

## *Supporting Information*

# **Synthesis of 3,4-Disubstituted Maleimide Derivatives via Phosphine-Catalyzed Isomerization of $\alpha$ -Succinimide Substituted Allenates Cascade $\gamma'$ -Addition with Aryl Imines**

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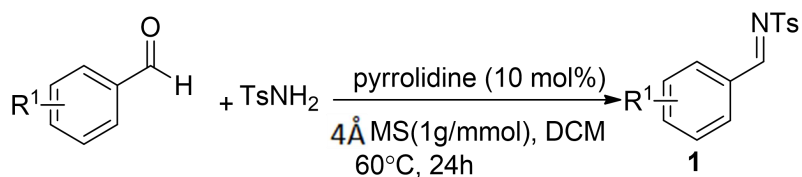
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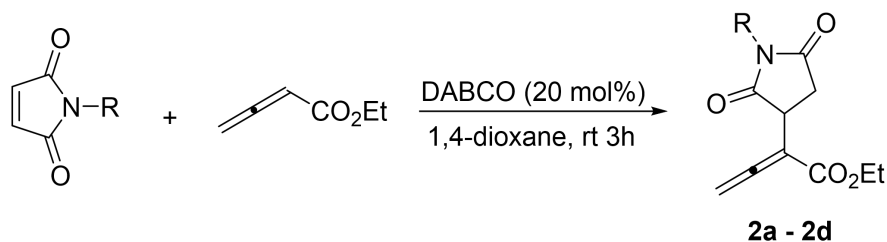
## General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were filtered and dried according to standard procedures ((1) Filter the solvents using vacuum filtration (2) Add anhydrous calcium chloride, stir and heat to reflux overnight (3) Collect the solvent by distillation (4) Store in a brown bottle and seal it) before use. All reactions were performed in dry glass vessels under nitrogen and magnetic stirring. The reaction was monitored by thin layer chromatography (TLC) on silica precoated glass plates. The chromatogram was viewed under 254 nm UV light. Qingdao Marine flash silica gel (100-200 mesh) (Qingdao, China) is used for flash column chromatography. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{CDCl}_3$  were recorded using a 500 MHz NMR instrument. Melting point was measured using an X-4 digital micromelting point meter (Shanghai, China). Accurate mass measurements were made using Agilent instruments and ESI-MS technology (Santa Clara, CA, USA). X-ray crystallographic data were obtained using using a Bruker D8 VENTURE instrument (Billerica, Germany).

**General Procedure for Synthesis of N-tosyl imines **1**<sup>[1]</sup> and  $\alpha$ -Succinimide-Substituted Allenolate **2**<sup>[2]</sup>**



Molecular Sieves (MS) 4Å was preactivated by microwave and dried under vacuum. A screw capped vial was charged with aldehyde (1.2 mmol), TsNH<sub>2</sub> (1.0 mmol) and preactivated MS 4Å (1.0 g). Dried dichloromethane (3.0 mL) and pyrrolidine (6.22  $\mu$ L, 0.10 mmol) were then added to the mixture. The resultant mixture was stirred at 60 °C for 24 h. The mixture was cooled to rt and filtered through a short pad of Celite<sup>®</sup>. The organic phase was concentrated under reduced pressure and the crude product was purified by crystallization (hexane/ethyl acetate system). The resulting solid was collected by filtration and then dried under vacuum.



Maleimide (0.15 mmol), allene (0.30 mmol), DABCO (0.030 mmol) , and 1,4-dioxane (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for 3 h or at room temperature for 3 h, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (PE/EA= 4/1~2/1) to afford products **2a-2d** .

[1] S. Morales, F.G. Guijarro, J. G. Ruano, M. B. Cid, *J. Am. Chem. Soc.* **2014**, 136, 1082.

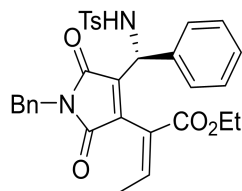
[2] Zhao Q Y, Pei C K, Guan X Y, et al. *Adv. Synth. Catal.* **2011**, 353, 1973 – 1979.

### **General Procedure for $\gamma'$ -addition reaction of N-tosyl imines and $\alpha$ -Succinimide-Substituted Allenolate**

Under argon atmosphere, to a mixture of N-tosyl imines **1** (0.10 mmol),  $\alpha$ -succinimide substituted allenolate **2** (0.15 mmol), catalyst  $\text{PR}_3$  (20 mol %, 0.02 mmol) and the additive (30 mol %, 0.03 mmol) in a Schlenk tube, 2 mL of DCM was added at room temperature. 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 (EtOAc / PE) to afford the corresponding products **3**.

### Characterization Data of the Products 3

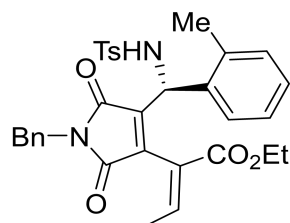
#### Ethyl (E)-2-(1-benzyl-4-(((4-methylphenyl)sulfonamido)(phenyl)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3aa)



**3aa**

White solid, 81% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 130.0- 131.0°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J$  = 7.9 Hz, 2H), 7.28 – 7.17 (m, 6H), 7.11 – 7.03 (m, 3H), 7.01 – 6.97 (m, 3H), 6.20 (s, 1H), 5.40 (d,  $J$  = 9.5 Hz, 1H), 4.55 (s, 2H), 4.12 – 3.84 (m, 2H), 2.25 (s, 3H), 1.54 (d,  $J$  = 5.6 Hz, 3H), 1.01 (t,  $J$  = 6.2 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 167.7, 163.2, 146.2, 142.3, 139.5, 136.6, 135.8, 134.8, 134.2, 128.4, 127.9, 127.7, 127.7, 127.5, 127.1, 127.08, 126.9, 126.0, 125.95, 125.8, 125.7, 121.1, 60.5, 52.7, 40.9, 20.4, 15.4, 12.9. HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  581.1722, found 581.1727.

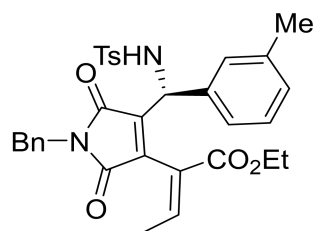
#### Ethyl (E)-2-(1-benzyl-4-(((4-methylphenyl)sulfonamido)(o-tolyl)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ba)



**3ba**

White solid, 83% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 124- 125°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J$  = 8.0 Hz, 2H), 7.25 – 7.18 (m, 6H), 7.10 (dd,  $J$  = 18.3, 7.5 Hz, 2H), 7.00 (t,  $J$  = 8.1 Hz, 2H), 6.96 – 6.87 (m, 2H), 6.24 – 6.02 (m, 1H), 5.64 (d,  $J$  = 9.3 Hz, 1H), 4.60 – 4.45 (m, 2H), 4.12 – 3.87 (m, 2H), 2.26 (s, 3H), 2.06 (s, 3H), 1.41 (d, 3H), 1.03 (t, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.15, 168.8, 164.3, 147.2, 143.3, 140.6, 138.0, 137.7, 135.9, 135.0, 133.8, 129.4, 129.3, 128.8, 128.2, 127.9, 127.0, 126.8, 122.2, 61.5, 53.7, 41.9, 26.9, 21.5, 21.0, 16.4, 13.9. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  595.1879, found 595.1883.

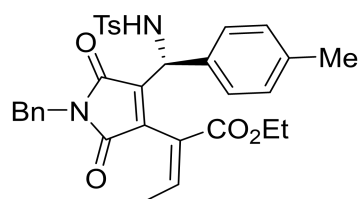
**Ethyl (E)-2-(1-benzyl-4-(((4-methylphenyl)sulfonamido)(m-tolyl)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ca)**



**3ca**

White solid, 77% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 93.5- 94.5°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.19 (m, 6H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.71 (s, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 5.35 (d, *J* = 9.6 Hz, 1H), 4.56 (s, 2H), 4.09 – 3.88 (m, 2H), 2.26 (s, 3H), 2.08 (s, 3H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.1, 167.8, 163.3, 146.0, 144.3, 142.2, 139.5, 137.3, 136.7, 135.6, 134.9, 134.1, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6, 127.2, 127.1, 126.9, 126.7, 126.5, 126.0, 122.9, 121.2, 60.8, 60.5, 52.8, 40.9, 28.7, 20.4, 20.2, 15.3, 13.0, 12.9. HRMS (ESI) calcd for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>NaS, [M+Na]<sup>+</sup> 595.1879, found 595.1881.

**Ethyl (E)-2-(1-benzyl-4-(((4-methylphenyl)sulfonamido)(p-tolyl)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3da)**

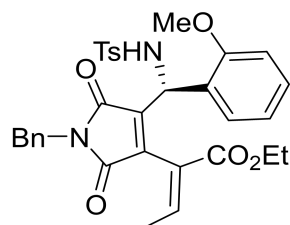


**3da**

White solid, 75% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 96-97°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 6H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.94 (s, 4H), 6.22 – 6.05 (m, 1H), 5.41 (d, *J* = 9.6 Hz, 1H), 4.62 (s, 2H), 4.18 – 3.97 (m, 3H), 2.33 (s, 3H), 2.24 (s, 3H), 1.62 (d, *J* = 7.4 Hz, 3H), 1.09 (t, *J* = 11.8, 4.8 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.1, 167.6, 163.4, 145.9, 142.2, 140.0, 136.6, 134.9, 134.3, 129.7, 128.3, 127.7, 127.1, 126.9, 126.1,

126.0, 125.3, 121.3, 60.6, 40.9, 28.7, 20.4, 18.2, 15.2, 12.9. HRMS (ESI) calcd for  $C_{32}H_{32}N_2O_6NaS$ ,  $[M+Na]^+$  595.1879, found 595.1873.

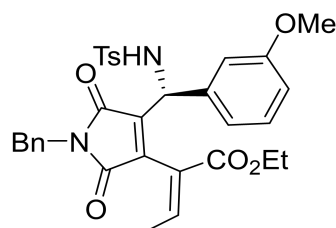
**Ethyl (E)-2-(1-benzyl-4-((2-methoxyphenyl)((4-methylphenyl)sulfonamido)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ea)**



**3ea**

White solid, 78% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 65–66°C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.50 (d,  $J$  = 8.1 Hz, 2H), 7.25 – 7.17 (m, 6H), 7.05 (dd,  $J$  = 13.5, 7.7 Hz, 2H), 6.99 (d,  $J$  = 8.1 Hz, 2H), 6.64 (t,  $J$  = 7.5 Hz, 1H), 6.52 (d,  $J$  = 8.2 Hz, 1H), 5.69 (d,  $J$  = 9.9 Hz, 1H), 4.54 (s, 2H), 4.05 (dd,  $J$  = 14.3, 7.1 Hz, 2H), 3.43 (s, 3H), 2.24 (s, 3H), 1.53 (dd,  $J$  = 47.1 Hz, 3H), 1.46 – 1.38 (m, 1H), 1.04 (m, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  170.1, 168.6, 167.9, 154.8, 142.0, 139.9, 136.7, 135.1, 128.1, 127.9, 127.6, 127.1, 126.8, 126.0, 124.2, 121.5, 119.5, 109.0, 60.3, 59.4, 53.8, 40.7, 20.4, 15.0, 13.2, 13.0. HRMS (ESI) calcd for  $C_{32}H_{32}N_2O_7NaS$ ,  $[M+Na]^+$  611.1828, found 611.1833.

**Ethyl (E)-2-(1-benzyl-4-((3-methoxyphenyl)((4-methylphenyl)sulfonamido)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3fa)**

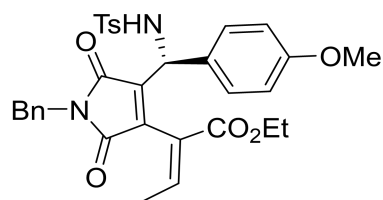


**3fa**

White solid, 73% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 103.5–104.5°C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.49 (d,  $J$  = 8.3 Hz, 2H), 7.25 – 7.17 (m, 7H), 7.04 – 6.95 (m, 3H), 6.64 – 6.54 (m, 2H), 6.53 – 6.47 (m, 1H), 6.16 (s, 1H), 5.36 (d,  $J$  = 9.0 Hz, 1H), 4.56 (s, 2H), 4.04 (q,  $J$  = 8.6, 5.7 Hz, 2H), 3.56 (s, 3H), 2.26 (s, 3H), 1.57 (d,  $J$  = 7.0 Hz, 3H), 1.04 (t, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  170.1,

169.1, 167.7, 163.3, 158.8, 146.1, 142.3, 139.3, 137.2, 136.7, 134.8, 134.2, 128.7, 128.4, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 126.9, 126.0, 121.1, 118.1, 112.9, 111.2, 60.5, 59.4, 54.1, 40.9, 20.4, 20.0, 15.4, 13.2, 12.9. HRMS (ESI) calcd for  $C_{32}H_{32}N_2O_7NaS$ ,  $[M+Na]^+$  611.1828, found 611.1827.

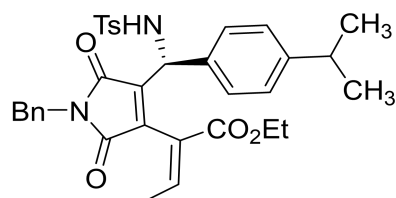
**Ethyl (E)-2-(1-benzyl-4-((4-methoxyphenyl)((4-methylphenyl)sulfonamido)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ga)**



**3ga**

White solid, 86% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 71.5- 72.5°C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.47 (d,  $J$  = 8.3 Hz, 2H), 7.27 – 7.23 (m, 3H), 7.23 – 7.19 (m, 3H), 7.01 (d,  $J$  = 8.0 Hz, 2H), 6.94 – 6.88 (m, 2H), 6.63 – 6.53 (m, 2H), 6.08 (s, 1H), 5.32 (d,  $J$  = 9.5 Hz, 1H), 4.55 (s, 2H), 4.12 – 3.94 (m, 2H), 3.65 (s, 3H), 2.27 (s, 3H), 1.56 (d,  $J$  = 6.2 Hz, 3H), 1.10 – 0.99 (m, 3H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  169.2, 167.8, 163.3, 158.4, 146.1, 142.2, 139.6, 136.7, 134.9, 133.8, 128.4, 127.9, 127.7, 127.2, 127.1, 126.9, 126.0, 121.2, 113.0, 60.5, 54.3, 52.4, 40.9, 20.4, 15.4, 12.9. HRMS (ESI) calcd for  $C_{32}H_{32}N_2O_7NaS$ ,  $[M+Na]^+$  611.1828, found 611.1830.

