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Synthesis of Thio-/Selenopyrrolines *via* $SnCl_4$-Catalyzed (3 + 2)-Cycloadditions of Donor-Acceptor Cyclopropanes with Thio-/Selenocyanates

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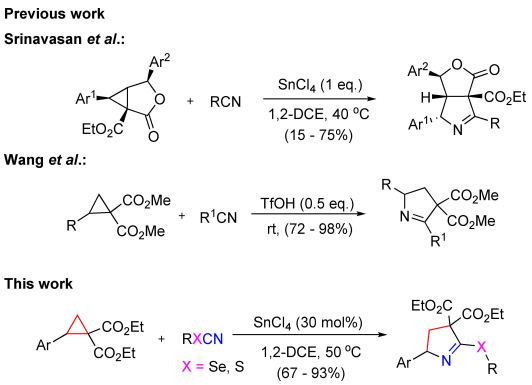
A straightforward protocol has been developed to access thio-/selenopyrrolines through a (3 + 2)-cycloaddition of aryl thio-/selenocyanates with donor-acceptor cyclopropanes (DACs) in the presence of $SnCl_4$ as a Lewis acid catalyst. Further, good chemoselectivity was observed when DACs were treated with 3-cyano phenyl thiocyanate. These results suggest that thiocyanate is more reactive than nitrile moiety in such (3 + 2)-cycloaddition reactions.

Introduction

During the past several decades, nitrogen-containing molecules are an important class of heterocyclic compounds that displays interesting applications in the field of medicinal chemistry.[1] Among the known nitrogen-containing heterocycles, pyrrolines are one of the most important classes of azaheterocycles found in a variety of natural products and bioactive molecules.[2] Furthermore, the heteroatom substituted pyrrolines have exhibited a number of interesting chemical and biological properties.[3] Literature survey has revealed that among numerous protocols to access pyrroline derivatives,[2a] (3 + 2)-cycloaddition of donor-acceptor cyclopropanes (DACs) are few.[4]

Over the past decades, DACs are known as one of the most strained rings, prompted chemists to explore their synthetic potential due to their remarkable and unique reactivity. The reactivity may be attributed due to both inherent strain and the push-pull effect of substituents.[5] A wide range of cycloadditions with various 1,2-, 1,3-, 1,4-, dipoles including dienes,[6] alkynes,[7] imines,[8] carbonyls,[9] have been reported using DACs as a reactive partner; however, any heteroatom (especially chalcogen) substituted pyrrolines has not been reported yet *via* mentioned cycloaddition protocol.

Encouraged by our previous work related to the synthesis of sulfur-/selenium-containing heterocycles,[10] we currently devote our attention for construction of the thiopyrrolines *via* cycloaddition strategy using DACs as one of the coupling partners. Pioneer work in this field includes the $SnCl_4$-promoted (3 + 2)-cycloaddition reaction between DACs and nitriles reported by Trushkov's group[11] and Srinivasan's group.[12] In 2014, Wang *et al.* disclosed the TfOH-catalyzed (3 + 2)-cycloaddition reaction of DACs with nitriles (Scheme 1).[13] Later in 2019, Srinivasan and co-workers have delineated the (3 + 2)-annulation of γ-butyrolactone-fused D–A cyclopropanes with nitriles to obtain γ-butyrolactone-fused 1-pyrrolines (Scheme 1).[14] However, all of these aforementioned methods are limited to alkyl or aryl nitriles. Recently, Werz *et. al.* investigated $Yb(OTf)_3$-catalyzed (3 + 2) cycloaddition of DACs with ammonium thio-/selenocyanate to achieve dihydrothio-/selenophenes.[15] Later, the same group delineated the synthesis of pyrrolidine-2-thiones allowing the treatment of D-A cyclopropanes with 1-methylimidazolium thiocyanate.[16]



Scheme 1. (3 + 2)-Cycloadditions of donor-acceptor cyclopropanes with nitriles.

Herein, we report a thio-/selenocyanate source dependent (3 + 2)-cycloaddition reactions protocol for the synthesis of thio-/selenopyrrolines in the presence of $SnCl_4$ as a Lewis acid catalyst.

Results and Discussion

At the onset, the exploration and optimization of (3 + 2)-cycloaddition reaction of donor-acceptor cyclopropane **1a** with phenyl selenocyanate **2a** was carried out. An array of Lewis acids involving Ti, Cu, Fe, Yb, In and Sn based complexes were employed in this survey, and the results are summarized in Table 1.

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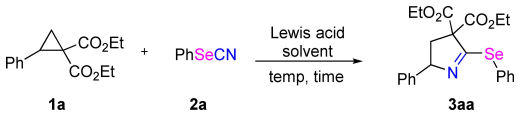
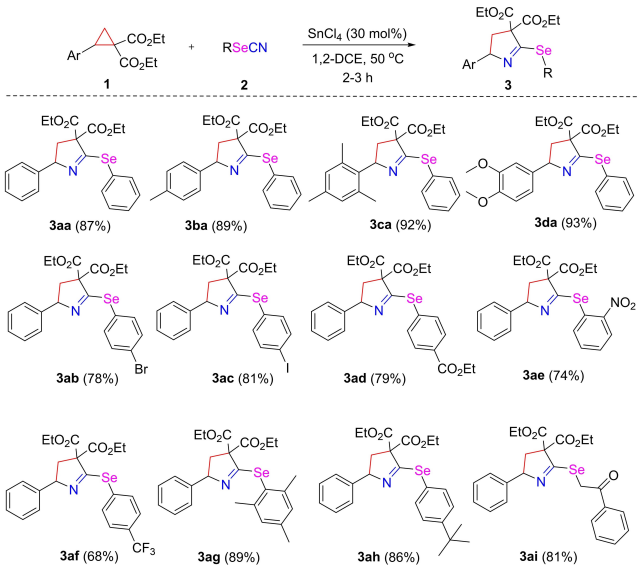
Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3aa**

