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FULL PAPER

Reductions of Imines Using Zirconocene Chloride Hydride

Denisa Vargová,[a] Brigita Mudráková,[a] Ivana Némethová, [a] and Radovan Šebesta*[a]

Abstract: Herein, we describe the fast, chemoselective, and clean reduction of imines with zirconocene chloride hydride. The reaction works well on aromatic and enolizable aliphatic aldimines, as well as ketimines. A range of *N*-protecting groups and various functional groups were tolerated in the imine structure. The corresponding amines were obtained in high yields (65% - quantitative) in short reaction time, and often, no purification was required other than standard aqueous workup and a short filtration.

Introduction

Zirconocene chloride hydride or chloridobis(η^5-cyclopentadienyl)hydridozirconium (**1**), also known as a Schwartz reagent, was introduced in the 1970s by Wailes and Weigold.[1] It performs hydrozirconations of alkenes and alkynes, thus providing access to alkyl or alkenylzirconium compounds with diverse applications in organic and organometallic chemistry.[2] Later, reducing capabilities of zirconocene chloride hydride towards polar groups were recognized.[3] Schwartz reagent effectively reduces cyclic ketones,[4] or semicyclic imides.[6] Zirconocene chloride hydride is highly useful reagent for reducing tertiary amides to aldehydes, what has been used in a number of syntheses of complex molecules.[5] Cyclic amides derived from sugars were reduced to corresponding cyclic imines.[7] In some cases, Schwartz reagent can be generated in situ from zirconocene dichloride and LiAlH(*t*-BuO)$_3$.[8] Snieckus also described reductive cleavage of *O*-aryl carbamates and heterocyclic *N*-amides using zirconocene chloride hydride. The reaction tolerated various functionalities, although functional groups prone to reduction were not assessed.[9] Amarante showed that azlactones are chemoselectively reduced by Schwartz reagent to functionalized α-amino aldehydes, which may be difficult to obtain by other means.[10] Zirconocene chloride hydride can reduce some other nitrogen-containing functional groups as well. Pace and co-workers showed that Schwartz reagent cleanly transforms isocyanates to formamides, and isothiocyanates to thioformamides.[11] Wipf reported reductive coupling of nitriles and allenes mediated by Schwartz reagent, which afforded homoallylic amines.[12] Early hint at hydrozirconation of imines was reported by Alper, who observed that enolizable imines afforded enamides upon treatment by Schwartz reagent and an acyl chloride.[13]

Preparation of amines is an important facet of organic synthesis.[14] Reduction of imines or reductive alkylation of carbonyl compounds are among the most typical methods. Besides traditional methods such as Eschweiler-Clarke methylation, borohydrides $NaBH_3CN$ or $NaBH(OAc)_3$ serve as reducing reagents for these transformations. However, these reagents often have compatibility issues, so chemoselective methods are indeed required. In this context, we wish to present new facet of Schwartz reagent reactivity, namely its fast, efficient, and chemoselective reduction of imines.

Results and Discussion

During our recent related work, we observed a fast reduction of tosyl protected aldimines by the Schwartz reagent (**1**). Therefore, we have tested the reduction of a range of variously *N*-protected imines. These imines were either commercially available or synthesized according to literature procedures (see Supporting information for more details). The reductions were fast, affording full conversions within 20 minutes at room temperature with only some exceptions (Scheme 1). Imines with various sulfonyl protecting groups (**2a**-**g**) afforded corresponding secondary amines **3a**-**g** in high yields. Boc and Cbz-protected imines (**2h**-**i**) were also cleanly reduced in 20 minutes. Diphenylphosphinoyl and 3-methylpyridin-2-yl groups were tolerated too and the corresponding amines **3j** and **3k** were obtained in quantitative yields. Slight excess, 1.2 equivalents, of Schwartz´s reagent (**1**) was optimal for efficient reduction. Lower amounts of Schwartz´s reagent led to incomplete conversions and lower yields. On the other hand, less reactive imines without electron withdrawing protecting group, such as *tert*-butyl protected imine **2l** did not give any product even after prolonged reaction time. Instead, the substrate **2l** slowly decomposed. Less stable imines, such as *p*-methoxyphenyl-protected glyoxylic imine **2m** gave full conversion after 15 minutes at 0°C. However, the corresponding product of this reaction could not be isolated as it quickly decomposed even in NMR-tube in both $CDCl_3$ and C_6D_6. Similar imine with trimethyl phenyl protecting group **2n** did not react even after prolonged reaction time, and only its decomposition was observed (Scheme 1).

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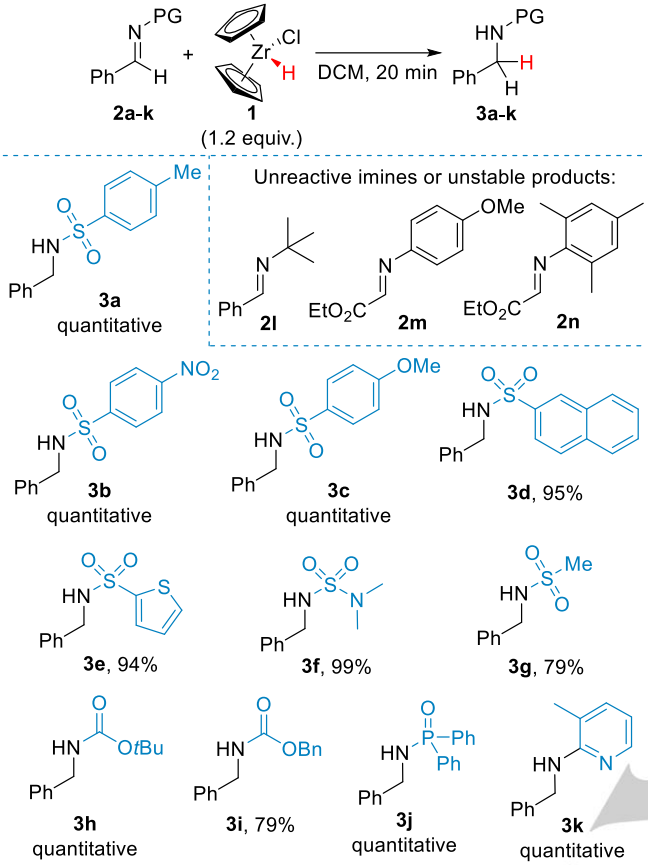
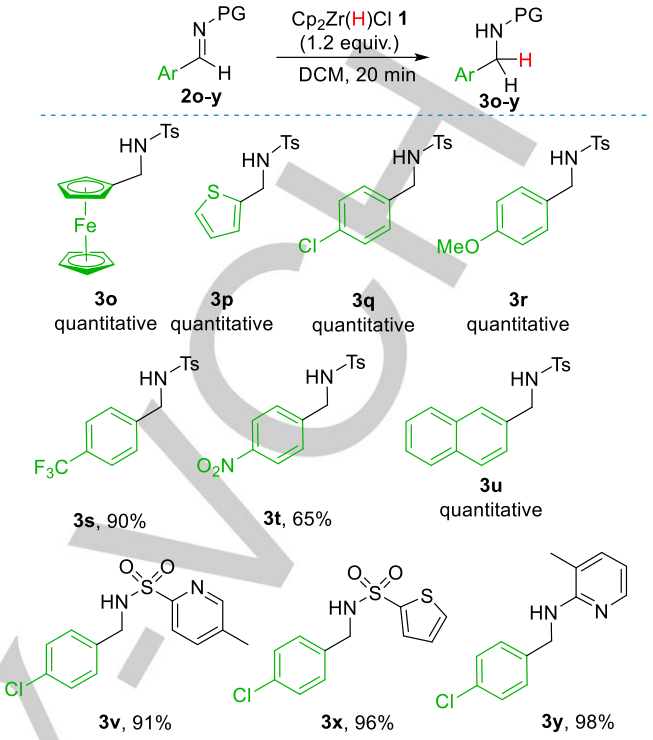


