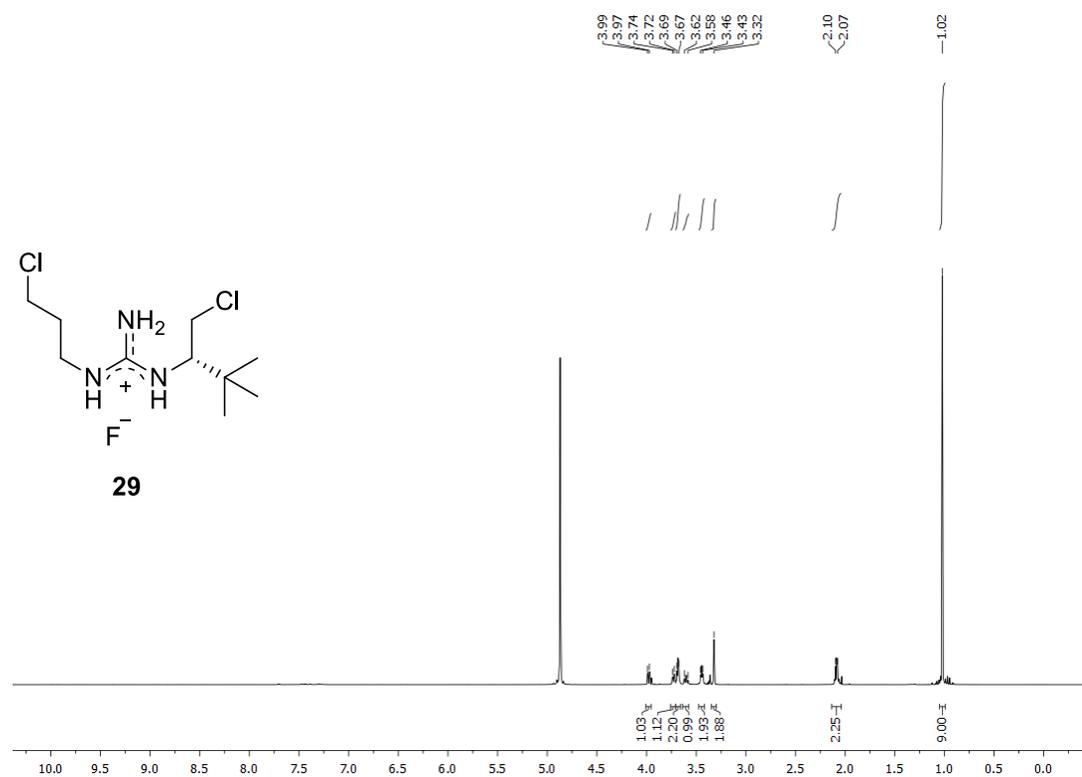


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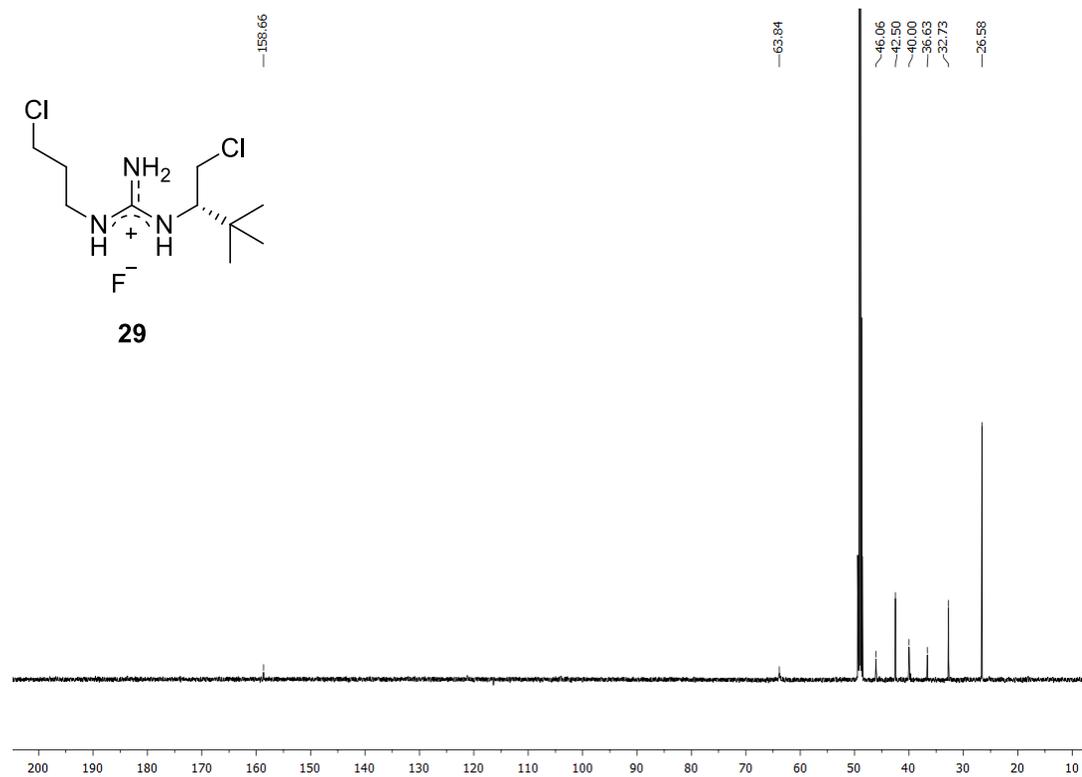


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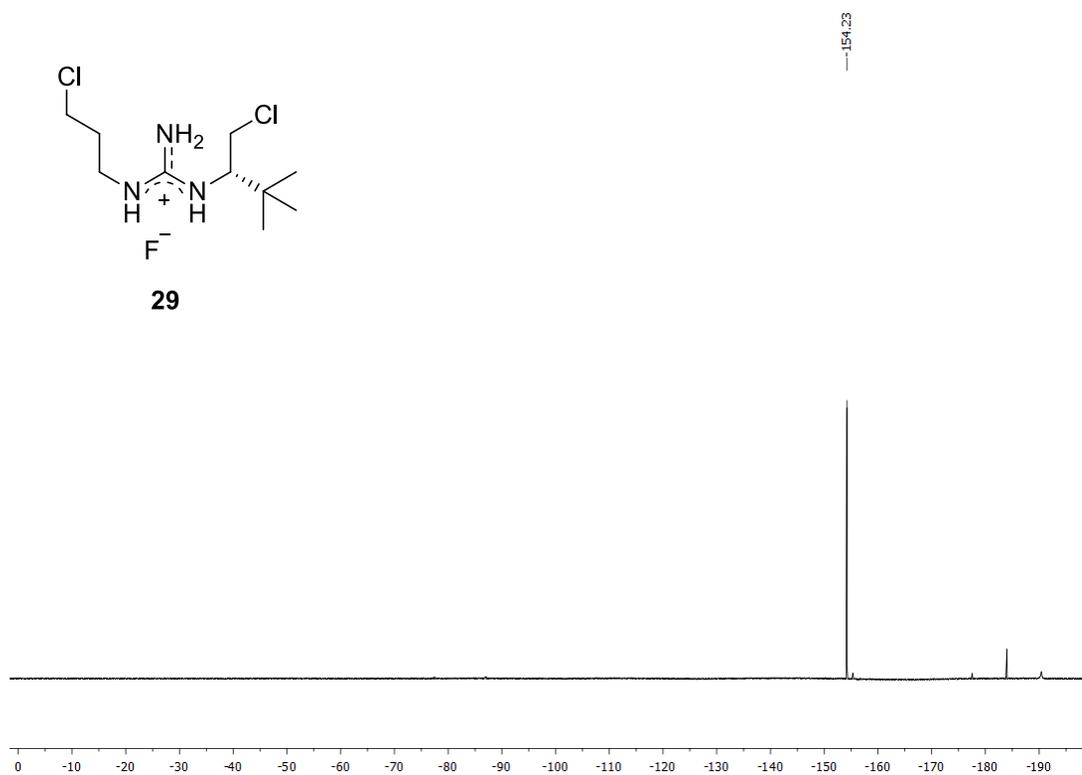
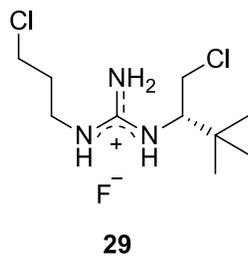


^{13}C NMR (151 MHz, CD_3OD)



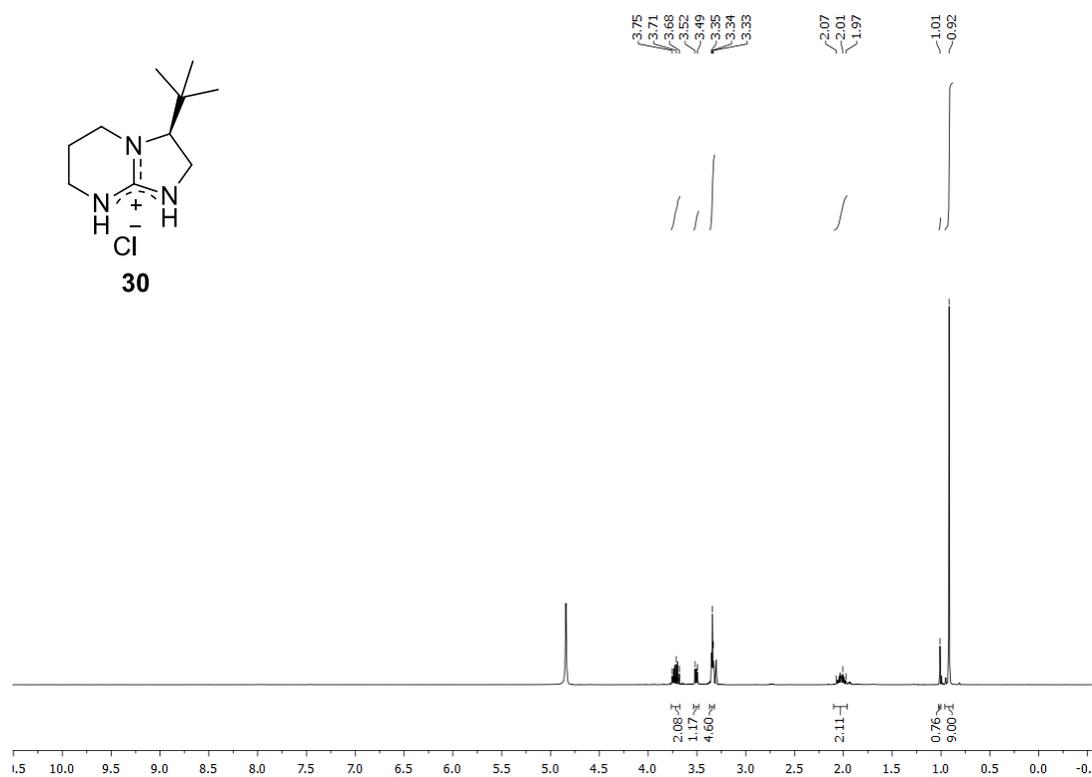
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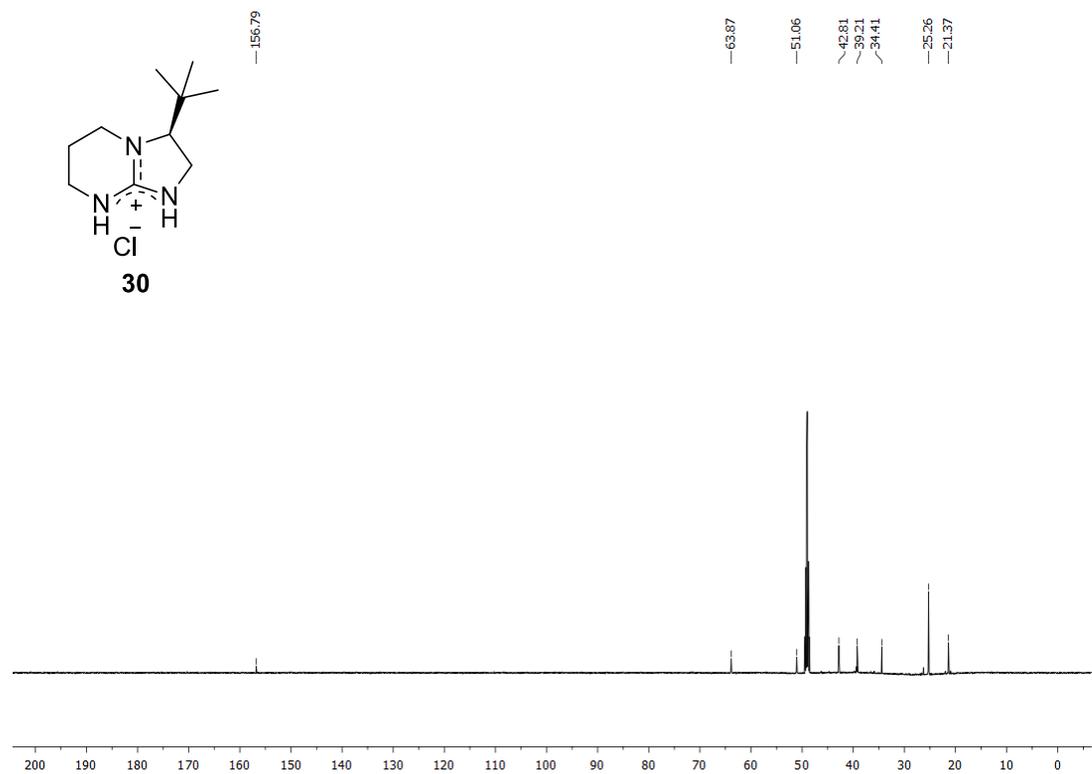


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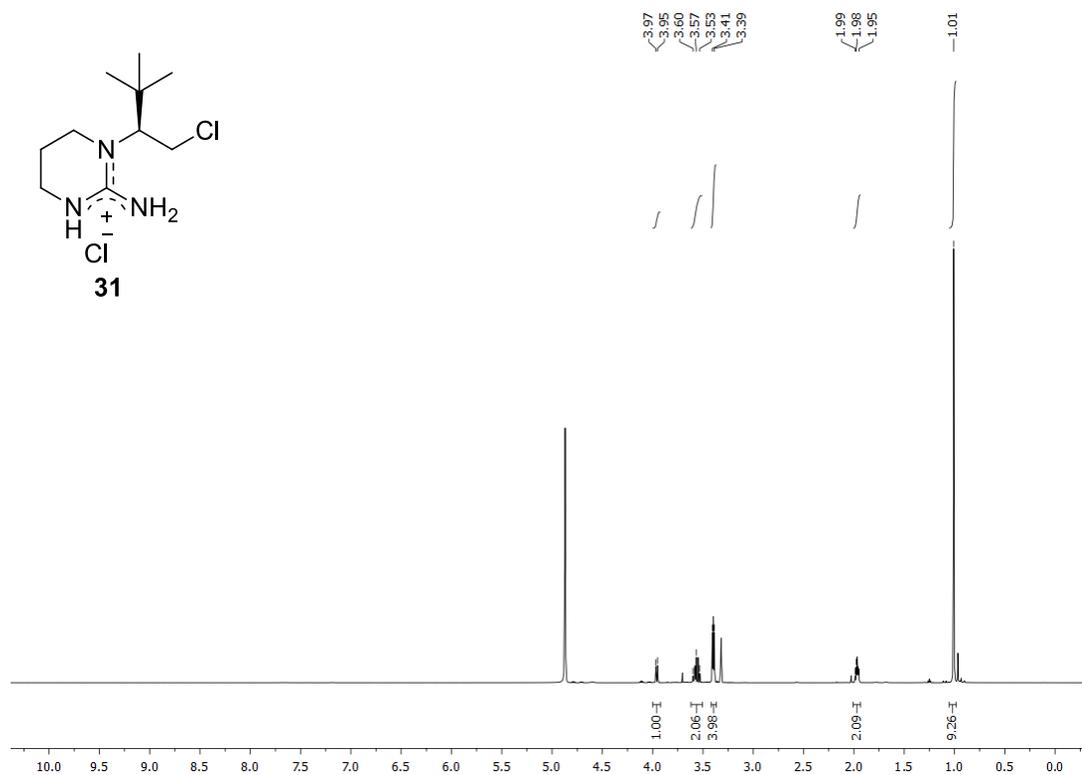


