Supporting Information

Aminothiolation of *α*-Bromocinnamaldehydes to Access Imidazo[2,1-*b*]thiazoles by Incorporation of Two Distinct Photoinduced Processes

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1. General information

General. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Inova-400 (400 MHz and 100 MHz, and 376 MHz, respectively) spectrometer. ^{1}H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 or $CDCl_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm) and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The HRMS analysis was obtained on a Agilent 6540 UHD Q-TOF mass spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL). X-ray single crystal diffraction data were collected on a Bruker D8 VENTURE. EPR spectra were recorded on a Bruker A300 spectrometer.

Materials. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. *Z*-*α*-bromocinnamaldehydes are known compounds and synthesized according to the reported method.[1]

The Light Source. Manufacturer： Xi'an WATTECS experimental equipment co. LTD

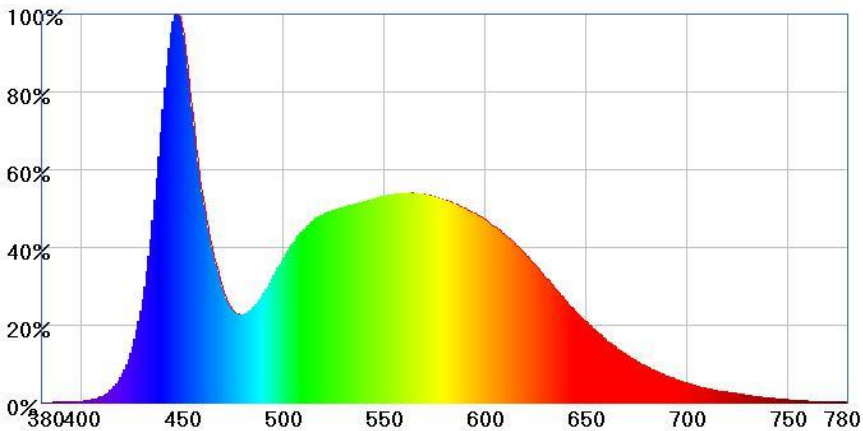


Figure S1. Emission spectrum of white LED light (6000-6500 K)

Figure S2. The reaction setup

2. Experimental procedures

2.1 Optimization of reaction conditions

2.1.1 Table S1. Light source screening[a]

Entry	Light sources	Yield (%)[b]
1	405-410 nm (10 W)	50
2	526-531 nm (10 W)	41
3	400-405 nm (10 W)	64
4	410-415 nm (10 W)	67
5	415-420 nm (10 W)	61
6	460-465 nm (10 W)	74
7	375-377 nm (10 W)	50
8	425-430 nm (10 W)	69
9	440-445 nm (10 W)	70
10	700-405 nm (10 W)	15
11	white light (7 W)	64

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), EosinY (5 mol%), K_2CO_3 (0.25 mmol), DMSO (1 mL), air, rt, 12 h. [b]Isolated yields.

2.1.2 Table S2. Additive screening[a]

Entry	Additive	Yield (%)[b]
1	Na_2CO_3	63
2	Cs_2CO_3	67

3	^{t}BuONa	21
4	^{t}BuOK	37
5	DMAP	12
6	DABCO	17
7	Et_3N	14
8	Pyridine	trace
9	K_3PO_4	20
10	KPF_6	trace
11	KH_2PO_4	trace
12	NaOAc	10
13	$NaHCO_3$	12
14	KOH	12
15	$K_2S_2O_8$	trace
16	*p*-TsOH	trace

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), EosinY (5 mol%), additive (0.25 mmol), DMSO (1 mL), 10 W white LED, air, rt, 12 h. [b]Isolated yields.

2.1.3 Table S3. Solvent screening[a]

Entry	Solvent	Yield (%)[b]
1	NMP	20
2	DMF	19
3	CF_3CH_2OH	trace
4	EtOH	18
5	THF	12
6	CH_3CN	13
7	DCE	11
8	H_2O	11
9	2-methyltetrahydrofuran	10
10	DMSO:H_2O (0.8:0.2)	12

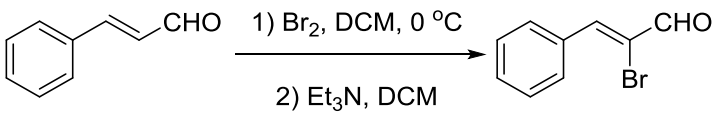
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), EosinY (5 mol%), K_2CO_3 (0.25 mmol), solvent (1 mL), 10 W white LED, air, rt, 12 h. [b]Isolated yields.

2.1.4 Table S4. Ratio of reactant and time screening[a]

Entry	Time (h)	Yield (%)[b]
1[c]	12	71
2[d]	12	59
3[e]	12	71
4	10	64
5	14	74

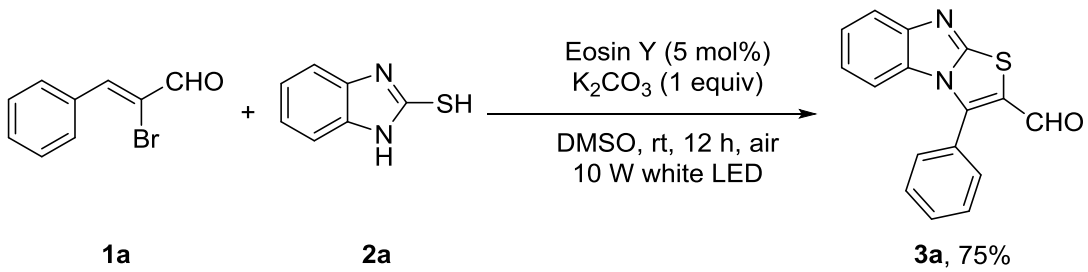
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.3 mmol), EosinY (5 mol%), K_2CO_3 (0.25 mmol), DMSO (1 mL), 10 W white LED, air, rt, 12 h. [b]Isolated yields. [c]**1a** (0.25 mmol), **2a** (0.25 mmol). [d]**1a** (0.25 mmol), **2a** (0.2 mmol). [e]**1a** (0.2 mmol), **2a** (0.3 mmol).

2.2 General procedure for synthesis of substrates[1]



To a solution of cinnamaldehyde (20.0 g, 151 mmol) in DCM (200 mL) was added Br_2 (9.4 mL, 183 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was stirred for 15 min, followed by the addition of Et_3N (36.0 mL, 258 mmol, 1.7 equiv.). After stirring for an additional 15 min, the reaction mixture was diluted with DCM and washed sequentially with a 10% $NaHSO_3$ solution, H_2O, and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated to yield orange oil. After keeping for 3 days at room temperature, the mixture crystallized completely as a bright yellow solid which was confirmed to be the desired *Z*-*α*-bromocinnamaldehyde.

2.3 General procedure for synthesis of products (taking 3a as an example)

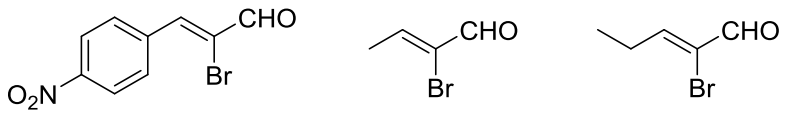


Z-*α*-bromocinnamaldehyde **1a** (52.8 mg, 0.25 mmol), 2-mercaptobenzoimidazole **2a** (45.1 mg, 0.3 mmol), Eosin Y (9.0 mg, 0.013 mmol), K_2CO_3 (34.6 mg, 0.25 mmol)

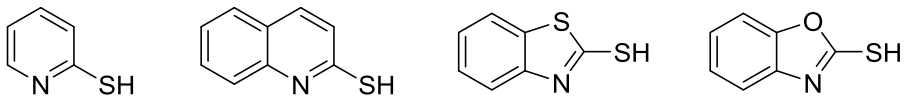
and DMSO (1 mL) were added to a 10 mL quartz tube. The reaction mixture was stirred and irradiated using 10 W white LED for 12 hours. After the reaction finished, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^oC)/EtOAc = 15:1, v/v) to afford the desired product **3a** in 75% yield.

2.4 Unreacted substrates

Unreacted *Z*-*a*-bromocinnamaldehydes:



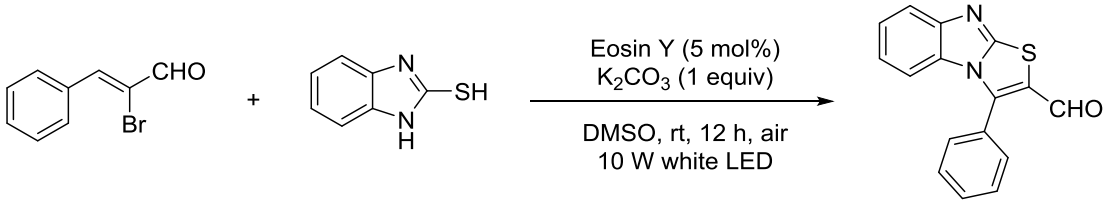
Unreacted 2-mercapto nitrogen heterocyclic compounds:



Scheme S1. Unreacted substrates

3. Gram-scale reaction and application of present work

3.1 Gram-scale reaction



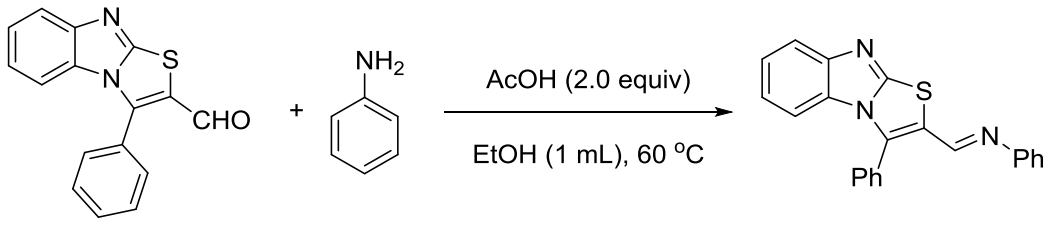
1a 1.85 g, 8.75mmol | **2a** 1.58g, 10.50 mmol | **3a**, 56% 1.35 g, 4.8 mmol

To a 100 mL round bottom flask with magnetic stirrer, *Z*-*α*-bromocinnamaldehyde **1a** (1.85 g, 8.75 mmol), 2-mercaptobenzoimidazole **2a** (1.58 g, 10.05 mmol), Eosin Y (0.318 g, 0.46 mmol) and K_2CO_3 (1.21 g, 8.75 mmol) were dissolved in DMSO (35.0 mL), and then the round bottom flask was stirred under the irradiation of white LED strip in open air at room temperature for 12 h. After reaction, the resulting mixture was extracted with EtOAc (4×40 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the

volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)/EtOAc = 15:1, v/v) to afford the desired product **3a** in 56% yield.

3.2 Application of present work

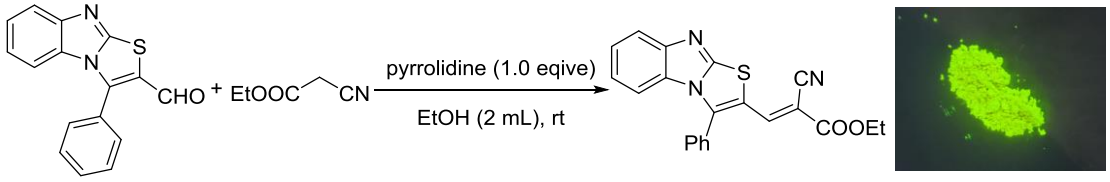
3.2.1 Procedure for synthesis of Schiff base product 3aa



3a **3aa**

A mixture of 3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde **3a** (55.7 mg, 0.2 mmol), aniline (19 μL, 0.2 mmol), acetic acid (23 μL, 0.4 mmol) and EtOH (1 mL) were added to a 25 mL tube. The reaction was stirred at 60 ^{o}C for 40 min. After cooling to ambient temperature, the resulting mixture was extracted with DCM (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^{o}C)/EtOAc = 8:1, v/v) to afford the desired product **3aa** in 98% yield.

3.2.2 Procedure for synthesis of Knoevenagel condensation reaction product 3ab

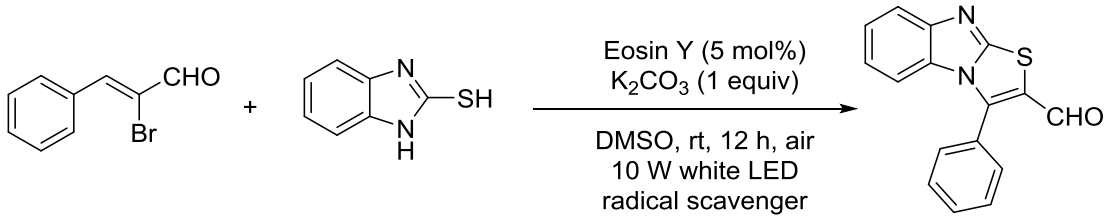


3a **3ab** irradiation of 365 nm

A mixture of 3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde **3a** (55.7 mg, 0.2 mmol), ethyl 2-cyanoacetate (32 μL, 0.3 mmol), pyrrolidine (17 μL, 0.2 mmol) and EtOH (2 mL) were added to a 25 mL tube. The reaction was stirred at room temperature for 3 h. After reaction, the resulting mixture was extracted with DCM (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purely crystallized by DCM to afford the desired product **3ab** in 95% yield.

4. Mechanistic studies

4.1 Radical trapping experiments



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

Entry	Radical scavenger (equiv)	Yield of **3a** (%)
1	TEMPO (2.0)	29
2	TEMPO (6.0)	18
3	BHT (2.0)	48
4	BHT (6.0)	32
5	1,1-diphenythylene (2.0)	43
6	1,1-diphenythylene (6.0)	32

Z-*α*-bromocinnamaldehyde **1a** (52.8 mg, 0.25 mmol), 2-mercaptobenzoimidazole **2a** (45.1 mg, 0.30 mmol), Eosin Y (9.0 mg, 0.013 mmol), K_2CO_3 (34.6 mg, 0.25 mmol), radical scavenger TEMPO, BHT or 1,1-diphenythylene (0.5 mmol or 1.5 mmol) and DMSO (1 mL) were added to a 10 mL Quartz tube. The reaction mixture was stirred and irradiated using 10 W white LED for 12 hours. After the reaction finished, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (35-60 ^oC)/EtOAc = 15:1, v/v).

After the reaction finished, the reaction mixture (Entry 2) was analyzed by HRMS. And, the TEMPO-trapped product was found (Figure S3). HRMS (ESI) m/z Calcd for $C_{16}H_{23}N_3OSK$ $[M+K]^+$: 344.1193; Found: 344.1401.

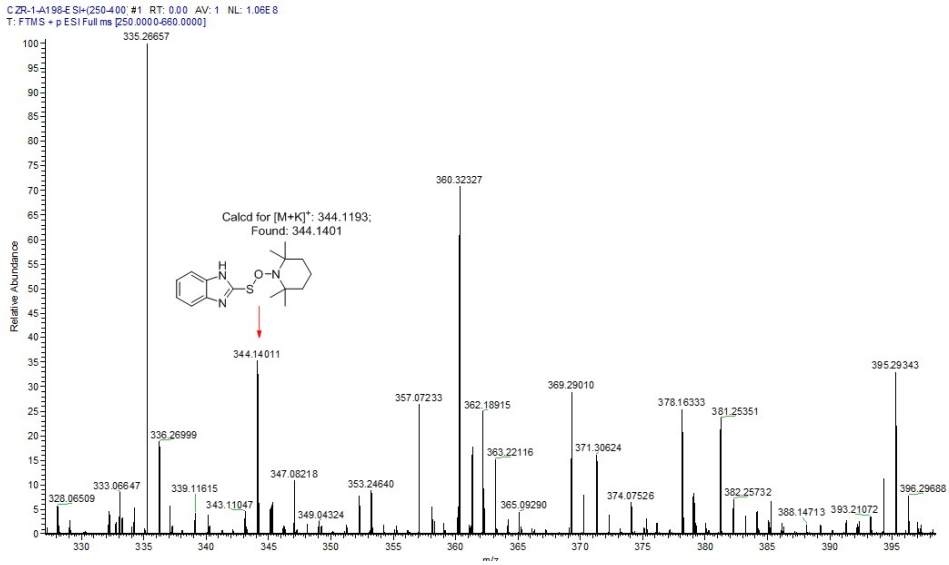


Figure S3. HRMS spectrum of the TEMPO trapping experiment

4.2 Eelectron paramagnetic resonance (EPR) experiment

Mixture of Eosin Y (3 mg), *Z*-*α*-bromocinnamaldehyde **1a** (18 mg), 2-mercaptobenzoimidazole **2a** (15 mg), K_2CO_3 (12 mg), and DMPO (10 μL) in DMSO was transferred to a capillary, and the EPR spectra were recorded (Figure S4). Notably, when the reaction mixture was irradiated with visible light (3 h), distinct signals of trapped radicals were observed. These results indicated that carbon and sulfur free radicals should be involved in the present reaction system.

Measurement conditions: Power 19.71 mW, Frequency 9.852 GHz, Center field 351 mT, Sweep width 10 mT, Modulation width 0.1 mT, Sweep time 1.0 min, Time constant 0.01 s.

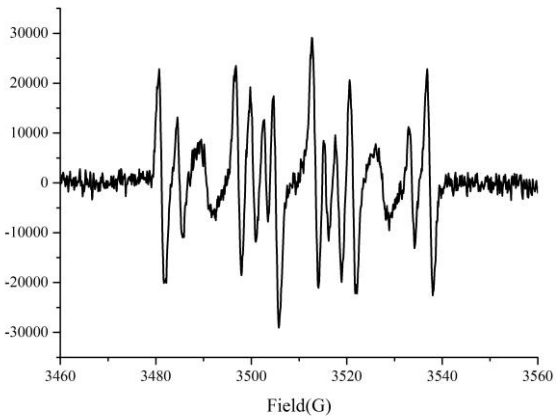


Figure S4. Eelectron Paramagnetic Resonance (EPR) Spectra

4.3 UV−vis spectroscopic measurements

The UV/vis absorption spectra of *Z*-*α*-bromocinnamaldehyde **1a** (0.017 M), 2-mercaptobenzoimidazole **2a** (0.020 M) with and K_2CO_3 (0.017 M) in DMSO were recorded in 1 cm path quartz cuvettes by using a UV-2550 UV-visible spectrophotometer, respectively (Figure S5).

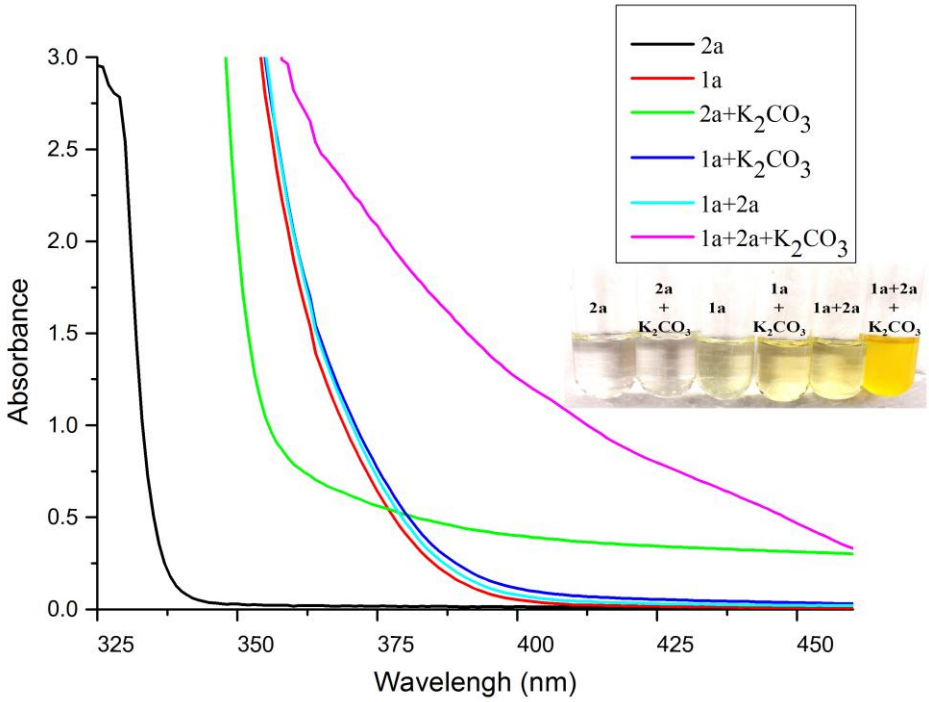
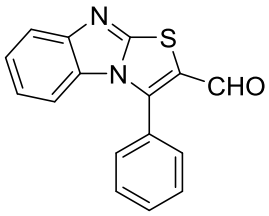


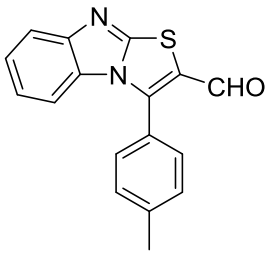
Figure S5. UV−vis spectroscopic measurements on various combinations of 1a, 2a, and K_2CO_3 in DMSO

5. Analytical data

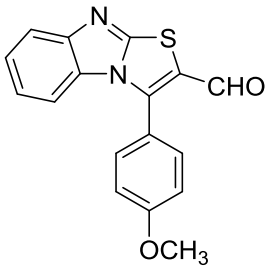


3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3a): New compound. 52.2 mg, 75% yield. Yellow solid. m.p.: 149.8-150.5 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.78-7.68 (m, 6H), 7.39-7.35 (m, 1H), 7.10-7.06 (m, 1H), 6.98-6.95 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.1, 155.9, 149.3, 143.8, 132.0, 130.2, 130.0,

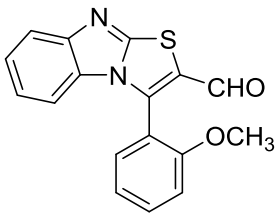
129.6, 126.1, 125.9, 125.3, 121.9, 119.8, 112.2. **HRMS** (ESI) m/z Calcd for $C_{16}H_{11}N_2OS$ $[M+H]^+$: 279.0587; Found: 279.0583.



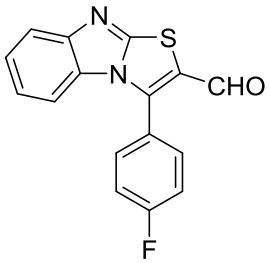
3-(*p*-tolyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3b): New compound. 43.7 mg, 60% yield. Yellow solid. m.p.: 184.3-184.9 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.65 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.10-7.02 (m, 2H), 2.57 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.3, 155.9, 149.3, 144.1, 142.6, 130.2, 130.0, 125.8, 125.1, 122.8, 121.7, 119.7, 112.3, 21.8. **HRMS** (ESI) m/z Calcd for $C_{17}H_{13}N_2OS$ $[M+H]^+$: 293.0743; Found: 293.0732.



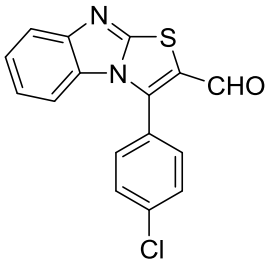
3-(4-methoxyphenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3c): New compound. 49.2 mg, 64% yield. Yellow solid. m.p.: 150.7-151.5 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.68 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.68-7.64 (m, 2H), 7.41-7.37 (m, 1H), 7.21-7.17 (m, 2H), 7.13-7.07 (m, 2H), 3.98 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.4, 162.5, 156.0, 149.0, 144.1, 131.8, 130.1, 125.9, 125.3, 121.9, 119.7, 117.6, 115.1, 112.4, 55.8. **HRMS** (ESI) m/z Calcd for $C_{17}H_{13}N_2O_2S$ $[M+H]^+$: 309.0692; Found: 309.0688.



3-(2-methoxyphenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3d): New compound. 63.2 mg, 82% yield. Yellow solid. m.p.: 160.4-161.2 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.64 (s, 1H), 7.77-7.69 (m, 2H), 7.53 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.24-7.17 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.3, 158.2, 156.0, 149.2, 141.3, 133.8, 132.5, 130.5, 126.1, 124.9, 121.8, 121.3, 119.6, 114.8, 111.9, 111.7, 55.8. **HRMS** (ESI) m/z Calcd for $C_{17}H_{13}N_2O_2S$ $[M+H]^+$: 309.0692; Found: 309.0704.

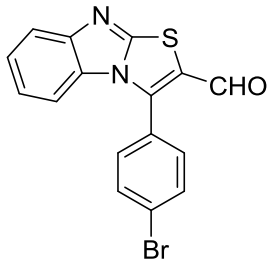


3-(4-fluorophenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3e): New compound. 49.5 mg, 67% yield. Yellow solid. m.p.: 185.2-185.9 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.65 (s, 1H), 7.79-7.73 (m, 3H), 7.44-7.36 (m, 3H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.96 (dd, *J* = 8.2, 0.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.8, 164.8 (d, *J* = 253.0 Hz), 155.8, 149.4, 142.5, 132.4 (d, *J* = 8.0 Hz), 130.0, 126.4, 125.4, 122.0, 121.9, 120.0, 117.1 (d, *J* = 22.0 Hz), 112.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -28.41--28.48 (m). **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}FN_2OS$ $[M+H]^+$: 297.0492; Found: 297.0488.

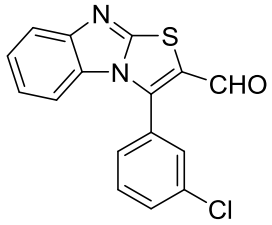


3-(4-chlorophenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3f): New compound. 48 mg, 61% yield. Yellow solid. m.p.: 191.1-191.7 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.72-7.67 (m, 4H), 7.42-7.38 (m, 1H), 7.14-7.10 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.7, 155.8, 149.3, 142.3, 138.7, 131.5, 130.1, 129.9, 126.6, 125.5, 124.3, 122.1,

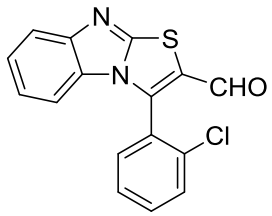
120.0, 112.1. **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}ClN_2OS$ $[M+H]^+$: 313.0197; Found: 313.0190.



3-(4-bromophenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3g): New compound. 53.4 mg, 60% yield. Yellow solid. m.p.: 194.0-195.7 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.88-7.84 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.63-7.60 (m, 2H), 7.42-7.37 (m, 1H), 7.14-7.10 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.7, 155.8, 149.2, 142.3, 133.1, 131.6, 129.9, 126.9, 126.6, 125.5, 124.8, 122.1, 120.0, 112.1. **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}BrN_2OS$ $[M+H]^+$: 358.9671; Found: 358.9662.

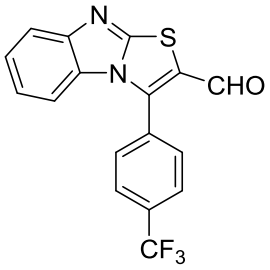


3-(3-chlorophenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3h): New compound. 52.3 mg, 67% yield. Yellow solid. m.p.: 148.3-148.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.77-7.72 (m, 3H), 7.69-7.63 (m, 2H), 7.40-7.36 (m, 1H), 7.13-7.09 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.6, 155.6, 149.3, 141.7, 135.8, 132.2, 131.0, 130.1, 129.8, 128.3, 127.6, 126.6, 125.4, 122.0, 120.0, 112.0. **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}ClN_2OS$ $[M+H]^+$: 313.0197; Found: 313.0186.

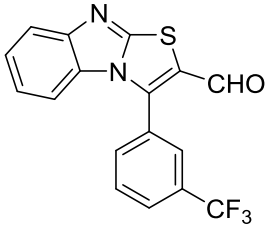


3-(2-chlorophenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3i): New

compound. 53.2 mg, 68% yield. Yellow solid. m.p.: 149.7-151.1 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.60 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.75-7.70 (m, 2H), 7.68-7.66 (m, 1H), 7.62-7.58 (m, 1H), 7.39-7.35 (m, 1H), 7.11-7.07 (m, 1H), 6.72 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.3, 155.4, 149.1, 140.1, 135.0, 133.4, 132.5, 130.9, 129.9, 127.9, 126.8, 125.5, 125.2, 122.1, 119.7, 111.6. **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}ClN_2OS$ $[M+H]^+$: 313.0197; Found: 313.0185.

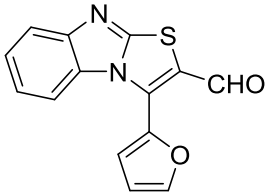


3-(4-(trifluoromethyl)phenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3j): New compound. 52.9 mg, 61% yield. Yellow solid. m.p.: 200.4-201.4 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.64 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.42-7.37 (m, 1H), 7.14-7.09 (m, 1H), 6.91 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.4, 155.7, 149.4, 141.5, 134.1 (q, *J* = 33.0 Hz), 130.8, 129.8, 129.7, 127.0, 126.7 (q, *J* = 3.0 Hz), 125.5, 122.2, 120.9 (q, *J* = 272.0 Hz), 120.2, 111.9. **^{19}F NMR** (376 MHz, CDCl3) δ 14.68 (s). **HRMS** (ESI) m/z Calcd for $C_{17}H_{10}F_3N_2OS$ $[M+H]^+$: 347.0460; Found: 347.0451.

