

Palladium-Catalyzed (3+2) Annulations of 1,3-Bis-Electrophilic motifs: Straightforward Synthesis of Functionalized Pyrrolidines

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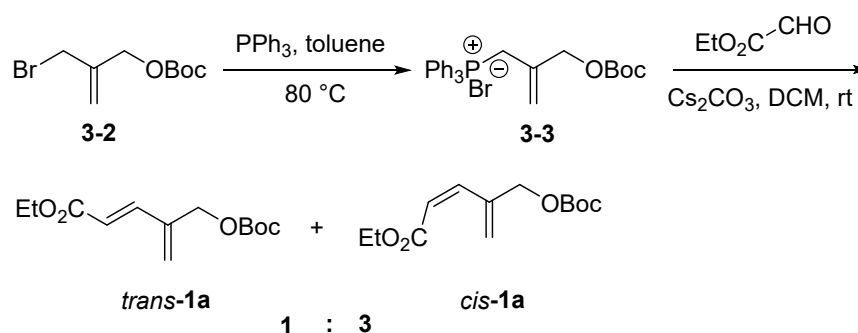
Table of Contents

Table of Contents	S2
1. General experimental details	S3
2. General procedure for the Synthesis of matrerails	S3
3. General procedure for the reaction	S10
5. Copies of ¹ H NMR, ¹³ C NMR spectra.....	S26
6. Copies of HPLC Chromatograms	S69
7. X-Ray single crystal data of product 3aa.....	S71

1. General experimental details

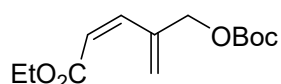
All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300/400 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-ToF HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4 °C/min, the thermometer was not corrected. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/IG/IB N-5 in comparison with the authentic racemates. Chiral HPLC analysis recorded on Shanghaiyice instruments and Equipment Co. Ltd. and Shimadzu LC-20A. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification.

2. General procedure for the Synthesis of matrerails



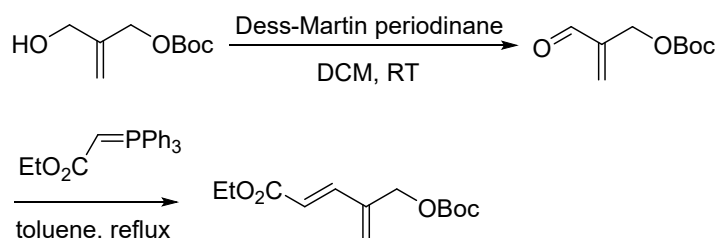
Triphenyl phosphorus (55 mol) and 2-(bromomethyl) allyl *tert*-butyl carbonate (50 mol) was added to a 250 mL round bottom flask, toluene (100 mL) was added and the mixture was stirred at 80 °C until triphenyl phosphorus dissolved. The mixture was refluxed at 80 °C for 48 h. The reaction solution is filtered to obtain white solid, and washed with petroleum ether to obtain crude product.

Dissolve the white solid (10 mmol) obtained in 50 mL DCM, add ethyl 2-oxoacetate (11 mmol) and Cesium carbonate (20 mmol) to the above system, and react at room temperature for two days. Remove the salt from the reaction solution through suction filtration to obtain the filtrate, remove the solvent from the filtrate through rotary evaporator, and separate the crude product through silica gel column chromatography to obtain *cis*-**1a** (petroleum ether: ethyl acetate=50:1).



Ethyl-(Z)-4-(((*tert*-butoxycarbonyl)oxy)methyl)penta-2,4-dienoate **1a**

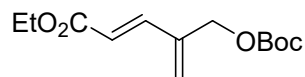
Yellow liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.44 (d, $J = 12.6$ Hz, 1H), 5.82 (d, $J = 12.6$ Hz, 1H), 5.50 (s, 1H), 5.43 (s, 1H), 4.79 (s, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.46 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 3H)ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 165.8, 153.2, 140.1, 139.6, 121.6, 121.1, 82.1, 67.8, 60.4, 27.7, 14.1ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{NaO}_5^+$: 279.1203; Found: 279.1205.



tert-Butyl (2 - (hydroxymethyl) allyl) (50 mmol) carbonate is added to a 250 mL round bottom flask, and then 120 mL dichloromethane is added, and stirred; The temperature of the reaction solution was reduced to 0 °C, Dais-Martin oxidant (55 mmol) was slowly added to the above system in batches, and the reaction was monitored after half an hour. Remove the solvent through the rotary evaporator, add ethyl acetate to dissolve the product, extract and filter the filtrate, remove the solvent through the rotary evaporator, and separate the oxide by silica gel column chromatography to obtain oxide (petroleum ether: ethyl acetate=10:1).

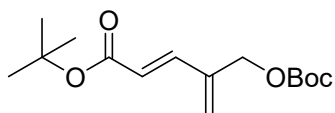
Oxide (10 mmol) is added to a 100mL round bottom flask, and then 30mL of toluene is added to dissolve it. Wittig reagent (12 mmol) is added, and then the

reaction solution is heated and refluxed for half an hour. The solvent was removed by rotary evaporation apparatus, and **trans-1a** (petroleum ether: ethyl acetate=30:1) was obtained by trans-silica column chromatography.



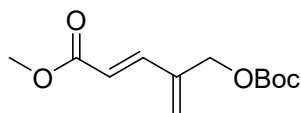
Ethyl (E)-4-(((tert-butoxycarbonyl)oxy)methyl)penta-2,4-dienoate 1a

Yellow liquid. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.28 (d, $J = 16.2$ Hz, 1H), 5.93 (d, $J = 16.2$ Hz, 1H), 5.60 (s, 1H), 5.56 (s, 1H), 4.72 (s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 1.46 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.6, 153.1, 143.0, 138.8, 125.3, 119.4, 82.5, 65.4, 60.5, 27.7, 14.2 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{NaO}_5^+$: 279.1203; Found: 279.1205.



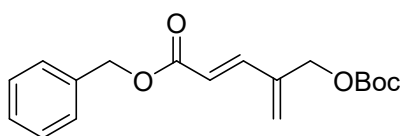
tert-Butyl (E)-4-(((tert-butoxycarbonyl)oxy)methyl)penta-2,4-dienoate 1b

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.21 (d, $J = 16.2$ Hz, 1H), 5.89 (d, $J = 16.2$ Hz, 1H), 5.60 (s, 1H), 5.56 (s, 1H), 4.73 (s, 2H), 1.50 (s, 18H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 165.9, 153.2, 142.0, 138.9, 124.7, 121.3, 82.6, 80.6, 65.6, 28.1, 27.7 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{24}\text{NaO}_5^+$: 307.1516; Found: 307.1520.



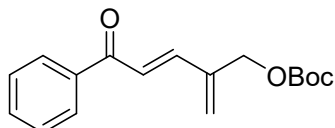
Methyl (E)-4-(((tert-butoxycarbonyl)oxy)methyl)penta-2,4-dienoate 1c

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32 (d, $J = 16.2$ Hz, 1H), 5.97 (d, $J = 16.2$ Hz, 1H), 5.64 (s, 1H), 5.60 (s, 1H), 4.74 (s, 2H), 3.76 (s, 3H), 1.49 (s, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 167.1, 153.1, 143.3, 138.8, 125.5, 119.0, 82.6, 65.5, 51.7, 27.7 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{NaO}_5^+$: 265.1046; Found: 265.1053.



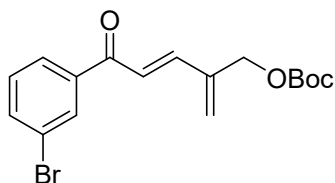
Benzyl (*E*)-4-(((*tert*-butoxycarbonyl)oxy)methyl)penta-2,4-dienoate 1d

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.42 - 7.33 (m, 6H), 6.03 (d, $J = 16.2$ Hz, 1H), 5.66 (s, 1H), 5.61 (s, 1H), 5.22 (s, 2H), 4.75 (s, 2H), 1.50 (s, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.4, 153.1, 143.6, 138.9, 135.9, 128.6, 128.3, 125.7, 119.1, 82.6, 66.4, 65.5, 27.7 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{NaO}_5^+$: 341.1359; Found: 341.1370.



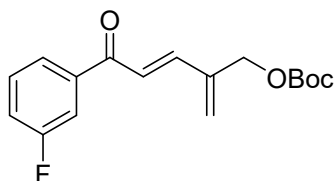
(*E*)-*Tert*-Butyl (2-methylene-5-oxo-5-phenylpent-3-en-1-yl) carbonate 1e

White solid. **MP**: 46.0 - 48.0 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 - 7.95 (m, 2H), 7.61 - 7.56 (m, 1H), 7.52 - 7.43 (m, 3H), 7.09 (d, $J = 15.9$ Hz, 1H), 5.75 (s, 1H), 5.73 (s, 1H), 4.90 (s, 2H), 1.52 (s, 9H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 190.2, 153.3, 143.0, 139.4, 137.8, 133.0, 128.6, 126.8, 122.8, 82.7, 65.6, 27.8 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{NaO}_4^+$: 311.1254; Found: 311.1268.



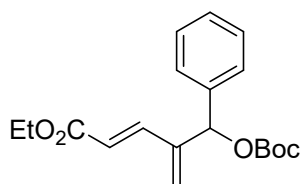
(*E*)-5-(4-Bromophenyl)-2-methylene-5-oxopent-3-en-1-yl *tert*-butyl carbonate 1f

Yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.09 (t, $J = 1.7$ Hz, 1H), 7.92 - 7.85 (m, 1H), 7.73 - 7.67 (m, 1H), 7.46 (d, $J = 15.8$ Hz, 1H), 7.41 - 7.34 (m, 1H), 7.02 (d, $J = 15.8$ Hz, 1H), 5.79 (s, 1H), 5.75 (s, 1H), 4.89 (s, 2H), 1.52 (s, 9H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 188.8, 153.3, 143.8, 139.6, 139.3, 135.8, 131.5, 130.2, 127.6, 127.0, 123.0, 122.2, 82.8, 65.6, 27.8 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{BrNaO}_4^+$: 389.0359; Found: 389.0363.



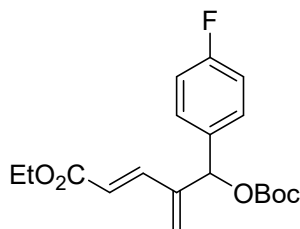
(*E*)-*tert*-Butyl (5-(3-fluorophenyl)-2-methylene-5-oxopent-3-en-1-yl) carbonate 1g

Yellow oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.69- 7.63 (m, 1H), 7.53 - 7.42 (m 2H), 7.34 - 7.24 (m, 1H), 7.04 (d, *J* = 15.9 Hz, 1H), 5.78 (s, 1H), 5.75 (s, 1H), 4.89 (s, 2H), 1.52 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃)** δ 188.9, 162.9 (d, *J* = 248.2 Hz), 153.3, 143.7, 139.9, 139.3, 130.3 (d, *J* = 7.6 Hz), 127.5, 124.2 (d, *J* = 3.0 Hz), 122.3, 120.0 (d, *J* = 21.4 Hz), 115.3 (d, *J* = 22.6 Hz), 82.8, 65.6, 27.8 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₁₇H₁₉FNaO₄⁺: 329.1160; Found: 329.1165



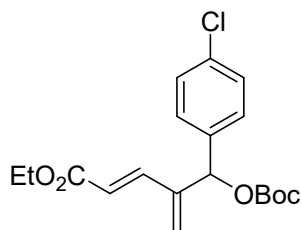
Ethyl-(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(phenyl)methyl)penta-2,4-dienoate 1h

Yellow oil. **¹H NMR (300 MHz, CDCl₃)** δ 7.51 - 7.19 (m, 6H), 6.31 (s, 1H), 5.90 (d, *J* = 16.2 Hz, 1H), 5.72 (s, 1H), 5.70 (s, 1H), 4.31 - 4.06 (m, 2H), 1.48 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 166.6, 152.6, 142.8, 142.7, 137.1, 128.7, 128.6, 127.6, 123.6, 120.2, 82.8, 77.0, 60.5, 27.8, 14.2 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₁₉H₂₄NaO₅⁺: 355.1516; Found: 355.1531



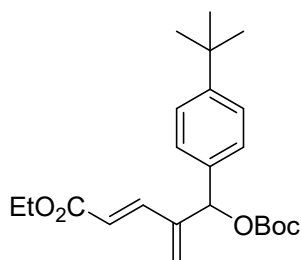
Ethyl-(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(4-fluorophenyl)methyl)penta-2,4-dienoate 1i

Light yellow solid. **MP:** 60.0 - 62.0 °C. **¹H NMR (300 MHz, CDCl₃)** δ 7.41 - 7.33 (m, 2H), 7.27 (d, *J* = 16.3 Hz, 1H), 7.05 (dd, *J* = 12.0, 5.3 Hz, 2H), 6.28 (s, 1H), 5.84 (d, *J* = 16.3 Hz, 1H), 5.72 (s, 1H), 5.70 (s, 1H), 4.29 - 4.08 (m, 2H), 1.47 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 166.5, 162.8 (d, *J* = 247.7 Hz), 152.5, 142.6, 142.4, 133.0, 129.5 (d, *J* = 8.3 Hz), 123.5, 120.3, 115.7 (d, *J* = 21.6 Hz), 82.9, 76.2, 60.6, 27.7, 14.2 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₁₉H₂₃FNaO₅⁺: 373.1422; Found: 373.1420



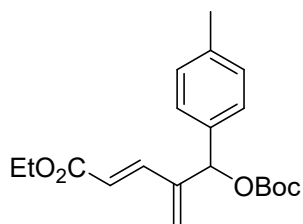
Ethyl(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(4-chlorophenyl)methyl)penta-2,4-dienoate 1j

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.33 (s, 4H), 7.27 (d, $J = 16.3$ Hz, 1H), 6.27 (s, 1H), 5.86 (d, $J = 16.3$ Hz, 1H), 5.71 (d, $J = 2.4$ Hz, 2H), 4.22 - 4.09 (m, 2H), 1.47 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.4, 152.5, 142.4, 142.3, 135.8, 134.6, 129.0, 128.9, 123.8, 120.3, 83.0 (s), 76.2, 60.6, 27.7, 14.2 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{23}\text{ClNaO}_5^+$: 389.1126; Found: 389.1133.



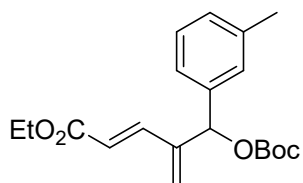
Ethyl(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(4-(*tert*-butyl)phenyl)methyl)penta-2,4-dienoate 1k

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.34 - 7.27 (m, 2H), 7.23 (d, $J = 14.6$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.28 (s, 1H), 5.89 (d, $J = 16.2$ Hz, 1H), 5.72 (s, 1H), 5.68 (s, 1H), 4.21 - 4.12 (m, 2H), 2.34 (s, 3H), 1.48 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.6, 152.7, 151.6, 142.9, 142.9, 134.0, 127.3, 125.6, 123.2, 120.1, 82.6, 76.8, 60.5, 34.6, 31.3, 27.8, 14.2 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{32}\text{NaO}_5^+$: 411.2142; Found: 411.2150.



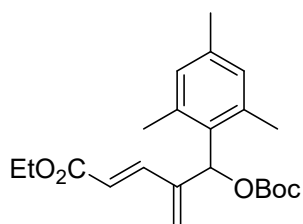
Ethyl-(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(*p*-tolyl)methyl)penta-2,4-dienoate 1l

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.35 - 7.14 (m, 5H), 6.28 (s, 1H), 5.89 (d, $J = 16.2$ Hz, 1H), 5.72 (s, 1H), 5.68 (s, 1H), 4.21 - 4.12 (m, 2H), 2.34 (s, 3H), 1.48 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.6, 152.7, 142.9, 142.8, 138.5, 134.2, 129.4, 127.6, 123.3, 120.1, 82.6, 76.8, 60.5, 27.8, 21.2, 14.2 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{NaO}_5^+$: 369.1672; Found: 369.1683.



Ethyl-(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(*m*-tolyl)methyl)penta-2,4-dienoate 1m

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.38 - 7.09 (m, 5H), 6.28 (s, 1H), 5.90 (d, $J = 16.2$ Hz, 1H), 5.72 (s, 1H), 5.69 (s, 1H), 4.24 - 4.12 (m, 2H), 2.35 (s, 3H), 1.48 (s, 9H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.6, 152.6, 142.9, 142.7, 138.4, 137.0, 129.5, 128.5, 128.2, 124.7, 123.4, 120.1, 82.7, 77.0, 60.5, 27.8, 21.4, 14.2 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{NaO}_5^+$: 369.1672; Found: 369.1685



Ethyl-(*E*)-4-(((*tert*-butoxycarbonyl)oxy)(mesityl)methyl)penta-2,4-dienoate 1n

Yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.34 (d, $J = 16.2$ Hz, 1H), 6.85 (s, 2H), 6.71 (s, 1H), 5.99 (d, $J = 16.1$ Hz, 1H), 5.61 (s, 1H), 5.17 (s, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.34 (s, 6H), 2.27 (s, 3H), 1.46 (s, 9H), 1.29 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.7, 153.1, 143.3, 141.5, 137.8, 137.3, 130.5, 123.0, 123.9,

119.8, 82.4, 74.0, 60.4, 27.8, 20.9, 20.7, 14.3 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{22}H_{30}NaO_5^+$: 397.1985; Found: 397.1998.

3. General procedure for the reaction

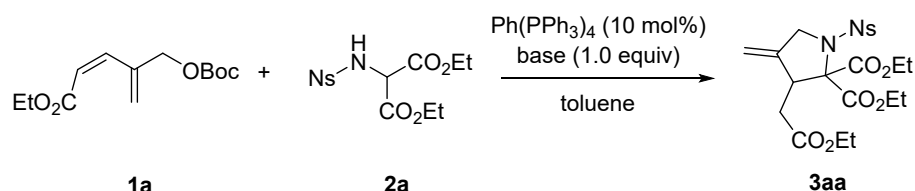
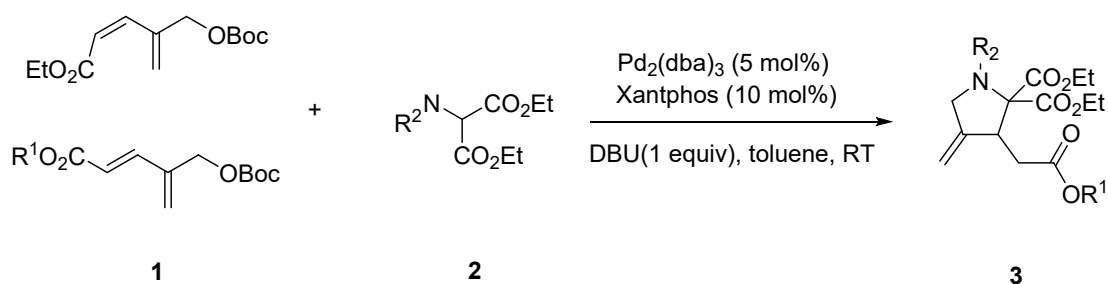


Table S1 Screening base

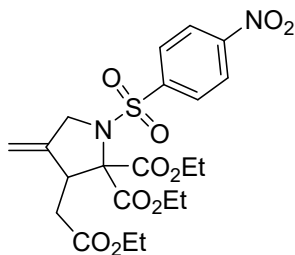
Entry	Base	Yields (%) ^b
1	Cs ₂ CO ₃	trace
2	K ₂ CO ₃	trace
3	Na ₂ CO ₃	trace
4	K ₃ PO ₄	trace
5	DBU	41
6	DMAP	26
7	DABCO	38

^a Reaction conditions: **1a** (0.13 mmol), **2a** (0.1 mmol), Boc = *tert*-butoxycarbonyl, solvent (1 mL). ^b Separation yield

General Procedure for (3+2) cycloaddition reaction.

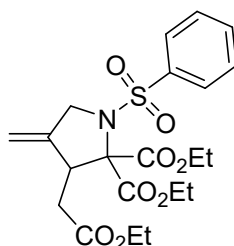


Xantphos (0.01 mmol) and Pd₂(dba)₃ (0.005 mmol) were dissolved in toluene (1.0 mL) in a 10 mL Schlenk tube under N₂. After stirring at room temperature for 0.5 h, material **1** (0.13 mmol), material **2** (0.1 mmol), DBU (0.1 mmol) were added. The reaction mixture was stirred at r.t. until the material **2** was totally consumed (monitored by TLC), and then was purified by flash column chromatography directly to afford the corresponding product **3aa - 3al**, **3bg - 3gg**.



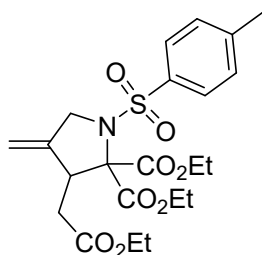
Diethyl-3-(2-ethoxy-2-oxoethyl)-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3aa

Light yellow solid (*cis-1a* 35.8 mg, 72% yield; *trans-1a* 37.4 mg, 75% yield). **MP:** 93.0 - 94.0 °C. **¹H NMR (300 MHz, CDCl₃)** δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 2H), 5.04 (d, *J* = 1.4 Hz, 1H), 4.97 (d, *J* = 1.6 Hz, 1H), 4.40 - 4.02 (m, 8H), 3.83 (s, 1H), 2.80 (dd, *J* = 16.9, 5.7 Hz, 1H), 2.47 (dd, *J* = 16.9, 8.1 Hz, 1H), 1.36 - 1.23 (m, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 170.9, 167.3, 166.4, 150.0, 145.7, 142.5, 129.1, 123.9, 109.0, 77.0, 63.0, 62.8, 61.0, 51.4, 49.4, 33.9, 14.1, 13.9 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₂₁H₂₆N₂NaO₁₀S⁺: 521.1200; Found: 521.1199.



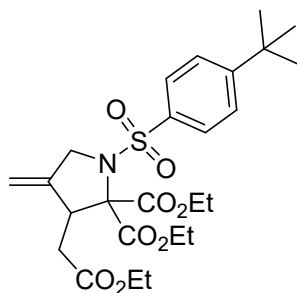
Diethyl-3-(2-ethoxy-2-oxoethyl)-4-methylene-1-(phenylsulfonyl)pyrrolidine-2,2-dicarboxylate 3ab

Yellow oil (*cis-1a* 27.4 mg, 60% yield; *trans-1a* 32.5 mg, 72% yield). **¹H NMR (300 MHz, CDCl₃)** δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.63 - 7.47 (m, 3H), 4.99 (s, 1H), 4.93 (d, *J* = 1.5 Hz, 1H), 4.39 - 3.98 (m, 8H), 3.85 (s, 1H), 2.80 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.47 (dd, *J* = 16.9, 8.3 Hz, 1H), 1.35 - 1.23 (m, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 171.0, 167.4, 166.5, 143.2, 140.0, 132.7, 128.7, 127.8, 108.3, 76.46, 62.7, 62.4, 60.9, 51.2, 49.5, 33.9, 14.1, 13.9 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₂₁H₂₇NNaO₈S⁺: 476.1350; Found: 476.1351.



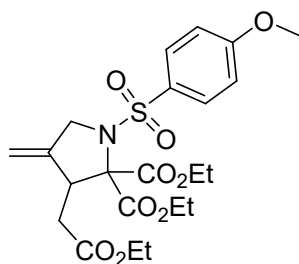
Diethyl 3-(2-ethoxy-2-oxoethyl)-4-methylene-1-tosylpyrrolidine-2,2-dicarboxylate
3ac

Yellow oil (*cis*-**1a** 25.2 mg, 54% yield; *trans*-**1a** 29.6 mg, 64% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 4.98 (s, 1H), 4.92 (d, $J = 1.2$ Hz, 1H), 4.40 - 4.10 (m, 6H), 4.09 - 3.96 (m, 2H), 3.84 (s, 1H), 2.80 (dd, $J = 16.8, 5.5$ Hz, 1H), 2.53 - 2.37 (m, 4H), 1.36 - 1.21 (m, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.1, 167.5, 166.6, 143.5, 143.3, 137.1, 129.3, 127.9, 108.2, 76.4, 62.7, 62.4, 60.9, 51.1, 49.5, 33.9, 21.6, 14.1, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{NNaO}_8\text{S}^+$: 490.1506 ; Found: 490.1509.



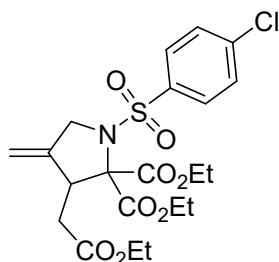
Diethyl 1-((4-(*tert*-butyl)phenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-
methylenepyrrolidine-2,2-dicarboxylate 3ad

Yellow oil (*cis*-**1a** 33.0 mg, 65% yield; *trans*-**1a** 48.6 mg, 95% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.91 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 4.98 (d, $J = 1.6$ Hz, 1H), 4.92 (d, $J = 1.8$ Hz, 1H), 4.40 - 3.97 (m, 8H), 3.85 (s, 1H), 2.81 (dd, $J = 16.9, 5.4$ Hz, 1H), 2.48 (dd, $J = 16.9, 8.4$ Hz, 1H), 1.34 (s, 9H), 1.32 - 1.22 (m, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.1, 167.5, 166.6, 156.4, 143.4, 137.0, 127.7, 125.8, 108.2, 76.4, 62.7, 62.4, 60.9, 51.1, 49.6, 35.1, 33.9, 31.1, 14.1, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{35}\text{NNaO}_8\text{S}^+$: 532.1976; Found: 532.1985.



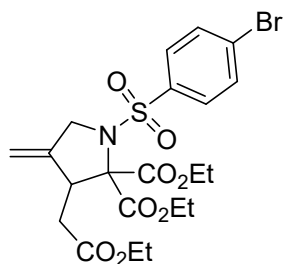
Diethyl-3-(2-ethoxy-2-oxoethyl)-1-((4-methoxyphenyl)sulfonyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3ae

Yellow oil (*cis-1a* 38.2 mg, 79% yield; *trans-1a* 45.5 mg, 94% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.94 (d, $J = 8.9$ Hz, 2H), 6.97 (d, $J = 8.9$ Hz, 2H), 4.97 (d, $J = 1.7$ Hz, 1H), 4.92 (d, $J = 1.9$ Hz, 1H), 4.36 - 4.09 (m, 6H), 4.06 - 3.93 (m, 2H), 3.88 - 3.80 (m, 4H), 2.79 (dd, $J = 16.9, 5.6$ Hz, 1H), 2.47 (dd, $J = 16.9, 8.3$ Hz, 1H), 1.35 - 1.23 (m, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.1, 167.61, 166.6, 163.0, 143.4, 131.7, 130.1, 113.9, 108.2, 76.5, 62.7, 62.4, 60.9, 55.6, 50.9, 49.6, 34.0, 14.1, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{NNaO}_9\text{S}^+$: 506.1455 ; Found: 506.1462.



