

## Supporting Information Section

**Title: “Selective *N,N*-dibenzylation of Primary Aliphatic Amines with Dibenzylcarbonate in the Presence of Onium Salts”**

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**General.** All compounds used were ACS grade and were employed without further purification.  $^1\text{H}$  NMR spectra were recorded on 300 MHz spectrometer. GLC and GC/MS (70 eV) analyses were run using HP5 capillary columns (30 m), respectively.

*Reaction methodology and Purification of products.* In a typical reaction (entry 7 of Table 1), a mixture of benzylamine (**2a**, 0.91 g, 8.5 mmol), DBnC (4.11 g, 17.0 mmol), and tetrabutylphosphonium bromide (**3b**, 1.44 g, 4.25 mmol) was loaded in a 10-mL glass reactor (shaped as a test tube) equipped with condenser, a magnetic bar, and a side screw-capped neck for the withdrawal of samples. The reactor was then dipped in an oil bath pre-heated at 170 °C, with stirring. At intervals, samples of the reaction mixture were withdrawn and analysed by GC and GC/MS. After 45 min, both heating and stirring were stopped. The condenser on the top of the reactor was replaced with a micro-Claisen distillation apparatus with a fused-on Liebig condenser.  $\text{PhCH}_2\text{OH}$  was removed under reduced pressure (95 °C/10 mm). Once the residue was cooled to rt, petroleum ether (25 mL) was added. The onium salt remained totally undissolved and it was filtered.

Two procedures [i) and ii)] were followed to purify the product (tribenzylamine, **5a**):

- i) *Flash chromatography.* The filtrate was rotary evaporated. The residue was transferred into a 150 x 50 mm (length x diameter) glass column filled with silica gel (F60, 120 g) previously conditioned with the eluant system (petroleum ether/diethyl ether, 95/5 v/v). Flash-chromatography was then performed.  $R_f$  were of 0.9, 0.4 and 0.1 for tribenzylamine, benzyl N-benzylcarbamate (**6a**), and  $\text{PhCH}_2\text{OH}$ , respectively. Tribenzylamine was isolated as a white solid (mp = 90-92 °C; 2.00 g, 6.97 mmol, 82%), and characterized as such.
- ii) *Recrystallization.* The liquid filtrate was cooled to -15 °C, and tribenzylamine separated as white needles (1.91 g, 6.65 mmol, 78%).

The same methodology was also used to run reactions of benzylamine (8.5 mmol) with DBnC (17.0 mmol) in the presence of a salt of onium- or imidazolium-type (**3a**: hexadecyltributylphosphonium bromide; **3c**: ethyltriphenyl phosphonium iodide; **3d**: cetylpyridinium chloride; **3e**: 1-butyl-3-methylimidazolium tetrafluoroborate;) which was added in the range of 0.05 to 0.5 molar equiv. with respect to **2a** (see Table 1).

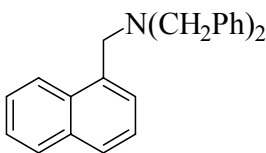
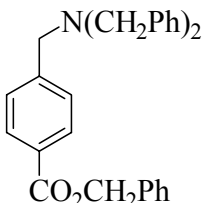
The same methodology was also used to run reactions of amines **2b-d** with DBnC in the presence of tetrabutylphosphonium bromide (**3b**) (see Table 2). The purification of liquid amines **5b-c** was performed either via flash chromatography (see above, procedure i) or by distillation. The latter case is exemplified for compound **5b**: a mixture of phenethylamine (1.03 g, 8.5 mmol), DBnC (4.11 g, 17.0 mmol), and tetrabutylphosphonium bromide (**3b**, 0.72 g, 2.12 mmol) was made to react at 170 °C (entry 1 of Table 2). After 100 min, both heating and stirring were stopped. The reactor was

equipped with a micro-Claisen distillation apparatus with a fused-on Liebig condenser. PhCH<sub>2</sub>OH and compound **5b** were distilled under reduced pressure at 95 °C/10 mm and 140-143 °C/0.3 mm, respectively. Amine **5b** (colourless liquid; 2.25 g, 7.48 mmol, 88%) was characterised as such.

