Supporting Information

A portal to a class of novel sultones functionalized pyridines *via* an annulative SuFEx process employing earth abundant Nickel catalyst

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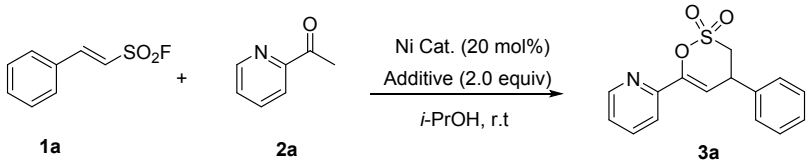
1. General Considerations

All reactions were carried out under an air atmosphere. Unless otherwise specified, NMR spectra are recorded in $CDCl_3$ on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), or 126 MHz (for ^{13}C) spectrometer. All chemical shifts are reported in ppm relative to TMS (^1H NMR, 0 ppm) as an internal standard. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The coupling constants are reported in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, Melting points were measured and uncorrected. MS experiments were performed on a TOF-Q ESI or CI/EI instrument. Reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Optimization of the Reaction Conditions.

Table 1 Screening of Ni Catalyst and additive[a]

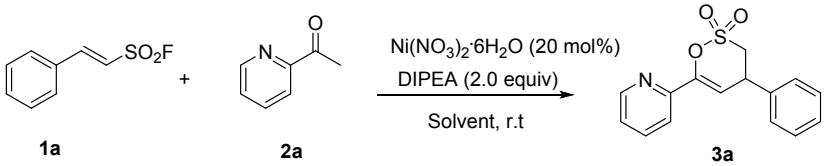


1a 2a 3a

Entry	Catalyst	Additive	Yield (**3a**, %)[b]
1	$Ni(acac)_2$	$NaHCO_3$	35
2	$NiBr_2$	$NaHCO_3$	16
3	$Ni(OAc)_2$ $4H_2O$	$NaHCO_3$	N.A
4	$NiCl_2$	$NaHCO_3$	16
5	NiI_2	$NaHCO_3$	7
6	$Ni(NO_3)_2{\cdot}6H_2O$	$NaHCO_3$	40
7	$Ni(OTf)_2$	$NaHCO_3$	14
8	$Ni(NO_3)_2{\cdot}6H_2O$	DBU	36
9	**$Ni(NO_3)_2{\cdot}6H_2O$**	**DIPEA**	**55**
10	$Ni(NO_3)_2{\cdot}6H_2O$	Cs_2CO_3	35

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine (**2a**, 0.2 mmol, 2.0 equiv), catalyst (20 mol%), additive (0.2 mmol, 2.0 equiv), *i*-PrOH (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 2 Screening of Solvent[a]



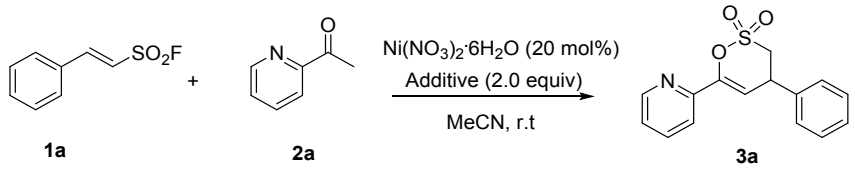
1a 2a 3a

Entry	Solvent	Yield (**3a**, %)[b]

1	DCM	40
2	THF	30
3	**MeCN**	**69**
4	Acetone	29
5	DMF	27
6	DMSO	65
7	*i*-PrOH	55
8	*t*-BuOH	56

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine (**2a**, 0.2 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (20 mol%), DIPEA (0.2 mmol, 2.0 equiv), solvent (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 3 Screening of Additive[a]



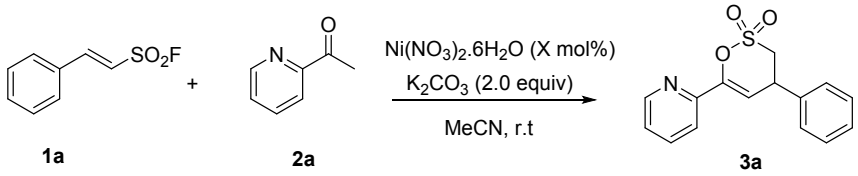
1a **2a** **3a**

Entry	Additive	Yield (**3a**, %)[b]
1	$NaHCO_3$	48
2	$KHCO_3$	47
3	Na_2CO_3	56
4	**K_2CO_3**	**91**
5	Cs_2CO_3	36
6	Na_3PO_4	68
7	K_3PO_4	84
8	K_2HPO_4	33
9	NaOAc	16
10	CH_3COOK	27
11	Et_3N	44
12	DBU	N.A
13	TMEDA	16

14	DABCO	<1
15	DIEA	69

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine (**2a**, 0.2 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (20 mol%), additive (0.2 mmol, 2.0 equiv), MeCN (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 4 Screening of Catalyst Loading[a]

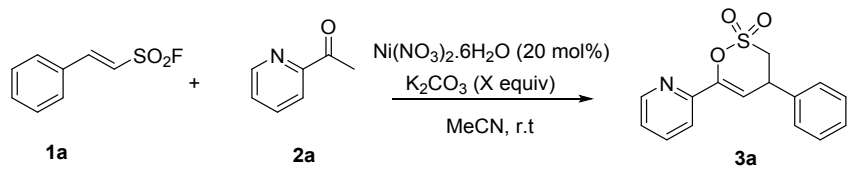


1a **2a** **3a**

Entry	Catalyst Loading (X mol%)	Yield (**3a**, %)[b]
1	/	7
2	1	50
3	5	69
4	10	77
5	**20**	**91**
6	50	92

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine (**2a**, 0.2 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (X mol%), K_2CO_3 (0.2 mmol, 2.0 equiv), MeCN (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 5 Screening of Additive Loading[a]

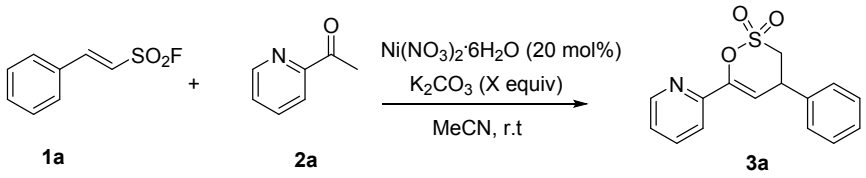


1a **2a** **3a**

Entry	Additive Loading (X equiv)	Yield (**3a**, %)[b]
1	/	21
2	0.5	52
3	1.0	55
4	1.5	77
5	**2.0**	**91**

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine (**2a**, 0.2 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (20 mol%), K_2CO_3 (X mmol, X equiv), MeCN (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 6 Screening the Ratio of Reactants[a]

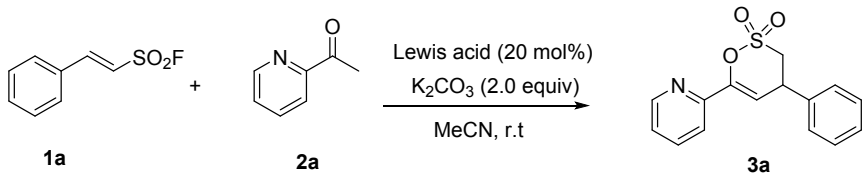


1a **2a** **3a**

Entry	Ratio (**1a**: **2a**)	Yield (**3a**, %)[b]
1	1 : 1	74
2	1 : 1.5	85
3	**1 : 2**	**91**

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine **2a**, $Ni(NO_3)_2{\cdot}6H_2O$ (20 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv), MeCN (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

Table 7 Screening the different Lewis acid under the optimal conditions[a]



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

Entry	Lewis acid	Yield (**3a**, %)[b]
1	$Ni(acac)_2$	92
2	$NiBr_2$	56
3	$NiCl_2$	66
4	$Ni(NO_3)_2{\cdot}6H_2O$	91
5	$Ni(OTf)_2$	76
6	$Ni(OAc)_2\ 4H_2O$	24
7	$AlCl_3$	N.A
8	$ZnCl_2$	25
9	$FeCl_3$	N.A
10	$Cu(OTf)_2$	40
11	AgOTf	3
12	$Cu(NO_3)_2{\cdot}2.5H_2O$	17
13	$AgNO_3$	N.A
14	$Co(acac)_2$	48

[a]Reaction conditions: (*E*)-2-phenylethenesulfonyl fluoride (**1a**, 0.1 mmol), 2-acetyl pyridine **2a**, Lewis acid (20 mol%), K_2CO_3 (0.2 mmol, 2.0 equiv), MeCN (1 mL) were added to a round-bottle flask (25 mL) and reacted at room temperature for 24 h. [b]The yield was determined by HPLC using **3a** as the external standard (t_R = 12.2 min, λ_{max} = 246.5 nm, methanol / water = 60 : 40 (v / v)).

3. Procedures and Characterizations for the Syntheses of 3.

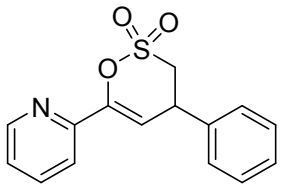
3.1 Preparation of Substrates

All the (hetero)arylethenesulfonyl fluorides **1** were prepared according to the literatures.[1, 2] The 2-acetyl azaarenes **2aa, 2ae, 2af, 2ah, 2ai** were purchased from commercial sources, **2ab, 2ac, 2ad, 2ag, 2aj** were prepared according to the literatures. [3, 4] All the homemade starting materials are identical to those reported regarding the ^1H and ^{13}C NMR and melting points (if applicable).

3.2 Procedures for Annulative SuFEx Reaction of 2-Acetyl Azaarenes with (Hetero)arylethenesulfonyl Fluorides

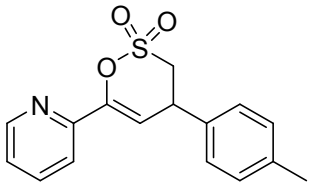
An oven-dried round-bottle flask (25 mL) was charged with (hetero)arylethenesulfonyl fluoride (**1**, 0.5 mmol), 2-acetyl azaarene (**2**, 1.0 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (29.1 mg, 20 mol%), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv), and MeCN (2 ml). The resulting mixture was stirred at room temperature under air atmosphere for 24-36 h with monitoring by TLC. The crude products were purified by column chromatography (Petroleum ether / ethyl acetate as eluent) on silica gel to give **3**.

3.3 Syntheses of 3



3a

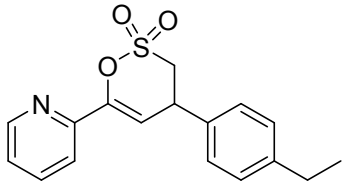
4-Phenyl-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3a**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 129 mg, 90% yield. Mp 112-114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.1 Hz, 1H), 7.78 (td, *J* = 7.8 Hz, *J* = 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 2H), 7.36-7.32 (m, 3H), 7.29 (dd, *J* = 6.7 Hz, *J* = 5.1 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 4.39 (ddd, *J* = 12.1 Hz, *J* = 6.3 Hz, *J* = 2.3 Hz, 1H), 3.69 (dd, *J* = 13.9 Hz, *J* = 6.2 Hz, 1H), 3.37 (dd, *J* = 13.6 Hz, *J* = 12.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.4, 149.2, 139.1, 137.1, 129.4, 128.3, 127.7, 124.1, 119.0, 108.1, 50.8, 41.2. ESI-MS HRMS calculated for $C_{15}H_{14}NO_3S$ $[M+H]^+$ 288.0689, found 288.0685.



3b

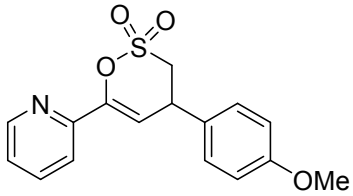
6-(Pyridin-2-yl)-4-(p-tolyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3b**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 146 mg, 97% yield. Mp 101-103 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 3.7 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.32-7.25 (m, 5H), 6.70 (s,

1H), 4.39-4.35 (m, 1H), 3.68 (dd, J = 13.8 Hz, J = 6.1 Hz, 1H), 3.35 (t, J = 12.8 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.4, 149.2, 138.9, 137.1, 135.7, 128.1, 127.3, 124.1, 119.0, 107.9, 50.7, 40.8, 15.8. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0844.



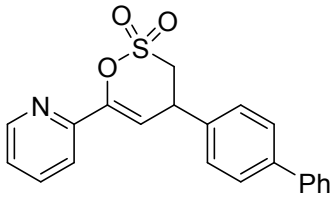
3c

4-(4-Ethylphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3c**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 140 mg, 89% yield. Mp 111-113°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, J = 3.7 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.29-7.23 (m, 5H), 6.69 (s, 1H), 4.38-4.34 (m, 1H), 3.67 (dd, J = 14.0 Hz, J = 6.6 Hz, 1H), 3.35 (t, J = 13.4 Hz, 1H), 2.66 (q, J = 7.4 Hz, 2H), 1.24 (t, J = 7.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.3, 149.2, 144.5, 137.0, 136.3, 128.8, 127.6, 124.0, 118.9, 108.4, 50.9, 40.9, 28.5, 15.6. ESI-MS HRMS calculated for $C_{17}H_{18}NO_3S$ $[M+H]^+$ 316.1002, found 316.1003.



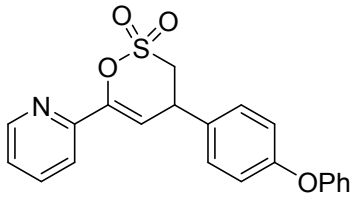
3d

4-(4-Methoxyphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3d**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 140 mg, 88% yield. Mp 107-109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, J = 4.0 Hz, 1H), 7.77 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.29-7.23 (m, 3H), 6.91 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 1.4 Hz, 1H), 4.34 (ddd, J = 11.6 Hz, J = 6.0 Hz, J = 2.0 Hz, 1H), 3.82 (s, 3H), 3.66 (dd, J = 13.8 Hz, J = 6.2 Hz, 1H), 3.33 (t, J = 13.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 149.6, 149.3, 149.1, 137.1, 131.1, 128.8, 124.1, 118.9, 114.7, 108.4, 55.4, 51.0, 40.5. ESI-MS HRMS calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$ 318.0795, found 318.0793.



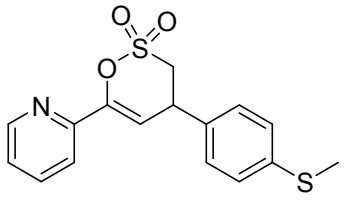
3e

4-([1,1'-Biphenyl]-4-yl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3e**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 127 mg, 70% yield. Mp 176-178 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.8 Hz, *J* = 0.8 Hz, 1H), 7.78 (td, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.60-7.58 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.41-7.36 (m, 3H), 7.29 (ddd, *J* = 7.5 Hz, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 4.44 (ddd, *J* = 12.1 Hz, *J* = 6.3 Hz, *J* = 2.6 Hz, 1H), 3.73 (ddd, *J* = 13.9 Hz, *J* = 6.3 Hz, *J* = 0.8 Hz, 1H), 3.41 (dd, *J* = 13.7 Hz, *J* = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.4, 149.2, 141.3, 140.3, 138.0, 137.1, 128.9, 128.11, 128.08, 127.7, 127.1, 124.1, 119.0, 108.0, 50.8, 40.9. ESI-MS HRMS calculated for $C_{21}H_{18}NO_3S$ $[M+H]^+$ 364.1002, found 364.0996.



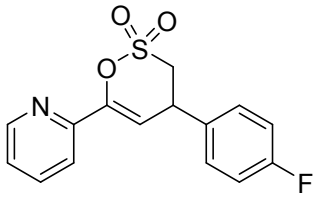
3f

4-(4-Phenoxyphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3f**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow solid, 123 mg, 65% yield. Mp 111-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.5 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.28-7.26 (m, 3H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 4H), 6.69 (s, 1H), 4.39-4.36 (m, 1H), 3.69 (dd, *J* = 13.9 Hz, *J* = 5.8 Hz, 1H), 3.35 (t, *J* = 12.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 156.8, 149.6, 149.3, 149.2, 137.1, 133.6, 129.9, 129.1, 124.2, 123.7, 119.4, 119.2, 119.0, 108.2, 50.9, 40.6. ESI-MS HRMS calculated for $C_{21}H_{18}NO_4S$ $[M+H]^+$ 380.0951, found 380.0948.



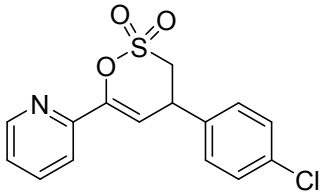
3g

4-(4-(Methylthio)phenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3g**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow solid, 135 mg, 81% yield. Mp 91-92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.5 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.29-7.21 (m, 5H), 6.67 (s, 1H), 4.37-4.33 (m, 1H), 3.66 (dd, *J* = 13.7 Hz, *J* = 6.1 Hz, 1H), 3.33 (t, *J* = 12.4 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.4, 149.2, 138.9, 137.1, 135.7, 128.1, 127.2, 124.1, 119.0, 107.9, 50.7, 40.7, 15.7. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S_2$ $[M+H]^+$ 334.0566, found 334.0561.



3h

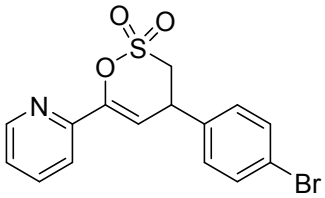
4-(4-Fluorophenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3h**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 115 mg, 75% yield. Mp 115-117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.8 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.32-7.29 (m, 3H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 4.40-4.37 (m, 1H), 3.68 (dd, *J* = 13.8 Hz, *J* = 6.3 Hz, 1H), 3.33 (t, *J* = 13.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.5 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.1 Hz), 149.6, 149.5, 149.1, 137.1, 134.9 (d, *J* = 2.7 Hz), 129.4 (d, *J* = 8.2 Hz), 124.2, 119.0, 116.3 (d, *J* = 20.9 Hz), 107.7, 50.9, 40.5. ESI-MS HRMS calculated for $C_{15}H_{13}FNO_3S$ $[M+H]^+$ 306.0595, found 306.0591.



3i

4-(4-Chlorophenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3i**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 113 mg, 70% yield. Mp 94-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.30-7.26 (m, 3H), 6.66 (s, 1H), 4.39-4.36 (m, 1H), 3.67 (dd, *J* = 13.7 Hz, *J* = 6.1 Hz, 1H), 3.32 (t, *J* = 12.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.0, 137.5, 137.1, 134.2, 129.5, 129.1, 124.3, 119.0, 107.4, 50.6, 40.6. ESI-MS HRMS calculated for $C_{15}H_{13}ClNO_3S$ $[M+H]^+$ 322.0299, found 322.0295.

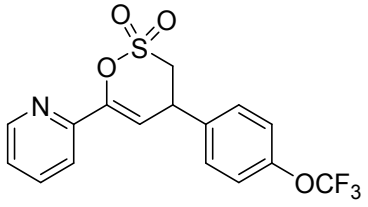
Note: In the ^{13}C NMR spectrum of **3i**, theoretically, there should be thirteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



3j

4-(4-Bromophenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3j**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow solid, 124 mg, 68% yield. Mp 135-137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 7.78 (td, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.53 (dt, *J* = 8.4 Hz, *J* = 1.9 Hz, 2H), 7.29 (ddd, *J* = 7.6 Hz, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 7.21 (dt, *J* = 8.4 Hz, *J* = 1.9 Hz, 2H), 6.67 (d, *J* = 2.0 Hz, 1H), 4.36 (ddd, *J* = 12.0 Hz, *J* = 6.4 Hz, *J* = 2.7 Hz, 1H), 3.67 (ddd, *J* = 13.9 Hz, *J* = 6.5 Hz, *J* = 1.0 Hz, 1H), 3.32 (dd, *J* = 13.7 Hz, *J* = 12.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.69, 149.67, 149.0, 138.1, 137.1, 132.5, 129.4, 124.3, 122.3, 119.0, 107.2, 50.6,

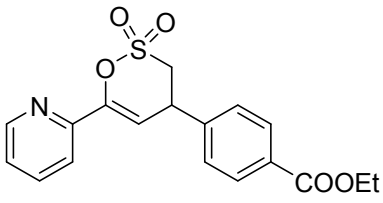
40.7. ESI-MS HRMS calculated for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$ 365.9794, found 365.9788.



3k

6-(Pyridin-2-yl)-4-(4-(trifluoromethoxy)phenyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3k**). Petroleum ether / ethyl acetate = 5 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 147 mg, 79% yield. Mp 125-126 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 4.6 Hz, *J* = 0.8 Hz, 1H), 7.78 (td, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.37 (dt, *J* = 8.7 Hz, *J* = 2.0 Hz, 2H), 7.30 (ddd, *J* = 7.5 Hz, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 1.9 Hz, 1H), 4.42 (ddd, *J* = 12.0 Hz, *J* = 6.4 Hz, *J* = 2.7 Hz, 1H), 3.69 (ddd, *J* = 13.8 Hz, *J* = 6.2 Hz, *J* = 0.9 Hz, 1H), 3.35 (dd, *J* = 13.9 Hz, *J* = 12.0 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.9 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 149.0, 137.8, 137.1, 129.2, 124.3, 121.9, 120.4 (q, *J* = 258.0 Hz), 119.0, 107.3, 50.6, 40.6. ESI-MS HRMS calculated for $C_{16}H_{13}F_3NO_4S$ $[M+H]^+$ 372.0512, found 372.0508.

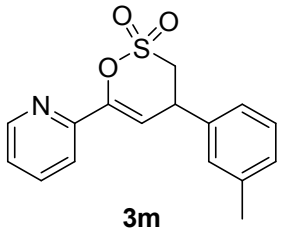
Note: In the ^{13}C NMR spectrum of **3k**, theoretically, there should be fourteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



3l

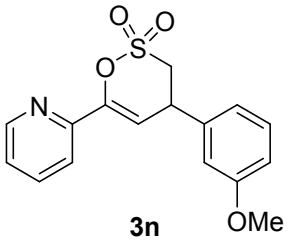
Ethyl 4-(2,2-dioxido-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiin-4-yl)benzoate (**3l**). Petroleum ether / ethyl acetate = 5 : 1 (v / v) as eluent for column chromatography. White solid, 79 mg, 44% yield. Mp 135-137 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 4.8 Hz, *J* = 1.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.78 (td, *J* = 7.7 Hz, *J* = 1.6

Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (ddd, *J* = 7.5 Hz, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 6.70 (d, *J* = 2.0 Hz, 1H), 4.45 (ddd, *J* = 12.1 Hz, *J* = 6.3 Hz, *J* = 2.6 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.70 (ddd, *J* = 13.9 Hz, *J* = 6.4 Hz, *J* = 0.9 Hz, 1H), 3.36 (dd, *J* = 13.7 Hz, *J* = 12.1 Hz, 1H), 1.40 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 149.8, 149.7, 149.0, 143.8, 137.1, 130.62, 130.58, 127.7, 124.3, 119.0, 107.1, 61.2, 50.5, 41.1, 14.3. ESI-MS HRMS calculated for $C_{18}H_{18}NO_5S$ $[M+H]^+$ 360.0900, found 360.0895.



3m

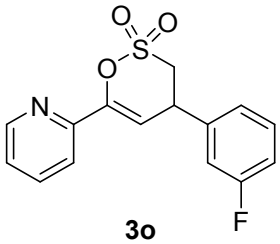
6-(Pyridin-2-yl)-4-(m-tolyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3m**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 134 mg, 89% yield. Mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.4 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.30-7.28 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 1.8 Hz, 1H), 4.35 (ddd, *J* = 12.0 Hz, *J* = 6.1 Hz, *J* = 2.2 Hz, 1H), 3.67 (dd, *J* = 13.9 Hz, *J* = 6.3 Hz, 1H), 3.36 (t, *J* = 12.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.3, 149.2, 139.2, 139.0, 137.1, 129.2, 129.0, 128.3, 124.7, 124.1, 119.0, 108.3, 50.8, 41.2, 21.4. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0844.



3n

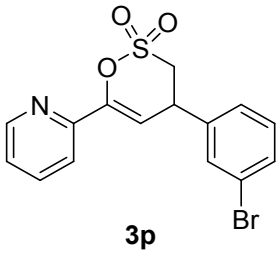
4-(3-Methoxyphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3n**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 140 mg, 88% yield. Mp 85-87 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 4.7 Hz, *J* = 0.9 Hz, 1H), 7.77 (td, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.32-7.27 (m, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.88-6.86 (m, 1H), 6.85 (t,

J = 1.9 Hz, 1H), 6.70 (d, *J* = 1.9 Hz, 1H), 4.35 (ddd, *J* = 12.2 Hz, *J* = 6.2 Hz, *J* = 2.6 Hz, 1H), 3.82 (s, 3H), 3.69 (ddd, *J* = 13.7 Hz, *J* = 6.2 Hz, *J* = 0.9 Hz, 1H), 3.37 (dd, *J* = 13.9 Hz, *J* = 12.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 149.6, 149.3, 149.2, 140.5, 137.1, 130.4, 124.1, 119.8, 119.0, 113.6, 113.4, 108.0, 55.4, 50.7, 41.2. ESI-MS HRMS calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$ 318.0795, found 318.0790.



3o

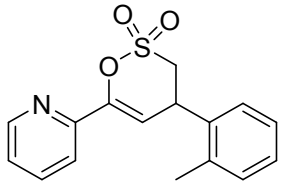
4-(3-Fluorophenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3o**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 122 mg, 80% yield. Mp 109-111 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.2 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 1H), 7.30 (t, *J* = 6.0 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.69 (s, 1H), 4.41-4.38 (m, 1H), 3.69 (dd, *J* = 13.2 Hz, *J* = 5.8 Hz, 1H), 3.35 (t, *J* = 13.0 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.2 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, *J* = 248.0 Hz), 149.7, 149.6, 149.0, 141.4 (d, *J* = 6.4 Hz), 137.1, 130.0 (d, *J* = 9.1 Hz), 124.3, 123.4 (d, *J* = 3.7 Hz), 119.0, 115.4 (d, *J* = 20.9 Hz), 114.8 (d, *J* = 21.8 Hz), 107.2, 50.6, 40.9 (d, *J* = 1.8 Hz). ESI-MS HRMS calculated for $C_{15}H_{13}FNO_3S$ $[M+H]^+$ 306.0595, found 306.0595.



3p

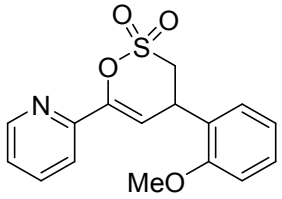
4-(3-Bromophenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3p**). Petroleum ether / ethyl acetate = 5 : 1 (v / v) as eluent for column chromatography. Yellow solid, 95 mg, 52% yield. Mp 115-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58-8.57 (m, 1H), 7.78 (td, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.49-7.47

(m, 2H), 7.30 (ddd, J = 7.6 Hz, J = 4.7 Hz, J = 0.7 Hz, 1H), 7.28-7.26 (m, 2H), 6.67 (d, J = 2.2 Hz, 1H), 4.36 (ddd, J = 12.1 Hz, J = 6.4 Hz, J = 2.7 Hz, 1H), 3.68 (ddd, J = 13.9 Hz, J = 6.4 Hz, J = 0.9 Hz, 1H), 3.34 (dd, J = 13.8 Hz, J = 12.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 149.6, 149.0, 141.2, 137.1, 131.5, 130.9, 130.8, 126.4, 124.3, 123.3, 119.0, 107.0, 50.6, 40.9. ESI-MS HRMS calculated for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$ 365.9794, found 365.9790.



3q

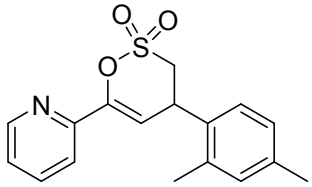
6-(Pyridin-2-yl)-4-(o-tolyl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3q**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 138 mg, 92% yield. Mp 139-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 2.3 Hz, 1H), 7.78 (t, J = 7.1 Hz, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.27-7.21 (m, 5H), 6.69 (s, 1H), 4.62-4.60 (m, 1H), 3.65 (dd, J = 13.6 Hz, J = 5.8 Hz, 1H), 3.31 (t, J = 12.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.5, 149.3, 137.13, 137.06, 135.3, 131.1, 128.2, 128.0, 127.2, 124.1, 118.9, 108.5, 49.6, 37.6, 19.3. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0843.



3r

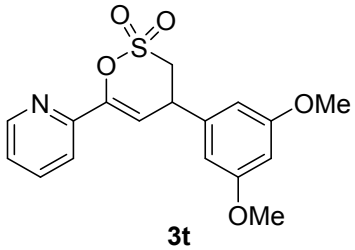
4-(2-Methoxyphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3r**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow solid, 144 mg, 91% yield. Mp 53-55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.79 (s, 1H), 7.69 (d, J = 6.9 Hz, 1H), 7.31-7.30 (m, 3H), 7.00-6.98 (m, 1H), 6.95 (d, J = 7.3 Hz, 1H), 6.74 (s, 1H), 4.78 (s, 1H), 3.90 (s, 3H), 3.86-3.83 (m, 1H), 3.35 (t, J = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 149.53, 149.47,

149.45, 137.1, 129.4, 128.7, 127.0, 124.0, 121.1, 118.8, 110.7, 108.4, 55.5, 48.8, 35.4. ESI-MS HRMS calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$ 318.0795, found 318.0790.



3s

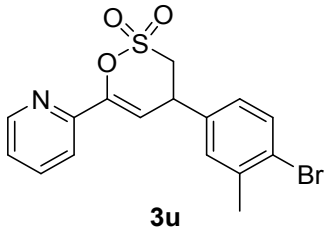
4-(2,4-Dimethylphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3s**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. white solid, 140 mg, 89% yield. Mp 104-106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 3.8 Hz, 1H), 7.78-7.75 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.29-7.28 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 6.6 Hz, 2H), 6.67 (d, *J* = 1.4 Hz, 1H), 4.56 (ddd, *J* = 11.8 Hz, *J* = 5.8 Hz, *J* = 2.2 Hz, 1H), 3.63 (dd, *J* = 13.8 Hz, *J* = 6.1 Hz, 1H), 3.31 (t, *J* = 13.4 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.4, 149.3, 137.9, 137.0, 135.1, 134.1, 131.9, 127.9, 127.8, 124.0, 118.8, 108.8, 49.7, 37.3, 21.0, 19.2. ESI-MS HRMS calculated for $C_{17}H_{18}NO_3S$ $[M+H]^+$ 316.1002, found 316.1001.



3t

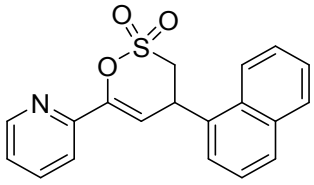
4-(3,5-Dimethoxyphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3t**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 139 mg, 80% yield. Mp 115-116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.5 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.32-7.30 (m, 1H), 6.99 (s, 1H), 6.94 (s, 2H), 6.71 (d, *J* = 2.0 Hz, 1H), 4.33 (ddd, *J* = 12.2 Hz, *J* = 6.1 Hz, *J* = 2.3 Hz, 1H), 3.68 (dd, *J* = 13.7 Hz, *J* = 6.2 Hz, 1H), 3.38 (t, *J* = 12.7 Hz, 1H), 2.34 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 149.6, 149.3, 149.2, 141.3, 137.0, 124.1, 118.9, 107.9, 105.8, 99.7, 55.5, 50.6, 41.4. ESI-MS HRMS calculated

for $C_{17}H_{18}NO_5S$ $[M+H]^+$ 348.0900, found 348.0894.



