CHAPTER-4

Synthesis of functionalized *S*-benzyl dithiocarbamates from diazo-compound via multi-component reactions with carbon disulfide and secondary amines

4.1 Introduction

Diazo compounds are important synthons in organic chemistry and they have been widely used as carbene precursors to construct various biologically active molecules [1]. Diazo compounds usually undergo cyclopropanation, nucleophilic insertion and rearrangement reactions [1a-b]. Among the different types of diazo compounds, α-aryl α-diazoesters are relatively stable and they are well explored in many organic transformations including nucleophilic insertion reactions with a variety of nucleophiles (e.g. nitrogen, oxygen, sulfur, phosphorous, silane, etc.) in the presence of transition metals [2], Lewis acids [3], Brønsted acids [4], and light conditions [5].

Over the past few decades, the importance of dithiocarbamate compounds has grown significantly due to their diverse applications in different fields [6]. Since 1940s, various metal-dithiocarbamates including zineb, maneb, nabam, ziram, mancozeb, etc., have been used for controlling the fungal infections in crops [7]. The organic dithiocarbamate, thiram (dimethyldithiocarbamate) has been used as a fungicide and ectoparasiticide to prevent fungal infections in seeds and crops. Moreover, organic dithiocarbamates display antioxidant, antibacterial, antifungal, anticancer and anti-Alzheimer activities [8]. On the other hand, dithiocarbamates are used as intermediates [9], protecting groups [10], linkers [11], polymerization agents [12], etc [13], in organic synthesis. Considering their importance, the synthesis of different classes of organic dithiocarbamates has been explored. Of the different types, *S*-benzyl dithiocarbamates received considerable attention due to their importance in biology and polymer chemistry[8] **(Figure 4.1**).

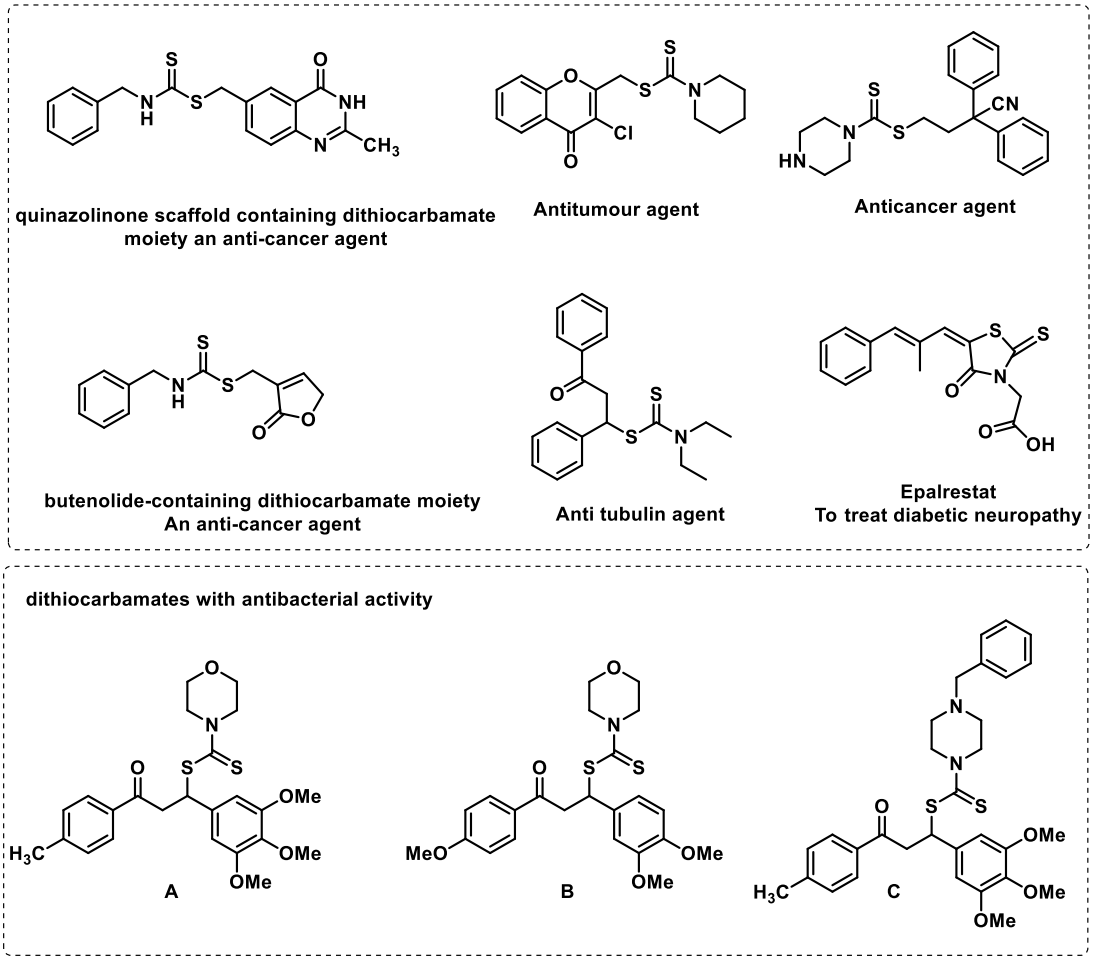
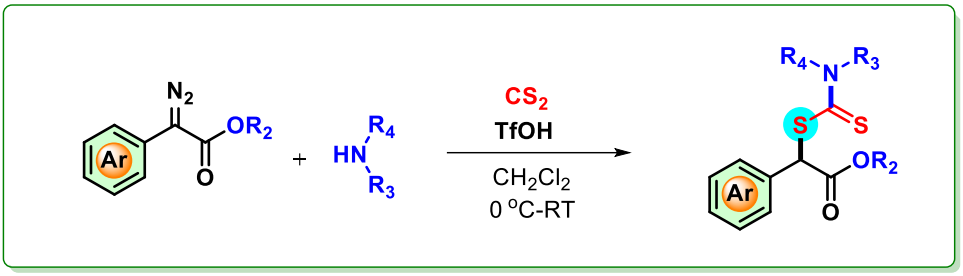


Figure 4.1 Biologically active dithiocarbamates and *S*-benzyl dithiocarbamates.

S-Benzyl dithiocarbamates are typically synthesized from benzyl halides through a multicomponent reaction with carbon disulfide and amines [14]. Nevertheless, methyl arenes [15] aryl alcohols [16] and aldehydes [17] were also used as a precursor for the preparation of *S*-benzyl dithiocarbamates. Alternatively, cross-coupling reaction of tetraalkylthiuram disulfides with benzylzinc bromide [18] or benzyl chlorides [19] affords *S*-benzyl dithiocarbamates. In this context, recently we have reported a catalyst-free

synthesis of *S*-benzyl dithiocarbamates from *para*-quinone methides (*p*-QMs), carbon disulfide and amines via a 1,6-Michael addition reaction [20]. In continuation of this work, here we explored the synthesis of *S*-benzyl dithiocarbamate derivatives from α-aryl α-diazoesters via triflic acid-promoted S-H insertion reaction at room temperature (**Scheme 4.1**).

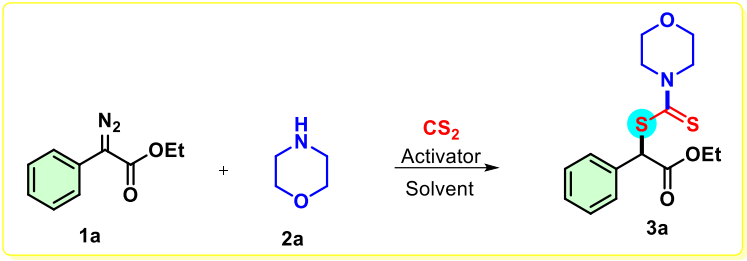


Scheme 4.1 Synthesis of *S*-benzyl dithiocarbamates from α-aryl α-diazoesters.

4.2 Results and Discussion

At the outset, optimization of the reaction condition was investigated by choosing ethyl α-diazo α-phenylacetate as a model substrate **(Table 4.1).** Initially, the insertion reaction was performed with *in situ* generated dithiocarbamic acid from morpholine and carbon disulfide in the presence of transition metal catalysts including $Rh_2(OAc)_4$, $Rh_2(esp)_4$, CuCl and $Cu(OAc)_2$. The reactions were performed in dichloromethane at 0 ^oC-room temperature. However, no reaction was observed with rhodium catalysts (**Table 4.1, entries 1-2**) while copper salts gave the desired product **3a** in 20-24% yields (**Table 4.1, entries 3-4**).

Table 4.1 Optimization of the Reaction Conditions.[a]



Entry	Activator	Solvent	Time (h)	Yield (%)[b]
1	$Rh_2(OAc)_4$ (0.1 eq.)	DCM	5	<5
2	$Rh_2(esp)_4$ (0.1 eq.)	DCM	5	<5
3	CuCl (0.1 eq.)	DCM	5	20
4	$Cu(OAc)_2$ (0.1 eq.)	DCM	5	24
5	$B(C_6F_5)_3$	DCM	1	<5
6	TfOH (0.2 eq.)	DCM	1	20
7	TfOH (0.5 eq.)	DCM	1	33
8[c]	TfOH (0.5 eq.)	DCM	1	41
9	TfOH (1.0 eq.)	DCM	1	50
10	**TfOH (2.0 eq.)**	**DCM**	**1**	**78**
11	TfOH (3.0 eq.)	DCM	1	70
12	PTSA (2.0 eq.)	DCM	1	28
13	CSA (2.0 eq.)	DCM	1	33
14	$HClO_4$ (2.0 eq.)	DCM	1	10
15	Eatons reagent ($CH_4O_8P_2S$) (2.0 eq.)	DCM	1	61
16	TfOH (2.0 eq.)	Dioxane	1	70
17	TfOH (2.0 eq.)	THF	1	50
18	TfOH (2.0 eq.)	AcCN	1	50

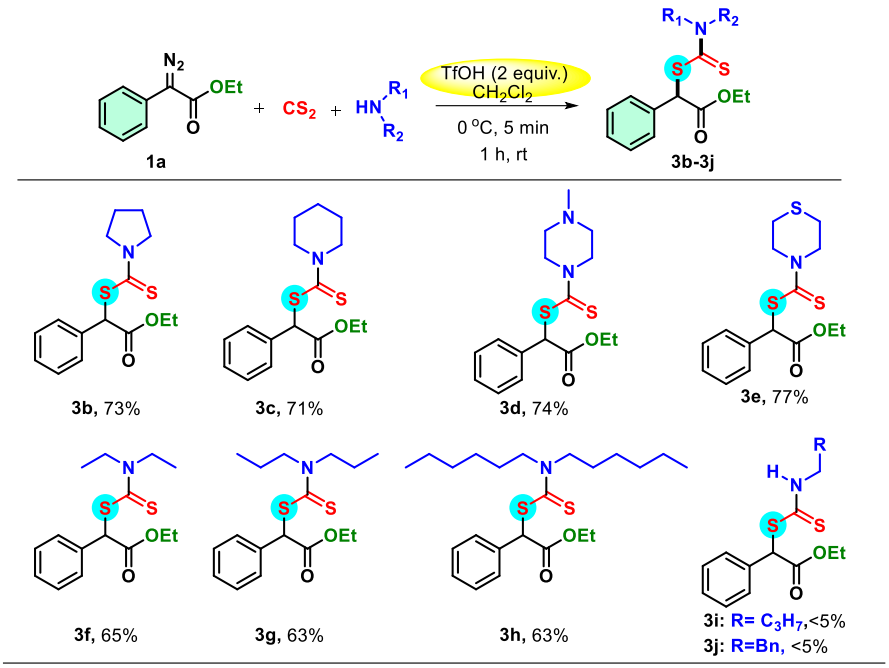
[a]**Reaction conditions:** Substrate **1a** (95 mg, 0.5 mmol), carbon disulfide (75 µL, 1.25 mmol) and amine **2a** (52 µL 0.6 mmol) were stirred in appropriate solvents (4 mL) for 5 min at 0 °C, then 1 h at room temperature. [b] Isolated yields. [c]The reaction was performed at 50 °C.

