Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2011

Microwave-assisted one-pot synthesis of 2-aryl-5,6-dihydro-1,3-thiazines via reaction between Lawesson's reagent and allyl arylamides derived from Morita-Baylis-Hillman acetates

Subhendu Bhowmik, Amita Mishra and Sanjay Batra*

Medicinal and Process Chemistry Division, Central Drug Research Institute, CSIR, PO Box 173, Lucknow 226001, India

e-mail: batra_san@yahoo.co.uk, s_batra@cdri.res.in

Contents

This journal is © The Royal Society of Chemistry 2011

Methyl 2-[(benzoylamino)(2-bromophenyl)methyl]acrylate (5b). 74 % as a white solid (0.89 g from 1.0 g), mp 100-102 ^{o}C; R_f= 0.29 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1664 (CONH), 1732 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.73 (s, 3H, OCH_3), 6.01 (s, 1H, $=CH_2$), 6.46 (s, 1H, $=CH_2$), 6.50 (d, 1H, *J*= 8.0 Hz, CH), 7.13-7.18 (m, 2H, ArH), 7.26-7.32 (m, 1H, ArH), 7.42-7.46 (m, 3H, ArH), 7.49-7.54 (m, 1H, ArH), 7.58-7.61 (m, 1H, ArH), 7.80-7.83 (m, 2H, ArH and NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 52.2, 54.8, 124.3, 127.2, 127.7, 128.3, 128.6, 128.7, 129.5, 131.8, 133.6, 134.0, 138.2, 138.6, 166.2, 166.5; mass (ES+) *m/z*= 374.0 (M^++1), 376.0 (M^++1; Anal. Calcd. for $C_{18}H_{16}BrNO_3$ (Exact mass: 373.0314); C, 57.77; H, 4.31; N, 3.74; Found: C, 57.59; H, 4.37; N, 3.63.

Methyl 2-[(benzoylamino)(2-fluorophenyl)methyl]acrylate (5c). 64 % as a white solid (0.8 g from 1.0 g), mp 62-64 ^{o}C; R_f= 0.28 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1645 (CONH), 1731 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.73 (s, 3H, OCH_3), 6.02 (s, 1H, $=CH_2$), 6.38 (s, 1H, $=CH_2$), 6.45 (d, 1H, *J*= 8.7 Hz, CH), 7.02-7.14 (m, 2H, ArH), 7.41-7.54 (m, 5H, ArH), 7.83 (d, 2H, *J*= 7.0 Hz, ArH), 8.13 (d, 1H, *J*= 7.2 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 50.4, 52.2, 115.9 (*J*= 21.5Hz), 124.3 (*J*= 1.8Hz), 127.2, 127.8, 128.5, 128.6, 128.7, 129.6 (*J*= 8.4 Hz), 130.2, 131.9, 133.7, 134.1, 138.3, 163.2, 166.3, 166.5; mass (ES+) *m/z*= 314.1 (M^++1); Anal. Calcd. for $C_{18}H_{16}FNO_3$ (Exact mass: 313.1114); C, 69.00; H, 5.15; N, 4.47; Found: C, 68.86; H, 5.33; N, 4.43.

Methyl 2-[(benzoylamino)(4-fluorophenyl)methyl]acrylate (5d). 79 % as a white solid (0.98 g from 1.0 g), 82-84 ^{o}C; R_f= 0.30 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1658 (CONH), 1731 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.74 (s, 3H, OCH_3), 6.03 (s, 1H, $=CH_2$), 6.20 (d, 1H, *J*= 8.9 Hz, CH), 6.41 (s, 1H, $=CH_2$), 7.02 (t, 2H, *J*= 8.6 Hz, ArH), 7.26-7.34 (m, 2H, ArH), 7.43-7.53 (m, 4H, ArH), 7.84 (d, 2H, *J*= 7.1 Hz, ArH and NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 52.4, 55.1, 115.6, 116.0, 127.3, 128.2, 128.3, 128.4, 128.9, 132.1, 134.3, 135.6, 135.7, 139.0, 160.0, 166.6, 166.8; mass (ES+) *m/z*= 314.1 (M^++1); Anal. Calcd. for $C_{18}H_{16}FNO_3$ (Exact mass: 313.1114); C, 69.00; H, 5.15; N, 4.47; Found: C, 68.73; H, 5.39; N, 4.36.

Methyl 2-[(benzoylamino)(4-methylphenyl)methyl]acrylate (5e). 63 % as a white solid (0.78 g from 1.0 g) mp 96-98 ^{o}C; R_f= 0.32 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1656 (CONH), 1733 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 2.32 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 6.01 (s, 1H, $=CH_2$), 6.19 (d, 1H, *J*= 8.7 Hz, CH), 6.39 (s, 1H, $=CH_2$), 7.14 (d, 2H, *J*= 8.0 Hz, ArH), 7.22-7.26 (m, 2H, ArH), 7.38-7.52 (m, 4H, ArH), 7.82-7.84 (m, 2H, ArH and NH); ^{13}C NMR (75

This journal is © The Royal Society of Chemistry 2011

MHz, $CDCl_3$) δ= 21.3, 52.3, 55.4, 126.6, 127.3, 127.8, 128.8, 129.6, 131.9, 134.4, 136.8, 137.5, 139.3, 166.6, 166.8; mass (ES+) *m/z*= 310.1 (M^++1). Anal. Calcd. for $C_{19}H_{19}NO_3$ (Exact mass: 309.1365); C, 73.77; H, 6.19; N, 4.53; Found: C, 73.86; H, 6.23; N, 4.39.

Methyl 2-[(benzoylamino)(2,4-dichlorophenyl)methyl]acrylate (5f). 71 % as a white solid (0.85 g from 1.0 g), mp 116-118 ^oC; R_f= 0.30 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1639 (CONH), 1729 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.74 (s, 3H, OCH_3), 6.02 (s, 1H, $=CH_2$), 6.44-6.48 (m, 2H, CH and $=CH_2$), 7.24-7.26 (m, 1H, ArH), 7.41-7.50 (m, 6H, ArH), 7.81 (d, 2H, *J*= 6.4 Hz, ArH and NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.4, 127.2, 127.4, 128.8, 129.0, 129.4, 130.0, 132.0, 133.8, 134.4, 134.5, 135.7, 137.4, 166.2, 166.5; mass (ES+) *m/z*= 364.0 (M^++1), 366.0 (M^++3). Anal. Calcd. for $C_{18}H_{15}Cl_2NO_3$ (Exact mass: 363.0429); C, 59.36; H, 4.15; N, 3.85; Found: C, 59.42; H, 4.33; N, 3.73.

Methyl 2-[(benzoylamino)(2-chloro-4-nitrophenyl)methyl]acrylate (5g). 88 % as a white solid (1.05 g from 1.0 g), mp 160-162 ^oC; R_f= 0.31 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1637 (CONH), 1734 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.77 (s, 3H, OCH_3), 6.10 (s, 1H, $=CH_2$), 6.50 (s, 1H, $=CH_2$), 6.56 (d, 1H, *J*= 8.2 Hz, CH), 7.47 (t, 2H, *J*= 6.6 Hz, ArH), 7.53-7.58 (m, 3H, ArH), 7.82-7.85 (m, 2H, ArH), 8.08-8.12 (m, 1H, ArH), 8.39 (d, 1H, *J*= 2.9 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 52.6, 123.6, 123.9, 127.3, 128.9, 130.1, 131.1, 132.2, 133.5, 136.8, 139.4, 140.6, 146.8, 166.2, 166.5; mass (ES+) *m/z*= 375.1 (M^++1), 377.1 (M^++3); Anal. Calcd. for $C_{18}H_{15}ClN_2O_5$ (Exact mass: 374.0670); C, 57.69; H, 4.03; N, 7.47; Found: C, 57.59; H, 4.23; N, 7.56.

Methyl 2-[(benzoylamino)(2-thienyl)methyl]acrylate (5h). 72 % as a yellow solid (0.90 g from 1.0 g), mp 67-69 ^oC; R_f= 0.29 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1655 (CONH), 1728 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.78 (s, 3H, OCH_3), 6.06 (s, 1H, $=CH_2$), 6.42 (d, 2H, *J*= 9.9 Hz, CH and $=CH_2$), 6.96 (t, 2H, *J*= 3.5 Hz, ArH), 7.23 (t, 1H, *J*= 1.4 Hz, ArH), 7.43-7.60 (m, 3H, ArH), 7.61 (d, 1H, *J*= 8.1 Hz, ArH), 7.82-7.85 (m, 2H, ArH and NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 52.1, 52.3, 124.8, 125.1, 127.3, 128.2, 128.8, 131.9, 134.1, 138.7, 144.1, 166.3, 166.5; mass (ES+) *m/z*= 302.1(M^++1). Anal. Calcd. for $C_{16}H_{15}NO_3S$ (Exact mass: 301.0773); C, 63.77; H, 5.02; N, 4.65; Found: C, 63.46; H, 5.11; N, 4.63.

***N*-(2-Cyano-1-phenylallyl)benzamide (6a).** 75 % as a white solid (0.98 g from 1.0 g), mp 97-99 ^oC; R_f= 0.27 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1638 (CONH), 2221 (CN) cm^{-1}; ^1H NMR

This journal is © The Royal Society of Chemistry 2011

(300 MHz, $CDCl_3$) δ= 5.95 (d, 1H, *J*= 7.7 Hz, CH), 6.09 (d, 1H, *J*= 0.9 Hz, $=CH_2$), 6.15 (s, 1H, $=CH_2$), 6.59 (d, 1H, *J*= 5.7 Hz, NH), 7.42-7.52 (m, 6H, ArH), 7.56 (d, 1H, *J*= 7.5 Hz, ArH), 7.81 (d, 2H, *J*= 7.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 55.1, 117.3, 123.7, 127.5, 127.6, 127.8, 128.0, 128.4, 128.8, 129.2, 131.3, 131.4, 132.3, 133.6, 137.1, 166.6; mass (ES+) *m/z*= 263.1(M^++1). Anal. Calcd. for $C_{17}H_{14}N_2O$ (Exact mass: 262.1106); C, 77.84; H, 5.38; N, 10.68; Found: C, 77.97; H, 5.56; N, 10.43.

***N*-(1-(2-Bromophenyl)-2-cyanoallyl)benzamide (6b).** 83 % as a white solid (1.01 g from 1.0 g), mp 108-110 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1649 (CONH), 2223 (CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 6.04 (d, 1H, *J*= 1.4 Hz, $=CH_2$), 6.19 (d, 1H, *J*= 1.2 Hz, $=CH_2$), 6.28 (d, 1H, *J*= 7.7 Hz, CH), 6.72 (d, 1H, J= 6.9 Hz, NH), 7.25-7.30 (m, 1H, ArH), 7.38-7.57 (m, 5H, ArH), 7.66 (d, 1H, *J*= 7.2 Hz, ArH), 7.81 (d, 2H, *J*= 7.1 Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 55.7, 117.1, 122.5, 124.0, 127.3, 128.4, 128.9, 129.2, 130.6, 132.3, 132.5, 133.3, 134.1, 136.2, 166.9; mass (ES+) *m/z*= 341.1 (M^++1), 343.1 (M^++3); Anal. Calcd. for $C_{17}H_{13}BrN_2O$ (Exact mass: 340.0211); C, 59.84; H, 3.84; N, 8.21; Found: C, 59.69; H, 3.88; N, 8.37.

***N*-(2-Cyano-1-(2-fluorophenyl)allyl)benzamide (6c).** 70 % as a white solid (0.90 g from 1.0 g), mp 132-134 ^{o}C; R_f= 0.30 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1650 (CONH), 2230 (CN) cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ= 6.00 (d, 1H, *J*= 2.0 Hz,$=CH_2$), 6.11 (d, 1H, *J*= 2.1 Hz,$=CH_2$), 6.18 (d, 1H, *J*= 12.5 Hz, CH), 6.83 (d, 1H, *J*= 10.4 Hz, NH), 7.11-7.22 (m, 2H, ArH), 7.37-7.55 (m, 5H, ArH), 7.79-7.86 (m, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 51.6 (*J*= 2.0 Hz, 116.8 (*J*= 11.4 Hz), 123.1, 124.3 (*J*= 13.0 Hz), 125.4 (*J*= 3.5 Hz), 127.3, 128.8, 129.0, 129.3 (*J*= 3.6 Hz), 130.9, 131.3 (*J*= 23.9 Hz), 132.2 (*J*= 9.7 Hz), 133.4, 160.7 (*J*= 246.0 Hz), 166.9; mass (ES+) *m/z*= 281.1 (M^++1); Anal. Calcd. for $C_{17}H_{13}FN_2O$ (Exact mass: 280.1012); C, 72.85; H, 4.67; N, 9.99; Found: C, 72.66; H, 4.39; N, 9.65.

***N*-(2-Cyano-1-(4-fluorophenyl)allyl)benzamide (6d).** 75 % as a white solid (0.96 g from 1.0 g), mp 110-112 ^{o}C; R_f= 0.29 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1648 (CONH), 2227 (CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 5.95 (d, 1H, *J*= 7.7 Hz, CH), 6.09 (d, 1H, *J*= 1.2 Hz, $=CH_2$), 6.16 (s, 1H, $=CH_2$), 6.55 (d, 1H, J= 6.5 Hz, NH), 7.09-7.15 (m, 2H, ArH), 7.37-7.55 (m, 5H, ArH), 7.79 (t, 2H, *J*= 7.0 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ= 54.4, 114.5, 115.7, 117.9, 123.7, 127.8, 128.5 (*J*= 18.8 Hz), 129.4, 130.1, 130.1 (*J*= 8.3 Hz), 130.8, 131.8, 132.9 (*J*= 11.2 Hz), 133.8, 134.1 (*J*= 2.9 Hz), 162.0 (*J*= 243.0 Hz), 166.4; mass (ES+) *m/z*= 281.1

This journal is © The Royal Society of Chemistry 2011

(M^++1); Anal. Calcd. for $C_{17}H_{13}FN_2O$ (Exact mass: 280.1012); C, 72.85; H, 4.67; N, 9.99; Found: C, 72.59; H, 4.46; N, 9.76.

***N*-(2-Cyano-1-(4-methylphenyl)allyl)benzamide (6e).** 66 % as a white solid (0.85 g from 1.0 g) , mp 87-89 ^oC; R_f= 0.28 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1647 (CONH), 2225 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 2.37 (s, 3H, CH_3), 5.89 (d, 1H, *J*= 7.4 Hz, CH), 6.08 (d, 1H, *J*= 1.0 Hz, $=CH_2$), 6.13 (s, 1H, $=CH_2$), 6.54-6.61 (d, 1H, *J*= 6.6 Hz, NH), 7.22-7.31 (m, 4H, ArH), 7.45 (t, 2H, *J*= 7.0 Hz, ArH), 7.53 (d, 1H, *J*= 7.1 Hz, ArH), 7.78 (d, 2H, *J*= 3.9 Hz, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 21.2, 56.1, 117.3, 123.8, 126.4, 127.1, 127.3, 127.9, 128.5, 128.8, 130.1, 131.6, 132.2, 133.6, 134.1, 139.0, 167.0; mass (ES+) *m/z*= 277.1 (M^++1). Anal. Calcd. for $C_{17}H_{13}BrN_2O$ (Exact mass: 276.1263); C, 78.24; H, 5.84; N, 10.14; Found: C, 78.06; H, 5.97; N, 10.07.

Methyl 2-[(2-furoylamino)(phenyl)methyl]acrylate (8A). 68 % as a white solid (0.83 g from 1.0 g) , mp 65-67 ^oC; R_f= 0.26 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1646 (CONH), 1725 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.72 (s, 3H, OCH_3), 6.00 (s, 1H, $=CH_2$), 6.19 (d, 1H, *J*= 9.0 Hz, CH), 6.41 (s, 1H, $=CH_2$), 6.50-6.52 (m, 1H, NH), 7.16 (d, 1H, *J*= 3.2 Hz, ArH), 7.26-7.35 (m, 5H, ArH), 7.46 (d, 2H, *J*= 0.9 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.2,, 54.4, 112.3, 114.9, 126.6, 127.7, 127.8, 128.5, 128.8, 139.1, 139.4, 144.3, 147.8, 157.5, 166.3; mass (ES+) *m/z*= 286.1 (M^++1). Anal. Calcd. for $C_{16}H_{15}NO_4$ (Exact mass: 285.1001); C, 67.36; H, 5.30; N, 4.91; Found: C, 67.09; H, 5.02; N, 4.77.

Methyl 2-[phenyl(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazole-3-carboxamido)methyl]acrylate (8B). 65 % as a yellow solid (1.25 g from 1.0 g), mp 71-73 ^oC; R_f= 0.27 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1662 (CONH), 1732 (CO_2Me) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ= 2.34 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 5.99 (s, 1H, $=CH_2$), 6.26 (d, 1H, *J*= 5.9 Hz, CH), 6.43 (s, 1H, $=CH_2$), 7.03-7.10 (m, 5H, ArH), 7.26-7.36 (m, 9H, ArH), 7.77 (d, 1H, *J*= 5.6 Hz, NH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 21.4, 52.1, 54.2, 108.2, 125.6, 126.9, 127.0, 127.7, 128.2, 128.7, 128.8, 129.1, 129.4, 129.8, 138.8, 139.6, 139.8, 145.2, 146.8, 161.2, 166.3; mass (ES+) *m/z*= 452.2 (M^++1). Anal. Calcd. for $C_{28}H_{25}N_3O_3$ (Exact mass: 451.1896); C, 74.48; H, 5.58; N, 9.31; Found: C, 74.66; H, 5.79; N, 9.40.

Methyl 2-[(3-(2-chlorophenyl)isoxazole-5-carboxamido)(phenyl)methyl]acrylate (8C). 77 % as a white solid (1.30 g from 1.0 g), mp 130-132 ^oC; R_f= 0.27 (hexanes: EtOAc, 70:30, v/v); ν_{max} (KBr) 1637 (CONH), 1733 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.74 (s, 3H, OCH_3),

6.02 (s, 1H, =CH_2), 6.21 (d, 1H, *J*= 8.9 Hz, CH), 6.46 (s, 1H, =CH_2), 7.30-7.46 (m, 8H, ArH), 7.51-7.54 (m, 1H, ArH), 7.71-7.77 (m, 2H, ArH and NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.3, 55.0, 108.8, 126.6, 127.3, 127.5, 128.1, 129.0, 130.7, 131.1, 131.5, 133.2, 138.7, 155.1, 162.2, 163.0, 166.1; mass (ES+) *m/z*= 397.1 (M^++1), 399.1 (M^++3); Anal. Calcd. for $C_{21}H_{17}ClN_2O_4$ (Exact mass: 396.0877); C, 63.56; H, 4.32; N, 7.06; Found: C, 63.43; H, 4.23; N, 6.92.

Methyl 2-[[(cyclohexylcarbonyl)amino](phenyl)methyl]acrylate (8D). 65 % as a white solid (0.83 g from 1.0 g), mp 91-93 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70:30, v/v), mp 91-93 ^{o}C; ν_{max} (KBr) 1672 (CONH), 1719 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 1.27-1.31 (m, 2H, CH_2), 1.41-1.53 (m, 2H, CH_2), 1.68-1.90 (m, 2H, CH_2), 2.12-2.22 (m, 1H, CH), 3.69 (s, 3H, OCH_3), 5.92 (s, 1H, =CH_2), 6.01 (d, 1H, *J*= 5.7 Hz, CH), 6.36 (s, 1H, =CH_2), 7.24-7.34 (m, 6H, ArH and NH); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6) δ= 25.3, 29.1, 29.3, 44.9, 51.5, 53.7, 72.5, 126.4, 126.5, 127.2, 128.2, 139.1, 139.6, 166.4, 176.3; mass (ES+) *m/z*= 302.1(M^++1). Anal. Calcd. for $C_{18}H_{23}NO_3$ (Exact mass: 301.1678); C, 71.73; H, 7.69; N, 4.65; Found: C, 71.49; H, 7.72; N, 4.56;

Methyl 2-[[(cyclopropylcarbonyl)amino](phenyl)methyl]acrylate (8E). 73 % as a white solid (0.80 g from 1.0 g), mp 82-84 ^{o}C; R_f= 0.29 (hexanes: EtOAc, 70:30, v/v), mp 82-84 ^{o}C; ν_{max} (KBr) 1642 (CONH), 1731 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.73-0.82 (m, 2H, CH_2), 0.98-1.03 (m, 2H, CH_2), 1.38-1.48 (m, 1H, CH), 3.70 (s, 3H, OCH_3), 5.96 (s, 1H, =CH_2), 6.04 (d, 1H, *J*= 13.3 Hz, CH), 6.38 (s, 1H, =CH_2), 6.75 (d, 1H, *J*= 12.5 Hz, NH), 7.23-7.42 (m, 5H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ= 7.4, 7.5, 15.0, 52.1, 55.0, 126.6, 127.5, 127.6, 128.7, 128.9, 129.8, 139.4, 139.9, 166.5, 172.8; mass (ES+) *m/z*= 260.1(M^++1). Anal. Calcd. for $C_{15}H_{17}NO_3$ (Exact mass: 259.1208); C, 69.48; H, 6.61; N, 5.40; Found: C, 69.29; H, 6.76; N, 5.13.

(4*R*,5*S*)-4-(4-Fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile. 3 % as brown oil (22 mg from 500 mg); R_f= 0.27 (hexanes: EtOAc, 80:20, v/v); ν_{max} (Neat) 2214 (CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.32 (dd, 1H, J_1= 12.3 Hz, J_2= 6.1 Hz, CH_2), 3.39-3.44 (m, 1H, CH), 3.55 (dd, 1H, J_1= 12.3 Hz, J_2= 3.6 Hz, CH_2), 5.09 (d, 1H, *J*= 3.4 Hz, CH), 7.13 (t, 2H, *J*= 8.6 Hz, ArH), 7.38-7.51 (m, 5H, ArH), 7.86-7.91 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 27.2, 29.8, 59.9, 115.7, 116.0, 126.7, 127.0, 127.6, 128.6, 128.7, 129.3, 129.4, 131.4, 132.1, 135.0, 159.7, 163.8; mass (ES+) *m/z*= 297.0 (M^++1); DART-HRMS calcd. for $C_{17}H_{14}FN_2S$ 297.0862, Found 297.0863.

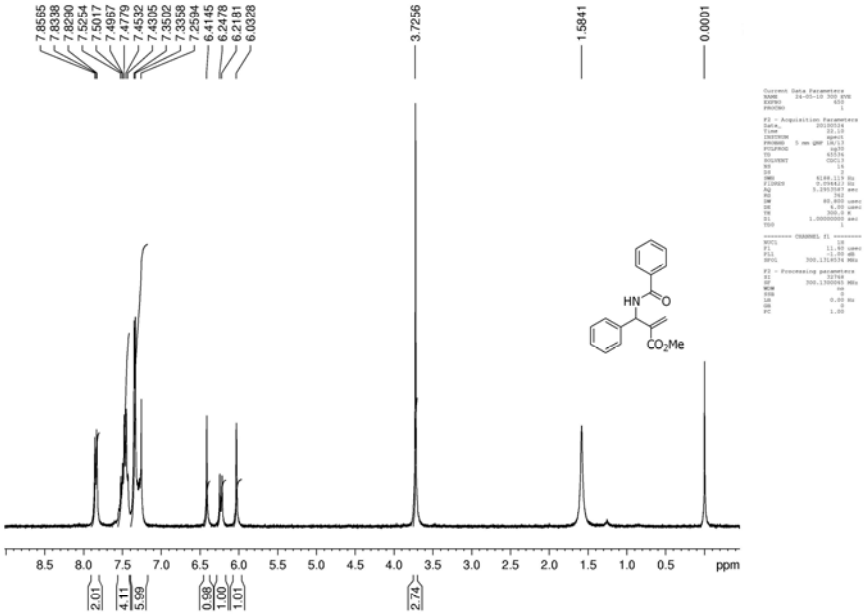

Fig:S-1 ^{1}H spectrum of Methyl 2-[(benzoylamino)(phenyl)methyl]acrylate (5a).