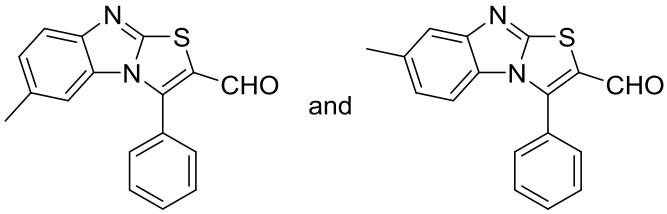


3-(3-(trifluoromethyl)phenyl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3k): New compound. 58.9 mg, 68% yield. Yellow solid. m.p.: 192.8-193.7 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.64 (s, 1H), 8.05 (d, *J* = 6.8 Hz, 2H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.90 (t, *J* =8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.41-7.37 (m, 1H), 7.13-7.09 (m, 1H), 6.87 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.3, 155.6, 149.3, 141.4, 133.5, 132.4 (q, *J* = 33.0 Hz), 130.4, 129.8, 128.8 (q, *J* = 3.0 Hz), 127.1 (q, *J* =4.0 Hz), 127.0, 126.9, 125.5, 123.4 (q, *J* = 272.0 Hz), 122.2, 120.1, 111.8. **^{19}F NMR**

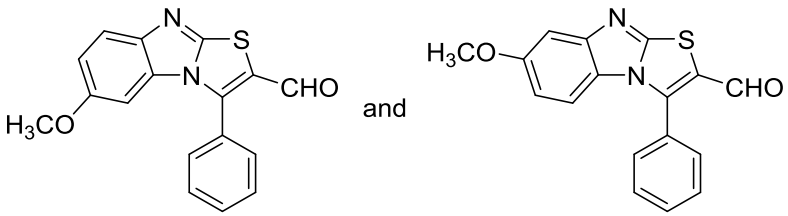
(376 MHz, CDCl3) δ 14.86 (s). **HRMS** (ESI) m/z Calcd for $C_{17}H_{10}F_3N_2OS$ $[M+H]^+$: 347.0460; Found: 347.0450.



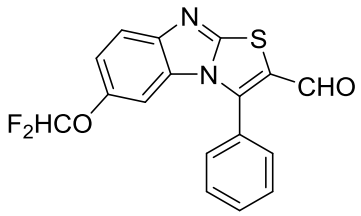
3-(furan-2-yl)benzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3l): New compound. 14 mg, 21% yield. Yellow solid. m.p.: 163.9-165.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.93 (s, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.81 (dd, *J* = 3.4, 1.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.9, 155.4, 149.2, 146.2, 139.2, 132.4, 130.1, 127.6, 125.4, 122.2, 119.8, 117.8, 112.8, 112.7. **HRMS** (ESI) m/z Calcd for $C_{14}H_9N_2O_2S$ $[M+H]^+$: 269.0379; Found: 269.0371.



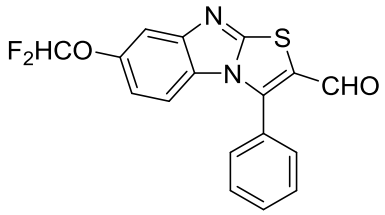
6-methyl-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3m) and 7-methyl-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3m'): New compound. 42.7 mg, 58% yield. Yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.64 (s, 1H), 9.63 (s, 1H), 7.79-7.67 (m, 10H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.53 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.2, 183.1, 155.8, 155.2, 149.6, 147.3, 143.8, 143.7, 135.3, 132.0, 131.9, 131.8, 130.1, 130.1, 129.5, 129.5, 127.9, 126.6, 125.9, 125.8, 125.7, 123.2, 119.6, 119.2, 112.2, 111.7, 21.8, 21.7. **HRMS** (ESI) m/z Calcd for $C_{17}H_{13}N_2OS$ $[M+H]^+$: 293.0743; Found: 293.0735.



6-methoxy-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3n) and 7-methoxy-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3n'): New compound. 52 mg, 67% yield. Yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 9.64 (s, 1H), 7.72 (s, 11H), 7.21 (s, 1H), 6.98 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 1H), 6.45 (s, 1H), 3.84 (s, 3H), 3.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.1, 183.0, 157.9, 155.3, 143.5, 132.0, 131.9, 130.2, 130.1, 129.6, 129.5, 126.0, 125.9, 125.9, 125.5, 120.1, 113.2, 112.6, 111.2, 102.3, 97.1, 55.8, 55.8. **HRMS** (ESI) m/z Calcd for $C_{17}H_{13}N_2O_2S$ $[M+H]^+$: 309.0692; Found: 309.0684.

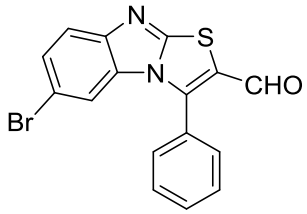


6-(difluoromethoxy)-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3o): New compound. 30.9 mg, 36% yield. White solid. m.p.: 172.2-173.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.68 (s, 1H), 7.79-7.71 (m, 6H), 7.18 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.37 (t, *J* = 73.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.1, 156.6, 147.0, 145.5 (t, *J* = 3.0 Hz), 143.4, 132.3, 130.1, 129.9, 129.8, 126.5, 125.5, 120.4, 118.1, 116.0 (t, *J* = 260.0 Hz), 104.7. ^{19}F NMR (376 MHz, CDCl3) δ -3.22 (s), -3.41 (s). **HRMS** (ESI) m/z Calcd for $C_{17}H_{11}F_2N_2O_2S$ $[M+H]^+$: 345.0504; Found: 345.0499.

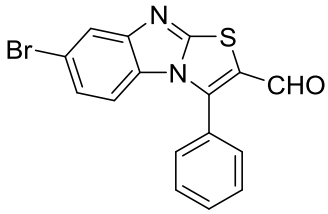


7-(difluoromethoxy)-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3o'): New compound. 37.1 mg, 43% yield. White solid. m.p.: 179.3-179.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.78-7.71 (m, 5H), 7.52 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 6.88 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.52 (t, *J* = 73.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.1, 157.3, 150.1, 148.7 (t, *J* = 3.0 Hz), 143.4, 132.2, 130.1, 129.8, 127.7, 126.4, 125.7, 116.1 (t, *J* = 260.0 Hz), 114.6, 112.7, 110.8. **^{19}F**

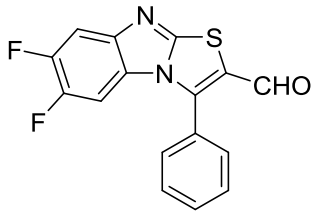
NMR (376 MHz, CDCl3) δ -3.07 (s), -3.27 (s). **HRMS** (ESI) m/z Calcd for $C_{17}H_{11}F_2N_2O_2S$ $[M+H]^+$: 345.0504; Found: 345.0498.



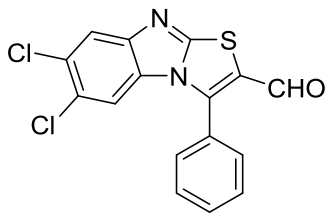
and



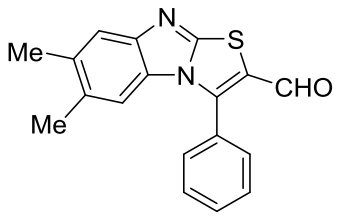
6-bromo-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3p) and 7-bromo-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3p'): New compound. 75.9 mg, 85% yield. White solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.67 (s, 2H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.79-7.71 (m, 10H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.48 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.18 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.10 (d, *J* = 1.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.1，183.0, 157.0, 156.4, 150.3, 148.2, 143.4, 132.4, 132.2, 130.8, 130.1 x 2, 129.8 x 2, 128.9, 128.5, 126.7, 126.6, 125.6, 125.4, 124.8, 122.7, 120.9, 118.5, 115.3, 114.8, 113.1. **HRMS** (ESI) m/z Calcd for $C_{16}H_{10}BrN_2OS$ $[M+H]^+$: 356.9692; Found: 356.9684.



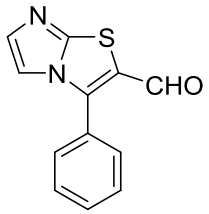
6,7-difluoro-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3q): New compound. 38.2 mg, 49% yield. Yellow solid. m.p.: 180.2-182.8 ^oC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.81-7.69 (m, 5H), 7.54 (dd, *J* = 10.3, 7.2 Hz, 1H), 6.76 (dd, *J* = 9.7, 7.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.0, 156.9, 149.2 (dd, *J* = 245.0, 15.0 Hz), 146.6 (dd, *J* = 243.0, 16.0 Hz), 144.9 (dd, *J* = 11.0, 2.0 Hz), 143.0, 132.4, 130.0, 129.9, 126.6, 125.3, 125.0 (dd, *J* = 11.0, 2.0 Hz), 107.4 (d, *J* = 20.0 Hz), 100.8 (d, *J* = 24.0 Hz). **^{19}F NMR** (376 MHz, CDCl3) δ -60.73--60.84 (m), -63.67--63.77 (m). **HRMS** (ESI) m/z Calcd for $C_{16}H_9F_2N_2OS$ $[M+H]^+$: 315.0398; Found: 315.0408.



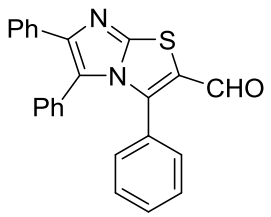
6,7-dichloro-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3r): New compound. 83.1 mg, 96% yield. Yellow solid. m.p.: 281.1-281.8 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.68 (s, 1H), 7.87 (s, 1H), 7.82-7.73 (m, 5H), 7.06 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.0, 157.7, 148.4, 143.1, 132.6, 130.1, 130.0, 129.6, 127.0, 125.9, 125.2, 120.9, 113.4. **HRMS** (ESI) m/z Calcd for $C_{16}H_9Cl_2N_2OS$ $[M+H]^+$: 346.9807; Found: 346.9800.



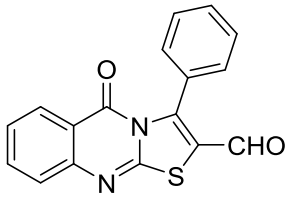
6,7-dimethyl-3-phenylbenzoimidazo[2,1-*b*]thiazole-2-carbaldehyde (3s): New compound. 50 mg, 65% yield. Yellow solid. m.p.: 232.8-234.4 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.63 (s, 1H), 7.77-7.67 (m, 5H), 7.51 (s, 1H), 6.71 (s, 1H), 2.34 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.2, 155.0, 148.0, 143.8, 134.4, 131.9, 130.9, 130.2, 129.5, 128.4, 126.1, 125.6, 119.9, 112.5, 20.6, 20.5. **HRMS** (ESI) m/z Calcd for $C_{18}H_{15}N_2OS$ $[M+H]^+$: 307.0900; Found: 307.0899.



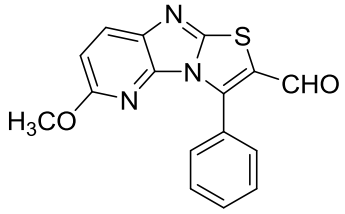
3-phenylimidazo[2,1-*b*]thiazole-2-carbaldehyde (3t): New compound. 20.9 mg, 37% yield. Yellow solid. m.p.: 159.7-160.5 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.81 (s, 1H), 7.70-7.63 (m, 5H), 7.47 (d, J = 1.5 Hz, 1H), 7.44 (d, J = 1.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.7, 149.4, 141.6, 137.1, 131.8, 129.8, 129.6, 128.2, 126.9, 112.3. **HRMS** (ESI) m/z Calcd for $C_{12}H_9N_2OS$ $[M+H]^+$: 229.0430; Found: 229.0424.



3,5,6-triphenylimidazo[2,1-*b*]thiazole-2-carbaldehyde (3u): New compound. 77 mg, 81% yield. Yellow solid. m.p.: 237.5-238.6 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.57 (s, 1H), 7.50-7.48 (m, 2H), 7.30-7.08 (m, 9H), 7.04-7.00 (m, 2H), 6.95-6.93 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.9, 149.4, 146.0, 143.6, 133.6, 131.0, 130.3, 130.2, 129.1, 128.4, 128.4, 128.2, 128.0, 127.7 x 2, 125.6, 124.4. **HRMS** (ESI) m/z Calcd for $C_{24}H_{17}N_2OS$ $[M+H]^+$: 381.1056; Found: 381.1072.

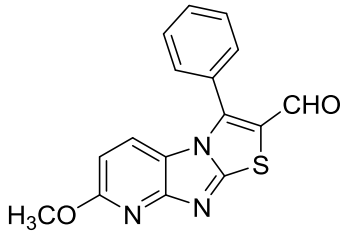


5-oxo-3-phenyl-5*H*-thiazolo[2,3-*b*]quinazoline-2-carbaldehyde (3v): New compound. 24.1 mg, 31% yield. Yellow solid. m.p.: 189.5-190.6 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.54 (s, 1H), 8.18 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.81-7.76 (m, 1H), 7.64-7.52 (m, 6H), 7.43-7.39 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.8, 159.9, 156.9, 147.4, 147.2, 135.8, 130.6, 130.0, 128.3, 128.2, 127.5, 126.2, 126.1, 124.4, 117.8. **HRMS** (ESI) m/z Calcd for $C_{17}H_{11}N_2O_2S$ $[M+H]^+$: 307.0536; Found: 307.0528.

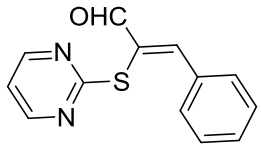


6-methoxy-3-phenylthiazolo[2',3':2,3]imidazo[4,5-*b*]pyridine-2-carbaldehyde (3w): New compound. 12.4 mg, 16% yield. Yellow solid. m.p.: 264.4-266.3 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.80 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.68-7.59 (m, 3H), 6.80 (d, *J* = 8.2 Hz, 1H), 3.63 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 183.9, 159.6, 143.8, 141.2, 136.2, 131.6, 131.5, 130.2, 128.3, 126.6, 125.2, 109.1, 53.9. **HRMS** (ESI) m/z Calcd for $C_{16}H_{12}N_3O_2S$ $[M+H]^+$: 310.0645; Found:

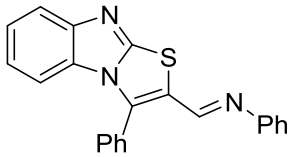
310.0641.



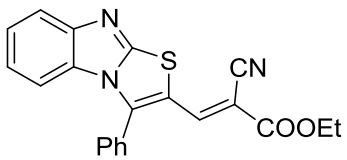
7-methoxy-3-phenylthiazolo[3',2':1,2]imidazo[4,5-*b*]pyridine-2-carbaldehyde (3w'): New compound. 46.3 mg, 60% yield. White solid. m.p.: 213.6-214.6 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.70 (s, 1H), 7.79-7.70 (m, 5H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 4.02 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 182.9, 162.7, 158.5, 156.5, 143.3, 132.2, 130.1, 129.8, 125.9, 125.7, 122.6, 117.8, 105.2, 54.1. **HRMS** (ESI) m/z Calcd for $C_{16}H_{12}N_3O_2S$ $[M+H]^+$: 310.0645; Found: 310.0637.



(*Z*)-3-phenyl-2-(pyrimidin-2-ylthio)acrylaldehyde (3x): New compound. 44.6 mg, 74% yield. Yellow solid. m.p.: 116.2-117.0 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.67 (s, 1H), 8.48 (d, *J* = 4.8 Hz, 2H), 7.98 (s, 1H), 7.92-7.89 (m, 2H), 7.45-7.41 (m, 3H), 7.00 (t, *J* = 4.8 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.2, 170.2, 157.7, 151.4, 133.6, 131.4, 131.2, 130.5, 128.8, 117.6. **HRMS** (ESI) m/z Calcd for $C_{13}H_{11}N_2OS$ $[M+H]^+$: 243.0587; Found: 243.0580.



(*E*)-*N*-phenyl-1-(3-phenylbenzoimidazo[2,1-*b*]thiazol-2-yl)methanimine (3aa): New compound. 69.6 mg, 98% yield. Yellow solid. m.p.: 214.0-214.8 ºC. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.31 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72-7.65 (m, 5H), 7.36-7.31 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16-7.14 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 150.8, 150.7, 137.4, 131.3, 130.3, 129.5, 129.3, 127.3, 126.8, 125.7, 124.3, 121.3, 121.2, 119.6, 111.8. **HRMS** (ESI) m/z Calcd for $C_{22}H_{16}N_3S$ $[M+H]^+$: 354.1059; Found: 354.1055.



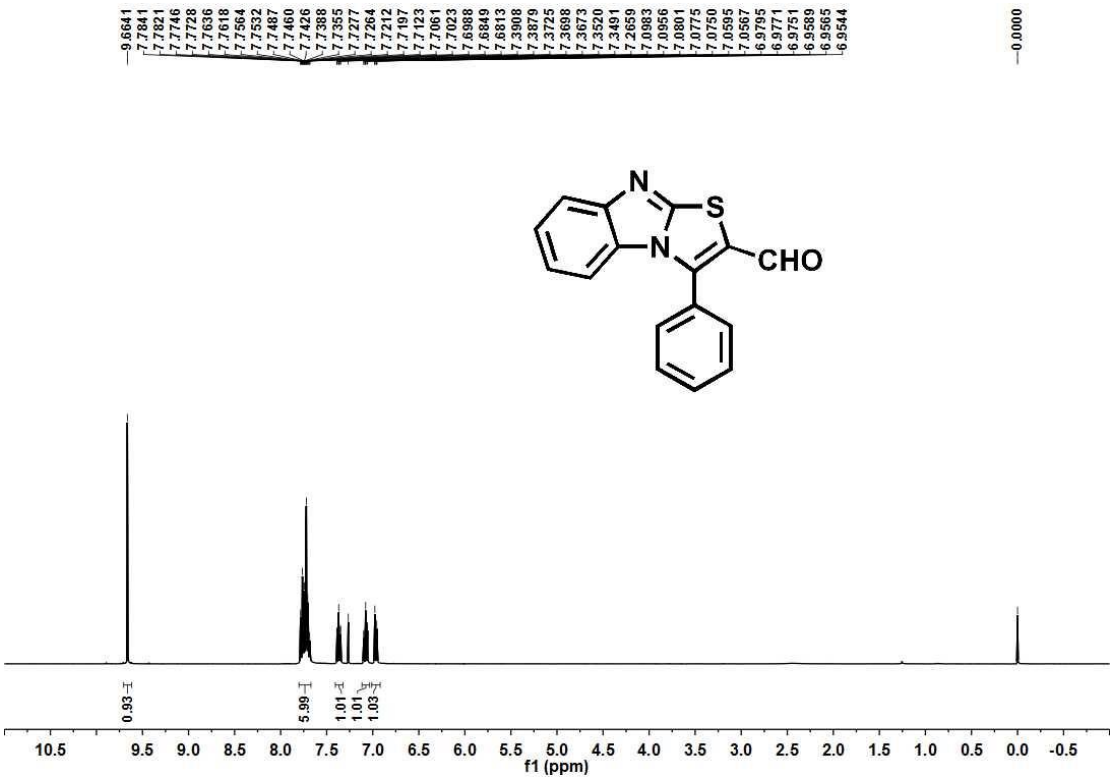
ethyl (*E*)-2-cyano-3-(3-phenylbenzoimidazo[2,1-*b*]thiazol-2-yl)acrylate (3ab): New compound. 71.3 mg, 95% yield. Yellow solid. m.p.: 277.5-278.4 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.06 (s, 1H), 7.80-7.69 (m, 4H), 7.61-7.59 (m, 2H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 162.4, 155.4, 149.1, 145.1, 142.8, 132.2, 130.3, 129.8, 129.6, 126.3, 125.6, 122.1, 120.0, 119.0, 115.3, 112.3, 100.6, 62.9, 14.3. **HRMS** (ESI) m/z Calcd for $C_{21}H_{16}N_3O_2S$ $[M+H]^+$: 374.0958; Found: 374.0952.

6. References

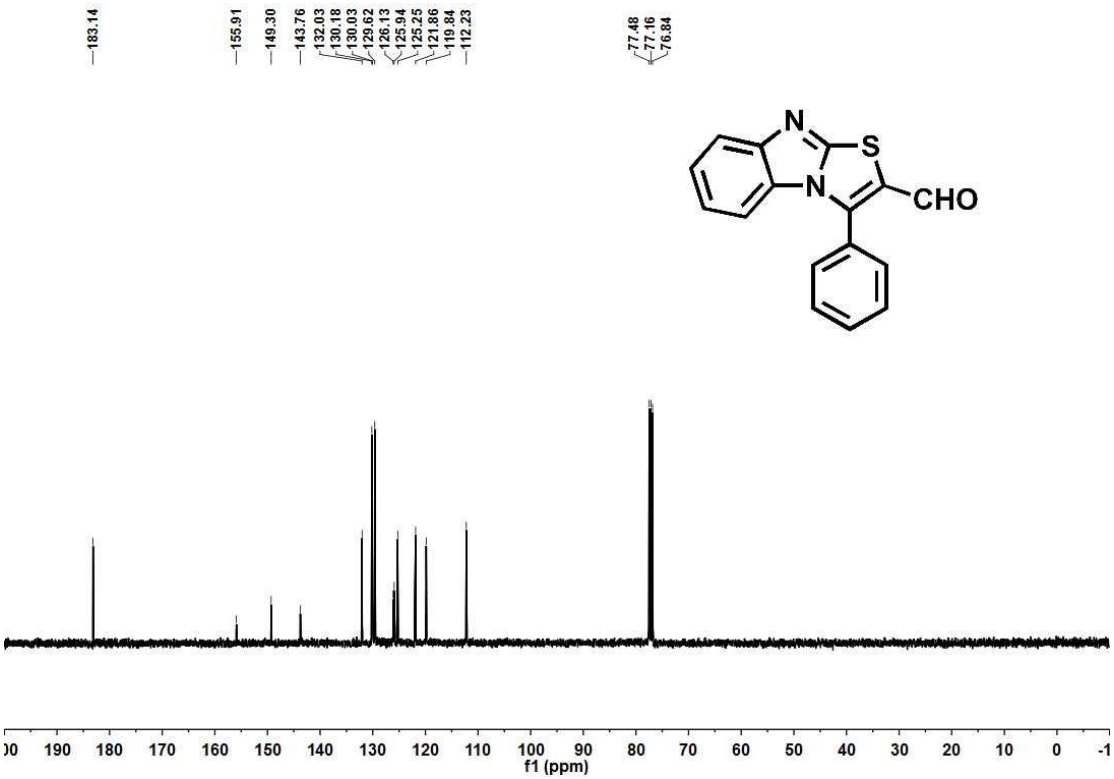
[1] (a) Gilley, C. B.; Buller, M. J.; Kobayashi, Y. *Org*. *Lett*. **2007**, *9*, 3631. (b) Liu, Y. F.; Chen, J. Z.; Zhang, Z. F.; Qin, J.; Zhao, M.; Zhang, W. B. *Org*. *Biomol*. *Chem*. **2016**, *14*, 7099.

7. Copies of NMR spectra

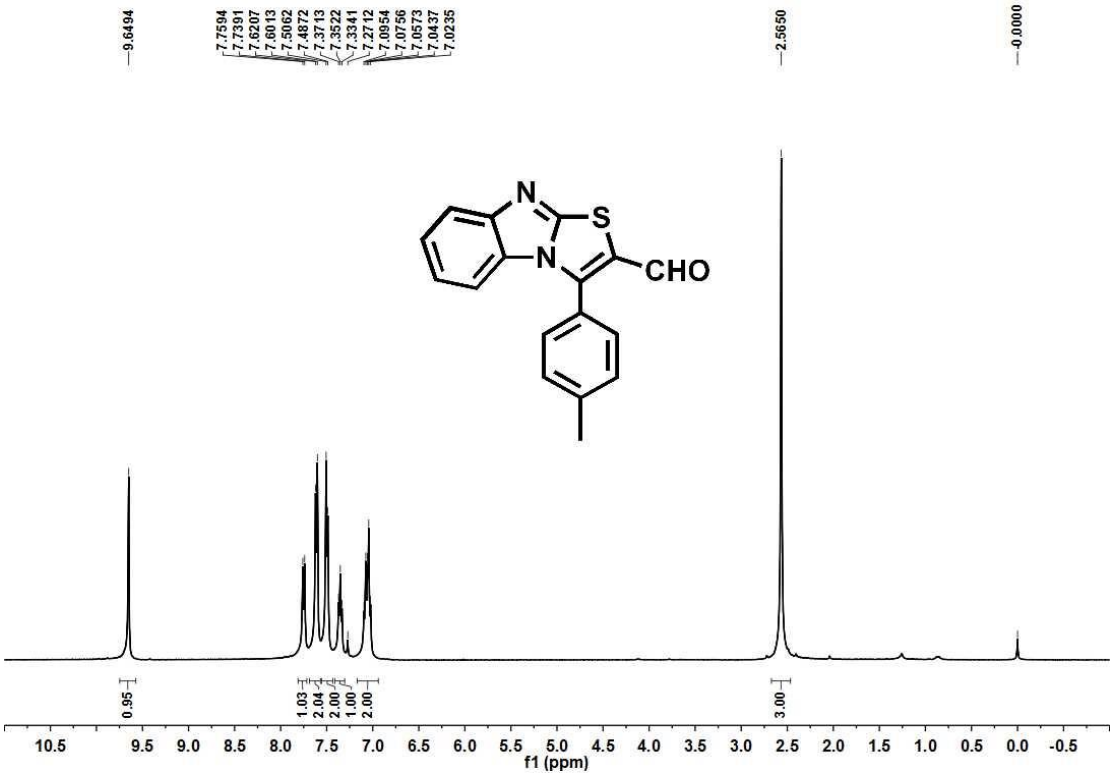
^{1}H NMR of product 3a in $CDCl_3$ (400 MHz)



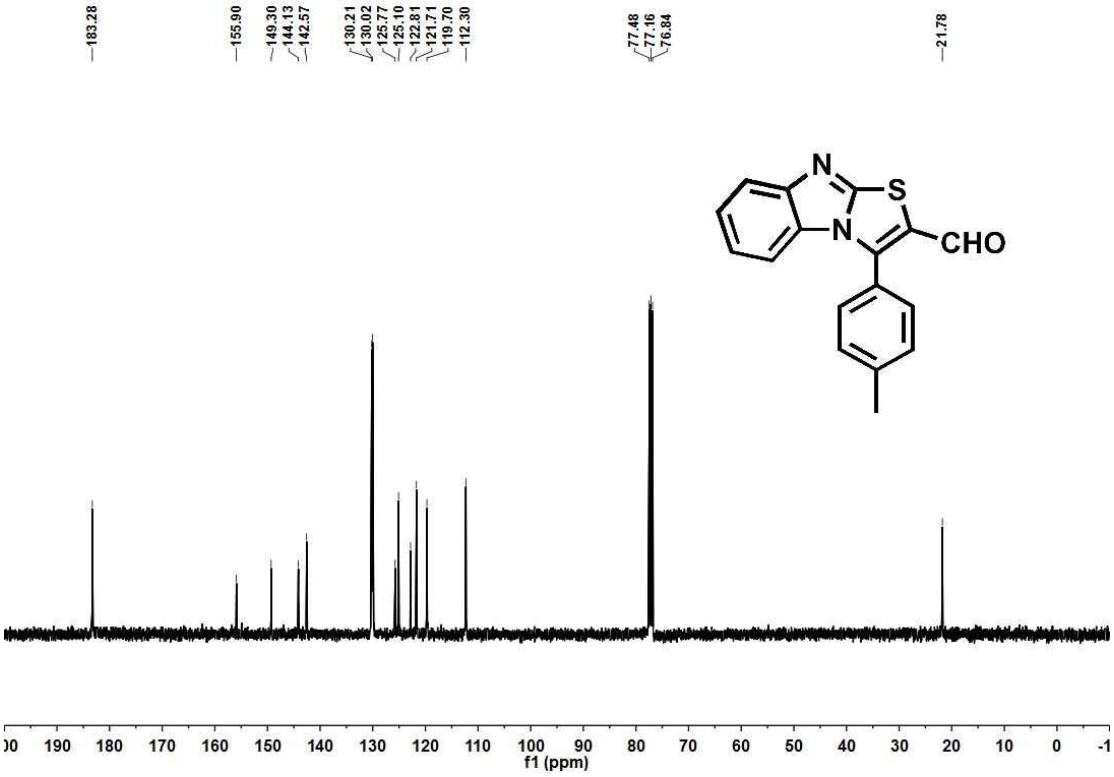
^{13}C NMR of product 3a in $CDCl_3$ (100 MHz)



