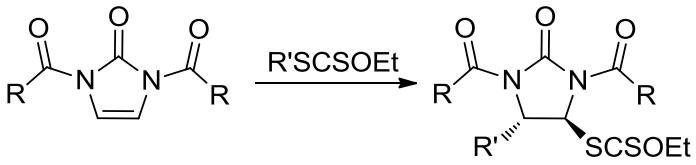
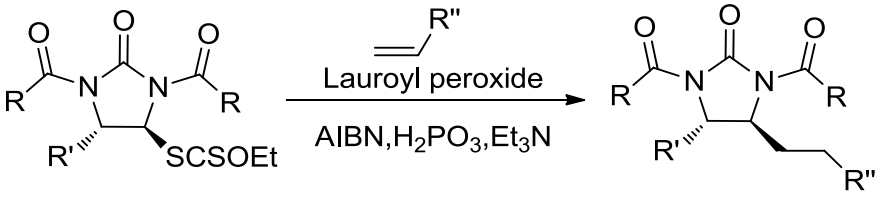
General procedure A for radical addition



A magnetically stirred solution of xanthate (2~3 equiv) and olefin (1.0 equiv) were dissolved in ethyl acetate (1 ml/mmol of xanthate) was refluxed for 15 min. DLP (5 mol%) was then added and additional DLP (5 mol%) was added every 60 min until total consumption of xanthate. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds. In cases of trisubstituted pyrroles synthesis, the residue could be purified by a quick flash chromatography on silica gel.

General procedure B for radical reduction

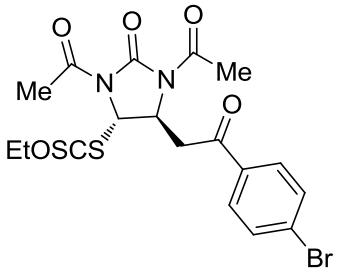


The residue was dissolved in dioxane (10 mL/mmol) then triethylamine (3.3 equiv.) and a solution of H_3PO_2 50% in water (3 equiv.) were added. The solution was refluxed for 15 min and AIBN (10%mol) was then added. After 1 hour, the solution was allowed to cool to room temperature, water and ethyl acetate were added. The organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

General procedure C for radical Cyclization

A magnetically stirred solution of the corresponding xanthate (1.0 equiv) in ethyl acetate (0.05 M of xanthate) was refluxed for about 15-30 min under nitrogen. Lauroyl peroxide (DLP) (20% mol) was then added to the refluxing solution every 60 min. The reaction was monitored by TLC every hour until the starting xanthate was completely consumed. The reaction mixture was then cooled down to room temperature, concentrated under reduced pressure and purified by flash chromatography on silica gel to yield the desired compounds.

S-((*4S,5S*)-1,3-Diacetyl-5-(2-(4-bromophenyl)-2-oxoethyl)-2-oxoimidazolidin-4-yl) -O-ethyl carbonodithioate (4-9a)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8a** (2.2 g, 7.14 mmol) and **RDC-2** (0.3g, 1.78 mmol), and needed 45 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 0.53g **4-9a** (yield: 62%) as a pale yellow oil.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.78 (d, 2H, J=8.6Hz, Ar), 7.61 (d, 2H, J=8.6Hz, Ar), 5.84 (d, 1H, J=1.1Hz, C*H*S), 4.85 (m, 1H, NC*H*CH_2), 4.63 (q, 2H, J=7.1Hz, SCSOC*H_2*), 3.78 (dd, 1H, J=5.7Hz, J=17.4Hz, COC*H*H), 3.63 (dd, 1H, J=3.5Hz, J=17.4Hz, COCH*H*), 2.59 (s, 3H, COC*H_3*), 2.51 (s, 3H, COC*H_3*), 1.39 (t, 3H, J=7.1Hz, $SCSOCH_2C$*H_3*);

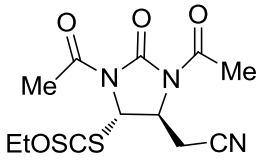
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 210.1 (*C*S), 195.6 (*C*OPhBr), 170.5 (*C*OCH_3), 169.2 (*C*OCH_3), 151.1 (N*C*ON), 134.8, 132.1, 129.5, 129.1 (Ar), 70.2 (SCSO*C*H_2), 62.7 (*C*HS), 57.5 (N*C*HCH_2), 40.7 (CO*C*H_2), 24.3, 24.2 (*C*OCH_3), 13.6

(SCSOCH$_2$*C*H$_3$);

IR (CCl$_4$): νmax 1054, 1244, 1374, 1558, 1704, 1732, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{15}H_{14}BrN_2O_4$: 365.0131 (365.0128).

S-((*4S,5S*)-1,3-Diacetyl-5-(cyanomethyl)-2-oxoimidazolidin-4-yl)-O-ethyl carbonodithioate (4-9b)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8b** (2.68g, 18 mmol) and **RDC-2** (1g, 6 mmol), and needed 10 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 1.5g **4-9b** (yield: 76%) as a white solid.

^{1}H NMR (400 MHz; CDCl$_3$): δ_H ppm 5.77 (s, 1H, C*H*S), 4.58-4.47 (m, 3H, NC*H*CH$_2$, SCSOC*H$_2$*), 3.09-3.01 (m, 2H, CNC*H$_2$*), 2.46 (s, 3H, COC*H$_3$*), 2.41 (s, 3H, COC*H$_3$*), 1.32 (t, 3H, J=7.1Hz, SCSOCH$_2$C*H$_3$*);

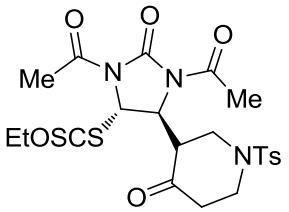
^{13}C NMR (100 MHz, CDCl$_3$): δ_C ppm 209.1 (*C*S), 169.7 (*C*OCH$_3$), 168.2 (*C*OCH$_3$), 149.4 (N*C*ON), 114.8 (CN), 70.2 (SCSO*C*H$_2$), 61.4 (*C*HS), 55.3 (N*C*HCH$_2$), 23.7, 23.5 (*C*OCH$_3$), 21.7 (CN*C*H$_2$), 13.2 (SCSOCH$_2$*C*H$_3$);

IR (CCl$_4$): νmax 1053, 1239, 1344, 1360, 1547, 1713, 1777, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{12}H_{15}N_3O_4S_2$: 329.0504 (329.0516);

MP: 115 - 116 ℃.

S-((*4S,5S*)-1,3-Diacetyl-2-oxo-5-((4-oxo-1-tosylpiperidin-3-yl)methyl)imidazolidin -4-yl) O-ethyl carbonodithioate (4-9c)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8c** (3.3g, 8.9 mmol) and **RDC-2** (0.5g, 2.9 mmol), and needed 55 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 0.86g **4-9c** (yield: 55%) as a pale yellow oil and a mixture of two diastereoisomers in a ratio 3:2.

