1,8-Disubstituted Naphthalenes by Directed Metalation and Subsequent Lithium–Manganese Exchange, Including Copper Catalysis[1]

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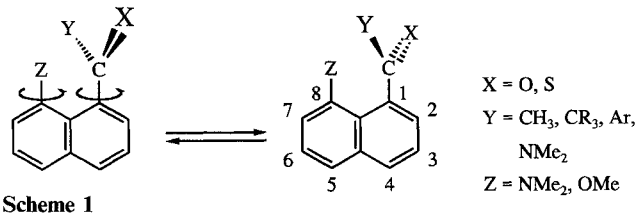
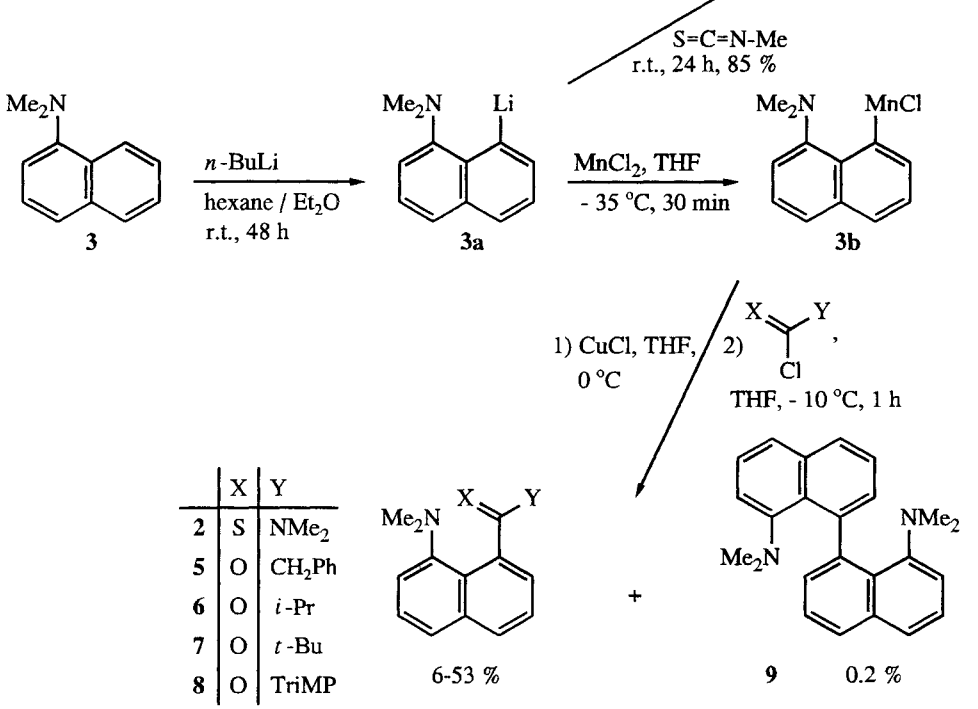
Directed lithiation of 1-dimethylamino- and 1-methoxynaphthalene, followed by Li–Mn exchange and reaction with electrophiles, provides regioselective syntheses of previously unknown racemic thioamides **2**, **11** and **12**, and ketones **5**–**8**.

Acceptor substituents such as acyl groups in the 1-position of naphthalene have been shown to be twisted out of the arene plane in many cases. The additional presence of a donor substituent Z in the 8-position (Scheme 1) leads to unusual details in the crystal structures[3] which are due to a donor–acceptor (nucleophile–electrophile) interaction. Such naphthalene derivatives have two rotor groups and may form interconvertible enantiomers. For some of these molecules, the rotational barriers can be related[2,4] to the gross stereostructures of their ground and transition states in solution. As we wanted to find more precise structure–barrier correlations, we intended to include the unknown chiral thioamides **2** and **12** as well as the ketones **5**–**8** (Schemes 2 and 3) into our investigation of stereodynamics.