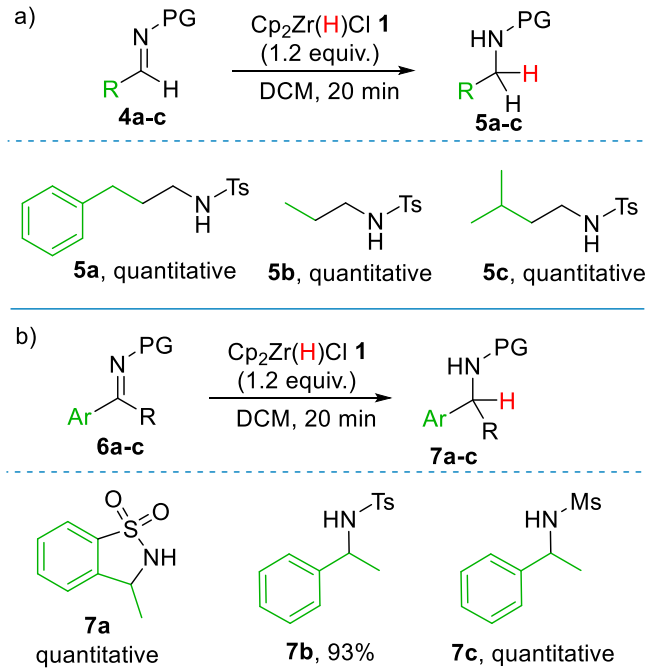
Scheme 1. Screening of *N*-protecting groups.

The scope of the reduction of imines with Schwartz reagent (**1**) was further assessed with a range of electronically different substrates **2o-y** (Scheme 2). This reduction tolerates a range of functionalities such as ferrocene, heterocycles, halogens, nitro, or alkoxy groups. Typically, all products were obtained in high yields. The reduction of nitro-containing imine **2t** afforded the corresponding amine **3t** in slightly lower, but still synthetically relevant, 65% yield. Notably, no reductive dehalogenation product was observed in the case of chloro-substituted imines **2q**, **2v**, **2x**, and **2y**. Neither trifluoromethyl group posed any problem for this reduction and the amine **3s** was isolated in 90% yield.



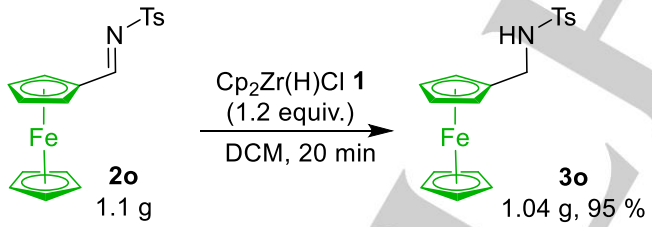
Scheme 2. Screening of imine types in the reduction.

Interestingly, also imines **4a-c** derived from enolizable aldehydes, cleanly afforded the corresponding amines **5a-c** in quantitative yields (Scheme 3a). Schwartz reagent (**1**) cleanly reduces also ketimines **6a-c** (Scheme 3b). Cyclic imine **6a** was suitable substrate for this reduction too and it afforded the corresponding amide **7a** in quantitative yield. Similarly, excellent yields were observed in case of ketimines **7b** and **7c** derive from acetophenone.



Scheme 3. Reduction of enolizable aldimines (a) and ketimines (b).

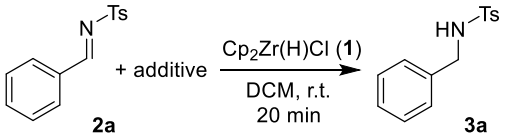
The reduction of imines with Schwartz reagent (**1**) is also easily scalable. We have performed a gram-scale experiment with 1.1 g of ferrocenyl-derived imine **2o**. Again, the imine was efficiently reduced in 20 min and afforded 1.04 g (95 %) of the corresponding amine **3o** (Scheme 4).

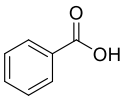
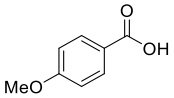
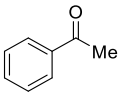
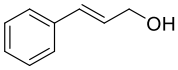
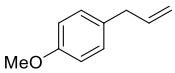
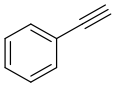


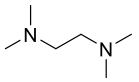
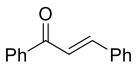
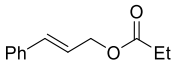
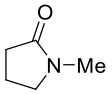
Scheme 4. Gram-scale reduction of imine **2o**.

