Vicarious Nucleophilic Substitution of (Chloroalkyl)heterocycles with Nitroarenes

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Keywords: Heterocycles / Vicarious nucleophilic substitution / Arenes / Regioselective synthesis

The vicarious nucleophilic substitution of potassium carbanions of the (chloromethyl)pyridines **1a** and **1b**, (chloromethyl)benzothiazole **1c**, (chloromethyl)thiazole **1d**, (chloroethyl)thiazole **1e** and (chloroethyl)benzothiazole **1f** with nitroarenes, leading to nitrobenzyl heterocycles **2** and **4**–**14** has been studied.

Introduction

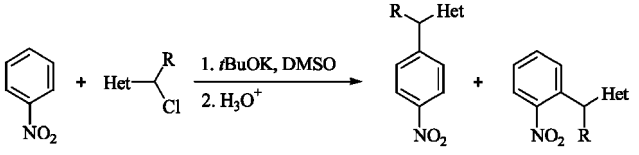
Nucleophilic substitution of hydrogen in an aromatic system is a versatile tool for functionalizing carbon and heterocyclic arenes.[1−3] Among the many variants which have been developed for the nucleophilic substitution of arenes with hydrogen, vicarious nucleophilic substitution (VNS), developed by Makosza and co-workers, has become a good method for the introduction of carbon, oxygen and nitrogen functional groups by the displacement of hydrogen from electron-deficient aromatic and heteroaromatic systems.[4−6] Vicarious nucleophilic substitution usually occurs when the nucleophile has a good leaving group at the nucleophilic centre.

In a previous paper we reported that carbanions of (chloroalkyl)oxazolines couple efficiently with nitroarenes to furnish (nitrobenzyl)oxazolines according to a VNS process.[7] In order to ascertain the generality of the VNS reaction of metallated (chloroalkyl)heterocycles, we embarked in a study focused on the reaction of carbanions of chloroalkyl derivatives of thiazole, benzothiazole and pyridine with nitroarenes.

Results and Discussion

When a mixture of nitrobenzene (1.1 equiv.) and 4-(chloromethyl)pyridine (**1a**, 1 equiv.) was added to a suspension of potassium *tert*-butoxide (3 equiv.) in dimethyl sulfoxide (DMSO) a dark red solution resulted. An acidic quench (satd. aq. NH_4Cl) gave, with poor regioselectivity, the (nitrobenzyl)pyridines **2a** and **3a**, which likely originated from the nucleophilic attack of the anion of **1a** at the positions *ortho* and *para* to the nitro group of the nitrobenzene. Comparable results were obtained when a mixture of nitrobenzene and 2-(chloromethyl)pyridine (**1b**), 2-(chloromethyl)benzothiazole (**1c**) or 2-(chloromethyl)-4-methylthiazole (**1d**) was added to a suspension of potassium *tert*-

Table 1. Reactions of nitrobenzene with **1a**−**f**



1a–f **2a–f** **3a–d**

Alkyl chloride	Het	R	% Total yield [a]	Products	Ratio of isomers [b] [%]
1a		H	65	**2a, 3a**	57:43
1b		H	66	**2b, 3b**	60:40
1c		H	46	**2c,3c**	60:40
1d		H	71	**2d, 3d**	58:42
1e		CH_3	41	**2e**	–
1f		CH_3	40	**2f**	–

[a] Yields of isolated products. [b] Determined by GC and ^1H NMR spectroscopy

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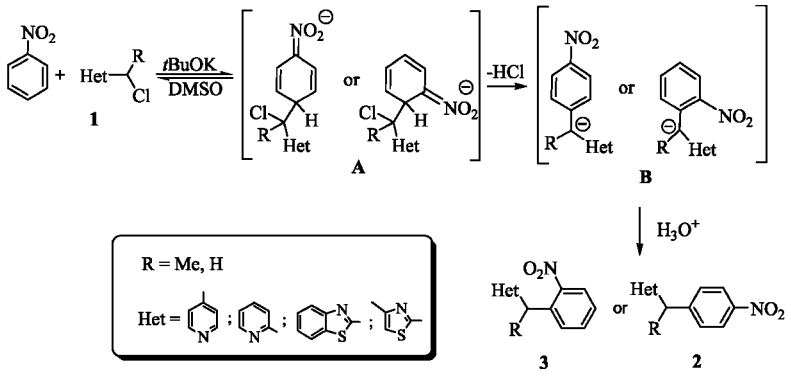
  DOI: 10.1002/ejoc.200300806



Scheme 1

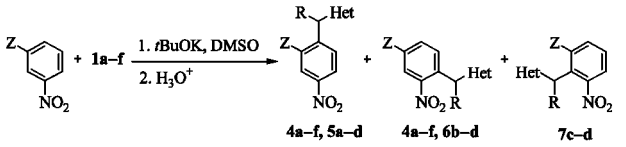
butoxide (3 equiv.) in DMSO. Quenching of the reaction mixture with satd. aq. NH_4Cl afforded (nitrobenzyl)-heterocycles **2b** + **3b**, **2c** + **3c**, and **2d** + **3d**, respectively, although with poor regioselectivity (Table 1).

In contrast, the reaction of nitrobenzene with the anions of 2-(1-chloroethyl)-4-methylthiazole (**1e**) and 2-(1-chloroethyl)benzothiazole (**1f**), leading to the formation of compounds **2e** and **2f**, respectively, was completely *para*-regioselective. These results can reasonably be accounted for in terms of a vicarious nucleophilic substitution mechanism, as illustrated in Scheme 1.

According to this mechanism, the anion of **1**, generated by deprotonation with *t*BuOK, would rapidly and reversibly add to the nitrobenzene at the hydrogen-bearing position, *ortho* and/or *para* to the nitro group, resulting in the formation of the σ^H adduct **A**. Base-induced β-elimination of HCl from the σ^H adduct **A**, which is likely the rate-limiting step of the reaction,[8,9] would then take place, to generate the benzylic carbanion **B** and subsequently compounds **2** and **3** upon acidic quenching. It has already been reported[10] that the orientation of the substitution is strongly influenced by the steric factor; inspection of the data listed in Table 1 shows, indeed, that the introduction of a methyl group on to the halogen-bearing carbon atom (as in **1e** and **1f**) suffices to make the reaction completely *para*-regioselective. The poor regioselectivity of the reaction of anions **1a**−**d** is intriguing, because the *para* isomer formation should be favoured both for steric and stability reasons. In our case, the formation of the *ortho* isomer can be explained by the fact that the addition of **1a**−**d** to the *ortho* position of nitrobenzene proceeds faster than to the *para* position (kinetic control). The preferential formation of the *ortho* regioisomer (with the respect to the alkoxy group) in the amination of 1-alkoxy-3,5-dinitrobenzenes has been ascribed to the higher thermodynamic stability of the corresponding σ^H complex.[11−12]