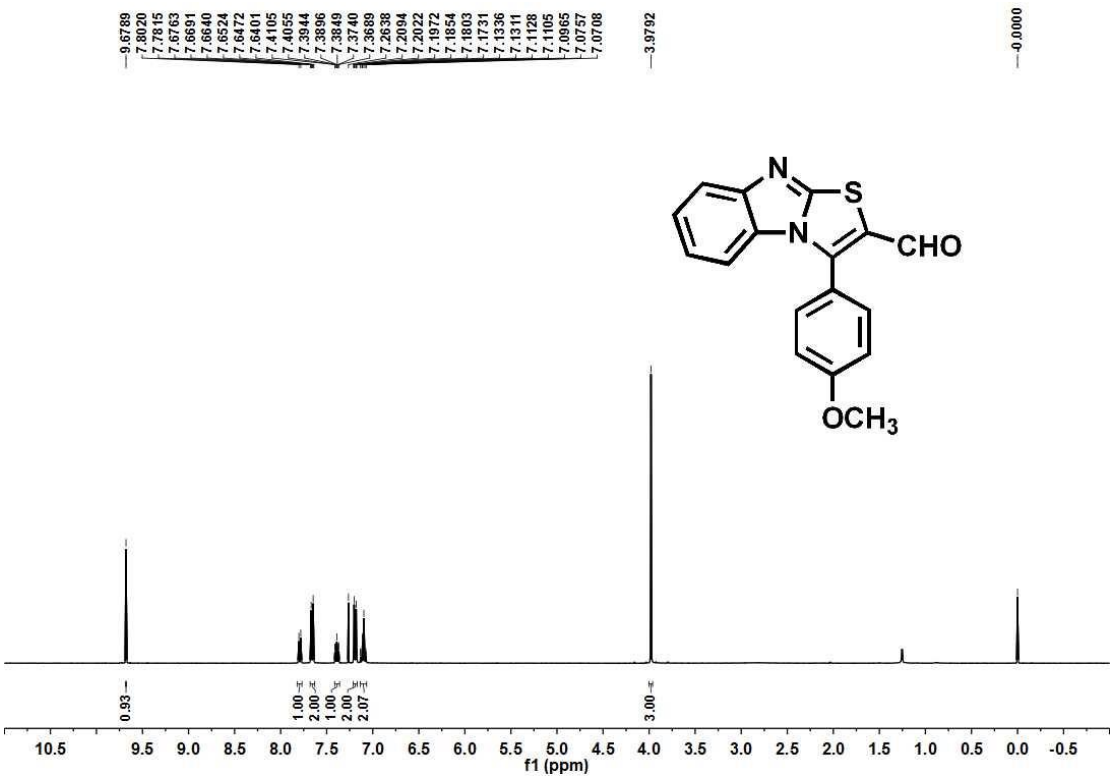
^{1}H NMR of product 3b in $CDCl_3$ (400 MHz)



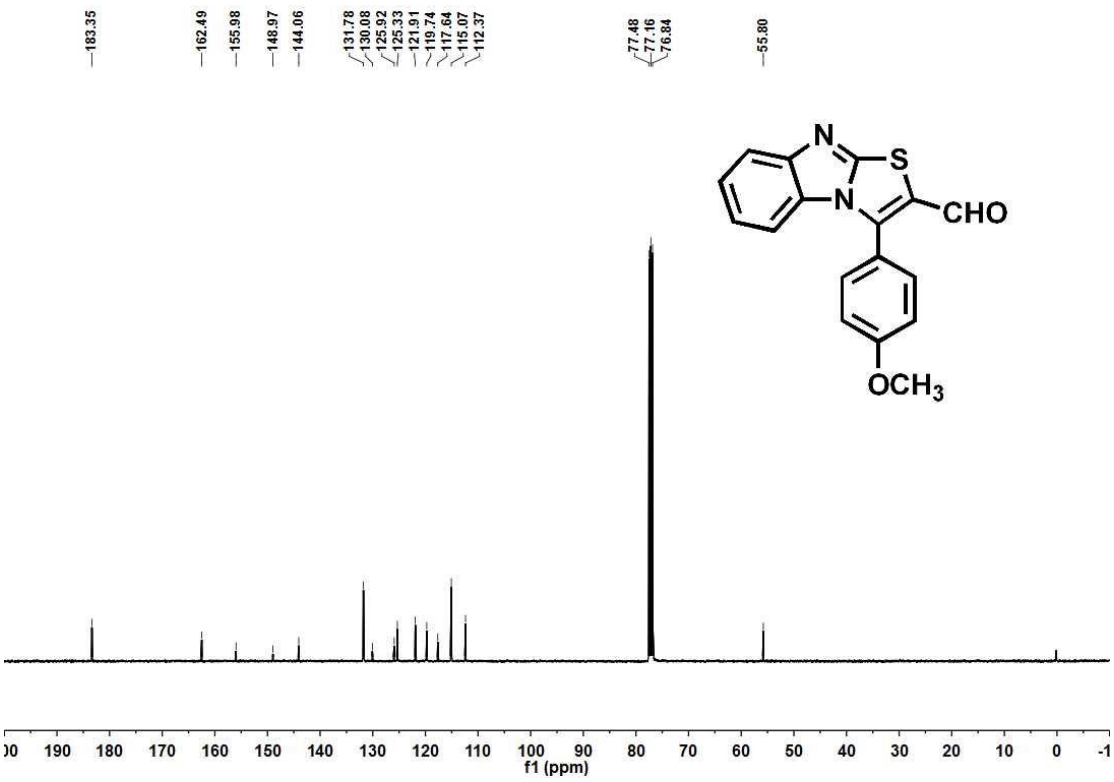
^{13}C NMR of product 3b in $CDCl_3$ (100 MHz)



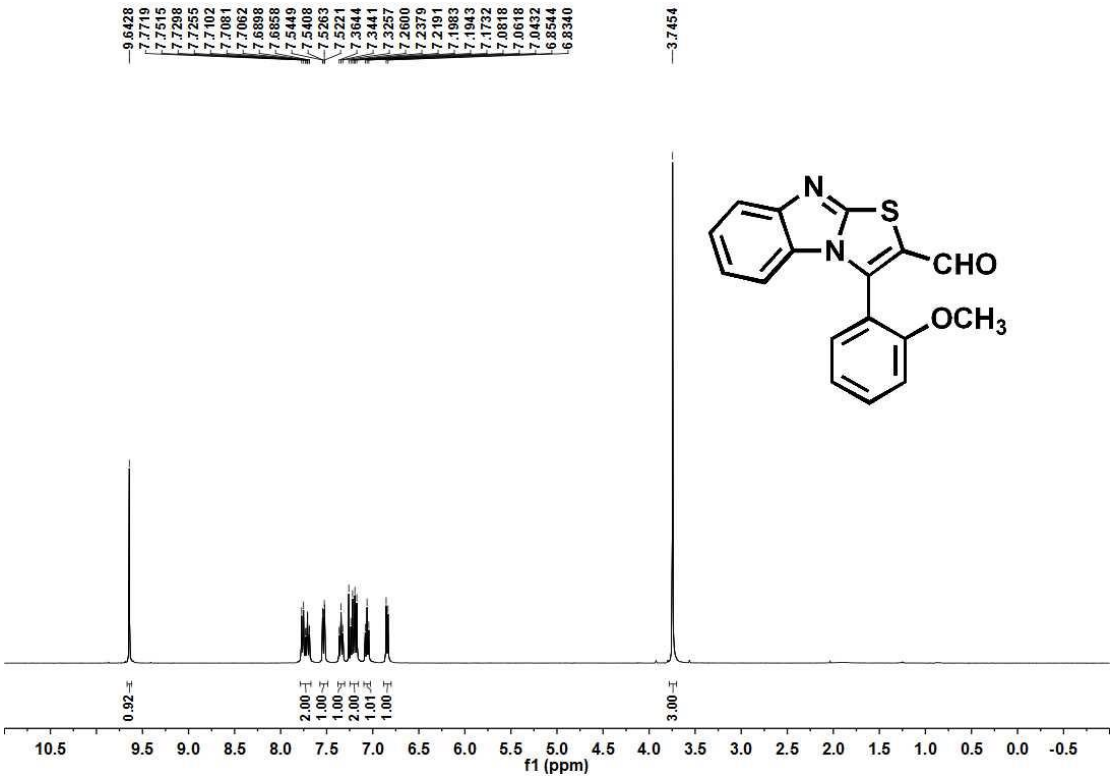
^{1}H NMR of product 3c in $CDCl_3$ (400 MHz)



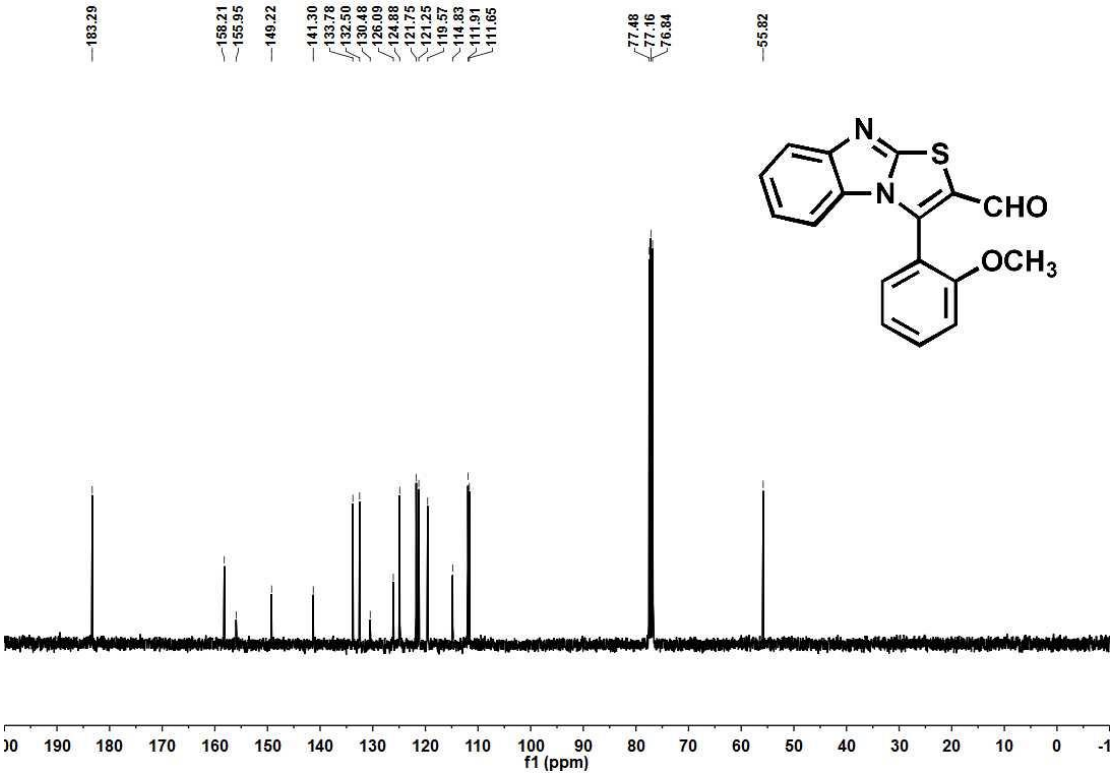
^{13}C NMR of product 3c in $CDCl_3$ (100 MHz)



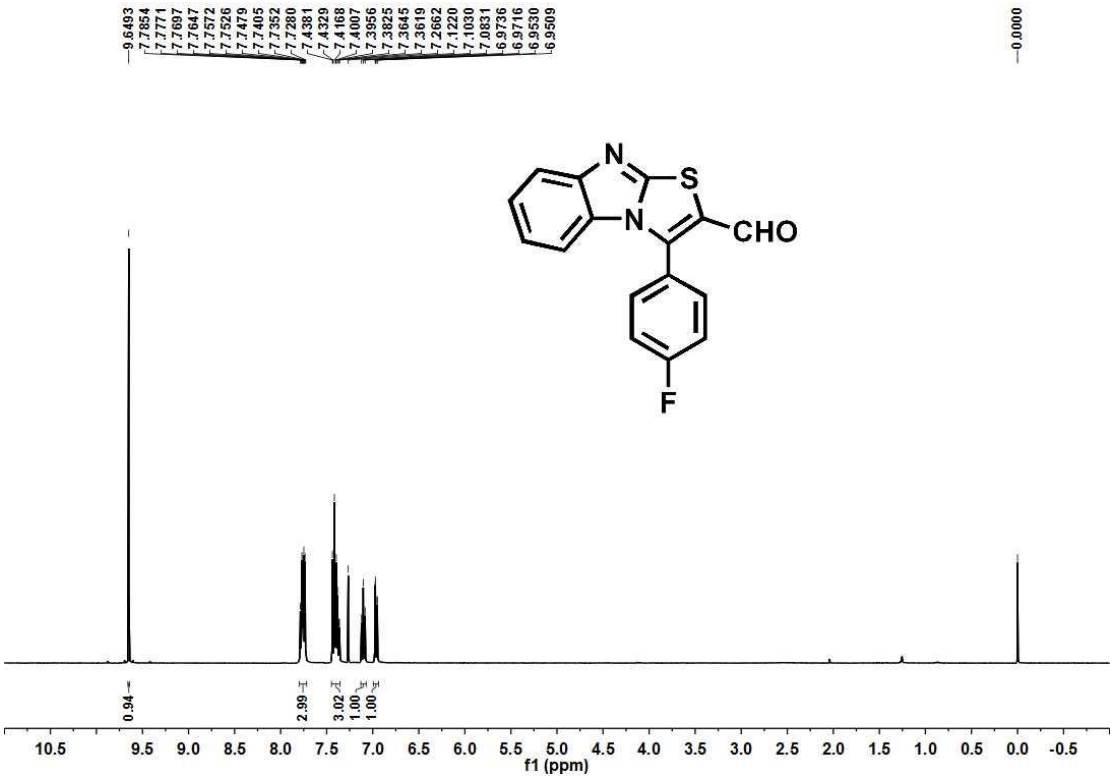
^{1}H NMR of product 3d in $CDCl_3$ (400 MHz)



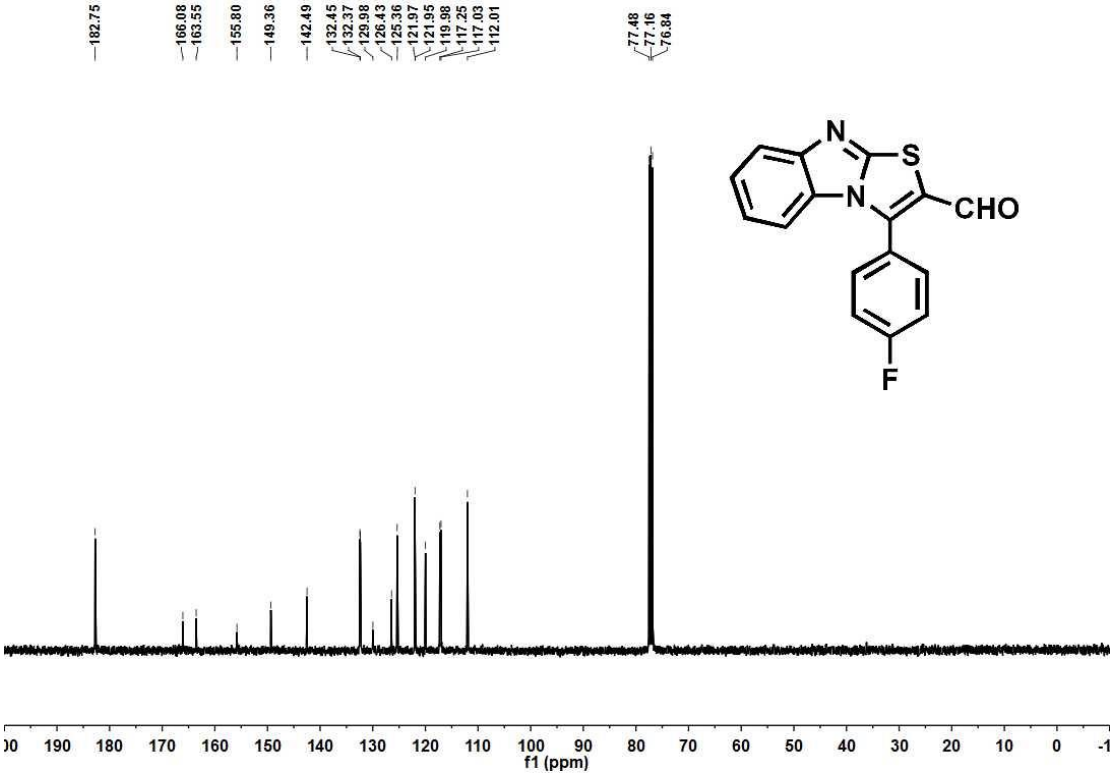
^{13}C NMR of product 3d in $CDCl_3$ (100 MHz)



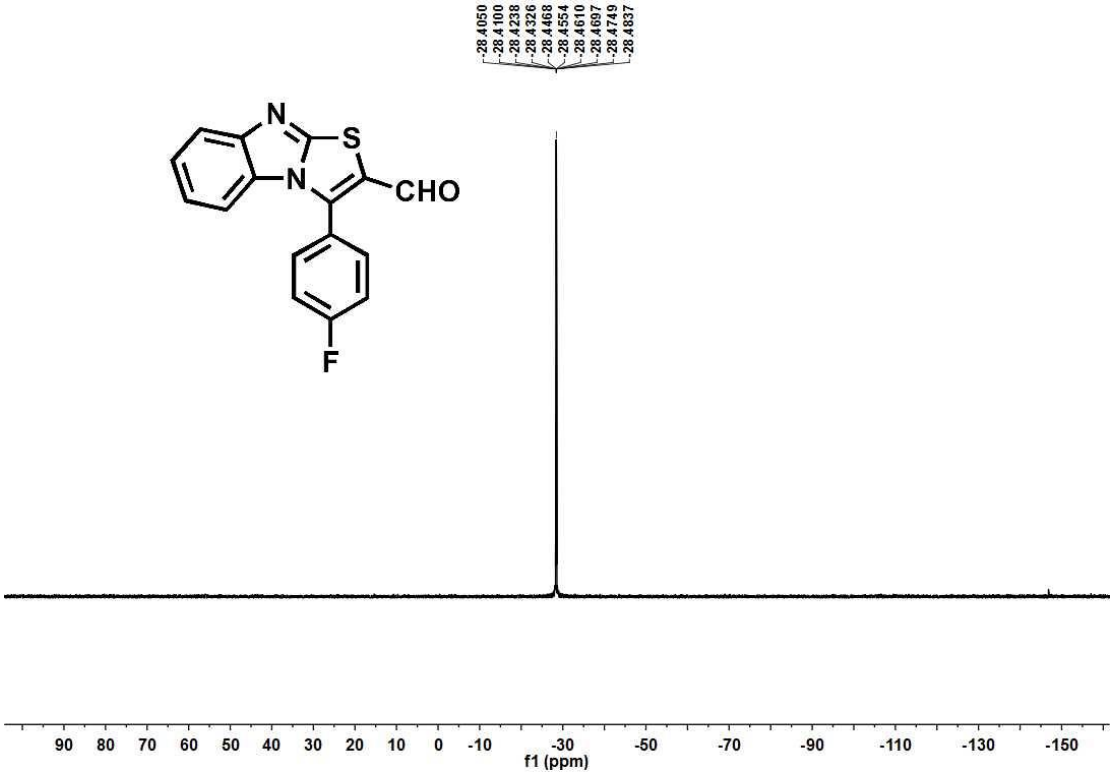
^{1}H NMR of product 3e in $CDCl_3$ (400 MHz)



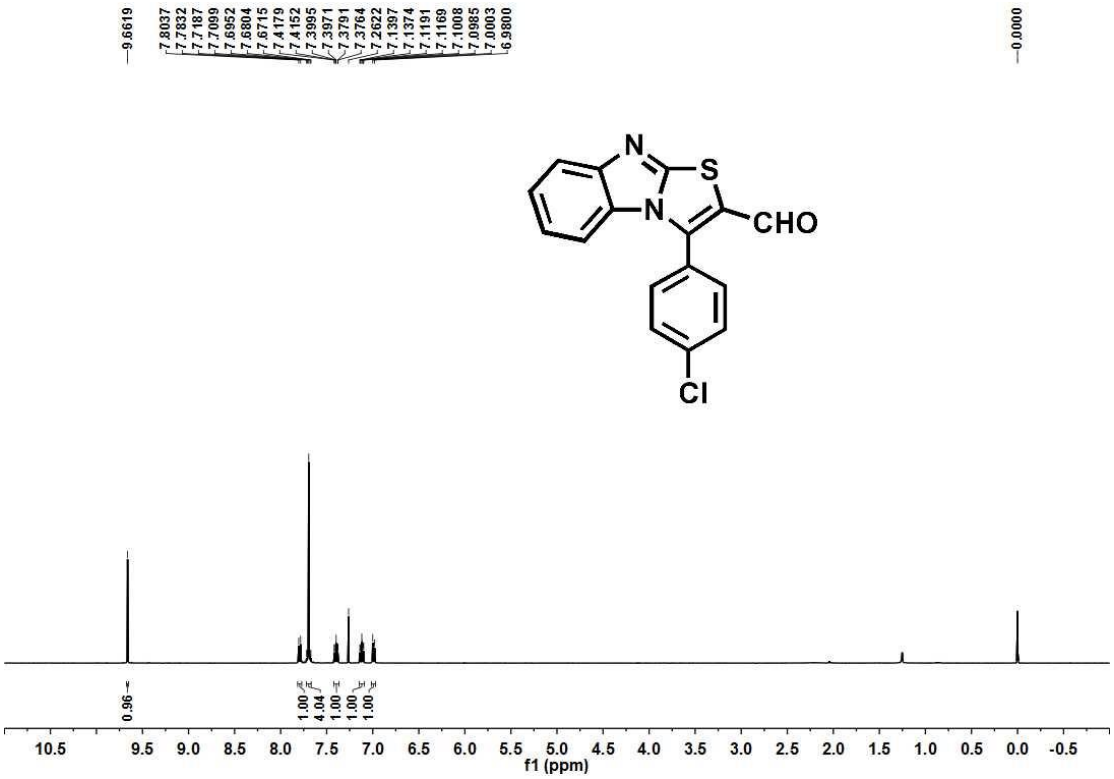
^{13}C NMR of product 3e in $CDCl_3$ (100 MHz)



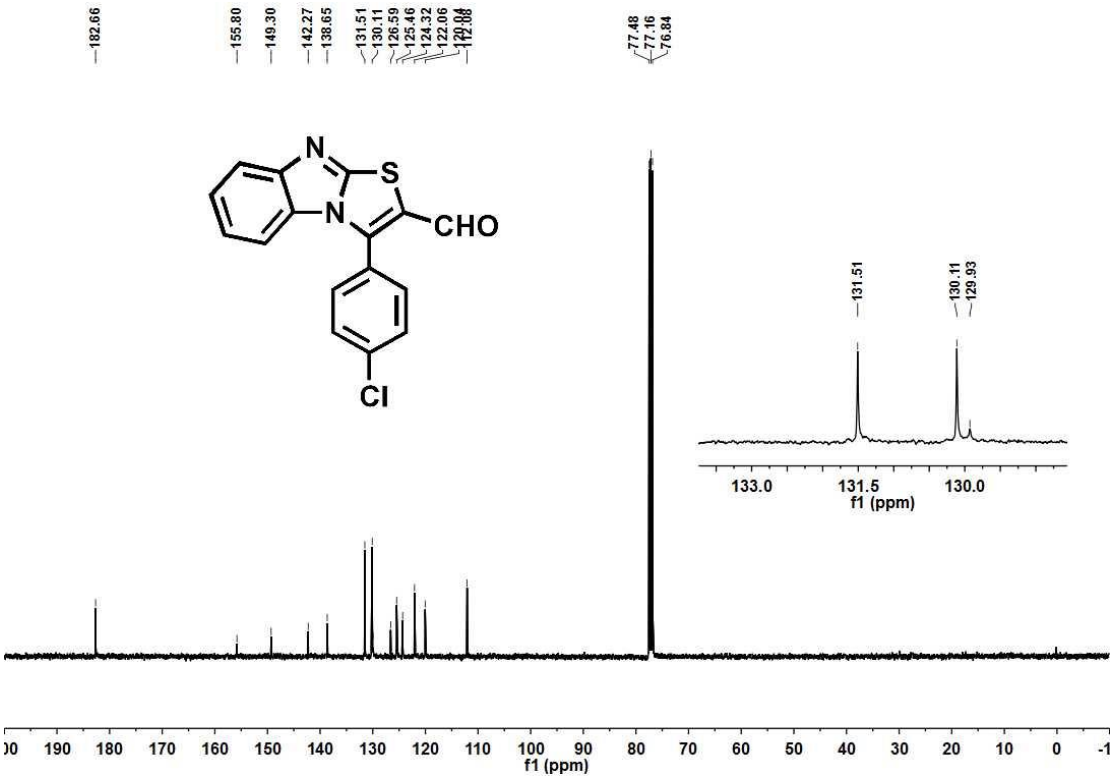
^{19}F NMR of product 3e in $CDCl_3$ (376 MHz)



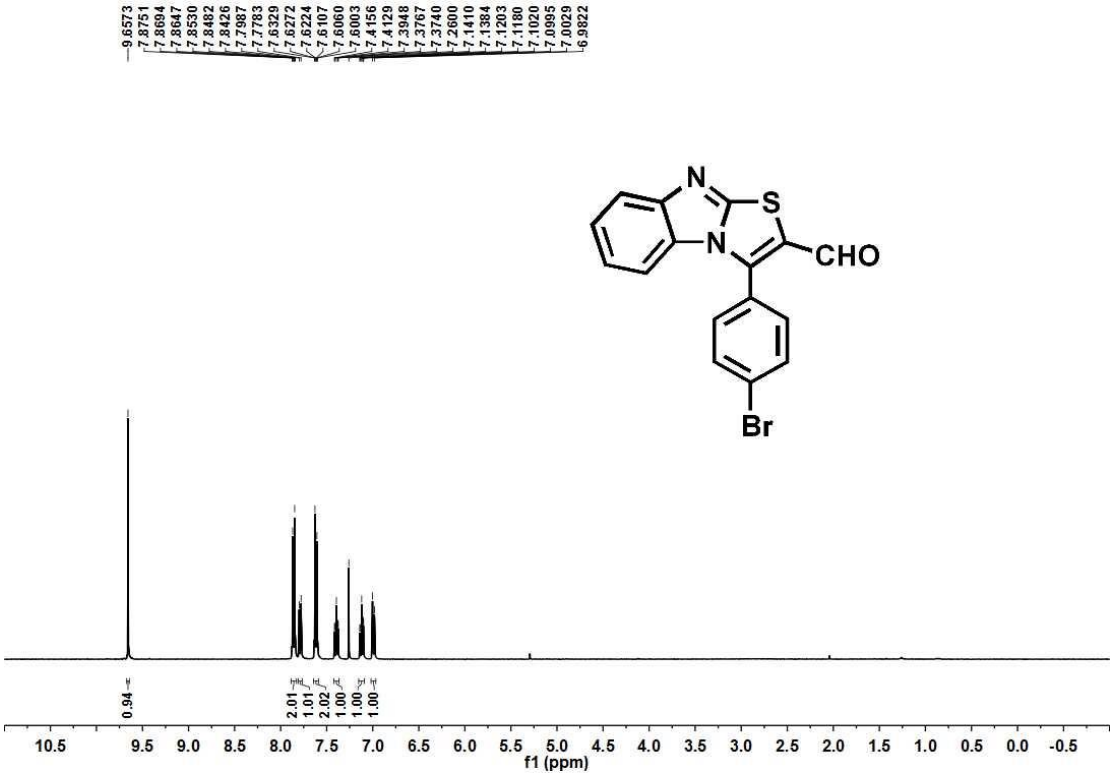
^{1}H NMR of product 3f in $CDCl_3$ (400 MHz)



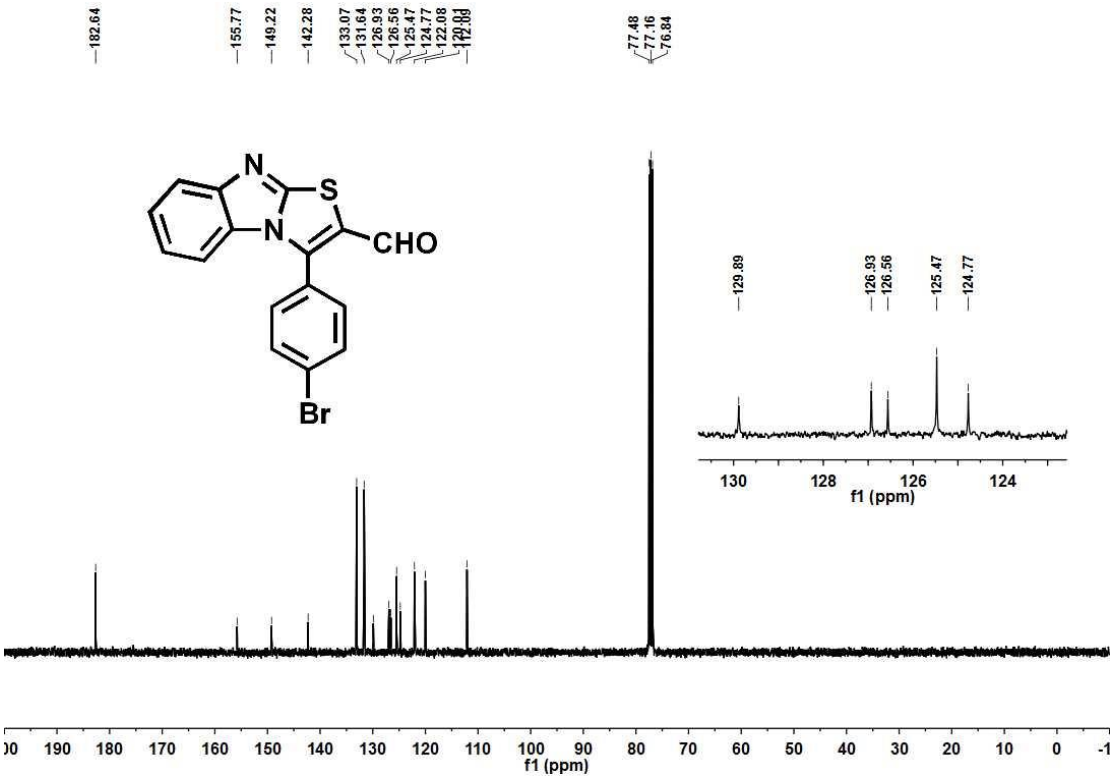
^{13}C NMR of product3f in $CDCl_3$ (100 MHz)



