Electronic Supplementary Information

Palladium-Catalyzed [3+2] Cycloaddition of 4-Vinyl-4-Butyrolactones with Sulfamate-Derived Cyclic Imines: Construction of Sulfamate-Fused Pyrrolidines

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Contents

General Information S2

Preparation of Starting Materials S2

General Procedure for Pd-Catalyzed [3+2] Annulation S2

The Scaled-up Reaction S2

Further Transformation of the Product S3

Investigation on Asymmetric [3+2] Cycloaddition S3

Characterization Data of Products S4

^{1}H NMR and ^{13}C NMR Spectra of Products S13

HPLC Chromatogram of Product **3aa** S40

X-Ray Crystallographic Data S41

General Information.

All reactions were performed under argon atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored by thin layer chromatography (TLC) on silica gel precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using flash silica gel (200−300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using 500 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Accurate mass measurements were performed using an instrument with the ESI-Linear ion trap-MS technique.

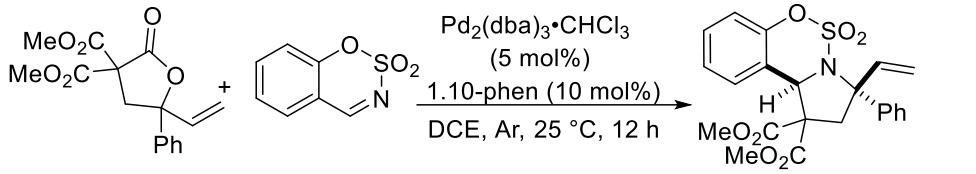
Preparation of Starting Materials

The 4-vinyl-4-butyrolactones **1**[1] and sulfamate-derived cyclic imines **2**[2] were synthesized using known literature procedures.

General Procedure for Pd-Catalyzed [3+2] Annulation

Under argon atmosphere, to a mixture of **1** (0.12 mmol), **2** (0.10 mmol), catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and 1.10-phen (10 mol%) in an oven-dried Schlenk tube was added 1 mL of DCE at 25 °C. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (petroleum ether/EtOAc) to give the corresponding products **3**.

The Scaled-up Reaction



1a (1.2 mmol) **2a** (1.0 mmol) **3aa** (403 mg, 91% yield, >20:1 dr)

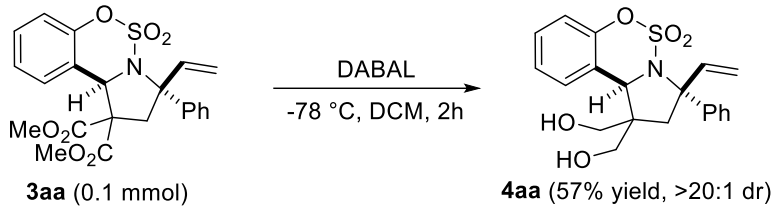
An oven-dried 100 mL of Schlenk tube was charged with **1a** (1.2 mmol, 365 mg), **2a** (1.0 mmol, 183 mg), $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%), 1.10-phen (10 mol%), and 10 mL of DCE under argon atmosphere. The reaction mixture was stirred at 25 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The

1. Sun, H.; Song, A.; Gu, S.; Tang, Y.; Yang, S.; Li, W.; Guo, H. *J. Org. Chem.* 2024, ***89,*** 14141-14150.

2. Liu, M.; Liao, J.; Dong, Y.; Shi, W.; Hu, Y.; Xu, J.; Wang, W.; Xu, Y.; Guo, H. *Adv. Synth. Catal.* 2022, ***364***, 2146–2151.

residue was purified by flash column chromatography (petroleum ether/EtOAc) to afford the product **3aa** (403 mg, 91% yield, >20:1 dr).

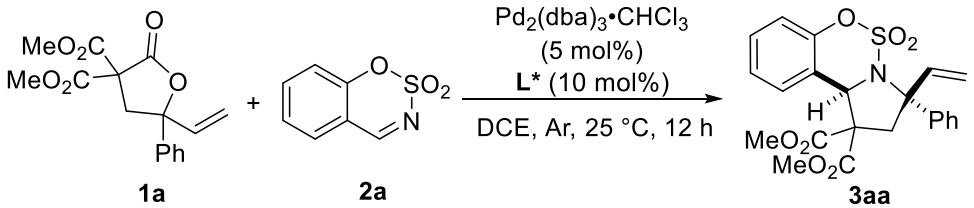
Further Transformation of the Product



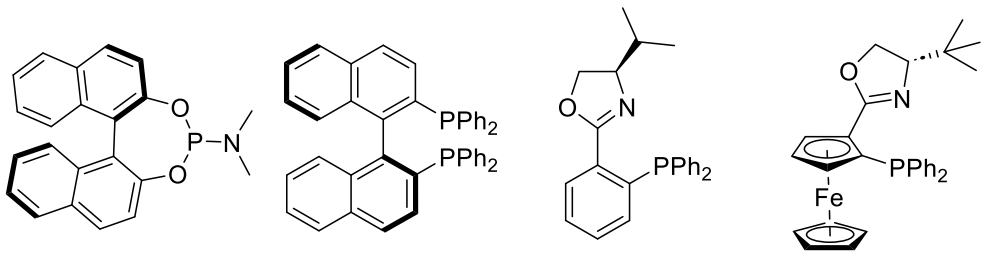
3aa (0.1 mmol) **4aa** (57% yield, >20:1 dr)

Under argon atmosphere, to a solution of **3aa** (0.1 mmol) in DCM was added DABAL (0.8 mmol) at –78 °C. Once the starting material was completely consumed (monitored by TLC), the mixture was concentrated to dryness. The residue was purified by flash column chromatography (petroleum ether/EtOAc) to afford the product **4aa** (57% yield, >20:1 dr).

Investigation on Asymmetric [3+2] Cycloaddition



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

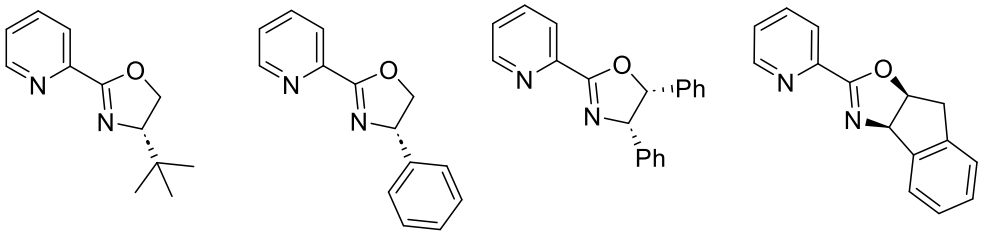


L1, 74% yield[a,b]
16% ee, 6:1 dr

L2, no reaction

L3, no reaction

L4, no reaction



L5, 74% yield
-16% ee, 18:1 dr

L6, 89% yield
21% ee, 19:1 dr

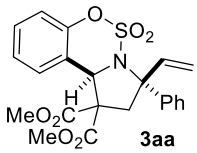
L7, 91% yield
24% ee, >20:1 dr

L8, 86% yield
8% ee, >20:1 dr

[a] Reactions of **1a** (0.12 mmol) and **2a** (0.10 mmol) were performed in the presence of $Pd_2(dba)_3$•$CHCl_3$ (5 mol%) and **L*** (10 mol%) in 1 mL of DCE at 15 °C for 12 h. [b] Isolated yield.

Characterization Data of Products

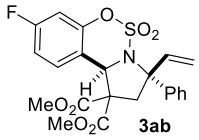
Dimethyl 3-phenyl-3-vinyl-2,3-dihydrobenzo[e]pyrrolo[1, 2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5-dioxide (3aa).



3aa

White solid (41.4 mg, 93% yield, >20:1 dr), mp: 134 – 135 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.19 (m, 4H), 7.07 (td, *J* = 7.7, 1.3 Hz, 1H), 6.97 (td, *J* = 7.8, 7.1, 1.3 Hz, 2H), 6.31 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.01 (s, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.57 (s, 3H), 3.26 (s, 3H), 3.08 (d, *J* = 13.7 Hz, 1H), 3.02 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.7, 151.7, 140.0, 138. 8, 129.9, 128.2, 127.8, 127.4, 126.0, 125.1, 119.6, 119.5, 118.3, 73.8, 67.0, 63.2, 53.13, 53.08, 45.5; HRMS (ESI) calculated for $C_{22}H_{22}NO_7S^+$ $[M + H]^+$ 444.1111, found 444.1121.

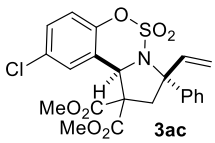
Dimethyl 8-fluoro-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ab).



3ab

White solid (41.2 mg, 89% yield, >20:1 dr), mp: 158 – 159 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.24 – 7.19 (m, 1H), 6.99 – 6.93 (m, 1H), 6.80 (m, 1H), 6.73 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.30 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.96 (s, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 3.59 (s, 3H), 3.28 (s, 3H), 3.09 (d, *J* = 13.8 Hz, 1H), 3.02 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 166.5, 161.5 (d, *J* = 251.2 Hz), 151.4 (d, *J* = 11.6 Hz), 138.8, 137.5, 127.2, 126.9, 126.5 (d, *J* = 9.2 Hz), 126.2, 117.4, 114.5 (d, *J* = 4.0 Hz), 111.5 (d, *J* = 21.7 Hz), 106.1 (d, *J* = 25.4 Hz), 72.9, 65.6, 62.1, 52.2, 52.1, 44.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.62; HRMS (ESI) calculated for $C_{22}H_{21}FNO_7S^+$ $[M + H]^+$ 462.1017, found 462.1027.

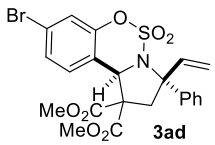
Dimethyl 9-chloro-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 - dioxide (3ac).



3ac

White solid (43.5 mg, 91% yield, >20:1 dr), mp: 156 – 157 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.05 – 6.98 (m, 2H), 6.35 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.06 (s, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 3.73 (s, 3H), 3.32 (s, 3H), 3.12 (q, *J* = 13.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 167.3, 150.3, 139.8, 138.5, 130.4, 129.9, 128.2, 127.9, 127.3, 126.3, 121.2, 120.8, 118.5, 73.9, 66.7, 63.2, 53.3, 53.2, 45.3; HRMS (ESI) calculated for $C_{22}H_{21}ClNO_7S^+$ $[M + H]^+$ 478.0722, found 478.0724.

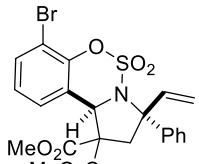
Dimethyl 8-bromo-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ad).



3ad

White solid (49.3 mg, 95% yield, >20:1 dr), mp: 160 – 161 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.36 (dd, *J* = 8.7, 6.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.92 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.36 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.00 (s, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 5.06 (d, *J* = 17.3 Hz, 1H), 3.66 (s, 3H), 3.35 (s, 3H), 3.15 (d, *J* = 13.8 Hz, 1H), 3.09 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5, 167.5, 152.0, 139.9, 138.5, 128.3, 128.2, 128.0, 127.3, 127.2, 122.8, 122.6, 118.7, 118.5, 74.0, 66.8, 63.0, 53.3, 53.2, 45.5; HRMS (ESI) calculated for $C_{22}H_{21}BrNO_7S^+$ $[M + H]^+$ 522.0217, found 522.0223.

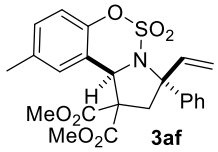
Dimethyl 7-bromo-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ae).



3ae

White solid (47.0 mg, 90% yield, >20:1 dr), mp: 142 – 143 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.38 – 7.33 (m, 2H), 7.29 (dd, *J* = 8.7, 6.9 Hz, 2H), 7.24 – 7.19 (m, 1H), 6.97 – 6.86 (m, 2H), 6.31 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.98 (s, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 3.55 (s, 3H), 3.29 (s, 3H), 3.09 (d, *J* = 13.8 Hz, 1H), 3.04 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.5, 148.5, 139.7, 138.4, 133.7, 128.3, 128.0, 127.2, 125.5, 125.2, 121.7, 118.5, 113.2, 74.3, 67.1, 63.4, 53.2, 45.6; HRMS (ESI) calculated for $C_{22}H_{21}BrNO_7S^+$ $[M + H]^+$ 522.0217, found 522.0221.

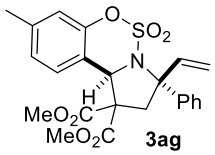
Dimethyl 9-methyl-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3af).



3af

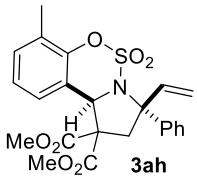
White solid (42.8 mg, 94% yield, >20:1 dr), mp: 154 – 155 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.35 (m, 2H), 7.29 – 7.24 (m, 1H), 7.12 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.83 – 6.75 (m, 1H), 6.36 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.08 (s, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.68 (s, 3H), 3.28 (s, 3H), 3.14 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.7 Hz, 1H)., 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.6, 149.7, 140.1, 138.9, 134.7, 130.5, 128.1, 127.7, 127.4, 126.4, 119.2, 119.0, 118.3, 73.6, 67.0, 63.2, 53.01, 52.99, 45.3, 21.0; HRMS (ESI) calculated for $C_{23}H_{24}NO_7S^+$ $[M + H]^+$ 458.1268, found 458.1272.

Dimethyl 8-methyl-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ag).



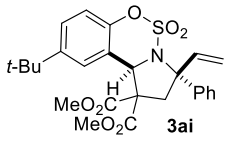
White solid (40.9 mg, 89% yield, >20:1 dr), mp: 164 – 165 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.28 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.23 – 7.18 (m, 1H), 6.87 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.84 – 6.72 (m, 2H), 6.29 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.99 (s, 1H), 5.27 (d, *J* = 10.7 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.60 (s, 3H), 3.21 (s, 3H), 3.07 (d, *J* = 13.7 Hz, 1H), 3.00 (d, *J* = 13.7 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 166.6, 150.5, 139.5, 139.1, 137.8, 127.0, 126.7, 126.4, 125.0, 124.6, 118.7, 117.2, 115.2, 72.6, 65.9, 62.0, 52.1, 52.0, 44.2, 19.9; HRMS (ESI) calculated for $C_{23}H_{24}NO_7S^+$ $[M + H]^+$ 458.1268, found 458.1272.

Dimethyl 7-methyl-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ah).



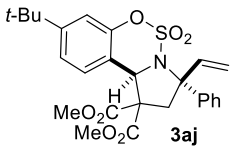
White solid (41.2 mg, 90% yield, >20:1 dr), mp: 145 – 146 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.36 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.19 – 7.15 (m, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.40 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.06 (s, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.62 (s, 3H), 3.34 (s, 3H), 3.16 (d, *J* = 13.7 Hz, 1H), 3.10 (d, *J* = 13.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 167.8, 150.1, 140.0, 138.9, 131.3, 128.7, 128.2, 127.8, 127.4, 124.4, 123.5, 119.3, 118.1, 73.9, 67.1, 63.4, 53.1, 53.0, 45.5, 15.7; HRMS (ESI) calculated for $C_{23}H_{24}NO_7S^+$ $[M + H]^+$ 458.1268, found 458.1264.

Dimethyl 9-(tert-butyl)-3-phenyl-3-vinyl-2,3-dihydrobenzo [e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10- bH)-dicarboxylate 5,5-dioxide (3ai).



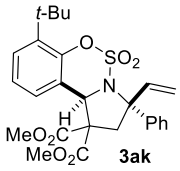
White solid (45.7 mg, 92% yield, >20:1 dr), mp: 163– 164 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.31 (m, 3H), 7.29 – 7.26 (m, 1H), 7.10 – 7.07 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.38 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.07 (s, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.67 (s, 3H), 3.32 (s, 3H), 3.15 (d, *J* = 13.7 Hz, 1H), 3.10 (d, *J* = 13.7 Hz, 1H), 1.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 167.7, 149.3, 148.1, 140.1, 138.9, 128.1, 127.7, 127.4, 127.0, 123.0, 118.8, 118.5, 118.3, 73.6, 67.1, 63.1, 53.3, 53.0, 45.5, 34.6, 31.3; HRMS (ESI) calculated for $C_{26}H_{30}NO_7S^+$ $[M + H]^+$ 500.1737, found 500.1732.

Dimethyl 8-(tert-butyl)-3-phenyl-3-vinyl-2,3-dihydrobenzo [e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10-bH)-dicarboxylate 5,5-dioxide (3aj).



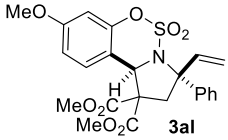
White solid (46.2 mg, 93% yield, >20:1 dr), mp: 134 – 135 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.08 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.29 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.01 (s, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.61 (s, 3H), 3.20 (s, 3H), 3.07 (d, *J* = 13.7 Hz, 1H), 3.01 (d, *J* = 13.7 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.6, 153.9, 151.6, 140.1, 138.9, 128.0, 127.7, 127.5, 125.4, 122.4, 118.4, 116.4, 116.1, 73.6, 66.8, 63.0, 53.1, 53.0, 45.3, 34.8, 31.0; HRMS (ESI) calculated for $C_{26}H_{30}NO_7S^+$ $[M + H]^+$ 500.1737, found 500.1735.

Dimethyl 7-(tert-butyl)-3-phenyl-3-vinyl-2,3-dihydrobenzo [e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10-bH)-dicarboxylate 5,5-dioxide (3ak).



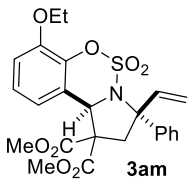
White solid (46.5 mg, 93% yield, >20:1 dr), mp: 154 – 155 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.29 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.25 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.23 – 7.18 (m, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.85 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.35 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.95 (s, 1H), 5.26 (d, *J* = 10.6 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.50 (s, 3H), 3.27 (s, 3H), 3.13 (d, *J* = 13.6 Hz, 1H), 3.02 (d, *J* = 13.7 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 167.9, 150.8, 140.4, 140.2, 138.8, 128.2, 127.8, 127.3, 127.3, 124.4, 124.3, 120.1, 117.8, 74.0, 67.2, 63.8, 53.0, 45.3, 35.0, 30.0; HRMS (ESI) calculated for $C_{26}H_{30}NO_7S^+$ $[M + H]^+$ 500.1737, found 500.1741.

Dimethyl 8-methoxy-3-phenyl-3-vinyl-2,3-dihydrobenzo [e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10-bH)-dicarboxylate 5,5-dioxide (3al).



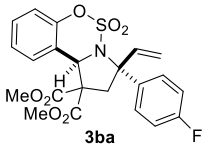
White solid (41.3 mg, 87% yield, >20:1 dr), mp: 194 – 195 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 3.7 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.62 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.30 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.97 (s, 1H), 5.28 (d, *J* = 10.7 Hz, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 3.72 (s, 3H), 3.61 (s, 3H), 3.22 (s, 3H), 3.08 (d, *J* = 13.7 Hz, 1H), 2.99 (d, *J* = 13.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.7, 160.5, 152.6, 140.1, 138.9, 128.1, 127.7, 127.4, 126.7, 118.3, 111.9, 111.0, 104.2, 73.6, 66.7, 63.0, 55.6, 53.2, 53.0, 45.2; HRMS (ESI) calculated for $C_{23}H_{24}NO_8S^+$ $[M + H]^+$ 474.1217, found 474.1221.

Dimethyl 7-ethoxy-3-phenyl-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3am).



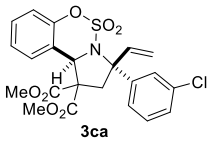
White solid (44.5 mg, 91% yield, >20:1 dr), mp: 146 – 147 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 2H), 7.28 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 1H), 6.96 (t, *J* = 8.1 Hz, 1H), 6.82 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.50 (dt, *J* = 8.1, 1.2 Hz, 1H), 6.33 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.00 (s, 1H), 5.28 (d, *J* = 10.7 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.00 (m, 2H), 3.56 (s, 3H), 3.24 (s, 3H), 3.06 (q, *J* = 13.7 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 167.7, 148.8, 141.7, 139.9, 138.9, 128.1, 127.8, 127.4, 124.7, 120.6, 118.2, 117.0, 113.6, 73.9, 67.1, 65.0, 63.3, 53.1, 53.0, 45.6, 14.7; HRMS (ESI) calculated for $C_{24}H_{26}NO_8S^+$ $[M + H]^+$ 488.1374, found 488.1377.

Dimethyl 3-(4-fluorophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ba).



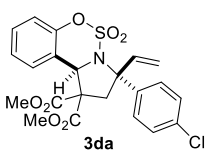
Pale yellow solid (42.9 mg, 93% yield, >20:1 dr), mp: 136 – 137 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.34 (tt, *J* = 8.2, 1.3 Hz, 1H), 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 – 7.00 (m, 4H), 6.36 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.08 (s, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.66 (s, 3H), 3.40 (s, 3H), 3.15 (d, *J* = 13.8 Hz, 1H), 3.04 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.5, 162.2 (d, *J* = 247.5 Hz), 151.6, 138.7, 135.9 (d, *J* = 3.1 Hz), 130.0, 129.3 (d, *J* = 8.3 Hz), 126. 0, 125.2, 119.5, 119.4, 118.5, 115.0 (d, *J* = 21.5 Hz), 73.2, 67.0, 63.1, 53.2, 45.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.61; HRMS (ESI) calculated for $C_{22}H_{21}FNO_7S^+$ $[M + H]^+$ 462.1017, found 462.1018.

Dimethyl 3-(3-chlorophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ca).



Pale yellow solid (44.5 mg, 93% yield, >20:1 dr), mp: 130 – 131 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 3.5, 1.9 Hz, 2H), 7.37 – 7.26 (m, 3H), 7.15 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.37 (dd, *J* = 17.2, 10.7 Hz, 1H), 6.08 (s, 1H), 5.39 (d, *J* = 10.7 Hz, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 3.67 (s, 3H), 3.43 (s, 3H), 3.17 (d, *J* = 13.8 Hz, 1H), 3.03 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.4, 151.6, 142.6, 138.1, 134.1, 130.0, 129.6, 128.0, 127.4, 126.0, 125.6, 125.2, 119.5, 119.3, 118.8, 73.2, 67.1, 63.1, 53.2, 45.2; HRMS (ESI) calculated for $C_{22}H_{21}ClNO_7S^+$ $[M + H]^+$ 478.0722, found 478.0724.

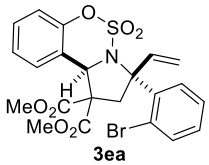
Dimethyl 3-(4-chlorophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3da).



3da

White solid (44.0 mg, 92% yield, >20:1 dr), mp: 138 – 139 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 7.08 (td, *J* = 7.7, 1.3 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.28 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.01 (s, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.59 (s, 3H), 3.32 (s, 3H), 3.08 (d, *J* = 13.8 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.4, 151.6, 138.9, 138.4, 133.8, 130.0, 128.9, 128.3, 126.0, 125.2, 119.5, 119.3, 118.6, 73.2, 67.0, 63.0, 53.2, 45.4; HRMS (ESI) calculated for $C_{22}H_{21}ClNO_7S^+$ $[M + H]^+$ 478.0722, found 478.0728.

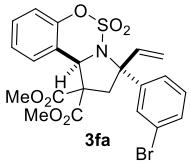
Dimethyl 3-(2-bromophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH) -dicarboxylate 5,5 -dioxide (3ea).



3ea

White solid (46.6 mg, 89% yield, >20:1 dr), mp: 140 – 141 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 2H), 7.54 – 7.47 (m, 2H), 7.31 – 7.25 (m, 1H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.93 (dt, *J* = 8.0, 1.2 Hz, 1H), 6.28 (dd, *J* = 17.3, 10.6 Hz, 1H), 6.05 (s, 1H), 5.35 (d, *J* = 10.7 Hz, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 3.64 (s, 3H), 3.28 (s, 3H), 3.14 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 13.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.4, 151.6, 142.9, 138.1, 131.0, 130.3, 130.0, 129.9, 126.1, 126.0, 125.2, 122.2, 119.5, 119.3, 118.8, 73.1, 67.1, 63.1, 53.3, 53.2, 45.2; HRMS (ESI) calculated for $C_{22}H_{21}BrNO_7S^+$ $[M + H]^+$ 522.0217, found 522.0220.

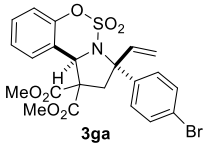
Dimethyl 3-(3-bromophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH) -dicarboxylate 5,5 -dioxide (3fa).



