Electronic Supplementary Material (ESI) for RSC Advances

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

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Contents

Methyl 2-[phenyl(3-phenylthioureido)methyl]acrylate (4.1aA). 70 % as a white solid (0.98 g from 1.0 g), mp 119-121 ^{o}C; R_t= 4.8 min; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1642 (CS), 1734 (CO_2Me), 3369 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.59 (s, 3H, OCH_3), 6.03 (s, 1H, =CH_2), 6.41 (s, 1H, =CH_2), 6.67 (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); ^{13}C NMR (75 MHz, $CDCl_3$) 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 $C_{18}H_{18}N_2O_2S$ (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 ^{o}C; R_f= 0.21 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1637 (CS), 2209 (CN) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ= 5.88 (s, 1H, =CH_2), 6.13 (s, 1H, =CH_2), 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); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ= 59.4, 117.1, 122.1, 123.8, 124.1, 125.8, 127.9, 129.1, 130.1, 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 $C_{17}H_{14}BrN_3S$ (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-phenylthioureido)methyl]acrylate (4.1dA). 69 % as a white solid (0.9 g from 1.0 g), mp 113-115 ^{o}C; R_f= 0.22 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1631 (CS), 1731 (CO_2Me), 3358 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.65 (s, 3H, OCH_3), 5.97 (s, 1H, =CH_2), 6.38 (s, 1H, =CH_2), 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); ^{13}C NMR (50 MHz, DMSO-d_6) 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 $C_{18}H_{17}ClN_2O_2S$ (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); R_f= 0.21 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1635 (CS), 2210 (CN), 3357 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.85 (s, 1H, =CH_2), 6.10 (s, 1H, =CH_2), 6.71-6.75 (m, 2H, CH and NH), 7.26-7.48 (m, 9H, ArH), 8.07 (s, 1H, NH); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6) 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 $C_{17}H_{14}ClN_3S$ (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-phenylthioureido)methyl]acrylate (4.1eA). 80 % as a white solid (0.55 g from 0.50 g), mp 116-118 ^{o}C; R_f = 0.27 (hexanes: EtOAc, 80:20, v/v); ν_{max} (KBr) 1711 (CO_2Me), 3347 (NH) cm^{-1}; ^{1}H 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), 8.00 (s, 1H, ArH); ^{13}C 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 ^{o}C; R_f = 0.26 (hexanes: EtOAc, 80:20, v/v); ν_{max} (KBr) 1624 (CS), 2225 (CN), 3402 (NH) cm^{-1}; ^{1}H 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); ^{13}C 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-phenylthioureido)methyl]acrylate (4.1fA). 79 % as a white solid (1.02 g from 1.0 g), mp 65-67 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1658 (CS), 1710 (CO_2Me), 3332 (NH) cm^{-1}; ^{1}H 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); ^{13}C 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)thioureido)methyl]acrylate (4.1fB). 89 % as a white solid (1.3 g from 1.0 g), mp 186-188 ^{o}C; R_f= 0.25 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1649 (CS), 1734 (CO_2Me), 3358 (NH) cm^{-1}; ^{1}H 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); ^{13}C 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 ^{o}C; R_f= 0.23 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1641 (CS), 2223(CN), 3410 (NH) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ= 6.03 (s, 1H, =CH_2), 6.16 (s, 1H, =CH_2), 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); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 60.2, 117.0, 122.2, 126.6, 129.7, 130.5, 133.5, 133.6, 134.3, 135.0, 135.1, 180.6; mass (ES+) *m/z*= 362.1(M^++1), 364.1 (M^++3). Anal. Calcd. for $C_{17}H_{13}Cl_2N_3S$ (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 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1644 (CS), 1734 (CO_2Me), 3369 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.62 (s, 3H, OCH_3), 6.07 (s, 1H, =CH_2), 6.43 (s, 1H, =CH_2), 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); ^{13}C NMR (50 MHz, $CDCl_3$) 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 $C_{18}H_{16}Cl_2N_2O_2S$ (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 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1641 (CS), 2209 (CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 6.06 (s, 1H, =CH_2), 6.19 (s, 1H, =CH_2), 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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, 136.9, 180.7; mass (ES+) m/z= 362.0 (M^++1), 364.0 (M^++1). Anal. Calcd. for $C_{17}H_{13}Cl_2N_3S$ (Exact mass: 361.0207); C, 56.36; H, 3.62; N, 11.60; Found C, 56.39; H, 3.77; N, 11.48.

Methyl (4*R*,5*S*)-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1aA). R_t= 4.0 min; R_f= 0.24 (hexanes: EtOAc, 80:20, v/v); ^{1}H NMR (300 MHz, $CDCl_3$) δ= 2.95-3.10 (m, 3H, CH and CH_2), 3.65 (s, 3H, OCH_3), 5.36 (brs, 1H, CH), 7.02 (brs, 2H, ArH), 7.25 (s, 6H, ArH), 7.35 (brs, 3H, ArH and NH). (The ^{1}H-NMR data included for this compound is the one obtained by deducting the peaks for *anti*-isomer from the ^{1}H-NMR of the mixture of *syn* and *anti* isomers)

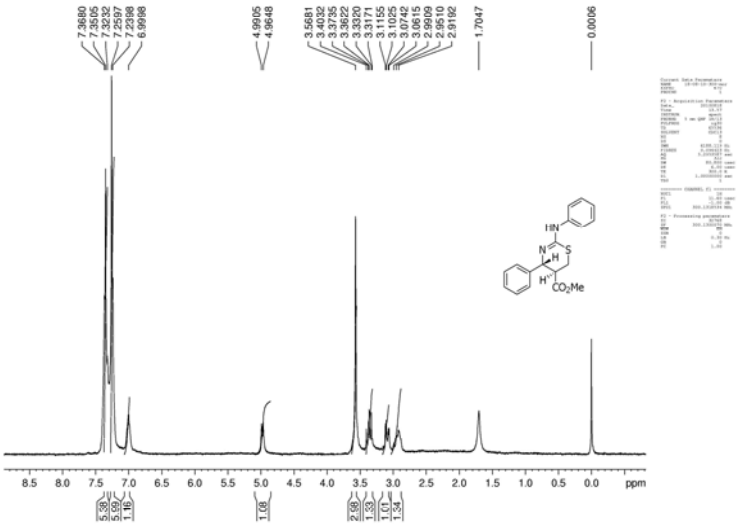

Fig:S-1 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aA).

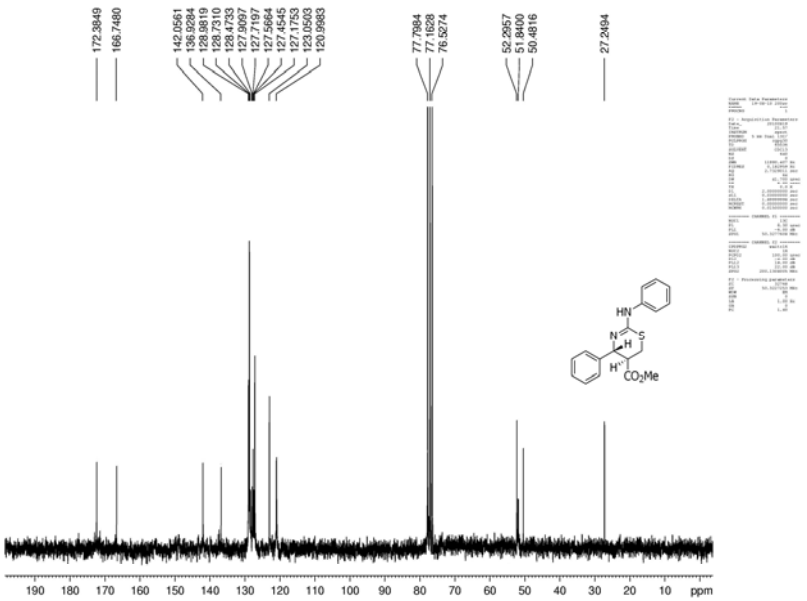

Fig:S-2 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aA).

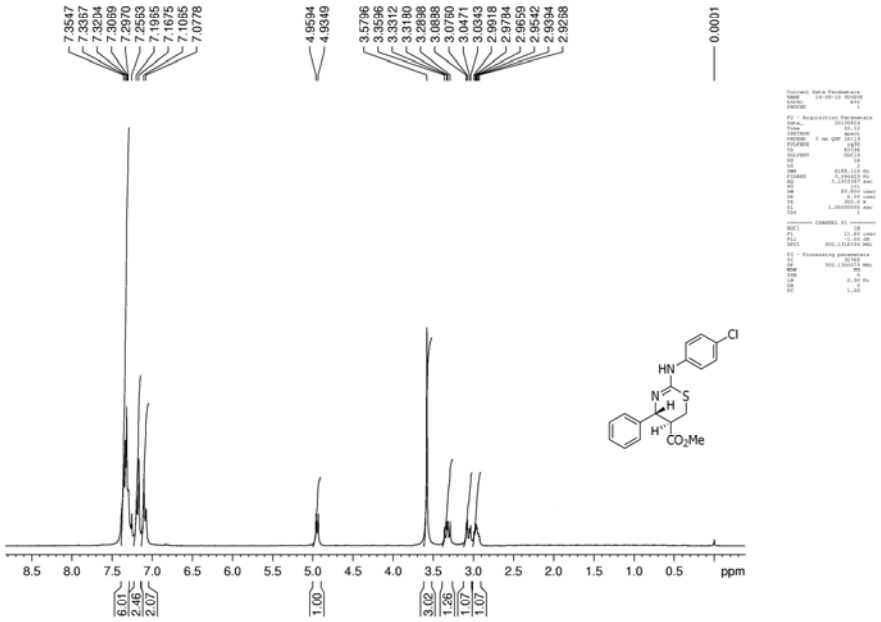

Fig:S-3 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aB).

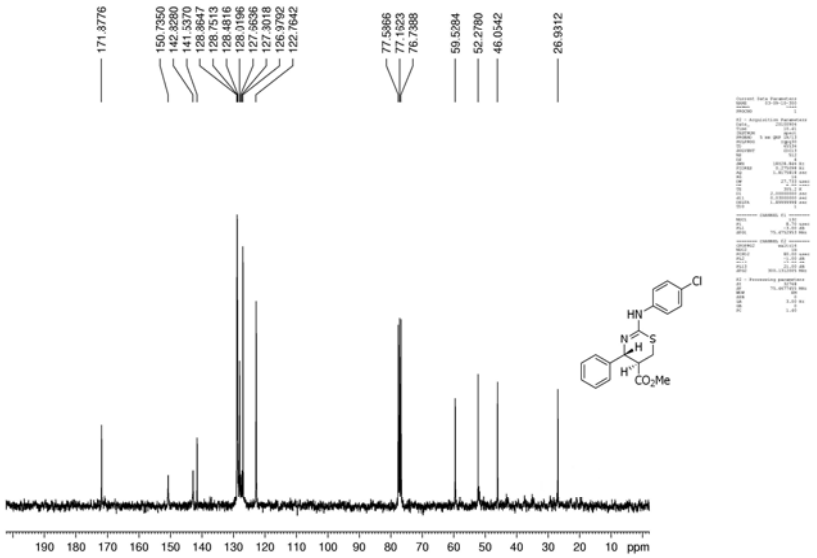

Fig:S-4 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aB).

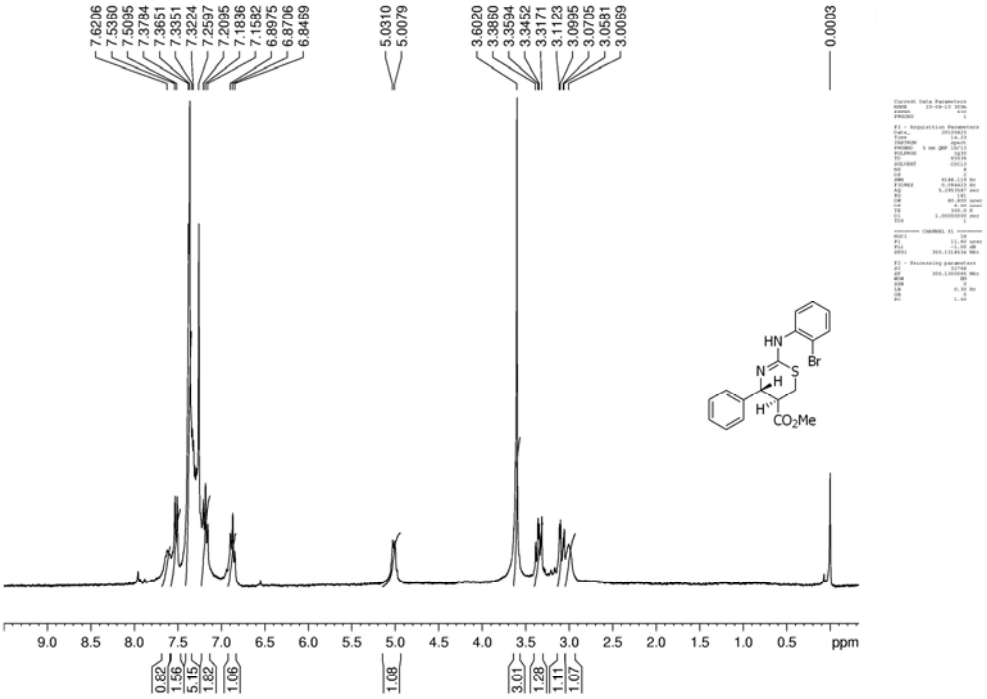

Fig:S-5 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-(2-bromoanilino)-4-phenyl-5,6- dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aC)

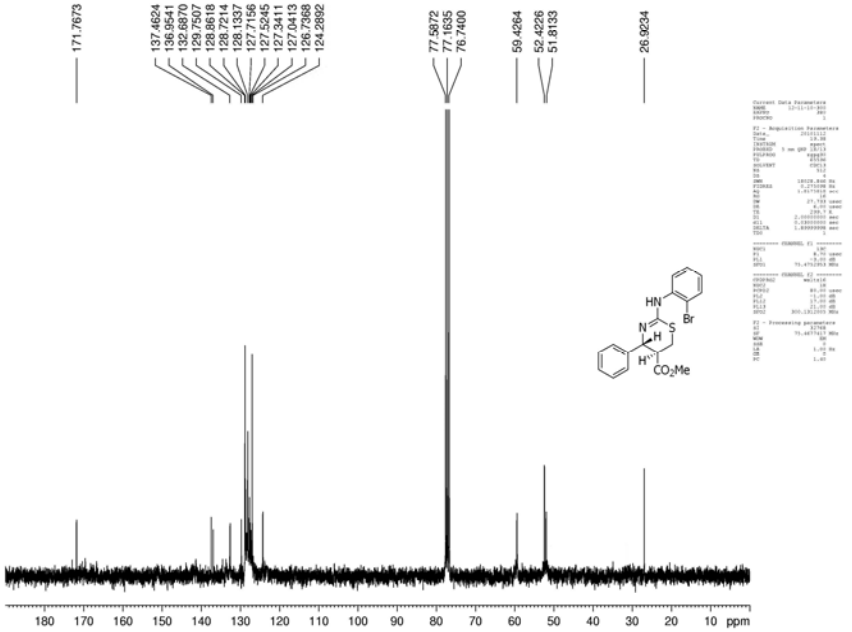

Fig:S-6 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-(2-bromoanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (3.1aC).

