

Supporting Information for

Intramolecular C-O/C-S bond insertion of α -diazoesters for the synthesis of 2-aryl-4*H*-benzo[d][1,3]oxazine and 2-aryl-4*H*-benzo[d][1,3]thiazine derivatives

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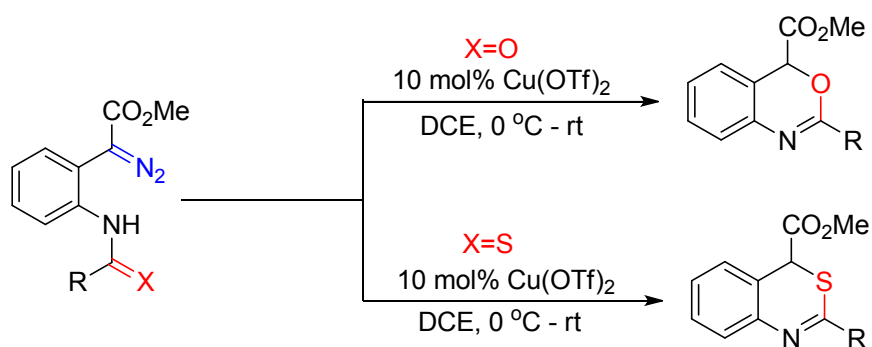


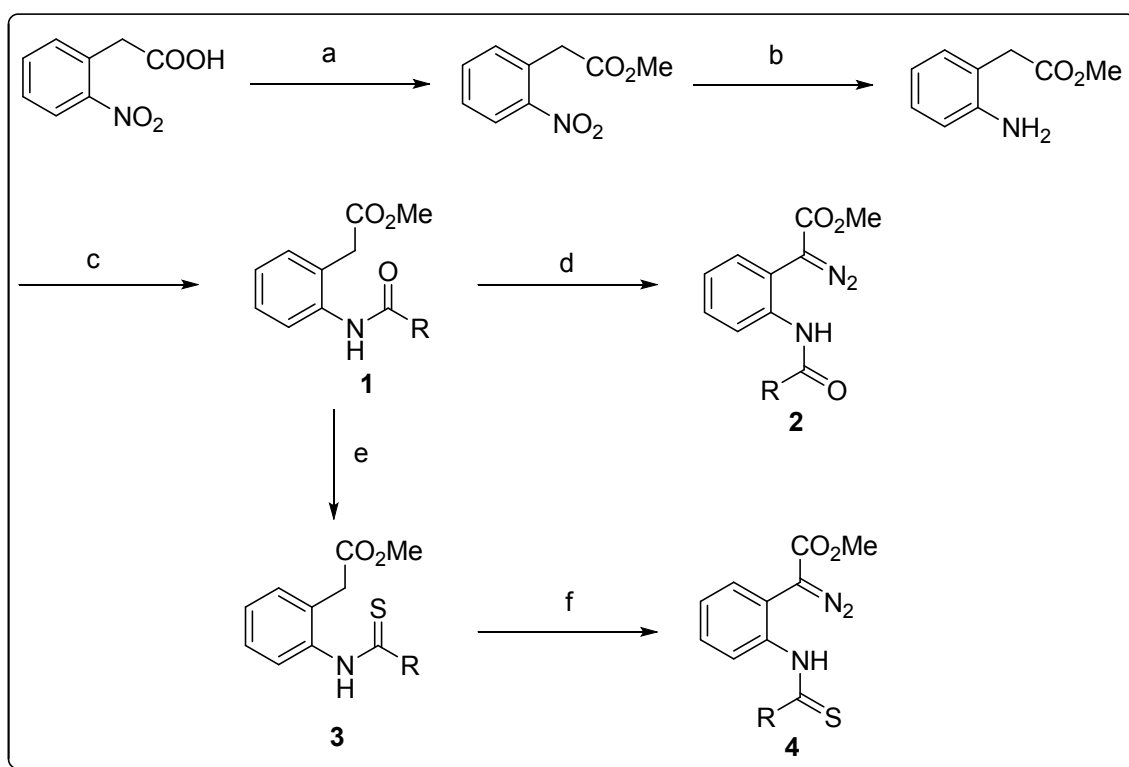
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1. General

IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimetres (cm⁻¹). ¹H NMR spectra were recorded at 500 MHz, 300 MHz and ¹³C NMR at 125 MHz, 75 MHz. For ¹H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and the coupling constants in Hz. For ¹³C NMR, CDCl₃ ($\delta = 77.27$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization. Melting points were measured on micro melting point apparatus. Commercially available amides, acid chlorides and Cu(OTf)₂ were used without further purification. dichloroethane were distilled from CaH under N₂ atmosphere.

Scheme 1. Synthetic procedure for **2** and **4**



Reagents & conditions: (a) MeOH, HCl, 0 °C to rt (b) H₂, 10% Pd/C, EtOAc, rt (c) RCOCl, Et₃N, DCM, rt (d) PMBSA, DBU, CH₃CN, 0 °C, rt, 90-95% yield (e) Lawesson's reagent, toluene, 70°C (f) PMBSA, DBU, CH₃CN, 0°C, rt, 85-90% yield

General procedure for the synthesis of methyl 2-(2-arylthioamidophenyl)acetate (3):

A solution of methyl 2-(2-aryl amidophenyl)acetate (**1**) (1 mmol) and Lawesson's reagent (1 mmol) in toluene (10 mL) was heated under reflux in inert atmosphere for 15 min. After removal of the solvent, the residue was purified by silica gel column chromatography using hexane-ethyl acetate to give the thioamidophenyl acetate (**3**).

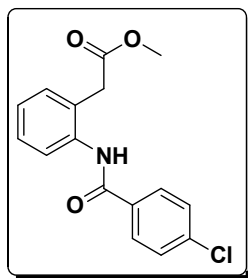
General procedure for the synthesis of diazo compound 2 or 4 (Scheme 1):

To a stirred solution of **1** or **3** (1 mmol) and *p*-methylbenzenesulfonylazide (1.5 mmol) in acetonitrile (5 mL) was added 1,8-Diazabicycloundec-7-ene (1.5 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 1 h, the reaction mixture was quenched with aqueous NH₄Cl, extracted with diethyl ether and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel to give the corresponding diazo compound **2** or **4**.

General procedure for the synthesis of benzoxazine or benzothiazine (5&6):

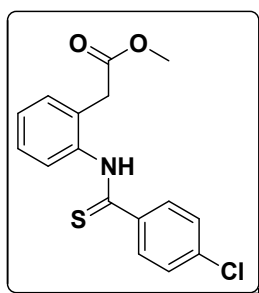
To a stirred solution of **2** or **4** (1 mmol) in dichloroethane (5 mL) was added Cu(OTf)₂ (10 mol %) at 0 °C. The resulting mixture was stirred at 25 °C under nitrogen atmosphere. The pale yellow mixture was stirred until it turned to pale red colour (10-30 min). The mixture was then quenched with saturated NaHCO₃ solution (1.0 mL) and extracted with dichloromethane (2-5 mL). The combined organic layers were washed with brine solution (3-5 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography (100–200 mesh) using ethyl acetate/hexane as eluent to afford the pure product.

Characterization data of products:**Methyl 2-(2-(4-chlorobenzamido)phenyl)acetate (1h):**



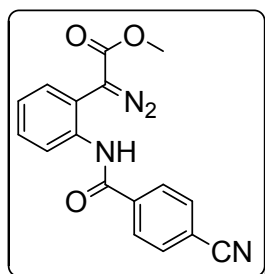
Solid, m.p.92-94 °C; ^1H NMR (500 MHz, CDCl_3): δ 9.80 (bs, 1H), 8.03-7.99 (m, 2H), 7.70 (d, $J= 8.6$ Hz, 1H), 7.50 (d, $J= 8.5$ Hz, 1H), 7.40-7.32 (m, 2H), 7.27-7.23 (m, 1H), 7.18-7.15 (m, 1H), 3.78 (s, 3H), 3.71 (s, 2H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 173.0, 171.3, 170.1, 163.8, 138.5, 137.6, 136.2, 132.4, 131.4, 130.4, 130.2, 128.5, 128.3, 128.1, 125.1, 125.0, 124.4, 52.9, 39.1 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 304.

Methyl 2-(2-(4-chlorophenylthioamido)phenyl)acetate (3d):



Solid, m.p.114-116 °C; ^1H NMR (300 MHz, CDCl_3): δ 10.47 (bs, 1H), 7.98-7.92 (m, 3H), 7.47-7.28 (m, 5H), 3.74 (s, 3H), 3.70 (s, 2H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 196.3, 172.7, 139.3, 138.1, 137.3, 130.6, 128.4, 127.9, 127.8, 127.3, 127.2, 52.9, 38.6 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 320.

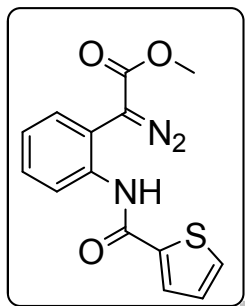
Methyl 2-(2-(4-cyanobenzamido)phenyl)-2-diazoacetate (2d):



Yellow Solid, m.p.112-114 °C; ^1H NMR (300 MHz, CDCl_3): δ 9.74 (bs, 1H), 8.07 (d, $J= 8.3$ Hz, 3H), 7.81 (d, $J= 8.4$ Hz, 3H), 7.32-7.25 (m, 2H), 3.92 (s, 3H) ppm; ^{13}C NMR (75 MHz,

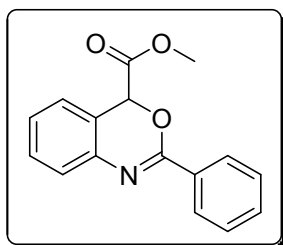
CDCl₃): δ 168.3, 153.9, 137.2, 131.6, 129.8, 128.3, 119.5, 118.1, 114.4, 74.4, 53.1 ppm; MS (ESI): m/z ([M+H]⁺): 321.

Methyl 2-diazo-2-(2-(thiophene-2-carboxamido)phenyl)acetate (2e):



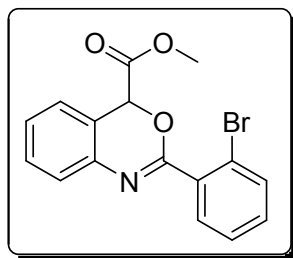
Yellow Solid, m.p. 108-110 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.41 (bs, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 4.7 Hz, 1H), 7.45 (d, J = 5.9 Hz, 1H), 7.28-7.20 (m, 2H), 7.14-7.09 (m, 2H), 3.93 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 173.6, 160.1, 139.8, 136.6, 130.8, 128.5, 128.4, 127.8, 125.2, 124.6, 52.7, 38.9 ppm; MS (ESI): m/z ([M+H]⁺): 302.

Methyl 2-phenyl-4H-benzo[d][1,3]oxazine-4-carboxylate (5a):



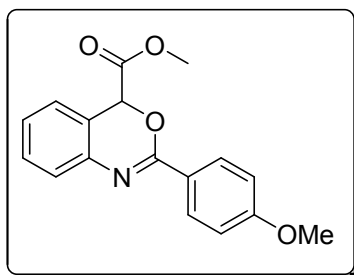
Solid, m.p. 104-106 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.01 (d, J = 7.9 Hz, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.48-7.19 (m, 6H), 4.32 (s, 1H), 3.59 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 168.5, 155.7, 137.8, 131.6, 131.1, 129.5, 127.8, 127.7, 126.3, 125.1, 124.8, 119.5, 74.2, 52.8 ppm; MS (ESI): m/z ([M+H]⁺): 268; HRMS (ESI): m/z calcd for C₁₆H₁₄O₃N: 268.09727; found: 268.09728.

Methyl 2-(2-bromophenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5b):



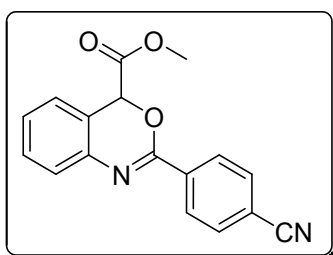
Solid, m.p.82-84 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.96 (d, $J= 9.3$ Hz, 1H), 7.70 (d, $J= 7.9$ Hz, 1H), 7.46-7.29 (m, 6H), 5.99 (s, 1H), 3.82 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 167.9, 155.1, 137.0, 133.0, 130.8, 129.4, 126.8, 126.6, 124.8, 124.8, 121.0, 118.8, 74.6, 53.1 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 346; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{NBr}$: 346.00825; found: 346.00827.

Methyl 2-(4-methoxyphenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5c):



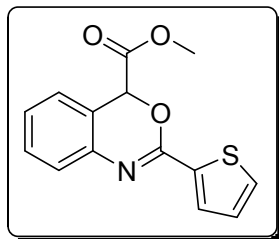
Solid, m.p.102-104 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.13 (d, $J= 8.9$ Hz, 2H), 7.37-7.17 (m, 4H), 6.95 (d, $J= 8.9$ Hz, 2H), 5.91 (s, 1H), 3.87 (s, 3H), 3.72 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 169.2, 166.0, 164.0, 155.4, 138.2, 130.6, 130.0, 126.7, 125.6, 125.1, 119.8, 115.4, 115.2, 74.3, 55.0, 52.8 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 298; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}$: 298.10731; found: 298.10750

Methyl 2-(4-cyanophenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5d):



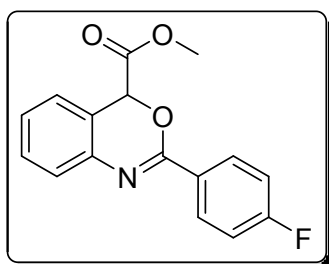
Solid, m.p.94-96 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.30 (d, $J= 8.3$ Hz, 2H), 7.75 (d, $J= 8.3$ Hz, 2H), 7.37-7.25 (m, 4H), 5.98 (s, 1H), 3.76 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 169.0, 154.4, 137.7, 136.2, 131.9, 130.1, 128.6, 127.6, 125.7, 119.8, 118.4, 114.6, 74.4, 52.9 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 293; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_2$: 293.0925; found: 293.0925

Methyl 2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5e):



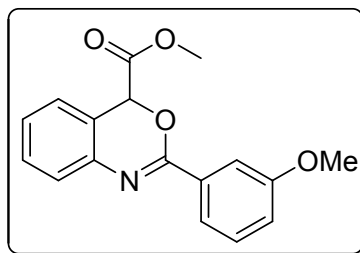
Solid, m.p.108-110 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.80 (d, $J= 3.7$ Hz, 1H), 7.52 (d, $J= 6.0$ Hz, 1H), 7.37-7.10 (m, 5H), 5.88 (s, 1H), 3.73 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 168.5, 152.2, 137.8, 135.7, 130.2, 130.1, 129.6, 127.3, 126.1, 125.2, 124.6, 119.4, 74.4, 53.0 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 274; HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NS}$: 274.0538; found: 274.0537.

