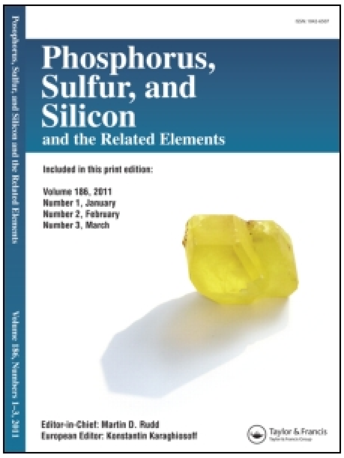

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An Efficient, Basic Resin-Mediated, One-Pot Synthesis of Dithiocarbazates Through Alcoholic Tosylates

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An Efficient, Basic Resin-Mediated, One-Pot Synthesis of Dithiocarbazates Through Alcoholic Tosylates

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A quick and efficient, one-pot synthesis of dithiocarbazates was accomplished in high yields by the reaction of various alcoholic tosylates of primary, secondary, and tertiary alcohols, with substituted hydrazines using an Amberlite IRA 400 (basic resin)/CS_2 system. The reaction conditions are mild with simpler work-up procedures than previously reported methods.

Keywords Alcoholic tosylates; Amberlite IRA 400; carbon disulfide; dithiocarbazates; substituted hydrazines

INTRODUCTION

Organic dithiocarbazates have attracted much attention due to their numerous remarkable medicinal, industrial, and synthetic applications.[1,2] They have been extensively used as pharmaceuticals,[3–6] agrochemicals,[7–10] intermediates in organic synthesis,[11–13] for the protection of amino groups in peptide synthesis,[14–17] as linkers in solid phase organic synthesis,[18,19] and as donor ligands in complexation reactions with transition metals.[20–22] To satisfy demand, their synthesis has been changed from the use of costly and toxic chemicals such as thiophosgene[23] and its derivatives,[24,25] directly or indirectly, to the more abundantly available, cheap, and safe reagents such as CS_2. However, their formation using CS_2 employed harsh reaction conditions such

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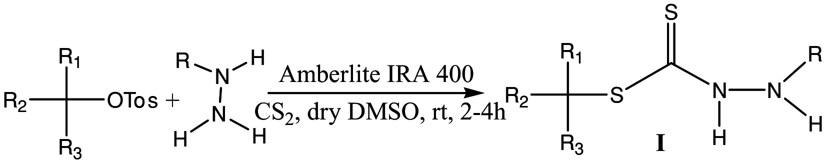
as the use of strong bases, higher reaction temperatures, and longer reaction times.[26,27] Thus, we were prompted to embark on developing improved procedures. Our group[28–40] has been engaged in the past several years in the development of new methodologies for the preparation of carbamates, dithiocarbamates, and related compounds using cheap, abundantly available, and safe reagents such as CO_2 and CS_2. More recently[41–47]we found that Amberlite IRA 400 (basic resin) is the best reagent for the synthesis of carbamates, dithiocarbamates, and dithiocarbonates (xanthates). Furthermore, use of basic resin has also been reported[48] for the tetrahydropyranylation of alcohols and phenols. In the present communication, we report here an efficient, one-pot synthesis of dithiocarbazates from variety of primary, secondary, and tertiary alcoholic tosylates and substituted hydrazines using basic resin/CS_2 system.

RESULTS AND DISCUSSION

In connection with our ongoing interest pertaining to the use of Amberlite IRA 400 (basic resin) for the synthesis of carbamates, dithiocarbamates, and dithiocarbonates (xanthates),[41–47] we now wish to report a simple and effective one-pot procedure for the preparation of dithiocarbazates from a variety of primary, secondary, and tertiary alcoholic tosylates and substituted hydrazines using a basic resin/CS_2 system. Thus, a mixture of substituted hydrazine and CS_2 were taken in dry DMSO, and Amberlite IRA 400 (basic resin) was added. The reaction was stirred for 30 min at room temperature and then the corresponding alcoholic tosylate was added. The reaction was further continued until the completion as determined by TLC (see Table I). It is proposed that the S^- of the dithiocarbazate ion produced will attach to the electrophilic carbon of the respective alcoholic tosylates to afford dithiocarbazates in high yields (80–98%) at room temperature in 2–4 h, as mentioned in Table I. The reaction proved to be successful, and the desired products were isolated and their identities confirmed by various spectroscopic and analytical techniques. Since the products were simply obtained by concentration of the organic layer after filtration of the basic resin from the reaction mixture, this indicates the novelty of the method among the reported procedures. Reactions have also been attempted without using Amberlite resin, but no products could be observed, which indicates the necessity of basic resin in carrying out the reaction. Alcoholic tosylates of primary, secondary, and tertiary alcohols were prepared following the standard procedure.[49] The whole reaction conditions are shown in Scheme 1.