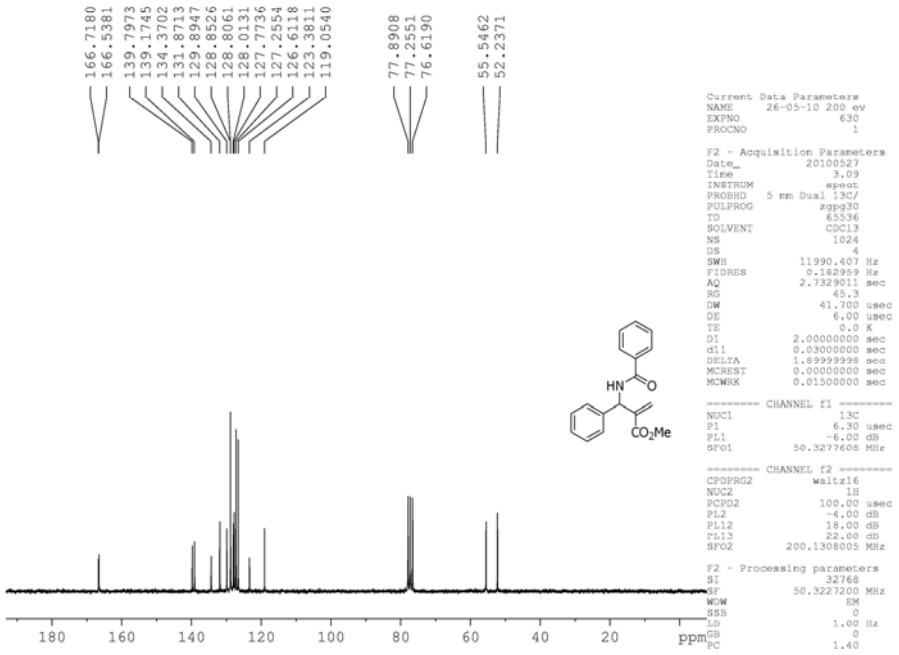

Fig:S-2 ^{13}C spectrum of Methyl (*E*)-2-({5-[1-(benzylamino)-1-methylpropyl]-1*H*-1,2,3,4-tetraazol-1-yl}methyl)-3-(4-fluorophenyl)prop-2-enoate (5a).

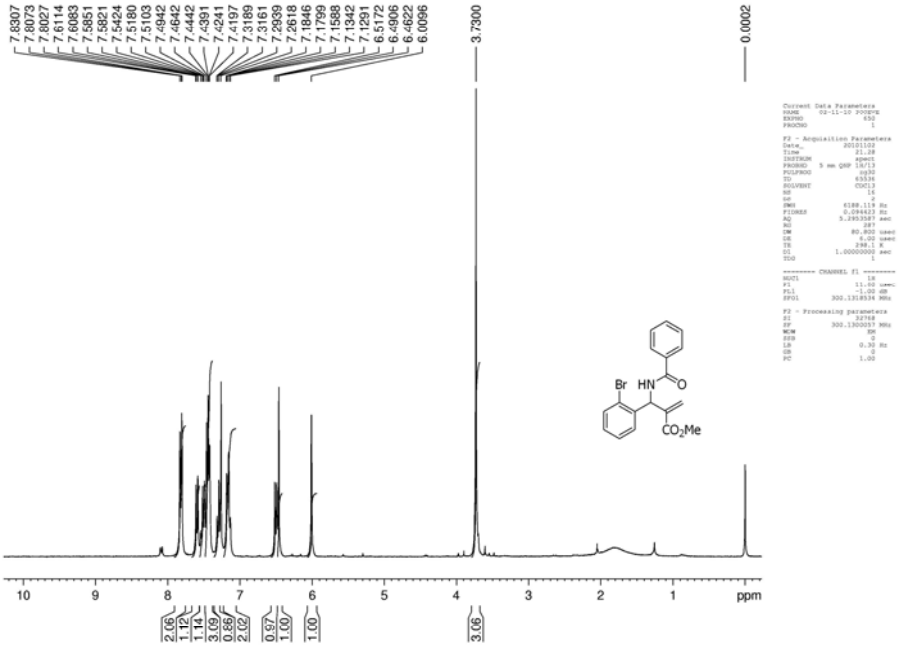

Fig:S- ^{1}H spectrum of Methyl 2-[(benzoylamino)(2-bromophenyl)methyl]acrylate (5b).

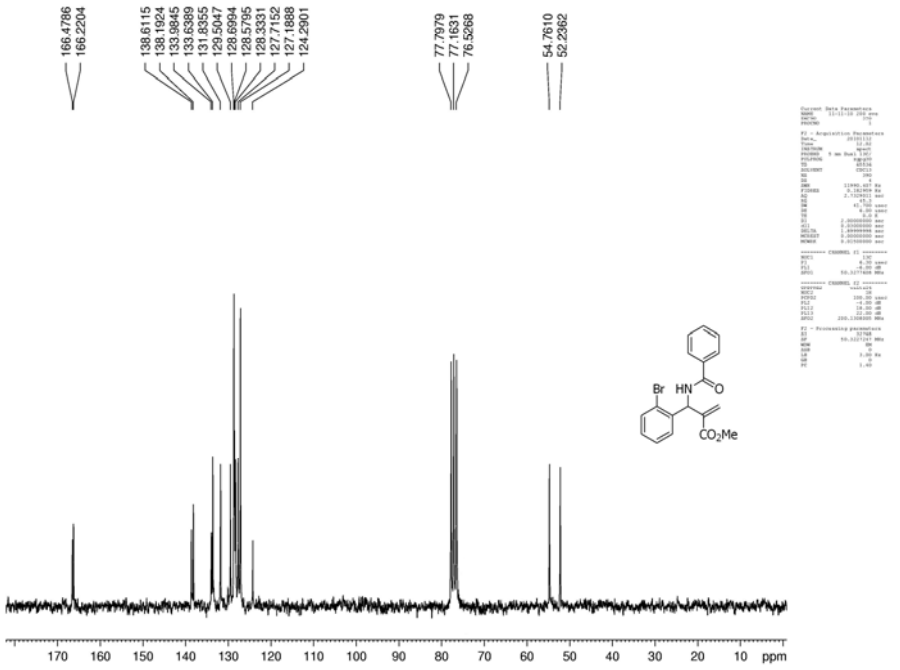

Fig:S-4 ^{13}C spectrum of Methyl 2-[(benzoylamino)(2-bromophenyl)methyl]acrylate (5b).

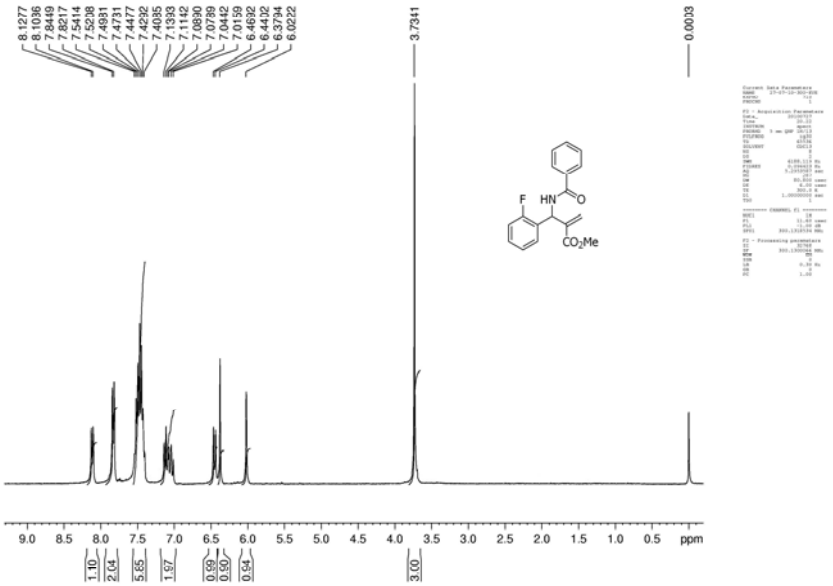

Fig:S-5 ^{1}H spectrum of Methyl 2-[(benzoylamino)(2-fluorophenyl)methyl]acrylate (5c).

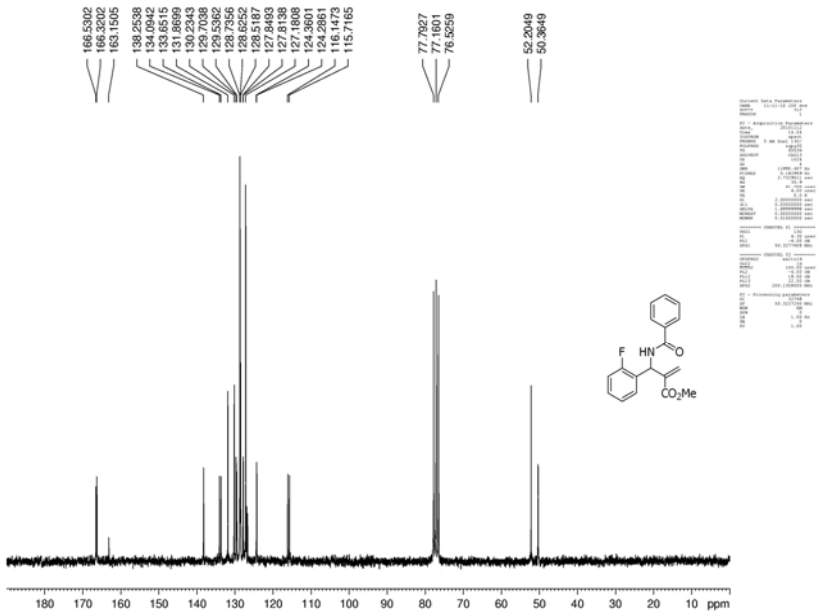

Fig:S-6 ^{13}C spectrum of Methyl 2-[(benzoylamino)(2-fluorophenyl)methyl]acrylate (5d).

This journal is © The Royal Society of Chemistry 2011

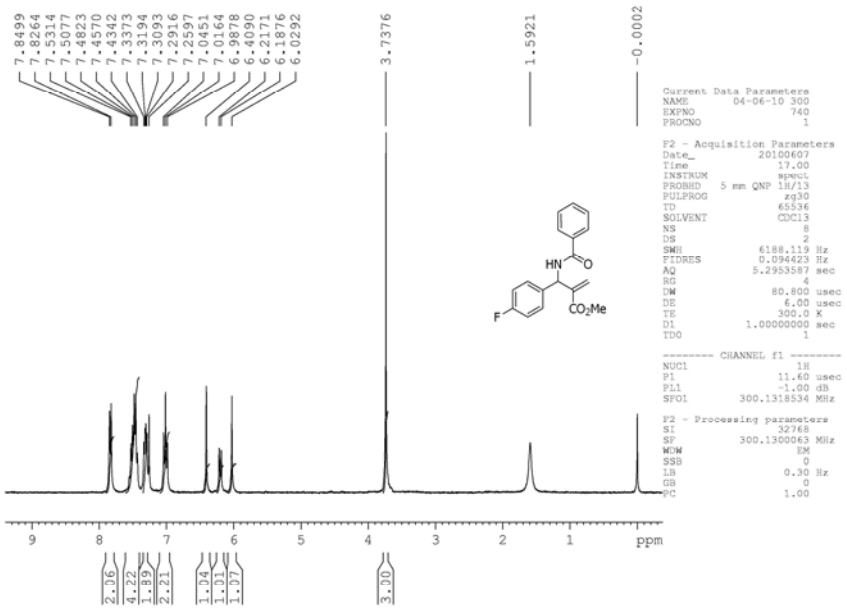

Fig:S-7 ^{1}H spectrum of Methyl 2-[(benzoylamino)(4-fluorophenyl)methyl]acrylate (5d).

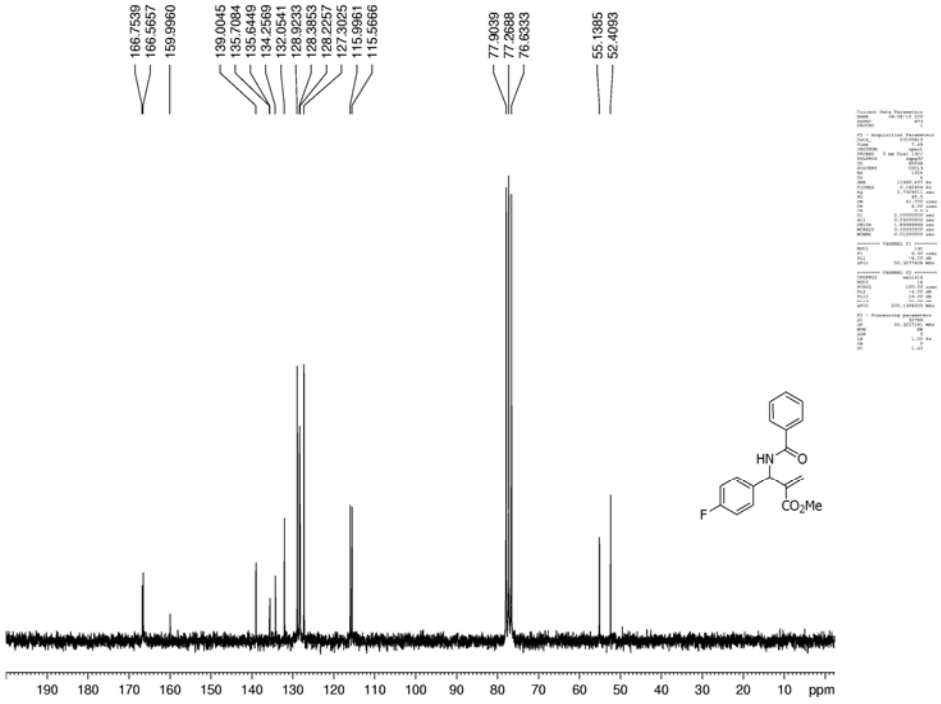

Fig:S-8 ^{13}C spectrum of Methyl 2-[(benzoylamino)(4-fluorophenyl)methyl]acrylate (5d).

This journal is © The Royal Society of Chemistry 2011

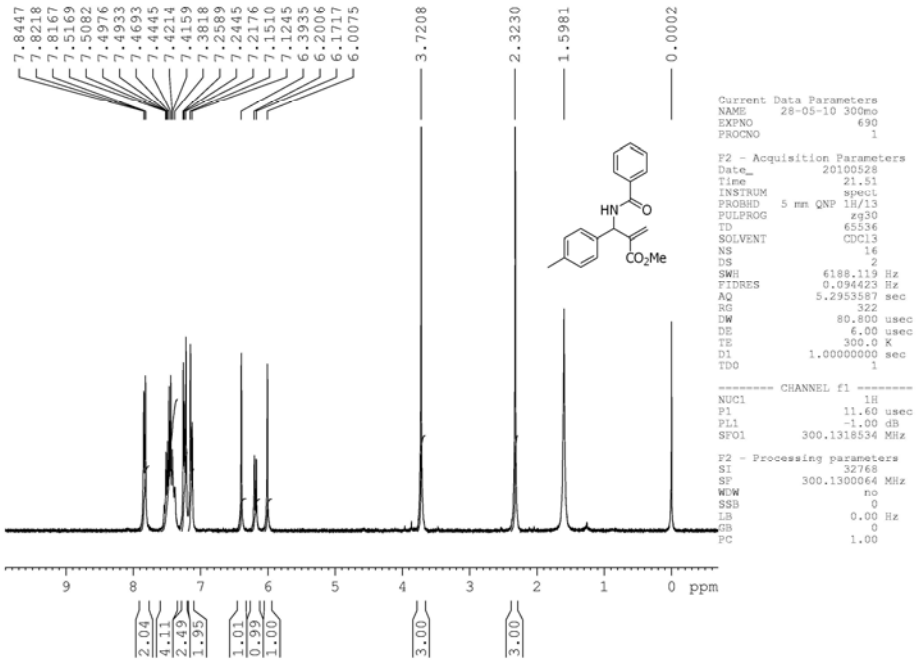

Fig:S-9 ^{1}H spectrum of Methyl 2-[(benzoylamino)(4-methylphenyl)methyl]acrylate (5e).

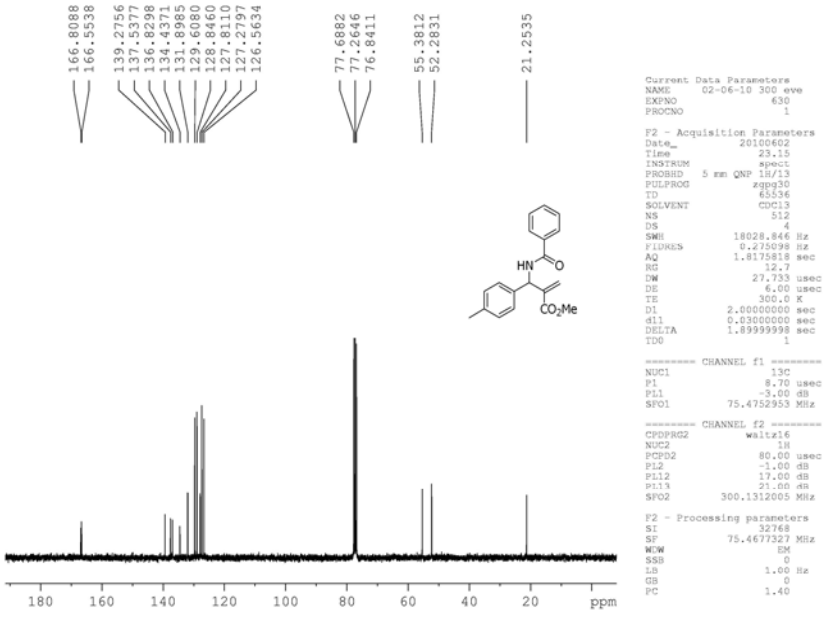

Fig:S-10 ^{13}C spectrum of Methyl 2-[(benzoylamino)(4-methylphenyl)methyl]acrylate (5e).

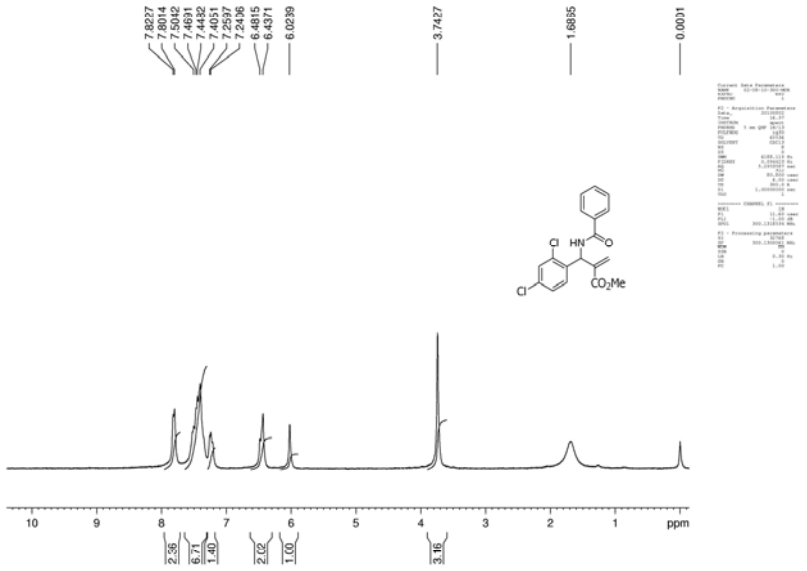

Fig:S-11 ^{1}H spectrum of Methyl 2-[(benzoylamino)(2,4-dichlorophenyl)methyl]acrylate (5f).

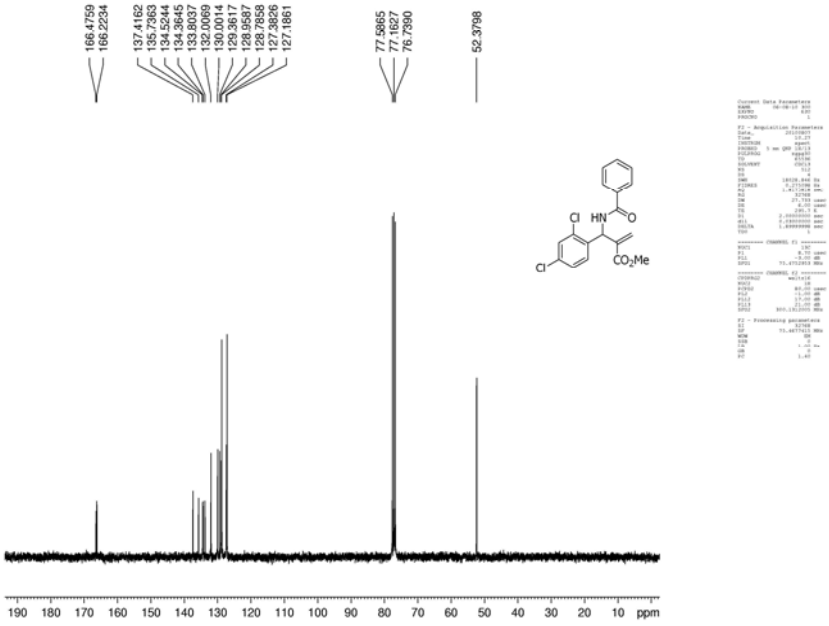

Fig:S-12 ^{13}C spectrum of Methyl 2-[(benzoylamino)(2,4-dichlorophenyl)methyl]acrylate (5f).

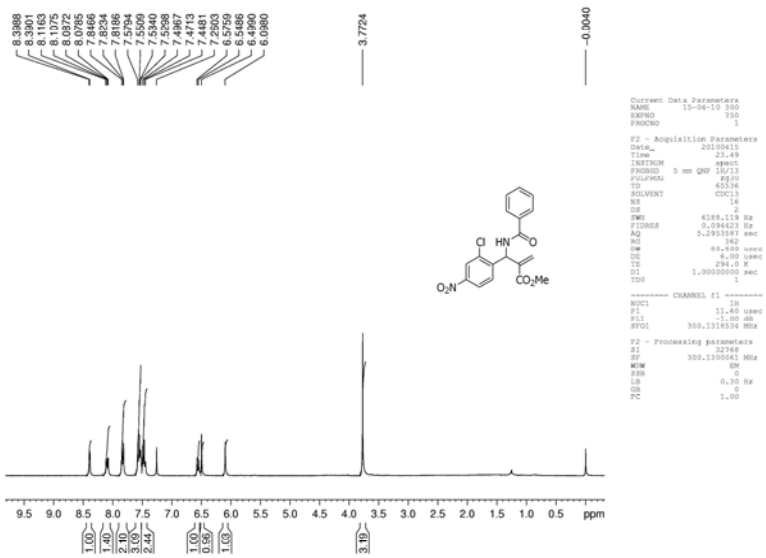

Fig:S-13 ^{1}H spectrum of Methyl 2-[(benzoylamino)(2-chloro-4-nitrophenyl)methyl]acrylate (5g).