Methyl 2-(4-fluorophenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5f):



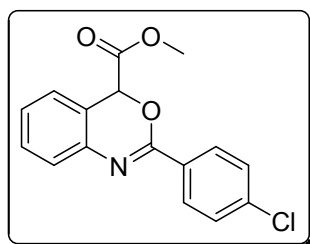
Solid, m.p.86-88 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.31-8.23 (m, 2H), 7.42-7.08 (m, 7H), 5.95 (s, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 169.2, 166.0, 164.0, 155.4, 138.2, 130.6, 130.0, 128.2, 126.7, 125.6, 125.1, 119.8, 115.4, 115.2, 74.3, 52.8 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 286; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{NF}$: 286.0877; found: 286.0877.

Methyl 2-(3-methoxyphenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5g):



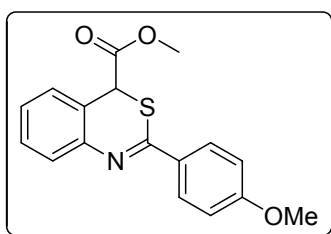
Semi Solid; ^1H NMR (500 MHz, CDCl_3): δ 7.79-7.70 (m, 2H), 7.42-7.20 (m, 5H), 7.09-7.05 (m, 1H), 5.95 (s, 1H), 3.90 (s, 3H), 3.74 (m, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 169.3, 159.4, 138.3, 133.4, 129.9, 129.2, 126.7, 125.5, 125.2, 120.8, 118.1, 112.7, 74.3, 55.4, 52.8 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 298; HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}$: 298.1070; found: 298.1072.

Methyl 2-(4-chlorophenyl)-4H-benzo[d][1,3]oxazine-4-carboxylate (5h):



Solid, m.p.72-74 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.25-8.17 (m, 2H), 7.42-7.13 (m, 6H), 5.95 (s, 1H), 3.75 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ 168.5, 154.8, 137.7, 137.3, 136.9, 130.2, 129.6, 129.2, 128.1, 126.5, 125.2, 124.9, 119.5, 74.3, 53.0 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 302; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{13}\text{ClNO}_3$: 302.0855; found: 302.0853.

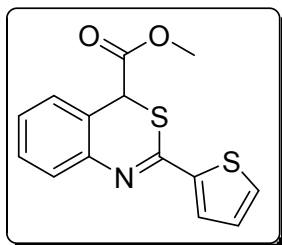
Methyl 2-(4-methoxyphenyl)-4H-benzo[d][1,3]thiazine-4-carboxylate (6b):



Solid, m.p.132-134 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.12 (d, J = 8.9 Hz, 2H), 7.54-7.43 (m, 2H), 7.32-7.22 (m, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.88 (s, 1H), 3.89 (s, 3H), 3.65 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 170.1, 162.6, 156.7, 143.6, 130.0, 129.4, 127.8, 127.3, 117.3,

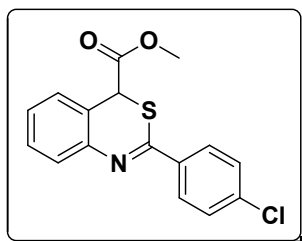
113.8, 55.4, 53.1, 44.2 ppm; MS (ESI): m/z ($[M+H]^+$): 314; HRMS (ESI): m/z calcd for $C_{17}H_{16}O_3NS$: 314.0846; found: 314.0847.

Methyl 2-(thiophen-2-yl)-4*H*-benzo[*d*][1,3]thiazine-4-carboxylate (6c):



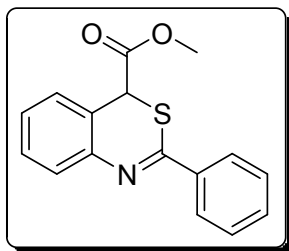
Solid, m.p.124-126 °C; 1H NMR (300 MHz, $CDCl_3$): δ 7.83-7.87 (m, 1H), 7.60-7.10 (m, 9H), 5.91 (s, 1H), 3.76 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 152.2, 137.8, 135.7, 130.5, 130.2, 130.1, 129.6, 129.1, 127.5, 127.3, 126.1, 125.2, 124.6, 119.4, 74.4, 53.0 ppm; MS (ESI): m/z ($[M+H]^+$): 290; HRMS (ESI): m/z calcd for $C_{14}H_{12}O_2NS_2$: 290.0306; found: 290.0306.

Methyl 2-(4-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazine-4-carboxylate (6d):



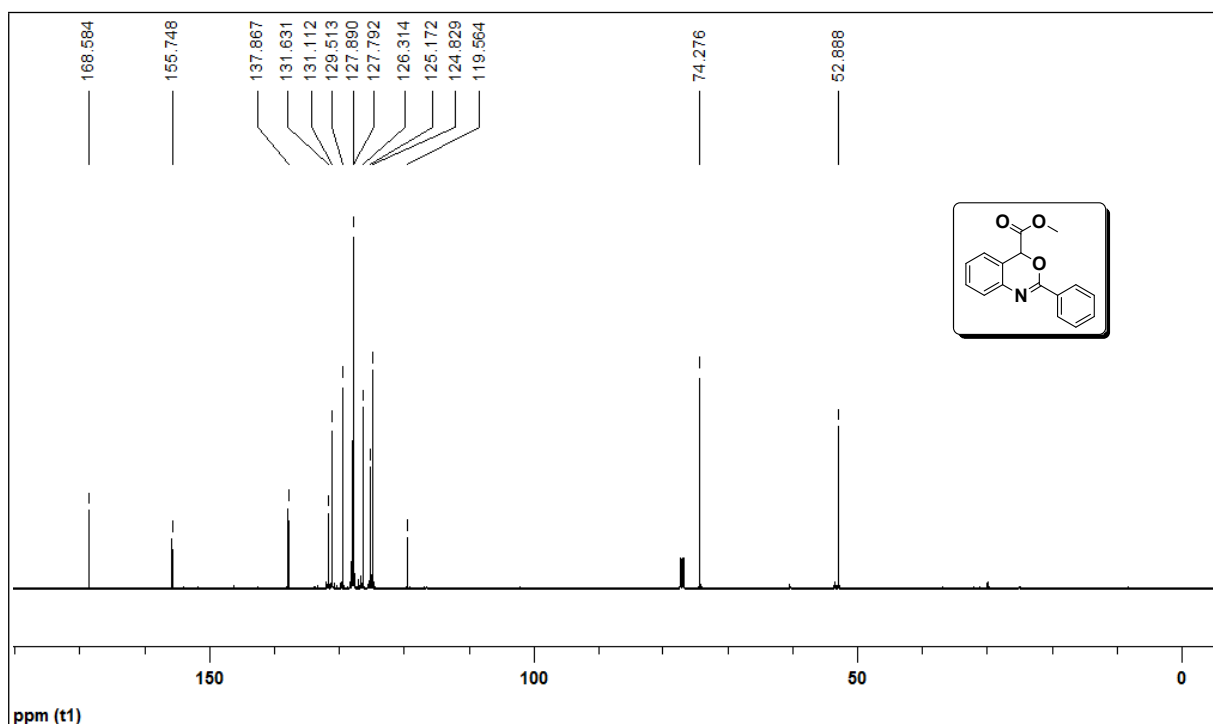
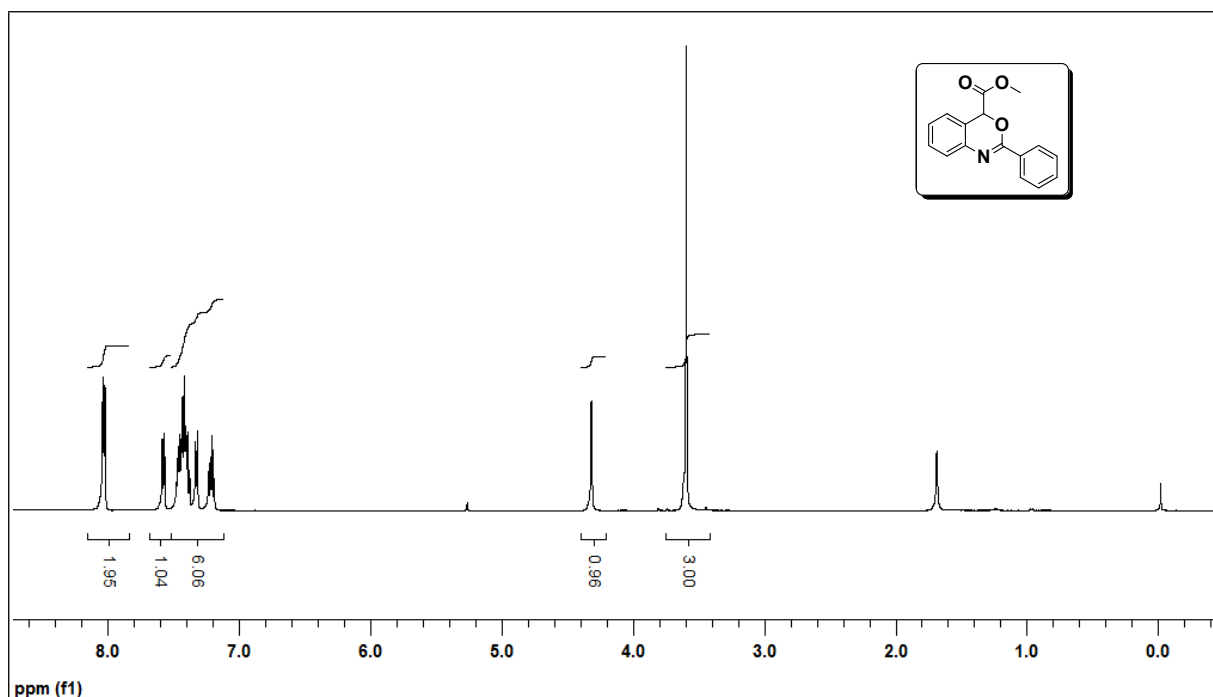
Solid, m.p.78-80 °C; 1H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, $J= 8.6$ Hz, 2H), 7.34-7.10 (m, 3H), 6.89 (d, $J= 8.7$ Hz, 2H), 5.96 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 166.4, 164.5, 155.5, 138.5, 130.5, 130.3, 126.3, 125.6, 125.3, 119.8, 115.5, 115.3, 74.5, 55.3, 52.7 ppm; MS (ESI): m/z ($[M+H]^+$): 318; HRMS (ESI): m/z calcd for $C_{16}H_{13}ClNO_2S$: 318.0357; found: 318.0349.

