Supporting Information

Chemoselective reactions under solvent-free conditions: lanthanide-catalyzed syntheses of 2-amino-3,1-benzothiazines and 3,4-dihydroquinazoline-2-thiones

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TABLE OF CONTENTS

General Information

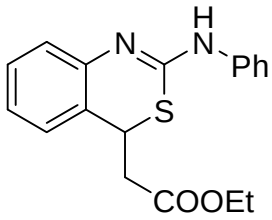
Air- or moisture-sensitive reactions were conducted under an atmosphere of dry Ar with flame-dried glassware. $Ln(OTf)_3$[1] and $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$[2] were synthesized according to the literature method. ^1H and ^{13}C NMR spectra were obtained on Varian INOVA-400 and System-300 spectrometers using tetramethylsilane (TMS) as an internal reference. HRMS data were obtained on a Micromass GCT instrument. IR spectra were obtained on a Nicolet FT-IR 1000 spectrophotometer.

Typical Experimental Procedure

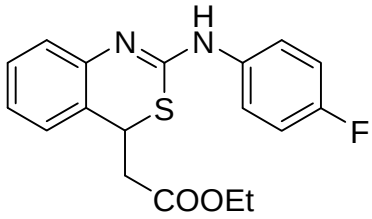
Typical Procedure for the $Yb(OTf)_3$-catalyzed Reactions of *o*-Aminocinnamate and Isothiocyanates. A mixture of ethyl *o*-aminocinnamate (191 mg, 1 mmol), isothiocyanate (1.2 mmol) and ytterbium triflate (6.2 mg, 0.01 mmol) was stirred at 50°C for 4 hours. Water was added, and the mixture was extracted with EtOAc. The combined organic layers were dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel [eluent: EtOAc/petroleum ether (60–90 °C) 1:10] to afford the desired 2-amino-4*H*-3,1-benzothiazine **3**.

Typical Procedure for the $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$-Catalyzed Reactions of *o*-Aminocinnamate and Isothiocyanates. A mixture of ethyl *o*-aminocinnamate (191 mg, 1 mmol), isothiocyanate (1.2 mmol) and $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$ (22 mg, 0.025 mmol) was stirred at 50°C for 5 hours. Water was added, and the mixture was extracted with EtOAc. The combined organic layers were dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by chromatography on silica gel [eluent: EtOAc/petroleum ether (60–90 °C) 1:10] to afford the desired 3,4-dihydroquinazoline-2-thione **4**.

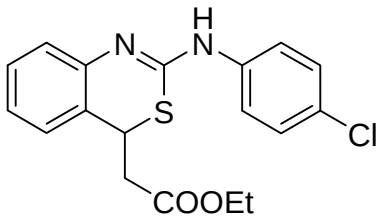
Characterization Data



Ethyl 2-(2-(phenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3a**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.0 Hz, 2H), 7.36–7.27 (m, 3H), 7.22–7.16 (m, 2H), 7.09 (t, J = 7.2 Hz, 2H), 6.71 (br s, 1H), 4.51 (dd, J = 8.8, 6.4 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.83 (dd, J = 16.0, 8.8 Hz, 1H), 2.75 (dd, J = 16.0，6.4 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H).

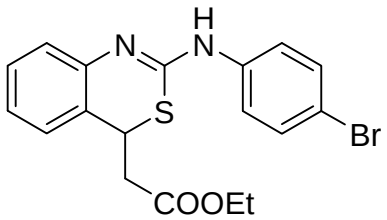


Ethyl 2-(2-(4-fluorophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3b**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.24 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.10–7.00 (m, 4H), 6.40 (br s, 1H), 4.50 (t, J = 7.6 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 2.84 (dd, J = 16.0, 8.8 Hz, 1H), 2.76 (dd, J = 16.0, 6.4 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 159.3 ($^1J_{CF}$ = 242 Hz), 150.6, 141.9, 138.6, 128.8, 126.6, 123.9, 123.0 ($^3J_{CF}$ = 8 Hz), 122.9, 122.5, 115.5 ($^2J_{CF}$ = 22 Hz), 61.0, 41.7, 40.3, 14.2.

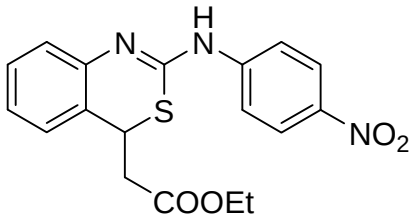


Ethyl 2-(2-(4-chlorophenylimino)-2,4-dihydro-1H-benzo[d][1,3]thiazin-4-yl)acetate (**3c**).[3] ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (br s, 1H), 7.96 (m, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.31–7.23 (m, 2H), 7.16–7.07 (m, 2H), 4.63 (t, J = 7.6 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 2.76 (dd, J = 16.0, 6.0 Hz, 1H), 2.69 (dd, J = 16.0, 8.8 Hz, 1H), 1.17

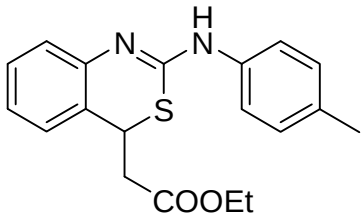
(t, *J* = 7.2 Hz, 3H).



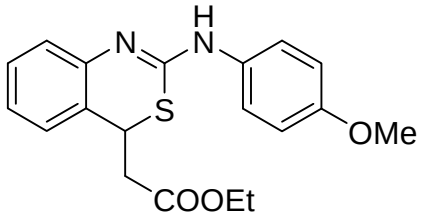
Ethyl 2-(2-(4-bromophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3d**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 4H), 7.30–7.28 (m, 1H), 7.17–7.07 (m, 3H), 6.95 (br s, 1H), 4.51 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.83 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.75 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).



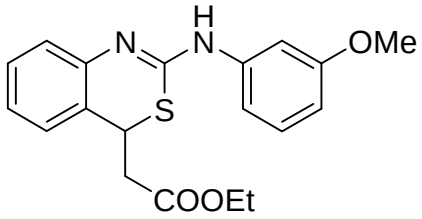
Ethyl 2-(2-(4-nitrophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3e**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.27–7.23 (m, 1H), 7.15–7.05 (m, 3H), 4.48 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.77 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.68 (dd, *J* = 16.4, 6.4 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).



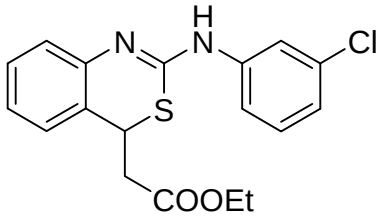
Ethyl 2-(2-(p-toluidino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3f**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.30–7.28 (m, 1H), 7.20–7.05 (m, 5H), 6.66 (br s, 1H), 4.50 (t, *J* = 7.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.82 (dd, *J* = 16.0, 8.4 Hz, 1H), 2.74 (dd, *J* = 16.0, 6.4 Hz, 1H), 2.33 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).



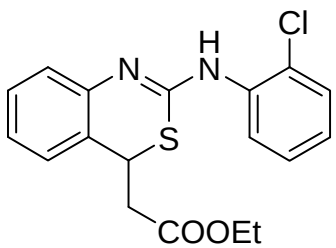
Ethyl 2-(2-(4-methoxyphenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3g**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.28–7.24 (m, 1H), 7.16–7.04 (m, 3H), 6.88 (d, J = 8.8 Hz, 2H), 4.49 (dd, J = 8.0, 6.8 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 2.83 (dd, J = 16.0, 8.4 Hz, 1H), 2.75 (dd, J = 16.0, 6.8 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H).



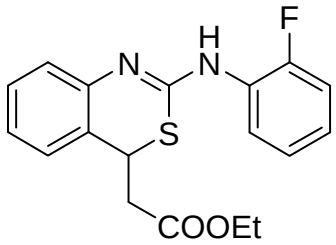
Ethyl 2-(2-(3-methoxyphenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3h**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.28–6.94 (m, 6H), 6.64 (d, J = 8.0 Hz, 1H), 4.50 (t, J = 7.6 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 2.84 (dd, J = 16.0, 8.4 Hz, 1H), 2.75 (dd, J = 16.0, 6.8 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H).



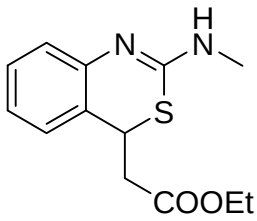
Ethyl 2-(2-(3-chlorophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3i**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 1H), 7.33–7.29 (m, 2H), 7.24–7.04 (m, 5H), 6.76 (br s, 1H), 4.52 (dd, J = 8.8, 6.8 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.83 (dd, J = 16.0, 8.8 Hz, 1H), 2.75 (dd, J = 16.0, 6.4 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H).



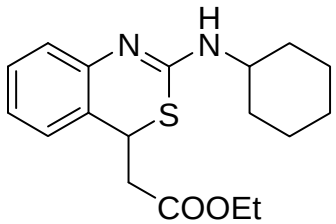
Ethyl 2-(2-(2-chlorophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3j**).[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (br s, 1H), 7.40–7.28 (m, 3H), 7.21–6.98 (m, 5H), 4.53 (dd, J = 8.7, 6.9 Hz, 1H), 4.20–4.09 (m, J = 7.2 Hz, 2H), 2.86 (dd, J = 16.2, 8.7 Hz, 1H), 2.76 (dd, J = 15.6, 6.6 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H).



Ethyl 2-(2-(2-fluorophenylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3k**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 7.31-6.99 (m, 8H), 4.52 (dd, J = 8.4, 6.8 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.85 (dd, J = 16.4, 8.8 Hz, 1H), 2.76 (dd, J = 16.0, 6.4 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 153.0 ($^1J_{CF}$ = 247 Hz), 149.9, 142.1, 130.5 ($^2J_{CF}$ = 19 Hz), 130.3, 128.8, 126.7, 124.5, 123.7, 122.8 ($^3J_{CF}$ = 8 Hz), 122.4, 118.0 ($^3J_{CF}$ = 8 Hz), 115.1 ($^2J_{CF}$ = 20 Hz), 61.0, 41.6, 40.4, 14.3.

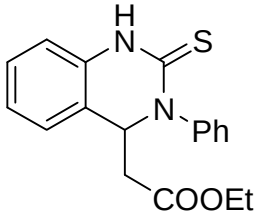


Ethyl 2-(2-(methylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3l**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 4.43 (t, J = 7.6 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.09 (s, 3H), 2.75 (dd, J = 16.0, 8.8 Hz, 1H), 2.68 (dd, J = 16.0, 6.8 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H).

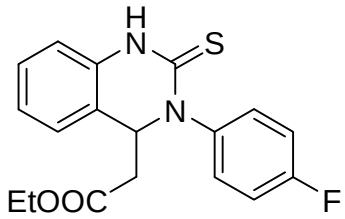


Ethyl 2-(2-(cyclohexylamino)-4H-benzo[d][1,3]thiazin-4-yl)acetate (**3m**).[3] ^{1}H NMR

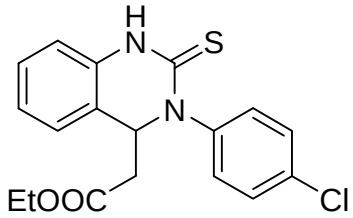
(400 MHz, $CDCl_3$) δ 7.25–6.99 (m, 4H), 4.59 (br s, 1H), 4.43 (dd, J = 8.4, 6.8 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 4.07–3.97 (m, 1H), 2.75 (dd, J = 16.0, 8.8 Hz, 1H), 2.69 (dd, J = 16.0, 6.4 Hz, 1H), 2.15–1.13 (m, 13H).



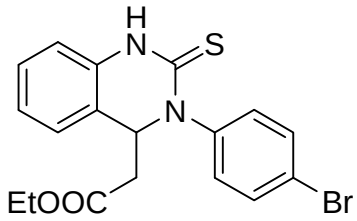
Ethyl 2-(3-phenyl-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4a**). White solid: mp 154–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.51–7.40 (m, 5H), 7.29–7.24 (m, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 5.26 (dd, J = 8.1, 4.8 Hz, 1H), 4.06–3.95 (m, 2H), 2.93 (dd, J = 15.0, 4.8 Hz, 1H), 2.85 (dd, J = 15.0, 8.4 Hz, 1H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.7, 143.9, 134.6, 129.6, 129.3, 128.8, 128.5, 126.0, 124.0, 120.8, 114.2, 61.2, 61.0, 40.0, 14.1; IR (cm^{-1}) 3332, 2980, 1730, 1594, 1514, 765; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1162, found 327.1164.



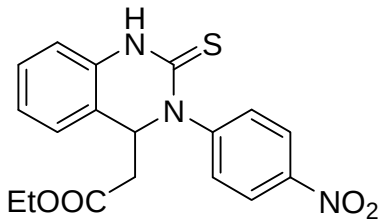
Ethyl 2-(3-(4-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4b**). White solid: mp 147–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.42–7.14 (m, 6H), 7.07 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 5.23 (dd, J = 7.8, 5.1 Hz, 1H), 4.07–3.96 (m, 2H), 2.90 (dd, J = 15.0, 5.1 Hz, 1H), 2.82 (dd, J = 15.0, 8.1 Hz, 1H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 169.5, 162.0 ($^1J_{CF}$ = 247 Hz), 139.7, 134.4, 130.6 ($^3J_{CF}$ = 8 Hz), 129.3, 125.8, 124.0, 120.6, 116.5 ($^2J_{CF}$ = 22 Hz), 114.2, 61.2, 61.0, 40.0, 14.1; IR (cm^{-1}) 3322, 2981, 1716, 1603, 1509, 1463, 1373, 1219, 837, 764; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O_2S$ 345.1068, found 345.1070.



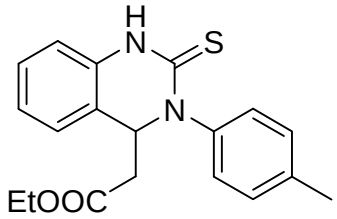
Ethyl 2-(3-(4-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4c**). White solid: mp 135–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.46–7.26 (m, 6H), 7.16 (d, J = 7.2 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 5.23 (dd, J = 7.8, 4.8 Hz, 1H), 4.07–3.97 (m, 2H), 2.89 (dd, J = 15.0, 4.8 Hz, 1H), 2.82 (dd, J = 15.0, 7.8 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 169.5, 142.2, 134.4, 134.2, 130.2, 129.8, 129.4, 125.9, 124.1, 120.6, 114.2, 61.2, 60.9, 40.0, 14.1; IR (cm^{-1}) 3342, 2977, 1716, 1618, 1493, 1462, 1374, 1092, 829, 754; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O_2S$ 361.0772, found 361.0770.



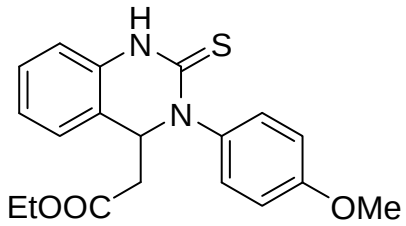
Ethyl 2-(3-(4-bromophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4d**). White solid: mp 146–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 5.23 (dd, J = 7.5, 5.1 Hz, 1H), 4.06–3.95 (m, 2H), 2.88 (dd, J = 14.7, 4.8 Hz, 1H), 2.81 (dd, J = 14.7, 7.5 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 169.5, 142.7, 134.3, 132.7, 130.5, 129.3, 125.8, 124.0, 122.3, 120.6, 114.3, 61.2, 60.8, 40.0, 14.1; IR (cm^{-1}) 3323, 2978, 1716, 1618, 1491, 1461, 1375, 1069, 826, 752; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrN_2O_2S$ 405.0267, found 405.0269.



Ethyl 2-(3-(4-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4e**). Yellow solid: mp 155–156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.80 (s, 1H), 8.33 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.28 (t, J = 6.9 Hz, 1H), 7.18 (d, J = 6.9 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 5.33 (dd, J = 7.5, 4.8 Hz, 1H), 4.08–3.97 (m, 2H), 2.90 (dd, J = 15.3, 5.1 Hz, 1H), 2.83 (dd, J = 15.5, 7.8 Hz, 1H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 169.3, 149.2, 146.9, 134.1, 129.9, 129.6, 125.9, 124.8, 124.5, 120.6, 114.4, 61.4, 60.7, 40.1, 14.1; IR (cm^{-1}) 3296, 3068, 2993, 1708, 1607, 1526, 1373, 1350, 862, 758; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}N_3O_4S$ 372.1013, found 372.1014.

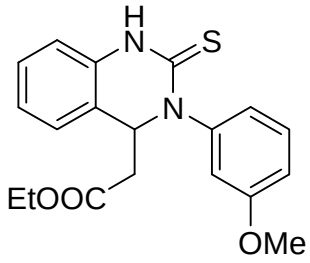


Ethyl 2-(2-thioxo-3-(p-tolyl)-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4f**). White solid: mp 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.30–7.26 (m, 5H), 7.16 (d, J = 7.2 Hz, 1H), 7.08–7.05 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 5.23 (dd, J = 8.4, 4.8 Hz, 1H), 4.05–3.96 (m, 2H), 2.92 (dd, J = 15.2, 4.8 Hz, 1H), 2.84 (dd, J = 15.2, 8.4 Hz, 1H), 2.40 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177. 2, 169.7, 141.3, 138.4, 134.6, 130.2, 129.3, 128.4, 126.0, 123.8, 120.8, 114.1, 61.1, 61.0, 39.9, 21.4, 14.1; IR (cm^{-1}) 3335, 3120, 2927, 1716, 1615, 1506, 1463, 1373, 821, 763; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2S$ 341.1318, found 341.1322.

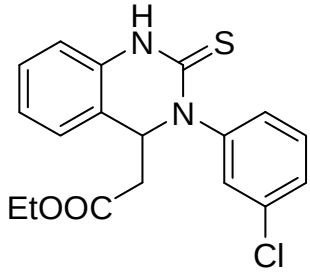


Ethyl 2-(3-(4-methoxyphenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4g**). White solid: mp 145–145.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.05–6.96 (m, 4H), 5.21 (dd, J = 7.5, 4.8 Hz, 1H), 4.02–3.99 (m, 2H), 3.84 (s, 3H), 2.91 (dd, J = 15.0, 5.1

Hz, 1H), 2.83 (dd, *J* = 15.0, 8.4 Hz, 1H), 1.13 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 169.7, 159.1, 136.6, 134.3, 129.8, 129.2, 125.9, 123.8, 120.8, 114.7, 114.1, 61.2, 61.1, 55.6, 39.9, 14.1; IR (cm^{-1}) 3180, 3020, 1743, 1604, 1507, 1444, 1378, 1246, 1024, 836, 751; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_3S$ 357.1267, found 357.1266.

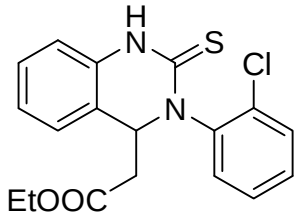


Ethyl 2-(3-(3-methoxyphenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4h**). White solid: mp 117–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.04–7.00 (m, 3H), 6.97–6.93 (m, 2H), 5.25 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.04–3.95 (m, 2H), 3.82 (s, 3H), 2.93 (dd, *J* = 15.2, 4.8 Hz, 1H), 2.85 (dd, *J* = 14.8, 8.4 Hz, 1H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 169.5, 160.2, 144.7, 134.5, 130.0, 129.1, 125.7, 123.7, 120.9, 120.6, 114.5, 114.2, 113.9, 61.0, 60.8, 55.4, 40.0, 14.0; IR (cm^{-1}) 3122, 3202, 2939, 1730, 1608, 1497, 1441, 1047, 857, 785, 750, 692; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_3S$ 357.1267, found 357.1267.

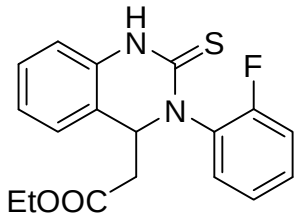


Ethyl 2-(3-(3-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4i**). White solid: mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.43–7.26 (m, 5H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.24 (dd, *J* = 8.0, 5.2 Hz, 1H), 4.06–3.97 (m, 2H), 2.90 (dd, *J* = 15.2, 4.8, 1H), 2.82 (dd, *J* = 15.2, 8.0, 1H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 169.5, 144.8, 134.9, 134.4, 130.4, 129.4, 129.2, 128.7, 127.3, 125.9, 124.1, 120.7, 114.3, 61.3, 60.9, 40.0, 14.1; IR (cm^{-1}) 3319, 2979, 1718, 1617, 1373, 1094, 856, 788,

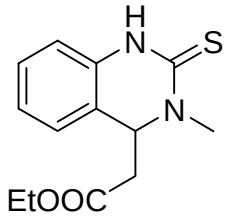
758, 686; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O_2S$ 361.0772, found 361.0773.



