Supplementary Information (SI) for ChemComm.
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Supporting Information

Synthesis of 1*H*-Isothiochromenes by Regioselective C–C and C–S Bonds Formation of Enaminothiones with Alkynes under Rhodium Catalysis

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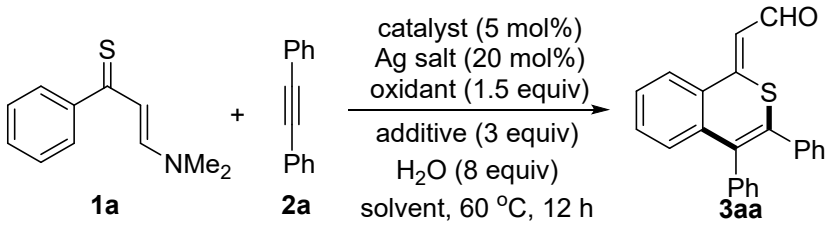
Contents

1. Experimental Section:

General Considerations. All products were prepared under argon atmosphere using standard Schlenk technique. ^{1}H, ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks, respectively. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) were done on an electrospray ionization (ESI) Fourier transform mass spectrometer (FTMS, Thermo QExactive Focus). X-ray diffraction (XRD) patterns were recorded on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Kα radiation. $[Cp^*MCl_2]_2$ (M = Rh/Ir) was prepared from $MCl_3.xH_2O$ (M = Rh/Ir) following a literature procedure.[1] Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Aldrich, Acros, Alfa Aesar, and Energy Chemical Company and used as received without any further purification.

2. Optimization Studies

(a) Table S1. Optimization Studies[a]



entry	catalyst	Ag salt	oxidant	additive	solvent	yield[b] (%)
1	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$Cu(OAc)_2$	HOAc	DCE	74
2	$[Cp^*RhCl_2]_2$	$AgBF_4$	$Cu(OAc)_2$	HOAc	DCE	48
3	$[Cp^*RhCl_2]_2$	AgOTf	$Cu(OAc)_2$	HOAc	DCE	71

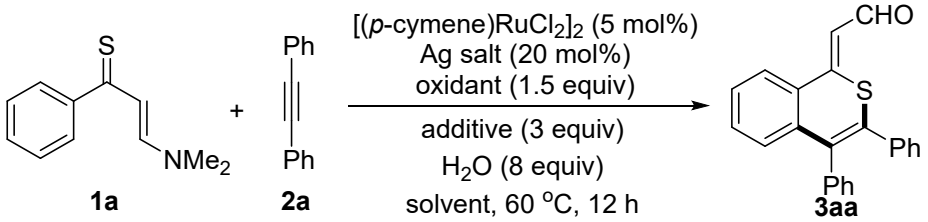
4	$[Cp^*RhCl_2]_2$	$AgNTf_2$	$Cu(OAc)_2$	HOAc	DCE	65
5	$[Cp^*RhCl_2]_2$	-	$Cu(OAc)_2$	HOAc	DCE	0
6	**$[Cp^*RhCl_2]_2$**	**$AgSbF_6$**	**AgOAc**	**HOAc**	**DCE**	**82**
7	$[Cp^*RhCl_2]_2$	$AgSbF_6$	$AgCO_3$	HOAc	DCE	61
8	$[Cp^*RhCl_2]_2$	$AgSbF_6$	Ag_2O	HOAc	DCE	27
9	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	TFA	DCE	0
10	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	PivOH	DCE	74
11	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	$MesCO_2H$	DCE	61
12	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	1-$AdCO_2H$	DCE	77
13	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCM	70
14	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	$CHCl_3$	66
15	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	MeOH	35
16	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	toluene	42
17	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	MeCN	17
18	[(*p*-cymene)$RuCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	55
19	$[Cp^*IrCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	0
20	$Cp^*Co(CO)I_2$	$AgSbF_6$	AgOAc	HOAc	DCE	0
21	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	71[c]
22	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	79[d]
23	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	74[e]
24	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	81[f]
25	$[Cp^*RhCl_2]_2$	$AgSbF_6$	AgOAc	HOAc	DCE	7[g]

[a] Reaction conditions: **1a** (0.2 mmol),**2a** (0.3 mmol), catalyst (5 mol%), Ag salt (20 mol%), oxidant (1.5 equiv), additive (3 equiv), H_2O (8 equiv), solvent (1.5 mL), 60 °C, 12 h, under N_2. [b] Isolated yields. [c] HOAc (2 equiv). [d] HOAc (4 equiv). [e] H_2O (6 equiv). [f] H_2O (10 equiv). [g] without H_2O.

Initially, (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (0.2 mmol, 1.0 equiv) was introduced to react with 1,2-diphenylethyne (**2a**) (0.3 mmol, 1.5 equiv)

accompanied by $[Cp^*RhCl_2]_2$ (5 mol%) $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (1.5 equiv), HOAc (3 equiv), and H_2O (8 equiv) in 1,2-dichloroethane (DCE) at 60 °C under nitrogen atmosphere for 12 h. The target product (*Z*)-2-(3,4-diphenyl-1H-isothiochromen-1-ylidene)acetaldehyde (**3aa**) was achieved with a yield of 74% (Table S1, entry 1). Then, several other Ag salts including $AgBF_4$, AgOTf, and $AgNTf_2$ were tested, and generated **3aa** in 48−71% yields (entries 2−4). The reaction without the participation of silver salt failed to generate product **3aa** (entry 5). When the oxidant was replaced by AgOAc, $AgCO_3$, and Ag_2O, the product **3aa** could be obtained in 27−82% yields (entries 6−8). The yields of **3aa** generated from reactions involving other additives such as 2,2,2-trifluoroacetic acid (TFA), PivOH, $MesCO_2H$, and 1-$AdCO_2H$ were not higher than 77% (entries 9−12). Tests on solvents showed that DCE is more suitable for this transformation than dichloromethane (DCM), $CHCl_3$, MeOH, toluene, and MeCN (entries 6, 13−17). However, **3aa** was obtained in 0−55% yields when other catalysts including $[(p\text{-cymene})RuCl_2]_2$, $[Cp^*IrCl_2]_2$, and $Cp^*Co(CO)I_2$ were employed (entries 18−20). In addition, adjusting the amounts of HOAc and H_2O did not promote the occurrence of this conversion (entries 21−24). When no additional H_2O was added, only 13% yield of product **3aa** was given (entry 25). Therefore, the factors in entry 6 were selected as the standard reaction conditions.

(b) Table S2. Optimization Studies Catalyzed by $[(p\text{-cymene})RuCl_2]_2$



entry	Ag salt	oxidant	additive	solvent	yield[b] (%)
1	**$AgSbF_6$**	**AgOAc**	**HOAc**	**DCE**	**55**
2	$AgBF_4$	AgOAc	HOAc	DCE	32
3	AgOTf	AgOAc	HOAc	DCE	50
4	$AgNTf_2$	AgOAc	HOAc	DCE	25
5	-	$AgOAc_2$	HOAc	DCE	0

6	$AgSbF_6$	$Cu(OAc)_2$	HOAc	DCE	42
7	$AgSbF_6$	$AgCO_3$	HOAc	DCE	51
8	$AgSbF_6$	Ag_2O	HOAc	DCE	20
9	$AgSbF_6$	AgOAc	TFA	DCE	0
10	$AgSbF_6$	AgOAc	PivOH	DCE	48
11	$AgSbF_6$	AgOAc	$MesCO_2H$	DCE	35
12	$AgSbF_6$	AgOAc	1-$AdCO_2H$	DCE	52
13	$AgSbF_6$	AgOAc	HOAc	DCM	33
14	$AgSbF_6$	AgOAc	HOAc	$CHCl_3$	30
15	$AgSbF_6$	AgOAc	HOAc	MeOH	25
16	$AgSbF_6$	AgOAc	HOAc	toluene	22
17	$AgSbF_6$	AgOAc	HOAc	MeCN	9
18	$AgSbF_6$	AgOAc	HOAc	DCE	42[c]
19	$AgSbF_6$	AgOAc	HOAc	DCE	53[d]
20	$AgSbF_6$	AgOAc	HOAc	DCE	46[e]
21	$AgSbF_6$	AgOAc	HOAc	DCE	55[f]
22	$AgSbF_6$	AgOAc	HOAc	DCE	0[g]

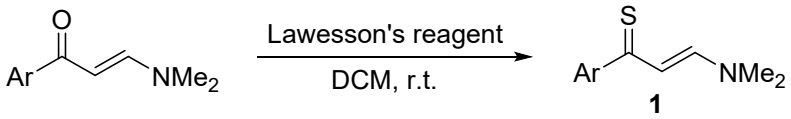
[a] Reaction conditions: **1a** (0.2 mmol),**2a** (0.3 mmol), [(*p*-cymene)$RuCl_2$]$_2$ (5 mol%), Ag salt (20 mol%), oxidant (1.5 equiv), additive (3 equiv), H_2O (8 equiv), solvent (1.5 mL), 60 °C, 12 h, under N_2. [b] Isolated yields. [c] HOAc (2 equiv). [d] HOAc (4 equiv). [e] H_2O (6 equiv). [f] H_2O (10 equiv). [g] without H_2O.

Optimization studies on the synthesis of 1*H*-isothiochromenes catalyzed by [(*p*-cymene)$RuCl_2$]$_2$ were carried out, and the results are summarized in Table S2. Initially, (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (0.2 mmol, 1.0 equiv) was introduced to react with 1,2-diphenylethyne (**2a**) (0.3 mmol, 1.5 equiv) accompanied by [(*p*-cymene)$RuCl_2$]$_2$ (5 mol%) $AgSbF_6$ (20 mol%), AgOAc (1.5 equiv), HOAc (3 equiv), and H_2O (8 equiv) in 1,2-dichloroethane (DCE) at 60 °C under nitrogen atmosphere for 12 h. The target product (*Z*)-2-(3,4-diphenyl-1H-isothiochromen-1-ylidene)acetaldehyde (**3aa**) was achieved with a yield of 55% (Table S2, entry 1). Then, a series of optimization studies on Ag salts, oxidants, additives, solvents as well

as the amount of HOAc and H_2O were carried out sequentially. However, these attempted reaction conditions did not provide product **3aa** with a yield higher than 55%. Therefore, the factors in entry 1 are currently the optimal conditions for synthesizing 1*H*-isothiochromenes catalyzed by [(*p*-cymene)$RuCl_2]_2$.

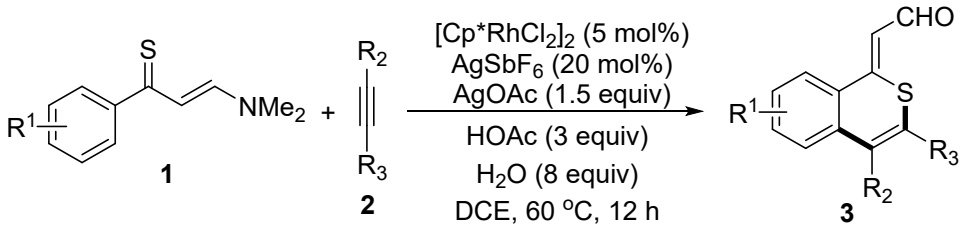
3. Synthetic Procedures

(a) General Procedure for the Preparation of 1



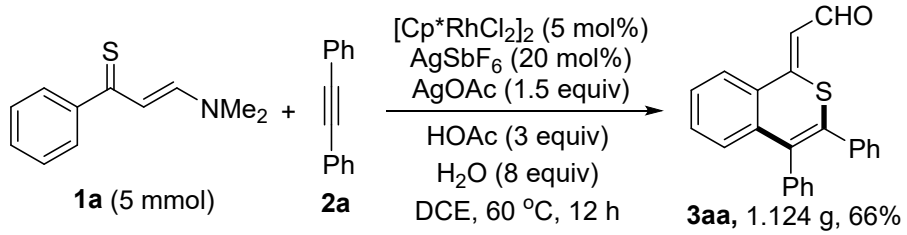
Enaminothiones (**1**) was prepared according to the previous work of Jiang.[2] To a stirred solution of Lawesson's reagent (2 mmol, 1.0 equiv) in DCM (20 mL), the enaminone (2 mmol, 1.0 equiv) was added. The reaction mixture was stired at room temperature for 1 h. Then, the mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

(b) General Procedure for the Rh(III)-Catalyzed Preparation of 3



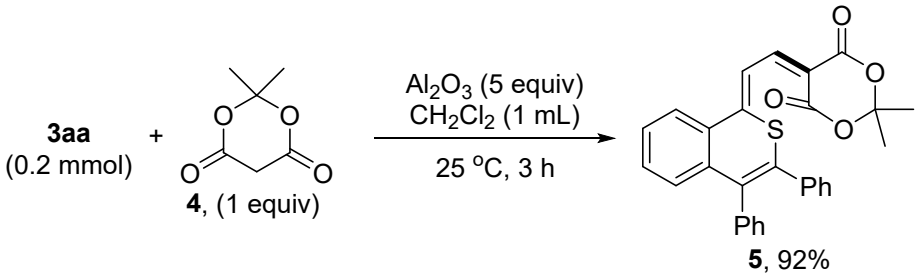
A mixture of substituted enaminothiones (**1**) (0.2 mmol, 1.0 equiv), alkynes (**2**) (0.3 mmol, 1.5 equiv), [(Cp*$RhCl_2]_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel with EtOAc/petroleum ether.

(c) Gram-Scale Preparation of 3aa



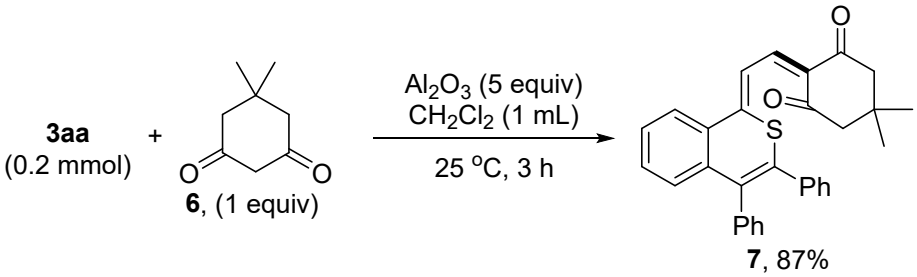
A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (955.4 mg, 5.0 mmol, 1.0 equiv), 1,2-diphenylethyne (**2a**) (1335.6 mg, 7.5 mmol, 1.5 equiv), [(Cp*$RhCl_2$]$_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether, the product **3aa** was affored as a yellow solid in 66% yield (1.124 g, 3.3 mmol).

(d) Condensation Reaction of 3aa for the Preparation of 5



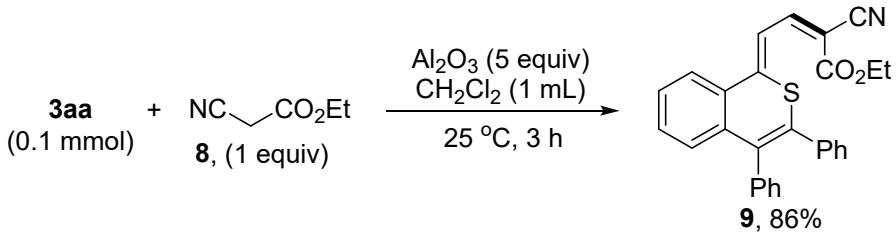
A mixture of (*Z*)-2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (**3aa**) (0.2 mmol, 1.0 equiv), 2,2-dimethyl-1,3-dioxane-4,6-dione (**4**) (0.2 mmol, 1 equiv), and Al_2O_3 (1 mmol, 5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (1 mL) was added and the mixture was stirred at 25 °C for 3 h. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give olefination product **5** in 92% yield.

(e) Condensation Reaction of 3aa for the Preparation of 7



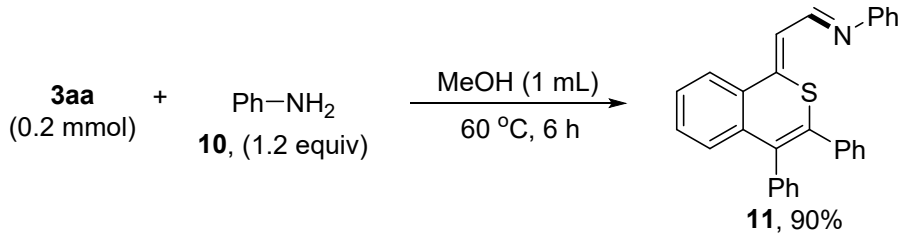
A mixture of (*Z*)-2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (**3aa**) (0.2 mmol, 1.0 equiv), 5,5-dimethylcyclohexane-1,3-dione (**6**) (0.2 mmol, 1 equiv), and Al_2O_3 (1 mmol, 5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (1 mL) was added and the mixture was stirred at 25 °C for 3 h. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give olefination product **7** in 87% yield.

(f) Condensation Reaction of 3aa for the Preparation of 9



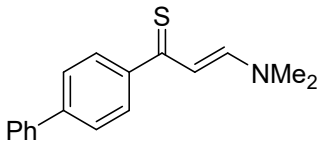
A mixture of (*Z*)-2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (**3aa**) (0.2 mmol, 1.0 equiv), ethyl 2-cyanoacetate (**8**) (0.2 mmol, 1 equiv), and Al_2O_3 (1 mmol, 5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (1 mL) was added and the mixture was stirred at 25 °C for 3 h. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give olefination product **9** in 86% yield.

(g) Condensation Reaction of 3aa for the Preparation of 11



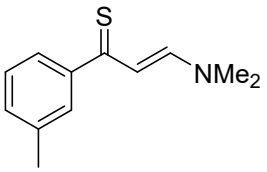
A mixture of (*Z*)-2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (**3aa**) (0.2 mmol, 1.0 equiv), and aniline (**10**) (0.24 mmol, 1.2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry MeOH (1 mL) was added and the mixture was stirred at 60 °C for 6 h. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give olefination product **11** in 90% yield.

4. Characterization of 3, 5,7, 9, and 11



(*E*)-1-([1,1'-biphenyl]-4-yl)-3-(dimethylamino)prop-2-ene-1-thione (1d)

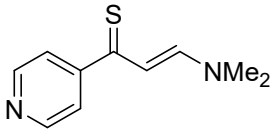
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red solid in 84% yield (448.7 mg, 1.68 mmol). Mp: 96 – 97 °C. **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 8.38 (d, *J* = 11.0 Hz, 1H), 7.98 (d, *J* = 7.3 Hz, 2H), 7.71– 7.65 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 11.1 Hz, 1H), 3.30 (s, 3H), 3.08 (s, 3H). **^{13}C NMR (DMSO-d_6, 125 MHz):** δ 208.7, 158.2, 146.1, 141.3, 139.4, 128.9, 127.7, 127.7, 126.6, 125.8, 110.3, 45.9, 38.4. **HRMS (ESI):** Calcd for $C_{17}H_{17}NNaS$ $[M+Na]^+$ 290.0974, found: 290.0976.



(*E*)-3-(dimethylamino)-1-(*m*-tolyl)prop-2-ene-1-thione (1l)

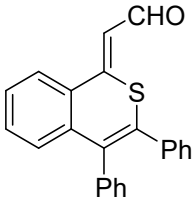
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red solid in 86% yield (352.8 mg, 1.72 mmol). Mp: 73 – 74 °C. **^{1}H NMR (DMSO-d_6, 500 MHz):** δ 8.33 (d, *J* = 10.9 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.27 – 7.19 (m, 2H), 6.64 (d, *J* = 11.2 Hz, 1H), 3.29 (s, 3H), 3.06 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (DMSO-d_6, 125 MHz):** δ 210.1, 158.0, 147.5,

136.6, 130.2, 127.5, 127.4, 124.1, 110.4, 45.8, 38.4, 21.0. **HRMS (ESI):** Calcd for $C_{12}H_{15}NNaS$ $[M+Na]^+$ 228.0817, found: 228.0819.



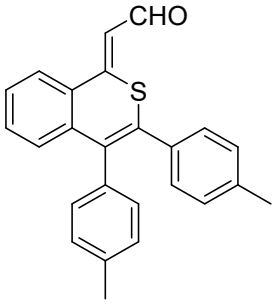
(*E*)-3-(dimethylamino)-1-(pyridin-4-yl)prop-2-ene-1-thione (1p)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red solid in 73% yield (280.4 mg, 1.46 mmol). Mp: 104 – 105 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.49 – 8.49 (m, 2H), 8.33 (d, *J* = 11.2 Hz, 1H), 7.51 – 7.51 (m, 2H), 6.43 (d, *J* = 11.3 Hz, 1H), 3.23 (s, 3H), 2.98 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 210.5, 157.8, 154.3, 149.3, 120.4, 111.1, 46.2, 38.4. **HRMS (ESI):** Calcd for $C_{10}H_{12}N_2NaS$ $[M+Na]^+$ 215.0613, found: 215.0612.



(*Z*)-2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3aa)

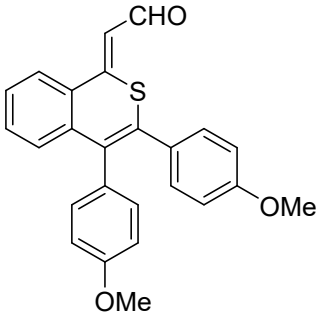
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 82% yield (55.8 mg, 0.164 mmol). Mp: 148 – 149 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.98 (d, *J* = 3.9 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.32 – 7.28 (m, 4H), 7.24 – 7.19 (m, 5H), 7.15 (d, *J* = 6.4 Hz, 2H), 6.98 (d, *J* = 4.0 Hz, 1H) **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 153.8, 137.4, 137.1, 135.4, 134.1, 132.5, 131.5, 131.1, 129.7, 129.3, 128.5, 128.2, 128.1, 128.0, 127.3, 126.1, 124.4, 113.3. **HRMS (ESI):** Calcd for $C_{23}H_{16}NaOS$ $[M+Na]^+$ 363.0814, found: 363.0812.



(*Z*)-2-(3,4-di-*p*-tolyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ab)

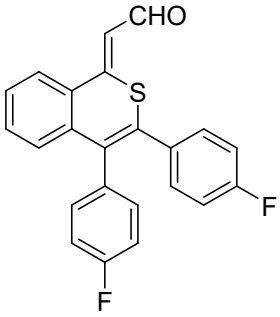
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 83% yield (61.1 mg, 0.166 mmol). Mp: 102 – 103 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 4.1 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.09 – 7.01 (m, 4H), 7.01 – 6.93 (m, 4H), 6.88 (d, *J* = 4.2 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 154.3, 137.9, 136.8, 135.8,

134.4, 134.2, 133.9, 132.2, 131.4, 130.9, 129.6, 129.2, 128.9, 128.8, 128.3, 126.1, 124.3, 113.3, 21.2. **HRMS (ESI):** Calcd for $C_{25}H_{20}NaOS$ $[M+Na]^+$ 391.1127, found: 391.1129.



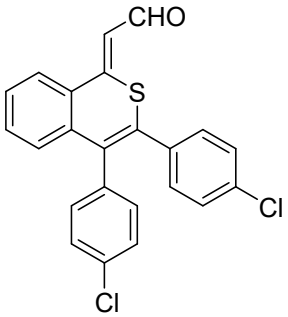
(*Z*)-2-(3,4-bis(4-methoxyphenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ac)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 77% yield (61.6 mg, 0.154 mmol). Mp: 90 – 91 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 4.1 Hz, 1H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.25 – 7.23 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 4.2 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 159.2, 158.6, 154.3, 135.9, 133.9, 132.7, 132.2, 132.0, 131.4, 131.1, 129.7, 129.2, 128.3, 126.1, 124.3, 113.7, 113.6, 113.3, 55.2, 55.2. **HRMS (ESI):** Calcd for $C_{25}H_{20}NaO_3S$ $[M+Na]^+$ 423.1025, found: 423.1029.



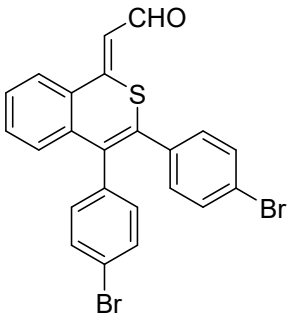
(*Z*)-2-(3,4-bis(4-fluorophenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ad)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 71% yield (53.4 mg, 0.142 mmol). Mp: 94 – 95 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.89 (d, *J* = 3.6 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.05 – 7.03 (m, 2H), 6.98 – 6.94 (m, 3H), 6.88 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 162.3 (d, *J* = 248.9 Hz), 161.9 (d, *J* = 247.7 Hz), 153.0, 135.1, 133.7, 133.1 (d, *J* = 3.7 Hz), 132.9 (d, *J* = 3.5 Hz), 132.6 (d, *J* = 8.0 Hz), 131.8, 131.6 (d, *J* = 8.1 Hz), 131.6, 129.0, 128.7, 126.0, 124.5, 115.4 (d, *J* = 21.6 Hz), 115.3 (d, *J* = 21.7 Hz), 113.2. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -112.4, -114.0. **HRMS (ESI):** Calcd for $C_{23}H_{14}F_2NaOS$ $[M+Na]^+$ 399.0626, found: 399.0629.



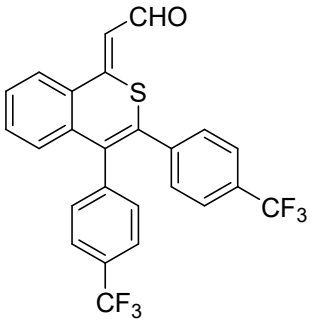
(*Z*)-2-(3,4-bis(4-chlorophenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ae)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 74% yield (60.4 mg, 0.148 mmol). Mp: 97 – 98 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.89 (d, *J* = 3.6 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.27 – 7.25 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 152.7, 135.6, 135.3, 134.9, 134.5, 133.6, 133.4, 132.3, 131.6, 131.6, 131.0, 129.0, 128.9, 128.7, 128.6, 126.1, 124.6, 113.5. **HRMS (ESI):** Calcd for $C_{23}H_{14}Cl_2NaOS$ $[M+Na]^+$ 431.0035, found: 431.0032.



(*Z*)-2-(3,4-bis(4-bromophenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3af)

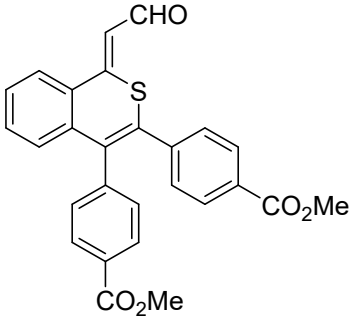
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 72% yield (71.4 mg, 0.144 mmol). Mp: 118 – 119 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.88 (d, *J* = 3.5 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.96 – 6.93 (m, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 152.6, 136.1, 135.7, 134.8, 133.4, 132.6, 131.7, 131.6, 131.5, 131.5, 131.2, 129.0, 128.9, 126.1, 124.6, 122.7, 121.8, 113.6. **HRMS (ESI):** Calcd for $C_{23}H_{14}Br_2NaOS$ $[M+Na]^+$ 520.9004 and 518.9024, found: 520.9002 and 518.9023.



(*Z*)-2-(3,4-bis(4-(trifluoromethyl)phenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ag)

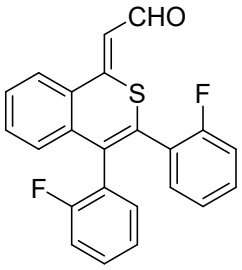
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 67% yield (63.8 mg, 0.134 mmol). Mp: 120 – 121 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.89 (d, *J* = 3.3 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.45 (m, 6H), 7.28– 7.23 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 3.4 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 152.0, 140.9, 140.3, 134.4, 133.5, 131.7, 131.7, 131.4, 130.5 (q, *J* = 32.8 Hz), 129.9 (q, *J* = 33.2 Hz), 129.3, 129.0, 126.1, 125.4 (q, *J* = 3.7 Hz),

125.3 (q, *J* = 3.9 Hz), 124.9, 124.7, 122.7, 122.6, 113.8. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -62.7, -62.9. **HRMS (ESI):** Calcd for $C_{25}H_{14}F_6NaOS$ $[M+Na]^+$ 499.0562, found: 499.0560.



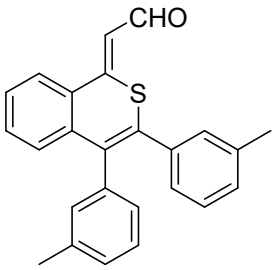
dimethyl 4,4'-(1-(2-oxoethylidene)-1*H*-isothiochromene-3,4-diyl)(*Z*)-dibenzoate (3ah)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 70% yield (63.9 mg, 0.140 mmol). Mp: 102 – 103 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.89 (d, *J* = 3.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 166.5, 166.3, 152.4, 142.1, 141.3, 134.5, 133.6, 132.0, 131.6, 131.1, 129.9, 129.8, 129.6, 129.5, 129.4, 129.1, 129.0, 126.1, 124.6, 113.6, 52.2. **HRMS (ESI):** Calcd for $C_{27}H_{20}NaO_5S$ $[M+Na]^+$ 479.0924, found: 479.0928.



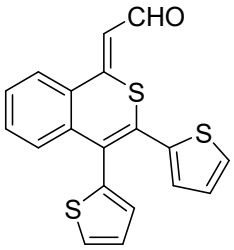
(*Z*)-2-(3,4-bis(2-fluorophenyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ai)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 47% yield (35.4 mg, 0.094 mmol). Mp: 150 – 151 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.88 (d, *J* = 3.4 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.25 – 7.18 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.02 – 6.98 (m, 4H), 6.89 (t, *J* = 8.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 159.3 (d, *J* = 249.0 Hz), 152.9, 134.2, 132.1 (d, *J* = 9.3 Hz), 132.0 (d, *J* = 9.9 Hz), 131.7, 131.3, 130.9 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 8.0 Hz), 129.9, 129.0, 128.4, 126.1, 124.7 (d, *J* = 16.7 Hz), 124.6, 124.3 (d, *J* = 15.7 Hz), 123.9, 115.5 (d, *J* = 21.1 Hz), 115.4 (d, *J* = 20.2 Hz), 113.2. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -112.5, -113.3. **HRMS (ESI):** Calcd for $C_{23}H_{14}F_2NaOS$ $[M+Na]^+$ 399.0626, found: 399.0624.



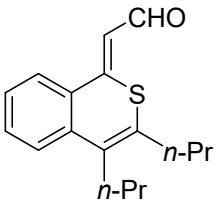
(*Z*)-2-(3,4-di-*m*-tolyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3aj)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 79% yield (58.2 mg, 0.158 mmol). Mp: 130 – 131 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 4.0 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.05 – 6.87 (m, 8H), 2.26 (s, 3H), 2.22 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 154.0, 137.7, 137.6, 137.3, 136.9, 135.6, 134.0, 132.4, 131.7, 131.4, 130.3, 129.3, 128.8, 128.4, 128.1, 128.0, 127.9, 127.8, 126.8, 126.0, 124.3, 113.2, 21.3, 21.2.. **HRMS (ESI):** Calcd for $C_{25}H_{20}NaOS$ $[M+Na]^+$ 391.1127, found: 391.1122.



(*Z*)-2-(3,4-di(thiophen-2-yl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ak)

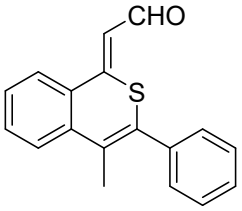
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a vermeil solid in 72% yield (50.7 mg, 0.144 mmol). Mp: 155 – 156 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.99 (d, *J* = 4.2 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.30 (d, *J* = 4.3 Hz, 2H), 7.12 (dd, *J* = 5.1, 3.5 Hz, 1H), 7.03 (d, *J* = 3.4 Hz, 1H), 6.96 – 6.92 (m, 1H), 6.89 (d, *J* = 4.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.8, 152.5, 138.2, 137.4, 135.7, 131.6, 130.8, 130.2, 129.5, 129.2, 129.1, 128.8, 127.8, 127.3, 126.5, 126.1, 124.4, 124.3, 114.8. **HRMS (ESI):** Calcd for $C_{19}H_{12}NaOS_3$ $[M+Na]^+$ 374.9942, found: 374.9945.



(*Z*)-2-(3,4-dipropyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3al)

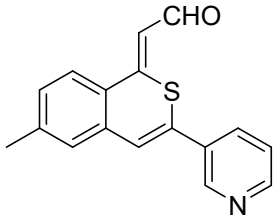
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 81% yield (44.1 mg, 0.162 mmol). Mp: 55 – 56 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.86 (d, *J* = 3.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 4.1 Hz, 1H), 2.77 – 2.70 (m, 2H), 2.61 – 2.54 (m, 2H), 1.74 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 1.06 – 1.02 (m, 6H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ

186.3, 154.4, 134.7, 133.0, 131.5, 128.3, 127.5, 126.6, 125.7, 124.8, 113.4, 36.3, 30.9, 23.6, 23.0, 14.3, 14.0. **HRMS (ESI):** Calcd for $C_{17}H_{20}NaOS$ $[M+Na]^+$ 295.1127, found: 295.1130.



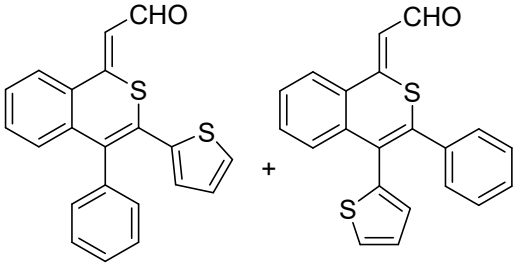
(*Z*)-2-(4-methyl-3-phenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3am)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as a yellow solid in 82% yield (45.6 mg, 0.164 mmol). Mp: 111 – 112 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.90 (d, *J* = 4.1 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.39 (m, 5H), 6.83 (d, *J* = 4.2 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.4, 153.8, 137.4, 135.5, 132.5, 131.7, 130.1, 128.8, 128.6, 128.3, 126.5, 126.2, 124.7, 113.6, 17.5. **HRMS (ESI):** Calcd for $C_{18}H_{14}NaOS$ $[M+Na]^+$ 301.0658, found: 301.0654.



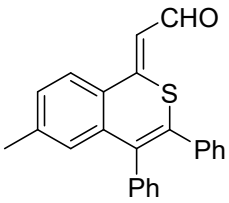
(Z)-2-(6-methyl-3-(pyridin-3-yl)-1H-isothiochromen-1-ylidene)acetaldehyde (3bn)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as a yellow solid in 23% yield (12.8 mg, 0.046 mmol). Mp: 106 – 107 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.87 (d, *J* = 3.0 Hz, 1H), 8.90 (s, 1H), 8.66 – 8.66 (m, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.39 – 7.39 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 1H), 7.17 (s, 1H), 6.93 (d, *J* = 3.1 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.1, 152.4, 150.2, 147.6, 142.7, 134.4, 134.0, 133.2, 132.8, 131.0, 130.8, 124.1, 123.6, 123.0, 122.0, 112.6, 21.3. **HRMS (ESI):** Calcd for $C_{17}H_{13}NNaOS$ $[M+Na]^+$ 302.0610, found: 302.0613.



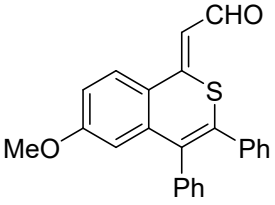
(*Z*)-2-(4-phenyl-3-(thiophen-2-yl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ao) and (Z)-2-(3-phenyl-4-(thiophen-2-yl)-1H-isothiochromen-1-ylidene)acetaldehyde (3ao') (**3ao**:**3ao'** = 1:1)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/10) as a orange red solid in 68% yield (47.1 mg, 0.136 mmol). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 9.99 (d, *J* = 4.2 Hz, 1H), 9.91 (d, *J* = 3.9 Hz, 1H), 8.02 (t, *J* = 9.0 Hz, 2H), 7.50 – 7.40 (m, 9H), 7.25 – 7.14 (m, 10H), 6.93 – 6.90 (m, 3H), 6.87 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.82 (d, *J* = 4.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 186.6, 186.5, 153.3, 152.9, 138.5, 137.6, 137.5, 137.4, 137.0, 135.6, 135.5, 132.3, 131.6, 131.4, 131.2, 129.8, 129.5, 129.3, 129.3, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.2, 128.1, 126.7, 126.7, 126.4, 126.1, 126.0, 124.9, 124.3, 124.3, 114.3, 113.7. **HRMS (ESI):** Calcd for $C_{21}H_{14}NaOS_2$ $[M+Na]^+$ 369.0378, found: 369.0375.



(*Z*)-2-(6-methyl-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ba)

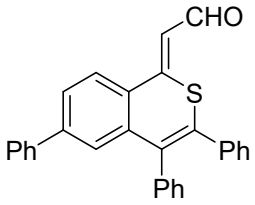
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 85% yield (60.2 mg, 0.170 mmol). Mp: 120 – 121 °C.**^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 3.9 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.19 – 7.19 (m, 5H), 7.12 (d, *J* = 6.5 Hz, 2H), 7.04 (s, 1H), 6.94 (d, *J* = 3.9 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.1, 154.0, 142.2, 137.4, 137.2, 135.4, 134.3, 132.4, 131.1, 129.8, 129.7, 129.4, 128.1, 128.0, 128.0, 127.2, 124.4, 123.7, 112.1, 21.6. **HRMS (ESI):** Calcd for $C_{24}H_{18}NaOS$ $[M+Na]^+$ 377.0971, found: 377.0966.



(*Z*)-2-(6-methoxy-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ca)

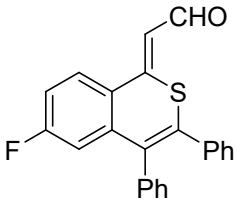
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 81% yield (60.0 mg, 0.162 mmol). Mp: 130 – 131 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.88 (d, *J* = 3.8 Hz, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.21 – 7.21 (m, 5H), 7.14 (d, *J* = 6.7 Hz, 2H), 7.08 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.88 (d, *J* = 3.9 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 185.7, 162.0, 153.8, 137.5, 137.3, 137.1, 135.2, 132.2,

131.0, 129.7, 128.2, 128.0, 127.9, 127.3, 126.5, 119.4, 115.6, 112.8, 110.7, 55.2. **HRMS (ESI):** Calcd for $C_{24}H_{18}NaO_2S$ $[M+Na]^+$ 393.0920, found: 393.0919.



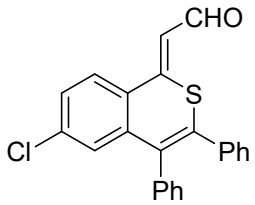
(*Z*)-2-(3,4,6-triphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3da)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 75% yield (62.4 mg, 0.150 mmol). Mp: 106 – 107 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.90 (d, *J* = 3.7 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 – 7.16 (m, 5H), 7.12 (d, *J* = 6.7 Hz, 2H), 6.94 (d, *J* = 3.8 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.2, 153.5, 143.9, 139.3, 137.2, 137.1, 135.9, 134.7, 132.5, 131.0, 129.7, 128.9, 128.2, 128.1, 128.0, 127.5, 127.4, 127.2, 127.0, 125.0, 125.0, 112.7. **HRMS (ESI):** Calcd for $C_{29}H_{20}NaOS$ $[M+Na]^+$ 439.1127, found: 439.1129.



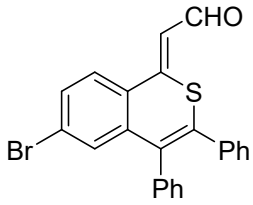
(*Z*)-2-(6-fluoro-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ea)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a vermeil solid in 73% yield (52.3 mg, 0.146 mmol). Mp: 123 – 124 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 3.8 Hz, 1H), 8.10 (dd, *J* = 9.1, 5.7 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.23 – 7.16 (m, 6H), 7.12 – 7.10 (m, 2H), 6.94 – 6.87 (m, 2H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.2, 164.4 (d, *J* = 252.5 Hz), 152.7, 138.2 (d, *J* = 8.9 Hz), 136.7 (d, *J* = 8.5 Hz), 136.0, 131.7 (d, *J* = 2.6 Hz), 130.9, 129.6, 128.4, 128.3, 128.1, 127.6, 127.1 (d, *J* = 9.1 Hz), 122.5 (d, *J* = 2.7 Hz), 116.4 (d, *J* = 22.7 Hz), 115.0 (d, *J* = 23.7 Hz), 112.9. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -106.9. **HRMS (ESI):** Calcd for $C_{23}H_{15}FNaOS$ $[M+Na]^+$ 381.0720, found: 381.0716.



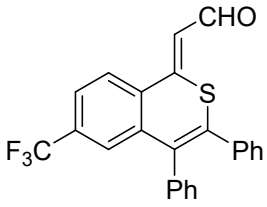
(*Z*)-2-(6-chloro-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3fa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 80% yield (59.8 mg, 0.160 mmol). Mp: 136 – 137 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 3.7 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.44 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 – 7.14 (m, 6H), 7.10 – 7.08 (m, 2H), 6.91 (d, *J* = 3.8 Hz, 1H) **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 152.5, 138.0, 137.0, 136.7, 136.6, 136.0, 131.5, 131.0, 129.6, 128.7, 128.6, 128.4, 128.3, 128.1, 127.6, 126.0, 124.6, 113.4. **HRMS (ESI):** Calcd for $C_{23}H_{15}ClNaOS$ $[M+Na]^+$ 397.0424, found: 397.0422.



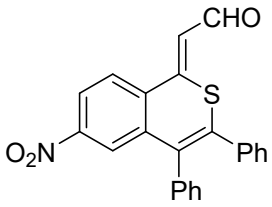
(*Z*)-2-(6-bromo-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ga)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 76% yield (63.5 mg, 0.152 mmol). Mp: 120 – 121 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 3.6 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.35 (d, *J* = 1.9 Hz, 1H), 7.31 – 7.28 (m, 3H), 7.21 – 7.14 (m, 5H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 3.7 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 152.5, 137.2, 136.7, 136.6, 136.0, 131.6, 131.6, 131.4, 131.0, 129.6, 128.4, 128.3, 128.1, 127.6, 126.5, 126.0, 124.9, 113.4. **HRMS (ESI):** Calcd for $C_{25}H_{15}BrNaOS$ $[M+Na]^+$ 440.9919 and 442.9899, found: 440.9921 and 442.9896.



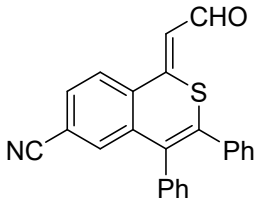
(*Z*)-2-(3,4-diphenyl-6-(trifluoromethyl)-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ha)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 71% yield (57.9 mg, 0.142 mmol). Mp: 113 – 114 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.96 (d, *J* = 3.7 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.46 (s, 1H), 7.31 – 7.27 (m, 3H), 7.21 – 7.15 (m, 5H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 3.7 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 151.7, 136.6, 136.3, 136.1, 135.9, 132.7, 131.9, 130.9, 129.6, 128.7, 128.5, 128.4, 128.2, 127.8, 125.8 (q, *J* = 4.3 Hz), 125.3, 124.7 (q, *J* = 3.4 Hz), 115.1. **^{19}F NMR ($CDCl_3$, 471 MHz):** δ -63.3. **HRMS (ESI):** Calcd for $C_{24}H_{15}F_3NaOS$ $[M+Na]^+$ 431.0688, found: 431.0686.



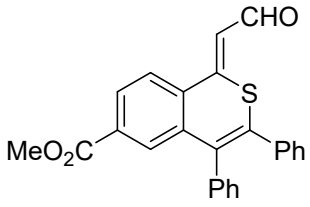
(*Z*)-2-(6-nitro-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3ia)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 67% yield (51.6 mg, 0.134 mmol). Mp: 152 – 153 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.96 (d, *J* = 3.6 Hz, 1H), 8.21 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 8.04 (d, *J* = 2.3 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.21 – 7.17 (m, 3H), 7.16 – 7.13 (m, 2H), 7.10 – 7.07 (m, 2H), 6.97 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 150.6, 149.1, 137.1, 136.8, 136.3, 135.9, 131.6, 130.9, 130.8, 129.5, 128.7, 128.6, 128.2, 128.1, 126.1, 123.7, 122.4, 116.3. **HRMS (ESI):** Calcd for $C_{23}H_{15}NNaO_3S$ $[M+Na]^+$ 408.0665, found: 408.0663.