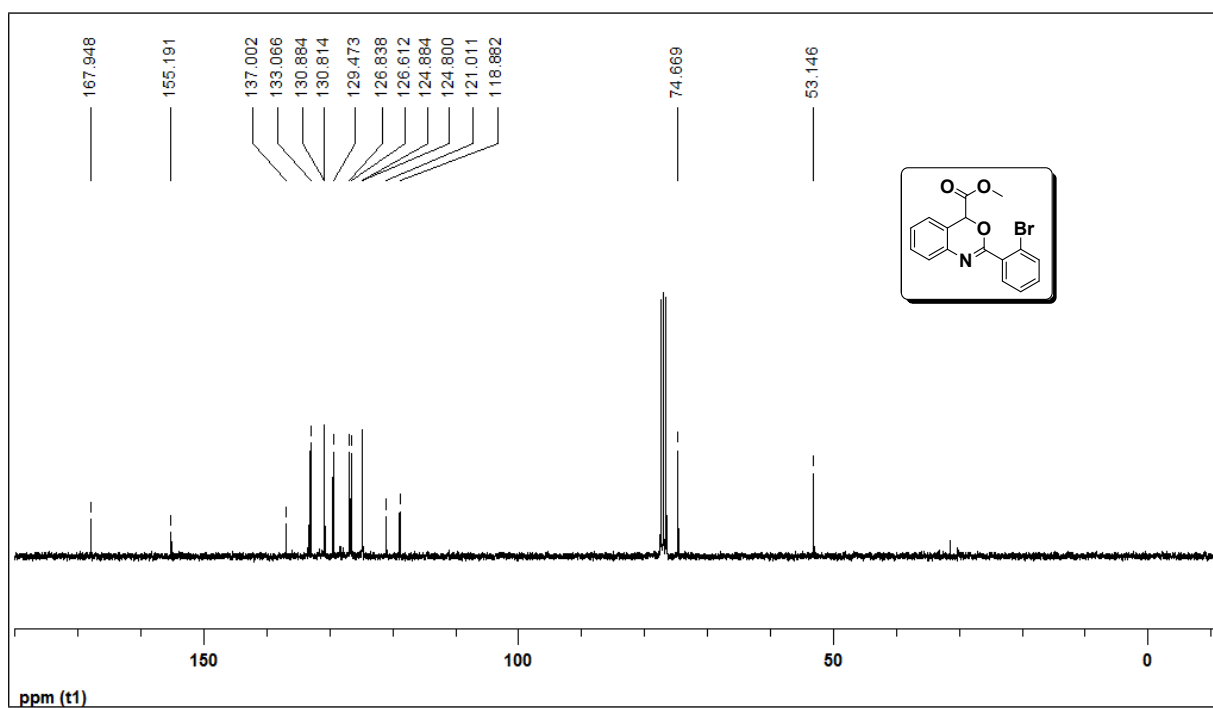
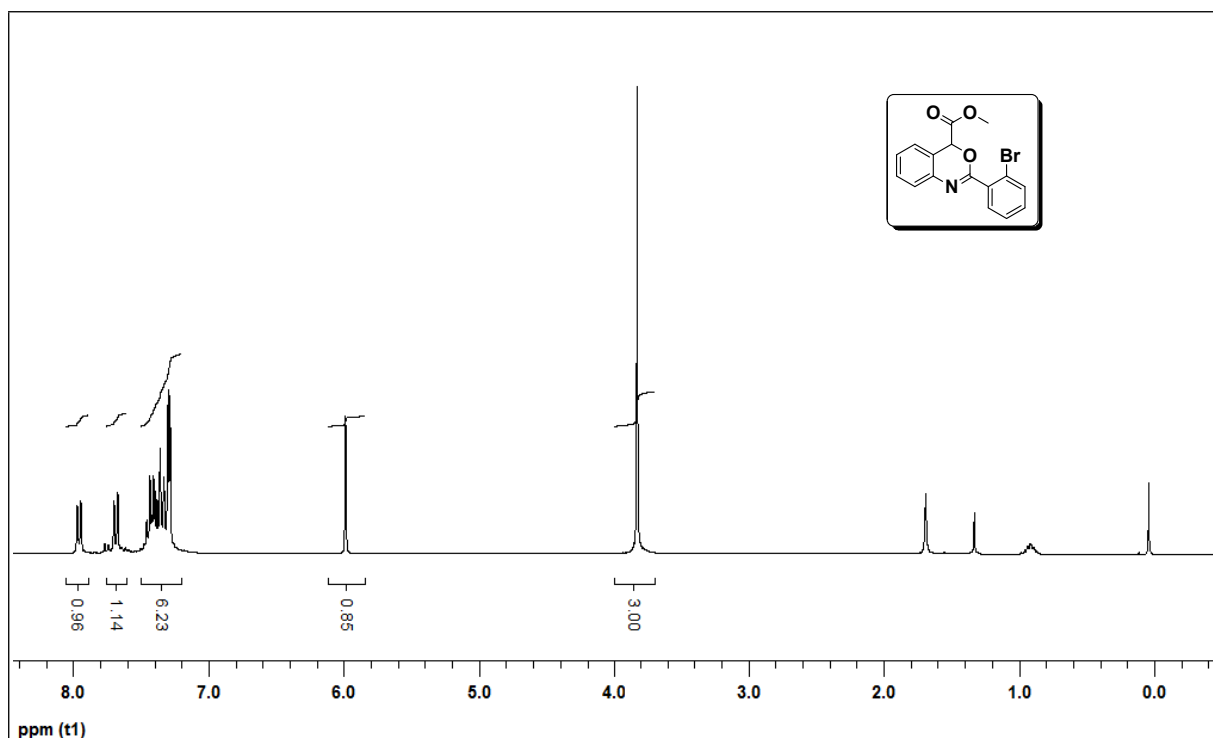
Methyl 2-phenyl-4*H*-benzo[*d*][1,3]thiazine-4-carboxylate (6a):

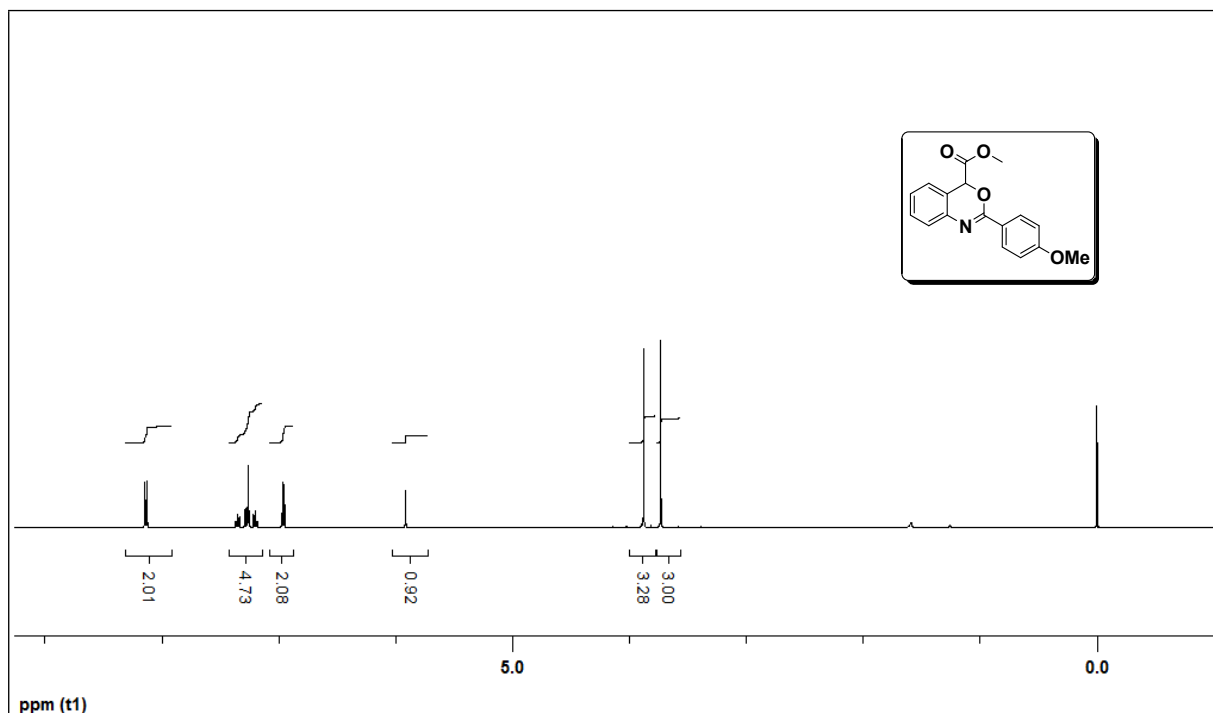


Solid, m.p.104-106 °C; ^1H NMR (500 MHz, CDCl_3): δ 8.07 (d, $J= 7.9$ Hz, 2H), 7.49-7.35 (m, 5H), 7.26-7.17 (m, 2H), 4.82 (s, 1H), 3.58 (s, 3H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ 168.5, 152.2, 137.8, 135.7, 130.2, 130.1, 129.6, 127.3, 126.1, 125.2, 124.6, 119.4, 74.4, 53.0 ppm; MS (ESI): m/z ($[\text{M}+\text{H}]^+$): 284; HRMS (ESI): m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{NS}$: 284.0744; found: 284.0745.

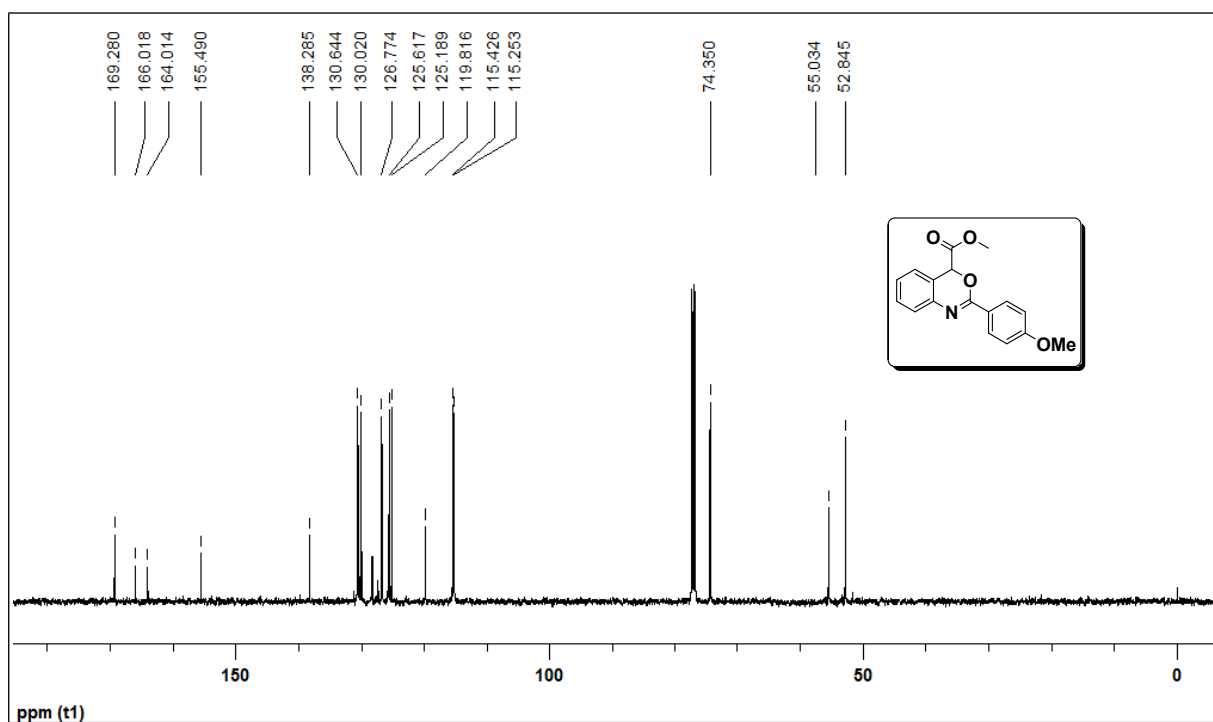
Copies of ^1H and ^{13}C NMR spectra:



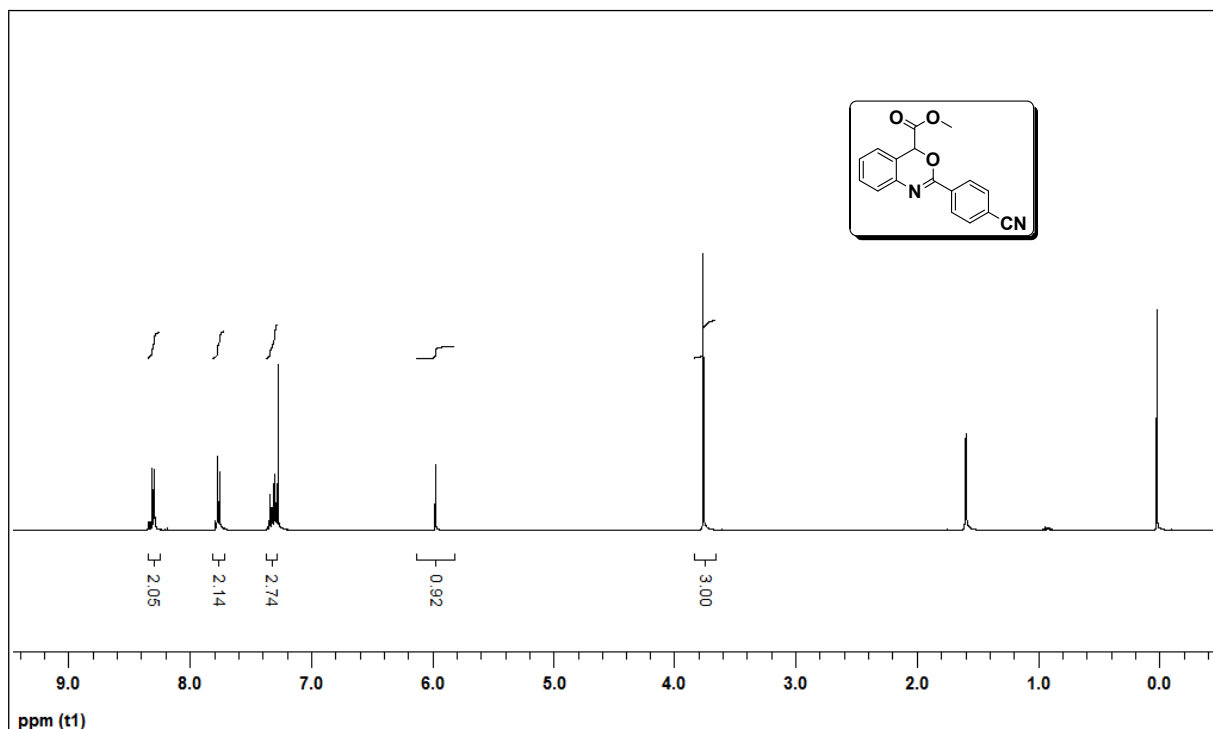




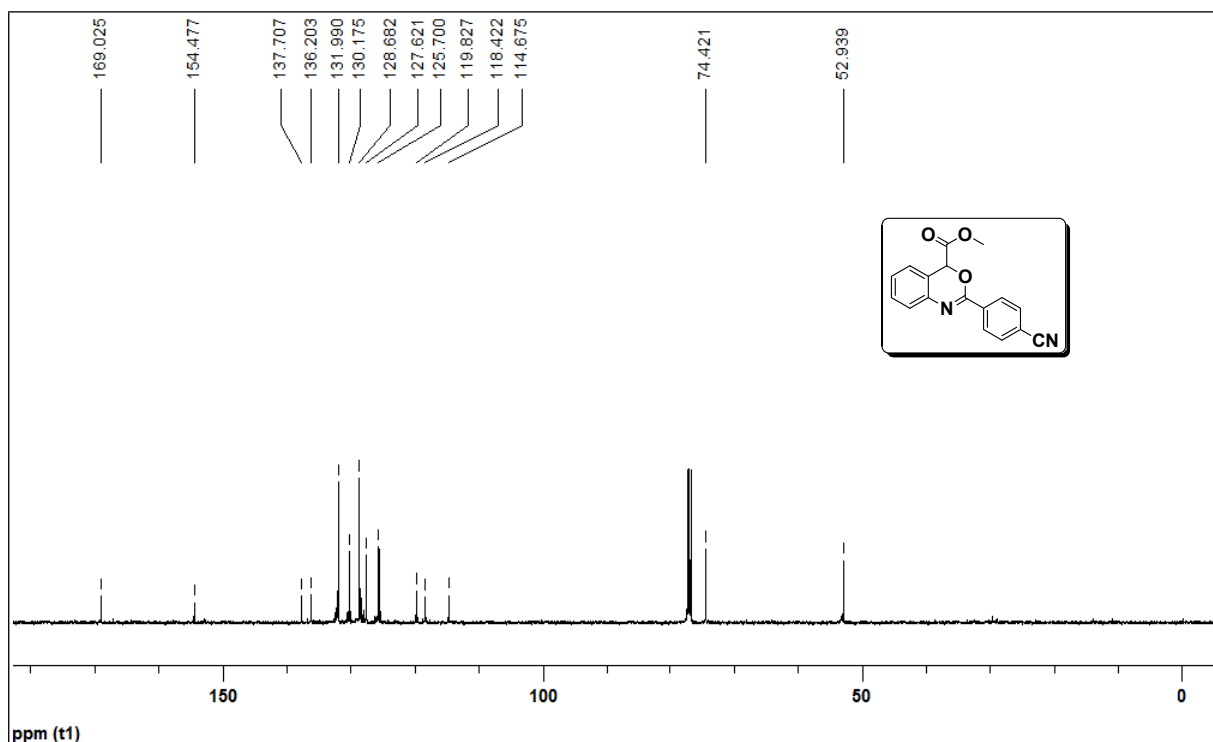
¹H NMR (500 MHz, CDCl₃) spectrum of compound 5c



