Reactions of 3-Nitro-ω-benzylideneacetophenone with Carbanions Containing Leaving Groups

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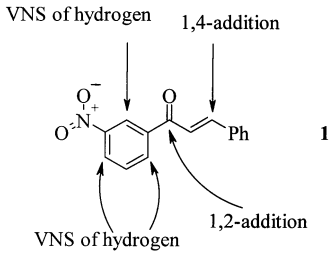
3-Nitro-ω-benzylideneacetophenone (**1**) reacts with carbanions containing leaving groups to give addition products to the electrophilic side chain. As a result of conjugated addition and subsequent intramolecular vicarious nucleophilic substitution of hydrogen (VNS) in the nitroaromatic ring of **1** in the position *para* to the nitro group, 4-cyano-7-nitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one and 4-cyano-7-nitro-3-phenylnaphth-1-ol are obtained. Smooth intramolecular VNS in the position *para* to the nitro group was observed for 4-chloro-1-(3-nitrophenyl)-3-phenyl-4-(*p*-tosyl)butanol.

Reactions of carbanions of general structure $^{-}$CXYR, containing leaving groups X at the carbanion centers, with nitroarenes proceed usually by an addition/β-elimination pathway resulting in overall nucleophilic replacement of hydrogen *ortho* and *para* to the nitro group with the carbanion moiety[1]. This process, known as vicarious nucleophilic substitution of hydrogen (VNS), is presently a general method of nucleophilic alkylation of nitroarenes. Amination of nitroarenes with a variety of aminating agents such as hydroxylamine[2], aminotriazole[3], sulfenamides[4] etc. and hydroxylation with alkylhydroperoxides[5] proceed by a similar pathway. There are only a few reported examples of the intramolecular variant of the VNS reaction and they are limited to the formation of C−C bonds[6]. In addition, very little is known about competition between the VNS and reaction of carbanions of general structure $^{-}$CXYR with other electrophilic functional groups present in nitroarenes. The reaction of *o*-, *p*-, and *m*-nitrobenzophenones with carbanions of phenyl chloromethyl sulphone proceeds along 2 pathways: VNS of hydrogen in the nitroaromatic ring (in *o*-nitrobenzophenone) and addition to the carbonyl group so that the Darzens condensation takes place (in the *para* isomer)[7]. *m*-Nitrobenzophenone reacts along both of these pathways depending on the reaction conditions. Similarly, these 2 reaction pathways were observed between nitrobenzophenones and other carbanions containing leaving groups[7b].

In order to learn more about this problem, the reactions of 3-nitro-ω-benzylideneacetophenone (**1**), a multifunctional model electrophile, with carbanions containing leaving groups were studied. Indeed **1** can add nucleophiles in five different positions: *o*, *o′*, and *p* positions of the nitroaromatic ring, the carbonyl group and the electrophilic double bond.

Scheme 1



The following compounds were used as the carbanion precursors: $CHCl_3$ (**2**), $PhOCH_2CN$ (**3**), *p*-$ClC_6H_4OCH_2CN$ (**4**), $BrCH_2COOtBu$ (**5**), $PhSCH_2CN$ (**6**), $Me_2NC(S)SCH_2CN$ (**7**), and *p*-$MeC_6H_4SO_2CH_2Cl$ (**8**). All of these compounds are known to enter readily into the VNS reaction. Addition of the carbanions of these compounds to **1** occurred exclusively at the electrophilic sites of the side chain, i.e. the carbonyl group and the double bond. Interestingly, the carbanions can be divided into 2 categories: those reacting with the carbonyl group (**2**, **3**, **4**, **5**) and those reacting with the double bond (**6**, **7**, and **8**).

Treatment of a mixture of **1** with **2**, **3**, or **4** with *t*BuOK in THF at −73°C resulted in the formation of the corresponding adducts to the carbonyl group, which upon quenching with acid gave **2a**, **3a**, and **4a**, isolated in 88, 37 and 76% yields, respectively.

Products **3a** and **4a** were formed as mixtures of diastereoisomers. Since the aim of this work was to learn how the multipositional electrophilic compound reacts with carbanions, mixtures of diastereomeric products were not

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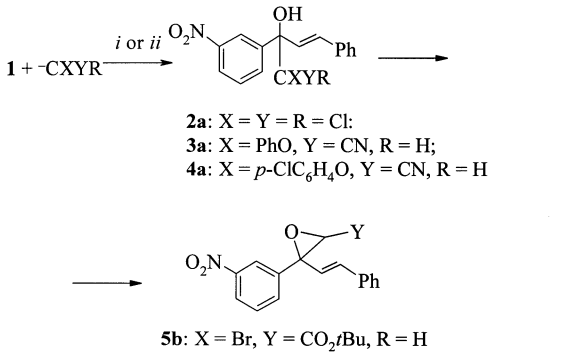
separated. The products were unambiguously identified as mixtures of diastereomers.

The reaction of **1** with **5** also proceeded through addition of the carbanion to the carbonyl group. However, this produced the bromohydrin anion, which reacted further to give oxirane **5b** as a product of the Darzens condensation in 45% yield.

Scheme 2



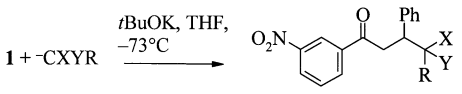
2a: X = Y = R = Cl:
3a: X = PhO, Y = CN, R = H;
4a: X = *p*-ClC_6H_4O, Y = CN, R = H

5b: X = Br, Y = CO_2tBu, R = H

Conditions: *i*. *t*BuOK, THF, DMF, –73°C; *ii*. *t*BuOK, THF, –73°C

Carbanions of **6**, **7**, and **8** reacted with **1** in a more complicated way. When the process was carried out in the presence of *t*BuOK in THF at −73°C and the mixture was quenched with acid at this temperature, adducts to the double bond **6a**, **7a**, and **8a** were obtained in yields of 73, 64, and 73% respectively.

Scheme 3

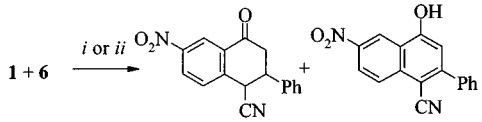


6a: X = PhS, Y = CN, R = H
7a: X = $Me_2NC(S)S$, Y = CN, R = H
8a: X = Cl, Y = Ts, R = H

However, when the reaction was carried out at higher temperatures the initial adducts reacted further along various pathways. Thus, when the reaction of **1** with **6** was carried out in the presence of KOH in DMSO at 20°C, substituted tetralone **6b** (a mixture of 2 diastereoisomers) was obtained as the main product along with small amounts of 4-cyano-7-nitro-3-phenylnaphth-1-ol (**6c**). Tetralone **6b** was the main product when this reaction was carried out in the presence KOH in DMF at 0°C. Clearly **6c** was formed by oxidation of anion of **6b** because the amount of this compound obtained depended on the reaction time. When the reaction mixture was treated with oxygen, **6c** was the sole reaction product obtained in 47% yield. Since all components of the mixture **6b** were converted into **6c**, there is no doubt that these components were diastereoisomers of **6b**.