To further explore potential limitations in the scope of the reduction of imines with Schwartz reagent, we employed the Glorius robustness screening method.[15] Inspired by this elegant methodology, we selected the reduction of imine **2a** as a benchmark reaction, to which we added additives possessing various functionalities. In this way, we could rapidly assess potential compatibility issues with the Schwartz reagent reduction. The reaction was monitored by ^{1}H NMR using benzyl benzoate as an internal standard (see Supporting information for more details). When benzoic acid was used as an additive, only a small amount of the reduced amine was found (Table 1, entry 1). Due to the overlap of the signals of benzoic acid and the signals of imine and amine, we were not able to determine the amount of consumed additive. Therefore, we also used 4-methoxybenzoic acid for more convenient identification of the methoxy group (entry 2). Evolution of gas was observed, because of the reaction between the acid and Schwartz reagent (**1**). Interestingly, portion of the imine was still reduced to the corresponding amine, although this result might be due to the reduction by hydrogen. When acetophenone, was used as additive, unsurprisingly a larger amount of the reduced alcohol was observed, but notably, 28% of amine **3a** still formed (entry 3). The reaction also tolerates alcohol functional group quite well (entry 4) – with only 35% of unreacted imine **2a** found in the reaction mixture. The reduction also took place in the presence of a C=C double bond, even though Schwartz reagent (**1**) is used for hydrozirconation reactions of alkenes (entry 5). Apparently, the imine reduction is faster than hydrozirconation of the alkene. A similar observation was made with phenylacetylene, though the alkyne was not found in the crude reaction mixture (entry 6). Coordinating compound like *N*,*N*,*N*´,*N*´-tetramethylethane-1,2-diamine completely inhibited the reaction (entry 7). The reduction was slow also in the presence of chalcone (entry 8). On the other hand, cinnamyl propionate possessing both alkene and ester moiety did not hamper the reaction and 61% of the amine **3a** was observed (entry 9). Addition of 1-methylpyrrolidin-2-one also harmed the reduction of imine **2a** (entry 10). This result is not surprising as Schwartz reagent reduces amides.

Table 1. Robustness screen of the imine reduction with Schwartz reagent using additives.[a]



Entry	Additive	Yield **3a** (%)	Unreacted **2a**/ consumed additive (%) [b]
1		8	97/n.d.
2		17	81/100
3		28	71/63
4		58	35/12
5		68	26/3
6		59	27/100

7		0		30 [c]/n.d.
8		20		76/72
9		61		23/0
10		26		63/12

[a] Experimental conditions: Imine (20 mg, 0.077 mmol), additive (0.077 mmol) and Schwarz reagent 1 (commercial, 95% purity, 20 mg, 0.077 mmol) were added to a flame-dried flask and dissolved in anhydrous DCM (0.4 mL) and stirred at r.t. for 20 min. After this time, DCM (3 mL) and benzyl benzoate (14 µL, 0.077 mmol) were added and the solvent was evaporated. The crude mixture was dissolved in CDCl3, filtered through a PTFE syringe filter to remove most of the Schwartz residue, and ^{1}H NMR was measured. [b] NMR yield, internal standard benzyl benzoate; [c] the reaction mixture was filtered two times due to its cloudiness.

To gain further insight into the reaction mechanism, we have performed DFT calculations, using the reduction of *N*-mesyl protected imine **2g** as a model reaction. Calculations were performed by the help of long-range corrected hybrid density ωB97X-D functional,[16] and LACVP (a combination of 6-31G* for H, C, N, O, S and LANL2DZ basis set for Zr) basis set. Solvent effects on the reduction were studied within the context of self-consistent reaction field theory using the polarizable continuum model (PCM)[17] and dichloromethane as solvent (ε = 8.93). These calculations suggest that the reduction of imines with zirconocene chloride hydride proceeds via 4-membered transition state (Figure 1a). The reaction proceeding via dimeric zirconocene species seem to have higher activation barrier 120.4 kJ.mol^{-1} than the reaction with monomeric **1** (98.3 kJ.mol^{-1}). This is probably caused by large steric hindrance of the two zirconocene fragments. See supporting information for more details. The reduction of enolizable imines may proceed via corresponding enamide intermediates as suggested by Alper.[13] However, following the reaction course by ^{1}H NMR, we were able to observe only traces of tentative enamide species. The intermediate zirconium salt was also detected by 1D NOESY experiment (see Supporting information for more details). By irradiation of the proton indicated by the blue color in figure 1b a positive signal at δ 6.24 ppm was detected.

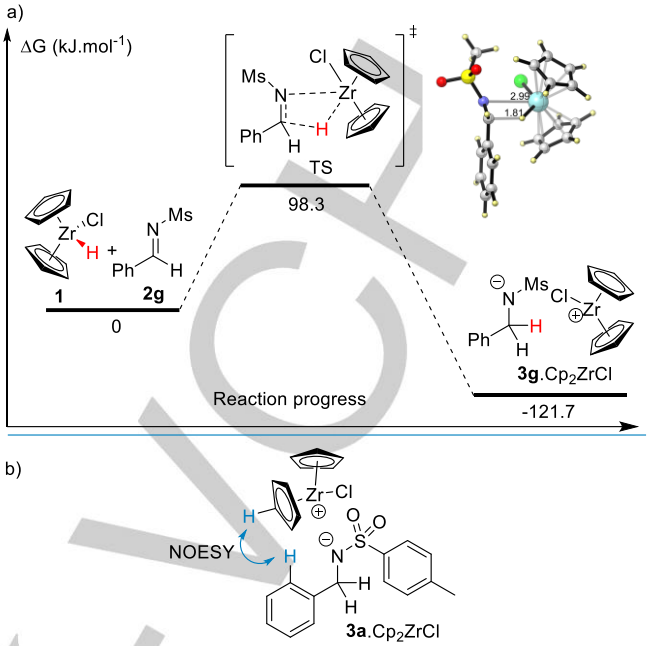


Figure 1. a) ωB97X-D/LACVP(DCM) calculated reaction profile for reduction of imines with Schwartz reagent; b) Detection of the Cp_2ZrCl-salt of **3a** by NOESY NMR.

Conclusions

We have found that zirconocene chloride hydride (**1**) reduces both aldimines as well as ketimines. The described reaction tolerates various N-protecting groups and other functionalities such as heterocycles, halogens, methoxide, or nitro group. Via additive robustness screen incompatibility with acidic and basic functionalities were revealed. On the other hand, the reduction tolerated also alkene, alkyne, and ester. Overall, the reduction is fast, clean, and chemoselective affording corresponding amines in high yields and purity. This protocol can be complementary to other conventional procedures for the reductive preparation of amines.

Experimental Section

General information

All reactions were carried out under protective atmosphere of Ar in heat-dried glassware; standard Schlenk techniques were used. Reaction flasks were always wrapped in Al-foil due to the light sensitivity of Schwartz reagent. DCM was dried over CaH_2 and freshly distilled under Ar prior to their use. Imines **2h**, **2j** and **2l** were commercially available. For filtration 40-60 ηm silica gel was used.