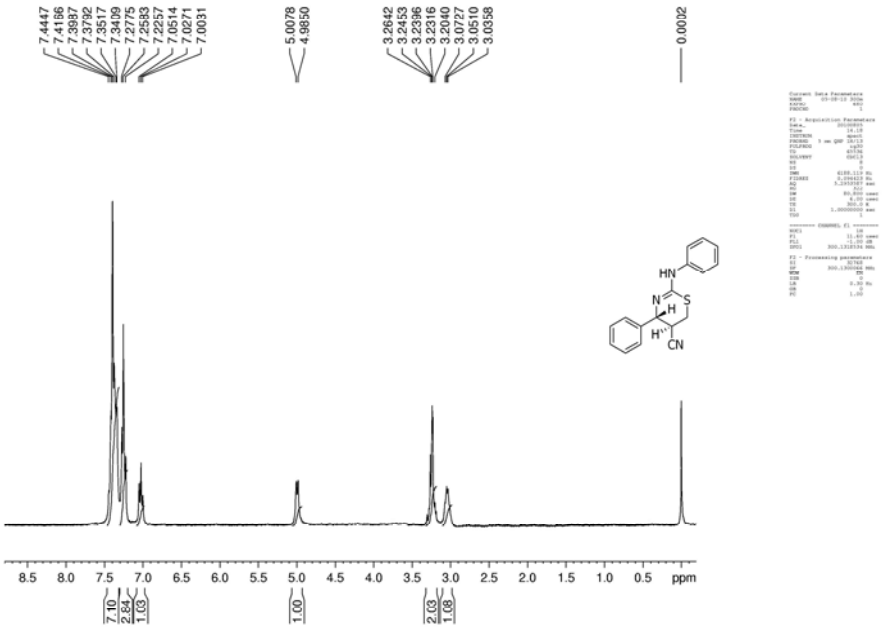

Fig:S-7 ^{1}H spectrum of (4*R*,5*R*)-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aA).

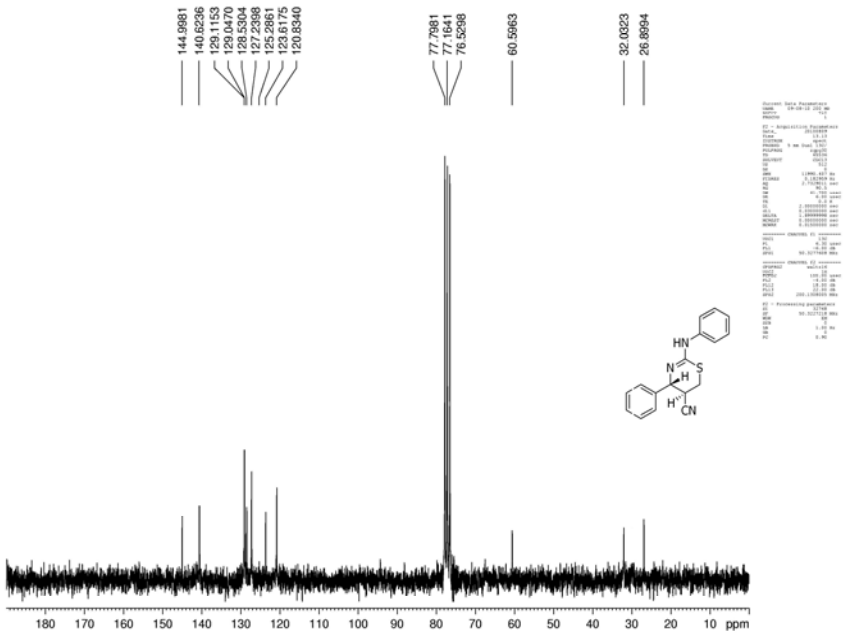

Fig:S-8 ^{13}C spectrum of (4*R*,5*R*)-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aA).

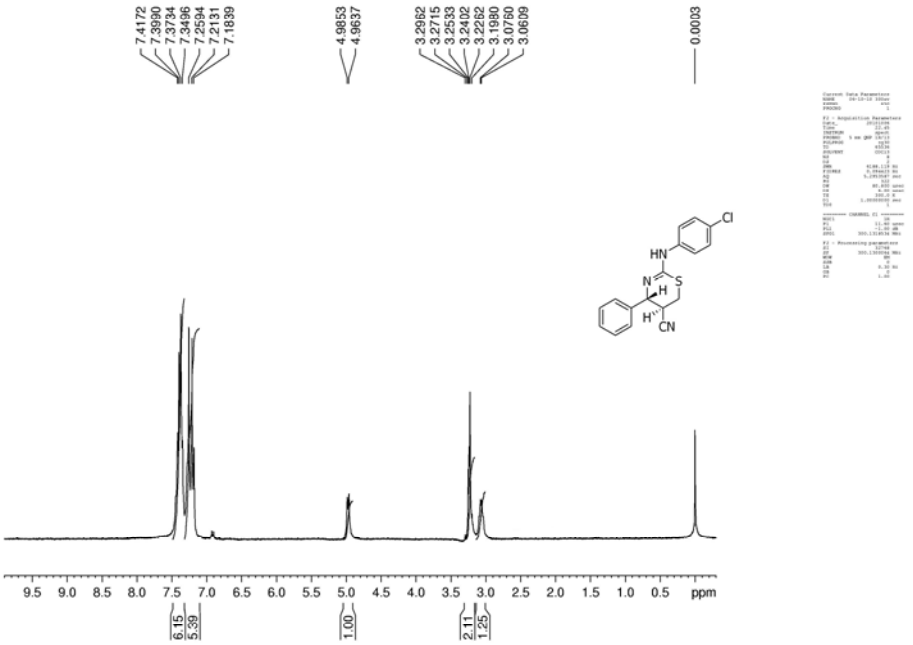

Fig:S-9 ^{1}H spectrum of (4*R*,5*R*)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aB).

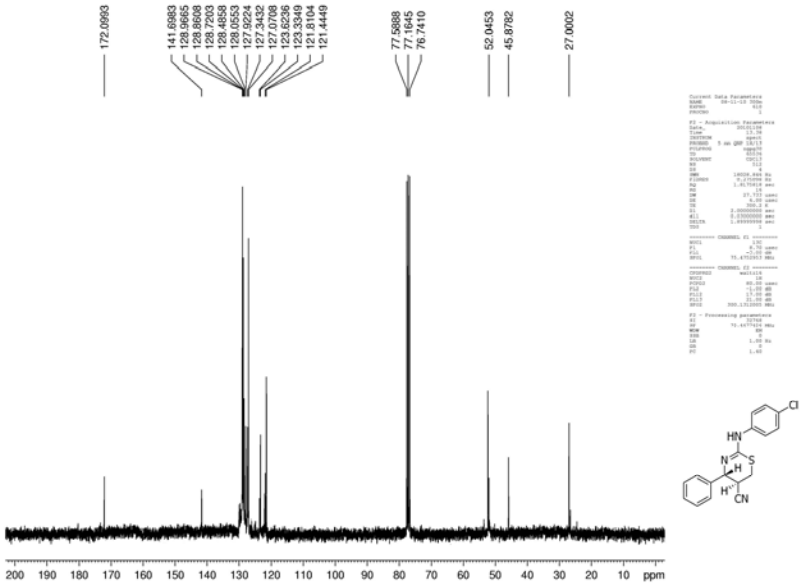

Fig:S-10 ^{13}C spectrum of (4*R*,5*R*)-2-(4-chloroanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aB).

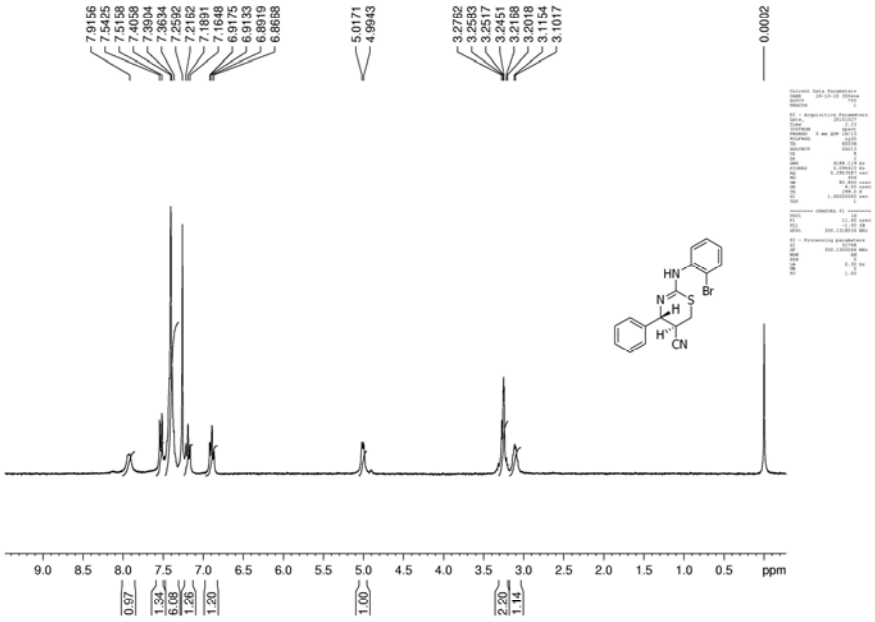

Fig:S-11 ^{1}H spectrum of (4*R*,5*R*)-2-(2-bromoanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aC).

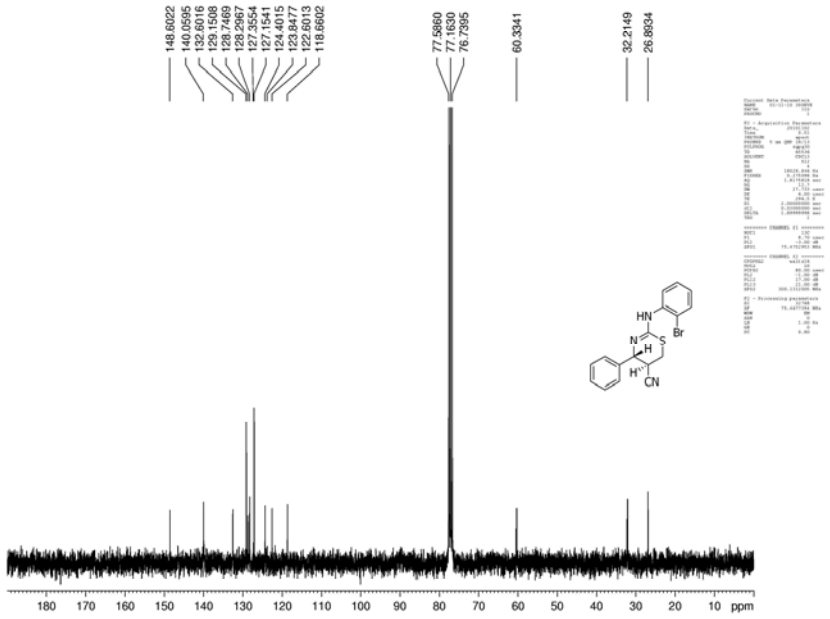

Fig:S-12 ^{13}C spectrum of (4*R*,5*R*)-2-(2-bromoanilino)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (3.2aC).

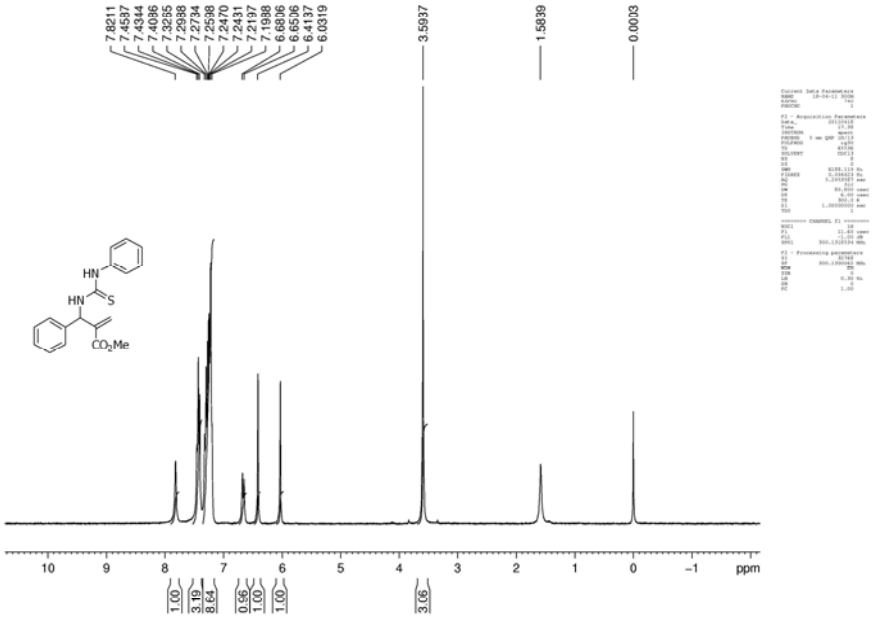

Fig:S-13 ^{1}H spectrum of Methyl 2-(phenyl(3-phenylthioureido)methyl)acrylate (4.1aA).

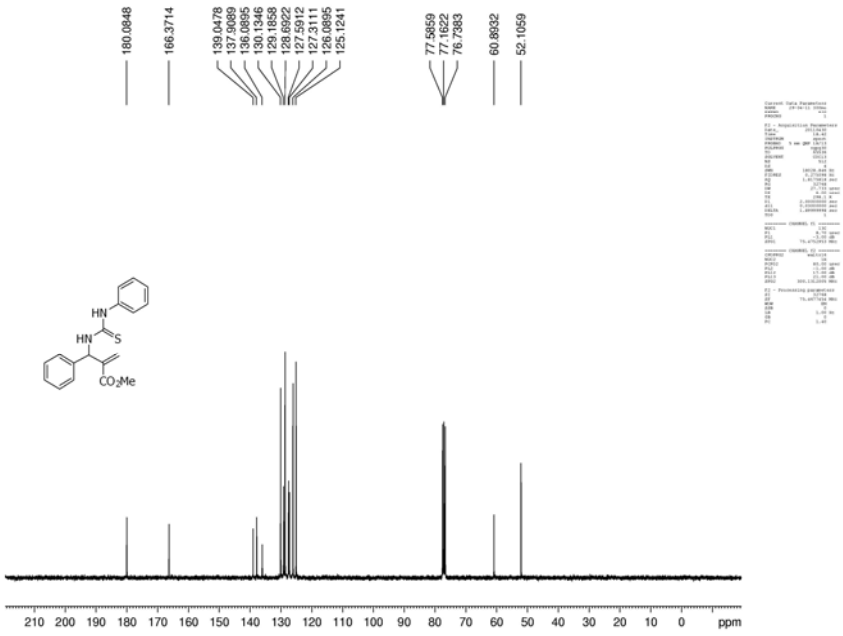

Fig:S-14 ^{13}C spectrum of Methyl 2-(phenyl(3-phenylthioureido)methyl)acrylate (4.1aA).

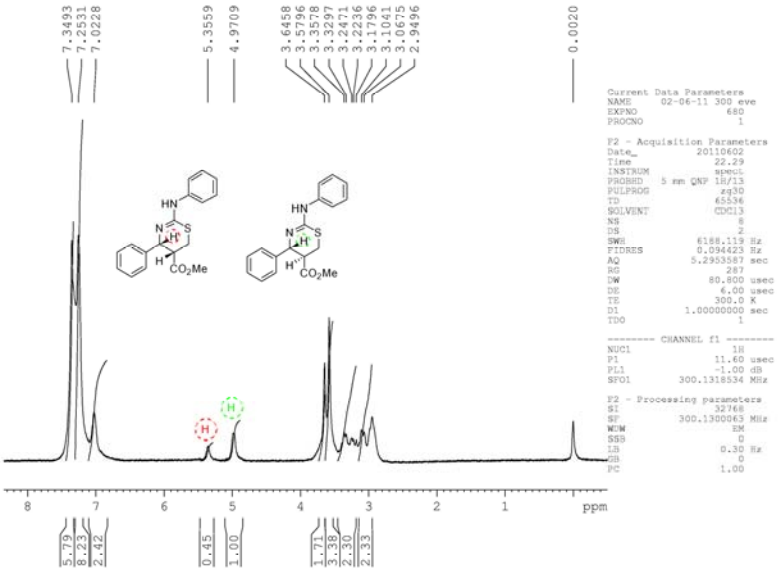

Fig:S-15 ^{1}H spectrum of Methyl-2-anilino-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* and *anti* as mixture) (3.1aA).