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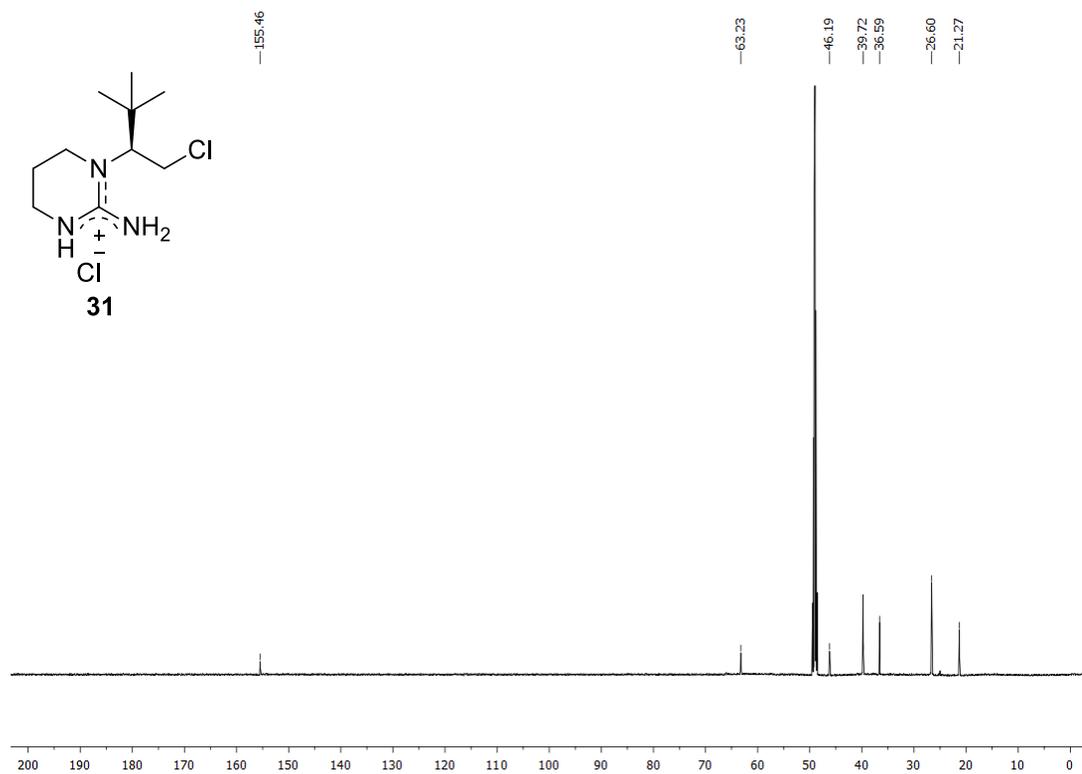


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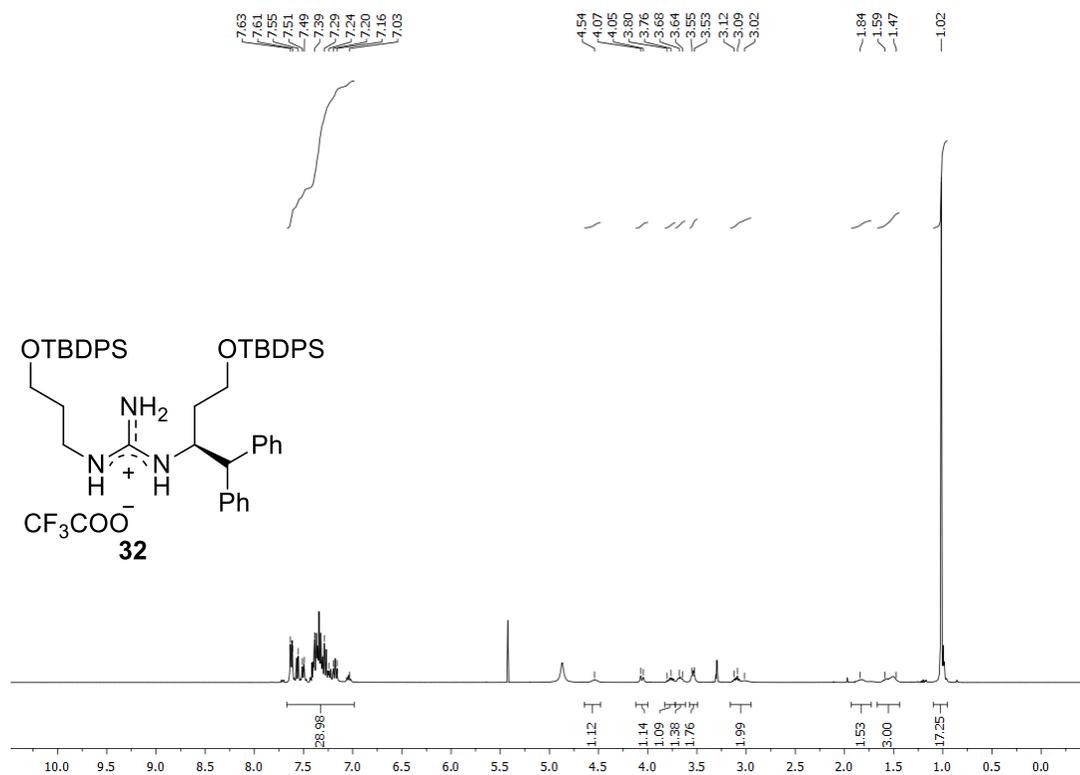


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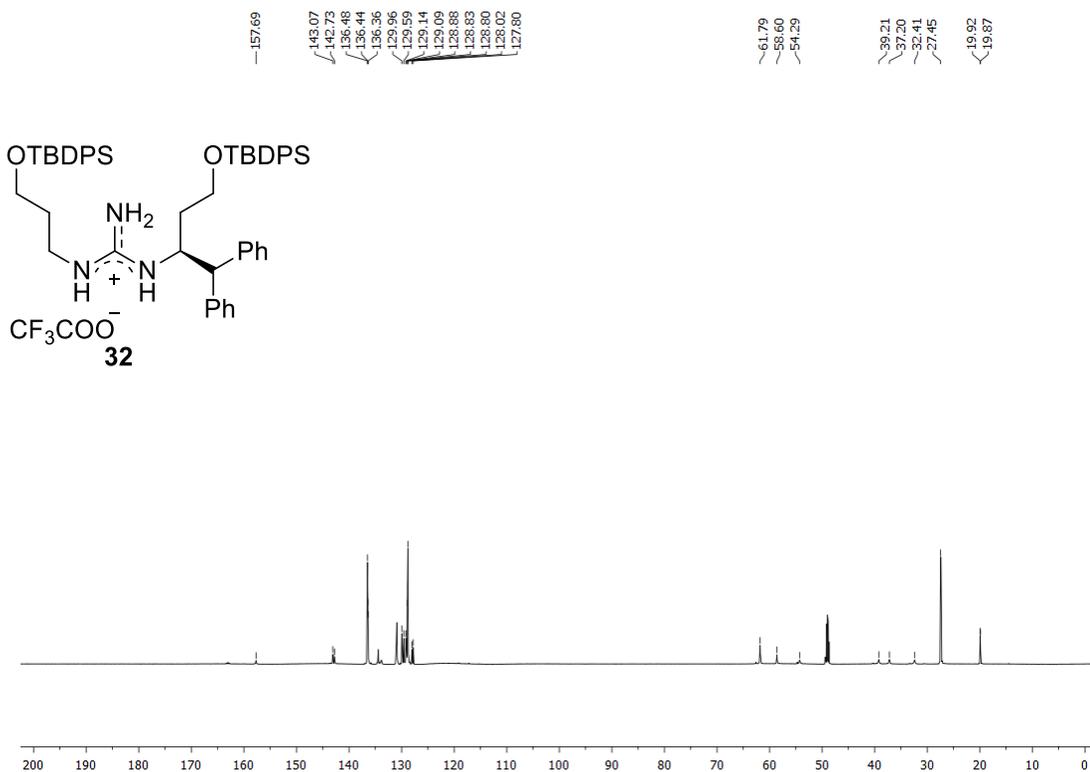


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^1H NMR (400 MHz, CD_3OD)

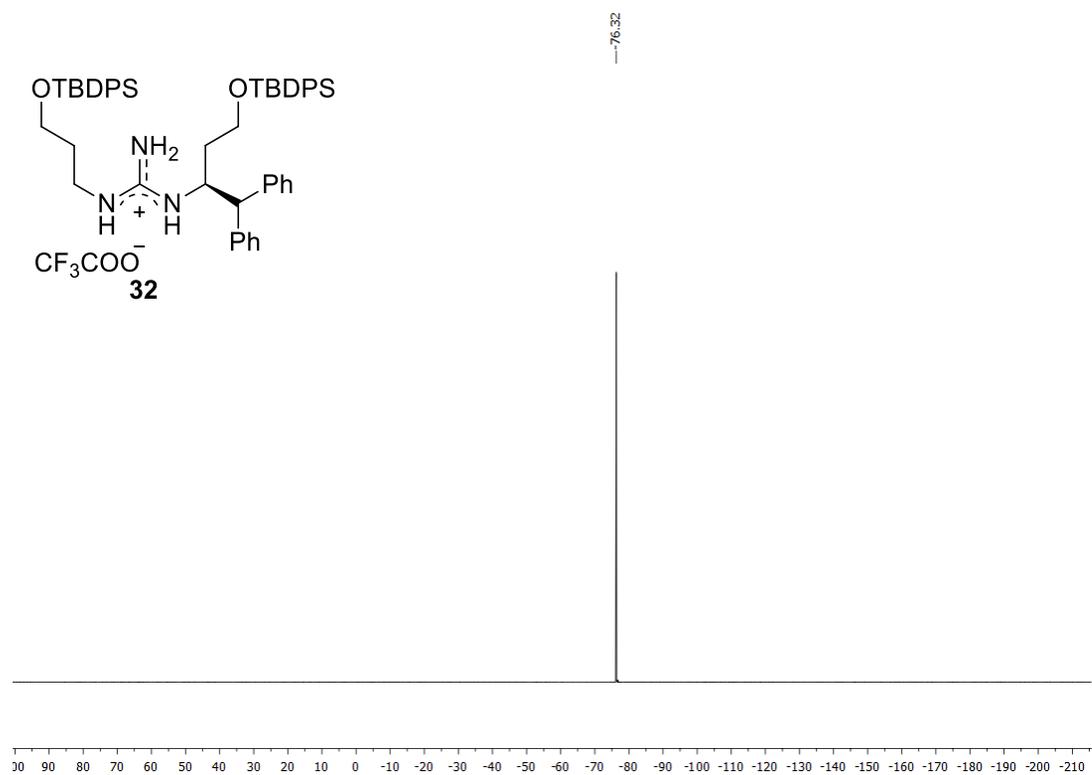


^{13}C NMR (151 MHz, CD_3OD)



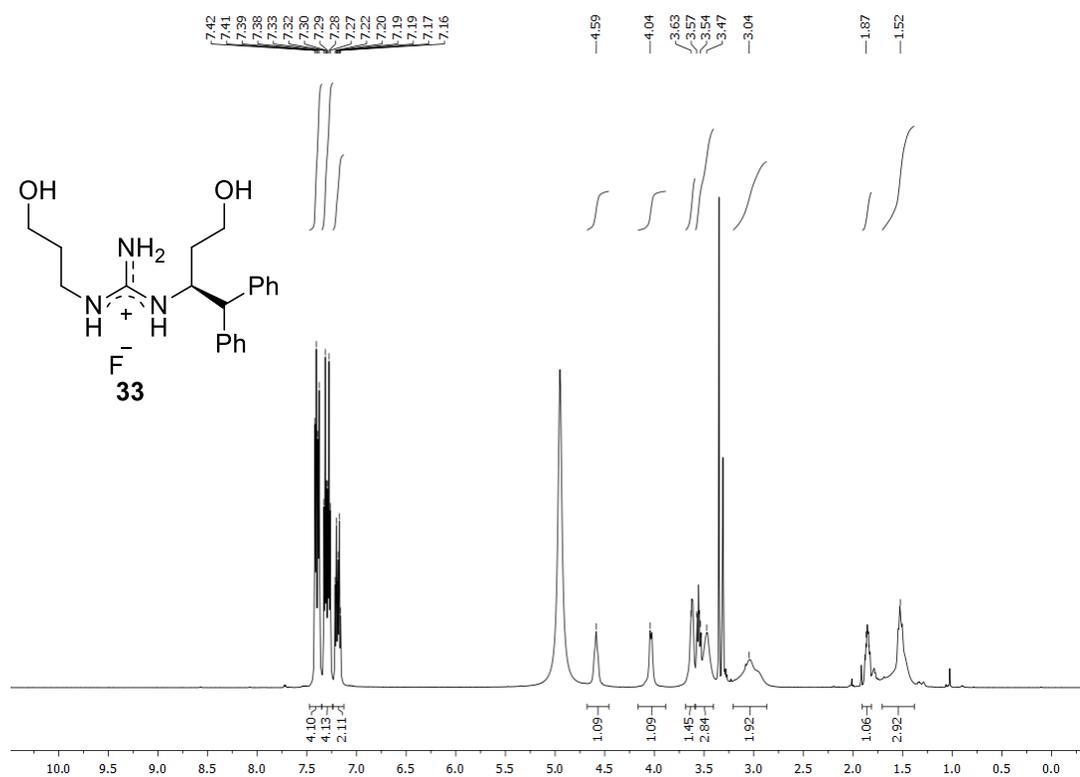
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^{19}F NMR (564 MHz, CD_3OD)