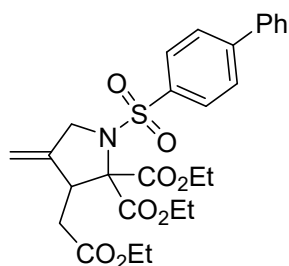
Diethyl-1-((4-chlorophenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3af

Light yellow solid (*cis-1a* 41.7 mg, 85% yield; *trans-1a* 34.2 mg, 71% yield). MP: 74.0 - 76.0 °C. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.94 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.7$ Hz, 2H), 5.00 (d, $J = 1.7$ Hz, 1H), 4.94 (d, $J = 1.9$ Hz, 1H), 4.40 - 3.97 (m, 8H), 3.83 (t, $J = 6.8$ Hz, 1H), 3.00 - 2.66 (m, 1H), 2.54 - 2.39 (m, 1H), 1.35 - 1.23 (m, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.0, 167.5, 166.5, 143.0, 139.2, 138.5, 129.4, 129.0, 108.6, 77.5, 77.1, 76.7, 76.6, 62.8, 62.6, 60.9, 51.1, 49.5, 34.0, 14.1, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{ClNNaO}_8\text{S}^+$: 510.0960; Found: 510.0969.



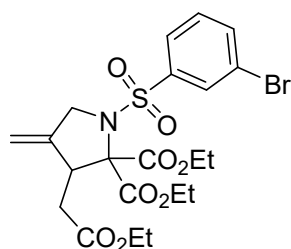
Diethyl-1-((4-bromophenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3ag

Light yellow solid (*cis-1a* 49.4 mg, 93% yield; *trans-1a* 41.7 mg, 79% yield). **MP:** 86.0 - 88.0 °C. **¹H NMR (300 MHz, CDCl₃)** δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 5.00 (s, 1H), 4.94 (s, 1H), 4.39 - 3.95 (m, 8H), 3.83 (s, 1H), 2.79 (dd, *J* = 16.9, 5.7 Hz, 1H), 2.46 (dd, *J* = 16.9, 8.1 Hz, 1H), 1.35 - 1.22 (m, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 171.0, 167.5, 166.5, 142.9, 139.0, 132.0, 129.5, 127.8, 108.6, 76.7, 62.8, 62.6, 61.0, 51.1, 49.5, 34.0, 14.2, 13.9 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₂₁H₂₆BrNNaO₈S⁺: 554.0455 ; Found: 554.0466.



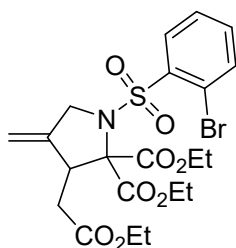
Diethyl-1-([1,1'-biphenyl]-4-ylsulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3ah

Yellow oil (*cis-1a* 51.6 mg, 98% yield; *trans-1a* 46.5 mg, 90% yield). **¹H NMR (300 MHz, CDCl₃)** δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.65 - 7.58 (m, 2H), 7.53 - 7.38 (m, 3H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.95 (d, *J* = 1.8 Hz, 1H), 4.42 - 4.03 (m, 8H), 3.88 (s, 1H), 2.83 (dd, *J* = 16.9, 5.6 Hz, 1H), 2.50 (dd, *J* = 16.9, 8.3 Hz, 1H), 1.37 - 1.23 (m, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 171.1, 167.5, 166.6, 145.6, 143.3, 139.5, 138.6, 129.0, 128.4, 127.4, 127.4, 108.4, 76.5, 62.8, 62.5, 60.9, 51.2, 49.6, 33.9, 14.2, 14.0 ppm. **HRMS (ESI) m/z:** [M+Na]⁺ calcd for C₂₇H₃₁BrNNaO₈S⁺: 552.1663 ; Found: 552.1669.



Diethyl-1-((3-bromophenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3ai

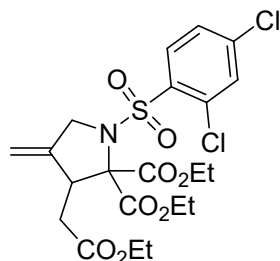
Yellow oil (*cis-1a* 29.7 mg, 51% yield; *trans-1a* 31.8 mg, 60% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.13 (t, $J = 1.7$ Hz, 1H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.75 - 7.67 (m, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 5.02 (d, $J = 1.7$ Hz, 1H), 4.95 (d, $J = 1.9$ Hz, 1H), 4.40 - 4.00 (m, 8H), 3.85 (t, $J = 6.8$ Hz, 1H), 2.80 (dd, $J = 16.9, 5.5$ Hz, 1H), 2.48 (dd, $J = 16.9, 8.3$ Hz, 1H), 1.36 - 1.23 (m, 9H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.0, 167.3, 166.4, 142.9, 141.8, 135.8, 130.7, 130.3, 126.4, 122.8, 108.6, 76.6, 62.8, 62.6, 61.0, 51.3, 49.5, 33.8, 14.2, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{BrNNaO}_8\text{S}^+$: 554.0455; Found: 554.0460.



Diethyl-1-((2-bromophenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3aj

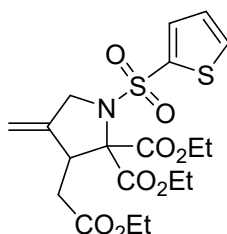
Yellow oil (*cis-1a* 32.8 mg, 62% yield; *trans-1a* 34.0 mg, 64% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.04 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.73 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.47 - 7.33 (m, 2H), 5.08 (d, $J = 1.9$ Hz, 1H), 4.93 (d, $J = 2.1$ Hz, 1H), 4.67 - 4.49 (m, 2H), 4.30 - 4.01 (m, 6H), 3.94 - 3.85 (m, 1H), 2.85 (dd, $J = 16.8, 4.2$ Hz, 1H), 2.46 (dd, $J = 16.8, 9.0$ Hz, 1H), 1.31 - 1.24 (m, 6H), 1.14 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.0, 166.7, 166.5, 143.3, 141.2, 135.3, 133.0, 131.0, 127.1, 119.6,

107.6, 76.0, 62.5, 62.4, 61.0, 54.2, 49.2, 33.6, 14.1, 14.0, 13.7 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{21}H_{26}BrNNaO_8S^+$: 554.0455; Found: 554.0475.



Diethyl-1-((2,4-dichlorophenyl)sulfonyl)-3-(2-ethoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3ak

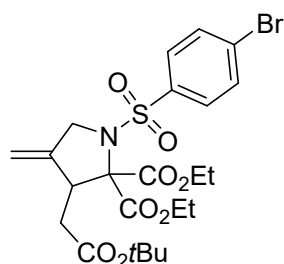
Yellow oil (*cis-1a* 41.8 mg, 80% yield; *trans-1a* 27.9 mg, 57% yield). **1H NMR (300 MHz, $CDCl_3$)** δ 7.95 (d, $J = 8.6$ Hz, 1H), 7.51 (d, $J = 2.0$ Hz, 1H), 7.36 (dd, $J = 8.6, 2.0$ Hz, 1H), 5.08 (d, $J = 1.8$ Hz, 1H), 4.93 (d, $J = 2.0$ Hz, 1H), 4.66 - 4.46 (m, 2H), 4.29 - 4.07 (m, 6H), 3.83 (dd, $J = 6.8, 1.9$ Hz, 1H), 2.85 (dd, $J = 16.7, 4.1$ Hz, 1H), 2.43 (dd, $J = 16.7, 9.0$ Hz, 1H), 1.31 - 1.17 (m, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.0, 166.7, 143.1, 138.8, 138.3, 132.6, 132.1, 131.4, 126.8, 107.7, 76.3, 62.6, 62.5, 61.0, 54.1, 49.1, 33.6, 14.1, 14.0, 13.8 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{21}H_{25}Cl_2NNaO_8S^+$: 544.0570; Found: 544.0579.



Diethyl-3-(2-ethoxy-2-oxoethyl)-4-methylene-1-(thiophen-2-ylsulfonyl)pyrrolidine-2,2-dicarboxylate 3al

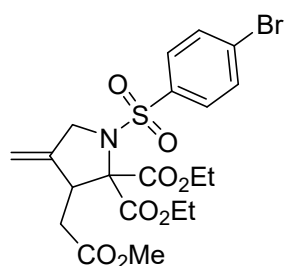
Yellow oil (*cis-1a* 19.0 mg, 41% yield; *trans-1a* 34.9 mg, 76% yield). **1H NMR (300 MHz, $CDCl_3$)** δ 7.76 (dd, $J = 3.7, 1.2$ Hz, 1H), 7.61 (dd, $J = 5.0, 1.2$ Hz, 1H), 7.09 (dd, $J = 4.9, 3.9$ Hz, 1H), 5.02 (d, $J = 1.7$ Hz, 1H), 4.96 (d, $J = 1.9$ Hz, 1H), 4.41 - 4.09 (m, 8H), 3.87 (t, $J = 6.8$ Hz, 1H), 2.82 (dd, $J = 16.8, 5.6$ Hz, 1H), 2.49 (dd, $J = 16.8, 8.3$ Hz, 1H), 1.37 - 1.24 (m, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.0, 167.3, 166.3, 142.9, 140.8, 133.4, 132.4, 127.0, 108.6, 76.7, 62.8, 62.5, 60.9, 51.1,

49.6, 33.9, 14.1, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{19}H_{25}BrNNaO_8S_2^+$: 482.0914; Found: 482.0915.



Diethyl-1-((4-bromophenyl)sulfonyl)-3-(2-(tert-butoxy)-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3bg

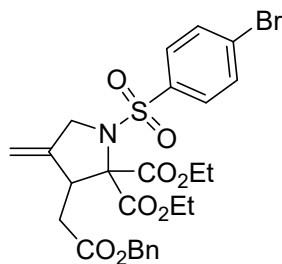
Yellow oil, 22.9 mg, 41% yield. 1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 5.00 (d, $J = 1.8$ Hz, 1H), 4.95 (d, $J = 1.9$ Hz, 1H), 4.39 - 4.17 (m, 4H), 4.10 - 3.96 (m, 2H), 3.79 (s, 1H), 2.74 (dd, $J = 16.8, 5.5$ Hz, 1H), 2.37 (dd, $J = 16.8, 8.3$ Hz, 1H), 1.45 (s, 9H), 1.35 - 1.28 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 167.5, 166.5, 143.2, 139.1, 132.0, 129.5, 127.7, 108.4, 81.2, 76.7, 62.7, 62.5, 51.2, 49.7, 35.0, 28.0, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{23}H_{30}BrNNaO_8S^+$: 582.0768; Found: 582.0770.



Diethyl-1-((4-bromophenyl)sulfonyl)-3-(2-methoxy-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3cg

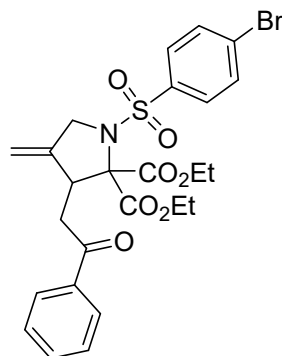
Yellow oil, 34.1 mg, 66% yield. 1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 5.00 (d, $J = 1.4$ Hz, 1H), 4.94 (d, $J = 1.6$ Hz, 1H), 4.39 - 4.18 (m, 4H), 4.09 - 3.96 (m, 2H), 3.84 (t, $J = 6.8$ Hz, 1H), 3.69 (s, 3H), 2.80 (dd, $J = 16.9, 6.0$ Hz, 1H), 2.49 (dd, $J = 16.9, 8.0$ Hz, 1H), 1.31 (q, $J = 7.1$ Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 167.4, 166.4, 142.9, 139.0, 132.0, 129.5, 127.8,

108.6, 76.7, 62.8, 62.6, 52.0, 51.0, 49.5, 33.8, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{20}H_{24}BrNNaO_8S^+$: 540.0298; Found: 540.0305.



Diethyl-3-(2-(benzyloxy)-2-oxoethyl)-1-((4-bromophenyl)sulfonyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3dg

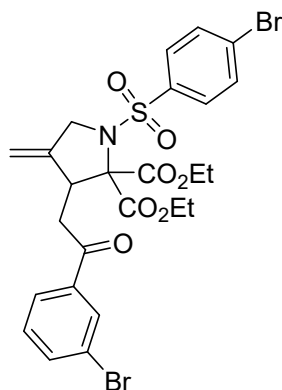
Yellow oil, 48.8 mg, 82% yield. 1H NMR (300 MHz, $CDCl_3$) δ 7.89 (t, $J = 9.5$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.36 (s, 5H), 5.11 (d, $J = 12.2$ Hz, 2H), 4.98 (d, $J = 1.3$ Hz, 1H), 4.91 (d, $J = 1.6$ Hz, 1H), 4.39 - 4.14 (m, 4H), 4.10 - 3.96 (m, 2H), 3.87 (t, $J = 6.7$ Hz, 1H), 2.87 (dd, $J = 17.0, 5.8$ Hz, 1H), 2.53 (dd, $J = 17.0, 8.1$ Hz, 1H), 1.34 - 1.25 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 167.4, 166.4, 142.8, 139.1, 135.5, 132.0, 129.5, 128.6, 128.4, 128.4, 127.8, 108.7, 76.7, 66.8, 62.8, 62.6, 51.1, 49.5, 34.0, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{26}H_{28}BrNNaO_8S^+$: 616.0611; Found: 616.0620.



Diethyl-1-((4-bromophenyl)sulfonyl)-4-methylene-3-(2-oxo-2-phenylethyl)pyrrolidine-2,2-dicarboxylate 3eg

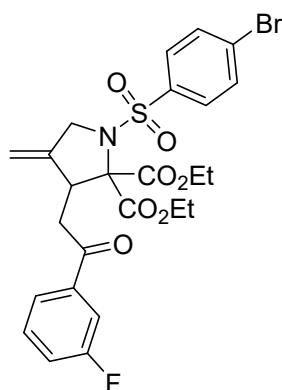
Yellow oil, 37.1 mg, 66% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.94 (m, 2H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.67 (d, $J = 8.6$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 5.00 (d, $J = 1.6$ Hz, 1H), 4.88 (d, $J = 1.8$ Hz, 1H), 4.40 - 4.19 (m, 4H), 4.19 - 4.03 (m, 3H), 3.57 (dd, $J = 18.2, 5.9$ Hz, 1H), 3.13 (dd, $J = 18.2, 6.9$ Hz, 1H), 1.33 - 1.26 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 167.6, 167.0, 143.5,

139.2, 136.4, 133.5, 132.0, 129.5, 128.8, 128.0, 127.8, 108.4, 76.8, 62.8, 62.6, 51.3, 48.7, 38.2, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{25}H_{26}BrNNaO_7S^+$: 586.0506; Found: 586.0512.



Diethyl-3-(2-(3-bromophenyl)-2-oxoethyl)-1-((4-bromophenyl)sulfonyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3fg

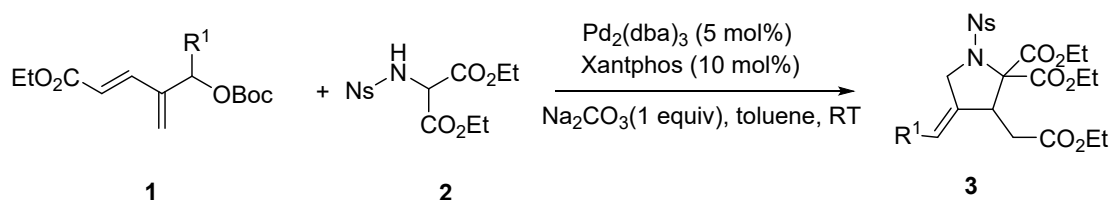
Yellow oil, 21.3 mg, 33% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 2H), 7.38 (t, $J = 7.9$ Hz, 1H), 5.02 (d, $J = 1.4$ Hz, 1H), 4.89 (d, $J = 1.7$ Hz, 1H), 4.42 - 4.19 (m, 4H), 4.16 - 4.02 (m, 3H), 3.55 (dd, $J = 18.3, 6.4$ Hz, 1H), 3.05 (dd, $J = 18.3, 6.4$ Hz, 1H), 1.35 - 1.27 (m, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 167.5, 166.9, 143.3, 139.1, 138.1, 136.3, 132.1, 131.1, 130.4, 129.5, 127.8, 126.6, 123.1, 108.6, 76.7, 62.9, 62.7, 51.0, 48.7, 38.4, 14.0, 13.9 ppm. **HRMS** (ESI) m/z : $[M+Na]^+$ calcd for $C_{25}H_{25}Br_2NNaO_7S^+$: 663.9611; Found: 663.9614.



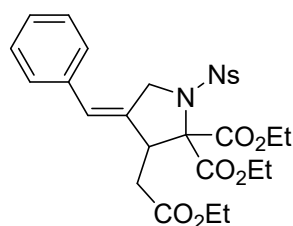
Diethyl-1-((4-bromophenyl)sulfonyl)-3-(2-(3-fluorophenyl)-2-oxoethyl)-4-methylenepyrrolidine-2,2-dicarboxylate 3gg

Yellow oil, 25.5 mg, 44% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.6$ Hz, 2H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 2H), 7.64 (dd, $J = 9.3, 2.0$ Hz, 1H), 7.52 - 7.45 (m, 1H), 7.35 - 7.29 (m, 1H), 5.02 (d, $J = 1.6$ Hz, 1H), 4.89 (d, $J = 1.8$ Hz, 1H), 4.41 - 4.19 (m, 4H), 4.17 - 4.02 (m, 3H), 3.56 (dd, $J = 18.3, 6.3$ Hz, 1H), 3.08 (dd, $J = 18.3, 6.5$ Hz, 1H), 1.34 - 1.27 (m, 6H) ppm. $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 195.4, 167.5, 166.9, 162.9 (d, $J = 248.3$ Hz), 143.3, 139.1, 138.4 (d, $J = 6.3$ Hz), 132.0, 130.5 (d, $J = 7.6$ Hz), 129.5, 127.9, 123.8 (d, $J = 2.8$ Hz), 120.6, 120.4, 114.8 (d, $J = 22.4$ Hz), 108.5, 76.7, 62.9, 62.7, 51.1, 48.7, 38.5, 13.9 ppm. **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{25}\text{BrFNNaO}_7\text{S}^+$: 604.0411; Found: 604.0414.

General Procedure for (3+2) cycloaddition reaction.



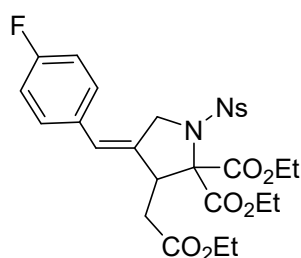
Xantphos (0.01 mmol) and $\text{Pd}_2(\text{dba})_3$ (0.005 mmol) were dissolved in toluene (1.0 mL) in a 10 mL Schlenk tube under N_2 . After stirring at room temperature for 0.5 h, material **1** (0.13 mmol), material **2** (0.1 mmol), Na_2CO_3 (0.1 mmol) were added. The reaction mixture was stirred at r.t. until the material **2** was totally consumed (monitored by TLC), and then was purified by flash column chromatography directly to afford the corresponding product **3ha-3na**.



Diethyl-(Z)-4-benzylidene-3-(2-ethoxy-2-oxoethyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate **3ha**

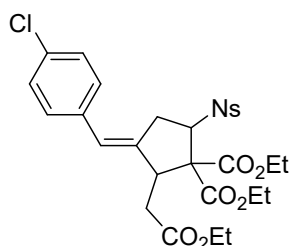
Yellow oil, 48.0 mg, 84% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 - 8.36 (m, 2H), 8.31 - 8.24 (m, 2H), 7.37 (t, $J = 7.4$ Hz, 2H), 7.32 - 7.29 (m, 1H), 7.11 (d, $J = 7.2$ Hz, 2H), 6.37 (d, $J = 1.8$ Hz, 1H), 4.41 - 4.13 (m, 8H), 4.08 (t, $J = 6.5$ Hz, 1H), 2.91 (dd, J

= 16.8, 6.1 Hz, 1H), 2.56 (dd, J = 16.8, 8.0 Hz, 1H), 1.36 - 1.26 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 167.5, 166.3, 145.8, 135.3, 134.5, 129.2, 128.7, 128.3, 127.9, 124.9, 124.1, 76.3, 63.1, 62.9, 61.1, 50.9, 49.6, 35.0, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{NaO}_{10}\text{S}^+$: 597.1513; Found: 597.1512.



Diethyl-(Z)-3-(2-ethoxy-2-oxoethyl)-4-(4-fluorobenzylidene)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3ia

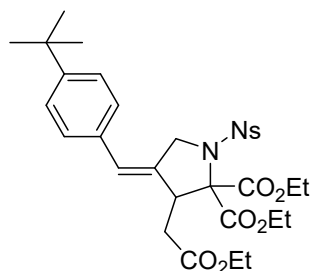
Yellow oil, 49.6 mg, 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.45 - 8.35 (m, 2H), 8.31 - 8.22 (m, 2H), 7.11 - 7.02 (m, 4H), 6.33 (d, J = 1.9 Hz, 1H), 4.41 - 4.13 (m, 8H), 4.06 (t, J = 6.5 Hz, 1H), 2.90 (dd, J = 16.8, 6.0 Hz, 1H), 2.54 (dd, J = 16.8, 8.0 Hz, 1H), 1.36 - 1.25 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 167.4, 166.3, 162.1 (d, J = 249.1 Hz), 150.1, 145.8, 134.3, 131.5 (d, J = 3.5 Hz), 130.0 (d, J = 8.2 Hz), 129.2, 124.1, 123.8, 115.8 (d, J = 21.6 Hz), 76.3, 63.0 (d, J = 18.8 Hz), 61.1, 50.8, 49.5, 34.9, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{29}\text{FN}_2\text{NaO}_{10}\text{S}^+$: 615.1419; Found: 615.1422.



Diethyl-(Z)-4-(4-chlorobenzylidene)-3-(2-ethoxy-2-oxoethyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3ja

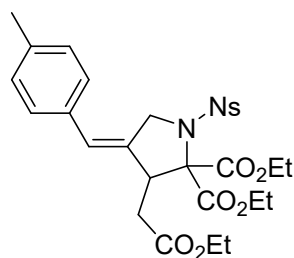
Yellow oil, 43.5 mg, 72% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.38 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 6.30 (d, J = 1.6 Hz, 1H), 4.41 - 4.22 (m, 6H), 4.19 - 4.11 (m, 2H), 4.04 (t, J = 6.5 Hz, 1H), 2.89 (dd, J = 16.8, 6.0 Hz, 1H), 2.53 (dd, J = 16.8, 8.0 Hz, 1H), 1.35 - 1.23 (m, 9H)

ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 167.4, 166.3, 150.1, 145.7, 135.3, 133.7, 129.5, 129.2, 128.9, 124.1, 123.7, 76.3, 63.1, 62.9, 61.1, 50.8, 49.6, 34.9, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{29}\text{ClN}_2\text{NaO}_{10}\text{S}^+$: 631.1124; Found: 631.1125.



Diethyl-(Z)-4-(4-(tert-butyl)benzylidene)-3-(2-ethoxy-2-oxoethyl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3ka

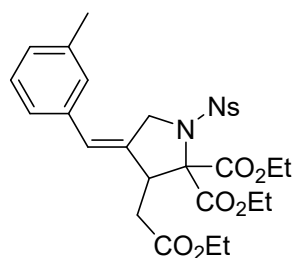
Yellow oil, 45.0 mg, 72% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.39 (d, $J = 8.9$ Hz, 2H), 8.27 (d, $J = 8.9$ Hz, 2H), 7.38 (d, $J = 8.3$ Hz, 2H), 7.04 (d, $J = 8.3$ Hz, 2H), 6.34 (s, 1H), 4.39 - 4.22 (m, 6H), 4.19 - 4.11 (m, 2H), 4.06 (t, $J = 6.6$ Hz, 1H), 2.88 (dd, $J = 16.8, 6.2$ Hz, 1H), 2.54 (dd, $J = 16.8, 7.9$ Hz, 1H), 1.36-1.26 (m, 18H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 171.0, 167.5, 166.4, 151.1, 150.1, 145.8, 133.5, 132.5, 129.3, 128.1, 125.6, 124.8, 124.1, 76.4, 63.0, 62.9, 61.0, 50.9, 49.6, 34.7, 31.2, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{38}\text{N}_2\text{NaO}_{10}\text{S}^+$: 653.2139 ; Found: 653.2151.



Diethyl-(Z)-3-(2-ethoxy-2-oxoethyl)-4-(4-methylbenzylidene)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3la

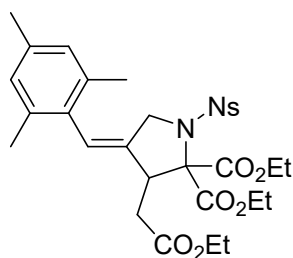
Yellow oil, 47.7 mg, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.41 - 8.37 (m, 2H), 8.30 - 8.24 (m, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 6.33 (d, $J = 1.7$ Hz, 1H), 4.40 - 4.21 (m, 6H), 4.19 - 4.12 (m, 2H), 4.06 (t, $J = 6.6$ Hz, 1H), 2.89 (dd, J

= 16.8, 6.2 Hz, 1H), 2.55 (dd, J = 16.8, 7.9 Hz, 1H), 2.36 (s, 3H), 1.36 - 1.25 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 171.0, 167.5, 166.4, 150.1, 145.8, 137.8, 133.4, 132.5, 129.4, 129.2, 128.3, 124.8, 124.0, 76.3, 63.0, 62.9, 61.0, 50.9, 49.6, 35.0, 21.2, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{NaO}_{10}\text{S}^+$: 611.1670 ; Found: 611.1675.



Diethyl-(Z)-3-(2-ethoxy-2-oxoethyl)-4-(3-methylbenzylidene)-1-((4-nitrophenyl)sulfonyl)pyrrolidine-2,2-dicarboxylate 3ma

Yellow oil, 51.4 mg, 87% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.43 - 8.36 (m, 2H), 8.31 - 8.23 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.13 - 7.09 (m, 1H), 6.95 - 6.88 (m, 2H), 6.34 (d, J = 1.8 Hz, 1H), 4.39 - 4.13 (m, 8H), 4.07 (t, J = 7.4 Hz, 1H), 2.90 (dd, J = 16.8, 6.1 Hz, 1H), 2.55 (dd, J = 16.8, 8.0 Hz, 1H), 2.36 (s, 3H), 1.35 - 1.26 (m, 9H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 167.5, 166.4, 145.8, 138.3, 135.3, 134.2, 129.2, 128.7, 128.6, 125.2, 124.1, 76.3, 63.1, 62.9, 61.0, 50.9, 49.5, 35.0, 21.5, 14.2, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{NaO}_{10}\text{S}^+$: 611.1670 ; Found: 611.1681.