(*Z*)-1-(2-oxoethylidene)-3,4-diphenyl-1*H*-isothiochromene-6-carbonitrile (3ja)

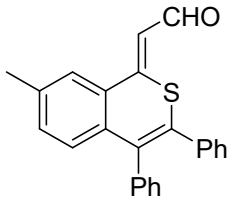
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 68% yield (49.7 mg, 0.136 mmol). Mp: 91 – 92 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.95 (d, *J* = 3.6 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.21 – 7.17 (m, 3H), 7.15 – 7.12 (m, 2H), 7.07 – 7.04 (m, 2H), 6.92 (d, *J* = 3.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 150.9, 136.8, 136.3, 136.2, 136.0, 133.0, 131.1, 130.9, 130.6, 129.5, 129.4, 128.7, 128.6, 128.2, 128.0, 125.5, 117.9, 115.7, 114.8. **HRMS (ESI):** Calcd for $C_{24}H_{15}NNaOS$ $[M+Na]^+$ 388.0767, found: 388.0763.



methyl (*Z*)-1-(2-oxoethylidene)-3,4-diphenyl-1*H*-isothiochromene-6-carboxylate (3ka)

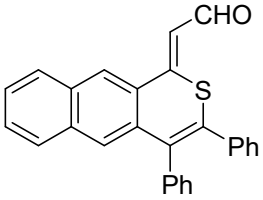
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 74% yield (58.9 mg, 0.148 mmol). Mp: 118 – 119 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.97 (d, *J* = 3.8 Hz, 1H), 8.12 – 8.06 (m, 2H), 7.91 (d, *J* = 1.4 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.21 – 7.16 (m, 5H), 7.12 – 7.10 (m, 2H), 6.99 (d, *J* = 3.8 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 165.9, 152.2, 136.8, 136.7, 135.5, 135.1, 132.4, 132.3, 131.0, 130.4, 129.7,

129.5, 128.7, 128.4, 128.3, 128.1, 127.6, 124.7, 114.9, 52.4. **HRMS (ESI):** Calcd for $C_{25}H_{18}NaO_3S$ $[M+Na]^+$ 421.0869, found: 421.0865.



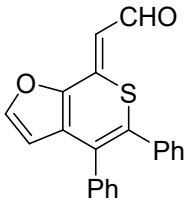
(*Z*)-2-(7-methyl-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)acetaldehyde (3la)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 81% yield (57.4 mg, 0.162 mmol). Mp: 164 – 165 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.91 (d, *J* = 4.0 Hz, 1H), 7.87 (s, 1H), 7.27 – 7.21 (m, 4H), 7.19 – 7.12 (m, 5H), 7.12 – 7.06 (m, 3H), 6.93 (d, *J* = 4.0 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.3, 154.0, 138.6, 137.5, 137.1, 133.1, 132.9, 132.7, 132.4, 131.1, 129.8, 129.3, 128.1, 128.0, 127.2, 125.9, 124.4, 112.8, 21.4. **HRMS (ESI):** Calcd for $C_{24}H_{18}NaOS$ $[M+Na]^+$ 377.0971, found: 377.0972.



(*Z*)-2-(3,4-diphenyl-1*H*-benzo[*g*]isothiochromen-1-ylidene)acetaldehyde (3ma)

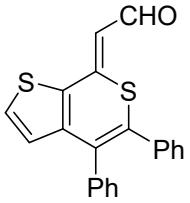
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 70% yield (54.6 mg, 0.140 mmol). Mp: 141 – 142 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 10.07 (d, *J* = 4.8 Hz, 1H), 8.53 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.59 (s, 1H), 7.53 – 7.48 (m, 2H), 7.31 – 7.28 (m, 3H), 7.20 – 7.14 (m, 7H), 7.07 (d, *J* = 4.8 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 187.1, 153.7, 137.7, 137.4, 134.4, 132.5, 132.4, 132.1, 131.7, 131.3, 129.7, 128.6, 128.4, 128.2, 128.2, 128.1, 128.1, 128.0, 127.3, 127.2, 125.2, 124.7, 116.4. **HRMS (ESI):** Calcd for $C_{27}H_{18}NaOS$ $[M+Na]^+$ 413.0971, found: 413.0972.



(*Z*)-2-(4,5-diphenyl-7*H*-thiopyrano[3,4-*b*]furan-7-ylidene)acetaldehyde (3na)

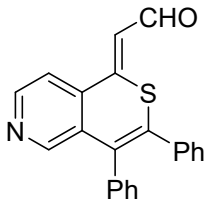
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 77% yield (50.8 mg, 0.154 mmol). Mp: 219 – 220 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.66 (d, *J* = 2.1 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.26 – 7.19 (m, 8H), 7.13 – 7.11 (m, 2H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.49 (d, *J* = 1.9 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 185.1, 146.2, 145.3, 142.8, 137.4,

136.4, 135.7, 131.2, 130.5, 129.9, 129.2, 128.5, 128.3, 128.2, 127.6, 110.6, 103.2. **HRMS (ESI):** Calcd for $C_{21}H_{14}NaO_2S$ $[M+Na]^+$ 353.0607, found: 353.0609.



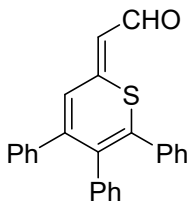
(*Z*)-2-(4,5-diphenyl-7*H*-thieno[2,3-*c*]thiopyran-7-ylidene)acetaldehyde (3oa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 84% yield (58.1 mg, 0.168 mmol). Mp: 234 – 235 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.64 (d, *J* = 2.5 Hz, 1H), 7.49 (d, *J* = 5.4 Hz, 1H), 7.27 – 7.25 (m, 3H), 7.19 – 7.19 (m, 5H), 7.14 – 7.12 (m, 2H), 6.92 (d, *J* = 5.4 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 184.8, 149.5, 143.3, 137.5, 137.3, 136.0, 132.3, 130.8, 130.3, 130.3, 129.1, 128.9, 128.4, 128.2, 128.1, 127.5, 107.1. **HRMS (ESI):** Calcd for $C_{21}H_{14}NaOS_2$ $[M+Na]^+$ 369.0378, found: 369.0375.



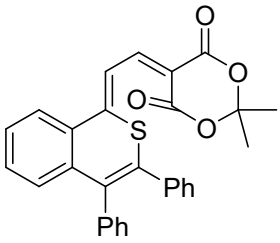
(*Z*)-2-(3,4-diphenyl-1*H*-thiopyrano[4,3-*c*]pyridin-1-ylidene)acetaldehyde (3pa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 61% yield (41.6 mg, 0.122 mmol). Mp: 81 – 82 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.92 (d, *J* = 3.0 Hz, 1H), 8.59 (d, *J* = 49.9 Hz, 2H), 7.77 (s, 1H), 7.25 – 7.22 (m, 3H), 7.18 – 7.11 (m, 5H), 7.08 (d, *J* = 6.5 Hz, 2H), 7.00 (d, *J* = 3.0 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 186.5, 151.6, 150.4, 148.3, 136.3, 136.3, 135.6, 131.6, 130.9, 130.3, 129.6, 128.8, 128.5, 128.2, 127.8, 116.4, 114.4. **HRMS (ESI):** Calcd for $C_{22}H_{16}NOS$ $[M+H]^+$ 342.0947, found: 342.0943.



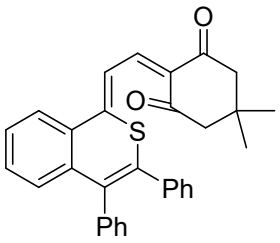
(*Z*)-2-(4,5,6-triphenyl-2*H*-thiopyran-2-ylidene)acetaldehyde (3qa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a yellow solid in 65% yield (47.6 mg, 0.30 mmol). Mp: 57 – 58 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 9.54 (d, *J* = 1.6 Hz, 1H), 7.19 – 7.12 (m, 8H), 7.03 – 6.99 (m, 2H), 6.96 – 6.90 (m, 4H), 6.75 – 6.70 (m, 2H), 6.23 (s, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 185.0, 153.2, 149.3, 143.7, 140.4, 137.0, 136.9, 134.0, 131.0, 129.8, 128.7, 128.4, 128.0, 127.7, 127.5, 127.4, 126.6, 126.5, 111.2. **HRMS (ESI):** Calcd for $C_{25}H_{18}NaOS$ $[M+Na]^+$ 389.0971, found: 389.0974.



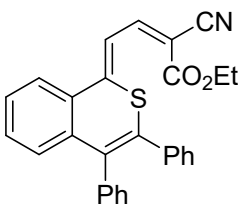
(*Z*)-5-(2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (5)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a purple solid in 92% yield (85.8 mg, 0.184 mmol). Mp: 159 – 160 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.77 (d, *J* = 12.9 Hz, 1H), 8.49 (d, *J* = 12.9 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.28 (m, 4H), 7.25 – 7.21 (m, 3H), 7.19 – 7.17 (m, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 6H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 164.1, 162.3, 160.5, 149.0, 136.8, 136.2, 136.1, 134.3, 134.0, 132.5, 131.0, 129.6, 129.2, 128.6, 128.3, 128.3, 127.8, 127.6, 125.1, 115.2, 105.1, 104.1, 27.5. **HRMS (ESI):** Calcd for $C_{29}H_{22}NaO_4S$ $[M+Na]^+$ 489.1131, found: 489.1137.



(*Z*)-2-(2-(3,4-diphenyl-1*H*-isothiochromen-1-ylidene)ethylidene)-5,5-dimethylcyclohexane-1,3-dione (7)

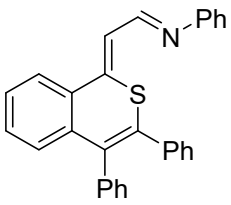
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a purple solid in 87% yield (80.4 mg, 0.174 mmol). Mp: 168 – 169 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.64 (d, *J* = 12.8 Hz, 1H), 8.45 (d, *J* = 12.8 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 8.3 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.20 – 7.13 (m, 6H), 7.09 – 7.07 (m, 2H), 2.54 (s, 2H), 2.51 (s, 2H), 1.09 (s, 6H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 199.4, 197.8, 158.9, 143.4, 137.1, 136.6, 135.8, 134.3, 133.5, 131.8, 131.1, 129.6, 129.3, 129.0, 128.3, 128.3, 128.2, 127.4, 125.0, 124.6, 116.8, 54.0, 52.2, 28.59. **HRMS (ESI):** Calcd for $C_{31}H_{26}NaO_2S$ $[M+Na]^+$ 485.1546, found: 485.1549.



ethyl (*Z*)-2-cyano-4-((*Z*)-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)but-2-enoate (9)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red solid in 86% yield (74.8 mg, 0.172 mmol). Mp: 172 – 173 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.46 (d, *J* = 12.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.27 – 7.23 (m, 3H),

7.20 – 7.18 (m, 4H), 7.16 – 7.13 (m, 3H), 7.09 – 7.08 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 163.3, 152.5, 148.2, 137.0, 136.6, 135.6, 133.0, 133.0, 131.6, 131.0, 129.4, 129.3, 129.1, 128.3, 128.3, 128.2, 127.5, 127.4, 124.4, 115.9, 113.7, 100.2, 61.9, 14.2. **HRMS (ESI):** Calcd for $C_{28}H_{21}NNaO_2S$ $[M+Na]^+$ 458.1185, found: 458.1187.



(*E*)-2-((*Z*)-3,4-diphenyl-1*H*-isothiochromen-1-ylidene)-*N*-phenylethan-1-imine (11)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/50) as a red solid in 90% yield (74.7 mg, 0.180 mmol). Mp: 111 – 112 °C. **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.75 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.14 (m, 11H), 7.10 – 7.08 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 156.5, 152.0, 144.5, 137.7, 137.4, 134.9, 132.3, 132.3, 131.1, 130.0, 129.2, 129.1, 128.7, 128.7, 128.6, 128.1, 128.1, 127.9, 127.1, 125.9, 124.3, 121.1, 120.2. **HRMS (ESI):** Calcd for $C_{29}H_{21}NNaS$ $[M+Na]^+$ 438.1287, found: 438.1285.

5. X-ray Crystallography of 3aa

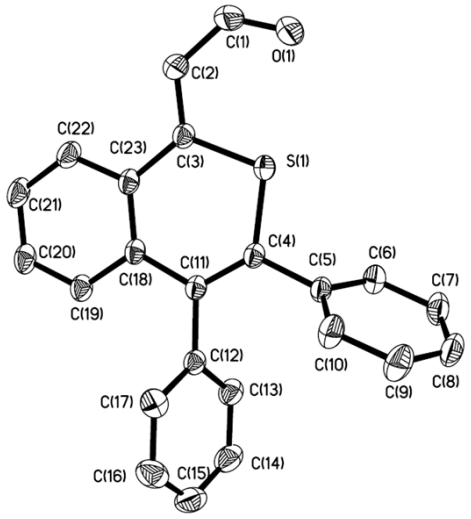


Figure S1. The molecular structure of **3aa**

Crystal preparation of compound 3aa.

Compound **3aa** (25 mg) was dissolved in 5 mL of dichloromethane/*n*-hexane (v1/v2 = 1:1), and it was crystallized to give crystal as colorless prisms after the solvent was slowly

volatilized in 4 days at room temperature (~ 25 °C).

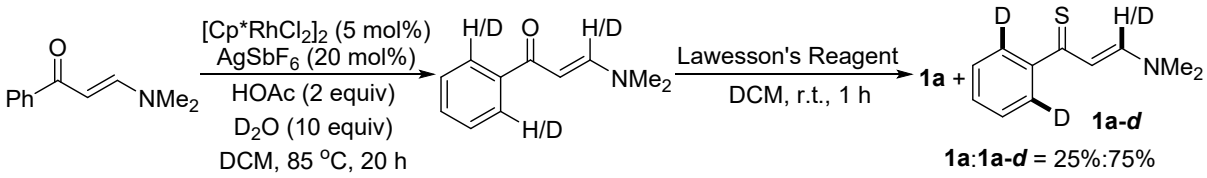
CCDC-2308326 (**3aa**), contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity. X-ray crystallographic data for **3aa** is available as Figure S1.

Table S3. Crystal Data and Summary of X-ray Data Collection for 3aa

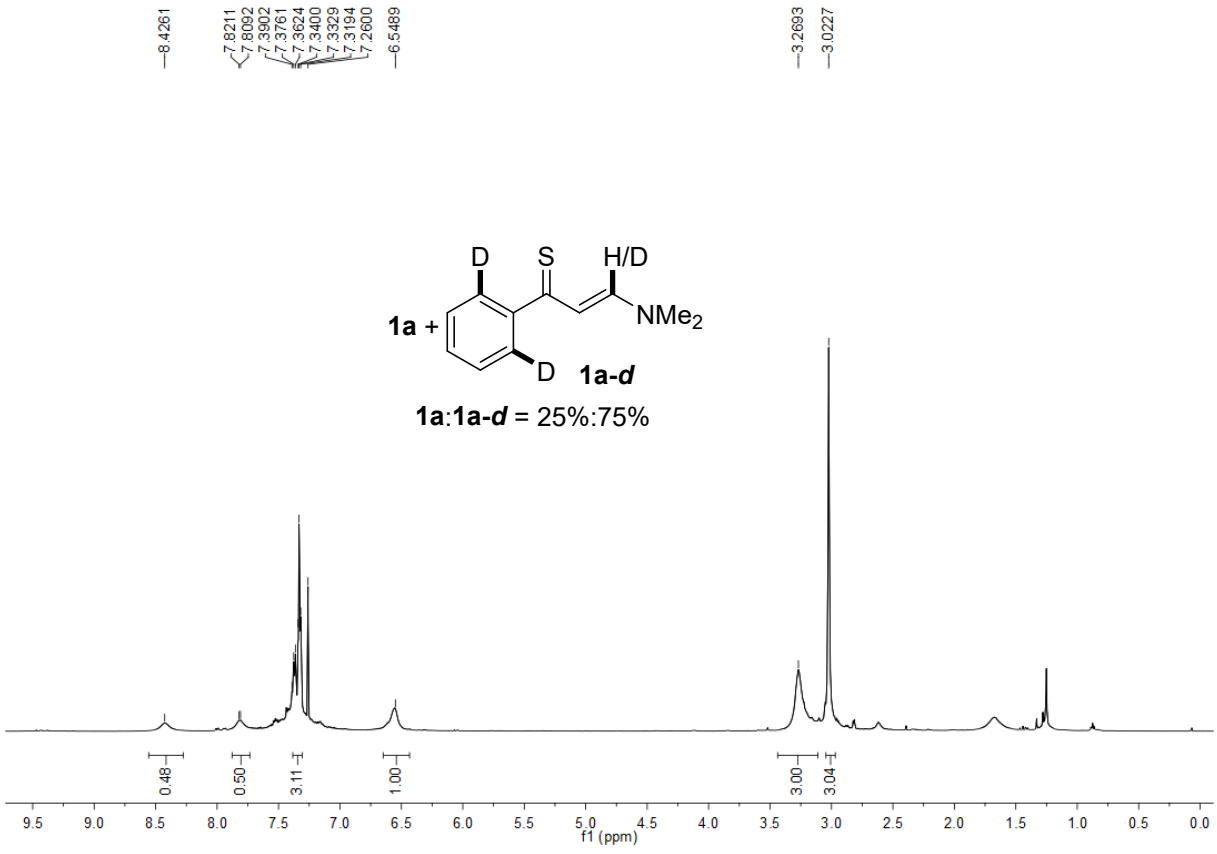
Empirical formula	C23 H16 O S
Formula weight	340.42
Temperature	273.15 K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 12.7462(15) A alpha = 90 deg.
	b = 9.1384(10) A beta = 95.183(4) deg.
	c = 15.0589(17) A gamma = 90 deg.
Volume	1746.9(3) A^3
Z, Calculated density	4, 1.294 Mg/m^3
Absorption coefficient	0.192 mm^-1
F(000)	712.0
Theta range for data collection	4.388 to 61.354 deg.
Limiting indices	-18<=h<=18, -10<=k<=13, -21<=l<=21
Reflections collected / unique	28047 / 2820 [R(int) = 0.0262]
Max. and min. transmission	0.6687 and 0.7461
Data / restraints / parameters	5329 / 6 / 226
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.1094
R indices (all data)	R1 = 0.0529, wR2 = 0.1182
Largest diff. peak and hole	0.27 and -0.26 e.A^-3

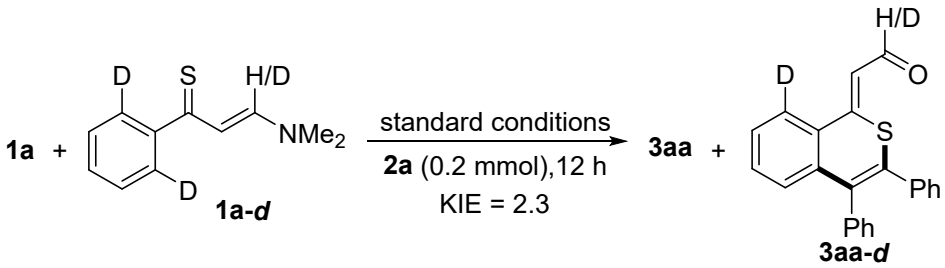
6. Mechanism Research

(a) Competition KIE Experiments

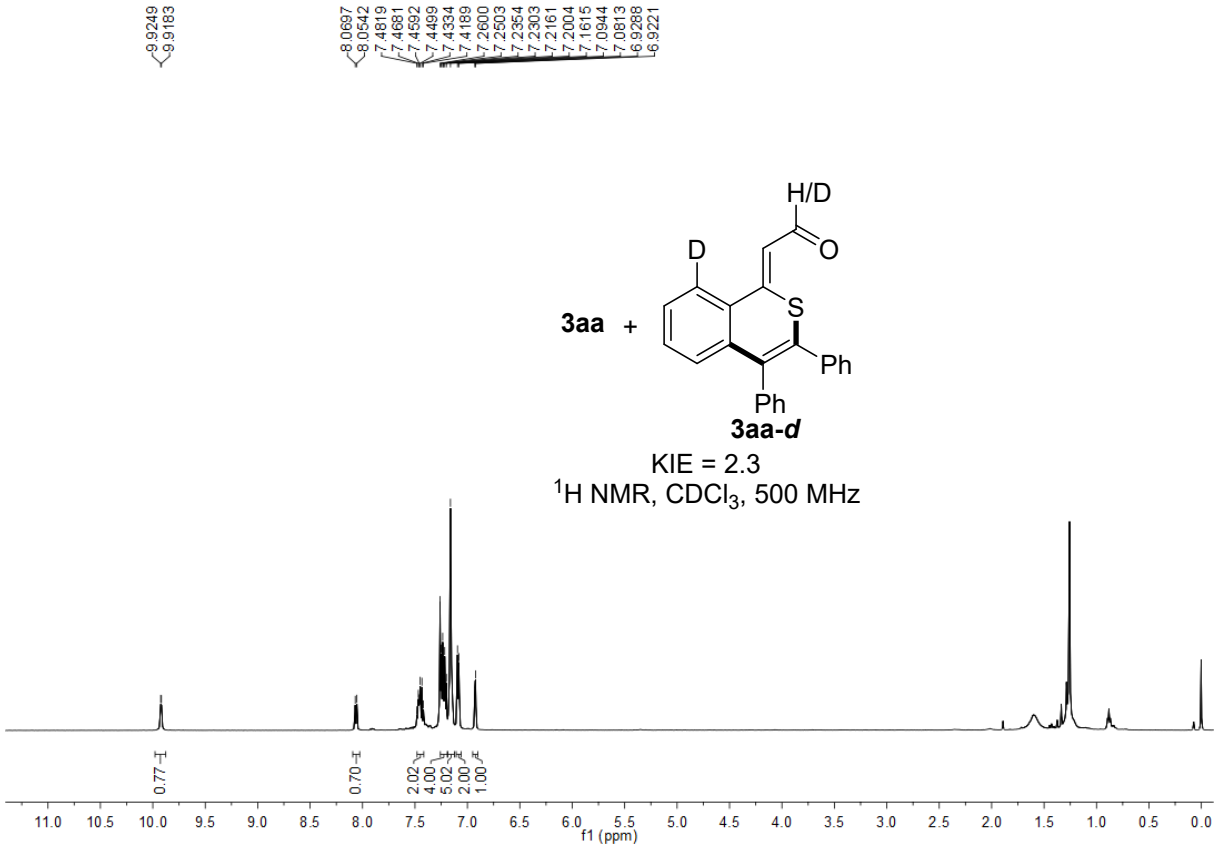


A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (175.1 mg, 1 mmol, 1.0 equiv), $[(Cp^*RhCl_2]_2$ (0.05 mmol, 5 mol%) and $AgSbF_6$ (0.2 mmol, 20 mol%) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (5 mL), HOAc (2 mmol, 2 equiv), and D_2O (20 mmol, 10 equiv) were added and the mixture was stirred at 85 °C in a pre-heated oil bath for 20 h under N_2 atmosphere. Then, deuterated enaminone was obtained by column chromatography on silica gel with EtOAc/petroleum ether, and treated by Lawesson's Reagent (1 equiv) in DCM (10 mL) at room temperature for 1 h. Finally, a mixture (71% yield) of **1a** and **1a-*d*** was presented by column chromatography on silica gel with EtOAc/petroleum ether with 25%:75%.

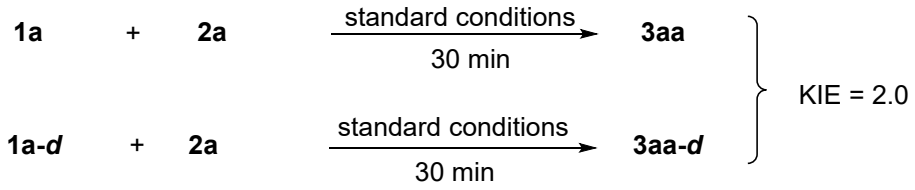




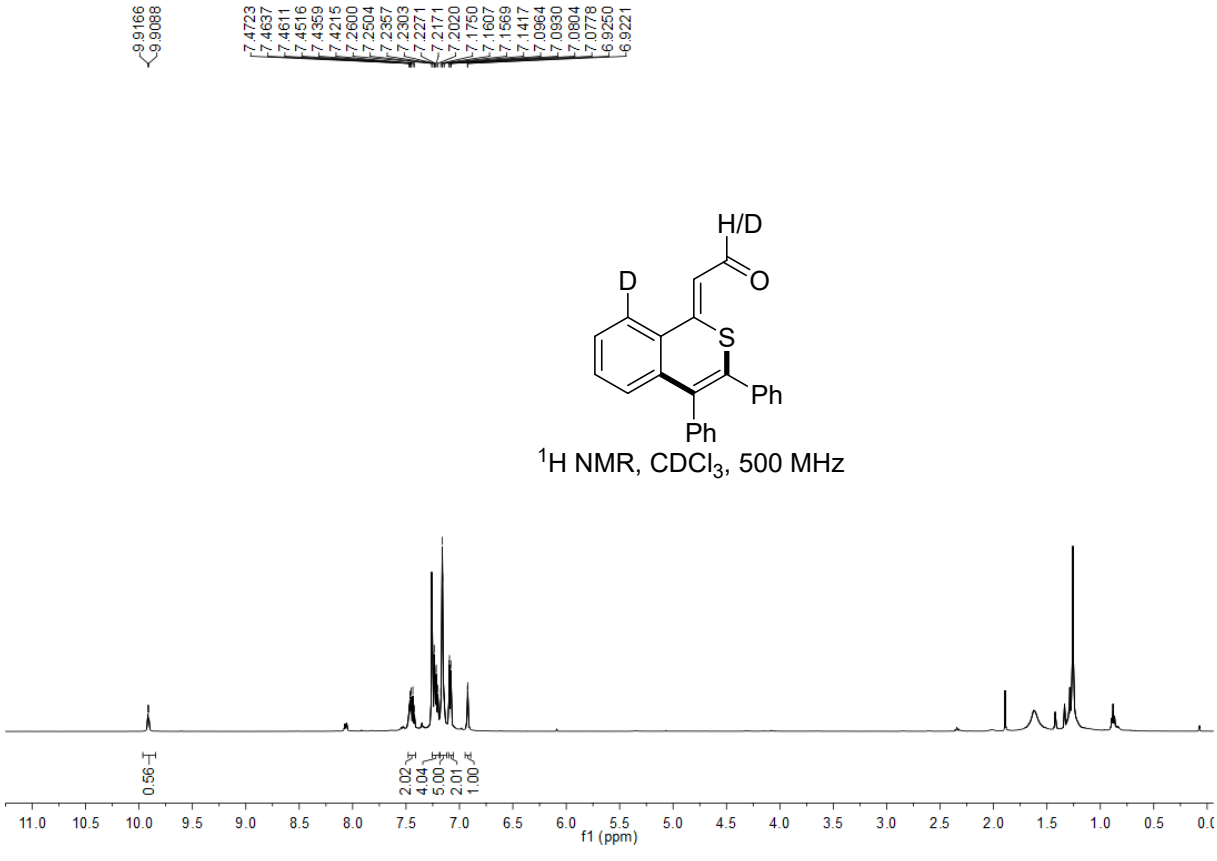
A mixture of (E)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (38.2 mg, 0.2 mmol, 1.0 equiv), **1a-*d*** (38.6 mg, 0.2 mmol, 1.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), $[(Cp^*RhCl_2]_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 ^oC in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether. The KIE value was determined to be k_H/k_D = 2.3 on the basis of ^1H NMR analysis.



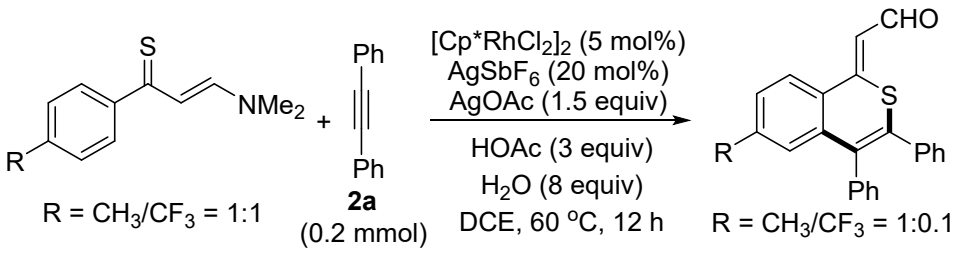
(b) Parallel KIE Experiments



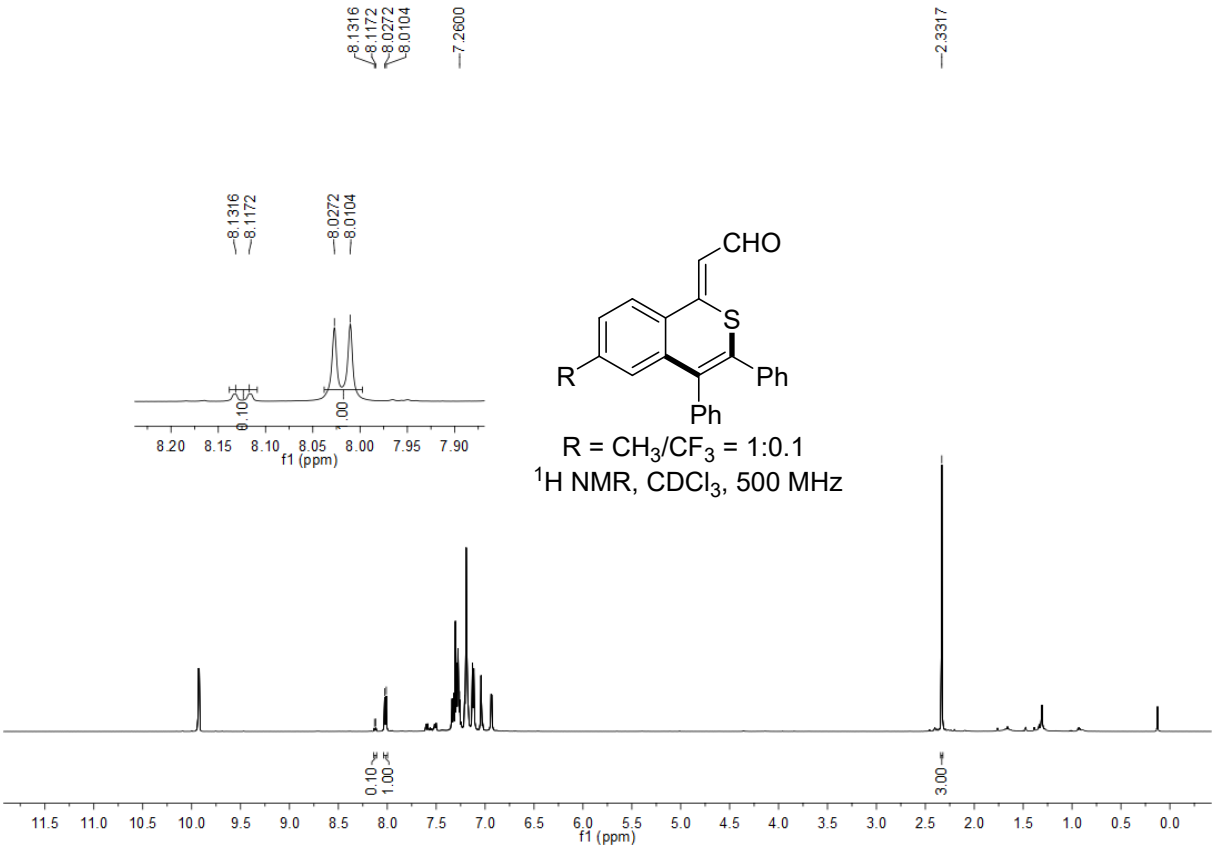
A mixture of **2a** (53.4 mg, 0.3 mmol, 1.5 equiv), $[(Cp^*RhCl_2]_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in each of two Schlenk tube equipped with a stir bar. To the parallel tubes was then separately introduced **1a** (38.2 mg, 0.2 mmol, 1.0 equiv) and **1a-*d*** (38.6 mg, 0.2 mmol, 1.0 equiv). Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give the desired product **3aa** in 21.6% yield (14.7 mg, 0.0432 mmol) or **3aa-*d*** in 10.3% yield (7.0 mg, 0.0205 mmol). The KIE value was calculated to be k_H/k_D = 2.0 according to isolated yields of **3aa** and **3aa-*d***.



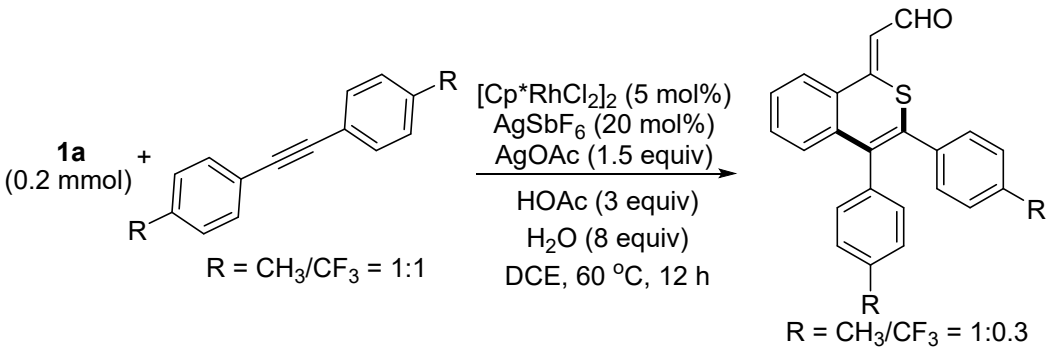
(c) Competition Experiment of 1b and 1h



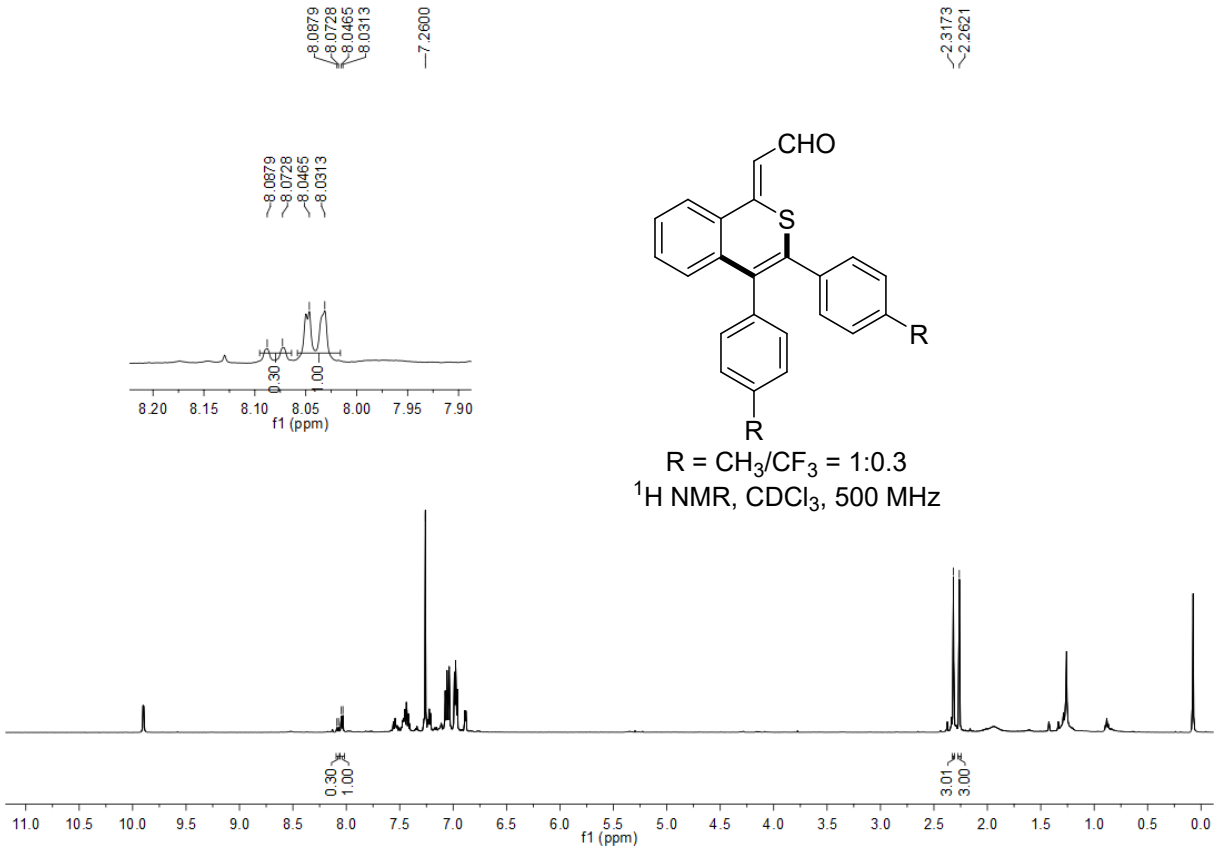
A mixture of (*E*)-3-(dimethylamino)-1-(*p*-tolyl)prop-2-ene-1-thione (**1b**) (41.0 mg, 0.2 mmol, 1.0 equiv), (*E*)-3-(dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-ene-1-thione (**1h**) (51.8 mg, 0.2 mmol, 1.0 equiv), 1,2-diphenylethyne (**2a**) (35.6 mg, 0.2 mmol, 1.0 equiv), [(Cp^*RhCl_2]$_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ba** and **3ha** at a ratio of 1:0.1.



(d) Competition Experiment of 2b and 2g



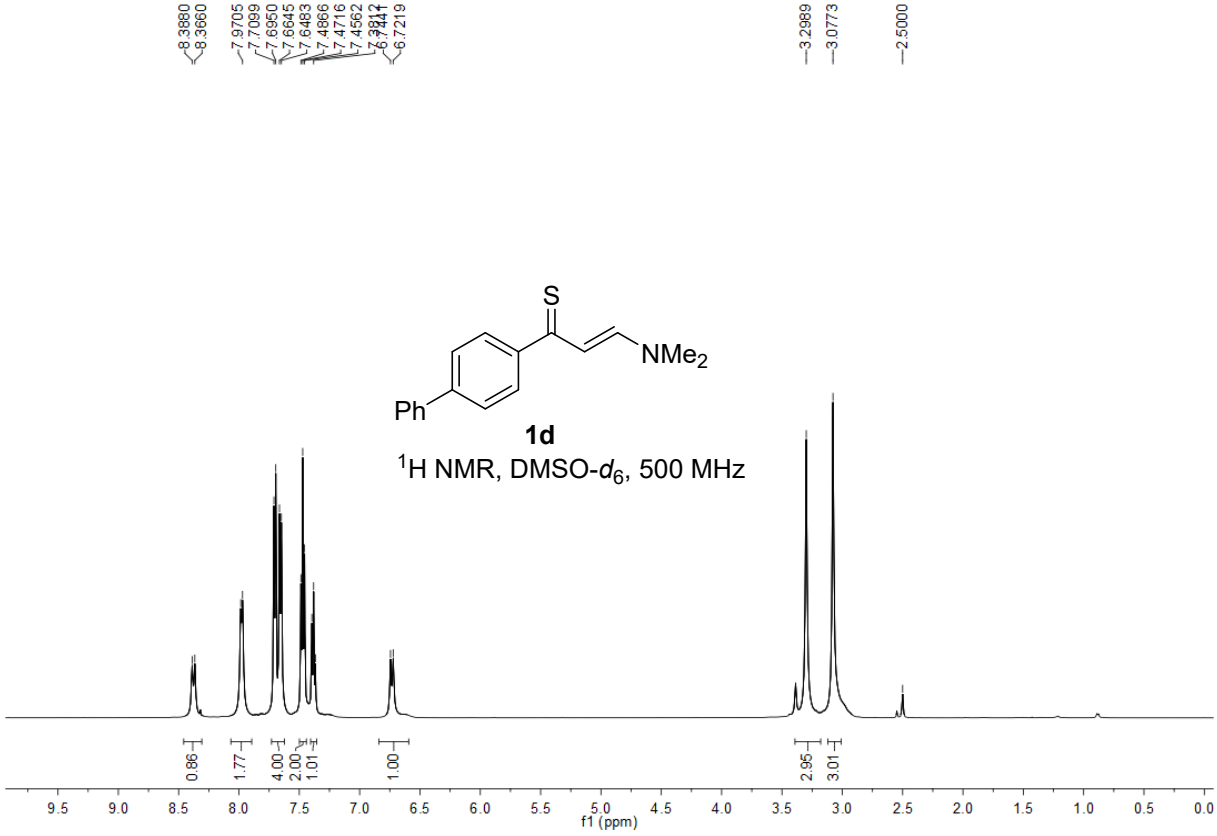
A mixture of (*E*)-3-(dimethylamino)-1-phenylprop-2-ene-1-thione (**1a**) (38.2 mg, 0.2 mmol, 1.0 equiv), (51.8 mg, 0.2 mmol, 1.0 equiv), 1,2-di-p-tolylethyne (**2b**) (41.2 mg, 0.2 mmol, 1.0 equiv), (51.8 mg, 0.2 mmol, 1.0 equiv), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (**2g**) (62.8 mg, 0.2 mmol, 1.0 equiv), $[(Cp^*RhCl_2]_2$ (0.01 mmol, 5 mol%), $AgSbF_6$ (0.04 mmol, 20 mol%), and AgOAc (0.3 mmol, 1.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (1.5 mL), HOAc (3 equiv), and H_2O (1.6 mmol, 8 equiv) were added and the mixture was stirred at 60 °C in a pre-heated oil bath for 12 h under N_2 atmosphere. Then, the mixture was cooled to room temperature and concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ab** and **3ag** at a ratio of 1:0.3.