^{1}H NMR (400 MHz; $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 7.63-7.54 (m, 2H, Ar), 7.32-7.22 (m, 2H, Ar), 5.69-5.62 (s, 1H, C*H*S), 4.66-4.40 (m, 3H, NC*H*CH, SCSOCH_2), 4.05-3.70 (m, 2H, NTsCH_2CH), 3.50-3.20 (m, 2H, NTsCH_2CH$_2$), 2.85-2.75 (m, 2H, NTsCH$_2$CH_2), 2.45-2.32 (m, 10H, 2COCH_3, CH_3, NCHC*H*), 1.34 (t, 3H, J=7.1Hz, SCSOCH$_2$CH_3);

Diastereoisomer 2: δ_H ppm 7.63-7.54 (m, 2H, Ar), 7.32-7.22 (m, 2H, Ar), 5.52-5.46 (s, 1H, C*H*S), 4.66-4.40 (m, 3H, NC*H*CH, SCSOCH_2), 4.05-3.70 (m, 2H, NTsCH_2CH), 3.50-3.20 (m, 2H, NTsCH_2CH$_2$), 2.69-2.55 (m, 3H, NTsCH$_2$CH_2, NCHC*H*), 2.45-2.32 (m, 9H, 2COCH_3, CH_3), 1.26 (t, 3H, J=7.1Hz, SCSOCH$_2$CH_3);

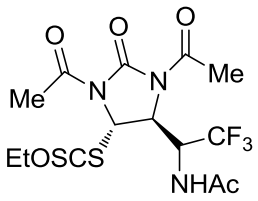
^{13}C NMR (100 MHz, $CDCl_3$): *Diastereoisomers 1:* δ_C ppm 208.2 (CS), 205.1 (CO), 170.2, 169.9 (CO), 150.8 (NCON), 143.8, 132.7, 129.5, 127 (Ar), 70.1 (SCSOCH_2CH$_3$), 62.2 (*C*HS), 58.2 (CONCH), 53.3 (COCH), 48, 45.4 (NCH$_2$), 40.1 (COCH$_2$), 23.9, 23.6 (*C*OCH$_3$), 21 (CH$_3$), 13.2 (SCSOCH$_2$CH_3);

Diastereoisomers 2: δ_C ppm 209 (CS), 204.3 (CO), 168.8, 168.6 (CO), 150.5 (NCON), 143.5, 132.1, 129.4, 126 (Ar), 70 (SCSOCH_2CH$_3$), 61.6 (*C*HS), 58 (CONCH), 49.3 (COCH), 47.3, 45.2 (NCH$_2$), 39.9 (COCH$_2$), 23.7, 23.6 (*C*OCH$_3$), 21 (CH$_3$), 13.1 (SCSOCH$_2$CH_3);

IR (CCl_4): νmax 1053, 1171, 1253, 1369, 1466, 1544, 1559, 1721, 1767, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{19}H_{22}N_3O_6S$: 420.1224 (420.1217).

S-((*4S,5S*)-5-((*R*)-1-Acetamido-2,2,2-trifluoroethyl)-1,3-diacetyl-2-oxoimidazolidin-4-yl) O-ethyl carbonodithioate (4-9d)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8d** (0.93g, 3.57mmol) and **RDC-2** (0.2g, 1.19mmol), and needed 45 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 346 mg **4-9d** (yield: 68%) as a pale yellow oil and a mixture of two diastereoisomers in a ratio 2:1.

^{1}H NMR (400 MHz; $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 7.42 (d, 1H, J=9.5Hz, N*H*Ac), 5.86 (d, 1H, J=5.7Hz, C*H*S), 5.43-5.38 (m, 1H, C*H*CF_3), 4.86-4.83 (m, 1H, NC*H*CH), 4.65 (q, 1H, J=7.1Hz, SCSOCH_2), 2.5 (s, 3H, COCH_3), 2.46 (s, 3H, COCH_3), 2.01 (s, 3H, COCH_3), 1.38 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

Diastereoisomer 2: δ_H ppm 7.81-7.76 (m, 1H, N*H*Ac), 6.08 (d, 1H, J=6.2Hz, C*H*S), 5.22-5.12 (m, 1H, C*H*CF_3), 4.86-4.83 (m, 1H, NC*H*CH), 4.65 (q, 1H, J=7.1Hz, SCSOCH_2), 2.51 (s, 3H, COCH_3), 2.48 (s, 3H, COCH_3), 1.99 (s, 3H, COCH_3), 1.22 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

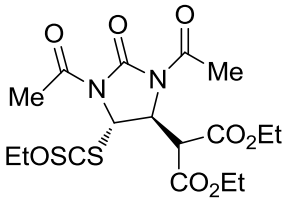
^{13}C NMR (100 MHz, $CDCl_3$): *Diastereoisomer 1:* δ_C ppm 208.4 (*C*S), 171.8, 170.2, 168.7 (*C*OCH_3), 150.1 (N*C*ON), 123.88 (q, J=282.4Hz, *C*F_3), 70.5 (SCSO*C*H_2), 61.3 (*C*HS), 58.2 (NCHCH), 52.39 (q, J=30.4Hz, *C*HCF_3), 24.2, 24.1, 22.4 (CO*C*H_3), 13.5 ($SCSOCH_2CH_3$);

Diastereoisomer 2: δ_C ppm 208.4 (*C*S), 171.8, 170.2, 168.7 (*C*OCH_3), 150.1 (N*C*ON), 123.88 (q, J=282.4Hz, *C*F_3), 70.5 (SCSO*C*H_2), 59.9 (*C*HS), 59.4 (NCHCH), 52.39 (q, J=30.4Hz, *C*HCF_3), 23.9, 23.8, 22.5 (CO*C*H_3), 13.6 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1053, 1137, 1233, 1253, 1347, 1370, 1465, 1506, 1559, 1705, 1774, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{11}H_{13}F_3N_3O_4$: 308.0853 (308.0854).

Diethyl-2-((*4S,5S*)-1,3-diacetyl-5-((ethoxycarbonothioyl)thio)-2-oxoimidazolidin-4-yl)malonate (4-9e)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8e** (0.99g, 3.57mmol) and **RDC-2** (0.2g, 1.19 mmol), and needed 15 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 468 mg **4-9e** (yield: 88%) as a pale yellow oil.

