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Au nanoparticle-catalyzed double hydrosilylation of nitriles by diethylsilane†

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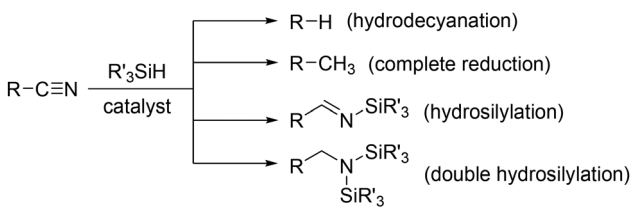
We present the first example of Au-catalyzed reduction of nitriles into primary amines. In contrast to monohydrosilanes which are completely unreactive, diethylsilane (a dihydrosilane) is capable of reducing aryl or alkyl nitriles into primary amines under catalysis by Au nanoparticles supported on TiO_2, *via* a smooth double hydrosilylation pathway. The produced labile *N*-disilylamines are readily deprotected by HCl in Et_2O to form the hydrochloric salts of the corresponding amines in very good to excellent yields. The catalyst is recyclable and reusable at least in 5 consecutive runs.

Introduction

The reduction of nitriles to amines[1] can be been achieved employing pyrophoric metal hydrides such as borohydrides and aluminum hydrides,[2] with such processes often suffering from serious safety issues,[3] or by the direct metal-catalyzed hydrogenation.[4] Apart from these traditional reducing conditions, several catalytic protocols were developed employing hydroboranes[5] or hydrosilanes. Particularly, the reaction between hydrosilanes and nitriles has gained significant attention, with four distinct pathways being observed depending on the catalytic conditions (Scheme 1). In the less common, hydrodecyanation[6] or complete reduction of the cyano functionality into a methyl group may occur.[7] The most common pathways are monohydrosilylation leading to *N*-silylated imines,[8] or depending on the catalyst, an additional hydrosilylation may occur leading to *N*-disilylamines. *N*-Silylamines[9] can be readily deprotected to primary amines. The double hydrosilylation pathway has been so far reported under catalysis by oxo-rhenium complexes,[10] a Fe(III) complex,[11] by Cp*Ir(III)-based iridacycles,[12] by $Co(OPiv)_2$ [13a] or $Co_2(CO)_8$,[13b] by tetrabutylammonium fluoride (TBAF),[14] by $Fe_3(CO)_{12}/InCl_3$ using a significant excess of nitrile,[15] by Mn(III) complexes,[16] by Ti$(OR)_4$,[17] and by *t*-BuOK applicable only to alkoxysilanes.[18] Mono *versus* double hydrosilylation can also be controlled by the appropriate use of the amount of hydrosilane using $B(C_6F_5)_3$,[19a] $[(C_6F_5)_3PF][B(C_6F_5)_4]$,[19b] or a Ru complex[19c] as catalysts. So far there is no reported example in the literature employing Au catalysts for the reduction of nitriles. Given that hydrosilanes and ammonia borane complex (NH_3BH_3) can be readily activated by supported Au(0) nanoparticles and other nano Au-based materials (Au NPs),[20] we attempted to study their ability to reduce nitriles in the presence of Au/TiO_2, a readily available and widely used catalyst in our lab. So far, hydrosilanes have been used under Au(0)-catalysis conditions as reducing agents of aldehydes/ketones,[21] imines,[22] amides,[23] nitro compounds,[24] quinolines,[25] and diazo compounds,[26] while ammonia borane for nitro compounds,[27] α-diazocarbonyl compounds,[28] and more recently to azoarenes.[29]

Results and discussion

Our exploration commenced with aryl-substituted benzonitrile (**1a**). To our disappointment, although NH_3BH_3 is capable of achieving reduction of nitriles under certain metal-catalyzed conditions,[30] it failed to provide any reaction in the presence of Au/TiO_2 (entry 10, Table 1). Additionally, common monohydrosilanes, such as Et_3SiH or $PhMe_2SiH$, did not react with **1a** even under prolonged refluxing conditions in the presence of Au/TiO_2 (entries 1 and 2, Table 1). Similar non-product forming results were observed for benzyl-substituted 2-(*p*-tolyl)



Scheme 1 Known reactivity pathways in the catalyzed reaction between hydrosilanes and nitriles.

