Metal-Free Reduction of Aromatic and Aliphatic Nitro Compounds to Amines: A $HSiCl_3$-Mediated Reaction of Wide General Applicability

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Supporting Information

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General information

Dry solvents were purchased and stored under nitrogen over molecular sieves (bottles with crown caps). Reactions were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 pre-coated glass plates (0.25 mm thickness) and visualized using UV light. Flash chromatography was carried out on silica gel (230-400 mesh). ^{1}H-NMR spectra were recorded on spectrometers operating at 300 MHz (Bruker Fourier 300 or AMX 300). ^{29}Si-NMR spectra were recorded on a spectrometer operating at 99.4 MHz (AMX 500). Proton and Silicon chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$ δ(1H)= 7.26 ppm, δ(29Si)= 0 ppm). ^{13}C-NMR spectra were recorded on 300 MHz spectrometers (Bruker Fourier 300 or AMX 300) operating at 75 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ = 77.0 ppm). Enantiomeric excess determinations were performed with Chiral Stationary Phase HPLC analysis on an Agilent 1200 series HPLC instrument.

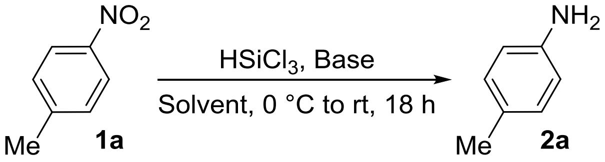
General procedure and reaction conditions optimization

In a round bottomed flask the nitro-compound (0.7 mmol) and the tertiary amine (3.5 mmol) were dissolved into the dry solvent (5 mL) under magnetic stirring and nitrogen atmosphere. A solution of freshly distilled $HSiCl_3$ (2.5 mmol) in 2 mL of dry solvent was prepared apart, and it was added drop-wise to the first solution over 10 minutes at 0 °C. After stirring the reaction mixture for 18 h, 5 mL of a saturated solution of $NaHCO_3$ was added drop-wise and the biphasic mixture was allowed to stir for 30 min. The crude mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and then dried under reduced pressure to afford the crude product.

The starting material conversion was evaluated through ^{1}H-NMR analysis of the crude products. **In some cases, deviations from the expected products' chemical shifts were observed due to the presence of residual tertiary amine hydrochlorides**. However, further purification of such crude mixtures by means of flash column chromatography (Hex/AcOEt mixtures) or by washing with DCM/NaOH 1M restored the NMR signals to the expected chemical shifts.

In the following table the optimization of the reaction conditions is reported. By varying both the solvent and the base the optimum reaction conditions were found to be the use of either acetonitrile or dichloromethane as solvent in combination with both TEA or DIPEA as bases of choice.

Table S1. Reaction conditions optimization



Entry	Solvent	Base	Conv. (%)
1	CH_2Cl_2	DIPEA	>99
2	CH_3CN	DIPEA	>99
3	$CHCl_3$	DIPEA	32
4	THF	DIPEA	n.r.
5	Toluene	DIPEA	n.r.
6	Hexane	DIPEA	n.r.
7	CH_3CN	TEA	90
8	CH_3CN	DMAP	17
9	CH_3CN	Pyridine	n.r.
10	CH_3CN	DABCO	n.r.
11	CH_3CN	DBU	54
12	CH_3CN	DMF	n.r.

Characterizations

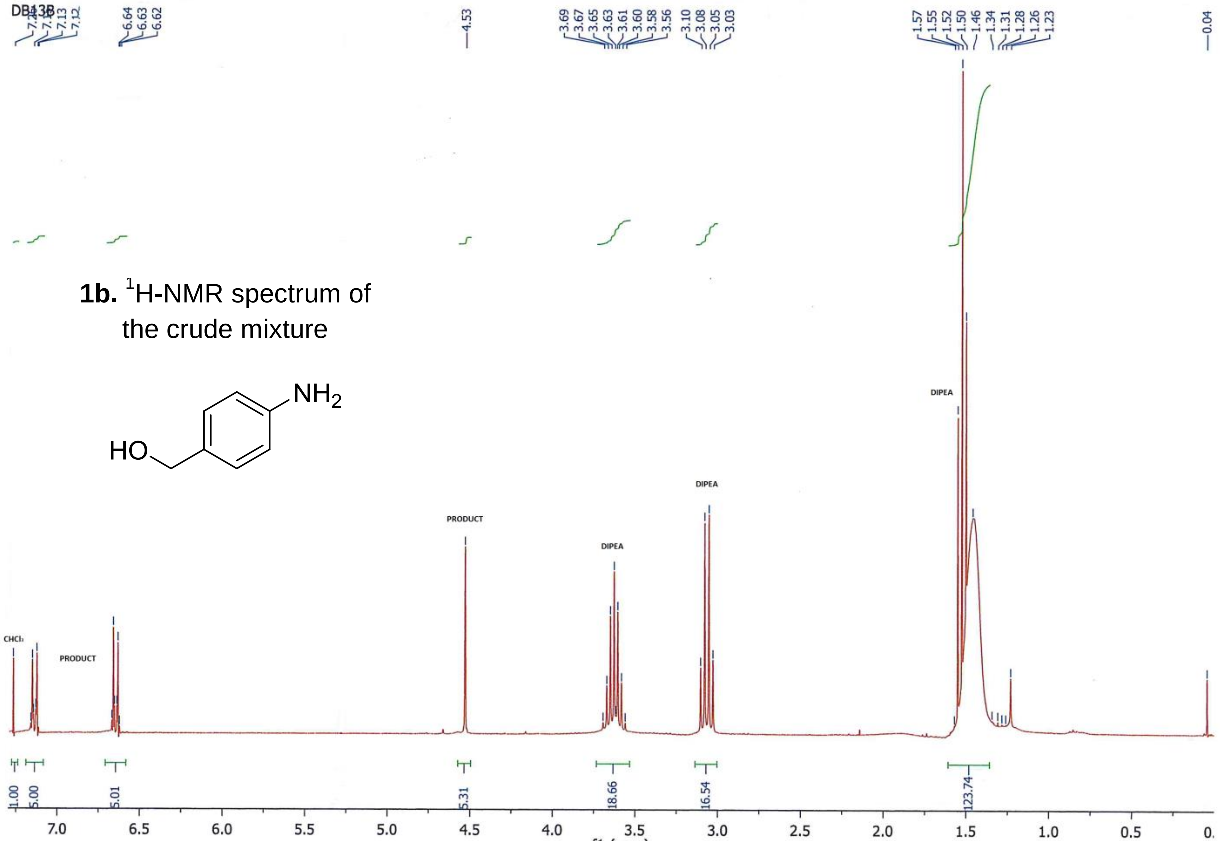
Characterizations of the products were found to agree with authentic samples (if commercially available) or with previously reported data. The ^{1}H-NMR spectra of some representative purified products are reported below the relative characterization. *In other cases the spectra of the crude mixtures are reported in order to prove the reported conversions.* Some products have been isolated in slightly lower yields with respect to the reported quantitative conversion. This is due to the combination of two factors: loss of material during the extraction process due to the hydrophilicity of the obtained amines, or during the chromatographic purification.

4-toluidine (1a)[1]

Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 69 mg (0.64 mmol) of the pure product as a white solid (91% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.95 (d, *J*=8.2 Hz, 2H), 6.63 (d, *J*=8.2 Hz, 2H), 3.52 (bs, 2H, NH), 2.27 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 143.9, 129.5,127.2, 115.1, 20.4.

4-aminobenzylalcohol (1b)[1]

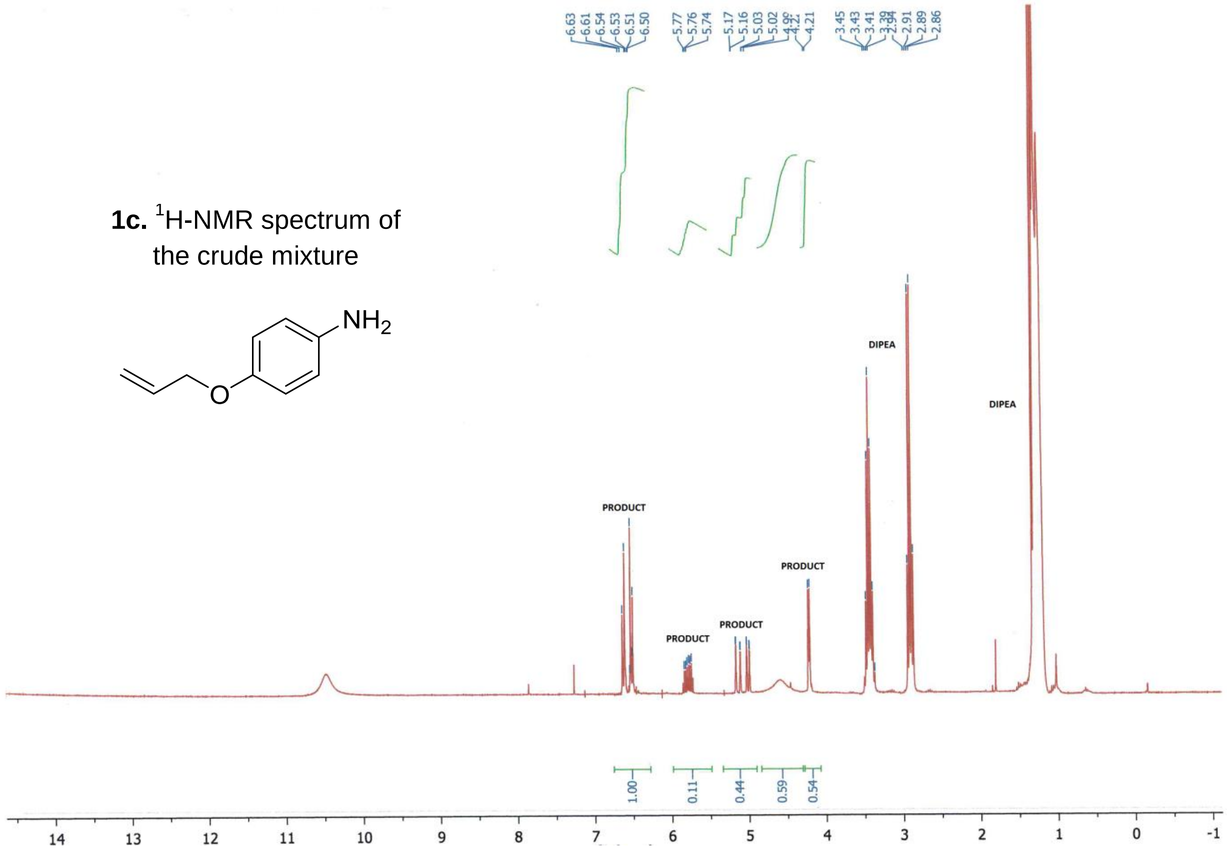
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 82 mg (0.67 mmol) of the pure product as a yellow solid (95% yield) ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.13 (d, *J*=8.6 Hz, 2H), 6.64 (d, *J*=8.6 Hz, 2H), 4.53 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 146.0, 131.1, 128.8, 115.2, 65.2.