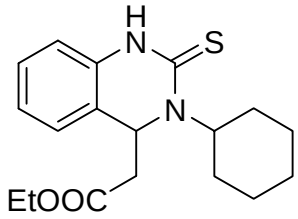
Ethyl 2-(3-(2-chlorophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4j**). White solid: mp 200–201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.64–7.62 (m, 1H), 7.55–7.53 (m, 1H), 7.40–7.25 (m, 3H), 7.17 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz,1H), 6.90 (d, J = 8.0 Hz, 1H), 5.16 (dd, J = 7.2, 5.6 Hz, 1H), 4.06–3.97 (m, 2H), 2.90 (dd, J = 14.8, 5.2 Hz, 1H), 2.85 (dd, J = 15.2, 7.6 Hz, 1H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.6, 140.5, 134.3, 133.2, 131.6, 130.9, 129.9, 129.2, 127.3, 126.0, 124.1, 120.7, 114.3, 61.2, 59.4, 40.2, 14.1; IR (cm^{-1}) 3315, 2926, 1730, 1618, 1480, 1373, 1219, 753; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ClN_2O_2S$ 361.0772, found 361.0777.



Ethyl 2-(3-(2-fluorophenyl)-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4k**). White solid: mp 164–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.40–7.23 (m, 5H), 7.15 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.20 (m, 1H), 4.05–3.96 (m, 2H), 3.02–2.92 (m, 1H), 2.83 (dd, J = 15.6, 8.4 Hz, 1H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 169.6 (J = 31 Hz), 156.7 ($^1J_{CF}$ = 212 Hz), 134.2 ($^3J_{CF}$ = 13 Hz), 133.0, 130.5 ($^3J_{CF}$ = 14 Hz), 130.1, 129.1, 125.6, 123.9 ($^2J_{CF}$ = 17 Hz), 120.8, 120.3, 117.0 ($^2J_{CF}$ = 20 Hz), 114.3, 61.0, 59.7, 40.3, 13.9; IR (cm^{-1}) 3321, 2898, 1724, 1602, 1518, 1464, 1175, 762; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}FN_2O_2S$ 345.1068, found 345.1060.



Ethyl 2-(3-methyl-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4l**). White solid: mp 77–78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 5.03 (dd, J = 7.2, 5.6 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.52 (s, 3H), 2.81 (dd, J = 15.2, 4.8 Hz, 1H), 2.65 (dd, J = 15.2, 8.0 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 170.1, 134.3, 129.1, 125.6, 123.7, 120.5, 113.7, 61.2, 59.1, 40.7, 39.3, 14.1; IR (cm^{-1}) 3192, 2978, 1720, 1602, 1367, 1203, 748; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005, found 265.1000.



Ethyl 2-(3-cyclohexyl-2-thioxo-1,2,3,4-tetrahydroquinazolin-4-yl)acetate (**4m**). White solid: mp 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.28–7.15 (m, 2H), 7.04–6.93 (m, 2H), 5.27–5.19 (m, 1H), 5.09 (dd, J = 10.5, 3.0 Hz, 1H), 4.09–3.99 (m, 2H), 2.79 (dd, J = 15.6, 10.8 Hz, 1H), 2.55 (dd, J = 15.6, 3.0 Hz, 1H), 2.19–1.22 (m, 10H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 170.1, 134.6, 128.9, 125.4, 123.6, 122.0, 113.8, 60.9, 60.8, 51.3, 40.4, 31.3, 30.7, 25.8, 25.7, 25.3, 14.1; IR (cm^{-1}) 3370, 2929, 1740, 1608, 1498, 1371, 1032, 935, 760; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_2S$ 333.1631, found 333.1628.

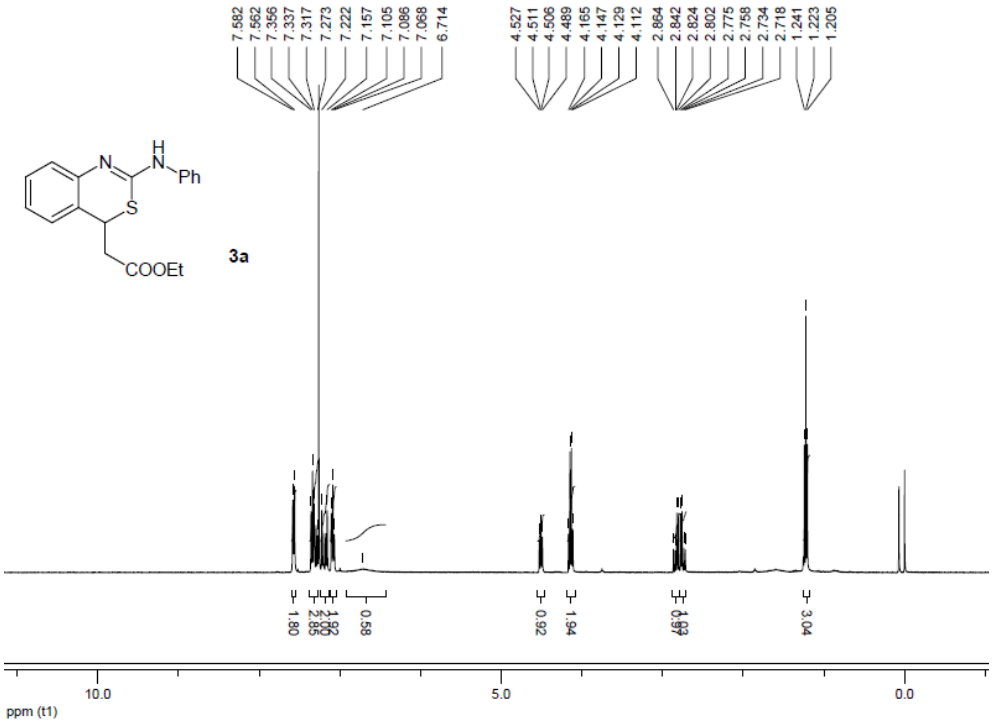
References

[1] a) J. H. Forsberg, V. T. Spaziano, T. M. Balasubramanian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown, J. L. Miller, *J. Org. Chem*. **1987**, *52*, 1017; b) S. Collins, Y. Hong, *Tetrahedron Lett*. **1987**, *28*, 4391.

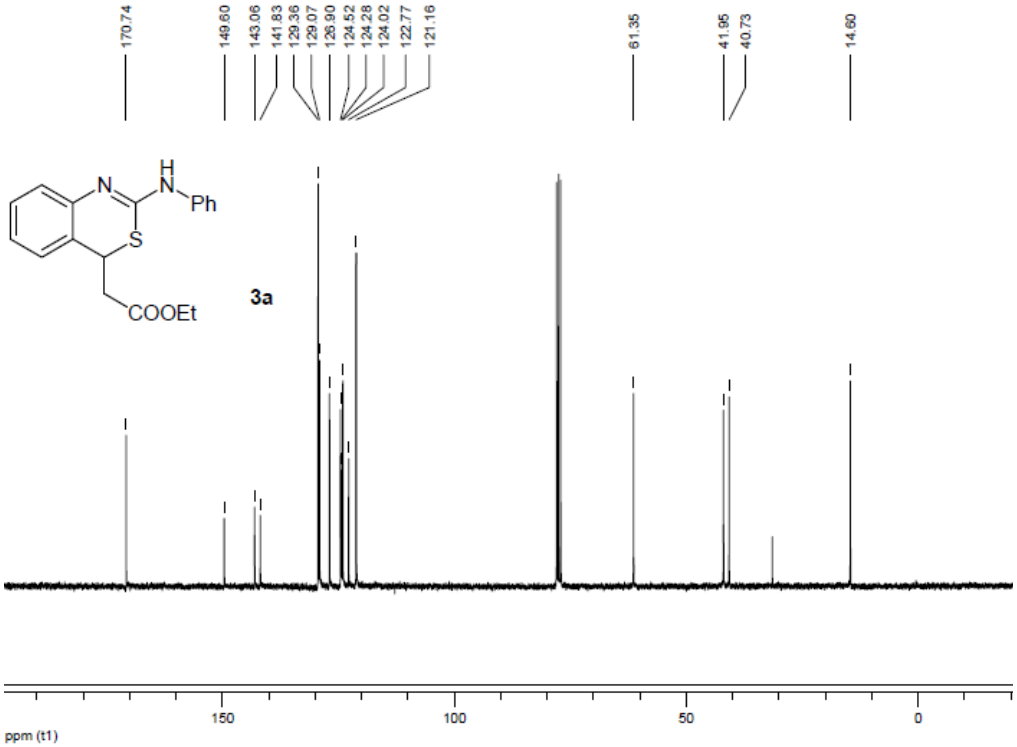
[2] a) E. Sheng, S. Wang, G. Yang, S. Zhou, L. Cheng, K. Zhang, Z. Huang, *Organometallics* **2003**, *22*, 684; b) S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng, Z. Huang, *Polyhedron* **2003**, *22*, 1019; c) M. Xie, X. Liu, S. Wang, L. Liu, Y. Wu, G. Yang, S. Zhou, E. Sheng, Z. Huang, *Chin. J. Chem.* **2004**, *22*, 678.

[3] J. Huang, Y. Yu, L. Hua, Z. Yao, F. Xu, Q. Shen, *Chin. Sci. Bull.* **2013**, *58*, 717.