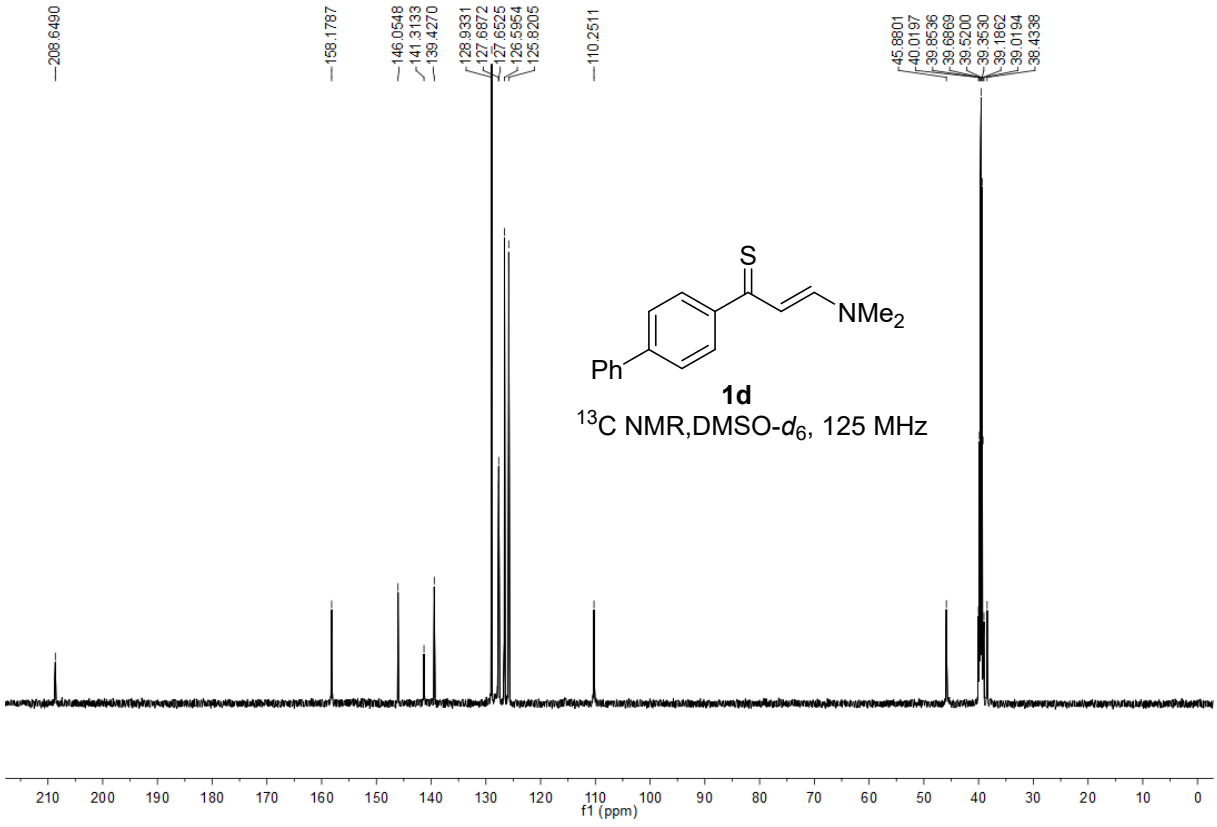


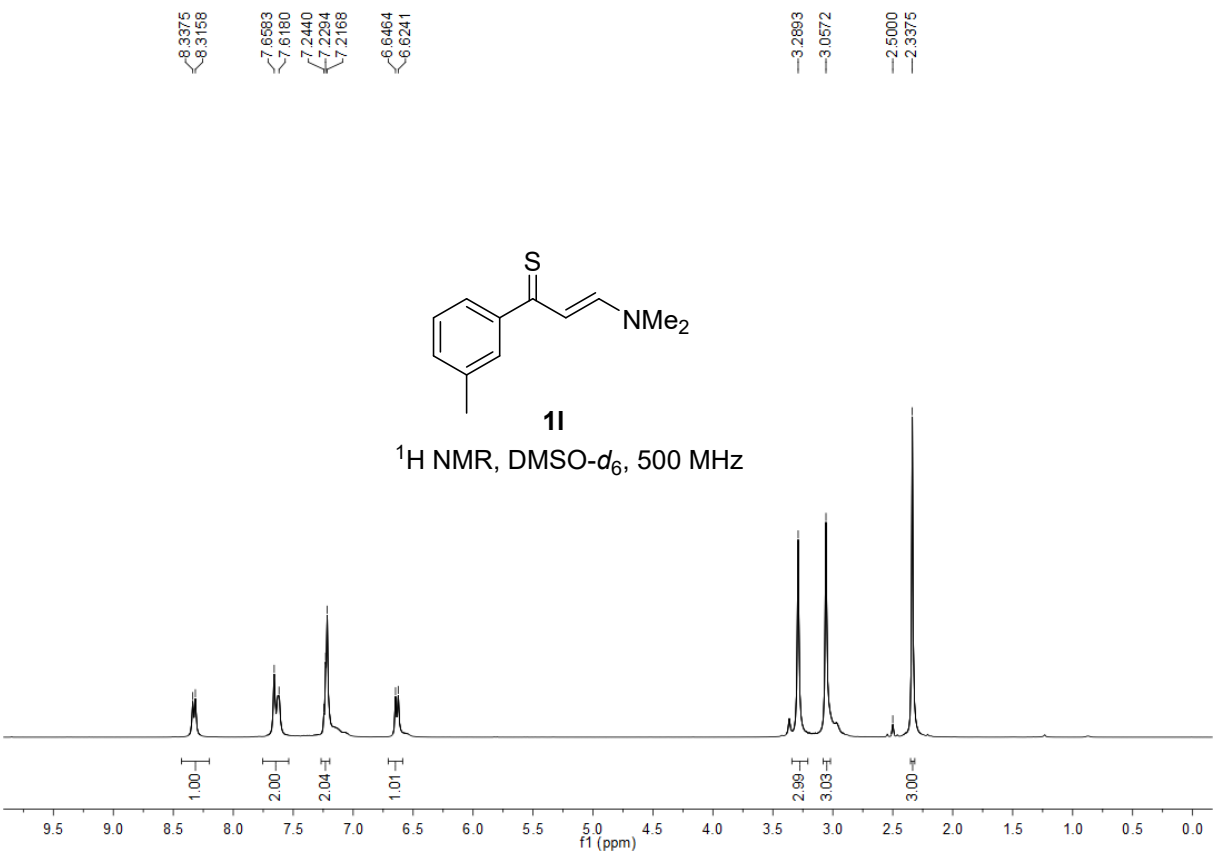
7. References:

(1) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228–234.
(2) Zhang, X.; Zhang, J.; Chen, J.; Zhou, B.; Zhang, J.; Chen, S.; Wu, J.; Jiang, Y. *Org. Biomol. Chem.* **2023**, *21*, 3345–3349.

8. NMR Spectra

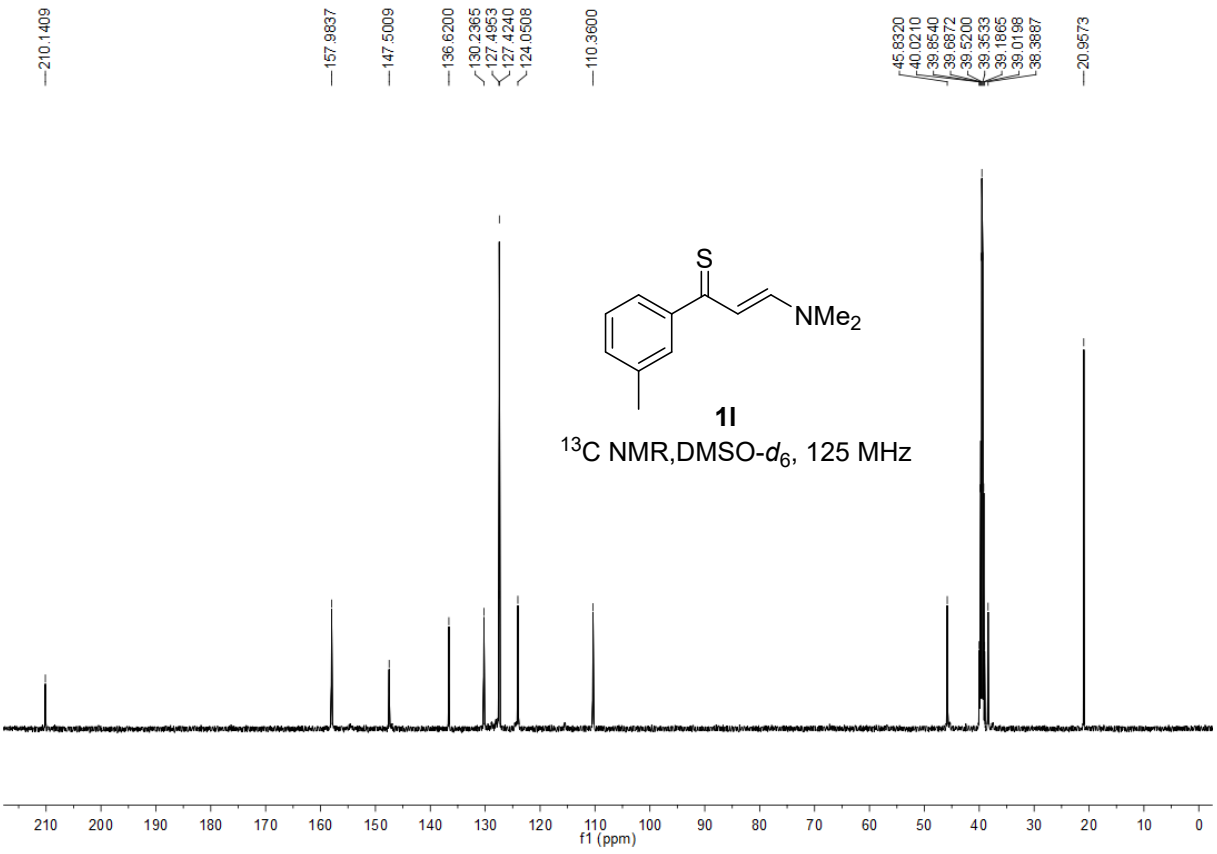






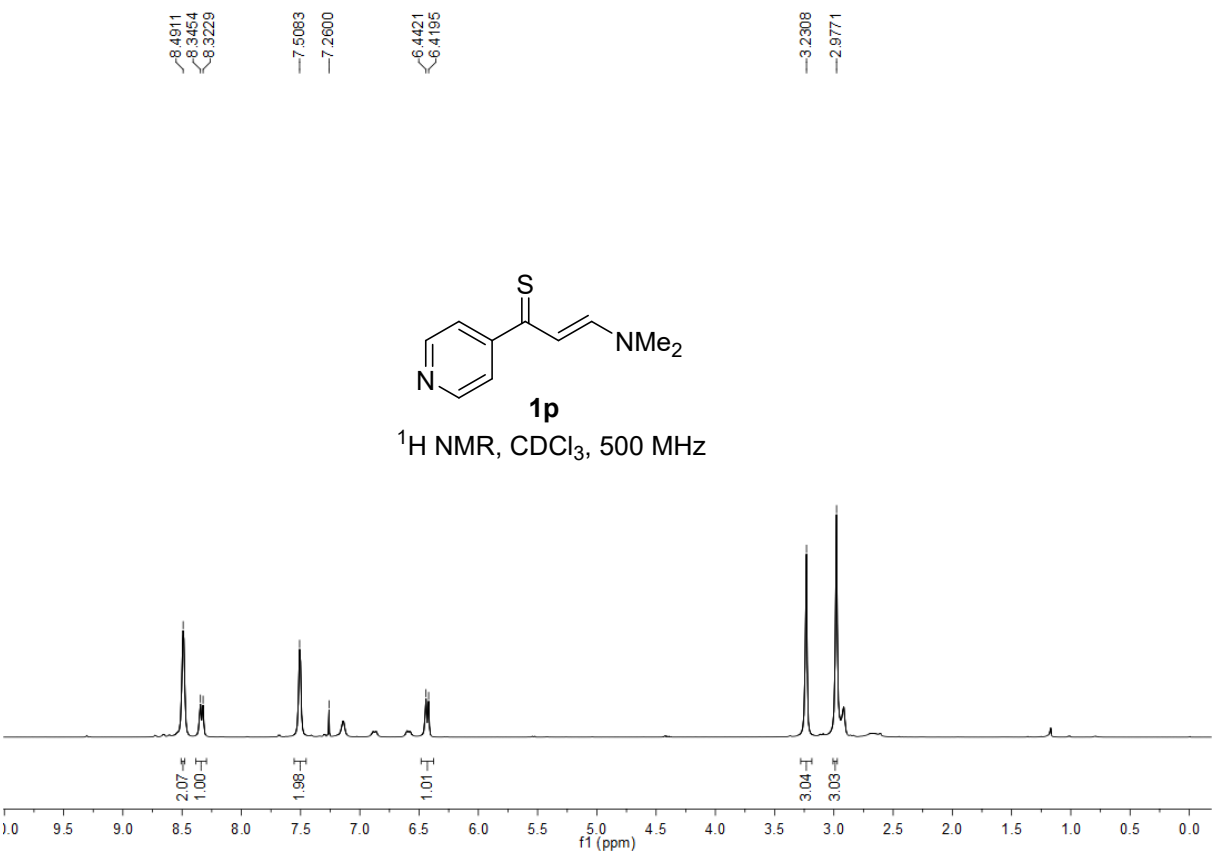
1l

^{1}H NMR, DMSO-d_6, 500 MHz



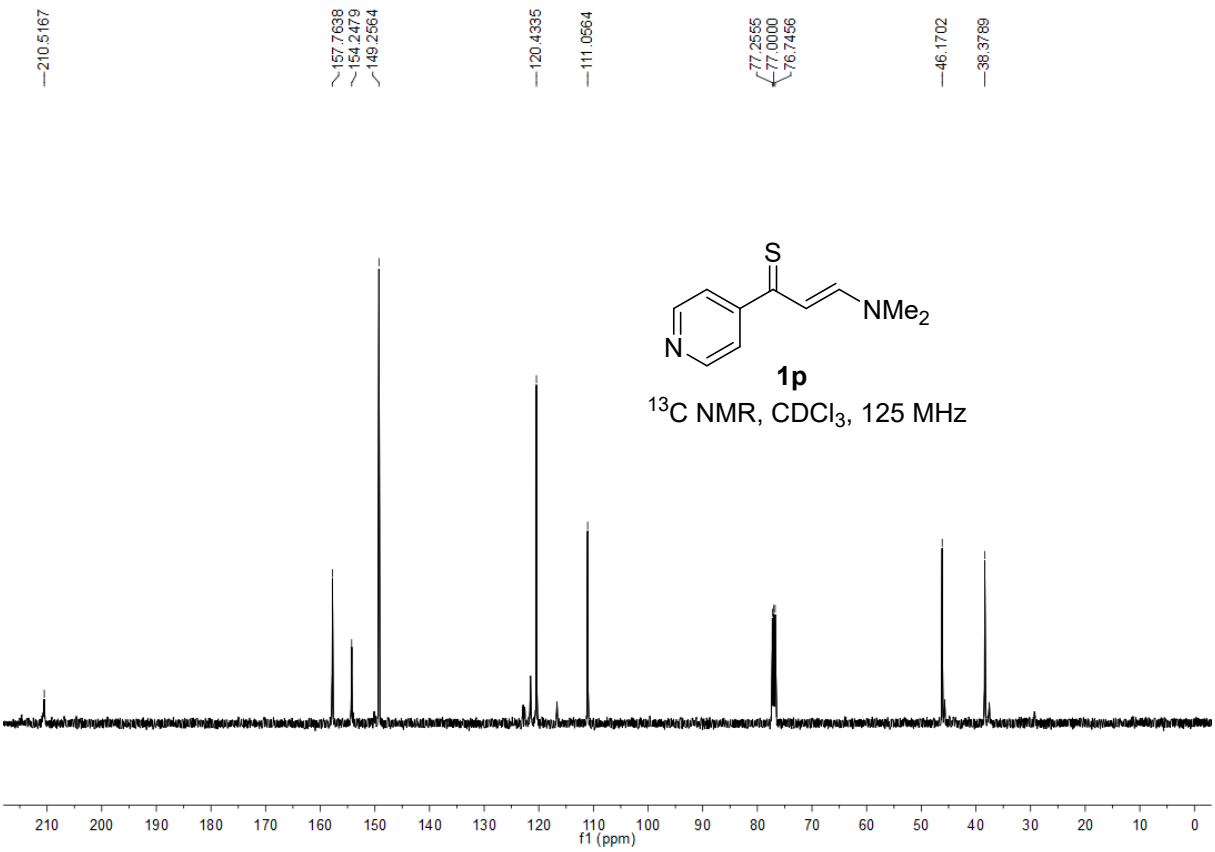
1l

^{13}C NMR,DMSO-d_6, 125 MHz



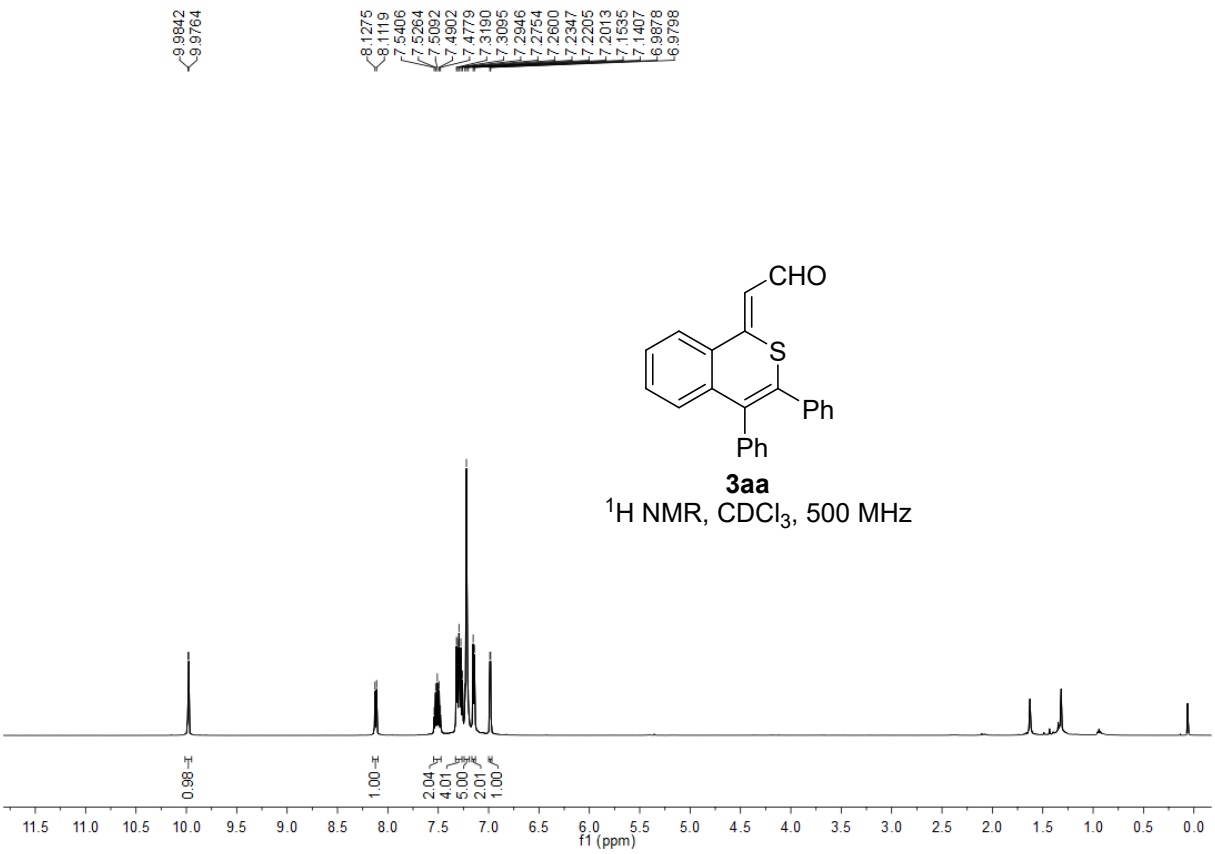
1p

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



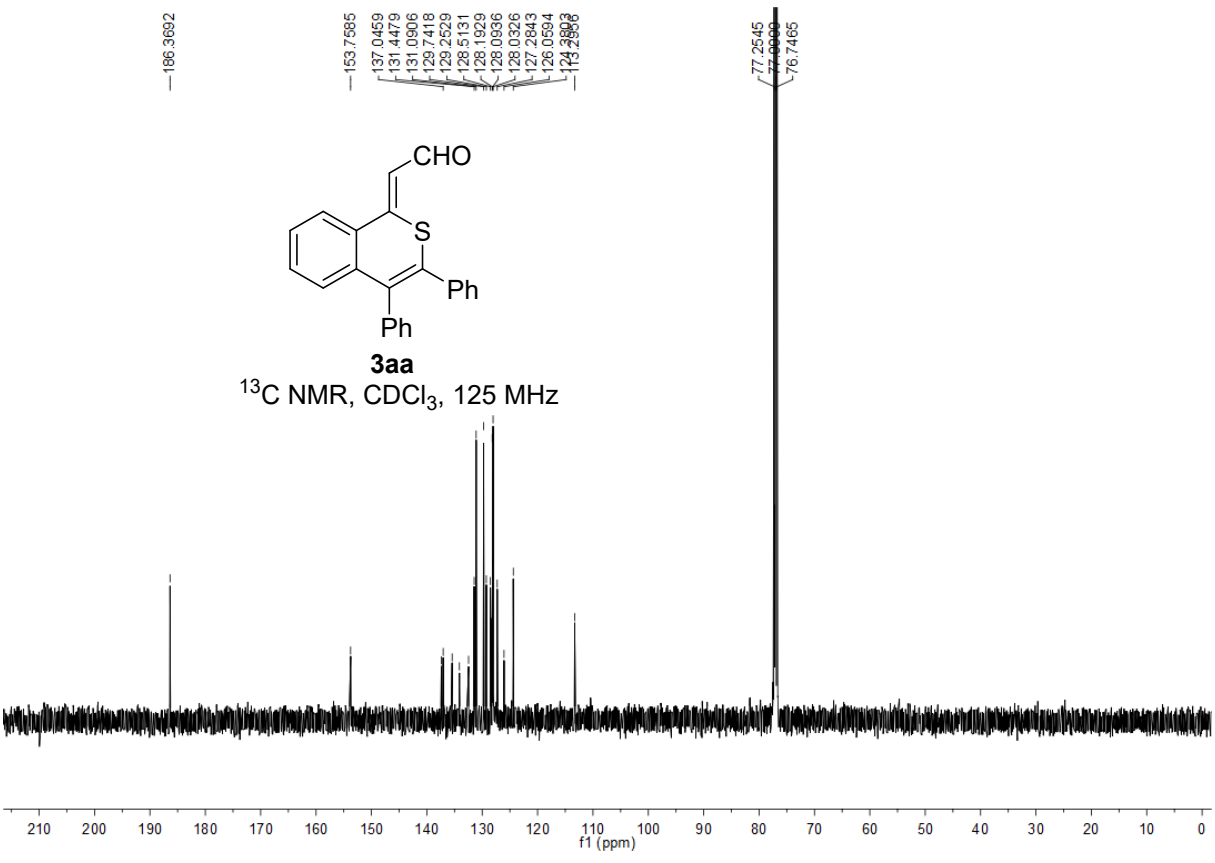
1p

^{13}C NMR, $CDCl_3$, 125 MHz



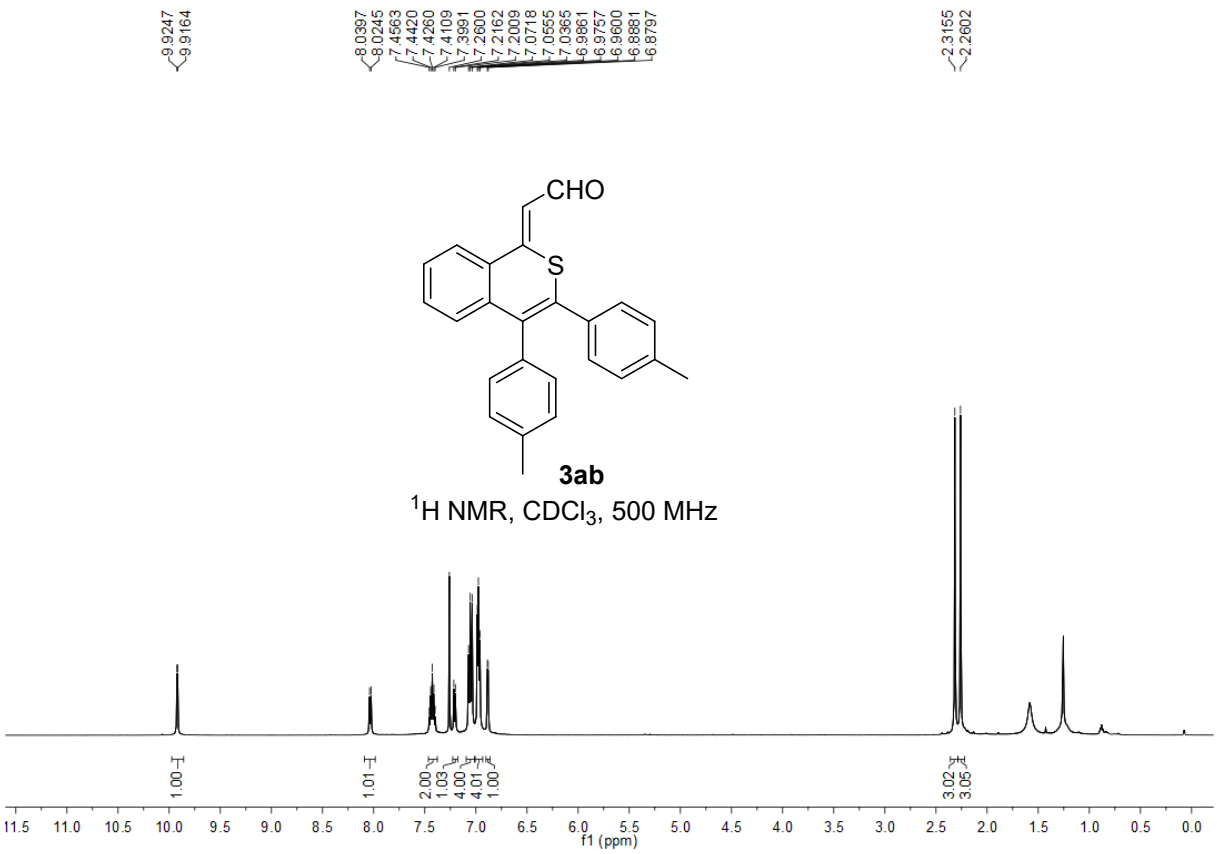
3aa

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



3aa

^{13}C NMR, $CDCl_3$, 125 MHz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8.0245
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7.2600
7.2162
7.2009
7.0718
7.0555
7.0365
6.9861
6.9757
6.9600
6.8881
6.8797
2.3155
2.2602
CHO
S
3ab
1H NMR, CDCl3, 500 MHz
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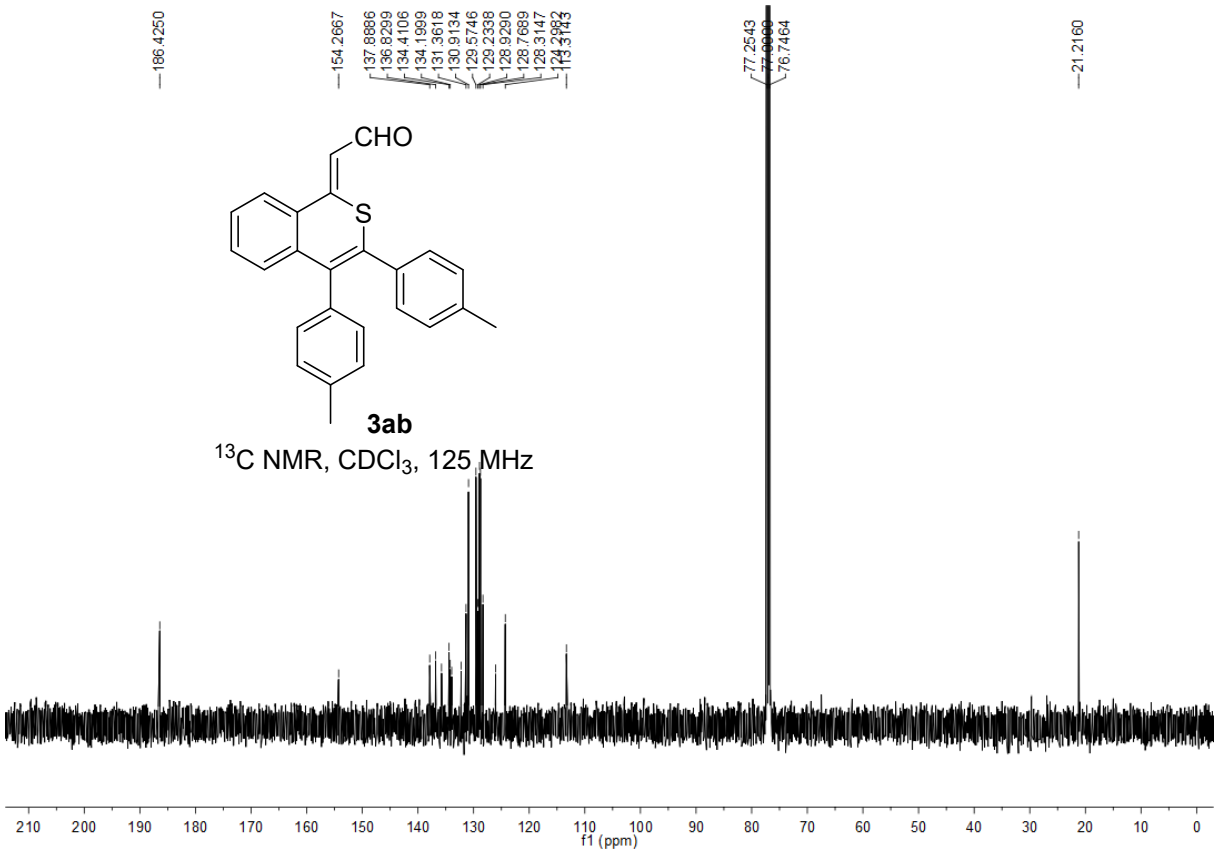
1.01
2.00
1.03
4.00
4.01
1.00
3.02
3.05
f1 (ppm)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76.7464
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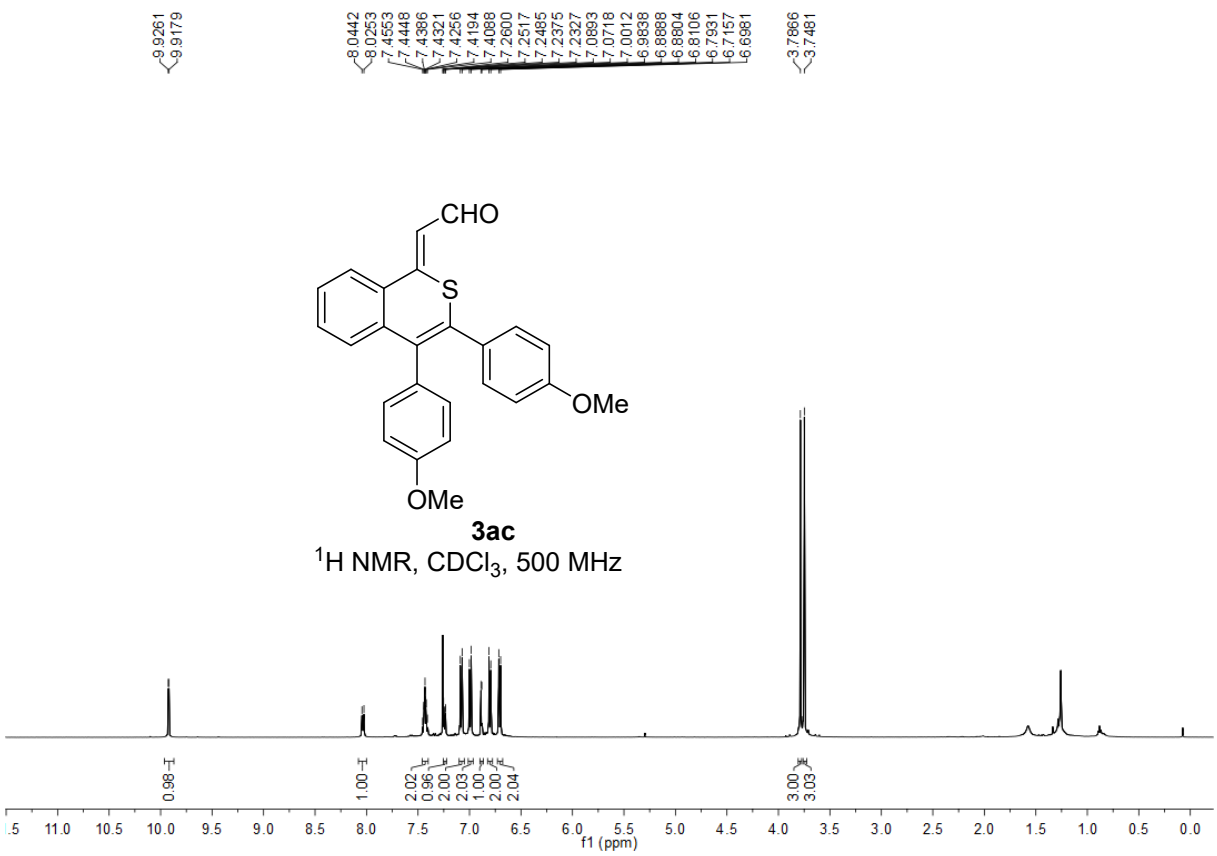
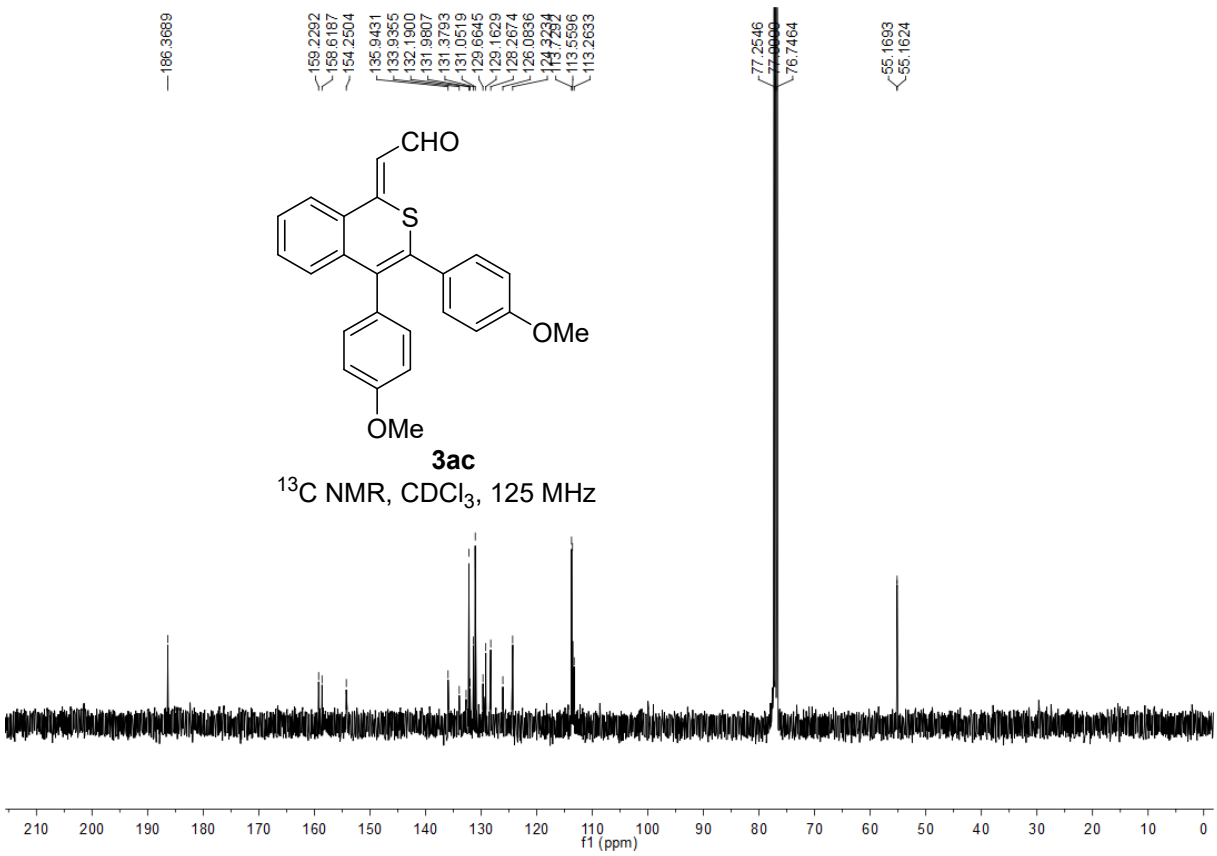
CHO
S
3ab
13C NMR, CDCl3, 125 MHz
f1 (ppm)