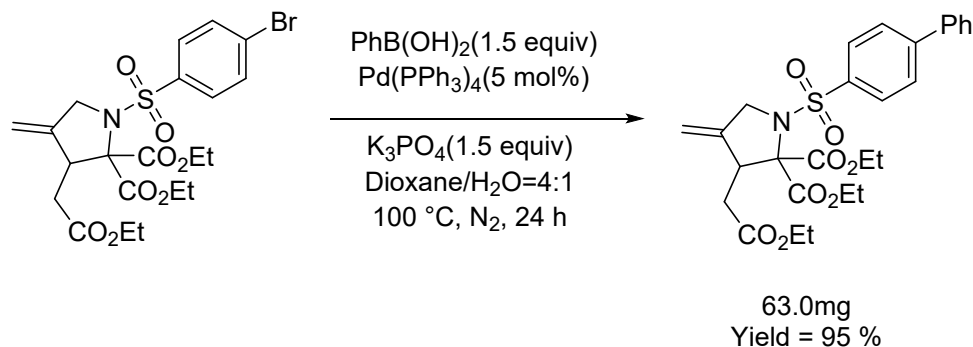
Diethyl-(Z)-3-(2-ethoxy-2-oxoethyl)-1-((4-nitrophenyl)sulfonyl)-4-(2,4,6-trimethylbenzylidene)pyrrolidine-2,2-dicarboxylate 3na

Yellow oil, 28.5 mg, 45% yield. ^1H NMR (300 MHz, CDCl_3) δ 8.39 - 8.26 (m, 2H), 8.13 (d, J = 8.9 Hz, 2H), 6.85 (s, 2H), 6.26 (s, 1H), 4.44 - 4.11 (m, 6H), 4.03 (t, J = 6.5 Hz, 1H), 3.81 - 3.59 (m, 2H), 2.92 (dd, J = 16.8, 5.5 Hz, 1H), 2.59 (dd, J = 16.8,

8.5 Hz, 1H), 2.28 (s, 3H), 2.05 (s, 6H), 1.40 - 1.25 (m, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 170.9, 167.6, 166.5, 150.0, 145.7, 137.2, 136.6, 135.2, 131.6, 129.1, 128.3, 123.9, 123.8, 77.3, 63.0, 62.9, 61.1, 49.4, 49.2, 34.6, 21.0, 19.8, 14.19, 14.0, 13.9 ppm. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{NaO}_{10}\text{S}^+$: 639.1983; Found: 639.1993.

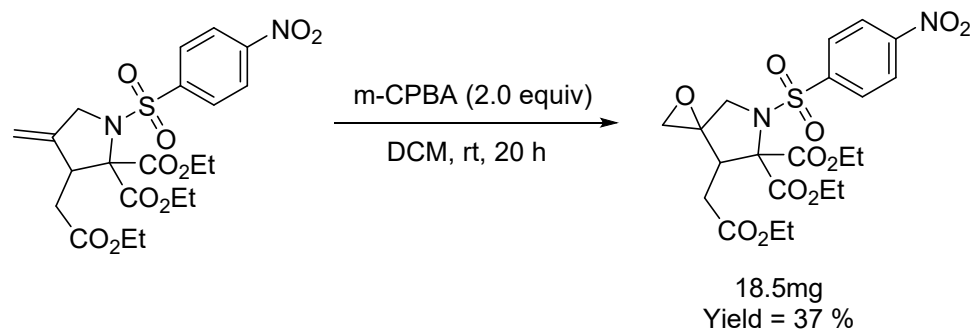
4. Transformations of products 3aa and 3ag

(1) The Suzuki Coupling Reaction of 3ag



3ag (66.8 mg, 0.125 mmol, 1.0 equiv), $\text{PhB}(\text{OH})_2$ (22.6 mg, 0.1875 mmol, 1.5 equiv), $\text{Pd}(\text{PPh}_3)_4$ (7.2 mg, 0.00625 mmol, 5 mol%), K_3PO_4 (39.7 mg, 0.1875 mmol, 1.5 equiv), 1,4-dioxane (2 mL) and H_2O (0.5 mL) were added into a 10 mL glass vial. The vial was purged with N_2 . The reaction mixture was heated at 100°C for 24 h. After being cooled to room temperature, the mixture was poured into water (3 mL), then extracted with EtOAc (5 mL \times 3). The combined organic layer was washed with brine (20 mL), dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo and the residue was purified by silica gel column chromatography to give the desired product **95** % yield (63.0 mg).

(2) Oxidation of 3aa with m-chloroperoxybenzoic acid (m-CPBA)

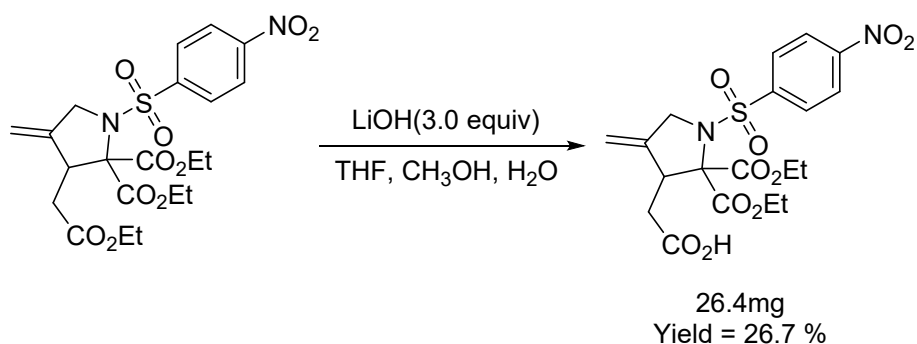


To a solution of **3aa** (49.8 mg, 0.10 mmol) in DCM (4 mL) was added 3-chloroperoxybenzoic acid (*m*-CPBA, 34.4 mg, 2.0 equiv.) at r.t. The reaction mixture was stirred for 20 h and poured into a saturated solution of aqueous sodium bicarbonate. The two layers were separated and the organic layer was washed with a saturated solution of aqueous sodium bicarbonate. This procedure was repeated twice more. The organic layer was dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was purified by column chromatography to give desired product in 37 % yield (18.5 mg).

Diethyl-7-(2-ethoxy-2-oxoethyl)-5-((4-nitrophenyl)sulfonyl)-1-oxa-5-azaspiro[2.4]heptane-6,6-dicarboxylate

Yellow oil. 18.5 mg, 37.1% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.44 - 8.34 (m, 2H), 8.23 - 8.13 (m, 2H), 4.45 - 4.24 (m, 4H), 4.19 - 4.09 (m, 2H), 3.86 (d, *J* = 10.5 Hz, 1H), 3.65 - 3.53 (m, 2H), 2.87 (d, *J* = 3.8 Hz, 1H), 2.79 (d, *J* = 3.8 Hz, 1H), 2.66 (dd, *J* = 17.8, 5.0 Hz, 1H), 2.35 (dd, *J* = 17.8, 7.8 Hz, 1H), 1.39 - 1.33 (m, 6H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 171.3, 167.2, 166.3, 150.1, 145.4, 129.2, 124.0, 76.5, 63.2, 62.9, 61.1, 52.1, 47.4, 46.7, 28.5, 14.1, 13.9, 13.9 ppm. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₁H₂₆N₂NaO₁₁S⁺: 537.1150; Found: 537.1157.

(3) Decarboxylation of 3aa



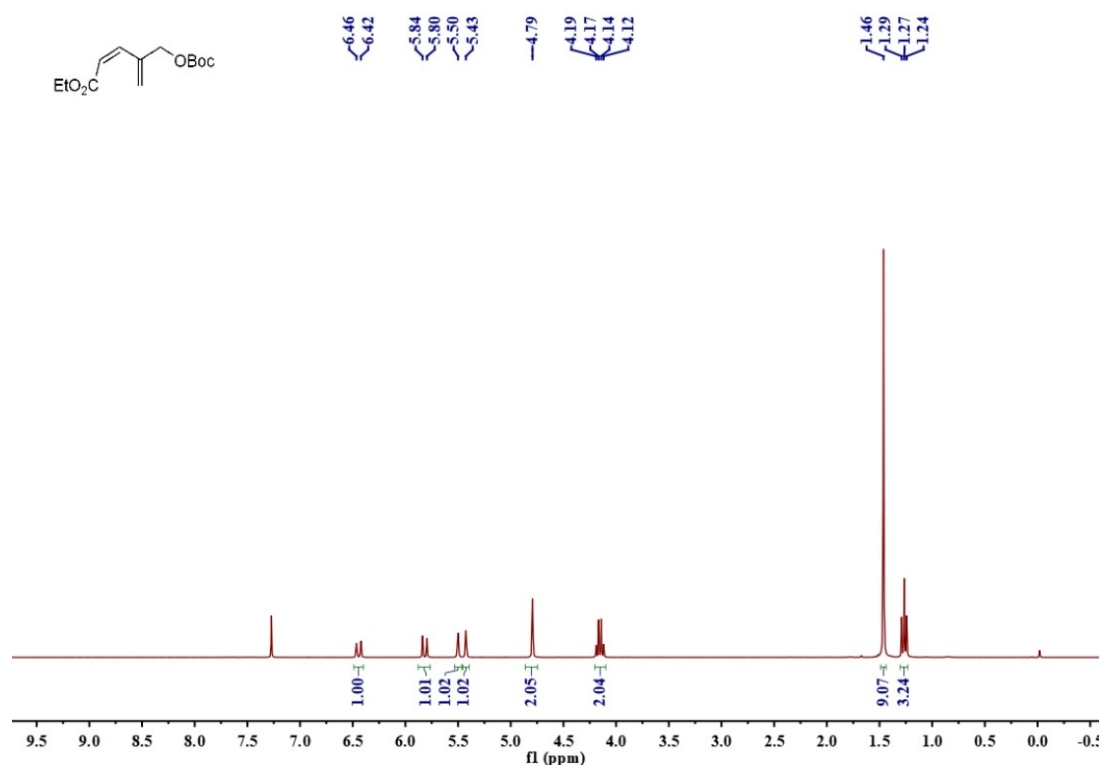
3aa (0.20 mmol) was added into a 50 mL round-bottomed flask, and 2 mL of tetrahydrofuran, 2 mL of methanol, 2 mL of water and LiOH·H₂O (0.60 mmol) were added, and reacted at room temperature for 12 hours. Remove solvent with rotary evaporator, extract with dichloromethane and water, and collect water phase. Add

dilute hydrochloric acid into the water phase until the pH is equal to 1-2. Extract the aqueous phase with dichloromethane, collect the organic phase, dry the organic phase with MgSO₄, filter, and concentrate on the rotary evaporator to remove the solvent. The crude product was purified by column chromatography, and the required product was obtained with 26.7% yield.

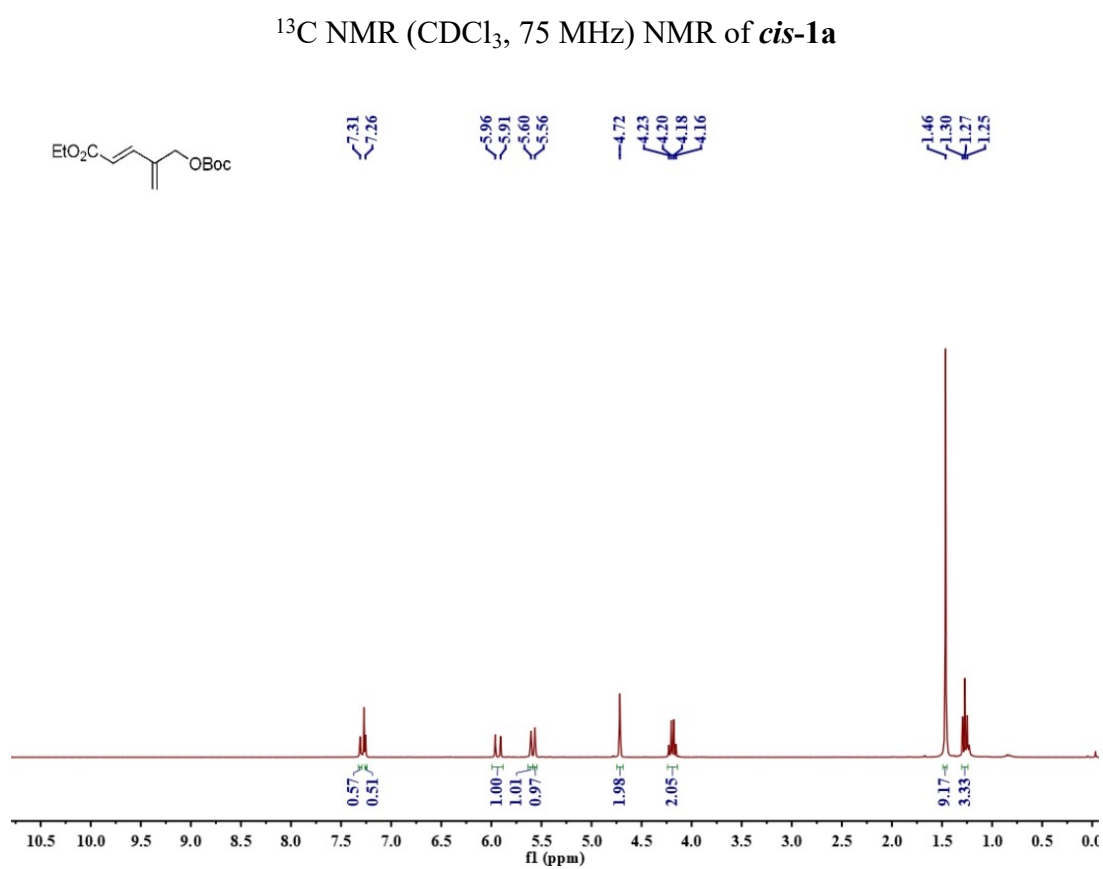
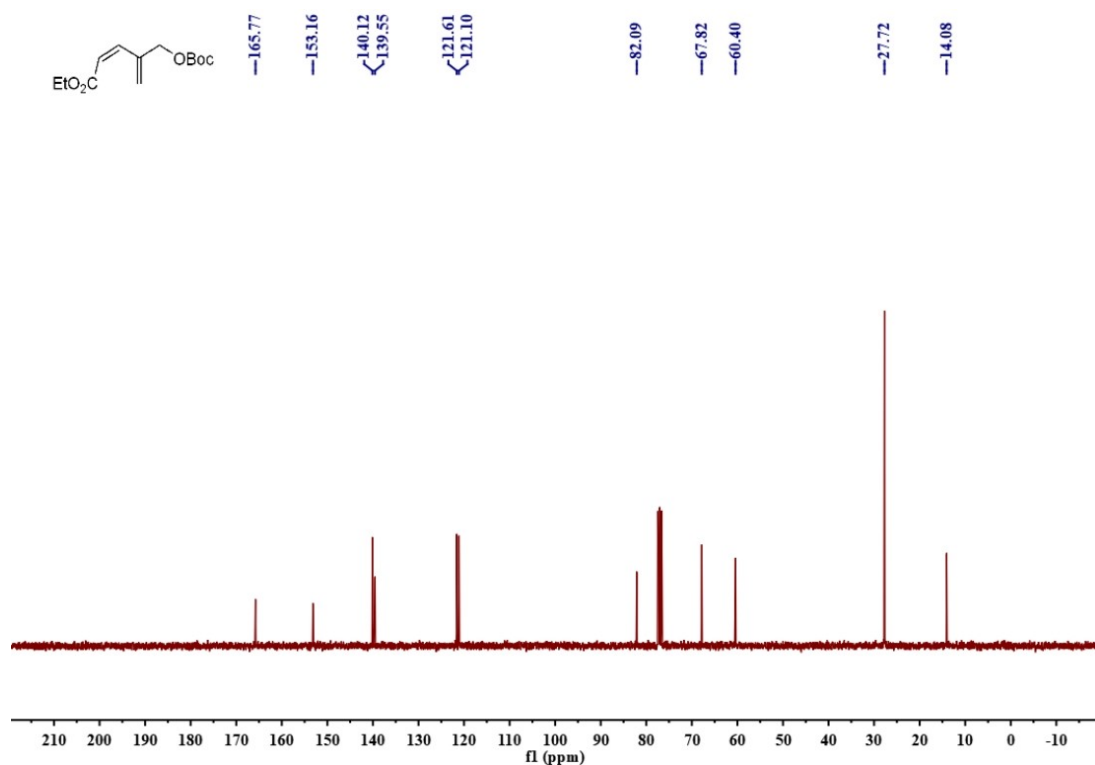
2-(2,2-Bis(ethoxycarbonyl)-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidin-3-yl)acetic acid

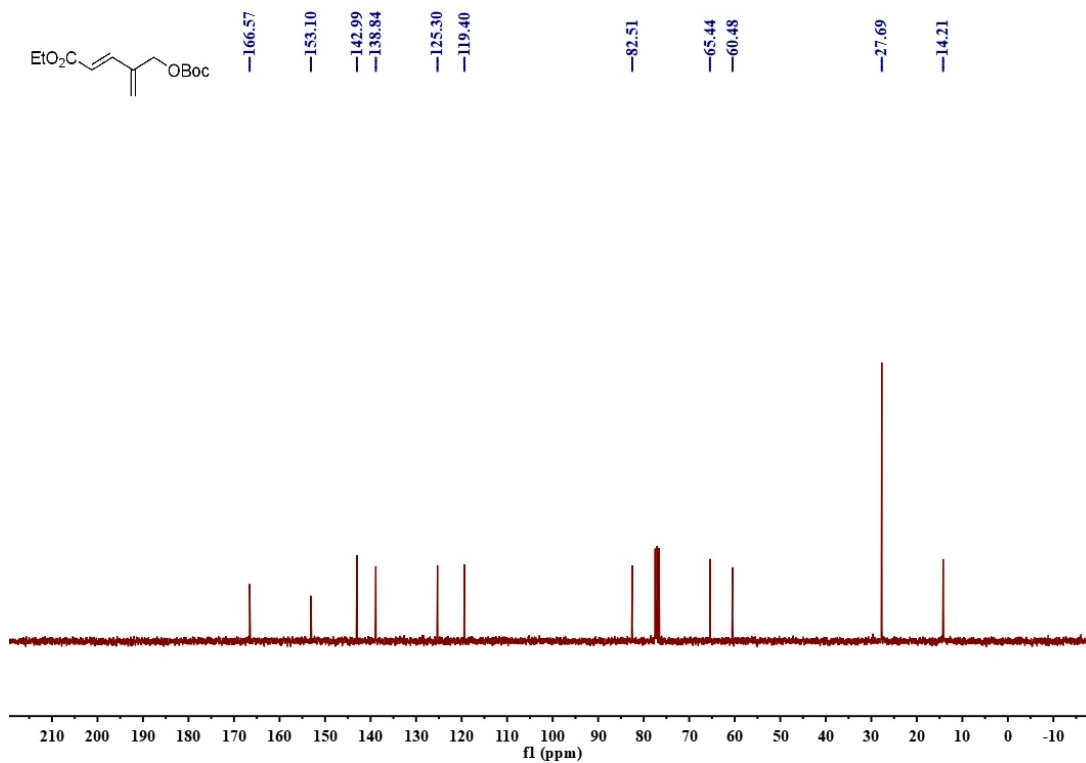
Colorless oil, 26.4 mg, 26.7% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.76 (s, 1H), 8.37 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 8.7 Hz, 2H), 4.35 - 4.06 (m, 6H), 3.86 (s, 1H), 2.62 - 2.37 (m, 2H), 1.26 - 1.15 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 168.0, 166.9, 150.1, 145.4, 143.0, 128.76, 124.1, 108.2, 76.1, 63.1, 62.8, 52.1, 50.9, 35.5, 13.9, 13.8 ppm. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₉H₂₂N₂NaO₁₀S⁺: 493.0887; Found: 493.0895.

5. Copies of ¹H NMR, ¹³C NMR spectra

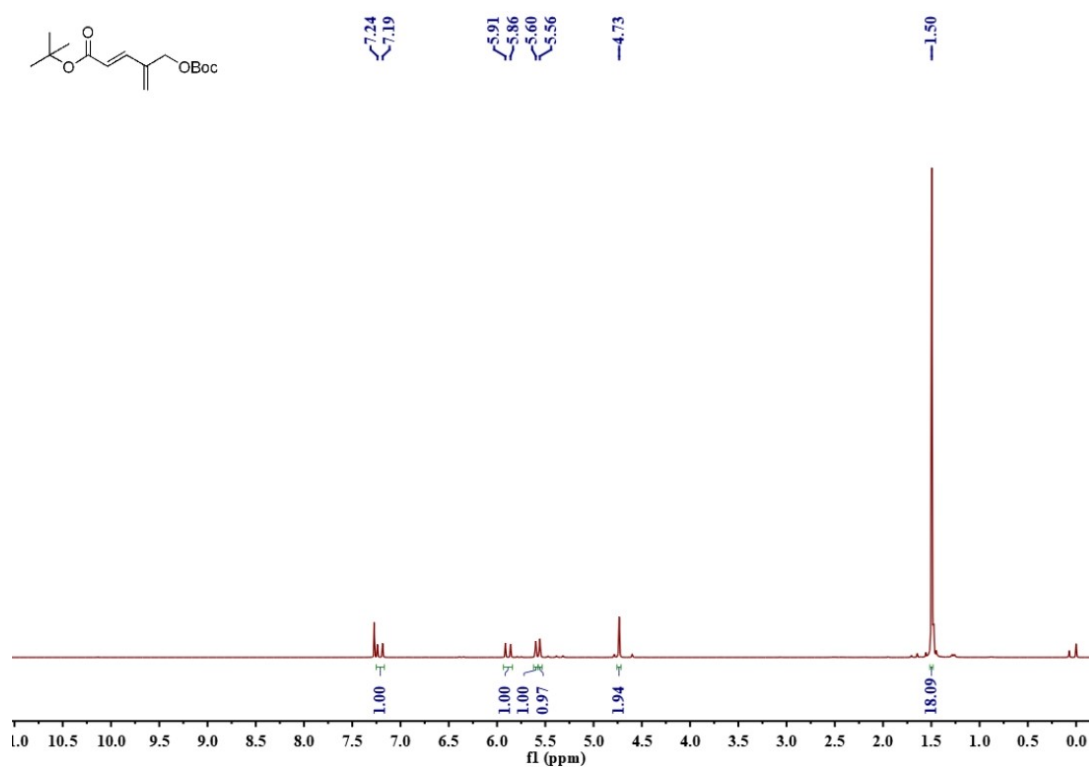


¹H NMR (CDCl₃, 300 MHz) NMR of *cis-1a*

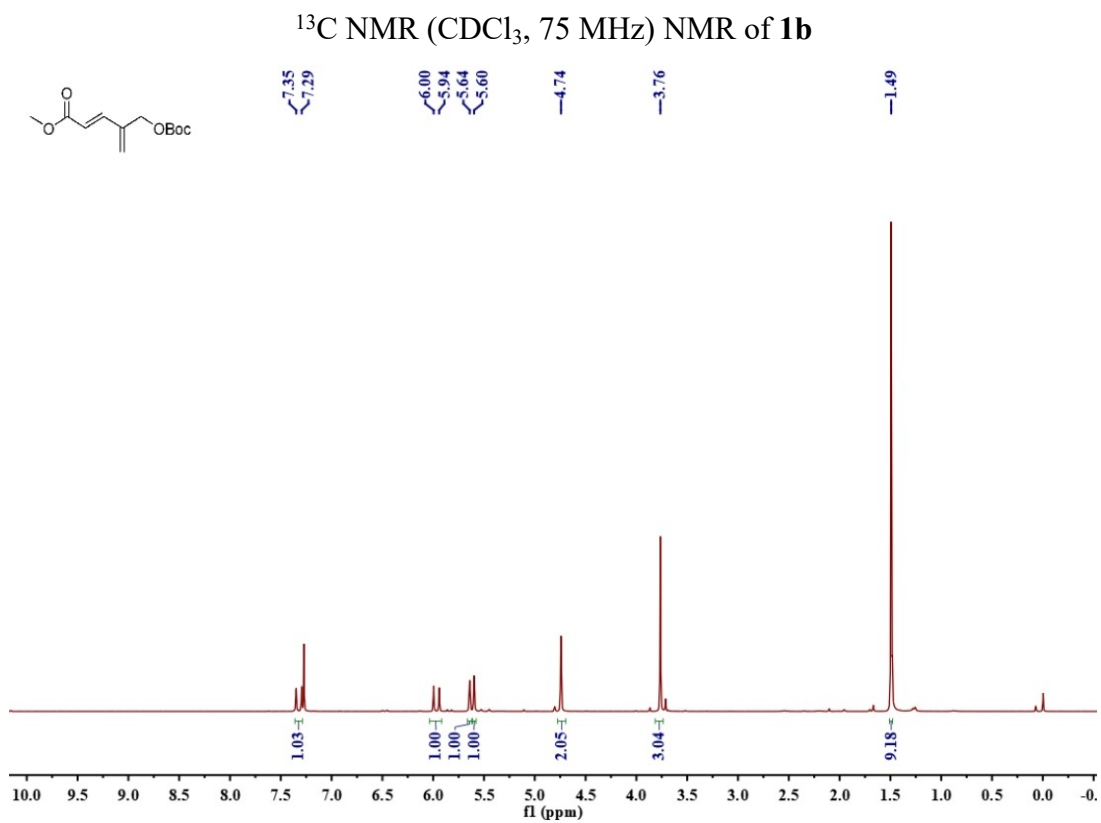
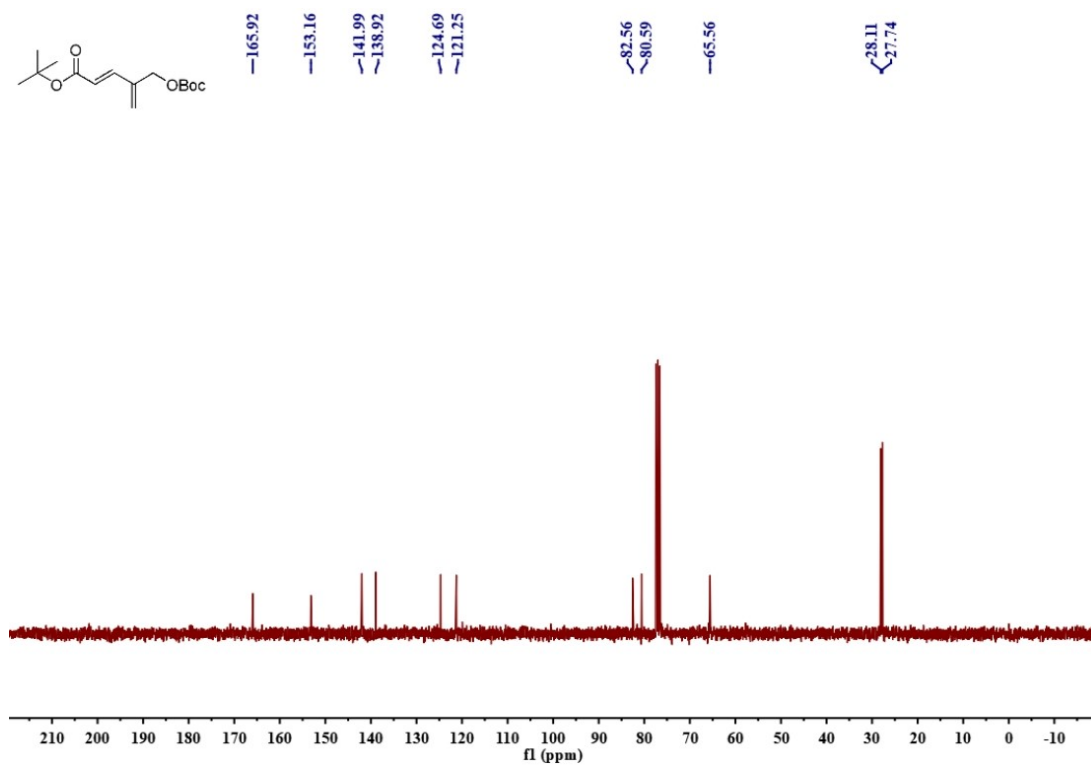