SCHEME 1

We tried several solvents such as *n*-heptane, *n*-hexane, acetonitrile, benzene, toluene, methanol, dichloromethane, chloroform, DMSO, dimethylformamide, and hexamethylphosphoric triamide, of which dry DMSO at room temperature proved to be the most suitable.

In conclusion, we have developed a convenient and efficient protocol for one-pot, three-component coupling of various amines with a variety of alcoholic tosylates of primary, secondary, and tertiary alcohols via a CS_2 bridge using basic resin (Amberlite IRA 400). This method generates the corresponding dithiocarbazates in good to excellent yields. Furthermore, this method exhibits substrate versatility, mild reaction conditions, and experimental convenience. This synthetic protocol developed in our laboratory is believed to offer a more general method for the formation of carbon–sulfur bonds essential to numerous organic syntheses.

TABLE I Conversion of Alcoholic Tosylates into Dithiocarbazates of General Formula I

Entry	R_1	R_2	R_3	R	Time (h)	Isolated Yield (%)
1	*n*-C_3H_7	H	H	4-MeOPh	2	93
2	$PhCH_2CH_2$	H	H	Ph	2	96
3	$PhCH_2$	H	H	Ph	2.5	86
4	Ph	H	H	Bn	3	91
5	C_2H_5	Me	H	Bn	3	89
6	4-MeOPh	H	H	3-NO_2Ph	3	84
7	C_3H_7	H	H	4-NO_2Ph	3	85
8	C_3H_7	H	H	2,4-NO_2Ph	4	80
9	C_3H_7	H	H	Naphthyl	3	84
10	C_4H_9	C_4H_9	H	Ph	3	91
11	C_4H_9	C_4H_9	C_4H_9	Ph	3	88
12	C_5H_{11}	H	H	Bn	2.5	95
13	C_7H_{15}	H	H	Ph	2.5	92
14.	C_9H_{19}	H	H	Bn	2	98
15.	C_3H_7	C_3H_7	H	Ph.	3	86
16.	Ph	CH_3	H	Ph	3.5	83

Note: All the products were characterized by IR, NMR, and mass spectroscopic data.

EXPERIMENTAL

Chemicals were procured from Merck, Aldrich, and Fluka chemical companies. Amberlite IRA 400 (basic resin) was also purchased from Merck. Reactions were carried out under an atmosphere of nitrogen. IR spectra (4000–200 cm^{-1}) were recorded on Bomem MB-104–FTIR spectrophotometer, whereas NMRs were scanned on an AC-300F NMR (300 MHz) instrument using $CDCl_3$ and TMS as internal standard. Elemental analysis were made on a Carlo-Erba EA 1110-CNNO-S analyzer and agreed favorably with the calculated values.

Typical Experimental Procedure

To a stirred solution of substituted hydrazine (3 mmol) in anhyd. DMSO (5 mL), carbon disulfide (8 mmol) and basic resin (5 mmol) were slowly added at room temperature. Then the mixture was stirred for 0.5 h, at which point the required alcoholic tosylates (3 mmol) was added over a period of 5 min. The reaction mixture was further continued until the completion of reaction (cf Table I) under argon. The reaction mixture was filtered to remove the resin. The filtrate was poured into water (20 mL), and the organic layer was extracted with EtOAc (3 × 10 mL). The organic layer was washed with 0.1 N HCl (20 mL), a saturated solution of sodium bicarbonate (25 mL), and brine (30 mL), and was dried (Na_2SO_4) and concentrated to get the desired compound.