Also, the reaction did not proceed with Lewis acid tris(penta-fluorophenyl)borane (**Table 4.1, entry 5**). Hence, the reaction was further investigated with various Brønsted acids including triflic acid (TfOH), p-toluenesulfonic acid (PTSA), camphorsulfonic acid

(CSA), perchloric acid and Eaton's reagent. With a catalytic amount of TfOH (i.e. 20 mol%), the desired product **3a** was observed only in 20% yield (**Table 4.1, entry 6**). A slight increment in the yield of **3a** was observed when the reaction was performed with 0.5 equivalent of TfOH at room temperature (**Table 4.1, entry 7**). Although the yield of **3a** was further increased at 50 ^{o}C, the rest of the starting material, i.e. diazo ester **1a** got decomposed (**Table 4.1, entry 8**). Hence, the reaction was performed with an increased amount of TfOH, i.e. from 1 to 3 equivalents. To our delight, the desired product **3a** was obtained in 78% yield with 2.0 equiv. of TfOH while low yields were obtained with 1.0 and 3.0 equivalents (**Table 4.1, entries 9-11**). The reaction with p-toluenesulfonic acid (PTSA), camphorsulfonic acid (CSA), perchloric acid and Eaton's reagent gave the product **3a** in 10-61% yield (**Table 4.1, entries 12-15**). Further, the effect of solvent in the insertion reaction was investigated. It was observed that the reaction in dichloromethane was better than in dioxane, THF and acetonitrile (AcCN) in terms of yield (**Table 4.1, entries 16-18**).

After the identification of optimized conditions, the scope of amines was investigated (**Table 4.2**). The reaction of five and six-membered heterocyclic secondary amines such as pyrrolidine, piperidine, N-methyl piperazine and thiomorpholine with α-aryl diazoester **1a** in the presence of carbon disulfide (CS_2) gave the desired *S*-benzyl dithiocarbamates **3b-3e** in 71-77% yields. Further, the reaction of di-alkyl amines with α-aryl diazoesters **1a** in the presence of triflic acid provided corresponding dithiocarbamates **3f-3h** in 63-65% yields. However, the reaction of primary amines with diazoester **1a** in the presence of CS_2 gave a complicated reaction mixture.

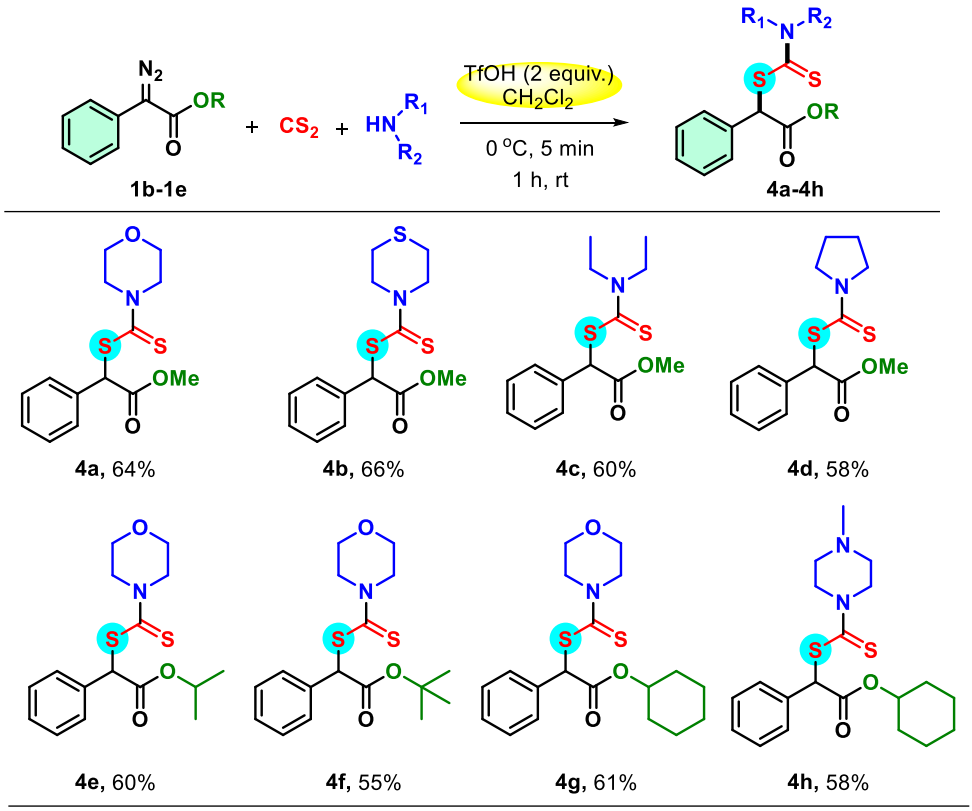
Table 4:2 Scope of the amines.[a,b]



[a]**Reaction condition:** diazoester **1a** (95 mg, 0.5 mmol), carbon disulfide (75 µL, 1.25 mmol), amine (0.6 mmol) and triflic acid (88 µL ,1.0 mmol) were stirred in dichloromethane (4 mL) for 5 min at 0 °C, then 1 h at room temperature. [b] Isolated yields.

After exploring the scope of the amines, we have investigated the insertion reaction of diazoesters bearing different *O*-alkyl groups (**Table 4.3**). Similar to ethyl α-diazoester, methyl α-diazoester also underwent *S*-insertion reaction with different dithiocarbamic acids under optimized conditions. These reactions gave functionalized *S*-benzyl dithiocarbamates **4a-4d** in 58-66% yields. Similarly, *iso*-propyl, *tert*-butyl and cyclohexyl functionalized α-diazoesters were successfully transformed into *S*-benzyl dithiocarbamates **4e-4h** in 55-61% yields.

Table 4.3 Scope of the diazoester.[a,b]

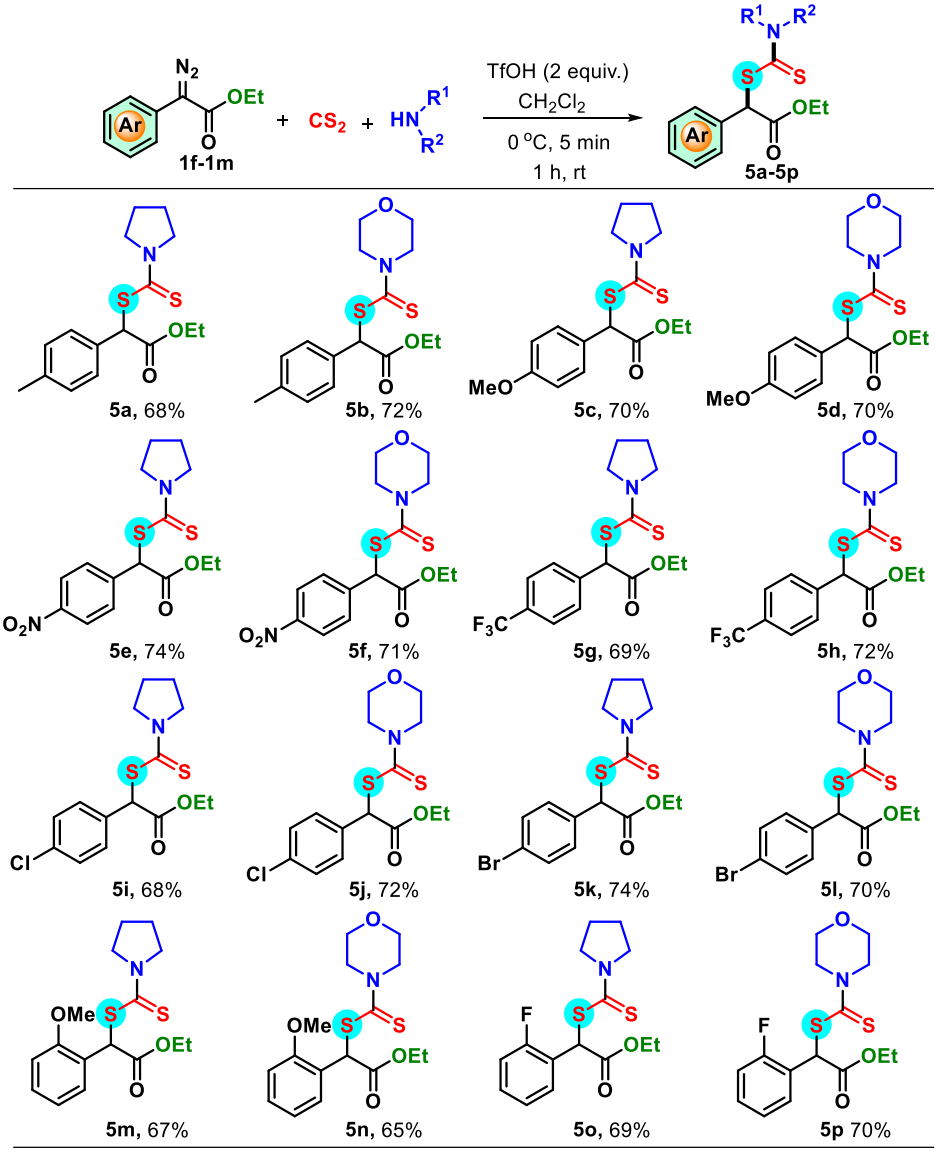


[a]**Reaction condition:** diazoester **1b-1e** (0.5 mmol), carbon disulfide (75 µL, 1.25 mmol), amine (0.6 mmol) and triflic acid (88 µL ,1.0 mmol) were stirred in dichloromethane (4 mL) for 5 min at 0 °C, then 1 h at room temperature. [b] Isolated yields.

Further, we have explored the substrate scope of α-diazoesters bearing different functionalized aryl groups (**Table 4.4**). Electron donating groups such as methyl and methoxy functionalized α-aryl α-diazoesters underwent smooth *S*-insertion reactions with dithiocarbamic acids generated from pyrrolidine and morpholine. These reactions gave corresponding *S*-benzyl dithiocarbamates **5a-5d** in 68-72% yields. Similarly, strongly electron withdrawing groups such as nitro and trifluoromethyl groups functionalized α-aryl diazoesters as well as halogens functionalized α-aryl diazoesters gave the desired products **5e-5l** in 68-74% yields. Moreover, sterically hindered *ortho*-functionalized α-

aryl diazoesters also participated in the *S*-insertion reactions smoothly and provided *S*-benzyl dithiocarbamates **5m-5p** in 65-70% yields.

