A General Synthesis of Amines and Hydrazines by Oxidation of Amidocuprates and Zinc-Amidocuprates

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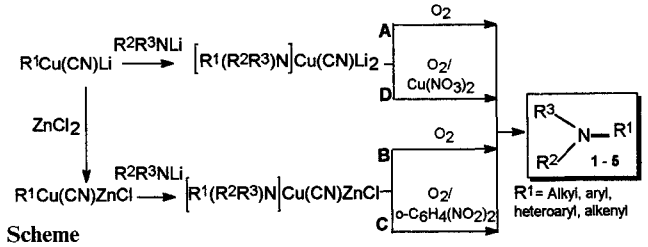
A wide range of amines and hydrazines were synthesized according to an electrophilic amination protocol by oxidative decomposition of readily generated lithium- and zinc-amidocyanocuprates. Optimization of the yields was achieved by the appropriate combination of the organometallic cluster and the nature of the oxidizing agent.

In previous papers[1,2] we have described a novel protocol for electrophilic amination,[3] by which a wide series of aliphatic, aromatic and heteroaromatic amines, several of them not accessible through the conventional synthetic routes, could be generated. The use of organocopper derivatives as the sources of the carbanionic ligands proved to be a key feature of this strategy, and we found[2] the presence of a good leaving group in the *N*-containing reagent unnecessary, provided that an oxidative step was applied to decompose the stable intermediate dimeric amidocuprate.

Accordingly, a number of *N*-alkylation, -vinylation, -arylation and -heteroarylation products were synthesized from simple primary and secondary amines. A limited number of substituted hydrazines were also generated, although in modest yields, since the usual combination of organocopper derivatives and lithium hydrazides led, in several cases, to sizeable amounts of azocompounds, most likely as a consequence of a copper-assisted hydrogen abstraction in the oxidative step.

This drawback, as well as the occurrence of dimeric by-products in some of the reactions so far studied, prompted us to investigate the variation of the organometallic species and of the oxidizing agent, with the purpose of identifying the procedures of choice for the optimization of the yields in this new version of the electrophilic amination reaction. Herein we report the results of this investigation.

The excellent transmetallation ability of zinc due to the low-lying empty orbitals, as well as its use[4] in a large number of recent synthetic applications prompted us to consider the Cu to Zn transmetallation as a way to modify the reactivity of the organometallic species. The procedures A–D based on the decomposition of cyanocuprates and zinc-cyanocuprates with different oxidants are illustrated in the Scheme.



Scheme

The relevant results for the application of procedures A–D to a wide series of amines and hydrazines are reported in the Table, in which the observations that the optimization in the yields of the electrophilic amination is related to right combination of the nature of the R^1, R^2, and R^3 groups in the reagents, the type of the organometallic system and the nature of the oxidizing agent, are clearly indicated.

Electrophilic amination, when applied to lithium hydrazides and performed according to procedure B via Cu to Zn transmetallation and followed by quenching with dioxygen of the intermediate zinc-amidocyanocuprate, led to a substantial improvement of the yields of *N*-substituted hydrazines **1b** and **1c** with respect to the original procedure A, even in those cases where hydrogens were present at the carbon of the newly formed C–N bond.

Extension of procedure B to a representative series of amines, however, afforded contrasting results. The expected products **2a–e** were obtained from the reaction run with zinc-cyanocuprates bearing aliphatic saturated ligands in similar or higher yields with respect to those obtained from procedure A, but a sizeable decrease in yields was noted when applying this procedure to *N*-arylation and *N*-heteroarylation (products **4d** and **5a–c**). In these latter cases, fairly large amounts of unreacted starting materials were recovered from the reaction mixture.