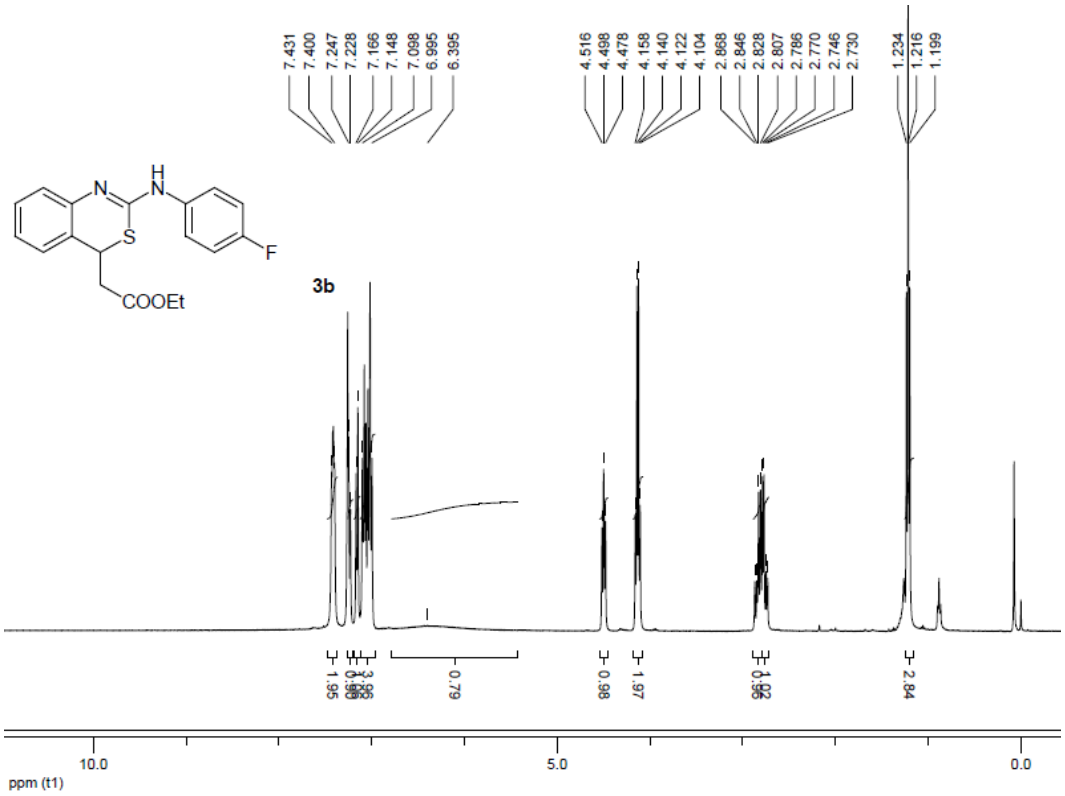
^{1}H NMR and ^{13}C NMR copies



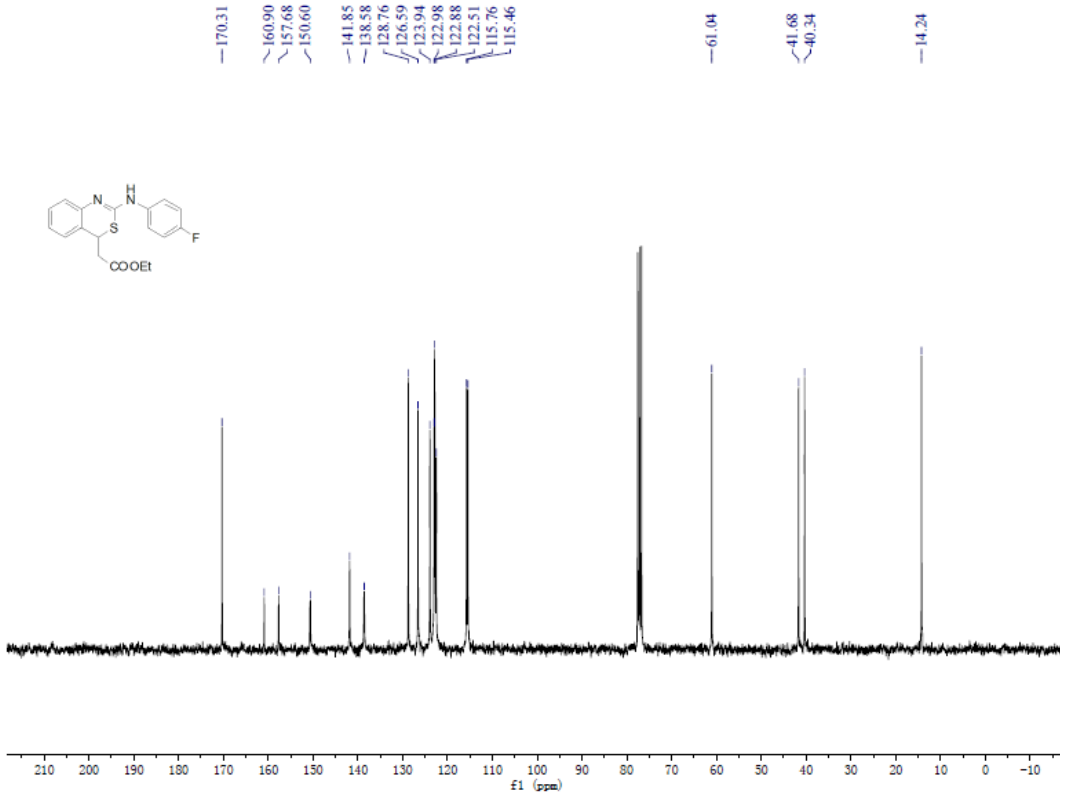
^{1}H NMR spectrum of compound **3a**



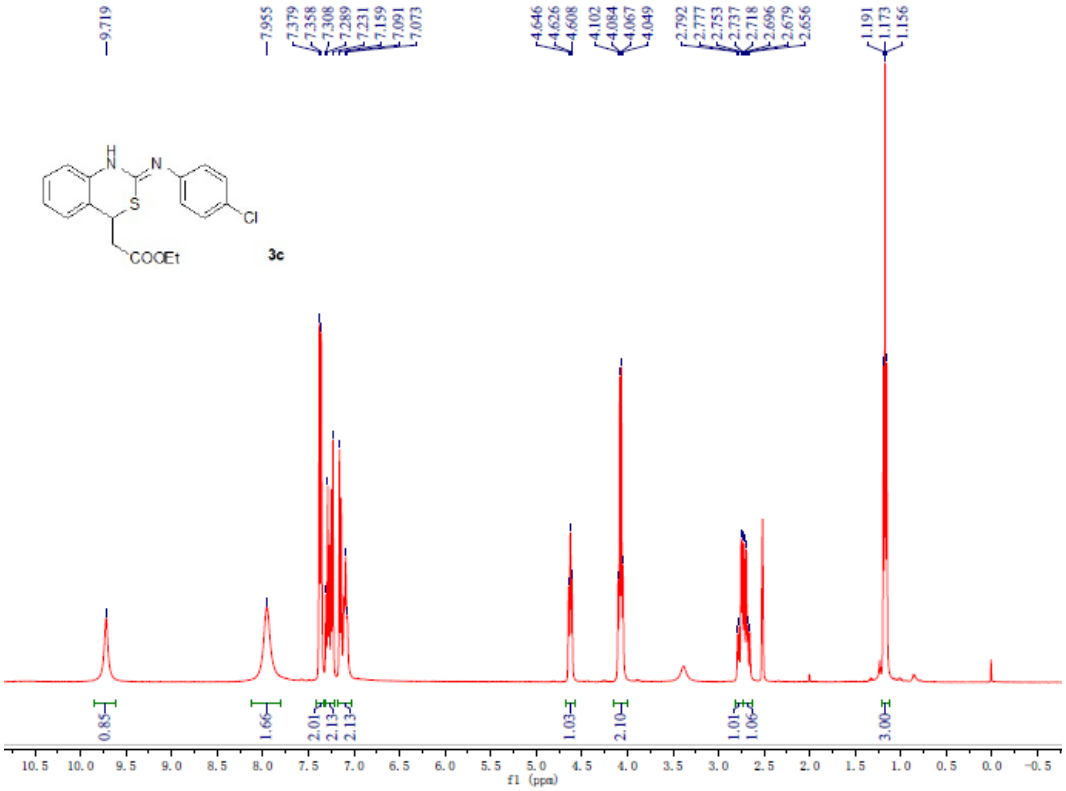
^{13}C NMR spectrum of compound **3a**



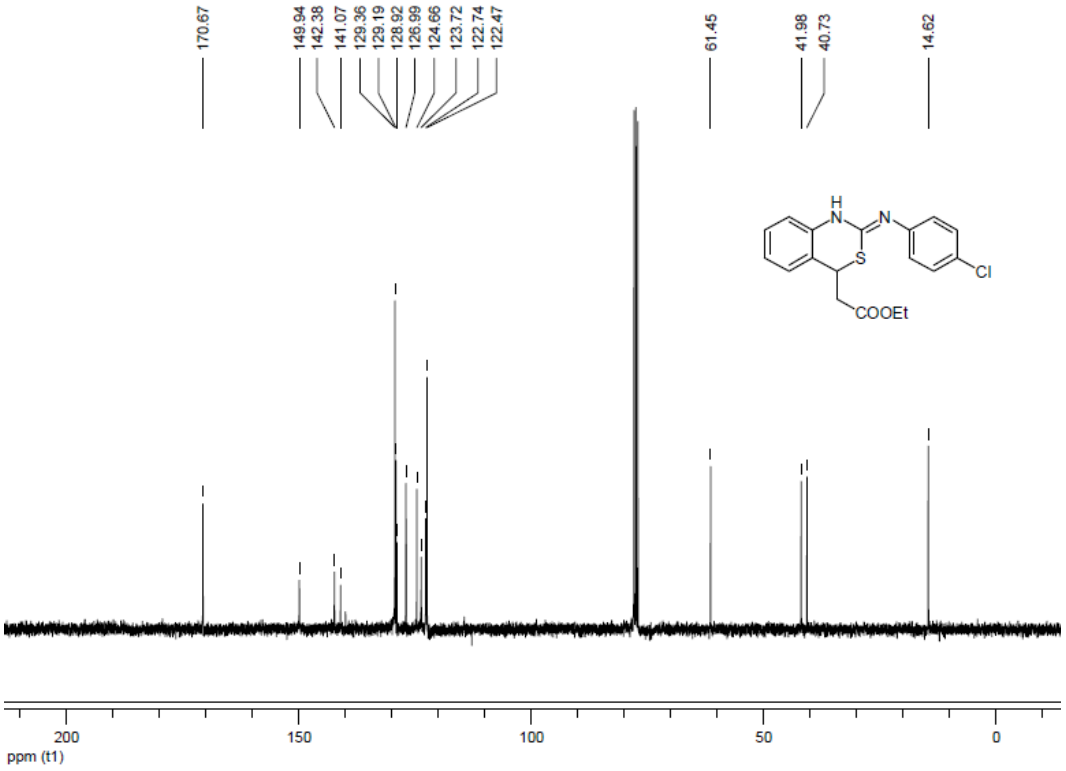
^{1}H NMR spectrum of compound **3b**



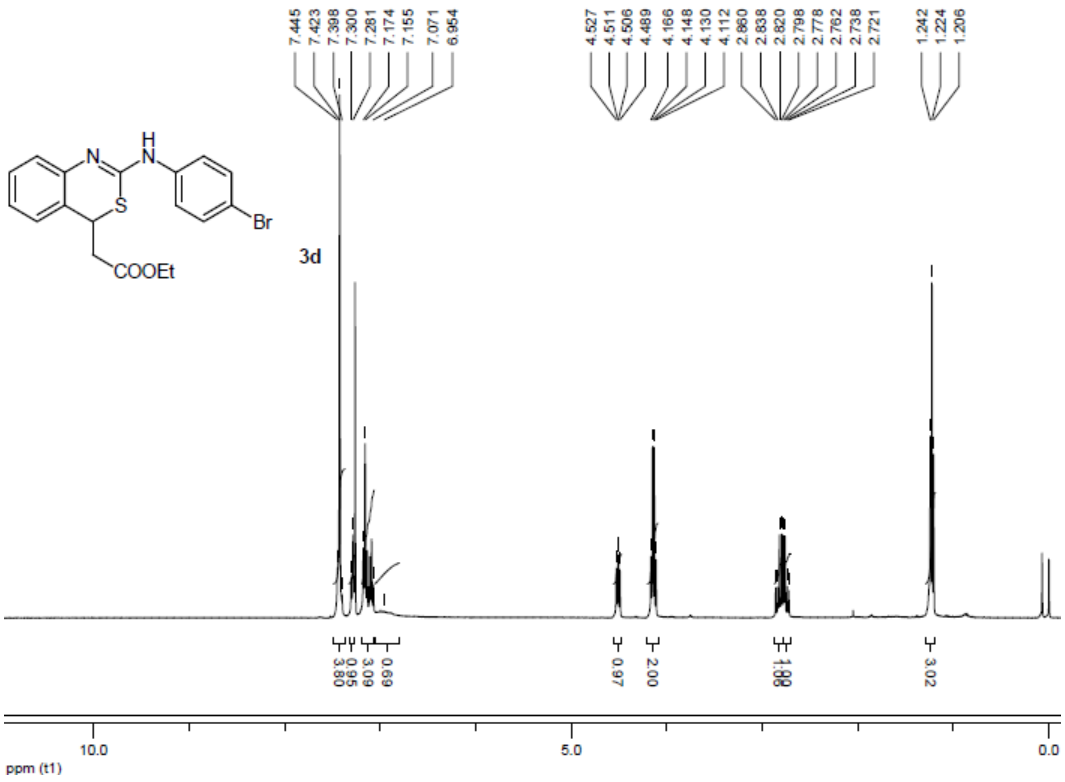
^{13}C NMR spectrum of compound **3b**



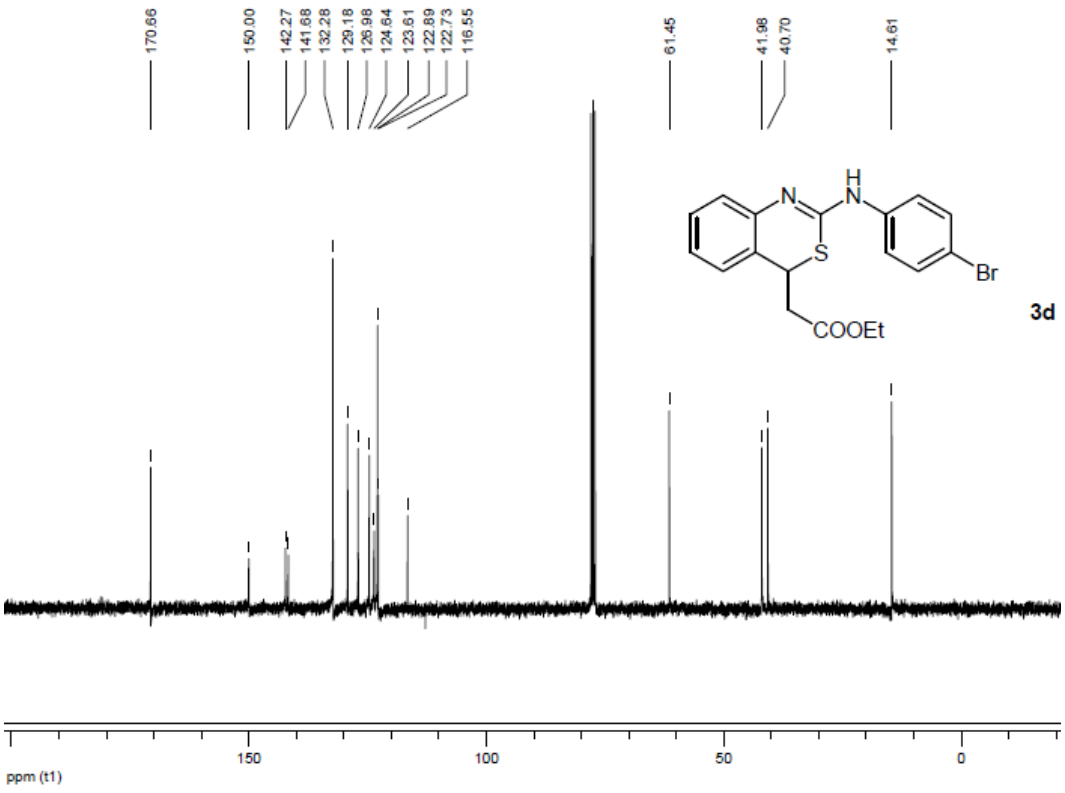
^{1}H NMR spectrum of compound **3c**



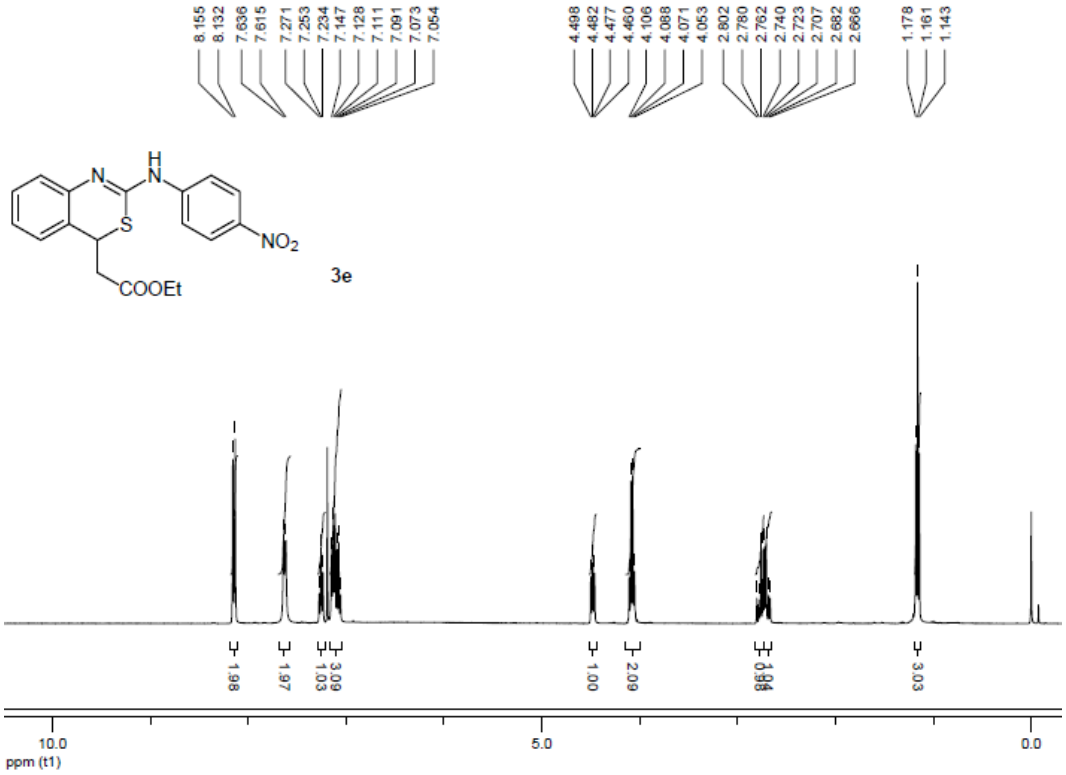
^{13}C NMR spectrum of compound **3c**



^{1}H NMR spectrum of compound **3d**



^{13}C NMR spectrum of compound **3d**



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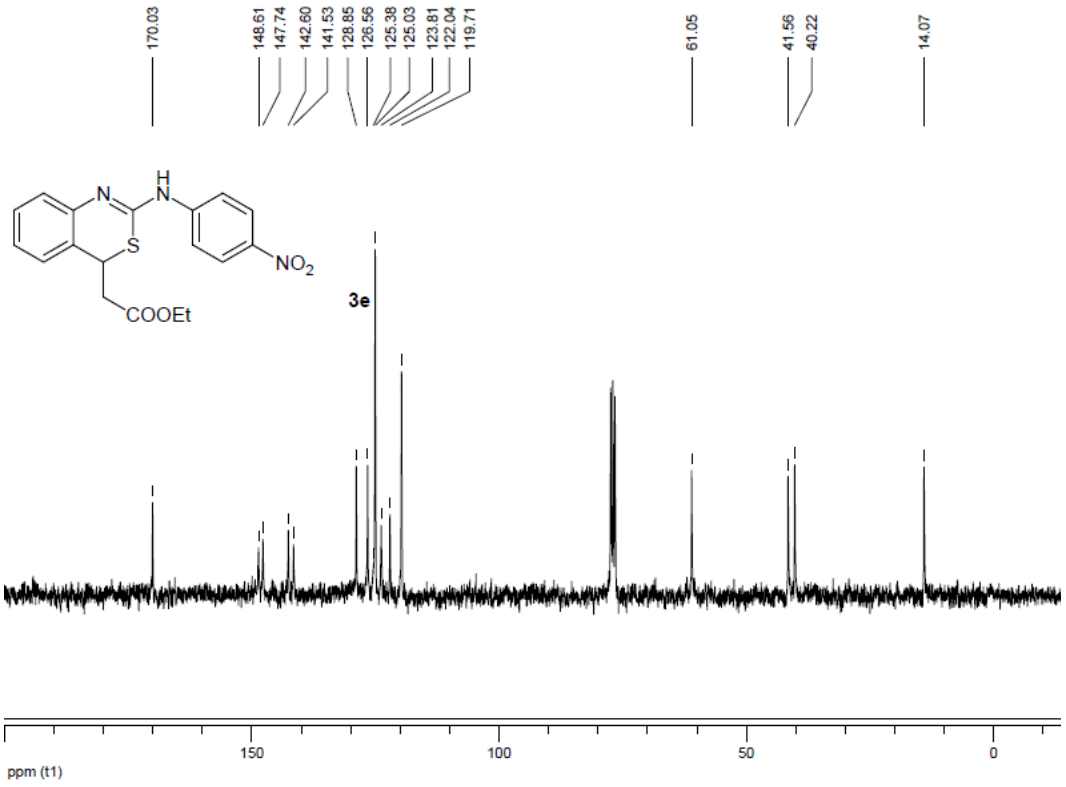

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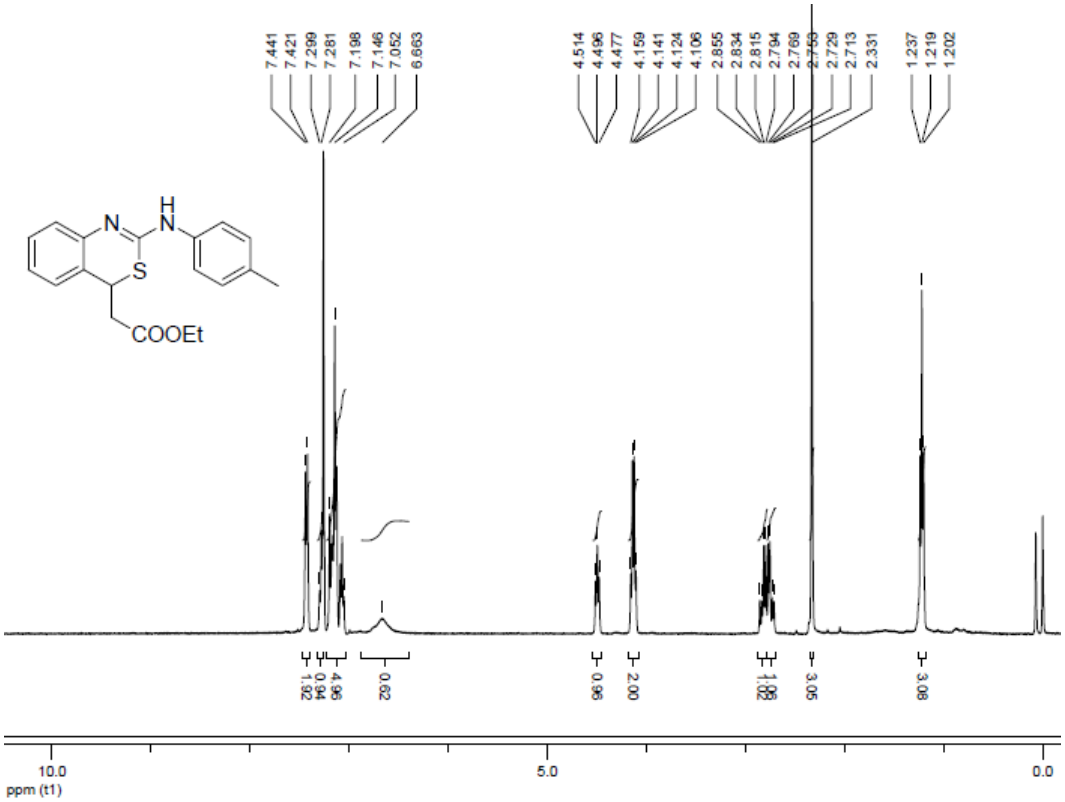
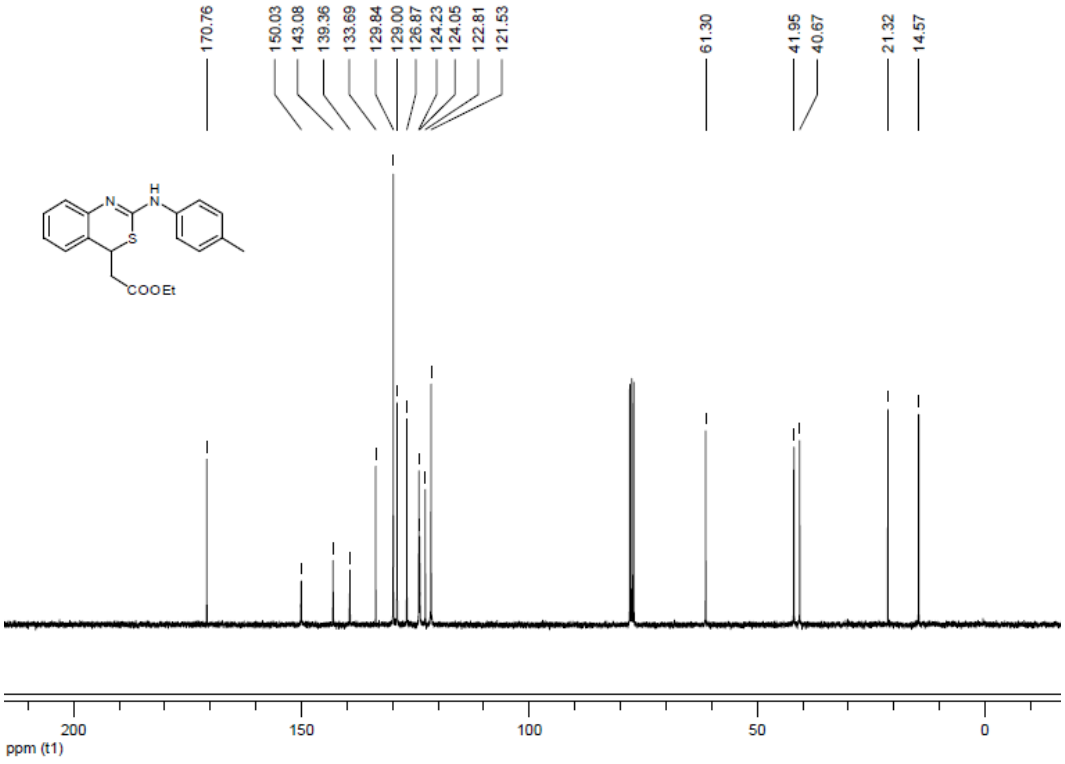
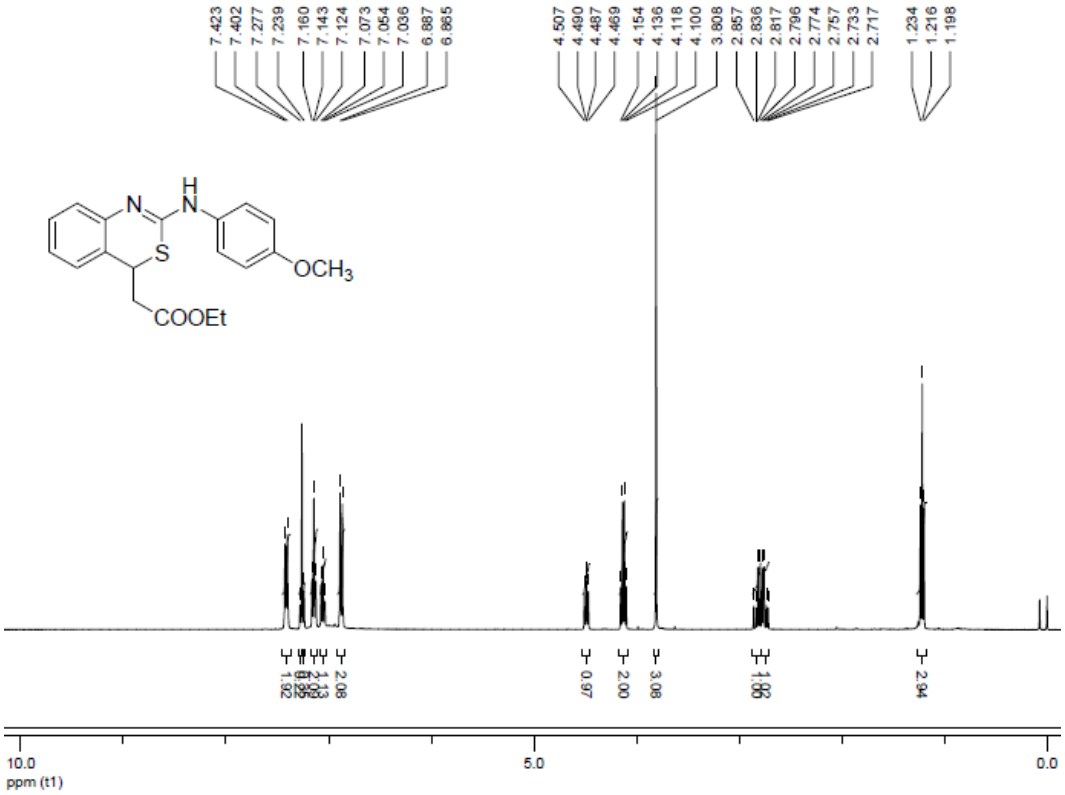