Scheme 1

However, thioamide **2** was not obtained by the usual thiation procedures starting from **1**[2] (Scheme 2), probably because the carbonyl group is twisted out of the naphthalene plane which reduces the accessibility of its carbon atom. Similarly, thioamide **12** (Scheme 3) was not easily available, as the corresponding 1-dimethylthiocarbamoyl-8-hydroxynaphthalene (to be methylated subsequently) was not obtained from 1-dimethylcarbamoyl-8-hydroxynaphthalene[3] and Lawesson's reagent. A failure of this type is described[5] for other OH, SH and NH_2 compounds, too. Therefore, the synthesis of the tertiary



	X	Y
2	S	NMe_2
5	O	CH_2Ph
6	O	*i*-Pr
7	O	*t*-Bu
8	O	TriMP

(LR: 2,4-Bis-(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide.
TriMP: 3,4,5-Trimethoxyphenyl. See text for occurence of **9**.)

Scheme 2

thioamide **2** was tried via 1-dimethylamino-8-lithionaphthalene (**3a**).[6,7] Indeed, **3a** reacted with methylisothiocyanate at r.t.[8] and gave access (85%) to the secondary thioamide **4**, the methylation of which unfortunately did not result in **2** (Scheme 2) but in its *S*-methylation product.[4] The desired thioamide **2** was again not obtained by trapping **3a** with dimethylthiocarbamoyl chloride under several conditions,[4] although quenching with the more reactive acetic anhydride makes 8-acetyl-1-dimethylaminonaphthalene **(13)** available (67%).[7] The latter procedure failed, under several conditions,[4] to yield **5** when phenylacetyl chloride was used, probably because the product underwent further reactions.

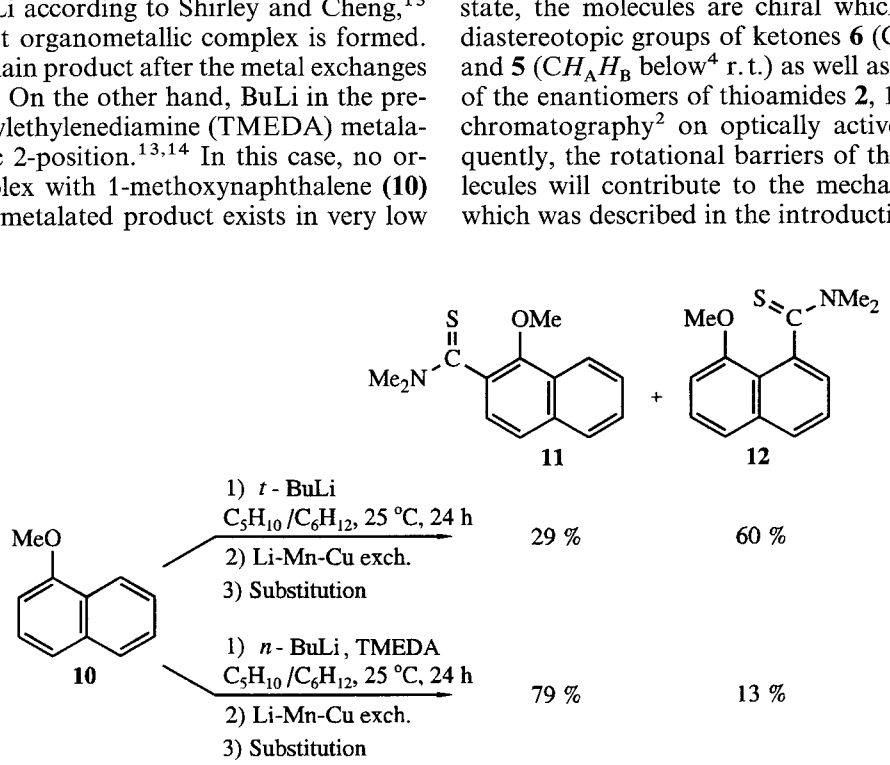
We were more successful when we replaced the Li atom in **3a** (Scheme 2) and in other lithium compounds, prepared according to Scheme 3, by MnCl at −35 °C, and subsequently added catalytic amounts of CuCl at 0 °C. Such exchanges have been described by Cahiez and coworkers for alkyl- and alkenyllithium,[9–11] and for phenylmagnesium chloride.[9] The structures of these Mn compounds are not yet known; we give the simplest possible formula for **3b**. A Cu-organic compound may be present as a mixed-metal cluster or even as a tetrameric Cu-cluster.[12]

When a dimethylamino group was present, the metalation was directed to the 8-position and we obtained the thioamide **2** and the ketones **5–8** (Scheme 2). In these preparations, coupling resulted in very small amounts of binaphthyl **9**.