3fa

White solid (45.4 mg, 87% yield, >20:1 dr), mp: 135 – 136 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 1.9 Hz, 1H), 7.36 (tdd, *J* = 6.7, 2.0, 1.0 Hz, 2H), 7.26 (ddt, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.08 (td, *J* = 7.6, 1.3 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.29 (dd, *J* = 17.2, 10.7 Hz, 1H), 6.00 (s, 1H), 5.32 (d, *J* = 10.7 Hz, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 3.59 (s, 3H), 3.36 (s, 3H), 3.09 (d, *J* = 13.9 Hz, 1H), 2.96 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.4, 151.6, 142.9, 138.1, 131.0, 130.3, 130.0, 129.9, 126.1, 126.0, 125.2, 122.2, 119.5, 119.3, 118.8, 73.1, 67.1, 63.1, 53.3, 53.2, 45.2; HRMS (ESI) calculated for $C_{22}H_{21}BrNO_7S^+$ $[M + H]^+$ 522.0217, found 522.0216.

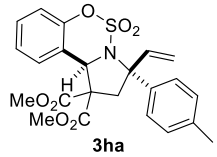
Dimethyl 3-(4-bromophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH) -dicarboxylate 5,5 -dioxide (3ga).



3ga

White solid (47.4 mg, 91% yield, >20:1 dr), mp: 130 – 131 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.36 – 7.30 (m, 3H), 7.15 (td, *J* = 7.7, 1.3 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.35 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.08 (s, 1H), 5.37 (d, *J* = 10.6 Hz, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 3.67 (s, 3H), 3.39 (s, 3H), 3.15 (d, *J* = 13.8 Hz, 1H), 3.02 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 167.4, 151.6, 139.4, 138.3, 131.3, 130.0, 129.2, 126.0, 125.2, 122.0, 119.5, 119.3, 118.7, 73.2, 67.0, 63.0, 53.0, 45.4; HRMS (ESI) calculated for $C_{22}H_{21}BrNO_7S^+$ $[M + H]^+$ 522.0217, found 522.0220.

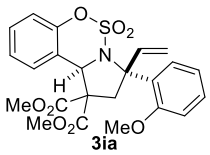
Dimethyl 3-(p-tolyl)-3-vinyl-2,3-dihydrobenzo[e]pyrrolo[1, 2-c][1,2,3]oxathiazine-1,1(10-bH)-dicarbo-xylate 5,5-dioxide (3ha).



3ha

White solid (40.7 mg, 89% yield, >20:1 dr), mp: 124 – 125 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.19 – 7.11 (m, 3H), 7.08 – 7.02 (m, 2H), 6.38 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.03 (s, 1H), 5.34 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.62 (s, 3H), 3.40 (s, 3H), 3.14 (d, *J* = 13.7 Hz, 1H), 3.09 (d, *J* = 13.7 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 167.8, 151.5, 139.0, 137.6, 136.9, 129.8, 128.9, 127.3, 126.1, 125.1, 119.7, 119.4, 118.0, 73.8, 66.9, 63.2, 53.13, 53.06, 45.6, 21.0; HRMS (ESI) calculated for $C_{23}H_{24}NO_7S^+$ $[M + H]^+$ 458.1268, found 458.1272.

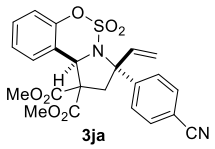
Dimethyl 3-(2-methoxyphenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10b H)-dicarboxylate 5,5 -dioxide (3ia).



3ia

White solid (40.7 mg, 86% yield, >20:1 dr), mp: 135 – 136 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.31 (td, *J* = 7.8, 1.6 Hz, 2H), 7.14 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.04 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.23 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.14 (s, 1H), 5.36 (d, *J* = 10.6 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 3.82 (s, 3H), 3.57 (d, *J* = 13.8 Hz, 4H), 3.50 (s, 3H), 2.98 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 168.2, 156.6, 151.3, 137.5, 129.8, 129.7, 129.5, 128.3, 126.0, 124.9, 120.6, 120.5, 119.2, 117.1, 111.6, 72.6, 67.2, 63.2, 55.2, 53.1, 52.8, 43.9; HRMS (ESI) calculated for $C_{23}H_{24}NO_8S^+$ $[M + H]^+$ 474.1217, found 474.1218.

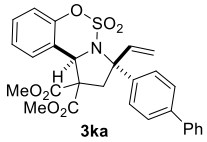
Dimethyl 3-(4-cyanophenyl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5 -dioxide (3ja).



3ja

White solid (43.1 mg, 92% yield, >20:1 dr), mp: 162 – 163 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.0 Hz, 1H), 7.36 (m, 2H), 7.26 (td, *J* = 8.0, 1.6 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.08 (td, *J* = 7.7, 1.3 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.29 (dd, *J* = 17.2, 10.7 Hz, 1H), 6.00 (s, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 3.59 (s, 3H), 3.36 (s, 3H), 3.09 (d, *J* = 13.9 Hz, 1H), 2.95 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 167.1, 151.6, 146.2, 137.6, 131.9, 130.2, 128.2, 125.9, 125.4, 119.6, 119.3, 119.0, 118.4, 111.8, 73.0, 67.2, 62.9, 53.3, 53.2, 45.1; HRMS (ESI) calculated for $C_{23}H_{21}N_2O_7S^+$ $[M + H]^+$ 469.1064, found 469.1068.

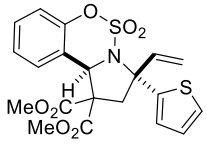
Dimethyl 3-([1,1'-biphenyl]-4-yl)-3-vinyl-2,3-dihydrobenzo [e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10 bH)-dicarboxylate 5,5-dioxide (3ka).



3ka

White solid (47.9 mg, 92% yield, >20:1 dr), mp: 146 – 147 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (td, *J* = 6.3, 3.0 Hz, 4H), 7.54 – 7.49 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.14 (td, *J* = 7.7, 1.3 Hz, 1H), 7.05 (tt, *J* = 6.7, 1.3 Hz, 2H), 6.42 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.12 (s, 1H), 5.39 (d, *J* = 10.6 Hz, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 3.65 (s, 3H), 3.35 (s, 3H), 3.15 (q, *J* = 13.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.6, 151.7, 140.6, 140.3, 139.1, 138.7, 129.9, 128.9, 127.9, 127.6, 127.1, 126.8, 126.1, 125.2, 119.6, 119.5, 118.4, 73.7, 67.1, 63.2, 53.2, 53.1, 45.5; HRMS (ESI) calculated for $C_{28}H_{26}NO_7S^+$ $[M + H]^+$ 520.1424, found 520.1419.

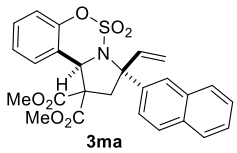
Dimethyl 3-(thiophen-2-yl)-3-vinyl-2,3-dihydrobenzo[e]py- rrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxylate 5,5-dioxide (3la).



3la, 1:1 dr

White solid (37.9 mg, 84% yield, 1:1 dr), mp: 121 – 122 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (td, *J* = 6.1, 5.1, 1.3 Hz, 2H), 7.19 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.07 – 6.97 (m, 4H), 6.48 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.92 (s, 1H), 5.30 (d, *J* = 10.7 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 3.82 (s, 3H), 3.54 (s, 3H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.33 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 168.1, 165.7, 165.7, 151.0, 144.0, 143.0, 139.2, 138.2, 129.8, 127.6, 127.1, 126.97, 126.94, 126.6, 125.94, 125.92, 125.1, 119.8, 119.1, 117.9, 116.4, 84.8, 70.9, 66.5, 63.3, 63.0, 54.01, 53.98, 53.5, 53.0, 48.0, 43.8; HRMS (ESI) calculated for $C_{20}H_{20}NO_7S_2^+$ $[M + H]^+$ 450.0676, found 450.0672.

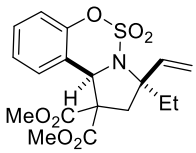
Dimethyl 3-(naphthalen-2-yl)-3-vinyl-2,3-dihydrobenzo[e] pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH) -dicarboxylate 5,5 -dioxide (3ma).



3ma

White solid (44.9 mg, 91% yield, >20:1 dr), mp: 167 – 168 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.3 Hz, 1H), 7.91 – 7.78 (m, 3H), 7.52 – 7.42 (m, 3H), 7.33 (td, *J* = 8.1, 1.6 Hz, 1H), 7.14 (td, *J* = 7.6, 1.3 Hz, 1H), 7.06 (m, 2H), 6.45 (dd, *J* = 17.3, 10.6 Hz, 1H), 6.14 (s, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.09 (d, *J* = 17.3 Hz, 1H), 3.64 (s, 3H), 3.19 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 167.7, 151.7, 138.6, 137.3, 132.8, 132.6, 129.9, 128.5, 128.0, 127.4, 126.61, 126.56, 126.5, 126.1, 125.2, 125.1, 119.6, 119.5, 118.7, 73.9, 67.2, 63.2, 53.2, 53.1, 45.1; HRMS (ESI) calculated for $C_{26}H_{24}NO_7S^+$ $[M + H]^+$ 494.1268, found 494.1265.

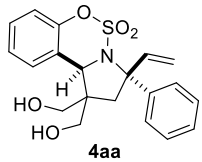
Dimethyl 3-ethyl-3-vinyl-2,3-dihydrobenzo[e]pyrrolo[1,2-c][1,2,3]oxathiazine-1,1(10bH)-dicarboxy-late 5,5-dioxide (3na).



3na

White solid (34.0 mg, 86% yield, >20:1 dr), mp: 103 – 104 °C. It was purified by flash column chromatography (petroleum ether/EtOAc =10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.29 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.69 (s, 1H), 5.24 – 5.13 (m, 2H), 3.91 (s, 3H), 3.44 (s, 3H), 2.86 (d, *J* = 13.8 Hz, 1H), 2.65 (d, *J* = 13.8 Hz, 1H), 2.12 – 1.98 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 168.2, 150.6, 139.3, 129.4, 126.6, 124.9, 120.4, 118.7, 114.7, 71.6, 66.9, 62.4, 53.7, 52.6, 42.9, 31.4, 8.7; HRMS (ESI) calculated for $C_{18}H_{22}NO_7S^+$ $[M + H]^+$ 396.1111, found 396.1115.

1,1-bis(hydroxymethyl)-3-phenyl-3-vinyl-1,2,3,10b-tetrah-ydrobenzo[e]pyrrolo[1,2-c][1,2,3]oxathia-zine 5,5-dioxide (4aa).

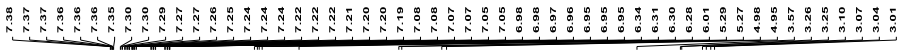


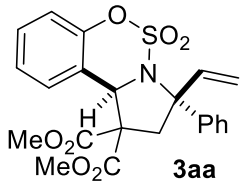
4aa

Pale yellow oil (22.2 mg, 57% yield, >20:1 dr). It was purified by flash column chromatography (petroleum ether/EtOAc =2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.33 – 7.19 (m, 4H), 7.13 – 7.07 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.56 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.41 – 5.30 (m, 3H), 3.87 (d, *J* = 10.7 Hz, 1H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.54 – 3.42 (m, 2H), 2.86 (d, *J* = 13.9 Hz, 1H), 2.40 (s, 1H), 2.15 – 1.94 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 143.0, 137.5, 128.2, 127.5, 126.7, 126.5, 125.0, 124.1, 119.0, 118.3, 115.8, 73.3, 66.9, 66.6, 62.3, 50.5, 42.7; HRMS (ESI) calculated for $C_{20}H_{22}NO_5S^+$ $[M + H]^+$ 388.1213, found 388.1214.

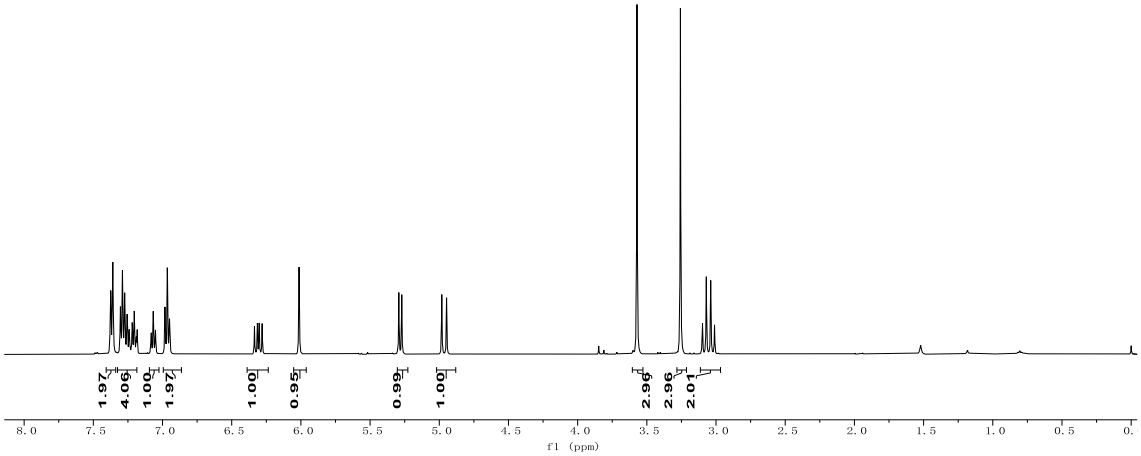
^{1}H NMR and ^{13}C NMR Spectra of Products

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

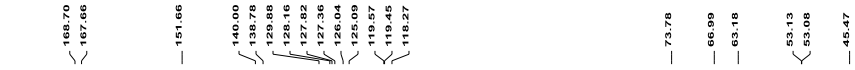


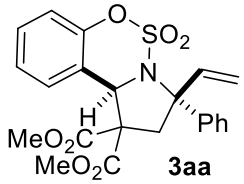


3aa

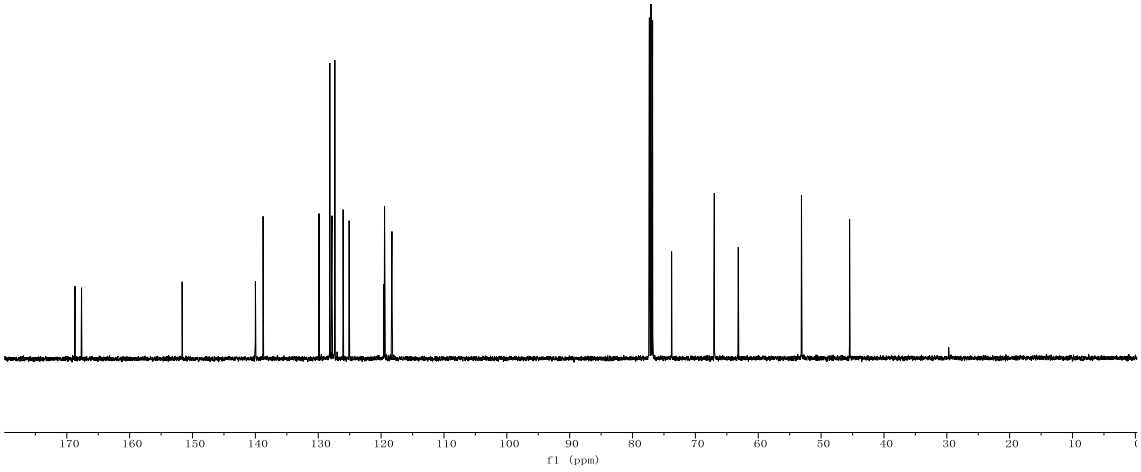


^{13}C NMR (126 MHz, $CDCl_3$)

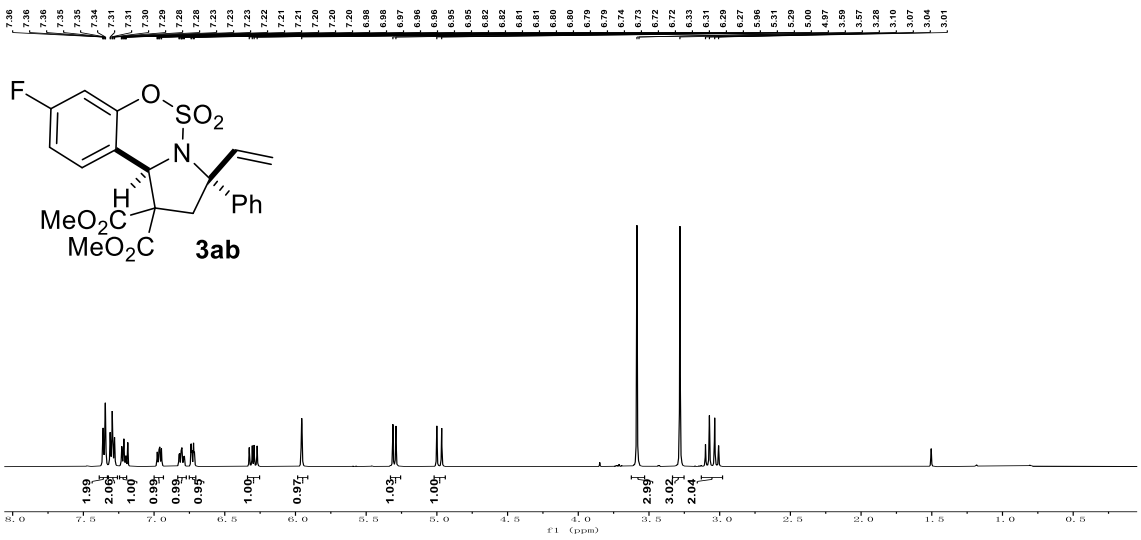




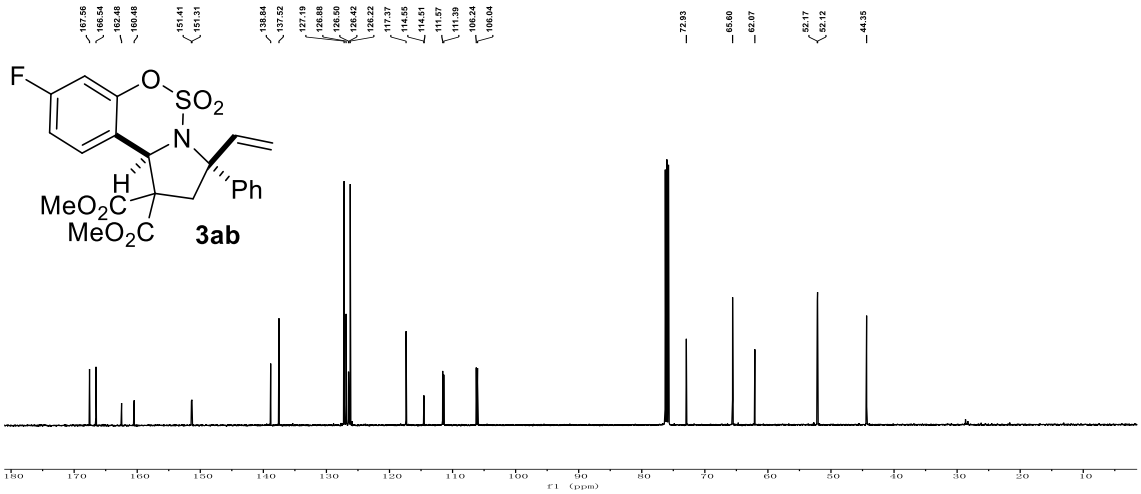
3aa



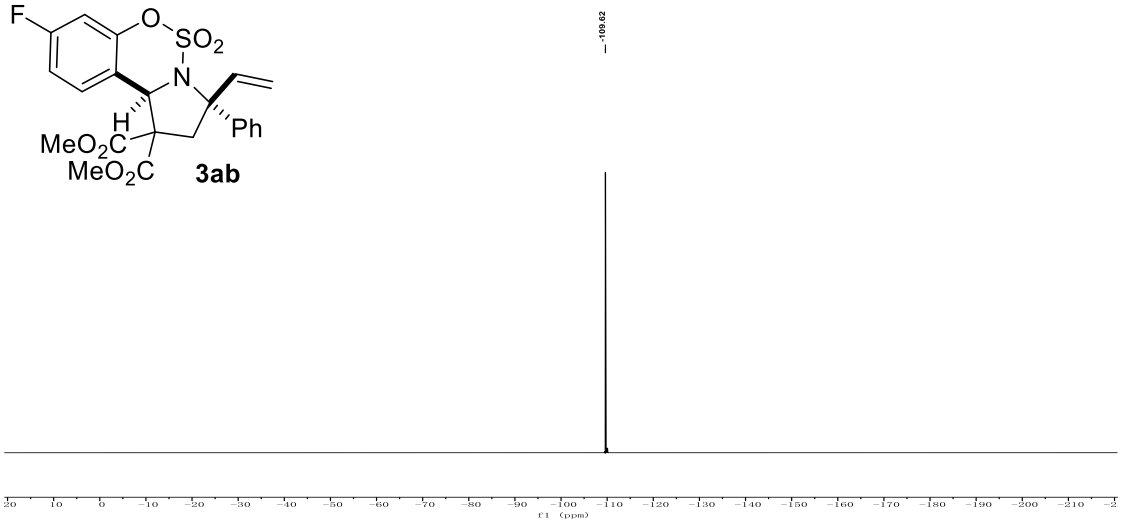
^{1}H NMR (500 MHz, $CDCl_3$)



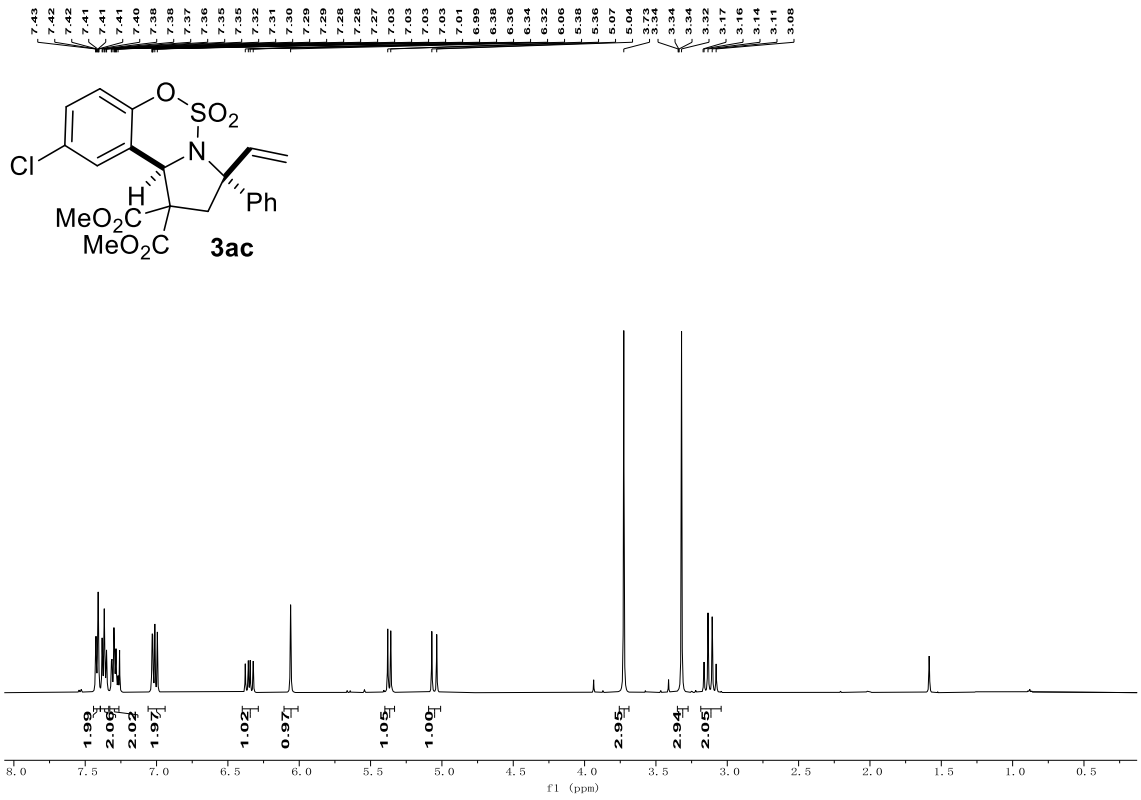
^{13}C NMR (126 MHz, $CDCl_3$)



