Addition of Trialkylalanes to Imines under Zirconium Catalysis

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Received 15 February 2005

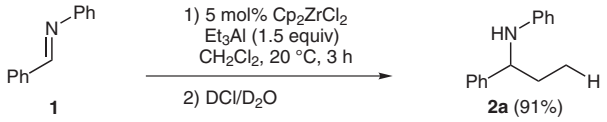
Abstract: Trialkylalanes, which are inert toward imines, undergo addition to them in the presence of a catalytic amount of dichlorodicyclopentadienylzirconium(IV) (Cp_2ZrCl_2). The reaction tolerates the presence of several functional groups in the starting imine such as halo, amide, nitrile, and hydroxy groups. A possible reaction pathway is proposed involving metallacyclic intermediates.

Key words: zirconium, catalysis, trialkylalanes, amine synthesis, imines

Recently, we[1] and others[2] reported that ketimines can undergo zirconium-catalyzed addition with ethylmagnesium reagents. This reaction has been demonstrated to be similar to the zirconium-catalyzed ethylmagnesation of alkenes[3] from both a mechanistic and synthetic point of view. In fact, as in the case of alkenes, zirconacycles have also been shown to be intermediates in the reaction with imines.[1a] The same synthetic limitation has been encountered in both reactions, i.e. alkylmagnesium halides higher than EtMgX appeared to be unreactive.[4]

Zirconium-catalyzed carboalumination of alkynes[5,6] and alkenes[5,7] has been shown to smoothly occur through multiple mechanistic pathways, depending upon the reaction conditions and substrates. Furthermore, in the absence of additives, trialkylalanes proved to be inert toward imines.[8] Based on these literature data, we focused on the possibility of performing zirconium-catalyzed addition of trialkylalanes to imines. We thought that such reactions could broaden the scope of the alkyl groups added while offering mild reaction conditions and selectivity. The zirconium-catalyzed reactions might then be a prerequisite for developing a new catalytic asymmetric synthesis of amines.[9]

At the outset of our study, we examined the reaction of triethylalane (Et_3Al) with *N*-phenylbenzaldimine (**1**). The reactions were carried out in hexane or chlorinated hydrocarbon solvents (CH_2Cl_2, DCE) in the presence of 5–20 mol% of Cp_2ZrCl_2 at 0–20 °C. In all cases, amine **2a** was obtained after hydrolysis in good to excellent yields. In contrast, in the absence of the zirconium catalyst, no alkylation occurred after a long reaction period (24 h). A particularly clean alkylation reaction took place in the chlorinated solvents. Thus, treatment of imine **1** with Et_3Al (1.5 equiv) and Cp_2ZrCl_2 (5 mol%) in dichloromethane at 20 °C for three hours produced, after hydrolysis, amine **2a** in 91% isolated yield (Scheme 1).



Scheme 1

In contrast to the catalytic ethylalumination of alkenes,[7] no deuterium incorporation at the β-carbon atom was observed after deuterolysis with deuterium chloride–deuterium oxide (DCl–D_2O), irrespective of the conditions employed. This result indicates a different mechanism occurring with imines than those postulated with alkenes (see below).

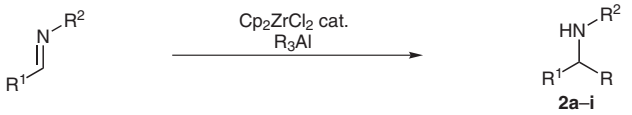
Various imines underwent the zirconium-catalyzed addition with Et_3Al.[10] The results are shown in Table 1.

The reactions proceeded smoothly with aromatic imines bearing *N*-aryl or *N*-alkyl groups (Table 1, entries 1–4). Interestingly, using a chiral imine, amine **2e** was isolated as a single diastereomer (Table 1, entry 5). To further explore the reaction, we next used a higher trialkylalane and noticed that, in contrast to the ethylmagnesation of imines,[1,2] the alkylalumination reaction is not limited to the use of Et_3Al. Thus, treatment of imine **1** with 1.5 equivalents of tributylalane (*n*-Bu_3Al) in the presence 5 mol% Cp_2ZrCl_2 gave amine **2f** (Table 1, entry 6). Similar to the reaction with Et_3Al, no deuterium incorporation was observed in this reaction after deuterolysis with DCl–D_2O. Compound **2f** was accompanied by the reduction side product, i.e. *N*-benzylaniline (28%). Contrary to the zirconium-catalyzed hydroalumination of alkenes,[5,7] the competing reduction of imine **1** by *n*-Bu_3Al proved to occur without adding Cp_2ZrCl_2. This side reaction could be slightly limited by lowering the reaction temperature to 10 °C (Table 1, entries 7 and 8). When using an imine derived from an aliphatic aldehyde, lower yields of the alkylation products **2h** and **2i** were obtained, probably due to a slower zirconium-mediated alkylalumination reaction with respect to the direct side reduction reaction (Table 1, entries 9 and 10).

