



A novel isocyanide-based three-component reaction: a facile synthesis of substituted 2*H*-pyran-3,4-dicarboxylates

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ABSTRACT

An efficient method for synthesis of 2*H*-pyran-3,4-dicarboxylates using the three-component reaction of dithiocarbamates, dialkyl acetylenedicarboxylates, and isocyanides in solvent-free conditions is described. In these reactions, synthesis of dithiocarbamates is possibly based on the one-pot reaction of secondary amines, CS₂, and alkyl halides in solvent-free conditions without using a catalyst. The mild reaction conditions and high yields of the reaction exhibit the good synthetic advantage of these methods.

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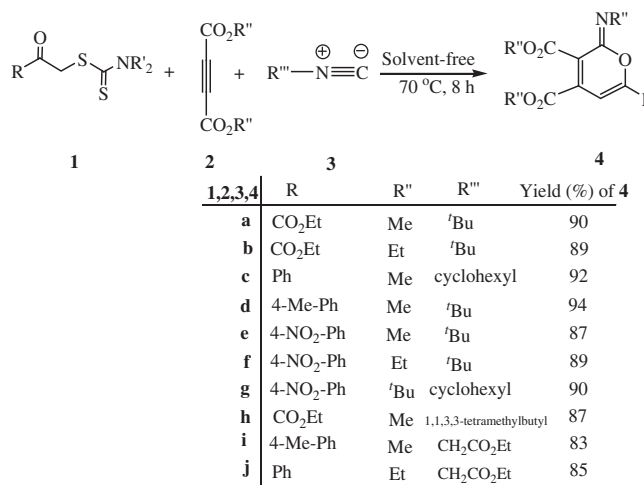
1. Introduction

Multicomponent reactions (MCRs) have been normally used by synthetic chemists as a basic means to generate molecular diversity from bifunctional substrates that react repeatedly in an intramolecular method.^{1–4} Devising such types of MCRs that include the formation of multiple bonds in a single action is one of the main challenges in new organic synthesis.^{5–9} They afford a great tool for the one-pot synthesis of various and complex compounds as well as small and drug-like heterocycles.¹⁰ MCRs that involve isocyanides are by far the most flexible reactions in terms of scaffolds and versatile compounds.^{1–5,11}

Here, we describe an efficient synthesis of 2*H*-pyran-3,4-dicarboxylates via the reaction of dithiocarbamates, dialkyl acetylenedicarboxylate, and isocyanides under solvent-free conditions at 70 °C (Scheme 1).

2. Result and discussion

As indicated in Scheme 1, dithiocarbamates **1**, activated acetylenes **2**, and isocyanides **3** undergo a smooth 1:1:1 addition reaction in solvent-free conditions at 70 °C (the activated acetylenes and dithiocarbamates are mixed first and then isocyanides is



Scheme 1. Three-component condensation reactions of isocyanides, activated acetylenes, and dithiocarbamates.

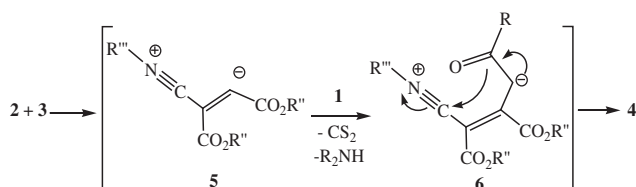
added) to produce 2*H*-pyran-3,4-dicarboxylate derivatives **4** in 83–94% yields (Scheme 1).

Structures of compounds **4a–4j** were deduced from their IR, mass, ¹H NMR and ¹³C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* values. The ¹H NMR spectrum of **4a** exhibited a triplet at δ=1.29

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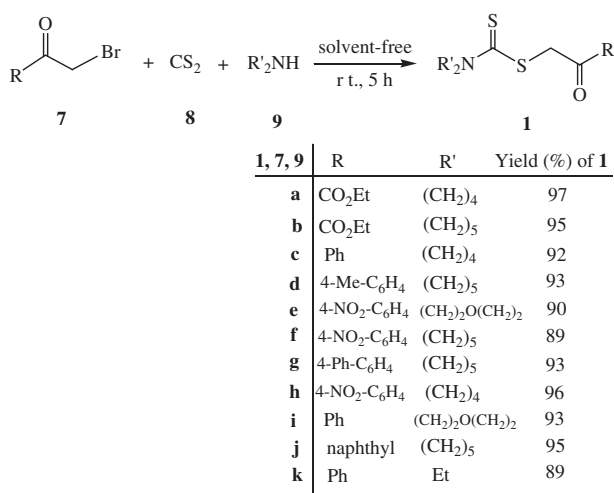
($^3J=7.2$ Hz) for the methyl group and four singlets for the *tert*-butyl (δ 1.27 ppm), methoxy (3.75 and 3.82 ppm), and olefinic (δ 6.57 ppm) protons. The proton-decoupled ^{13}C NMR spectrum of **4a** showed 16 distinct resonances in agreement with the proposed structure. Three singlet resonances at $\delta=160.4$, 162.3, and 163.8 ppm are observed in the ^{13}C NMR spectrum of **4a**, which are attributed to the carbonyl groups.