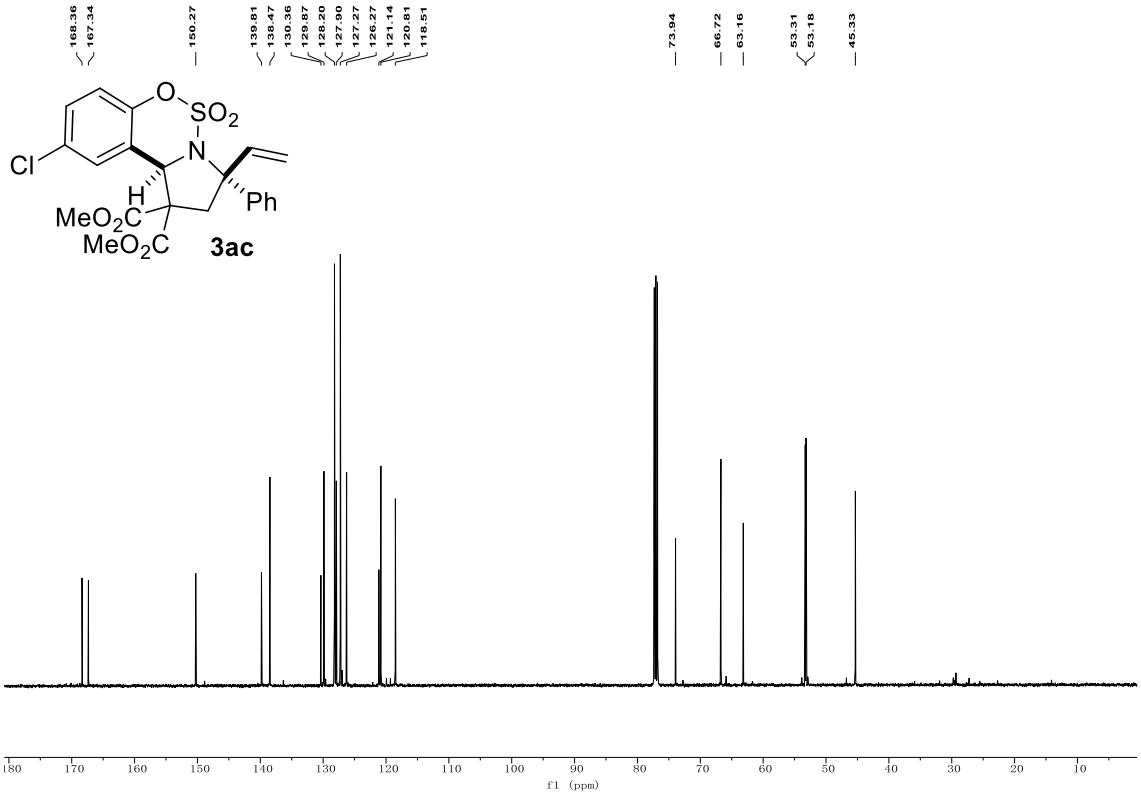
^{19}F NMR (471 MHz, $CDCl_3$)



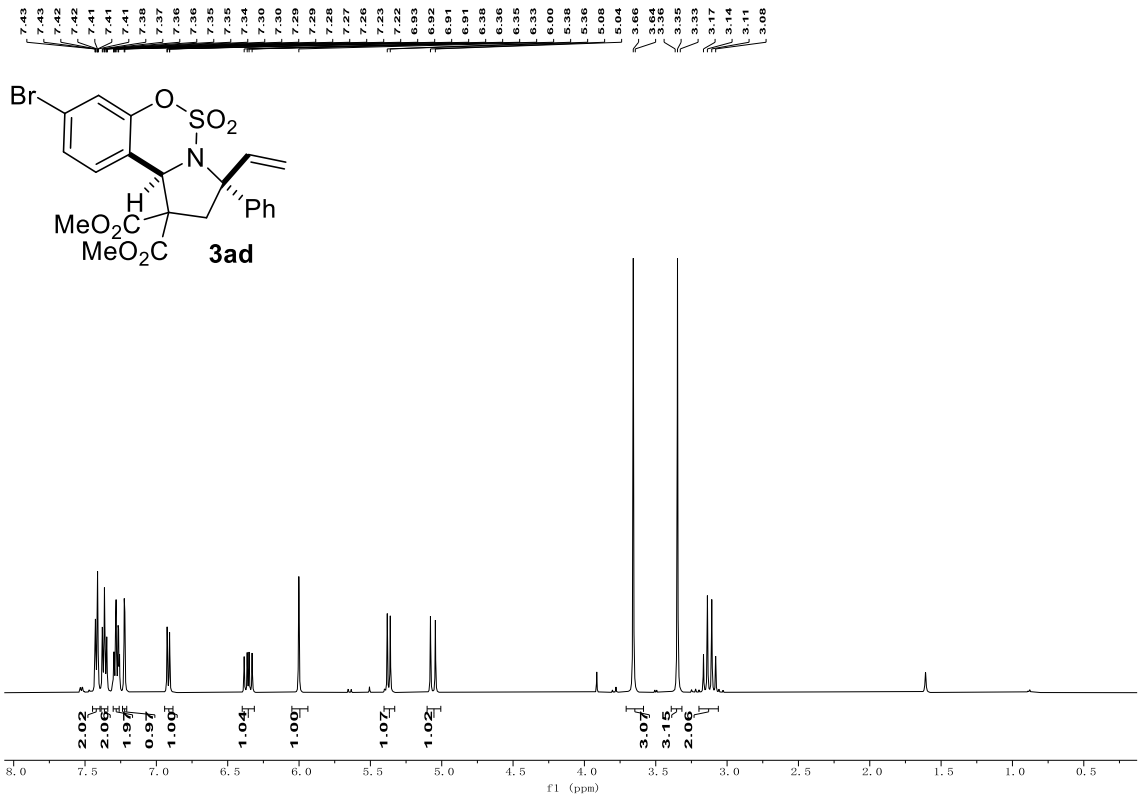
^{1}H NMR (500 MHz, $CDCl_3$)



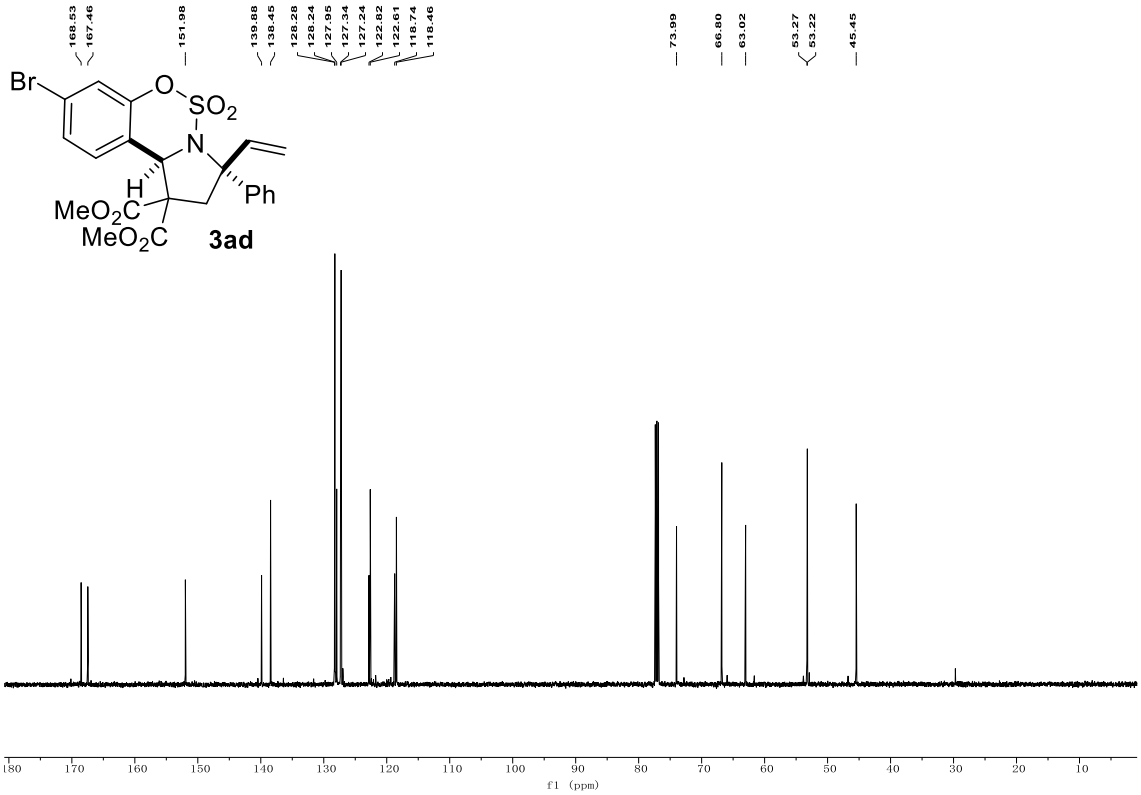
^{13}C NMR (126 MHz, $CDCl_3$)



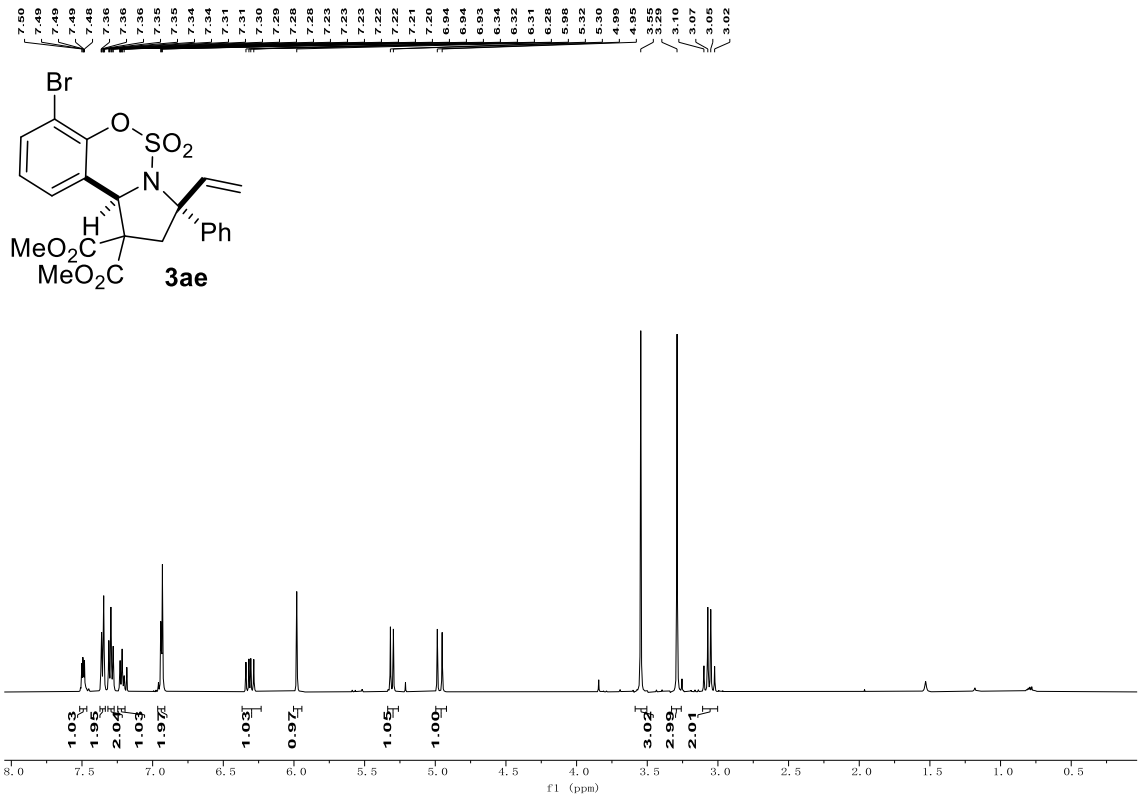
^{1}H NMR (500 MHz, $CDCl_3$)



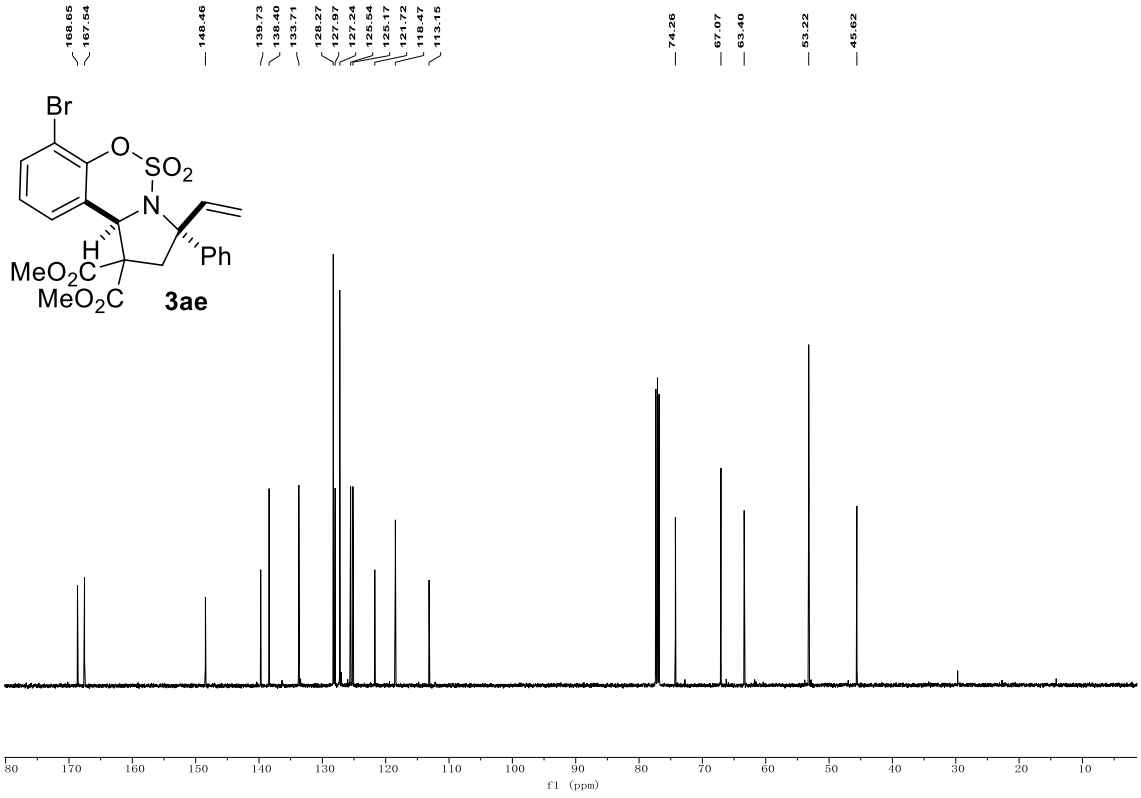
^{13}C NMR (126 MHz, $CDCl_3$)



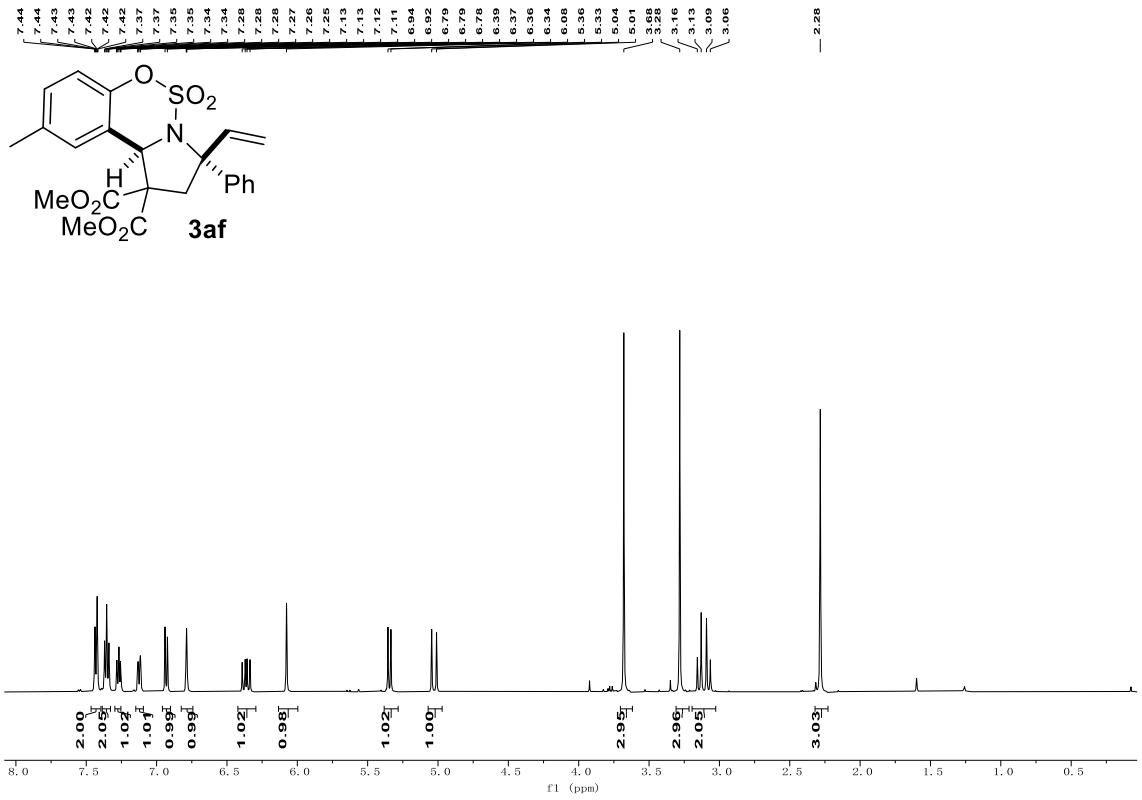
^{1}H NMR (500 MHz, $CDCl_3$)



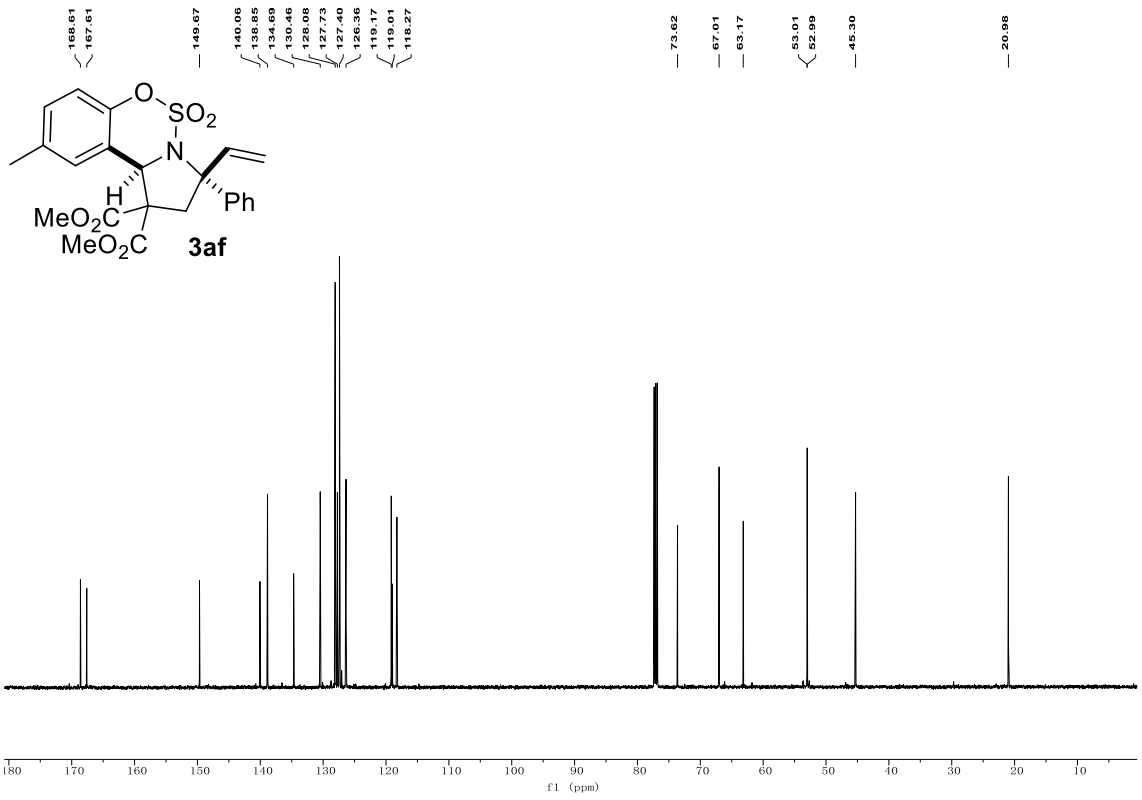
^{13}C NMR (126 MHz, $CDCl_3$)



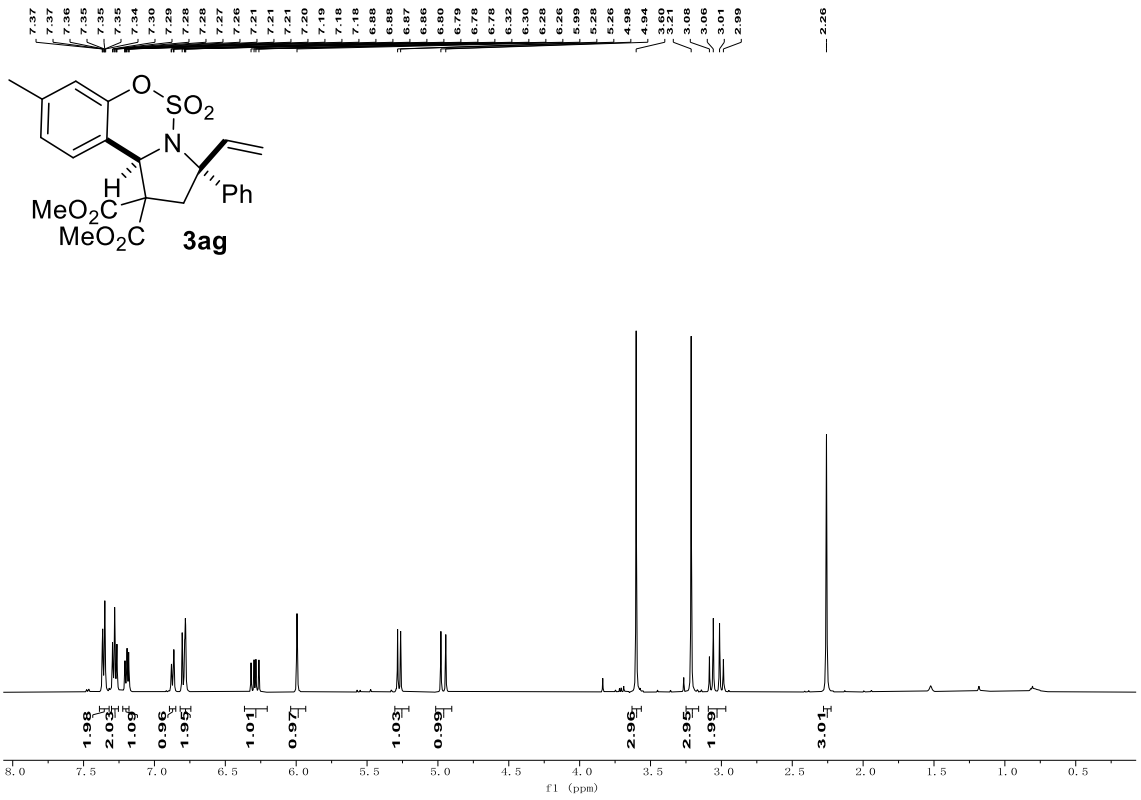
^{1}H NMR (500 MHz, $CDCl_3$)



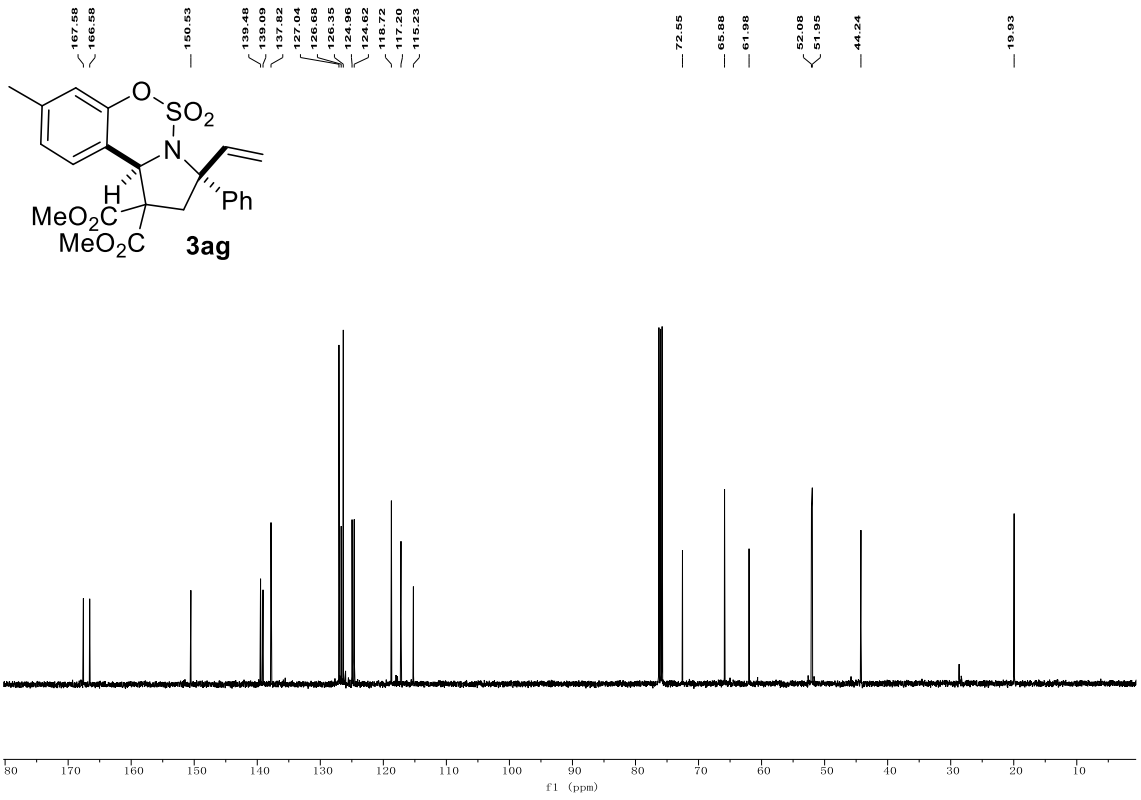
^{13}C NMR (126 MHz, $CDCl_3$)