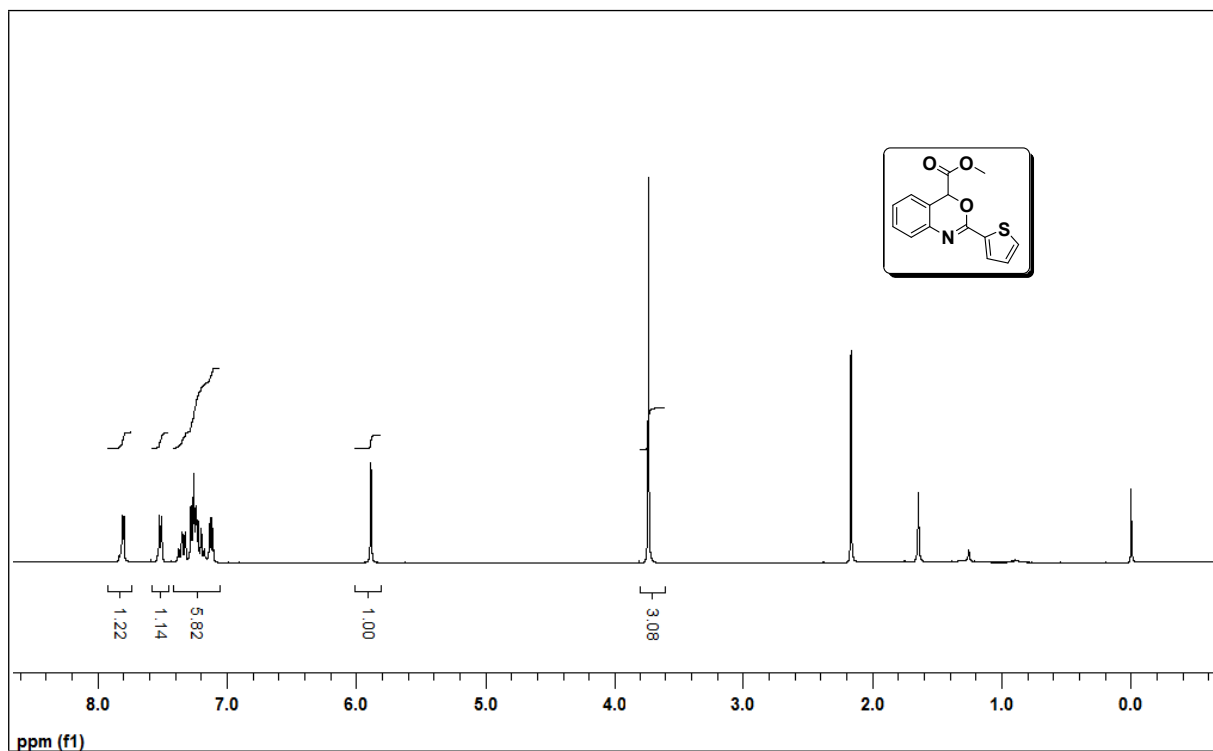
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 5c



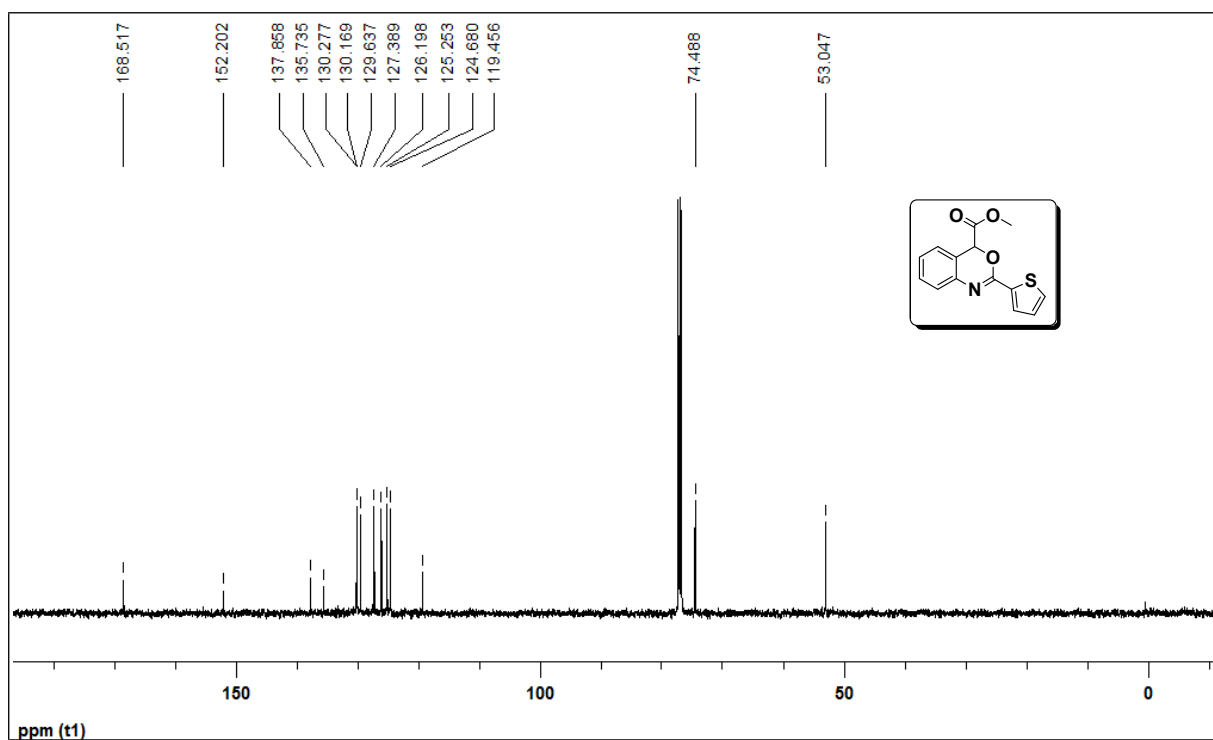
¹H NMR (500 MHz, CDCl₃) spectrum of compound 5d



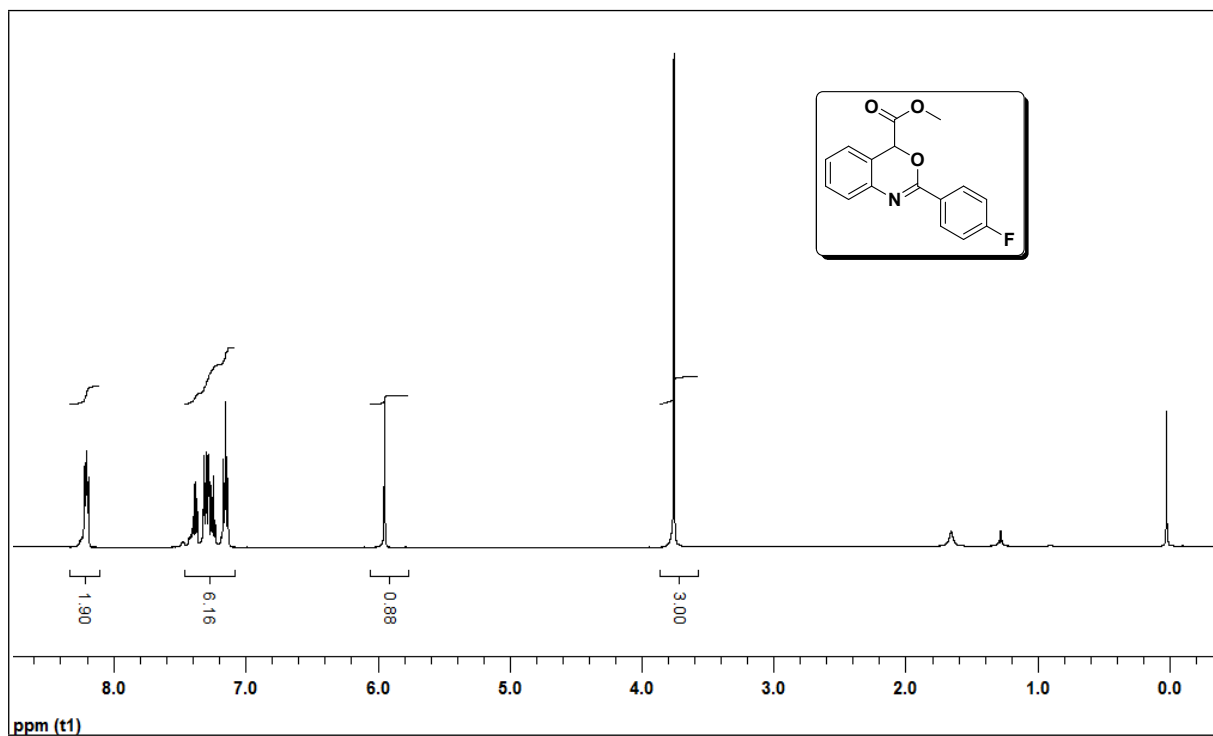
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 5d



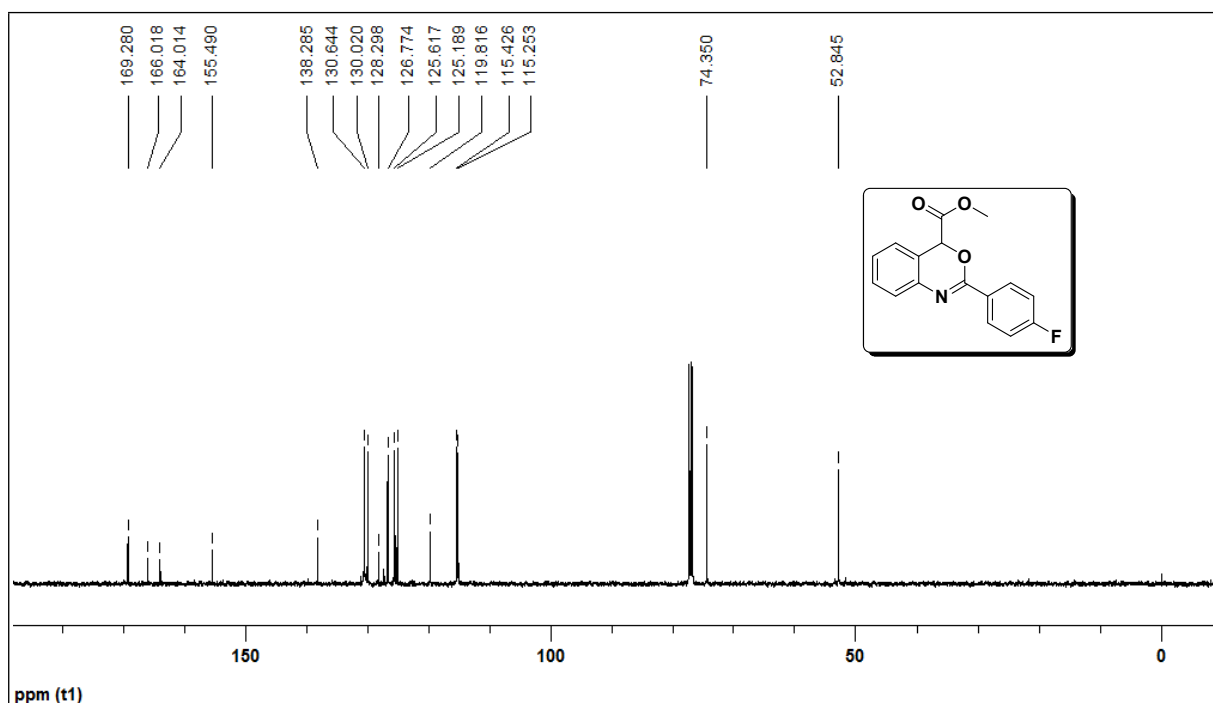
$^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of compound 5e