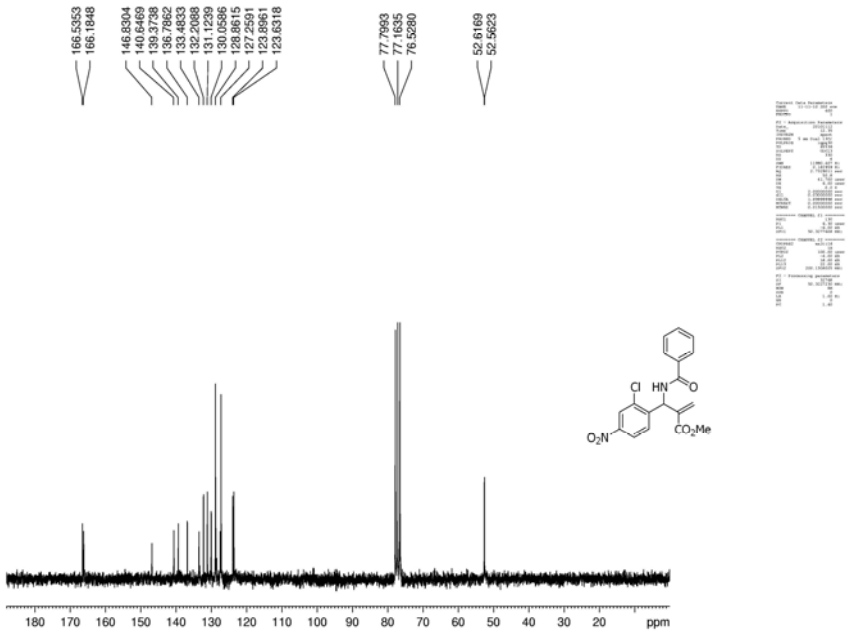

Fig:S-14 ^{13}C spectrum of Methyl 2-[(benzoylamino)(2-chloro-4-nitrophenyl)methyl]acrylate (5g).

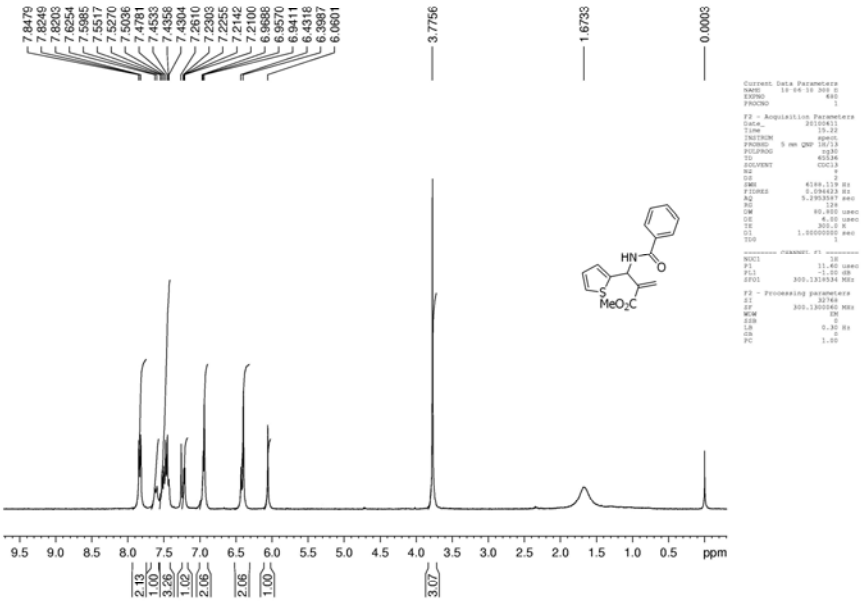

Fig:S-15 ^{1}H spectrum of Methyl 2-[(benzoylamino)(2-thienyl)methyl]acrylate (5h).

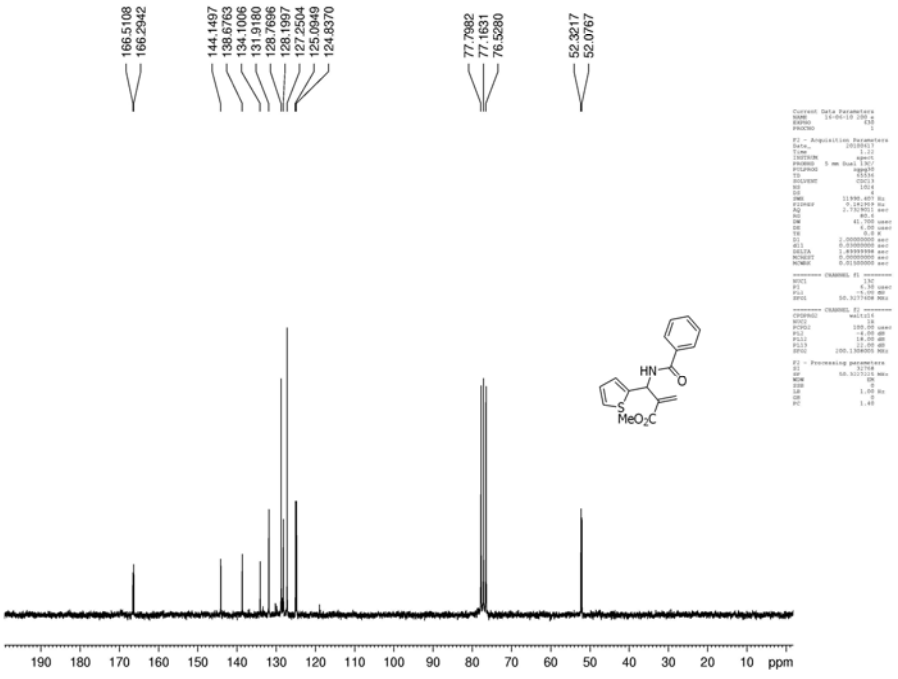

Fig:S-16 ^{13}C spectrum of Methyl 2-[(benzoylamino)(2-thienyl)methyl]acrylate (5h).

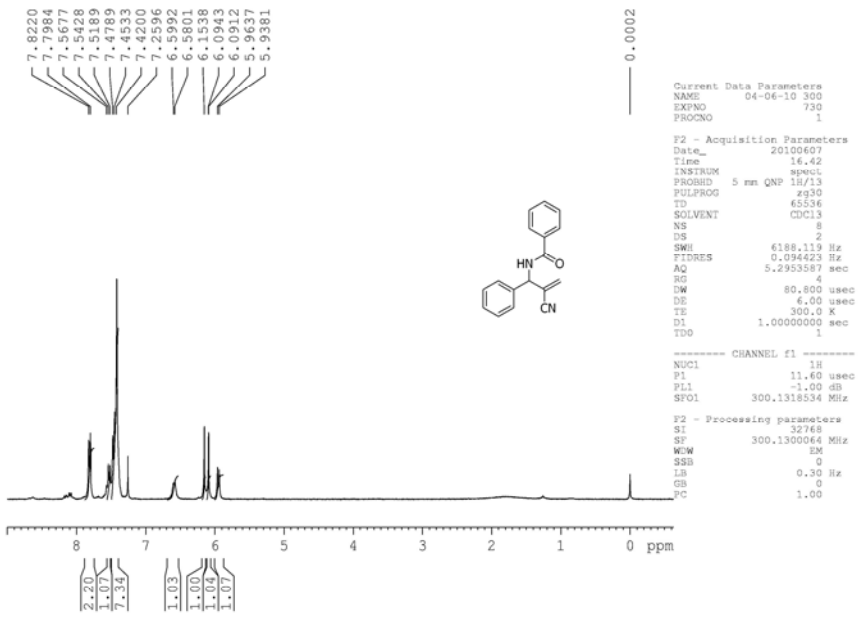

Fig:S-17 ^{1}H spectrum of *N*-(2-cyano-1-phenylallyl)benzamide (6a).

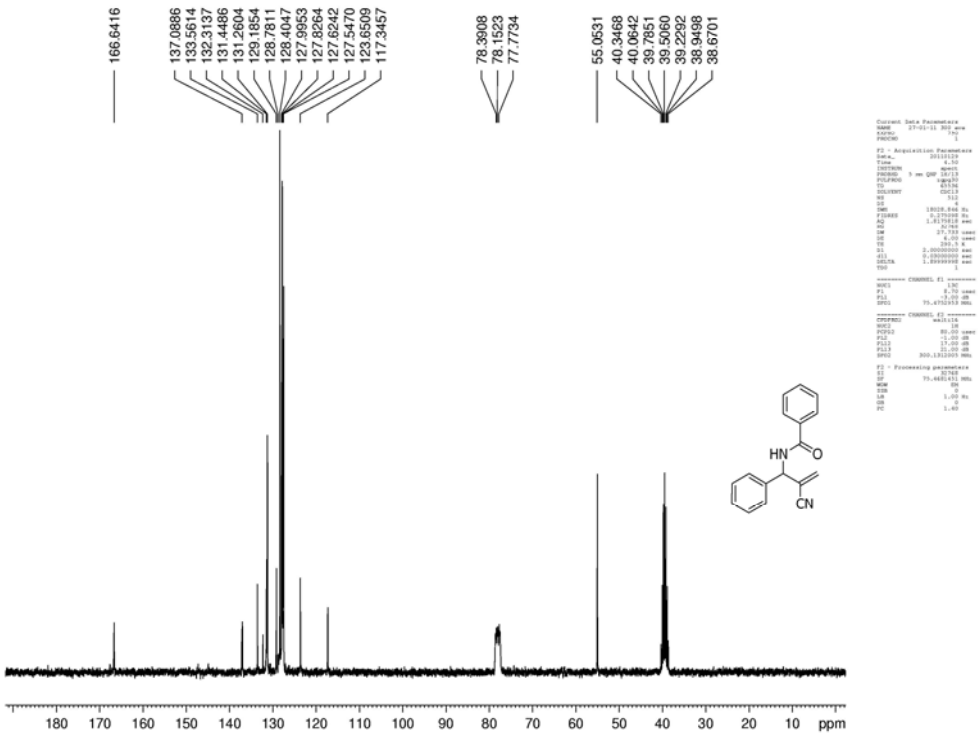

Fig:S-18 ^{13}C spectrum of *N*-(2-cyano-1-phenylallyl)benzamide (6a).

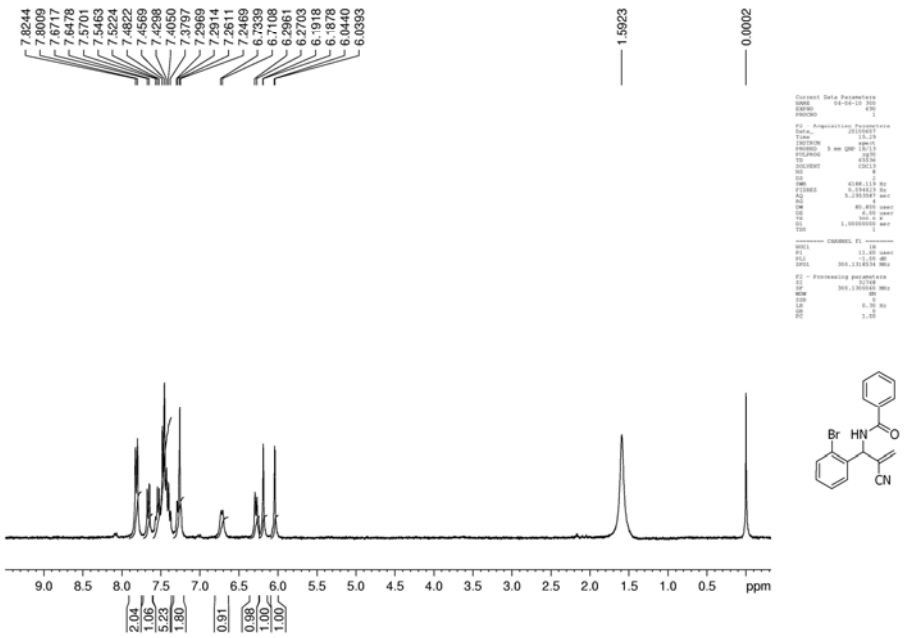

Fig:S-19 ^{1}H spectrum of *N*-(1-(2-bromophenyl)-2-cyanoallyl)benzamide (6b).

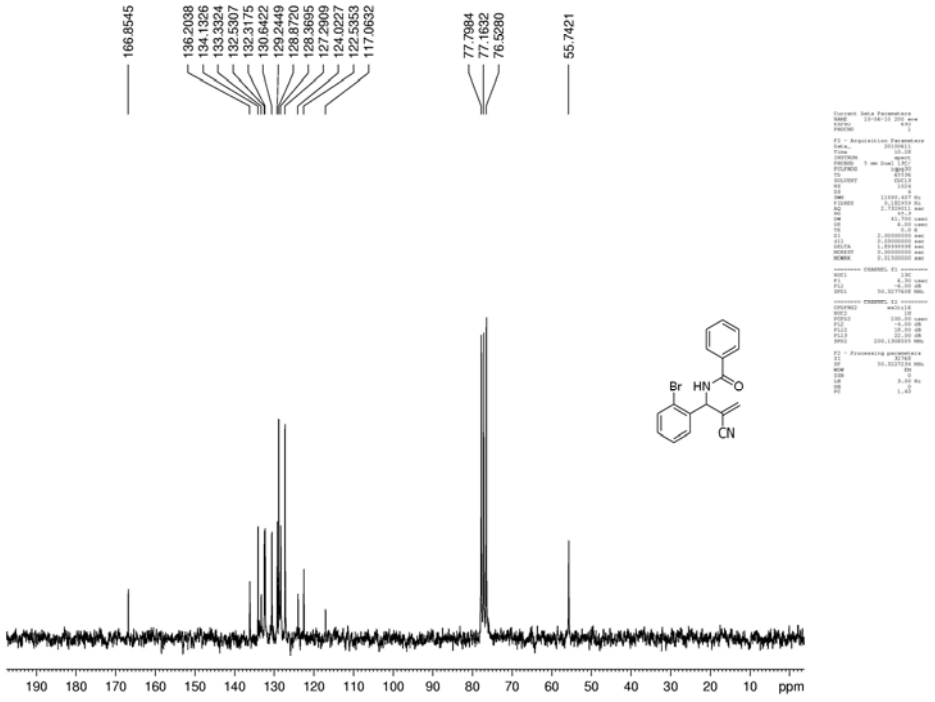

Fig:S-20 ^{13}C spectrum of *N*-[1-(2-bromophenyl)-2-cyanoallyl]benzamide (6b).

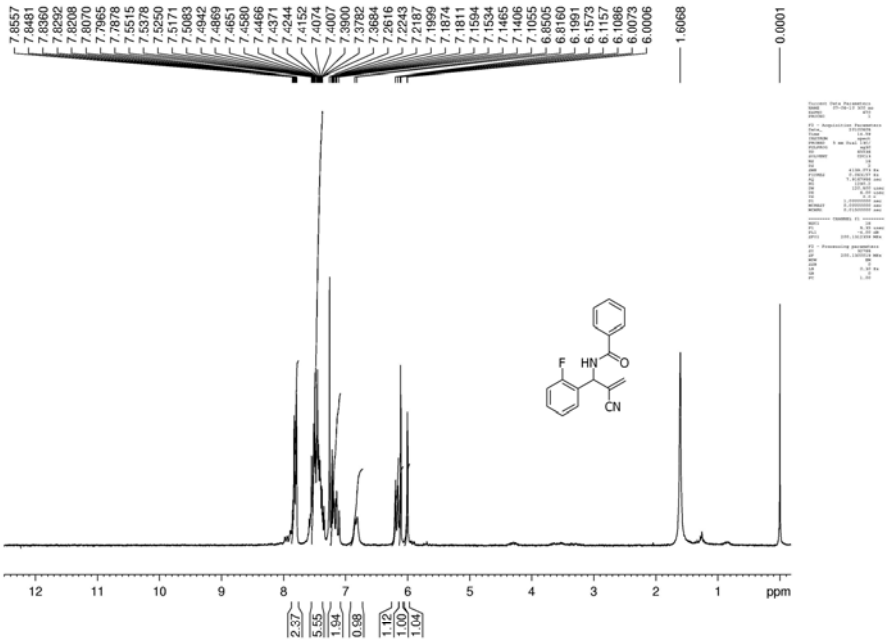

Fig:S-21 ^{1}H spectrum of *N*-[2-cyano-1-(2-fluorophenyl)allyl]benzamide (6c).

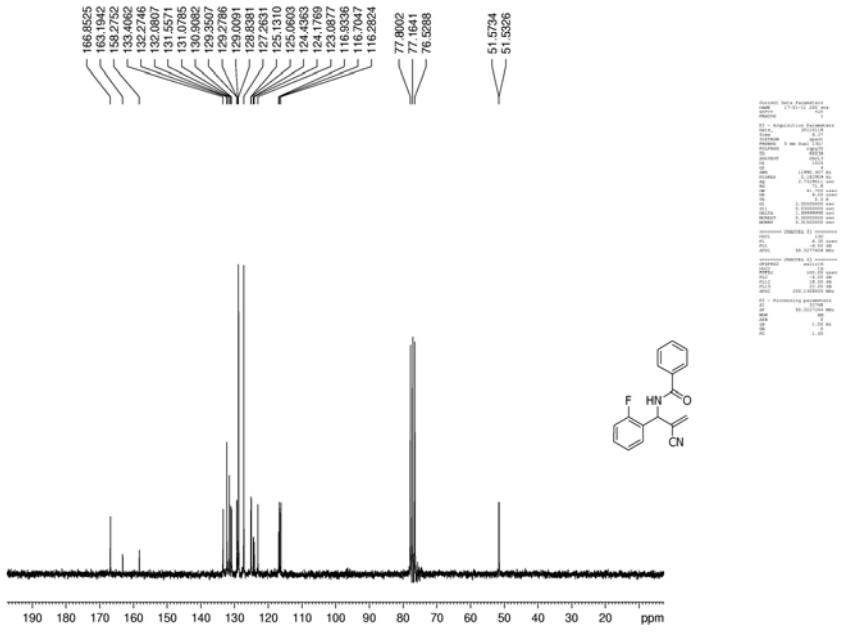

Fig:S-22 ^{13}C spectrum of *N*-[2-cyano-1-(2-fluorophenyl)allyl]benzamide (6c).

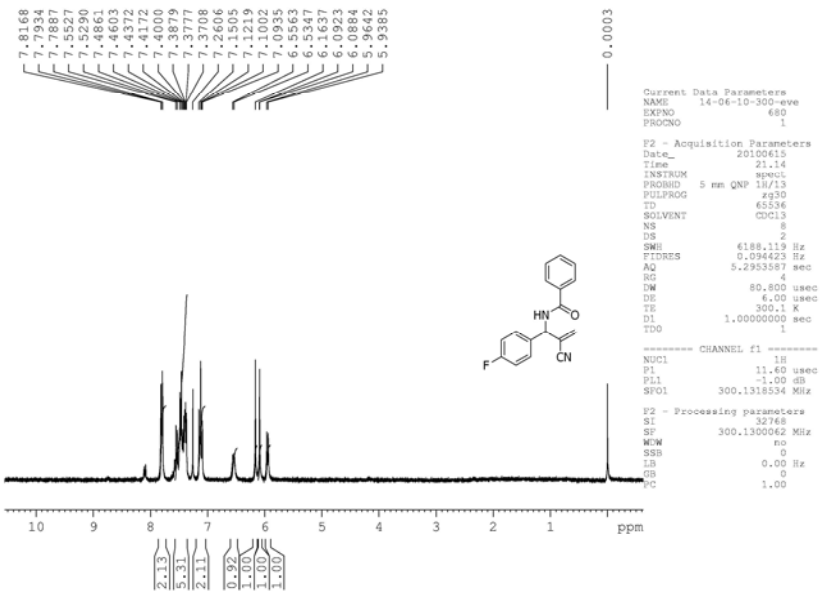

Fig:S-23 ^{1}H spectrum of *N*-[2-cyano-1-(4-fluorophenyl)allyl]benzamide (6d).

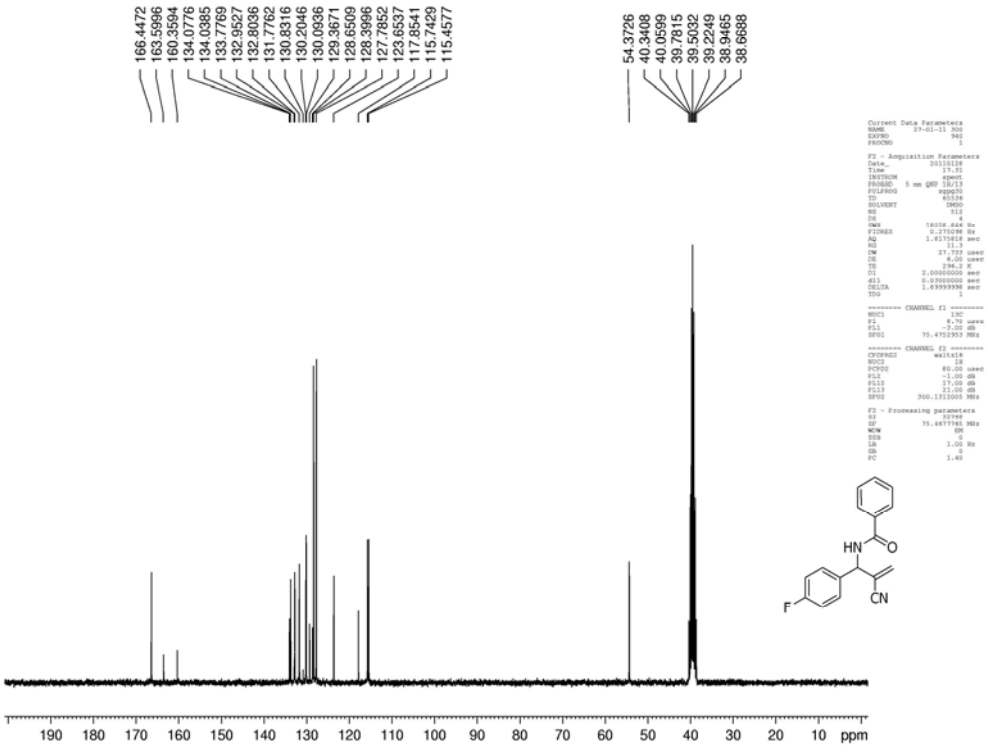

Fig:S-24 ^{13}C spectrum of *N*-[2-cyano-1-(4-fluorophenyl)allyl]benzamide (6d).

