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Reactions of α-Nitroacrylates with Thiophenols

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Abstract—Reactions of α-nitroacrylates with aromatic thiols like 4-methyl- and 4-chlorothiophenols afford a series of new 3-arylsulfanyl-2-nitropropanoates. The latter were isolated as diastereomerically pure substances or mixtures of two diastereomers. Structures of the obtained *S*-adducts were confirmed by IR, ^{1}H and $^{13}C–\{^{1}H\}$ NMR spectroscopy using HMQC and HMBC experiments.

Keywords: nitroalkenes, nitroacrylates, thiophenols, nucleophilic addition

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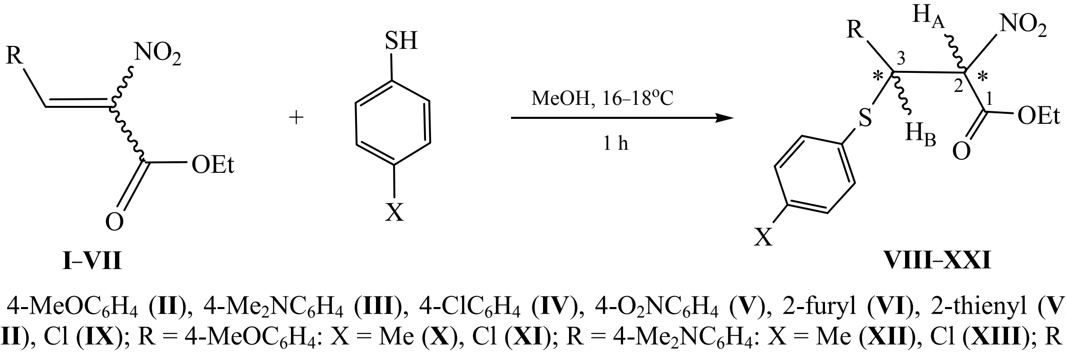
A wide spectrum of the practically useful properties of organosulfur compounds (drugs, pesticides, antioxidants, etc.) attracts a large interest in developing new methods for the synthesis of their derivatives. *para*-Benzoyloxy-containing α-nitrocinnamate is known to add thiomethanol at the double bond in the presence of pyridine at low temperature [1]. According to [2–4], the reactions of furylnitroacrylates with benzylmercaptan, 2-mercaptoethanol, 2-mercaptoethylamine, etc., occurred in water or methanol at room temperature. However, Šturdík et al. did not preparatively isolate the resulting *S*-adducts, the latter were only spectrally detected. We have recently shown that the reactions of β-aryl(hetaryl)-α-nitroacrilates and their analogs, *gem*-benzoylnitrostyrenes, with *N*,*S*-binucleophile like *o*-aminothiophenol occurred in MeOH in a short time to give the linear *S*-adducts [5, 6]. However, the reactions of α-nitroacrylates with aromatic *S*-mononucleophiles are not described in the literature.

In the present work we found that α-nitroacrylates **I**–**VII** react with 4-methyl- and 4-chlorothiophenols in methanol in the absence of any catalyst at 16–18°C within 1 h to afford linear *S*-adducts **VIII**–**XXI** in up to 97% yield (Scheme 1).

The structures of **VIII**–**XXI** were confirmed by the spectral data. In the IR spectra (Table 1) absorption bands are observed from the non-conjugated nitro (1560–1570, 1370–1375 cm^{-1}) and carbonyl (1750–1755 cm^{-1}) groups.

Scheme 1.



I–**VII** **VIII**–**XXI**

R = Ph (**I**), 4-MeOC$_6$H$_4$ (**II**), 4-Me$_2$NC$_6$H$_4$ (**III**), 4-ClC$_6$H$_4$ (**IV**), 4-O$_2$NC$_6$H$_4$ (**V**), 2-furyl (**VI**), 2-thienyl (**VII**); R = Ph: X = Me (**VIII**), Cl (**IX**); R = 4-MeOC$_6$H$_4$: X = Me (**X**), Cl (**XI**); R = 4-Me$_2$NC$_6$H$_4$: X = Me (**XII**), Cl (**XIII**); R = 4-ClC$_6$H$_4$: X = Me (**XIV**), Cl (**XV**); R = 4-O$_2$NC$_6$H$_4$: X = Me (**XVI**), Cl (**XVII**); R = 2-furyl: X = Me (**XVIII**), Cl (**XIX**); R = 2-thienyl: X = Me (**XX**), Cl (**XXI**).