This behaviour can be rationalized by taking into account the nature of the organometallic system as well as the stability of the C–M bond in the case of aromatic ligands. The formation, in the conditions employed, of a highly organized pseudo-planar dimeric amidocuprate cluster **II**, consisting of a metal core to which each of the ligands is bound to two metals is well established in the literature.[5] In the zinc-amidocyanocuprates **III**, the high affinity of the Cu towards N, and the replacement of a C–Li with a more covalent C–Zn bond[6] would make these systems more stable with respect to standard cyanocuprates **I**, as well as to amidocyanocuprates **II**. Such a stabilizing effect is likely to be particularly high with aromatic ligands due to the more favourable formation of the three center-two electron bond,[7] and would prevent the collapse of type **III** clusters upon oxidation with dioxygen.

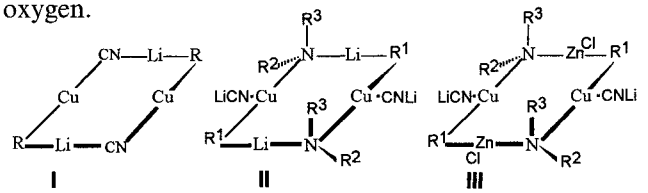


Table. Amines, Enamines and Hydrazines Prepared by Reaction of $R^1M(CN)M'$ with R^2R^3NLi Followed by Oxidative Decomposition

Product	R^1	R^2	R^3	Method[a]	Yield[b] (%)	Product	R^1	R^2	R^3	Method[a]	Yield[b] (%)
1a	*t*-Bu	H	Ph_2N	A	30[c]	**3b**	$CH=CH_2Ph$	Me	CH_2Ph	A	40
				C	**60**					C	**55**
1b	Bu	H	Ph_2N	A	2[c]	**4a**	Ph	*i*-Pr	*i*-Pr	A	60[c]
				B	18					B	30
				C	**34**					C	**70**
1c	Bu	H	Me_2N	A	2	**4b**	Ph	H	Ph	B	54
				B	18					C	**69**
				C	**50**					D	52
1d	Ph	H	Me_2N	A	40[c]	**4c**	Ph	Ph	Ph	A	50[c]
				B	40					C	76
				C	**62**	**4d**	Ph	Ph	CH_2Ph	A	54
2a	Bu	*i*-Pr	*i*-Pr	A	50[c]					B	32
				B	**85**					C	**68**
2b	Bu	H	Ph	A	62[c]					D	62
				B	**70**	**5a**	2-thienyl	Me	Ph	A	52[c]
2c	Bu	Ph	Ph	A	50					B	**5**
				B	3					C	20
				C	18					D	**70**
				D	**60**	**5b**	2-thienyl	Ph	$PhCH_2$	A	25
2d	Bu	Me	CH_2Ph	A	45[c]					B	7
				B	**45**					C	**75**
				C	57	**5c**	2-benzofuryl	Me	Ph	A	25[c]
2e	Me	Ph	CH_2Ph	A	50[c]					B	5
				B	40					C	20
				C	**60**					D	**76**
3a	CH=CHPh	*i*-Pr	*i*-Pr	A	45[c]						
				C	**60**						

[a] Method A: $R^1M(CN)M'$ stands for $R^1Cu(CN)Li$, oxidation run with O_2. Method B: $R^1Cu(CN)M'$ stands for $R^1Cu(CN)ZnCl/LiCl$, oxidation run with O_2. Method C: $R^1M(CN)M'$ stands for $R^1Cu(CN)ZnCl/LiCl$, oxidation run with $O_2/o\text{-}C_6H_4(NO_2)_2$ (cat.). Method D: $R^1M(CN)M'$ stands for $R^1Cu(CN)Li$, oxidation run with $O_2/Cu(NO_3)_2$ (cat.).

[b] Yields of isolated materials.

[c] From Ref. 2.