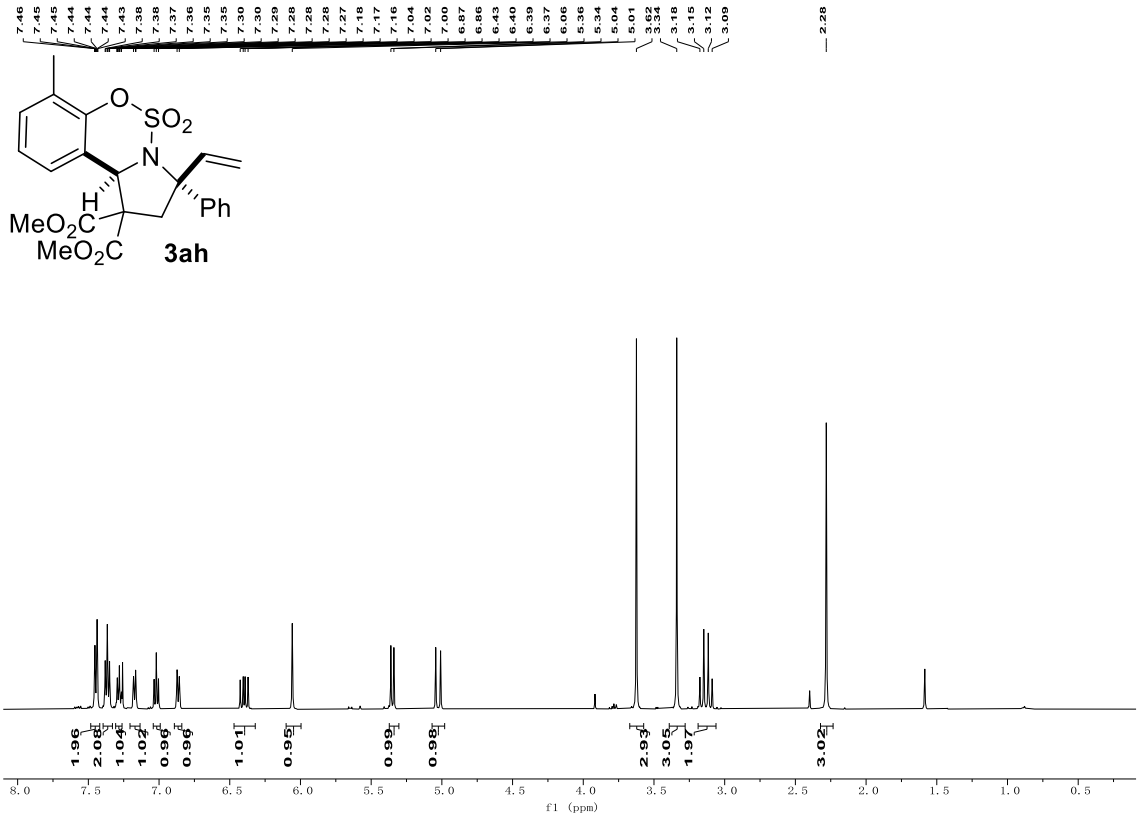
^{1}H NMR (500 MHz, $CDCl_3$)



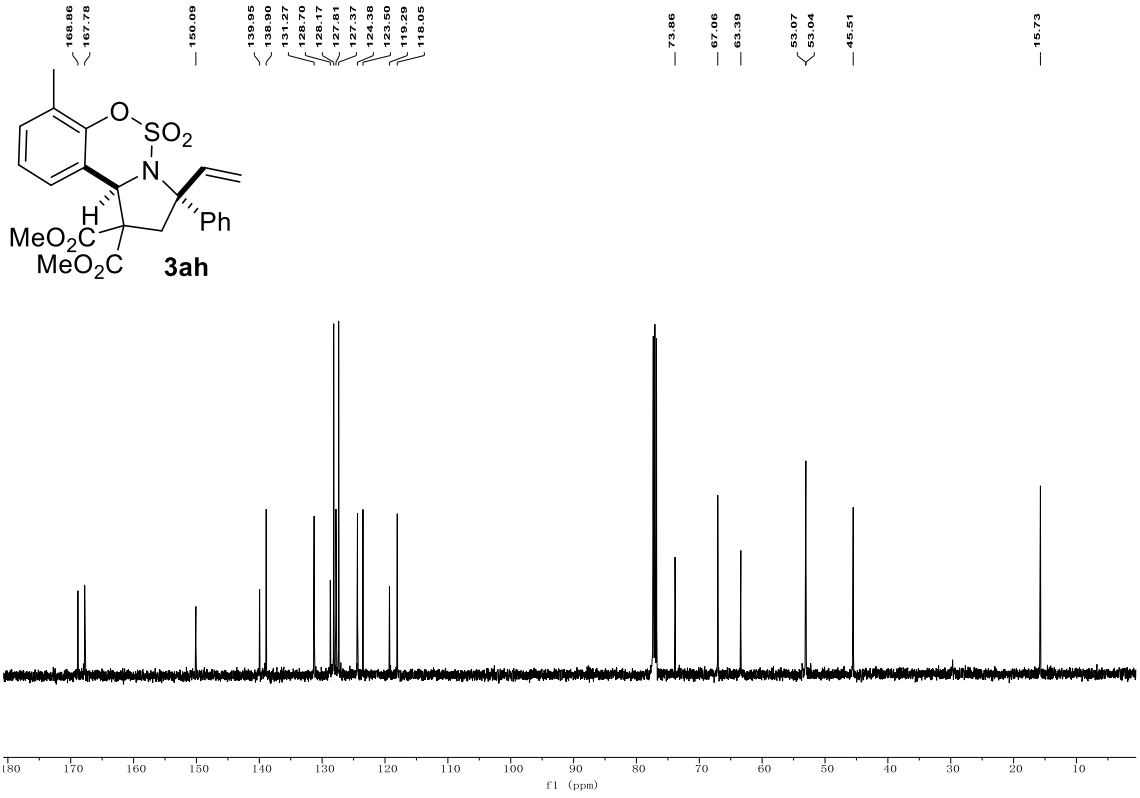
^{13}C NMR (126 MHz, $CDCl_3$)



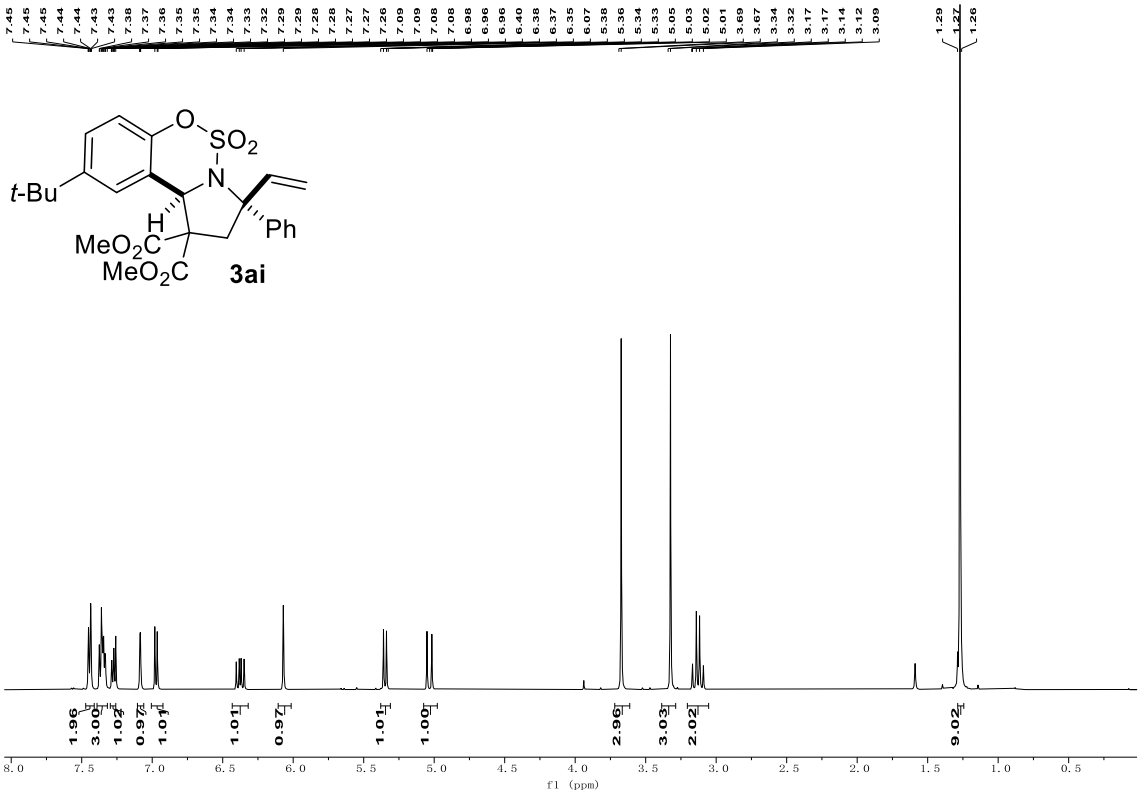
^{1}H NMR (500 MHz, $CDCl_3$)



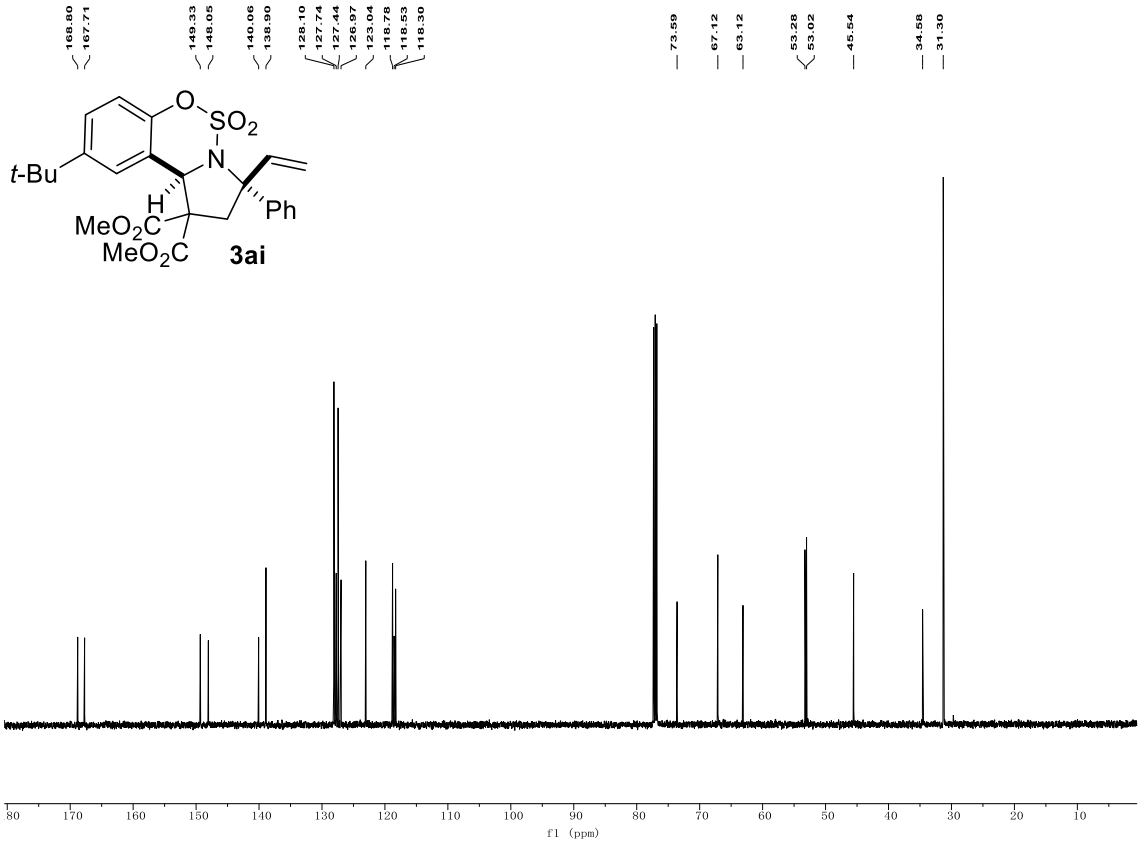
^{13}C NMR (126 MHz, $CDCl_3$)



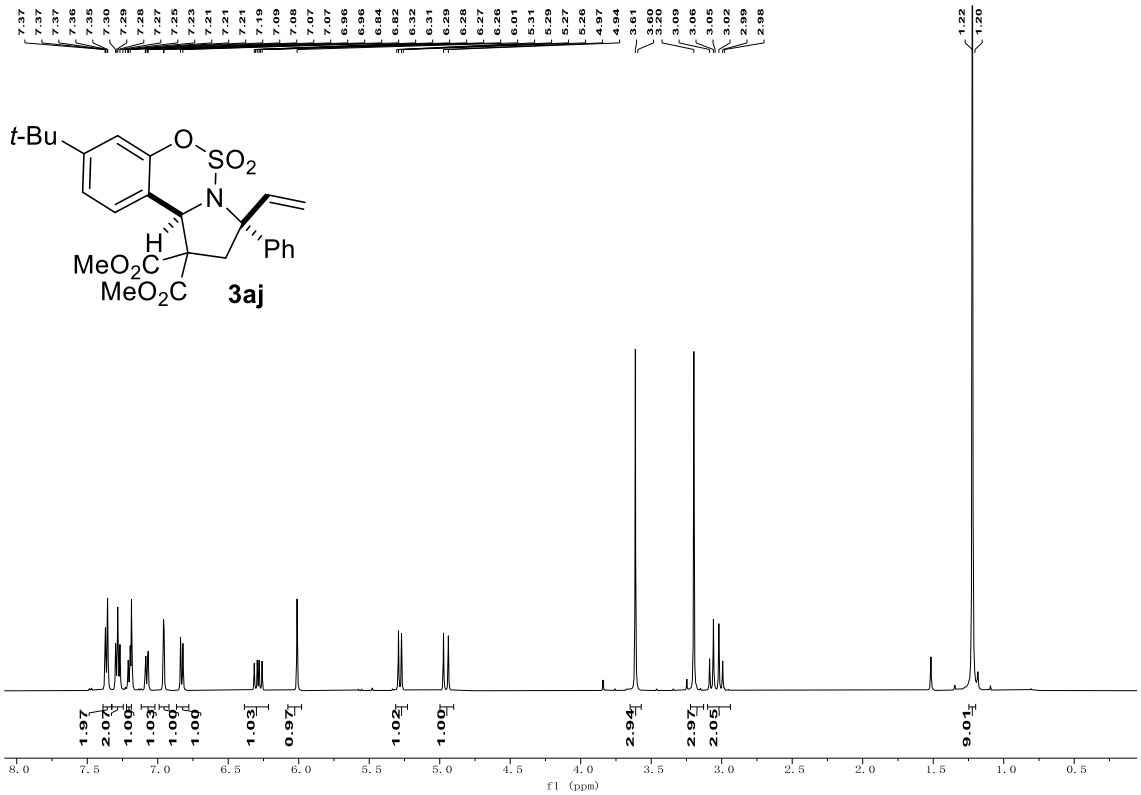
^{1}H NMR (500 MHz, $CDCl_3$)



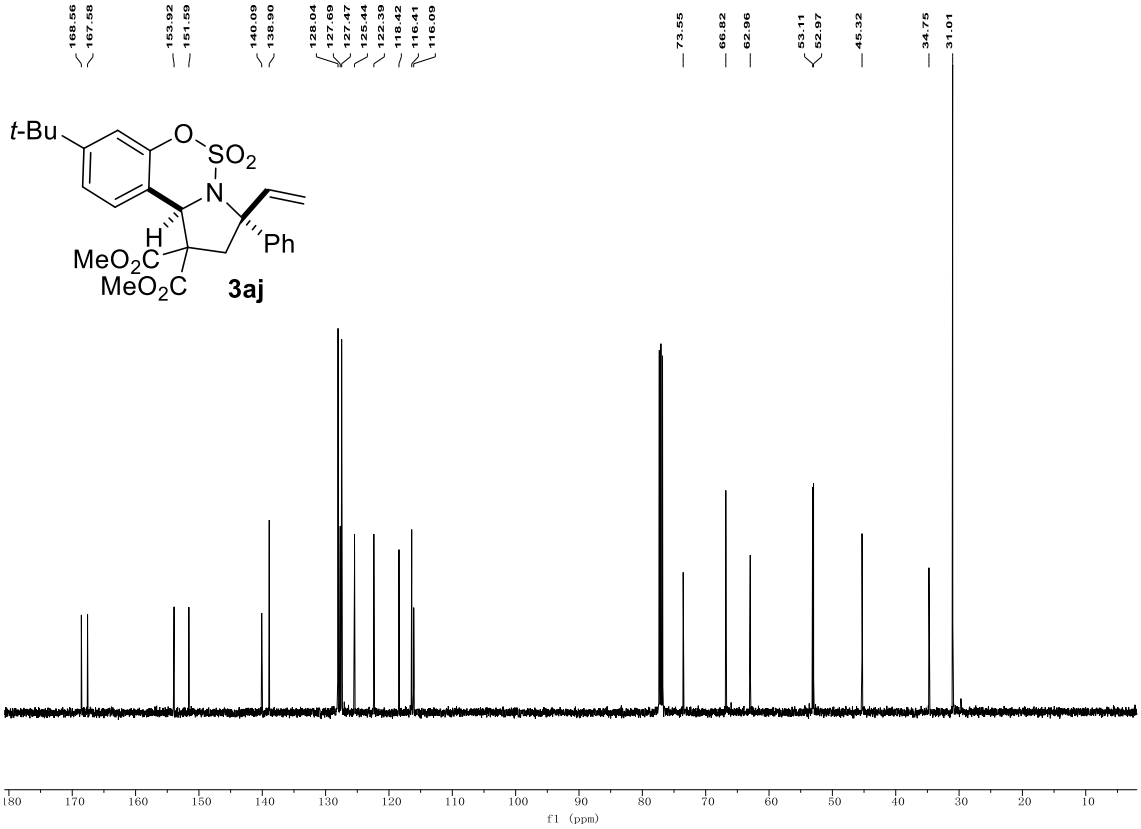
^{13}C NMR (126 MHz, $CDCl_3$)



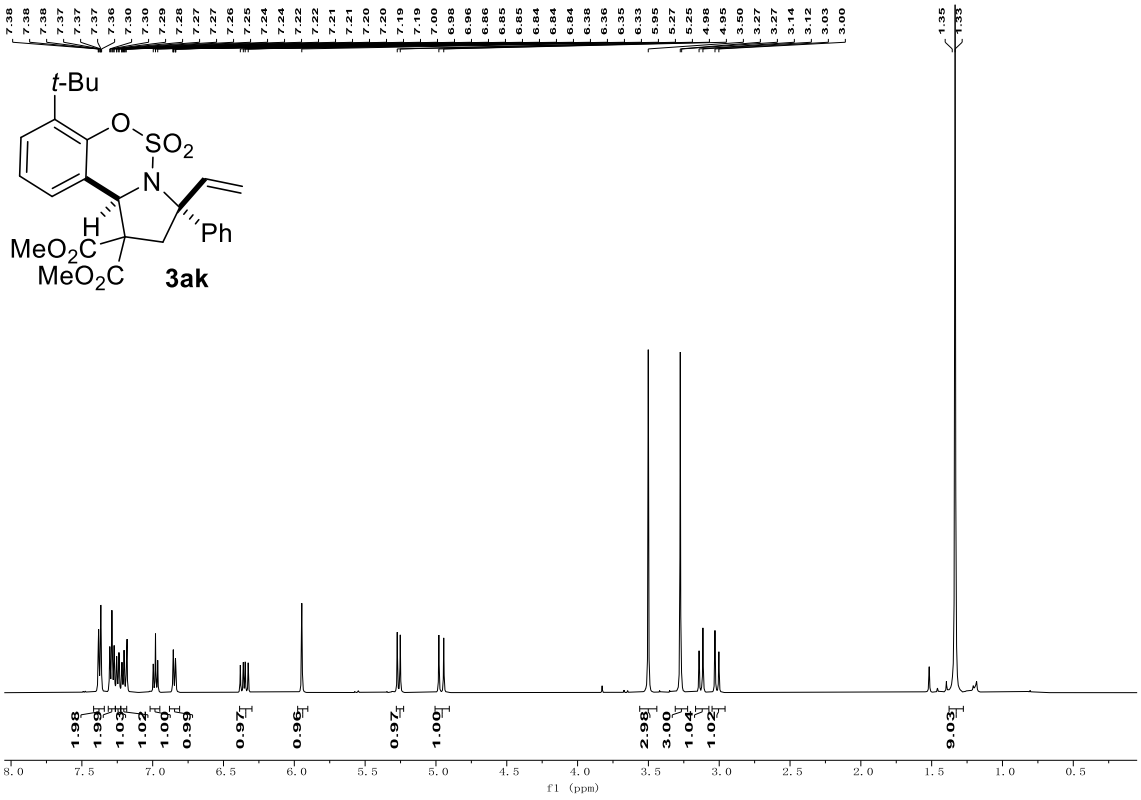
^{1}H NMR (500 MHz, $CDCl_3$)



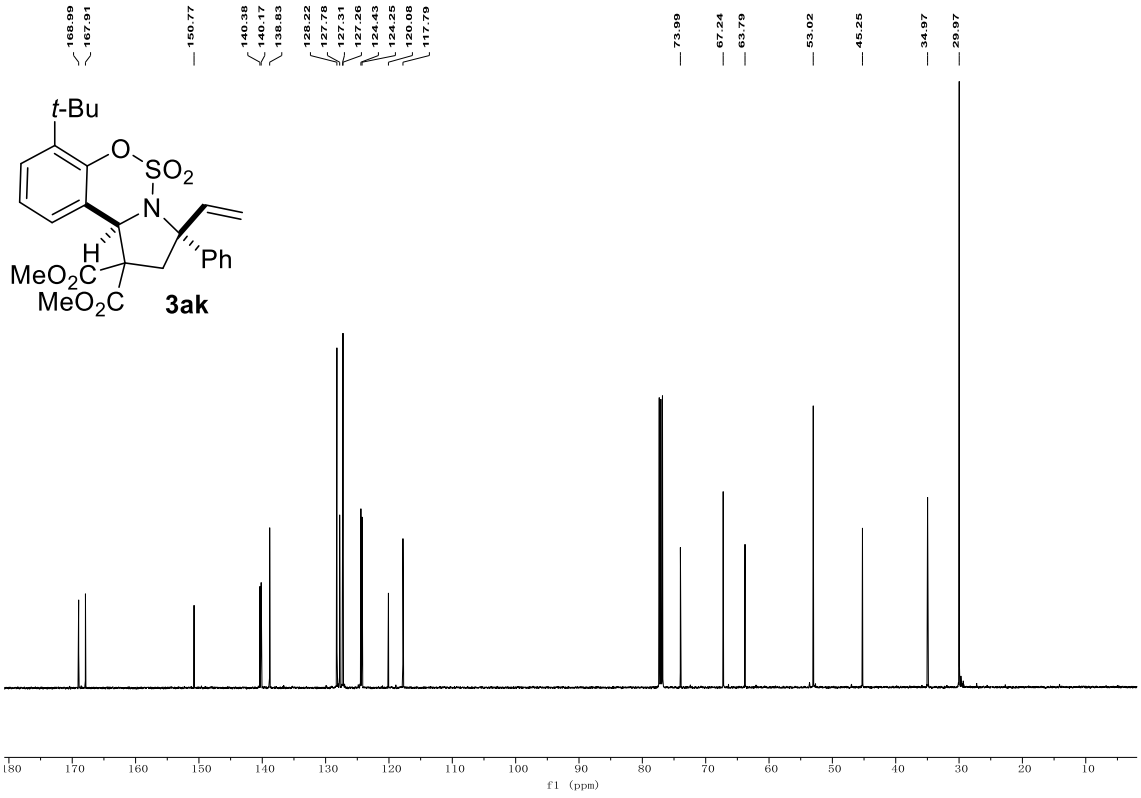
^{13}C NMR (126 MHz, $CDCl_3$)