The alkylation reactions involving main-group organometallics frequently exhibit poor chemoselectivity. In contrast, the described reaction was found to be compatible with the presence of several groups (Table 2). Thus, halo, amide, nitrile, and hydroxy groups can be present in the substrate and tolerated by the reaction conditions

SYNTHESIS 2005, No. 12, pp 2075–2079
Advanced online publication: 14.07.2005
DOI: 10.1055/s-2005-870028; Art ID: C03905SS

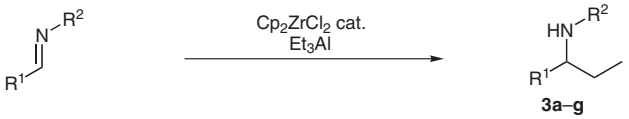
Table 1 Zirconium-Catalyzed Alkylation of Aldimines by Trialkylalanes[a]



Entry	R^1	R^2	R	Time (h)	Product[b] (%)
1	Ph	Ph	Et	3	**2a** (91)
2	Ph	PMP	Et	3	**2b** (86)
3	Ph	Bn	Et	6	**2c** (88)
4	Ph	*n*-Pr	Et	8	**2d** (85)
5[c,d]	Ph	R*	Et	3	**2e** (92)[e]
6	Ph	Ph	*n*-Bu	12	**2f** (67)[f]
7	Ph	Ph	*n*-Bu	24	**2f** (75)[f]
8	Ph	PMP	*n*-Bu	24	**2g** (71)[f]
9	Et	Ph	Et	24	**2h** (32)[f,g]
10	Et	Ph	*n*-Bu	24	**2i** (24)[f,g]

[a] The reactions were run using Cp_2ZrCl_2 (5 mol%) and R_3Al (1.5 equiv) in CH_2Cl_2 at 20 °C, except for entries 7 and 8 (10 °C).
[b] Isolated yields.
[c] R* = (*R*)-2-hydroxy-1-phenylethyl.
[d] 2.5 equivalents of Et_3Al.
[e] de >95% determined by ^1H NMR on the crude product.
[f] Accompanied by the reduction product: entry 6 (28%), entry 7 (20%), entry 8 (22%), entry 9 (65%), entry 10 (73%).
[g] NMR yields.

Table 2 Chemoselective Zirconium-Catalyzed Alkylation of Aldimines by Triethylalane[a]



Entry	R^1	R^2	Product[b] (%)
1	2-BrC_6H_4	Ph	**3a** (89)
2	Ph	2-IC_6H_4	**3b** (88)
3	4-$MeCONHC_6H_4$	Ph	**3c** (88)
4	4-NCC_6H_4	Ph	**3d** (88)
5	3-MeO-4-HOC_6H_3	Ph	**3e** (89)
6	2-pyridyl	Ph	**3f** (95)
7	3-pyridyl	Ph	**3g** (95)

[a] The reactions were run using Cp_2ZrCl_2 (5 mol%) and Et_3Al (1.5 equiv, except entries 3 and 5 where 2.5 equiv were used) in CH_2Cl_2 at 20 °C for 3 hours.
[b] Isolated yields.

(Table 2, entries 1–5). In addition, amines **3f** and **3g** were obtained both in 95% yield starting from 2- and 3-pyridylimines (Table 2, entries 6 and 7). The wide chemoselectivity of the reaction and the mild reaction conditions should be synthetically useful.