This assumption prompted us to envision a new procedure for the oxidative decomposition of the intermediate polymetallic cluster **III**. The use of nitroarenes for the oxidation of organocuprates has already been reported[8] to lead to the dimer of the organic residue. Of the dozen oxidizing agents screened, and in the oxidation of mixed cuprates RR'CuLi, the dinitrobenzenes gave the best results in terms of unsymmetrical ligand coupling. The combination of dioxygen with catalytic amounts (20%) of *o*-dinitrobenzene as the co-oxidant is, to our knowledge, unprecedented since nitroarenes have been used only in stoichiometric amounts. When applied to zinc-amidocyanocuprates (procedure C), this combination proved to be successful,[9] since a faster reaction and a general improvement of the yields were observed. This improvement was particularly remarkable in the *N*-arylation (products **4a–d**) and *N*-heteroarylation (product **5b**) reactions. Regarding the compatibility of this oxidative quenching with more fragile compounds, enamines **3a,b** from *N*-vinylation were formed in satisfactory yields to some extent, better with respect to those obtained according to procedure A. Furthermore, a sizeable increase in the yields was obtained in the synthesis of hydrazines **1a–c**. Surprisingly, in the *N*-heteroarylation of *N*-methylaniline extensive decomposition occurred probably due to overoxidation of **5a** and **5c**.

In order to run the oxidative quench under milder conditions, a metallic nitrate was used as the co-catalyst in combination with dioxygen. This choice was dictated by the fact that several metallic nitrates on silica gel efficiently oxidize[10] primary alcohols to the corresponding aldehydes without overoxidation, and when used without silica gel exhibit an even lower activity. Among the various metallic nitrates, unsupported $Cu(NO_3)_2$ was chosen as the co-oxidant of choice with the purpose of avoiding unwanted transmetallation reactions on the intermediate clusters. The oxidative decomposition of the stable zinc-amidocyanocuprates by the $Cu(NO_3)_2/O_2$ system did not take place but was effective (procedure D) when performed on the more fragile amidocyanocuprates **II**. The beneficial effect of the combination of a more reactive cluster and a milder oxidizing reagent allowed us to overcome the previously mentioned oxidative decomposition of the reaction products, leading to the expected products **2c**, **5a** and **5c** in satisfactory to good yields.

In conclusion, a good combination of the organometallic reagents and of the oxidizing system in the intramolecular oxidative coupling of metalloamides is a general and flexible system for the generation of new C–N bonds, leading to a wide series of aliphatic, aromatic and heteroaromatic amines and hydrazines. On account of its effi-

ciency, flexibility and operational simplicity, this method should find further practical use in the synthesis of amines and hydrazines not readily accessible by the conventional routes.

Solvents were purified and dried under the standard conditions. All reactions involving air-sensitive reagents were performed using syringe-septum cap techniques in oven dried glassware under nitrogen. Thiophene, benzofuran, BuLi, PhLi, MeLi, CuCN, $Cu(NO_3)_2$ (30 % wt. on Celite) and *o*-dinitrobenzene were purchased from Aldrich Chemical Company and used as received. The purity of the organolithium derivatives was checked according to Gilman.[11] Column chromatography was performed on silica gel (70–230 mesh) and on alumina at normal pressure, or on silica gel 60 (230–400 mesh) at 0.2–0.4 mPa, using the solvent mixtures mentioned below. GC was performed on a Varian 3300 chromatograph equipped with a 25 m × 0.25 mm, cross-linked 5 % methylphenylsilicone capillary column. Mass spectra were obtained with a GC–MS Hewlett-Packard 5890/Mass Selective detector 5972. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 (200 MHz for ^1H and 50.3 MHz for ^{13}C), using $CDCl_3$ and C_6D_6 as solvents. δ Values are given relative to TMS; *J* values in Hz. HRMS (EI/DP) were obtained at 70 eV on a VG 7070-E spectrometer. Satisfactory analytical data were obtained for new compounds **1c**, **2c**, **3b**, **4d**, **5b**: C ± 0.40, H ± 0.21, N ± 0.28.