Entry	Lewis acid [equiv.]	Solvent	T °C	Time [h]	Yield **3aa** [%])[b]
1	$TiCl_4$ (1)	DCM	−5 °C to rt	24	–
2	$Yb(OTf)_3$ (1)	1,2-DCE	40 °C	24	–
3	$FeCl_3$ (1)	1,2-DCE	40 °C	24	–
4	$Cu(OTf)_2$ (1)	1,2-DCE	40 °C	24	–
5	$InCl_3$ (1)	1,2-DCE	40 °C	24	–
6	TfOH (1)	DCM	rt	5	trace
7	TfOH (1)	1,2-DCE	rt	5	42
8	TfOH (1)	1,2-DCE	40 °C	4	37
9	$AlCl_3$ (1)	1,2-DCE	40 °C	6	51
10	$SnCl_4$ (1)	1,2-DCE	40 °C	4	66
11	$SnCl_4$ (1)	1,2-DCE	rt	5	54
12	$SnCl_4$ (1)	DCM	40 °C	5	59
13	$SnCl_4$ (1)	$CHCl_3$	40 °C	5	62
14	$SnCl_4$ (1)	Toluene	60 °C	5	–
15	**$SnCl_4$ (0.3)**	**1,2-DCE**	**50 °C**	**2**	**87**
16	$SnCl_4$ (1.5)	1,2-DCE	40 °C	4	65
17	TMSOTf (1)	$MeNO_2$	rt	5	–
18	$BF_3.OEt_2$ (1)	DCM	rt	5	–

[a] Optimized reaction conditions for **3aa**: **1a** (78.6 mg, 0.30 mmol), **2a** (65.5 mg, 0.36 mmol), $SnCl_4$ (0.01 mL, 0.3 eq.), 1,2-DCE (2.0 mL), 50 °C, inert atmosphere, 2 h. [b] Isolated yield.



Scheme 2. $SnCl_4$-catalyzed synthesis of various selenopyrroline derivatives **3** via (3 + 2)-cycloadditions.[a] [a] Reaction Conditions: **1** (0.30 mmol), **2** (0.36 mmol), $SnCl_4$ (0.01 mL, 30 mol %), 1,2-DCE (2.0 mL), 50 °C, inert conditions, 2–3 h.

The cycloaddition was initially investigated with Ti, Fe, Yb, and In-based Lewis acids; however, none of them could deliver the expected product **3aa** (Table 1, entries 1–5). Taking the lead from the previous work,[12] the cycloaddition was performed in the presence of TfOH in DCM at room temperature. The cycloaddition resulted in the formation of product in trace amount (Table 1, entry 6). Further tuning the reaction conditions, the cycloaddition increased the yield up to 42% (Table 1, entries 7–8). Unfortunately, the reaction, even with the replacement of TfOH with $AlCl_3$, was not much effective (Table 1, entry 9). In order to achieve the product with a higher yield, cycloaddition was further explored in the presence of $SnCl_4$ as a Lewis acid (Table 1, entries 10–15). To our delight, the cycloaddition furnished the product with 66% yield using 1 eq. of $SnCl_4$ in DCE at 40 °C for 4 h. Further optimization towards the other reaction parameters like the amount of catalyst, solvent, and temperature successfully delivered the product in 87% yield (Table 1, entry 15). Other commercially available Lewis acids, like TMSOTf, and $BF_3.OEt_2$, failed to catalyze the transformation (Table 1, entries 17–18).

Employing the optimized reaction conditions, a plethora of selenopyrrolines could be accessed exclusively (Scheme 2). Electron-deficient (**2b**, **2e**), and electron-rich (**2a**, **2g**, **2h**) aryl selenocyanates reacted to deliver the selenopyrroline cycloadducts in good to excellent yields. Additionally, substitutions at *ortho*-positions of the aryl selenocyanates were tolerated, giving the cycloadduct **3ae** and **3ag** in yield of 74% and 89% respectively. A broad range of functional groups was compatible, including bromo (**3ab**), iodo (**3ac**), ester (**3ad**), nitro (**3ae**), and *tert*-butyl (**3ah**) groups.

The reaction of α-carbonyl selenocyanate **2i** with cyclopropane **1a** furnished selenopyrroline **3ai** in 81% yield. It is noteworthy that the yields were higher for aromatic selenocyanates having electron-donating substituents in the *para*-position as compared to those with electron-withdrawing substituents in the position. (Scheme 2).

Encouraged by the results, the scope of the protocol was also explored for the tin (IV)-catalyzed (3 + 2)-cycloaddition of DACs **1** and alkyl/arylthiocyanates **4** for the synthesis of thiopyrroline derivatives **5**, and the results are shown in Scheme 3. At first, a number of DACs were examined. Cyclopropane, bears a substituent such as a methoxy at the aryl ring, was an effective coupling partner, affording the corresponding product **5ea** in 89% yield. On the other hand, DACs bearing nitro group at aryl ring offered the desired cycloadduct **5fa** with a relatively lower yield. Next, we focused on investigating the scope of thiocyanates **4** with cyclopropane **1a**. The reaction proceeded smoothly to provide thiopyrrolines **5ab** and **5ac** in 88% and 82% yields for thiocyanates **4b** and **4c** bearing methyl and methoxy group at *para*-position, respectively. Aryl thiocyanates, containing electron-withdrawing substituents at the *para*-position, including nitro and acetyl, were well tolerated, and the reaction provided compounds **5ae** and **5ad** in 76% and 81% yields, respectively. Treating methyl thiocyanate **4f** with cyclopropane **1a**, the corresponding cycloadduct **5af** was obtained in 91% yield. The cycloaddition also proceeded smoothly with benzyl thiocyanate, and the corresponding cycloadduct **5ag** was produced in 93% yield.