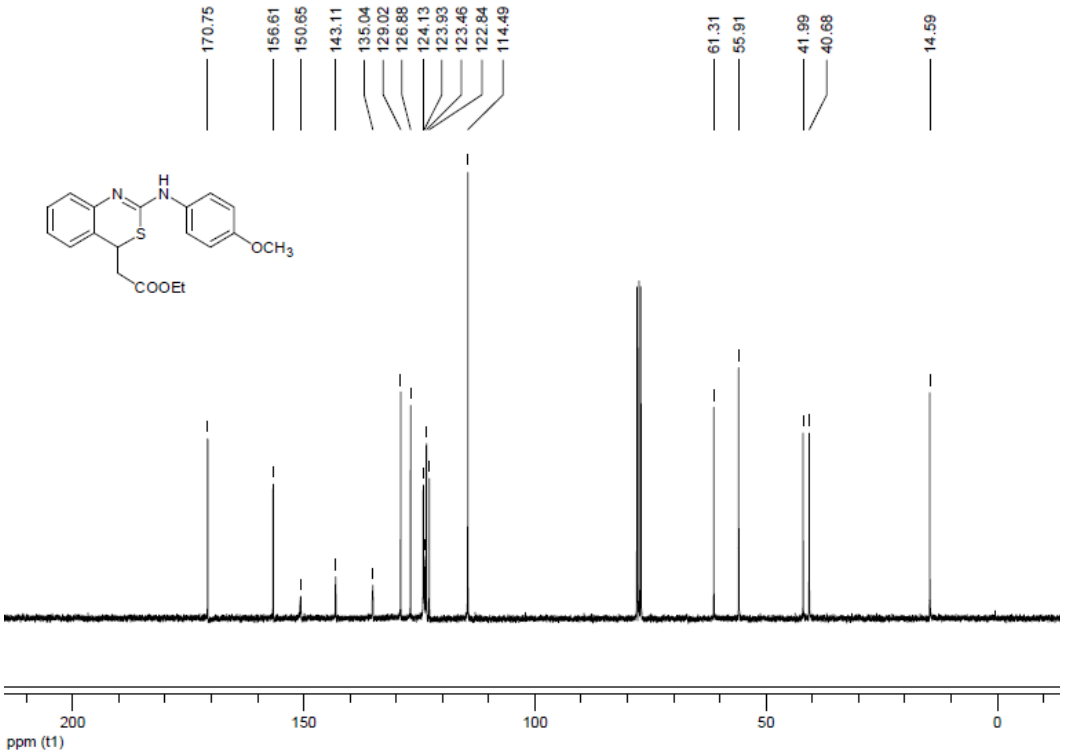
^{1}H NMR spectrum of compound **3f**



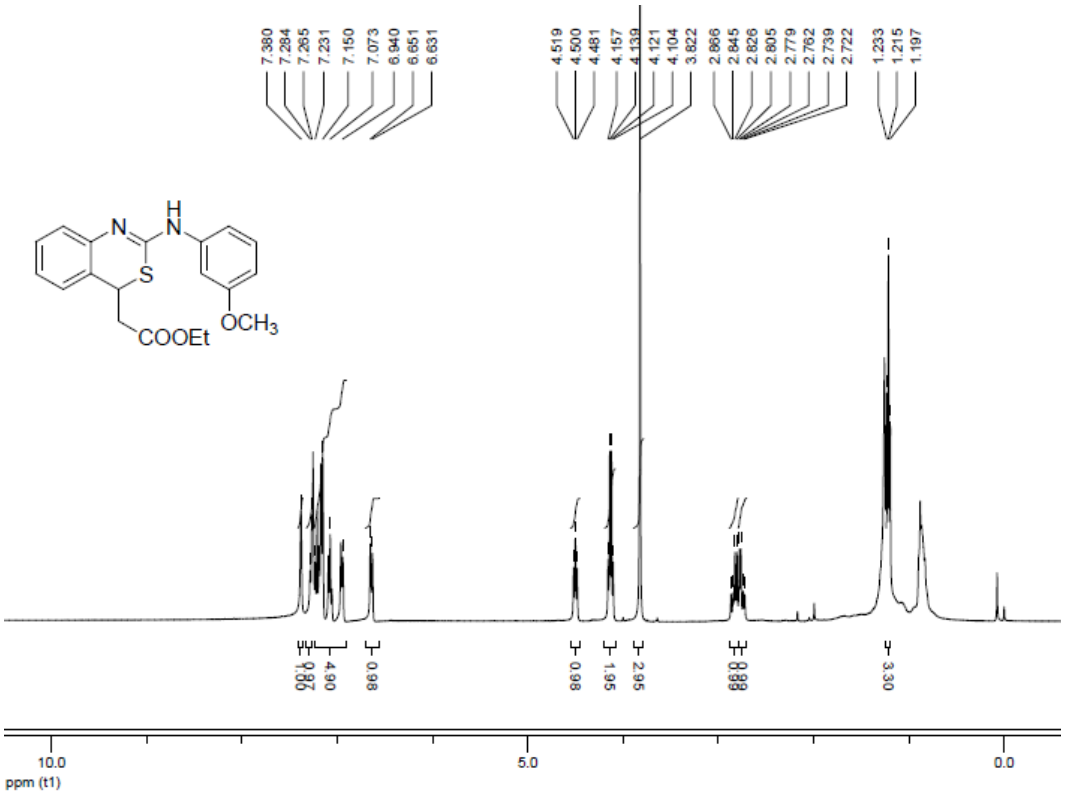
^{13}C NMR spectrum of compound **3f**



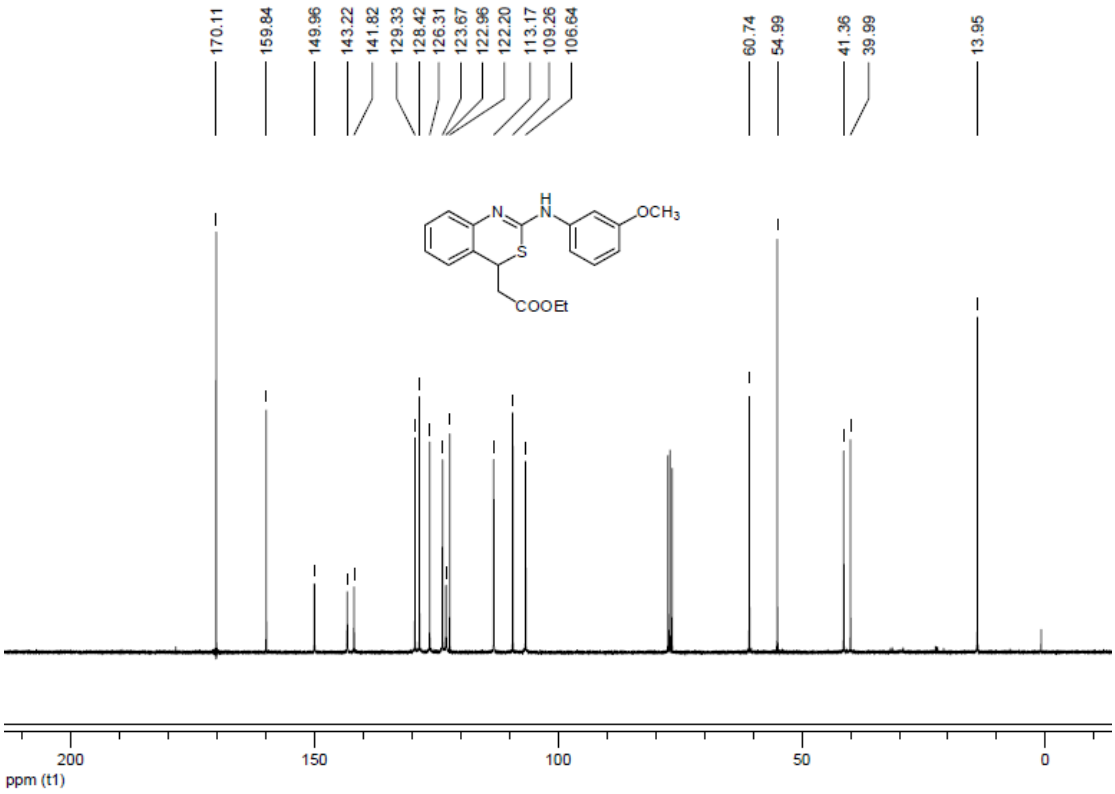
^{1}H NMR spectrum of compound **3g**



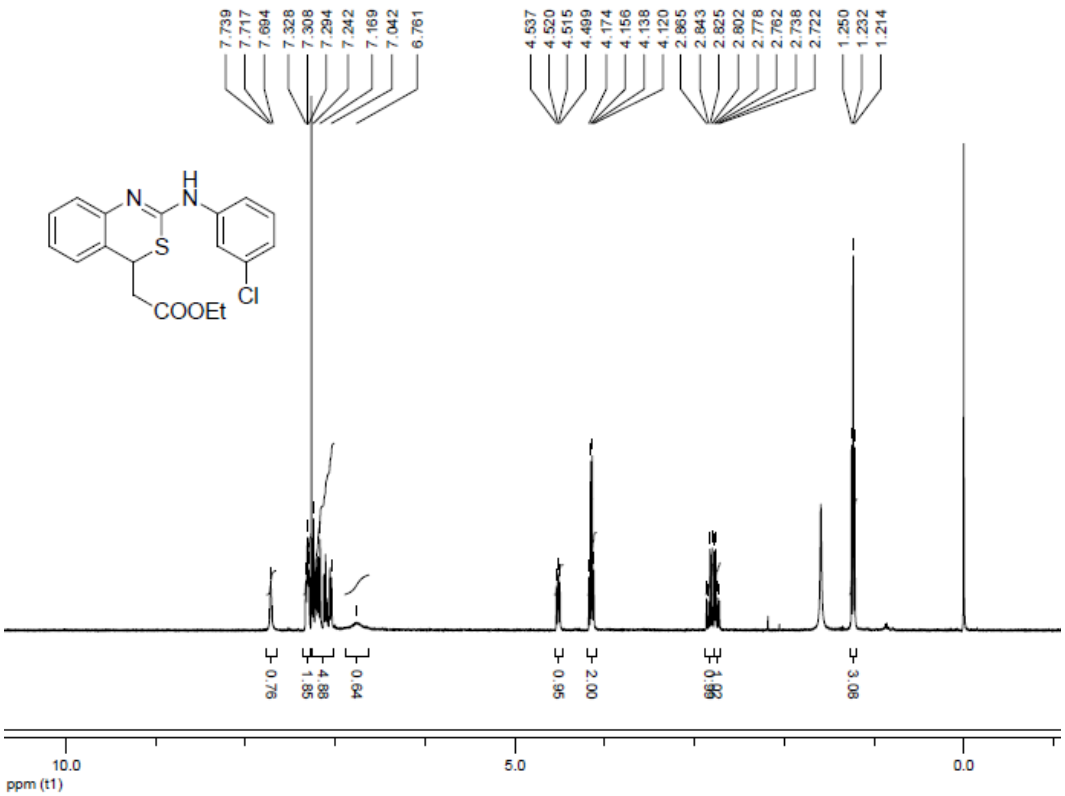
^{13}C NMR spectrum of compound **3g**



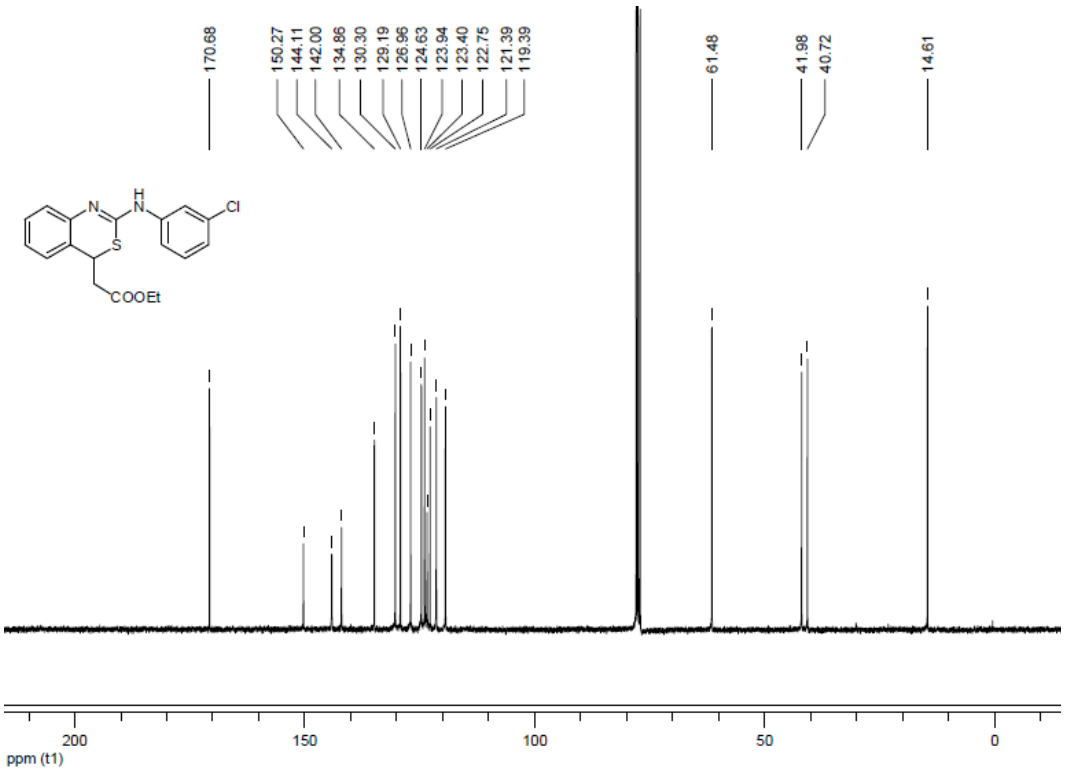
^{1}H NMR spectrum of compound **3h**



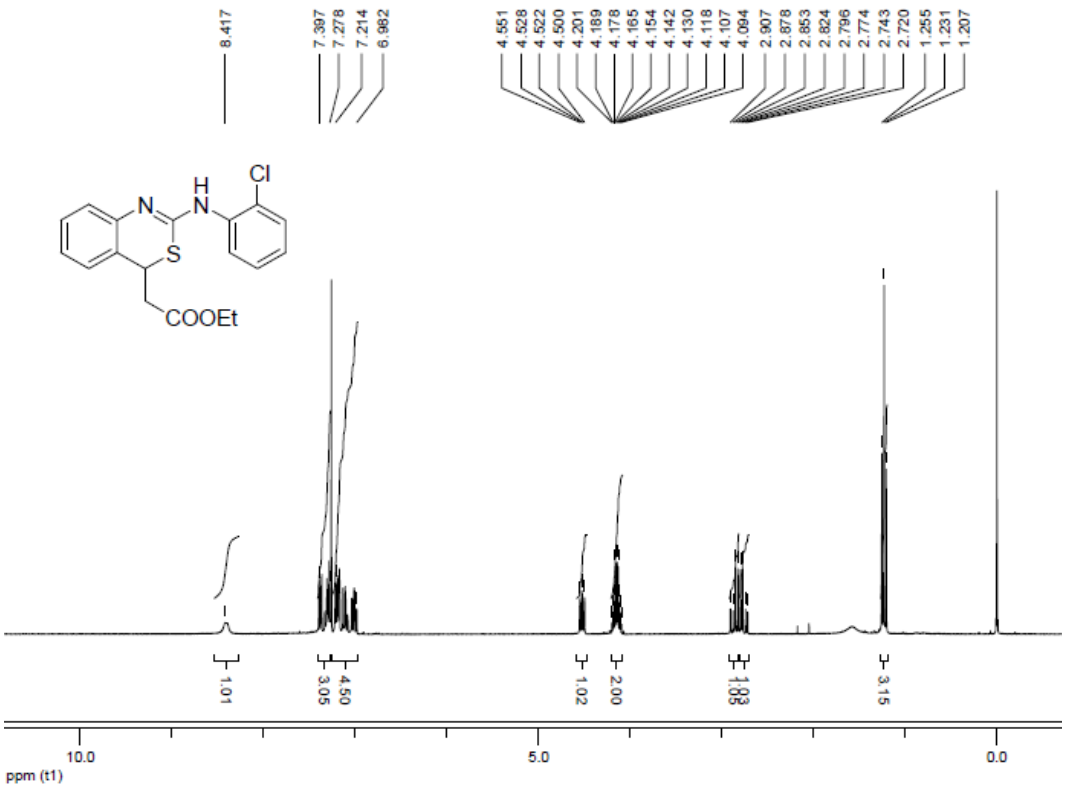
^{13}C NMR spectrum of compound **3h**



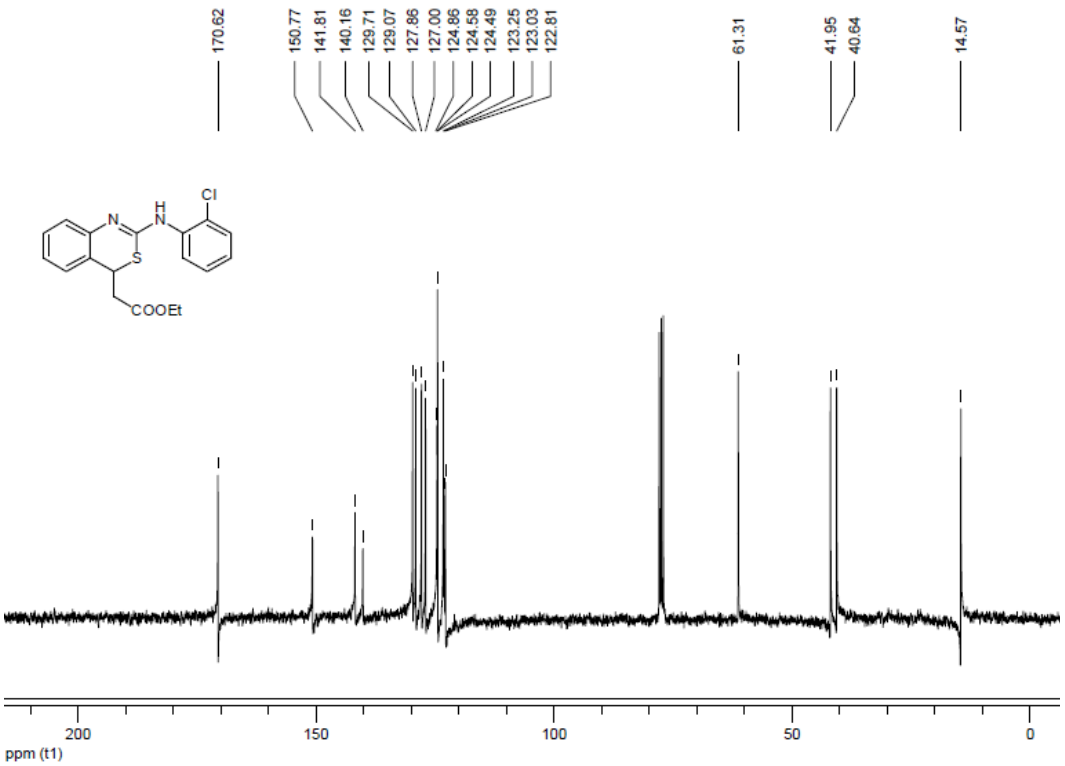
^{1}H NMR spectrum of compound **3i**



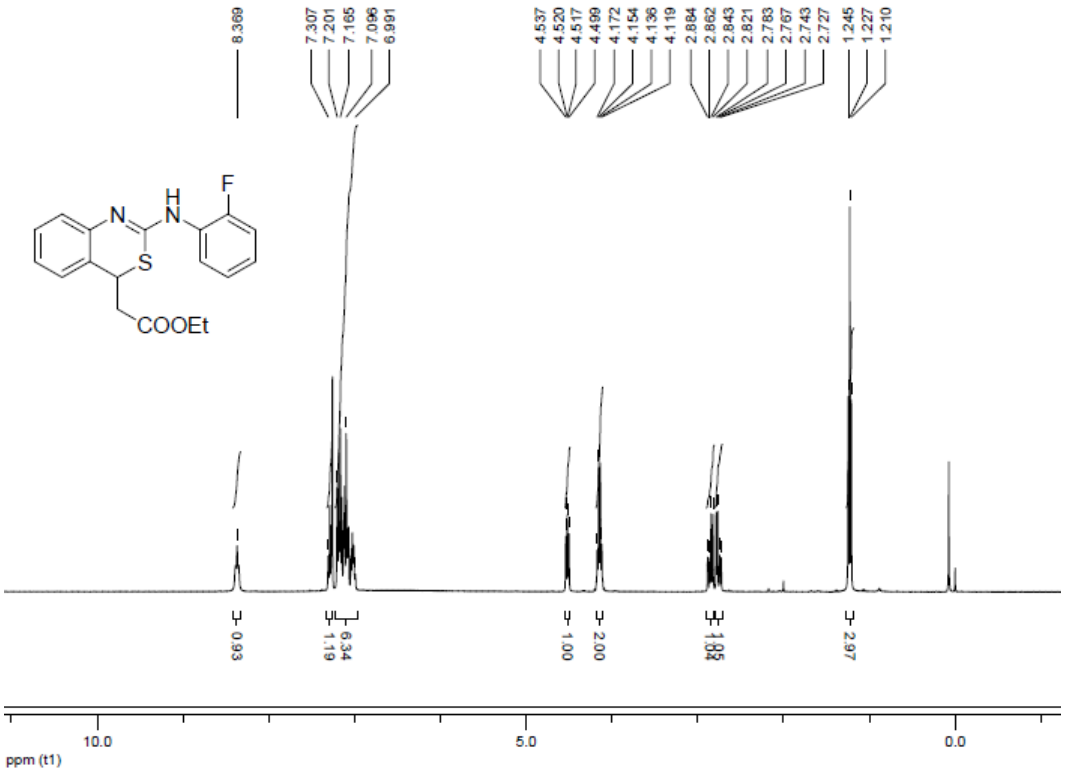
^{13}C NMR spectrum of compound **3i**



