Synthesis X. Bai et al. Paper

Hydrogen-Borrowing Amination of Secondary Alcohols Promoted by a (Cyclopentadienone)iron Complex

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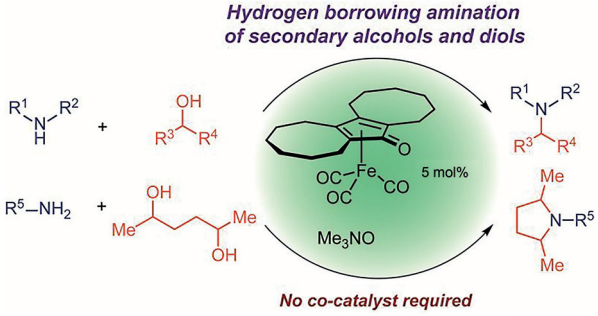
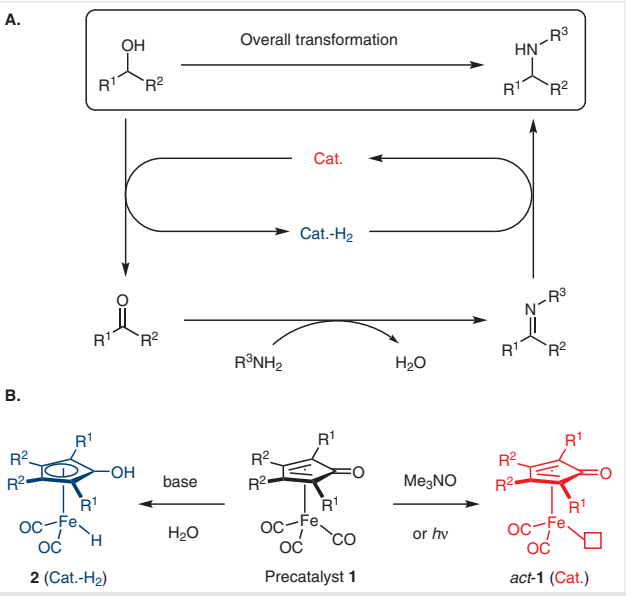


Received: 18.04.2019
Accepted after revision: 27.05.2019
Published online: 26.06.2019
DOI: 10.1055/s-0039-1690101; Art ID: ss-2019-t0234-op

Abstract Thanks to a highly active catalyst, the scope of the (cyclopentadienone)iron complex-promoted 'hydrogen-borrowing' (HB) amination has been expanded to secondary alcohols, which had previously been reported to react only in the presence of large amounts of co-catalysts. A range of cyclic and acyclic secondary alcohols were reacted with aromatic and aliphatic amines giving fair to excellent yields of the substitution products. The catalyst was also able to promote the cyclization of diols bearing a secondary alcohol group with primary amines to generate saturated N-heterocycles.

Key words hydrogen borrowing, iron, amination, alcohols, (cyclopentadienone)iron complexes

Alcohol amination is an attractive and atom-economic reaction which provides access to amines – a valuable class of fine chemicals[1] – generating H_2O as the only by-product. As OH^- is a poor leaving group, this transformation cannot occur via the S_N2 mechanism and, on the other hand, its acid-promoted version requires harsh conditions.[2] Catalytic processes involving the 'hydrogen-borrowing' (HB) mechanism (also known as 'hydrogen autotransfer')[3] are the most effective way to perform alcohol amination. In these reactions, an alcohol dehydrogenation/imine formation/imine hydrogenation sequence takes place (Scheme 1 A), with no net consumption or release of hydrogen. The catalyst has the role to temporarily store a H_2 molecule taken from the substrate and then transfer it to the imine intermediate, thus forming the amine product. Rhodium, ruthenium, and iridium complexes were initially used to catalyze HB aminations[4] and, after remarkable progress in the area,[3] most recent studies have focused on the latter two noble metals.[5,6] Cheaper metals such as copper,[7] cobalt[8] and iron[9] have been much less exploited for HB amination until recent years, when catalytic methodologies relying on base metals have been increasingly studied.[3a] In this context, Feringa, Barta et al. reported in 2014 the first application of a well-defined homogeneous iron catalyst for the HB amination of alcohols: the 'Knölker complex' **1a** (Figure 1) was shown to promote the amination of several primary alcohols and diols.[10c]



Scheme 1 A: general mechanism of HB amination of alcohols. B: formation of HB amination catalysts (***act*-1** and **2**) from (cyclopentadienone)iron complexes **1**

This methodology had the advantage of using a highly stable and easy-to-handle pre-catalyst, which can be readily activated in situ (see Scheme 1 B). The main limitation was that the substrate scope is restricted to primary alco-

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hols. Further reports on the use of (cyclopentadienone)iron complexes **1**[11] in HB amination by Feringa/Barta,[10a,b] Poater/Renaud,[12] and Morrill[13a] (Figure 1) did not expand the scope to the more challenging secondary alcohols.[13] To this end, Wills and co-workers (Figure 1) showed that pre-catalysts **1c–h** can promote the amination of a few cycloalkanols.[14] Zhao et al. reported that the isolated catalyst **2a**, in the presence AgF (40 mol%) as co-catalyst, is able to promote the HB amination of secondary alcohols in fair to good yields.[15]

However, the latter methodology suffers from serious limitations such as high catalyst loading (10 mol%) and sensitivity of the isolated complex **2a**, which cannot be handled in the air. Most importantly, the necessity of large amounts of a semi-precious metal co-catalyst (AgF) offsets the economic and environmental advantages of using an iron catalyst.

This paper accounts for the effort taken by our research group – building on its expertise in this area[16] – to extend the use of (cyclopentadienone)iron complexes to the *HB amination of secondary alcohols*. To this end, we exploited our previously reported pre-catalyst **1i** (Figure 1).[16d] This complex showed superior activity compared to other (cyclopentadienone)iron complexes, such as the 'Knölker complex' **1a**, in the catalytic transfer hydrogenation (CTH) of ketimines and in the CTH-based reductive amination of ketones.[16b,c] As these reactions share the same elementary steps of the HB amination, we expected **1i** to display sufficient activity to promote the amination of secondary alcohols.