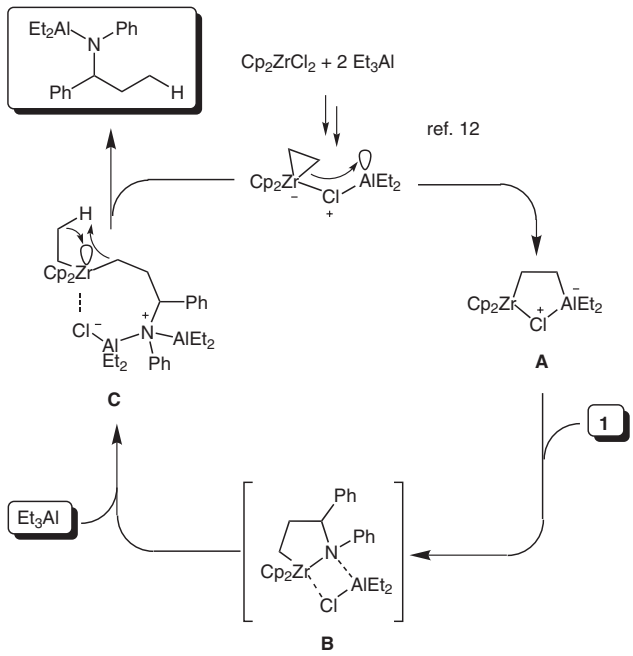
Surprisingly, the protocol employed for the zirconium-catalyzed addition of trialkylalanes (R = Et, *n*-Bu) to imines appeared inefficient when using trimethylalane (Me_3Al). We found that the reaction of **1** with Me_3Al did not give the expected amine in detectable yields with either catalytic or stoichiometric amounts of Cp_2ZrCl_2. The use of hexane or chlorinated solvents, an excess of Me_3Al (>2 equiv), and a temperature increase up to 40 °C had no effect on the reaction. The imine was almost entirely recovered in these cases. Other imines from Table 1 also did not react with Me_3Al.

Methylalumination of alkynes and alkenes with Me_3Al and Cp_2ZrCl_2 has been postulated to proceed by direct C—M bond addition via a four-centered concerted process involving bimetallic polarization (acyclic mechanism).[7] In sharp contrast, zirconium-catalyzed carboalumination of alkynes with higher alanes involves a β-CH activation process and formation of metallacyclic intermediates (cyclic mechanism).[6c]

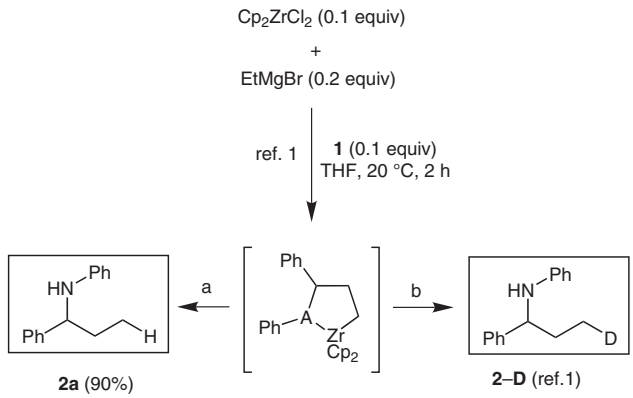
Within this context, the lack of reactivity of Me_3Al toward imines together with the efficient catalyzed addition of higher alanes is mechanistically relevant. It indicates that a direct acyclic addition mechanism does not operate with Me_3Al and, accordingly, such a mechanism should also be ruled out with higher alanes. A cyclic mechanism could be envisaged in the latter case, irrespective of the conditions and solvent.[11] However, if a cyclic mechanism is invariably involved with imines, then no deuterium incorporation in the product might be questionable. To rationalize this, we tentatively assumed a cyclic mechanism in which a second β-CH activation would remove the metal (Zr) from the carbon (Scheme 2).

The catalytic process is initiated by the reaction of Cp_2ZrCl_2 with two equivalents of Et_3Al to afford the bimetallic complex **A**. The formation of **A** from Cp_2ZrCl_2 and two equivalents of Et_3Al has been reported[12] and is postulated to proceed via a bimetallic β-CH activation process.[6c] Subsequent reaction of imine **1** with **A** gives azametallacycle **B**, which would exist as a chlorine-bridged species. In the next step, Et_3Al reacts with **B** to produce the zirconium-ethylated complex **C**. The β-CH activation from **C** completes the catalytic cycle by regenerating **A** and by affording the final product in which no metal atom is attached to the β-carbon of the alkyl group.

In support of the mechanism proposed, we independently prepared a catalytic quantity (0.1 equiv) of the azazirconacyclopentane corresponding to complex **B** in Scheme 2,[1] and subjected it to 0.1 equivalents of diethylaluminum chloride (Et_2AlCl), imine **1** (1 equiv), and Et_3Al (1.5 equiv) (Scheme 3).