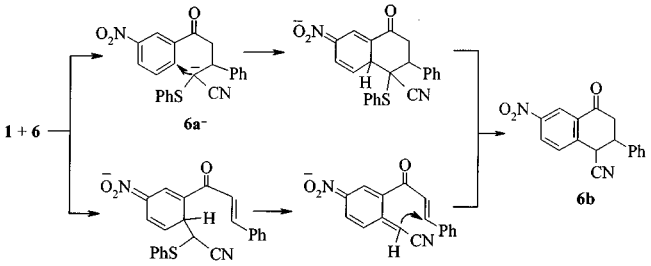
Formation of **6b** can proceed through the intramolecular VNS reaction of the initial adduct **6a** after 1,3-proton migration or, alternatively, by VNS in **1** with the carbanion of **6** followed by intramolecular Michael addition of the carbanion produced to the electrophilic double bond.

Scheme 4



Conditions: *i*. KOH, DMSO, 20°C; *ii*. KOH, DMF, 0°C.

Scheme 5

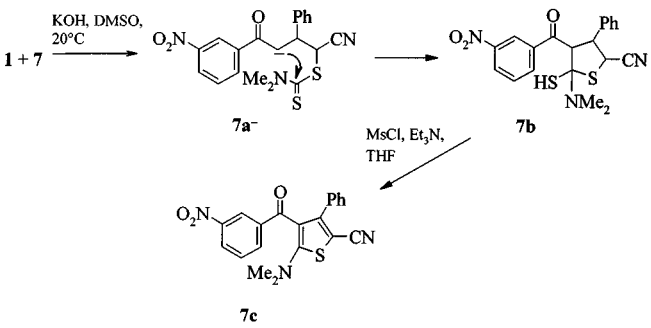


The latter reaction pathway implies a total change in the mode of the addition with a change in temperature and, moreover, a similar process should occur, at least partially, in other positions to give a VNS product that is unable to cyclize. Since such products were not observed one can suppose that **6b** is formed through the intramolecular VNS reaction of **6a**. Indeed, treatment of the isolated product **6a** with KOH in DMF at 0°C also gave a mixture of **6b** and **6c**.

A peculiar reaction took place between **1** and **7** at higher temperature (KOH, DMSO, 20°C) to give **7b** (47%). The structure of **7b** was elucidated on the basis of IR, ^1H-, ^{13}C-NMR spectroscopy and MS spectrometry data.

The stability of dithioacetal **7b** is remarkable and this compound can be recrystallized and stored without decomposition. Its formation apparently proceeds by the reaction sequence shown in Scheme 6. It should be noted that treatment of isolated **7a** with KOH in DMSO at 20°C gave the same product (**7b**), thus confirming the intermediacy of **7a**.

Scheme 6

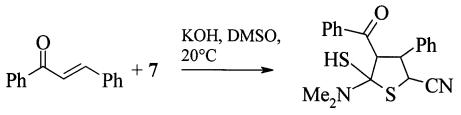


Treatment of compound **7b** with mesyl chloride in an excess of triethylamine gave 2-dimethylamino-5-cyano-3-(3-nitrobenzoyl)-4-phenylthiophene in 44% yield confirming the structure tetrahydrothiophene **7b**.

The different ways of transformation of the rather similar adducts **6a** and **7a** is apparently due to the possibility of rapid intramolecular addition of carbanion **7a**$^-$ to the thiocarbonyl group. In contrast, such a possibility is not available for **6a**$^-$, therefore the intramolecular VNS takes place in this case.

Reaction of **7** with chalcone **9** under similar conditions (KOH, DMSO, 20°C) gave the analogous product **9b** as a mixture of 2 diastereoisomers in 43% yield.

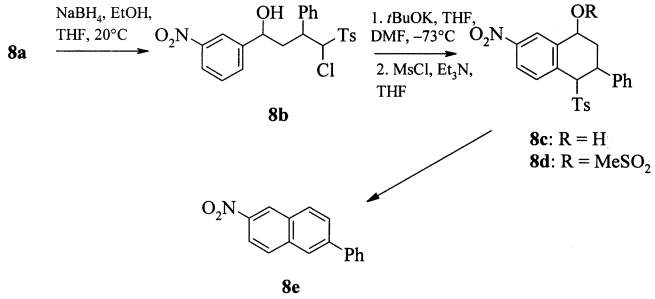
Scheme 7



9 **9b**

On the other hand, adduct **8a**, when treated with a strong base, underwent total decomposition without formation of a definite product. It appears that this decomposition proceeds by a multidirectional retro Michael reaction. This supposition is supported by a smooth intramolecular VNS when the possibility of the retro Michael reaction was excluded. Thus, when alcohol **8b**, obtained by borohydride reduction of **8a**, was treated with a strong base, **8c** was produced in high yield. Alcohol **8b** and tetraline derivative **8c** were obtained as mixtures of diastereoisomers.

Scheme 8



Treatment of **8c** (mixture of diastereoisomers in the ratio 2:1) with mesyl chloride and an excess of triethylamine gave mesylate **8d**. Compound **8d** underwent elimination of methanesulfonic acid and toluenesulfinic acid to form 2-nitro-6-phenylnaphthalene (**8e**) either under the reaction conditions or upon isolation and subsequent treatment with base.

It was shown that addition of carbanions to 3-nitro-ω-benzylideneacetophenone takes place at the carbonyl group or electrophilic double bond. The fact that this reaction mode is strongly preferred over addition to the nitroaromatic ring is apparently because the latter destroys the aromatic system. Surprisingly, differences in the addition sites of the carbanions studied were observed.

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Experimental Section

General: Melting points are uncorrected. Solvents were distilled before use: THF from potassium/benzophenone ketyl, DMF from CaH_2. Starting 3-nitro-ω-benzylideneacetophenone was prepared according to a known procedure[8]. − Column chromatography: Silica gel (230−400 mesh, Merck). − TLC monitoring: Kieselgel 60 (F_{254}) sheets. − NMR: Varian "Gemini" (200 MHz for ^1H and 50.3 MHz for ^{13}C). $CDCl_3$ was used as solvent, TMS as internal standard. Signals due to CH atoms are marked with an asterisk. − IR: Perkin-Elmer 1640. − MS: AMD-604 spectrometer.