A preliminary test in the HB amination of a primary alcohol [1-octanol (**4a**)] with *p*-anisidine (**3a**) showed that **1i** is indeed more active than **1a**, giving >95% (Table 1, entry 1) versus 69% yield (reported by Barta, Feringa et al. using **1a**).[17] Thus, we tested pre-catalyst **1i** in the reaction of **3a** with 1-phenylethanol (**4b**) under the same conditions used with 1-octanol, and observed a poor conversion to the desired product **P2** (entry 2). The presence of 3Å molecular sieves in the reaction environment positively affected the conversion (entry 3 vs 2), possibly accelerating the imine formation step (see Scheme 1). Varying the reaction stoichiometry was found to remarkably affect the conversion (entries 4–10), the best result (76%) being obtained with 4:1 alcohol/amine ratio (entry 5). The addition of a Brønsted acid to the reaction environment – expected to accelerate the imine formation step – did not significantly impact on the conversion (entries 11, 12). Next, the amination of **4b** was carried out in several different aprotic solvents (entries 13–17), but lower conversions than in toluene were observed. To conclude the optimization, the reaction temperature was increased from 130 to 150 °C (entry 18 vs 5), which allowed to increase the conversion to 89%.

With the optimized conditions in hand, a number of secondary alcohols were screened in the reaction with *p*-anisidine (**3a**). To our delight, good to excellent yields were achieved in several cases (Table 2), thus demonstrating the synthetic value of our **1i**-based catalytic methodology.

A careful examination of the data allows to recognize the following general trends:

1) Yields roughly decreased with the increasing steric bulk surrounding the OH group, that is, along the series **4b** → **4c** → **4l** → **4m** → **4n** for benzylic alcohols (Table 2, entries 1, 2, 11–13), **4d** → **4e** → **4g** → **4h** → **4f** for aliphatic alcohols (entries 3–7), and **4i** → **4k** → **4j** for allylic alcohols (entries 8–10).

2) Extending the reaction time to 72 hours allowed to significantly improve the yield of the reactions, which were incomplete after 24 hours (Table 2, entries 2, 5, 7–9, 11–13). Hence, it is evident that the catalytic complex undergoes no or slow decomposition under the reaction conditions, and thus remains active for a long time.

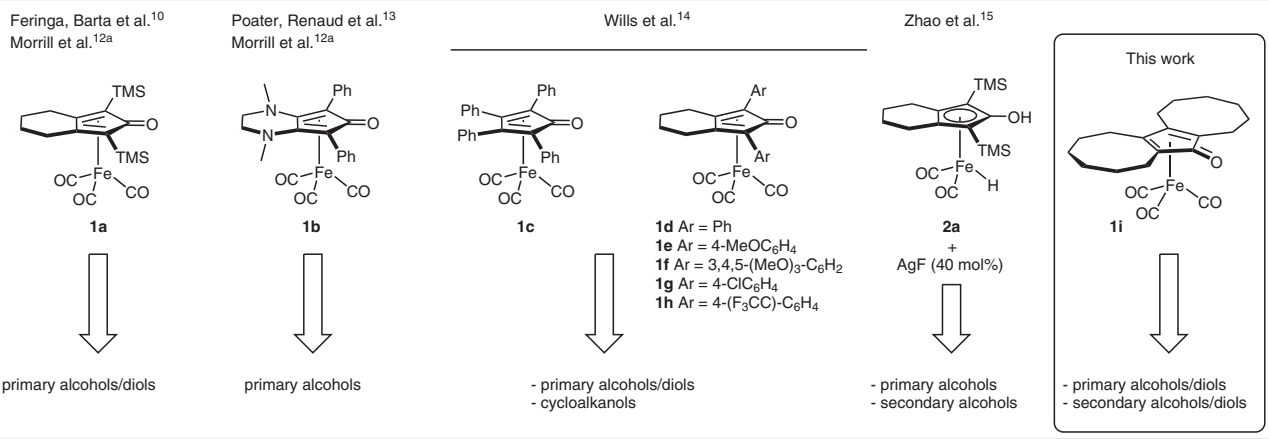
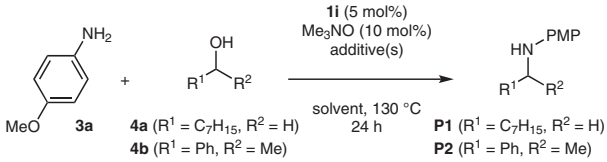


Figure 1 Previous applications of (cyclopentadienone)iron complexes in HB amination

Table 1 HB Amination of Alcohols with *p*-Anisidine Promoted by Precatalyst **1i** – Optimization[a]