1b. ^{1}H-NMR spectrum of the crude mixture

4-allyloxyaniline (1c)[2]

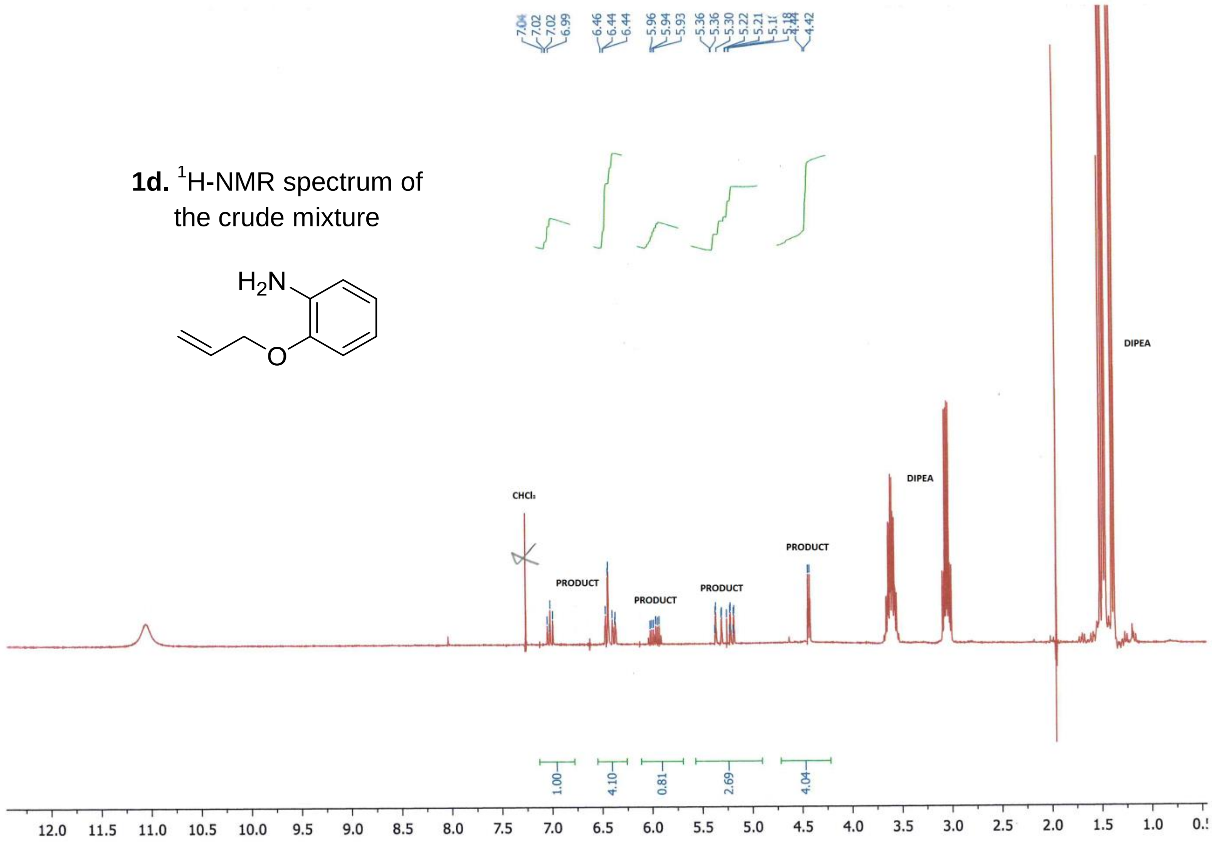
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 103 mg (0.69 mmol) of the pure product as a solid (98% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 6.62 (d, *J*=6.2 Hz, 2H), 6.51 (d, *J*=6.2 Hz, 2H), 5.89 (ddt, *J*=16.3 Hz, 11.9 Hz, 2.8 Hz, 1H), 5.16 (d, *J*=16.3 Hz, 1H), 4.97 (d, *J*=11.9 Hz, 1H), 4.21 (d, *J*=2.8 Hz, 2H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 152.0, 140.3, 134.1, 117.5, 116.7, 116.2, 69.9.



1c. ^{1}H-NMR spectrum of the crude mixture

2-allyloxyaniline (1d)[3]

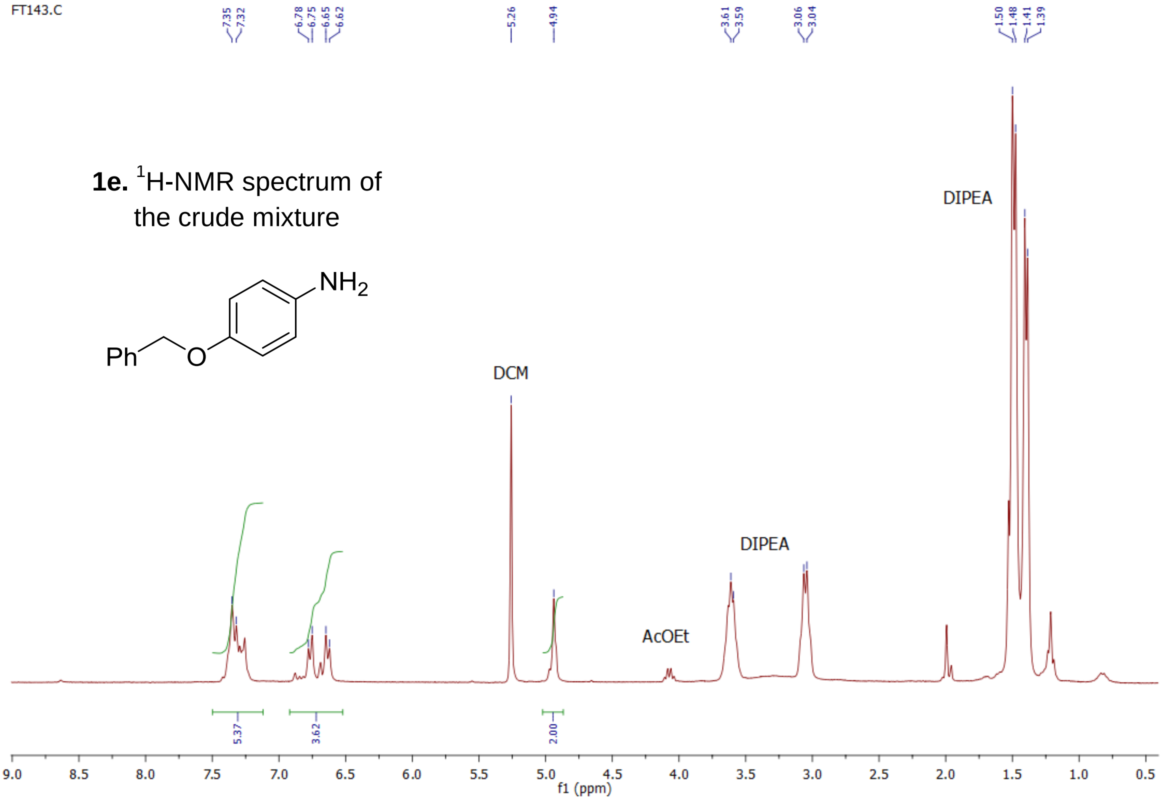
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 95 mg (0.64 mmol) of the pure product as a solid (91% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.02 (m, 1H), 6.45 (m, 3H), 5.93 (ddt, *J*=17.7 Hz, 12.1 Hz, 4.8 Hz, 1H), 5.33 (d, *J*=17.8 Hz, 1H), 5.20 (d, *J*=12.1 Hz, 1H), 4.43 (d, *J*=4.8 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 69.2, 112.1, 115.2, 117.4, 118.4, 121.4, 133.6, 136.5, 146.3



1d. ^{1}H-NMR spectrum of the crude mixture

4-benzyloxyaniline (1e)[4]

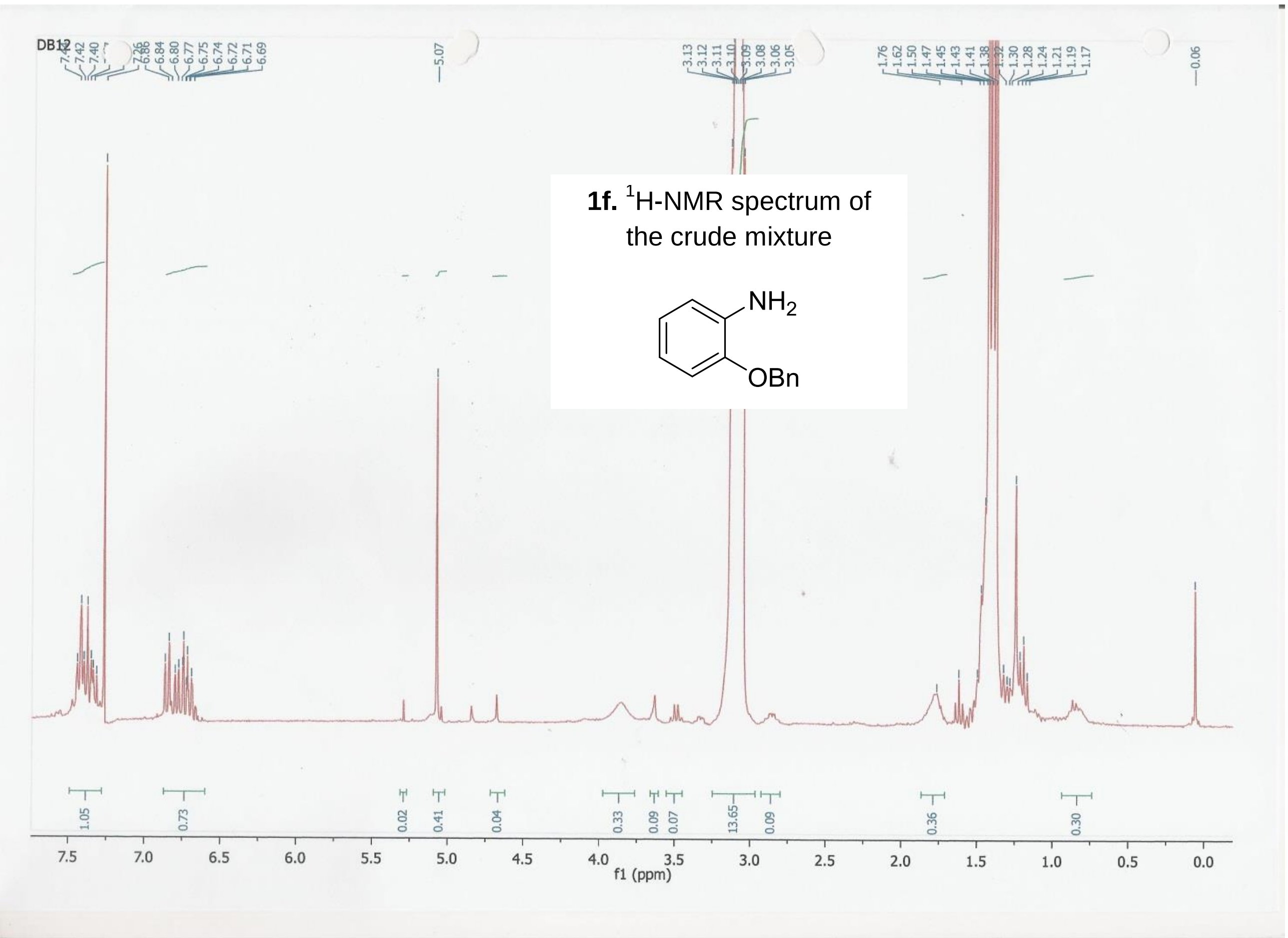
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 133 mg (0.67 mmol) of the pure product as a solid (95% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40 (m, 5H), 6.85 (d, *J*=8.7 Hz, 2H), 6.66 (s, *J*=8.7 Hz, 2H), 5.02 (s, 2H), 3.37 (bs, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 152.0, 140.3, 137.6, 128.4, 127.7, 127.4, 116.3, 116.2, 70.9.