NMR spectra were measured on 600 MHz spectrometer (600 MHz of ^{1}H-NMR experiments, 150 MHz for ^{13}C-NMR spectra). Chemical sifts (δ) were down-fielded to TMS as an internal standard and are given in ppm. Interaction constants (*J*) are in Hz. The following abbreviations are used to describe the multiplicity of observed signals - s (singlet), d (doublet), t

(triplet), q (quartet) and m (multiplet). High resolution mass spectroscopy was measured using HESI/heated electrospray ionization.

Synthesis of starting materials

Although commercially available Schwartz reagent could also be used, for better reproducibility of the results, it was prepared from zirconocene dichloride. Imines were synthesized according to literature procedures; see supporting information for corresponding references.

Preparation of Schwartz reagent

Schwartz reagent was prepared according to the modified procedure:[18]

Zirconocene dichloride (Cp_2ZrCl_2, 17 mmol, 5.00 g) was placed into a flame-dried amberised 100 mL round bottom flask flushed with Ar. It was then connected to the high-vac source and purged three times with Ar, before being attached to the external Ar-source. Cp_2ZrCl_2 was suspended in anhydrous THF (32 mL) and heated up to 55-60°C until the solution became transparent. Then it was slowly cooled to room temperature.

Freshly ground $LiAlH_4$ (4.7 mmol, 0.18 g) from pellets was placed into 50 mL round bottom flask flushed with Ar. It is advised to use only freshly ground $LiAlH_4$, otherwise the yield of product would drop to 10%. The flask was then connected to the high-vac via needle and carefully purged three times with Ar, before being attached to the outside Ar-source. This reducing agent was then suspended in anhydrous Et_2O (9 mL). It formed grey slurry, which was stirred for approximately 10 min before being transferred into the new 20 mL syringe equipped with PTFE (2 cm in diameter) syringe filter. Large amount of the $LiAlH_4$ stayed in the flask.

To the solution of Cp_2ZrCl_2 cooled at approximately 30-35°C (indicated by slow formation of precipitate), the solution of $LiAlH_4$ was added dropwise via syringe pump in over 30 min. The $LiAlH_4$ must be filtered prior being added; otherwise the formed $Cp_2Zr(H)Cl$ (1) might be contaminated by traces of Al from $LiAlH_4$, that can drastically change its properties. During the addition, white precipitate formed immediately. After complete addition of $LiAlH_4$, the resulting slurry was stirred for at least 1.5 h.

Even though the original procedure advised to use strict Schlenk techniques to filtrate the reagent **1**, in our experience it is more practical to quickly filter (in less than 5 min) it via sintered funnel (S3) connected to the vacuum pump. The reaction mixture was poured into the sintered funnel and quickly washed with anhydrous THF (20 mL), followed by anhydrous DCM (20 mL) and anhydrous Et_2O (20 mL). Almost dry reagent 1 was quickly transferred to the 50 mL round bottom flask, where it would be stored, and dried at reduced pressure for at least 2 h, then stored under Ar at -10°C wrapped in Al-foil. Schwartz reagent prepared by this methodology was obtained in 100% purity.

Determination of purity of Schwartz reagent 1 via ^{1}H NMR

Approximately 5 mg of 1 was suspended in C_6D_6 in a test tube. Then one drop of acetone (p.a.) was added via microsyringe. Resulting white slurry was filtered to the NMR tube via syringe equipped by PTFE syringe filter (1 cm in diameter).

In the NMR spectra in the area of 1.1-0.85 ppm, the signals of product of the reaction between $Cp_2Zr(H)Cl$ (**1**) (and Cp_2ZrH_2 by-product) and acetone could be seen in background noise. Signals for $Cp_2Zr(O$*i*-$Pr)Cl$ are at 0.9 ppm and for $Cp_2Zr(O$*i*-$Pr)_2$ at 1.05 ppm, although they might be slightly shifted downfield if too much acetone is present in the mixture.

4-Methyl-N-(ferrocenylmethylene)benzenesulfonamide (2o): A procedure by Cid was used instead of literature procedure for imine **2n**.[19] A mixture of sulfonamide (1.7 g, 10 mmol), ferrocenecarbaldehyde (3.0 g, 10 mmol), activated 4Å MS, and a catalytic amount of pyrrolidine (1.0 mmol, 0.1 ml) in anhydrous DCM (50 mL) was stirred overnight at ambient temperature. Subsequently, the reaction mixture was filtered through a pad of SiO_2 and concentrated under reduced pressure. The resulting residue was purified by crystallization DCM/pentane to yield the pure product as dark red crystals (2.5 g, 69%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.05 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.86 – 4.81 (m, 2H), 4.75 – 4.70 (m, 2H), 4.19 (s, 5H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.9, 143.9, 136.3, 129.7, 127.6, 75.2, 74.6, 71.3, 70.2, 21.6. MS (APCI, *m/z*): calcd for $C_{18}H_{18}FeNO_2S$ $[M+H]^+$: 368.0, found: 368.0.

Imine reductions

Typical procedure for reductions

Schwartz reagent (**1**, 1.2 equiv) and imine (1.0 equiv) were dissolved in anhydrous DCM (0.2 mL for 20 mg of Schwartz reagent **1**) and stirred at room temperature until the full conversion of the starting material was detected via TLC. Also, the full conversion was apparent after a change of the reaction mixture from being cloudy to clear. The reaction was quenched by addition of 10 % NH_4Cl solution and extracted to DCM. After drying over Na_2SO_4, and evaporation of the solvent, the Schwartz reagent residue was filtered through a minimal amount of SiO_2 (hexane/EA 2:1). The products were obtained pure without further purification.

Characterization data

***N*-Benzyl-4-methylbenzenesulfonamide (3a)**: This compound was prepared from 0.11 mmol of imine **2a** to give **3a** as yellow solid in quantitative yield (29 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 (dd, *J* = 9.3, 7.2 Hz, 3H), 7.21 – 7.18 (m, 2H), 4.76 (t, *J* = 5.9 Hz, 1H), 4.12 (d, *J* = 6.2 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.5, 136.8, 136.3, 129.7, 128.7, 127.8, 127.2, 126.4, 47.3, 21.5 ppm. Spectral data are consistent with those in the literature.[20] MS (APCI, *m/z*): calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$: 262.1, found: 262.1.