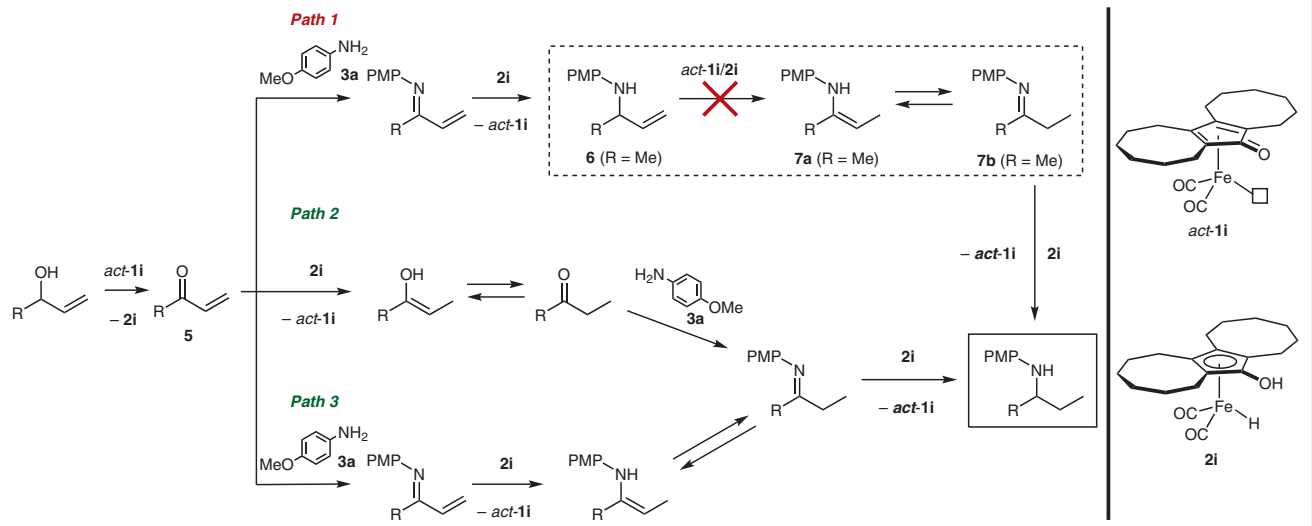
Entry	Solvent	Alcohol	Alcohol/**3a**	Additive(s)	Conv. (%)[b]
1	toluene	**4a**	1.5:1	–	95[c]
2	toluene	**4b**	1.5:1	–	17
3	toluene	**4b**	1.5:1	3Å MS (400 mg)	48
4	toluene	**4b**	3:1	3Å MS (400 mg)	42
5	toluene	**4b**	4:1	3Å MS (400 mg)	76
6	toluene	**4b**	6:1	3Å MS (400 mg)	46
7	toluene	**4b**	10:1	3Å MS (400 mg)	0
8	toluene	**4b**	1:1	3Å MS (400 mg)	58
9	toluene	**4b**	1:1.5	3Å MS (400 mg)	35
10	toluene	**4b**	1:4	3Å MS (400 mg)	34
11	toluene	**4b**	4:1	3Å MS (400 mg) TFA (1 mol%)	53
12	toluene	**4b**	4:1	3Å MS (400 mg) AcOH (1 mol%)	64
13	CPME[d]	**4b**	4:1	3Å MS (400 mg)	24
14	1,4-dioxane	**4b**	4:1	3Å MS (400 mg)	22
15	DMF	**4b**	4:1	3Å MS (400 mg)	0
16	DME	**4b**	4:1	3Å MS (400 mg)	19
17	DCE	**4b**	4:1	3Å MS (400 mg)	5
18[e]	toluene	**4b**	4:1	3Å MS (400 mg)	89

[a] Reaction conditions: **3a**/**1i**/Me_3NO = 100:5:10. Catalyst activation: solvent, Me_3NO, r.t., 15 min, $C_{0,cat.}$ = 0.1 M; HB amination: solvent, $C_{0,sub.}$ = 0.25 M (0.5 mmol), 130 °C, 24 h.
[b] Determined by ^1H NMR analysis of the reaction crude.
[c] Isolated yield.
[d] CPME: Cyclopentyl methyl ether.
[e] Reaction run at 150 °C.

The latter finding is in agreement with the kinetic studies previously reported by our group for the catalytic hydrogenation of ketones, showing that **1i** retains its activity for a longer period than **1a**.[16d] Such remarkable stability is possibly due to the presence of bulky cyclooctane rings fused to the cyclopentadienone and may explain the higher observed activity of complex **1i** compared to other members of its family.[16b,c] Consistent with this interpretation, when the HB amination of cyclohexanol **4h** (Table 2, entry 7, pre-catalyst **1i**) was repeated using pre-catalyst **1a** under the same conditions, a much lower yield of product **P8** was obtained (32% at 24 h and 63% at 72 h).

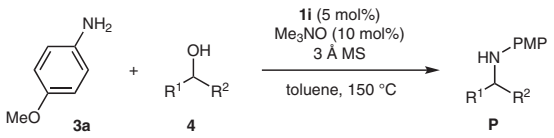
The **1i**-catalyzed synthesis of amine **P7** was uneventfully repeated on gram-scale (Table 2, entry 6). Interestingly, the amination of allylic alcohols took place along with partial (entry 10) or complete (entries 8 and 9) reduction of the C=C bond. This outcome is due to the presence of excess alcohol which acts as terminal reducing agent. After the initial dehydrogenation step, generating the α,β-unsaturated ketone **5**, three possible pathways may be conceived (Scheme 2). Path 1, involving two C=N 1,2-reduction steps, was ruled out on the basis of a control experiment showing that allylic amine **6**, prepared according to known procedures,[18] is unreactive at 150 °C in the presence of catalyst **1i** and alcohol **4i** (see the Supporting Information). Path 2 and Path 3, involving a 1,4-reduction[19] followed by a C=N 1,2-reduction, are both viable and probably operating.

We screened also other functionalized alcohols and achieved a good result with alcohol **4o**, possessing a tertiary amino group, which gave the corresponding secondary amine **P15** in good yields (Table 2, entry 14). α-Hydroxyesters (e.g., methyl lactate, methyl mandelate, ethyl malate) were also tested but failed to afford the desired amination products.