1e. ^{1}H-NMR spectrum of the crude mixture

2-benzyloxyaniline (1f)[5]

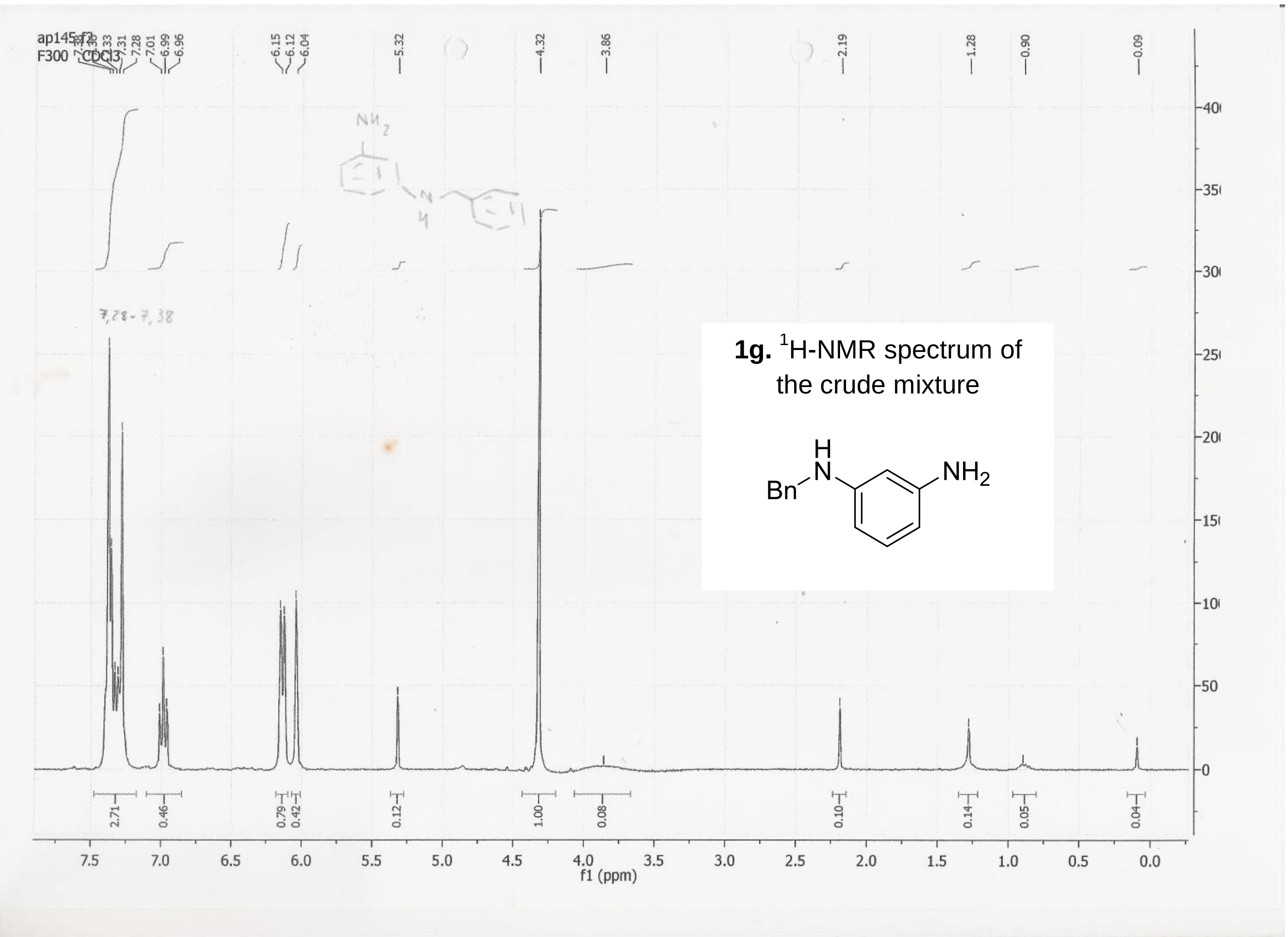
Conv. 98%. Purification through flash column chromatography gave 129 mg (0.65 mmol) of the pure product as a solid (93% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40 (m, 5H), 6.77 (m, 4H), 5.07 (s, 2H), 3.80 (bs, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 70.4, 112.1, 115.2, 118.4, 121.5, 127.5, 127.9, 128.5, 136.5, 137.2, 146.5.



1f. ^{1}H-NMR spectrum of the crude mixture

N-Benzyl-3-phenylene diamine (1g)[6]

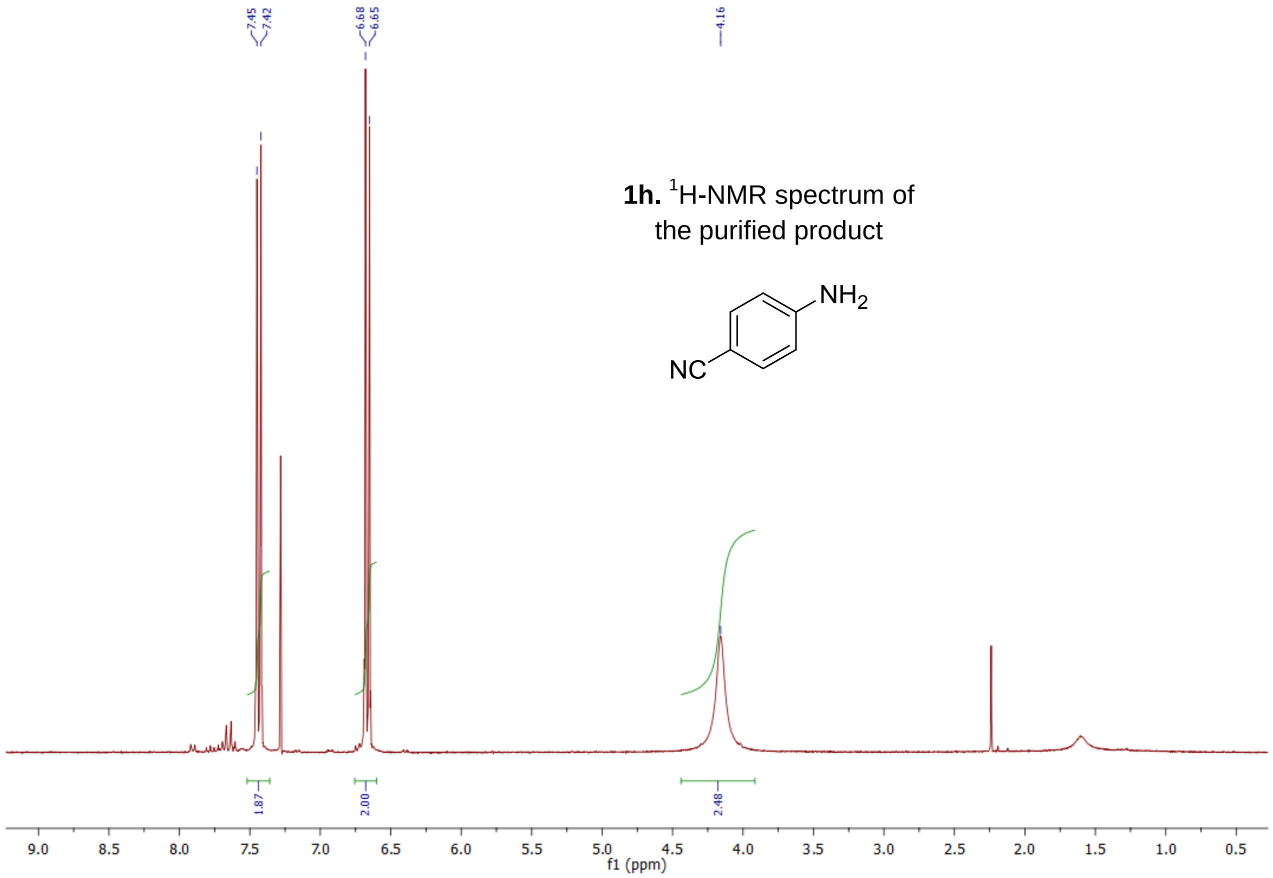
The starting material conversion was not determinable from the NMR spectrum of the crude mixture. Hence, the product was isolated through flash column chromatography in 88% yield as a solid (122 mg, 0.62 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.30 (m, 5H), 6.99 (t, *J*=7.5 Hz, 1H), 6.13 (d, *J*=7.5 Hz, 2H), 6.04 (s, 1H), 4.32 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 149.3, 147.4, 139.5, 130.1, 128.6, 127.5, 127.2, 105.2, 104.2, 99.6, 48.3.



1g. ^{1}H-NMR spectrum of the crude mixture

4-aminobenzonitrile (1h)[7]

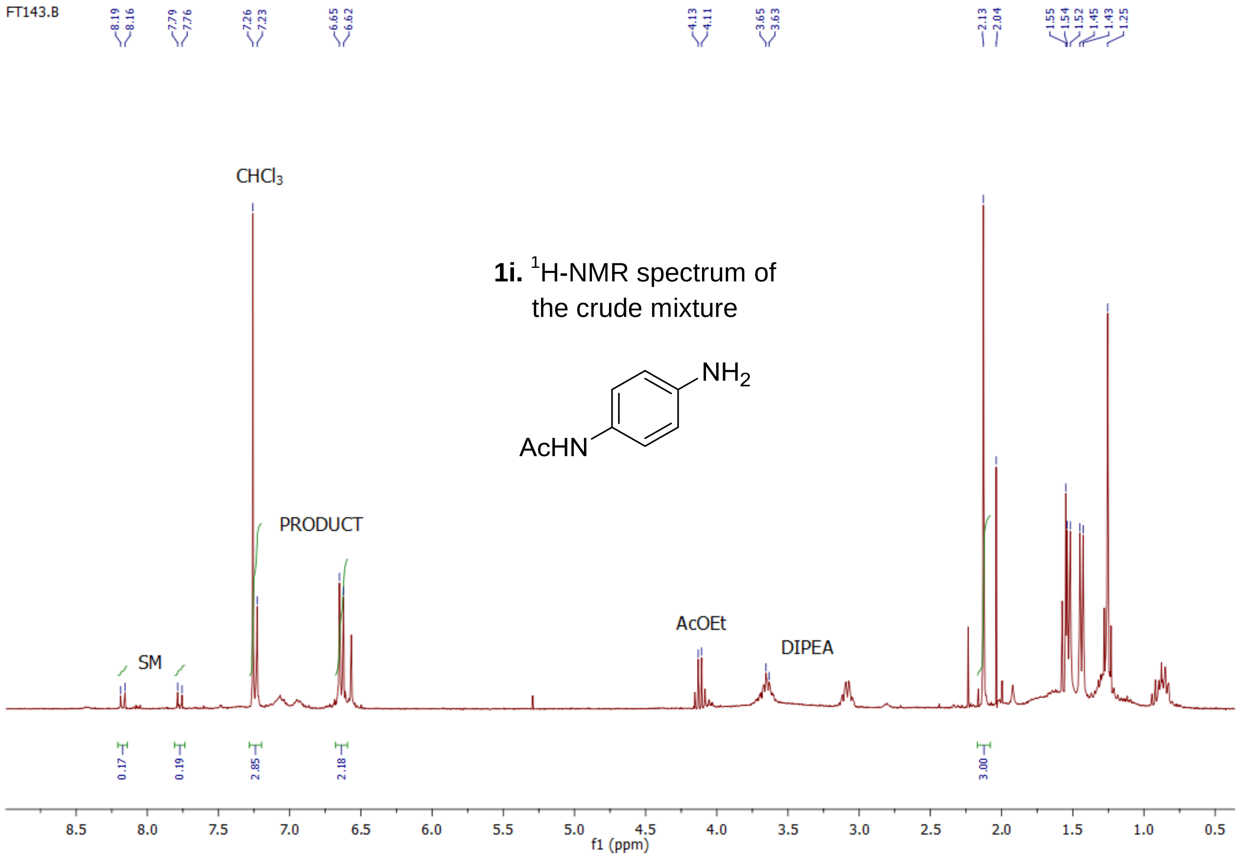
Conv. 93%. Purification through flash column chromatography gave 74 mg (0.63) of the pure product a solid (89% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.43 (d, *J*=8.7 Hz, 2H), 6.67 (d, *J*=8.7 Hz, 2H), 4.16 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 150.8, 133.7, 120.4, 114.3, 99.3.