Table 1. IR and ^{1}H NMR spectral data of the *S*-adducts **VIII**–**XXI**

Comp. no.	IR spectrum (CHCl$_3$), ν, cm^{-1}		^{1}H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz)				
	NO$_2$	C=O	H$_A$	H$_B$	OCH$_2$CH$_3$	CH$_3$ (OCH$_3$) [N(CH$_3$)$_2$]	Ar
VIIIa	1565, 1375	1750	5.52 d $^3J_{AB}$ 10.68	4.85 d	0.96 t, 3.97 d.q, 4.01 d.q (^3J 7.15, ^2J 10.75)	2.31 s	6.98–7.13 m, 7.18–7.28 m
VIIIb			5.54 d $^3J_{AB}$ 11.60	4.88 d	1.37 t, 4.30 d.q, 4.36 d.q (^3J 7.15, ^2J 10.75)	2.31 s	
VIIIb	1565, 1375	1750	5.54 d $^3J_{AB}$ 11.60	4.88 d	1.37 t, 4.30 d.q, 4.36 d.q (^3J 7.15, ^2J 10.75)	2.31 s	6.98–7.07 m, 7.08 d, 7.18–7.28 m
IXb	1560, 1375	1750	5.51 d $^3J_{AB}$ 11.60	4.91 d	1.37 t, 4.32 d.q, 4.37 d.q (^3J 7.15, ^2J 10.80)	–	7.03–7.08 m, 7.12 d, 7.20 d, 7.22–7.29 m
IXa	–	–	5.50 d $^3J_{AB}$ 10.66	4.86 d	0.98 t, 3.99 d.q, 4.03 d.q (^3J 7.15, ^2J 10.75)	–	7.00–7.30 m
IXb			5.51 d $^3J_{AB}$ 11.60	4.91 d	1.37 t, 4.32 d.q, 4.37 d.q (^3J 7.15, ^2J 10.80)	–	
Xa	1565, 1375	1750	5.47 d $^3J_{AB}$ 10.68	4.82 d	1.00 t, 3.98 d.q, 4.02 d.q (^3J 7.15, ^2J 10.75)	2.31 s (3.76 s)	6.76 d, 7.00 d, 7.04 d, 7.12 d
Xa [a]	–	–	5.47 d $^3J_{AB}$ 10.68	4.82 d	1.00 t, 3.98 d.q, 4.02 d.q (^3J 7.15, ^2J 10.75)	2.31 s (3.77 s)	6.76 d, 7.00 d, 7.04 d, 7.12 d
Xb			5.48 d $^3J_{AB}$ 11.44	4.85 d	1.36 t, 4.28 d.q, 4.34 d.q (^3J 7.15, ^2J 10.75)	2.32 s (3.76 s)	6.75 d, 6.97 d, 7.04 d, 7.09 d
XIa	1565, 1375	1750	5.46 d $^3J_{AB}$ 10.53	4.84 d	1.01 t, 4.00 d.q, 4.04 d.q (^3J 7.15, ^2J 10.60)	(3.77 s)	6.76 d, 6.99 d, 7.13 d, 7.21 d
XIb			5.47 d $^3J_{AB}$ 11.44	4.88 d	1.36 t, 4.30 d.q, 4.35 d.q (^3J 7.15, ^2J 10.50)	(3.76 s)	6.78 d, 7.02 d, 7.15 d, 7.21 d
XIIa	1565, 1370	1750	5.47 d $^3J_{AB}$ 10.60	4.80 d	1.01 t, 3.99 d.q, 4.02 d.q (^3J 7.15, ^2J 10.75)	2.31 s [2.92 s]	6.50–6.60 m, 6.88–6.98 m, 7.00–7.08 m, 7.10–7.18 m
XIIb			5.49 d $^3J_{AB}$ 11.44	4.84 d	1.34 t, 4.24 d.q, 4.30 d.q (^3J 7.15, ^2J 10.75)	2.32 s [2.91 s]	
XIIIa	1565, 1370	1750	5.45 d $^3J_{AB}$ 10.68	4.82 d	1.02 t, 4.00 d.q, 4.04 d.q (^3J 7.15, ^2J 10.75)	[2.92 s]	6.50–6.60 m, 6.88–7.00 m, 7.10–7.24 m
XIIIb			5.47 d $^3J_{AB}$ 11.60	4.86 d	1.35 t, 4.28 d.q, 4.32 d.q (^3J 7.15, ^2J 10.65)	[2.91 s]	

Table 1. (Contd.)

Comp. no.	IR spectrum ($CHCl_3$), ν, cm^{-1}		^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz)				
	NO_2	C=O	H_A	H_B	OCH_2CH_3	CH_3 (OCH_3) [$N(CH_3)_2$]	Ar
XIV	1570, 1375	1750	5.46 d $^3J_{AB}$ 10.68	4.81 d	1.02 t, 4.01 d.q, 4.05 d.q (^3J 7.15, ^2J 10.80)	2.32 s	6.99 d, 7.22 d, 7.05 d, 7.10 d
XVa	1570, 1375	1750	5.42 d $^3J_{AB}$ 10.65	4.81 d	1.06 t, 4.03 d.q, 4.07 d.q (^3J 7.15, ^2J 10.80)	–	7.04 d, 7.14 d, 7.20–7.28 m
XVb			5.41 d $^3J_{AB}$ 11.60	4.85 d	1.39 t, 4.34 d.q, 4.38 d.q (^3J 7.15, ^2J 10.80)	–	7.00 d, 7.16 d, 7.20–7.28 m
XVIa	1570, 1375 (1525, 1350)	1755	5.54 d $^3J_{AB}$ 10.78	4.92 d	1.05 t, 4.03 d.q, 4.08 d.q (^3J 7.15, ^2J 10.95)	2.32 s	7.08 br.s, 7.20 d, 8.10 d
XVIb			5.53 d $^3J_{AB}$ 11.56	4.94 d	1.41 t, 4.38 d.q, 4.43 d.q (^3J 7.15, ^2J 10.85)	2.32 s	7.06 br.s, 7.16 d, 8.08 d
XVIIa	1570, 1375 (1530, 1350)	1755	5.53 d $^3J_{AB}$ 10.68	4.93 d	1.07 t, 4.05 d.q, 4.10 d.q (^3J 7.15, ^2J 10.85)	–	7.11–7.17 m, 7.20–7.30 m, 8.14 d
XVIIb			5.51 d $^3J_{AB}$ 11.29	4.97 d	1.40 t, 4.38 d.q, 4.42 d.q (^3J 7.15, ^2J 10.75)	–	7.11–7.17 m, 7.20–7.30 m, 8.12 d
XVIIIa	1565, 1375	1750	5.52 d $^3J_{AB}$ 10.17	4.94 d	1.12 t, 4.11 d.q, 4.15 d.q (^3J 7.15, ^2J 10.70)	2.33 s	7.05–7.11 m, 7.17 d (6.04 d, 6.26 d.d, 7.30 d)
XVIIIb			5.45 d $^3J_{AB}$ 11.19	4.99 d	1.37 t, 4.34 d.q, 4.39 d.q (^3J 7.15, ^2J 10.75)	2.33 s	7.05–7.11 m, 7.13 d (5.99 d, 6.23 d.d, 7.32 d)
XIXa	1570, 1375	1750	5.53 d $^3J_{AB}$ 10.12	4.96 d	1.12 t, 4.11 d.q, 4.15 d.q (^3J 7.15, ^2J 10.75)	–	7.14–7.26 m (6.04 d, 6.24 d.d, 7.32 d)
XIXb			5.45 d $^3J_{AB}$ 11.15	5.02 d	1.36 t, 4.34 d.q, 4.39 d.q (^3J 7.15, ^2J 10.70)	–	7.14–7.26 m (6.08 d, 6.26 d.d, 7.29 d)
XXa	1565, 1375	1750	5.48 d $^3J_{AB}$ 9.97	5.13 d	1.09 t, 4.08 d.q, 4.12 d.q (^3J 7.15, ^2J 10.70)	2.32 s	7.04–7.11 m, 7.19 d (6.62 d, 6.83 d.d, 7.20–7.25 m)
XXb			5.44 d $^3J_{AB}$ 11.02	5.16 d	1.37 t, 4.33 d.q, 4.37 d.q (^3J 7.15, ^2J 10.80)	2.32 s	7.04–7.11 m, 7.15 d (6.55 d, 6.79 d.d, 7.20–7.25 m)
XXIa	1570, 1375	1750	5.48 d $^3J_{AB}$ 9.77	5.15 d	1.10 t, 4.10 d.q, 4.13 d.q (^3J 7.15, ^2J 10.75)	–	7.16–7.29 m (6.67 d, 6.85 d.d, 7.24–7.29 m)
XXIb			5.43 d $^3J_{AB}$ 10.99	5.19 d	1.37 t, 4.34 d.q, 4.38 d.q (^3J 7.15, ^2J 10.75)	–	7.16–7.29 m (6.60 d, 6.81 d.d, 7.24–7.29 m)