***N*-Benzyl-4-nitrobenzenesulfonamide (3b):** This compound was prepared from 0.12 mmol of imine **2b** to give **3b** as brown oil in quantitative yield (35 mg).^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 – 8.28 (m, 2H), 8.02 – 7.97 (m, 2H), 7.32 – 7.25 (m, 3H), 7.21 – 7.15 (m, 2H), 4.94 (t, *J* = 5.7 Hz, 1H), 4.24 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.9, 146.0, 135.4, 128.8, 128.8, 128.3, 128.2, 127.9, 124.3, 47.4 ppm. Spectral data are consistent with those in the literature.[21] MS (APCI, *m/z*): calcd for $C_{13}H_{11}N_2O_4S$ $[M-H]^-$: 291.0, found: 291.1.

***N*-Benzyl-4-methoxybenzenesulfonamide (3c):** This compound was prepared from 0.11 mmol of imine **2c** to give **3c** as colorless powder in quantitative yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.9 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.21 – 7.17 (m, 2H) 6.97 (d, *J* = 8.9 Hz, 2H), 4.70 (t, *J* = 5.9 Hz, 1H), 4.11 (d, *J* = 6.2 Hz, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.9, 136.3, 131.4, 129.3, 128.7, 127.89, 127.85, 114.3, 55.6, 47.2 ppm. Spectral data are consistent with those in the literature.[22] MS (APCI, *m/z*): calcd for $C_{14}H_{16}NO_3S$ $[M+H]^+$: 278.1, found: 278.1.

***N*-Benzylnaphthalene-2-sulfonamide (3d):** This compound was prepared from 0.068 mmol of imine **2d** to give **3d** as colorless solid in 95% yield (19 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.96 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.64 – 7.60 (m, 1H), 7.28 – 7.15 (m, 5H), 4.85 (t, *J* = 6.0 Hz, 1H), 4.17 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.6, 136.1, 134.8, 132.1, 129.5, 129.2, 128.8, 128.7, 128.6, 127.9, 127.9, 127.9, 127.6, 122.3, 47.4 ppm. Spectral data are consistent with those in the literature.[23] MS (APCI, *m/z*): calcd for $C_{17}H_{14}NO_2S$ $[M-H]^-$: 296.1, found: 296.1.

***N*-Benzylthiophene-2-sulfonamide (3e):** This compound was prepared from 0.068 mmol of imine **2e** to give **3e** as colorless solid in 94% yield (15 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (ddd, *J* = 6.2, 4.4, 1.2 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.22 (d, *J* = 6.6 Hz, 2H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.77 (s, 1H), 4.23 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.1, 131.1, 127.6, 127.3, 124.0, 123.3, 123.1, 122.7, 42.8. Spectral data are consistent with those in the literature.[24] HRMS (ESI+, *m/z*): calcd for $C_{11}H_{12}NO_2S_2$ $[M+H]^+$: 254.03040, found: 254.03043.

***N*-Benzyldimethylaminosulfonamide (3f):** This compound was prepared from 0.117 mmol of imine **2f** to give **3f** as colorless solid in 99% yield (27 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.25 (m, 5H), 4.51 (s, 1H), 4.22 (d, *J* = 6.1 Hz, 2H), 2.77 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 137.0, 128.7, 127.9, 116.0, 47.7, 37.9. Structure was reported in literature before, but spectra was recorded in CCl_4.[25] MS (APCI, *m/z*): calcd for $C_9H_{15}N_2O_2S$ $[M+H]^+$: 215.1, found: 215.1.

***N*-Benzylmethanesulfonamide (3g):** This compound was prepared from 0.163 mmol of imine **2g** to give **3g** as colorless solid in quantitative yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 5H), 4.52 (s, 1H), 4.34 (d, *J* = 6.1 Hz, 2H), 2.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 136.7, 128.9, 128.1, 127.9, 47.2, 41.1. Spectral data are consistent with those in the literature.[26] MS (APCI, *m/z*): calcd for $C_8H_{10}NO_2S$ $[M+H]^+$: 184.0, found: 184.1.

***tert*-Butyl benzylcarbamate (3h):** This compound was prepared from 0.11 mmol of imine **2h** to give **3h** as colorless oil in quantitative yield (24 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.24 (m, 3H), 4.84 (br. s, 1H), 4.32 (d, *J* = 5.0 Hz, 2H), 1.46 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 155.9, 138.9, 128.6, 127.5, 127.3, 79.4, 44.7, 28.4 ppm. Spectral data are consistent with those in the literature.[27] MS (APCI, *m/z*): calcd for $C_7H_{10}N$ $[M+H]^+$: 108.1, found: 108.1.

***N*-Carbobenzyloxybenzylamine (3i):** This compound was prepared from 0.11 mmol of imine **2i** to give **3i** as white solid in 79% yield (21 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.34 (m, 4H), 7.33 (d, *J* = 7.3 Hz, 3H), 7.28 (dd, *J* = 8.4, 2.8 Hz, 3H), 5.14 (s, 2H), 5.06 (s, 1H), 4.39 (d, *J* = 5.8 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 156.4, 138.4, 136.5, 128.7, 128.5, 128.1, 127.5, 66.9, 45.2 ppm. Spectral data are consistent with those in the literature.[28] MS (APCI, *m/z*): calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1, found: 242.2.

***N*-Benzyl-*P*,*P*-diphenylphosphinic amide (3j):** This compound was prepared from 0.11 mmol of imine **2j** to give **3j** as yellow oil in quantitative yield (34 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.50 (dd, *J* = 10.5, 4.2 Hz, 2H), 7.45 (td, *J* = 7.4, 3.2 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 4.14 (t, *J* = 7.4 Hz, 2H), 3.15 (d, *J* = 5.7 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 132.2, 132.1, 131.98, 131.96, 128.66, 128.65, 128.56, 127.7, 127.5, 44.7 ppm. Spectral data are consistent with those in the literature.[29] MS (APCI, *m/z*): calcd for $C_{19}H_{17}NOP$ $[M-H]^-$: 306.1, found: 306.2.

***N*-Benzyl-3-methylpyridin-2-amine (3k):** This compound was prepared from 0.11 mmol of imine 2f to give 3f as colorless solid in quantitative yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.24 (dd, *J* = 7.1, 0.8 Hz, 1H), 6.56 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.69 (d, *J* = 5.1 Hz, 2H), 4.36 (s, 1H), 2.09 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 156.6, 145.5, 140.0, 136.8, 128.6, 127.9, 127.4, 116.5, 112.9, 45.8, 17.0 ppm. Spectral data are consistent with those in the literature.[30] MS (APCI, *m/z*): calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1, found: 199.2.