Scheme 2 Possible pathways for the amination of allylic alcohols with concomitant C=C bond reduction

Table 2 Screening of Alcohol Substrates in the HB Amination with *p*-Anisidine Promoted by Precatalyst **1i**[a]



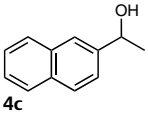
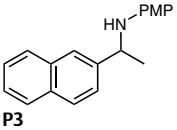
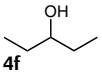
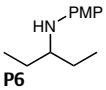
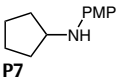
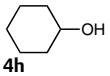
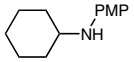
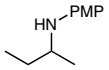
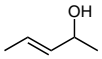
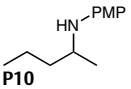
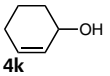
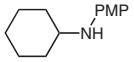
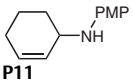
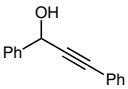
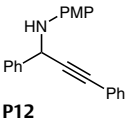
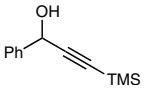
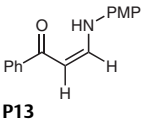
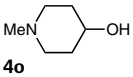
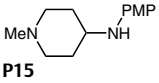
Entry	Alcohol	Product	Yield (%)[b]	
			t = 24 h	*t* = 72 h
1	 **4b**	 **P2**	87	95
2	 **4c**	 **P3**	14	64
3	 **4d**	 **P4**	95	96
4	 **4e**	 **P5**	99	99
5	 **4f**	 **P6**	19	53
6	 **4g**	 **P7**	99 (99)[c]	99

Table 2 (continued)

Entry	Alcohol	Product		Yield (%)[b]	
				t = 24 h	*t* = 72 h
7	 **4h**	 **P8**		89	95
8	 **4i**	 **P9**		10	31
9	 **4j**	 **P10**		6	28
10	 **4k**	 **P8**	 **P11**	40 (1:1)[d]	49 (1:1)[d]
11	 **4l**	 **P12**		16	27
12	 **4m**	 **P13**		6	29
13	 **4n**	 **P14**		10	30
14	 **4o**	 **P15**		84	82

[a] Reaction conditions: alcohol/**3a**/**1i**/Me_3NO = 400:100:5:10. Catalyst activation: toluene, Me_3NO, r.t., 15 min, $C_{0,cat.}$ = 0.1 M; HB amination: toluene, $C_{0,sub.}$ = 0.25 M(0.5 mmol), 150 °C.
[b] Isolated yield after column chromatography.
[c] Yield of gram-scale experiment.
[d] Ratio **P8**:**P11**.

Next, a series of different amine nucleophiles were screened in the HB amination of 1-phenylethanol **4b** (Table 3).

Analogously to what we observed in the alcohol screening (Table 2), increasing the steric bulk of the nucleophile decreased the yields: *N*-methylbenzylamine (**3f**) gave lower yields than benzylamine (**3e**) (Table 3, entry 6 vs 5) and 2,4-dimethoxyaniline (**3b**) was found less reactive than *p*-anisidine (**3a**), yet giving useful yields (entry 2 vs 1). Aliphatic **3c**,**d** and benzylic amines **3e**,**f** showed lower reactivity than anilines **3a**,**b** (entries 3–6 vs 1, 2), although also in this case extended reaction times (72 vs 24 h) allowed to remarkably improve the yields.

(Cyclopentadienone)iron complexes have been reported to promote the reaction of diols with primary amines to yield saturated N-heterocycles,[10b,c,14a] but so far the scope was limited to substrates bearing primary alcohol groups.[20] Thus, we tested pre-catalyst **1i** in the cyclization of 2,5-hexanediol (**8**) with several primary amines (Table 4).

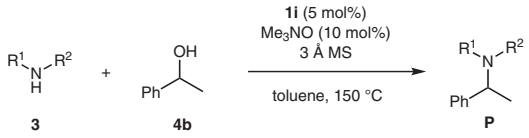
Delightfully, 2,5-dimethylpyrrolidine products were obtained in good yields from aniline **3a** and the benzylic amines **3e**, **3g**, and **3h**; while in the former case a long reaction time positively affected the yield (Table 4, entry 1), with benzylic amines a reaction time of 24 hours led to similar (entry 3) or even higher yields (entries 2 and 4) than an extended one (72 h). 2,5-Dimethylpyrrolidines **P21**–**P24** were obtained as *cis*/*trans*-diastereoisomer mixtures, as determined by ^1H NMR analysis,[21] and the *cis*-product was the most abundant in all cases.

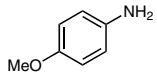
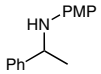
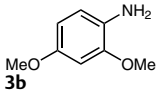
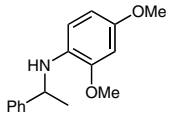
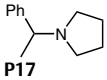
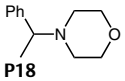
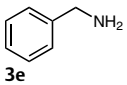
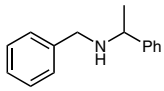
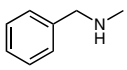
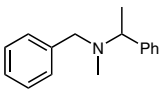
In conclusion, in this paper the scope of the HB amination of alcohols promoted by (cyclopentadienone)iron-complexes has been remarkably expanded, thanks to the

high activity of pre-catalyst **1i**.[16b–d] In the presence of 5 mol% **1i** and Me_3NO, a range of cyclic and acyclic secondary alcohols were aminated in good yields without need of expensive co-catalysts such AgF.[15] Notably, this reaction has been extended for the first time to a secondary diol [2,5-hexanediol (**8**)], which afforded the corresponding 2,5-dimethylpyrrolidine products in good yields. We believe that these achievements represent an important step towards the replacement of precious metal catalysts with cheap and environmentally friendly base metal complexes in a very important and atom-economic transformation such as the HB amination of alcohols.