Although we have not established the mechanism of the reaction between the isocyanides and the acetylenic esters in the presence of the dithiocarbamate derivatives **1**, a possible explanation is proposed in Scheme 2. On the basis of the well-established chemistry of isocyanides,^{4,12–15} it is reasonable to assume that compound **5** results from an initial addition of the isocyanide to the acetylenic ester adds to dithiocarbamate **1** resulting in the formation of **6**, which undergoes cyclization to generate the 2*H*-pyran-3,4-dicarboxylate **4a–j**.



Scheme 2. Possible mechanism for the formation of products **4**.

Dithiocarbamates are important compounds due to their numerous biological activities¹⁶ and their essential function in agriculture¹⁷ and as linkers in solid-phase organic synthesis.¹⁸ They are also used in the rubber industry as vulcanization accelerators.¹⁹ *S*-Alkyl dithiocarbamates are used as herbicides, insecticides, fungicides, and in the treatment of cancer.²⁰ Dithiocarbamates **1** in these reactions were produced from the reaction of alkyl bromides **7**, carbon disulfide **8**, and secondary amines **9** under solvent-free conditions in excellent yields (Scheme 3).



Scheme 3. Three-component reactions of phenacyl bromides, disulfide carbon, and secondary amines.

In conclusion, we have developed the most useful and dependable procedure currently available for the synthesis of *S*-alkyl dithiocarbamates and 2*H*-pyran-3,4-dicarboxylate by using low-cost and readily available starting materials in one pot. This method represents a simple procedure, uses mild reaction conditions, and has general applicability.

3. Experimental

3.1. General

All chemicals were obtained from commercial sources. Melting points were measured on a Kofler hot stage apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker FT-500 spectrometer in chloroform, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded with a Finnigan Mat TSQ-70 spectrometer. Infrared (IR) spectra were acquired on a Nicolet Magna 550-FT spectrometer. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values.

3.2. Typical procedure for the preparation of 2*H*-pyran-3,4,6-tricarboxylate (**4**)

A mixture of dithiocarbamates (2 mmol) and dialkyl acetylenedicarboxylates (2 mmol) was warmed at about 70 °C for 2 h. Then, the isocyanide (2 mmol) was added slowly. The reaction mixture was stirred for 6 h at room temperature, and then poured into water (15 mL). The resulting precipitate was separated by filtration and recrystallized from diethyl ether (Et₂O) to afford the pure title compounds.

3.2.1. 6-Ethyl 3,4-dimethyl-2-(tert-butylimino)-2*H*-pyran-3,4,6-tricarboxylate (4a**).** White powder, mp 124–127 °C, yield: 0.61 g (90%). IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 1738, 1732, 1723, 1547 and 1245 cm^{-1} . ^1H NMR: $\delta=1.27$ (9H, s, Me₃C), 1.29 (3H, t, $^3J=7.6$ Hz, Me), 3.75 (3H, s, MeO), 3.82 (3H, s, MeO), 4.32 (2H, q, $^3J=7.6$ Hz, CH₂O), 6.57 (1H, s, CH) ppm. ^{13}C NMR: $\delta=14.0$ (Me), 29.6 (Me₃C), 51.6 (MeO), 52.3 (MeO), 55.3 (C–N), 63.1 (CH₂O), 117.4 (CH), 135.4 (C), 143.2 (C), 145.4 (C), 149.8 (C=N), 160.4 (C=O), 162.3 (C=O), 163.8 (C=O) ppm. MS: m/z (%)=339 (M⁺, 15), 308 (45), 282 (85), 57 (100), 31(86). Anal. Calcd for C₁₆H₂₁NO₇ (339.34): C, 56.63; H, 6.24; N, 4.13. Found: C, 56.58; H, 6.12; N, 4.02%.