[a] The ^1H NMR spectrum was recorded after exposure of the individual diastereomer **Xa** in $CDCl_3$ solution for 1 day.

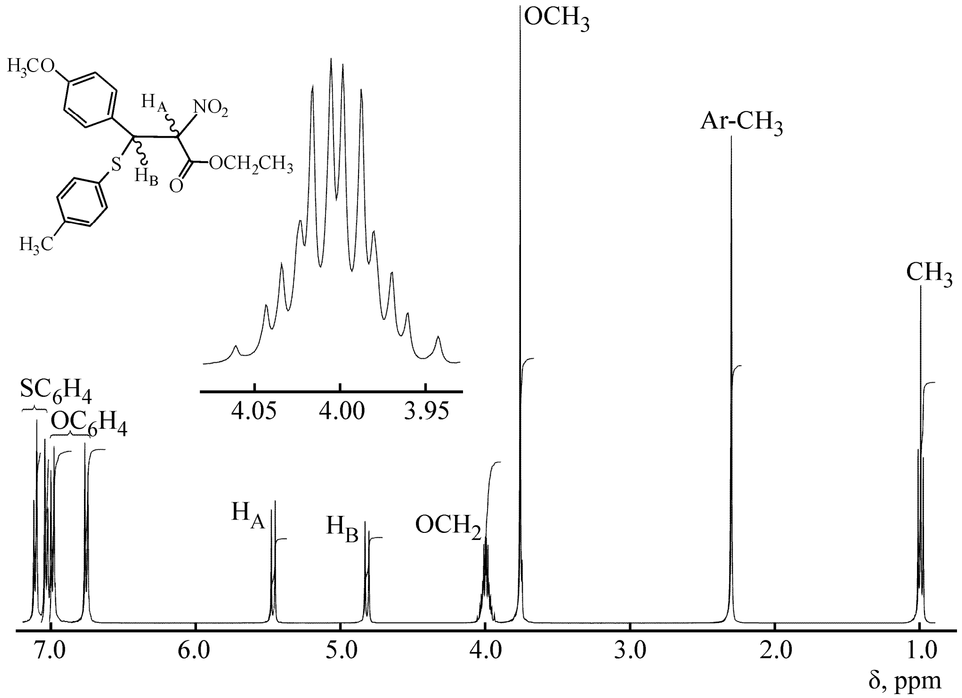


Fig. 1. ^{1}H NMR spectrum of **Xa** in CDCl$_3$.

The ^{1}H NMR spectral data of **VIII–XXI** are given in Table 1.

The synthesized β-aryl(hetaryl)-β-arylsulfanyl-α-nitropropanoates are diastereomerically pure compounds (**IXb**, **Xa**, **XIV**) or a mixtures of two diastereomers (**VIIIa**, **VIIIb**, **XIa**, **XIb–XIIIa**, **XIIIb**, **XVa**, **XVb–XXIa**, **XXIb**) (stereoisomers with the lower values of $^3J_{AB}$ are marked with the letter "**a**," and with the higher ones, with the letter "**b**"). Single diastereomer **VIIIb** was isolated by repeated recrystallization of **VIIIa**, **VIIIb** (**a** : **b** ~ 1 : 2).

The ^{1}H NMR spectra of **VIII–XXI** are similar (Table 1, Figs. 1, 2). Thus, the ^{1}H NMR spectrum (CDCl$_3$) of **VIIIb** contained two doublets of the methine protons H$_A$ and H$_B$ at 5.54 and 4.88 ppm, $^3J_{AB}$ 11.60 Hz. The protons of the methyl and methylene groups of the ester moiety resonated as a triplet at 1.37 and two doublets of quartets (due to magnetic nonequivalence of the diastereotopic methylene protons) at 4.30 and 4.36 ppm (^3J 7.15, ^2J 10.75 Hz). The protons of phenyl substituents appeared as multiplets in the range of 6.98–7.28 ppm. The signal at 2.31 ppm corresponds to the protons of the methyl group at the aromatic ring. Figures 1 and 2 show the ^{1}H NMR spectra of **Xa** and **XVIIIa**, **XVIIIb**.

A single diastereomer **Xa** was found to transform into a mixture of diastereomers in a ratio of **a** : **b** = 1.47 : 1 when kept in a CDCl$_3$ solution for 1 day. ^{1}H NMR spectral data of the resulting mixture of diastereomers are given in Table 1.

In the ^{13}C NMR spectra of **VIII–XXI** there are the signals of all carbon atoms (Table 2, Figs. 3, 4). Thus, the signals of the atoms C^2 and C^3 appeared in the ranges of 89.08–91.67 and 45.82–53.62 ppm, respectively. The carbon atoms of COOEt moiety resonated at 161.60–162.94 (C^1), 63.05–64.18 (OCH$_2$), 13.63–14.03 ppm (CH$_3$). In the spectra of **VIII**, **X**, **XII**, **XIV**, **XVI**, **XVIII**, **XX** the carbon atom of the methyl group at the benzene ring resonated in the range of 21.33–21.36 ppm. The carbon atoms of methoxy and dimethylamino groups were registered at 55.36–55.37 (**X**, **XI**) and 40.38–40.45 ppm (**XII**, **XIII**), respectively.