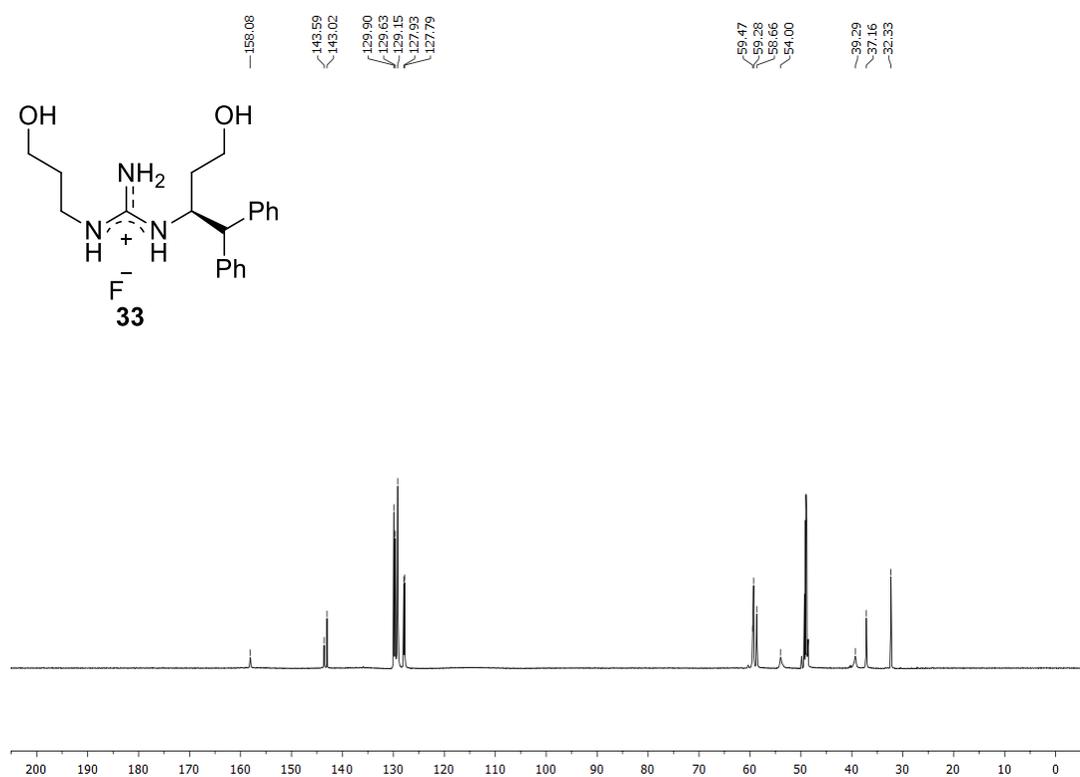


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^1H NMR (600 MHz, CD_3OD)

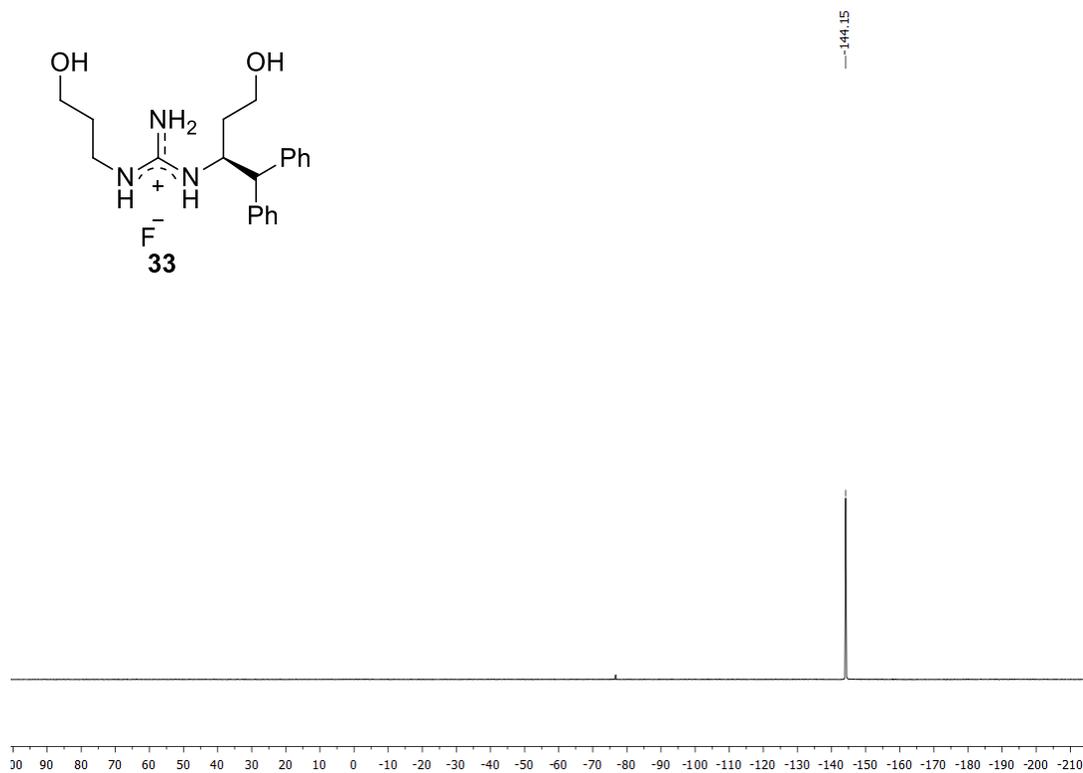
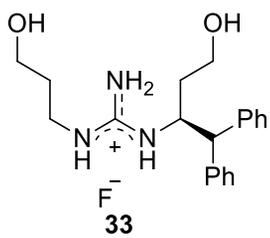


^{13}C NMR (151 MHz, CD_3OD)



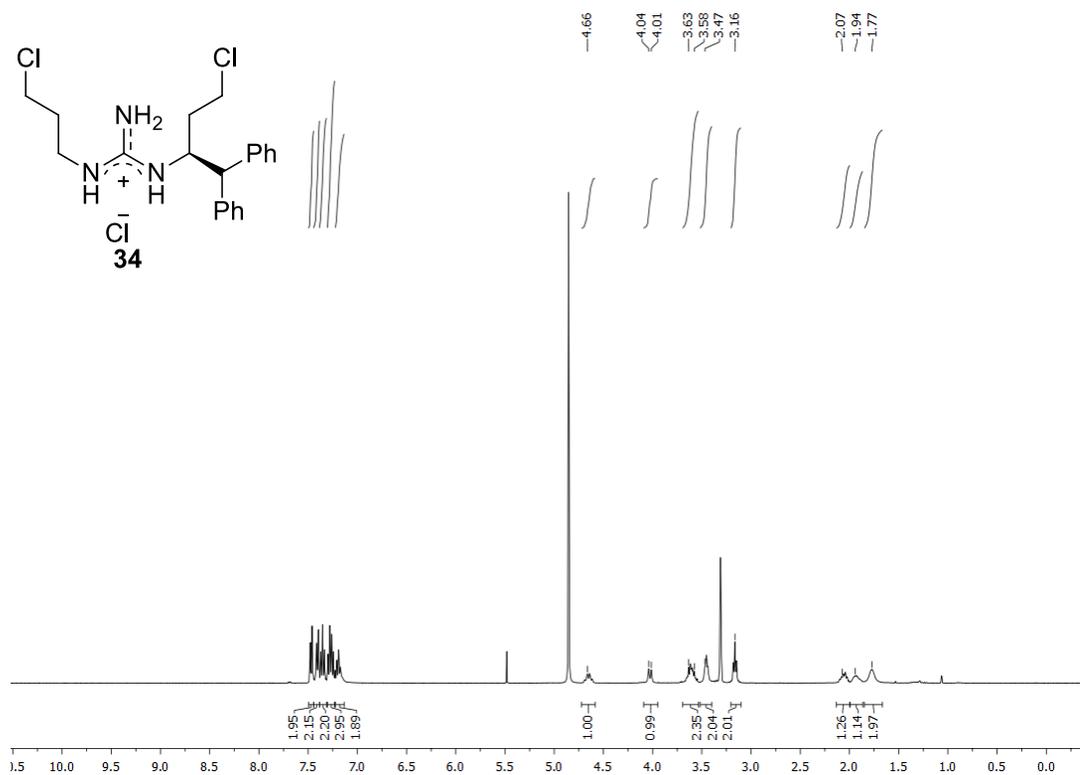
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^{19}F NMR (564 MHz, CD_3OD)

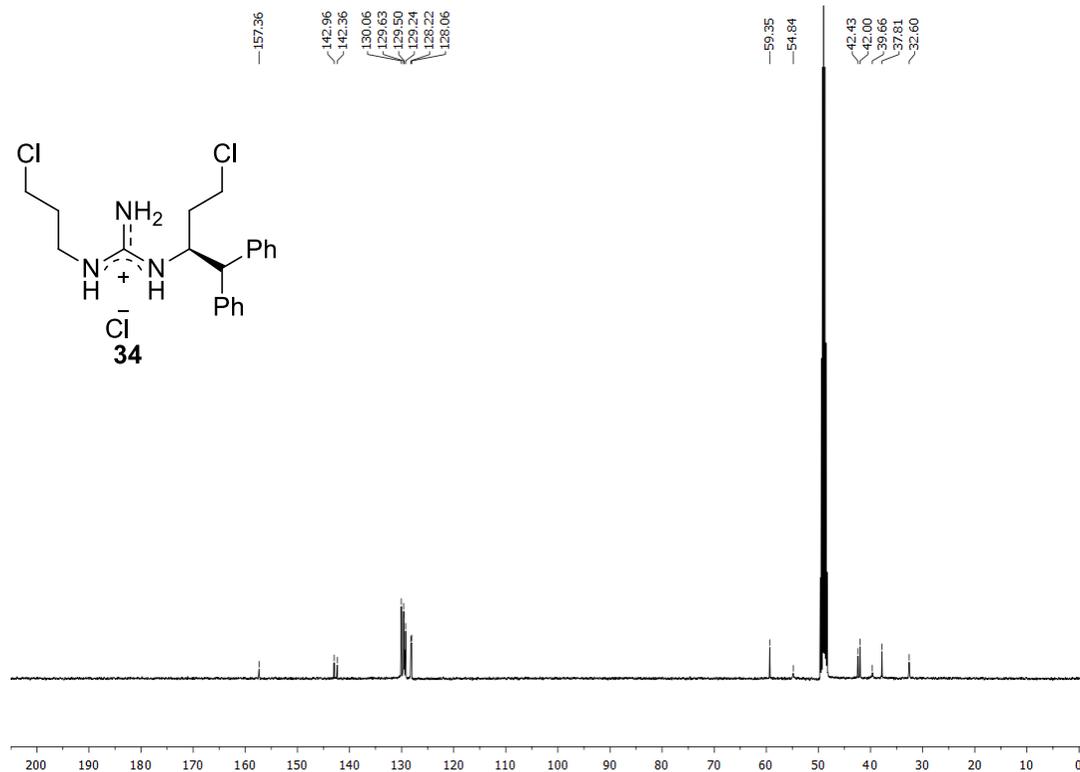


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^1H NMR (400 MHz, CD_3OD)

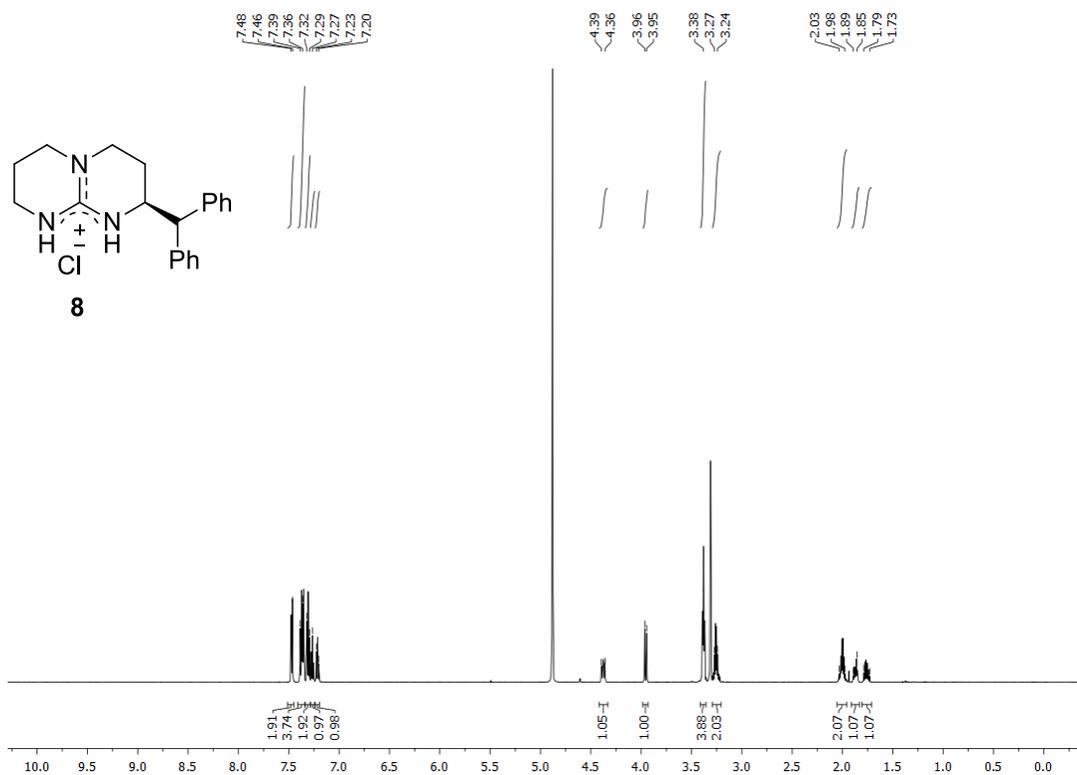


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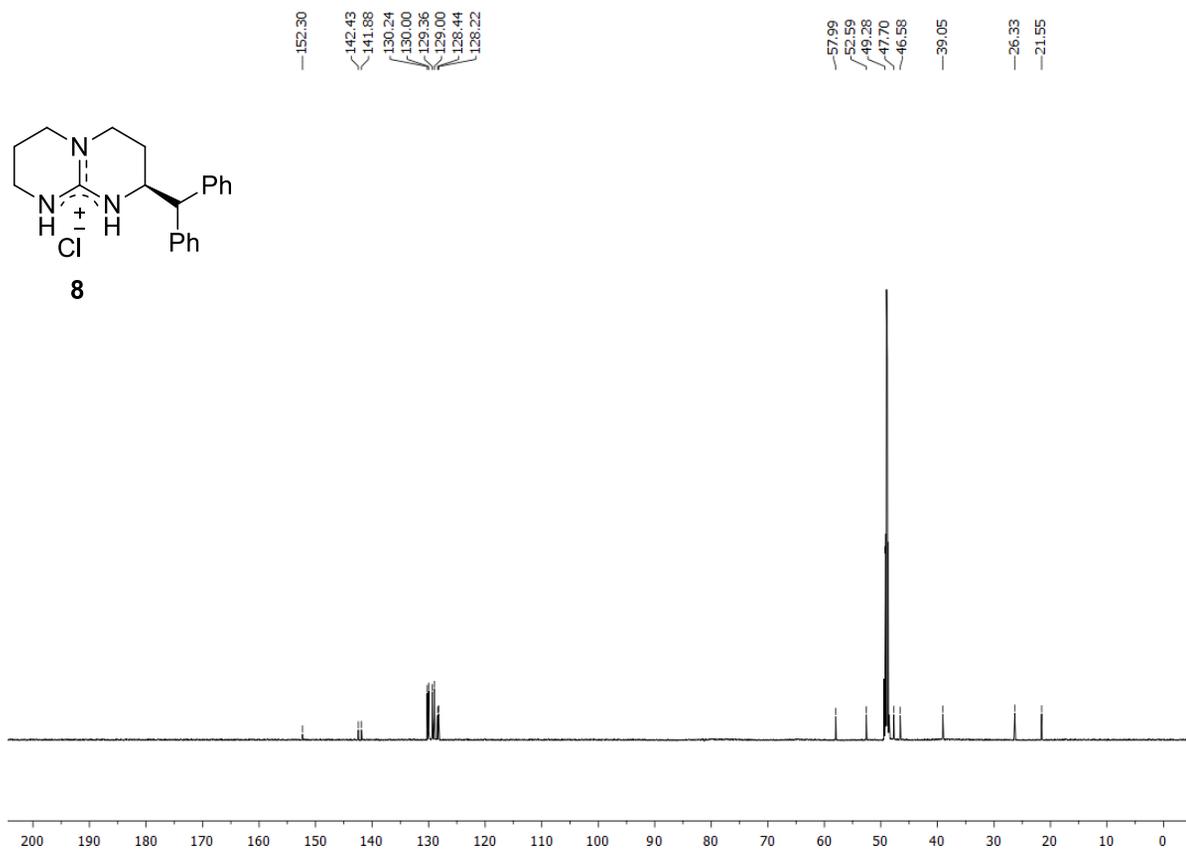