The above VNS reaction of **1a**−**f** anions takes place also with other nitroarenes. As shown in Table 2, treatment of 1,3-dinitrobenzene with the anions of (chloroalkyl)heterocycles **1a**−**f** afforded (dinitrophenylmethyl)- and (dinitrophenylethyl)heterocycles **4a**−**f**. Unfortunately, chemical yields were often rather poor, even when the temperature was changed. The reactions of **1b**, **1c**, and **1d** with 3-chloronitrobenzene afforded mixtures of regioisomers **5b** + **6b**, **5c** + **6c** + **7c**, and **5d** + **6d** + **7d**, respectively, whereas the reaction of **1a** led regioselectively to compound **5a**. In the case of 4-(chloromethyl)pyridine (**1a**), the *para*-substituted isomer **5a** was the exclusive product, and in the cases of **1b**, **1c**, and **1d**, the *para*-substituted isomers **5b**, **5c**, **5d** were the major products. When three isomers were formed, the less hindered *ortho* isomer predominated over the more hin-

Table 2. Reactions of *m*-substituted nitrobenzenes with **1a**−**f**



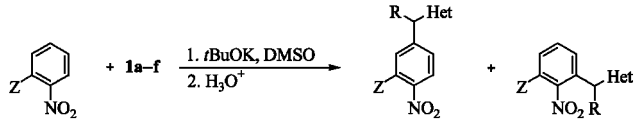
Alkyl chloride	Z	Het	R	% Total yield [a]	Products	Ratio of isomers [b] [%]
1a	NO_2		H	20	**4a**[c]	–
1b	NO_2		H	38	**4b**[c]	–
1c	NO_2		H	54	**4c**[c]	–
1d	NO_2		H	20	**4d**[c]	–
1e	NO_2		CH_3	12	**4e**[c]	–
1f	NO_2		CH_3	25	**4f**[c]	–
1a	Cl		H	45	**5a**	–
1b	Cl		H	41	**5b, 6b**	85:15
1c	Cl		H	77	**5c, 6c, 7c**	98:traces:traces
1d	Cl		H	69	**5d, 6d, 7d**	77:16:7

[a] Yields of isolated products. [b] Determined by GC and ^1H NMR spectroscopy. [c] The Z = NO_2 isomers **5** and **6** are identical, and correspond to **4**.

dered *ortho'* isomer (as in the reaction of **1d**), whereas both isomers were found in traces in the reaction of **1c**.

Replacement of hydrogen in 1,2-dinitrobenzene and 2-chloro-1-nitrobenzene could occur at both the *para* and *ortho* positions with respect to the nitro group, giving two isomeric products. The reaction, however, proceeds in a quite regioselective way, with the prevalence of the *para* substituted product. However, the reaction with 2-(chloromethyl)-benzothiazole (**1c**) afforded only the *ortho*-hydrogen substitution product **9c** (Table 3).

Table 3. Reactions of *o*-substituted nitrobenzenes with **1a−f**

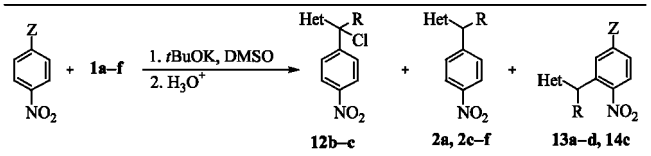


Alkyl chloride	Z	Het	R	% Total yield [a]	Products	Ratio of isomers [b] [%]
1a	NO_2		H	34	**8a**	–
1b	NO_2		H	68	**8b, 9b**	93:7
1c	NO_2		H	30	**9c**	–
1d	NO_2		H	25	**8d, 9d**	98:traces
1e	NO_2		CH_3	38	**8e**	–
1a	Cl		H	40	**10a**	–
1b	Cl		H	40	**10b**	–
1c	Cl		H	28	**10c, 11c**	98:traces
1d	Cl		H	45	**10d, 11d**	77:23
1e	Cl		CH_3	30	**10e**	–
1f	Cl		CH_3	64	**10f**	–

[a] Yields of isolated products. [b] Determined by GC and ^{1}H NMR spectroscopy.

As expected, when the carbanions of heterocycles **1a−d** were treated with 4-chloronitrobenzene, the VNS reaction occurred exclusively *ortho* to the nitro group to give compounds **13a−d**. Exceptionally, the anion of 2-(1-chloroethyl)-4-methylthiazole (**1e**) reacted with 4-chloronitrobenzene to generate compound **2e**, which is likely to derive from an S_NAr process involving the replacement of the chlorine *para* to the nitro group followed by the *t*BuOK-induced reduction of the chlorobenzylic group. All this can be explained by the well established reactivity of 4-chloronitrobenzene with nucleophiles and the reducing ability of *t*BuOK (Table 4).

Table 4. Reactions of *p*-substituted nitrobenzenes with **1a−f**



Alkyl chloride	Z	Het	R	% Total yield [a]	Products	Ratio of isomers [b] [%]
1a	NO_2		H	41	**2a**	–
1b	NO_2		H	61	**12b**	–
1c	NO_2		H	67	**12c, 2c**	16:84
1d	NO_2		H	60	**2d**	–
1e	NO_2		CH_3	50	**2e**	–
1f	NO_2		CH_3	48	**2f**	–
1a	Cl		H	86	**13a**	–
1b	Cl		H	53	**13b**	–
1c	Cl		H	70	**13c**	–
1d	Cl		H	41	**13d**	–
1e	Cl		CH_3	20	**2e**	–
1c	OCH_3		H	35	**14c**	–

[a] Yields of isolated products. [b] Determined by GC and ^{1}H NMR spectroscopy.

The dehalogenation of the S_NAr product has been reported in the reaction of carbanions of (chloromethyl)sulfones with fluoronitrobenzenes.[10a] The anion of 2-(chloromethyl)benzothiazole (**1c**) was treated with *p*-nitroanisole to generate compound **14c**, in accordance with the above-mentioned pattern for *para*-substituted nitrobenzenes.

