SUPPORTING INFORMATION FOR

Efficient metal–free hydrosilylation of tertiary, secondary and primary amides to amines

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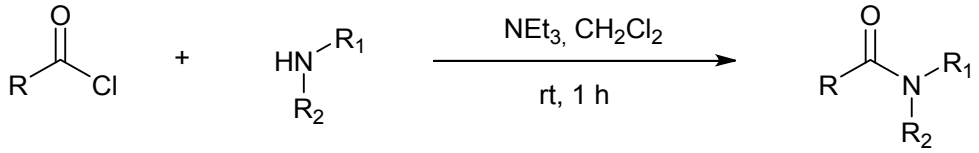
1. Experimental details

1.1. General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 ºC before use. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to solvent residual peaks. Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB^{TM}-ms fused silica capillary column (30 m x 0.25 mm x 0.25 μm). Unless otherwise noted, reagents were purchased from commercial suppliers. Toluene was dried over a sodium(0)/benzophenone mixture and distilled before use. CD_3CN and CD_2Cl_2 were dried over CaH_2 and distilled before use. The following amides are commercially available and samples were purchased from Aldrich, Acros or Alfa Aesar (CAS given in parenthesis): **1a** (1485-70-7), **1b** (93-98-1), **1c** (103-84-4), **1d** (613-93-4), **1e** (5894-65-5), **3a** (611-74-5), **3b** (20383-28-2).

1.2. General procedure for the preparation of amides



A 50 mL round bottom flask equipped with a stirring bar is charged with the amine (6.0 mmol, 1.2 eq), NEt_3 (6.0 mmol) and dichloromethane (10 mL). At room temperature, the acyl chloride (5.0 mmol, 1 eq.) is slowly added, resulting in a boiling solution. The reaction mixture is stirred for 1 h at room, then diluted with dichloromethane (10 mL), transferred to a separating funnel and washed with 1M HCl aqueous solution (2 x 20 mL). The organic layer was filtered through a short silica gel column, washed with ethyl acetate/hexane (1:1), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The corresponding amine is identified by ^{1}H NMR and obtained as a white powder or colorless/pale yellow oil with good to excellent yield. All ^{1}H NMR and ^{13}C NMR correspond to those reported in the literature.

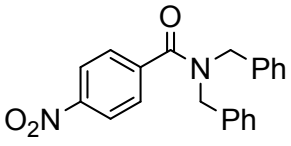
Characterization of secondary amides:

^{1}H NMR and ^{13}C NMR of the following amides products are identical to reported data: **1f**[1], **1g**[1], **1h**[1], **1i**[1], **1j**[1], **1k**[2]

Characterization of tertiary amides:

^{1}H NMR and ^{13}C NMR of the following amides products are identified to reported data: **3c**[3], **3d**[3], **3e**[3], **3f**[4], **3g**[3], **3h**[3], **3i**[3], **3j**[3], **3k**[3], **3l**[4], **3m**[3], **3p**[3], **5**[1], **7**[3]

- **3n (*N*,*N*-dibenzyl-4-nitrobenzamide):**



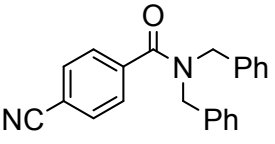
White powder, yield = 92 %

^{1}H NMR (*CDCl*$_3$, 298 K): δ 4.47 (s, 2H, NC*H*$_2$Ph); 4.86 (s, 2H, NC*H*$_2$Ph); 7.47 (m, 10H, N(CH$_2$C$_6$*H*$_5$)$_2$); 7.76 (d, 2H, COC$_6$*H*$_4$NO$_2$, $^{3}J_{HH}$ = 10.0 Hz); 8.36 (d, 2H, COC$_6$*H*$_4$NO$_2$, $^{3}J_{HH}$ = 10.0 Hz) ppm.

^{13}C NMR (*CDCl*$_3$, 298 K): δ 47.35 (N*C*H$_2$Ph); 51.43 (N*C*H$_2$Ph); 124.00 (Ar); 126.81 (Ar); 127.79 (Ar); 127.95 (Ar); 128.08 (Ar); 128.59 (Ar); 128.96 (Ar); 129.18 (Ar); 135.65 (Ar); 136.38 (Ar); 142.37 (Ar); 148.35 (Ar); 170.09 (*C*O) ppm.

EI (+) (m/z): 346 [M]$^{+}$ (2), 255 (57), 150 (100), 134 (3), 120 (10), 104 (31), 91 (52), 76 (16), 65 (16), 51 (4), 39 (4).

- **3o (*N*,*N*-dibenzyl-4-cyanobenzamide):**



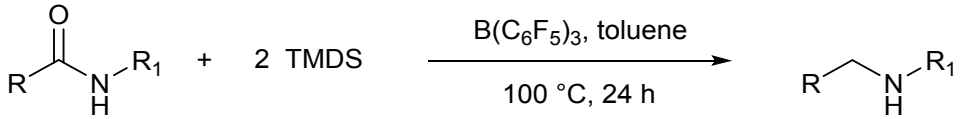
White powder, yield = 89 %

^{1}H NMR (*CDCl*$_3$, 298 K): δ 4.48 (s, 2H, NC*H*$_2$Ph); 4.86 (s, 2H, NC*H*$_2$Ph); 7.23-7.52 (m, 10H, N(CH$_2$C$_6$H$_5$)$_2$); 7.68-7.84 (m, 4H, COC$_6$*H*$_4$CN) ppm.

^{13}C NMR (*CDCl*$_3$, 298 K): δ 47.25 (N*C*H$_2$Ph); 51.44 (N*C*H$_2$Ph); 113.52 (Ar); 118.13 (*C*N); 126.82 (Ar); 127.44 (Ar); 127.91 (Ar); 128.03 (Ar); 128.91 (Ar); 129.13 (Ar); 132.53 (Ar); 135.69 (Ar); 136.37 (Ar); 140.50 (Ar); 170.35 (*C*O) ppm.

EI (+) (m/z): 326 $[M]^+$ (2), 235 (30), 130 (100), 102 (30), 91 (38), 77 (3), 75 (3), 65 (13), 51 (5), 39 (3).

1.3. General procedure for the reduction of secondary amides



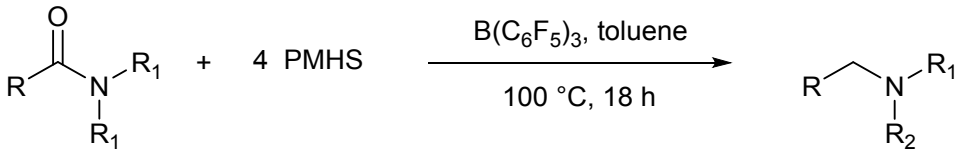
An NMR tube equipped with a J. Young valve is charged with the amine (0.10 mmol, 1 eq.), $B(C_6F_5)_3$ (2.6 mg, 0.0050 mmol, 5.0 mol%) and dry toluene (300 µL). TMDS (35 µL, 0.20 mmol, 2 eq., 4 eq. of Si–H functionalities) is added to the solution mixture. The tube is sealed and the solution is heated at 100 °C for 18 h. The corresponding amine is identified and its yield determined by GC/MS and/or ^{1}H NMR by comparison with mesitylene as an internal standard. The crude mixture is then purified by flash chromatography on silica gel (0.069-0.200 mm, standard grade). Silicon by-products are first recovered using diethylether as the eluent and the amine is then collected as a colorless or pale yellow oil using ethyl acetate / petrol ether (5/5) as the eluent.