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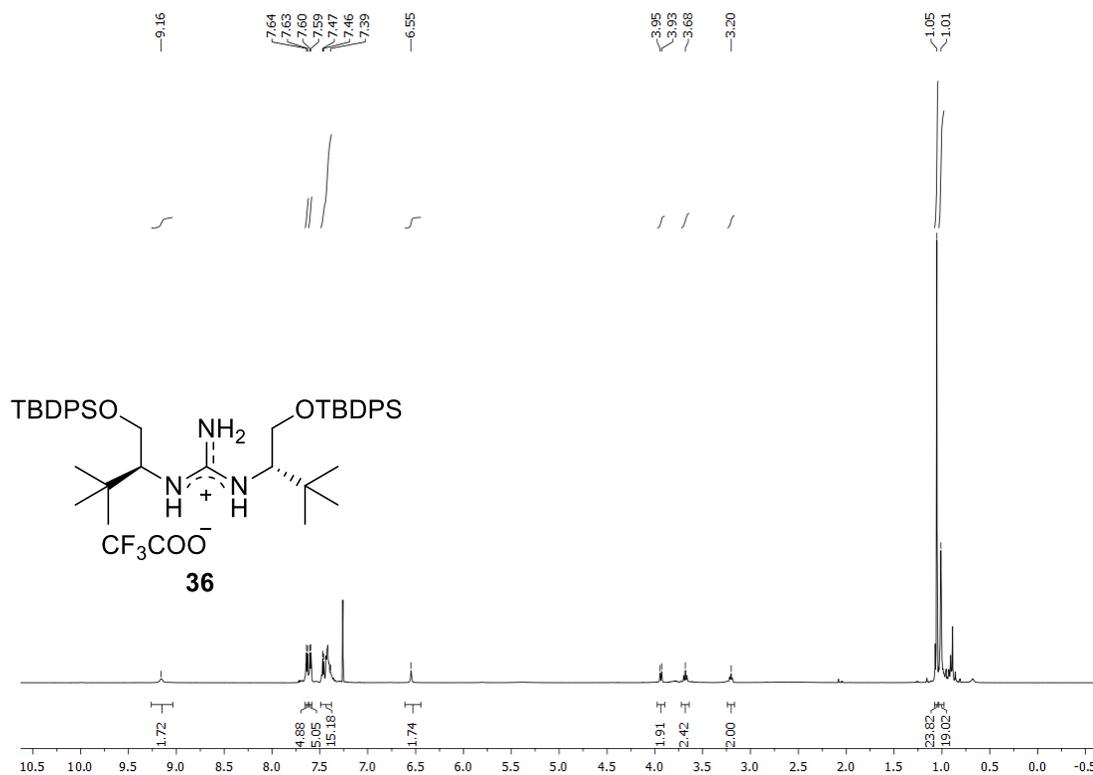


^{13}C NMR (151 MHz, CD_3OD)

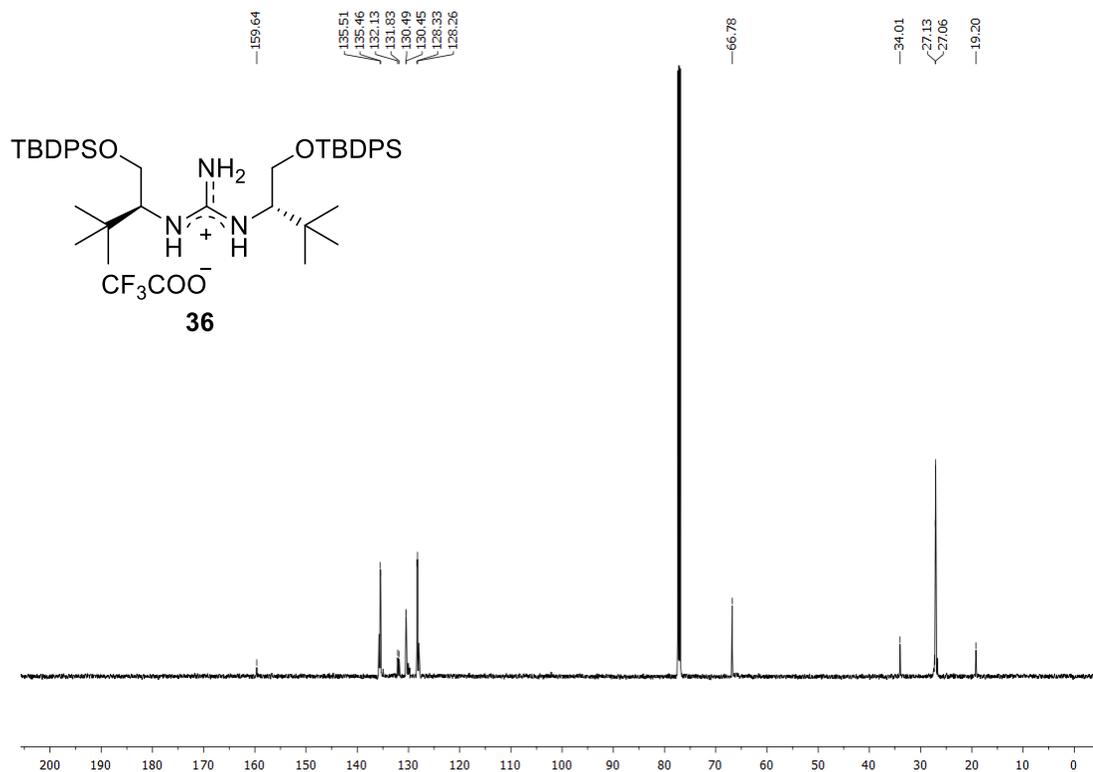


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^1H NMR (600 MHz, CDCl_3)

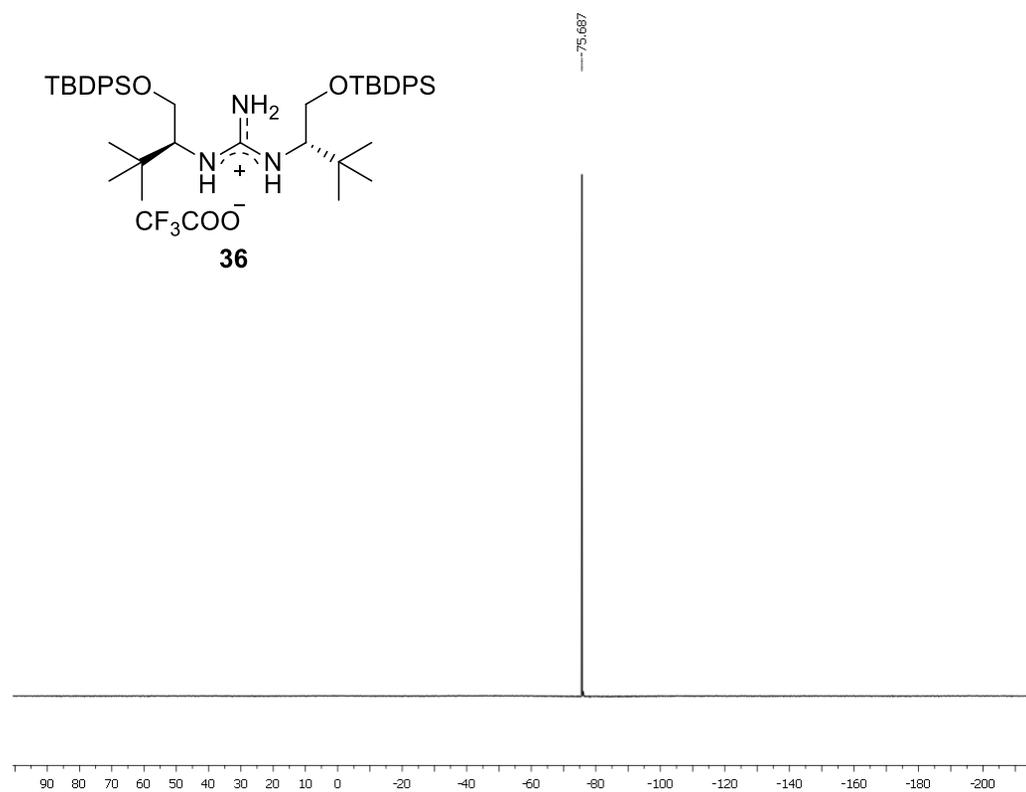


^{13}C NMR (151 MHz, CDCl_3)



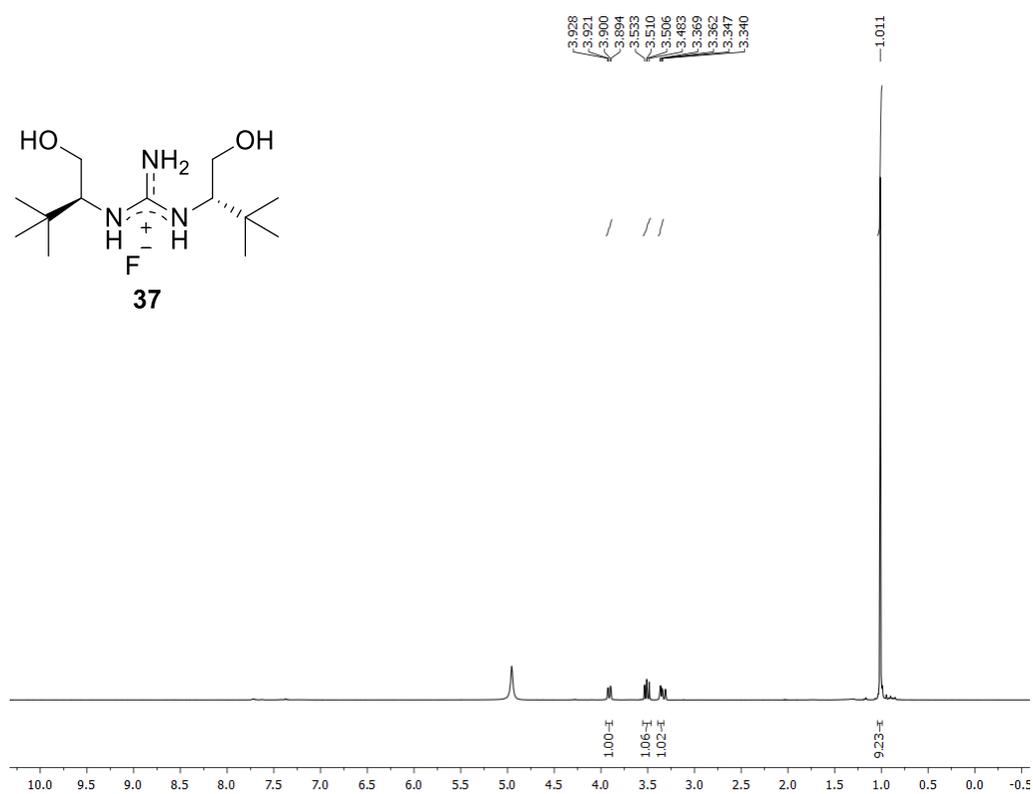
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^{19}F NMR (564 MHz, CDCl_3)

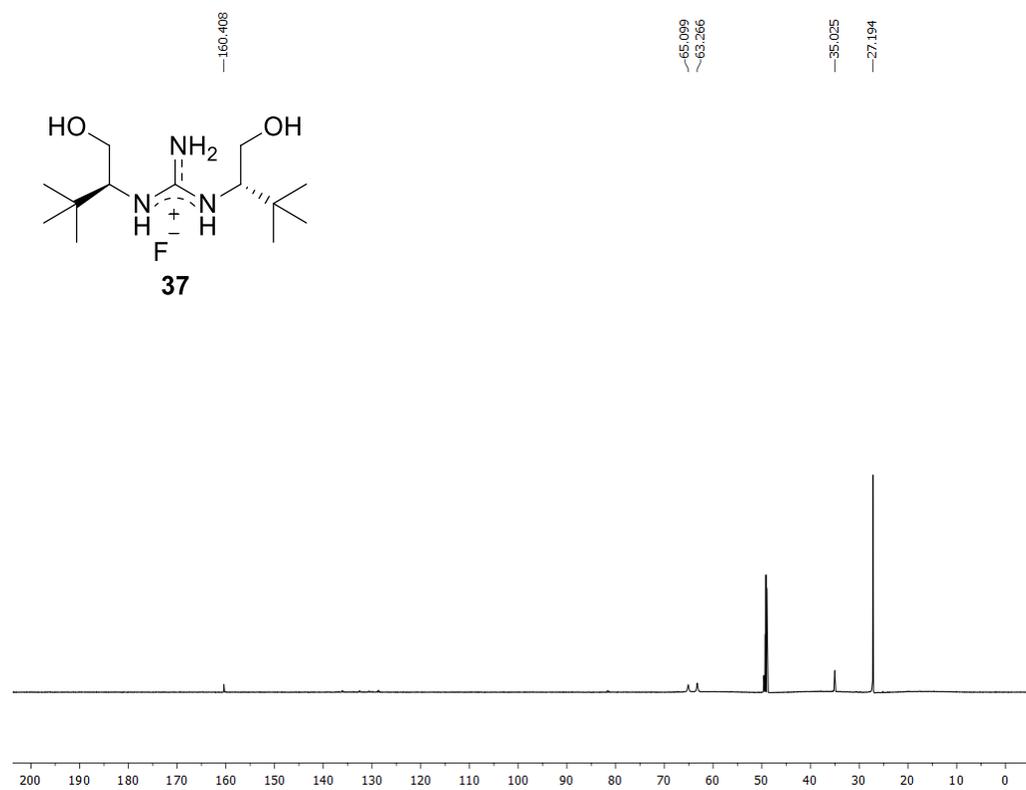


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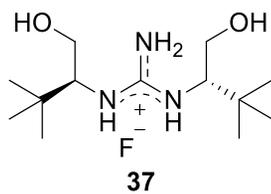


^{13}C NMR (151 MHz, CD_3OD)