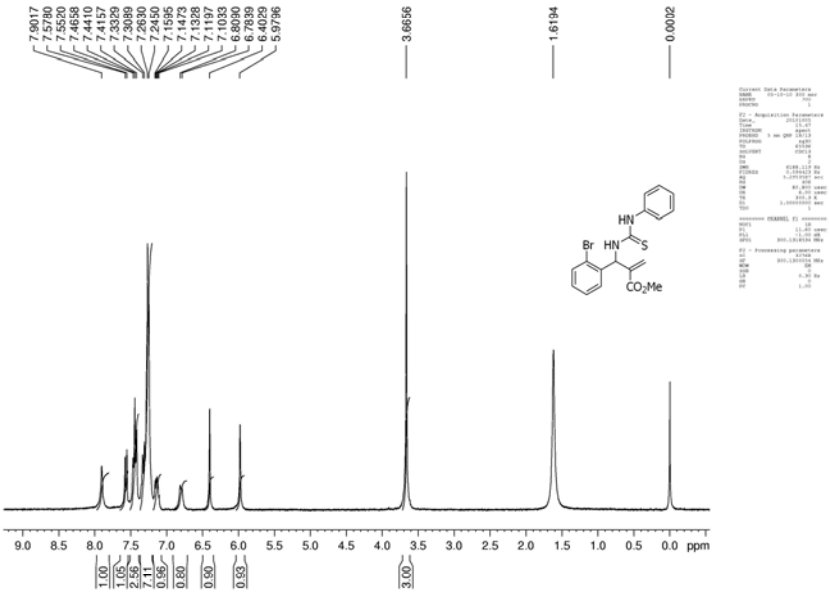

Fig:S-16 ^{1}H spectrum of Methyl 2-[(2-bromophenyl)(3-phenylthioureido)methyl]acrylate (4.1cA).

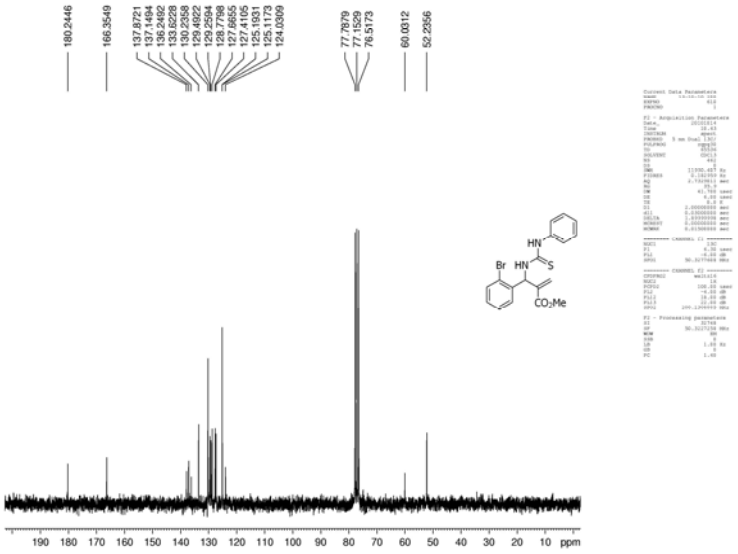

Fig:S-17 ^{13}C spectrum of Methyl 2-[(2-bromophenyl)(3-phenylthioureido)methyl]acrylate (4.1cA).

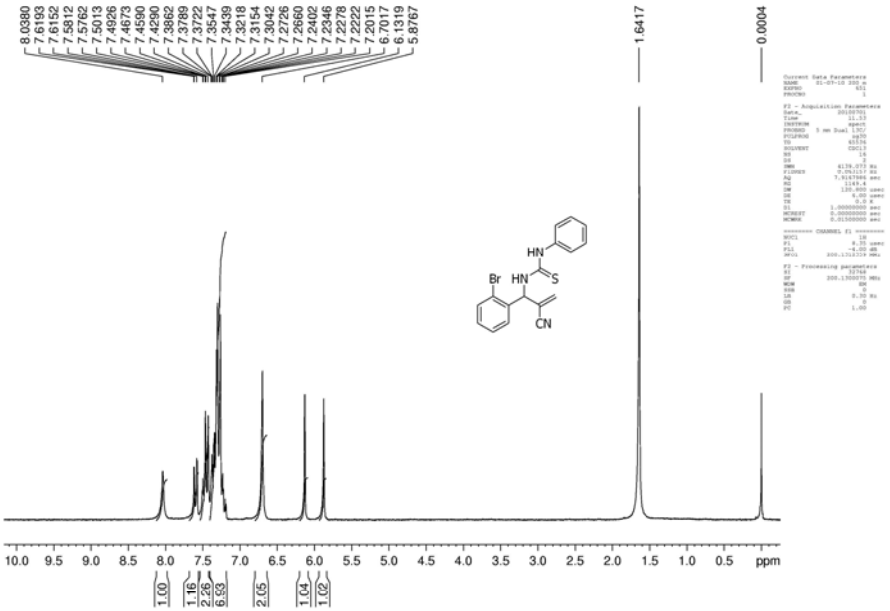

Fig:S-18 ^{1}H spectrum of *N*-[1-(2-bromophenyl)-2-cyanoallyl]-3-*N*'-phenylthiourea (4.2cA).

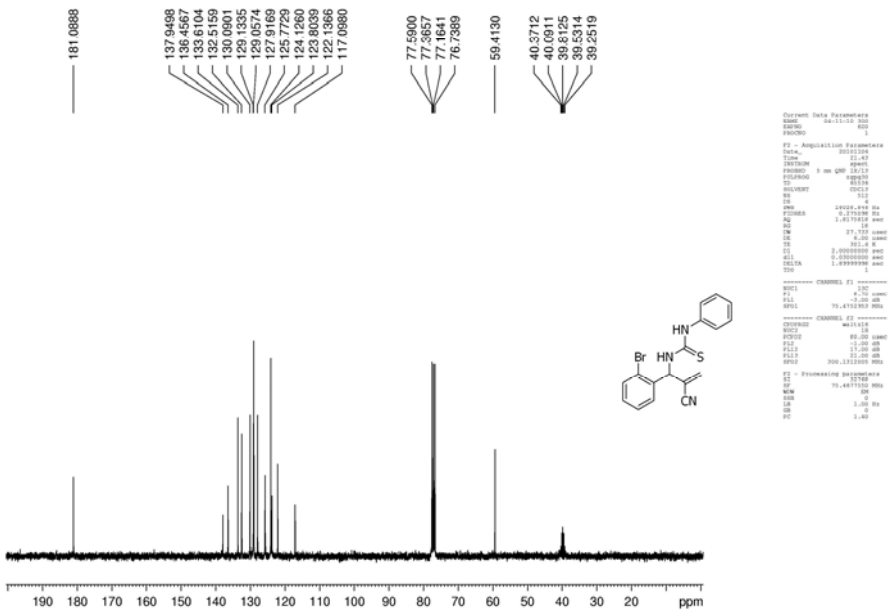

Fig:S-19 ^{13}C spectrum of *N*-[1-(2-bromophenyl)-2-cyanoallyl]-3-*N*'-phenylthiourea (4.2cA).

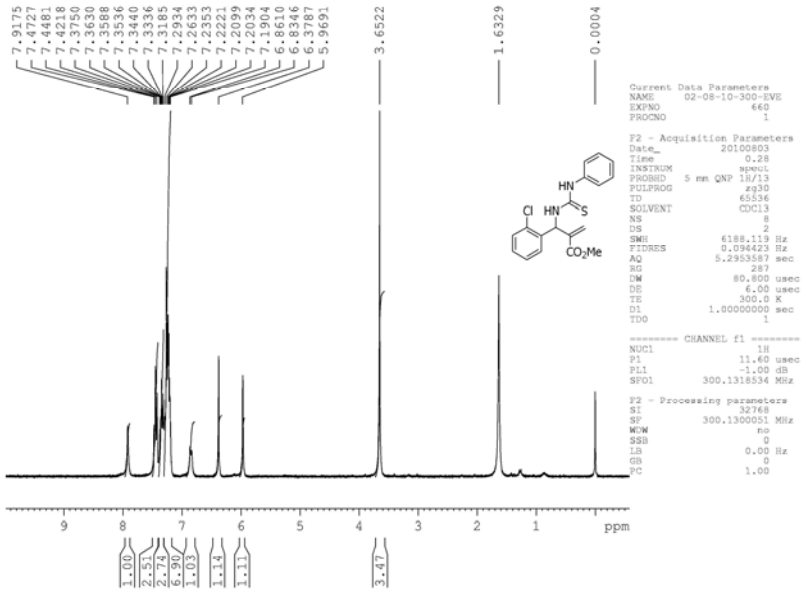

Fig:S-20 ^{1}H spectrum of Methyl 2-[(2-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1dA).

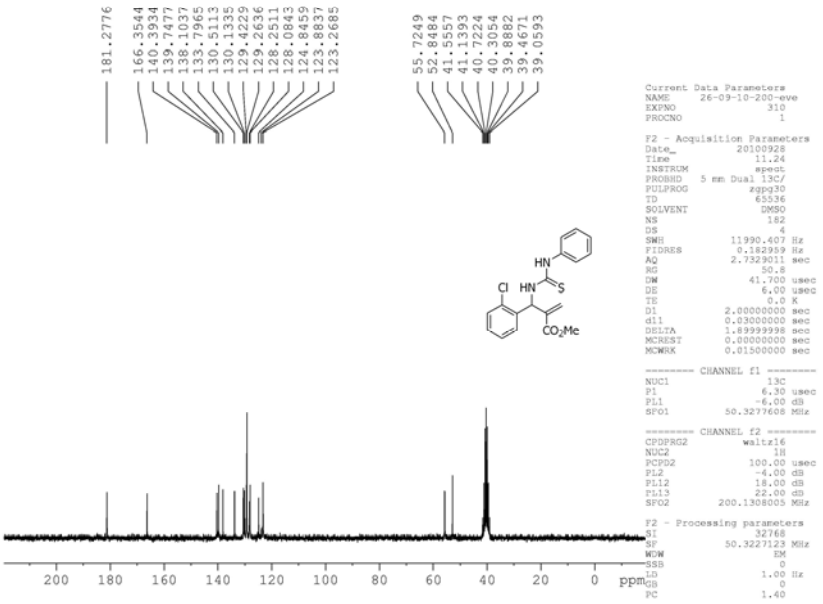

Fig:S-21 ^{13}C spectrum of Methyl 2-[(2-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1dA).

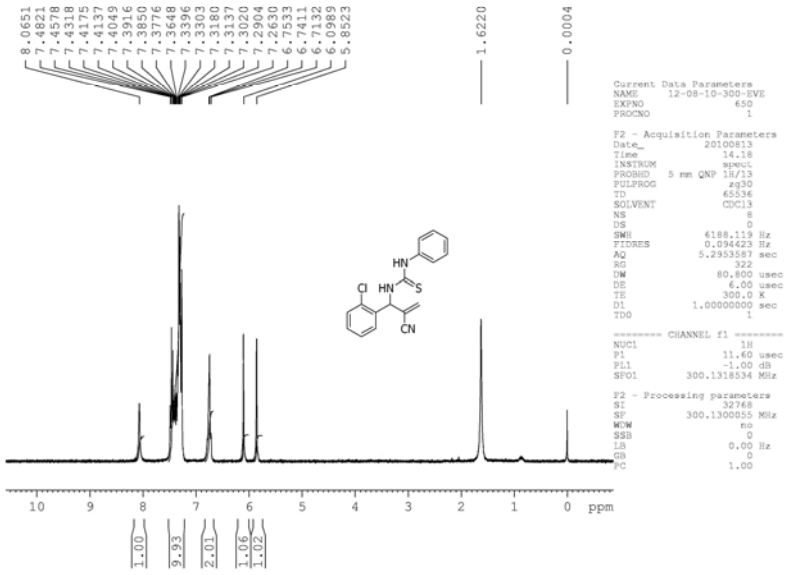

Fig:S-22 ^{1}H spectrum of *N*-[1-(2-Chloro-phenyl)-2-cyano-allyl]-3-*N*'-phenyl-thiourea (4.2dA).

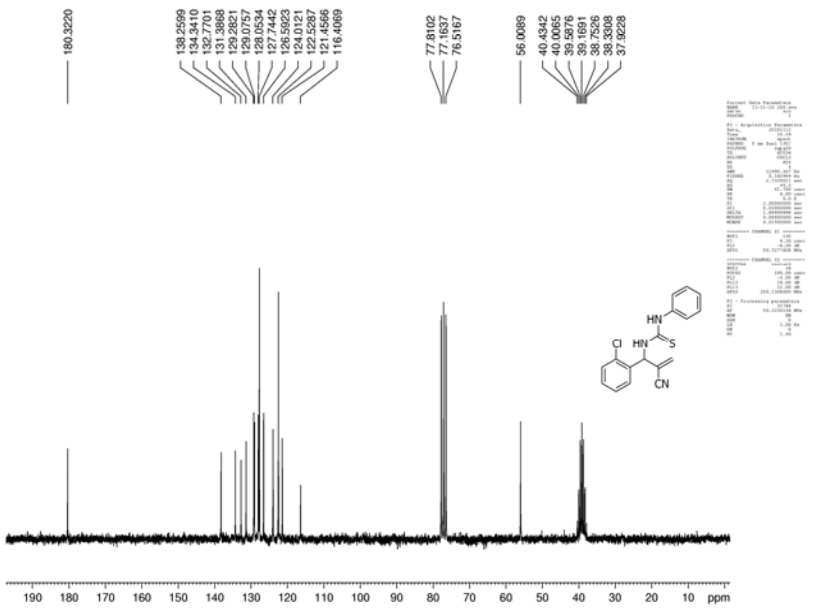

Fig:S-23 ^{13}C spectrum of *N*-[1-(2-Chloro-phenyl)-2-cyano-allyl]-3-*N*'-phenyl-thiourea (4.2dA).

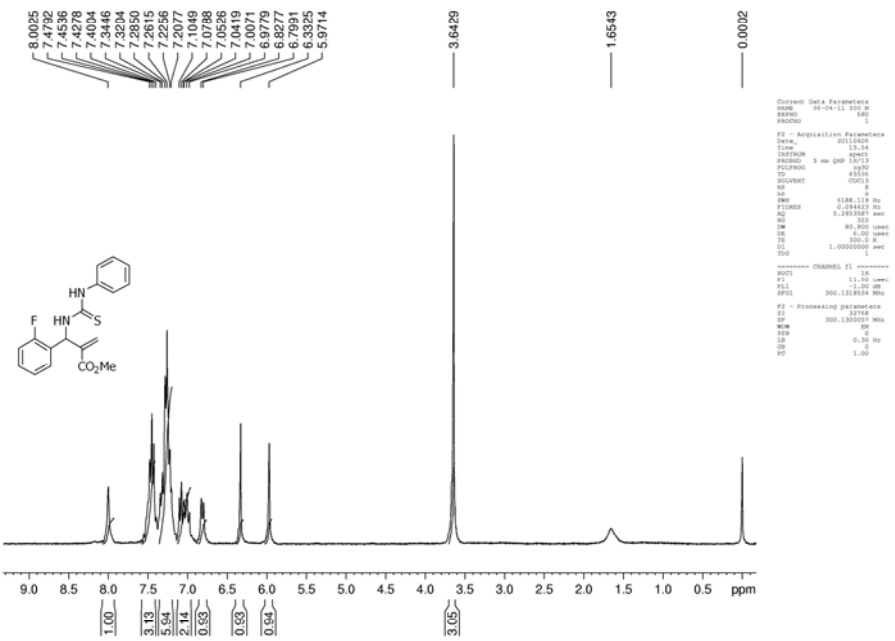

Fig:S-24 ^{1}H spectrum of Methyl 2-[(2-fluorophenyl)(3-phenylthioureido)methyl]acrylate (4.1eA).

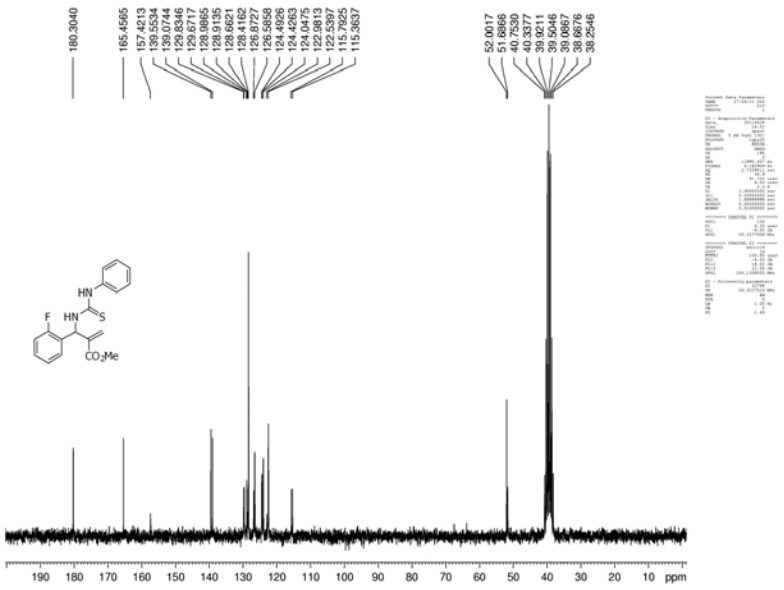

Fig:S-25 ^{13}C spectrum of Methyl Methyl 2-[(2-fluorophenyl)(3-phenylthioureido)methyl]acrylate (4.1eA).