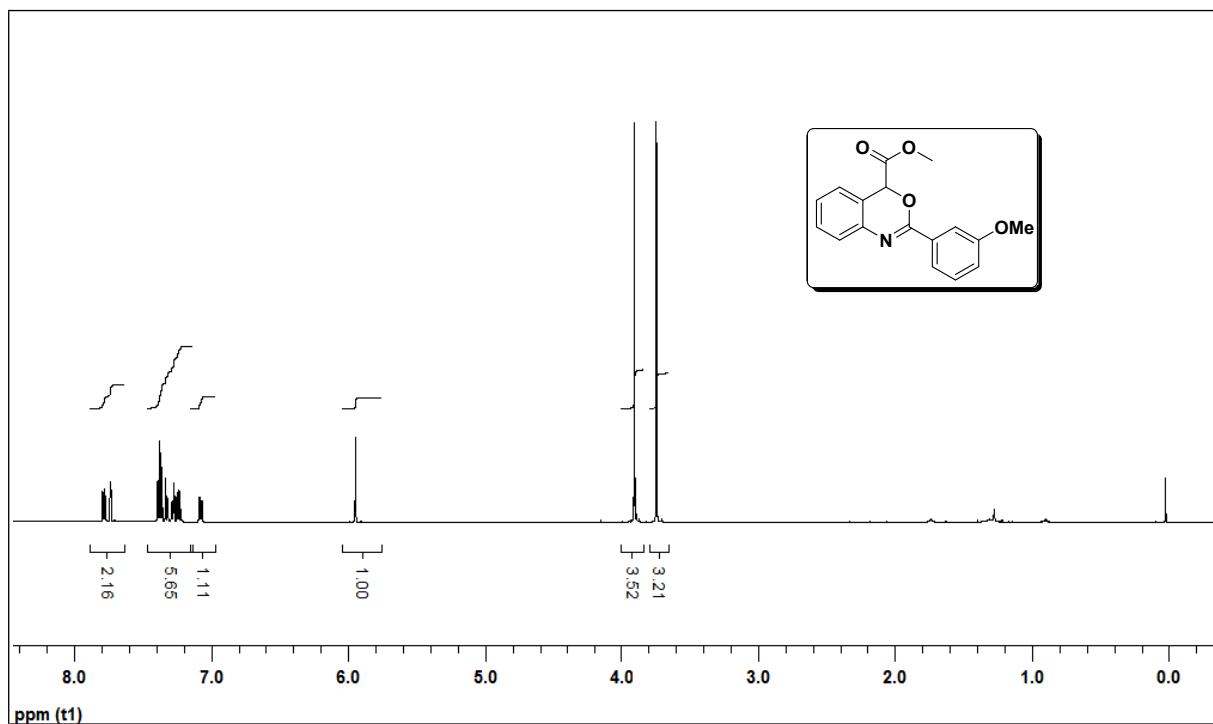
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) spectrum of compound 5e



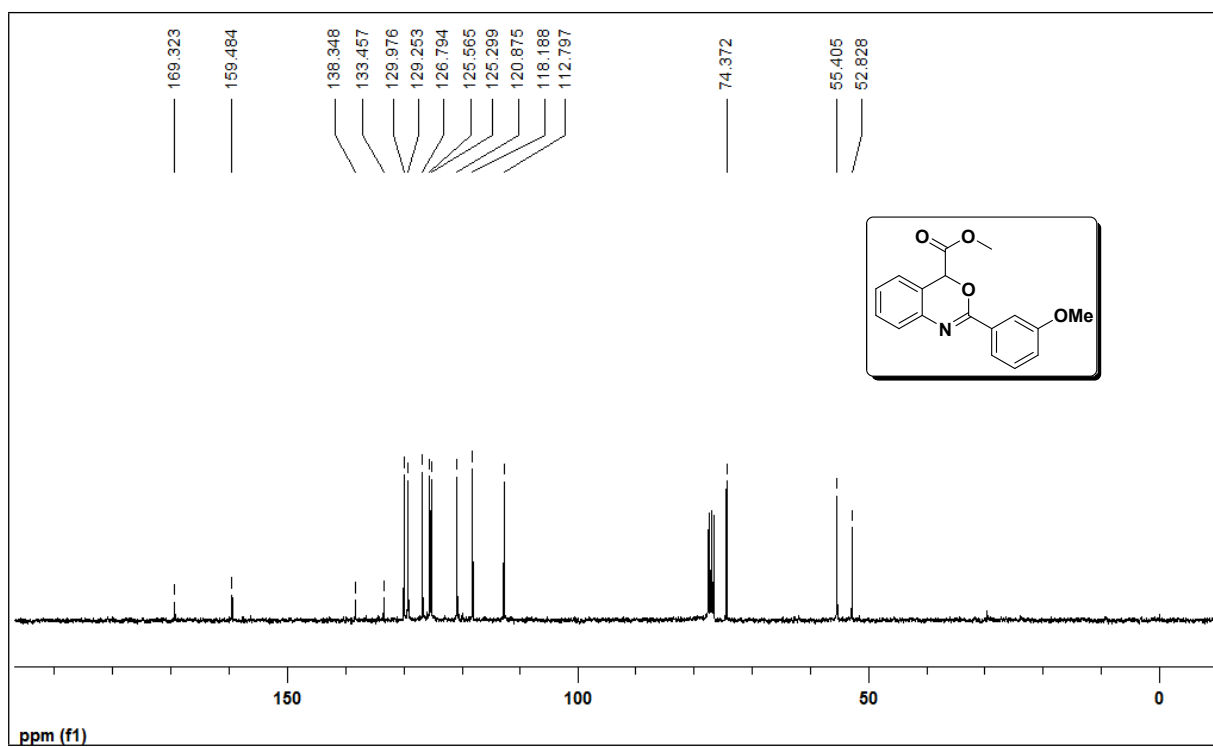
¹H NMR (500 MHz, CDCl₃) spectrum of compound 5f



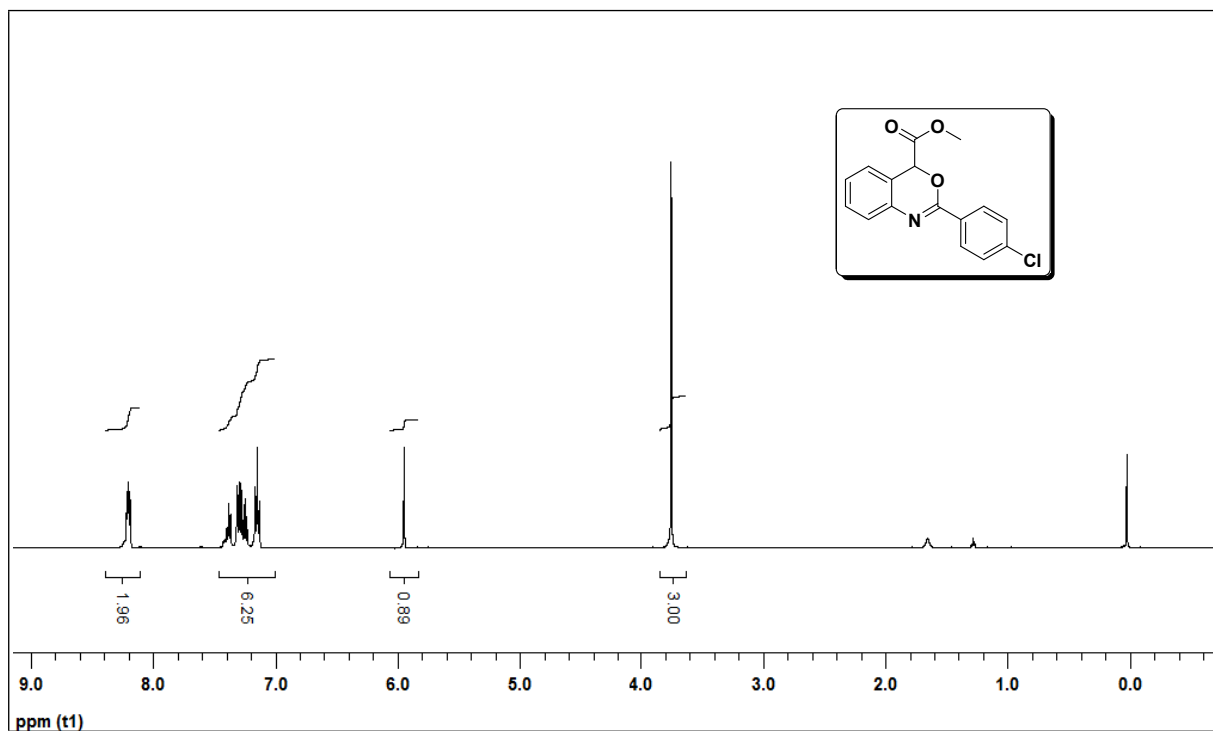
¹³C NMR (125 MHz, CDCl₃) spectrum of compound 5f



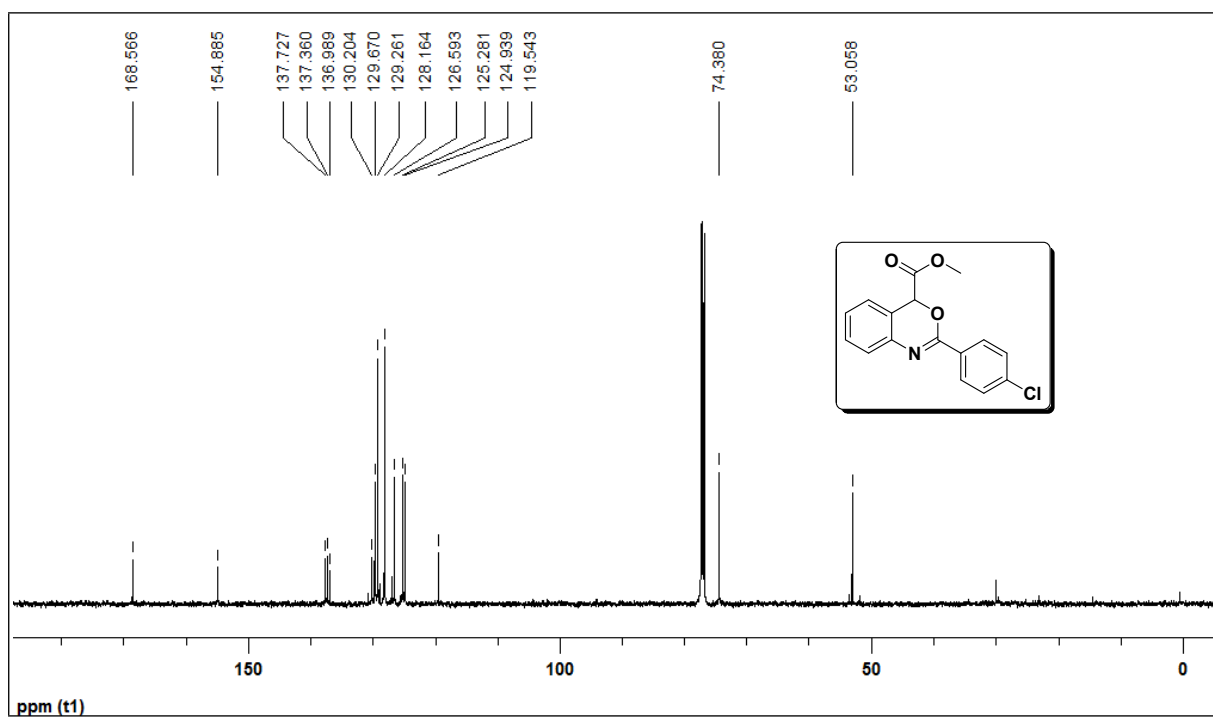
¹H NMR (500 MHz, CDCl₃) spectrum of compound 5g



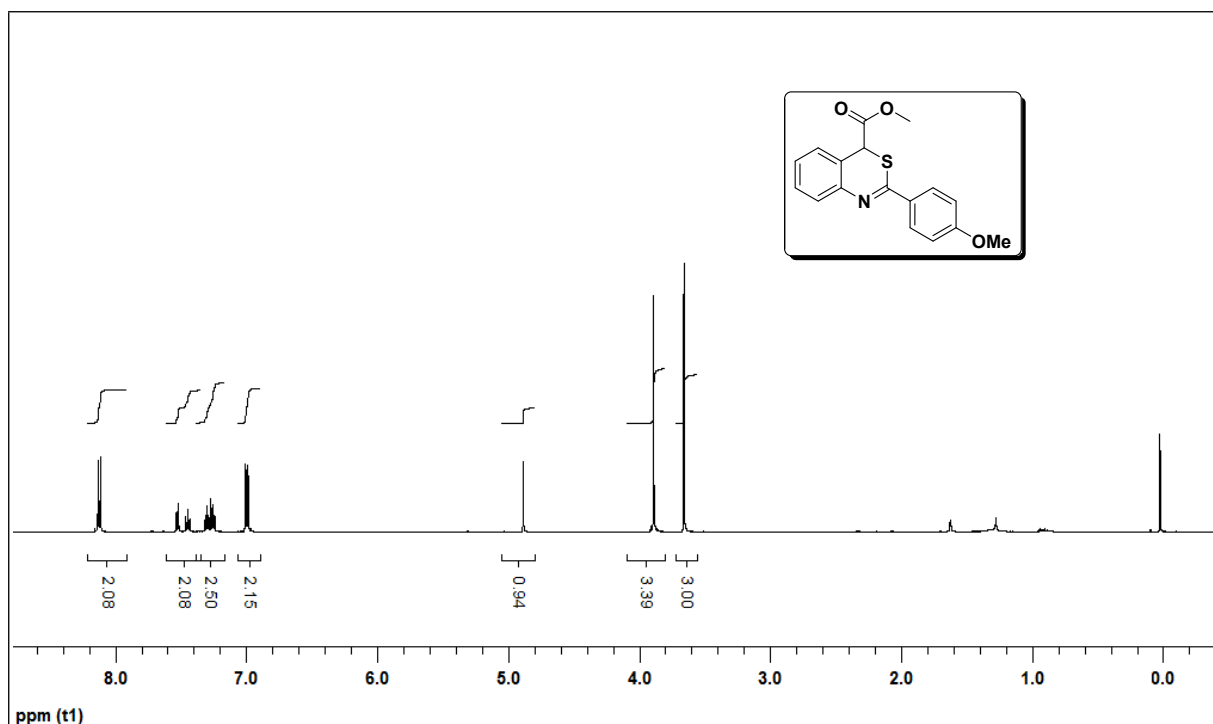
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 5g