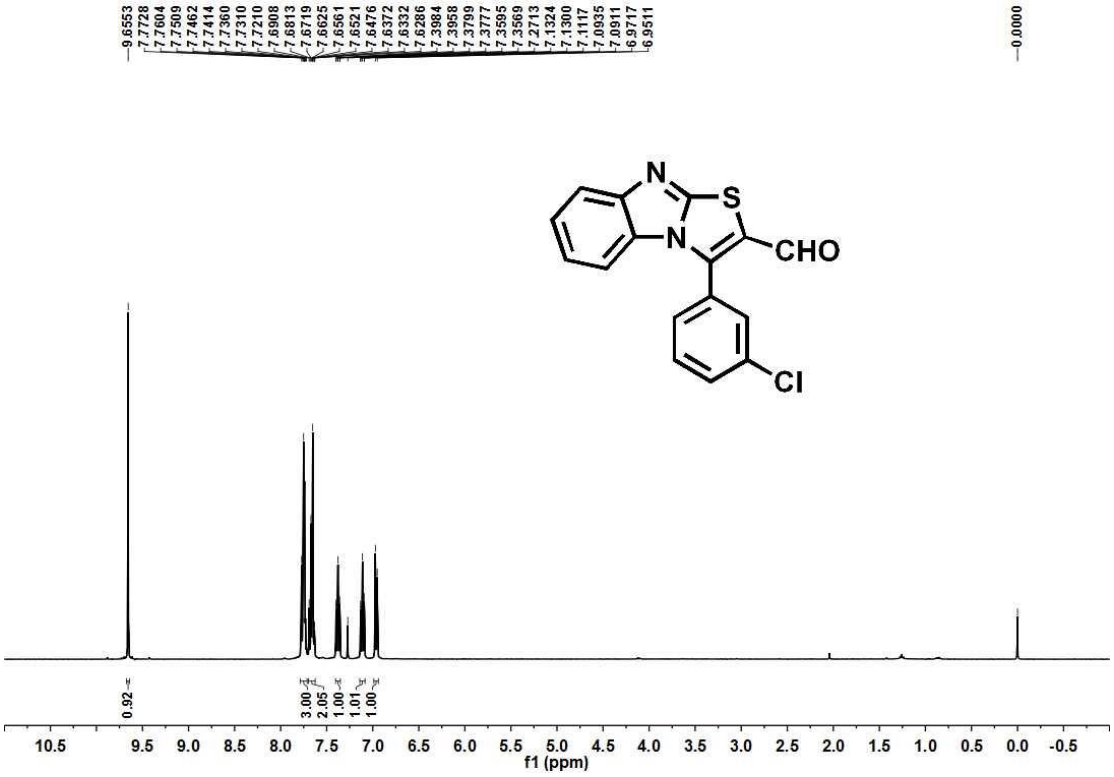
^{1}H NMR of product 3g in $CDCl_3$ (400 MHz)



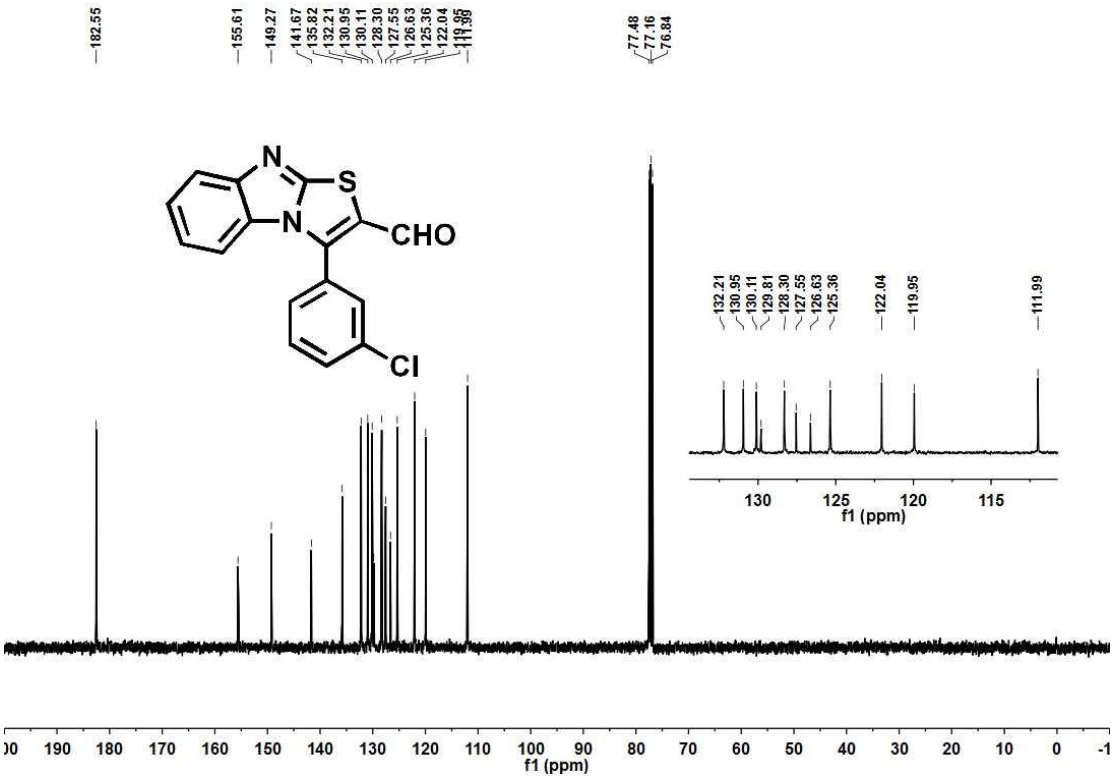
^{13}C NMR of product 3g in $CDCl_3$ (100 MHz)



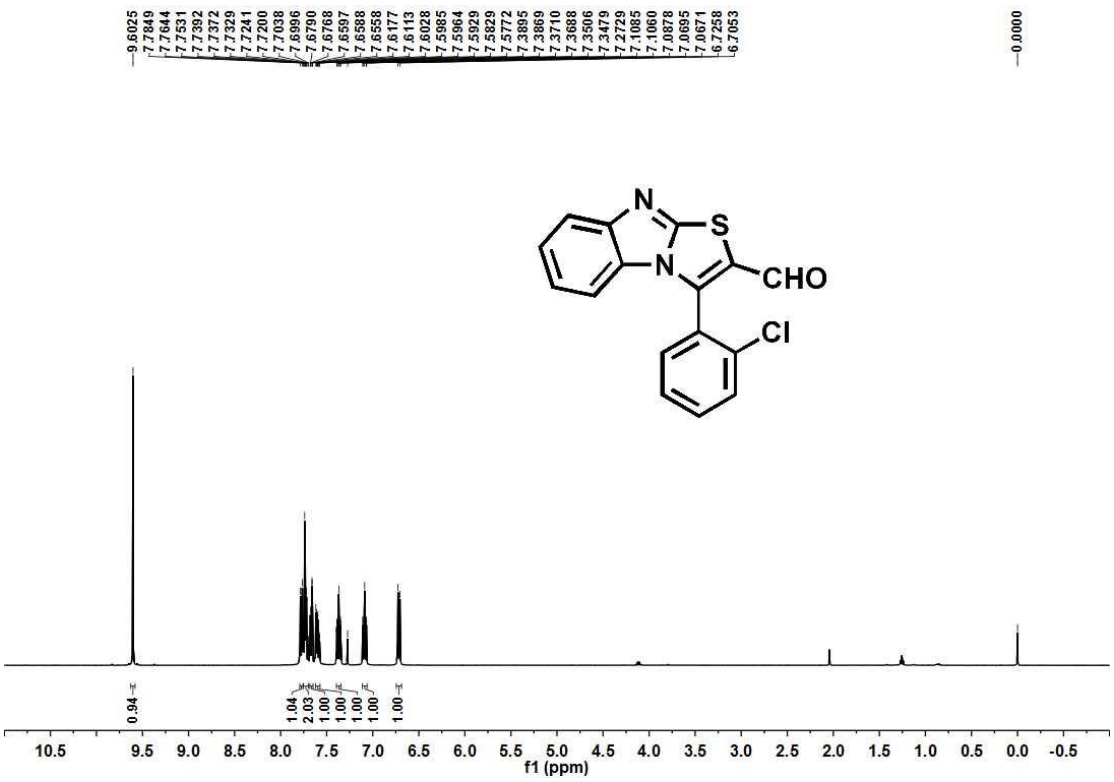
^{1}H NMR of product 3h in $CDCl_3$ (400 MHz)



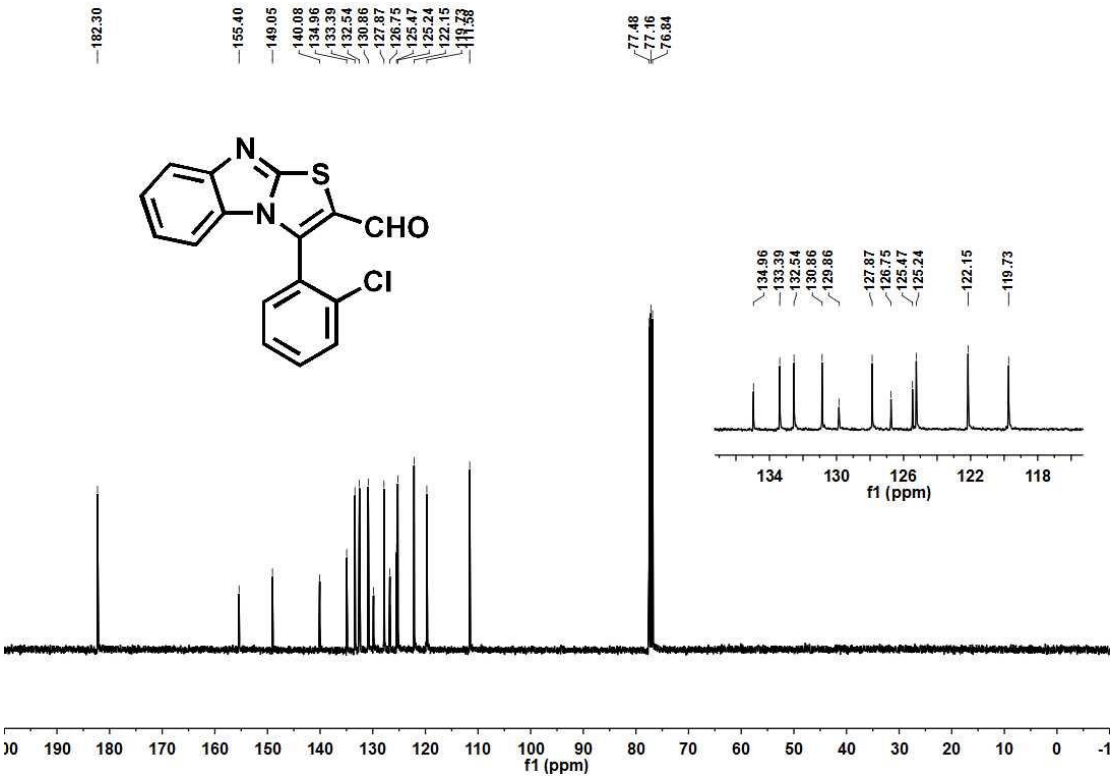
^{13}C NMR of product 3h in $CDCl_3$ (100 MHz)



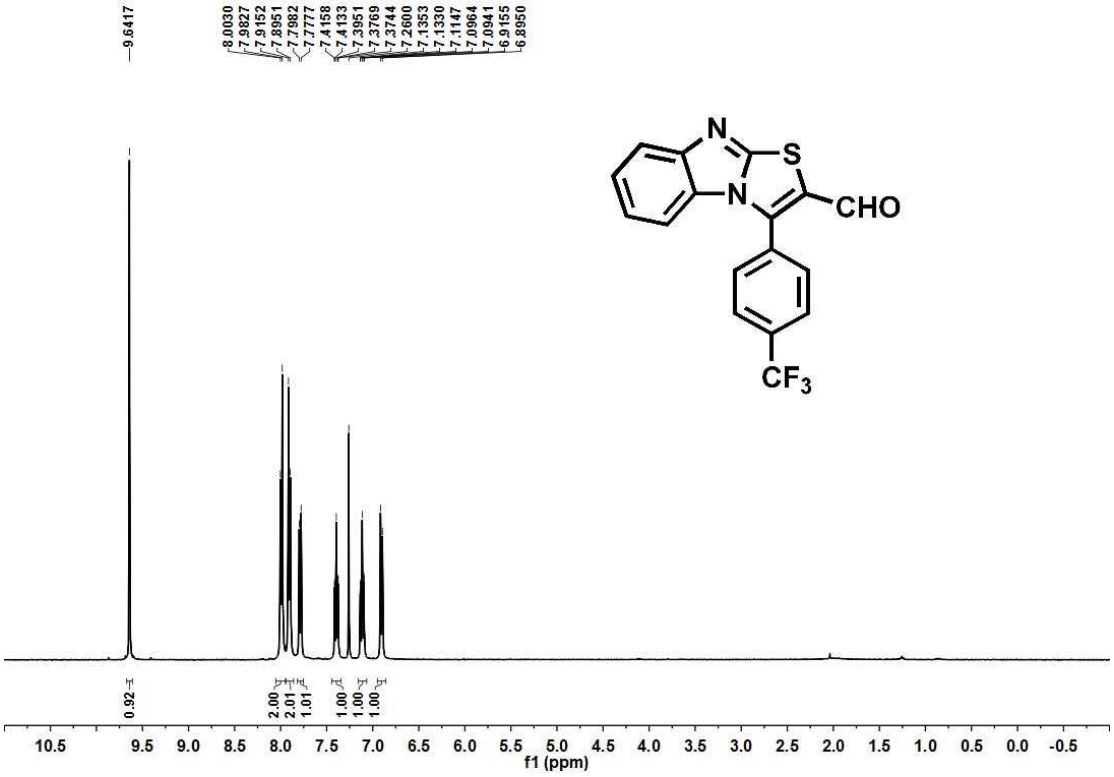
^{1}H NMR of product 3i in $CDCl_3$ (400 MHz)



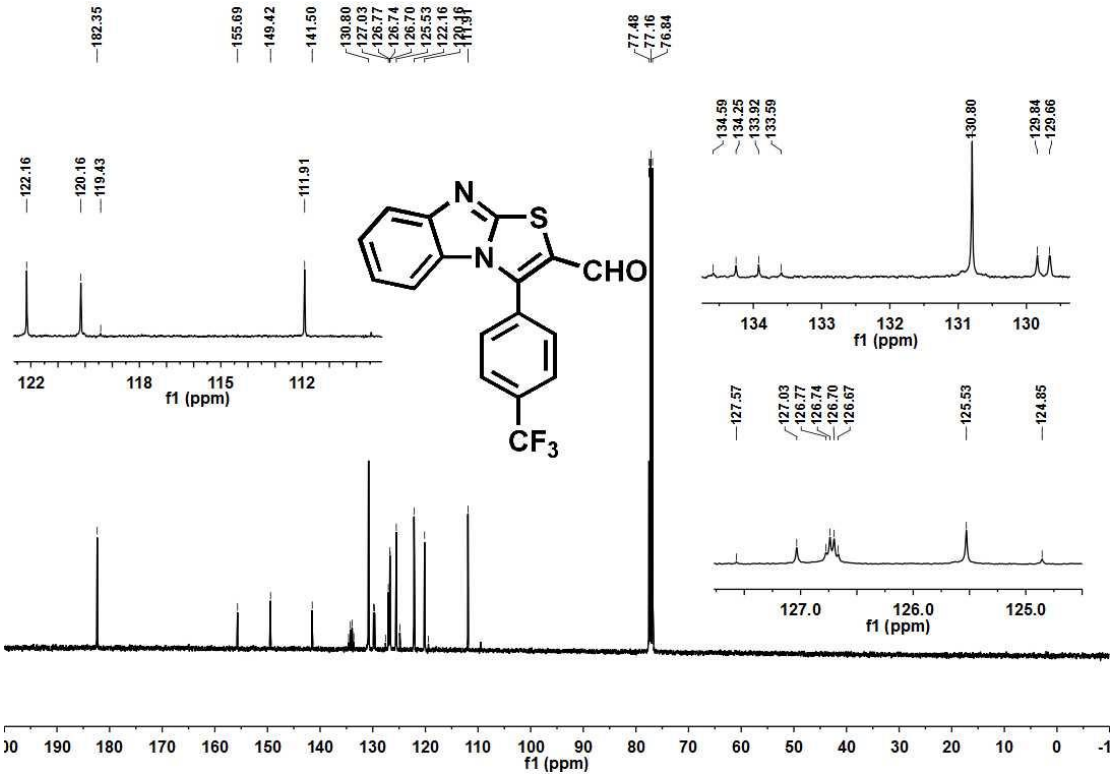
^{13}C NMR of product 3i in $CDCl_3$ (100 MHz)



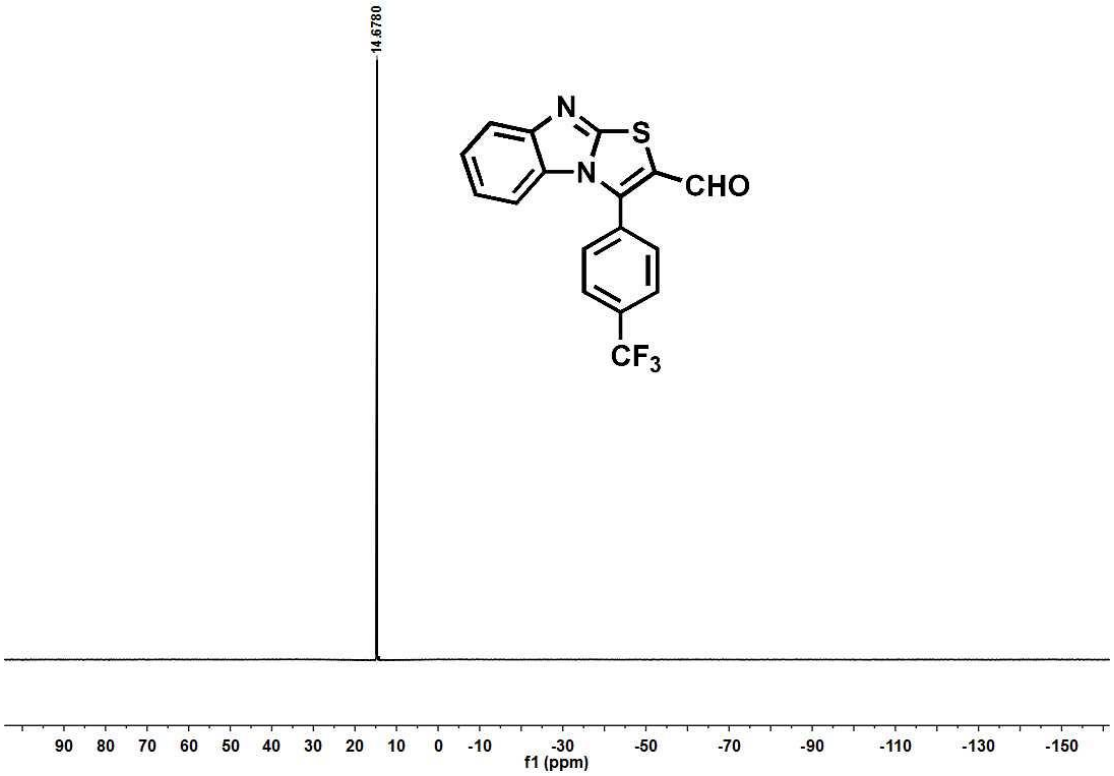
^{1}H NMR of product 3j in $CDCl_3$ (400 MHz)



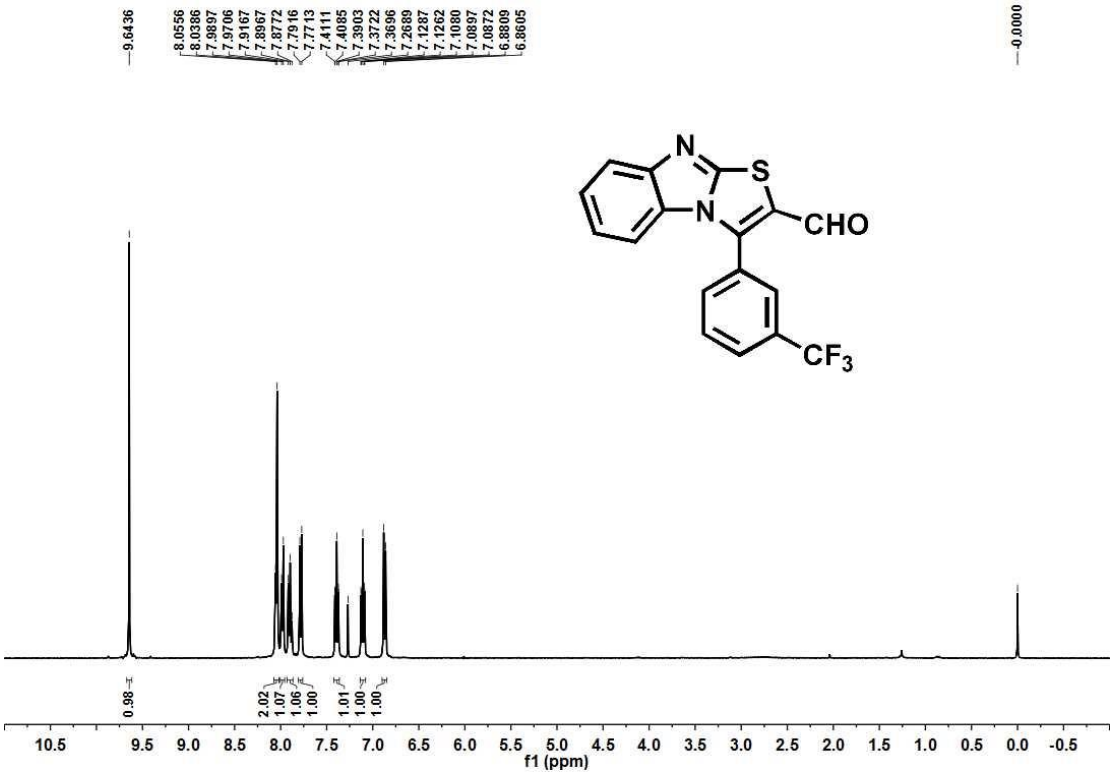
^{13}C NMR of product 3j in $CDCl_3$ (100 MHz)



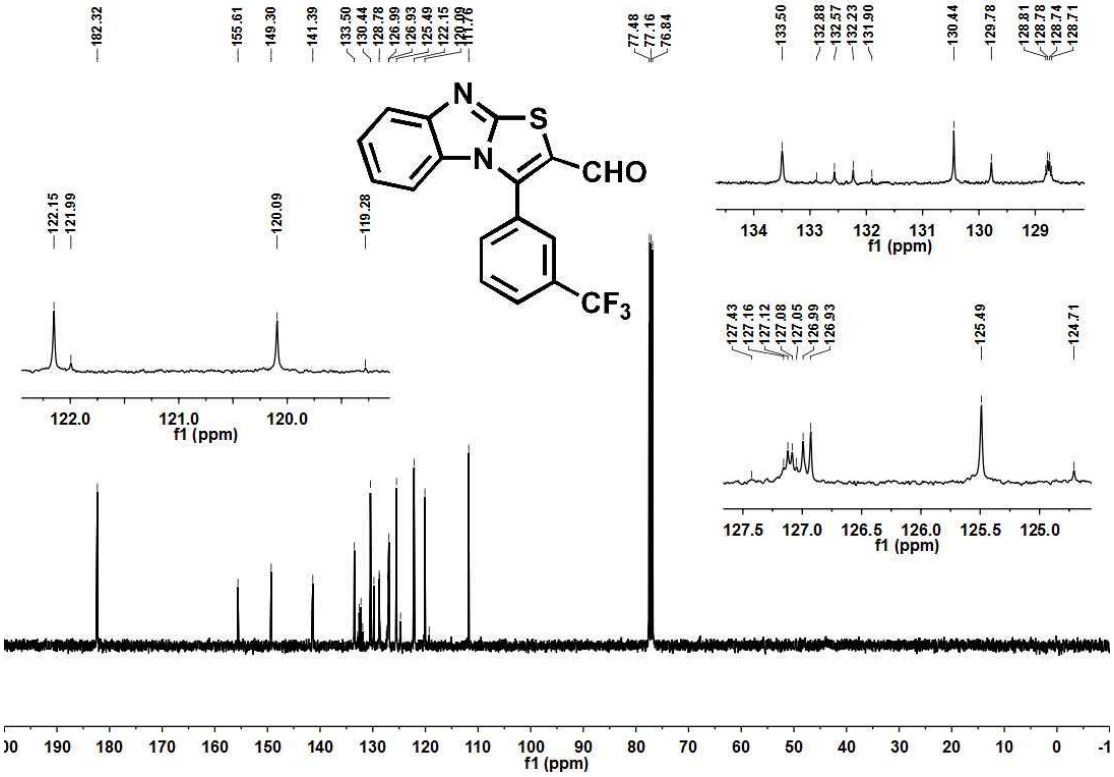
^{19}F NMR of product 3j in $CDCl_3$ (376 MHz)



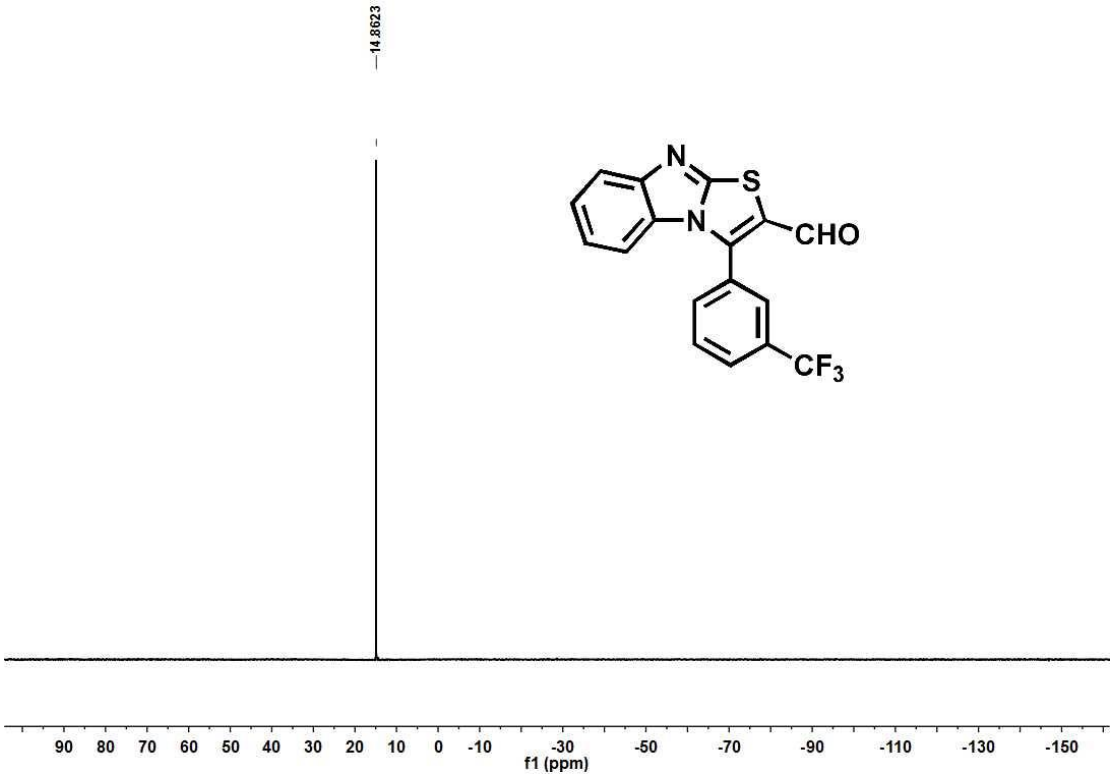
^{1}H NMR of product 3k in $CDCl_3$ (400 MHz)