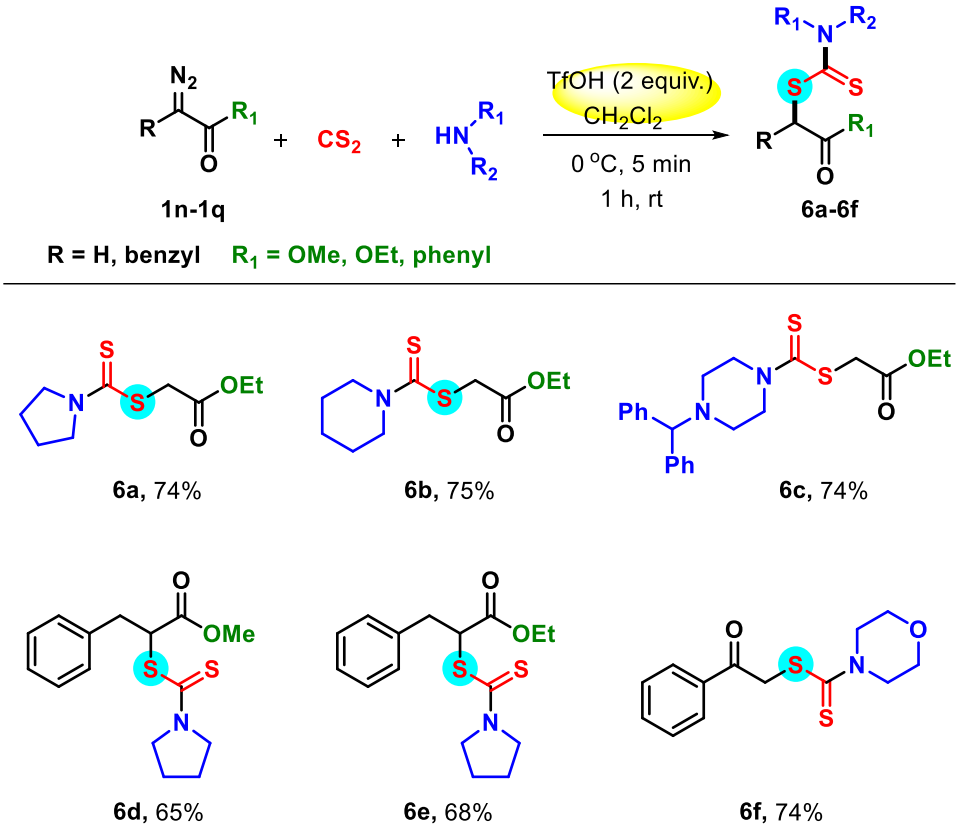
Table 4.4 Scope of the diazoester and amines.[a,b]



[a]**Reaction condition:** Diazoester **1f-1m** (0.5 mmol), carbon disulfide (75 µL, 1.25 mmol), amine (0.6 mmol) and triflic acid (88 µL ,1.0 mmol) were stirred in dichloromethane (4 mL) for 5 min at 0 °C, then 1 h at room temperature. [b] Isolated yields.

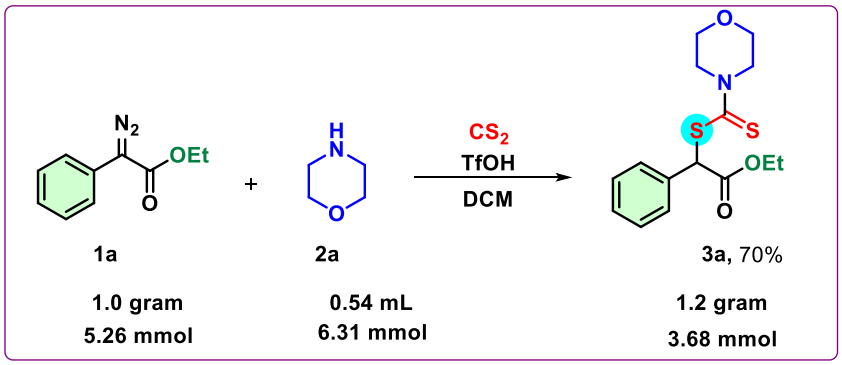
after exploring the scope of aryl α-diazoesters, we investigated the reactivities of alkyl diazo compounds in the preparation of dithiocarbamates. To our delight, methyl α-diazobenzenepropanoate, ethyl α-diazobenzenepropanoate, diazoacetophenone and ethyl diazoacetate underwent S-insertion smoothly and gave the desired products **6a–6f** in good yields (**Table 4.5**).

Table 4.5 Scope of alkyl diazoester compounds.[a,b]



[a]**Reaction condition:** diazo compound 1n–1q (0.5 mmol), carbon disulfide (75 µL, 1.25 mmol), amine (0.6 mmol) and triflic acid (88 µL, 1.0 mmol) were stirred in dichloromethane (4 mL) for 5 min at 0 °C, then 1 h at room temperature. [b] Isolated yields.

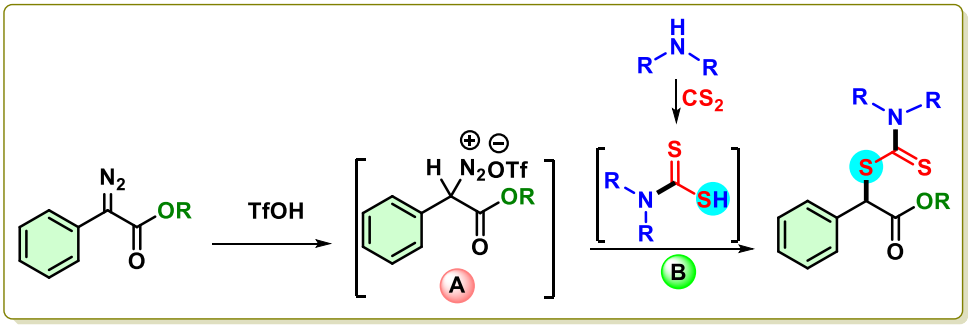
Further, a gram-scale reaction was performed with model substrates **1a** and **2a** in the presence of CS_2 (**Scheme 4.2**). To our delight, this reaction provided the desired product **3a** in 70% yield under optimized conditions.



Scheme 4.2 Gram-scale reaction.

4.3 Plausible Reaction Mechanism

A plausible mechanism of the reaction has been provided in (**Scheme 4.3**). In step 1, diazoester is converted into diazonium triflate **A** in the presence of triflic acid. In step 2, *in situ* generated dithiocarbamic acid **B** reacts with **A** and provides the desired product. We used 1.25 equivalents of secondary amines and 2.5 equivalents carbon disulfide, resulting no free secondary amines available for the protonation.



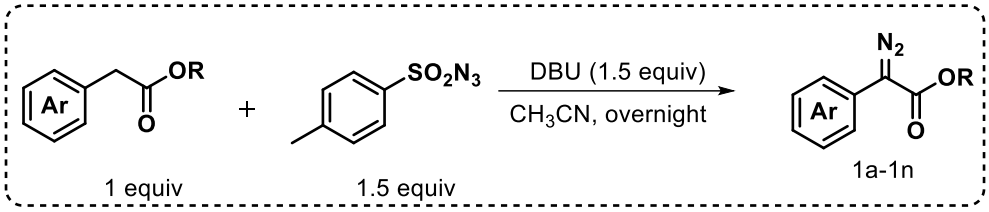
Scheme 4.3 Plausible reaction mechanism.

4.4 Conclusion

In conclusion, we have demonstrated the triflic acid promoted synthesis of various functionalized *S*-benzyl dithiocarbamates from α-aryl diazoesters *via* multicomponent reaction involving carbon disulfide and amines. The reactions proceed at room temperature and gave the desired dithiocarbamates in good yields. Broad substrate scope and easy operations are the important features of the reactions.

4.5 Experimental Procedures

4.5.1 General Procedure for Preparation of α-Diazoester [21 a-d] (1a-1m)



To a stirred solution of ester (10 mmol, 1 equiv) and tosyl azide (2.96 g, 15 mmol, 1.5 equiv) in anhydrous CH_3CN (15 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.24 mL, 2.28 g, 15 mmol, 1.5 equiv) at room temperature. The reaction mixture was allowed to stir for overnight. After completion, the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (2× 50 mL), and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the α-diazoesters.

4.5.2 Starting Materials Prepared

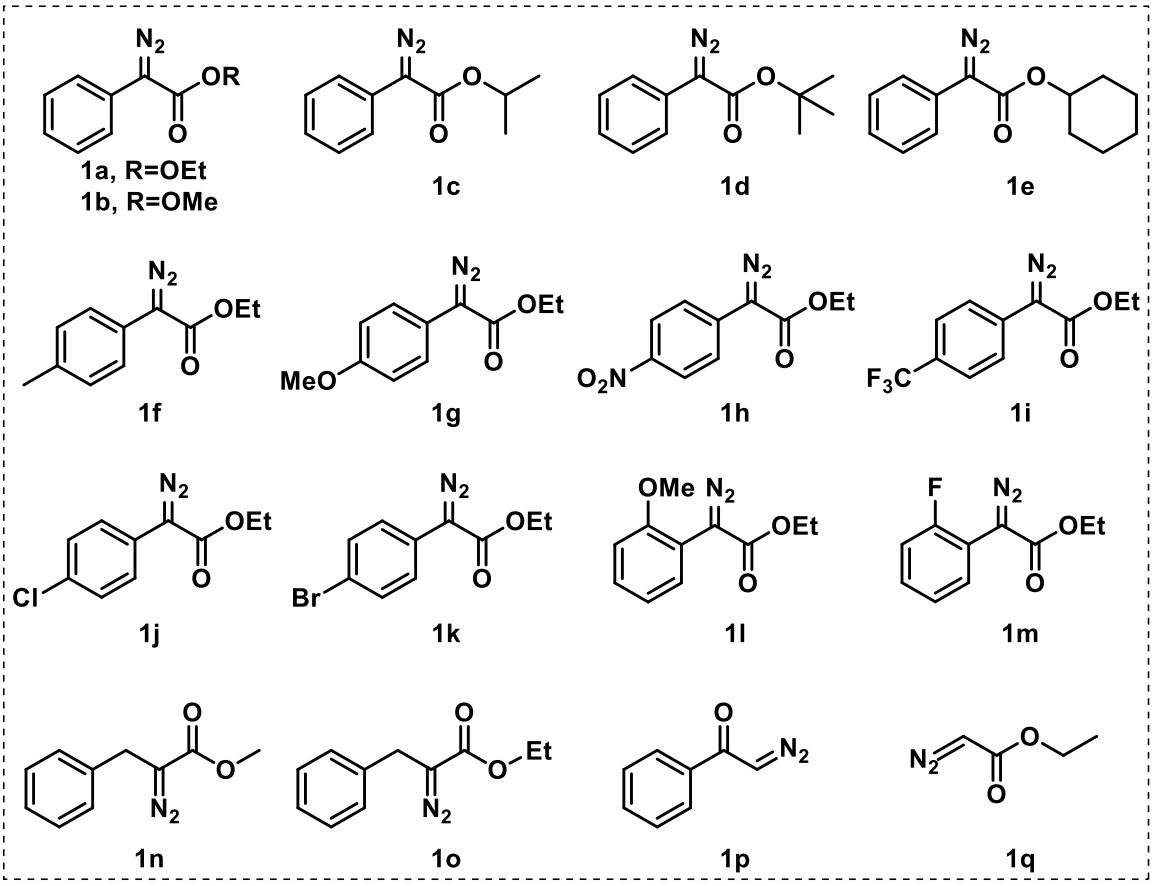


Figure 4.2 Starting materials used for the synthesis of S-benzyl dithiocarbamates

4.5.3 Synthesis of Diazo-ester [22 a-c] (1n and 1o)

A solution of the amino acid ester (5. 0 mmol), isoamyl nitrite (6.0 mmol) and acetic acid (0.5 mmol) in chloroform (40 mL) was refluxed for 3 h. The mixture was diluted with ethyl acetate (50 mL) and washed with saturated $NaHCO_3$ solution (3 × 20 mL). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography (20% EtOAc in petroleum ether) to give pure **1n** (714 mg, 3.75 mmol, 75%) and **1o** products. (735 mg, 3.60 mmol, 72%).

