A novel stereoselective one-pot synthesis of 2-susbstituted amino-5,6-dihydro-4H-1,3-thiazines via primary allylamines afforded from Morita-Baylis-Hillman acetates

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Methyl 2-[phenyl(3-phenylthiourea)methyl]acrylate (4.1aA). 70 % as a white solid (0.98 g from 1.0 g), mp 119-121 °C; Rf = 4.8 min; Rf= 0.24 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1642 (CS), 1734 (CO2Me), 3369 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ= 3.59 (s, 3H, OCH₃), 6.03 (s, 1H, =CH₂), 6.41 (d, 1H, J= 9.0 Hz, CH), 7.20-7.33 (m, 8H, ArH and NH), 7.43 (t, 3H, J= 7.3 Hz, ArH), 7.82 (s, 1H, NH); ¹³C NMR (75 MHz, CDCl₃) δ= 52.1, 60.9, 125.1, 126.1, 127.3, 127.6, 128.7, 129.2, 130.1, 136.1, 137.9, 139.0, 166.4, 180.1; mass (ES+) m/z= 327.1 (M⁺+1). Anal. Calcd. for C₁₈H₁₈N₂O₂S (Exact mass: 326.1089); C, 66.23; H, 5.56; N, 8.58; Found C, 66.19; H, 5.69; N, 8.49.

N-[1-(2-Bromophenyl)-2-cyanoallyl]-3-N'-phenylthiourea (4.2cA). 73 % as a white solid (0.97 g from 1.0 g), mp 130-132 °C; Rf= 0.21 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1637 (CS), 2209 (CN) cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ= 5.88 (s, 1H, =CH₂), 6.13 (s, 1H, =CH₂), 6.70 (s, 2H, CH and NH), 7.20-7.39 (m, 6H, ArH), 7.43-7.58 (m, 2H, ArH), 7.58-7.61 (m, 1H, ArH), 8.04 (s, 1H, NH); ¹³C NMR (75 MHz, CDCl₃ + DMSO-d₆) δ= 59.4, 117.1, 122.1, 123.8, 124.1, 125.8, 127.9, 129.1, 132.5, 133.6, 136.5, 137.9, 181.1; mass (ES+) m/z= 372.0 (M⁺+1), 374.0 (M⁺+3). Anal. Calcd. for C₁₇H₁₄BrN₃S (Exact mass: 371.0092); C, 54.85; H, 3.79; N, 11.29; Found C, 54.65; H, 3.81; N, 11.17.

Methyl 2-[2-chlorophenyl(3-phenylthiourea)methyl]acrylate (4.1dA). 69 % as a white solid (0.9 g from 1.0 g), mp 113-115 °C; Rf= 0.22 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1631 (CS), 1731 (CO₂Me), 3358 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ= 3.65 (s, 3H, OCH₃), 5.97 (s, 1H, =CH₂), 6.38 (s, 1H, =CH₂), 6.85 (d, 1H, J= 7.9 Hz, CH), 7.19-7.29 (m, 6H, ArH), 7.32-7.38 (m, 2H, ArH), 7.45 (t, 2H, J= 7.4 Hz, ArH), 7.92 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-d₆) δ= 52.8, 55.7, 123.3, 123.9, 124.8, 128.1, 128.3, 129.3, 129.4, 130.1, 130.5, 133.8, 138.1, 139.7, 140.4, 166.4, 181.3; mass (ES+) m/z= 361.1 (M⁺+1), 363.0 (M⁺+3). Anal. Calcd. for C₁₈H₁₇ClN₂O₂S (Exact mass: 360.0699); C, 59.91; H, 4.75; N, 7.76; Found C, 59.69; H, 4.63; N, 7.58.