Data for Dithiocarbazates

N′-(4-Methoxyphenyl) Hydrazine Carbodithioc Acid Butyl Ester (1, $C_{12}H_{18}N_2OS_2$)

IR υ (cm^{-1}) = 675, 1210; ^1H NMR ($CDCl_3$) $\delta = 0.85$(t, 3H, J= 7.3 Hz), 1.33(m, 2H), 1.85(m, 2H), 2.0 (s, NH), 2.95 (t, 2H, J= 6.3 Hz), 3.73 (s, 3H), 4.05(m, NH), 6.75–7.60(m, 4H); ^{13}CNMR ($CDCl_3$) $\delta = 13.5$, 21.8, 32.4, 33.9, 43.7, 55.6, 112.5, 114.9, 134.5, 152.4, 222.5 (C=S) ppm; MS (EI): $m/z = 270$; Analysis: $C_{12}H_{18}N_2OS_2$, Calcd: C, 53.30; H, 6.71; N, 10.36; S, 23.72; Found: C, 53.24; H, 6.65; N, 10.33; S, 23.58.

N′-Phenyl Hydrazine Carbodithioc Acid 3-Phenyl Propyl Ester (2, $C_{16}H_{18}N_2S_2$)

IR υ (cm^{-1}) = 676, 1205; H^1NMR ($CDCl_3$) $\delta = 2.05$ (s, H, NH), 2.30 (m, 2H, Ph.CH_2. CH_2.CH_2-S)), 2.56 (t, 2H, $J = 7.2$ Hz, Ph.CH_2), 2.87(t, 2H, Ph.CH_2.CH_2. CH_2.S), 4.03 (m, H, Ph.*NH*), 6.66–7.12 (m, 10H, Ar-H); ^{13}C NMR ($CDCl_3$), $\delta = 32.2$, 33.6, 34.4, 112.5, 119.2, 125.8, 128.6, 129.5, 138.6, 221.6 (C = S) ppm; MS: $m/z = 302$; Analysis: $C_{16}H_{18}N_2S_2$, Calcd: C, 63.54; H, 6.00; N, 9.26; S, 21.20; Found: C, 63.35; H, 6.26; N, 9.17; S, 21.28.

N′-Phenyl-hydrazine Carbodithioc Acid Phenethyl Ester (3, $C_{15}H_{16}N_2S_2$)

IR υ (cm^{-1}) = 673, 1203; H^1NMR ($CDCl_3$) δ = 2.10 (s, H, NH), 3.20 (2H, t, $J = 6.5,$ Hz, Ph.CH_2*CH_2*S), 3.24 (m, 2H, $J = 7.2$ *Hz*, Ph*CH_2*), 4.52 (m, H, Ph*NH*), 6.69–7.15 (m, 10H, Ar-H); ^{13}CNMR ($CDCl_3$), δ = 34.5, 37.3, 47.2, 49.9, 118.6, 192.7, 223.3 (C=S) ppm; MS: m/z = 288; Analysis: $C_{15}H_{16}N_2S_2$, Calcd: C, 62.46; H, 5.59; N, 9.71; S, 22.23; Found: C, 62.70; H, 6.64; N, 9.59; S, 22.10.

N′-Butyl Hydrazine Carbodithioc Acid Benzyl Ester (4, $C_{12}H_{18}N_2S_2$)

IR υ (cm^{-1}) = 676, 1207; H^1NMR ($CDCl_3$) δ = 1.05 (t, 3H, CH_3), 1.33 (m,2H, *CH_2*CH_3), 1.56 (m, 2H, *CH_2*.CH_2CH_3), 2.05(br, NH), 2.65 (m, 2H, NH*CH_2*), 4.13 (s, 2H, Ph*CH_2*), 7.06–7.15 (m, 5H, Ar-H)); ^{13}CNMR ($CDCl_3$), δ = 13.7, 20.2, 31.5, 38.5, 50.9, 126.8, 127.6, 128.5, 141.8, 223.5 ppm; MS: m/z = 254; Analysis: $C_{12}H_{18}N_2S_2$, Calcd: C, 56.65; H, 7.13; N, 11.01; S, 25.21; Found: C, 56.46; H, 7.35; N, 11.27; S, 25.12.