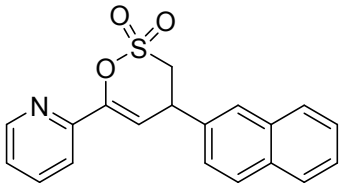
3u

4-(4-Bromo-3-methylphenyl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3u**). Petroleum ether / ethyl acetate = 5 : 1 (v / v) as eluent for column chromatography. Yellow solid, 139 mg, 73% yield. Mp 136-138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dq, *J* = 4.6 Hz, *J* = 0.7 Hz, 1H), 7.77 (td, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.29 (ddd, *J* = 7.5 Hz, *J* = 4.8 Hz, *J* = 0.9 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 7.01 (dd, *J* = 8.1 Hz, *J* = 2.3 Hz, 1H), 6.66 (d, *J* = 1.9 Hz, 1H), 4.32 (ddd, *J* = 12.6 Hz, *J* = 6.2 Hz, *J* = 2.6 Hz, 1H), 3.66 (ddd, *J* = 13.8 Hz, *J* = 6.3 Hz, *J* = 1.0 Hz, 1H), 3.32 (dd, *J* = 13.9 Hz, *J* = 12.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.5, 149.1, 139.1, 138.3, 137.1, 133.2, 130.1, 126.6, 124.3, 124.2, 119.0, 107.5, 50.6, 40.7, 23.0. ESI-MS HRMS calculated for $C_{16}H_{15}BrNO_3S$ $[M+H]^+$ 379.9951, found 379.9943.



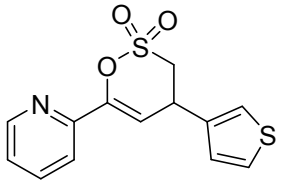
3v

4-(Naphthalen-1-yl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3v**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 89 mg, 53% yield. Mp 159-160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 3.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.58-7.53 (m, 2H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.32-7.29 (m, 1H), 6.89 (s, 1H), 5.20 (s, 1H), 3.89 (dd, *J* = 13.9 Hz, *J* = 6.0 Hz, 1H), 3.49-3.44 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 149.7, 149.3, 137.1, 134.7, 134.1, 130.4, 129.5, 129.0, 127.2, 126.3, 126.0, 125.8, 124.1, 122.0, 118.9, 108.4, 50.0, 37.3. ESI-MS HRMS calculated for $C_{19}H_{16}NO_3S$ $[M+H]^+$ 338.0845, found 338.0840.



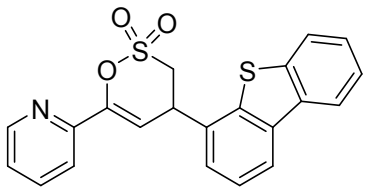
3w

4-(Naphthalen-2-yl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3w**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 125 mg, 74% yield. Mp 154-156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.4 Hz, 1H), 7.89-7.83 (m, 3H), 7.81-7.78 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.43-7.41 (m, 1H), 7.30 (dd, *J* = 7.0 Hz, *J* = 5.0 Hz, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 4.57 (ddd, *J* = 12.1 Hz, *J* = 6.2 Hz, *J* = 2.3 Hz, 1H), 3.77 (dd, *J* = 13.8 Hz, *J* = 6.2 Hz, 1H), 3.46 (t, *J* = 13.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.5, 149.3, 137.1, 136.3, 133.5, 133.0, 129.4, 127.9, 127.8, 126.8, 126.7, 126.5, 125.2, 124.2, 119.0, 108.0, 50.8, 41.4. ESI-MS HRMS calculated for $C_{19}H_{16}NO_3S$ $[M+H]^+$ 338.0845, found 338.0841.



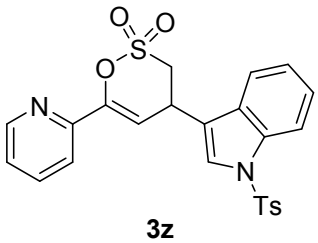
3x

6-(Pyridin-2-yl)-4-(thiophen-3-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3x**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 123 mg, 84% yield. Mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 3.4 Hz, 1H), 7.77 (t, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.38 (s, 1H), 7.30-7.26 (m, 1H), 7.24 (s, 1H), 7.06 (d, *J* = 4.6 Hz, 1H), 6.72 (s, 1H), 4.54-4.51 (m, 1H), 3.72 (dd, *J* = 14.1 Hz, *J* = 6.6 Hz, 1H), 3.39 (t, *J* = 12.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.2, 148.8, 139.2, 137.1, 127.4, 126.4, 124.1, 122.5, 119.0, 107.7, 50.1, 36.4. ESI-MS HRMS calculated for $C_{13}H_{12}NO_3S_2$ $[M+H]^+$ 294.0253, found 294.0249.



3y

4-(Dibenzo[b,d]thiophen-4-yl)-6-(pyridin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3y**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 139 mg, 71% yield. Mp 159-161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.6 Hz, 1H), 8.19-8.16 (m, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.87-7.84 (m, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.52-7.47 (m, 3H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.30 (dd, *J* = 7.0 Hz, *J* = 5.0 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 4.72 (ddd, *J* = 11.8 Hz, *J* = 6.4 Hz, *J* = 2.6 Hz, 1H), 3.87 (dd, *J* = 13.9 Hz, *J* = 6.4 Hz, 1H), 3.64 (t, *J* = 12.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 149.7, 149.2, 138.8, 138.0, 137.1, 136.9, 135.6, 133.0, 127.3, 126.0, 125.5, 124.9, 124.2, 122.7, 121.9, 121.6, 119.0, 106.9, 48.2, 40.8. ESI-MS HRMS calculated for $C_{21}H_{16}NO_3S_2$ $[M+H]^+$ 394.0566, found 394.0565.

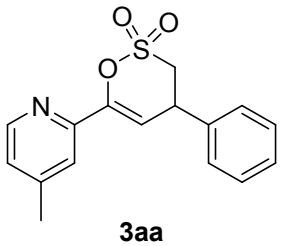


3z

6-(Pyridin-2-yl)-4-(1-tosyl-1H-indol-3-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3z**). Petroleum ether / ethyl acetate = 5 : 1 (v / v) as eluent for column chromatography. White solid, 120 mg, 50% yield. Mp 188-190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.3 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.80-7.77 (m, 3H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31-7.25 (m, 4H), 6.75 (d, *J* = 3.6 Hz, 1H), 4.66-4.62 (m, 1H), 3.76 (dd, *J* = 13.9 Hz, *J* = 6.3 Hz, 1H), 3.47 (dd, *J* = 13.7 Hz, *J* = 11.5 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 149.5, 149.0, 145.4, 137.1, 135.4, 135.0, 130.1, 128.5, 127.0, 125.4, 124.3, 123.9, 123.6, 119.6, 119.0, 114.1, 106.6, 48.9, 32.7, 21.6. ESI-MS HRMS calculated

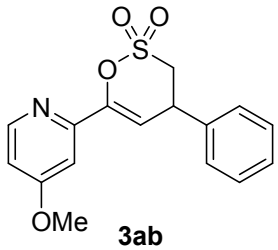
for $C_{24}H_{21}N_2O_5S_2$ $[M+H]^+$ 481.0886, found 481.0877.

Note: In the ^{13}C NMR spectrum of **3z**, theoretically, there should be twenty-two peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



3aa

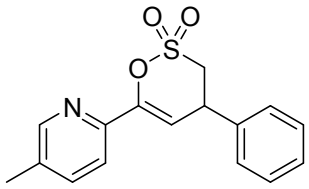
6-(4-Methylpyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3aa**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 123 mg, 82% yield. Mp 145-147 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 4.1 Hz, 1H), 7.51 (s, 1H), 7.39-7.31 (m, 5H), 7.10 (s, 1H), 6.68 (s, 1H), 4.39-4.38 (m, 1H), 3.69 (dd, *J* = 13.7 Hz, *J* = 6.1 Hz, 1H), 3.36 (t, *J* = 12.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 149.4, 149.1, 148.4, 139.1, 129.4, 128.2, 127.7, 125.0, 120.0, 107.9, 50.8, 41.2, 21.2. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0844.



3ab

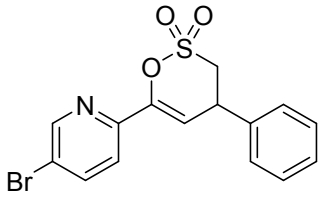
6-(4-Methoxypyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ab**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 122 mg, 77% yield. Mp 135-137 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.5 Hz, 1H), 7.40-7.38 (m, 2H), 7.35-7.31 (m, 3H), 7.19 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 5.6 Hz, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 4.37 (ddd, *J* = 12.2 Hz, *J* = 6.3 Hz, *J* = 2.6 Hz, 1H), 3.90 (s, 3H), 3.69 (ddd, *J* = 13.9 Hz, *J* = 6.4 Hz, 1H), 3.36 (dd, *J* = 13.8 Hz, *J* = 12.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 150.9, 150.8, 149.2, 139.0, 129.4, 128.2, 127.7, 110.1, 108.4, 105.3, 55.5, 50.8, 41.2. ESI-

MS HRMS calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$ 318.0795, found 318.0792.



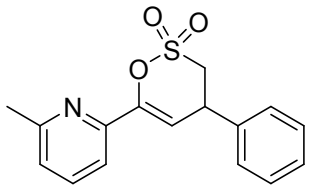
3ac

6-(5-Methylpyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ac**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 100 mg, 66% yield. Mp 165-167 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.58-7.55 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 3H), 6.63 (d, *J* = 2.2 Hz, 1H), 4.37 (ddd, *J* = 12.2 Hz, *J* = 6.3 Hz, *J* = 2.6 Hz, 1H), 3.68 (ddd, *J* = 13.9 Hz, *J* = 6.4 Hz, *J* = 0.9 Hz, 1H), 3.35 (dd, *J* = 13.7 Hz, *J* = 12.3 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 149.5, 146.7, 139.2, 137.3, 134.0, 129.3, 128.2, 127.7, 118.5, 107.0, 50.8, 41.2, 18.3. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0845.



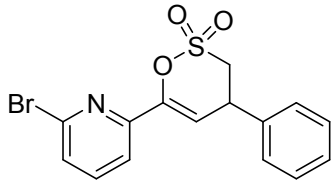
3ad

6-(5-Bromopyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ad**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Yellow solid, 82 mg, 45% yield. Mp 174-176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.8 Hz, 1H), 7.90 (dd, *J* = 8.4 Hz, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.42-7.39 (m, 2H), 7.37-7.34 (m, 1H), 7.32-7.30 (m, 2H), 6.71 (d, *J* = 1.9 Hz, 1H), 4.37 (ddd, *J* = 12.1 Hz, *J* = 6.3 Hz, *J* = 2.6 Hz, 1H), 3.69 (ddd, *J* = 13.9 Hz, *J* = 6.4 Hz, *J* = 0.9 Hz, 1H), 3.36 (dd, *J* = 13.9 Hz, *J* = 12.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 148.7, 147.7, 139.6, 138.9, 129.4, 128.3, 127.6, 121.2, 120.0, 108.7, 50.8, 41.3. ESI-MS HRMS calculated for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$ 365.9794, found 365.9792.



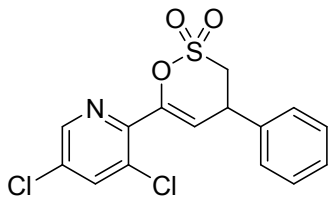
3ae

6-(6-Methylpyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ae**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 68 mg, 45% yield. Mp 107-109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.36-7.33 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 4.38-4.37 (m, 1H), 3.67 (dd, *J* = 14.3 Hz, *J* = 6.5 Hz, 1H), 3.36 (t, *J* = 13.0 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 149.6, 148.5, 139.3, 137.1, 129.4, 128.2, 127.8, 123.9, 115.9, 107.6, 50.8, 41.3, 24.6. ESI-MS HRMS calculated for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0845, found 302.0845.



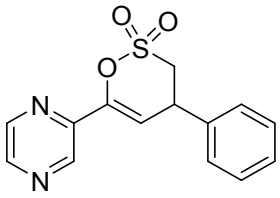
3af

6-(6-Bromopyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3af**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 90 mg, 49% yield. Mp 164-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.48-7.45 (m, 1H), 7.43-7.40 (m, 2H), 7.37-7.34 (m, 1H), 7.32-7.31 (m, 2H), 6.75 (d, *J* = 2.2 Hz, 1H), 4.38 (ddd, *J* = 12.2 Hz, *J* = 6.4 Hz, *J* = 2.7 Hz, 1H), 3.69 (ddd, *J* = 13.9 Hz, *J* = 6.2 Hz, *J* = 0.8 Hz, 1H), 3.37 (dd, *J* = 13.9 Hz, *J* = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 147.9, 141.9, 139.3, 138.7, 129.4, 128.5, 128.4, 127.7, 117.6, 109.5, 50.8, 41.4. ESI-MS HRMS calculated for $C_{15}H_{13}BrNO_3S$ $[M+H]^+$ 365.9794, found 365.9788.



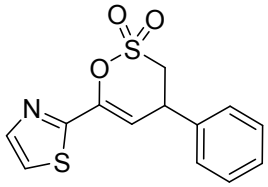
3ag

6-(3,5-Dichloropyridin-2-yl)-4-phenyl-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ag**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. White solid, 60 mg, 34% yield. Mp 152-153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37-7.34 (m, 3H), 6.02 (d, *J* = 2.0 Hz, 1H), 4.40 (ddd, *J* = 12.1 Hz, *J* = 6.3 Hz, *J* = 2.5 Hz, 1H), 3.68 (ddd, *J* = 13.9 Hz, *J* = 6.4 Hz, 1H), 3.38 (dd, *J* = 13.7 Hz, *J* = 12.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 146.5, 146.2, 138.7, 138.0, 132.8, 131.0, 129.5, 128.4, 127.6, 113.4, 50.9, 41.6. ESI-MS HRMS calculated for $C_{15}H_{12}Cl_2NO_3S$ $[M+H]^+$ 355.9909, found 355.9905.



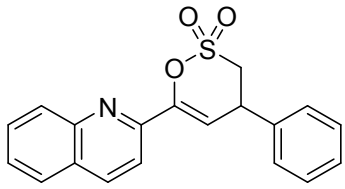
3ah

4-Phenyl-6-(pyrazin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ah**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Brown solid, 45 mg, 31% yield. Mp 164-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.60 (d, *J* = 2.0 Hz, 1H), 8.53 (s, 1H), 7.41 (t, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 7.1 Hz, 2H), 6.73 (d, *J* = 2.0 Hz, 1H), 4.41 (ddd, *J* = 12.0 Hz, *J* = 6.2 Hz, *J* = 2.4 Hz, 1H), 3.73 (dd, *J* = 13.9 Hz, *J* = 6.2 Hz, 1H), 3.40 (t, *J* = 12.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 145.2, 144.8, 144.1, 140.4, 138.6, 129.5, 128.5, 127.6, 110.2, 50.9, 41.4. ESI-MS HRMS calculated for $C_{14}H_{13}N_2O_3S$ $[M+H]^+$ 289.0641, found 289.0639.



3ai

4-Phenyl-6-(thiazol-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3ai**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 53 mg, 36% yield. Mp 93-95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 3.2 Hz, 1H), 7.45 (d, *J* = 3.0 Hz, 1H), 7.42-7.39 (m, 2H), 7.36 (dt, *J* = 7.2 Hz, *J* = 2.7 Hz, 1H), 7.33-7.31 (m, 2H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.39 (ddd, *J* = 12.2 Hz, *J* = 6.2 Hz, *J* = 2.7 Hz, 1H), 3.71 (ddd, *J* = 13.8 Hz, *J* = 6.2 Hz, *J* = 0.9 Hz, 1H), 3.39 (dd, *J* = 14.0 Hz, *J* = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 145.3, 144.2, 138.4, 129.5, 128.5, 127.6, 120.6, 107.5, 51.1, 41.3. ESI-MS HRMS calculated for $C_{13}H_{12}NO_3S_2$ $[M+H]^+$ 294.0253, found 294.0251.



3aj

4-Phenyl-6-(quinolin-2-yl)-3,4-dihydro-1,2-oxathiine 2,2-dioxide (**3aj**). Petroleum ether / ethyl acetate = 10 : 1 (v / v) as eluent for column chromatography. Red solid, 51 mg, 30% yield. Mp 172-174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.83 (t, *J* = 8.5 Hz, 2H), 7.73-7.70 (m, 1H), 7.57-7.53 (m, 1H), 7.45-7.42 (m, 2H), 7.39-7.36 (m, 3H), 6.93 (d, *J* = 2.0 Hz, 1H), 4.45 (ddd, *J* = 12.0 Hz, *J* = 6.2 Hz, *J* = 2.6 Hz, 1H), 3.72 (ddd, *J* = 13.7 Hz, *J* = 6.2 Hz, *J* = 0.8 Hz, 1H), 3.42 (dd, *J* = 13.8 Hz, *J* = 12.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 149.3, 147.8, 139.1, 137.2, 130.1, 129.6, 129.4, 128.3, 128.1, 127.8, 127.6, 127.2, 116.7, 109.0, 50.8, 41.4. ESI-MS HRMS calculated for $C_{19}H_{16}NO_3S$ $[M+H]^+$ 338.0845, found 338.0844.

4. Procedures and Characterizations for the Syntheses of 5.

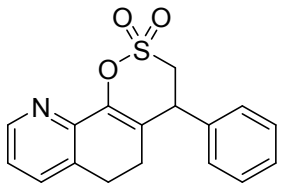
4.1 Preparation of Substrates

All the substituted-ethenesulfonyl fluorides **1** were prepared according to the literatures.[1, 2] All the homemade starting materials are identical to those reported regarding the ^{1}H and ^{13}C NMR and melting points (if applicable). 6,7-dihydroquinolin-8(5*H*)-one (**4)** was purchased from commercial sources.

4.2 Procedures for Annulative SuFEx Reactions of Substituted-Ethenesulfonyl Fluorides with 6,7-Dihydroquinolin-8(5*H*)-One

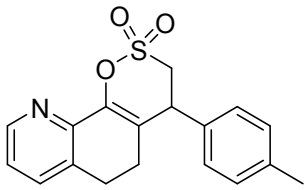
An oven-dried round-bottle flask (25 mL) was charged with substituted-ethenesulfonyl fluoride (**1**, 0.5 mmol), 6,7-dihydroquinolin-8(5*H*)-one (**4**, 147.2 mg, 1.0 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (29.1 mg, 20 mol%), K_2CO_3 (138.2 mg, 1.0 mmol, 2.0 equiv), and MeCN (2 ml). The resulting mixture was stirred at room temperature under air atmosphere for 24 h. The crude products were purified by column chromatography (Petroleum ether / ethyl acetate as eluent) on silica gel to give **5**.

4.3 Syntheses of 5



5a

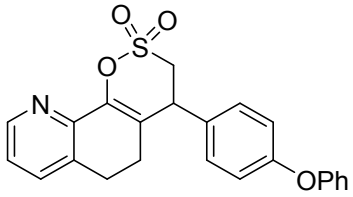
4-Phenyl-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5a**). Petroleum ether / ethyl acetate = 2 : 1 (v / v) as eluent for column chromatography. White solid, 155 mg, 99% yield. Mp 178-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.3 Hz, 1H), 7.42-7.38 (m, 3H), 7.36-7.33 (m, 1H), 7.29-7.27 (m, 2H), 7.15 (dd, *J* = 7.7 Hz, *J* = 5.1 Hz, 1H), 4.26 (dd, *J* = 11.6 Hz, *J* = 6.7 Hz, 1H), 3.69 (dd, *J* = 14.0 Hz, *J* = 6.7 Hz, 1H), 3.49 (dd, *J* = 13.9 Hz, *J* = 11.6 Hz, 1H), 2.89-2.82 (m, 1H), 2.77-2.71 (m, 1H), 2.20-2.08 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 147.0, 144.5, 138.0, 134.9, 131.3, 129.5, 128.5, 128.3, 123.4, 120.5, 51.6, 46.1, 26.3, 25.0. ESI-MS HRMS calculated for $C_{17}H_{16}NO_3S$ $[M+H]^+$ 314.0845, found 314.0844.



5b

4-(P-tolyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5b**). Petroleum ether / ethyl acetate = 2 : 1 (v / v) as eluent for column chromatography. White solid, 162 mg, 99% yield. Mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.6 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.18-7.11 (m, 5H), 4.21 (dd, *J* = 11.6 Hz, *J* = 6.9 Hz, 1H), 3.65 (dd, *J* = 14.0 Hz, *J* = 6.8 Hz, 1H), 3.45 (dd, *J* = 13.9 Hz, *J* = 11.6 Hz, 1H), 2.85-2.78 (m, 1H), 2.74-2.68 (m, 1H), 2.33 (s, 3H), 2.17-2.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 147.0, 144.2, 138.3, 134.9, 131.4, 130.1, 128.2, 123.3, 120.9, 51.6, 45.6, 26.3, 25.0, 21.1. ESI-MS HRMS calculated for $C_{18}H_{18}NO_3S$ $[M+H]^+$ 328.1002, found 328.1003.

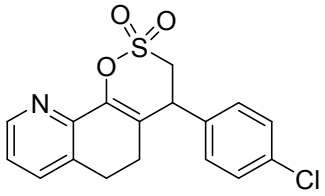
Note: In the ^{13}C NMR spectrum of **5b**, theoretically, there should be sixteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



5c

4-(4-Phenoxyphenyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5c**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 194 mg, 96% yield. Mp 178-180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.16-7.13 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 8.5 Hz, 2H), 4.25 (dd, *J* = 11.5 Hz, *J* = 6.9 Hz, 1H), 3.70 (dd, *J* = 14.1 Hz, *J* = 6.7 Hz, 1H), 3.49 (dd, *J* = 13.7 Hz, *J* = 11.6 Hz, 1H), 2.90-2.84 (m, 1H), 2.78-2.72 (m, 1H),

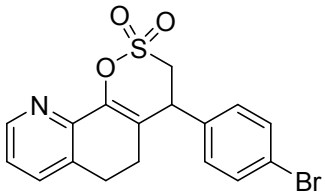
2.22-2.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 156.4, 147.7, 147.0, 144.3, 134.9, 132.3, 131.4, 130.0, 129.7, 124.0, 123.4, 120.6, 119.4, 119.2, 51.6, 45.3, 26.3, 25.0. ESI-MS HRMS calculated for $C_{23}H_{20}NO_4S$ $[M+H]^+$ 406.1108, found 406.1103.



5d

4-(4-Chlorophenyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5d**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 172 mg, 99% yield. Mp 98-100 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.2 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.16 (dd, *J* = 7.3 Hz, *J* = 4.9 Hz, 1H), 4.25 (dd, *J* = 11.0 Hz, *J* = 6.8 Hz, 1H), 3.69 (dd, *J* = 14.0 Hz, *J* = 6.7 Hz, 1H), 3.46 (dd, *J* = 13.9 Hz, *J* = 11.6 Hz, 1H), 2.89-2.82 (m, 1H), 2.77-2.71 (m, 1H), 2.19-2.07 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 146.7, 144.6, 136.5, 135.0, 134.4, 131.4, 129.7, 123.5, 119.9, 51.4, 45.4, 26.3, 25.0. ESI-MS HRMS calculated for $C_{17}H_{15}ClNO_3S$ $[M+H]^+$ 348.0456, found 348.0452.

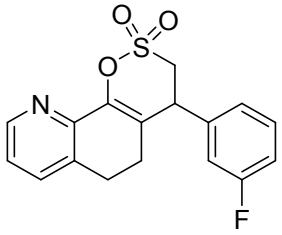
Note: In the ^{13}C NMR spectrum of **5d**, theoretically, there should be fifteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



5e

4-(4-Bromophenyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5e**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 195 mg, 99% yield. Mp 99-101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H

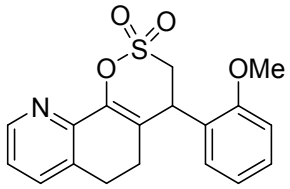
NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.6 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 4.24 (dd, *J* = 11.0 Hz, *J* = 6.7 Hz, 1H), 3.69 (dd, *J* = 14.0 Hz, *J* = 6.9 Hz, 1H), 3.45 (dd, *J* = 13.9 Hz, *J* = 11.3 Hz, 1H), 2.88-2.82 (m, 1H), 2.77-2.71 (m, 1H), 2.19-2.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 146.8, 144.6, 137.0, 135.0, 132.7, 131.4, 130.0, 123.5, 122.5, 119.8, 51.3, 45.4, 26.3, 25.0. ESI-MS HRMS calculated for $C_{17}H_{15}BrNO_3S$ $[M+H]^+$ 391.9951, found 391.9945.



5f

4-(3-Fluorophenyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5f**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 160 mg, 97% yield. Mp 172-174 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.7 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.28-7.26 (m, 2H), 7.15 (dd, *J* = 7.5 Hz, *J* = 4.9 Hz, 1H), 7.08 (t, *J* = 8.5 Hz, 2H), 4.27 (dd, *J* = 11.3 Hz, *J* = 6.9 Hz, 1H), 3.69 (dd, *J* = 14.1 Hz, *J* = 6.9 Hz, 1H), 3.47 (dd, *J* = 14.0 Hz, *J* = 11.4 Hz, 1H), 2.89-2.82 (m, 1H), 2.77-2.71 (m, 1H), 2.19-2.07 (m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.0 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.9 Hz), 148.0, 146.9, 144.5, 134.9, 133.7 (d, *J* = 2.7 Hz), 131.3, 130.0 (d, *J* = 8.2 Hz), 123.5, 120.1, 116.5 (d, *J* = 21.8 Hz), 51.6, 45.3, 26.3, 25.0. ESI-MS HRMS calculated for $C_{17}H_{15}FNO_3S$ $[M+H]^+$ 332.0751, found 332.0748.

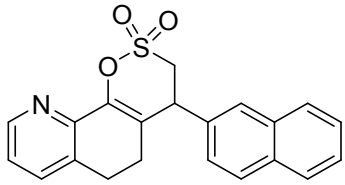
Note: In the ^{13}C NMR spectrum of **5f**, theoretically, there should be seventeen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



5g

4-(2-Methoxyphenyl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5g**). Petroleum ether / ethyl acetate = 2 : 1 (v / v) as eluent for column chromatography. White solid, 168 mg, 98% yield. Mp 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.4 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.33-7.30 (m, 1H), 7.22-7.20 (m, 1H), 7.14 (dd, *J* = 7.4 Hz, *J* = 4.9 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.61 (s, 1H), 3.83 (s, 3H), 3.62 (d, *J* = 8.1 Hz, 2H), 2.88-2.81 (m, 1H), 2.79-2.73(m, 1H), 2.18-2.14 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 147.6, 147.2, 143.8, 134.8, 131.3, 129.9, 129.7, 125.4, 123.1, 121.2, 111.1, 55.5, 49.4, 40.3, 28.4, 24.8. ESI-MS HRMS calculated for $C_{18}H_{18}NO_4S$ $[M+H]^+$ 344.0951, found 344.0948.

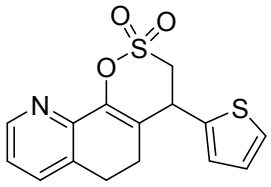
Note: In the ^{13}C NMR spectrum of **5g**, theoretically, there should be eighteen peaks. Due to the compact overlaying, it is difficult to specify the overlaying peaks.



5h

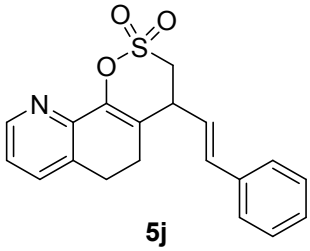
4-(Naphthalen-2-yl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5h**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 176 mg, 97% yield. Mp 119-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.3 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.85 (t, *J* = 9.3 Hz, 2H), 7.78 (s, 1H), 7.55-7.51 (m, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 7.2 Hz, *J* = 5.0 Hz, 1H), 4.40 (dd, *J* = 11.3 Hz, *J* = 6.8 Hz, 1H), 3.75 (dd, *J* = 14.0 Hz, *J* = 6.7 Hz, 1H), 3.61 (t, *J* = 11.7, 1H), 2.88-2.82 (m, 1H), 2.76-

2.70 (m, 1H), 2.24-2.10 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 147.0, 144.5, 135.2, 134.9, 133.5, 133.1, 131.4, 129.7, 127.88, 127.85, 127.81, 127.0, 126.7, 125.2, 123.4, 120.5, 51.5, 46.2, 26.3, 25.1. ESI-MS HRMS calculated for $C_{21}H_{18}NO_3S$ $[M+H]^+$ 364.1002, found 364.0996.



5i

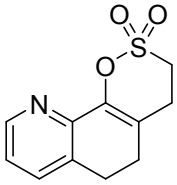
4-(Thiophen-2-yl)-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5i**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. Light yellow solid, 142 mg, 89% yield. Mp 132-134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.5 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.16 (dd, *J* = 7.5 Hz, *J* = 5.0 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 7.00 (t, *J* = 5.1 Hz, 1H), 4.61 (dd, *J* = 11.5 Hz, *J* = 6.7 Hz, 1H), 3.77 (dd, *J* = 14.0 Hz, *J* = 6.7 Hz, 1H), 3.59 (dd, *J* = 13.8 Hz, *J* = 11.4 Hz, 1H), 2.90-2.83 (m, 1H), 2.81-2.75 (m, 1H), 2.32-2.22 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 147.0, 143.6, 140.5, 134.9, 131.5, 127.4, 127.3, 126.1, 123.5, 120.1, 51.9, 40.9, 26.3, 24.6. ESI-MS HRMS calculated for $C_{15}H_{14}NO_3S_2$ $[M+H]^+$ 320.0410, found 320.0405.



5j

(*E*)-4-styryl-3,4,5,6-tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5j**). Petroleum ether / ethyl acetate = 2 : 1 (v / v) as eluent for column chromatography. Gray solid, 103 mg, 61% yield. Mp 87-89 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 3.9 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 6.9 Hz, 1H), 6.66 (d, *J* = 15.5 Hz, 1H), 6.20 (dd, *J* = 15.5 Hz, *J* = 9.6 Hz, 1H), 3.80 (dd, *J* = 15.2 Hz, *J* = 7.8 Hz, 1H), 3.62 (dd, *J* = 14.9 Hz, *J* = 7.7 Hz,

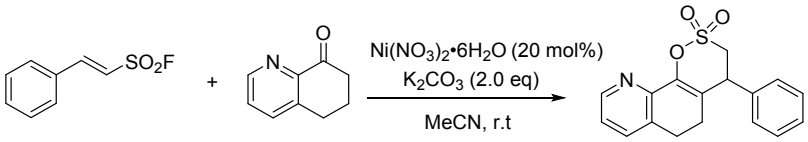
1H), 3.42 (dd, *J* = 13.9 Hz, *J* = 8.5 Hz, 1H), 2.92-2.78 (m, 2H), 2.52-2.46 (m, 1H), 2.40-2.34 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 146.9, 143.6, 135.6, 135.4, 134.9, 131.3, 128.8, 128.5, 126.6, 125.2, 123.4, 119.7, 49.5, 43.8, 26.3, 25.0. ESI-MS HRMS calculated for $C_{19}H_{18}NO_3S$ $[M+H]^+$ 340.1002, found 340.0997.



