Highly active and selective synthesis of imines from alcohols and amines or nitroarenes catalyzed by Pd/DNA in water with dehydrogenation

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General Remarks

All substrates were purchased commercially without further purification. Fish sperm DNA (CAS: 100403-24-5) were purchased from BBI. Starch soluble (CAS: 9005-25-8), Gum Arabic powder (CAS: 9000-01-5), Polyvinyl pyrrolidone (PVP K-30, CAS: 9003-39-8), were purchased from Sinopharm Chemical Reagent Co., Ltd. UV-Vis tests were taken on a Persee TU1901 UV-Vis spectrometer. All the solutions were diluted to similar concentration and gained the desirable normalized curves. The morphology and size of the Pd NPs were characterized on transmission electron microscopy (TEM) (JEOL–2010 and Hitachi H7650). The diluted solutions of the as-synthesized Pd-DNA nanohybrid were used as samples directly and dried on the carbon-coated Cu grids. X-ray powder diffraction (XRD) experiments were carried out with a Philips X’Pert Pro Super diffractometer with Cu KR radiation (λ = 1.54178 Å). The accurate concentrations of Pd/DNA nanohybrid and other supported Pd catalysts were directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV. $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR were recorded on a Bruker AC-300 FT ($^1$H NMR 300 MHz, $^{13}$C NMR 75 MHz) or Bruker AC-400 FT($^1$H NMR 400 MHz, $^{13}$C NMR 100 MHz) using TMS as internal reference. Infrared samples of DNA and Pd/DNA were recorded on a Thermo Scientific Nicolet 8700 spectrometer. HRMS were recorded on a MicroMass GCT TOF-MS. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yields were determined using 1,3,5-trimethylbenzene as an internal standard. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 electron spectrometer using monochromatized Al Kα excitation source (hν = 1486.6 eV). $\text{H}_2$ was detected by an online mass spectrometry (Hiden-QIC20).

General procedures for the synthesis of heterogeneous Pd catalysts

0.2 mmol of the corresponding metal salt (PdCl$_2$, KAuCl$_4$, AgNO$_3$, K$_2$PtCl$_6$) and 20 mg of fish sperm DNA were dissolved in 24 ml Tris buffer (10mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion (Pd$^{2+}$, Ag$^+$, Au$^{3+}$, Pt$^{4+}$) thoroughly bind to DNA. After this aging process, 1.0 mmol of freshly dissolved NaBH$_4$ in 16 ml Tris buffer was added dropwise under N$_2$ atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N$_2$ from 0 °C to room temperature to obtain the resulting M/DNA nanohybrids (c.a. 5 mM in Tris). This synthesis method can be scaled up to hundreds of millilitres easily at a time.

Other water-soluble palladium nanoparticles, such as Pd/starch, Pd/PVP and Au/gum arabic, were was synthesized by similar procedure according to the synthesis of M/DNA. For example, 0.05 mmol of PdCl$_2$ and 50 mg of water-soluble starch were dissolved in 5 ml H$_2$O. The combined solution was stirred for 24 h. After this aging process, 0.25 mmol of freshly dissolved NaBH$_4$ in 5 ml H$_2$O was added dropwise under N$_2$ atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in N$_2$ from 0 °C to room temperature to obtain the resulting Pd/starch (c.a. 5 mM in H$_2$O).

The Pd/diatomite nanoparticles were synthesized according to previous report.$^{[s1]}$ The
Pd/MMT nanoparticles were synthesized according the similar method using Na-MMT instead of diatomite. Pd/C (10%) was supplied by Sinopharm Chemical Reagent Co., Ltd.