N′-Butyl-hydrazine Carbodithioc Acid Sec-butyl Ester (5, $C_9H_{20}N_2S_2$)

IR υ (cm^{-1}) = 682, 1214; H^1NMR ($CDCl_3$) δ = 0.99 (t, 3H, CH_3), 1.05 (t, 3H, CH_3), 1.35 (m, 2H, CH_2.*CH_3*), 1.41(d, 3H, CH*CH_3*), 1.55 (m, 2H, CH_3CH_2*CH_2*), 1.96 (m, 2H, CH*CH_2*), 2.0 (br, H, NH), 2.65 (m, 2H, NH*CH_2*), 2.70 (m, H, *CH*-S), ^{13}C NMR ($CDCl_3$) δ = 10.2, 13.7, 20.2, 21.5, 31.2, 32.3, 40.1, 49.9, 223.4 ppm; MS: m/z = 220; Analysis: $C_9H_{20}N_2S_2$, Calcd: C,49.05; H, 9.15; N, 12.71; S, 29.10; Found: C, 49.33; H, 9.01; N, 12.75; S, 29.32.

N′-(3-Nitrophenyl)-hydrazine Carbodithioc Acid 4-Methoxy Benzyl Ester (6, $C_{15}H_{15}N_3O_3S_2$)

IR υ (cm^{-1}) = 678, 1211; H^1NMR ($CDCl_3$) δ = 2.05 (br, H, *NH*Ph.OMe), 3.73(s, 3H, O*CH_3*), 4.06 (br, H, *NH*Ph.NO_2), 6.65–7.66(m, 8H, Ar-H); ^{13}C NMR ($CDCl_3$) δ = 38.3, 56.7, 107.5, 114.6, 118.4, 128.5, 129.9, 133.6, 143.6, 148.7, 160.6, 223.2 ppm; MS: m/z = 349; Analysis: $C_{15}H_{15}N_3O_3S_2$, Calcd: C, 51.56; H, 4.33; N, 12.03; S, 18.35; Found: C, 51.23; H, 4.50; N, 12.24; S, 18.03.

N′-(4-Nitrophenyl)-hydrazine Carbodithioc Acid Butyl Ester (7, $C_{11}H_{15}N_3O_2S_2$)

IR υ (cm^{-1}) = 666, 1203; H^{1}NMR (CDCl$_3$) $\delta = 0.96$ (t, 3H, CH$_3$), 1.33 (m, 2H, *CH*$_2$CH$_3$), 1.96 (m, 2H, SCH$_2$.*CH*$_2$), 2.05 (br, H, N*H*), 2.87 (t, 2H, S*CH*$_2$), 4.04 (br, N, *NH*ArNO$_2$), 6.92-8.15 (m, 4H, Ar-H); ^{13}C NMR (CDCl$_3$) δ = 13.7, 21.6, 32.2, 33.7, 113.5, 124.6, 138.8, 143.3, 223.5 ppm; MS: m/z = 285; Analysis: $C_{11}H_{15}N_3O_2S_2$, Calcd: C, 46.29; H, 5.30; N, 14.72; S, 22.47; Found: C, 46.45; H, 5.17; N, 14.47; S, 22.21.

N′-(2,4-Dinitro-phenyl)hydrazinecarbodithioc Acid Butyl Ester (8, $C_{11}H_{14}N_4O_4S_2$)

IR υ (cm^{-1}) = 670, 1212; H^{1}NMR (CDCl$_3$) $\delta = 0.94$ (t, 3H, CH$_3$), 1.32 (m, 2H, *CH*$_2$CH$_3$), 1.95(m, 2H, SCH$_2$. *CH*$_2$), 2.02 (br, H, N*H*), 2.83 (t, 2H, S*CH*$_2$), 4.04 (br, N, *NH*ArNO$_2$), 7.19–9.50 (m, 3H, Ar-H); ^{13}CNMR (CDCl$_3$) δ = 13.8, 21.9, 32.3, 33.8, 113.6, 119.2, 130.2, 132.8, 139.7, 143.3, 222.5 ppm; MS: m/z = 330; Analysis: $C_{11}H_{14}N_4O_4S_2$, Calcd: C, 39.99; H, 4.27; N, 16.96; S, 19.41; Found: C, 40.22; H, 4.05; N, 16.76, S, 19.50.