5k

3,4,5,6-Tetrahydro-[1,2]oxathiino[5,6-h]quinoline 2,2-dioxide (**5k**). Petroleum ether / ethyl acetate = 1 : 1 (v / v) as eluent for column chromatography. White solid, 44 mg, 37% yield. Mp 187-189 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.1 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.13 (dd, *J* = 7.5 Hz, *J* = 4.9 Hz, 1H), 3.44 (t, *J* = 6.9 Hz, 2H), 2.93-2.90 (m, 4H), 2.46 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 146.9, 144.0, 134.8, 130.7, 123.1, 117.5, 44.0, 28.4, 26.3, 26.2. ESI-MS HRMS calculated for $C_{11}H_{12}NO_3S$ $[M+H]^+$ 238.0532, found 238.0528.

5. Scaled-up reaction.



1a **4** **5a**, 1.49 g, 95% yield

An oven-dried reaction flask (100 mL) was charged with (*E*)-2-phenylethene-1-sulfonyl fluoride (**1a**, 0.93 g, 5.0 mmol), 6,7-dihydroquinolin-8(5*H*)-one (**4**, 1.47 g, 10.0 mmol, 2.0 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (0.29 g, 20 mol%), K_2CO_3 (1.38 g, 1.0 mmol, 2.0 equiv), and MeCN (20 ml). The resulting mixture was stirred at room temperature under air atmosphere for 24 h, The crude products were purified by column chromatography on silica gel (Petroleum ether / ethyl acetate = 2 : 1 (v / v) as eluent) to give **5a** as white solid, 1.49 g, 95% yield.

6. Reference

[1] H.-L. Qin, Q. Zheng, G. A. L. Bare, P. Wu and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2016, **55**, 14155−14158.

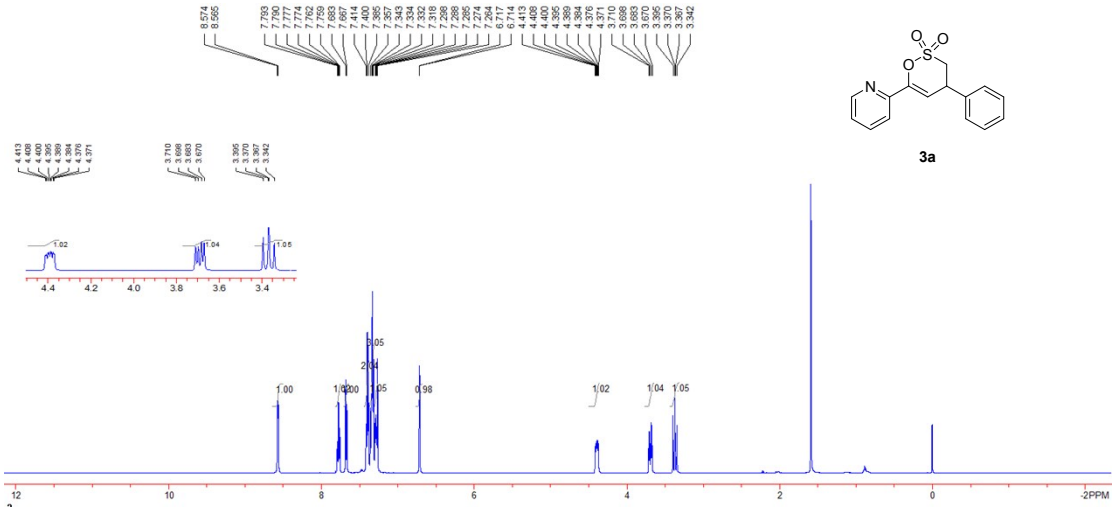
[2] G.-F. Zha, Q. Zheng, J. Leng, P. Wu, H.-L. Qin and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2017, **56**, 4849-4852.

[3] D. Bhuniya, R. Mukkavilli, R. Shivahare, D. Launay, R.T. Dere, A. Deshpande, A. Verma, P. Vishwakarma, M. Moger, A. Pradhan, H. Pati, V.S. Gopinath, S. Gupta, S. K. Puri and D. Martin, *Eur. J. Med. Chem*. 2015, **102**, 582-593.

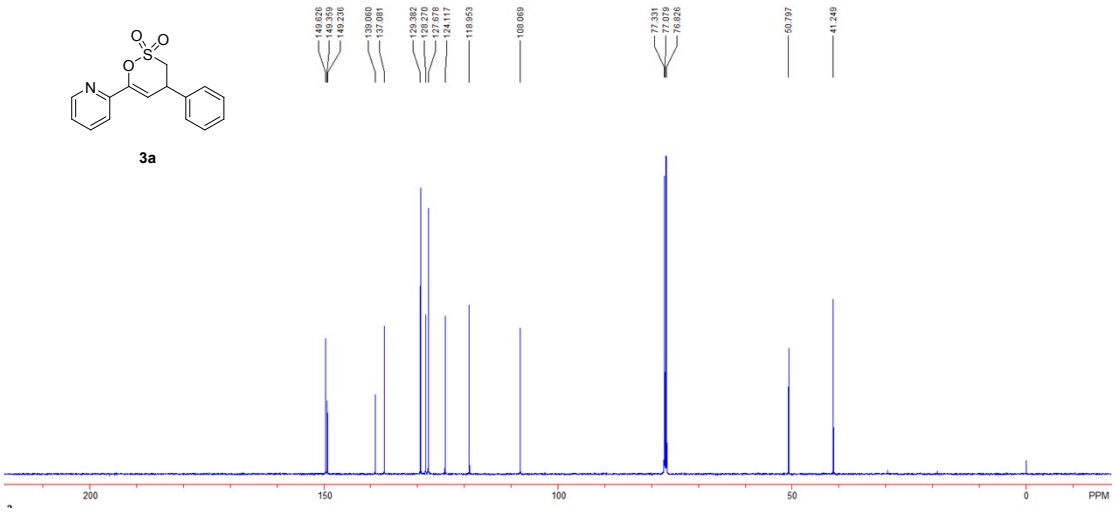
[4] M. Y. Fosso, H. LeVine 3rd, K. D. Green, O. V. Tsodikov and S. Garneau-Tsodikova, *Org. Biomol. Chem*., 2015, **13**, 9418-9426.

7. Spectra

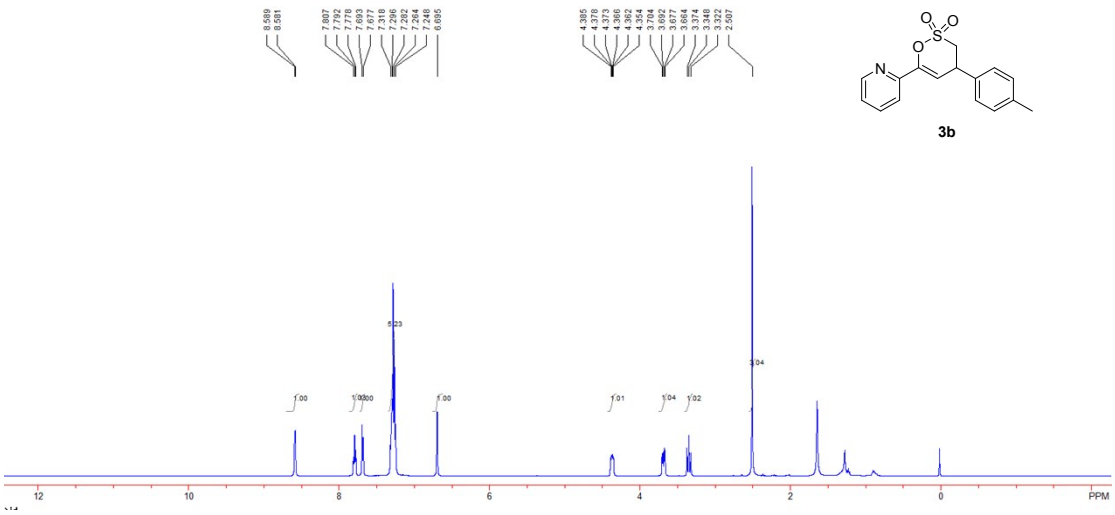
3a, ^{1}H NMR, 500 MHz, $CDCl_3$



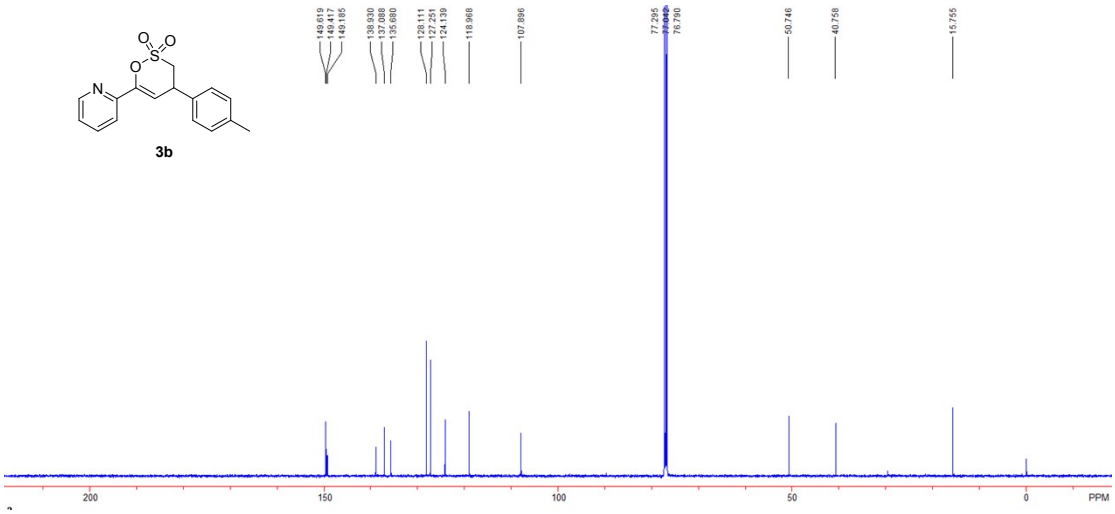
3a, ^{13}C NMR, 126 MHz, $CDCl_3$



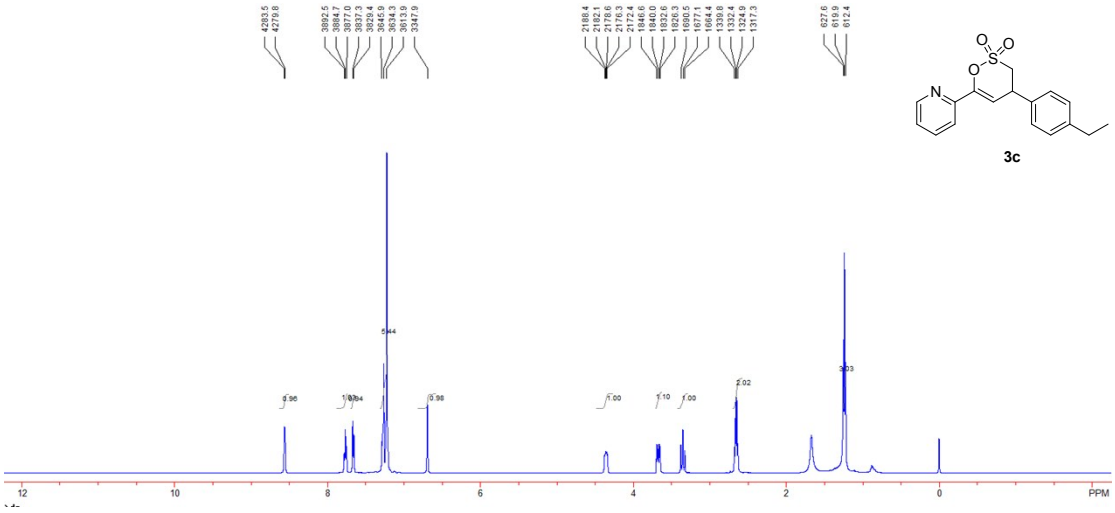
3b, ^{1}H NMR, 500 MHz, $CDCl_3$



3b, ^{13}C NMR, 126 MHz, $CDCl_3$



3c, ^{1}H NMR, 500 MHz, $CDCl_3$



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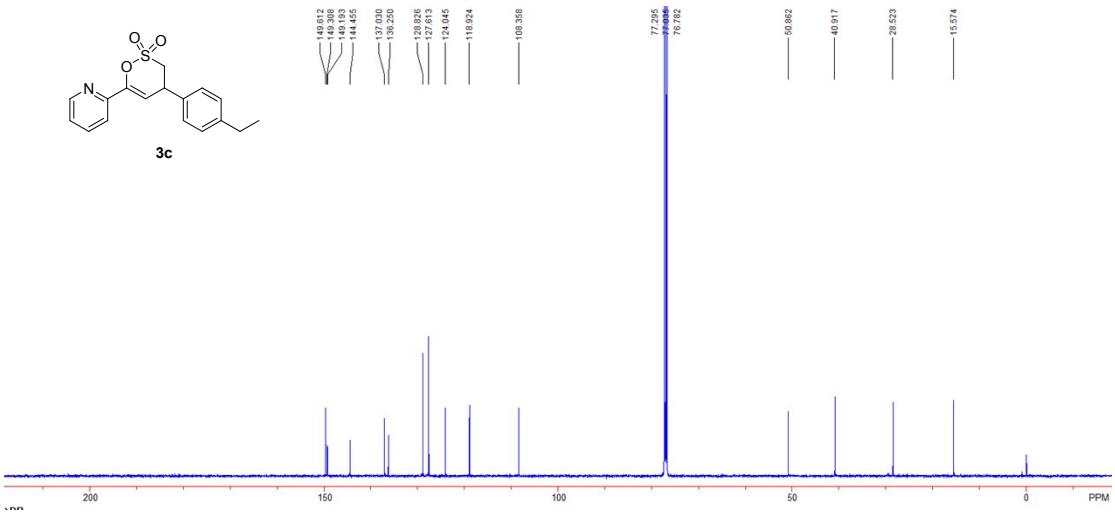

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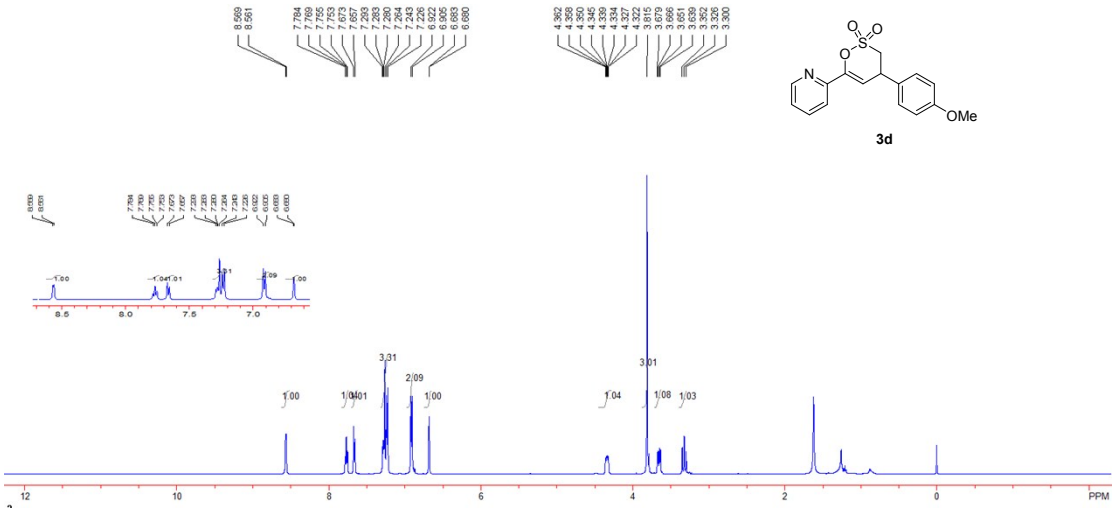
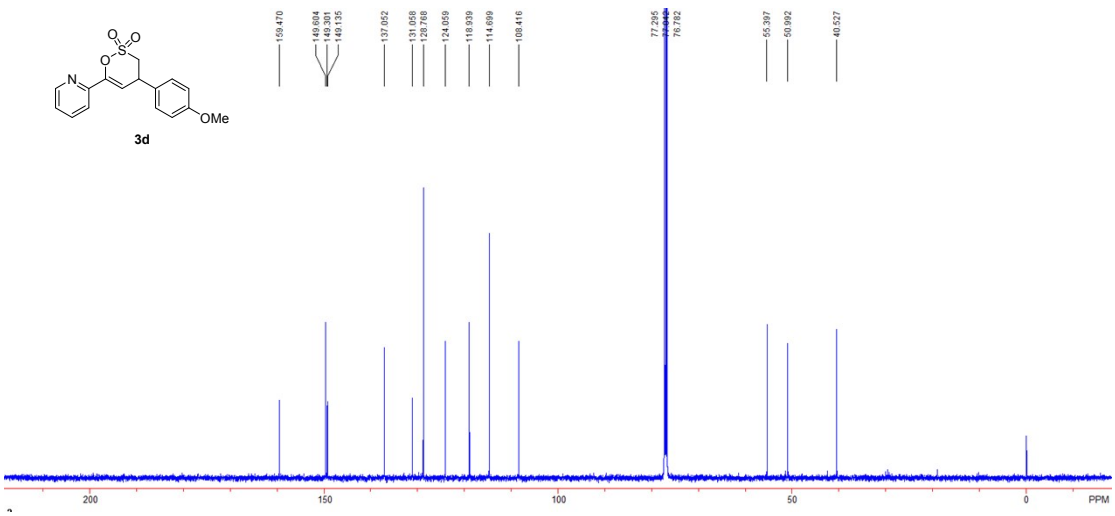


3d, ^{13}C NMR, 126 MHz, $CDCl_3$



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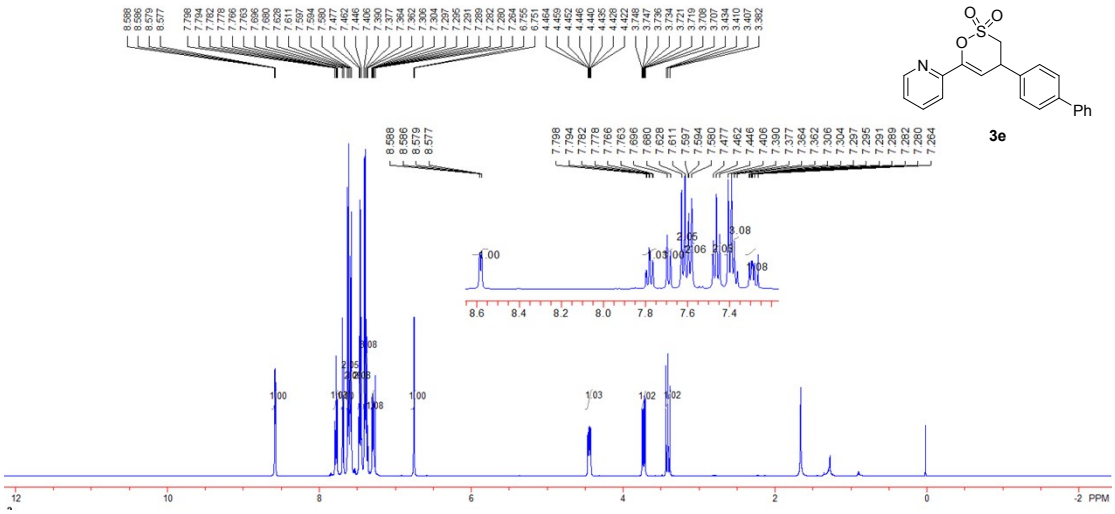

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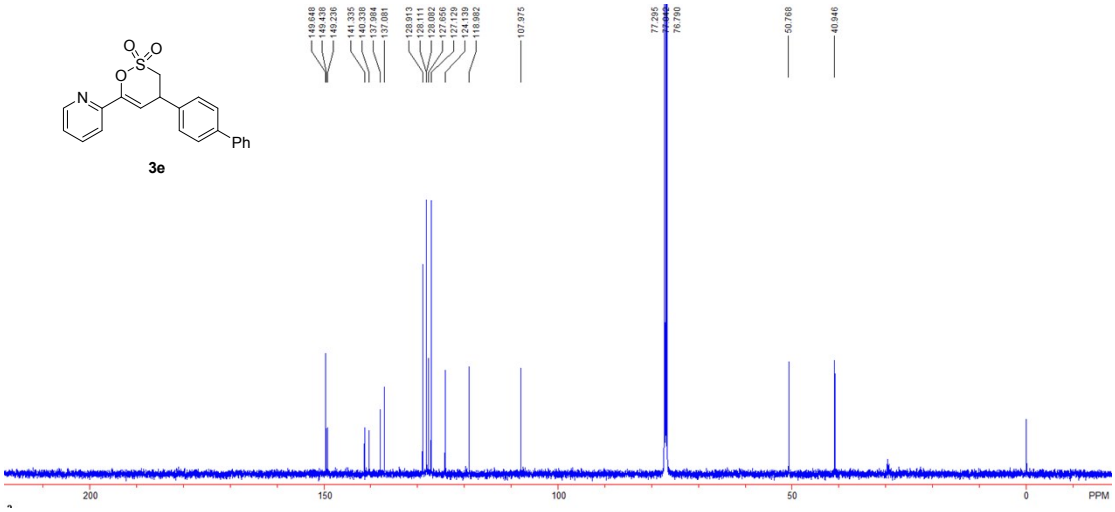
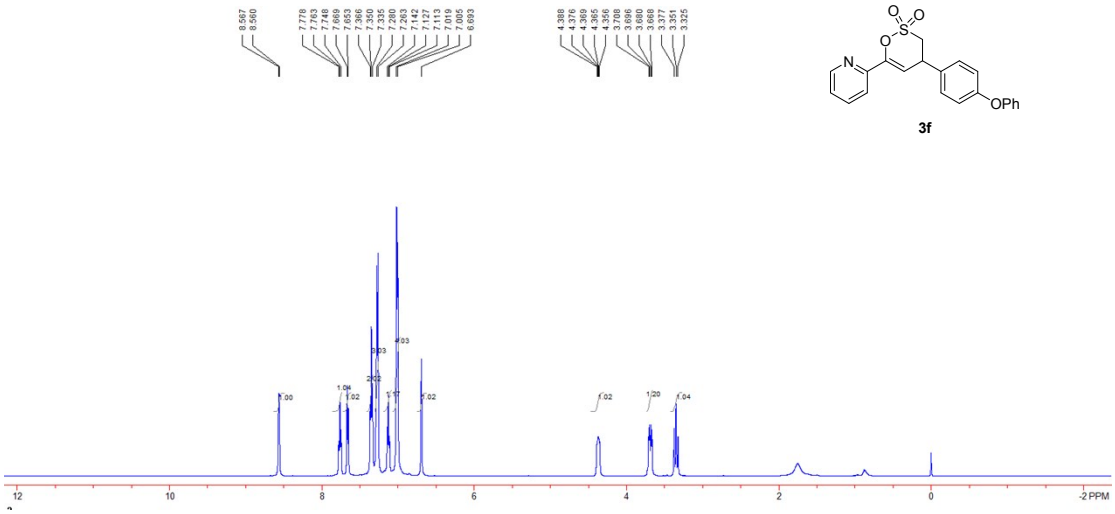
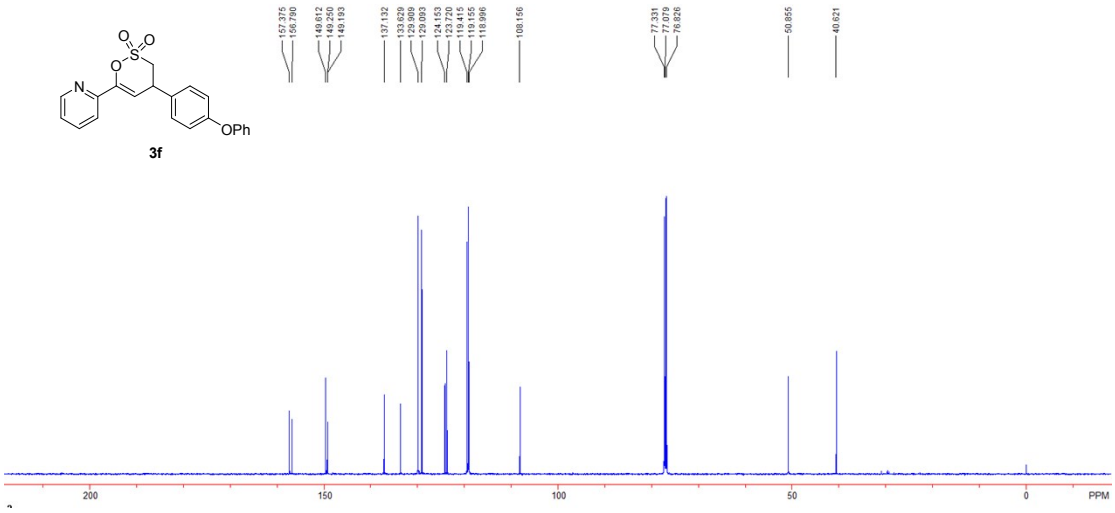


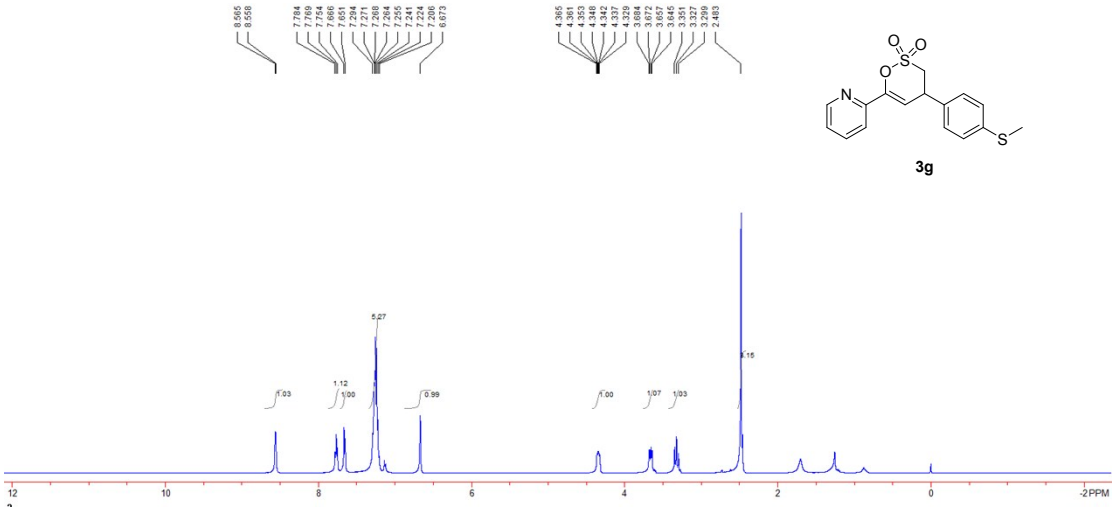
3f, ^{1}H NMR, 500 MHz, $CDCl_3$



3f, ^{13}C NMR, 126 MHz, $CDCl_3$



3g, ^{1}H NMR, 500 MHz, $CDCl_3$



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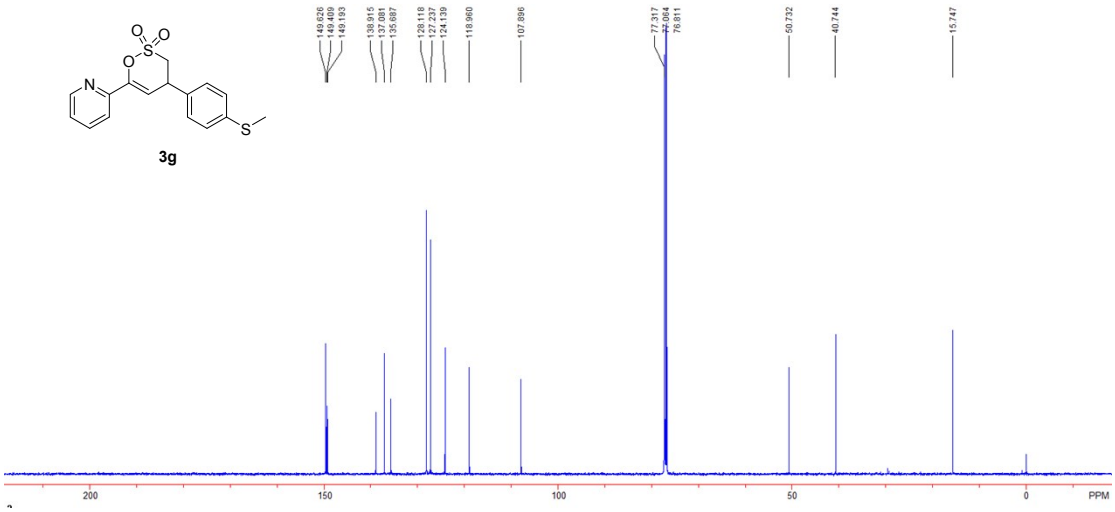
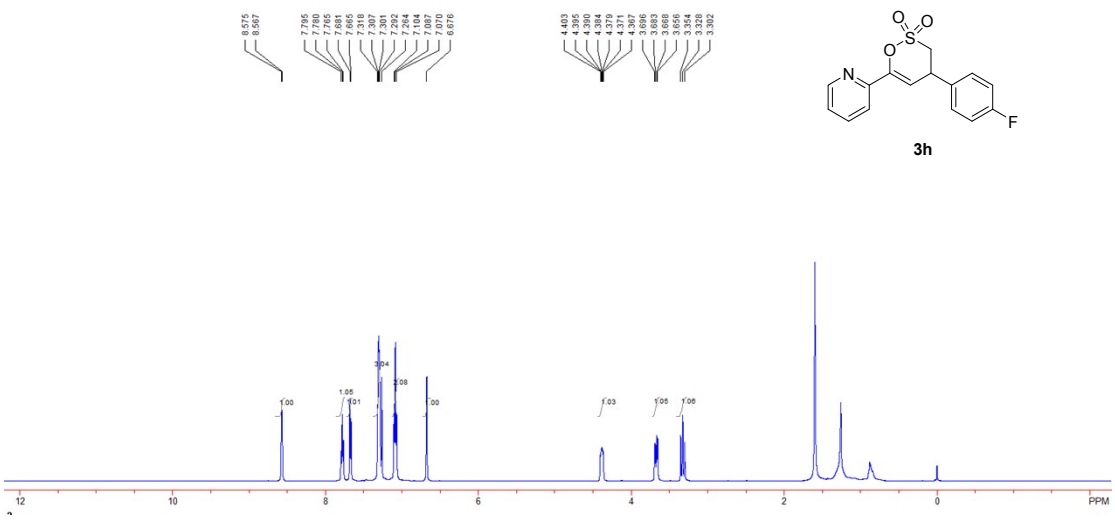
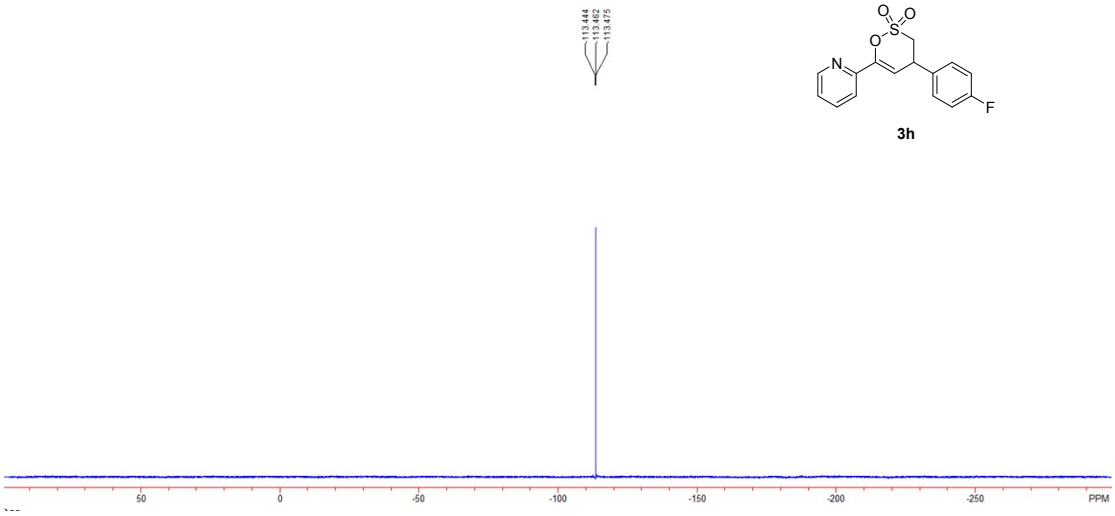