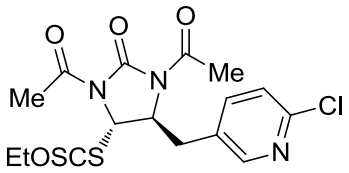
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 5.89 (d, 1H, J=1.6Hz, C*H*S), 5.08-5.01 (m, 1H, NC*H*CH_2), 4.63 (q, 1H, J=7.1Hz, SCSOC*H*$_2$), 4.26-4.18 (m, 5H, 2COC*H*$_2$$CH_3$, C*H*$(CO_2Et)_2$), 2.53 (s, 3H, COC*H*$_3$), 2.50 (s, 3H, COC*H*$_3$), 1.38 (t, 3H, J=7.1Hz, SCSOCH$_2$C*H*$_3$), 1.28-1.18 (m, 6H, 2COCH$_2$C*H*$_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 208.4 (*C*S), 170.2 (*C*OCH_3), 168.8 (*C*OCH_3), 166 (*C*OCH_2CH_3), 165.8 (*C*OCH_2CH_3), 150.9 (N*C*ON), 70.1 (SCSO*C*H_2), 62.2 (*C*HS), 62.1, 60.8 (CO_2*C*H_2CH_3), 57.4 (N*C*HCH_2), 52.2 (*C*H$(CO_2Et)_2$), 24.3, 24.1 (*C*OCH_3), 13.8 (SCSOCH$_2$*C*H_3), 13.7, 13.5 (CO_2CH_2*C*H_3),

IR (CCl_4): νmax 1053, 1232, 1370, 1553, 1682, 1741, 2855, 2984;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{14}H_{19}N_2O_7$: 327.1187 (327.1192).

_S_-((_4S,5S_)-1,3-Diacetyl-5-((6-chloropyridin-3-yl)methyl)-2-oxoimidazolidin-4-yl)-O-ethyl carbonodithioate (4-9f)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8f** (293mg, 1.19 mmol) and **RDC-2** (80mg, 0.476 mmol), and needed 60 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 106 mg **4-9f** (yield: 54%) as a pale yellow oil.

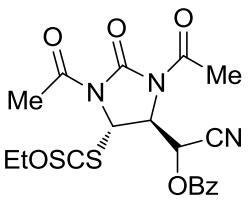
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 8.22 (s, 1H, =C*H*-N=), 7.56-7.48 (m, 1H, -C*H*=), 7.32-7.26 (m, 1H, =C*H*-Cq), 5.84 (s, 1H, C*H*S), 4.77 (t, 2H, J=4.5Hz, NC*H*CH_2), 4.62 (q, 1H, J=7.1Hz, SCSOCH_2), 3.20 (t, 2H, J=5.0Hz, NCHCH_2), 2.56 (s, 3H, COCH_3), 2.21 (s, 3H, COCH_3), 1.40 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 209.6 (*C*S), 170.2, 168.3 (*C*OCH_3), 150.9 (N*C*ON), 150.3, 150, 139.6, 129, 124.2 (Pyridyl), 70.4 (SCSO*C*H_2), 62.2 (*C*HS), 60 (N*C*HCH_2), 34.9 (NCH*C*H_2), 24.3, 23.5 (*C*OCH_3), 13.6 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1053, 1110, 1234, 1248, 1363, 1459, 1711, 1769;

HRMS (EI+): *m/z* calculated (found) for $C_{16}H_{18}ClN_3O_4S_2$: 415.0427 (415.0443).

(_R_)-Cyano((4S,5S)-1,3-diacetyl-5-((ethoxycarbonothioyl)thio)-2-oxoimidazolidin-4-yl)methyl benzoate (4-9g)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8g** (924mg, 3.29mmol) and **RDC-2** (184mg, 1.09 mmol), and

needed 45 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 332mg **4-9g** (yield: 68%) as a pale yellow oil and a mixture of two diastereoisomers in a ratio 2:1.

^{1}H NMR (400 MHz; $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 8.07-8.02 (m, 2H, J=7.1Hz, Ar), 7.51-7.44 (m, 3H, J=7.5Hz, Ar), 6.15 (d, 1H, J=0.6Hz, C*H*CN), 6.12 (d, 1H, J=2.4Hz, C*H*S), 5.08 (d, 1H, J=1.7Hz, NC*H*CH_2), 4.64-4.57 (m, 2H, SCSOC*H_2*), 2.62 (s, 3H, COC*H_3*), 2.49 (s, 3H, COC*H_3*), 1.35 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

Diastereoisomer 2: δ_H ppm 7.91-7.87 (m, 2H, J=7.1Hz, Ar), 7.67-7.61 (m, 3H, J=7.5Hz, Ar), 6.26 (d, 1H, J=0.7Hz, C*H*CN), 6.20 (d, 1H, J=2.5Hz, C*H*S), 5.09 (d, 1H, J=1.1Hz, NC*H*CH_2), 4.82-4.75 (m, 2H, SCSOC*H_2*), 2.53 (s, 3H, COC*H_3*), 2.35 (s, 3H, COC*H_3*), 1.44 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

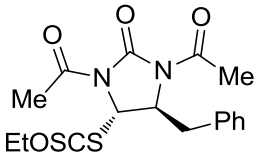
^{13}C NMR (100 MHz, $CDCl_3$): *Diastereoisomer 1:* δ_C ppm 207.3 (*C*S), 170 (O*C*OPh), 168.2, 163.8 (*C*OCH_3), 149.9 (N*C*ON), 134.7, 129.9, 128.9, 126.8 (Ar), 113.5 (*C*N), 70.7 ($SCSOCH_2$), 61 (*C*HS), 59.6 (N*C*HCH_2), 58.8 (CN*C*H), 24, 23.7 (*C*OCH_3), 13.7 ($SCSOCH_2CH_3$);

Diastereoisomer 2: δ_C ppm 207.2 (*C*S), 169.9 (O*C*OPh), 168.2, 163.7 (*C*OCH_3), 149.8 (N*C*ON), 134.6, 129.8, 128.8, 126.8 (Ar), 113.5 (*C*N), 70.6 ($SCSOCH_2$), 61 (*C*HS), 59.5 (N*C*HCH_2), 58.8 (CN*C*H), 23.9, 23.7 (*C*OCH_3), 13.6 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1054, 1085, 1242, 1370, 1453, 1721, 1748, 1773, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{16}H_{14}N_3O_5$: 328.0928 (328.0943).

S-((*4S,5S*)-1,3-Diacetyl-5-benzyl-2-oxoimidazolidin-4-yl)-O-ethylcarbonodithioa--te (4-9h)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8h** (1.48 g, 7.05 mmol) and **RDC-2** (400 mg, 2.35 mmol),

and needed 45 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 498 mg **4-9h** (yield: 56%) as white solid.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.32-7.24 (m, 3H, Ar), 7.19-7.11 (m, 2H, Ar), 5.91 (s, 1H, C*H*S), 4.82-4.74 (m, 1H, NC*H*CH_2), 4.62 (q, 1H, J=7.1Hz, 2H, SCSOC*H*$_2$), 3.28 (dd, 1H, J=4.8Hz, J=14.0Hz, CH*H*Ph), 3.15 (dd, 1H, J=3.0Hz, J=14.0Hz, C*H*HPh), 2.57 (s, 3H, COC*H*$_3$), 1.96 (s, 3H, COC*H*$_3$), 1.41 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

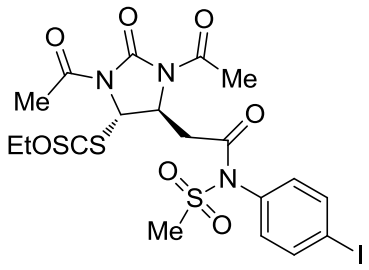
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 210 (*C*S), 170.2, 168.2 (*C*OCH_3), 150.7 (N*C*ON), 134, 129.3, 128.7, 127.4 (Ar), 70.1 (SCSO*C*H_2), 62.1 (*C*HS), 60.3 (N*C*HCH_2), 37.8 (*C*H_2Ph), 24.4, 23.1 (*C*OCH_3), 13.6 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1054, 1240, 1260, 1466, 1558, 1708, 1766, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{14}H_{15}N_2O_3$: 259.1077 (259.1083).