All reactions were carried out in flame-dried glassware with magnetic stirring under inert atmosphere (N_2 or argon), unless otherwise stated. The reactions were monitored by analytical TLC using silica gel 60 F254 pre-coated glass plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with an alkaline $KMnO_4$ solution or with a ninhydrin solution. Flash column chromatography was performed using silica gel (60 Å, particle size 40–64 μm) as stationary phase, following the procedure by Still and co-workers.[22] ^1H NMR spectra were recorded on a spectrometer operating at 400.13 MHz. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to TMS as the internal standard ($CDCl_3$, δ = 7.26; CD_2Cl_2 δ = 5.32). Standard abbreviations are used to describe spin multiplicity. ^{13}C NMR spectra were recorded on a 400 MHz spectrometer operating at 100 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$ δ = 77.16; CD_2Cl_2 δ = 54.00). The coupling constant values are given in hertz (Hz). ^{19}F NMR spectra were recorded on a 300 MHz spectrometer operating at 282 MHz, with complete proton decoupling. Fluorine chemical shifts are reported in ppm (δ) relative to external $CFCl_3$ at 0 ppm (positive values downfield). IR spectra were recorded on a standard FT/IR spectrophotometer. High-resolution mass

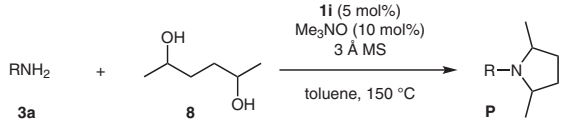
Table 3 Screening of Amine Nucleophiles in the HB Amination of 1-Phenylethanol Promoted by Precatalyst **1i**[a]

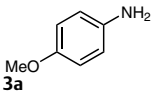
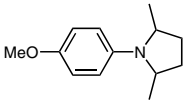
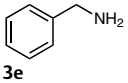
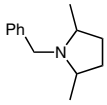
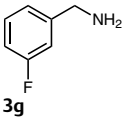
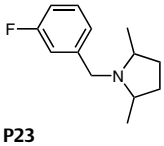
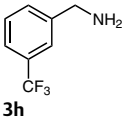
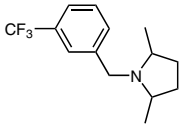


Entry	Amine	Product	Yield (%)[b]	
			t = 24 h	*t* = 72 h
1	 **3a**	 **P2**	87	95
2	 **3b**	 **P16**	51	71
3	 **3c**	 **P17**	45	75
4	 **3d**	 **P18**	15	54
5	 **3e**	 **P19**	22	78
6	 **3f**	 **P20**	20	43

[a] Reaction conditions: **4b**/amine/**1i**/Me_3NO = 400:100:5:10. Catalyst activation: toluene, Me_3NO, r.t., 15 min, $C_{0,cat.}$ = 0.1 M; HB amination: toluene, $C_{0,sub.}$ = 0.25 M (0.5 mmol), 150 °C.
[b] Isolated yield after column chromatography.

Table 4 Amination of Primary Amines with 2,5-Hexanediol Promoted by Precatalyst **1i**[a]



Entry	Amine	Product	Yield (%)[b]	
			t = 24 h	*t* = 72 h
1	 **3a**	 **P21**	25 (57:43)[c]	71 (58:42)[c]
2	 **3e**	 **P22**	66 (79:21)[c]	43 (79:21)[c]
3	 **3g**	 **P23**	55 (76:24)[c]	60 (79:21)[c]
4	 **3h**	 **P24**	72 (73:27)[c]	66 (76:24)[c]

[a] Reaction conditions: **8**/amine/**1i**/Me_3NO = 400:100:5:10. Catalyst activation: toluene, Me_3NO, r.t., 15 min, $C_{0,cat.}$ = 0.1 M; HB amination: toluene, $C_{0,sub.}$ = 0.25 M (0.5 mmol), 150 °C.
[b] Isolated yield after column chromatography.
[c] *cis*/*trans* Ratio determined by ^1H NMR of the reaction crude.[21]

spectra (HRMS) were performed on a ESI QTof SYNAPT G2 Si mass spectrometer (Waters), available at the UNITECH-COSPECT laboratories (Università degli Studi di Milano).

Toluene was distilled from Na/benzophenone before use, and transferred under N_2. Alcohols and amines used in the substrate screening were purchased from commercial suppliers (TCI Chemicals, ACROS, Sigma Aldrich). The liquid amines were distilled before use, whereas the other reagents were used as received. Pre-catalyst **1i** was prepared as previously described by our group.[16d] 3Å MS were dried under high vacuum at 200 °C and then stored in an oven at 110 °C.

HB Amination of Alcohols; General Procedure

Toluene (0.25 mL) was added to a mixture of pre-catalyst **1i** (9.6 mg, 0.025 mmol, 0.05 equiv) and Me_3NO (3.8 mg, 0.050 mmol, 0.010 equiv) under argon in a Schlenk vessel fitted with a Teflon screw cap. The resulting solution, which gradually turned from yellow to dark red, was stirred for 20 minutes at r.t. The amine substrate **3** (0.5 mmol, 1 equiv) was added, followed by 3Å MS (beads, 400 mg), the respective alcohol (2.0 mmol, 4.0 equiv), and additional toluene (1.75 mL). The reaction vessel was sealed and stirred in a pre-heated oil bath at 150 °C for 24 h or 72 h. After cooling down, the mixture was filtered through Celite (rinsing several times with EtOAc), and then the solvent was removed with a rotavapor. The product was purified by flash chromatography.

4-*N*-Octylamino-1-methoxybenzene (P1)[10c]

Reaction time: 24 h; yield: 111.8 mg (95%); yellow oil; R_f = 0.24 (95:5 hexane/EtOAc).

^1H NMR (400 MHz, $CDCl_3$): δ = 6.78 (d, *J* = 8.9 Hz, 2 H), 6.58 (d, *J* = 8.9 Hz, 2 H), 3.75 (s, 3 H), 3.06 (t, *J* = 7.1 Hz, 2 H), 1.62–1.56 (m, 2 H), 1.41–1.26 (m, 10 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

4-Methoxy-*N*-(1-phenylethyl)aniline (P2)[23]

Reaction time: 72 h; yield: 108.0 mg (95%); yellow oil; R_f = 0.23 (98:2 hexane/EtOAc + 0.1% Et_3N).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.34 (m, 4 H), 7.28–7.24 (m, 1 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 4.45 (q, *J* = 6.8 Hz, 1 H), 3.73 (s, 3 H), 1.53 (d, *J* = 6.8 Hz, 3 H).