3h, ^{1}H NMR, 500 MHz, $CDCl_3$



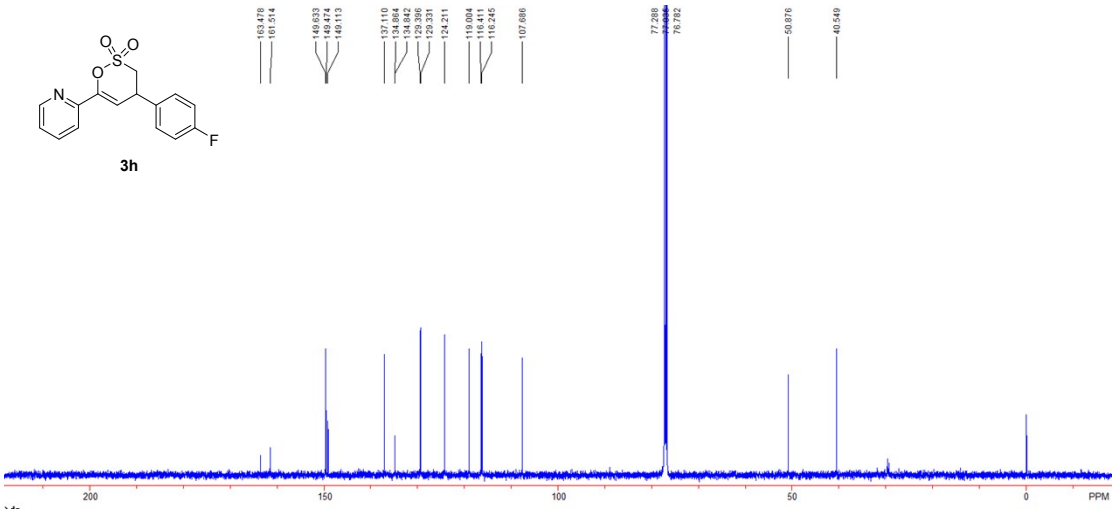
3h

3h, ^{19}F NMR, 376 MHz, $CDCl_3$



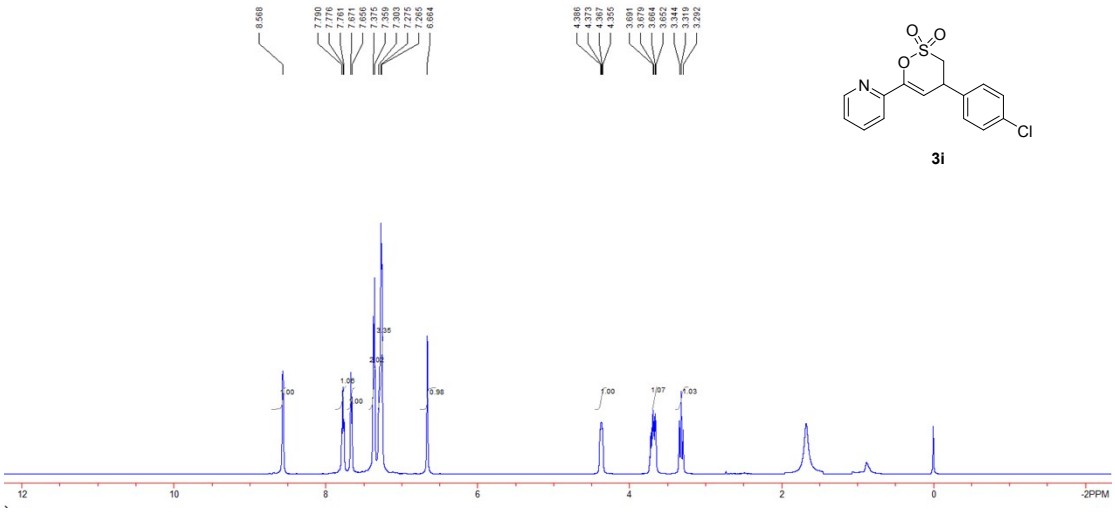
3h

3h, ^{13}C NMR, 126 MHz, $CDCl_3$



3h

3i, ^{1}H NMR, 500 MHz, $CDCl_3$



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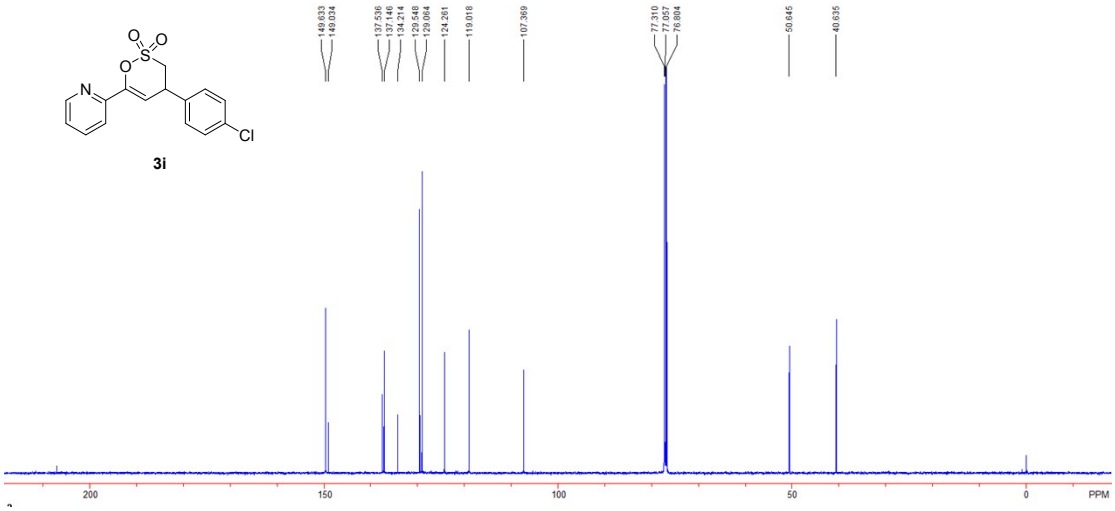
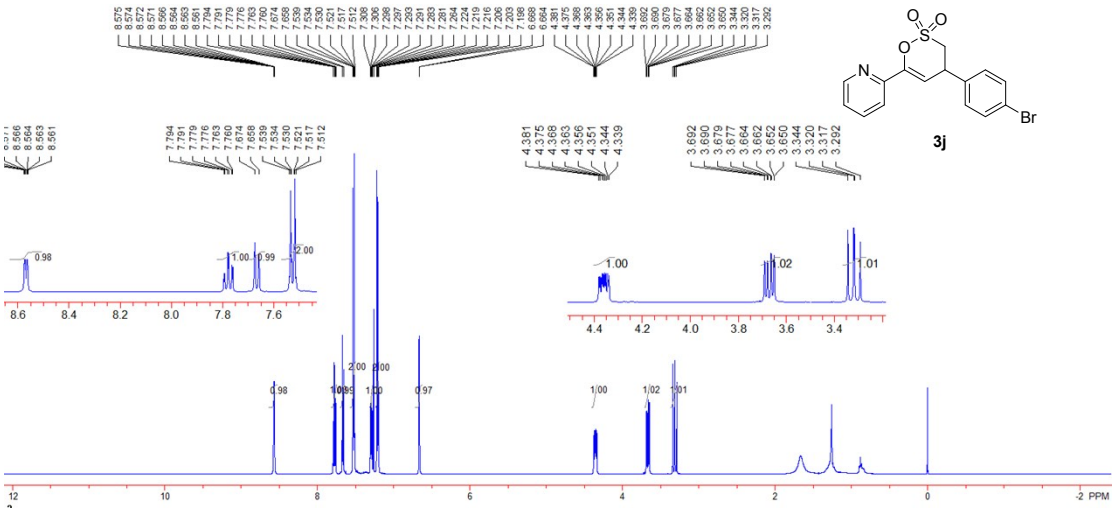


3j, ^{1}H NMR, 500 MHz, $CDCl_3$



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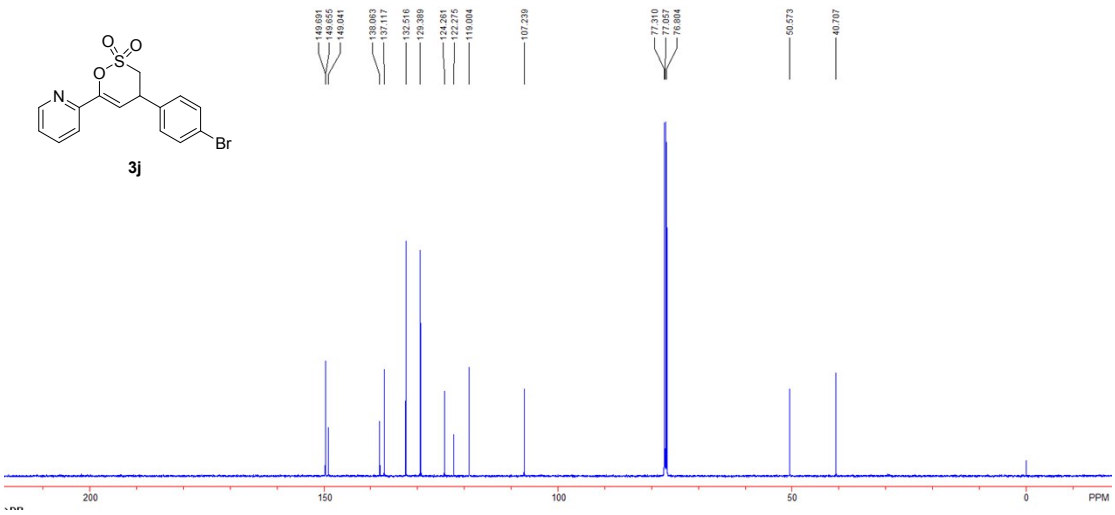

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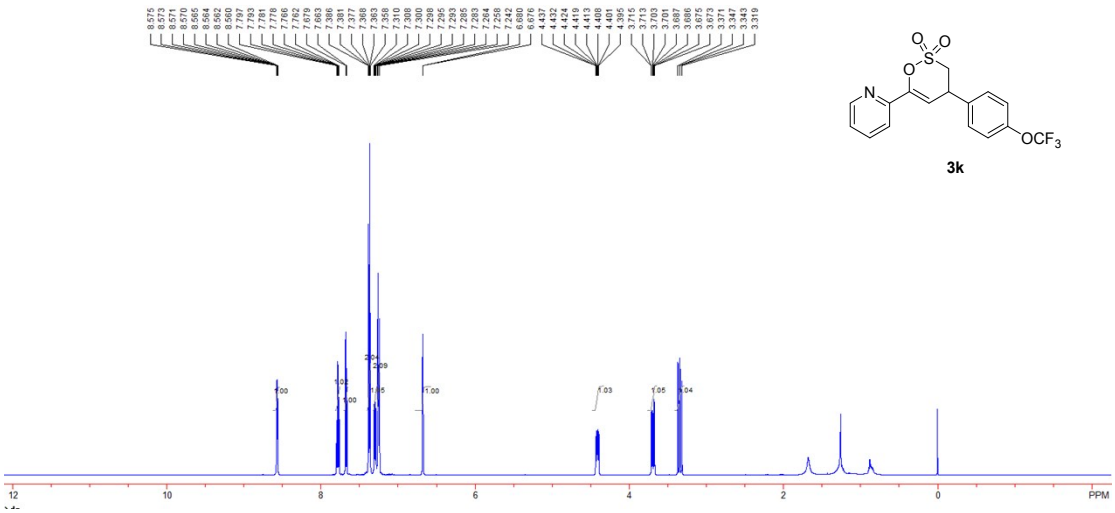
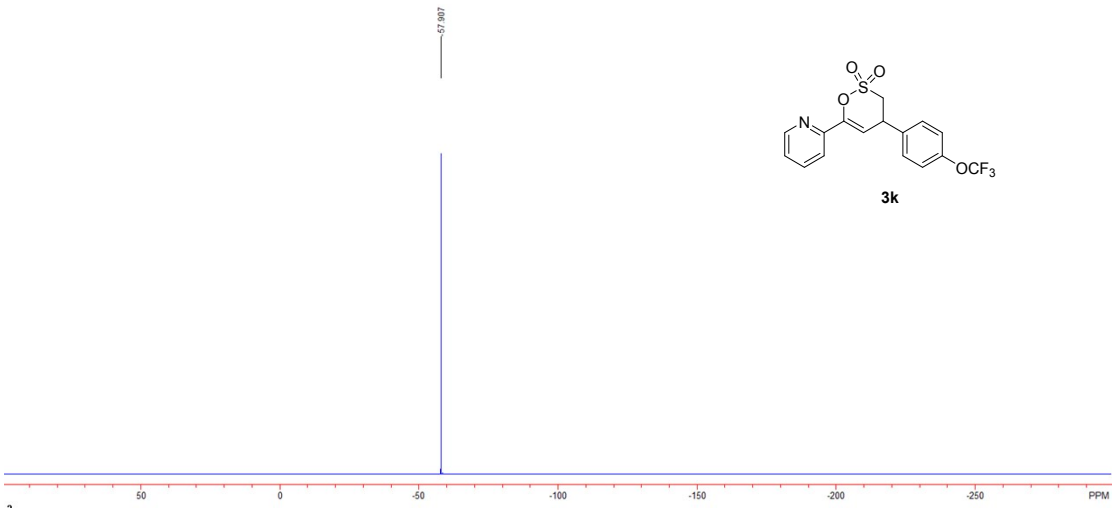
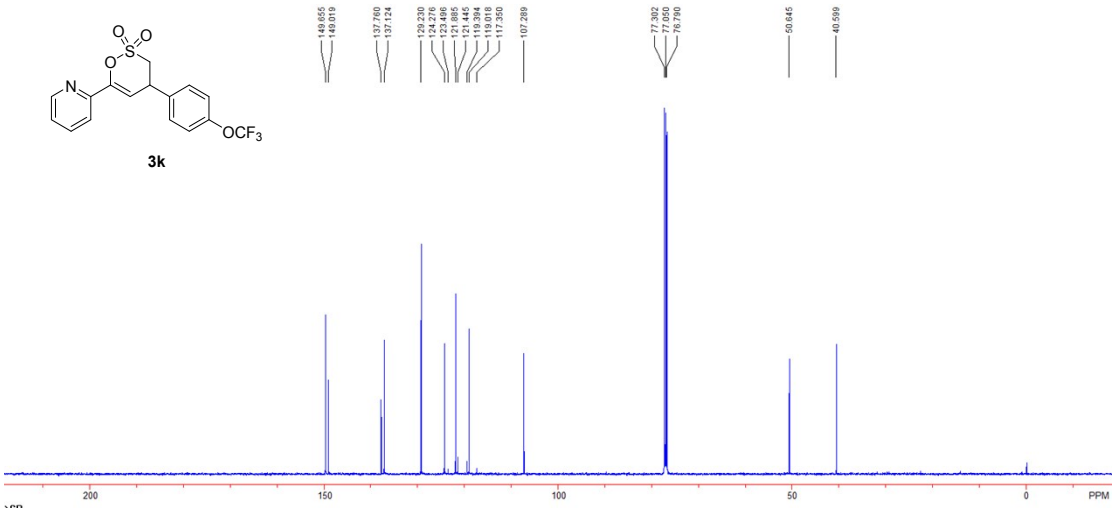


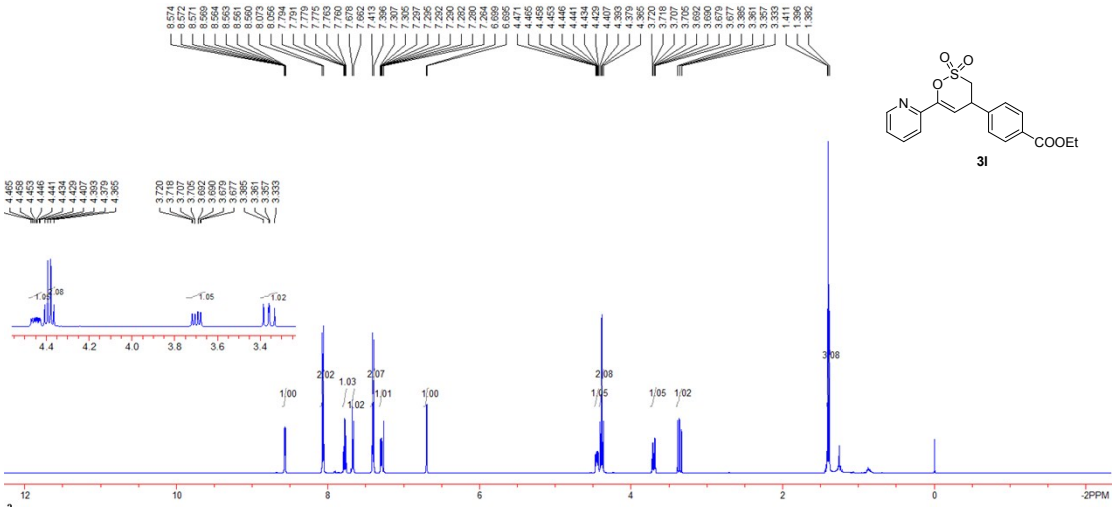
3k, ^{19}F NMR, 376 MHz, $CDCl_3$



3k, ^{13}C NMR, 126 MHz, $CDCl_3$



3l, ^{1}H NMR, 500 MHz, $CDCl_3$



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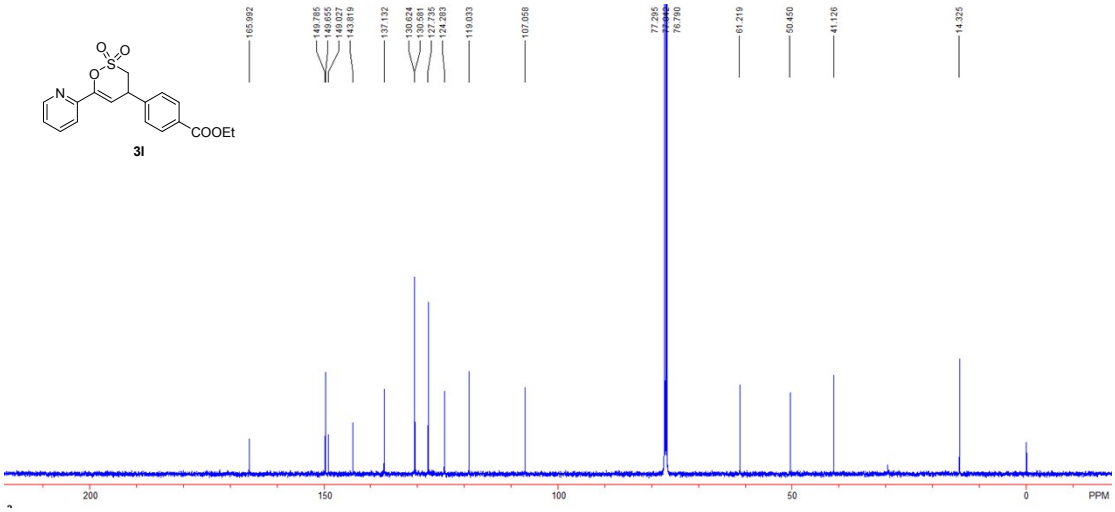

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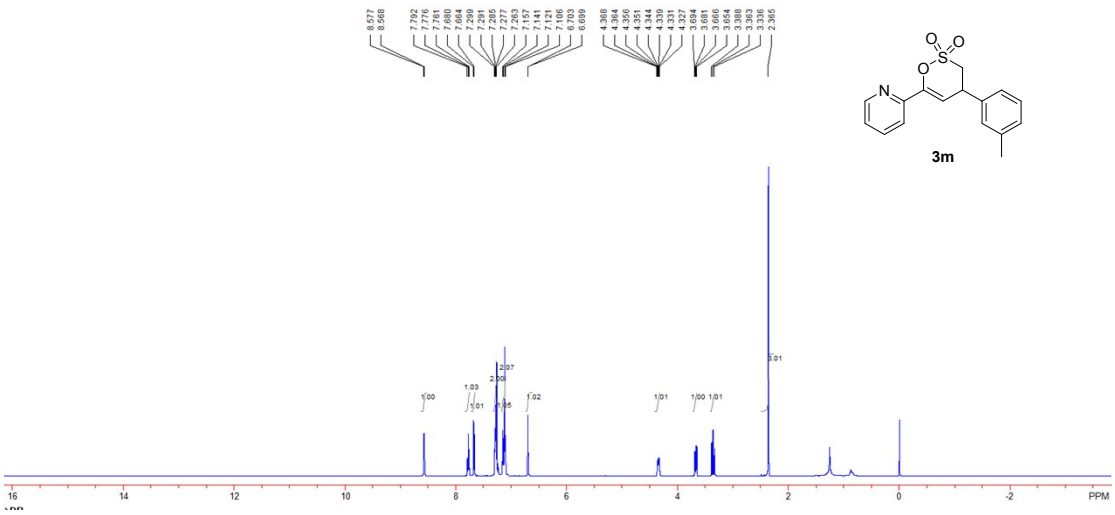

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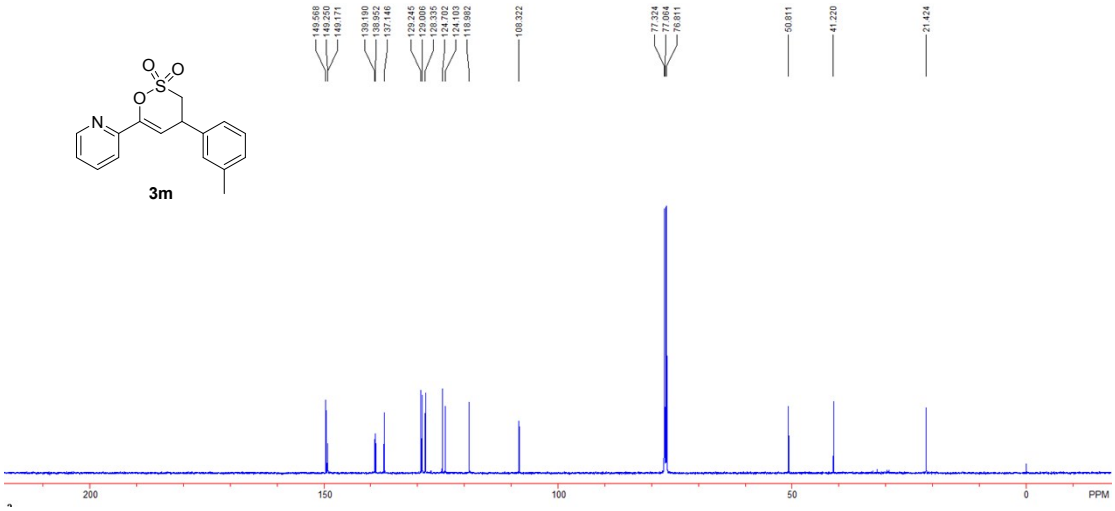

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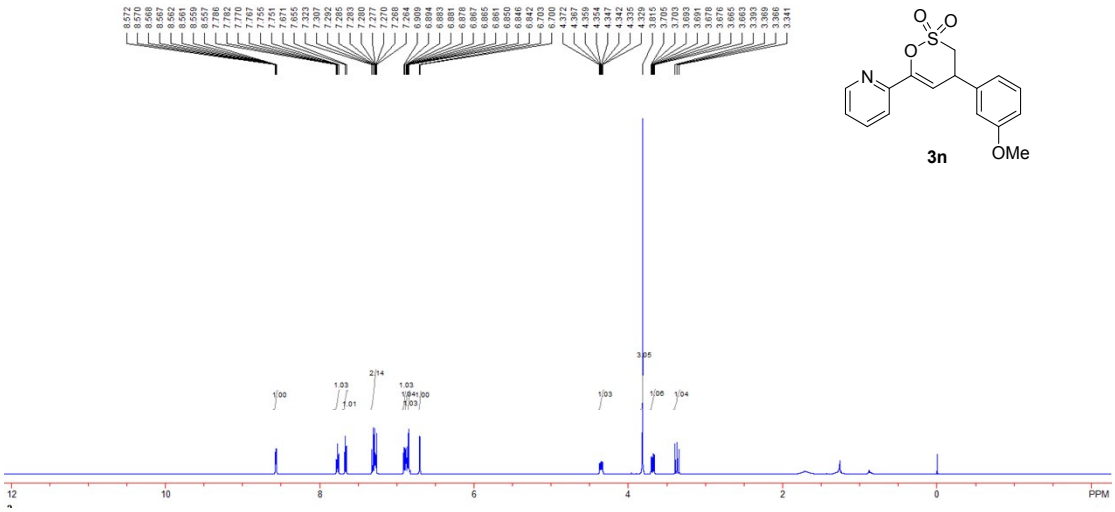

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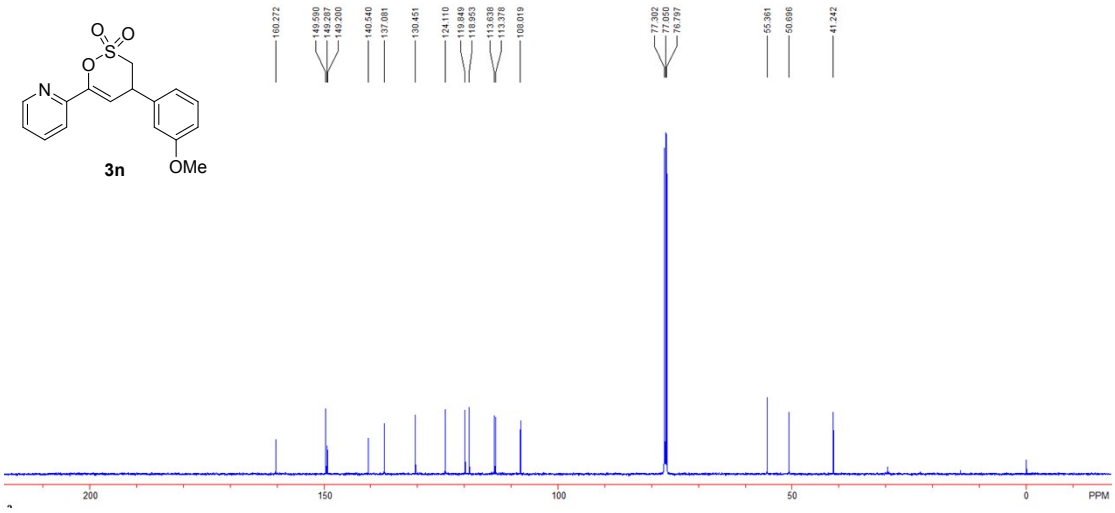

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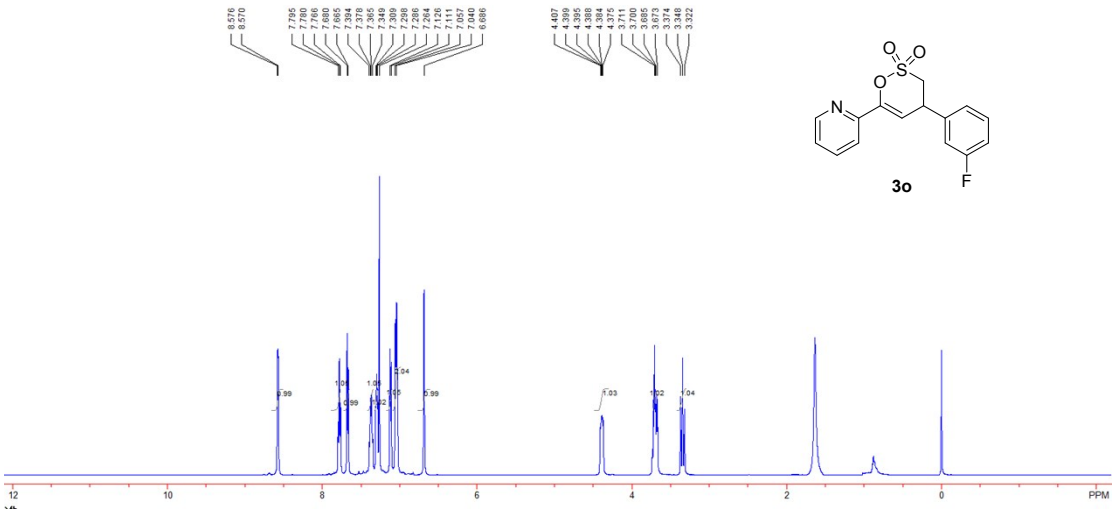
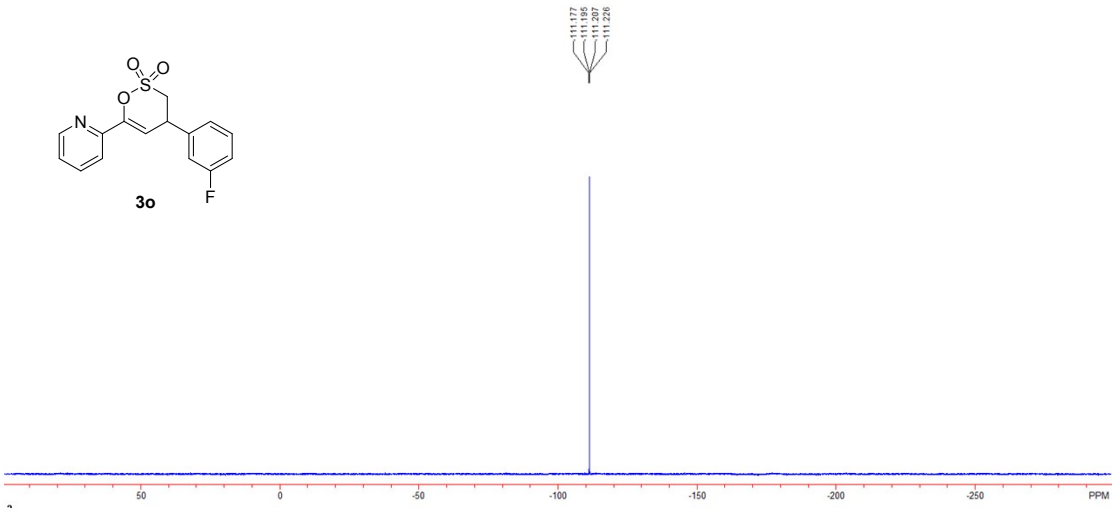