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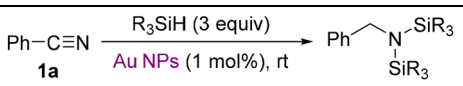
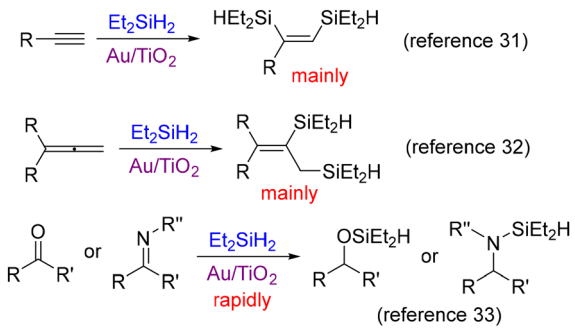
Table 1 Optimization of conditions in the Au/TiO_2-catalyzed reduction of benzonitrile (**1a**)



	Reductant	Catalyst	Solvent	Time	Conversion
1	Et_3SiH	Au/TiO_2	Benzene	5 h[a]	—
2	$PhMe_2SiH$	Au/TiO_2	Benzene	5 h[a]	—
3	Et_2SiH_2	—	Benzene	5 h	—
4	Et_2SiH_2	Au/TiO_2	Benzene[b]	0.5 h	>99%
5	Et_2SiH_2	Au/TiO_2	DCE	0.5 h	85%
6	Et_2SiH_2	Au/TiO_2	THF	0.5 h	12%
7	Et_2SiH_2	Au/Al_2O_3	Benzene	0.5 h	8%
8	Et_2SiH_2	Au/ZnO	Benzene	0.5 h	28%
9	$(HMe_2Si)_2O$	Au/TiO_2	Benzene	2 h[a]	12%[c]
10	NH_3BH_3	Au/TiO_2	MeOH	5 h[a]	—

[a] 70 °C. [b] Identical results were obtained in toluene instead of benzene. [c] Benzylamine.



Scheme 2 The unique reactivity of Et_2SiH_2 with several functionalities under Au/TiO_2 catalysis conditions.

acetonitrile (**1o**). Then we turned to diethylsilane (Et_2SiH_2). This specific dihydrosilane has shown in the recent past a surprising reactivity and unprecedented reaction pathways if activated by Au(0) nanoparticles (Scheme 2). For example, in contrast to monohydrosilanes which in the presence of Au/TiO_2 add to alkynes or allenes (hydrosilylation pathway), Et_2SiH_2 provides unique dehydrogenative 1,2-disilylation pathways.[31,32] In addition, aldehydes/ketones or imines[33] are rapidly reduced by diethylsilane, whereas monohydrosilanes perform the reduction at orders of magnitude lower rates.

To our delight, in the presence of 1 mol% Au/TiO_2, **1a** underwent at room temperature double hydrosilylation with 3 molar equivalents of Et_2SiH_2, forming **2a** within 30 min (entry 4, Table 1). Suitable solvents are primarily benzene and toluene or 1,2-dichloroethane (DCE), and they must by as dry as possible. The only side-products in the crude reaction mixture (see ESI†) were oligosiloxanes from the partial dehydrogenative hydrolysis of the excess of diethylsilane by traces of moisture. Di-adduct **2a** is unstable and cannot be purified by column chromatography. Yet, after evaporation of the supernatant solvent from the crude reaction slurry we managed to characterize it properly (see ESI†). Upon treatment of **2a** with 1 M HCl/Et_2O, the hydrochloric salt of benzylamine (**3a**) was isolated as a solid in 87% yield. Labile disilylamine **2a** has been previously reported by Chang and co-workers[19a] as an intermediate in their $B(C_6F_5)_3$-catalyzed silylative reduction of nitriles, but no spectroscopic data were provided. Au/Al_2O_3 or Au/ZnO are also active, but less efficient catalysts. Finally, 1,1,3,3-tetramethyldisiloxane (TMDS), a highly reactive reducing agent of carbonyl compounds in the presence of Au/TiO_2 [21c] resulted to merely 12% product after 2 h at 70 °C.