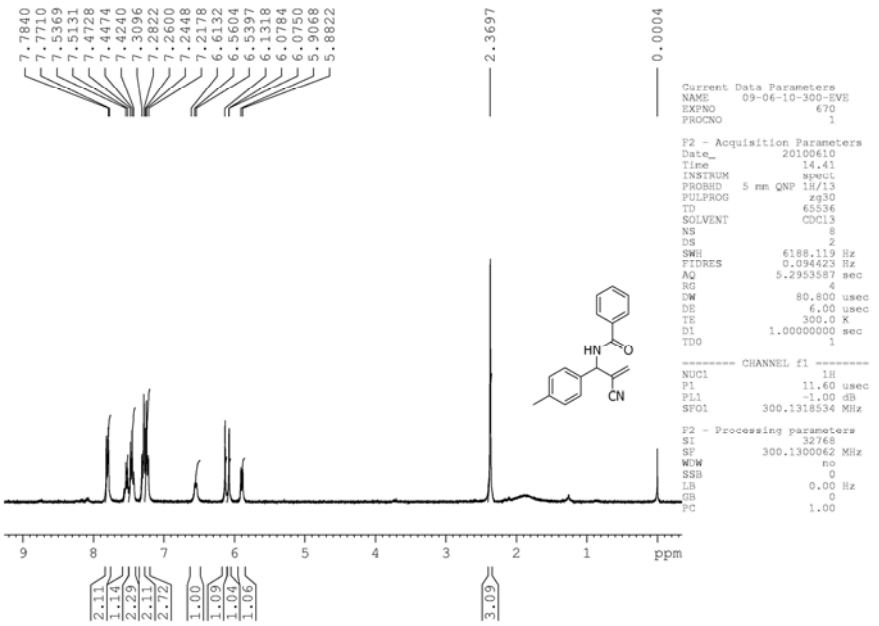

Fig:S-25 ^{1}H spectrum of *N*-(2-cyano-1-*p*-tolylallyl)benzamide (6e).

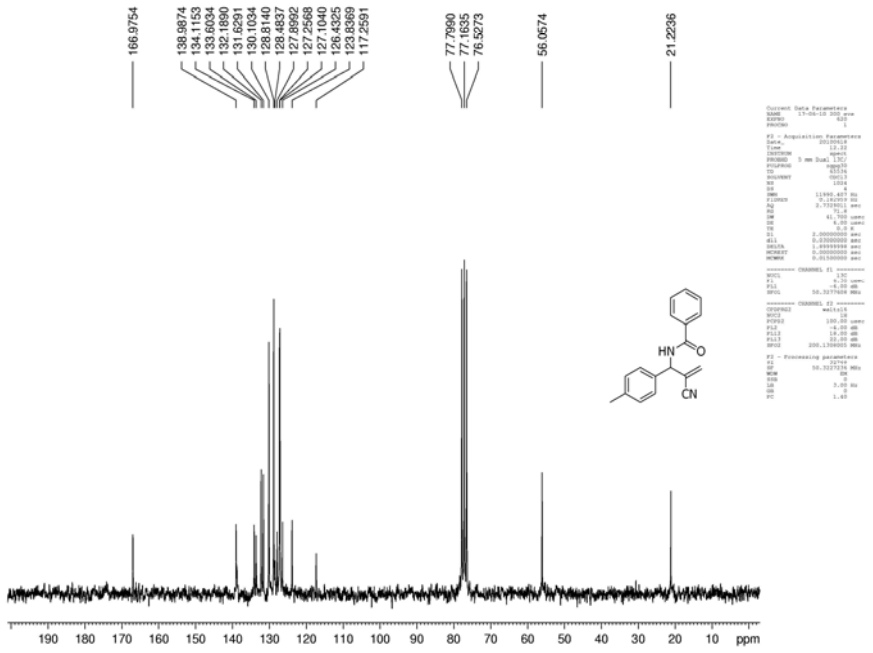

Fig:S-26 ^{13}C spectrum of *N*-(2-cyano-1-*p*-tolylallyl)benzamide (6e).

This journal is © The Royal Society of Chemistry 2011

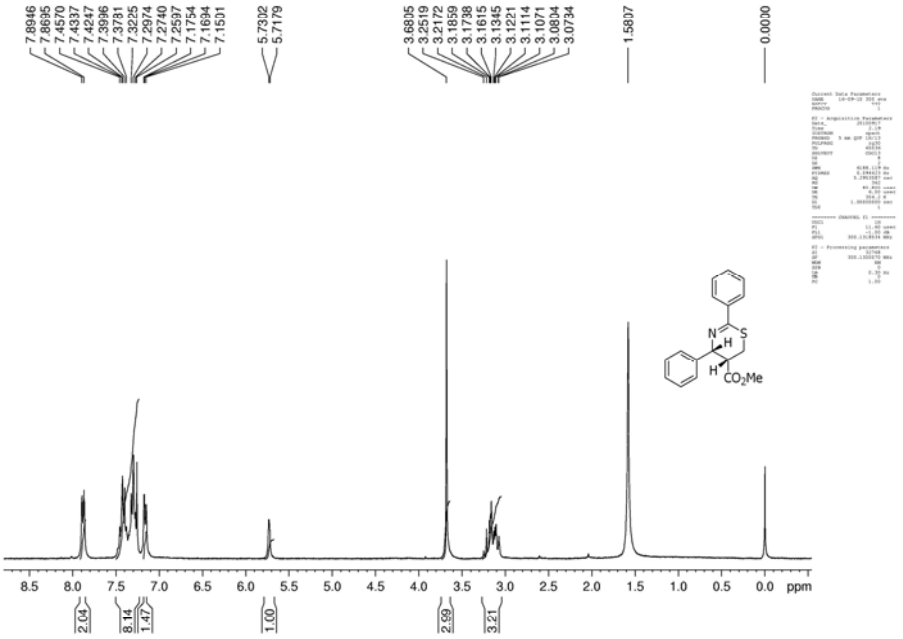

Fig:S-27 ^{1}H spectrum of Methyl (4*R*,5*S*)-2,4-diphenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7a).

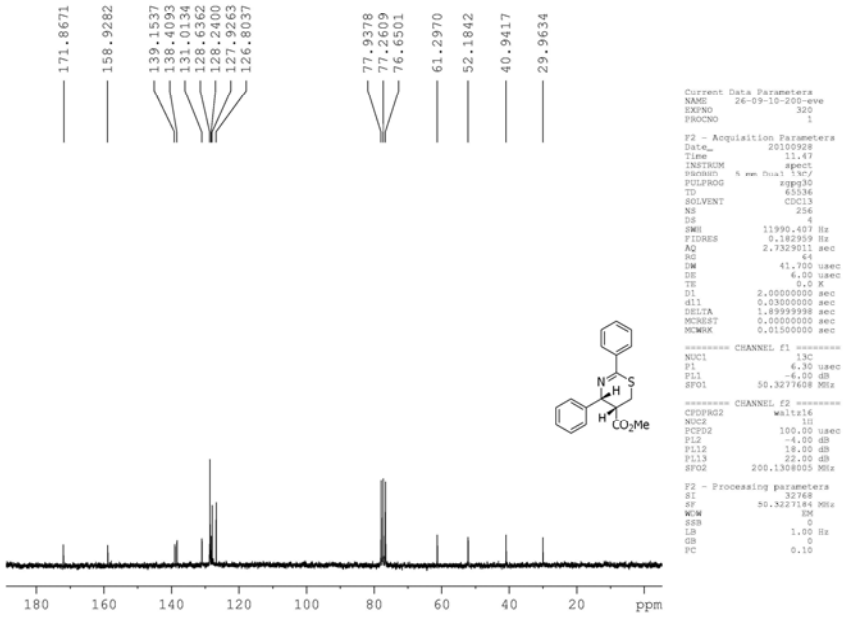

Fig:S-28 ^{13}C spectrum of Methyl (4*R*,5*S*)-2,4-diphenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7a).

This journal is © The Royal Society of Chemistry 2011

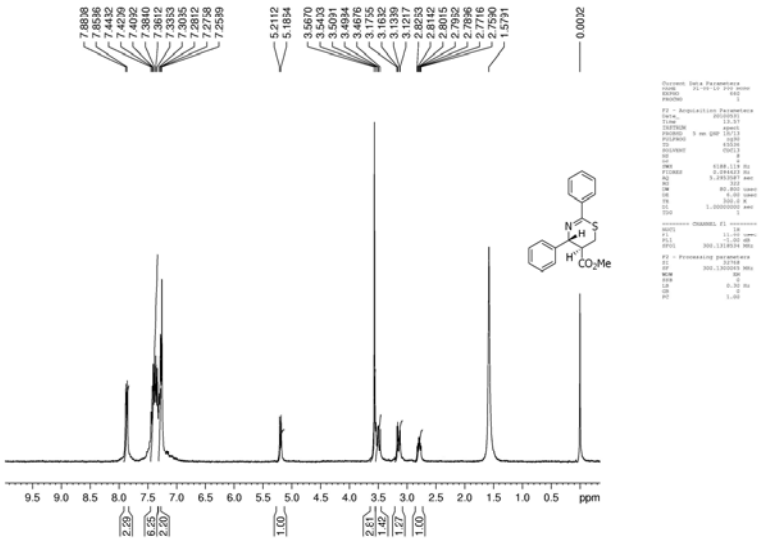

Fig:S-29 ^{1}H spectrum of Methyl (4*R*,5*R*)-2,4-diphenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7a).

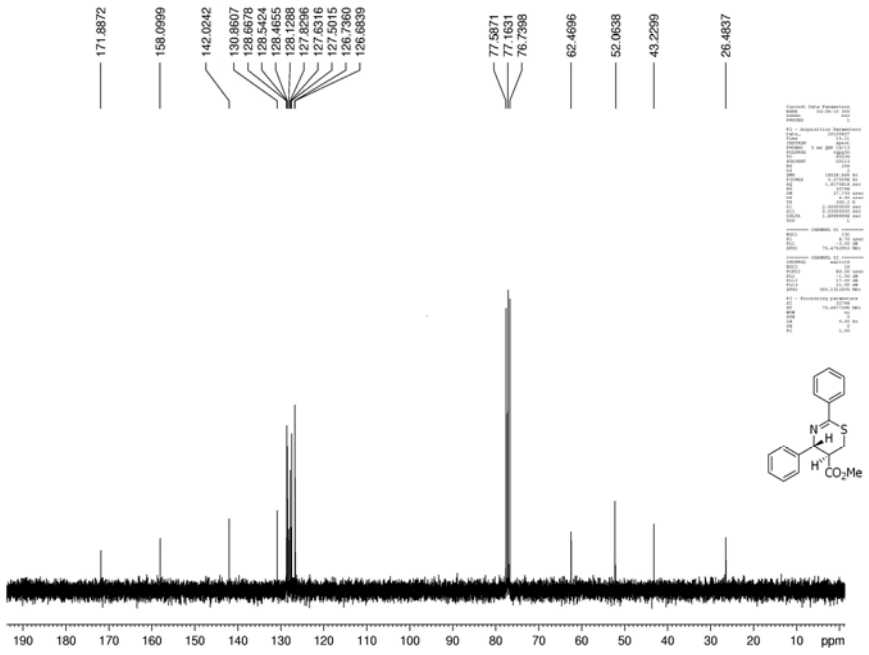

Fig:S-30 ^{13}C spectrum of Methyl (4*R*,5*R*)-2,4-diphenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7a).

This journal is © The Royal Society of Chemistry 2011

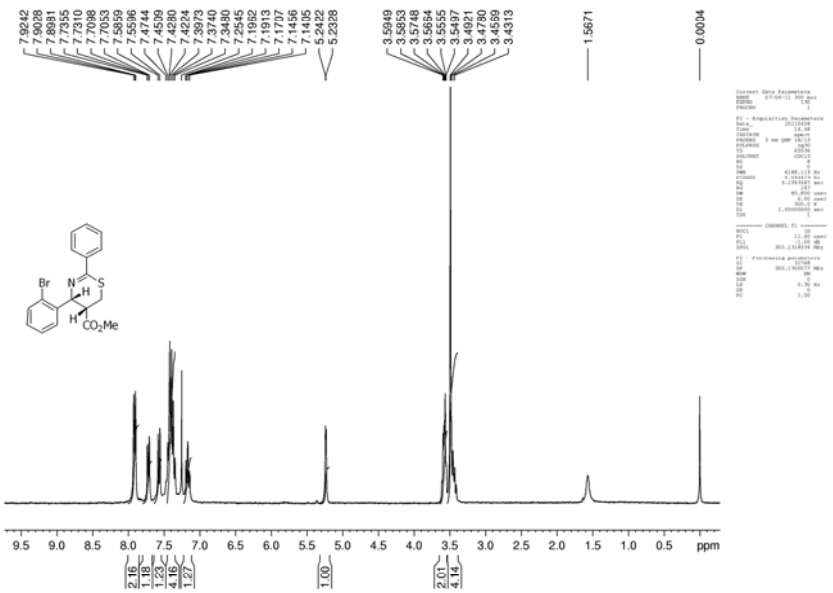

Fig:S-31 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7b).

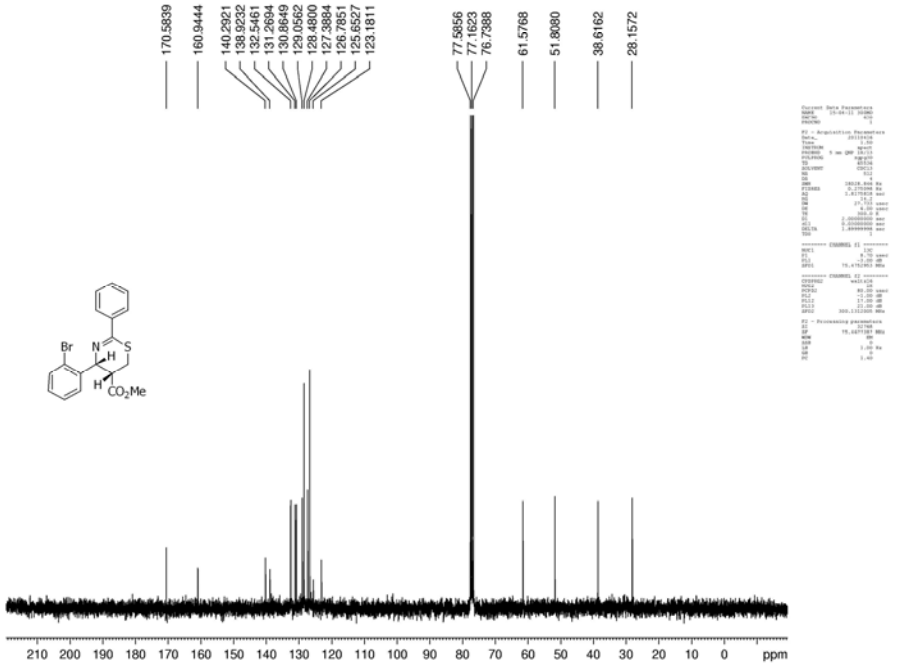

Fig:S-32 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7b).

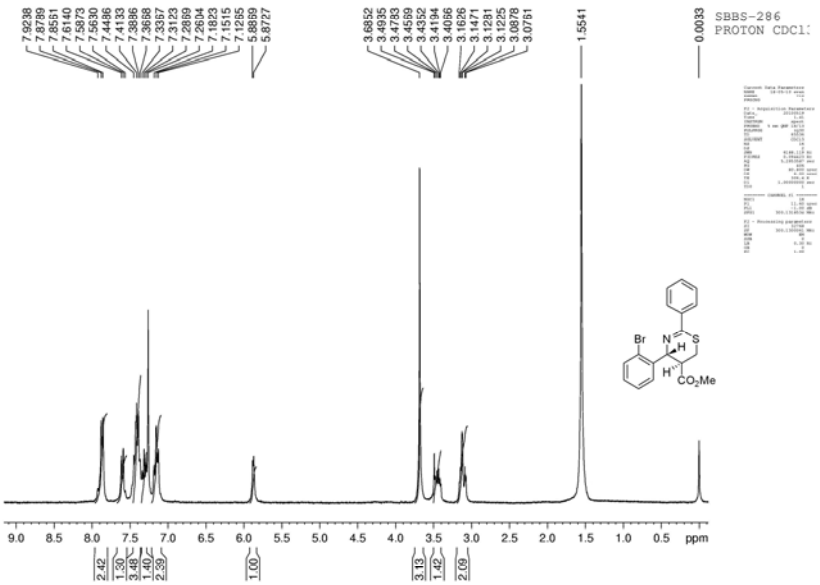

Fig:S-33 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti*7b).

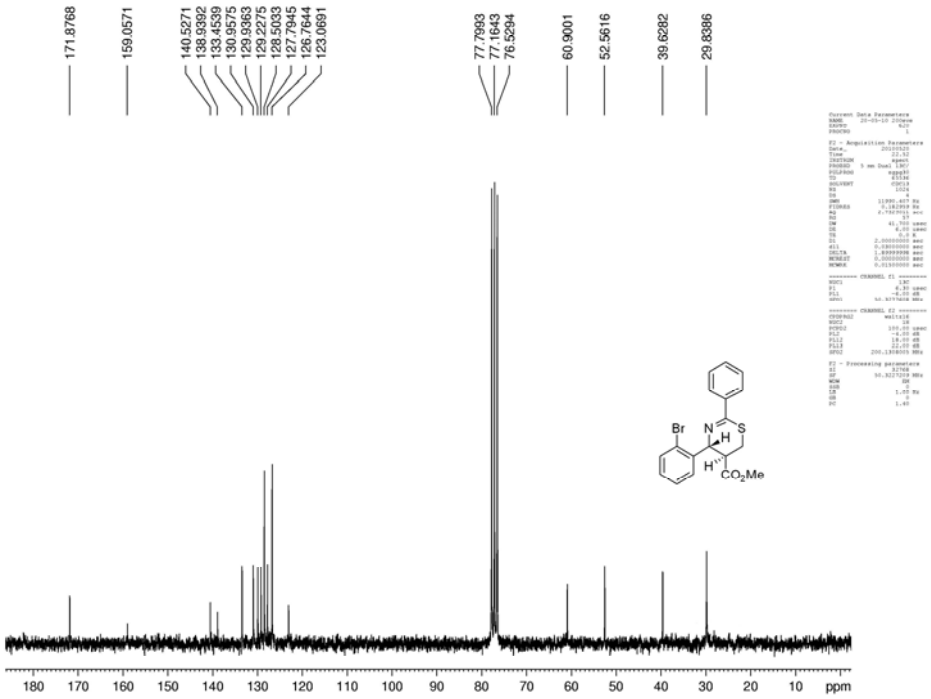

Fig:S-34 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-bromophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7b).

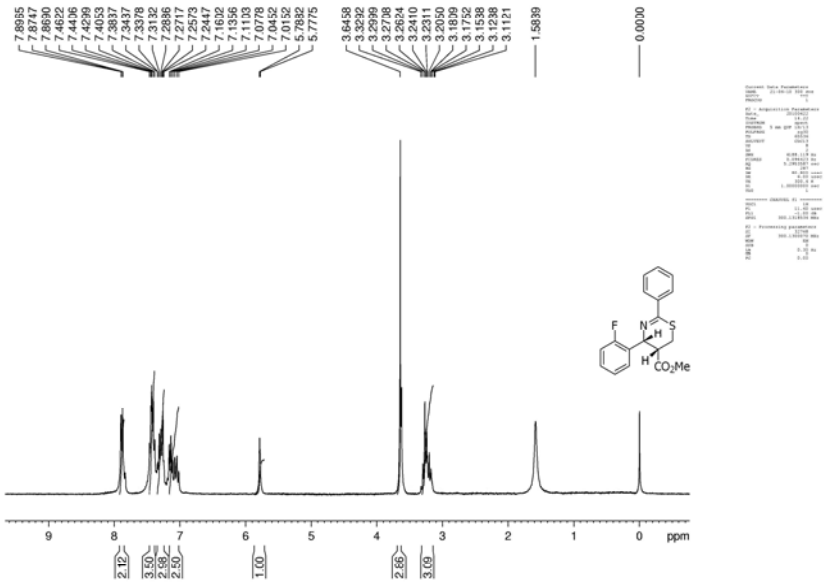

Fig:S-35 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(2-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7c).

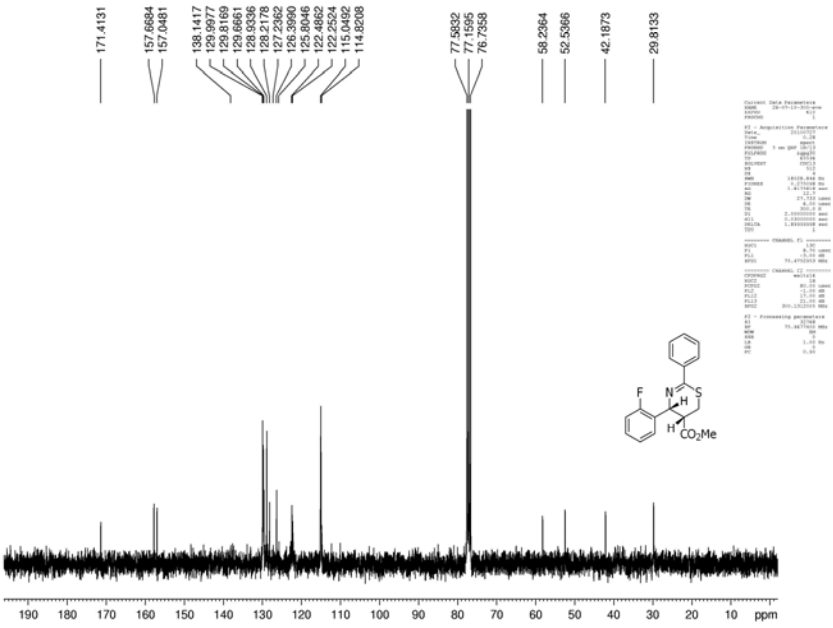

Fig:S-36 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 7c).

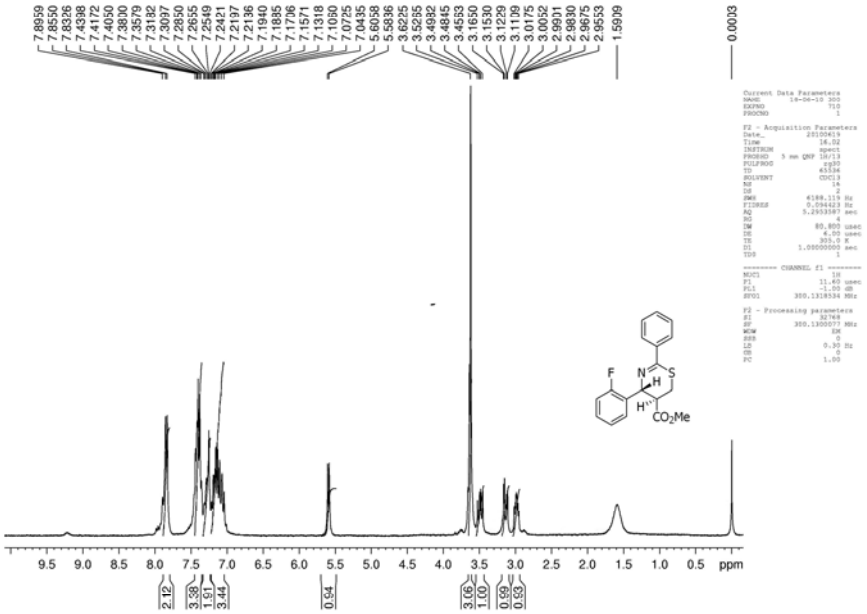

Fig:S-37 ^{1}H spectrum of Methyl (4*R*,5*R*)-4-(2-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7c).

