Supporting Information

Domino Synthesis of 2-Substituted Benzothiazoles by Base Promoted Intramolecular C-S Bond Formation

Yogendra Kumar and Hiriyakkanavar Ila*

New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur,

Bangalore-560064, India,

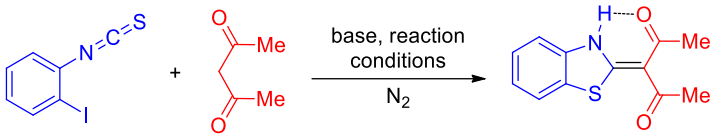
E–mail: hila@jncasr.ac.in

Supporting information–Table of contents

Experimental Section

General Information. All the reagents were purchased from commercial suppliers and used without further purification. Solvents were dried according to the standard procedures. All the reactions were monitored by thin layer chromatography (TLC) using standard TLC silica gel plates and visualized with UV light. Column chromatography was performed using silica gel (100−200 mesh). Nuclear magnetic resonance spectra were recorded on (400 and 600 MHz) FT-NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts were reported in δ (ppm) using residual solvent protons as the internal standard (δ 7.26 for $CDCl_3$ and δ 2.50 for DMSO-d_6, in ^{1}H NMR, δ 77.16 for $CDCl_3$, and δ 39.52 for DMSO-d_6 in ^{13}C NMR and ^{19}F NMR spectra were recorded at 564.65 MHz with the Brucker spectrometer). Coupling constants were reported as *J* values in hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (doublet of triplet), td (triplet of doublet), m (multiplet), and br (broad). Infrared spectra of neat samples were recorded in attenuated total reflectance (ATR) mode using a FT-IR instrument, and HRMS spectra were recorded using a Q-TOF spectrometer. Melting points were recorded using an electro thermal capillary melting point apparatus and are uncorrected. All the 2-halophenylisothiocyanates **1a**,[2,3,4] **1e-g**,[1,2,3] substituted 2-iodophenylisothiocyanates **1b-d**[4] and 3-iodophenylisothiocyanate **1h**[1] were prepared according to the reported procedures. The active methylene compounds **2j-k**,[5-6] **2m**[7] and **2p**[8] were also synthesized according to the reported procedures.

Table S1. Optimization of Reaction Conditions for the Synthesis of 3a



1a **2a** **3a**

Entry	Base (2 equiv)	Solvent	Temp (°C)	Time (h)	% Yield (**3a**)[a]
1	**NaH**	**DMSO**	**rt**	**1**	**92**
2	t-BuOK	DMSO	rt	48	78
3	t-BuOK	DMSO	90	6	80
4	KOH	DMSO	90	12	75
5	K_2CO_3	DMSO	90	6	78
6	Cs_2CO_3	DMSO	90	5	83
7	NaH	DMF	60	12	50
8	NaH	Toluene	90	12	39
9	NaH	THF	65	18	35
10	NaH	CH_3CN	70	18	30
11[b]	NaH	DMSO	rt	10	80

[a]Yields of pure isolated product. [b]Reaction with 1 equiv of NaH.

General Procedure for copper-catalyzed synthesis of 3-(benzo[*d*]thiazol-2(3*H*)-ylidene)pentane-2,4-dione (3a). To a stirred suspension of NaH (67 mg, 2.0 mmol) in dry DMSO (3 ml), a solution of acetylacetone **2a** (100 mg, 1.0 mmol) in DMSO (3 ml) was added dropwise, at room temperature under N_2 atmosphere, and the stirring was further continued for 10-20 min, followed by addition of a solution of 2-iodophenylisothiocyanate **1a** (261 mg, 1.0 mmol) in DMSO (4 ml) with CuI (19 mg, 0.1 mmol) and ligand (0.2 mmol). After stirring for 4-5 h (monitored by TLC), the reaction mixture was quenched with saturated NH_4Cl solution (25 ml), extracted with EtOAc (3 X 25 ml), the combined organic layer was washed with water (3 X 25 ml), and brine (25 mL), dried over Na_2SO_4, and evaporated organic solvent under vacuum to give product **3a**, which was further purified by column chromatography using hexane/ethyl acetate as eluent.

General procedure for the synthesis of 2-substituted 1,3-benzothiazoles 3. To a stirred suspension of NaH (67 mg, 2.0 mmol) in dry DMSO (3 ml), a solution of appropriate activated methylene compound (**2a-r**) (1.0 mmol) in DMSO (3 ml) was added dropwise, at room temperature under N_2 atmosphere, and the stirring was further continued for 10-20 min, followed by addition of a solution of 2-iodophenylisothiocyanate (**1a-h**) (1.0 mmol) in DMSO (4 ml). After stirring for 1-3 h (monitored by TLC), the reaction mixture was quenched with saturated NH_4Cl solution (25 ml), extracted with EtOAc (3 X 25 ml), the combined organic layer was washed with water (3 X 25 ml), and brine (25 mL), dried over Na_2SO_4, and evaporated under vacuum to give products **3**, which were further purified by column chromatography using hexane/ethyl acetate as eluent.

3-(Benzo[*d*]thiazol-2(3*H*)-ylidene)pentane-2,4-dione (3a). Yield 95% (222 mg, 0.95 mmol); white solid; mp 160-161 °C (reported compound)[9]; R_f 0.37 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3255, 3001, 1669, 1596, 1543, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.58 (br, 1H), 7.79 (d, J = 8.0 Hz, 1H) 7.56 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 2.65 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 193.0, 169.1, 138.0, 129.5, 127.2, 124.5, 122.1, 114.1, 109.8, 31.6, 31.2; HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_2S$ $[M+H]^+$ 234.0589, found 234.0581.

2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1,3-diphenylpropane-1,3-dione (3b). Yield 99% (353 mg, 0.99 mmol); yellow solid; mp 188-190 °C; R_f 0.37 (1:4 EtOAc/hexane); IR (neat, cm^{-1}) 3205, 1752, 1594, 1571, 1487, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.64 (br, 1H); 7.83 (d, J = 8.0 Hz, 1H); 7.6 (d, J = 8.0 Hz, 1H); 7.51 (dt, J = 8.0, 0.8 Hz, 1H); 7.43-7.37 (m, 5H); 7.14-7.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 193.5, 169.6, 141.3, 140.9, 138.4, 130.6, 130.5, 129.24, 129.2, 128.8, 127.7, 127.6, 127.4, 124.6, 122.3, 113.9, 106.2; HRMS (ESI) m/z calcd for $C_{22}H_{16}NO_2S$ $[M+H]^+$ 358.0902, found 358.0892.

Diethyl 2-(benzo[*d*]thiazol-2(3*H*)-ylidene)malonate (3c). Yield 97% (284 mg, 0.97 mmol); white solid; mp 138-139 °C (reported compound)[9]; R_f 0.40 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3250, 2986, 1750, 1639, 1581, 1452, 746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.58 (br, 1H); 7.93-7.90 (m, 2H); 7.41 (dt, J = 8.0, 1.6 Hz, 1H); 7.03 (dt, J = 7.6, 1.6 Hz, 1H); 4.29 (q, J = 7.2 Hz, 4H); 1.35 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.2, 167.7, 138.5, 128.2, 126.8, 123.6, 121.8, 112.7, 103.0, 60.5, 60.4, 14.4, 14.3; HRMS (ESI) m/z calcd for $C_{14}H_{16}NO_4S$ $[M+H]^+$ 294.0800, found 294.0694.

(*Z*)-Ethyl 2-(benzo[*d*]thiazol-2(3*H*)-ylidene)-3-oxobutanoate (3d). Yield 87% (229 mg, 0.87 mmol); off-white solid; mp 127-128 °C (reported compound)[9]; R_f 0.36 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3280, 2986, 1750, 1639, 1581, 746; ^{1}H NMR (600 MHz, $CDCl_3$) δ 15.79 (br, 1H); 7.73 (d, J = 7.8 Hz, 1H); 7.52 (d, J = 8.4 Hz, 1H); 7.43 (t, J = 7.8 Hz, 1H); 7.31 (t, J = 7.8 Hz, 1H); 4.38 (q, J = 7.2 Hz, 2H); 2.61 (s, 3H); 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.9, 170.1, 167.9, 139.5, 137.4, 126.9, 124.2, 121.7, 114.3, 104.7, 60.6, 30.9, 14.6; HRMS (ESI) m/z calcd for $C_{13}H_{14}NO_3S$ $[M+H]^+$ 264.0694, found 264.0669.

(*E*)-Ethyl 2-(benzo[*d*]thiazol-2(3*H*)-ylidene)-2-cyanoacetate (3e). Yield 89% (219 mg, 0.89 mmol); white solid; mp 220-221 °C (reported compound)[9]; R_f 0.56 (3:7 EtOAc/hexane); IR (neat, cm^{-1}) 3400, 3025, 2202, 1750, 1663, 1526, 744; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.16 (br, 1H); 7.89 (d, J = 7.8 Hz, 1H); 7.57 (d, J = 7.8 Hz, 1H); 7.44 (t, J = 7.8 Hz, 1H);

7.28 (t, *J* = 7.8 Hz, 1H); 4.19 (q, *J* = 7.2 Hz, 2H); 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 168.2, 165.9, 139.3, 127.2, 126.8, 123.6, 122.4, 117.0, 113.6, 112.8, 60.1, 14.5; HRMS (ESI) *m*/z calcd for $C_{12}H_{11}N_2O_2S$ $[M+H]^+$ 247.0541, found 247.0509.

2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)malononitrile (3f). Yield 99% (196 mg, 0.99 mmol); off-white solid; mp 290-292 °C (reported compound)[9]; R_f 0.25 (1:3 EtOAc/hexane); IR (neat, cm^{-1}) 3066, 2201, 1604, 1567, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, *J* = 7.6 Hz, 1H); 7.51-7.43 (m, 3H); 7.29 (dt, *J* = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.9, 147.3, 136.5, 130.0, 128.4, 127.7, 114.1, 113.9, 113.2, 69.8; HRMS (ESI) *m*/z calcd for $C_{10}H_6N_3S$ $[M+H]^+$ 200.0282, found 200.0267.

2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)cyclopentane-1,3-dione (3g). Yield 98% (226 mg, 0.98 mmol); white solid; mp 176-178 °C; R_f 0.53 (2:3 EtOAc/hexane); IR (neat, cm^{-1}) 3239, 3010, 1734, 1664, 1566, 1441, 768; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.32 (br, 1H); 7.94 (d, *J* = 8.0 Hz, 1H); 7.70 (d, *J* = 8.0 Hz, 1H); 7.42 (t, *J* = 7.6 Hz, 1H); 7.06 (t, *J* = 7.6 Hz, 1H); 2.86 (t, *J* = 5.6 Hz, 2H); 2.59 (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 199.7, 187.7, 139.7, 138.9, 129.3, 128.5, 128.1, 110.5, 95.7, 31.6, 28.4; HRMS (ESI) *m*/z calcd for $C_{12}H_{10}NO_2S$ $[M+H]^+$ 232.0432, found 232.0421.

2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)cyclohexane-1,3-dione (3h). Yield 98% (240 mg, 0.98 mmol); white solid; mp 190-192 °C; R_f 0.53 (2:3 EtOAc/hexane); IR (neat, cm^{-1}) 3278, 3001, 1739, 1630, 1563, 1441, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.92 (br, 1H); 7.82 (d, *J* = 7.6 Hz, 1H); 7.60 (d, *J* = 8.0 Hz, 1H); 7.50 (dt, *J* = 7.2, 1.2 Hz, 1H); 7.38 (dt, *J* = 8.0, 1.2 Hz, 1H); 2.67 (t, *J* = 6.4 Hz, 2H); 2.64 (t, *J* = 6.4 Hz, 2H); 2.07 (quin, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 194.6, 166.6, 137.8, 128.7, 127.5, 124.8, 122.5, 114.2, 106.1, 37.2, 36.6, 20.2; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{12}NO_2S$ $[M+H]^+$ 246.0589, found 246.0577.

2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1*H*-indene-1,3(2*H*)-dione (3i). Yield 97% (271 mg, 0.97 mmol); greenish yellow solid; mp 354-356 °C; R_f 0.45 (3:7 EtOAc/hexane); IR (neat, cm^{-1}) 3450, 3158, 1678, 1631, 1576, 751; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.27 (br, 1H); 8.03 (d, *J* = 7.6 Hz, 1H); 7.97 (d, *J* = 8.0 Hz, 1H); 7.68 (br, 4H); 7.52 (t, *J* = 7.8 Hz, 1H); 7.38 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.0, 192.4, 168.7, 159.9, 139.1, 133.2, 127.5, 125.6, 124.5, 122.9, 121.5, 121.0, 115.2, 100.0; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{10}NO_2S$ $[M+H]^+$ 280.0432, found 280.0420.

5-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (3j). Yield 87% (252 mg, 0.87 mmol); brown solid; mp 302-303 °C; R_f 0.17 (3:7 EtOAc/hexane); IR (neat, cm^{-1}) 3287, 3172, 2963, 1702, 1605, 1504, 787; ^{1}H NMR (400 MHz, $CDCl_3$) δ

13.81 (br, 1H); 7.81 (d, *J* = 8.0 Hz, 1H); 7.57 (d, *J* = 8.0 Hz, 1H); 7.51 (t, *J* = 8.2 Hz, 1H); 7.39 (t, *J* = 8.4 Hz, 1H); 3.434 (s, 3H); 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.6, 163.6, 162.2, 137.7, 128.1, 127.7, 124.9, 122.5, 113.8, 99.7, 27.9, 27.7; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{12}N_3O_3S$ $[M+H]^+$ 290.0599, found 290.0587.

5-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1,3-dimethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (3k). Yield 87% (266 mg, 0.87 mmol); brown solid; mp 253-254 °C; R_f 0.21 (2:3 EtOAc/hexane); IR (neat, cm^{-1}) 3293, 2983, 2857, 1745, 1645, 1625, 1527, 750; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.96 (br, 1H); 7.89 (d, *J* = 6.6 Hz, 1H); 7.85 (d, *J* = 7.2 Hz, 1H); 7.56 (t, *J* = 8.4 Hz, 1H); 7.04 (t, *J* = 7.8 Hz, 1H); 3.85 (s, 3H); 3.84 (s,3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.8, 167.7, 163.9, 160.9, 139.8, 129.3, 128.1, 125.3, 122.5, 114.2, 98.8, 35.2, 34.9; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{12}N_3O_2S_2$ $[M+H]^+$ 306.0371, found 306.0358.

5-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3l). Yield 92% (256 mg, 0.92 mmol); off-white solid; mp (decomposed at 206°C); R_f 0.36 (3:7 EtOAc/hexane); IR (neat, cm^{-1}) 3403, 3100, 1750, 1663, 1519, 1459, 750; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.83 (br, 1H); 7.78 (d, *J* = 7.8 Hz, 1H); 7.60 (d, *J* = 8.4 Hz, 1H); 7.51 (t, *J* = 8.4 Hz, 1H); 7.39 (t, *J* = 7.8 Hz, 1H); 1.78 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 165.1, 163.4, 137.9, 127.9, 127.8, 125.1, 122.5, 114.0, 113.9, 104.9, 26.9; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{12}NO_4S$ $[M+H]^+$ 278.0487, found 278.0473.

(*E*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-3-(4-chlorophenyl)-3-oxopropanenitrile (3m). Yield 98% (306 mg, 0.98 mmol); white solid; mp 279-281 °C; R_f 0.25 (3:2 EtOAc/hexane); IR (neat, cm^{-1}) 3165, 3020, 2198, 1745, 1615, 1598, 746; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.75 (br, 1H); 8.02 (d, *J* = 7.8 Hz, 1H); 7.84 (d, *J* = 7.8 Hz, 2H); 7.75 (d, *J* = 7.8 Hz, 1H); 7.59 (d, *J* = 7.8 Hz, 2H); 7.54 (t, *J* = 7.8 Hz, 1H); 7.39 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 184.3, 168.2, 140.4, 137.3, 135.8, 129.6, 128.3, 127.6, 127.2, 124.4, 122.8, 119.1, 114.4, 75.7; HRMS (ESI) *m*/*z* calcd for $C_{16}H_{10}ClN_2OS$ $[M+H]^+$, $[M+H+2]^+$ 313.0202, 315.0202 found 313.0193, 315.0172.

(*Z*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-2-phenylacetonitrile (3n). Yield 95% (237 mg, 0.95 mmol); off-white solid; mp 108-109 °C (reported compound)[9]; R_f 0.61 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 2929, 2861, 2150, 1634, 1480, 763; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.8 Hz, 2H); 8.25 (d, *J* = 8.4 Hz, 1H); 8.02 (d, *J* = 7.8 Hz, 1H); 7.67 (t, *J* = 7.2 Hz, 1H); 7.60-7.54 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 154.1, 137.2, 135.1, 134.1, 131.4, 128.7, 127.8, 127.1, 125.9, 122.3, 82.9; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{11}N_2S$ $[M+H]^+$ 251.0643, found 251.0539.

(*Z*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-2-(4-fluorophenyl)acetonitrile (3o). Yield 99% (265 mg, 0.99 mmol); yellow solid; mp 94-95 °C; R_f 0.56 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3083, 2922, 2199, 1620, 1590, 757; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (dd, J = 7.2, 1.8 Hz, 2H); 8.21 (dd, J = 8.4, 1.2 Hz, 1H); 8.00 (dd, J = 8.1, 1.5 Hz, 1H); 7.55 (dt, J = 7.8, 1.2 Hz, 1H); 7.50 (dt, J = 7.8, 1.2 Hz, 1H); 6.75 (dd, J = 7.2, 1.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4, 165.7, 137.2, 134.4, 134.3, 131.4, 127.9, 127.2, 125.9, 122.3, 115.9, 115.8, 85.3; ^{19}F{^{1}H} NMR (564.65 MHz, $CDCl_3$) δ -103.01; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{10}FN_2S$ $[M+H]^+$ 269.0549, found 269.0493.

(*Z*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-2-(pyridin-2-yl)acetonitrile (3p). Yield 96% (241 mg, 0.96 mmol); yellow solid; mp 149-150 °C; R_f 0.51 (3:7 EtOAc/hexane); IR (neat, cm^{-1}) 3401, 3025, 2183, 1640, 1580746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1521 (br, 1H); 7.83 (d, J = 6.0 Hz, 1H); 7.72 (dd, J = 8.0, 1.2 Hz, 1H); 7.66 (dd, J = 8.0, 1.2 Hz, 1H); 7.57-7.52 (m, 1H); 7.39-7.33 (m, 2H); 7.21 (dt, J = 7.6, 1.2 Hz, 1H); 6.68 (dt, J = 7.2, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 152.3, 150.9, 138.1, 135.7, 130.7, 126.1, 123.1, 121.3, 120.6, 120.2, 118.3, 112.9, 68.4; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}N_3S$ $[M+H]^+$ 252.0595, found 252.0584.

(*E*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(4-chlorophenyl)ethanone (3q). Yield 94% (270 mg, 0.94 mmol); pale yellow solid; mp 142-144 °C (reported compound)[9]; R_f 0.60 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3296, 3055, 3015, 1754, 1615, 1596, 724; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.41 (br, 1H); 8.06 (d, J = 9.0 Hz, 1H); 7.94 (d, J = 8.4 Hz, 2H); 7.50 (d, J = 8.4 Hz, 1H); 7.44 (t, J = 7.8 Hz, 1H); 7.37 (d, J = 8.4 Hz, 2H); 7.07 (t, J = 7.5 Hz, 1H); 6.10 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 168.2, 142.1, 140.4, 139.7, 133.7, 130.5, 129.5, 129.1, 127.9, 127.8, 109.3, 91.5; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{11}ClNOS$ $[M+H]^+$, $[M+H+2]^+$ 288.0250, 290.0250 found 288.0237, 290.0203.

(*E*)-2-(Benzo[*d*]thiazol-2(3*H*)-ylidene)-1-(pyridin-4-yl)ethanone (3r). Yield 93% (236 mg, 0.93 mmol); red solid; mp 124-126 °C; R_f 0.31 (1:1 EtOAc/hexane); IR (neat, cm^{-1}) 3335, 3035, 2941, 1737, 1620, 1593, 746; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (br, 1H); 8.79 (d, J = 5.2 Hz, 2H); 7.98 (d, J = 7.6 Hz, 1H); 7.74 (d, J = 4.8 Hz, 2H); 7.50 (t, J = 7.6 Hz, 1H); 7.39 (d, J = 7.6 Hz, 1H); 7.16 (t, J = 7.6 Hz, 1H); 6.74 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.6, 167.4, 162.3, 150.2, 142.3, 131.8, 126.9, 124.8, 121.6, 120.5, 119.8, 92.9; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{11}N_2OS$ $[M+H]^+$ 255.0592, found 255.0586.

3-(6-Chlorobenzo[*d*]thiazol-2(3*H*)-ylidene)pentane-2,4-dione (3s). Yield 93% (249 mg, 0.93 mmol); white solid; mp 189-191 °C; R_f 0.36 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3390,

3099, 1670, 1610, 1591, 808; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.72 (br, 1H); 7.76 (d, J = 2.4 Hz, 1H); 7.46 (s, 1H); 7.42 (d, J = 2.0 Hz, 1H); 2.65 (s, 3H); 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 193.1, 169.3, 136.9, 131.3, 130.2, 127.7, 121.8, 115.0, 109.9, 31.4, 31.1; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{11}ClNO_2S$ $[M+H]^+$, $[M+H+2]^+$ 268.0199, 270.0199 found 268.0186, 270.0157.

Diethyl 2-(6-chlorobenzo[*d*]thiazol-2(3*H*)-ylidene)malonate (3t). Yield 95% (310 mg, 0.95 mmol); white solid; mp 194-195 °C; R_f 0.48 (3:17 EtOAc/hexane); IR (neat, cm^{-1}) 3310, 3012, 1750, 1639, 1581, 806; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.22 (br, 1H); 7.62 (d, J = 2.0 Hz, 1H); 7.32 (d, J = 1.6 Hz, 1H); 7.28 (s, 1H); 4.34 (q, J = 7.1 Hz, 4H); 1.38 (q, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.2, 167.8, 137.3, 130.0, 129.3, 127.4, 121.7, 113.5, 86.7, 60.7, 60.1, 14.5, 14.4; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{15}ClNO_4S$ $[M+H]^+$, $[M+H+2]^+$ 328.0410, 330.0410 found 328.0380, 330.0315.

(*Z*)-2-(6-Chlorobenzo[*d*]thiazol-2(3*H*)-ylidene)-2-(pyridin-2-yl)acetonitrile (3u). Yield 91% (260 mg, 0.91 mmol); brown solid; mp 218-220 °C; R_f 0.48 (1:4 EtOAc/hexane); IR (neat, cm^{-1}) 3350, 3005, 2173, 1627, 1578, 810; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.15 (br, 1H); 7.79 (t, J = 6.4 Hz, 1H); 7.71 (d, J = 2.0 Hz, 1H); 7.61-7.56 (m, 2H); 7.37 (d, J = 8.8 Hz, 1H); 7.33 (dd, J = 8.6, 2.2 Hz, 1H); 6.69 (dt, J = 6.7, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.1, 150.8, 138.6, 134.7, 132.7, 128.6, 126.7, 121.0, 120.6, 120.4, 119.6, 112.8, 68.2; HRMS (ESI) *m*/*z* calcd for $C_{14}H_9ClN_3S$ $[M+H]^+$, $[M+H+2]^+$ 286.0206, 288.0206 found 286.0196, 288.0178.

3-(6-(Trifluoromethyl)benzo[*d*]thiazol-2(3*H*)-ylidene)pentane-2,4-dione (3v). Yield 94% (283 mg, 0.94 mmol); yellow solid; mp 187-189 °C; R_f 0.35 (1:4 EtOAc/hexane); IR (neat, cm^{-1}) 3280, 3020, 1738, 1600, 1540, 839; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.80 (br, 1H); 8.07 (s, 1H); 7.72 (d, J = 8.4 Hz, 1H); 7.64 (d, J = 8.8 Hz, 1H); 2.67 (s, 3H), 2.64(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 193.2, 170.3, 140.7, 130.2, 127.1, 126.8, 124.4, 124.3, 119.8, 119.79, 119.75, 114.4, 110.3, 31.4, 31.1; ^{19}F{^{1}H} NMR (564.65 MHz, $CDCl_3$) δ -61.32; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{11}F_3NO_2S$ $[M+H]^+$, 302.0463, found 302.0450.

1,3-Diphenyl-2-(6-(trifluoromethyl)benzo[*d*]thiazol-2(3*H*)-ylidene)propane-1,3-dione (3w). Yield 94% (400 mg, 0.94 mmol), white solid; mp 295-296 °C; R_f 0.30 (1:4 EtOAc/hexane); IR (neat, cm^{-1}) 3338, 3037, 1739, 1637, 1655, 715; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.66 (br, 1H); 8.12 (s, 1H); 7.84 (d, J = 8.0 Hz, 1H); 7.61 (d, J = 8.0 Hz, 1H); 7.45-7.38 (m, 5H); 7.15-7.03 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 194.4, 170.5, 143.5, 142.2, 141.8, 139.3,

131.5, 131.4, 130.2, 130.1, 129.7, 128.6, 128.5, 128.3, 125.6, 125.2, 124.9, 123.2, 121.7, 114.8, 107.1; $^{19}F\{^{1}H\}$ NMR (564.65 MHz, $CDCl_3$) δ -62.61; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{15}F_3NO_2S$ $[M+H]^+$, 426.0776, found 426.0767.

2-(6-(Trifluoromethyl)benzo[*d*]thiazol-2(3*H*)-ylidene)cyclohexane-1,3-dione (3x). yield 93% (291 mg, 0.93 mmol); white solid; mp 278-280 °C; R_f 0.47 (2:3 EtOAc/hexane); IR (neat, cm^{-1}) 3358, 3092, 2962, 1735, 1605, 1560, 828; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.09 (br, 1H); 8.09 (s, 1H); 7.75 (d, *J* = 8.4 Hz, 1H); 7.69 (d, *J* = 8.4 Hz, 1H); 2.69 (t, *J* = 6.4 Hz, 2H); 2.65 (t, *J* = 6.4 Hz, 2H); 2.09 (quin, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 194.8, 167.7, 140.5, 129.4, 127.4, 127.1, 124.7, 124.6, 124.3, 120.1, 120.0, 114.6, 106.6, 36.8, 36.5; $^{19}F\{^{1}H\}$ NMR (564.65 MHz, $CDCl_3$) δ -61.38; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{11}F_3NO_2S$ $[M+H]^+$, 314.0463, found 314.0369.

3-(5,6-Dimethoxybenzo[*d*]thiazol-2(3*H*)-ylidene)pentane-2,4-dione (3y). Yield 67% (197 mg, 0.67 mmol); off-white solid; mp 120-121 °C; R_f 0.47 (2:3 EtOAc/hexane); IR (neat, cm^{-1}) 3309, 3025, 2982, 1745, 1615, 1541, 1075, 815; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.72 (br, 1H); 7.20 (s, 1H); 7.06 (s, 1H); 3.96 (s, 6H); 2.63(s, 3H); 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 192.6, 168.4, 150.1, 148.0, 132.3, 121.6, 109.9, 103.6, 97.4, 56.6, 56.5, 31.5, 31.2; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{16}NO_4S$ $[M+H]^+$, 294.0800, found 294.0730.

2-(5,6-Dimethoxybenzo[*d*]thiazol-2(3*H*)-ylidene)-1*H*-indene-1,3(2*H*)-dione (3z). Yield 60% (204 mg, 0.60 mmol); pale yellow solid; mp 178-180 °C; R_f 0.43 (1:1 EtOAc/hexane); IR (neat, cm^{-1}) 3310, 3006, 2945, 1745, 1628, 1586, 1028, 766; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (br, 1H); 7.66 (dd, *J* = 5.4, 3.0 Hz, 1H); 7.55 (dd, *J* = 5.2, 3.2 Hz, 1H); 6.56 (s, 1H); 6.55 (s, 1H); 6.53 (d, *J* = 2.4 Hz, 1H); 6.45 (d, *J* = 2.4 Hz, 1H); 3.76 (s, 3H); 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 192.1, 168.7, 155.4, 148.9, 147.4, 139.1, 132.7, 132.0, 129.6, 120.9, 120.4, 116.2, 110.9, 108.2, 94.5, 56.2, 55.9; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{14}NO_4S$ $[M+H]^+$, 340.0644, found 340.0629.