4.5.4 Synthesis of α-Diazoacetophenone [23] (1p)

α-Bromoacetophenone (400 mg, 2.00 mmol) and N, N′-ditosylhydrazine (1.37 g, 4.00 mmol) were dissolved in 10 mL of dry THF. The flask was kept in an ice bath, and DBU (1.5 mL, 10 mmol, 5 equiv) was added dropwise. After 20 min the reaction mixture was concentrated and purified by column chromatography (20% EtOAc in hexane) to give product **1p** (264 mg, 1.81 mmol, 90%) as a yellow oil. Rf = 0.35 (4:1 petroleum ether: EtOAc).

4.5.5 General Procedure for Preparation of S-Benzyl Dithiocarbamates

A 25 mL round bottom flask was charged with CS_2 (75 µL, 1.25 mmol, 2.5 equiv) in dry DCM (4 mL) and respective amines (0.6 mmol, 1.2 equiv) were added dropwise at 0 oC. The resulting reaction mixture was stirred for 5 minutes after which diazoester (0.5 mmol, 1.0 equiv) and triflic acid (88 µL, 2.0 equiv) were added at 0 ^oC. The resulting mixture was allowed to stir at room temperature for 1 h. After completion, the reaction was quenched with saturated sodium bicarbonate and extracted with CH_2Cl_2 (2× 50 mL). The organic layer was washed with brine (2 × 15 mL) and dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford S-benzyl dithiocarbamates.

4.6 Analytical Data

4.6.1 Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (3a):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.45. Yield 78% (126.8 mg). IR (KBr): ν_{max} = 3025, 2978, 2876,

1937, 1732, 1627, 1625, 1560, 1489, 1476, 1311, 1265, 1244, 934, 835, 730, 545 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.8, 1.6 Hz, 2H), 7.36-7.32 (m, 3H), 5.78 (s, 1H), 4.31-4.12 (m, 4H), 3.92 (s, 2H), 3.75 (s, 4H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.2, 169.8, 133.5, 128.9, 128.8, 128.6, 66.1, 62.1, 58.8, 50.7, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{20}NO_3S_2$: 326.0885; found: 326.0890.

4.6.2 Ethyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate (3b):

The title compound hexane was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in): 0.45. Yield 73% (112.8 mg). IR (KBr): ν_{max} = 3028, 2980, 2866, 1909, 1731, 1599, 1448, 1360, 1308, 1222, 1080, 950, 835, 780, 508 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.35-7.31 (m, 3H), 5.84 (s, 1H), 4.30-4.14 (m, 2H), 3.91-3.87 (m, 2H), 3.74-3.55 (m, 2H), 2.08-1.94 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.4, 170.1, 134.2, 128.8, 128.7, 128.4, 62.0, 58.3, 54.9, 50.5, 26.1, 24.2, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{20}NO_2S_2$: 310.0935; found: 310.0945.

4.6.3 Ethyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate (3c):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.5. Yield 71% (114.7 mg). IR (KBr): ν_{max} = 3040, 2985, 2875, 1925, 1730, 1628, 1626, 1547, 1490, 1309, 1265, 1244, 924, 824, 725, 544 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.36-7.31 (m, 3H), 5.79 (s, 1H), 4.31-4.24 (m, 2H), 4.18-4.12 (m, 2H), 3.88-3.81 (m, 2H), 1.69 (s, 6H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.3, 170.1, 133.9, 128.8, 128.8, 128.5, 61.9, 58.9, 52.3,

24.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_2S_2$: 324.1092; found: 324.1099.

4.6.4 Ethyl 2-((4-methylpiperazine-1-carbonothioyl)thio)-2-phenylacetate (3d):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (40 % ethyl acetate in hexane): 0.35. Yield 74% (125.1 mg). IR (KBr): ν_{max} = 3045, 2985, 2876, 1928, 1747, 1653, 1632, 1478, 1451, 1300, 1269, 1231, 933, 845, 738, 549cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 2H), 7.36-7.30 (m, 3H), 5.76 (s, 1H), 4.30-4.11 (m, 4H), 3.90 (s, 2H), 2.47 (s, 4H), 2.30 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.5, 169.8, 133.6, 128.8, 128.7, 128.5, 61.9, 58.8, 54.2, 50.7, 49.8, 45.5, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{23}N_2O_2S_2$: 339.1201; found: 339.1206.

4.6.5 Ethyl 2-phenyl-2-((thiomorpholine-4-carbonothioyl)thio)acetate (3e):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.43. Yield 77% (131.3 mg). IR (KBr): ν_{max} = 3031, 2980, 28645, 1947, 170, 1648, 1619, 1561, 1489, 1449, 1318, 1289, 1247, 817, 735, 550 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.7, 1.7 Hz, 2H), 7.36-7.32 (m, 3H), 5.75 (s, 1H), 4.48-4.06 (m, 6H), 2.74 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.5, 169.7, 133.5, 128.9, 128.8, 128.7, 62.1, 59.0, 52.2, 27.2, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{20}NO_2S_3$: 342.0656; found: 342.0652.

4.6.6 Ethyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate (3f):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.6. Yield 65% (101.1 mg). IR (KBr): ν_{max} = 3049, 2976, 2873, 1937, 1730, 1639, 1617, 1587, 1478, 1466, 1315, 1292, 1216, 943, 725, 502 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.9, 1.6 Hz, 2H), 7.36-7.31 (m, 3H), 5.76 (s, 1H), 4.29-4.13 (m, 2H), 3.99 (q, J = 7.0 Hz, 2H), 3.79-3.64 (m, 2H), 1.30-1.27 (m, 3H), 1.25 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.3, 170.0, 133.9, 128.8, 128.8, 128.4, 61.9, 58.9, 49.3, 46.9, 14.0, 12.5, 11.5. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{22}NO_2S_2$: 312.1092; found: 312.1099.

4.6.7 Ethyl 2-((dipropylcarbamothioyl)thio)-2-phenylacetate (3g):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.6. Yield 63% (106.8 mg). IR (KBr): ν_{max} = 3056, 2869, 1941, 1734, 1655, 1636, 1547, 1468, 1476, 1291, 1282, 1256, 843, 749, 556 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.35-7.31 (m, 3H), 5.77 (s, 1H), 4.29-4.14 (m, 2H), 3.90-3.83 (m, 2H), 3.68-3.52 (m, 2H), 1.79-1.70 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.9, 170.0, 133.9, 128.8, 128.8, 128.4, 61.9, 59.0, 56.6, 54.5, 20.7, 19.5, 14.0, 11.1 HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{17}H_{26}NO_2S_2$: 340.1405; found: 340.1413.

4.6.8 Ethyl 2-((dihexylcarbamothioyl)thio)-2-phenylacetate (3h):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.55. Yield 63% (133.3 mg). IR (KBr): ν_{max} = 3041, 2976,

2873, 1936, 1727, 1646, 1624, 1562, 1496, 1473, 1325, 1293, 1252, 944, 838, 737 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.9, 1.6 Hz, 2H), 7.36-7.30 (m, 3H), 5.77 (s, 1H), 4.29-4.12 (m, 2H), 3.92-3.85 (m, 2H), 3.70-3.54 (m, 2H), 1.71 (d, J = 5.6 Hz, 4H), 1.33-1.28 (m, 12H), 1.24 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.5, 170.0, 133.9, 128.8, 128.7, 128.4, 61.8, 58.9, 55.1, 52.9, 31.4, 31.2, 29.6, 27.2, 26.4, 26.4, 26.0, 22.5, 22.4, 13.9, 13.9, 13.8. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{23}H_{38}NO_2S_2$: 424.2344; found: 424.2347.

4.6.9 Methyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4a):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 64% (99.7 mg). IR (KBr): ν_{max} = 3049, 2978, 2850, 1920, 1721, 1630, 1611, 1550, 1478, 1451, 1289, 1283, 1245, 931, 814, 715, 524 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.7, 1.7 Hz, 2H), 7.38-7.32 (m, 3H), 5.80 (s, 1H), 4.27 (s, 2H), 3.90 (s, 2H), 3.76 (s, 7H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.0, 170.3, 133.3, 128.9, 128.8, 128.7, 66.1, 58.6, 53.0, 50.8. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{14}H_{18}NO_3S_2$: 312.0728; found: 312.0726.

4.6.10 Methyl 2-phenyl-2-((thiomorpholine-4-carbonothioyl)thio)acetate (4b):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 66% (108.0 mg). IR (KBr): ν_{max} = 3022, 2983, 2879, 1929, 1719, 1638, 1624, 1568, 1472, 1460, 1317, 1266, 954, 884, 765, 564 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.7, 1.8 Hz, 2H), 7.37-7.33 (m, 3H), 5.76 (s, 1H), 4.72-4.13 (m, 4H), 3.75 (s, 3H), 2.73 (s, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.3,

170.3, 133.2, 128.9, 128.8, 128.7, 58.8, 53.0, 27.2. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{14}H_{18}NO_2S_3$: 328.0500; found: 328.0504.

4.6.11 Methyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate (4c):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.6. Yield 60% (89.2 mg). IR (KBr): ν_{max} = 3048, 2980, 2887, 1937, 1733, 1645, 1628, 1548, 1471, 1449, 1315, 1277, 1254, 967, 836, 741, 544 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, J = 7.8, 1.6 Hz, 2H), 7.35-7.33 (m, 3H), 5.79 (s, 1H), 3.99 (q, J = 7.0 Hz, 2H), 3.75 (s, 3H), 3.75-3.66 (m, 2H), 1.30-1.25 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.2, 170.6, 133.7, 128.9, 128.8, 128.5, 58.7, 53.0, 49.3, 46.9, 12.5, 11.4. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{14}H_{20}NO_2S_2$: 298.0935; found: 298.0939.

4.6.12 Methyl 2-((diisopropylcarbamothioyl)thio)-2-phenylacetate (4d):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.45. Yield 58% (86.2 mg). IR (KBr): ν_{max} = 3045, 2971, 2865, 1901, 1735, 1592, 1444, 1366, 1301, 1215, 1071, 1015, 938, 778, 505 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2H), 7.37-7.30 (m, 3H), 5.85 (s, 1H), 3.91-3.87 (m, 2H), 3.75 (s, 3H), 3.73-3.53 (m, 2H), 2.09-1.93 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.2, 170.6, 133.9, 128.9, 128.7, 128.5, 58.1, 54.9, 53.0, 50.5, 26.1, 24.2. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{14}H_{18}NO_2S_2$: 296.0779; found: 296.0784.

4.6.13 Isopropyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4e):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.46. Yield 60% (101.8 mg). IR (KBr): ν_{max} = 3036, 2975, 2866, 1923, 1735, 1635, 1616, 1557, 1488, 1456, 1301, 1272, 1236, 924, 824, 725, 544 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.5, 1.7 Hz, 2H), 7.37-7.31 (m, 3H), 5.72 (s, 1H), 5.12-5.03 (m, 1H), 4.28 (s, 2H), 3.90 (s, 2H), 3.75 (s, 4H), 1.30 (d, J = 6.3 Hz, 3H), 1.14 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.2, 169.2, 133.6, 128.9, 128.8, 128.6, 69.7, 66.1, 59.0, 50.6, 21.6, 21.4. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_3S_2$: 340.1041; found: 340.1047.