N′-Naphthalen-2-yl Hydrazine Carbodithioc Acid Butyl Ester (9, $C_{15}H_{18}N_2S_2$)

IR υ (cm^{-1}) = 677, 1209; ^{1}H NMR (CDCl$_3$) $\delta = 0.95$ (t, 3H, CH$_3$), 1.33 (m, 2H, *CH*$_2$CH$_3$), 1.97 (m, 2H, SCH$_2$.*CH*$_2$), 2.05 (br, H, N*H*), 2.84 (t, 2H, S*CH*$_2$), 4.05 (br, N, *NH*ArNO$_2$), 6.76–7.55 (m, 7H, Ar-H); ^{13}CNMR (CDCl$_3$) δ = 13.9, 22.1, 32.5, 33.9, 107.4, 117.2, 121.3, 124.5, 126.6, 127.2, 133.5, 142.6, 224.1 ppm; MS: m/z = 290; Analysis: $C_{15}H_{18}N_2S_2$, Calcd: C, 62.03; H, 6.25; N, 9.64; S, 22.08; Found: C, 62.44; H, 6.33; N, 9.53; S, 22.25.

N′-Phenyl-hydrazine Carbodithioc Acid 1-Butyl Pentyl Ester (10, $C_{16}H_{26}N_2S_2$)

IR υ (cm^{-1}) = 677, 1212; ^{1}H NMR (CDCl$_3$) $\delta = 0.96$ (t, 6H, CH$_3$), 1.29 (m, 4H, *CH*$_2$CH$_2$CH), 1.33 (m, 4H, *CH*$_2$CH$_3$), 1.92 (m, 4H, CH*CH*$_2$), 2.05 (br, H, N*H*), 2.52 (t, H, S*CH*), 4.05 (br, H, *NH*Ar), 6.66-7.18 (m, 5H, Ar-H); ^{13}C NMR (CDCl$_3$) δ = 14.2, 23.1, 28.5, 36.2, 41.4, 112.2, 119.3, 129.0, 142.4, 223.3 ppm; MS: m/z = 310; Analysis: $C_{16}H_{26}N_2S_2$, Calcd: C, 61.89; H, 8.44; N, 9.02; S, 20.65; Found: C, 61.77; H, 8.54; N, 9.22; S, 20.46.

N′-Phenyl-hydrazine Carbodithioc Acid 1,1-Dibutyl Pentyl Ester (11, $C_{20}H_{34}N_2S_2$)

IR υ (cm^{-1}) = 669, 1210; ^{1}H NMR (CDCl$_3$) δ = 0.96 (t, 6H, CH$_3$), 1.29 (m, 4H, *CH*$_2$CH$_2$C), 1.33 (m, 4H, *CH*$_2$CH$_3$), 1.88 (m, 4H, CH*CH*$_2$), 2.04 (br, H, N*H*), 4.0 (br, H, *NH*-Ar), 6.67-7.19 (m, 5H, Ar-H); ^{13}C NMR

(CDCl$_3$) $\delta = 14.1, 23.4, 26.7, 39.6, 41.1, 112.5, 119.3, 129.6, 142.2, 223.5$ ppm; MS: m/z = 366; Analysis: $C_{20}H_{34}N_2S_2$, Calcd: C, 65.52; H, 9.35; N, 7.64; S, 17.49; Found: C, 65.27; H, 9.11; N, 7.44; S, 17.49.

N′-Butyl-hydrazine Carbodithioc Acid Hexyl Ester (12, $C_{11}H_{24}N_2S_2$)

IR υ (cm^{-1}) = 674, 1208; ^{1}H NMR (CDCl$_3$) δ = 0.96 (t, 6H, CH$_3$), 1.29 (m, 4H, *CH*$_2$*CH*$_2$CH$_2$CH$_3$), 1.33 (t, 2H, *CH*$_2$CH$_3$), 1.55 (m, 2H, NHCH$_2$*CH*$_2$), 1.96 (m, 2H, SCH$_2$*CH*$_2$), 2.0 (br, 2H, NH), 2.65 (t, 2H, NH*CH*$_2$), 2.87 (t, 2H, S*CH*$_2$), ^{13}C NMR (CDCl$_3$) $\delta = 13.7, 14.1, 20.2, 23.1, 28.6, 31.5, 32.6, 49.9, 223.1$ ppm; MS: m/z = 248; Analysis: $C_{11}H_{24}N_2S_2$, Calcd: C, 53.18; H, 9.74; N, 11.28; S, 25.81; Found: C, 53.33; H, 9.54; N, 11.39; S, 25.64.