The correctness of the assignment of the signals of the methine protons was confirmed by ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC experiments. For example, in the HMQC spectrum of **VIIIb** (Fig. 5) the more downfield signal of H$_A$ (5.54 ppm) correlates with the more downfield signal of C^2 (90.43 ppm); the more upfield signal of H$_B$ (4.88 ppm) correlates with the more upfield signal of C^3 (52.28 ppm).

In the HMBC spectrum there are cross-peaks between the signal of H$_A$ at 5.41–5.54 ppm and the signal of C^1 atom at 161.60–162.94 ppm (a cross-peak between the signals of H$_B$ and C^1 is absent). The

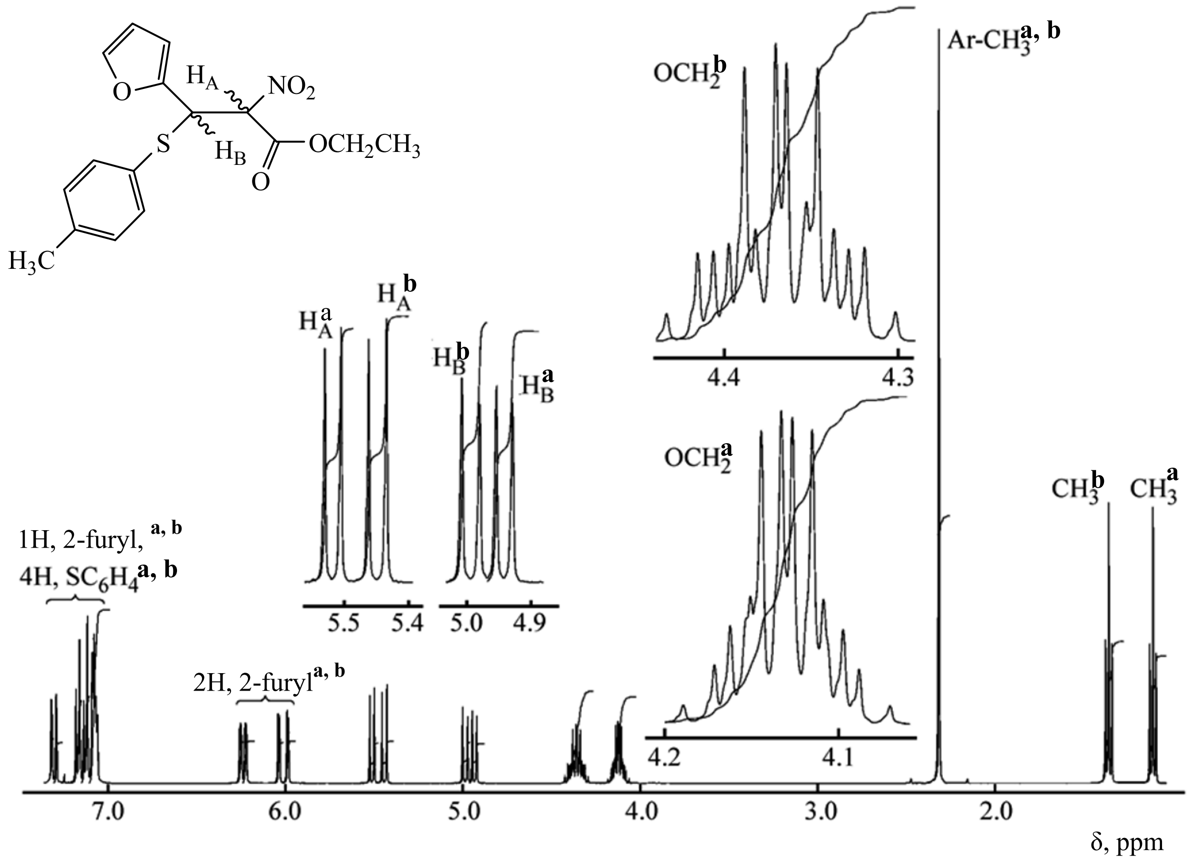


Fig. 2. ^{1}H NMR spectrum of **XVIIIa**, **XVIIIb** in $CDCl_3$.

HMBC spectrum of a single diastereomer **IXb** is represented in Fig. 6.

In conclusion, based on the reactions of α-nitroacrylates with arylthiols we developed preparatively available and suitable for scaling procedure for the synthesis of a series of β-aryl(hetaryl)-β-arylsulfanyl-α-nitropropanoates. The latter are of interest as precursors for the synthesis of modified α-amino acids (phenylalanine and its analogs) containing arylthiol group in β-position. The pharmacophore β-aminothiol fragment is known to be constituent of penicillin antibiotics, penicillamine (heavy metal chelator), vitamin H (biotin), carbocystein (mucolytic), sulconazole (fungicide), leucogen (stimulant of leucopoiesis, and arbidol (antiviral drug) [7, 8].

EXPERIMENTAL

The ^{1}H, ^{13}C–{^{1}H}, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC NMR spectra were recorded on a Jeol ECX400A spec-trometer [399.78 (^{1}H), 100.525 (^{13}C) MHz] in chloro-form-d_1; the residual proton signals of deuterated solvent were used as internal standard. The IR spectra were registered on a Shimadzu IRPrestige-21 Fourier spectrometer in chloroform solution (c ~ 40 mg mL^{-1}). Elemental analysis was performed on an EuroVector EA 3000 analyzer CHNS mode. TLC analysis was performed using Silufol UV254 plates and eluting with hexane–acetone, 3 : 1 (**XII**, **XVIII**–**XX**), 3 : 2 (**XV**, **XXI**).

α-Nitroacrylates were obtained as described in [9] (**I**–**IV**), [10] (**V**) and in [11] (**VI**, **VII**).