2-Acetyl-*N*-(3-iodophenyl)-3-oxobutanethioamide (5). Yield 94% (340 mg, 0.94 mmol); yellow solid; mp 82-84 °C; R_f 0.46 (1:4 EtOAc/hexane); IR (neat, cm^{-1}) 3201, 2986, 1750, 1598, 1570, 709; ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.32 (br, 1H); 8.21 (d, *J* = 2.0 Hz, 1H); 7.79 (dd, *J* = 8.2, 2.2 Hz, 1H); 7.65 (dd, *J* = 7.8, 1.4 Hz, 1H); 7.18 (t, *J* = 8.0 Hz, 1H); 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 189.4, 189.2, 139.5, 136.3, 131.5, 130.6, 122.1, 93.9, 82.0, 23.9, 23.4; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{13}INO_2S$ $[M+H]^+$, 361.9712, found 361.9685.

X-Ray Crystal data and ORTEP diagram of compound 3h:

Experimental

Single crystals of $C_{13}H_{11}NO_2S$ **[3h]** were recrystallized from **[ethanol + dichloromethane]** mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal structure determination of [3h]

Crystal Data. $C_{13}H_{11}NO_2S$, M =245.29, Triclinic, a = 10.0303(17) Å, b = 4.7560(7) Å, c = 12.3563(19) Å, β = 111.075(7)°, U = 550.02(15) Å^3, T = 296.0, space group P2$_1$ (no. 1), Z = 2, μ(Mo-Kα) = 0.281, 5519 reflections measured, 2440 unique (R_{int} = 0.0893) which were used in all calculations. The final $wR(F^2)$ was 0.1577 (all data).

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXL-2018/3 (Sheldrick, 2018)

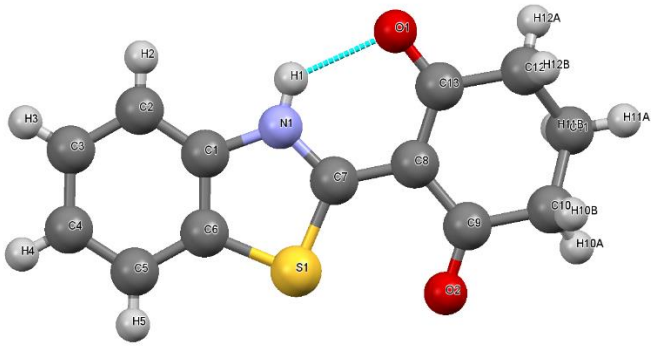
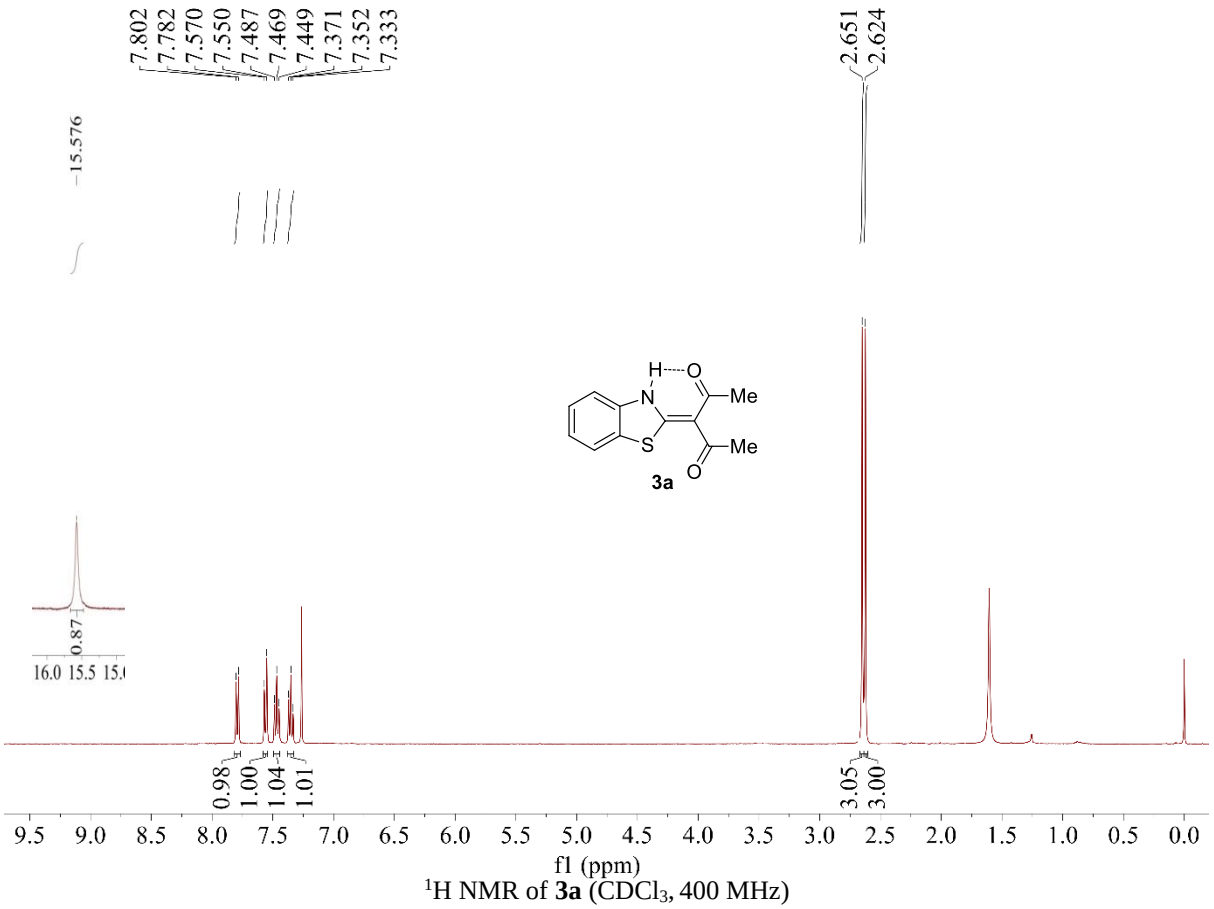
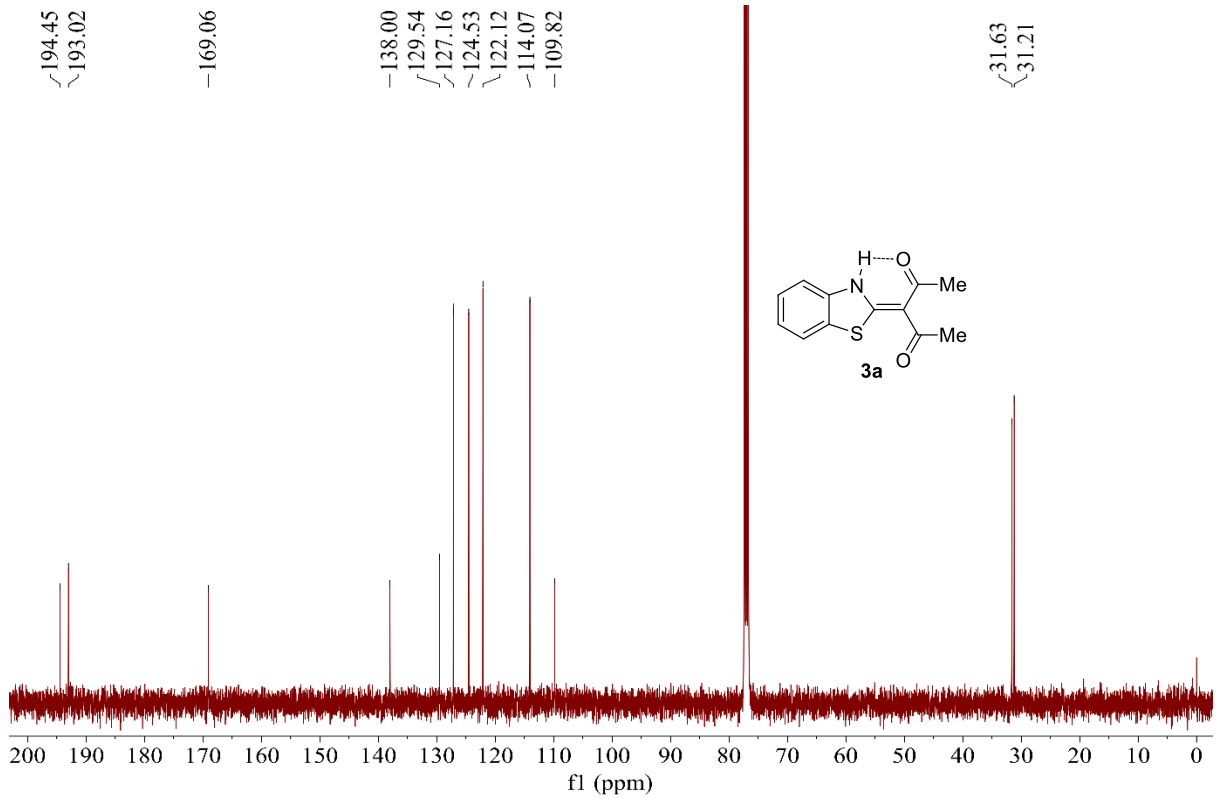


Figure S1: ORTEP (with 50% probability) diagram for **3h**.

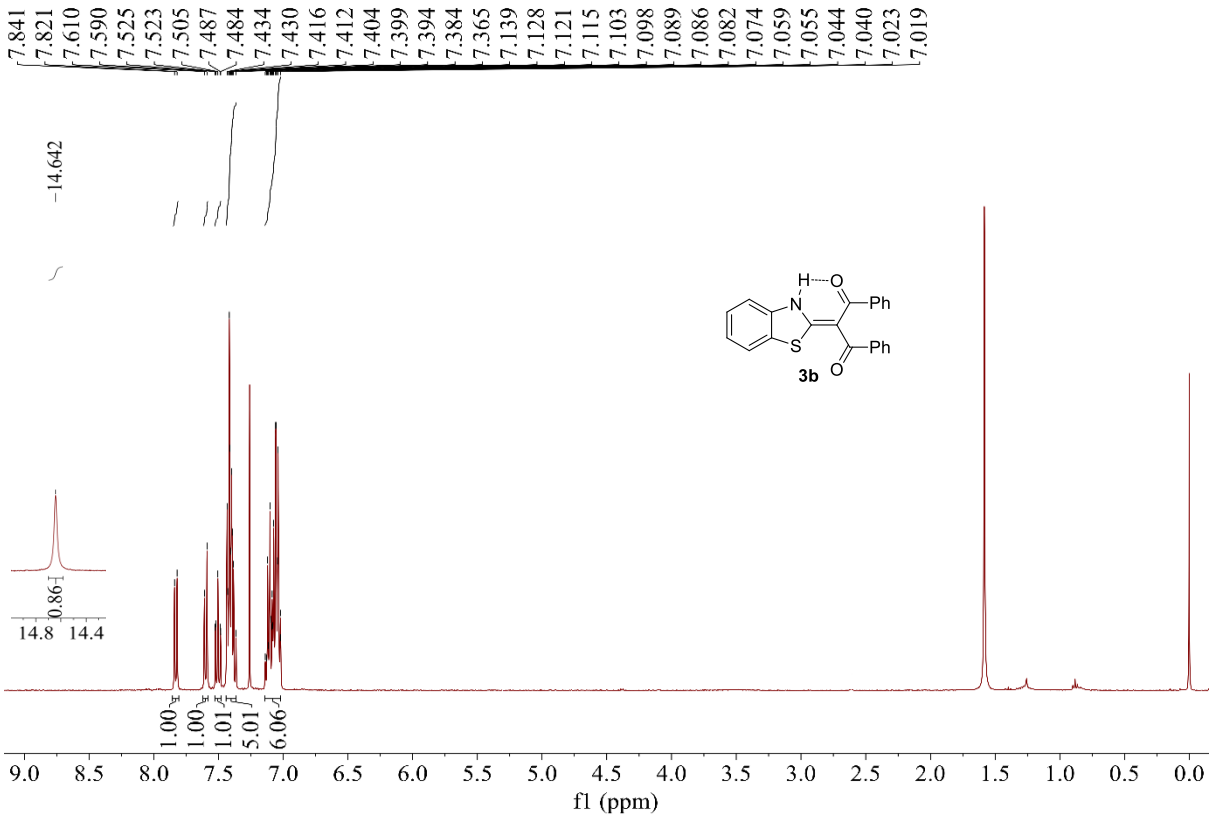
1. Wong, R.; Dolman, S. J. *J. Org. Chem.* 2007, *72*, 3969-3971.
2. Liu, P.; Li, C.; Zhang, I. Xu, X.; *Synthetic* Communications 2013, *43*, 3342-3351.
3. Janczewski, L.; Gajda, A.; Gajda, T. *Eur. J. Org. Chem.* 2019, *14*, 2528-2532.
4. Pinapati, S.; Mandapti, U.; Rudraraju, R. R. *Chemistry Select* 2017, *2*, 295-299.
5. Devi, I.; Bhuyan, P. J. *Tetrahedron Lett.* 2005, *46*, 5727-5729.
6. Kalaiaras, N.; Manivarman, S. *Orient. J. Chem.* 2017, *33*, 304-317.
7. Joubran, L.; Jackson, W. R.; Campi, E. M.; Robinson, A. J.; Wells, B. A.; Godfrey, P. D.; Callaway, J. K.; Jarrott, B. *Aust. J. Chem.* 2003, *56*, 597-605.
8. Klapars, A.; Waldman, J. H.; Campos, K. R.; Jensen, M. S.; McLaughlin, M.; Chung, J. Y. L.; Cvetovich, R. J.; Chen, C-Y. *J. Org. Chem.* 2005, *70*, 10186-10189.
9. Synthesis, reactions, and tautomerism of ketene N,S-acetals with benzothiazoline ring: Huang, Z.-T.; Shi, X. *Chem. Ber*. 1990, *123*, 541-547.



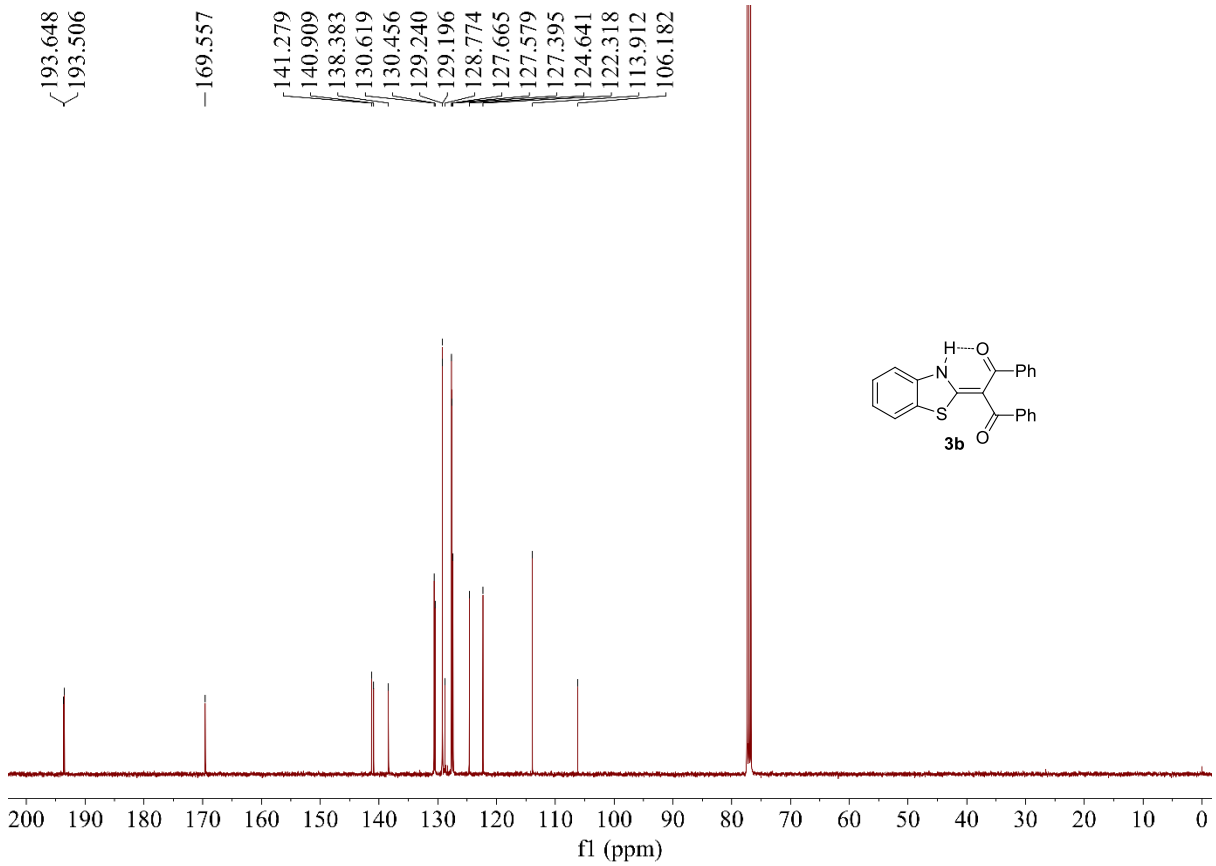
^{1}H NMR of **3a** ($CDCl_3$, 400 MHz)



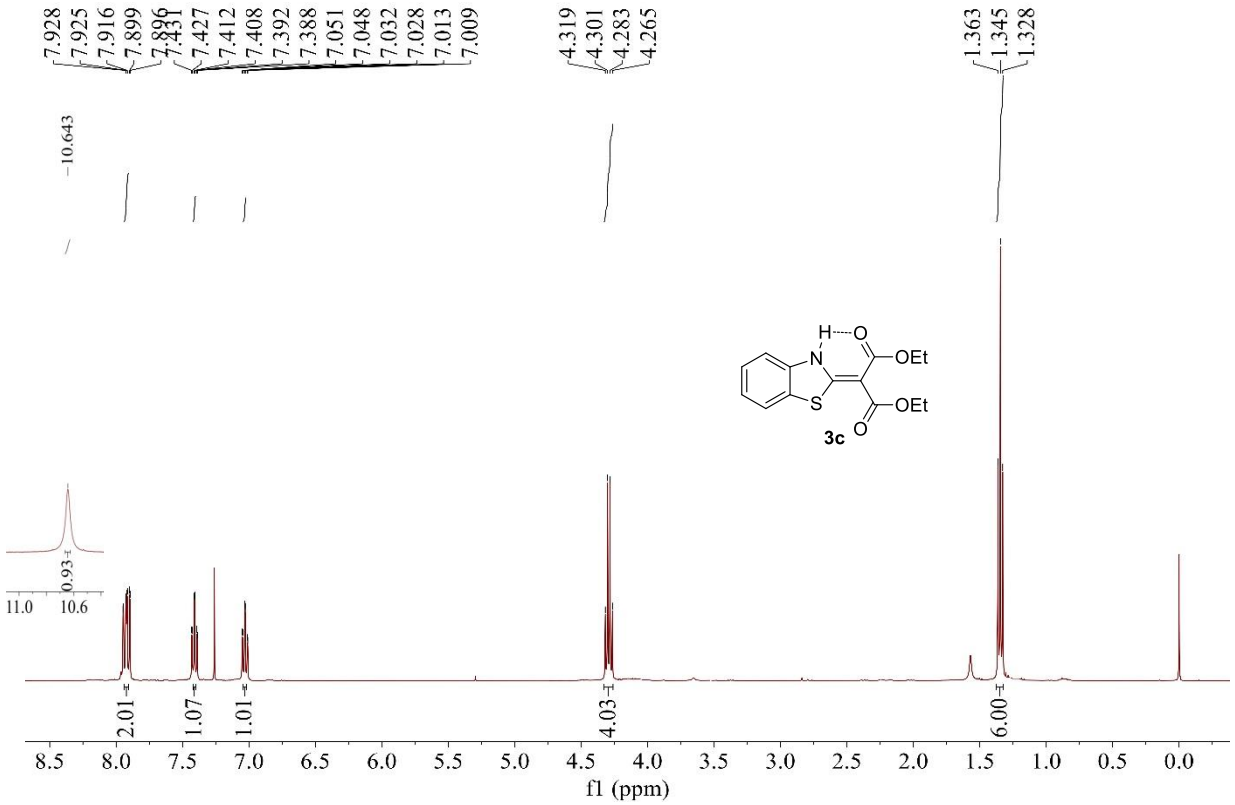
^{13}C NMR of **3a** ($CDCl_3$, 100 MHz)



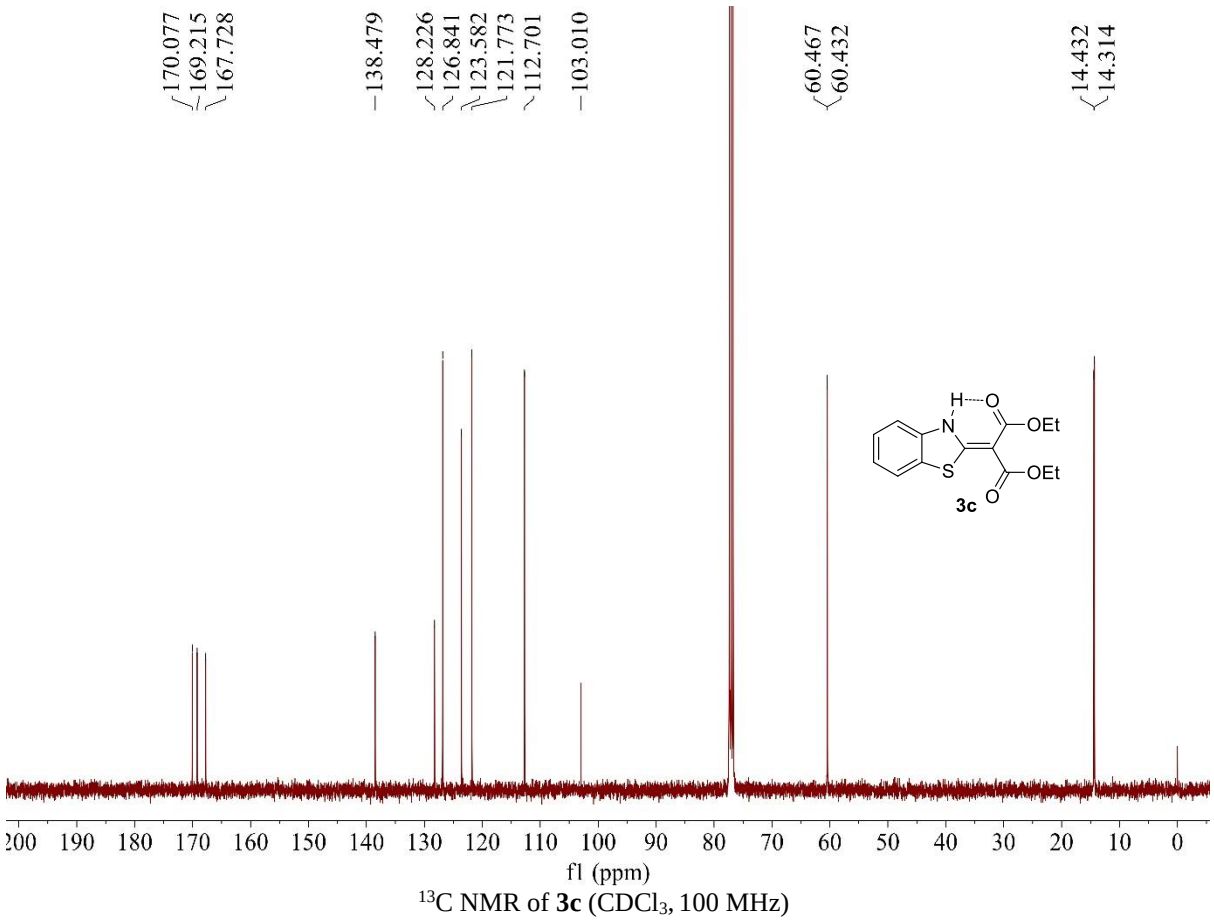
^{1}H NMR of **3b** ($CDCl_3$, 400 MHz)



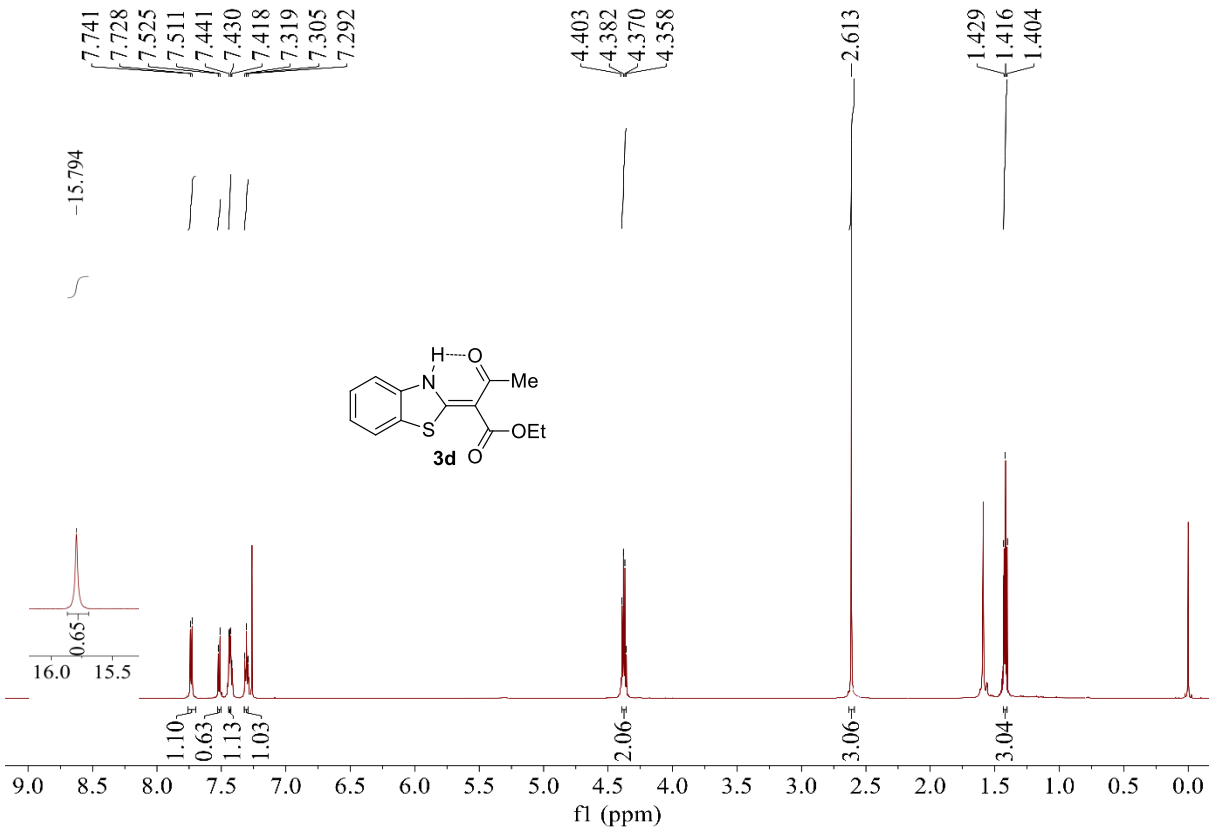
^{13}C NMR of **3b** ($CDCl_3$, 100 MHz)