Amines and Hydrazines 1–5 by Oxidation of Amidocuprates and Zinc-Amidocuprates; General Procedures:

Procedure A: The amidocyanocuprates were prepared by rapidly adding CuCN (3.00 mmol, 0.268 g) under N_2 flow to the lithium compound (3.00 mmol) in THF (10 mL), cooled at −40 °C. The reaction mixture was stirred until dissolution of the salt, which was generally complete after 20 min. To the clear solution of cyanocuprate was added a THF solution of the lithium amide (3.00 mmol). After 20 min the mixture, cooled at −78 °C, was quenched with a vigorous stream of O_2 for an additional 30 min. A dark precipitate formed during this time. The mixture was allowed to rise to r.t., filtered through a Celite pad, concentrated, and the crude material was purified appropriately.

Procedure B: Commercial $ZnCl_2$ (3.00 mmol, 0.406 g) was melted under reduced pressure (0.02 Torr) and cooled under Ar several times. The anhydrous salt was dissolved in anhyd THF (5 mL) and added to a solution of cyanocuprate (3 mmol) cooled at −78 °C and prepared according to procedure A. To the clear solution of zinc-cyanocuprate was added a THF solution of the lithium amide (3.00 mmol). The reaction was allowed to reach −40 °C and after 40 min was cooled at −78 °C and quenched with a stream of O_2. A dark precipitate was formed during this time. The mixture was allowed to rise to r.t., filtered through a Celite pad, concentrated and the crude material was purified appropriately.

Procedure C: To a THF solution of zinc-amidocyanocuprate (3.00 mmol) at −78 °C, prepared according to procedure B, was added a THF solution of *o*-dinitrobenzene (0.6 mmol) and after 30 min a stream of O_2 was bubbled in for 30 min. A dark precipitate formed during this time. The mixture was allowed to rise to r.t. filtered through a Celite pad, concentrated, and the crude material was purified appropriately.

Procedure D: To a reaction mixture of the amidocyanocuprate (3.00 mmol) prepared according to procedure A, and cooled at −78 °C, was added a THF solution of $Cu(NO_3)_2$ (0.5 mmol). After 5 min a stream of O_2 was bubbled in for 30 min. A dark precipitate was formed during this time. The mixture was filtered through a Celite pad, the solvent evaporated, and the crude material was purified appropriately.

tert-Butyl-1,1-diphenylhydrazine (**1a**):

The typical procedure C was followed by adding lithium-1,1-diphenylhydrazide (3.00 mmol) to *t*-BuCu(CN)ZnCl/LiCl. After standard workup, the crude material was purified by flash chromatography on alumina, using pentane/Et_2O (1:1) to give 0.432 (60 %) of **1a** as a red solid; mp 62–64 °C.

^1H NMR (C_6D_6): δ = 7.35–7.10 (m, 10 H_{arom}), 3.50 (br s, 1 H, NH), 1.40 (s, 9 H, *t*-C_4H_9).

^{13}C NMR ($CDCl_3$): δ = 152.45, 129.84, 123.24, 122.16, 55.92, 29.60.

MS (EI, 70 eV): *m/z* (%) = 240 (M+, 48), 183 (100), 168 (87), 77 (67), 51 (23).

HRMS: *m/z* calc. for $C_{16}H_{20}N_2$: 240.1626; found: 240.1627.

Butyl-1,1-diphenylhydrazine (**1b**):

Following procedure C, and after purification by Kugelrohr distillation (pot temperature 150 °C/0.02 Torr), 0.226 g (34 %) of **1b** was obtained as a yellow-red oil.

^1H NMR ($CDCl_3$): δ = 7.40–6.90 (m, 10 H_{arom}), 3.90 (br s, 1 H, NH), 2.84 (t, 2 H, *J* = 6 Hz, CH_2), 1.6–1.35 [m, 4 H, $(CH_2)_2$], 0.9 (t, 3 H, *J* = 7.5 Hz, CH_3).