N-[1-(2-Chlorophenyl)-2-cyano-allyl]-3-N'-phenyl-thiourea (4.2dA). 77 % as a white solid (1.07 g from 1.0 g); Rf= 0.21 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1635 (CS), 2210 (CN), 3357 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ= 5.85 (s, 1H, =CH₂), 6.10 (s, 1H, =CH₂), 6.71-6.75 (m, 2H, CH and NH), 7.26-7.48 (m, 9H, ArH), 8.07 (s, 1H, NH); ¹³C NMR (50 MHz, CDCl₃ + DMSO-d₆) δ= 56.0, 116.4, 121.5, 122.5, 124.0, 126.6, 127.7, 128.1, 129.1, 129.3, 131.4, 132.8, 134.3, 138.3, 180.3; mass (ES+) m/z= 328.1 (M⁺+1), 330.1 (M⁺+3). Anal. Calcd. for C₁₇H₁₄ClN₃S (Exact mass: 327.0597); C, 62.28; H, 4.30; N, 12.82; Found C, 62.28; H, 4.30; N, 12.82.
Methyl 2-[(2-fluorophenyl)(3-phenylthiourea) methyl]acrylate (4.1eA). 80 % as a white solid (0.55 g from 0.50 g), mp 116-118 °C; R_f = 0.27 (hexanes: EtOAc, 80:20, v/v); ν_max (KBr) 1711 (CO_2Me), 3347 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl_3) δ = 3.64 (s, 3H, OCH_3), 5.97 (s, 1H, =CH_2), 6.33 (s, 1H, =CH_2), 6.81 (d, 1H, J = 8.6 Hz, CH), 7.01-7.10 (m, 2H, ArH and NH), 7.21-7.34 (m, 5H, ArH), 7.40-7.48 (m, 3H, ArH); 13C NMR (50 MHz, CDCl_3 + DMSO-d_6) δ = 51.7, 52.0, 115.6 (J = 21.4 Hz), 122.8 (J = 22.1 Hz), 124.5 (J = 3.3 Hz), 126.6, 126.9, 128.4, 128.7, 129.0 (J = 3.7 Hz), 129.8 (J = 8.1 Hz), 139.1, 139.6, 157.4, 165.5, 180.3; mass (ES+) m/z = 345.0 (M⁺+1). Anal. Calcd. for C_{18}H_{17}FN_2O_2S (Exact mass: 344.0995); C, 62.77; H, 4.98; N, 8.13; Found C, 62.59; H, 4.99; N, 8.16.

1-[2-Cyano-1-(2-fluorophenyl)allyl]-3-phenylthiourea (4.2eA). 85 % as a white solid (1.2 g from 1.0 g), mp 127-129 °C; R_f = 0.26 (hexanes: EtOAc, 80:20, v/v); ν_max (KBr) 1624 (CS), 2225 (CN), 3402 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl_3) δ = 5.89 (s, 1H, =CH_2), 6.07 (s, 1H, =CH_2), 6.60-6.74 (m, 2H, CH and NH), 7.04-7.52 (m, 9H, ArH), 7.97 (s, 1H, NH); 13C NMR (50 MHz, CDCl_3 + DMSO-d_6) δ = 53.9, 115.1, 115.6, 116.5, 122.2, 122.9, 124.2 (J = 15.4 Hz), 128.0, 128.6, 130.0, 130.7, 138.3, 159.7 (J = 246.5 Hz), 180.5; mass (ES+) m/z = 312.0 (M⁺+1). Anal. Calcd. for C_{17}H_{14}FN_3S (Exact mass: 311.0892); C, 65.57; H, 4.53; N, 13.49; Found C, 65.55; H, 4.67; N, 13.39.

Methyl 2-[(4-chlorophenyl)(3-phenylthiourea) methyl]acrylate (4.1fA). 79 % as a white solid (1.02 g from 1.0 g), mp 65-67 °C; R_f = 0.24 (hexanes: EtOAc, 70:30, v/v); ν_max (KBr) 1658 (CS), 1710 (CO_2Me), 3332 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl_3) δ = 3.60 (s, 3H, OCH_3), 6.04 (s, 1H, =CH_2), 6.41 (s, 1H, =CH_2), 6.62 (d, 1H, J = 8.9 Hz, CH), 7.15 (d, 2H, J = 8.4 Hz, ArH and NH), 7.21-7.34 (m, 5H, ArH), 7.44 (t, 3H, J = 7.2 Hz, ArH), 7.91 (s, 1H, NH); 13C NMR (50 MHz, CDCl_3) δ = 52.2, 60.5, 125.0, 125.1, 127.5, 127.6, 128.9, 129.6, 130.2, 133.5, 136.0, 136.6, 137.6, 137.8, 166.3, 180.2; mass (ES+) m/z = 361.1 (M⁺+1), 363.1 (M⁺+3). Anal. Calcd. for C_{18}H_{17}ClN_2O_2S (Exact mass: 360.0699); C, 59.91; H, 4.75; N, 7.76; Found C, 59.63; H, 4.46; N, 7.43.