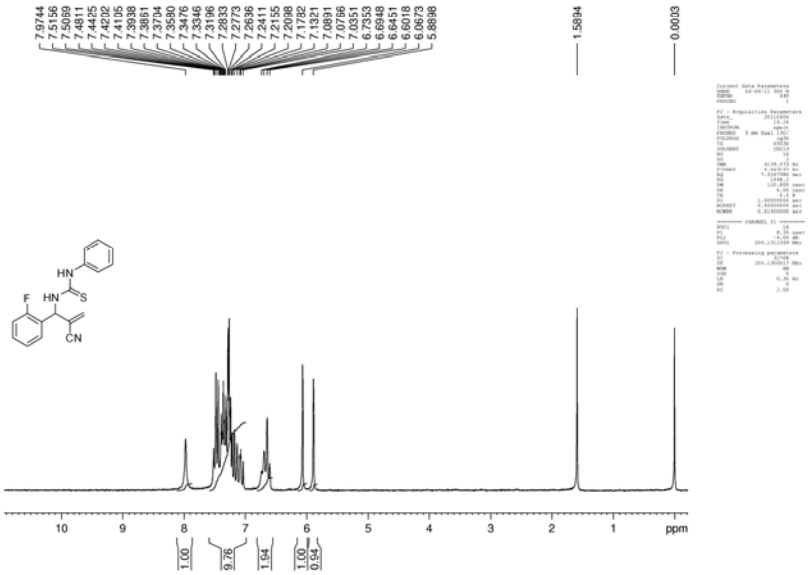

Fig:S-26 ^{1}H spectrum of 1-[2-Cyano-1-(2-fluorophenyl)allyl]-3-phenylthiourea (4.2eA).

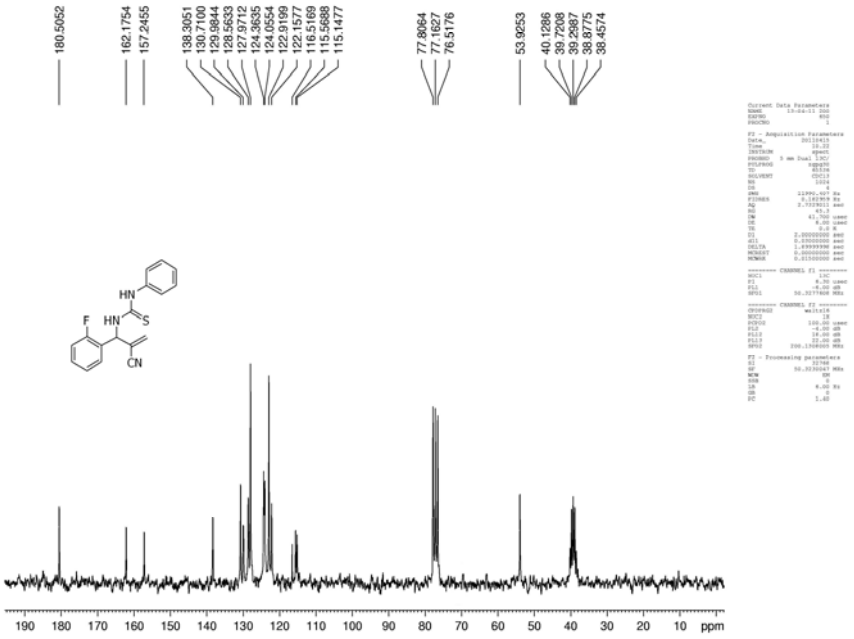

Fig:S-27 ^{13}C spectrum of 1-[2-Cyano-1-(2-fluorophenyl)allyl]-3-phenylthiourea (4.2eA).

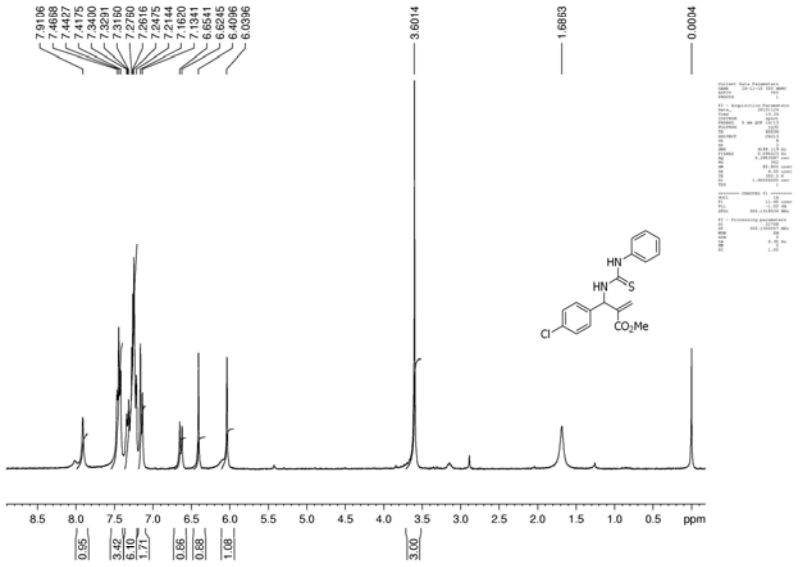

Fig:S-28 ^{1}H spectrum of Methyl 2-[(4-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1fA).

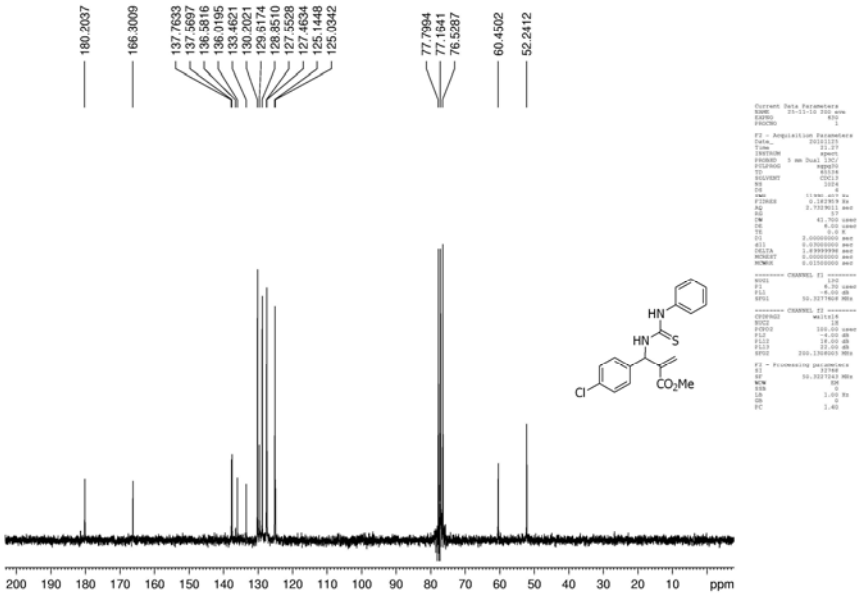

Fig:S-29 ^{13}C spectrum of Methyl 2-[(4-chlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1fA).

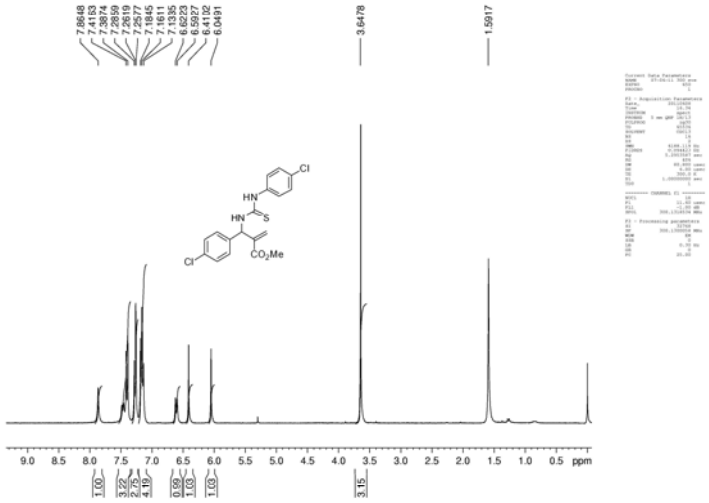

Fig:S-30 ^{1}H spectrum of Methyl 2-[(4-chlorophenyl)(3-(4-chlorophenyl)thioureido)methyl]acrylate (4.1fB).

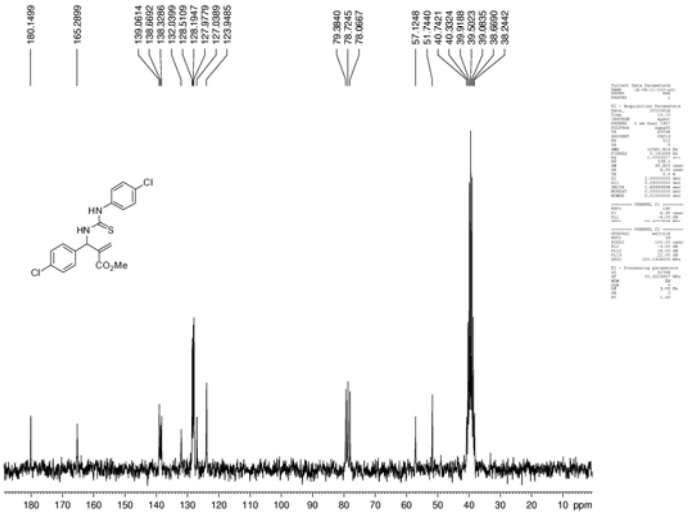

Fig:S-31 ^{13}C spectrum of Methyl 2-[(4-chlorophenyl)(3-(4-chlorophenyl)thioureido)methyl]acrylate (4.1fB).

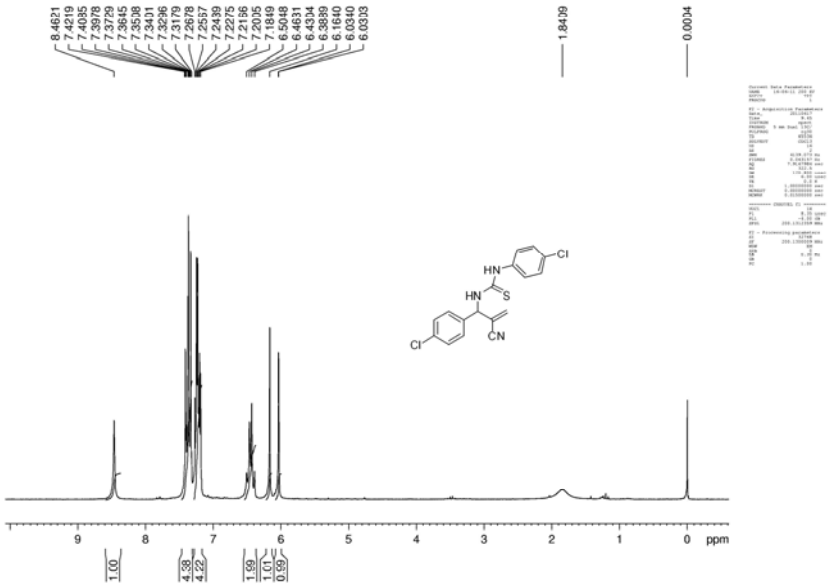

Fig:S-32 ^{1}H spectrum of 1-(4-Chlorophenyl)-3-(1-(4-chlorophenyl)-2-cyanoallyl)thiourea (4.2fB).

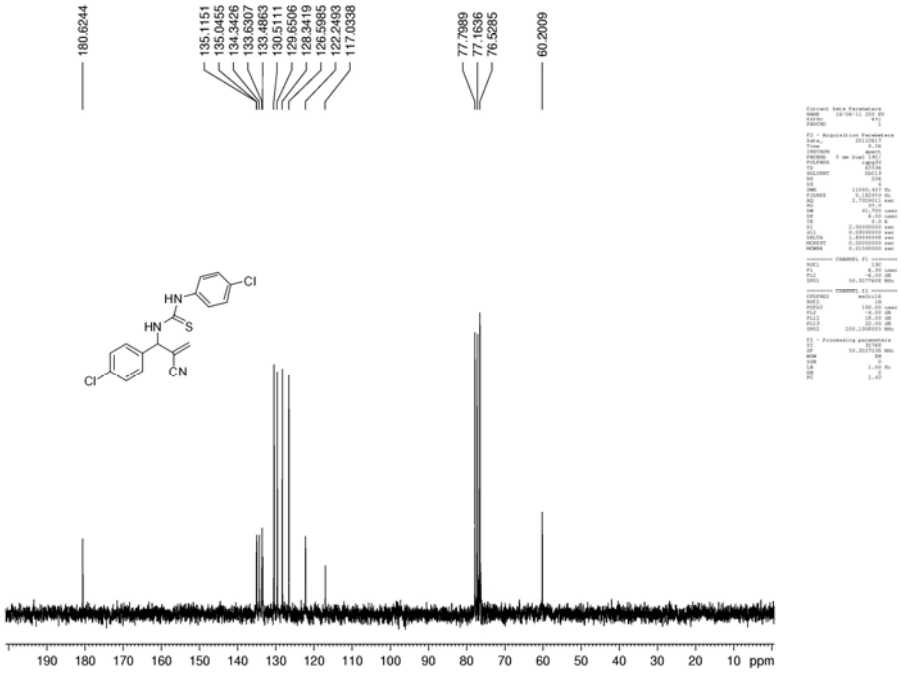

Fig:S-33 ^{13}C spectrum of 1-(4-Chlorophenyl)-3-(1-(4-chlorophenyl)-2-cyanoallyl)thiourea (4.2fB).

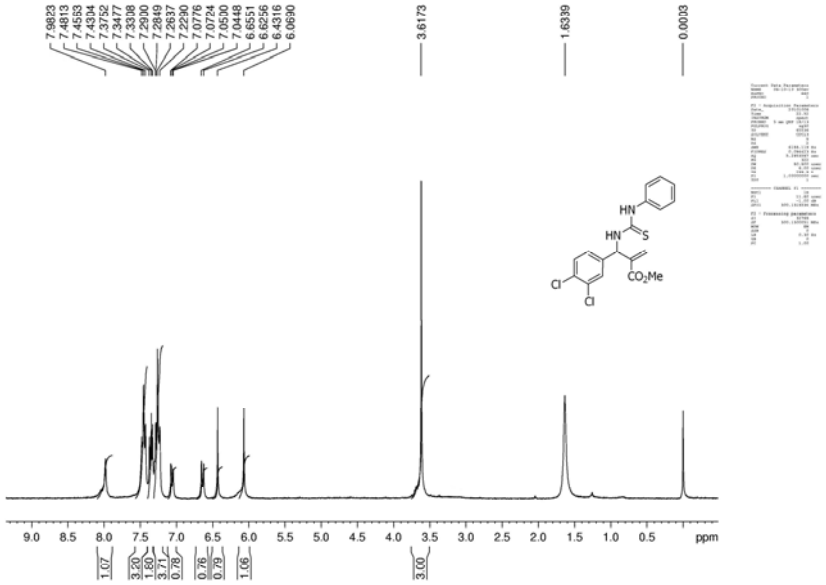

Fig:S-34 ^{1}H spectrum of Methyl 2-[(3,4-dichlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1gA).