MS (EI, 70 eV): *m/z* (%): 240 (M^+, 48), 183 (100), 168 (80), 77 (67), 51 (23), 41 (9).

HRMS: *m/z* calc. for $C_{16}H_{20}N_2$: 240.1626; found: 240.1619.

Butyl-1,1-dimethylhydrazine (**1c**):

Following procedure C, and after purification by Kugelrohr distillation (pot temperature 90 °C/20 Torr), 0.174 g (34 %) of **1c** was obtained as a yellow oil.

^1H NMR ($CDCl_3$): δ = 3.90 (br s, 1 H, NH), 2.83 (t, 2 H, *J* = 6 Hz, CH_2), 1.85 [s, 6 H, $(CH_3)_2$], 1.60–1.32 (m, 4 H, CH_2CH_2), 0.91 (t, 3 H, *J* = 7.5 Hz, CH_3).

MS (EI, 70 eV): *m/z* (%): 116 (M^+, 25), 73 (28), 59 (100), 42 (17).

HRMS: *m/z* calc. for $C_6H_{16}N_2$: 116.1313; found 116.1321.

1,1-Dimethyl-2-phenylhydrazine (**1d**):

Following procedure C, and after purification by Kugelrohr distillation (pot temperature 90 °C/20 Torr), and then by flash chromatography on alumina with pentane/Et_2O (6:4) 0.252 g (62 %) of **1d** was obtained as a dark oil.

^1H NMR (C_6D_6): δ = 6.90–6.20 (m, 5 H_{arom}), 3.40 (br, 1 H, NH), 1.85 [s, 6 H, $(CH_3)_2$].

MS (EI, 70 eV): *m/z* (%): 136 (M+, 71), 183 (100), 121 (49), 92 (100), 77 (23), 65 (50), 59 (10), 51 (16), 42 (24).

HRMS: *m/z* calc. for $C_8H_{12}N_2$: 136.1000; found: 136.0997.

N-Butyldiisopropylamine (**2a**):

Following procedure B and after purification by Kugelrohr distillation (pot temperature 75 °C/20 Torr), 0.40 g (85 %) of **2a** was obtained as a pale yellow oil.

^1H NMR ($CDCl_3$): δ = 3.8 (m, 2 H), 2.39 (t, 2 H, *J* = 6.6 Hz, CH_2), 1.68–1.20 (m, 4 H, CH_2CH_2), 1.24 [d, 12 H, *J* = 6.3 Hz, $CH(CH_3)_2$], 0.95 (t, 3 H, *J* = 6.6 Hz, CH_3).

MS (EI, 70 eV): *m/z* (%) = 157 (M^+, 30), 142 (89), 114 (100), 100 (94), 72 (96), 58 (48), 56 (35).

HRMS: *m/z* calc. for $C_{10}H_{23}N$: 157.1830; found: 157.1827.

N-Butylaniline (**2b**):

Following procedure B and after purification by flash chromatography on silica gel with pentane/Et_2O (8:2), 0.313 g (70 %) of **2b** was obtained as a pale yellow liquid.

Spectroscopic data are fully consistent with those of a commercial sample.

N,N-Diphenylbutylamine (**2c**):

Following procedure A and after purification by flash chromatography on silica gel with pentane/Et_2O (7:3), 0.337 g (50 %) of **2c** was obtained as a yellow viscous oil.

^1H NMR ($CDCl_3$): δ = 7.40–6.87 (m, 10 H_{arom}), 2.84 (t, 2 H, *J* = 6.6 Hz, CH_2), 1.66–1.27 [m, 4 H, $(CH_2)_2$], 0.94 (t, 3 H, *J* = 6.6 Hz, CH_3).

^{13}C NMR ($CDCl_3$): δ = 148.22, 129.21, 118.16, 52.11, 29.68, 20.29, 13.89.