Compound **5c** (entry 2 in Table 2), was purified by distillation at 172-176 °C/0.2 mm to yield a colourless liquid (2.38 g, 7.06 mmol, 83%).

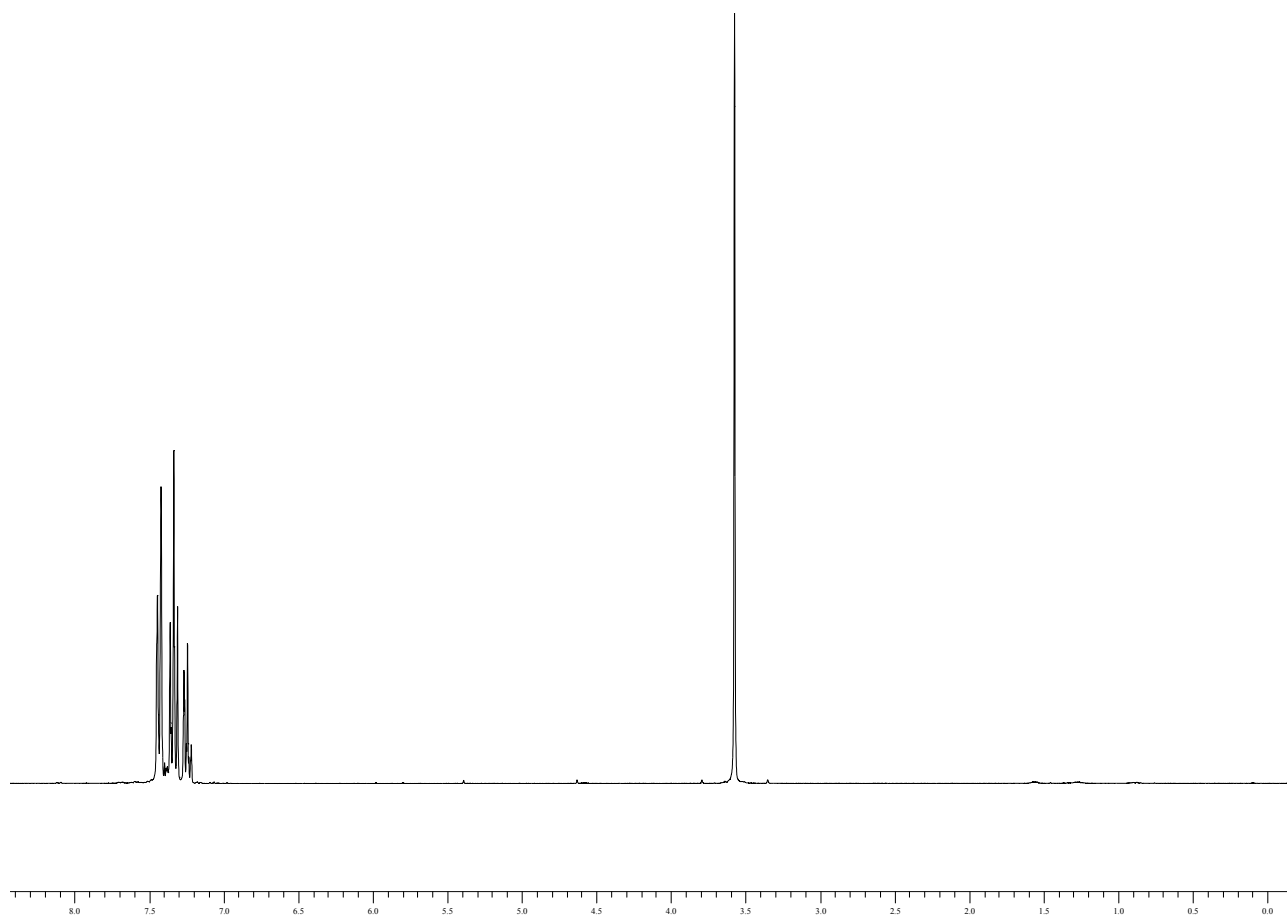
After removal of PhCH<sub>2</sub>OH and DBnC (165 °C/5 mm) by distillation, crude amines **5d** and **5e** had 93 and 90 % purity (by GC/MS and <sup>1</sup>H NMR, respectively). They were both purified through flash chromatography (see above, procedure i) to yield **5d** as a white solid and **5e** as a highly viscous liquid.