(3-Nitrophenyl)(trans-β-styryl)(trichloromethyl)carbinol (**2a**): To a solution of *t*BuOK (0.88 g, 7.9 mmol) in a mixture of THF (5 ml) and DMF (5 ml) was added a solution of chalcone **1** (0.5 g, 1.97 mmol) and $CHCl_3$ (0.28 g, 2.1 mmol) in THF (5 ml) at −73°C under argon. The mixture was stirred for 3 min, then poured into ice-cooled diluted aq. HCl (5%), and extracted with EtOAc. The organic phase was washed with water and dried with Na_2SO_4, the solvent was evaporated in vacuo and the residue was purified by column chromatography [hexane/EtOAc (4:1) as eluent] to give carbinol **2a** (0.64 g, 88%) as a yellow oil. − IR (film): $\tilde{\nu}$ = 6531 cm^{-1} (OH), 1614 (C=C), 1529, 1348 (NO_2). − ^1H NMR ($CDCl_3$): δ = 8.75 (t, *J* = 2.0 Hz, 1 H), 8.27 (dm, *J* = 8.2 Hz, 1 H), 8.19 (dm, *J* = 7.9 Hz, 1 H), 7.58 (t, *J* = 8.2, 7.9 Hz, 1 H), 7.37 (d, *J* = 15.8 Hz, 1 H), 7.55−7.35 (m, 5 H), 6.98 (d, *J* = 15.8 Hz, 1 H), 3.51 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 147.53, 140.46, 135.25*, 129.01*, 128.90*, 128.30*, 127.93*, 127.05*, 124.36*, 123.66*, 106.55, 84.69. − MS (70eV); *m/z* (%): 254 [$M^+ - CCl_3$] (100), 236 [$M^+ - CCl_3 - H_2O$] (4), 208 [$M^+ - NO_2 - CCl_3$] (7), 189 (3), 178 (6), 165 (3), 150 [$NO_2C_6H_4CO^+$] (16), 131 [$PhCH{=}CHCO^+$] (9), 103 [$PhCH{=}CH^+$] (8), 77 [Ph^+] (7). − EIHR: calcd. for [$M^+ - CCl_3$] 254.0817 ($C_{15}H_{12}NO_3$), found 254.0791.

4-Cyano-3-hydroxy-3-(3-nitrophenyl)-4-phenoxy-1-phenylbut-1-ene (**3a**) was obtained from **1** (0.5 g, 1.97 mmol) and **3** (0.28 g, 2.1 mmol) as described for compound **2a** and isolated in 37% yield (0.28 g) as a mixture of 2 stereoisomers in the ratio 1:1 [hexane/EtOAc (5:1) as eluent], m.p. for this mixture 30°C. − ^1H NMR ($CDCl_3$): for mixture of isomers: δ = 8.60 (m, 1 H), 8.24 and 8.21 (2 dm, *J* = 8.1 Hz, 1 H), 8.09 and 8.03 (2 dm, *J* = 7.9 Hz, 1 H), 7.61 (t, *J* = 8.1, 7.9 Hz, 1 H), 7.5−7.3 (m, 7 H), 7.2−7.0 (m, 3 H), 6.99 and 6.95 (2 d, *J* = 16 Hz, 1 H), 6.83 and 6.78 (2 d, *J* = 16 Hz, 1 H), 5.10 and 5.05 (2 s, 1 H), 3.65 and 3.62 (2 s, 1 H). − ^{13}C NMR ($CDCl_3$): for a mixture of isomers: δ = 156.25, 156.12, 148.44, 148.40, 142.43, 135.37, 134.36, 134.10, 132.65, 132.67, 130.17, 129.68, 128.90, 127.83, 127.36, 127.11, 124.25, 124.16, 123.63, 121.93, 121.80, 116.46, 116.35, 115.58, 115.50, 77.31, 77.04, 75.17, 75.03. − MS (70 eV); *m/z* (%): 356 [$M^+ - NO$] (0.2), 254 [$M^+ - PhOCHCN$] (100), 34 (3), 224 (4), 208 (6), 178 (5), 150 [$NO_2C_6H_4CO^+$] (22), 131 (10), 103 [$PhCH{=}CH^+$] (10), 94 (7), 77 [Ph^+] (9), 65 (6). − LSIMS: 409 [$M + Na^+$], 369 [$M - H_2O + H^+$].

4-(4-Chlorophenoxy)-4-cyano-3-hydroxy-3-(3-nitrophenyl)-1-phenylbut-1-ene (**4a**) was obtained from **1** (0.5 g, 1.97 mmol) and **4** (0.35 g, 2.1 mmol) according to the procedure described for carbinol **2a** and isolated in 76% yield (0.64 g) as a mixture of 2 stereoisomers in the ratio 1:1 [hexane/EtOAc (3:1) as eluent], m.p. 38−40°C. − IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1} (OH), 2250 (CN), 1585 (C=C), 1529, 1349 (NO_2). − ^1H NMR ($CDCl_3$): for mixture of isomers: δ = 8.60 and 8.57 (2 t, *J* = 1.9, 2.0 Hz, 1 H), 8.29 and 8.26 (2 dm, *J* = 8.1 Hz, 1 H), 8.09 and 8.02 (2 dm, *J* = 7.8 Hz, 1 H), 7.65 (t, *J* = 8.1,

7.8 Hz, 1 H), 7.5−7.26 (m, 6 H), 7.02−6.89 (m, 4 H), 6.78 and 6.75 (2 d, J = 16 Hz, 1 H), 5.04 and 4.99 (2 s, 1 H), 3.34 and 3.32 (2 s, 1 H, OH). − MS (70 eV); *m/z* (%): 293 [$M^+ - ClC_6H_4O$] (2.5), 254 [$M^+ - ClC_6H_4OCHCN$] (100), 236 (5), 206 (8), 178 (6), 167 (8), 150 [$NO_2C_6H_4CO^+$] (22), 131 [$PhCH{=}CHCO^+$] (15), 127 [$ClC_6H_4O^+$] (16), 103 [$PhCH{=}CH^+$] (15), 77 [Ph^+] (10). − LSIMS: 443 [$M + Na^+$], 403 [$M - H_2O + H^+$]. − LSIMSHR: calcd. for [$M + Na^+$] 443.07745 ($C_{23}H_{17}ClN_2O_4Na$), found 443.07736.