A completely different pattern was observed when the anions of **1a−f** were reacted with 1,4-dinitrobenzene. The products, compounds **12** and **2**, are very likely to be the S_NAr products; one of the two nitro groups could be displaced by the anion of the heterocycle used (the ability of NO_2 to act as a leaving group in a S_NAr process is well-known[1]). Compounds **2** might be the result of the reduction of **12** by the excess of *t*BuOK.[13]

Conclusion

In conclusion, the work carried out in this paper shows that carbanions of (chloroalkyl)heterocycles are VNS reagents, and provide the synthetic organic chemist with a convenient route to α-substituted (nitrobenzyl)pyridines, (nitrobenzyl)benzothiazoles, and (nitrobenzyl)thiazoles, which have potential for elaboration to a variety of other substances and, are therefore useful in synthetic organic chemistry.

Experimental Section

General Remarks: ^{1}H and the ^{13}C NMR spectra were recorded with a Bruker Avance 400 apparatus (400.13 MHz and 100.62 MHz, for ^{1}H and ^{13}C, respectively) and a Bruker AC200 apparatus (200 MHz and 50.3 MHz, for ^{1}H and ^{13}C, respectively); with $CDCl_3$ as the solvent (δ = 7.24 ppm for ^{1}H spectra; δ = 77.0 ppm for ^{13}C spectra) and TMS as an internal standard. IR spectra were recorded with a Perkin−Elmer spectrometer Model 283. GC-MS analyses were performed with a Shimadzu GC−17A gas chromatograph (5% diphenyl, 95% dimethylpolysiloxane capillary column, 30 m, 0.25 mm i.d.), equipped with a Shimadzu GCMS−QP5050A mass-selective detector operating at 70 eV (EI). TLC analysis was performed on Merck silica gel plates with F−254 indicator; visualization was by UV light (254 nm). Column chromatography was performed on silica gel (63−200 μm), with petroleum ether/ethyl acetate mixtures as the eluent. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe/septum cap techniques. DMSO was distilled and stored over molecular sieves (5 Å) prior to use. Starting materials were commercially available or were prepared by known methods. In particular, 4-(chloromethyl)pyridine (**1a**) and 2-(chloromethyl)pyridine (**1b**) were obtained from the corresponding hydrochlorides upon treatment with 5% NaOH, extraction with diethyl ether, drying (Na_2SO_4) and evaporation of the solvent under reduced pressure. Substrates **1c** and **1f** were obtained by the reaction of 2-aminothiophenol with glycolic or lactic acid and subsequent halogenation.[14−17] Compound **1d** was prepared by formylation of 4-methylthiazole, reduction of the thiazol-2-carbaldehyde thus obtained, and subsequent halogenation, following reported synthetic protocols.[18] **1e** was obtained by the coupling of 2-(4-methyl)thiazolyllithium with acetaldehyde and subsequent halogenation.[18]

General Procedure for the Preparation of α-Substituted (Nitrobenzyl)heterocycles: A solution of **1a**−**f** (1 mmol) and the nitroarene (1.1 mmol) in DMSO (2 mL) was added dropwise, under N_2, to a vigorously stirred suspension of powdered *t*BuOK (3 mmol) in DMSO (10 mL). The reaction was kept at room temperature for 1 h, quenched with saturated aqueous NH_4Cl solution (10−20 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The crude products were purified by column chromatography (silica gel; petroleum ether/EtOAc, 1:1) to afford the α-substituted (nitrobenzyl)heterocycles in yields of 12−86%.

4-(4-Nitrobenzyl)pyridine (2a): Yield: 80 mg (37%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.08 (s, 2 H), 7.10 (d, *J* = 5.9 Hz, 2 H), 7.34 (d, *J* = 8.7 Hz, 2 H), 8.16 (d, *J* = 8.7 Hz, 2 H), 8.53 (d, *J* = 5.9 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz): δ = 40.8, 123.8, 124.0, 129.7, 146.3, 147.9, 149.8, 150.1 ppm. GC-MS: *m*/*z* (%) = 214 (100) [M$^+$], 197 (5), 184 (17), 168 (78), 139 (19). IR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 2950, 1600, 1510, 1345, 860.

2-(4-Nitrobenzyl)pyridine (2b): Yield: 85 mg (40%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.23 (s, 2 H), 7.15−7.17 (m, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 7.61−7.65 (m, 1 H), 8.13 (d, *J* = 8.5 Hz, 2 H), 8.55 (d, *J* = 3.7 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 44.7, 122.2, 123.7, 124.2, 130.2, 137.3, 147.1, 147.6, 150.1, 159.4 ppm. GC-MS: *m*/*z* (%) = 214 (2) [M$^+$], 213 (12), 197 (35), 196 (28), 169 (77), 168 (100), 167 (96), 169 (77), 166 (74), 139 (66), 92 (46). IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2920, 1590, 1510, 1430, 1345, 1150, 1050.

2-(4-Nitrobenzyl)benzothiazole (2c): Yield: 76 mg (28%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.54 (s, 2 H), 7.38 (t, *J* = 8.1 Hz, 1 H), 7.48 (t, *J* = 8.1 Hz, 1 H), 7.54 (d, *J* = 8.7 Hz, 2 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 8.00 (d, *J* = 8.1 Hz, 1 H), 8.20 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 40.4, 122.0, 123.4, 124.4, 125.7, 126.7, 130.4, 135.9, 144.8, 147.6, 153.6, 168.5 ppm. GC-MS: *m*/*z* (%) = 270 (100) [M$^+$], 269 (90), 240 (61), 224 (80), 223 (91), 111 (83). IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2960, 1600, 1500, 1350, 1100.

4-Methyl-2-(4-nitrobenzyl)thiazole (2d): Yield: 96 mg (41%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 4.40 (s, 2 H), 6.80 (s, 1 H), 7.48 (d, *J* = 8.5 Hz, 2 H), 8.16 (d, *J* = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 16.8, 38.8, 113.7, 123.7, 129.5, 145.1, 146.7, 152.7, 166.4 ppm. GC-MS: *m*/*z* (%) = 234 (100) [M$^+$], 233 (85), 204 (30), 187 (70), 89 (50), 71 (96). IR (film): $\tilde{\nu}$ = 3100 cm^{-1}, 2950, 2850, 1600, 1510, 1350, 1100, 730.