The smooth double hydrosilylation of benzonitrile by diethysilane urged us to explore the scope and limitations of the Au/TiO_2-catalyzed reaction. The results are collectively presented in Fig. 1, and were performed on an approximately 0.15–0.20 mmol scale of nitriles. Aryl, heteroaryl or alkyl nitriles react smoothly within 30 min to 2 h affording the corresponding amines as hydrochloric acid salts in isolated yields >75%. Labile disilylamines from double hydrosilylation are formed in all cases and can be seen by *in situ* NMR, however, following a generalized protocol, after the reaction was complete (TLC or GC), the slurry was immediately filtered with the aid of DCM through a short pad of Celite, the solvents were evaporated, and the residue was treated with 1 M HCl in Et_2O. The hydrochloric salts of the amines precipitate and can be isolated *via* filtration. The catalyst is recyclable and reusable in five consecutive runs at 0.2 mmol scale without any obvious deterioration of its activity. After each run, the catalyst was

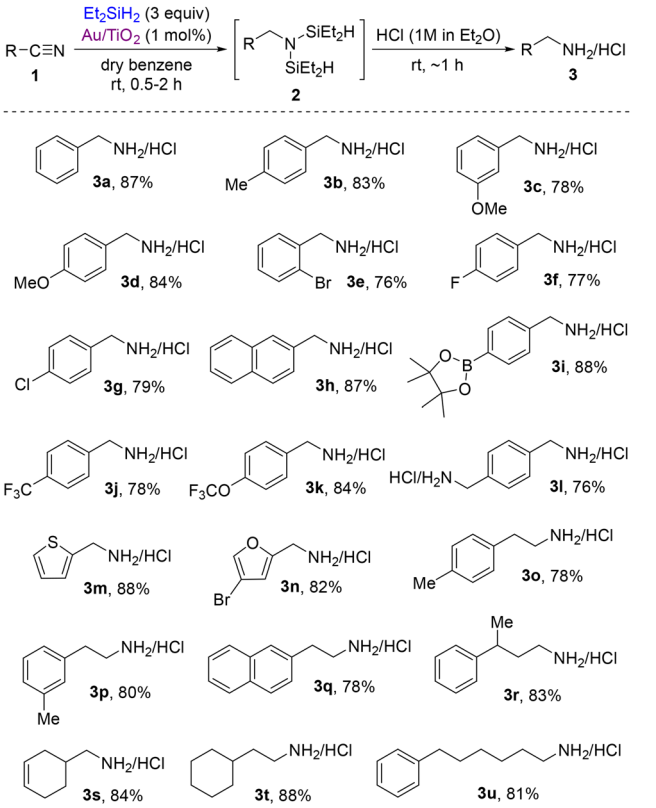


Fig. 1 Reduction of nitriles with Et_2SiH_2 catalyzed by Au/TiO_2.

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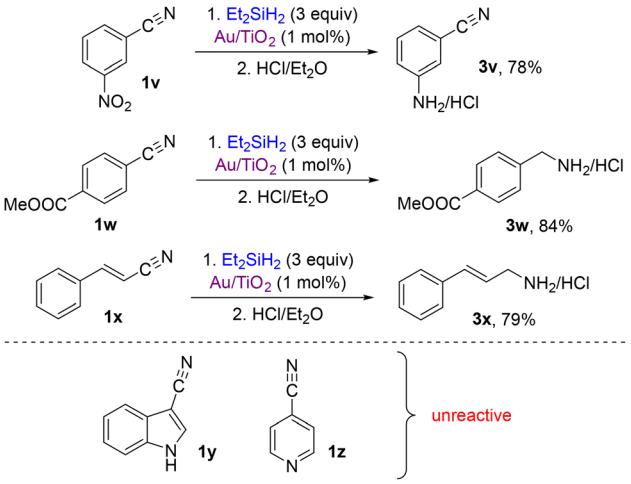
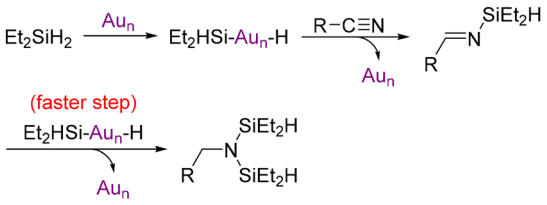


Scheme 3 Chemoselectivity issues and limitations in the reduction of functionalized nitriles.

recovered by supernatant solution decantation, washed, dried in the oven at 100 °C for 1 h, and then reused.