3.2.2. Triethyl 2-(tert-butylimino)-2*H*-pyran-3,4,6-tricarboxylate (4b**).** Yellow powder, mp 130–132 °C, yield: 0.65 g (89%). IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 1738, 1735, 1724, 1582 and 1195 cm^{-1} . ^1H NMR: $\delta=1.26$ (9H, s, Me₃C), 1.29 (3H, t, $^3J=7.3$ Hz, Me), 1.32 (3H, t, $^3J=7.3$ Hz, Me), 1.36 (3H, t, $^3J=7.4$ Hz, Me), 4.13 (2H, q, $^3J=7.3$ Hz, CH₂O), 4.15 (2H, q, $^3J=7.3$ Hz, CH₂O), 4.24 (2H, q, $^3J=7.4$ Hz, CH₂O), 6.64 (1H, s, CH) ppm. ^{13}C NMR: $\delta=13.8$ (Me), 14.1 (Me), 14.3 (Me), 30.2 (Me₃C), 55.6 (C–N), 62.3 (CH₂O), 62.6 (CH₂O), 63.0 (CH₂O), 119.2 (CH), 136.8 (C), 142.6 (C), 145.4 (C), 148.4 (C=N), 161.5 (C=O), 162.8 (C=O), 163.3 (C=O) ppm. MS: m/z (%)=367 (M⁺, 10), 339 (62), 310 (84), 57 (100), 45 (48). Anal. Calcd for C₁₈H₂₅NO₇ (367.39): C, 58.85; H, 6.86; N, 3.81. Found: C, 58.78; H, 6.73; N, 3.75%.

3.2.3. Dimethyl 2-(cyclohexylimino)-6-phenyl-2*H*-pyran-3,4-dicarboxylate (4c**).** Yellow powder, mp 135–137 °C, yield: 0.68 g (92%). IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 1730, 1725, 1548 and 1278 cm^{-1} . ^1H NMR: $\delta=1.34$ (2H, m, CH₂), 1.40 (2H, m, CH₂), 1.47 (2H, m, CH₂), 1.66 (2H, m, CH₂), 1.84 (2H, m, CH₂), 3.75 (3H, s, MeO), 3.79 (1H, m, N–CH), 3.82 (3H, s, MeO), 6.68 (1H, s, CH), 7.16 (2H, t, $^3J=7.2$ Hz, 2CH), 7.30 (1H, t, $^3J=7.5$ Hz, CH), 7.63 (2H, d, $^3J=7.4$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=24.3$ (CH₂), 24.5 (CH₂), 25.5 (CH₂), 33.3 (CH₂), 33.5 (CH₂), 51.5 (3H, s, Me), 52.4 (3H, s, Me), 56.9 (C–N), 105.8 (CH), 128.3 (2CH), 129.5 (2CH), 131.5 (CH), 134.0 (C), 136.4 (C), 140.6 (C), 155.2 (C=N), 158.6 (C), 163.5 (C=O), 165.9 (C=O) ppm. Anal. Calcd for C₂₁H₂₃NO₅ (369.41): C, 68.28; H, 6.28; N, 3.79. Found: C, 68.32; H, 6.37; N, 3.84%.

3.2.4. Dimethyl 2-(tert-butylimino)-6-(4-methylphenyl)-2*H*-pyran-3,4-dicarboxylate (4d**).** Pale yellow powder, mp 143–145 °C, yield:

0.67 g (94%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1732, 1725, 1557, 1410 and 1127 cm^{-1} . ^1H NMR: $\delta=1.25$ (9H, s, CMe_3), 2.35 (3H, s, Me), 3.78 (3H, s, MeO), 3.83 (3H, s, MeO), 6.42 (1H, s, CH), 7.42 (2H, d, $^3J=7.6$ Hz, 2CH), 7.84 (2H, d, $^3J=7.6$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=21.7$ (Me), 30.6 (CMe_3), 51.6 (MeO), 52.4 (MeO), 57.2 (C–N), 108.6 (CH), 125.7 (2CH), 129.3 (2CH), 133.2 (C), 134.5 (C), 137.0 (C), 142.4 (C), 155.2 (C=N), 156.8 (C), 163.8 (C=O), 164.7 (C=O) ppm. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_5$ (357.40): C, 67.21; H, 6.49; N, 3.92. Found: C, 67.18; H, 6.53; N, 4.02%.

