Metal-free oxidative carbonylation on enaminone C=C bond for the cascade synthesis of benzothiazole−containing vicinal diketones

Jie-Ping Wan,*[,a] Youyi Zhou,[a] Yunyun Liu[a] and Shouri Sheng*[,a]

[a]College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P.R. China

Email: wanjieping@jxnu.edu.cn; shengsr@jxnu.edu.cn

Contents

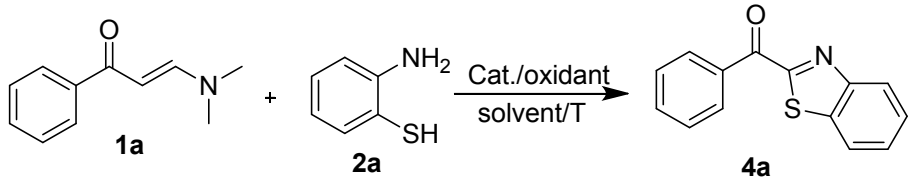
General information

Enaminones **1** were synthesized following literature process,[1] all other chemicals and solvents were obtained from commercial source and used directly without further treatment. Unless otherwise specified, all reaction were performed under air atmosphere. The ^{1}H and ^{13}C NMR were recorded in an 400 MHz apparatus by using $CDCl_3$ as solvent. The chemical shift was reported in ppm with TMS as internal standard (0 ppm). HRMS data were tested under ESI model in the spectrometer equipped TOF analyzer, and the melting points were measured in a X-4A apparatus without correcting the temperature.

General procedure for the synthesis of vicinal didketones

In a 25 mL round-bottom flask equipped with a stirring bar were located enaminone **1** (0.3 mmol), *o*-aminothiophenol **2** (0.3 mmol), I_2 (0.06mmol) and DMSO (2 mL). The resulting mixture was then stirred at 110 ^{o}C for 12 h under air atmosphere. Upon completion of the reaction (TCL), water (5 mL) was added to the vessel and the suspension was extracted with ethyl acetate (3 × 10 mL). The combined organic solution was dried over anhydrous Na_2SO_4. After filtration, the organic solvent was removed from the solution under reduced pressure. The resulting residue was then subjected to silica gel chromatography to give pure product by using mixed ethyl acetate/petroleum ether as eluent (v/v = 1/15).

Optimization data for the synthesis of 2-aroylbenzothiazole (Table 1)



Entry	Catalyst	Oxidant	Solvent	T(^{o}C)	Yield(%)[b]
1	$FeCl_3$	-	DMSO	120	27
2	*p*-TSA	-	DMSO	120	19
3	CAN	-	DMSO	120	trace
4	Rose Bengal	-	DMSO	120	nr
5	CuI	-	DMSO	120	33
6	CuI	TBHP	DMSO	120	42
7	CuI	$KMnO_4$	DMSO	120	nr
8	CuI	$PhI(AcO)_2$	DMSO	120	trace
9	CuI	MnO_2	DMSO	120	nr
10	CuI	DDQ	DMSO	120	trace
11[c]	CuI	TBHP	DMSO	120	52
12[d]	CuI	TBHP	DMSO	120	46
13[c]	**CuI**	**TBHP**	**DMSO**	**110**	**54**
14[c]	CuI	TBHP	DMSO	100	48
15[c,e]	CuI	TBHP	DMSO	110	39
16[c,f]	CuI	TBHP	DMSO	110	47
17[c]	CuBr	TBHP	DMSO	110	51
18[c]	CuCl	TBHP	DMSO	110	43
19[c]	$CuBr_2$	TBHP	DMSO	110	37
20[c]	$Cu(AcO)_2$	TBHP	DMSO	110	36
21[c,g]	CuI	TBHP	DMF	110	21
22[c,g]	CuI	TBHP	Toluene	110	trace
23[c,g]	CuI	TBHP	EtOH	110	nr
24[c,g]	CuI	TBHP	CH_3CN	110	nr

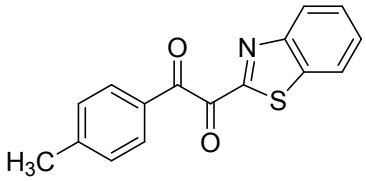
[a] Unless otherwise specified, the reaction conditions are: **1a** (0.3 m mol), **2a** (0.3 m mol), catalyst (0.06 mmol) and oxidant (0.6 mmol) in 2 mL of solvent(s), stirred for 12 h at air atmosphere. [b] Yield of isolated product. [c] The TBHP was 0.45 mmol. [d] The TBHP was 0.3 mmol. [e] The CuI was 0.03 mmol. [f] The CuI was 0.09 mol. [g] The reactions were run at reflux.

General procedure procedure for the synthesis of 2-aroylbenzothiazole

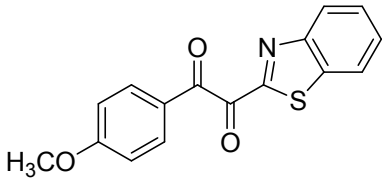
In a 25 mL round-bottom flask equipped with a stirring bar were added enaminone **1** (0.3 mmol), *o*-aminothiophenol **2** (0.3 mmol), CuI (0.06mmol), TBHP (0.45 mmol) and DMSO (2 mL). The resulting mixture was stirred at 110 ^{o}C for 12 h under air atmosphere. Upon completion of the reaction (TCL), the water (5 mL) was added to

the vessel and the resulting suspension was extracted with ethyl acetate (3×10 mL). The combined organic solution was dried over anhydrous Na_2SO_4. After filtration, the organic solvent was removed from the solution under reduced pressure. The retained residue was then subjected to silica gel chromatography to give pure product by using mixed ethyl acetate/petroleum ether as eluent (v/v = 1/50).

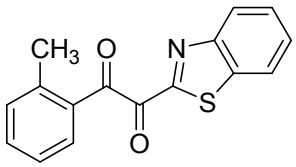
Characterization data of all products



1-Benzothiazol-2-yl-2-p-tolyl-ethane-1,2-dione (**3a**). Orange solid; m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.16 (m, 1 H), 8.04-8.01 (m, 1 H), 7.91 (d, *J* = 8.0 Hz, 2 H), 7.58-7.56 (m, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 188.0, 162.9, 153.8, 146.6, 137.3, 130.2, 130.0, 129.8, 128.6, 127.4, 126.3, 122.4, 22.0; ESI-HRMS: Calcd for $C_{16}H_{12}NO_2S$ $[M+H]^+$: 282.0589; Found: 282.0589.

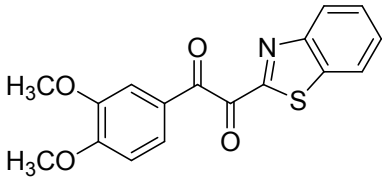


1-Benzothiazol-2-yl-2-(4-methoxy-phenyl)-ethane-1,2-dione (**3b**). Orange solid; m.p. 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.17 (m, 1 H), 8.03-8.00 (m, 2 H), 7.99 (d, *J* = 7.2 Hz, 1 H), 7.58-7.55 (m, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 187.9, 165.3, 162.9, 153.8, 137.0, 132.6, 128.6, 127.4, 126.3, 125.4, 122.4, 114.5, 55.7; ESI-HRMS: Calcd for $C_{16}H_{12}NO_3S$ $[M+H]^+$: 298.0538; Found: 298.0545.

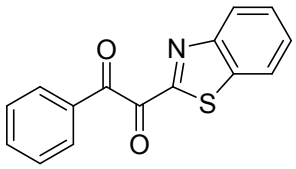


1-Benzothiazol-2-yl-2-o-tolyl-ethane-1,2-dione (**3c**). Yellow solid; m.p. 118-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 1 H), 8.03-8.01 (m, 1 H), 7.69 (d, *J* = 8.0

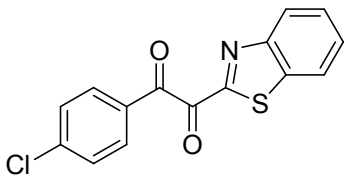
Hz, 1 H), 7.58-7.55 (m, 2 H), 7.50 (t, J = 8.0 Hz, 1 H), 7.36 (d, J = 7.6 Hz, 1 H), 7.29 (d, J = 7.2 Hz, 1 H), 2.76 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.1, 187.9, 163.0, 153.8, 141.8, 137.0, 134.0, 133.1, 132.6, 131.1, 128.6, 127.4, 126.3, 126.0, 122.4, 21.9; ESI-HRMS: Calcd for $C_{16}H_{12}NO_2S$ $[M+H]^+$: 282.0589; Found: 282.0582.



1-Benzothiazol-2-yl-2-(3,4-dimethoxy-phenyl)-ethane-1,2-dione (**3d**). Green solid; m.p. 127-129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20-8.19 (m, 1 H), 8.04-8.03 (m, 1 H), 7.67 (s, 1 H), 7.59-7.57 (m, 2 H), 7.52 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1 H), 6.91 (d, J = 8.4 Hz, 1 H), 3.98 (s, 3 H), 3.96 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.6, 187.7, 163.0, 155.3, 153.8, 149.8, 137.0, 128.6, 127.4, 126.6, 126.3, 125.6, 122.4, 110.4, 110.3, 56.3, 56.1; ESI-HRMS: Calcd for $C_{17}H_{14}NO_4S$ $[M+H]^+$: 328.0644; Found: 328.0637.

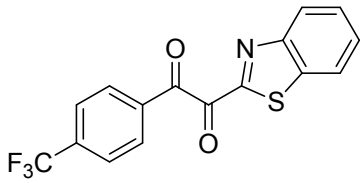


1-Benzothiazol-2-yl-2-phenyl-ethane-1,2-dione (**3e**). Yellow solid; m.p. 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.16 (m, 1 H), 8.03 (t, J = 7.2 Hz, 3 H), 7.68 (t, J = 7.2 Hz, 1 H), 7.59-7.52 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 187.8, 162.7, 153.8, 137.1, 135.0, 132.5, 130.0, 129.0, 128.6, 127.4, 126.3, 122.4; ESI-HRMS: Calcd for $C_{15}H_{10}NO_2S$ $[M+H]^+$: 268.0427; Found: 268.0427.

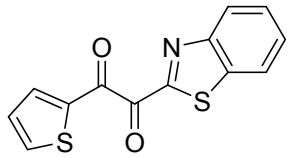


1-Benzothiazol-2-yl-2-(4-chloro-phenyl)-ethane-1,2-dione (**3f**). Yellow solid; m.p. 208-210 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19-8.18 (m, 1 H), 8.05-8.04 (m, 1 H), 7.96 (d, J = 8.4 Hz, 2 H), 7.60-7.59 (m, 2 H), 7.52 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 187.4, 162.5, 153.8, 141.9, 137.0, 131.3, 130.8, 129.5, 128.8,

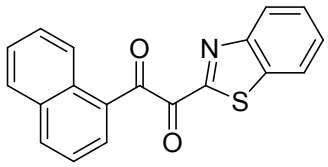
127.5, 126.4, 122.5; ESI-HRMS: Calcd for $C_{15}H_9ClNO_2S$ $[M+H]^+$: 302.0037; Found: 302.0047.



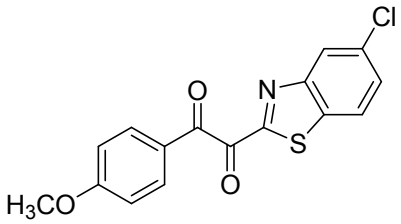
1-Benzothiazol-2-yl-2-(4-trifluoromethyl-phenyl)-ethane-1,2-dione (**3g**). Orange solid; m.p. 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.13 (m, 3 H), 8.05 (t, *J* = 4.4 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 4.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 187.0, 162.2, 153.7, 137.1, 136.3, 135.9, 135.0, 130.3, 129.0, 127.6, 126.4, 126.1 (t, *J* = 3.6 Hz), 122.5; ESI-HRMS: Calcd for $C_{16}H_9F_3NO_2S$ $[M+H]^+$: 336.0301; Found: 336.0310.



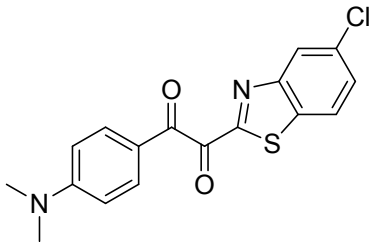
1-Benzothiazol-2-yl-2-thiophen-2-yl-ethane-1,2-dione (**3h**). Brown solid; m.p. 100-102 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25-8.23 (m, 1 H), 8.04-8.02 (m, 1 H), 7.90-7.88 (m, 2 H), 7.60-7.58 (m, 2 H), 7.21 (t, *J* = 4.2 Hz, 1 H);^{13}C NMR (150 MHz, $CDCl_3$) δ 184.8, 182.9, 161.7, 153.7, 139.0, 137.5, 137.3, 137.1, 128.9, 128.7, 127.5, 126.4, 122.4; ESI-HRMS: Calcd for $C_{13}H_8NO_2S_2$ $[M+H]^+$: 273.9991; Found: 273.9989.



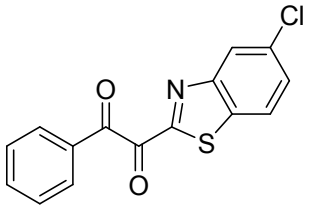
1-Benzothiazol-2-yl-2-naphthalen-1-yl-ethane-1,2-dione (**3i**). Green solid; m.p. 168-170 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.37 (d, *J* = 8.4 Hz, 1 H), 8.14 (d, *J* = 7.8 Hz, 2 H), 8.05 (d, *J* = 1.8 Hz, 1 H), 8.04-7.94 (m, 2 H), 7.79-7.76 (m, 1 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.58-7.55 (m, 2 H), 7.51 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.3, 187.6, 163.3, 153.9, 137.1, 136.3, 135.3, 134.1, 131.1, 129.6, 128.7, 128.6, 127.9, 127.4, 127.2, 126.3, 126.2, 124.4, 122.4; ESI-HRMS: Calcd for $C_{19}H_{12}NO_2S$ $[M+H]^+$: 318.0589; Found: 318.0588.



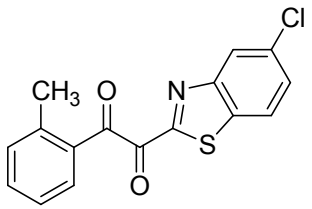
1-(5-Chloro-benzothiazol-2-yl)-2-(4-methoxy-phenyl)-ethane-1,2-dione (**3j**). Orange solid; m.p. 186-187 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1 H), 7.98 (d, *J* = 9.0 Hz, 2 H), 7.95 (d, *J* = 9.0 Hz, 1 H), 7.55-7.54 (m, 1 H), 7.01 (d, *J* = 9.0 Hz, 2 H), 3.90 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 187.4, 165.4, 164.6, 154.5, 135.2, 133.6, 132.6, 129.2, 125.7, 125.3, 123.2, 114.6, 55.7; ESI-HRMS: Calcd for $C_{16}H_{11}ClNO_3S$ $[M+H]^+$: 332.0148; Found: 332.0140.



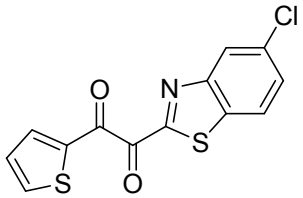
1-(5-Chloro-benzothiazol-2-yl)-2-(4-dimethylamino-phenyl)-ethane-1,2-dione (**3k**). Orange solid; m.p. 154-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.2 Hz, 1 H), 7.93 (d, *J* = 9.0 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.53-7.51 (m, 1 H), 6.69 (d, *J* = 9.0 Hz, 2 H), 3.11 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.0, 187.8, 165.2, 154.8, 154.5, 135.2, 133.4, 132.6, 128.9, 125.7, 123.1, 120.0, 111.1, 40.1; ESI-HRMS: Calcd for $C_{17}H_{14}ClN_2O_2S$ $[M+H]^+$: 345.0464; Found: 345.0463.



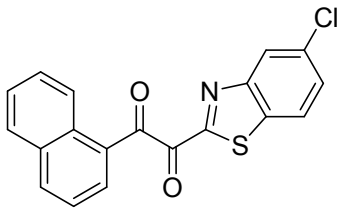
1-(5-Chloro-benzothiazol-2-yl)-2-phenyl-ethane-1,2-dione (**3l**). Reseda solid; m.p. 77-79 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1 H), 8.01 (d, *J* = 7.2 Hz, 2 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 7.70 (t, *J* = 7.8 Hz, 1 H), 7.57-7.54 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 187.4, 164.3, 154.4, 135.3, 135.2, 133.7, 132.3, 130.0, 129.3, 129.1, 125.7, 123.2; ESI-HRMS: Calcd for $C_{15}H_9ClNO_2S$ $[M+H]^+$: 302.0043; Found: 302.0074.



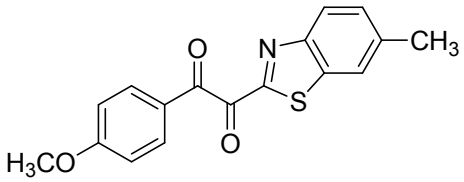
1-(5-Chloro-benzothiazol-2-yl)-2-o-tolyl-ethane-1,2-dione (**3m**).Yellow solid; m.p. 139-141 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 2.4 Hz, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.55 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1 H), 7.52 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2 H), 7.38 (d, J = 7.8 Hz, 1 H), 7.29 (t, J = 7.8 Hz, 1 H), 2.75 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.8, 187.4, 164.7, 154.5, 141.8, 135.2, 134.1, 133.6, 133.0, 132.7, 130.9, 129.2, 126.1, 125.7, 123.2, 21.9; ESI-HRMS: Calcd for $C_{16}H_{10}ClNO_2SNa$ $[M+Na]^+$: 338.0018; Found: 338.0028.



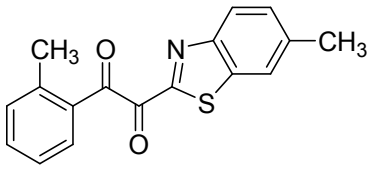
1-(5-Chloro-benzothiazol-2-yl)-2-thiophen-2-yl-ethane-1,2-dione (**3n**). Brown solid; m.p. 143-145 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1 H), 7.96 (d, J = 9.0 Hz, 1 H), 7.92-7.90 (m, 2 H), 7.56 (d, J = 9.0 Hz, 1 H), 7.24-7.22 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.2, 182.3, 163.1, 154.3,138.7, 137.8, 137.3, 135.5, 133.7, 129.4, 129.0, 125.8, 123.2; ESI-HRMS: Calcd for $C_{13}H_7ClNO_2S_2$ $[M+H]^+$: 307.9607; Found: 307.9598.



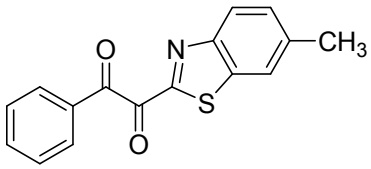
1-(5-Chloro-benzothiazol-2-yl)-2-naphthalen-1-yl-ethane-1,2-dione (**3o**). Brown solid; m.p. 92-94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (d, J = 8.4 Hz, 1 H), 8.15 (d, J = 8.4 Hz, 1 H), 8.12 (s, 1 H), 7.97-7.94 (m, 3 H), 7.78 (t, J = 7.2 Hz, 1 H), 7.65 (t, J = 7.8 Hz, 1 H), 7.55-7.51 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 187.1, 164.9, 154.4, 136.4, 135.3, 135.2, 134.1, 133.5, 131.0, 129.7, 129.2, 128.8, 127.7, 127.3, 126.1, 125.7, 124.4, 123.2; ESI-HRMS: Calcd for $C_{19}H_{10}ClNO_2SNa$ $[M+Na]^+$: 374.0018; Found: 374.0025.



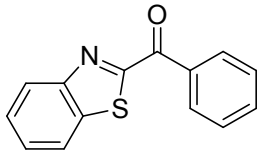
1-(4-Methoxy-phenyl)-2-(6-methyl-benzothiazol-2-yl)-ethane-1,2-dione (**3p**). Orange solid; m.p. 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1 H), 7.98 (d, *J* = 9.2 Hz, 2 H), 7.79 (s, 1 H), 7.38-7.35 (m, 1 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 3.88 (s, 3 H), 2.52 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.6, 188.1, 165.2, 161.9, 152.1, 139.5, 137.4, 132.6, 129.4, 125.8, 125.6, 121.9, 114.4, 55.7, 21.9; ESI-HRMS: Calcd for $C_{17}H_{14}NO_3S$ $[M+H]^+$: 312.0694; Found: 312.0700.