In order to investigate the chemoselectivity, we embarked on probing the reaction of thiocyanate **4h** with cyclopropane **1a**. To our delight, the reaction of 1 eq. of **1a** with 1 eq. of **4h** delivered the separable mixture of cycloadducts **5ah** and **5′′ah** in 76% and 12% yields, respectively. Increasing the equivalence

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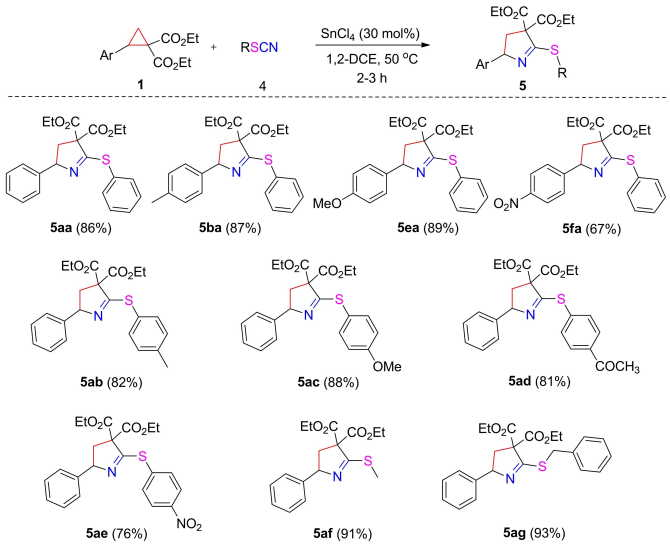
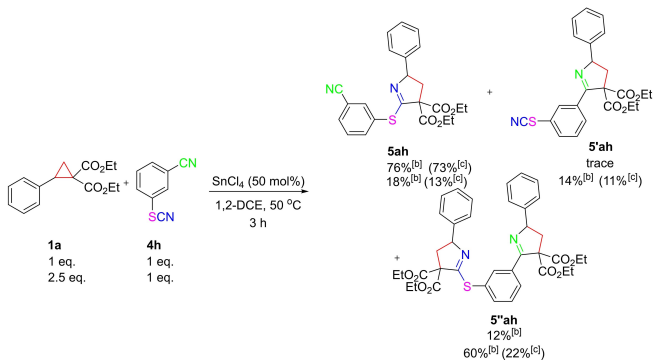
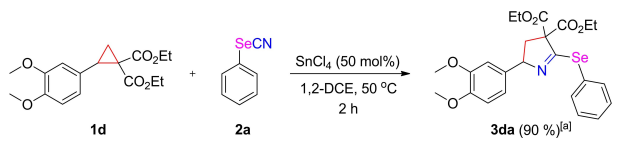


Scheme 3. Synthesis of thiopyrroline derivatives **5** *via* $SnCl_4$-catalyzed (3 + 2)-cycloadditions.[a] [a] Reaction conditions: **1** (0.30 mmol), **4** (0.36 mmol), $SnCl_4$ (0.01 mL, 30 mol %), 1,2-DCE (2.0 mL), 50 °C, inert conditions, 2–3 h.

of cyclopropane **1 a** to 2.5 eq., (3 + 2)-cycloaddition provided the compounds **5 ah**, **5′ah** and **5′′ah** in 18%, 14% and 60% yields, respectively. These results clearly indicate that thiocyanate moiety undergoes (3 + 2)-cycloaddition faster than the nitrile group (Scheme 4).These results clearly indicate that the aforementioned protocol has a remarkable practicable applicability.



Scheme 4. $SnCl_4$-catalyzed chemoselectivity studies of DACs with 3-cyano phenyl thiocyanate.[a] [a] Reaction Conditions: **1 a** (0.50–1.25 mmol), **4 h** (0.50 mmol), $SnCl_4$ (50 mol %), 1,2-DCE (2.0 mL), 50 °C, inert conditions, 3 h. [b] Isolated yield. [c] From NMR of crude mixture.



Scheme 5. Gram scale synthesis of **3 da**.[a][a]Reaction conditions: **1 d** (1.61 g, 5.00 mmol), **2 a** (1.09 g, 6.00 mmol) $SnCl_4$ (0.175 mL, 50.0 mol %), 1,2-DCE (5.0 mL),

After successfully constructing a range of heteroatom-substituted pyrrolines, the gram-scale synthesis of selenopyrroline **3 da** was carried out using the optimized reaction conditions. To our delight, the protocol was amenable to the gram-scale synthesis of selenopyrroline **3 da** based on 5 mmol of cyclopropane **1 a** with 6 mmol of phenyl selenocyanate **2 a** (Scheme 5). Of note, the large-scale synthesis proceeded as efficiently as the small-scale synthesis (Scheme 2), giving **3 da** in 90 % yield (Scheme 5).

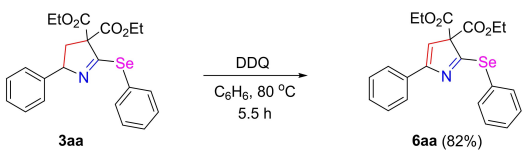
The versatility of the products as synthons was demonstrated by the follow-up reaction of selenopyrroline **3 aa**. The 3*H*-pyrrole **6 aa** was obtained *via* dehydrogenation of selenopyrroline **3 aa**. In this study, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was employed as an oxidant in benzene at 80 °C (Scheme 6).

Conclusion

To conclude, we have documented a $SnCl_4$-catalyzed (3 + 2)-cycloaddition of DACs with thio-/selenocyanates for the synthesis of thio-/selenopyrrolines under mild conditions. These transformations are well tolerant to a wide range of functional groups on aryl thio-/selenocyanate building blocks as well as D-A cyclopropanes. The procedure provides a general, atom-economical, and straightforward way to construct chalcogen substituted azacycles in good to excellent yields. Further utilization of thus obtained thio-/selenopyrrolines is underway.

Experimental Section

General information: All the reactions were carried out under an inert atmosphere using the Schlenk technique. All solvents were dried and stored over molecular sieves under argon atmosphere. All chemicals and reagents were purchased from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). ^1H, ^{13}C, and DPT-135 NMR spectra were recorded in $CDCl_3$, on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz (^1H) or 100 MHz (^{13}C) as indicated in the individual spectrum. Chemical shifts (δ) are given in parts per million (ppm) relative to residual solvent (chloroform, $\delta = 7.26$ for ^1H and 77.16 for proton decoupled ^{13}C NMR) and coupling constants (J) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet, and m for multiplet. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on waters mass spectrometer (XEVO G2-XS QTOF). All cyclopropane-1,1-diester derivatives(**1 a**–**1 h**),[17] arylselenocyanates (**2 a**–



Scheme 6. Preparation of seleno-substituted 3H-pyrrol **6 aa**.