Caracterization of secondary amines:

The following amines are commercially available and their spectra were compared to authentic samples purchased from Aldrich or Acros (CAS given in parenthesis): **2a** (103-49-1), **2b** (103-32-2), **2c** (103-69-5), **2d** (103-67-3).

^{1}H NMR and ^{13}C NMR of the following amines products are identified to reported data: **2e**[1], **2f**[1], **2g**[1], **2h**[1], **2i**[1], **2j**[5], **2k**[6]

1.4. General procedure for the reduction of tertiary amides



An NMR tube equipped with a J. Young valve is charged with the amine (0.10 mmol, 1 eq.), $B(C_6F_5)_3$ (2.6 mg, 0.0050 mmol, 5.0 mol%) and toluene (300 µL). PMHS (24 µL, 0.40 mmol, 4 eq., 4 eq. of Si–H functionalities) is added to the solution mixture. The tube is sealed and the solution is heated at 100 °C for 18 h. The corresponding amine is identified and its yield determined by GC/MS and/or ^{1}H NMR by comparison with mesitylene as an internal

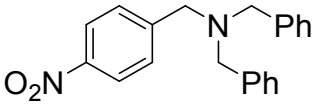
standard. The crude mixture is then purified by flash chromatography on silica gel (0.069-0.200 mm, standard grade). Silicium by-products are first recovered using diethylether as the eluent and the amine is then collected as an analytically pure colorless or pale yellow oil using ethyl acetate / petrol ether (5/5) as the eluent.

Caracterization of tertiary amines:

The following amines are commercially available and their spectra were compared to authentic samples purchased from Aldrich (CAS given in parenthesis): **4a** (103-83-3).

^{1}H NMR and ^{13}C NMR of the following amines products are identified to reported data: **4b**[3], **4c**[3], **4d**[3], **4e**[3], **4f**[3], **4g**[3], **4h**[3], **4i**[4], **4j**[3], **4k**[3], **4l**[4], **4m**[3]**, 4p**[3].

- **4n (*N*,*N*-dibenzyl-1-(4-nitrophenyl)methanamine):**



Viscous yellow oil

^{1}H NMR (*$CDCl_3$*, 298 K): δ 3.58 (s, 4H, NC*H_2*Ph); 3.64 (s, 2H, NC*H_2*PhNO_2); 7.30-7.40 (m, 10H, N($CH_2C_6H_5$)$_2$); 7.58 (d, 2H, $C_6H_4NO_2$, $^{3}J_{HH}$ = 8.0 Hz); 8.18 (d, 2H, $C_6H_4NO_2$, $^{3}J_{HH}$ = 8.0 Hz) ppm.

^{13}C NMR (*$CDCl_3$*, 298 K): δ 55.36 (N*C*H$_2$PhNO_2); 57.09 (N(*C*H$_2$Ph)$_2$); 123.66 (Ar); 127.34 (Ar); 128.53 (Ar); 128.84 (Ar); 129.32 (Ar); 138.97 (Ar); 147.14 (Ar); 147.98 (Ar) ppm.

EI (+) (m/z): 332 [M]$^{+}$ (7), 315 (1), 255 (6), 241 (10), 210 (3), 196 (1), 165 (1), 136 (2), 118 (1), 106 (2), 91 (100), 78 (3), 65 (11), 51 (2), 39 (2).

4n *was first isolated as a hydrochloride salt:*

^{1}H NMR (*$CDCl_3$*, 298 K): δ 4.20 (s, broad, 6H, N(C*H_2*Ph)$_3$); 7.44 (s, 6H, N($CH_2C_6H_5$)$_2$); 7.64 (s, 4H, N($CH_2C_6H_5$)$_2$); 8.00 (d, 2H, $C_6H_4NO_2$, $^{3}J_{HH}$ = 8.0 Hz); 8.23 (d, 2H, $C_6H_4NO_2$, $^{3}J_{HH}$ = 8.0 Hz) ppm.

^{13}C NMR (*$CDCl_3$*, 298 K): δ 57.41 (N*C*H$_2$PhNO_2); 58.34 (N(*C*H$_2$Ph)$_2$); 124.32 (Ar); 128.27 (Ar); 129.61 (Ar); 130.38 (Ar); 131.56 (Ar); 132.39 (Ar); 136.43 (Ar); 148.65 (Ar) ppm.

- **4o (*N*,*N*-dibenzyl-1-(4-cyanophenyl)methanamine):**

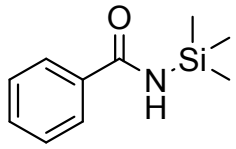
Due to absence of conversion of **3o**, spectroscopic data for **4o** were not collected.

1.5. General procedure for the trimethylsilylation of primary amides

A 25 mL round bottom flask equipped with a stirring bar is charged with 3-methoxybenzamide (498.8 mg, 3.30 mmol), triethylamine (1.38 µL, 9.90 mmol, 3 eq.) and ether (15 mL). The solution is stirred at RT for 1 h. TMSCl (1.26 µL, 9.90 mmol, 3 eq.) is added to the solution, resulting in the precipitation of a white powder. Diethylether (15 mL) is added and the mixture is filtered and washed with diethylether (2 x 10 mL). The solution is recovered and the volatiles are removed under reduced pressure to afford 3-methoxy-*N*-(trimethylsilyl)benzamide (**10b**) as a white powder in 95 % yield (701.3 mg, 3.14 mmol).

Characterization of primary amides and silylated primary amides:

- **10a (*N*-(trimethylsilyl)benzamide):**



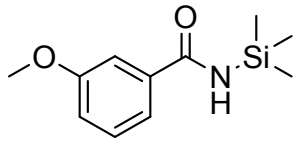
White powder, yield = 95 %

^{1}H NMR (CD_2Cl_2, 298 K): δ 0.31 (s, 9H, Si(CH_3)$_3$); 5.82 (s broad, 1H, N*H*); 7.46 (m, 3H, Ar); 7.77 (dd, 2H, Ar, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz) ppm.

^{1}H NMR ($CDCl_3$, 298 K): δ 0.33 (s, 9H, Si(CH_3)$_3$); 5.83 (s broad, 1H, N*H*); 7.39 (m, 3H, Ar); 7.82 (dd, 2H, Ar, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz) ppm.

^{13}C NMR ($CDCl_3$, 298 K): δ 0.58 (Si(CH_3)$_3$); 127.36 (Ar); 128.52 (Ar); 131.68 (Ar); 134.98 (Ar); 172.26 (*C*O) ppm.