In the case of co-existence of a second formally reducible group in reacting nitriles, the following selectivity modes were observed (Scheme 3). In nitro-substituted benzonitrile **1v**, the nitro functionality was selectively reduced relative to the cyano. There are several reports in the literature concerning the competing chemoselectivity of such reductions. Generally, treatment of cyano and nitro bearing substrates with specific boron hydrides,[34] and primarily in the metal-catalyzed reduction with hydrosilanes,[8a,17,19a] the cyano group is selectively reduced. The opposite selectivity, such as under our conditions, occurs performing catalytic hydrogenation,[4] or employing hydrosilanes with Au/Fe_3O_4 [24] or Cu(OTf)$_2$ [35] as catalysts. The reduction of ester-bearing benzonitrile **1w** provides exclusively product **3w** in which only the cyano was reduced. In contrast, metal hydrides react unselectively with **1w**, reducing both functional groups,[36] although under several modifications only the ester can be reduced.[37] Our observed chemoselectivity has precedents in the literature, primarily *via* catalytic hydrogenation[4] or hydroboration,[34b] and is complementary to metal-catalyzed protocols employing hydrosilanes as reducing agents, in which the ester functionality is reduced over cyano.[14,38] Another chemoselective reduction is that of cinnamonitrile (**1x**) in which the double bond remains unaffected. In reactions involving hydrosilanes as reductants, the Fe(III)-catalyzed process[11] provides similar selectivity to our protocol, while the B(C_6F_5)$_3$-catalyzed reaction of dihydrosilanes with conjugated nitriles affords Michael-type addition of silyl group on the double bond.[39] Apart from these selective reductions, we observed some limitations, with indole-carbonitrile **1y** and 4-cyanopyridine (**1z**) being completely unreactive. We postulate that the strong coordination of their sp^2-N on Au NPs disfavors reduction of the cyano functionality.

In Scheme 4, we propose a simplified mechanism of the transformation catalyzed by Au NPs (denoted as Au_n). The first



Scheme 4 Proposed mechanism of the double hydrosilylation of nitriles catalyzed by Au nanoparticles (Au_n).

hydrosilylation provides a *N*-silyl imine followed by a second addition. Since imines are rapidly reduced by Et_2SiH_2 in the presence of Au/TiO_2,[33] we reasonably postulate that the second hydrosilylation occurs much faster than the first one. In fact, no silyl imines were detected in the crude reaction mixture, interrupting the progress of the reaction at any stage.

Conclusions

In conclusion, we report the first example of reduction of nitriles to amines under Au-catalysis conditions. The process occurs at ambient conditions *via* double hydrosilylation of the cyano functionality in the presence of recyclable and reusable Au nanoparticles supported on TiO_2 as catalyst. The only hydrosilane that is capable of reacting is diethylsilane, which is proven once more a unique reagent under Au NP catalysis conditions.[31–33] The initially formed labile disilylamines undergo deprotection with etherated HCl and the amines are isolated as their hydrochloric salts in very good to excellent yields. These results exemplify once more the unique potency of supported Au nanoparticles in catalyzing organic transformations of high synthetic utility, but also the superior activity of a dihydrosilane (Et_2SiH_2) as a reducing agent,[40] relative to simple monohydrosilanes.