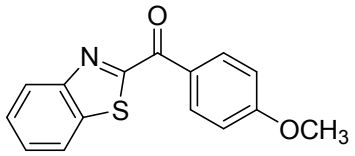
1-(6-Methyl-benzothiazol-2-yl)-2-o-tolyl-ethane-1,2-dione (**3q**). Orange solid; m.p. 115-117 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1 H), 7.81 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.2 Hz, 1 H), 7.39-7.35 (m, 2 H), 7.29-7.25 (m, 1 H), 2.75 (s, 3 H), 2.53 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.3, 188.0, 162.0, 152.1, 141.8, 139.5, 137.4, 133.9, 133.1, 132.6, 131.1, 129.4, 126.0, 125.8, 121.9, 21.9, 21.8; ESI-HRMS: Calcd for $C_{17}H_{14}NO_2S$ $[M+H]^+$: 296.0745; Found: 296.0718.



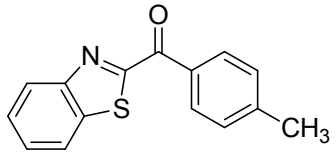
1-(6-Methyl-benzothiazol-2-yl)-2-phenyl-ethane-1,2-dione (**3r**). Orange solid; m.p. 101-103 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1 H), 8.02 (d, *J* = 7.2 Hz, 2 H), 7.81 (s, 1 H), 7.68 (t, *J* = 7.8 Hz, 1 H), 7.53 (t, *J* = 7.8 Hz, 2 H), 7.38 (t, *J* = 9.6 Hz, 1 H), 2.54 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.3, 187.9, 161.7, 152.1, 139.7, 137.5, 135.1, 132.5, 130.1, 129.4, 129.0, 125.9, 121.9, 22.0; ESI-HRMS: Calcd for $C_{16}H_{12}NO_2S$ $[M+H]^+$: 282.0589; Found: 282.0584.



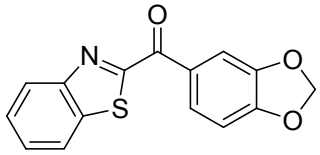
Benzothiazol-2-yl-phenyl-methanone (**4a**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 7.6 Hz, 2 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.61-7.53 (m, 4 H).



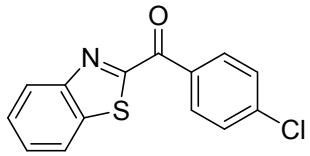
Benzothiazol-2-yl-(4-methoxyphenyl)-methanone (**4b**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.8 Hz, 2 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.02 (d, *J* = 7.6 Hz, 1 H), 7.60-7.52 (m, 2 H), 7.04 (d, *J* = 9.2 Hz, 2 H), 3.92 (s, 3 H).



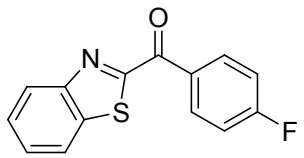
Benzothiazol-2-yl-p-tolyl-methanone (**4c**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.0 Hz, 2 H), 8.22 (d, *J* = 8.0 Hz, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.58-7.50 (m, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H).



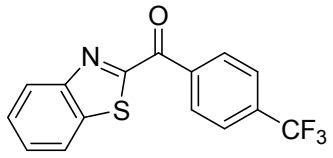
Benzothiazol-2-yl-(1,3-dihydro-isobenzofuran-5-yl)-methanone (**4d**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.0 Hz, 1 H), 8.22 (d, *J* = 7.6 Hz, 1 H), 8.06 (s, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.58-7.51 (m, 2 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 6.10 (s, 2H).



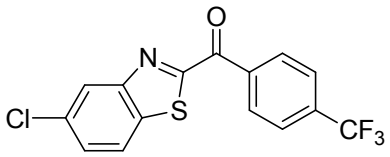
Benzothiazol-2-yl-(4-chlorophenyl)-methanone (**4e**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 2 H), 8.24 (d, *J* = 7.6 Hz, 1 H), 8.02 (d, *J* = 7.6 Hz, 1 H), 7.60-7.53 (m, 4 H).



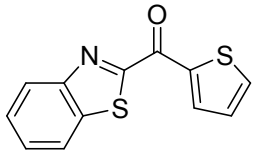
Benzothiazol-2-yl-(4-fluorophenyl)-methanone (**4f**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.65 (m, 2 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 7.6 Hz, 1 H), 7.61-7.53 (m, 2 H), 7.23 (t, *J* = 8.8 Hz, 2 H).



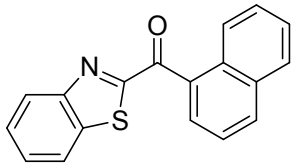
Benzothiazol-2-yl-(4-trifluoromethyl-phenyl)-methanone (**4g**). Yellow solid; m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 7.6 Hz, 2 H), 8.23 (d, *J* = 7.6 Hz, 1 H), 8.01 (d, *J* = 7.2 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.62-7.54 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 166.3, 153.8, 137.8, 137.1, 135.0, 134.7, 131.6, 128.0, 127.2, 125.9, 125.4 (q, *J* = 3.6 Hz), 122.2; ESI-HRMS: Calcd for $C_{15}H_9F_3NOS$ $[M+H]^+$: 308.0351; Found: 308.0330.



(5-Chloro-benzothiazol-2-yl)-(4-trifluoromethyl-phenyl)-methanone (**4h**). Orange solid; m.p. 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 2 H), 8.23 (s, 1 H), 7.94 (d, *J* = 4.8 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 7.55-7.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 168.0, 154.5, 137.4, 135.3, 135.2, 134.9, 133.3, 131.6, 128.6, 125.5 (q, *J* = 3.6 Hz), 125.4, 123.0; ESI-HRMS: Calcd for $C_{15}H_8ClF_3NOS$ $[M+H]^+$: 341.9962; Found: 341.9933.



Benzothiazol-2-yl-(thiophen-2-yl)-methanone (**4i**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.0 Hz, 1 H), 8.24 (d, *J* = 8.8 Hz, 1 H), 8.00 (d, *J* = 7.6 Hz, 1 H), 7.84 (d, *J* = 5.2 Hz, 1 H), 7.61-7.52 (m, 2 H), 7.26 (d, *J* = 4.0 Hz, 1 H).



Benzothiazol-2-yl-(naphthalen-1-yl)-methanone (**4j**).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.0 Hz, 1 H), 8.35 (d, *J* = 7.6 Hz, 1 H), 8.19-8.17 (m, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 8.03-8.01 (m, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.62-7.54 (m, 5 H).

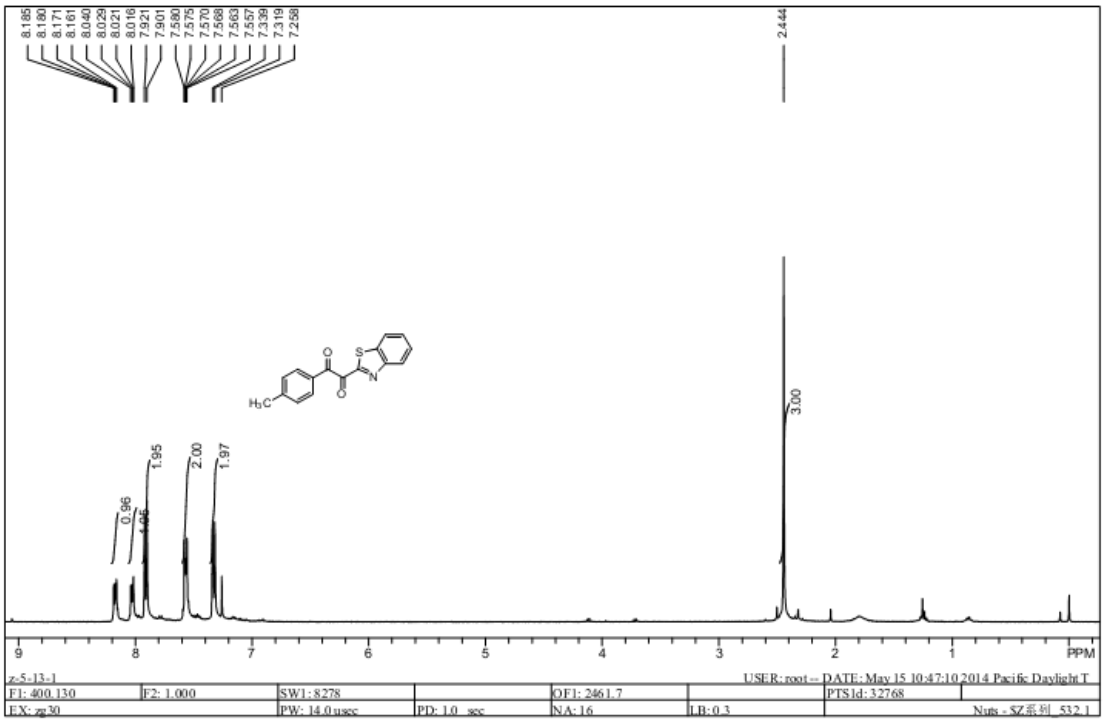
References

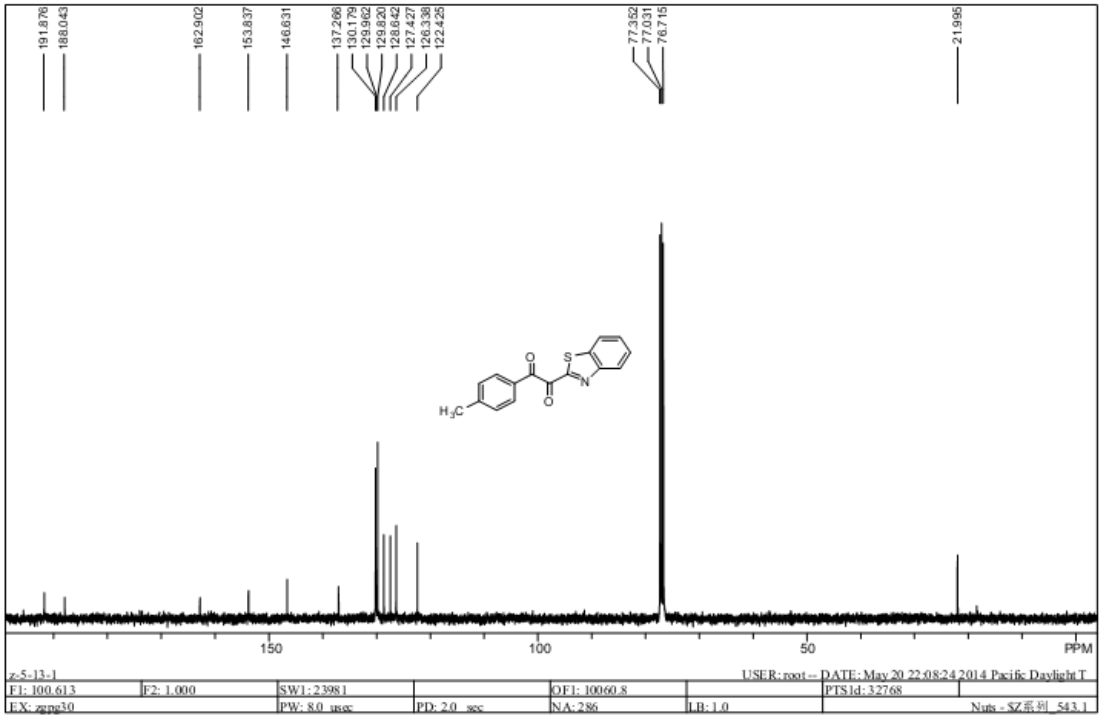
[1] F. M. A. A. El-Taweel, M. H. Elnagdi, *J. Heterocyclic Chem.* 2001, **38**, 981.

[2] Q.-H. Gao, X. Wu, F.-C. Jia, M.-C. Liu, Y.-P. Zhu, Q. Cai, A.-X. Wu, *J. Org. Chem.* **2013***, 78,* 2792.

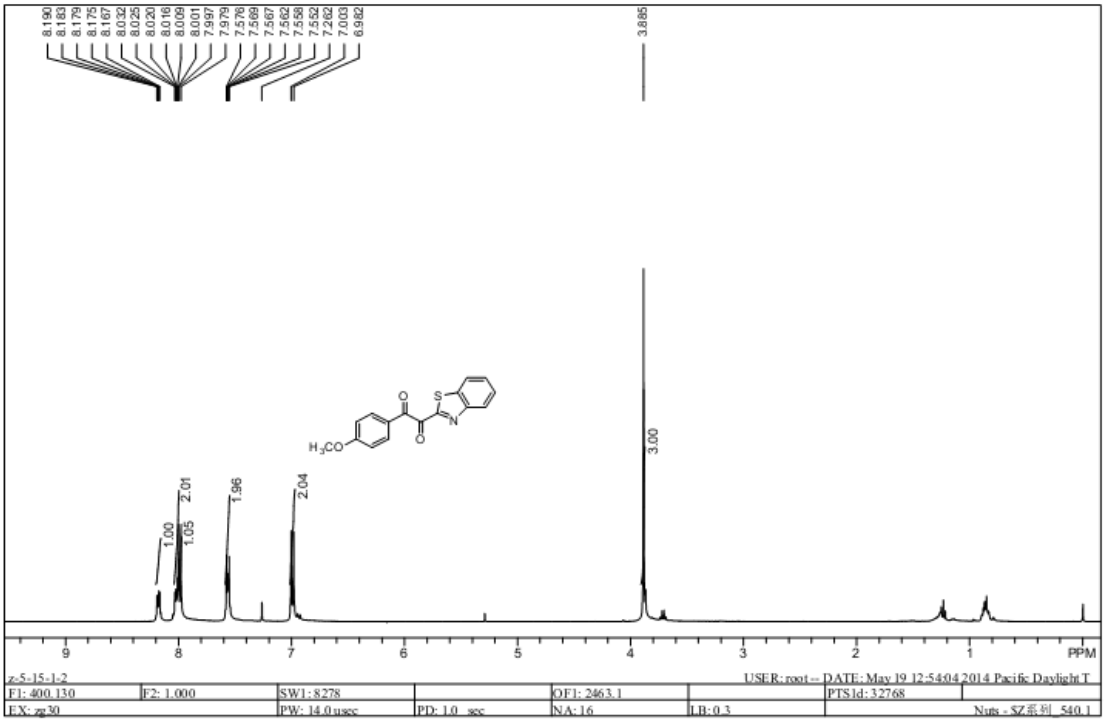
^{1}H and ^{13}C NMR spectra of all products