**Table.** <sup>1</sup>H NMR and GC/MS spectra of *N,N*-dibenzylamines **5b-d**.

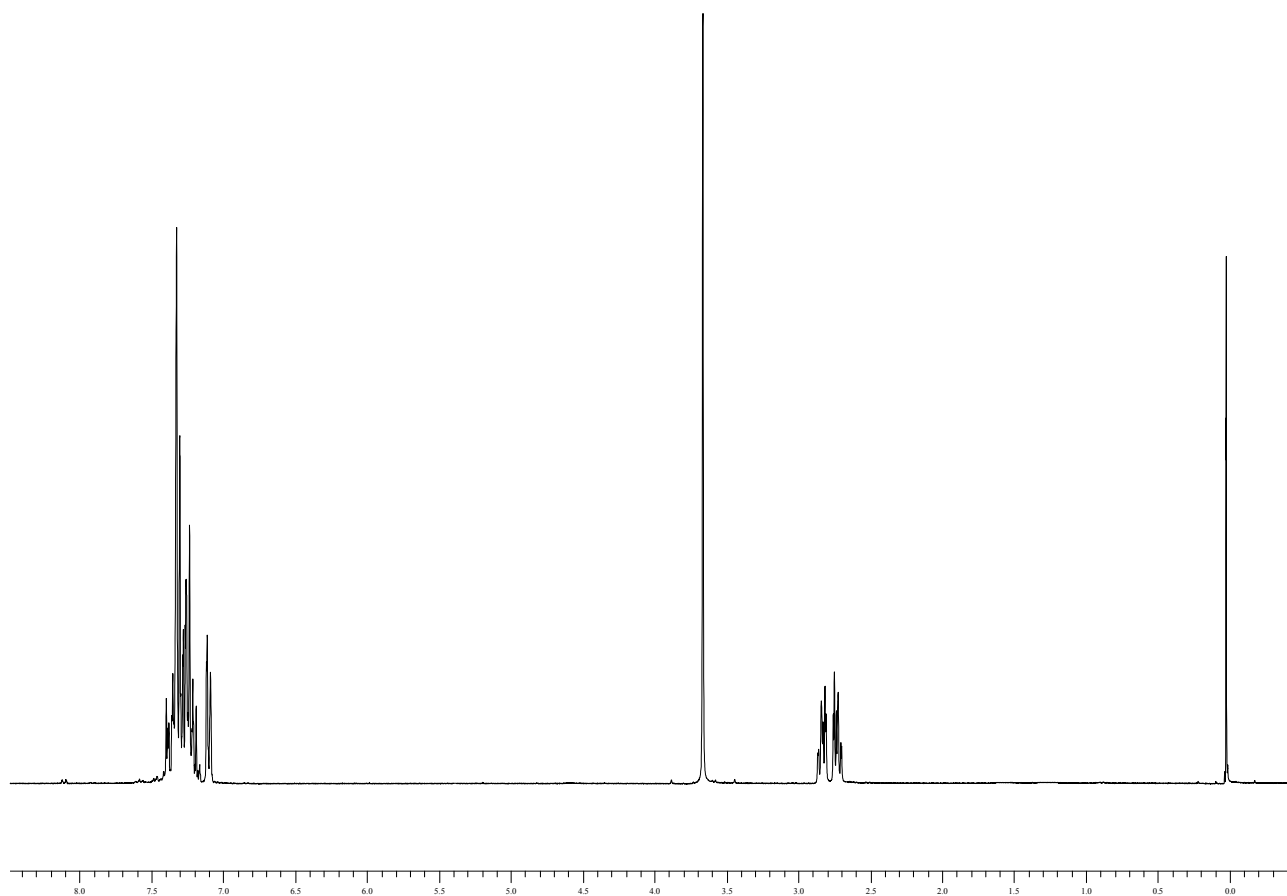
Amine	<sup>1</sup> H NMR (300 MHz), δ <sup>i</sup>	GC/MS (70 eV), m/z
(PhCH <sub>2</sub> ) <sub>3</sub> N <b>5a</b>	3.57 (s, 6H, 3CH <sub>2</sub> ), 7.22-7.44 (m, 15H, 3Ph)	
PhCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>2</sub> Ph) <sub>2</sub> <b>5b</b>	2.67-2.84 (m, 4H, 2CH <sub>2</sub> ), 3.64 (s, 4H, 2CH <sub>2</sub> ), 7.06-7.37 (m, 15H, 3Ph) <sup>ii</sup>	301 (M <sup>+</sup> , <1 %), 211 (17), 210 ([M-PhCH <sub>2</sub> ] <sup>+</sup> , 100), 91 ([M-CH <sub>2</sub> N(PhCH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> , 77)
<i>n</i> -C <sub>10</sub> H <sub>21</sub> N(CH <sub>2</sub> Ph) <sub>2</sub> <b>5c</b>	0.87 (t, 3H, CH <sub>3</sub> , J = 7.0 Hz), 1.15-1.29 (m, 14H, 7CH <sub>2</sub> ), 1.44-1.54 (m, 2H, CH <sub>2</sub> ), 2.39 (t, 2H, CH <sub>2</sub> , J = 7.17 Hz), 3.54 (s, 4H, 2CH <sub>2</sub> ), 7.18-7.37 (m, 10H, 2Ph)	337 (M <sup>+</sup> , 1 %), 246 ([M-PhCH <sub>2</sub> ] <sup>+</sup> , 5), 211 (19), 210 ([M-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> ] <sup>+</sup> , 100), 91 ([M-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> NCH <sub>2</sub> Ph] <sup>+</sup> , 45)