When a methoxy group is present in order to direct the positions of metal atoms, the less acidic 8-position is metalated by *t*-BuLi according to Shirley and Cheng,[13] because the stablest organometallic complex is formed. Accordingly, our main product after the metal exchanges was **12** (Scheme 3). On the other hand, BuLi in the presence of tetramethylethylenediamine (TMEDA) metalates the more acidic 2-position.[13,14] In this case, no organometallic complex with 1-methoxynaphthalene **(10)** is formed, but the metalated product exists in very low concentration.[14] Therefore, we obtained mainly **11** after the metal exchanges (Scheme 3). The yields (89 and 92%) are much better than in the cases of Shirley and Cheng (35 and 59%), but their regioselectivities (1:99 and 99:1)[13] were not obtained (29:60 and 79:13).

In conclusion, a dimethylamino or methoxy group in the 1-position of naphthalene and the complexing additives served to direct the lithiation reaction. Subsequent Li–Mn exchange, including Cu-catalysis, is described for naphthyllithium for the first time and provided regioselective syntheses of the unknown thioamides **2**, **11** and **12** as well as the ketones **5–8** which are not easily accessible by other methods. The yields given are not optimized because our aim was not to develop a method of synthesis but to include these compounds into our investigation of stereodynamics.

As far as the properties of our products are concerned, their luminescence should be mentioned first. In the cases of **2** and **9**, the maxima given in the experimental part show large Stokes shifts of ca. 200 nm; a similar value had been found for **1**.[2] Among the naphthalene protons of the ketones, H-2 shows the lowest δ-value (Table 1) which probably results from an out-of-plane twist[15] (Scheme 1) of the acyl substituents. A similar trend is not easily seen for the thioamides (Table 1 and **12** in Table 2) because of the stronger effect of the S=C–N anisotropy. The coupling constants in Table 1 and the ones for **12** in Table 2 resemble one another and prove a common substitution pattern for these products. The 1-dimethylaminonaphthalenes **2**, **5–8** and **10** shown *two* *N*-methyl signals at r.t. which are in agreement with the twist mentioned above. As a consequence of this ground state, the molecules are chiral which is shown by the diastereotopic groups of ketones **6** ($CHMe^1Me^2$ at r.t.) and **5** (CH_AH_B below[4] r.t.) as well as by the separation[4] of the enantiomers of thioamides **2**, **11** and **12** by liquid chromatography[2] on optically active sorbents. Consequently, the rotational barriers of these new chiral molecules will contribute to the mechanistic investigation which was described in the introduction. In addition, an

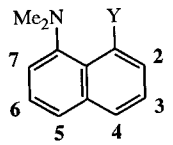


(Li-Mn-Cu exchange: a) $MnCl_2$, THF, -35°C, 30 min; b) CuCl, THF, 0°C.

Substitution: Me_2N-CSCl, THF, -10 °C, 1h.)

Scheme 3

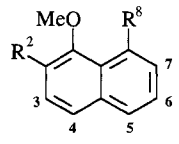
Table 1. ^{1}H NMR Shifts and Coupling Constants (Hz) of Dimethylaminonaphthalenes in $CDCl_3$



Compound	Y	δ^2(dd)	δ^3(m)	δ^4(m)	δ^5(m)	δ^6(dd)	δ^7(dd)	$^3J_{2,3}$	$^4J_{2,4}$	$^3J_{3,4}$	$^4J_{4,5}$	$^3J_{5,6}$	$^4J_{5,7}$	$^3J_{6,7}$
4	S=C-NHMe	7.54	7.39	7.79	7.61	7.45	7.32	7.1	1.1	8.1	0.4	8.1	1.1	7.4
2	S=C-NMe_2	7.57	7.14	7.48	7.43	7.19	7.04	7.1	1.0	8.2	0.4	8.1	1.0	7.5
13	O=C-Me	7.25	7.46	7.82	7.64	7.48	7.32	7.0	1.1	8.2	0.3	8.1	1.0	7.4
6	O=C-Pr-*i*	7.20	7.44	7.82	7.62	7.46	7.27	7.0	1.1	8.2	0.3	8.1	1.1	7.5
7	O=C-Bu-*t*	7.13	7.42	7.80	7.59	7.44	7.23	7.0	1.2	8.2	0.3	8.1	1.0	7.4
5	O=C-CH_2Ph	6.88	7.33	7.80	7.65	7.50	7.10	7.0	1.1	8.2	0.3	8.1	1.1	7.4
8	O=C-TriMP[a]	7.24	7.47	7.91	7.70	7.55	7.42	7.2	1.1	8.2	0.3	8.2	1.0	7.5