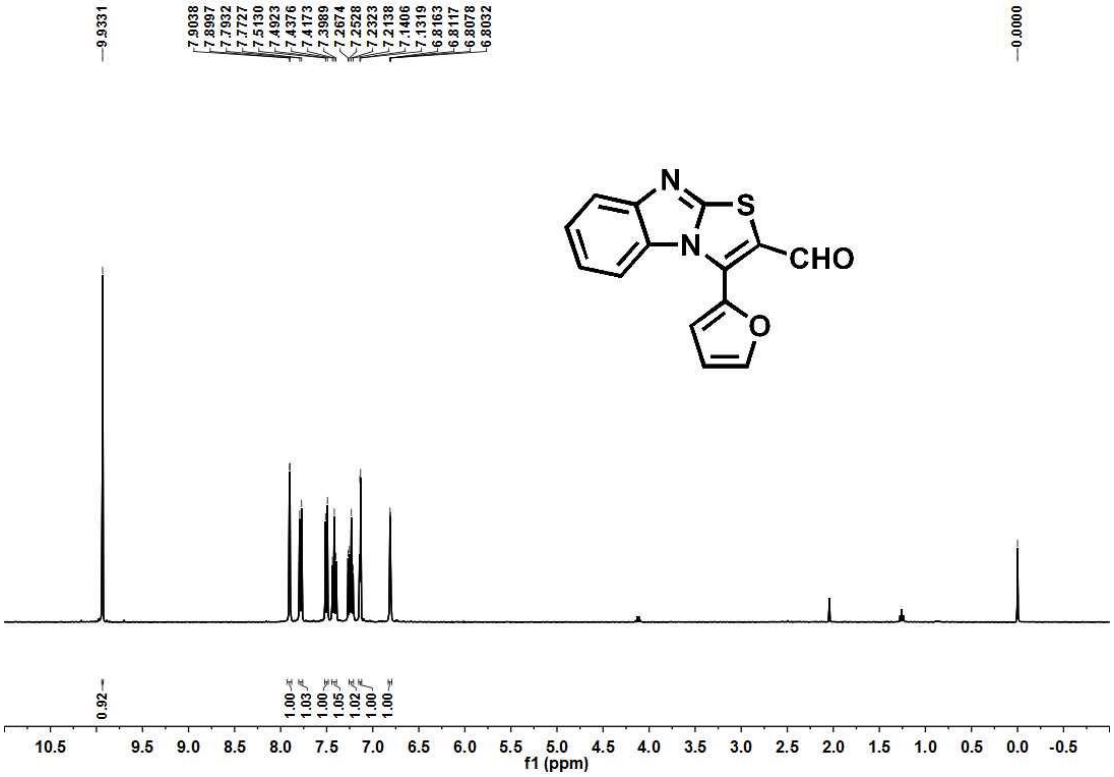
^{13}C NMR of product 3k in $CDCl_3$ (100 MHz)



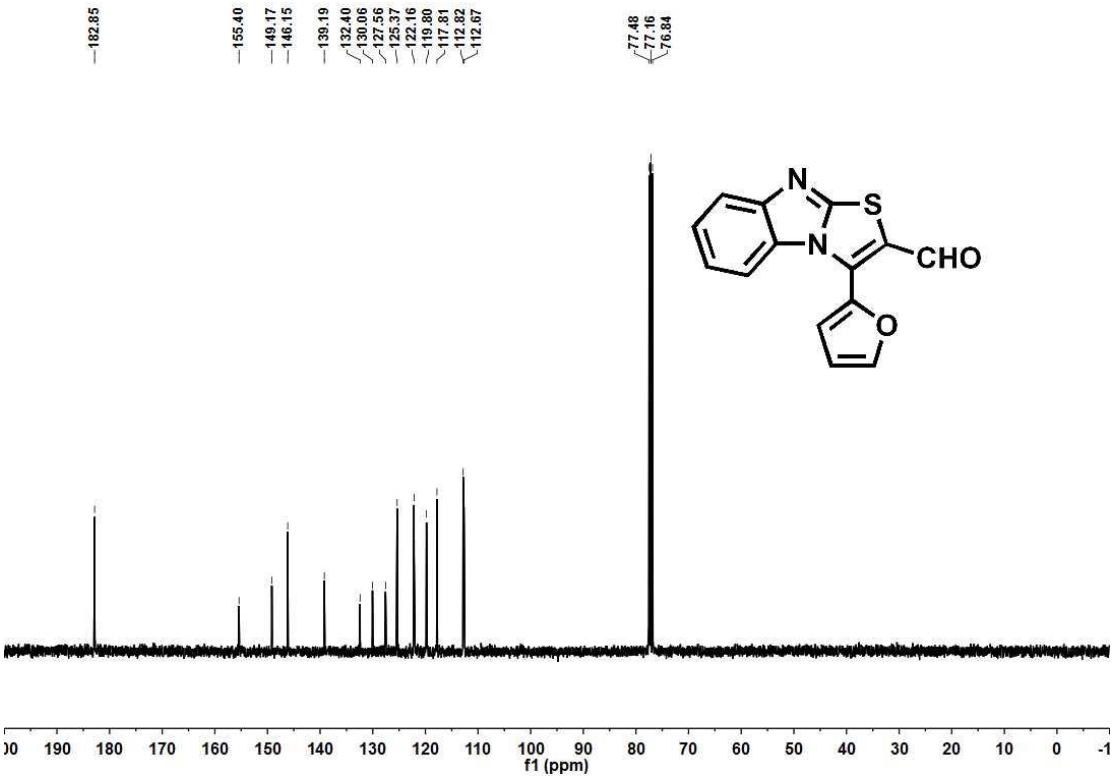
^{19}F NMR of product 3k in $CDCl_3$ (376 MHz)



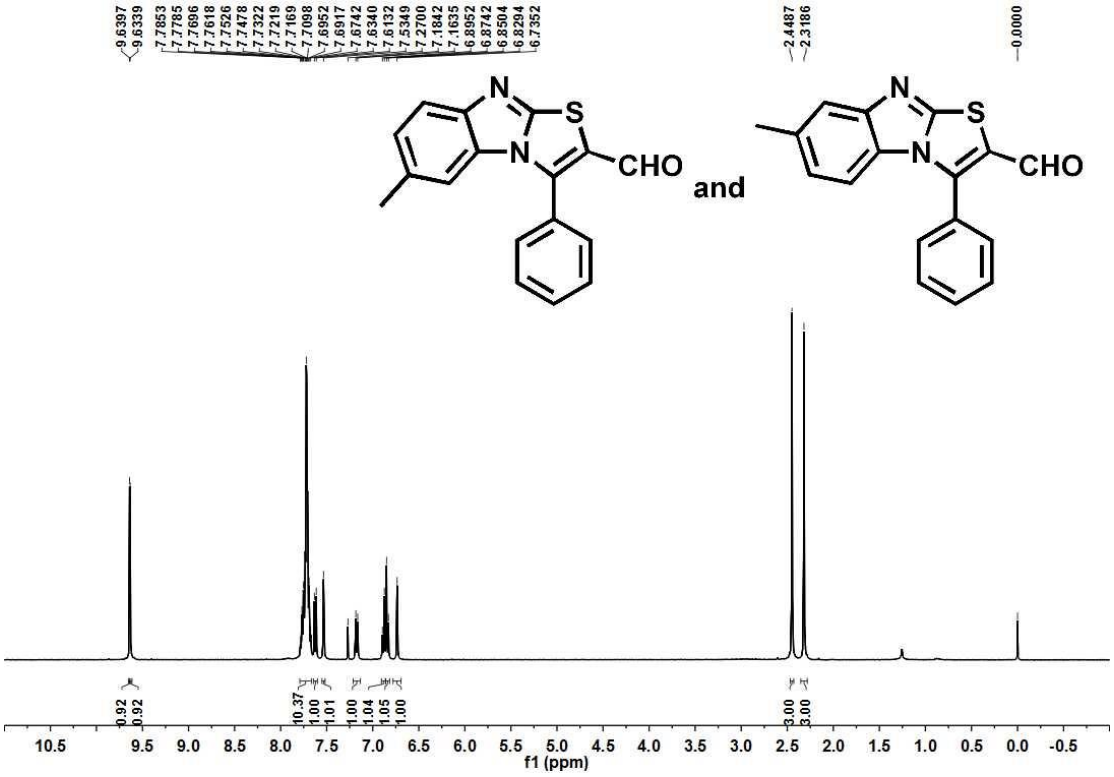
^{1}H NMR of product 3l in $CDCl_3$ (400 MHz)



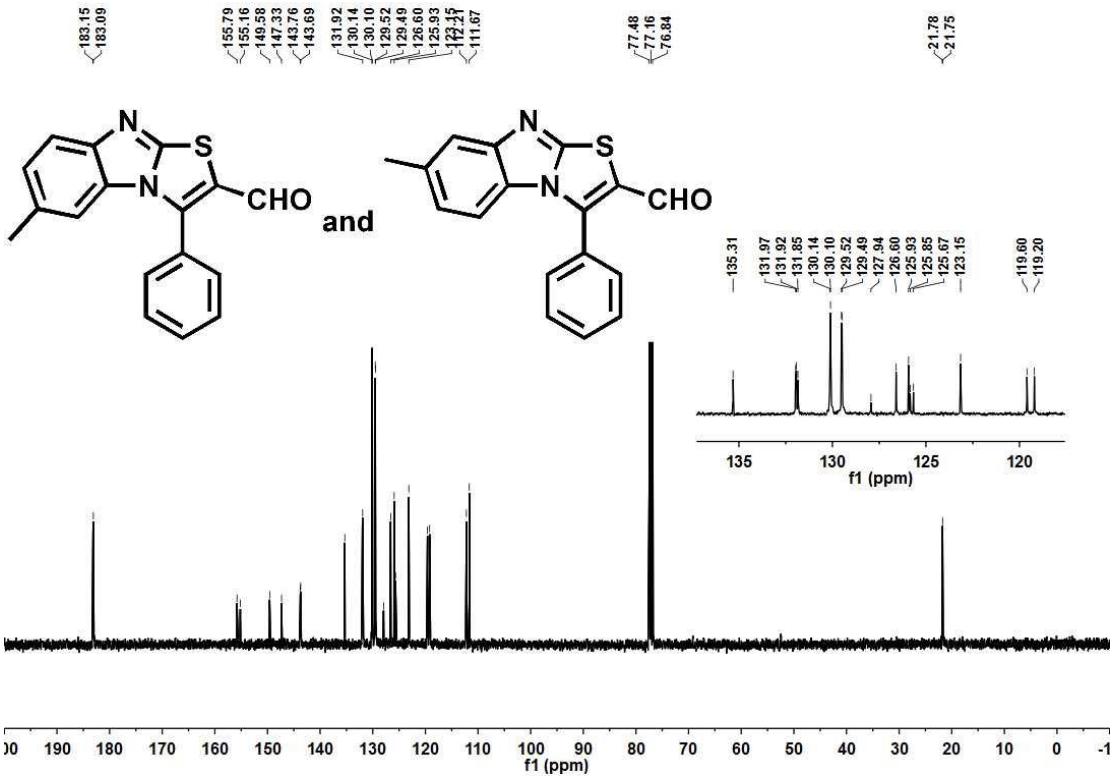
^{13}C NMR of product 3l in $CDCl_3$ (100 MHz)



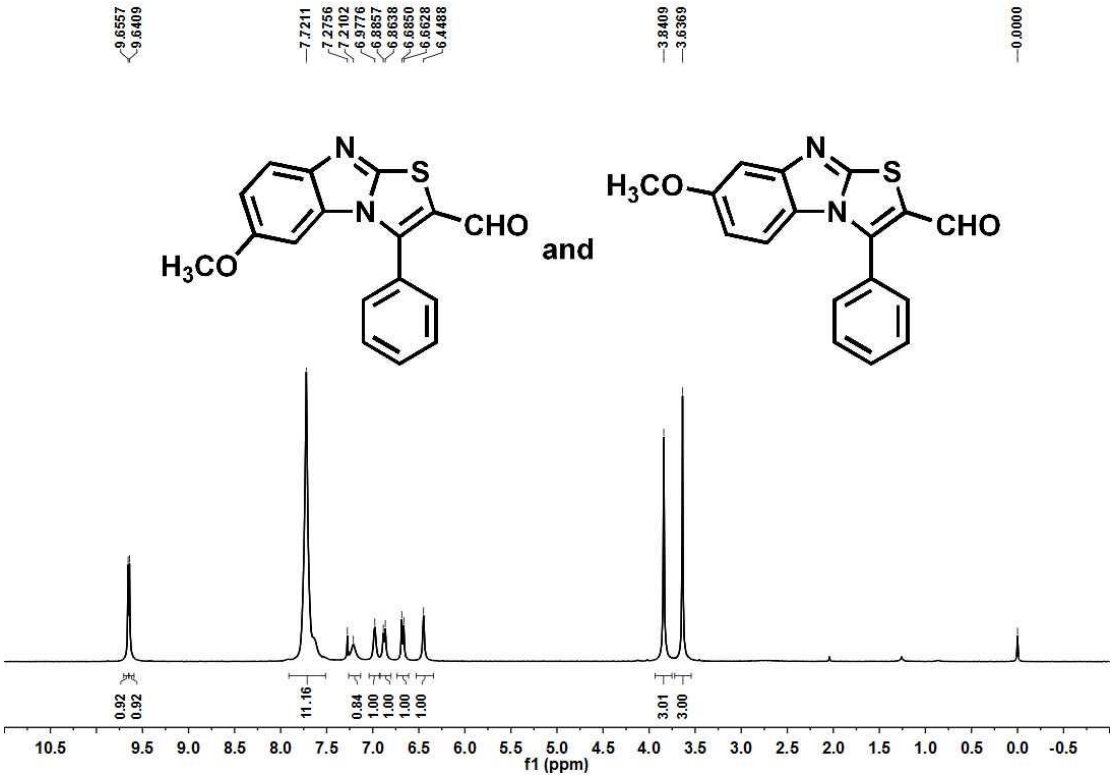
^{1}H NMR of product 3m and 3m' in $CDCl_3$ (400 MHz)



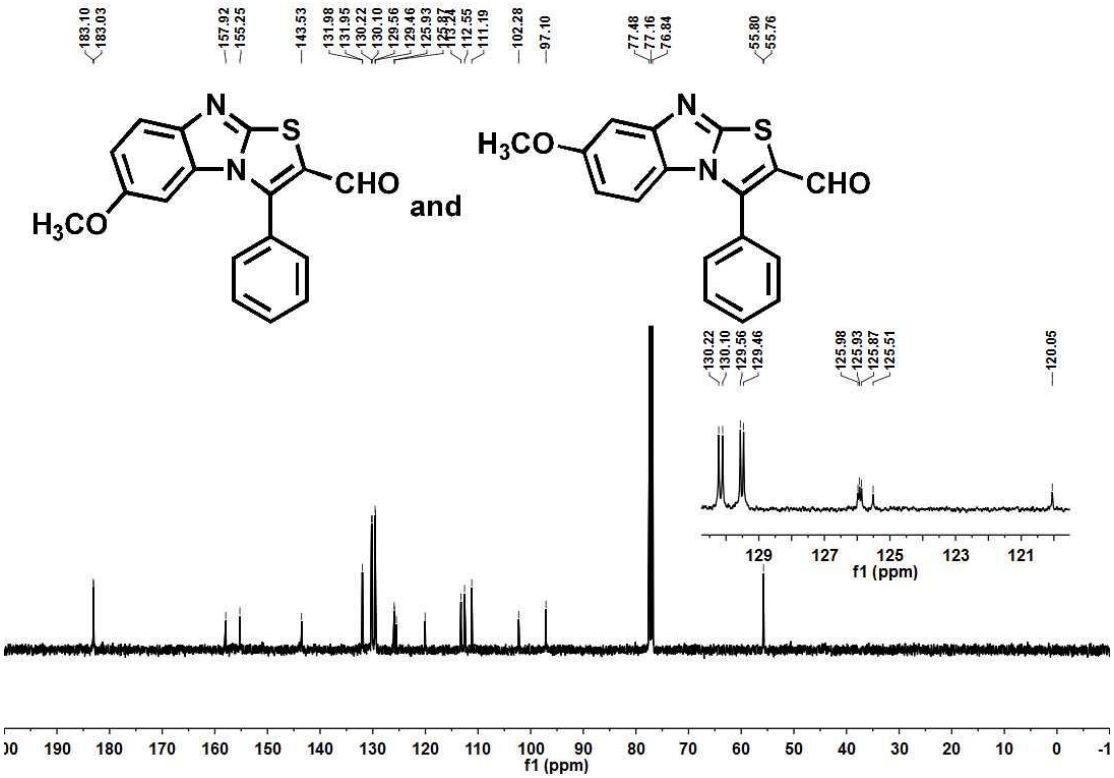
^{13}C NMR of product 3m and 3m' in $CDCl_3$ (100 MHz)



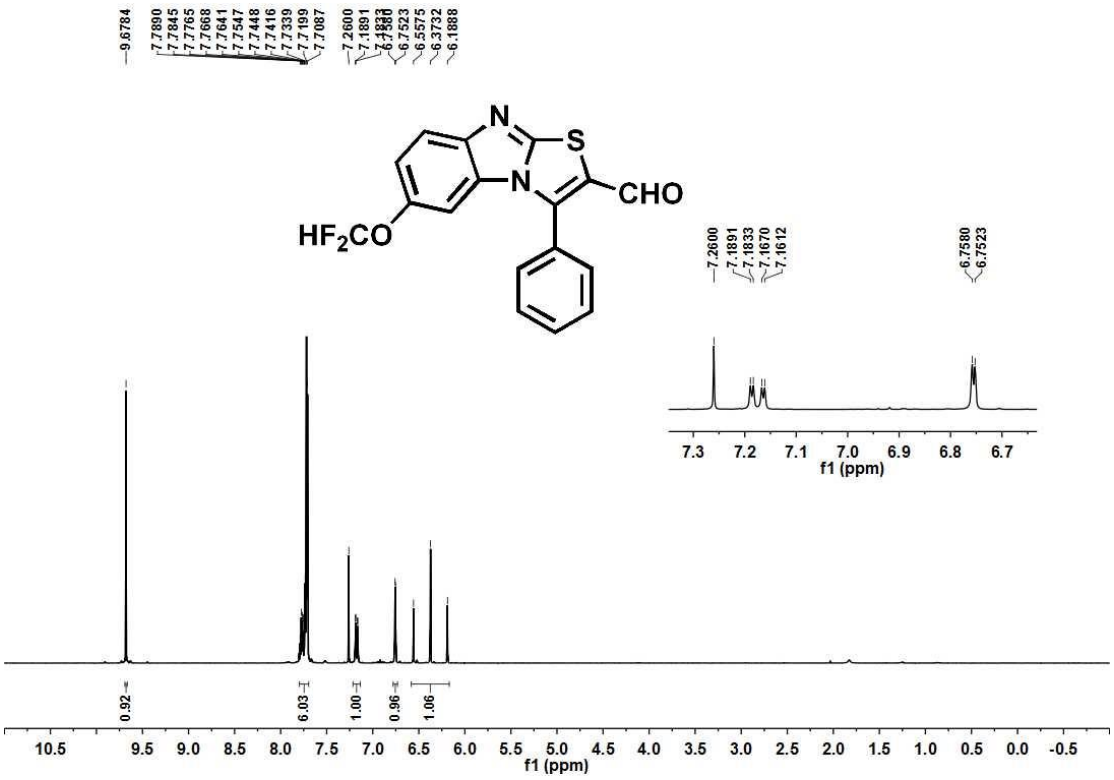
^{1}H NMR of product 3n and 3n' in $CDCl_3$ (400 MHz)



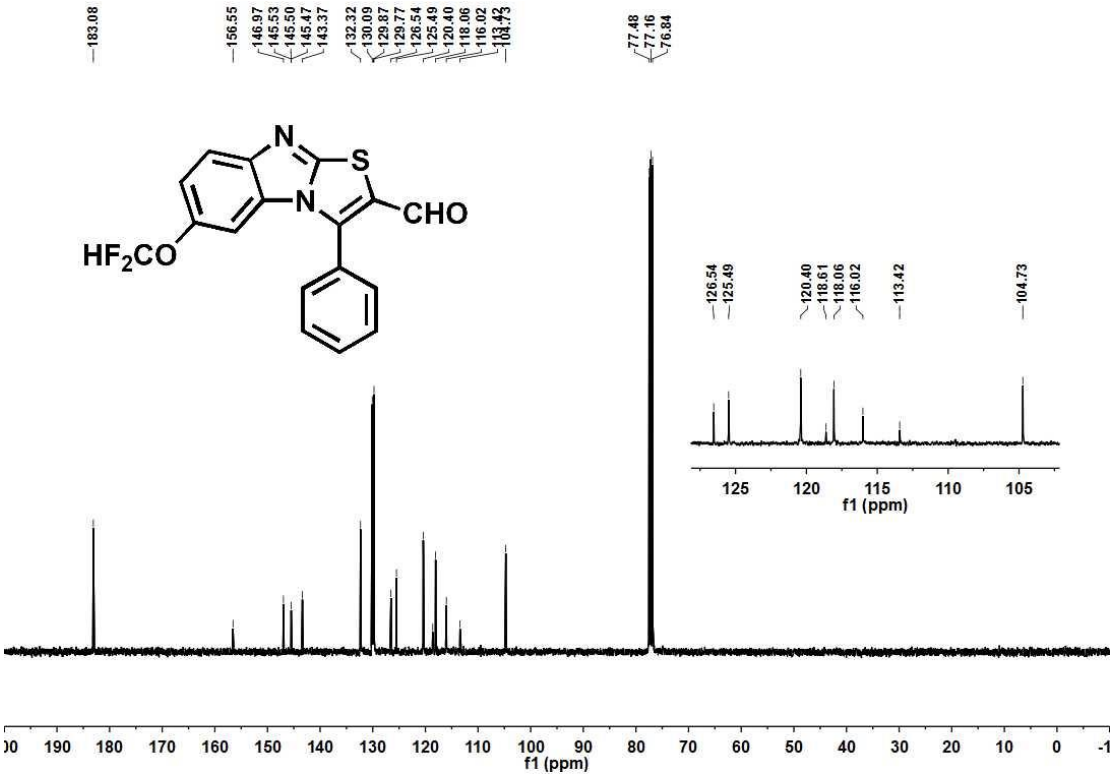
^{13}C NMR of product 3n and 3n' in $CDCl_3$ (100 MHz)



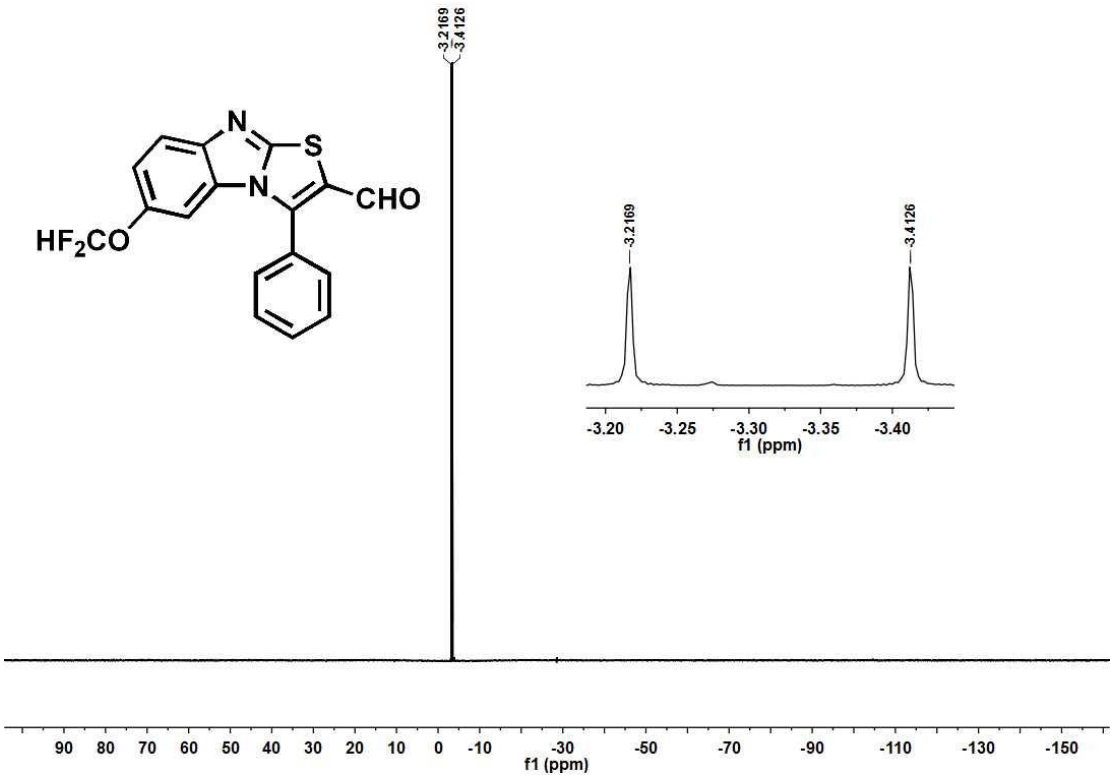
^{1}H NMR of product 3o in $CDCl_3$ (400 MHz)



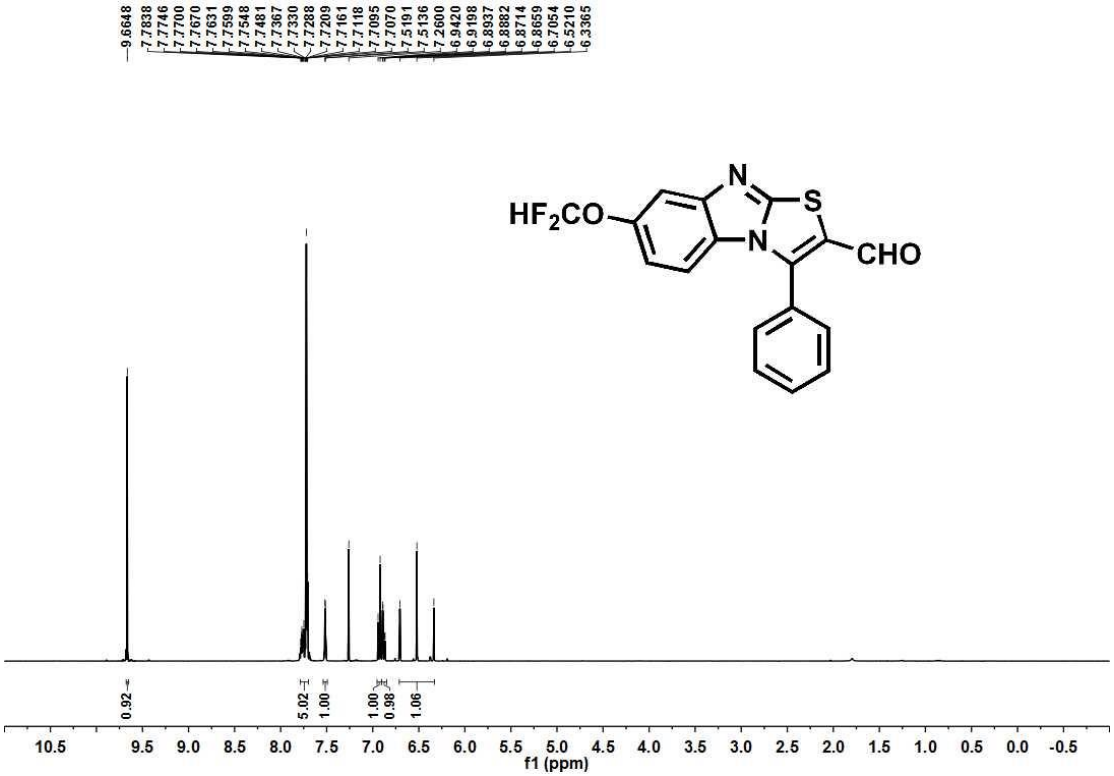
^{13}C NMR of product 3o in $CDCl_3$ (100 MHz)



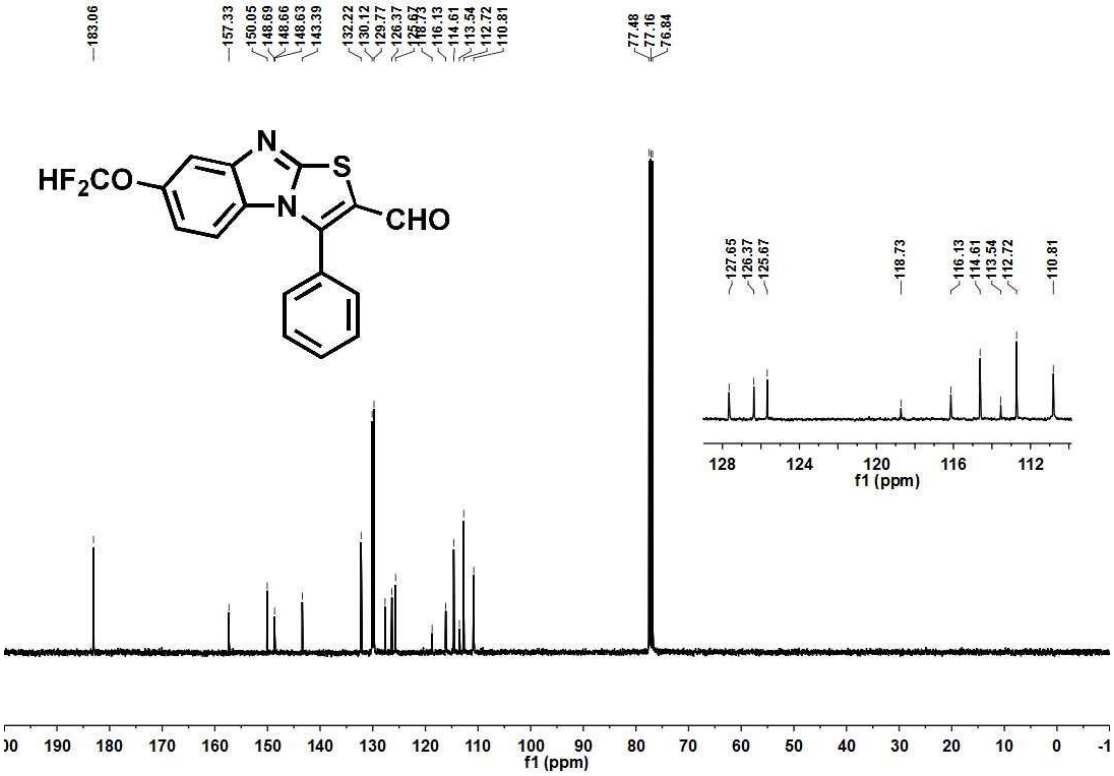
^{19}F NMR of product 3o in $CDCl_3$ (376 MHz)