4-Methyl-2-[1-(4-nitrophenyl)ethyl]thiazole (2e): Yield: 101 mg (41%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72 (d, *J* = 7.1 Hz, 3 H), 2.33 (s, 3 H), 4.50 (q, *J* = 7.1 Hz, 1 H), 6.70 (s, 1 H), 7.40 (d, *J* = 8.7 Hz, 2 H), 8.10 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz): δ = 17.0, 21.6, 43.6, 113.2, 123.8, 128.4, 147.3, 151.1, 152.8, 172.3 ppm. GC-MS: *m*/*z* (%) = 248 (100) [M$^+$], 233 (16), 215 (21), 201 (36), 187 (90), 126 (63), 112 (37), 71 (60). IR (film): $\tilde{\nu}$ = 3100 cm^{-1}, 2960, 2920, 1600, 1510, 1340, 850, 740.

2-[1-(4-Nitrophenyl)ethyl]benzothiazole (2f): Yield: 114 mg (40%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.88 (d, *J* = 7.1 Hz, 3 H), 4.68 (q, *J* = 7.1 Hz, 1 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.7 Hz, 2 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 8.0 (d, *J* = 8.0 Hz, 1 H), 8.17 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 21.2, 44.4, 121.5, 122.9, 123.9, 125.1, 126.1, 128.5, 134.9, 147.0, 150.2, 153.0, 173.4 ppm. GC-MS: *m*/*z* (%) = 284 (100), 269 (5), 254 (8), 237 (22), 223 (40), 262 (20). IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2960, 1600, 1530, 1340, 1100.

4-(2-Nitrobenzyl)pyridine (3a): Yield: 60 mg (28%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.22 (s, 2 H), 6.97 (d, *J* = 5.6 Hz, 2 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.36 (dd, *J* = 7.4, 7.5 Hz, 1 H), 7.50 (dd, *J* = 7.4, 7.5 Hz, 1 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 8.40 (d, *J* = 5.6 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz): δ = 37.9, 123.8, 125.0, 128.0, 132.6, 133.2, 133.4, 147.7, 149.8 ppm. GC-MS: *m*/*z* (%) = 214 (4) [M$^+$], 213 (15), 197 (100), 184 (20), 168 (31), 167 (25), 139 (40). IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2925, 1595, 1515, 1410, 1340, 850.

2-(2-Nitrobenzyl)pyridine (3b): Yield: 56 mg (26%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.48 (s, 2 H), 7.09−7.12 (m, 1 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 7.36−7.41 (m, 2 H), 7.50−7.60 (m, 2 H), 8.95 (d, *J* = 8.1 Hz, 1 H), 8.49 (d, *J* = 4.4 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 41.6, 121.9, 123.7, 125.2, 128.1, 133.4, 133.5, 134.5, 137.8, 149.7, 149.8, 159.0 ppm. GC-MS: *m*/*z* (%) = 214 (83) [M$^+$], 213 (100), 197 (8), 196 (10), 184 (18), 183 (23), 168 (70), 167 (93), 166 (72), 92 (7). IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2920, 1530, 1510, 1430, 1350, 1150, 1050.

2-(2-Nitrobenzyl)benzothiazole (3c): Yield: 49 mg (18%), oil. ^{1}H NMR, ^{13}C NMR, GC-MS, IR are measured on the mixture with

2c. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.80 (s, 2 H), 7.32−7.53 (m, 4 H), 7.58 (t, *J* = 7.8 Hz, 1 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.95 (d, *J* = 8.1 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 38.0, 121.9, 123.3, 125.4, 125.7, 126.4,0, 126.5, 129.0, 132.5, 133.3, 134.1, 149.1, 153.5, 168.6 ppm. GC-MS: *m*/*z* (%) = 270 (13) [M$^+$], 253 (100), 252 (55), 225 (70), 224 (70), 223 (74), 136 (62), 111 (87). IR (film): ṽ = 3050 cm^{-1}, 2960, 1600, 1500, 1350, 1100.

4-Methyl-2-(2-nitrobenzyl)thiazole (3d): Yield: 70 mg (30%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 4.64 (s, 2 H), 6.75 (s, 1 H), 7.41−7.48 (m, 2 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 8.0 (d, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 16.8, 36.4, 113.6, 124.9, 128.2, 132.5, 132.7, 133.4, 148.4, 152.3, 166.4 ppm. GC-MS: *m*/*z* (%) = 234 (1) [M$^+$], 217 (100), 187 (29), 100 (43), 89 (56), 71 (90). IR (film): ṽ = 3080 cm^{-1}, 2950, 2850, 1605, 1520, 1350.

4-(2,4-Dinitrobenzyl)pyridine (4a): Yield: 52 mg (20%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.40 (s, 2 H), 7.06 (d, *J* = 5.4 Hz, 2 H), 7.53 (d, *J* = 8.5 Hz, 1 H), 8.40 (dd, *J* = 2.1, 8.5 Hz, 1 H), 8.51 (d, *J* = 5.4 Hz, 2 H), 8.83 (d, *J* = 2.1 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.9, 120.6, 123.9, 127.3, 133.8, 140.3, 145.9, 146.9, 149.0, 150.2 ppm. GC-MS: *m*/*z* (%) = 259 (7) [M$^+$], 258 (14), 242 (100), 231 (10) 228 (8); 196 (70), 139 (55). IR (film): ṽ = 3050 cm^{-1}, 2925, 1595, 1515, 1410, 1340, 850.

2-(2,4-Dinitrobenzyl)pyridine (4b): Yield: 98 mg (38%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.60 (s, 2 H), 7.15−7.17 (m, 1 H), 7.28 (d, *J* = 7.1 Hz, 1 H), 7.64−7.70 (m, 2 H), 8.37−8.46 (m, 2 H), 8.81 (s, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 41.5, 120.7, 122.5, 123.9, 127.3, 134.8, 137.3, 141.5, 147.1, 149.6, 150.0, 157.2 ppm. GC-MS: *m*/*z* (%) = 259 (1) [M$^+$], 258 (8), 213 (100), 196 (29) 183 (33); 167 (85), 166 (71), 92 (24). IR (film): ṽ = 3060 cm^{-1}, 1600, 1510, 1340, 1110

2-(2,4-Dinitrobenzyl)benzothiazole (4c): Yield: 170 mg (54%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.90 (s, 2 H), 7.37 (t, *J* = 7.9 Hz, 1 H), 7.45 (t, *J* = 7.9 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 1 H), 7.84 (d, *J* = 7.9 Hz, 1 H), 7.92 (d, *J* = 7.9 Hz, 1 H), 8.43 (dd, *J* = 2.3, 8.4 Hz, 1 H), 8.93 (d, *J* = 2.3 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.8, 121.2, 122.0, 123.5, 125.9, 126.7, 127.1, 127.9, 134.7, 135.7, 139.1, 147.7, 153.3, 166.1 ppm. GC-MS: *m*/*z* (%) = 315 (8) [M$^+$], 298 (100), 285 (20), 252 (62), 224 (28), 223 (30), 222 (27), 135 (30). IR (film): ṽ = 3060 cm^{-1}, 2920, 1600, 1515, 1340.