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2 i),[18] thiocyanates (**4 a**–**4 h**)[19] were synthesized according to the reported literature procedures.

General Procedure for the Synthesis of Seleno-/Thio Substituted Pyrrolins 3 and 5: Cyclopropanediester (0.30 mmol, 1.0 eq.) and seleno-/thiocyanate (0.36 mmol, 1.2 eq.) were dissolved in 1,2-DCE under nitrogen atmosphere. The solution was stirred at 50 °C for two min and $SnCl_4$ (30 mol %) was added. Reaction was continued until TLC analysis showed complete consumption of cyclopropane. The reaction mixture was passed through celite pad and concentrated in *vacuo*. Then the residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

Gram Scale Synthesis of 3 da: Cyclopropanediester **1 d** (1.61 g, 5 mmol, 1.0 eq.) and selenocyanate **2 a** (1.10 g, 6 mmol, 1.2 eq.) were dissolved in 1,2-DCE under nitrogen atmosphere. The solution was stirred at 50 °C for two min and $SnCl_4$ (0.175 mL, 50 mol %) was added. Reaction was continued until TLC analysis showed complete consumption of cyclopropane. The reaction mixture was passed through celite pad and concentrated in *vacuo*. Then the residue was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

Synthesis of Diethyl 5-Phenyl-2-(phenylselanyl)-3*H*-pyrrole-3,3-dicarboxylate (6 aa): DDQ (25 mg, 0.1 mmol, 1 eq.) was added to the solution of **3 aa** (44.6 mg, 0.1 mmol, 1 eq.) in benzene (3 mL) and refluxed for 5.5 h. After full consumption of starting material, the crude was purified by silica gel column chromatography using ethyl acetate/hexane solution as eluent.

Characterization Data of Compounds

Diethyl 5-phenyl-2-(phenylselanyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 aa): Yield: 116 mg (87 %); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.66 (m, 2H), 7.35–7.31 (m, 3H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.25–7.22 (m, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 5.20 (t, *J* = 7.7 Hz, 1H), 4.33 (q, *J* = 7.16, 2H), 4.28 (q, *J* = 7.12, 2H), 3.19 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.45 (dd, *J* = 13.0, 8.4 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 167.6, 165.6, 142.6, 135.3, 129.2, 128.6, 128.5, 128.0, 127.2, 126.4, 75.5, 74.9, 62.7, 62.6, 42.3, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2981, 2931, 1729, 1587, 1444, 1250, 1186, 1094, 743, 686 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{24}NO_4Se$ $[M+H]^+$ 446.0871, found 446.0864.

Diethyl 2-(phenylselanyl)-5-(*p*-tolyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 ba): Yield: 122 mg (89 %); Yellow solid (m.p. = 99–102 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.66 (m, 2H), 7.35–7.28 (m, 3H), 7.11–7.05 (m, 4H), 5.15 (t, *J* = 7.7 Hz, 1H), 4.32 (q, *J* = 6.88, 2H), 4.27 (q, *J* = 7.12, 2H), 3.16 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.43 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.31 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 167.7, 165.3, 139.7, 136.8, 135.3, 129.2, 129.1, 128.6, 128.1, 126.4, 75.3, 74.9, 62.7, 62.6, 42.4, 21.2, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 3089, 2981, 2919, 1706, 1428, 1251, 1065, 720 cm^{-1};HRMS: *m/z* calculated for $C_{23}H_{26}NO_4Se$ $[M+H]^+$ 460.1027, found 460.1021.

Diethyl 5-mesityl-2-(phenylselanyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 ca): Yield: 134 mg (92 %); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.25–7.22 (m, 1H), 7.19–7.15 (m, 2H), 5.20 (t, *J* = 7.7 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 6.7 Hz, 2H), 3.17 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.44 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.32–1.28 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 167.6, 162.6, 136.7, 136.5, 136.0, 134.0, 130.1, 129.2, 128.8, 127.3, 74.6, 73.0, 62.6, 62.6, 40.1, 20.9, 20.8, 14.2, 14.2; IR (neat) ($\tilde{\nu}$): 3056, 2932, 1733, 1566, 1450, 1261, 1093, 1021, 730 cm^{-1}; HRMS: *m/z* calculated for $C_{25}H_{30}NO_4Se$ $[M+H]^+$ 488.1340 found 488.1348.

Diethyl 5-(3,4-dimethoxyphenyl)-2-(phenylselanyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 da): Yield: 141 mg (93 %); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl^3$): δ 7.72–7.67 (m, 2H), 7.33–7.29 (m, 3H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.73–6.68 (m, 2H), 5.14 (t, *J* = 7.6 Hz, 1H), 4.33 (q, *J* = 7.2, 2H), 4.30–4.25 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 3.17 (dd, *J* = 13.5, 7.5 Hz, 1H), 2.43 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 167.6, 165.5, 148.9, 148.0, 135.4, 135.3, 129.2, 128.6, 128.0, 118.4, 110.9, 109.5, 75.1, 74.9, 62.7, 62.6, 55.9, 55.8, 42.2, 14.1, 14.1; IR (neat) ($\tilde{\nu}$): 2988, 2941, 1750, 1520, 1384, 1229, 1136, 1080, 751 cm^{-1}; HRMS: *m/z* calculated for $C_{24}H_{28}NO_6Se$ $[M+H]^+$ 506.1082, found 506.1088.

Diethyl 2-((4-bromophenyl)selanyl)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 ab): Yield: 122 mg (78 %); Pale yellow gum; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.43–7.39 (m, 2H), 7.38–7.33 (m, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 5.16 (t, *J* = 7.7 Hz, 1H), 4.30 (q, *J* = 7.16, 2H), 4.25 (q, *J* = 7.16, 2H), 3.15 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.42 (dd, *J* = 13.5, 7.9 Hz, 1H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.6, 165.2, 142.4, 136.8, 133.5, 132.3, 128.6, 127.3, 126.4, 123.2, 75.5, 74.8, 62.8, 62.7, 42.2, 14.1, 14.1; IR (neat) ($\tilde{\nu}$): 2983, 2923, 1740, 1584, 1458, 1376, 1250, 1175, 1063, 803 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{23}NO_4SeBr$ $[M+H]^+$ 523.9976, found 523.9968.