2-tert-Butoxycarbonyl-3-(3-nitrophenyl)-3-(trans-β-styryl)-oxirane (**5b**): To a solution of *t*BuOK (0.88 g, 7.9 mmol) in THF (30 ml) was added a solution of *tert*-butyl bromoacetate (0.38 g, 1.97 mmol) and chalcone **1** (0.5 g, 1.97 mmol) in THF (5 ml) at −70°C under argon. The mixture was stirred at this temperature for 5 min and then poured into ice-cooled sat. NH_4Cl, and extracted with EtOAc. The organic phase was washed with water and dried with $MgSO_4$. The residue, after evaporation of the solvent, was purified by flash chromatography [hexane/EtOAc (10:1) as eluent] to give oxirane **5d** as a mixture of 2 isomers in the ratio 1.7:1 (oil, 0.32 g, 45%). − IR (film): $\tilde{\nu}$ = 1744 cm^{-1} (CO), 1531, 1350 (NO_2). − ^1H NMR ($CDCl_3$): δ = 8.36 (m, 1 H), 8.24 (dm, J = 8.1 Hz, 1 H), 7.86 (dm, J = 7.7 Hz, 1 H), 7.60 (t, J = 8.1, 7.7 Hz, 1 H), 7.3 (m, 5 H), 6.64 (d, J = 16.1 Hz, PhC*H*= for major isomer), 6.51 (d, J = 16.1 Hz, CCH= for major isomer), 6.50 (d, J = 16.1 Hz, PhC*H*= for minor isomer), 6.26 (d, J = 16.1 Hz, CCH= for minor isomer), 3.87 (s, C*H*CO_2tBu for minor isomer), 3.71 (s, C*H*CO_2tBu for major isomer), 1.51 (s, *t*Bu for major isomer), 1.19 (s, *t*Bu for minor isomer). − ^{13}C NMR ($CDCl_3$): for a mixture of isomers: δ = 165.44, 165.05, 148.38, 147.98, 139.93, 137.36*, 136.82*, 135.87*, 135.50, 135.27, 134.21*, 133.23*, 129.77*, 129.30*, 128.80*, 128.75*, 126.99*, 126.84*, 126.78*, 123.52*, 123.38*, 123.07*, 122.24*, 121.91*, 83.33, 82.91, 64.64, 64.19, 62.80, 62.44 (CH of oxirane), 28.16, 27.72 (CH_3). − MS (70eV); *m/z* (%): 367 [M^+] (2), 339 (0.6), 311 [$M^+ - Me_2C{=}CH_2$] (20), 294 (5), 283 (2), 266 [$M - CO_2t$Bu$^+$] (58), 250 (18), 238 (13), 220 (16), 189 (36), 178 (7), 165 (11), 150 (55), 144 (47), 131 (4), 115 (9), 105 (15), 91 (14), 77 [Ph^+] (8), 57 [Bu^+] (100). − EIHR: calcd. for $C_{21}H_{21}NO_5$ 367.1419, found 367.1432.

4-Cyano-1-(3-nitrophenyl)-3-phenyl-4-thiophenoxybuten-1-one (**6a**): A solution of chalcone **1** (0.5 g, 1.97 mmol) and thiophenoxyacetonitrile (0.3 g, 1.97 mmol) in THF (10 ml) was added to a solution of *t*BuOK (0.88 g, 7.9 mmol) in THF (40 ml) at −73°C under argon. The mixture was stirred for 15 min. The subsequent work up was as described for carbinol **2a**. Compound **6a** was isolated by column chromatography in 73% yield (0.58 g) as a mixture of 2 isomers in the ratio 1:1 [hexane/EtOAc (5:1) as eluent], m.p. 56°C.

When the system *t*BuOK, DMF, −30°C was used for this reaction compound **6a** was isolated in 49% yield. − IR (KBr): $\tilde{\nu}$ = 2235 cm^{-1} (CN), 1693 (CO), 1613 (Ph), 1531, 1350 (NO_2). − ^1H NMR ($CDCl_3$): δ = 8.75 (m, 1 H), 8.44 (dm, J = 8.2 Hz, 1 H), 8.33 (dm, J = 7.8 Hz, 1 H), 7.69 (t, J = 8.2, 7.8 Hz, 1 H), 7.63−7.51 (m, 2 H), 7.5−7.3 (m, 8 H), 4.35 (d, J = 6.7 Hz, 1 H, CHCN for first isomer), 4.21 (d, J = 5.4 Hz, 1 H, CHCN for second isomer), 4.0−3.6 (m, 3 H). − MS (70 eV); *m/z* (%): 402 [M^+] (0.2), 384 [$M^+ - H_2O$] (0.4), 372 [$M^+ - NO$] (0.1), 298 (0.2), 270 (0.25), 260 (0.4), 252 [$M^+ - NO_2C_6H_4CO$] (19), 237 (78), 210 (5), 206 (6), 178 (3), 167 (6), 150 [$NO_2C_6H_4CO^+$] (100), 131 (7), 109 (18), 104 (17), 76 (8), 65 (4), 51 (3). − EIHR: calcd. for $C_{23}H_{18}N_2O_3S$ 402.1038, found 402.1033.

4-Cyano-7-nitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-one (**6b**) − *A:* A solution of chalcone **1** (1 g, 3.9 mmol) and thiophenoxyacetonitrile (0.58 g, 3.9 mmol) in DMF (20 ml) was added to a solution of KOH (1.1 g, 9.7 mmol) in DMF (20 ml) at 0°C under argon. The mixture was stirred at this temperature for 2 min, poured into ice-cooled diluted aq. HCl (5%) and extracted with EtOAc. The extract was washed with water (3 × 30 ml) and dried with $MgSO_4$. The solvent was evaporated and $CHCl_3$ was added to the residue, the precipitate was filtered off, and washed with $CHCl_3$ (0.45 g of compound **6b**). The solvent from the filtrate was evaporated and from the residue, after purification by column chromatography [hexane/EtOAc (2:1) as eluent], an additional 0.223 g of compound **6b** was obtained. Overall yield of compound **6b** was 58% (0.53 g), m.p. 209−210°C (dec.).

B: A solution of chalcone **1** (1 g, 4 mmol) and thiophenoxyacetonitrile (0.6 g, 4 mmol) in DMSO (10 ml) was added to a mixture of KOH (2.2 g, 40 mmol) in DMSO (15 ml) at 20°C under argon. The mixture was stirred at this temperature for 2 min, poured into diluted aq. HCl (5%) and extracted with EtOAc. The organic extract was washed with water and dried with Na_2SO_4. After evaporation of the solvent, the brown residue was purified by column chromatography to give compounds **6b** (0.474 g, 41%) and **6c** (0.067 g, 5%). − IR (KBr): $\tilde{\nu}$ = 2242 cm^{-1} (CN), 1692 (CO), 1612 (Ph), 1538, 1353 (NO_2). − ^1H NMR ($CDCl_3$): for first isomer: δ = 8.97 (d, J = 2.4 Hz, 1 H), 8.52 (dd, J = 8.5, 2.4 Hz, 1 H), 7.98 (dd, J = 8.5, 0.8 Hz, 1 H), 7.52−7.33 (m, 5 H), 4.50 (dd, J = 11.0, 0.9 Hz, 1 H), 3.73 (ddd, J = 12.5, 11.0, 4.4 Hz, 1 H), 3.20 (dd, J = 17.4, 4.4 Hz, 1 H), 3.04 (dd, J = 17.4, 12.5 Hz, 1 H); for second isomer: δ = 8.99 (d, J = 2.5 Hz, 1 H), 8.49 (dd, J = 8.4, 2.5 Hz, 1 H), 7.69 (d, J = 8.7 Hz, 1 H), 7.53−7.32 (m, 5 H), 4.43 (d, J = 4.2 Hz, 1 H), 3.81 (ddd, J = 13.1, 4.2, 3.6 Hz, 1 H), 3.46 (dd, J = 17.4, 13.1 Hz, 1 H), 3.14 (ddd, J = 17.4, 3.6, 1.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): for first isomer: δ = 192.23, 141.74, 148.8, 138.13, 132.44, 129.97*, 129.58*, 128.95*, 128.58*, 127.13*, 123.14*, 117.57, 44.53*, 44.40 (CH_2), 39.73*; for second isomer: δ = 192.79, 148.63, 142.11, 137.47, 132.67, 130.43*, 129.36*, 128.85*, 128.55*, 127.38*, 123.54*, 116.30, 41.86*, 40.23 (CH_2), 39.34*. − MS (70 eV); *m/z* (%): 292 [M^+] (22), 260 (13), 231 (5), 214 [$M^+ - C_6H_6$] (2.5), 188 (100), 158 (2.5), 142 (11), 130 (8), 114 (22), 104 (6), 77 [Ph^+] (4), 63 (3), 51 (2.5). − EIHR: calcd. for $C_{17}H_{12}N_2O_3$ 292.0847, found 292.0846. − $C_{17}H_{12}N_2O_3$ (292.29): calcd. C 69.85, H 4.13, N 9.58, found C 69.82, H 4.01, N 9.34.