Scheme 2



Scheme 3 (a) Et_2AlCl (0.1 equiv), **1** (1 equiv), Et_3Al (1.5 equiv), CH_2Cl_2, 20 °C, 3 h, then DCl–D_2O; (b) DCl–D_2O

The intermediate thus formed was demonstrated to be catalytically active in these conditions, since **2a** was obtained in 90% yield. Significantly, no deuterium incorporation in the product was observed in this case. The above results are in accordance with the mechanistic proposal in Scheme 2. Nevertheless, further studies are clearly desirable to fully elucidate the mechanism of the reaction.

In conclusion, we have described a new method for the alkylation of imines using trialkylalanes under zirconium catalysis. Further developments of this new reaction will be reported in due course.

All reactions were conducted under an atmosphere of argon using standard Schlenk techniques. Prior to use, tetrahydrofuran and heptane were distilled under argon from sodium benzophenone ketyl, CH_2Cl_2 was distilled under argon from CaH_2, Cp_2ZrCl_2 (Strem), Et_3Al, and Grignard reagents (Aldrich) were used as received. All imines were prepared according to known procedures[12] and gave satisfactory analysis. Unless otherwise stated, ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker AC-250. Mass spectra were recorded on a Micromass Q-TOF micro MS spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer.

Preparation of Tributylalane[13]

To a refluxing suspension of Al (2.7 g, 100 mmol) and Mg (3.6 g, 150 mmol) in heptane (120 mL) was added *n*-BuI (55.2 g, 300 mmol) over 45 min. The mixture was stirred for 2 h under reflux. The reaction was cooled to r.t. and the solid was filtered off under an argon atmosphere. The solvent was removed by distillation, and the residue was distilled under vacuum to give *n*-Bu_3Al in 58% yield.

Preparation of Amines 2; General Procedure

In an oven-dried Schlenk tube and under an argon atmosphere, the trialkylalane (1.5 mmol) was added to a solution of imine (1 mmol) and Cp_2ZrCl_2 (14.5 mg, 0.05 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at 20 °C for the time specified in Tables 1 and 2 (deviations from the above conditions are listed in the Tables). The reaction was then quenched at 0 °C with 15% aq NaOH and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by column chromatography (silica gel, petroleum ether–Et_2O, 20:1) as eluent to give the corresponding amine **2**.

Phenyl(1-phenylpropyl)amine (2a)[14]

Yellow oil; yield: 91%.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 6.8 Hz, 3 H), 1.85 (m, 2 H), 4.07 (br s, 1 H), 4.24 (t, *J* = 6.8 Hz, 1 H), 6.52 (d, *J* = 7.7 Hz, 2 H), 6.64 (t, *J* = 7.4 Hz, 1 H), 7.04–7.11 (m, 2 H), 7.21–7.25 (m, 1 H), 7.30–7.35 (m, 4 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 11.0, 31.8, 59.9, 113.4, 117.3, 126.7, 127.0, 128.7, 129.2, 144.1, 147.7.

4-Methoxyphenyl(1-phenylpropyl)amine (2b)[15]

Yellow oil; yield: 86%.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.4 Hz, 3 H), 1.80 (m, 2 H), 3.68 (s, 3 H), 3.81 (br s, 1 H), 4.15 (dd, *J* = 12.1, 6.3 Hz, 1 H), 6.47 (d, *J* = 8.8 Hz, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 7.32 (m, 5 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 11.0, 31.8, 55.9, 60.7, 114.6, 114.9, 126.7, 127.0, 128.6, 142.0, 144.3, 152.0.

Benzyl(1-phenylpropyl)amine (2c)[1a]

Yellow oil; yield: 88%.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.67–1.95 (m, 2 H), 3.63 (dd, *J* = 7.5, 5.9 Hz, 1 H), 3.64 (d, *J* = 13.2 Hz, 1 H), 3.77 (d, *J* = 13.2 Hz, 1 H), 7.28–7.50 (m, 10 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.8, 11.7, 23.3, 30.9, 19.7, 65.1, 126.7, 127.3, 128.2, 144.3.

(1-Phenylpropyl)propylamine (2d)

Yellow oil; yield: 85%.

IR (film): 3421, 2963, 1582, 1459, 764, 701 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.7 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H), 1.39–1.84 (m, 4 H), 2.31–2.50 (m, 2 H), 3.48 (dd, *J* = 8.0, 5.7 Hz, 1 H), 7.20–7.40 (m, 5 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.7, 31.0, 51.4, 64.1, 126.7, 126.8, 127.4, 128.0, 128.2, 140.6, 143.9.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{12}H_{20}N$: 178.1596; found: 178.1600.