3o, ^{19}F NMR, 376 MHz, $CDCl_3$



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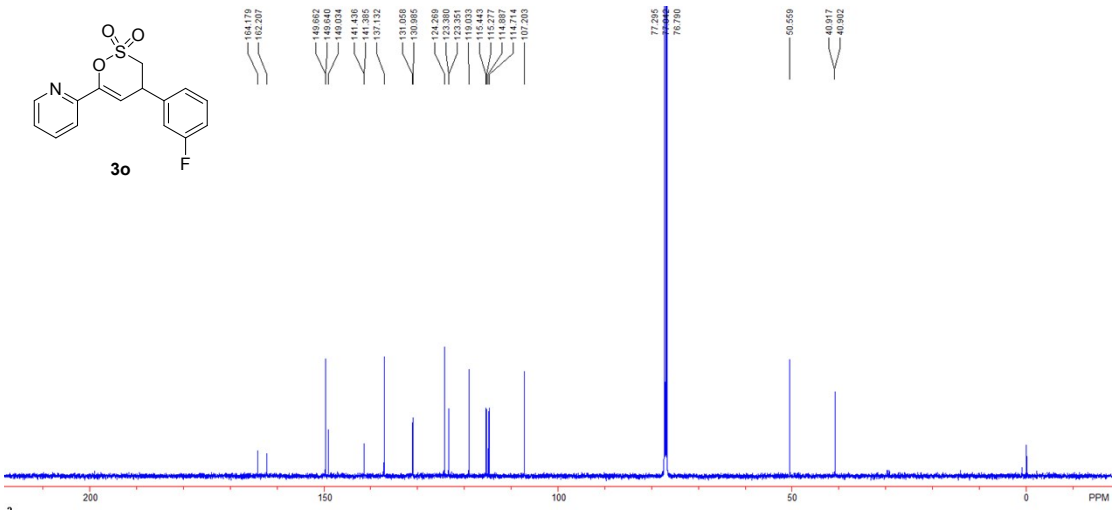

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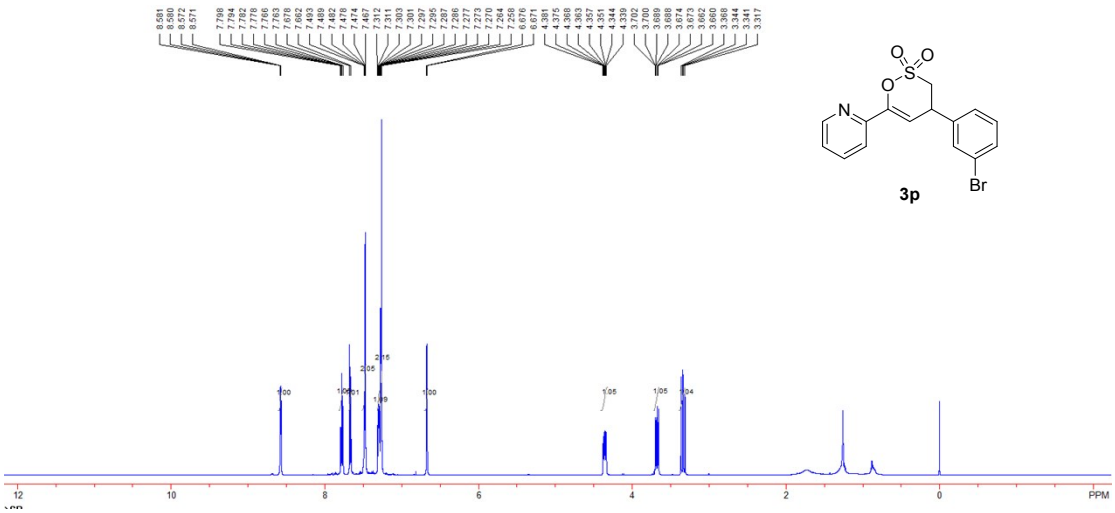

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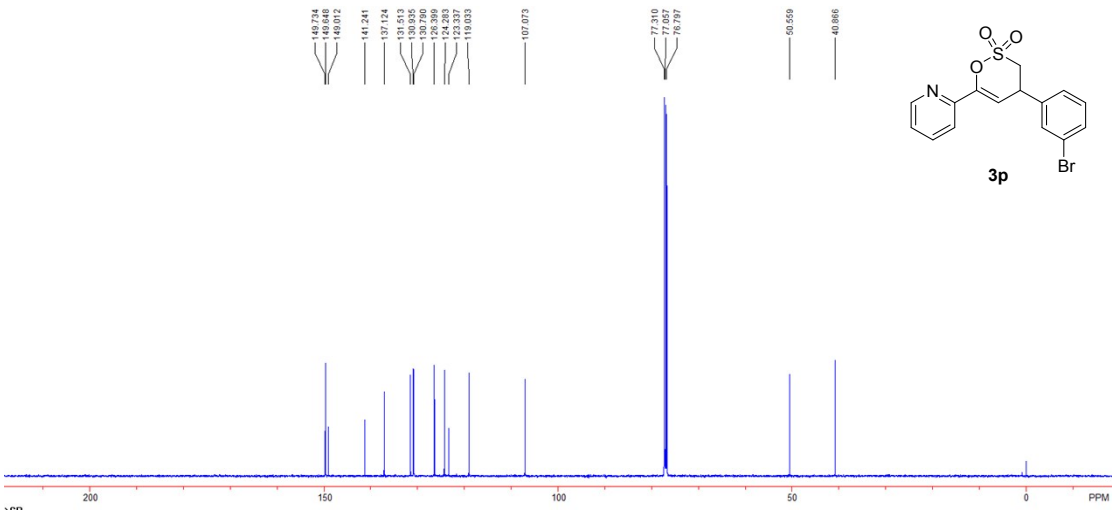

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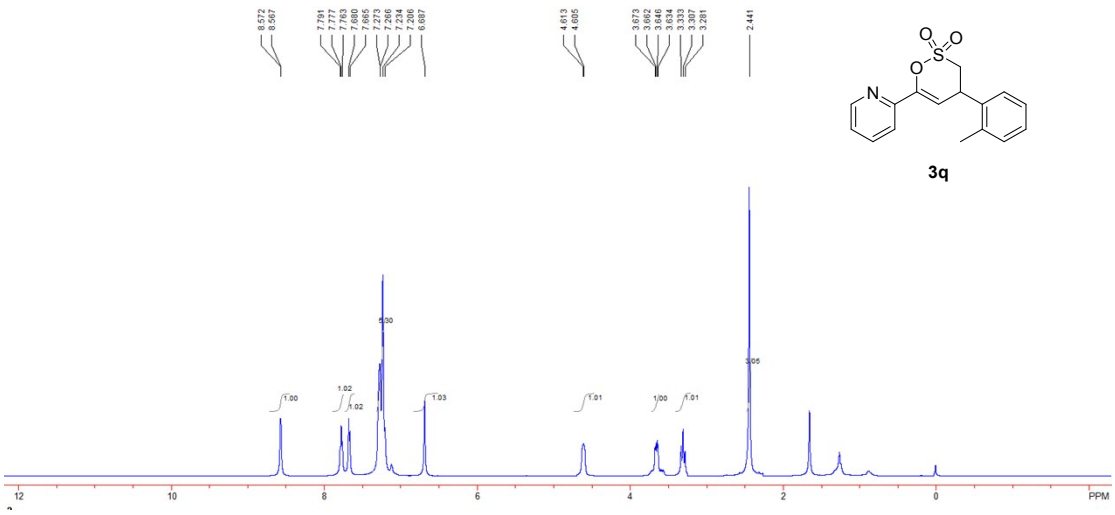

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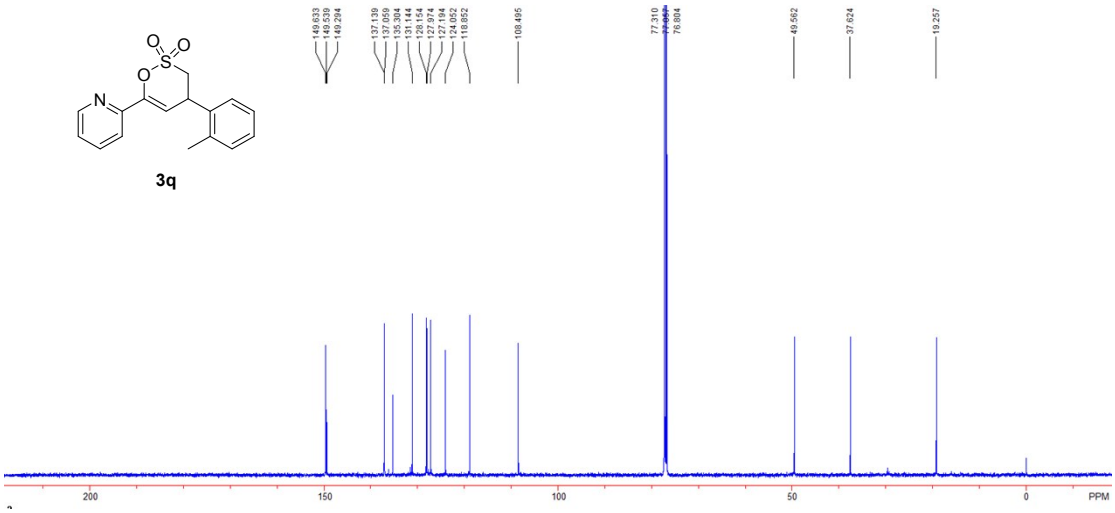

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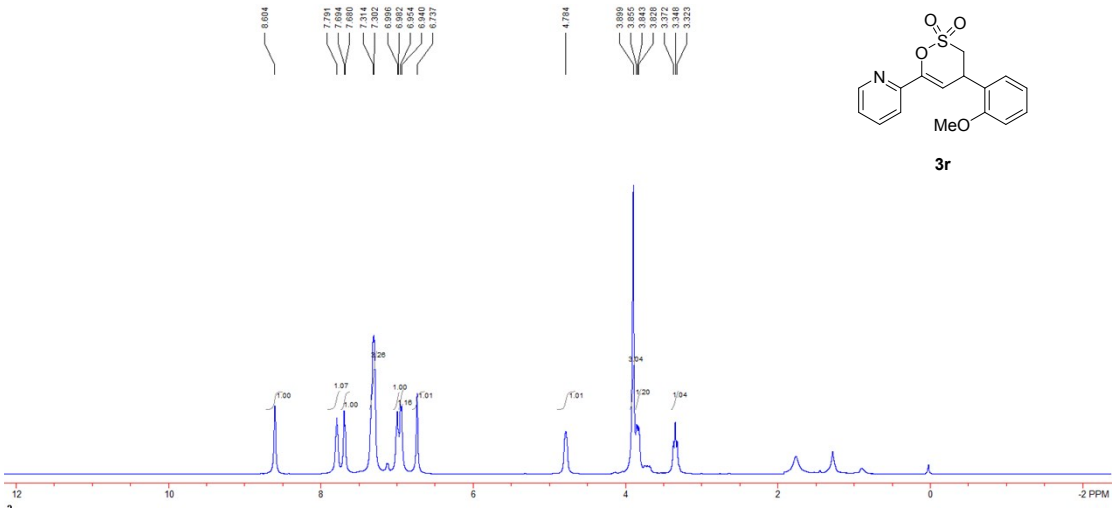

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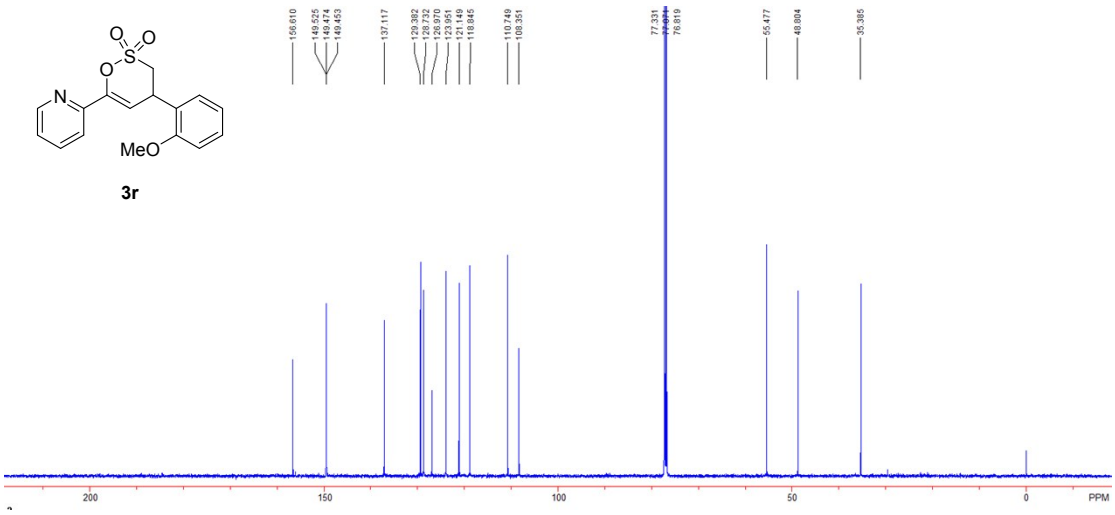

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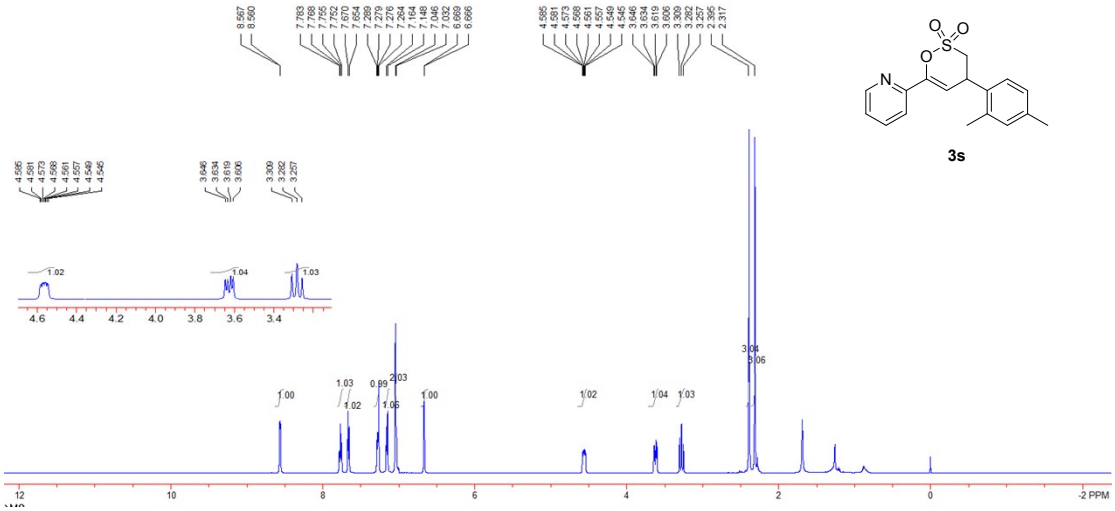

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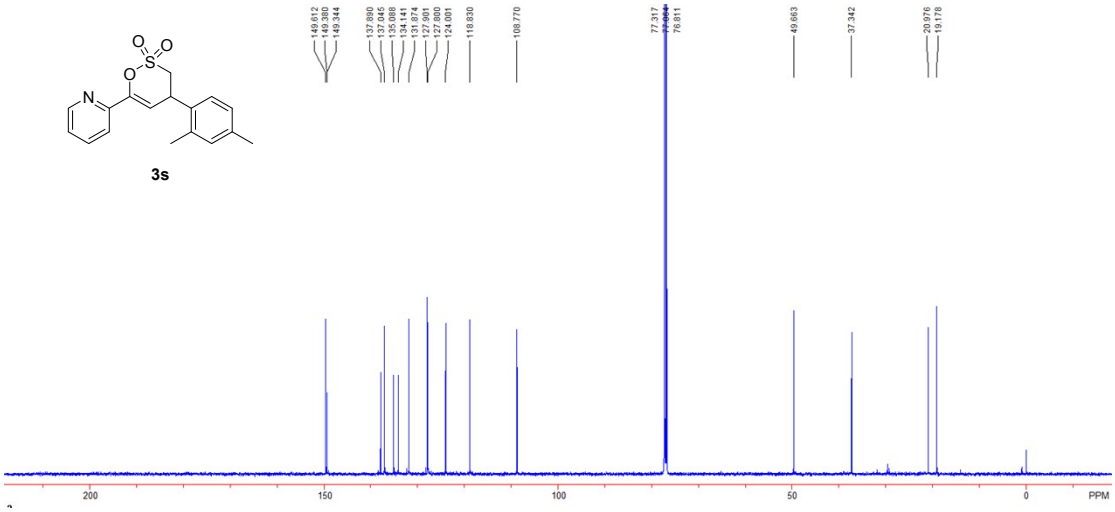

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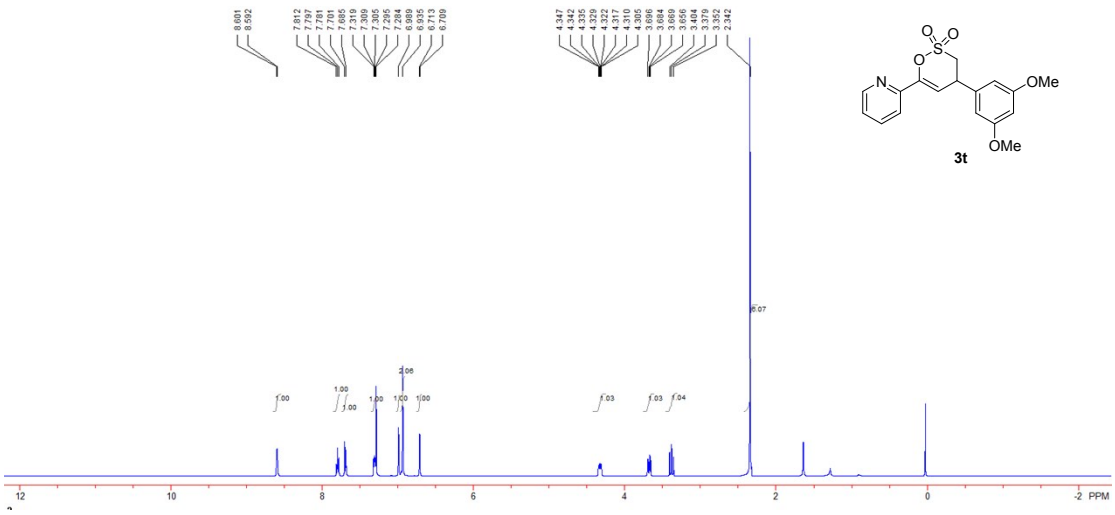
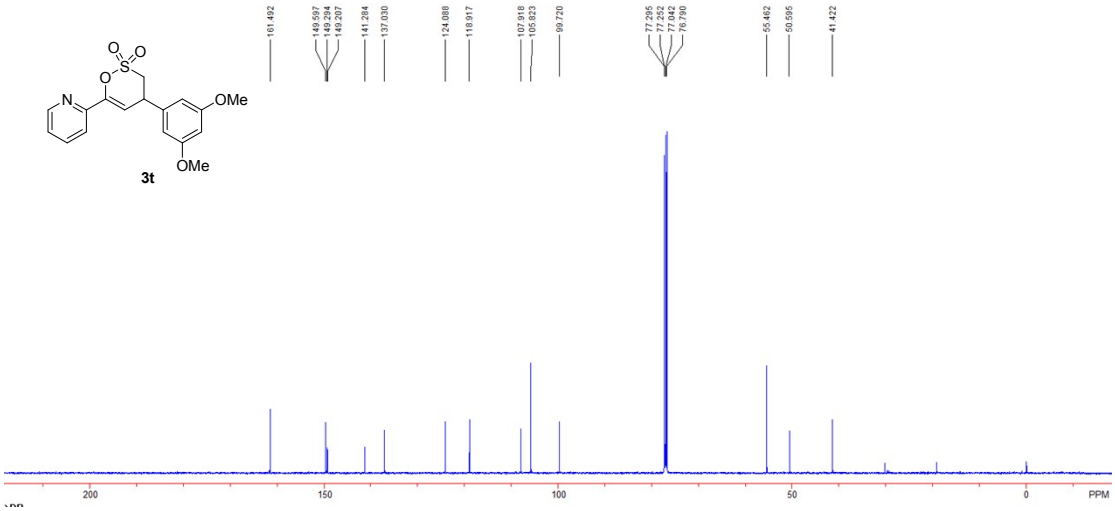


3t, ^{13}C NMR, 126 MHz, $CDCl_3$



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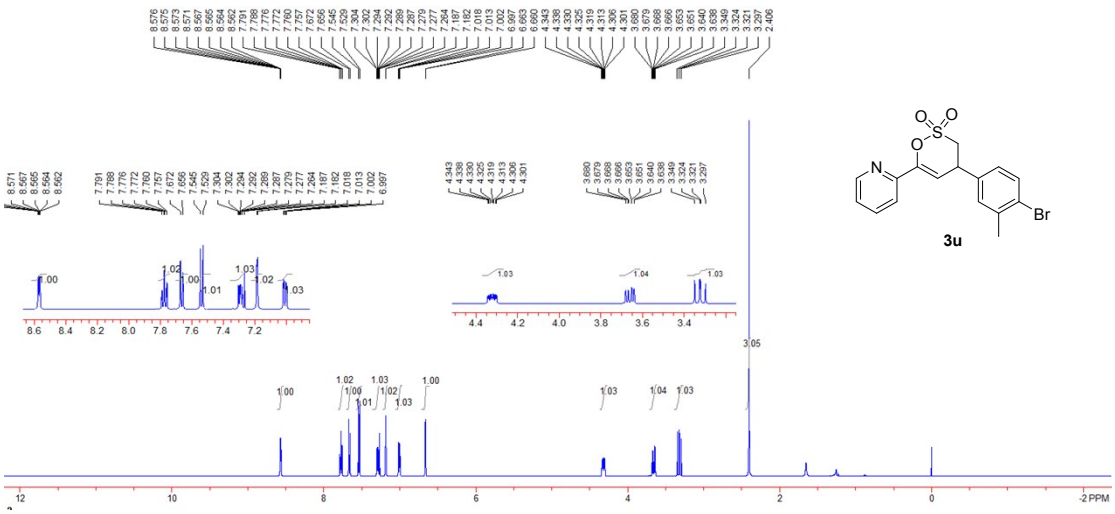

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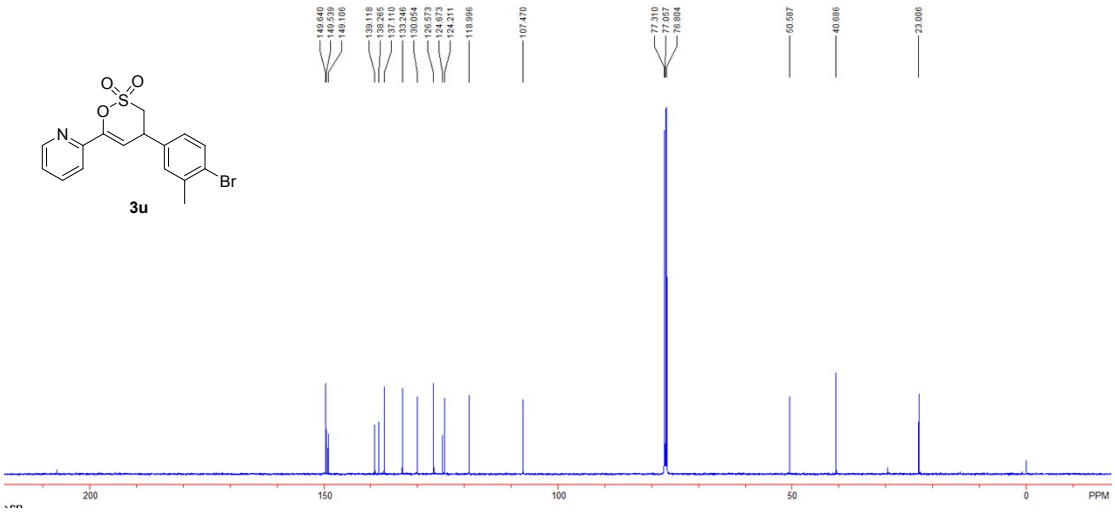

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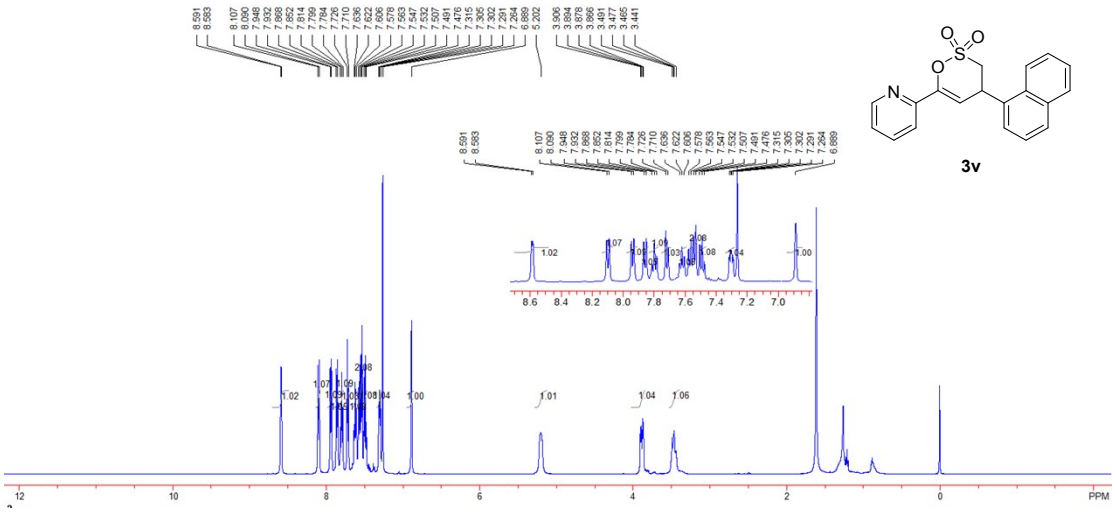

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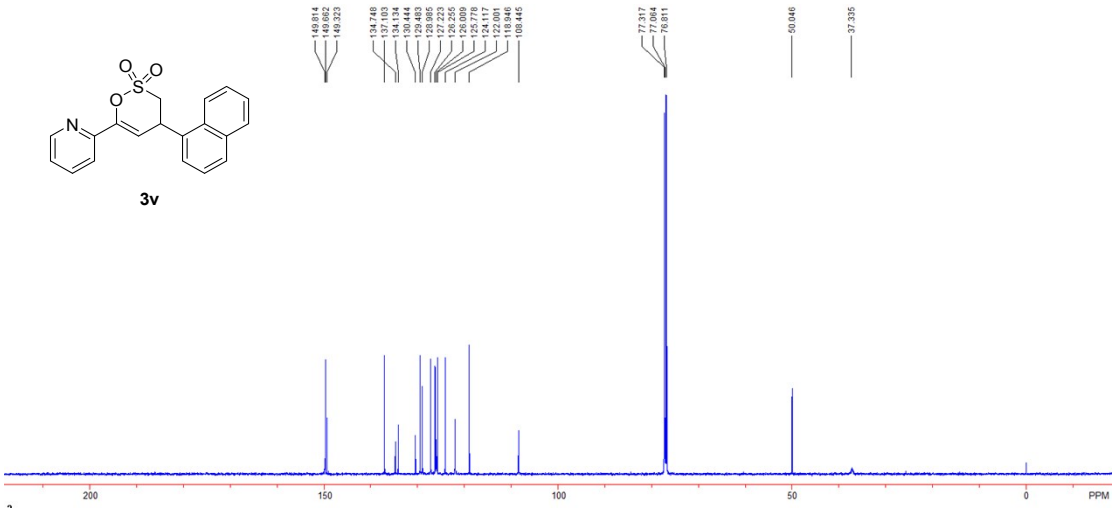

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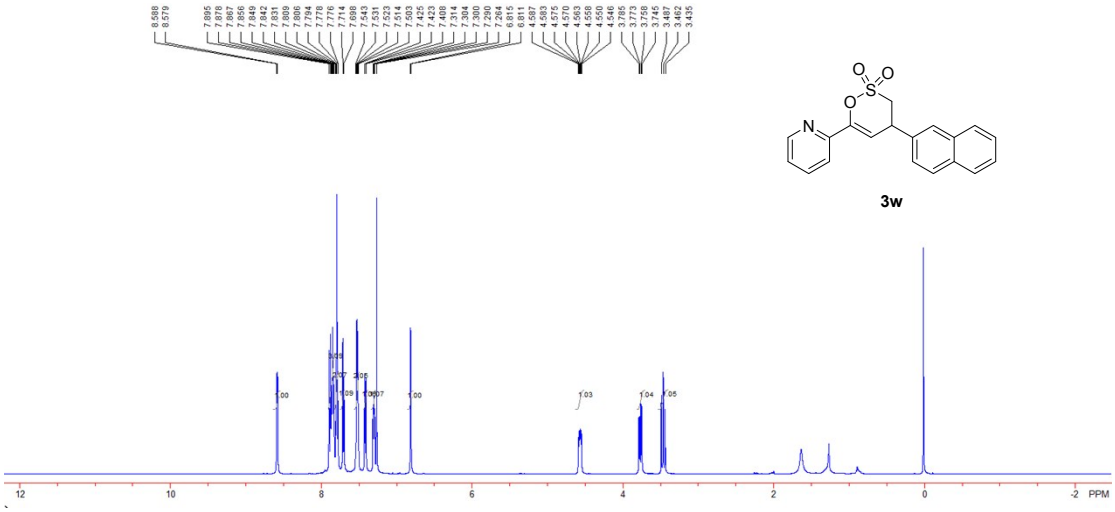