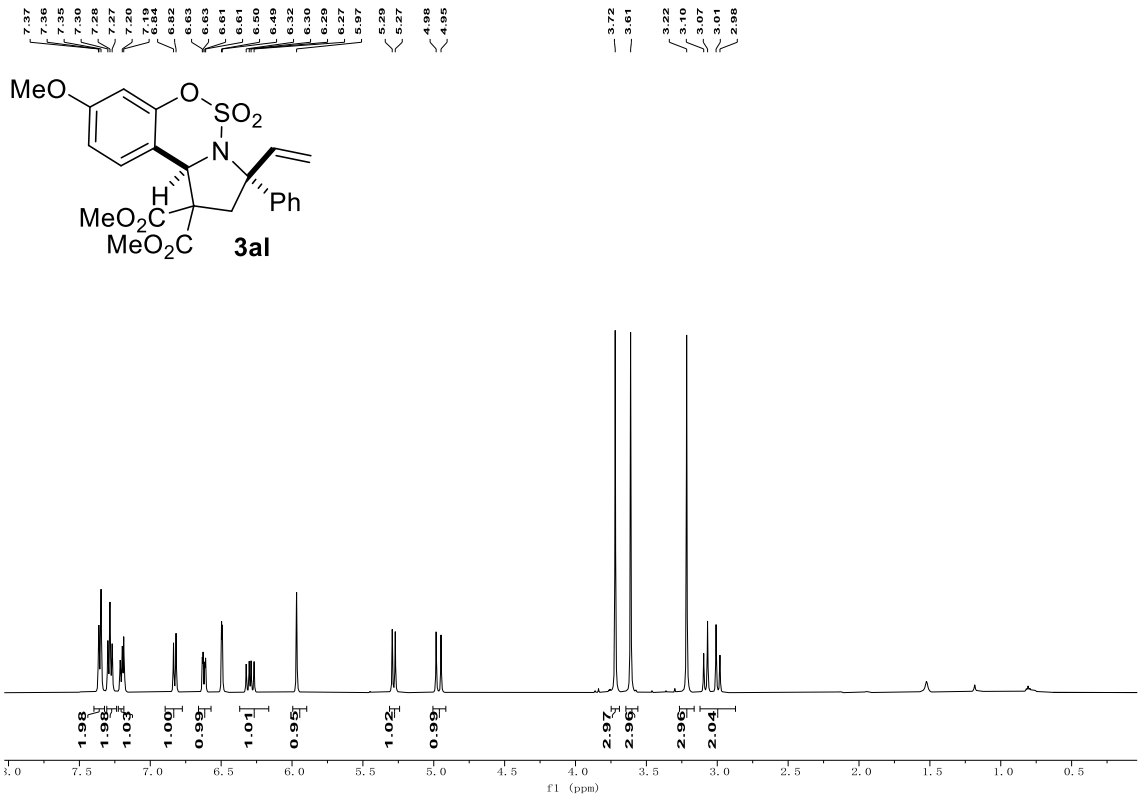
^{1}H NMR (500 MHz, $CDCl_3$)



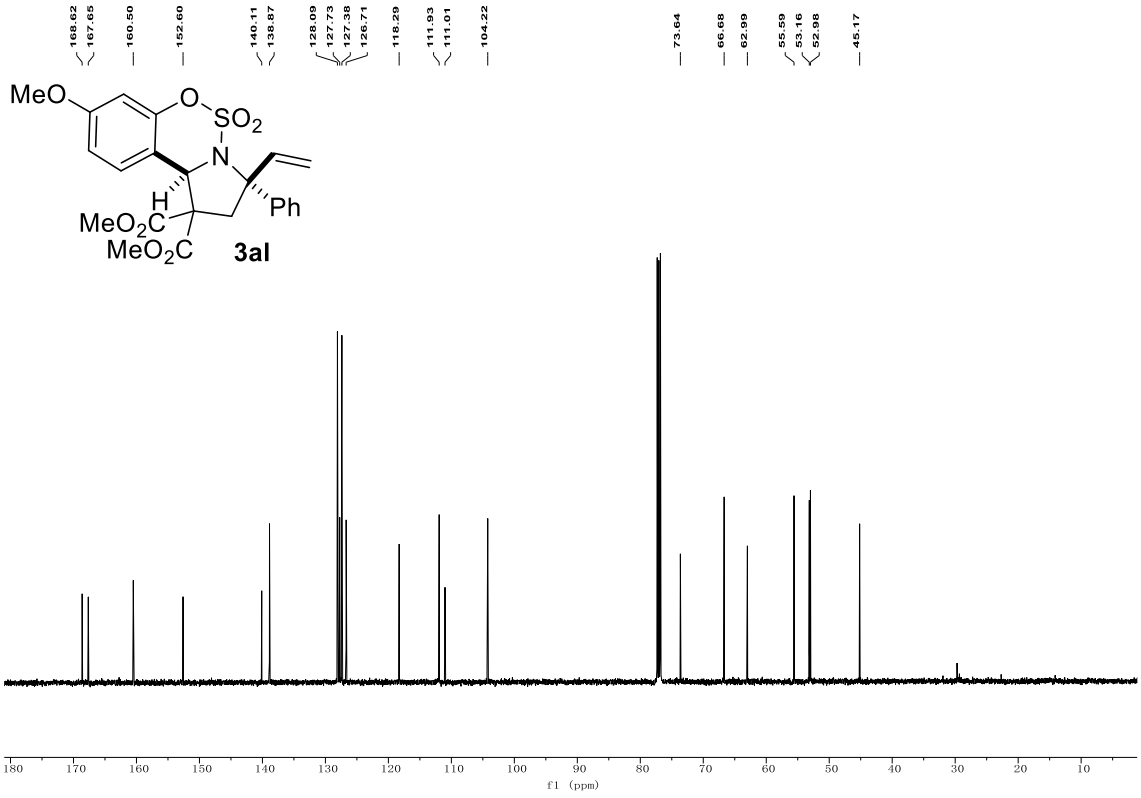
^{13}C NMR (126 MHz, $CDCl_3$)



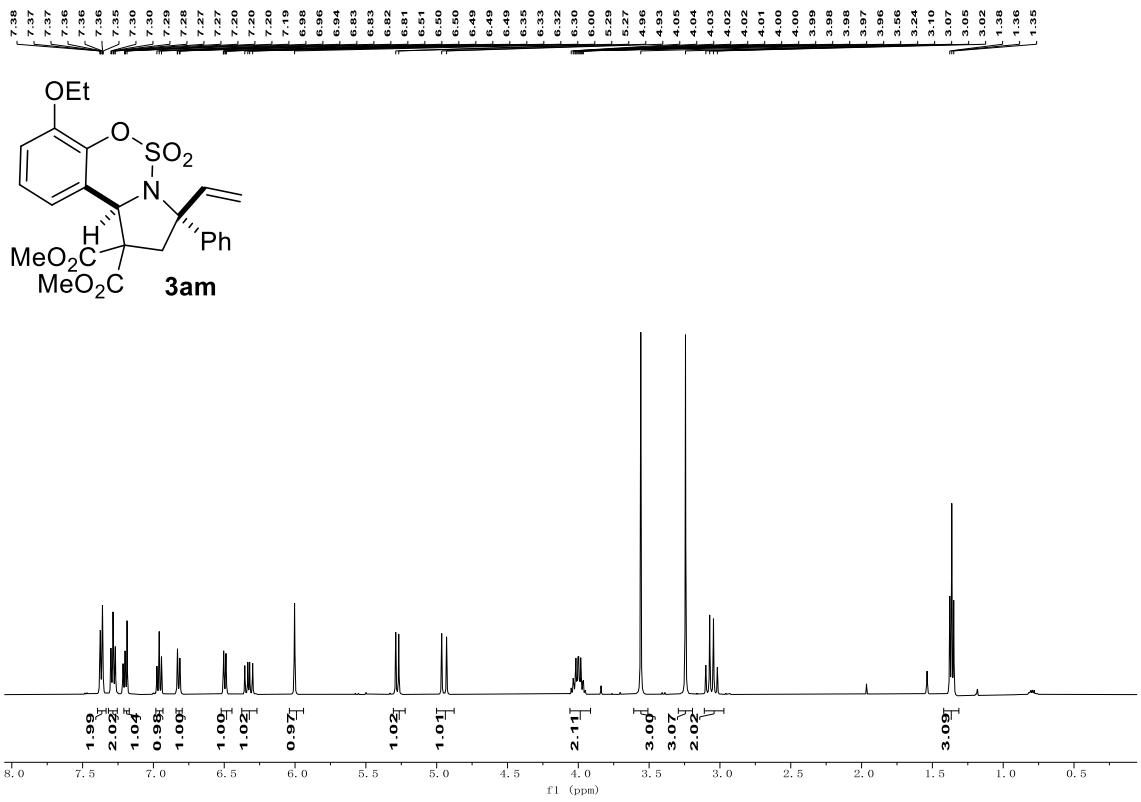
^{1}H NMR (500 MHz, $CDCl_3$)



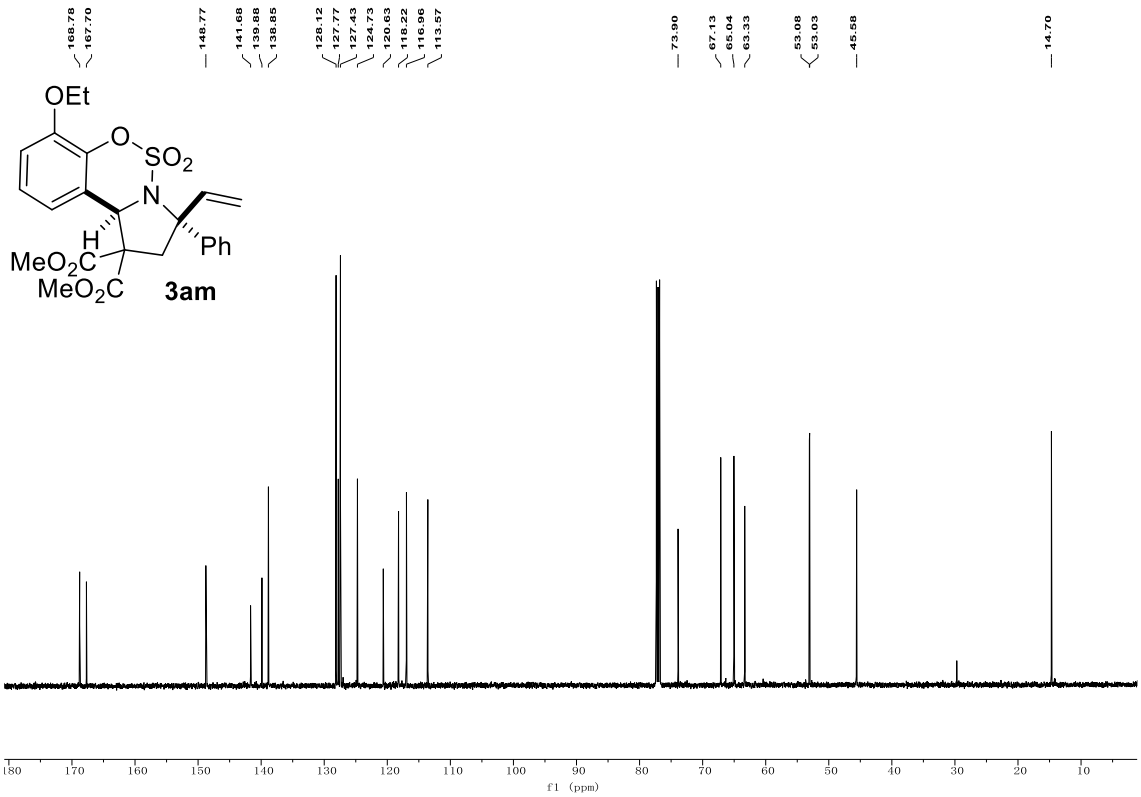
^{13}C NMR (126 MHz, $CDCl_3$)



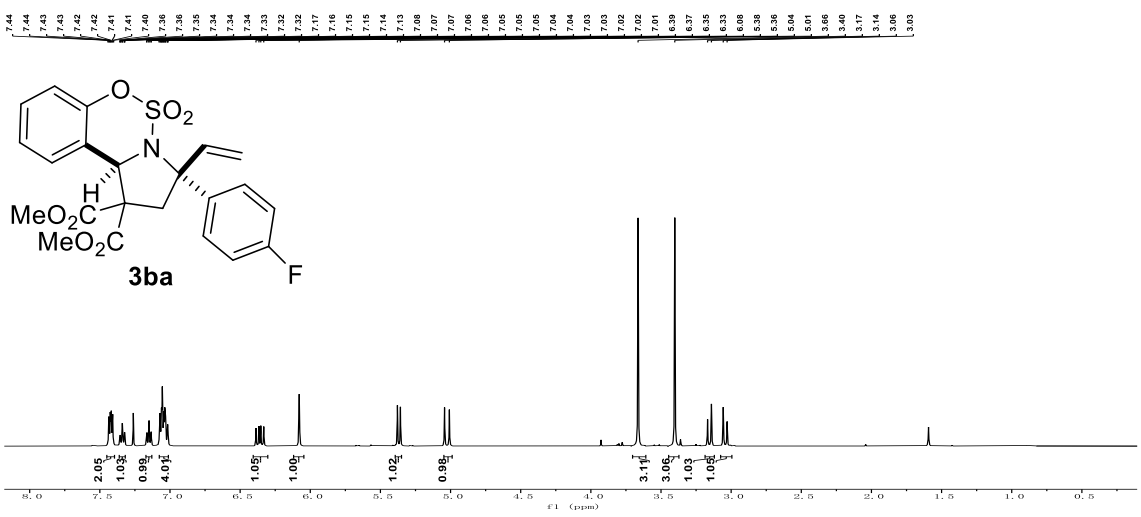
^{1}H NMR (500 MHz, $CDCl_3$)



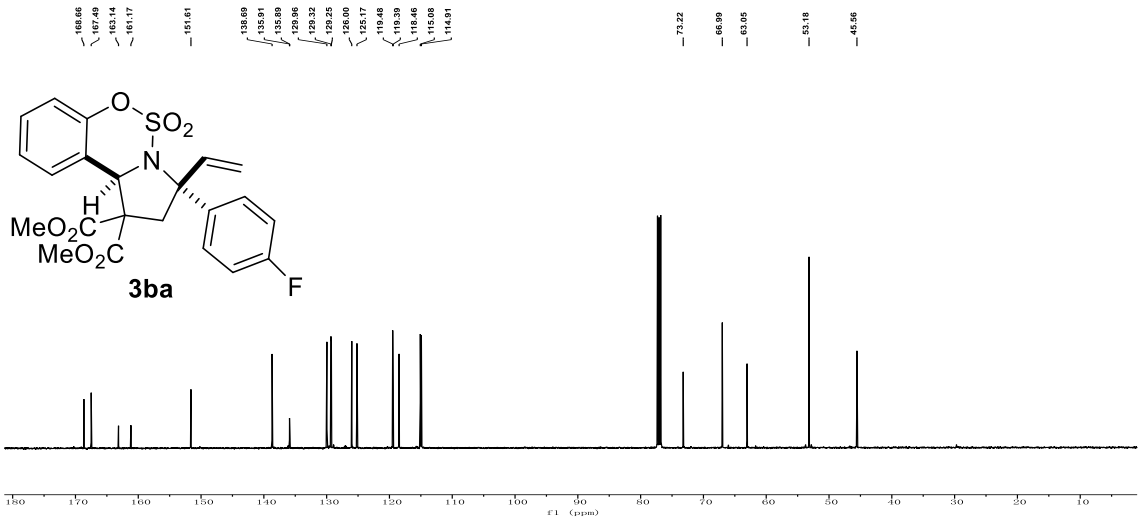
^{13}C NMR (126 MHz, $CDCl_3$)



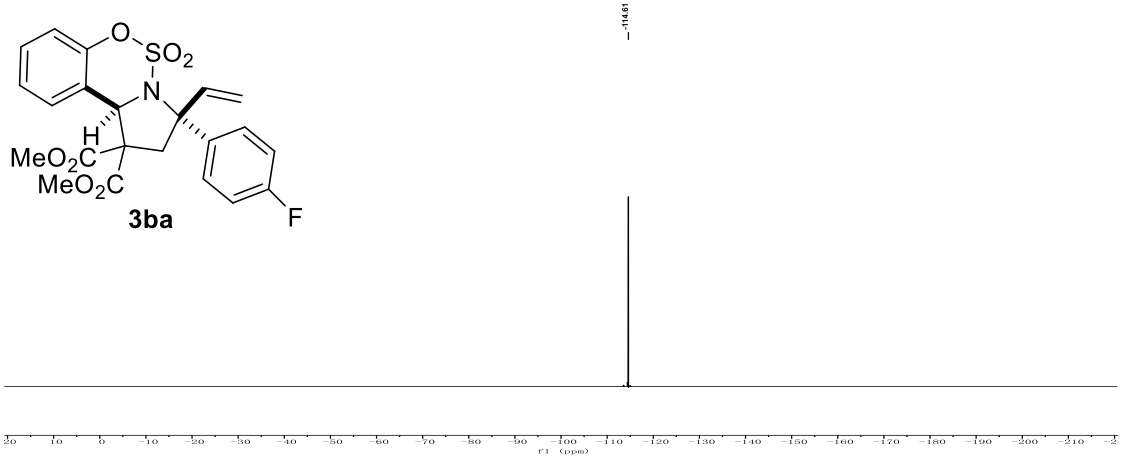
^{1}H NMR (500 MHz, $CDCl_3$)



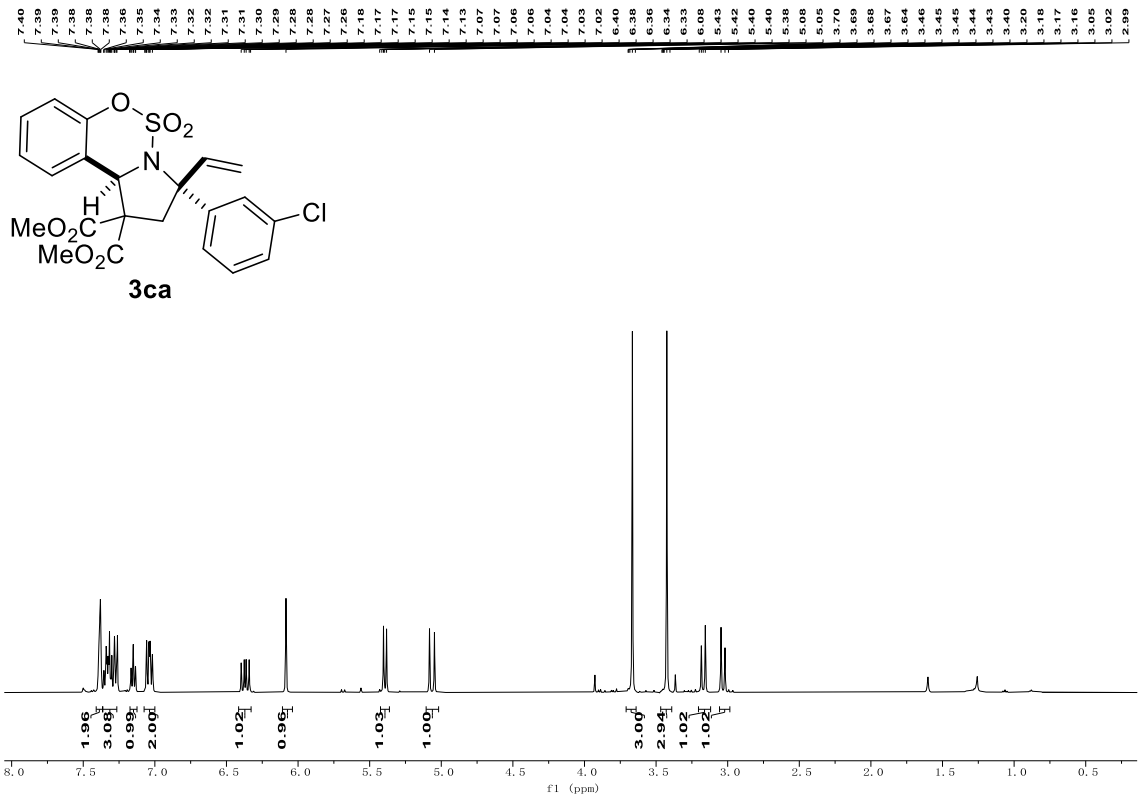
^{13}C NMR (126 MHz, $CDCl_3$)



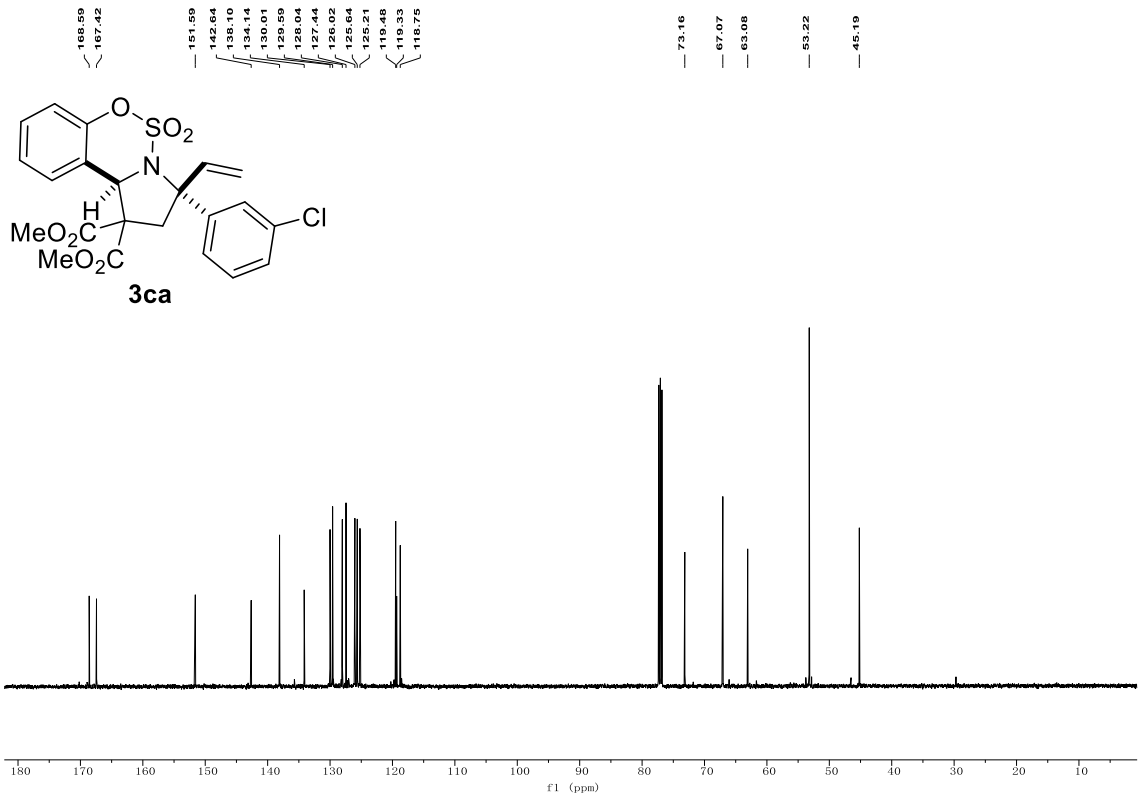
^{19}F NMR (471 MHz, $CDCl_3$)