Ethyl 3-(4-methylphenylsulfanyl)-2-nitro-3-phenyl-propanoate (VIIIa, VIIIb). To 0.44 g (2 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** was added 0.25 g (2 mmol) of 4-methylthiophenol dissolved in 10 mL of anhydrous methanol. The mixture was kept at 16–18°C for 1 h. Next, the solution was poured into a Petri dish and evaporated. The residue was treated with ethanol. Yield 0.56 g (81%), mixture of diastereomers in a ratio of **a** : **b** = 1 : 2, white crystals, mp 74–76°C. A single diastereomer **VIIIb** [mp 60–62°C (ethanol)] was isolated by repeated recrystallization of the mixture of diastereomers **VIIIa**, **VIIIb**. Found, %: C 62.79; H

Table 2. ^{13}C–{^{1}H} NMR spectral of the *S*-adducts **VIII–XXI** in CDCl$_3$ (δ, ppm)

Comp. no.	C^1 (OCH$_2$CH$_3$)	C^2	C^3	CH$_3$ (OCH$_3$) [(CH$_3$)$_2$N]	Ar (Het)
VIIIb	162.79 (14.00, 63.64)	90.43	52.28	21.34	126.61, 127.85, 128.44, 128.74, 129.91, 135.67, 135.93, 139.73
IXb	162.65 (14.01, 63.76)	90.23	52.37	–	127.84, 128.72, 128.85, 128.90, 129.35, 135.49, 135.88, 136.67
Xa	162.26 (13.66, 63.22)	91.36	53.25	21.35 (55.36)	113.98, 127.57, 127.69, 129.68, 129.93, 135.32, 139.41, 159.57
Xa	162.26 (13.66, 63.22)	91.36	53.25	21.35 (55.36)	113.98, 127.57, 127.69, 129.68, 129.93, 135.32, 139.41, 159.57
Xb	162.79 (13.99, 63.55)	90.74	51.96	21.35 (55.36)	114.09, 127.57, 127.69, 129.13, 129.93, 135.60, 139.58, 159.55
XIa	162.07 (13.67, 63.35)	91.29	53.36	(55.37)	114.15, 127.12, 129.16, 129.65, 130.03, 135.51, 136.23, 159.76
XIb	162.67 (14.00, 63.70)	90.53	52.08	(55.37)	114.24, 127.29, 129.33, 129.65, 130.01, 135.74, 136.61, 159.72
XIIa	162.38 (13.97, 63.05)	91.67	53.55	21.33 [40.43]	112.16, 122.63, 127.51, 128.74, 129.81, 135.12, 139.06, 150.39
XIIb	162.94 (13.68, 63.41)	90.99	52.32	21.33 [40.45]	112.24, 122.84, 127.32, 129.25, 129.78, 135.41, 139.24, 150.35
XIIIa	162.20 (13.69, 63.22)	91.55	53.62	[40.40]	112.15, 121.94, 128.76, 129.21, 130.56, 135.18, 136.08, 150.49
XIIIb	162.84 (13.99, 63.55)	90.74	52.42	[40.38]	112.22, 122.14, 128.76, 129.21, 129.69, 135.40, 136.46, 150.45
XIV	162.02 (13.63, 63.41)	90.86	53.07	21.33	127.04, 126.99, 128.84, 129.76, 130.08, 134.37, 135.44, 139.80
XVa	161.69 (13.67, 63.38)	90.70	53.22	–	129.01, 129.17, 129.68, 128.51, 134.12, 134.72, 135.98, 136.36
XVb	162.25 (14.03, 63.68)	89.98	51.89	–	129.10, 129.17, 129.40, 129.51, 134.17, 134.72, 136.20, 136.68
XVIa	161.78 (13.69, 63.71)	90.27	52.92	21.36	123.83, 126.14, 129.29, 130.33, 135.69, 140.41, 143.38, 147.63
XVIb	162.31 (14.03, 64.03)	89.66	51.54	21.36	123.93, 125.30, 128.76, 130.33, 135.95, 140.64, 143.38, 147.63
XVIIa	161.60 (13.71, 63.89)	90.25	53.12	–	124.04, 128.53, 129.28, 129.81, 136.47, 136.54, 143.00, 147.63
XVIIb	162.16 (14.03, 64.18)	89.52	51.74	–	124.12, 127.65, 128.80, 129.81, 136.71, 136.84, 143.00, 147.79
XVIIIa	162.43 (14.00, 63.48)	89.18	47.09	21.35	127.22, 129.97, 135.59, 140.05 (109.24, 110.72, 142.88, 148.36)
XVIIIb	162.18 (13.76, 63.70)	88.69	45.83	21.35	126.14, 129.94, 135.94, 139.80 (108.91, 110.74, 142.79, 148.36)
XIXa	161.99 (14.00, 63.84)	88.48	47.09	–	129.40, 129.45, 135.94, 136.65 (109.50, 110.83, 143.05, 147.93)
XIXb	162.30 (13.76, 63.64)	89.08	45.82	–	128.33, 129.37, 136.21, 137.07 (109.23, 110.85, 143.12, 147.94)

Table 2. (Contd.)

Comp. no.	C^1 (OCH_2CH_3)	C^2	C^3	CH_3 (OCH_3) [$(CH_3)_2N$]	Ar (Het)
XXa	162.05 (13.98, 63.71)	91.23	48.99	21.36	126.62, 130.01, 135.24, 139.74 (126.24, 126.54, 126.96, 138.52)
XXb	162.38 (13.67, 63.46)	91.04	47.92	21.36	127.59, 129.99, 135.62, 139.97 (126.14, 126.75, 126.79, 138.62)
XXIa	161.89 (13.70, 63.62)	91.17	49.08	–	129.46, 129.81, 136.15, 136.20 (126.58, 126.80, 127.15, 138.19)
XXIb	162.25 (13.99, 63.84)	90.87	48.02	–	128.80, 129.44, 135.87, 136.66 (126.51, 126.90, 126.95, 138.30)

5.42; N 3.99; S 9.18. $C_{18}H_{19}NO_4S$. Calculated, %: C 62.61; H 5.51; N 4.06; S 9.28.