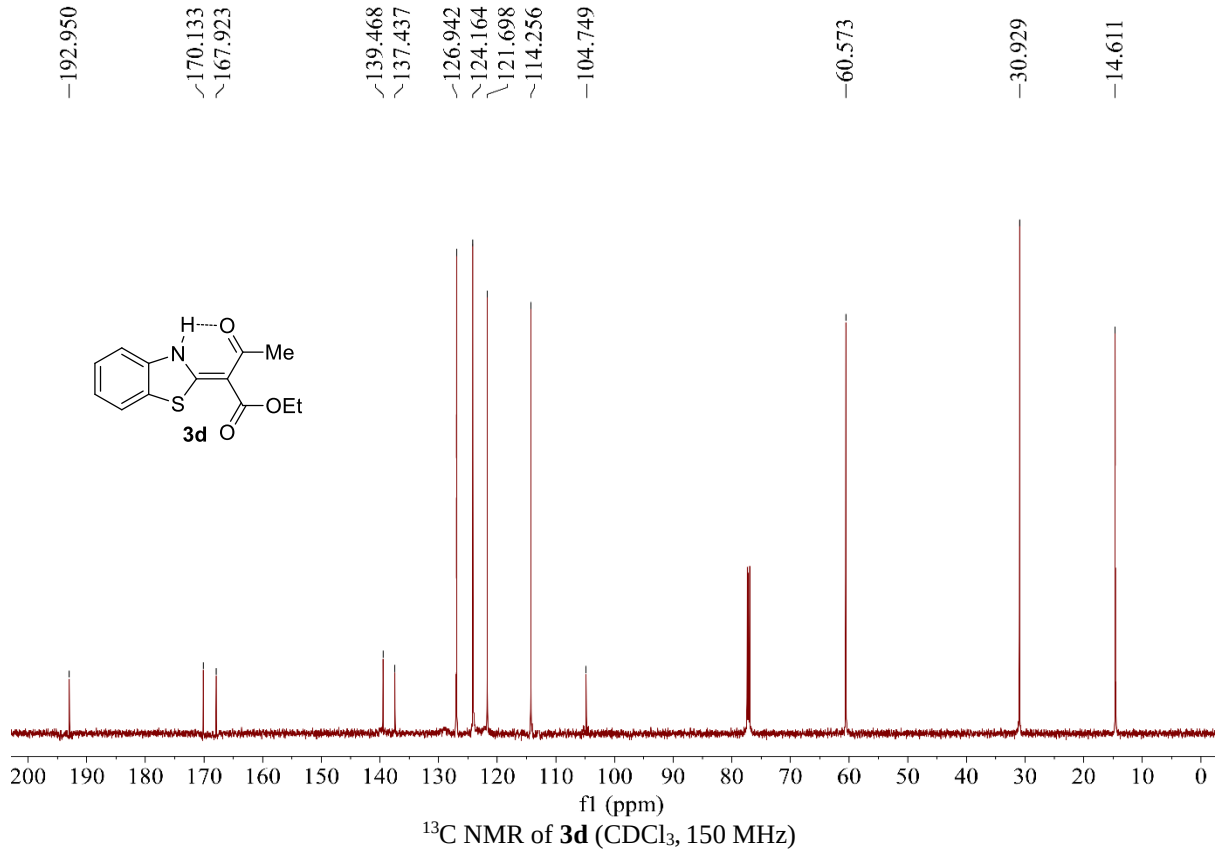
^{1}H NMR of **3c** ($CDCl_3$, 400 MHz)



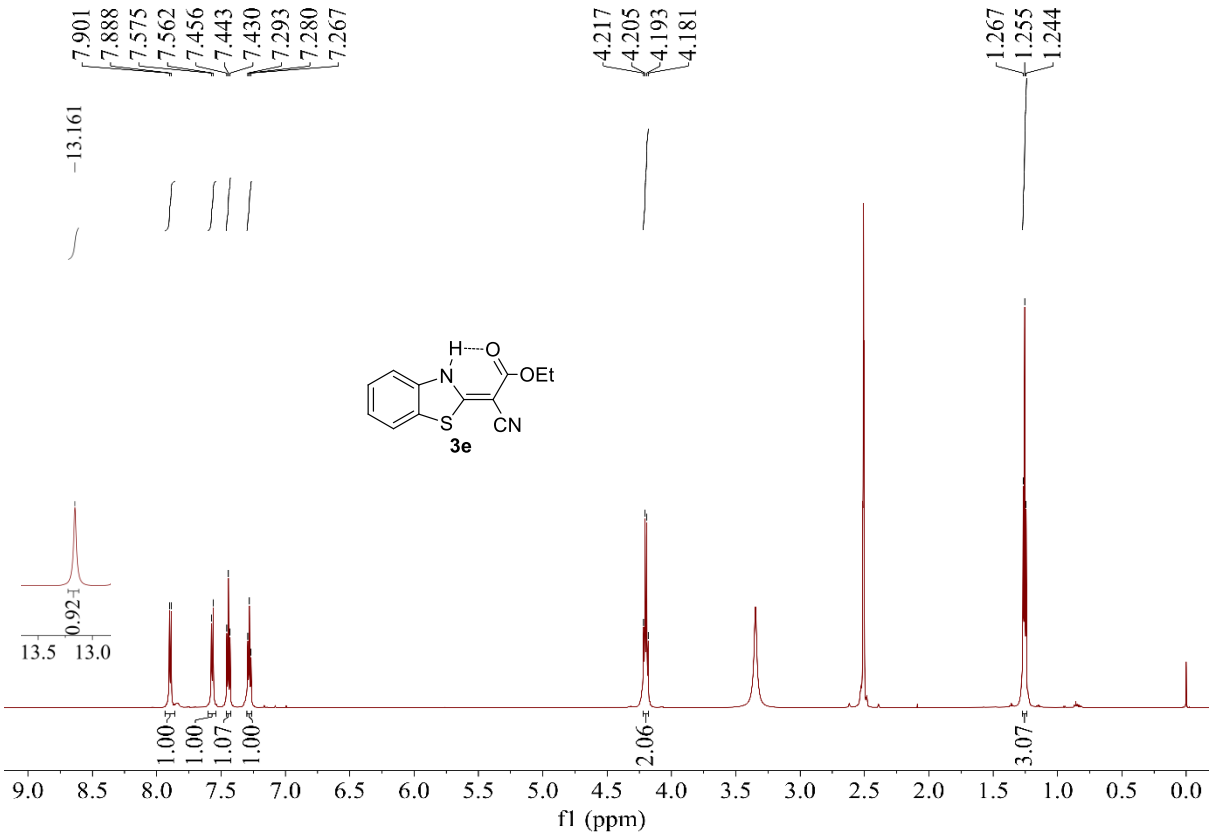
^{13}C NMR of **3c** ($CDCl_3$, 100 MHz)



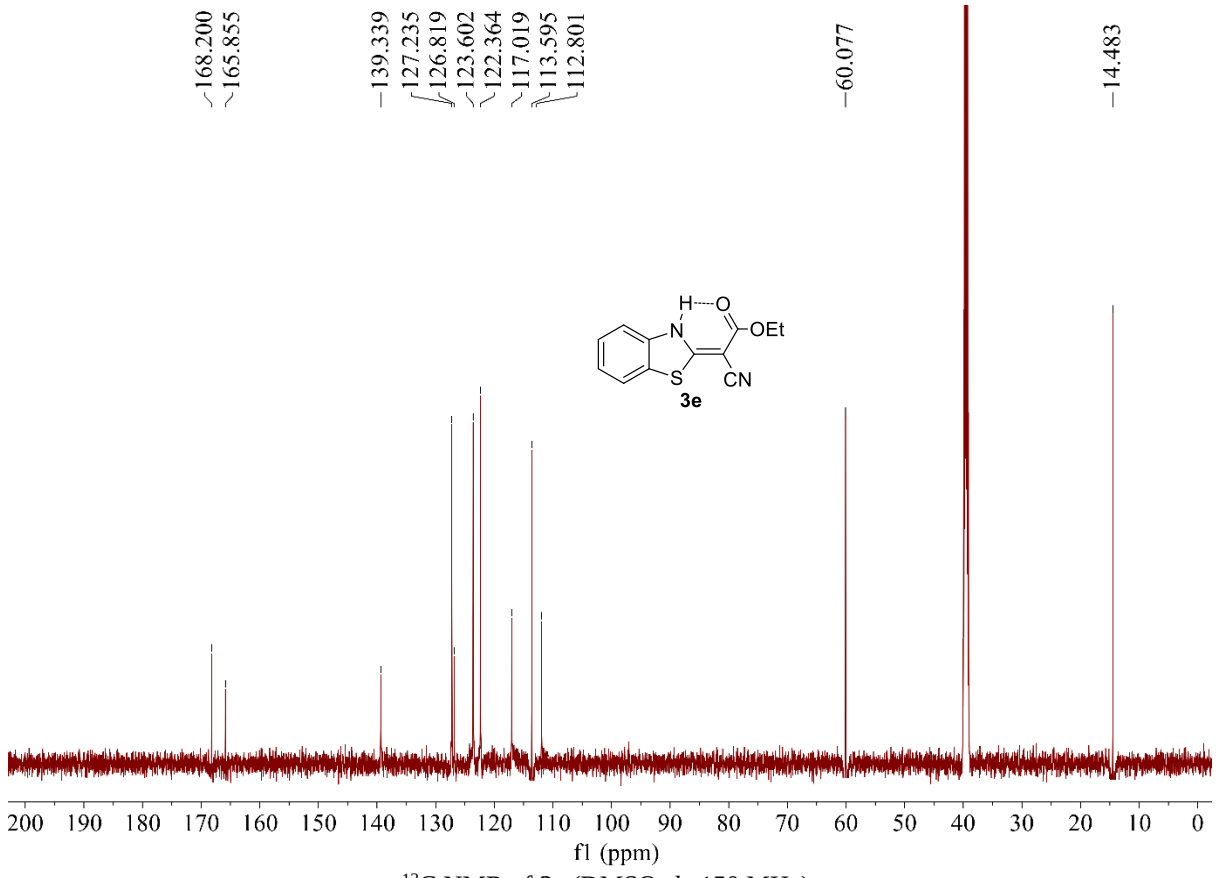
^{1}H NMR of **3d** ($CDCl_3$, 600 MHz)



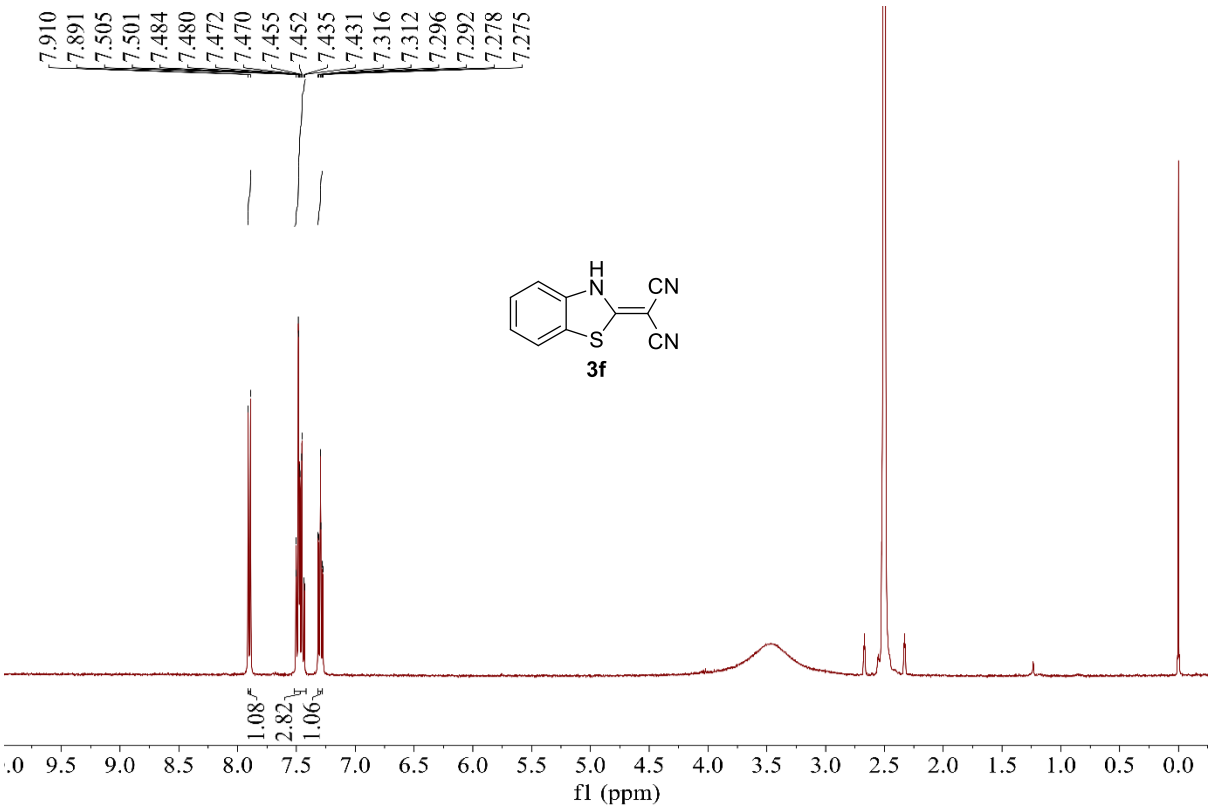
^{13}C NMR of **3d** ($CDCl_3$, 150 MHz)



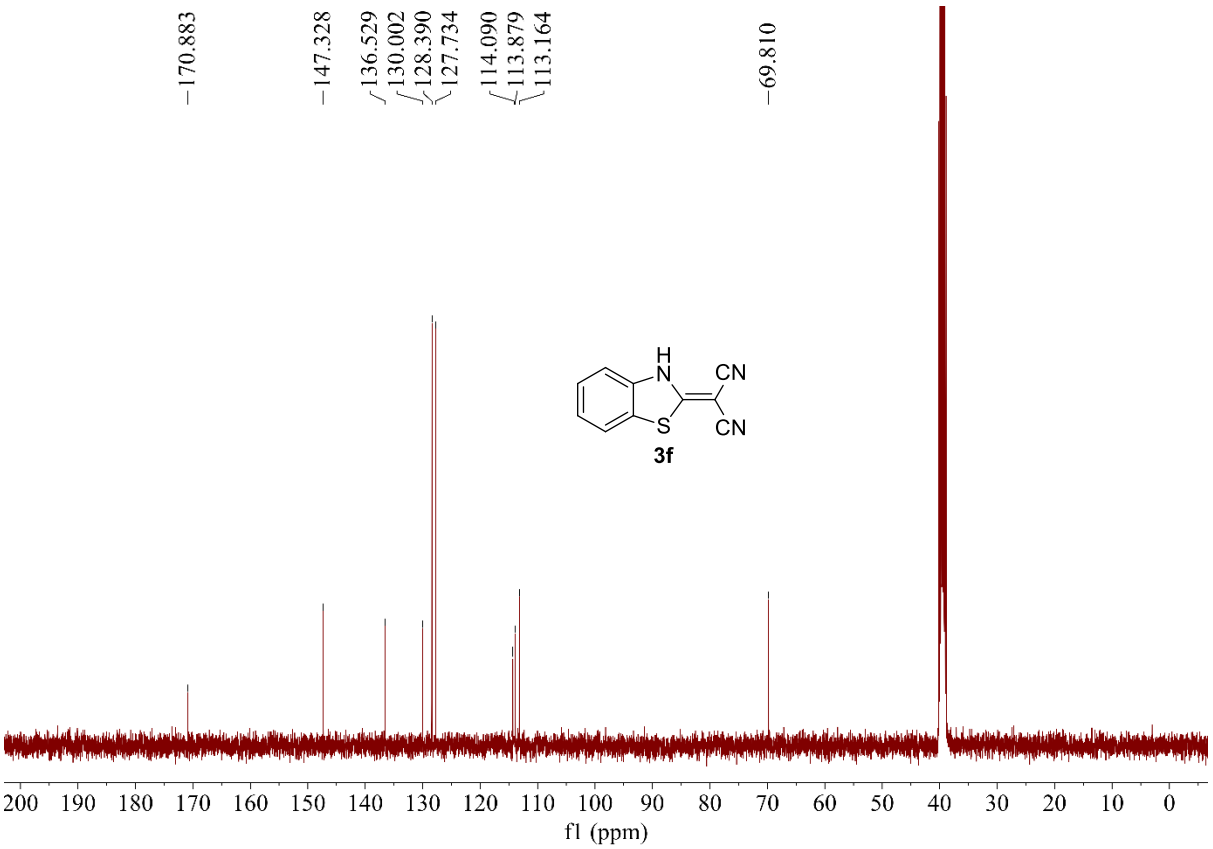
^{1}H NMR of **3e** (DMSO-d_6, 600 MHz)



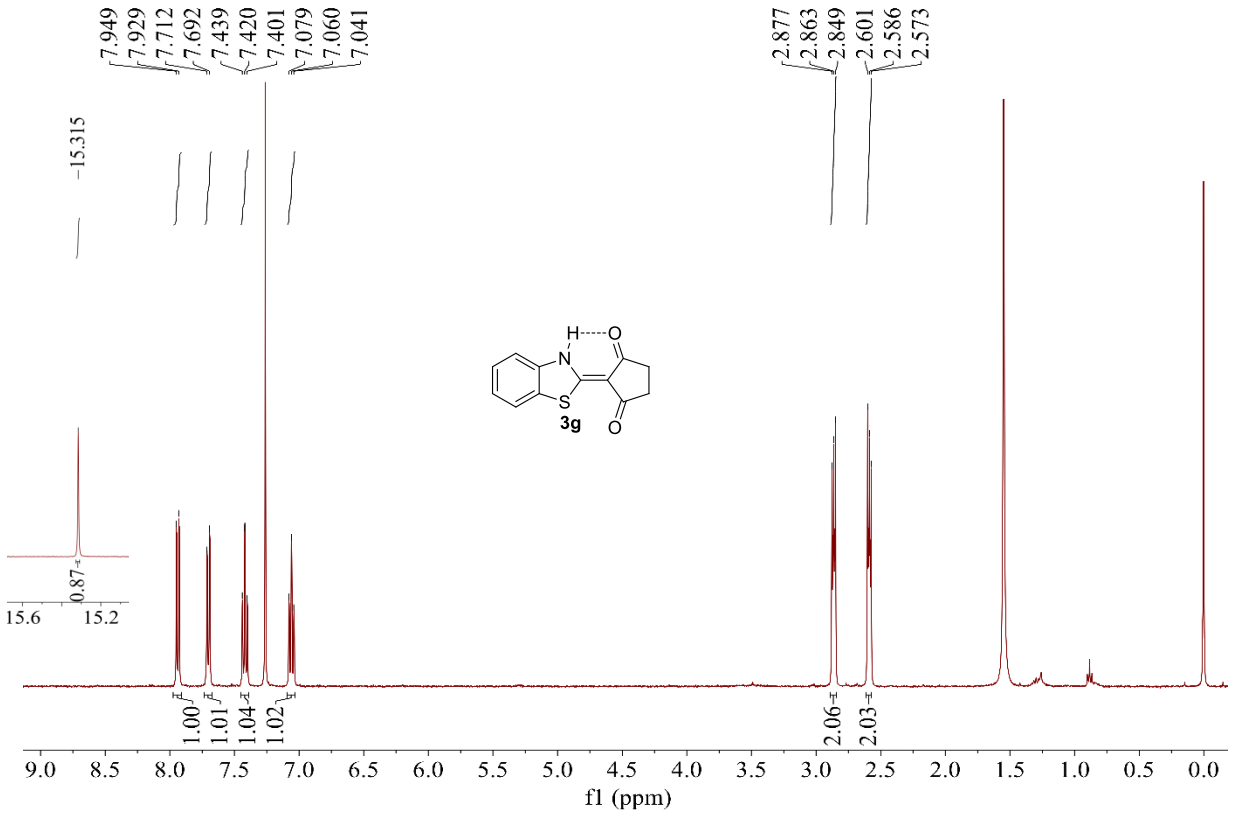
^{13}C NMR of **3e** (DMSO-d_6, 150 MHz)



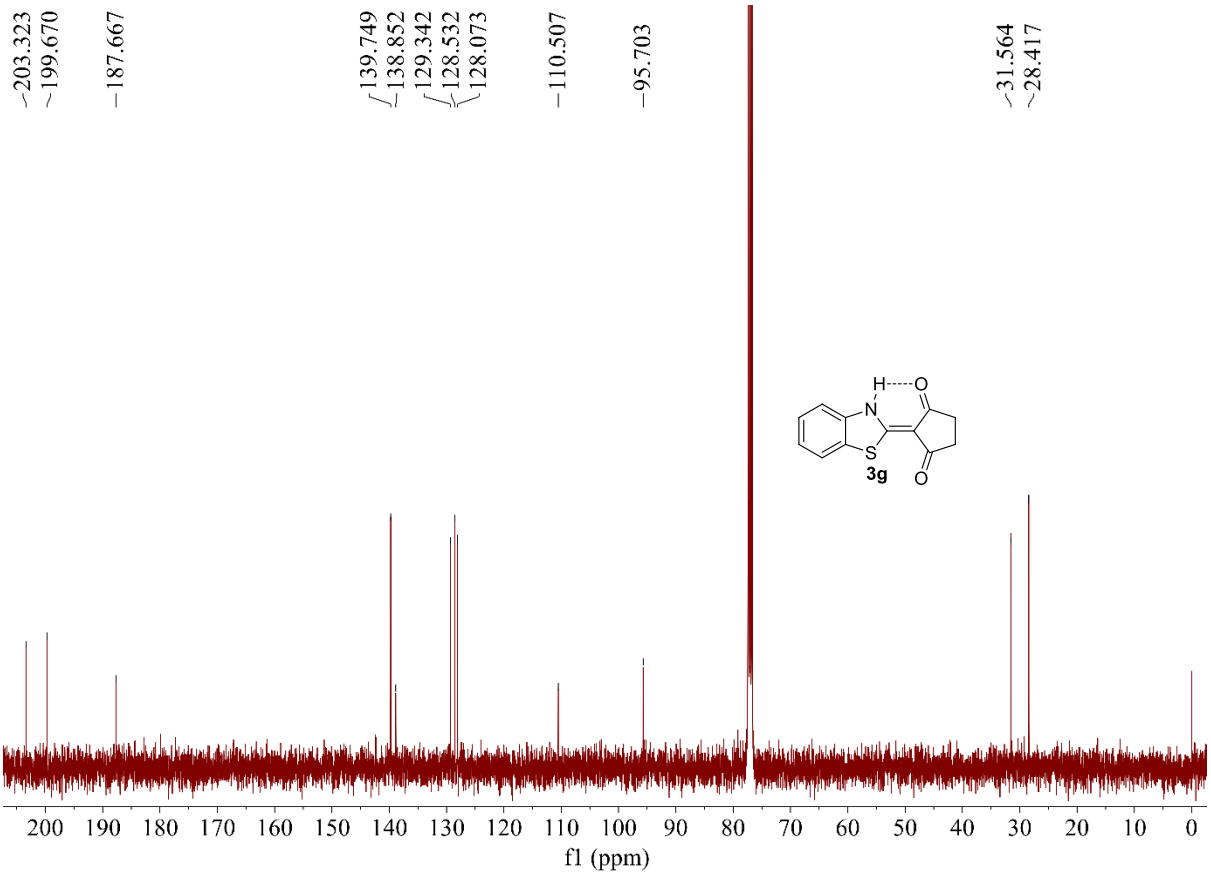
^{1}H NMR of **3f** (DMSO-d_6, 400 MHz)



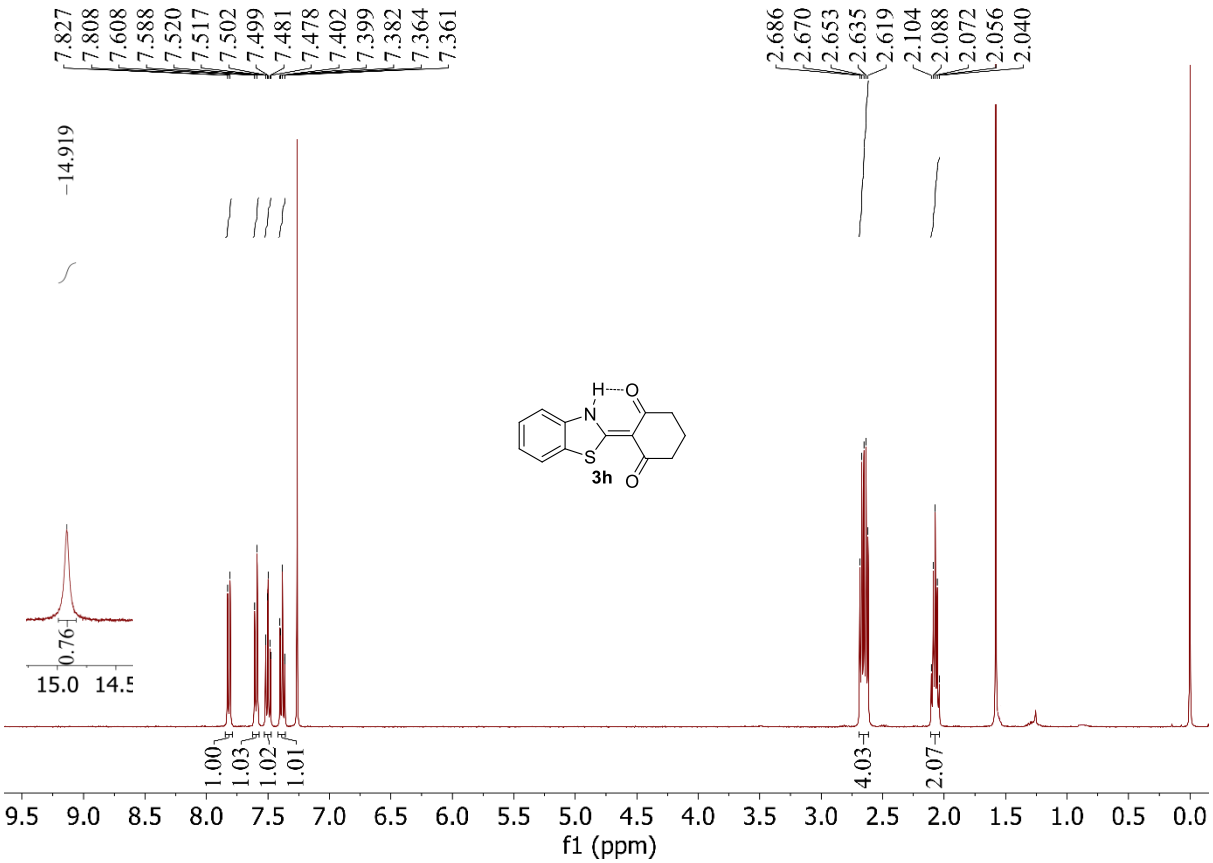
^{13}C NMR of **3f** (DMSO-d_6, 100 MHz)