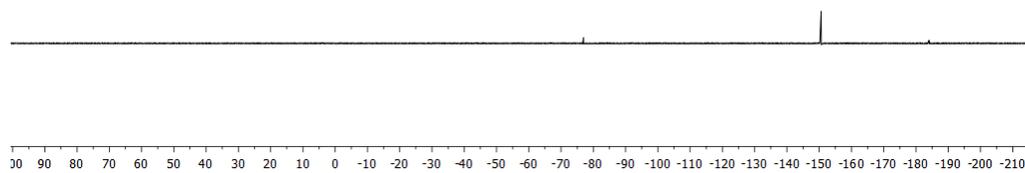


Supporting information

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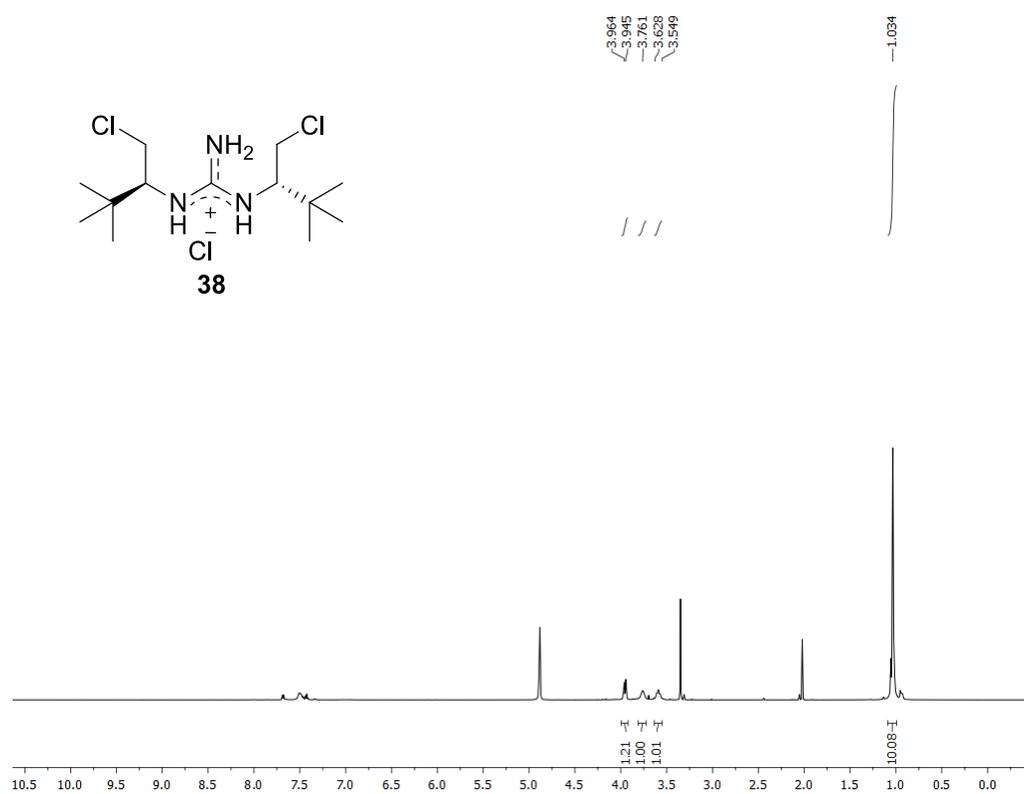


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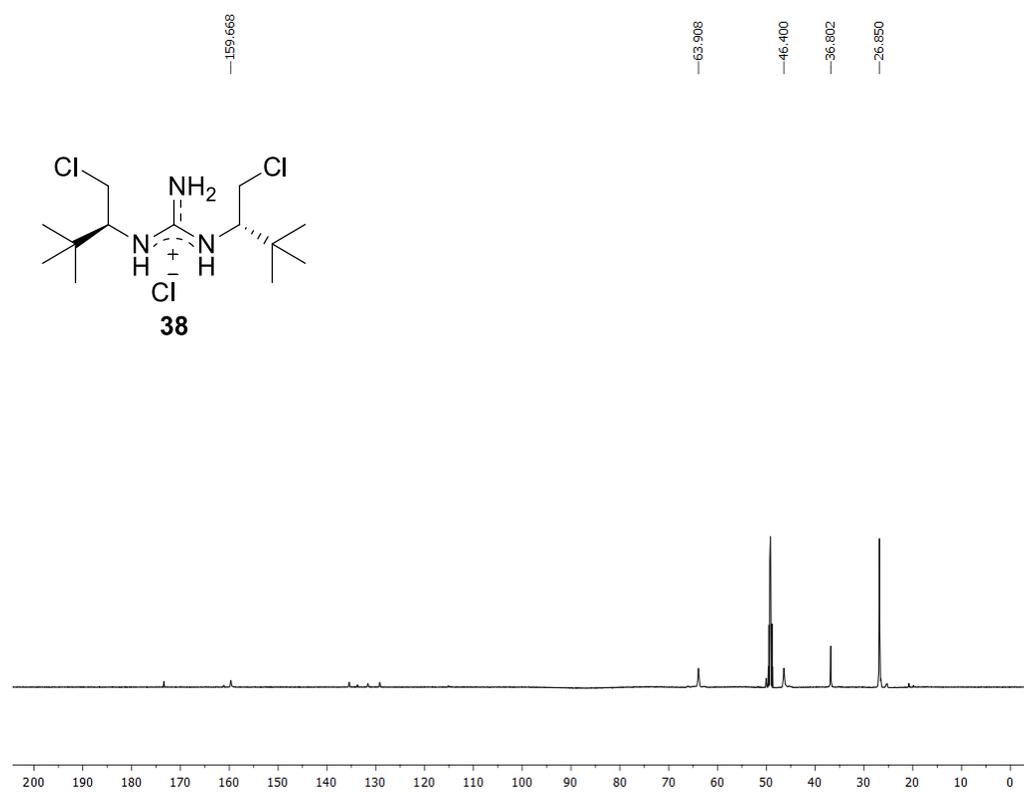


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^1H NMR (600 MHz, CD_3OD)

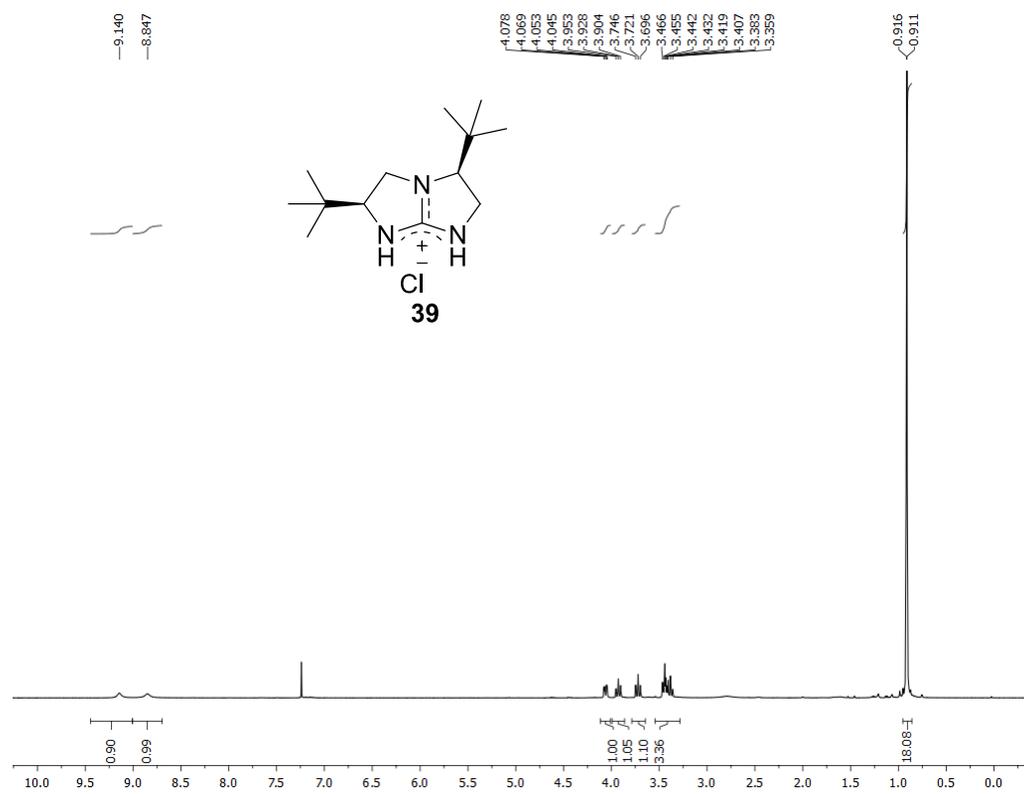


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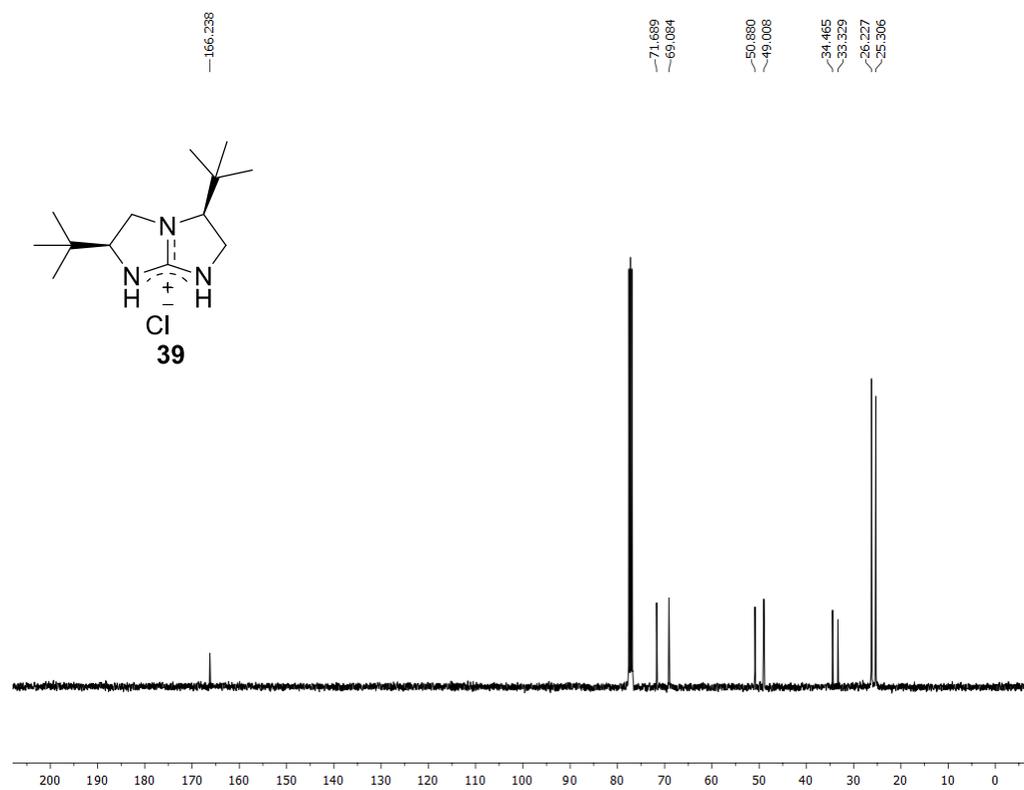


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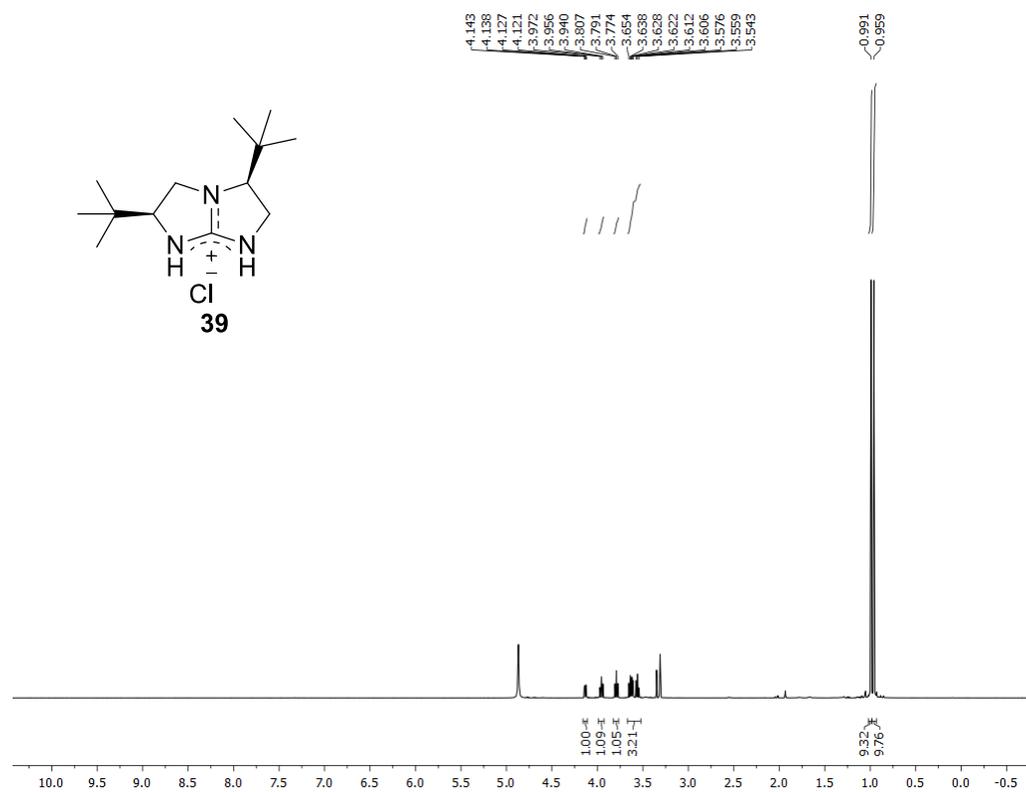


^{13}C NMR (101 MHz, CDCl_3)

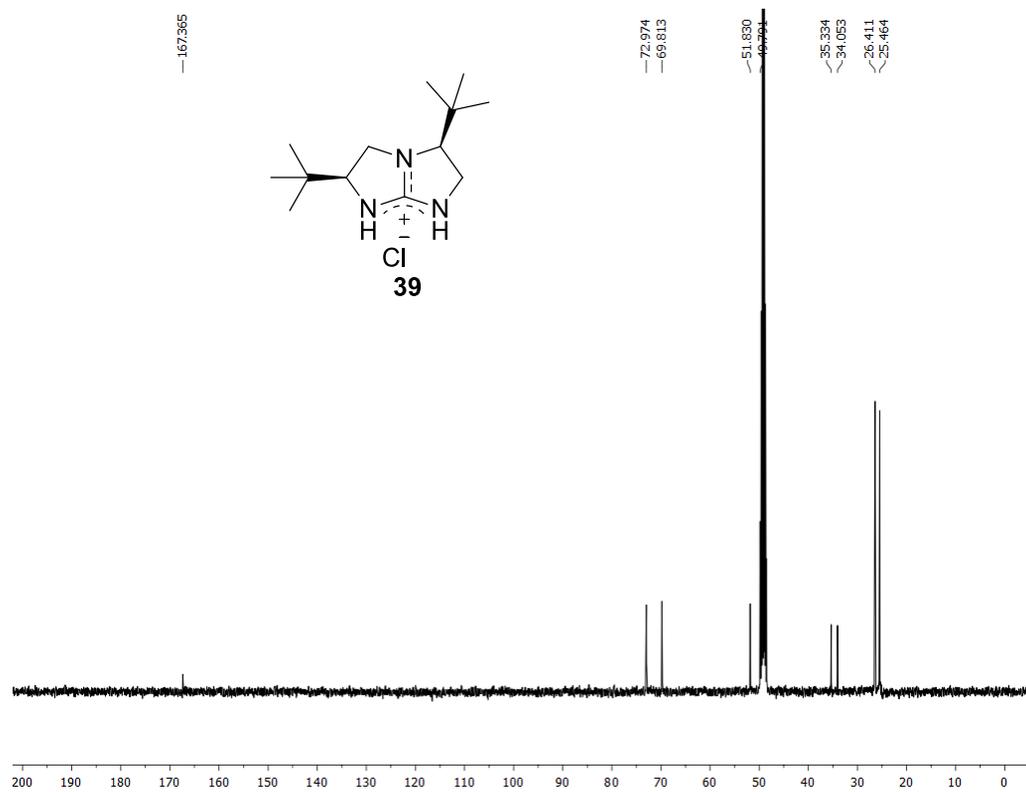


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^1H NMR (600 MHz, CD_3OD)

