Lewis Acid-Catalyzed Ring-Opening 1,3-Aminothiolation of Donor-Acceptor Cyclopropanes Using Sulfenamides

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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 25 °C Corresponds to the room temperature of the lab when the experiments were carried out. Dry DCE was purchased from commercial sources and was stored under argon over 4Å molecular sieves. Yb(OTf)₃ was purchased from commercial sources and was stored in argon filled Glove-box. All D-A cyclopropane derivatives¹ and functionalized sulfenamides² were synthesized following literature procedures.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light or KMnO₄ staining solutions followed by heating. Unless and otherwise specified flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker Ultrashield spectrometer in CDCl₃ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν-max in cm⁻¹. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument. HPLC analysis was performed on Agilent Technologies 1260 Infinity with UV detector.

Procedure for the preparation of Sulfenamides

Sulfenamides were prepared following the reported procedure.² Benzene sulfonyl chloride (3.9 g, 27 mmol) was dissolved in 14 mL dry diethyl ether under argon atmosphere and the solution was added dropwise over 20 min to substituted aniline (40 mmol) and Et₃N (8.25 g, 81 mmol)

¹ (a) Augustin, A. U.; Busse, M.; Jones, P. G.; Werz, D. W. *Org. Lett.* **2018**, *20*, 820. (b) Goldberg, A. F. G.; Connor, N. R. O.; Craig, R. A.; Stoltz, B. M. *Org. Lett.* **2012**, *14*, 5314. (c) Pohlhaus, P. D.; Sanders, S. D.; Parsons, A. T.; Li, W.; Johnson, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 8642.

² Gaykar, R. N.; Bhattacharjee, S.; Biju, A. T. *Org. Lett.* **2019**, *21*, 737.

in 14 mL of dry diethyl ether, and then the reaction mixture was cooled to -78 °C. The reaction mixture was allowed to stir for an additional 30 min at -78 °C. Then 40 mL of *n*-hexane was added and the solution was allowed to warm to 0 °C. After the precipitated salts were filtered off, the filtrate was washed with water (2×40 mL) and dried over Na₂SO₄. Removal of the solvent gave an oil, which was dissolved in *n*-hexane/ether and cooled to -78 °C. The solid or liquid were collected [the solid product was crystallized from *n*-hexane at low temperature, while the liquid product was purified by silica gel column chromatography].

2. General Procedure for 1, 3-Aminothiolation of D-A Cyclopropanes

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (10 mol %) in a glove-box. The mixture was dissolved in DCE (4 mL per mmol) under argon atmosphere. The cyclopropane **1** (1.2 equiv) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2** (1.0 equiv) was added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel to afford the corresponding derivatives **3** in moderate to good yield.

Procedure for the 1.0 mmol Scale Reaction for the Synthesis of 3a

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.062g, 10 mol %) in a glove-box. The mixture was dissolved in 4 mL DCE under argon atmosphere. The cyclopropane **1a** (0.280 g, 1.2 mmol) was added outside the

glove-box under argon atmosphere. To the stirring solution, sulfenamide **2a** (0.229 g, 1.0 mmol) was added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford **3a** as a white solid (0.324 g, 70%).

3. General Procedure for 1, 3-Aminothiolation of Chiral D-A Cyclopropane

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.006 g, 0.01 mmol) in a glove-box. The mixture was dissolved in DCE (0.5 mL) under argon atmosphere at 10 °C. The enantiopure cyclopropane (S)-**1a** (0.028 g, 0.12 mmol) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2** (0.023 g, 0.1 mmol) was added. Then, the reaction mixture was allowed to react at 10 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford (R)-**3a** in 68% yield and >99% ee. (*The absolute stereochemistry of the chiral centre was not unequivocally determined*)

4. Mechanistic Experiments

(a) Reaction using N,3-Dimethylaniline-derived sulfenamide

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.015 g, 0.025 mmol) in a glove-box. The mixture was dissolved in DCE (1.0

mL) under argon atmosphere. The cyclopropane **1a** (0.070 g, 0.3 mmol) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2k** / **2l** (0.25 mmol) was added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column on silica gel to afford **4a** / **4b** in 79% and 81% yields respectively.

(4b) Reaction of 2k without D-A cyclopropane 1a

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.015 g, 0.025 mmol) in a glove-box. The mixture was dissolved in DCE (1.0 mL) under argon atmosphere. To the stirring solution, sulfenamide **2k** (0.057 g, 0.25 mmol) was added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 93/07) on silica gel to afford **5** in 93% yield.

(4c) Envisioned Three-Component Coupling

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.015 g, 0.025 mmol) in a glove-box. The mixture was dissolved in DCE (1.0 mL) under argon atmosphere. The cyclopropane **1a** (0.070 g, 0.3 mmol) was added outside the

glove-box under argon atmosphere. To the stirring solution, *N*,4-dimethylaniline **6a** (0.030 g, 0.25 mmol) and phenyl hypochlorothioite **7a** (0.036 g, 0.25 mmol) were added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether /EtOAc = 91/09) on silica gel to afford **8a** in 91% yield.

The desired 1,3-aminothiolated product 3a was not formed under this conditions and instead the N-H insertion of 6a to 1a took place leading to the formation of 8a in 91% yield. Moreover, the insertion product 9a derived from 7a was not observed under this condition. These studies indicate the role of preformed sulfenamides in this insertion reaction.

(4d) Study Towards the Enantioselective version of the reaction

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (0.006 g, 0.01 mmol) in the glove-box. The mixture was dissolved in DCE (0.5 mL) under argon atmosphere at 25 °C. The enantiopure cyclopropane **1a** (0.028 g, 0.12 mmol) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2a** (0.023 g, 0.1 mmol) was added. Then, the reaction mixture was allowed to stir at 25 °C. After a definite time-interval, a small sample of reaction mixture was taken out, and was analyzed using HPLC.

Enantiomeric excess of the product **3a** was found to slightly decrease under the optimized reaction conditions at different time interval, which is tabulated as below:

Table S1. The variation of ee during progress of the reaction

Time	ee (%) of 3a	ee (%) of 1a
15 min	62	>99
30 min	60	>99
45 min	57	>99
1 h	55	>99
1.5 h	53	>99
2 h	52	>99
3 h	52	>99
4 h	52	>99

5 h	52	>99
6 h	52	>99
7 h	52	>99
8 h	52	>99
9 h	52	>99
10 h	52	>99
11 h	52	>99
12 h	52	>99

Enantiomeric excess of the product and the cyclopropane was monitored in regular interval of time. After every 15 minutes of time for 1 hour, ee of the product was analyzed and found to be decreased slightly in due course of time. Dropping of ee was observed up to 2 hours and then it remained almost constant (52% ee) after 2 hours. But, the ee of cyclopropane (*S*)-**1a** was remained intact during the progress of the reaction. So, it was observed that the ee of chiral D-A cyclopropane was remained unchanged but slight racemization was observed for the product at 25 °C. This has been represented in the Figure below:

(4e) Crossover experiment using two different sulfenamides

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the Yb(OTf)₃ (10 mol %) in a glove-box. The mixture was dissolved in 1 mL DCE under argon atmosphere. The cyclopropane **1a** (0.070 g, 0.3 mmol) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2e** (0.025 g, 0.125 mmol) and **2h** (0.029 g, 0.125 mmol) were added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the crude mixture was passed through a small

pad of silica and then the filtrate was evaporated and the crude products were analyzed using HRMS. In HRMS data, crossover products mass $[M+H]^+$ was detected along with normal products mass $[M+H]^+$.