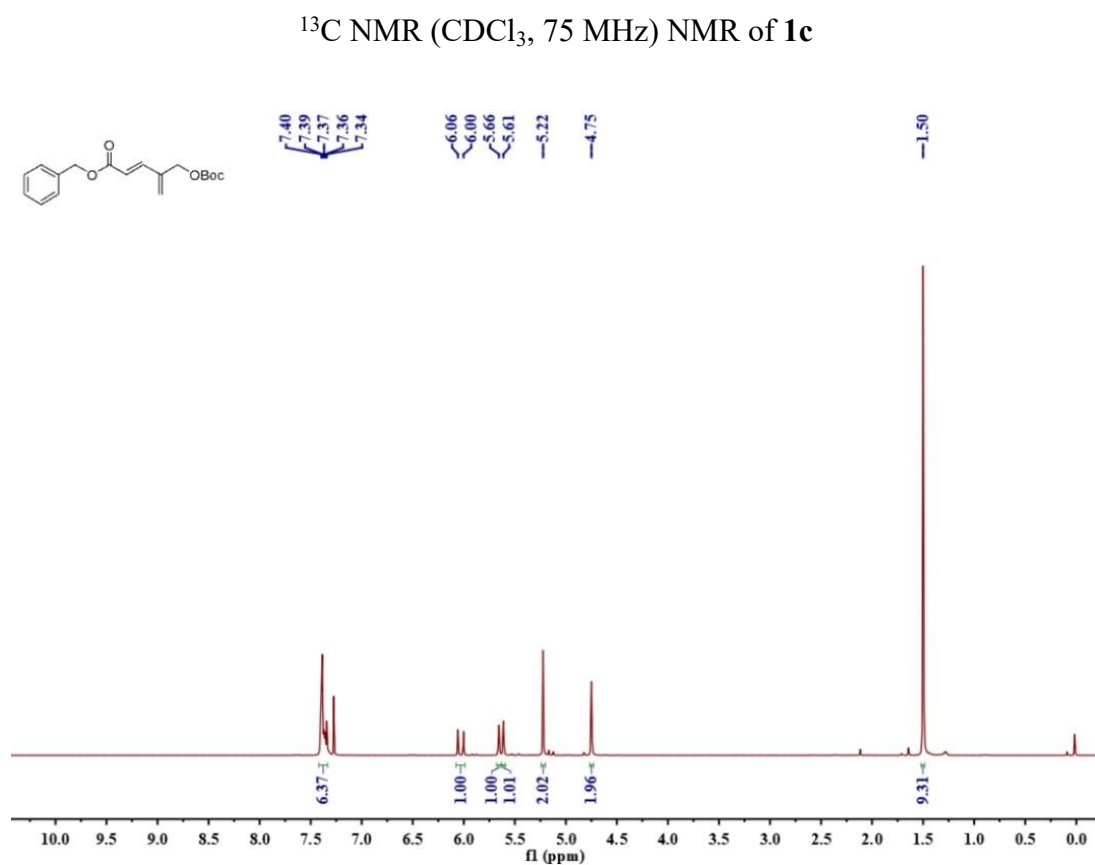
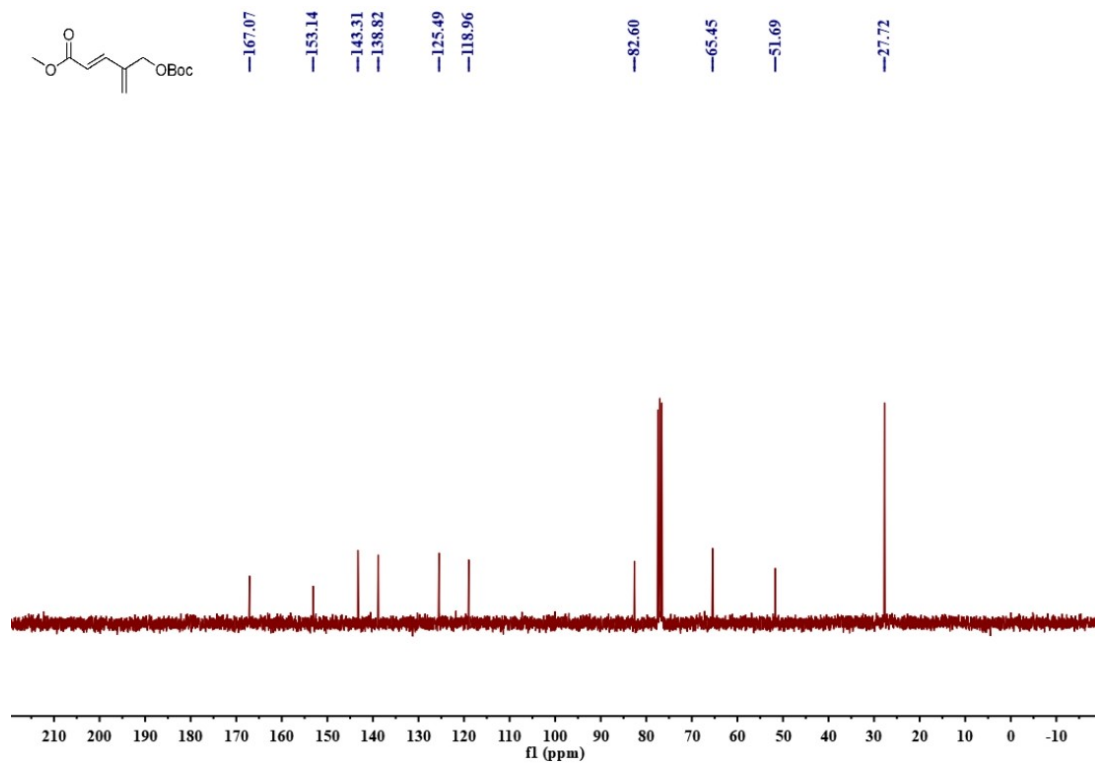


^{13}C NMR (CDCl₃, 75 MHz) NMR of *trans*-1a

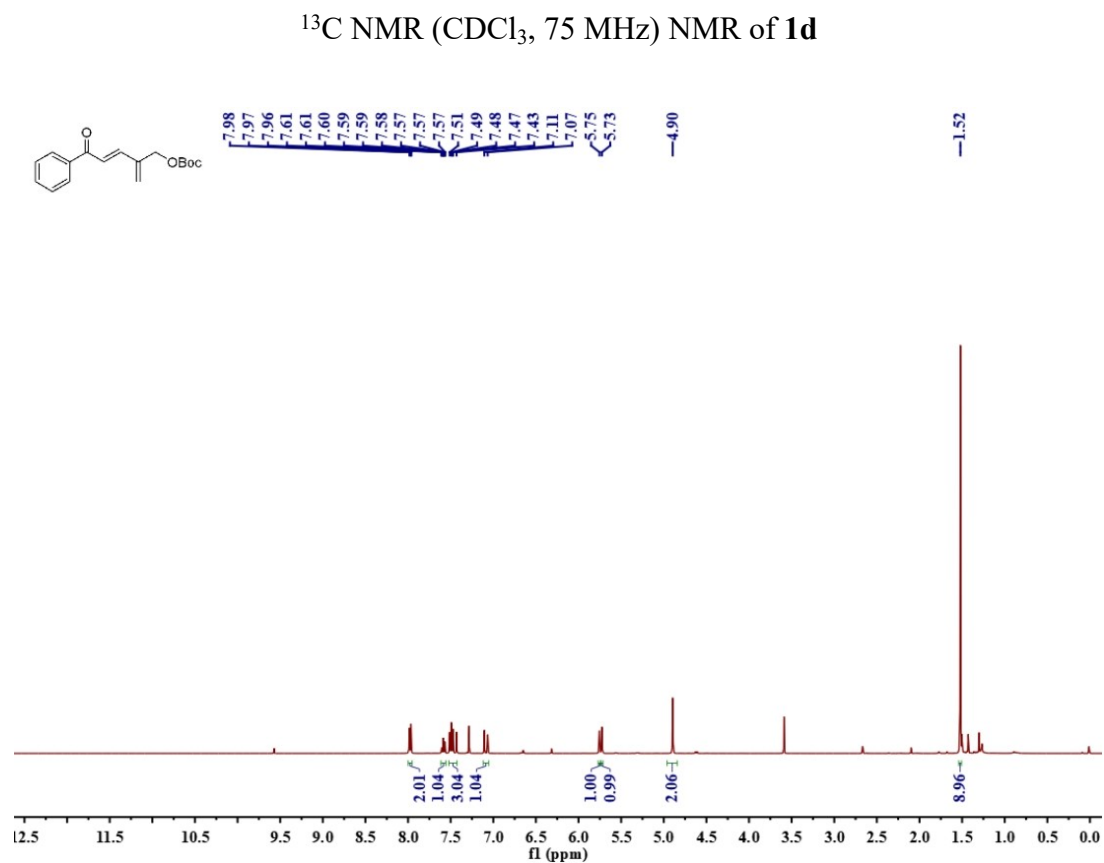
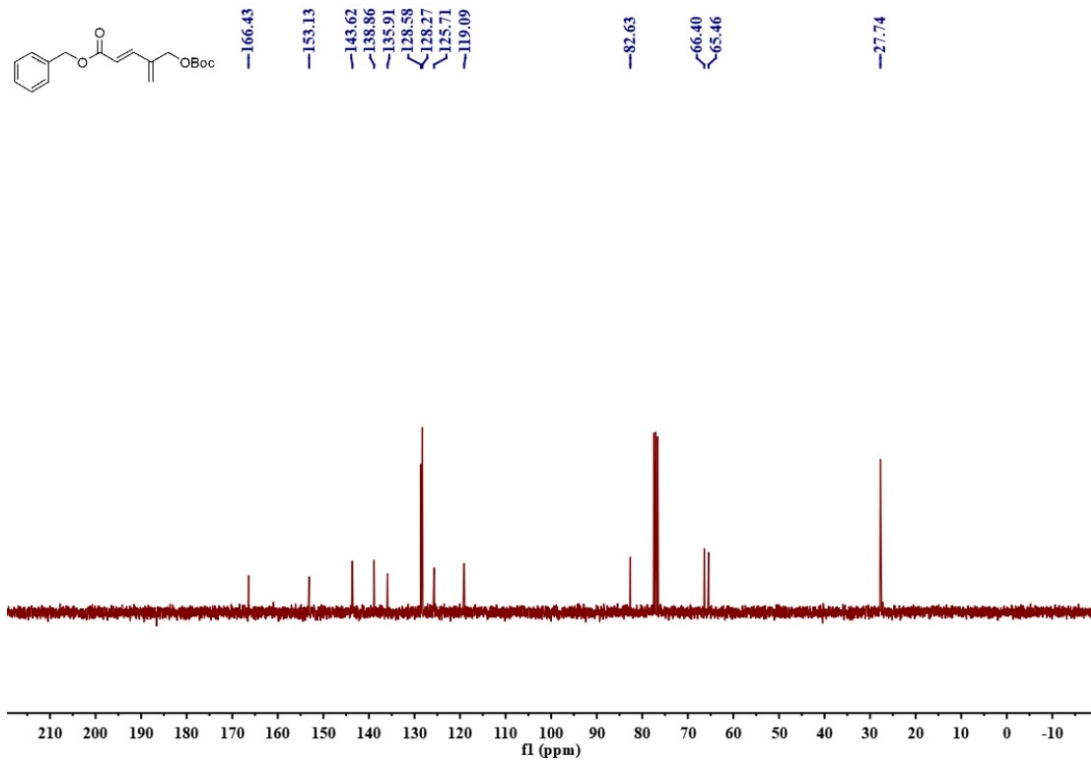


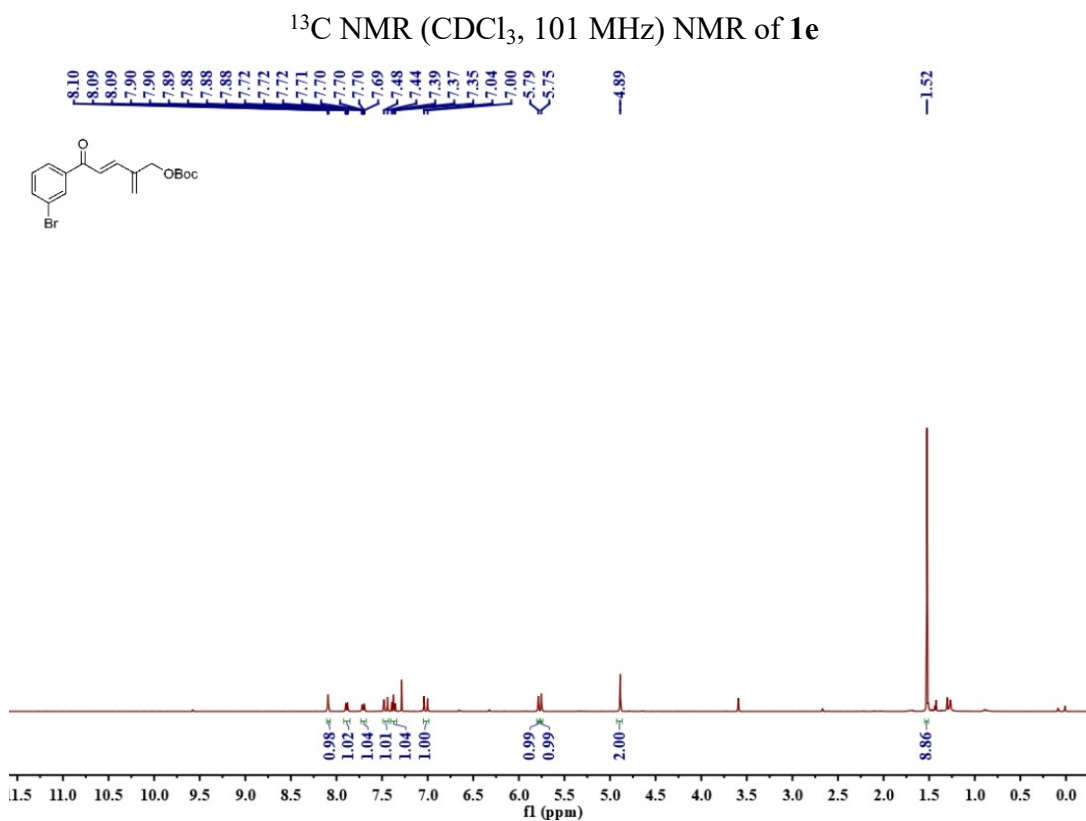
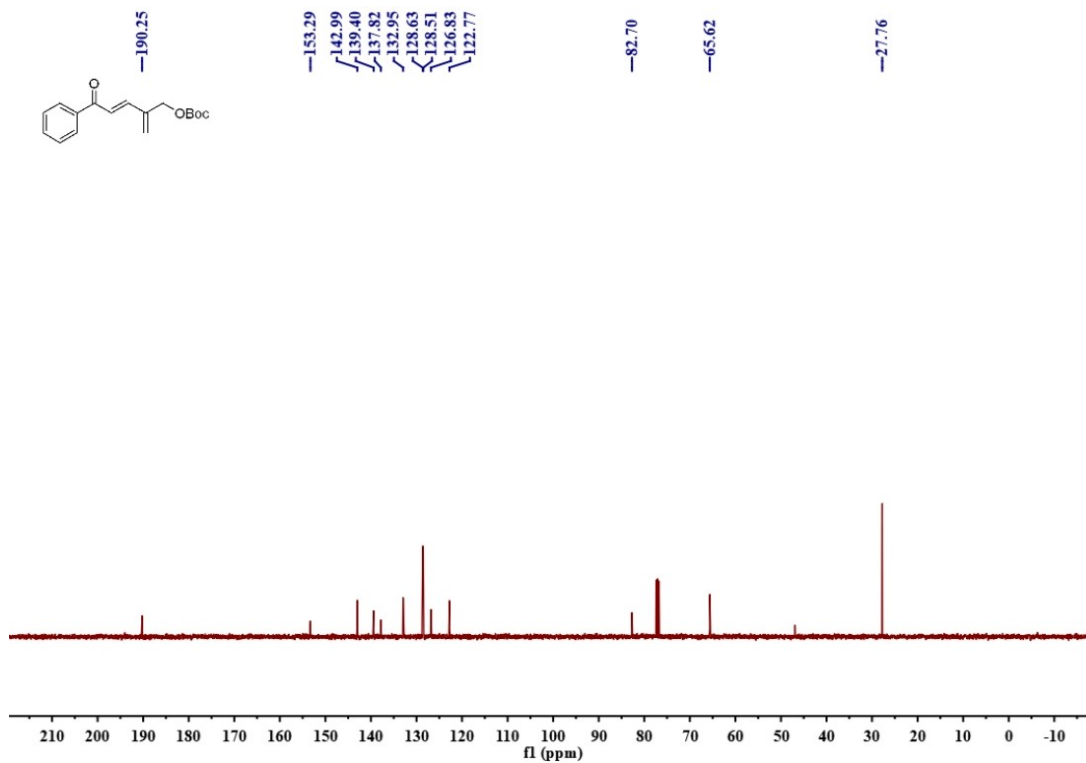
^1H NMR (CDCl₃, 300 MHz) NMR of *trans*-1b

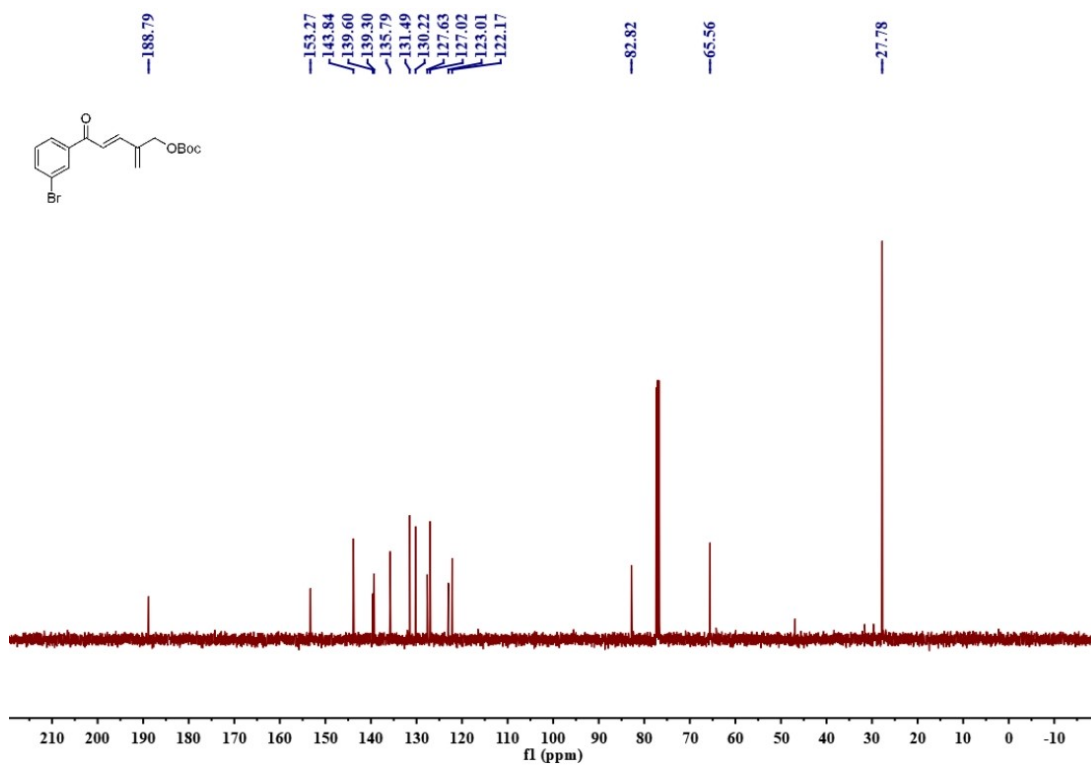




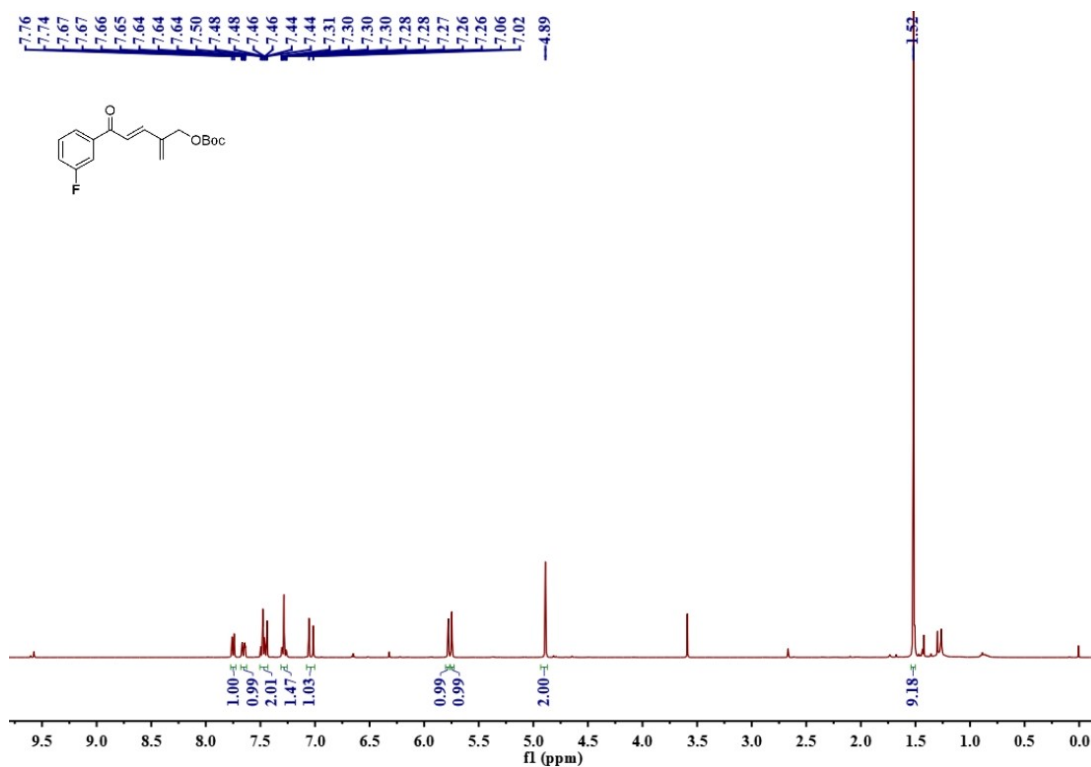
^1H NMR (CDCl₃, 300 MHz) NMR of **1d**



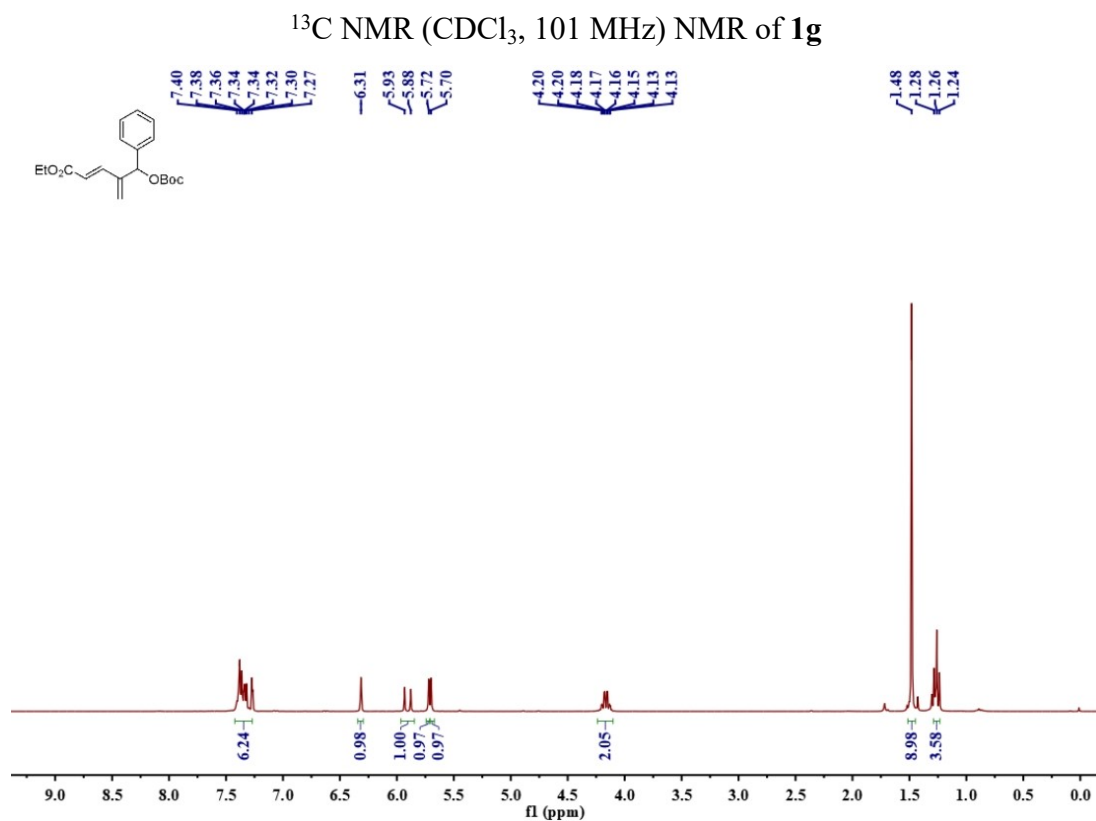
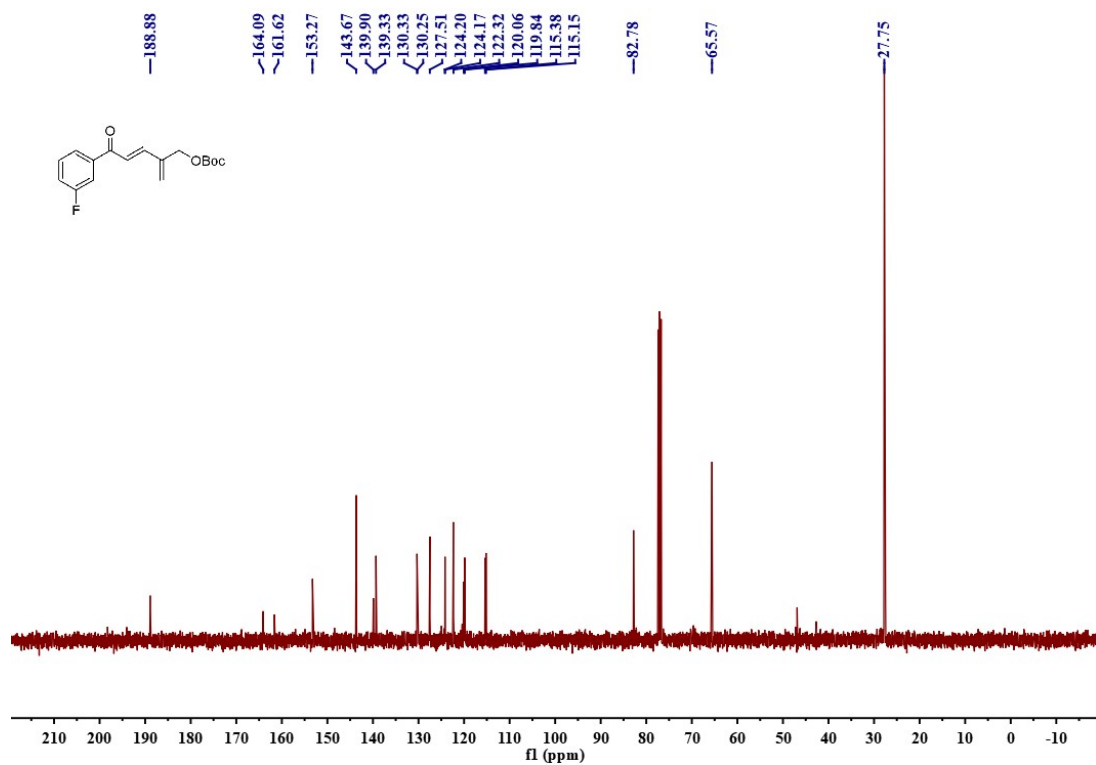