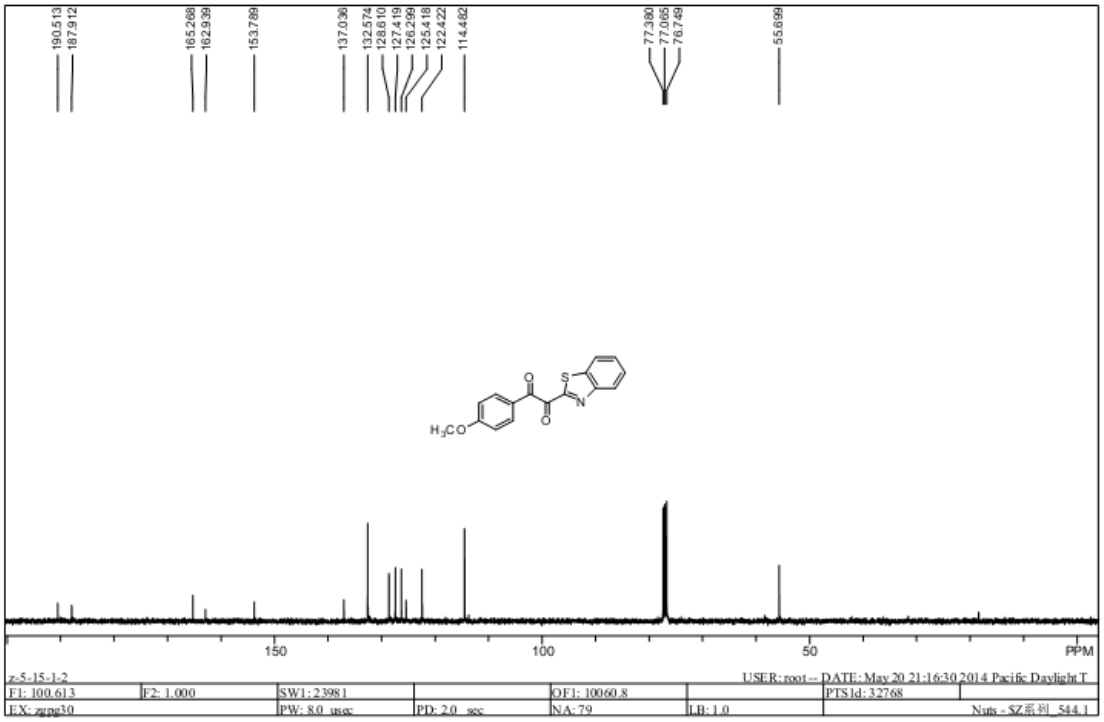
^{1}H and ^{13}C NMR spectra of **3a**



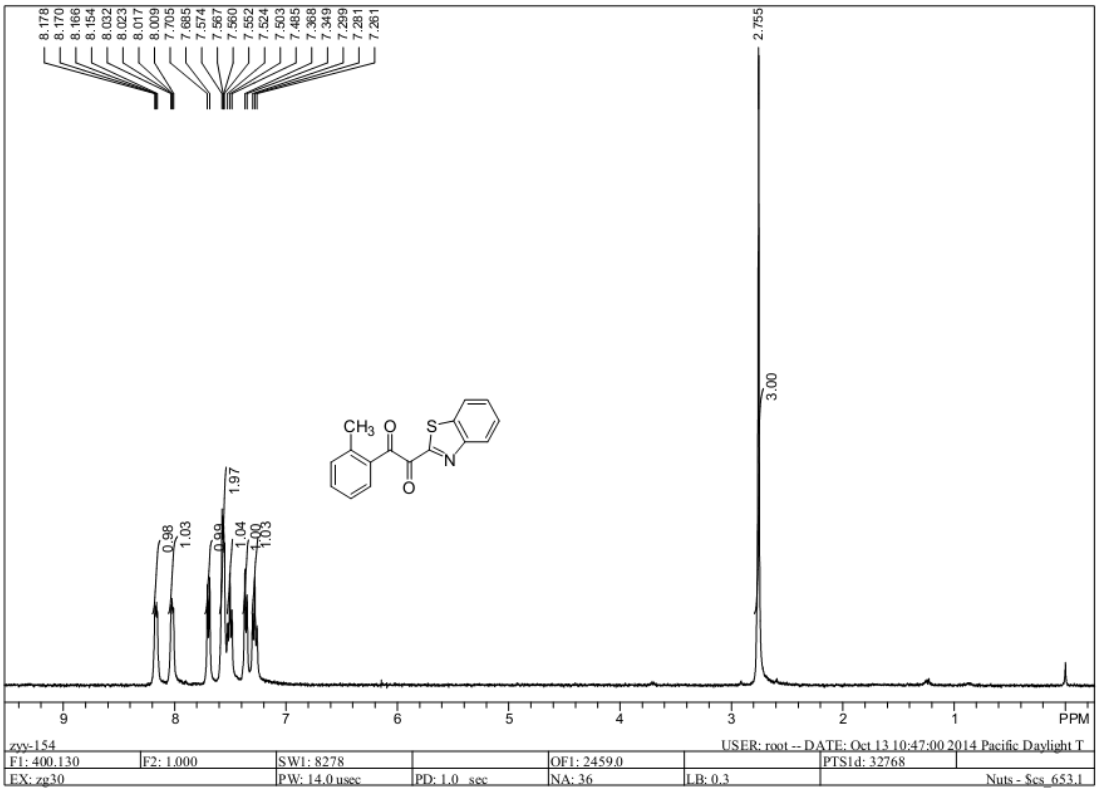


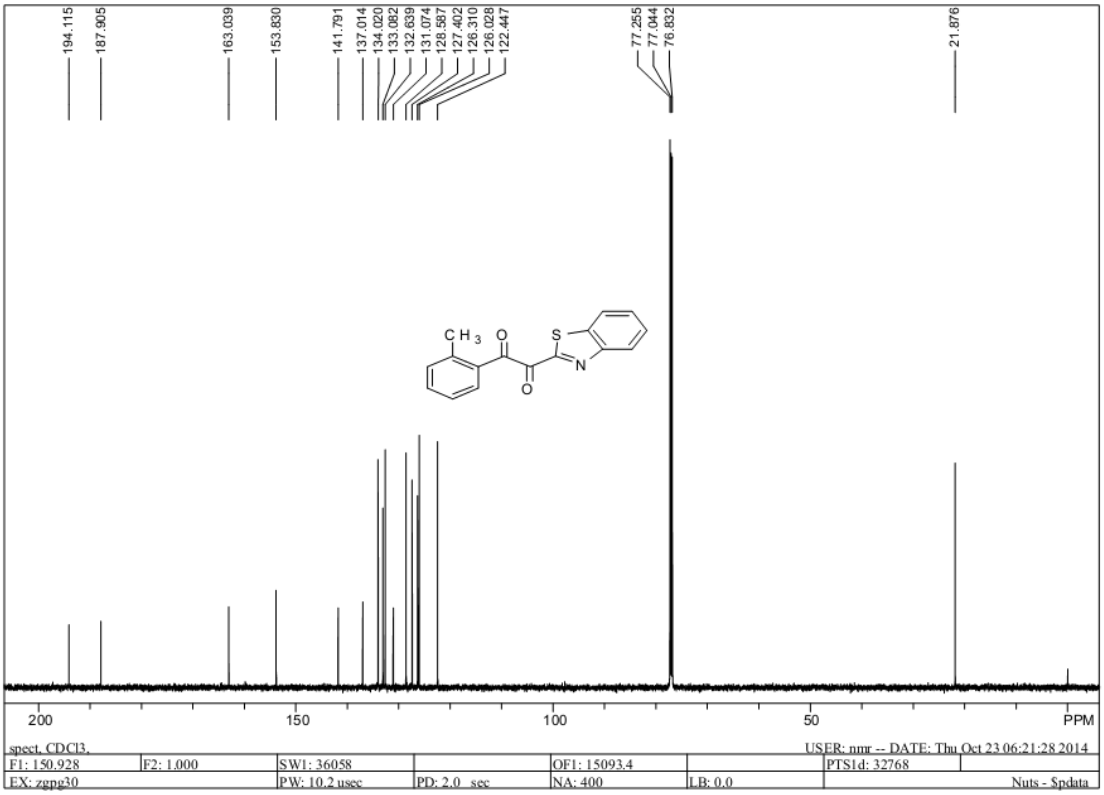
^{1}H and ^{13}C NMR spectra of **3b**



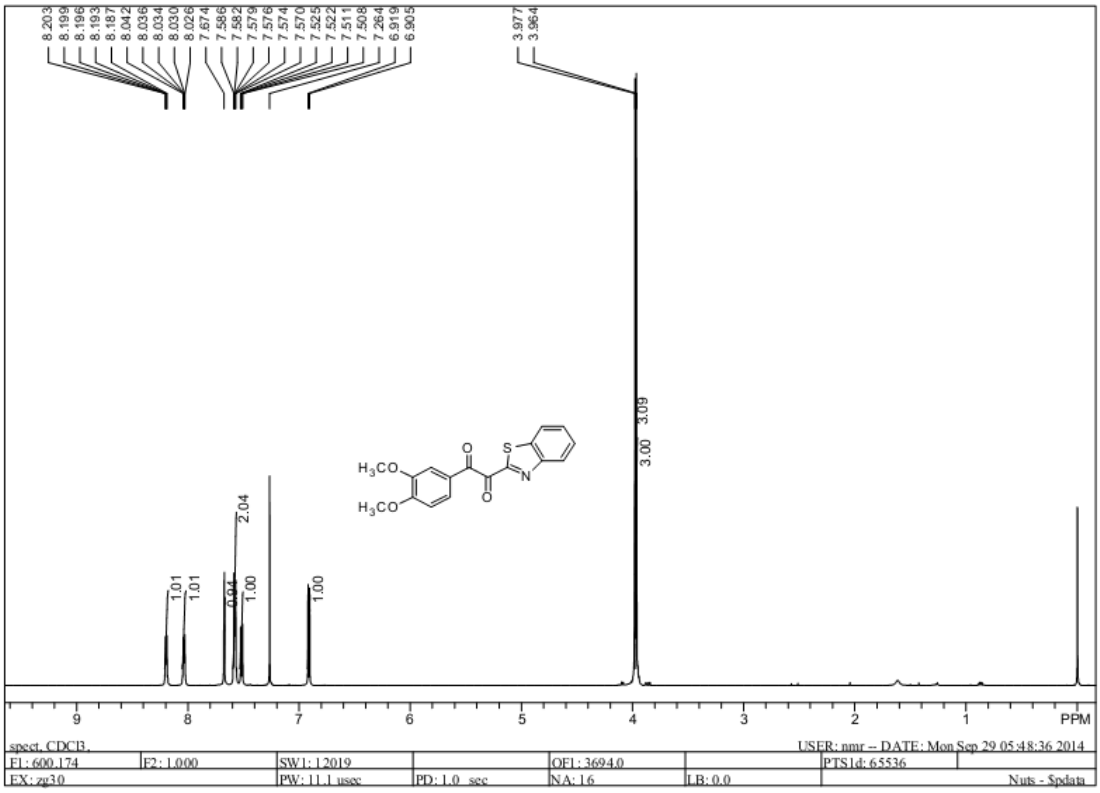


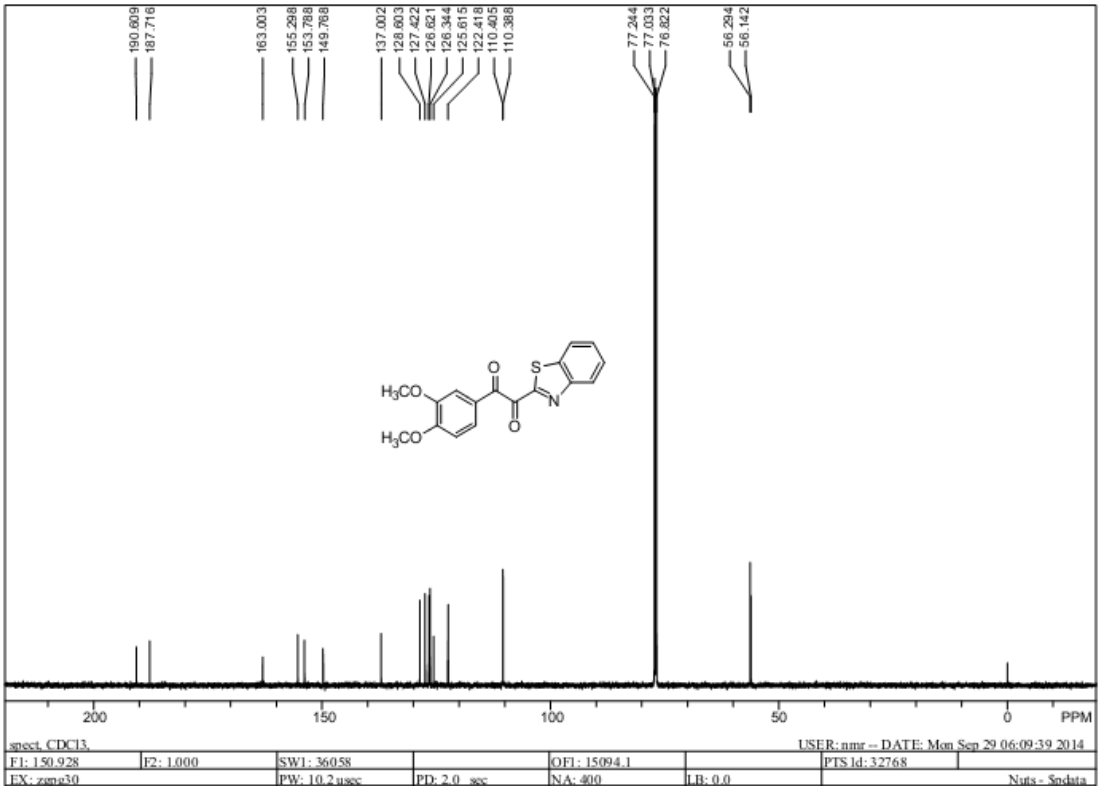
^{1}H and ^{13}C NMR spectra of **3c**



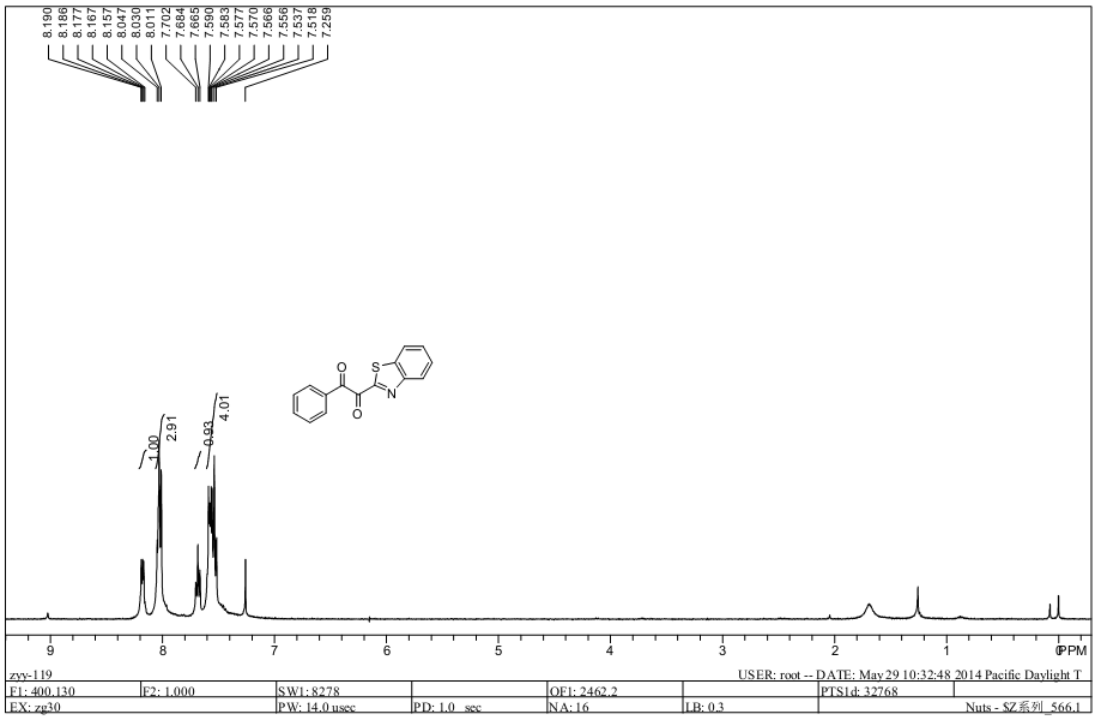


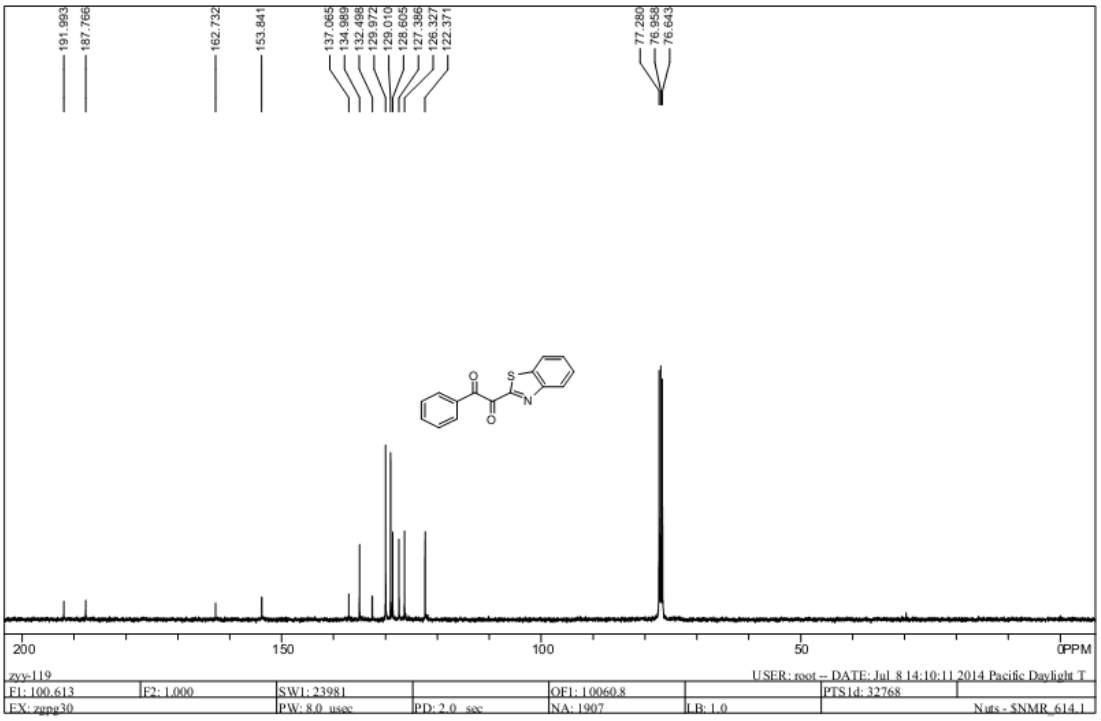
^{1}H and ^{13}C NMR spectra of **3d**



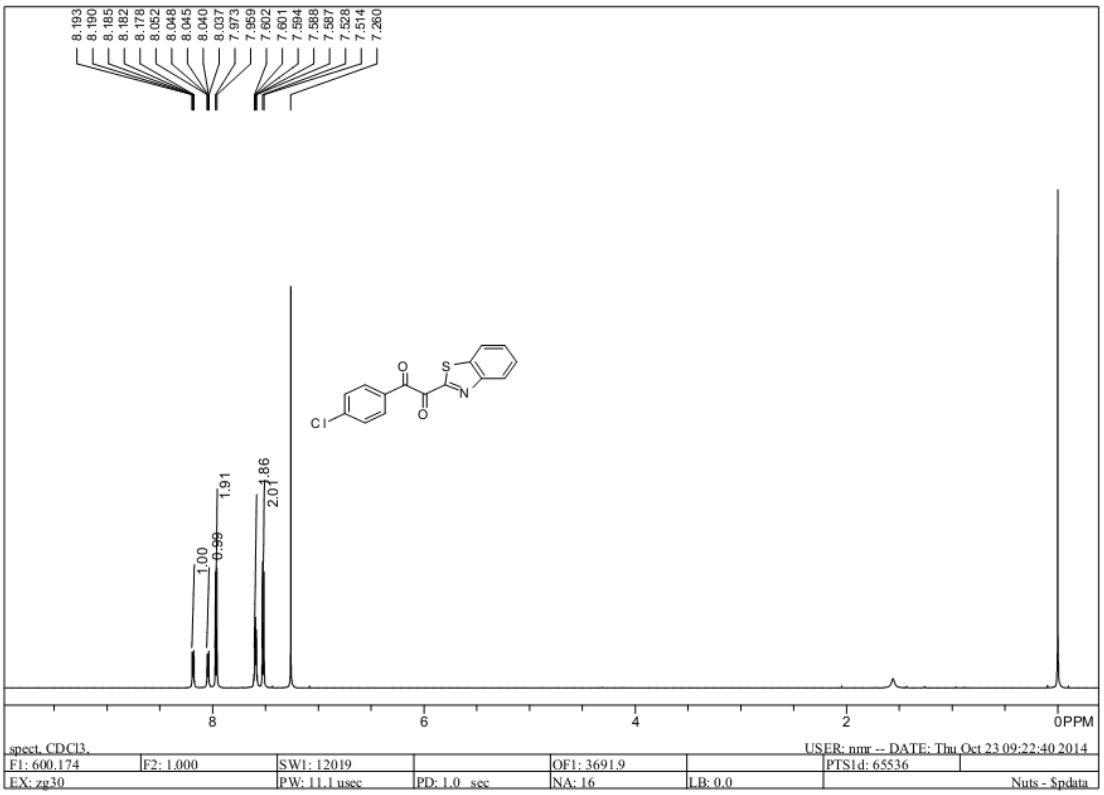