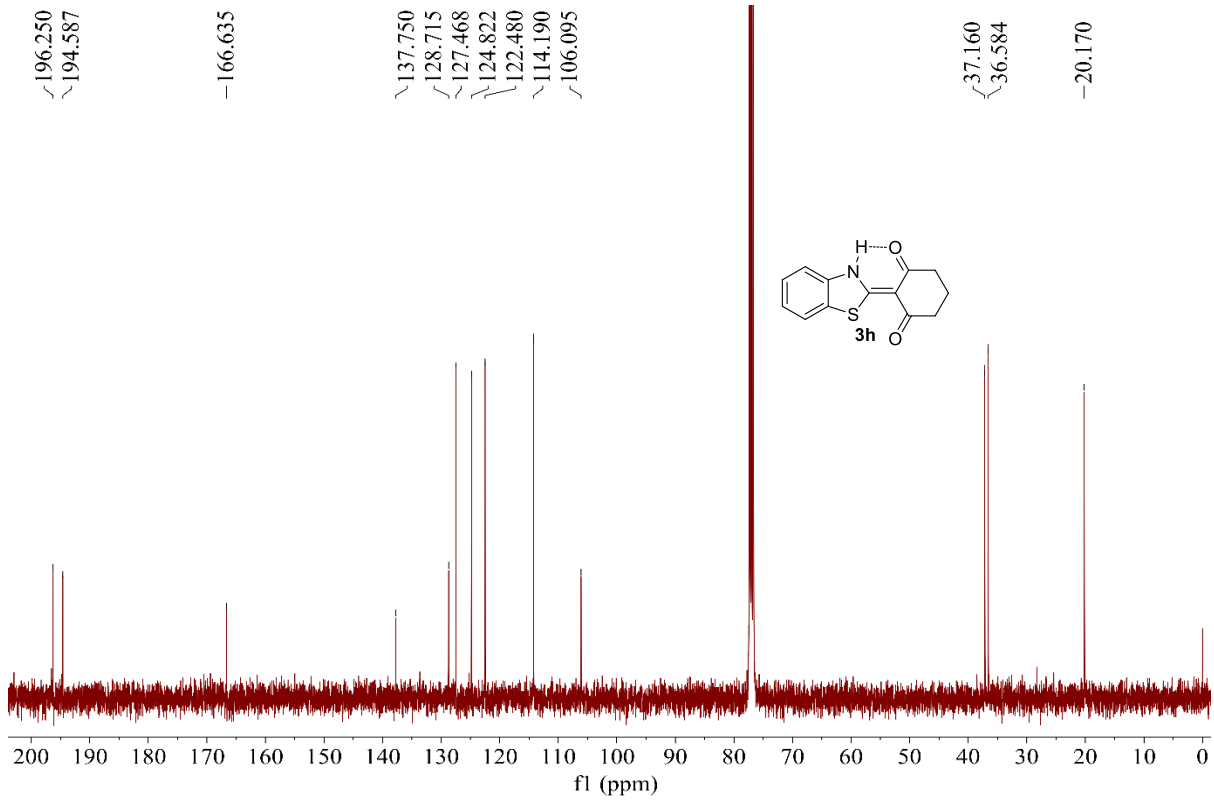
^{1}H NMR of **3g** ($CDCl_3$, 400 MHz)



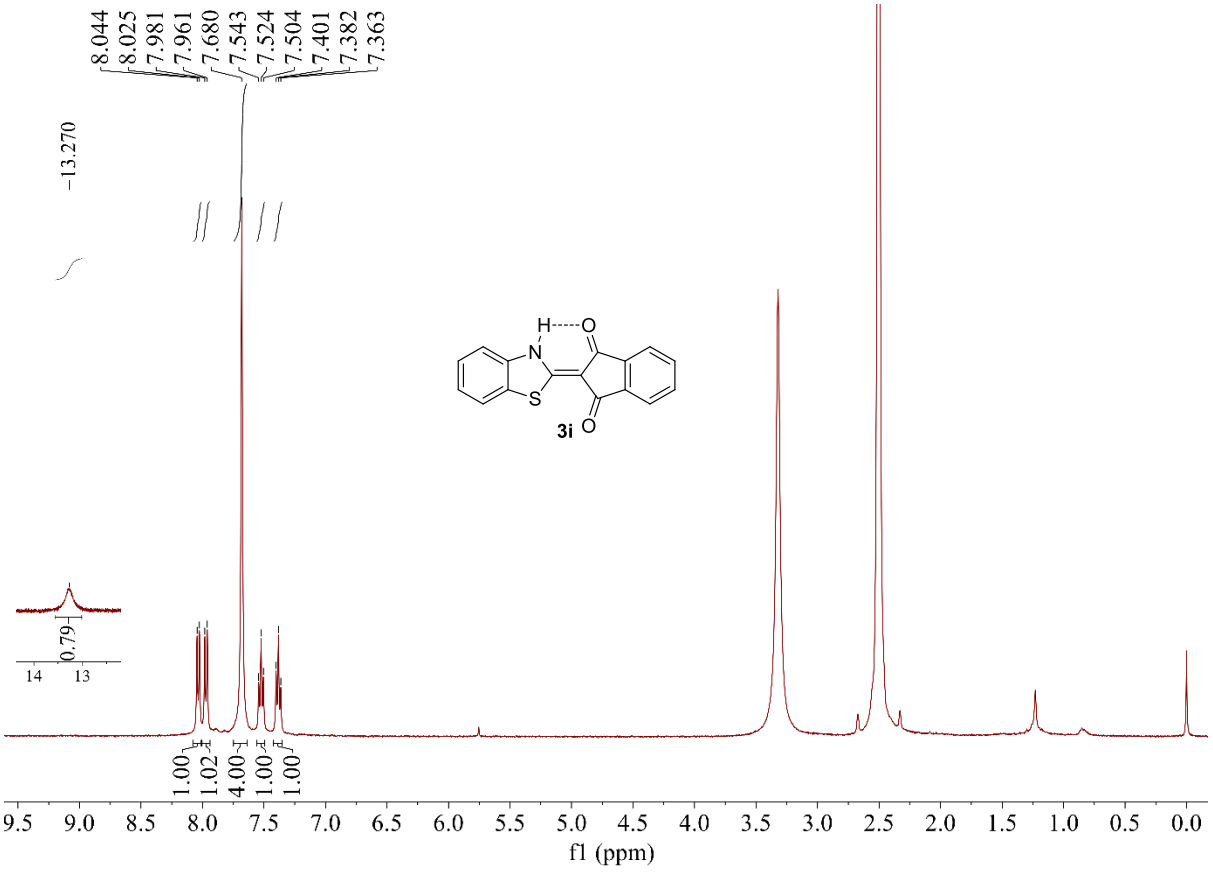
^{13}C NMR of **3g** ($CDCl_3$, 100 MHz)



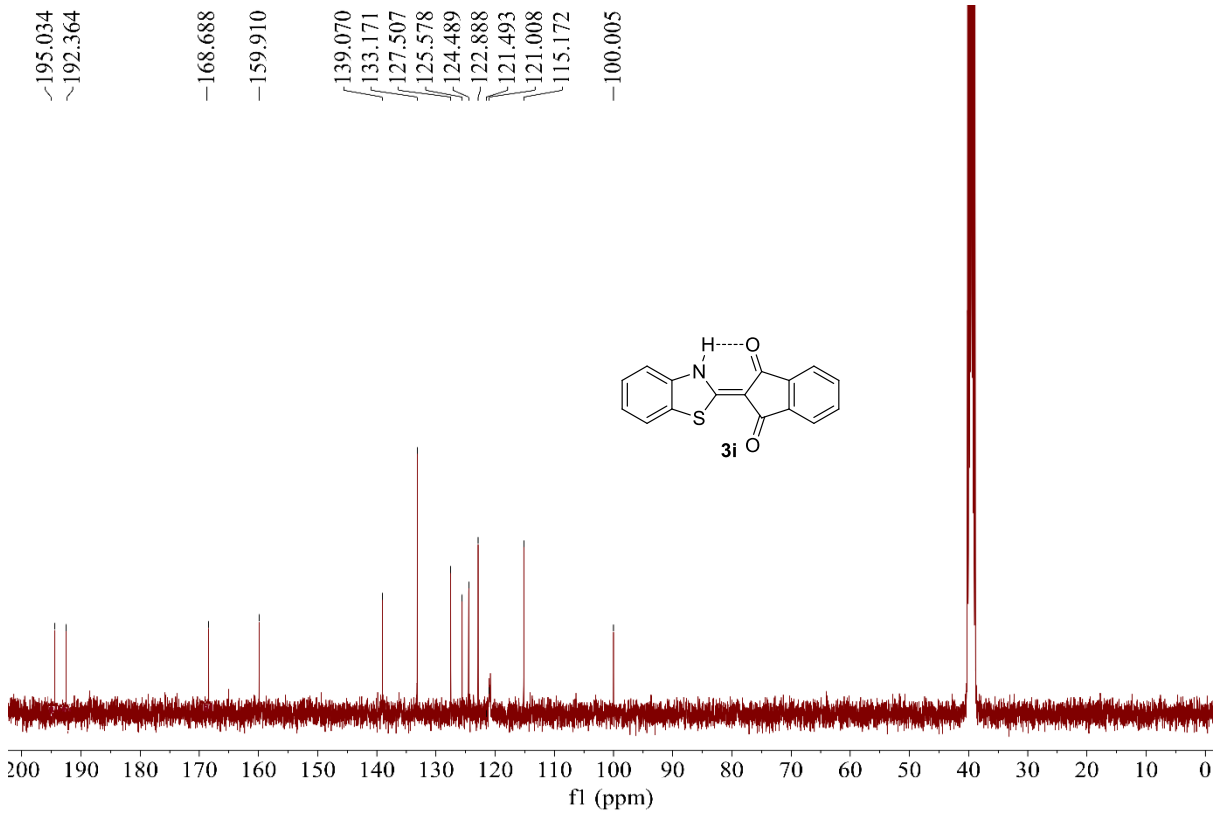
^{1}H NMR of **3h** ($CDCl_3$, 400 MHz)



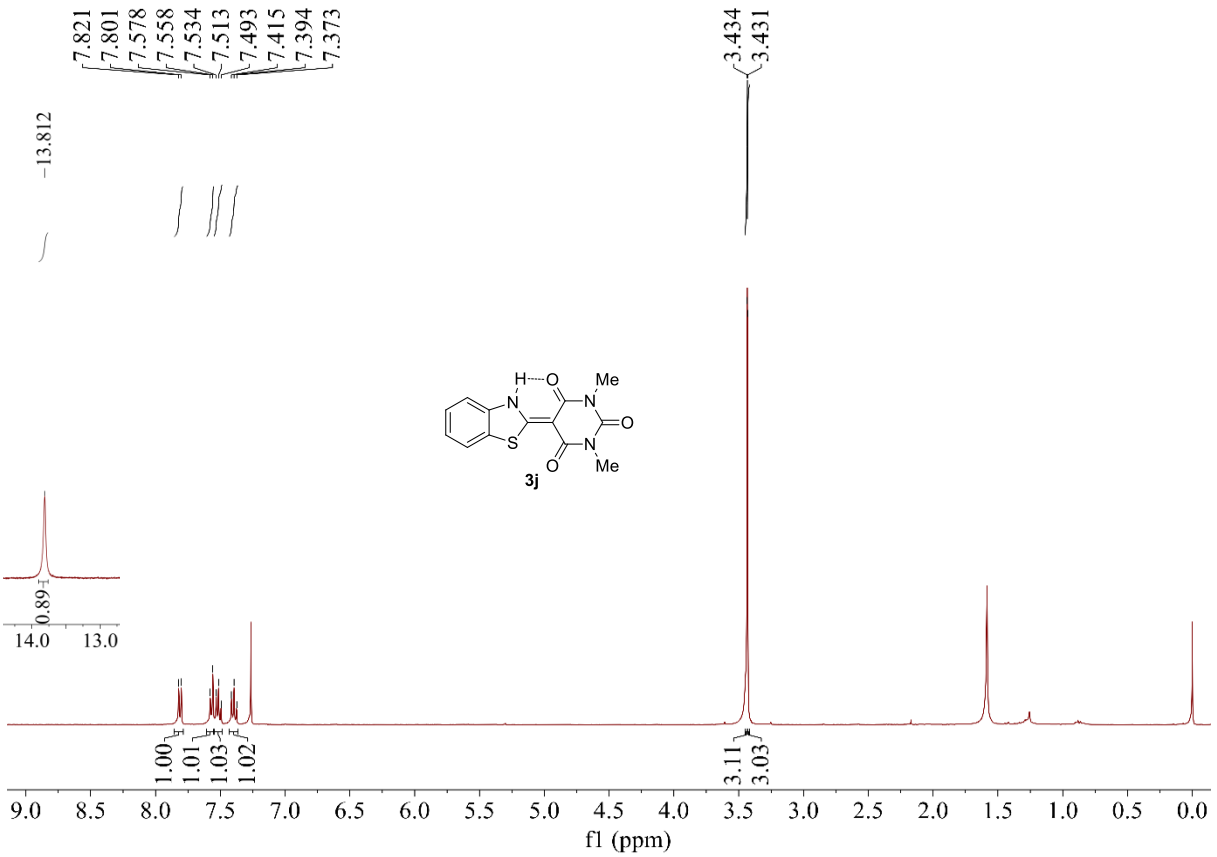
^{13}C NMR of **3h** ($CDCl_3$, 100 MHz)



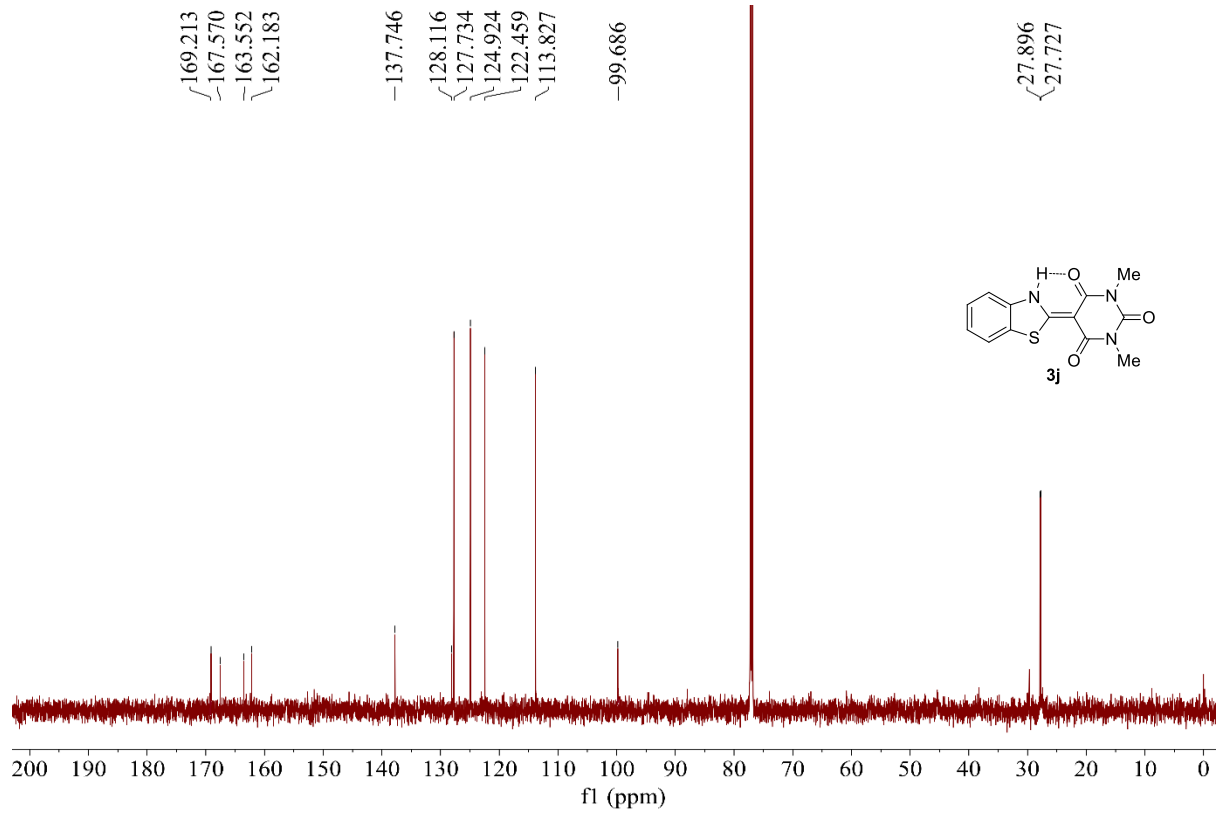
^{1}H NMR of **3i** (DMSO-d_6, 400 MHz)



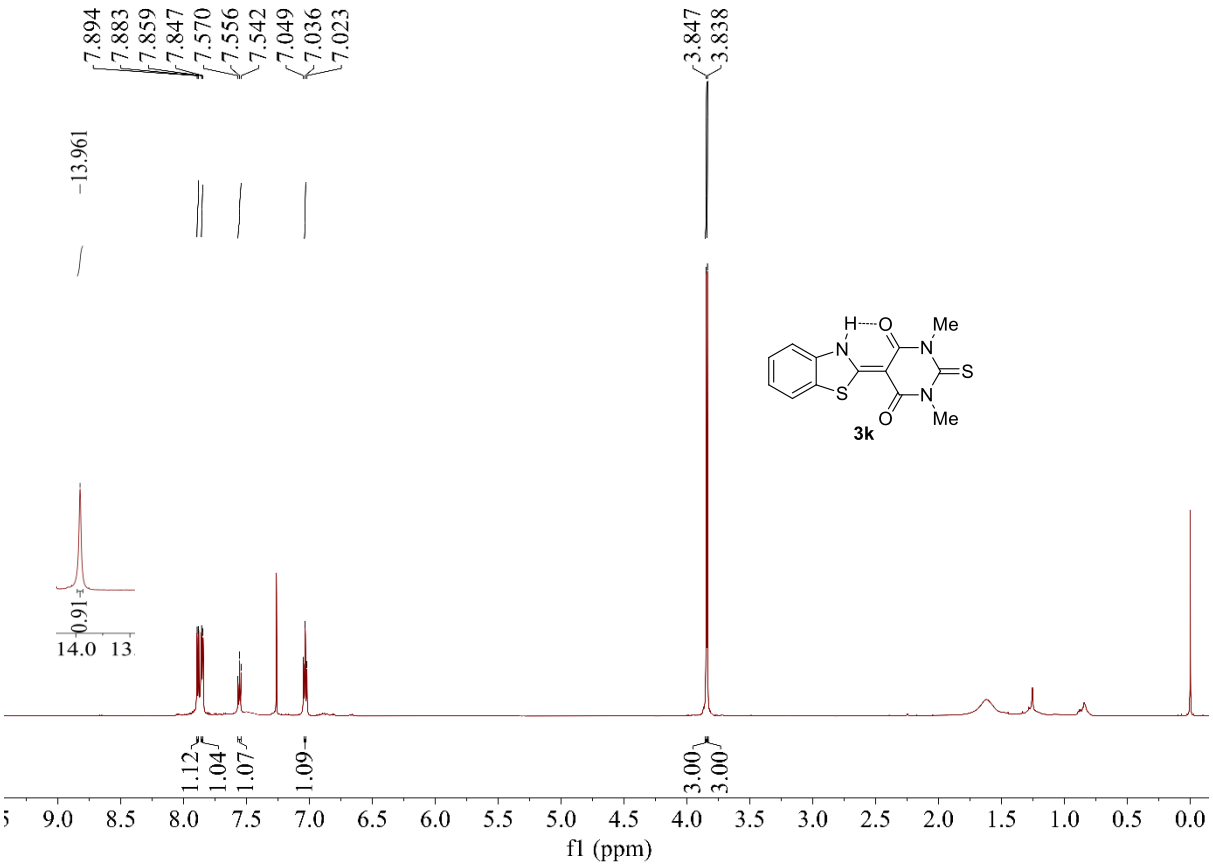
^{13}C NMR of **3i** (DMSO-d_6, 100 MHz)



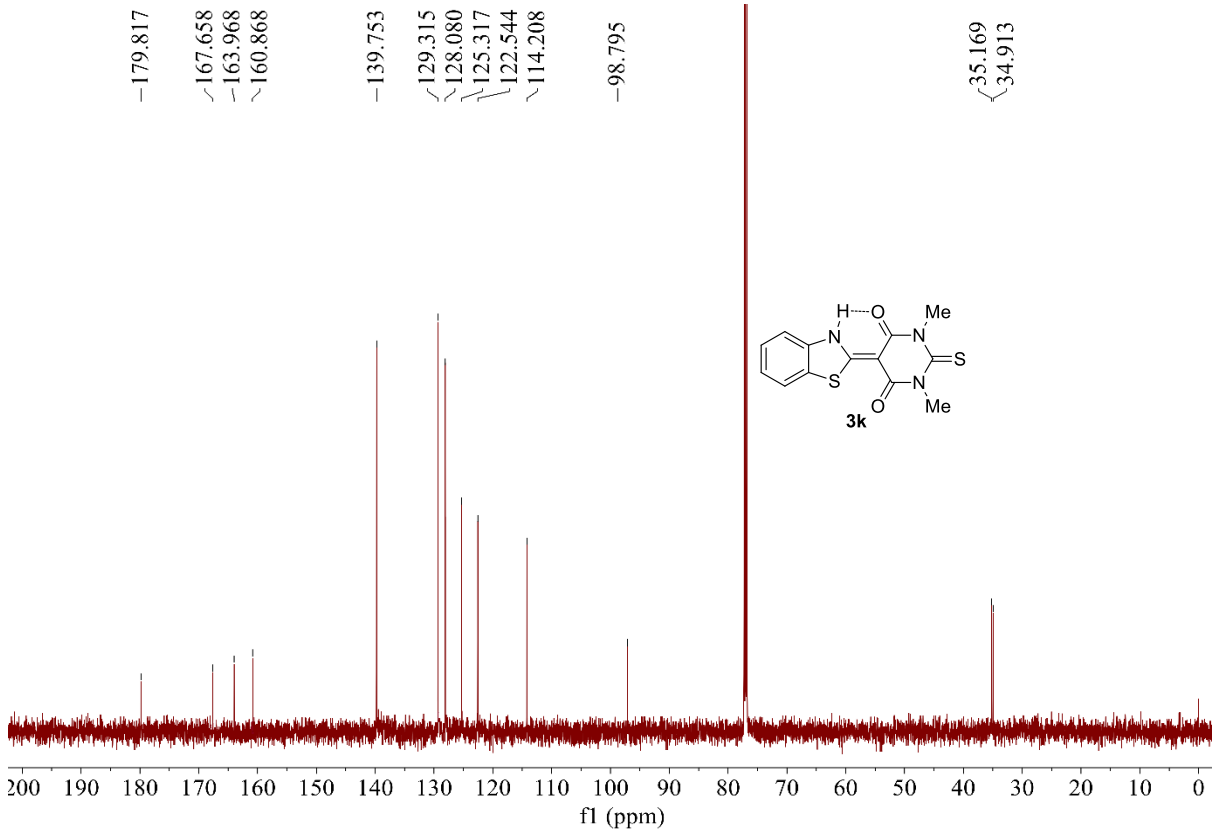
^{1}H NMR of **3j** ($CDCl_3$, 400 MHz)



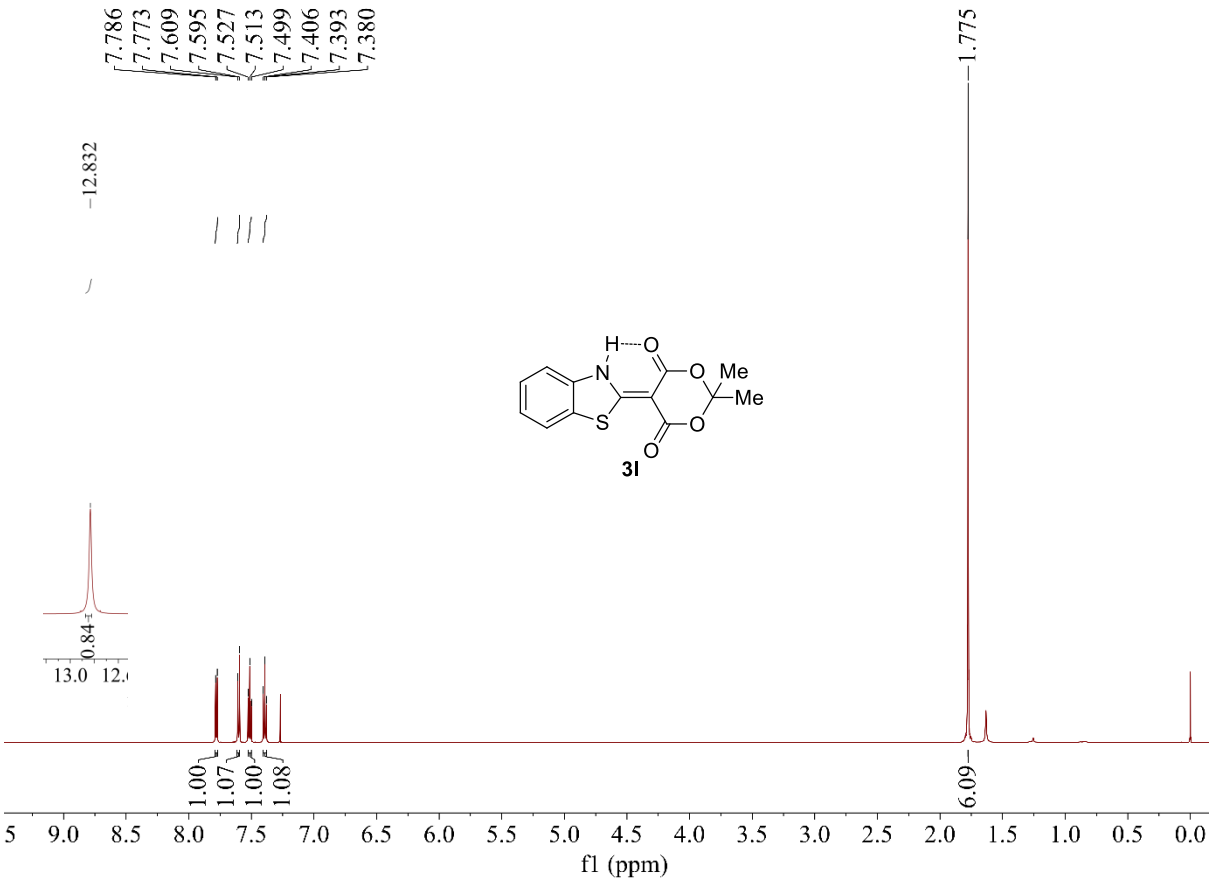
^{13}C NMR of **3j** ($CDCl_3$, 100 MHz)



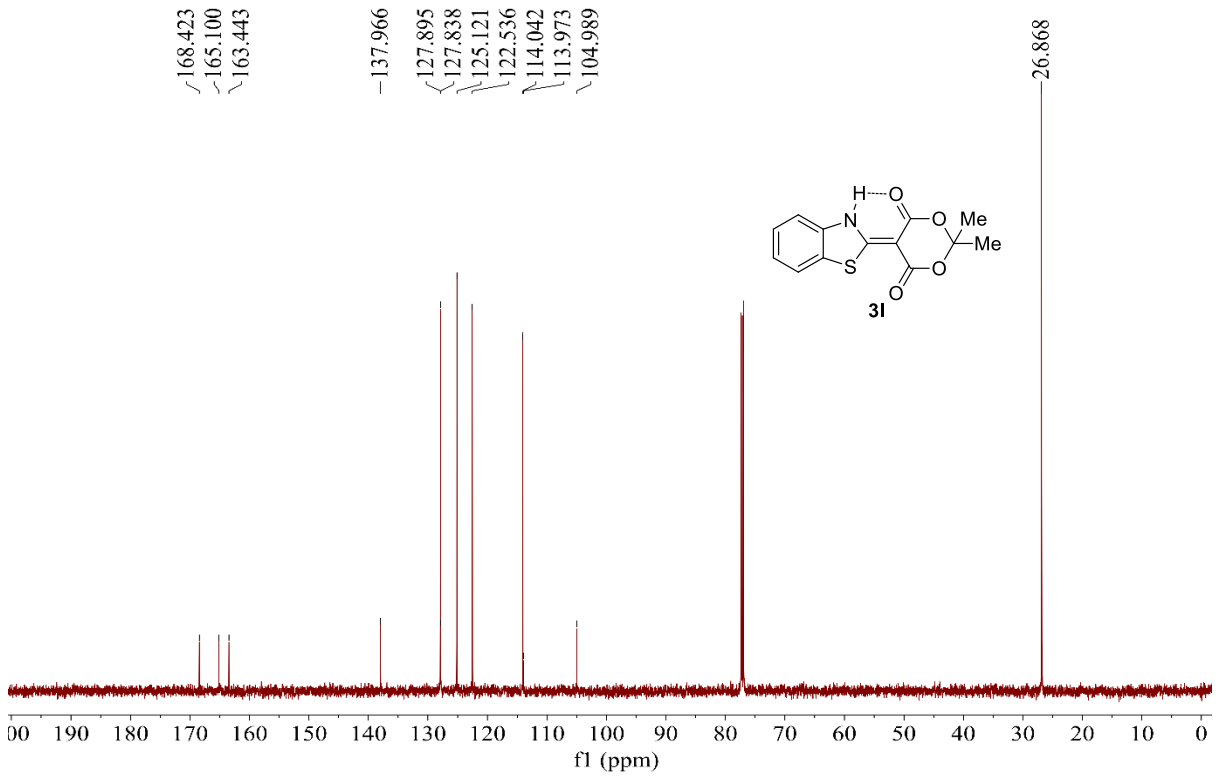
^{1}H NMR of **3k** ($CDCl_3$, 600 MHz)