***N*-Ferrocenylmethyl-4-methylbenzenesulfonamide (3o):** This compound was prepared from 0.12 mmol of imine **2o** to give **3o** as orange solid in quantitative yield (44 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 5.6 Hz, 1H), 4.13 – 4.07 (m, 7H), 4.06 – 4.03 (m, 2H), 3.83 (d, *J* = 5.7 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 136.9, 129.7, 127.1, 83.5, 68.5, 68.3, 67.9, 42.6, 21.5 ppm. Spectral data are consistent with those in the literature.[23] MS (APCI, *m/z*): calcd for $C_{18}H_{18}FeNO_2S$ $[M-H]^-$: 368.0, found: 368.0.

4-Methyl-*N*-(thiophen-2-ylmethyl)benzenesulfonamide (3p): This compound was prepared from 0.12 mmol of imine 2p to give 3p as white solid in quantitative yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 4.8 Hz, 1H), 6.87 (dd, *J* = 11.3, 6.5 Hz, 2H), 4.81 (s, 1H), 4.33 (d, *J* = 6.0 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.6, 138.9, 136.8, 129.7, 127.2, 126.9, 126.5, 125.8, 42.1, 21.5 ppm. Spectral data are consistent with those in the literature.[23] MS (APCI, *m/z*): calcd for $C_{12}H_{12}NO_2S_2$ $[M-H]^-$: 266.0, found: 266.0.

***N*-(4-Chlorobenzyl)-4-methylbenzenesulfonamide (3q):** This compound was prepared from 0.12 mmol of imine **2q** to give **3q** as colorless oil in quantitative yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.93 (t, *J* = 6.0 Hz, 1H), 4.08 (d, *J* = 6.3 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.7, 136.8, 134.8, 133.8, 129.8, 129.2, 128.8, 127.1, 46.6, 21.5 ppm. Spectral data are consistent with those in the literature.[31] MS (APCI, *m/z*): calcd for $C_{14}H_{13}ClNO_2S$ $[M-H]^-$: 294.0, found: 294.0.

***N*-(4-Methoxybenzyl)-4-methylbenzenesulfonamide (3r):** This compound was prepared from 0.12 mmol of imine **2r** to give **3r** as colorless crystals in quantitative yield (35 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.81 (t, *J* = 5.8 Hz, 1H), 4.04 (d, *J* = 6.1 Hz, 2H), 3.76 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.3, 143.4, 136.9, 129.7, 129.7, 129.7, 129.7, 129.2, 128.3, 127., 114.0, 55.3, 46.7, 21.5 ppm. Spectral data are consistent with those in the literature.[23] MS (APCI, *m/z*): calcd for $C_{15}H_{16}NO_3S$ $[M-H]^-$: 290.0, found: 290.0.

4-Methyl-*N*-(4-(trifluoromethyl)benzyl)benzenesulfonamide (3s): This compound was prepared from 0.12 mmol of imine **2s** to give **3s** as white

needles in 90% yield (35 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.78 (t, *J* = 6.2 Hz, 1H), 4.21 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.7, 140.4, 136.7, 130.4, 130.2, 129.9, 129.8, 129.7, 128.0, 127.1, 126.6, 125.5, 125.5, 124.8, 123.0, 121.2, 46.7, 21.5 ppm. Spectral data are in agreement with literature data.[23] MS (APCI, *m/z*): calcd for $C_{15}H_{13}F_3NO_2S$ [M-H]$^-$: 328.0, found: 328.0.

4-Methyl-*N*-[(4-nitrophenyl)methyl]-benzenesulfonamide (3t): This compound was prepared from 0.11 mmol of imine **2t** to give **3t** as yellow solid in 65% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.85 (t, *J* = 6.3 Hz, 1H), 4.26 (d, *J* = 6.5 Hz, 2H), 2.44 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 144.4, 143.8, 136.7, 129.9, 128.4, 127.1, 126.4, 46.4, 21.5 ppm. Spectral data are consistent with those in the literature.[32] MS (APCI, *m/z*): calcd for $C_{14}H_{13}N_2O_4S$ [M-H]$^-$: 305.1, found: 305.2.

4-Methyl-*N*-(naphthalen-2-ylmethyl)benzenesulfonamide (3u): This compound was prepared from 0.11 mmol of imine **2u** to give **3u** as white solid in quantitative yield (34 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.77 – 7.73 (m, 3H), 7.71 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.59 (s, 1H), 7.46 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.30 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.95 (t, *J* = 5.8 Hz, 1H), 4.27 (d, *J* = 6.3 Hz, 2H), 2.39 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.5, 136.9, 133.6, 133.2, 132.8, 129.7, 128.5, 127.73, 127.68, 127.2, 126.7, 126.3, 126.1, 125.7, 47.4, 21.5 ppm. Spectral data are consistent with those in the literature.[33] MS (APCI, *m/z*): calcd for $C_{18}H_{16}NO_2S$ [M-H]$^-$: 310.1, found: 310.2.

***N*-(4-Chlorobenzyl)-5-methylpyridine-2-sulfonamide (3v):** This compound was prepared from 0.068 mmol of imine **2v** to give **3v** as colorless crystals in 91% yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.19 (s, 4H), 6.32 (t, *J* = 6.0 Hz, 1H), 4.17 (d, *J* = 6.4 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 154.5, 150.3, 138.1, 137.3, 135.1, 133.5, 129.5, 128.6, 128.6, 122.1, 46.8, 18.5 ppm. HRMS (ESI+, *m/z*): calcd for $C_{13}H_{13}ClN_2O_2SK$ [M+K]$^+$: 335.00178, found: 335.00193.

***N*-(4-Chlorobenzyl)thiophene-2-sulfonamide (3x):** This compound was prepared from 0.068 mmol of imine **2x** to give **3x** as colorless solid in 96% yield (15 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 2H), 7.27 (dd, *J* = 6.9, 1.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.09 (dt, *J* = 8.2, 4.1 Hz, 1H), 4.94 (t, *J* = 5.8 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 135.9, 129.7, 129.1, 127.7, 127.4, 124.5, 124.1, 124.1, 122.7, 42.0 ppm. HRMS (ESI+, *m/z*): calcd for $C_{11}H_{10}ClNO_2S_2K$ [M+K]$^+$: 327.9444, found: 327.9441.