**Ethyl (E)-2-(1-benzyl-4-((4-isopropylphenyl)((4-methylphenyl)sulfonamido)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ha)**

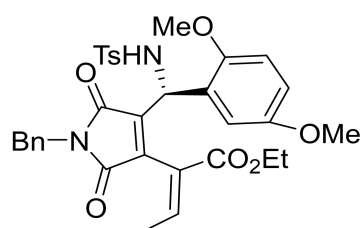


**3ha**

White solid, 72% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 103- 104°C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.44 (d,  $J$  = 8.3 Hz, 2H), 7.28 – 7.19 (m, 6H), 6.97 (d,  $J$  = 8.1 Hz, 2H), 6.89 – 6.88 (m, 3H), 6.17 (d,  $J$  = 7.4 Hz, 1H), 5.34 (d,  $J$

= 9.6 Hz, 1H), 4.56 (s, 2H), 4.09 – 3.84 (m, 2H), 2.71 (dt,  $J$  = 13.8, 6.9 Hz, 1H), 2.24 (s, 3H), 1.57 (d,  $J$  = 6.3 Hz, 3H), 1.08 (s, 3H), 1.07 (s, 3H), 0.99 (t,  $J$  = 6.7 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 167.8, 163.2, 148.0, 146.1, 142.1, 139.5, 136.6, 134.8, 133.9, 133.0, 128.3, 127.7, 127.1, 126.9, 126.0, 125.9, 125.7, 121.1, 60.4, 52.8, 40.9, 32.7, 22.9, 22.8, 20.4, 15.3, 12.9. HRMS (ESI) calcd for  $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  623.2186, found 623.2182.

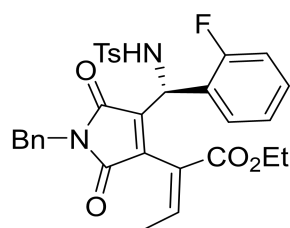
**Ethyl (E)-2-(1-benzyl-4-((2,5-dimethoxyphenyl)((4-methylphenyl)sulfonamido)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ia)**



**3ia**

White solid, 84% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 76–77°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 8.1 Hz, 2H), 7.24 – 7.21 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 – 7.02 (m, 1H), 6.99 (d,  $J$  = 8.1 Hz, 2H), 6.66 – 6.58 (m, 1H), 6.58 – 6.49 (m, 1H), 6.49 – 6.33 (m, 2H), 5.68 (d,  $J$  = 9.9 Hz, 1H), 4.54 (s, 2H), 4.12 – 3.89 (m, 2H), 3.54 (s, 3H), 3.40 (s, 3H), 2.24 (s, 3H), 1.64 – 1.48 (m, 3H), 1.11 – 0.97 (m, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 167.9, 152.4, 149.0, 142.0, 139.7, 136.7, 135.1, 128.1, 127.8, 127.6, 127.1, 126.8, 126.0, 124.9, 121.5, 113.0, 110.0, 60.4, 54.6, 54.3, 40.8, 20.4, 15.1, 12.9. HRMS (ESI) calcd for  $\text{C}_{33}\text{H}_{34}\text{N}_2\text{O}_8\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  641.1934, found 641.1934.

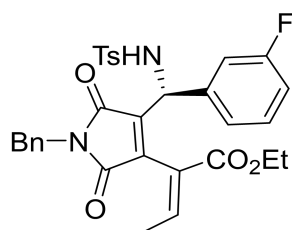
**Ethyl (E)-2-(1-benzyl-4-((2-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ja)**



**3ja**

White solid, 51% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 104.1- 105.1°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.29 (m, 1H), 7.27 – 7.20 (m, 4H), 7.18 – 7.14 (m, 2H), 7.11 – 7.08 (m, 1H), 7.07 – 7.05 (m, 2H), 7.04 – 7.01 (m, 1H), 6.93 (s, 1H), 6.48 (s, 1H), 5.88 (d, *J* = 9.6 Hz, 1H), 4.55 (s, 2H), 4.15 – 3.98 (m, 2H), 2.28 (s, 3H), 1.45 (d, *J* = 5.6 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 167.6, 145.7, 142.2, 139.4, 136.8, 134.9, 134.23, 128.5, 128.3, 128.2, 127.7, 127.0, 126.8, 126.1, 121.0, 60.7, 41.0, 28.7, 20.5, 15.3, 13.0. HRMS (ESI) calcd for C<sub>31</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>6</sub>NaS, [M+Na]<sup>+</sup> 599.1628, found 599.1630.

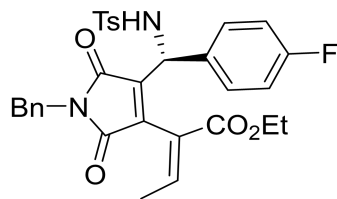
**Ethyl (E)-2-(1-benzyl-4-((3-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ka)**



**3ka**

White solid, 54% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 107.0- 108.0°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.23 – 7.20 (m, 2H), 7.09 – 6.99 (m, 3H), 6.85 – 6.73 (m, 2H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 4.56 (s, 2H), 4.12 – 3.96 (m, 2H), 2.27 (s, 3H), 1.59 (dd, *J* = 12.9, 7.3 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.9, 167.5, 163.3, 162.7, 160.7, 146.3, 142.5, 138.9, 138.4, 138.4, 136.6, 134.7, 134.5, 129.3, 129.2, 128.4, 127.8, 127.2, 127.0, 125.9, 121.5, 121.0, 114.2, 114.0, 113.0, 112.9, 60.7, 52.0, 41.0, 28.7, 20.4, 15.4, 12.9. HRMS (ESI) calcd for C<sub>31</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>6</sub>NaS, [M+Na]<sup>+</sup> 599.1628, found 599.1633.

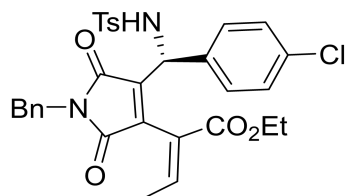
**Ethyl (E)-2-(1-benzyl-4-((4-fluorophenyl)((4-methylphenyl)sulfonamido)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3la)**



**3la**

White solid, 67% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 100.5- 101.5°C; <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.19 (m, 6H), 7.06 – 6.94 (m, 4H), 6.76 (t, *J* = 8.6 Hz, 2H), 6.15 (d, *J* = 9.6 Hz, 1H), 5.39 (d, *J* = 9.5 Hz, 1H), 4.56 (s, 2H), 4.12 – 3.92 (m, 2H), 2.27 (s, 3H), 1.57 (d, *J* = 7.3 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.0, 167.6, 163.3, 162.3, 160.4, 146.3, 142.5, 139.2, 136.6, 134.7, 134.2, 131.7, 131.7, 128.4, 127.8, 127.72, 127.66, 127.4, 127.2, 127.0, 125.9, 125.6, 121.0, 114.7, 114.5, 60.6, 52.1, 41.0, 28.7, 20.4, 15.4, 12.9. HRMS (ESI) calcd for C<sub>31</sub>H<sub>29</sub>FN<sub>2</sub>O<sub>6</sub>NaS, [M+Na]<sup>+</sup> 599.1628, found 599.1631.

**Ethyl (E)-2-(1-benzyl-4-((4-chlorophenyl)((4-methylphenyl)sulfonamido)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ma)**

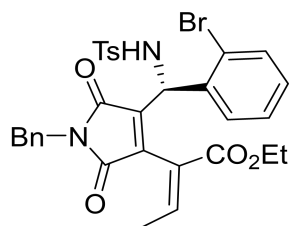


**3ma**

White solid, 65% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 74.0- 75.0°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.15 (m, 7H), 7.06 – 6.98 (m, 4H), 6.96 – 6.92 (m, 2H), 6.27 – 6.09 (m, 1H), 5.37 (d, *J* = 9.6 Hz, 1H), 4.55 (s, 2H), 4.13 – 3.93 (m, 2H), 2.28 (s, 3H), 1.58 (d, *J* = 6.5 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.9, 167.5, 163.2, 146.4, 142.6, 138.9, 136.5, 134.7, 134.3, 133.1, 128.4, 127.8, 127.3, 127.2, 127.0, 125.9, 121.0, 60.6, 52.2, 41.0, 20.4, 15.5, 12.9. HRMS (ESI) calcd for C<sub>31</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>6</sub>NaS, [M+Na]<sup>+</sup> 615.1333, found 615.1340.

**Ethyl (E)-2-(1-benzyl-4-((2-bromophenyl)((4-methylphenyl)sulfonamido)-**

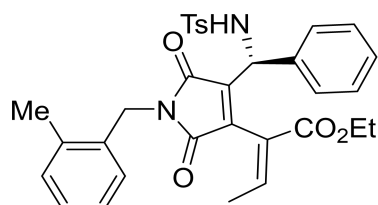
**methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3na)**



**3na**

White solid, 49% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 134.5- 135.5°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 8.2 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.23 – 7.20 (m, 2H), 7.09 – 6.99 (m, 3H), 6.85 – 6.73 (m, 2H), 6.70 (d,  $J$  = 9.6 Hz, 1H), 6.19 (d,  $J$  = 7.6 Hz, 1H), 5.42 (d,  $J$  = 9.6 Hz, 1H), 4.56 (s, 2H), 4.12 – 3.96 (m, 2H), 2.27 (s, 3H), 1.59 (dd,  $J$  = 12.9, 7.3 Hz, 3H), 1.07 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 145.8, 142.2, 139.8, 136.9, 136.1, 134.9, 131.8, 128.4, 128.3, 127.7, 126.9, 126.8, 126.1, 121.0, 60.8, 41.0, 28.7, 20.5, 15.4, 13.1. HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{29}\text{BrN}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  659.0827, found 659.0829.

**Ethyl (E)-2-(1-(2-methylbenzyl)-4-(((4-methylphenyl)sulfonamido)(phenyl)-methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ab)**

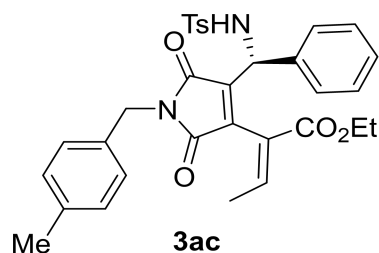


**3ab**

White solid, 59% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 119.0- 120.0°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J$  = 8.2 Hz, 2H), 7.25 (q,  $J$  = 7.2 Hz, 1H), 7.13 – 7.04 (m, 6H), 7.04 – 6.98 (m, 5H), 6.16 (s, 1H), 5.41 (d,  $J$  = 9.5 Hz, 1H), 4.58 (s, 2H), 4.09 – 3.92 (m, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 1.58 (d,  $J$  = 6.2 Hz, 3H), 1.03 (t,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 167.8, 163.2, 146.1, 142.3, 139.5, 136.6, 135.9, 134.9, 134.2, 132.6, 129.5, 128.4, 127.7, 127.1, 127.0, 126.8, 126.0, 125.8, 125.2, 121.1, 60.5, 52.7, 38.7, 28.7, 20.4, 18.3, 15.4, 12.9. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  595.1879, found 595.1882.

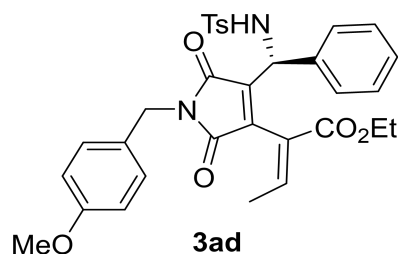
**Ethyl (E)-2-(1-(4-methylbenzyl)-4-(((4-methylphenyl)sulfonamido)(phenyl)-**

**ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate**



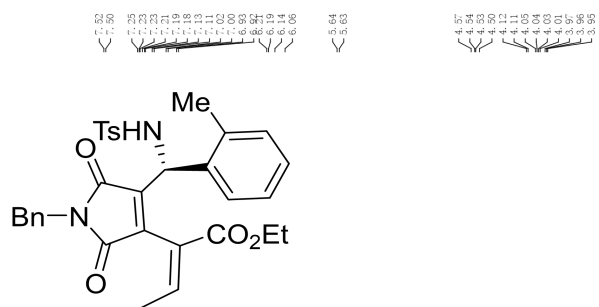
White solid, 65% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 103.3- 104.3°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J$  = 8.2 Hz, 2H), 7.23 (q,  $J$  = 7.3 Hz, 1H), 7.12 – 7.07 (m, 4H), 7.07 – 7.03 (m, 3H), 7.00 (d,  $J$  = 8.1 Hz, 4H), 6.23 – 6.11 (m, 1H), 5.39 (d,  $J$  = 9.5 Hz, 1H), 4.51 (s, 2H), 4.09 – 3.93 (m, 2H), 2.26 (s, 6H), 1.55 – 1.51 (m, 3H), 1.03 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 167.7, 163.3, 146.1, 142.3, 139.4, 136.7, 135.9, 134.2, 131.9, 128.4, 128.4, 127.7, 127.2, 127.1, 126.0, 125.8, 121.1, 60.5, 52.7, 40.7, 28.7, 20.4, 20.1, 15.4, 12.9. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_6\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  595.1879, found 595.1885.

**Ethyl (E)-2-(1-(4-methoxybenzyl)-4-(((4-methylphenyl)sulfonamido)(phenyl)methyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)but-2-enoate (3ad)**



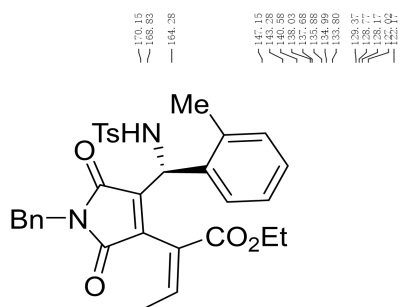
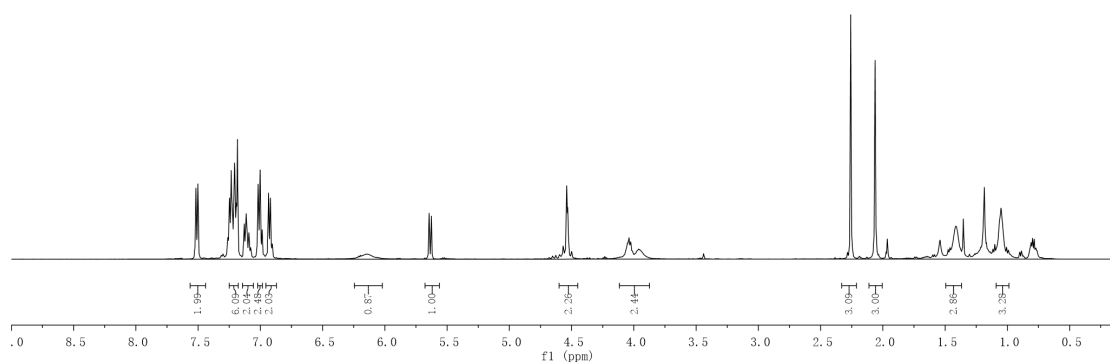
White solid, 64% yield. Purified by flash chromatography (12% EtOAc/PE). mp = 126.5- 127.5°C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J$  = 8.3 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.18 – 7.13 (m, 2H), 7.10 – 7.03 (m, 3H), 7.02 – 6.95 (m, 4H), 6.77 (dd,  $J$  = 6.7, 4.8 Hz, 2H), 6.19 (d,  $J$  = 7.8 Hz, 1H), 5.39 (d,  $J$  = 9.6 Hz, 1H), 4.49 (s, 2H), 4.10 – 3.92 (m, 2H), 3.72 (s, 3H), 2.25 (s, 3H), 1.53 (d,  $J$  = 6.8 Hz, 3H), 1.02 (t,  $J$  = 7.0 Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 167.8, 163.3, 158.3, 146.1, 142.3, 139.4, 136.6, 135.8, 134.1, 128.7, 128.4, 127.7, 127.1, 126.0, 125.8, 121.1, 113.1, 60.5, 54.3, 52.7, 40.4, 20.4, 15.4, 12.9. HRMS (ESI) calcd for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_7\text{NaS}$ ,  $[\text{M}+\text{Na}]^+$  611.1828, found 611.1832.