MP: 153~156 ℃.

***S*-((*4S,5S*)-1,3-Diacetyl-5-((4-iodophenyl)(methylsulfonyl)carbamoyl)-2-oxoimidazolidin-4-yl) O-ethyl carbonodithioate (4-9i)**



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8i** (1g, 2.38 mmol) and **RDC-2** (100 mg, 0.6 mmol), and needed 30 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 190 mg **4-9i** (yield: 52%) as a pale yellow oil.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.81 (d, 1H, J=8.6Hz, Ar), 7.13 (d, 1H,

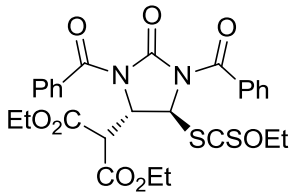
J=8.5Hz, Ar), 5.60 (d, 1H, J=0.6Hz, C*H*S), 4.62-4.57 (m, 2H, SCSOCH_2), 4.52 (t, 1H, J=5.5Hz, NC*H*CH_2), 3.37 (s, 3H, SO_2CH_3), 2.92 (dd, 1H, J=4.8Hz, J=15.5Hz, C*H*HCON), 2.66 (dd, 1H, J=6.4Hz, J=15.5Hz, CH*H*CON), 2.52 (s, 6H, 2CO*C*H_3), 1.36 (t, 1H, J=7.1Hz, $SCSOCH_2CH_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 209.5 (*C*S), 170.7 (*C*ONSO_2Me), 169.3, 169.1 (*C*OCH_3), 150.2 (N*C*ON), 139.4, 134.5, 131.5, 96.8 (Ar), 70.4 (SCSO*C*H_2), 62.7 (*C*HS), 57.1 (N*C*HCH_2), 41.7 (SO_2CH_3), 39.3 (*C*H_2CON), 24.2, 24 (*C*OCH_3), 13.5 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1053, 1229, 1369, 1543, 1558, 1724, 1767, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{18}H_{20}IN_3O_7S_3$ 612.9508 (612.9515).

Diethyl-2-((*4S,5S*)-1,3-dibenzoyl-5-((ethoxycarbonothioyl)thio)-2-oxoimidazolidin-4-yl)malonate (4-11a)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8e** (2.86 g, 10.27 mmol) and **4-10** (0.75 g, 2.57 mmol), and needed 12 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 1.35 g **4-11a** (yield: 92%) as a pale yellow oil.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.64-7.58 (m, 4H, Ar), 7.50-7.44 (m, 2H, Ar), 7.32-7.40 (m, 4H, Ar), 6.23 (d, 1H, J=2.8Hz, C*H*S), 5.47 (dd, 1H, J=2.9Hz, J=3.7Hz, NC*H*), 4.71 (q, 1H, J=7.1Hz, SCSOC*H*$_2$), 4.35 (d, 1H, J=3.8Hz, C*H*$(CO_2Et)_2$), 4.34-4.20 (m, 4H, 2$CO_2CH_2CH_3$), 1.44 (t, 1H, J=7.1Hz, $SCSOCH_2CH_3$), 1.33 (t, 1H, J=7.1Hz, $CO_2CH_2CH_3$), 1.23 (t, 1H, J=7.2Hz, $CO_2CH_2CH_3$);

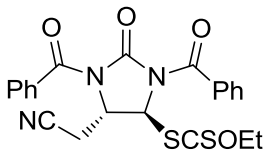
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 208.7 (*C*S), 169.5, 168.1 (*C*OPh), 166.1, 165.9 (*C*OCH_2CH_3), 149.4 (N*C*ON), 133.1, 133, 132.4, 132.2, 129, 129, 127.8, 127.7

(Ar), 70.4 (SCSO*C*H_2), 62.4 (*C*HS), 62.4, 61.9 (CO*C*H_2CH$_3$), 57.4 (N*C*HCH$_2$), 53.3 (*C*H(CO$_2$Et)$_2$), 13.9, 13.8 (COCH$_2$*C*H$_3$), 13.5 (SCSOCH$_2$*C*H$_3$);

IR (CCl$_4$): νmax 1045, 1154, 1228, 1276, 1449, 1693, 1736, 1778, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{24}H_{23}N_2O_7$: 451.1500 (451.1501).

_S_-((_4S,5S_)-1,3-dibenzoyl-5-(cyanomethyl)-2-oxoimidazolidin-4-yl)-O-ethyl carbonodithioate (4-11b)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8b** (205 mg, 1.37 mmol) and **4-10** (100 mg, 0.34 mmol), and needed 20 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 130 mg **4-11b** (yield: 85%) as a pale yellow oil.

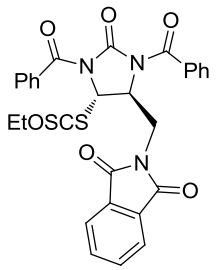
^{1}H NMR (400 MHz; CDCl$_3$): δ_H ppm 7.69 (d, 2H, J=7.2Hz, Ar), 7.61 (d, 2H, J=7.1Hz, Ar) 7.51-7.39 (m, 6H, Ar), 6.07 (d, 1H, J=1.0Hz, C*H*S), 4.96-4.88 (m, 1H, NC*H*CH$_2$), 4.75-4.68 (m, 2H, SCSOC*H*$_2$), 3.58 (dd, 1H, J=4.9Hz, J=17.4Hz, C*H*HCN), 3.24 (dd, 1H, J=2.7Hz, J=17.4Hz, CH*H*CN), 1.47 (t, 3H, J=7.1Hz, SCSOCH$_2$C*H*$_3$);

^{13}C NMR (100 MHz, CDCl$_3$): δ_C ppm 209.7 (*C*S), 169.8, 168 (*C*OPh), 148.7 (N*C*ON), 132.7, 132.5, 132.3, 132.2, 128.8, 128.8, 128, 127.9 (Ar), 115.7 (*C*N), 70.7 (SCSO*C*H$_2$), 64.2 (*C*HS), 57.4 (N*C*HCH$_2$), 22.2 (*C*H$_2$CN), 13.6 (SCSOCH$_2$*C*H$_3$);

IR (CCl$_4$): νmax 1054, 1150, 1213, 1276, 1449, 1699, 1787, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{22}H_{19}N_3O_4S_2$: 453.0817 (453.0829).