***N*-(4-Chlorobenzyl)-3-methylpyridin-2-amine (3y):** This compound was prepared from 0.11 mmol of imine **2y** to give **3y** as white solid in quantitative yield (25 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.05 – 8.01 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 (dd, *J* = 7.1, 0.8 Hz, 1H), 6.56 (dd, *J* = 7.1, 5.1 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 2H), 4.37 (s, 1H), 2.10 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 156.4, 145.5, 138.7, 136.9, 132.8, 129.1, 116.5, 113.1, 45.0, 17.0 ppm. HRMS (ESI+, *m/z*): calcd for $C_{13}H_{14}ClN_2$ [M+H]$^+$: 233.0840, found: 233.08400.

***N*-(3-Phenylpropyl)-4-methylbenzenesulfonamide (5a):** This compound was prepared from 0.11 mmol of imine **4a** to give **5a** as yellow liquid in quantitative yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.3 2Hz, 1H), 4.72 (t, *J* = 6.0 Hz, 1H), 2.95 (q, *J* = 6.7 Hz, 2H), 2.63 – 2.55 (m, 2H), 2.42 (s, 3H), 1.83 – 1.72 (m, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.4, 140.9, 136.9, 129.7, 128.4, 128.3, 127.1, 126.0, 42.6, 32.7, 31.1, 21.5 ppm. Spectral data are in agreement with literature data.[34] MS (APCI, *m/z*): calcd for $C_{16}H_{20}NO_2S$ [M-H]$^+$: 290.1, found: 290.1.

4-Methyl-*N*-propylbenzenesulfonamide (5b): This compound was prepared from 0.11 mmol of imine **4b** to give **5b** as yellow liquid in quantitative yield (23 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.62 (t, *J* = 5.6 Hz, 1H), 2.90 (dd, *J* = 13.6, 6.8 Hz, 2H), 2.43 (s, 3H), 1.55 – 1.41 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.3, 137.0, 129.7, 127.1, 44.9, 22.9, 21.5, 11.1 ppm. Spectral data are consistent with those in the literature.[35] MS (APCI, *m/z*): calcd for $C_{10}H_{16}NO_2S$ [M+H]$^+$: 214.1, found: 214.1.

***N*-(3-Methylbutyl)-4-methylbenzenesulfonamide (5c):** This compound was prepared from 0.11 mmol of imine **4c** to give **5c** as yellow liquid in quantitative yield (27 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.61 (bs, 1H), 2.94 (dd, *J* = 13.8, 6.8 Hz, 2H), 2.43 (s, 2H), 1.58 (tt, *J* = 13.2, 6.6 Hz, 1H), 1.34 (dd, *J* = 14.3, 7.1 Hz, 1H), 0.82 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.3, 136.9, 129.6, 127.1, 41.5, 38.3, 25.4, 22.2, 21.5 ppm. Spectral data are consistent with those in the literature.[36] MS (APCI, *m/z*): calcd for $C_{12}H_{20}NO_2S$ [M+H]$^+$: 241.1, found: 242.1.

3-Methyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (7a): This compound was prepared from 0.12 mmol of imine **6a** to give **7a** as colorless solid in quantitative yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 4.90 (s, 1H), 4.83 – 4.75 (m, 1H), 1.62 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 141.7, 135.5, 133.2, 129.2, 123.9, 121.2, 53.4, 21.4 ppm. Spectral data are in agreement with literature data.[37] MS (APCI, *m/z*): calcd for $C_8H_8NO_2S$ [M-H]$^-$: 182.0, found: 182.0.

1-Phenyl-*N*-tosylethanamine (7b): This compound was prepared from 0.11 mmol of imine **6b** to give **7b** as white solid in 93% yield (28 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 5H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.95 (d, *J* = 6.8 Hz, 1H), 4.46 (p, *J* = 6.9 Hz, 1H), 2.38 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 143.1, 142.0, 137.6, 129.4, 128.5, 127.4, 127.1, 126.1, 53.6, 23.5, 21.5 ppm. Spectral data are in agreement with literature data.[38] MS (APCI, *m/z*): calcd for $C_{15}H_{16}NO_2S$ [M-H]$^-$: 274.1, found: 274.1.

***N*-(1-Phenylethyl)methanesulfonamide (7c):** This compound was prepared from 0.11 mmol of imine **6c** to give **7c** as colorless oil in quantitative yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.33 (m,4H), 7.32 – 7.28 (m, 1H), 4.98 (d, *J* = 6.5 Hz, 1H), 4.65 (p, *J* = 6.9 Hz, 1H), 2.61 (s, 3H), 1.54 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ 142.6, 129.2, 128.2, 126.4, 54.0, 42.0, 24.2 ppm. Spectral data are in agreement with literature data.[39] MS (APCI, m/z): calcd for $C_9H_{12}NO_2S$ [M-H]$^-$: 198.1, found: 198.1.

NMR tests of functional group tolerance

Imine 2a (20 mg, 0.077 mmol, 1.0 equiv), additive (0.077 mmol, 1.0 equiv) and Schwarz reagent (20 mg, 0.077 mmol, 1.0 equiv) were added to a flame-dried flask and dissolved in anhydrous DCM (0.4 mL) and stirred at r.t. for 20 min. After this time, DCM (3 mL) and benzoyl benzoate (14µL, 0.077 mmol, 1.0 equiv) were added and the solvent was evaporated. The crude mixture was dissolved in $CDCl_3$, filtered through a syringe filter to remove most of the Schwartz residue, and ^{1}H NMR was measured.

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Keywords: imine • reduction • Schwartz reagent • zirconocene chloride hydride • amine