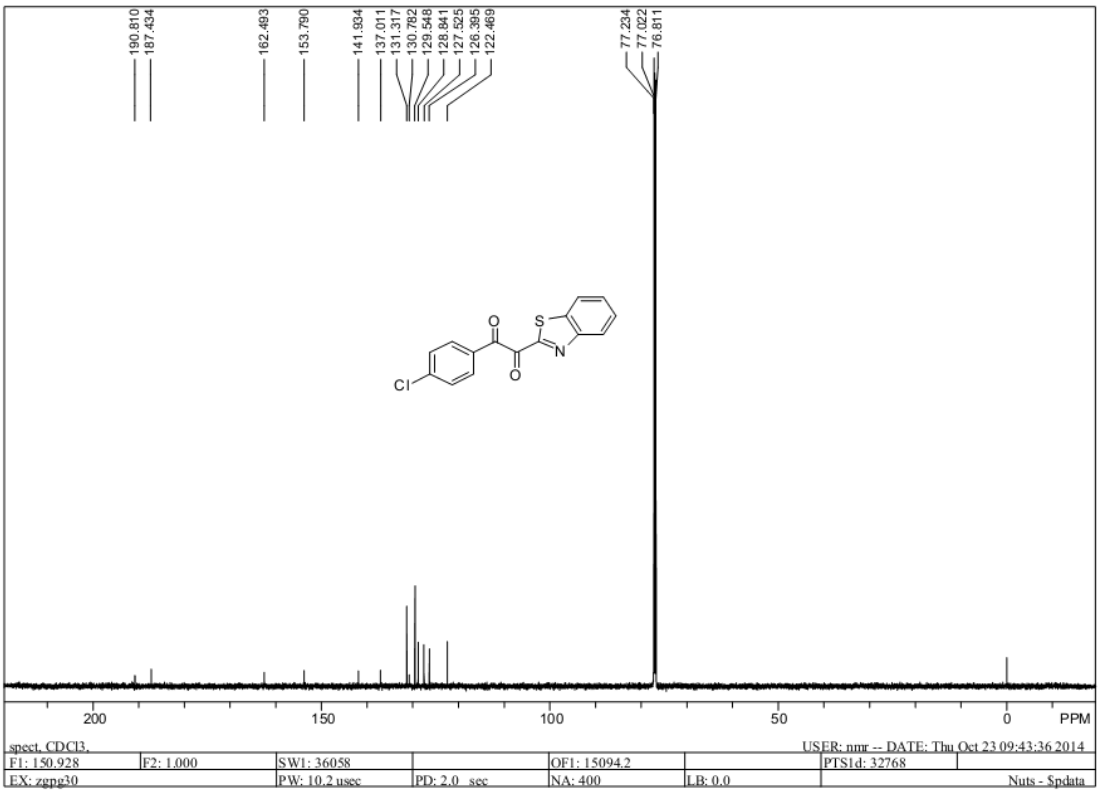
^{1}H and ^{13}C NMR spectra of **3e**



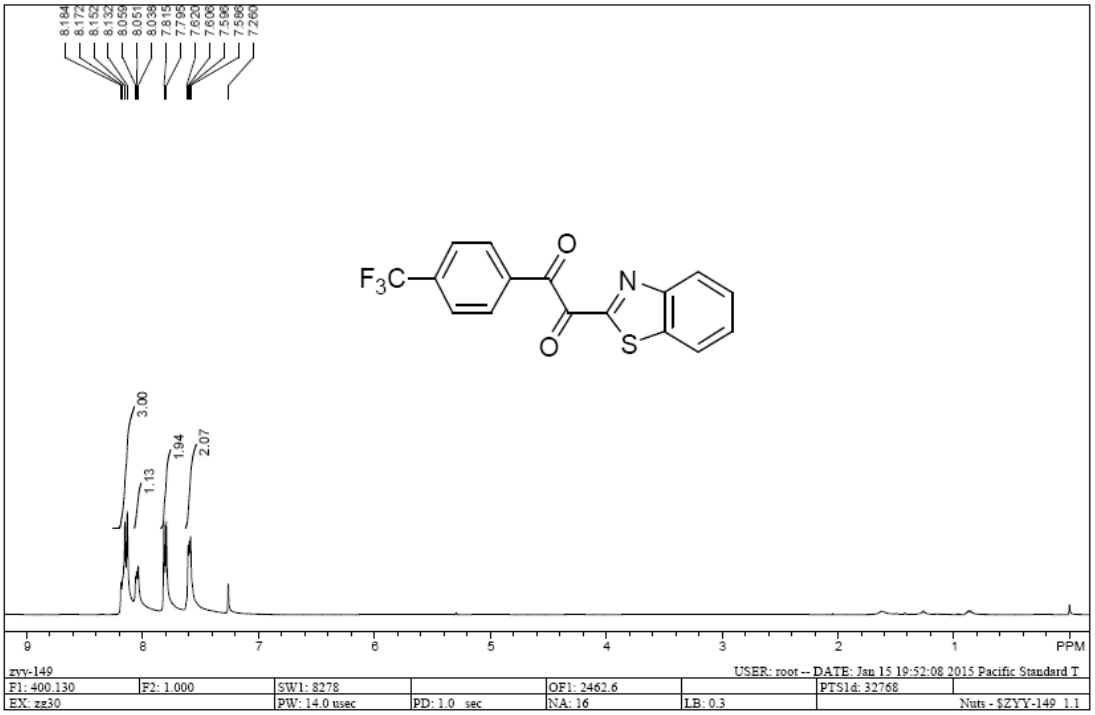


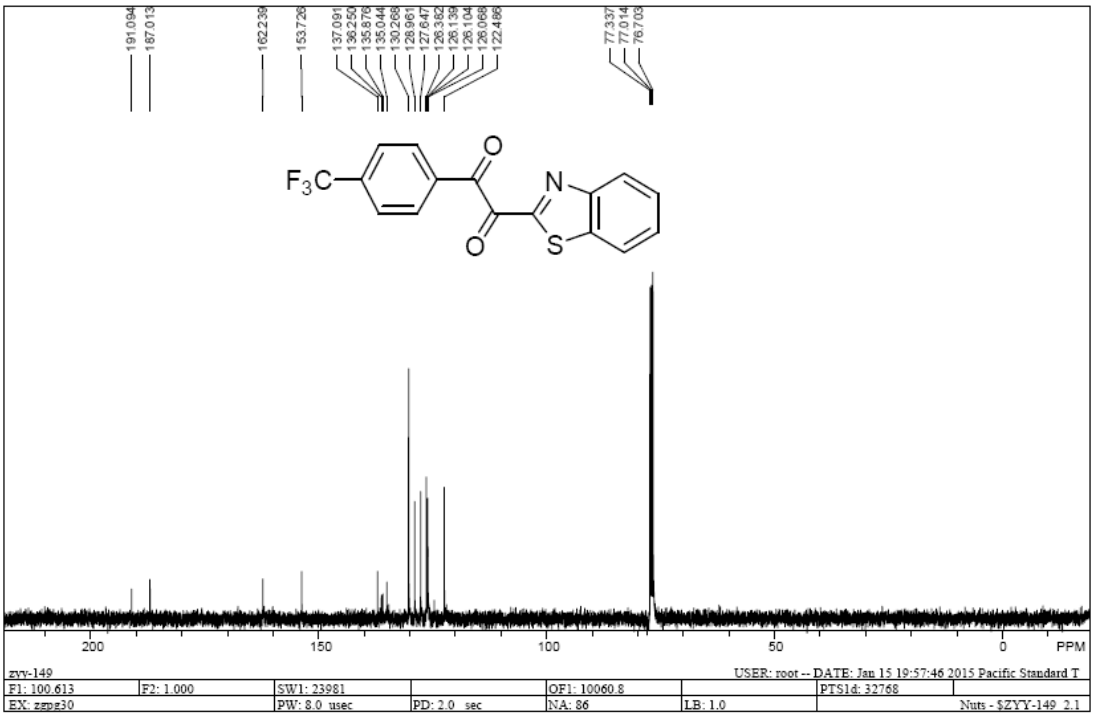
^{1}H and ^{13}C NMR spectra of **3f**



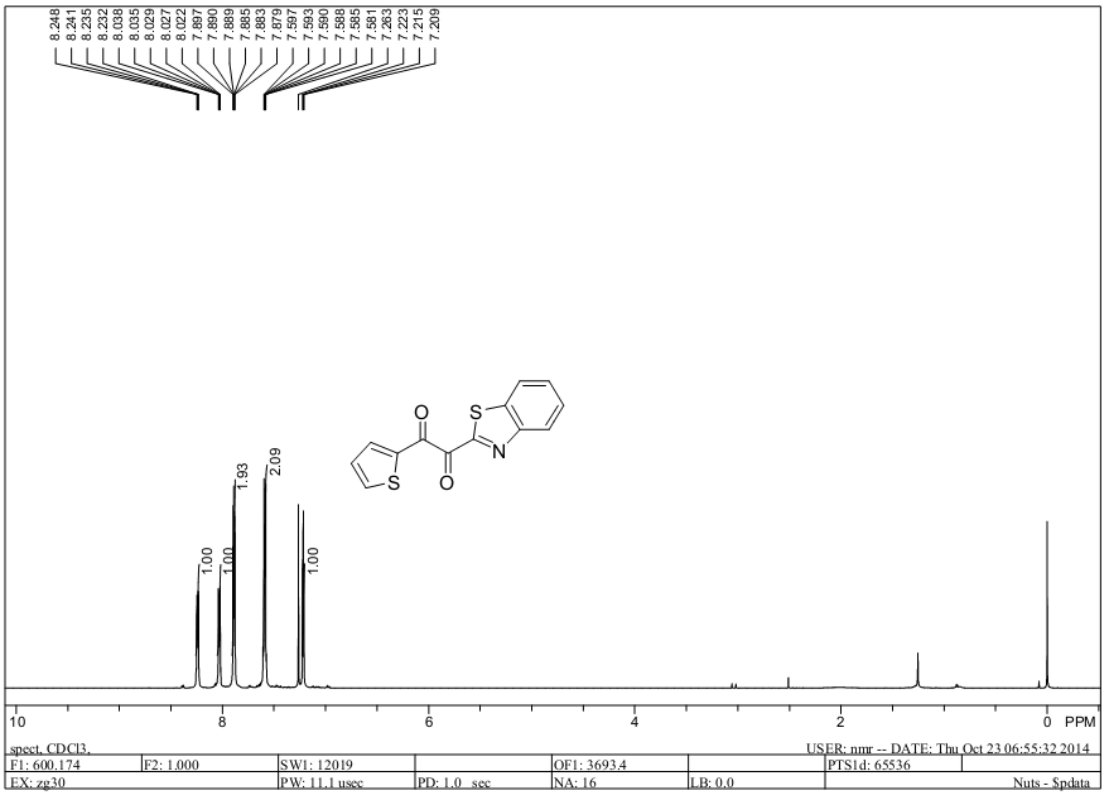


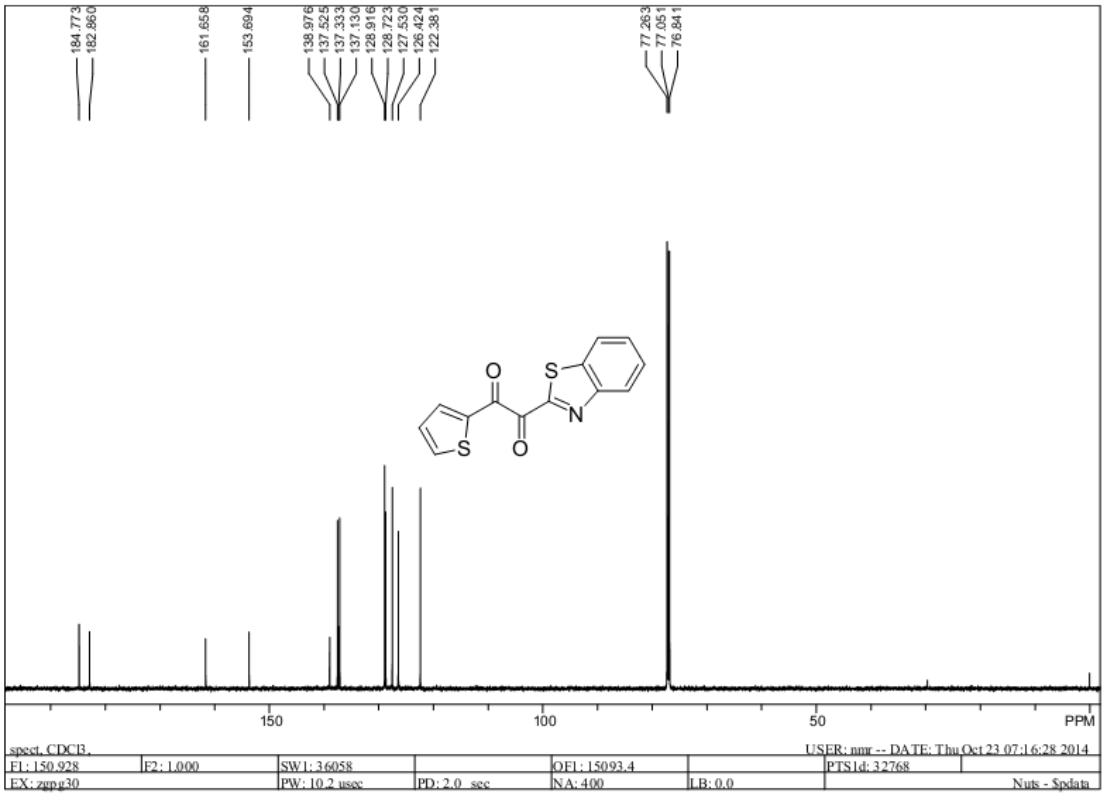
^{1}H and ^{13}C NMR spectra of **3g**



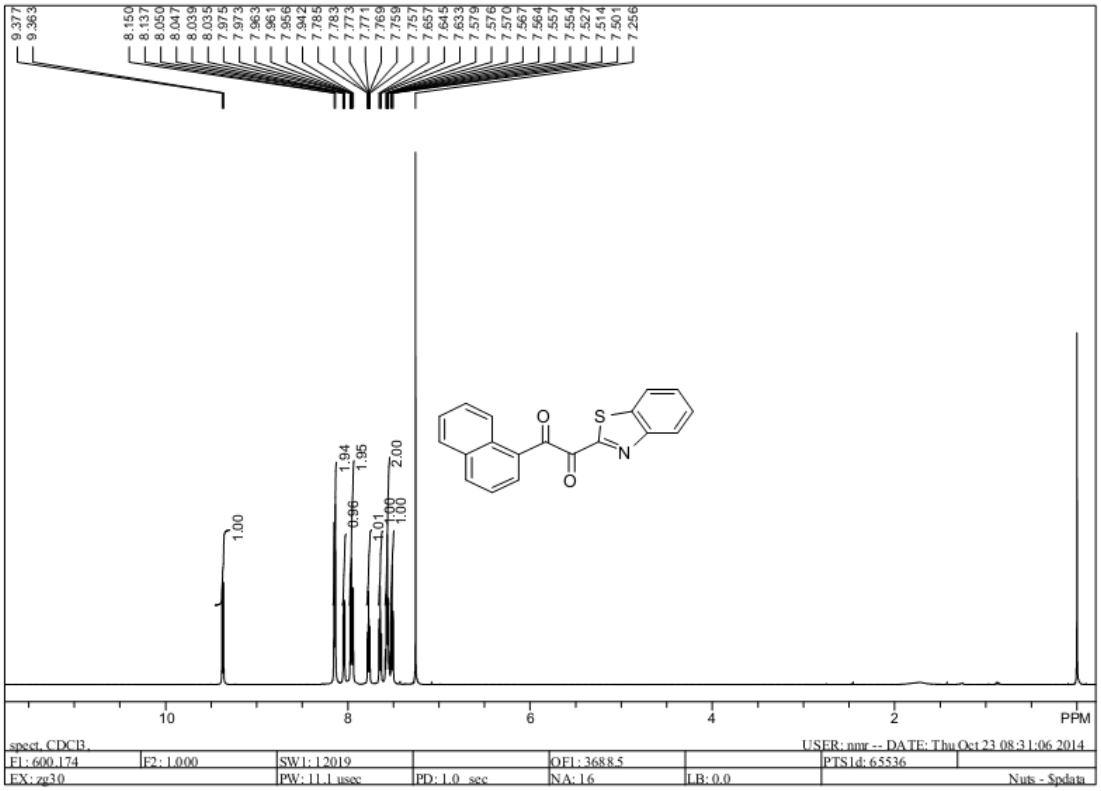


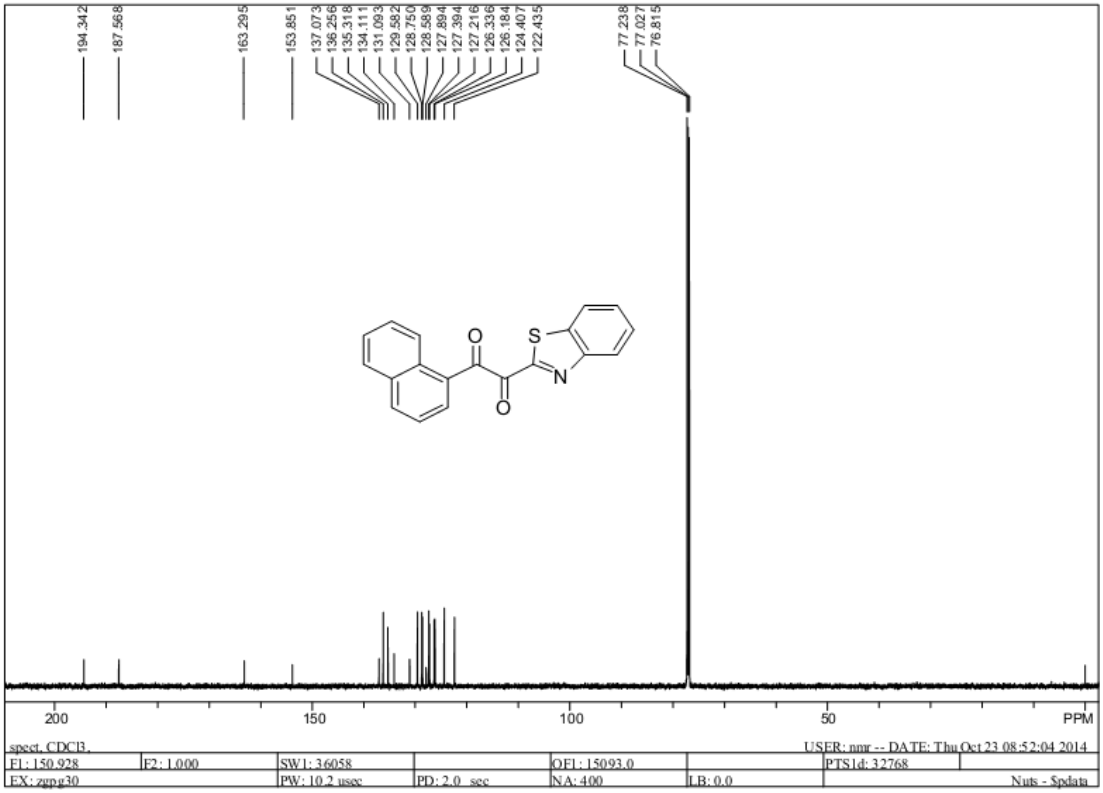
^{1}H and ^{13}C NMR spectra of **3h**



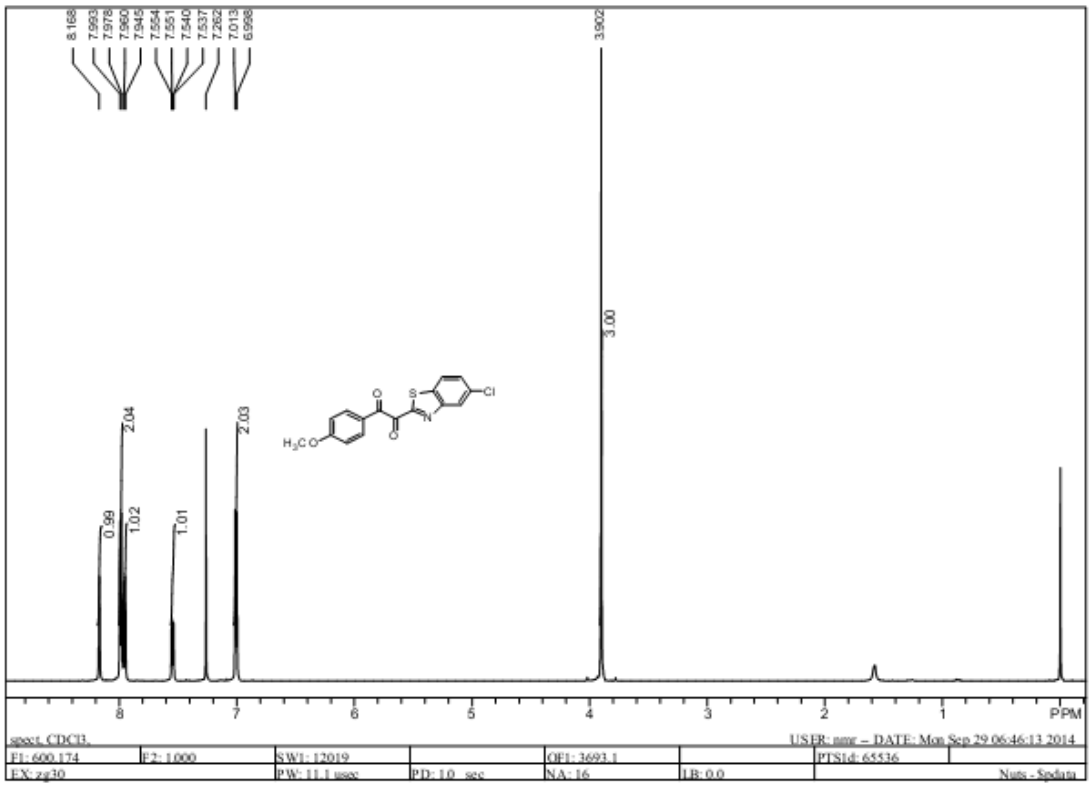