2-(2,4-Dinitrobenzyl)-4-methylthiazole (4d): Yield: 56 mg (20%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 4.76 (s, 2 H), 6.82 (s, 1 H), 7.73 (d, *J* = 8.5 Hz, 1 H), 8.42 (dd, *J* = 2.3, 8.5 Hz, 1 H), 8.87 (d, *J* = 2.3 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 17.4, 36.7, 114.6, 121.0, 127.8, 134.4, 140.0, 147.5, 153.4, 155.5, 164.3 ppm. GC-MS: *m*/*z* (%) = 279 (2) [M$^+$], 262 (100), 216 (90), 187 (43), 186 (40), 115 (66), 71 (90). IR (film): ṽ = 3100 cm^{-1}, 2920, 2850, 1670, 1600, 1420, 1350, 830.

2-[1-(2,4-Dinitrophenyl)ethyl]-4-methylthiazole (4e): Yield: 35 mg (12%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.87 (d, *J* = 7.1 Hz, 3 H), 2.41 (s, 3 H), 5.17 (q, *J* = 7.1 Hz, 1 H), 6.83 (s, 1 H), 7.77 (d, *J* = 8.7 Hz, 1 H), 8.37 (dd, *J* = 2.2, 8.7 Hz, 1 H), 8.73 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 17.1, 21.8, 38.4, 113.6, 119.1, 127.1, 128.9, 130.7, 131.7, 145.1, 153.2, 170.0 ppm. GC-MS: *m*/*z* (%) = 293 (3) [M$^+$], 276 (17), 262 (25), 245 (32), 234 (56), 230 (30), 200 (44), 188 (58), 71 (100). IR (film): ṽ = 3100 cm^{-1}, 2920, 2850, 1600, 1430, 1350, 900, 710.

2-[1-(2,4-Dinitrophenyl)ethyl]benzothiazole (4f): Yield: 83 mg (25%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.96 (d, *J* = 7.0 Hz, 3 H), 5.29 (q, *J* = 7.0 Hz, 1 H), 7.37 (t, *J* = 8.1 Hz, 1 H), 7.46 (t, *J* = 8.1 Hz, 1 H), 7.81−7.87 (m, 2 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 8.35 (dd, *J* = 2.1, 8.6 Hz, 1 H), 8.73 (d, *J* = 2.1 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 21.4, 39.2, 120.0, 121.5, 123.1, 125.4, 126.2, 127.1, 131.7, 134.9, 144.1, 147.7, 148.5, 152.9, 172.0 ppm. GC-MS: *m*/*z* (%) = 330 (4) [M$^+$], 329 (20), 224 (98), 151 (100), 136 (70), 135 (72), 123 (40), 77 (75). IR (film): ṽ = 3060 cm^{-1}, 2980, 1600, 1520, 1340.

4-(2-Chloro-4-nitrobenzyl)pyridine (5a): Yield: 111 mg (45%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.20 (s, 2 H), 7.11 (d, *J* = 4.0 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 1 H), 8.08 (d, *J* = 8.3 Hz, 1 H), 8.27 (s, 1 H), 8.54 (d, *J* = 4.0 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 38.4, 121.8, 123.6, 123.8, 124.6, 125.0, 131.4, 143.9, 146.4, 149.0 ppm. GC-MS: *m*/*z* (%) = 248 (100) [M$^+$], 232 (5), 202 (15), 167 (98), 139 (32). IR (film): ṽ = 3040 cm^{-1}, 2920, 1590, 1520, 1350, 1260, 735.

2-(2-Chloro-4-nitrobenzyl)pyridine (5b): Yield: 87 mg (35%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.36 (s, 2 H), 7.18−7.28 (m, 2 H), 7.46 (d, *J* = 8.5 Hz, 1 H), 7.64 (t, *J* = 7.7 Hz 1 H), 8.06 (d, *J* = 8.5 Hz, 1 H), 8.25 (s, 1 H), 8.55 (d, *J* = 4.6 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 42.2, 122.2, 122.3, 123.8, 125.0, 132.3, 135.5, 137.2, 145.2, 147.5, 150.2, 158.1 ppm. GC-MS: *m*/*z* (%) = 248 (1) [M$^+$], 247 (3), 213 (100), 202 (3), 183 (29), 167 (82). IR (film): ṽ = 3060 cm^{-1}, 1600, 1510, 1340, 1110.

2-(2-Chloro-4-nitrobenzyl)benzothiazole (5c): Yield: 229 mg (75%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.57 (s, 2 H), 7.29−7.33 (m, 1 H), 7.36−7.42 (m, 1 H), 7.51 (d, *J* = 8.6 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.2 Hz, 1 H), 8.00 (dd, *J* = 2.2, 8.6 Hz, 1 H), 8.19 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.1, 121.6, 122.1, 123.0, 123.6, 124.9, 126.1, 126.3, 130.6, 134.4, 135.4, 142.2, 152.9, 167.3 ppm. GC-MS: *m*/*z* (%) = 304 (5) [M$^+$], 269 (100), 239 (30), 223 (76) 136 (17). IR (film): ṽ = 3040 cm^{-1}, 2950, 1600, 1520, 1350, 1250

2-(2-Chloro-4-nitrobenzyl)-4-methylthiazole (5d) and 2-(4-Chloro-2-nitrobenzyl)-4-methylthiazole (6d): Inseparable mixture of isomers: 83:17. Overall yield: 171 mg (64%), oil. ^{1}H NMR, ^{13}C NMR, GC-MS, IR were measured on the mixture of the isomers. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.43 (d, *J* = 0.8 Hz, 3 H), 4.50 (s, 2 H), 6.80 (q, *J* = 0.8 Hz, 1 H), 7.52 (d, *J* = 8.5 Hz, 1 H), 8.06 (dd, *J* = 2.2, 8.5 Hz, 1 H), 8.25 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 16.8, 16.9, 35.8, 36.7, 113.7, 113.8, 121.8, 121.9, 124.6, 125.0, 131.4, 131.5, 133.4, 133.6, 134.8, 134.9, 142.9, 143.0, 152.9, 153.0, 164.9, 165.1 ppm. GC-MS: *m*/*z* (%) = 268 (2) [M$^+$], 238 (5), 233 (100), 203 (72), 187 (56), 140 (13), 71 (43). IR (film): ṽ = 3090 cm^{-1}, 2920, 1520, 1345, 1120, 890, 730.