- **10b (3-methoxy-*N*-(trimethylsilyl)benzamide):**



White powder, yield = 95 %

^{1}H NMR (*d8*-THF, 298 K): δ 0.28 (s, 9H, Si(CH_3)$_3$); 3.79 (s, 3H, CH_3O); 6.83 (s broad, 1H, N*H*); 7.01 (d, 1H, Ar, $^3J_{HH}$ = 8.0 Hz); 7.27 (t, 1H , Ar, $^3J_{HH}$ = 8.0 Hz); 7.43 (m, 2H, Ar) ppm.

^{1}H NMR (*d8*-tol, 298 K): δ 0.29 (s, 9H, Si(CH_3)$_3$); 3.27 (s, 3H, CH_3O); 5.46 (s broad, 1H, N*H*); 6.82 (d, 1H, $^3J_{HH}$ = 8.0 Hz); 6.96 (t, 1H, Ar, $^3J_{HH}$ = 8.0 Hz); 7.09 (d, 1H, Ar, $^3J_{HH}$ = 8.0 Hz); 7.53 (s, 1H, Ar) ppm.

^{1}H NMR (CDCl$_3$, 298 K): δ 0.27 (s, 9H, Si(CH_3)$_3$); 3.74 (s, 3H, CH_3O); 5.89 (s broad, 1H, N*H*); 6.97 (s, 1H, Ar); 7.26 (m, 3H, Ar) ppm.

^{13}C NMR (CDCl$_3$, 298 K): δ 0.66 (Si(CH$_3$)$_3$); 55.35 (CH$_3$O); 112.38 (Ar); 118.00 (Ar); 119.15 (Ar); 129.35 (Ar); 136.39 (Ar); 159.72 (Ar); 172.04 (CO) ppm.

Anal. Calc. for $C_{11}H_{16}NO_2Si$ (mol. wt. 223.35): C, 59.16; H, 7.67; N, 6.28. Found: C, 59.06 H, 6.81; N, 7.25.

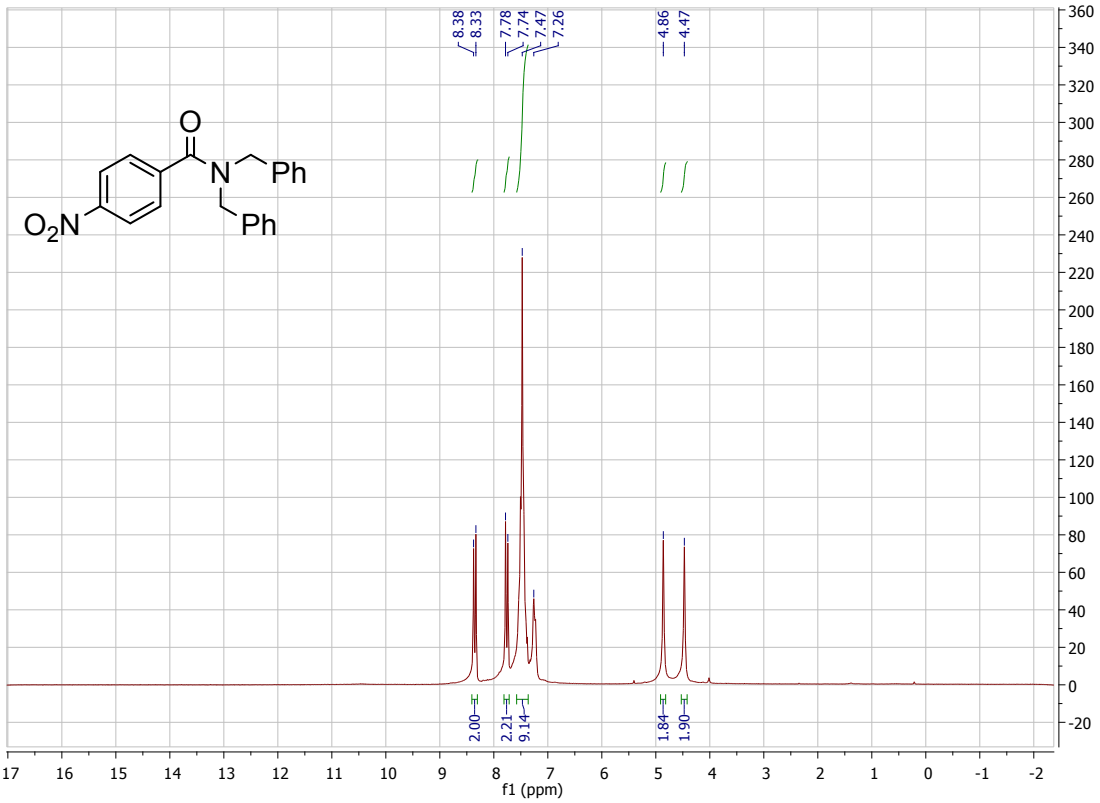
The following amines are commercially available and their spectra were compared to authentic samples purchased from Aldrich or Acros (CAS given in parenthesis): **9a** (55-21-0), **9b** (5813-86-5), **11a** (100-46-9), **11b** (5071-96-5).

1.6. General procedure for the reduction of silylated primary amines

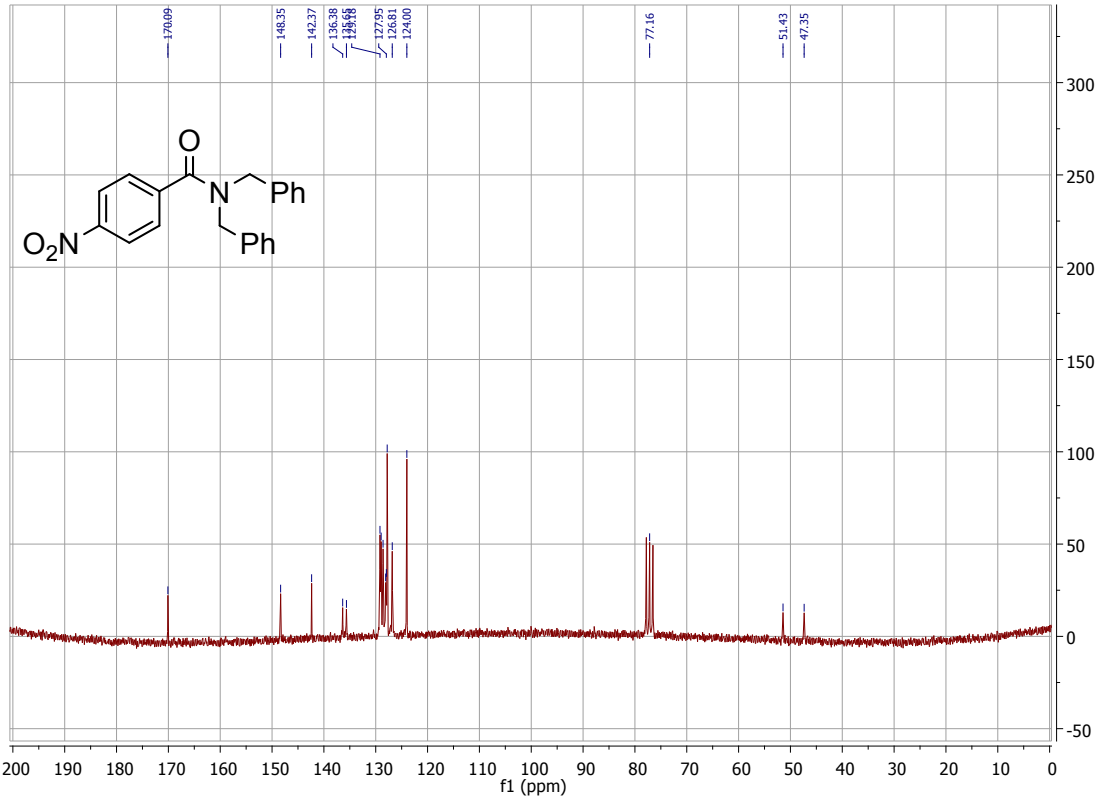
An NMR tube equipped with a J. Young valve is charged with the amine (0.10 mmol, 1 eq.), B(C_6F_5)$_3$ (5.2 mg, 0.010 mmol, 10.0 mol%) and dry toluene (300 µL). TMDS (35 µL, 0.20 mmol, 2 eq., 4 eq. of Si–H functionalities) is added to the reaction mixture. The tube is sealed and the solution is heated at 100 °C for 18 h. The corresponding amine is identified and its yield determined by GC/MS by comparison with mesitylene as an internal standard. Aqueous solution of NaOH 1M is added and the solution is agitated for 4h. The crude mixture is then purified by flash chromatography on silica gel (0.069-0.200 mm, standard grade) using ethyl acetate / petrol ether (5/5) as the eluent.