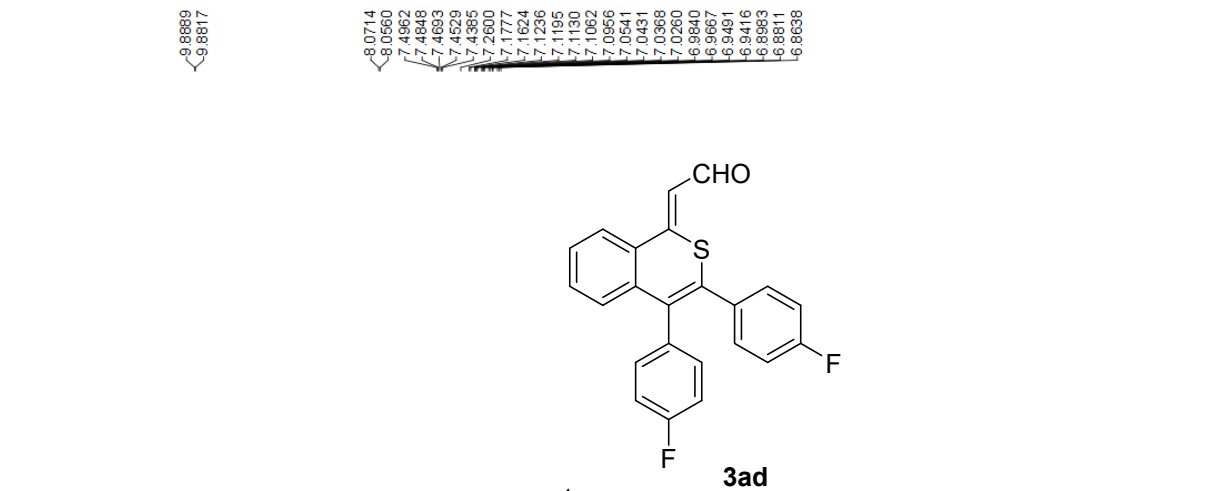
3ac

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



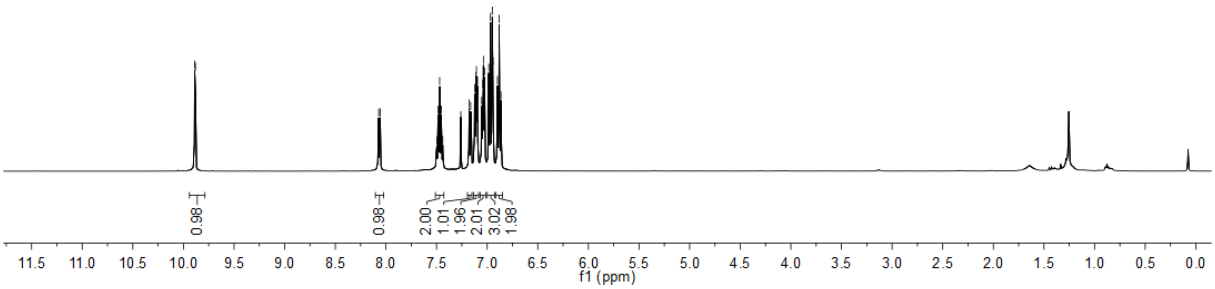
3ac

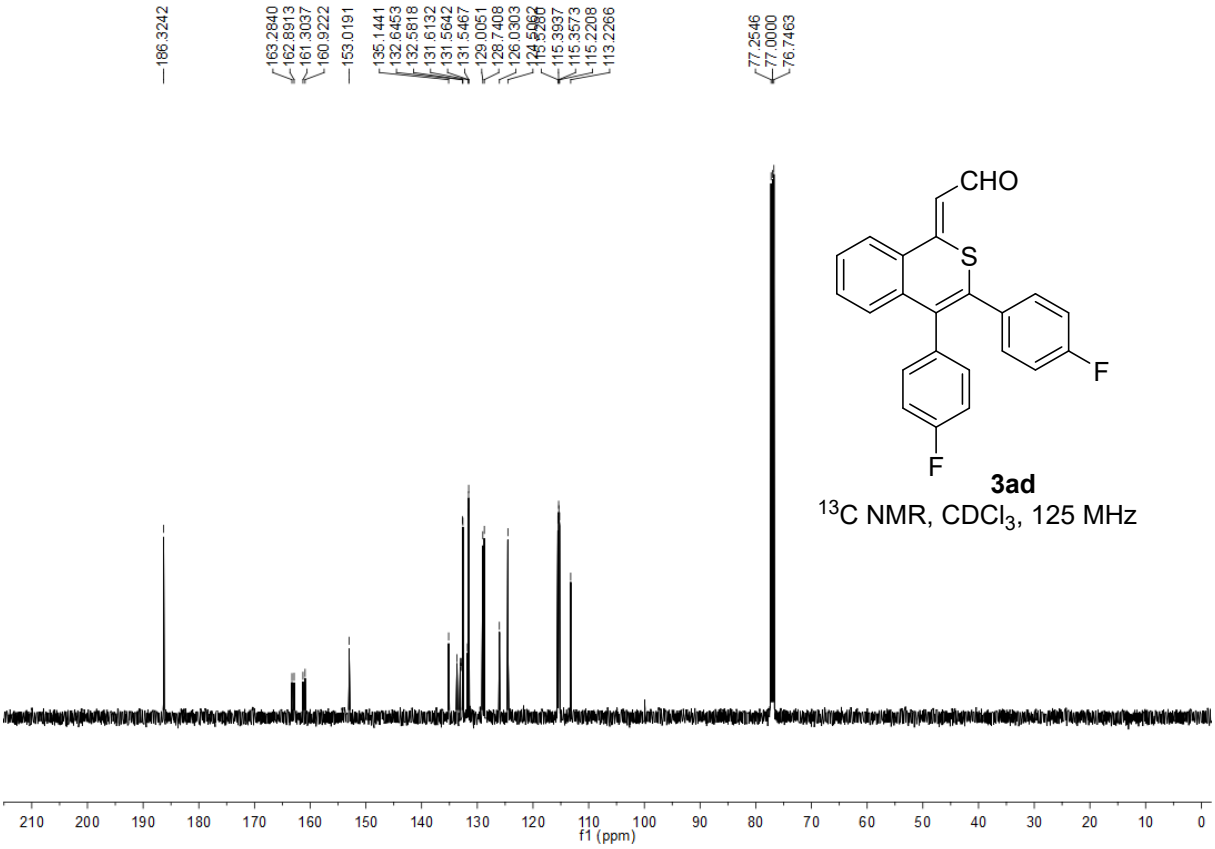
^{13}C NMR, $CDCl_3$, 125 MHz



3ad

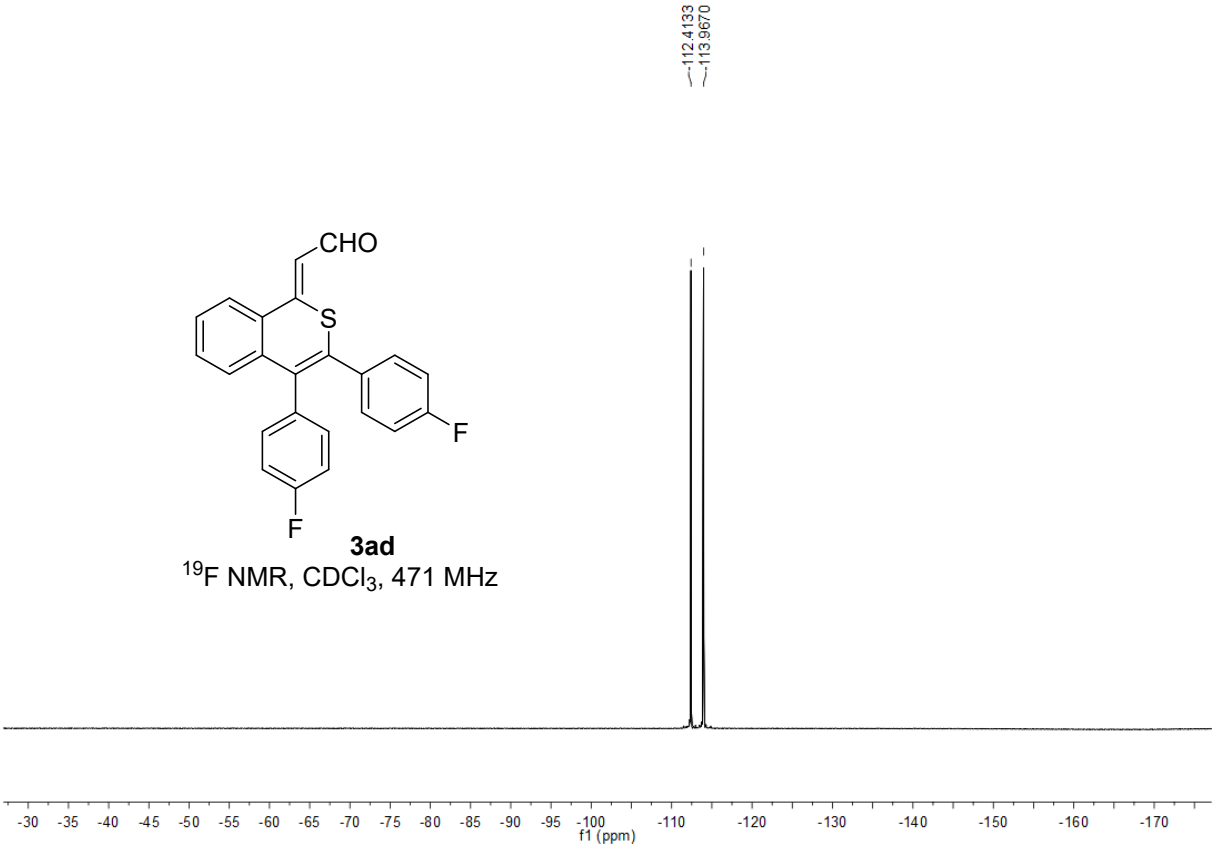
^{1}H NMR, $CDCl_3$, 500 MHz





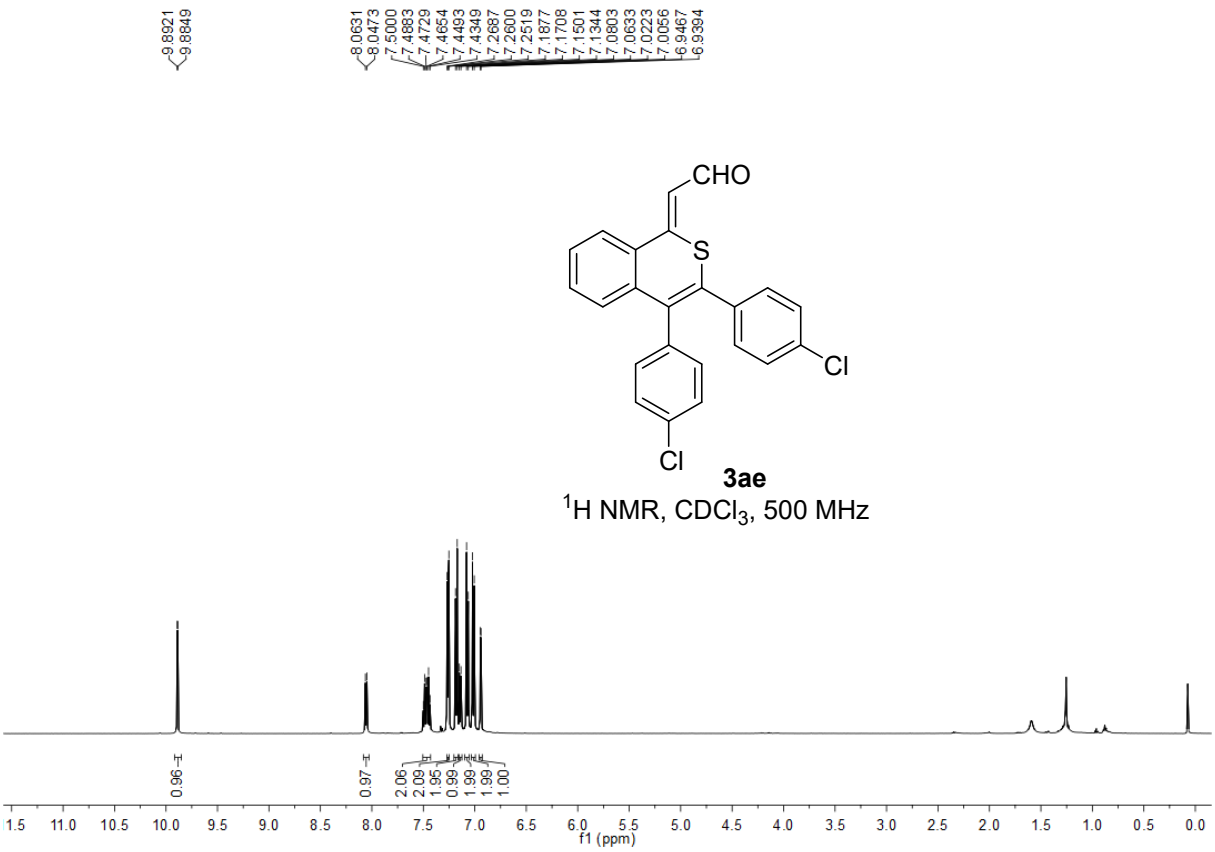
3ad

^{13}C NMR, $CDCl_3$, 125 MHz



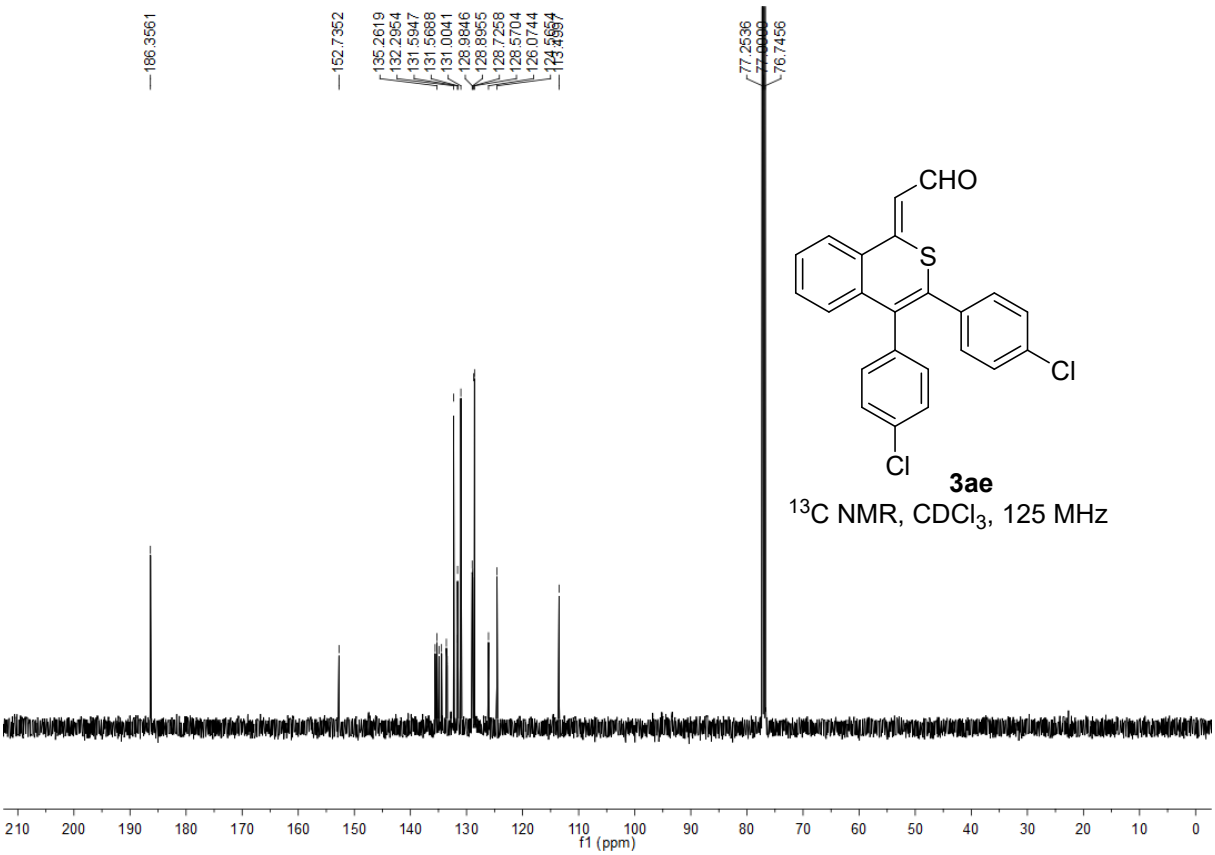
3ad

^{19}F NMR, $CDCl_3$, 471 MHz



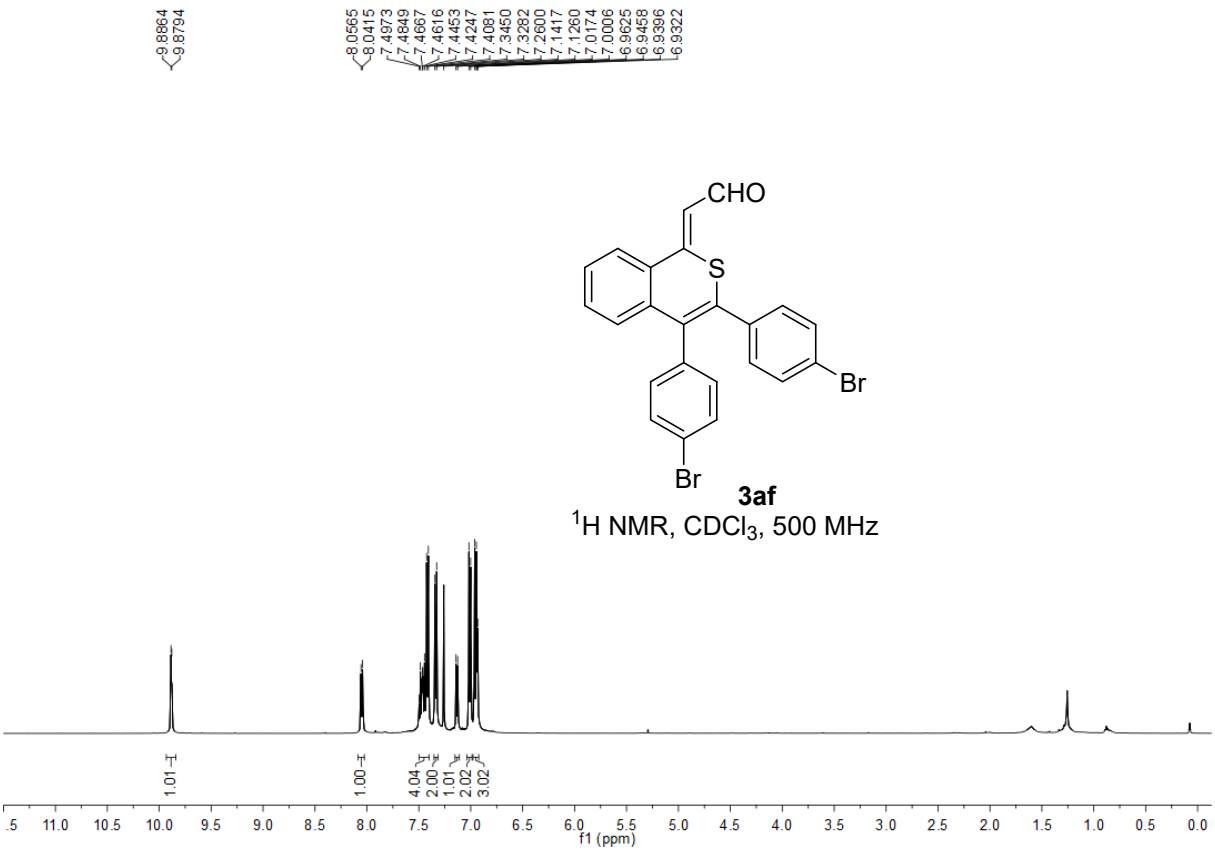
3ae

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



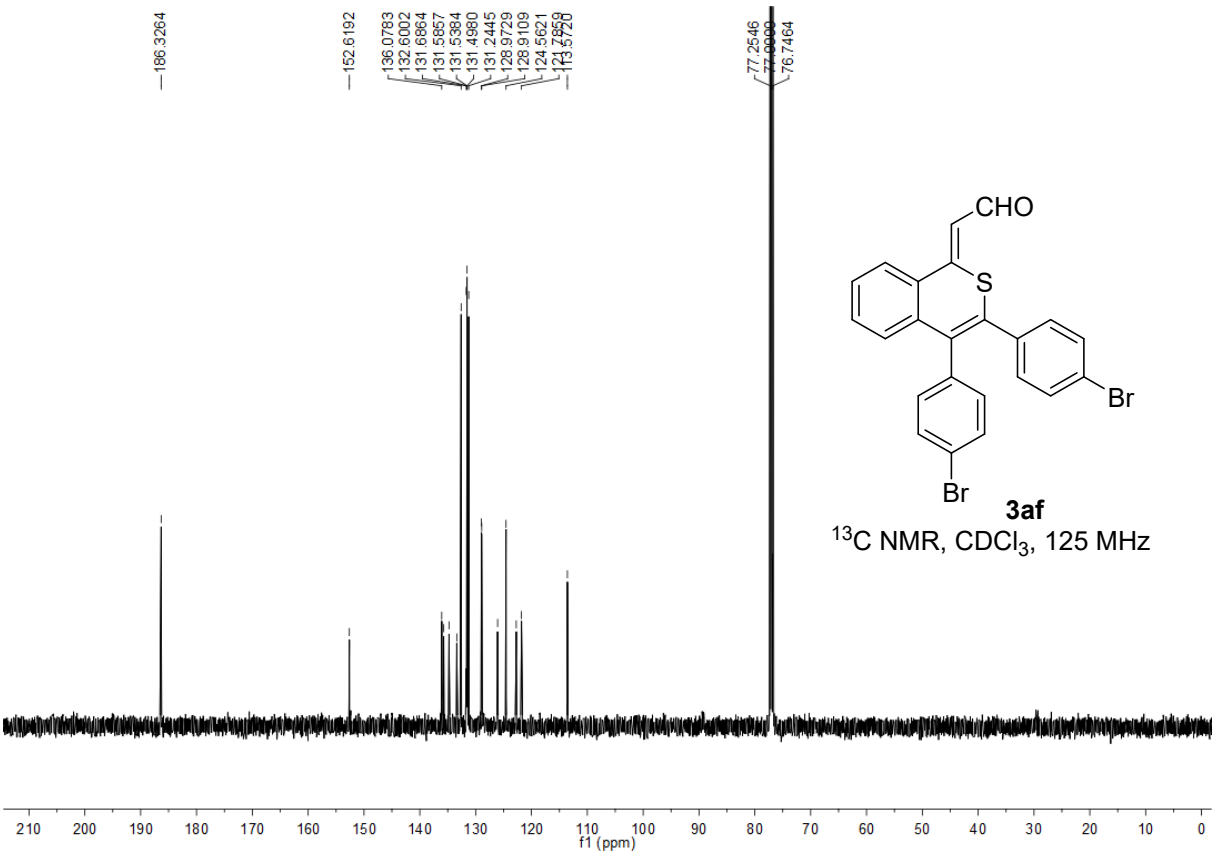
3ae

^{13}C NMR, $CDCl_3$, 125 MHz



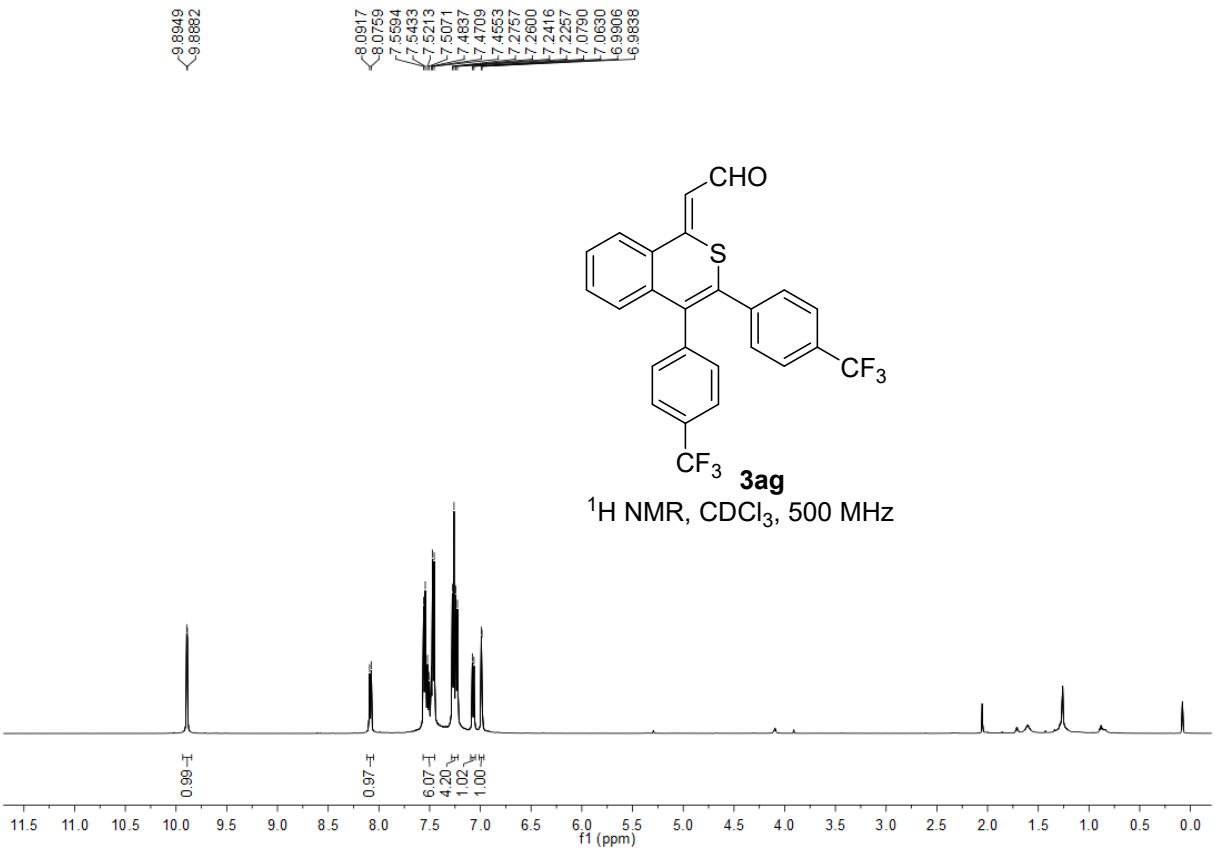
3af

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



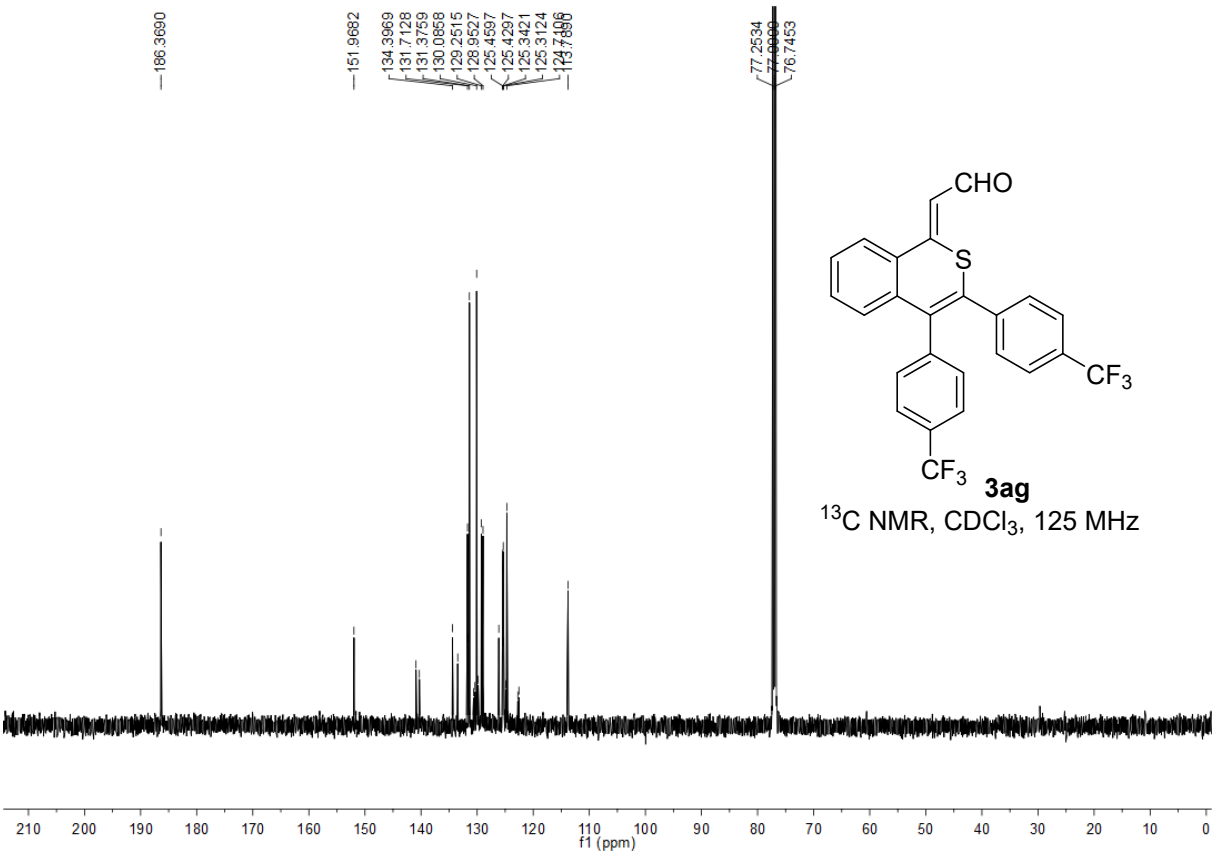
3af

^{13}C NMR, $CDCl_3$, 125 MHz



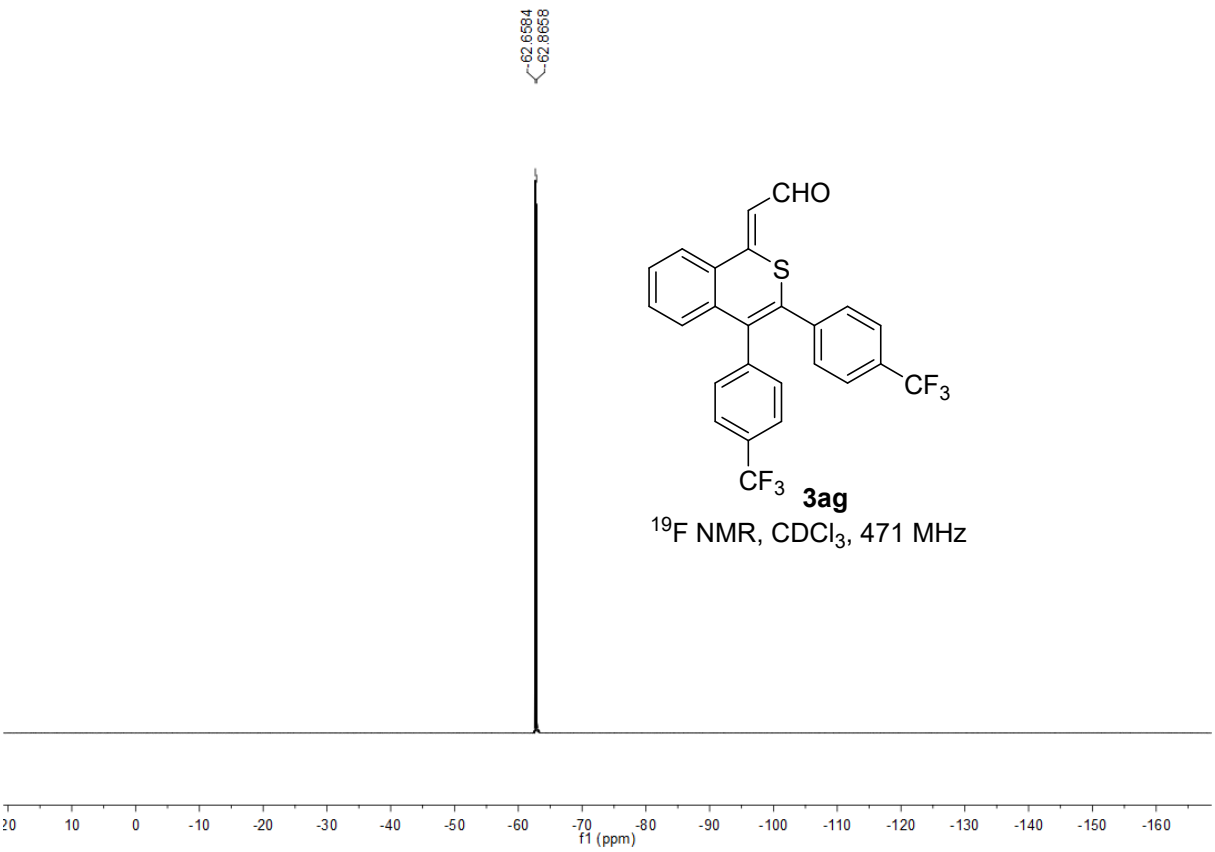
3ag

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



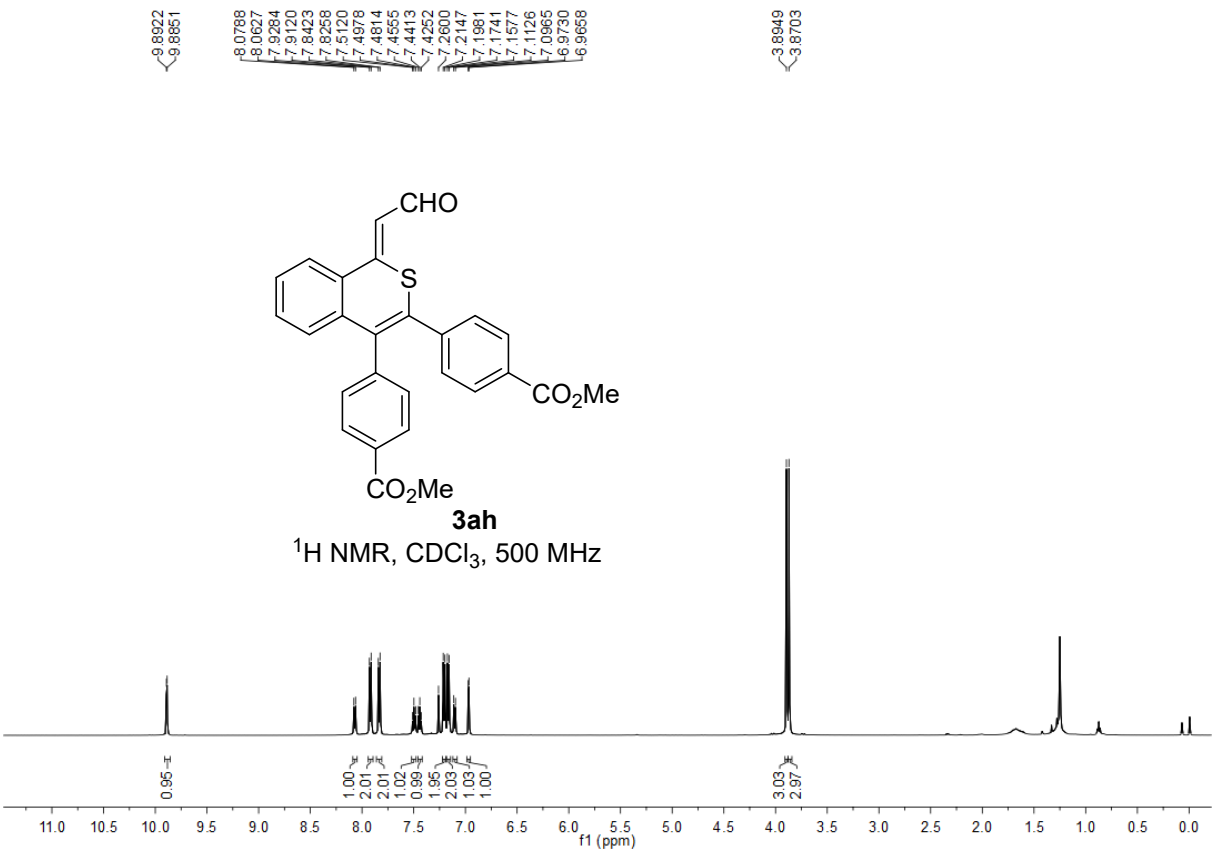
3ag

^{13}C NMR, $CDCl_3$, 125 MHz



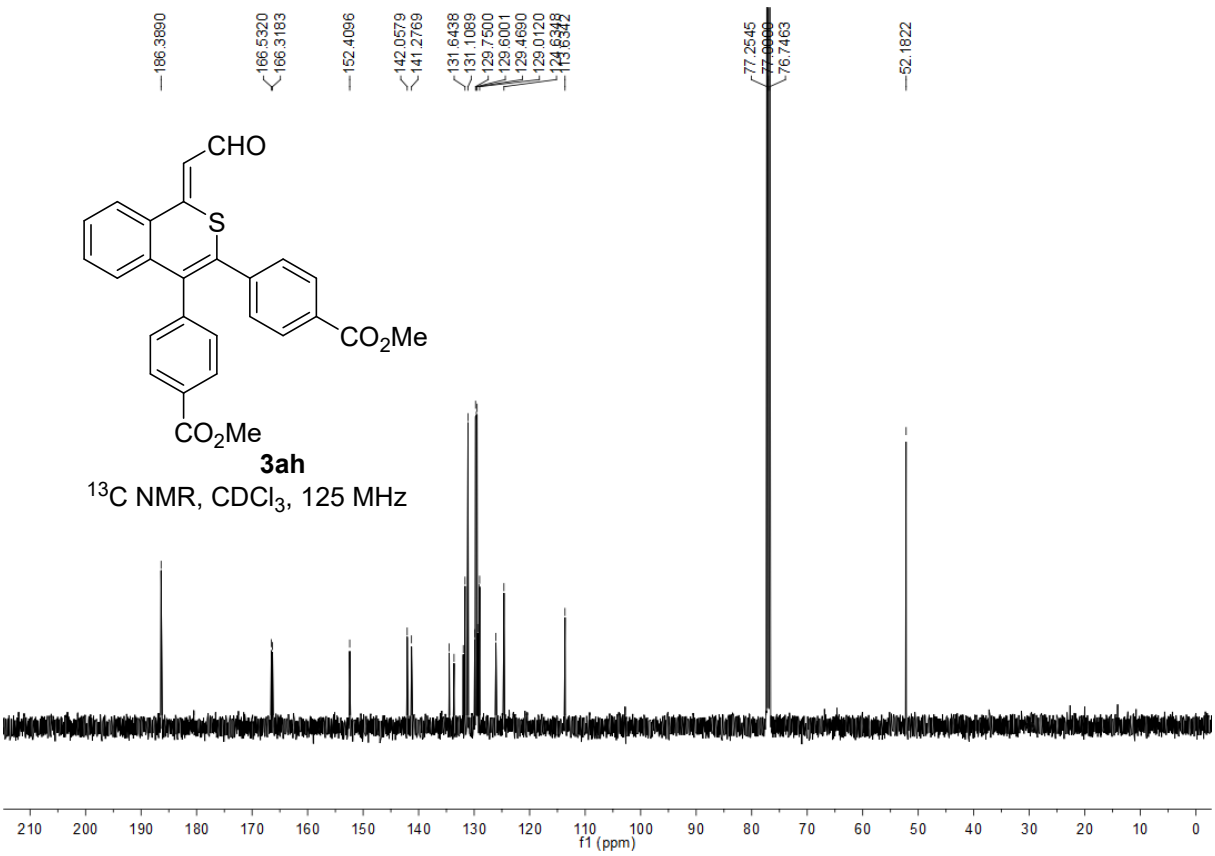
3ag

^{19}F NMR, $CDCl_3$, 471 MHz



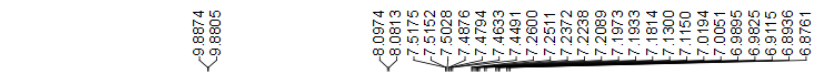
3ah

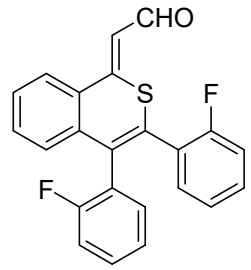
^{1}H NMR, $CDCl_3$, 500 MHz



3ah

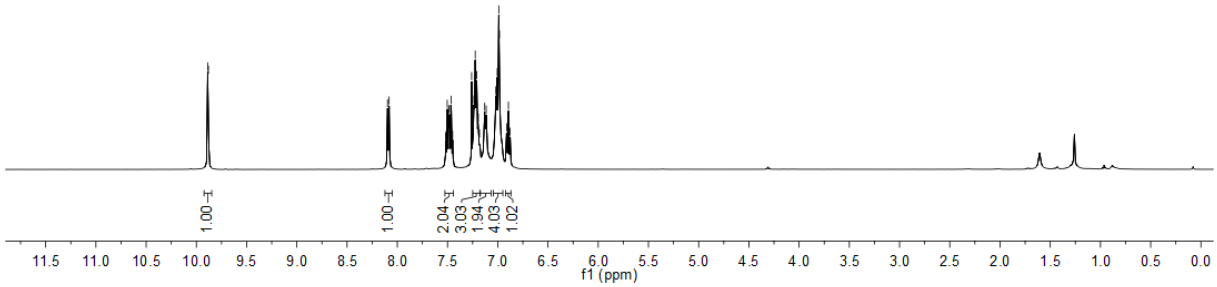
^{13}C NMR, $CDCl_3$, 125 MHz

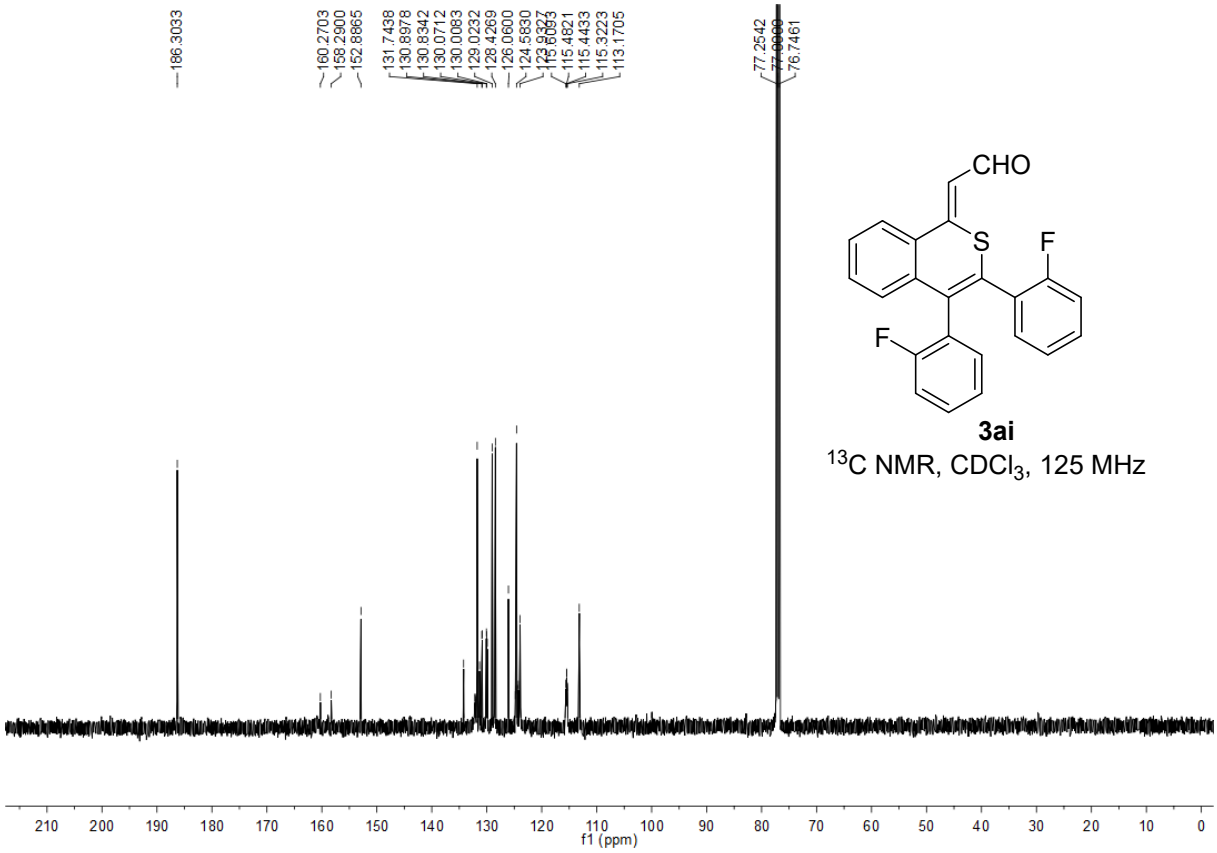




3ai

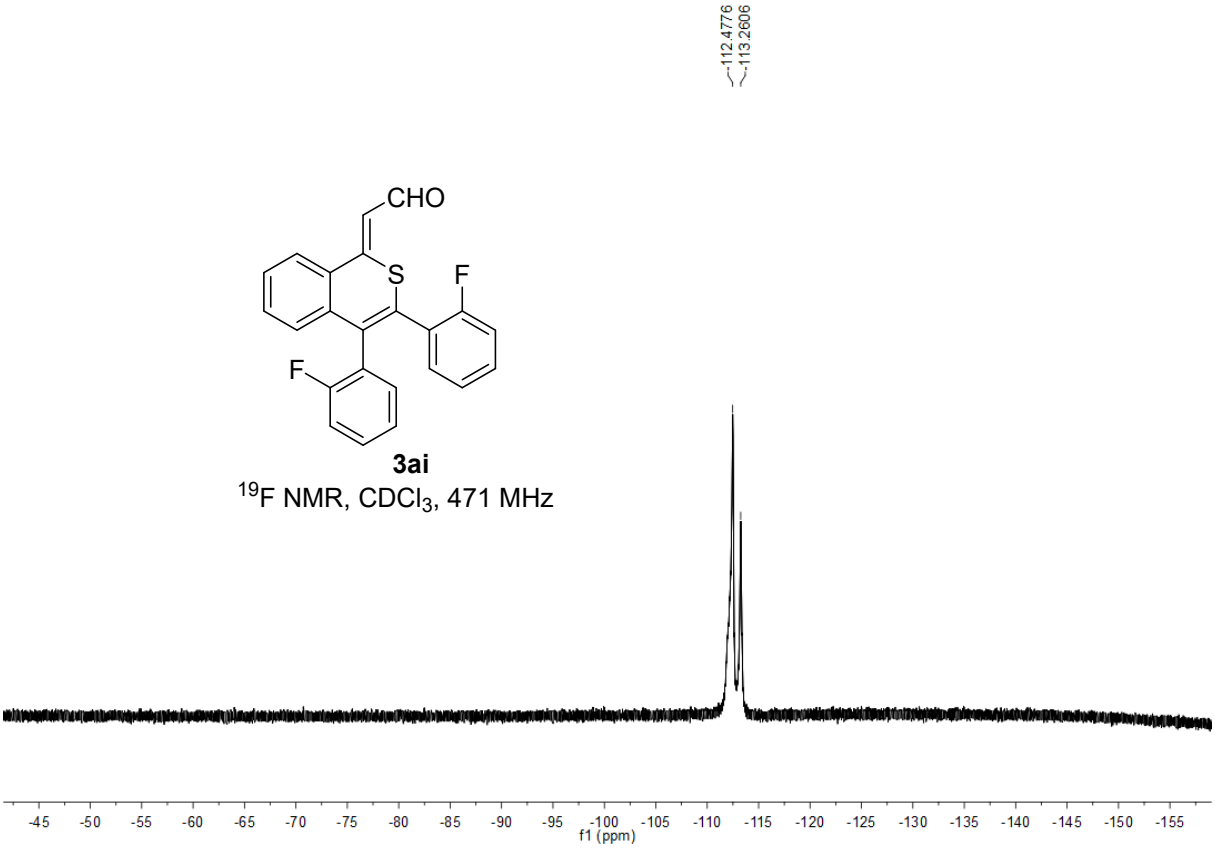
^{1}H NMR, $CDCl_3$, 500 MHz





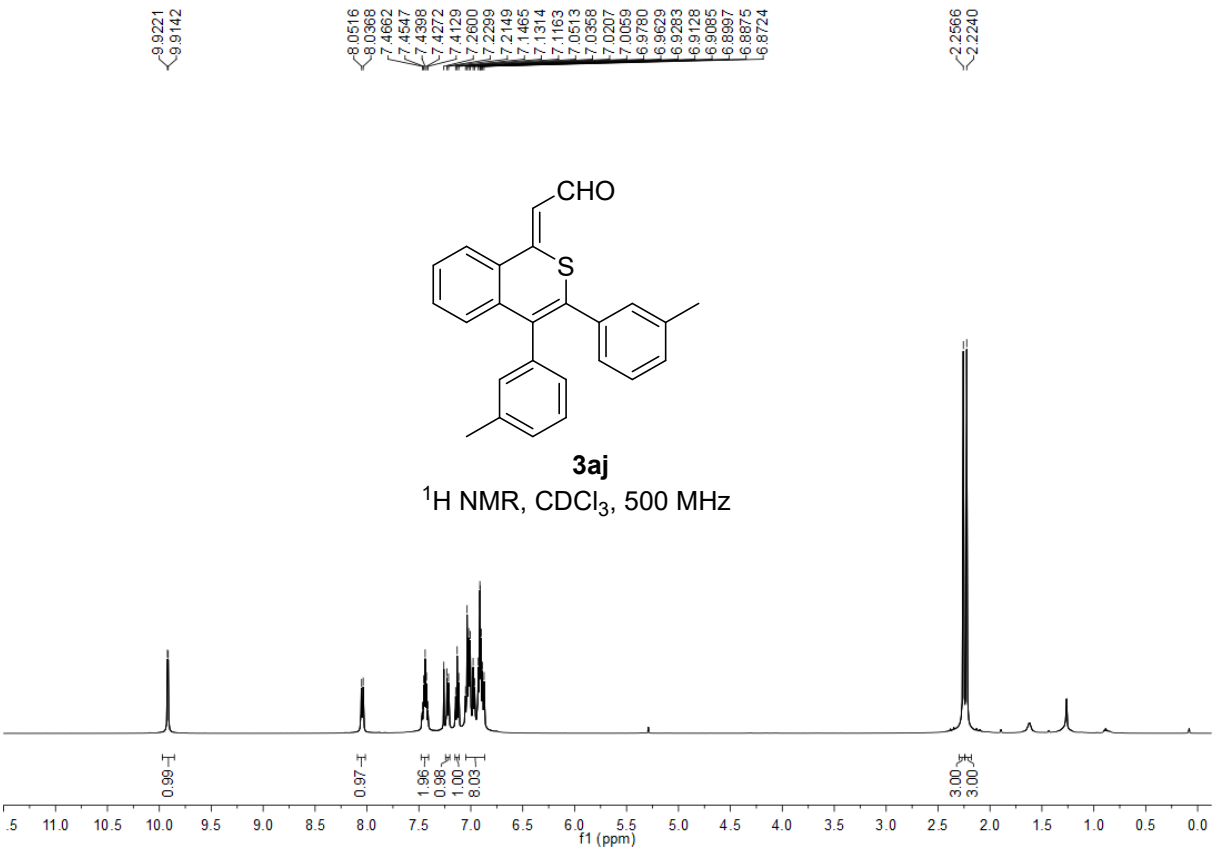
3ai

^{13}C NMR, $CDCl_3$, 125 MHz



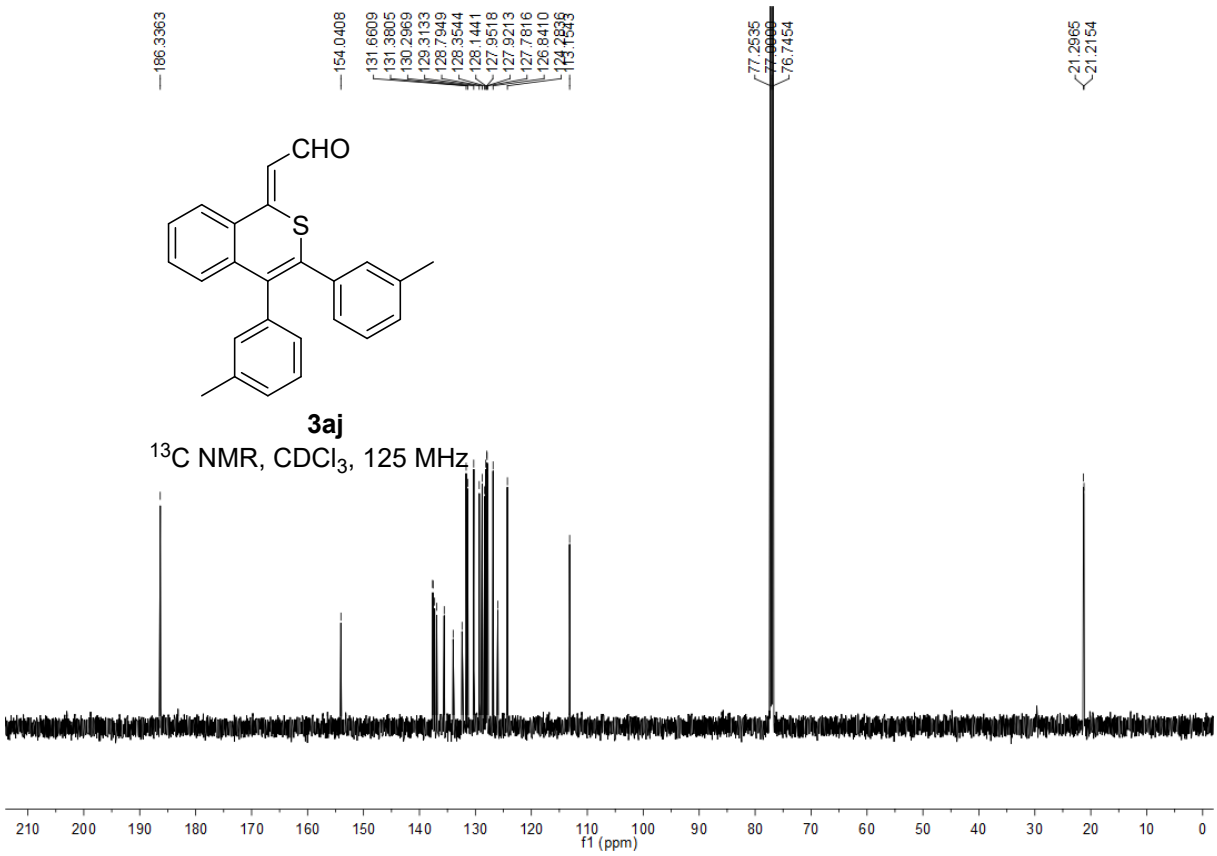
3ai

^{19}F NMR, $CDCl_3$, 471 MHz



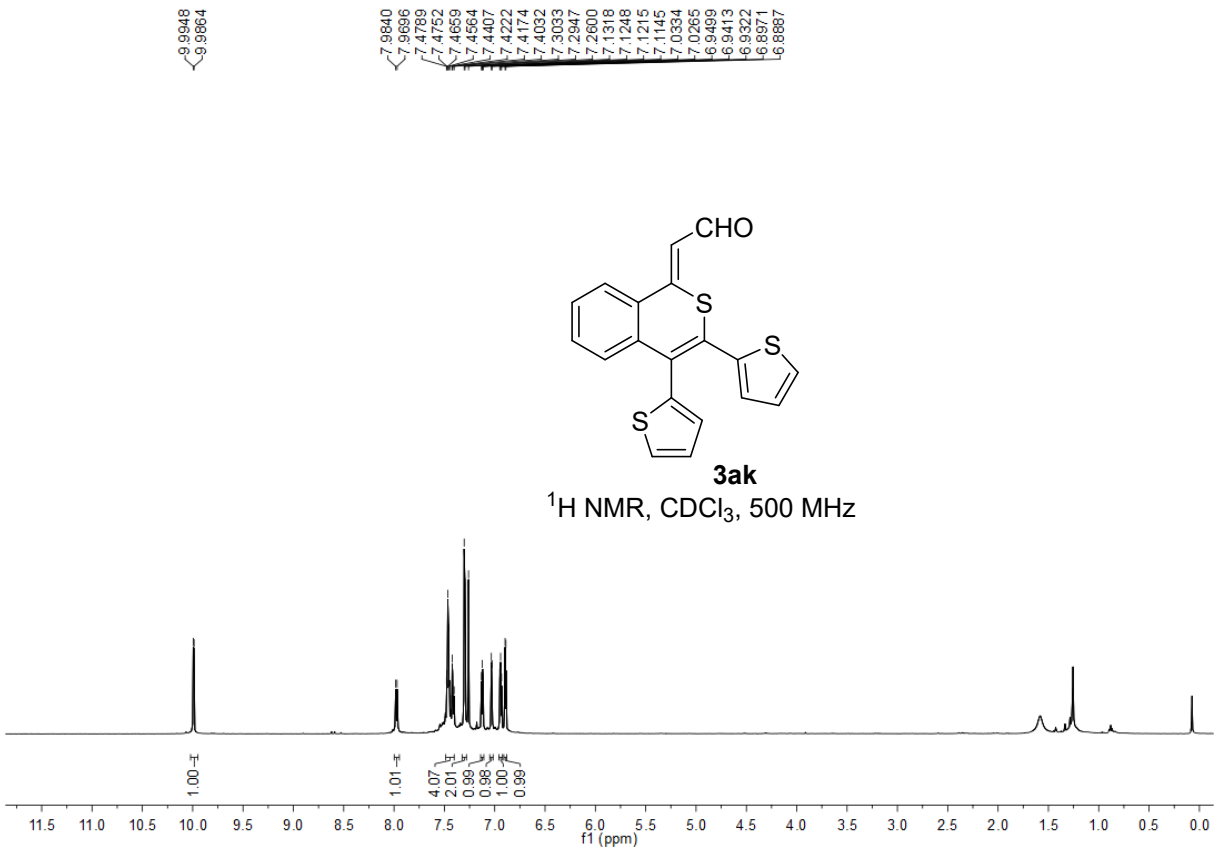
3aj

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



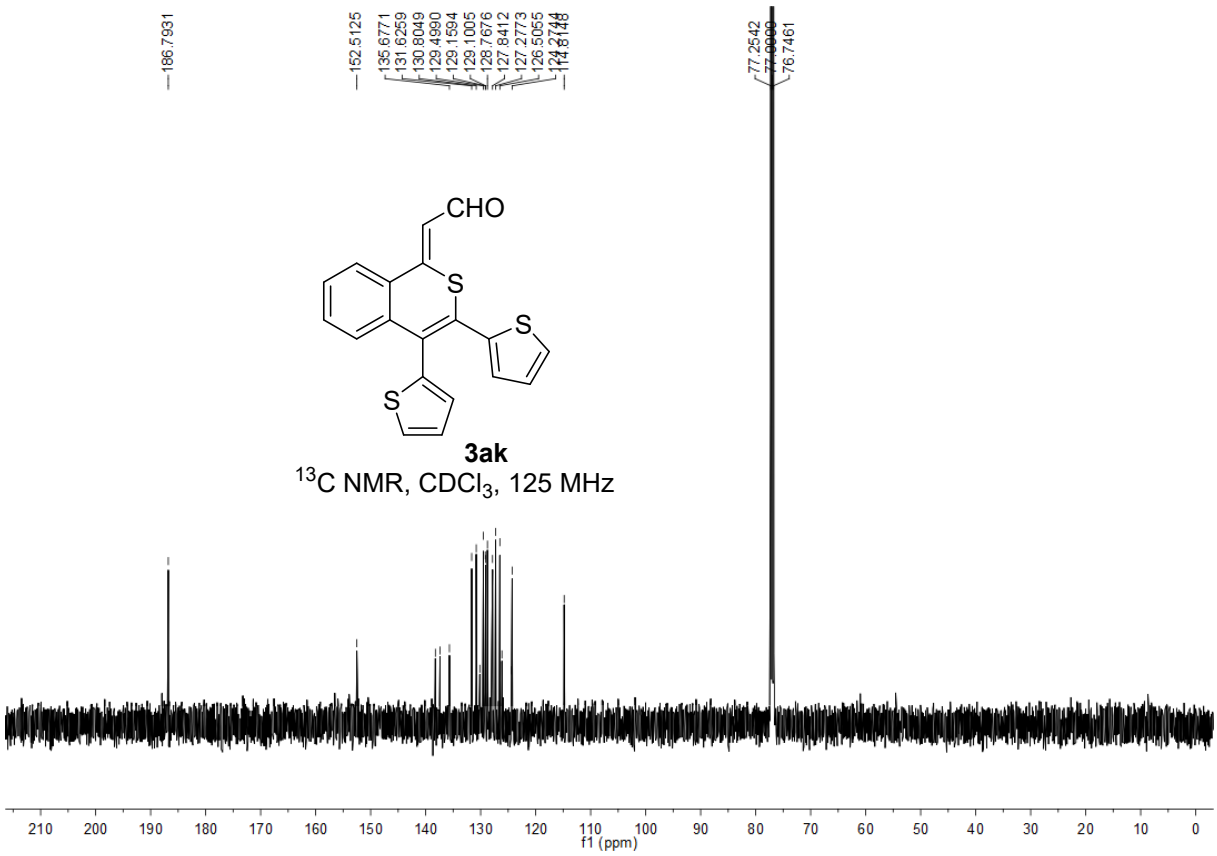
3aj

^{13}C NMR, $CDCl_3$, 125 MHz



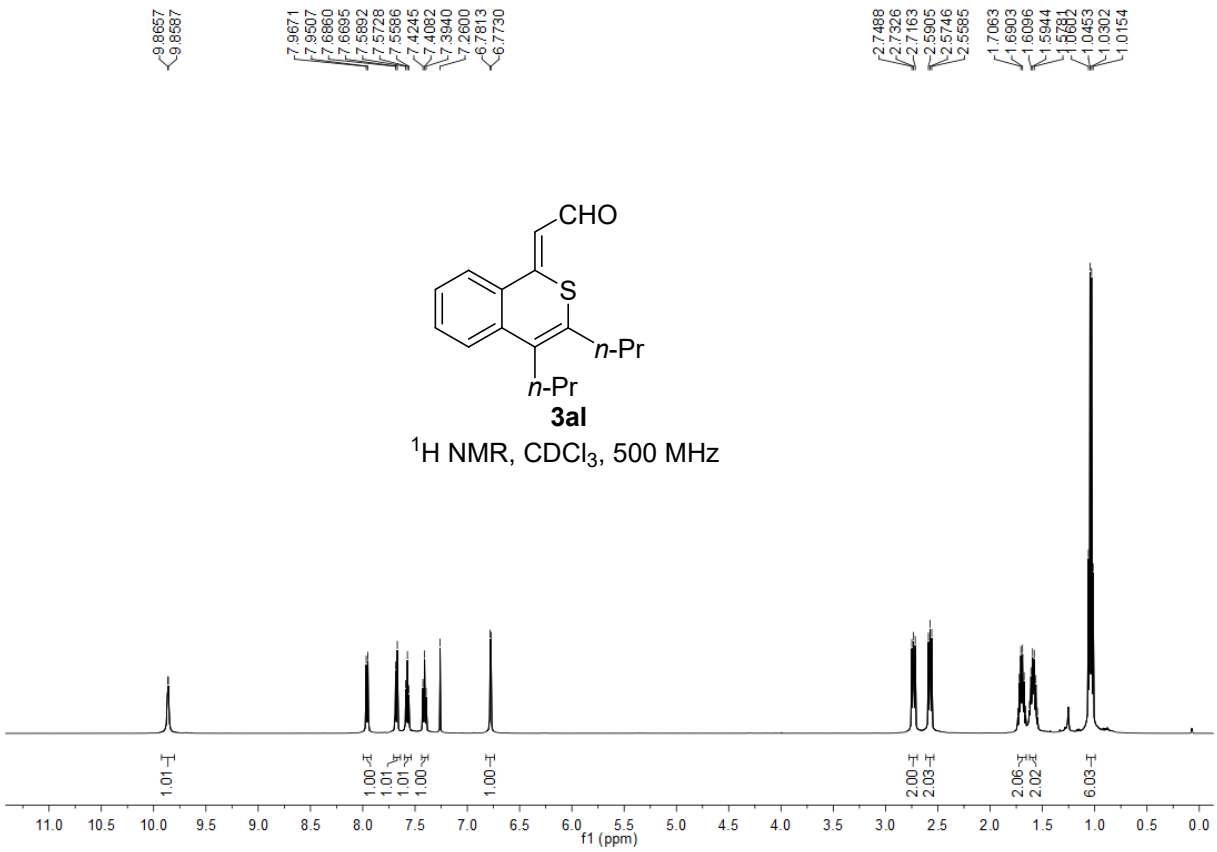
3ak