Diethyl 5-((4-iodophenyl)selanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ac): Yield: 138 mg (81 %); Pale yellow gum; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.32–7.28 (m, 2H), 7.26–7.23 (m, 1H), 7.20–7.14 (m, 2H), 5.18 (t, *J* = 7.7 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.29–4.24 (m, 2H), 3.17 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.44 (dd, *J* = 13.5, 7.9 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.6, 165.1, 142.4, 138.3, 136.9, 128.6, 127.8, 127.3, 126.4, 95.0, 75.6, 74.9, 62.8, 62.7, 42.2, 14.1, 14.0.; IR (neat) ($\tilde{\nu}$): 2986, 2925, 1723, 1589, 1448, 1374, 1247, 1180, 1099, 984, 750 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{23}NO_4SeI$ $[M+H]^+$ 571.9837, found 571.9839.

Diethyl 5-((4-(ethoxycarbonyl)phenyl)selanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ad): Yield: 122.5 mg (79 %); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.33–7.27 (m, 2H), 7.25–7.21 (m, 1H), 7.20–7.16 (m, 2H), 5.21 (t, *J* = 7.7 Hz, 1H), 4.38–4.27 (m, 6H), 3.18 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.45 (dd, *J* = 13.5, 8.0 Hz, 1H), 1.38–1.36 (m, 6H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.5, 166.3, 164.7, 142.3, 134.7, 130.3, 130.0, 128.6, 127.3, 126.4, 75.7, 75.0, 62.8, 62.7, 61.2, 42.0, 14.4, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2927, 2862, 1723, 1590, 1458, 1266, 1176, 1103, 1013, 755 cm^{-1}; HRMS: *m/z* calculated for $C_{25}H_{28}NO_6Se$ $[M+H]^+$ 518.1082, found 518.1075.

Diethyl 5-((2-nitrophenyl)selanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ae): Yield: 108 mg (74 %); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 6.9 Hz, 1H), 8.15 (d, *J* = 6.7 Hz, 1H), 7.51–7.46 (m, 1H), 7.40–7.32 (m, 3H), 7.29–7.27 (m, 3H), 5.36 (t, *J* = 7.8 Hz, 1H), 4.36–4.27 (m, 4H), 3.24 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.48 (dd, *J* = 13.6, 8.0 Hz, 1H), 1.34–1.29 (m, 6H); ^{13}C NMR (100 MHz,$CDCl_3$): δ 168.1, 167.4, 165.1, 148.2, 141.7, 134.6, 133.5, 129.7, 128.8, 127.7, 127.6, 126.6, 125.5, 76.6, 75.7, 63.1, 62.9, 41.8, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2986, 2929, 1727, 1592, 1520, 1449, 1256, 1177, 1098, 1012, 734 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{23}N_2O_6Se$ $[M+H]^+$ 491.0721, found 491.0717.

Diethyl 5-phenyl-2-((4-(trifluoromethyl)phenyl)selanyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (3 af): Yield: 105 mg (68 %); Yellow solid (m.p. = 80–82 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.34–7.28 (m, 3H), 7.17–7.15 (m, 2H), 5.18 (t, *J* = 7.7 Hz, 1H), 4.32 (q, *J* = 7.16, 2H), 4.29–4.24 (m, 2H), 3.17 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.44 (dd, *J* = 13.6, 7.9 Hz, 1H), 1.35 (t,

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J=7.1 Hz, 3H), 1.30 (t, J=7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.5, 165.1, 142.4, 138.2, 136.9, 129.0 (q, J=4.1 Hz), 128.6, 127.8 (q, J=245 Hz), 127.3, 126.4, 95.0, 75.6, 74.8, 62.8, 62.7, 42.2, 14.1, 14.0.; ^{19}F NMR (283 MHz, $CDCl_3$): δ–62.6.; IR (neat) ($\tilde{\nu}$): 2924, 2857, 1723, 1469, 1379, 1267, 1178, 1067, 991, 806, 737 cm^{-1}; D-Mass: *m/z* calculated for $C_{23}H_{22}F_3NO_4Se$ $[M+H]^+$ is 513.0666 found 572.9927, 571.9888, 569.9934, 446.0907, 306,1384.

Diethyl 5-(mesitylselanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ag): Yield: 130 mg (89%); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 2H), 7.24–7.18 (m, 1H), 7.14 (d, J= 7.0 Hz, 2H), 6.96 (s, 2H), 5.12 (t, J=7.6 Hz, 1H), 4.38–4.26 (m, 4H), 3.15 (dd, J=13.5, 7.5 Hz, 1H), 2.52 (s, 6H), 2.44 (dd, J=13.5, 7.8 Hz, 1H), 2.26 (s, 3H), 1.39 (t, J=7.2 Hz, 3H), 1.33 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 168.0, 165.1, 143.4, 143.0, 139.5, 128.8, 128.4, 127.5, 126.4, 125.8, 75.2, 74.6, 62.7, 62.5, 42.8, 24.2, 21.2, 14.2, 14.1; IR (neat) ($\tilde{\nu}$): 3041, 2901, 1734, 1550, 1446, 1255, 1083, 997, 935, 722 cm^{-1}. HRMS: *m/z* calculated for $C_{25}H_{30}NO_4Se$ $[M+H]^+$ 488.1340 found 488.1346.

Diethyl 5-((4-(*tert*-butyl)phenyl)selanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ah): Yield: 129.2 mg (86%); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J=8.5 Hz, 2H), 7.34 (d, J=8.5 Hz, 2H), 7.28 (d, J=7.5 Hz, 2H), 7.25–7.21 (m, 1H), 7.17 (d, J= 7.0 Hz, 2H), 5.20 (t, J=7.7 Hz, 1H), 4.32 (q, J=7.2 Hz, 2H), 4.27 (q, J=6.7 Hz, 2H), 3.17 (dd, J=13.5, 7.6 Hz, 1H), 2.44 (dd, J=13.6, 7.8 Hz, 1H), 1.36 (t, J=7.1 Hz, 3H), 1.32–1.28 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 167.7, 165.9, 151.7, 142.7, 135.0, 128.5, 127.2, 126.5, 126.4, 124.5, 75.5, 74.9, 62.7, 62.6, 42.4, 34.8, 31.3, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 3197, 3022, 2985, 2884, 1741, 1437, 1263, 1078 cm^{-1}; HRMS: *m/z* calculated for $C_{26}H_{32}NO_4Se$ $[M+H]^+$ 502.1497 found 502.1498.