2. NMR spectra

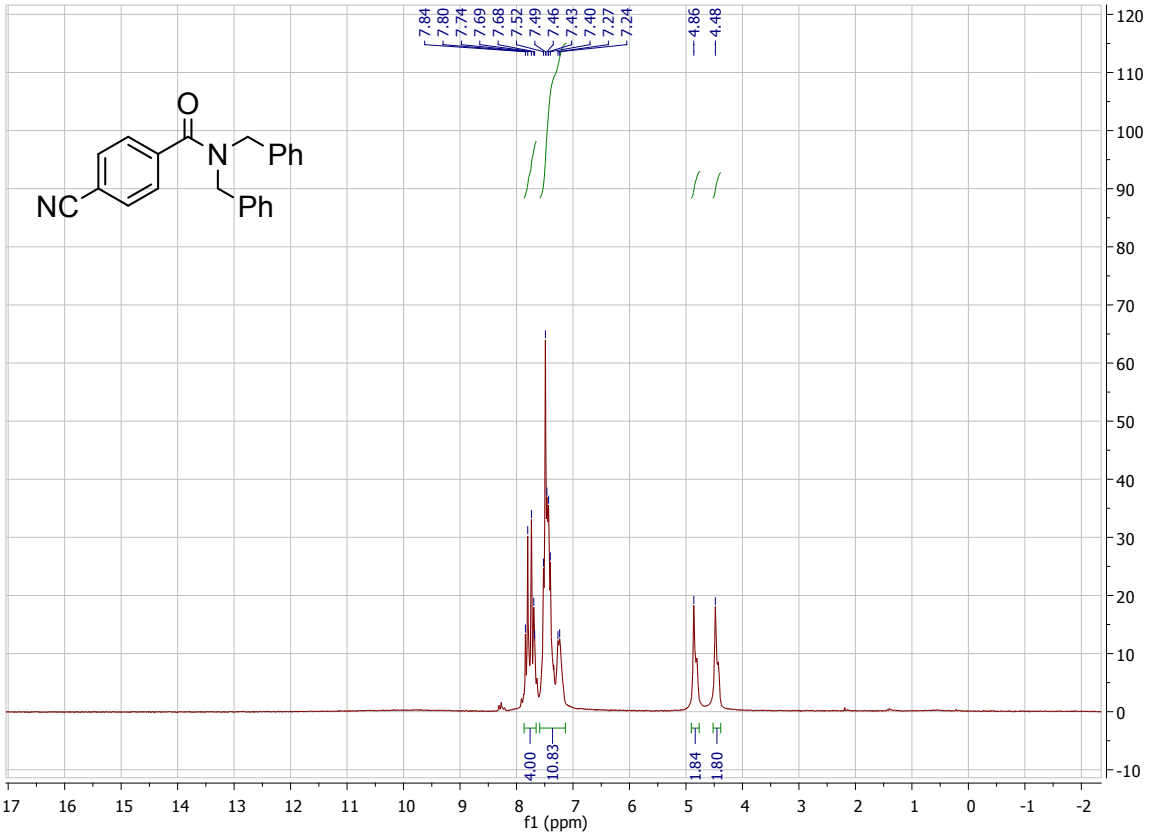
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-4-nitrobenzamide (**3n**)



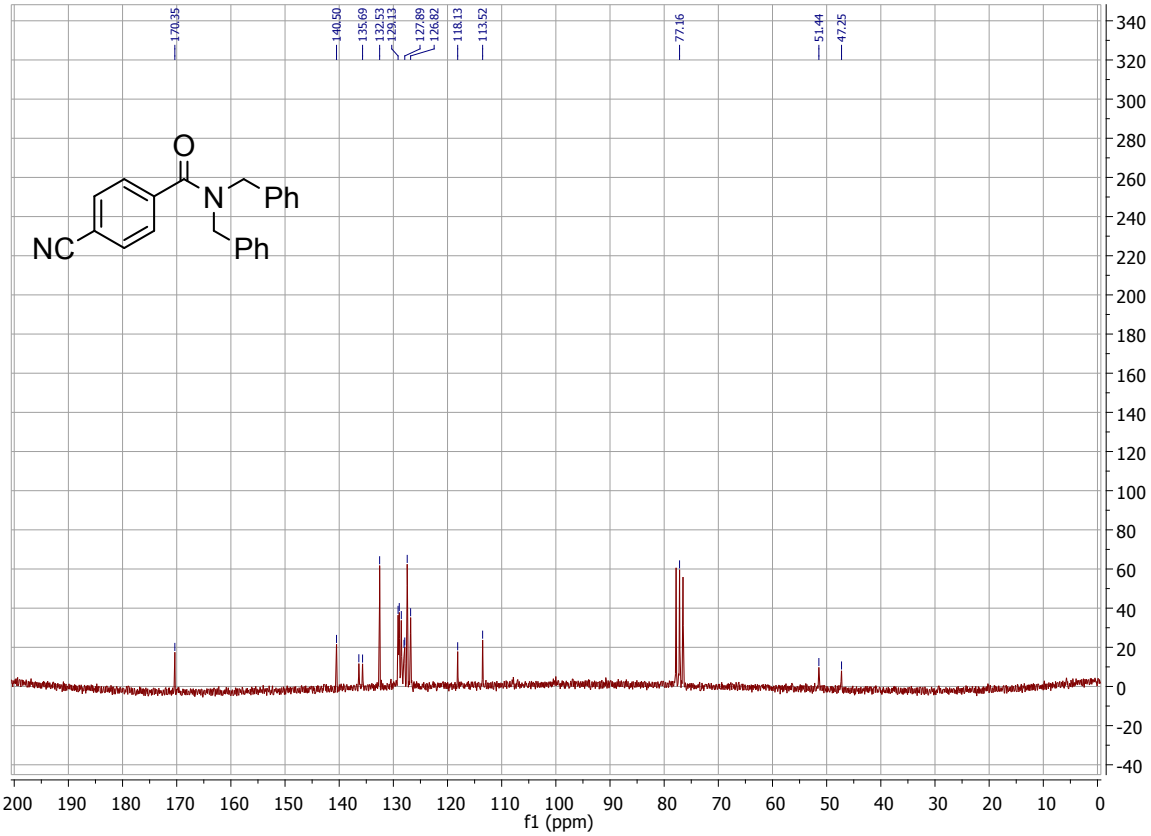
^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-4-nitrobenzamide (**3n**)