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



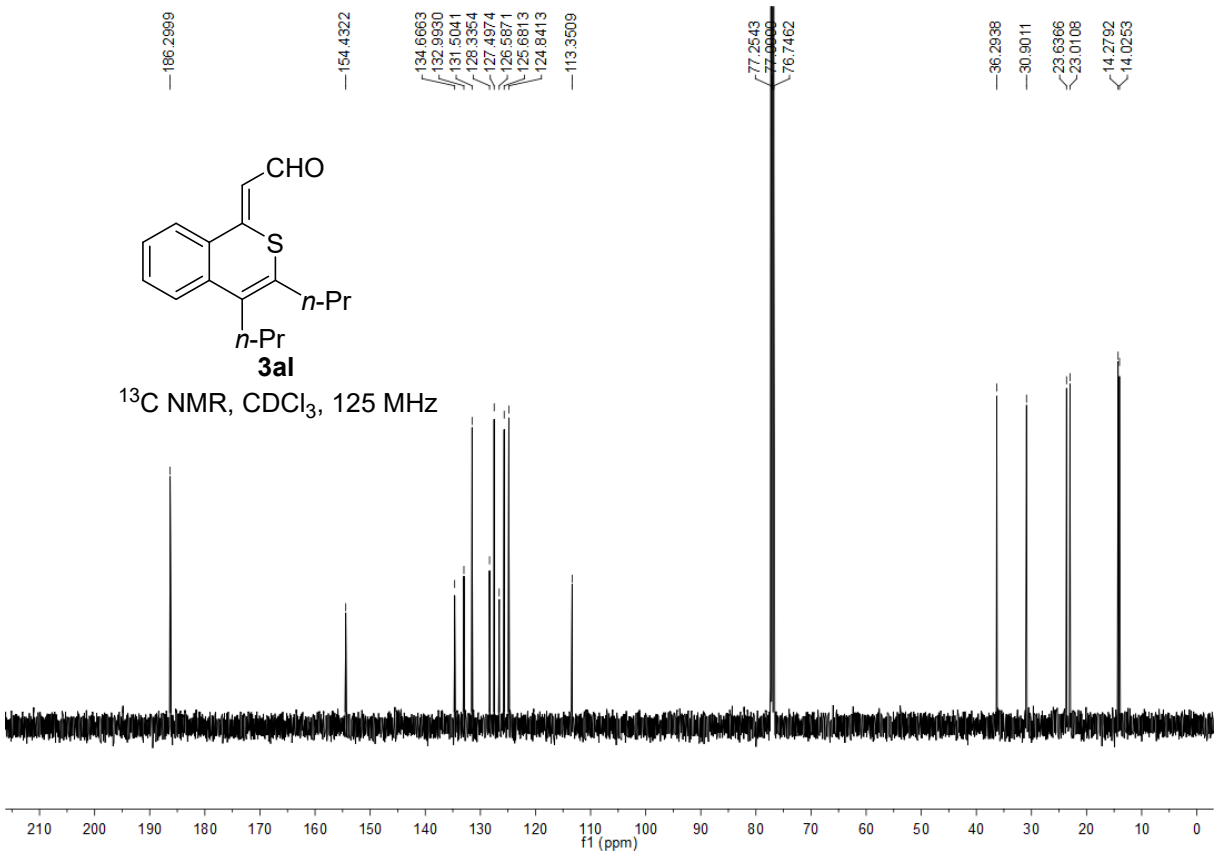
3ak

^{13}C NMR, $CDCl_3$, 125 MHz



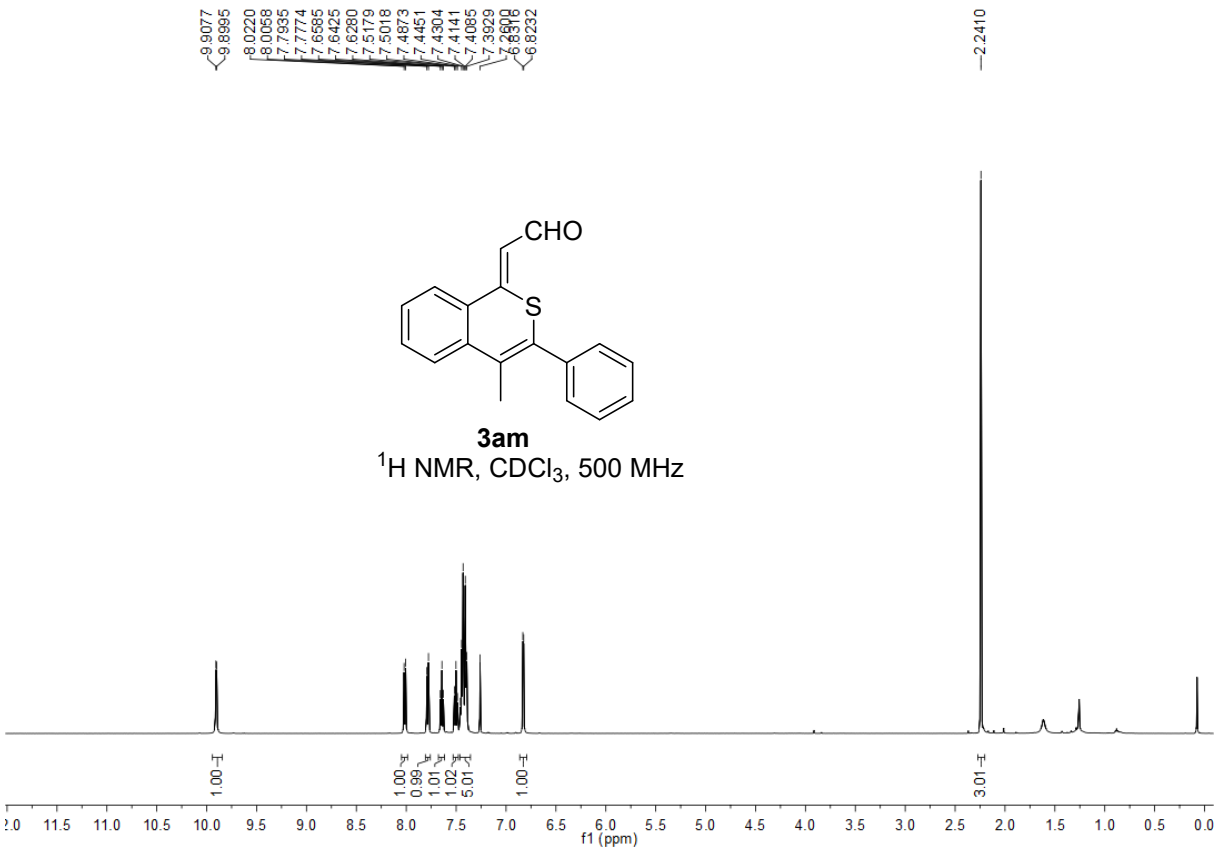
3al

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



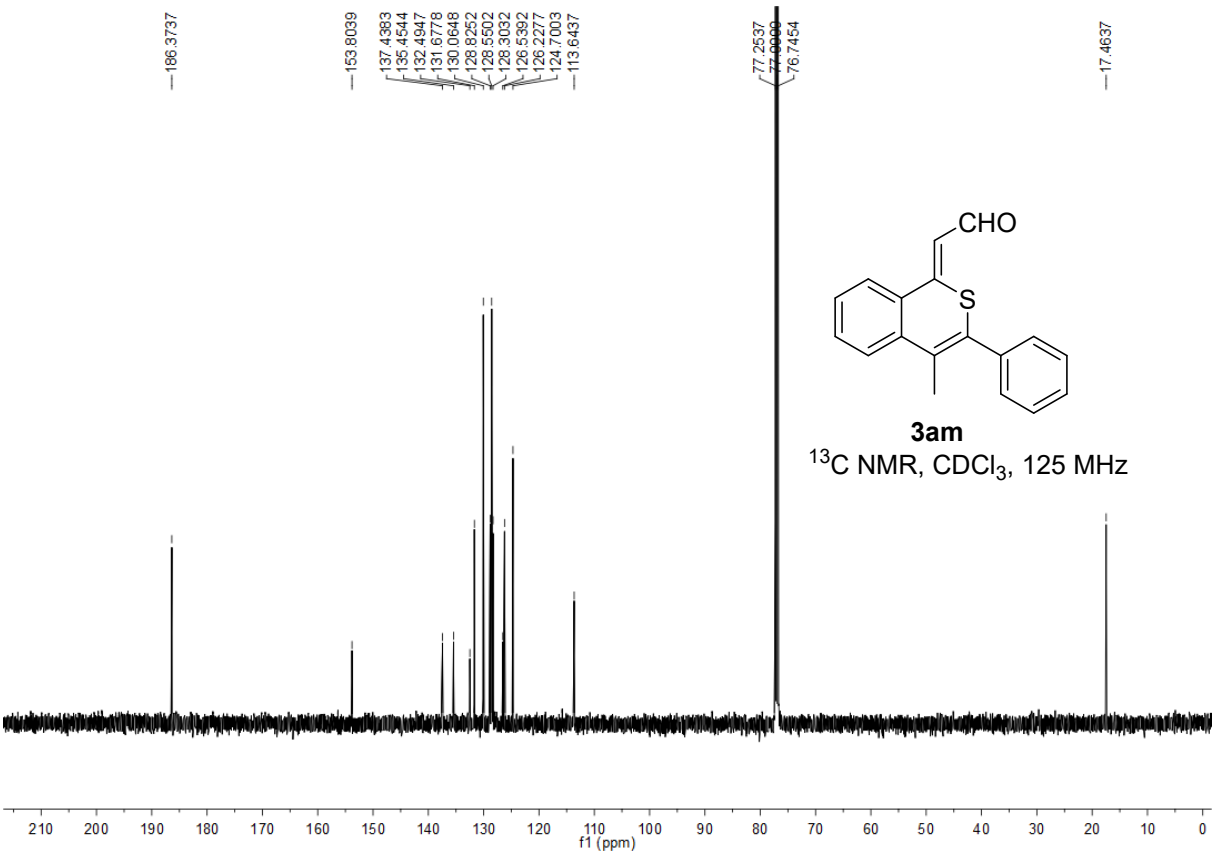
3al

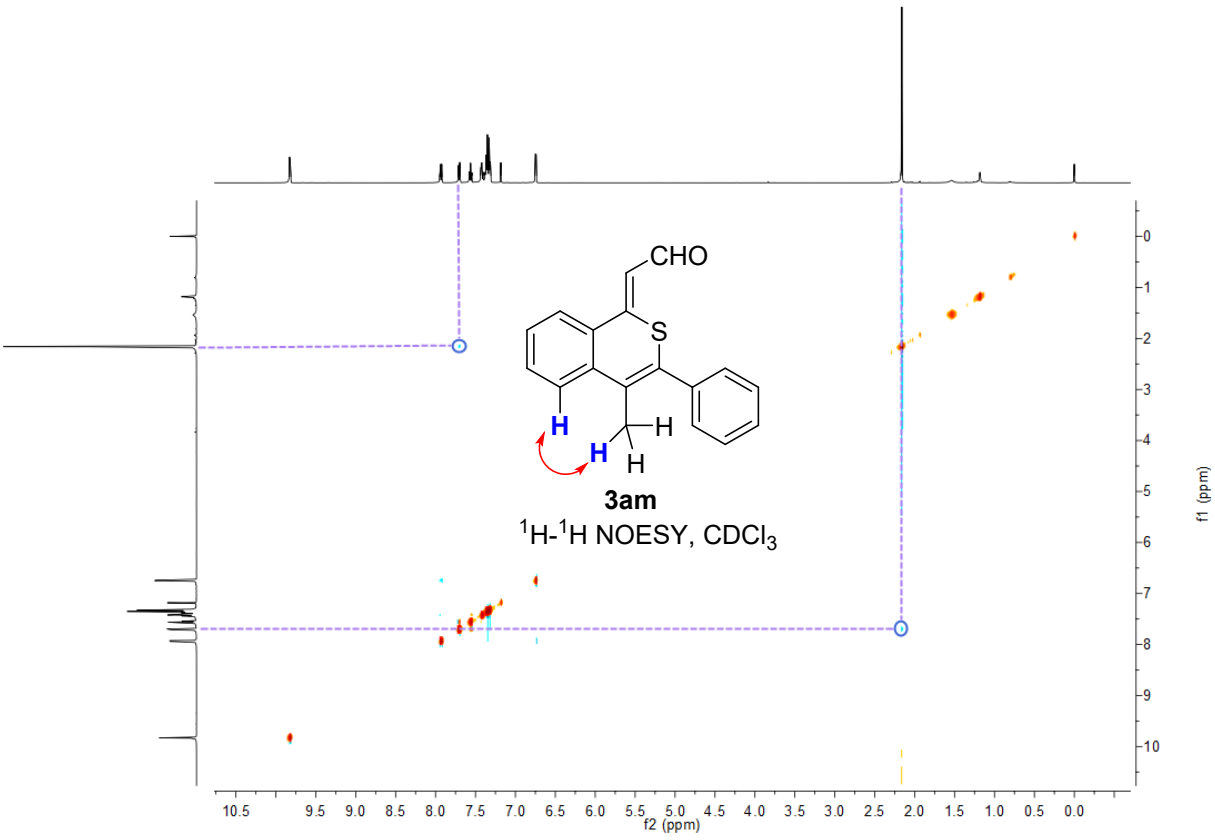
^{13}C NMR, $CDCl_3$, 125 MHz

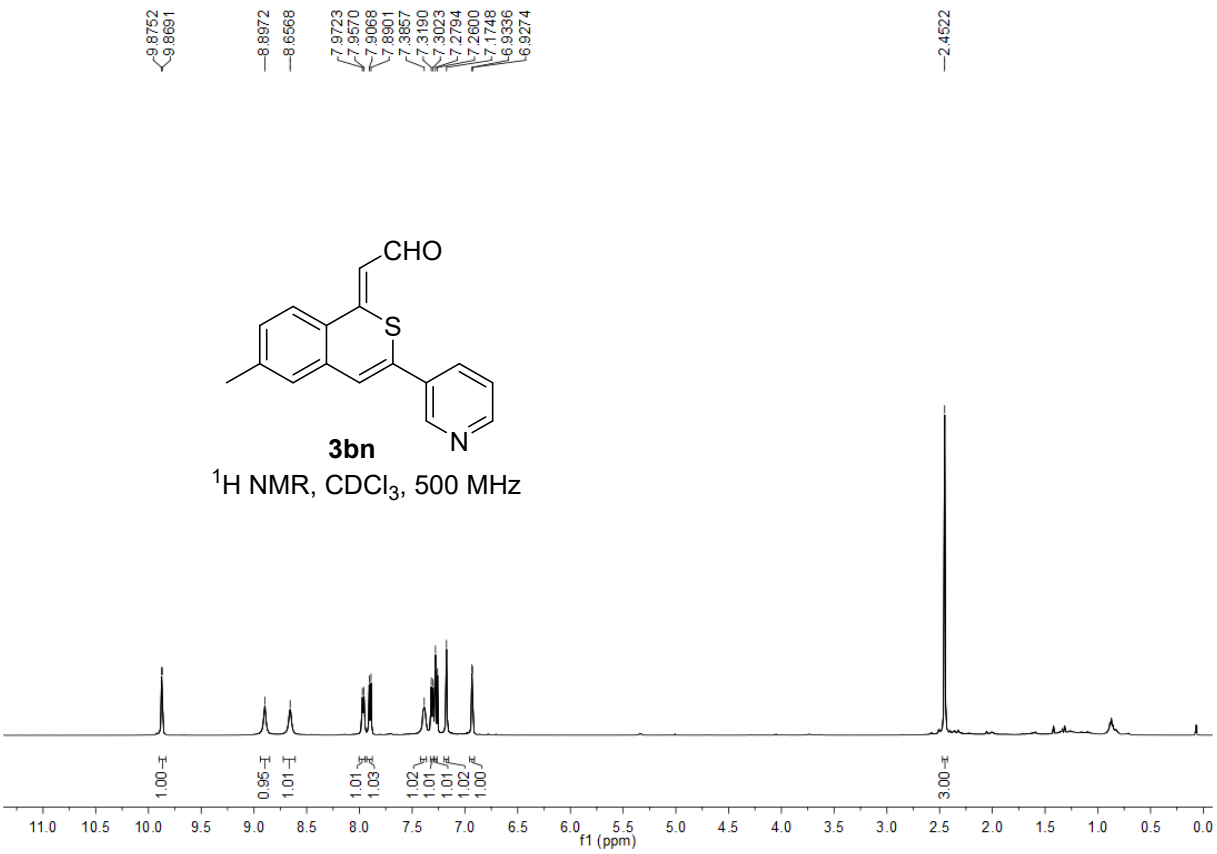


3am

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

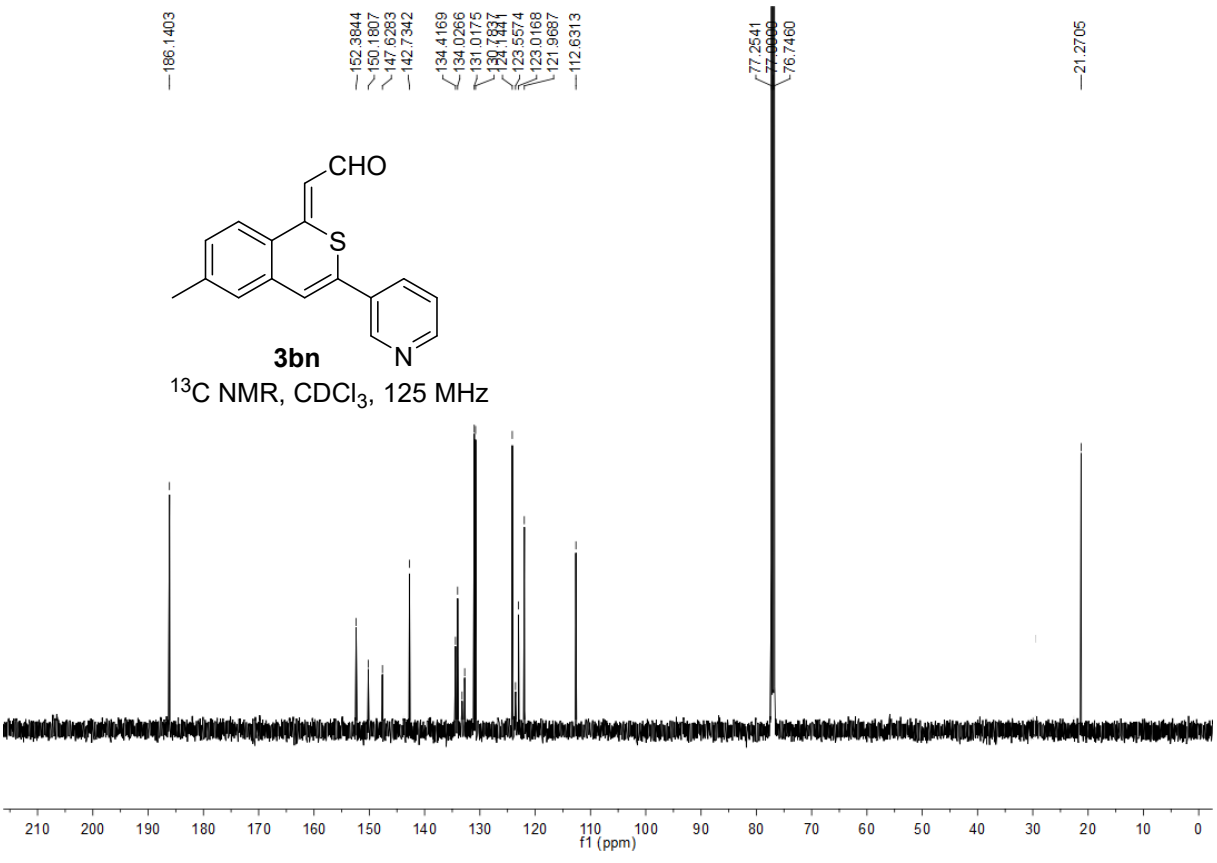

186.3737
153.8039
137.4383
135.4544
132.4947
131.6778
130.0648
128.8252
128.5502
128.3032
126.5392
126.2277
124.7003
113.6437
77.2537
77.0000
76.7454
17.4637
CHO
S
3am
13C NMR, CDCl3, 125 MHz
f1 (ppm)


CHO
S
H
H
H
H
3am
1H-1H NOESY, CDCl3
f2 (ppm)
f1 (ppm)



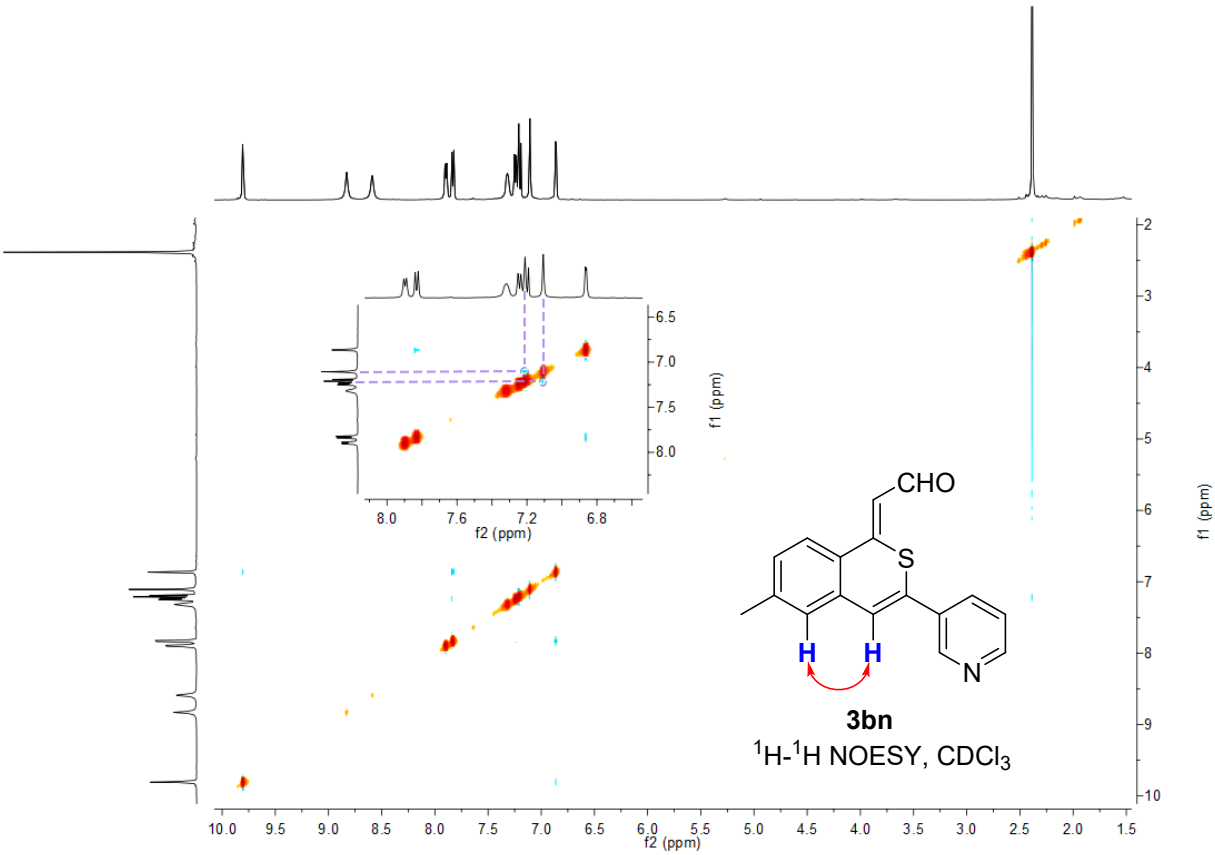
3bn

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



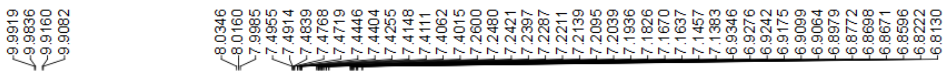
3bn

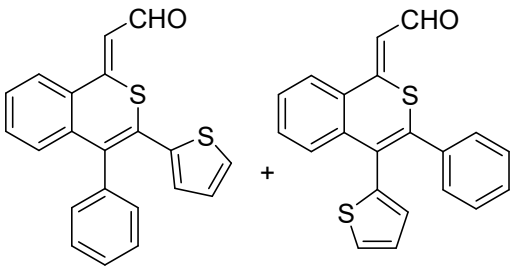
^{13}C NMR, $CDCl_3$, 125 MHz



3bn

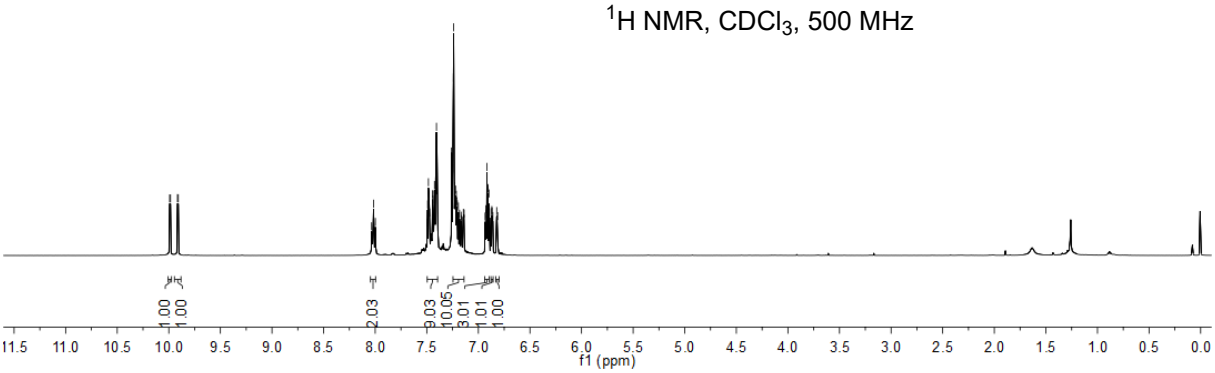
^{1}H-^{1}H NOESY, $CDCl_3$

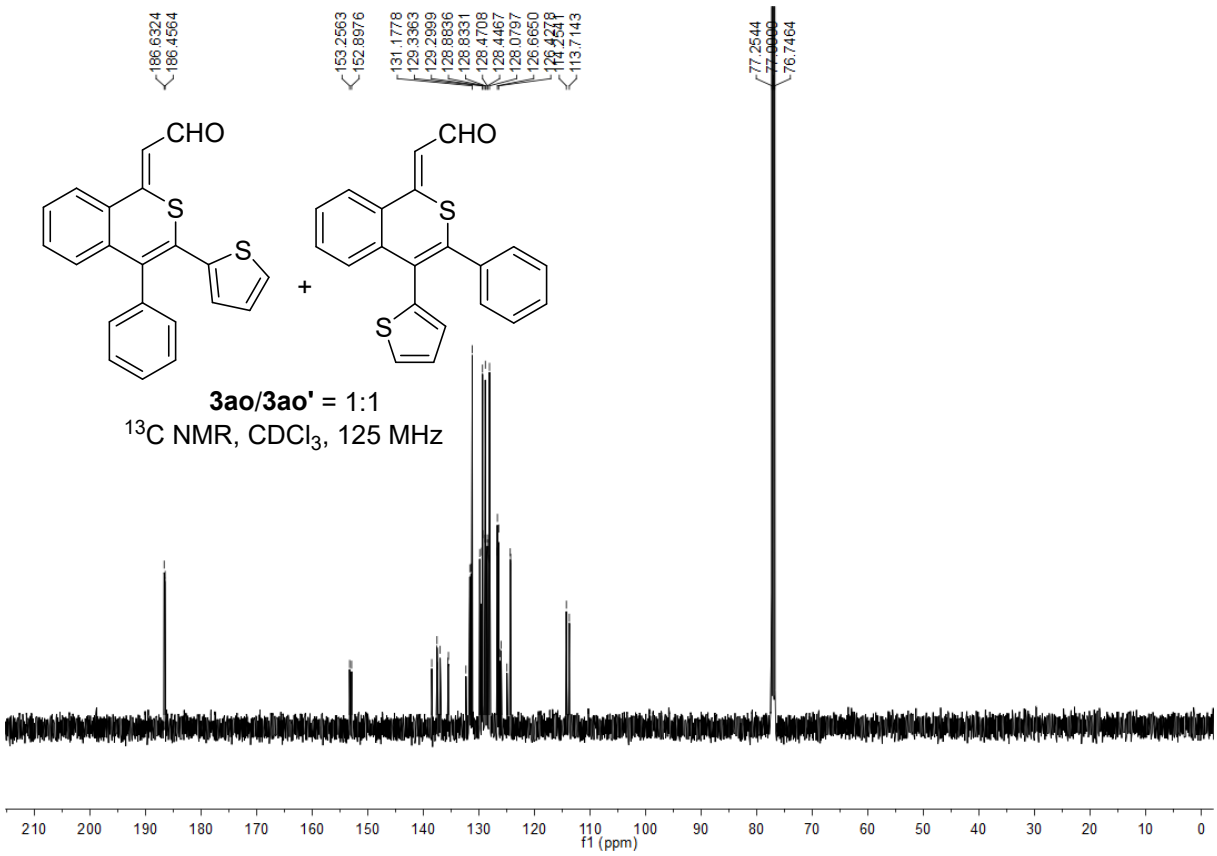


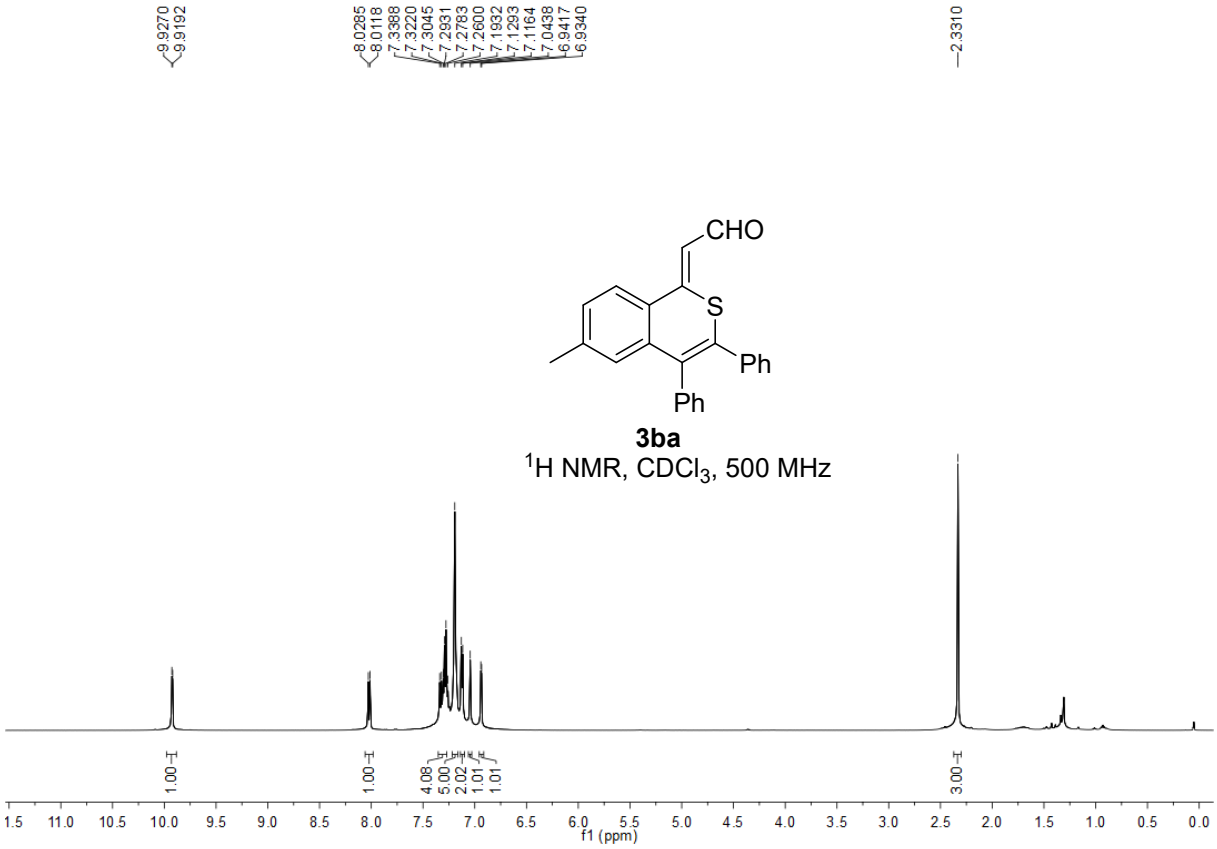


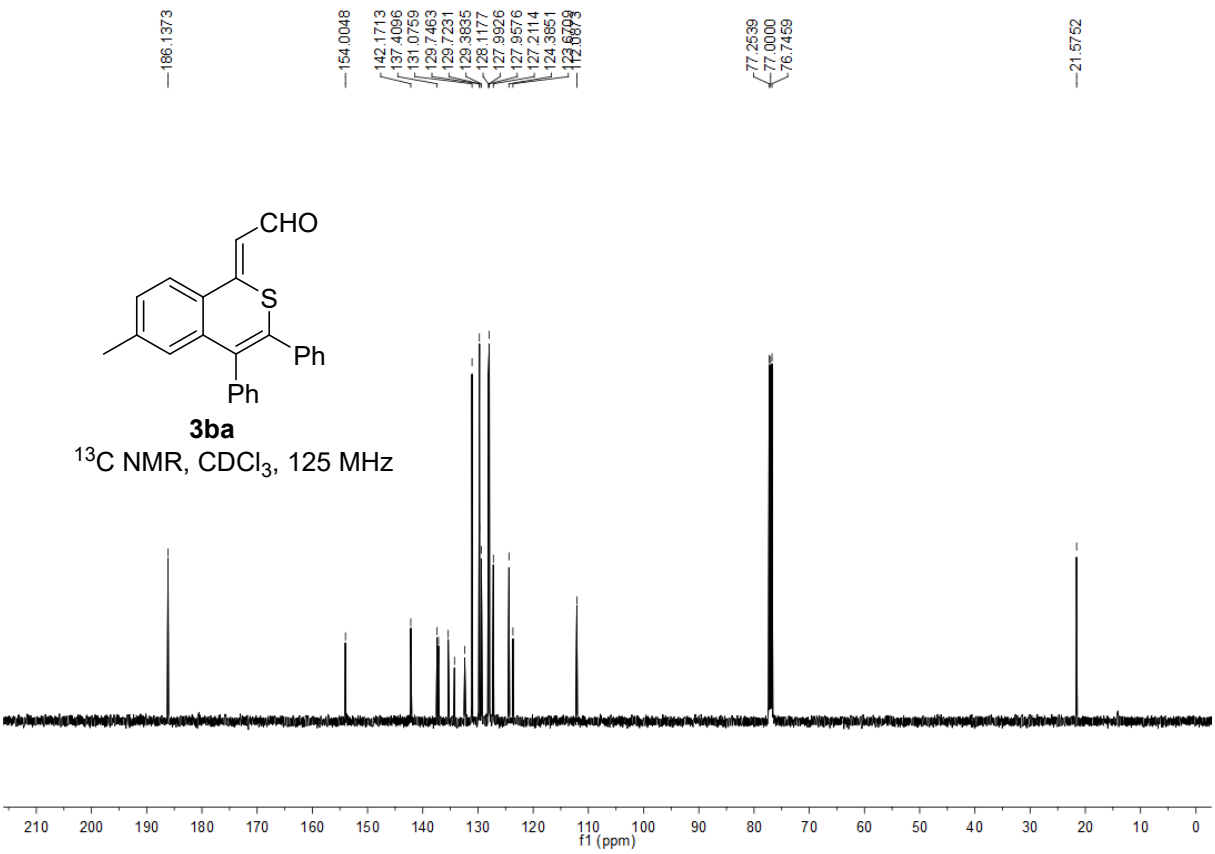
3ao/3ao' = 1:1

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



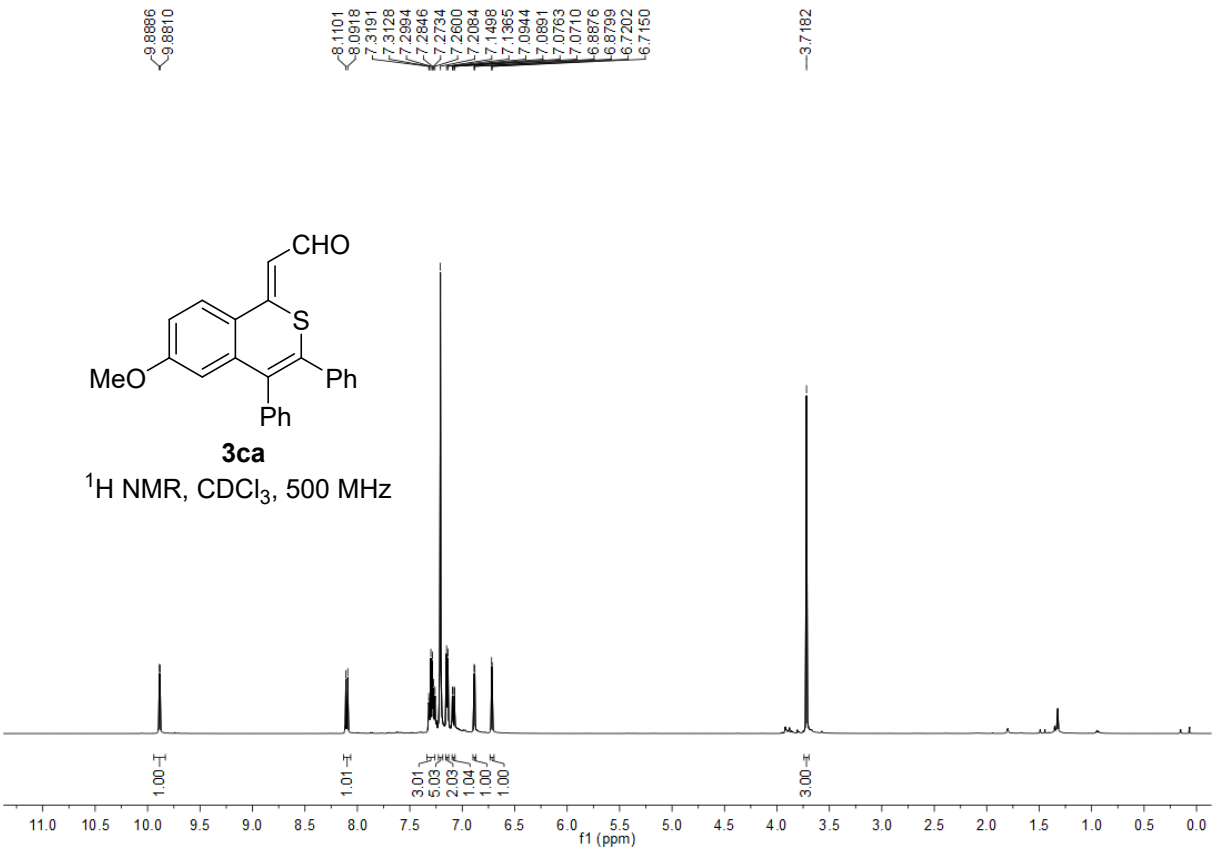

186.6324
186.4564
153.2563
152.8976
131.1778
129.3363
129.2999
128.8836
128.8331
128.4708
128.4467
128.0797
126.6650
126.4278
114.2541
113.7143
77.2544
77.0000
76.7464
CHO
S
S
+
CHO
S
S
3ao/3ao' = 1:1
13C NMR, CDCl3, 125 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.9270
9.9192
8.0285
8.0118
7.3388
7.3220
7.3045
7.2931
7.2783
7.2600
7.1932
7.1293
7.1164
7.0438
6.9417
6.9340
2.3310
CHO
S
Ph
Ph
3ba
1H NMR, CDCl3, 500 MHz
1.00
1.00
4.08
5.00
2.02
1.01
1.01
3.00
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