Anal. Calcd for $C_{12}H_{19}N{\cdot}HCl$: C, 67.73; N, 6.55; H, 9.43. Found: C, 67.57; N, 6.55; H, 9.66.

(2*R*)-2-(1-Phenylpropylamino)-2-phenylethanol (2e)[16]
Yellow oil; yield: 92%.

$[\alpha]_D^{24}$ –37.5 (*c* 0.8, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 (t, *J* = 7.4 Hz, 3 H), 1.66 (m, 1 H), 1.86 (m, 1 H), 1.92 (br s, 1 H), 3.51 (dd, *J* = 10.7, 7.2 Hz, 1 H), 3.54 (dd, *J* = 8.3, 5.1 Hz, 1 H), 3.74 (dd, *J* = 10.7, 4.6 Hz, 1 H), 3.82 (dd, *J* = 7.0, 4.6 Hz, 1 H), 7.17–7.30 (m, 10 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.4, 29.4, 61.2, 61.6, 65.5, 127.1, 127.2, 127.4, 128.4, 128.5, 141.3, 143.9.

Phenyl(1-phenylpentyl)amine (2f)[17a,b]
Yellow oil; yield: 75%.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 8.1 Hz, 3 H), 1.26–1.40 (m, 4 H), 1.79 (m, 2 H), 3.82 (br s, 1 H), 4.20 (t, *J* = 6.5 Hz, 1 H), 6.51 (dd, *J* = 8.2, 1.0 Hz, 2 H), 6.51 (td, *J* = 7.3, 1.0 Hz, 1 H), 7.06 (dd, *J* = 8.2, 7.3 Hz, 2 H), 7.05–7.33 (m, 5 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 13.9, 22.6, 28.5, 38.7, 58.2, 113.2, 117.1, 126.4, 126.8, 128.5, 129.1, 144.4, 147.5.

4-Methoxyphenyl(1-phenylpentyl)amine (2g)
Yellow oil; yield: 71%.

IR (film): 3406, 2950, 2853, 1506, 1235 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3 H), 1.24–1.37 (m, 4 H), 1.76 (m, 2 H), 3.68 (s, 3 H), 4.21 (t, *J* = 6.6 Hz, 1 H), 4.28 (br s, 1 H), 6.46 (d, *J* = 8.7 Hz, 2 H), 6.67 (d, *J* = 8.7 Hz, 2 H), 7.15–7.32 (m, 5 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.5, 38.7, 55.7, 59.0, 114.4, 114.7, 126.4, 126.7, 128.4, 141.8, 144.5, 151.7.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{18}H_{24}NO$: 270.1858; found: 270.1861.

Pentan-3-yl(phenyl)amine (2h)[18]
Pale yellow oil; yield: 32%.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.9 Hz, 6 H), 1.30–1.80 (m, 4 H), 3.05–3.50 (m, 2 H), 6.50–6.80 (m, 3 H), 7.0–7.30 (m, 2 H).

[1-(2-Bromophenyl)propyl]phenylamine (3a)
Yellow oil; yield: 89%.

IR (film): 3410, 1567, 1495, 759, 693 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.83 (m, 2 H), 4.14 (d, *J* = 5.1 Hz, 1 H), 4.22 (dd, *J* = 6.4, 12.5 Hz, 1 H), 6.46 (d, *J* = 8.5 Hz, 2 H), 6.63 (t, *J* = 7.3 Hz, 1 H), 7.09 (t, *J* = 7.9 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 1 H), 7.37 (m, 2 H), 7.55 (d, *J* = 7.9 Hz, 1 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.2, 27.2, 68.0, 124.6, 129.4, 129.9, 130.7, 131.2, 132.5, 134.7, 140.3, 145.1.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{15}H_{17}NBr$: 290.0544; found: 290.0546.

2-Iodophenyl(1-phenylpropyl)amine (3b)
Pale-yellow oil; yield: 88%.