[a] TriMP: 3,4,5-trimethoxyphenyl.

Table 2. ^{1}H NMR Shifts and Coupling Constants (Hz) of Methoxynaphthalenes in $CDCl_3$



Compound	R^2	R^8	δ^2(dd)	δ^3	δ^4(m)	δ^5(m)	δ^6(m)	δ^7(m)	δ^8(m)
12	H	S=C-NMe_2	6.86	7.39m	7.43	7.74	7.42	7.29	–
11	S=C-NMe_2	H	–	7.42d	7.61	7.82	7.50	7.53	8.11

Compound	R^2	R^8	$^3J_{2,3}$	$^4J_{2,4}$	$^3J_{3,4}$	$^4J_{4,5}$	$^5J_{4,8}$	$^3J_{5,6}$	$^4J_{5,7}$	$^5J_{5,8}$	$^3J_{6,7}$	$^4J_{6,8}$	$^3J_{7,8}$
12	H	S=C-NMe_2	7.1	1.0	8.3	0.4	–	8.3	1.2	–	7.0	–	–
11	S=C-NMe_2	H	–	–	8.5	0.5	0.7	7.9	1.7	0.6	7.0	1.0	8.8

anomalous X-ray analysis[16] of $(+)_{365}$-**12** resulted in its absolute helicity which, in turn, may provide the absolute stereostructures of further thioamides[4] via circular dichroism.

^{1}H NMR spectra were recorded on Bruker WM-250 or AC-250 instruments at 24 and 21 °C, respectively. Successful simulations with the program LAME,[17] including the peri-coupling constants $^4J_{45}$, and some ^{1}H/^{1}H-COSY experiments are in agreement with the assignments given in Tables 1 and 2. IR spectra were measured on Beckmann Acculab 1 or on JASCO IR 810, mass spectra (MS) on Finnigan (MAT 112S/SS200, 70 eV) or Varian (MAT CH 5, 70 eV) spectrometers. UV spectra were recorded on a Hitachi U-2000, luminescence spectra on a Hitachi F-3000 instrument. The latter were obtained for 10^{-4} M solutions, with a light path of 1 cm, excitation at 300 nm, at 25 °C; they are not corrected. Melting points were determined on a Büchi SMP-20 or an SMP-530 apparatus and are corrected.

BuLi and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Co. THF and Et_2O were freshly distilled from sodium with benzophenone. All metalation reactions were performed in flame-dried glassware under N_2 using the syringe–septum cap techniques. Column chromatography was carried out on ICN silica gel 60 F_{254} (63–200 μm).

Compounds **2**, **4–6**, **8**, **11** and **12** gave C, H, N analysis ± 0.18%; except **6**, N ± 0.4%.

1-Dimethylamino-8-lithionaphthalene (3a):[7]
A solution of BuLi (20.6 mL, 1.6 M, 33 mmol) in hexane was added to a stirred solution of 1-dimethylaminonaphthalene (**3**; 5.14 g, 4.94 mL, 30 mmol) in dry Et_2O (50 mL) at r.t. After 48 h the precipitation of yellow **3a** was complete.

1-Dimethylamino-8-methylthiocarbamoylnaphthalene (4):
A solution of methylisothiocyanate (2.42 g, 33 mmol) in dry Et_2O (80 mL) was added dropwise to the suspension of **3a** (30 mmol) at r.t. The mixture was stirred for 24 h. After the addition of MeOH (10 mL) the suspension was stirred for 1 h, diluted with Et_2O, washed with water (2 × 150 mL), then with sat. aq NaCl (2 × 150 mL) and dried (Na_2SO_4). The ether phase was evaporated under reduced pressure. Crystallisation of the residue from EtOH yielded colourless or slightly yellow crystals of **4** (6.23 g, 85%), mp 172–174 °C (decomp.).