 <b>5d</b>	3.59 (s, 4H, 2CH <sub>2</sub> ), 3.98 (s, 2H, CH <sub>2</sub> ), 7.19-8.12 (m, 17H, Ar)	338 (10), 337 (M <sup>+</sup> , 35 %), 260 ([M-Ph] <sup>+</sup> , 11), 246 ([M-PhCH <sub>2</sub> ] <sup>+</sup> , 18), 210 ([M-C <sub>10</sub> H <sub>7</sub> ] <sup>+</sup> , 15), 142 (29), 198 (38), 141 ([M-N(CH <sub>2</sub> Ph) <sub>2</sub> ] <sup>+</sup> , 100), 115 (18), 91 ([M-PhCH <sub>2</sub> NCH <sub>2</sub> C <sub>10</sub> H <sub>7</sub> ] <sup>+</sup> , 61)
	<sup>1</sup> H NMR (300 MHz), δ <sup>i</sup>	<sup>13</sup> C NMR (300 MHz), δ <sup>i</sup>
 <b>5e</b>	3.51 (s, 4H, 2 N-CH <sub>2</sub> ), 3.56 (s, 2H, N-CH <sub>2</sub> ), 5.32 (s, 2H, O-CH <sub>2</sub> ), 7.17-7.42 (m, 15H, Ar), 7.46 (d, 2H, Ph, J = 8.19 Hz), 8.01 (d, 2H, Ph, J = 8.19 Hz),	57.6, 58.0, 66.5, 127.0, 128.0, 128.1, 128.3, 128.6, 128.7, 128.8, 129.7, 136.1, 139.2, 145.4, 166.3

<sup>i</sup> CDCl<sub>3</sub> was always used as a solvent for NMR spectra.