4.6.14 Tert-butyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4f):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 55% (97.1 mg). IR (KBr): ν_{max} = 3056, 2961, 2874, 1931, 1730, 1655, 1660, 1573, 1501, 1459, 1321, 1252, 1239, 843, 734, 505 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.9, 1.5 Hz, 2H), 7.35-7.31 (m, 3H), 5.67 (s, 1H), 4.28 (s, 2H), 3.91 (s, 2H), 3.75 (s, 4H), 1.43 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.5, 168.6, 134.0, 128.8, 128.7, 128.4, 82.4, ,59.6, 29.6, 27.8. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{17}H_{24}NO_3S_2$: 354.1198; found: 354.1189.

4.6.15 Cyclohexyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate (4g):

The title compound was obtained as white foam using the general procedure 2.2. R_f (5 % ethyl acetate in hexane): 0.44. Yield 61% (115.7 mg). IR (KBr): ν_{max} = 3040, 2970, 2862, 1921, 1720, 1636, 1619, 1551, 1451, 1307, 1278, 1239, 930, 821, 722, 549 cm^{-1}. **^{1}H**

NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.7, 1.6 Hz, 2H), 7.35-7.30 (m, 3H), 5.74 (s, 1H), 4.86-4.81 (m, 1H), 4.27 (s, 2H), 3.90 (s, 2H), 3.73 (s, 4H), 1.93-1.86 (m, 1H), 1.73-1.69 (m, 1H), 1.59-1.55 (m, 1H), 1.52-1.34 (m, 3H), 1.31-1.21 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.1, 169.0, 133.6, 128.8, 128.7, 128.5, 74.2, 66.1, 58.9, 50.6, 31.2, 30.9, 25.2, 23.4, 23.3. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{26}NO_3S_2$: 380.1354; found: 380.1355.

4.6.16 Cyclohexyl 2-((4-methylpiperazine-1-carbonothioyl)thio)-2-phenylacetate (4h):

The title compound was obtained as white foam using the general procedure 2.2. R_f (40 % ethyl acetate in hexane): 0.4. Yield 58% (102.2 mg). IR (KBr): ν_{max} = 3051, 2972, 2863, 1931, 1728, 1631, 1621, 1562, 1491, 1463, 1311, 1281, 1247, 935, 705, 501 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.8, 1.6 Hz, 2H), 7.36-7.29 (m, 3H), 5.74 (s, 1H), 4.88-4.81 (m, 1H), 4.30 (s, 2H), 3.92 (s, 2H), 2.48 (s, 4H), 2.31 (s, 3H), 1.92-1.86 (m, 1H), 1.73-1.69 (m, 1H), 1.61-1.56 (m, 1H), 1.52-1.34 (m, 3H), 1.31-1.23 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.7, 169.2, 133.9, 128.8, 128.4, 74.2, 59.1, 54.2, 45.5, 31.3, 31.0, 25.3, 23.4, 23.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for : $C_{20}H_{28}N_2NaO_2S_2$: 415.1490; found: 415.1503.

4.6.17 Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(p-tolyl)acetate (5a):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.45. Yield 68% (109.9 mg). IR (KBr): ν_{max} = 3031, 2959, 2857, 1920, 1729, 1582, 1454, 1386, 1307, 1219, 1069, 1024, 941, 833, 515 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.77 (s, 1H), 4.29-

4.11 (m, 2H), 3.89-3.85 (m, 2H), 3.71-3.52 (m, 2H), 2.32 (s, 3H), 2.05-2.00 (m, 2H), 1.96-1.92 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.3, 170.0, 138.2, 130.8, 129.4, 128.4, 61.8, 57.9, 54.7, 50.4, 26.0, 24.1, 21.0, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_2S_2$: 324.1092; found: 324.1094.

4.6.18 Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-(p-tolyl)acetate (5b):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.44. Yield 72% (122.2 mg). IR (KBr): ν_{max} = 3029, 2968, 2878, 1921, 1732, 1649, 1611, 1552, 1489, 1458, 1311, 1259, 1242, 942, 841, 746, 546 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 5.72 (s, 1H), 4.36-4.10 (m, 4H), 3.90 (s, 2H), 3.75 (s, 4H), 2.34 (s, 3H), 1.27-1.24 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.3, 169.9, 138.6, 130.3, 129.6, 128.7, 62.0, 58.5, 29.6, 21.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_3S_2$: 340.1041; found: 340.1043.

4.6.19 Ethyl 2-(4-methoxyphenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5c):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0. 38. Yield 70% (118.8 mg). IR (KBr): ν_{max} = 3045, 2971, 2865, 1901, 1733, 1592, 1459, 1367, 1319, 1228, 1089, 1028, 936, 825, 777, 515 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, J = 8.6 Hz, 2H), 6.88-6.84 (m, 2H), 5.75 (s, 1H), 4.30-4.10 (m, 2H), 3.89-3.85 (m, 2H), 3.78 (s, 3H), 3.71-3.52 (m, 2H), 2.06-1.91 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.5, 170.2, 159.6, 129.9, 125.8, 114.2, 61.9, 57.6, 55.1, 54.7, 50.5, 26.0, 24.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_3S_2$: 340.1041; found: 340.1051.

4.6.20 Ethyl 2-(4-methoxyphenyl)-2-((morpholine-4-carbonothioyl)thio)acetate (5d):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.35. Yield 70% (124.4 mg). IR (KBr): ν_{max} = 3031, 2961, 2861, 1923, 1734, 1631, 1610, 1550, 1484, 1457, 1327, 1292, 1256, 939, 859, 750, 551 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.70 (s, 1H), 4.31-4.11 (m, 4H), 3.89 (s, 2H), 3.79 (s, 3H), 3.74 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.3, 170.0, 159.8, 130.0, 125.1, 114.3, 66.1, 62.0, 58.2, 55.2, 50.6, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_4S_2$: 356.0990; found: 356.0983.

4.6.21 Ethyl 2-(4-nitrophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5e):

The title compound was obtained as yellow foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 74% (131.1 mg). IR (KBr): ν_{max} = 3053, 2971, 2865, 1901, 1737, 1592, 1476, 1381, 1317, 1200, 1050, 998, 914, 814, 754, 527 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20-8.11 (m, 2H), 7.67-7.60 (m, 2H), 6.07 (s, 1H), 4.29-4.09 (m, 2H), 3.91-3.54 (m, 4H), 2.07-1.90 (m, 4H), 1.21 (t, J = 4.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.5, 168.8, 147.4, 142.5, 129.7, 123.6, 62.3, 57.2, 55.2, 50.5, 25.9, 24.0, 13.8. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}N_2O_4S_2$: 355.0786; found: 355.0785.

4.6.22 Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-(4-nitrophenyl)acetate (5f):

The title compound was obtained as yellow foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 71% (131.5 mg). IR (KBr): ν_{max} = 3052, 2975, 2853, 1933, 1741, 1639, 1611, 1551, 1498, 1474, 1304, 1266, 1232, 939, 821, 731, 528 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H),

6.03 (s, 1H), 4.33-4.13 (m, 4H), 3.92 (s, 2H), 3.75 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.4, 168.7, 147.8, 141.9, 129.9, 123.9, 62.6, 57.9, 29.6, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}N_2O_5S_2$: 371.0735; found: 371.0730.

4.6.23 Ethyl 2-((pyrrolidine-1-carbonothioyl)-2-(4-trifluoromethyl)phenyl)acetate (5g)

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.45. Yield 69% (130.2 mg). IR (KBr): ν_{max} = 3045, 2971, 2865, 1901, 1724, 1589, 1481, 1355, 1313, 1212, 1055, 1019, 934, 819, 758, 543 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (s, 4H), 5.99 (s, 1H), 4.29-4.14 (m, 2H), 3.90-3.86 (m, 2H), 3.72-3.56 (m, 2H), 2.10-1.95 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.3, 169.4, 138.9, 130.45 (q, J = 31.2 Hz), 129.2, 125.67 (q, J = 3.75 Hz), 123.83 (q, J = 270 Hz), 62.3, 57.6, 55.1, 50.5, 26.0, 24.1, 13.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.7. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{19}F_3NO_2S_2$: 378.0809; found: 378.0813.

4.6.24 Ethyl 2-((morpholine-4-carbonothioyl)thio)-2-(4(trifluoromethyl)phenyl) acetate (5h)

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 72% (141.6 mg). IR (KBr): ν_{max} = 3047, 2961, 2872, 1945, 1722, 1635, 1628, 1548, 1460, 1471, 1331, 1268, 1247, 937, 837, 733, 537 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.56 (m, 4H), 5.92 (s, 1H), 4.32-4.13 (m, 4H), 3.91 (s, 2H), 3.75 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.1, 169.2, 138.2, 130.71 (q, J = 32.5 Hz), 129.2, 125.77 (q, J = 3.7 Hz), 123.79 (q, J = 270

Hz), 66.0, 62.4, 58.2, 50.6, 13.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.7. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{19}F_3NO_3S_2$: 394.0758; found: 394.0757.

4.6.25 Ethyl 2-(4-chlorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5i):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 68% (116.9 mg). IR (KBr): ν_{max} = 3021, 2956, 2831, 1917, 1735, 1581, 1437, 1334, 1316, 1226, 1064, 1045, 922, 838, 751, 643 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 5.85 (s, 1H), 4.28-4.14 (m, 2H), 3.90-3.86 (m, 2H), 3.71-3.54 (m, 2H), 2.08-1.93 (m, 4H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.7, 169.7, 134.4, 133.1, 130.1, 128.9, 128.6, 127.8, 62.1, 57.5, 55.0, 50.5, 26.1, 24.2, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}ClNO_2S_2$: 344.0546; found: 344.0541.

4.6.26 Ethyl 2-(4-chlorophenyl)-2-((morpholine-4-carbonothioyl)thio)acetate (5j):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.38. Yield 72% (123.8 mg). IR (KBr): ν_{max} = 3043, 2962, 2859, 1929, 1761, 1656, 1661, 1582, 1471, 1461, 1318, 1261, 1216, 971, 893, 761, 632 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.78 (s, 1H), 4.33-4.09 (m, 4H), 3.90 (s, 2H), 3.74 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.5, 169.4, 134.6, 132.4, 130.1, 129.0, 66.0, 62.2, 58.0, 50.7, 13.9. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}ClNO_3S_2$: 360.0495; found: 360.0491.

4.6.27 Ethyl 2-(4-bromophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5k):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 74% (143.6 mg). IR (KBr): ν_{max} = 3031, 2971, 2865, 1901, 1730, 1592, 1474, 1387, 1333, 1227, 1112, 1012, 917, 817, 765, 536 cm^{-1}. **^{1}H**

NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 5.84 (s, 1H), 4.29-4.13 (m, 2H), 3.90-3.86 (m, 2H), 3.71-3.55 (m, 2H), 2.08-1.93 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.7, 169.7, 133.7, 131.9, 130.4, 122.6, 62.2, 57.6, 55.0, 50.6, 29.6, 26.1, 24.2, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}BrNO_2S_2$: 388.0041; found: 388.0030.