Methyl 2-[(4-chlorophenyl)(3-(4-chlorophenyl)thiourea) methyl]acrylate (4.1fB). 89 % as a white solid (1.3 g from 1.0 g), mp 186-188 °C; R_f = 0.25 (hexanes: EtOAc, 70:30, v/v); ν_max (KBr) 1649 (CS), 1734 (CO_2Me), 3358 (NH) cm⁻¹; ¹H NMR (300 MHz, CDCl_3) δ = 3.65 (s, 3H, OCH_3), 6.05 (s, 1H, =CH_2), 6.41 (s, 1H, =CH_2), 6.61 (d, 1H, J = 8.9 Hz, CH), 7.13-7.18 (m, 4H, ArH and NH), 7.26-7.29 (m, 2H, ArH), 7.39-7.42 (m, 3H, ArH), 7.86 (s, 1H, NH); 13C NMR (50 MHz, CDCl_3+ DMSO-d_6) δ = 51.7, 51.1, 123.9, 127.0, 128.0, 128.2, 128.5, 132.0, 138.3, 138.7, 139.1, 165.3, 180.1; mass (ES+) m/z = 395.1 (M⁺+1), 397.2 (M⁺+3). Anal. Calcd. for C_{18}H_{17}ClN_2O_2S (Exact mass: 394.0310); C, 54.69; H, 4.08; N, 7.09; Found C, 54.82; H, 4.16; N, 7.01.
1-(4-Chlorophenyl)-3-(1-(4-chlorophenyl)-2-cyanoallyl)thiourea (4.2fB). 80 % as a white solid (0.31 g from 0.25 g), mp 126-128 °C; Rf = 0.23 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1641 (CS), 2223(CN), 3410 (NH) cm-1; 1H NMR (200 MHz, CDCl3) δ= 6.03 (s, 1H, =CH2), 6.16 (s, 1H, =CH2), 6.39-6.50 (m, 2H, CH and NH), 7.18-7.27 (m, 4H, ArH), 7.32-7.42 (M, 4H, ArH), 8.46 (s, 1H, NH); 13C NMR (50 MHz, CDCl3) δ= 60.2, 117.0, 122.2, 126.6, 129.7, 130.5, 133.5, 133.6, 134.3, 135.1, 180.6; mass (ES+) m/z = 362.1(M++1), 364.1 (M++3). Anal. Calcd. for C17H13Cl2N3S (Exact mass: 361.0207); C, 56.36; H, 3.62; N, 11.60; Found: C, 56.33; H, 3.47; N, 11.69.

Methyl 2-[(3,4-dichlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1gA). 79 % as a white solid (1.02 g from 1.0 g), mp 103-105 °C; Rf = 0.24 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1644 (CS), 1734 (CO2Me), 3369 (NH) cm-1; 1H NMR (300 MHz, CDCl3) δ= 3.62 (s, 3H, OCH3), 6.07 (s, 1H, =CH 2), 6.43 (s, 1H, =CH2), 6.64 (d, 1H, J= 8.9 Hz, CH), 7.04-7.08 (m, 1H, NH), 7.23-7.29 (m, 3H, ArH), 7.33-7.38 (m, 2H, ArH), 7.46 (t, 3H, J= 7.5 Hz, ArH), 7.98 (s, 1H, NH); 13C NMR (50 MHz, CDCl3) δ= 52.2, 59.7, 124.7, 124.9, 125.6, 127.1, 128.2, 129.9, 130.5, 131.5, 132.6, 136.2, 136.7, 137.1, 139.7, 166.0, 180.1; mass (ES+) m/z= 395.1 (M++1), 397.1 (M++3). Anal. Calcd. for C18H16Cl2N2O2S (Exact mass: 394.0310); C, 54.69; H, 4.08; N, 7.09; Found C, 54.43; H, 4.12; N, 7.00.

N-[2-Cyano-1-(3,4-dichloro-phenyl)-allyl]-3-N'-phenyl-thiourea (4.2gA). 76 % as a white solid (1.02 g from 1.0 g), mp 138-140 °C; Rf= 0.24 (hexanes: EtOAc, 70:30, v/v); νmax (KBr) 1641 (CS), 2209 (CN) cm-1; 1H NMR (300 MHz, CDCl3) δ= 6.06 (s, 1H, =CH2), 6.19 (s, 1H, =CH2), 6.32 (d, 1H, J= 8.2 Hz, CH), 6.48 (d, 1H, J= 8.4 Hz, NH), 7.11 (d, 1H, J= 8.3 Hz, ArH), 7.27 (d, 2H, J= 6.0 Hz, ArH), 7.35-7.39 (m, 2H, ArH), 7.44-7.50 (m, 3H, ArH), 7.97 (s, 1H, NH); 13C NMR (75 MHz, CDCl3) δ= 59.8, 116.7, 121.9, 125.5, 126.2, 128.2, 129.1, 130.6, 131.3, 133.3, 133.6, 133.8, 135.5, 180.7; mass (ES+) m/z= 362.0 (M++1), 364.0 (M++1). Anal. Calcd. for C17H13Cl2N3S (Exact mass: 361.0207); C, 56.36; H, 3.62; N, 11.60; Found C, 56.39; H, 3.77; N, 11.48.