4-Methoxy-*N*-[1-(naphthalen-2-yl)ethyl]aniline (P3)[24]

Reaction time: 72 h; yield: 89.0 mg (64%); pale yellow solid; mp 97–99 °C (Lit.[25] mp 98–100 °C); R_f = 0.28 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.79 (m, 4 H), 7.52 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.48–7.41 (m, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 6.55 (d, *J* = 9.0 Hz, 2 H), 4.58 (q, *J* = 6.8 Hz, 1 H), 3.68 (s, 3 H), 1.60 (d, *J* = 6.8 Hz, 3 H).

4-(Isopropylamino)anisole (P4)[10c]

Reaction time: 24 h; yield: 79.0 mg (95%); yellow oil; R_f = 0.30 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.8 Hz, 2 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H), 3.57 (m, 1 H), 1.20 (d, *J* = 6.6 Hz, 6 H).

4-Methoxy-*N*-(octan-2-yl)aniline (P5)[26]

Reaction time: 24 h; yield: 117.0 mg (99%); yellow oil; R_f = 0.28 (99:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 9.0 Hz, 2 H), 6.62–6.59 (m, 2 H), 3.75 (s, 3 H), 3.36 (q, *J* = 6.0 Hz, 1 H), 1.43–1.27 (m, 10 H), 1.16 (d, *J* = 6.0 Hz, 3 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

4-Methoxy-*N*-(3-pentyl)aniline (P6)[27]

Reaction time: 72 h; yield: 51.2 mg (53%); light orange oil; R_f = 0.26 (99:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83–6.75 (d, *J* = 8.9 Hz, 2 H), 6.61–6.55 (d, *J* = 8.9 Hz, 2 H), 3.77 (s, 3 H), 3.17 (pent, *J* = 5.9 Hz, 1 H), 1.61–1.42 (m, 4 H), 0.95 (t, *J* = 7.4 Hz, 6 H).

***N*-Cyclopentyl-4-methoxyaniline (P7)**[28]

Reaction time: 24 h; yield: 94.7 mg (99%). Gram-scale experiment; yield: 1.51 g (99%) using 0.995 g (8.0 mmol) of *p*-anisidine; pale yellow oil; R_f = 0.30 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.9 Hz, 2 H), 6.60 (d, *J* = 8.9 Hz, 2 H), 3.77 (s, 3 H), 3.75 (m, 1 H), 2.02 (m, 2 H), 1.75 (m, 2 H), 1.63 (m, 2 H), 1.54–1.40 (m, 2 H).

***N*-Cyclohexyl-4-methoxyaniline (P8)**[10c]

Reaction time: 72 h; yield: 97.5 mg (95%); white solid; mp 43–44 °C (Lit.[28] mp 45–46 °C); R_f = 0.42 (9:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 8.8 Hz, 2 H), 6.59 (d, *J* = 8.8 Hz, 2 H), 3.74 (s, 3 H), 3.20–3.14 (m, 1 H), 2.08–2.02 (m, 2 H), 1.79–1.76 (m, 2 H), 1.67–1.61 (m, 1 H), 1.40–1.11 (m, 5 H).

***N*-(*sec*-Butyl)-4-methoxyaniline (P9)**[29]

Reaction time: 72 h; yield: 27.8 mg (31%); light brown oil; R_f = 0.32 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.9 Hz, 2 H), 6.64 (d, *J* = 8.9 Hz, 2 H), 3.77 (s, 3 H), 3.38–3.28 (m, 1 H), 1.70–1.57 (m, 1 H), 1.53–1.41 (m, 1 H), 1.18 (d, *J* = 6.3 Hz, 3 H), 0.97 (t, *J* = 7.4 Hz, 3 H).

4-Methoxy-*N*-(pentan-2-yl)aniline (P10)[28]

Reaction time: 72 h; yield: 27.1 mg (28%); yellow oil; R_f = 0.28 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (d, *J* = 8.9 Hz, 2 H), 6.61 (d, *J* = 8.9 Hz, 2 H), 3.77 (s, 3 H), 3.41 (m, 1 H), 1.63–1.53 (m, 1 H), 1.48–1.37 (m, 3 H), 1.18 (d, *J* = 6.3 Hz, 3 H), 0.95 (t, *J* = 7.1 Hz, 3 H).

***N*-(Cyclohex-2-en-1-yl)-4-methoxyaniline (P11)**[30]

Reaction time: 72 h; yield: 25.4 mg (25%); yellow oil; R_f = 0.27 (98:2 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (d, *J* = 8.9 Hz, 2 H), 6.61 (d, *J* = 8.8 Hz, 2 H), 5.86–5.74 (m, 2 H), 3.92 (br s, 1 H), 3.77 (s, 3 H), 2.11–2.03 (m, 2 H), 1.94–1.87 (m, 1 H), 1.76–1.55 (m, 3 H).

***N*-(1,3-Diphenylprop-2-yn-1-yl)-4-methoxyaniline (P12)**[31]

Reaction time: 72 h; yield: 42.3 mg (27%); yellow oil; R_f = 0.20 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.65 (m, 2 H), 7.42–7.38 (m, 4 H), 7.36–7.27 (m, 4 H), 6.82–6.75 (m, 4 H), 5.41 (s, 1 H), 3.88 (br s, 1 H), 3.76 (s, 3 H).

(*Z*)-3-(4-Methoxyphenylamino)-1-phenylprop-2-en-1-one (P13)[32]

Reaction time: 72 h; yield: 34.5 mg (29%); colorless oil; R_f = 0.26 (98:2 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.12 (d, *J* = 12.2 Hz, 1 H), 7.90–7.82 (d, *J* = 6.5 Hz, 2 H), 7.51–7.42 (m, 4 H), 6.99 (d, *J* = 8.9 Hz, 2 H), 6.83 (d, *J* = 8.9 Hz, 2 H), 5.91 (d, *J* = 7.7 Hz, 1 H), 3.74 (s, 3 H).