MS (EI, 70 eV): *m/z* (%): 225, (M^+, 23), 182 (100), 167 (11), 77 (26).

HRMS: *m/z* calc. for $C_{16}H_{19}N$: 225.2517; found: 225.2522.

N-Butyl-N-methylbenzylamine (**2d**):

Following procedure C and after purification by Kugelrohr distil-

lation (pot temperature 100°C/20 Torr), 0.302 g (57%) of **2d** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.31–7.29 (m, 5H), 3.51 (s, 2H), 2.39 (t, 2H, J = 6.6 Hz), 2.21 (s, 3H), 1.68–1.60 (m, 4H), 0.95 (t, 3H, J = 6.6 Hz).

MS (EI, 70 eV): m/z (%): 177, (M^+, 13), 135 (18), 134 (85), 92 (23), 91 (100), 65 (25).

HRMS: m/z calc. for $C_{12}H_{19}N$: 177.1517; found: 177.1520.

N-Methyl-N-phenylbenzylamine (**2e**):

Following procedure C and after purification by Kugelrohr distillation (pot temperature 130°C/20 Torr), 0.345 g (60%) of **2e** was obtained as a pale yellow viscous oil.

^{1}H NMR ($CDCl_3$): δ = 7.51–7.10 (m, 5H), 3.51 (s, 2H, CH_2), 2.91 (s, 3H, NCH_3).

MS (EI, 70 eV): m/z (%): 197, (M^+, 84), 180 (34), 120 (84), 91 (100), 77 (73), 65 (34).

HRMS: m/z calc. for $C_{14}H_{15}N$: 197.1204; found: 197.1202.

Diisopropylstyrylamine (**3a**):

The lithium derivative PhCH=CHLi[12] was converted into the corresponding zinc-cyanocuprate and reacted with LDA according to procedure C to give, after standard workup and purification by Kugelrohr distillation (pot temperature, 155°C/20 Torr), 0.244 g (60%) of **3a** as a pale yellow liquid.

^{1}H NMR ($CDCl_3$): δ = 7.30–7.10 (m, 5H_{arom}), 6.88 (d, 1H, CH, J = 14 Hz), 5.36 (d, 1H, CH, J = 14 Hz), 3.70 (m, 2H, NCH_2), 1.21 (d, 12H, J = 6.6 Hz, 4 CH_3).

MS (EI, 70 eV): m/z (%): 203, (M^+, 92), 188 (68), 160 (100), 146 (60), 129 (32), 118 (34), 91 (53), 70 (28).

HRMS: m/z calc. for $C_{14}H_{21}N$: 203.1674; found: 203.1672.

N-Methyl-N-styrylbenzylamine (**3b**):

The lithium derivative PhCH=CHLi[12] was converted into the corresponding zinc-cyanocuprate and reacted with lithium *N*-benzylmethylamide according to procedure C to give, after standard workup and purification by Kugelrohr distillation (pot temperature, 180°C/20 Torr), 0.335 g (55%) of **3b** as a yellow oil.

^{1}H NMR ($CDCl_3$) δ = 7.40–7.08 (m, 10H_{arom}), 6.88 (d, 1H, CH, J = 15 Hz), 5.36 (d, 1H, CH, J = 15 Hz), 3.84 (s, 1H), 2.38 (s, 1H).

MS (EI, 70 eV): m/z (%): 223, (M^+, 81), 167 (44), 117 (85), 91 (100), 77 (25), 65 (57).

HRMS: m/z calc. for $C_{16}H_{17}N$: 223.1361; found: 223.1361.

N,N-Diisopropylaniline (**4a**):

Following procedure C and after purification by Kugelrohr distillation (pot temperature 100°C/20 Torr), 0.371 g (70%) of **4a** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.69–7.33 (m, 5H_{arom}), 3.80 (m, 2H), 1.24 (d, 12H, J = 6.3 Hz).