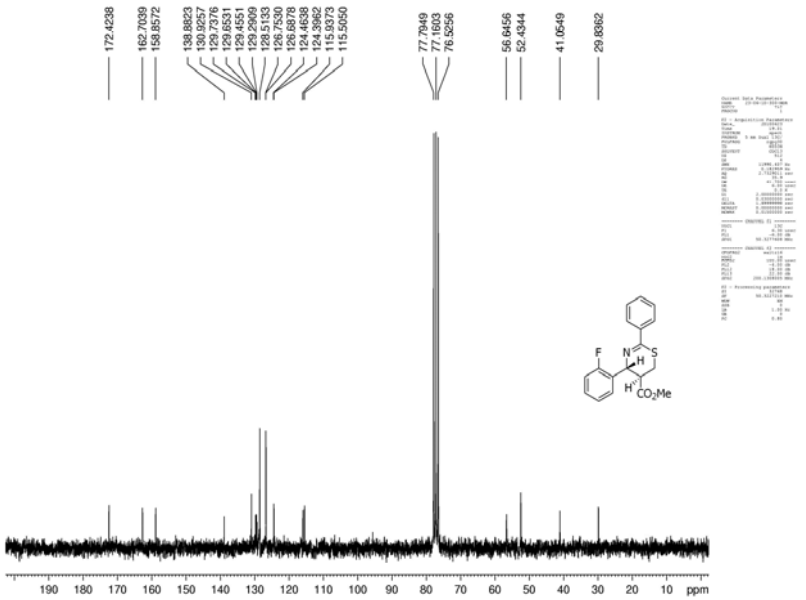

Fig:S-38 ^{13}C spectrum of Methyl (4*R*,5*R*)-4-(2-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7c).

This journal is © The Royal Society of Chemistry 2011

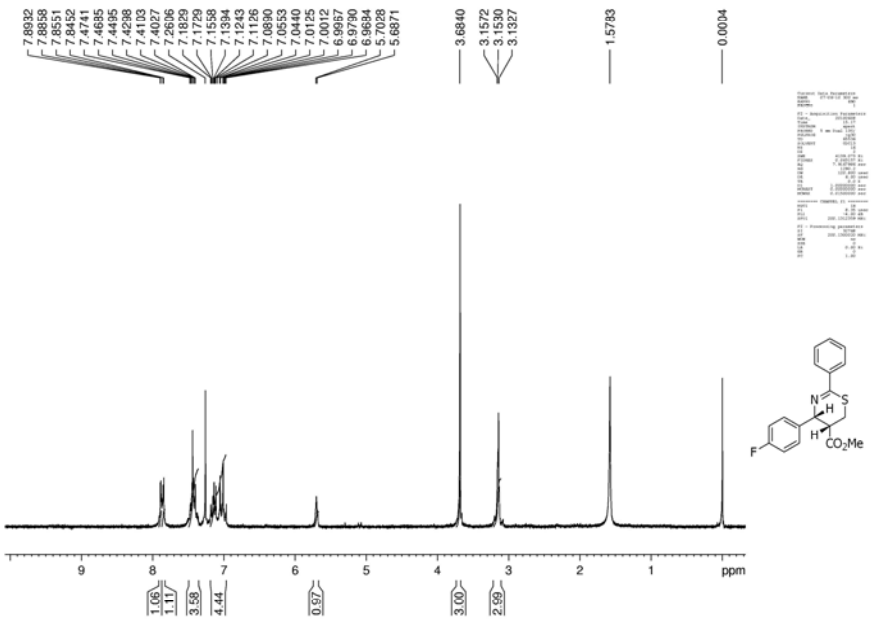

Fig:S-39 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7d).

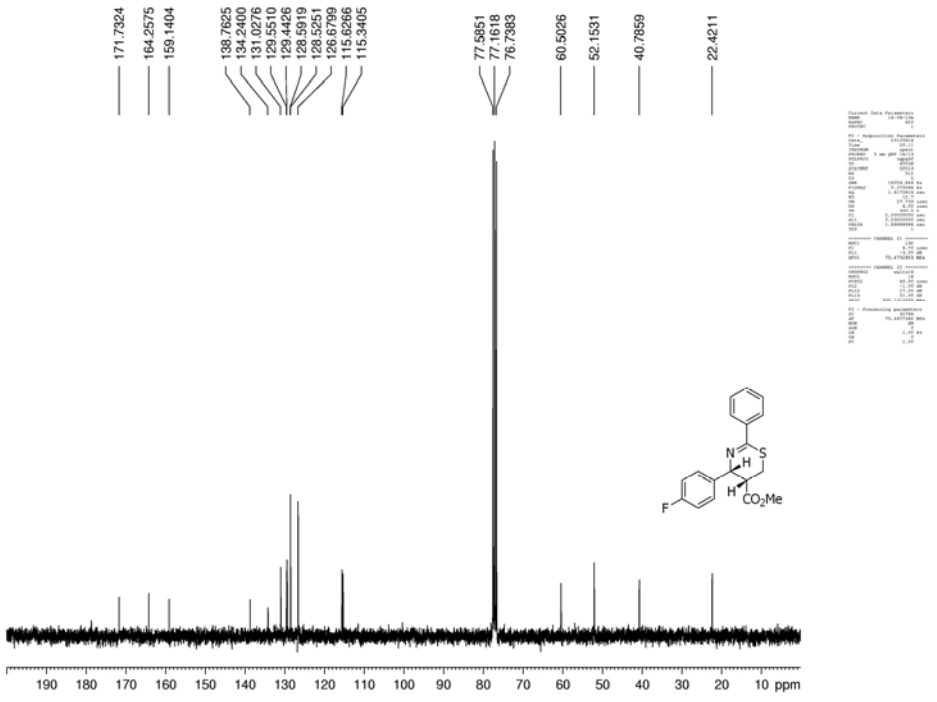

Fig:S-40 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7d).

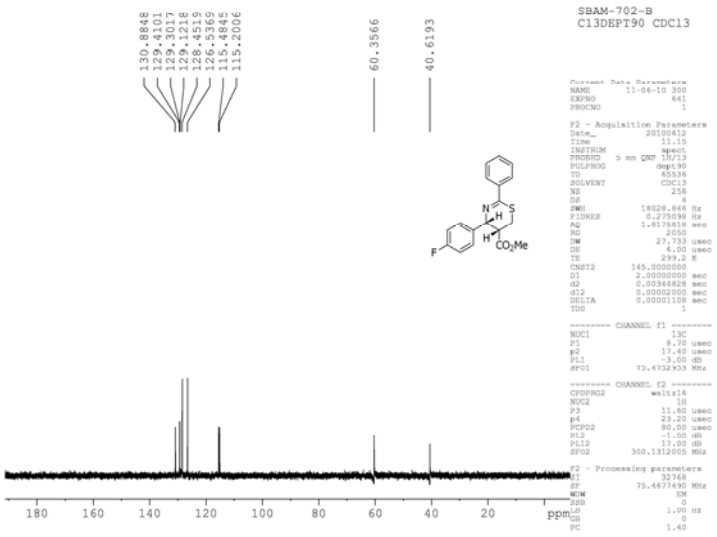

Fig:S-41 DEPT-90 spectrum of Methyl (4*R*,5*S*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7d).

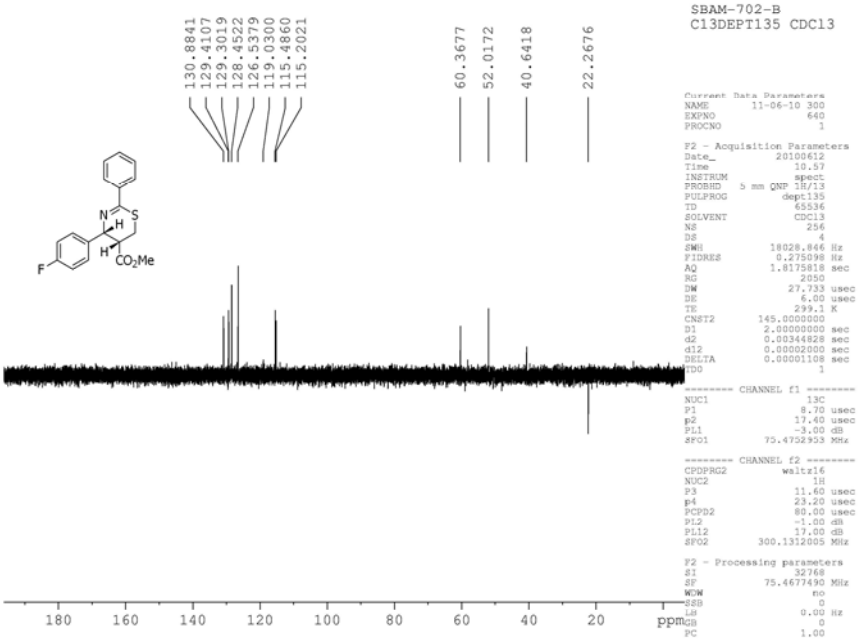

Fig:S-42 DEPT-135 spectrum of Methyl (4*R*,5*S*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7d).

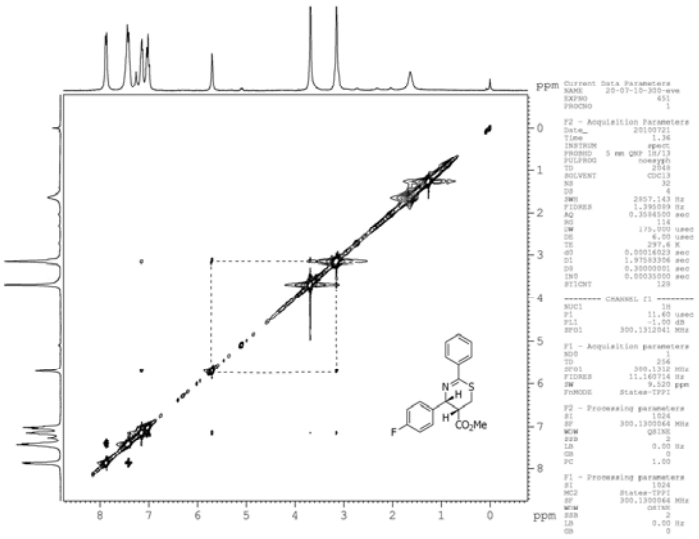

Fig:S-43 NOESY spectrum of Methyl (4*R*,5*S*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7d).

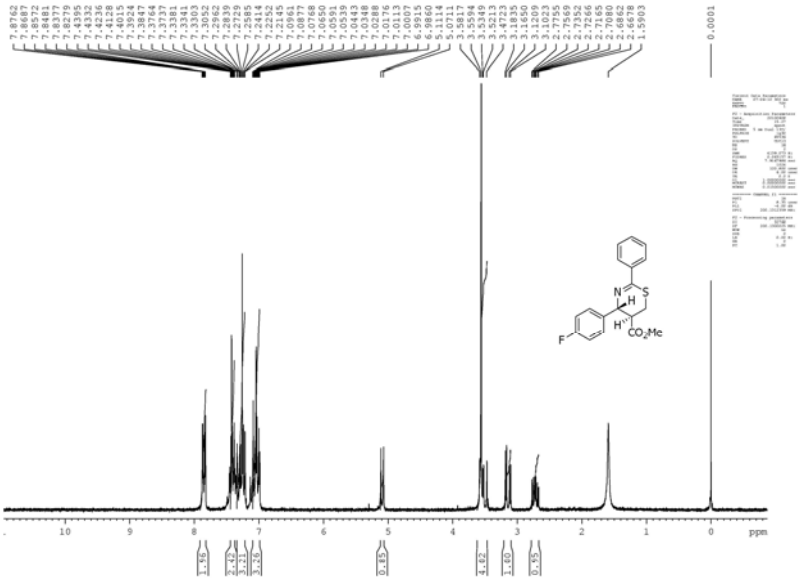

Fig:S-44 ^{1}H spectrum of Methyl (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7d).

This journal is © The Royal Society of Chemistry 2011

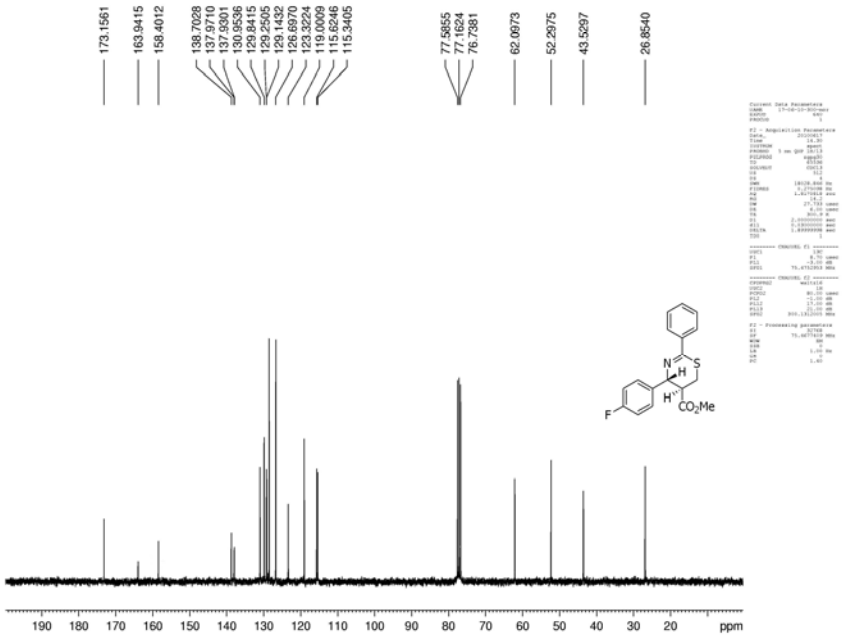

Fig:S-45 ^{13}C spectrum of Methyl (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7d).

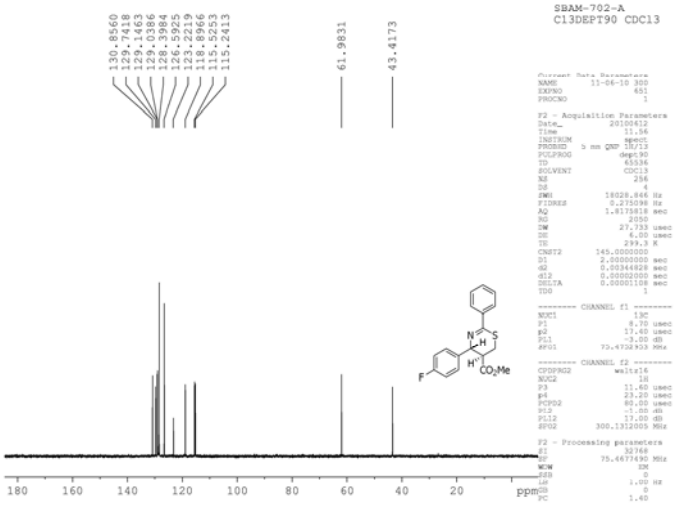

Fig:S-46 DEPT-90 spectrum of Methyl (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7d).

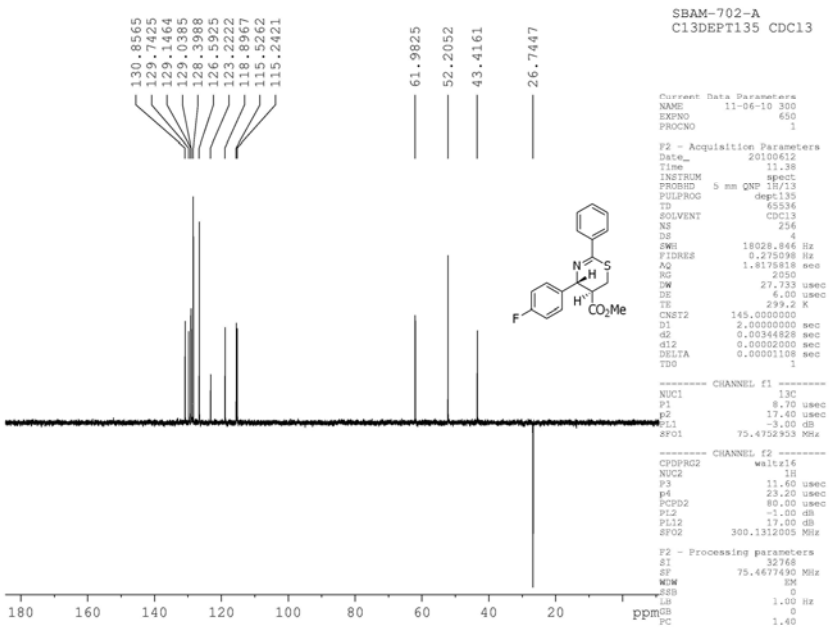

Fig:S-47 DEPT-135 spectrum of Methyl (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7d).

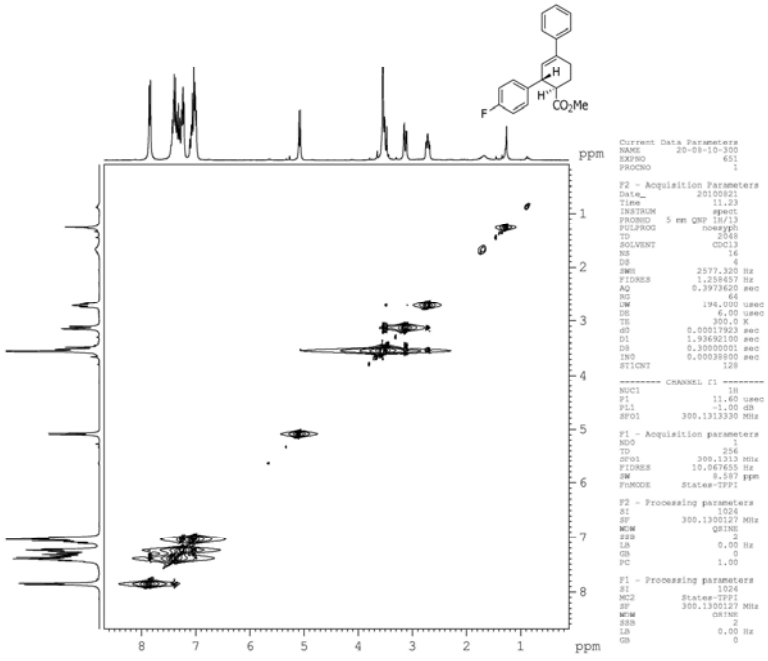

Fig:S-48 NOESY spectrum of Methyl (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7d).

This journal is © The Royal Society of Chemistry 2011

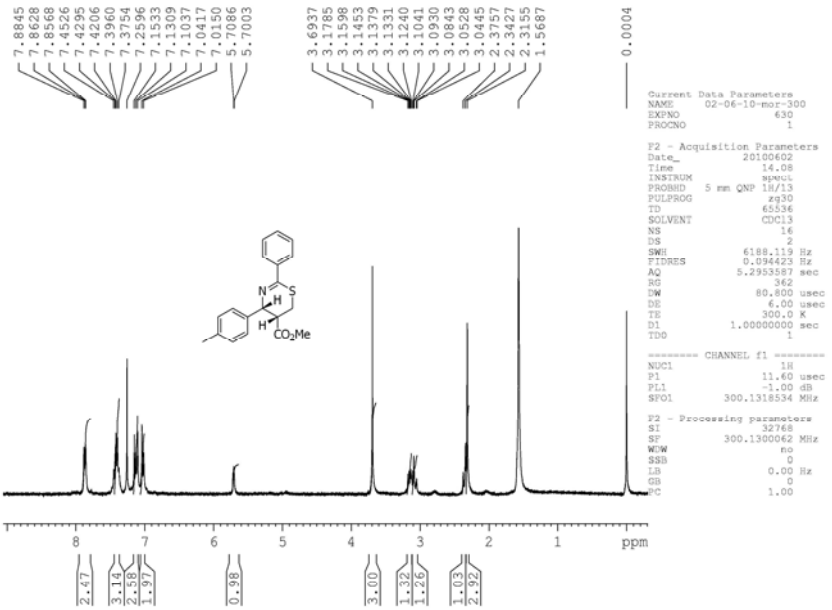

Fig:S-49 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(4-methylphenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate(*syn* 7e).

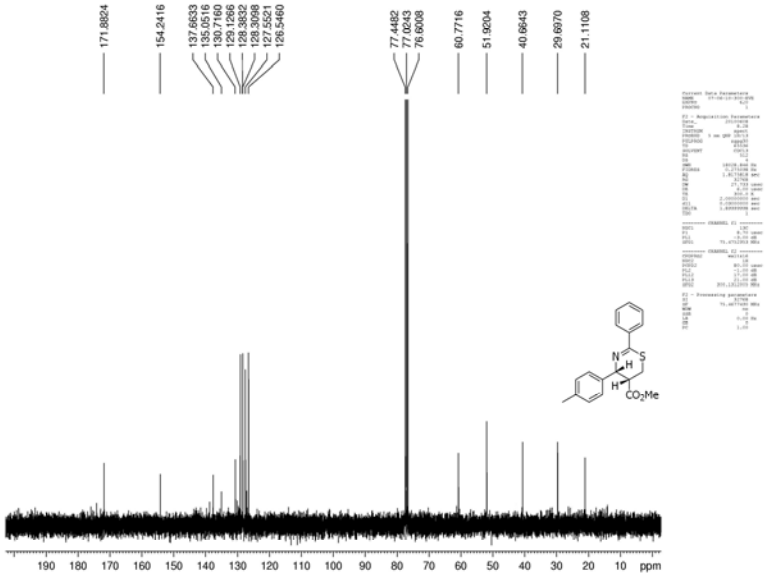

Fig:S-50 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(4-methylphenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn*7e).

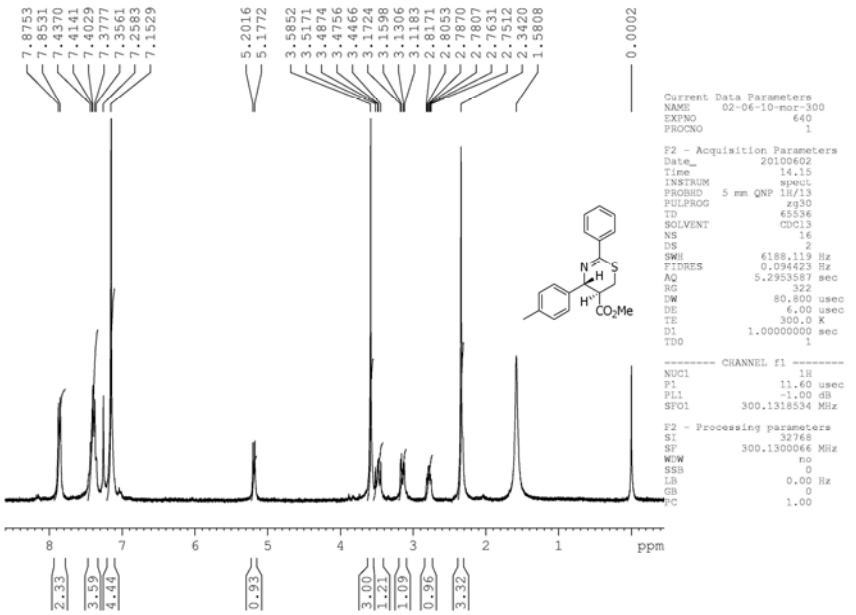

Fig:S-51 ^{1}H spectrum of Methyl (4*R*,5*R*)-4-(4-methylphenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7e).