3.2.5. Dimethyl 2-(tert-butylimino)-6-(4-nitrophenyl)-2H-pyran-3,4-dicarboxylate (4e). Yellow powder, mp 152–154 °C, yield: 0.68 g (87%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1738, 1732, 1545, 1412 and 1175 cm^{-1} . ^1H NMR: $\delta=1.27$ (9H, s, CMe_3), 3.80 (3H, s, MeO), 3.85 (3H, s, MeO), 6.48 (1H, s, CH), 7.87 (2H, d, $^3J=8.2$ Hz, 2CH), 8.45 (2H, d, $^3J=8.2$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=29.8$ (CMe_3), 52.0 (MeO), 52.6 (MeO), 56.8 (C–N), 107.6 (CH), 125.2 (2CH), 129.8 (2CH), 133.9 (C), 139.7 (C), 142.9 (C), 146.8 (C), 156.4 (C=N), 158.9 (C), 162.4 (C=O), 164.6 (C=O) ppm. MS: m/z (%)=388 (M^+ , 15), 357 (54), 266 (52), 120 (85), 57 (100), 31 (78). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_7$ (388.37): C, 58.76; H, 5.19; N, 7.21. Found: C, 58.68; H, 5.04; N, 7.14%.

3.2.6. Diethyl 2-(tert-butylimino)-6-(4-nitrophenyl)-2H-pyran-3,4-dicarboxylate (4f). Pale yellow powder, mp 154–156 °C, yield: 0.74 g (89%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1730, 1727, 1645, 1548 and 1232 cm^{-1} . ^1H NMR: $\delta=1.27$ (9H, s, CMe_3), 1.31 (3H, t, $^3J=7.4$ Hz, Me), 1.37 (3H, t, $^3J=7.3$ Hz, Me), 4.12 (2H, q, $^3J=7.4$ Hz, CH_2O), 4.25 (2H, q, $^3J=7.3$ Hz, CH_2O), 6.45 (1H, s, CH), 8.05 (2H, d, $^3J=8.0$ Hz, 2CH), 8.37 (2H, d, $^3J=8.0$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=13.8$ (Me), 14.2 (Me), 30.4 (CMe_3), 57.0 (C–N), 61.4 (CH_2O), 52.6 (CH_2O), 107.5 (CH), 126.0 (2CH), 130.1 (2CH), 140.2 (C), 141.3 (C), 143.0 (C), 146.5 (C), 157.2 (C=N), 157.6 (C), 162.5 (C=O), 165.3 (C=O) ppm. Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_7$ (416.43): C, 60.57; H, 5.81; N, 6.73. Found: C, 60.49; H, 5.75; N, 6.68%.

3.2.7. Di(tert-butyl) 2-(cyclohexylimino)-6-(4-nitrophenyl)-2H-pyran-3,4-dicarboxylate (4g). Yellow powder, mp 147–149 °C, yield: 0.82 g (90%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1728, 1718, 1654, 1568 and 1258 cm^{-1} . ^1H NMR: $\delta=1.32$ (2H, m, CH_2), 1.38 (2H, m, CH_2), 1.45 (2H, m, CH_2), 1.65 (2H, m, CH_2), 1.67 (9H, s, CMe_3), 1.71 (9H, s, CMe_3), 1.83 (2H, m, CH_2), 3.75 (1H, m, N–CH), 6.48 (1H, s, CH), 7.68 (2H, d, $^3J=7.8$ Hz, 2CH), 7.92 (2H, d, $^3J=7.8$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=24.5$ (CH_2), 24.7 (CH_2), 25.8 (CH_2), 28.2 (CMe_3), 29.4 (CMe_3), 34.3 (CH_2), 35.0 (CH_2), 57.0 (C–N), 79.2 (CMe_3), 82.3 (CMe_3), 108.3 (CH), 125.6 (2CH), 129.8 (2CH), 135.8 (C), 138.5 (C), 142.0 (C), 148.3 (C), 154.8 (C=N), 159.2 (C), 163.4 (C=O), 165.7 (C=O) ppm. Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{NO}_5$ (453.58): C, 71.50; H, 7.78; N, 3.09. Found: C, 71.45; H, 7.70; N, 2.98%.

3.2.8. 6-Ethyl 3,4-dimethyl-2-(1,1,3,3-tetramethylbutylimino)-2H-pyran-3,4,6-tricarboxylate (4h). Yellow powder, mp 137–139 °C, yield: 0.69 g (87%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1730, 1722, 1720, 1545, 1425 and 1167 cm^{-1} . ^1H NMR: $\delta=1.03$ (9H, s, CMe_3), 1.24 (3H, t, $^3J=7.3$ Hz, Me), 1.55 (3H, s, Me), 1.56 (3H, s, Me), 1.83 (2H, s, CH_2), 3.74 (3H, s, MeO), 3.82 (3H, s, MeO), 4.23 (2H, q, $^3J=7.3$ Hz, Me), 6.84 (1H, s, CH) ppm. ^{13}C NMR: $\delta=13.9$ (Me), 29.7 (C), 29.8 (Me), 31.6 (CMe_3), 31.9 (Me), 51.5 (MeO), 52.7 (MeO), 55.0 (CH_2), 59.2 (C–N), 61.2 (CH_2O), 109.4 (CH), 139.0 (C), 141.3 (C), 144.5 (C), 158.4 (C), 160.2 (C=O), 161.3 (C=O), 163.5 (C=O) ppm. Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_7$ (395.45): C, 60.75; H, 7.39; N, 3.54. Found: C, 60.68; H, 7.32; N, 3.43%.