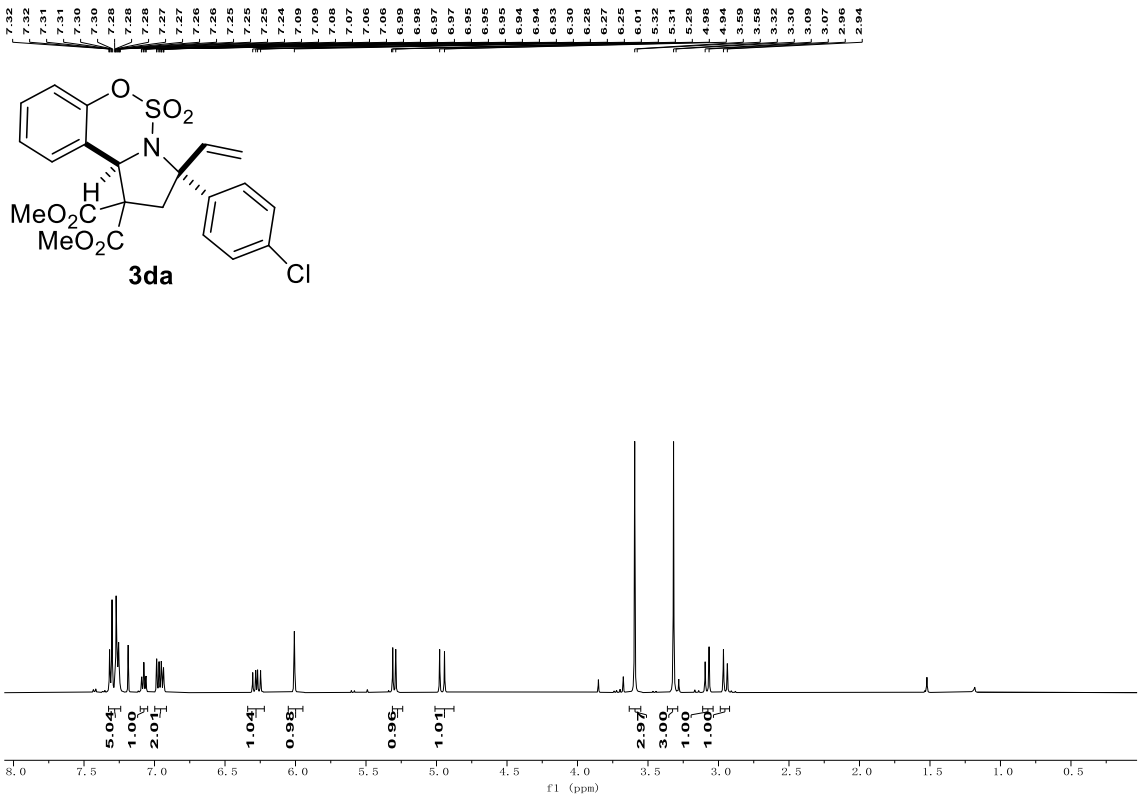
^{1}H NMR (500 MHz, $CDCl_3$)



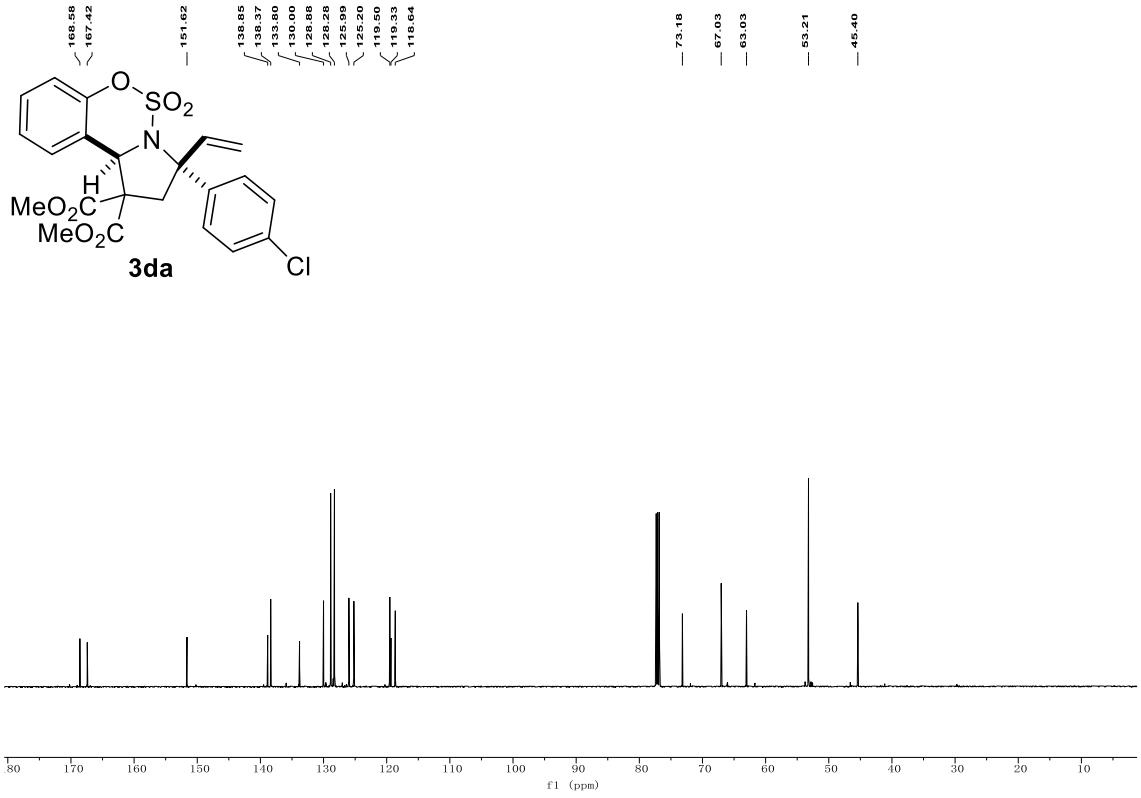
^{13}C NMR (126 MHz, $CDCl_3$)



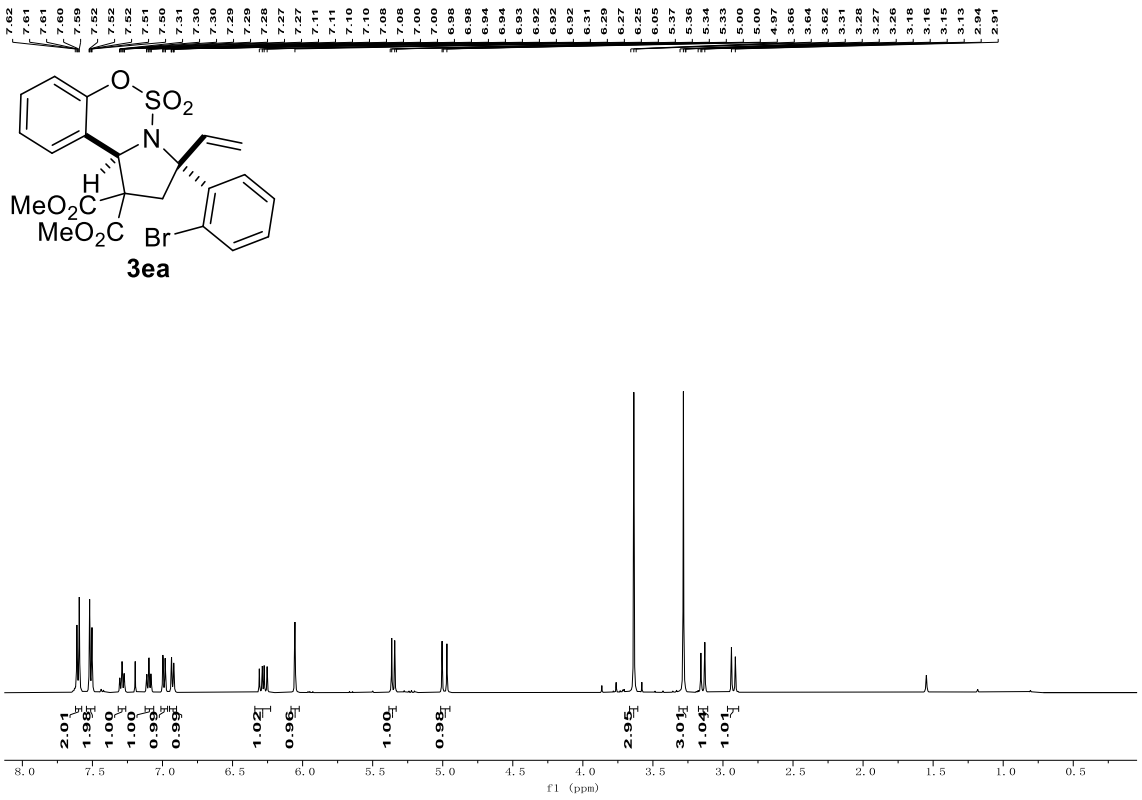
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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



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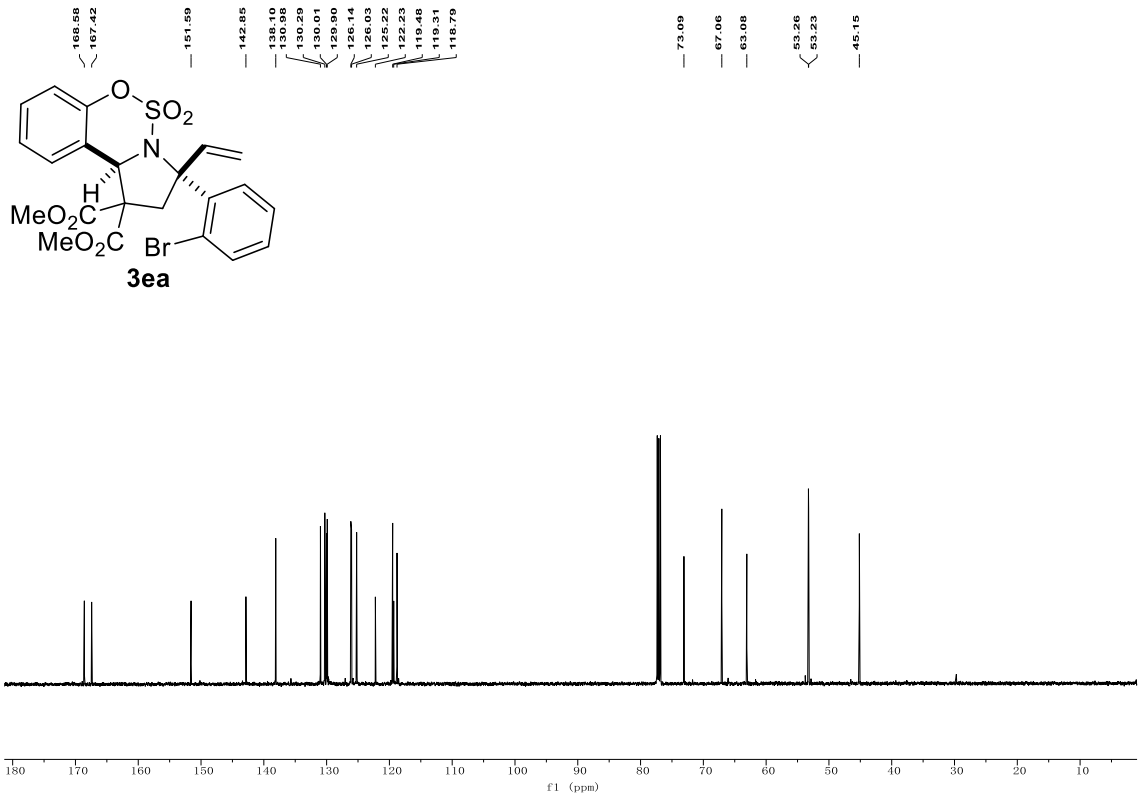
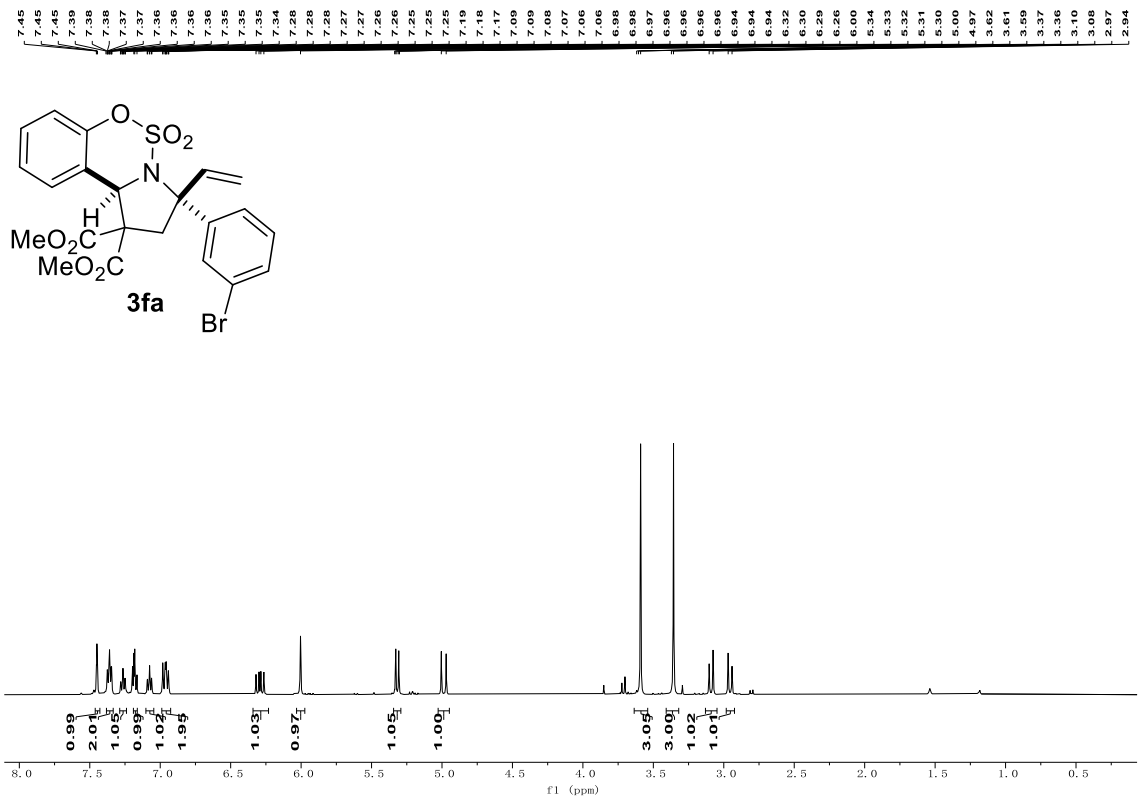
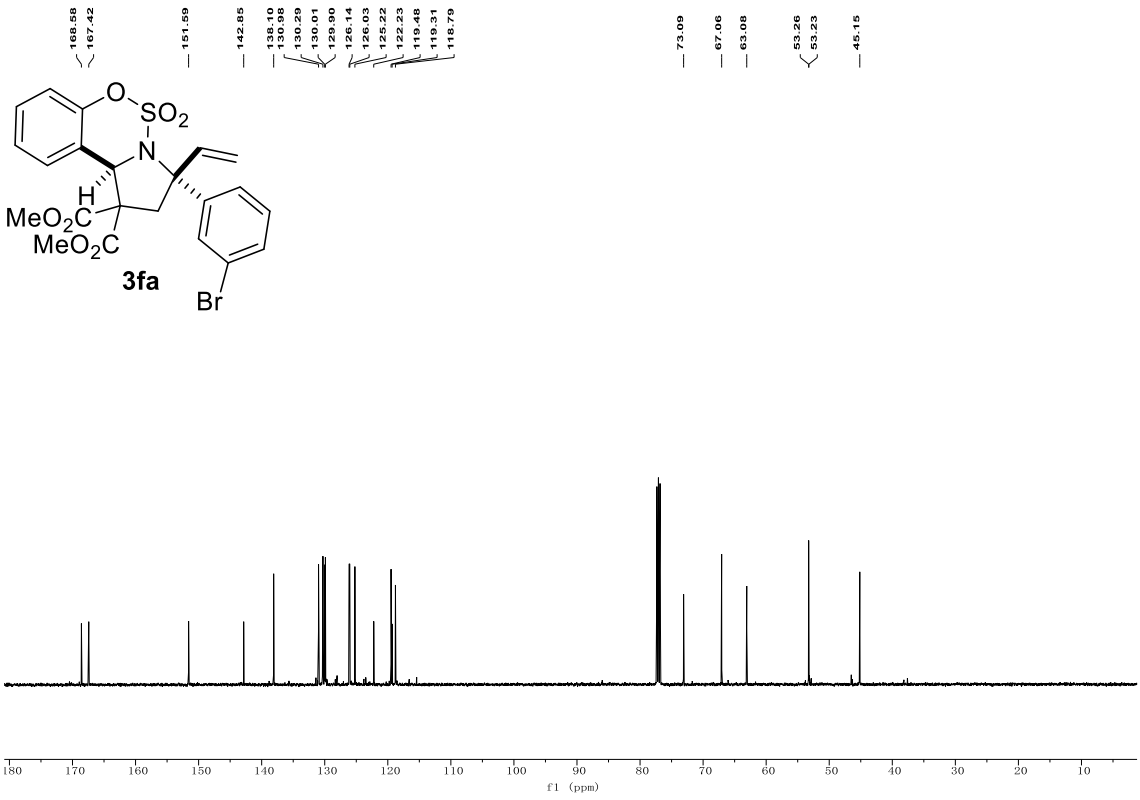


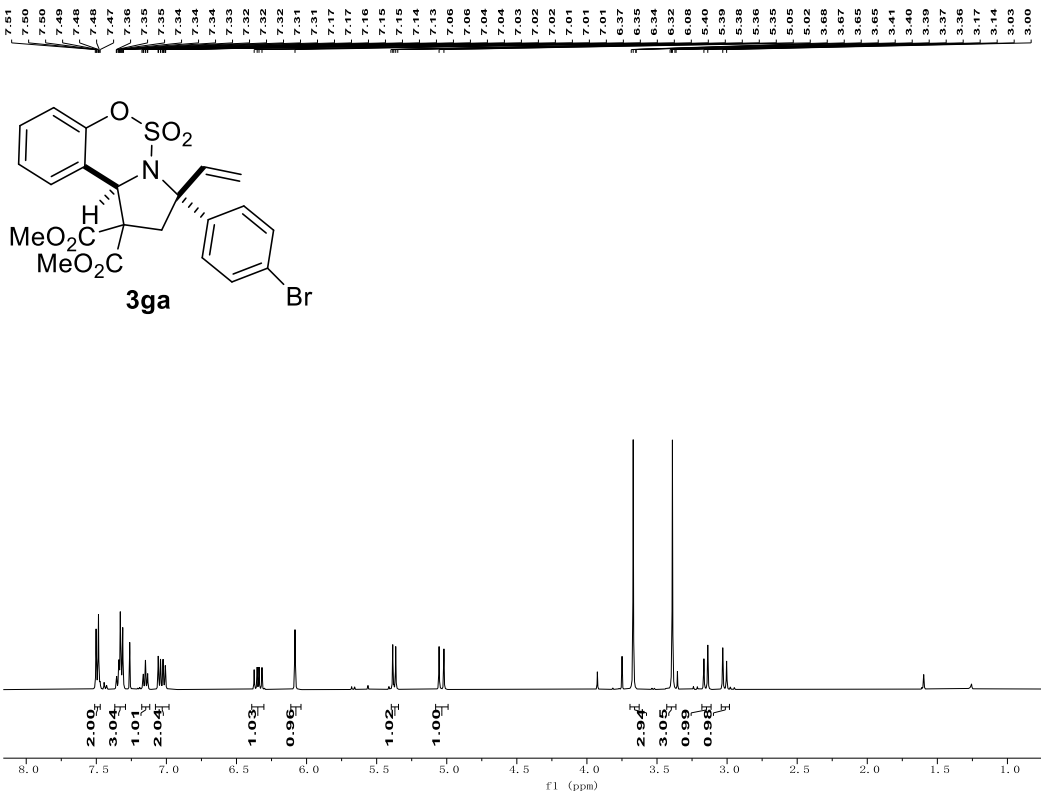
^{1}H NMR (500 MHz, $CDCl_3$)



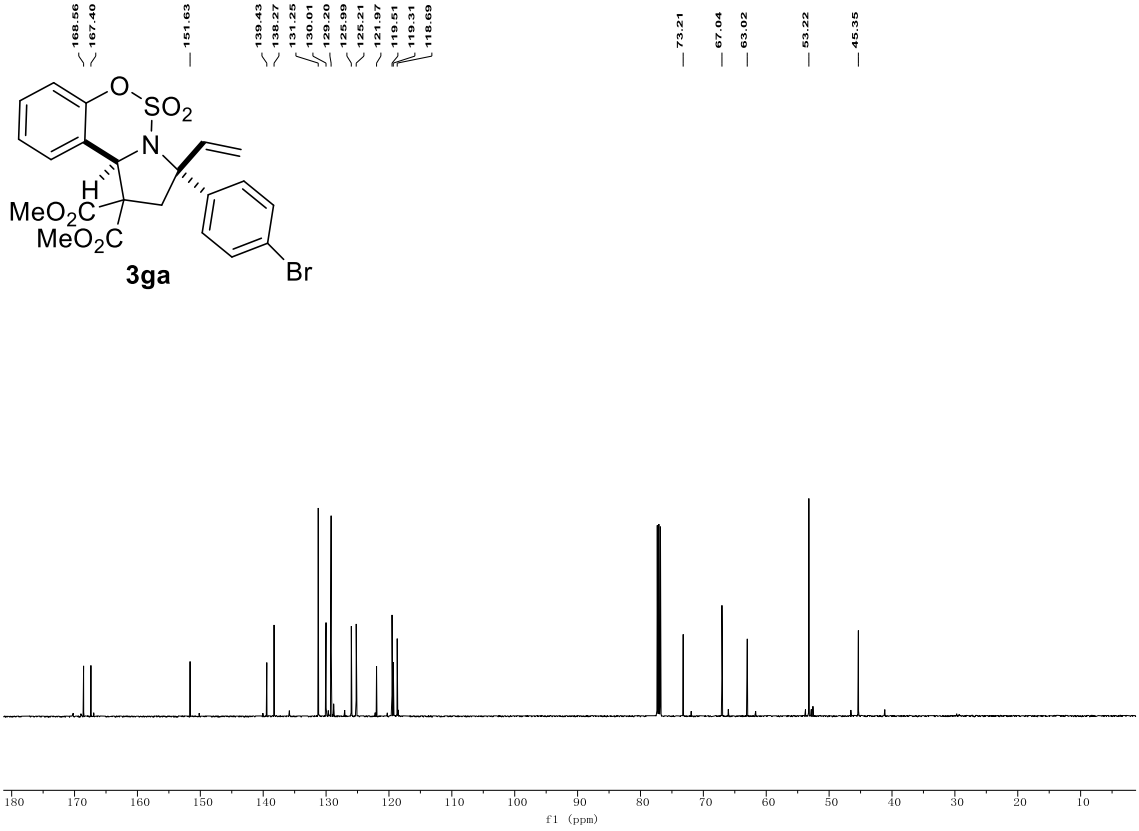
^{13}C NMR (126 MHz, $CDCl_3$)



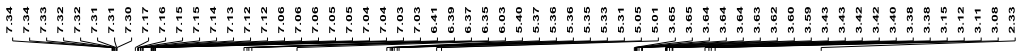
^{1}H NMR (500 MHz, $CDCl_3$)

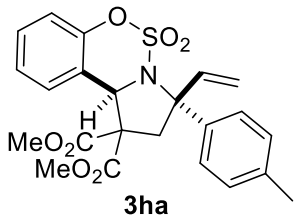


^{13}C NMR (126 MHz, $CDCl_3$)

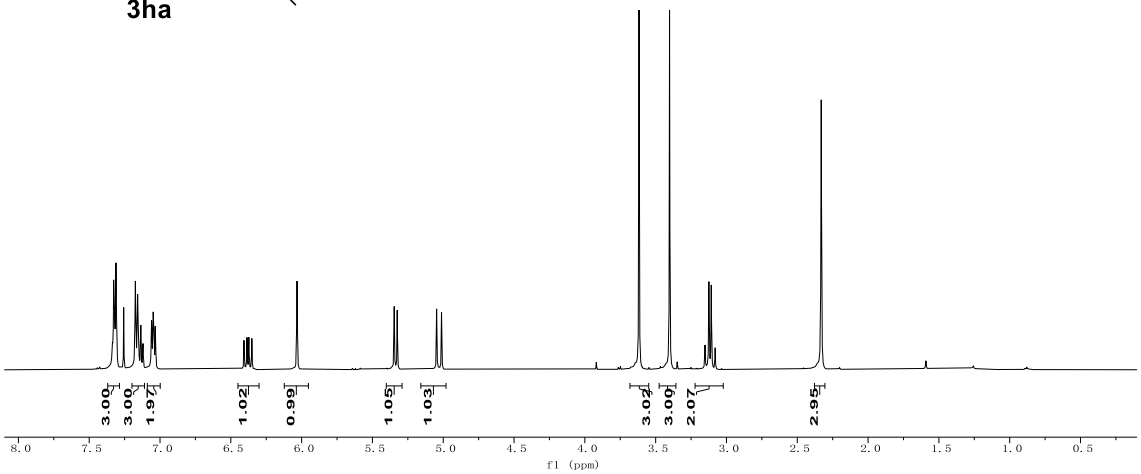


^{1}H NMR (500 MHz, $CDCl_3$)