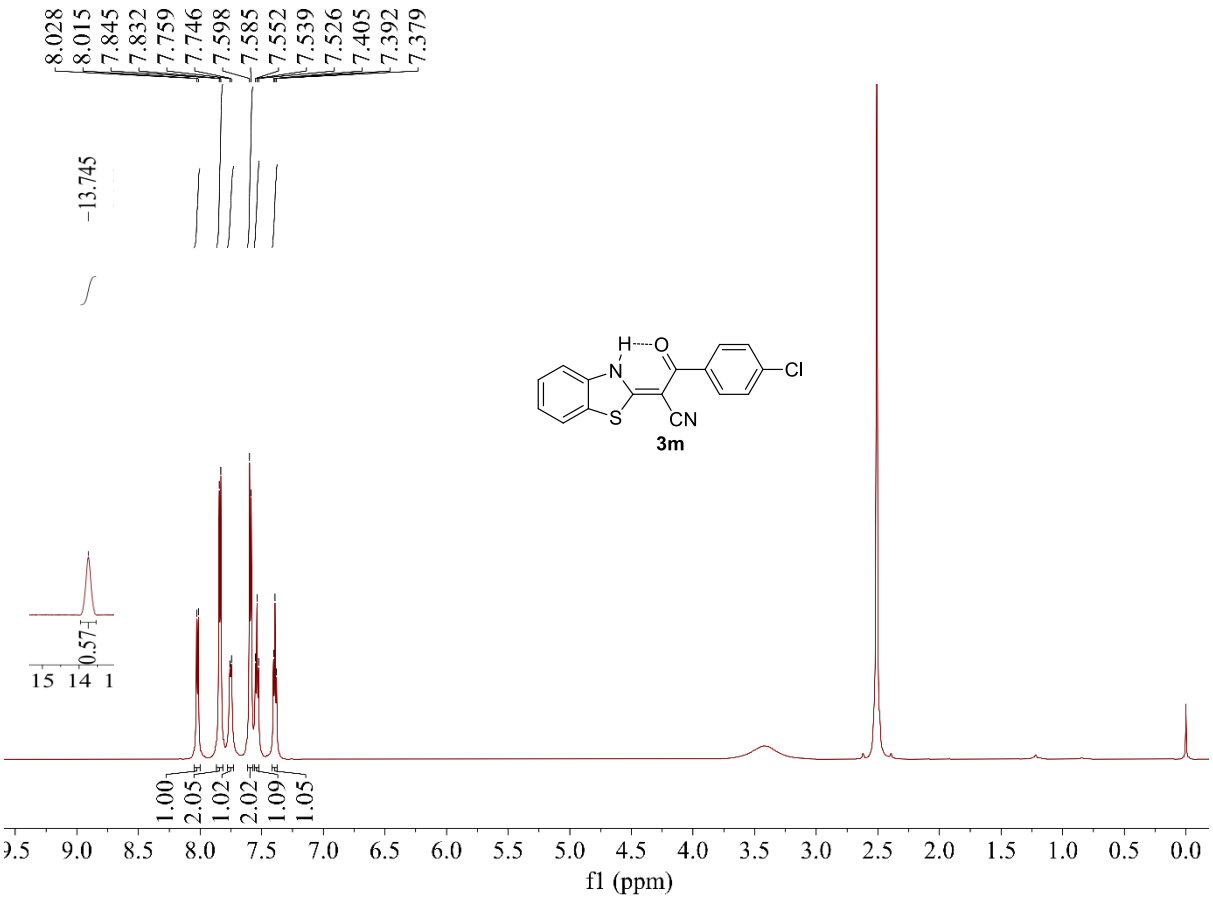
^{13}C NMR of **3k** ($CDCl_3$, 150 MHz)



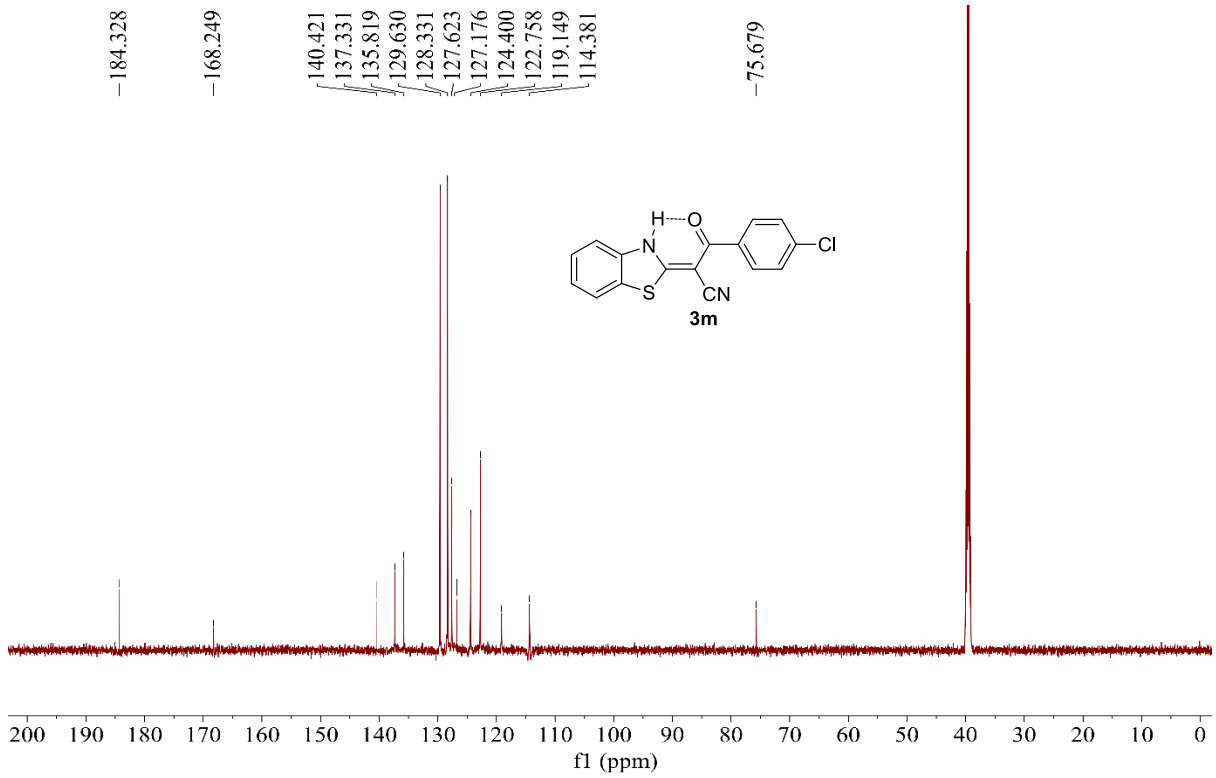
^{1}H NMR of **3l** ($CDCl_3$, 600 MHz)



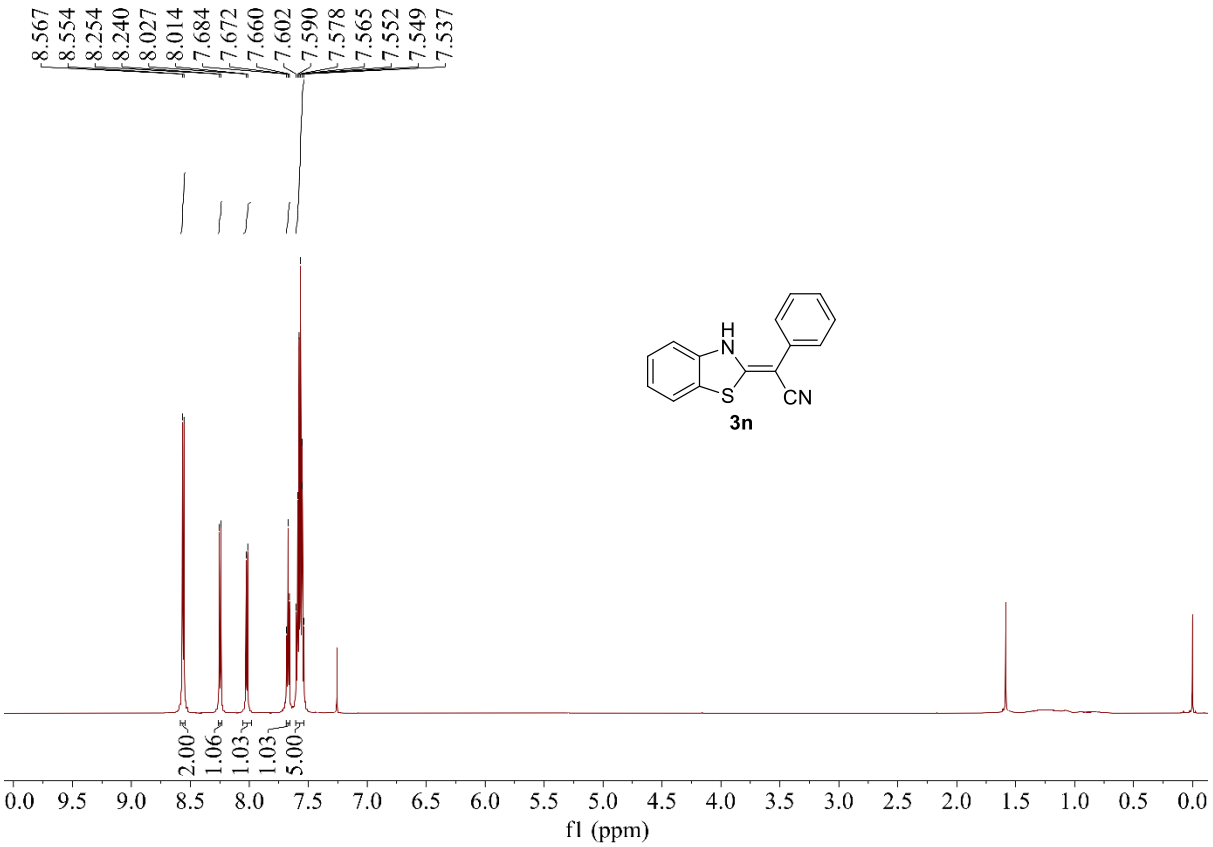
^{13}C NMR of **3l** ($CDCl_3$, 150 MHz)



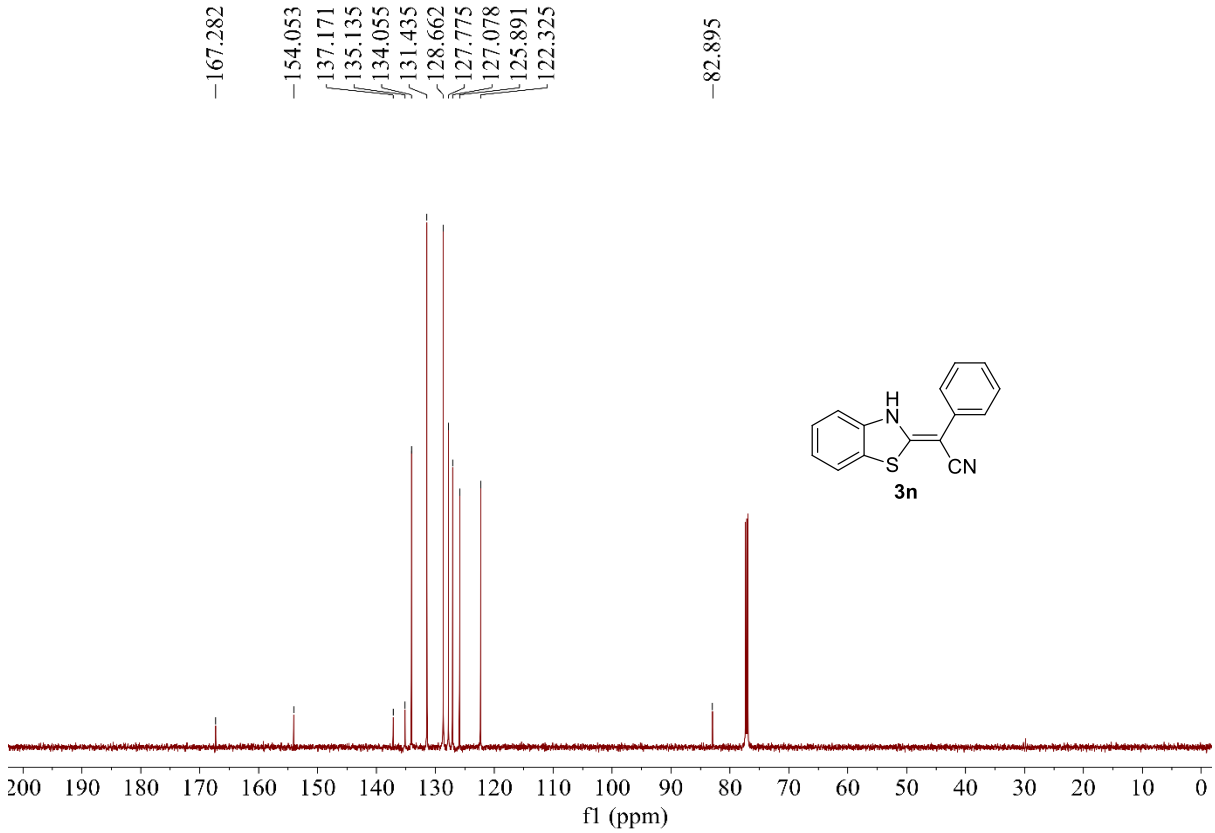
^{1}H NMR of **3m** (DMSO-d_6, 600 MHz)



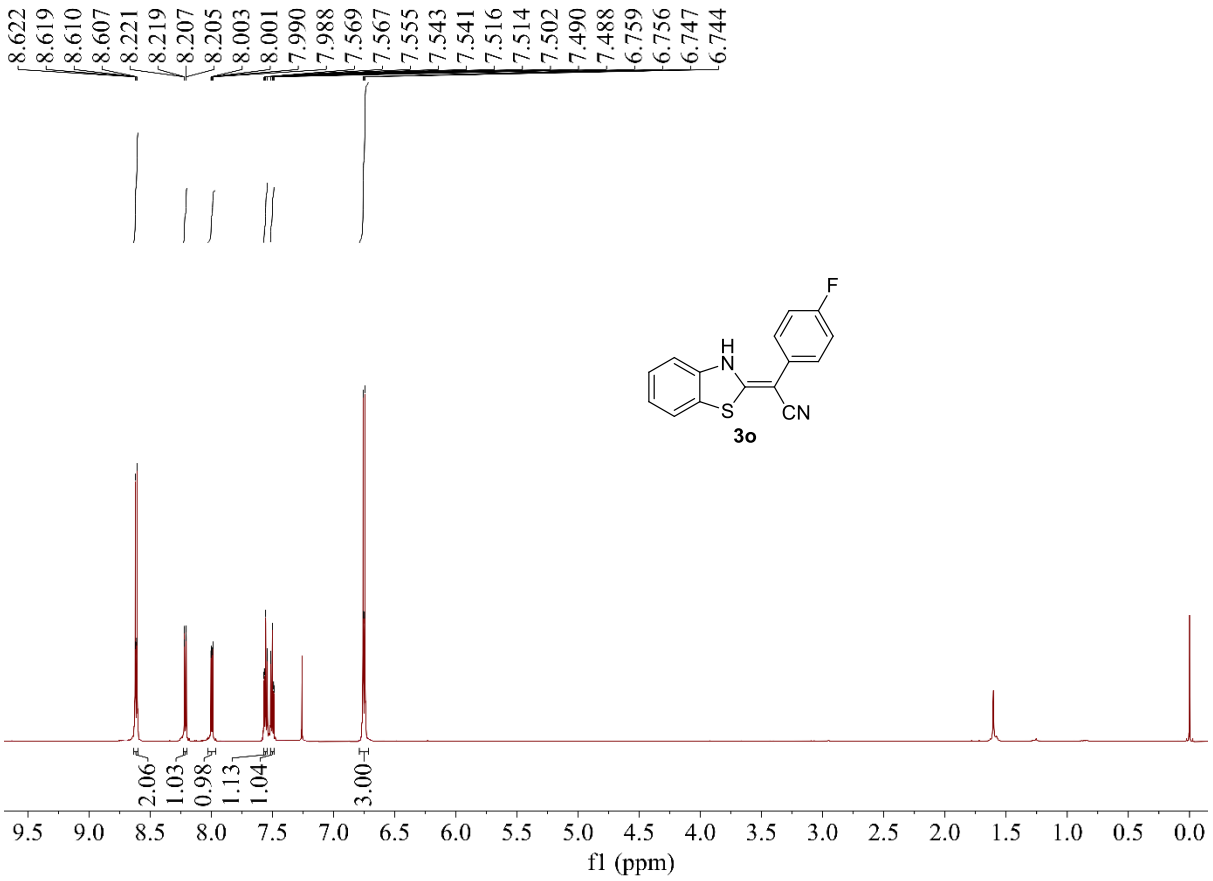
^{13}C NMR of **3m** (DMSO-d_6, 150 MHz)



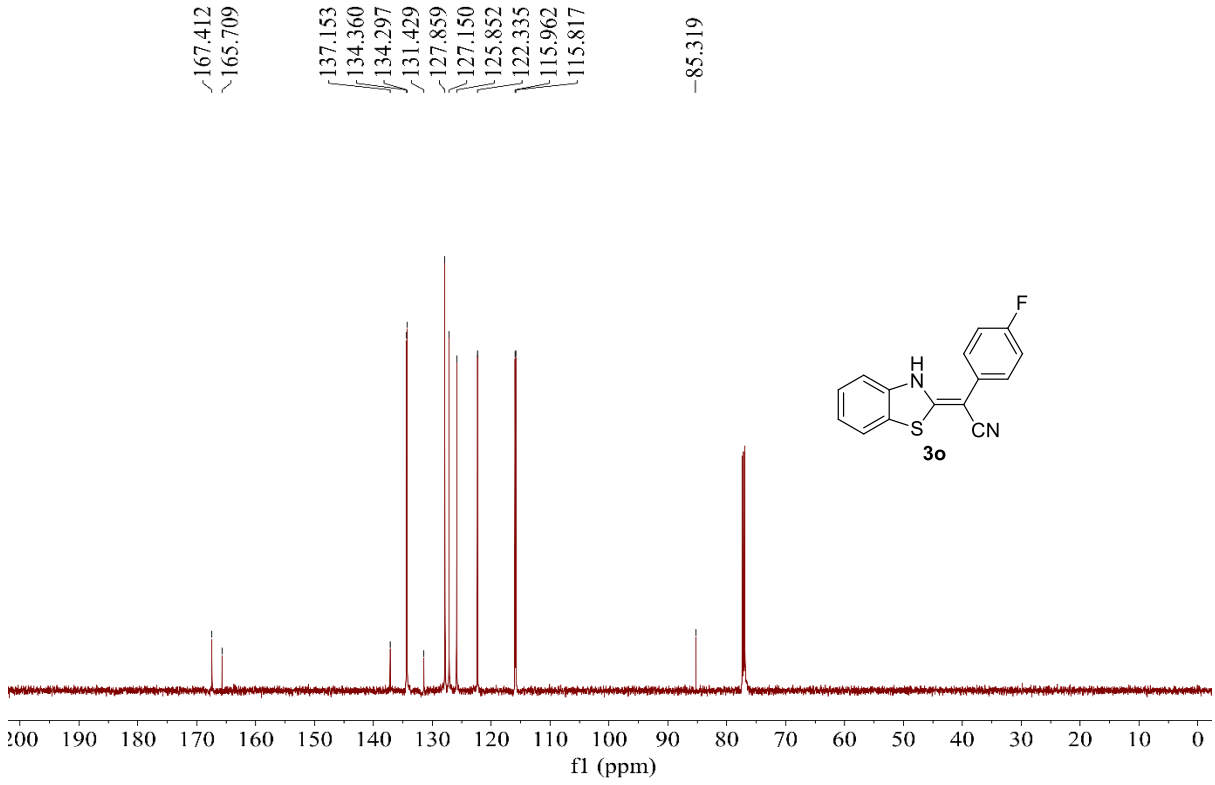
^{1}H NMR of **3n** ($CDCl_3$, 600 MHz)



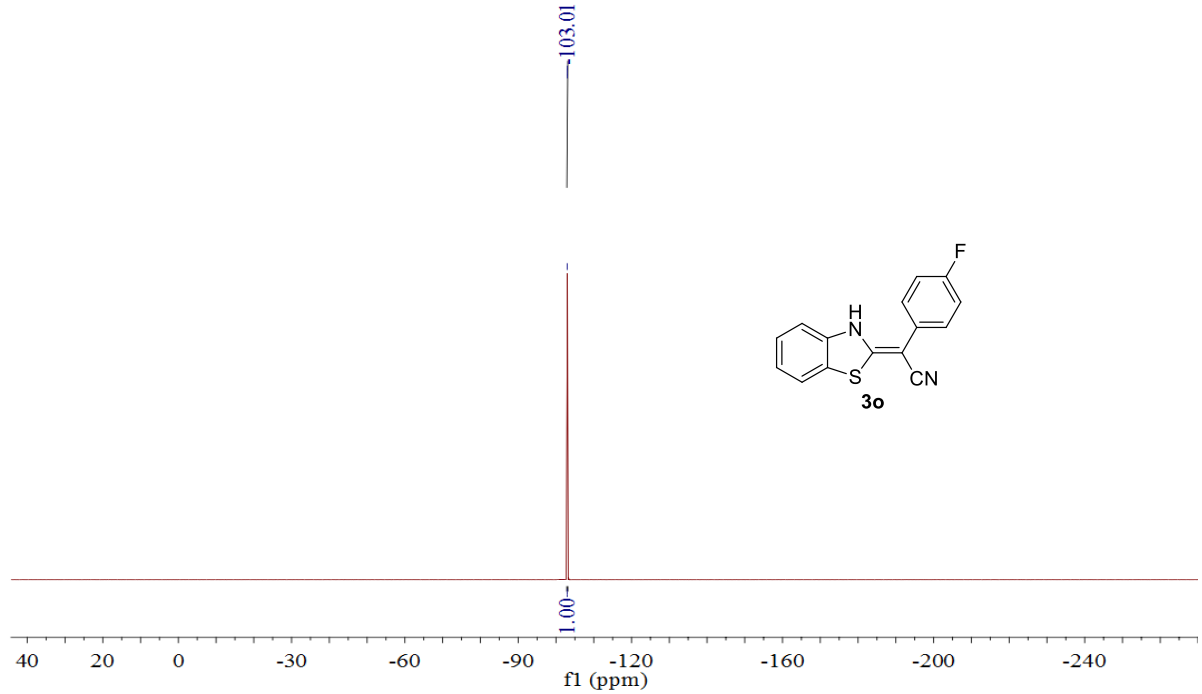
^{13}C NMR of **3n** ($CDCl_3$, 150 MHz)



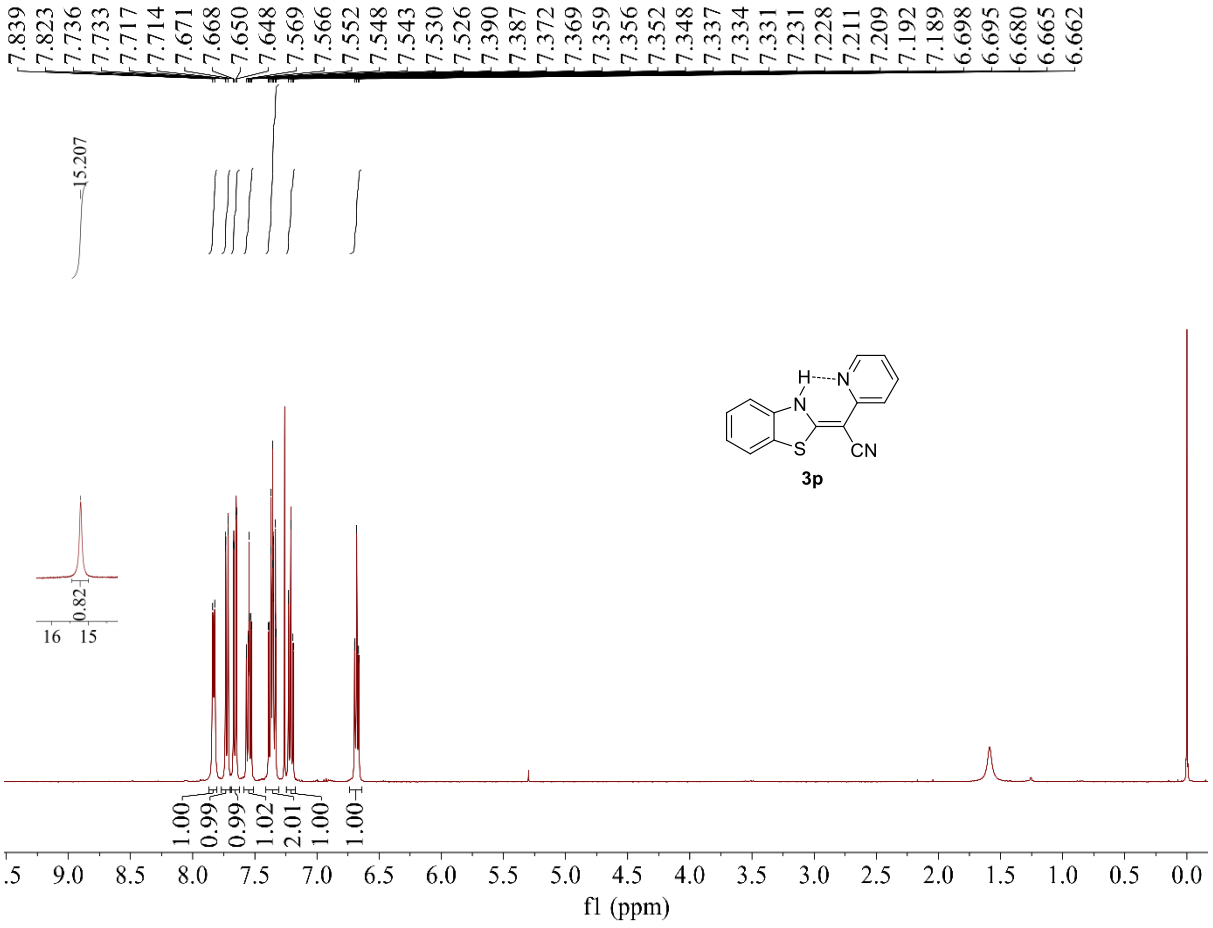
^{1}H NMR of **3o** ($CDCl_3$, 600 MHz)