2-(4-Chloro-2-nitrobenzyl)pyridine (6b): Yield: 15 mg (6%), oil. ^{1}H NMR, ^{13}C NMR, GC-MS, IR were measured on the mixture with **5b**. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.45 (s, 2 H), 7.18−7.28 (m, 2 H), 7.39 (d, *J* = 8.3 Hz, 1 H), 7.52 (d, *J* = 8.3 1 H), 7.55 (t, *J* = 7.7 Hz, 1 H), 7.96 (s, 1 H). 8.48 (d, *J* = 4.5 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 41.1, 122.1, 123.7, 125.6, 128.8, 133.5, 134.6, 137.0, 147.7, 149.9, 153.0, 158.4 ppm. GC-MS: *m*/*z* (%) = 248 (1) [M$^+$], 247 (2), 202 (85), 183 (11), 167 (100). IR (film): ṽ = 3060 cm^{-1}, 1600, 1510, 1340, 1110.

2-(4-Chloro-2-nitrobenzyl)-4-methylthiazole (6d): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39 (d, *J* = 0.8 Hz, 3 H), 4.60 (s, 2 H), 6.76 (q, *J* = 0.8 Hz, 1 H), 7.40−7.55 (m, 2 H), 7.99 (d, *J* = 2.1 Hz, 1 H) ppm. GC-MS: *m*/*z* (%) = 268 (1) [M$^+$], 251 (100), 238 (60), 164 (40), 71 (65). ^{13}C NMR and IR see **5d**.

2-(2-Chloro-6-nitrobenzyl)-4-methylthiazole (7d): Yield: 14 mg (5%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39 (d, *J* = 0.8 Hz, 3 H), 4.77 (s, 2 H), 6.72 (q, *J* = 0.8 Hz, 1 H), 7.42 (t, *J* = 8.2 Hz, 1 H), 7.69 (dd, *J* = 1.2, 8.2 Hz, 1 H), 7.86 (dd, *J* = 1.2, 8.2 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz): δ = 17.0, 33.4, 113.2, 123.5, 128.8, 131.1, 134.2, 147.0, 152.5, 165.2 ppm. GC-MS: *m*/*z* (%) = 268 (1) [M$^+$], 251 (100), 238 (35), 164 (30), 71 (50). IR (film): ṽ = 3040 cm^{-1}, 2905, 1520, 1250, 730.

4-(3,4-Dinitrobenzyl)pyridine (8a): Yield: 88 mg (34%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.20 (s, 2 H), 7.22 (d, *J* = 5.6 Hz, 2 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.93 (s, 1 H), 8.02 (d, *J* = 7.5 Hz, 1 H), 8.55 (d, *J* = 5.6 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 39.5, 122.9, 124.2, 124.5, 129.8, 132.8, 145.7, 145.8, 148.8, 149.8 ppm. GC-MS: *m*/*z* (%) = 259 (100) [M$^+$], 229 (2), 211 (11), 168 (15), 167 (20), 154 (25), 139 (18). IR (film): ṽ = 3050 cm^{-1}, 2925, 1595, 1515, 1410, 1340, 850.

2-(3,4-Dinitrobenzyl)pyridine (8b) and 2-(2,3-Dinitrobenzyl)pyridine (9b): Inseparable mixture of isomers: 93:7. Overall yield: 176 mg (68%). ^{1}H NMR, ^{13}C NMR, GC-MS, IR were measured on the mixture of the isomers. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.30 (s, 2 H), 7.22 (t, *J* = 5.7 Hz 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 7.68−7.63 (m, 2 H), 7.86 (s, 1 H), 7.92 (d, *J* = 8.3 Hz, 1 H). 8.55 (d, *J* = 4.6 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 43.7, 43.8, 122.5, 123.1, 123.8, 124.2, 124.9, 125.5, 125.6, 125.7, 126.1, 129.1, 137.7, 134.1, 134.5, 137.5, 137.8, 137.9, 147.6, 149.1, 149.9, 150.1, 157.7, 157.8 ppm. GC-MS: *m*/*z* (%) = 259 (27) [M$^+$], 258 (100), 242 (30), 212 (25), 166 (86). IR (film): ṽ = 3050 cm^{-1}, 2930, 1600, 1450, 1350, 1020.

2-(3,4-Dinitrobenzyl)-4-methylthiazole (8d): Yield: 70 mg (25%), oil.^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 4.44 (s, 2 H), 6.84 (s, 1 H), 7.70 (d, *J* = 8.2 Hz, 1 H), 7.76 (s, 1 H), 7.91 (d, *J* = 8.2 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 16.9, 38.4, 114.2, 125.2, 125.4, 131.0, 133.4, 136.9, 145.0, 153.5, 164.3 ppm. GC-MS: *m*/*z* (%) = 279 (42) [M$^+$], 262 (12), 232 (21), 186 (30), 71 (100). IR (film): ṽ = 3100 cm^{-1}, 2960, 2850, 1540, 1380, 1350, 1100.

2-[1-(3,4-Dinitrophenyl)ethyl]-4-methylthiazole (8e): Yield: 111 mg (38%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.82 (d, *J* = 7.2 Hz, 3 H), 2.40 (s, 3 H), 4.62 (q, *J* = 7.2 Hz, 1 H), 6.83 (s, 1 H), 7.70−7.90 (m, 3 H) ppm. ^{13}C NMR (50.3 MHz): δ = 17.0, 21.6, 43.2, 113.5, 124.1, 125.1, 125.4, 132.3, 133.5, 150.9, 153.3, 170.4 ppm. GC-MS: *m*/*z* (%) = 293 (100) [M$^+$], 292 (43), 276 (69), 246 (78), 200 (90), 186 (74), 126 (72), 71 (93). IR (film): ṽ = 3090 cm^{-1}, 2960, 2910, 1540, 1350, 840, 730.

2-(2,3-Dinitrobenzyl)pyridine (9b): ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.20 (s, 2 H), 7.36 (d, *J* = 7.8 Hz, 1 H), 7.49−7.53 (m, 1 H), 7.60−7.68 (m, 2 H), 7.90 (d, *J* = 8.3 Hz, 1 H), 7.96 (d, *J* = 6.9 Hz, 1 H), 8.60 (d, *J* = 4.4 Hz, 1 H) ppm. GC-MS: *m*/*z* (%) = 259 (1) [M$^+$], 242 (3), 224 (5), 212 (65), 166 (100), 139 (35). ^{13}C NMR and IR see **8b**.