^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 6H, NMe^1Me^2), 3.27 (d, 3H, ^3J = 4.9 Hz, CSNH*Me*), 7.15 (s br, 1H, NH), naphthalene protons see Table 1.

IR (KBr): ν = 3200, 3040, 2980–2790, 1540 cm^{-1}.

MS (70 eV): m/z (%) = 244 (13, M^+), 211 (61, $M^+ - SH$), 200 (19, $M^+ - NMe_2$), 181 (100, $M^+ - SH - 2CH_3$), 127 (11, $C_{10}H_7^+$).

8-Dimethylamino-1-naphthylmanganese Chloride (3b), Containing Copper-Catalyst:

The Li–Mn exchange was performed by a method analogous to the literature.[10] The suspension of **3a** (30 mmol) was added to a stirred suspension of dry $MnCl_2$ (4.16 g, 33 mmol) in dry THF (50 mL) at −35 °C. After further stirring for 30 min at r.t., the manganese compound **3b** formed a brown slurry. Dry CuCl (30 mg, 0.3 mmol) was added at 0 °C.

Quenching of the 3b Suspension, Containing Copper-Catalyst; General Procedure:

A solution of freshly distilled acyl or dimethylthiocarbamoyl chloride (30 mmol) in dry THF (10 mL) was added dropwise to the stirred suspension of **3b**, containing the copper catalyst, at −10 °C. After stirring for 1 h at r.t., the mixture was hydrolysed by 1 N aq HCl (40 mL), diluted with Et_2O (100 mL), washed with water (100 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographically purified using a mixture (4:1) of petroleum ether (bp 40–60 °C) (PE) and EtOAc (EA), then separated using mixtures (10:1 and 20:1) of hexane and Et_2O as eluents. The first fraction contained **9**, the second 1-dimethylaminonaphthalene **(3)**, and the third 1-dimethylaminonaphthalenes **2** or **5–8**.

1-Dimethylamino-8-dimethylthiocarbamoylnaphthalene **(2)**:

In the general procedure, the separation of **9**, **3** and **2** was accomplished by a mixture (4:1) of PE and EA as eluent. Crystallisation of the brown oil from hexane/acetone and EtOH yielded colourless or slightly yellow crystals (5.6 g, 53 %), mp 120–121 °C.

^{1}H NMR ($CDCl_3$): δ = 2.57, 2.77 (2 s, 6 H, ArNMe^1Me^2), 2.78 (s, 3 H, $CSNCH_3^E$), 3.64 (s, 3 H, $CSNCH_3^Z$), naphthalene protons see Table 1.

IR (KBr): ν = 3020, 2960–2760, 1510 cm^{-1}.

UV (MeOH): λ (log ε) = 263 (4.13), 274 (sh, 4.1), 304 (sh, 3.8), 329 nm (sh, 3.2).

Luminescence (MeOH): λ = 514 nm; compare with naphthalene **9** for relative intensities.

MS (70 eV): m/z (%) = 258 (4, M^+), 225 (52, $M^+ - SH$), 214 (11, $M^+ - NMe_2$), 181 (100, $M^+ - SH - NMe_2$), 166 (20, $M^+ - SH - NMe_2 - CH_3$), 127 (7, $C_{10}H_7^+$).

8,8′-Bis(dimethylamino)-1,1′-binaphthyl **(9)**:[12]

The first fraction of the purification of **2** (see above) was crystallised from hexane/acetone and yielded colourless crystals (20 mg, 0.2 %), mp 131–132 °C (not given in lit. 12).

^{1}H NMR ($CDCl_3$): δ = 1.60, 1.65 (2 s, 12 H, NMe^1Me^2), 6.86 (dd, 2 H, H-2), 7.27 (t, 2 H, H-6), 7.45 (m, 2 H, H-3), 7.57 (m, 2 H, H-5), 7.58 (m, 2 H, H-4), 7.73 (t, 2 H, H-7), $^3J_{2,3}$ = 7.0, $^4J_{2,4}$ = 1.3, $^3J_{3,4}$ = 8.2, $^4J_{4,5}$ = 0.4, $^3J_{5,6}$ = 8.0, $^4J_{5,7}$ = 1.2, $^3J_{6,7}$ = 7.4 Hz.