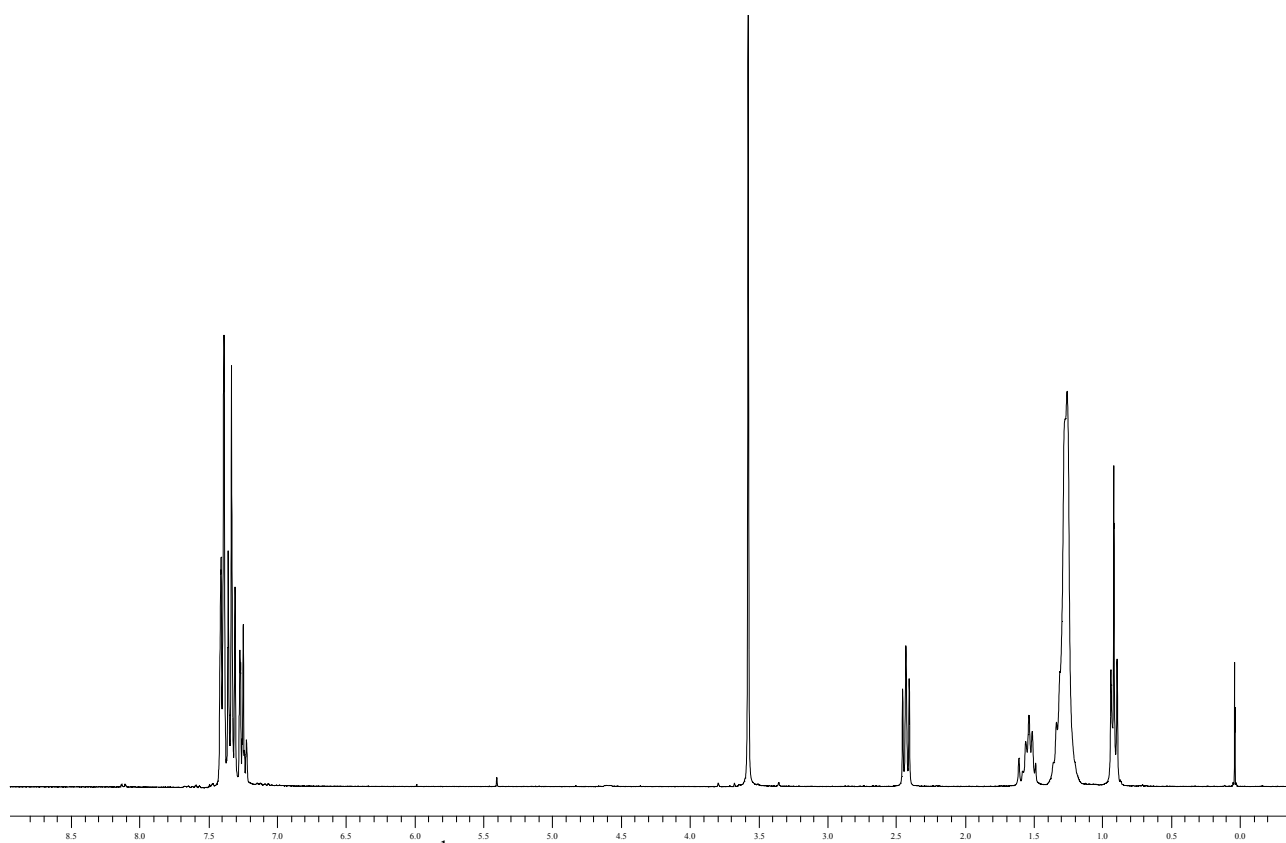
<sup>ii</sup> Salvatore, R. N.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2002**, 67, 674-683