To check the generality, another two different sulfenamides were taken and conducted the same experiment.

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the $\text{Yb}(\text{OTf})_3$ (10 mol %) in a glove-box. The mixture was dissolved in 1 mL DCE under argon atmosphere. The cyclopropane **1a** (0.070 g, 0.3 mmol) was added outside the glove-box under argon atmosphere. To the stirring solution, sulfenamide **2f** (0.031 g, 0.125 mmol) and **2h** (0.029 g, 0.125 mmol) was added. Then, the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the crude mixture was passed through a small pad of silica and then the filtrate was evaporated to get the crude products, which was subsequently analyzed

using HRMS. In HRMS data, crossover product mass $[M+H]^+$ was detected along with normal products mass $[M+H]^+$.

Tentative mechanism of the reaction

5. X-Ray Data of **3k**

Single crystal of **3k** (recrystallized from CH₂Cl₂/*n*-hexane at 25 °C) was mounted and the diffraction data was collected at 296 K on a Bruker APEX-II CCD diffractometer using SMART/SAINT software. Intensity data were collected using MoK α radiation (λ =0.71073 Å). The single crystal was affixed to a Hampton Research cryoloop using Paratone-N oil. Data collection and reduction was performed using Bruker APEX2 and Bruker SAINT, respectively. The structure was solved by direct methods using the SHELX-97 and refined by full-matrix leastsquares on F². Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and Mercury-3. CCDC 1978915 (**3k**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystallographic refinement parameters are given below:

Table S2 Crystal data and structure refinement for **3k**

Compounds	3k
CCDC no.	1978915
Chemical formula	C ₂₈ H ₃₁ N O ₄ S
Formula weight	477.60
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	17.473(4)
<i>b</i> (Å)	11.243(3)
<i>c</i> (Å)	13.763(3)
α (°)	90
β (°)	110.138(11)
γ (°)	90
<i>V</i> (Å ³)	2538.44
<i>Z</i>	4
<i>T</i> (K)	296(2)
<i>D</i> _{calc} (g cm ⁻³)	1.25
Abs. coefficient (mm ⁻¹)	0.161
<i>F</i> (000)	1016.0
θ Range for data collection (°)	1.2 - 32.2
Limiting indices	-25 ≤ <i>h</i> ≤ 25, -15 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 19
Reflections collected	42471

Unique reflections (R_{int})	7880 (0.086)
Completeness of θ	27.42 (99.77%)
Data/restraints/parameters	7880/1/302
GOF	1.308
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.145$, $wR_2 = 0.354$
R indices (all data)	$R_1 = 0.248$, $wR_2 = 0.452$
$\Delta\rho_{max}(\text{e. \AA}^{-3})$	0.879
$\Delta\rho_{min}(\text{e. \AA}^{-3})$	-0.685

Figure S2. Crystal structure of **3k** (Thermal ellipsoids are shown with 50% probability)

6. Synthesis and Characterization of γ -Aminated α -Thiolated Malonic Diesters

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (**3a**)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.070 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3a** as a white solid (0.085 g, 73% yield).

*R*_f (Pet. ether / EtOAc = 90/10): 0.43; ¹H NMR (400 MHz, CDCl₃) δ 7.41–7.39 (m, 2H), 7.37–7.34 (m, 1H), 7.27–7.22 (m, 5H), 7.10–7.07 (m, 4H), 6.98 (d, *J* = 8.6 Hz, 2 H), 5.69 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.5 Hz, 1H), 3.63 (s, 3H), 3.46 (s, 3H), 3.03 (dd, *J*₁ = 15.2 Hz, *J*₂ = 11.0 Hz, 1H), 2.43 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.8 Hz, 1H), 2.37 (s, 3H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 167.9, 148.5, 138.5, 137.1, 130.2, 129.6, 129.4, 129.2, 128.2, 127.8, 127.4, 116.5, 64.7, 60.2, 53.0, 34.7, 32.2, 20.5. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₇H₃₀NO₄S 464.1890; Found 464.1896. FTIR (cm⁻¹) 2952, 1734, 1614, 1515, 1437, 1263.

Dimethyl-2-(2-(4-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (**3b**)

Following the general procedure, treatment of dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate **1b** (0.079 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 85/15) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(4-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3b** as a white solid (0.108 g, 87% yield).

*R*_f (Pet. ether / EtOAc = 90/10): 0.38; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.33 (m, 3H), 7.26–7.25 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.98 (dd, *J*₁ = 8.6 Hz, *J*₂ = 6.6 Hz, 4H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.62 (s, 3H), 3.46 (s, 3H), 2.99 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.9 Hz, 1H), 2.37 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.8 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ

169.2, 168.0, 158.8, 148.7, 137.1, 130.8, 130.1, 129.6, 129.4, 129.2, 128.5, 127.8, 116.7, 113.5, 64.7, 59.8, 55.3, 53.0, 53.0, 34.9, 32.1, 20.6. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{28}H_{32}NO_5S$ 494.1996; Found 494.2001. **FTIR (cm⁻¹)** 2953, 1733, 1611, 1513, 1436, 1250.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*p*-tolyl)ethyl)-2-(phenylthio)malonate (3c)

Following the general procedure, treatment of dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate **1c** (0.074 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography

(Pet.ether/ EtOAc = 93/07) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*p*-tolyl)ethyl)-2-(phenylthio)malonate **3c** as a white solid (0.097 g, 81% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.45; **¹H NMR (400 MHz, CDCl₃)** δ 7.42-7.39 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.27-7.24 (m, 2H), 7.08 (d, J = 8.4 Hz, 2 H), 7.03 (d, J = 7.8 Hz, 2 H), 6.99-6.95 (m, 4H), 5.65 (dd, J_1 = 10.8 Hz, J_2 = 2.5 Hz, 1H), 3.63 (s, 3H), 3.46 (s, 3H), 3.02 (dd, J_1 = 15.1 Hz, J_2 = 10.8 Hz, 1H), 2.41 (dd, J_1 = 15.2 Hz, J_2 = 2.7 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 6H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 168.0, 148.6, 137.1, 136.9, 135.5, 130.1, 129.6, 129.4, 129.2, 128.9, 127.7, 127.3, 116.5, 64.7, 59.9, 53.0, 52.9, 34.8, 32.2, 21.1, 20.5. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{28}H_{32}NO_4S$ 478.2047; Found 478.2054. **FTIR (cm⁻¹)** 2952, 1735, 1515, 1437, 1260, 1175.