***S*-(((*4R,5S*)-1,3-Dibenzoyl-5-((1,3-dioxoisoindolin-2-yl)methyl)-2-oxoimidazolidin-4-yl)methyl) O-ethyl carbonodithioate (4-11c)**



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-8h** (962 mg, 3.42 mmol) and **4-10** (200 mg, 0.68 mmol), and needed 45 mol% of DLP to go to completion. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 247 mg **4-11c** (yield: 62%) as a white solid.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.89-7.83 (m, 3H, PhthN, Ar), 7.75-7.68 (m, 3H, PhthN, Ar), 7.54-7.50 (m, 2H, Ar), 7.43-7.37 (m, 2H, Ar), 7.36-7.30 (m, 2H, Ar), 7.26-7.20 (m, 2H, Ar), 6.16 (s, 1H, C*H*S), 5.16-5.12 (m, 1H, NC*H*CH_2), 4.71-4.64 (m, 2H, SCSOC*H*$_2$), 4.48-4.43 (m, 2H, C*H*$_2$NthPh), 1.45 (t, 3H, J=7.1Hz);

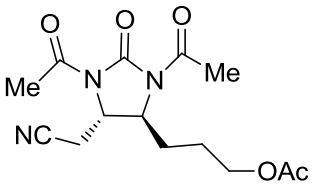
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 209.2 (*C*S), 169.5, 168 (*C*OPh), 167.9 (*C*ON), 149.1 (N*C*ON), 134.3, 134.1 (PhthN), 133, 132.3, 132.1, 131.8, 131.6, 128.7, 128.3, 127.7, 123.6 (Ar), 70.3 (SCSO*C*H_2), 63.2 (*C*HS), 53.4 (N*C*HCH_2), 38.9 (PhthN*C*H_2), 13.6 (SCSOCH$_2$*C*H_3);

IR (CCl_4): νmax 1054, 1233, 1280, 1449, 1544, 1711, 1741, 1774, 2855, 2924, 3031;

HRMS (EI+): *m/z* calculated (found) for $C_{30}H_{25}N_3O_6S_2$: 587.1185 (587.1178).

MP: 232 ~ 234 ℃..

3-((*4S,5S*)-1,3-Diacetyl-5-(cyanomethyl)-2-oxoimidazolidin-4-yl)propylacetate (4-12a)



Following the general procedure A for radical addition and procedure B for removal of xanthate group afford crude **4-12a**. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded **4-12a** (yield: 54%) as a pale yellow oil.

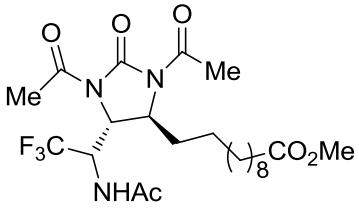
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 4.24-4.20 (m, 2H, 2NC*H*CH_2), 4.05 (t, 2H, J=5.5Hz, C*H*$_2$OAc), 2.84 (dd, 1H, J=6.6Hz, J=16.9Hz, CH*H*CN), 2.75 (dd, 1H, J=3.4Hz, J=16.9Hz, C*H*HCN), 2.53 (s, 3H, COC*H*$_3$), 2.49 (s, 3H, COC*H*$_3$), 2.01 (s, 3H, COC*H*$_3$), 1.88-1.82 (m, 1H, C*H*HCH$_2$OAc), 1.63 (s, 3H, NCHC*H*$_2$, CH*H*CH$_2$OAc);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 170.8, 170.7, 170 (*C*OCH_3), 150.4 (N*C*ON), 115.3 (*C*N), 63.2 (*C*H$_2$OAc), 55.2 (N*C*H), 51.6 (N*C*H), 29.4 (*C*H$_2$), 24.2, 24.2 (*C*OCH_3), 23.5 (*C*H$_2$CH$_2$CN), 21.8 (*C*H$_2$CN), 20.7 (*C*OCH_3);

IR (CCl_4): νmax 1054, 1145, 1233, 1287, 1454, 1715, 1792, 2845, 2933;

HRMS (EI+): *m/z* calculated (found) for $C_{14}H_{19}N_3O_5$: 309.1325 (309.1331).

Methyl-11-((*4S,5S*)-5-((*R*)-1-acetamido-2,2,2-trifluoroethyl)-1,3-diacetyl-2-oxoimidazolidin-4-yl)undecanoate (4-12b)



Following the general procedure A for radical addition and procedure B for

removal of xanthate group afford crude **4-12b**. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded **4-12b** (yield: 68%) as a pale yellow oil and a mixture of two diastereoisomers in a ratio 3:1.

^{1}H NMR (400 MHz; $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 7.20 (d, 1H, J=9.9Hz, NH), 5.24-5.18 (m, 1H, CF_3CH), 4.49-4.27 (m, 2H, 2NCH), 3.64 (s, 3H, CO_2CH_3), 2.51 (s, 3H, $COCH_3$), 2.49 (s, 3H, $COCH_3$), 2.28 (t, 2H, J=7.5Hz, CH_2COOCH_3), 1.99 (s, 3H, $COCH_3$), 1.61-1.56 (m, 2H, CH_2), 1.26-1.2 (m, 16H, $8CH_2$);

Diastereoisomer 2: δ_H ppm 6.34 (d, 1H, J=9.9Hz, NH), 4.89-4.82 (m, 1H, CF_3CH), 4.49-4.27 (m, 2H, 2NCH), 3.64 (s, 3H, CO_2CH_3), 2.5 (s, 3H, $COCH_3$), 2.45 (s, 3H, $COCH_3$), 2.28 (t, 2H, J=7.5Hz, CH_2COOCH_3), 1.98 (s, 3H, $COCH_3$), 1.61-1.56 (m, 2H, CH_2), 1.26-1.2 (m, 16H, $8CH_2$);

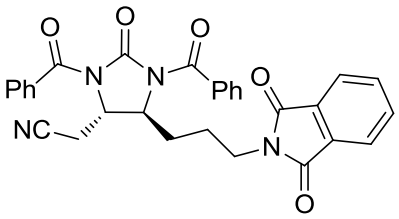
^{13}C NMR (100 MHz, $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 174.4, 171.1, 170.4 (CO), 151.1 (NCON), 123.96 (q, J=282.1Hz, CF_3), 68.6 (N*C*HCH), 54.6 (N*C*HCH_2), 51.4 (OCH_3), 51.56 (q, J=31.4Hz, *C*HCF_3), 34.1 (NCH*C*H_2), 29.7, 29.6, 29.5, 29.4 29.3, 29.2, 29.1, 29.1, 29.1 (CH_2), 24.3, 24.2, 23.9 ($COCH_3$), 22.4 ($COOCH_3$);

Diastereoisomer 2: δ_H ppm 172.3, 170.7, 170.3 (CO), 150.8 (NCON), 124.34 (q, J=278.6Hz, CF_3), 66.3 (N*C*HCH), 62.6 (N*C*HCH_2), 52 (OCH_3), 52.45 (q, J=31.4Hz, *C*HCF_3), 32.7 (NCH*C*H_2), 29.7, 29.6, 29.5, 29.4 29.3, 29.2, 29.1, 29.1, 29.1 (CH_2), 24.3, 24.2, 24 ($COCH_3$), 23.9 ($COOCH_3$);

IR (CCl_4): νmax 1138, 1260, 1370, 1706, 1742, 1765, 2855, 2927, 3342;

HRMS (EI+): *m/z* calculated (found) for $C_{23}H_{36}F_3N_3O_6$: 507.2556 (507.2558).