[1] P. C. Wailes, H. Weigold, *J. Organomet. Chem.* **1970**, *24*, 405-411.
[2] a) J. Schwartz, J. A. Labinger, *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 333-340; b) P. Wipf, H. Jahn, *Tetrahedron* **1996**, *52*, 12853-12910; c) D. L. J. Pinheiro, P. P. de Castro, G. W. Amarante, *Eur. J. Org. Chem.* **2018**, 4828-4844.
[3] M. M. Więcław, S. Stecko, *Eur. J. Org. Chem.* **2018**, 6601-6623.
[4] E. Cesarotti, A. Chiesa, S. Maffi, R. Ugo, *Inorg. Chim. Acta* **1982**, *64*, L207-L208.
[5] a) J. M. White, A. R. Tunoori, G. I. Georg, *J. Am. Chem. Soc.* **2000**, *122*, 11995-11996; b) J. T. Spletstoser, J. M. White, A. R. Tunoori, G. I. Georg, *J. Am. Chem. Soc.* **2007**, *129*, 3408-3419; c) J. T. Spletstoser, J. M. White, G. I. Georg, *Tetrahedron Lett.* **2004**, *45*, 2787-2789; d) B. Ganem, R. R. Franke, *J. Org. Chem.* **2007**, *72*, 3981-3987; e) M. Iwata, R. Yazaki, Y. Suzuki, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 18244-18245; f) V. B. Gondi, K. Hagihara, V. H. Rawal, *Chem. Commun.* **2010**, *46*, 904-906; g) M. Iwata, R. Yazaki, I. H. Chen, D. Sureshkumar, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2011**, *133*, 5554-5560.
[6] G. Lanza, M. A. Chiacchio, S. V. Giofrè, R. Romeo, P. Merino, *Eur. J. Org. Chem.* **2013**, 95-104.
[7] a) P. Szcześniak, S. Stecko, O. Staszewska-Krajewska, B. Furman, *Tetrahedron* **2014**, *70*, 1880-1888; b) P. Szcześniak, S. Stecko, E. Maziarz, O. Staszewska-Krajewska, B. Furman, *J. Org. Chem.* **2014**, *79*, 10487-10503; c) P. Szcześniak, E. Maziarz, S. Stecko, B. Furman, *J. Org. Chem.* **2015**, *80*, 3621-3633.
[8] Y. Zhao, V. Snieckus, *Org. Lett.* **2014**, *16*, 390-393.
[9] J. Morin, Y. Zhao, V. Snieckus, *Org. Lett.* **2013**, *15*, 4102-4105.
[10] D. L. J. Pinheiro, E. P. Ávila, G. M. F. Batista, G. W. Amarante, *J. Org. Chem.* **2017**, *82*, 5981-5985.
[11] a) V. Pace, K. de la Vega-Hernández, E. Urban, T. Langer, *Org. Lett.* **2016**, *18*, 2750-2753; b) K. de la Vega-Hernández, R. Senatore, M. Miele, E. Urban, W. Holzer, V. Pace, *Org. Biomol. Chem.* **2019**, *17*, 1970-1978.
[12] P. Wipf, M. D. Manojlovic, *Beilstein J. Org. Chem.* **2011**, *7*, 824-830.
[13] K. S. Ng, D. E. Laycock, H. Alper, *J. Org. Chem.* **1981**, *46*, 2899-2901.
[14] A. Ricci, ed., Amino Group Chemistry: From Synthesis to the Life Sciences, Wiley-VCH, Weinheim, **2008**.
[15] K. D. Collins, F. Glorius, *Nat. Chem.* **2013**, *5*, 597-601.
[16] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.
[17] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001.
[18] S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, S. M. King, *Org. Synth.* **1993**, *71*, 77.
[19] S. Morales, F. G. Guijarro, J. L. García Ruano, M. B. Cid, *J. Am. Chem. Soc.* **2014**, *136*, 1082-1089.
[20] H. Clavier, A. Lepronier, N. Bengobesse-Mintsa, D. Gatineau, H. Pellissier, L. Giordano, A. Tenaglia, G. Buono, *Adv. Synth. Catal.* **2013**, *355*, 403-408.
[21] R. Plamont, L. V. Graux, H. Clavier, *Eur. J. Org. Chem.* **2018**, 1372-1376.
[22] D. A. Powell, H. Fan, *J. Org. Chem.* **2010**, *75*, 2726-2729.
[23] P. Qu, C. Sun, J. Ma, F. Li, *Adv. Synth. Catal.* **2014**, *356*, 447-459.
[24] B. G. Reed-Berendt, L. C. Morrill, *J. Org. Chem.* **2019**, *84*, 3715-3724.
[25] B. Unterhalt, E. Seebach, *Arch. Pharm.* **1981**, *314*, 51-57.
[26] Z.-l. Li, L.-k. Jin, C. Cai, *Org. Biomol. Chem.* **2017**, *15*, 1317-1320.
[27] E. Speckmeier, M. Klimkait, K. Zeitler, *J. Org. Chem.* **2018**, *83*, 3738-3745.
[28] Z. Aouf, R. Mansouri, S. Lakrout, M. Berredjem, N. E. Aouf, *J. Korean Chem. Soc.* **2017**, *61*, 151-156.
[29] A. Martínez-Asencio, D. J. Ramón, M. Yus, *Tetrahedron* **2011**, *67*, 3140-3149.
[30] N. Dastbaravardeh, M. Schnürch, M. D. Mihovilovic, *Org. Lett.* **2012**, *14*, 1930-1933.
[31] L. J. Wesenberg, S. Herold, A. Shimizu, J.-i. Yoshida, S. R. Waldvogel, *Chem. Eur. J.* **2017**, *23*, 12096-12099.
[32] M. D. Hopkins, Z. C. Brandeburg, A. J. Hanson, A. A. Lamar, *Molecules* **2018**, *23*, 1838.
[33] R. Cano, D. J. Ramón, M. Yus, *J. Org. Chem.* **2011**, *76*, 5547-5557.
[34] M. Zhu, K.-i. Fujita, R. Yamaguchi, *Org. Lett.* **2010**, *12*, 1336-1339.
[35] X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun.* **2013**, *49*, 6102-6104.
[36] X. Liu, Y. Liu, Y. Zhang, *Tetrahedron Lett.* **2002**, *43*, 6787-6789.
[37] Y. Tao, S. R. Gilbertson, *Chem. Commun.* **2018**, *54*, 11292-11295.
[38] J. G. Taylor, N. Whittall, K. K. Hii, *Org. Lett.* **2006**, *8*, 3561-3564.
[39] D. R. Wallach, J. D. Chisholm, *J. Org. Chem.* **2016**, *81*, 8035-8042.

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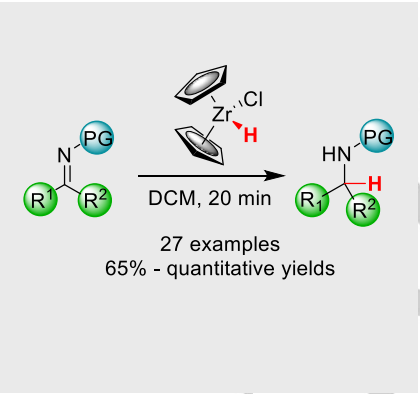
FULL PAPER

Zirconocene chloride hydride (Schwartz´s reagent) can reduce aromatic and aliphatic aldimines as well as ketimines. The reaction is fast (complete in 20 min) and chemoselective. It tolerates a range of functional groups and afford corresponding *N*-protected amines in high yields.



Organometallic reagents*

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Reductions of Imines Using Zirconocene Chloride Hydride

*one or two words that highlight the emphasis of the paper or the field of the study