Reference


General procedure for the tandem imination

Synthesis of imine from alcohol and amine: For M/DNA nanohybrids: To 2 ml of as-synthesized Pd/DNA nanohybrids were precipitated by adding excess EtOH (3 times of the volume). After sitting for 1 h and then centrifuged at 6000 r min⁻¹ for 4 min, the decantate was poured off. The obtained solid residue was dried by N₂ flow and redispersed in a water solution (1 mL) containing LiOH•H₂O (15.7 mg, 0.375 mmol). Benzyl alcohol (29.7 mg, 0.275 mmol) and aniline (23.3 mg, 0.25 mmol) were then added to the solution. The air in the reaction mixture was removed under vacuum and the reaction vessel refilled with N₂. This procedure was repeated for three times. The reaction mixture was then stirred under an N₂ balloon at 50 °C for 12 h. After the reaction was finished, 3 times the volume of EtOH and 5 times the volume of EtOAc was added to the reaction mixture. This mixture was left undisturbed for 2 h to allow precipitation and then centrifuged at 6000 r min⁻¹ for 4 min. The decantate was poured off. The solid residue was dried and used as the catalyst for the next round. The decantate was evaporated with a rotary evaporator. The obtained mixture was dissolved in EtOAc and yield with conversion were determined by GC-MS using 1,3,5-trimethylbenzene as an internal standard. And the reaction was carried out at a higher scale with alcohol (5.1 mmol) and amine (5.0 mmol) to afford the pure imine by recrystallization or vacuum distillation. The resulting products were characterized by ¹H NMR, ¹³C NMR and HRMS.

Synthesis of imines from alcohols and nitroarenes compound: The tandem reaction was carried out with alcohol (1.0 mmol) and nitroarene (0.25 mmol) for 24 h under the standard reaction conditions.

Detailed characterization of heterogeneous Pd catalysts

TEM characterization of Pd/DNA

![TEM characterization of Pd/DNA](image-url)
**Fig. ESI-1.** Pd/DNA average diameter = 2.87 nm.

**XRD patterns for Pd/DNA nanohybrids**

![XRD patterns of Pd/DNA](image)

**Fig. ESI-2** XRD patterns of Pd/DNA

**Uv-Vis Spectra of Pd/DNA compared with only DNA and NaBH₄**

![Uv-Vis Spectra](image)
**Fig. ESI-3** Uv-Vis spectra of DNA (red line), Pd/DNA (black line) and DNA after only adding NaBH₄ (green line).

**IR spectra of DNA and Pd/DNA.**

![IR spectra](image)

**Fig. ESI-4** IR spectra of Pd/DNA and DNA

No obvious variation was found before and after reduction at 1060 and 1230 cm⁻¹, which were the symmetric and antisymmetric stretching modes of PO₂⁻, showing that Pd NPs didn’t bind to this area. The variation at 1650 - 1685 cm⁻¹, which was contributed from C=C, C-N, C=O stretching modes, indicated that the base pairs of the DNA may interacted with Pd NPs. Especially, the weakening of 1480 cm⁻¹ (C=N) implied that Pd NPs may had interaction with the nitrogen atom of the base pairs. All of these indicated that Pd/DNA nanohybrid was formed.
$^{31}$P NMR spectra of DNA and Pd/DNA.

**Fig. ESI-5** $^{31}$P NMR spectra of DNA and Pd/DNA

The $^{31}$P NMR spectra of pure fish sperm DNA in Tris and the Pd/DNA solution which
was gained through precipitating and re-dissolving procedure by adding excess EtOH indicated that after pouring out the fair solution, DNA remained in the black precipitation. Secondly, the chemical shift of $^{31}$P in Pd/DNA system was almost the same as the pure DNA showed that Pd did not bind with the P atoms in the DNA.

**The procedure for the detection of the hydrogen**

The reaction mixture was stirred under an N$_2$ balloon at 50 °C in the reaction vessel (see Experimental Section for details). After the reaction was finished, the balloon was closed. Then the balloon was connect to an online mass spectroscopy (Hiden-QIC20), we set N$_2$ as the carrier gas to detect the H$_2$ liberated from this reaction. Opening the piston of the balloon, the gas entered into the system of this online mass spectroscopy. When H$_2$ had been detected, the piston was closed. This procedure was repeated for three times.