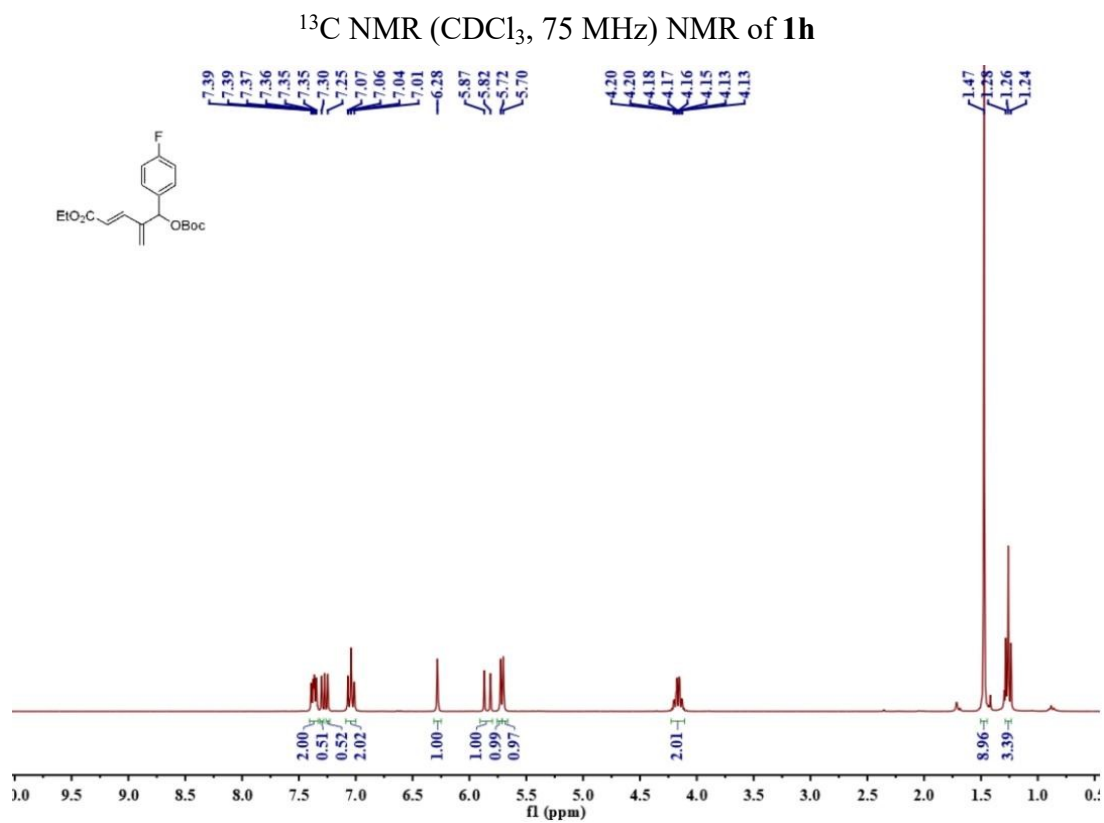
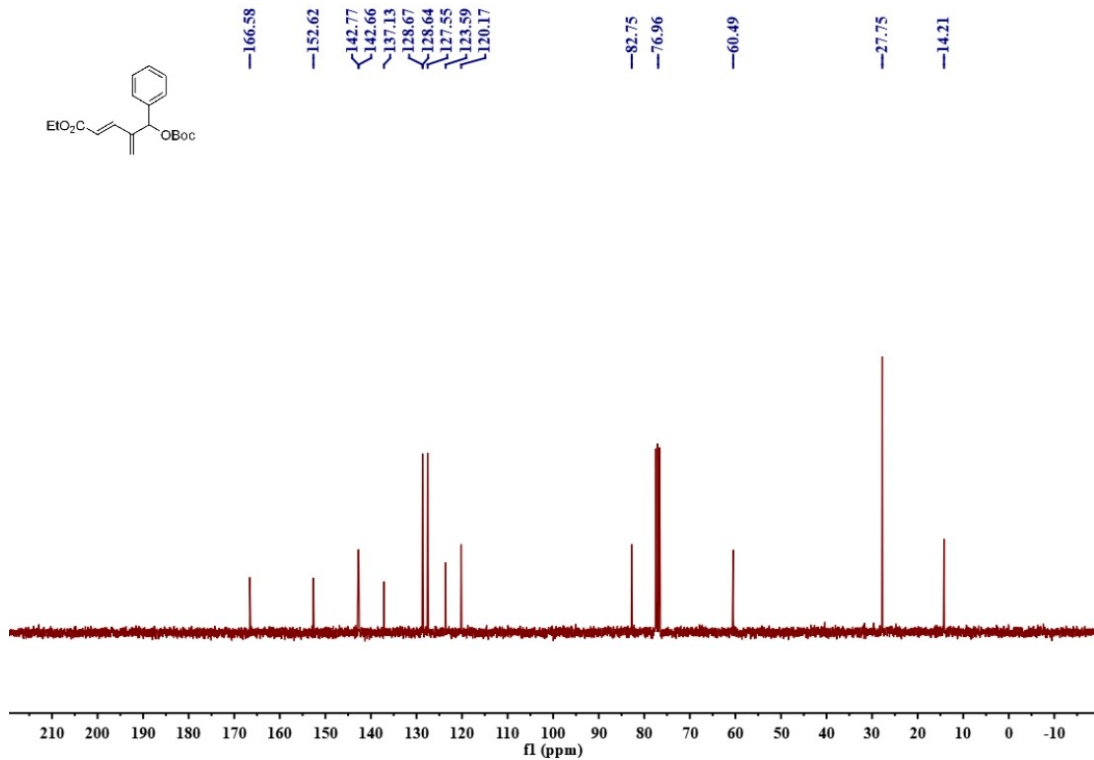


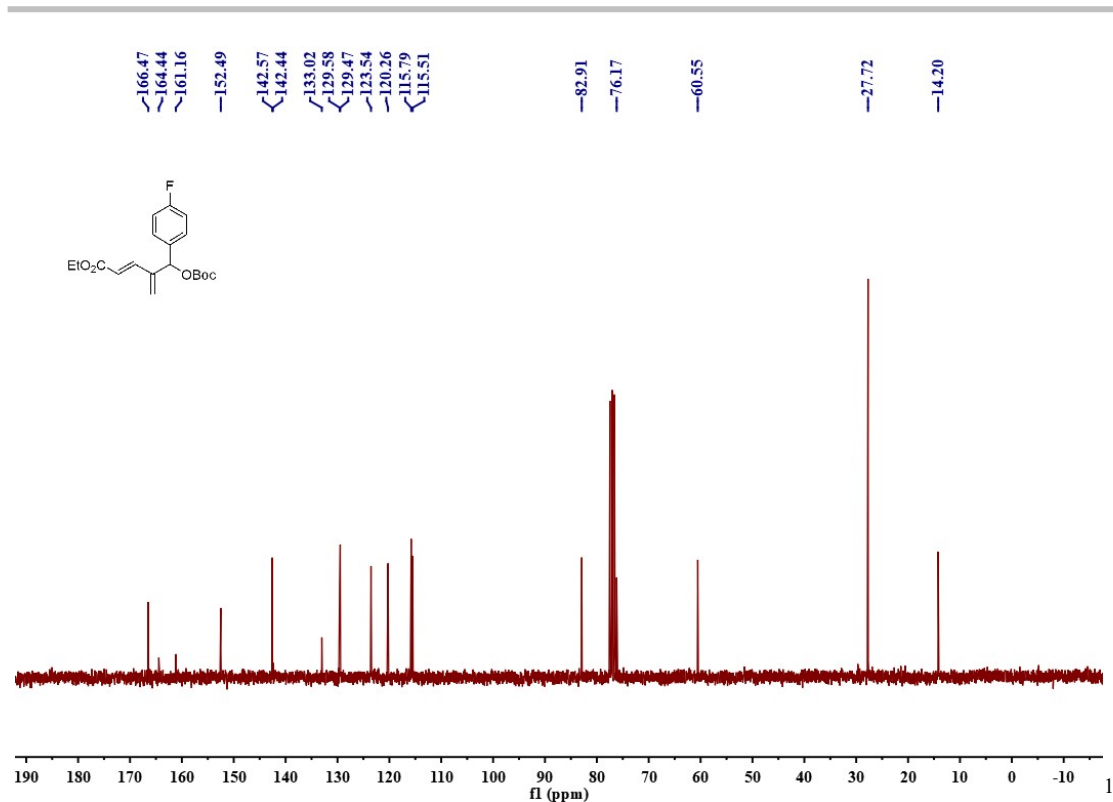
¹³C NMR (CDCl₃, 101 MHz) NMR of **1f**



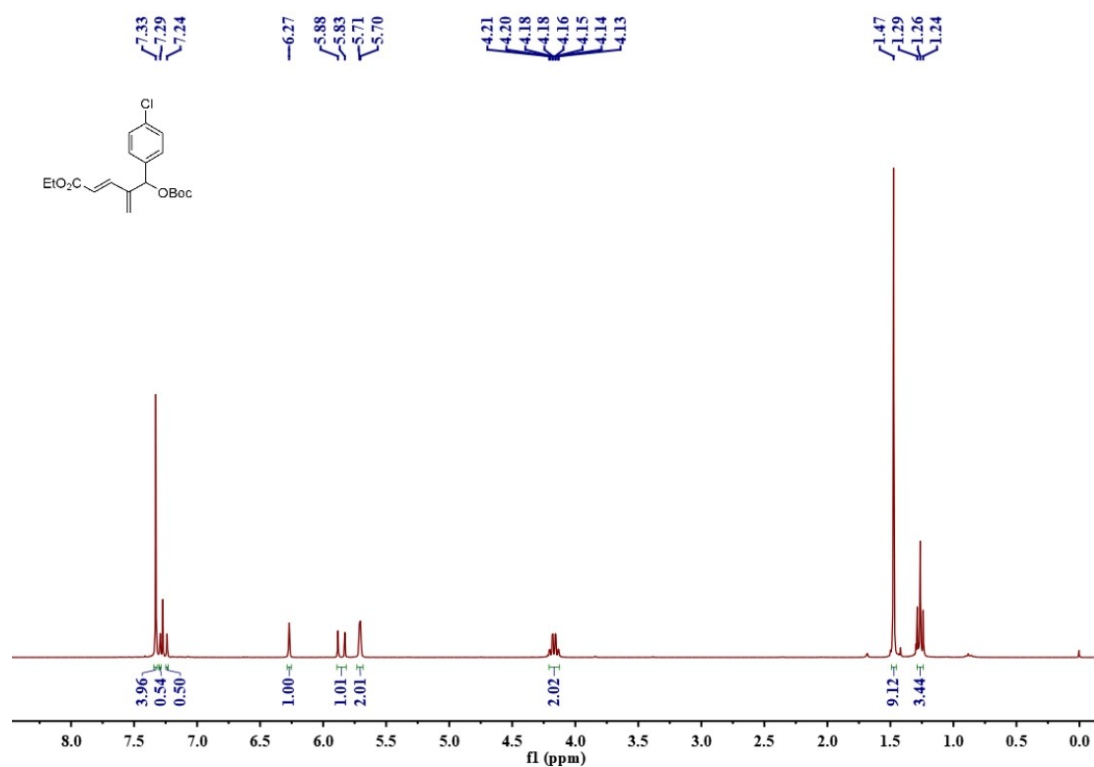
¹H NMR (CDCl₃, 400 MHz) NMR of **1g**



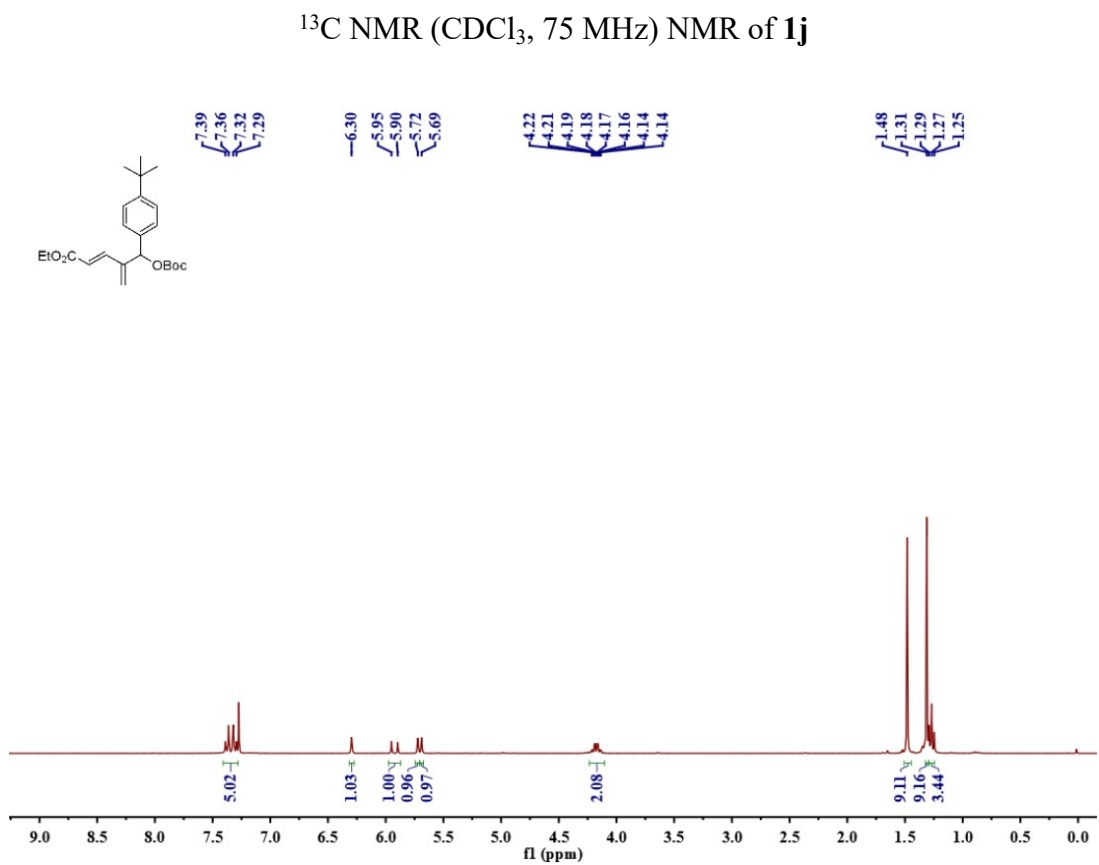
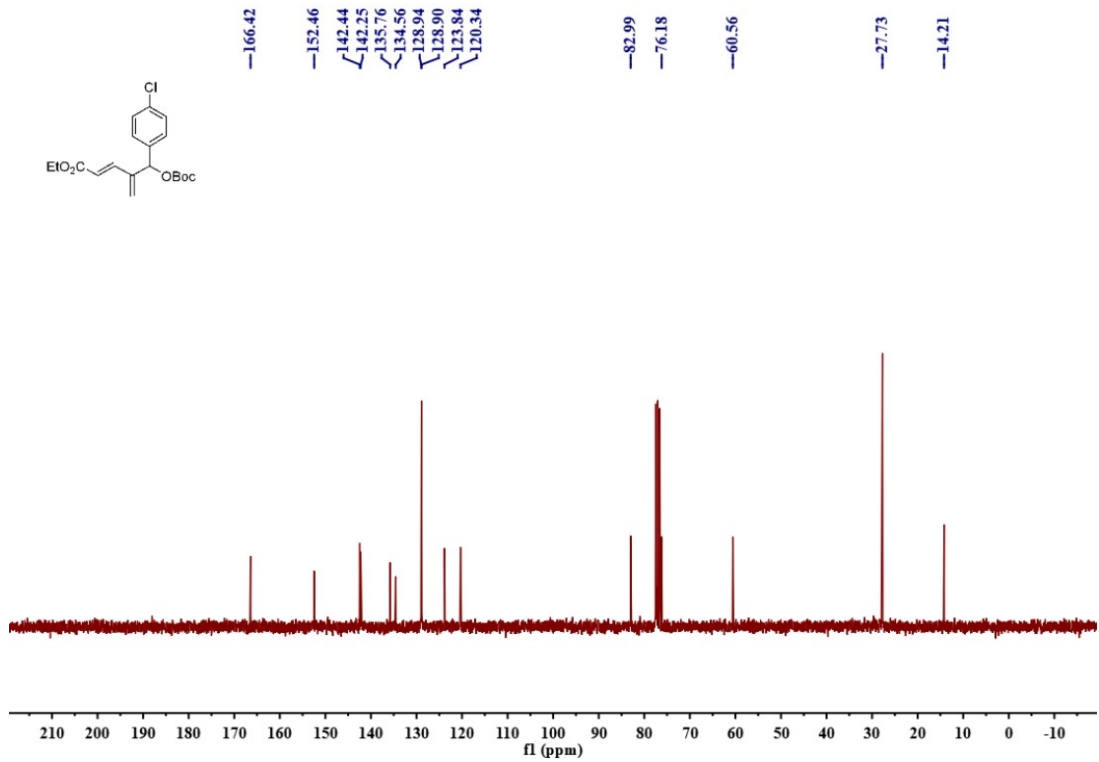


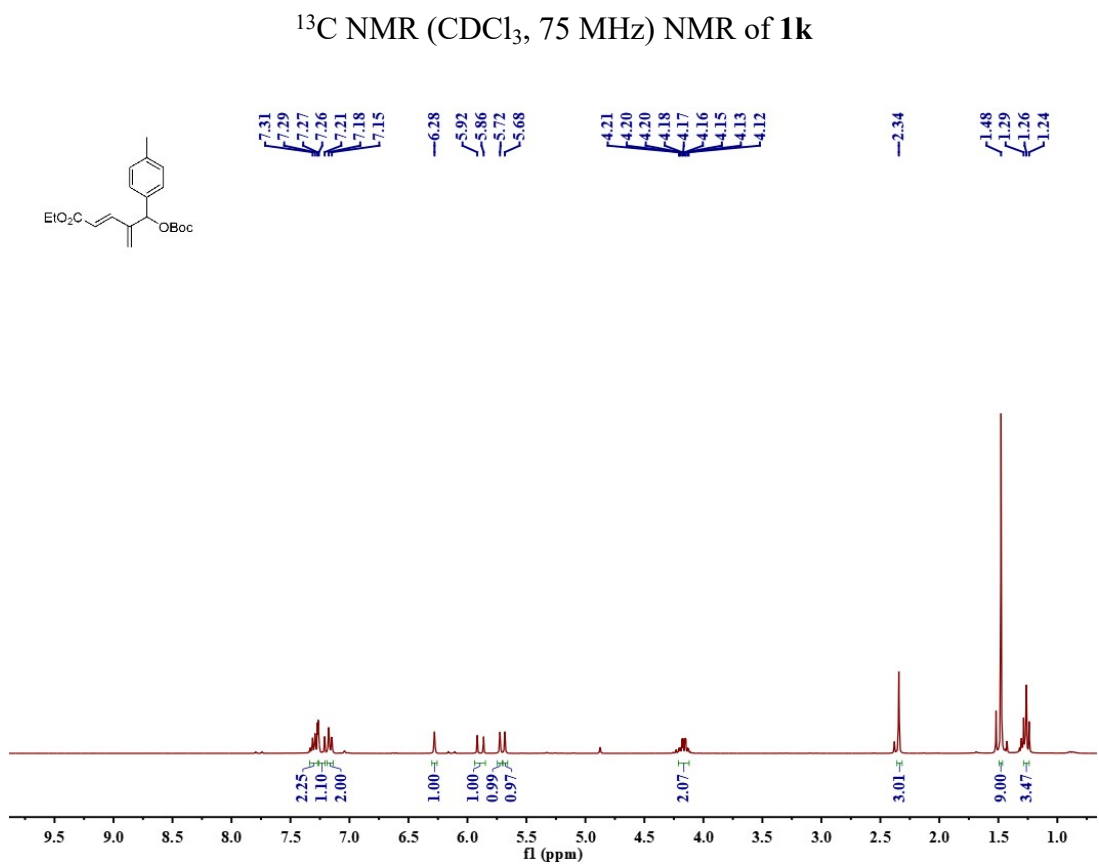
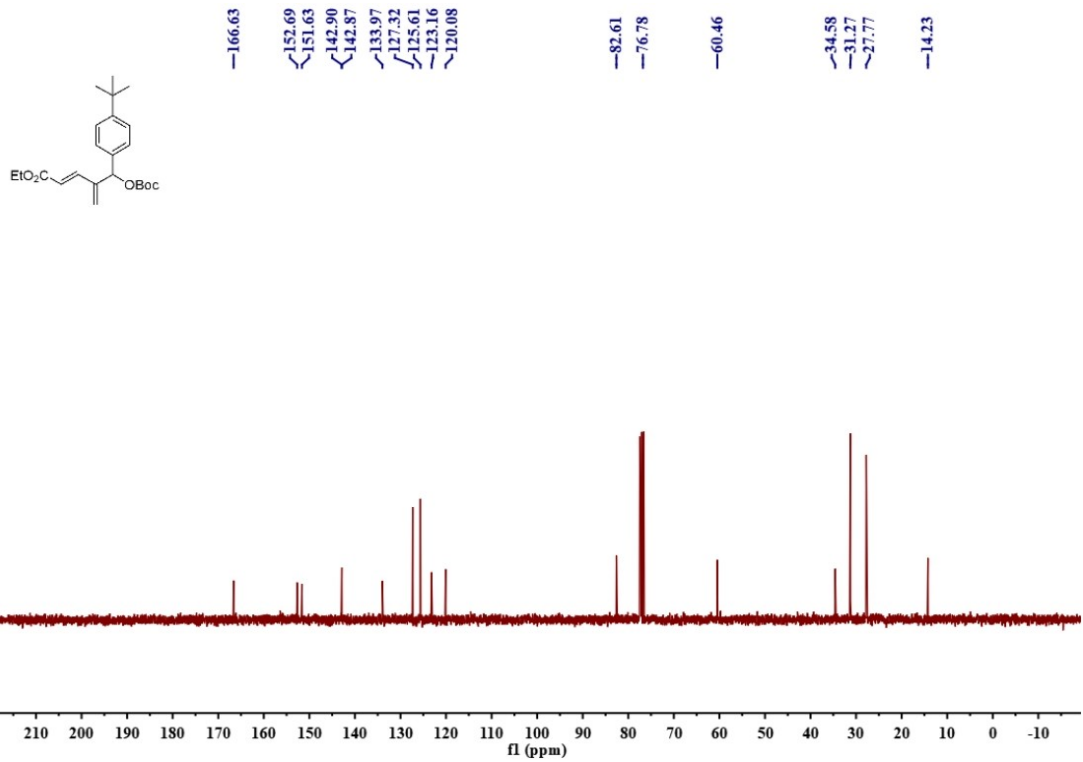


³C NMR (CDCl₃, 75 MHz) NMR of **1i**

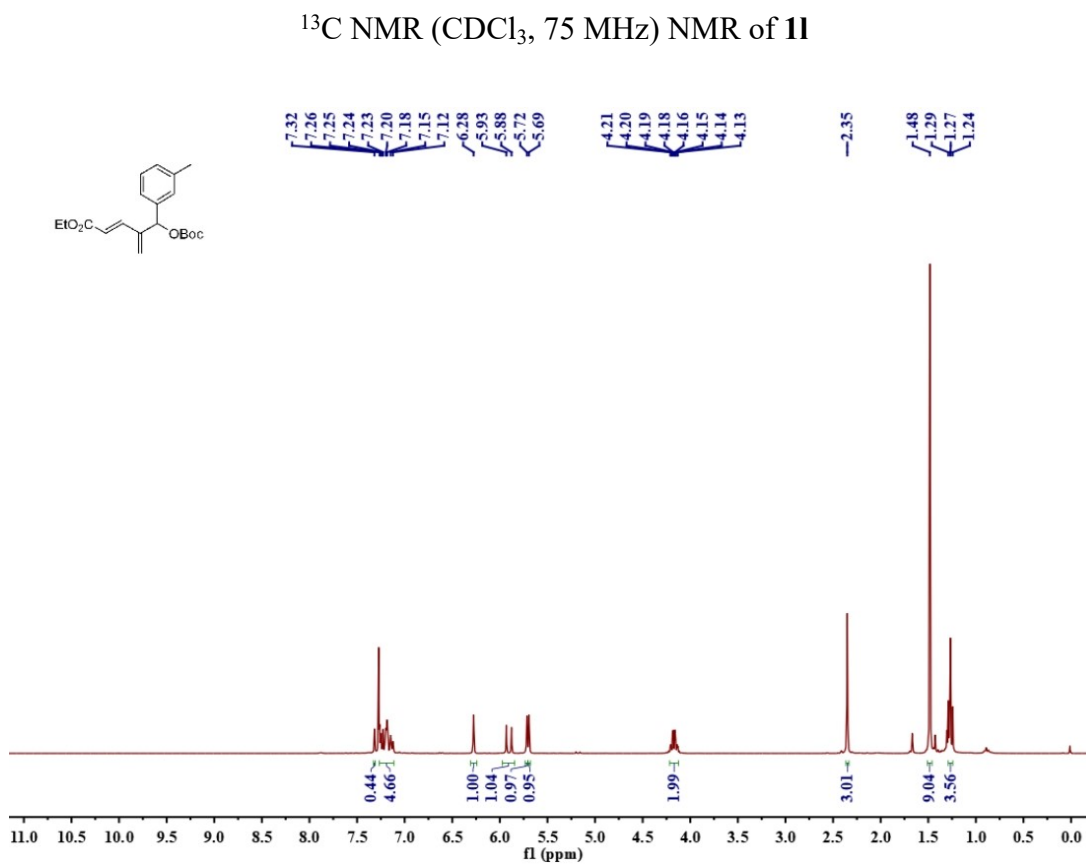
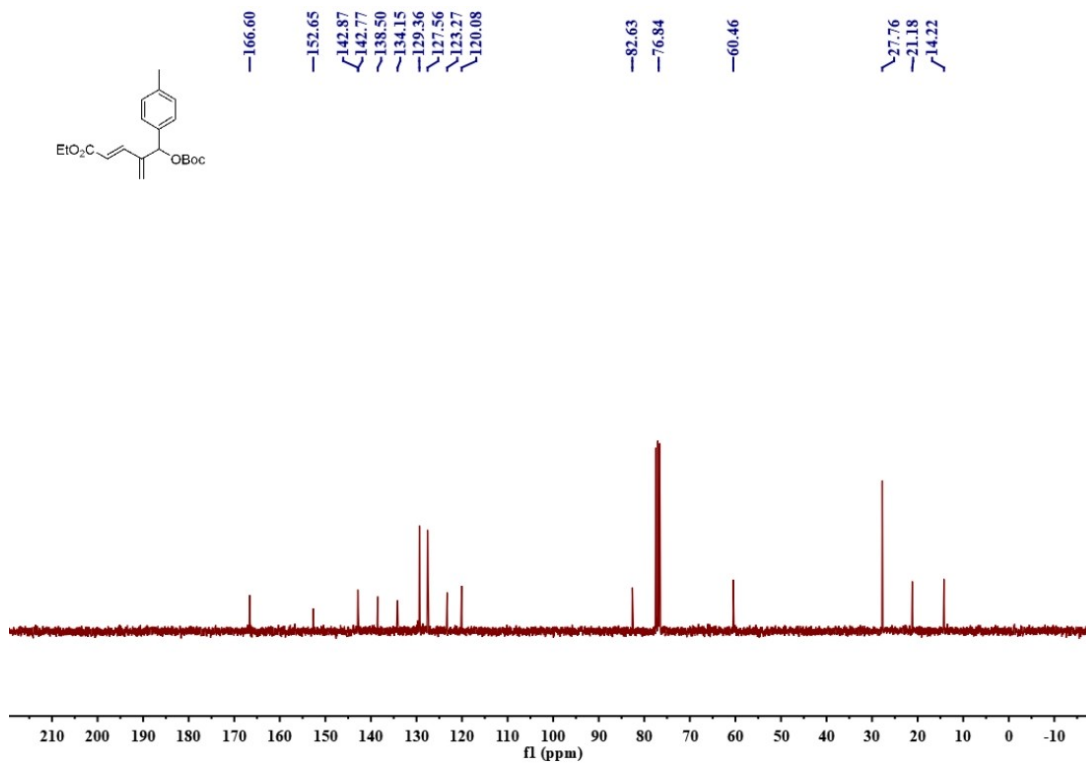