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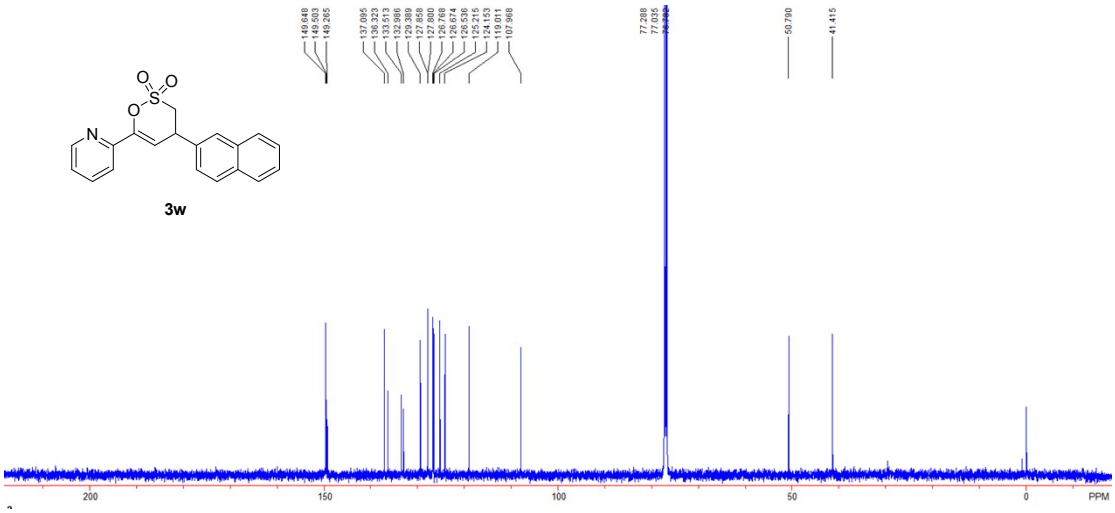

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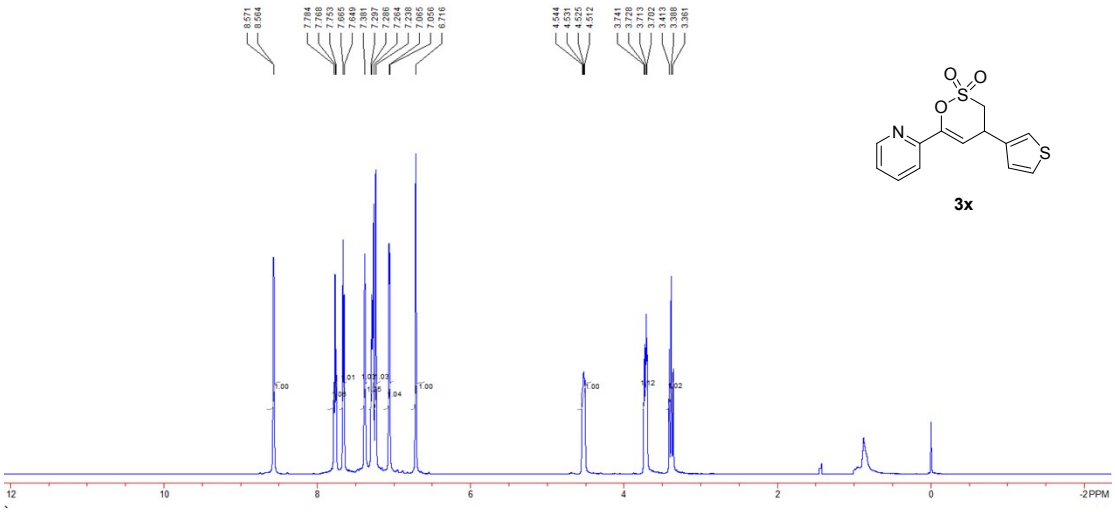
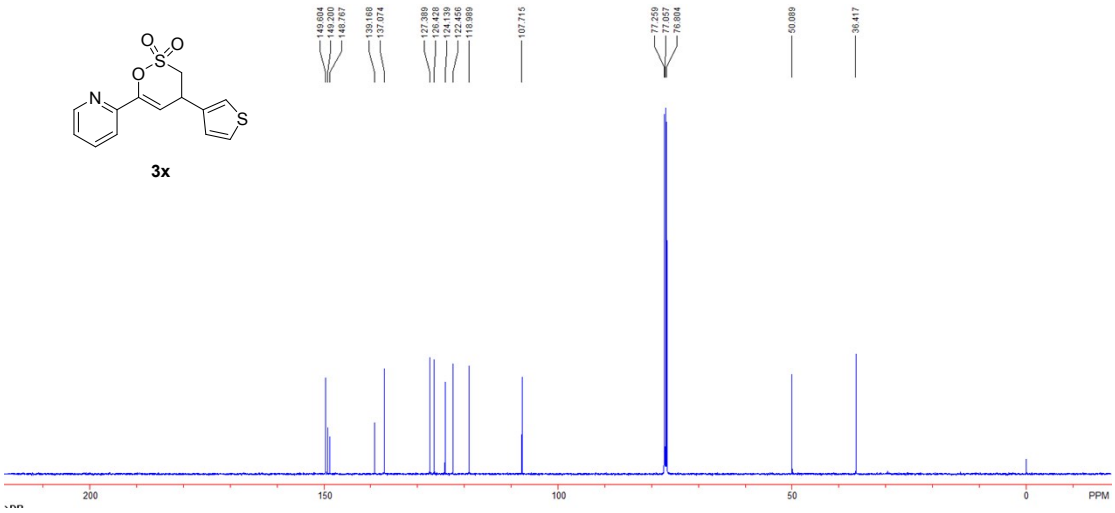
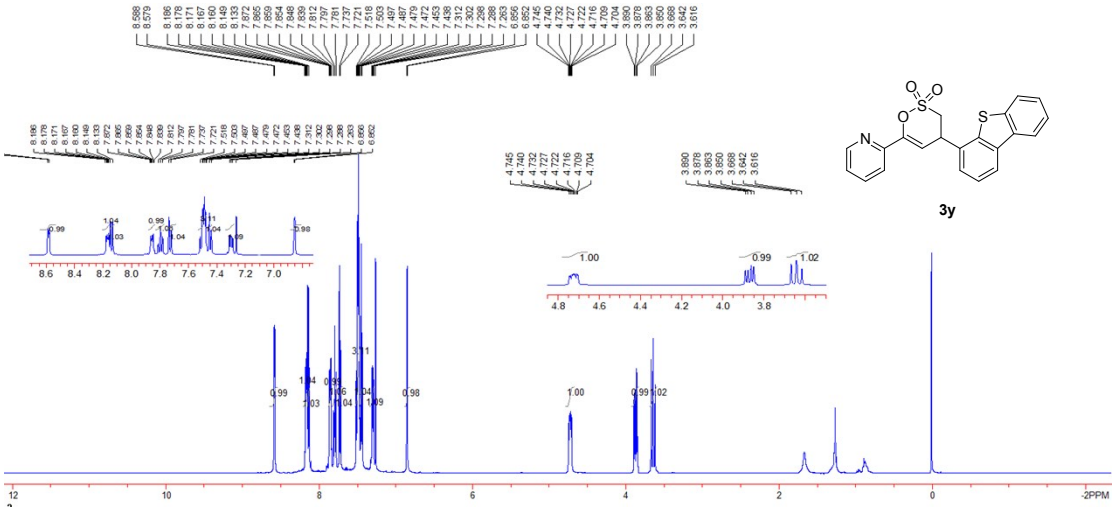