Experimental section

The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254). Benzene was passed though silica gel and kept over 4 Å molecular sieves. NMR spectra were recorded on a Bruker Avance-500 instrument. HRMS were recorded with a Q-Exactive Plus Orbitrap MS from Thermo Scientific, with a direct infusion of the corresponding product. GC-MS analyses were performed on a Shimadzu GC-MS 2030 model equipped with a 30 m MEGA-5 HT capillary column. Flash column chromatography for the purification of compounds was carried out on SiO_2 (silica gel 60, particle size 0.040–0.063 mm). The Au catalyst is commercially available and has a gold content of 1% w/w. Its nanoparticles have an average crystallite size of 2–3 nm. The catalyst was ground in a mortar to become a fine dust and was kept in the dark. Diethylsilane was obtained from commercial suppliers. Apart from **1a**, **1i–1l**, **1o–1q** and **1z** which were obtained

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from commercial suppliers, all aryl or heteroaryl nitriles were prepared from the corresponding aldehydes *via* the triflic acid-mediated Schmidt reaction,[41] while the alkyl ones *via* treatment of aldehydes with hydroxylamine hydrochloride in DMSO.[42] The spectroscopic data of synthesized nitriles (see ESI†) are in agreement with those of the commercially available substances. The only nitrile that is a new compound in the literature is **1n**.

4-Bromofuran-2-carbonitrile (1n)

White solid (45 mg, 35% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.59 (d, J = 0.5 Hz, 1H), 7.12 (d, J = 0.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 145.6, 127.3, 124.3, 110.2, 100.7. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for C_5H_2BrNO + H, 171.9393; found 171.9391.

General procedure of the Au/TiO_2-catalyzed double hydrosilylation of nitriles

To a properly dried vial containing a solution of 0.15 mmol of nitrile in dry benzene (0.5 mL) are added 0.45 mmol of Et_2SiH_2 followed by the addition of 29 mg of Au/TiO_2 (1.0 mol% in Au) at room temperature for a certain period of time (30 min to 2 h depending on the substrate), until the reaction was complete (TLC or GC-MS). The slurry is filtered with the aid of dichloromethane under a low pressure through a short pad of silica gel and the filtrate is evaporated. The residue was treated at 25 °C with a 1 M solution of HCl in Et_2O (1 mL) for 1 h. The hydrochloric salts of the amines precipitate and are isolated in pure form as white solids *via* filtration. Apart from the 0.15–0.20 mmol scale in which the reduction experiments of Fig. 1 were performed, the double hydrosilylation was also achieved on a larger scale using 103 mg (1.0 mmol) of parent benzonitrile (**1a**), 390 μL of diethylsilane (3.0 mmol), 3 mL of benzene and 197 mg of Au/TiO_2 (2.0 mg of Au, as the catalyst contains 1 w/w% Au). After 30 min at 25 °C the reaction was complete. The crude filtrate was evaporated at reduced pressure and the residue was treated with 6 mL of a 1 M solution of HCl in Et_2O. The precipitated hydrochloric salt **3a** was isolated *via* filtration and was dried in the oven for 12 h at 100 °C (130 mg, 91% yield).

Spectroscopic data of products

***N*-Benzyl-*N*-(diethylsilyl)-1,1-diethylsilanamine (2a).**[19a] Colorless oil (37 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 7.29–7.19 (m, 5H), 4.25 (quintet, J = 3.0 Hz, 2H), 4.07 (s, 2H), 0.95 (t, 12H, J = 8.0 Hz), 0.65–0.56 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): 142.9, 128.0, 127.3, 126.5, 49.7, 7.8, 6.0. MS (EI): 279 (M^+, 7%), 250 (M^+-Et, 100%), 222 (40%), 162 (34%). HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{15}H_{29}NSi_2$ + H, 280.1911; found 280.1914.

Phenylmethanamine hydrochloride (3a).[11] White solid (29 mg, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.54 (br s, 3H), 7.51 (d, J = 7.0 Hz, 2H), 7.42–7.35 (m, 3H), 4.00 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 134.1, 128.9, 128.5, 128.3, 42.1.

***p*-Tolylmethanamine hydrochloride (3b).**[11] Yellowish solid (27 mg, 83% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.48 (br s, 3H), 7.38 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.94 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 137.7, 131.0, 129.0, 128.9, 41.9, 20.7.

(3-Methoxyphenyl)methanamine hydrochloride (3c).[4a] White solid (26 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.51 (br s, 3H), 7.31 (t, J = 8.0 Hz, 1H), 7.15 (br s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.97 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 159.3, 135.5, 129.7, 120.9, 114.5, 113.9, 55.2, 42.1.