Methyl (4R,5S)-2-anilino-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (syn-3.1aA). Rt= 4.0 min; Rf= 0.24 (hexanes: EtOAc, 80:20, v/v); 1H NMR (300 MHz, CDCl3) δ= 2.95-3.10 (m, 3H, CH and CH2), 3.65 (s, 3H, OCH3), 5.36 (brs, 1H, CH), 7.02 (brs, 2H, ArH), 7.25 (s, 6H, ArH), 7.35 (brs, 3H, ArH and NH). (The 1H-NMR data included for this compound is the one obtained by deducting the peaks for anti-isomer from the 1H-NMR of the mixture of syn and anti isomers)
Fig:S-1 $^1$H spectrum of Methyl (4$R$,5$R$)-2-anilino-4-phenyl-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate (3.1aA).

Fig:S-2 $^{13}$C spectrum of Methyl (4$R$,5$R$)-2-anilino-4-phenyl-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate (3.1aA).
Fig:S-3 $^1$H spectrum of Methyl (4R,5R)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (3.1aB).

Fig:S-4 $^{13}$C spectrum of Methyl (4R,5R)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (3.1aB).
Fig:S-5 $^1$H spectrum of Methyl (4R,5R)-2-(2-bromoanilino)-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (3.1aC)

Fig:S-6 $^{13}$C spectrum of Methyl (4R,5R)-2-(2-bromoanilino)-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (3.1aC).
Fig. S-7 $^1$H spectrum of (4R,5R)-2-anilino-4-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (3.2aA).

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Fig:S-14 $^{13}$C spectrum of Methyl 2-(phenyl(3-phenylthioureido)methyl)acrylate (4.1aA).
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Fig:S-18 $^1$H spectrum of N-[1-(2-bromophenyl)-2-cyanoallyl]-3-$N'$-phenylthiourea (4.2cA).
Fig:S-19 $^{13}$C spectrum of $N$-[1-(2-bromophenyl)-2-cyanoallyl]-3-$N'$-phenylthiourea (4.2cA).

Fig:S-20 $^1$H spectrum of Methyl 2-[(2-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1dA).
Fig:S-21 $^{13}$C spectrum of Methyl 2-[(2-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1dA).

Fig:S-22 $^1$H spectrum of $N$-[1-(2-Chloro-phenyl)-2-cyano-allyl]-3-$N'$-phenyl-thiourea (4.2dA).
Fig:S-23 $^{13}$C spectrum of $N$-[1-(2-Chloro-phenyl)-2-cyano-allyl]-3-$N'$-phenylthiourea (4.2dA).

Fig:S-24 $^1$H spectrum of Methyl 2-[(2-fluorophenyl)(3-phenylthioureido)methyl]acrylate (4.1eA).
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Fig:S-26 $^1$H spectrum of 1-[2-Cyano-1-(2-fluorophenyl)allyl]-3-phenylthiourea (4.2eA).
Fig:S-27 $^{13}$C spectrum of 1-[2-Cyano-1-(2-fluorophenyl)allyl]-3-phenylthiourea (4.2eA).

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Fig:S-29 $^{13}$C spectrum of Methyl 2-[(4-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1fA).

Fig:S-30 $^1$H spectrum of Methyl 2-[(4-chlorophenyl)(3-(4-chlorophenyl)thioureido)methyl]acrylate (4.1fB).
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Fig:S-32 $^1$H spectrum of 1-(4-Chlorophenyl)-3-(1-(4-chlorophenyl)-2-cyanoallyl)thiourea (4.2fB).
Fig:S-33 $^{13}$C spectrum of 1-(4-Chlorophenyl)-3-(1-(4-chlorophenyl)-2-cyanoallyl)thiourea (4.2fB).

Fig:S-34 $^1$H spectrum of Methyl 2-[(3,4-dichlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1gA).
Fig:S-35 $^{13}$C spectrum of Methyl 2-[(3,4-dichlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1gA).

Fig:S-36 $^1$H spectrum of N-[2-Cyano-1-(3,4-dichloro-phenyl)-allyl]-3-$N'$-phenyl-thiourea (4.2gA).
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Fig:S-38 $^1$H spectrum of (4$R$,5$R$)-Methyl 2-anilino-4-(4-methylphenyl)-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate (anti-3.1bA).
**Fig:S-39** $^{13}$C spectrum of $(4R,5R)$-Methyl 2-anilino-4-(4-methylphenyl)-5,6-dihydro-$4H$-1,3-thiazine-5-carboxylate ($anti$-$3.1bA$).