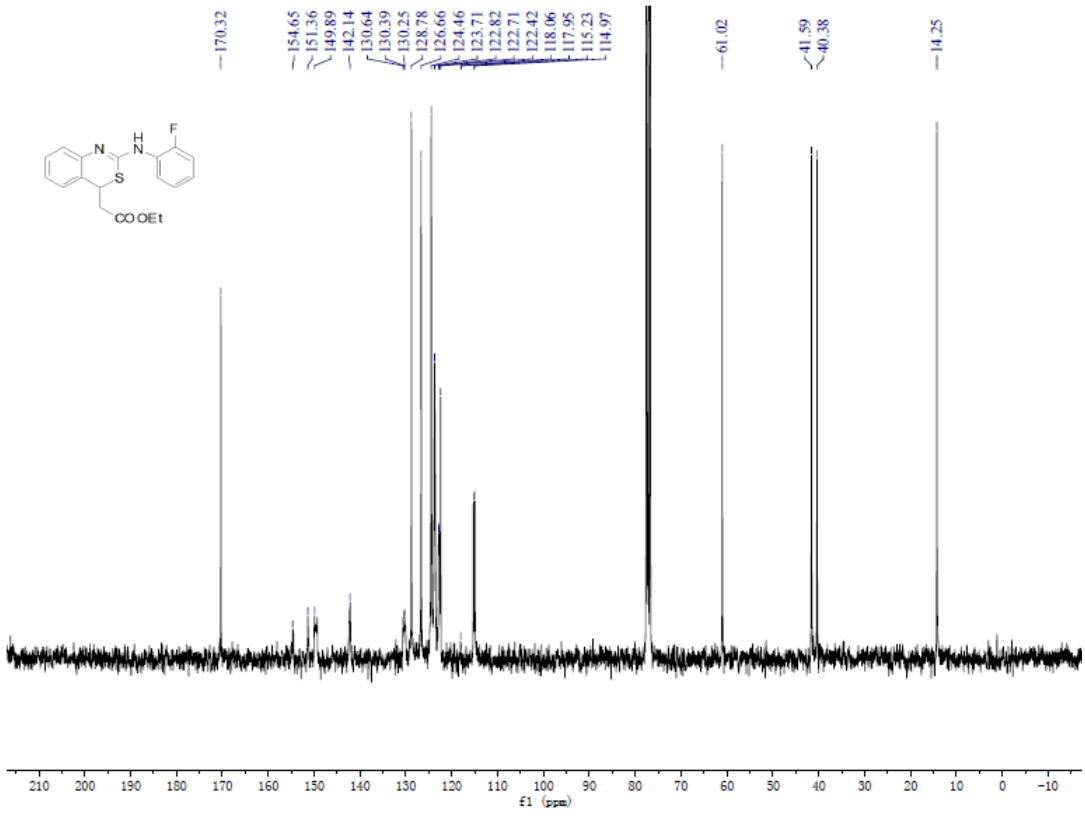
^{1}H NMR spectrum of compound **3j**



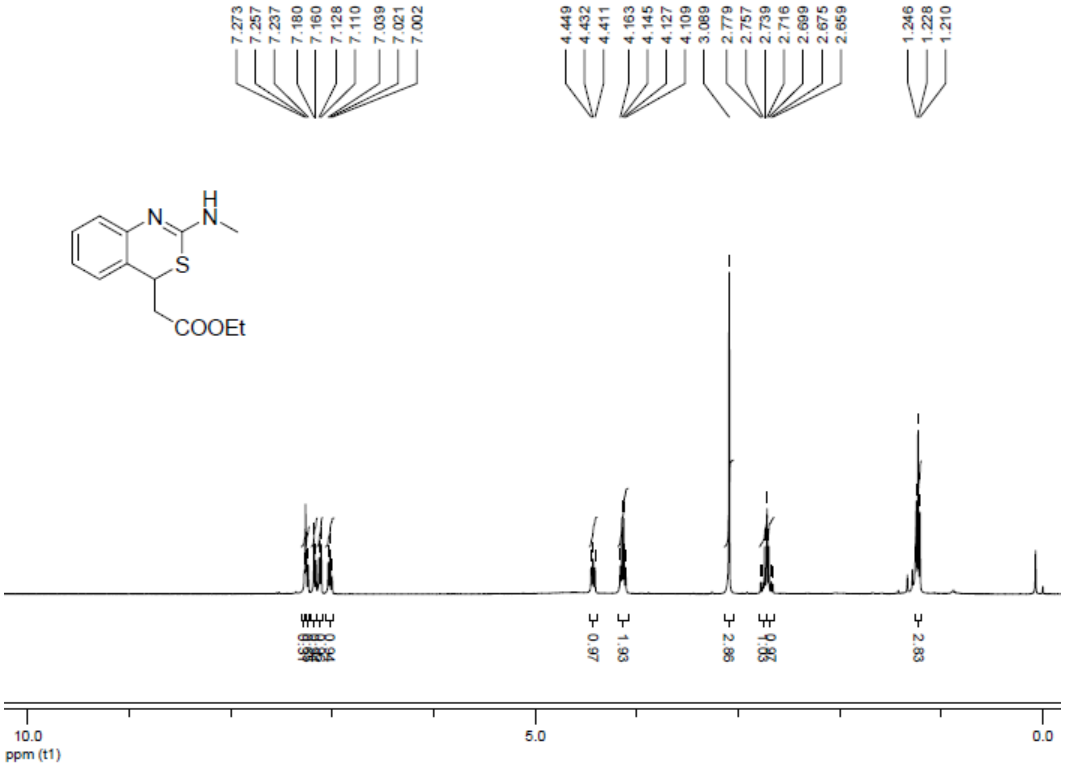
^{13}C NMR spectrum of compound **3j**



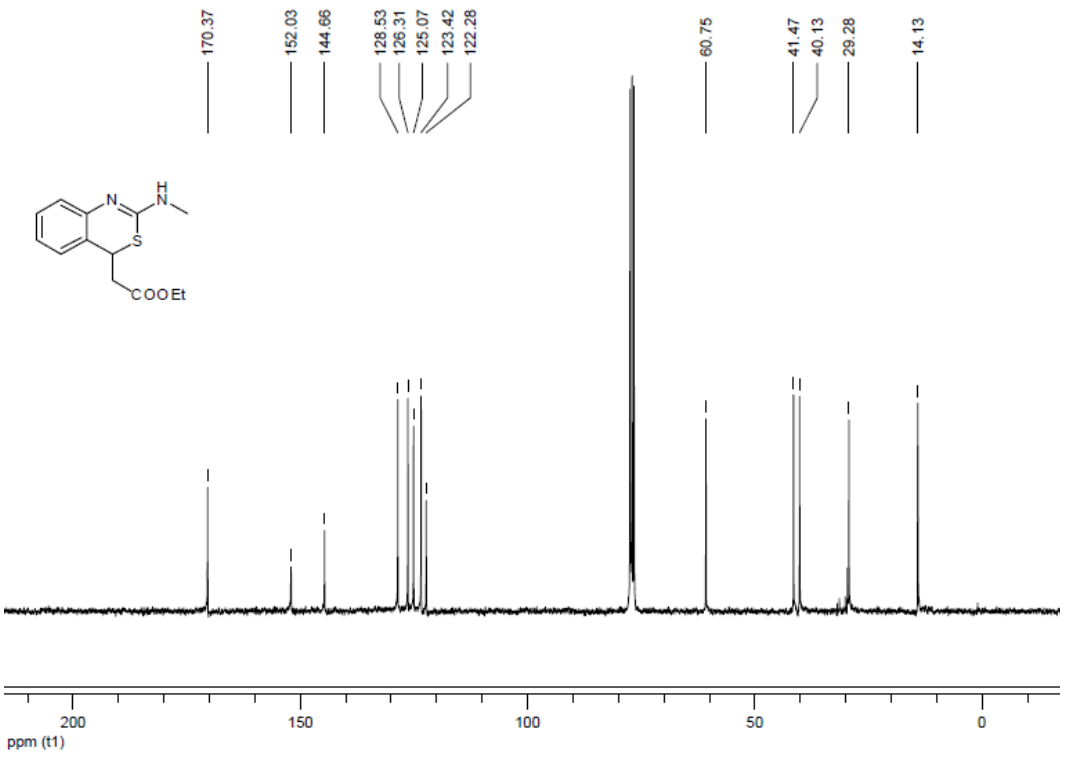
^{1}H NMR spectrum of compound **3k**



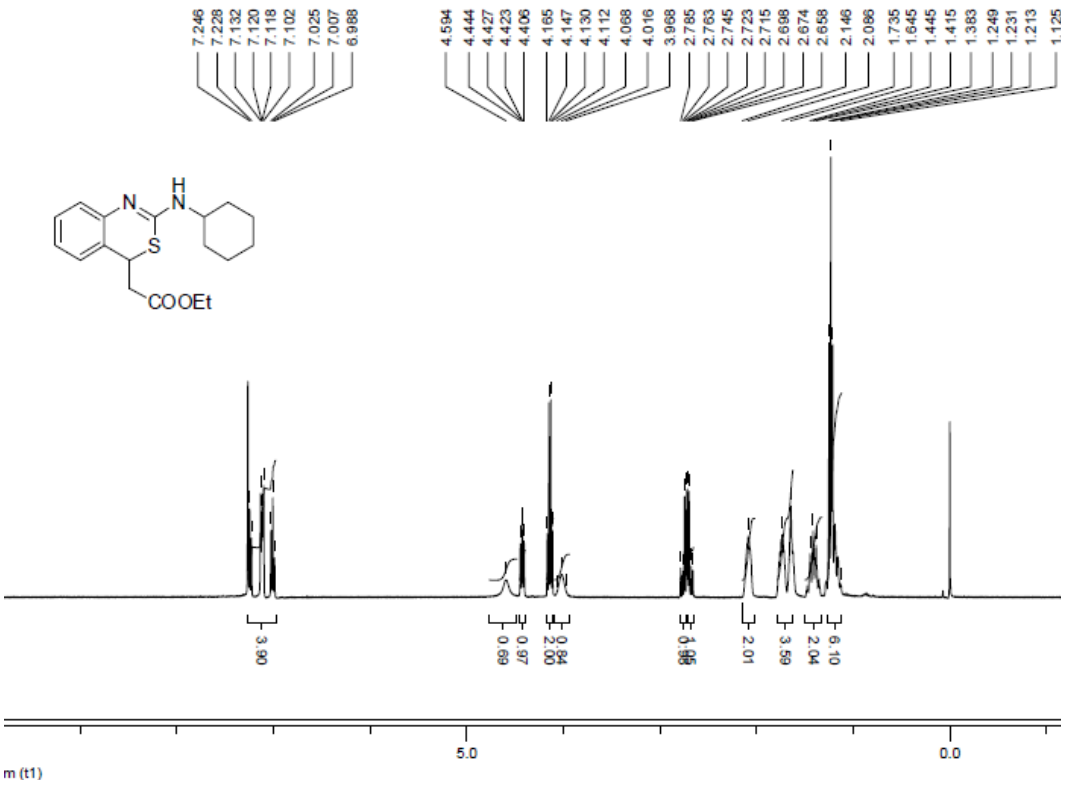
^{13}C NMR spectrum of compound **3k**



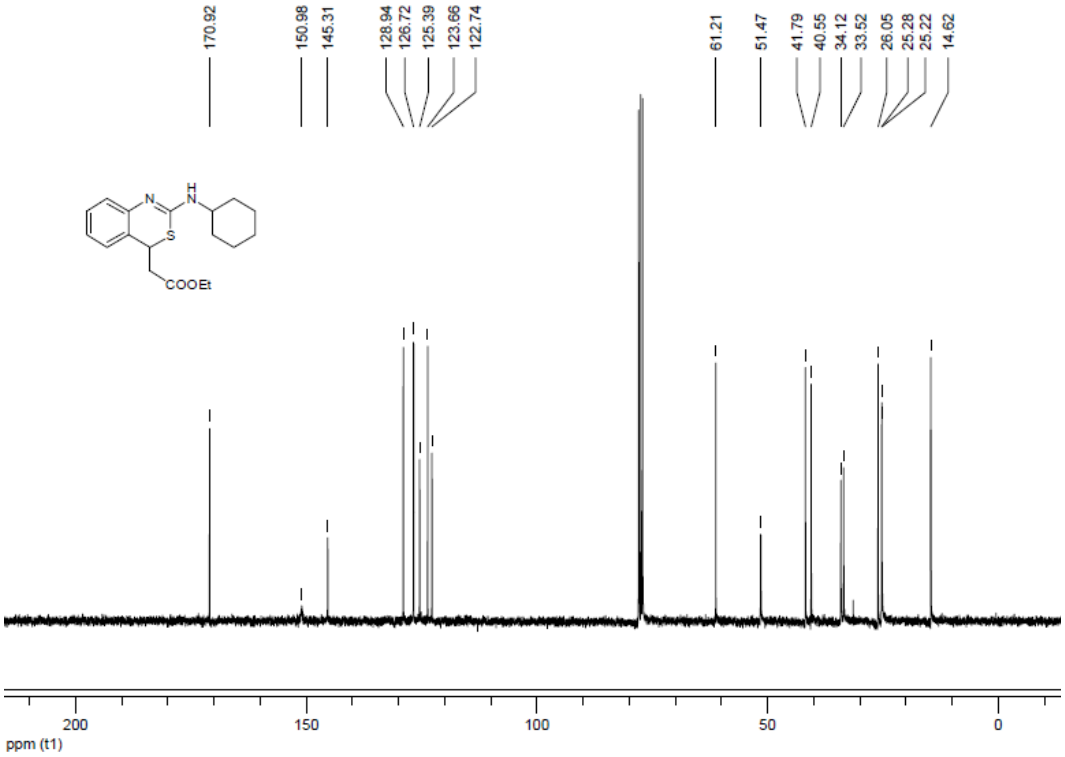
^{1}H NMR spectrum of compound **3l**



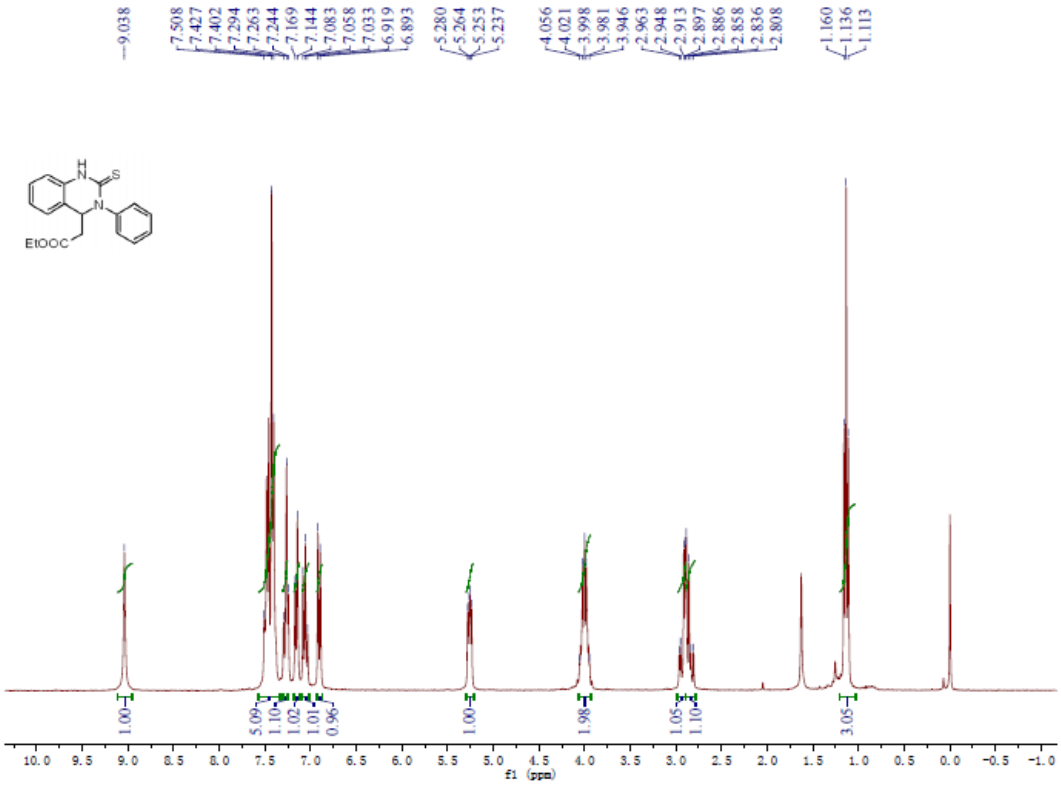
^{13}C NMR spectrum of compound **3l**



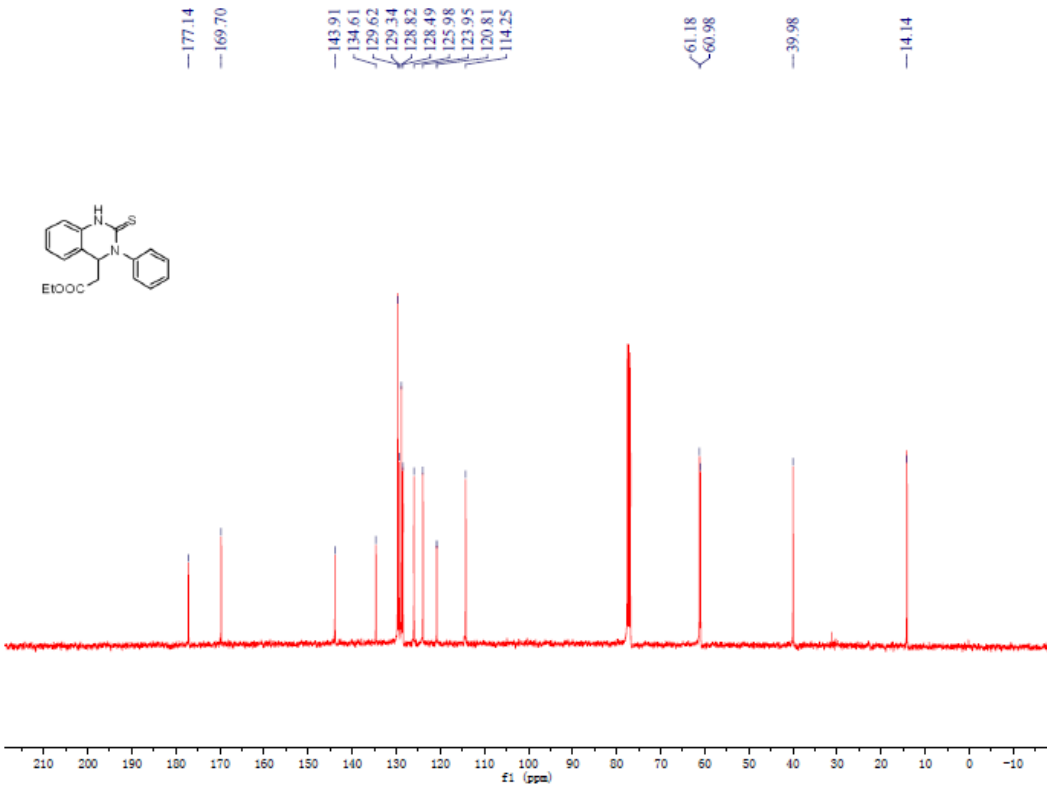
^{1}H NMR spectrum of compound **3m**



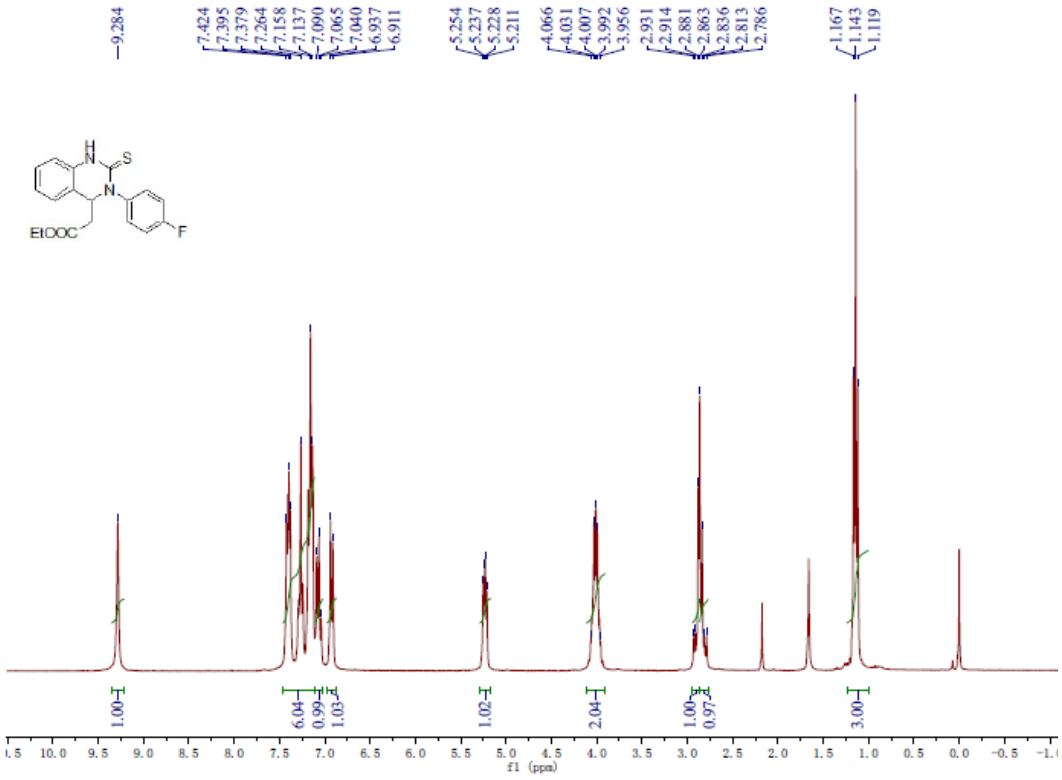
^{13}C NMR spectrum of compound **3m**