1h. ^{1}H-NMR spectrum of the purified product

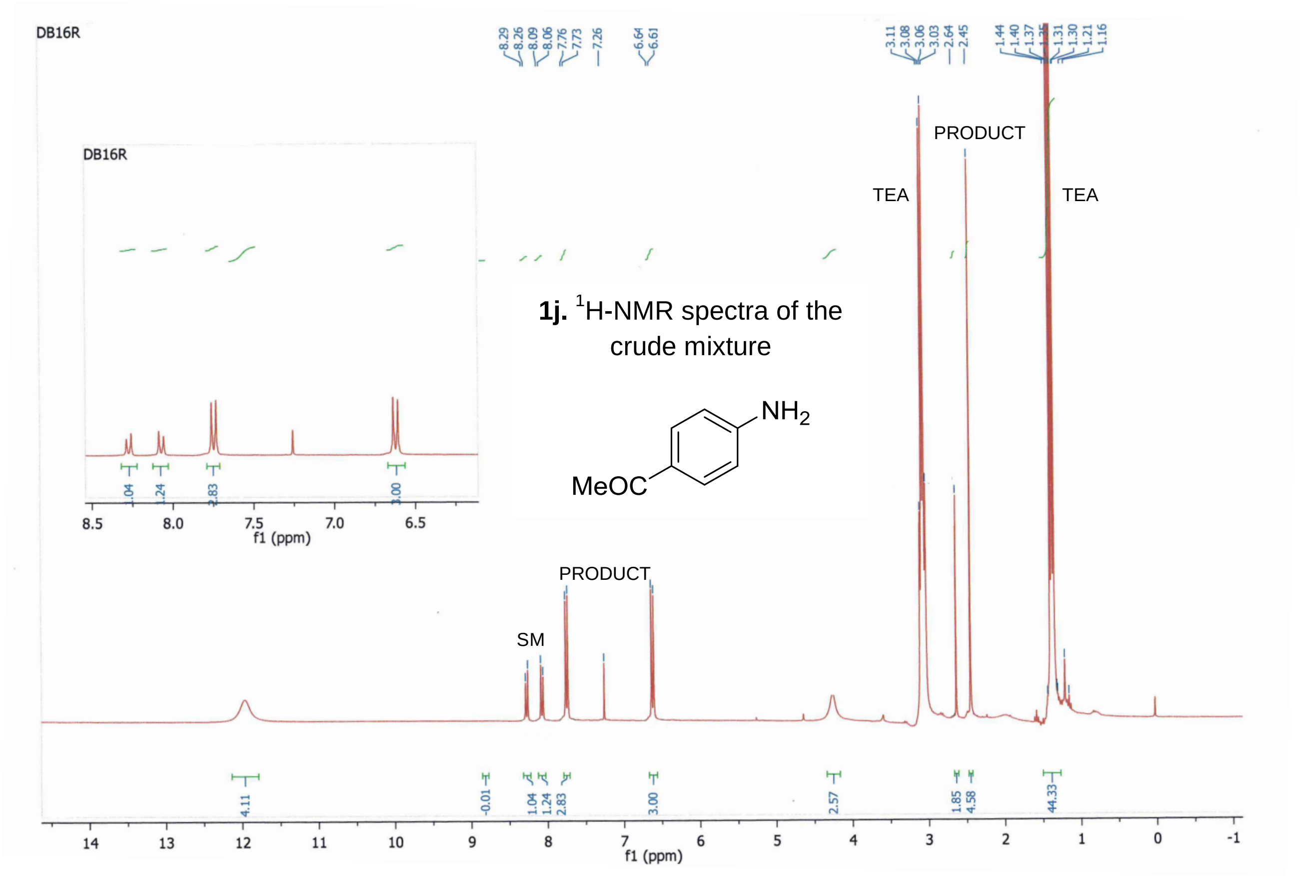
4’-aminoacetanilide (1i)[8]

Conv. 92%. In the following spectrum 8% integrating signals of the starting material (SM) with respect to the product are detectable. Purification through flash column chromatography gave 95 mg (0.63 mmol) of the pure product a solid (90% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.22 (d, *J*=8.5 Hz, 2H), 6.63 (d, *J*=8.5 Hz, 2H), 2.13 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 167.2, 144.3, 128.2, 120.7, 114.5, 23.8.


1i. ^{1}H-NMR spectrum of the crude mixture

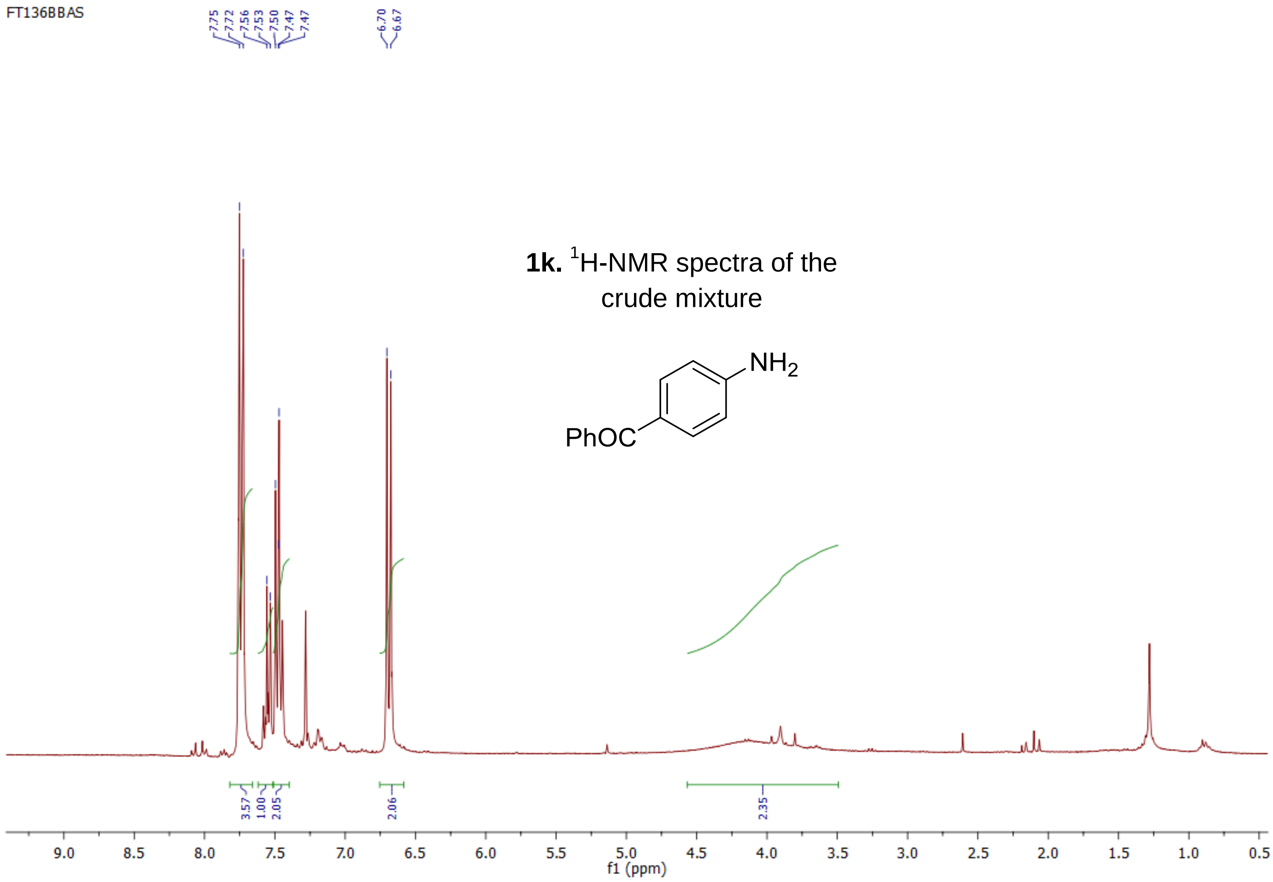
4-aminoacetophenone (1j)[9]

Conv. 70%. In the following spectrum 30% integrating signals of the starting material (SM) with respect to the product are detectable. Purification through flash column chromatography gave 68 mg (0.5 mmol) of the pure product as a yellow solid (70% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.72 (d, *J*=8.7 Hz, 2H), 6.63 (d, *J*=8.7 Hz, 2H), 4.03 (bs, 2H), 2.44 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 196.3, 151.0, 130.7, 128.0, 113.7, 25.9


1j. ^{1}H-NMR spectra of the crude mixture

4-aminobenzophenone (1k)[10]