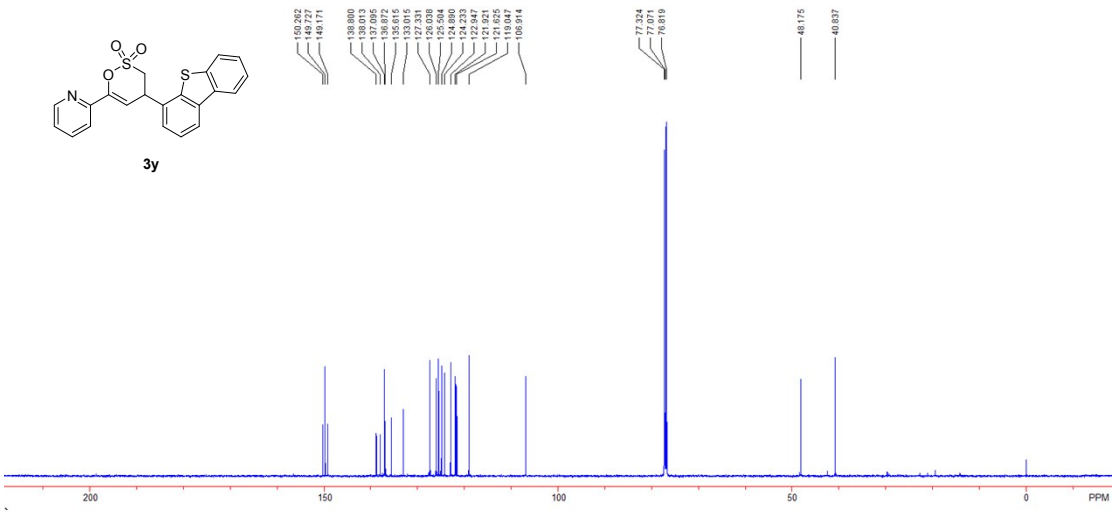
3x, ^{13}C NMR, 126 MHz, $CDCl_3$



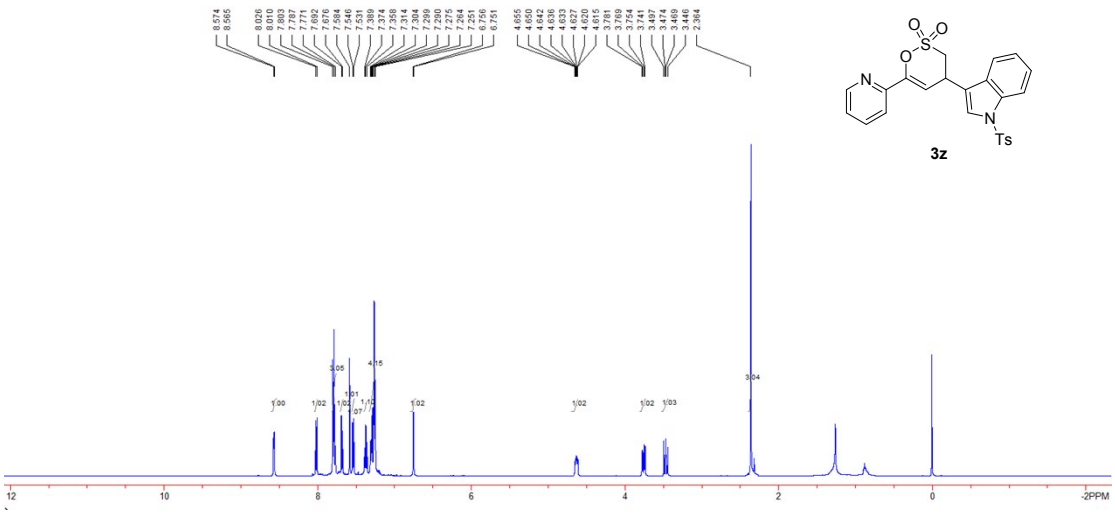
3y, ^{1}H NMR, 500 MHz, $CDCl_3$



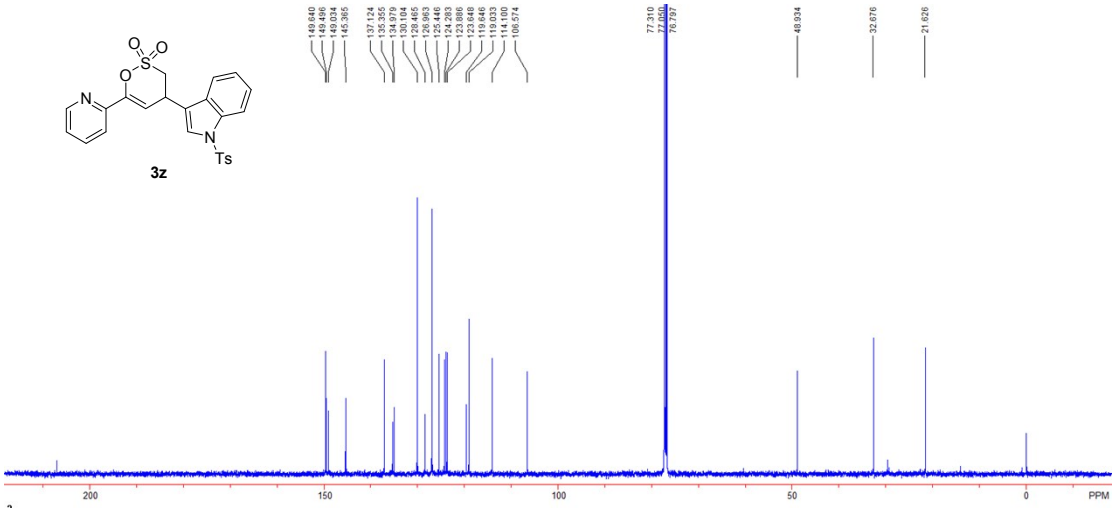
3y, ^{13}C NMR, 126 MHz, $CDCl_3$



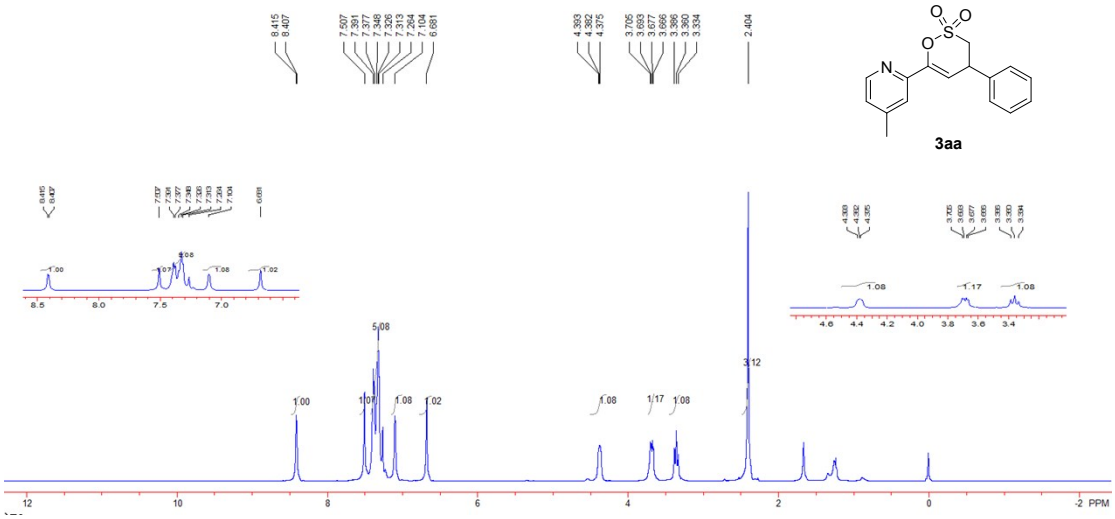
3z, ^{1}H NMR, 500 MHz, $CDCl_3$



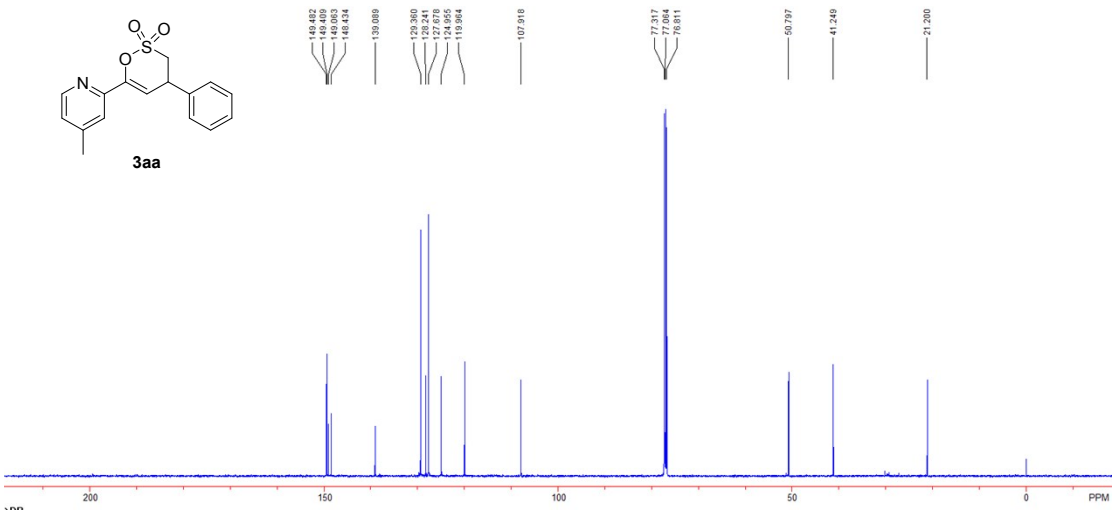
3z, ^{13}C NMR, 126 MHz, $CDCl_3$



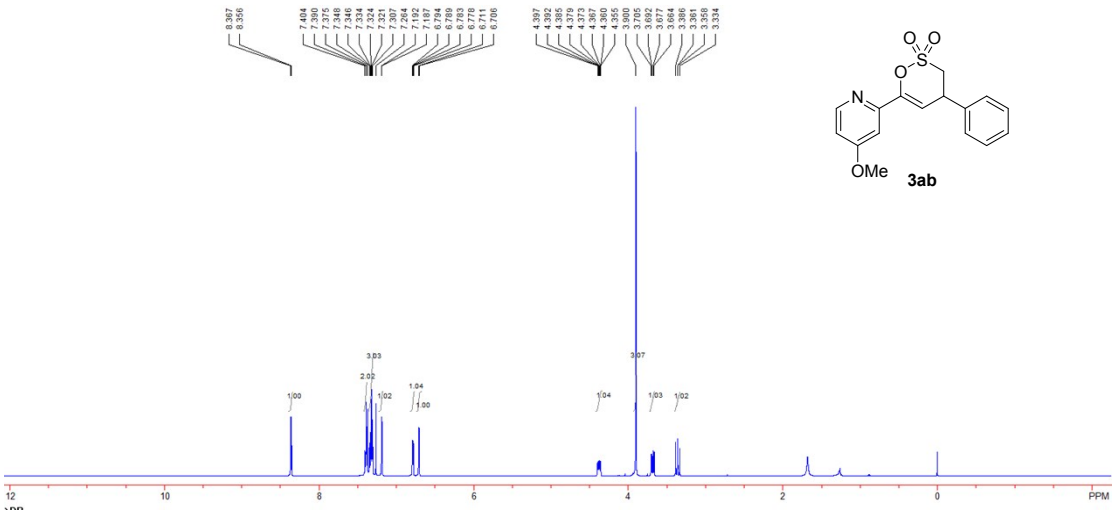
3aa, ^{1}H NMR, 500 MHz, $CDCl_3$



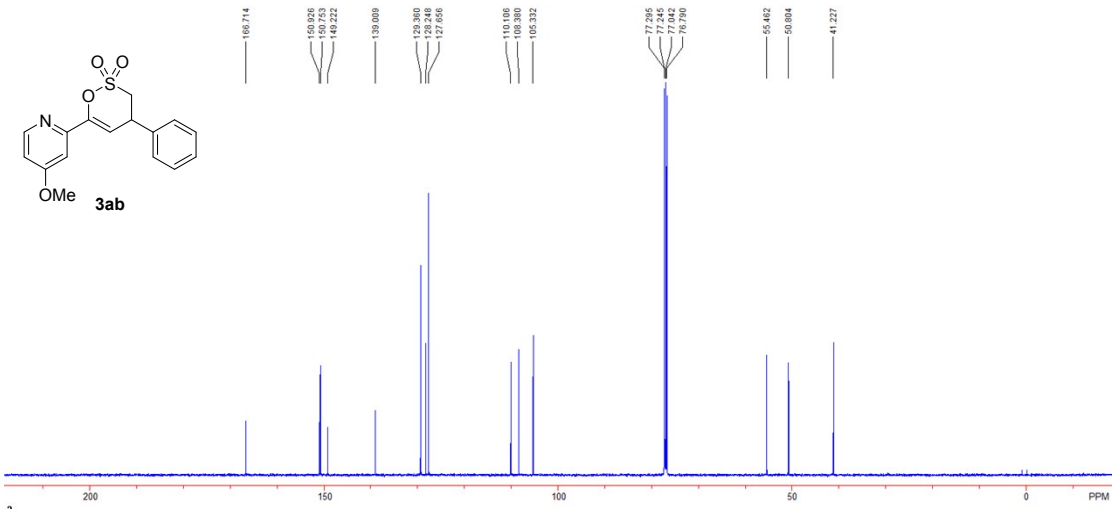
3aa, ^{13}C NMR, 126 MHz, $CDCl_3$



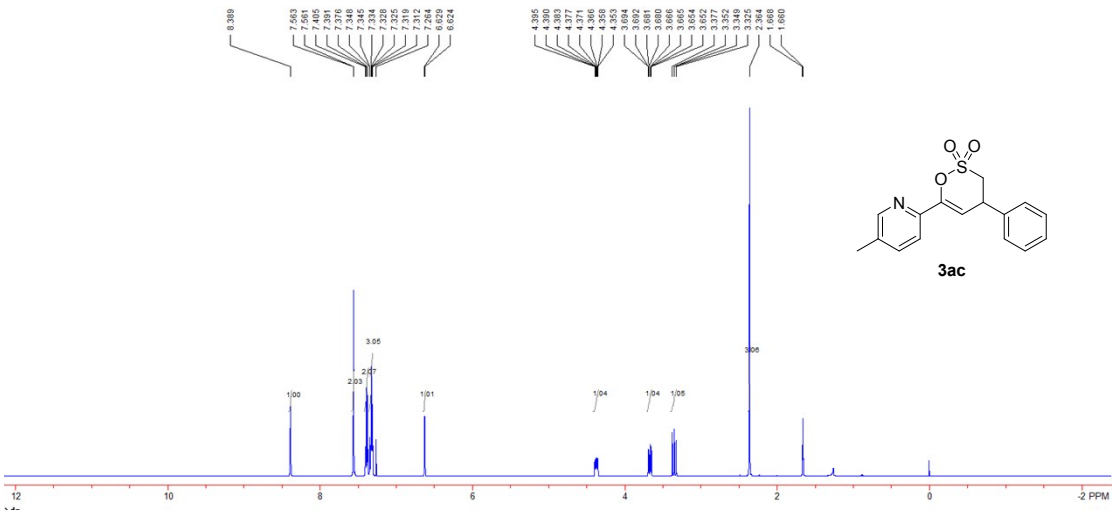
3ab, ^{1}H NMR, 500 MHz, $CDCl_3$



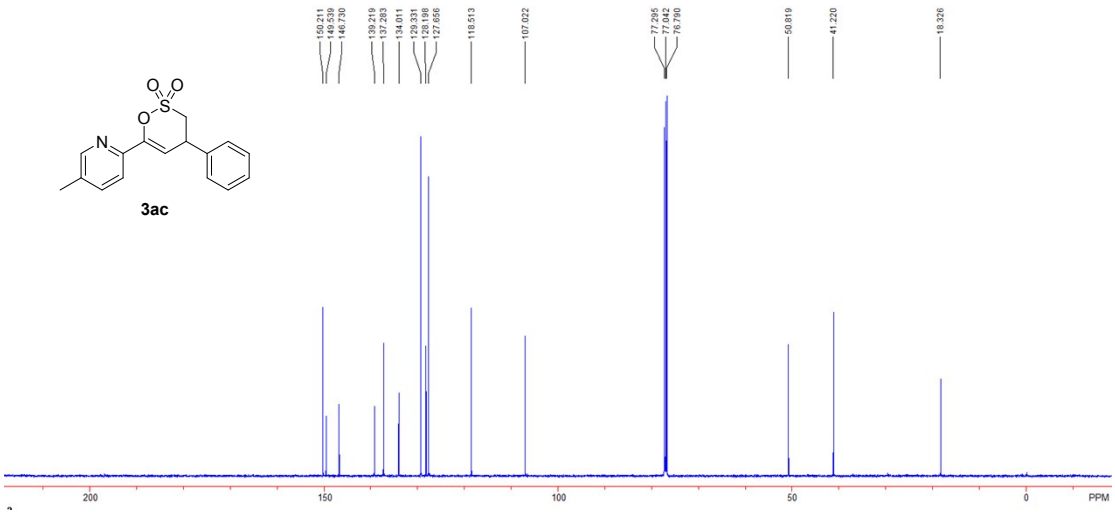
3ab, ^{13}C NMR, 126 MHz, $CDCl_3$



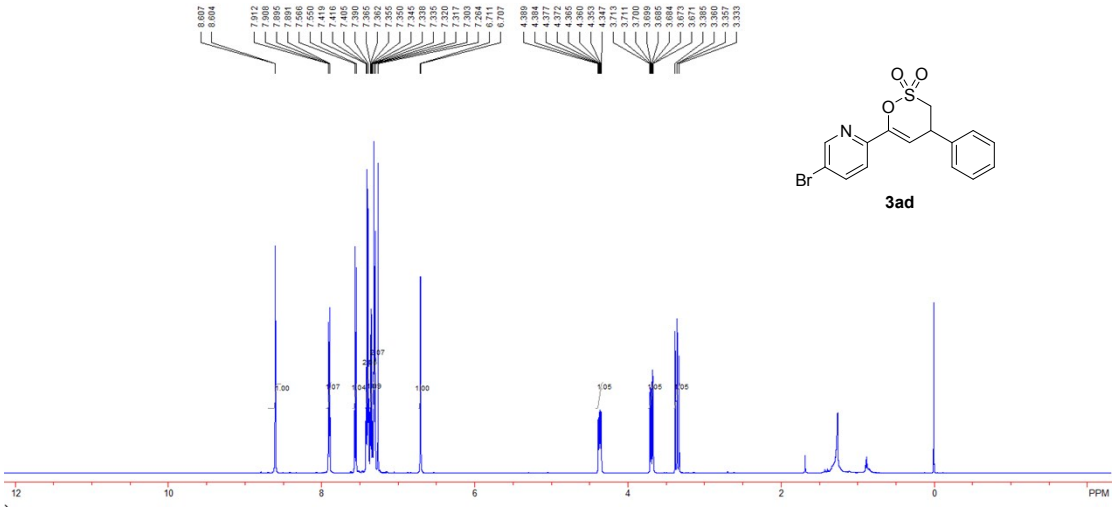
3ac, ^{1}H NMR, 500 MHz, $CDCl_3$



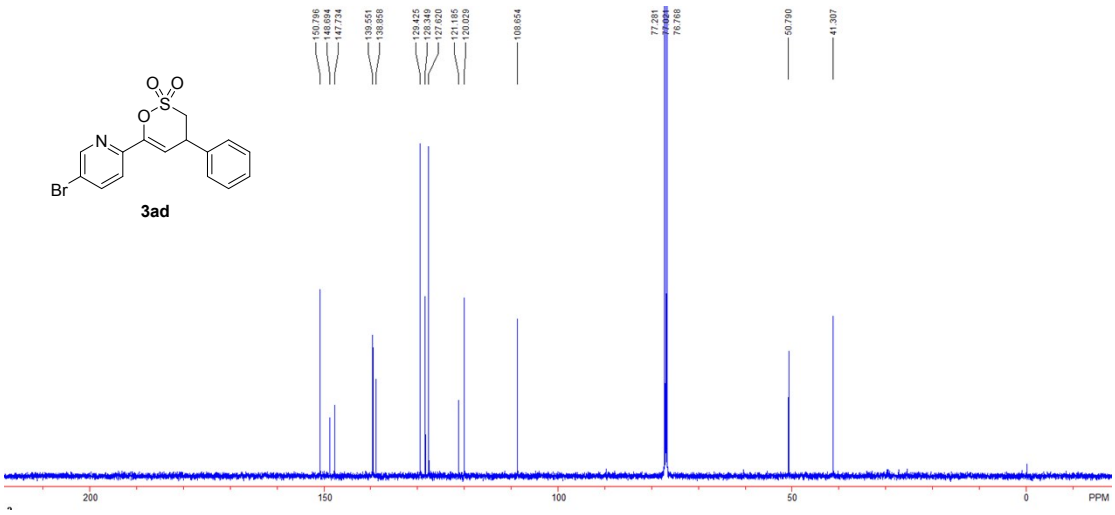
3ac, ^{13}C NMR, 126 MHz, $CDCl_3$



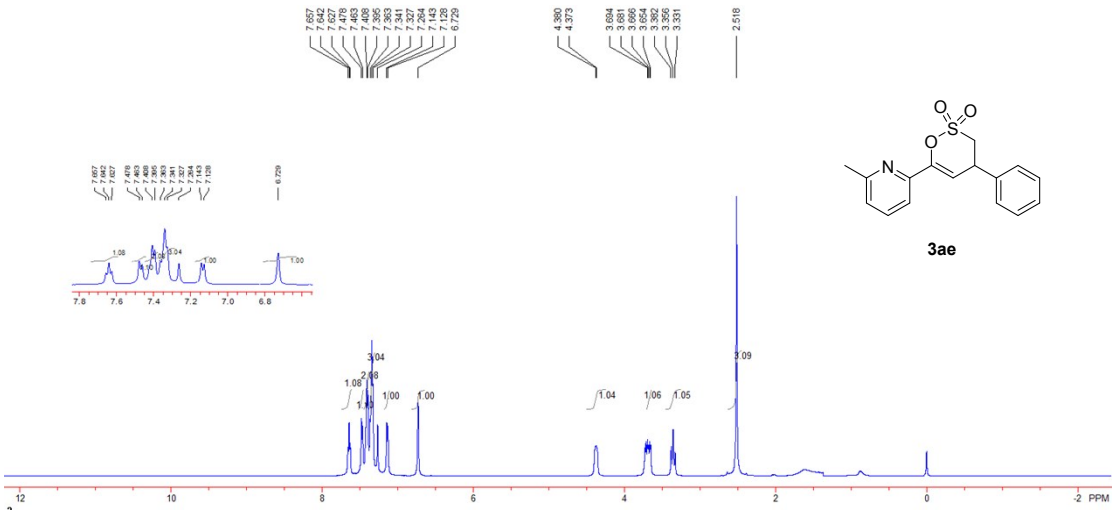
3ad, ^{1}H NMR, 500 MHz, $CDCl_3$



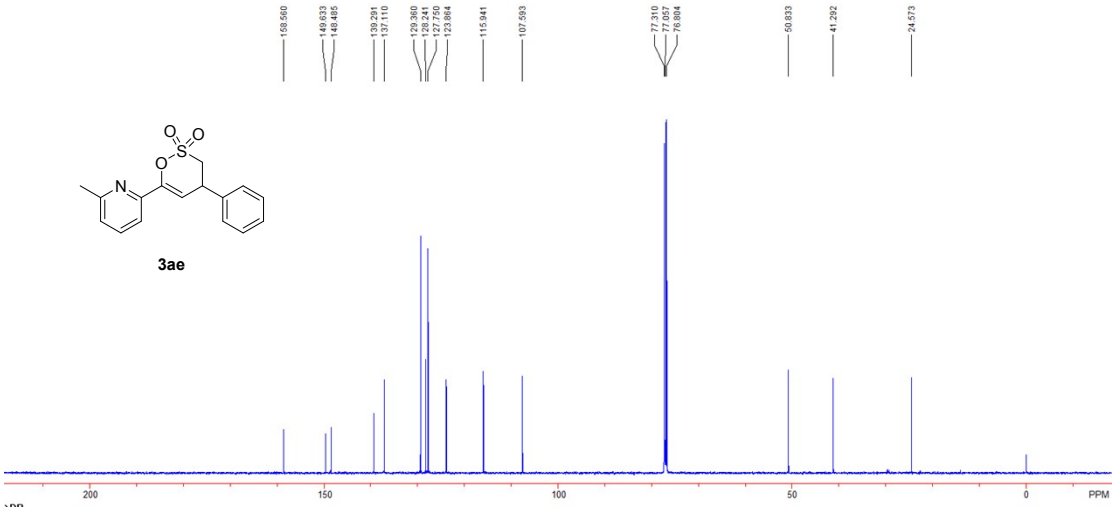
3ad, ^{13}C NMR, 126 MHz, $CDCl_3$



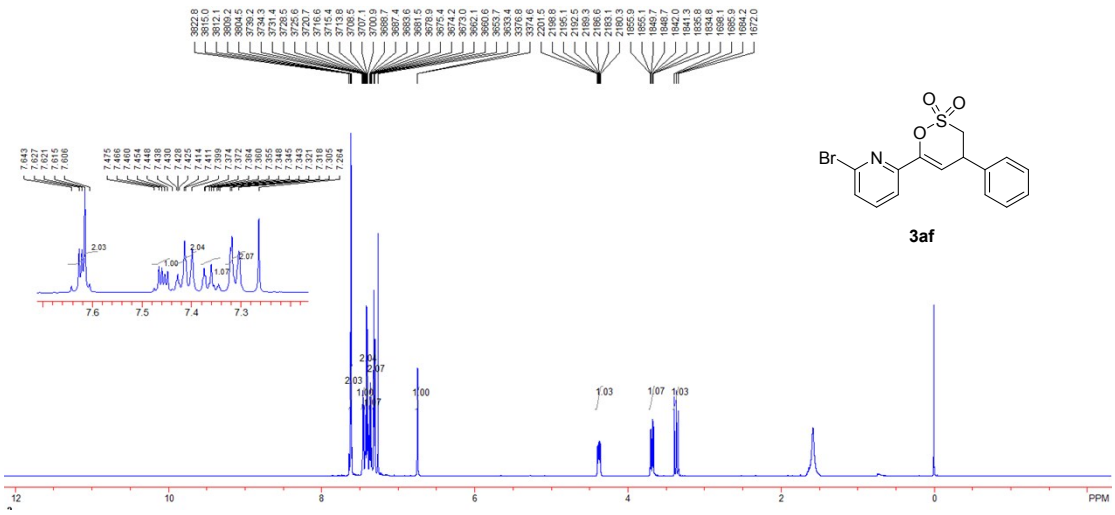
3ae, ^{1}H NMR, 500 MHz, $CDCl_3$



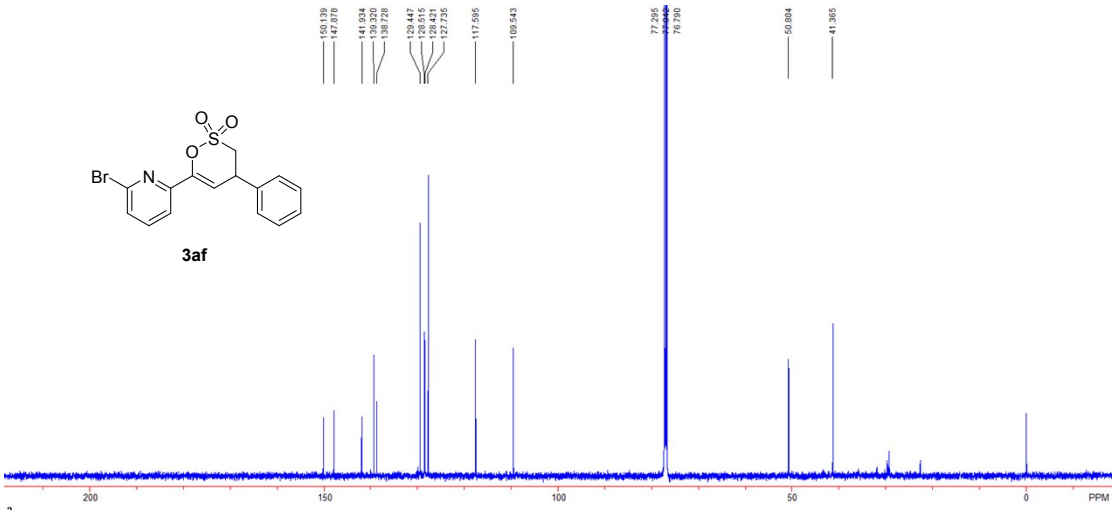
3ae, ^{13}C NMR, 126 MHz, $CDCl_3$



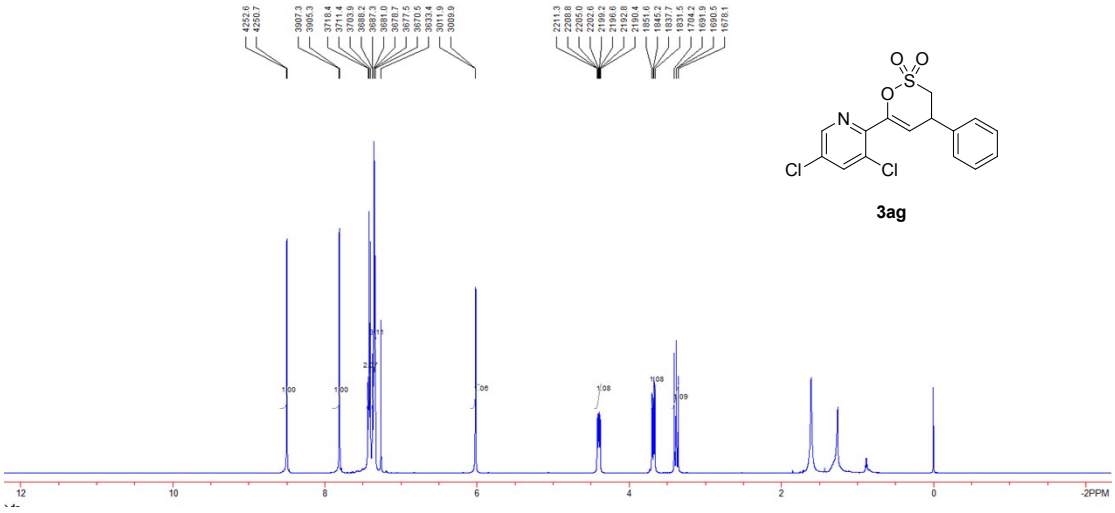
3af, ^{1}H NMR, 500 MHz, $CDCl_3$



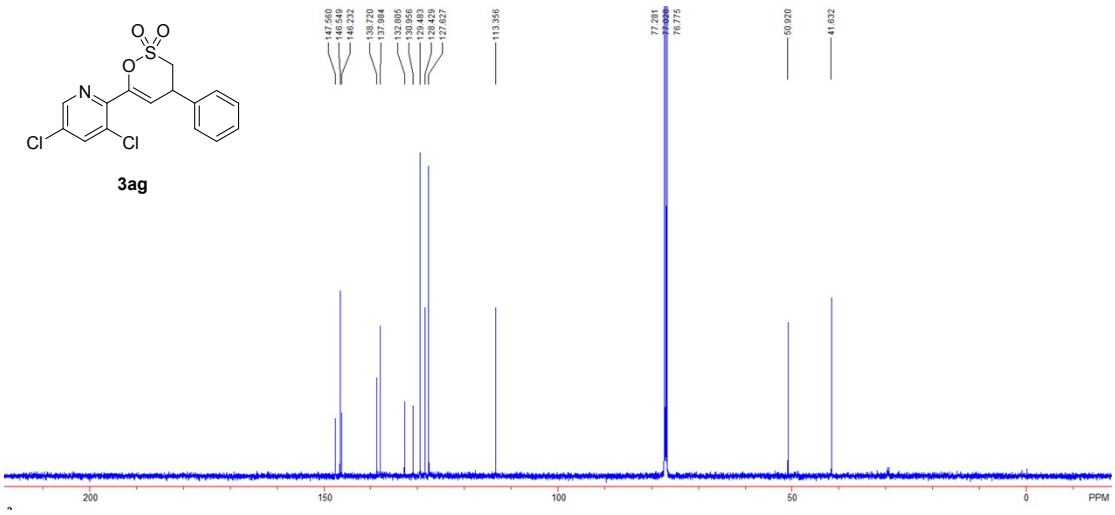
3af, ^{13}C NMR, 126 MHz, $CDCl_3$



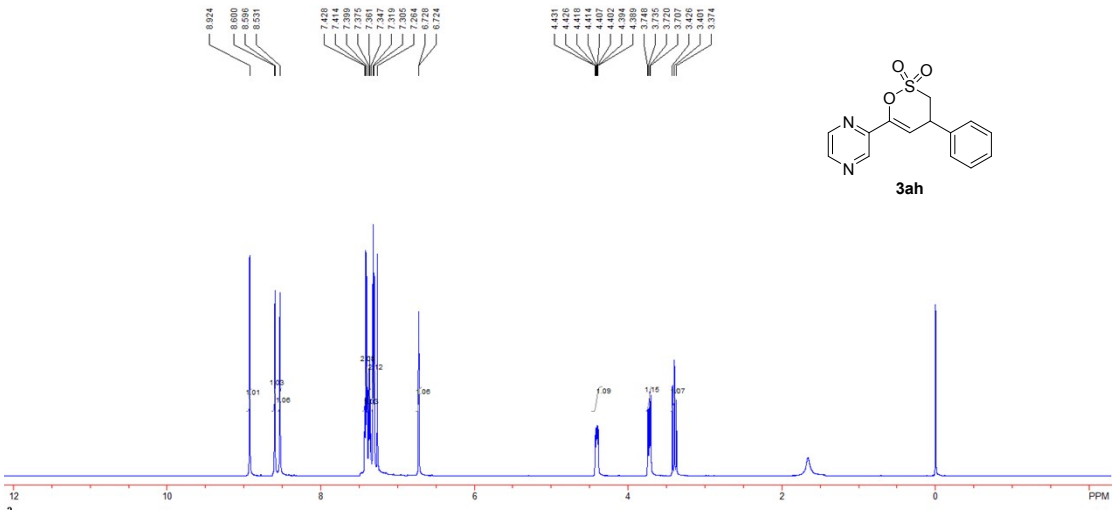
3ag, ^{1}H NMR, 500 MHz, $CDCl_3$



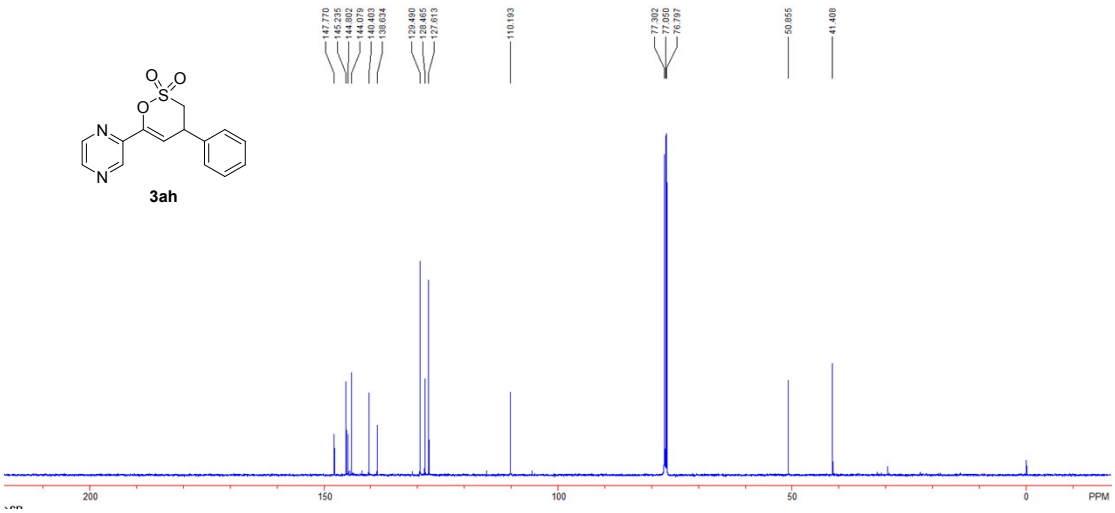
3ag, ^{13}C NMR, 126 MHz, $CDCl_3$



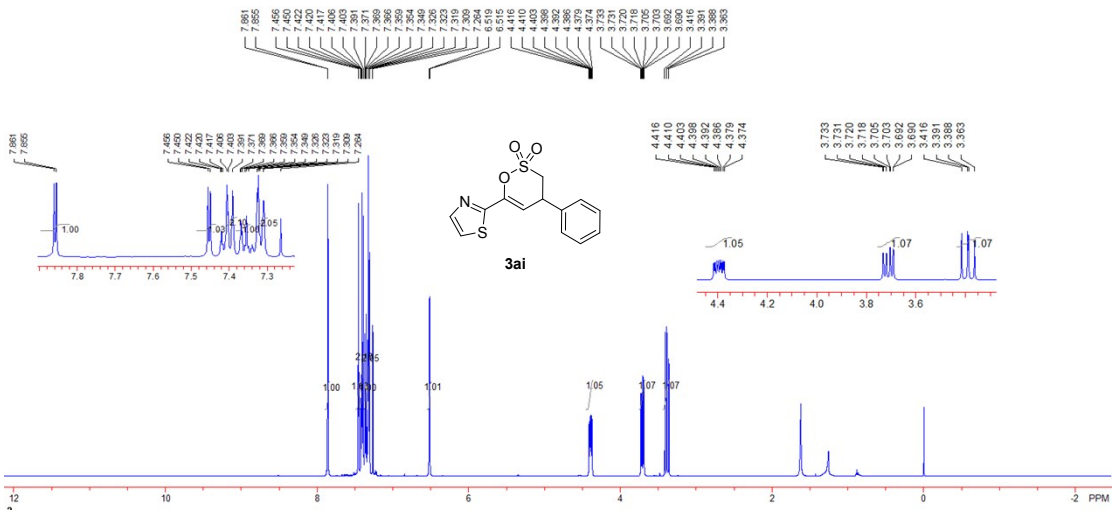
3ah, ^{1}H NMR, 500 MHz, $CDCl_3$



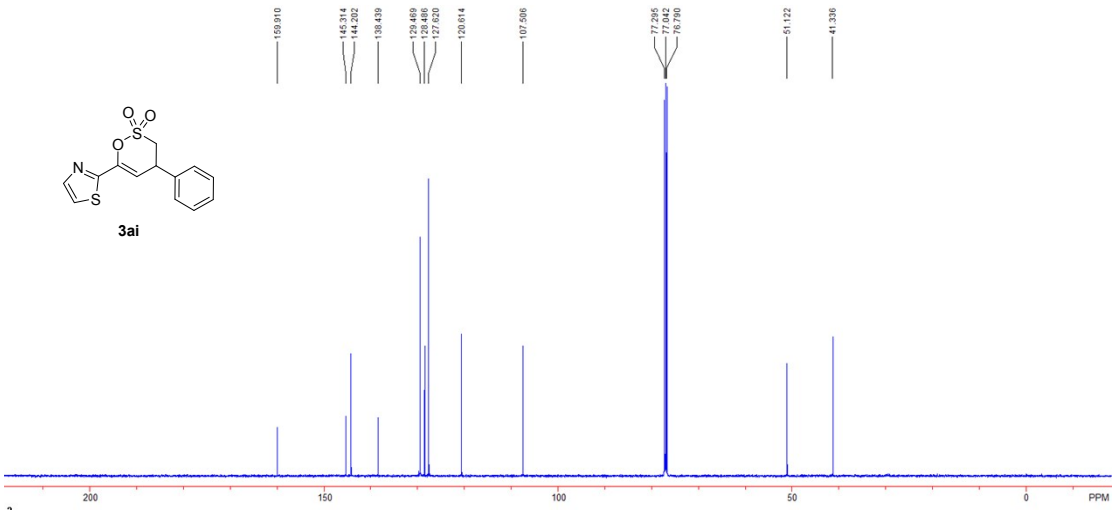
3ah, ^{13}C NMR, 126 MHz, $CDCl_3$



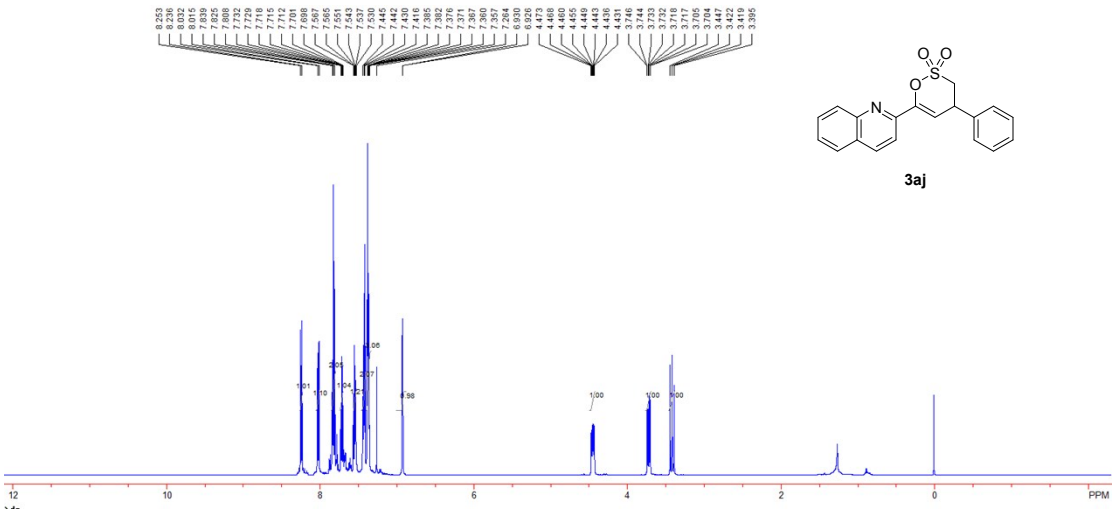
3ai, ^{1}H NMR, 500 MHz, $CDCl_3$



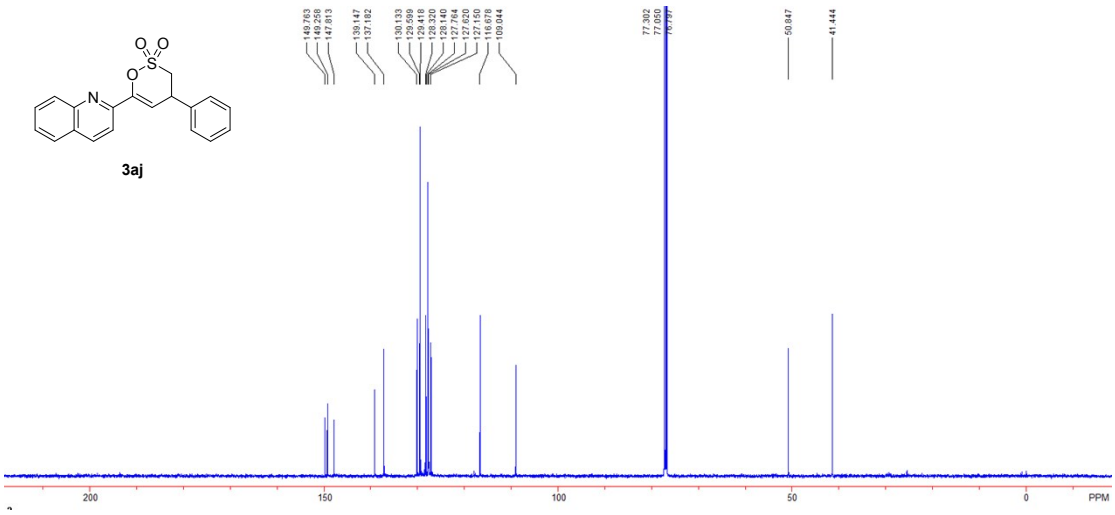
3ai, ^{13}C NMR, 126 MHz, $CDCl_3$