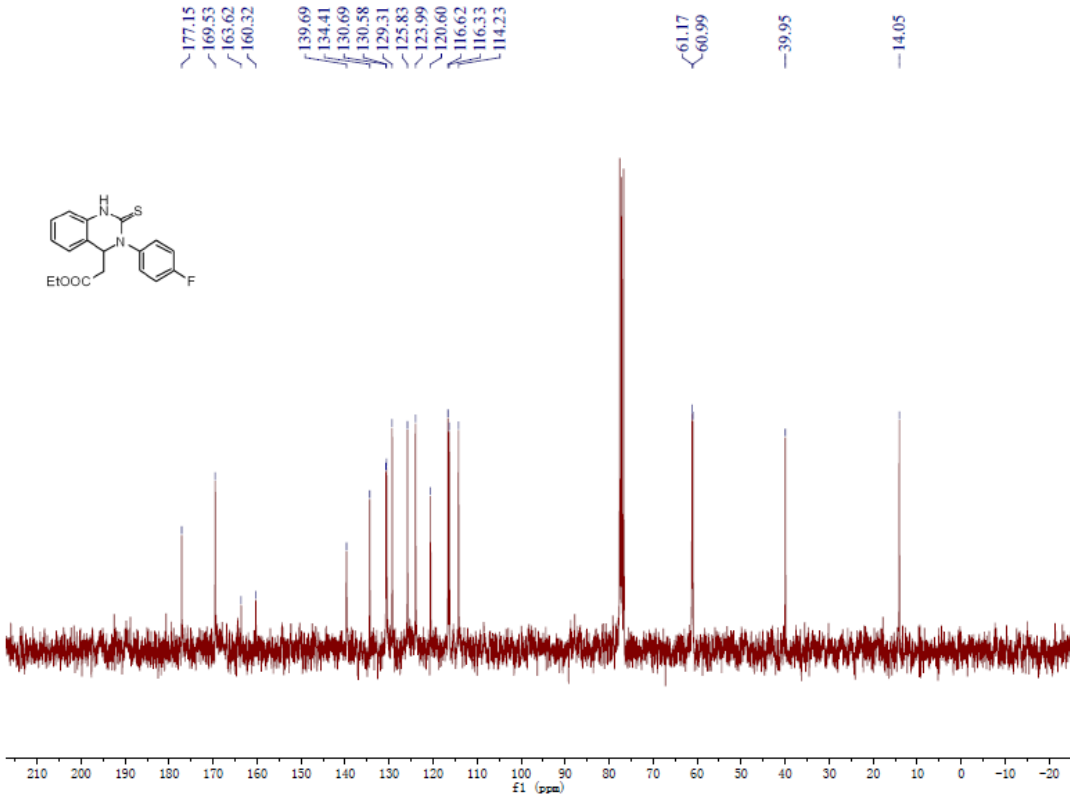
^{1}H NMR spectrum of compound **4a**



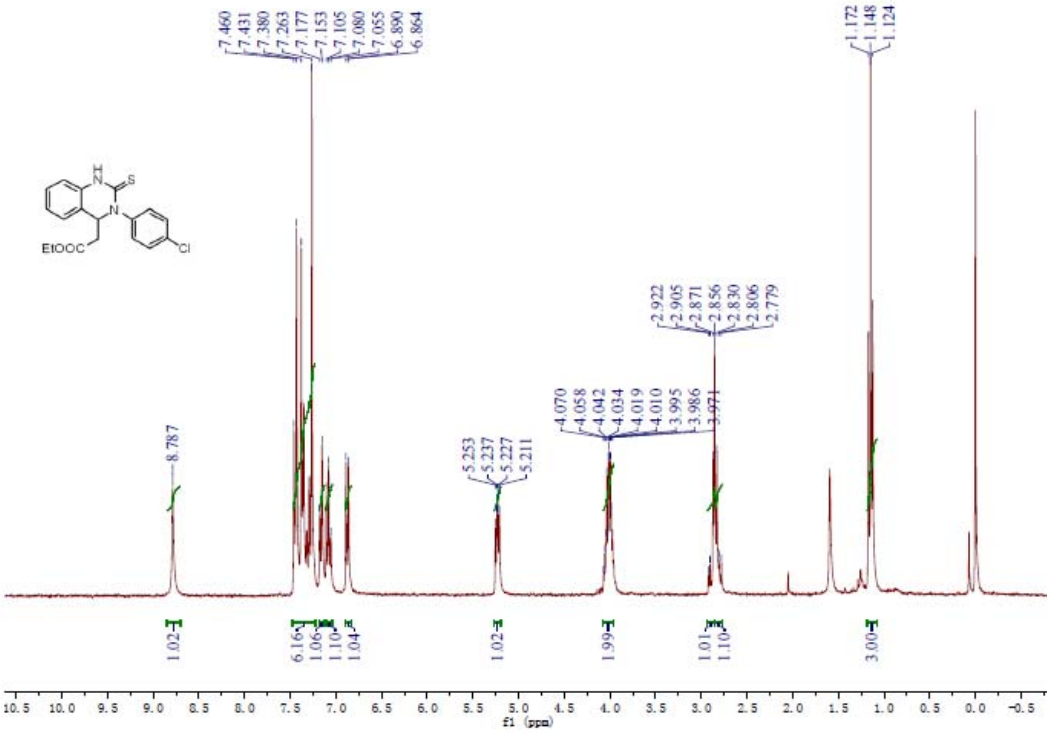
^{13}C NMR spectrum of compound **4a**



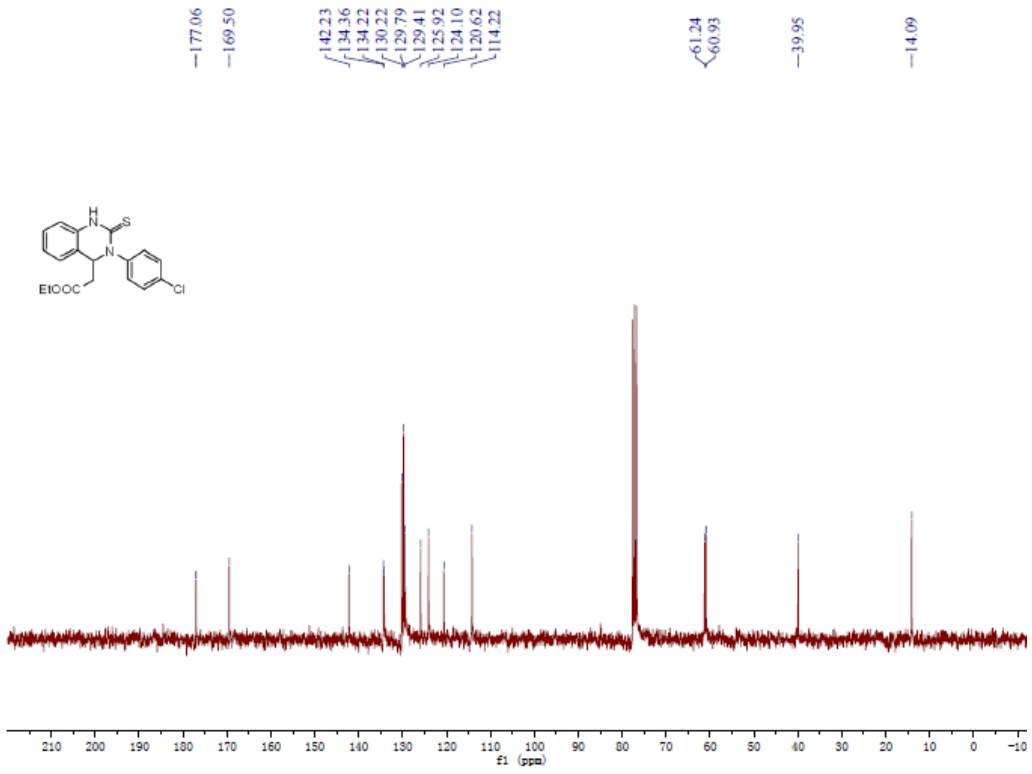
^{1}H NMR spectrum of compound **4b**



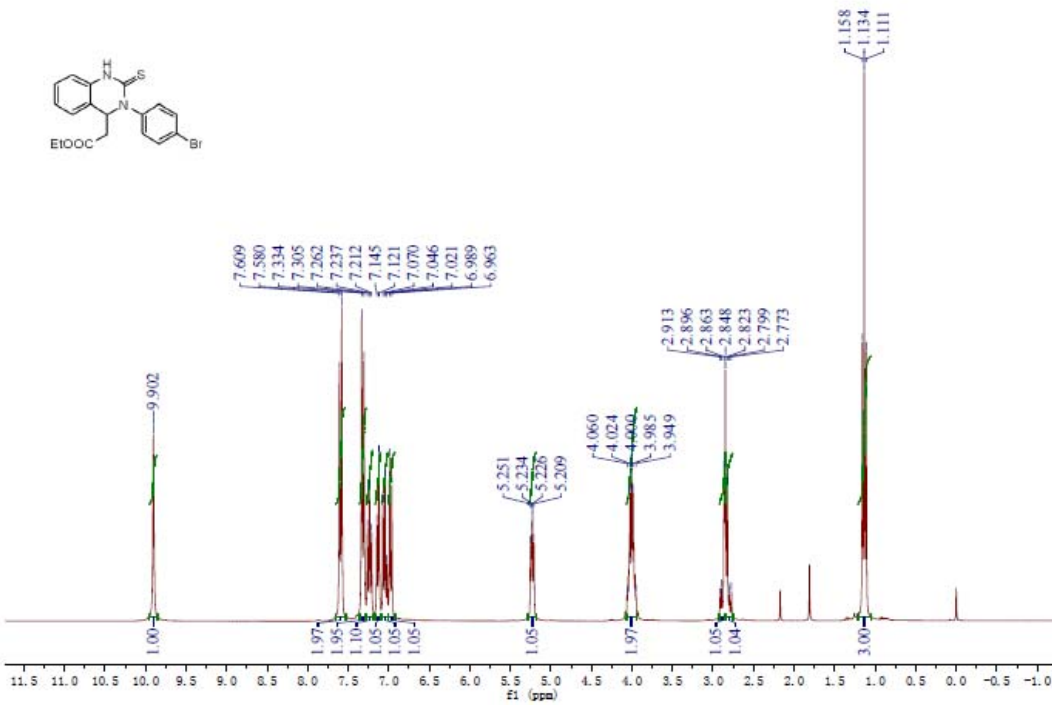
^{13}C NMR spectrum of compound **4b**



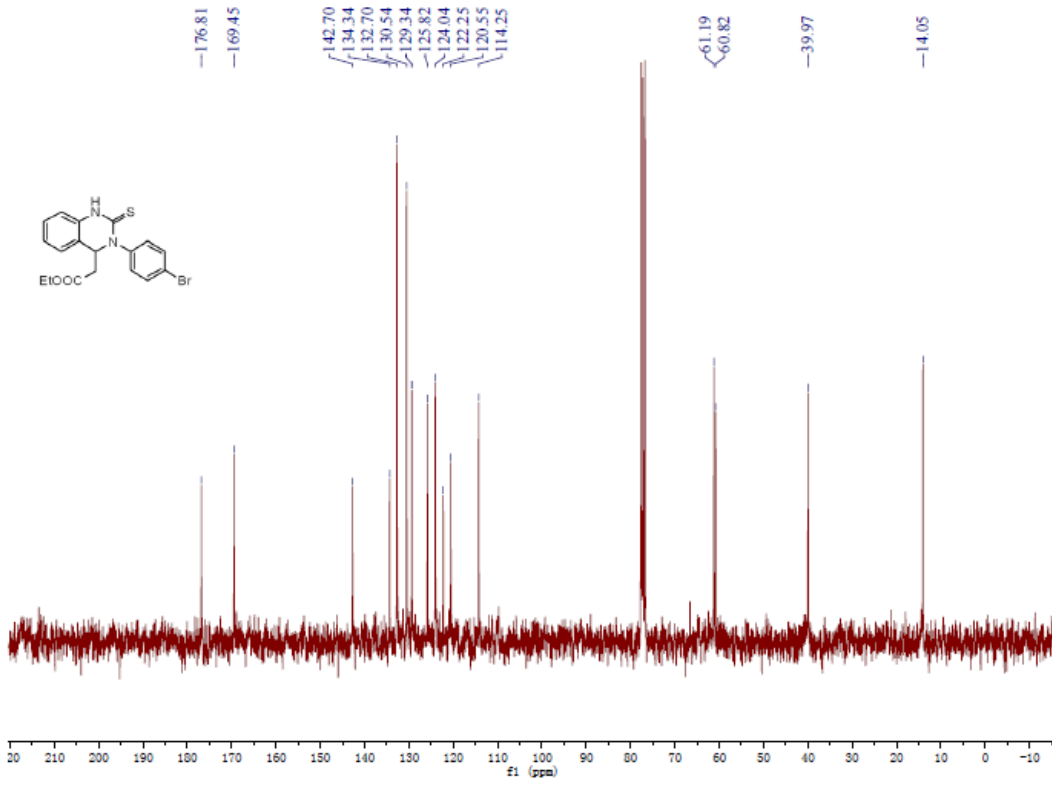
^{1}H NMR spectrum of compound **4c**



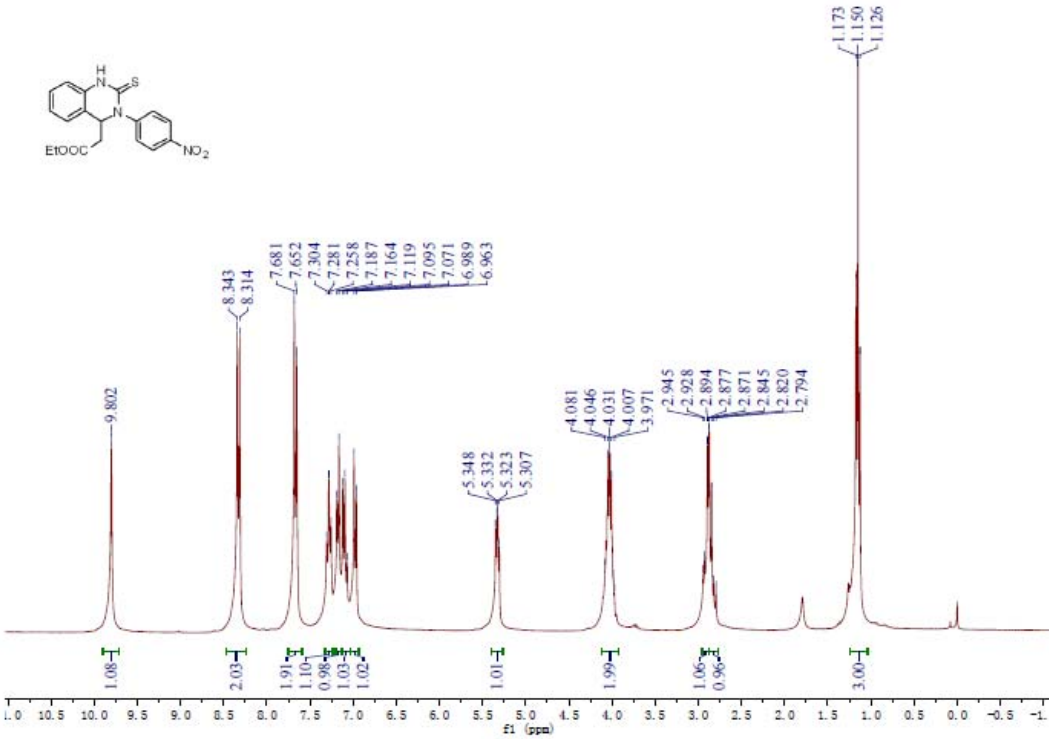
^{13}C NMR spectrum of compound **4c**



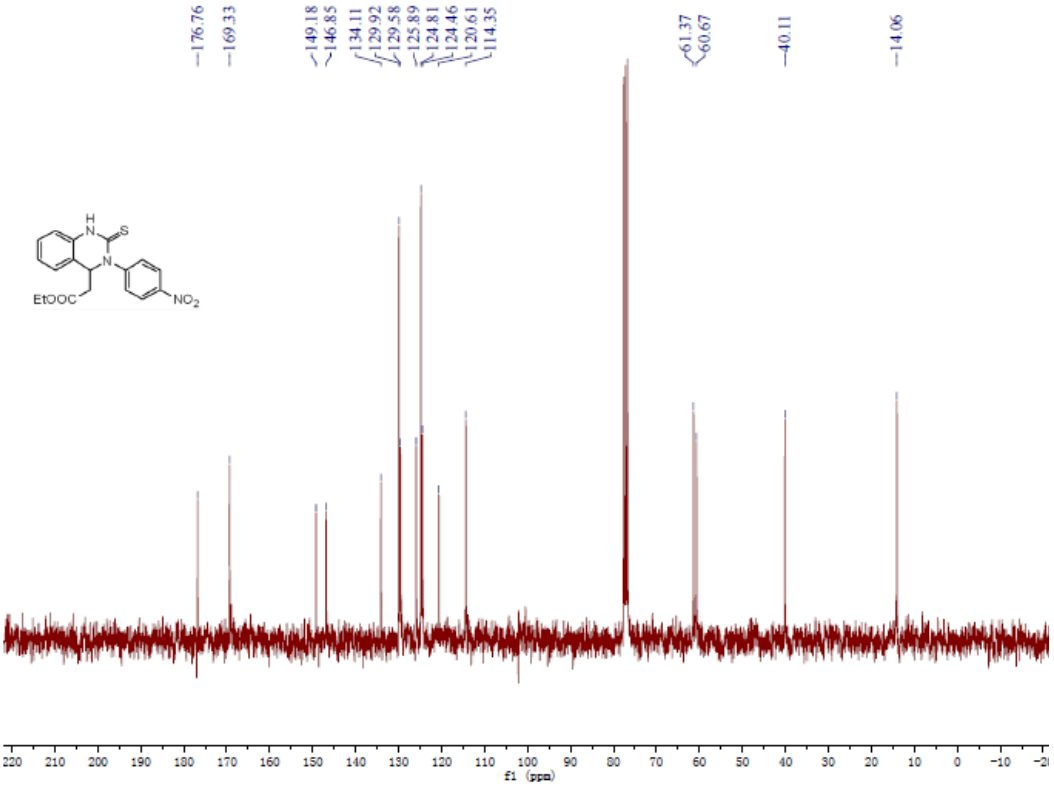
^{1}H NMR spectrum of compound **4d**



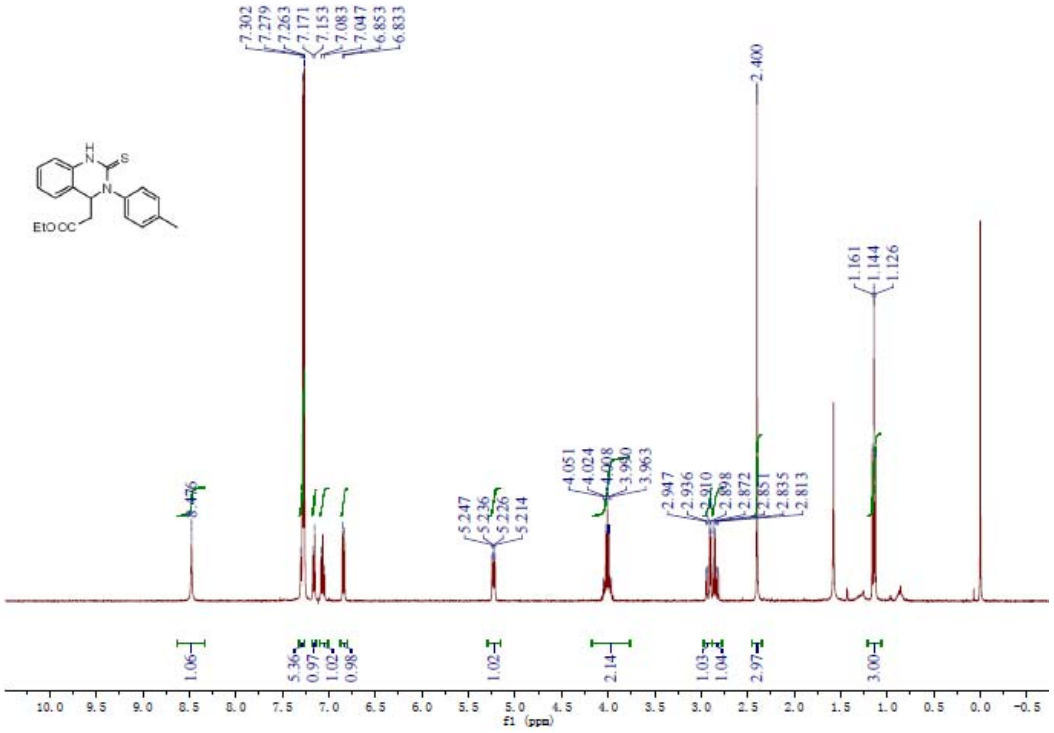
^{13}C NMR spectrum of compound **4d**



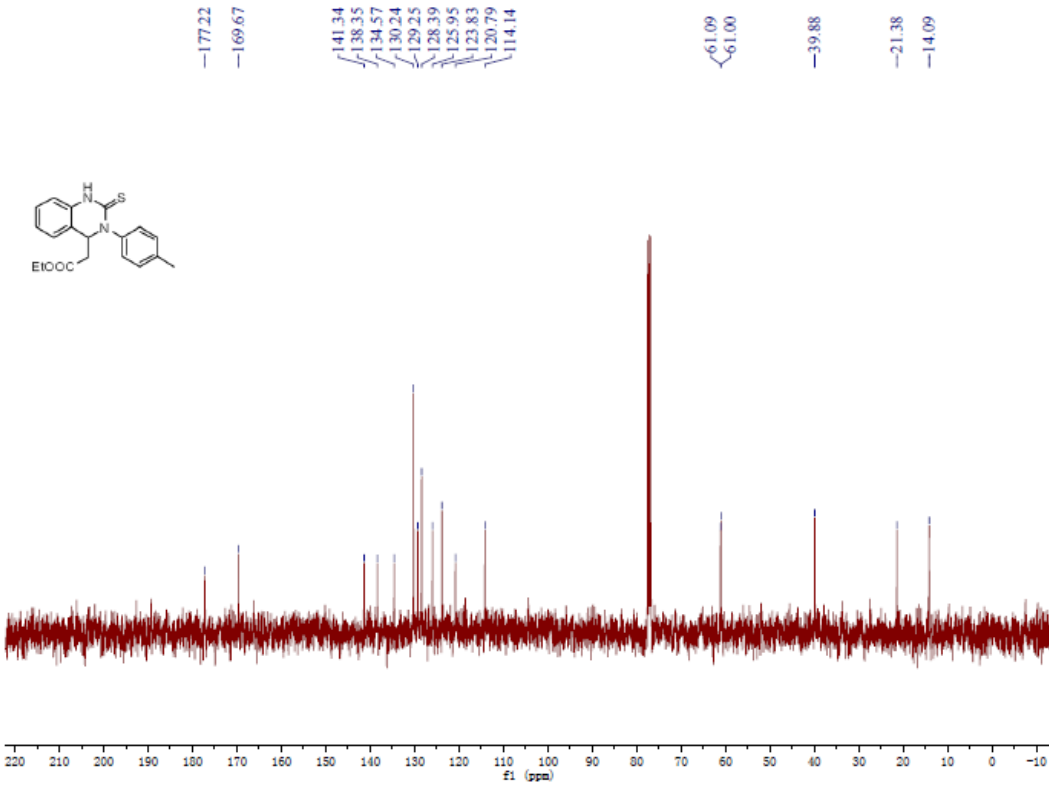