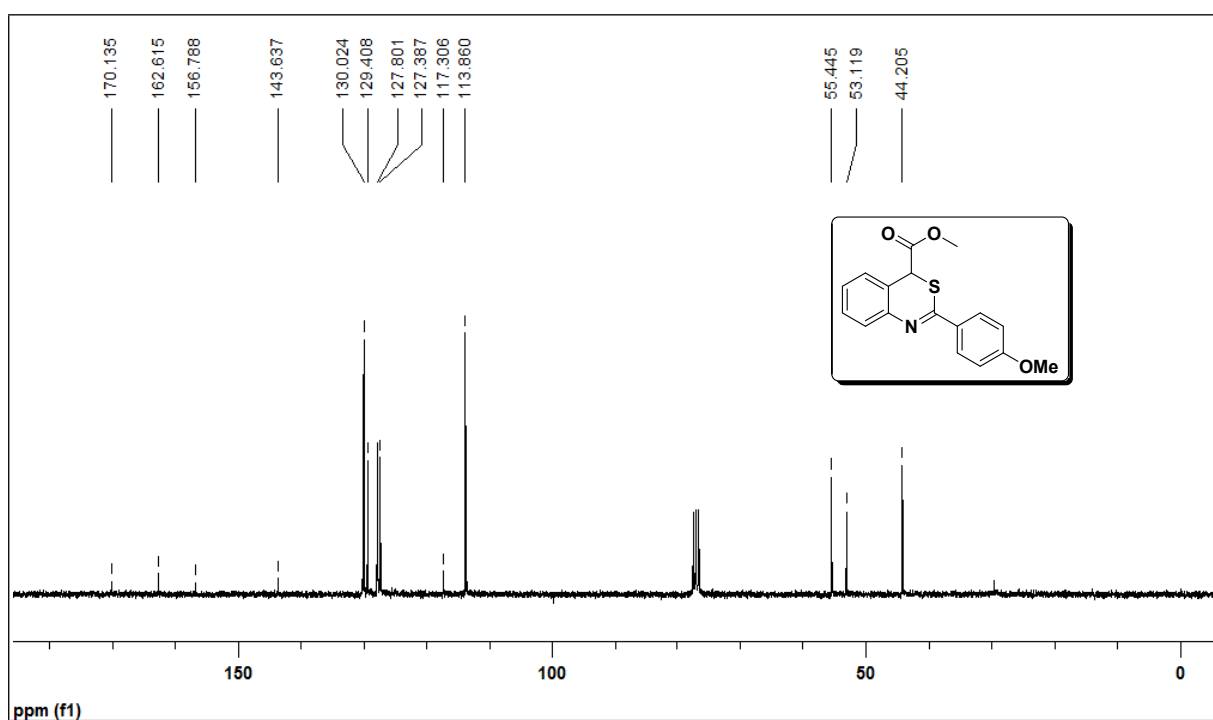
¹H NMR (300 MHz, CDCl₃) spectrum of compound 5h



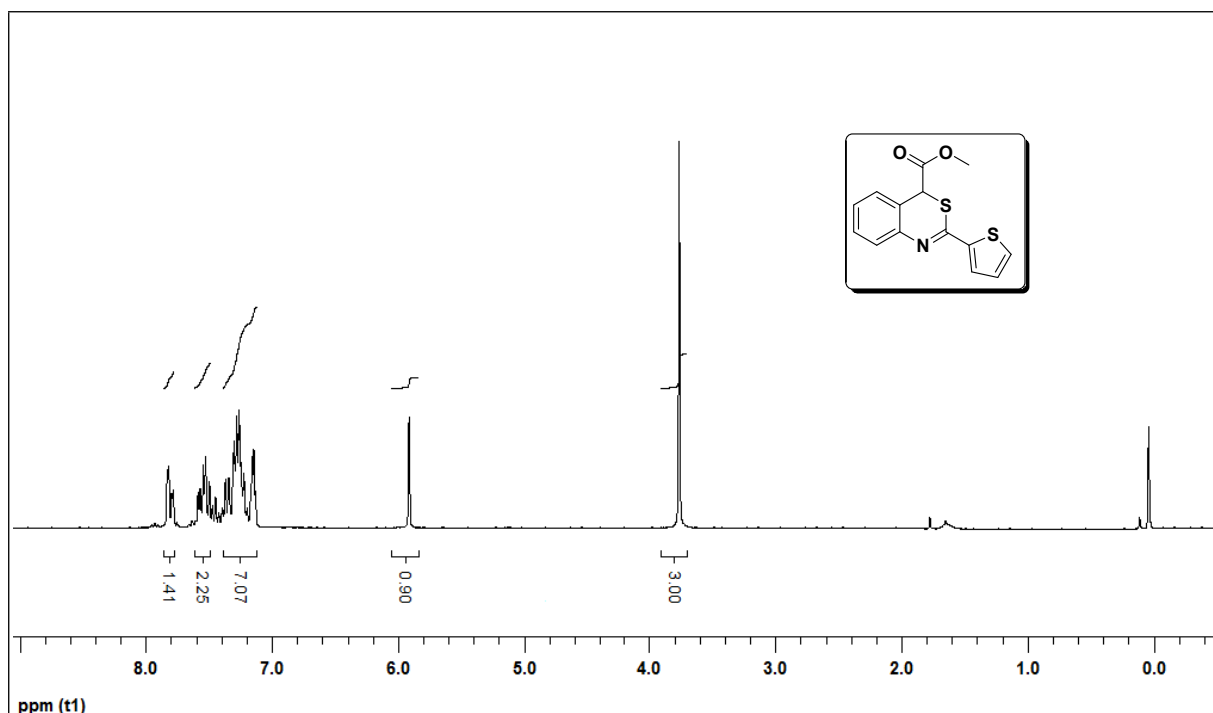
¹³C NMR (125 MHz, CDCl₃) spectrum of compound 5h



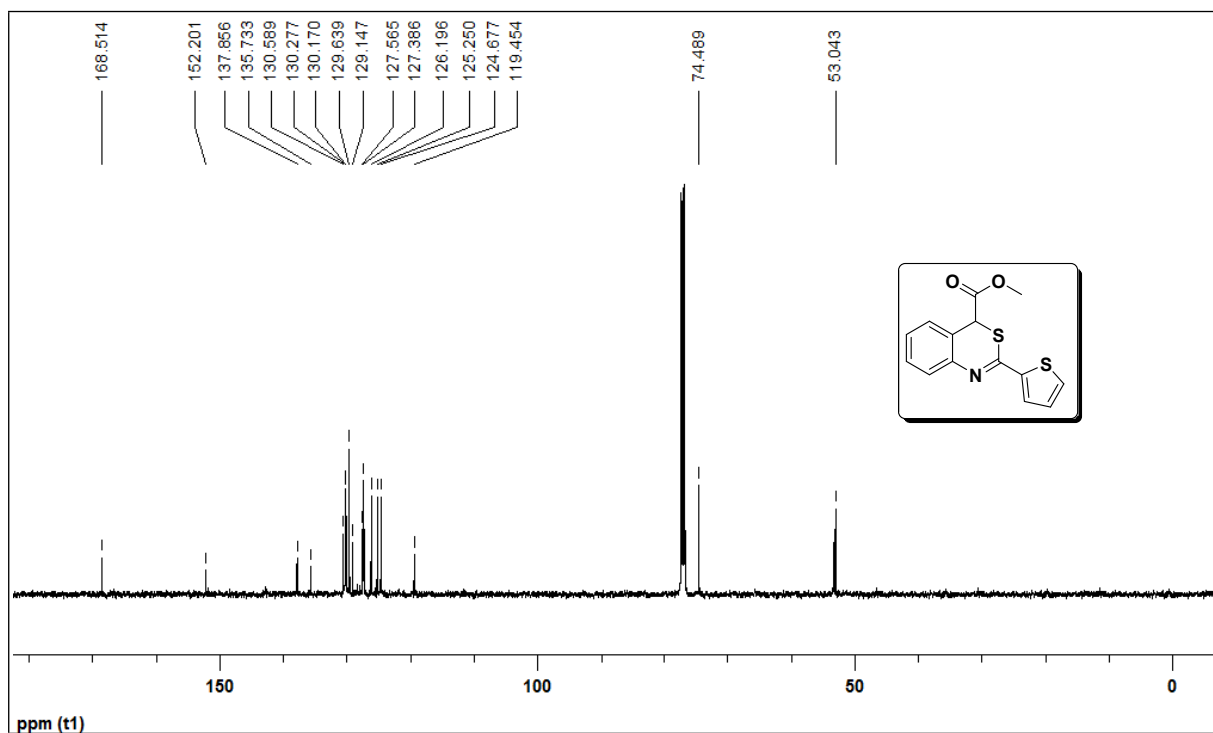
¹H NMR (500 MHz, CDCl₃) spectrum of compound 6b



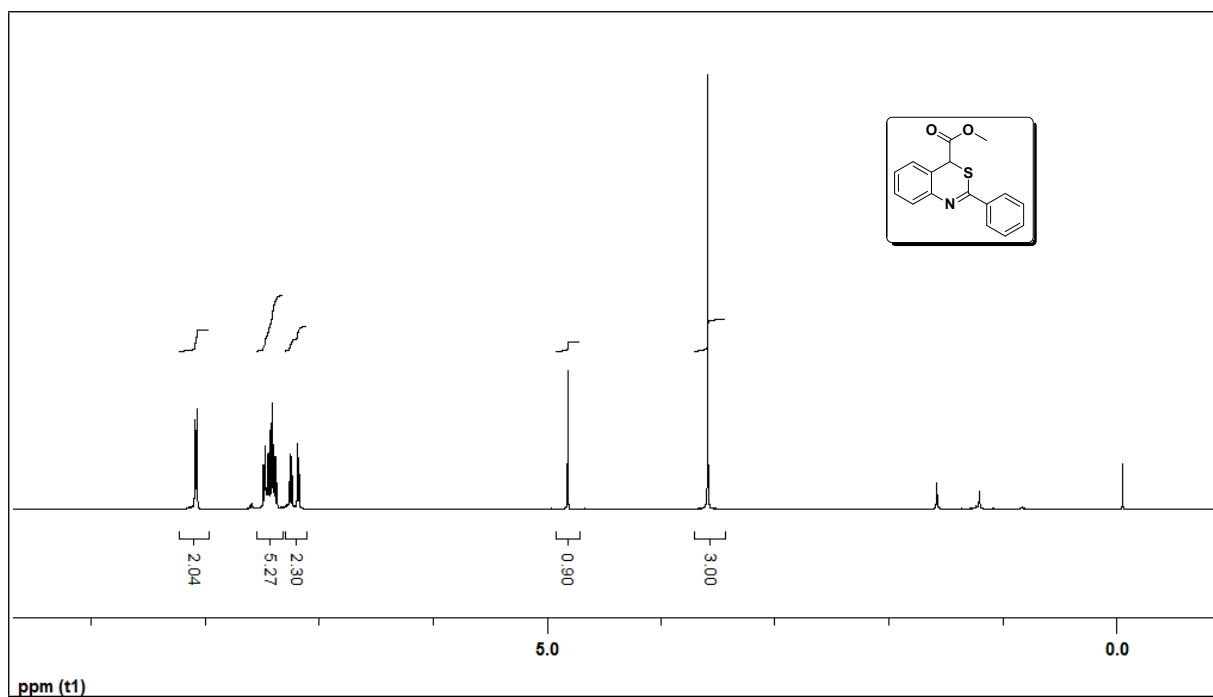
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 6b



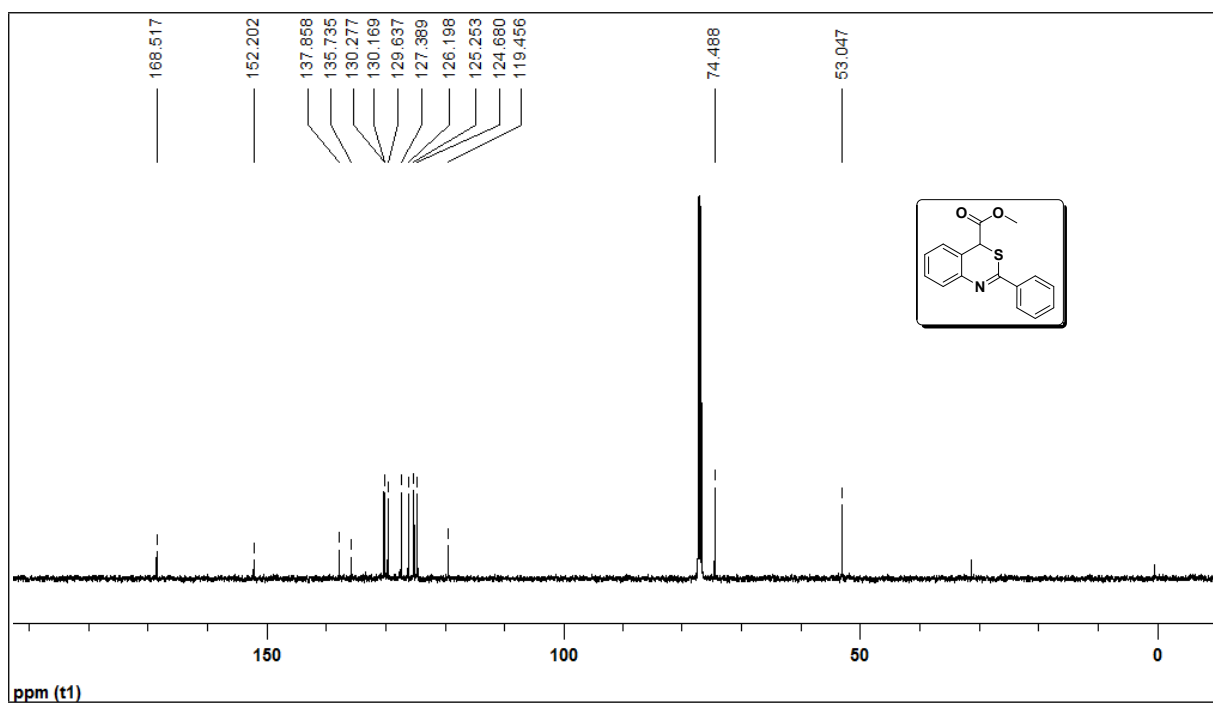
¹H NMR (300 MHz, CDCl₃) spectrum of compound 6c