Dimethyl-2-(2-(4-bromophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3d)

Following the general procedure, treatment of dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **1d** (0.094 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in

DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 93/07) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(4-bromophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3d** as a white solid (0.092 g, 68% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.46; **¹H NMR (400 MHz, CDCl₃)** δ 7.38-7.33 (m, 5H), 7.27-7.23 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.96-6.90 (m, 4H), 5.60 (dd, *J*₁ = 10.9 Hz, *J*₂ = 2.4 Hz, 1H), 3.64 (s, 3H), 3.46 (s, 3H), 2.99 (dd, *J*₁ = 15.0 Hz, *J*₂ = 10.9 Hz, 1H), 2.35-2.31 (m, 1H), 2.34 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 167.9, 148.3, 137.4, 137.0, 131.4, 130.3, 129.7, 129.3, 129.1, 128.3, 121.4, 116.8, 64.5, 60.0, 53.1, 53.0, 34.6, 32.1, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉BrNO₄S 542.0995; Found 542.1003. **FTIR (cm⁻¹)** 2952, 1734, 1515, 1436, 1260, 1103.

Dimethyl-2-(2-(4-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3e)

Following the general procedure, treatment of dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate **1e** (0.081 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(4-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3e** as a white solid (0.080 g, 64% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.47; **¹H NMR (400 MHz, CDCl₃)** δ 7.38-7.34 (m, 3H), 7.27-7.23 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.08(d, *J* = 8.4 Hz, 2 H), 6.96 (t, *J* = 8.9 Hz, 4 H), 5.62 (dd, *J*₁ = 10.9 Hz, *J*₂ = 2.4 Hz, 1H), 3.64 (s, 3H), 3.46 (s, 3H), 2.98 (dd, *J*₁ = 15.3 Hz, *J*₂ = 10.7 Hz, 1H), 2.35 (dd, *J*₁ = 15.1 Hz, *J*₂ = 2.5 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 167.9, 148.3, 137.1, 136.9, 133.2, 130.3, 129.7, 129.3, 129.3, 128.7, 128.4, 128.3, 116.8, 64.5, 60.0, 53.1, 53.0, 34.7, 32.1, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉ClNO₄S 498.15; Found 498.1506. **FTIR (cm⁻¹)** 2952, 1731, 1615, 1516, 1436, 1266.

Dimethyl-2-(2-(4-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3f)

Following the general procedure, treatment of dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate **1f** (0.076 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column

chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(4-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio) malonate **3f** as a white solid (0.076 g, 63% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.39-7.34 (m, 3H), 7.27-7.23 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.03-7.00 (m, 2H), 6.97-6.88 (m, 4H), 5.63 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.4 Hz, 1H), 3.64 (s, 3H), 3.47 (s, 3H), 2.99 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.8 Hz, 1H), 2.36-2.33 (m, 1H), 2.33 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 167.9, 162.1 (*J* = 246.8 Hz), 148.4, 137.1, 134.3 (*J* = 3.3 Hz), 130.2, 129.7, 129.3, 129.2, 128.9 (*J* = 7.9 Hz), 128.2, 116.8, 115.0 (*J* = 21.3 Hz), 64.6, 59.9, 53.0, 34.8, 32.1, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉FN₂O₄S 482.1796; Found 482.1803. **FTIR (cm⁻¹)** 2954, 2364, 1734, 1513, 1436, 1225.

Dimethyl-2-(2-(4-(methoxycarbonyl)phenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3g**)**

Following the general procedure, treatment of dimethyl 2-(4-(methoxycarbonyl)phenyl)cyclopropane-1,1-dicarboxylate **1g** (0.088 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C

for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 86/14) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(4-(methoxycarbonyl)phenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2 (phenylthio)malonate **3g** as a white solid (0.074 g, 57% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.37; **¹H NMR (400 MHz, CDCl₃)** δ 7.89 (d, *J* = 8.1 Hz, 2 H), 7.38-7.33 (m, 3H), 7.26-7.22 (m, 2H), 7.12-7.07 (m, 4H), 6.95 (d, *J* = 8.6 Hz, 2 H), 5.68 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.4 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 3.47 (s, 3H), 3.03 (dd, *J*₁ = 15.1 Hz, *J*₂ = 10.8 Hz, 1H), 2.40-2.35 (m, 1H), 2.35 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 167.8, 167.0, 148.2, 143.5, 137.0, 130.3, 129.9, 129.7, 129.6, 129.3, 129.2, 128.4, 127.3, 116.8, 64.5, 60.3, 53.1, 53.1, 52.2, 34.5, 32.3, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₉H₃₂NO₆S 522.1945; Found 522.1948. **FTIR (cm⁻¹)** 2954, 1748, 1612, 1516, 1437, 1284.

Dimethyl-2-(2-(3-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3h)

Following the general procedure, treatment of dimethyl 2-(3-methoxyphenyl)cyclopropane-1,1-dicarboxylate **1h** (0.079 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 87/13) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(3-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3h** as a white solid (0.078 g, 63% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.39; **¹H NMR (400 MHz, CDCl₃)** δ 7.41-7.33 (m, 3H), 7.27-7.23 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.75 (dd, *J*₁ = 15.1 Hz, *J*₂ = 10.8 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 5.64 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.4 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 3.46 (s, 3H), 3.00 (dd, *J*₁ = 15.1 Hz, *J*₂ = 10.9 Hz, 1H), 2.40 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.7 Hz, 1H), 2.37 (s, 3H), 2.28 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 168.0, 159.4, 148.6, 140.2, 137.1, 130.2, 129.6, 129.4, 129.2, 127.9, 119.8, 116.6, 113.3, 112.5, 64.7, 60.3, 55.2, 53.0, 34.7, 32.3, 20.5. **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₂₈H₃₂NO₅S 494.1996; Found 494.2000. **FTIR (cm⁻¹)** 2952, 2363, 1734, 1608, 1516, 1262.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate (3i)

Following the general procedure, treatment of dimethyl 2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate **1i** (0.075 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate **3i** as a white solid (0.097 g, 81% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.42-7.34 (m, 3H), 7.28-7.24 (m, 2H), 7.13-7.07 (m, 3H), 7.03 (d, *J* = 7.5 Hz, 1 H), 6.97 (d, *J* = 8.6 Hz, 2 H), 6.89-6.85 (m, 2H), 5.64 (dd, *J*₁ = 10.7 Hz, *J*₂ = 2.6 Hz, 1H), 3.62 (s, 3H), 3.46 (s, 3H), 3.02 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.8 Hz, 1H), 2.43 (dd, *J*₁ = 15.2 Hz, *J*₂ = 3.1 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.28

(s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 168.5, 168.0, 148.5, 138.6, 137.7, 137.1, 130.1, 129.6, 129.5, 129.2, 128.1, 128.0, 127.6, 125.7, 124.7, 122.1, 64.7, 60.0, 53.0, 34.9, 32.3, 21.7, 20.5. **HRMS (ESI)** m/z: [M+H]⁺ Calcd for C₂₈H₃₂NO₄S 478.2047; Found 478.2052. **FTIR (cm⁻¹)** 2952, 1733, 1612, 1516, 1436, 1265.