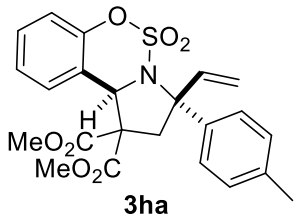




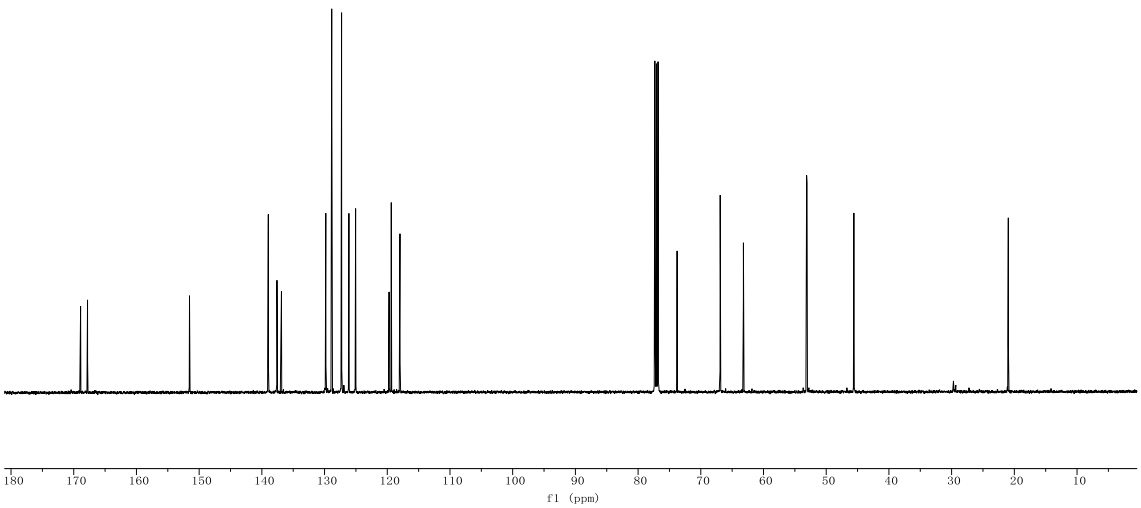
3ha



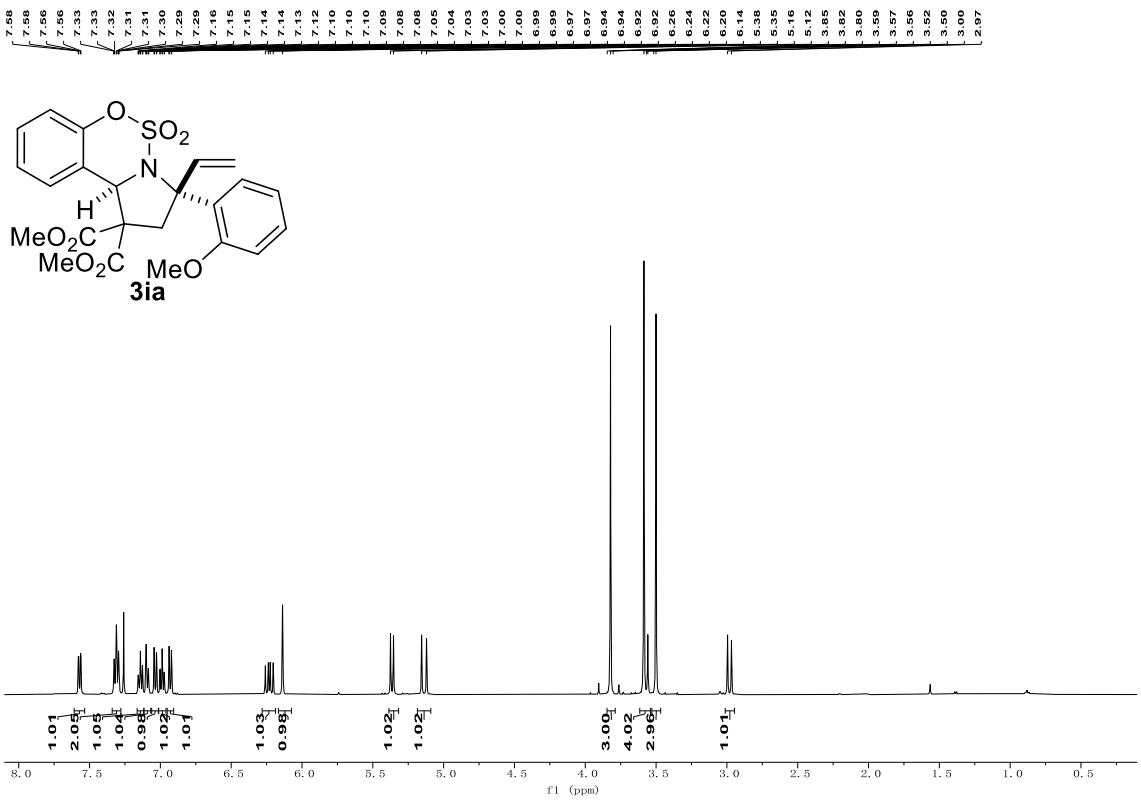
^{13}C NMR (126 MHz, $CDCl_3$)



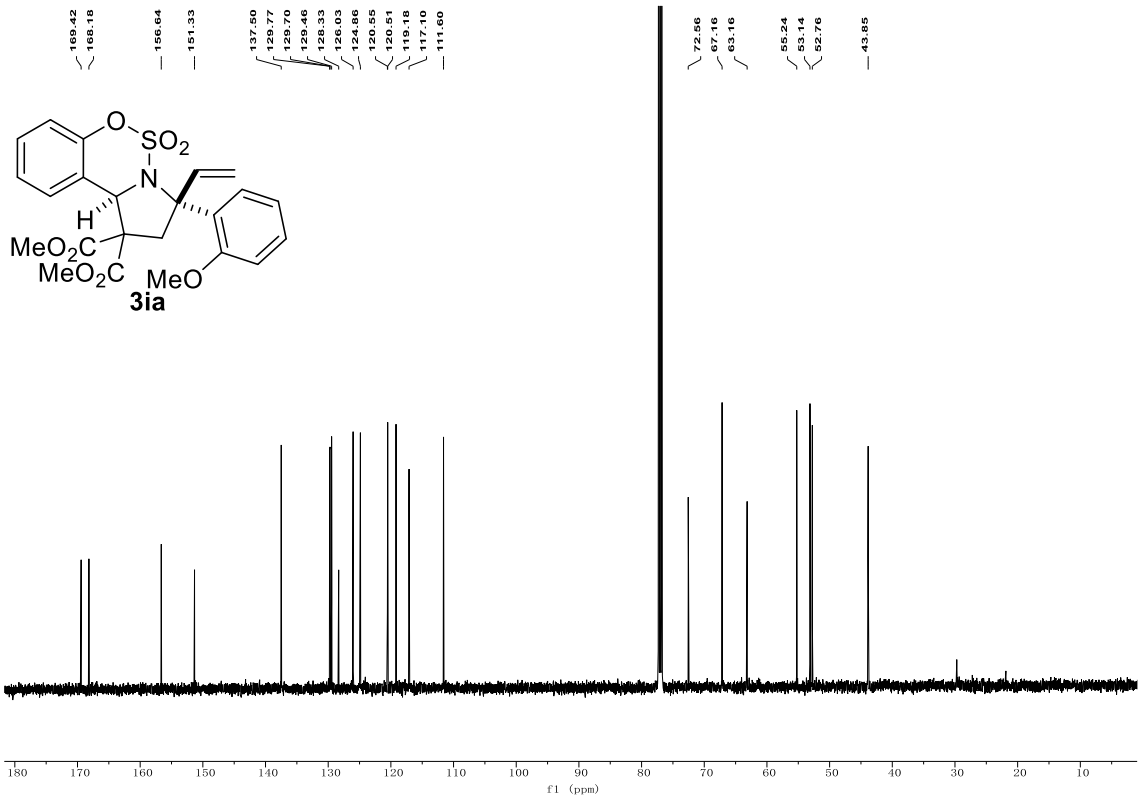
3ha



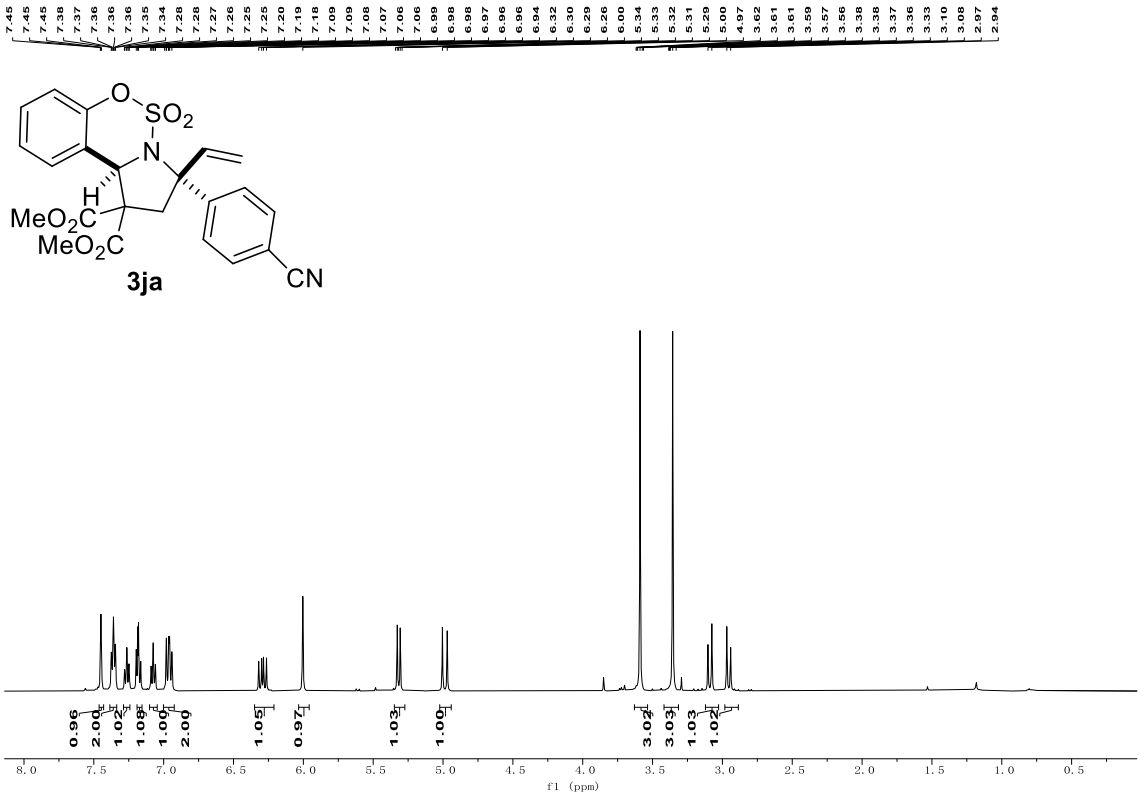
^{1}H NMR (500 MHz, $CDCl_3$)



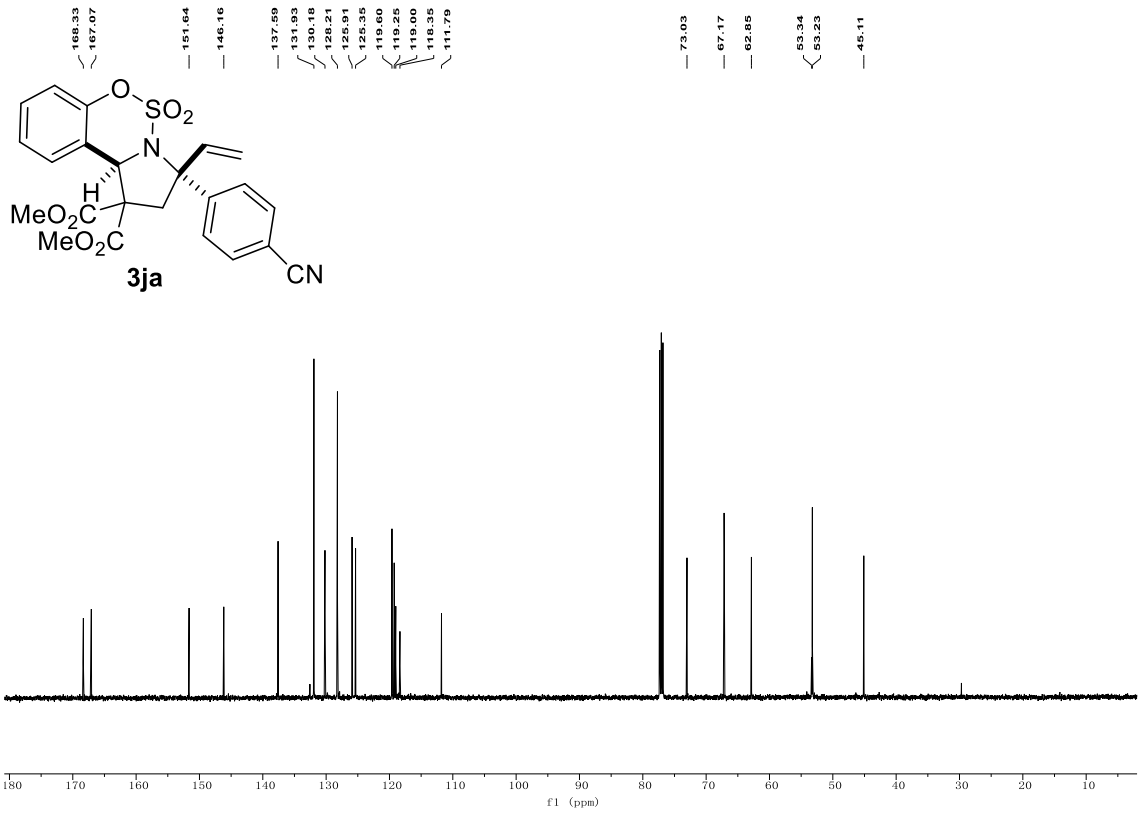
^{13}C NMR (126 MHz, $CDCl_3$)



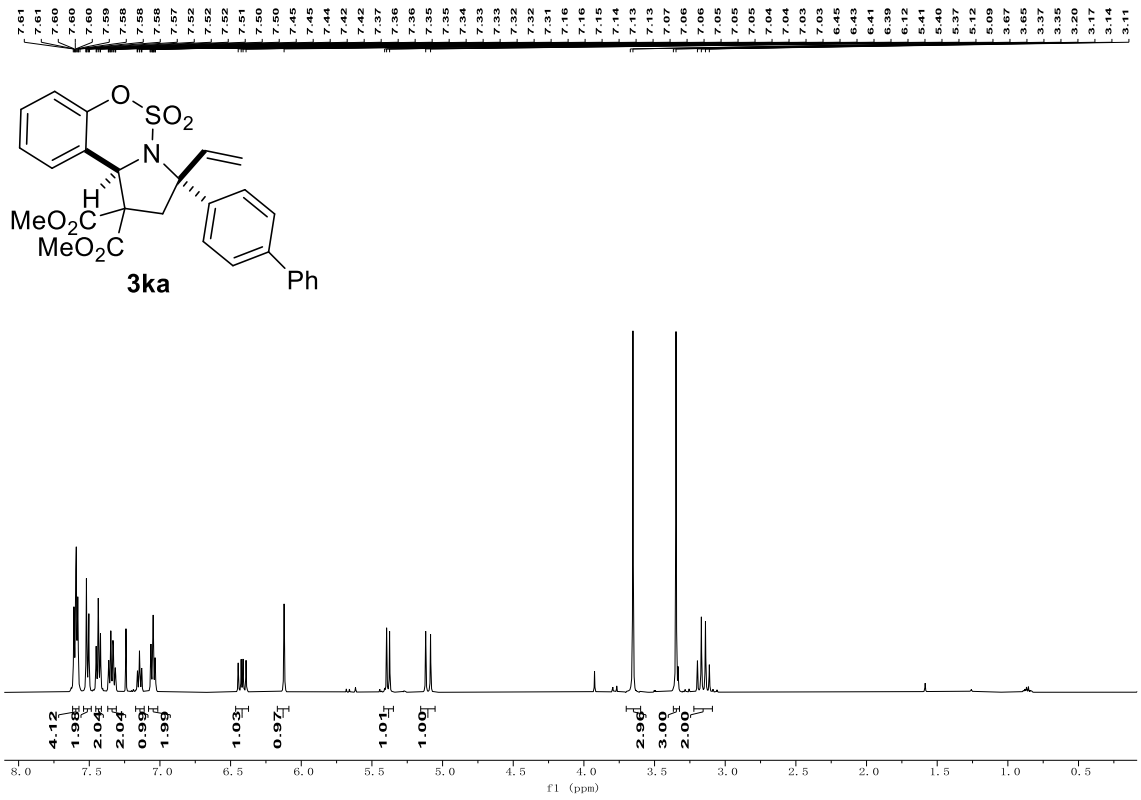
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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



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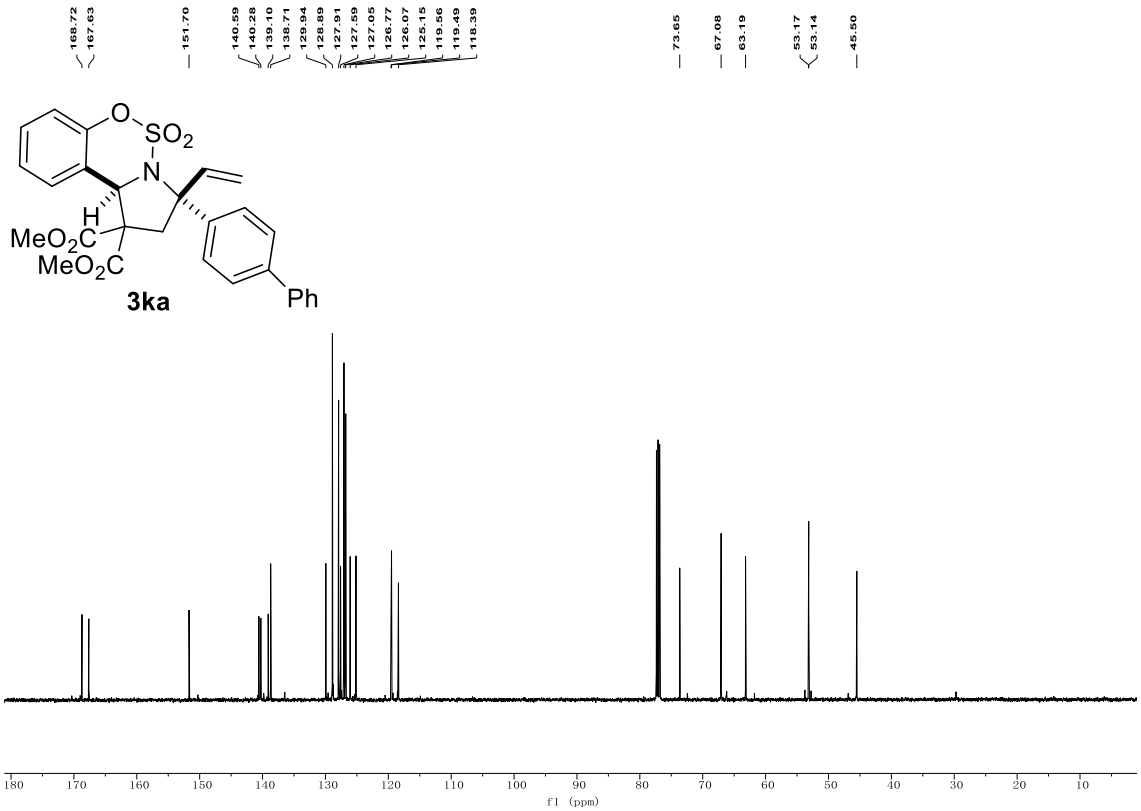
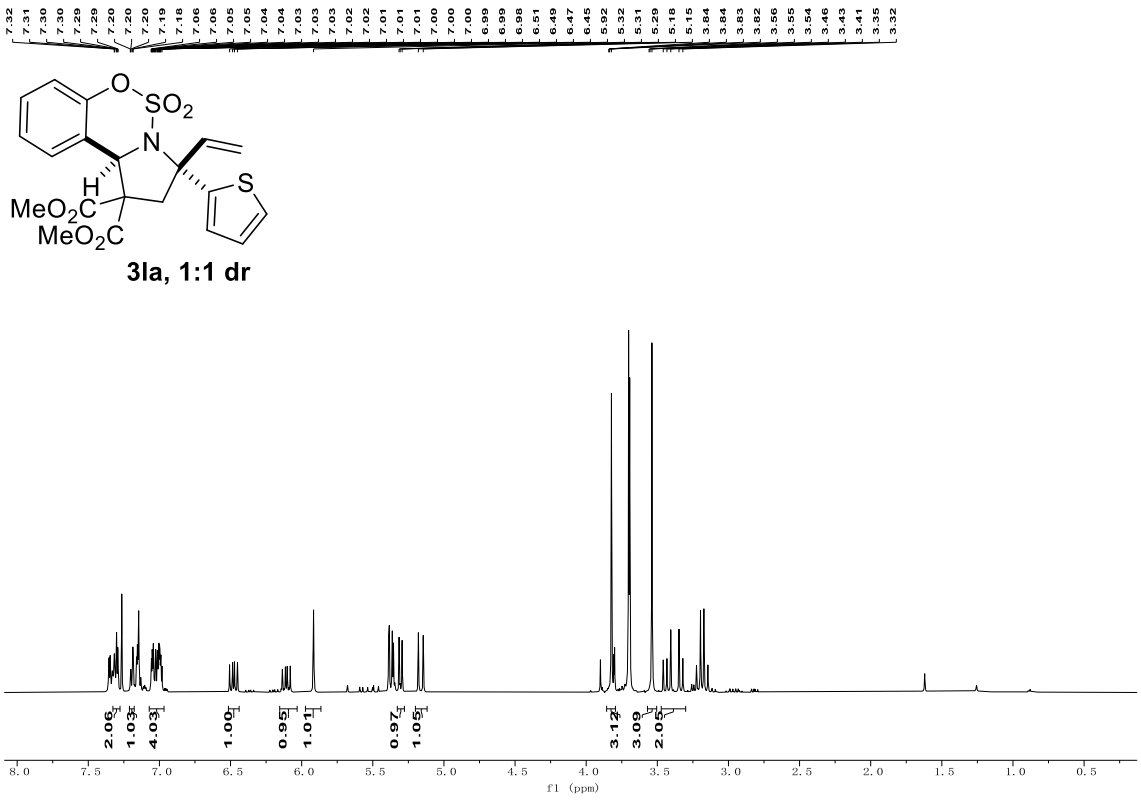
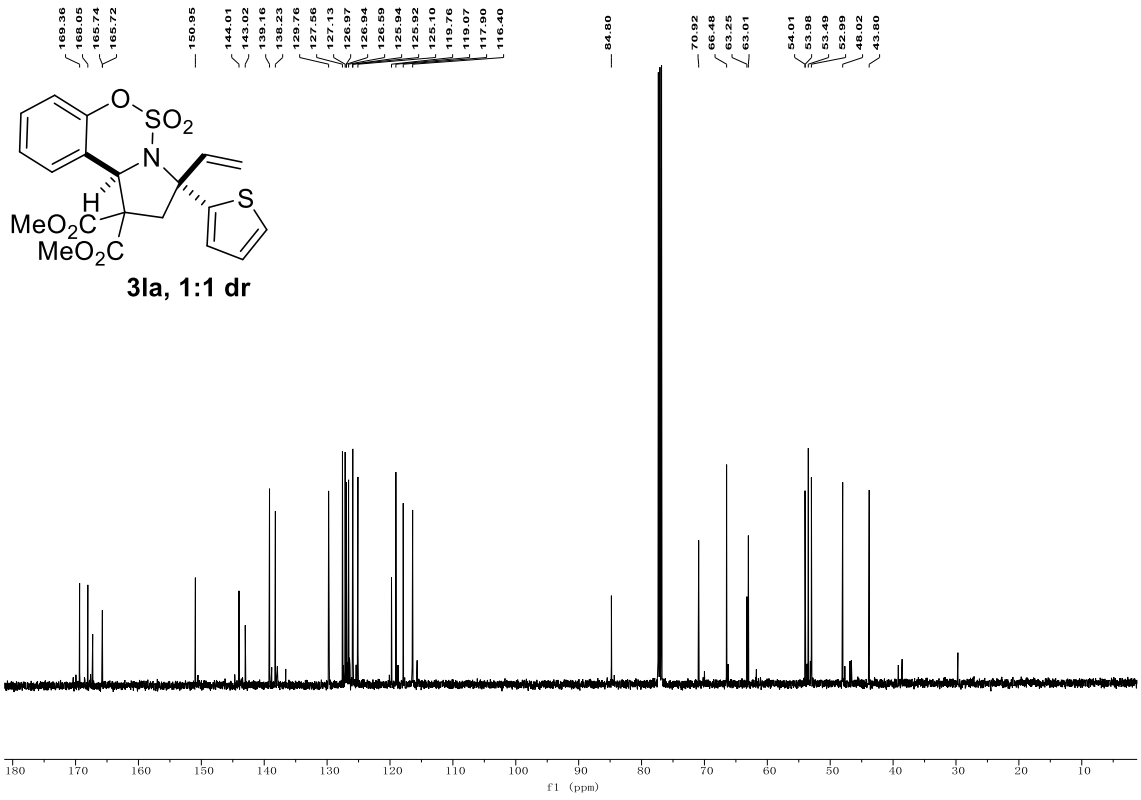