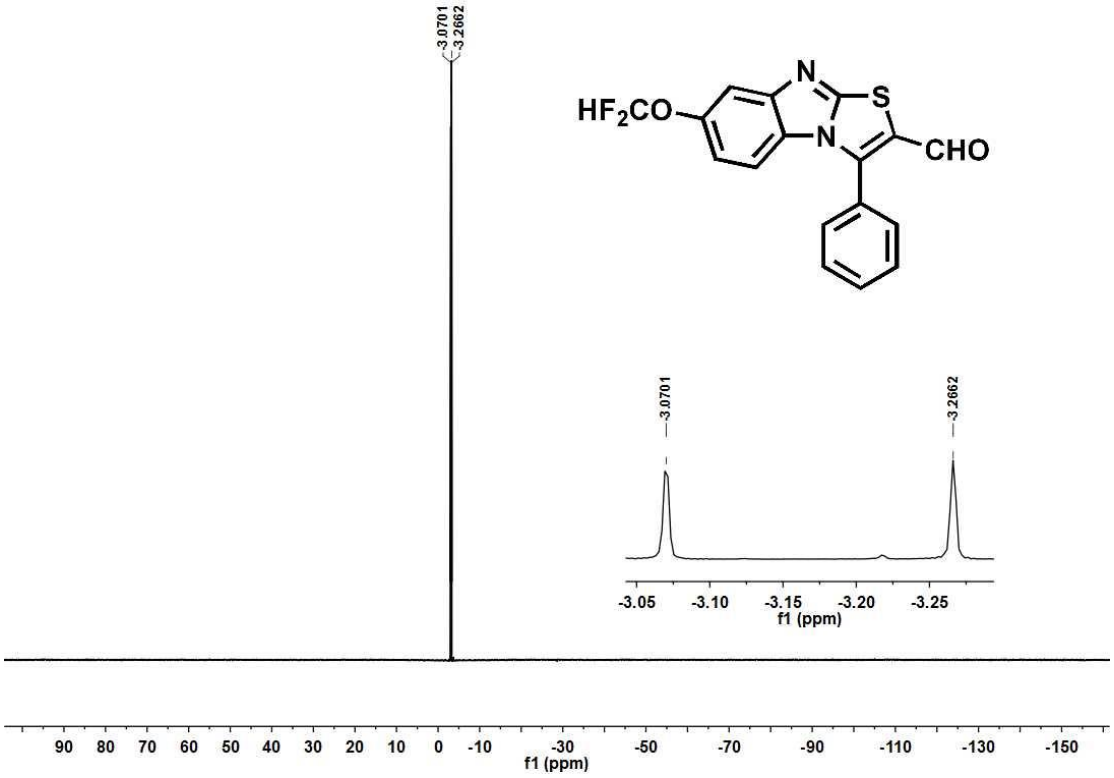
^{1}H NMR of product 3o' in $CDCl_3$ (400 MHz)



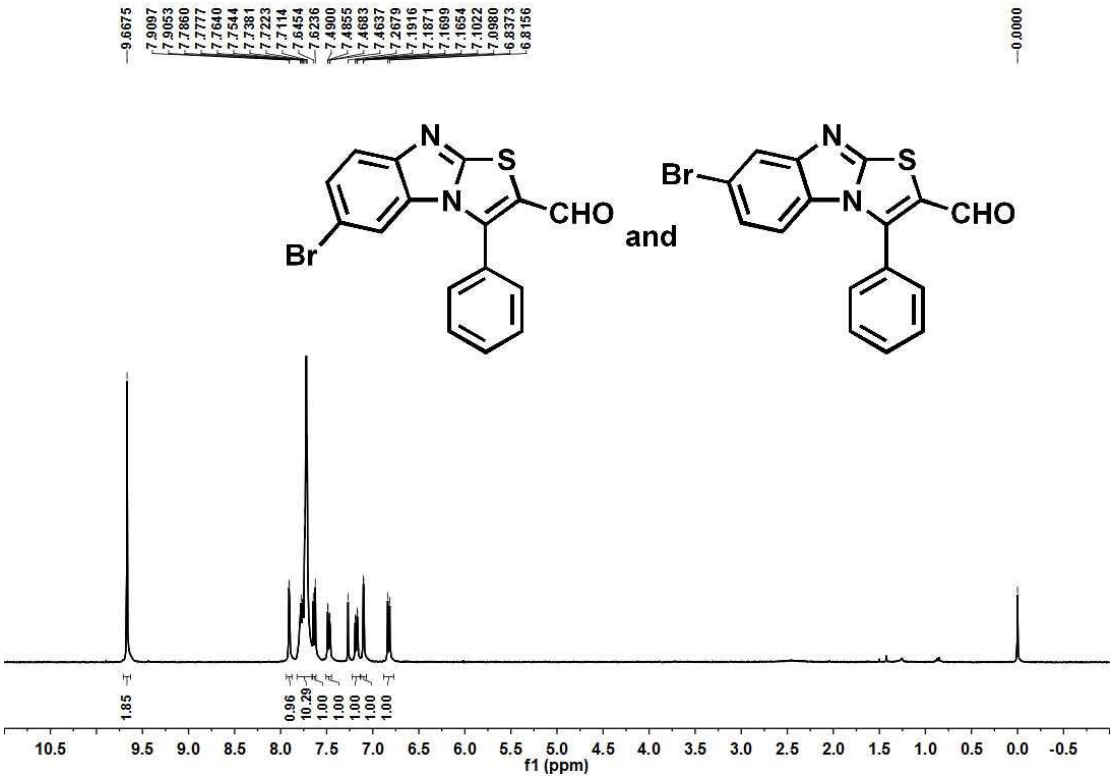
^{13}C NMR of product 3o' in $CDCl_3$ (100 MHz)



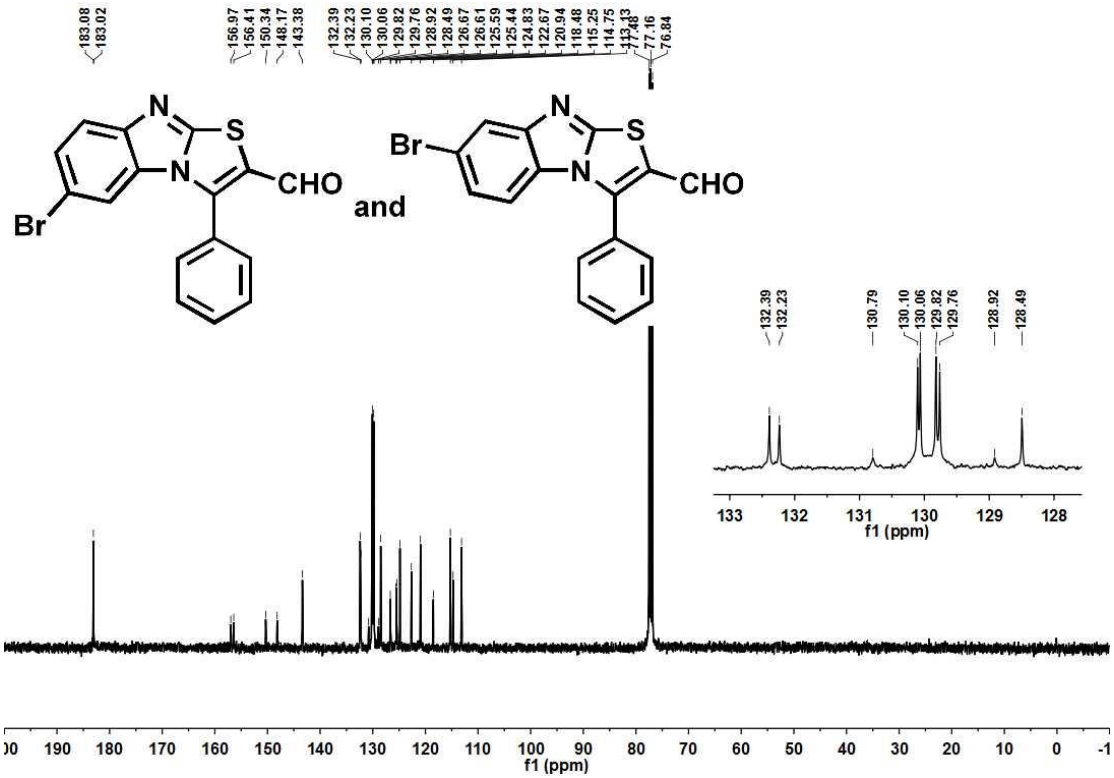
^{19}F NMR of product 3o' in $CDCl_3$ (376 MHz)



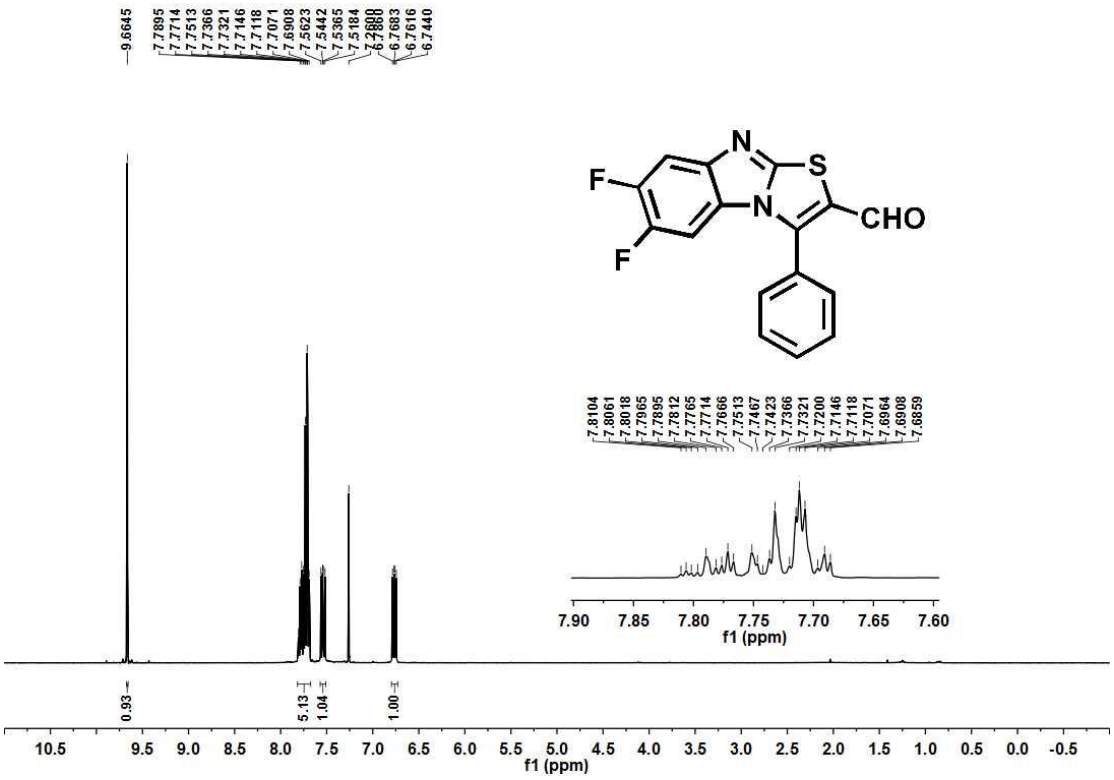
^{1}H NMR of product 3p and 3p' in $CDCl_3$ (400 MHz)



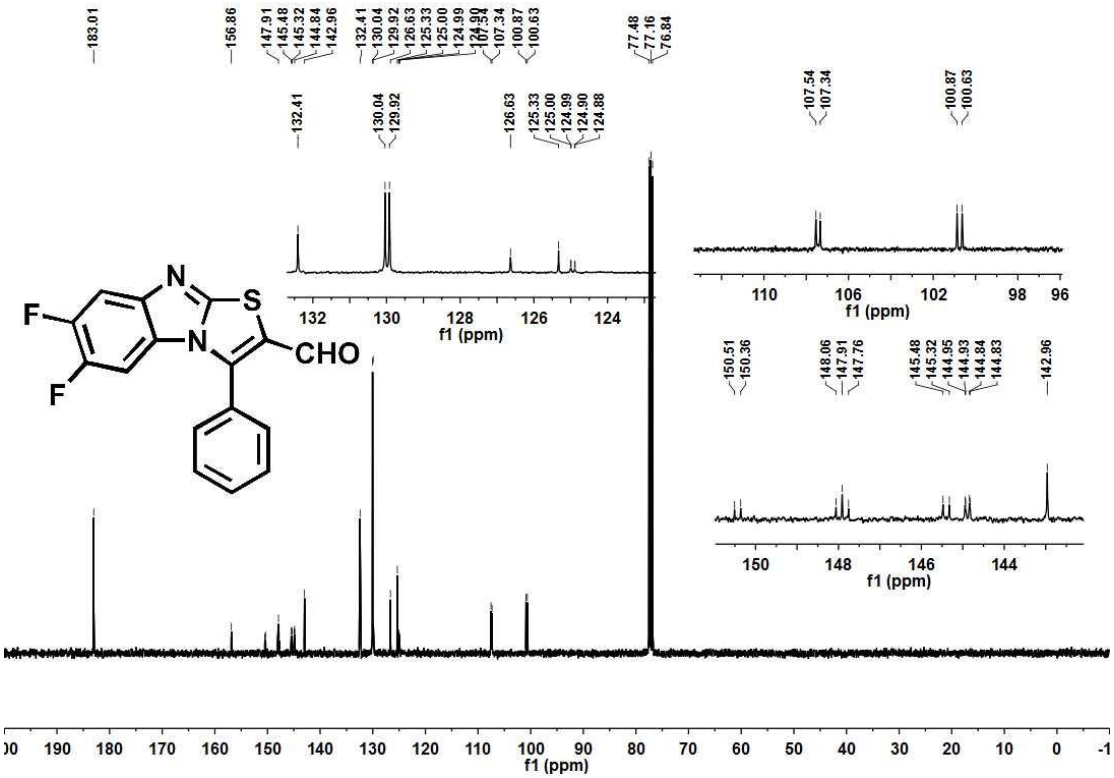
^{13}C NMR of product 3p and 3p' in $CDCl_3$ (100 MHz)



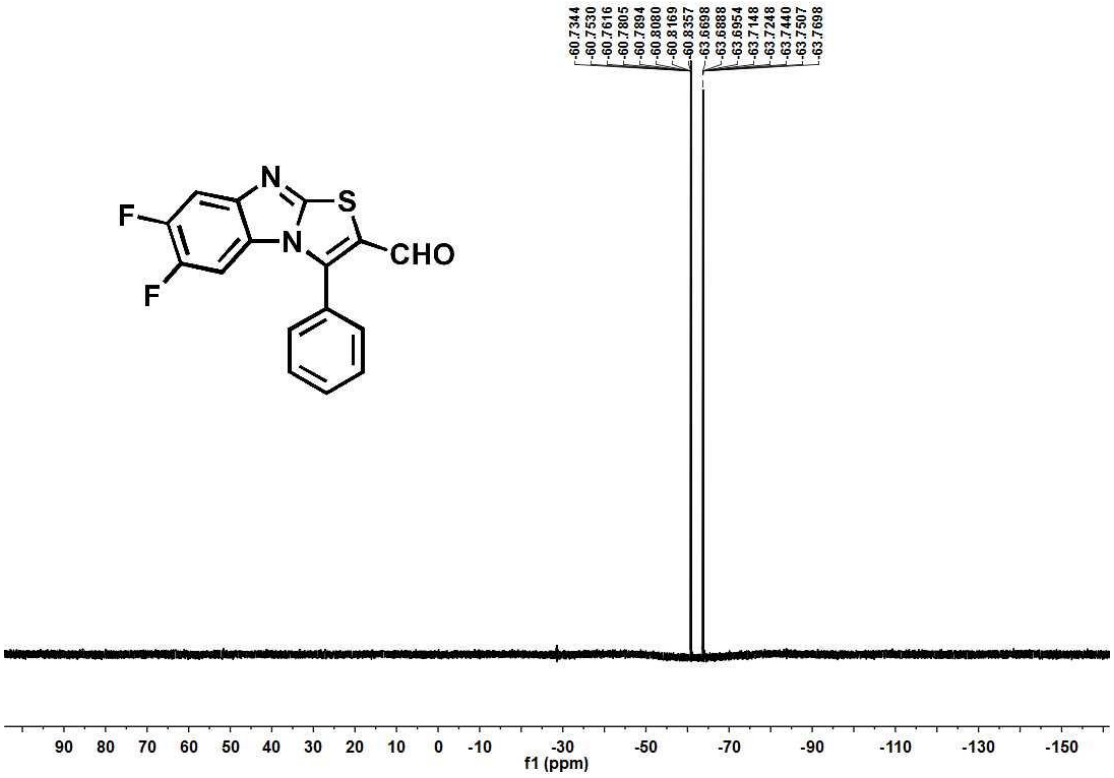
^{1}H NMR of product 3q in $CDCl_3$ (400 MHz)



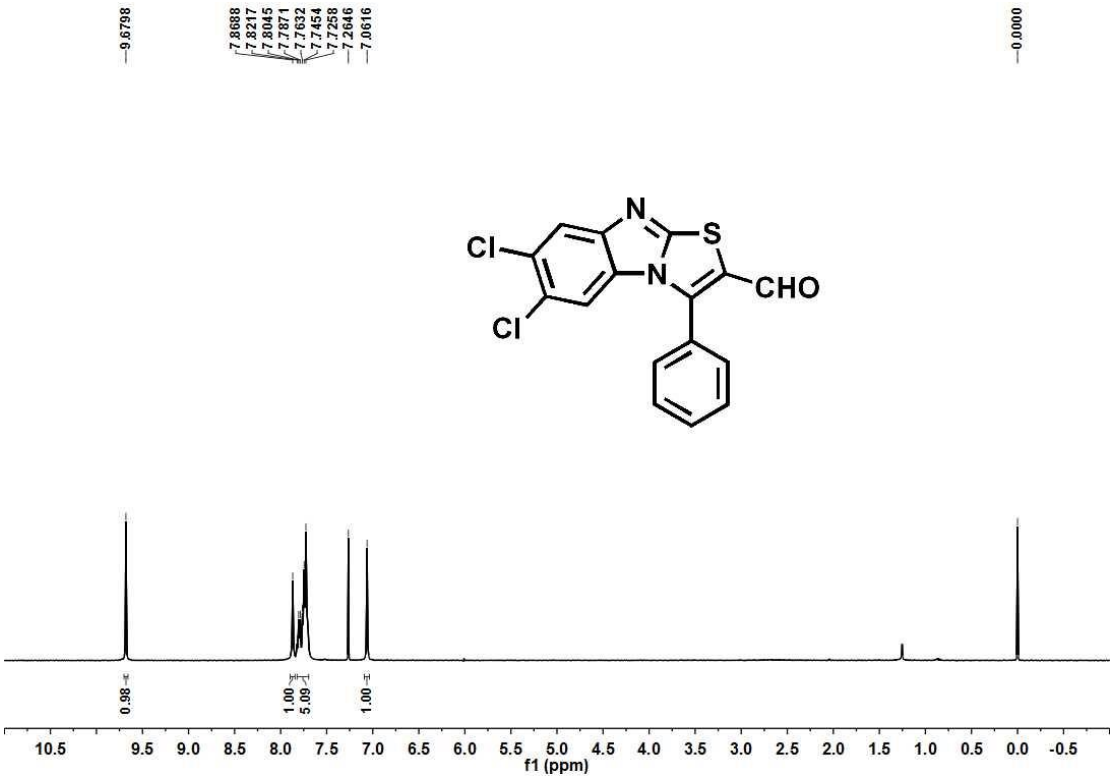
^{13}C NMR of product 3q in $CDCl_3$ (100 MHz)



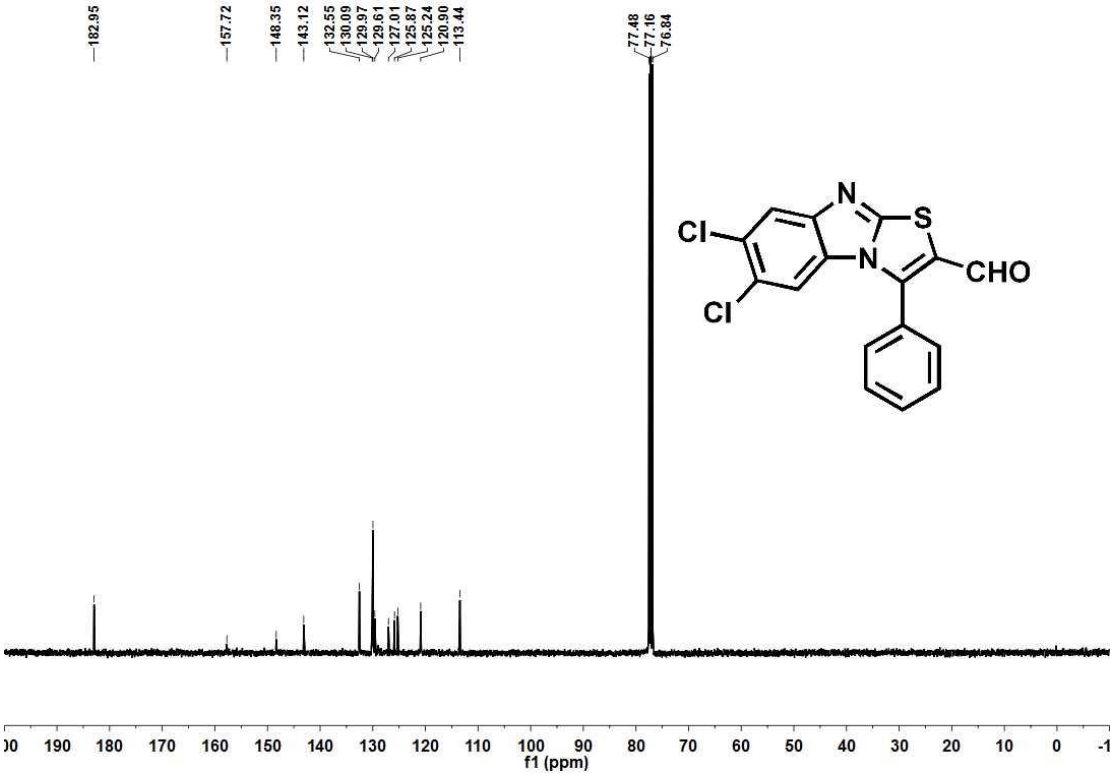
^{19}F NMR of product 3q in $CDCl_3$ (376 MHz)



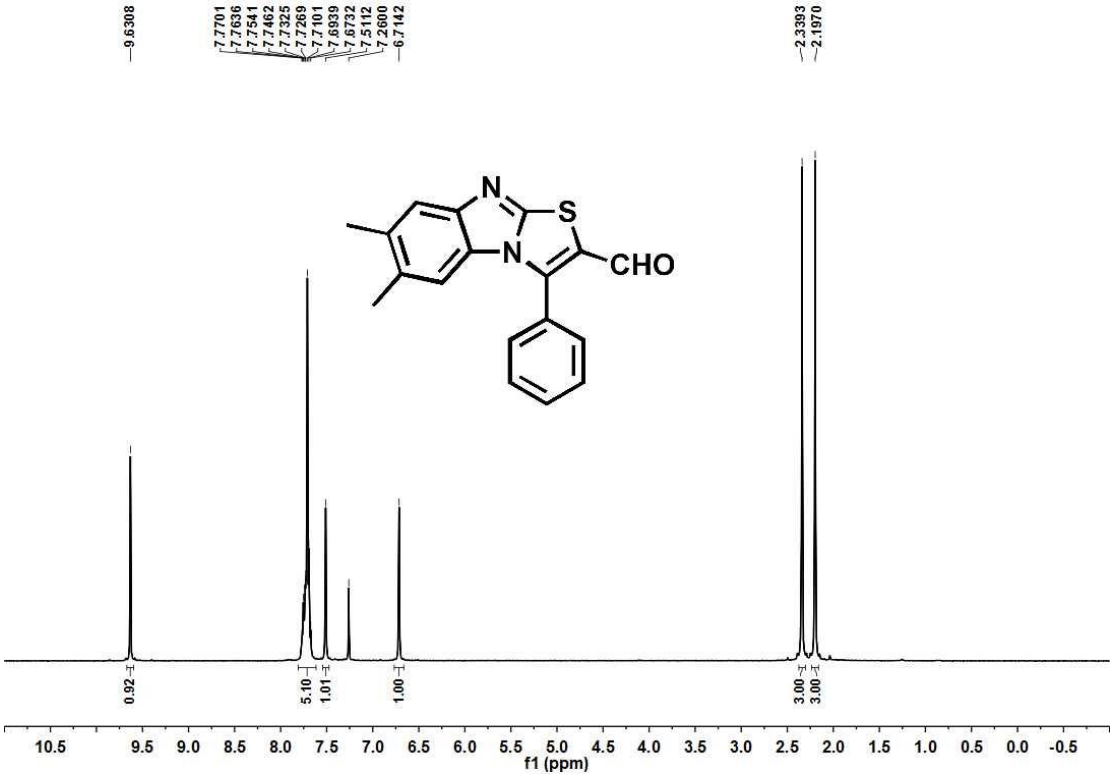
^{1}H NMR of product 3r in $CDCl_3$ (400 MHz)



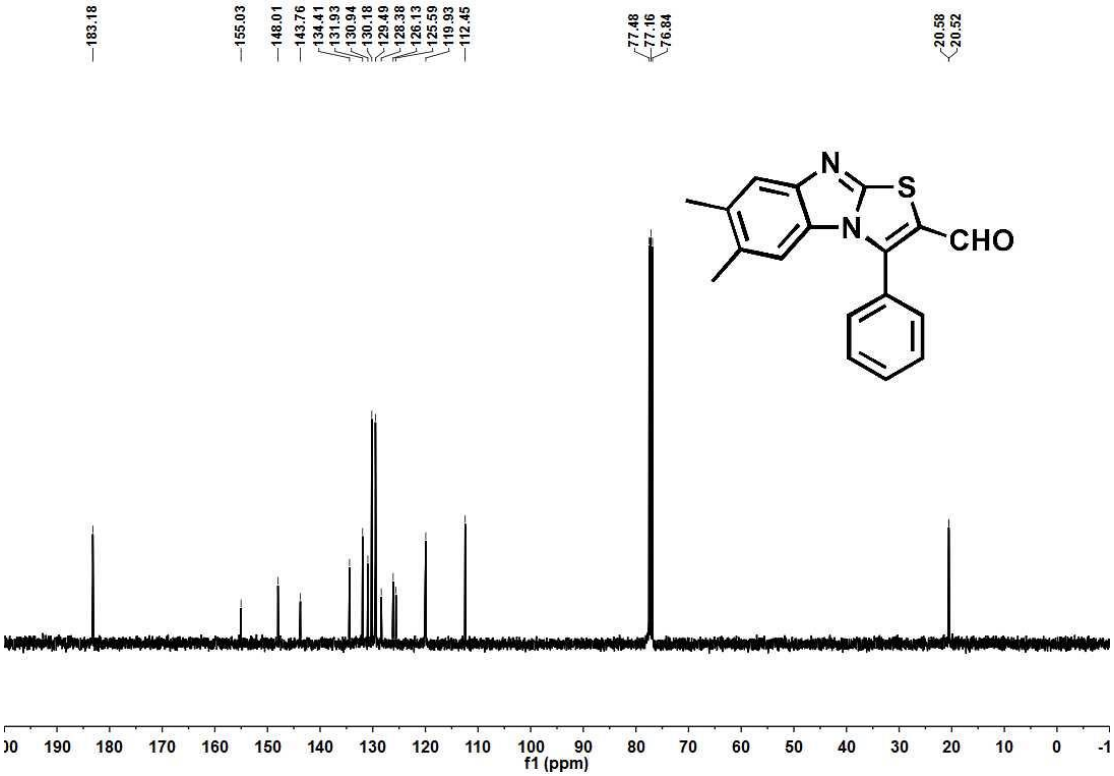
^{13}C NMR of product 3r in $CDCl_3$ (100 MHz)