4.6.28 Ethyl 2-(4-bromophenyl)-2-((morpholine-4-carbonothioyl)thio)acetate (5l):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 70% (141.5 mg). IR (KBr): ν_{max} = 3042, 2961, 2872, 1918, 1729, 1639, 1619, 1555, 1452, 1303, 1275, 1236, 936, 838, 718, 521 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.78 (s, 1H), 4.30-4.09 (m, 4H), 3.90 (s, 2H), 3.75 (s, 4H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.5, 169.4, 133.0, 132.0, 130.5, 122.8, 62.3, 58.1, 29.6, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}BrNO_3S_2$: 403.9990; found: 403.9982.

4.6.29 Ethyl 2-(2-methoxyphenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5m):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.42. Yield 67% (113.7 mg). IR (KBr): ν_{max} = 3045, 2877, 1911, 1730, 1588, 1466, 1351, 1322, 1218, 1066, 1015, 942, 855, 768, 505 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.5 Hz, 1H), 7.26-7.21 (m, 1H), 6.87-6.83 (m, 2H), 6.29 (s, 1H), 4.20-4.09 (m, 2H), 3.85-3.80 (m, 2H), 3.78 (s, 3H), 3.66-3.47 (m, 2H), 1.98-1.85 (m, 4H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.8, 169.8, 156.3, 129.4, 129.2, 123.0, 120.2, 110.6, 61.4, 55.3, 54.7, 52.6, 50.1, 25.7, 23.8, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_3S_2$: 340.1041; found: 340.1040.

4.6.30 Ethyl 2-(2-methoxyphenyl)-2-((morpholine-4-carbonothioyl)thio)acetate (5n):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 65% (115.5 mg). IR (KBr): ν_{max} = 3027, 2971, 2863, 1921, 1731, 1634, 1619, 1558, 1489, 1457, 1301, 1273, 1236, 925, 823, 724, 509 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.5, 1.6 Hz, 1H), 7.32-7.28 (m, 1H), 6.93-6.89 (m, 2H), 6.31 (s, 1H), 4.34-4.14 (m, 4H), 3.86 (s, 3H), 3.74 (s, 4H), 1.23 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.3, 170.0, 156.7, 129.9, 129.7, 122.6, 120.7, 111.0, 66.1, 61.9, 55.6, 53.2, 51.1, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_4S_2$: 356.0990; found: 356.0989.

4.6.31 Ethyl 2-(2-fluorophenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate (5o):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.35. Yield 69% (113 mg). IR (KBr): ν_{max} = 3031, 2967, 2867, 1914, 1736, 1578, 1456, 1369, 1316, 1227, 1092, 1027, 901, 841, 759, 549 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 (t, J = 7.5 Hz, 1H), 7.31-7.27 (m, 1H), 7.16-7.02 (m, 2H), 6.26 (s, 1H), 4.28-4.14 (m, 2H), 3.93-3.86 (m, 2H), 3.74-3.54 (m, 2H), 2.04 (dd, J = 6.6, 3.5 Hz, 2H), 2.00-1.91 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.0, 169.3, 160.19 (d, J = 248.5 Hz), 130.16 (d, J = 3.7 Hz), 130.12, 124.26 (d, J = 2.5 Hz), 122.41 (d, J = 15 Hz), 115.75 (d, J = 21.25 Hz), 62.1, 55.1, 51.8, 50.4, 26.0, 24.1, 13.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.6. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}FNO_2S_2$: 328.0841; found: 328.0836.

4.6.32 Ethyl 2-(2-fluorophenyl)-2-((morpholine-4-carbonothioyl)thio)acetate (5p):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 70% (120.1 mg). IR (KBr): ν_{max} = 3051, 2961, 2874,

1928, 1734, 1656, 1661, 1567, 1494, 1467, 1376, 1290, 1281, 939, 814, 715, 594 cm^{-1}. 1H NMR (500 MHz, $CDCl_3$) δ 7.46-7.41 (m, 1H), 7.34-7.28 (m, 1H), 7.13-7.06 (m, 2H), 6.20 (s, 1H), 4.35-4.14 (m, 4H), 3.90 (s, 2H), 3.74 (s, 4H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.8, 169.1, 160.18 (d, J = 247.5 Hz), 130.38 (d, J = 8.7 Hz), 130.12 (d, J = 2.5 Hz), 124.33 (d, J = 3.7 Hz), 121.68 (d, J = 13.75 Hz), 115.87 (d, J = 21.25 Hz), 66.0, 62.2, 52.0, 52.0, 50.5, 13.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.6. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{19}FNO_3S_2$: 344.0790; found: 344.0787.

4.6.33 Methyl 3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (6a):

The title compound was obtained as yellow liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.2. Yield 65% (100 mg). IR (KBr): ν_{max} = 3039, 2963, 2863, 1927, 1729, 1612, 1451, 1349, 1321, 1216, 1073, 1035, 961, 871, 731, 549 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 4.22-4.19 (m, 1H), 3.93 (t, J = 6.9 Hz, 2H), 3.84-3.80 (m, 1H), 3.75-3.70 (m, 1H), 3.69 (s, 3H), 3.65 – 3.56 (m, 2H), 2.08-1.95 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.0, 173.3, 137.8, 128.8, 127.7, 127.7, 55.0, 52.1, 51.1, 50.6, 38.7, 26.0, 24.2. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{15}H_{20}NO_2S_2$: 310.0935; found: 310.0929.

4.6.34 Ethyl 3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (6b):

The title compound was obtained as yellow liquid foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.2. Yield 68% (109 mg). IR (KBr): ν_{max} = 3033, 2962, 2847, 1931, 1721, 1567, 1502, 1398, 1329, 1233, 1055, 1012, 971, 819, 795, 555 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 4.21-4.10 (m, 3H), 3.94 (t, J = 6.8 Hz, 2H), 3.84-3.81 (m, 1H), 3.74-3.69 (m, 1H), 3.64-3.56 (m, 2H), 2.07-1.96 (m, 4H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.1, 172.8, 138.0, 128.7, 127.7, 127.6,

61.0, 55.0, 51.2, 50.6, 38.8, 26.0, 24.2, 14.0. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{16}H_{22}NO_2S_2$: 324.1092; found: 324.1093.

4.6.35 2-oxo-2-Phenylethyl morpholine-4-carbodithioate (6c):

The title compound was obtained as white foam using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.3. Yield 74% (104 mg). IR (KBr): ν_{max} = 3047, 2961, 2867, 1926, 1710, 1518, 1414, 1323, 1300, 1255, 1080, 1019, 908, 835, 787, 518 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.4, 1.2 Hz, 2H), 7.63-7.57 (m, 1H), 7.53-7.48 (m, 2H), 4.92 (s, 2H), 4.30-4.04 (m, 4H), 3.80-3.75 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.9, 193.0, 136.0, 133.5, 128.7, 128.5, 66.1, 50.5, 44.7. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{13}H_{16}NO_2S_2$: 282.0622; found: 282.0634.

4.6.36 Ethyl 2-((pyrrolidine-1-carbonothioyl)thio)acetate (6d):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.5. Yield 74% (86 mg). IR (KBr): ν_{max} = 1733, 1518, 1414, 1323, 1300, 1255, 1080, 1019, 908, 835, 787, 685 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.22 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 3.91 (t, J = 7.0 Hz, 2H), 3.70 (t, J = 6.9 Hz, 2H), 2.12- 1.96 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.8, 168.7, 61.8, 55.3, 50.6, 38.5, 26.0, 24.2, 14.1. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_9H_{16}NO_2S_2$: 234.0622; found: 234.0636.

4.6.37 Ethyl 2-((piperidine-1-carbonothioyl)thio)acetate (6e):

The title compound was obtained as colourless liquid using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.5. Yield 75% (93 mg). IR (KBr): ν_{max} = 1725, 1518, 1414, 1323, 1300, 1255, 1110, 1019, 908, 835, 787, 671 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.31-4.19 (m, 4H), 4.16 (s, 2H), 3.91 (s, 2H), 1.70-1.68 (m, 6H), 1.29 (t, J = 7.1

Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 168.7, 61.7, 53.3, 51.5, 39.1, 26.0, 25.3, 24.1, 14.1. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{10}H_{18}NO_2S_2$: 248.0779; found: 248.0785.

4.6.38 Ethyl 2-((4-benzhydrylpiperazine-1-carbonothioyl)thio)acetate (6f):

The title compound was obtained as yellow oil using the general procedure 2.2. R_f (10 % ethyl acetate in hexane): 0.4. Yield 74% (153 mg). IR (KBr): ν_{max} = 3012, 2923, 2856, 1910, 1735, 1576, 1450, 1359, 1315, 1259, 1081, 1051, 948, 858, 757, 509 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 4H), 7.29 (t, J = 7.6 Hz, 4H), 7.21-7.18 (m, 2H), 4.31 (s, 2H), 4.26 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.14 (s, 2H), 3.95 (s, 2H), 2.55-2.45 (m, 4H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.7, 168.6, 141.7, 128.6, 127.7, 127.2, 75.6, 61.8, 51.2, 38.9, 14.1. HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{22}H_{27}N_2O_2S_2$: 415.1514; found: 415.1526