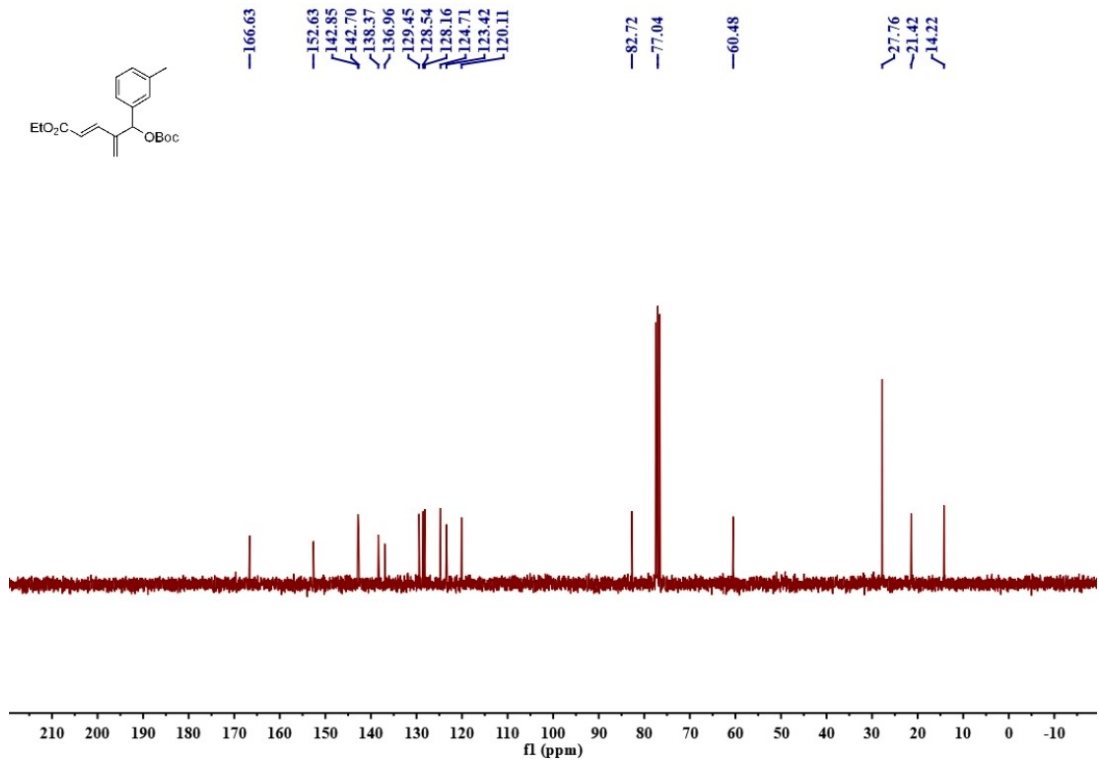
¹H NMR (CDCl₃, 300 MHz) NMR of **1j**



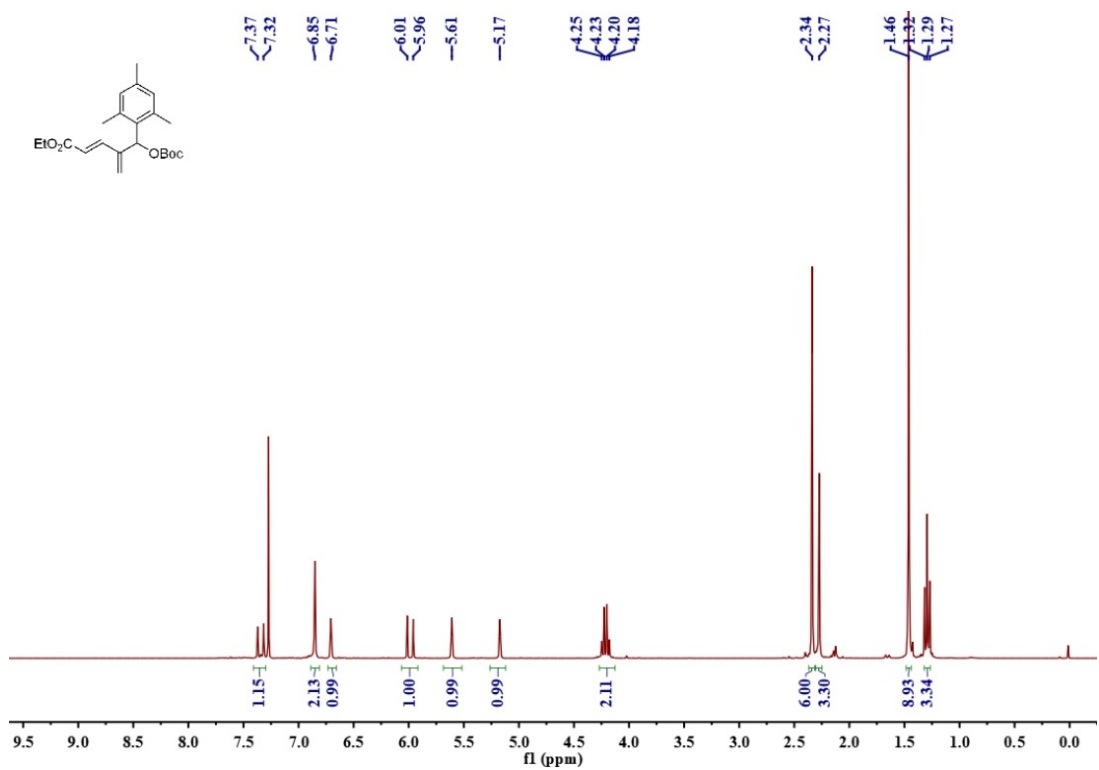


^1H NMR (CDCl₃, 300 MHz) NMR of **1l**

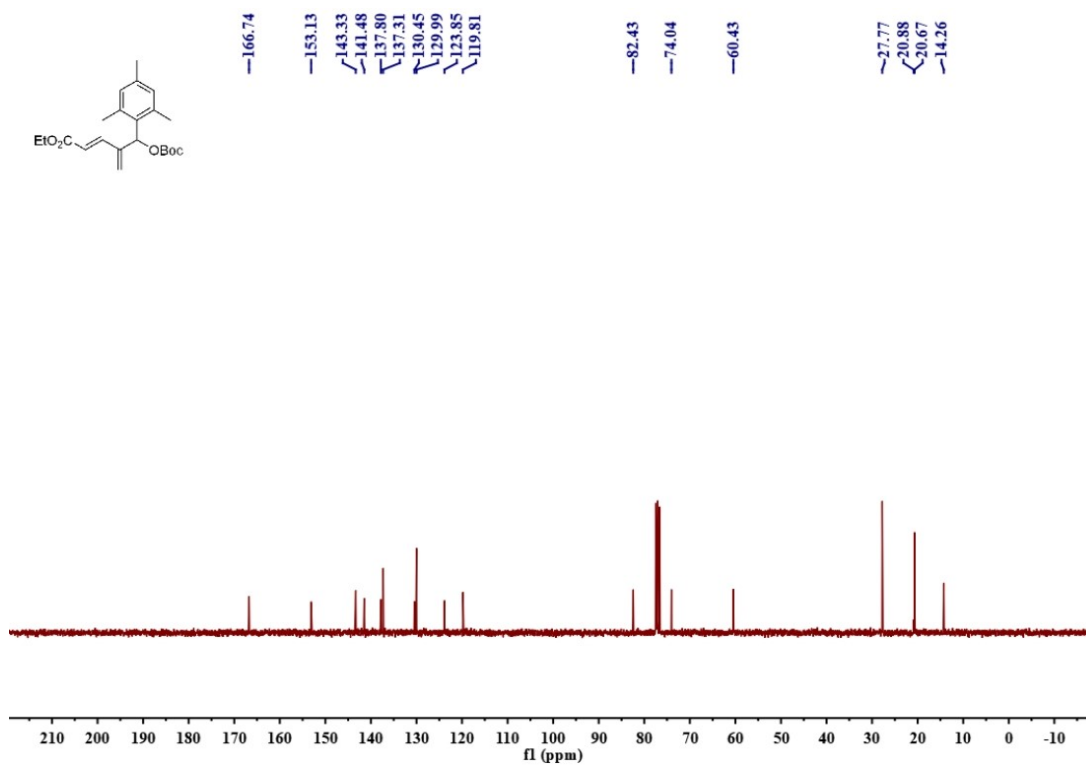




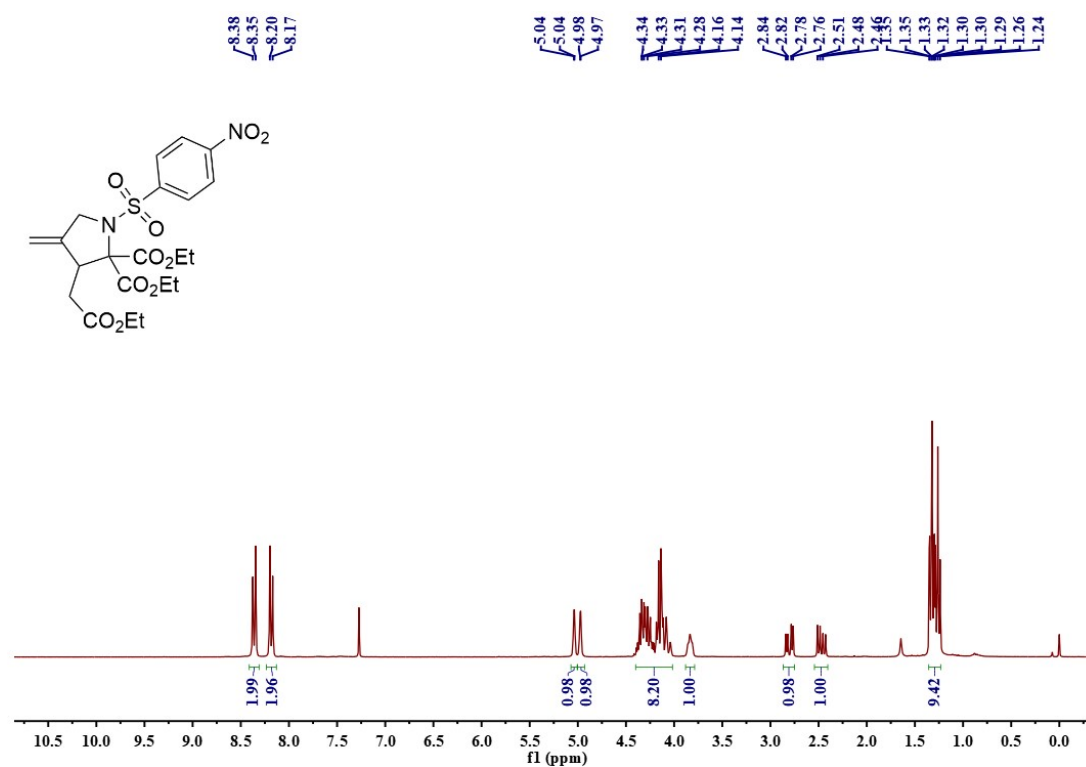
¹³C NMR (CDCl₃, 75 MHz) NMR of **1m**



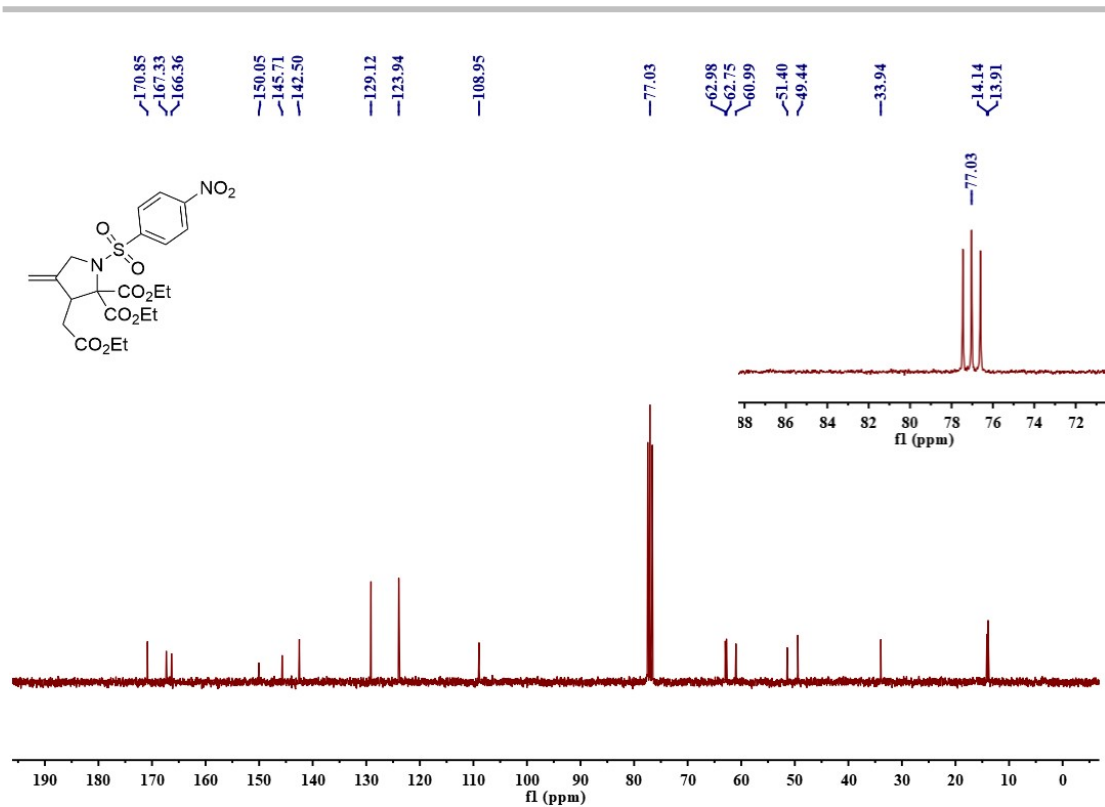
¹H NMR (CDCl₃, 300 MHz) NMR of **1n**



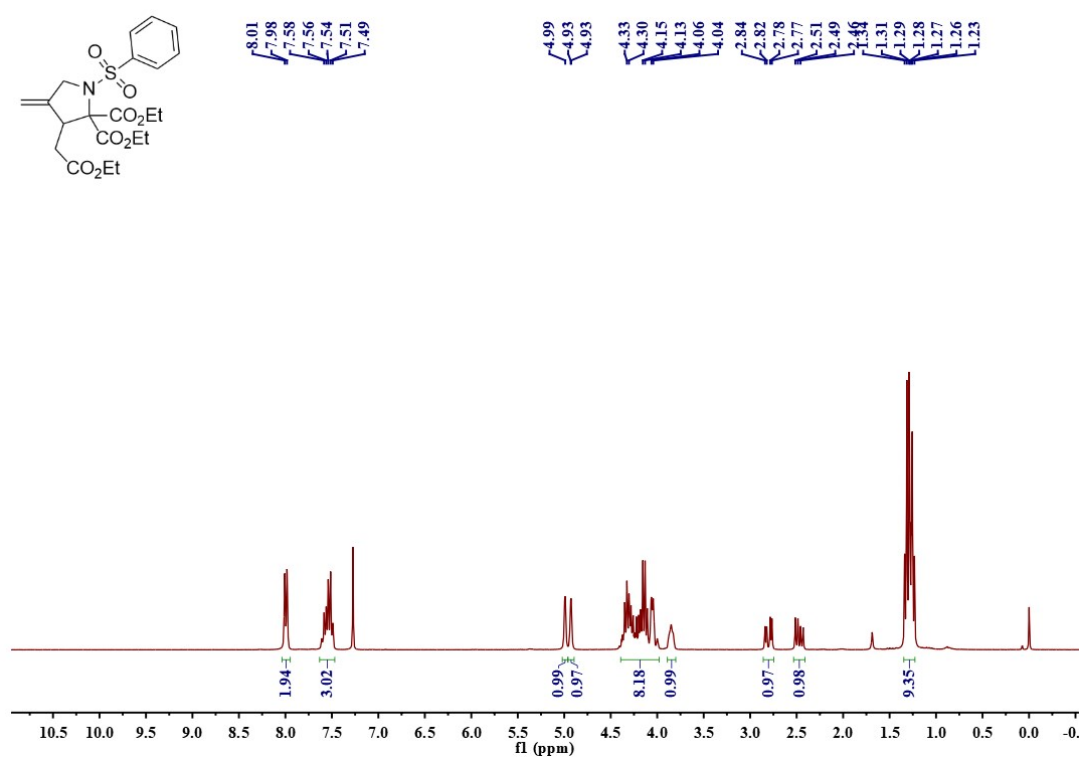
^{13}C NMR (CDCl₃, 75 MHz) NMR of **1n**



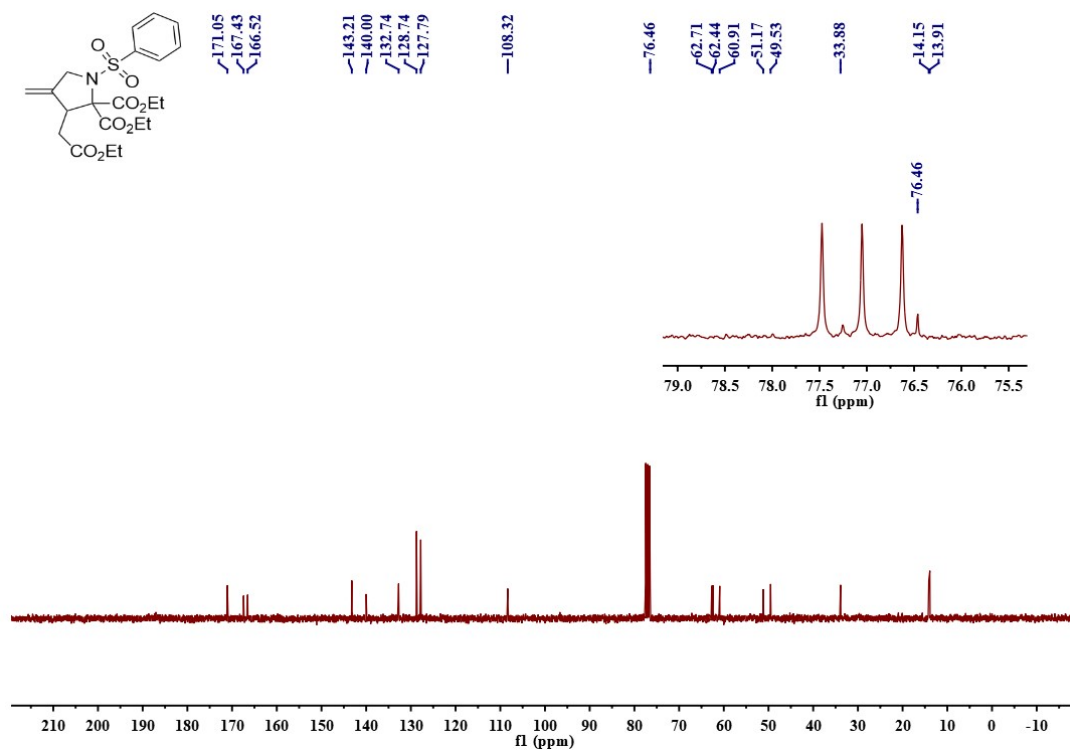
^1H NMR (CDCl₃, 300 MHz) NMR of **3aa**



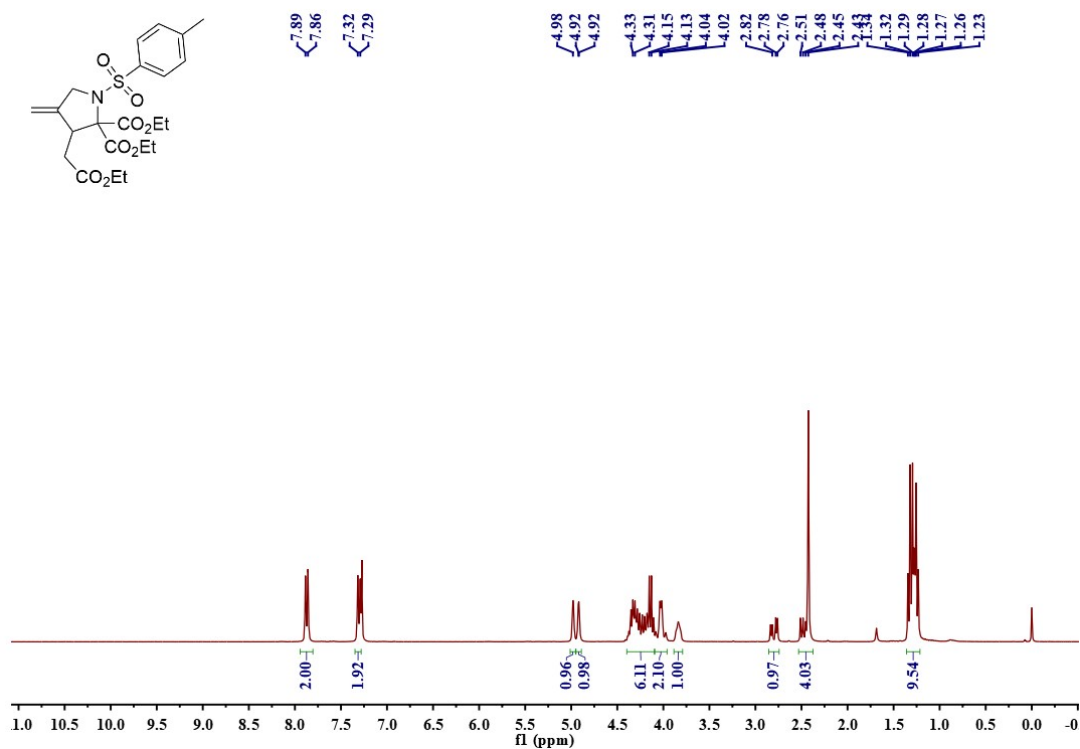
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3aa**



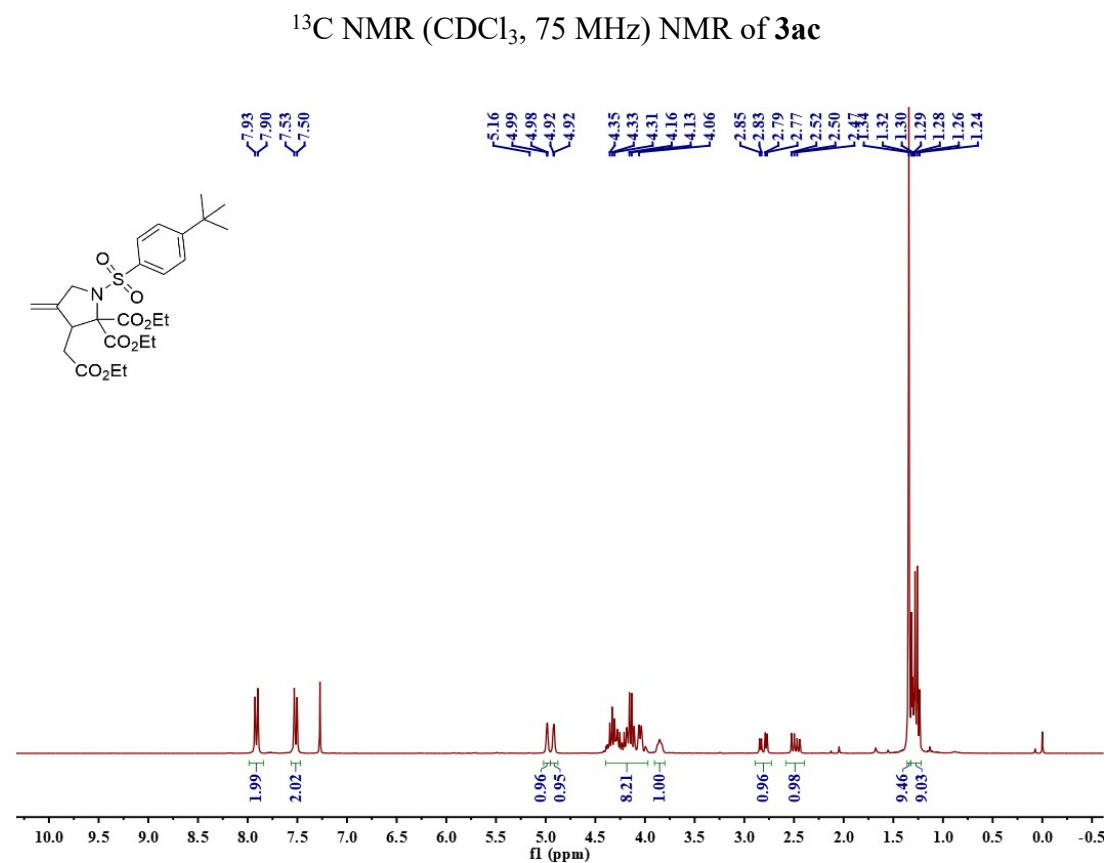
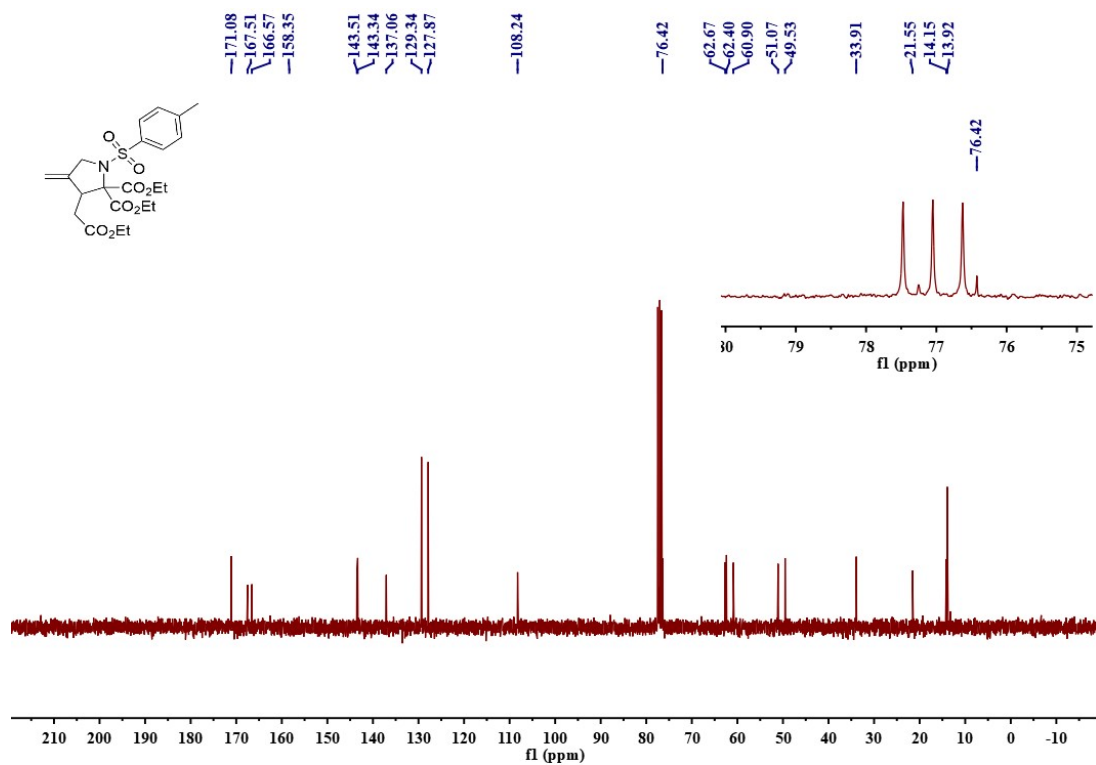
^1H NMR (CDCl₃, 300 MHz) NMR of **3ab**