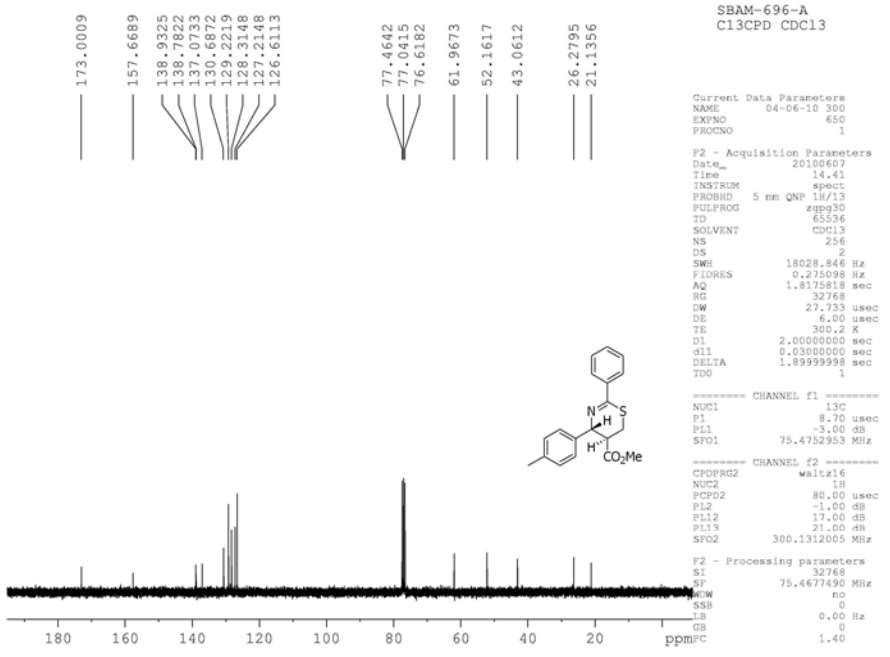

Fig:S-52 ^{13}C spectrum of Methyl (4*R*,5*R*)-4-(4-methylphenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7e).

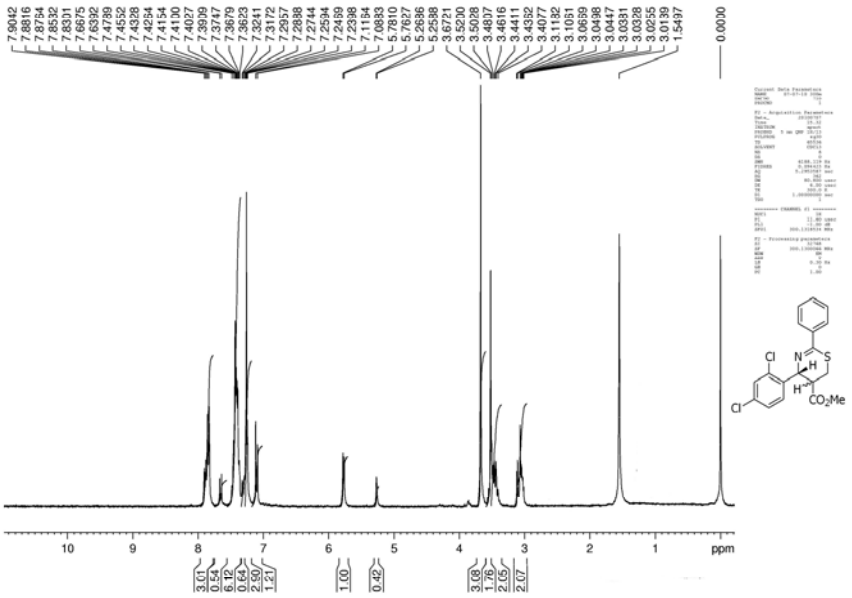

Fig:S-53 ^{1}H spectrum of Methyl 4-(2,4-dichlorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (7f).

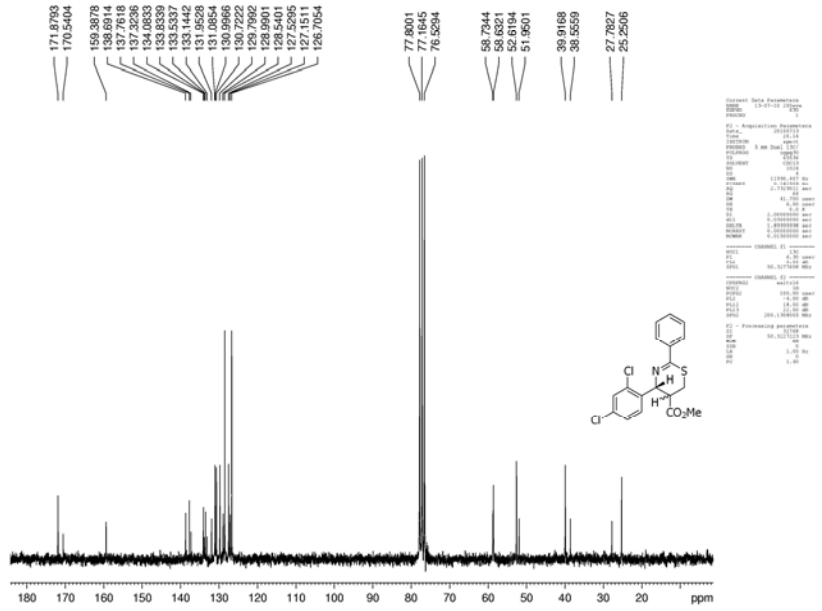

Fig:S-54 ^{13}C spectrum of Methyl 4-(2,4-dichlorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (7f).

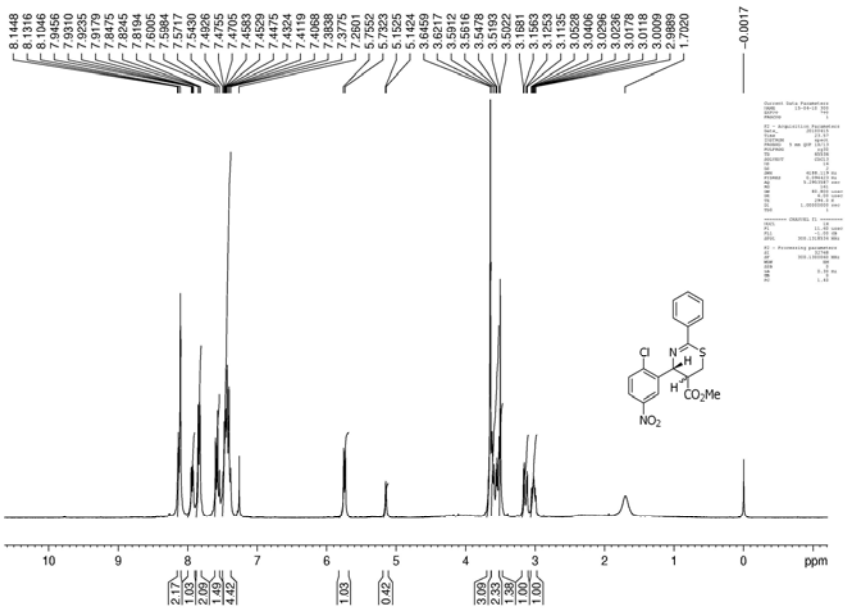

Fig:S-55 ^{1}H spectrum of Methyl 4-(2-chloro-4-nitrophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (7g).

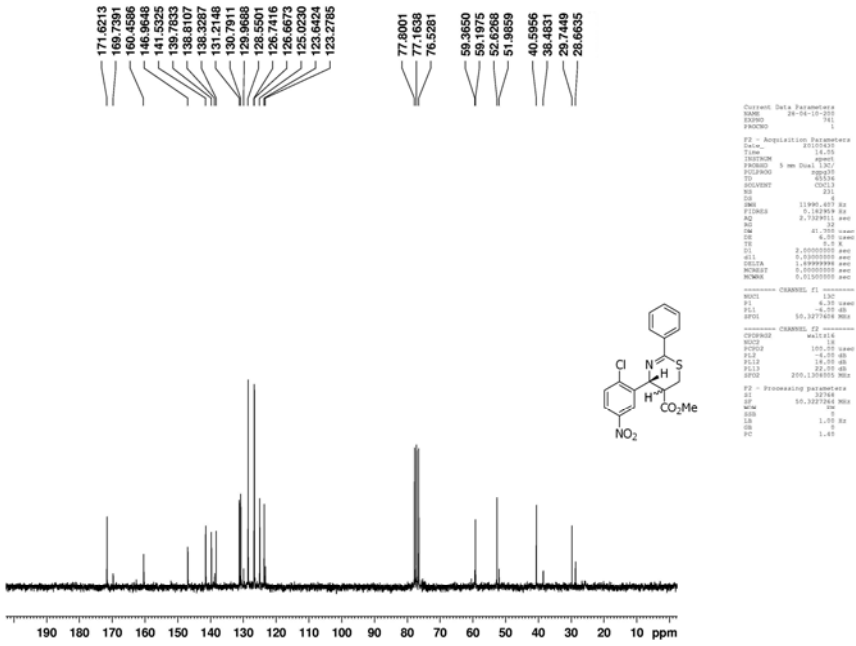

Fig:S-56 ^{13}C spectrum of Methyl 4-(2-chloro-4-nitrophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-oxazine-5-carboxylate (7g).

This journal is © The Royal Society of Chemistry 2011

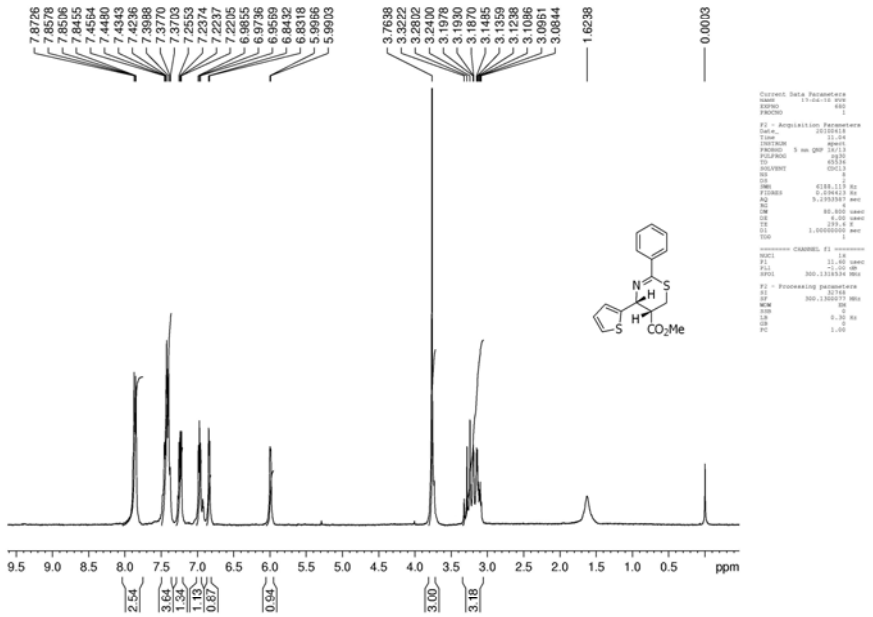

Fig:S-57 ^{1}H spectrum of Methyl (4*R*,5*S*)-4-(2-thienyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 7h).

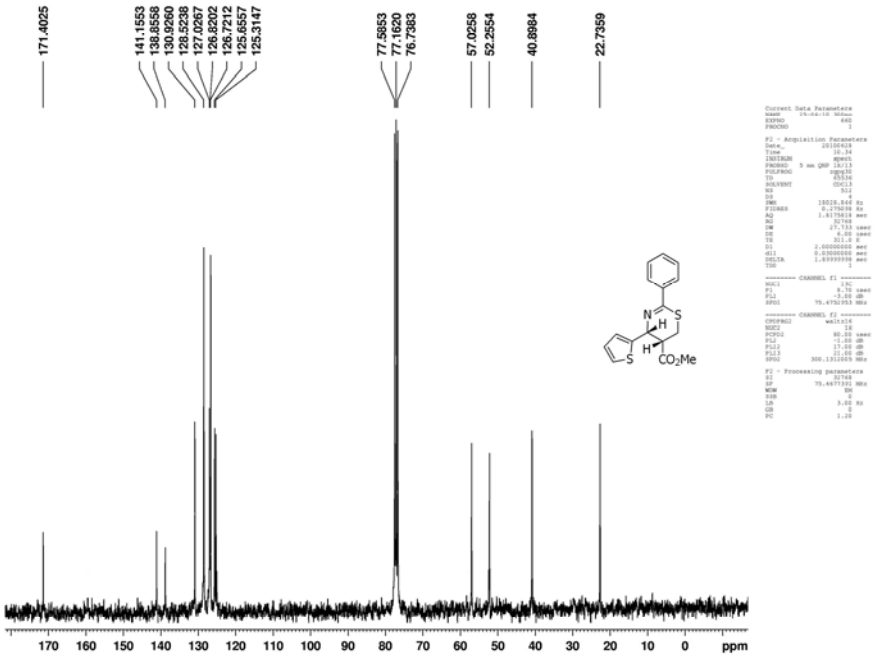

Fig:S-58 ^{13}C spectrum of Methyl (4*R*,5*S*)-4-(2-thienyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 7h).

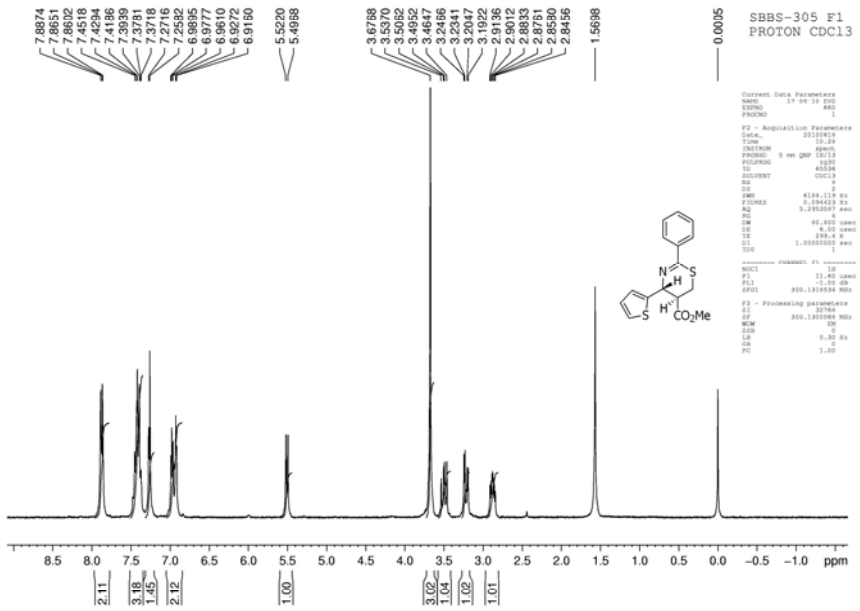

Fig:S-59 ^{1}H spectrum of Methyl (4*R*,5*R*)-4-(2-thienyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7h).

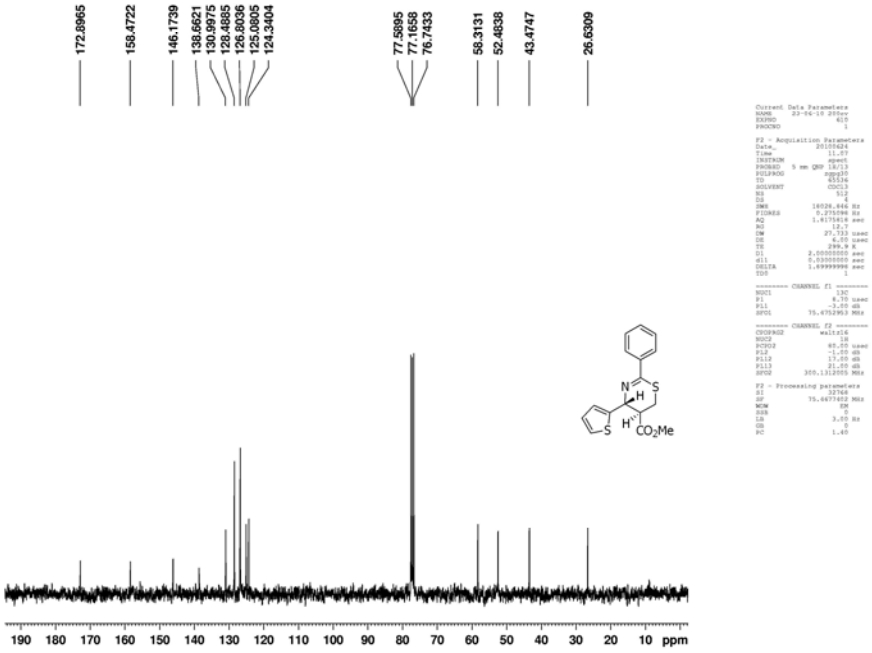

Fig:S-60 ^{13}C spectrum of Methyl (4*R*,5*R*)-4-(2-thienyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 7h).

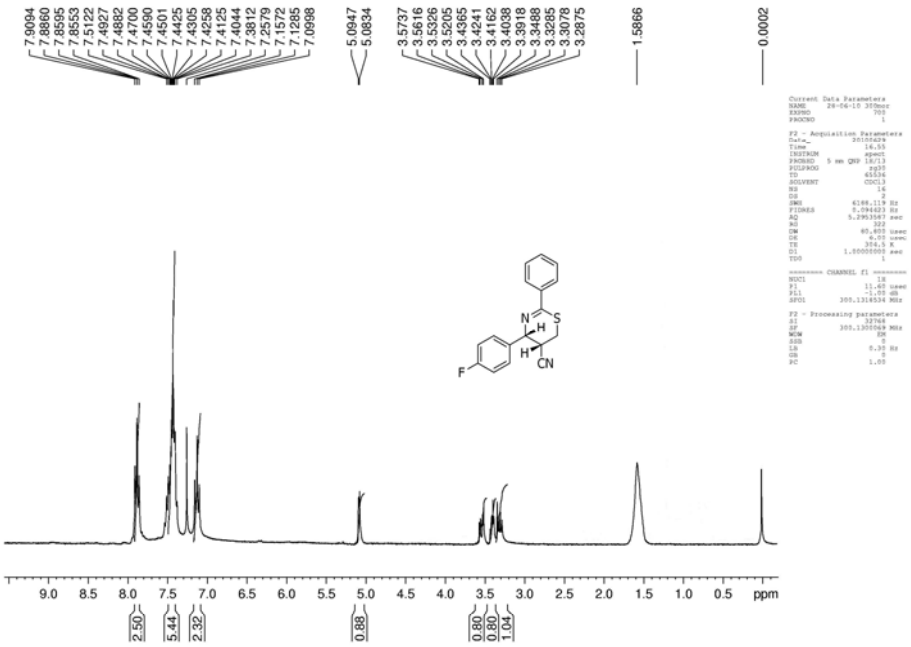

Fig:S-61 ^{1}H spectrum of (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4H-1,3-thiazine-5-carbonitrile.

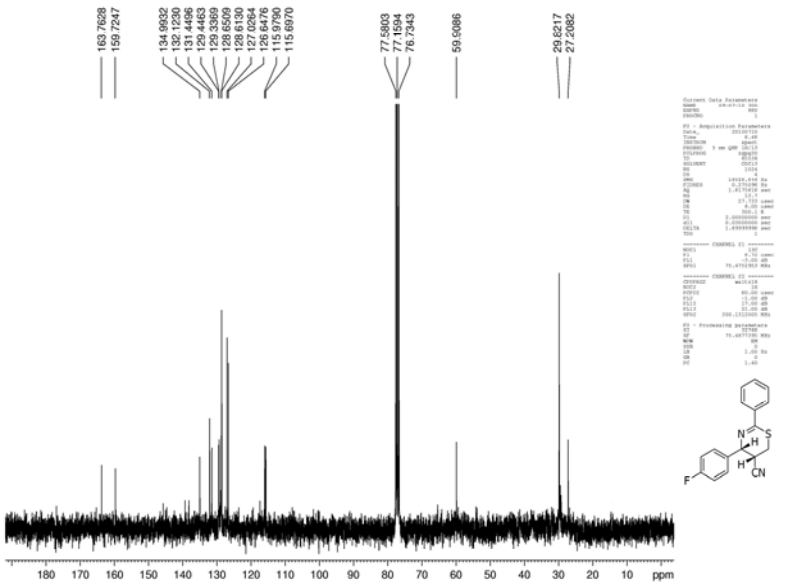

Fig:S-62 ^{13}C spectrum of (4*R*,5*R*)-4-(4-fluorophenyl)-2-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carbonitrile.

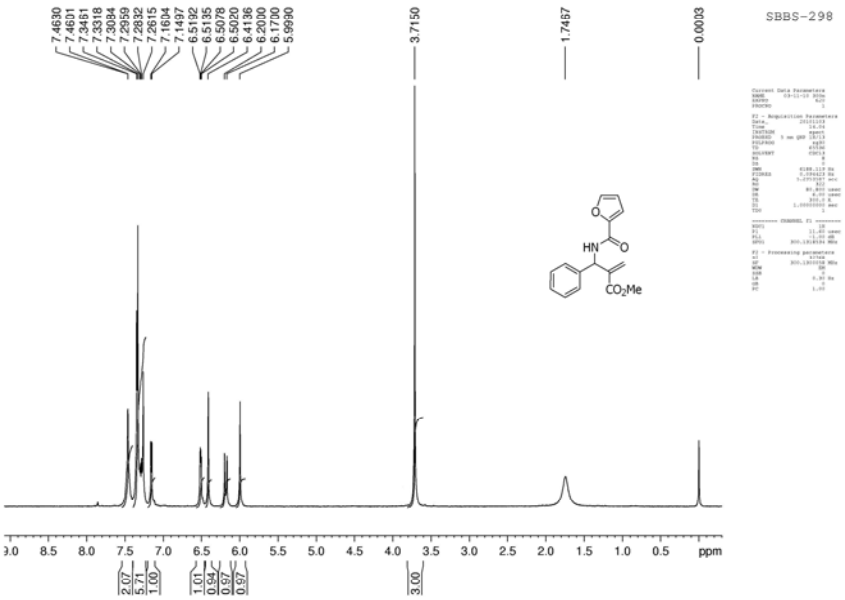

Fig:S-63 ^{1}H spectrum of Methyl 2-[(2-furoylamino)(phenyl)methyl]acrylate (8A).