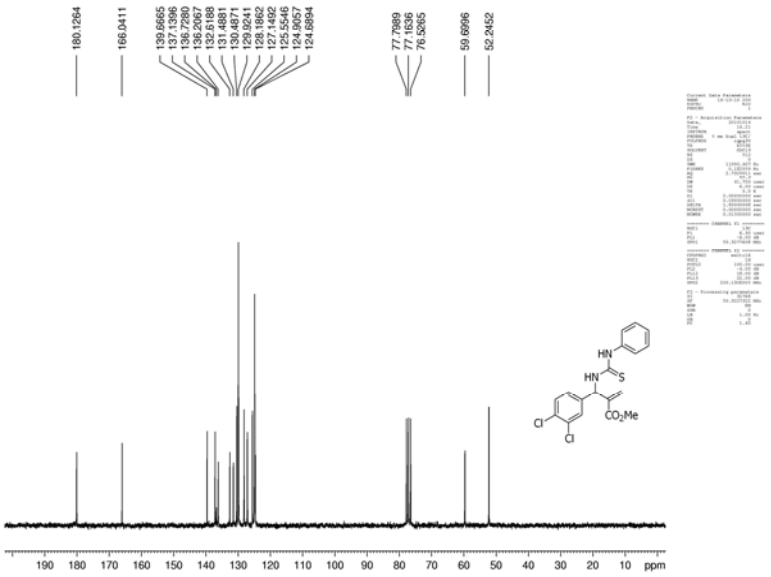

Fig:S-35 ^{13}C spectrum of Methyl 2-[(3,4-dichlorophenyl)(3-phenylthioureido)methyl]acrylate (4.1gA).

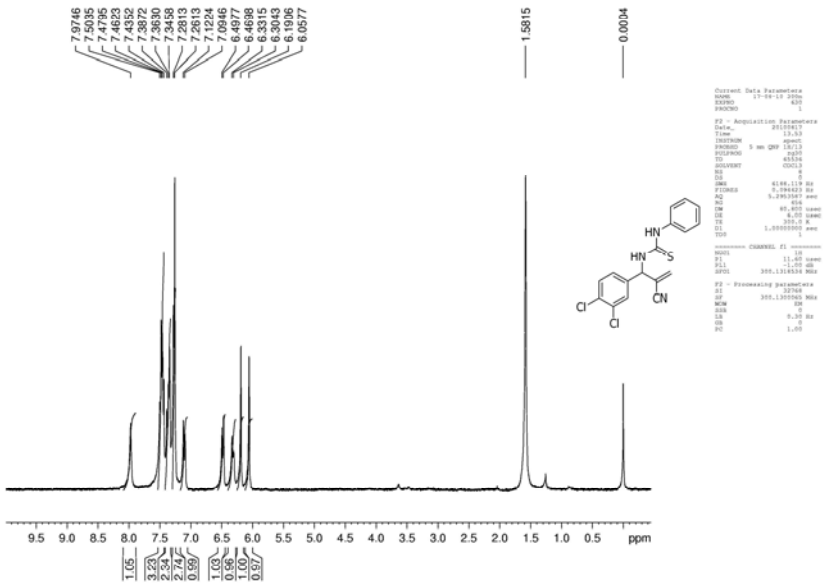

Fig:S-36 ^{1}H spectrum of *N*-[2-Cyano-1-(3,4-dichloro-phenyl)-allyl]-3-*N*'-phenyl-thiourea (4.2gA).

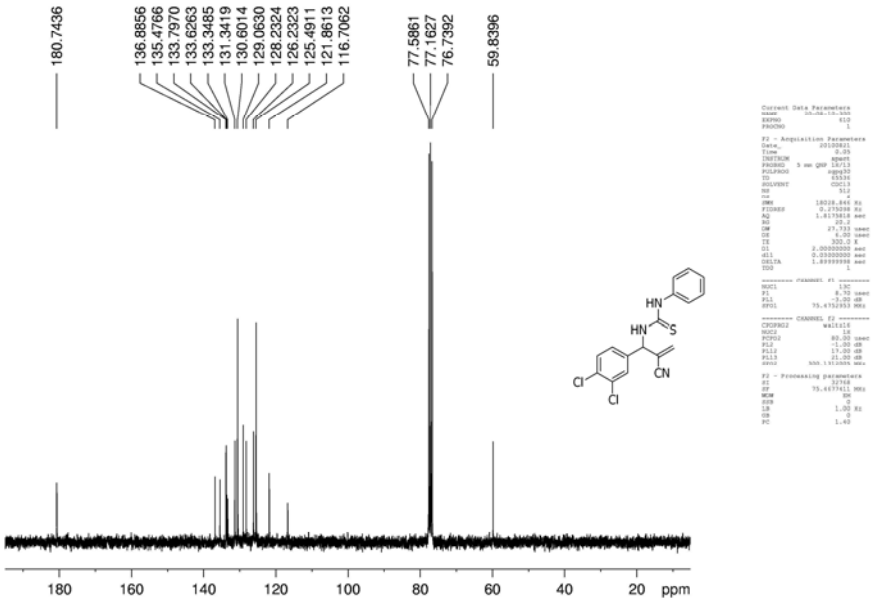

Fig:S-37 ^{13}C spectrum of *N*-[2-Cyano-1-(3,4-dichloro-phenyl)-allyl]-3-*N*'-phenyl-thiourea (4.2gA).

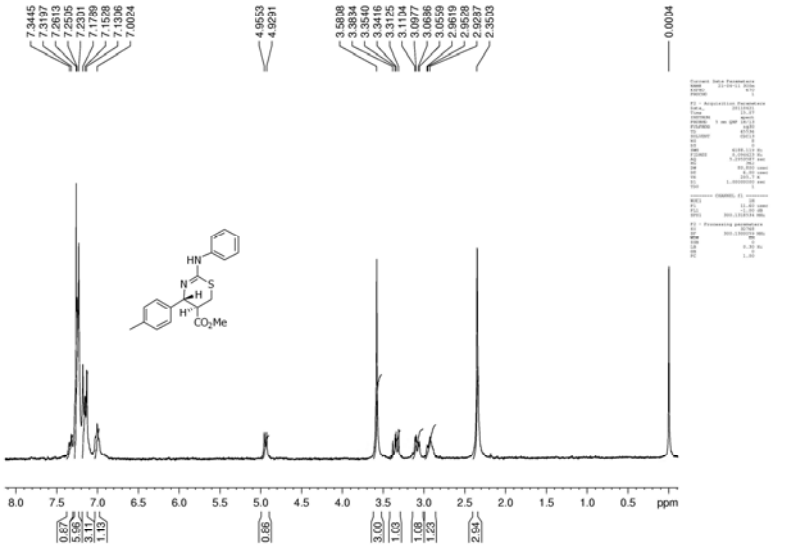

Fig:S-38 ^{1}H spectrum of (4*R*,5*R*)-Methyl 2-anilino-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1bA).

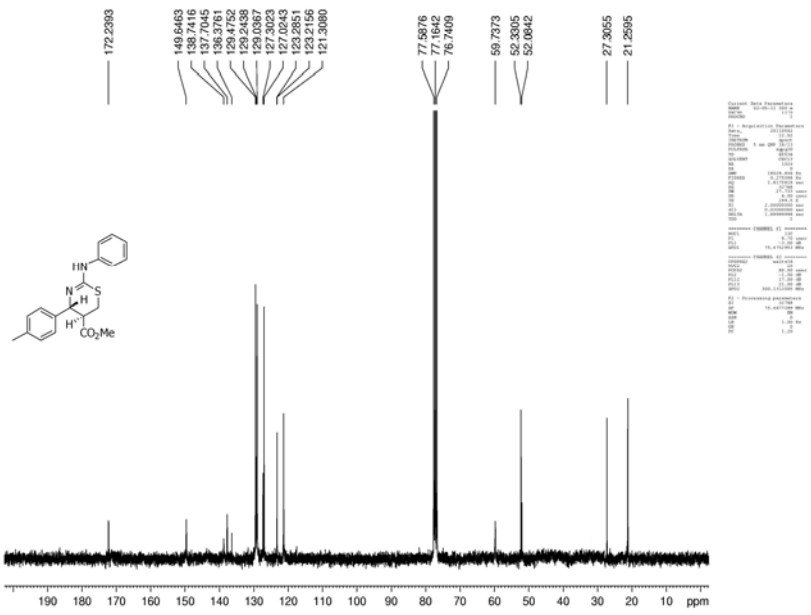

Fig:S-39 ^{13}C spectrum of (4*R*,5*R*)-Methyl 2-anilino-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1bA).

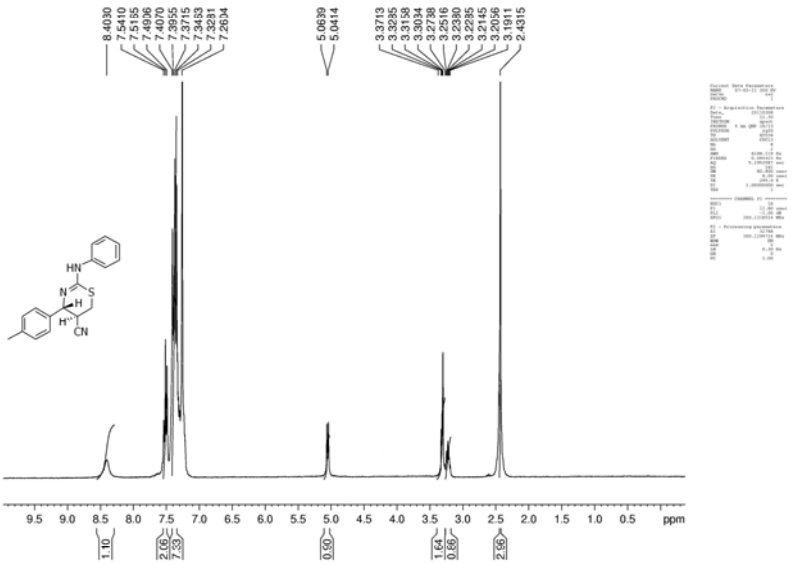

Fig:S-40 ^{1}H spectrum of (4*R*,5*R*)-2-(Phenylamino)-4-(4-methylphenyl)-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile (*anti*-3.2bA).

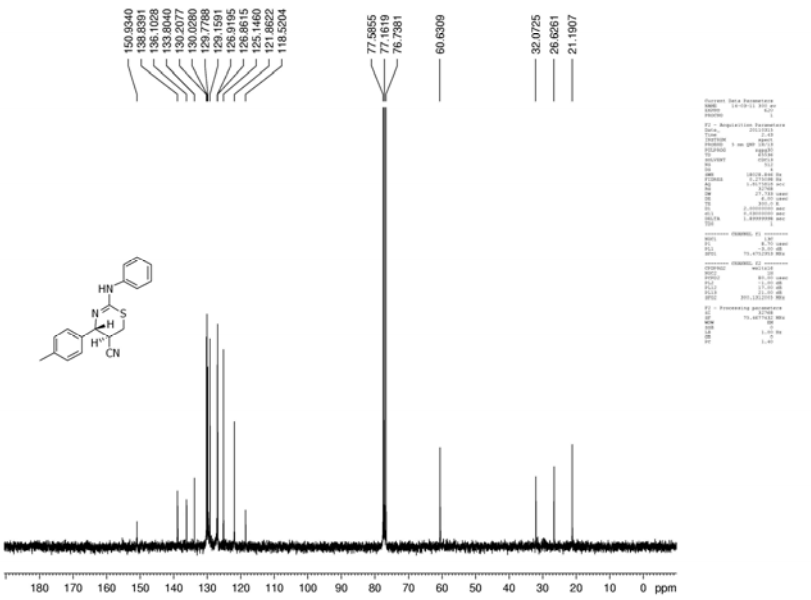

Fig:S-41 ^{13}C spectrum of (4*R*,5*R*)-2-(Phenylamino)-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2bA).

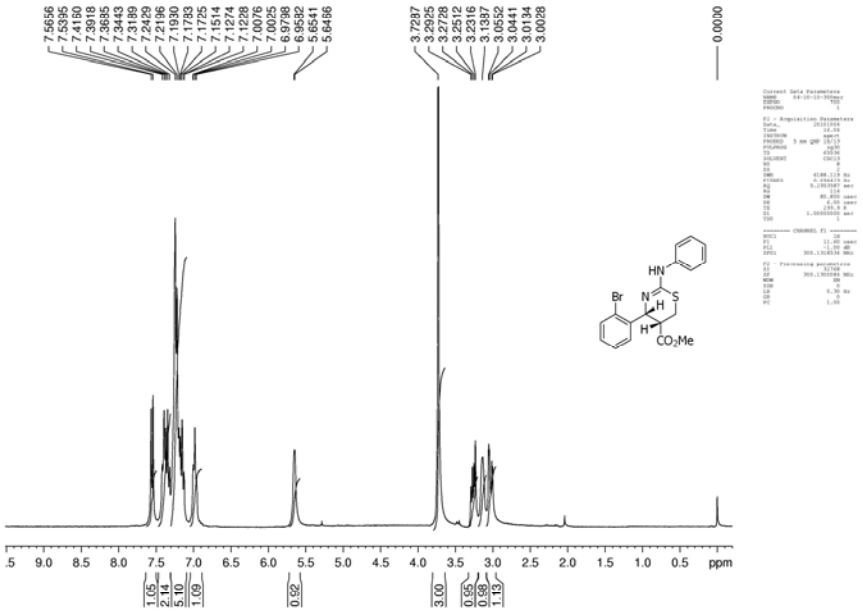

Fig:S-42 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1cA).

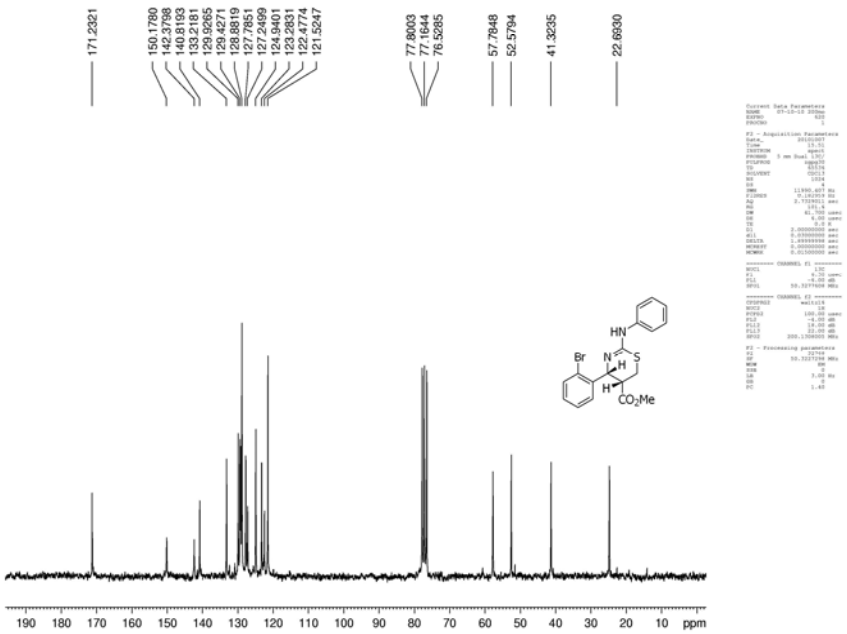

Fig:S-43 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1cA).

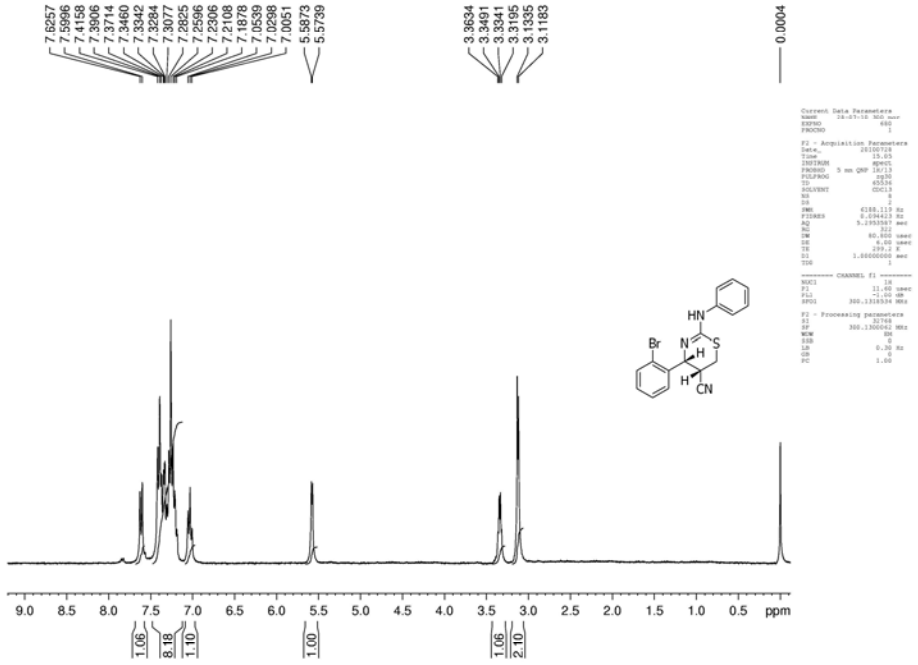

Fig:S-44 ^{1}H spectrum of (4*R*,5*S*)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (syn-3.2cA).