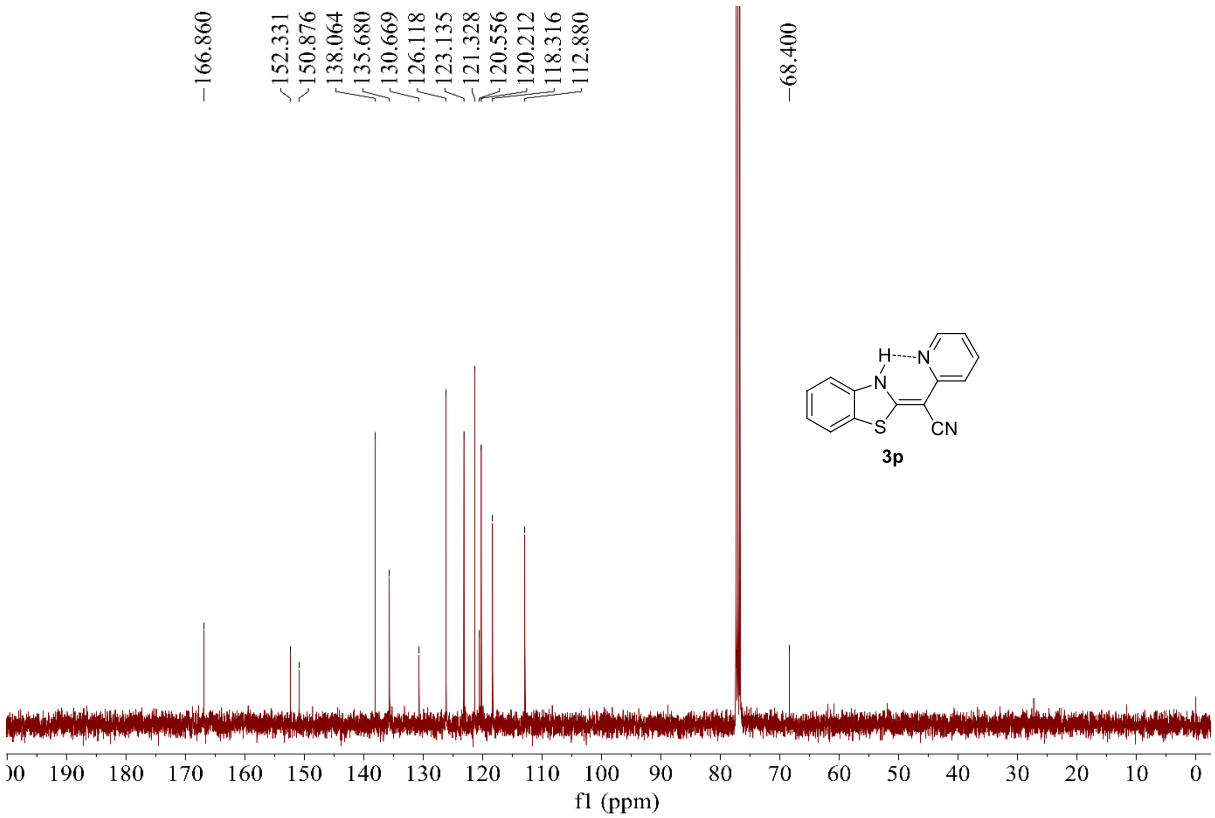
^{13}C NMR of **3o** ($CDCl_3$, 150 MHz)



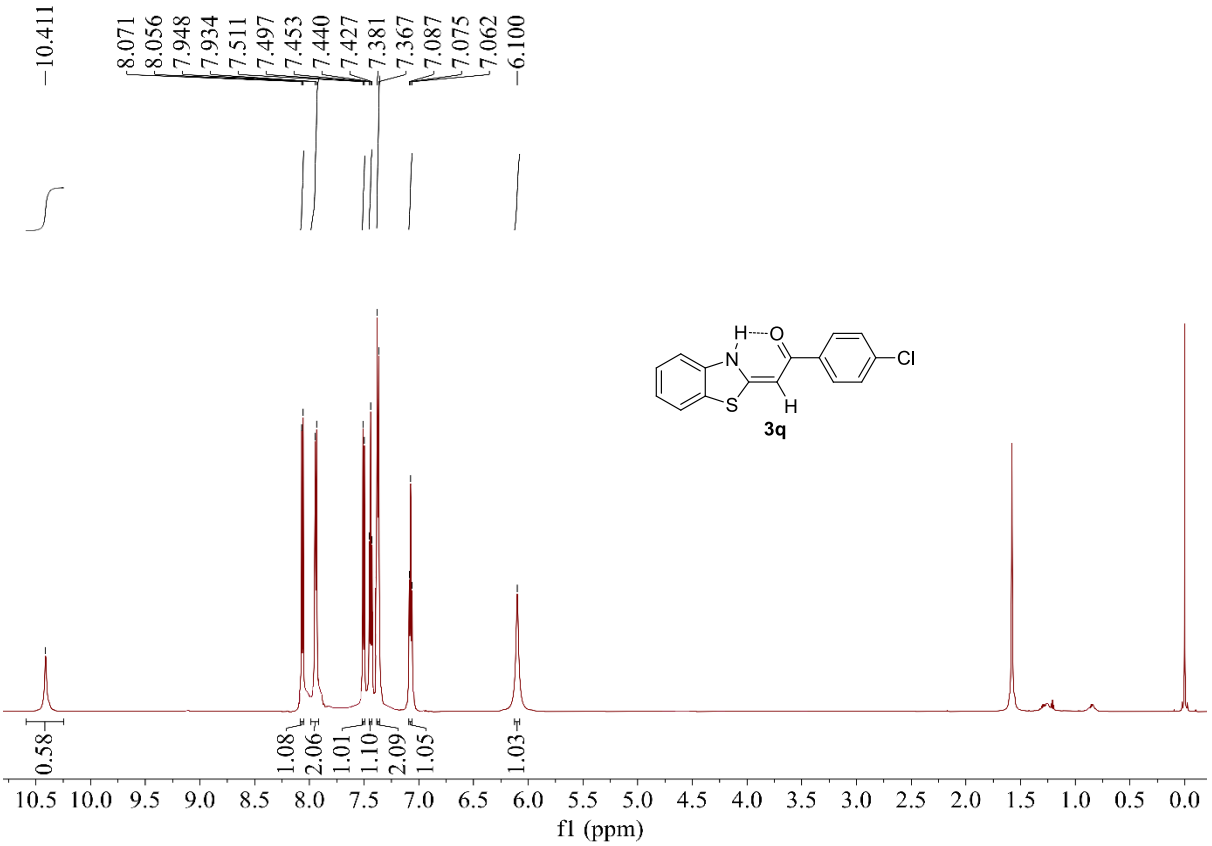
^{19}F NMR of **3o** ($CDCl_3$, 564.65 MHz)



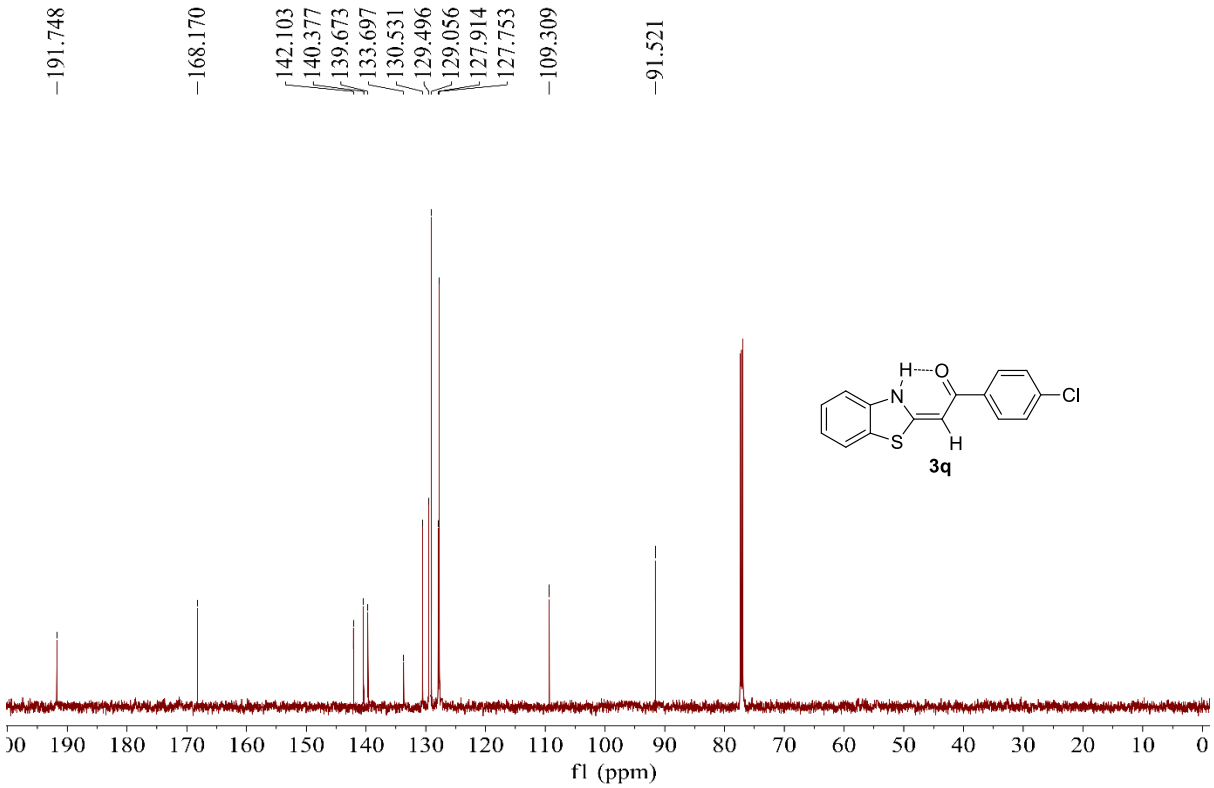
^{1}H NMR of **3p** ($CDCl_3$, 400 MHz)



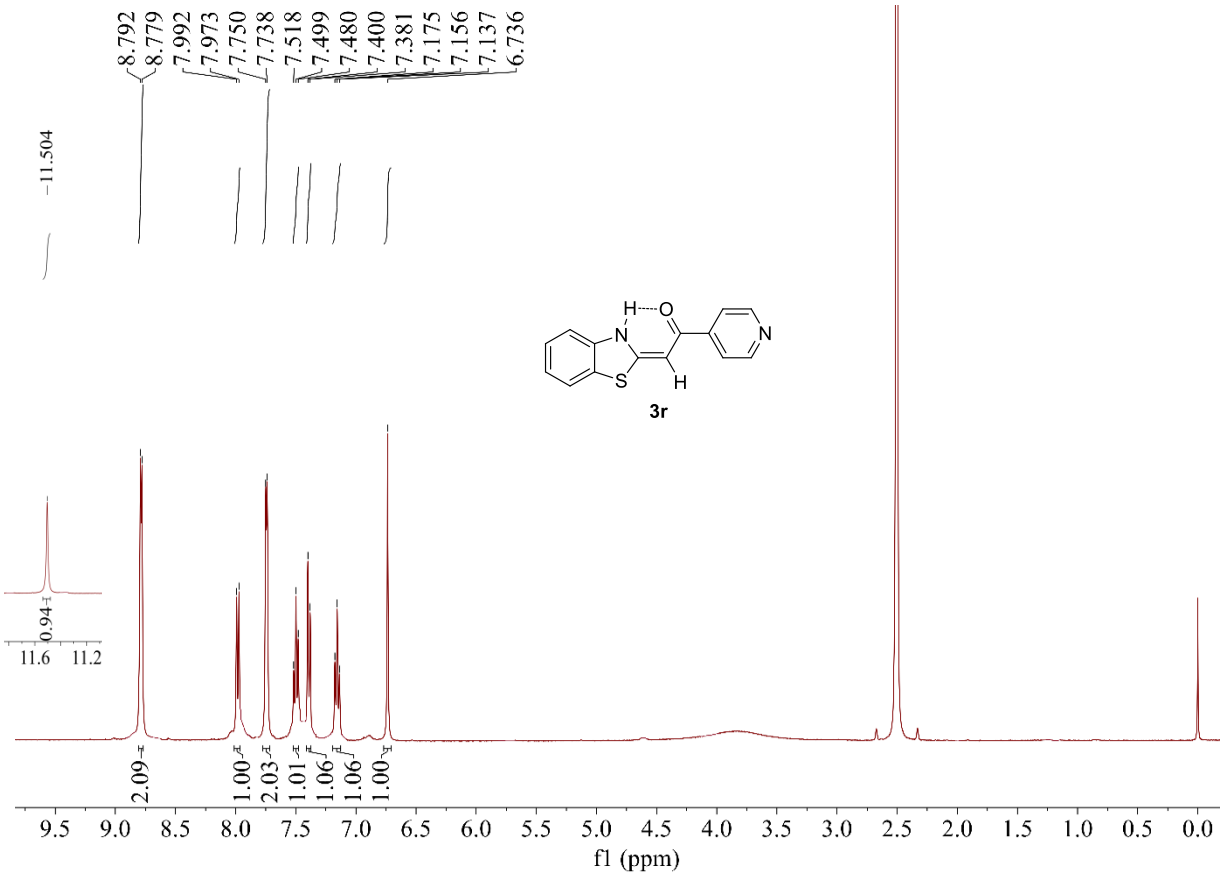
^{13}C NMR of **3p** ($CDCl_3$, 100 MHz)



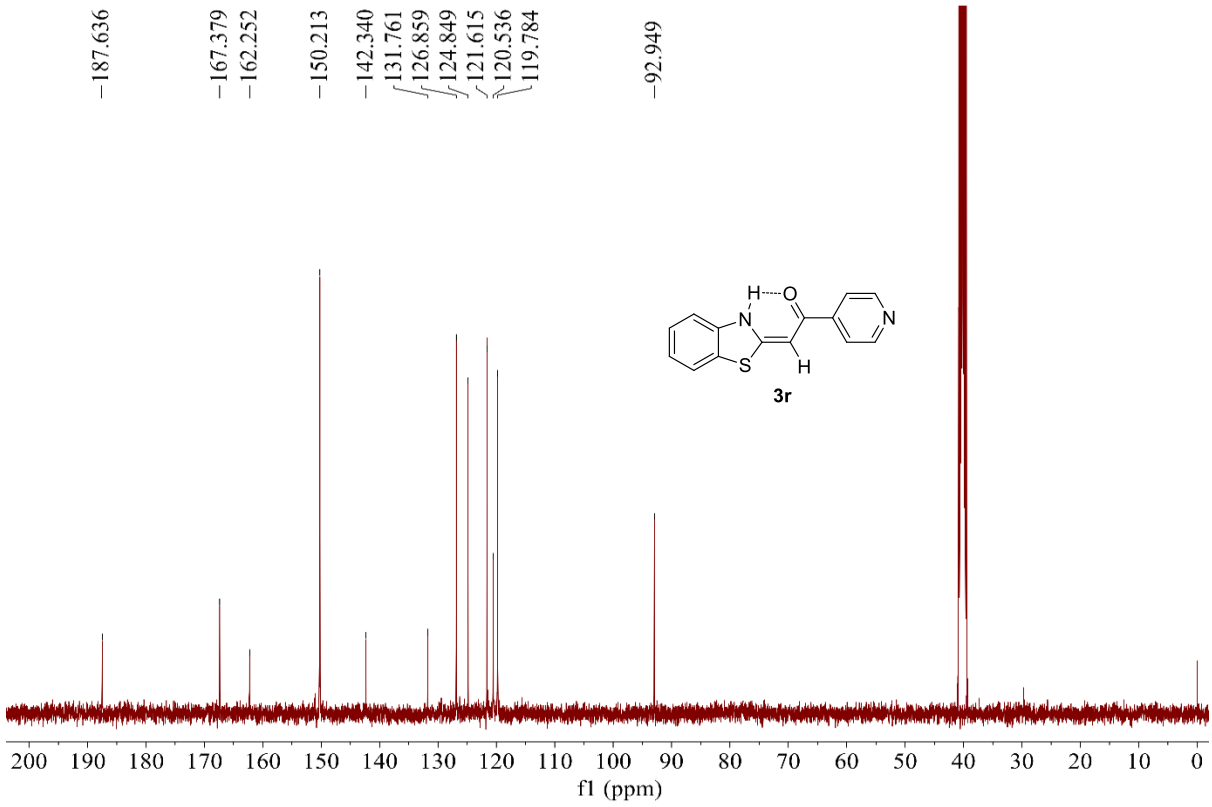
^{1}H NMR of **3q** ($CDCl_3$, 600 MHz)



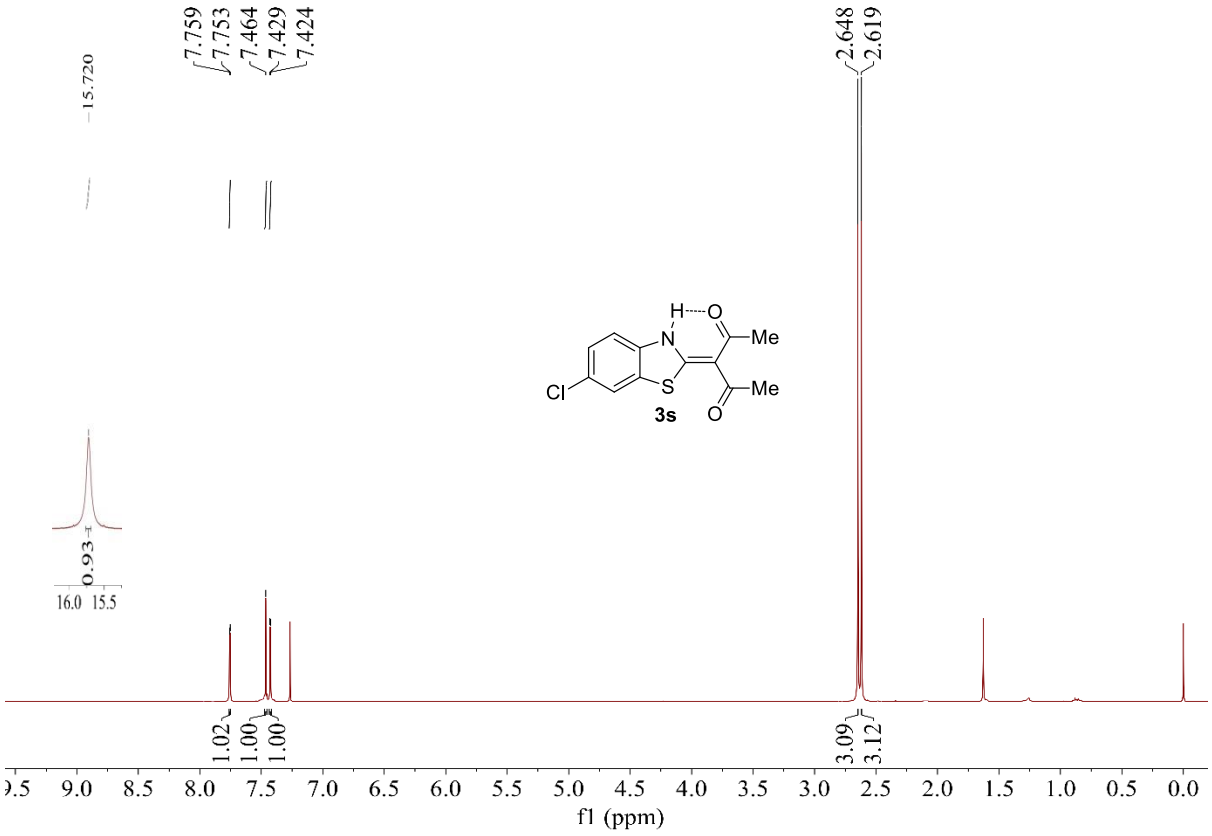
^{13}C NMR of **3q** ($CDCl_3$, 150 MHz)



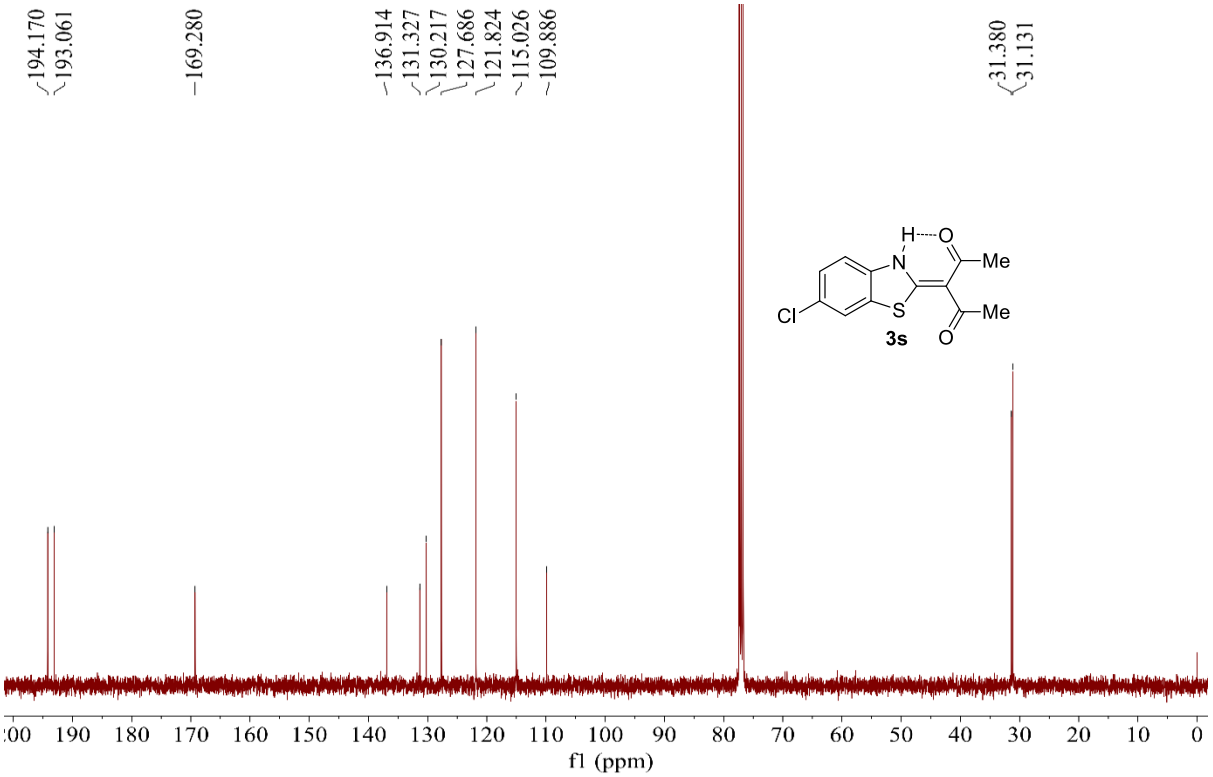
^{1}H NMR of **3r** (DMSO-d_6, 400 MHz)



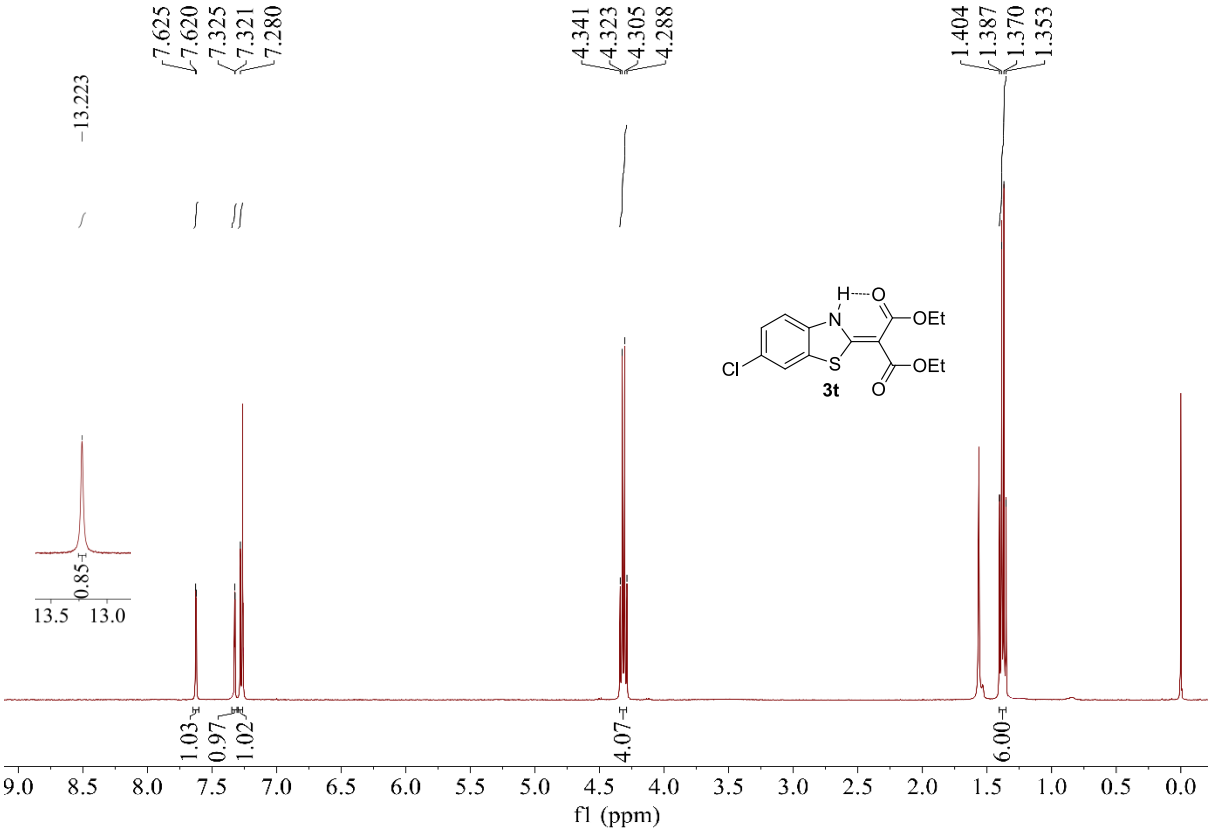
^{13}C NMR of **3r** (DMSO-d_6, 100 MHz)



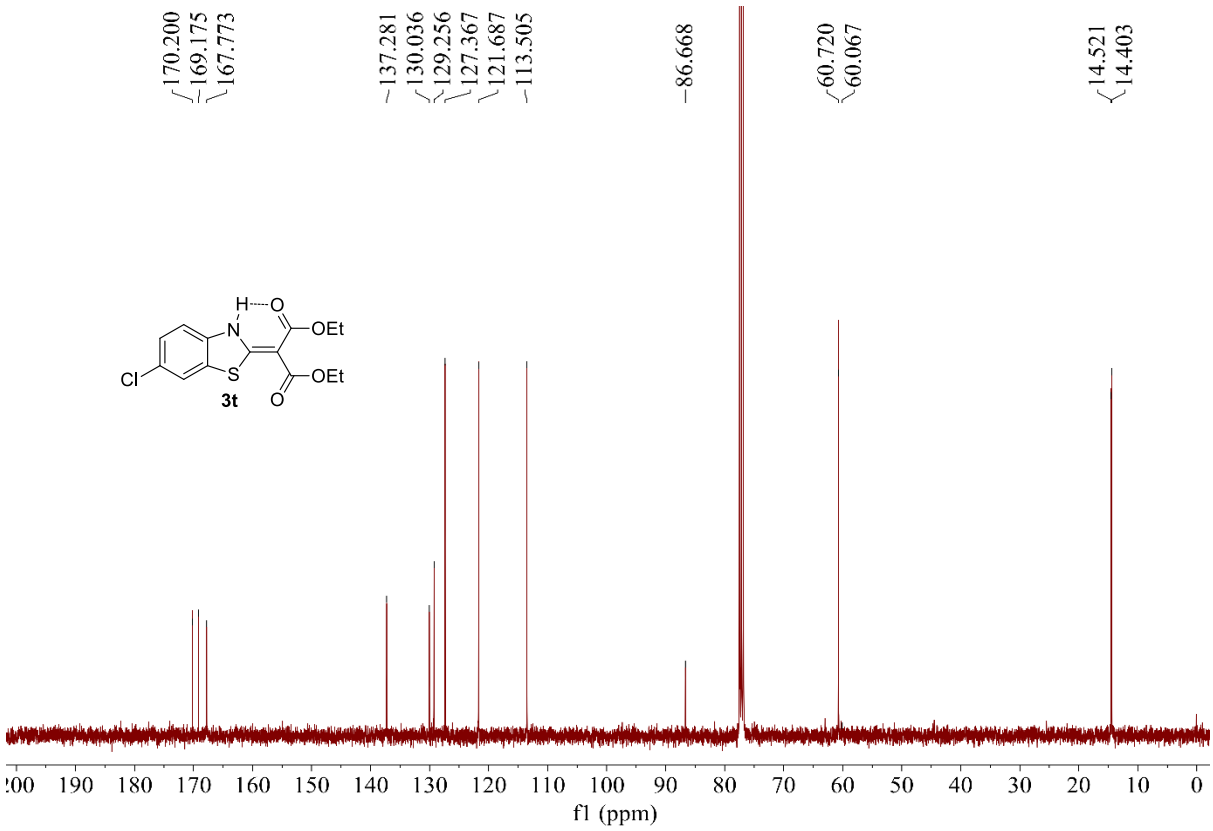
^{1}H NMR of **3s** ($CDCl_3$, 400 MHz)