(4-Methoxyphenyl)methanamine hydrochloride (3d).[4a] White solid (27 mg, 84% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.31 (br s, 3H), 7.41 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 3.93 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 159.3, 130.5, 125.9, 113.9, 55.2, 41.7.

(2-Bromophenyl)methanamine hydrochloride (3e).[19a] White solid (24 mg, 76% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.58 (br s, 3H), 7.70 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.47 (br t, 1H), 7.34 (br t, 1H), 4.11 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 133.3, 132.7, 130.5, 130.4, 128.0, 123.3, 42.0.

(4-Fluorophenyl)methanamine hydrochloride (3f).[19a] White solid (27 mg, 77% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.51 (br s, 3H), 7.58–7.55 (m, 2H), 7.25 (t, $J_1 = J_2$ = 8.0 Hz, 2H), 4.00 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 162.0 (d, J_{C-F} = 244.5 Hz), 131.3 (d, J_{C-F} = 8.5 Hz), 130.4 (d, J_{C-F} = 3.5 Hz), 115.3 (d, J_{C-F} = 21.5 Hz), 41.4.

(4-Chlorophenyl)methanamine hydrochloride (3g).[19a] White solid (22 mg, 79% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.45 (br s, 3H), 7.52 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 4.01 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 133.2, 133.1, 130.9, 128.5, 41.5.

Naphthalen-2-ylmethanamine hydrochloride (3h).[19a] White solid (29 mg, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.56 (br s, 3H), 8.01 (s, 1H), 7.98–7.90 (m, 3H), 7.64 (d, J = 8.5 Hz, 1H), 7.57–7.55 (m, 2H), 4.18 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 132.71, 132.70, 131.6, 128.3, 128.0, 127.9, 127.7, 126.71, 126.68, 126.6, 42.5.

(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) methanamine hydrochloride (3i).[43] White solid (35 mg, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.54 (br s, 3H), 7.69 (d, J = 7.0 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 4.02 (s, 2H), 1.29 (s, 12H). ^{13}C NMR (125 MHz, DMSO-d_6): 137.3, 134.5, 128.2, 83.7, 42.0, 24.6.

(4-(Trifluoromethyl)phenyl)methanamine hydrochloride (3j).[43] White solid (27 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.68 (br s, 3H), 7.78 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 4.12 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 138.8, 129.8, 128.9 (q, J_{C-F} = 32.0 Hz), 125.3 (q, J_{C-F} = 3.5 Hz), 124.1 (q, J_{C-F} = 272.5 Hz), 41.6.

(4-(Trifluoromethoxy)phenyl)methanamine hydrochloride (3k).[43] White solid (30 mg, 84% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.60 (br s, 3H), 7.66 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 4.05 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 148.3, 133.6, 131.2, 121.1, 120.0 (q, J_{C-F} = 256.5 Hz), 41.3.

***p*-Xylylenediamine dihydrochloride (3l).**[44] White solid (18 mg, 76% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.49 (br s, 6H), 7.52 (s, 4H), 4.02 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): 134.2, 129.0, 41.8.

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Thiophen-2-ylmethanamine hydrochloride (3m).[19a] Yellowish solid (25 mg, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.58 (br s, 3H), 7.57 (d, J = 4.5 Hz, 1H), 7.28 (d, J = 3.5 Hz, 1H), 7.06 (dd, J_1 = 4.5 Hz, J_2 = 3.5 Hz, 1H), 4.21 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 135.3, 129.1, 127.21, 127.18, 36.6.

(4-Bromofuran-2-yl)methanamine hydrochloride (3n). Yellowish solid (23 mg, 82% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.49 (br s, 3H), 8.00 (s, 1H), 6.74 (s, 1H), 4.07 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 149.2, 142.1, 113.2, 99.6, 34.9. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for C_5H_6BrNO + H, 175.9706; 175.9706.