^{1}H NMR spectrum of compound **4e**



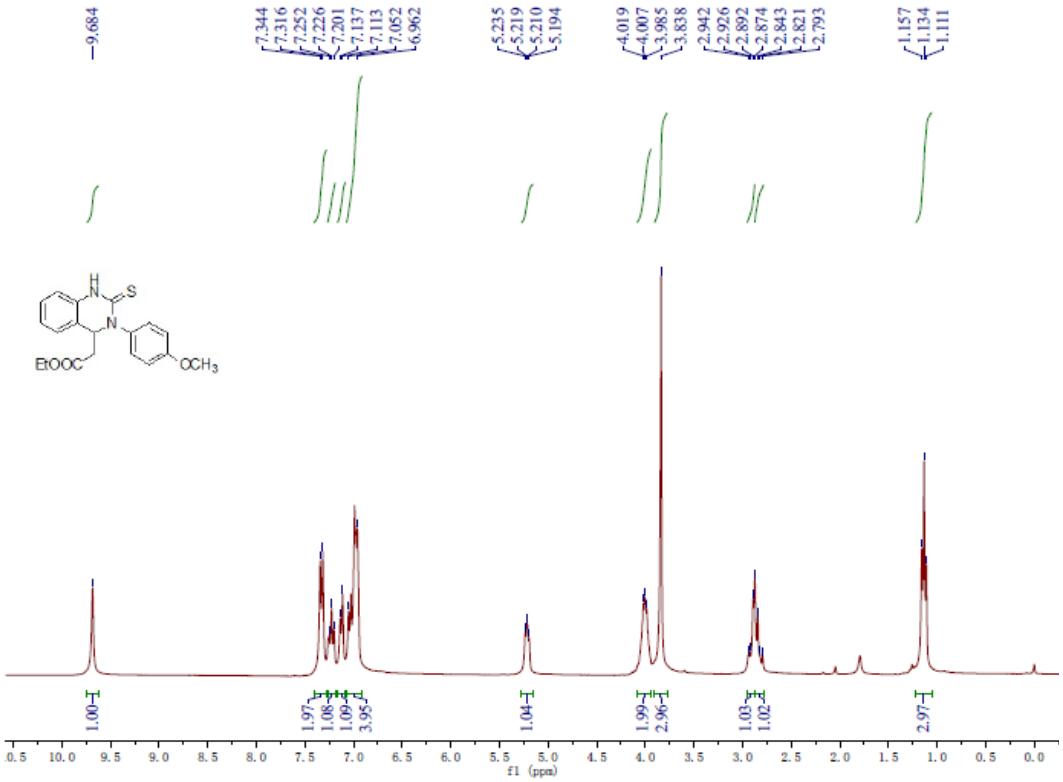
^{13}C NMR spectrum of compound **4e**



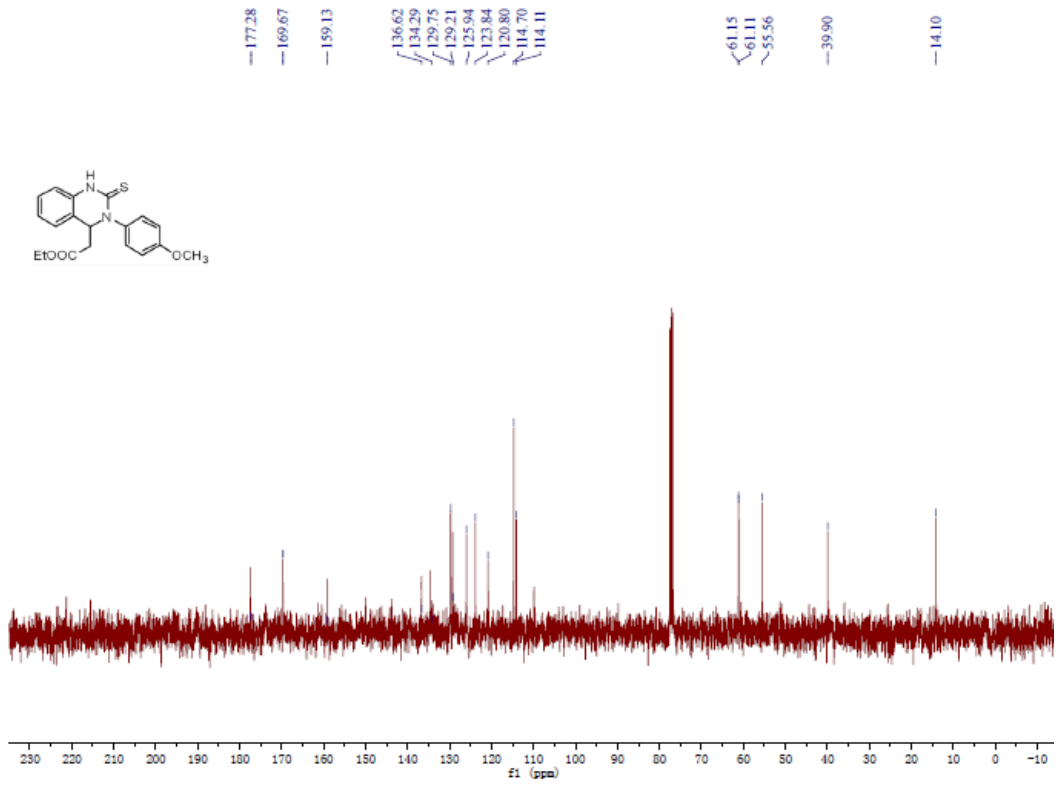
^{1}H NMR spectrum of compound **4f**



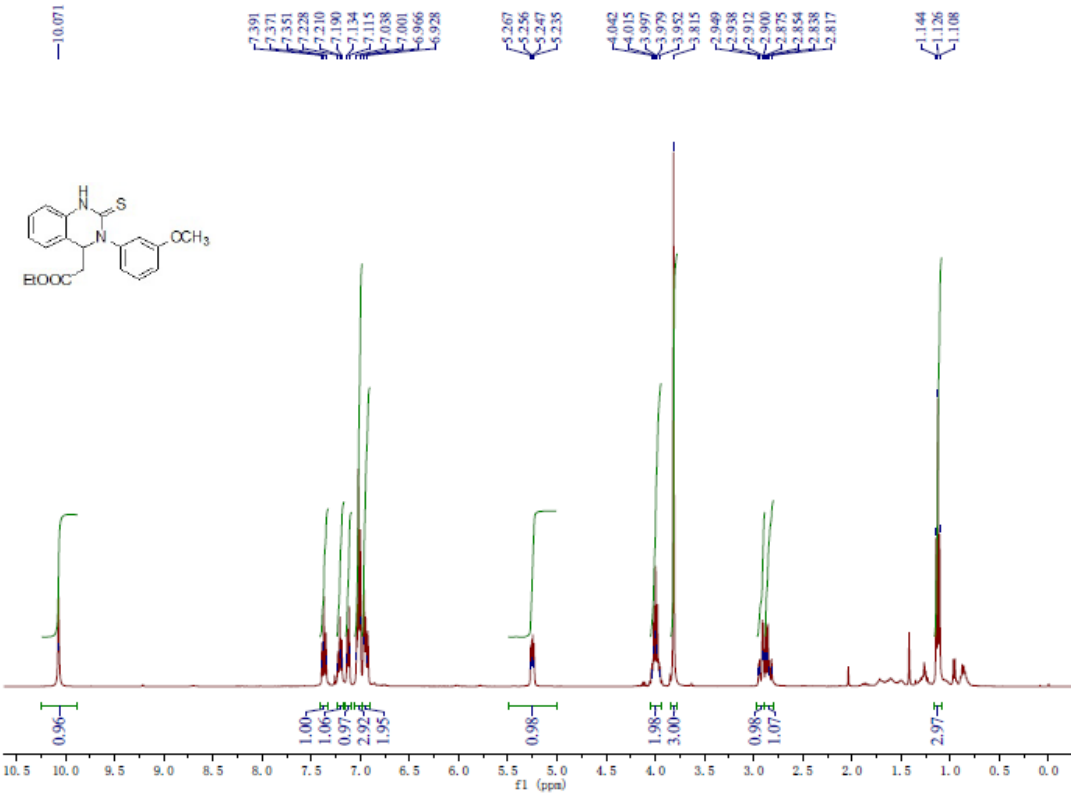
^{13}C NMR spectrum of compound **4f**



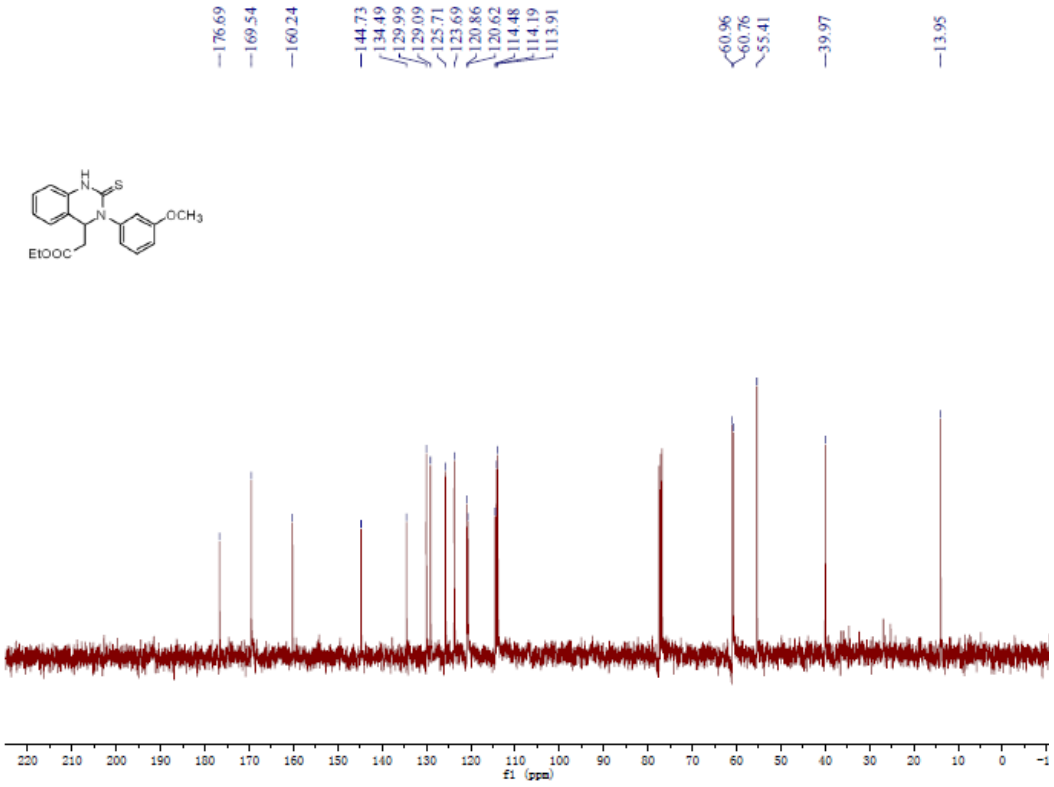
^{1}H NMR spectrum of compound **4g**



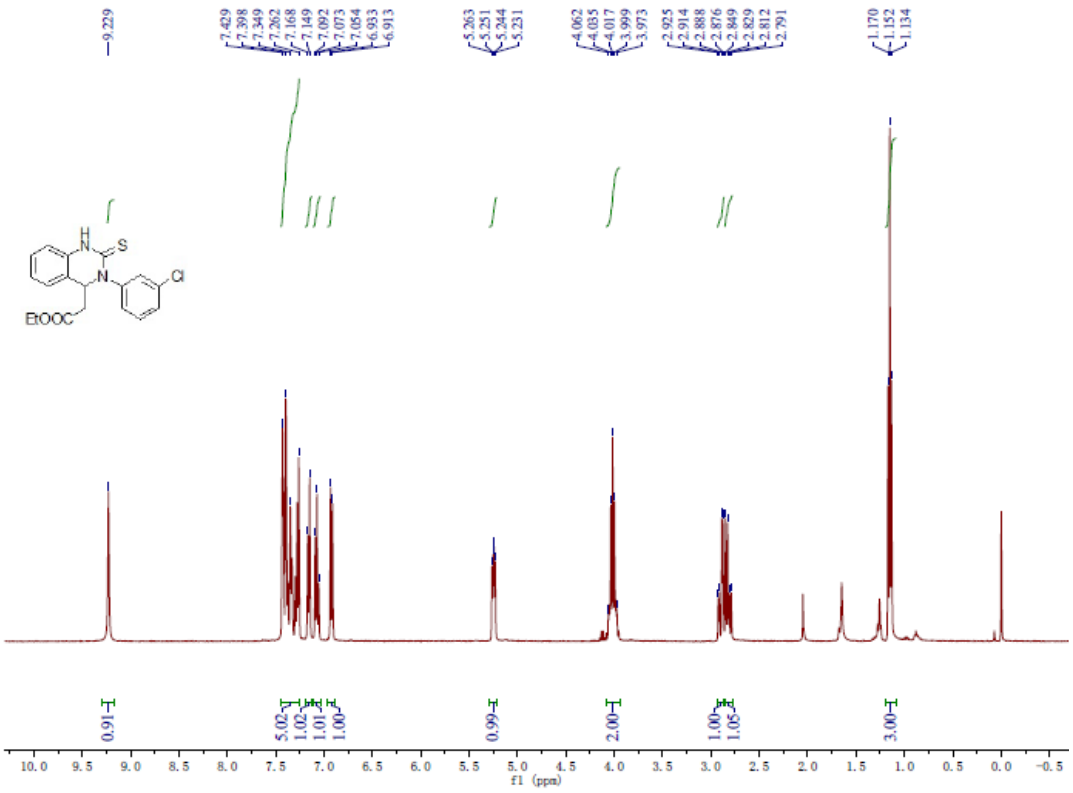
^{13}C NMR spectrum of compound **4g**



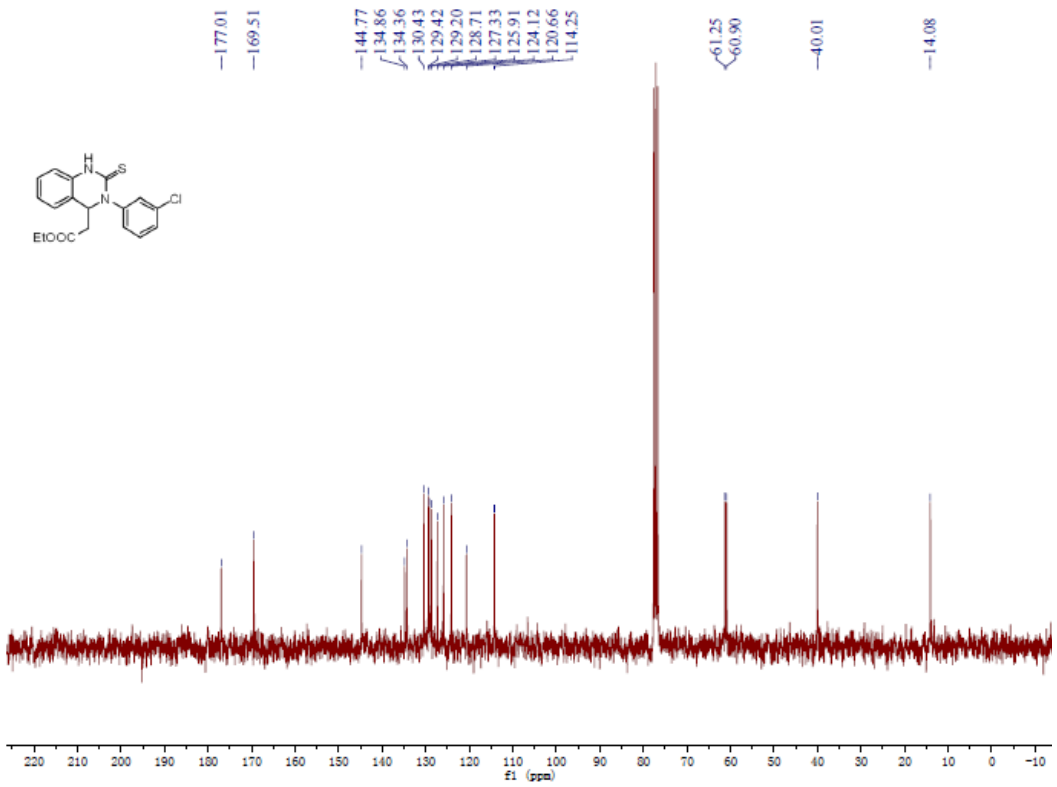
^{1}H NMR spectrum of compound **4h**



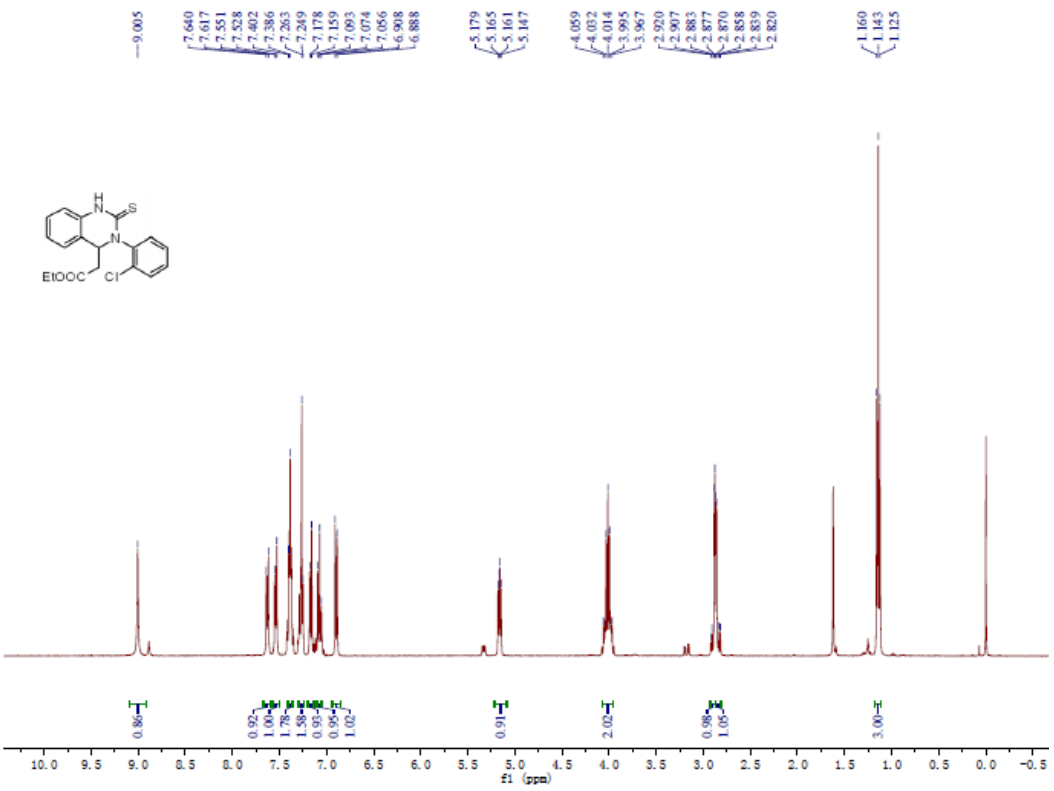
^{13}C NMR spectrum of compound **4h**



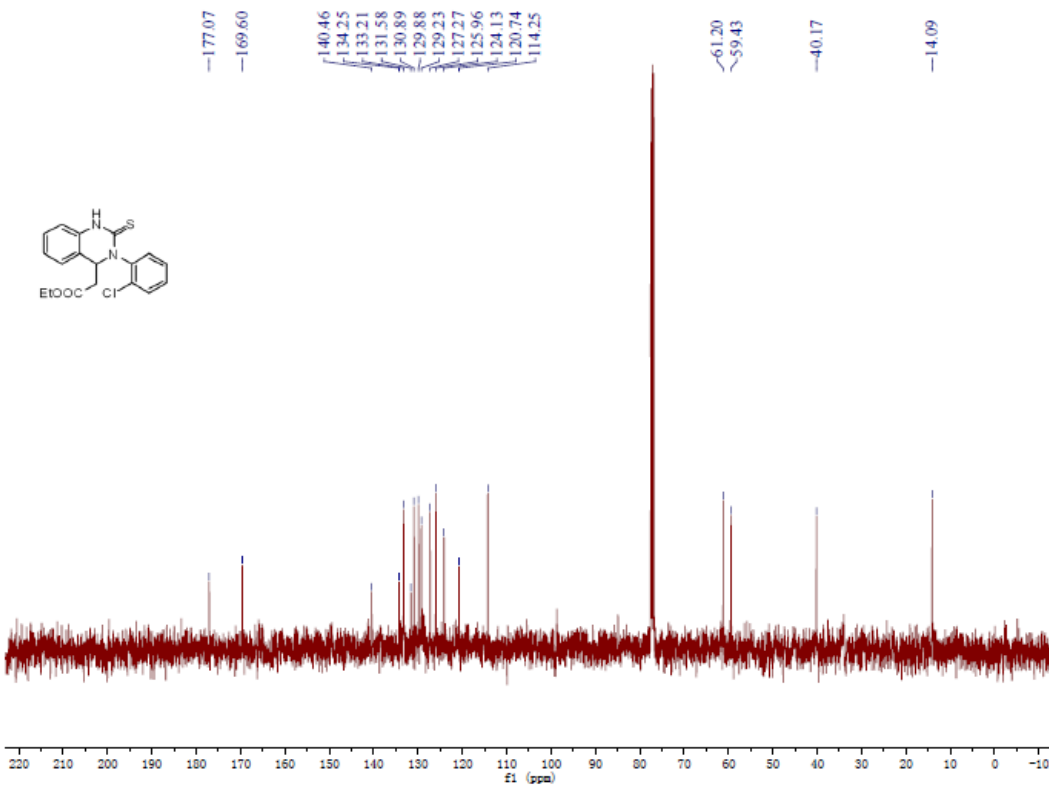