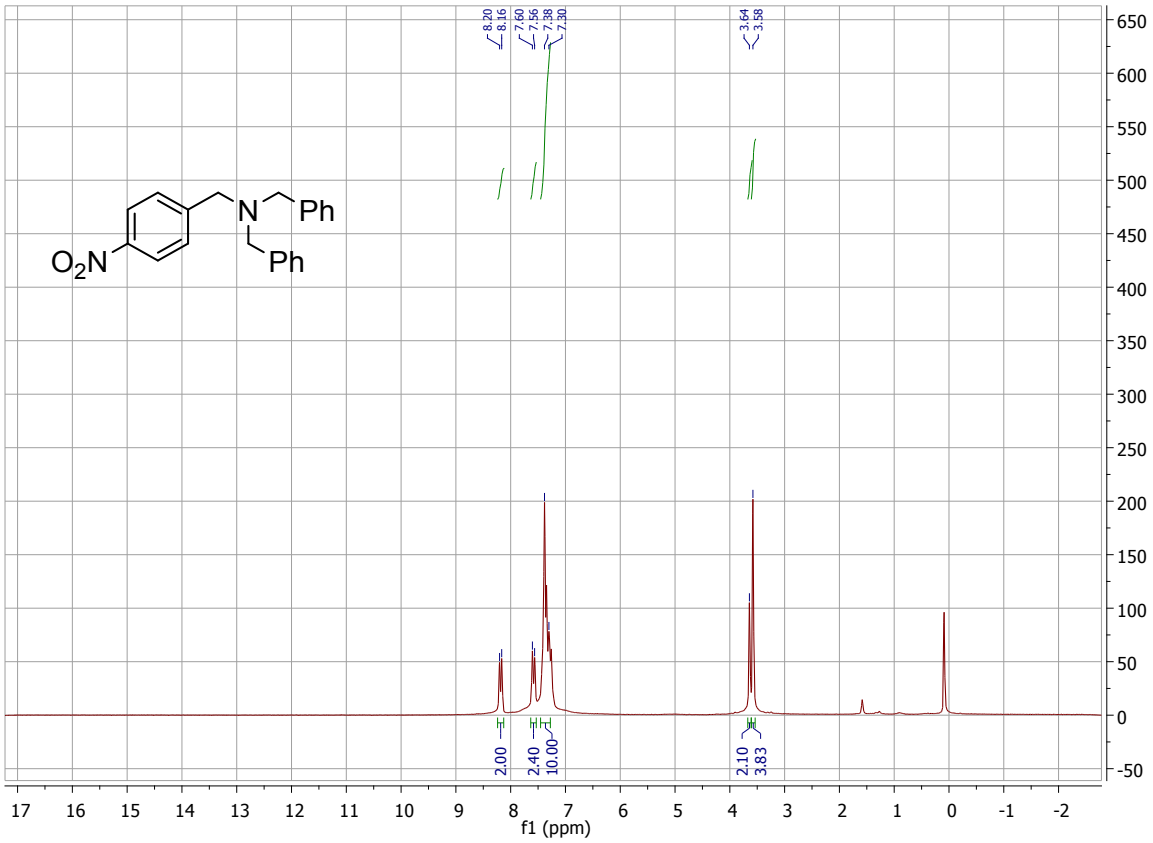
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-4-cyanobenzamide (**3o**)



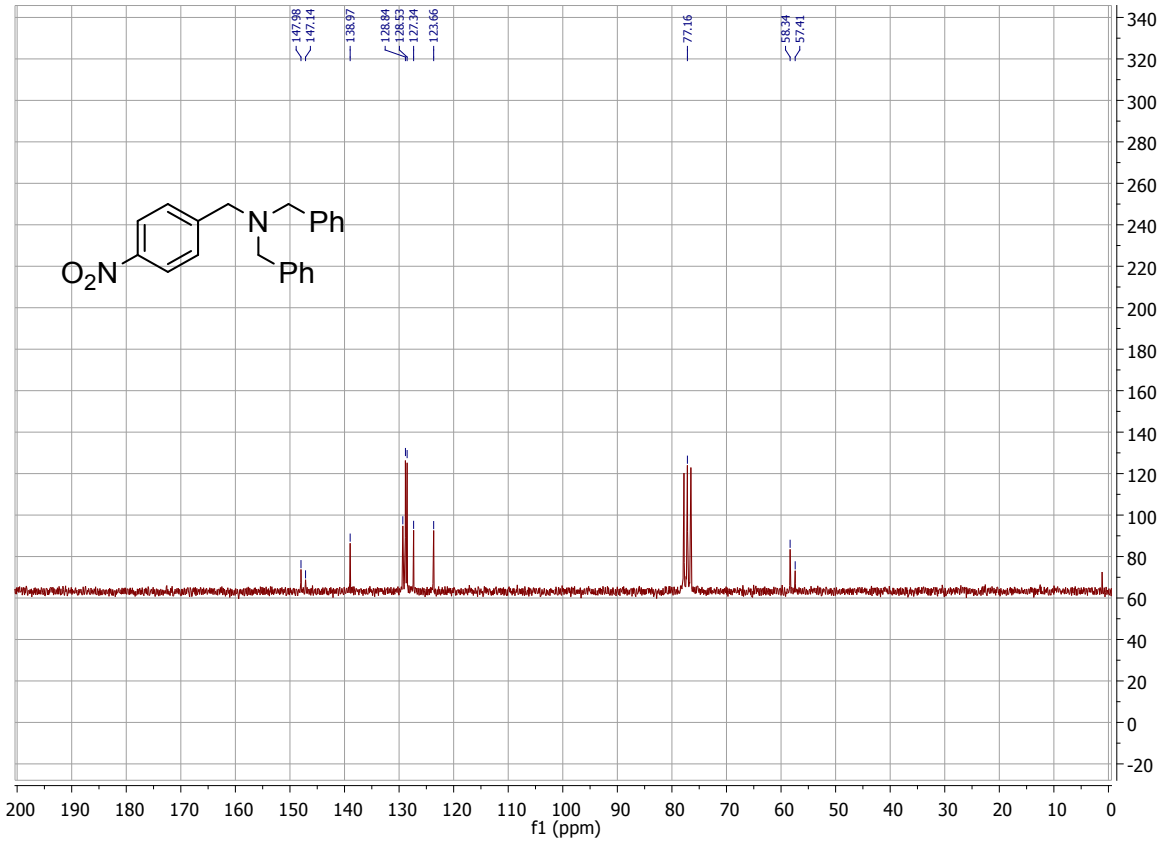
^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-4-cyanobenzamide (**3o**)