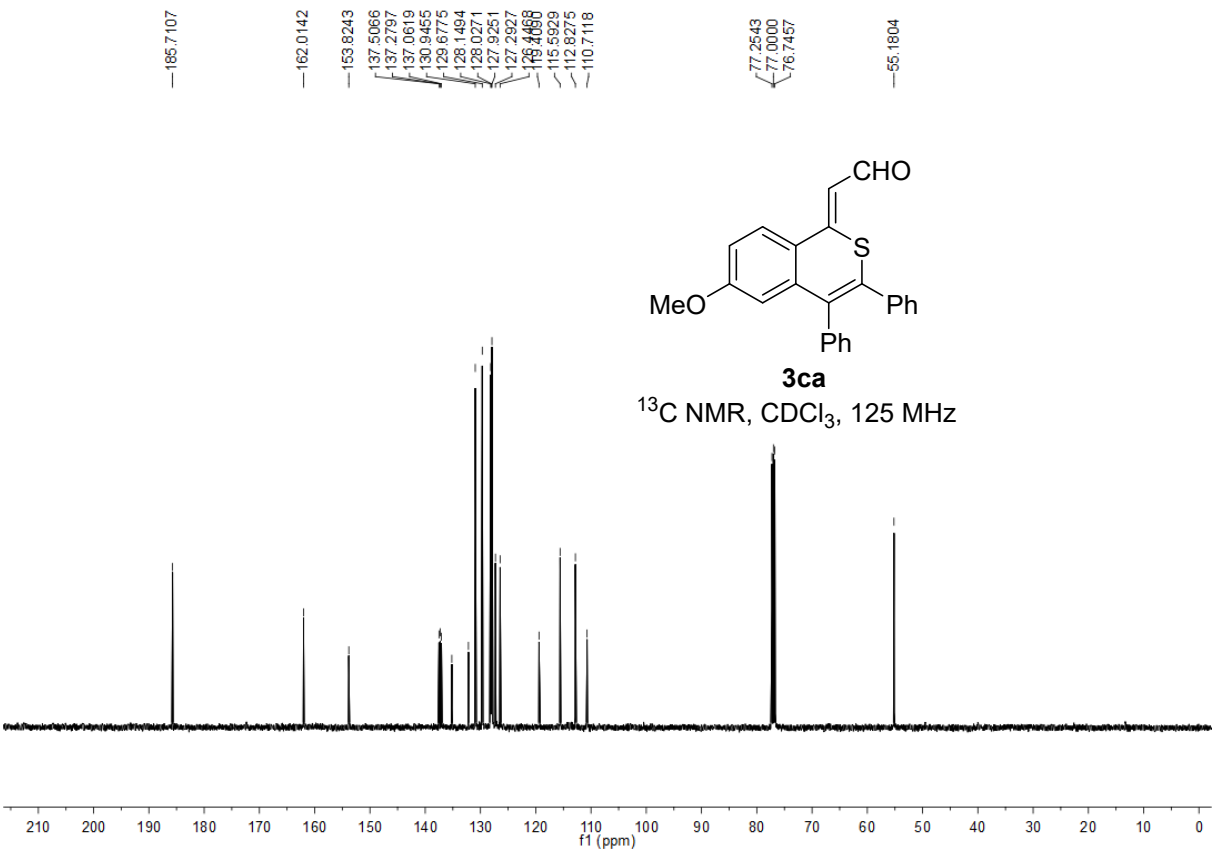
3ba

^{13}C NMR, $CDCl_3$, 125 MHz



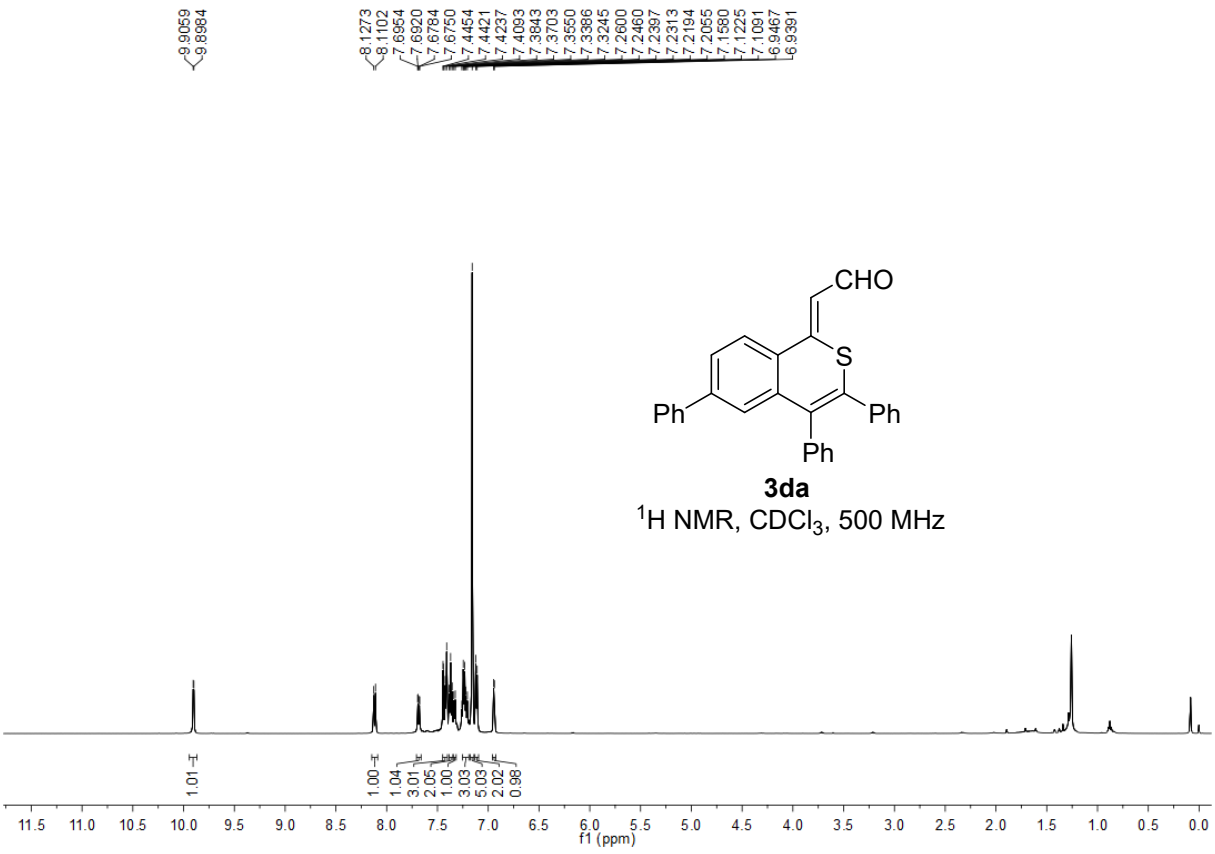
3ca

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



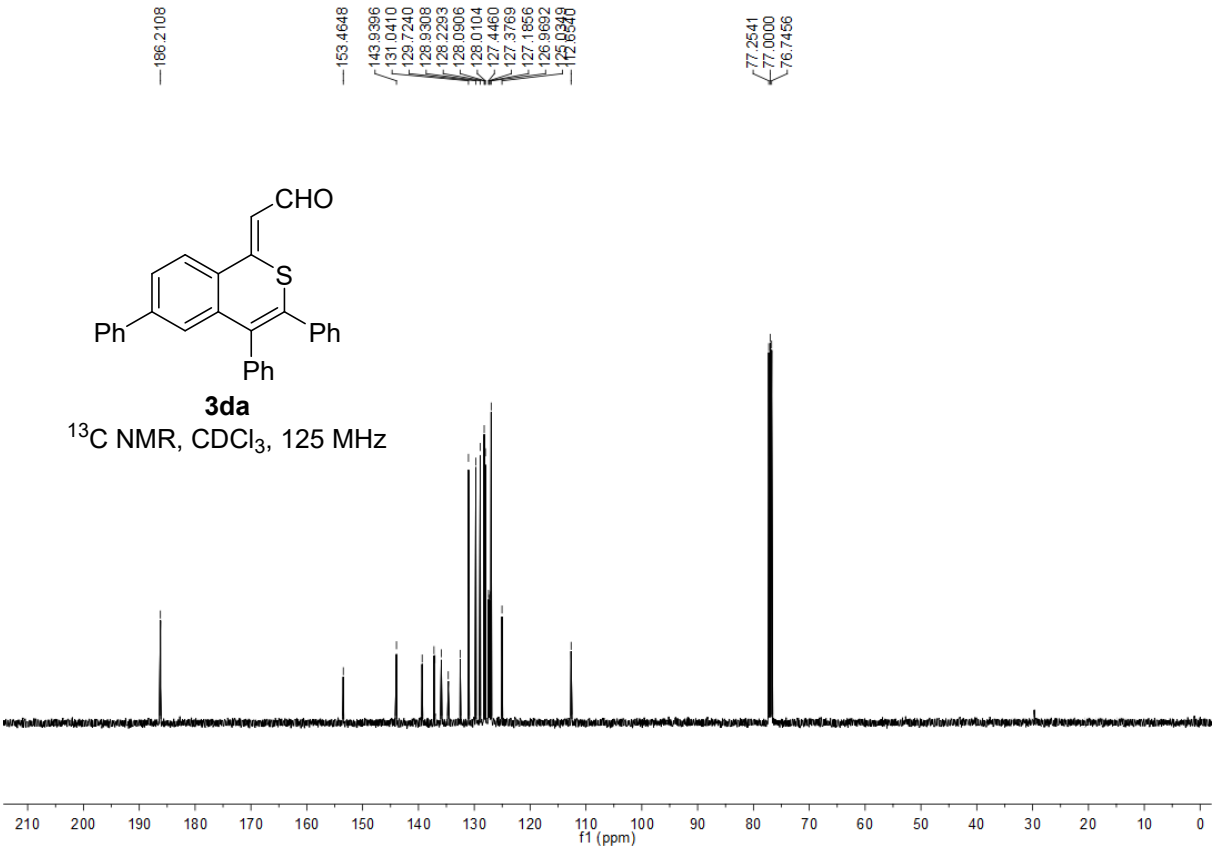
3ca

^{13}C NMR, $CDCl_3$, 125 MHz



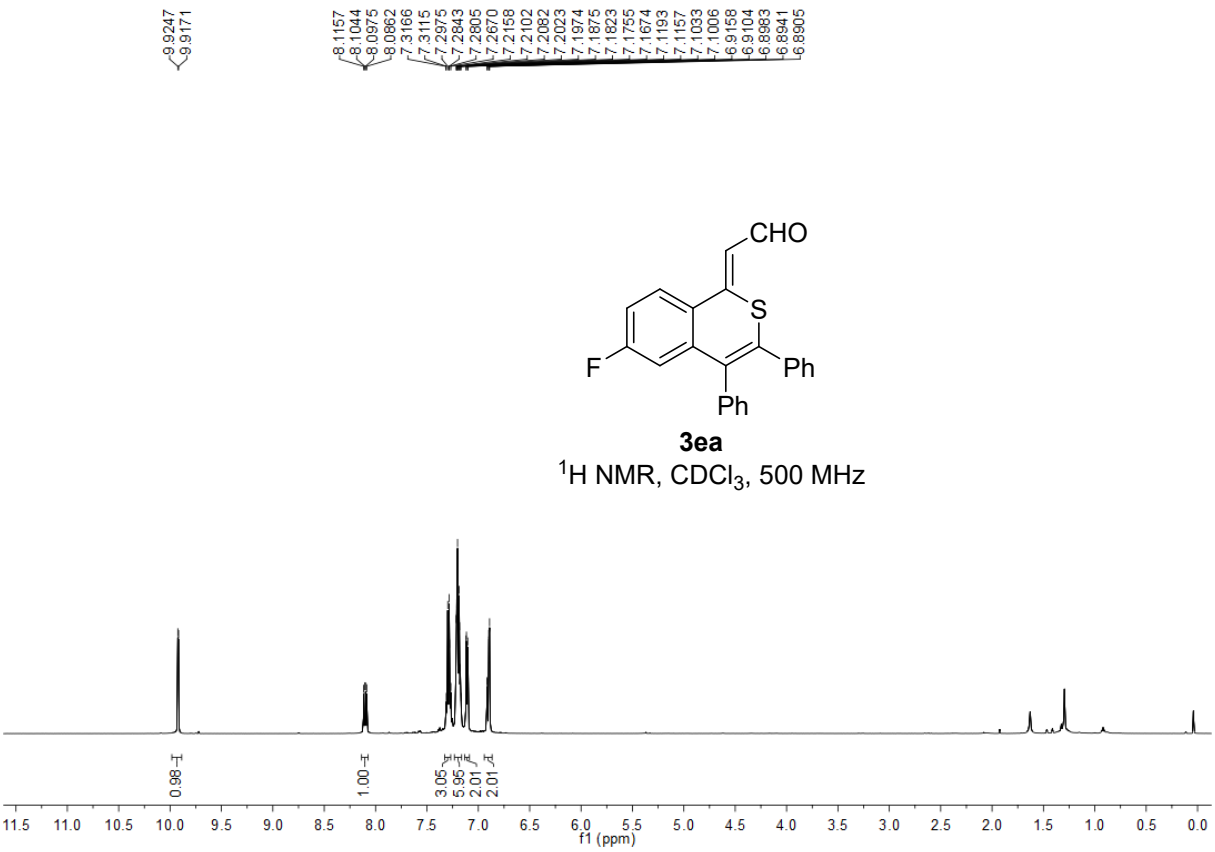
3da

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



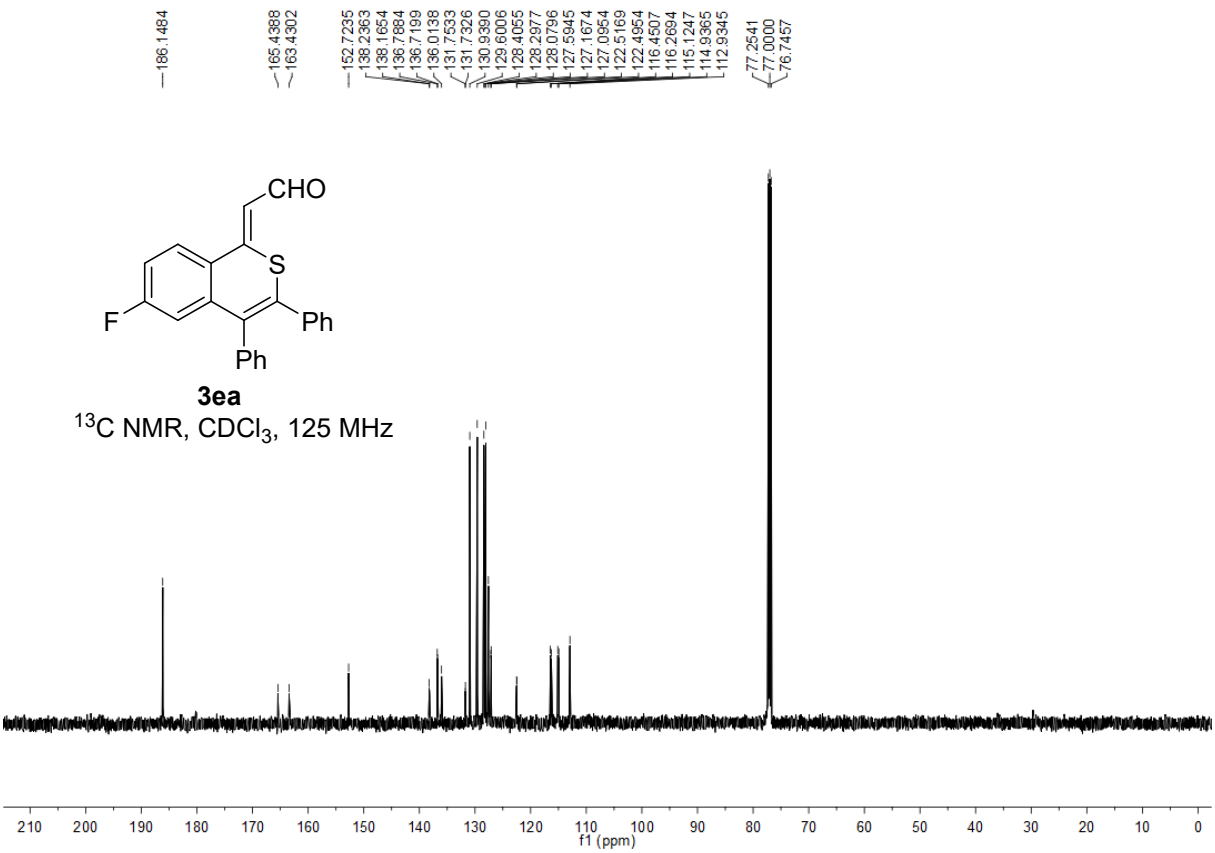
3da

^{13}C NMR, $CDCl_3$, 125 MHz



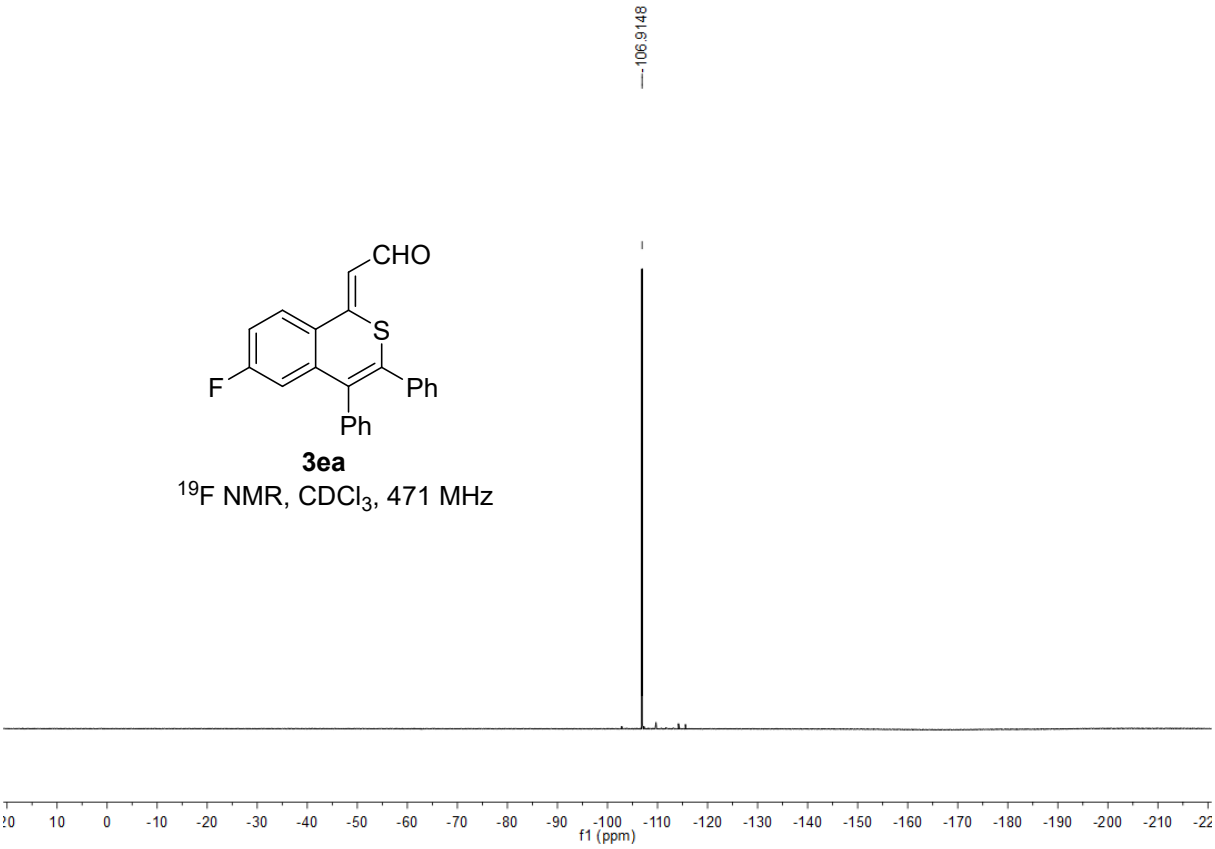
3ea

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



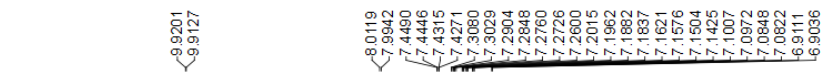
3ea

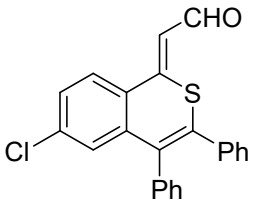
^{13}C NMR, $CDCl_3$, 125 MHz



3ea

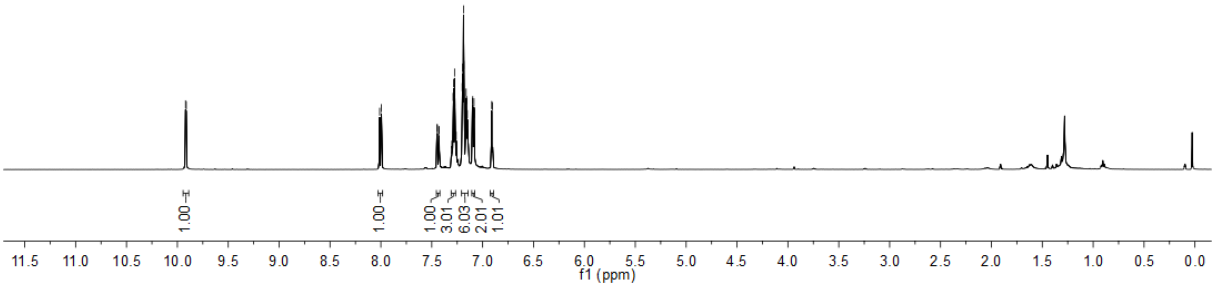
^{19}F NMR, $CDCl_3$, 471 MHz

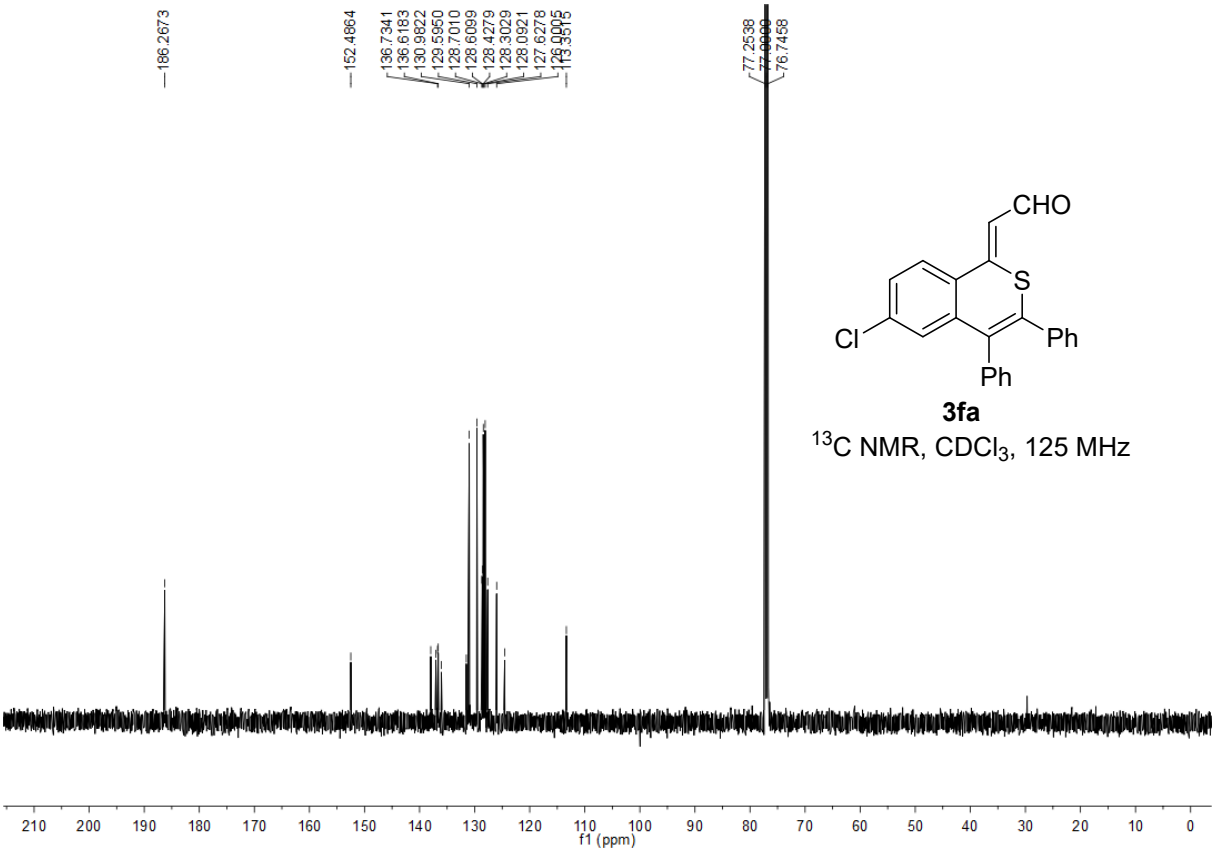




3fa

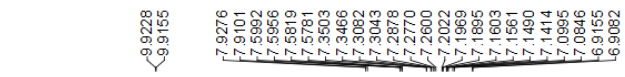
^{1}H NMR, $CDCl_3$, 500 MHz

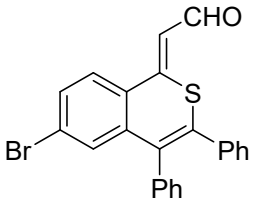




3fa

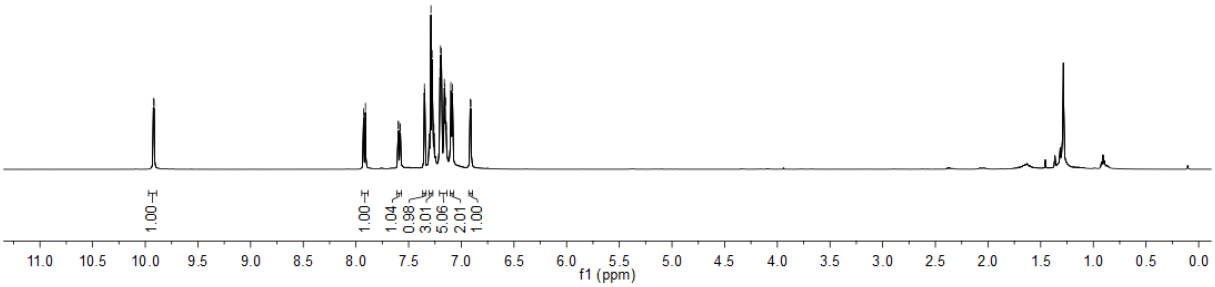
^{13}C NMR, $CDCl_3$, 125 MHz

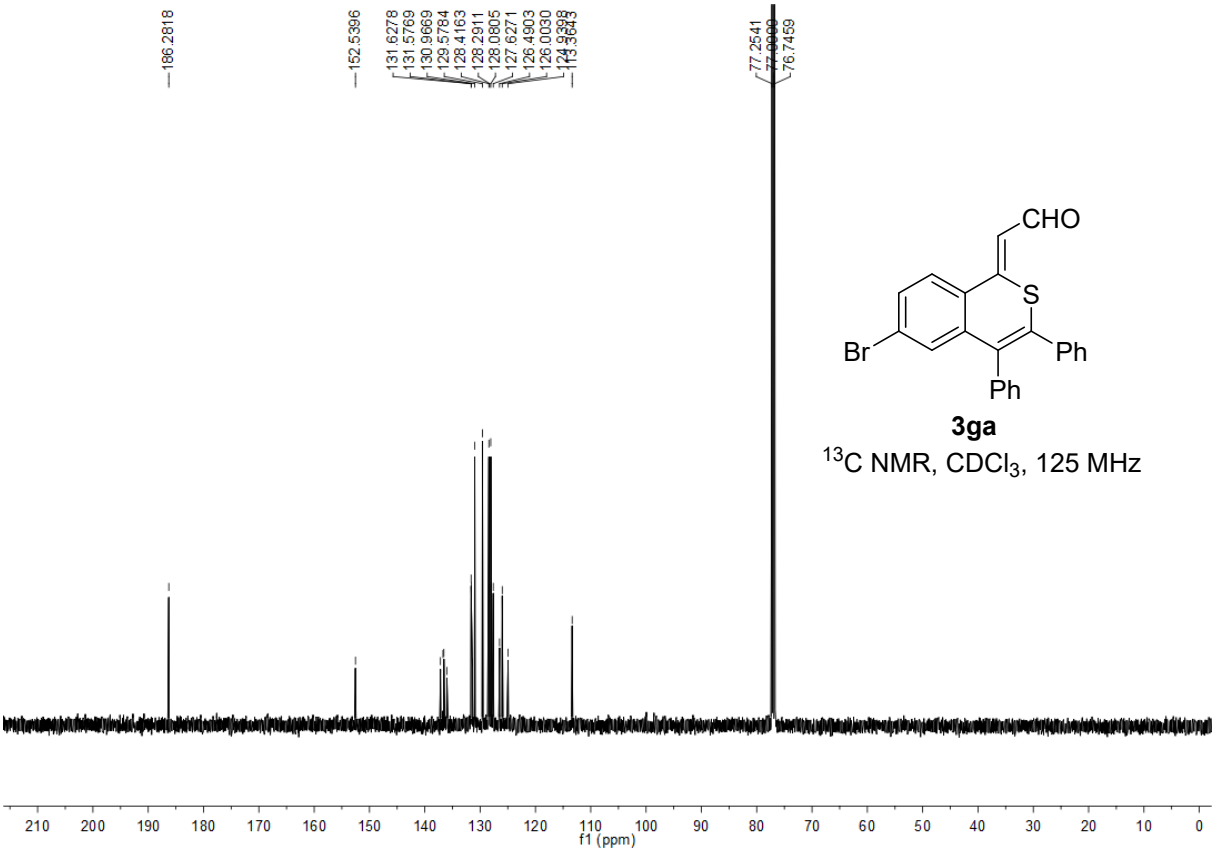




3ga

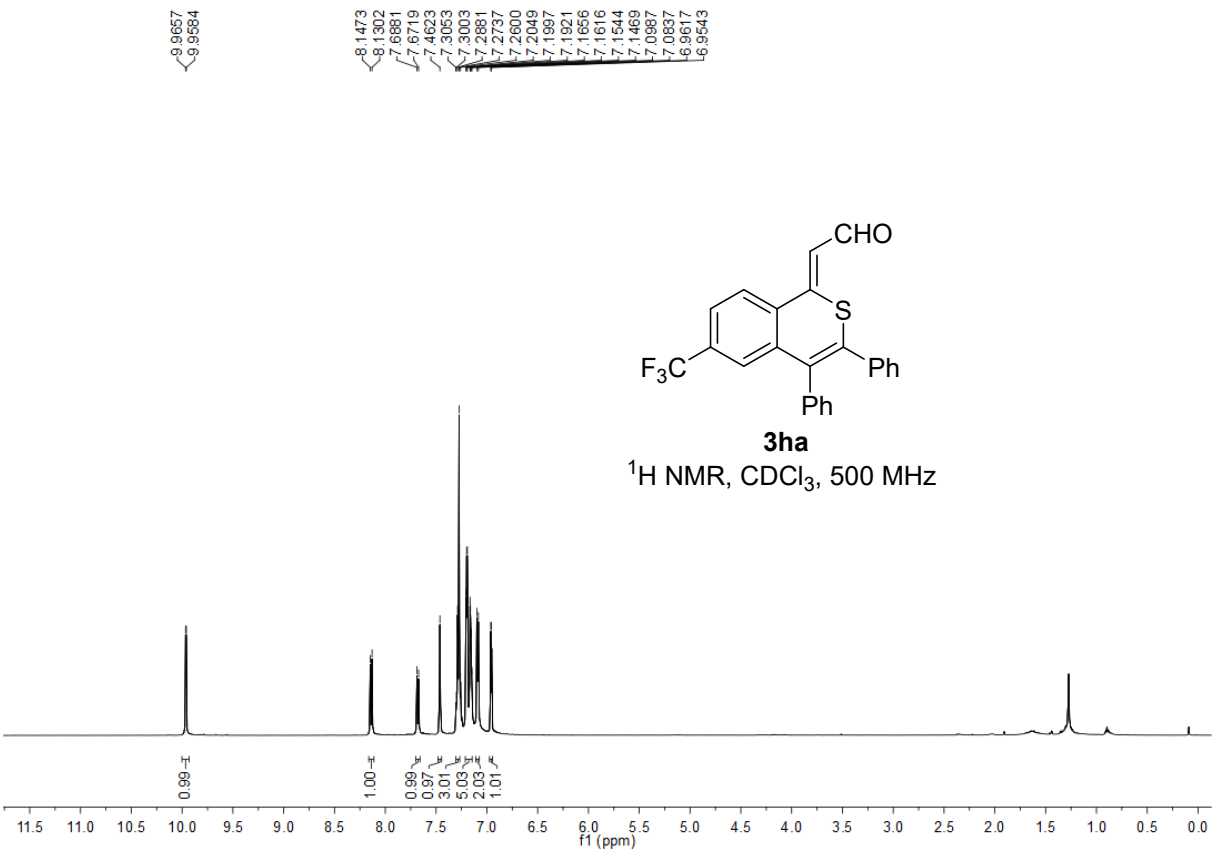
^{1}H NMR, $CDCl_3$, 500 MHz





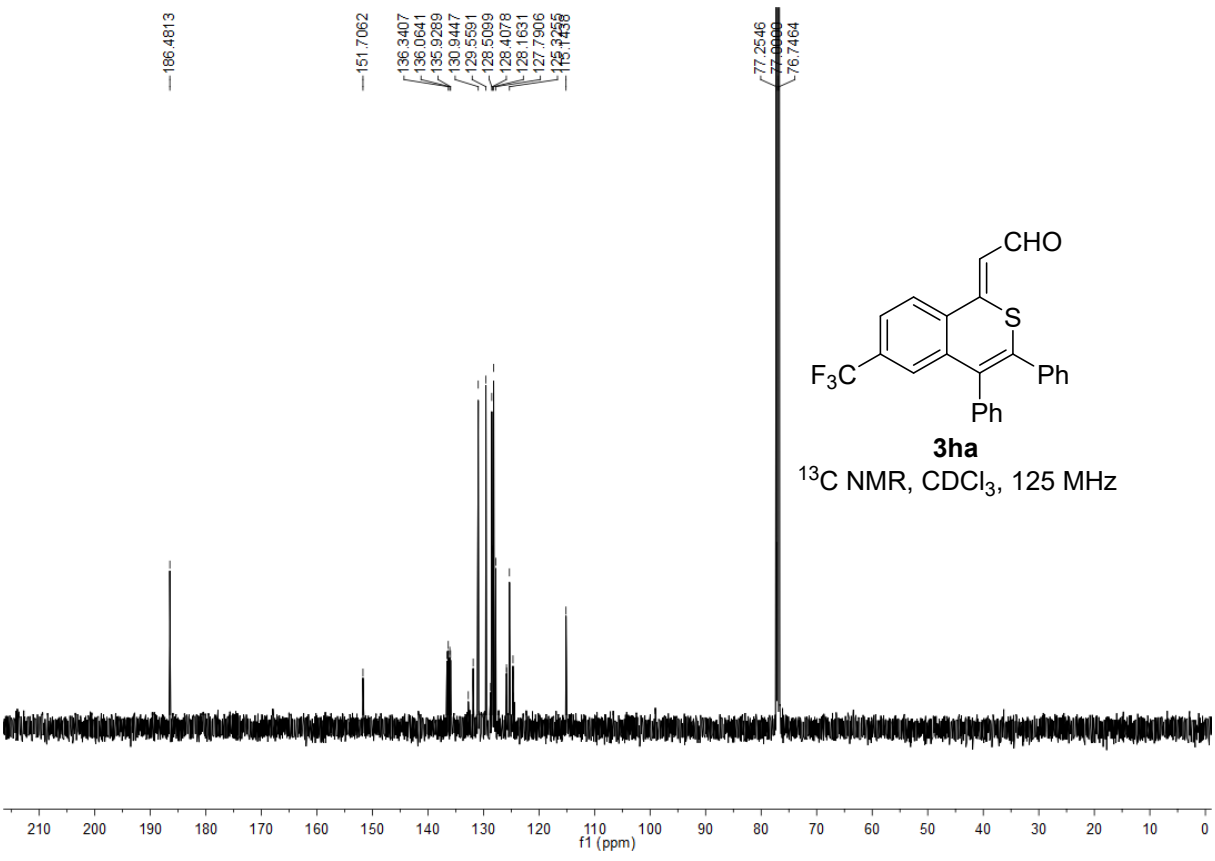
3ga

^{13}C NMR, $CDCl_3$, 125 MHz



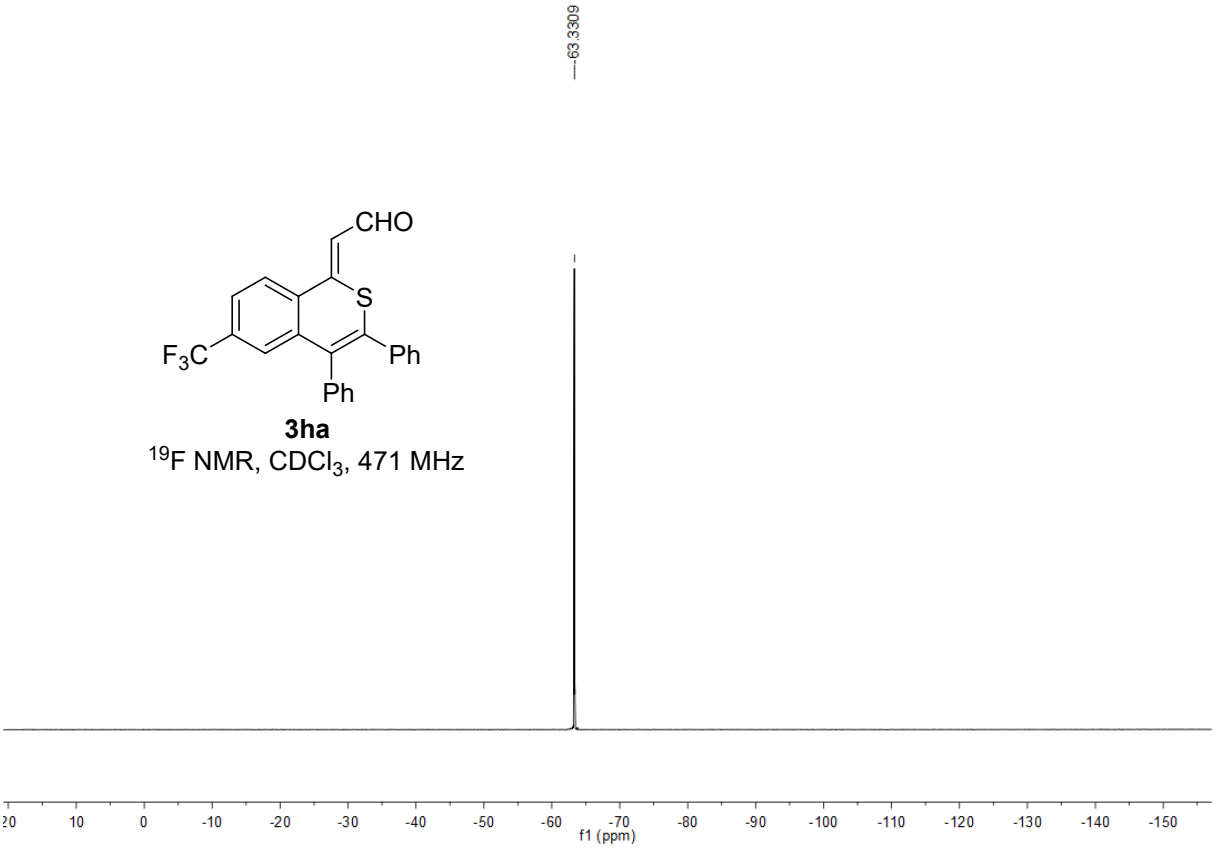
3ha

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



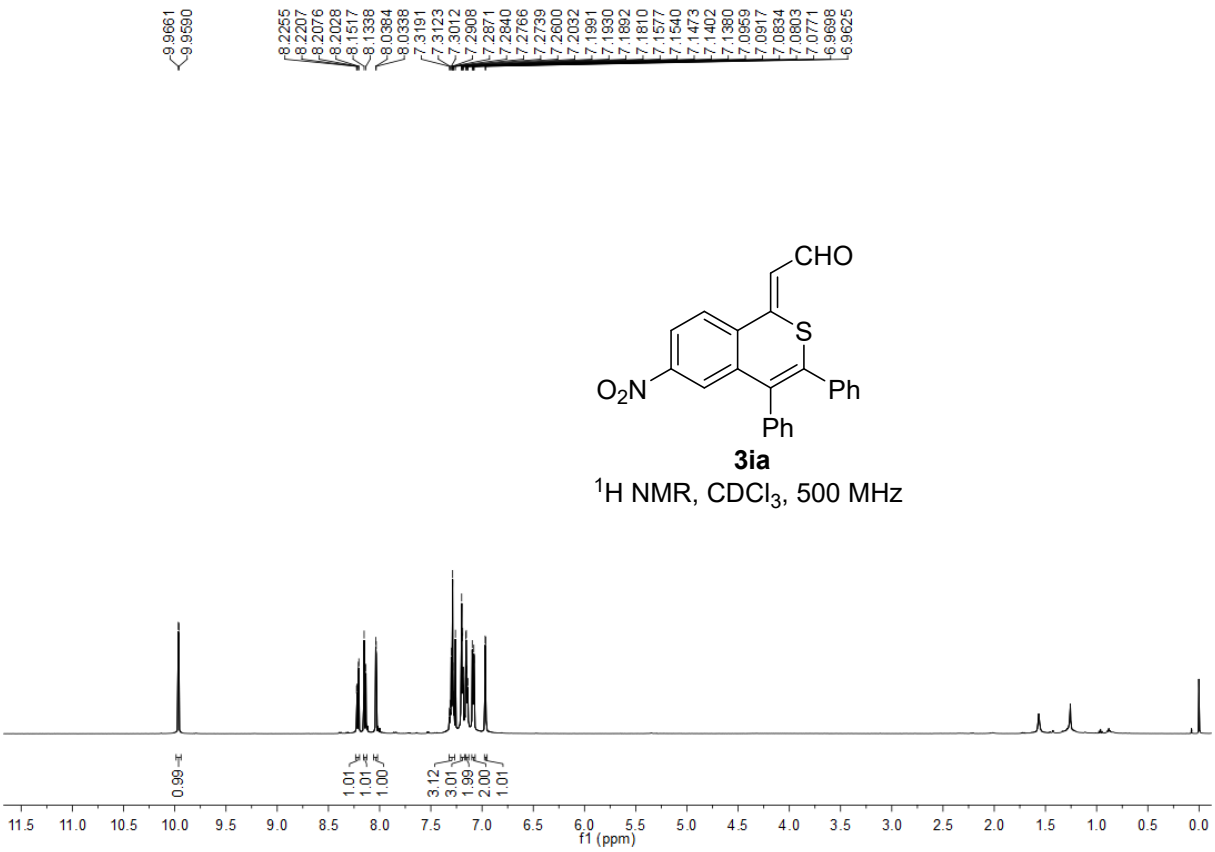
3ha

^{13}C NMR, $CDCl_3$, 125 MHz