2-((*4S,5S*)-1,3-Dibenzoyl-5-(3-(1,3-dioxoisoindolin-2-yl)propyl)-2-oxoimidazolidin-4-yl)acetonitrile (4-12c)



Following the general procedure A for radical addition and procedure B for

removal of xanthate group afford crude **4-12c**. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded **4-12c** (yield: 64%) as a pale yellow oil.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.86-7.83 (m, 2H, Ar), 7.74-7.71 (m, 2H, Ar), 7.6-7.54 (m, 4H, Ar), 7.5-7.43 (m, 2H, Ar), 7.38-7.33 (m, 4H, Ar), 4.53-4.45 (m, 1H, NCH), 4.25-4.21 (m, 1H, NCH), 3.83-3.71 (m, 2H, PhthNCH_2), 3.28 (dd, 1H, J=5.9Hz, J=17.1Hz, CNC*H*H), 2.98 (dd, 1H, J=2.8Hz, J=17.1Hz, CNCH*H*), 2.21-2.16 (m, 1H, CHCH*H*CH_2), 1.93-1.87 (m, 3H, $CHCH_2CH_2$, CHC*H*HCH_2);

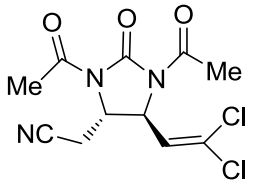
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 170.2, 169.6, 168.3 (CO), 149.3 (NCON), 134.1, 133.3, 132.8, 132.5, 132, 131.9, 128.9, 128.6, 127.9, 127.9, 123.3 (Ar), 115.6 (CN), 56.5, 53.1 (NCH), 37 (PhthNCH_2), 30.2 (NCHCH_2CH_2), 23.9 ($NCHCH_2CH_2$), 22.1 (CNCH_2);

IR (CCl_4): νmax 1233, 1281, 1377, 1466, 1542, 1718, 1776, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) $C_{30}H_{24}N_4O_5$: 520.1747 (520.1739);

MP: 263~265 °C.

2-((*4S,5S*)-1,3-Diacetyl-5-(2,2-dichlorovinyl)-2-oxoimidazolidin-4-yl)acetonitrile (4-13)



A solution of **4-9b** (154 mg, 0.367 mmol) and 1,1-dichloro-2-(ethylsulfonyl)ethane (139 mg, 0.735 mmol) in 0.4 mL chlorobenzene was heated to reflux under N_2 atmosphere for 10 min. To the solution 3 drops of DTBP was added at intervals of 4 h. After refluxing for 12 h, the solution was allowed to cool to room temperature. The solvent was removed under vacuum and the residue was purified via flash chromatography (SiO_2, petroleum ether: ethyl acetate = 4:1) to afford 76 mg **4-13** (yield: 69%) as a yellow oil.

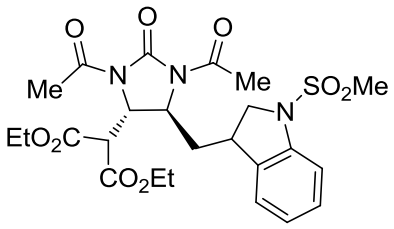
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 5.85 (d, 1H, J=7.9Hz, CH=CCl_2), 4.92 (dd, 1H, J=1.7Hz, J=7.9Hz, NC*H*CH), 4.35-4.32 (m, 1H, NC*H*CH_2), 3.04 (dd, 1H, J=5.8Hz, J=17.1Hz, CNC*H*H), 2.80 (dd, 1H, J=3.1Hz, J=17.1Hz, CNCH*H*), 2.55 (s, 3H, COCH_3), 2.52 (s, 3H, COCH_3);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 170.4, 169.7 (*C*OCH_3), 149.9 (N*C*ON), 126.4 (*C*Cl_2), 126.3 (*C*=CCl_2), 114.8 (CN), 54.4 (N*C*HCH=), 52.7 (N*C*HCH_2), 24.1, 24 (*C*OCH_3), 21.9 (CN*C*H_2);

IR (CCl_4): νmax 1246, 1367, 1378, 1465, 1559, 1711, 1769, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{11}H_{11}C_{l2}N_3O_3$: 303.0177 (303.0175).

Diethyl-2-((*4S,5S*)-1,3-diacetyl-5-((1-(methylsulfonyl)indolin-3-yl)methyl)-2-oxoi midazolidin-4-yl)malonate (4-15)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-9e** (170 mg, 0.38 mmol) and *N*-allyl-*N*-phenylmethane-sulfonamide (171 mg, 0.76 mmol), and needed 10 mol% of DLP to go to completion. The solution was concentrated in vacuo to obtain the residue which was purified by a quick column to afford 202 mg crude **4-14** (yield: 81%). Then following the procedure C for radical cyclization, a magnetically stirred solution of **4-14** (202 mg, 0.3 mmol) in AcOEt (6.2 ml) was refluxed for about 15-30 min under nitrogen. Lauroyl peroxide (DLP) (20%mol) was then added to the refluxing solution every 60 min. The reaction was monitored by TLC every hour until the starting xanthate was completely consumed. The reaction mixture was then cooled down to room temperature, concentrated under reduced pressure. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 90 mg **4-15** (yield: 56 %) as a pale yellow oil and a mixture of two diastereoisomers in a ratio 1:1.

^{1}H NMR (400 MHz; $CDCl_3$): *Diastereoisomer 1:* δ_H ppm 7.42-7.36 (m, 1H, Ar), 7.20-7.10 (m, 2H, Ar), 7.04-6.96 (m, 1H, Ar), 4.72-4.66 (m, 1H, NC*H*CH_2), 4.64-4.60 (m, 1H, NC*H*CH), 4.30-4.02 (m, 6H, $2CO_2CH_2CH_3$, C*H*$(CO_2Et)_2$, CH*H*NSO_2Me), 3.92-3.86 (m, 1H, C*H*HNSO_2Me), 3.76-3.70 (m, 1H, C*H*CH_2NSO_2Me), 2.90 (s, 3H, SO_2CH_3), 2.56 (s, 3H, $COCH_3$), 2.47 (s, 3H, $COCH_3$), 2.10-2.04 (m, 1H, CHCH*H*CH), 1.98-1.94 (m, 1H, CHC*H*HCH), 1.25 (m, 6H, $2COCH_2CH_3$);