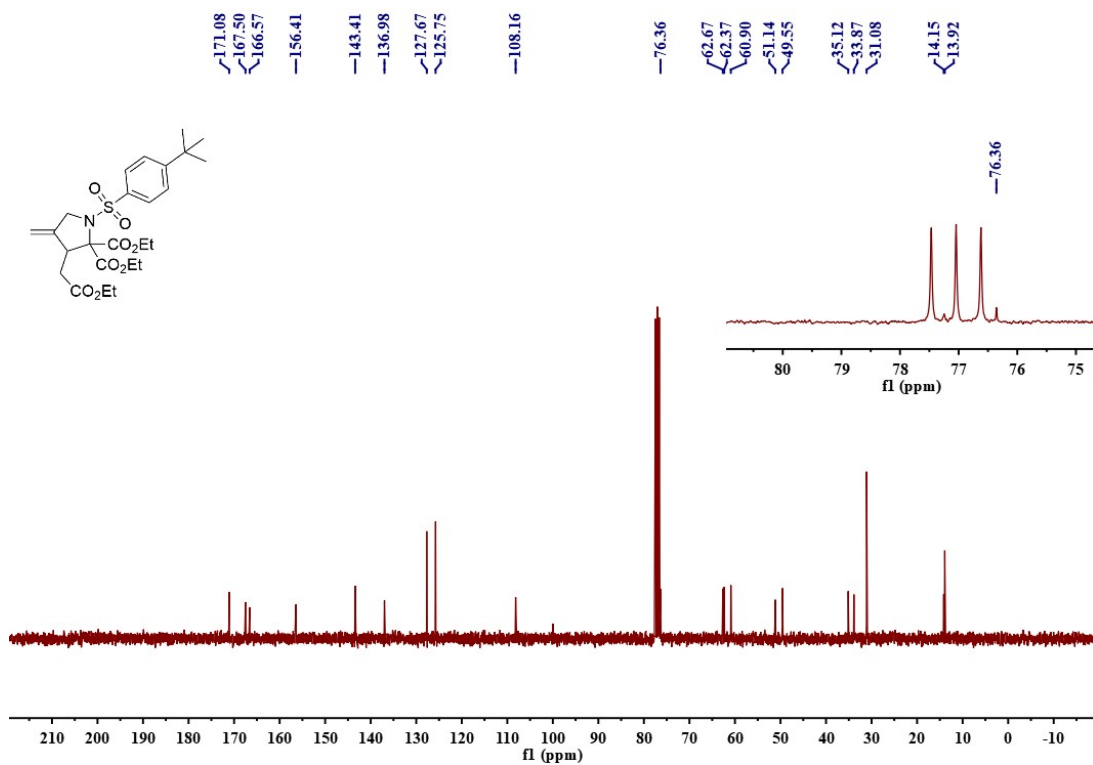
¹³C NMR (CDCl₃, 75 MHz) NMR of **3ab**



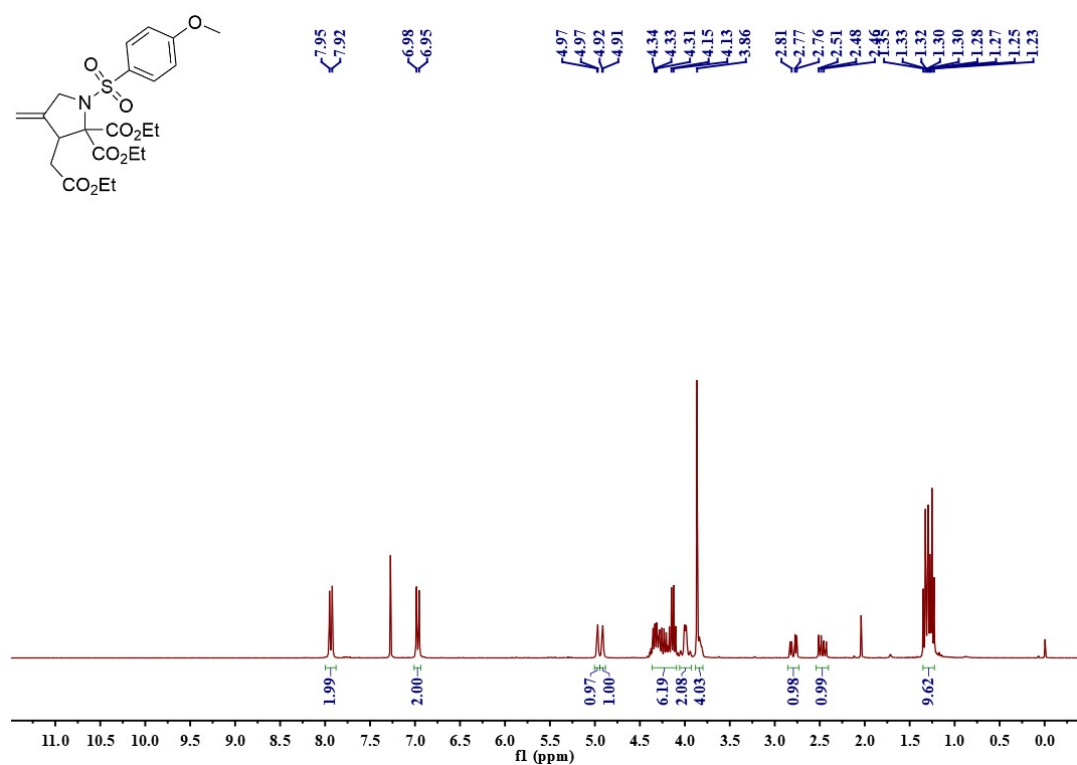
¹H NMR (CDCl₃, 300 MHz) NMR of **3ac**



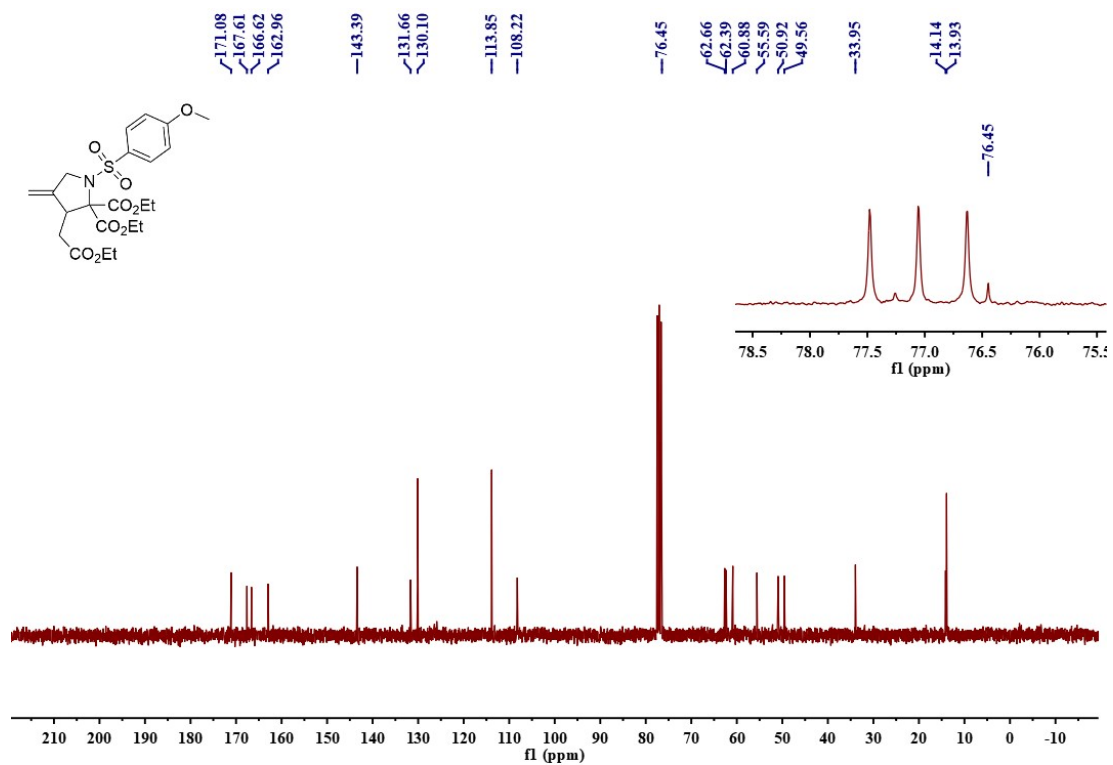
^1H NMR (CDCl₃, 300 MHz) NMR of **3ad**



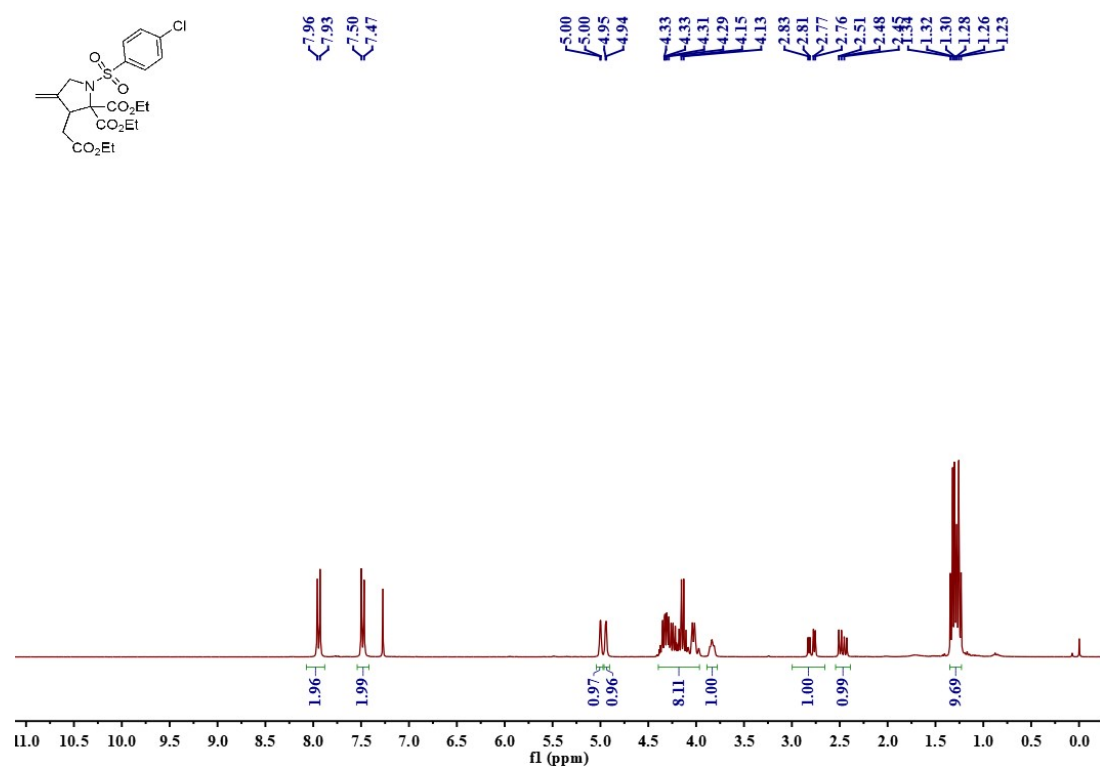
¹³C NMR (CDCl₃, 75 MHz) NMR of **3ad**



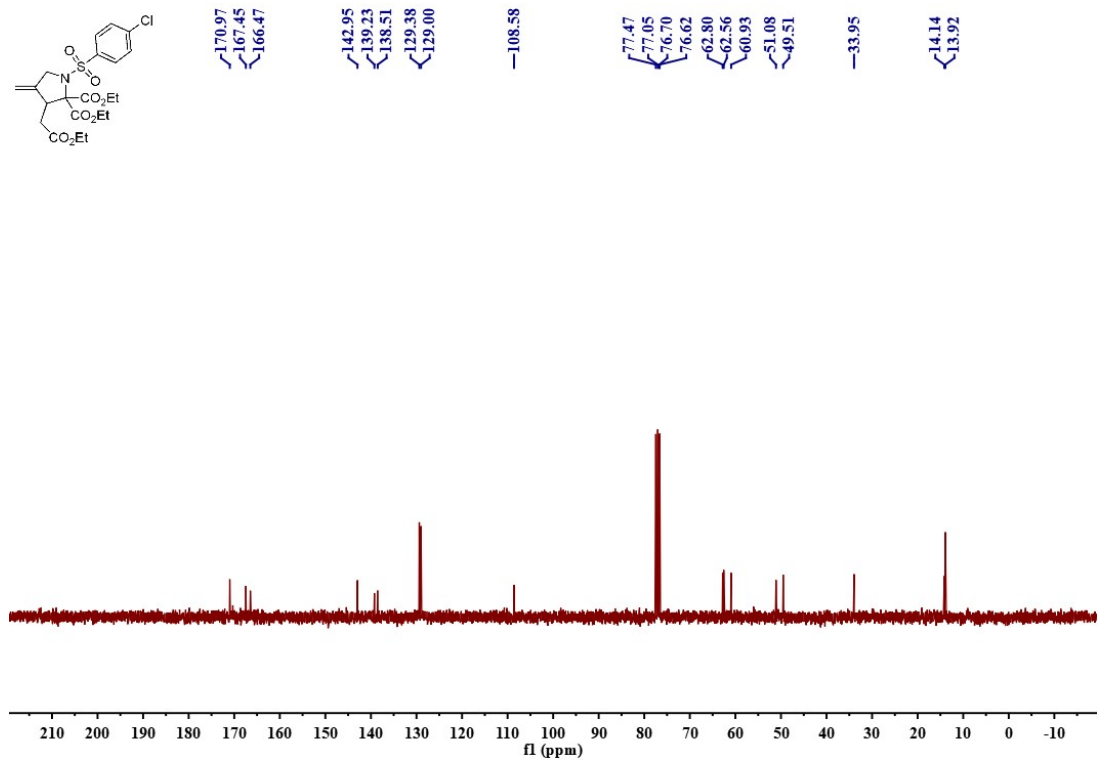
¹H NMR (CDCl₃, 300 MHz) NMR of **3ae**



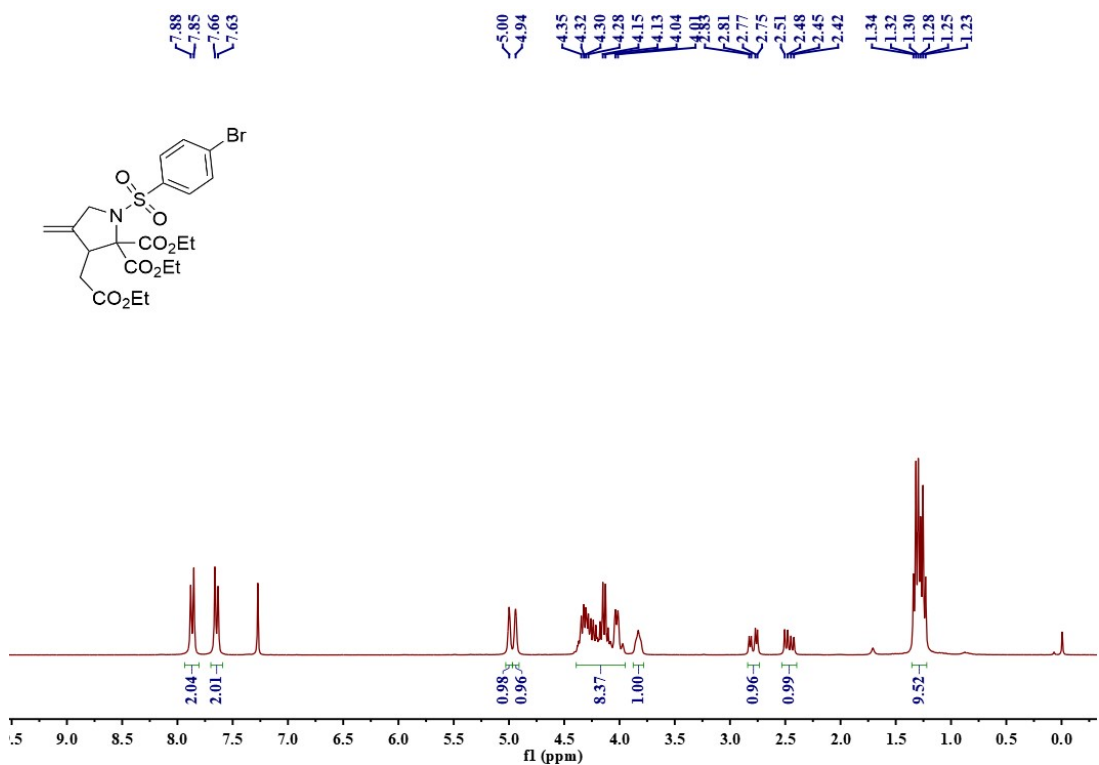
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3ae**



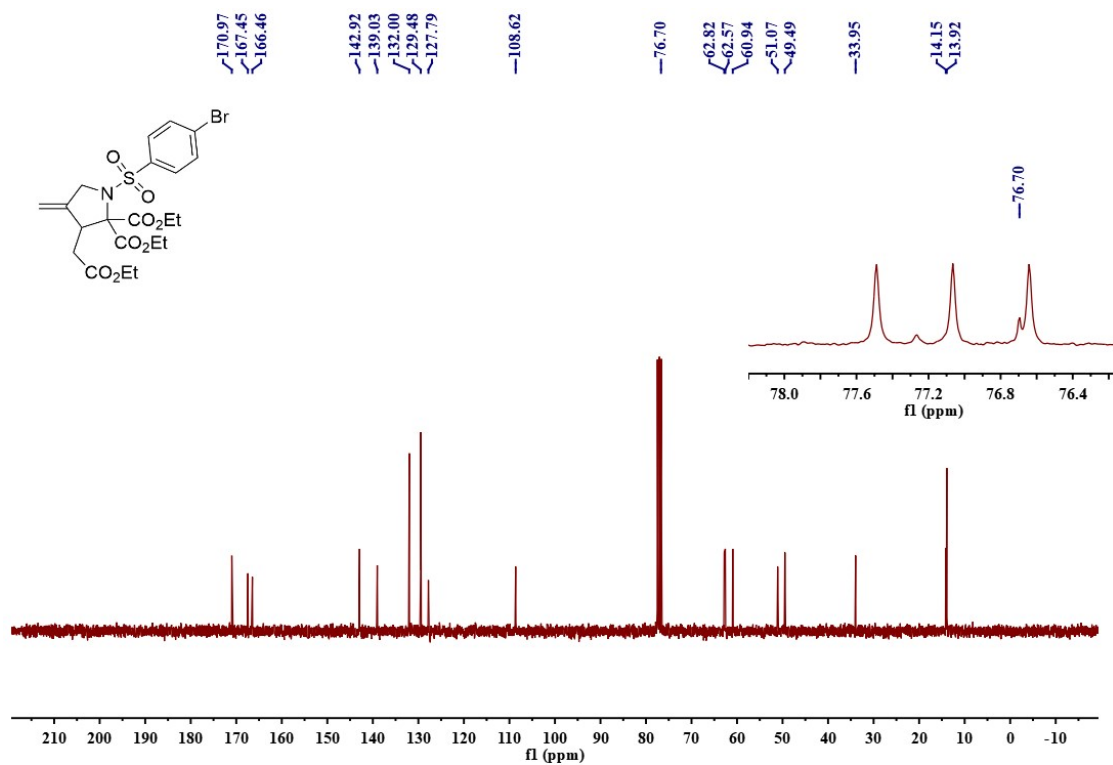
^1H NMR (CDCl₃, 300 MHz) NMR of **3af**



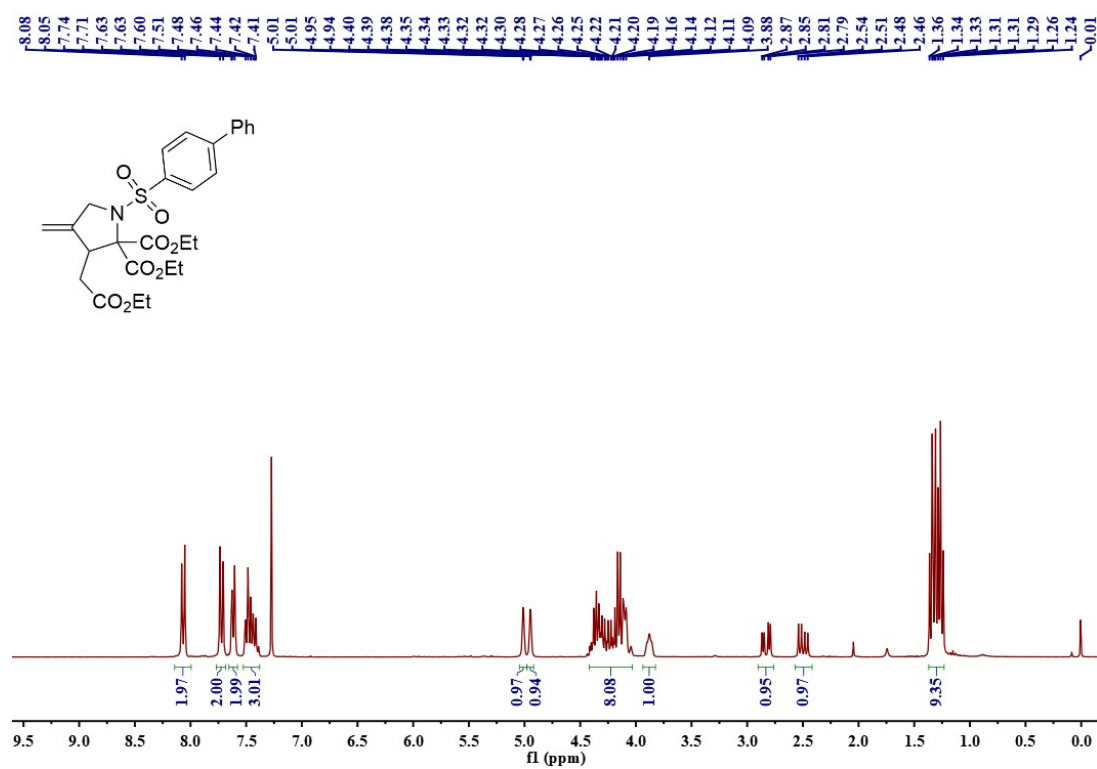
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3af**