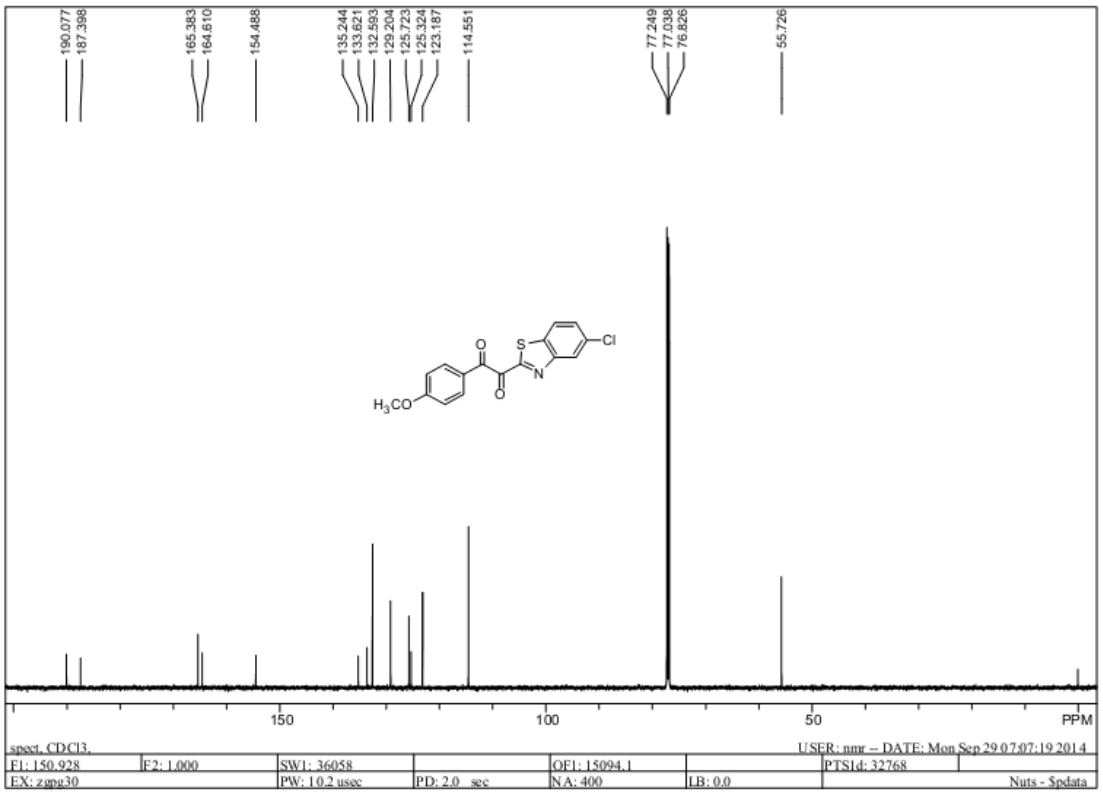
^{1}H and ^{13}C NMR spectra of **3i**



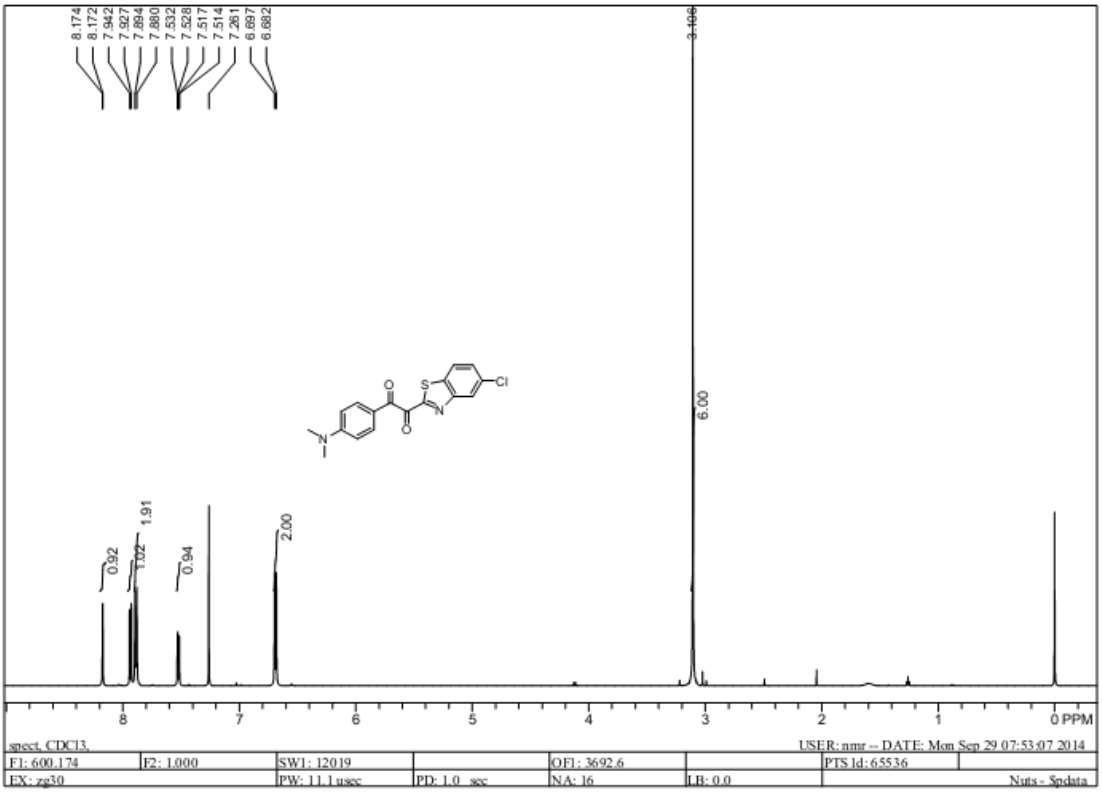


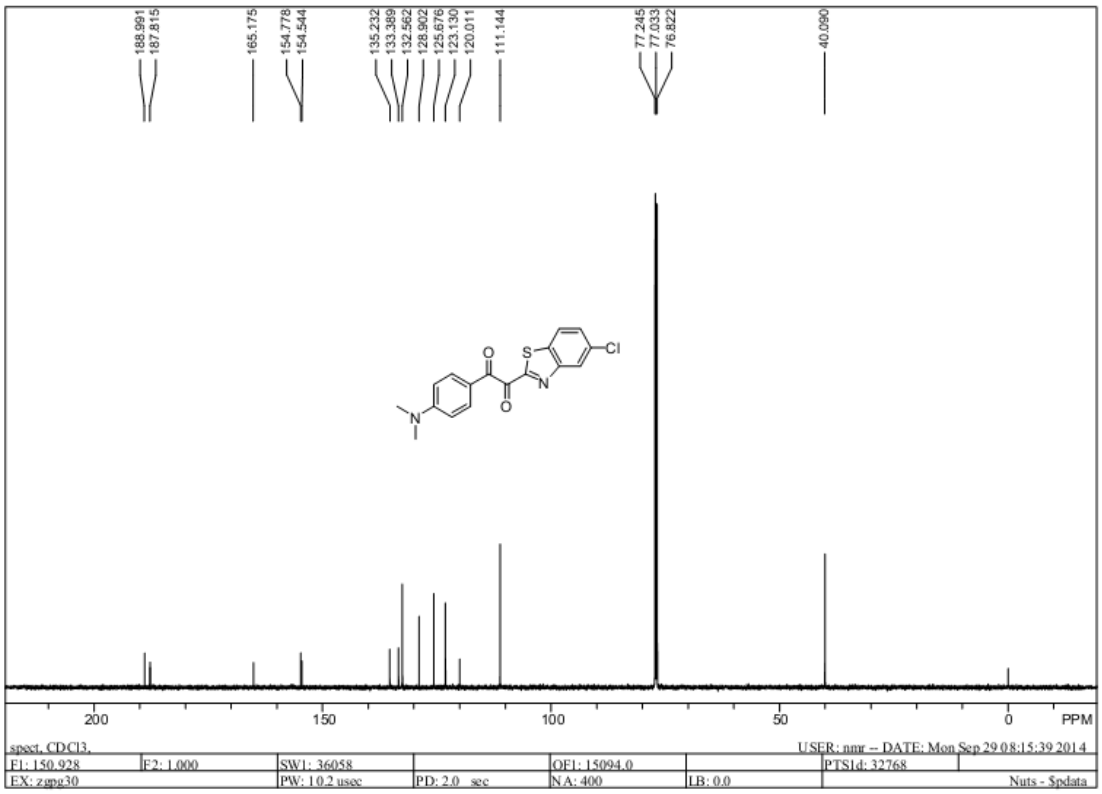
^{1}H and ^{13}C NMR spectra of **3j**



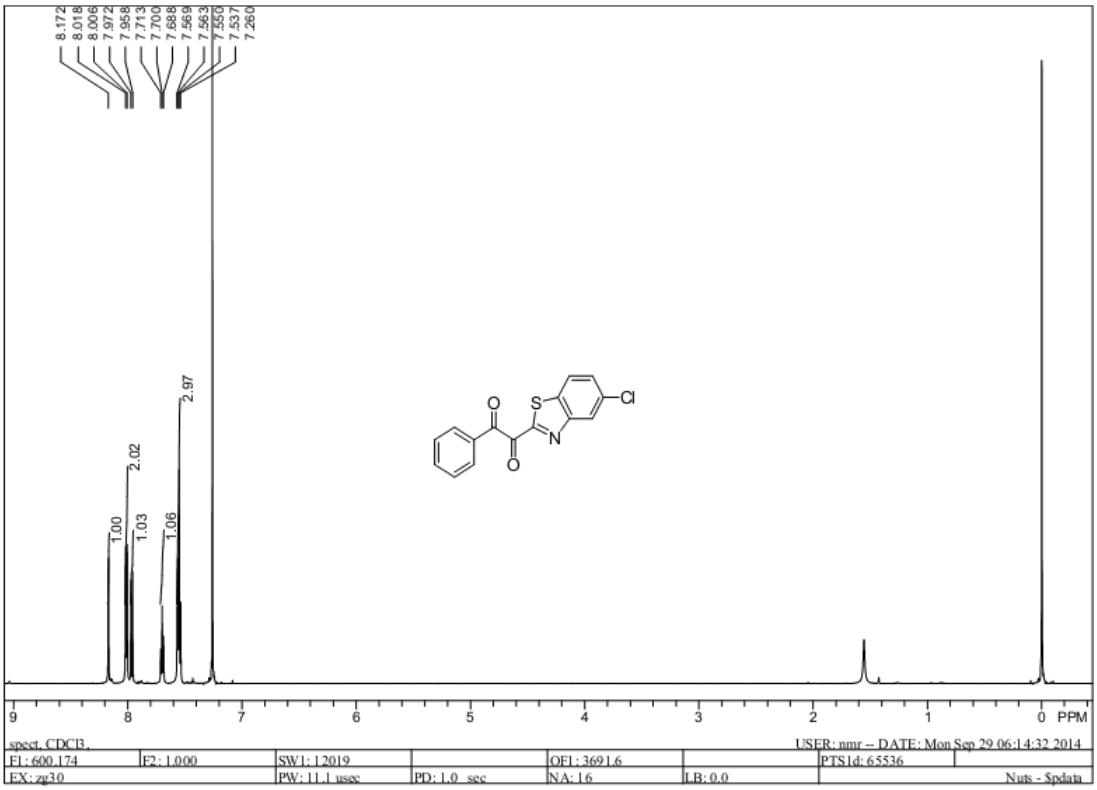


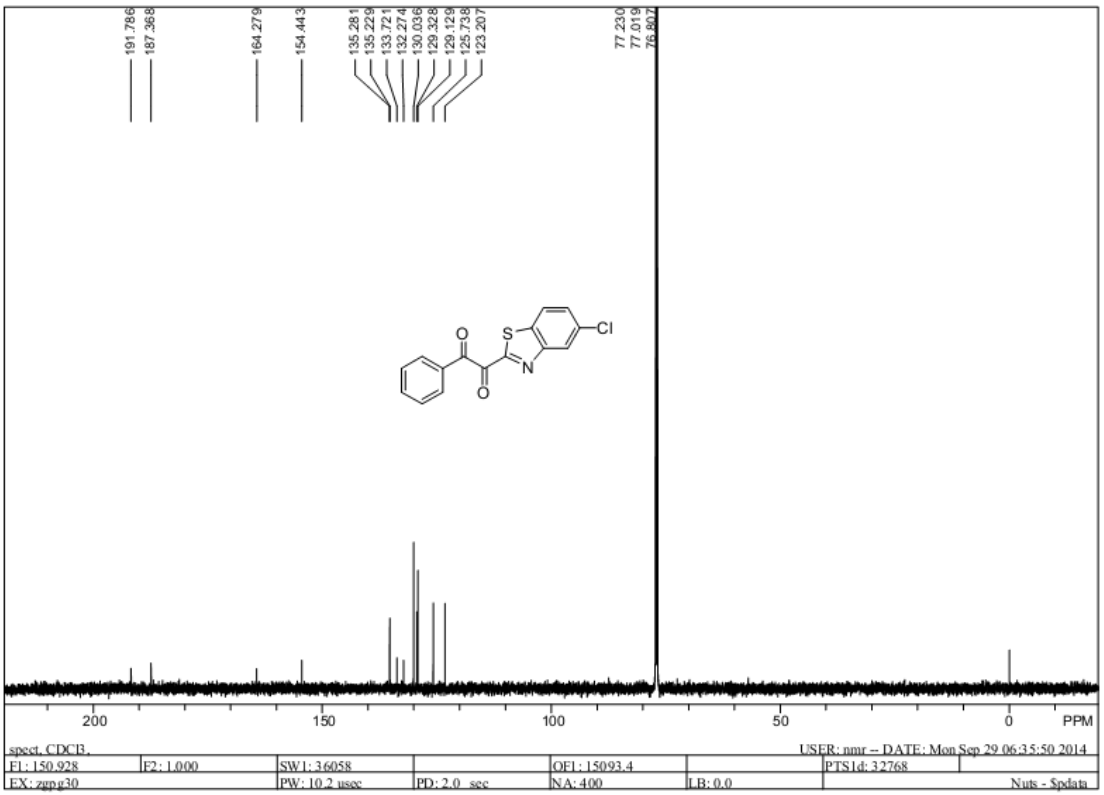
^{1}H and ^{13}C NMR spectra of **3k**



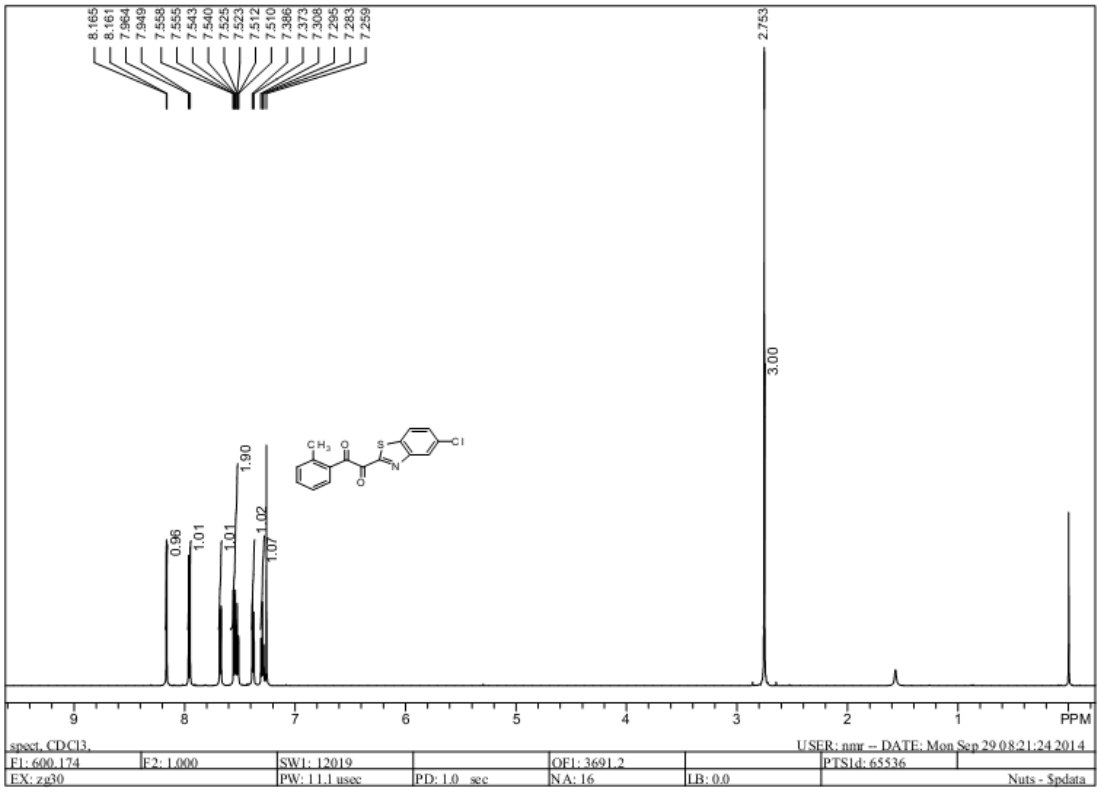


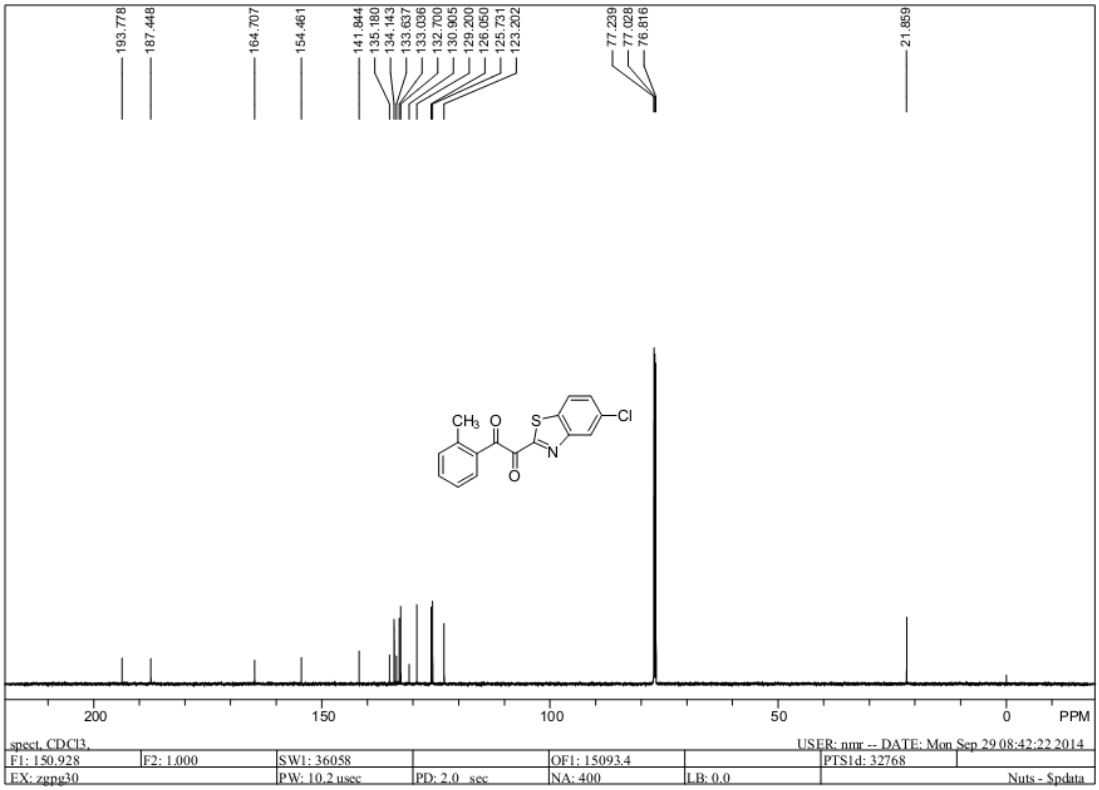
^{1}H and ^{13}C NMR spectra of **3l**



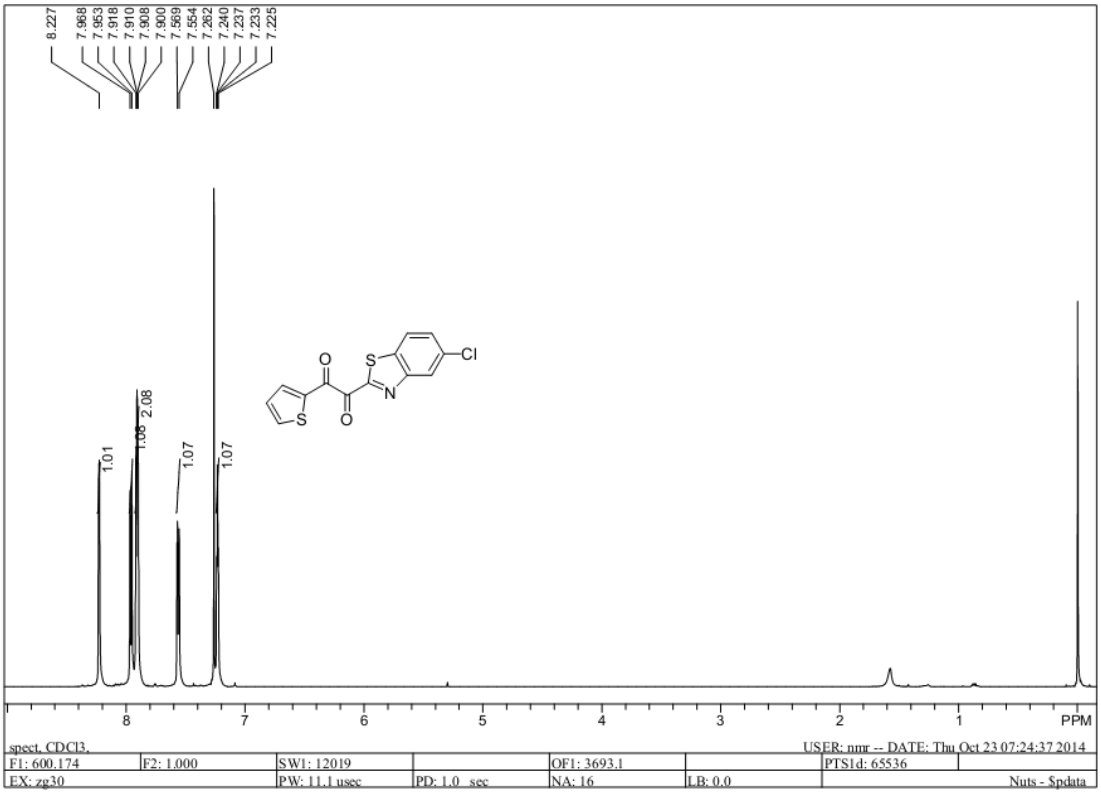