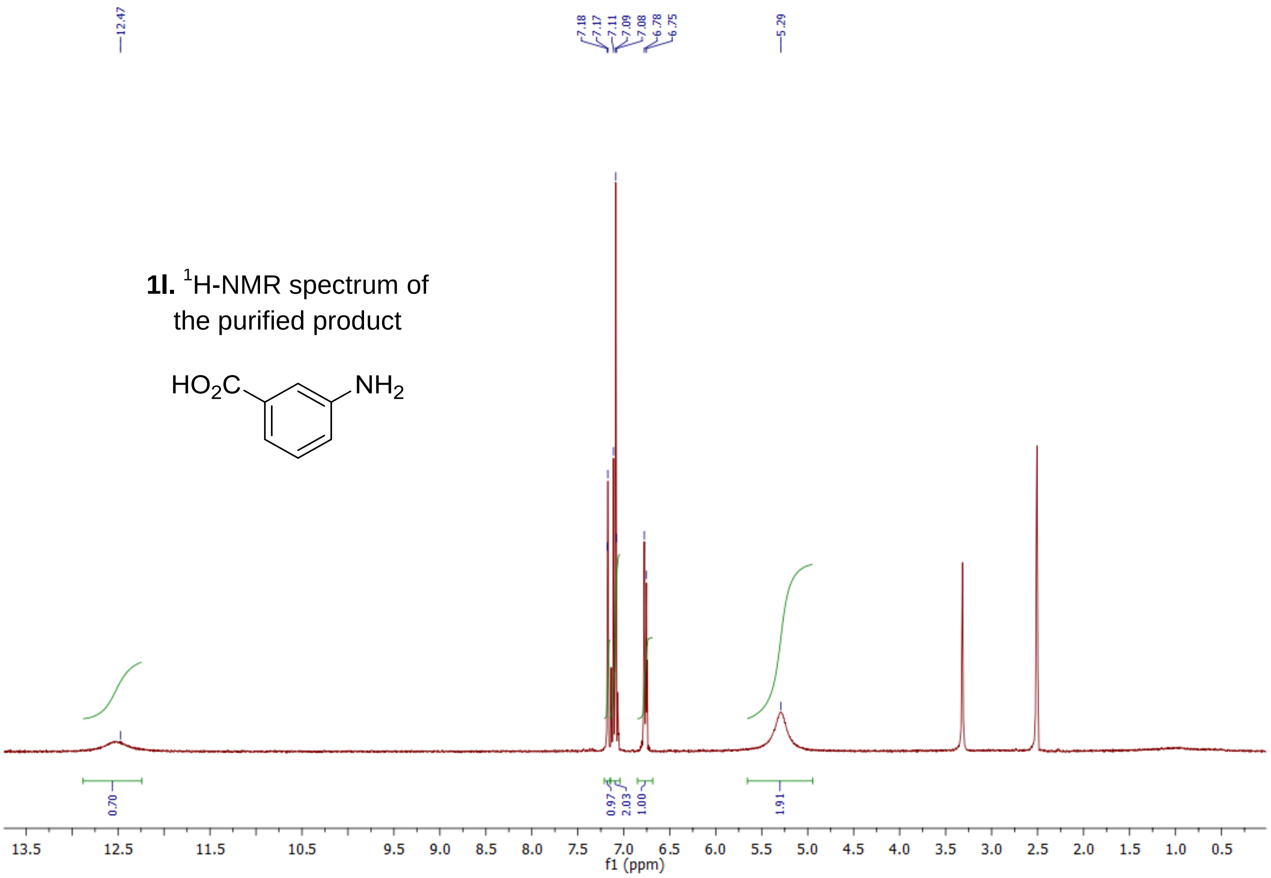
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 129 mg (0.65 mmol) of the pure product a solid (93% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.72 (m, 4H), 7.54 (t, *J*=7.4 Hz, 1H), 7.46 (t, *J*=7.4 Hz, 2H), 6.68 (d, *J*=8.4 Hz, 2H), 4.10 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 195.4, 151.5, 138.9, 132.9, 131.4, 129.4, 128.1, 126.9, 113.6.



1k. ^{1}H-NMR spectra of the crude mixture

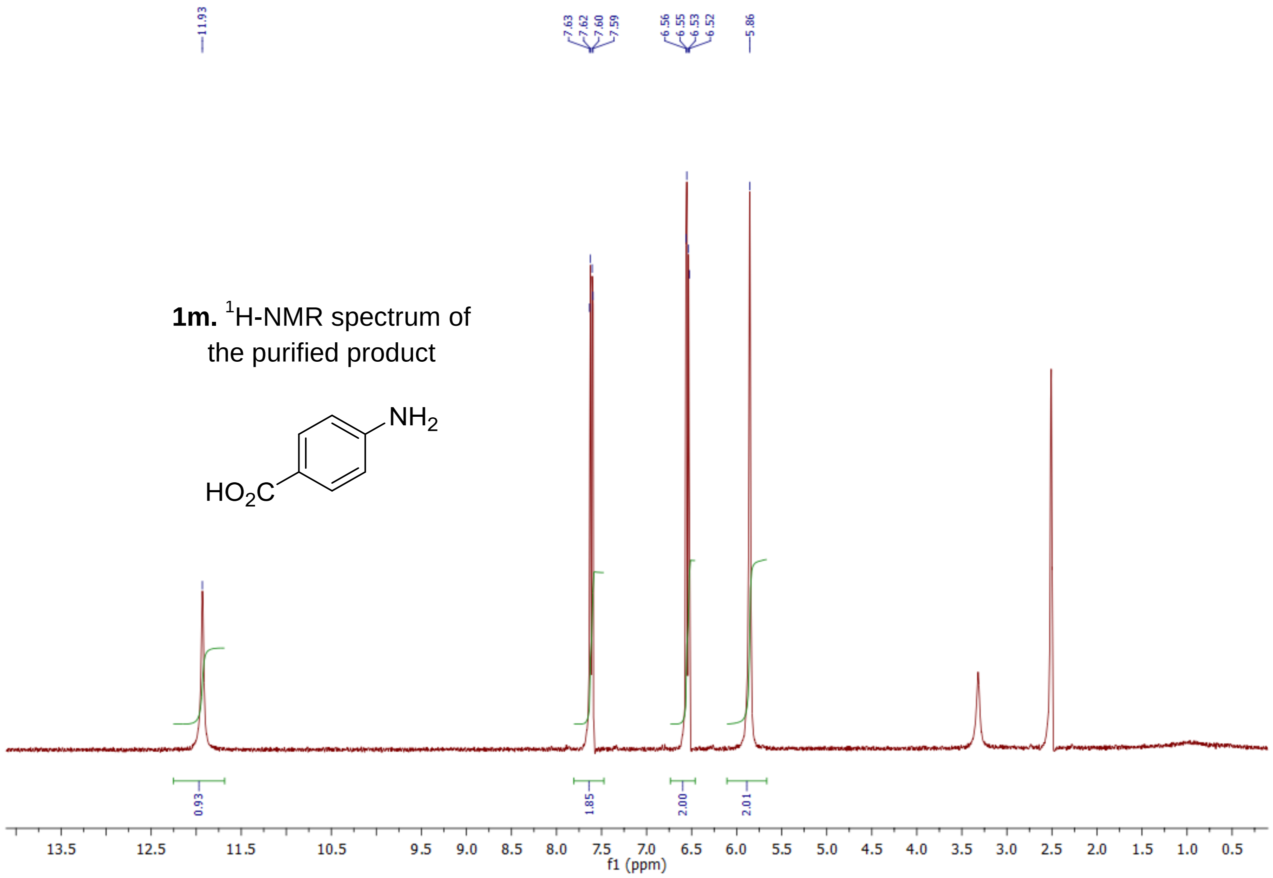
3-aminobenzoic acid (1l)[1]

Conv. 60%. Purification through flash column chromatography gave 55 mg (0.4 mmol) of the pure product as a white solid (57% yield). ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 12.47 (m, 1H), 7.08-7.18 (m, 3H), 6.76(m, 1H), 5.29 (bs, 2H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ: 167.9, 148.8, 131.3, 128.9, 118.0, 116.6, 114.4.


1l. ^{1}H-NMR spectrum of the purified product

4-aminobenzoic acid (1m)[10]

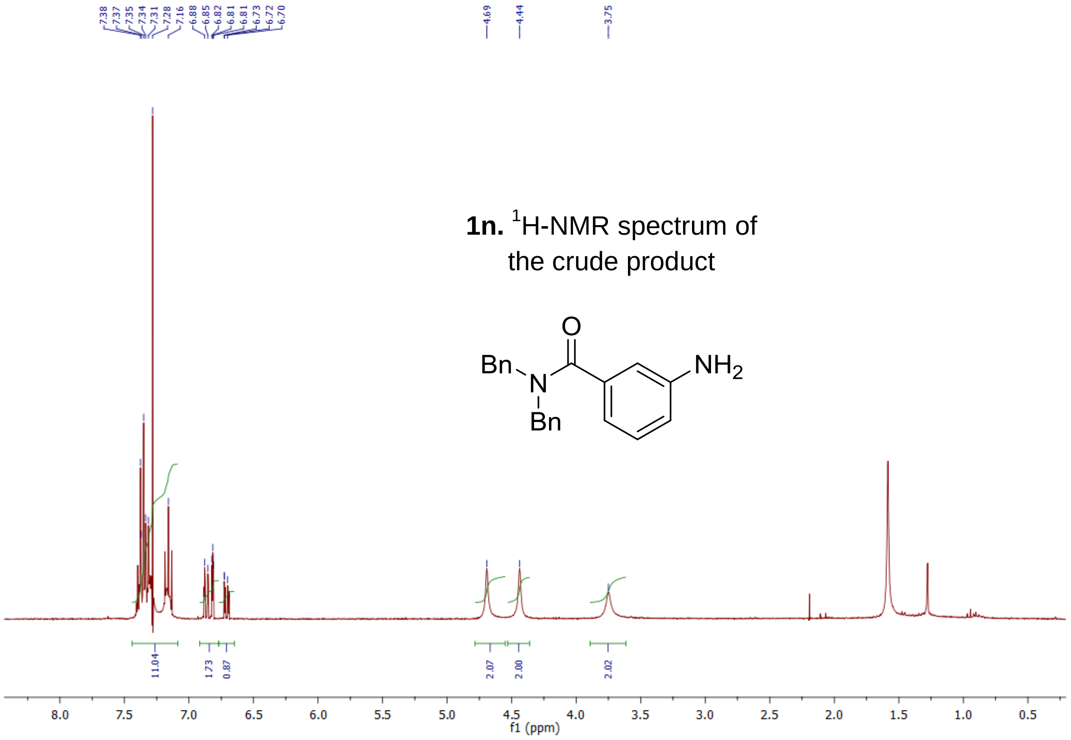
Conv. 70%. Purification through flash column chromatography gave 62 mg (0.45 mmol) of the pure product as white solid (65% yield). ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 11.93 (bs, 1H), 7.62 (d, *J*=8.6 Hz, 2H), 6.55 (d, *J*=8.6 Hz, 2H), 5.86 (bs, 2H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ: 167.9, 153.6, 131.7, 117.4, 113.1.