Diethyl 5-((2-oxo-2-phenylethyl)selanyl)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (3 ai):Yield: 118 mg (81%); Brown gum; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.01 (m, 2H), 7.58–7.53 (m, 1H), 7.44–7.34 (m, 4H), 7.32–7.27 (m, 3H), 5.22 (t, J=7.9 Hz, 1H), 4.69 (d, J= 13.8 Hz, 1H), 4.60 (d, J=13.9 Hz, 1H), 4.23 (q, J=7.1 Hz, 4H), 3.14 (dd, J=13.6, 7.4 Hz, 1H), 2.49 (dd, J=13.6, 8.4 Hz, 1H), 1.27 (td, J= 7.1, 1.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 167.5, 167.5, 164.9, 142.3, 135.5, 133.6, 128.9, 128.7, 128.7, 127.5, 126.63, 75.1, 74.3, 62.8, 62.7, 42.5, 33.1, 14.0, 14.0; IR (neat) ($\tilde{\nu}$): 2988, 2929, 1730, 1584, 1446, 1257, 1170, 1090, 1002, 690 cm^{-1}; HRMS: *m/z* calculated for $C_{24}H_{26}NO_5Se$ $[M+H]^+$ 488.0976, found 488.0975.

Diethyl 2-phenyl-5-(phenylthio)-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 aa): Yield: 102 mg (86%); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 2H), 7.40–7.33 (m, 3H), 7.31–7.26 (m, 2H), 7.22 (d, J=6.9 Hz, 1H), 7.17 (d, J=7.2 Hz, 2H), 5.15 (t, J=7.6 Hz, 1H), 4.35 (q, J=6.8 Hz, 2H), 4.28 (q, J=7.1 Hz, 2H), 3.21 (dd, J=13.3, 7.7 Hz, 1H), 2.53 (dd, J=13.6, 8.1 Hz, 1H), 1.37 (t, J=7.0 Hz, 3H), 1.31 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.7, 167.7, 142.8, 134.3, 130.0, 129.2, 129.0, 128.5, 127.2, 126.4, 73.8, 73.1, 62.7, 62.6, 43.3, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2979, 2928, 1718, 1446, 1368, 1267, 1096, 1011, 755, 687 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{24}NO_4S$ $[M+H]^+$ 398.1426, found 398.1435.

Diethyl 5-(phenylthio)-2-(*p*-tolyl)-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ba): Yield: 107 (87%); Colourless viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.59 (m, 2H), 7.39–7.29 (m, 3H), 7.10–7.05 (m„ 4H), 5.10 (t, J=7.6 Hz, 1H), 4.34 (q, J=7.16, 2H), 4.28 (q, J=7.12, 2H), 3.18 (dd, J=13.4, 7.4 Hz, 1H), 2.51 (dd, J=13.5, 7.9 Hz, 1H), 2.31 (s, 3H), 1.36 (t, J=7.1 Hz, 3H), 1.31 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 167.7, 167.3, 139.8, 136.8, 134.3, 130.1, 129.1, 129.0, 126.3, 73.73, 73.2, 62.6, 62.5, 43.4, 21.2, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2981, 2929, 2856, 1729, 1583, 1451, 1246, 1180, 1078, 1012, 741 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{26}NO_4S$ $[M+H]^+$ 412.1583, found 412.1589.

Diethyl 2-(4-methoxyphenyl)-5-(phenylthio)-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ea):Yield: 114 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J=8.1 Hz, 2H), 7.39–7.31 (m, 3H), 7.09 (d, J=8.6 Hz, 2H), 6.82 (d, J=8.6 Hz, 2H), 5.09 (t, J=7.5 Hz, 1H), 4.34 (q, J=7.12, 2H), 4.28 (q, J=7.12, 2H), 3.77 (s, 3H), 3.16 (dd, J=13.4, 7.3 Hz, 1H), 2.50 (dd, J=13.5, 7.8 Hz, 1H), 1.36 (t, J=7.1 Hz, 3H), 1.31 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 167.7, 167.3, 158.7, 134.9, 134.3, 130.1, 129.2, 129.0, 127.6, 113.8, 73.5, 73.1, 62.7, 62.5, 55.3, 43.4, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2986, 2866, 1733, 1483, 1423, 1236, 1167, 1016, 712 cm^{-1}; HRMS*: m/z* calculated for $C_{23}H_{26}NO_5S$ $[M+H]^+$ 428.1532, found 428.1545.

Diethyl 2-(4-nitrophenyl)-5-(phenylthio)-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 fa): Yield: 89 mg (67%); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J=8.5 Hz, 2H), 7.65–7.60 (m, 2H), 7.43–7.38 (m, 3H), 7.32 (d, J=8.7 Hz, 2H), 5.21 (t, J=7.7 Hz, 1H), 4.36 (q, J=7.1 Hz, 2H), 4.31–4.26 (m, 2H), 3.26 (dd, J=13.5, 7.7 Hz, 1H), 2.49 (dd, J=13.4, 8.0 Hz, 1H), 1.38 (t, J=7.2 Hz, 3H), 1.31 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 167.5, 167.3, 150.2, 147.1, 134.6, 134.6, 129.5, 129.3, 127.2, 123.8, 73.1, 72.9, 62.9, 62.8, 42.7, 14.1, 14.0; IR (neat) ($\tilde{\nu}$): 2987, 2923, 1728, 1577, 1474, 1241, 1164, 1032, 986, 761 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{23}N_2O_6S$ $[M+H]^+$ 443.1277, found 443.1291.