Diastereoisomer 2: δ_H ppm 7.42-7.36 (m, 1H, Ar), 7.20-7.10 (m, 2H, Ar), 7.04-6.96 (m, 1H, Ar), 4.52-4.46 (m, 1H, NC*H*CH_2), 4.41 (dd, 1H, J=1.1Hz, J=4.0Hz, NC*H*CH), 4.30-4.02 (m, 6H, $2CO_2CH_2CH_3$, C*H*$(CO_2Et)_2$, CH*H*NSO_2Me), 3.82-3.76 (m, 1H, C*H*HNSO_2Me), 3.44-3.36 (m, 1H, C*H*CH_2NSO_2Me), 2.87 (s, 3H, SO_2CH_3), 2.55 (s, 3H, $COCH_3$), 2.41 (s, 3H, $COCH_3$), 1.92-1.88 (m, 2H, $CHCH_2CH$), 1.25 (m, 6H, $2COCH_2CH_3$);

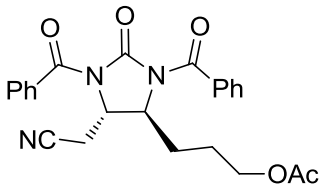
^{13}C NMR (100 MHz, $CDCl_3$): *Diastereoisomer 1:* δ_C ppm 170.9, 170.7 (*C*OCH_3), 166.7, 166.3 (*C*OCH_2CH_3), 151.4 (N*C*ON), 141.6, 134.1, 128.4, 124.4, 123.7, 114.2 (Ar), 62.2, 62.1 ($CO_2CH_2CH_3$), 55.9 (N*C*HCH_2), 55.3 (*C*H$(CO_2Et)_2$), 52.1 (*C*H_2NSO_2Me), 50.9 (N*C*HCH), 41.2 (SO_2CH_3), 36.9 (*C*HCH_2NSO_2Me), 34.6 (CH*C*H_2CH), 24.3, 24 (*C*OCH_3), 13.8, 13.7 ($CO_2CH_2CH_3$);

Diastereoisomer 2: δ_C ppm 170.5, 169.5 (*C*OCH_3), 166.7, 166.3 (*C*OCH_2CH_3), 150.8 (N*C*ON), 141.5, 134, 128.4, 124.2, 123.7, 113.8 (Ar), 62.2, 62.1 ($CO_2CH_2CH_3$), 55.6 (N*C*HCH_2), 54.1 (*C*H$(CO_2Et)_2$), 52 (*C*H_2NSO_2Me), 50.8 (N*C*HCH), 39.1 (SO_2CH_3), 36.3 (*C*HCH_2NSO_2Me), 34.4 (CH*C*H_2CH), 24.2, 23.9 (*C*OCH_3), 13.8, 13.7 ($CO_2CH_2CH_3$);

IR (CCl_4): νmax 1029, 1117, 1165, 1259, 1368, 1558, 1706, 1731, 1747, 1763, 2930, 2984;

HRMS (EI+): *m/z* calculated (found) for $C_{24}H_{31}N_3O_9S$: 537.1781 (537.1778).

3-((*4S,5S*)-1,3-Dibenzoyl-5-(cyanomethyl)-2-oxoimidazolidin-4-yl)propyl acetate (4-18)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-11b** (165 mg, 0.37 mmol) and allyl acetate (75 mg, 0.75 mmol), and needed 10 mol% of DLP to go to completion. The solution was concentrated *in vacuo* to obtain the residue which was used in the next step without purification. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 115 mg **4-18** (yield: 72%) as a white solid.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.62-7.57 (m, 4H, Ar), 7.52-7.45 (m, 2H, Ar), 7.4-7.34 (m, 4H, Ar), 4.52-4.43 (m, 2H, 2NCH), 4.18-4.14 (m, 2H, C*H*$_2$OAc), 3.20 (dd, 1H, J=6.1Hz, J=17.1Hz, CNC*H*H), 2.94 (dd, 1H, J=2.9Hz, J=17.1Hz, CNCH*H*), 2.19-2.13 (m, 1H, NCHCH$_2$C*H*H), 2.06 (s, 3H, $COCH_3$), 1.98-1.93 (m, 1H, NCHCH$_2$CH*H*), 1.85-1.78 (m, 2H, NCHC*H*$_2$CH$_2$);

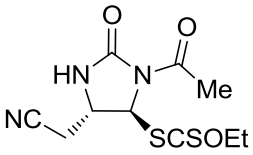
^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 170.9, 170.2, 169.5 (CO), 149.4 (NCON), 133.3, 132.7, 132.6, 132.1, 128.8, 128.5, 128, 127.9 (Ar), 115.6 (CN), 63.3 (CH_2OAc), 56.7, 53 (NCH), 29.3 (NCH*C*H$_2$CH$_2$), 23.7 (CO*C*H$_3$), 22.1 (NCHCH$_2$*C*H$_2$), 20.8 (CN*C*H$_2$);

IR (CCl_4): νmax 1123, 1233, 1281, 1688, 1744, 1777, 2856, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{24}H_{23}N_3O_5$: 433.1638 (433.1641);

MP: 154~155 °C.

S-((*4S,5S*)-3-Acetyl-5-(cyanomethyl)-2-oxoimidazolidin-4-yl)-*O*-ethyl carbonodithioate (4-21)



To a solution of **4-9b** (268 mg, 0.64 mmol) in methanol (1.28 ml) was added DIPEA (83 mg, 0.64 mmol). The reaction was monitored by TLC every hour until the starting material was completely consumed. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 132 mg **4-21** (yield: 72%) as a pale yellow oil.

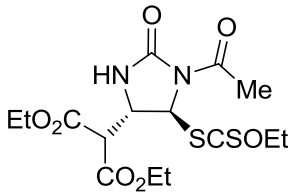
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 6.96 (br, 1H, N*H*), 5.84 (s, 1H, C*H*S), 4.68-4.61 (m, 2H, SCSOCH_2)), 4.19-4.11 (m, 1H, NC*H*CH_2), 2.97 (dd, 1H, J=3.2Hz, J=16.7Hz, CH*H*CN), 2.85 (dd, 1H, J=7.1Hz, J=16.7Hz, C*H*HCN), 2.49 (s, 3H, COCH_3), 1.42 (t, 3H, J=7.1Hz, $SCSOCH_2CH_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 210.7 (*C*S), 169.1 (*C*OCH_3), 154.2 (N*C*ON), 115.8 (CN), 70.4 (SCSO*C*H_2), 65.3 (*C*HS), 54.5 (N*C*HCH_2), 24.8 (*C*OCH_3), 23.6 (CN*C*H_2), 13.6 ($SCSOCH_2CH_3$);

IR (CCl_4): νmax 1053, 1228, 1307, 1373, 1716, 1771, 2932;

HRMS (EI+): *m/z* calculated (found) for $C_{10}H_{13}N_3O_3S_2$: 287.0398 (287.0404).