3.2.9. Dimethyl 2-(2-ethoxy-2-oxoethylimino)-6-(4-methylphenyl)-2H-pyran-3,4-dicarboxylate (4i). White powder, mp 138–140 °C, yield: 0.64 g (83%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1738, 1730, 1728, 1624, 1557, 1410 and 1127 cm^{-1} . ^1H NMR: $\delta=1.30$ (3H, t, $^3J=7.2$ Hz, Me), 2.35 (3H, s, Me), 3.76 (3H, s, MeO), 3.83 (3H, s, MeO), 4.20 (2H, s, CH_2), 4.28 (2H, q, $^3J=7.2$ Hz, OCH_2), 6.47 (1H, s, CH), 7.54 (2H, d,

$^3J=7.5$ Hz, 2CH), 7.85 (2H, d, $^3J=7.6$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=14.1$ (Me), 21.4 (Me), 50.3 ($\text{CH}_2\text{–N}$), 51.6 (MeO), 52.4 (MeO), 61.3 (OCH_2), 107.4 (CH), 126.3 (2CH), 129.7 (2CH), 134.8 (C), 135.2 (C), 137.3 (C), 142.8 (C), 153.6 (C), 156.5 (C=N), 160.2 (C=O), 162.7 (C=O), 164.3 (C=O) ppm. Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_7$ (387.39): C, 62.01; H, 5.46; N, 3.62. Found: C, 61.96; H, 5.38; N, 3.54%.

3.2.10. Diethyl 2-(2-ethoxy-2-oxoethylimino)-6-phenyl-2H-pyran-3,4-dicarboxylate (4j). White powder, mp 144–146 °C, yield: 0.58 g (85%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1732, 1728, 1725, 1612, 1547, 1385 and 1215 cm^{-1} . ^1H NMR: $\delta=1.23$ (3H, t, $^3J=7.4$ Hz, Me), 1.26 (3H, t, $^3J=7.5$ Hz, Me), 1.29 (3H, t, $^3J=7.3$ Hz, Me), 4.12 (2H, q, $^3J=7.4$ Hz, OCH_2), 4.15 (2H, q, $^3J=7.5$ Hz, OCH_2), 4.18 (2H, s, CH_2), 4.20 (2H, q, $^3J=7.5$ Hz, OCH_2), 6.52 (1H, s, CH), 7.21 (2H, t, $^3J=7.8$ Hz, 2CH), 7.42 (1H, t, $^3J=7.6$ Hz, CH), 7.79 (2H, t, $^3J=7.6$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=13.8$ (Me), 14.0 (Me), 14.3 (Me), 52.4 ($\text{CH}_2\text{–N}$), 60.3 (OCH_2), 61.5 (OCH_2), 62.0 (OCH_2), 108.0 (CH), 128.2 (2CH), 129.5 (2CH), 131.4 (CH), 135.0 (C), 135.8 (C), 142.3 (C), 154.8 (C), 158.5 (C=N), 162.3 (C=O), 163.5 (C=O), 164.8 (C=O) ppm. Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_7$ (401.41): C, 62.84; H, 5.78; N, 3.49. Found: C, 62.75; H, 5.69; N, 3.38%.

3.3. Typical procedure for the preparation of dithiocarbamate (1)

To a mixture of the alkyl bromide (2 mmol) and carbon disulfide (4 mmol) in the test tube, amine (4 mmol) was added and stirred at 0 °C for 30 min, then warmed to room temperature and stirring was continued until the reaction was complete (reaction mixture solidified or monitored by TLC). The reaction was quenched by the addition of water (10 mL) and was extracted with EtOAc (3×5 mL), dried over anhydrous Na_2SO_4 , and evaporated to give NMR pure product. Further purification in all cases can be achieved by silica gel column chromatography eluted with *n*-hexane and ethyl acetate to afford the pure dithiocarbamate.