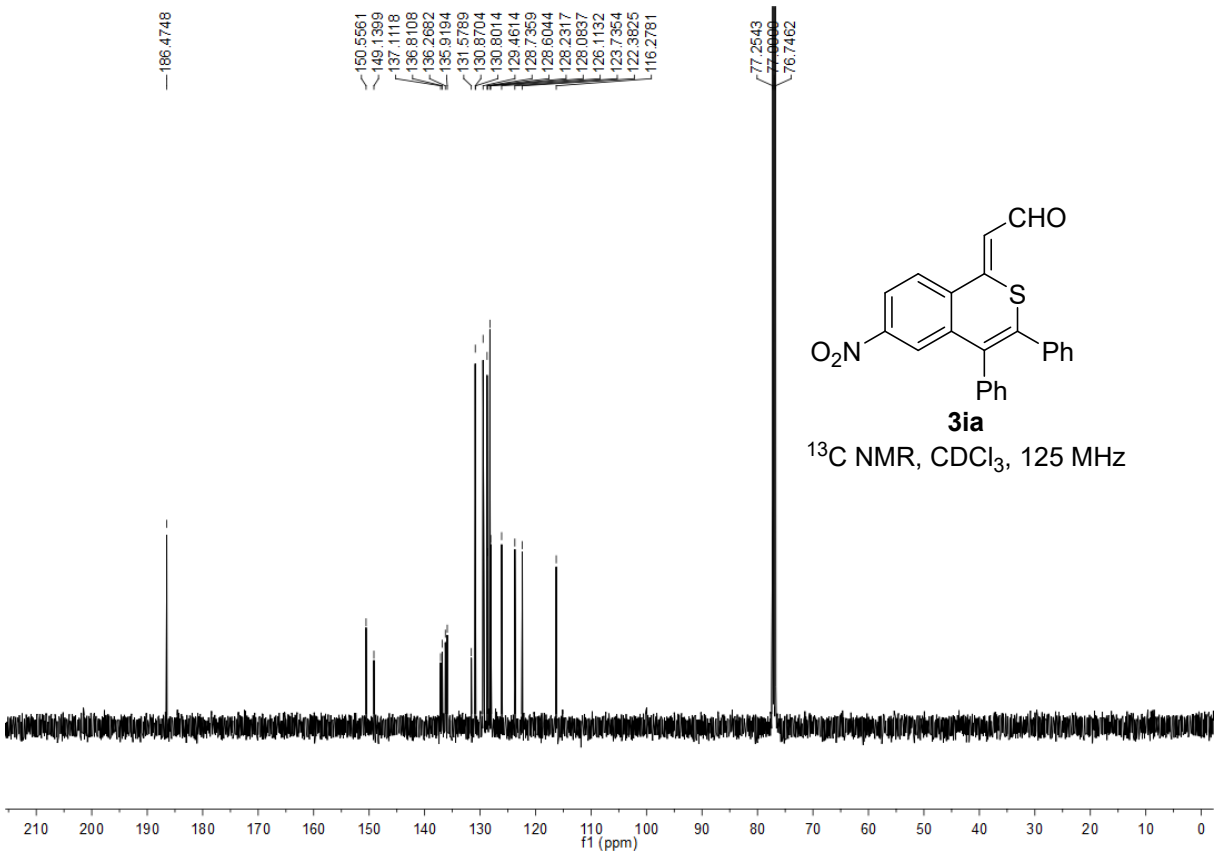
3ha

^{19}F NMR, $CDCl_3$, 471 MHz



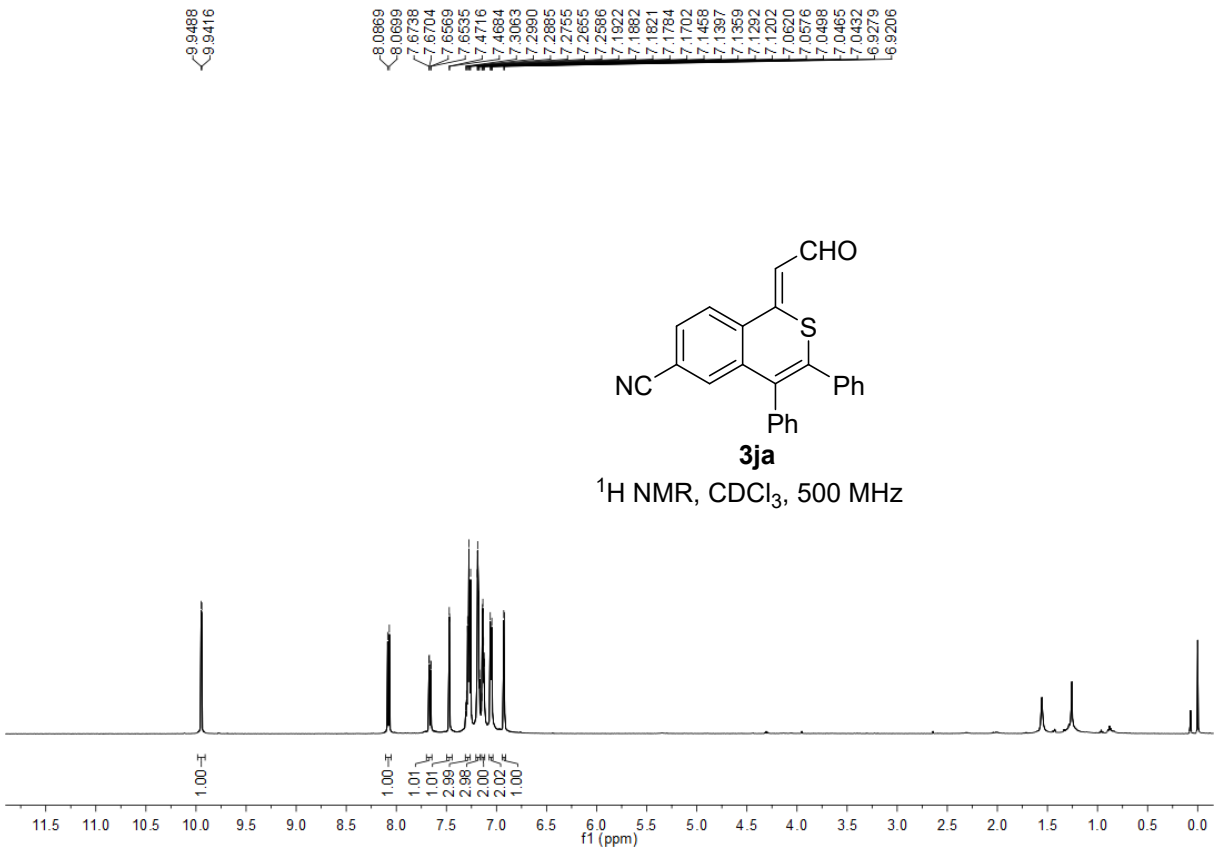
3ia

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



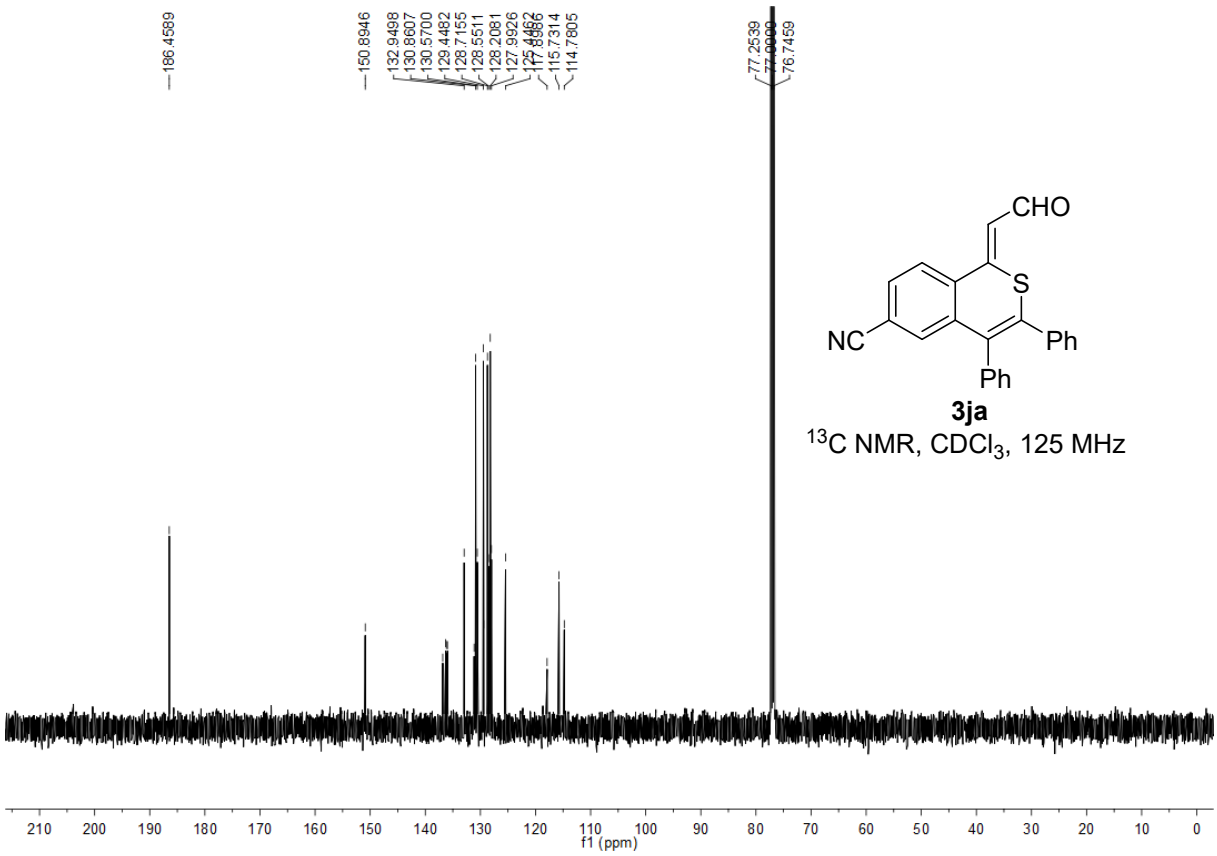
3ia

^{13}C NMR, $CDCl_3$, 125 MHz



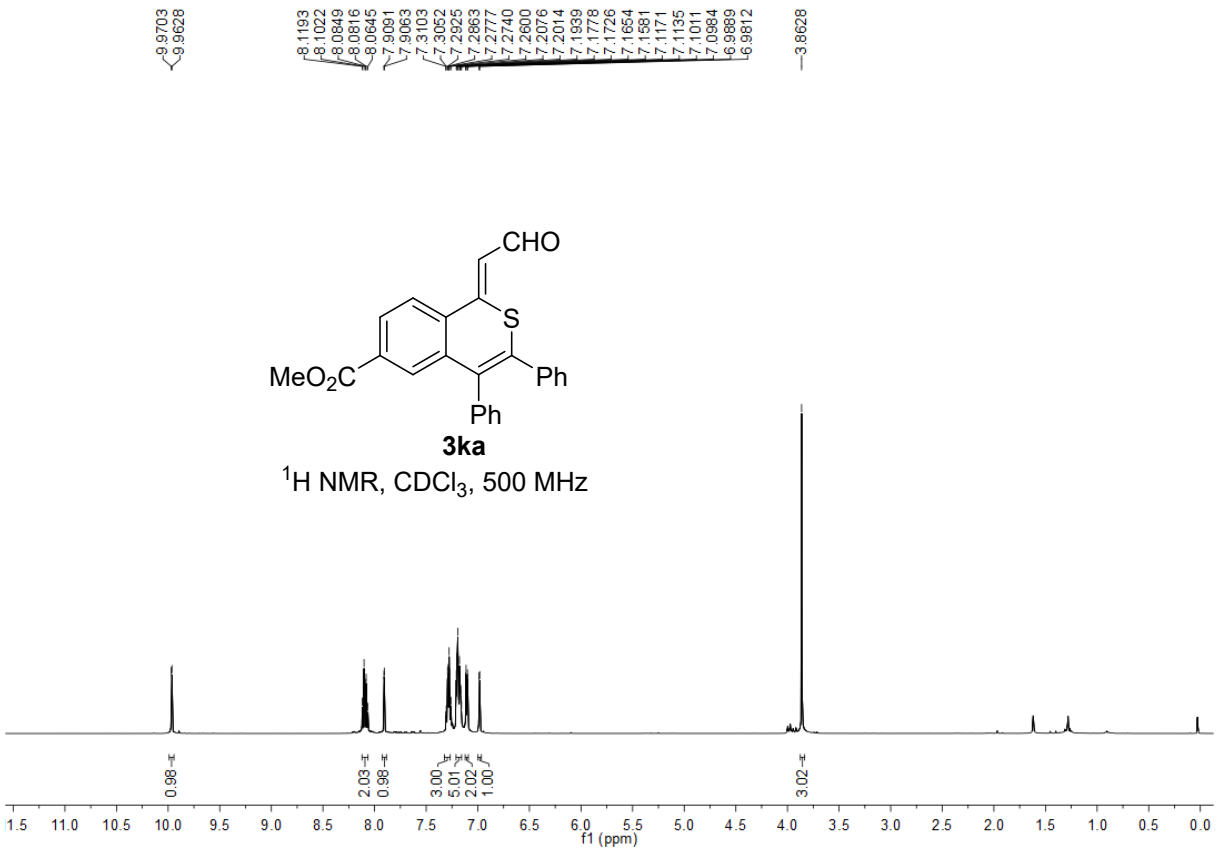
3ja

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



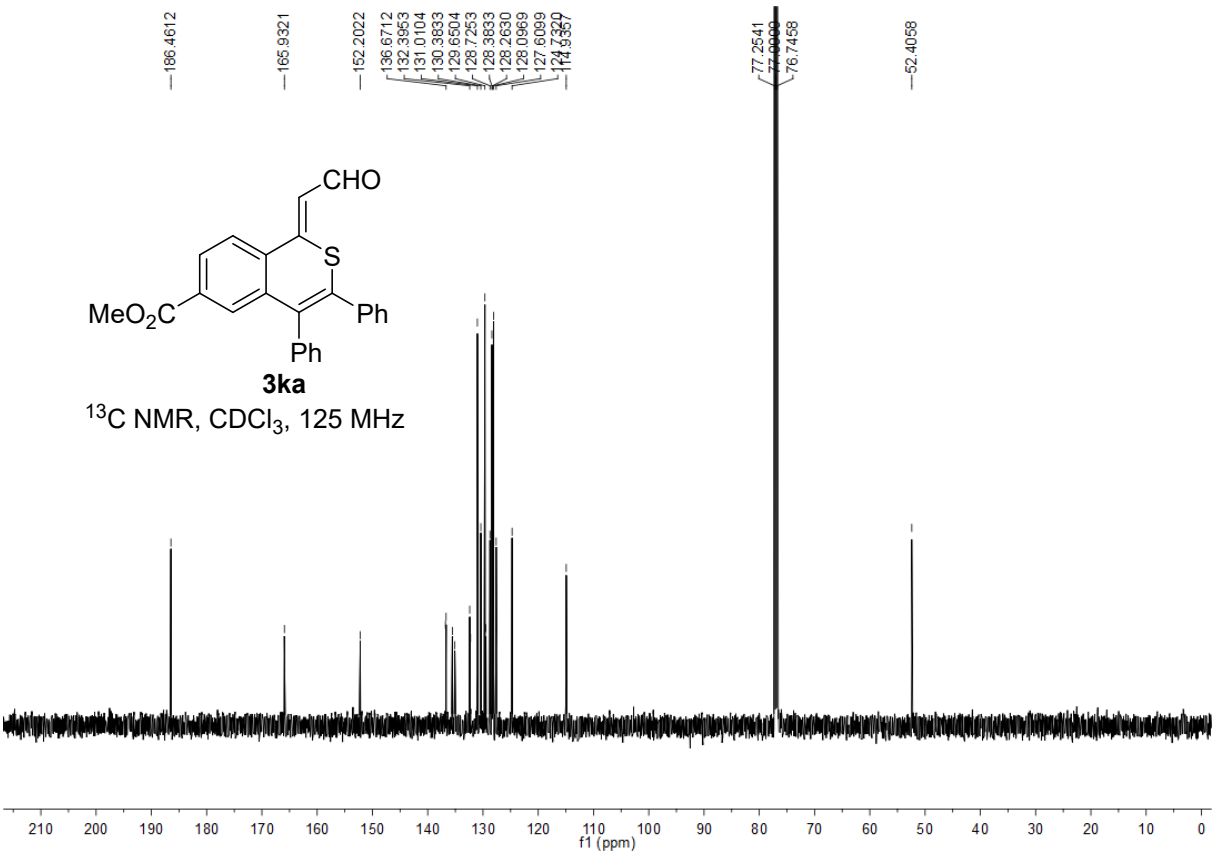
3ja

^{13}C NMR, $CDCl_3$, 125 MHz



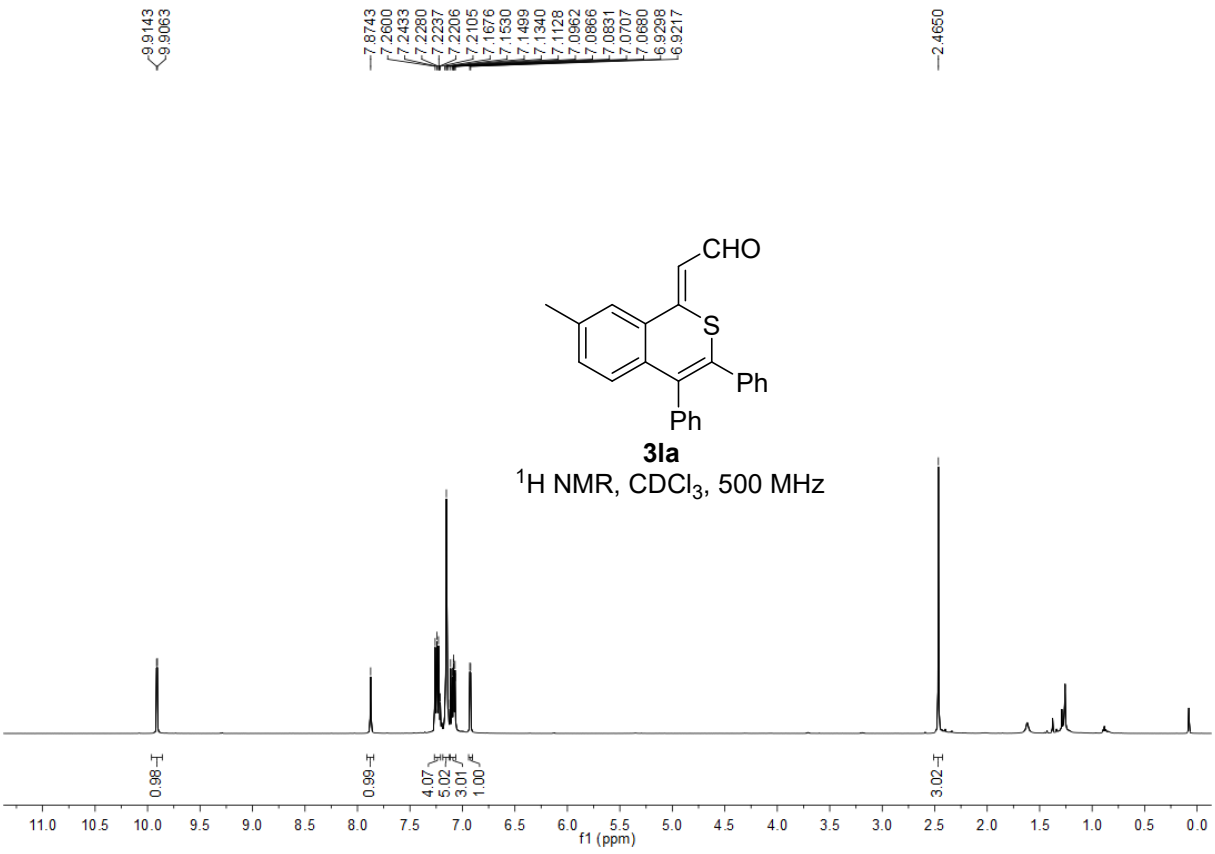
3ka

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



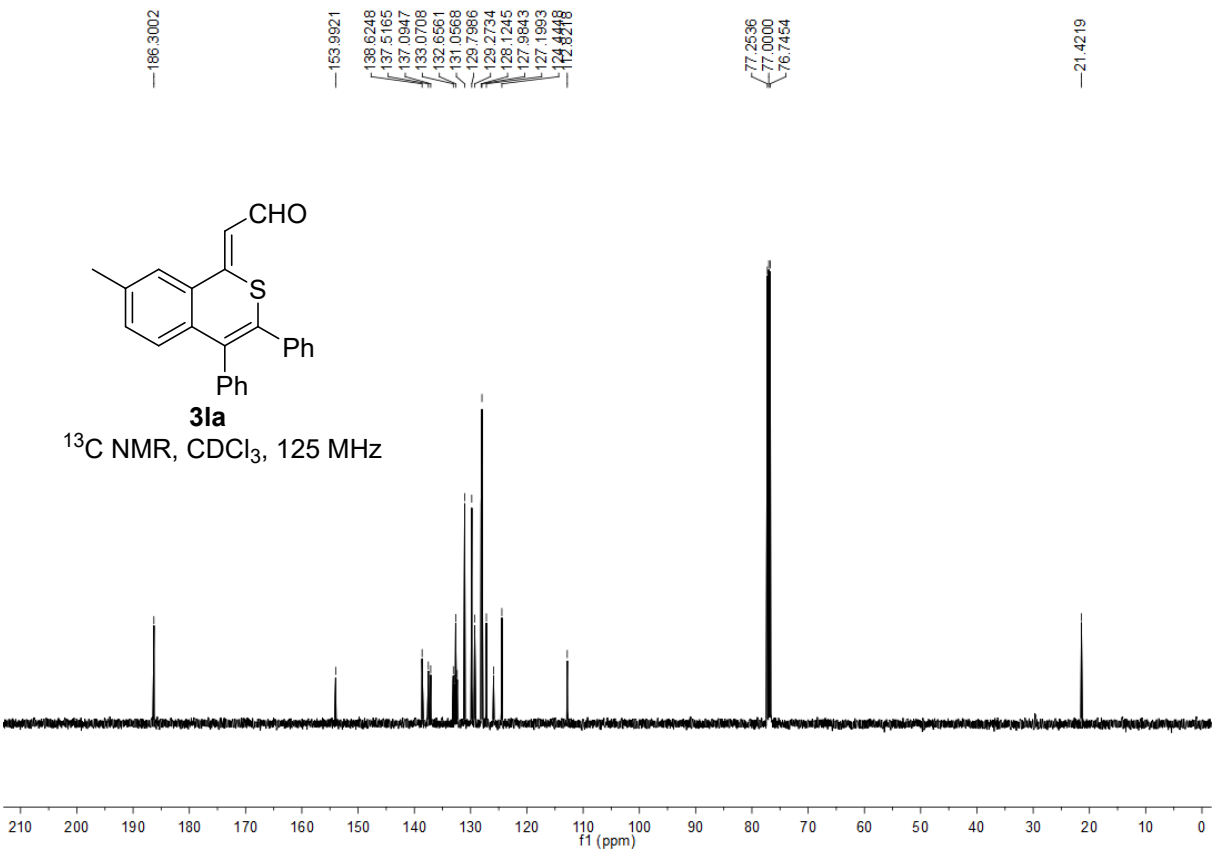
3ka

^{13}C NMR, $CDCl_3$, 125 MHz



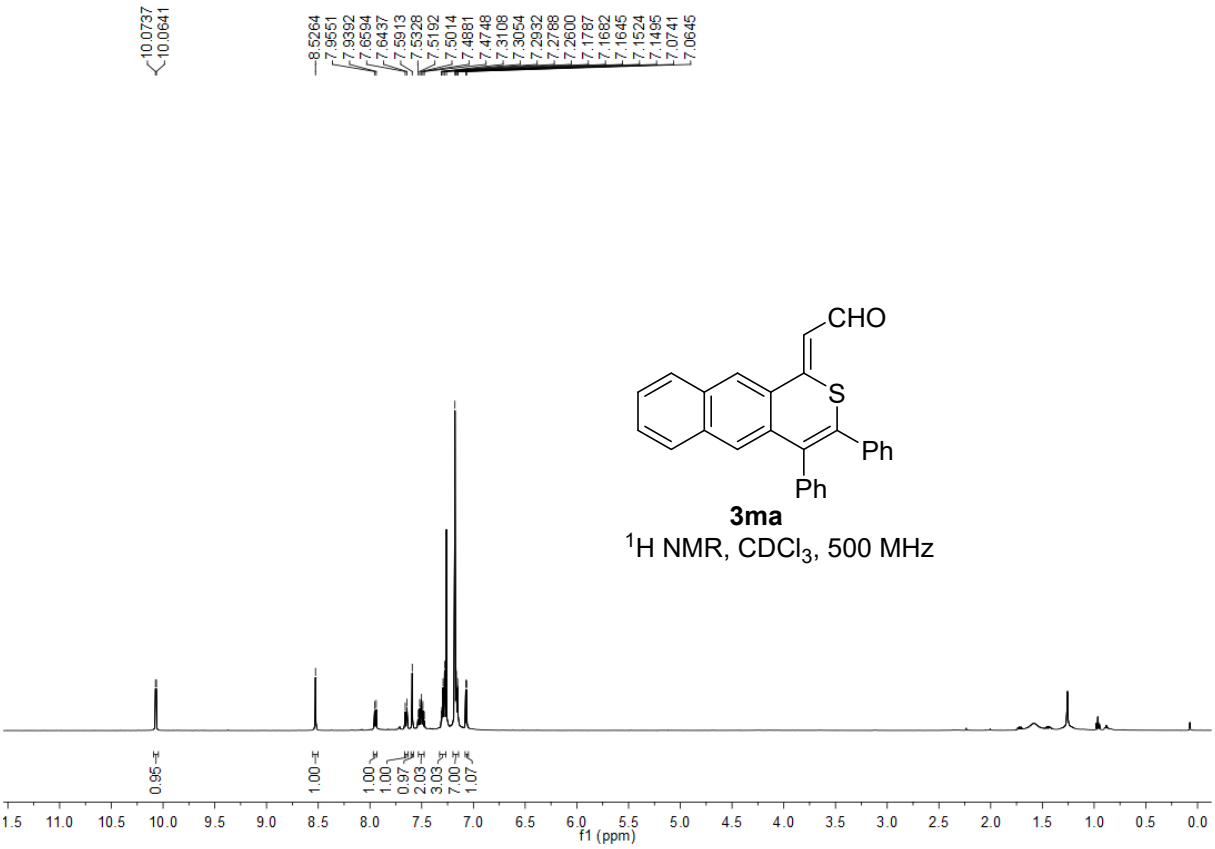
3la

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



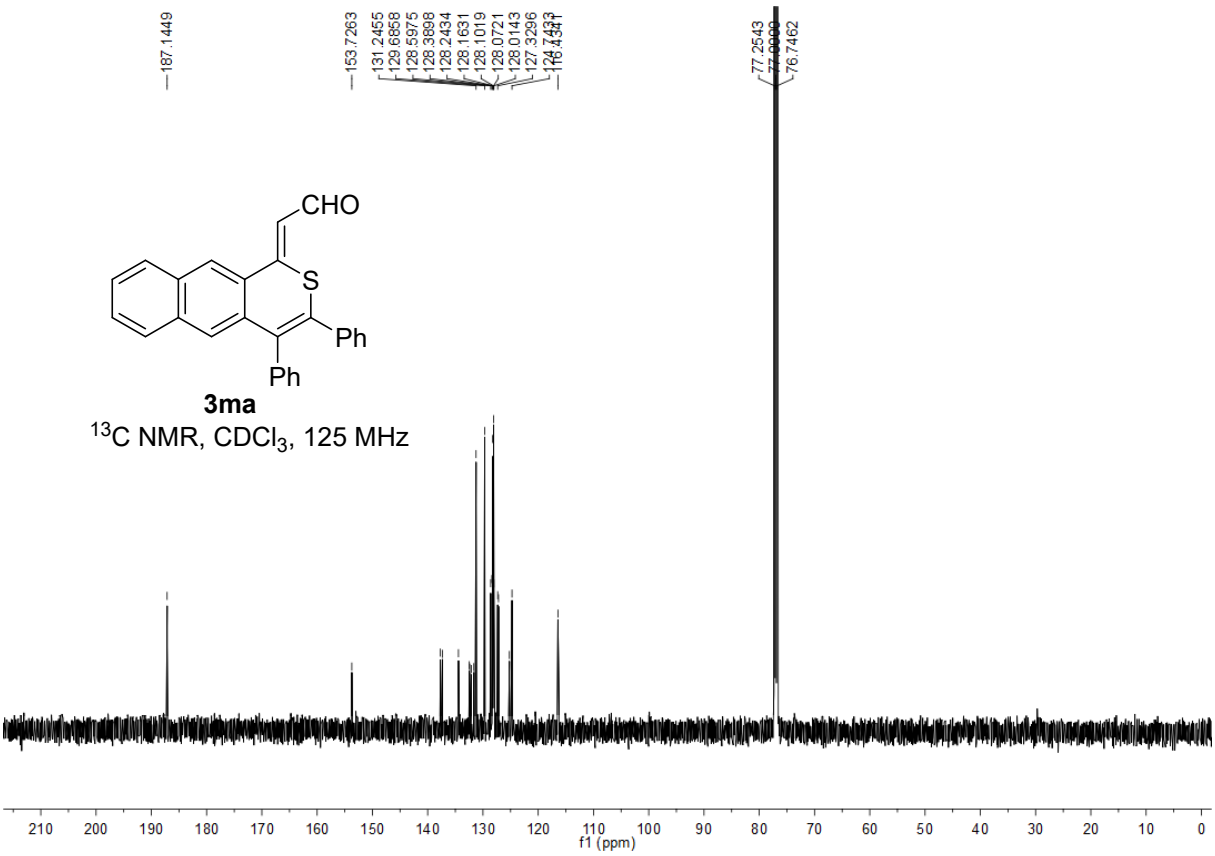
3la

^{13}C NMR, $CDCl_3$, 125 MHz



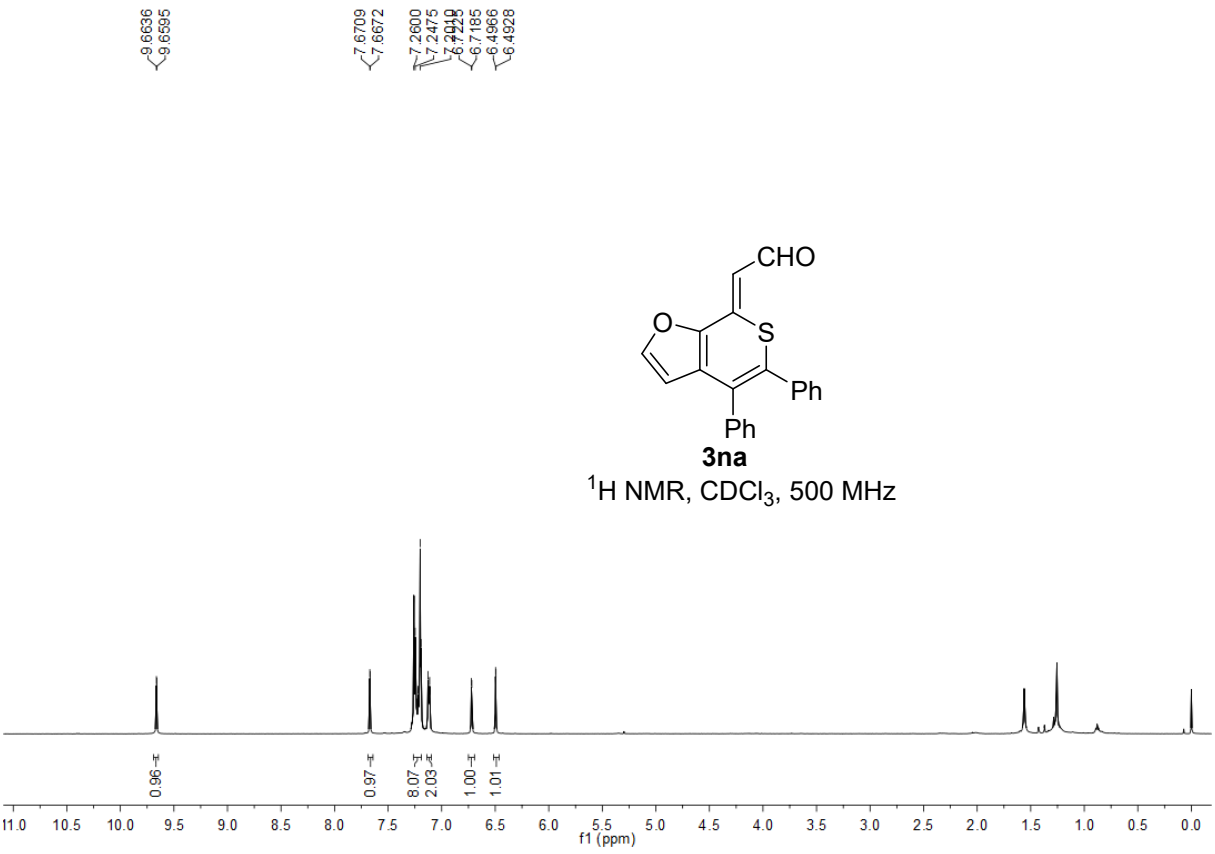
3ma

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



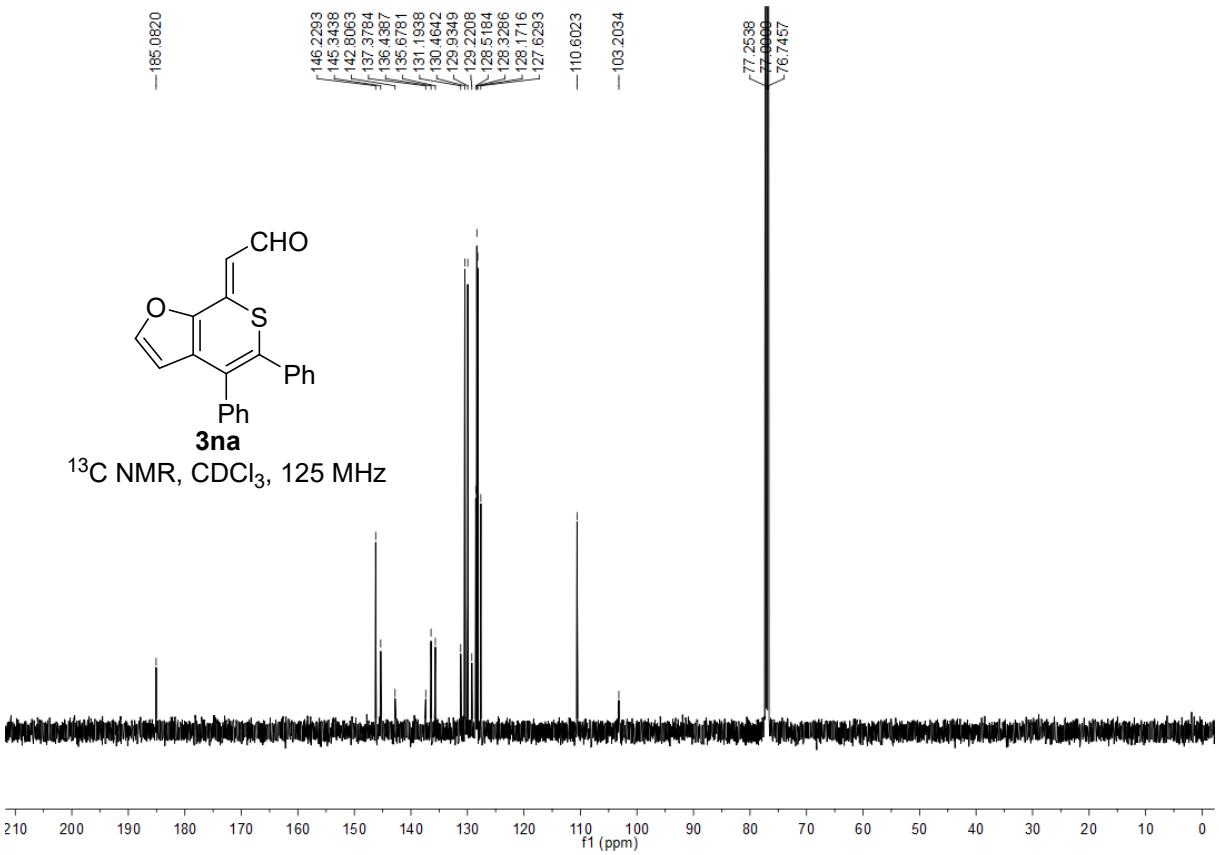
3ma

^{13}C NMR, $CDCl_3$, 125 MHz



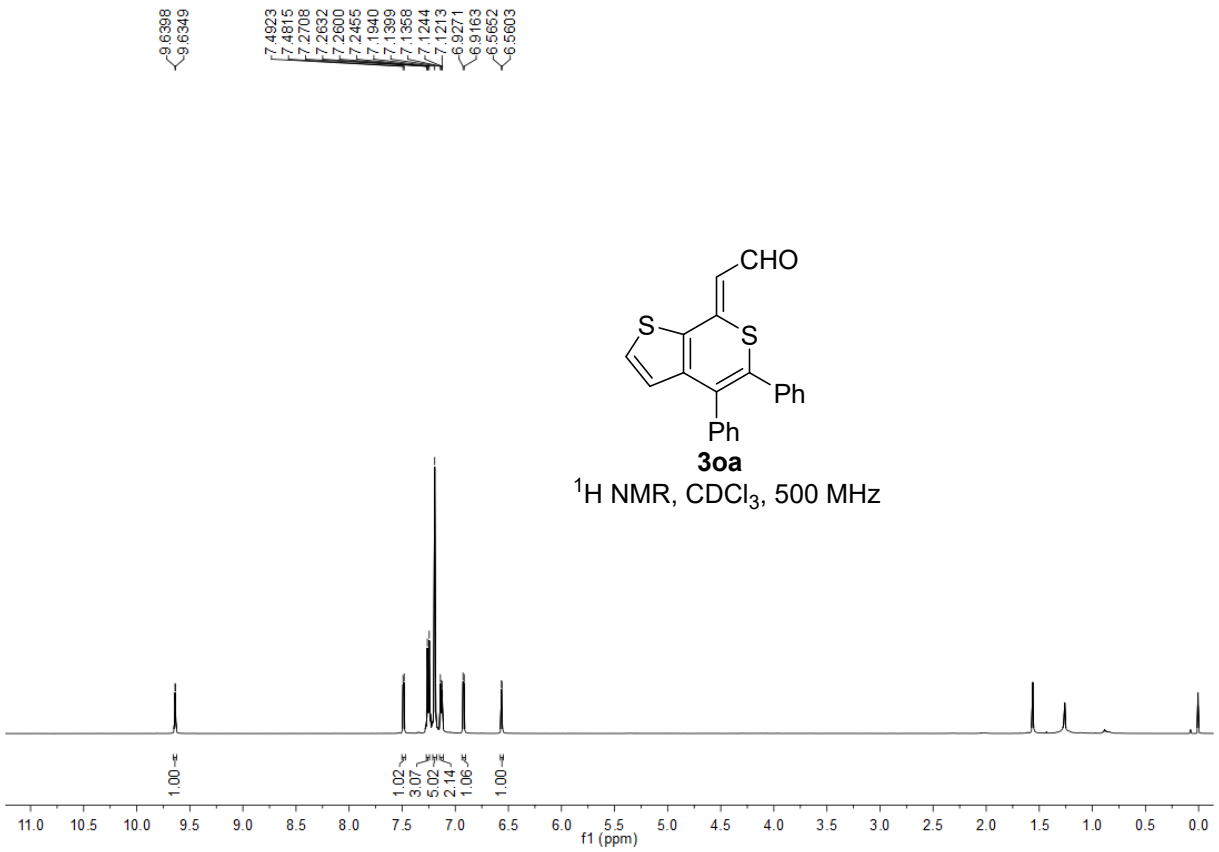
3na

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



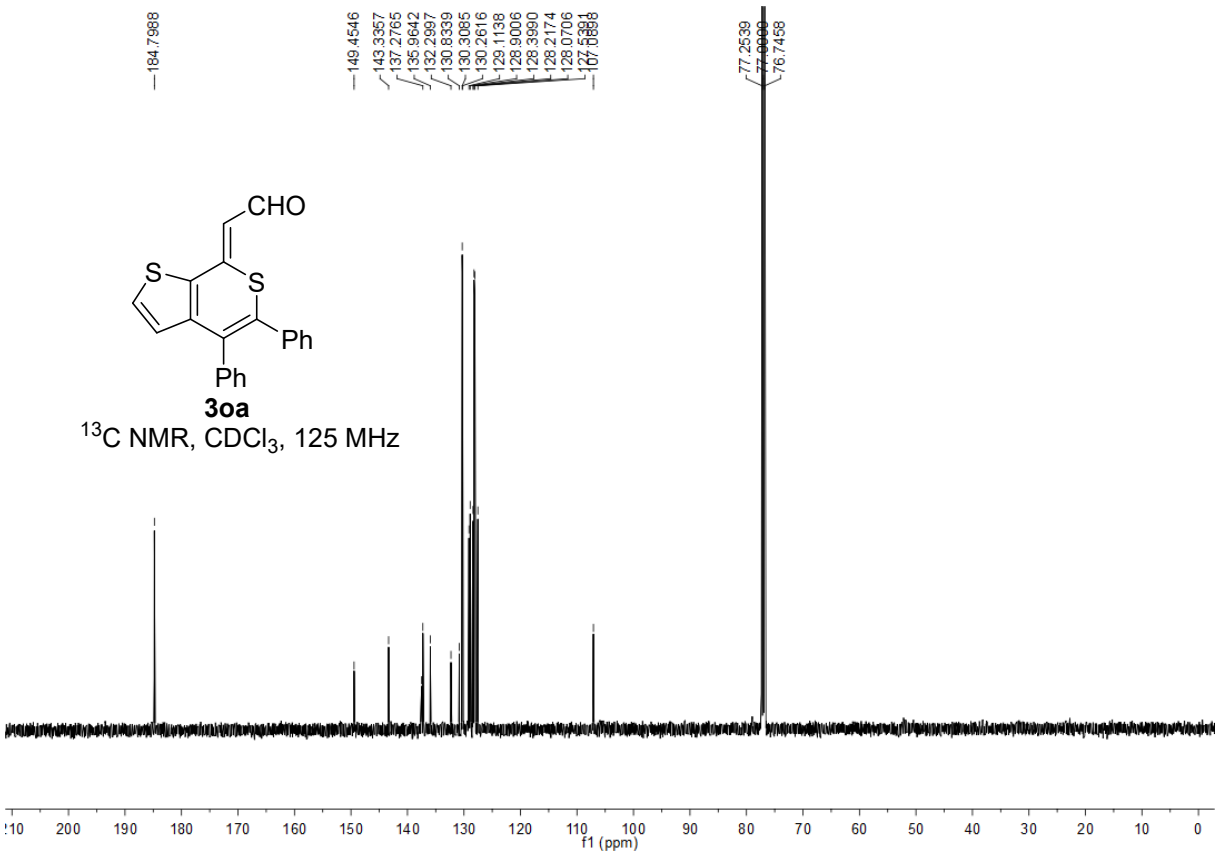
3na

^{13}C NMR, $CDCl_3$, 125 MHz



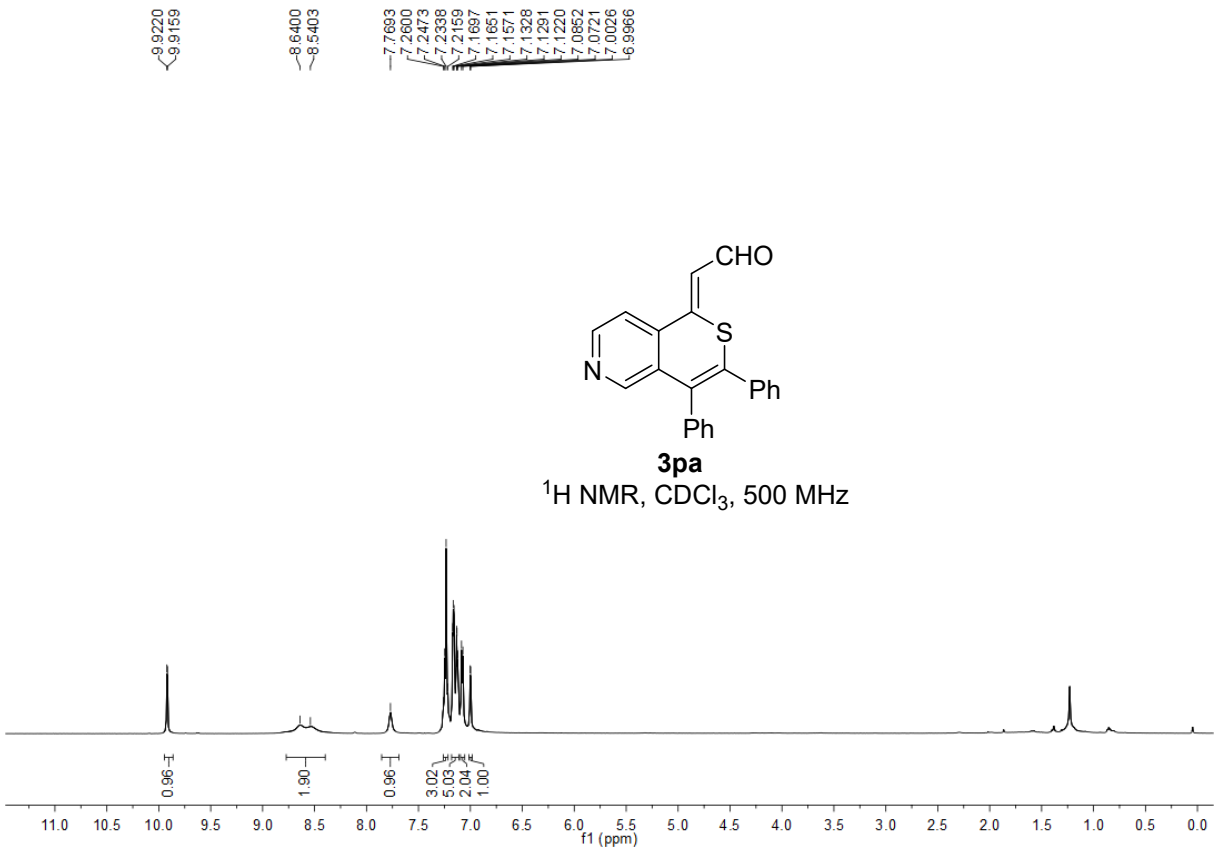
3oa

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



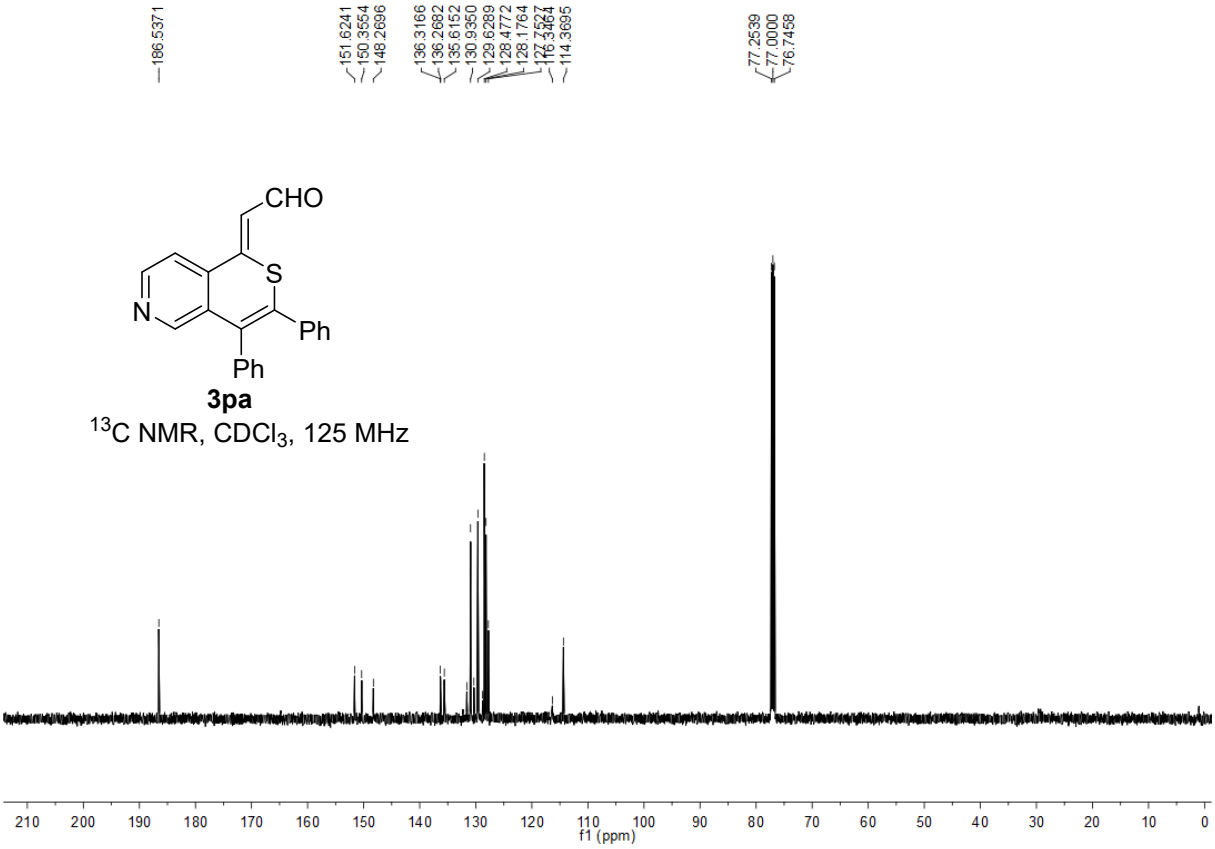
3oa

^{13}C NMR, $CDCl_3$, 125 MHz



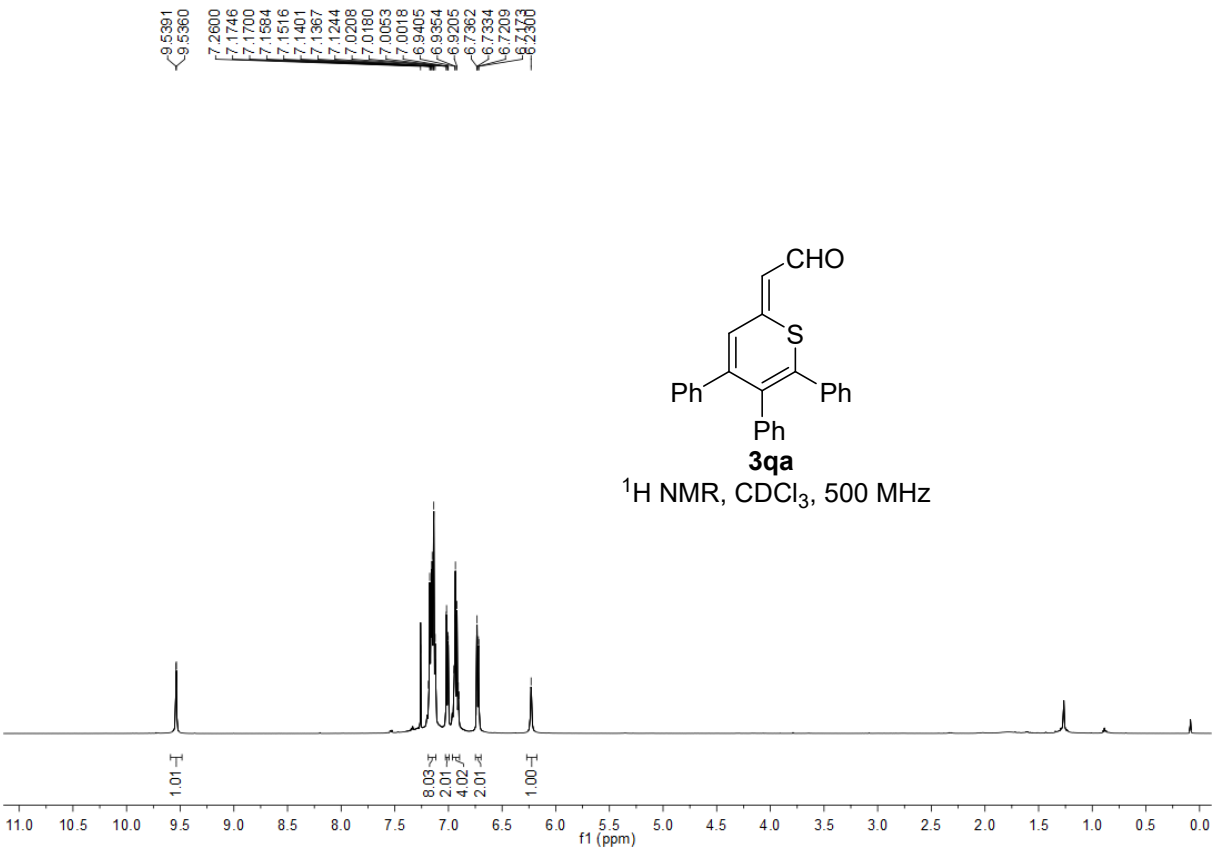