^{1}H NMR spectrum of compound **4i**



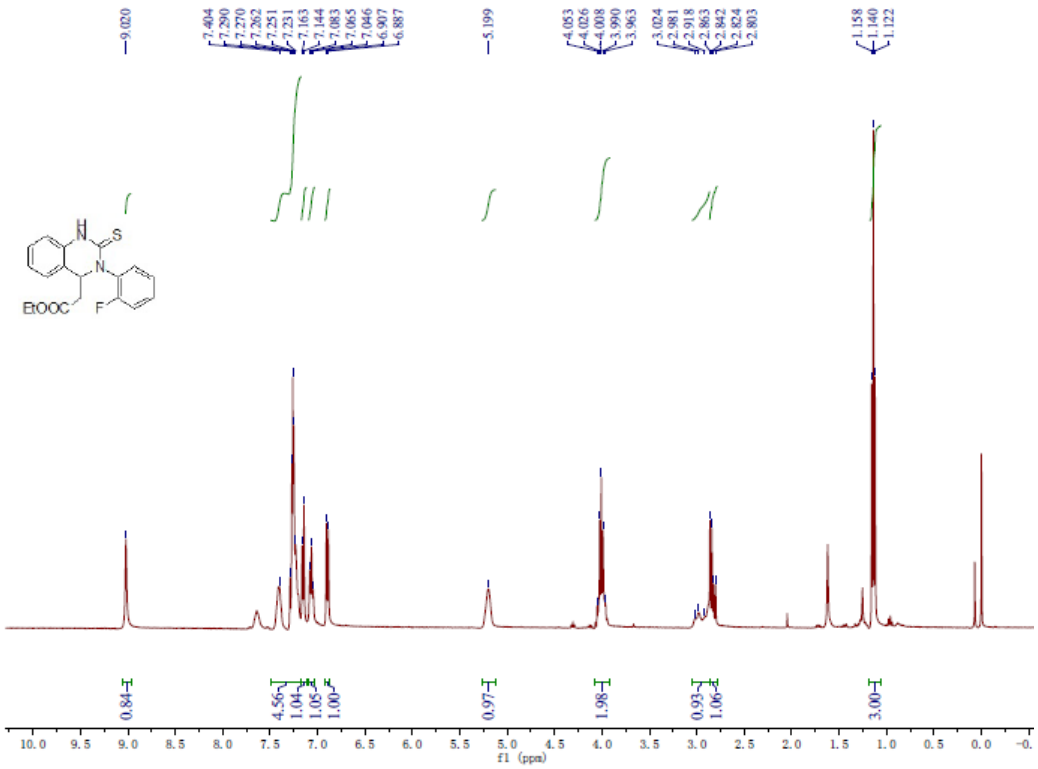
^{13}C NMR spectrum of compound **4i**



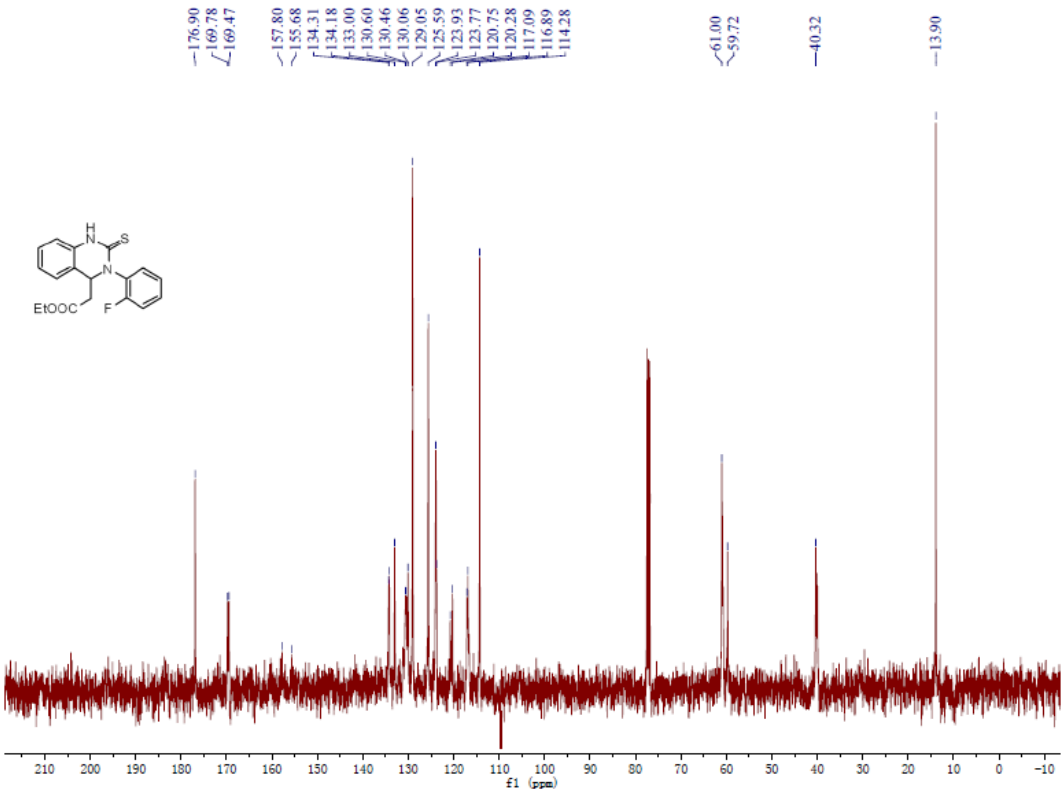
^{1}H NMR spectrum of compound **4j**



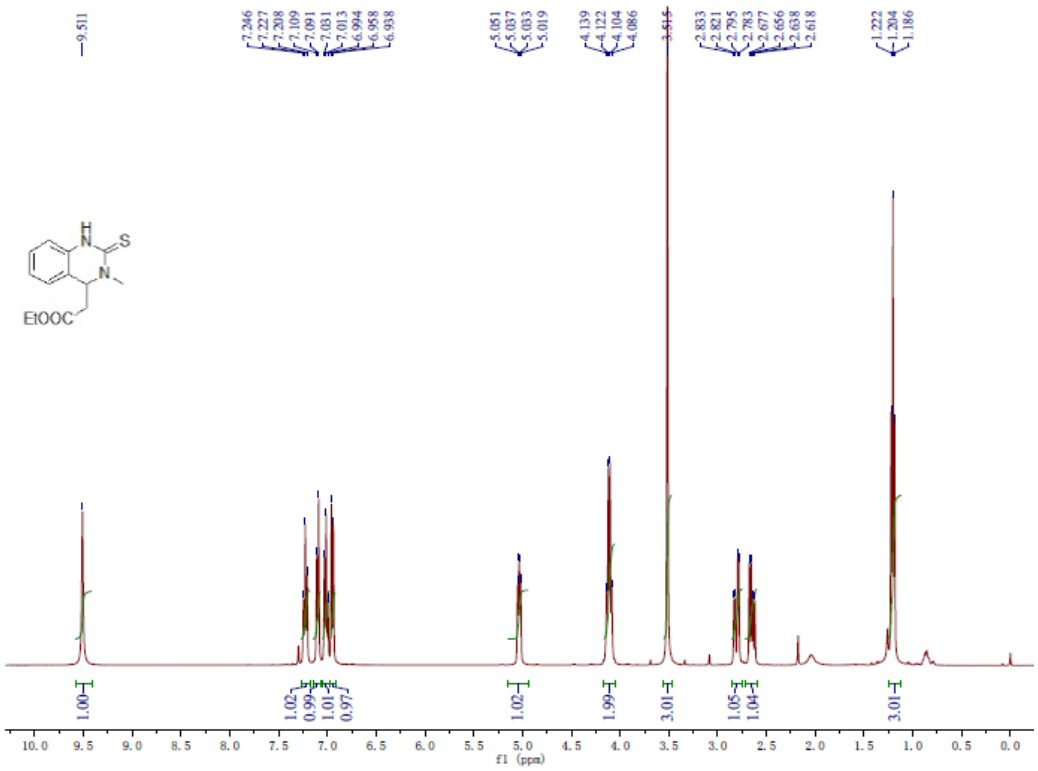
^{13}C NMR spectrum of compound **4j**



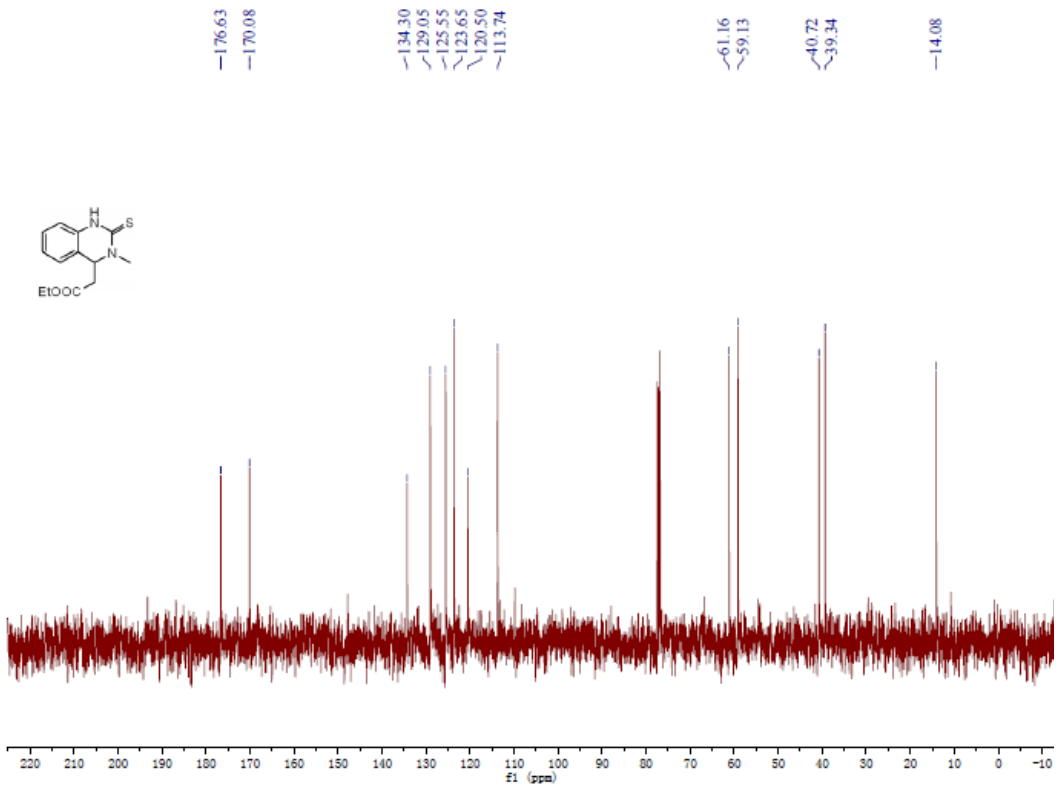
^{1}H NMR spectrum of compound **4k**



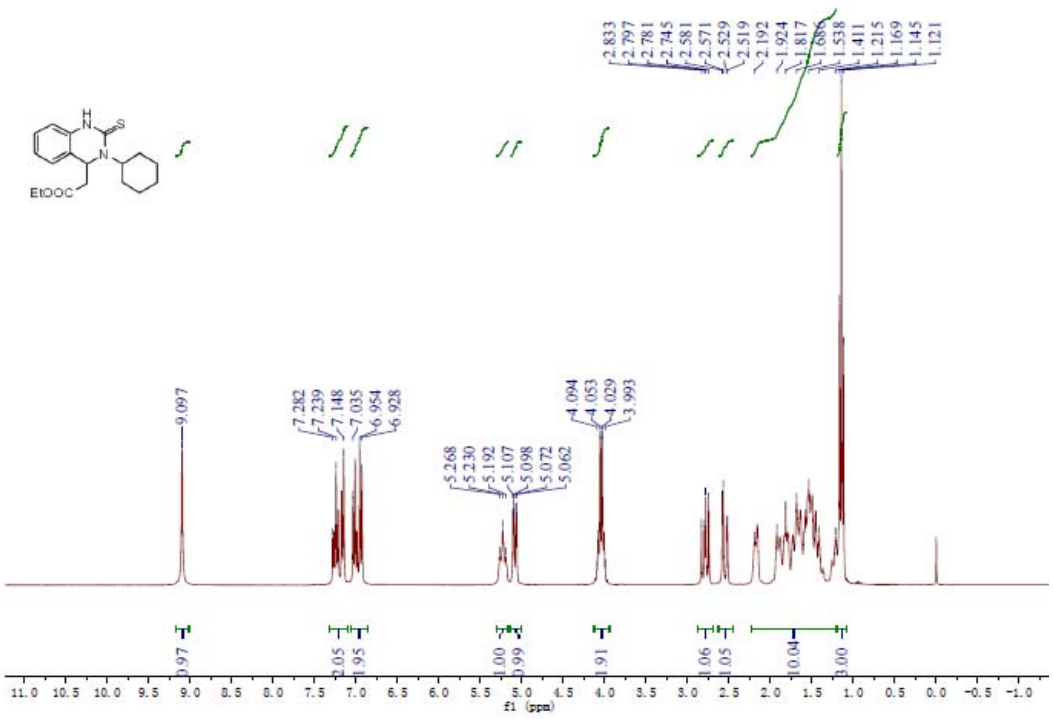
^{13}C NMR spectrum of compound **4k**



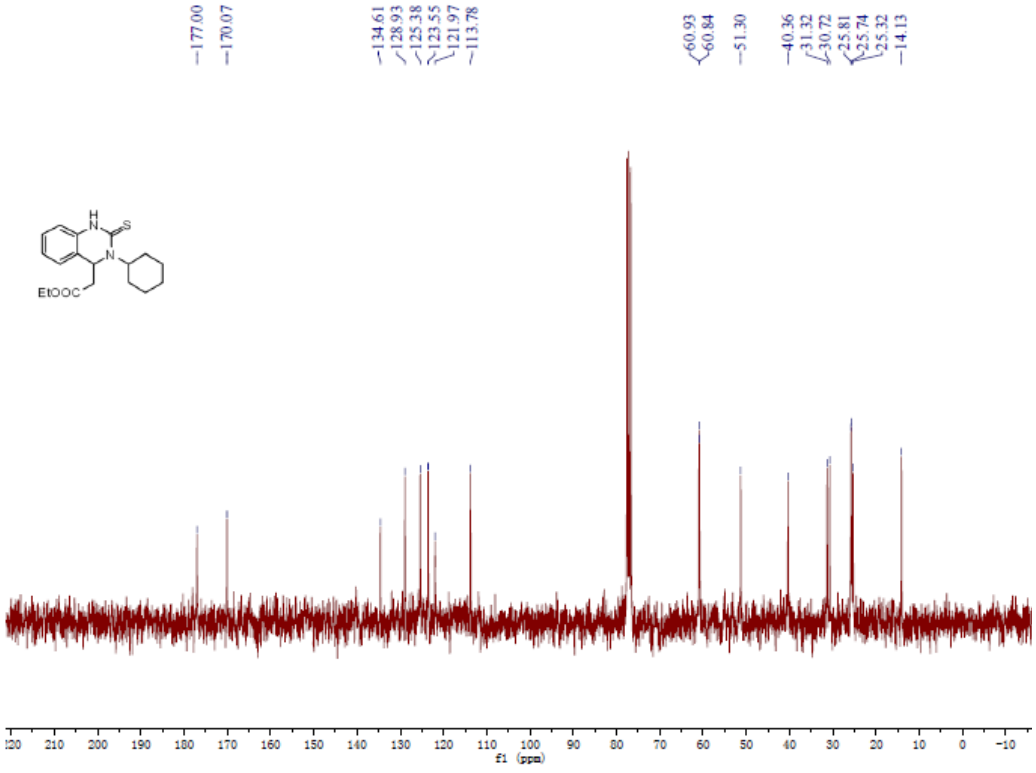
^{1}H NMR spectrum of compound **4l**



^{13}C NMR spectrum of compound **4l**



^{1}H NMR spectrum of compound **4m**



^{13}C NMR spectrum of compound **4m**