![Graph showing the detection of H$_2$](image)

**Fig. ESI-6** H$_2$ was detected by a online mass spectroscopy (Hiden-QIC20).
Characterization of Pd/DNA after recycles

Fig. ESI-7 TEM image of the Pd/DNA after fifth round

Fig. ESI-8 UV-Vis of the Pd/DNA before reaction, after first, third and fifth round
Fig. ESI-9 Pd 3d XPS analysis of Pd/DNA after fifth round

Fig. ESI-10 Pd 3d XPS analysis of Pd leached in the water after reaction
ICP-OES measurement of Pd/DNA

For the as-synthesized Pd/DNA nanohybrids (2 mL), with the aid of centrifugation at 5000 r/min for 5 minutes, then the decantate were poured out. The residues were dried by N₂ flow. And it was dissolved in aqua regia with constant volume of 50 ml. The accurate palladium content was 0.774 mg with ICP-OES measurement, after five cycles the Pd/DNA content was decreased to 0.577 mg.

GC-MS analysis for the reaction of 4-methoxybenzyl alcohol and 4-methylbenzyl alcohol with nitrobenzene

1. The GC-MS analysis for the reaction of 4-methoxybenzyl alcohol with nitrobenzene.
The MS analysis indicated that the peak of 1, 2 and 3 belonged to N-(4-methoxybenzylidene)aniline, 4-methoxy benzaldehyde and nitrobenzene respectively. This meant that 4-methoxybenzyl alcohol was almost completely converted to 4-methoxy benzaldehyde. A poor reduction of nitrobenzene into aniline was observed. A low yield of N-(4-methoxybenzylidene)aniline were observed either.

2. The GC-MS analysis for the reaction of 4-methylbenzyl alcohol with nitrobenzene.
The MS analysis indicated that the peak of 1, 2, 3 and 4 belong to 
N-(4-methylbenzylidene)aniline, 4-methylbenzyl alcohol, 4-methylbenzaldehyde and 
aniline respectively. The 4-methoxybenzyl alcohol was converted to 4-methoxy 
benzaldehyde with a good yield, and an excellent reduction of nitrobenzene and an 
excellent yield of N-(4-methylbenzylidene)aniline were observed.

**Characterization data of products**

**N-Benzylideneaniline (3aa)**

![N-Benzylideneaniline (3aa)](image)

This compound was prepared according to the general procedure and purified by recrystallization with 
Et₂O/hexane to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.45 (s, 1 H), 
7.92-7.89 (m, 2H), 7.39 (t, J = 9.0 Hz, 2H), 7.23 (t, J = 9.0 Hz, 3H); ¹³C NMR (75 MHz, 
CDCl₃): δ [ppm] = 160.4, 152.1, 136.3, 131.4, 129.1, 128.81, 128.77, 125.9, 120.9; HRMS (M+) calcd 
for C₁₃H₁₁N: 181.0891, found 181.0894.

**N-(4-methoxybenzylidene)aniline (3ba)**

![N-(4-methoxybenzylidene)aniline (3ba)](image)

This compound was prepared according to the general procedure and purified by recrystallization with 
Et₂O/hexane to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.38 (s, 1 H), 
7.86-7.83 (m, 2H), 7.40-7.35 (m, 2H), 7.23-7.17 (m, 3H), 6.99-6.96 (m, 2H), 3.87 (s, 3H); ¹³C NMR 
(75 MHz, CDCl₃): δ [ppm] = 162.3, 159.7, 152.4, 130.5, 129.3, 129.1, 125.6, 120.9, 114.2, 55.4; 
HRMS (M+) calcd for C₁₄H₁₃NO: 211.0997 found 211.0995.