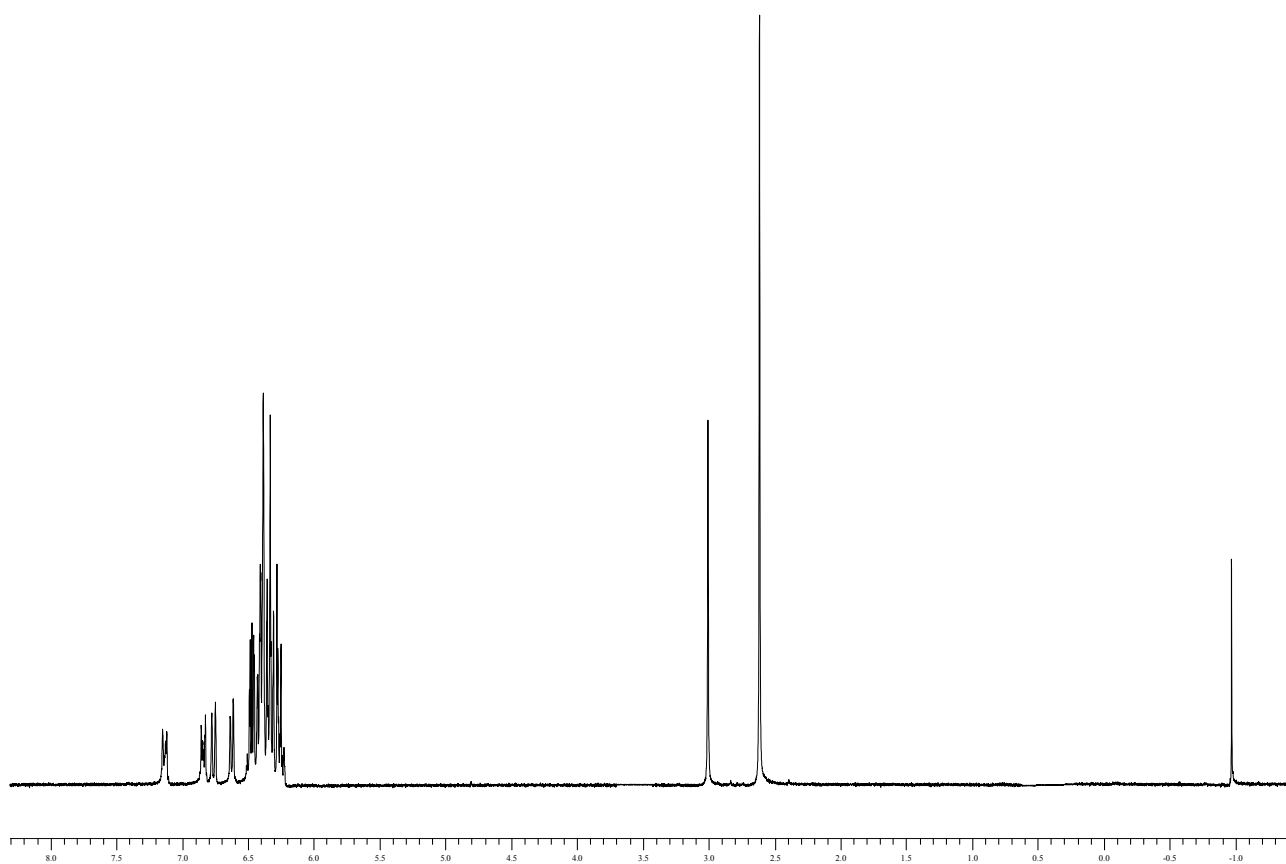
**Figure 1.**  $^1\text{H}$  NMR of tribenzylamine **5a**.