[illegible]



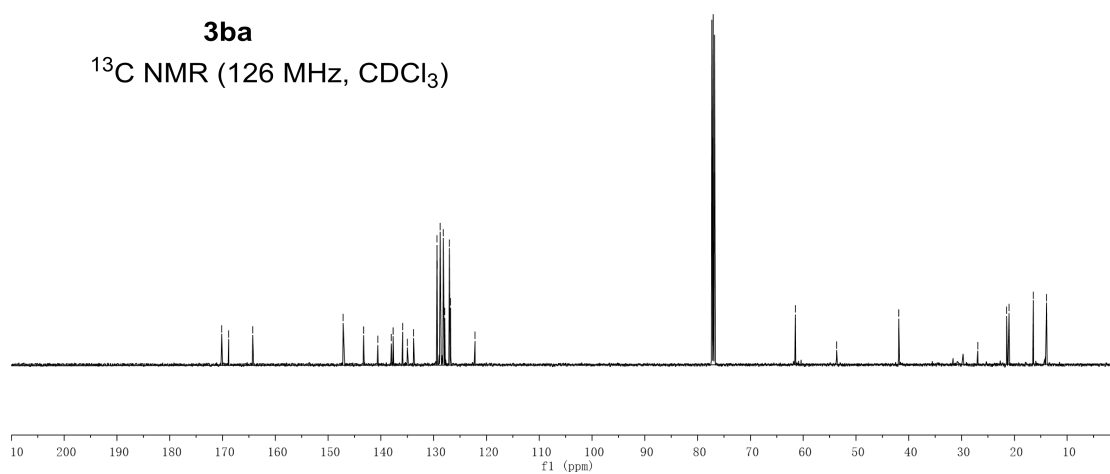
**3ba**

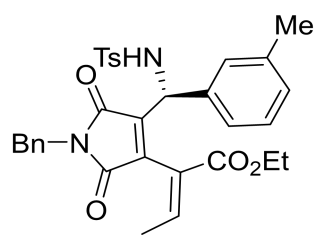
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



**3ba**

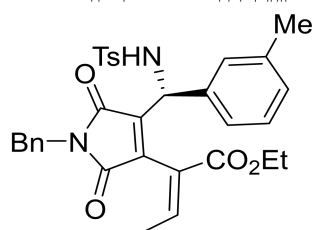
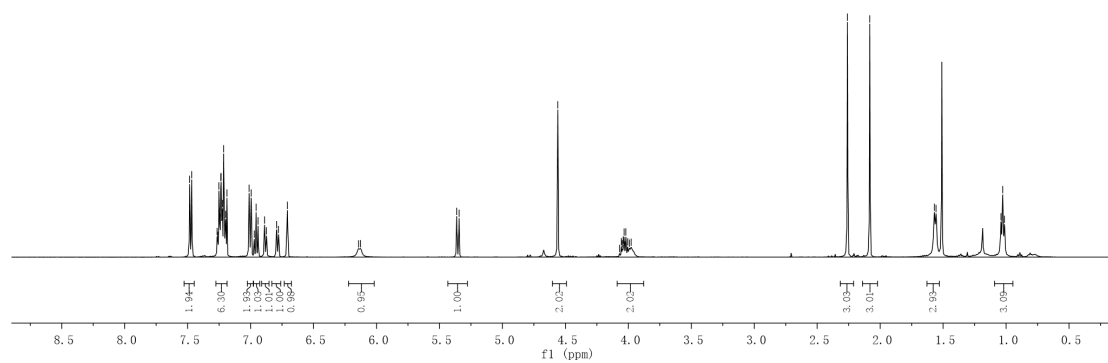
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)





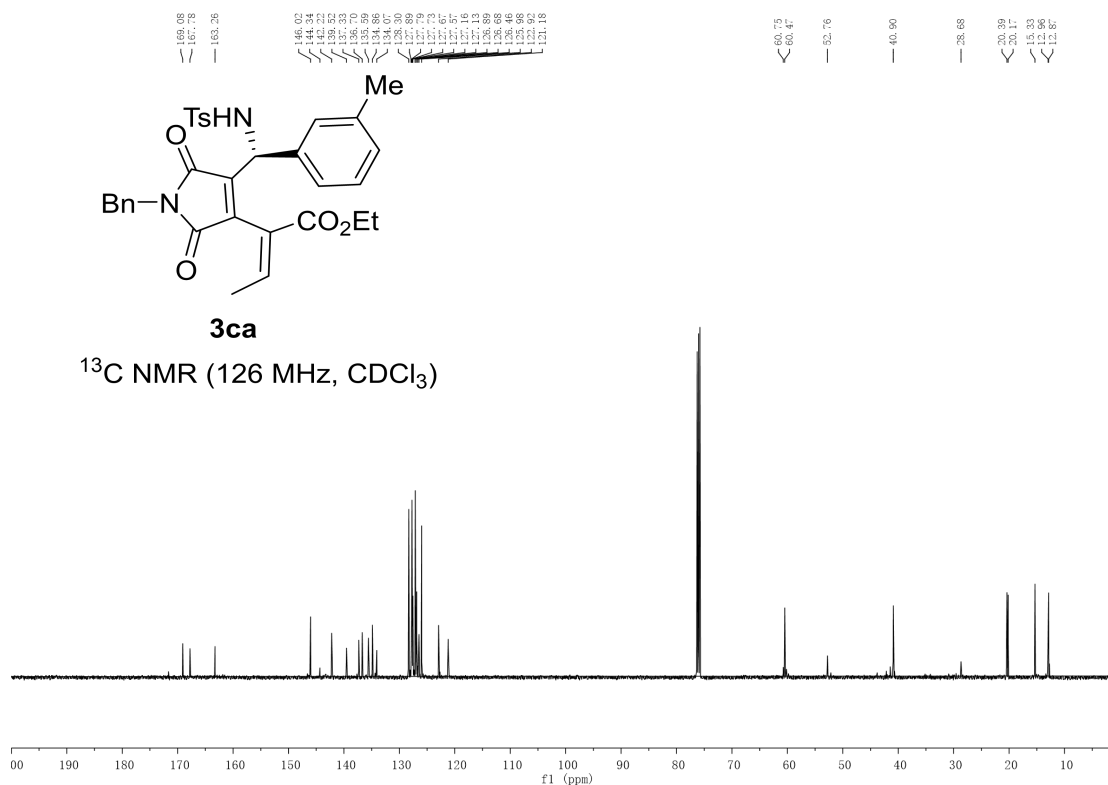
**3ca**

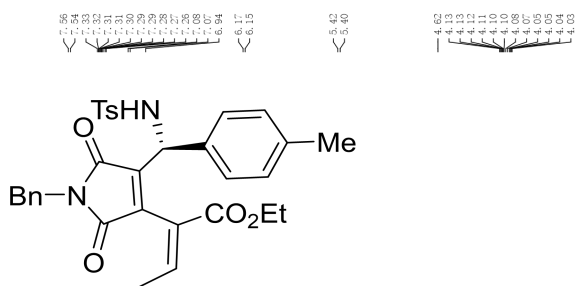
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



**3ca**

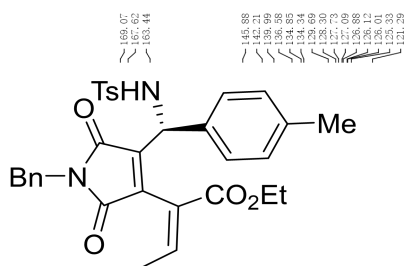
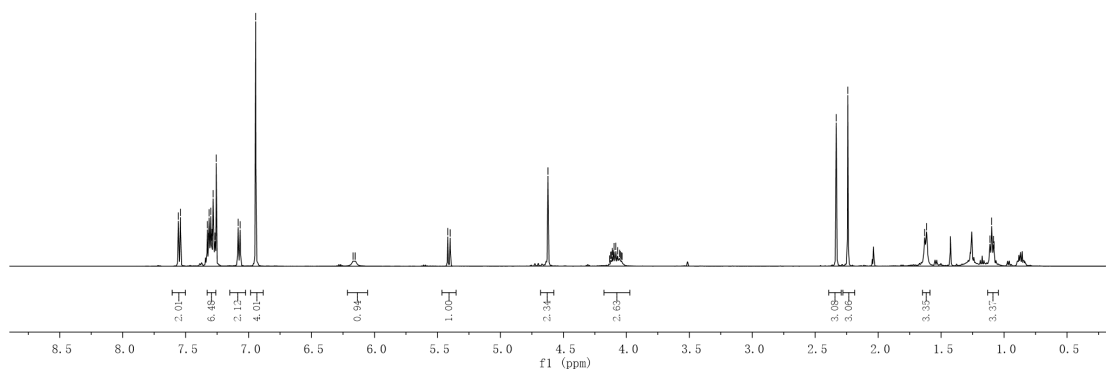
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)





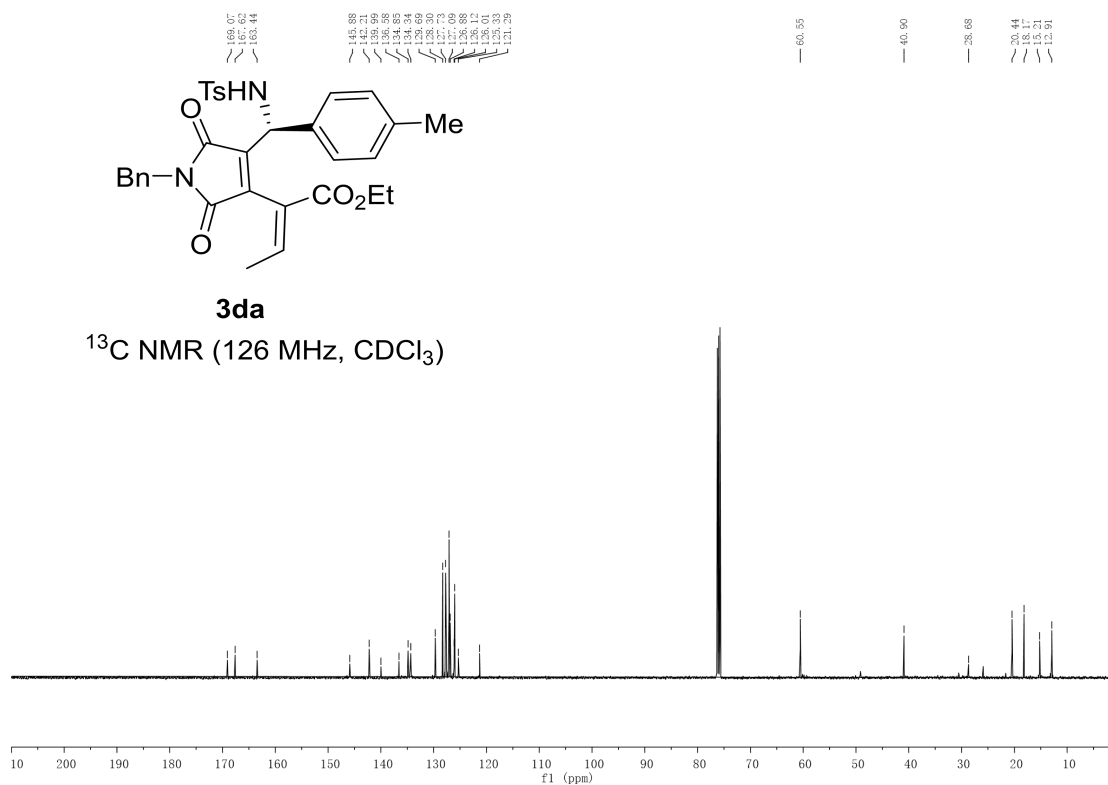
**3da**

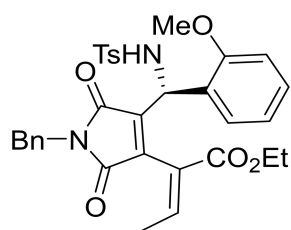
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



**3da**

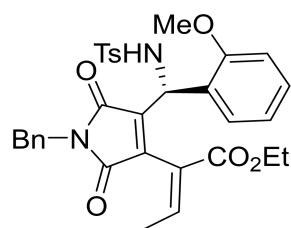
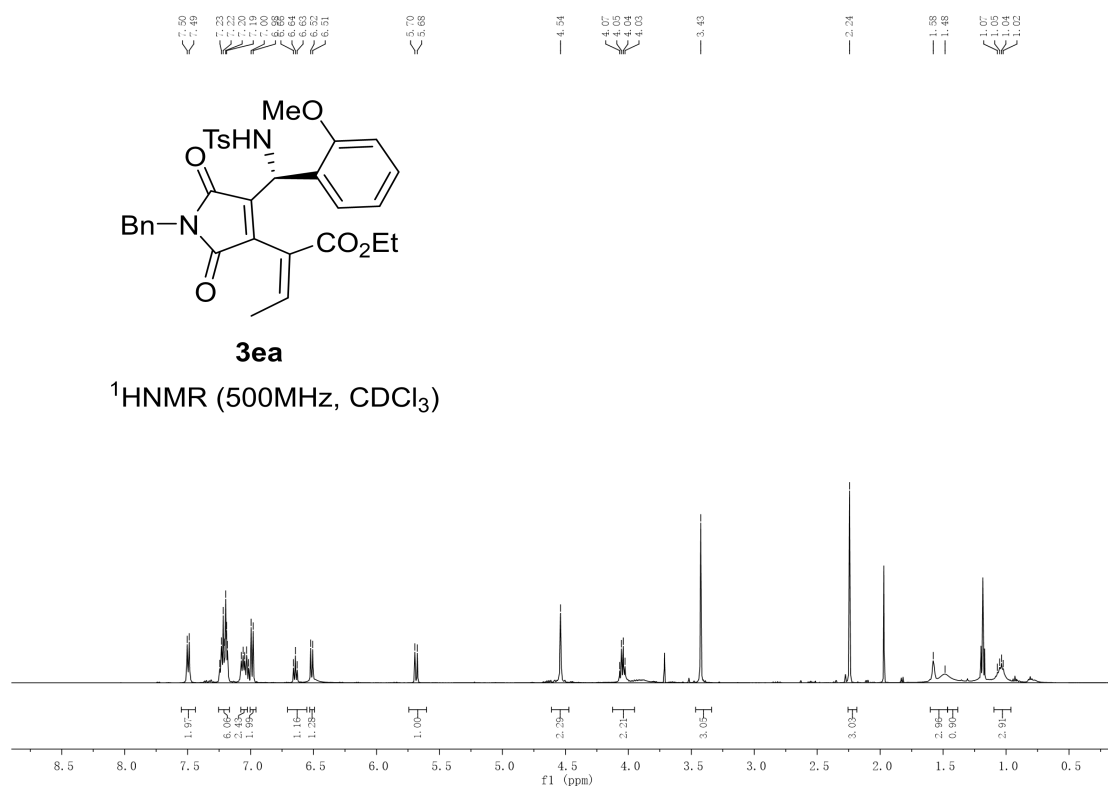
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)