**N-(3-methoxybenzylidene)aniline (3ca)**

![N-(3-methoxybenzylidene)aniline (3ca)](image)

This compound was prepared according to the general procedure and purified by recrystallization with 
Et₂O/hexane to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 8.42 (s, 1 H), 
7.53 (s, 1H), 7.53-7.34 (m, 4H), 7.25-7.20 (m, 3H), 7.06-7.02 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 
[ppm] = 160.3, 160.1, 152.0, 137.7, 129.7, 129.2, 126.0, 122.4, 120.9, 118.4, 111.9, 55.5; HRMS (M+) 
calcd for C₁₄H₁₃NO: 211.0997 found 211.0994.

**N-(2-methoxybenzylidene)aniline (3da)**

![N-(2-methoxybenzylidene)aniline (3da)](image)
This compound was prepared according to the general procedure and purified by recrystallization with 
Et<sub>2</sub>O/hexane to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): \( \delta \text{ [ppm]} = 8.92 \) (s, 1H), 8.17-8.14 (m, 1H), 7.46-7.35 (m, 3H), 7.25-7.18 (m, 3H), 7.07-7.02 (m, 1H), 6.95 (d, \( J_CF \) = 6.0 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): \( \delta \text{ [ppm]} = 159.5, 156.4, 152.8, 132.7, 129.0, 127.5, 125.6, 124.8, 121.1, 120.9, 111.1, 55.5; \) HRMS (M+) calcd for C₁₄H₁₃NO: 211.0997 found 211.0996.

N,N-dimethyl-4-((phenylimino)methyl)aniline (3ea)

This compound was prepared according to the general procedure and purified by recrystallization with 
Et<sub>2</sub>O/hexane to give the product as a yellow solid. ¹H NMR (300 MHz, CDCl₃): \( \delta \text{ [ppm]} = 8.33 \) (s, 1H), 7.87 (d, \( J = 8.7 \) Hz, 2H), 7.37 (t, \( J = 7.5 \) Hz, 2H), 7.20 (d, \( J = 7.5 \) Hz, 3H), 6.74 (d, \( J = 8.7 \) Hz, 2H), 3.06 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): \( \delta \text{ [ppm]} = 160.3, 153.1, 152.7, 130.6, 129.2, 125.1, 124.7, 121.1, 111.7, 40.3; \) HRMS (M+) calcd for C₁₅H₁₆N₂: 224.1313 found 224.1319.

N-(4-methylbenzylidene)aniline (3fa)

This compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether : EtOAc = 10:1 (2% Et₃N) v/v) to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): \( \delta \text{ [ppm]} = 8.41 \) (s, 1H), 7.79 (d, \( J = 8.0 \) Hz, 2H), 7.40-7.35 (m, 2H), 7.27 (d, \( J = 7.9 \) Hz, 2H), 7.20 (d, \( J = 8.0 \) Hz, 3H), 2.41 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): \( \delta \text{ [ppm]} = 160.3, 152.3, 141.9, 133.7, 129.5, 129.1, 128.8, 125.7, 120.9, 21.6; \) HRMS (M+) calcd for C₁₄H₁₃N: 195.1048 found 195.1047.

N-(3-methylbenzylidene)aniline (3ga)

This compound was prepared according to the general procedure and purified by column...
chromatography (Petroleum Ether : EtOAc = 10:1 (2% Et3N) v/v) to give the product as a yellow oil. 

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.39 (s, 1H), 7.74 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.39-7.33 (m, 3H), 7.31-7.25 (m, 1H), 7.22-7.18 (m, 3H), 2.39 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 160.6, 152.2, 138.6, 136.2, 132.3, 129.1, 129.0, 128.7, 126.4, 125.9, 120.9, 21.3; HRMS (M+) calcd for C$_{14}$H$_{13}$N: 195.1048 found 195.1045.