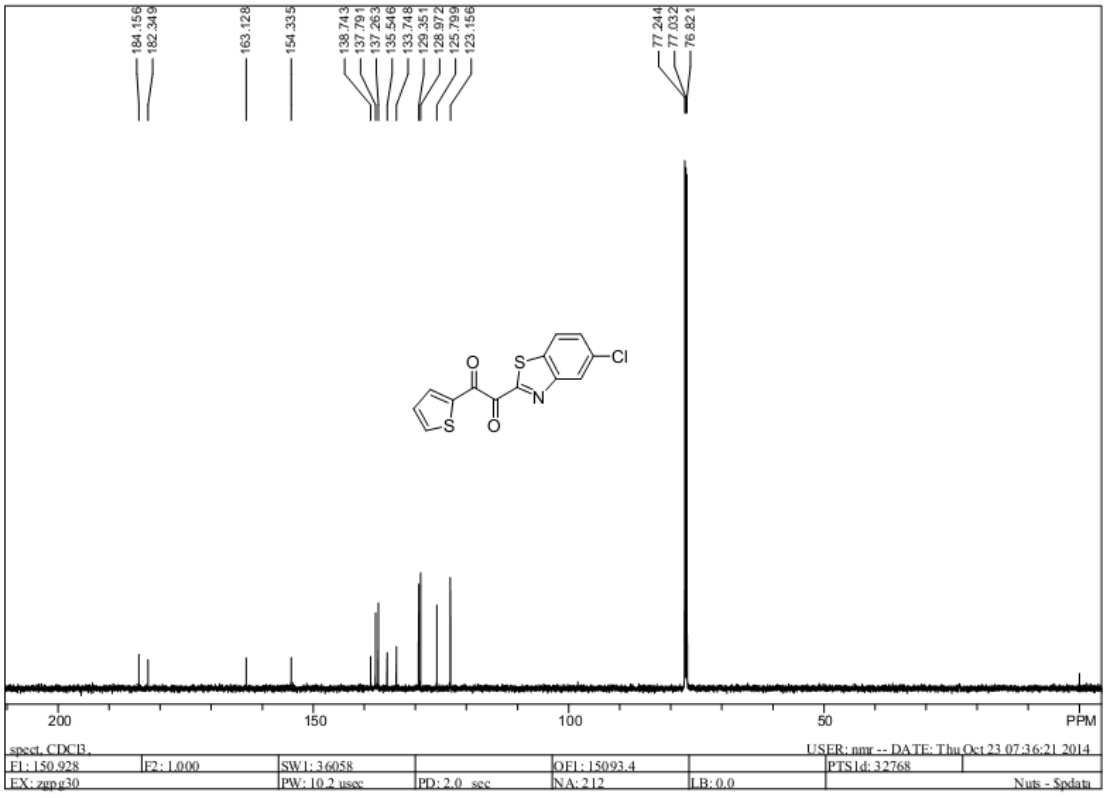
^{1}H and ^{13}C NMR spectra of **3m**



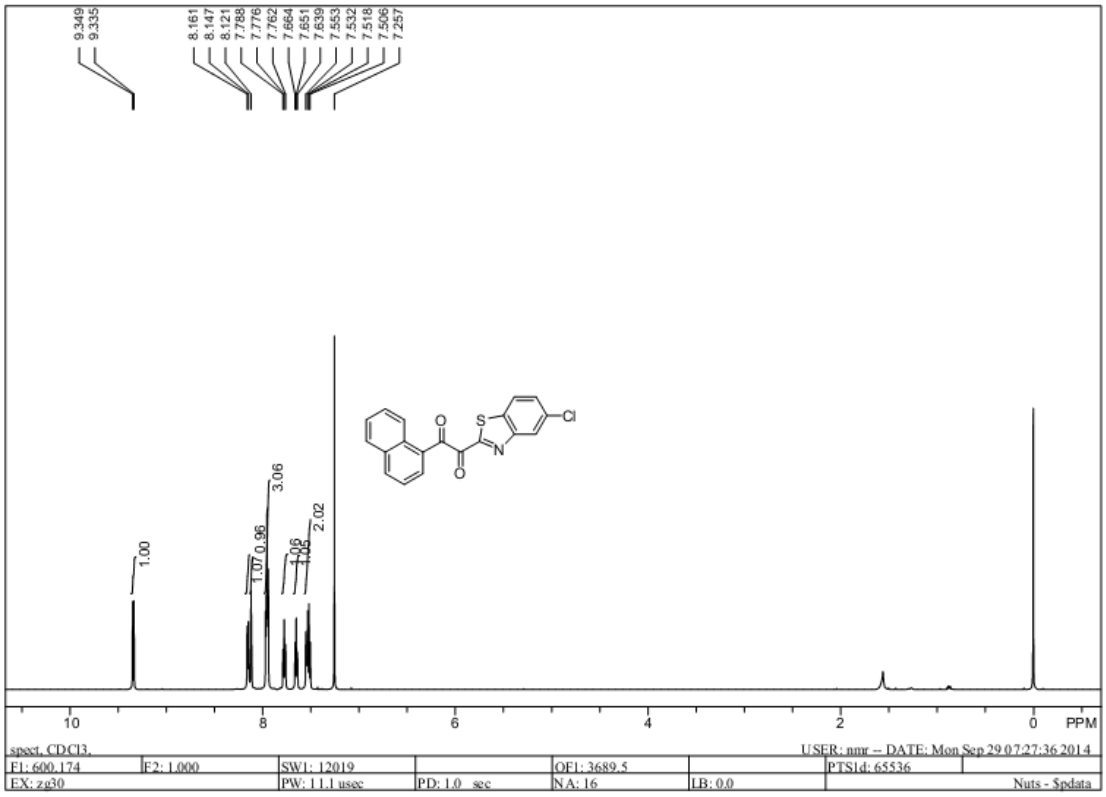


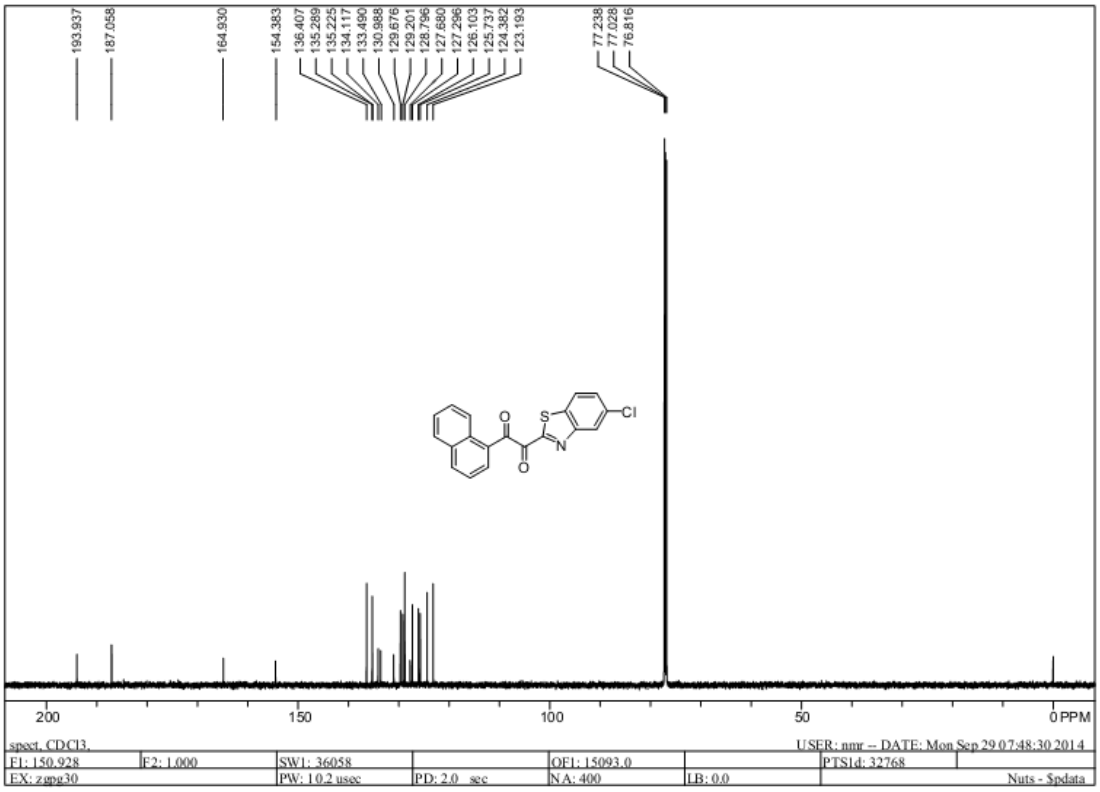
^{1}H and ^{13}C NMR spectra of **3n**



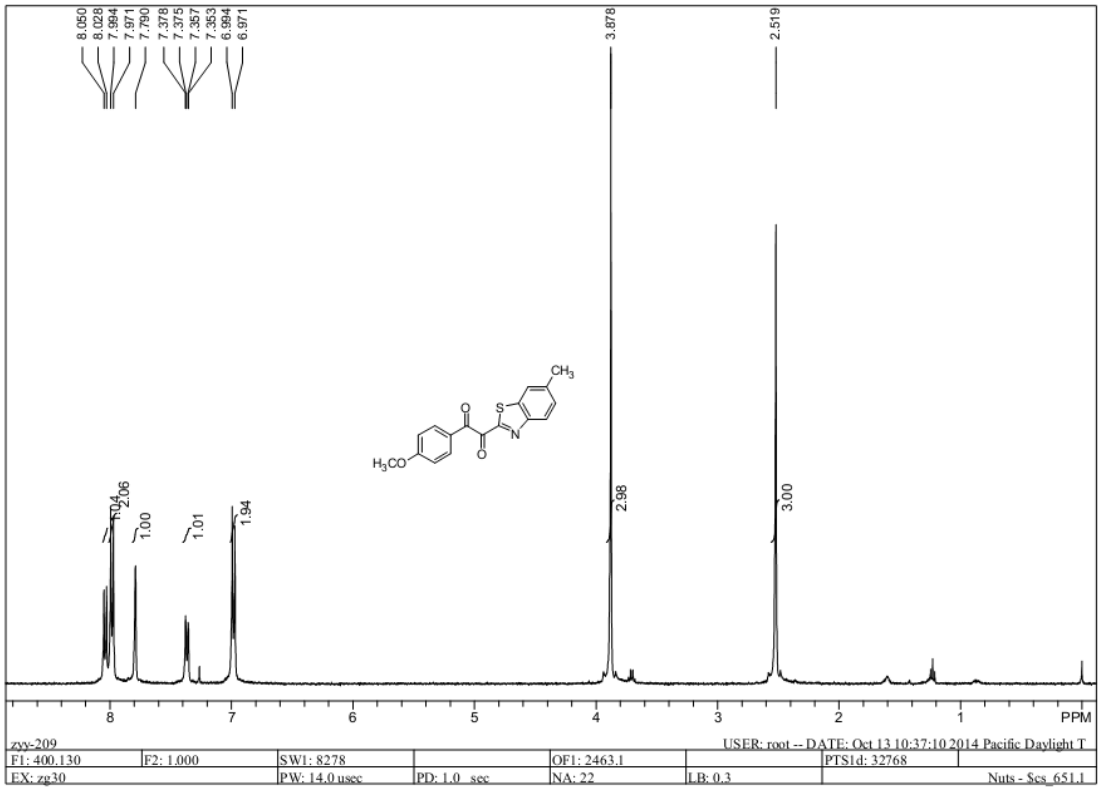


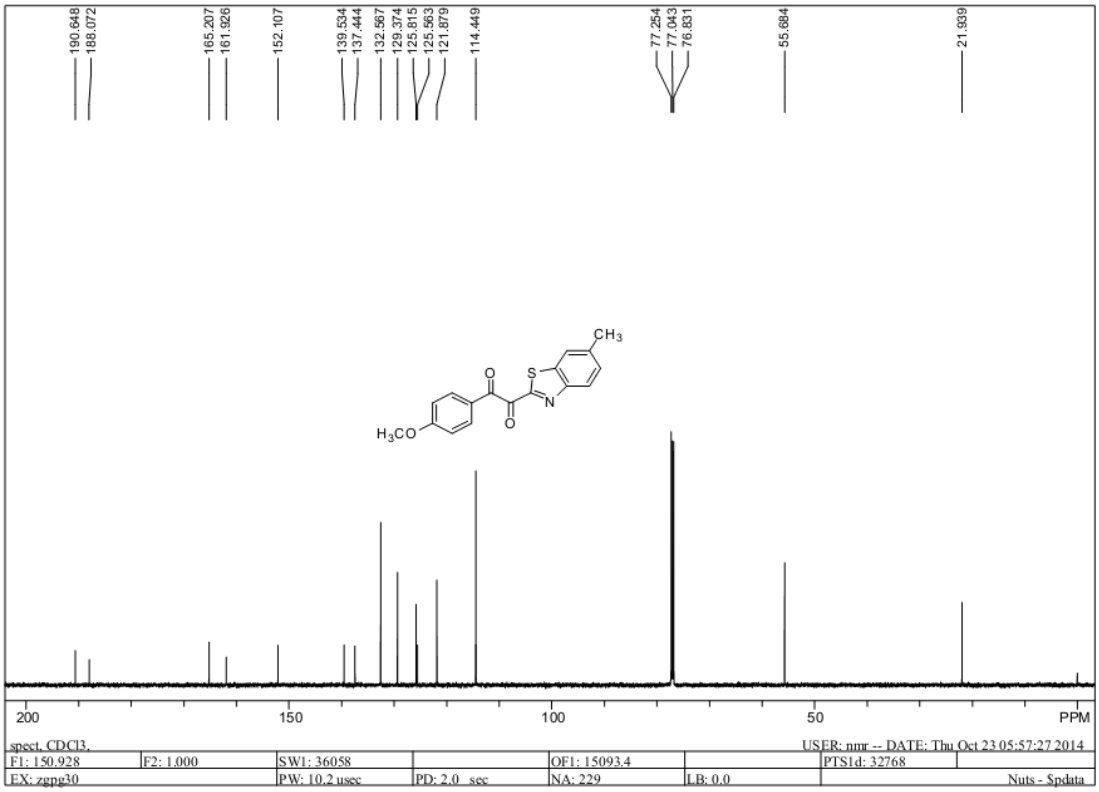
^{1}H and ^{13}C NMR spectra of **3o**



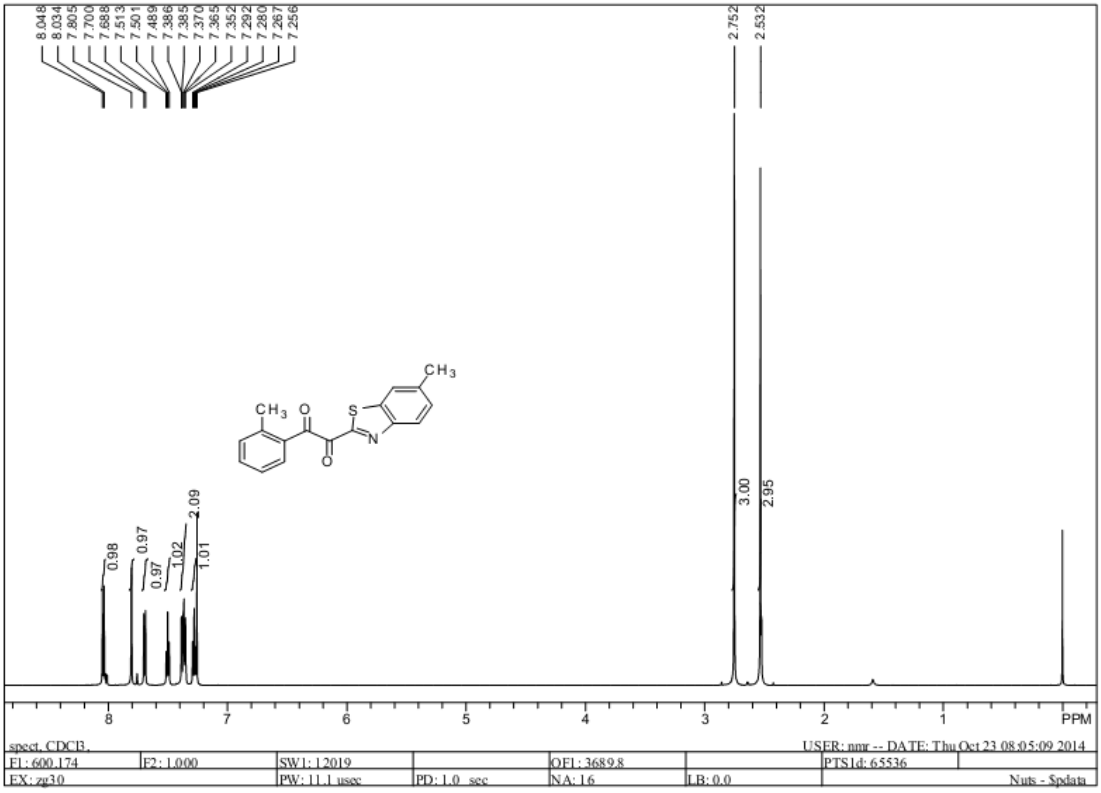


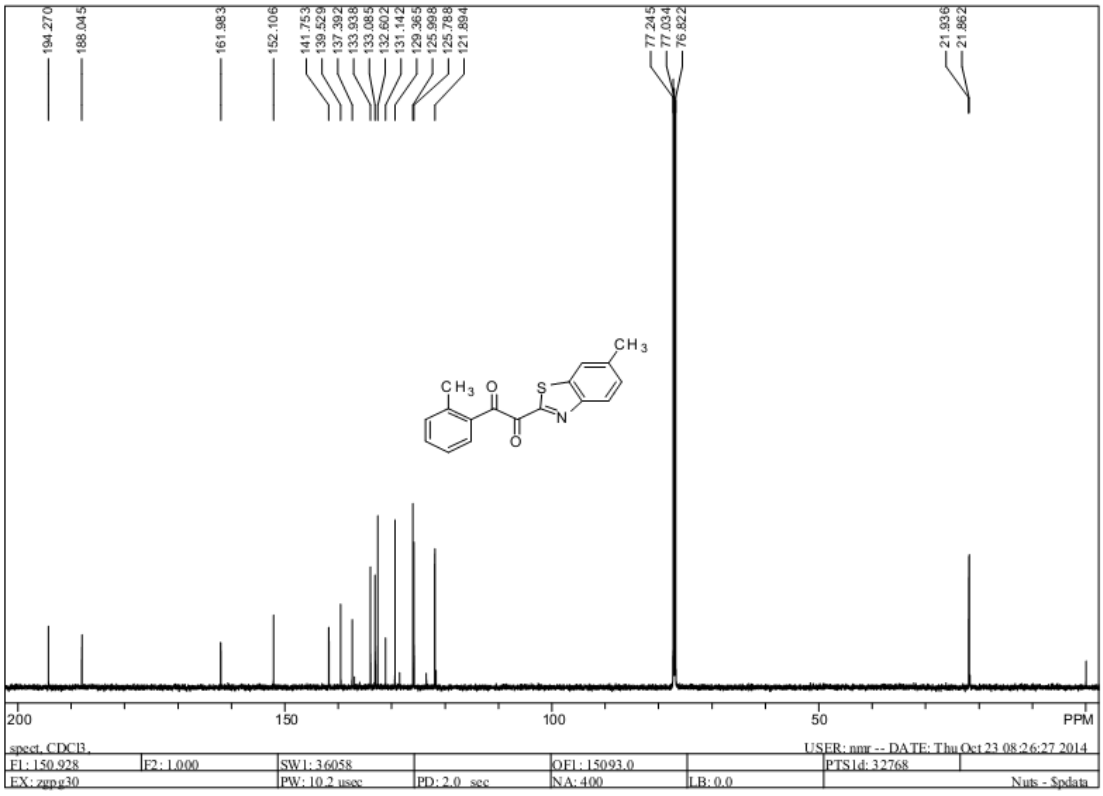
^{1}H and ^{13}C NMR spectra of **3p**



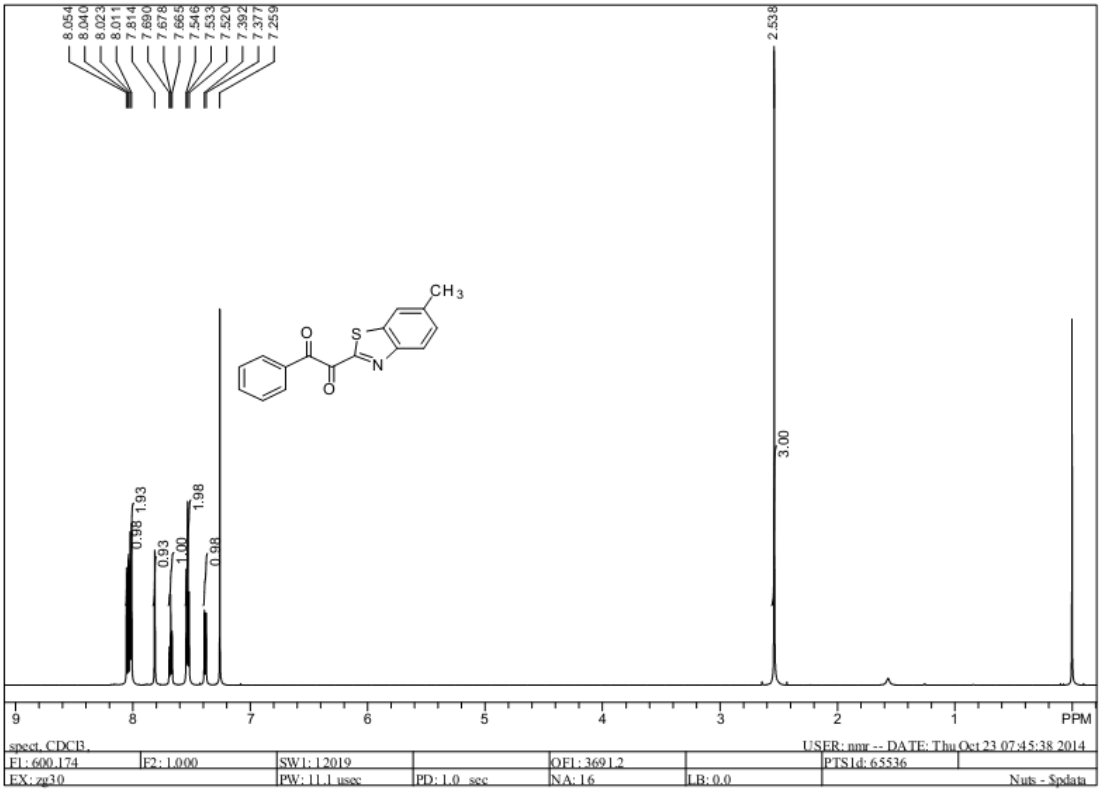