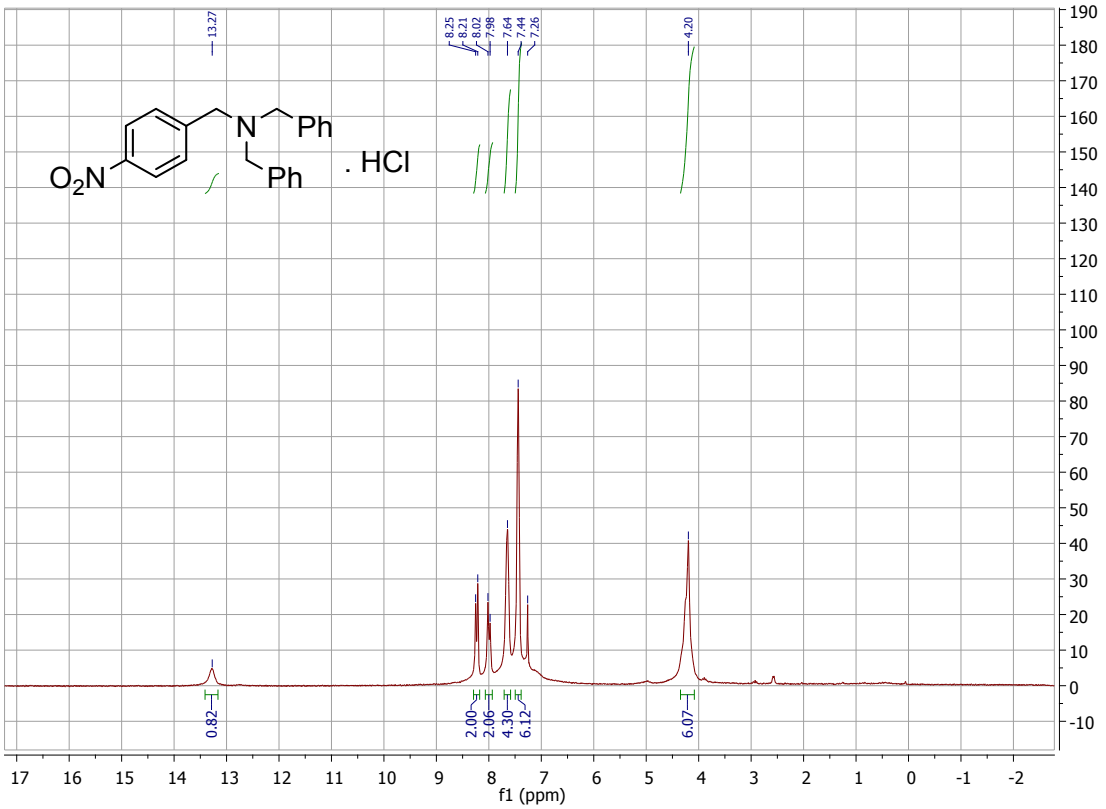
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-1-(4-nitrophenyl)methanamine (**4n**)



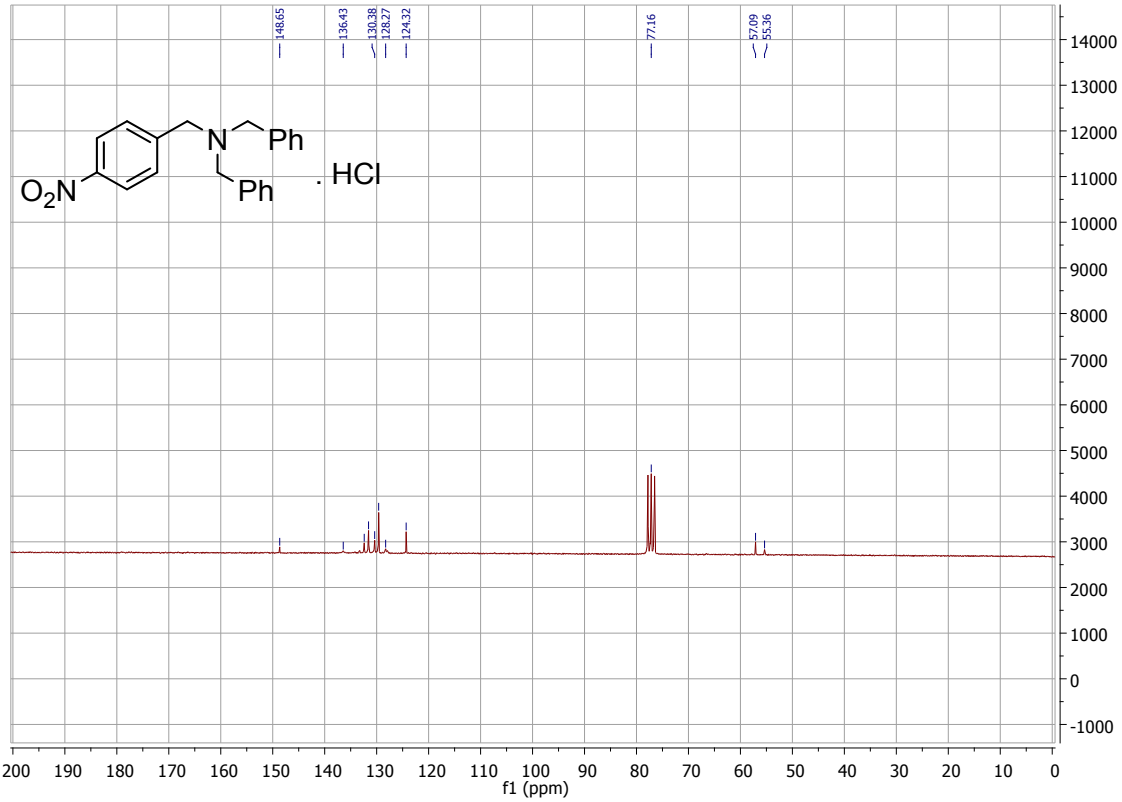
^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-1-(4-nitrophenyl)methanamine (**4n**)