UV (MeOH): λ (log ε) = 300 nm (3.03).

Luminescence (MeOH): λ = 517 nm; intensity amounts to 16 times that of naphthalene **2**.

MS (70 eV): m/z (%) = 340 (63, M^+), 295 (100, $M^+ - HNMe_2$), 252 (18, $M^+ - HNMe_2 - H_2C{=}N{-}Me$).

1-Dimethylamino-8-(phenylacetyl)naphthalene **(5)**:

According to the general procedure, **5** was obtained as a colourless or slightly yellow oil (2.8 g, 32 %).

^{1}H NMR ($CDCl_3$): δ = 2.44, 2.87 (2 s, br, 6 H, NMe^1Me^2), 3.94 (s, br, 2 H, CH_2), 7.21–7.24 (m, 5 H, Ph–H), naphthalene protons see Table 1.

IR (film): ν = 3350, 3080–3030, 2980–2790, 1675 cm^{-1}.

1-Dimethylamino-8-(2-methylpropanoyl)naphthalene **(6)**:

According to the general procedure, **6** was obtained as a colourless or slightly yellow oil (2.03 g, 28 %).

^{1}H NMR ($CDCl_3$): δ = 0.91, 1.24 (2 d, br, 6 H, CHMe^1Me^2), 2.39, 2.82 (2 s, br, 6 H, NMe^1Me^2), 2.97 (sept, 1 H, C*H*Me^1Me^2), naphthalene protons see Table 1.

IR (film): ν = 3360, 3060, 2980–2800, 1680 cm^{-1}.

MS (70 eV): m/z (%) = 241 (34, M^+), 198 (100, $M^+ - C_3H_7$), 183 (70, $M^+ - C_3H_7 - CH_3$), 170 (5, $M^+ - C_3H_7 - CO$), 155 (6, $M^+ - C_3H_7 - CH_3 - CO$), 154 (23, $M^+ - C_3H_7 - CH_3 - CO - H$), 127 (26, $C_{10}H_7^+$).

1-Dimethylamino-8-(2,2-dimethylpropanoyl)naphthalene **(7)**:

According to the general procedure, **7** was obtained as a colourless or slightly yellow oil (450 mg, 6 %).

^{1}H NMR ($CDCl_3$): δ = 1.09 (s, 9 H, CMe_3), 2.35, 2.85 (2 s, 6 H, NMe^1Me^2), naphthalene protons see Table 1.

IR (film): ν = 3350, 3050–2790, 1670 cm^{-1}.

MS (70 eV): m/z (%) = 255 (30, M^+), 198 (100, $M^+ - C_4H_9$), 183 (51, $M^+ - C_4H_9 - CH_3$).

1-Dimethylamino-8-(3,4,5-trimethoxybenzoyl)naphthalene **(8)**:

The general procedure and a crystallisation from hexane/acetone yield colourless crystals of **8** (1.7 g, 15.5 %), mp 112–113 °C.

^{1}H NMR ($CDCl_3$): δ = 2.05, 2.37 (2 s, 6 H, NMe^1Me^2), 3.66 (s, 6 H, OMe-3, OMe-5), 3.84 (s, 3 H, OMe-4), 6.75 (s, 2 H, H-2, H-6), naphthalene protons see Table 1.

IR (KBr): ν = 3280, 3060, 3040, 2990–2790, 1635 cm^{-1}.

Lithio-1-methoxynaphthalenes, Prepared in the Absence of TMEDA:[13]

A solution of *t*-BuLi (25 mL, 1.4 M, 33 mmol) in pentane was added slowly to a well stirred solution of 1-methoxynaphthalene (**10**, 4.75 g, 30 mmol) in dry cyclohexane (50 mL) at r.t. After 24 h the yellow lithium compounds precipitated.