4-Cyano-7-nitro-3-phenylnaphth-1-ol (**6c**) was obtained as orange crystals with m.p. 238−240°C (dec.) in 42% yield according to procedure *B* (described above for compound **6b**) when the mixture was stirred for 1 h and $CHCl_3$ was used as the eluent.

Naphthol **6c** was isolated in 38% yield when this reaction was carried out at 25−30°C for 5 min. When the reaction mixture was stirred under O_2 at 20°C for 5 min, naphthol **6c** was isolated by column chromatography in 47% yield [hexane/EtOAc (3:1) as eluent].

A solution of **6a** (0.5 g, 1.2 mmol) in DMSO (2 ml) was added to a mixture of KOH (0.7 g, 12 mmol) in DMSO (4 ml) at 20°C. The reaction mixture was stirred for 5 min. The subsequent work up was carried out according to procedure *B* (as described for compound **6b**). Purification of the residue by column chromatography led to **6c** (0.18 g, 52%). − IR (KBr): $\tilde{\nu}$ = 3587, 3487 cm^{-1} (OH), 2217 (CN), 1496, 1337 (NO_2). − ^1H NMR ([D_6]acetone): δ = 9.17 (d, J = 2.3 Hz, 1 H), 8.52 (dd, J = 9.3, 2.3 Hz, 1 H), 8.34 (d, J = 9.3 Hz, 1 H), 7.77−7.70 (m, 2 H), 7.65−7.56 (m, 3 H), 7.25 (s, 1 H), 3.1 (br. s, 1 H). − ^{13}C NMR ([D_6]acetone): δ = 159.61, 151.86, 146.34, 139.21, 138.08, 130.22*, 129.79*, 129.61*, 127.83*, 123.47*, 120.49*, 117.62 (CN), 112.43*. − MS (70 eV); *m/z* (%): 290 [M^+] (100), 274 (2), 260 [$M^+ - NO$] (13), 243 (3), 232 (22), 216 (36),

203 (4), 189 (12), 177 (2), 107 (2.5), 94 (3), 63 (2), 51 (1). − EIHR: calcd. for $C_{17}H_{10}N_2O_3$ 290.0691, found 290.0688.

4-Cyano-4-(N,N-dimethylaminodithiocarbamyl)-1-(3-nitrophenyl)-3-phenylbutan-1-one (**7a**) was obtained according to the procedure described for compound **6a** and isolated in 64% yield as a mixture of 2 isomers in the ratio 1.3:1 [hexane/EtOAc (3:1) as eluent], m.p. 129−130°C. − IR (KBr): $\tilde{\nu}$ = 2229 cm^{-1} (CN), 1695 (CO), 1612 (Ph), 1526, 1372 (NO_2), 1347, 1245 (SO_2). − ^1H NMR ($CDCl_3$): δ = 8.75 (t, *J* = 1.8 Hz, 1 H), 8.43 (dm, *J* = 8.2 Hz, 1 H), 8.27 and 8.26 (2 dm, *J* = 7.8 Hz, 1 H), 7.68 (t, *J* = 8.2, 7.8 Hz, 1 H), 7.51−7.30 (m, 5 H), 5.80 (d, *J* = 7.2 Hz, CHCN for major isomer) and 5.60 (d, *J* = 4.8 Hz, CHCN for minor isomer), 4.14 (m, PhC*H* for minor isomer), 3.96 (dd, *J* = 13.5, 7.2 Hz, PhC*H* for major isomer), 3.85−3.65 (m, 2 H), 3.57 (s, 3 H, CH_3 for major isomer), 3.54 (s, 3 H, CH_3, for minor isomer), 3.32 (s, 3 H, CH_3 for major isomer), 3.37 (s, 3 H, CH_3, for minor isomer). − MS (70 eV); *m*/*z* (%): 414 [M + H^+] (0.2), 413 [M^+] (0.1), 379 (0.2), 362 (0.5), 293 [M^+ − SC(S)NMe_2] (3), 263 (5), 252 (8), 206 (3), 160 (5), 150 [$NO_2C_6H_4CO^+$] (35), 121 [$Me_2NC(S)SH$] (100), 104 (14), 88 [Me_2NCS^+] (86), 76 (12), 44 [Me_2N^+] (33). − EIHR: calcd. for $C_{20}H_{19}N_3O_3S_2$ 413.08648, found 413.08650, calcd. for [M + H^+] 414.09461 ($C_{20}H_{20}N_3O_3S_2$), found 414.09450. − $C_{20}H_{19}N_3O_3S_2$ (413.52): calcd. C 58.09, H 4.63, N 10.16, S 15.50, found C 58.13, H 4.63, N 9.77, S 15.50.

5-Cyano-2-dimethylamino-2-mercapto-3-(3-nitrobenzoyl)-4-phenyltetrahydrothiophene (**7b**) was obtained according to procedure *B* (as described for compound **6c**) and isolated ($CHCl_3$ as eluent) in 47% yield as a mixture of 2 isomers in the ratio 6:1, m.p. 54°C.

Compound **7b** was prepared from **7a** in 57% yield according to procedure *B* (as described for compound **6c**) and purified by column chromatography using hexane/EtOAc (2:1) as eluent. − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (SH), 2238 (CN), 1529, 1348 (NO_2). − ^1H NMR ($CDCl_3$): for major isomer: δ = 8.56 (t, *J* = 2.0 Hz, 1 H), 8.20 (dm, *J* = 8.2 Hz, 1 H), 8.10 (dm, *J* = 7.8 Hz, 1 H), 7.88 (s, 1 H, SH), 7.59 (t, *J* = 8.2, 7.8 Hz, 1 H), 7.41 (m, 5 H), 4.8 (dd, *J* = 11.3, 8.0 Hz, 1 H), 4.67 (d, *J* = 8.0 Hz, 1 H), 4.52 (d, *J* = 11.3 Hz, 1 H), 3.07 (s, 3 H), 2.64 (s, 3H); for minor isomer: δ = 8.64 (t, *J* = 2.1 Hz, 1 H), 8.3−8.2 (m, 2 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 4.89 (dd, *J* = 12.2, 7.0 Hz, 1 H), 4.55 (d, *J* = 7.0 Hz, 1 H), 4.55 (d, *J* = 12.2 Hz, 1 H), 3.17 (s, 3 H), 2.73 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 196.19, 148.38, 142.82, 135.85, 132.79*, 129.94*, 129.51*, 129.17*, 127.64*, 123.81*, 121.31*, 119.29, 94.86, 66.06*, 59.44*, 45.00 (CH_3), 41.90 (CH_3), 37.97*. − MS (70 eV); *m*/*z* (%) for major isomer: 413 [M^+] (1), 393 (0.5), 380 (11), 362 (13), 252 (33), 237 (40), 229 (14), 223 (7), 203 (17), 190 (13), 178 (5), 167 (6), 158 (18), 150 [$NO_2C_6H_4CO^+$] (100), 135 (26), 128 (38), 120 (23), 115 (17), 109 (19), 104 (33), 88 [Me_2NCS^+] (42), 84 (75) 77 [Ph^+] (25), 65 (23), 44 [Me_2N^+] (28). − EIHR: calcd. for $C_{20}H_{19}N_3O_3S_2$ 413.0867, found 413.0865.