3.3.1. Ethyl 2-oxo-3-[(pyrrolidinylcarbothioyl)sulfanyl] propanoate (1a). Pale yellow powder, mp 125–127 °C, yield: 0.51 g (97%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1738, 1695, 1614, 1531, 1430, 1334, 1194 and 1157 cm^{-1} . ^1H NMR: $\delta=0.89$ (3H, t, $^3J=7.2$ Hz, Me), 2.10 (4H, m, 2 CH_2), 3.77 (2H, t, $^3J=6.8$ Hz, CH_2), 3.94 (2H, t, $^3J=6.8$ Hz, CH_2), 4.02 (2H, q, $^3J=7.2$ Hz, OCH_2), 4.35 (2H, s, CH_2) ppm. ^{13}C NMR: $\delta=13.5$ (Me), 25.8 (2 CH_2), 42.6 (CH_2), 48.6 (CH_2NCH_2), 62.0 (OCH_2), 160.5 (C=O), 187.6 (C=O), 198.2 (C=S) ppm. MS: m/z (%)=261 (M^+ , 20), 216 (56), 191 (86), 70 (94), 45 (100). Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_3\text{S}_2$ (261.35): C, 45.96; H, 5.78; N, 5.36. Found: C, 45.87; H, 5.67; N, 5.28%.

3.3.2. Ethyl 2-oxo-3-[(piperidinocarbothioyl)sulfanyl] propanoate (1b). Yellow powder, mp 128–130 °C, yield: 0.50 g (95%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1732, 1695, 1595, 1465, 1386, 1248 and 1194 cm^{-1} . ^1H NMR: $\delta=1.38$ (3H, t, $^3J=7.3$ Hz, Me), 1.52–1.63 (6H, m, 3 CH_2), 3.75 (2H, t, $^3J=7.2$ Hz, CH_2), 3.94 (2H, t, $^3J=7.2$ Hz, CH_2), 4.37 (2H, q, $^3J=7.3$ Hz, OCH_2), 4.38 (2H, s, CH_2) ppm. ^{13}C NMR: $\delta=13.9$ (Me), 23.8 (CH_2), 25.9 (CH_2), 41.7 (CH_2), 52.4 (CH_2), 53.8 (CH_2), 62.5 (OCH_2), 160.56 (C=O), 187.2 (C=O), 193.4 (C=S) ppm. MS: m/z (%)=275 (M^+ , 15), 230 (45), 191 (52), 45 (100). Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{S}_2$ (275.38): C, 47.98; H, 6.22; N, 5.09. Found: C, 47.85; H, 6.14; N, 4.96%.

3.3.3. 2-Oxo-2-phenylethyl-1-pyrrolidinecarbothioate (1c). Pale yellow powder, mp 135–137 °C, yield: 0.49 g (92%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1685, 1585, 1457, 1324, 1283 and 1168 cm^{-1} . ^1H NMR: $\delta=1.97$ –2.03 (2H, m, CH_2), 2.09–2.14 (2H, m, CH_2), 3.77 (2H, t, $^3J=6.8$ Hz, CH_2), 3.94 (2H, t, $^3J=6.8$ Hz, CH_2), 4.92 (2H, s, CH_2), 7.48 (2H, t, $^3J=7.5$ Hz, 2CH), 7.59 (1H, t, $^3J=7.4$ Hz, CH), 8.08 (2H, d, $^3J=7.4$ Hz, 2CH) ppm. ^{13}C NMR: $\delta=24.4$ (CH_2), 26.2 (CH_2), 44.5 (CH_2), 50.8 (CH_2), 55.5 (CH_2), 128.6 (2CH), 128.9 (2CH), 133.5 (CH),

136.2 (C), 191.1 (C=O), 193.5 (C=S) ppm. Anal. Calcd for C₁₃H₁₅NOS₂ (265.39): C, 58.84; H, 5.70; N, 5.28. Found: C, 58.90; H, 5.76; N, 5.32%.

3.3.4. 2-(4-Methylphenyl)-2-oxoethyl tetrahydro-1(2H)-pyridine carbodithioate (1d). White powder, mp 142–144 °C, yield: 0.58 g (54%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1683, 1586, 1328, 1269 and 1153 cm^{-1} . ¹H NMR: δ =1.59–1.73 (6H, m, 3CH₂), 2.41 (3H, s, Me), 3.72 (2H, t, ³J=6.5 Hz, CH₂), 3.96 (2H, t, ³J=6.5 Hz, CH₂), 4.90 (2H, s, CH₂), 7.83 (2H, d, ³J=7.6 Hz, 2CH), 7.95 (2H, d, ³J=7.6 Hz, 2CH) ppm. ¹³C NMR: δ =21.4 (Me), 24.4 (CH₂), 25.7 (2CH₂), 37.8 (CH₂), 45.4 (CH₂), 50.1 (CH₂), 128.7 (2CH), 129.5 (2CH), 132.9 (C), 144.3 (C), 187.3 (C=O), 193.9 (C=S) ppm. Anal. Calcd for C₁₅H₁₉NOS₂ (293.44): C, 61.40; H, 6.53; N, 4.77. Found: C, 61.32; H, 6.46; N, 4.65%.