$N$-(4-fluorobenzylidene)aniline (3ia)

![Structure of 3ia](image)

This compound was prepared according to the general procedure and purified by recrystallization with Et$_2$O/hexane to give the product as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.42 (s, 1H), 7.94-7.87 (m, 2H), 7.43-7.36 (m, 2H), 7.24-7.12 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 164.7 (d, $J$$_{CF}$ = 250.5 Hz), 158.8, 151.9, 132.6 (d, $J$$_{CF}$ = 2.8 Hz), 130.8 (d, $J$$_{CF}$ = 8.7 Hz), 129.2, 126.0, 120.8, 115.9 (d, $J$$_{CF}$ = 21.8 Hz); HRMS (M+) calcd for C$_{13}$H$_{10}$FN: 199.0797 found 199.0795.

$N$-(3-fluorobenzylidene)aniline (3ja)

![Structure of 3ja](image)

This compound was prepared according to the general procedure and purified by recrystallization with Et$_2$O/hexane to give the product as a yellow oil. $^1$H NMR (300 MHz, d$_6$-acetone): $\delta$ [ppm] = 8.61 (s, 1H), 7.79-7.73 (m, 2H), 7.60-7.53 (m, 1H), 7.45-7.40 (m, 2H), 7.33-7.24 (m, 4H); $^{13}$C NMR (75 MHz, d$_6$-acetone): $\delta$ [ppm] = 164.7 (d, $J$$_{CF}$ = 243 Hz), 160.6 (d, $J$$_{CF}$ = 3.0 Hz), 153.3, 140.9 (d, $J$$_{CF}$ = 7.8 Hz), 132.4 (d, $J$$_{CF}$ = 7.8Hz), 130.9, 127.9, 126.9 (d, $J$$_{CF}$ = 3.0 Hz), 122.7, 119.7 (d, $J$$_{CF}$ = 21.7 Hz), 115.9 (d, $J$$_{CF}$ = 22.5 Hz); HRMS (M+) calcd for C$_{13}$H$_{10}$FN: 199.0797 found 199.0801.

$N$-(4-(trifluoromethyl)benzylidene)aniline (3ka)

![Structure of 3ka](image)

This compound was prepared according to the general procedure and purified by recrystallization with Et$_2$O/hexane to give the product as a yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.51 (s, 1H), 8.02 (d, J = 6.0 Hz, 2H), 7.73 (d, J = 6.0 Hz, 2H), 7.44-7.39 (m, 2H), 7.29-7.22 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 158.5, 151.4, 139.3, 132.1 (q, $J$$_{CF}$ = 32.3 Hz), 129.9, 129.3, 129.0, 126.6, 125.7 (q, $J$$_{CF}$ = 3.8 Hz), 122.1 (q, $J$$_{CF}$ = 270 Hz), 120.9; HRMS (M+) calcd for C$_{14}$H$_{10}$F$_3$N: 249.0765 found 249.0771.
**N-(Thiophen-2-ylmethylene)aniline (3la)**

![Structure (3la)](image)

This compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether : EtOAc = 10:1 (1% Et₃N) v/v) to give the product as a yellow solid. 

$^1$H NMR (300 MHz, CDCl₃): $\delta$ [ppm] = 8.55 (s, 1H), 7.51-7.47 (m, 2H), 7.40-7.35 (m, 2H), 7.23-7.19 (m, 3H), 7.13-7.11 (m, 1H); $^{13}$C NMR (75 MHz, CDCl₃): $\delta$ [ppm] = 153.0, 151.4, 142.8, 132.2, 130.3, 129.1, 127.7, 126.1, 121.0; HRMS (M+) calcd for C₁₁H₉NS: 187.0456 found 187.0459.

**N-(3-Phenylallylidene)aniline (3ma)**

![Structure (3ma)](image)

This compound was prepared according to the general procedure and purified by recrystallization with Et₂O/hexane to give the product as a yellow solid. 