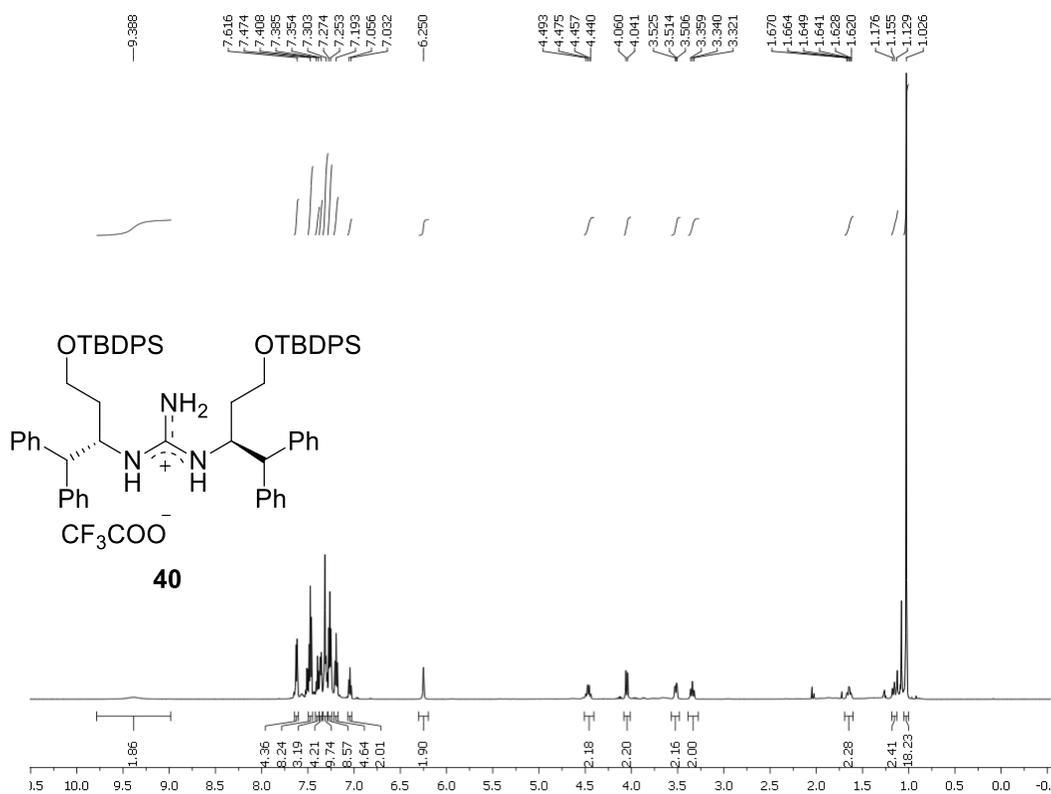


^{13}C NMR (101 MHz, CD_3OD)

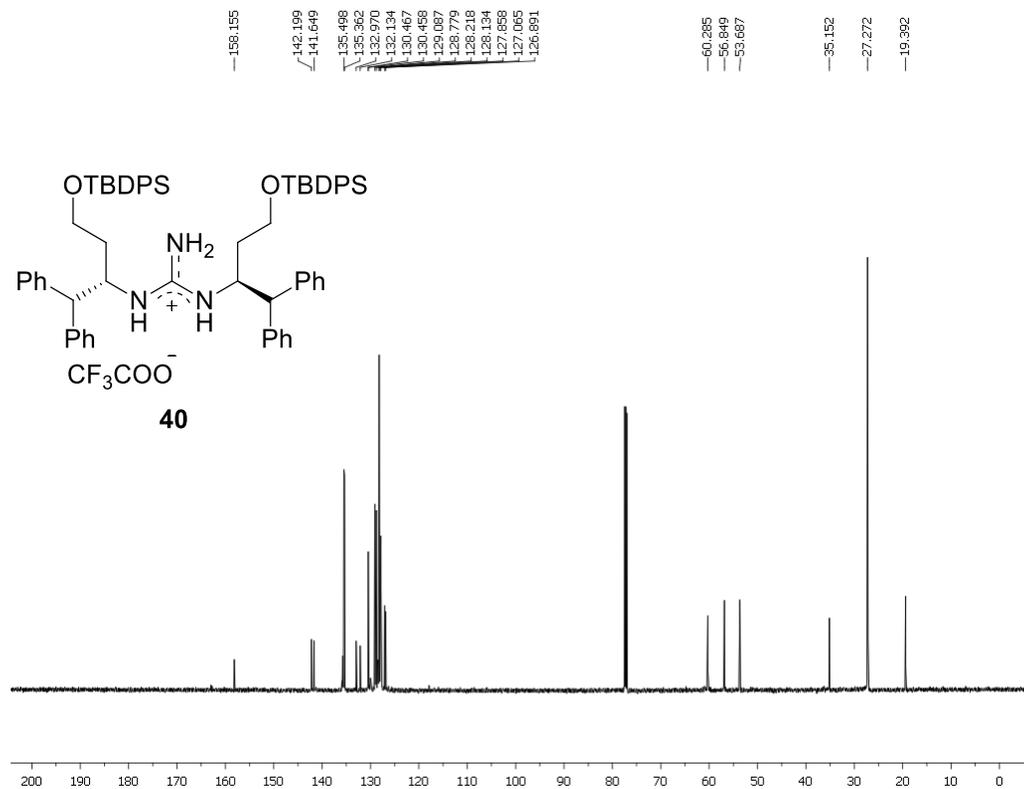


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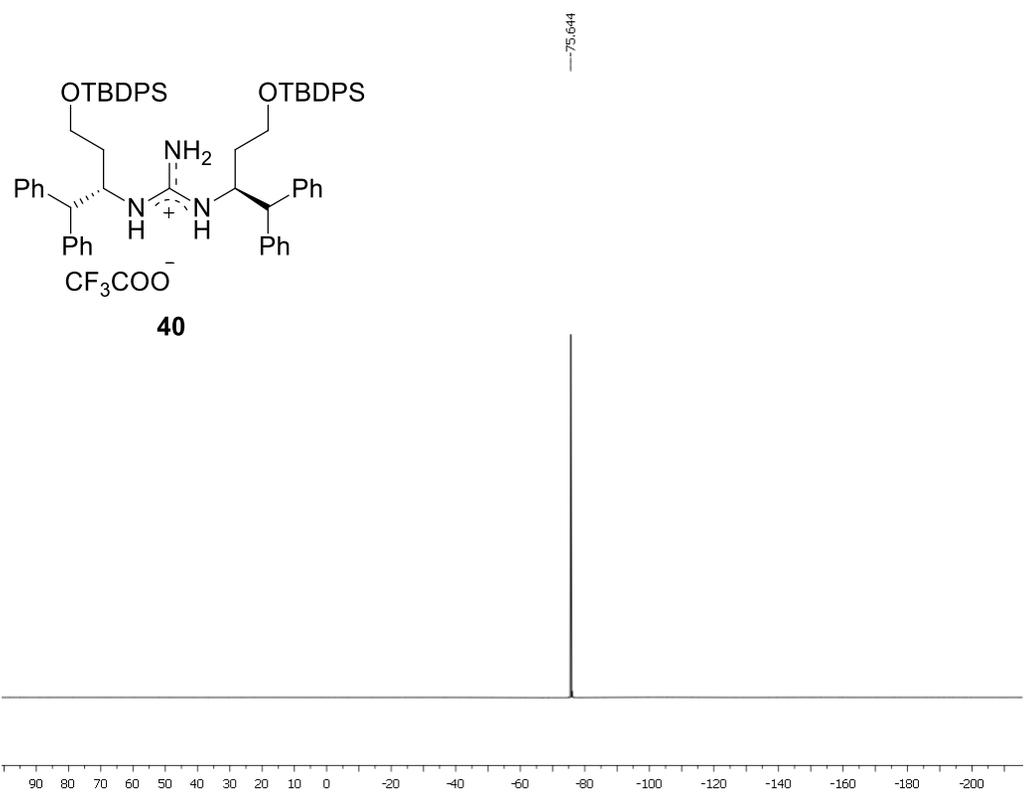


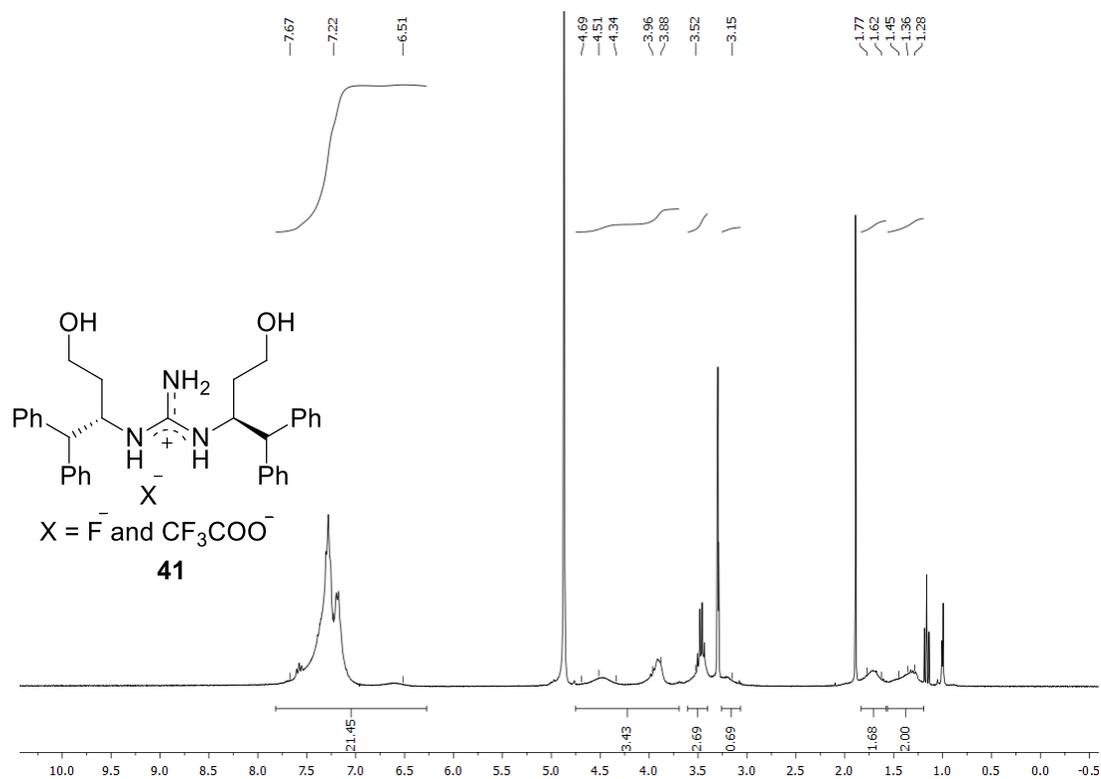
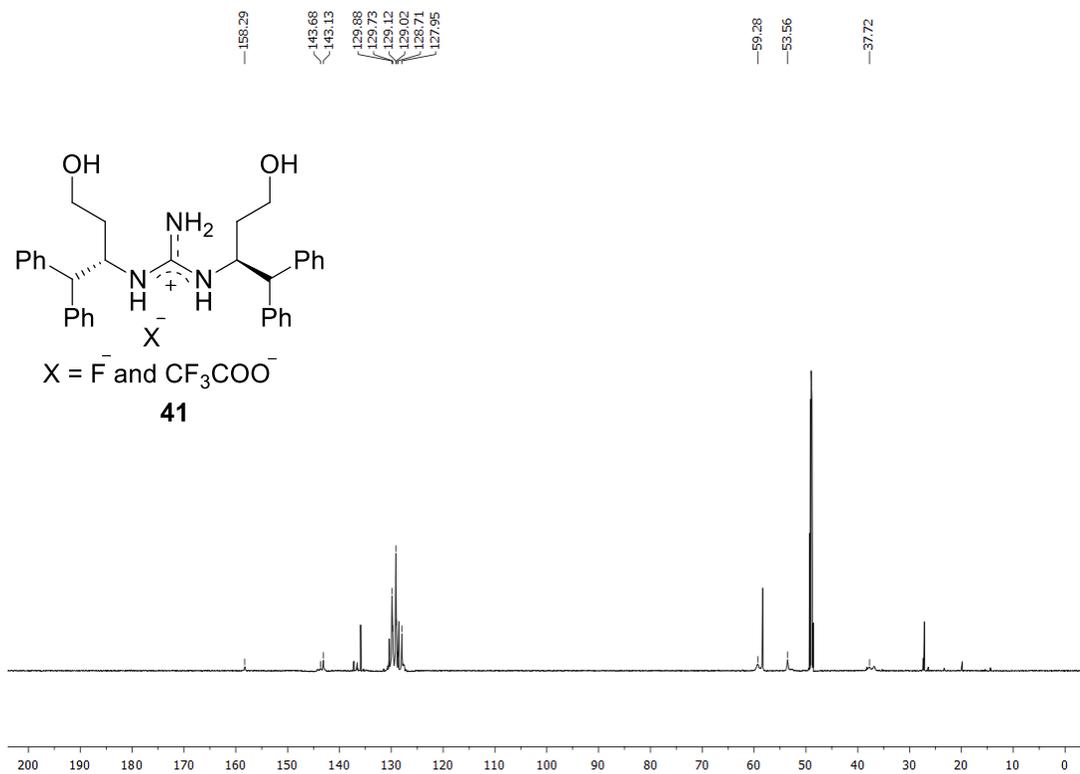
^{13}C NMR (151 MHz, CDCl_3)



Supporting information

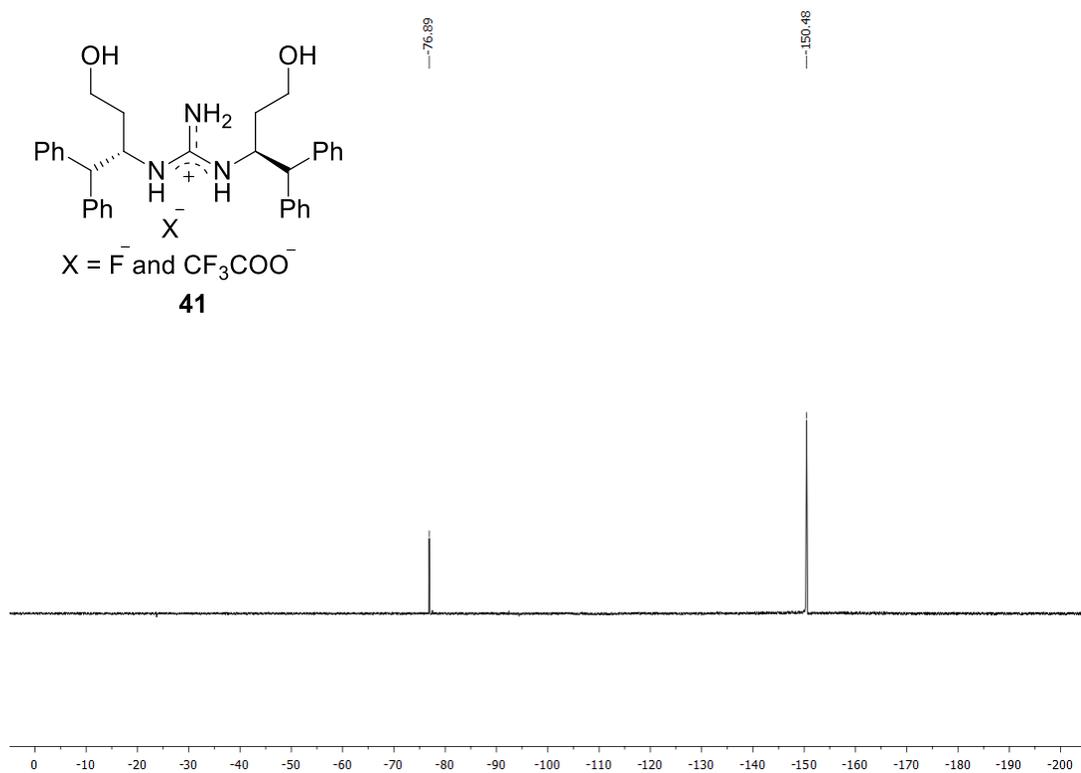
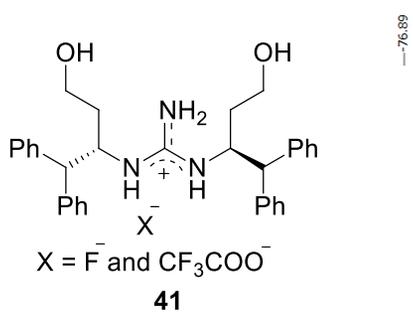
^{19}F NMR (282 MHz, CDCl_3)