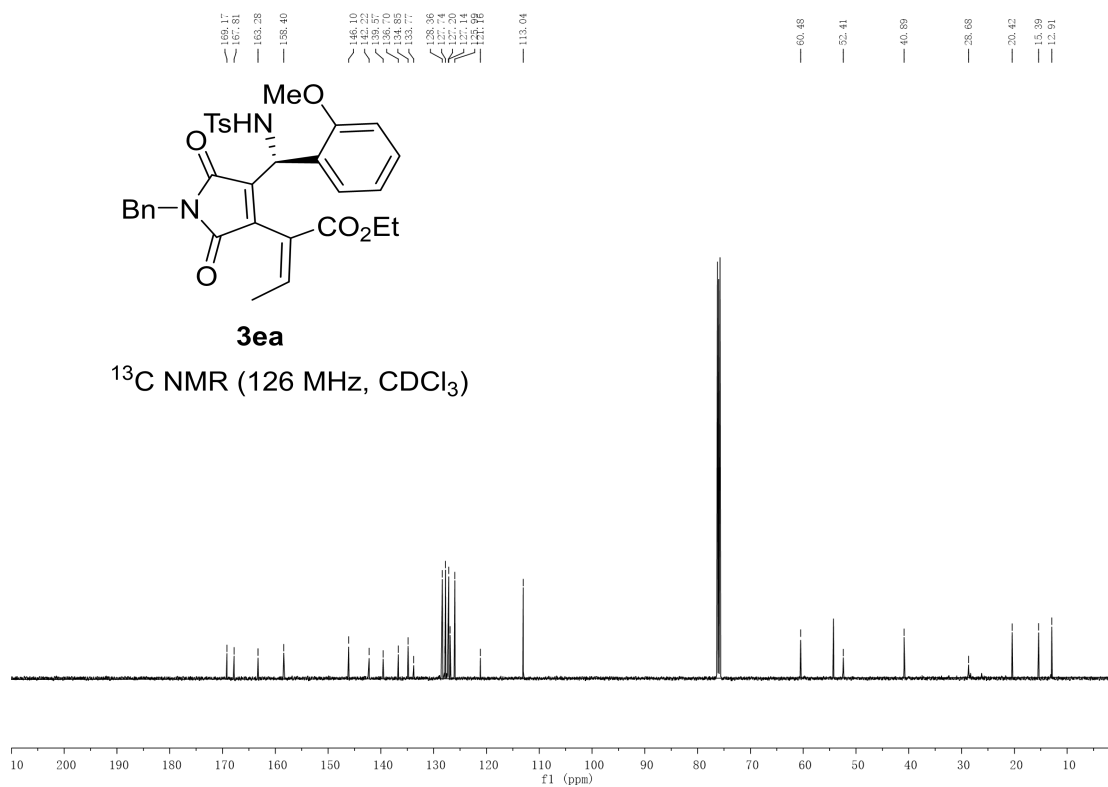
**3ea**

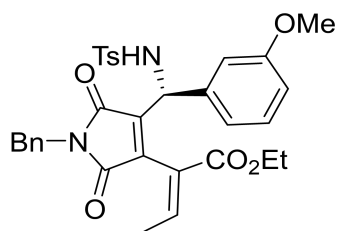
$^1\text{H}$ NMR (500MHz,  $\text{CDCl}_3$ )



**3ea**

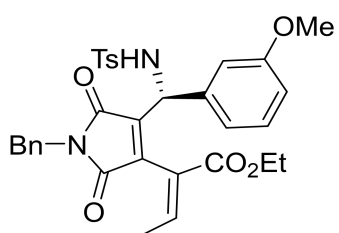
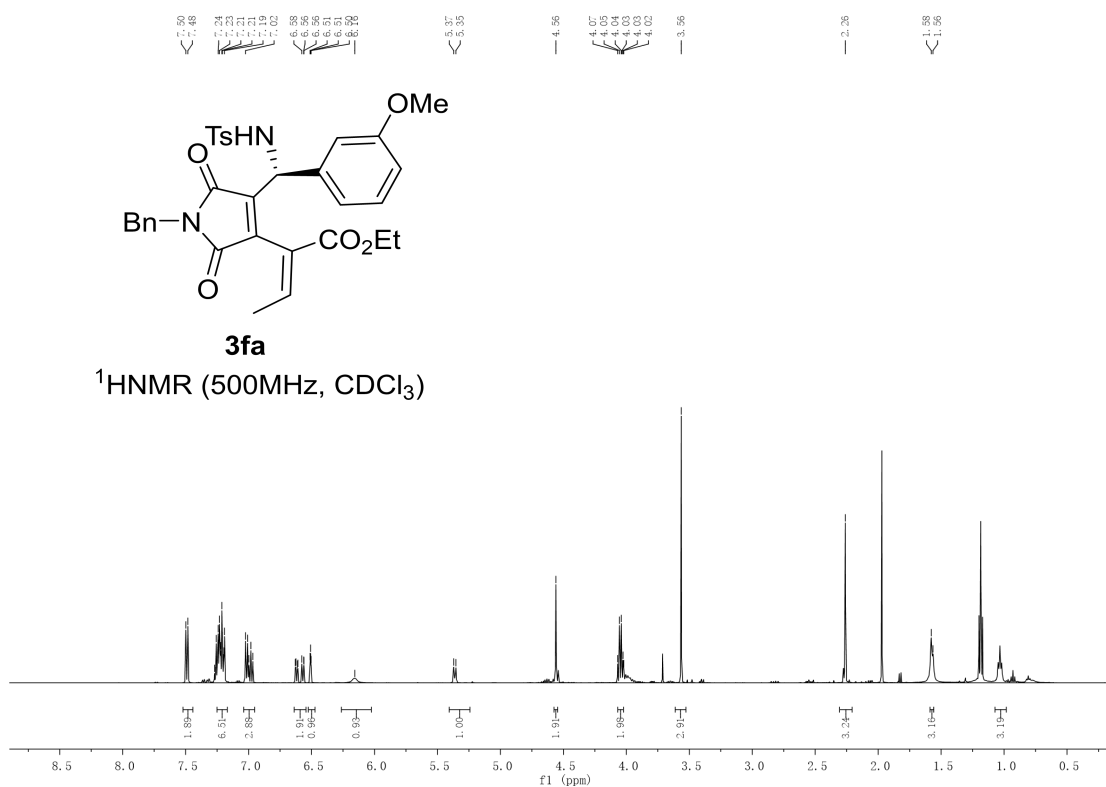
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )





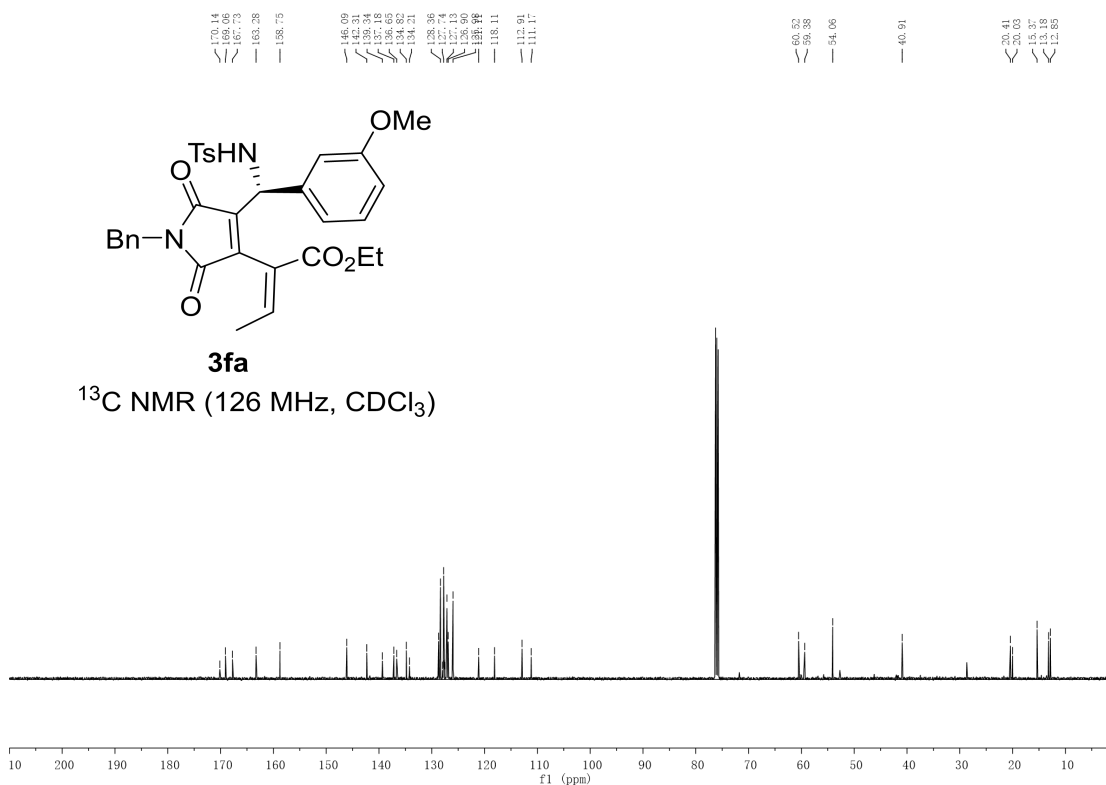
**3fa**

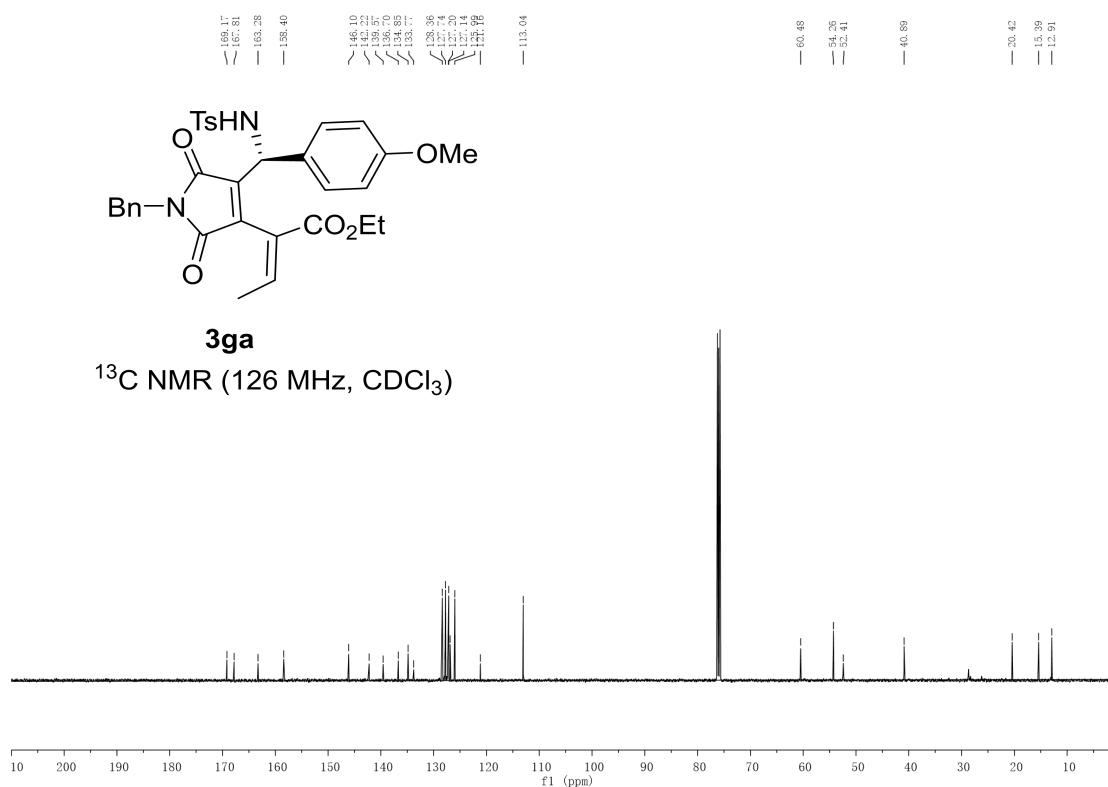
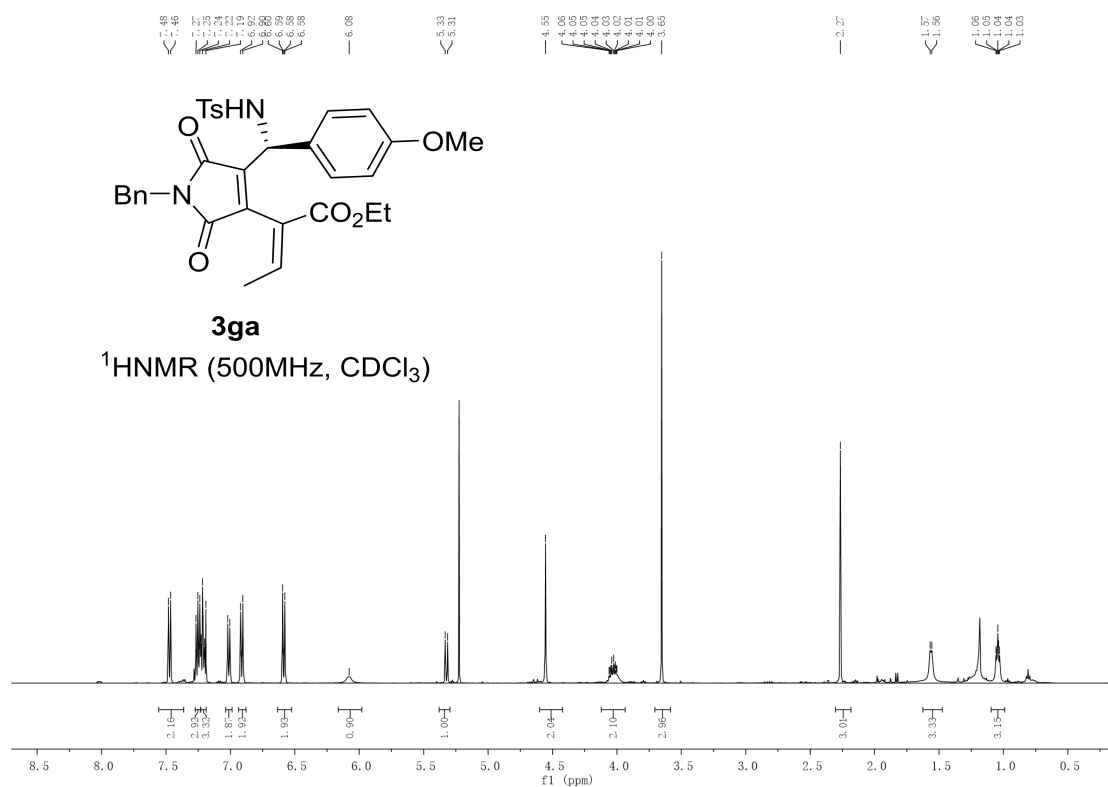
$^1\text{H}$ NMR (500MHz,  $\text{CDCl}_3$ )