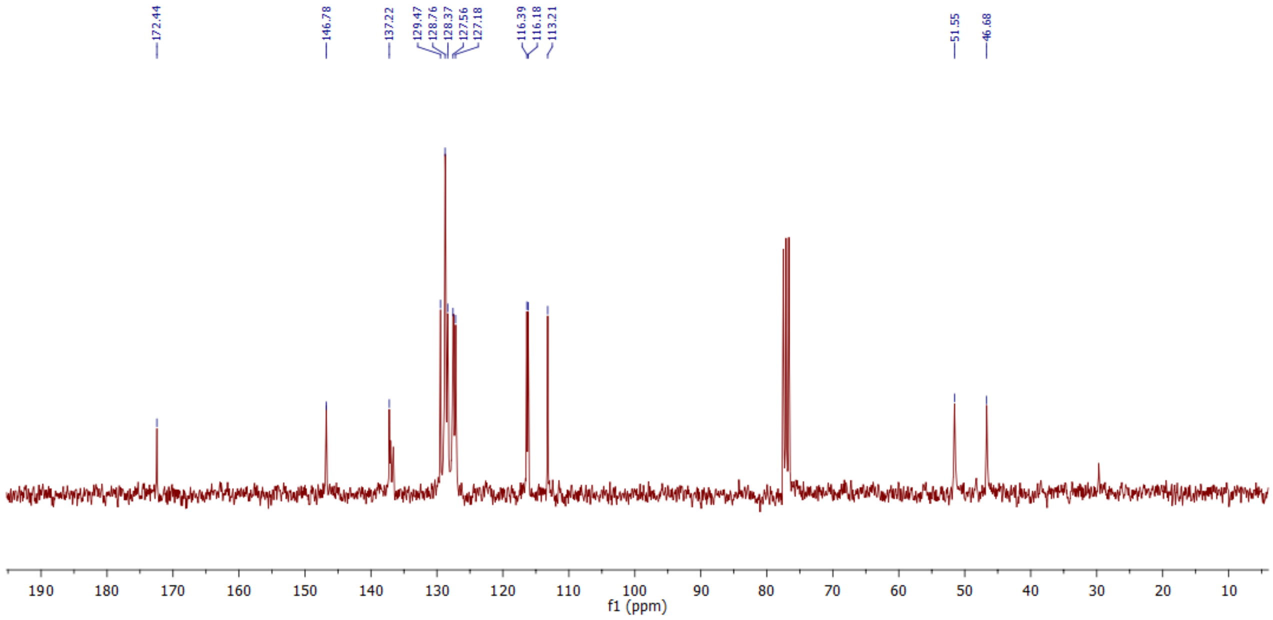
1m. ^{1}H-NMR spectrum of the purified product

3-amino-N,N-dibenzylbenzamide (1n)

Conv. >98%. Purification through flash column chromatography gave 210 mg (0.66 mmol) of the pure product as a white solid (95% yield). By NMR analysis, two benzyl groups are detectable at rt. ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 7.40-7.10 (m, 11H), 6.86 (m, 1H), 6.81 (m, 1H), 6.71 (ddd, *J*=8.0, 2.5, 1.0 Hz, 1H), 4.69 (s, 2H), 4.44 (s, 2H), 2.02 (bs, 2H, NH). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 172.4, 146.8, 137.2, 136.6, 129.5, 128.7, 128.4, 127.6, 127.2, 116.4, 116.2, 113.2, 51.5, 46.7. HRMS (ESI) m/z Calc for $C_{21}H_{21}N_2O^+$ [M+H]$^+$ 317.16484, found 317.16454.

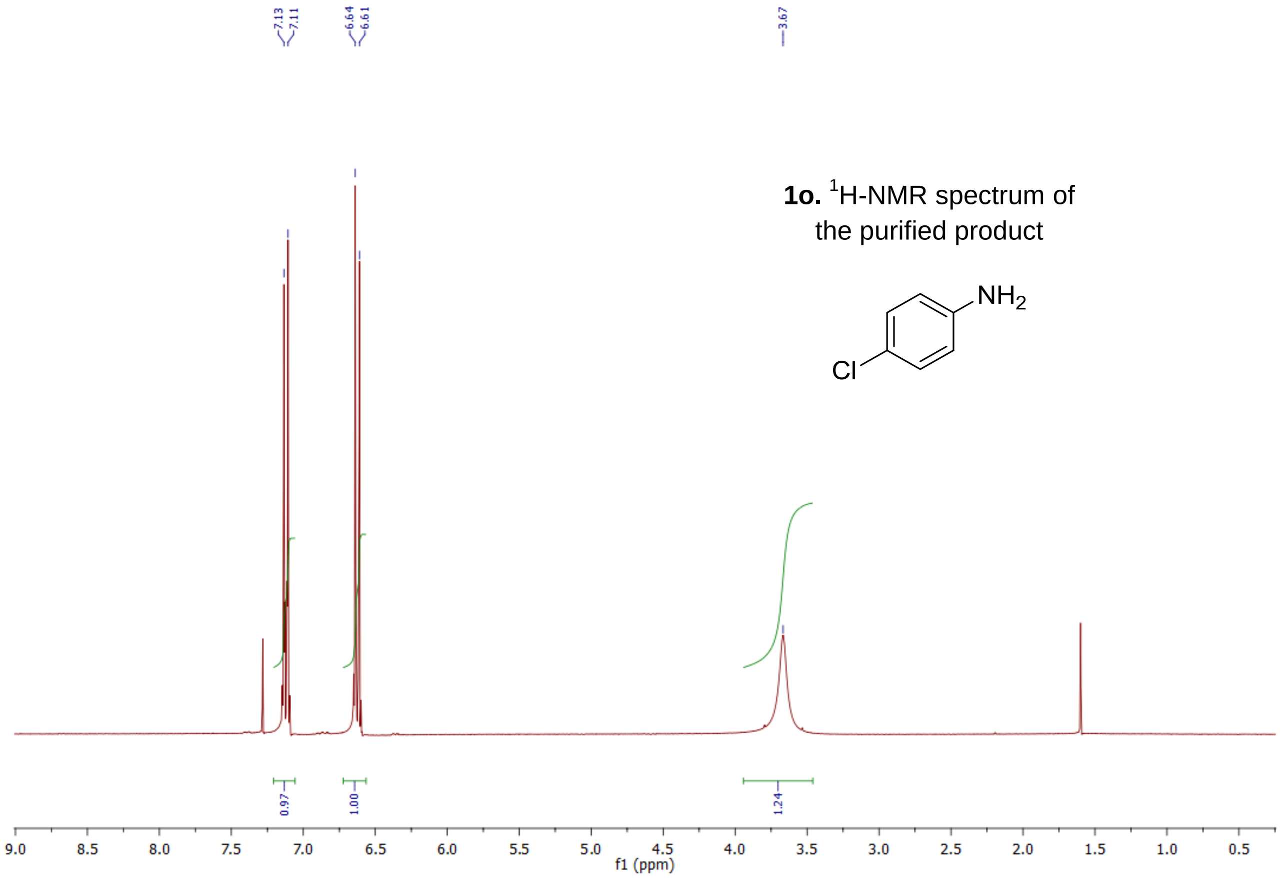


1n. ^{1}H-NMR spectrum of the crude product



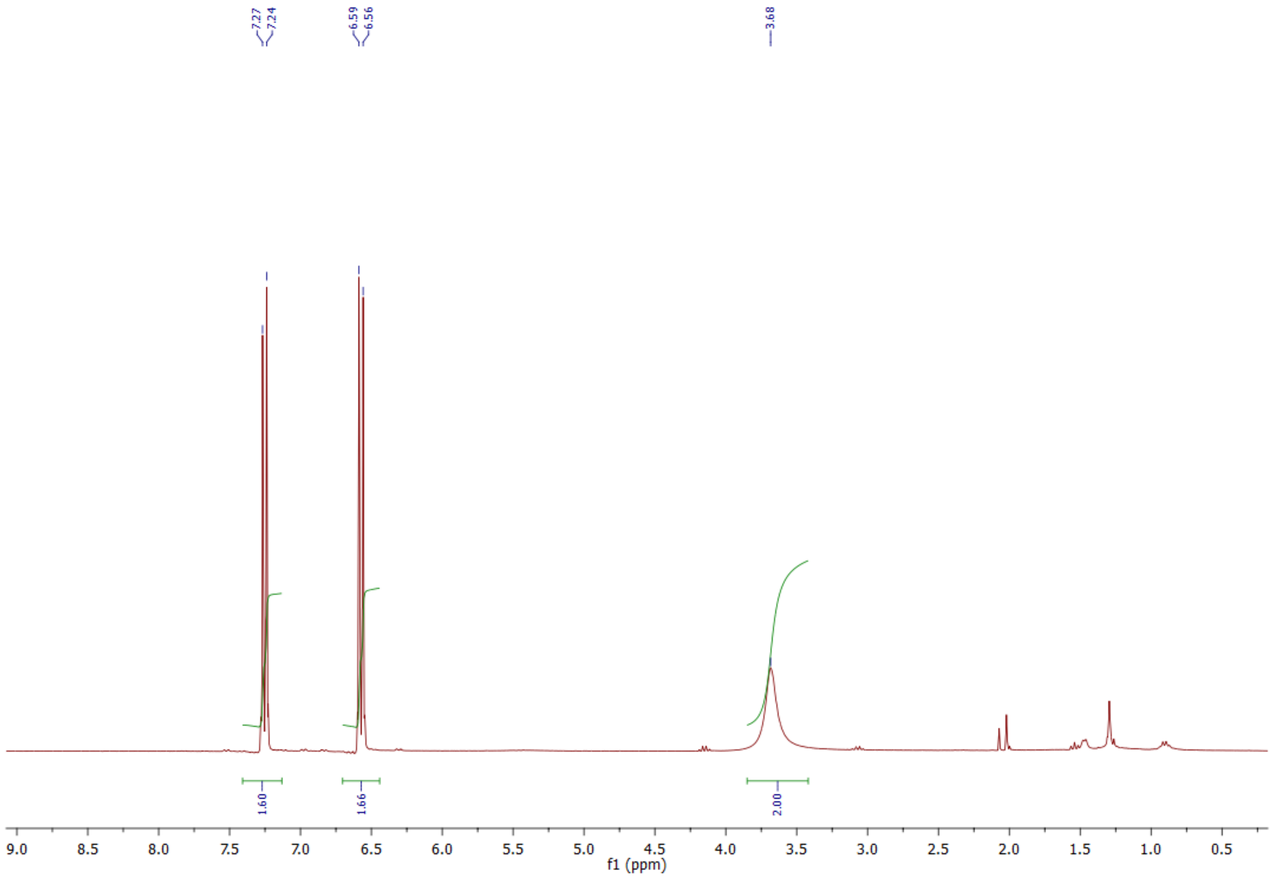
4-chloroaniline (1o)[10]

Conv. >98%. Purification through flash column chromatography gave 87 mg (0.68 mmol) of the pure product as a solid (97% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.12 (d, *J*=8.9 Hz, 2H), 6.63 (d, *J*=8.9 Hz, 2H), 3.67 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 144.8, 128.9, 123.0, 116.0.