Diethyl 2-phenyl-5-(*p*-tolylthio)-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ab): Yield: 101 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J= 8.1 Hz, 2H), 7.31–7.25 (m, 2H), 7.24–7.13 (m, 5H), 5.13 (t, J=7.5 Hz, 1H), 4.34 (q, J=6.9 Hz, 2H), 4.27 (q, J=7.2 Hz, 2H), 3.19 (dd, J=13.4, 7.4 Hz, 1H), 2.52 (dd, J=13.4, 7.7 Hz, 1H), 2.33 (s, 3H), 1.36 (t, J= 7.1 Hz, 3H), 1.30 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 167.7, 142.9, 139.4, 135.5, 134.5, 130.1, 128.5, 127.2, 126.5, 73.7, 73.0, 62.7, 62.6, 43.4, 21.5, 14.2, 14.1; IR (neat) ($\tilde{\nu}$): 2980, 2932, 1727, 1446, 1247, 1054, 798, 687 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{26}NO_4S$ $[M+H]^+$ 412.1583, found 412.1591.

Diethyl 5-((4-methoxyphenyl)thio)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ac): Yield: 112 mg (88%); Colourless viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J=8.5 Hz, 2H), 7.29 (d, J= 7.1 Hz, 2H), 7.22–7.19 (m, 1H), 7.15 (d, J=7.1 Hz, 2H), 6.90 (d, J= 8.6 Hz, 2H), 5.12 (t, J=7.5 Hz, 1H), 4.34 (q, J=7.1 Hz, 2H), 4.26 (q, J=7.1 Hz, 2H), 3.79 (s, 3H), 3.19 (dd, J=13.4, 7.4 Hz, 1H), 2.51 (dd, J=13.6, 7.7 Hz, 1H), 1.37 (t, J=7.1 Hz, 3H), 1.30 (t, J=7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 167.9, 167.7, 160.4, 142.2, 136.2, 128.4, 127.1, 126.4, 120.3, 114.8, 73.6, 72.9, 62.6, 62.5, 55.3, 43.4, 14.1, 14.0.; IR (neat) ($\tilde{\nu}$): 2981, 2930, 1731, 1487, 1451, 1252, 1170, 1016, 935, 603 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{26}NO_5S$ $[M+H]^+$ 428.1532 found, 428.1530.

Diethyl 5-((4-acetylphenyl)thio)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ad): Yield: 106 mg (81%); Yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.93 (d, J=8.2 Hz, 2H), 7.75 (d, J=8.2 Hz, 2H), 7.33–7.23 (m, 3H), 7.18 (d, J=7.1 Hz, 2H), 5.17 (t, J=7.7 Hz, 1H), 4.35 (q, J=7.16, 2H), 4.28 (q, J=7.08, 2H), 3.22 (dd, J=13.6, 7.4 Hz, 1H), 2.63–2.49 (m, 4H), 1.36 (t, J=7.1 Hz, 3H), 1.31 (t, J=7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 167.7, 167.5, 166.5, 142.4, 136.9, 136.6, 133.5, 128.8, 128.6, 127.4, 126.4, 74.2, 73.3, 62.8, 62.7, 43.0, 26.7, 14.1, 14.0.; IR (neat) ($\tilde{\nu}$): 2987, 2926, 1733, 1680, 1588, 1442, 1358, 1251, 1174, 1082, 1014, 762 cm^{-1}; HRMS: *m/z* calculated for $C_{24}H_{26}NO_5S$ $[M+H]^+$ 440.1532, found 440.1523.

Diethyl 5-((4-nitrophenyl)thio)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5 ae):Yield: 101 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J=8.7 Hz, 2H), 7.84 (d, J=8.8 Hz, 2H), 7.33–7.27 (m, 3H), 7.19 (d, J=7.1 Hz, 2H), 5.19 (t, J=7.7 Hz, 1H), 4.35 (q, J=7.12, 2H), 4.30 (m, 2H), 3.22 (dd, J=13.6, 7.4 Hz, 1H), 2.55 (dd, J=13.6, 8.0 Hz, 1H), 1.36 (t, J=7.2 Hz, 2H), 1.32 (t, J=7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 167.3, 165.7, 147.6, 142.0, 139.4, 133.7, 128.7, 127.5, 126.4, 123.9, 74.3, 73.4, 62.9, 62.8, 42.7, 14.1, 14.0; IR

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(neat) ($\tilde{\nu}$): 2988, 2929, 1728, 1580, 1520, 1461, 1335, 1247, 1173, 1083 cm^{-1}; HRMS: m/z calculated for $C_{22}H_{23}N_2O_6S$ $[M+H]^+$ 443.1277 found, 443.1281.

Diethyl 5-(methylthio)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5af): Yield: 91 mg (91%); Colourless viscous liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.25 (m, 5H), 5.15 (t, $J=7.7$ Hz, 1H), 4.34–4.20 (m, 4 H), 3.16 (dd, $J=13.5$, 7.2 Hz, 1H), 2.59–2.48 (m, 4H), 1.32 (t, $J=7.1$ Hz, 3H), 1.28 (t, $J=7.1$ Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 168.8, 167.8, 142.8, 128.6, 127.4, 126.6, 73.6, 72.8, 62.6, 62.5, 43.6, 15.0, 14.1, 14.0.; IR (neat) ($\tilde{\nu}$) :2986, 2934, 1728, 1576, 1455, 1250, 1174, 1091, 1023, 757, 696 cm^{-1}; HRMS: *m/z* calculated for $C_{17}H_{22}NO_4S$ $[M+H]^+$ 336.1270 found, 336.1261.

Diethyl 5-(benzylthio)-2-phenyl-2*H*-pyrrole-4,4(3*H*)-dicarboxylate (5ag): Yield: 114 mg (93%); Yellow viscous liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.23 (m, 10H), 5.18 (t, $J=7.7$ Hz, 1H), 4.42–4.33 (m, 2H), 4.30–4.18 (m, 4H), 3.16 (dd, $J=13.5$, 7.2 Hz, 1H), 2.53 (dd, $J=13.4$, 8.3 Hz, 1H), 1.29 (t, $J=7.2$ Hz, 3H), 1.24 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 167.7, 167.7, 142.7, 137.0, 129.3, 128.6, 128.5, 127.4, 127.3, 126.6, 73.7, 73.0, 62.6, 62.5, 43.4, 36.5, 14.0, 14.0; IR (neat) ($\tilde{\nu}$): 2981, 2925, 1724, 1580, 1450, 1248, 1177, 1095, 1015, 701 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{26}NO_4S$ $[M+H]^+$ 412.1583, found 412.1596.