IR (film): 3397, 2961, 1589, 1505, 742 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.3 Hz, 3 H), 1.85 (m, 2 H), 4.26 (q, *J* = 6.0 Hz, 1 H), 4.64 (br, 1 H), 6.29 (d, *J* = 8.2 Hz, 1 H), 6.37 (t, *J* = 7.6 Hz, 1 H), 7.00 (t, *J* = 7.9 Hz, 1 H), 7.30 (m, 5 H), 7.64 (d, *J* = 6.3 Hz, 1 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.8, 31.85, 60.0, 81.1, 111.7, 118.4, 124.8, 126.2, 126.9, 128.5, 129.1, 138.7, 143.2, 147.3.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{15}H_{17}NI$: 338.0406; found: 338.0398.

***N*-{4-[(1-Phenylamino)propyl]phenyl}acetamide (3c)**
Red solid; yield: 88%.

IR (KBr): 3321, 2965, 1661, 1604, 749 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3 H), 1.79 (m, 2 H), 2.14 (s, 3 H), 4.18 (t, *J* = 6.6 Hz, 1 H), 4.24 (br s, 1 H), 6.50 (d, *J* = 8.1 Hz, 2 H), 6.63 (t, *J* = 7.3 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.33 (br s, 1 H), 7.43 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.7, 24.5, 31.4, 59.4, 113.4, 120.0, 127.0, 129.0, 133.5, 136.5, 139.6, 172.2.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{17}H_{21}N_2O$: 269.1654; found: 269.1660.

4-(1-Phenylaminopropyl)benzonitrile (3d)[8b]
Pale-green oil; yield: 88%.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 1.81 (m, 2 H), 4.10 (d, *J* = 4.5 Hz, 1 H), 4.27 (dd, *J* = 11.6, 6.4 Hz, 1 H), 6.44 (d, *J* = 7.8 Hz, 2 H), 6.66 (t, *J* = 7.3 Hz, 1 H), 7.08 (t, *J* = 7.9 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.60 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.6, 31.5, 59.4, 113.1, 117.7, 118.9, 127.2, 129.1, 132.4, 132.8, 146.7, 149.8.

2-Methoxy-4-(1-phenylaminopropyl)phenol (3e)
Red oil; yield: 89%.

IR (film): 3505, 3407, 2964, 1603, 750 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3 H), 1.80 (m, 2 H), 3.85 (s, 3 H), 3.95 (m, 1 H), 4.12 (t, *J* = 6.7 Hz, 1 H), 5.53 (br s, 1 H), 6.50 (d, *J* = 7.6 Hz, 2 H), 6.63 (t, *J* = 7.3 Hz, 1 H), 6.84 (m, 3 H), 7.08 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 11.2, 32.1, 56.3, 60.2, 109.1, 113.7, 114.6, 117.5, 119.7, 129.4, 135.1, 144.8, 148.7.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{16}H_{20}NO_2$: 258.1494; found: 258.1493.

Phenyl[1-(2-pyridyl)propyl]amine (3f)[8b]
Pale green oil; yield: 95%.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.5 Hz, 3 H), 1.85–1.96 (m, 2 H), 4.43 (t, *J* = 7.5 Hz, 1 H), 4.24 (br s, 1 H), 6.57 (d, *J* = 8.0 Hz, 2 H), 6.64 (t, *J* = 2.0 Hz, 1 H), 7.11 (m, 3 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.59 (t, *J* = 2 Hz, 1 H), 8.58 (d, *J* = 2 Hz, 1 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.6, 25.2, 55.9, 108.6, 112.7, 116.5, 117.2, 124.4, 131.8, 142.7, 144.6, 158.1.

Phenyl[1-(3-pyridyl)propyl]amine (3g)
Pale green oil; yield: 95%.

IR (film): 3251, 3109, 2930, 2875, 1603 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 1.83 (m, 2 H), 4.09 (d, *J* = 4.6 Hz, 1 H), 4.28 (dd, *J* = 6.5, 12.1 Hz, 1 H), 6.49 (d, *J* = 8.3 Hz, 2 H), 6.65 (t, *J* = 7.3 Hz, 1 H), 7.09 (t, *J* = 7.9 Hz, 2 H), 7.23 (dd, *J* = 5.2, 8.2 Hz, 1 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 8.48 (dd, *J* = 4.7, 1.4 Hz, 1 H), 8.61 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 10.6, 31.52, 57.4, 113.2, 117.5, 123.5, 129.1, 133.8, 139.1, 146.8, 148.4, 148.7.

HRMS-ESI: *m/z* $[M + H]^+$ calcd for $C_{14}H_{17}N_2$: 213.1392; found: 213.1395.

Acknowledgment

We thank the CNRS and the Ministère de l'Education Nationale for their financial support.

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