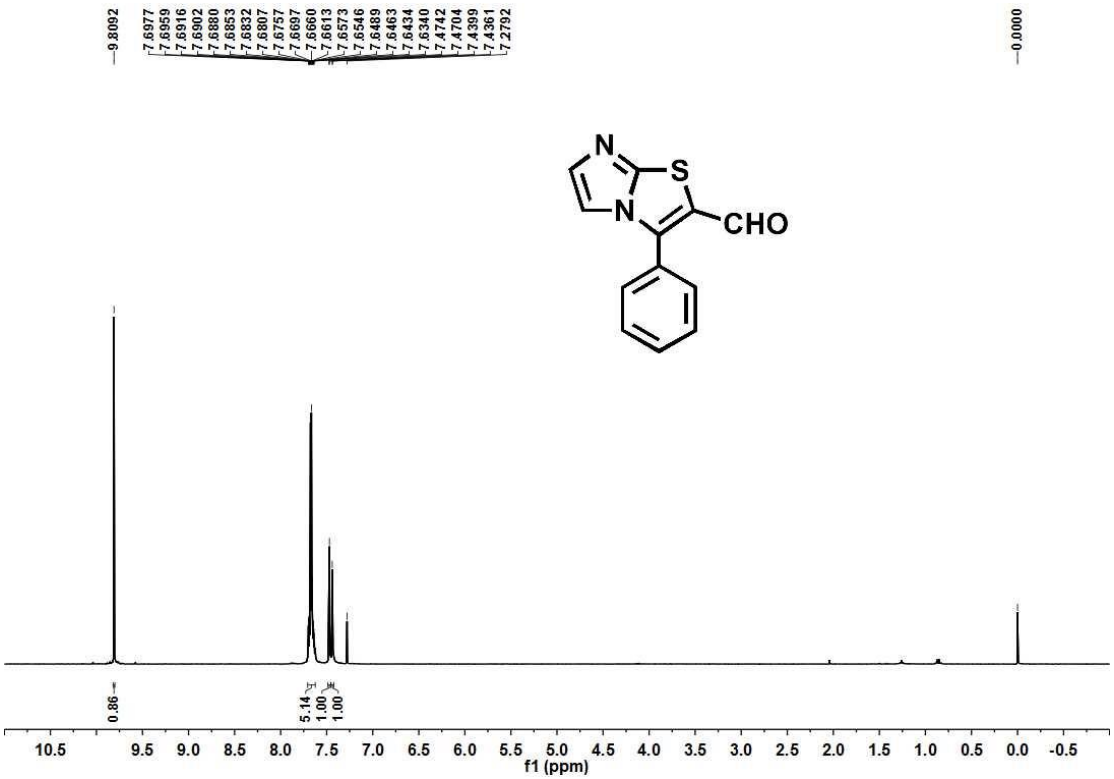
^{1}H NMR of product 3s in $CDCl_3$ (400 MHz)



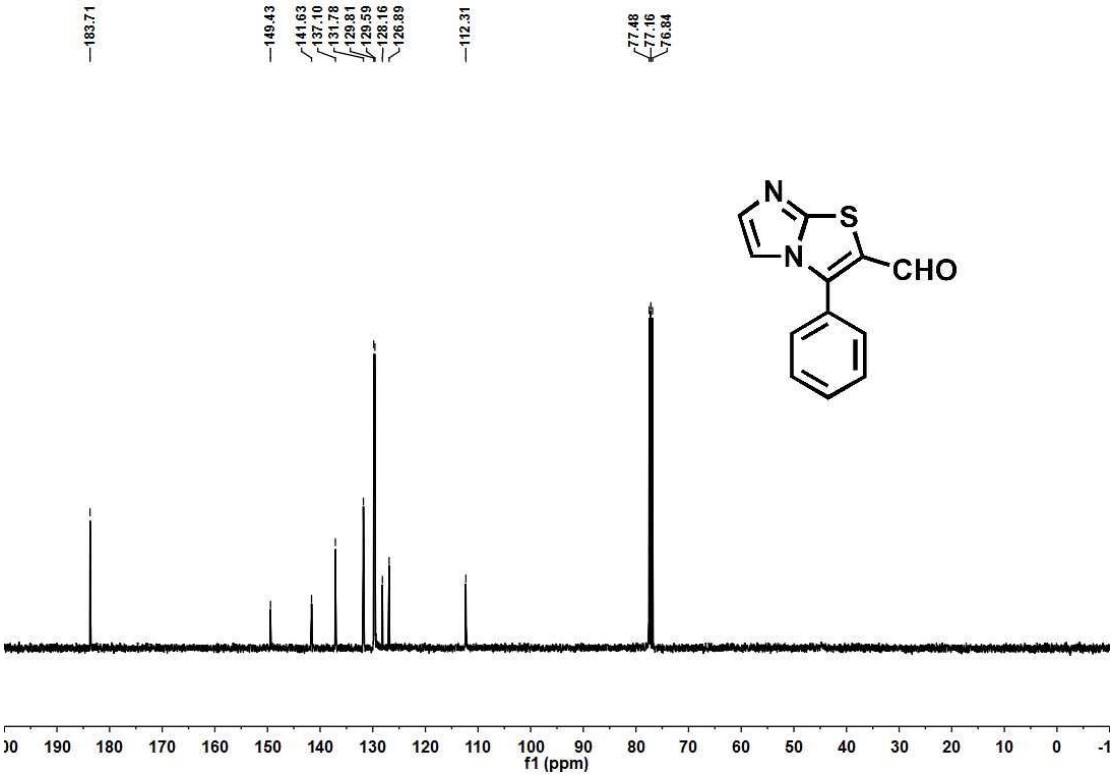
^{13}C NMR of product 3s in $CDCl_3$ (100 MHz)



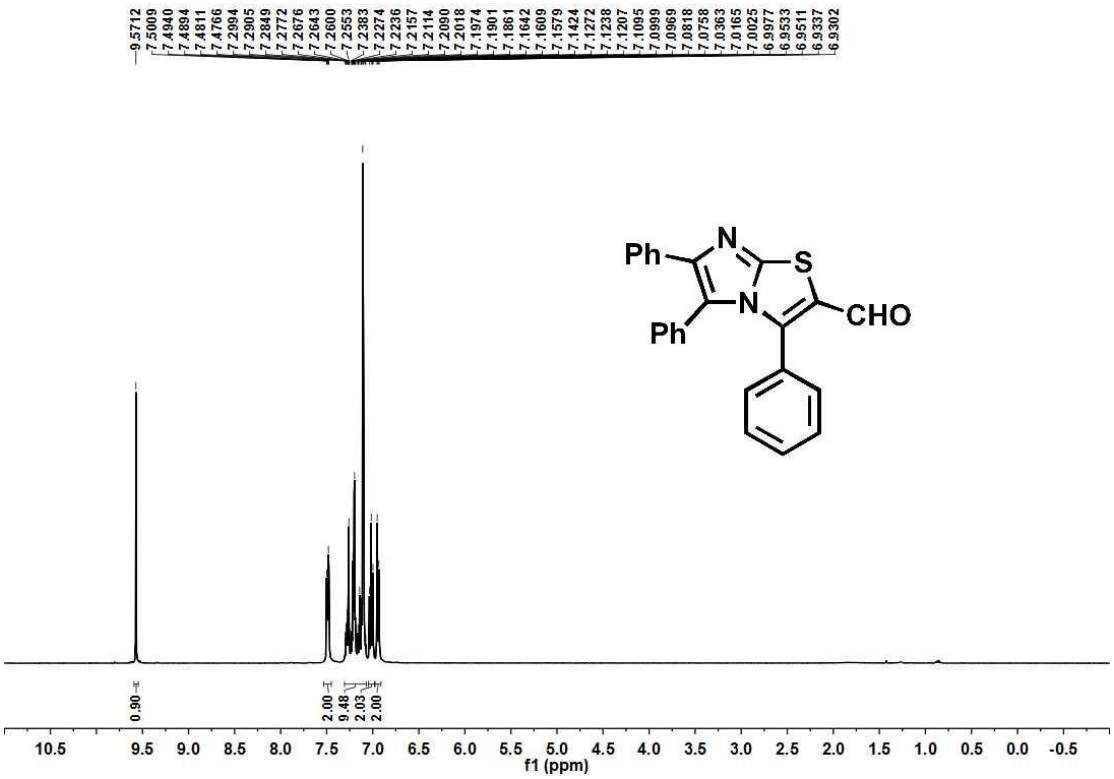
^{1}H NMR of product 3t in $CDCl_3$ (400 MHz)



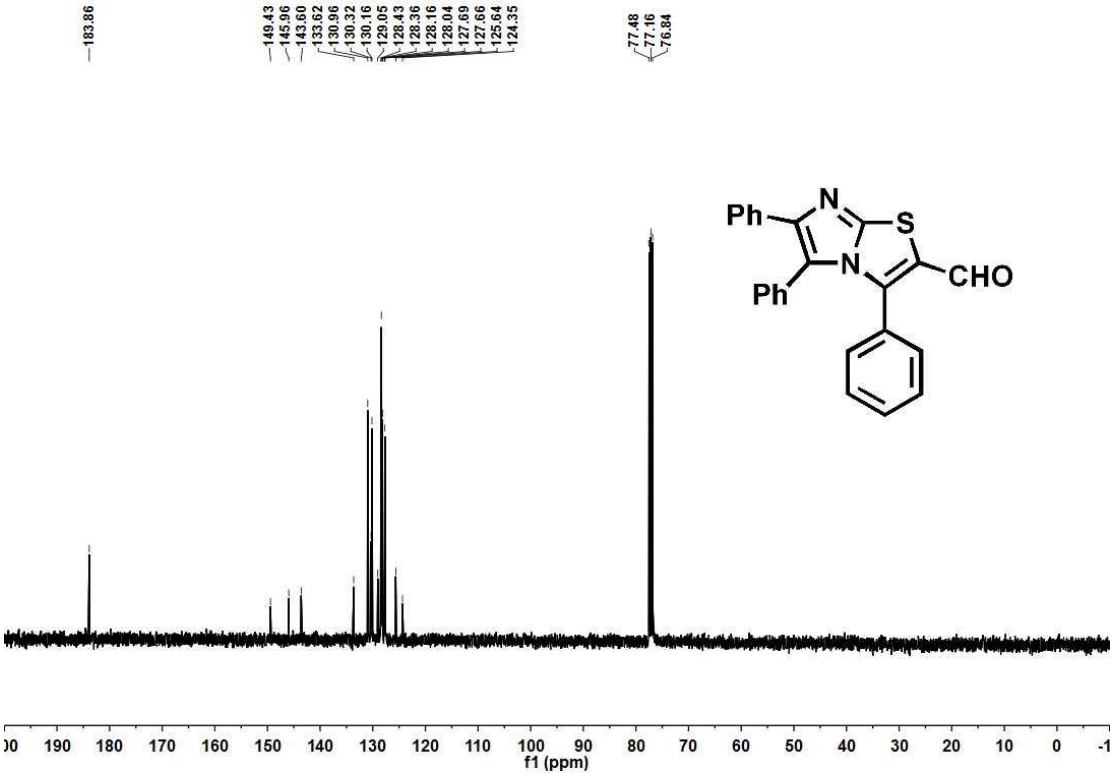
^{13}C NMR of product 3t in $CDCl_3$ (100 MHz)



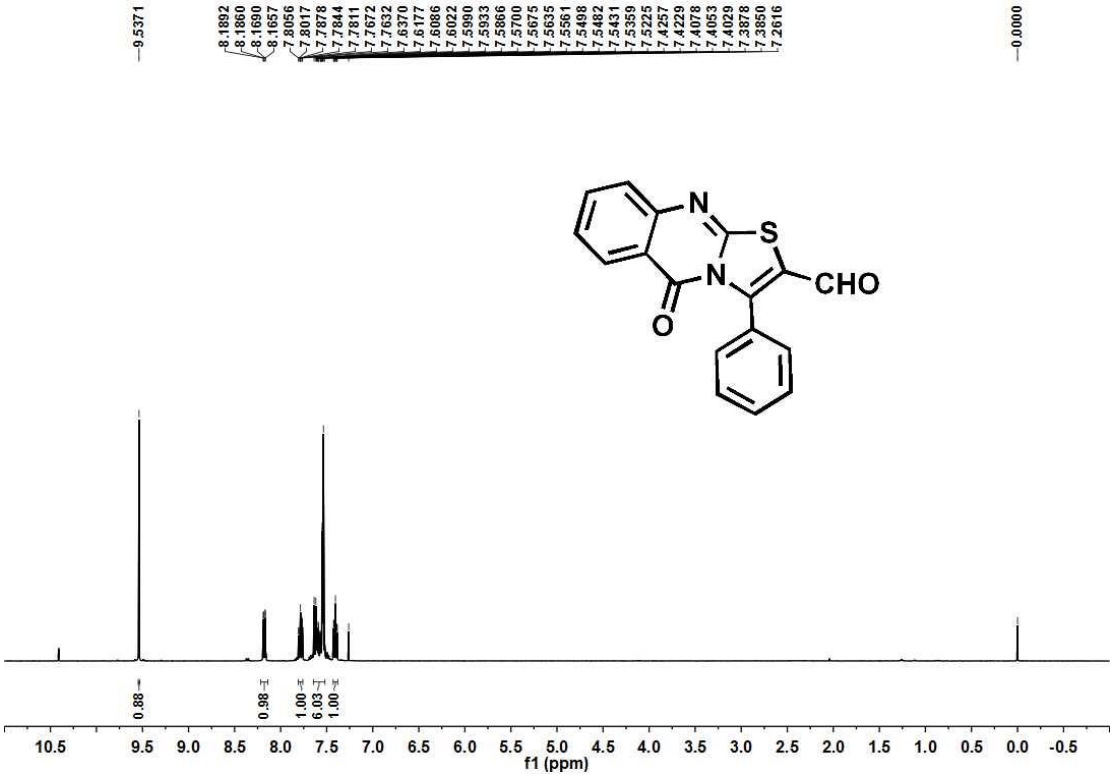
^{1}H NMR of product 3u in $CDCl_3$ (400 MHz)



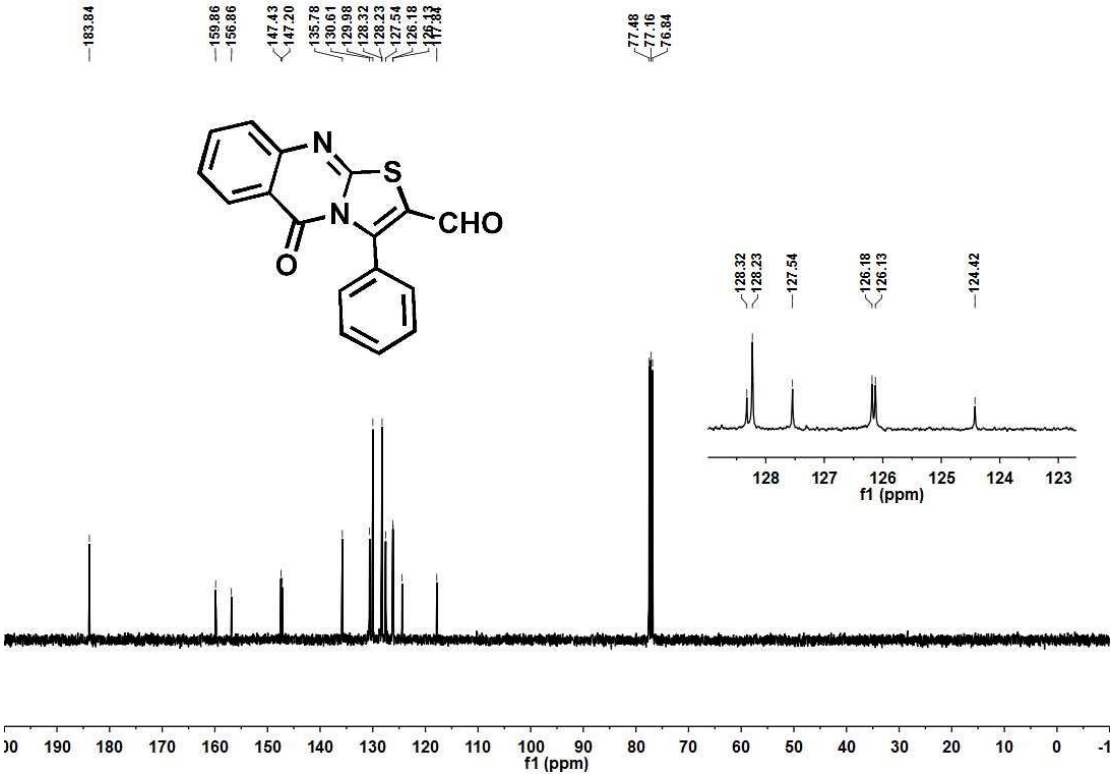
^{13}C NMR of product 3u in $CDCl_3$ (100 MHz)



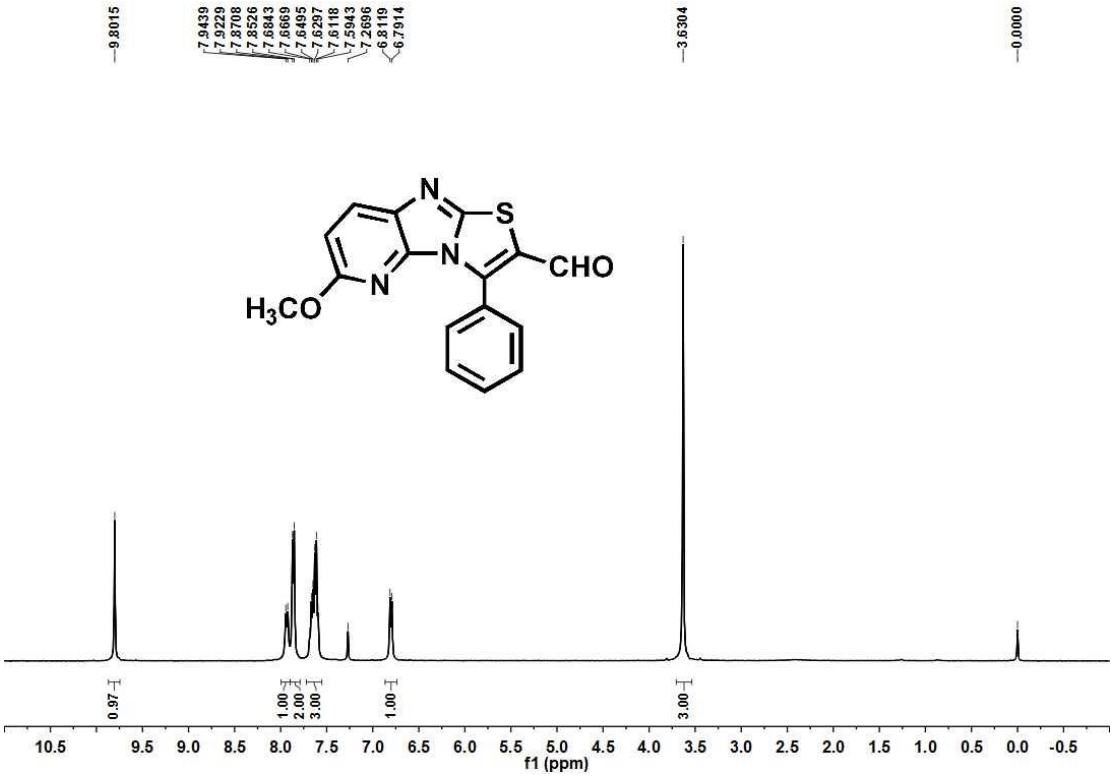
^{1}H NMR of product 3v in $CDCl_3$ (400 MHz)



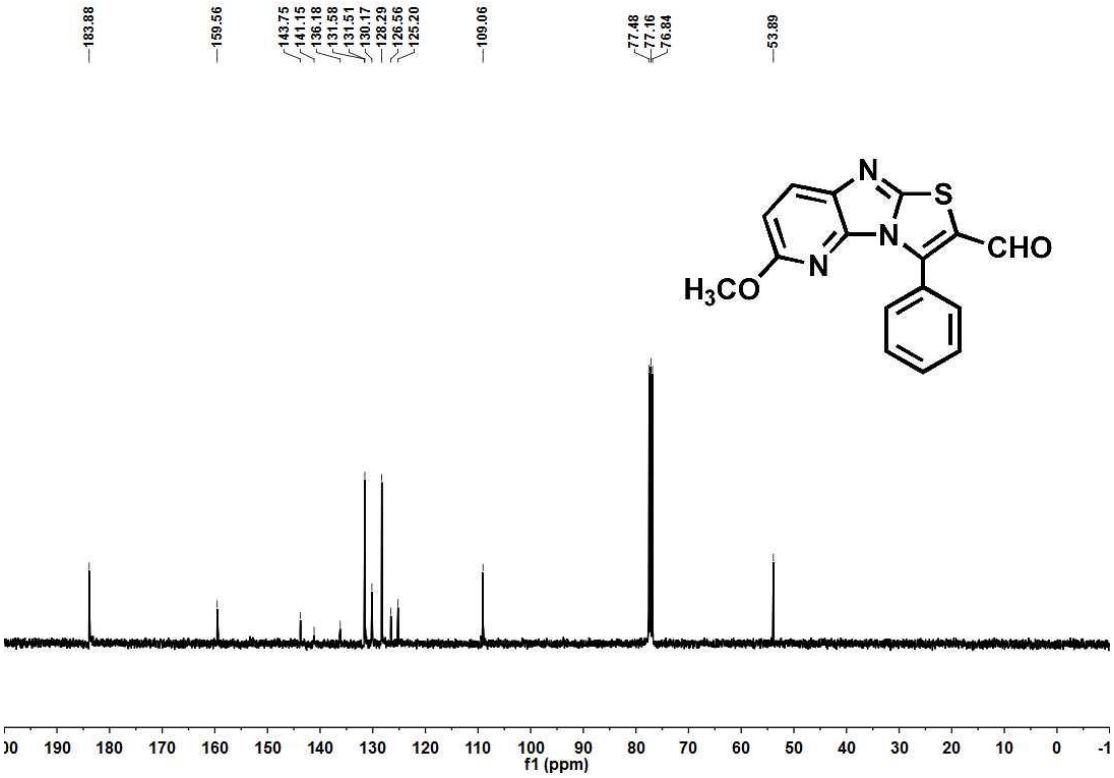
^{13}C NMR of product 3v in $CDCl_3$ (100 MHz)



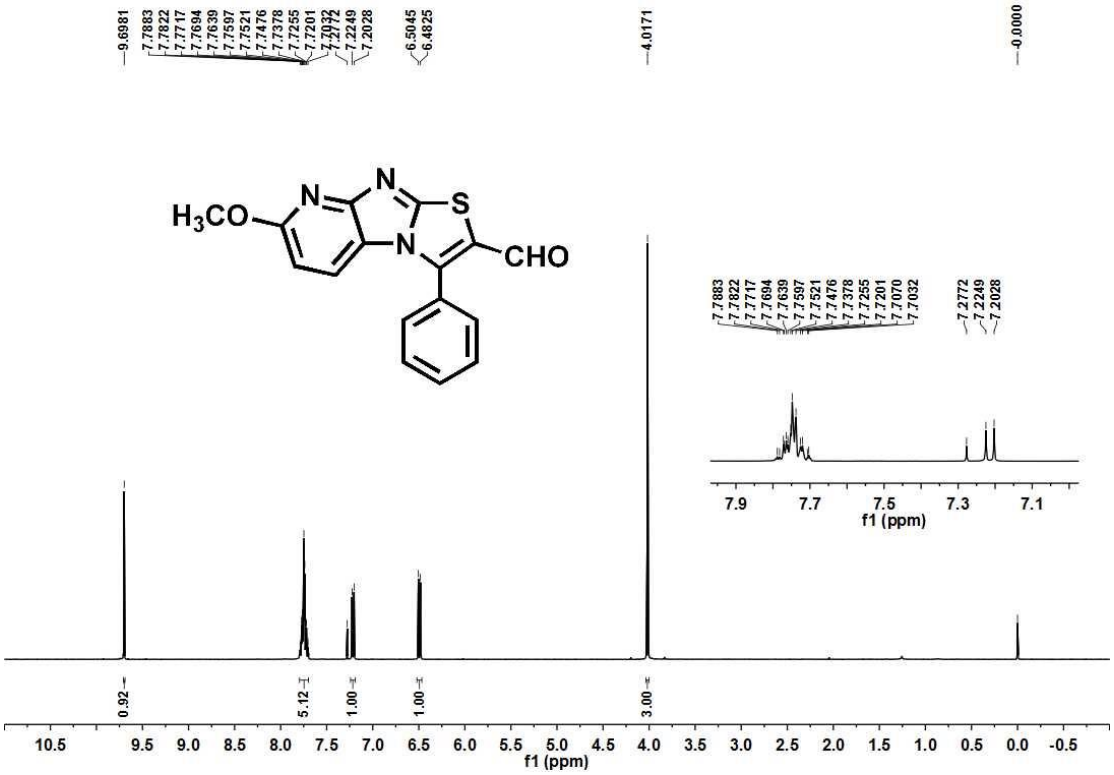
^{1}H NMR of product 3w in $CDCl_3$ (400 MHz)



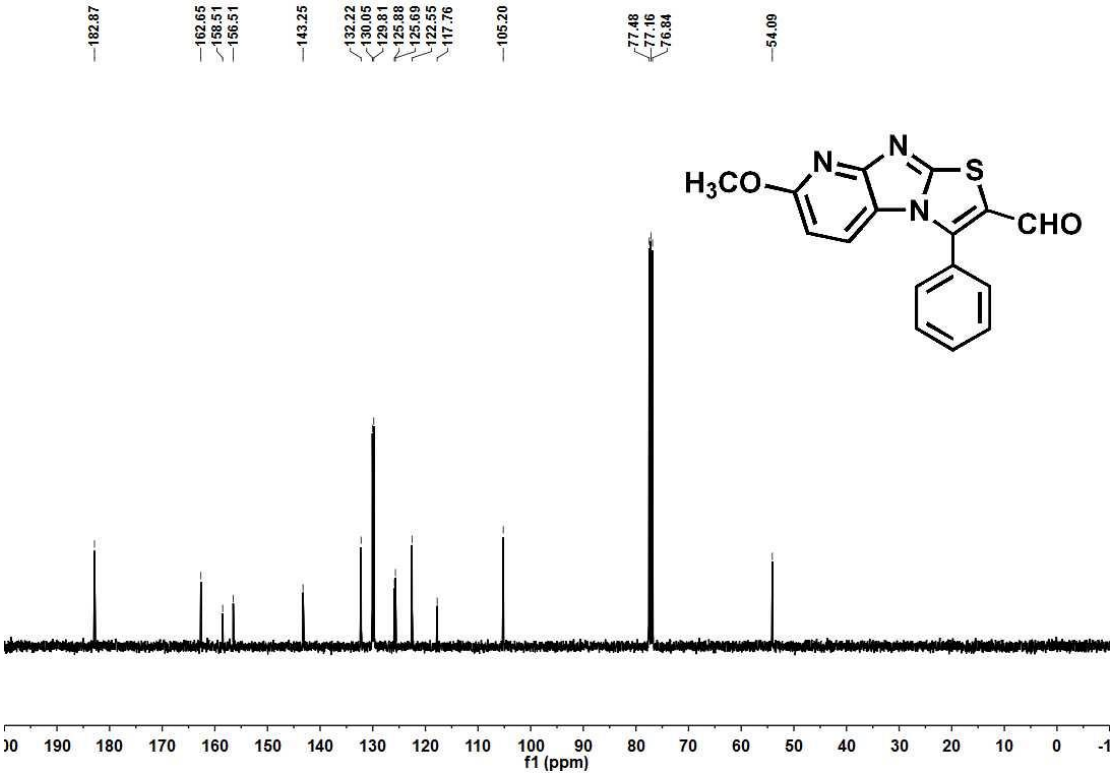
^{13}C NMR of product 3w in $CDCl_3$ (100 MHz)



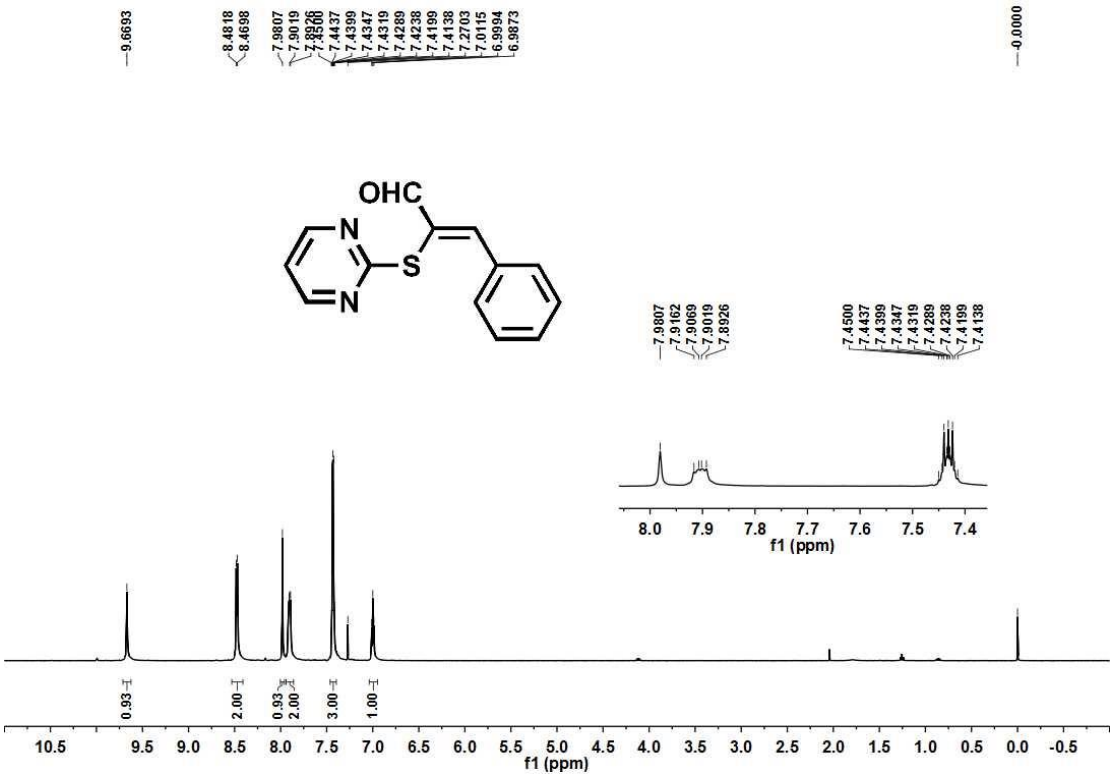
^{1}H NMR of product 3w' in $CDCl_3$ (400 MHz)