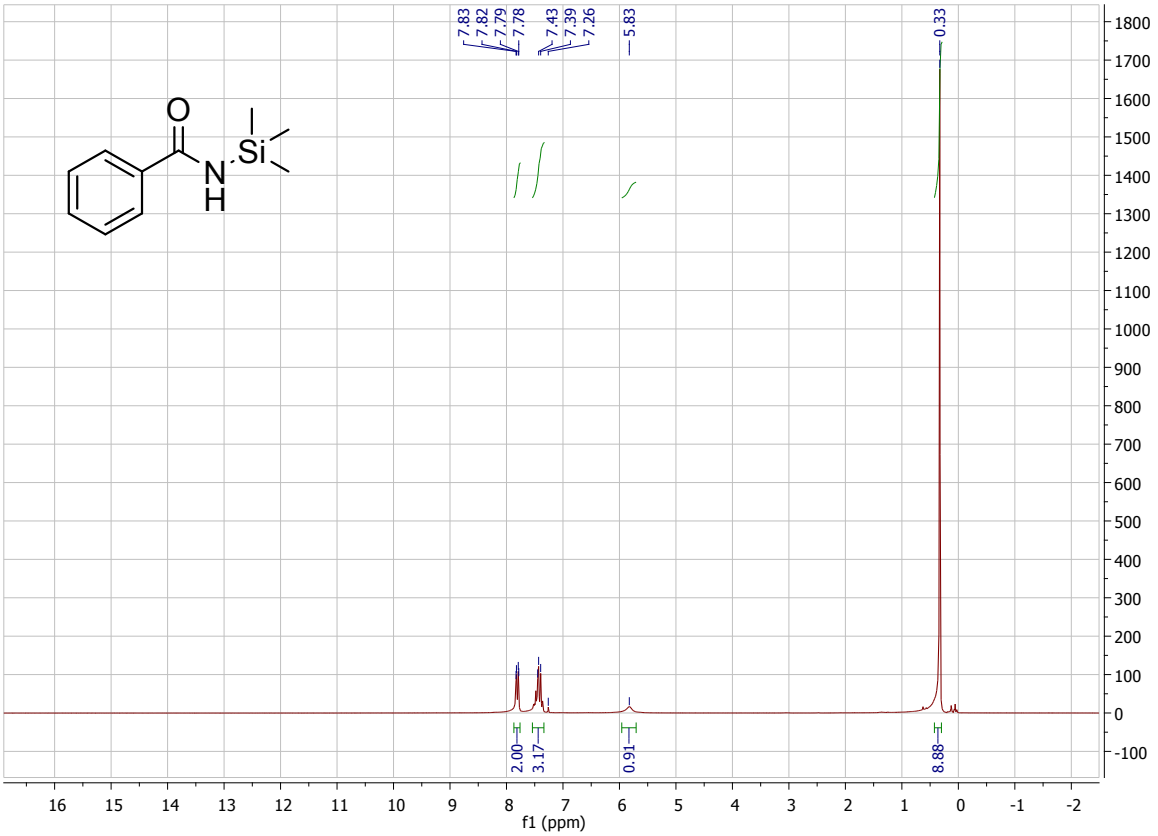
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-1-(4-nitrophenyl)methanamine hydrochloride (**4n.HCl**)



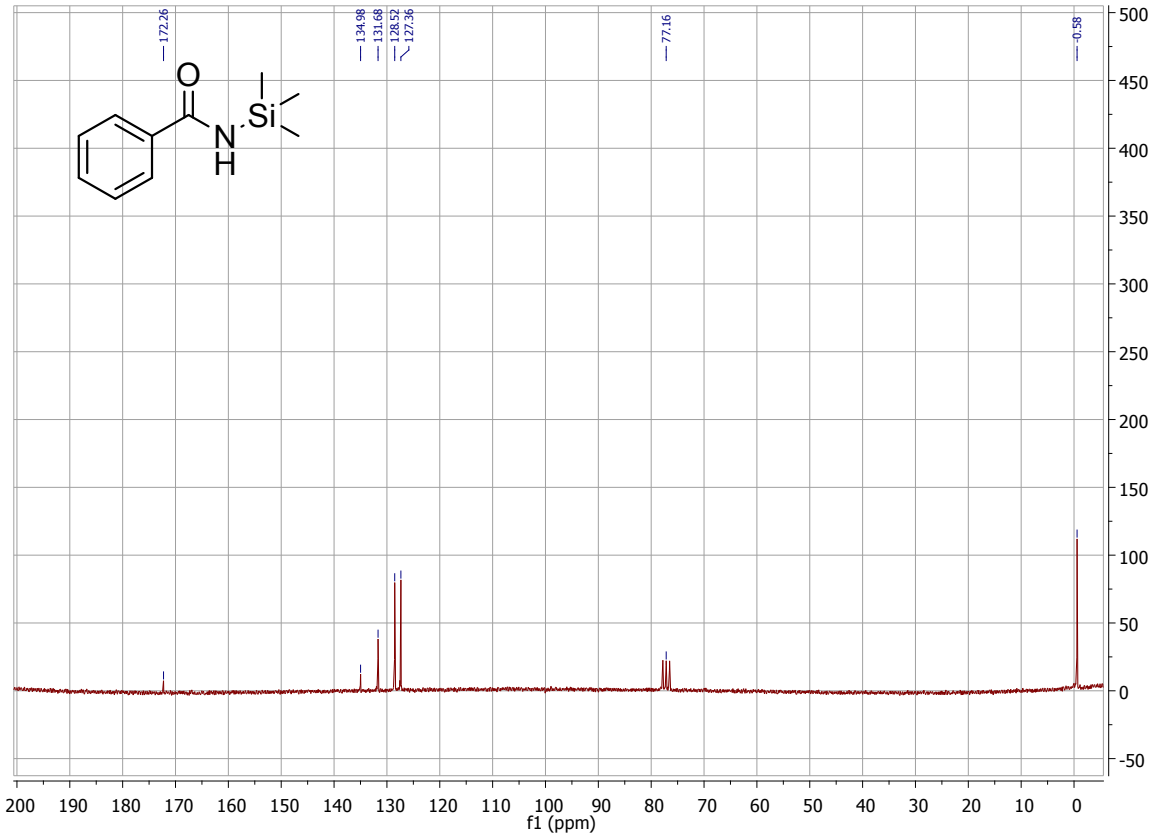
^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*,*N*-dibenzyl-1-(4-nitrophenyl)methanamine hydrochloride (**4n.HCl**)