Dimethyl-2-(2-(3-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3j)

Following the general procedure, treatment of dimethyl 2-(3-chlorophenyl)cyclopropane-1,1-dicarboxylate **1j** (0.081 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 92/08) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(3-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3j** as a white solid (0.105 g, 84% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.44; **¹H NMR (400 MHz, CDCl₃)** δ 7.42-7.36 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.14 (m, 2H), 7.12-7.08 (m, 3H), 6.98-6.93 (m, 3H), 5.65 (dd, *J*₁ = 10.7 Hz, *J*₂ = 2.6 Hz, 1H), 3.66 (s, 3H), 3.49 (s, 3H), 3.01 (dd, *J*₁ = 15.1 Hz, *J*₂ = 10.8 Hz, 1H), 2.40 (s, 3H), 2.40-2.36 (m, 1H), 2.31 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 167.8, 148.2, 140.6, 137.1, 134.1, 130.3, 129.7, 129.5, 129.2, 128.2, 127.6, 127.2, 125.8, 116.6, 64.5, 60.0, 53.0, 53.0, 34.6, 32.3, 20.5. **HRMS (ESI)** m/z: [M+H]⁺ Calcd for C₂₇H₂₉ClNO₄S 498.1500; Found 498.1504. **FTIR (cm⁻¹)** 2951, 1734, 1612, 1570, 1435, 1262.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*o*-tolyl)ethyl)-2-(phenylthio)malonate (3k)

Following the general procedure, treatment of dimethyl 2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate **1k** (0.074 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 92/8) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*o*-tolyl)ethyl)-2-(phenylthio)malonate **3k** as a white solid (0.079 g, 66% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.48; **¹H NMR (400 MHz, CDCl₃)** δ 7.34-7.26 (m, 4H), 7.23-7.19 (m, 2H), 7.17-7.04 (m, 7H), 5.68 (dd, *J*₁ = 8.5 Hz, *J*₂ = 4.8 Hz, 1H), 3.49 (s, 3H), 3.44 (s, 3H), 2.99 (dd, *J*₁ = 15.2 Hz, *J*₂ = 8.6 Hz, 1H), 2.48-2.44 (m, 1H), 2.44 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.8, 168.1, 148.9, 137.6, 137.0, 136.4, 131.0, 130.1, 129.6, 129.4, 129.1, 128.8, 128.0, 127.2, 125.0, 118.3, 64.8, 57.5, 52.9, 52.8, 35.6, 32.1, 21.0, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₈H₃₂NO₄S 478.2047; Found 478.2052. **FTIR (cm⁻¹)** 2953, 1734, 1515, 1436, 1261, 1224.

Dimethyl-2-(2-(2-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3l)

Following the general procedure, treatment of dimethyl 2-(2-fluorophenyl)cyclopropane-1,1-dicarboxylate **1l** (0.076 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(2-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3l** as a white solid (0.076 g, 63% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23-7.14 (m, 4H), 7.08-6.95 (m, 6H), 5.88 (dd, *J*₁ = 10.3 Hz, *J*₂ = 3.3 Hz, 1H), 3.61 (s, 3H), 3.49 (s, 3H), 3.12 (dd, *J*₁ = 15.0 Hz, *J*₂ = 10.5 Hz, 1H), 2.46 (s, 3H), 2.28 (s, 3H), 2.27-2.23 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 167.9, 160.8 (d, *J* = 246.5 Hz), 148.2, 137.1, 130.1, 129.7, (d, *J* = 5.2 Hz), 129.3, 129.2, 129.1, 129.0 (d, *J* = 8.2 Hz), 128.6, 125.0 (d, *J* = 16.1 Hz), 123.6 (d, *J* = 3.3 Hz), 117.5, 115.9 (d, *J* = 24.1 Hz), 64.7, 55.7, 53.0, 34.8, 32.1, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉FNO₄S 482.1796; Found 482.1802. **FTIR (cm⁻¹)** 2953, 1734, 1614, 1516, 1437, 1225.

Dimethyl-2-(2-(3,4-dimethoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3m)

Following the general procedure, treatment of dimethyl 2-(3,4-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate **1m** (0.088 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc

= 85/15) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(3,4-dimethoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3m** as a white solid

(0.097 g, 74% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.37; **¹H NMR (400 MHz, CDCl₃)** δ 7.40-7.33 (m, 3H), 7.27-7.23 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2 H), 6.97 (d, *J* = 8.6 Hz, 2 H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.62 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.6 Hz, 1H), 6.47 (d, *J* = 1.6 Hz, 1H),

5.58 (dd, *J*₁ = 10.7 Hz, *J*₂ = 2.5 Hz, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 3.63 (s, 3H), 3.48 (s, 3H), 2.98 (dd, *J*₁ = 15.3 Hz, *J*₂ = 10.9 Hz, 1H), 2.38 (dd, *J*₁ = 15.3 Hz, *J*₂ = 2.7 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 168.0, 148.9, 148.4, 148.2, 137.1, 131.2, 130.2, 129.5, 129.4, 129.2, 128.1, 119.3, 117.1, 110.9, 110.6, 64.7, 60.5, 55.9, 55.8, 53.0, 34.7, 32.1, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₉H₃₄NO₆S 524.2101; Found 524.2108. **FTIR (cm⁻¹)** 2955, 1733, 1613, 1515, 1439, 1263.

Dimethyl-2-(2-(3,4-dichlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (**3n**)

Following the general procedure, treatment of dimethyl 2-(3,4-dichlorophenyl)cyclopropane-1,1-dicarboxylate **1n** (0.091 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 88/12) of the crude reaction

mixture using silica gel afforded dimethyl-2-(2-(3,4-dichlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3n** as a white solid (0.099 g, 74% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.41; **¹H NMR (400 MHz, CDCl₃)** δ 7.39-7.36 (m, 3H), 7.29-7.25 (m, 3H), 7.14-7.08 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2 H), 6.84 (dd, *J*₁ = 8.3 Hz, *J*₂ = 1.9 Hz, 1H), 5.59 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.3 Hz, 1H), 3.66 (s, 3H), 3.47 (s, 3H), 2.98 (dd, *J*₁ = 15.0 Hz, *J*₂ = 11.0 Hz, 1H), 2.36 (s, 3H), 2.32-2.28 (m, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 167.7, 148.0, 138.7, 137.0, 132.3, 131.4, 130.3, 130.2, 129.8, 129.3, 129.1, 129.0, 128.6, 127.0, 116.8, 64.3, 59.8, 53.1, 53.1, 34.5, 32.2, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₈Cl₂NO₄S 532.1111; Found 532.1116. **FTIR (cm⁻¹)** 2952, 2364, 1733, 1615, 1515, 1264.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(naphthalen-2-yl)ethyl)-2-(phenylthio)malonate (3o)

Following the general procedure, treatment of dimethyl 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate **1o** (0.085 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h

followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(naphthalen-2-yl)ethyl)-2-(phenylthio)malonate **3o** as a white solid (0.085 g, 66% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.79-7.76 (m, 2H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.57 (s, 1H), 7.48-7.41 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.26-7.21 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 5.56 (dd, *J*₁ = 10.5 Hz, *J*₂ = 1.8 Hz, 1H), 3.64 (s, 3H), 3.48 (s, 3H), 3.16 (dd, *J*₁ = 15.2 Hz, *J*₂ = 11.0 Hz, 1H), 2.58 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.6 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 167.9, 137.1, 136.4, 133.2, 132.8, 130.2, 129.7, 129.3, 129.2, 128.2, 127.8, 127.6, 126.2, 126.1, 125.9, 125.4, 64.6, 60.1, 53.1, 53.0, 34.6, 32.3, 20.6. **HRMS (ESI) m/z**: [M+H]⁺ Calcd for C₃₁H₃₂NO₄S 514.2047; Found 514.2053. **FTIR (cm⁻¹)** 2953, 1732, 1612, 1515, 1435, 1224.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(pyren-2-yl)ethyl)-2-(phenylthio)malonate (3p)