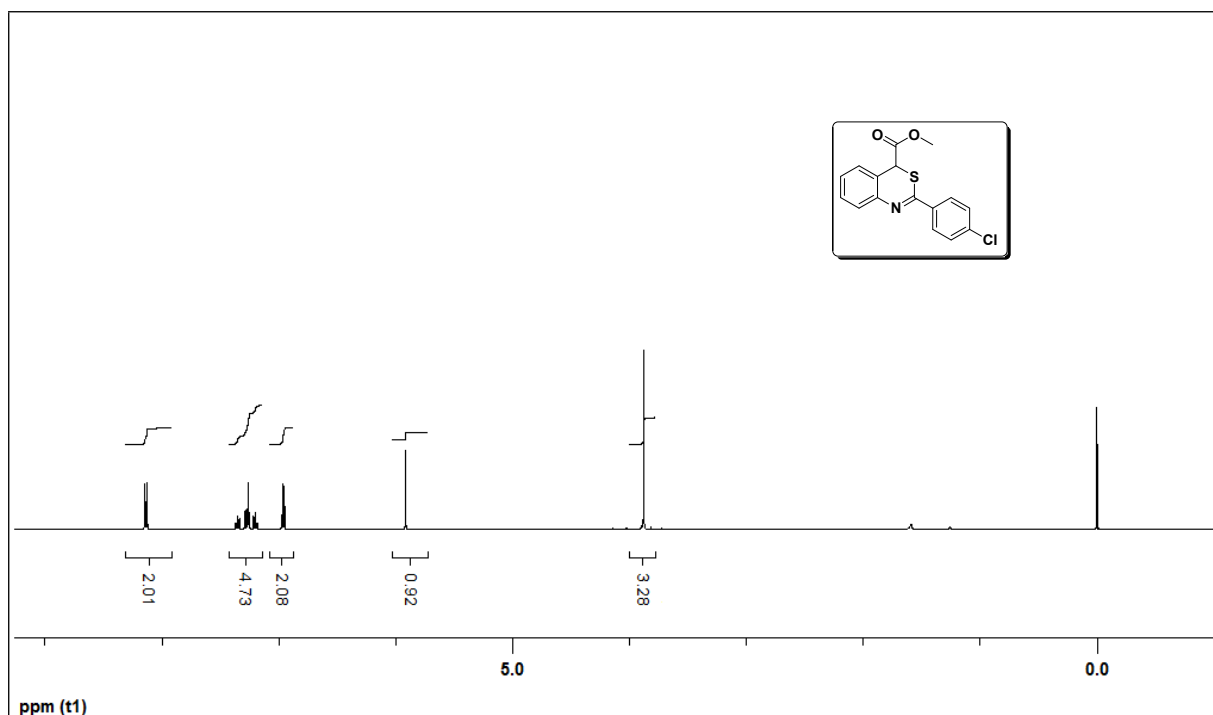
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 6c



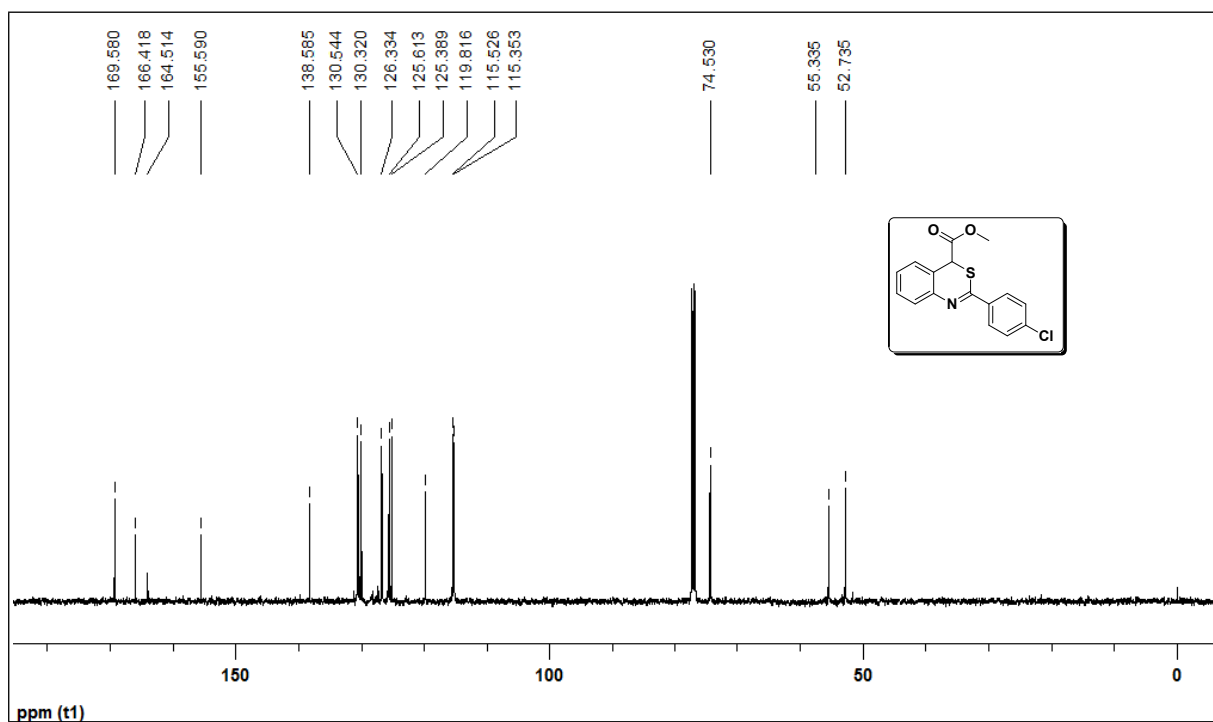
¹H NMR (500 MHz, CDCl₃) spectrum of compound 6a



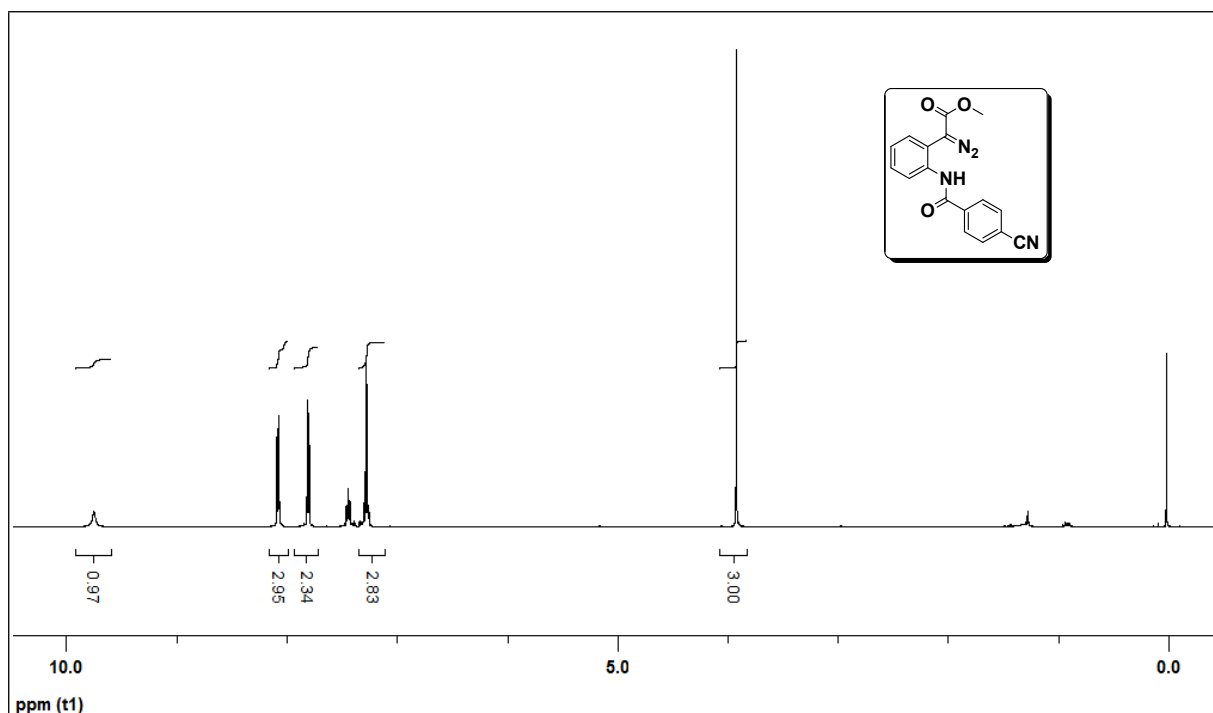
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 6a



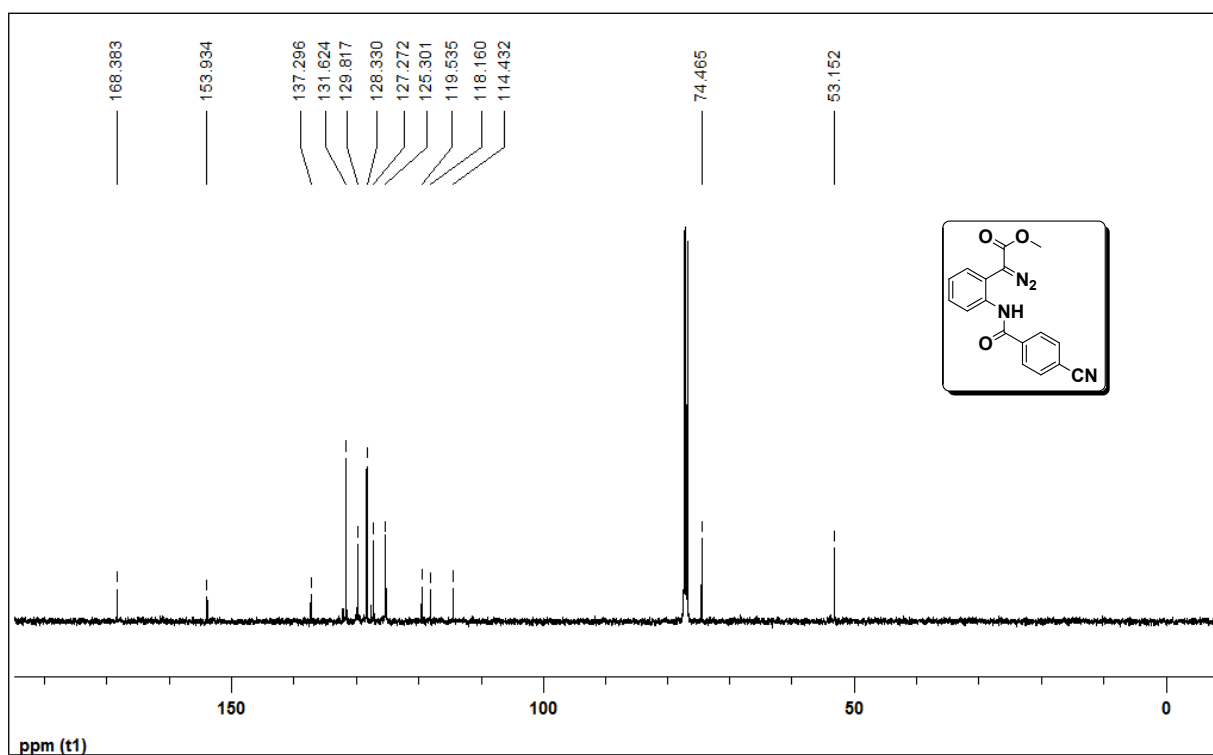
¹H NMR (500 MHz, CDCl₃) spectrum of compound 6d



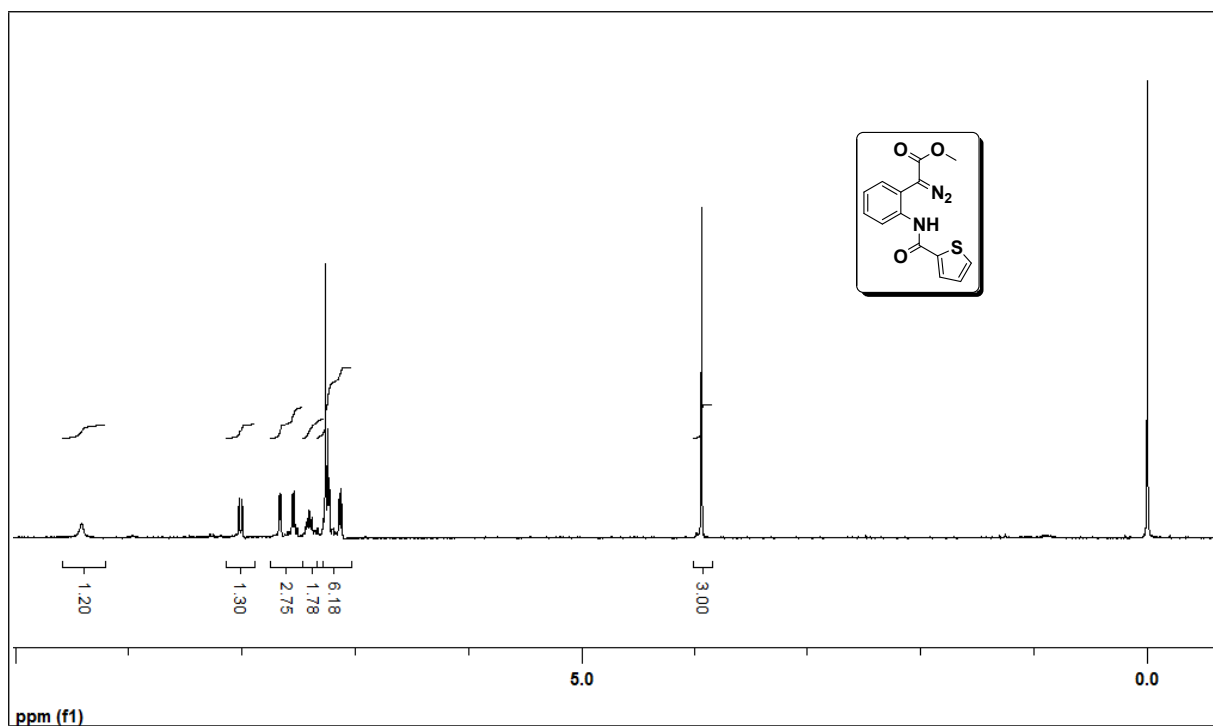
¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6d