***N*-Benzhydryl-4-methoxyaniline (P14)**[33]

Reaction time: 72 h: yield 43.4 mg (30%); yellow solid; mp 78–80 °C (Lit.[34] mp 81 °C); R_f = 0.29 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.39–7.30 (m, 8 H), 7.27–7.23 (m, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 5.44 (s, 1 H), 4.12 (br s, 1 H), 3.67 (s, 3 H).

***N*-(4-Methoxyphenyl)-1-methylpiperidin-4-amine (P15)**[35]

Reaction time: 24 h; yield: 92.5 mg (84%); yellow oil; R_f = 0.21 (9:1 DCM/MeOH + 0.5% Et_3N).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 8.9 Hz, 2 H), 6.58 (d, *J* = 8.9 Hz, 2 H), 3.74 (s, 3 H), 3.24–3.17 (m, 1 H), 2.85–2.82 (m, 2 H), 2.31 (s, 3 H), 2.17–2.03 (m, 4 H), 1.53–1.44 (m, 2 H).

2,4-Dimethoxy-*N*-(1-phenylethyl)aniline (P16)[36]

Reaction time: 72 h; yield: 91.4 mg (71%); white solid; mp 77–78 °C (Lit.[36] mp 78 °C); R_f = 0.20 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.29 (m, 4 H), 7.23–7.19 (m, 1 H), 6.44 (t, *J* = 1.4 Hz, 1 H), 6.24–6.23 (m, 2 H), 4.40 (q, *J* = 6.7 Hz, 1 H), 4.29 (br s, 1 H), 3.86 (s, 3 H), 3.69 (s, 3 H), 1.53 (d, *J* = 6.7 Hz, 3 H).

1-(1-Phenylethyl)pyrrolidine (P17)[37]

Reaction time: 72 h; yield: 65.7 mg (75%); colorless oil; R_f = 0.22 (8:2 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 5 H), 3.21 (q, *J* = 6.6 Hz, 1 H), 2.58 (m, 2 H), 2.44–2.34 (m, 2 H), 1.82–1.75 (m, 4 H), 1.43 (d, *J* = 6.6 Hz, 3 H).

4-(1-Phenylethyl)morpholine (P18)[38]

Reaction time: 72 h; yield: 52.0 mg (54%); colorless oil; R_f = 0.14 (8:2 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 4 H), 7.30–7.23 (m, 1 H), 3.71 (t, *J* = 4.7 Hz, 4 H), 3.32 (q, *J* = 6.7 Hz, 1 H), 2.56–2.47 (m, 2 H), 2.42–2.32 (m, 2 H), 1.38 (d, *J* = 6.7 Hz, 3 H).

***N*-Benzyl-1-phenylethylamine (P19)**[39]

Reaction time: 72 h; yield 82.4 mg (78%); yellow oil; R_f = 0.21 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 10 H), 3.82 (q, *J* = 6.8 Hz, 1 H), 3.67 (d, J = 13.1 Hz, 1 H), 3.60 (d, J = 13.1 Hz, 1 H), 1.37 (d, *J* = 6.4 Hz, 3 H).

_N_-Benzyl-_N_-methyl-1-phenylethylamine (P20)[40]

Reaction time: 72 h; yield: 48.4 mg (43%); yellow oil; R_f = 0.35 (95:5 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.20 (m, 10 H), 3.67 (q, *J* = 6.8 Hz, 1 H), 3.61 (d, *J* = 13.3 Hz, 1 H), 3.33 (d, *J* = 13.3 Hz, 1 H), 2.16 (s, 3 H), 1.45 (d, *J* = 6.8 Hz, 3 H).

1-(4-Methoxyphenyl)-2,5-dimethylpyrrolidine (P21, mixture of diastereomers)[21]

Reaction time: 72 h; yield: 72.9 mg (71%); yellow oil; R_f = 0.28 (99:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.86 (m, 2 H), 6.65 (d, *J* = 9.1 Hz, 2 H, *cis*-isomer), 6.58 (d, *J* = 9.1 Hz, 2 H, *trans*-isomer), 4.01–3.93 (m, 2 H, *trans*-isomer), 3.78 (s, 3 H), 3.71–3.62 (m, 2 H, *cis*-isomer), 2.37–2.15 (m, 2 H, *trans*-isomer), 2.07–1.99 (m, 2 H, *cis*-isomer), 1.77–1.67 (m, 2 H, *cis*-isomer), 1.67–1.59 (m, 2 H, *trans*-isomer), 1.27 (d, *J* = 6.2 Hz, 6 H, *cis*-isomer), 1.09 (d, *J* = 6.1 Hz, 6 H, *trans*-isomer).

1-Benzyl-2,5-dimethylpyrrolidine (P22, mixture of diastereomers)[21]

Reaction time: 24 h; yield: 62.5 mg (66%); yellow oil; R_f = 0.50 (95:5 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 4 H), 7.24–7.20 (m, 1 H), 3.83 (d, *J* = 13.6 Hz, 1 H, *trans*-isomer), 3.74 (s, 2 H, *cis*-isomer), 3.52 (d, *J* = 13.6 Hz, 1 H, *trans*-isomer), 3.04–3.00 (m, 2 H, *trans*-isomer), 2.60–2.55 (m, 2 H, *cis*-isomer), 2.05–1.97 (m, 2 H, *trans*-isomer), 1.81–1.75 (m, 2 H, *cis*-isomer), 1.40–1.34 (m, 2 H, *cis*- and *trans*-isomer), 1.05 (d, *J* = 6.0 Hz, 6 H, *cis*-isomer), 0.97 (d, *J* = 6.0 Hz, 6 H, *trans*-isomer).

1-(3-Fluorobenzyl)-2,5-dimethylpyrrolidine (P23, mixture of diastereomers)

Reaction time: 72 h; yield: 62.2 mg (60%); light yellow oil; R_f = 0.21 (98:2 DCM/MeOH).