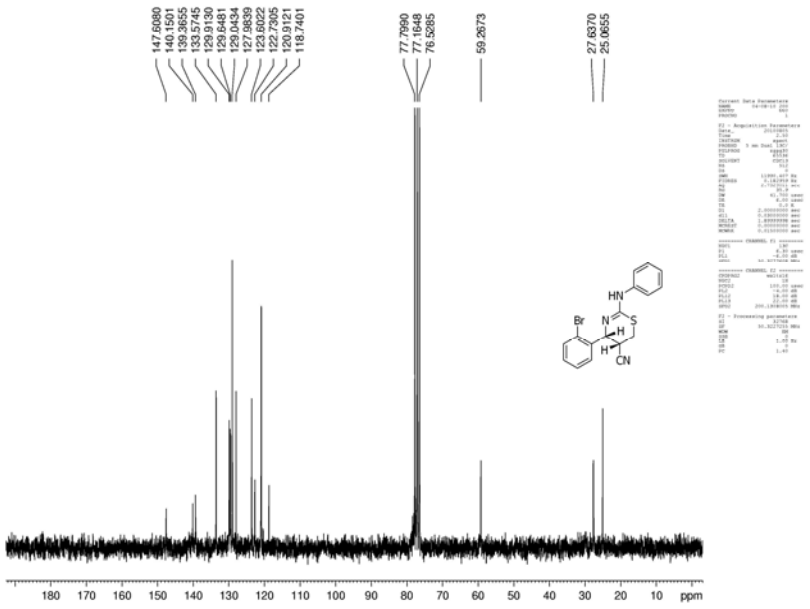

Fig:S-45 ^{13}C spectrum of (4*R*,5*S*)-4-(2-bromophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*syn*-3.2cA).

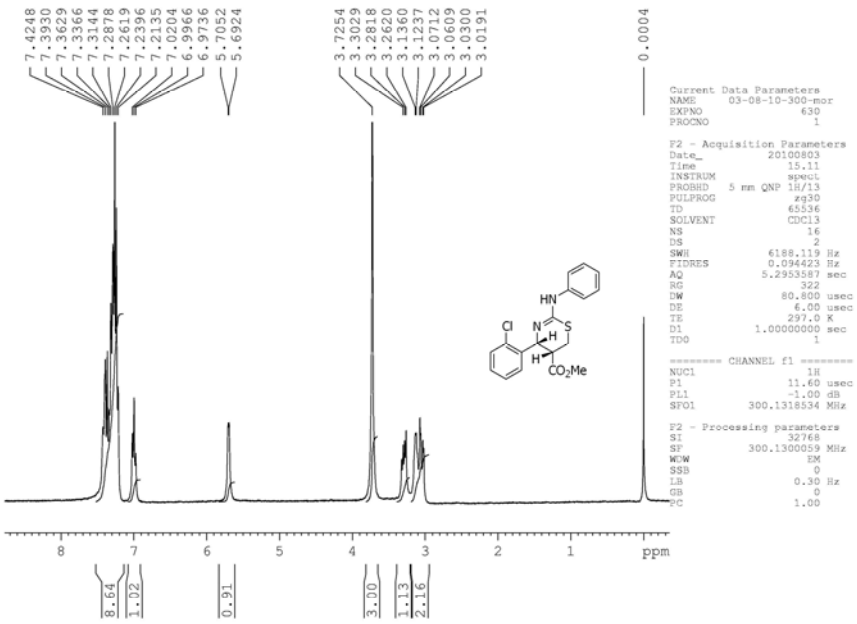

Fig:S-46 ^{1}H spectrum of Methyl (4*R*,5*S*)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1dA).

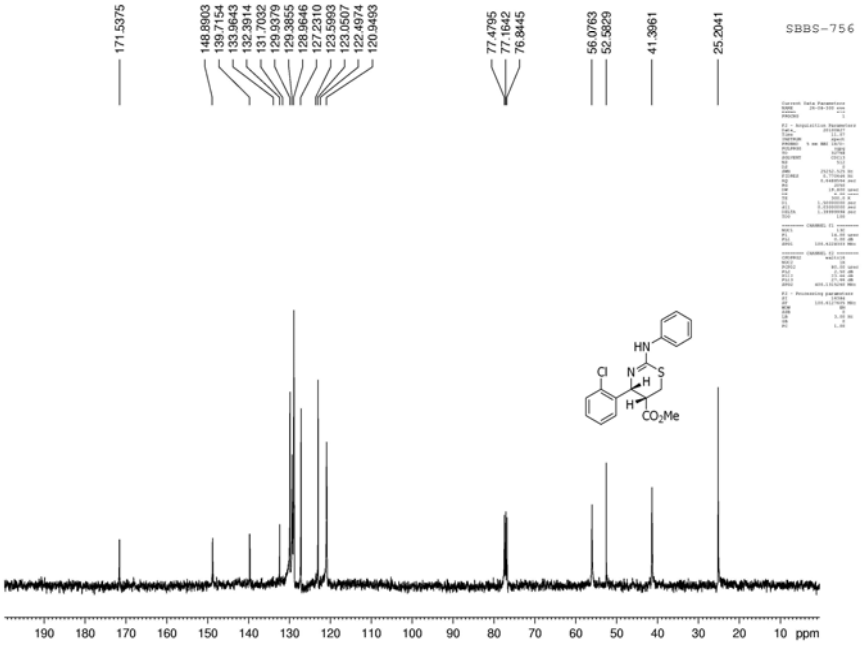

Fig:S-47 ^{13}C spectrum of Methyl (4*R*,5*S*)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1dA).

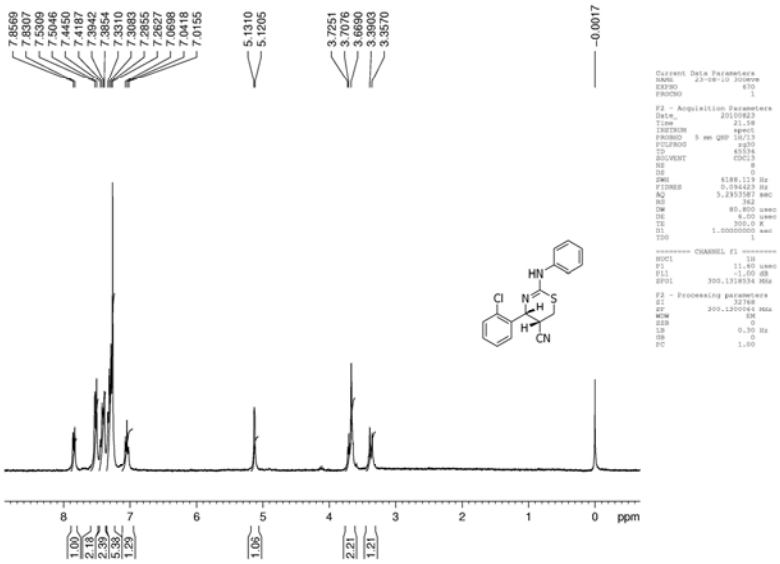

Fig:S-48 ^{1}H spectrum of (4*R*,5*S*)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*syn*-3.2dA).

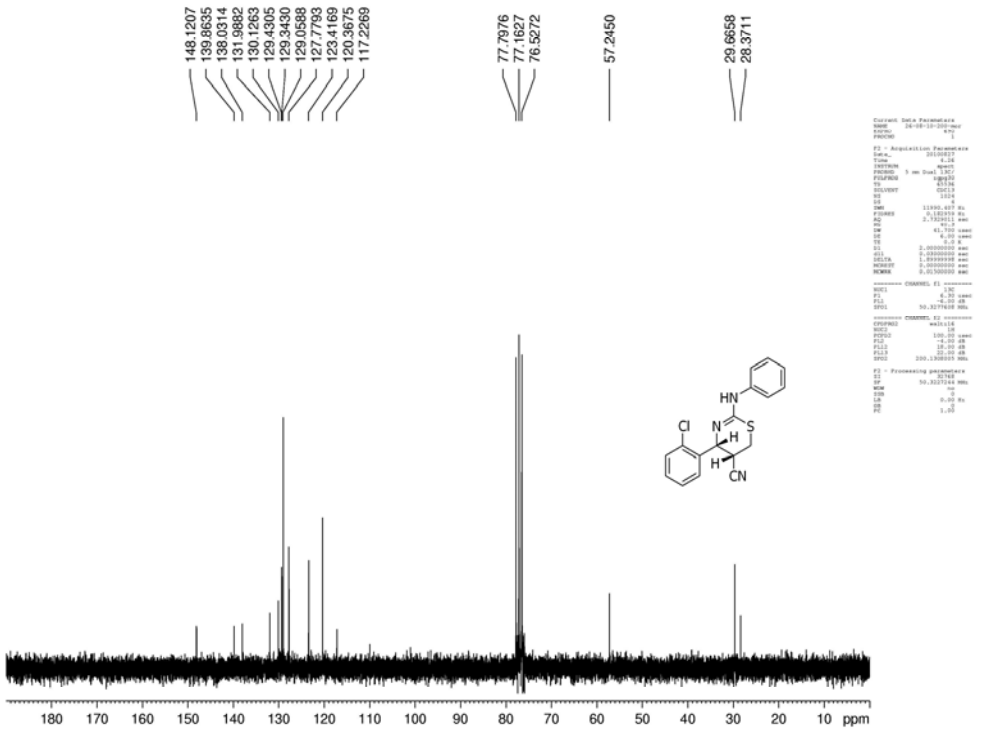

Fig:S-49 ^{13}C spectrum of (4*R*,5*S*)-2-anilino-4-(2-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitril (*syn*-3.2dA).

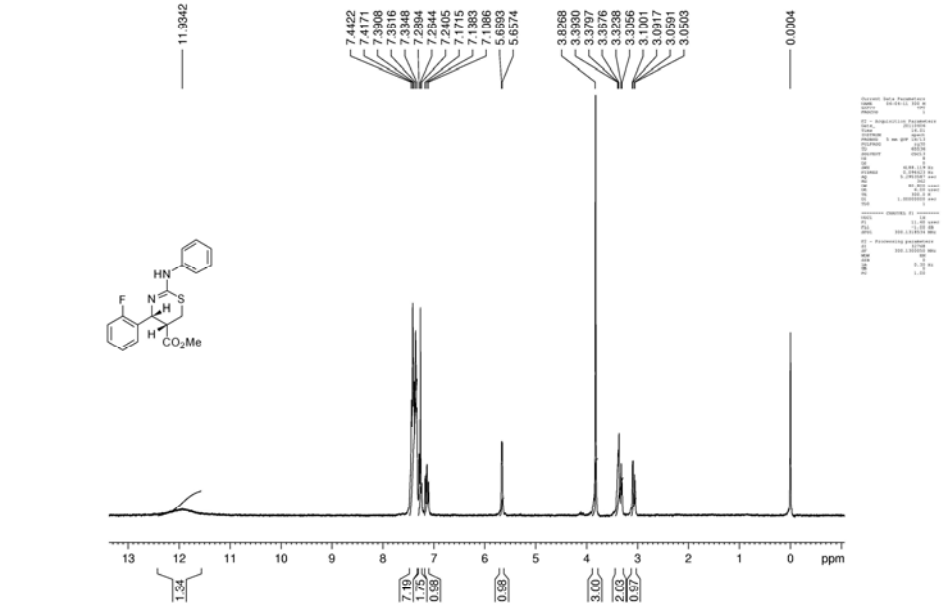

Fig:S-50 ^{1}H spectrum of (4*R*,5*S*)-Methyl 4-(2-fluorophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1eA).

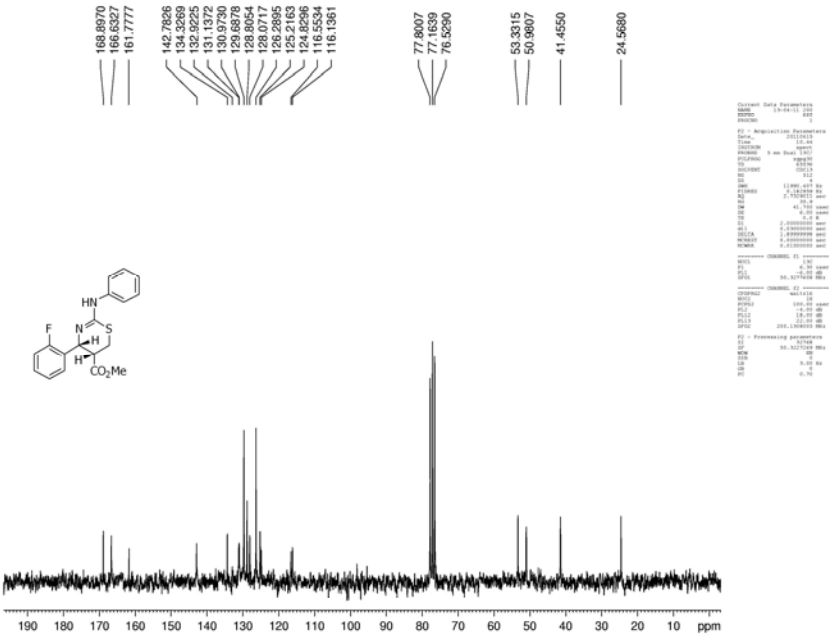

Fig:S-51 ^{13}C spectrum of (4*R*,5*S*)-Methyl 4-(2-fluorophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*-3.1eA).

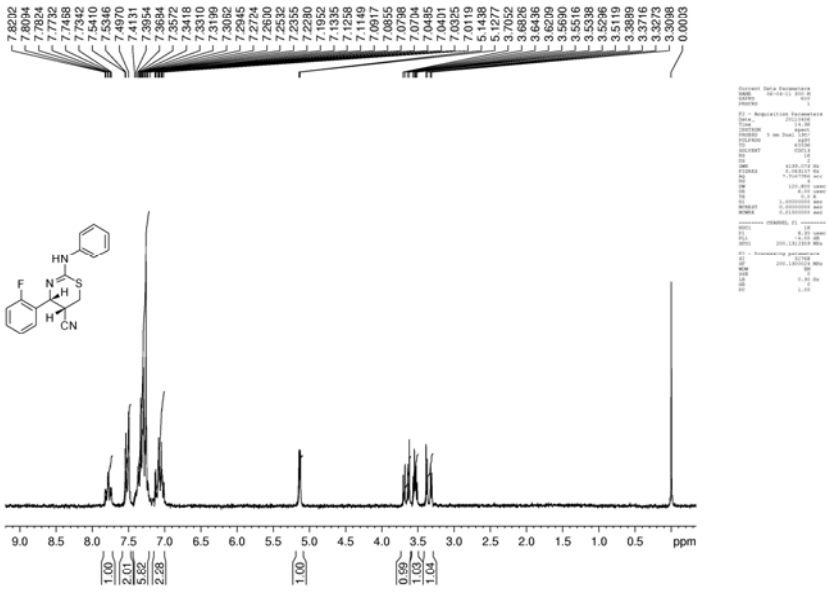

Fig:S-52 ^{1}H spectrum of (4*R*,5*S*)-2-anilino-4-(2-fluorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*syn*-3.2eA).