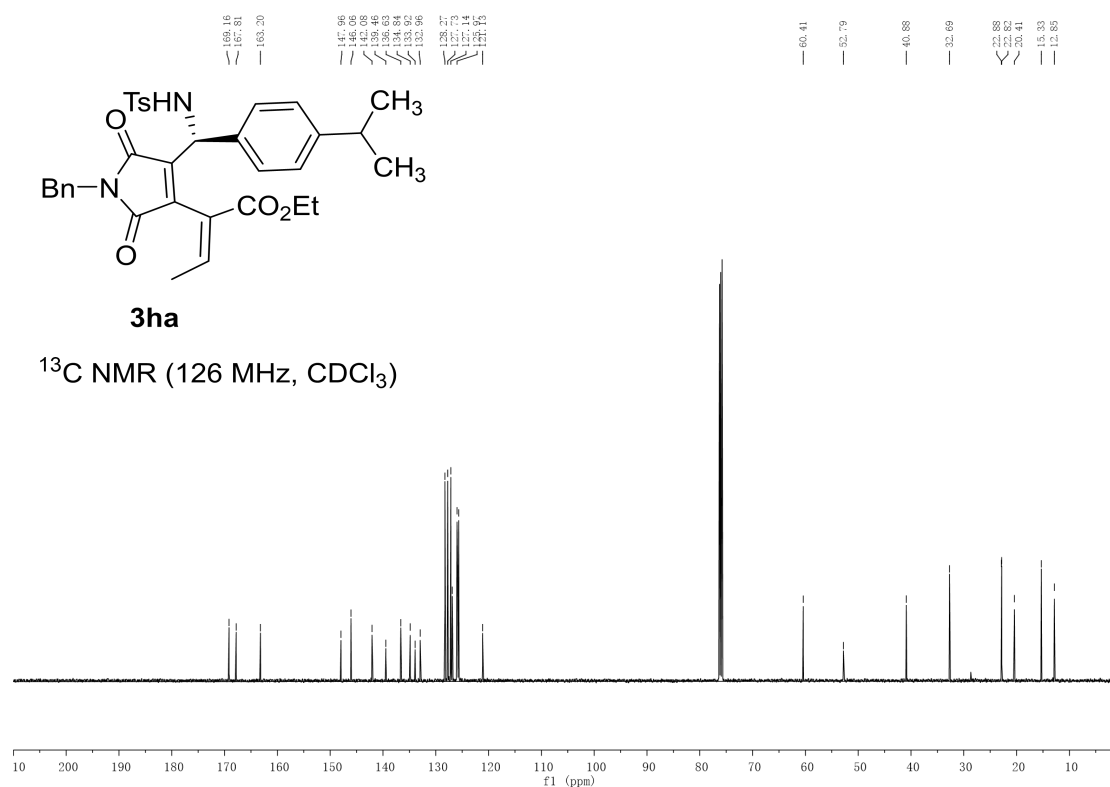
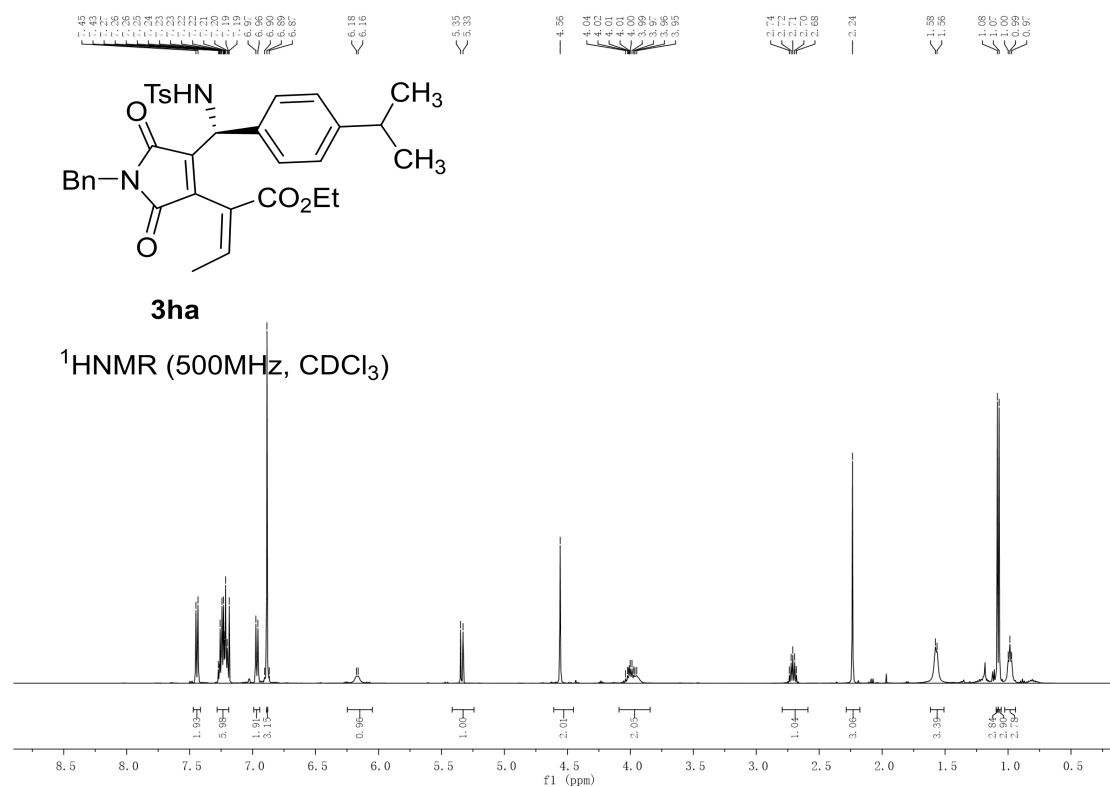


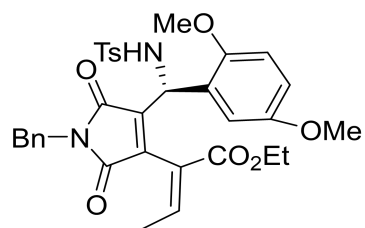
**3fa**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



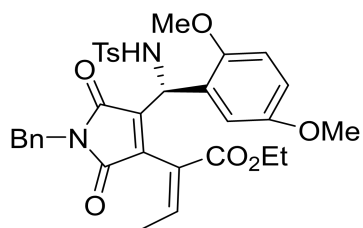
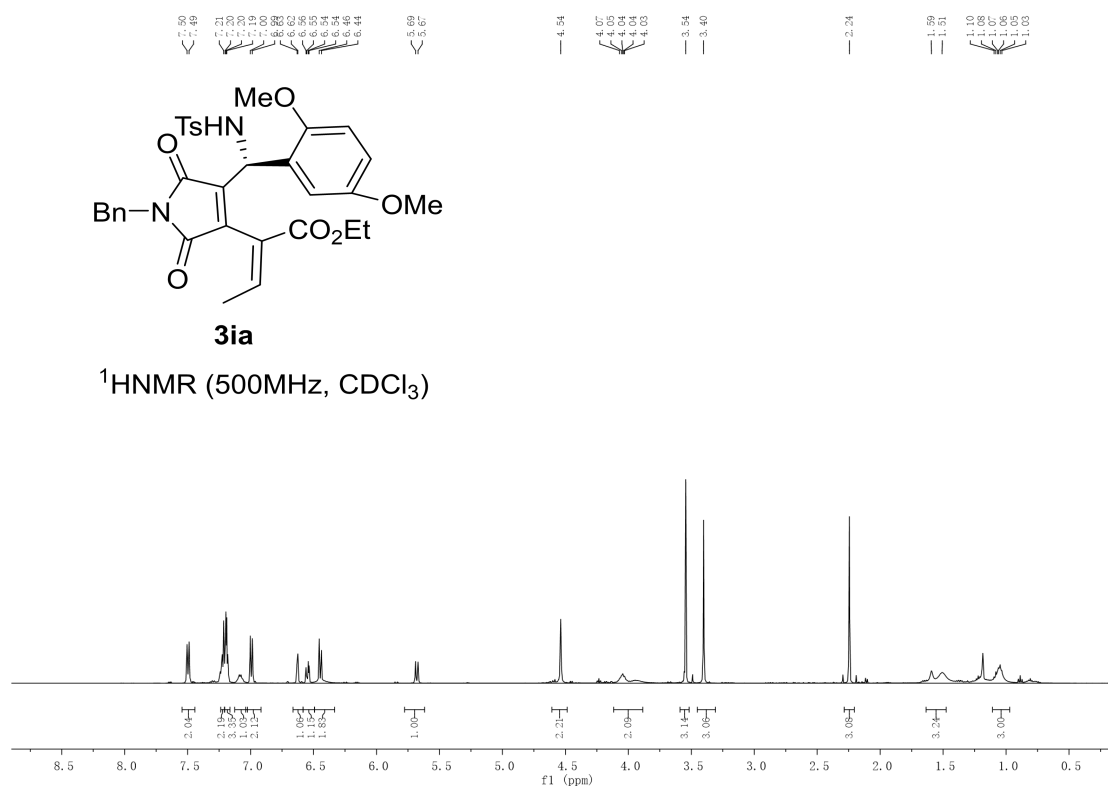






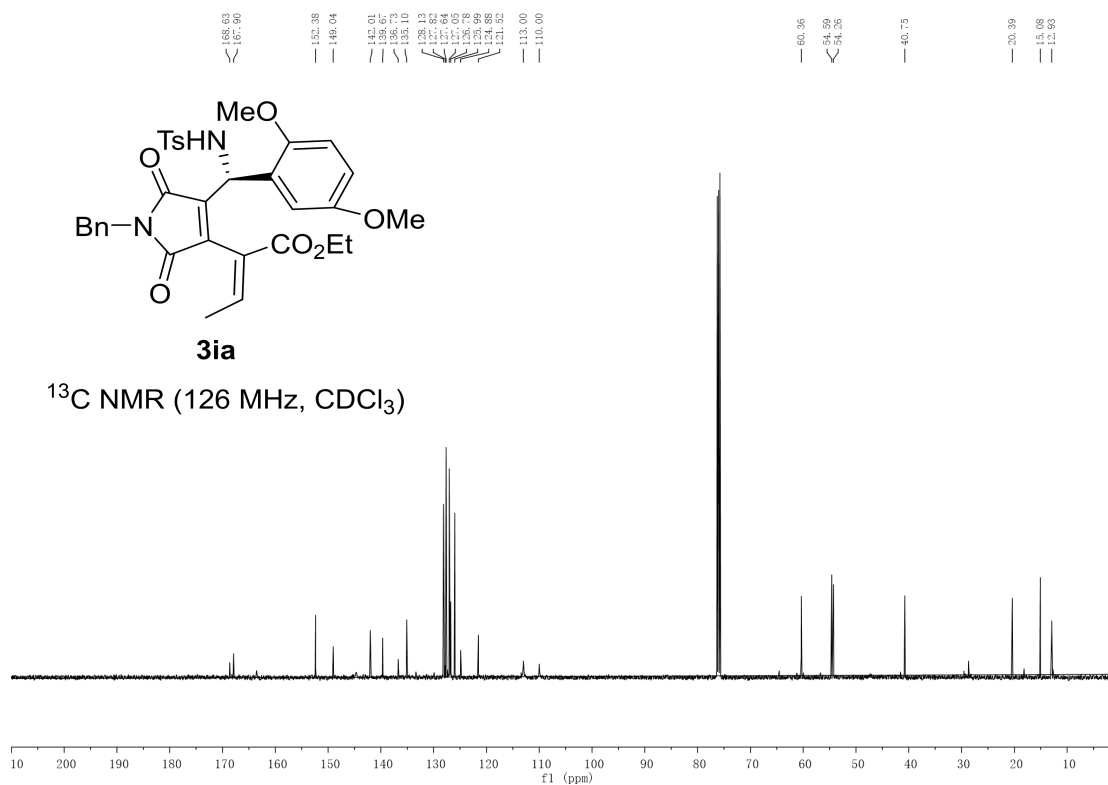
**3ia**

$^1\text{H}$ NMR (500MHz,  $\text{CDCl}_3$ )

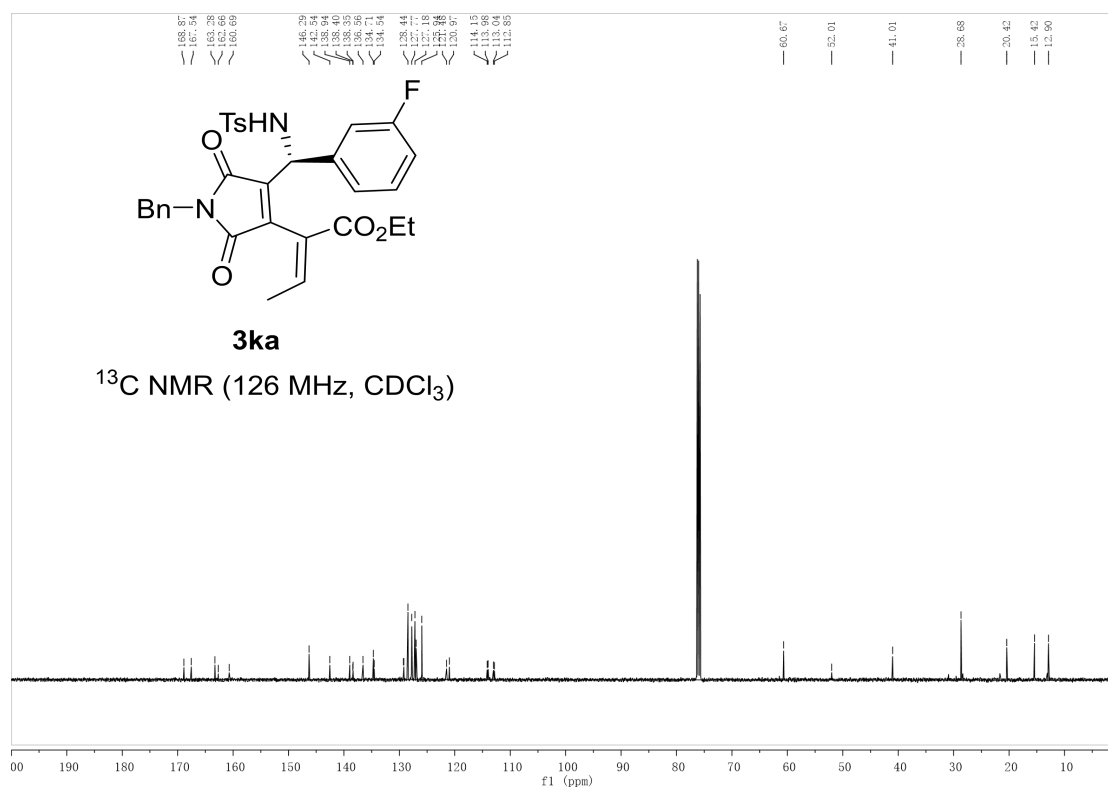
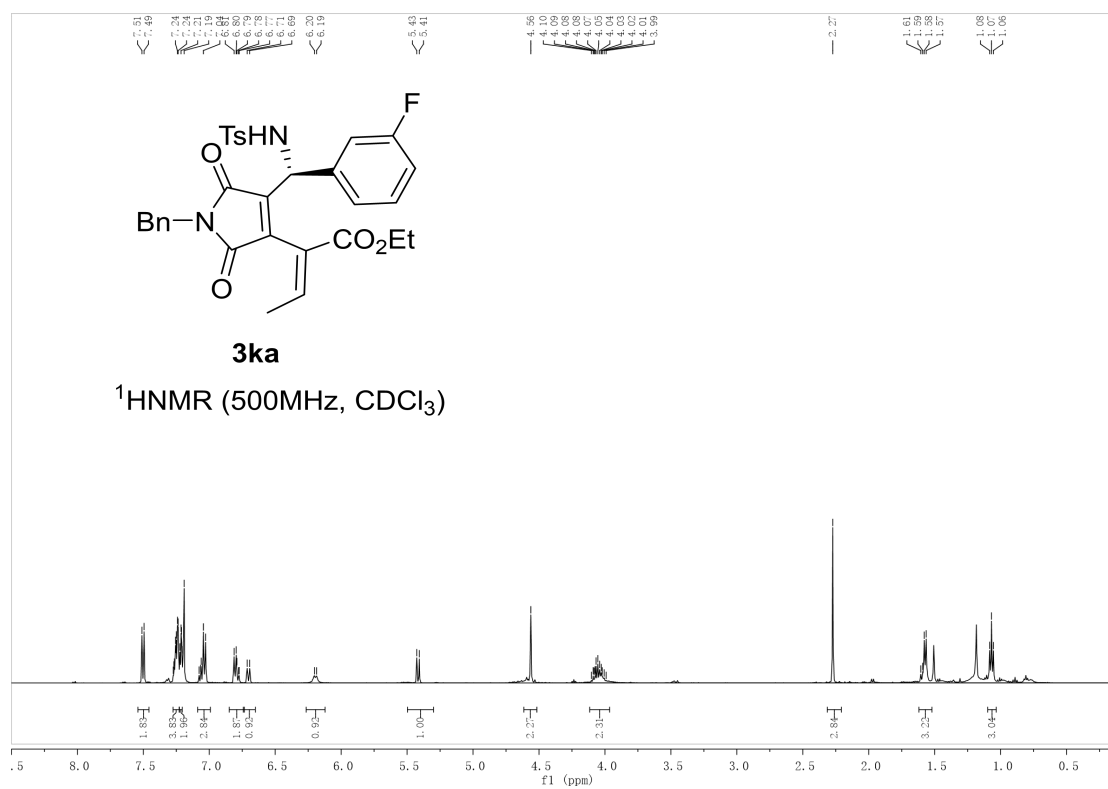