4.7 Spectra of Few Synthesized Compounds

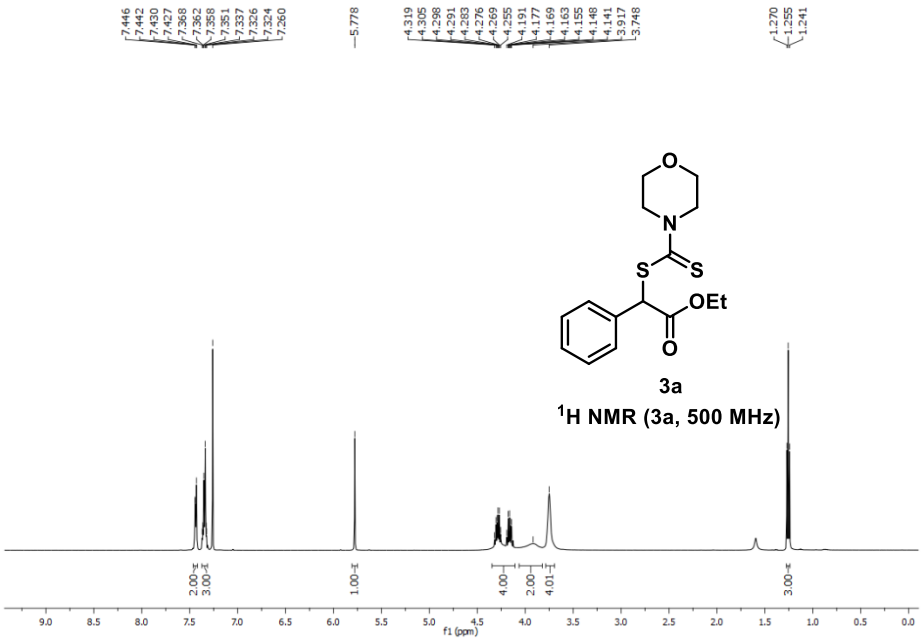


Figure 4.3 ^{1}H NMR Spectra of product 3a in $CDCl_3$

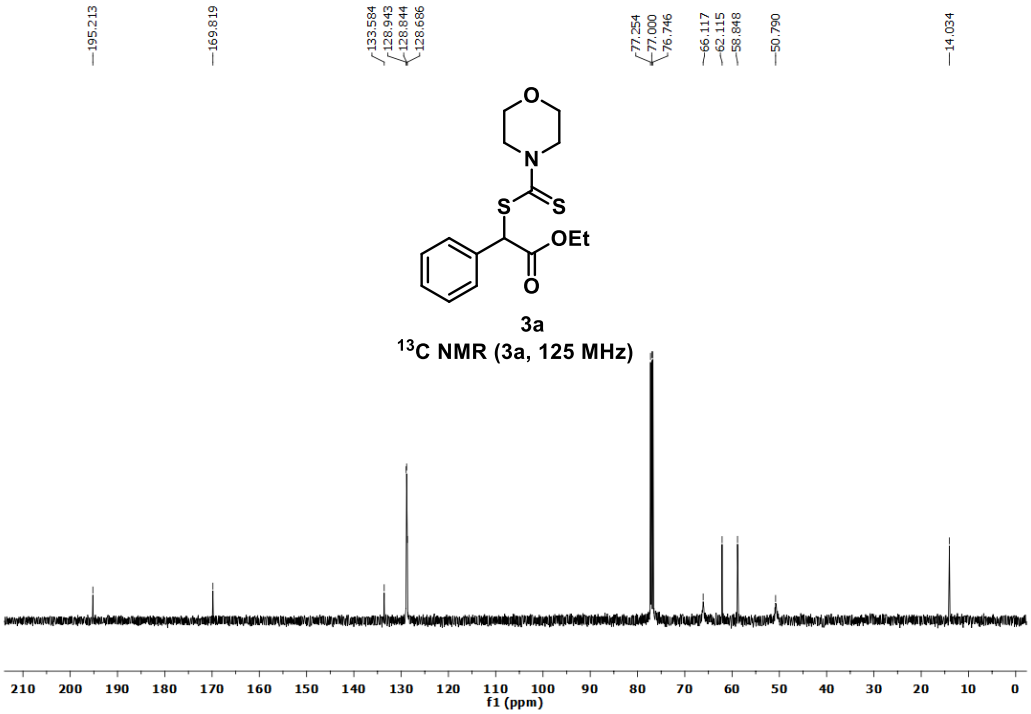


Figure 4.4 ^{13}C NMR Spectra of product 3a in $CDCl_3$

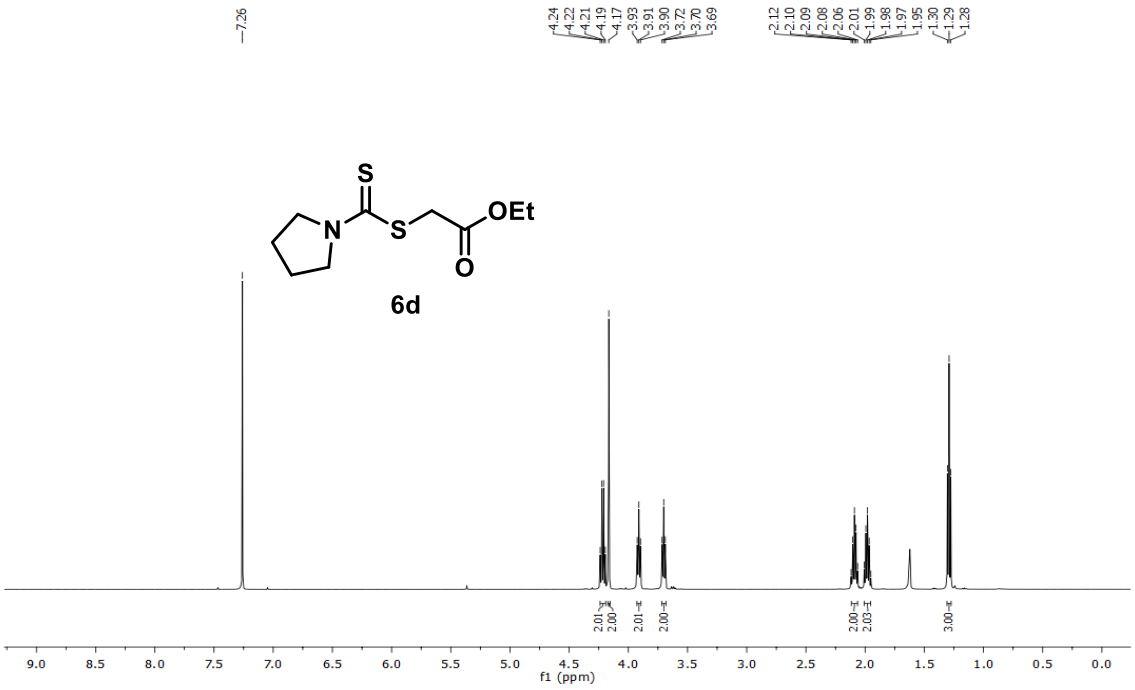


Figure 4.5 ^{1}H NMR Spectra of product 6d in $CDCl_3$

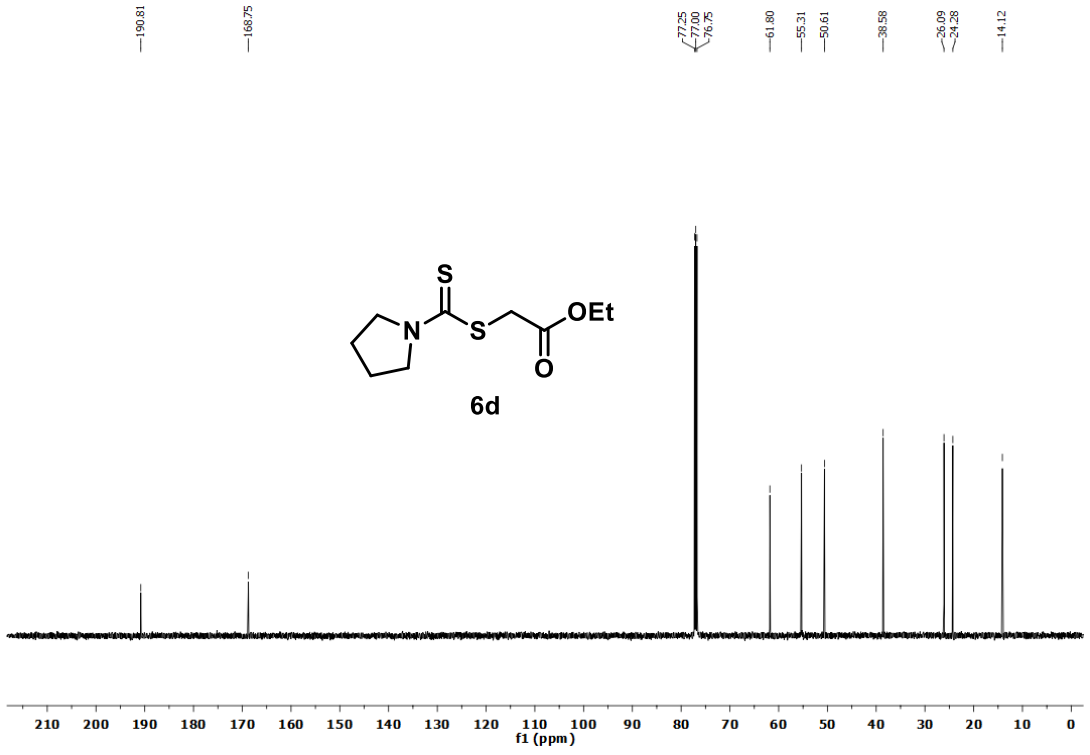


Figure 4.6 ^{13}C NMR Spectra of product 6d in $CDCl_3$

4.8 References

[1] (a) M. P. Doyle, M. A. McKervey, T. Ye, "Modern catalytic methods for organic synthesis with diazo compounds," *John Wiley & Sons, New York*, 1998; (b) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKervey, "Modern organic synthesis with α-diazocarbonyl compounds," *Chemical Reviews*, **115** (2015) 9981-10080. (c) K. A. Mix, M. R. Aronoff, R. T. Raines, "Diazo compounds: versatile tools for chemical biology," *ACS Chemical Biology*, **11** (2016) 3233-3244. (d) T. Ye, M. A. McKervey, "Organic synthesis with alpha-diazo carbonyl compounds," *Chemical Reviews*, **94** (1994) 1091-1160; (e) M. P. Doyle, D. C. Forbes, "Recent advances in asymmetric catalytic metal carbene transformations," *Chemical Reviews*, **98** (1998) 911-936; (f) Y. Zhang, J. Wang, "Recent development of reactions with α-diazocarbonyl compounds as nucleophiles," *Chemical Communications*, **36** (2009) 5350-5361; (g) Z. Zhang and J. Wang, *Tetrahedron Letter*, **64** (2008) 6577-6605; (h) X. Zhao, Y. Zhang, J. Wang, "Recent developments in copper-catalyzed reactions of diazo compounds," *Chemical Communications*, **48** (2012) 10162-10173; (i) Ł. W. Ciszewski, K. Rybicka-Jasińska, D. Gryko, "Recent developments in photochemical reactions of diazo compounds," *Organic & Biomolecular Chemistry*, **17** (2019) 432-448.

[2] (a) H. Keipour, A. Jalba, L. Delage-Laurin, T. Ollevier, "Copper-catalyzed carbenoid insertion reactions of α-diazoesters and α-diazoketones into Si–H and S–H bonds," *The Journal of Organic Chemistry*, **82** (2017) 3000-3010; (b) H. Jiang, H. Jin, A. Abdukader, A. Lin, Y. Cheng, C. Zhu, "Catalyst-controlled switchable phosphination of α-diazoesters," *Organic & Biomolecular Chemistry*, **11** (2013) 3612-3615; (c) B. D. Bergstrom, L. A. Nickerson, J. T. Shaw, L. W. Souza, "Deconvoluting nonlinear catalyst–substrate effects in the intramolecular dirhodium-catalyzed C–H insertion of donor/donor carbenes using data sciencet," *ACS Catalysis*, **14** (2023) 104-115; (d) M. Y. Huang, S. F. Zhu, "Uncommon carbene insertion reactions," *Chemical Science*, **12** (2021) 15790-15801; (e) H. Keipour, T. Ollevier, "Iron-catalyzed carbene insertion reactions of α-diazoesters into Si–H bonds," *Organic Letters*, **19** (2017) 5736-5739; (f) Q. H. Deng, H. W. Xu, A. W.-H. Yuen, Z.-J. Xu, C. M. Che, "Ruthenium-catalyzed one-pot carbenoid N-H insertion reactions and diastereoselective synthesis of prolines," *Organic Letters*, **10** (2008) 1529-1532; (g) M. E. Morilla, M. M. Díaz-Requejo, T. R. Belderrain, M. C. Nicasio, S. Trofimenko, P. J. Pérez, "Catalytic insertion of diazo compounds into N-H bonds: the copper alternative," *Chemical Communications*, **24** (2002) 2998-2999; (h) K. Ramakrishna, C. Sivasankar, "Synthesis of aminobenzoic acid derivatives via chemoselective carbene insertion

into the -NH bond catalyzed by Cu (I) complex," *The Journal of Organic Chemistry*, **81** (2016) 6609-6616.