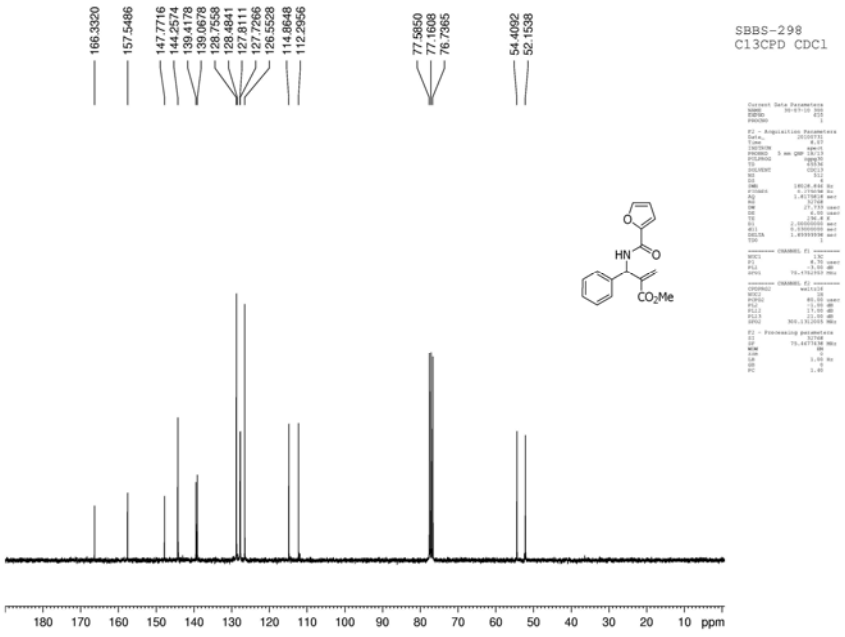

Fig:S-64 ^{13}C spectrum of Methyl 2-[(2-furoylamino)(phenyl)methyl]acrylate (8A).

This journal is © The Royal Society of Chemistry 2011

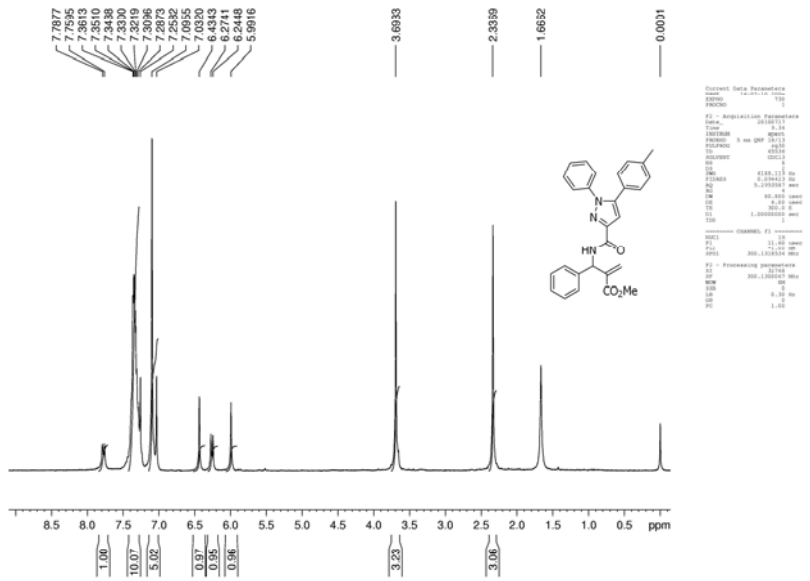

Fig:S-65 ^{1}H spectrum of Methyl 2-(phenyl(1-phenyl-5-*p*-tolyl-1*H*-pyrazole-3-carboxamido)methyl)acrylate (8B).

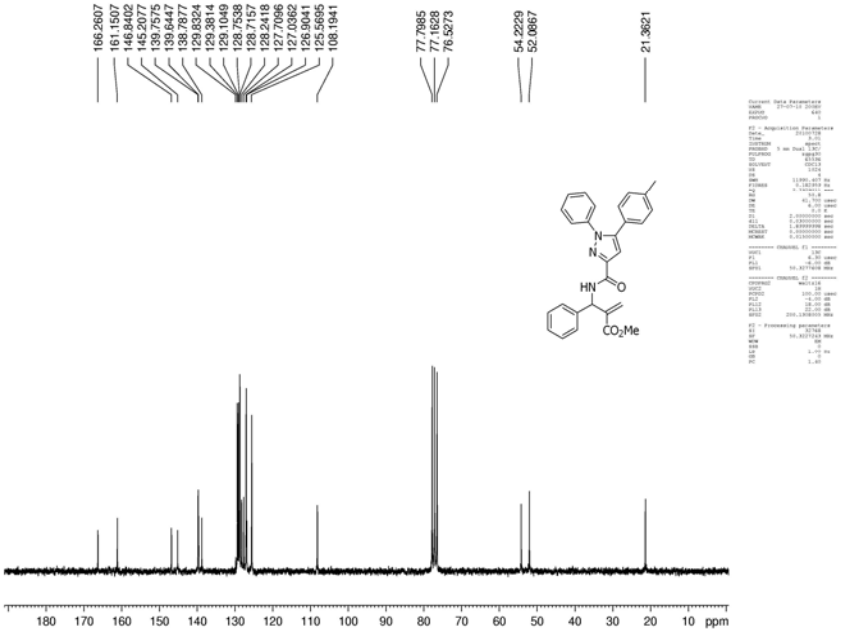

Fig:S-66 ^{13}C spectrum of Methyl 2-[phenyl(1-phenyl-5-*p*-tolyl-1*H*-pyrazole-3-carboxamido)methyl]acrylate (8B).

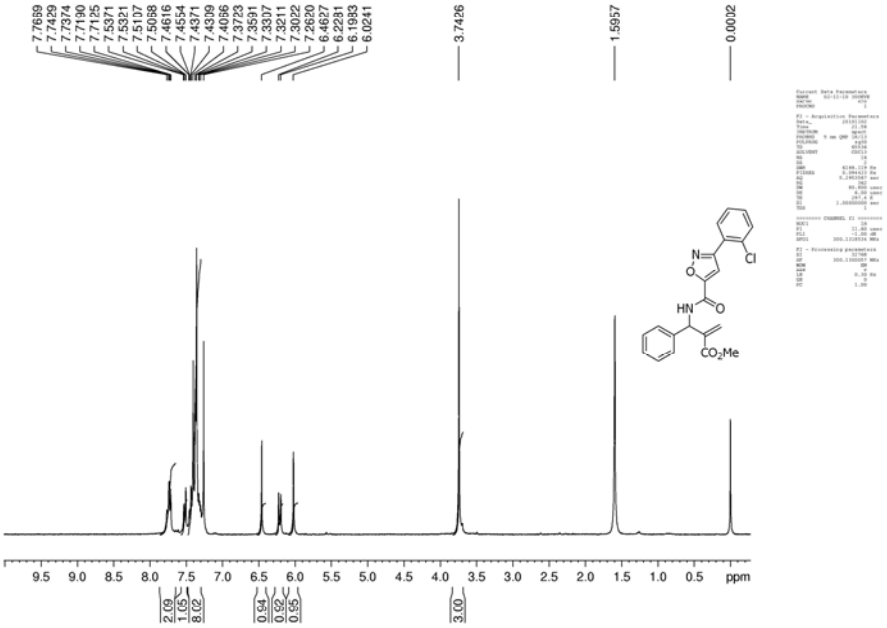

Fig:S-67 ^{1}H spectrum of Methyl 2-[(3-(2-chlorophenyl)isoxazole-5-carboxamido)(phenyl)methyl]acrylate (8C).

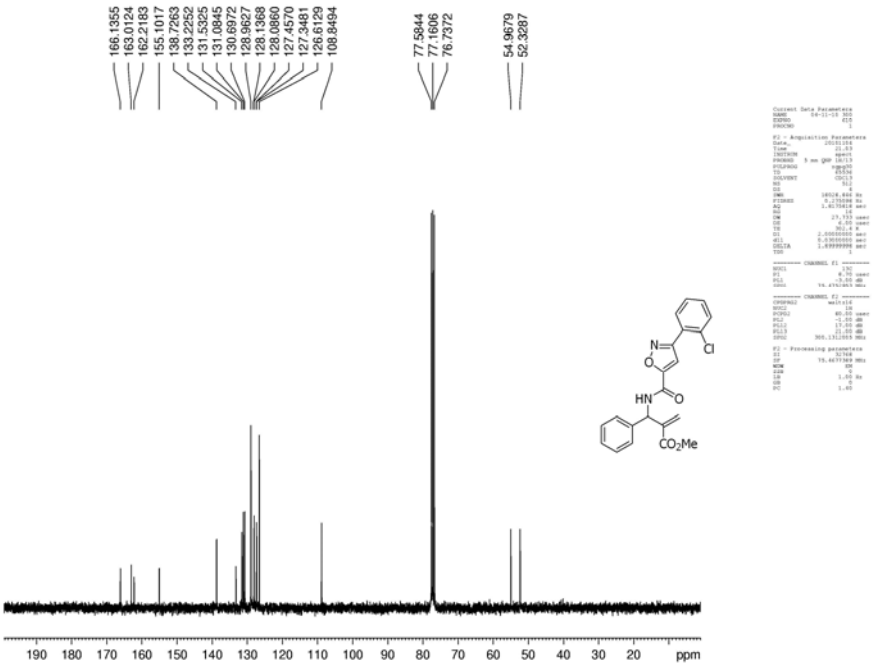

Fig:S-68 ^{13}C spectrum of Methyl 2-[(3-(2-chlorophenyl)isoxazole-5-carboxamido)(phenyl)methyl]acrylate (8C).

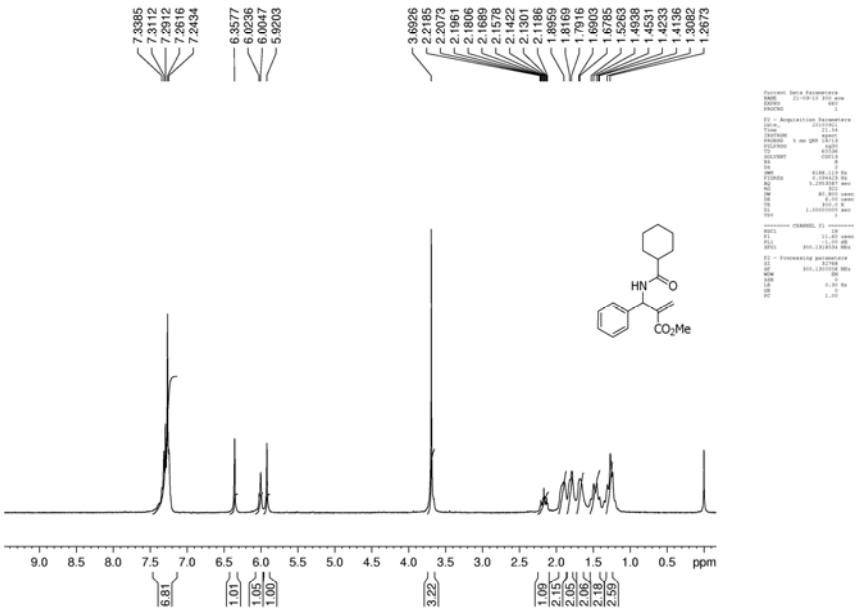

Fig:S-69 ^{1}H spectrum of Methyl 2-[[(cyclohexylcarbonyl)amino](phenyl)methyl]acrylate (8D).

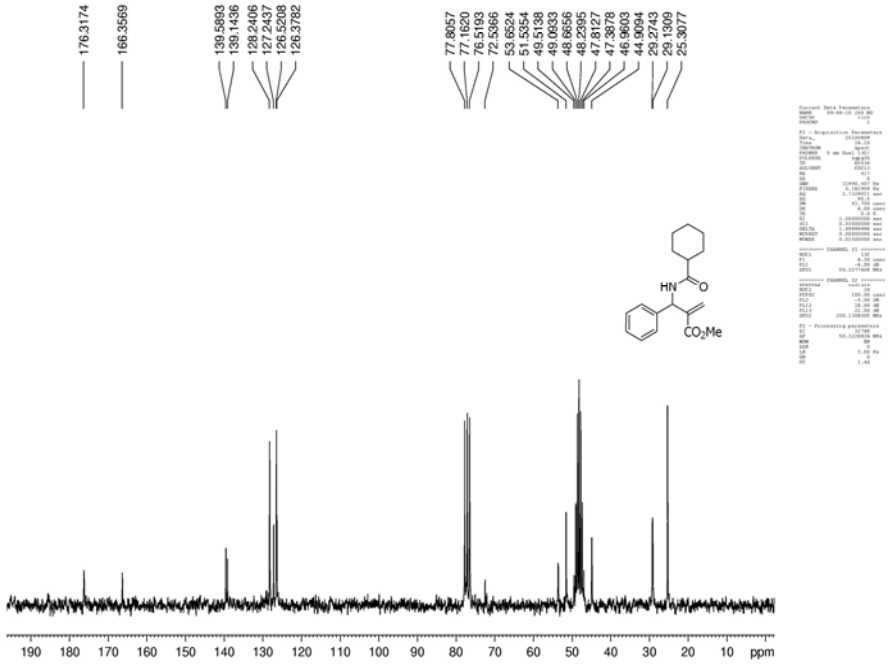

Fig:S-70 ^{13}C spectrum of Methyl 2-[[(cyclohexylcarbonyl)amino](phenyl)methyl]acrylate (8D).

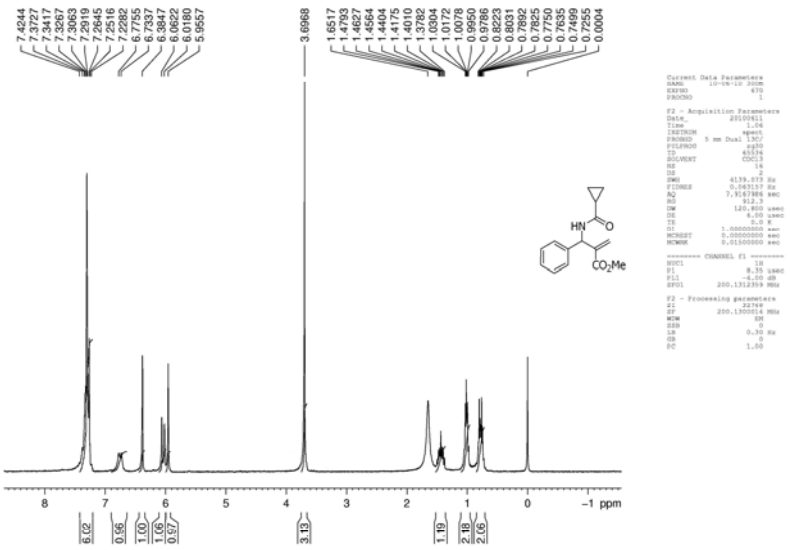

Fig:S-71 ^{1}H spectrum of Methyl 2-[[(cyclopropylcarbonyl)amino](phenyl)methyl]acrylate (8E).

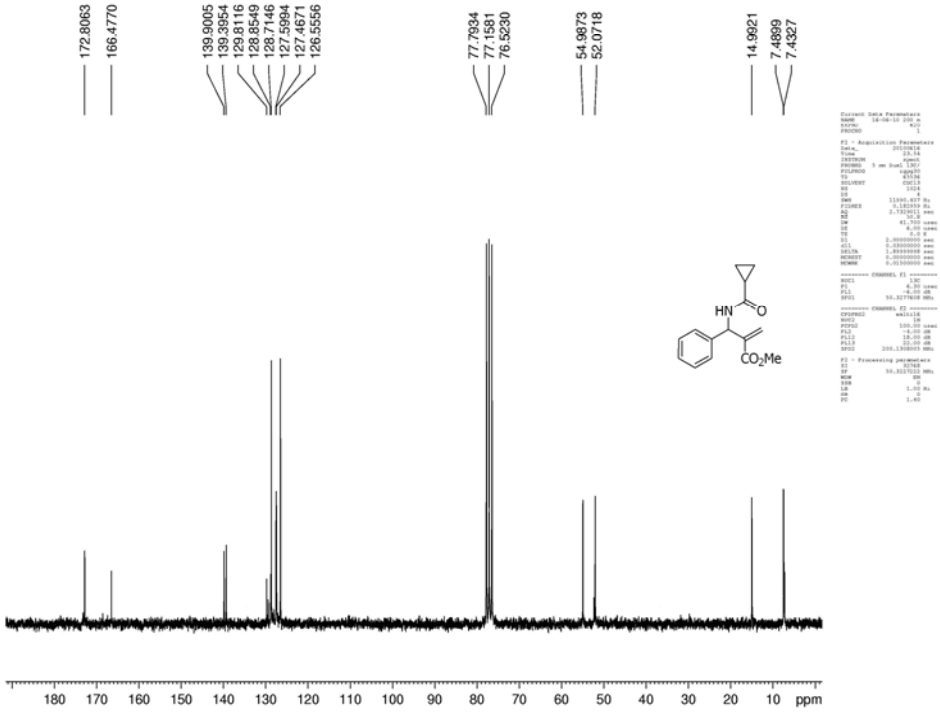

Fig:S-72 ^{13}C spectrum of Methyl 2-[[(cyclopropylcarbonyl)amino](phenyl)methyl]acrylate (8E).

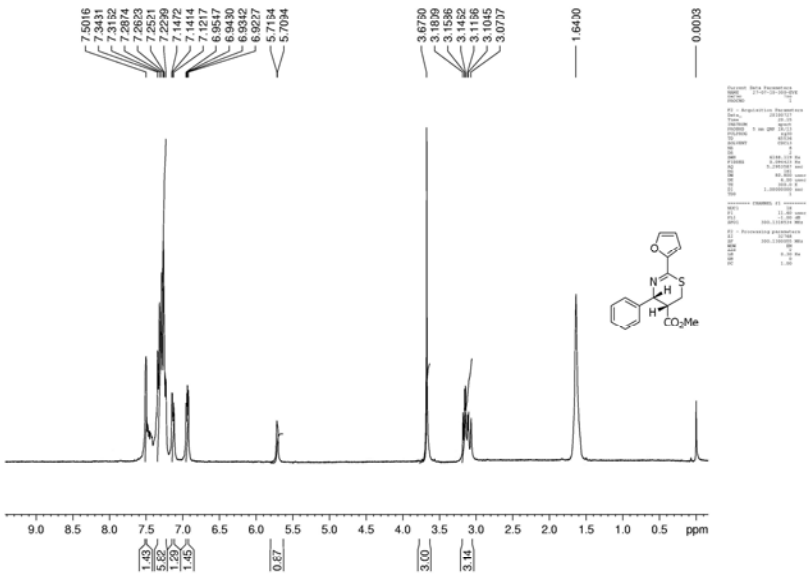

Fig:S-73 ^{1}H spectrum of Methyl (4*R*,5*S*)-2-(2-furyl)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 9A).

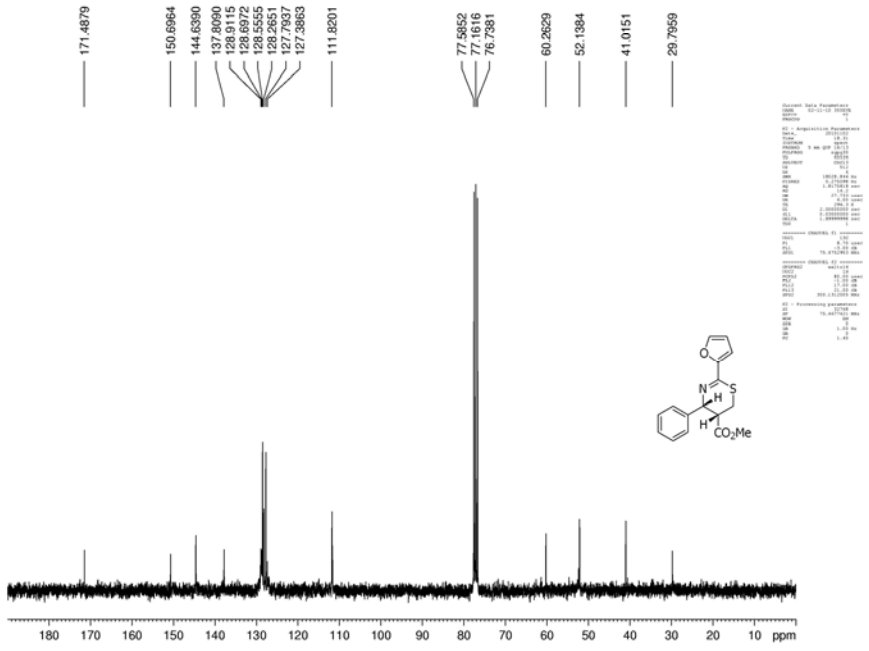

Fig:S-74 ^{13}C spectrum of Methyl (4*R*,5*S*)-2-(2-furyl)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 9A).

This journal is © The Royal Society of Chemistry 2011

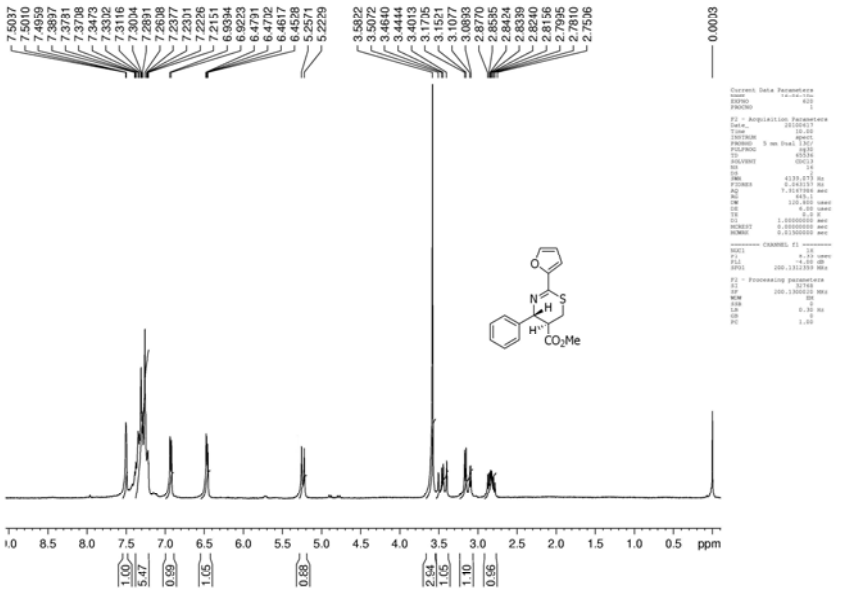

Fig:S-75 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-(2-furyl)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9A).