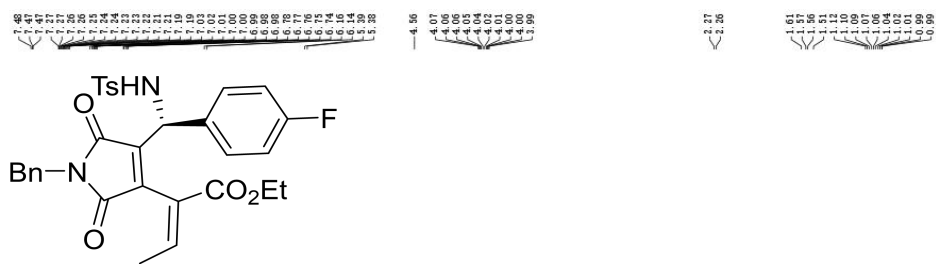
**3ia**

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )



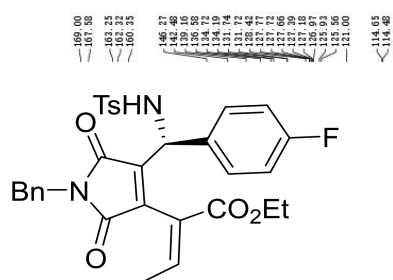
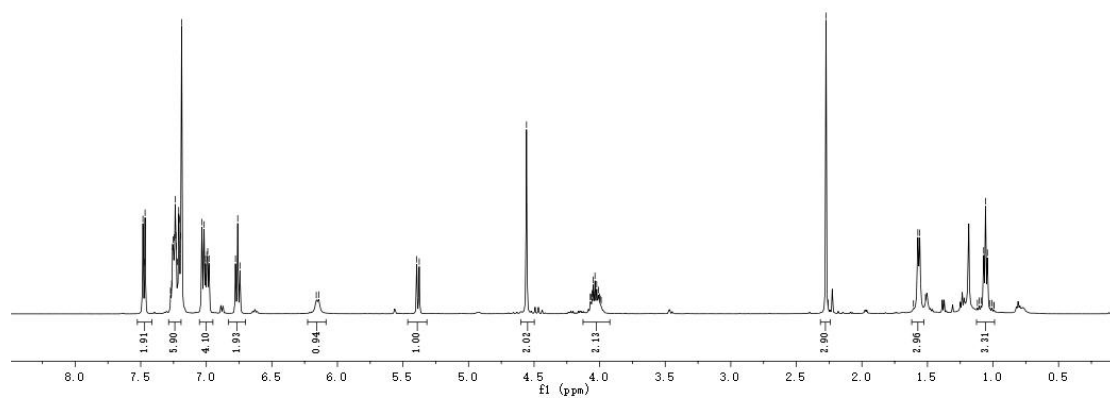






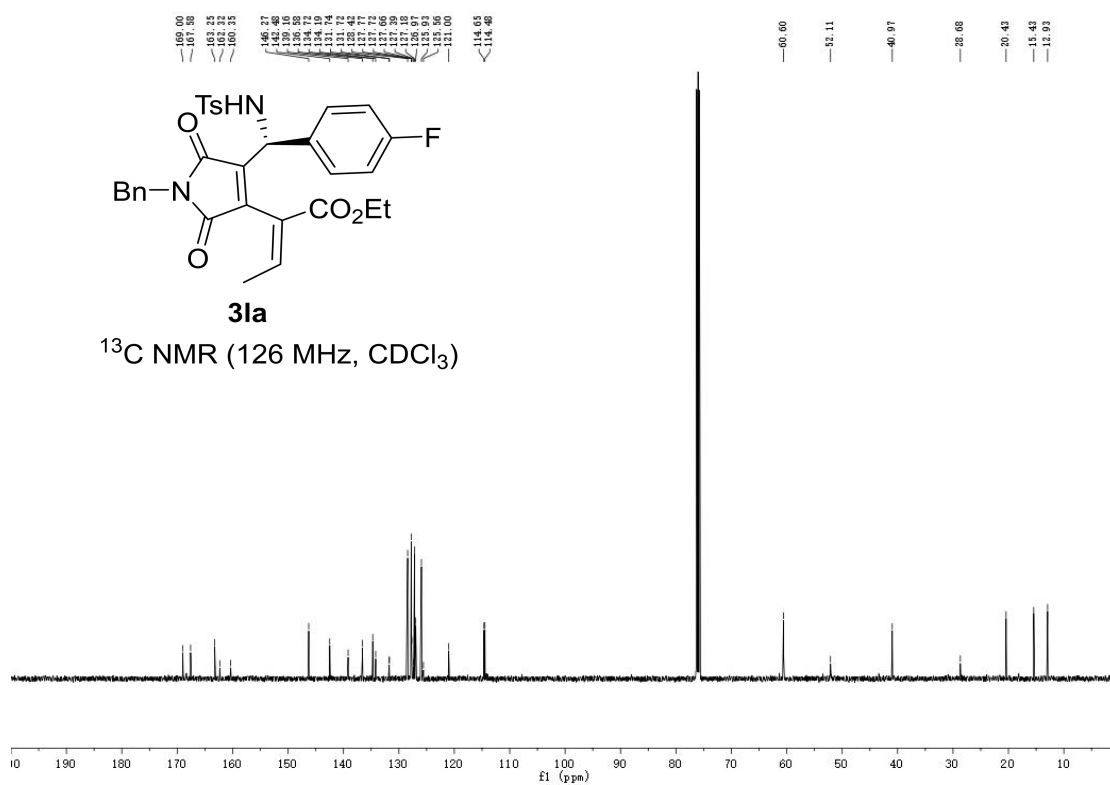
**3la**

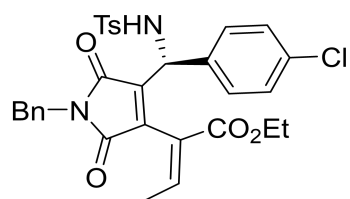
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



**3la**

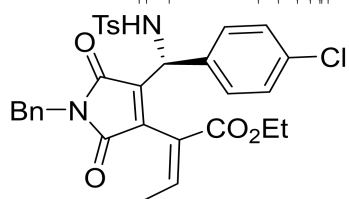
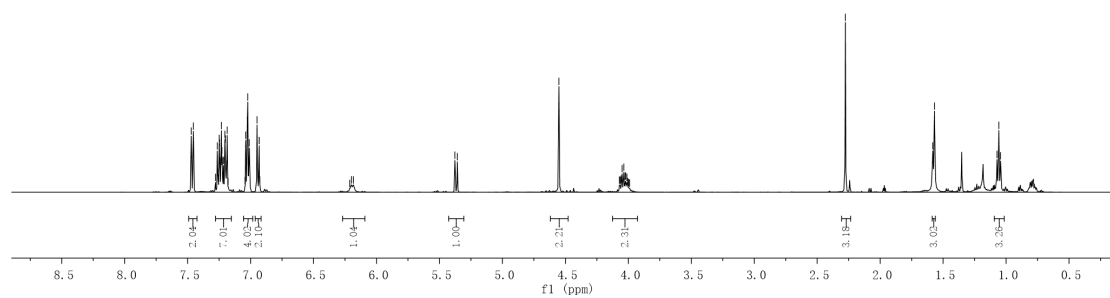
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)





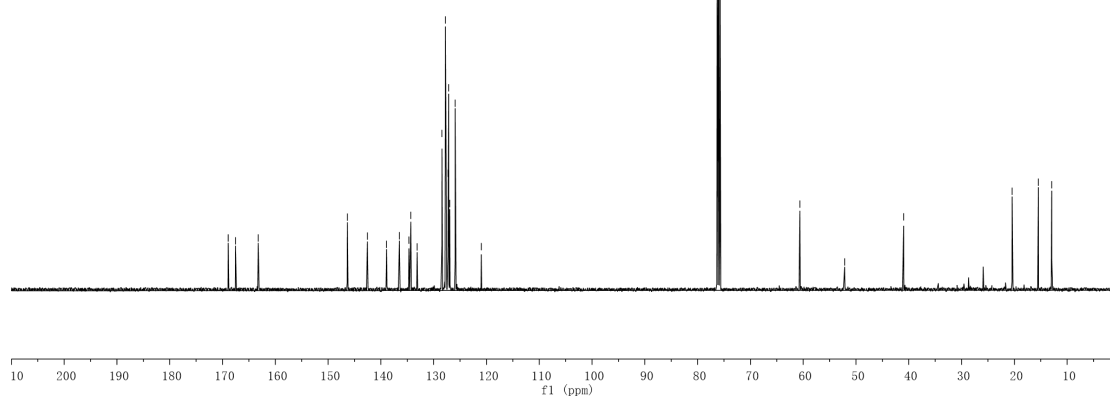
**3ma**

$^1\text{H}$ NMR (500MHz,  $\text{CDCl}_3$ )

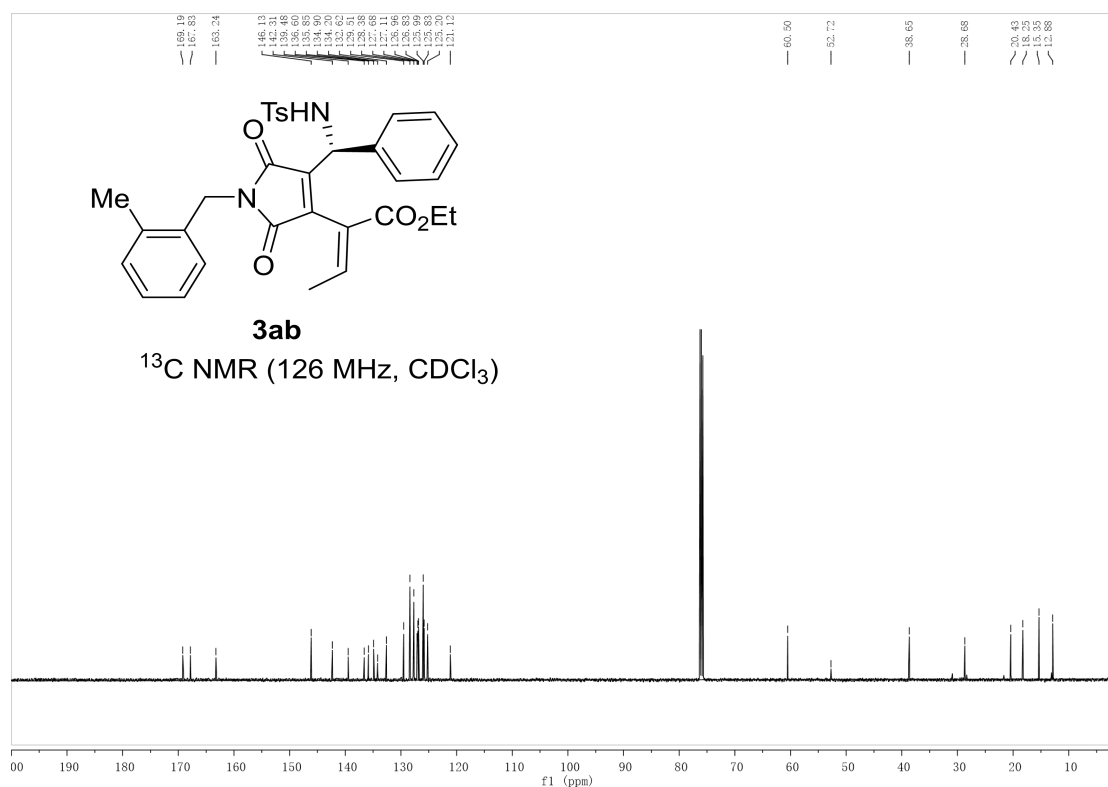
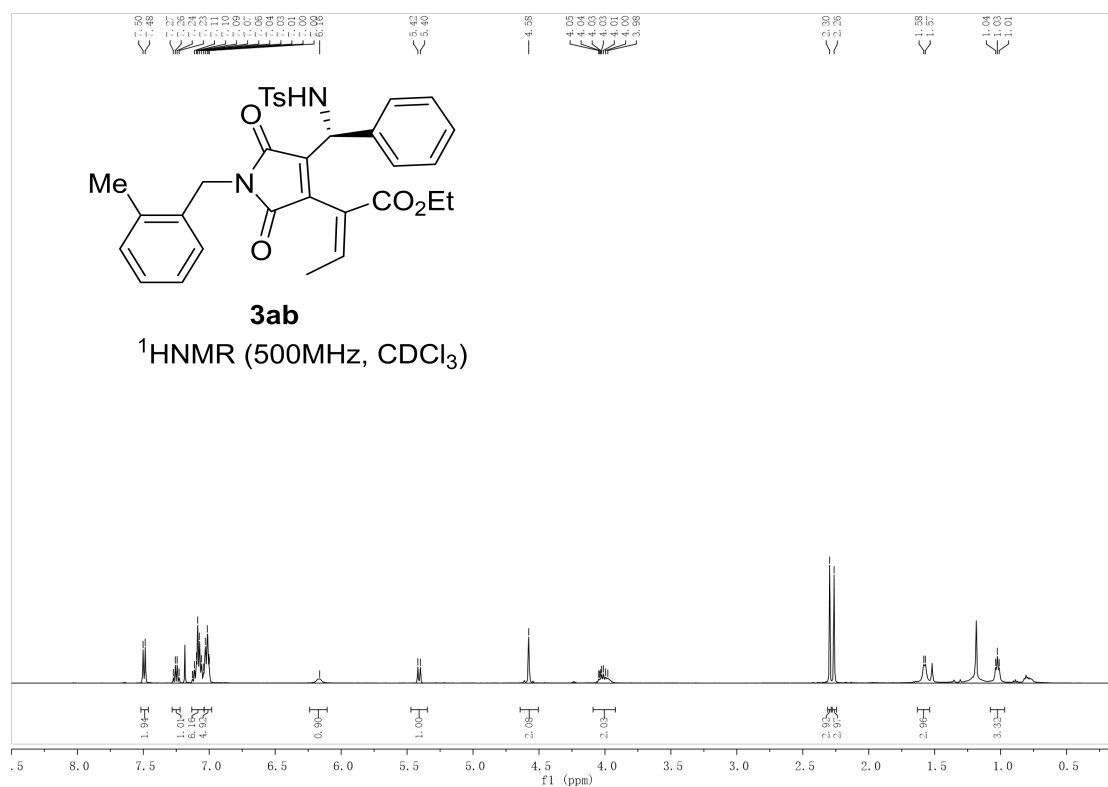