IR (film): 2962.13, 2927.41, 2870.52, 2802.06, 1616.06, 1590.99, 1485.88, 1450.21, 1373.07, 1350.89, 1328.71, 1254.47, 1203.36, 1130.08, 1073.19, 992.20, 944.95, 926.63, 871.67, 783.92, 745.35, 686.53 cm^{-1}.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.27–7.22 (m, 1 H), 7.15–7.08 (m, 2 H), 6.92–6.87 (m, 1 H), 3.80 (d, *J* = 14.4 Hz, 1 H, *trans*-isomer), 3.67 (s, 2 H, *cis*-isomer), 3.56 (d, *J* = 14.4 Hz, 1 H, *trans*-isomer), 3.02–3.00 (m, 2 H, *trans*-isomer), 2.63–2.57 (m, 2 H, *cis*-isomer), 2.02–1.97 (m, 2 H, *trans*-isomer), 1.83–1.78 (m, 2 H, *cis*-isomer), 1.38–1.35 (m, 2 H), 0.98 (d, *J* = 6.4 Hz, 6 H, *cis*-isomer), 0.95 (d, *J* = 6.4 Hz, 6 H, *trans*-isomer).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 163.6 (d, $J_{C,F}$ = 242.4 Hz, *trans*-isomer), 163.4 (d, $J_{C,F}$ = 242.5 Hz, *cis*-isomer), 144.8 (d, $J_{C,F}$ = 9.2 Hz), 130.0 (d, $J_{C,F}$ = 9 Hz, *trans*-isomer), 129.8 (d, $J_{C,F}$ = 8.3 Hz, *cis*-isomer), 124.8 (d, $J_{C,F}$ = 2.6 Hz, *cis*-isomer), 124.5 (d, $J_{C,F}$ = 2.6 Hz, *trans*-isomer), 116.0 (d, *J* = 21.1 Hz, *cis*-isomer), 115.6 (d, *J* = 21.2 Hz, *trans*-isomer), 113.7 (d, $J_{C,F}$ = 21.1 Hz, *trans*-isomer), 113.7 (d, *J* = 21.1 Hz, *cis*-isomer), 61.6 (*cis*-isomer), 56.4 (*cis*-isomer), 55.6 (*trans*-isomer), 51.6 (*trans*-isomer), 32.1 (*cis*-isomer), 31.6 (*trans*-isomer), 21.4 (*cis*-isomer), 17.5 (*trans*-isomer).

^{19}F NMR (282 MHz, CD_2Cl_2): δ = –115.15.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{19}FN$: 208.1502; found: 208.1501.

2,5-Dimethyl-1-(3-(trifluoromethyl)benzyl)pyrrolidine (P24, mixture of diastereomers)

Reaction time: 24 h; yield: 92.6 mg (72%); yellow oil; R_f = 0.24 (97:3 hexane/EtOAc 85:15 + 0.1% Et_3N).

IR (film): 2964.05, 2928.38, 2871.49, 2803.03, 2611.14, 1676.80, 1615.09, 1597.73, 1491.67, 1451.17, 1374.03, 1329.68, 1256.40, 1199.51, 1163.83, 1126.22, 1091.51, 1073.19, 948.81, 920.84, 889.99, 799.35, 750.17, 702.93, 660.50 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 1 H, *trans*-isomer), 7.59 (s, 1 H, *cis*-isomer), 7.56 (d, *J* = 7.6 Hz, 1 H, *trans*-isomer), 7.52 (d, *J* = 7.8 Hz, 1 H, *cis*-isomer), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.39 (t, *J* = 7.6 Hz, 1 H), 3.85 (d, *J* = 14.4 Hz, 1 H, *trans*-isomer), 3.75 (s, 2 H, *cis*-isomer), 3.60 (d, *J* = 14.4 Hz, 1 H, *trans*-isomer), 3.04–3.00 (m, 2 H, *trans*-isomer), 2.61–2.56 (m, 2 H, *cis*-isomer), 2.04–1.98 (m, 2 H, *trans*-isomer), 1.85–1.79 (m, 2 H, *cis*-isomer), 1.43–1.35 (m, 2 H), 1.00 (d, *J* = 6.0 Hz, 6 H, *cis*-isomer), 0.96 (d, *J* = 6.4 Hz, 6 H, *trans*-isomer).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2 (*trans*-isomer), 141.9 (*cis*-isomer), 132.2 (q, $J_{C,F}$ = 1.5 Hz, *cis*-isomer), 131.8 (q, $J_{C,F}$ = 1.5 Hz, *trans*-isomer), 130.5 (q, $J_{C,F}$ = 31.7 Hz, *trans*-isomer), 130.4 (q, $J_{C,F}$ = 31.7 Hz, *cis*-isomer), 128.5 (*trans*-isomer), 128.4 (*cis*-isomer), 125.5 (q, $J_{C,F}$ = 4 Hz, *cis*-isomer), 125.1 (q, $J_{C,F}$ = 4 Hz, *trans*-isomer), 124.5 (d, $J_{C,F}$ = 270.5 Hz, *trans*-isomer), 124.5 (d, $J_{C,F}$ = 270.4 Hz, *cis*-isomer), 123.5 (q, $J_{C,F}$ = 4 Hz, *cis*- and *trans*-isomer), 60.9 (*cis*-isomer), 55.9 (*cis*-isomer), 55.1 (*trans*-isomer), 51.4 (*trans*-isomer), 31.5 (*cis*-isomer), 31.1 (*trans*-isomer), 21.0 (*cis*-isomer), 17.3 (*trans*-isomer).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.46.

HRMS (ESI+): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}F_3N$: 258.1470; found: 258.1472.

Funding Information

X. Bai thanks the China Scholarship Council for a Ph.D. fellowship (CSC No. 201608410107). L. Pignataro thanks 'Piano di Sostegno alla Ricerca 2015–2017' (Dipartimento di Chimica, Università degli Studi di Milano) and PRIN 2017 – Progetto 20174SYJAF (MIUR) for financial support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690101.

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