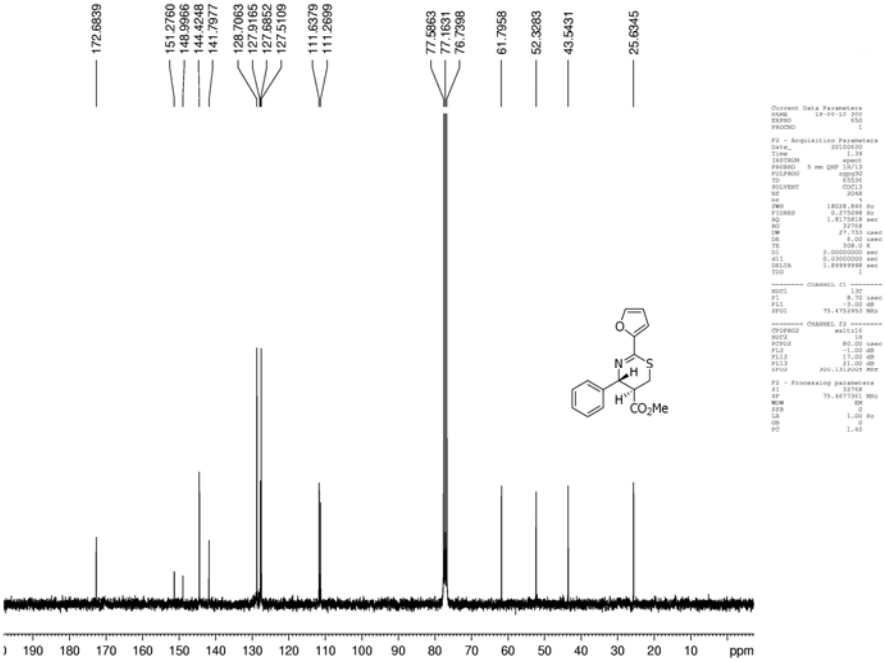

Fig:S-76 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-(2-furyl)-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9A).

This journal is © The Royal Society of Chemistry 2011

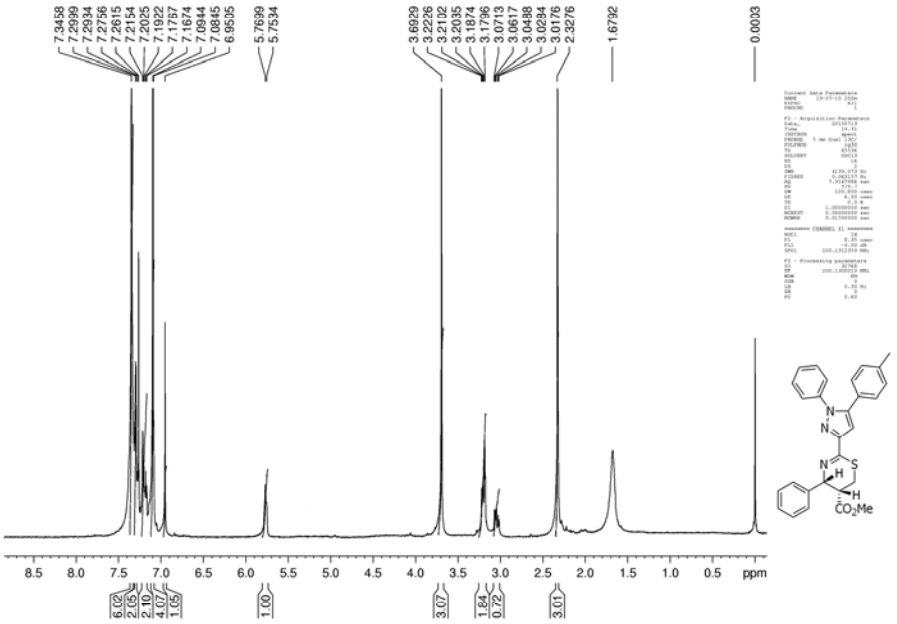

Fig:S-77 ^{1}H spectrum of Methyl (4*R*,5*S*)-2-[5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 9B).

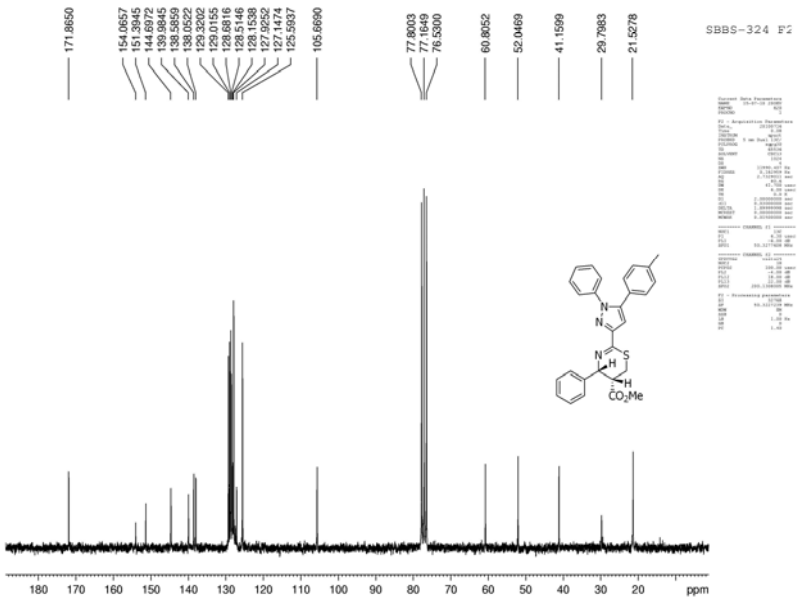

Fig:S-78 ^{13}C spectrum of Methyl (4*R*,5*S*)-2-[5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*syn* 9B).

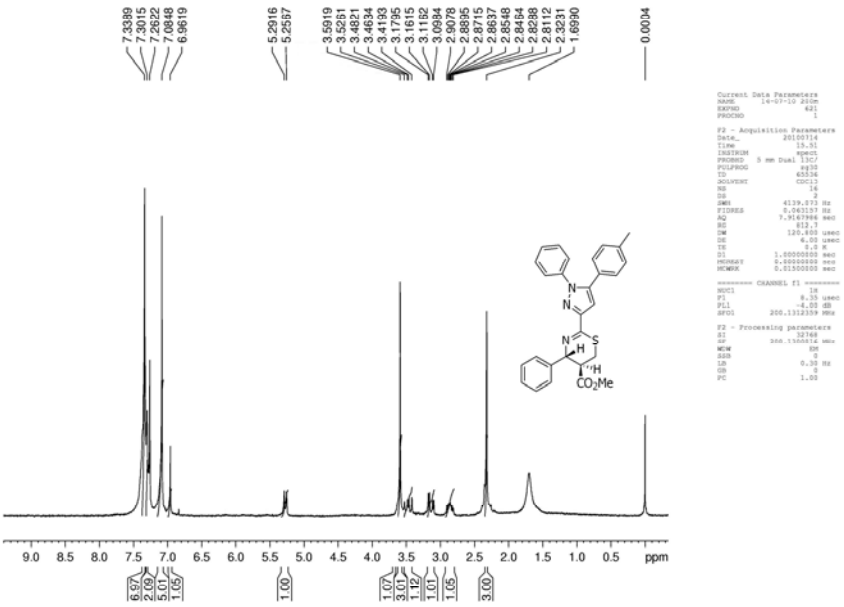

Fig:S-79 ^{1}H spectrum of Methyl (4*R*,5*R*)-2-[5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9B).

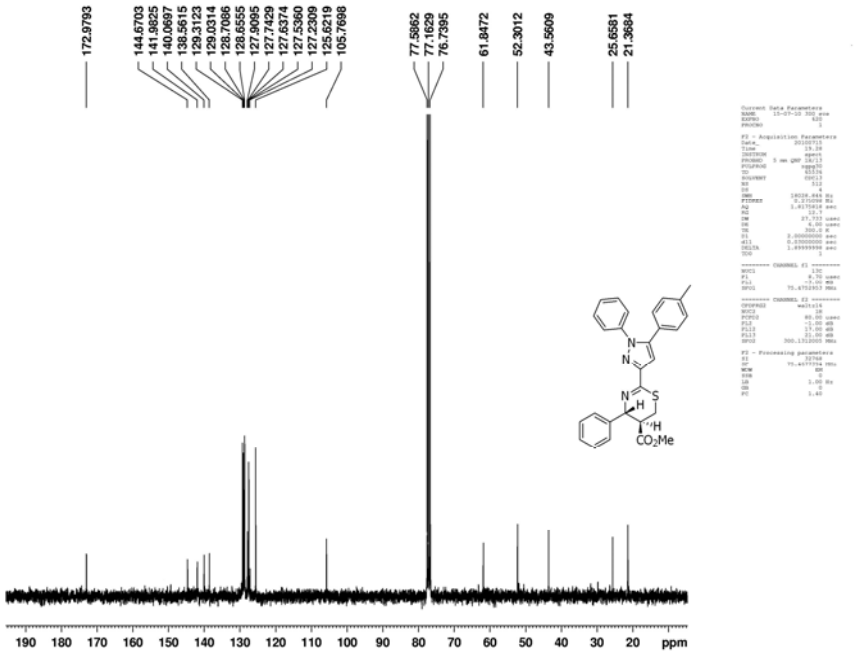

Fig:S-80 ^{13}C spectrum of Methyl (4*R*,5*R*)-2-[5-(4-methylphenyl)-1-phenyl-1*H*-pyrazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9B).

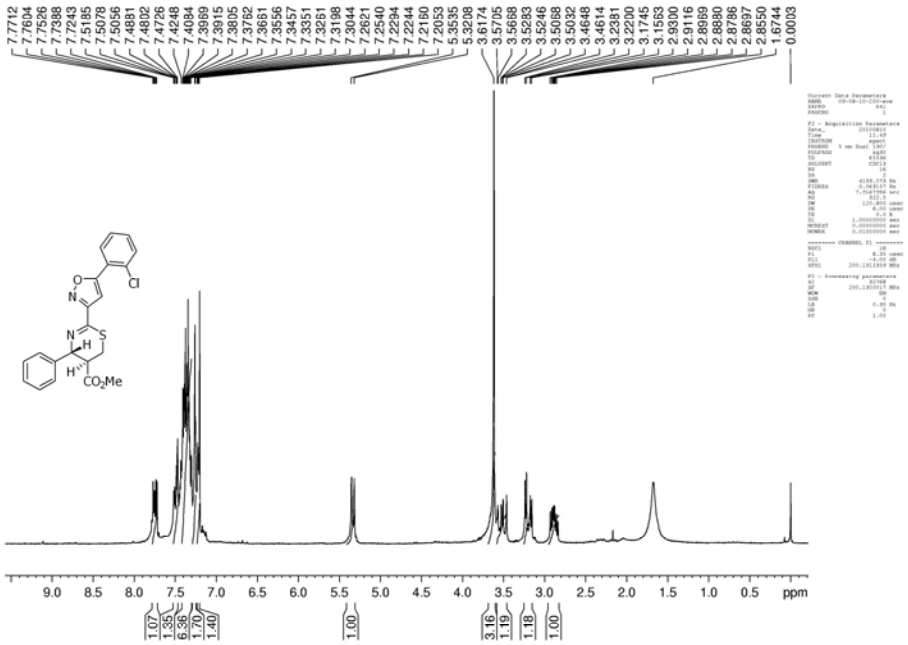

Fig:S-81 ^{1}H spectrum of Methyl (4*R*,5*S*)-2-2-[5-(2-chlorophenyl)isoxazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9C).

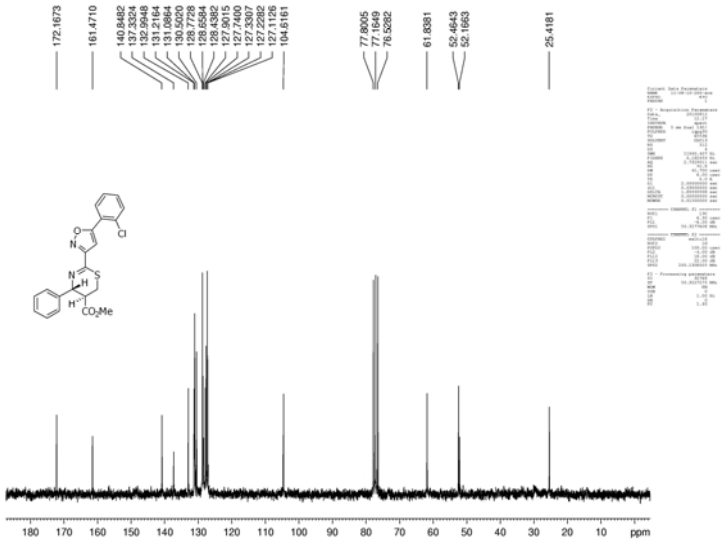

Fig:S-82 ^{13}C spectrum of Methyl (4*R*,5*S*)-2-2-[5-(2-chlorophenyl)isoxazol-3-yl]-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (*anti* 9C).

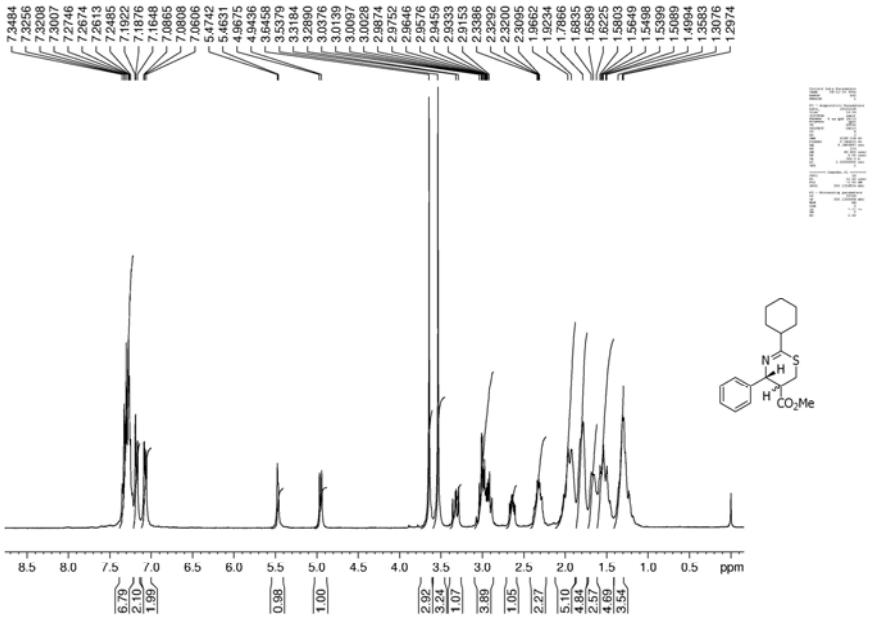

Fig:S-83 ^{1}H spectrum of Methyl 2-cyclohexyl-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (9D).

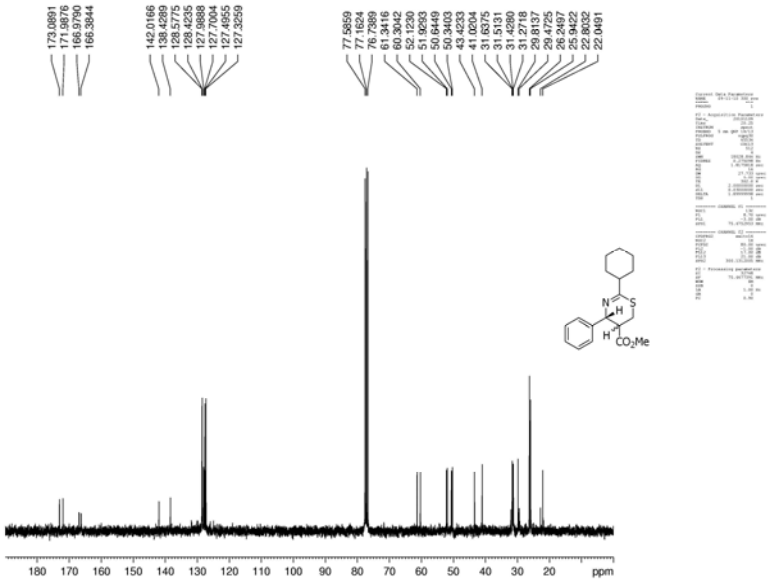

Fig:S-84 ^{13}C spectrum of Methyl 2-cyclohexyl-4-phenyl-5,6-dihydro-4*H*-1,3-thiazine-5-carboxylate (9D).

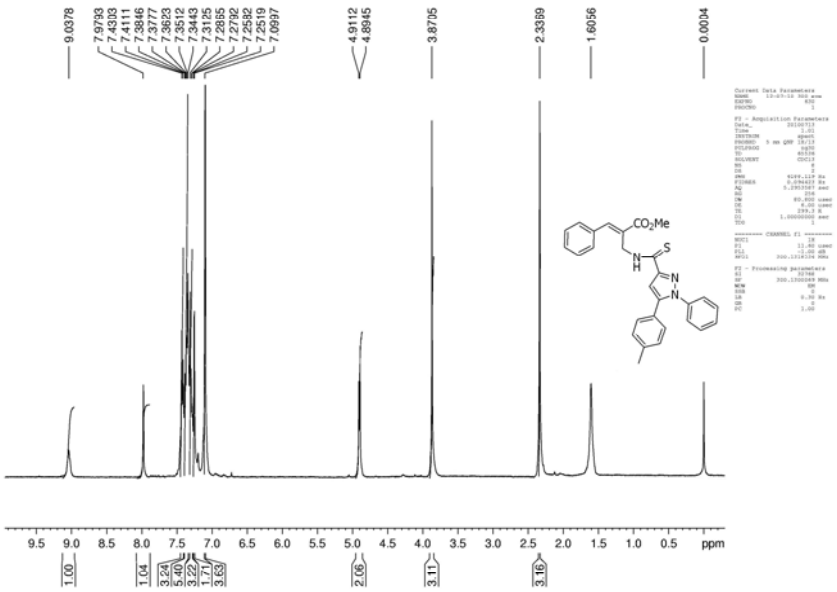

Fig:S-85 ^{1}H spectrum of Methyl (*Z*)-2-{[(3-carbothionyl-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazole)amino]methyl}-3-phenylprop-2-enoate (10B).

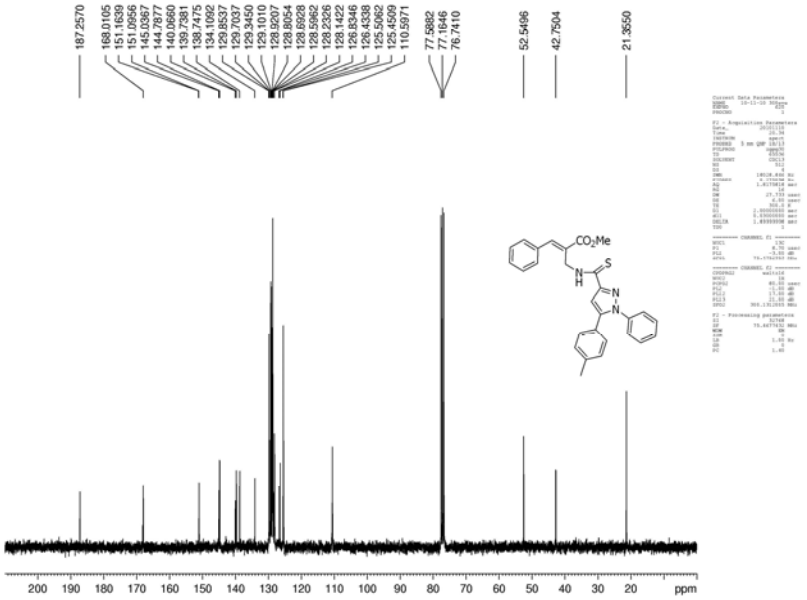

Fig:S-86 ^{13}C spectrum of Methyl (*Z*)-2-{[(3-carbothionyl-5-(4-methylphenyl)-1-phenyl-1*H*-pyrazole)amino]methyl}-3-phenylprop-2-enoate (10B).

This journal is © The Royal Society of Chemistry 2011

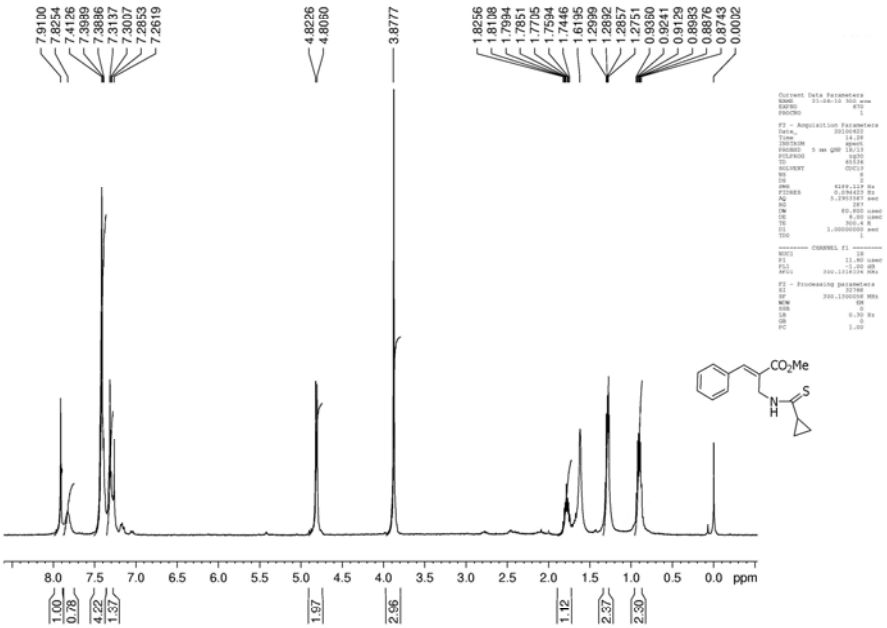

Fig:S-87 ^{1}H spectrum of Methyl (*Z*)-2-{[(cyclopropylcarbothioyl)amino]methyl}-3-phenylprop-2-enoate (10E).

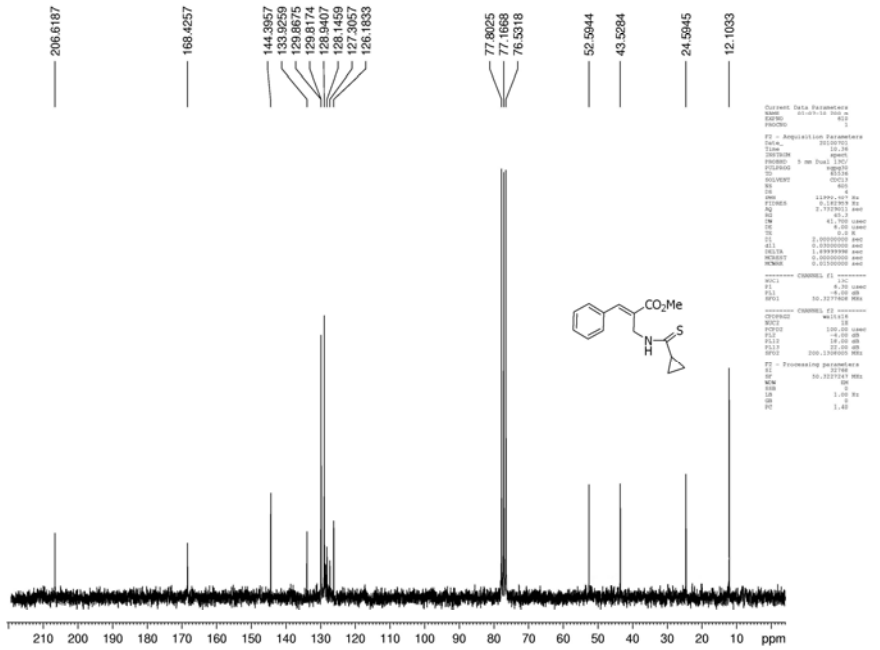

Fig:S-88 ^{13}C spectrum of Methyl (*Z*)-2-{[(cyclopropylcarbothioyl)amino]methyl}-3-phenylprop-2-enoate (10E).