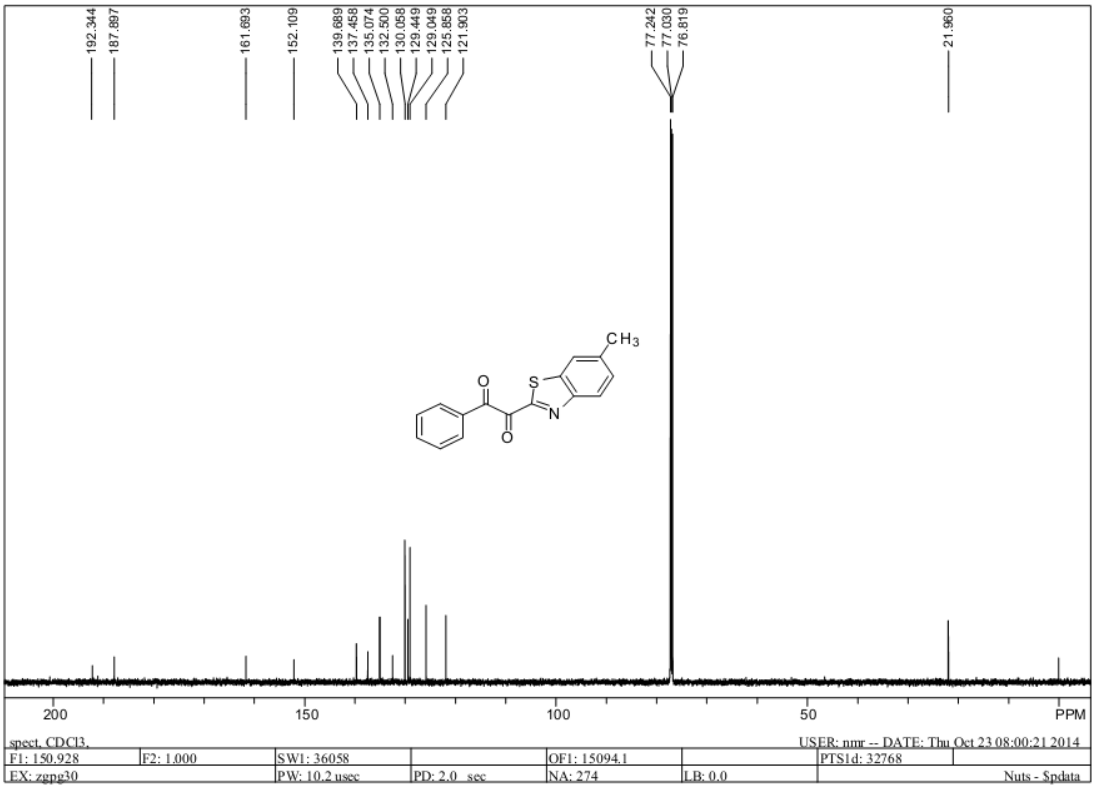
^{1}H and ^{13}C NMR spectra of **3q**



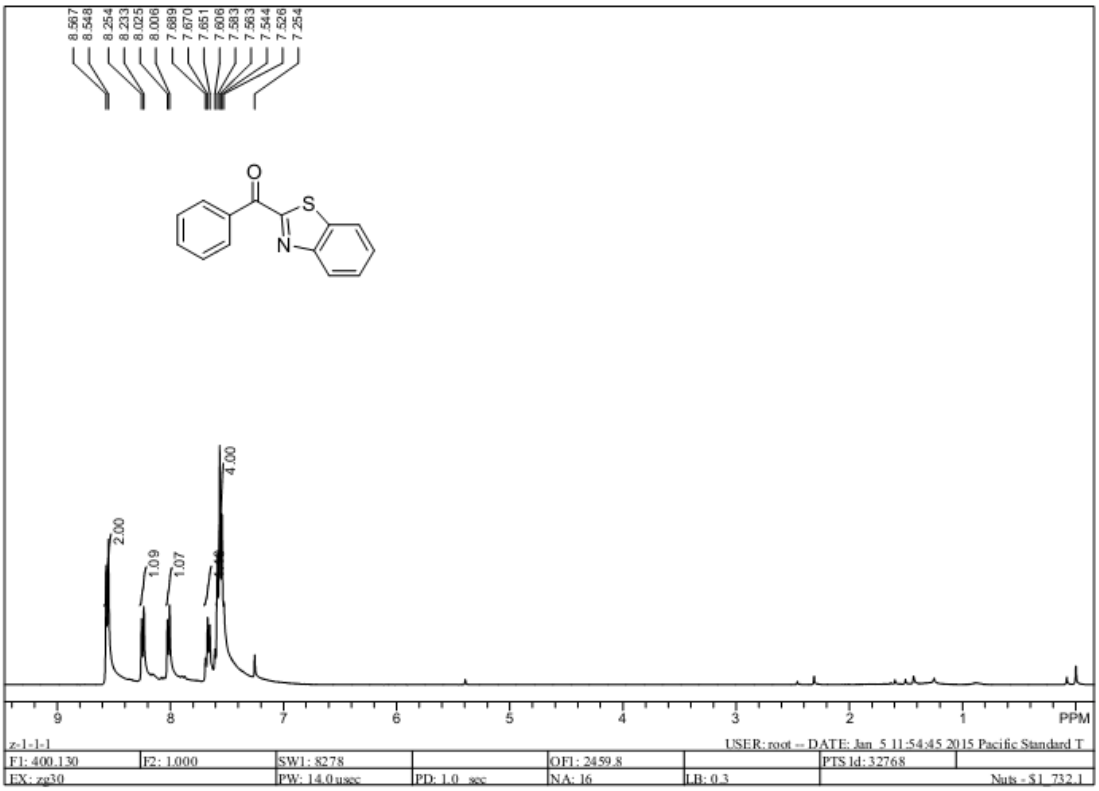


^{1}H and ^{13}C NMR spectra of **3r**

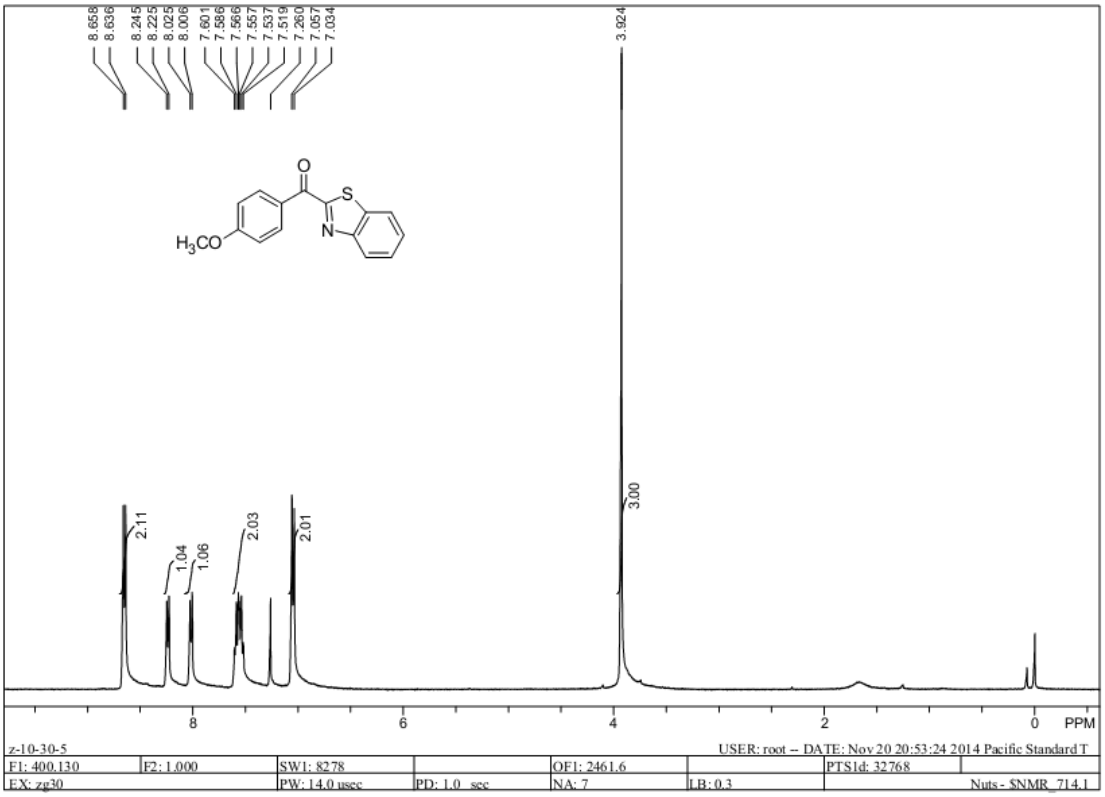




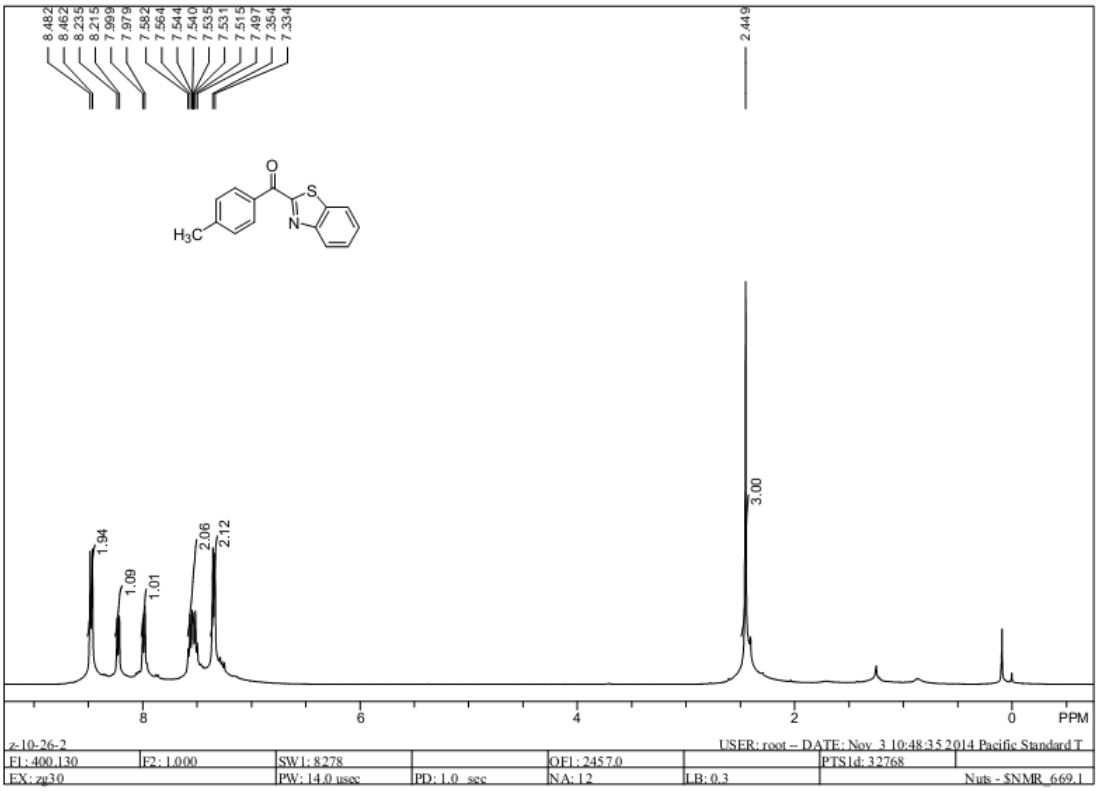
^{1}H NMR spectrum of **4a** (Known compound)



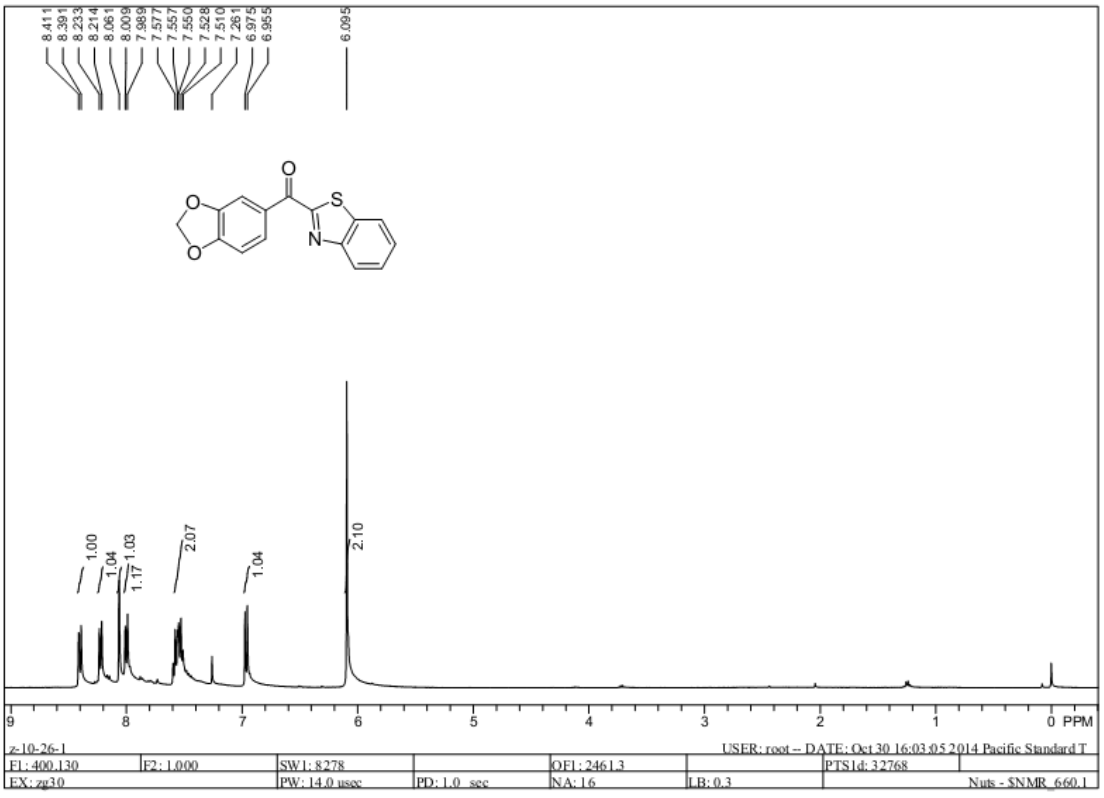
^{1}H NMR spectrum of **4b** (Known compound)



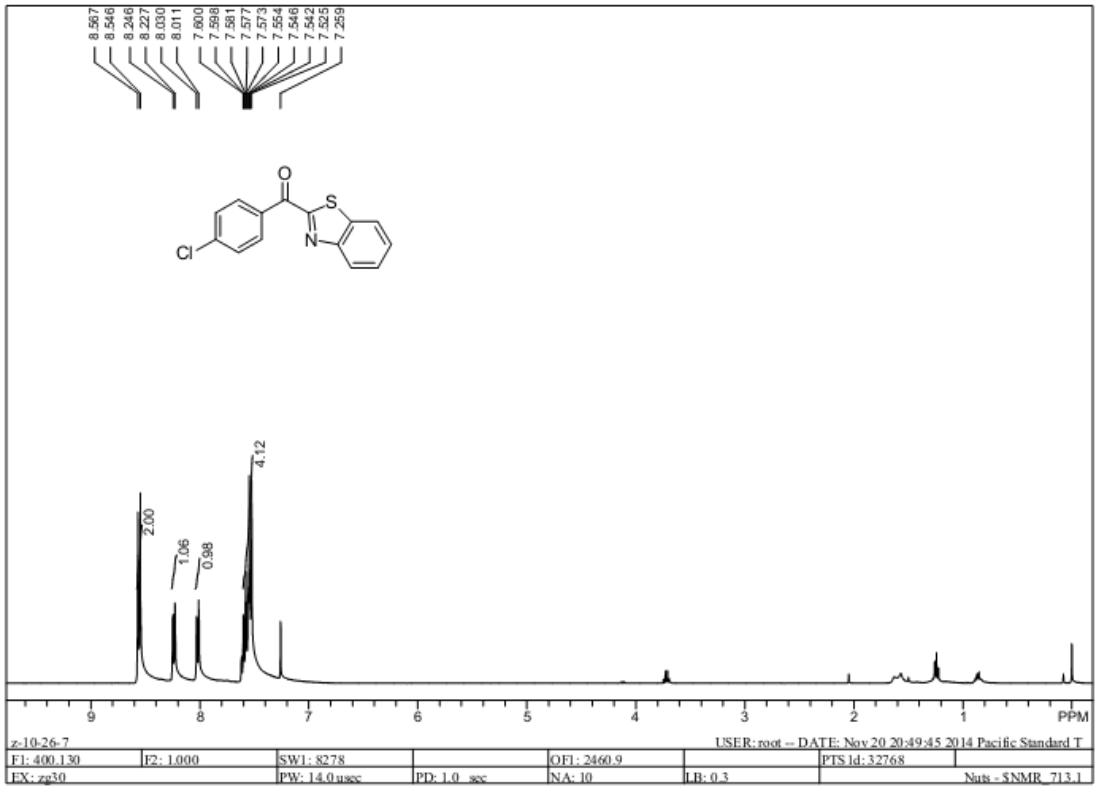
^{1}H NMR spectrum of **4c** (Known compound)



