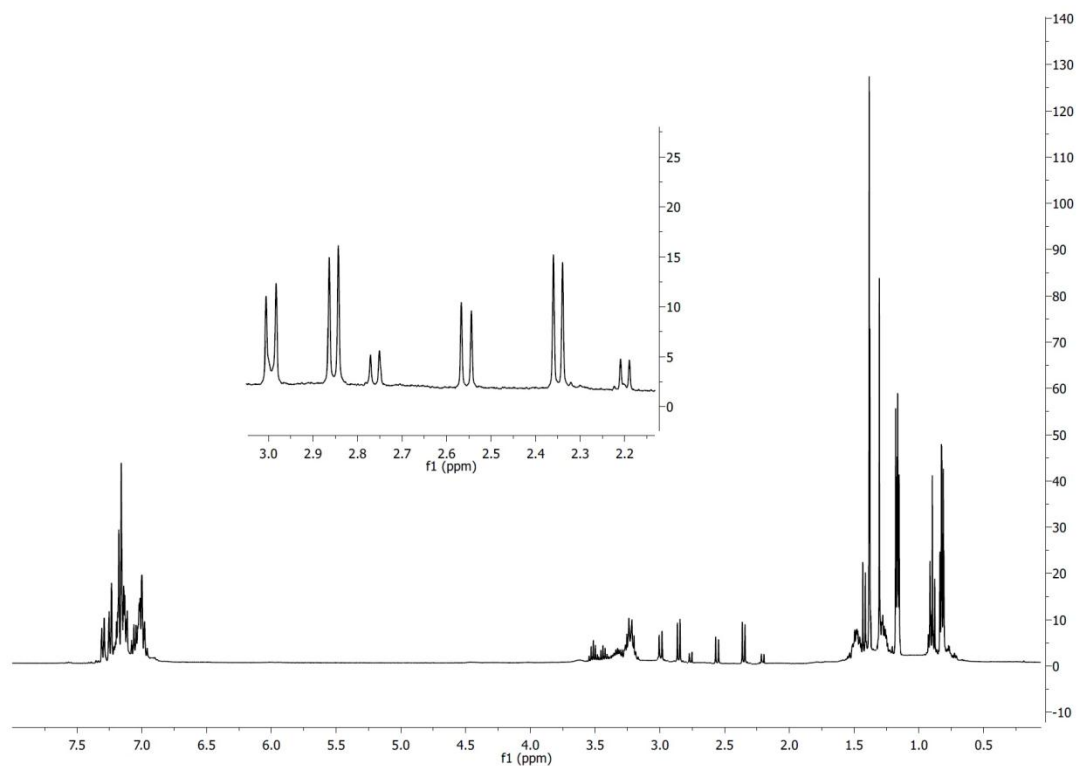
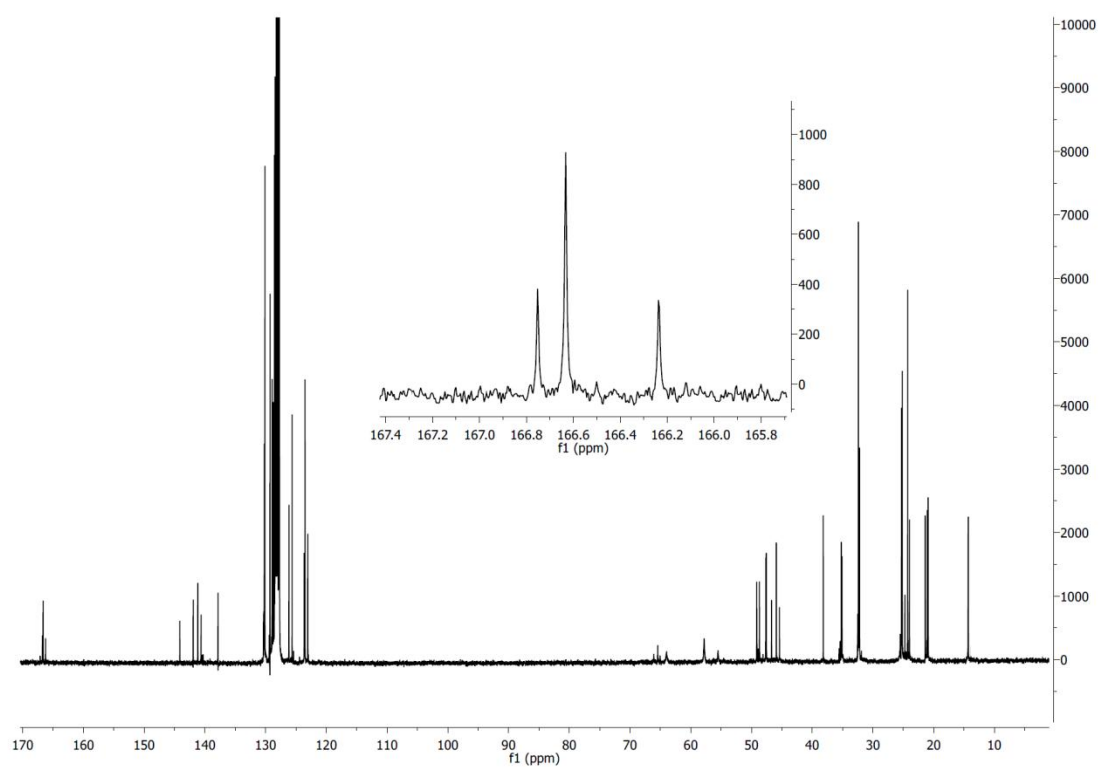