3.3.5. 2-(4-Nitrophenyl)-2-oxoethyl tetrahydro-1(2H)-morpholine carbodithioate (1e). Yellow powder, mp 152–154 °C, yield: 0.59 g (90%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1687, 1564, 1487, 1326 and 1147 cm^{-1} . ¹H NMR: δ =3.79–3.82 (4H, m, 2CH₂), 4.02–4.30 (4H, m, 2CH₂), 4.86 (2H, s, CH₂), 8.16 (2H, d, ³J=7.8 Hz, 2CH), 8.35 (2H, d, ³J=7.8 Hz, 2CH) ppm. ¹³C NMR: δ =44.0 (CH₂), 46.4 (CH₂), 52.1 (CH₂), 66.6 (CH₂), 67.0 (CH₂), 124.6 (2CH), 129.6 (2CH), 130.8 (C), 142.6 (C), 192.1 (C=O), 195.3 (C=S) ppm. Anal. Calcd for C₁₃H₁₄N₂O₄S₂ (326.38): C, 47.84; H, 4.32; N, 8.58. Found: C, 47.75; H, 4.26; N, 8.47%.

3.3.6. 2-(4-Nitrophenyl)-2-oxoethyl tetrahydro-1(2H)-pyridine carbodithioate (1f). Yellow powder, mp 158–160 °C, yield: 0.58 g (89%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1692, 1587, 1423, 1322 and 1285 cm^{-1} . ¹H NMR: δ =1.43–1.71 (6H, m, 3CH₂), 3.94 (2H, t, ³J=6.5 Hz, CH₂), 4.10 (2H, t, ³J=6.5 Hz, CH₂), 5.28 (2H, s, CH₂), 8.15 (2H, d, ³J=7.5 Hz, 2CH), 8.33 (2H, d, ³J=7.5 Hz, 2CH) ppm. ¹³C NMR: δ =24.5 (CH₂), 26.9 (2CH₂), 45.1 (CH₂), 52.7 (CH₂), 54.8 (CH₂), 124.5 (2CH), 130.5 (2CH), 139.8 (C), 141.6 (C), 189.6 (C=O), 196.4 (C=S) ppm. Anal. Calcd for C₁₄H₁₆N₂O₃S₂ (324.41): C, 51.83; H, 4.97; N, 8.64. Found: C, 51.75; H, 4.90; N, 8.54%.

3.3.7. 2-Biphenyl-2-oxoethyl tetrahydro-1(2H)-pyridine carbodithioate (1g). Orange powder, mp 136–138 °C, yield: 0.66 g (93%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1683, 1576, 1388, 1242 and 1147 cm^{-1} . ¹H NMR: δ =1.43–1.71 (6H, m, 3CH₂), 4.02 (4H, m, 2CH₂), 4.95 (2H, s, CH₂), 7.41 (2H, t, ³J=7.4 Hz, 2CH), 7.48 (1H, t, ³J=7.4 Hz, CH), 7.63 (2H, d, ³J=7.5 Hz, 2CH), 7.72 (2H, t, ³J=7.8 Hz, 2CH), 8.16 (2H, d, ³J=7.8 Hz, 2CH) ppm. ¹³C NMR: δ =24.5 (CH₂), 26.9 (2CH₂), 44.6 (CH₂), 51.7 (CH₂), 53.6 (CH₂), 126.9 (2CH), 127.2 (CH), 127.6 (2CH), 128.9 (2CH), 129.4 (2CH), 134.9 (C), 139.8 (C), 142.8 (C), 189.9 (C=O), 194.0 (C=S) ppm. Anal. Calcd for C₂₀H₂₁NOS₂ (355.51): C, 67.57; H, 5.95; N, 3.94. Found: C, 67.48; H, 5.87; N, 3.89%.