**Fig:S-40** $^1$H spectrum of $(4R,5R)$-2-(Phenylamino)-4-(4-methylphenyl)-5,6-dihydro-$4H$-1,3-thiazine-5-carbonitrile ($anti$-$3.2bA$).
Fig:S-41 $^{13}$C spectrum of $(4R,5R)$-2-(Phenylamino)-4-(4-methylphenyl)-5,6-dihydro-4$H$-1,3-thiazine-5-carbonitrile ($anti$-3.2bA).

Fig:S-42 $^1$H spectrum of Methyl $(4R,5S)$-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate ($syn$-3.1cA).
Fig:S-43 $^{13}$C spectrum of Methyl (4$R$,5$S$)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate (syn-3.1cA).

Fig:S-44 $^1$H spectrum of (4$R$,5$S$)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4$H$-1,3-thiazine-5-carbonitrile (syn-3.2cA).
Fig:S-45 $^{13}$C spectrum of (4R,5S)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (syn-3.2cA).

Fig:S-46 $^1$H spectrum of Methyl (4R,5S)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (syn-3.1dA).
Fig:S-47 $^{13}$C spectrum of Methyl (4R,5S)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (syn-3.1dA).

Fig:S-48 $^1$H spectrum of (4R,5S)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (syn-3.2dA).
Fig:S-49 $^{13}\text{C}$ spectrum of (4$R$,5$S$)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-$4H$-1,3-thiazine-5-carbonitril (syn-3.2dA).

Fig:S-50 $^1\text{H}$ spectrum of (4$R$,5$S$)-Methyl 4-(2-fluorophenyl)-2-(phenylamino)-5,6-dihydro-$4H$-1,3-thiazine-5-carboxylate (syn-3.1eA).
Fig:S-51 $^{13}$C spectrum of (4R,5S)-Methyl 4-(2-fluorophenyl)-2-(phenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (syn-3.1eA).

Fig:S-52 $^1$H spectrum of (4R,5S)-2-anilino-4-(2-fluorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (syn-3.2eA).
Fig:S-53 $^{13}$C spectrum of (4R,5S)-2-anilino-4-(2-fluorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (syn-3.2eA).

Fig:S-54 $^1$H spectrum of Methyl (4R,5R) 4-(4-chlorophenyl)-2-(phenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1fA).
Fig: S-55 $^{13}$C spectrum of Methyl (4R,5R) 4-(4-chlorophenyl)-2-(phenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1fA).

Fig: S-56 $^1$H spectrum of (4R,5R)-2-anilino-4-(4-chlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2fA).
Fig:S-57 $^{13}$C spectrum of (4R,5R)-2-anilino-4-(4-chlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2fA).
Fig:S-58 $^1$H spectrum of Methyl (4R,5R)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1gA).

Fig:S-59 $^{13}$C spectrum of Methyl (4R,5R)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1gA).

Fig:S-60 $^1$H spectrum of (4R,5R)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2gA).
Fig:S-61 $^{13}$C spectrum of (4R,5R)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2gA).

Fig:S-62 $^1$H spectrum of (4R,5R)-4-(4-Methoxyphenyl)-2-(phenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2hA).
Fig:S-63 $^{13}$C spectrum of (4$R$,5$R$)-4-(4-Methoxyphenyl)-2-(phenylamino)-5,6-dihydro-4$H$-1,3-thiazine-5-carbonitrile (anti-3.2hA).

Fig:S-64 $^1$H spectrum of (4$R$,5$R$)-Methyl 2-(2-bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4$H$-1,3-thiazine-5-carboxylate (anti-3.1bC).
Fig:S-65 $^{13}$C spectrum of (4R,5R)-Methyl 2-(2-bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1bC).

Fig:S-66 $^1$H spectrum of (4R,5R)-2-(2-Bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2bC).
Fig:S-67 $^{13}$C spectrum of (4$R$,5$R$)-2-(2-Bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-$4H$-1,3-thiazine-5-carbonitrile (anti-3.2bC).

Fig:S-68 $^1$H spectrum of (4$R$,5$R$)-Methyl 4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-$4H$-1,3-thiazine-5-carboxylate (anti-3.1fB).
Fig:S-69 $^{13}\text{C}$ spectrum of (4R,5R)-Methyl 4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (anti-3.1fB).

Fig:S-70 $^1\text{H}$ spectrum of (4R,5R)-4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2fB).
Fig:S-71 $^{13}$C spectrum of (4$R$,5$R$)-4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (anti-3.2fB).