1-Methoxynaphthylmanganese Chlorides, Prepared in the Absence of TMEDA, Containing Copper-Catalyst:

The Li–Mn exchange was performed by a method analogous to the literature.[10] The suspension of lithium compounds (30 mmol) described above was added to a stirred suspension of dry $MnCl_2$ (4.16 g, 33 mmol) in dry THF (50 mL) at −35 °C. After stirring for 30 min at r.t., the manganese compounds formed a brown solution. Dry CuCl (30 mg, 0.3 mmol) was added at 0 °C.

Lithio-1-methoxynaphthalenes, Prepared in the Presence of TMEDA:[13]

A solution of BuLi (20.6 mL, 1.6 M, 33 mmol) in hexane was added slowly to a well stirred solution of 1-methoxynaphthalene (**10**, 4.75 g, 30 mmol) and TMEDA (3.49 g, 30 mmol) in dry cyclohexane (50 mL) at r.t. After 24 h the lithium compounds form a dark-red solution.

1-Methoxynaphthylmanganese Chlorides, Prepared in the Presence of TMEDA, Containing Copper-Catalyst:

The solution of lithium compounds (30 mmol) described above was added dropwise to a well stirred suspension of dry $MnCl_2$ (4.16 g, 33 mmol) in dry THF (50 mL) at −35 °C. After stirring for 30 min at r.t., the manganese compounds formed a brown solution. Dry CuCl (30 mg, 0.3 mmol) was added at 0 °C.

Dimethylthiocarbamoyl(methoxy)naphthalenes (11) and (12); General Procedure:

A solution of dimethylthiocarbamoyl chloride (3.71 g, 30 mmol) in dry THF (10 mL) was added dropwise to the stirred solution of 1-methoxynaphthylmanganese chlorides, prepared in the absence *or* presence of TMEDA, containing the copper catalyst, both described above, at −10 °C. After stirring for 1 h at r.t., the mixture was hydrolysed with 1 N aq HCl (40 mL), diluted with Et_2O (100 mL), washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The remaining brown oil was separated by repeated chromatography using a PE/EA mixture (3:1) as eluent. The first fraction contained 1-methoxynaphthalene **(10)**, the second, **11**, and the third, **12**.

2-Dimethylthiocarbamoyl-1-methoxynaphthalene **(11)**:

In the case of 1-methoxynaphthylmanganese chlorides prepared in the *presence* of TMEDA, the second fraction contained **11**, and the third one **12** (0.95 g, 13%), characterised above. Compound **11** was recrystallised from EtOH yielding yellow crystals (5.8 g, 79%), mp 94.5–95.5°C.

^{1}H NMR ($CDCl_3$): $\delta = 3.17$ (s, 3H, $CSNCH_3^E$), 3.68 (s, 3H, $CSNCH_3^Z$), 3.99 (s, 3H, OMe), naphthalene protons see Table 2.

IR (KBr): $\nu = 3040$, 2980–2820, 1515 cm^{-1}.

UV (MeOH): λ (log ε) = 244 (4.50), 282 (4.2), 299 (sh, 4.0), 331 (sh, 3.0), 363 nm (2.7).

1-Dimethylthiocarbamoyl-8-methoxynaphthalene **(12)**:

In the case of 1-methoxynaphthylmanganese chlorides prepared in the *absence* of TMEDA, the second fraction contained **11** (2.16 g, 29%), characterised below, and the third fraction **12**. Crystallisation from hexane/acetone, 5:1, yielded colourless or slightly yellow crystals (4.4 g, 60%), mp 124–126°C.

^{1}H NMR ($CDCl_3$): $\delta = 2.94$ (s, 3H, $CSNCH_3^E$), 3.66 (s, 3H, $CSNCH_3^Z$), 3.91 (s, 3H, OMe), naphthalene protons see Table 2.

IR (KBr): $\nu = 3040$, 2990–2830, 1510 cm^{-1}.

UV (MeOH): λ (log ε) = 234 (4.54), 256 (sh, 4.1), 263 (4.14), 273 (4.13), 278 (sh, 4.1), 286 (sh, 4.0), 300 (sh, 4.0), 313 (sh, 3.9), 324 nm (sh, 3.7).

1-Acetyl-8-dimethylaminonaphthalene **(13)**:[7]

^{1}H NMR ($CDCl_3$): $\delta = 2.35$ (s, 3H, $COCH_3$), 2.60 (s br, 6H, NMe_2), naphthalene protons see Table 1.

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