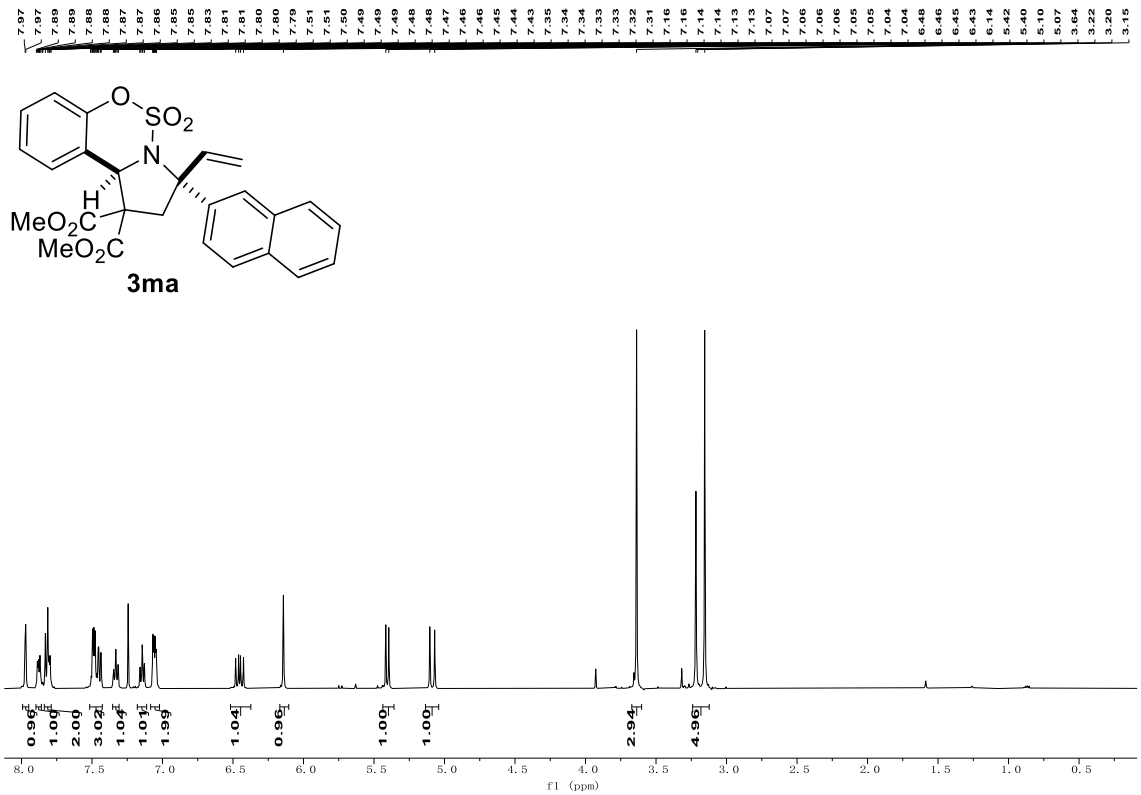
^{1}H NMR (500 MHz, $CDCl_3$)



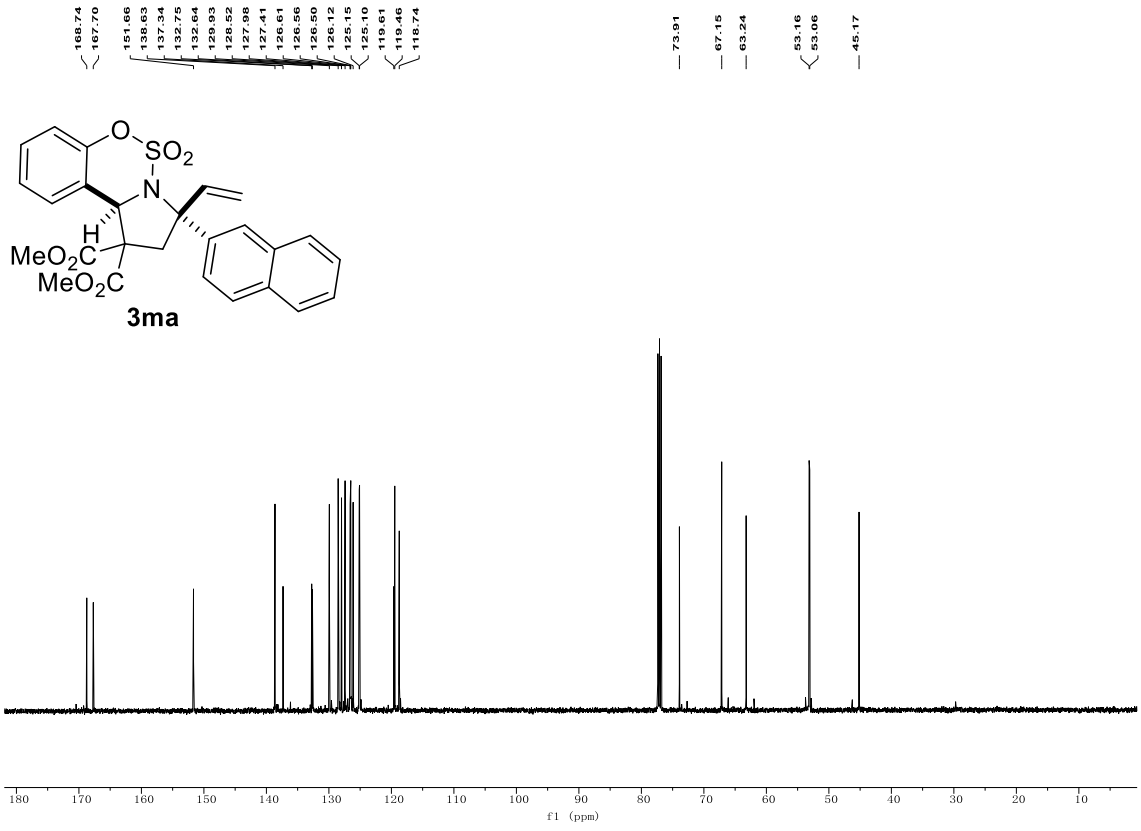
^{13}C NMR (126 MHz, $CDCl_3$)



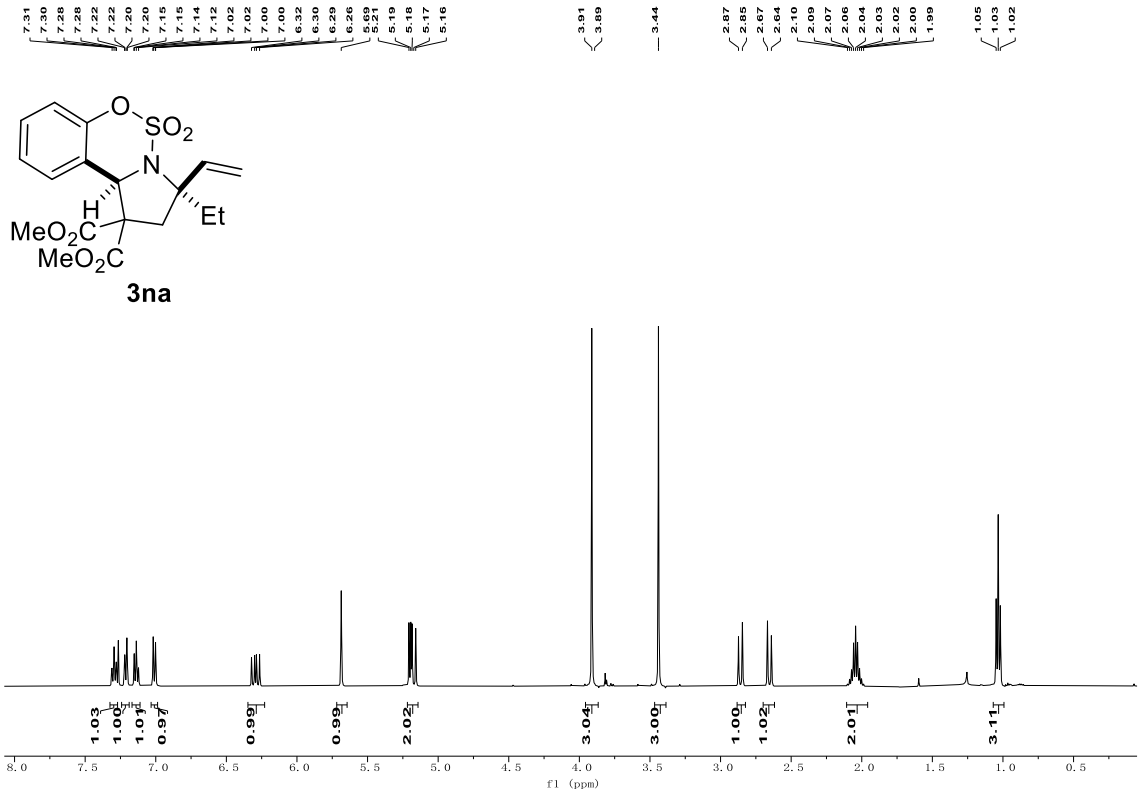
^{1}H NMR (500 MHz, $CDCl_3$)



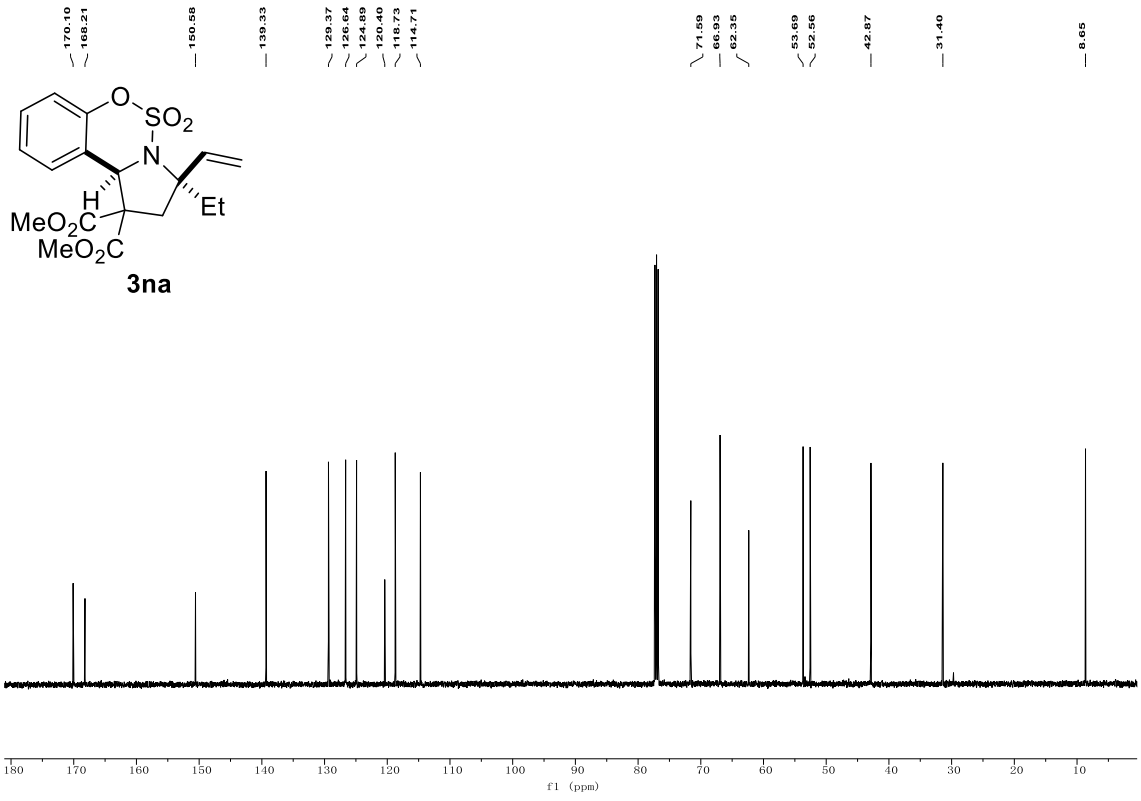
^{13}C NMR (126 MHz, $CDCl_3$)



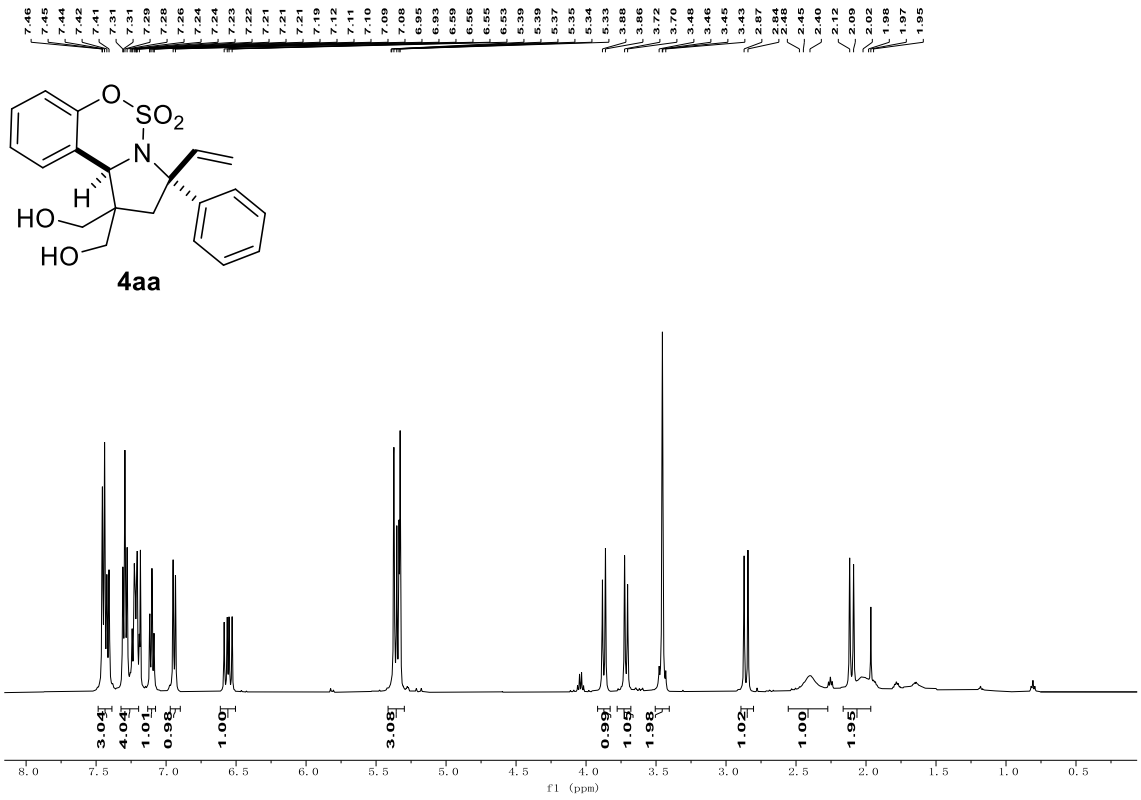
^{1}H NMR (500 MHz, $CDCl_3$)



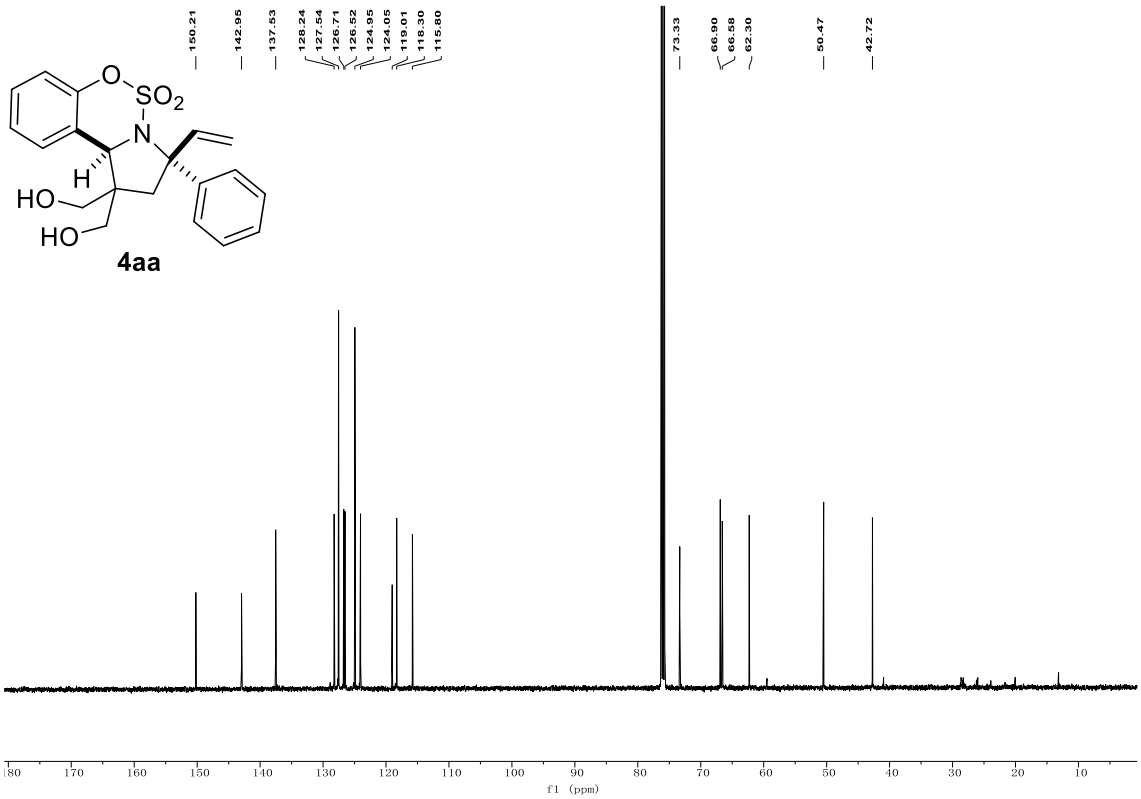
^{13}C NMR (126 MHz, $CDCl_3$)



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

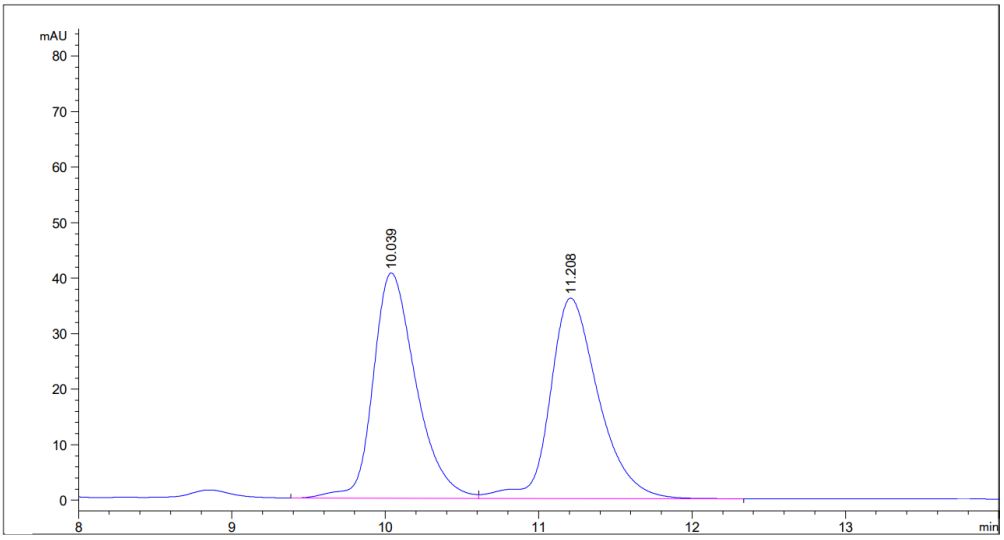


^{13}C NMR (126 MHz, $CDCl_3$)



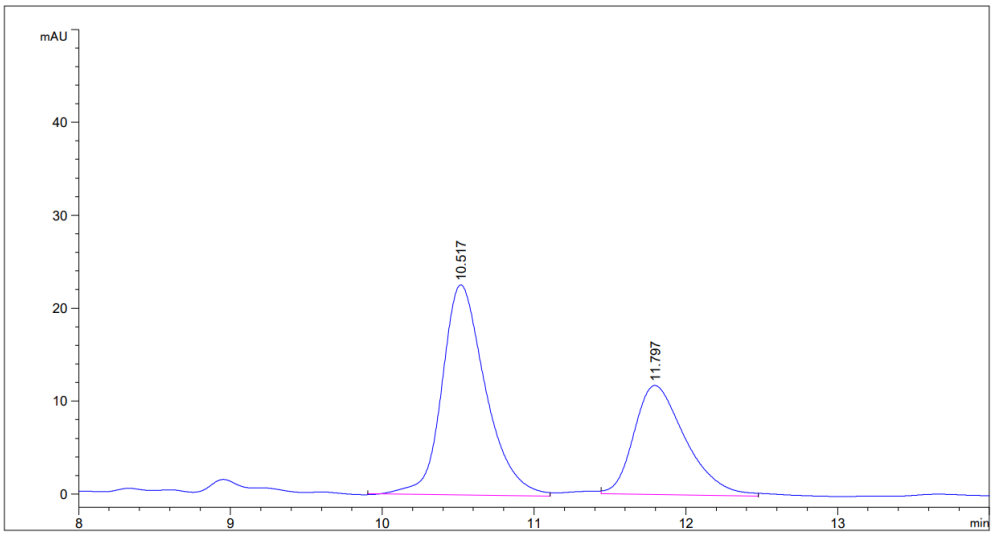
HPLC Chromatogram of Product 3aa

HPLC chromatogram of racemic product **3aa**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.039	BV	0.2951	786.57825	40.58231	49.7736
2	11.208	VB	0.3326	793.73364	36.09402	50.2264

HPLC chromatogram of chiral product **3aa**

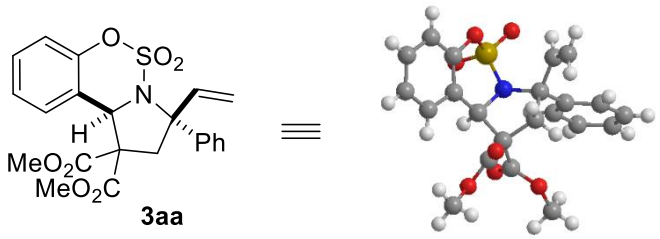


Peak #	Ret Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.517	MM R	0.3320	450.32135	22.60950	62.0011
2	11.797	MM R	0.3922	275.99091	11.72741	37.9989

X-ray Crystallographic Data of Product 3aa

Crystallographic data for **3aa** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2366186. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request- @ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from ethyl acetate/ petroleum ether(V/V=5/1) at RT. X-ray structure of complex **3aa** with 50% ellipsoid probability Crystal data.



3aa

Table 1 Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{22}H_{21}NO_7S$
Formula weight	443.46
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.98380(10)
b/Å	20.9681(2)
c/Å	11.6909(2)
α/°	90
β/°	109.1210(10)
γ/°	90
Volume/Å^3	2080.75(5)
Z	4
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	1.781
F(000)	928.0
Crystal size/mm^3	0.06 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.434 to 135.928
Index ranges	$-10 \le h \le 10$, $-24 \le k \le 25$, $-12 \le l \le 13$
Reflections collected	20398
Independent reflections	3749 [R_{int} = 0.0323, R_{sigma} = 0.0177]
Data/restraints/parameters	3749/0/283
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.1063
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.1072
Largest diff. peak/hole / e Å^{-3}	0.34/-0.41