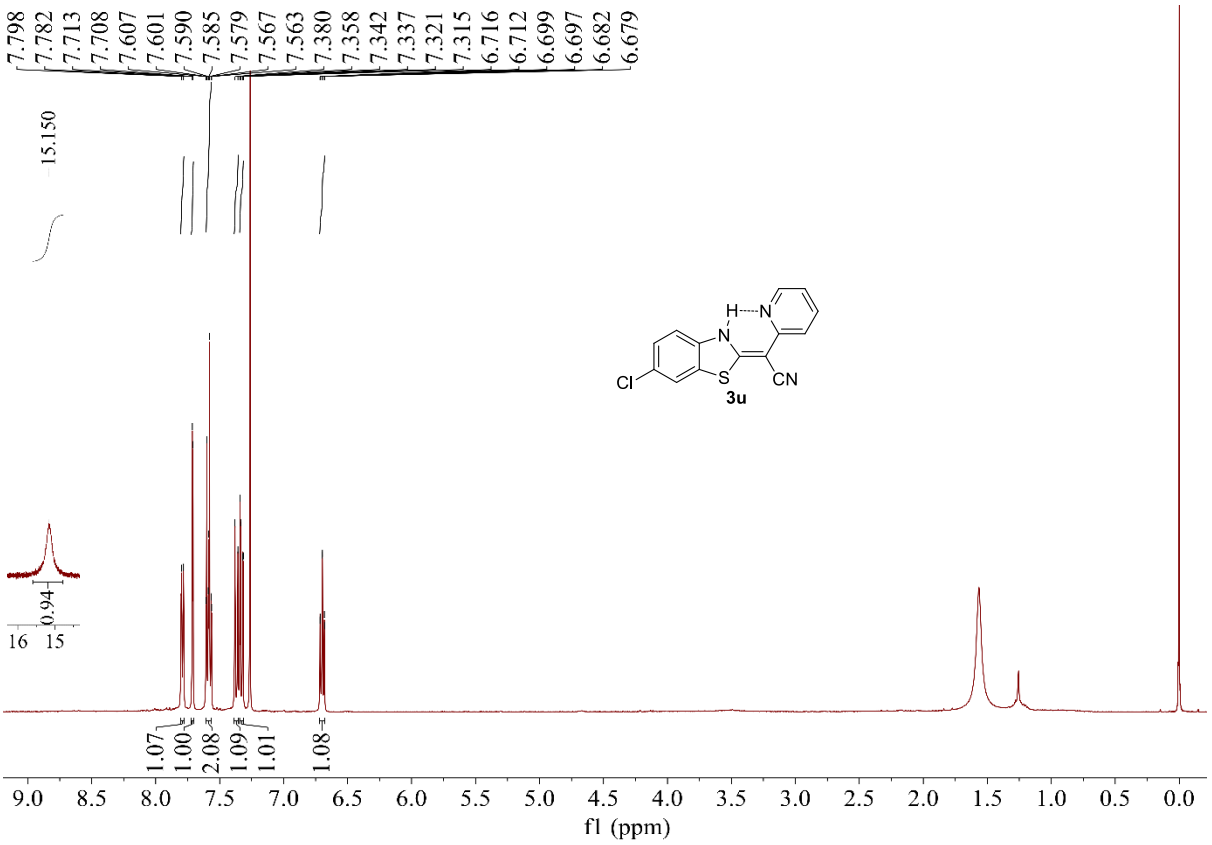
^{13}C NMR of **3s** ($CDCl_3$, 100 MHz)



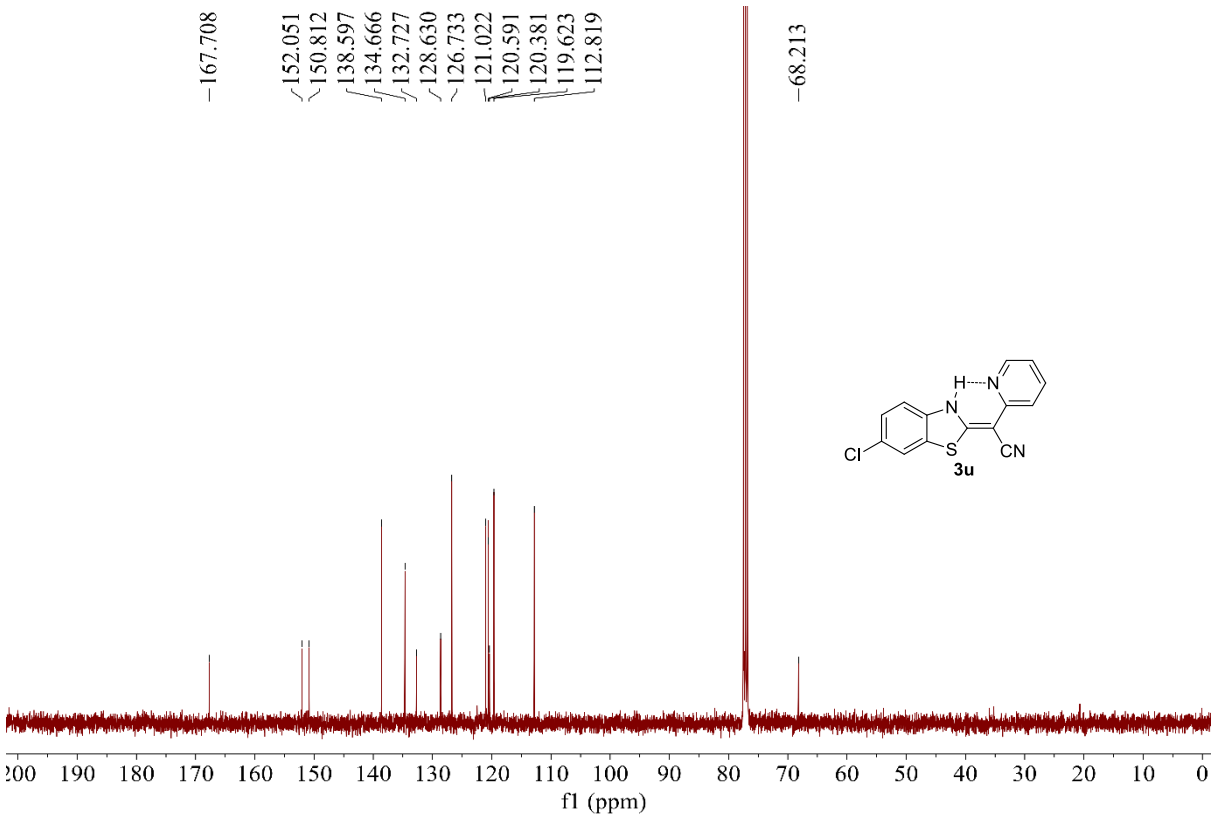
^{1}H NMR of **3t** ($CDCl_3$, 400 MHz)



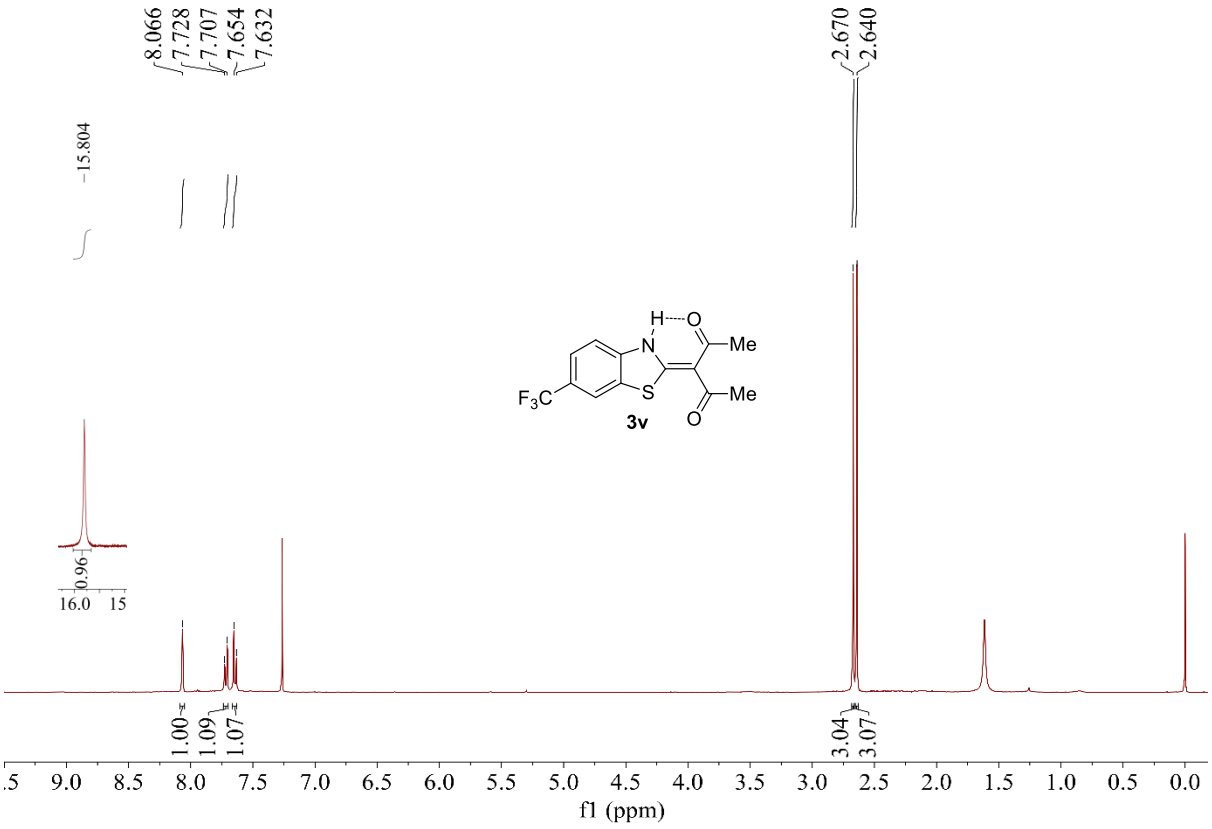
^{13}C NMR of **3t** ($CDCl_3$, 100 MHz)



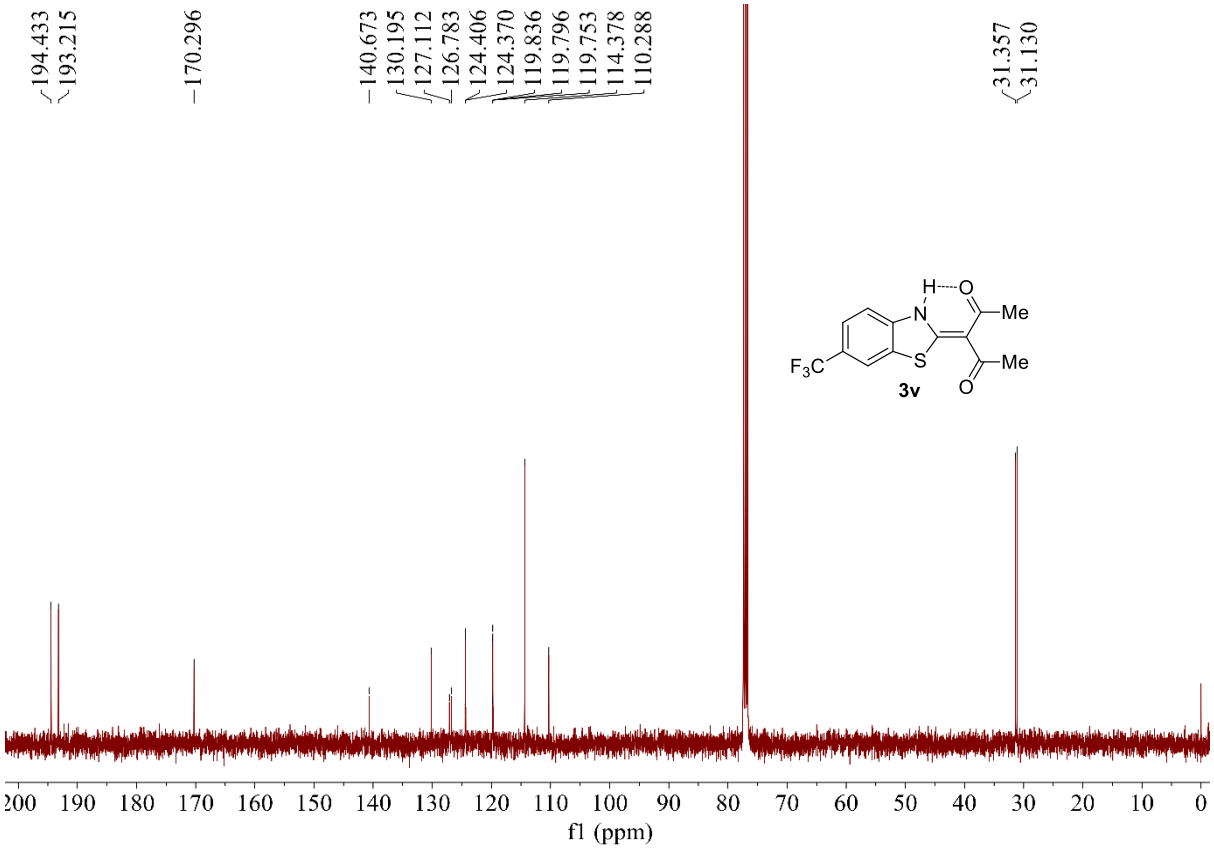
^{1}H NMR of **3u** ($CDCl_3$, 400 MHz)



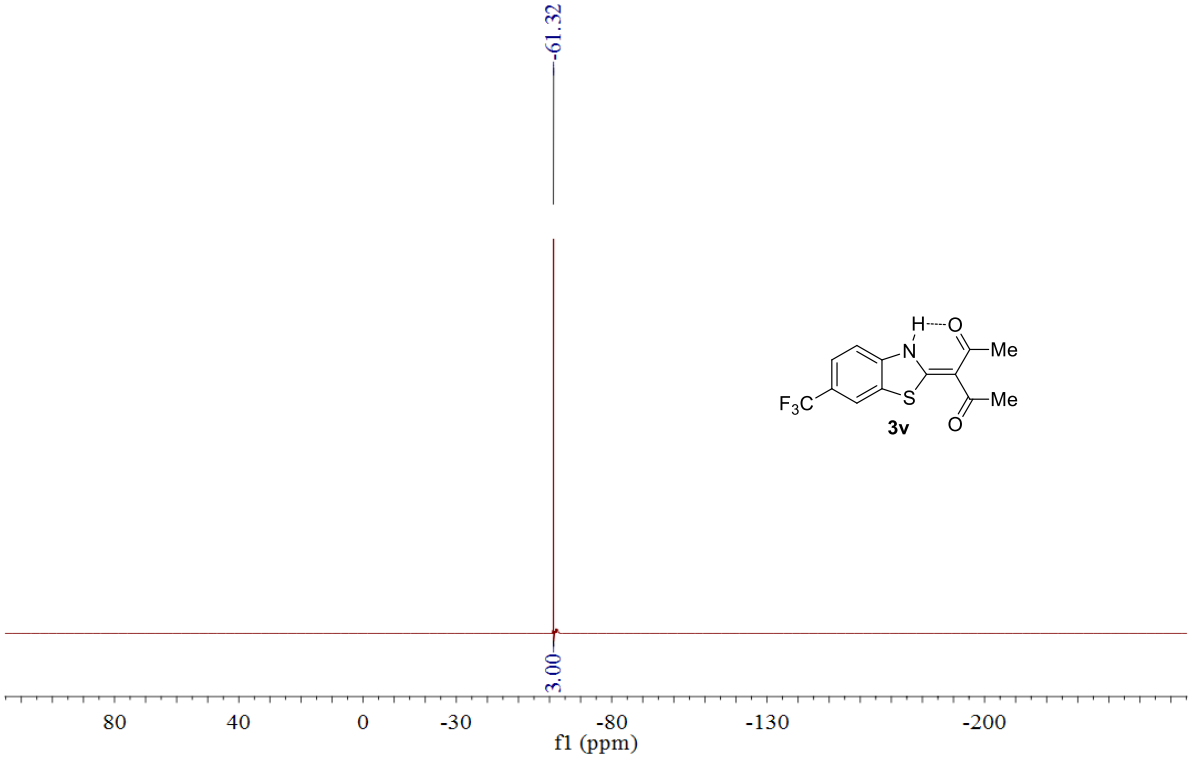
^{13}C NMR of **3u** ($CDCl_3$, 100 MHz)



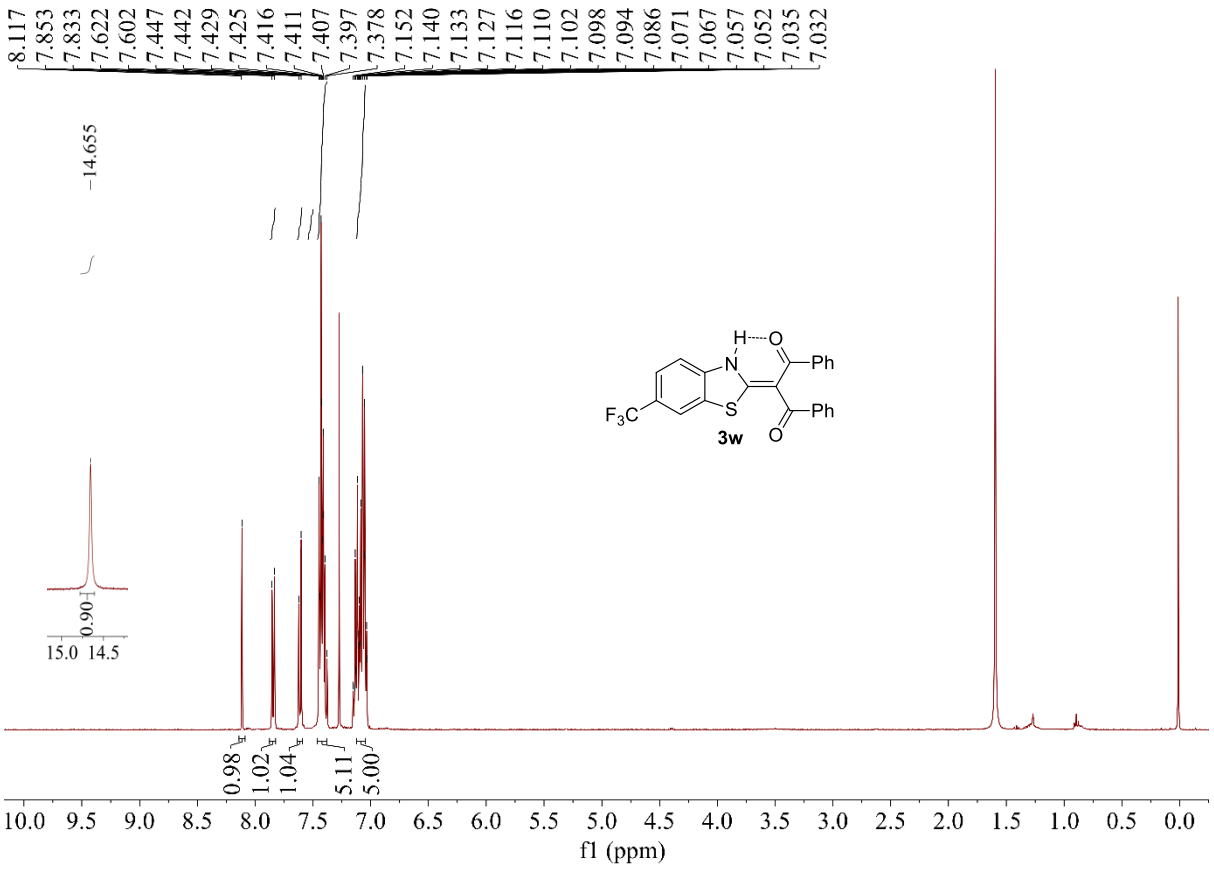
^{1}H NMR of **3v** ($CDCl_3$, 400 MHz)



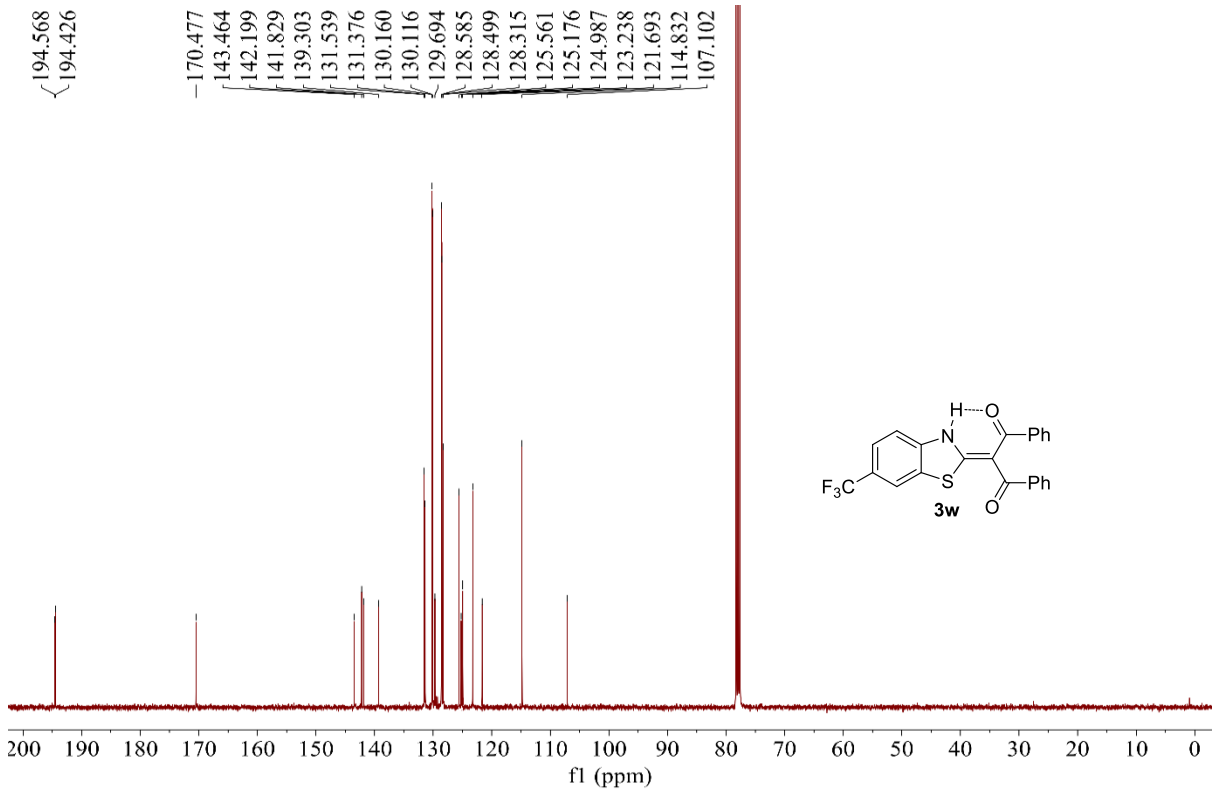
^{13}C NMR of **3v** ($CDCl_3$, 100 MHz)



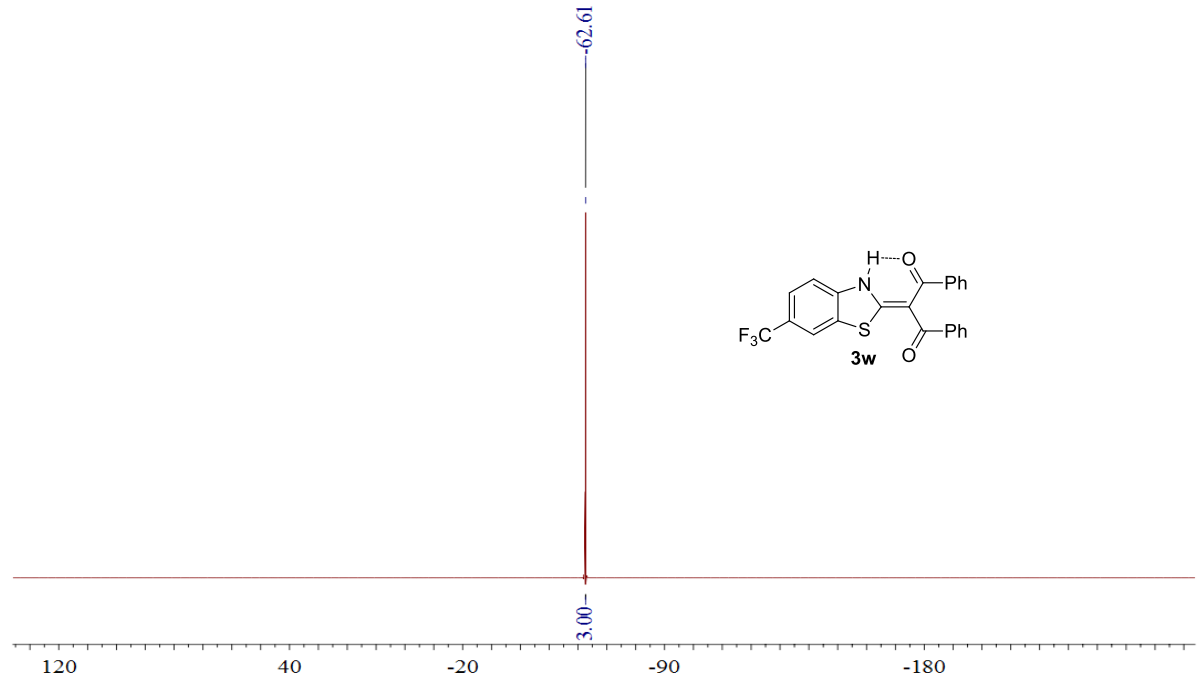
^{19}F NMR of **3v** ($CDCl_3$, 564.65 MHz)



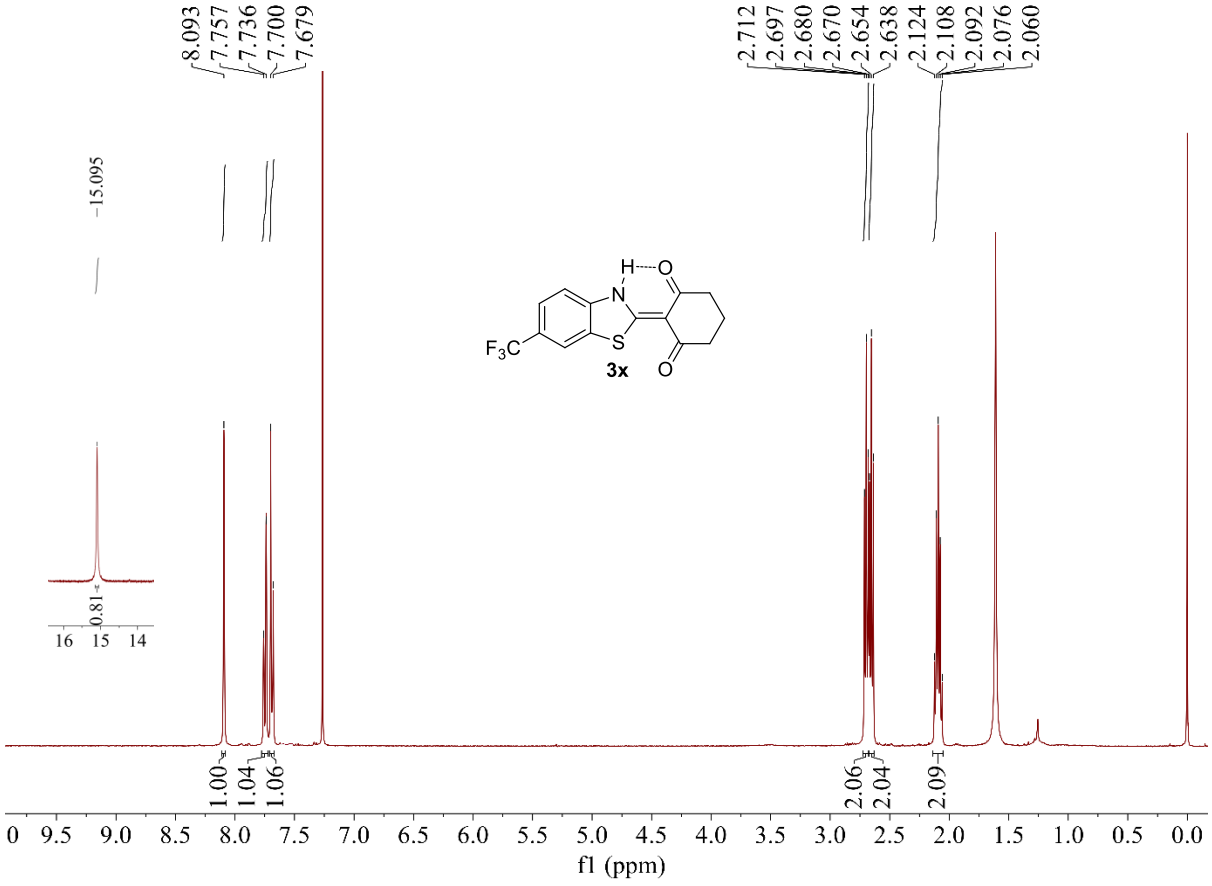
^{1}H NMR of **3w** ($CDCl_3$, 400 MHz)