Ethyl 2-nitro-3-phenyl-3-(4-chlorophenylsulfanylphenyl)propanoate (IXa, IXb). To 0.44 g (2 mmol) of ethyl 2-nitro-3-phenylpropenoate **I** was added 0.29 g of (2 mmol) of 4-chlorothiophenol dissolved in 10 mL of anhydrous methanol. The mixture was kept at 16–18°C for 1 h. The precipitate was filtered off to yield 0.25 g (34%) of **IXb** as pale gray crystals, mp 109–110°C (ethanol). A mixture **IXa**, **IXb** (**a** : **b** = 1 : 1.1), mp 90–91°C, was isolated from the mother liquor in the yield of 0.425 g (58%). Total yield of **IX** 0.675 g (92%). Found, %: C 55.79; H 4.39; S 8.68. $C_{17}H_{16}ClNO_4S$. Calculated, %: C 55.81; H 4.38; S 8.76.

Ethyl 3-(4-methylphenylsulfanyl)-3-(4-methoxyphenyl)-2-nitropropanoate (Xa) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 70%, pale yellow crystals (single diastereomer), mp 58–60°C (ethanol). Found, %: C 61.02; H 5.44; N 3.65; S 8.56. $C_{19}H_{21}NO_5S$. Calculated, %: C 60.80; H 5.60; N 3.73; S 8.53.

Ethyl 3-(4-methoxyphenyl)-2-nitro-3-(4-chlorophenylsulfanyl)propanoate (XIa, XIb) was obtained

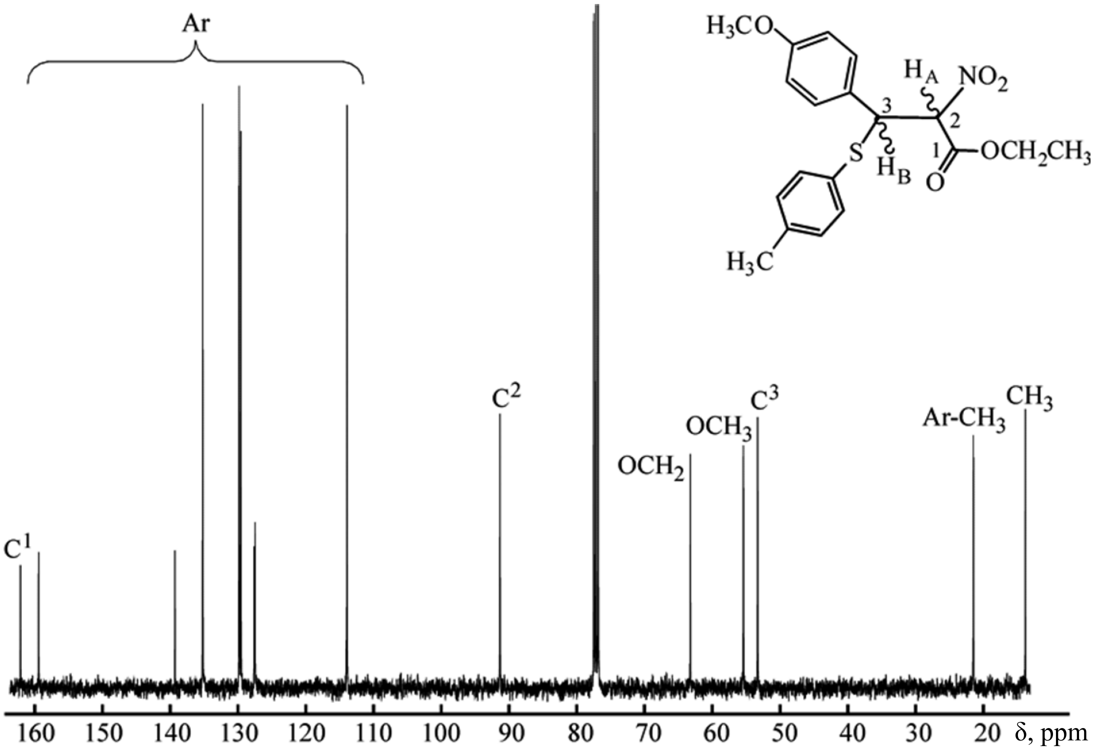


Fig. 3. ^{13}C–{^1H} NMR spectrum of **Xa** in $CDCl_3$.