2-(2,3-Dinitrobenzyl)benzothiazole (9c): Yield: 95 mg (30%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.81 (s, 2 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.42−7.58 (m, 2 H), 7.60 (t, *J* = 7.6 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 8.24 (d, *J* = 7.4 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.6, 121.5, 122.8, 125.1, 125.3, 126.1, 128.6, 132.0, 132.9, 133.7, 135.4, 140.2, 152.9, 168.3 ppm. GC-MS: *m*/*z* (%) = 315 (1) [M$^+$], 253 (100), 225 (35), 224 (29), 223 (36), 111 (17). IR (film): ṽ = 3050 cm^{-1}, 2960, 1600, 1510, 1340, 1100.

4-(3-Chloro-4-nitrobenzyl)pyridine (10a): Yield: 99 mg (40%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.04 (s, 2 H), 7.11 (d, *J* = 5.0 Hz, 2 H), 7.22 (d, *J* = 8.3 Hz, 1 H), 7.37 (s, 1 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 8.56 (d, *J* = 5.0 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 40.2, 123.9, 125.9, 127.3, 127.9, 132.0, 145.2, 147.1, 150.0, 167.5 ppm. GC-MS: *m*/*z* (%) = 248 (100) [M$^+$], 232 (5), 218 (30) 202 (12), 183 (21), 167 (72), 139 (45). IR (film): ṽ = 3050 cm^{-1}, 2920, 1585, 1515, 1350, 1040, 740.

2-(3-Chloro-4-nitrobenzyl)pyridine (10b): Yield: 99 mg (40%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.16 (s, 2 H), 7.13−7.26 (m, 2 H), 7.28 (d, *J* = 8.3 Hz, 1 H), 7.43 (s, 1 H), 7.63 (dd, *J* = 7.6, 7.8 Hz, 1 H), 7.80 (d, *J* = 8.3 Hz, 1 H), 8.55 (d, *J* = 4.4 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz): δ = 43.7, 121.9, 123.2, 125.8, 127.2, 128.2, 132.2, 136.9, 146.1, 149.8, 153.0, 158.0 ppm. GC-MS: *m*/*z* (%) = 248 (31) [M$^+$], 247 (100), 218 (41) 202 (11), 201 (47), 167 (48). IR (film): ṽ = 3060 cm^{-1}, 2920, 1590, 1520, 1350, 1050.

2-(3-Chloro-4-nitrobenzyl)benzothiazole (10c): Yield: 85 mg (28%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.45 (s, 2 H), 7.35−7.56 (m, 4 H), 7.81−7.86 (m, 2 H), 7.99 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 39.4, 121.6, 123.0, 125.4, 126.0, 126.2, 126.3, 128.2, 129.7, 132.3, 135.4, 143.3, 153.2, 167.1 ppm. GC-MS: *m*/*z* (%) = 304 (4) [M$^+$], 287 (100), 274 (20), 224 (23), 223 (40), 136 (24), 111 (20). IR (film): ṽ = 3050 cm^{-1}, 2905, 1590, 1525, 1350, 730.

2-(3-Chloro-4-nitrobenzyl)-4-methylthiazole (10d): Yield: 94 mg (35%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 4.34 (s, 2 H), 6.81 (s, 1 H), 7.35 (dd, *J* = 1.6, 8.5 Hz, 1 H), 7.50 (d, *J* = 1.6 Hz, 1 H), 7.85 (d, *J* = 8.5 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz): δ = 16.9, 38.5, 113.9, 125.9, 127.9, 129.4, 131.0, 132.1, 144.1, 153.1, 165.2 ppm. GC-MS: *m*/*z* (%) = 268 (100) [M$^+$], 238 (72), 203 (34), 187 (61), 140 (34), 71 (99). IR (film): ṽ = 3100 cm^{-1}, 2910, 1580, 1520, 1340, 730.

2-[1-(3-Chloro-4-nitrophenyl)ethyl]-4-methylthiazole (10e): Yield: 85 mg (30%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78 (d, *J* = 7.2 Hz, 3 H), 2.43 (s, 3 H), 4.49 (q, *J* = 7.2 Hz, 1 H), 6.80 (s, 1 H), 7.35 (dd, *J* = 1.5, 8.3 Hz, 1 H), 7.51 (d, *J* = 1.5 Hz, 1 H), 7.84 (d, *J* = 7.3 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz): δ = 17.1, 21.5, 43.3, 113.3, 125.9, 126.7, 127.1, 128.0, 130.9, 150.0, 153.0, 171.5 ppm. GC-MS: *m*/*z* (%) = 282 (93) [M$^+$], 260 (62), 252 (35), 237 (39), 201 (44), 126 (44), 113 (45), 71 (100). IR (film): ṽ = 3050 cm^{-1}, 2920, 1580, 1520, 1340, 1260, 730.

2-[1-(3-Chloro-4-nitrophenyl)ethyl]benzothiazole (10f): Yield: 203 mg (64%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.87 (d, *J* = 7.2 Hz, 3 H), 4.63 (q, *J* = 7.2 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.43 (dd, *J* = 1.8, 8.7 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 7.57 (d, *J* = 1.8 Hz, 1 H), 7.83 (d, *J* = 8.7 Hz, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 8.00 (d, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 21.1, 44.1, 121.6, 123.1, 125.3, 126.0, 126.3, 126.9, 127.5, 131.0, 134.9, 142.1, 149.2, 153.1, 172.7 ppm. GC-MS: *m*/*z* (%) = 318 (100) [M$^+$], 283 (30), 257 (28), 236 (33), 162 (48), 136 (12), 135 (13). IR (film): ṽ = 3060 cm^{-1}, 2970, 1590, 1510, 1340, 1110.

2-(2-Chloro-6-nitrobenzyl)-4-methylthiazole (11d): Yield: 27 mg (10%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.42 (s, 3 H), 4.28 (s, 2 H), 6.80 (s, 1 H), 7.35−7.58 (m, 3 H) ppm. ^{13}C NMR (50.3 MHz): δ = 16.9, 34.6, 114.2, 125.1, 128.3, 129.5, 131.0, 133.5, 145.0, 153.1, 165.0 ppm. GC-MS: *m*/*z* (%) = 268 (1) [M$^+$], 251 (85), 187 (22), 100 (33), 90 (39), 71 (100). IR (film): ṽ = 3050 cm^{-1}, 2910, 1600, 1520, 1350, 1260, 730.