Diethyl-2-((*4S,5S*)-1-acetyl-5-((ethoxycarbonothioyl)thio)-2-oxoimidazolidin-4-yl) malonate (4-22)



To a solution of **4-9e** (28 mg, 0.063 mmol) in methanol (0.13 ml) was added DIPEA (8 mg, 0.063 mmol). The reaction was monitored by TLC every hour until the starting material was completely consumed. Flash chromatography on silica gel

(petroleum ether: ethyl acetate, 2:1 v/v) afforded 18mg **4-22** (yield: 74%) as a pale yellow oil.

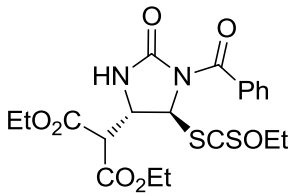
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 6.10 (s, 1H, N*H*), 5.86 (s, 1H, C*H*S), 4.68-4.61 (m, 2H, SCSOC*H*$_2$), 4.35 (d, 1H, J=4.2Hz, NC*H*CH$_2$), 4.28-4.22 (m, 4H, 2COC*H*$_2$CH$_3$), 3.99 (d, 1H, J=4.2Hz, C*H*(CO$_2$Et)$_2$), 2.47 (s, 3H, COC*H*$_3$), 1.42 (t, 3H, J=7.1Hz, SCSOCH$_2$C*H*$_3$), 1.33-1.26 (m, 6H, J=7.2Hz, 2COCH$_2$C*H*$_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 210.8 (*C*S), 168.8, 167.2, 166.1 (*C*OCH$_3$), 153.8 (N*C*ON), 70.2 (SCSO*C*H$_2$), 64.2 (*C*HS), 62.5, 62.4 (CO$_2$*C*H$_2$CH$_3$), 57 (N*C*HCH$_2$), 55.4 (*C*H(CO$_2$Et)$_2$), 23.5 (*C*OCH$_3$), 13.9 (SCSOCH$_2$*C*H$_3$), 13.8, 13.7 (CO$_2$CH$_2$*C*H$_3$);

IR (CCl_4): νmax 1023, 1243, 1261, 1712, 1777, 2843, 2922;

HRMS (EI+): *m/z* calculated (found) for $C_{15}H_{22}N_2O_7S_2$: 406.0868 (406.0861).

Diethyl-2-((*4S,5S*)-1-benzoyl-5-((ethoxycarbonothioyl)thio)-2-oxoimidazolidin-4-yl)malonate (4-23)



To a solution of **4-11a** (895 mg, 1.58 mmol) in methanol (10 ml) was added DIPEA (202 mg, 1.58 mmol). The reaction was monitored by TLC every hour until the starting material was completely consumed. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 1:1 v/v) afforded 576 mg **4-23** (yield: 78%) as a pale yellow oil.

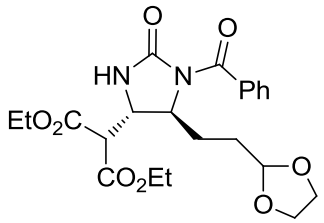
^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.62-7.56 (m, 2H, Ar), 7.52-7.46 (m, 1H, Ar), 7.42-7.34 (m, 2H, Ar), 6.28 (s, 1H, C*H*S), 6.23 (br, 1H, N*H*), 4.72-4.62 (m, 2H, SCSOC*H*$_2$), 4.44 (d, 1H, J=3.8Hz, C*H*(CO$_2$Et)$_2$), 4.30-4.10 (m, 4H, 2CO$_2$C*H*$_2$CH$_3$), 4.02-3.98 (m, 1H, NHC*H*CH), 1.43 (t, 3H, J=7.1Hz, SCSOCH$_2$C*H*$_3$), 1.30-1.20 (s, 6H, 2CO$_2$CH$_2$C*H*$_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 210.3 (*C*S), 168 (*C*OPh), 166.8, 166 (*C*OCH_2CH_3), 153.2 (N*C*ON), 133.3, 131.7, 128.8, 127.4 (Ar), 70.2 (SCSO*C*H_2), 65.1 (*C*HS), 62.3, 62.3 (CO*C*H_2CH_3), 56.8 (N*C*HCH_2), 55.4 (*C*H$(CO_2Et)_2$), 13.8, 13.8 (COCH_2*C*H_3), 13.5 (SCSOCH_2*C*H_3);

IR (CCl_4): νmax 1054, 1271, 1722, 1777, 2853, 2927;

HRMS (EI+): *m/z* calculated (found) for [M-SCSOEt] $C_{17}H_{19}N_2O_6$: 347.1238 (347.1242).

Diethyl-2-((*4S,5S*)-5-(2-(1,3-dioxolan-2-yl)ethyl)-1-benzoyl-2-oxoimidazolidin-4-yl)malonate (4-24)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **4-23** (312 mg, 0.67 mmol) and 2-vinyl-1,3-dioxolane (134 mg, 1.34 mmol), and needed 10 mol% of DLP to go to completion. The solution was concentrated *in vacuo* to obtain the residue which was used in the next step without purification. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1~1:1 v/v) afforded 189 mg **4-24** (yield: 63%) as a colorless oil.

^{1}H NMR (400 MHz; $CDCl_3$): δ_H ppm 7.56-7.52 (m, 2H, Ar), 7.46-7.42 (m, 1H, Ar), 7.38-7.33 (m, 2H, J=7.5Hz, Ar), 6 (br, 1H, N*H*), 4.90 (t, 1H, J=4.3Hz, OCHO), 4.56-4.53 (m, 1H, NHC*H*), 4.22-4.18 (m, 2H, CO_2C*H*$_2CH_3$), 4.13 (q, 2H, J=7.1Hz, CO_2C*H*$_2CH_3$), 3.96-3.93 (m, 3H, NC*H*CH_2, OCH_2), 3.84-3.82 (m, 2H, OCH_2), 3.55 (d, 1H, J=7.5Hz, C*H*$(CO_2Et)_2$), 2.02-1.91 (m, 2H, CH_2), 1.8-1.75 (m, 2H, CH_2), 1.27 (t, 3H, J=7.1Hz, CO_2CH_2C*H*$_3$), 1.21 (t, 3H, J=7.1Hz, CO_2CH_2C*H*$_3$);

^{13}C NMR (100 MHz, $CDCl_3$): δ_C ppm 169.4 (*C*OPh), 166.6, 166.5 (*C*OCH_2CH_3), 154.1 (N*C*ON), 134.4, 131.1, 128.4, 127.3 (Ar), 103.5 (OCHO), 64.9, 64.8 (OCH_2),

62.1, 62.1 (CO*C*$H_2$$CH_3$), 57.4 (N*C*HCH$_2$), 56.1 (*C*H($CO_2Et)_2$), 52.4 (NH*C*H), 28.3 ($CH_2$), 26.8 ($CH_2$), 13.8, 13.8 (COCH$_2$*C*$H_3$);

IR (CCl_4): νmax 1148, 1241, 1332, 1448, 1670, 1732, 2855, 2927;

HRMS (EI+): *m/z* calculated (found) for $C_{22}H_{28}N_2O_8$: 448.1846 (448.1841).