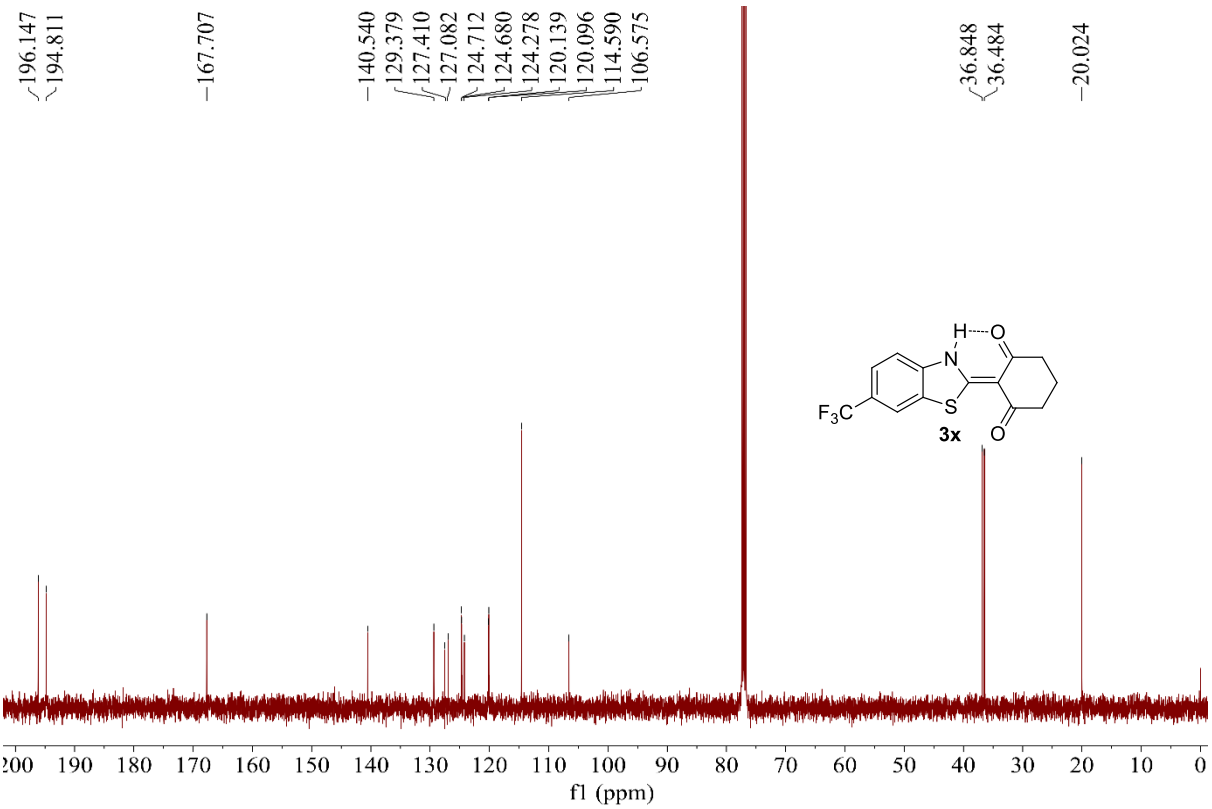
^{13}C NMR of **3w** ($CDCl_3$, 100 MHz)



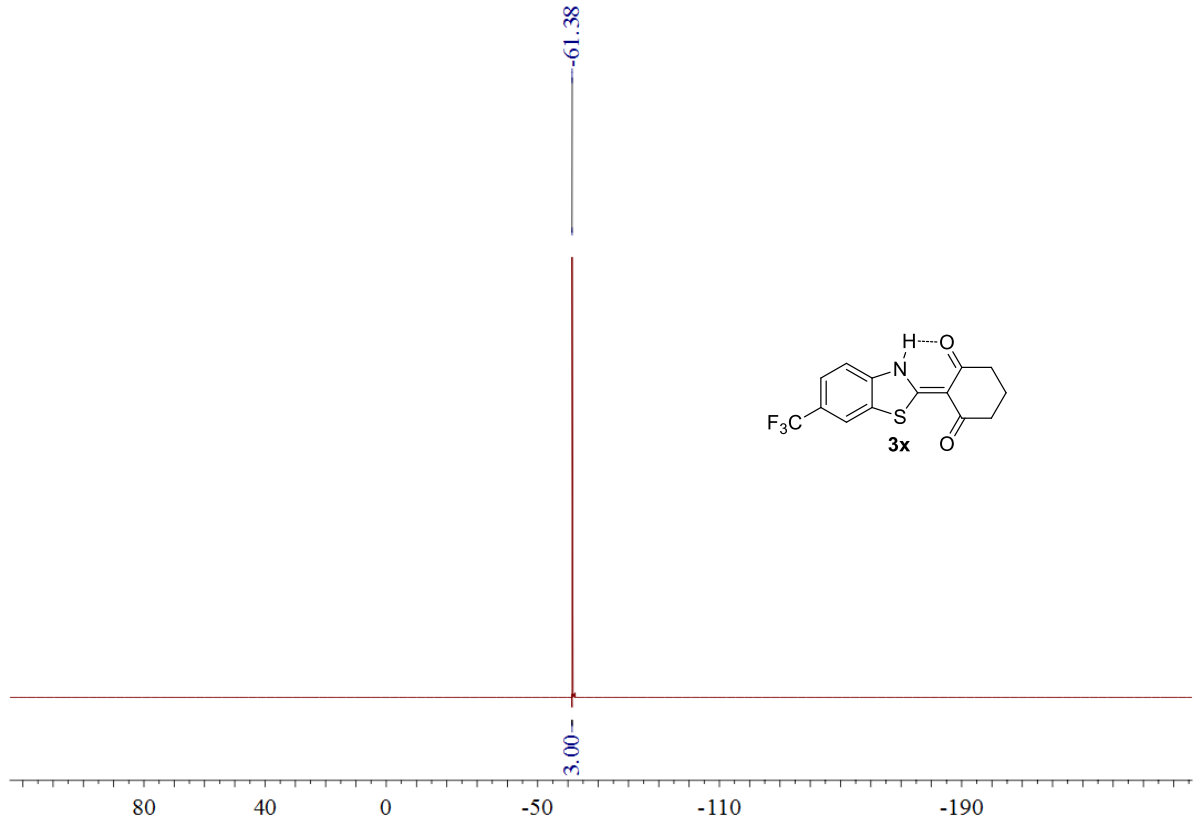
^{19}F NMR of **3w** ($CDCl_3$, 564.65 MHz)



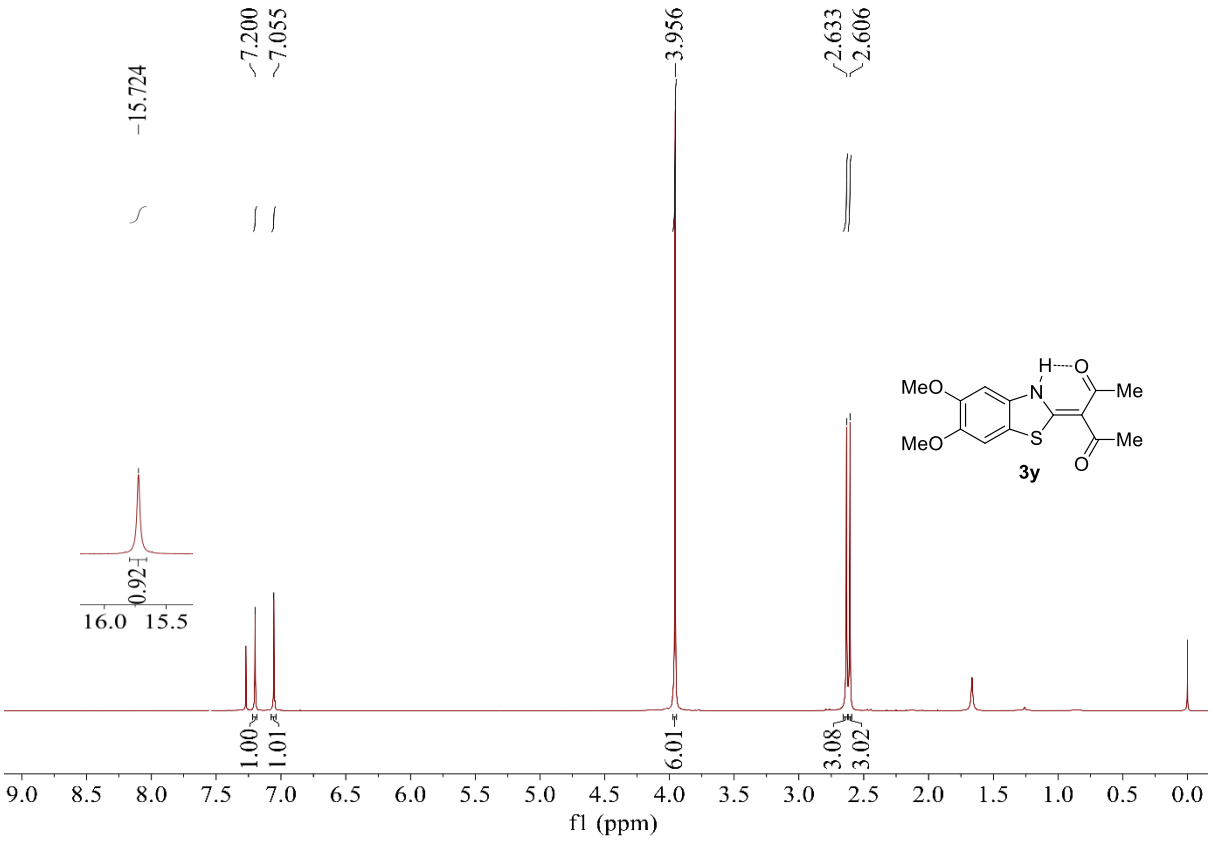
^{1}H NMR of **3x** ($CDCl_3$, 400 MHz)



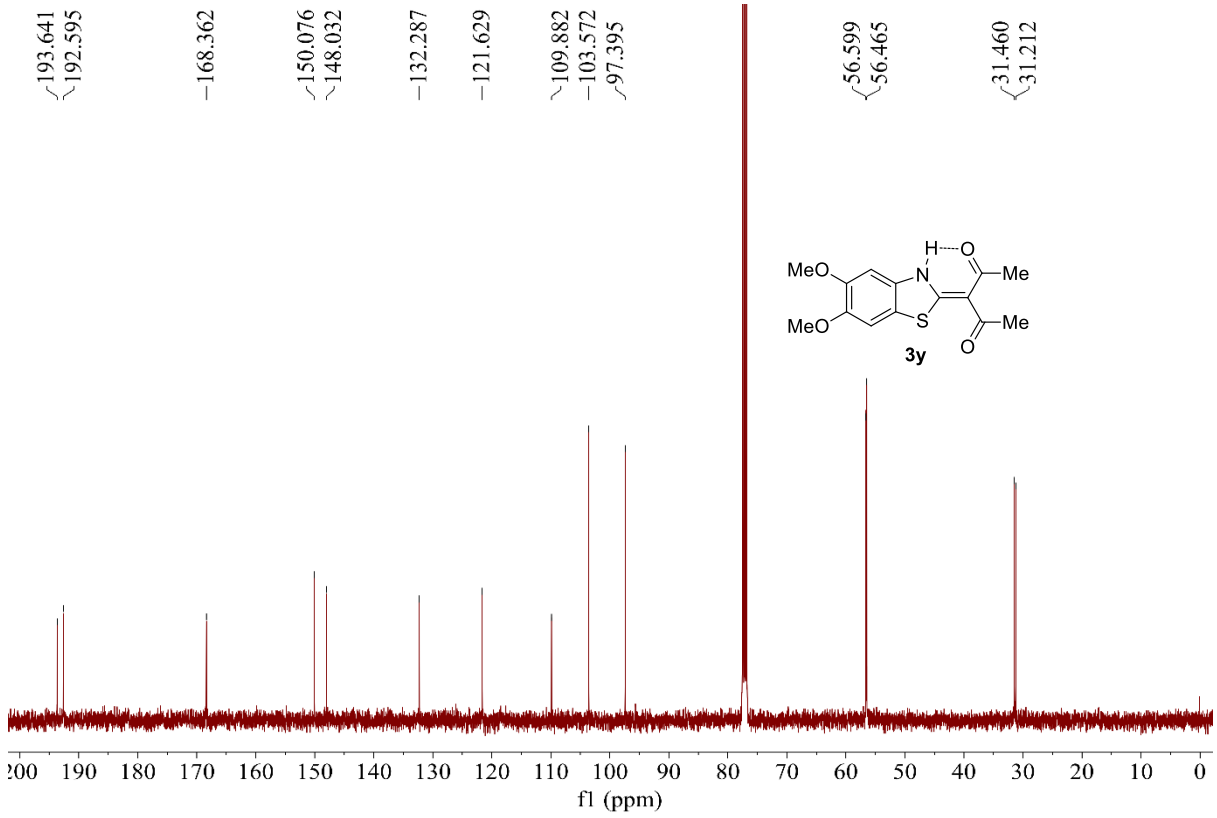
^{13}C NMR of **3x** ($CDCl_3$, 100 MHz)



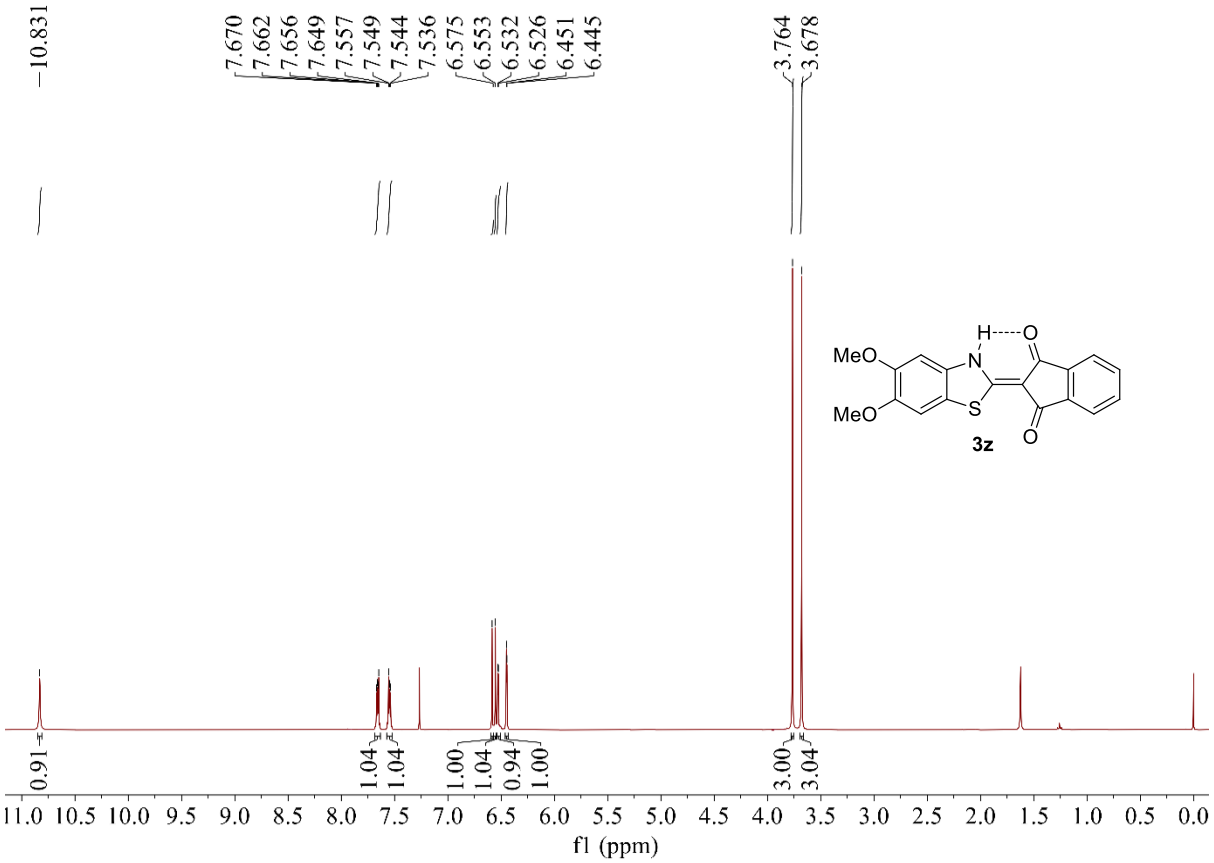
^{19}F NMR of **3x** ($CDCl_3$, 564.65 MHz)



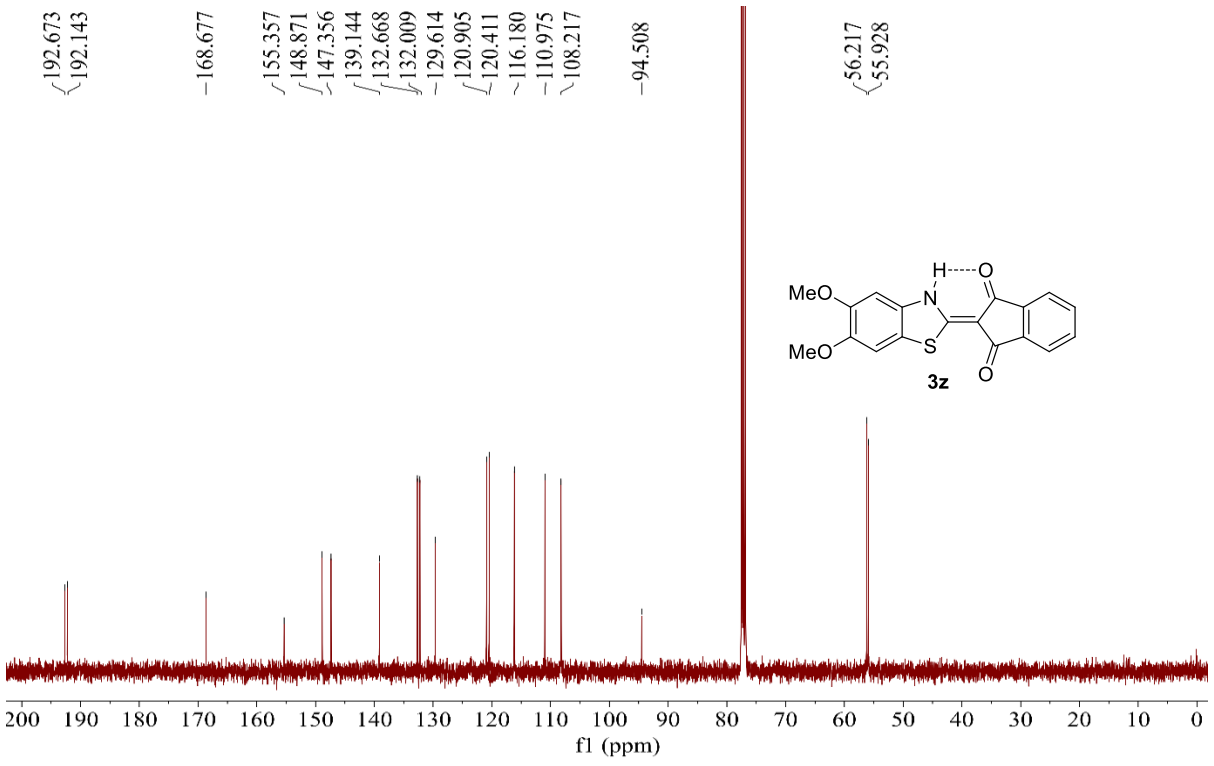
^{1}H NMR of **3y** ($CDCl_3$, 400 MHz)



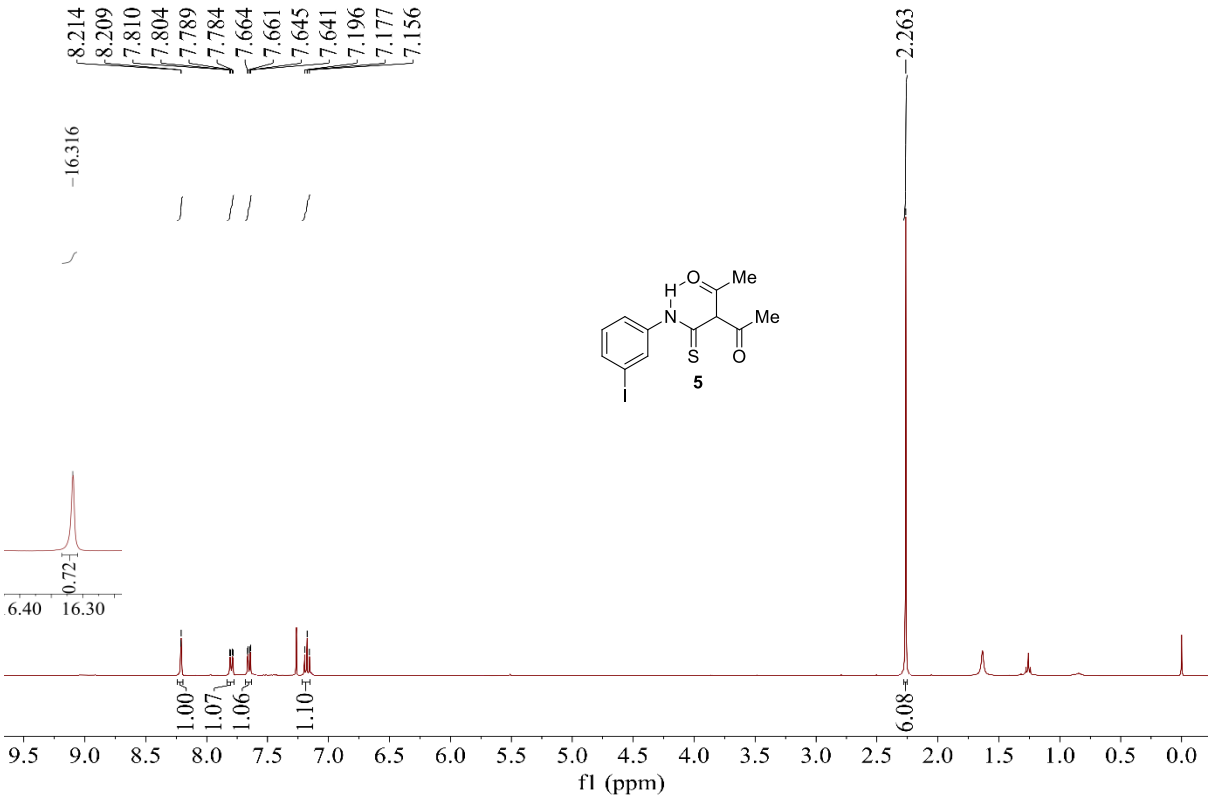
^{13}C NMR of **3y** ($CDCl_3$, 100 MHz)



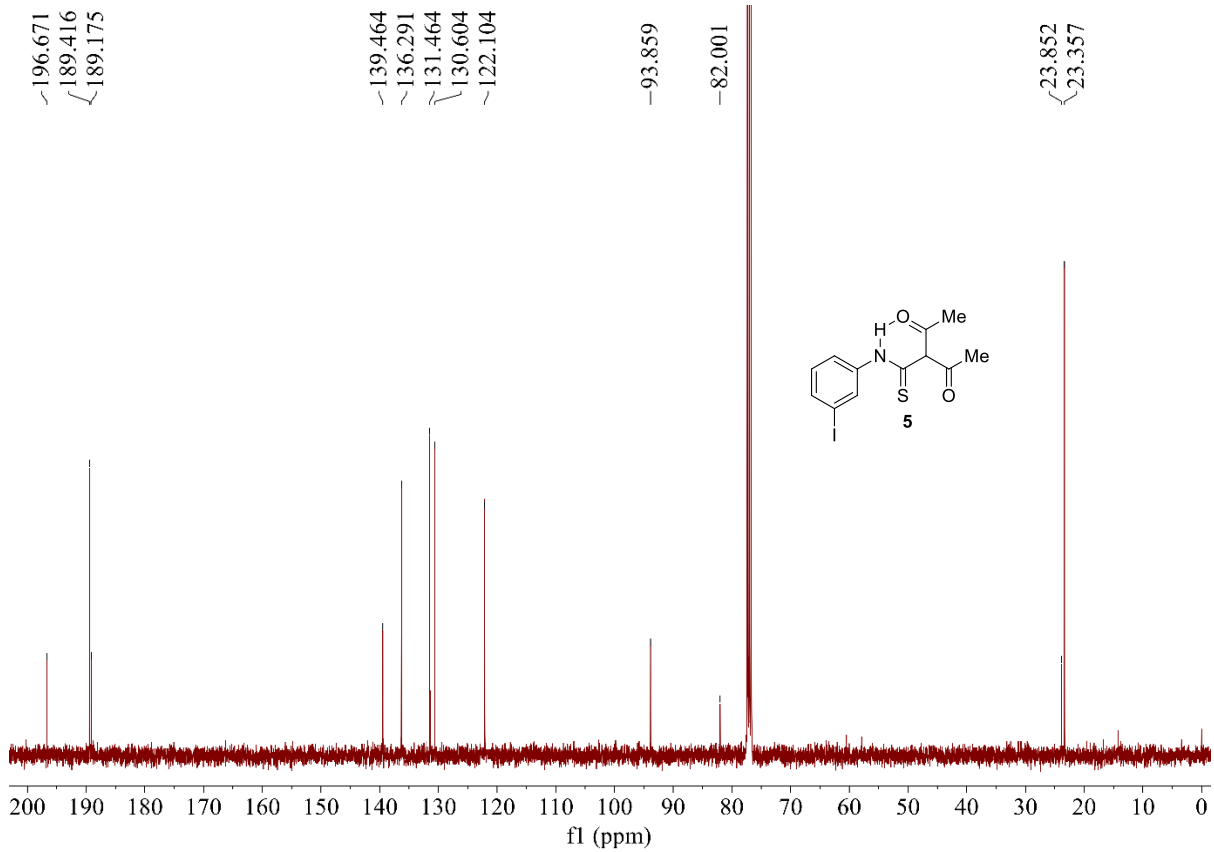
^{1}H NMR of **3z** ($CDCl_3$, 400 MHz)



^{13}C NMR of **3z** ($CDCl_3$, 100 MHz)



^{1}H NMR of **5** ($CDCl_3$, 400 MHz)



^{13}C NMR of **5** ($CDCl_3$, 100 MHz)