5-Cyano-2-dimethylamino-3-(3-nitrobenzoyl)-4-phenylthiophene (**7c**). To a mixture of **7b** (0.089 g, 0.22 mmol) in dry THF (2 ml) was added Et_3N (0.066 g, 0.66 mmol). The mixture was cooled and at −30°C a solution of $MeSO_2Cl$ (0.042 g, 0.33 mmol) in dry THF (0.5 ml) was added. The mixture was stirred while the temperature was allowed to reach 20°C and stirred at this temperature for 24 h. The precipitate was then filtered off and washed with ether, the organic layer was diluted with ether and washed successively with water, 5% aq. HCl, water, and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography [hexane/EtOAc (3:1) as eluent] to give thiophene **7c** (0.036 g, 44%), m.p. 147−148°C (MeOH). − IR (KBr) $\tilde{\nu}$ = 2201 cm^{-1} (CN), 1649 (CO), 1531, 1348 (NO_2). − ^1H NMR ($CDCl_3$): δ = 8.04 (m, 1 H), 8.02 (dm, *J* = 7.0 Hz, 1 H), 7.67−7.5 (m, 2 H), 7.45−7.32 (m, 3 H), 7.31−7.2 (m, 2 H), 3.00 (s, 6 H). − ^{13}C NMR ($CDCl_3$): δ = 192.35, 164.35, 150.72, 147.73, 138.27, 135.23, 134.86*, 133.50*, 129.57*, 129.43*, 128.54*, 124.09*, 123.46*, 116.85*, 114.81*, 44.97 (CH_3). − MS (70 eV); *m*/*z* (%): 377 [M^+] (86), 360 (100), 343 (5), 330 (9), 314 (13), 300 (28), 91 (4), 81 (2), 58 (5), 43 (14). − EIHR calcd. for $C_{20}H_{15}O_3N_3S$ 377.0834, found 377.0828.

4-Chloro-1-(3-nitrophenyl)-3-phenyl-4-(p-tosyl)butan-1-one (**8a**) was obtained by the procedure described for compound **6a** and isolated in 73% yield as a mixture of 2 isomers in the ratio 1:1 [hexane/EtOAc (4:1) as eluent], m.p. 149°C. − IR (KBr): for first isomer: $\tilde{\nu}$ = 1694 cm^{-1} (CO), 1525, 1352 (NO_2), 1326, 1151 (SO_2); for second isomer: $\tilde{\nu}$ = 1693 cm^{-1} (CO), 1531, 1351 (NO_2), 1323, 1151 (SO_2). − ^1H NMR ($CDCl_3$) for first isomer: δ = 8.73 (t, *J* = 1.9 Hz, 1 H), 8.43 (dm, *J* = 8.2 Hz, 1 H), 8.31 (dm, *J* = 7.8 Hz, 1 H), 7.87 (dm, *J* = 8.4 Hz, 2 H), 7.69 (t, *J* = 8.2, 7.8 Hz, 1 H), 7.44−7.24 (m, 7 H), 4.81 and 4.85−4.76 (d with *J* = 1.3 Hz and m, 2 H, CHCl and PhCH respectively), 4.05 (dd, *J* = 18.0, 3.3 Hz, 1 H), 3.86 (dd, *J* = 18.0, 9.7 Hz, 1 H), 2.48 (s, 3 H); for second isomer: δ = 8.74 (t, *J* = 1.9 Hz, 1 H), 8.42 (dm, *J* = 8.1 Hz, 1 H), 8.27 (dm, *J* = 7.8 Hz, 1 H), 7.76 (dm, *J* = 8.3 Hz, 2 H), 7.67 (t, *J* = 8.1, 7.8 Hz, 1 H), 7.5−7.2 (m, 7 H), 5.36 (d, *J* = 6.0 Hz, 1 H), 4.51 (m, 1 H), 3.94 (dd, *J* = 18.3, 6.8 Hz, 1 H), 3.7 (dd, *J* = 18.3, 6.3 Hz, 1 H), 2.44 (s, 3 H). − ^{13}C NMR ($CDCl_3$): for first isomer: δ = 194.31, 148.31, 146.05, 139.27, 137.70, 133.61, 132.64, 129.91, 129.86, 129.55, 128.83, 127.87 (br.), 127.39, 122.82, 78.71, 39.18, 38.88, 21.66. − MS (70 eV); *m*/*z* (%): for mixture of isomers: 458 [M + H^+] (0.04), 427 [M^+ − NO] (0.54), 302 [M^+ − $SO_2C_6H_4CCH_3$] (19), 266 (19), 236 (7), 220 (1), 191 (2), 150 [$NO_2C_6H_4CO^+$] (100), 139 (2), 120 (10), 104 (15), 91 (10), 76 [$C_6H_4^+$] (7), 65 (3). − LSIMS: 458 [M + H^+], 480 [M + Na^+].