$^1$H NMR (300 MHz, CDCl₃): $\delta$ [ppm] = 8.27-8.25 (m, 1H), 7.55-7.52 (m, 2H), 7.42-7.32 (m, 5H), 7.19 (t, $J$ = 6.0 Hz, 3H), 7.14-7.12 (m, 2H); $^{13}$C NMR (75 MHz, CDCl₃): $\delta$ [ppm] = 161.6, 151.8, 144.0, 135.6, 129.6, 129.2, 128.9, 128.7, 127.5, 126.1, 120.9; HRMS (M+) calcd for C₁₅H₁₃N: 207.1048 found 207.1044.

**N-(naphthalen-1-ylmethylene)aniline (3na)**

![Structure (3na)](image)

This compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether : EtOAc = 10:1 (2% Et₃N) v/v) to give the product as a light yellow solid. 

$^1$H NMR (300 MHz, d₆-acetone): $\delta$ [ppm] = 9.32 (d, $J$ = 9 Hz, 1H), 9.18 (s, 1H), 8.17 (d, $J$ = 9 Hz, 1H), 8.07 (d, $J$ = 8.3 Hz, 1H), 8.01 (d, $J$ = 7.6 Hz, 1H), 7.68-7.57 (m, 3H), 7.47-7.42 (m, 2H), 7.37-7.34 (m, 2H), 7.29-7.24 (m, 1H); $^{13}$C NMR (75 MHz, d₆-acetone): $\delta$ [ppm] = 162.0, 154.4, 135.8, 133.6, 133.3, 133.2, 132.3, 130.9, 130.4, 129.1, 128.0, 127.6, 127.0, 126.5, 122.7; HRMS (M+) calcd for C₁₇H₁₃N: 231.1048 found 231.1050.

**N-benzylidene-4-methylaniline (3ab)**

![Structure (3ab)](image)
This compound was prepared according to the general procedure and purified by recrystallization with \( \text{Et}_2\text{O}/\text{hexane} \) to give the product as a white solid. \(^1\text{H NMR} (300 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 8.46 \text{ (s, 1H), 7.91-7.88 \text{ (m, 2H), 7.21-7.12 \text{ (m, 4H), 2.37 \text{ (s, 3H)}}; } ^{13}\text{C NMR} (75 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 159.6, 149.5, 136.4, 135.8, 131.2, 129.8, 128.74, 128.72, 120.8, 21.0; \text{ HRMS (M+) calcd for C}_{14}\text{H}_{13}\text{N: 195.1048, found 195.1047.}

\textit{N-benzylidene-3-methylaniline} (3ac)

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a faint yellow oil. \(^1\text{H NMR} (300 \text{ MHz, d}_6\text{-acetone}): \delta \text{ [ppm]} = 8.57 \text{ (s, 1H), 7.98-7.95 \text{ (m, 2H), 7.54-7.49 \text{ (m, 3H), 7.31-7.25 \text{ (m, 1H), 7.07-7.04 \text{ (m, 3H)}}; } ^{13}\text{C NMR} (75 \text{ MHz, d}_6\text{-acetone): } \delta \text{ [ppm]} = 161.6, 153.9, 140.5, 138.4, 132.9, 130.61, 130.38, 130.33, 128.2, 123.2, 119.6, 22.2; \text{ HRMS (M+) calcd for C}_{14}\text{H}_{13}\text{N: 195.1048, found 195.1046.}

\textit{N-benzylidene-4-methoxyaniline} (3ae)

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

This compound was prepared according to the general procedure and purified by recrystallization with \( \text{Et}_2\text{O}/\text{hexane} \) to give the product as a white solid. \(^1\text{H NMR} (300 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 8.48 \text{ (s, 1H), 7.90-7.87 \text{ (m, 2H), 7.47-7.45 \text{ (m, 3H), 7.52-7.21 \text{ (m, 2H), 6.95-6.92 \text{ (m, 2H), 3.83 \text{ (s, 3H)}}; } ^{13}\text{C NMR} (75 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 158.4, 158.3, 144.9, 136.4, 131.0, 128.7, 128.6, 122.2, 114.4, 55.5; \text{ HRMS (M+) calcd for C}_{14}\text{H}_{13}\text{NO: 211.0997, found 211.0996.}