2-(*p*-Tolyl)ethan-1-amine hydrochloride (3o). White solid (22 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.17 (br s, 3H), 7.13 (s, 4H), 2.97 (br s, 2H), 2.85 (t, J = 7.5 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 135.7, 134.3, 129.1, 128.5, 40.0, 32.5, 20.6. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_9H_{13}N$ + H, 136.1121; found 136.1122.

2-(*m*-Tolyl)ethan-1-amine hydrochloride (3p).[45] Yellowish solid (24 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.09 (br s, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.07–7.03 (m, 3H), 3.00 (br s, 2H), 2.85 (t, J = 7.5 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 137.7, 137.2, 129.2, 128.5, 127.3, 125.6, 40.1, 20.9.

2-(Naphthalen-2-yl)ethan-1-amine hydrochloride (3q).[45] Yellowish solid (27 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.21 (br s, 3H), 7.89–7.86 (m, 3H), 7.77 (s, 1H), 7.52–7.43 (m, 3H), 3.10 (br s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): 135.0, 133.1, 131.9, 128.1, 127.5, 127.4, 127.1, 126.9, 126.2, 125.7, 39.7, 33.0.

3-Phenylbutan-1-amine hydrochloride (3r). White solid (25 mg, 83% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 7.89 (br s, 3H), 7.32 (t, J = 7.5 Hz, 2H), 7.25–7.19 (m, 3H), 2.80 (m, 1H), 2.72–2.63 (m, 2H), 1.85–1.80 (m, 2H), 1.21 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 145.8, 128.5, 126.8, 126.3, 37.4, 36.4, 35.1, 21.9. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{10}H_{15}N$ + H, 150.1277; found 150.1279.

Cyclohex-3-en-1-ylmethanamine hydrochloride (3s). Yellowish solid (21 mg, 84% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.05 (br s, 3H), 5.65–5.64 (m, 2H), 2.70 (d, J = 6.0 Hz, 2H), 2.13–2.02 (m, 3H), 1.84–1.72 (m, 3H), 1.23–1.21 (m, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): 126.7, 125.2, 43.6, 31.5, 28.4, 25.3, 23.8. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for$C_7H_{13}N$ + H, 112.1121; found 112.1124.

2-Cyclohexylethan-1-amine hydrochloride (3t). White solid (23 mg, 88% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 7.97 (br s, 3H), 2.76 (t, J = 8.0 Hz, 2H), 1.66–1.59 (m, 5H), 1.47–1.42 (m, 2H), 1.31 (m, 1H), 1.23–1.08 (m, 3H), 0.90–0.84 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 36.7, 34.3, 34.2, 32.4, 25.9, 25.5. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_8H_{17}N$ + H, 128.1434; found 128.1437.

6-Phenylhexan-1-amine hydrochloride (3u).[46] White solid (28 mg, 81% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 7.99 (br s, 3H), 7.27 (t, J = 7.5 Hz, 2H), 7.19–7.15 (m, 3H), 2.76–2.69 (m, 2H), 2.57 (t, J = 7.5 Hz, 2H), 1.59–1.51 (m, 4H), 1.36–1.25 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): 142.2, 128.21, 128.20, 125.6, 38.6, 34.9, 30.7, 28.0, 26.8, 25.6.

3-Aminobenzonitrile hydrochloride (3v). Yellow solid (19 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 7.32 (t, J = 8.0 Hz, 1H), 7.13–7.07 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 142.9, 130.6, 124.3, 122.6, 120.3, 118.9, 111.9. HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_7H_6N_2$ + H, 119.0607; found 119.0604.

Methyl 4-(aminomethyl)benzoate hydrochloride (3w).[4a] White solid (28 mg, 84% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.66 (br s, 3H), 7.98 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 4.10 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): 165.9, 139.4, 129.5, 129.23, 129.17, 52.2, 41.7.

(*E*)-3-Phenylprop-2-en-1-amine hydrochloride (3x).[11] White solid (22 mg, 79% yield). ^{1}H NMR (500 MHz, DMSO-d_6): 8.19 (br s, 3H), 7.44–7.30 (m, 5H), 6.74 (d, J = 16.0 Hz, 1H), 6.32–6.26 (m, 1H), 3.61 (br s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 135.7, 134.4, 128.8, 128.2, 126.4, 121.9, 40.5.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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