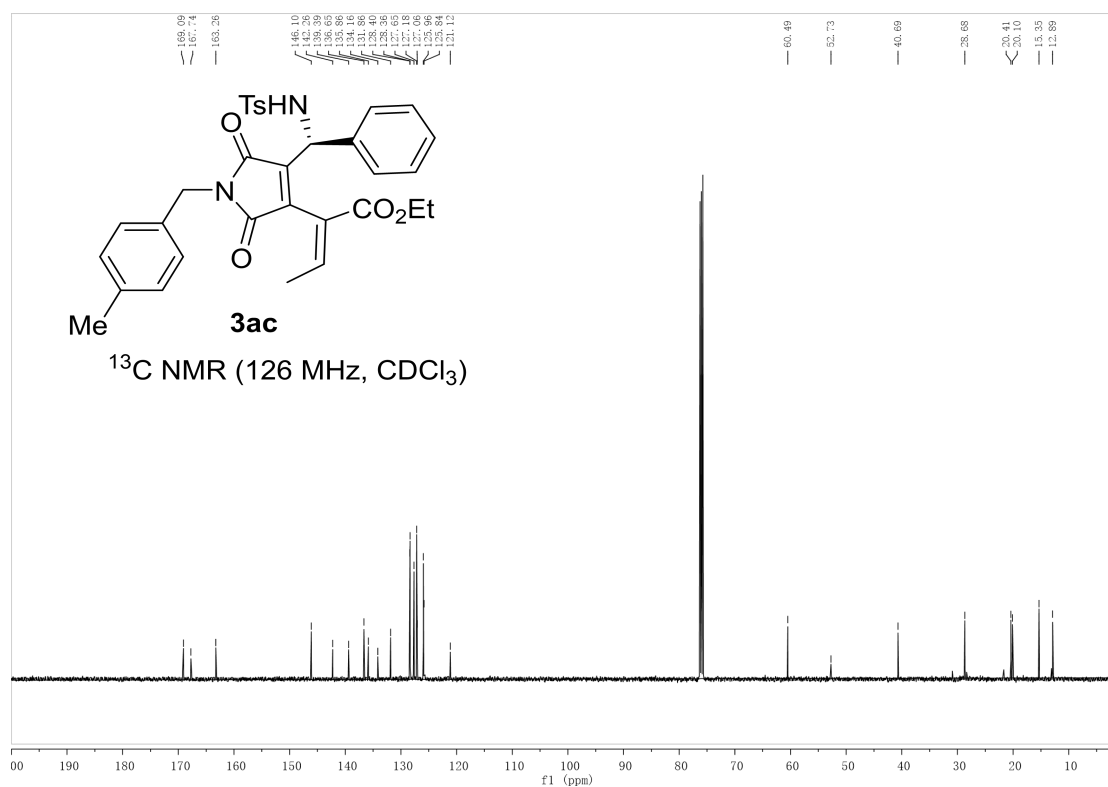
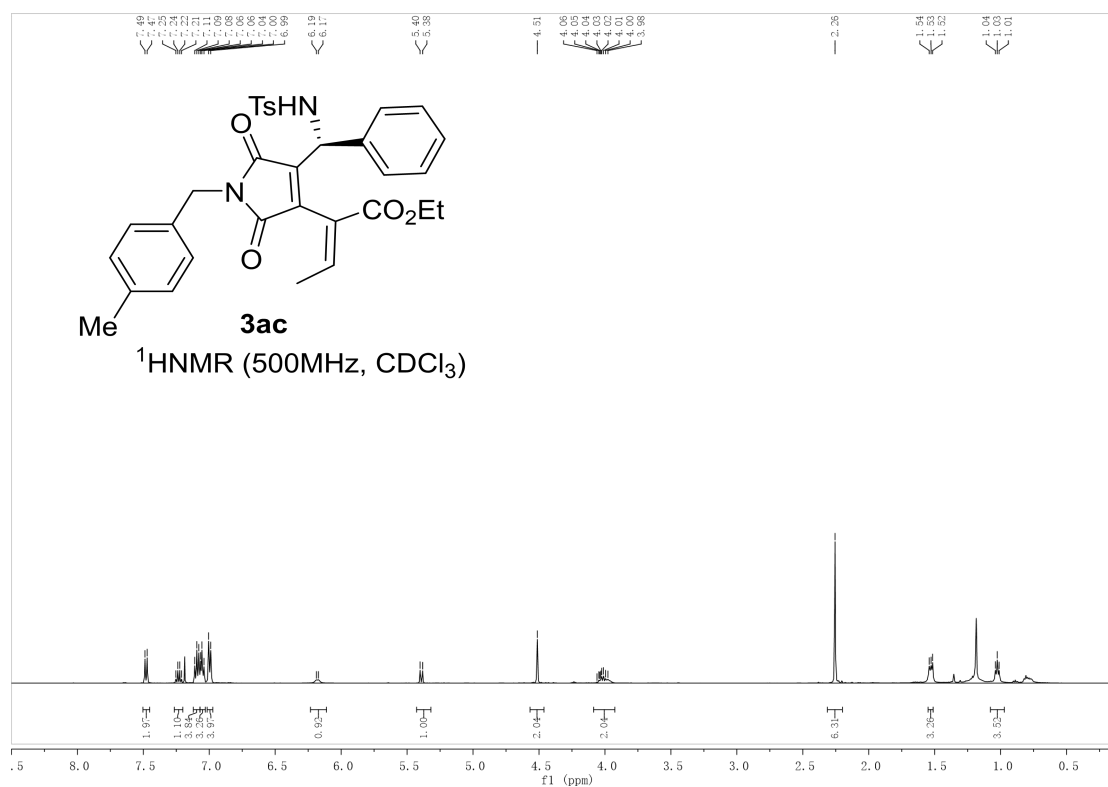
**3ma**

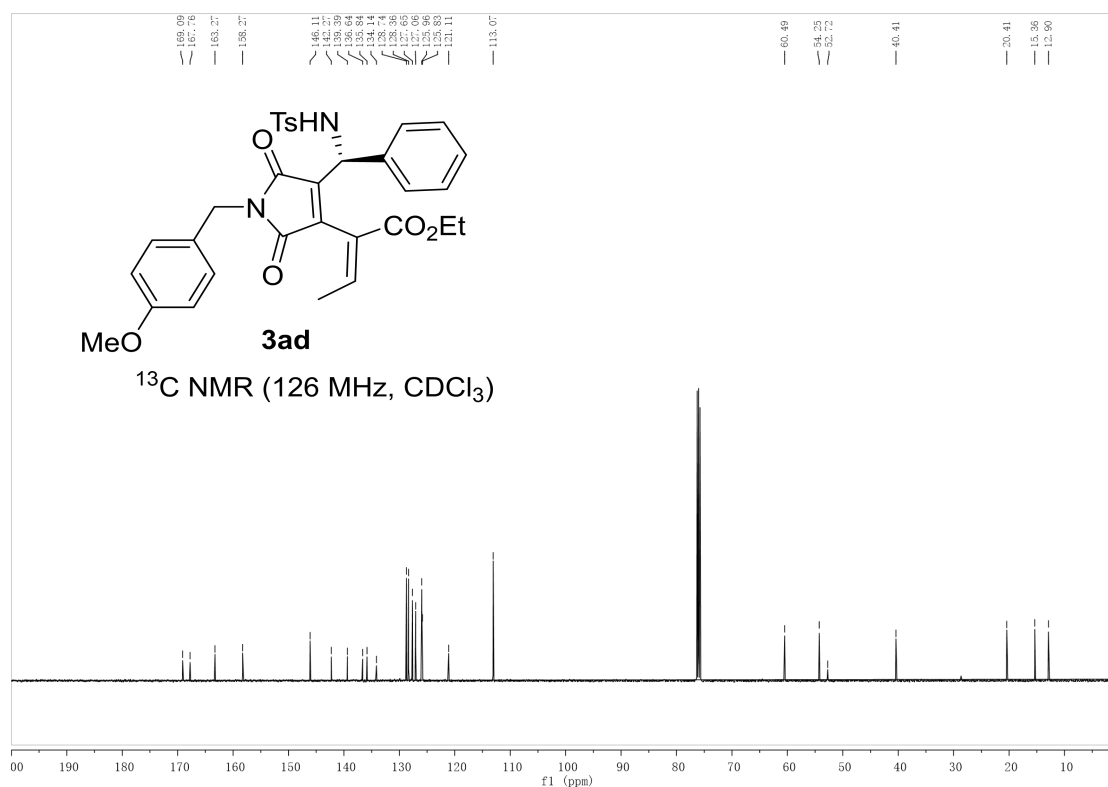
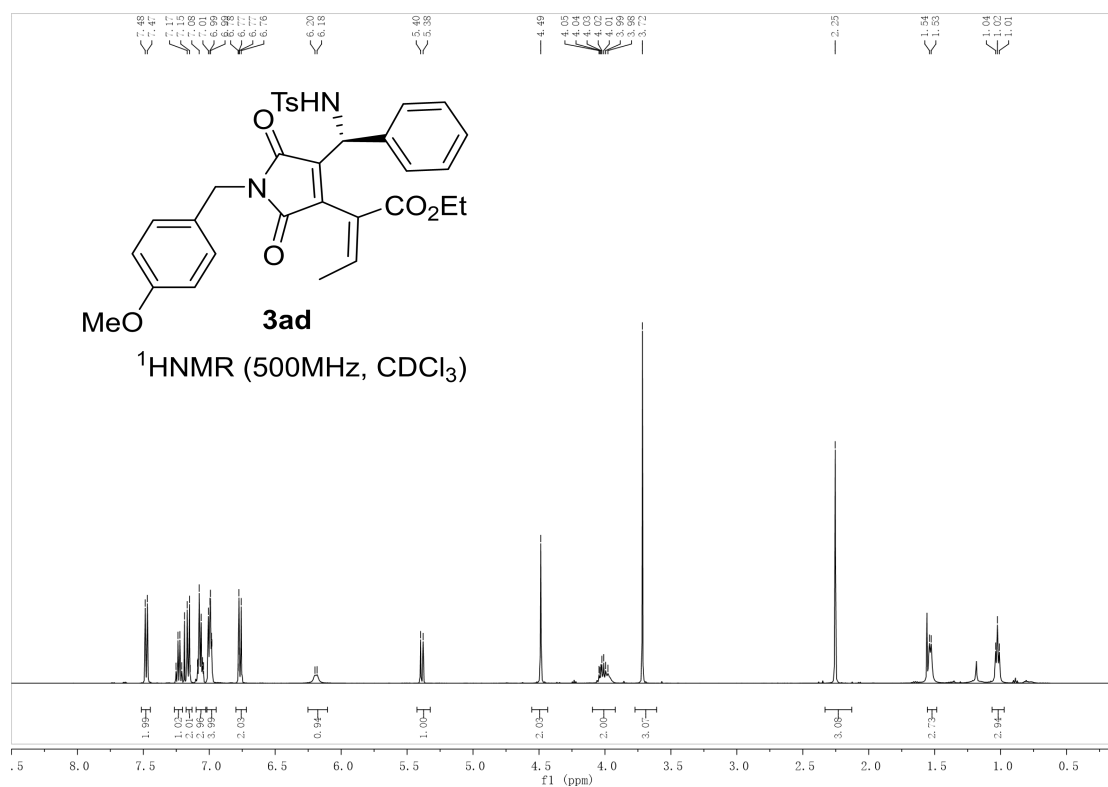
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )











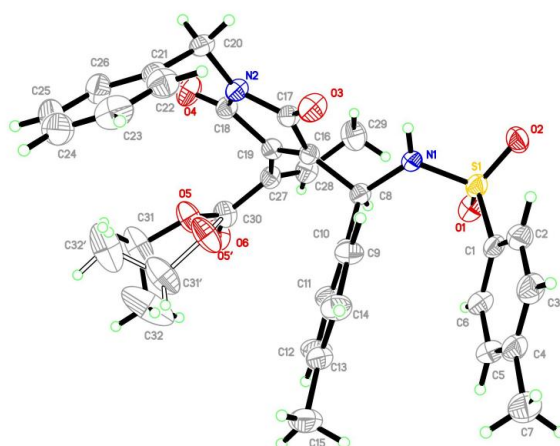
### X-Ray Crystallographic Data of 3da

**Sample preparation:** Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a saturated solution of compound **3da** (Dichloromethane/methanol) in a loosely capped vial.

**Crystal measurement:** A crystal of **3da** was picked up with paratone oil and mounted on a Bruker Smart Apexii diffractometer equipped with a Mo K $\alpha$  ( $\lambda = 1.54184$  Å) radiation source at 293 K.

Crystallographic data for **3da** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 2258229.

Thermal ellipsoids are drawn at 50% probability level.