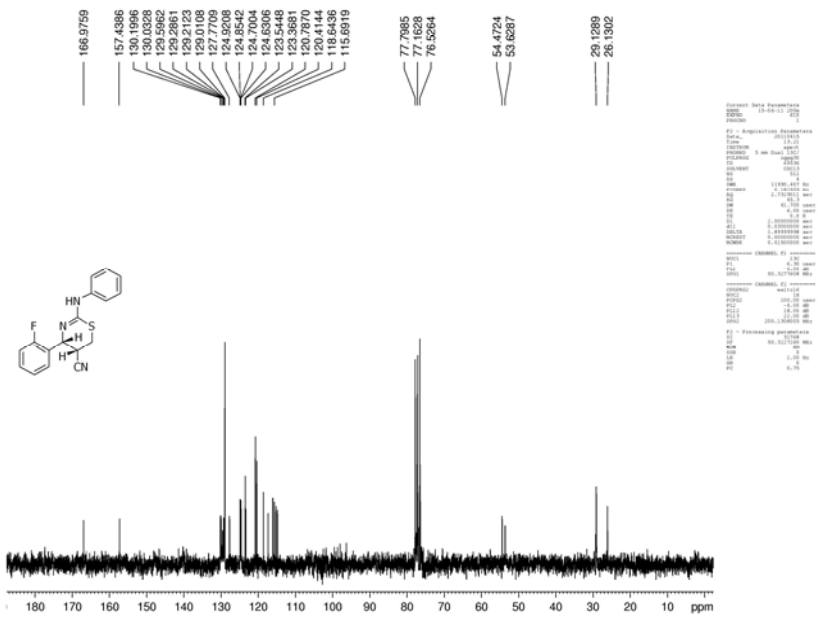

Fig:S-53 ^{13}C spectrum of (4*R*,5*S*)-2-anilino-4-(2-fluorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*syn*-3.2eA).

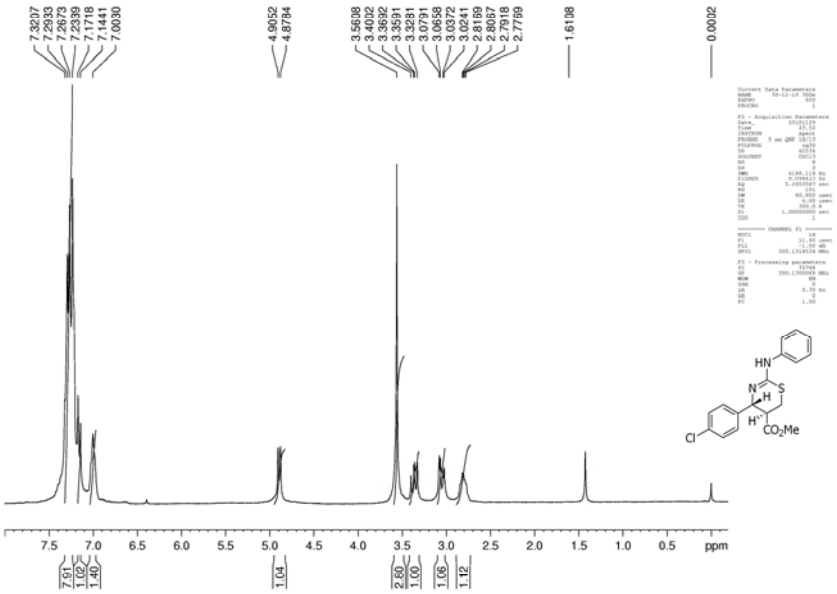

Fig:S-54 ^{1}H spectrum of Methyl (4*R*,5*R*) 4-(4-chlorophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1fA).

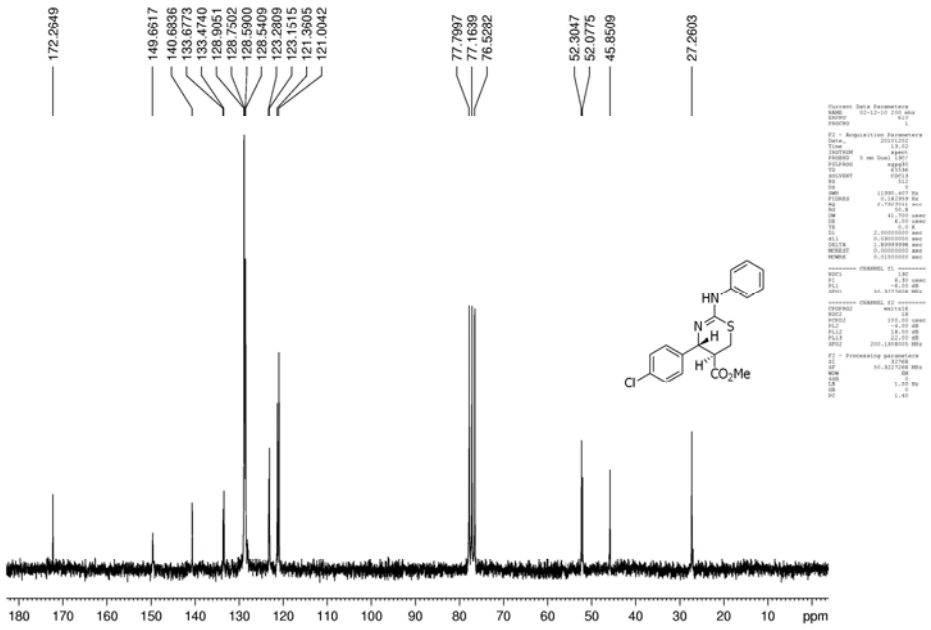

Fig:S-55 ^{13}C spectrum of Methyl (4*R*,5*R*) 4-(4-chlorophenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1fA).

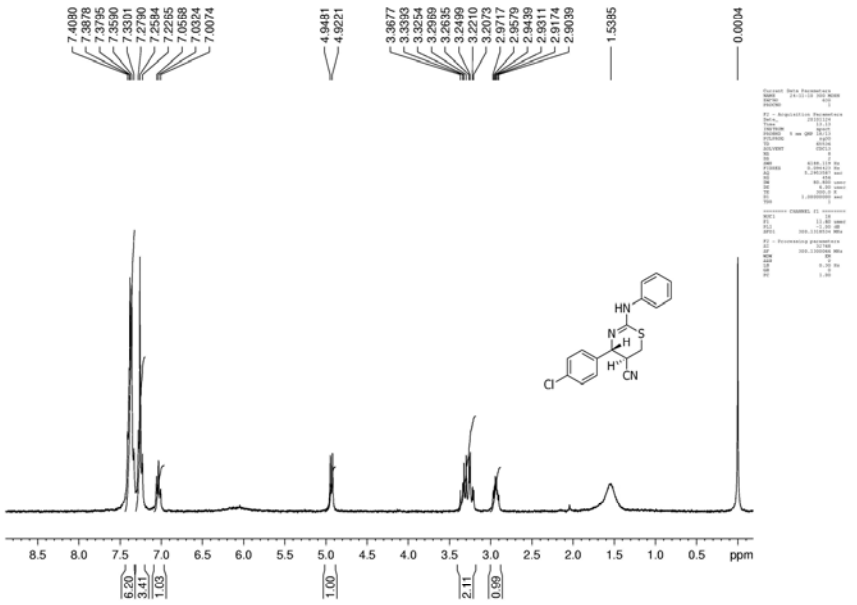

Fig:S-56 ^{1}H spectrum of (4*R*,5*R*)-2-anilino-4-(4-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2fA).

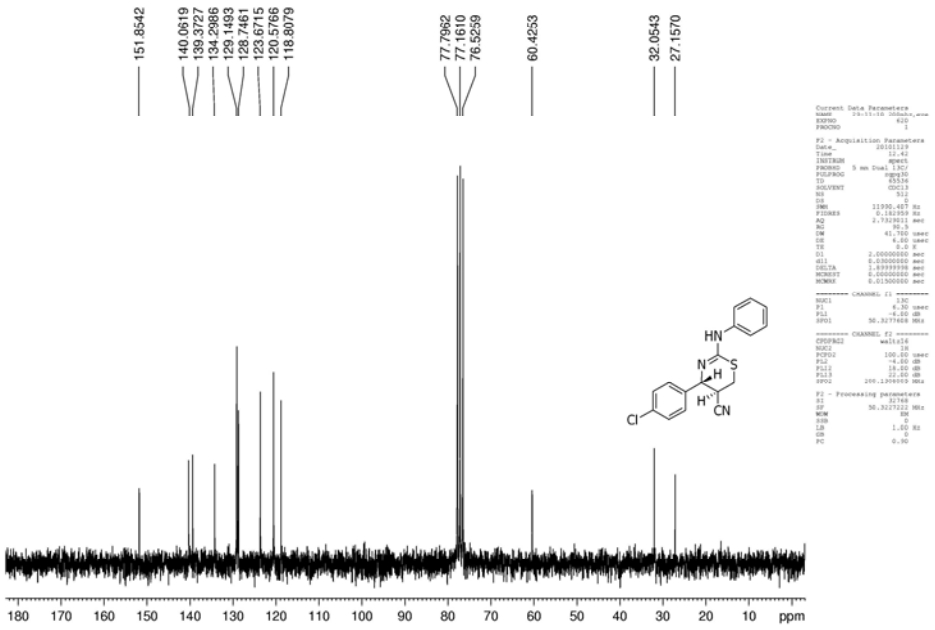

Fig:S-57 ^{13}C spectrum of (4*R*,5*R*)-2-anilino-4-(4-chlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2fA).

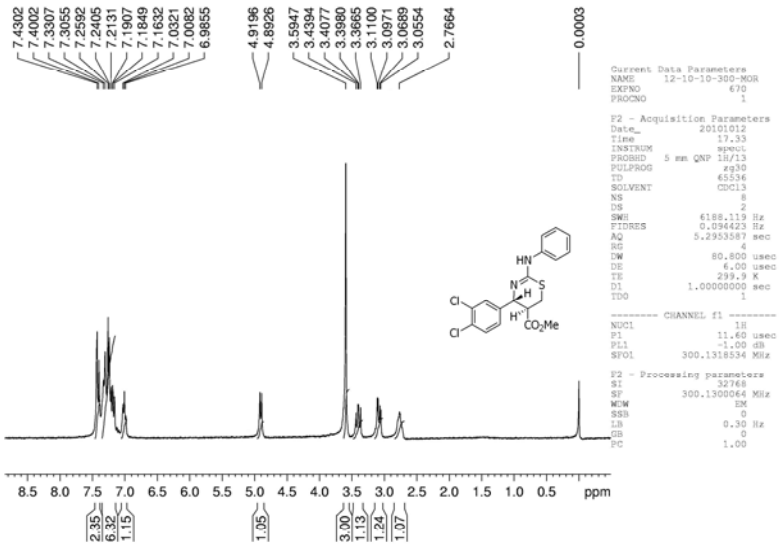

Fig:S-58 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1gA).

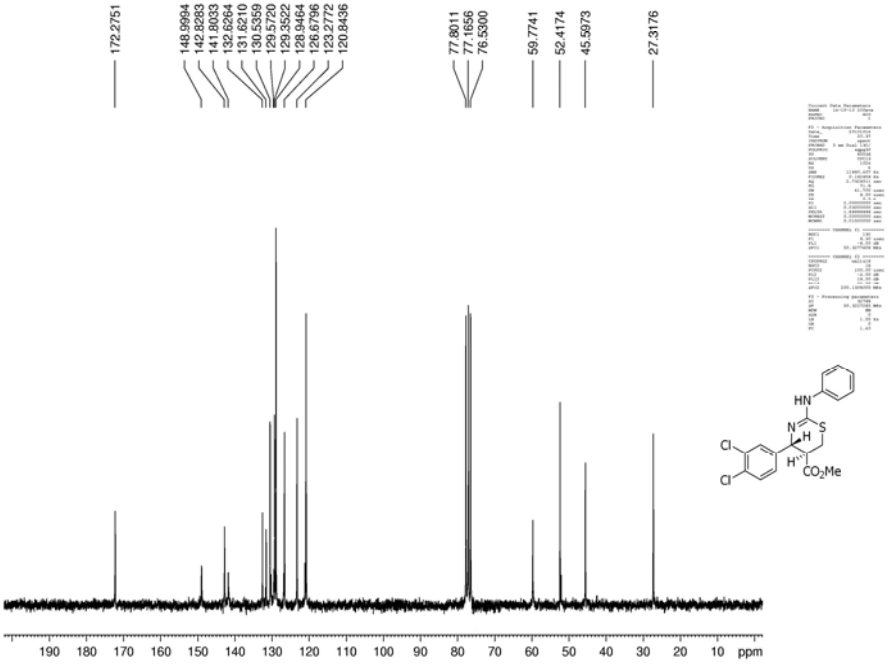

Fig:S-59 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1gA).

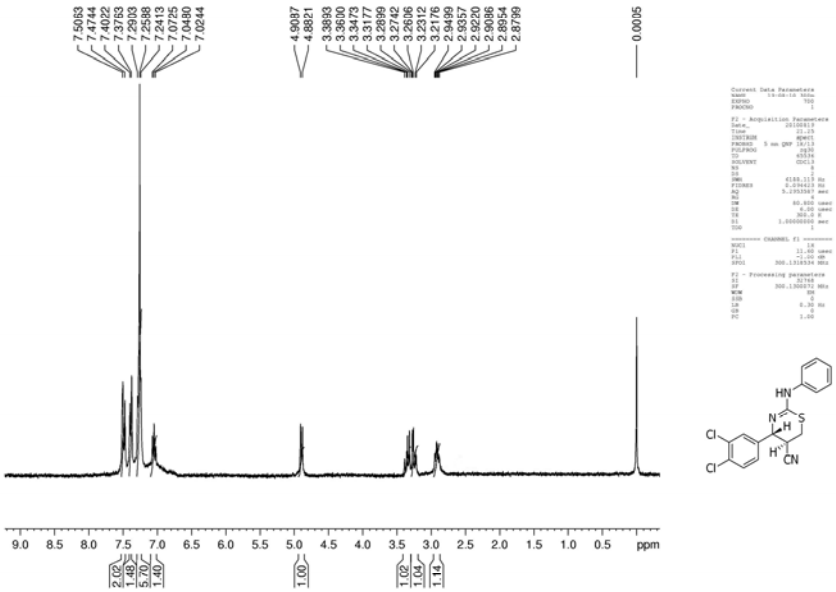

Fig:S-60 ^{1}H spectrum of (4*R*,5*R*)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2gA).

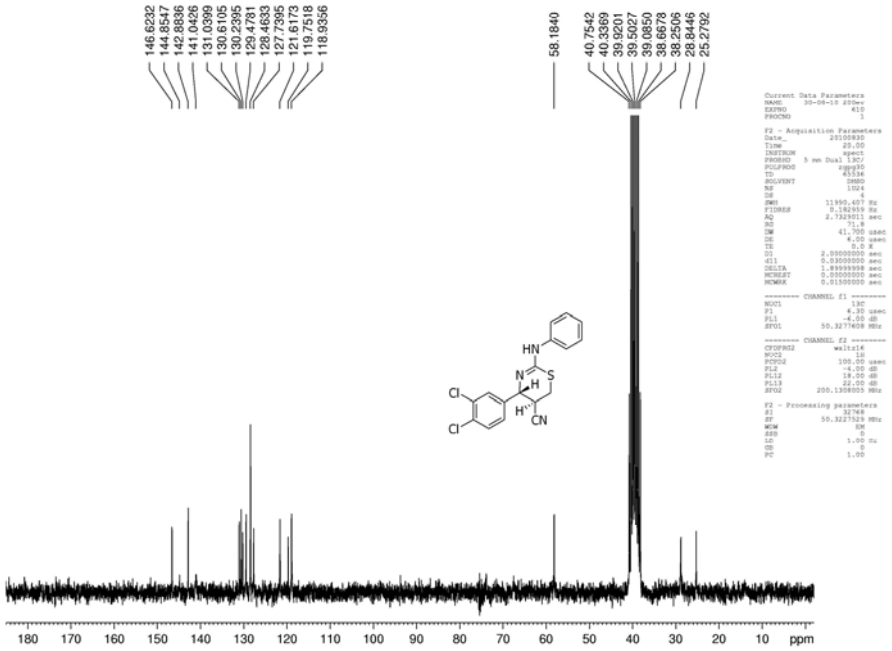

Fig:S-61 ^{13}C spectrum of (4*R*,5*R*)-2-anilino-4-(3,4-dichlorophenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2gA).