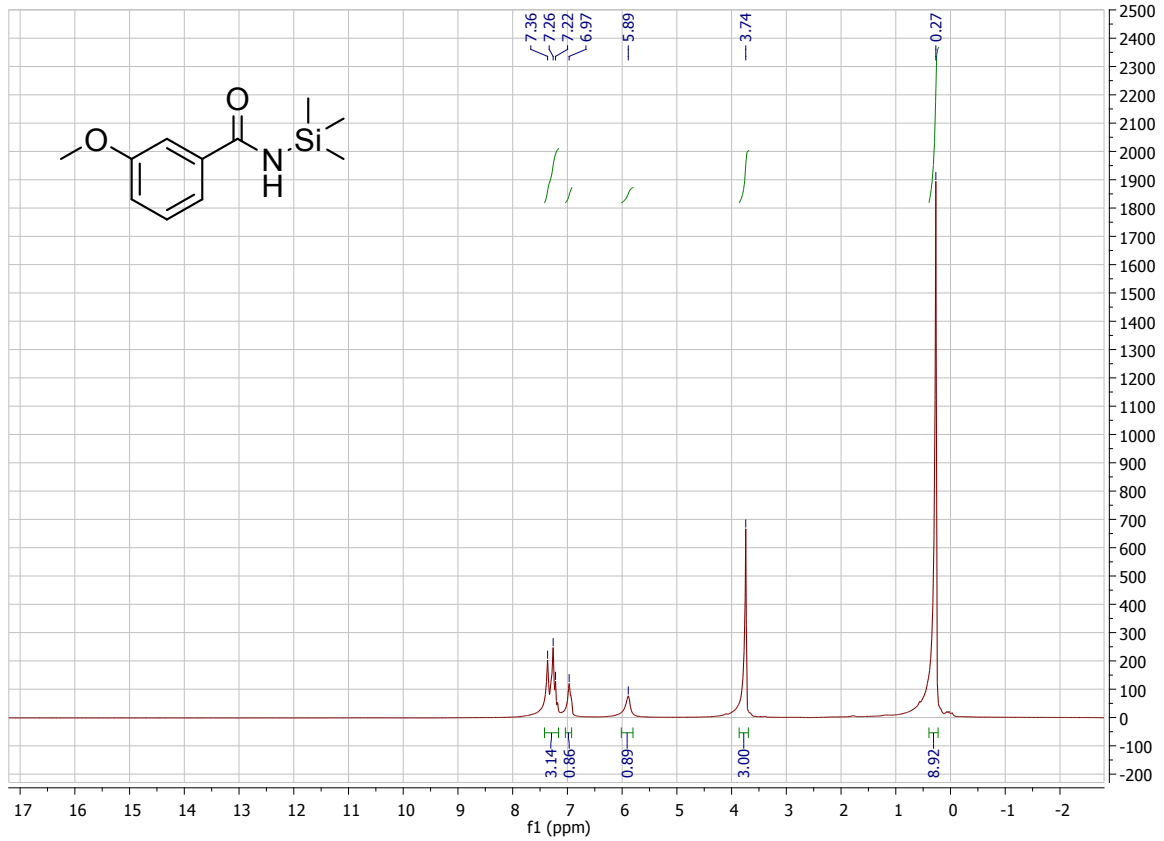
^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*-(trimethylsilyl)benzamide (**10a**)



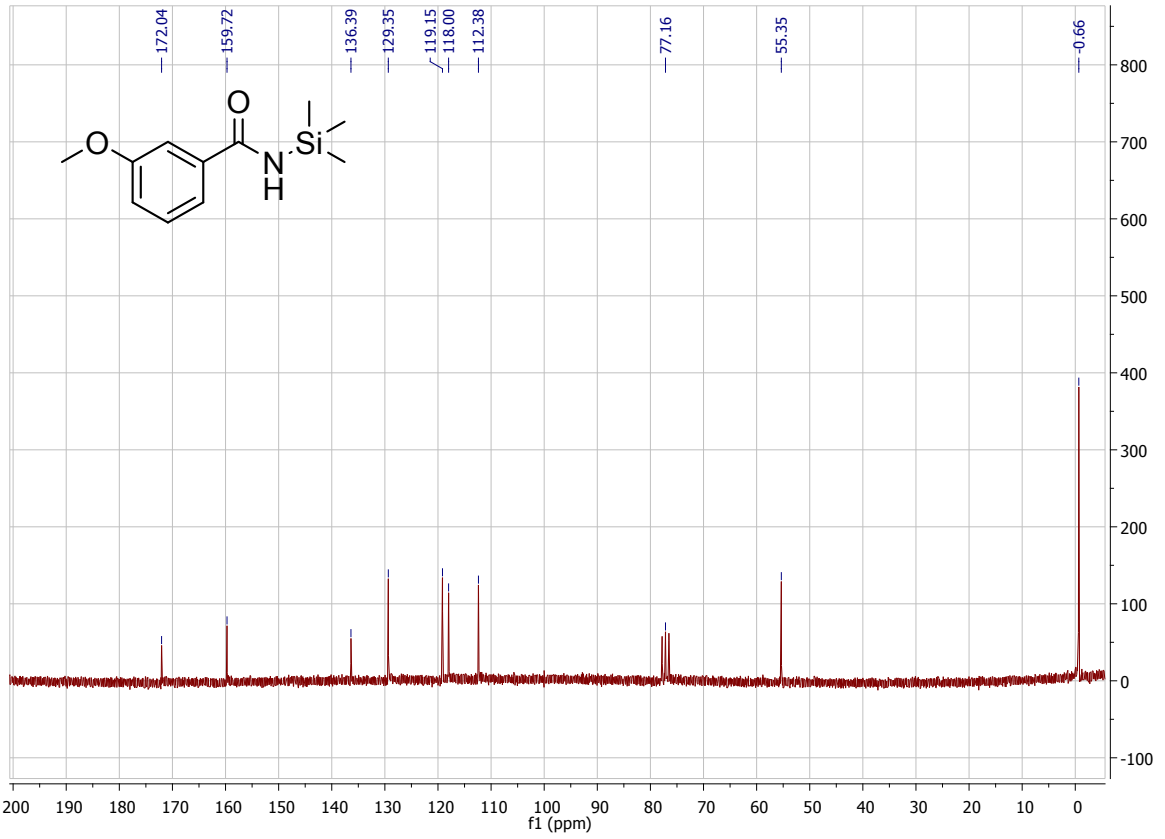
^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of *N*-(trimethylsilyl)benzamide (**10a**)



^{1}H NMR (200 MHz, $CDCl_3$, 298 K) spectrum of 3-methoxy-*N*-(trimethylsilyl)benzamide (**10b**)

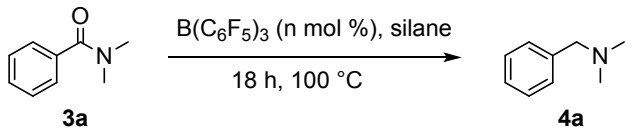


^{13}C NMR (200 MHz, $CDCl_3$, 298 K) spectrum of 3-methoxy-*N*-(trimethylsilyl)benzamide (**10b**)



3. Appendix

3.1. Reduction of 3a: influence of the silane and the catalyst loading



3a **4a**

Entry	Silane	Catalytic loading [mol%]	Temp [°C]	Yield [%][a]
1	$PhSiH_3$	2	100	92
2	$PhSiH_3$	1	100	>99
3	$PhSiH_3$	0.5	100	2
4	TMDS	2	100	>99
5	PMHS	2	100	68
6	PMHS	5	100	>99

[a] GC yield using mesitylene as an internal standard [b] Reaction conditions: *N,N*-dimethylbenzamide (0.10 mmol), silane (4 equiv. "Si–H"), 18 h under an inert athmosphere

1. S. Das, D. Addis, K. Junge and M. Beller, *Chemistry*, 2011, **17**, 12186.
2. W. Wu, Z. Zhang and L. S. Liebeskind, *J. Am. Chem. Soc.*, 2011, **133**, 14256.
3. S. Zhou, K. Junge, D. Addis, S. Das and M. Beller, *Angew. Chem. Int. Ed.*, 2009, **48**, 9507.
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