3.3.8. 2-(4-Nitrophenyl)-2-oxoethyl tetrahydro-1(2H)-pyrrolidine carbodithioate (1h). Yellow powder, mp 143–145 °C, yield: 0.59 g (96%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1695, 1580, 1454, 1325 and 1185 cm^{-1} . ¹H NMR: δ =1.98–2.04 (2H, m, CH₂), 2.09–2.17 (2H, m, CH₂), 3.76 (2H, t, ³J=7.2 Hz, CH₂), 3.91 (2H, t, ³J=7.2 Hz, CH₂), 4.86 (2H, s, CH₂), 8.24 (2H, d, ³J=7.6 Hz, 2CH), 8.34 (2H, d, ³J=7.6 Hz, 2CH) ppm. ¹³C NMR: δ =24.3 (CH₂), 26.1 (CH₂), 43.9 (CH₂), 50.9 (CH₂), 55.7 (CH₂), 123.9 (2CH), 129.7 (2CH), 140.8 (C), 146.9 (C), 190.3 (C=O), 192.5 (C=S) ppm. Anal. Calcd for C₁₃H₁₄N₂O₃S₂ (310.38): C, 50.31; H, 4.55; N, 9.03. Found: C, 50.38; H, 4.62; N, 9.12%.

3.3.9. 2-Oxo-2-phenylethyl-1-morpholine carbodithioate (1i). Pale yellow powder, mp 130–132 °C, yield: 0.52 g (93%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1700, 1690, 1573, 1458, 1322 and 1274 cm^{-1} . ¹H NMR:

δ =3.77–3.79 (4H, m, 2CH₂), 4.08–4.26 (4H, m, 2CH₂), 4.92 (2H, s, CH₂), 7.49 (2H, t, ³J=7.4, 2CH), 7.60 (1H, t, ³J=7.3 Hz, CH), 8.07 (2H, d, ³J=7.4 Hz, CH) ppm. ¹³C NMR: δ =44.8 (CH₂), 50.9 (CH₂), 51.3 (CH₂), 66.2 (2CH₂), 128.6 (2CH), 128.8 (2CH), 133.6 (CH), 136.2 (C), 193.0 (C=O), 196.0 (C=S) ppm. Anal. Calcd for C₁₃H₁₅NOS₂ (281.39): C, 55.49; H, 5.37; N, 4.98. Found: C, 55.38; H, 5.28; N, 4.86%.

3.3.10. 2-(Naphthyl)-2-oxoethyl tetrahydro-1(2H)-pyridine carbodithioate (1j). White powder, mp 138–140 °C, yield: 0.63 g (95%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1698, 1583, 1447, 1338 and 1236 cm^{-1} . ¹H NMR: δ =1.45–1.73 (6H, m, 3CH₂), 3.99–4.29 (4H, m, 2CH₂), 5.05 (2H, s, CH₂), 7.57 (1H, t, ³J=7.6 Hz, CH), 7.62 (1H, t, ³J=7.5 Hz, CH), 7.88 (1H, d, ³J=7.5 Hz, CH), 7.92 (1H, d, ³J=7.5 Hz, CH), 8.01 (1H, d, ³J=7.8 Hz, CH), 8.10 (1H, d, ³J=7.8 Hz, CH), 8.66 (1H, s, CH) ppm. ¹³C NMR: δ =24.2 (CH₂), 26.0 (2CH₂), 45.0 (CH₂), 51.7 (CH₂), 53.7 (CH₂), 124.2 (CH), 126.8 (CH), 127.8 (CH), 128.5 (CH), 128.7 (CH), 129.9 (CH), 130.4 (CH), 132.5 (C), 133.6 (C), 135.8 (C), 193.5 (C=O), 194.1 (C=S) ppm. Anal. Calcd for C₁₈H₁₉NOS₂ (329.47): C, 65.62; H, 5.81; N, 4.25. Found: C, 65.53; H, 5.74; N, 4.14%.

3.3.11. 2-Oxo-2-phenylethyl-1-diethylamine carbodithioate (1k). Pale yellow powder, mp 124–126 °C, yield: 0.48 g (89%). IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 1694, 1625, 1595, 1454, 1342 and 1126 cm^{-1} . ¹H NMR: δ =1.26 (3H, t, ³J=7.3 Hz, Me), 1.34 (3H, t, ³J=7.3 Hz, Me), 3.83 (2H, d, ³J=7.3 Hz, CH₂), 4.02 (2H, d, ³J=7.3 Hz, CH₂), 4.90 (2H, s, CH₂), 7.48 (2H, t, ³J=7.5, 2CH), 7.58 (1H, t, ³J=7.5 Hz, CH), 8.07 (2H, t, ³J=7.5, 2CH) ppm. ¹³C NMR: δ =11.5 (Me), 12.6 (Me), 45.0 (CH₂), 47.0 (CH₂), 50.1 (CH₂), 128.5 (2CH), 128.6 (2CH), 133.4 (CH), 136.2 (C), 193.4 (C=O), 194.0 (C=S) ppm. Anal. Calcd for C₁₃H₁₇NOS₂ (267.40): C, 58.39; H, 6.41; N, 5.24. Found: C, 58.28; H, 6.32; N, 5.12%.

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