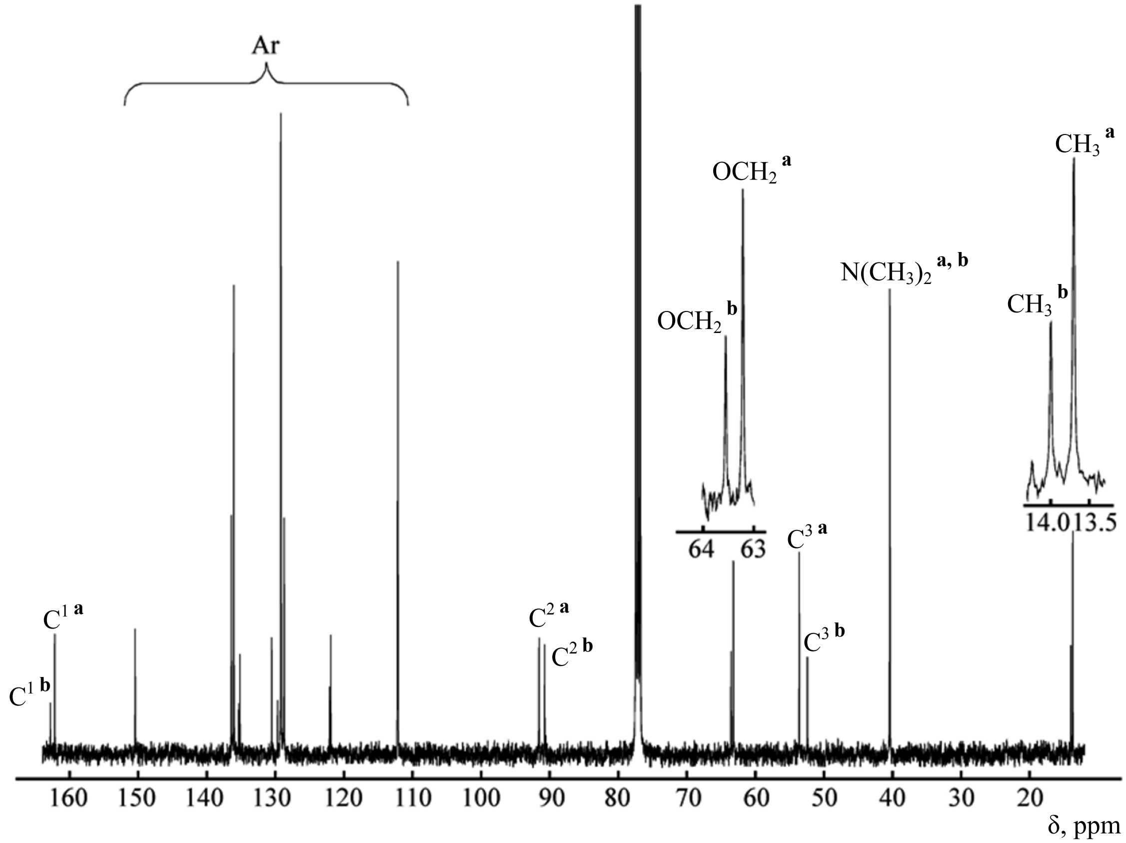


Fig. 4. $^{13}C–\{^1H\}$ NMR spectrum of **XIIIa**, **XIIIb** in $CDCl_3$.

similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 67%, colorless crystals (a mixture of diastereomers in a ratio of **a** : **b** = 1 : 1.1), mp 82–84°C (ethanol). Found, %: C 54.89; H 4.38; S 8.08. $C_{18}H_{18}ClNO_5S$. Calculated, %: C 54.61; H 4.55; S 8.09.

Ethyl 3-(4-dimethylaminophenyl)-3-(4-methylphenylsulfanyl)-2-nitropropanoate (XIIa, XIIb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 89%, oily substance (a mixture of diastereomers in a ratio of **a** : **b** = 1 : 1.1), R_f 0.70 (hexane–acetone, ~ 3 : 1). Found N, %: 7.38. $C_{20}H_{24}N_2O_4S$. Calculated N, %: 7.22.

Ethyl 3-(4-dimethylaminophenyl)-2-nitro-3-(4-chlorophenylsulfanyl)propanoate (XIIIa, XIIIb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 88%, pale orange crystals (a mixture of diastereomers in a ratio of **a** : **b** = 2.14 : 1), mp 82–84°C (ethanol). Found, %: C 55.56; H 5.25; N 6.72. $C_{19}H_{21}ClN_2O_4S$. Calculated, %: C 55.81; H 5.14; N 6.85.

Ethyl 3-(4-methylphenylsulfanyl)-2-nitro-3-(4-chlorophenyl)propanoate (XIV) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 56%, colorless crystals (single diastereomer), mp 78–80°C (ethanol). Found, %: C 57.04; H 4.77; N 3.69; S 8.56. $C_{18}H_{18}ClNO_4S$. Calculated, %: C 56.92; H 4.74; N 3.69; S 8.43.

Ethyl 2-nitro-3-(4-chlorophenyl)-3-(4-chlorophenylsulfanyl)propanoate (XVa, XVb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 79%, colorless oil (a mixture of diastereomers in a ratio of **a** : **b** = 1 : 1.15), R_f 0.78 (hexane–acetone, ~3 : 2). Found N, %: 3.71. $C_{17}H_{15}Cl_2NO_4S$. Calculated N, %: 3.50.

Ethyl 3-(4-methylphenylsulfanyl)-2-nitro-3-(4-nitrophenyl)propanoate (XVIa, XVIa b) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 90%, white crystals (a mixture of diastereomers in a ratio of **a** : **b** = 1.47 : 1), mp 96–98°C (ethanol). Found, %: C 55.40; H 4.64; N 7.34; S 8.12. $C_{18}H_{18}N_2O_6S$. Calculated, %: C 55.38; H 4.62; N 7.18; S 8.21.

Ethyl 2-nitro-3-(4-nitrophenyl)-3-(4-chlorophenylsulfanyl)propanoate (XVIIa, XVIIa b) was

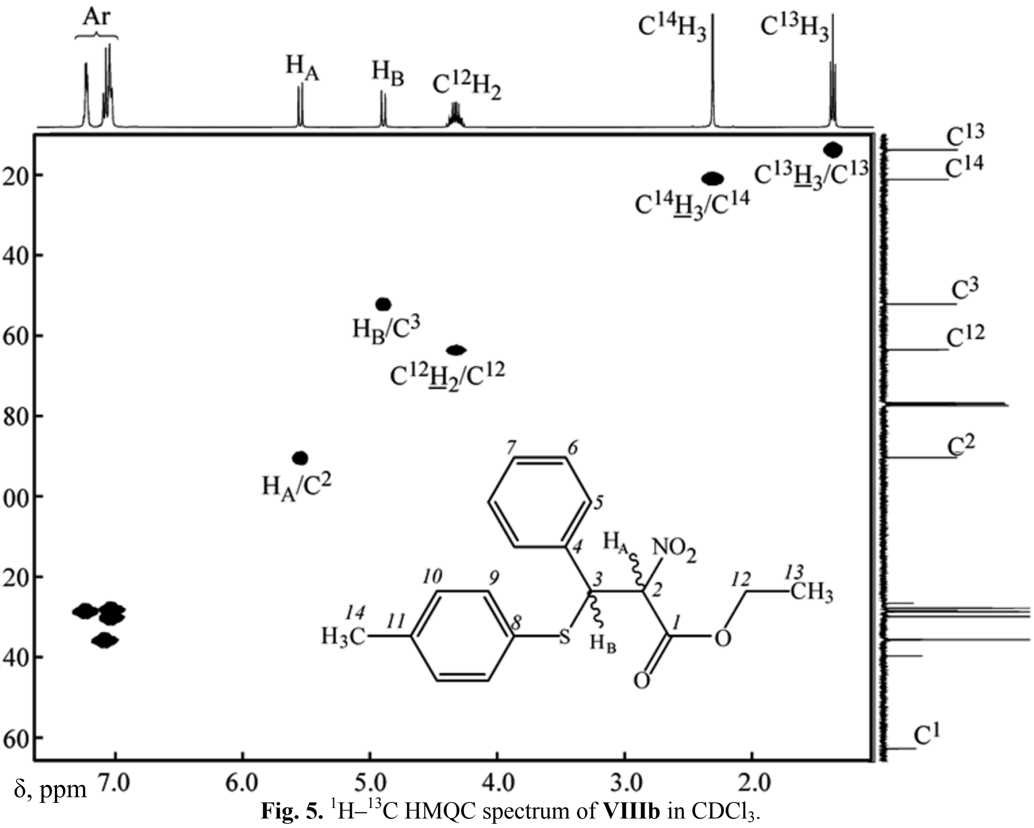


Fig. 5. $^1H-^{13}C$ HMQC spectrum of **VIIIb** in $CDCl_3$.