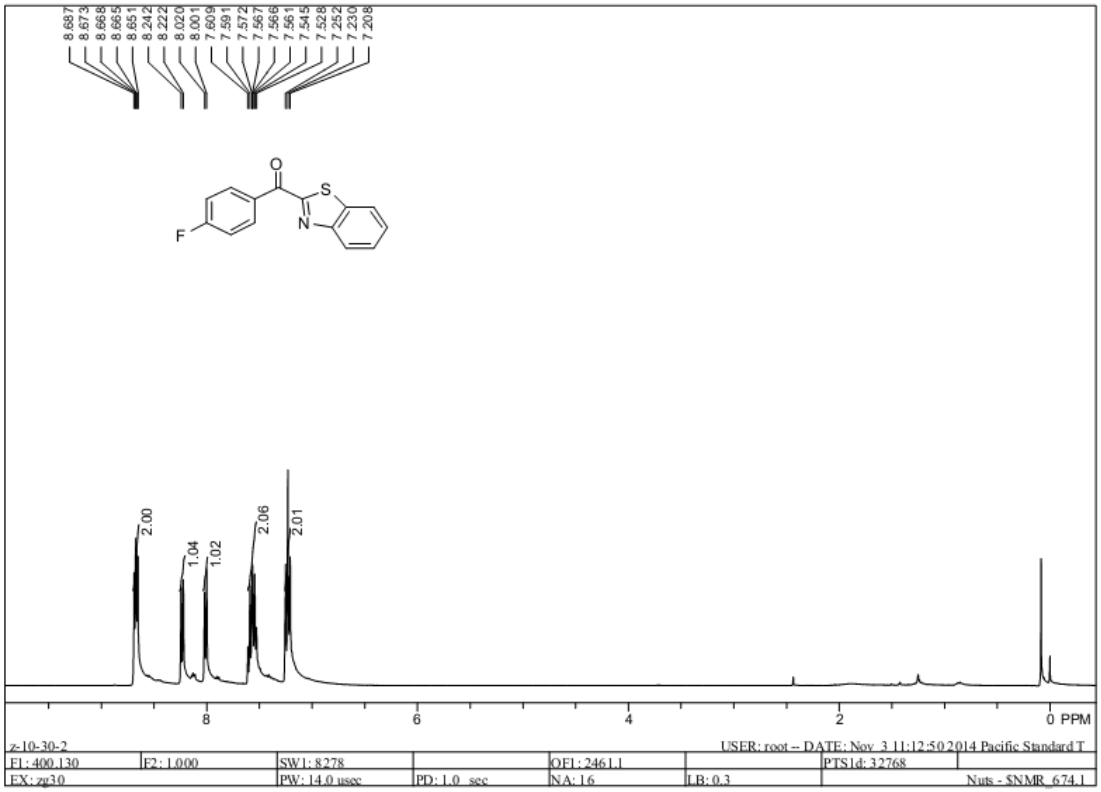
^{1}H NMR spectrum of **4d** (Known compound)



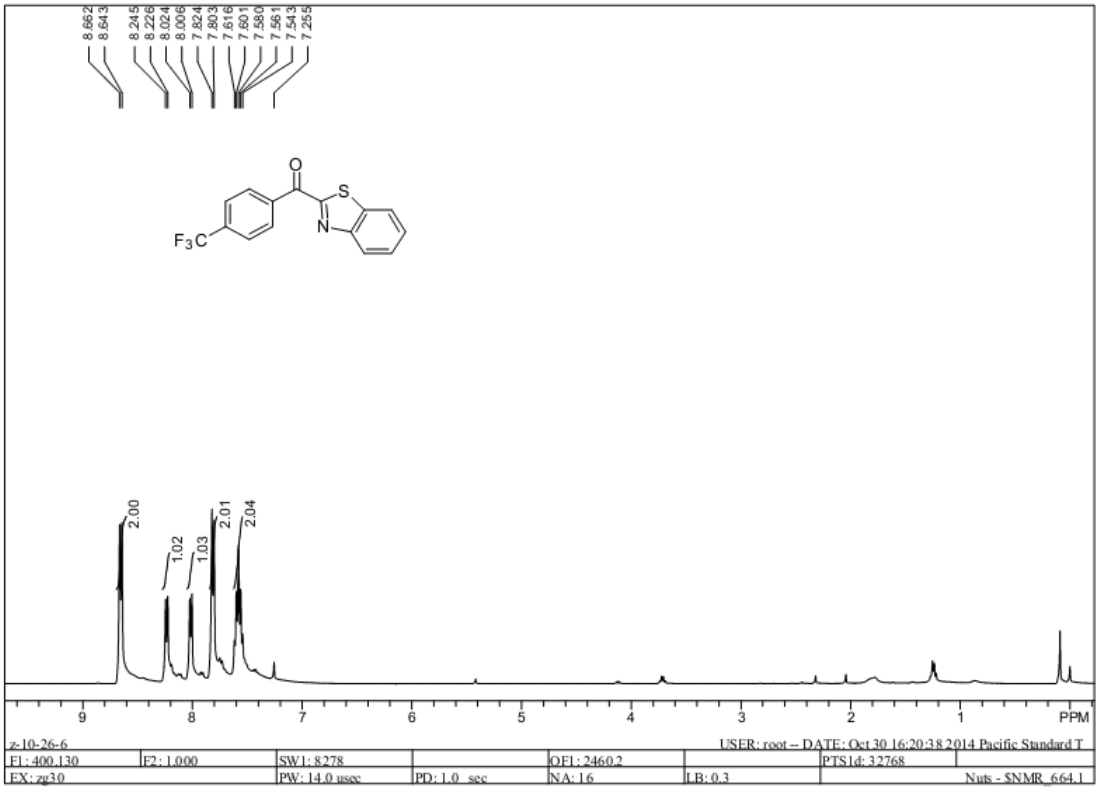
^{1}H NMR spectrum of **4e** (Known compound)

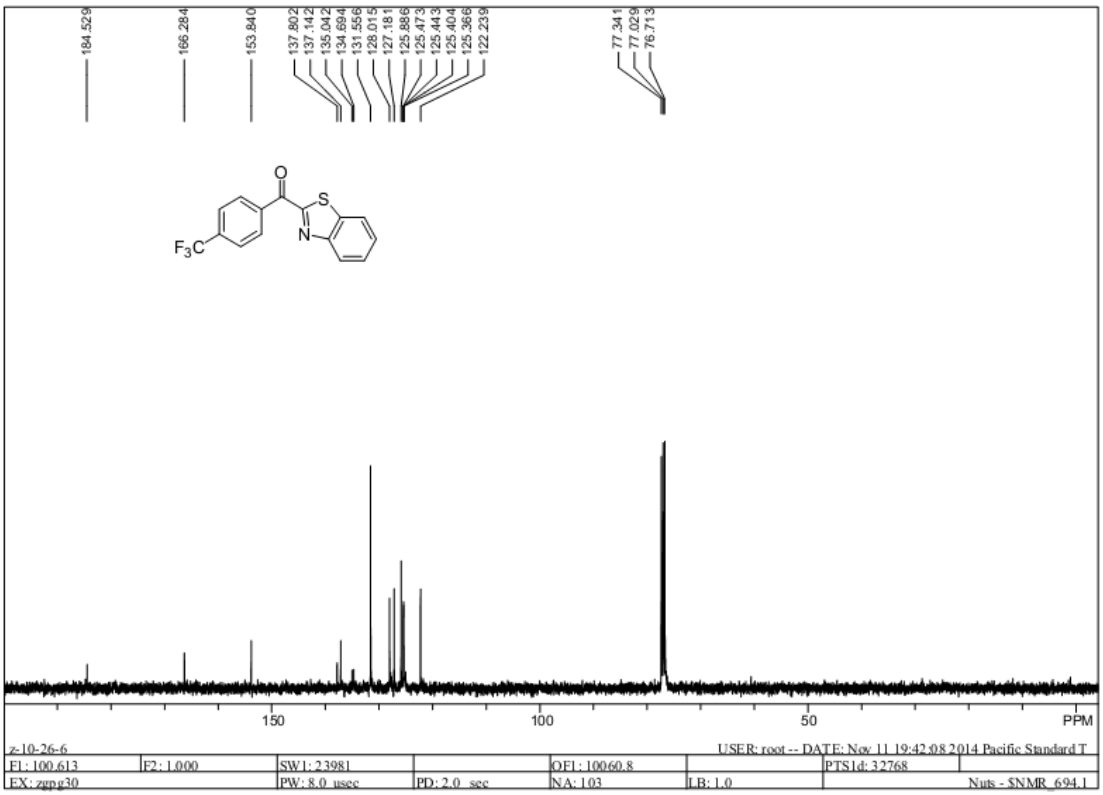


^{1}H NMR spectrum of **4f** (Known compound)

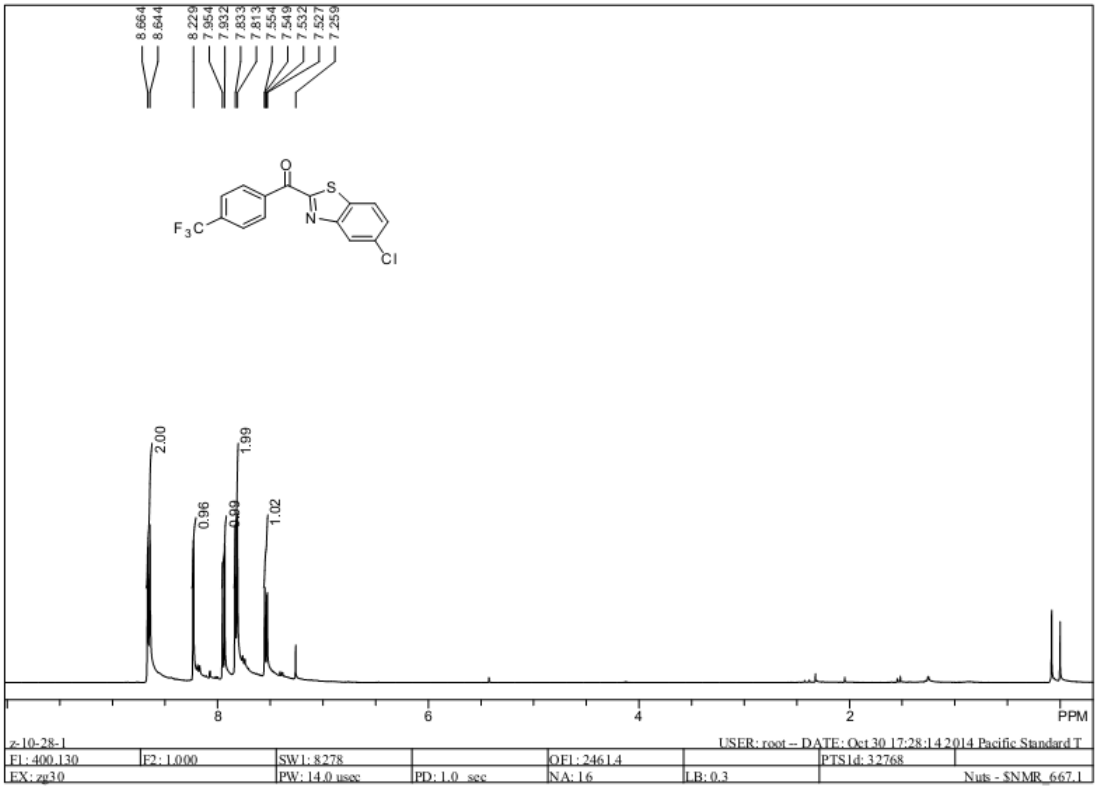


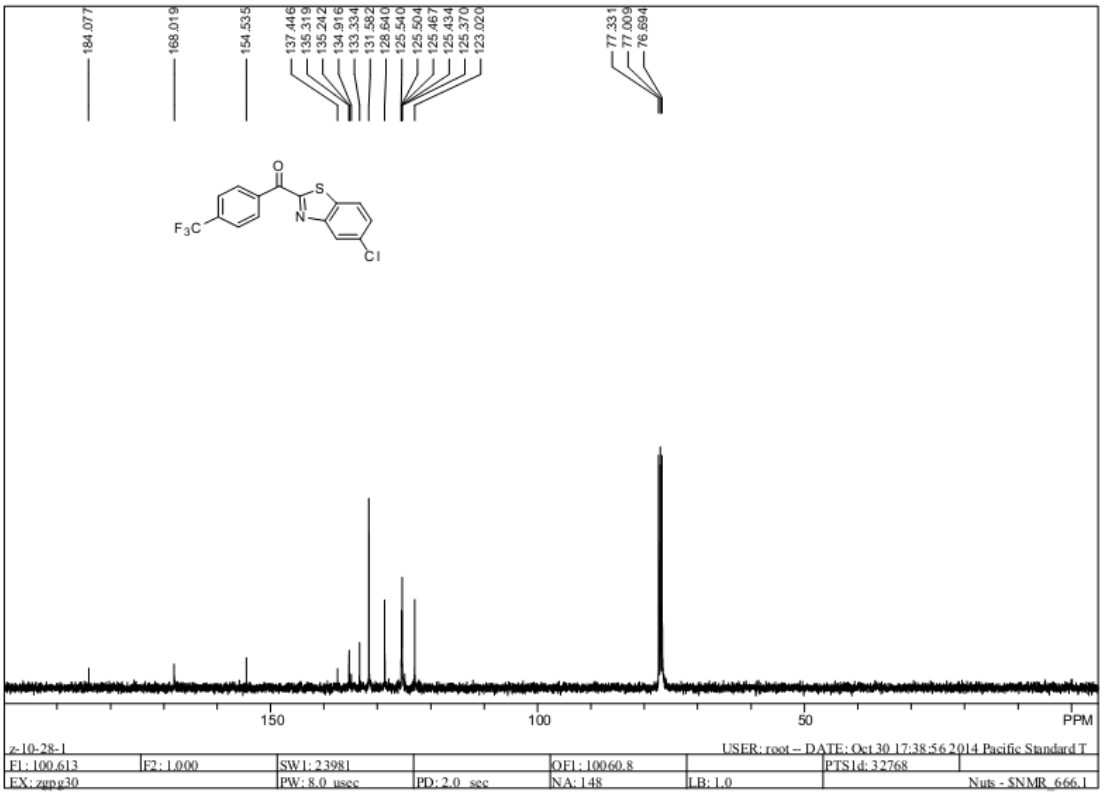
^{1}H and ^{13}C NMR spectra of **4g**



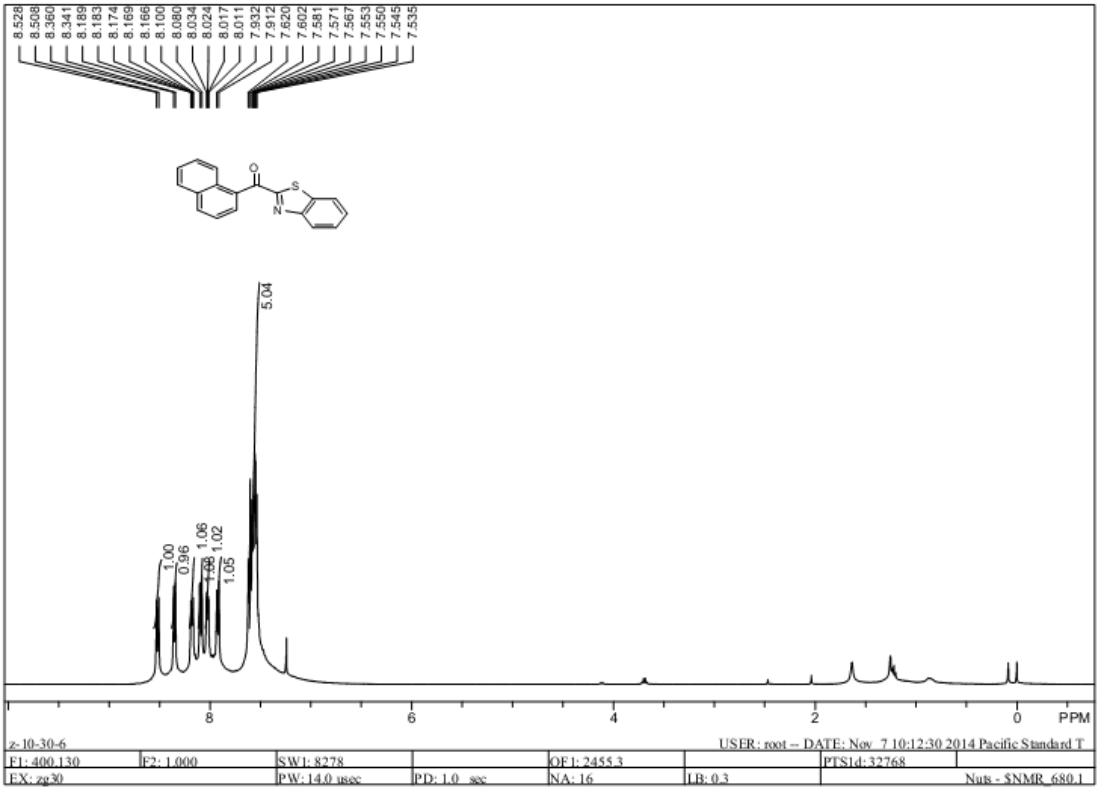


^{1}H and ^{13}C NMR spectra of **4h**

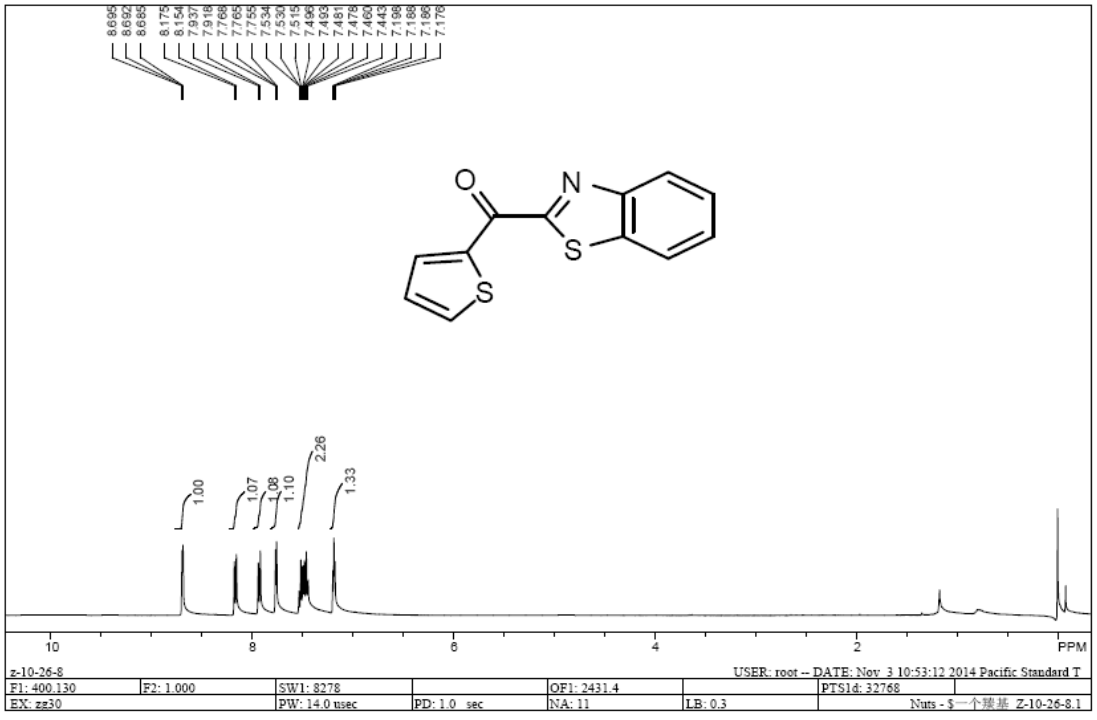




^{1}H NMR spectrum of **4i** (Known compound)



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



Crystal structure of **3i**