4-Chloro-1-(3-nitrophenyl)-3-phenyl-4-(p-tosyl)butan-1-ol (**8b**). A solution of $NaBH_4$ (0.015 g, 0.38 mol) in EtOH (2 ml) and water (0.5 ml) was added dropwise to a stirred solution of sulfone **8a** (0.5 g, 1.1 mmol) in a mixture of THF (10 ml) and EtOH (3 ml) under argon at 20°C. The mixture was stirred for 1 h, then diluted aq. HCl (2%) was added until no more gas was formed. The neutralized mixture was extracted with CH_2Cl_2, the extract was washed with water and dried with $MgSO_4$. The solvent was evaporated in vacuo, the crude product was purified by column chromatography [hexane/EtOAc (4:1) as eluent] to give 0.38 g of alcohol **8b** (76%) as a mixture of four stereoisomers. −IR (KBr): $\tilde{\nu}$ = 3506 cm^{-1} (OH), 1528, 1349 (NO_2), 1323, 1149 (SO_2). − ^1H NMR ($CDCl_3$): for the mixture of first and second isomers in the ratio 2:1: δ = 8.17−8.07 (m, 2 H), 7.87 and 7.72 (2 dm, *J* = 8.3 Hz, 2 H), 7.52 (t, *J* = 8.1, 7.7 Hz, 1 H), 7.46−7.2 (m, 8 H), 4.91 (m, 1 H), 4.76 and 4.64 (2 d, *J* = 1.9 Hz for minor and *J* = 1.7 Hz for major isomers respectively, 1 H), 4.43 and 3.88 (2 m, 1 H), 2.77 and 2.70 (2 dd, *J* = 6.6, 4.5 Hz, 1 H), 2.49 (m, 1 H), 2.46 (s, 3 H) and 2.45 (s, 3 H), 2.34 (m, 1 H); for third isomer: δ = 8.12 (m, 1 H), 8.1 (dm, *J* = 7.7 Hz, 1 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 7.61 (dm, *J* = 7.8 Hz, 1 H), 7.54−7.25 (m, 9 H), 5.01 (d, *J* = 5.0 Hz, 1 H), 4.49 (m, 1 H), 4.32 (ddd, *J* = 9.8, 4.9, 5.0 Hz, 1 H), 2.43 (s, 3 H), 2.31 (m, 2 H), 2.19 (d, *J* = 4.6 Hz, 1 H); for fourth isomer: δ = 8.14 (dm, *J* = 8.2 Hz, 1 H), 8.12 (m, 1 H), 7.68 (dm, *J* = 8.3 Hz, 2 H), 7.64 (dm, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.7, 7.2 Hz, 1 H), 7.32 (s, 5 H), 7.29 (dm, *J* = 8.3 Hz, 2 H), 5.12 (d, *J* = 5.9 Hz, 1 H), 4.75 (m, 1 H), 3.79 (m, 1 H), 2.51 (m, 2 H), 2.43 (s, 3 H). − ^{13}C NMR ($CDCl_3$): for a mixture of first and second isomers: δ = 148.04, 147.94, 146.84, 145.89, 145.46, 139.66, 138.94, 132.68, 132.33, 131.74, 129.77, 129.70, 129.53, 129.38, 129.30, 129.01, 128.96,

128.30, 127.98 (br.), 127.91, 127.55, 122.49, 122.26, 121.24, 120.47, 79.59, 79.52, 71.34, 70.06, 40.95, 40.75, 39.05, 38.48, 21.60. − MS (70 eV); *m*/*z* (%): for a mixture of first and second isomers: 459 [M^+] (0.8), 442 [M^+ − OH] (0.34), 429 [M^+ − NO] (0.7), 308 (3), 286 (20), 268 (5), 250 (10), 204 (12), 152 [$NO_2C_6H_4CHOH^+$] (100), 134 (35), 117 (40), 105 (22), 91 (33), 77 [Ph^+] (8), 65 (5). − EIHR: calcd. for $C_{23}H_{22}ClNO_5S$ 459.0907, found 459.0908, calcd. for [M^+ − OH] 442.0879 ($C_{23}H_{21}ClNO_4S$), found 442.0880. − $C_{23}H_{22}ClNO_5S$ (459.95) calcd. C 60.06, H 4.73, Cl 7.70, N 3.05, S 6.97, found C 60.13, H 4.96, Cl 7.66, N 3.19, S 6.98.

7-Nitro-3-phenyl-4-(p-tosyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**8c**). To a solution of *t*BuOK (1.1 g, 10 mmol) in a mixture of THF (5 ml) and DMF (5 ml) was added a solution of crude alcohol **8b** (1.8 g, 4 mmol) in a mixture of DMF (2 ml) and THF (2 ml) at −73°C under argon and the mixture was stirred for 2 min. The mixture was then poured into ice-cooled diluted hydrochloric acid (5%) and extracted with EtOAc. The organic phase was washed with water and dried with $MgSO_4$. The solvent was evaporated in vacuo and $CHCl_3$ (5 ml) was added to the residue. After cooling, the precipitate was filtered off and washed with $CHCl_3$ (alcohol **8c**, 0.70 g). The solvent from the filtrate was evaporated and, from the residue, an additional amount of alcohol **8c** (0.54 g) was isolated by column chromatography [hexane/EtOAc (3:1) as eluent]. Overall yield of 7-nitro-3-phenyl-4-(*p*-tosyl)-1,2,3,4-tetrahydronaphthalen-1-ol (1.24 g, 73%) as a mixture of three stereoisomers. For first isomer: IR (KBr): $\tilde{\nu}$ = 3454 cm^{-1} (OH), 1524, 1344 (NO_2), 1289, 1138 (SO_2). − ^1H NMR ($CDCl_3$, 500 MHz): δ = 8.39 (d, *J* = 2.4 Hz, 1 H), 8.11 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.59 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 1 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.17 (m, 3 H), 6.85 (m, 2 H), 4.81 (m, 1 H), 4.71 (d, *J* = 4.1 Hz, 1 H), 3.98 (m, 1 H), 3.46 (br. s, 1H), 2.52 (dt, *J* = 5.7, 13.9 Hz, 1 H), 2.46 (s, 3 H), 1.94 (ddd, *J* = 13.9, 10.2, 3.4 Hz, 1 H). − For second isomer: m.p. 208°C. − IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1} (OH), 1525, 1344 (NO_2), 1306, 1140 (SO_2). − ^1H NMR ($CDCl_3$): δ = 8.58 (d, *J* = 2.4 Hz, 1 H), 8.02 (dd, *J* = 8.4, 2.4 Hz, 1 H), 7.45 (dm, *J* = 8.4 Hz, 2 H), 7.29−7.20 (m, 5 H), 7.10−7.0 (m, 3 H), 4.95 (m, 1 H), 4.56 (d, *J* = 3.8 Hz, 1 H), 3.97 (ddd, *J* = 11.5, 6.7, 3.8 Hz, 1 H), 2.57 (ddd, *J* = 12.5, 6.7, 4.4 Hz, 1 H), 2.46 (s, 3 H), 2.19 (d, *J* = 6.4 Hz, 1 H), 1.72 (dd, *J* = 12.5, 11.5 Hz, 1 H). − For third isomer: m.p. 199°C. − IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (OH), 1523, 1347 (NO_2), 1285, 1139 (SO_2). − ^1H NMR ([D_6]acetone): δ = 8.47 (d, *J* = 2.3 Hz, 1 H), 8.09 (dd, *J* = 8.5, 2.3 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 1 H), 7.35−7.25 (m, 4H), 7.17−7.09 (m, 5 H), 5.34 (d, *J* = 4.0 Hz, 1 H), 5.25 (m, 1 H), 4.82 (d, *J* = 5.1 Hz, 1 H), 3.89 (dm, *J* = 13.8 Hz, 1 H), 3.48 (td, *J* = 13.8, 5.3 Hz, 1 H), 2.35 (s, 3 H), 2.29 (m, 1 H). − ^{13}C NMR ([D_6]acetone): δ = 149.05, 144.64, 144.00, 140.60, 138.75, 136.98, 135.13*, 130.08*, 129.21*,128.99*,128.75*, 127.19*, 125.68*, 121.45*, 69.62*, 66.37*, 37.30*, 31.76 (CH_2), 21.37 (CH_3). − MS (70 eV); *m*/*z* (%): 267 (60), 250 [M^+ − H_2O − Ts] (100), 237 (26), 219 (35), 204 [M^+ − H_2O − Ts − NO_2] (95), 191 (25), 178 (14), 165 (17), 139 (18), 115 (15), 105 (22), 91 (78), 77 [Ph^+] (19), 65 (20), 51 (18). − LSIMS: 446 [M + Na^+], 250 [M^+ − H_2O − Ts]. − $C_{23}H_{21}NO_5S$ (423.50): calcd. C 65.23, H 4.99, N 3.30, S 7.57, found C 64.87, H 5.07, N 2.87, S 7.61.