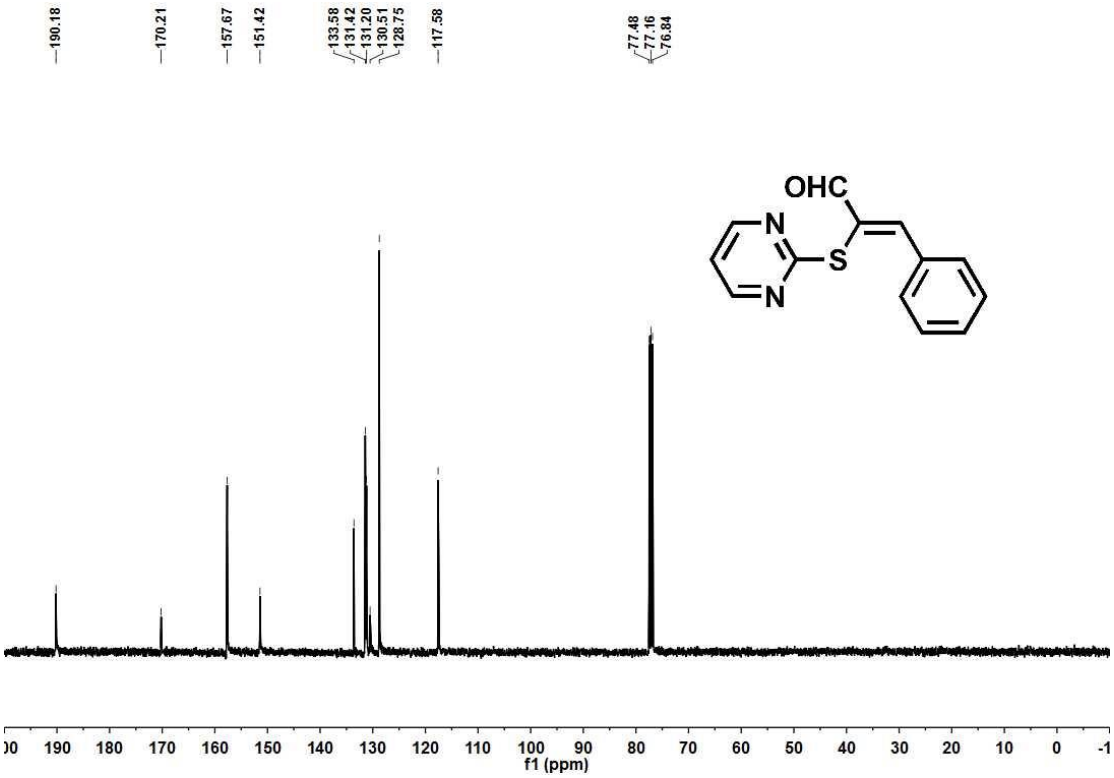
^{13}C NMR of product 3w' in $CDCl_3$ (100 MHz)



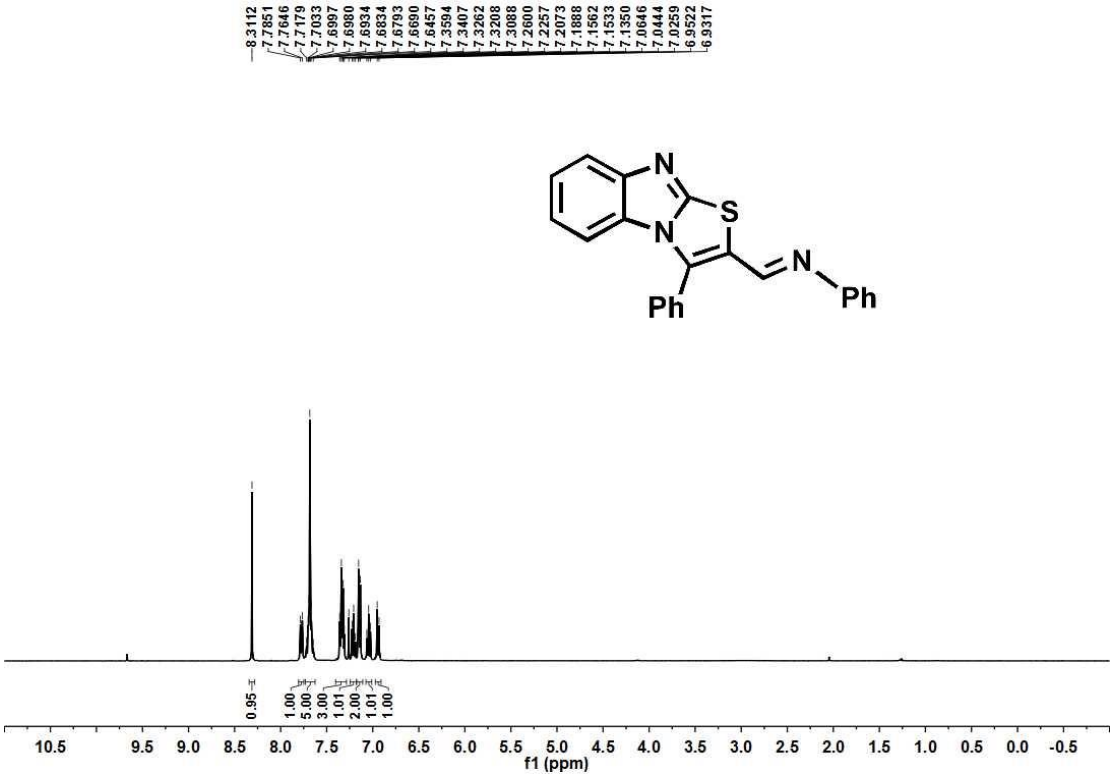
^{1}H NMR of product 3x in $CDCl_3$ (400 MHz)



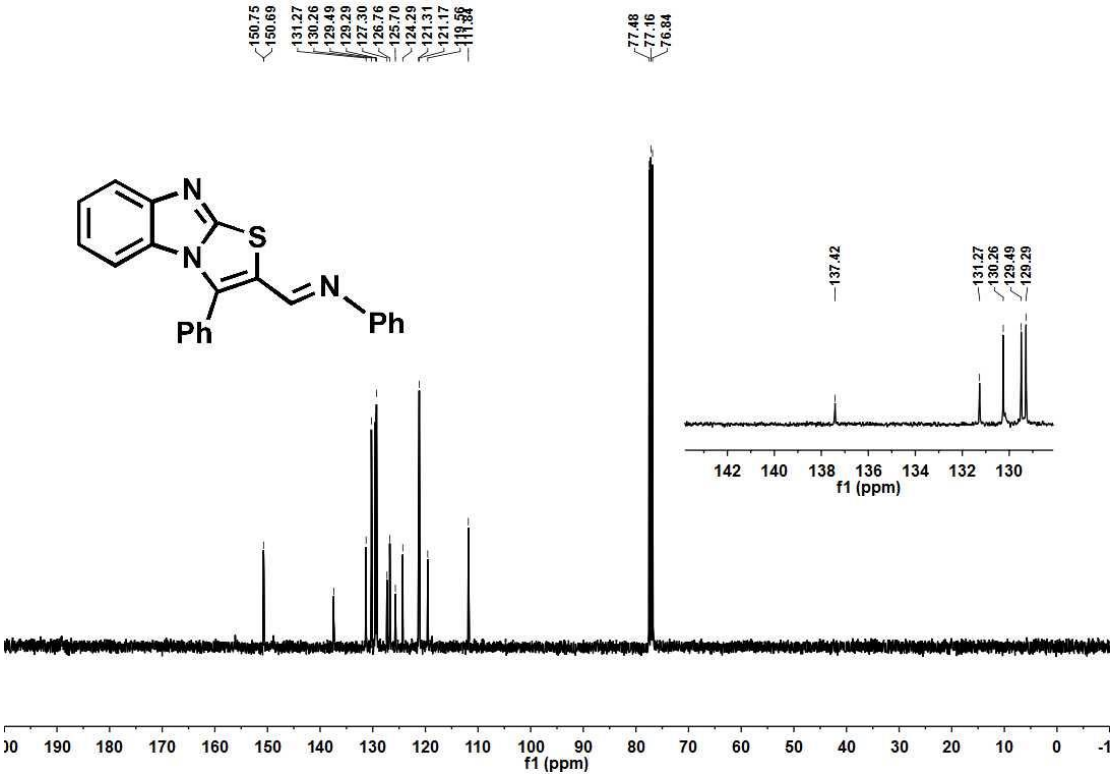
^{13}C NMR of product 3x in $CDCl_3$ (100 MHz)



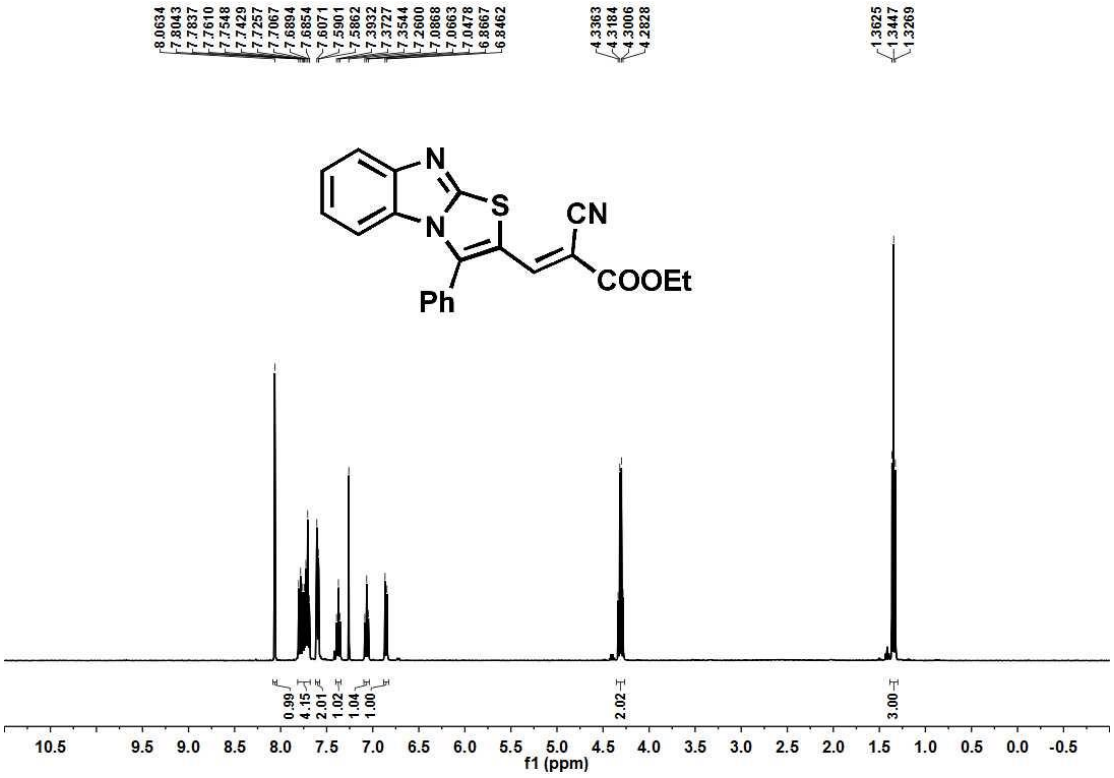
^{1}H NMR of product 3aa in $CDCl_3$ (400 MHz)



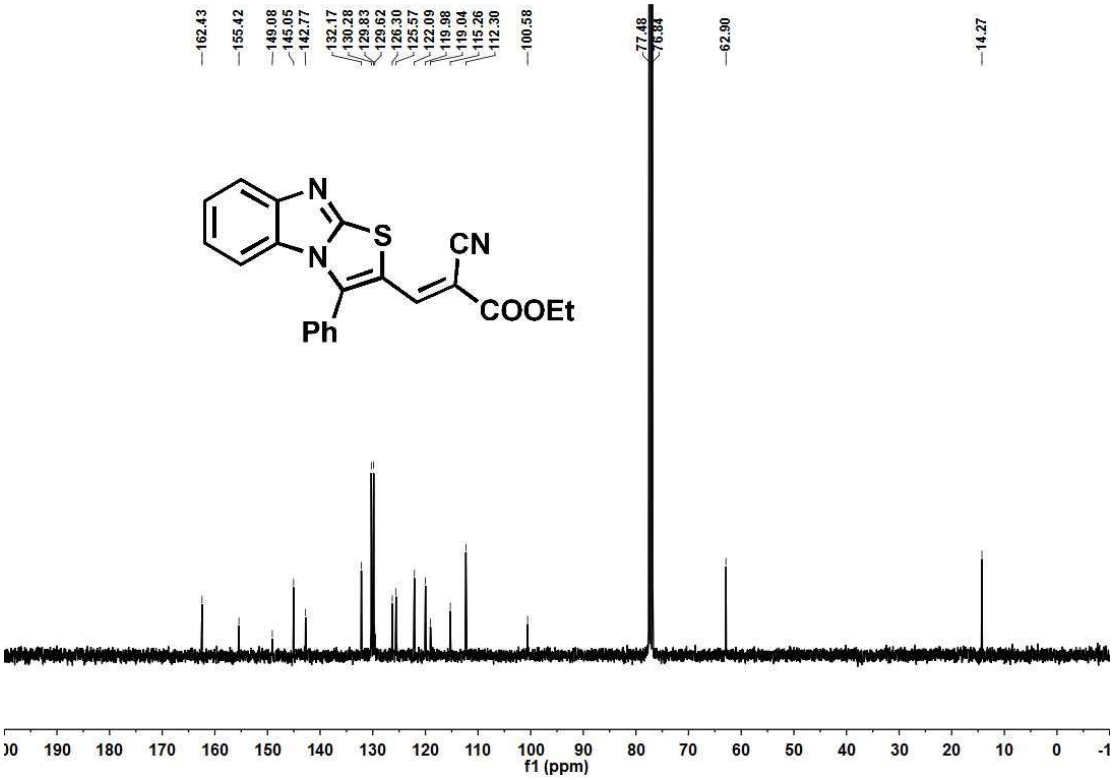
^{13}C NMR of product 3aa in $CDCl_3$ (100 MHz)



^{1}H NMR of product 3ab in $CDCl_3$ (400 MHz)



^{13}C NMR of product 3ab in $CDCl_3$ (100 MHz)



8. X-Ray crystallography data of 3a, 3o, 3v, 3w and 3x

The suitable crystals were selected on a **XtaLAB Synergy**, **Dualflex**, **HyPix** diffractometer. The crystals were kept at 100.03(10) K during data collection. Using Olex2[1], the structures were solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

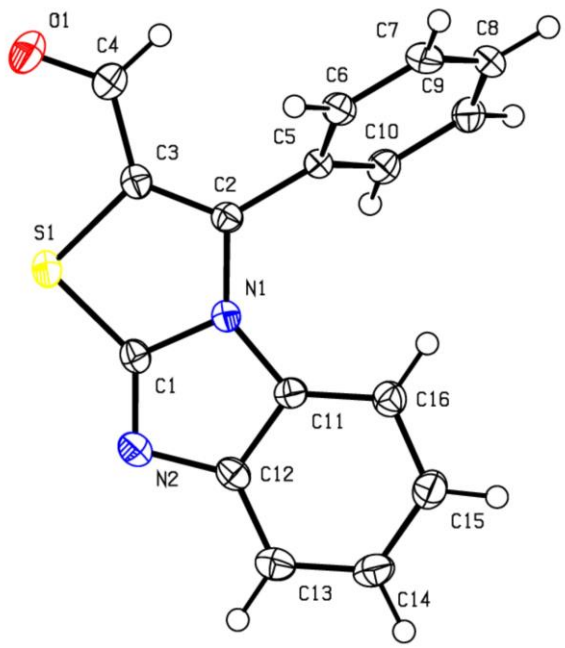
[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Single-crystals suitable for X-ray diffraction analysis were grown from the recrystallization in chloroform and petroleum ether (1/1, v/v) at 25 ^{o}C. Thermal ellipsoids of the crystal structures of 3a, 3o, 3v, 3w and 3x was set at 50%.

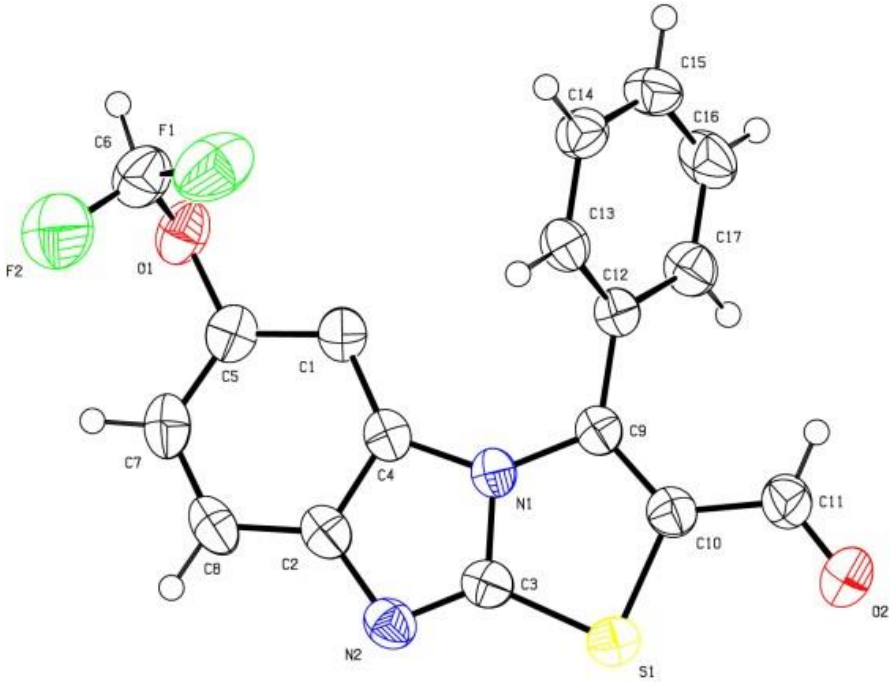
8.1 X-Ray crystallography data of 3a (CCDC 2000586)



Identification code	CCDC 2000586
Empirical formula	$C_{16}H_{11}N_2OS$
Formula weight	279.33
Temperature	150.0 K

Wavelength	0.71076 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5014(5) Å	α = 77.458(3)°.
	b = 10.8939(7) Å	β = 85.285(3)°.
	c = 17.7605(10) Å	γ = 80.774(3)°.
Volume	1396.73(15) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	0.228 mm^{-1}	
F(000)	580	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.352 to 26.022°.	
Index ranges	-9<=h<=9, -13<=k<=13, -21<=l<=21	
Reflections collected	26128	
Independent reflections	5490 [R(int) = 0.0661]	
Completeness to theta = 25.243°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.7454 and 0.6794	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5490 / 0 / 361	
Goodness-of-fit on F^2	1.885	
Final R indices [I>2sigma(I)]	R1 = 0.1347, wR2 = 0.4130	
R indices (all data)	R1 = 0.1663, wR2 = 0.4447	
Extinction coefficient	n/a	
Largest diff. peak and hole	5.000 and -0.691 e.$Å^{-3}$	

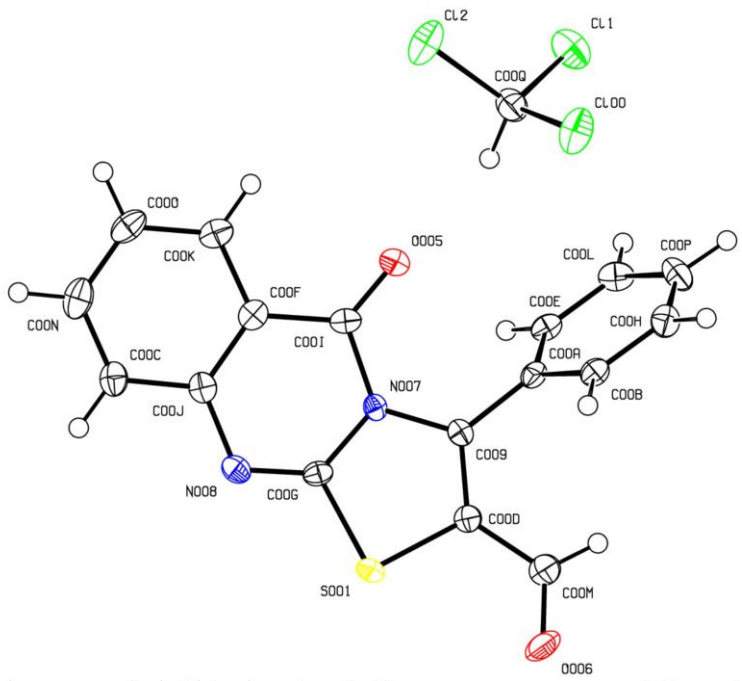
8.2 X-Ray crystallography data of 3o (CCDC 2000587)



Identification code	CCDC 2000587	
Empirical formula	$C_{17}H_9F_2N_2O_2S$	
Formula weight	343.32	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.311(6) Å	α = 90°.
	b = 7.438(5) Å	β = 90.0010(10)°.
	c = 21.236(13) Å	γ = 90°.
Volume	1470.7(16) $Å^3$	
Z	4	
Density (calculated)	1.551 Mg/m^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	700	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	0.959 to 27.800°.	
Index ranges	-11<=h<=11, -9<=k<=5, -27<=l<=26	
Reflections collected	8035	

Independent reflections	3272 [R(int) = 0.0715]
Completeness to theta = 25.242°	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4710
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3272 / 0 / 218
Goodness-of-fit on F^2	0.980
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1547
R indices (all data)	R1 = 0.0938, wR2 = 0.1730
Extinction coefficient	n/a
Largest diff. peak and hole	0.395 and -0.347 e.$Å^{-3}$

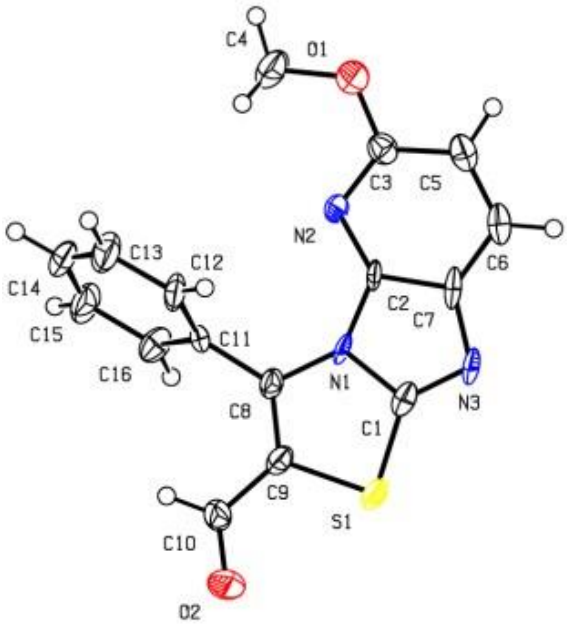
8.3 X-Ray crystallography data of 3v (CCDC 2000589)



Identification code	CCDC 2000589
Empirical formula	$C_{18}H_{11}Cl_3N_2O_2S$
Formula weight	425.70
Temperature/K	150.02
Crystal system	monoclinic
Space group	P21/c
a/Å	7.8666(15)

b/Å	19.734(4)
c/Å	11.832(2)
α/°	90
β/°	102.683(7)
γ/°	90
Volume/Å3	1791.9(6)
Z	4
ρcalcg/cm3	1.578
μ/mm-1	0.644
F(000)	864.0
Crystal size/mm3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.308 to 52.042
Index ranges	-8 ≤ h ≤ 9, -24 ≤ k ≤ 24, -14 ≤ l ≤ 14
Reflections collected	16228
Independent reflections	3417 [Rint = 0.0849, Rsigma = 0.0638]
Data/restraints/parameters	3417/0/235
Goodness-of-fit on F2	1.120
Final R indexes [I>=2σ (I)]	R1 = 0.0807, wR2 = 0.2108
Final R indexes [all data]	R1 = 0.1052, wR2 = 0.2232
Largest diff. peak/hole / e Å-3	0.86/-0.66

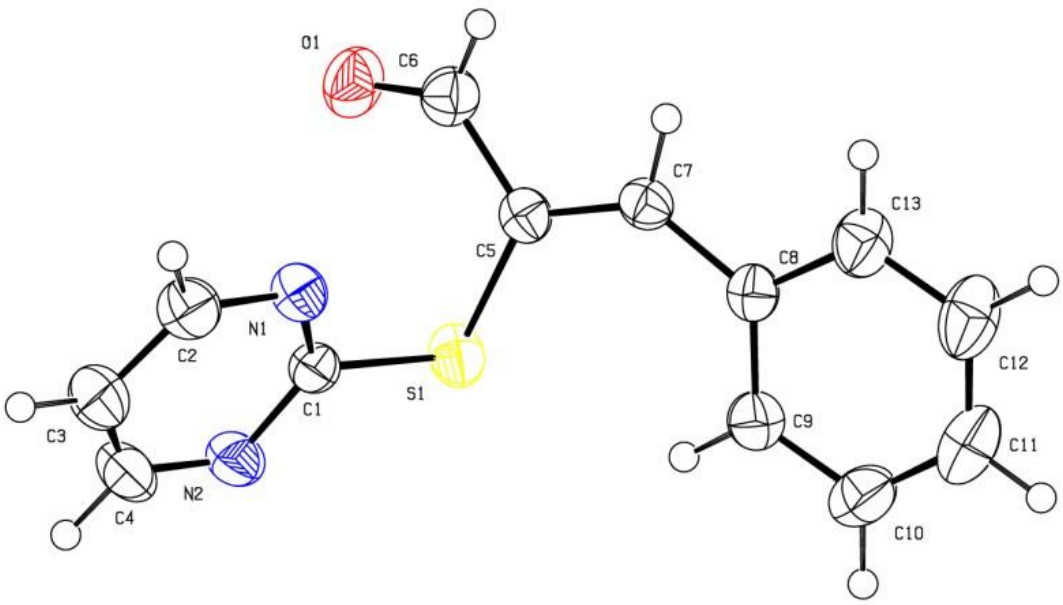
8.4 X-Ray crystallography data of 3w (CCDC 2000591)



Identification code	CCDC 2000591	
Empirical formula	$C_{16}H_{11}N_3O_2S$	
Formula weight	309.34	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.931(7) Å	α = 77.926(12)°.
	b = 9.750(10) Å	β = 86.891(13)°.
	c = 21.38(2) Å	γ = 82.136(13)°.
Volume	1399(2) $Å^3$	
Z	4	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	0.242 mm^{-1}	
F(000)	640	
Crystal size	? x ? x ? mm^3	

Theta range for data collection	0.974 to 24.998°.
Index ranges	-8<=h<=8, -11<=k<=11, -10<=l<=25
Reflections collected	4876
Independent reflections	4876 [R(int) = ?]
Completeness to theta = 24.998°	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5475
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4876 / 0 / 400
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.1104, wR2 = 0.2852
R indices (all data)	R1 = 0.1381, wR2 = 0.3006
Extinction coefficient	n/a
Largest diff. peak and hole	0.710 and -0.707 e.$Å^{-3}$

8.5 X-Ray crystallography data of 3x (CCDC 2000590)



Identification code	CCDC 2000590
Empirical formula	$C_{13}H_{10}N_2OS$
Formula weight	242.29
Temperature	100.15 K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.498(4) Å	α = 90°.
	b = 8.270(2) Å	β = 90.787(4)°.
	c = 10.268(3) Å	γ = 90°.
Volume	1146.1(6) $Å^3$	
Z	4	
Density (calculated)	1.404 Mg/m^3	
Absorption coefficient	0.265 mm^{-1}	
F(000)	504	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.889 to 27.687°.	
Index ranges	-17<=h<=15, -10<=k<=10, -13<=l<=13	
Reflections collected	6759	
Independent reflections	2615 [R(int) = 0.0342]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5310	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2615 / 0 / 154	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.1008	
R indices (all data)	R1 = 0.0478, wR2 = 0.1065	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.320 and -0.295 $e.Å^{-3}$	