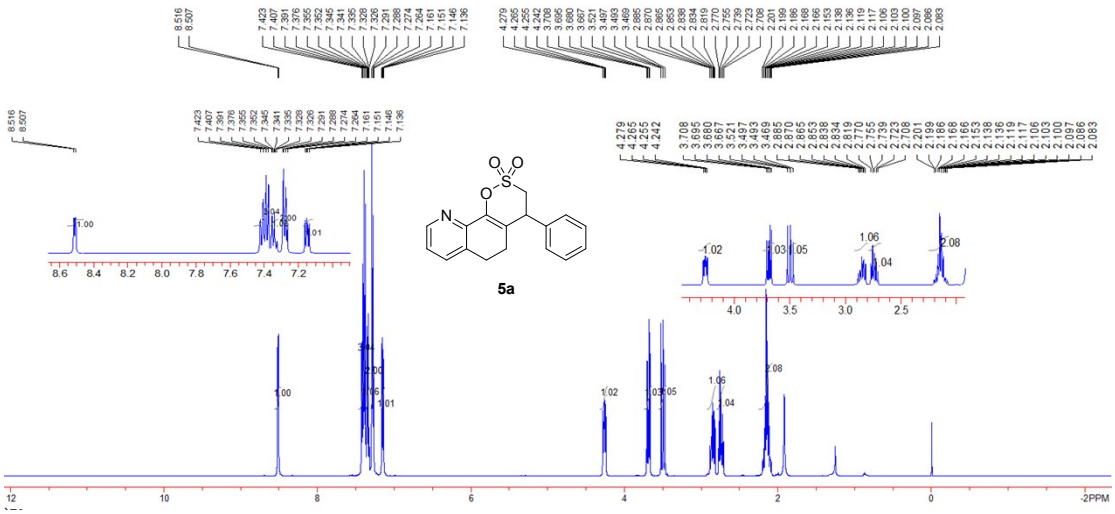
3aj, ^{1}H NMR, 500 MHz, $CDCl_3$



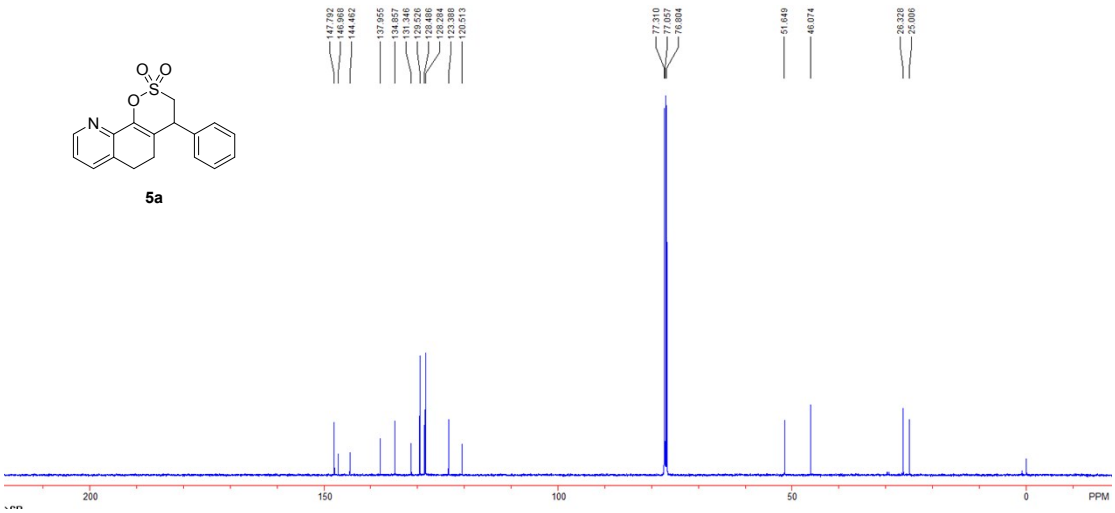
3aj, ^{13}C NMR, 126 MHz, $CDCl_3$



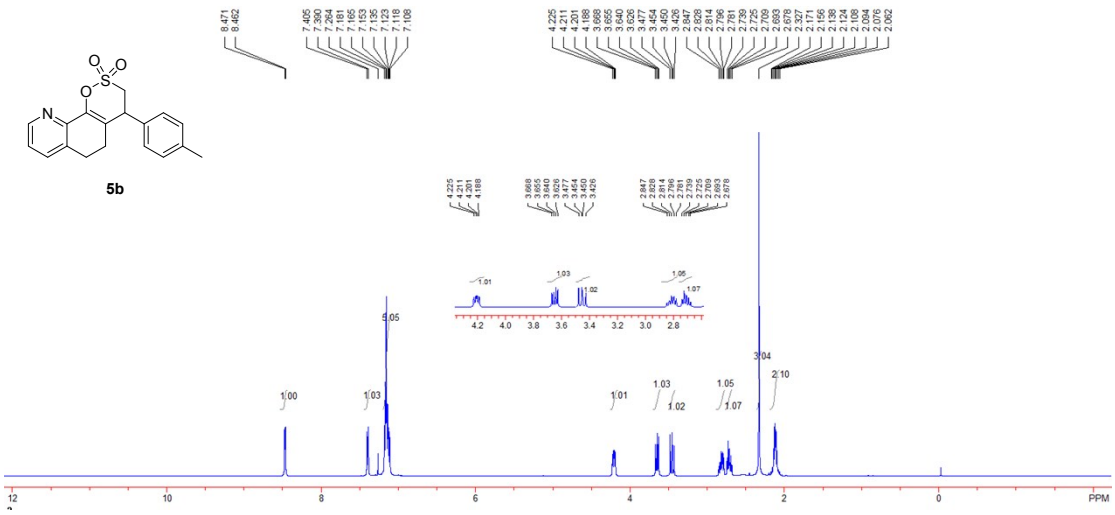
5a, ^{1}H NMR, 500 MHz, $CDCl_3$



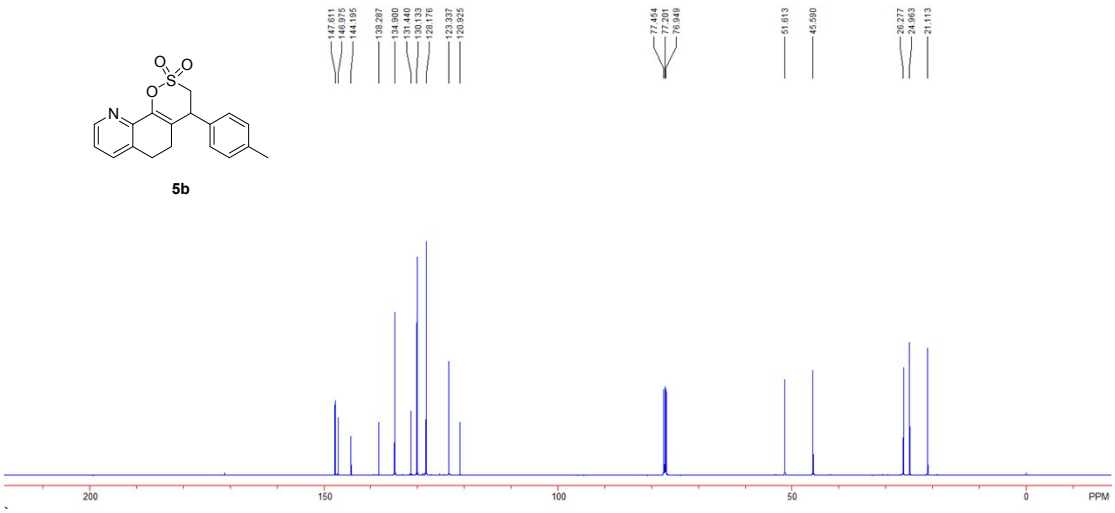
5a, ^{13}C NMR, 126 MHz, $CDCl_3$



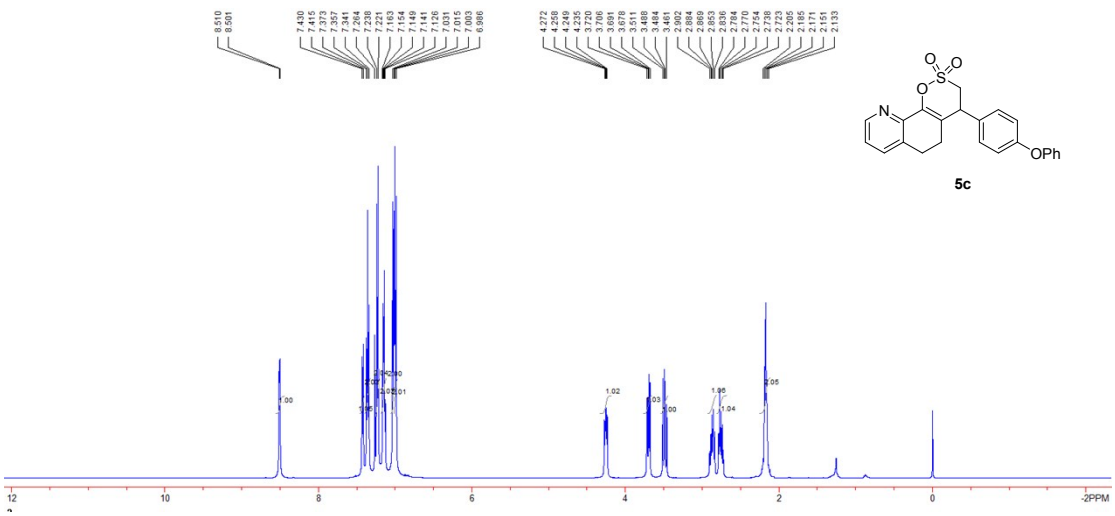
5b, ^{1}H NMR, 500 MHz, $CDCl_3$



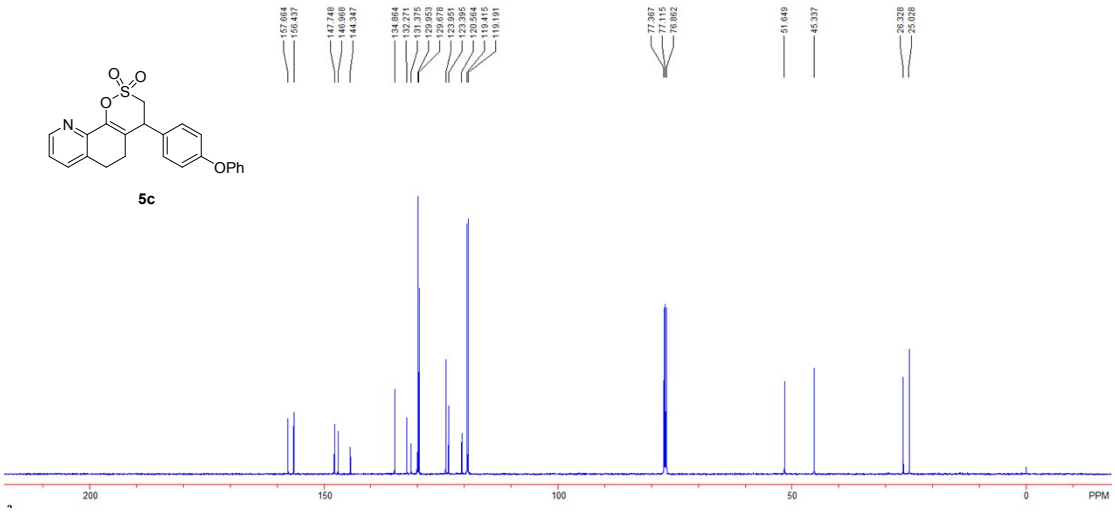
5b, ^{13}C NMR, 126 MHz, $CDCl_3$



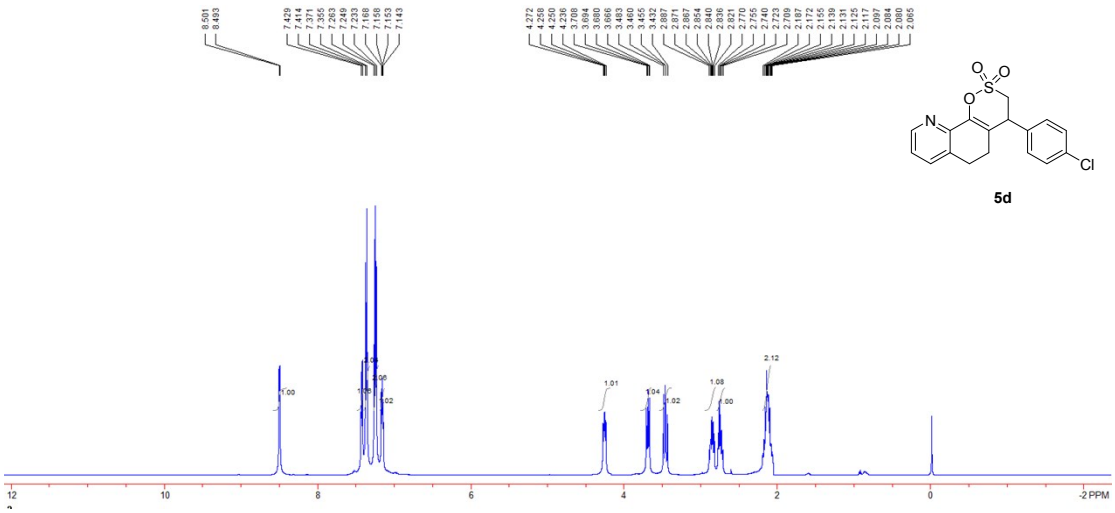
5c, ^{1}H NMR, 500 MHz, $CDCl_3$



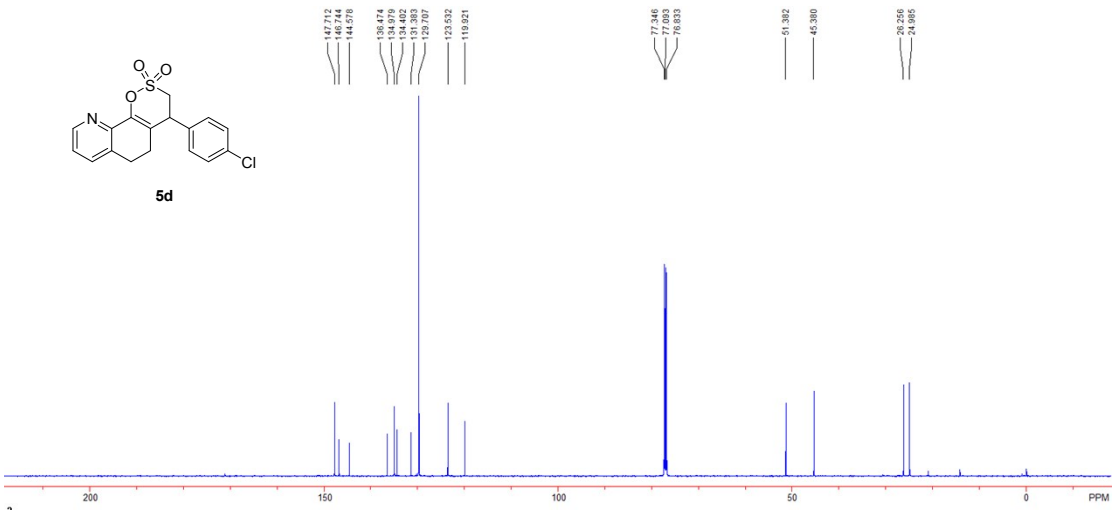
5c, ^{13}C NMR, 126 MHz, $CDCl_3$



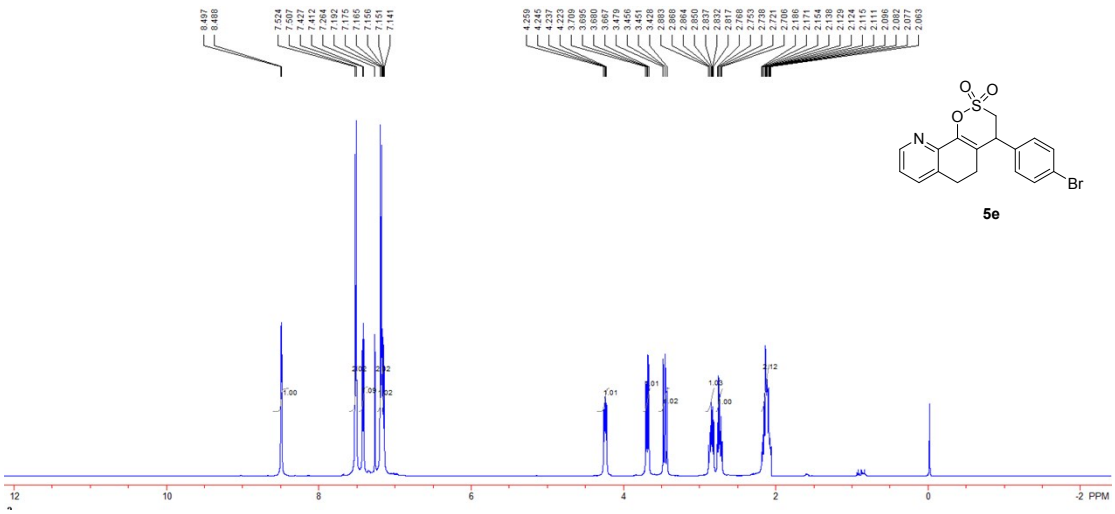
5d, ^{1}H NMR, 500 MHz, $CDCl_3$



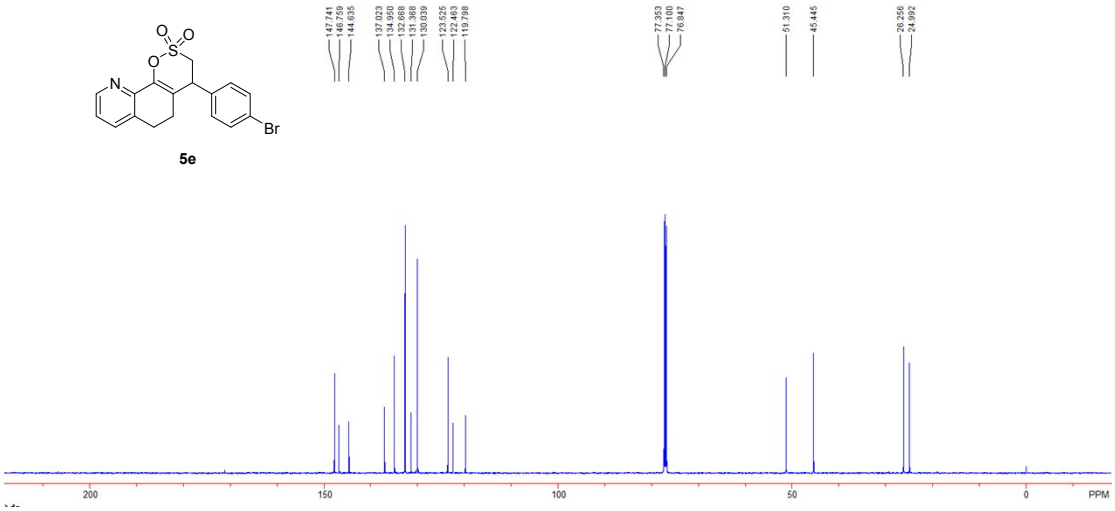
5d, ^{13}C NMR, 126 MHz, $CDCl_3$



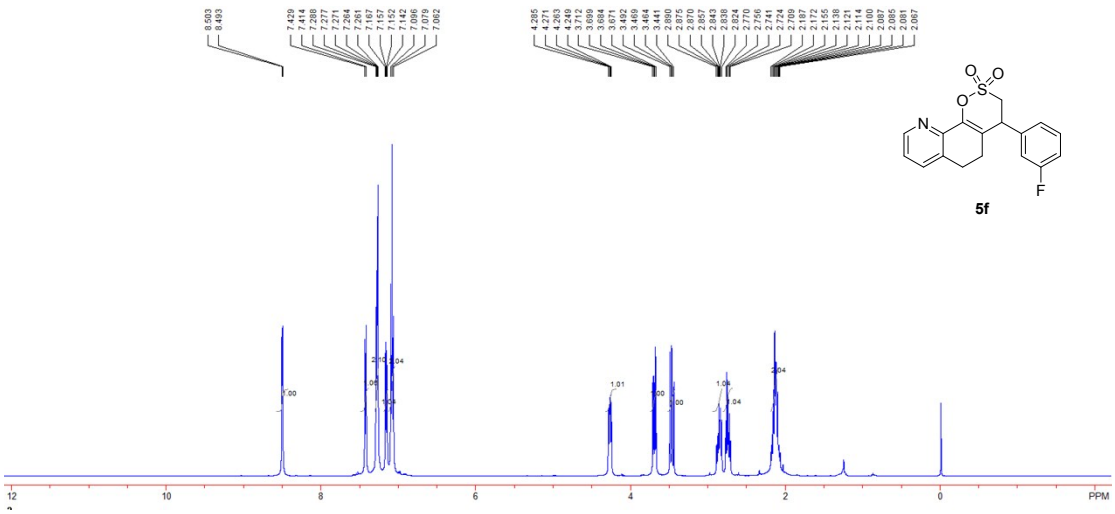
5e, ^{1}H NMR, 500 MHz, $CDCl_3$



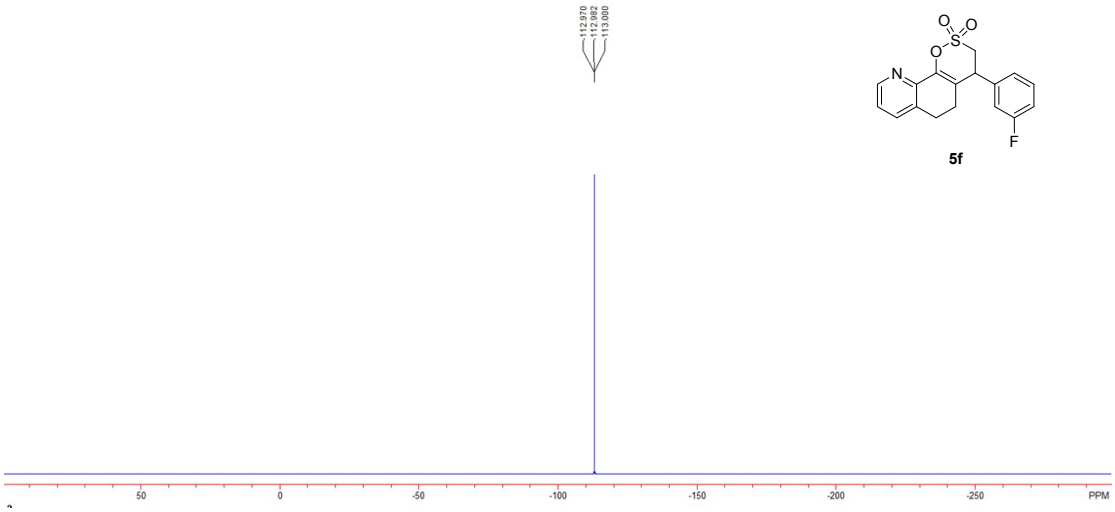
5e, ^{13}C NMR, 126 MHz, $CDCl_3$



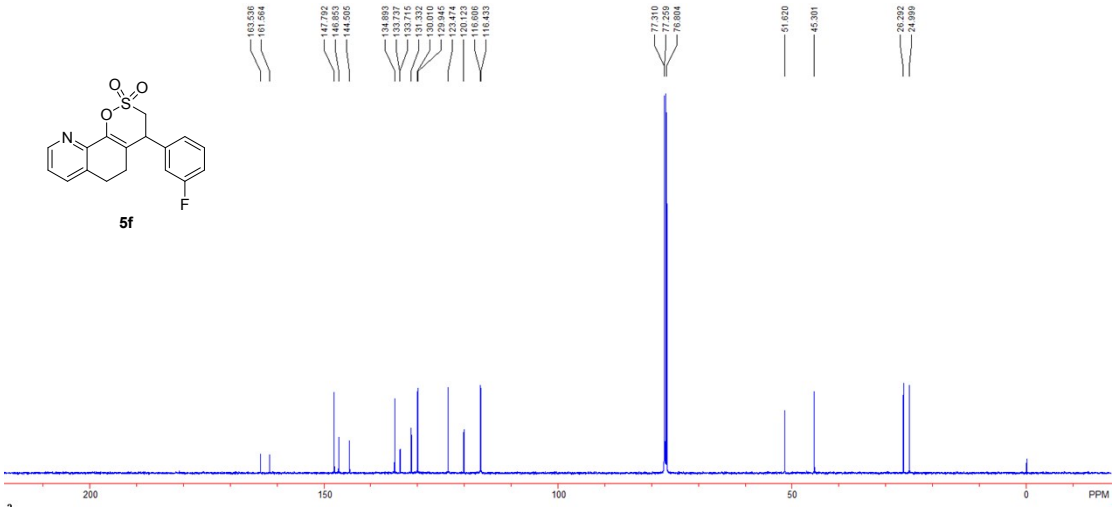
5f, ^{1}H NMR, 500 MHz, $CDCl_3$



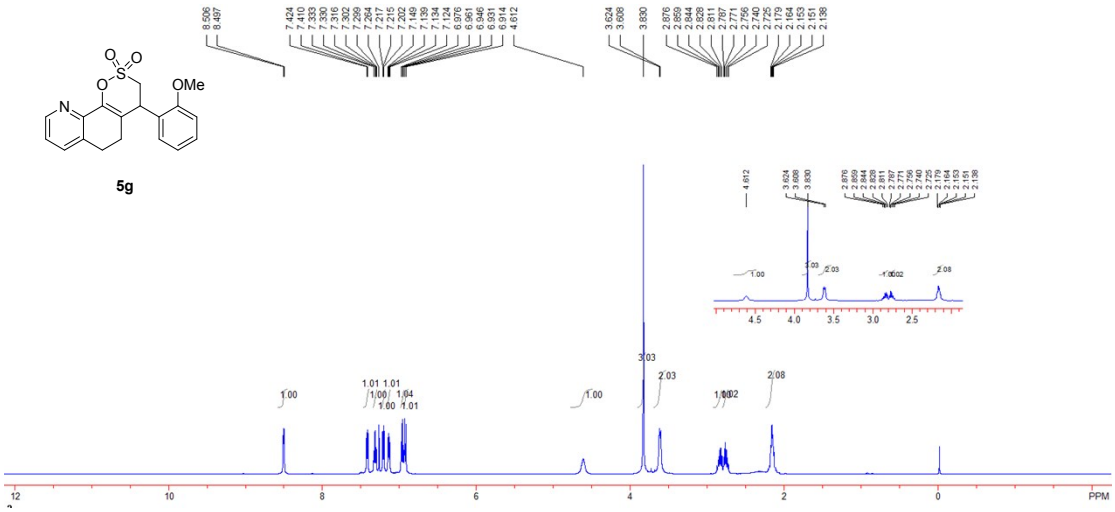
5f, ^{19}F NMR, 376 MHz, $CDCl_3$



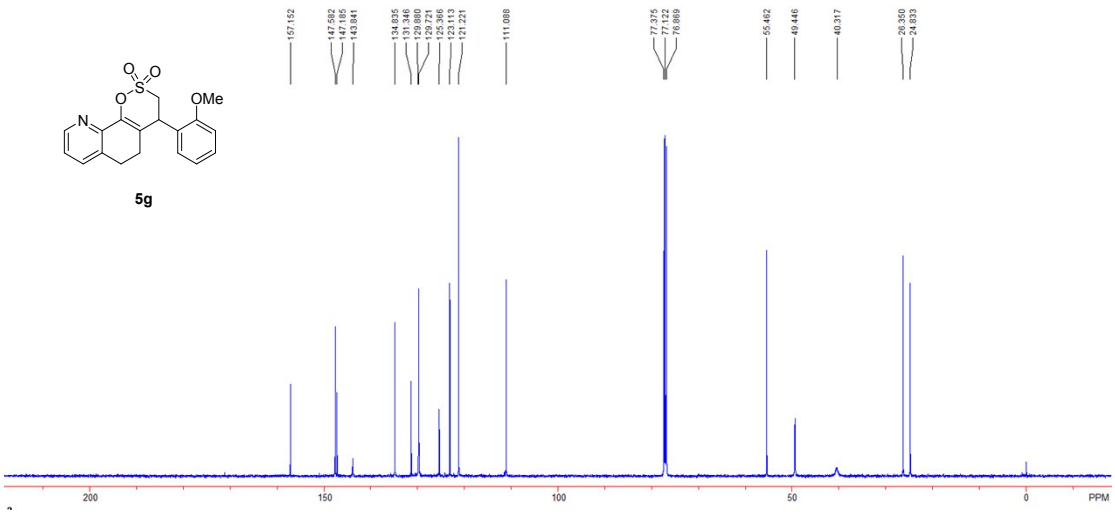
5f, ^{13}C NMR, 126 MHz, $CDCl_3$



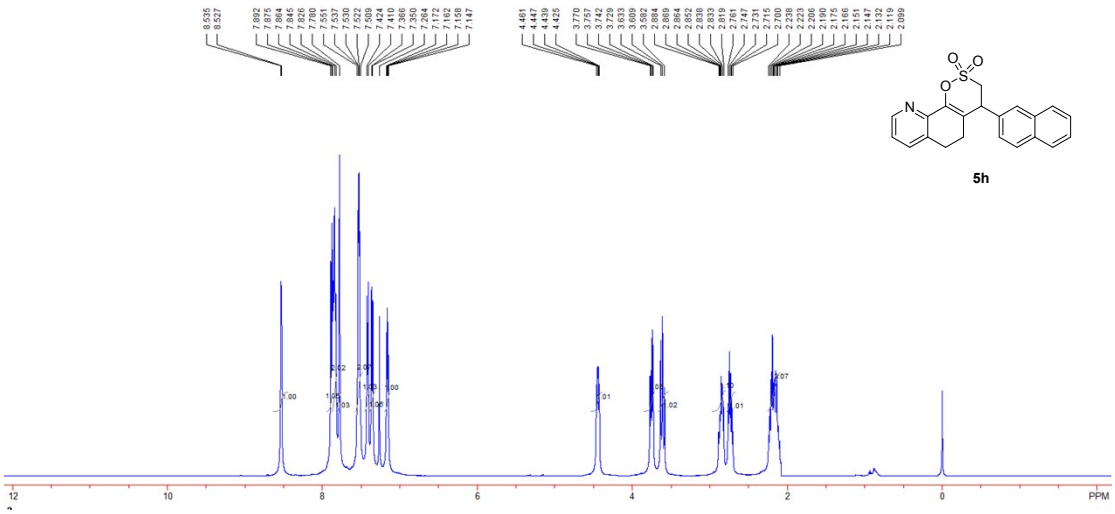
5g, ^{1}H NMR, 500 MHz, $CDCl_3$



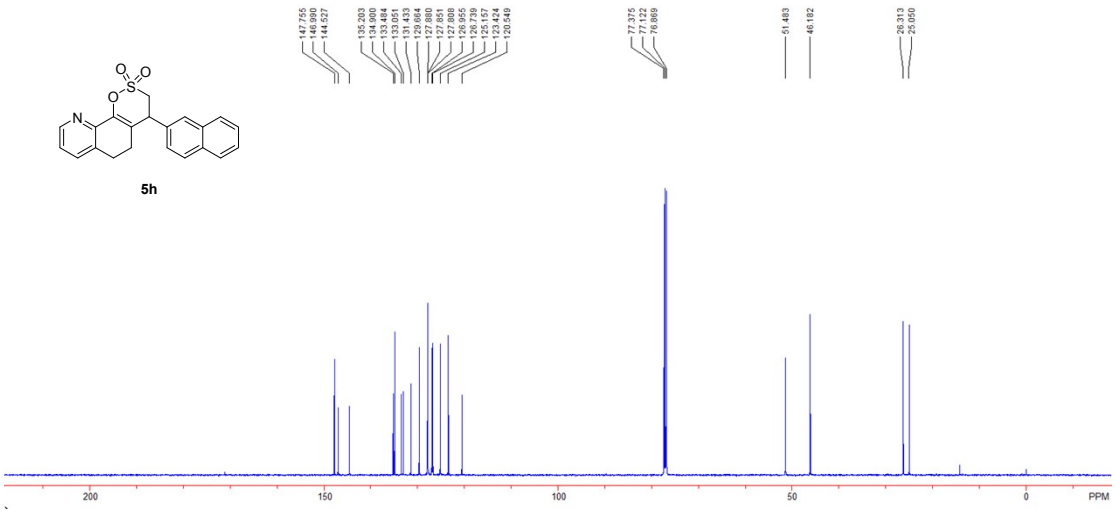
5g, ^{13}C NMR, 126 MHz, $CDCl_3$



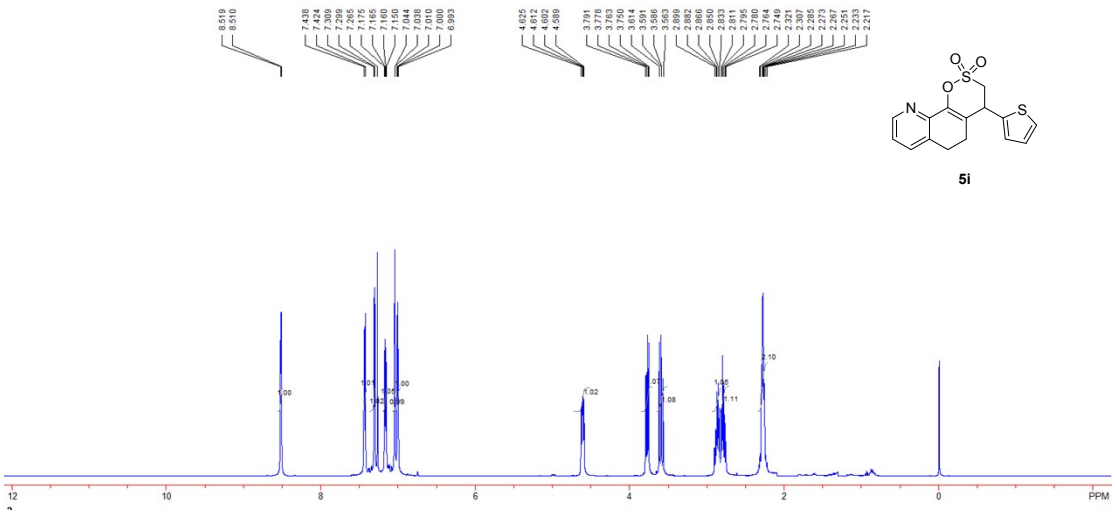
5h, ^{1}H NMR, 500 MHz, $CDCl_3$



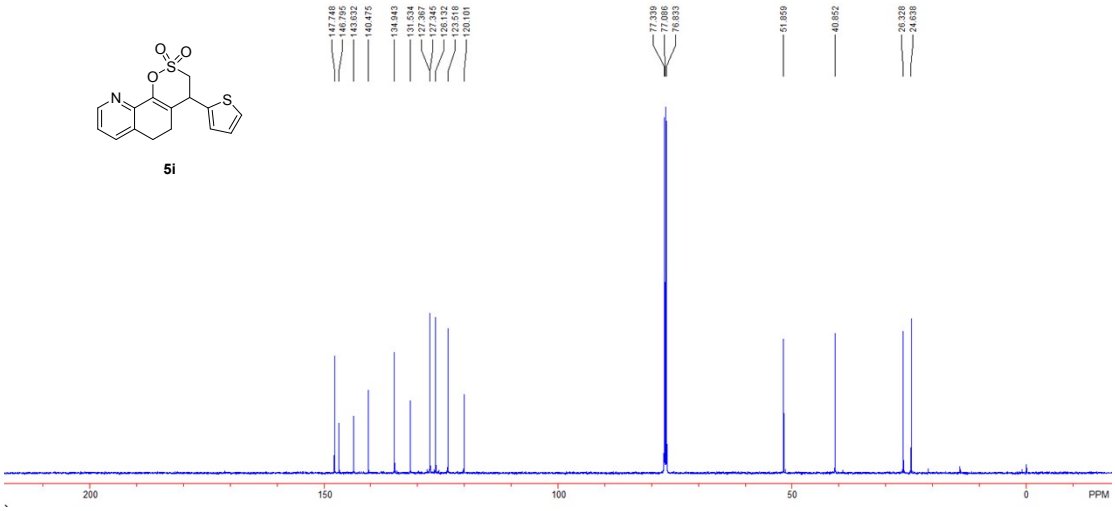
5h, ^{13}C NMR, 126 MHz, $CDCl_3$



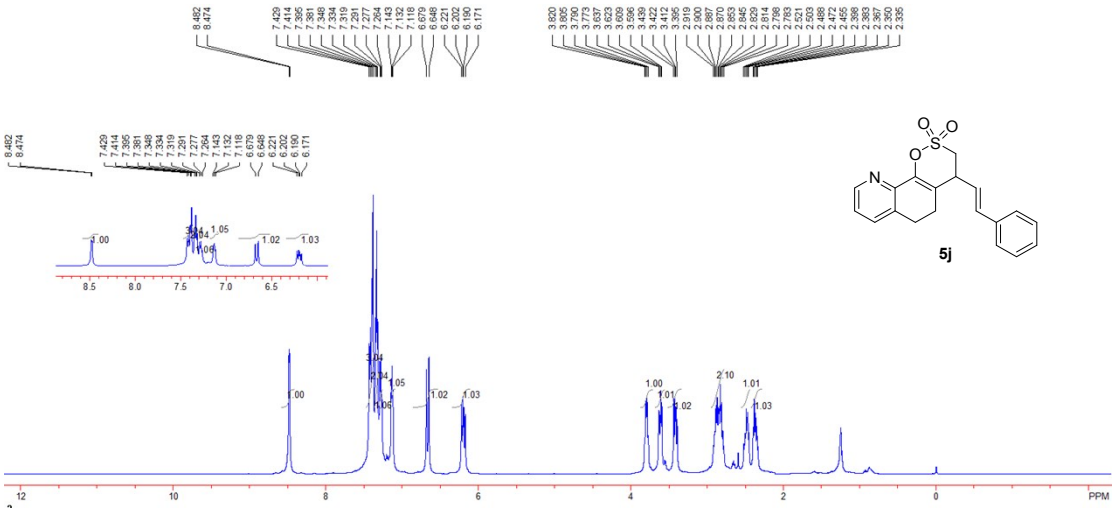
5i, ^{1}H NMR, 500 MHz, $CDCl_3$



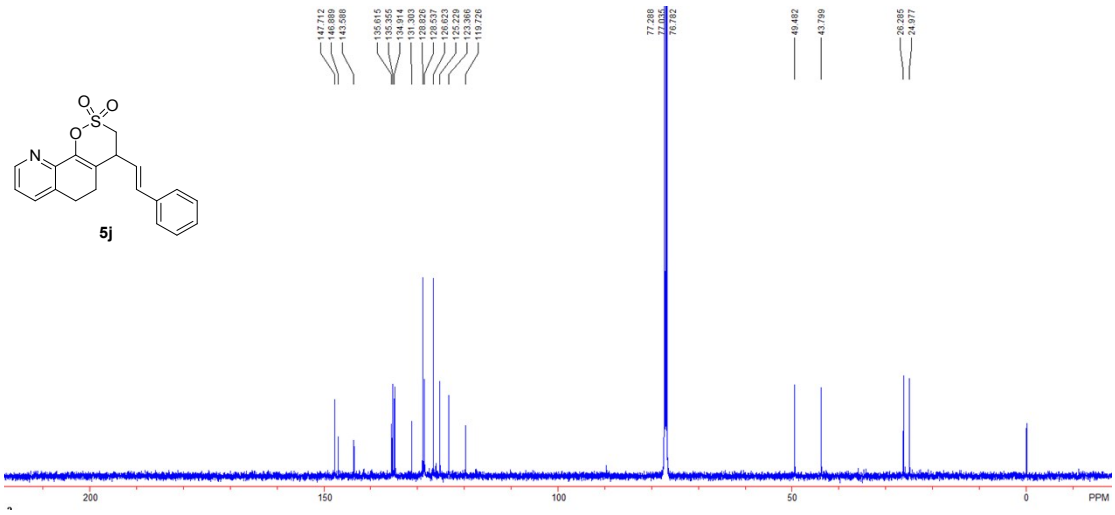
5i, ^{13}C NMR, 126 MHz, $CDCl_3$



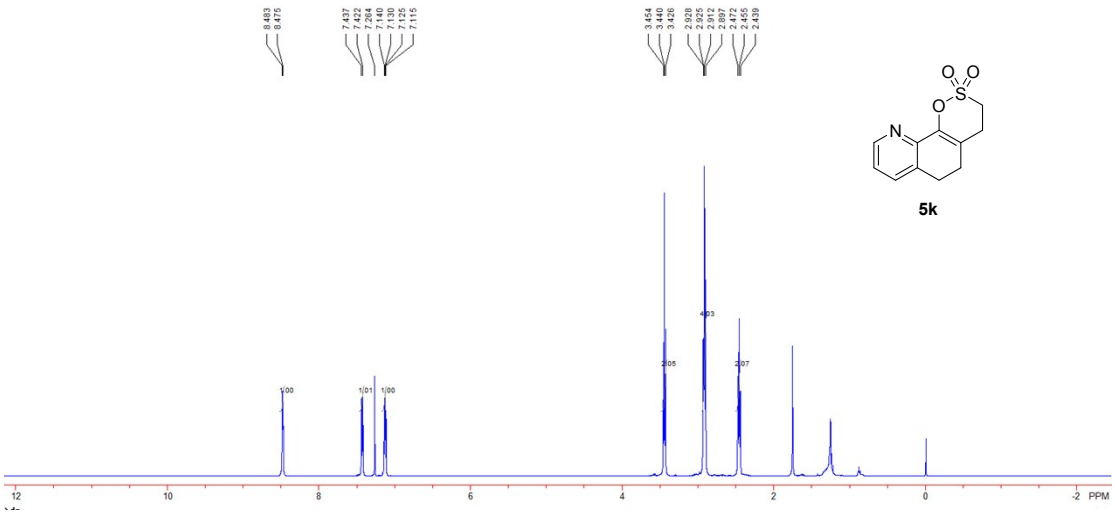
5j, ^{1}H NMR, 500 MHz, $CDCl_3$



5j, ^{13}C NMR, 126 MHz, $CDCl_3$



5k, ^{1}H NMR, 500 MHz, $CDCl_3$



5k, ^{13}C NMR, 126 MHz, $CDCl_3$