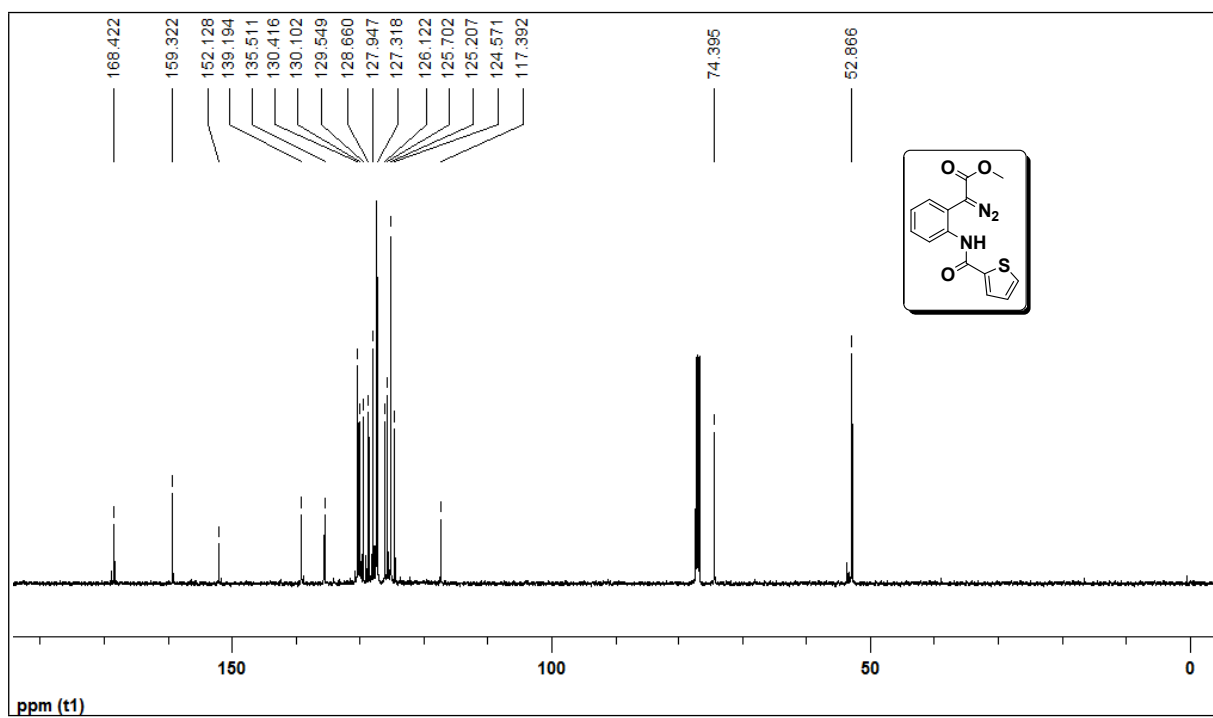
¹H NMR (500 MHz, CDCl₃) spectrum of compound 2d



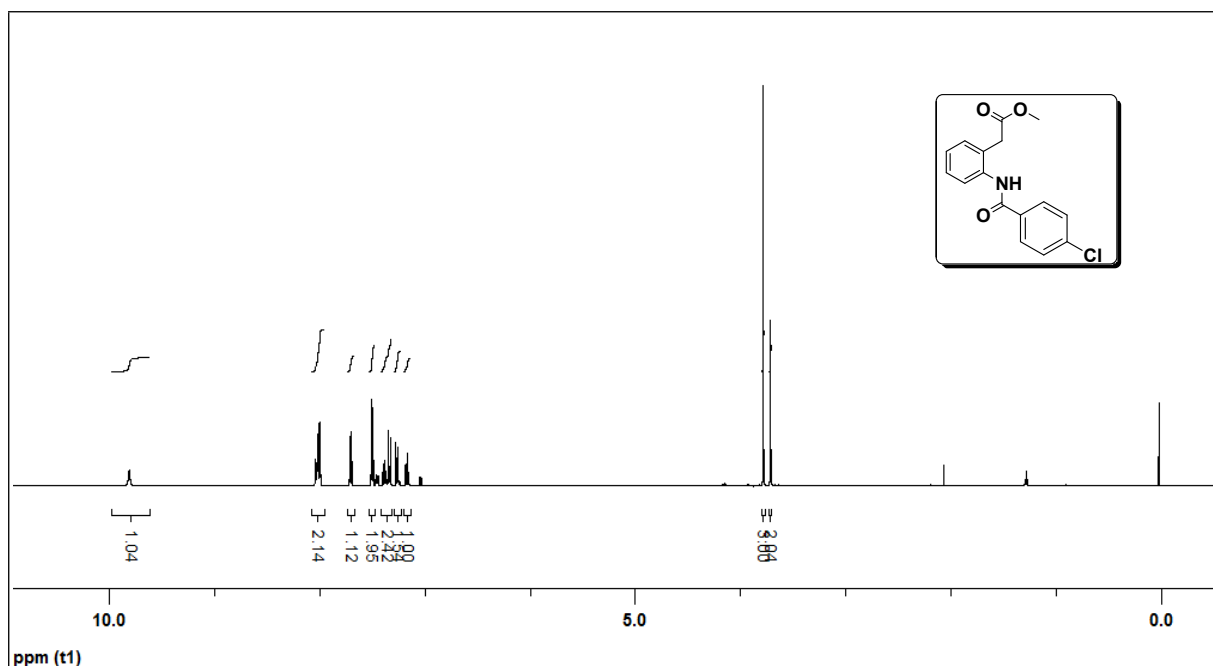
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 2d



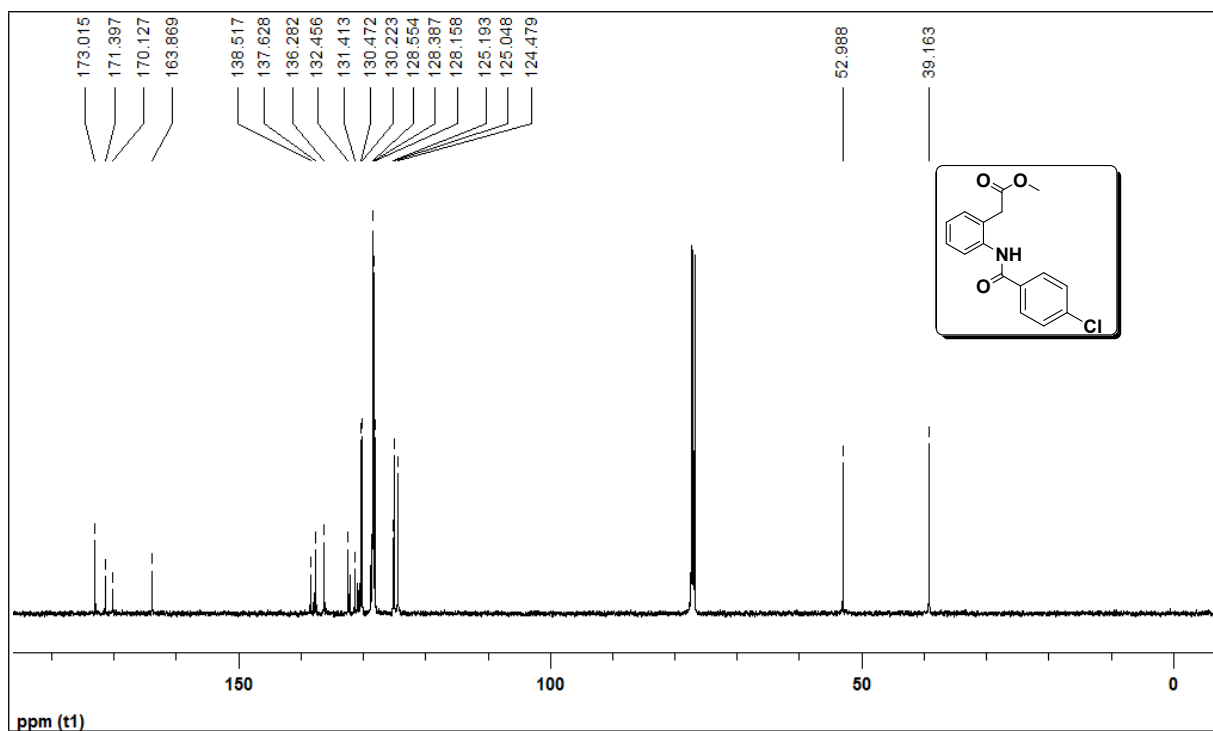
¹H NMR (300 MHz, CDCl₃) spectrum of compound 2e



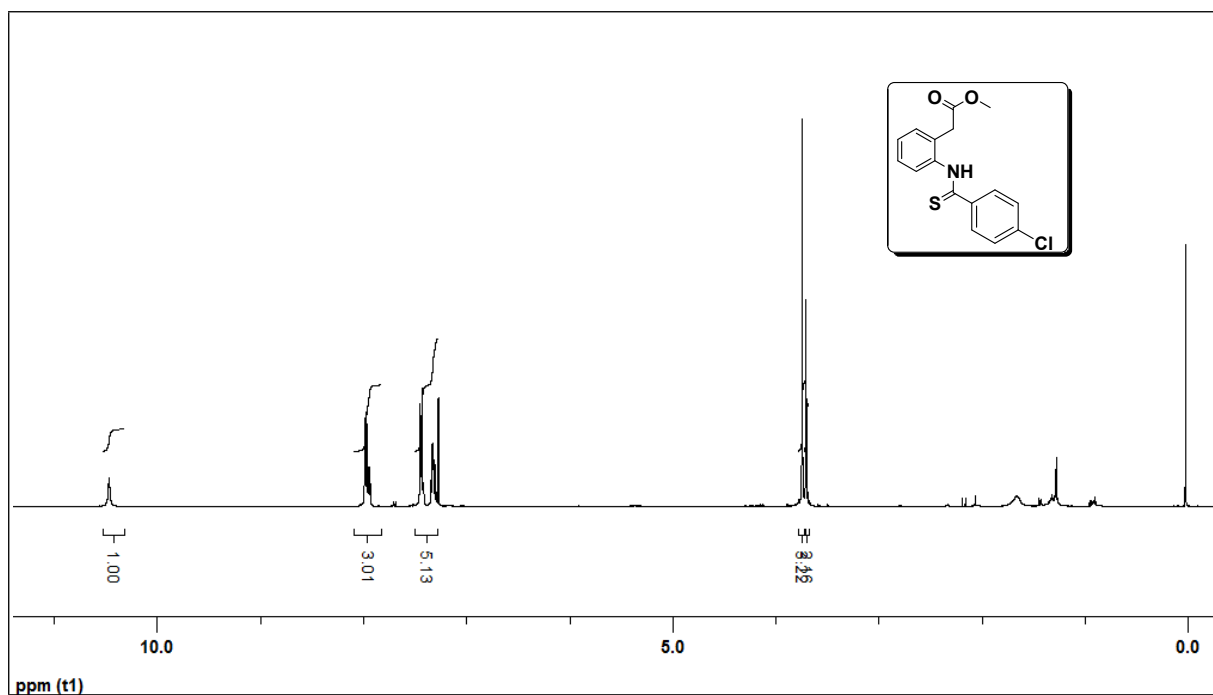
¹³C NMR (75 MHz, CDCl₃) spectrum of compound 2e



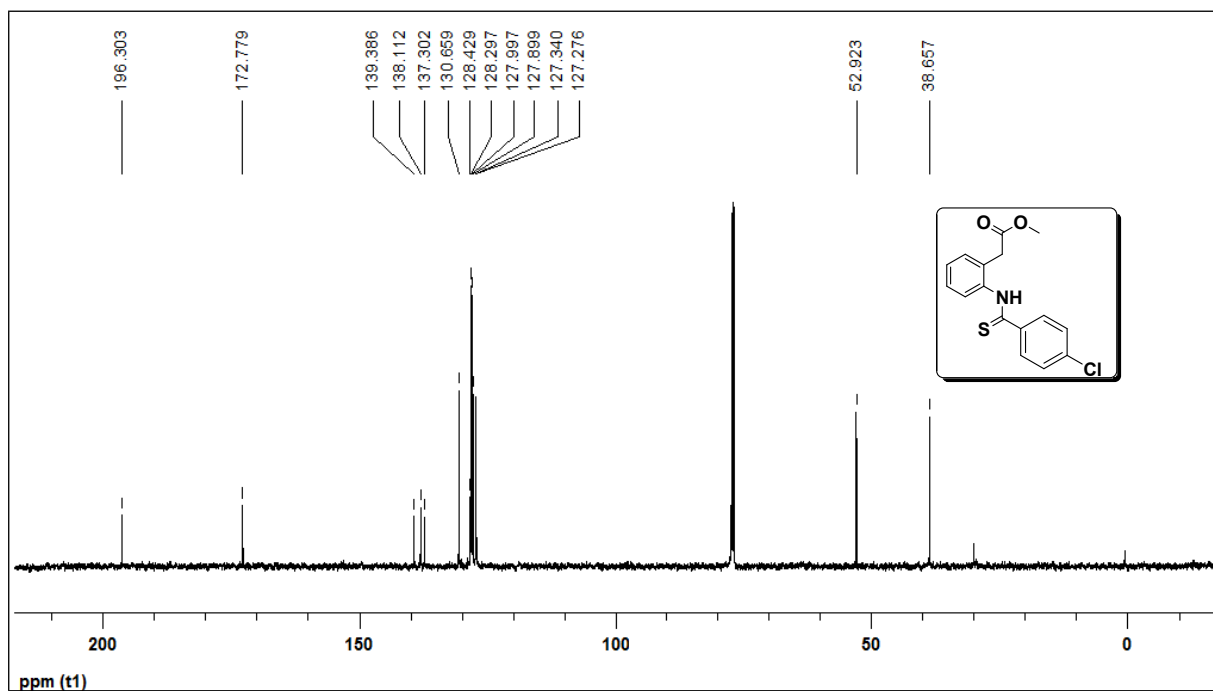
¹H NMR (500 MHz, CDCl₃) spectrum of compound 1h



¹³C NMR (75 MHz, CDCl₃) spectrum of compound 1h



¹H NMR (300 MHz, CDCl₃) spectrum of compound 3d



¹³C NMR (75 MHz, CDCl₃) spectrum of compound 3d