2-[Chloro-(4-nitrophenyl)methyl]pyridine (12b): Yield: 151 mg (61%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.22 (s, 1 H), 7.25

(dd, J = 4.8, 7.4 Hz 1 H), 7.58 (d, J = 7.9 Hz, 1 H), 7.67 (d, J = 8.8 Hz, 2 H), 7.73−7.77 (m, 1 H), 8.18 (d, J = 8.8 Hz, 2 H), 8.57 (d, J = 4.8 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 62.7, 121.9, 123.2, 123.6, 128.7, 137.3, 146.7, 147.8, 149.3, 158.0 ppm. GC-MS: *m*/*z* (%) = 248 (3) [M$^+$], 213 (99), 167 (100), 166 (30), 139 (13). IR (film): ṽ = 3050 cm^{-1}, 2960, 1530, 1510, 1345, 1100.

2-[Chloro-(4-nitrophenyl)methyl]benzothiazole (12c): Yield: 34 mg (11%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.46 (s, 1 H), 7.44 (t, J = 8.1 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 1 H), 7.76 (d, J = 8.7 Hz, 2 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 8.24 (d, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 59.6, 122.2, 124.2, 124.5, 126.5, 127.1, 129.4, 136.0, 145.4, 148.5, 153.3, 169.6 ppm. GC-MS: *m*/*z* (%) = 304 (20) [M$^+$], 269 (85), 240 (44), 223 (100), 207 (35), 106 (30). IR (film): ṽ = 3050 cm^{-1}, 2920, 1600, 1515, 1350, 730.

4-(5-Chloro-2-nitrobenzyl)pyridine (13a): Yield: 213 mg (86%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.30 (s, 2 H), 7.08 (d, J = 5.4 Hz, 2 H), 7.31 (d, J = 2.0 Hz, 1 H), 7.43 (dd, J = 2.0, 8.7 Hz, 1 H), 7.98 (d, J = 8.7 Hz, 1 H), 8.51 (d, J = 5.4 Hz, 2 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.8, 123.7, 126.6, 128.2, 132.4, 135.5, 139.6, 146.8, 147.1, 149.8 ppm. GC-MS: *m*/*z* (%) = 248 (10) [M$^+$], 247 (11), 231 (100), 218 (23), 196 (79), 168 (42), 167 (38), 139 (60). IR (film): ṽ = 3060 cm^{-1}, 2920, 1595, 1515, 1340, 900, 830.

2-(5-Chloro-2-nitrobenzyl)pyridine (13b): Yield: 131 mg (53%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.46 (s, 2 H), 7.08−7.21 (m, 2 H), 7.33 (dd, J = 2.0, 8.7 Hz, 1 H), 7.40 (d, J = 2.0 Hz, 1 H), 7.60 (dd, J = 7.5, 7.7 Hz, 1 H), 7.92 (d, J = 8.7 Hz, 1 H). 8.48 (d, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 40.8, 121.6, 123.1, 123.4, 126.1, 127.6, 132.6, 136.0, 136.5, 139.1, 147.3, 149.3, 157.5 ppm. GC-MS: *m*/*z* (%) = 248 (1) [M$^+$], 218 (10), 202 (88), 167 (100) 78 (22). IR (film): ṽ = 3060 cm^{-1}, 2920, 1600, 1550, 1350, 1030.

2-(5-Chloro-2-nitrobenzyl)benzothiazole (13c): Yield: 213 mg (70%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.75 (s, 2 H), 7.32 (t, J = 7.9 Hz, 1 H), 7.39 (dd, J = 2.0, 8.8 Hz, 1 H), 7.42 (t, J = 7.9 Hz, 1 H), 7.50 (d, J = 2.0 Hz, 1 H), 7.78 (d, J = 7.9 Hz, 1 H), 7.93 (d, J = 7.9 Hz, 1 H), 8.01 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 37.3, 121.4, 122.8, 125.1, 126.0, 126.6, 128.6, 132.6, 133.9, 135.3, 139.9, 146.7, 152.8, 166.9 ppm. GC-MS: *m*/*z* (%) = 304 (1) [M$^+$], 287 (100), 274 (15), 259 (19), 239 (8), 223 (25), 136 (20). IR (film): ṽ = 3030 cm^{-1}, 2950, 1600, 1510, 1340.

2-(5-Chloro-2-nitrobenzyl)-4-methylthiazole (13d): Yield: 110 mg (41%), oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 4.53 (s, 2 H), 6.68 (s, 1 H), 7.28 (dd, J = 2.0, 8.6 Hz, 1 H), 7.35 (d, J = 2.0 Hz, 1 H), 7.90 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz): δ = 16.8, 36.2, 113.8, 126.5, 128.3, 132.3, 134.7, 139.7, 152.6, 165.1 ppm. GC-MS: *m*/*z* (%) = 268 (1) [M$^+$], 251 (100), 250 (25), 223 (14), 100 (25), 90 (19), 71 (60). IR (film): ṽ = 3100 cm^{-1}, 2950, 2850, 1600, 1570, 1515, 1340, 1090.

2-(5-Methoxy-2-nitrobenzyl)benzothiazole (14c): Yield: 105 mg (35%), oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.87 (s, 3 H), 4.83 (s, 2 H), 6.91 (dd, J = 2.7, 9.1 Hz, 1 H), 6.98 (d, J = 2.7 1 H), 7.32−7.36 (m, 1 H), 7.42−7.46 (m, 1 H), 7.80 (d, J = 7.8 Hz, 1 H), 7.96 (d, J = 8.2 Hz, 1 H), 8.18 (d, J = 9.1 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz): δ = 38.4, 55.9, 113.3, 117.9, 121.6, 122.8, 125.0, 126.0, 128.2, 135.1, 135.5, 153.0, 163.5, 168.3 ppm. GC-MS: *m*/*z* (%) = 300 (1) [M$^+$], 283 (68), 270 (17), 267 (28), 254 (100), 240 (40), 210 (53), 136 (40), 106 (39), 77 (28). IR (film): ṽ = 3020 cm^{-1}, 2940, 1610, 1510, 1350, 1100.

Acknowledgments

This work was carried out under the framework of the National Project "Stereoselezione in Sintesi Organica. Metodologie ed Applicazioni" supported by the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Rome) and by the University of Bari and University of Lecce and CNR (Rome).

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Received December 22, 2003