1o. ^{1}H-NMR spectrum of the purified product

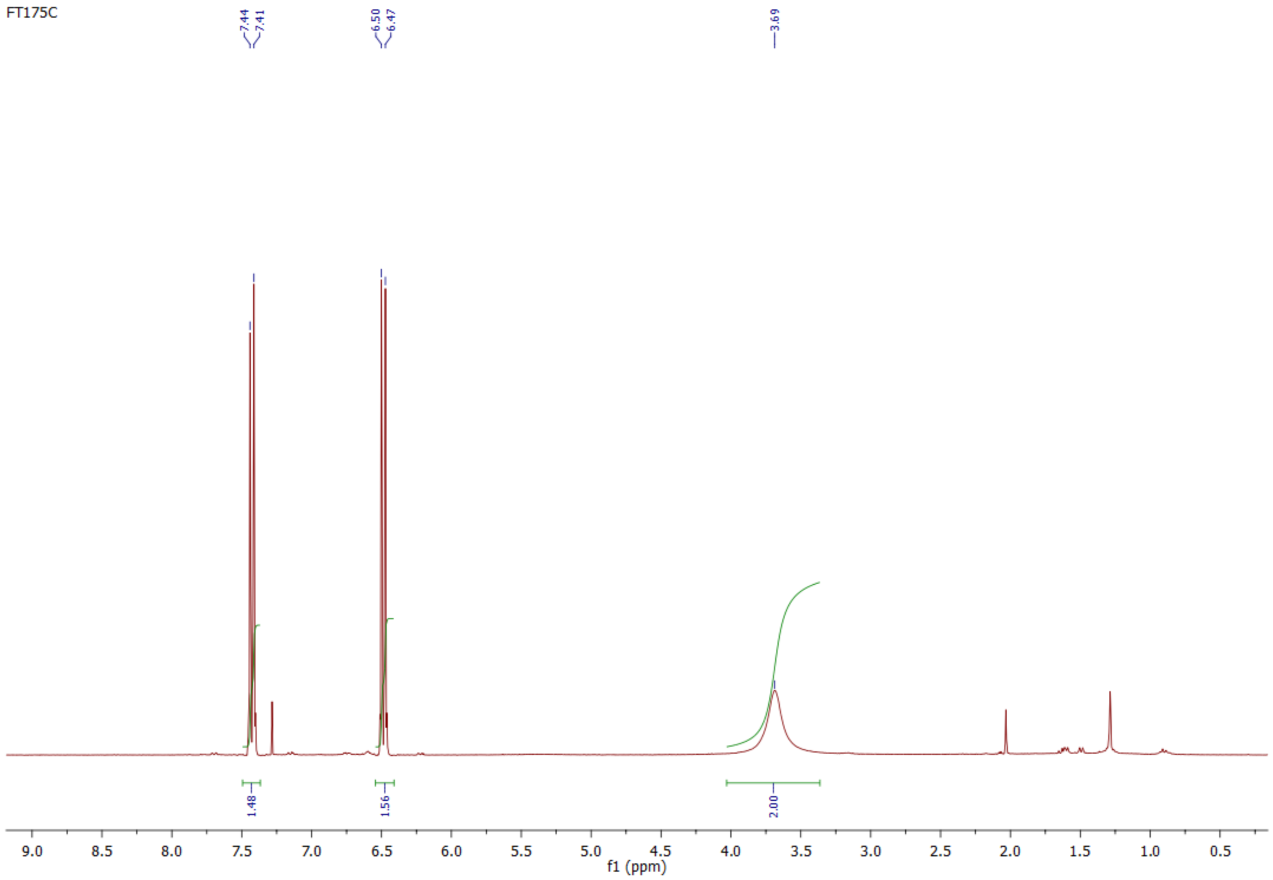
4-bromoaniline (1p)[11]

Conv. >98%. The crude product (117 mg, 0.68 mmol) was found to be pure (97% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.25 (d, *J*=8.6 Hz, 2H), 6.57 (d, *J*=8.6 Hz, 2H), 3.68 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 110.4, 116.9, 132.2, 145.6.



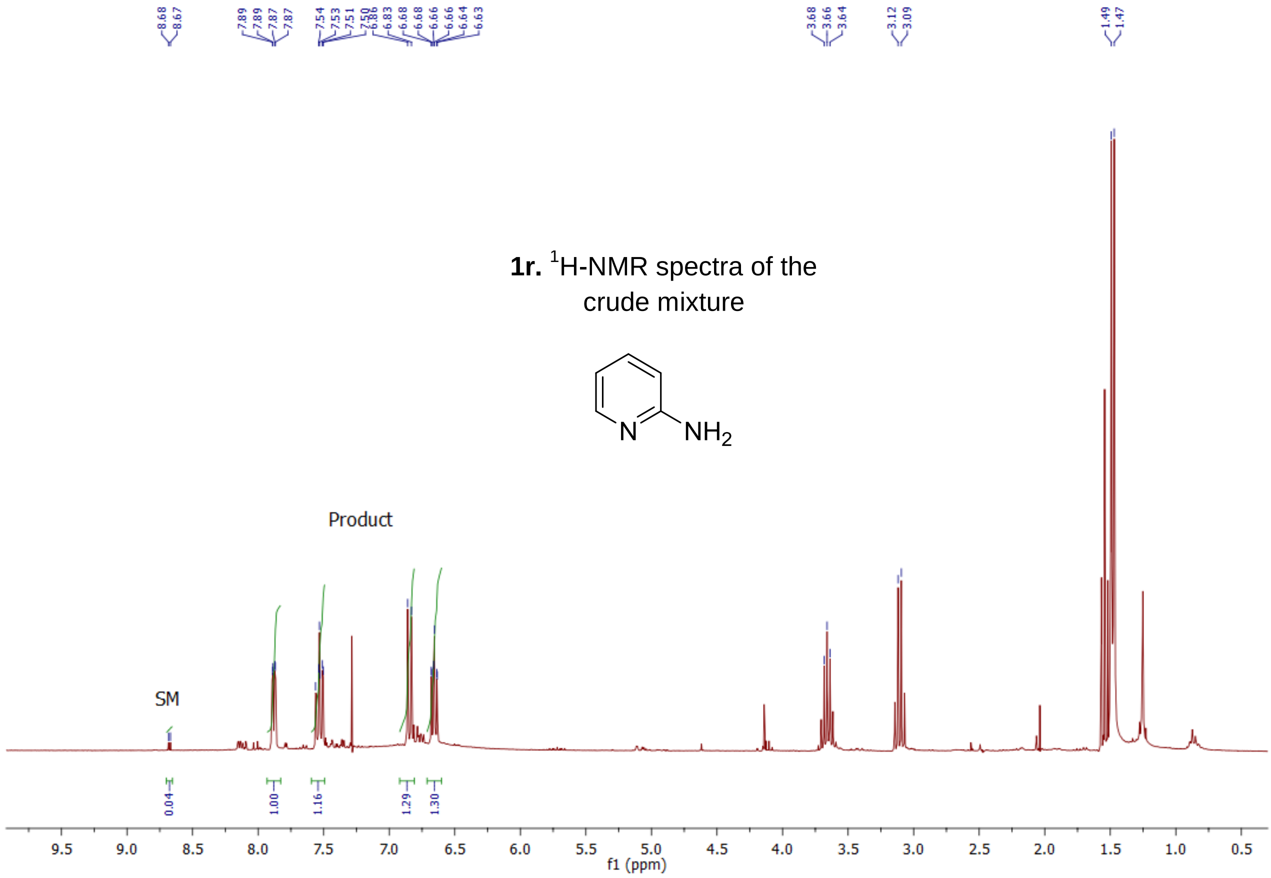
4-iodoaniline (1q)[12]

Conv. >98%. The crude product (150 mg, 0.68 mmol) was found to be pure (98% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, *J*=8.6 Hz, 2H), 6.48 (d, *J*=8.6 Hz, 2H), 3.69 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 79.6, 117.5, 138.1, 146.3.



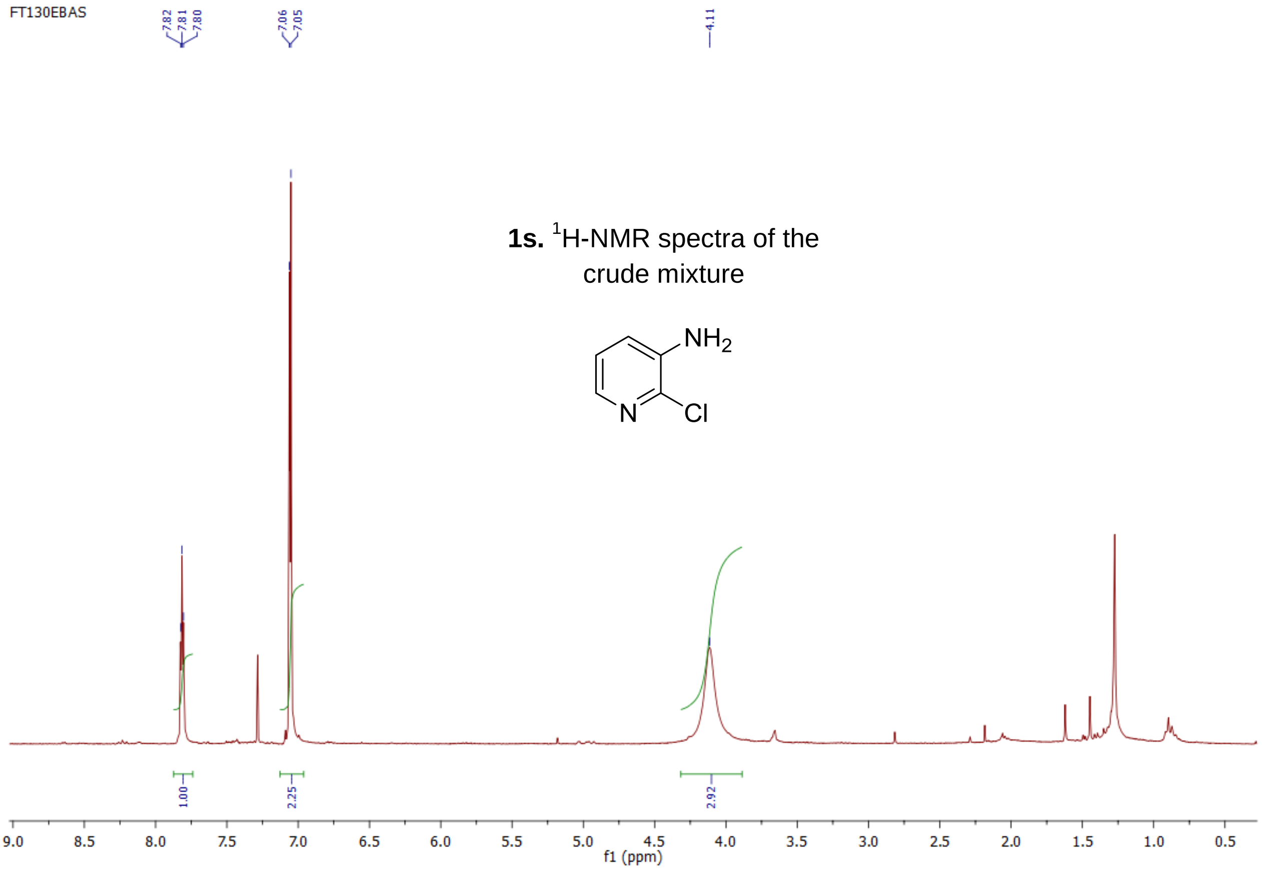
2-aminopyridine (1r)[8]

Conv. 96%. Purification through flash column chromatography gave 61 mg (0.65 mmol) of the pure product as a white solid (94% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 8.05 (m, 1H), 7.42 (m, 1H), 6.62 (m, 1H), 6.49 (d, 1H), 4,10 (bs, 2H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 158.3, 148.1, 137.7, 114.0, 108,6.