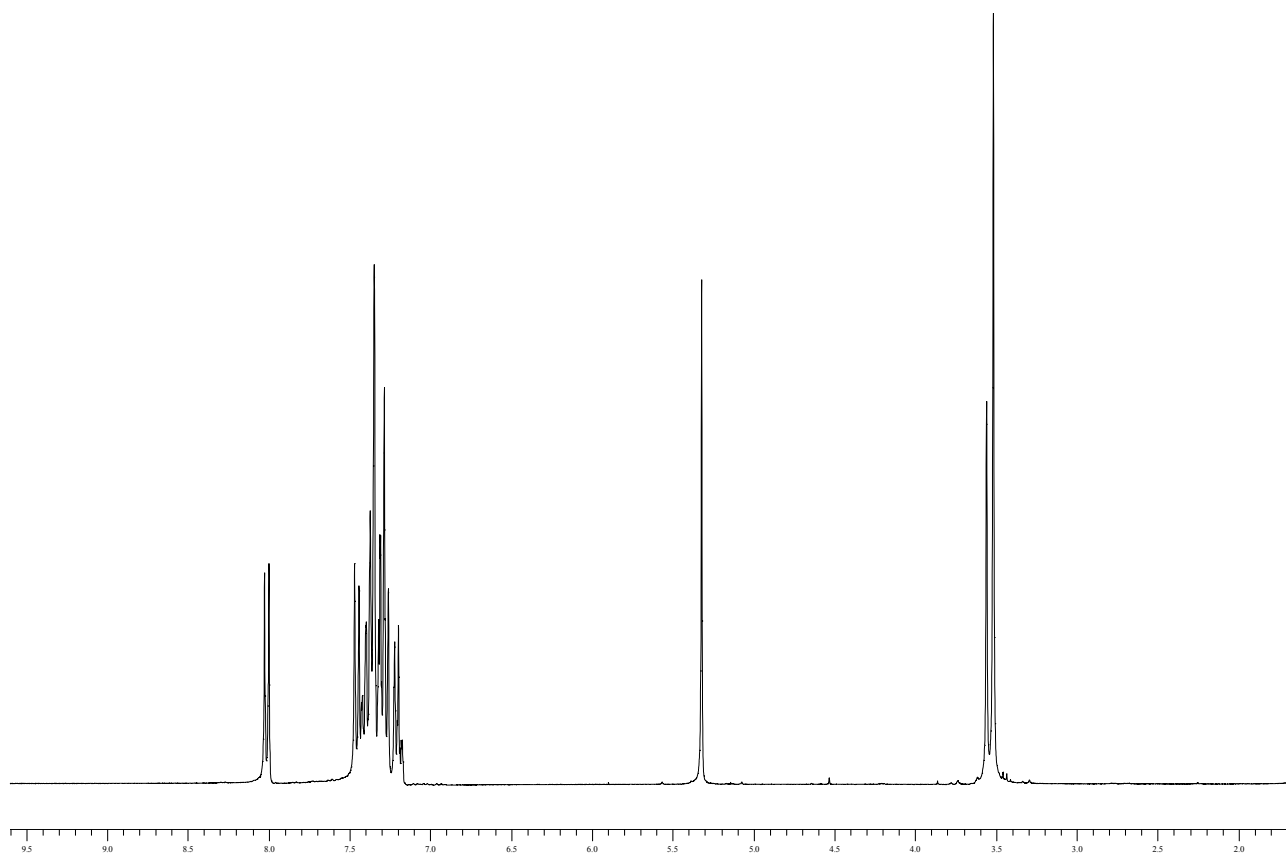
**Figure 2.**  $^1\text{H}$  NMR of *N,N*-dibenzyl phenethylamine **5b**