### Supporting Information:

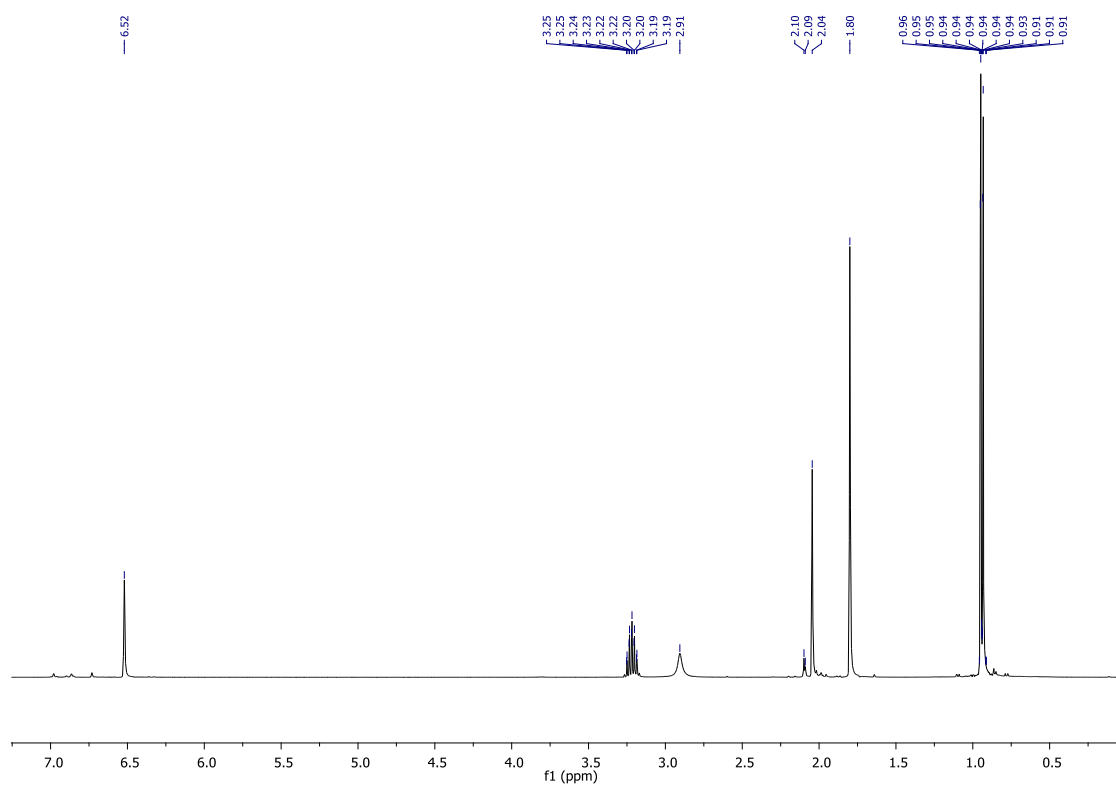
1.  $^1\text{H}$ -NMR of **4a-c** mixture in  $\text{C}_6\text{D}_6$ .
2.  $^{13}\text{C}$ -NMR of **4a-c** mixture in  $\text{C}_6\text{D}_6$ .
3.  $^1\text{H}$ -NMR of the product mixture of the catalytic guanylation of 2,4,6-trimethylaniline in toluene- $\text{d}^8$ , as an example of guanylation with complex **2**. Conditions: amine (1 mmol); *N,N'*-Diisopropylcarbodiimide (1 mmol). Time: 24 h. Temp.: 50°C. 2 mol% catalyst.
4. Preparative Scale Synthesis of the (4-tert-butylphenyl)-2,3-diisopropylguanidine.
5.  $^1\text{H}$ -NMR of isolated (4-tert-butylphenyl)-2,3-diisopropylguanidine in  $\text{CDCl}_3$ .



$^1\text{H-NMR}$  of **4a-c** mixture in  $\text{C}_6\text{D}_6$ , with an enlarged view of the methylene region.