^1H NMR (600 MHz, CD_3OD) ^{13}C NMR (151 MHz, CD_3OD)

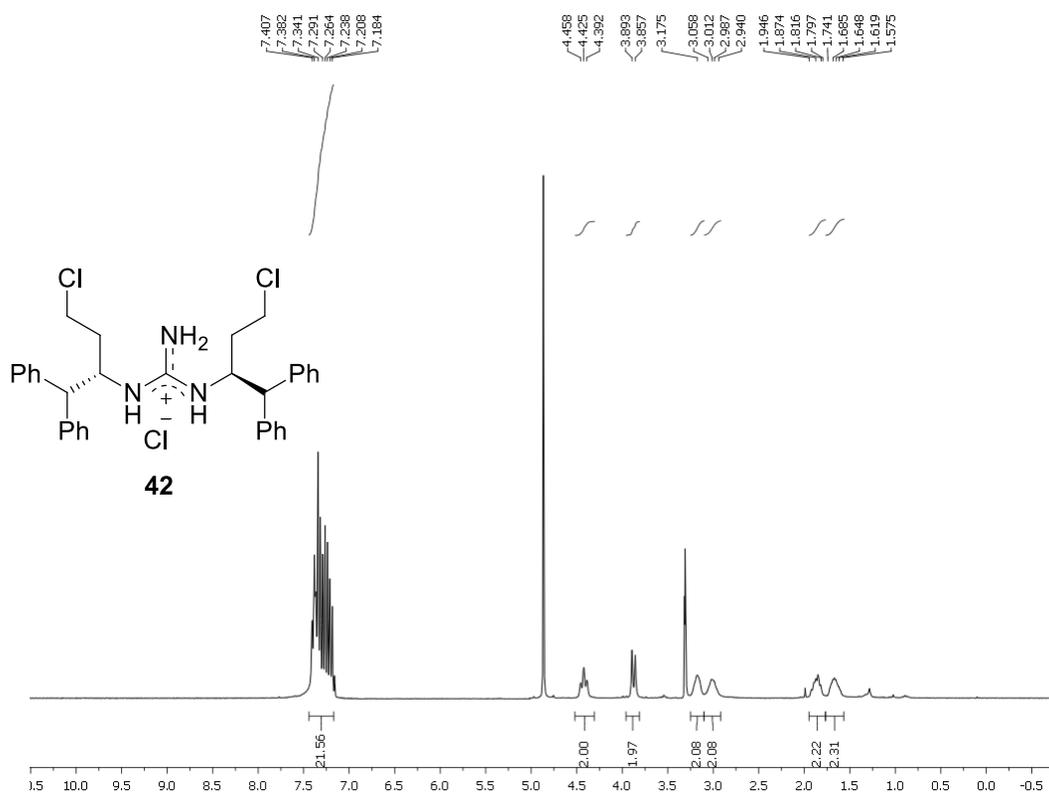
Supporting information

^{19}F NMR (282 MHz, CD_3OD)

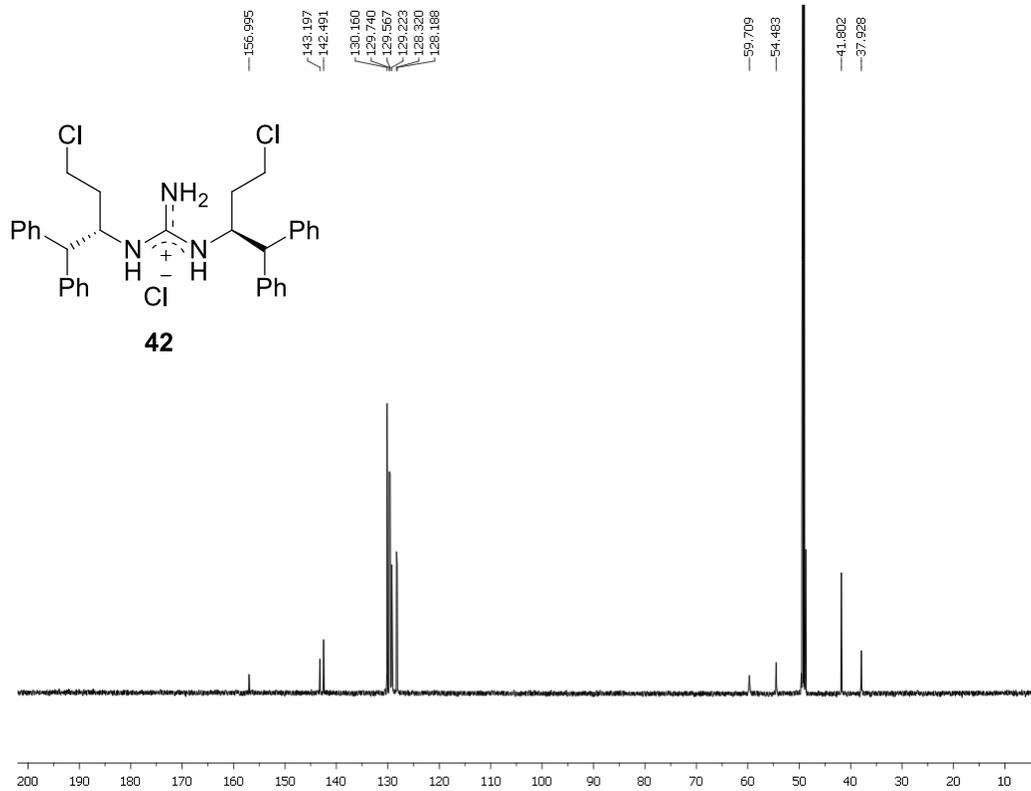


Supporting information

^1H NMR (300 MHz, CD_3OD)

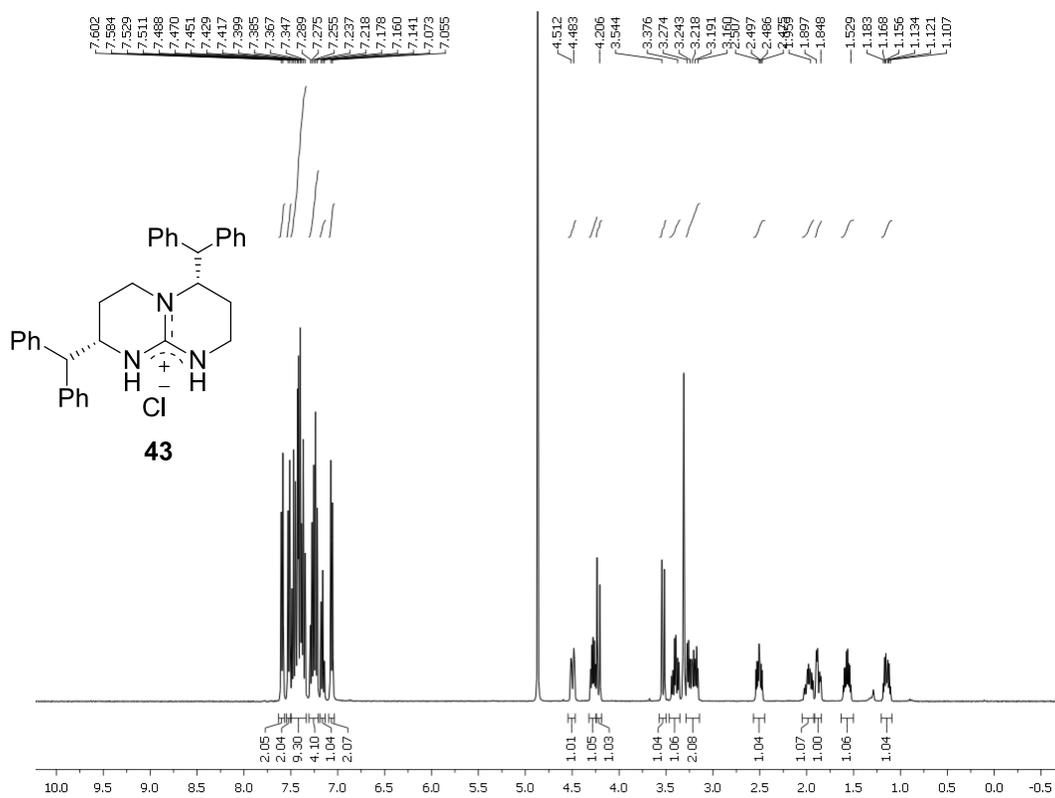


^{13}C NMR (151 MHz, CD_3OD)

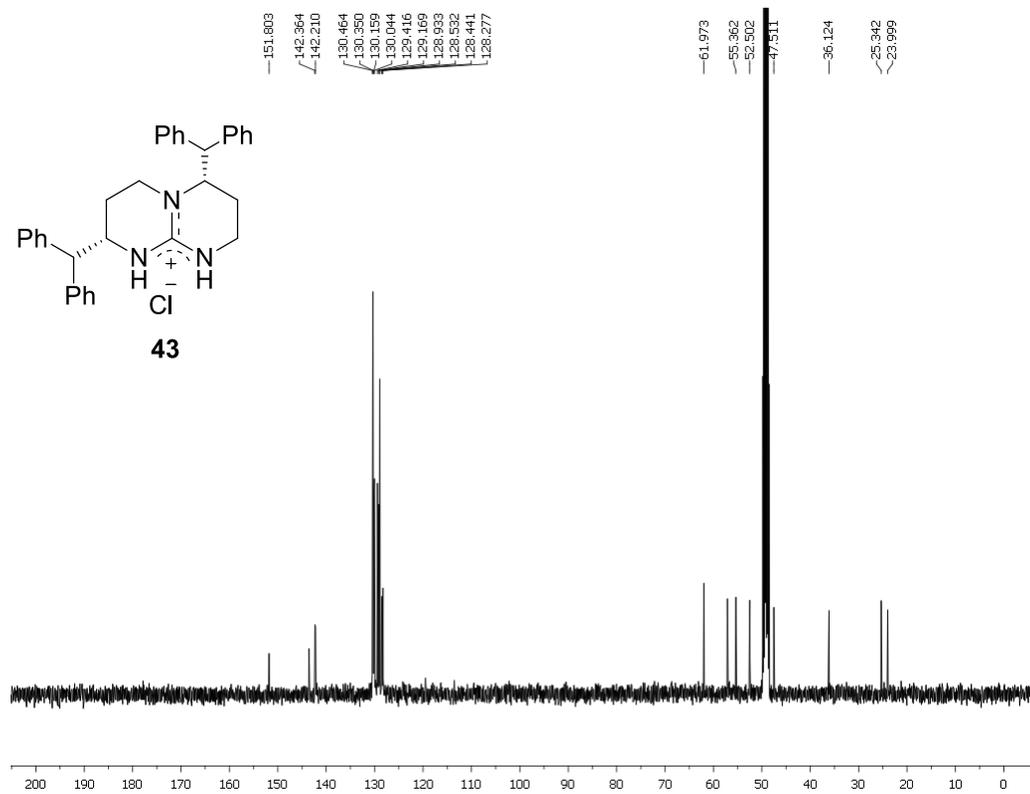


Supporting information

^1H NMR (400 MHz, CD_3OD)

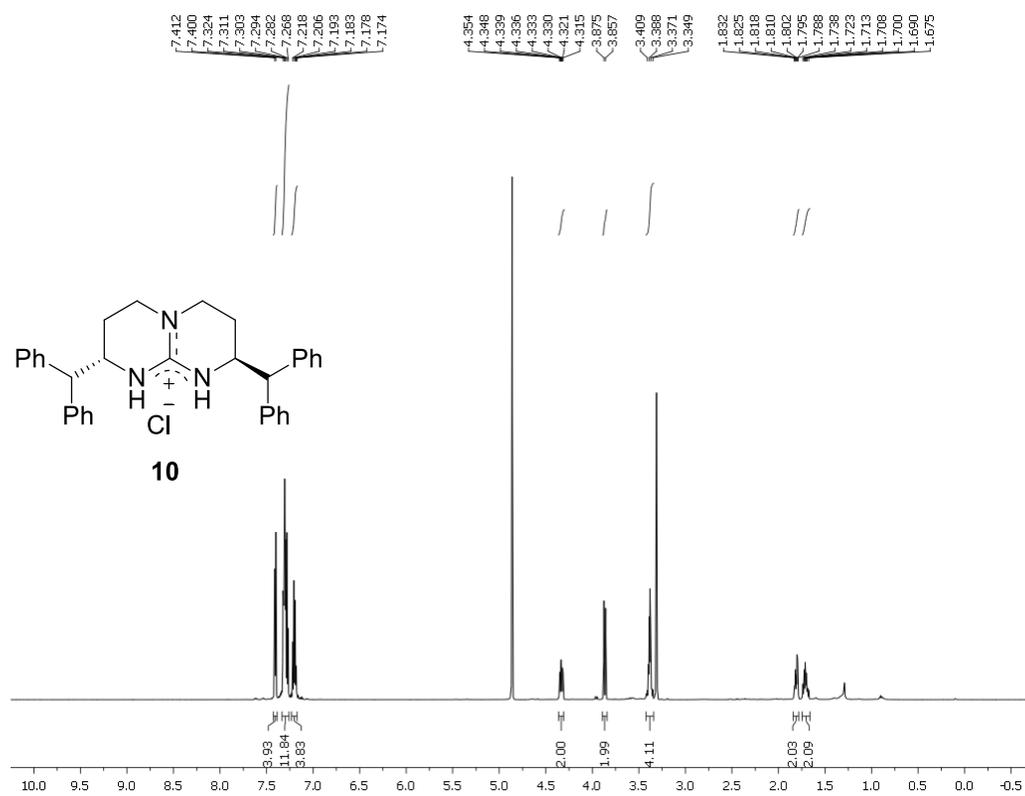


^{13}C NMR (101 MHz, CD_3OD)