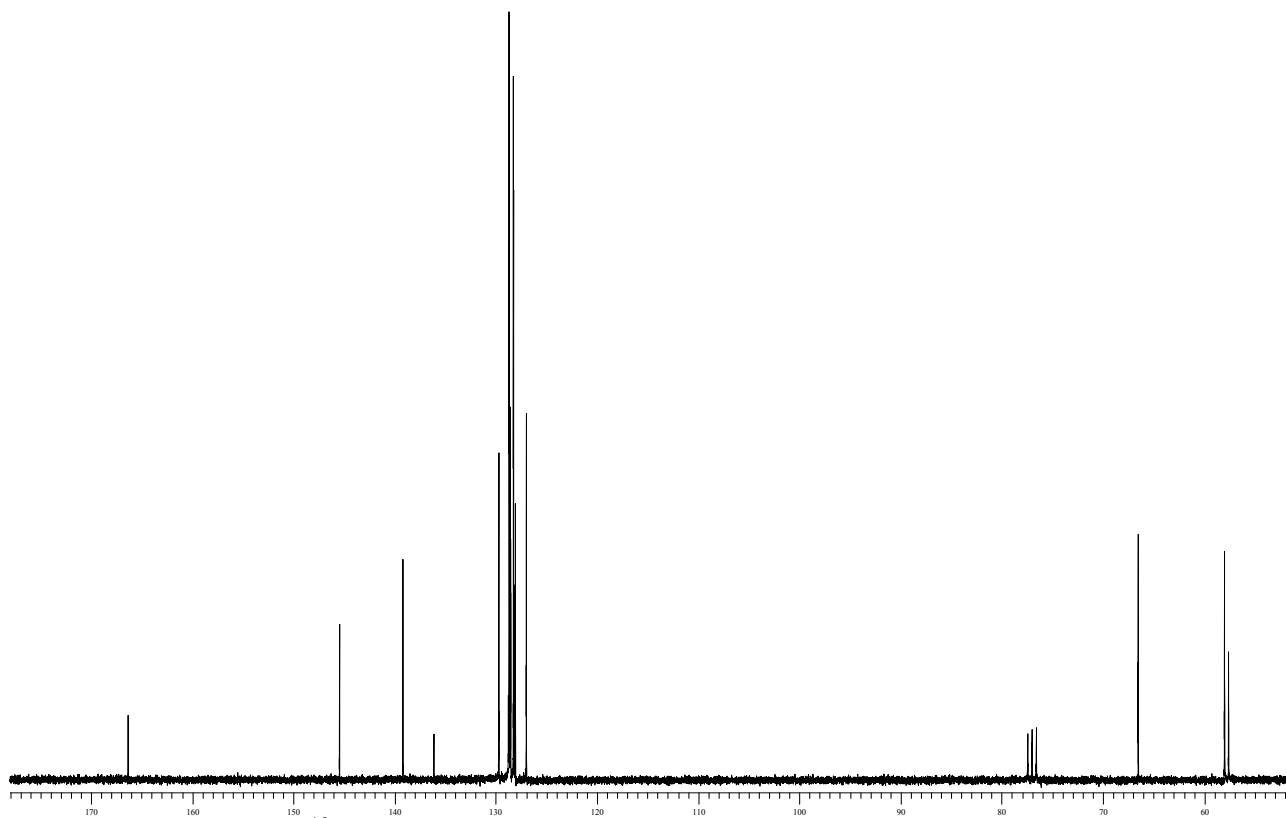
**Figure 3.**  $^1\text{H}$  NMR of *N,N*-dibenzyl *n*-decylamine **5c**.



**Figure 4.**  $^1\text{H}$  NMR of *N,N*-dibenzyl 1-naphthylamine **5d**.



**Figure 5.**  $^1\text{H}$  NMR of benzyl 4-( $N,N$ -dibenzylaminomethyl)benzoate **5e**.



**Figure 6.**  $^{13}\text{C}$  NMR of benzyl 4-( $N,N$ -dibenzylaminomethyl)benzoate **5e**.