\textit{N-benzylidene-3-methoxyaniline} (3af)

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a yellow oil. \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 8.47 \text{ (s, 1H), 7.92-7.90 \text{ (m, 2H), 7.50-7.48 \text{ (m, 3H), 7.30 \text{ (t, J = 8.0 Hz, 1H), 6.82-6.79 \text{ (m, 3H), 3.85 \text{ (s, 3H)}}; } ^{13}\text{C NMR} (75 \text{ MHz, CDCl}_3): \delta \text{ [ppm]} = 160.6, 160.5, 153.6, 136.3, 131.5, 130.0, 129.0, 128.9, 113.0, 112.0, 106.8, 55.4; \text{ HRMS (M+) calcd for C}_{14}\text{H}_{13}\text{NO: 211.0997, found 211.0990.}

\textit{N-benzylidene-4-fluoroaniline} (3ah)
This compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether : EtOAc = 10:1 (2% Et3N v/v) to give the product as a faint yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.44 (s, 1H), 7.89 (s, 2H), 7.48 (s, 3H), 7.25-7.20 (m, 2H), 7.09-7.08 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 161.3 (d, $J_{CF}$ = 243.0 Hz), 160.2, 148.05 (d, $J_{CF}$ = 3 Hz), 136.1, 131.5, 128.80, 128.78, 122.3 (d, $J_{CF}$ = 8.3 Hz), 115.9 (d, $J_{CF}$ = 22.5 Hz); HRMS (M+) calcd for C$_{13}$H$_{10}$FN: 199.0797, found 199.0798.

$N$-benzylidene-4-trifluoromethylaniline (3ai)

This compound was prepared according to the general procedure and purified by recrystallization with Et$_2$O/hexane to give the product as a white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.42 (s, 1H), 7.92-7.89 (m, 2H), 7.64 (d, $J$ = 8.3 Hz, 2H), 7.53-7.45 (m, 3H), 7.24 (d, $J$ = 8.3 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 161.9, 155.3, 135.7, 132.0, 129.1, 128.9, 127.7 (q, $J_{CF}$ = 32.3 Hz), 126.4 (q, $J_{CF}$ = 3.8 Hz), 124.3 (q, $J_{CF}$ = 270 Hz), 121.0; HRMS (M+) calcd for C$_{14}$H$_{10}$F$_3$N: 249.0765 found 249.0766.

$N$-benzylidenenaphthalen-1-amine (3aj)

This compound was prepared according to the general procedure and purified by column chromatography (Petroleum Ether : EtOAc = 10:1 (2% Et3N v/v) to give the product as a light yellow solid. $^1$H NMR (300 MHz, d$_6$-acetone): $\delta$ [ppm] = 8.68 (s) and 8.67 (s, E and Z, 1H), 8.39-8.36 (m, 1H), 8.11-8.08 (m, 2H), 7.93-7.90 (m, 1H), 7.78 (d, $J$ = 9 Hz, 1H), 7.57-7.48 (m, 6H), 7.18 (d, 7.3 Hz, 1H); $^{13}$C NMR (75 MHz, d$_6$-acetone): $\delta$ [ppm] = 162.2, 150.9, 138.5, 135.9, 133.2, 130.8, 130.64, 130.55, 129.4, 128.1, 127.9, 127.44, 127.36, 125.5, 114.4; HRMS (M+) calcd for C$_{17}$H$_{15}$N: 231.1048 found 231.1047.