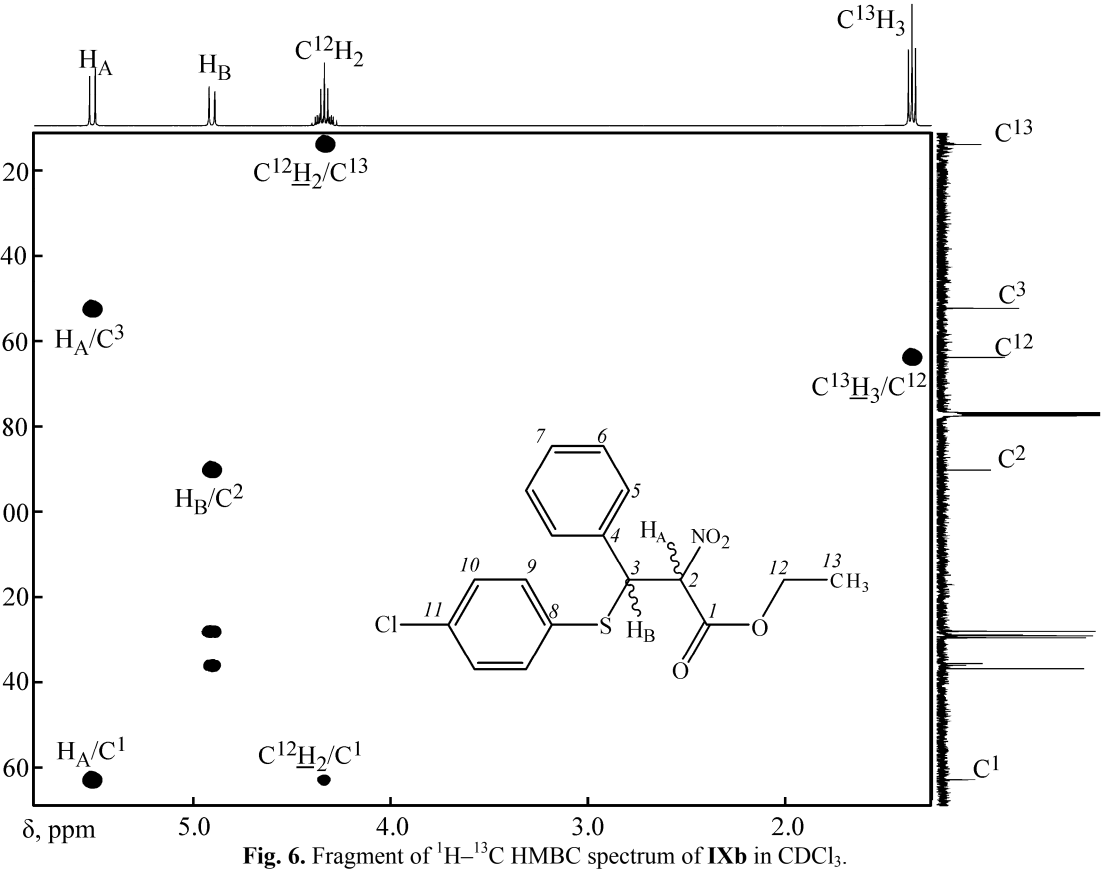


Fig. 6. Fragment of $^1H-^{13}C$ HMBC spectrum of **IXb** in $CDCl_3$.

obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 92%, colorless crystals (a mixture of diastereomers in a ratio of **a** : **b** = 1 : 1.47), mp 82–84°C (ethanol). Found, %: C 49.54; H 3.66; N 7.05; S 8.02. $C_{17}H_{15}ClN_2O_6S$. Calculated, %: C 49.70; H 3.65; N 6.82; S 7.80.

Ethyl 3-(4-methylphenylsulfanyl)-2-nitro-3-(2-furyl)propionate (XVIIIa, XVIIIa b) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 97%, oily substance (a mixture of diastereomers in a ratio of **a** : **b** = 1 : 1.04), R_f 0.45 (hexane–acetone, ~3 : 1). Found, %: C 57.11; H 4.83; N 3.97. $C_{16}H_{17}NO_5S$. Calculated, %: C 57.31; H 5.07; N 4.18.

Ethyl 2-nitro-3-(2-furyl)-3-(4-chlorophenylsulfanyl)propanoate (XIXa, XIXb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 89%, oily substance (a mixture of diastereomers in a ratio of **a** : **b** = 1.02:1), R_f 0.44 (hexane–acetone, ~3 : 1). Found, %: C 50.48; H 3.79; N 3.79. $C_{15}H_{14}ClNO_5S$. Calculated, %: C 50.63; H 3.94; N 3.94.

Ethyl 3-(4-methylphenylsulfanyl)-2-nitro-3-(2-thienyl)propanoate (XXa, XXb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 90%, colorless oil (a mixture of diastereomers in a ratio of **a** : **b** = 1.08 : 1), R_f 0.54 (hexane–acetone, ~3 : 1). Found N, %: 4.12. $C_{16}H_{17}NO_4S_2$. Calculated N, %: 3.99.

Ethyl 2-nitro-3-(2-thienyl)-3-(4-chlorophenylsulfanyl)propanoate (XXIa, XXIb) was obtained similarly to the synthesis of **VIIIa**, **VIIIb**. Yield 97%, colorless oil (a mixture of diastereomers in a ratio of **a** : **b** = 1.1 : 1), R_f 0.68 (hexane–acetone, ~3 : 2). Found N, %: 3.61. $C_{15}H_{14}ClNO_4S_2$. Calculated N, %: 3.77.

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