1r. ^{1}H-NMR spectra of the crude mixture

2-chloro-3-aminopyridine (1s)[13]

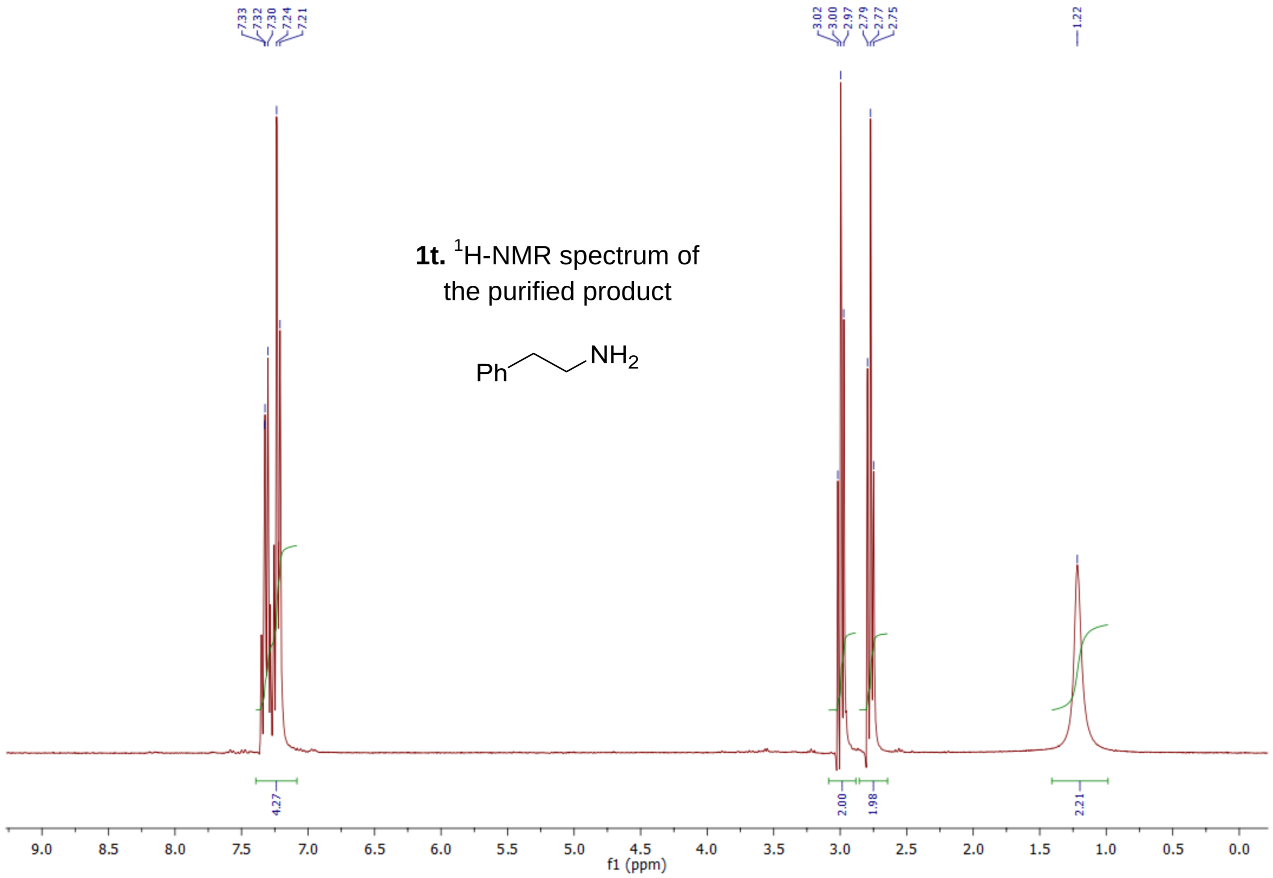
Conv. >98%. In the following spectrum no signals of the starting material are detectable. Purification through flash column chromatography gave 81 mg (0.63 mmol) of the pure product as a white solid (90% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.80 (m, 1H), 7.05 (m, 2H), 4.20 (bs, 2H, NH). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 141.5, 135.1, 134.6, 123.7, 121.6.



1s. ^{1}H-NMR spectra of the crude mixture

2-phenethylamine (1t)

Conv. >98%. Purification through flash column chromatography gave 83 mg (0.68 mmol) of the pure product as a pale yellow liquid (98% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 7.23 (m, 5H), 2.94 (t, *J*=6.2 Hz, 2H), 2.72 (t, *J*=6.2 Hz, 2H), 1.25 (bs, 2H, NH). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 40.0, 43.5, 126.0, 128.3, 128.7, 139.7.



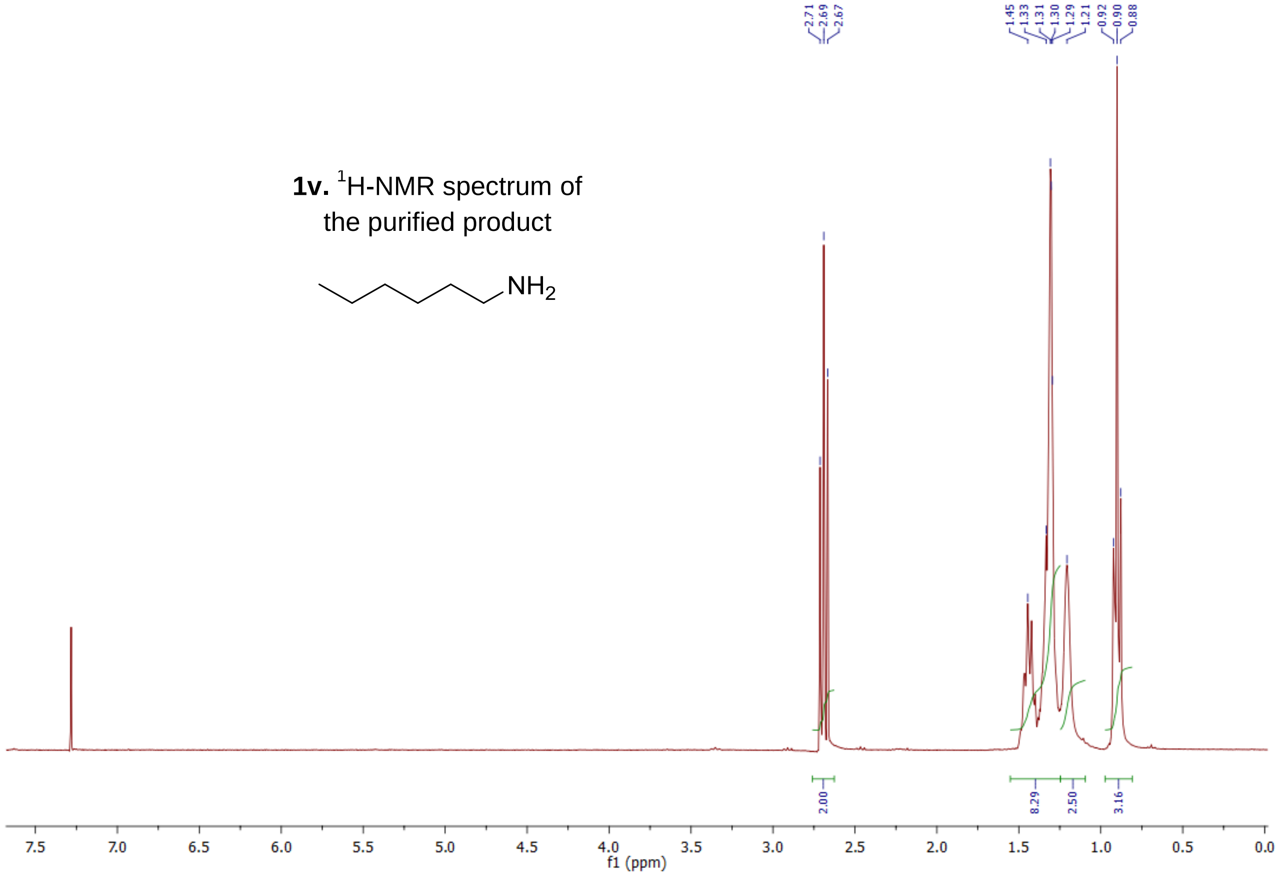
1t. ^{1}H-NMR spectrum of the purified product

2-aminopropanol (1u)

Conv. >98%. Purification through flash column chromatography gave 47 mg (0.62 mmol) of the pure product as a colourless liquid (90% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 2.82-3.63 (m, 3H), 2.53 (bs, 3H), 1.03 (d, *J*=6.2 Hz, 3H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 68.2, 48.4, 19.9.

Hexylamine (1v)

Conv. >98%. Purification through flash column chromatography gave 66 mg (0.65 mmol) of the pure product as a colourless liquid (93% yield). ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 2.69 (t, *J*=6.5 Hz, 2H), 1.50-1.05 (m, 10H), 0.89 (t, *J*=5.6 Hz, 3H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ: 42.3, 34.1, 31.7, 26.3, 22.8, 14.0.



1v. ^{1}H-NMR spectrum of the purified product

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Preliminary Theoretical Studies

In order to provide any evidence of the preference of nitro groups for one of the two silicon species DFT computational studies have been performed. To limit the computational efforts in these preliminary studies, we focused on the first step of the reduction (from nitro to nitroso). Indeed, since the only observed species in solution were the starting material, if any, and the silylated amine, we hypothesized the reduction of the nitro to the nitroso group to be the reaction rate determining step. Moreover, by monitoring the reaction through NMR spectroscopy, neither 4-nitrosotoluene nor hydroxylamine were detected, and the reduction of 4-nitrosotoluene was completed in short times.

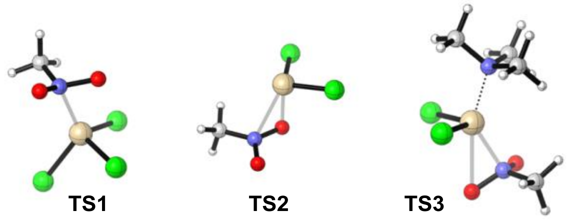
Calculations have been performed using three different DFT functionals: B3LYP,[1] M06-2X[2] and wB97X[3] with Gaussian 09 package.[4] The used basis set is 6-311++G(3df,3pd) and the PCM solvation model[5] for chloroform was used. These computational set up have been used both in the optimization and frequencies analysis steps. To minimize computational efforts, nitromethane was chosen as the substrate and trimethylamine as a model tertiary amine.

According to previous reports,[6] we calculated $SiCl_2$ to exist in the singlet state, rather than in the triplet one.

We investigated three different possible mechanisms: i) the addition of $SiCl_3^-$, ii) the addition of naked $SiCl_2$ and iii) the addition of a trimethylamine stabilized $SiCl_2$ species. It is important to point out that further mechanisms could be hypothesized, but we present here the simplest ones as basic hypothesis.

As reported in Figure 1, the addition of $SiCl_3^-$ to nitromethane occurs with a higher energy barrier (30.6-33.5 kcal/mol). Interestingly, the most favorite pathway for M06-2X and wB97XD seems to be the addition of a stabilized dichlorosilylene; the stabilization of the $SiCl_2$ species by means of the trimethylamine provide an advantage in terms of energy of several kcal/mol, depending on the functional (compare activation energies for naked and stabilized silylene: 22.5-26.2 kcal/mol *vs* 15.8-23.0 kcal/mol).

Figure 1. Energy barriers relative to: **TS1** for the addition of $SiCl_3^-$ to nitromethane; **TS2** for the addition of naked $SiCl_2$ to nitromethane and **TS3** for the addition of a stabilized $SiCl_2$ to nitromethane. The activation Gibbs free energies are calculated with respect to the separated reagents. The energies are reported in kcal/mol.



Functional[a]	$\Delta G^{\ddagger}$ (TS1)	$\Delta G^{\ddagger}$ (TS2)	$\Delta G^{\ddagger}$ (TS3)
B3LYP	33.5	**27.0**	34.8
M06-2X	30.6	22.5	**15.8**
wB97XD	32.7	26.2	**23.0**

[a] All the calculations are performed with the 6-311++G(3df,3pd)[PCM-chloroform] level of theory.

The presented calculations suggest that the addition of a stabilized dichlorosilylene seems to be the most likely mechanism for the presented reaction. However, further experimental and computational studies for the determination of a more detailed reaction mechanism are still ongoing in our laboratories.

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