Following the general procedure, treatment of dimethyl 2-(pyren-1-yl)cyclopropane-1,1-dicarboxylate **1p** (0.108 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude

reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(pyren-2-yl)ethyl)-2-(phenylthio)malonate **3p** as a white solid (0.087 g, 59% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.41; **¹H NMR (400 MHz, CDCl₃)** δ 8.16-8.09 (m, 4H), 8.07-7.95 (m, 4H), 7.84 (d, *J* = 9.7 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11-7.03 (m, 6H), 6.60 (dd, *J*₁ = 10.1 Hz, *J*₂ = 3.1 Hz, 1H), 3.57 (s, 3H), 3.56 (s, 3H), 3.50 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.1 Hz, 1H), 2.54 (dd, *J*₁ = 15.1 Hz, *J*₂ = 3.3 Hz, 1H), 2.50 (s, 3H), 2.31 (s,

3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 168.1, 148.7, 137.0, 132.1, 131.4, 130.7, 130.5, 130.1, 129.6, 129.5, 129.3, 129.2, 129.1, 127.6, 127.3, 126.0, 125.7, 125.2, 125.2, 124.9, 124.1, 123.9, 118.9, 65.1, 57.2, 53.1, 53.0, 36.2, 32.6, 20.7. **HRMS (ESI)** m/z: [M+H]⁺ Calcd for C₃₇H₃₄NO₄S 588.2203; Found 588.2206. **FTIR (cm⁻¹)** 2952, 1732, 1514, 1263, 1230, 1113.

Dibenzyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (**3q**)

Following the general procedure, treatment of dibenzyl 2-phenylcyclopropane-1,1-dicarboxylate **1q** (0.116 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography

(Pet.ether/ EtOAc = 93/07) of the crude reaction mixture using silica gel afforded dibenzyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3q** as a white solid (0.115 g, 75% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.60; **¹H NMR (400 MHz, CDCl₃)** δ 7.36-7.35 (m, 3H), 7.33-7.23 (m, 11H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.12-7.10 (m, 6H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.75 (dd, *J_I* = 10.9 Hz, *J₂* = 2.4 Hz, 1H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.92-4.88 (m, 2H), 4.82 (d, *J* = 12.3 Hz, 1H), 3.12 (dd, *J_I* = 15.1 Hz, *J₂* = 11.0 Hz, 1H), 2.49 (dd, *J_I* = 15.1 Hz, *J₂* = 2.6 Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.4, 167.3, 148.5, 138.6, 137.2, 135.2, 135.0, 130.0, 129.6, 129.3, 129.1, 128.6, 128.5, 128.4, 128.4, 128.2, 127.7, 127.3, 116.5, 67.9, 67.6, 64.6, 60.1, 34.7, 32.5, 20.5. **HRMS (ESI)** m/z: [M+H]⁺ Calcd for C₃₉H₃₈NO₄S 616.2516; Found 616.2519. **FTIR (cm⁻¹)** 2953, 2364, 1731, 1514, 1262, 1217, 1106.

Dimethyl-2-(2-(furan-2-yl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (**3r**)

Following the general procedure, treatment of dimethyl 2-(furan-2-yl)cyclopropane-1,1-dicarboxylate **1r** (0.067 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography

(Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(furan-2-yl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate **3r** as a white solid (0.085 g, 75% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.43-7.37 (m, 3H), 7.31-7.27 (m, 3H), 7.09 (d, *J* = 8.5 Hz, 2 H), 6.99 (d, *J* = 8.6 Hz, 2 H), 6.25-6.24 (m, 1H), 6.03 (d, *J* = 3.1 Hz, 1 H), 5.62 (dd, *J*₁ = 10.1 Hz, *J*₂ = 3.0 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 3H), 2.89 (dd, *J*₁ = 15.3 Hz, *J*₂ = 10.1 Hz, 1H), 2.50 (s, 3H), 2.44 (dd, *J*₁ = 15.3 Hz, *J*₂ = 3.1 Hz, 1H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 167.9, 153.8, 148.5, 141.9, 137.2, 130.2, 129.6, 129.2, 128.0, 116.1, 109.9, 107.0, 64.3, 55.0, 53.0, 53.0, 34.2, 32.9, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₅H₂₈NO₅S 454.1683; Found 454.1687. **FTIR (cm⁻¹)** 2953, 1735, 1516, 1436, 1264, 1232.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(thiophen-2-yl)ethyl)-2-(phenylthio)malonate (3s)

Following the general procedure, treatment of dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate **1s** (0.072 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12

h followed by flash column chromatography (Pet. ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(thiophen-2-yl)ethyl)-2-(phenylthio)malonate **3s** as a light yellow solid (0.094 g, 80% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.39; **¹H NMR (400 MHz, CDCl₃)** δ 7.44-7.37 (m, 3H), 7.31-7.27 (m, 2H), 7.12-7.10 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.91-6.86 (m, 1H), 6.75 (d, *J* = 3.5 Hz, 1H), 5.87 (dd, *J*₁ = 10.5 Hz, *J*₂ = 2.0 Hz, 1H), 3.67 (s, 3H), 3.48 (s, 3H), 3.02 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.7 Hz, 1H), 2.49-2.44 (m, 4H), 2.30 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 167.8, 148.0, 142.3, 137.2, 130.3, 129.7, 129.2, 129.2, 128.3, 126.4, 124.6, 124.0, 116.5, 64.5, 56.7, 53.1, 36.1, 32.2, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₅H₂₈NO₄S₂ 470.1454; Found 470.1460. **FTIR (cm⁻¹)** 3003, 2861, 1722, 1614, 1515, 1435, 1268, 1097, 924.

Dimethyl (*E*)-2-(2-(methyl(*p*-tolyl)amino)-4-phenylbut-3-en-1-yl)-2-(phenylthio)malonate (3t)

Following the general procedure, treatment of dimethyl (*E*)-2-styrylcyclopropane-1,1-dicarboxylate **1t** (0.078 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*p*-tolyl)thiohydroxylamine **2a** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0

mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl (*E*)-2-(2-(methyl(*p*-tolyl)amino)-4-phenylbut-3-en-1-yl)-2-(phenylthio)malonate **3t** as a white solid (0.061 g, 50% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.45; **¹H NMR (400 MHz, CDCl₃)** δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33-7.26 (m, 6H), 7.23-7.19 (m, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.15 (dd, *J₁* = 16.3 Hz, *J₂* = 6.0 Hz, 1H), 5.14-5.10 (m, 1H), 3.67 (s, 3H), 3.48 (s, 3H), 2.73 (dd, *J₁* = 15.2 Hz, *J₂* = 9.8 Hz, 1H), 2.63 (s, 3H), 2.29 (s, 3H), 2.24 (dd, *J₁* = 15.2 Hz, *J₂* = 3.3 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 168.0, 148.2, 137.1, 136.9, 131.5, 130.2, 129.7, 129.4, 129.2, 128.6, 127.8, 127.7, 127.6, 126.5, 116.1, 64.3, 58.2, 53.1, 53.0, 35.4, 32.6, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₉H₃₂NO₄S 490.2047; Found 490.2053. **FTIR (cm⁻¹)** 3026, 2953, 1731, 1614, 1516, 1437, 1264.