3pa

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



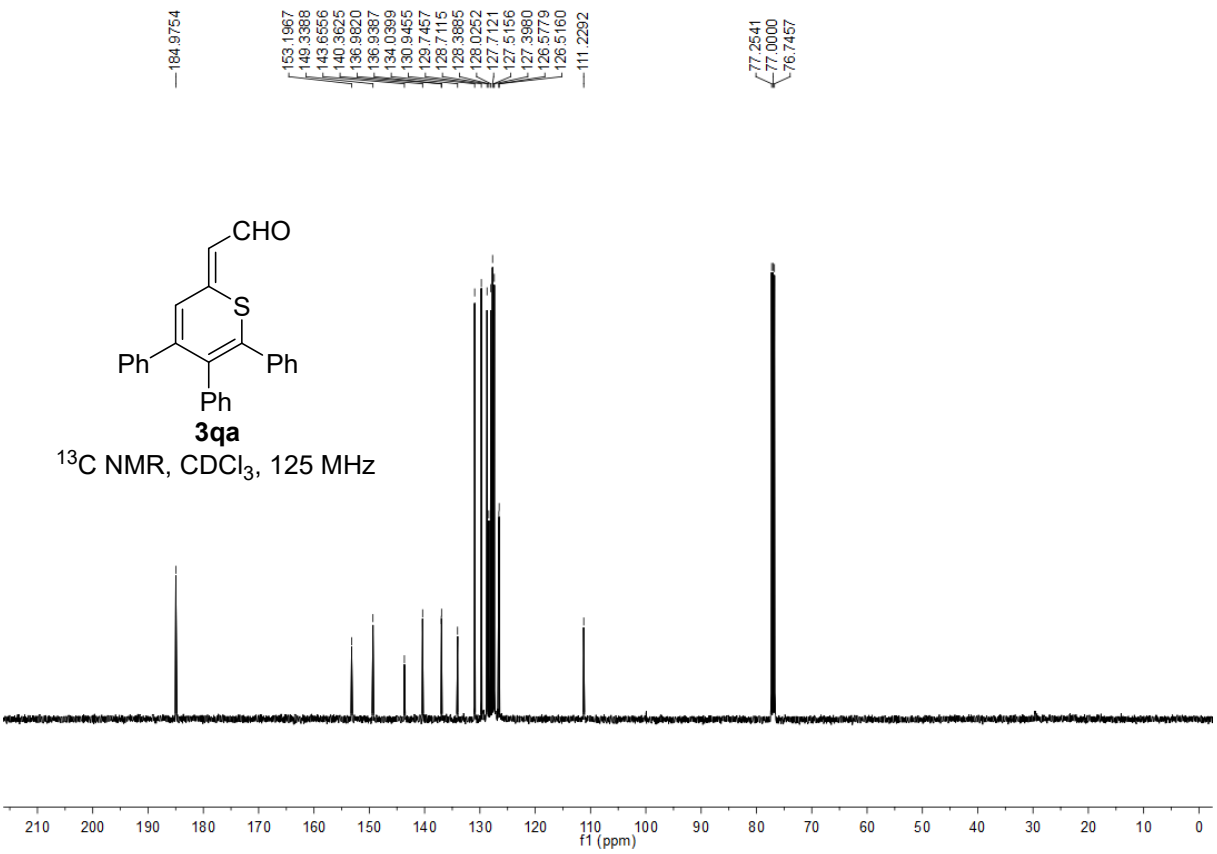
3pa

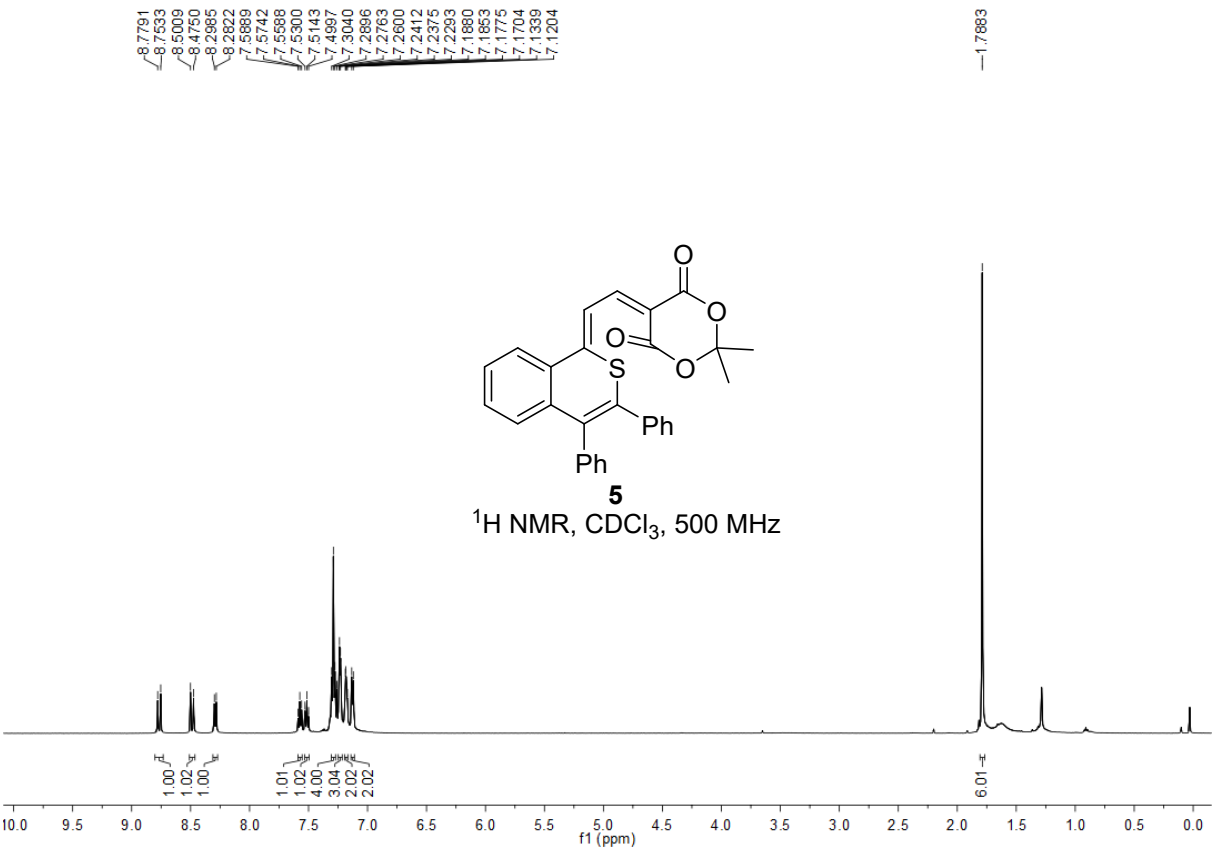
^{13}C NMR, $CDCl_3$, 125 MHz

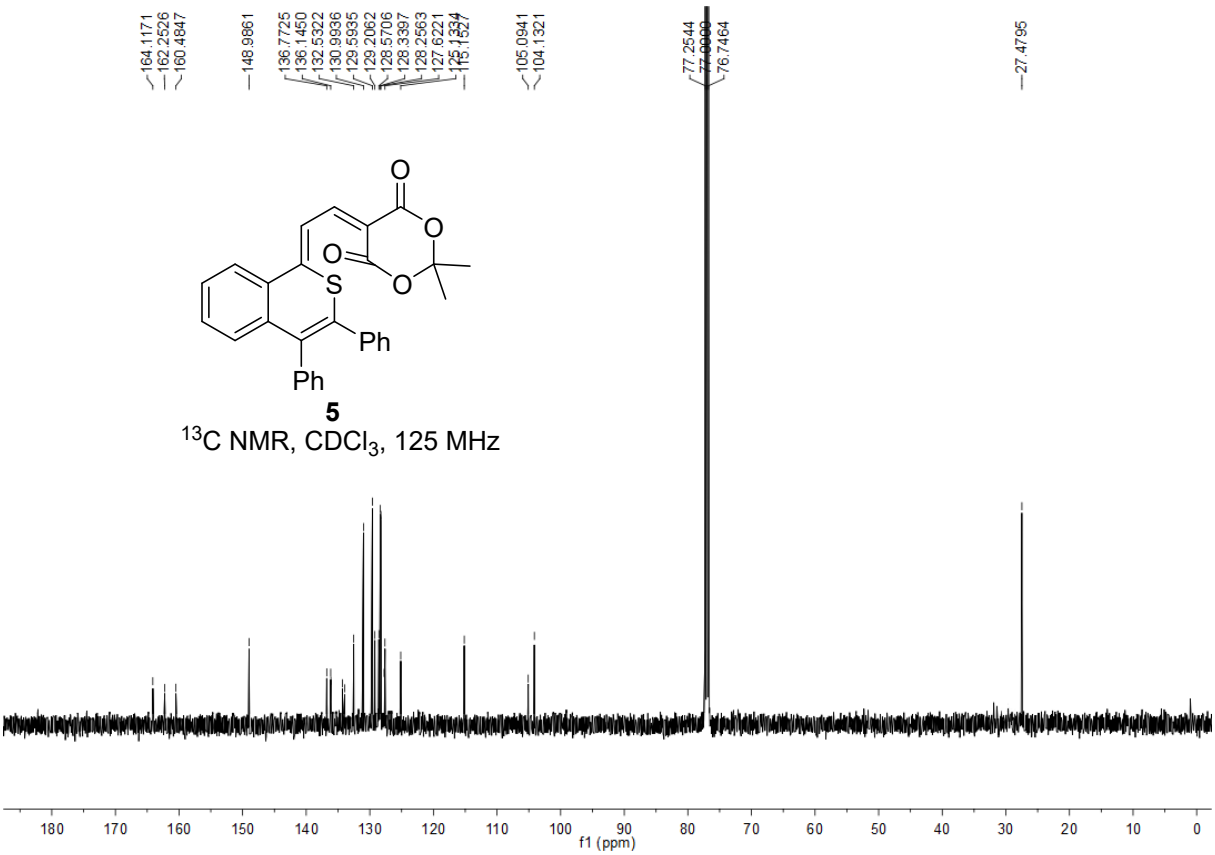


3qa

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

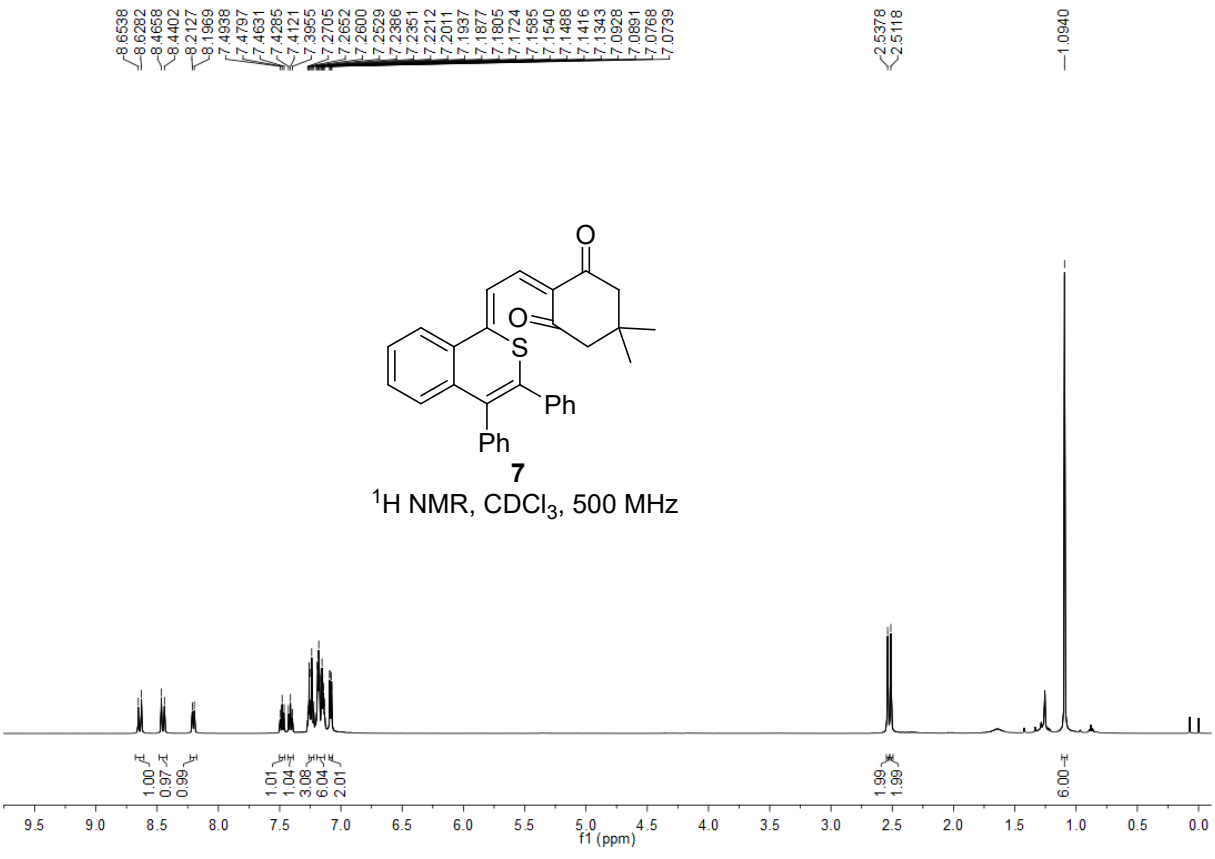

184.9754
153.1967
149.3388
143.6556
140.3625
136.9820
136.9387
134.0399
130.9455
129.7457
128.7115
128.3885
128.0252
127.7121
127.5156
127.3980
126.5779
126.5160
111.2292
77.2541
77.0000
76.7457
CHO
S
Ph
Ph
Ph
3qa
13C NMR, CDCl3, 125 MHz
f1 (ppm)


8.7791
8.7533
8.5009
8.4750
8.2985
8.2822
7.5889
7.5742
7.5688
7.5300
7.5143
7.4997
7.3040
7.2896
7.2763
7.2600
7.2412
7.2375
7.2293
7.1880
7.1853
7.1775
7.1704
7.1339
7.1204
1.7883
O
O
O
O
S
Ph
Ph
5
1H NMR, CDCl3, 500 MHz
1.00
1.02
1.00
1.01
1.02
4.00
3.04
2.02
2.02
6.01
f1 (ppm)



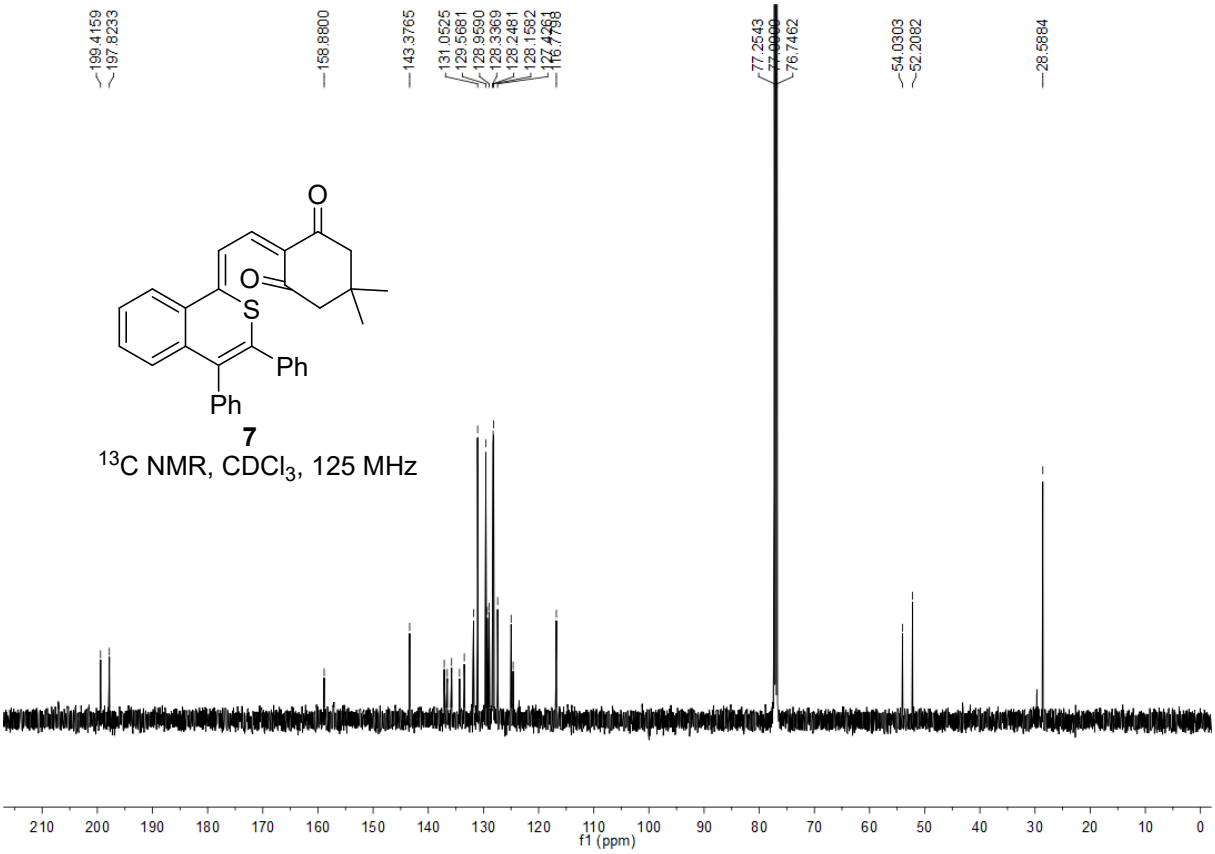
5

^{13}C NMR, $CDCl_3$, 125 MHz



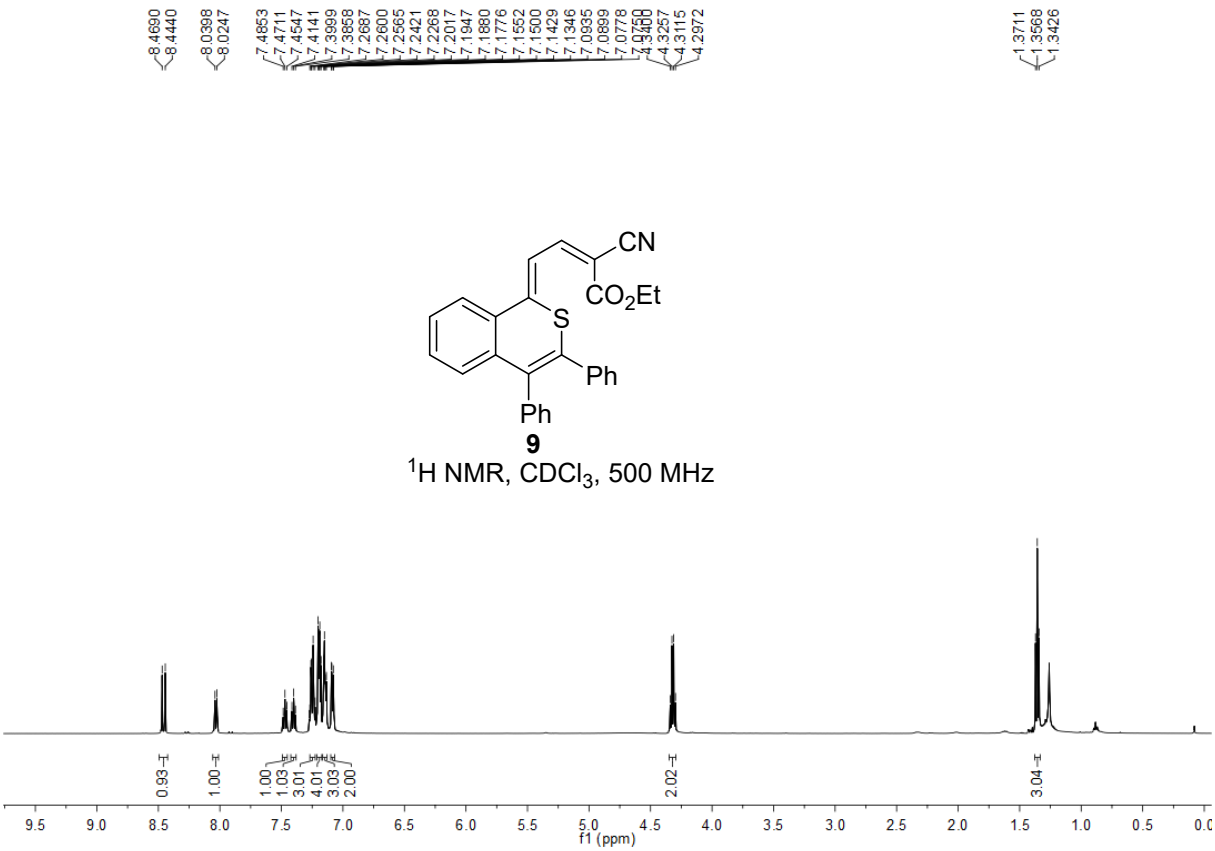
7

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



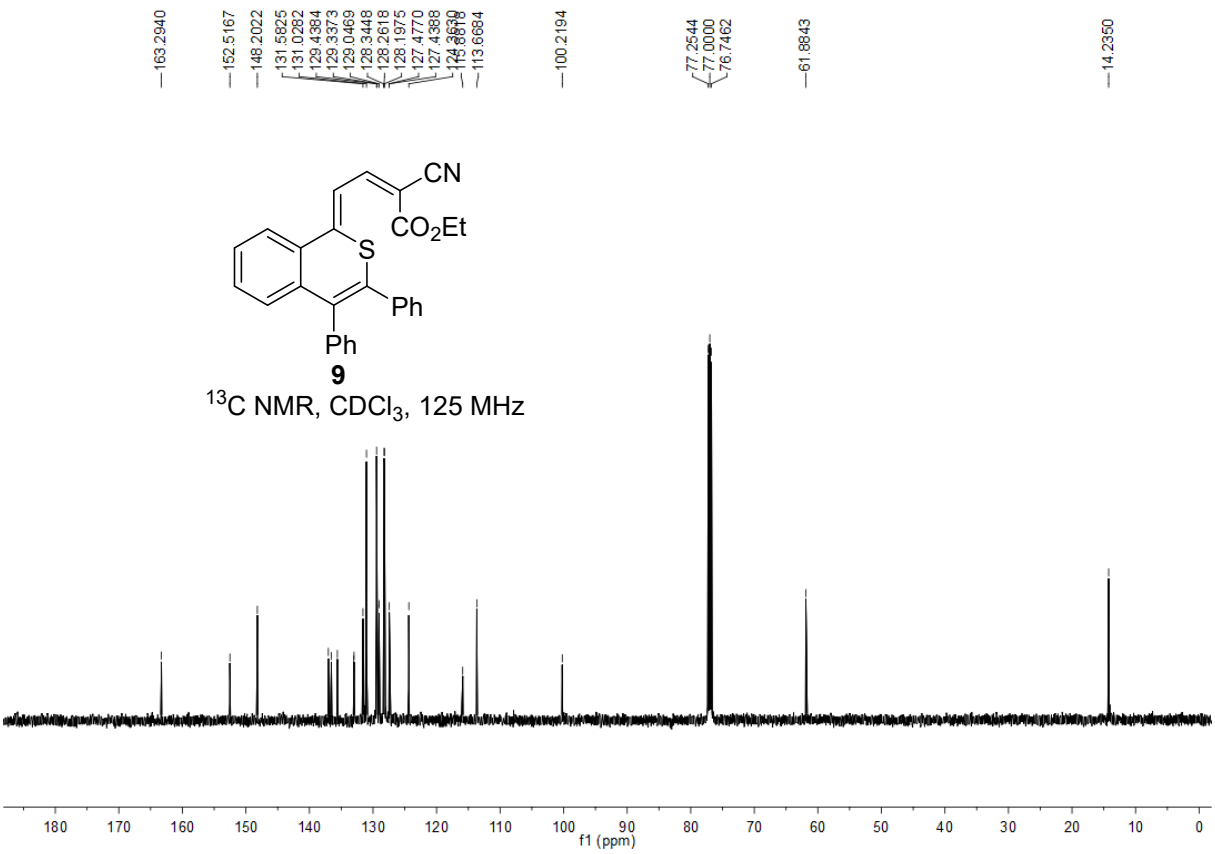
7

^{13}C NMR, $CDCl_3$, 125 MHz



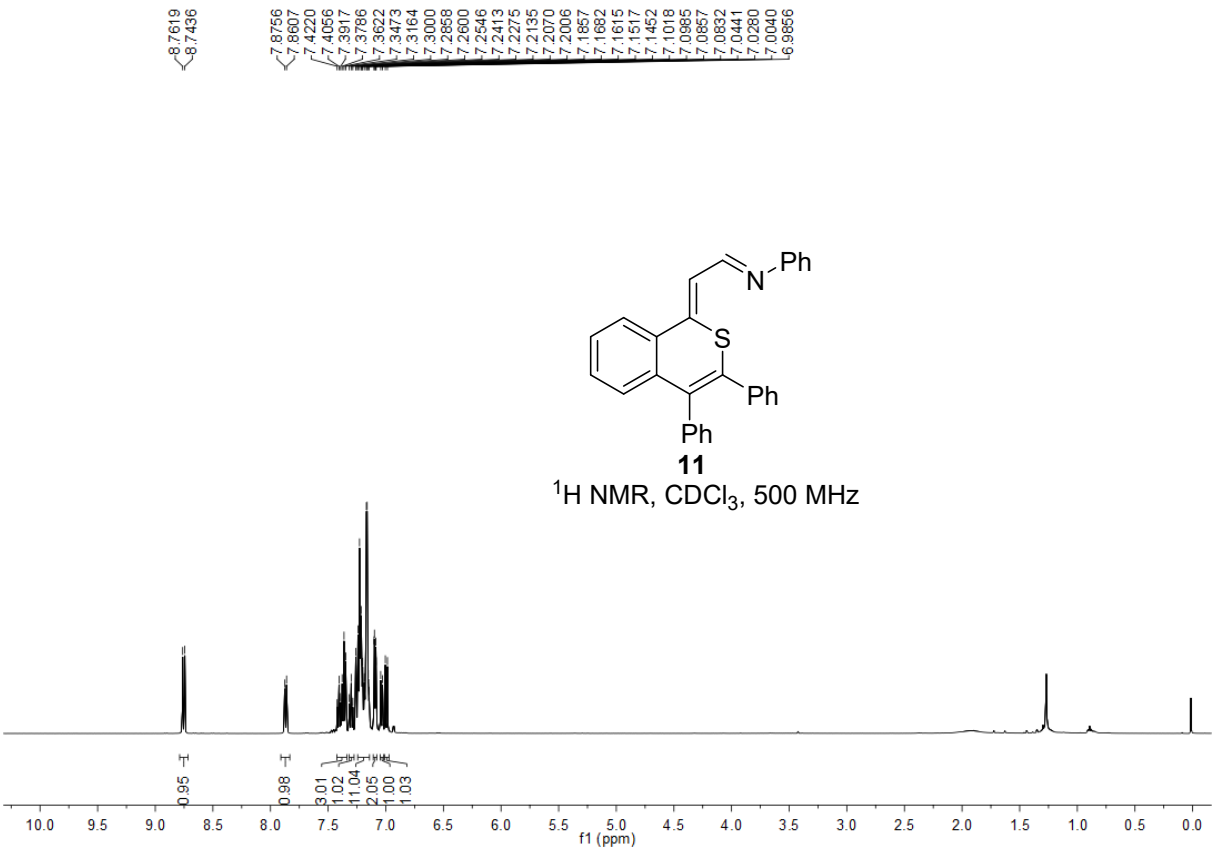
9

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



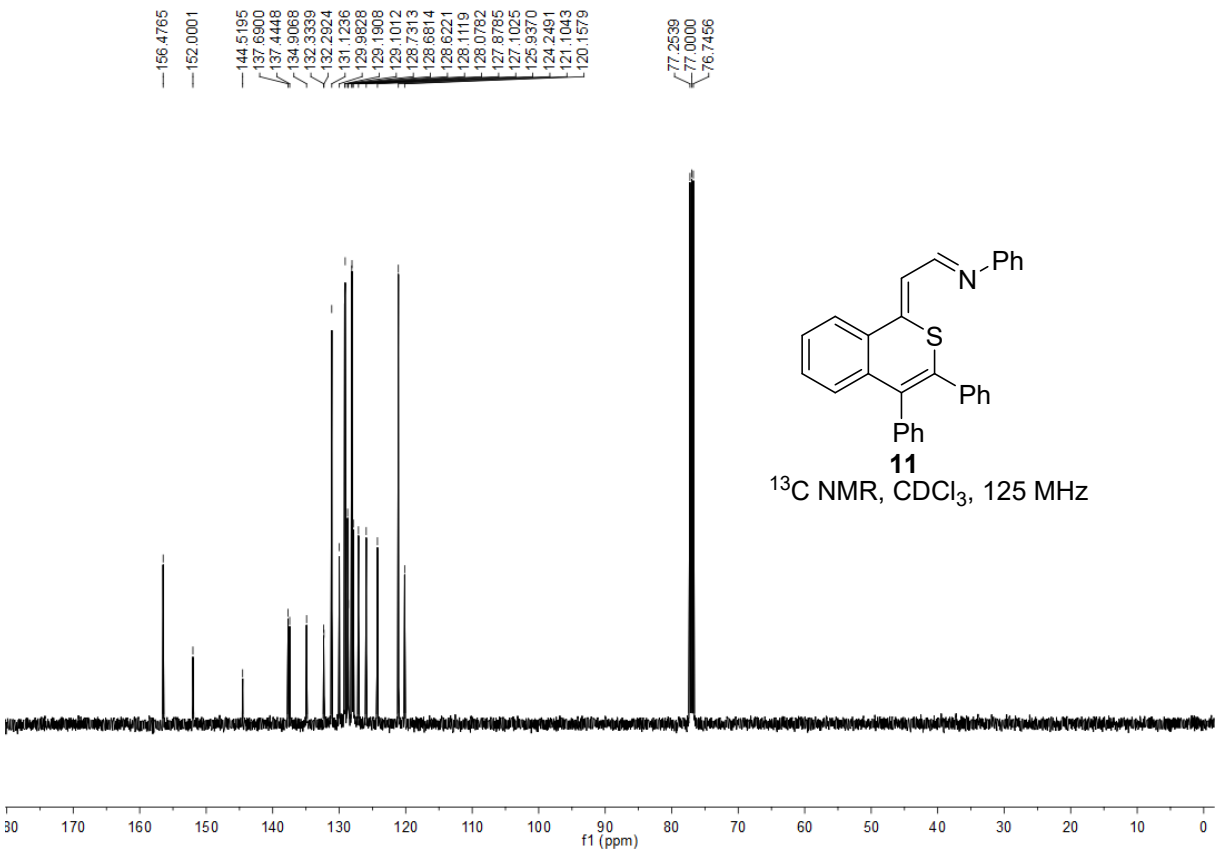
9

^{13}C NMR, $CDCl_3$, 125 MHz



11

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



11

^{13}C NMR, $CDCl_3$, 125 MHz