Diethyl 2-((3-cyanophenyl)thio)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (5ah): Yield (a): 154.1 mg (73%) (0.5 mmol of aryl thiocyanate **4h** and 0.5 mmol of cyclopropane **1a**); Yield (b): 27 mg (13%) (0.5 mmol of aryl thiocyanate **4h** and 1.25 mmol of cyclopropane **1a**); Yellow oil; ^1H NMR (400 MHz, $CDCl_3$):δ 7.93–7.92 (m, 1H), 7.87–7.84 (m, 1H), 7.62–7.60 (m, 1H), 7.49–7.45 (m, 1H), 7.33–7.29 (m, 2H), 7.24–7.22 (m, 1H), 7.17–7.15 (m, 2H), 5.15 (t, $J=7.7$ Hz, 1H), 4.35 (q, $J=7.1$ Hz, 2H), 4.31–4.26 (m, 2H), 3.21 (dd, $J=13.6$, 7.4 Hz, 1H), 2.54 (dd, $J=13.6$, 7.9 Hz, 1H), 1.37 (t, $J=7.1$ Hz, 3H), 1.31 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 167.4, 166.5, 142.2, 138.5, 137.4, 132.5, 132.4, 129.8, 128.7, 127.5, 126.4, 118.2, 113.4, 74.1, 73.2, 62.9, 62.8, 42.9, 14.2, 14.1; IR (neat) ($\tilde{\nu}$): 2957, 2231, 1729, 1259, 1018, 700 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{23}N_2O_4S$ $[M+H]^+$ 423.1379, found 423.1385.

Diethyl 5-phenyl-2-(3-thiocyanatophenyl)-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (5′ah): Yield: 23 mg (11%) (0.5 mmol of aryl thiocyanate **4h** and 1.25 mmol of cyclopropane **1a**); Yellow oil; ^1H NMR (400 MHz, $CDCl_3$):δ 8.20–8.19 (m, 1H), 8.03–7.99 (m, 1H), 7.64–7.61 (m, 1H), 7.47 (t, $J=8.2$ Hz, 1H), 7.41–7.30 (m, 5H), 5.36–5.32 (m, 1H), 4.34–4.25 (m, 2H), 4.19 (q, $J=7.1$ Hz, 2H), 3.38 (dd, $J=13.1$, 7.0 Hz, 1H), 2.59 (dd, $J=13.1$, 8.4 Hz, 1H), 1.27 (t, $J=7.1$ Hz, 3H), 1.16 (t, $J=7.1$ Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 168.1, 166.8, 141.9, 135.3, 131.9, 130.7, 130.4, 130.0, 128.8, 127.7, 126.8, 124.7, 110.3, 73.8, 71.2, 62.8, 62.7, 45.5, 14.1, 14.0.; IR (neat) ($\tilde{\nu}$): 2981, 2187, 1752, 1236, 992, 717 cm^{-1}; HRMS: *m/z* calculated for $C_{23}H_{23}N_2O_4S$ $[M+H]^+$ 423.1379, found 423.1387.

Diethyl 2-((3-(4,4-bis(ethoxycarbonyl)-2-phenyl-3,4-dihydro-2*H*-pyrrol-5-yl)phenyl)thio)-5-phenyl-4,5-dihydro-3*H*-pyrrole-3,3-dicarboxylate (5′′ah): Yield : 75 mg (22%) (0.5 mmol of aryl thiocyanate **4h** and 1.25 mmol of cyclopropane **1a**); Blue oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94–7.84 (m, 1H), 7.82–7.68 (m, 4H), 7.59 (t, $J=7.7$ Hz, 2H), 7.50–7.45 (m, 1H), 7.39–7.33 (m, 4H), 7.17–7.14 (m, 2H), 5.37–5.28 (m, 1H), 5.18–5.09 (m, 1H), 4.36–4.20 (m, 8H), 3.40–3.31 (m, 1H), 3.25–3.14 (m, 1H), 2.60–2.50 (m, 2H), 1.44–1.30 (m, 8H), 1.18–1.08 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 167.6, 167.4, 166.4, 142.2, 138.5, 137.3, 132.5, 132.4, 131.0, 129.8, 128.7, 127.5, 126.4, 118.2, 113.4, 74.0, 73.1, 68.2, 62.9, 62.8, 43.0, 38.8, 32.0, 14.3, 14.2, 14.2, 14.1.; IR (neat) ($\tilde{\nu}$): 2927, 1728, 1258, 1066, 699 cm^{-1}; HRMS: *m/z* calculated for $C_{38}H_{41}N_2O_8S$ $[M+H]^+$ 685.2584, found 685.2585.

Diethyl 5-phenyl-2-(phenylselanyl)-3*H*-pyrrole-3,3-dicarboxylate (6aa): Yield: 36.2 mg (82%); Yellow viscous liquid; ^1H NMR (400 MHz, $CDCl_3$):δ 7.78–7.74 (m, 4H), 7.41–7.38 (m, 3H), 7.35–7.30 (m, 3H), 6.63 (s, 1H), 4.33–4.27 (m, 4H), 1.33 (t, $J=7.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 173.8, 164.5, 158.2, 135.2, 132.4, 129.2, 128.7, 128.5, 127.3, 126.8, 114.9, 81.0, 63.1, 14.0; IR (neat) ($\tilde{\nu}$): 2986, 2914, 1743, 1481, 1247, 1093, 757 cm^{-1}; HRMS: *m/z* calculated for $C_{22}H_{21}NO_4Se$ $[M+H]^+$ 444.0714, found 444.0702.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cyclopropanes · Cycloaddition · Lewis acids · Selenopyrrolines · Thiopyrrolines

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