Dimethyl-2-(2-((4-methoxyphenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (**3u**)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-(4-methoxyphenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2b** (0.123 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash

column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-((4-methoxyphenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3u** as a white solid (0.115 g, 48% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.37; **¹H NMR (400 MHz, CDCl₃)** δ 7.39-7.37 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.26-7.20 (m, 5H), 7.02-6.99 (m, 4H), 6.86-6.84 (m, 2H), 5.51 (dd, *J₁* = 11.0 Hz, *J₂* = 2.7 Hz, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.50 (s, 3H), 3.04 (dd, *J₁* = 15.2 Hz, *J₂* = 11.0 Hz, 1H), 2.43 (dd, *J₁* = 15.3 Hz, *J₂* = 2.9 Hz, 1H), 2.31 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.2, 168.0, 153.2, 145.2, 137.9, 137.1, 130.2, 129.4, 129.2, 128.1, 127.6, 127.4, 118.9, 114.4, 64.8, 61.9, 55.7, 53.0, 34.6, 32.4. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉NO₅S 479.1766; Found 479.1767. **FTIR (cm⁻¹)** 2951, 1734, 1579, 1511, 1438, 1256.

Dimethyl-2-(2-((4-ethylphenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3v)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-(4-ethylphenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2c** (0.122 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-((4-ethylphenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3v** as a white solid (0.165 g, 69% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.45; **¹H NMR (400 MHz, CDCl₃)** δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27-7.22 (m, 5H), 7.12-7.07 (m, 4H), 6.99 (d, *J* = 8.6 Hz, 2 H), 5.69 (dd, *J_I* = 10.6 Hz, *J₂* = 2.8 Hz, 1H), 3.61 (s, 3H), 3.45 (s, 3H), 3.03 (dd, *J_I* = 15.2 Hz, *J₂* = 10.6 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.44 (dd, *J_I* = 15.2 Hz, *J₂* = 3.0 Hz, 1H), 2.39 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 168.0, 148.6, 138.6, 137.1, 134.3, 130.2, 129.4, 129.2, 128.3, 128.2, 127.4, 127.4, 116.5, 64.7, 60.1, 53.0, 52.9, 34.9, 32.3, 28.0, 15.8. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₈H₃₂NO₄S 478.2047; Found 478.2052. **FTIR (cm⁻¹)** 2957, 1735, 1612, 1437, 1256, 1222.

Dimethyl-2-(2-((4-chlorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3w)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-(4-chlorophenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2d** (0.125 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-((4-chlorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3w** as a white solid (0.152 g, 63% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.45; **¹H NMR (400 MHz, CDCl₃)** δ 7.40-7.34 (m, 3H), 7.27-7.21 (m, 7H), 7.08-7.05 (m, 2H), 6.99 (d, *J* = 9.2 Hz, 2 H), 5.69 (dd, *J_I* = 11.0 Hz, *J₂* = 2.4 Hz, 1H), 3.64 (s, 3H), 3.45 (s, 3H), 3.02 (dd, *J_I* = 15.3 Hz, *J₂* = 11.0 Hz, 1H), 2.44 (dd, *J_I* = 15.3 Hz, *J₂* = 2.7 Hz, 1H), 2.38 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 167.9, 149.2, 138.3,

137.0, 130.3, 129.3, 129.1, 128.9, 128.4, 127.7, 127.12, 123.4, 117.3, 64.5, 60.0, 53.1, 53.0, 34.6, 32.4. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{26}H_{27}ClNO_4S$ 484.1344; Found 484.1349. **FTIR (cm⁻¹)** 2952, 1734, 1594, 1497, 1437, 1263.

Dimethyl-2-(2-((4-fluorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3x)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-(4-fluorophenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2e** (0.116 g, 0.5 mmol) with $Yb(OTf)_3$ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded Dimethyl-2-(2-((4-fluorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3x** as a white solid (0.140 g, 60% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.42; **¹H NMR (400 MHz, CDCl₃)** δ 7.42-7.36 (m, 3H), 7.29-7.25 (m, 5H), 7.06-6.98 (m, 6H), 5.61 (dd, $J_1 = 11.0$ Hz, $J_2 = 2.5$ Hz, 1H), 3.67 (s, 3H), 3.52 (s, 3H), 3.08 (dd, $J_1 = 15.2$ Hz, $J_2 = 11.1$ Hz, 1H), 2.41 (dd, $J_1 = 15.3$ Hz, $J_2 = 2.7$ Hz, 1H), 2.37 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 168.0, 156.7 (d, $J = 237.9$ Hz), 147.3 (d, $J = 2.0$ Hz), 137.8, 137.1, 130.3, 129.2, 128.3, 127.6, 127.4, 118.2 (d, $J = 7.4$ Hz), 115.4 (d, $J = 21.6$ Hz), 64.7, 61.4, 53.1, 53.0, 34.5, 32.4. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{26}H_{27}FNO_4S$ 468.1639; Found 468.1646. **FTIR (cm⁻¹)** 2952, 1733, 1509, 1436, 1224, 1103.

Dimethyl-2-(2-((3,4-difluorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3y)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-(3,4-difluorophenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2f** (0.126 g, 0.5 mmol) with $Yb(OTf)_3$ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-((3,4-difluorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate **3y** as a white solid (0.131 g, 54% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.47; **¹H NMR (400 MHz, CDCl₃)** δ 7.39-7.33 (m, 3H), 7.26-7.22 (m, 5H), 7.09-7.02 (m, 3H), 6.86-6.77 (m, 2 H), 5.58 (dd, *J*₁ = 11.0 Hz, *J*₂ = 2.5 Hz, 1H), 3.63 (s, 3H), 3.48 (s, 3H), 3.01 (dd, *J*₁ = 15.2 Hz, *J*₂ = 11.0 Hz, 1H), 2.40 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.7 Hz, 1H), 2.33 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 167.9, 150.5 (dd, *J*₁ = 245.0 Hz, *J*₂ = 13.0 Hz), 147.9 (dd, *J*₁ = 7.9 Hz, *J*₂ = 2.1 Hz), 143.8 (dd, *J*₁ = 238.8 Hz, *J*₂ = 12.8 Hz), 137.9, 137.0, 130.3, 129.3, 129.1, 128.4, 127.8, 127.2, 117.2 (dd, *J*₁ = 17.7 Hz, *J*₂ = 1.5 Hz), 111.8 (dd, *J*₁ = 5.2 Hz, *J*₂ = 2.9 Hz), 105.3 (d, *J* = 20.6 Hz), 64.5, 60.8, 53.1, 53.0, 34.60, 32.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₆H₂₆F₂NO₄S 486.1545; Found 486.1551. **FTIR (cm⁻¹)** 2953, 1730, 1598, 1517, 1437, 1246.