N′-Phenyl-hydrazine Carbodithioc Acid N-octyl Ester (13, $C_{15}H_{24}N_2S_2$)

IR υ (cm^{-1}) = 679, 1211; ^{1}H NMR (CDCl$_3$) δ = 0.96 (t, 3H, CH$_3$), 1.29 (m, 8H, CH$_2$), 1.33 (m, 2H, *CH*$_2$CH$_3$), 1.96 (m, 2H, SCH$_2$*CH*$_2$), 2.0 (br, H, NH), 2.88 (t, 2H, S*CH*$_2$), 4.0 (br, H, Ph.*NH*), 6.65-7.20 (m, 5H, Ar-H), ^{13}C NMR (CDCl$_3$) $\delta = 14.5, 23.10, 28.9, 30.5, 31.5, 32.5, 112.2, 129.6, 118.9, 142.2, 223.6$ ppm; MS: m/z = 296; Analysis: $C_{15}H_{24}N_2S_2$, Calcd: C, 60.76; H, 8.16; N, 9.45; S, 21.63; Found: 60.55; H, 8.33 N, 9.30; S, 21.77.

N′-Butyl Hydrazine Carbodithioc Acid Decyl Ester (14, $C_{15}H_{32}N_2S_2$)

IR υ (cm^{-1}) = 673, 1220; ^{1}HNMR (CDCl$_3$), δ = 0.97 (s, 3H, CH$_3$), 0.99 (s, 3H, CH$_3$), 1.29 (m, 12H, CH$_2$), 1.34 (m, 4H, *CH*$_2$CH$_3$), 1.55 (m, 2H, *CH*$_2$CH$_2$CH$_3$), 1.96 (m, 2H, SCH$_2$*CH*$_2$), 2.0 (br, 2H, NH.NH), 2.65 (m, 2H, NH*CH*$_2$), 2.87 (t, 2H, S*CH*$_2$), ^{13}CNMR (CDCl$_3$) $\delta = 13.7, 14.5, 20.3, 23.1, 28.9, 30.6, 30.9, 31.5, 32.5, 222.1$ ppm; MS: m/z = 304; Analysis: $C_{15}H_{32}N_2S_2$, Calcd: C, 59.15; H, 10.59; N, 9.20; S, 21.06; Found: C, 59.30; H, 10.34; N, 9.21; S, 21.24.

N′-Phenyl Hydrazine Carbodithioc Acid 1-Propyl Butyl Ester (15, $C_{14}H_{22}N_2S_2$)

IR υ (cm^{-1}) = 675, 1210; ^{1}H NMR (CDCl$_3$) δ = 0.97 (s, 3H, CH$_3$), 1.33 (m, 4H, *CH*$_2$CH$_3$), 1.92 (m, 4H, CH*CH*$_2$), 2.0 (br, H, NH), 2.52 (m, H, C*H*-S), 4.1 (br, H, NH-Ar), 6.66–7.22 (m, 5H, Ar-H); ^{13}C NMR (CDCl$_3$) $\delta = 14.5, 20.1, 38.4, 40.8, 112.5, 118.3, 129.6, 143.3, 222.1$ ppm; MS: m/z = 282; Analysis: $C_{14}H_{22}N_2S_2$, Calcd: C, 59.53; H, 7.85; N, 9.92; S, 22.70; Found: C, 59.75; H, 7.66; N, 9.92; S, 22.44.

N′-Phenyl Hydrazine Carbodithioc Acid 1-Phenyl Ethyl Ester (16, $C_{15}H_{16}N_2S_2$)

IR υ (cm^{-1}) = 678, 1210; ^1H NMR ($CDCl_3$) $\delta = 1.69$ (d, 3H, CH_3), 2.2(br, H, NH), 3.98 (m, H, *CH*-S), 4.2 (br, H, NH-Ar), 6.66–7.22 (m, 10H, Ar-H), ^{13}CNMR ($CDCl_3$) $\delta = 23.4$, 41.1, 112.5, 118.9, 126.5, 128.5, 129.7, 141.3, 142.5, 222.1 ppm; MS: m/z = 288; Analysis: $C_{15}H_{16}N_2S_2$, Calcd: C, 62.46; H, 5.59; N, 9.71; S, 22.23; Found: C, 62.33; H, 5.46; N, 9.99; S, 22.36.

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