[3] (a) H. H. San, C. Y. Wang, H. P. Zeng, S. T. Fu, M. Jiang, X. Y. Tang, "Boron-catalyzed azide insertion of α-aryl α-diazoesters," *The Journal of Organic Chemistry*, **84** (2019) 4478-4485; (b) Y. Zhang, X. Zhang, J. Zhao, J. Jiang, "B (C_6F_5) 3-catalyzed O-H insertion reactions of diazoalkanes with phosphinic acids," *Organic & Biomolecular Chemistry*, **19** (2021) 5772-5776; (c) C. Empel, T. V. Nguyen, R. M. Koenigs, "Tropylium-catalyzed O-H insertion reactions of diazoalkanes with carboxylic acids," *Organic Letters*, **23** (2021) 548-553; (d) A. Dasgupta, K. Stefkova, R. Babaahmadi, L. Gierlichs, A. Ariafard, R. L. Melen, "Triarylborane-catalyzed alkenylation reactions of aryl esters with diazo compounds," *Angewandte Chemie*, **59** (2020) 15492-15496.

[4] (a) S. Hu, J. Wu, Z. Lu, J. Wang, Y. Tao, M. Jiang, F. Chen, "TfOH-catalyzed N-H insertion of α-substituted-α-diazoesters with anilines provides access to unnatural α-amino esters," *The Journal of Organic Chemistry*, **86** (2020) 3223-3231; (b) K. A. Mix, R. T. Raines, "Optimized diazo scaffold for protein esterification," *Organic Letters*, **17** (2015) 2358-2361; (c) X. Yi, J. Feng, F. Huang, J. B. Baell, "Metal-free C-C, C-O, C-S and C-N bond formation enabled by SBA-15 supported TFMSA," *Chemical Communications*, **56** (2020) 1243-1246; (d) Z. Zhang, Z. He, Y. Xie, T. He, Y. Fu, Y. Yu, F. Huang, "Brønsted acid-catalyzed homogeneous O-H and S-H insertion reactions under metal-and ligand-free conditions," *Organic Chemistry Frontiers*, **8** (2021) 1233-1242.

[5] (a) F. He, F. Li, R. M. Koenigs, "Metal-free insertion reactions of silanes with aryldiazoacetates," *The Journal of Organic Chemistry*, **85** (2019) 1240-1246; (b) D. Maiti, R. Das, S. Sen, "Blue LED-mediated N-H insertion of indoles into aryldiazoesters at room temperature in batch and flow: reaction kinetics, density functional theory, and mechanistic study," *The Journal of Organic Chemistry*, **86** (2021) 2522-2533; (c) M. L. Stivanin, R. D.Gallo, J. P. M. Spadeo, R. A. Cormanich, I. D. Jurberg, "A visible light-mediated three-component strategy based on the ring-opening of cyclic ethers with aryldiazoacetates and nucleophiles," *Organic Chemistry Frontiers*, **9** (2022) 1321-1326.

[6] G. D. Thorn, R. A. Ludwig, "The dithiocarbamates and related compounds." The dithiocarbamates and related compounds. (1962).

[7] L. G. Costa, M. Aschner, Toxicology of Pesticides. "Perspective on halogenated organic compounds," *Advances in Neurotoxicology*, **10** (2023) 1.

[8] (a) V. Bala, G. Gupta, V. L. Sharma, "Chemical and medicinal versatility of dithiocarbamates: an overview," *Mini-Reviews in Medicinal Chemistry*, **14** (2014) 1021-1032; (b) S. D. Shinde, A. P. Sakla, N. Shankaraiah, "An insight into medicinal attributes of dithiocarbamates: Bird's eye view," *Bioorganic*

Chemistry, **105** (2020) 104346; (c) M. A. H. Zahran, T. A. R. Salem, R. M. Samaka, H. S. AgwaAwad, A. R. "Design, synthesis and antitumor evaluation of novel thalidomide dithiocarbamate and dithioate analogs against ehrlich ascites carcinoma-induced solid tumor in Swiss albino mice," *Bioorganic & Medicinal Chemistry*, **16** (2008) 9708-9718; (d) C. K. Adokoh, "Therapeutic potential of dithiocarbamate supported gold compounds," *RSC Advances*, **10** (2020) 2975-2988; (e) L. Ronconi, L. Giovagnini, C. Marzano, F. Bettìo, R. Graziani, G. Pilloni, D. Fregona, "Gold dithiocarbamate derivatives as potential antineoplastic agents: design, spectroscopic properties, and in vitro antitumor activity," *Inorganic Chemistry*, **44** (2005) 1867-1881; (f) M. Ayman, S. M. El-Messery, E. E. Habib, S. T. Al-Rashood, A. A. Almehizia, H. M. Alkahtani, G. S. Hassan, "Targeting microbial resistance: Synthesis, antibacterial evaluation, DNA binding and modeling study of new chalcone-based dithiocarbamate derivatives," *Bioorganic Chemistry*, **85** (2019) 282-292.

[9] (a) Y. Guillaneuf, J. L. Couturier, D. Gigmes, S. R. A. Marque, P. Tordo, D. Bertin, "Synthesis of highly labile SG1-based alkoxyamines under photochemical conditions," *The Journal of Organic Chemistry*, **73** (2008) 4728-4731; (b) M. Betou, L. Male, J. W. Steed, R. S. Grainger, "Carbamoyl radical-mediated synthesis and semipinacol rearrangement of β-lactam diols," *Chemistry-A European Journal*, **20** (2014) 6505-6517; (c) R. Wong, S. J. Dolman, "Isothiocyanates from tosyl chloride mediated decomposition of in situ generated dithiocarbamic acid salts," *The Journal of Organic Chemistry*, **72** (2007) 3969-3971; (d) G. Li, M. Noguchi, G. Arisaka, Y. Tanaka, S. I. Shoda, "A protecting group-free approach for synthesizing C-glycosides through glycosyl dithiocarbamates," *Organic & Biomolecular Chemistry*, **19** (2021) 3134-3138.

[10] A. Z. Halimehjani, M. H. Shayegan, M. M. Hashemi, B. Notash, "Investigation of the reaction of dithiocarbamic acid salts with aromatic aldehydes," *Organic Letters*, **14** (2012) 3838-3841.

[11] P. Morf, F. Raimondi, H. G. Nothofer, B. Schnyder, A. Yasuda, J. M. Wessels, T. A. Jung, "Dithiocarbamates: functional and versatile linkers for the formation of self-assembled monolayers," *Langmuir*, **22** (2006) 658-663.

[12] J. T. Lai, R. Shea, "Controlled radical polymerization by carboxyl-and hydroxyl-terminated dithiocarbamates and xanthates," *Journal of Polymer Science Part A: Polymer Chemistry*, **44** (2006) 4298-4316.

[13] (a) A. Saha, R. B. N. Baig, J. Leazer, R. S. Varma, "A modular synthesis of dithiocarbamate pendant unnatural α-amino acids," *Chemical Communications*, **48** (2012) 8889-8891; (b) P. J. Nieuwenhuizen, A. W. Ehlers, J. G. Haasnoot, S. R. Janse, J. Reedijk, E. J. Baerends, "The mechanism of zinc (II)-dithiocarbamate-accelerated vulcanization uncovered; theoretical and experimental

evidence," *Journal of the American Chemical Society*, **121** (1999) 163-168; (c) I. Kaur, S. K. Verma, "Living radical polymerization and grafting of diethyl (acryloyloxy) ethylthiophosphoramidate onto cotton fabric to impart flame retardancy," *Surface and Coatings Technology*, **205** (2010) 2082-2090; (d) J. Zhang, N. R. Myllenbeck, T. L. Andrew, "Synthesis and properties of dithiocarbamate-linked acenes," *Organic Letters*, **19** (2017) 210-213.

[14] N. Azizi, F. Aryanasab, M. R. Saidi, "Straightforward and highly efficient catalyst-free one-pot synthesis of dithiocarbamates under solvent-free conditions," *Organic Letters*, **8** (2006) 5275-5277.

[15] T. Guntreddi, R. Vanjari, K. N. Singh, "Direct conversion of methylarenes into dithiocarbamates, thioamides and benzyl esters," *Tetrahedron*, **70** (2014) 3887-3892.

[16] S. Dutta, A. Saha, "Iodine mediated direct coupling of benzylic alcohols with dithiocarbamate anions: an easy access of S-benzyl dithiocarbamate esters under neat reaction condition," *Tetrahedron Letters*, **61** (2020) 152382.

[17] N. Azizi, M. Khajeh, M. Hasani, S. Dezfooli, "An efficient four-component synthesis of dithiocarbamate derivatives," *Tetrahedron Letters*, **54** (2013) 5407-5410.

[18] A. Krasovskiy, A. Gavryushin, Knochel, "Highly stereoselective access to sulfur derivatives starting from zinc organometallics," *Synlett*, **2006** (2006) 0792-0794.

[19] Z. Wu, M. Lai, S. Zhang, X. Zhong, H. Song, M. Zhao, "An efficient synthesis of benzyl dithiocarbamates by base-promoted cross-Coupling reactions of benzyl chlorides with tetraalkylthiuram disulfides at room temperature," *European Journal of Organic Chemistry*, **2018** (2018) 7033-7036.

[20] R. Venkatesh, G. Shankar, A. C. Narayanan, G. Modi, S. Sabiah and J. Kandasamy, "Multicomponent synthesis of S-benzyl dithiocarbamates from para-quinone methides and their biological evaluation for the treatment of alzheimer's disease," *The Journal of Organic Chemistry*, **87** (2022) 6730-6741.

[21] (a) S.Thurow, A. A. Fernandes, Y. Quevedo-Acosta, M. F. de Oliveira, M. G. de Oliveira, I. D. Jurberg, "Preparation of organic nitrates from aryldiazoacetates and Fe $(NO_3)_3 \cdot 9H_2O$," *Organic Letters*, **21** (2019) 6909-6913; (b) J. Zheng, J. H. Lin, L. Y. Yu, Y. Wei, X. Zheng, J. C. Xiao, "Cross-coupling between difluorocarbene and carbene-derived intermediates generated from diazocompounds for the synthesis of gem-difluoroolefins," *Organic Letters*, **17** (2015) 6150-6153; (c) H. Keipour, and T. Ollevier, "Iron-catalyzed carbene insertion reactions of α-diazoesters into Si–H bonds," *Organic Letters* **19** (2017) 5736-5739; (d) G. Liu, J. Li, L. Qiu, L. Liu, G. Xu, B. Ma, J. Sun, "Palladium-catalyzed carbenoid based N–H bond insertions: application to the synthesis of chiral α-amino esters," *Organic & Biomolecular Chemistry*, **11** (2013) 5998-6002.

[22] (a) C. Matheis, T. Krause, V. Bragoni, L. J. Goossen, "Trifluoromethylthiolation and trifluoromethylselenolation of α-diazo esters catalyzed by copper," *Chemistry-A European Journal*, **22** (2016) 12270-12273; (b) E. Yasui, K. Ishimine, S. Nitanai, N. Hatakeyama, S. Nagumo, "Synthesis of α-diazoesters from α-hydrazonoesters: Utilization of α-hydrazonoesters and α-diazoesters for convenient interconversion," *Tetrahedron Letters*, **96** (2022) 153730; (c) A. Röske, I. Alt and B. Plietker, "Scope and limitations of TBA [Fe]-catalyzed carbene transfer to X-H-bonds indication of a mechanistic dichotomy," *ChemCatChem*, **11** (2019) 5260-5263.

[23] N. D. Koduri, Z. Wang, G. Cannell, K. Cooley, T. M. Lemma, K. Miao, M. Nguyen, B. Frohock, M. Castaneda, H. Scott, D. Albinescu and S. R. Hussaini, "Enaminones via ruthenium-catalyzed coupling of thioamides and α-diazocarbonyl compounds," *The Journal of Organic Chemistry*, **79** (2014) 7405-7414.