1-Methylsulfonato-7-nitro-3-phenyl-4-(p-tosyl)-1,2,3,4-tetrahydronaphthalene (**8d**): To a solution of alcohol **8c** [mixture of 2 stereoisomers (2:1), 0.119 g, 0.24 mmol] in dry THF (5 ml) containing Et_3N (0.021 g, 0.36 mmol) was added $MeSO_2Cl$ (0.034 g, 0.26 mmol) at −20°C. The mixture was stirred while the temperature was allowed to reach 20°C and stirred at 20°C for 30 min. The resulting precipitate was filtered off and washed with ether. The organic phase was diluted with ether and washed successively with water, 5% aq. HCl, water, and dried with $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography [hexane/EtOAc (3:1) as eluent] to give ether **8d** (0.072 g, 62%) as a mixture of 2 stereoisomers in the ratio 2:1, m.p. of this mixture 106−108°C, and 2-nitro-6-phenylnaphthalene (0.004 g, 7%). − For **8d**: IR (KBr): $\tilde{\nu}$ = 1527, 1339 cm^{-1} (NO_2), 1324, 1147 (SO_2). − ^1H NMR ($CDCl_3$): δ = 8.42 and 8.39 (2 d, *J* = 2.3 Hz, 1 H for minor and major isomer respectively), 8.28 (dd, *J* = 8.7, 2.3 Hz, 1 H for minor isomer), 8.13 (dd, *J* = 8.2, 2.3 Hz, 1 H for major isomer), 7.8 (d, *J* = 8.7 Hz, 1 H for minor isomer), 7.58 and 7.48 (2 dm, *J* = 8.3 Hz, 2 H), 7.31−7.16 (m, 5 H + 1 H for major isomer), 6.98 (m, 2 H for major isomer), 6.89 (m, 2 H for minor isomer), 5.72 (m, 1 H), 4.87 and 4.6 (2 d, with *J* = 4.9 Hz for minor and *J* = 3.7 Hz for major isomers respectively, 1 H), 3.97 (m, 1 H), 3.11 and 2.99 (2 s, 3 H, for major isomer and minor isomer respectively), 3.0−2.62 (m, 1 H), 2.46 and 2.42 (2 s, 3 H for major isomer and minor isomer respectively), 2.23−1.94 (m, 1 H_2). − LSIMS: 524 [M + Na^+].

2-Nitro-6-phenylnaphthalene (**8e**). To a solution of mesylate **8d** (mixture of isomers in the ratio 2:1, 0.060 g, 0.12 mmol) in THF (2 ml) was added Et_3N (0.021 g, 0.36 mmol) in THF (1 ml) and the mixture was stirred at 40°C for 24 h. The mixture was cooled to room temperature, diluted with ether and washed successively with water, 5% aq. HCl, water, and dried with $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography [hexane/EtOAc (10:1) as eluent] to give 2-nitro-6-phenylnaphthalene (**8e**) (0.024 g, 73%), m.p. 124°C (EtOH). − IR (KBr): $\tilde{\nu}$ = 1527, 1339 cm^{-1} (NO_2). − ^1H NMR ($CDCl_3$): δ = 8.82 (d, *J* = 2.3 Hz, 1 H), 8.29 (dd, *J* = 9.0, 2.3 Hz, 1 H), 8.15 (s, 1 H), 8.13 (d, *J* = 8.6 Hz, 1 H), 8.03 (d, *J* = 9.0 Hz, 1 H), 7.93 (dd, *J* = 9.0, 2.3 Hz, 1 H), 7.79−7.73 (m, 2H), 7.60−7.45 (m, 3H). − MS (70 eV); *m*/*z* (%): 249 [M^+] (100), 219 [M^+ − NO] (26), 203 [M^+ − NO_2] (45), 202 [M^+ − HNO_2] (84), 191 (39), 101 (14), 88 (11). − $C_{16}H_{11}NO_2$ (249.28): calcd. C 77.09, H 4.45, N 5.62, found C 77.09, H 4.29, N 5.72.

3-Benzoyl-2-(N,N-dimethylamino)-5-cyano-2-mercapto-4-phenyltetrahydrothiophene (**9b**) was obtained according to procedure *B* (as described for compound **6c**) and isolated in 43% yield as a mixture of 2 isomers in the ratio 21:1 [hexane/EtOAc (3:1) as eluent]. − IR (KBr): $\tilde{\nu}$ = 3195 cm^{-1} (SH), 2233 (CN). − ^1H NMR ($CDCl_3$): for major isomer: δ = 7.72 (m, 2 H), 7.46 (m, 1 H), 7.37 (m, 8 H), 4.84 (dd, *J* = 11.5, 8.2 Hz, 1 H), 4.55 (d, *J* = 8.2 Hz, 1 H), 4.45 (d, *J* = 11.5 Hz, 1 H), 3.07 (s, 3 H), 2.53 (s, 3 H); for minor isomer: δ = 7.84 (m, 2 H), 7.48−7.25 (m, 8 H), 6.90 (s, 1 H, SH), 4.9 (dd, *J* = 12.3, 7.0 Hz, 1 H), 4.50 (d, *J* = 7.0 Hz, 1 H), 4.50 (d, *J* = 12.3 Hz, 1 H), 3.17 (s, 3 H), 2.59 (s, 3 H). − ^{13}C NMR ($CDCl_3$): for major isomer: δ = 196.57, 140.37, 136.76, 129.39*, 128.86*, 128.79*, 128.67*, 127.57*, 126.24*, 119.45, 96.12, 67.12*, 59.52*, 44.97 (CH_3), 41.56 (CH_3), 38.13*; for minor isomer: δ = 196.03, 142.33, 134.88, 129.01, 128.82 (br), 128.70, 128.42, 126.81, 119.00, 94.34, 63.47, 57.62, 45.10 (CH_3), 41.39 (CH_3), 38.82. − LSIMS for major isomer: 391 [M + Na^+], 369 [M + H^+], 351 [M^+ − H_2O + H], 335 [M^+ − H_2O − CH_3]. − LSIMSHR: calcd. for [M^+ + H] 369.1095 ($C_{20}H_{21}N_2OS_2$), found 369.1094. − $C_{20}H_{20}N_2OS_2$ (368.52): calcd. C 65.18, H 5.47, N 7.60, S 17.39; found C 65.17, H 5.49, N 7.72, S 17.31.

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