**Table S1. Crystal data and structure refinement for 3da.**

Identification code	<b>3da</b>
Empirical formula	C <sub>32</sub> H <sub>32</sub> N <sub>2</sub> O <sub>6</sub> S
Formula weight	572.65
Temperature/K	293
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	9.1784(3)
b/Å	12.7700(4) Å
c/Å	25.7633(6) Å
$\alpha$ /°	90
$\beta$ /°	98.165(3)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	2989.06(15)
Z	4

$\rho_{\text{calc}}/\text{cm}^3$	1.273
$\mu/\text{mm}^{-1}$	1.343
F(000)	1208
Crystal size/ $\text{mm}^3$	0.120 x 0.120 x 0.110
2 $\Theta$ range for data collection/ $^\circ$	3.466 to 67.244
Index ranges	-10 $\leq h \leq$ 6, -14 $\leq k \leq$ 15, -30 $\leq l \leq$ 30
Reflections collected	10268
Independent reflections	5334 [R(int) = 0.0342]
Data/restraints/parameters	5334 / 94 / 404
Goodness-of-fit on F <sup>2</sup>	1.052
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0494, wR <sub>2</sub> = 0.1340
Final R indexes [all data]	R <sub>1</sub> = 0.0686, wR <sub>2</sub> = 0.1531
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.295 and -0.387
Flack parameter	0.0031(3)

**Table S2 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3da.  $U_{\text{eq}}$  is defined as 1/3 of of the trace of the orthogonalised  $U_{ij}$  tensor.**

Atom	x	y	z	U(eq)
S(1)	7648(1)	9580(1)	931(1)	50(1)
N(1)	7253(2)	8545(2)	1255(1)	43(1)
N(2)	5862(2)	6036(2)	2193(1)	47(1)
O(1)	6342(2)	10205(1)	852(1)	66(1)
O(2)	8979(2)	9990(2)	1214(1)	69(1)
O(3)	7802(2)	6390(2)	1743(1)	62(1)
O(4)	3637(2)	6193(2)	2496(1)	72(1)
O(5)	1931(8)	6202(6)	1394(3)	74(2)
C(31)	766(9)	5458(7)	1249(3)	110(3)
C(32)	468(10)	5417(9)	667(3)	179(5)
O(5')	2050(20)	6394(16)	1187(7)	93(4)
C(31')	910(20)	5727(13)	919(9)	115(5)
C(32')	610(30)	4839(19)	1277(9)	178(7)
O(6)	325(2)	7532(2)	1338(1)	79(1)
C(1)	8036(3)	9181(2)	310(1)	49(1)
C(2)	9428(3)	8832(2)	258(1)	61(1)
C(3)	9695(3)	8447(2)	-221(1)	69(1)
C(4)	8591(4)	8399(2)	-644(1)	65(1)
C(5)	7228(3)	8770(3)	-584(1)	67(1)
C(6)	6931(3)	9166(2)	-114(1)	58(1)
C(7)	8892(4)	7943(3)	-1160(1)	95(1)
C(8)	5813(2)	8032(2)	1118(1)	42(1)

C(9)	5634(3)	7387(2)	616(1)	44(1)
C(10)	6745(3)	6762(2)	485(1)	54(1)
C(11)	6570(3)	6209(2)	23(1)	64(1)
C(12)	5291(3)	6245(2)	-324(1)	62(1)
C(13)	4171(3)	6864(3)	-191(1)	74(1)
C(14)	4346(3)	7433(3)	272(1)	64(1)
C(15)	5118(4)	5640(3)	-834(1)	86(1)
C(16)	5508(2)	7364(2)	1574(1)	40(1)
C(17)	6566(3)	6564(2)	1828(1)	44(1)
C(18)	4486(3)	6455(2)	2202(1)	49(1)
C(19)	4270(2)	7293(2)	1788(1)	43(1)
C(20)	6555(3)	5216(2)	2540(1)	56(1)
C(21)	6381(3)	4147(2)	2302(1)	50(1)
C(22)	7463(3)	3708(3)	2047(1)	69(1)
C(23)	7259(4)	2717(3)	1818(1)	86(1)
C(24)	5997(5)	2175(3)	1847(1)	87(1)
C(25)	4949(4)	2585(3)	2106(1)	86(1)
C(26)	5139(3)	3555(2)	2330(1)	68(1)
C(27)	2862(3)	7851(2)	1656(1)	48(1)
C(28)	2681(3)	8869(2)	1724(1)	59(1)
C(29)	3831(4)	9624(2)	1947(1)	81(1)
C(30)	1566(3)	7221(2)	1433(1)	62(1)

**Table S3. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 3da. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$**

Atom	U11	U22	U33	U23	U13	U12
S(1)	65(1)	47(1)	43(1)	-4(1)	19(1)	-9(1)
N(1)	43(1)	52(1)	35(1)	4(1)	7(1)	-7(1)
N(2)	51(1)	49(1)	42(1)	7(1)	8(1)	1(1)
O(1)	84(1)	51(1)	67(1)	4(1)	28(1)	12(1)
O(2)	81(1)	76(1)	53(1)	-16(1)	18(1)	-37(1)
O(3)	40(1)	80(1)	68(1)	17(1)	13(1)	14(1)
O(4)	74(1)	80(1)	69(1)	16(1)	37(1)	-2(1)
O(5)	45(2)	65(3)	111(4)	-22(3)	13(2)	-6(2)
C(31)	71(4)	82(5)	178(7)	-39(5)	17(5)	-15(4)
C(32)	96(5)	218(9)	210(9)	-134(8)	-21(6)	21(6)
O(5')	44(5)	89(8)	145(10)	-43(8)	13(7)	-13(5)
C(31')	66(7)	106(9)	169(11)	-52(9)	4(9)	-6(7)
C(32')	152(13)	122(13)	264(16)	-48(14)	41(13)	-51(12)
O(6)	37(1)	85(2)	115(2)	7(1)	13(1)	6(1)
C(1)	60(2)	49(1)	39(1)	2(1)	18(1)	-7(1)
C(2)	57(2)	77(2)	50(1)	0(1)	14(1)	-6(2)

C(3)	68(2)	78(2)	66(2)	-4(2)	30(1)	-4(2)
C(4)	83(2)	68(2)	48(1)	-4(1)	25(1)	-14(2)
C(5)	76(2)	81(2)	43(1)	6(1)	6(1)	-9(2)
C(6)	64(2)	66(2)	46(1)	8(1)	12(1)	2(1)
C(7)	123(3)	106(3)	65(2)	-24(2)	41(2)	-24(2)
C(8)	36(1)	47(1)	42(1)	4(1)	7(1)	1(1)
C(9)	46(1)	49(1)	39(1)	6(1)	6(1)	-4(1)
C(10)	52(2)	62(2)	46(1)	-3(1)	1(1)	9(1)
C(11)	75(2)	64(2)	54(1)	-4(1)	9(1)	11(2)
C(12)	82(2)	60(2)	42(1)	1(1)	4(1)	-7(2)
C(13)	63(2)	99(2)	54(2)	-4(2)	-11(1)	-3(2)
C(14)	50(2)	85(2)	53(1)	0(1)	0(1)	5(2)
C(15)	126(3)	81(2)	49(2)	-9(2)	-1(2)	-7(2)
C(16)	38(1)	44(1)	38(1)	-1(1)	7(1)	-1(1)
C(17)	44(1)	47(1)	41(1)	0(1)	4(1)	0(1)
C(18)	54(2)	50(1)	43(1)	-1(1)	13(1)	-4(1)
C(19)	41(1)	44(1)	43(1)	-4(1)	10(1)	1(1)
C(20)	69(2)	54(2)	41(1)	8(1)	-2(1)	0(1)
C(21)	60(2)	51(1)	37(1)	9(1)	-1(1)	4(1)
C(22)	59(2)	78(2)	70(2)	4(2)	7(1)	8(2)
C(23)	97(3)	82(2)	79(2)	-1(2)	16(2)	34(2)
C(24)	114(3)	55(2)	85(2)	-2(2)	-6(2)	8(2)
C(25)	96(3)	61(2)	98(2)	4(2)	5(2)	-17(2)
C(26)	73(2)	62(2)	72(2)	7(2)	18(2)	-7(2)
C(27)	42(1)	55(2)	50(1)	2(1)	16(1)	0(1)
C(28)	50(2)	62(2)	69(2)	5(1)	20(1)	7(1)
C(29)	83(2)	60(2)	103(2)	-11(2)	20(2)	1(2)
C(30)	45(2)	69(2)	75(2)	-1(2)	17(1)	-1(1)

**Table S4 Bond Lengths for 3da.**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
S(1)-O(1)	1.4301(19)	S(1)-O(2)	1.4305(18)
S(1)-N(1)	1.6306(19)	S(1)-C(1)	1.764(2)
N(1)-C(8)	1.473(3)	N(2)-C(18)	1.374(3)
N(2)-C(17)	1.387(3)	N(2)-C(20)	1.464(3)
O(3)-C(17)	1.207(3)	O(4)-C(18)	1.209(3)
O(5)-C(30)	1.351(8)	O(5)-C(31)	1.439(6)
C(31)-C(32)	1.486(8)	O(5')-C(30)	1.341(19)
O(5')-C(31')	1.449(9)	C(31')-C(32')	1.512(10)
O(6)-C(30)	1.198(3)	C(1)-C(2)	1.377(4)
C(1)-C(6)	1.380(3)	C(2)-C(3)	1.383(4)
C(3)-C(4)	1.380(4)	C(4)-C(5)	1.367(4)

C(4)-C(7)	1.512(4)	C(5)-C(6)	1.375(4)
C(8)-C(16)	1.509(3)	C(8)-C(9)	1.522(3)
C(9)-C(14)	1.374(3)	C(9)-C(10)	1.374(3)
C(10)-C(11)	1.373(3)	C(11)-C(12)	1.371(4)
C(12)-C(13)	1.378(4)	C(12)-C(15)	1.513(4)
C(13)-C(14)	1.387(4)	C(16)-C(19)	1.335(3)
C(16)-C(17)	1.495(3)	C(18)-C(19)	1.505(3)
C(19)-C(27)	1.472(3)	C(20)-C(21)	1.497(4)
C(21)-C(26)	1.378(4)	C(21)-C(22)	1.385(4)
C(22)-C(23)	1.397(5)	C(23)-C(24)	1.360(5)
C(24)-C(25)	1.350(5)	C(25)-C(26)	1.369(5)
C(27)-C(28)	1.326(4)	C(27)-C(30)	1.482(4)
C(28)-C(29)	1.484(4)		

**Table S5 Bond Angles for 3da.**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O(1)-S(1)-O(2)	120.44(13)	O(1)-S(1)-N(1)	106.41(11)
O(2)-S(1)-N(1)	105.73(11)	O(1)-S(1)-C(1)	107.74(12)
O(2)-S(1)-C(1)	107.50(12)	N(1)-S(1)-C(1)	108.57(11)
C(8)-N(1)-S(1)	119.68(14)	C(18)-N(2)-C(17)	109.92(19)
C(18)-N(2)-C(20)	126.0(2)	C(17)-N(2)-C(20)	123.9(2)
C(30)-O(5)-C(31)	118.2(6)	O(5)-C(31)-C(32)	108.0(10)
C(30)-O(5')-C(31')	114.8(15)	O(5')-C(31')-C(32')	109(2)
C(2)-C(1)-C(6)	120.4(2)	C(2)-C(1)-S(1)	119.41(19)
C(6)-C(1)-S(1)	120.1(2)	C(1)-C(2)-C(3)	119.1(3)
C(4)-C(3)-C(2)	121.2(3)	C(5)-C(4)-C(3)	118.4(3)
C(5)-C(4)-C(7)	121.2(3)	C(3)-C(4)-C(7)	120.4(3)
C(4)-C(5)-C(6)	121.8(3)	C(5)-C(6)-C(1)	119.1(3)
N(1)-C(8)-C(16)	108.91(16)	N(1)-C(8)-C(9)	115.42(18)
C(16)-C(8)-C(9)	110.23(19)	C(14)-C(9)-C(10)	117.8(2)
C(14)-C(9)-C(8)	120.2(2)	C(10)-C(9)-C(8)	121.9(2)
C(11)-C(10)-C(9)	120.8(2)	C(12)-C(11)-C(10)	122.1(3)
C(11)-C(12)-C(13)	117.2(3)	C(11)-C(12)-C(15)	121.5(3)
C(13)-C(12)-C(15)	121.3(3)	C(12)-C(13)-C(14)	121.1(3)
C(9)-C(14)-C(13)	121.0(3)	C(19)-C(16)-C(17)	108.08(19)
C(19)-C(16)-C(8)	128.5(2)	C(17)-C(16)-C(8)	123.14(19)
O(3)-C(17)-N(2)	125.1(2)	O(3)-C(17)-C(16)	127.9(2)
N(2)-C(17)-C(16)	107.02(19)	O(4)-C(18)-N(2)	125.4(2)
O(4)-C(18)-C(19)	127.5(2)	N(2)-C(18)-C(19)	107.03(19)
C(16)-C(19)-C(27)	130.0(2)	C(16)-C(19)-C(18)	107.9(2)
C(27)-C(19)-C(18)	122.1(2)	N(2)-C(20)-C(21)	112.93(19)
C(26)-C(21)-C(22)	117.3(3)	C(26)-C(21)-C(20)	121.3(3)

C(22)-C(21)-C(20)	121.5(3)	C(21)-C(22)-C(23)	120.3(3)
C(24)-C(23)-C(22)	120.1(3)	C(25)-C(24)-C(23)	120.1(3)
C(24)-C(25)-C(26)	120.2(3)	C(25)-C(26)-C(21)	122.0(3)
C(28)-C(27)-C(19)	124.5(2)	C(28)-C(27)-C(30)	118.4(2)
C(19)-C(27)-C(30)	117.2(2)	C(27)-C(28)-C(29)	126.4(3)
O(6)-C(30)-O(5')	122.4(8)	O(6)-C(30)-O(5)	122.9(4)
O(6)-C(30)-C(27)	125.9(3)	O(5')-C(30)-C(27)	107.8(7)
O(5)-C(30)-C(27)	111.0(4)		

**Table S6 Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for 3da.**

Atom	x	y	z	U(eq)
H(1)	7883	8300	1504	52
H(31A)	-114	5673	1389	132
H(31B)	1057	4773	1388	132
H(32A)	278	6111	531	268
H(32B)	-375	4982	561	268
H(32C)	1307	5131	533	268
H(31C)	1218	5448	602	138
H(31D)	19	6133	821	138
H(32D)	204	5116	1573	267
H(32E)	1508	4477	1397	267
H(32F)	-85	4362	1089	267
H(2)	10178	8854	541	73
H(3)	10635	8216	-259	82
H(5)	6482	8755	-868	80
H(6)	5999	9420	-82	70
H(7A)	8137	7446	-1284	142
H(7B)	9831	7600	-1111	142
H(7C)	8898	8495	-1413	142
H(8)	5066	8585	1072	50
H(10)	7626	6712	712	65
H(11)	7343	5797	-57	77
H(13)	3284	6900	-415	89
H(14)	3580	7853	352	76
H(15A)	4090	5553	-961	130
H(15B)	5571	4965	-775	130
H(15C)	5581	6017	-1088	130
H(20A)	6126	5221	2863	67
H(20B)	7596	5371	2628	67
H(22)	8329	4074	2027	83
H(23)	7987	2427	1646	103