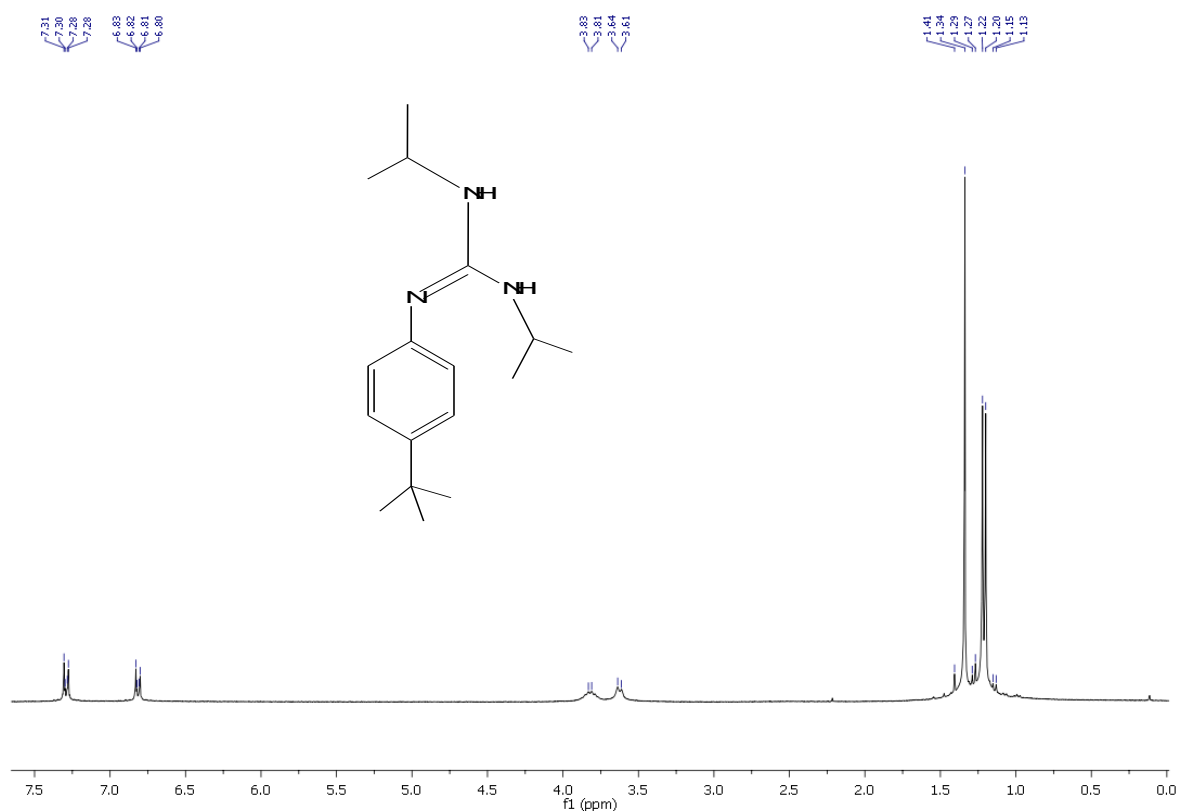
$^{13}\text{C-NMR}$  of **4a-c** mixture in  $\text{C}_6\text{D}_6$ , with an enlarged view of the "CN<sub>3</sub>" region.



$^1\text{H-NMR}$  of the product mixture of the catalytic guanylation of 2,4,6-trimethylaniline in toluene- $\text{d}^8$ , as an example of guanylation with complex **2**. Conditions: amine (1 mmol);  $N,N'$ -Diisopropylcarbodiimide (1 mmol). Time: 24 h. 2 mol% catalyst. Performed under an inert atmosphere in a J. Young valve NMR tube.

### Preparative Scale Synthesis of the (4-tert-butylphenyl)-2,3-diisopropylguanidine.

In a glovebox, a solution of *p*-tertbutylaniline (6.00 mmol) in toluene (10 mL) was added to a solution of [NbBz<sub>3</sub>(N<sup>t</sup>Bu)] (0.12 mmol) in toluene (10 mL) in a Schlenk tube. The *N,N'*-diisopropylcarbodiimide (6.00 mmol) was then added to the above reaction mixture. The Schlenk tube was taken outside the glovebox and the reaction was carried out at 50 °C for 24 hours. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether (20 mL) and filtered to give a clear solution. The solvent was removed under vacuum and the residue was recrystallized from ether at -30°C to provide the guanidine product as a white solid (1.54 g, 95% yield).



<sup>1</sup>H-NMR of isolated (4-tert-butylphenyl)-2,3-diisopropylguanidine in CDCl<sub>3</sub>.