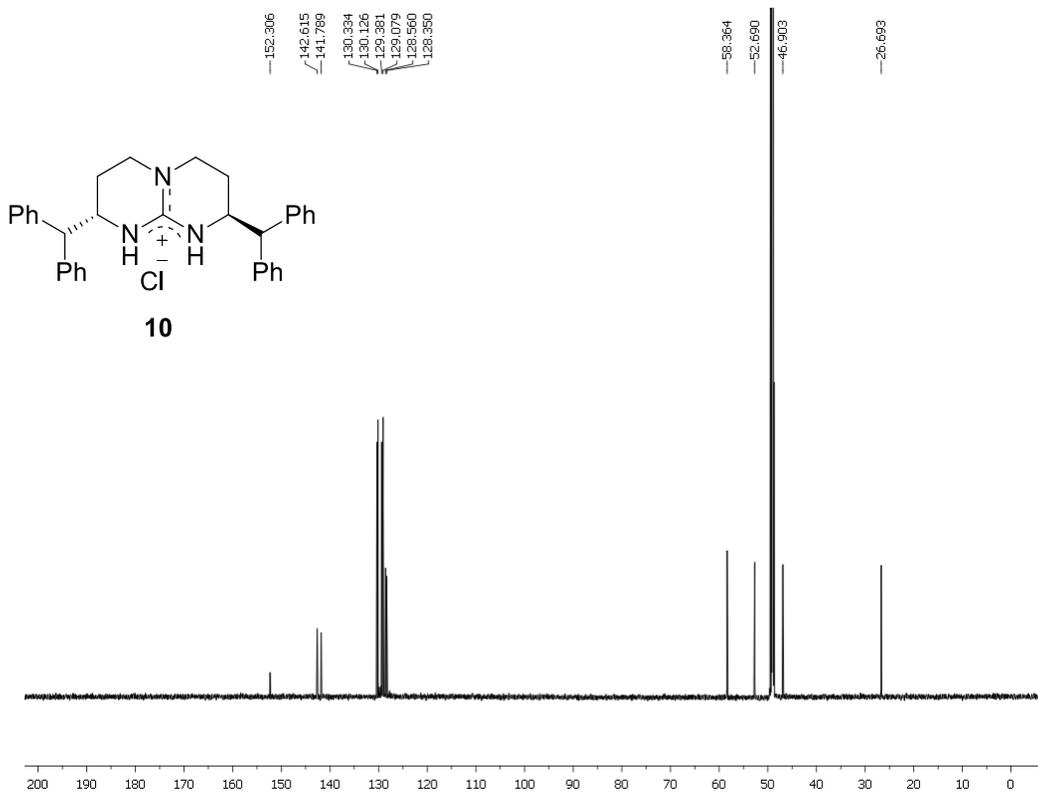


Supporting information

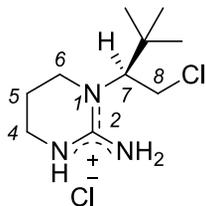
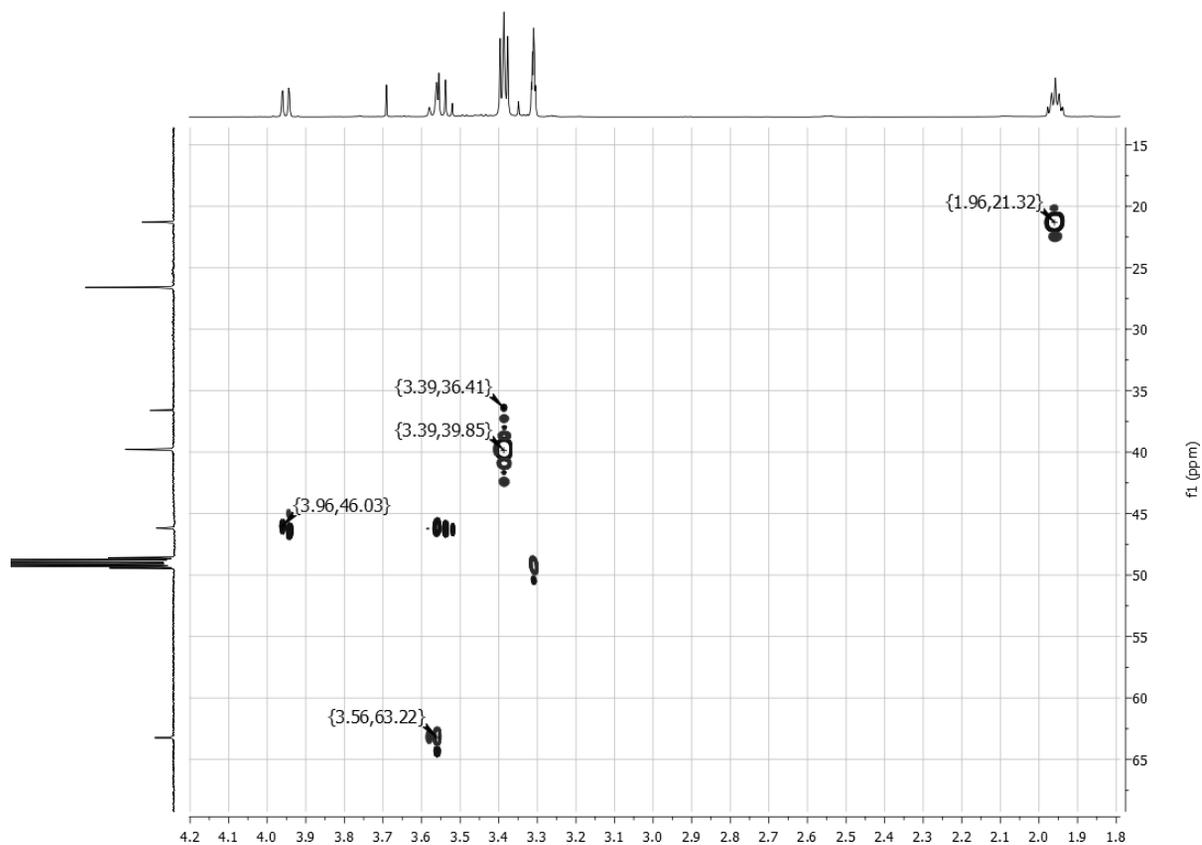
^1H NMR (600 MHz, CD_3OD)



^{13}C NMR (151 MHz, CD_3OD)

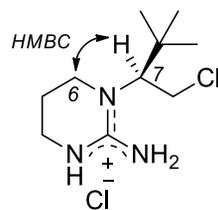
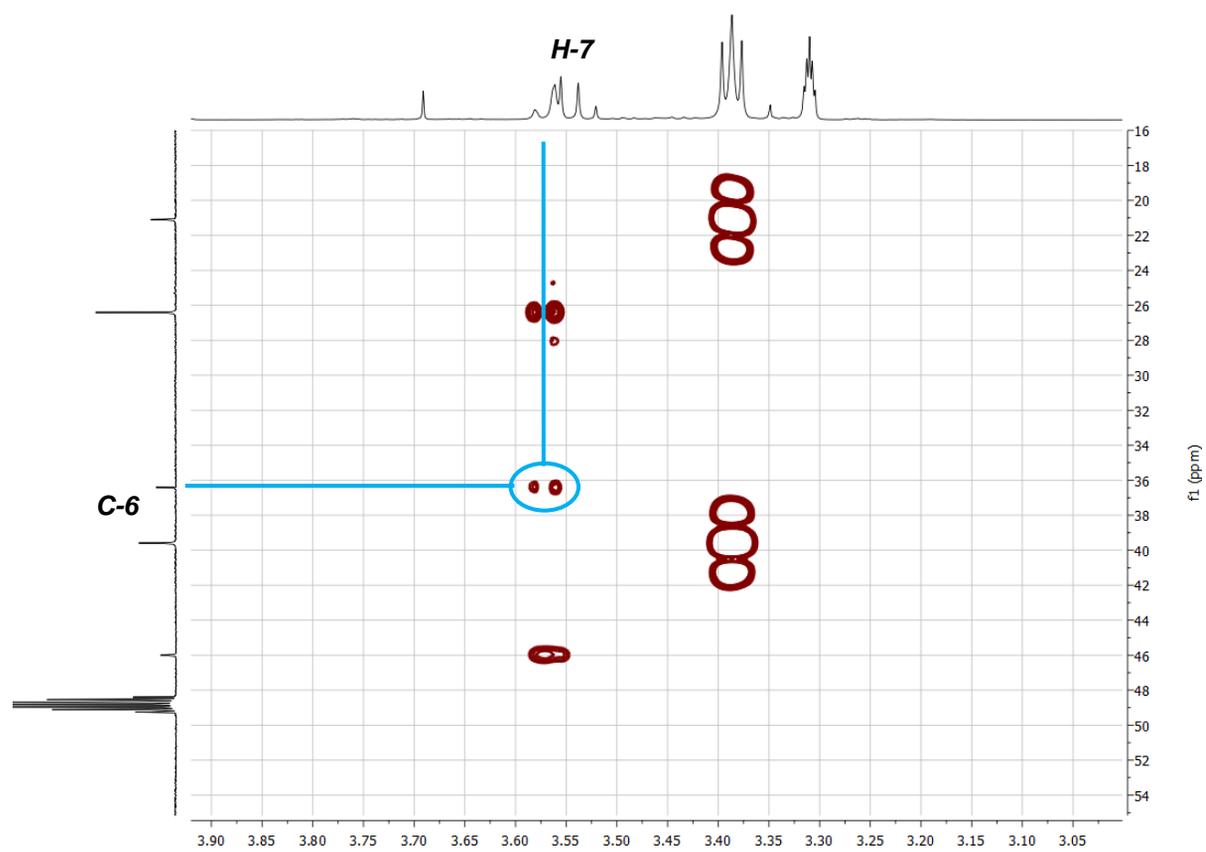


2. HSQC Spectrum of 31 and Assignment of Relevant Signals



Atom Number	¹³ C Chemical Shifts [ppm]	¹ H Chemical Shifts [ppm]
4 and 6	39.85 and 36.41	3.39
5	21.32	1.96
7	63.22	3.56
8	46.03	3.55 and 3.96

Relevant HMBC Correlation in 31



3. Crystal Structure Determination

Intensity data were collected with a Bruker APEX area detector equipped with an Incoatec microsource (Mo- K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$, multilayer optics) at 100 K (Oxford Cryostream 700 instrument). Data were integrated with SAINT (Bruker AXS, SAINT, Program for Reduction of Data collected on Bruker, CCD Area Detector Diffractometer V. 6.02, Bruker AXS Inc.: Madison, WI, USA, 1999) and corrected for absorption by multi-scan methods (SADABS: Program for Empirical Absorption Correction of Area Detector Data V 2004/1, Bruker AXS Inc.: Madison, WI, USA, 2004.) The structure was solved by direct methods (SHELXS-13). and were refined by full matrix least squares procedures based on F^2 as implemented in SHELXL-13. Non-hydrogen atoms were assigned anisotropic displacement parameters and hydrogen atoms were found, yet not anisotropically refined. No cases of twinning or disorder have been encountered.

3.1 Crystal Structure Determination of **8**:

Crystal data: orthorhombic space group $P 2_12_12_1$, $Z = 4$, $a = 10.807(2) \text{ \AA}$, $b = 11.284(2) \text{ \AA}$, $c = 15.094(3) \text{ \AA}$, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $V = 1840.6(6) \text{ \AA}^3$, 22832 reflections, 4781 unique, $wR_2 = 0.0915$, $R_1 = 0.0365$, $S = 1.033$, Flack parameter: $-0.03(3)$.

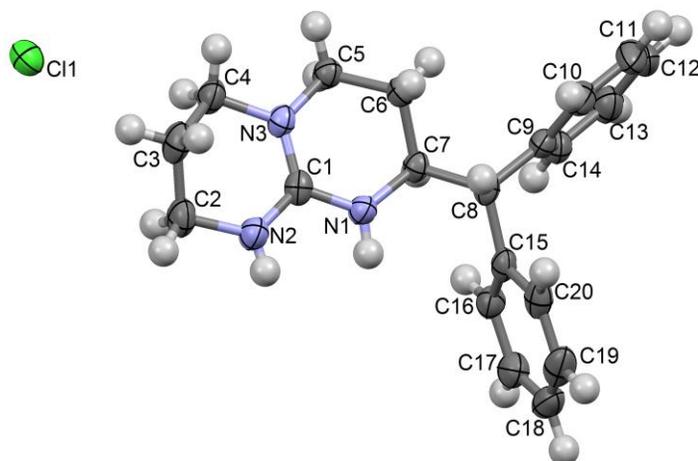


Figure s1: Displacement ellipsoid plot (Mercury¹) of **8** in the crystal structure. Ellipsoids are drawn at 80 % probability. A water molecule has been omitted for clarity.

¹ C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.*, **2008**, 41, 466-470.

3.2 Crystal Structure Determination of 10:

Crystal data: orthorhombic space group $C222_1$, $Z = 4$, $a = 7.1107(11)$ Å, $b = 16.739(3)$ Å, $c = 23.312(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $V = 2774.7(7)$ Å³, 15776 reflections, 2573 unique, $wR_2 = 0.1062$, $R_1 = 0.0492$, $S = 1.049$, Flack parameter: 0.08(7).

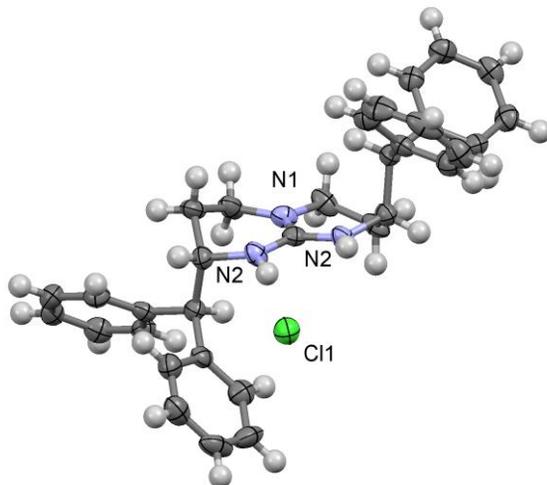


Figure s2: Displacement ellipsoid plot (Mercury¹) of **10** in the crystal structure. Ellipsoids are drawn at 80 % probability. Water molecules have been omitted for clarity.

3.3 Crystal Structure Determination of 38:

Crystal data: tetragonal space group $P4_12_12$, $Z = 8$, $a = b = 15.5961(9)$ Å, $c = 14.7319(9)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90$, $V = 3583.4(5)$ Å³, 38342 reflections, 3694 unique, $wR_2 = 0.0776$, $R_1 = 0.0296$, $S = 1.039$, Flack parameter: -0.04(2).

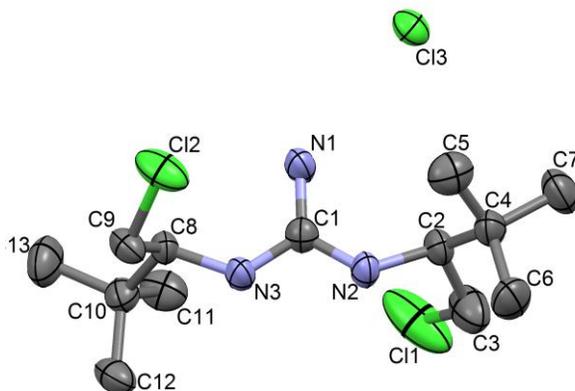


Figure s3: Displacement ellipsoid plot (Mercury¹) of **38** in the crystal structure. Ellipsoids are drawn at 80 % probability. A water molecule has been omitted for clarity.