MS (EI, 70 eV): m/z (%): 177, (M^+, 58), 163 (27), 162 (60), 134 (17), 121 (28), 120 (100), 77 (59).

HRMS: m/z calc. for $C_{12}H_{19}N$: 177.1517; found: 177.1514.

Diphenylamine (**4b**):

Following procedure C and after purification by flash chromatography on silica gel with Et_2O, 0.359 g (69%) of **4b** was obtained as a white powder.

Spectroscopic data are fully consistent with those of a commercial sample.

Triphenylamine (**4c**):

Following procedure C and after purification by flash chromatography on silica gel with hexane/EtOAc (5:1), 0.558 g (76%) of **4c** was obtained as a colourless oil.

Spectroscopic data are fully consistent with those of a commercial sample.

N,N-Diphenylbenzylamine (**4d**):

Following procedure C and after purification by flash chromatography on silica gel with pentane/Et_2O (5:1), 0.529 g (68%) of **4d** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.70–6.60 (m, 15H_{arom}), 5.02 (s, 2H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 148.16, 139.24, 129.25, 128.54, 127.22, 126.57, 121.39, 120.75, 56.3.

MS (EI, 70 eV): m/z (%): 259, (M^+, 84), 182 (17), 168 (64), 91 (100), 77 (24), 51 (20).

HRMS: m/z calc. for $C_{19}H_{17}N$: 259.1361; found: 259.1359.

2-(Methylphenylamino)thiophene (**5a**):

Following procedure D and after purification by flash chromatography on silica gel with pentane/Et_2O (8:2), 0.396 g (70%) of **4d** was obtained as a yellow viscous oil.

^{1}H NMR ($CDCl_3$): δ = 7.35–7.16 (m, 3$H_{thiophene}$), 7.1–6.8 (m, 4H_{arom}), 6.68 (m, 1H_{arom}), 3.34 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 128.97, 127.79, 125.76, 124.37, 123.78, 119.94, 119.48, 116.29, 42.02.

MS (EI, 70 eV): m/z (%): 189 (M^+, 100), 174 (31), 173 (36), 130 (10), 77 (19).

HRMS: m/z calc. for $C_{11}H_{11}NS$: 189.0612; found: 189.0610.

2-(Benzylphenylamino)thiophene (**5b**):

Following procedure C and after purification by chromatography on alumina with pentane/Et_2O (7:3), 0.596 g (75%) of **5b** was obtained as a yellow viscous oil.

^{1}H NMR ($CDCl_3$): δ = 7.19–5.58 (m, 13$H_{arom+thiophene}$), 4.53 (s, CH_2).

^{13}C NMR (C_6D_6): δ = 149.22, 138.69, 137.75, 129.45, 129.33, 129.14, 125.96, 124.49, 124.09, 120.34, 116.73, 113.19, 58.29.

MS (EI, 70 eV): m/z (%): 265, (M^+, 77), 174 (100), 147 (5), 130 (19), 91 (51), 77 (35), 51 (22).

HRMS: m/z calc. for $C_{17}H_{15}NS$: 265.0925; found: 265.0922.

2-(Methylphenylamino)benzofuran (**5c**):

Following procedure D and after purification by flash chromatography on alumina with pentane/Et_2O (8:2), 0.508 g (76%) of **5c** was obtained as a yellow viscous oil.

^{1}H NMR ($CDCl_3$): δ = 7.50–7.00 (m, 10H, Ar), 3.45 (s, 3H, CH_3).

^{13}C NMR (C_6D_6): δ = 158.03, 150.84, 154.92, 130.23, 129.16, 122.66, 121.35, 120.36, 118.70, 112.51, 110.11, 85.72, 38.61.

MS (EI, 70 eV): m/z (%) = 223, (M^+, 100), 208 (25), 181 (11), 180 (22), 91 (10), 77 (26), 51 (19).

HRMS: m/z calc. for $C_{15}H_{13}NO$: 223.0997; found: 223.0994.

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