$N$-benzylidenebenzylamine (3ak)

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.38 (s, 1H), 7.79-7.76 (m, 2H), 7.42-7.38 (m, 3H), 7.34-7.33 (m, 4H), 7.30-7.23 (m, 1H), 4.81 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 162.0, 139.3, 136.2, 130.7, 128.59, 128.49, 128.28, 127.98, 127.0, 65.0; HRMS
(M+) calcd for C$_{14}$H$_{13}$N: 195.1048, found 195.1045.

**N-benzylidene-2-phenylethanamine (3al)**

![N-benzylidene-2-phenylethanamine](image)

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a colourless oil. $^1$H NMR (400 MHz, d$_6$-acetone): $\delta$ [ppm] = 8.27 (s, 1H), 7.79 (t, $J = 1.6$ Hz, 2H), 7.46 (d, $J = 5.2$ Hz, 3H), 7.30 (d, $J = 4.0$ Hz, 4H), 7.22-7.18 (m, 1H), 3.88 (t, $J = 7.2$ Hz, 2H), 3.01 (t, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, d$_6$-acetone): $\delta$ [ppm] = 161.1, 140.3, 136.8, 130.5, 129.1, 128.6, 128.3, 128.1, 126.0, 62.7, 37.3; HRMS (M+) calcd for C$_{15}$H$_{15}$N: 209.1204, found 209.1211.

**N-benzylidenebutan-1-amine (3am)**

![N-benzylidenebutan-1-amine](image)

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a yellow oil. $^1$H NMR (300 MHz, d$_6$-acetone): $\delta$ [ppm] = 8.36 (s, 1H), 7.82-7.79 (m, 2H), 7.47 (t, $J = 4.0$ Hz, 3H), 3.62 (t, $J = 9.2$ Hz, 2H), 1.73-1.63 (m, 2H), 1.49-1.36 (m, 2H), 0.97 (t, $J = 10.0$ Hz, 3H); $^{13}$C NMR (75 MHz, d$_6$-acetone): $\delta$ [ppm] = 160.4, 136.8, 130.4, 128.6, 128.0, 60.9, 33.0, 20.2, 13.3; HRMS (M+) calcd for C$_{11}$H$_{15}$N: 161.1204, found 161.1209.

**N-benzylideneterbutylamine (3an)**

![N-benzylideneterbutylamine](image)

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.27 (s, 1H), 7.76-7.73 (m, 2H), 7.40-7.37 (m, 3H), 1.29 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 155.1, 137.2, 130.1, 128.5, 127.9, 57.2, 29.7; HRMS (M+) calcd for C$_{11}$H$_{15}$N: 161.1204 found 161.1202.

**N-benzylidenedodecylamine (3ap)**

![N-benzylidenedodecylamine](image)

This compound was prepared according to the general procedure and purified by vacuum distillation to give the product as a colourless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 8.27 (s, 1H), 7.72 (d, $J = 3.0$ Hz, 2H), 7.40 (t, $J = 3.0$ Hz, 3H), 3.60 (t, $J = 6.0$ Hz, 2H), 1.69 (t, $J = 6.0$ Hz, 2H), 1.29 (d, $J = 20.6$ Hz, 18H), 0.88 (t, $J = 6.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 160.6, 136.4, 130.4, 128.5, 128.0, 61.8, 31.9, 31.0, 29.68, 29.64, 29.61, 29.47, 29.35, 27.4, 22.7, 14.1; HRMS (M+) calcd for C$_{19}$H$_{31}$N: 273.2457 found 273.2461.
1-benzylidene-2-phenylhydrazine (3aq)

This compound was prepared according to the general procedure and purified by recrystallization with Et₂O/hexane to give the product as a white solid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.67-7.64 (m, 3H), 7.39-7.31 (m, 2H), 7.30-7.24 (m, 3H), 7.12-7.10 (m, 2H), 6.89-6.84 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 144.7, 137.3, 135.3, 129.3, 128.6, 128.4, 126.2, 120.1, 112.8; HRMS (M+) calcd for C₁₃H₁₂N₂: 196.1000 found 196.1011.
NMR Spectra of products