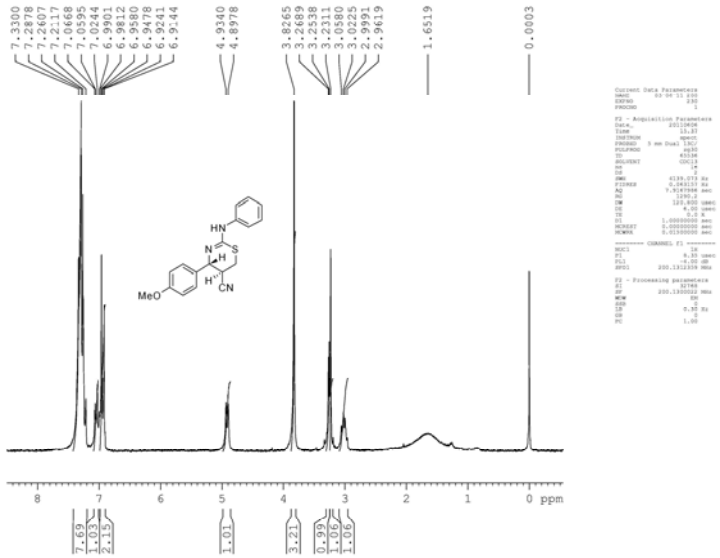

Fig:S-62 ^{1}H spectrum of (4*R*,5*R*)-4-(4-Methoxyphenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2hA).

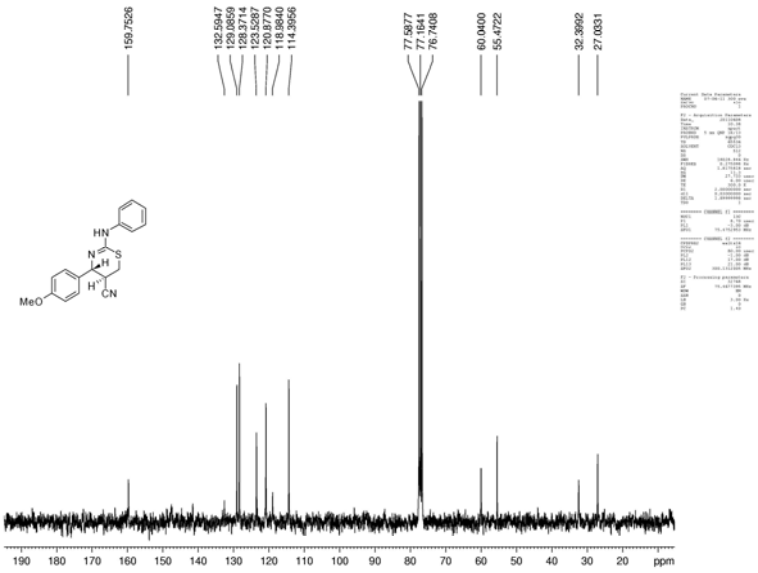

Fig:S-63 ^{13}C spectrum of (4*R*,5*R*)-4-(4-Methoxyphenyl)-2-(phenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2hA).

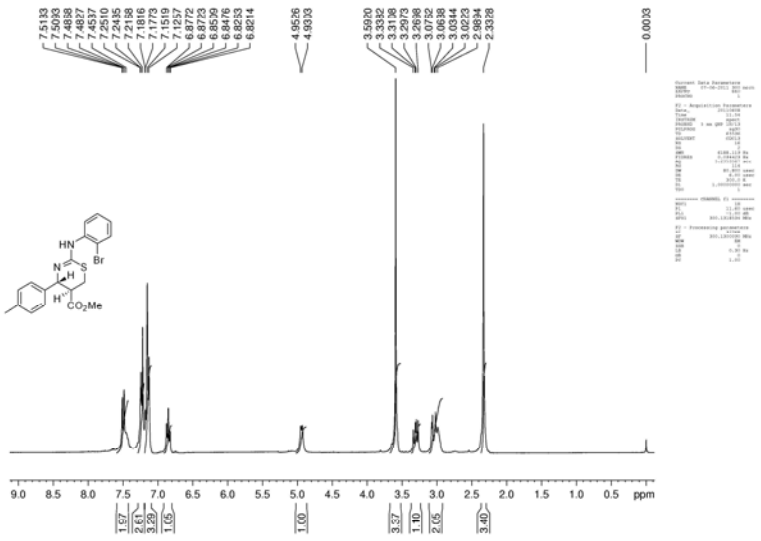

Fig:S-64 ^{1}H spectrum of (4*R*,5*R*)-Methyl 2-(2-bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1bC).

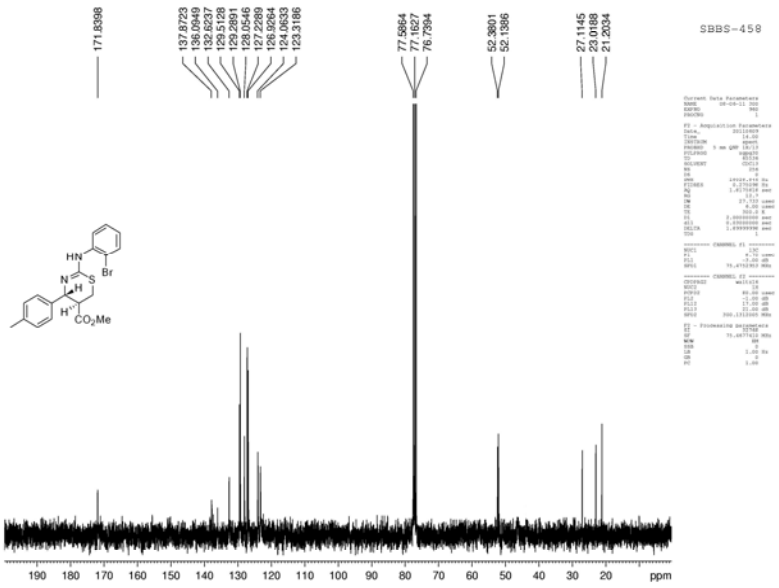

Fig:S-65 ^{13}C spectrum of (4*R*,5*R*)-Methyl 2-(2-bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1bC).

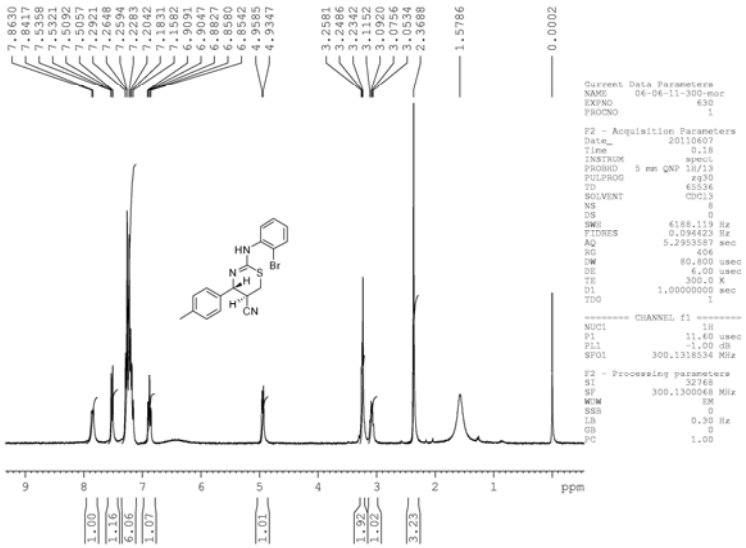

Fig:S-66 ^{1}H spectrum of (4*R*,5*R*)-2-(2-Bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2bC).

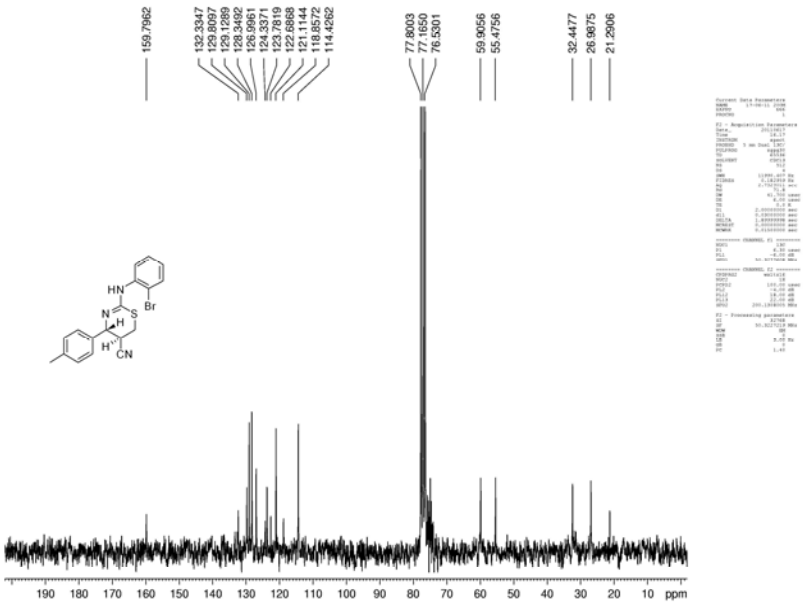

Fig:S-67 ^{13}C spectrum of (4*R*,5*R*)-2-(2-Bromophenylamino)-4-(4-methylphenyl)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2bC).

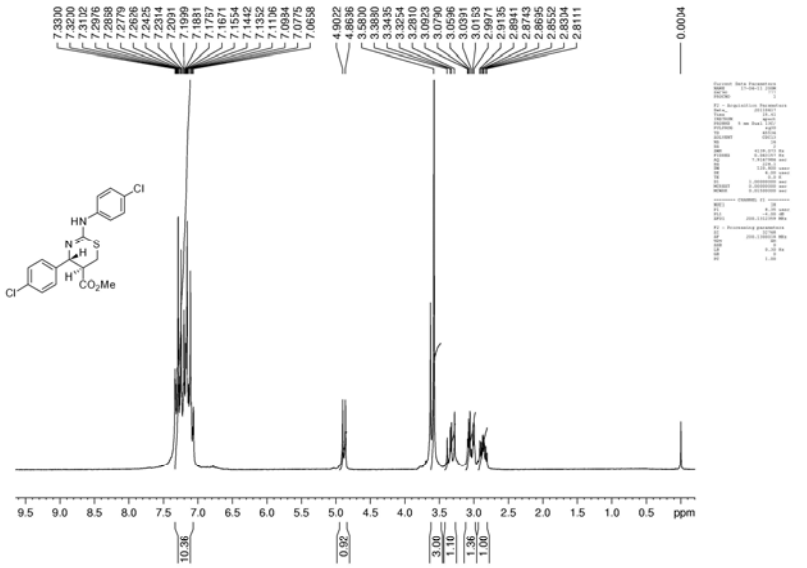

Fig:S-68 ^{1}H spectrum of (4*R*,5*R*)-Methyl 4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4H-1,3-thiazine-5-carboxylate (*anti*-3.1fB).

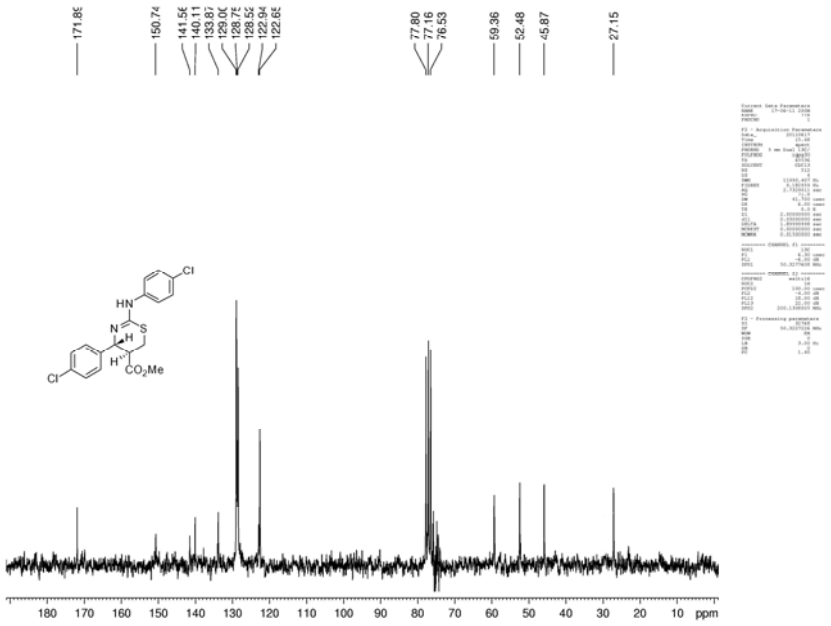

Fig:S-69 ^{13}C spectrum of (4*R*,5*R*)-Methyl 4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*-3.1fB).

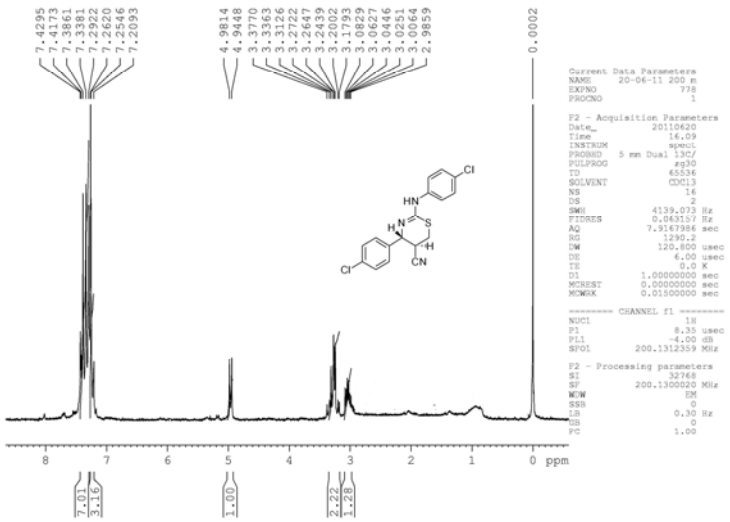

Fig:S-70 ^{1}H spectrum of (4*R*,5*R*)-4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2fB).

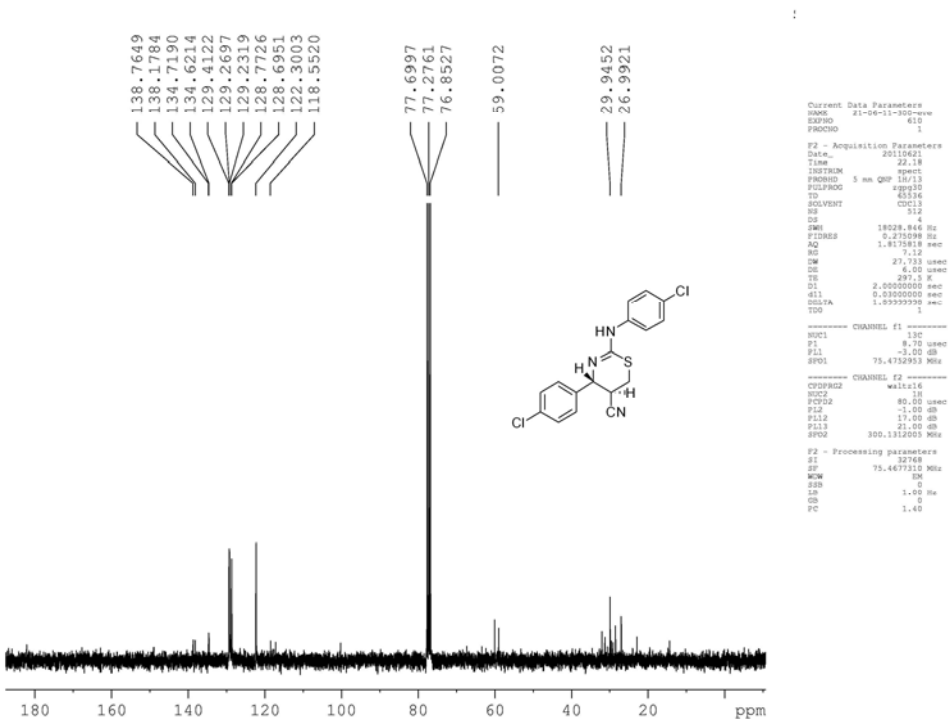

Fig:S-71 ^{13}C spectrum of (4*R*,5*R*)-4-(4-chlorophenyl)-2-(4-chlorophenylamino)-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile (*anti*-3.2fB).