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(*p*-tolylthio)malonate (3z)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *N*-methyl-*N,S*-di-*p*-tolylthiohydroxylamine **2g** (0.122 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h

followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(*p*-tolylthio)malonate **3z** as a white solid

(0.177 g, 74% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.47; **¹H NMR (400 MHz, CDCl₃)** δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.26-7.23 (m, 3H), 7.11-7.05 (m, 6H), 7.00 (d, *J* = 8.5 Hz, 2 H), 5.72 (dd, *J*₁ = 10.7 Hz, *J*₂ = 2.5 Hz, 1H), 3.65 (s, 3H), 3.47 (s, 3H), 3.03 (dd, *J*₁ = 15.1 Hz, *J*₂ = 10.9 Hz, 1H), 2.43 (dd, *J*₁ = 15.2 Hz, *J*₂ = 2.7 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.1, 167.9, 148.5, 140.5, 138.5, 137.0, 130.0, 129.5, 128.2, 127.7, 127.3, 127.3, 125.7, 116.5, 64.6, 60.1, 52.9, 52.9, 34.6, 32.2, 21.3, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₈H₃₂NO₄S 478.2047; Found 478.2049. **FTIR (cm⁻¹)** 2952, 1734, 1613, 1516, 1435, 1263.

Dimethyl-2-((4-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (3aa)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *S*-(4-chlorophenyl)-*N*-methyl-*N*-(*p*-tolyl)thiohydroxylamine **2h** (0.132 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05

mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-((4-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl) malonate **3aa** as a white solid (0.194 g, 78% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.40; **¹H NMR (400 MHz, CDCl₃)** δ 7.33-7.31 (m, 2H), 7.26-7.21 (m, 5H), 7.09-7.07 (m, 4H), 6.95 (d, *J* = 8.6 Hz, 2 H), 5.61 (dd, *J*₁ = 10.6 Hz, *J*₂ = 2.7 Hz, 1H), 3.61 (s, 3H), 3.47 (s, 3H), 3.02 (dd, *J*₁ = 15.2 Hz, *J*₂ = 10.6 Hz, 1H), 2.43 (dd, *J*₁ = 15.2 Hz, *J*₂ = 3.0 Hz, 1H), 2.37 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 167.8, 148.5, 138.4, 138.3, 136.8, 129.6, 129.4, 128.3, 128.0, 127.5, 127.4, 116.6, 64.8, 60.3, 53.1, 53.0, 34.8, 32.2, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉ClNO₄S 498.1500; Found 498.1506. **FTIR (cm⁻¹)** 2952, 1730, 1613, 1516, 1437, 1265.

Dimethyl-2-((3-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (**3ab**)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *S*-(3-chlorophenyl)-*N*-methyl-*N*-(*p*-

tolyl)thiohydroxylamine **2i** (0.132 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-((3-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-

phenylethyl)malonate **3ab** as a white solid (0.110 g, 44% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.40; **¹H NMR (400 MHz, CDCl₃)** δ 7.41-7.41 (m, 1H), 7.34-7.22 (m, 1H), 7.28-7.15 (m, 5H), 7.08-7.06 (m, 4H), 6.94 (d, *J* = 8.6 Hz, 2 H), 5.59 (dd, *J*₁ = 10.6 Hz, *J*₂ = 2.6 Hz, 1H), 3.62 (s, 3H), 3.47 (s, 3H), 3.04 (dd, *J*₁ = 15.3 Hz, *J*₂ = 10.7 Hz, 1H), 2.43 (dd, *J*₁ = 15.3 Hz, *J*₂ = 2.9 Hz, 1H), 2.38 (s, 3H), 2.28 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 167.7, 148.4, 138.4, 136.8, 135.1, 134.6, 131.3, 130.4, 130.1, 129.6, 128.3, 128.0, 127.5, 127.4, 116.6, 64.9, 60.2, 53.1, 53.1, 34.9, 32.3, 20.6. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉ClNO₄S 498.1500; Found 498.1504. **FTIR (cm⁻¹)** 2952, 1735, 1613, 1515, 1433, 1262.

Dimethyl-2-((2-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (3ac)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.140 g, 0.6 mmol) and *S*-(2-chlorophenyl)-*N*-methyl-*N*-(*p*-tolyl)thiohydroxylamine **2j** (0.132 g, 0.5 mmol) with Yb(OTf)₃ (0.031 g, 0.05 mmol) in DCE (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-((2-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate **3ac** as a white solid (0.115 g, 46% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.40; **¹H NMR (400 MHz, CDCl₃)** δ 7.48 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.4 Hz, 1H), 7.40 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.22-7.20 (m, 3H), 7.14-7.04 (m, 5H), 6.98 (d, *J* = 8.6 Hz, 2 H), 5.77 (dd, *J*₁ = 11.1 Hz, *J*₂ = 2.1 Hz, 1H), 3.68 (s, 3H), 3.45 (s, 3H), 3.08 (dd, *J*₁ = 15.1 Hz, *J*₂ = 11.0 Hz, 1H), 2.43 (dd, *J*₁ = 15.3 Hz, *J*₂ = 2.5 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.0, 167.7, 148.5, 141.0, 139.2, 138.5, 131.5, 130.5, 129.6, 128.9, 128.1, 127.8, 127.4, 127.3, 127.2, 116.6, 64.8, 60.3, 53.2, 53.1, 34.8, 32.1, 20.5. **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd for C₂₇H₂₉ClNO₄S 498.1500; Found 498.1503. **FTIR (cm⁻¹)** 2951, 1734, 1613, 1517, 1436, 1262.

Dimethyl-2-(2-(methyl(3-methyl-4-(phenylthio)phenyl)amino)-2-phenylethyl)malonate (4a)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.070 g, 0.3 mmol) and *N*-methyl-*S*-phenyl-*N*-(*m*-tolyl)thiohydroxylamine **2k** (0.057 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-(methyl(3-methyl-4-(phenylthio)phenyl)amino)-2-phenylethyl)malonate **4a** as a white solid (0.092 g, 79% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.41 (d, *J* = 8.6 Hz, 1H), 7.37-7.33 (m, 2H), 7.30-7.26 (m, 3H), 7.24-7.20 (m, 2H), 7.10-7.04 (m, 3H), 6.78 (d, *J* = 2.7 Hz, 1H), 6.69 (dd, *J*₁ = 8.6 Hz, *J*₂ = 2.8 Hz, 1H), 5.22 (dd, *J*₁ = 10.7 Hz, *J*₂ = 4.7 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.54 (dd, *J*₁ = 8.9 Hz, *J*₂ = 5.5 Hz, 1H), 2.77 (ddd, *J*₁ = 13.9 Hz, *J*₂ = 8.9 Hz, *J*₃ = 4.8 Hz, 1H), 2.66-2.59 (m, 4H), 2.36 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.8,

169.7, 151.4, 143.7, 139.7, 139.6, 137.8, 128.8, 128.7, 127.6, 127.1, 126.3, 124.8, 117.7, 115.0, 111.5, 58.7, 52.7, 49.0, 31.6, 30.6, 21.5. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{27}H_{30}NO_4S$ 464.1890; Found 464.1895. **FTIR (cm⁻¹)** 2952, 1754, 1731, 1591, 1488, 1438, 1264, 1152.

Dimethyl-2-(2-((3-chloro-4-(phenylthio)phenyl)(methyl)amino)-2-phenylethyl)malonate (4b)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.070 g, 0.3 mmol) and *N*-(3-chlorophenyl)-*N*-methyl-*S*-phenylthiohydroxylamine **2l** (0.062 g, 0.25 mmol) with $Yb(OTf)_3$ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded dimethyl-2-(2-((3-chloro-4-(phenylthio)phenyl)(methyl)amino)-2-phenylethyl) malonate **4b** as a white solid (0.098 g, 81% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR (400 MHz, CDCl₃)** δ 7.38-7.22 (m, 8H), 7.18-7.14 (m, 3H), 6.93 (d, $J = 2.7$ Hz, 1 H), 6.71 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.8$ Hz, 1H), 5.14 (dd, $J_1 = 10.6$ Hz, $J_2 = 4.9$ Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 3.49-3.46 (m, 1H), 2.78-2.71 (m, 1H), 2.62 (s, 3H), 2.61-2.55 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 169.7, 169.6, 151.7, 139.8, 139.0, 137.8, 137.2, 129.1, 128.9, 128.1, 127.9, 127.0, 125.9, 118.2, 114.2, 112.2, 58.9, 52.9, 52.9, 48.9, 31.8, 30.5. **HRMS (ESI)** m/z : $[M+H]^+$ Calcd for $C_{26}H_{27}ClNO_4S$ 484.1344; Found 484.1350. **FTIR (cm⁻¹)** 2952, 1753, 1731, 1587, 1486, 1434.

***N*,3-Dimethyl-4-(phenylthio)aniline (5)**

Following the general procedure, *N*-methyl-*S*-phenyl-*N*-(*m*-tolyl)thiohydroxylamine **2k** (0.057 g, 0.25 mmol) with $Yb(OTf)_3$ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 98/02) of the crude reaction mixture using silica gel afforded *N*,3-dimethyl-4-(phenylthio)aniline **5** as a colourless oil (0.053 g, 93% yield).

R_f (Pet. ether / EtOAc = 100/00): 0.31; **¹H NMR (400 MHz, CDCl₃)** δ 7.44 (d, $J = 8.3$ Hz, 1 H), 7.26-7.22 (m, 2H), 7.13-7.07 (m, 3H), 6.59 (d, $J = 1.7$ Hz, 1 H), 6.50 (dd, $J_1 = 8.2$ Hz, $J_2 = 2.4$ Hz, 1H), 3.87 (bs, 1H), 2.88 (s, 3H), 2.38 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 150.5, 143.9, 140.0, 138.1, 128.8, 126.0, 124.6, 117.2, 114.4, 110.8, 30.5, 21.1. **HRMS (ESI)** m/z :

$[M]^+$ Calcd for $C_{14}H_{15}NS$ 229.0925; Found 229.0926. **FTIR** (cm^{-1}) 3423, 2921, 1603, 1504, 1474, 1326.

Dimethyl 2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (8a)

Following the general procedure, treatment of dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (0.085 g, 0.3 mmol), *N*,4-dimethylaniline **6a** (0.030 g, 0.25 mmol) and phenyl hypochlorothioite **7a** (0.036 g, 0.25 mmol) with Yb(OTf)₃ (0.015 g, 0.025 mmol) in DCE (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/ EtOAc = 90/10) of the crude reaction mixture using silica gel afforded Dimethyl 2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate **8a** as a white solid (0.080 g, 91% yield).

R_f (Pet. ether / EtOAc = 90/10): 0.43; **¹H NMR** (400 MHz, CDCl₃) δ 7.32-7.24 (m, 3H), 7.21 (d, *J* = 6.9 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 5.07 (t, *J* = 8.4 Hz, 1H), 3.69 (s, 6H), 3.61 (t, *J* = 7.2 Hz, 1H), 2.69-2.65 (m, 2H), 2.57 (s, 3H), 2.28 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 13C NMR (101 MHz, CDCl₃) δ 169.9, 169.8, 148.5, 139.6, 129.7, 128.4, 127.3, 127.2, 126.9, 114.3, 60.2, 52.6, 49.2, 31.8, 30.6, 20.3. **HRMS (ESI)** *m/z*: $[M+H]^+$ Calcd for C₂₁H₂₆NO₄ 356.1856; Found 356.1861. **FTIR** (cm^{-1}) 2953, 1759, 1615, 1518, 1435, 1262.

7. ^1H and ^{13}C NMR Spectra of all Products

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (**3a**)

Dimethyl-2-(2-(4-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3b**)**

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*p*-tolyl)ethyl)-2-(phenylthio)malonate (3c**)**

Dimethyl-2-(2-(4-bromophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3d)

Dimethyl-2-(2-(4-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3e)

Dimethyl-2-(2-(4-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3f)

Dimethyl-2-(2-(4-(methoxycarbonyl)phenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3g)

Dimethyl-2-(2-(3-methoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3h)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate (3i**)**

Dimethyl-2-(2-(3-chlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3j)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(*o*-tolyl)ethyl)-2-(phenylthio)malonate (3k)

Dimethyl-2-(2-(2-fluorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3I)

Dimethyl-2-(2-(3,4-dimethoxyphenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3m)

Dimethyl-2-(2-(3,4-dichlorophenyl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3n)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(naphthalen-2-yl)ethyl)-2-(phenylthio)malonate (3o)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(pyren-2-yl)ethyl)-2-(phenylthio)malonate (3p)

Dibenzyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3q)

Dimethyl-2-(2-(furan-2-yl)-2-(methyl(*p*-tolyl)amino)ethyl)-2-(phenylthio)malonate (3r)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-(thiophen-2-yl)ethyl)-2-(phenylthio)malonate (3s)

Dimethyl (*E*)-2-(2-(methyl(*p*-tolyl)amino)-4-phenylbut-3-en-1-yl)-2-(phenylthio)malonate (3t**)**

Dimethyl-2-((4-methoxyphenyl)(methyl)amino)-2-phenylethyl-2-(phenylthio)malonate (3u)

Dimethyl-2-((4-ethylphenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3v)

Dimethyl-2-((4-chlorophenyl)(methyl)amino)-2-phenylethyl-2-(phenylthio)malonate (3w)

Dimethyl-2-(2-((4-fluorophenyl)(methyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (3x)

Dimethyl-2-((3,4-difluorophenyl)(methyl)amino)-2-phenylethyl)-2-phenylthio)malonate (3y)

Dimethyl-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(*p*-tolylthio)malonate (3z)

Dimethyl-2-((4-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (3aa)

Dimethyl-2-((3-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (3ab)

Dimethyl-2-((2-chlorophenyl)thio)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (3ac)

Dimethyl-2-(2-(methyl(3-methyl-4-(phenylthio)phenyl)amino)-2-phenylethyl)malonate (4a)

Dimethyl-2-((3-chloro-4-(phenylthio)phenyl)(methyl)amino)-2-phenylethylmalonate (4b)

***N*,3-Dimethyl-4-(phenylthio)aniline (5)**

Dimethyl 2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)malonate (8a**)**

8. HPLC Data

Dimethyl (*R*)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-(phenylthio)malonate (**3a**) at 25 °C

Sample Info : CHIRALPAK OD-H , 5 %IPA-HEXANE, 1 mL -min, 254 nm

Dimethyl (*R*)-2-(2-(methyl(*p*-tolyl)amino)-2-phenylethyl)-2-phenylthio)malonate (3a**) at 10 °C**

Sample Info : CHIRALPAK OD-H, 2 % IPA-HEXANE, 1.0 mL -min, 254 nm