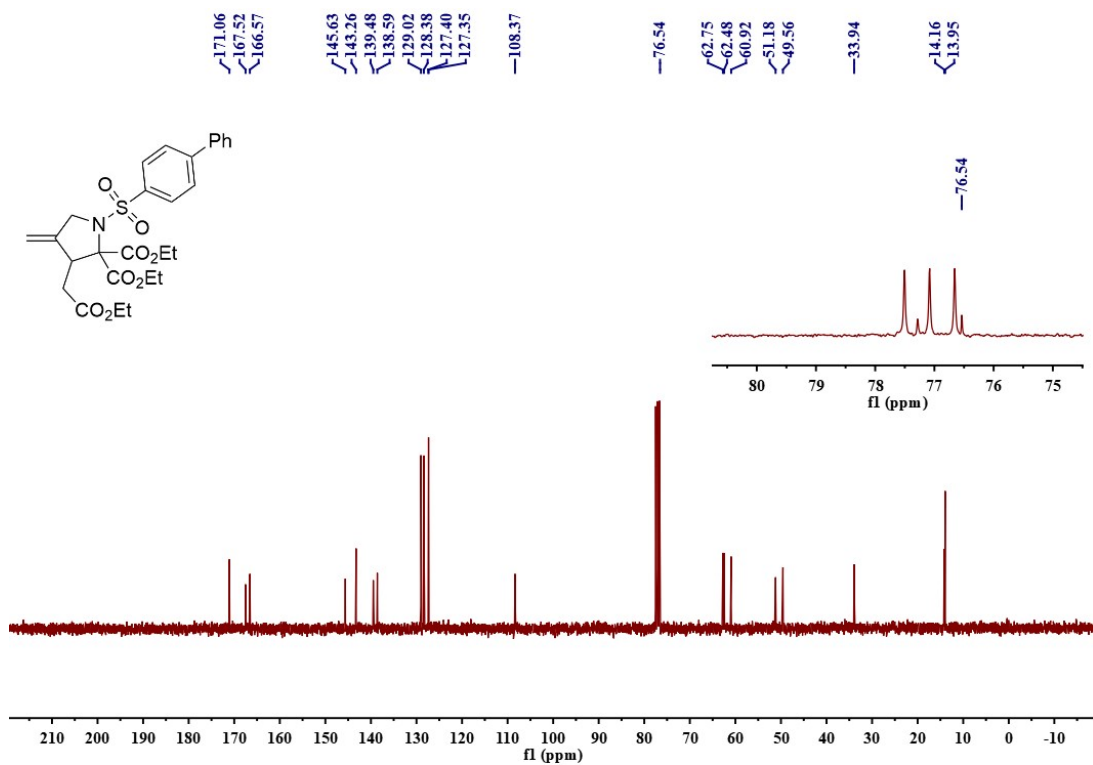
^1H NMR (CDCl₃, 300 MHz) NMR of **3ag**



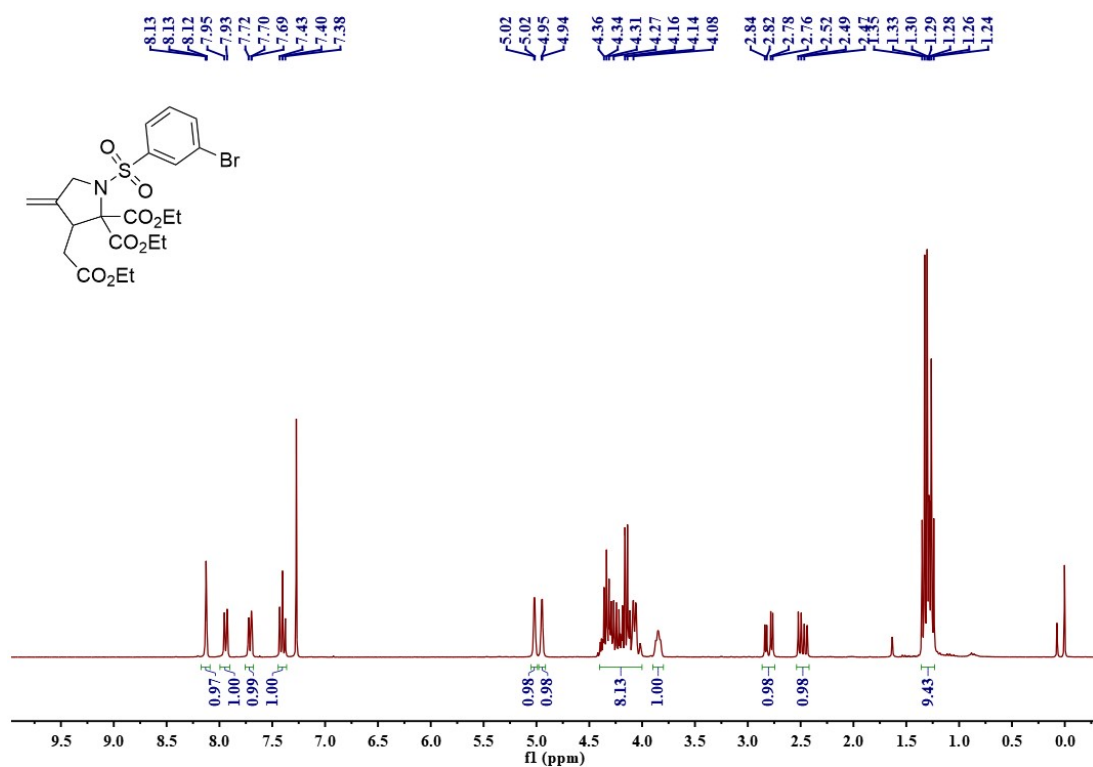
¹³C NMR (CDCl₃, 75 MHz) NMR of **3ag**



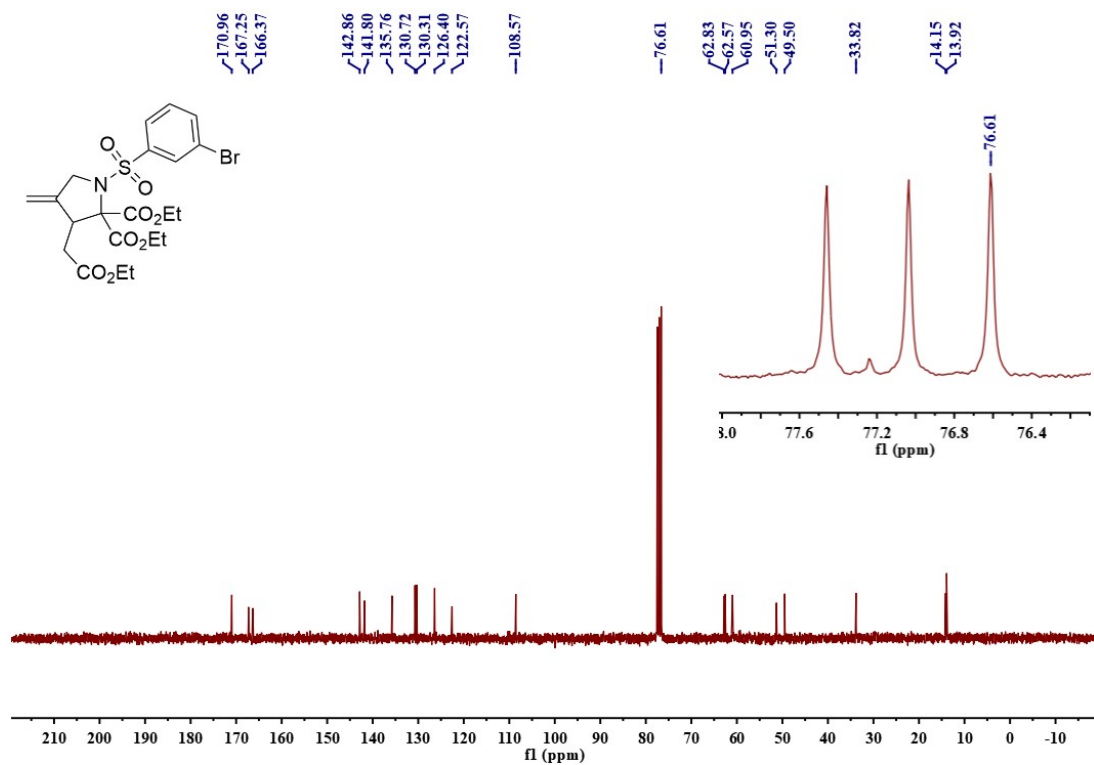
¹H NMR (CDCl₃, 300 MHz) NMR of **3ah**



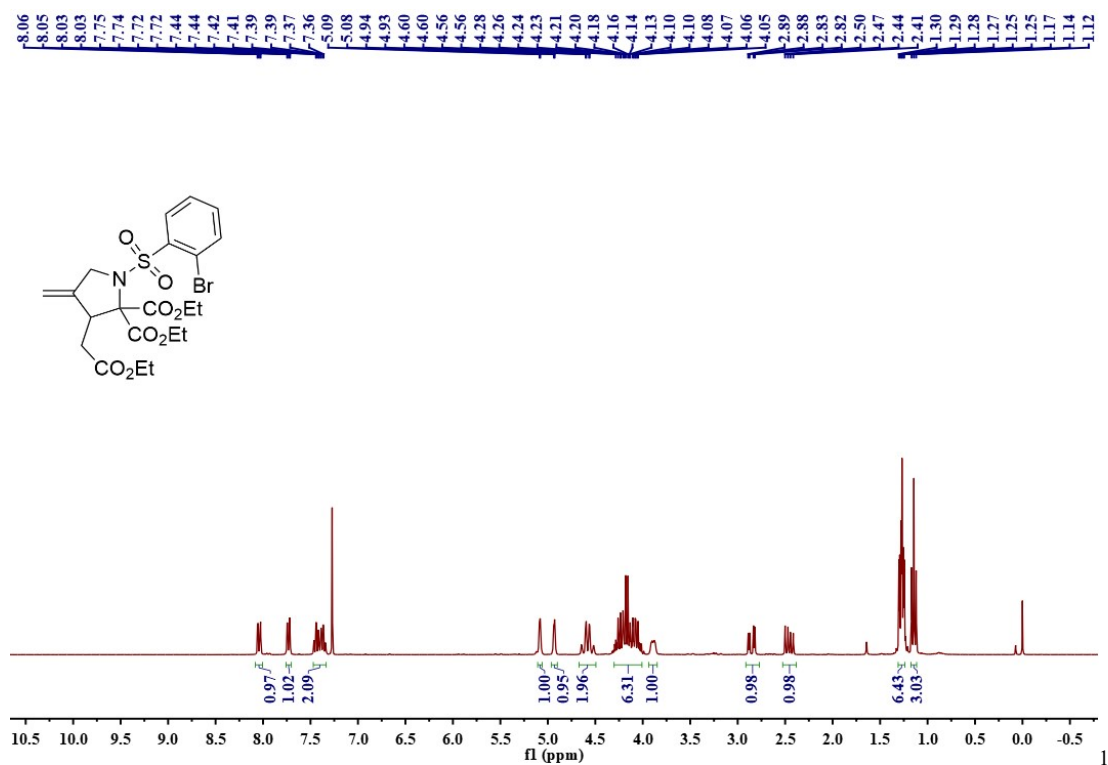
¹³C NMR (CDCl₃, 75 MHz) NMR of 3ah



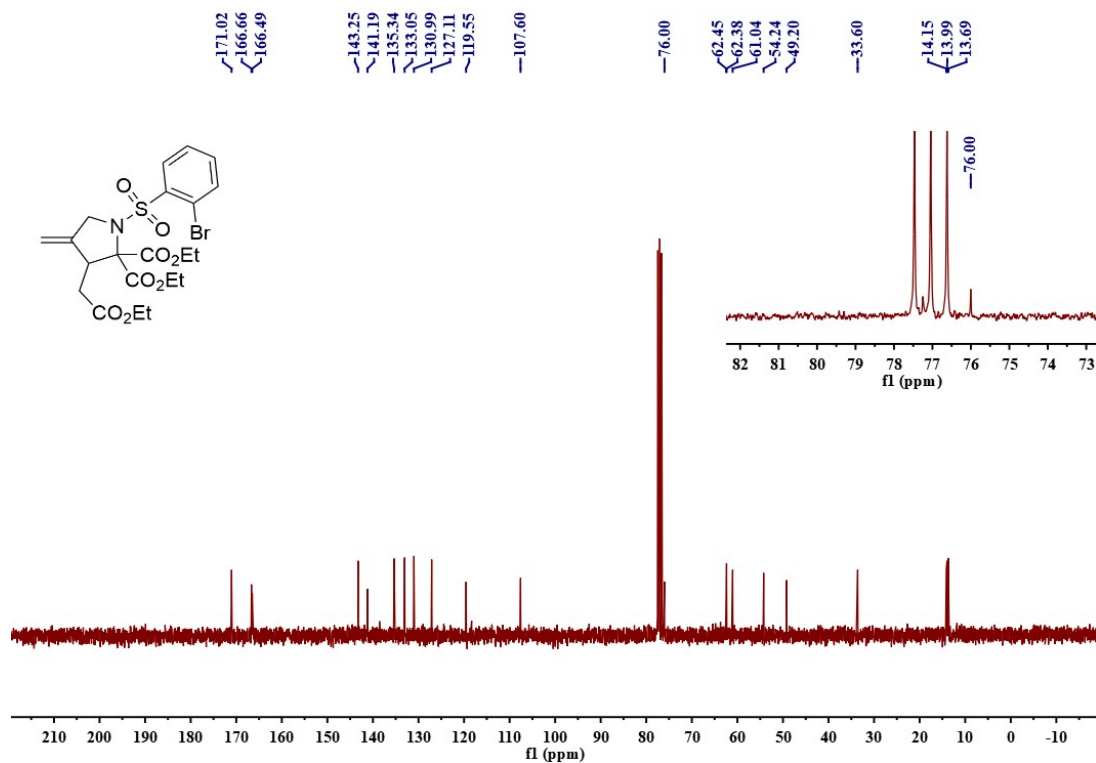
¹H NMR (CDCl₃, 300 MHz) NMR of 3ai



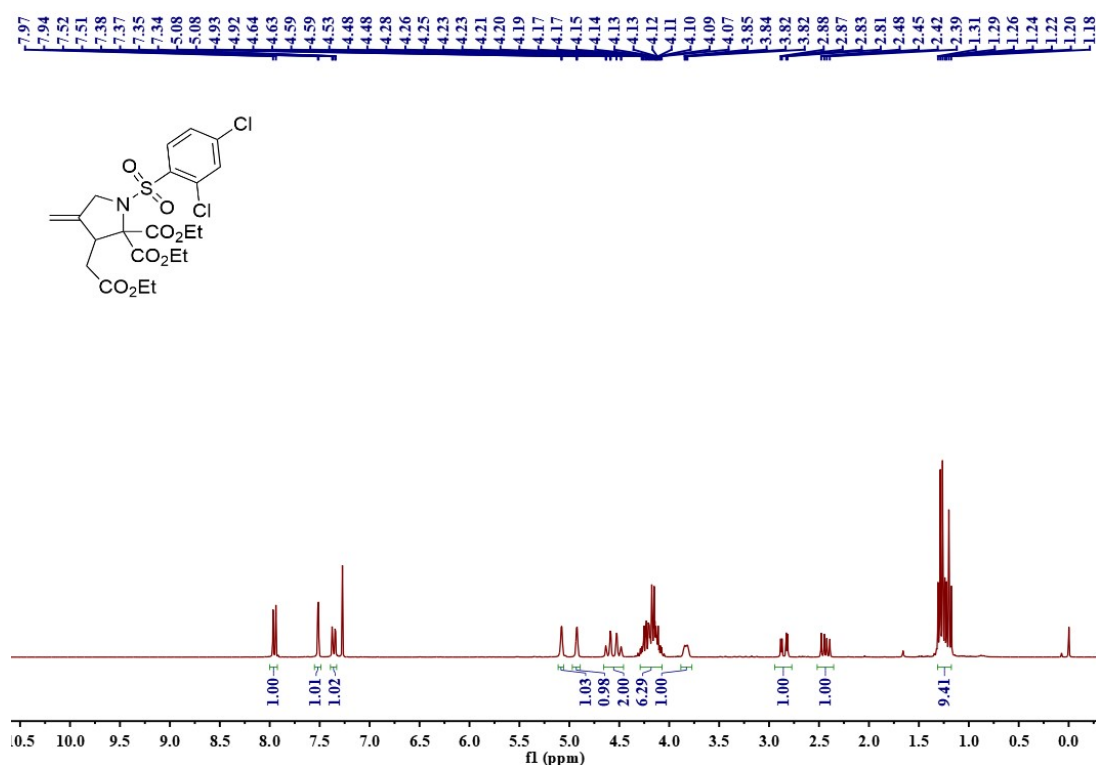
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3ai**



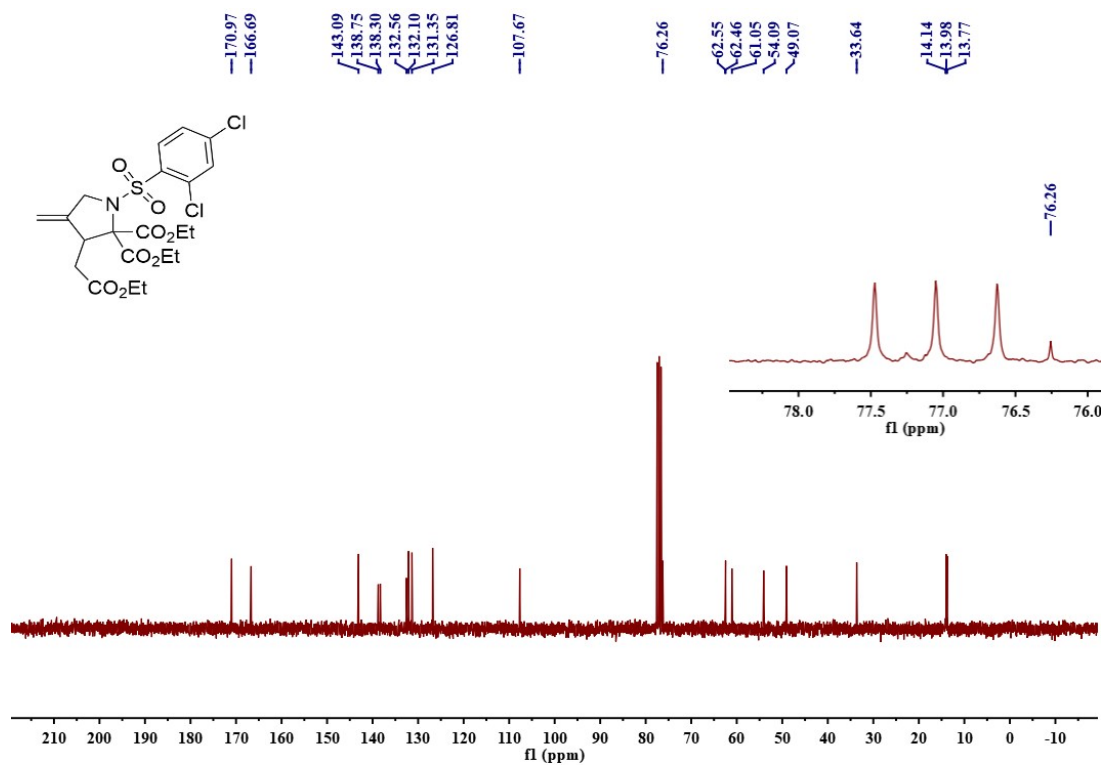
^1H NMR (CDCl₃, 300 MHz) NMR of **3aj**



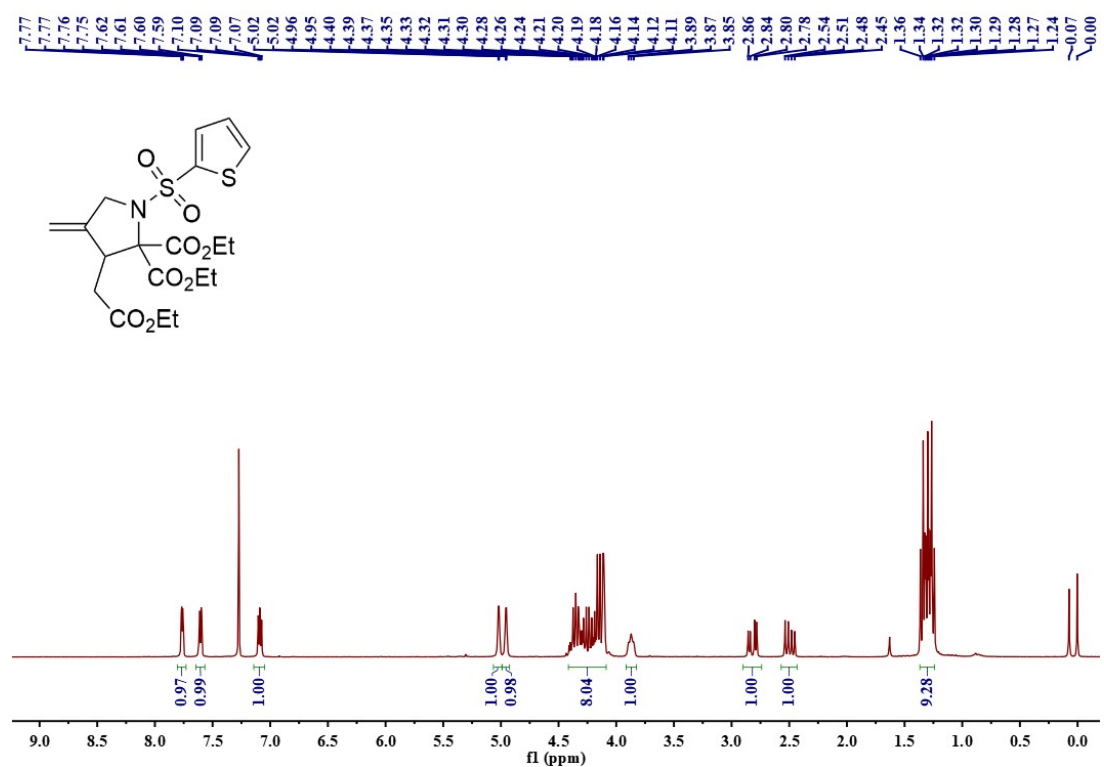
¹³C NMR (CDCl₃, 75 MHz) NMR of **3aj**



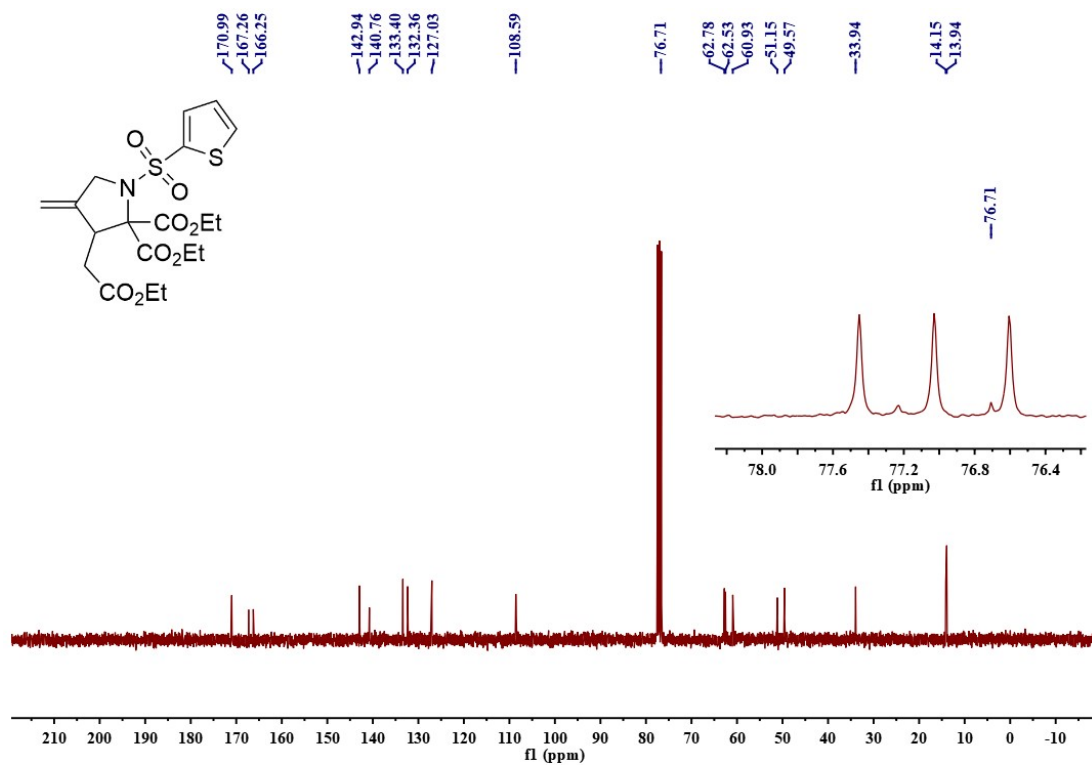
¹H NMR (CDCl₃, 300 MHz) NMR of **3ak**



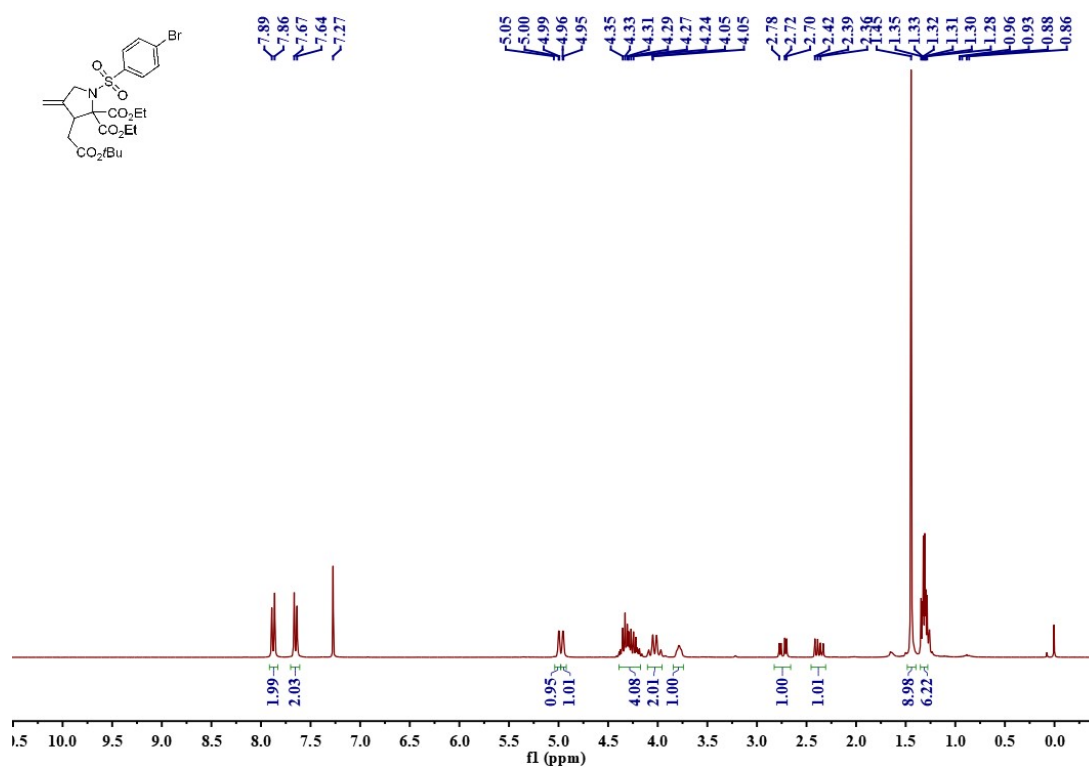
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3ak**



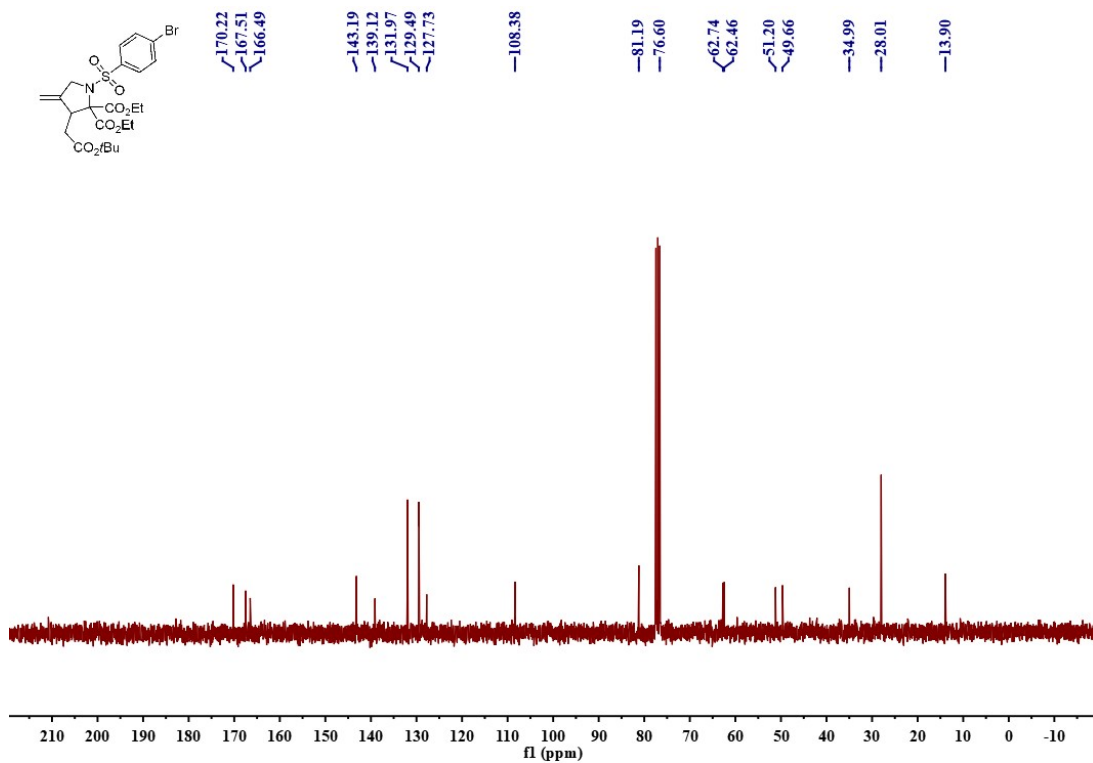
^1H NMR (CDCl₃, 300 MHz) NMR of **3al**



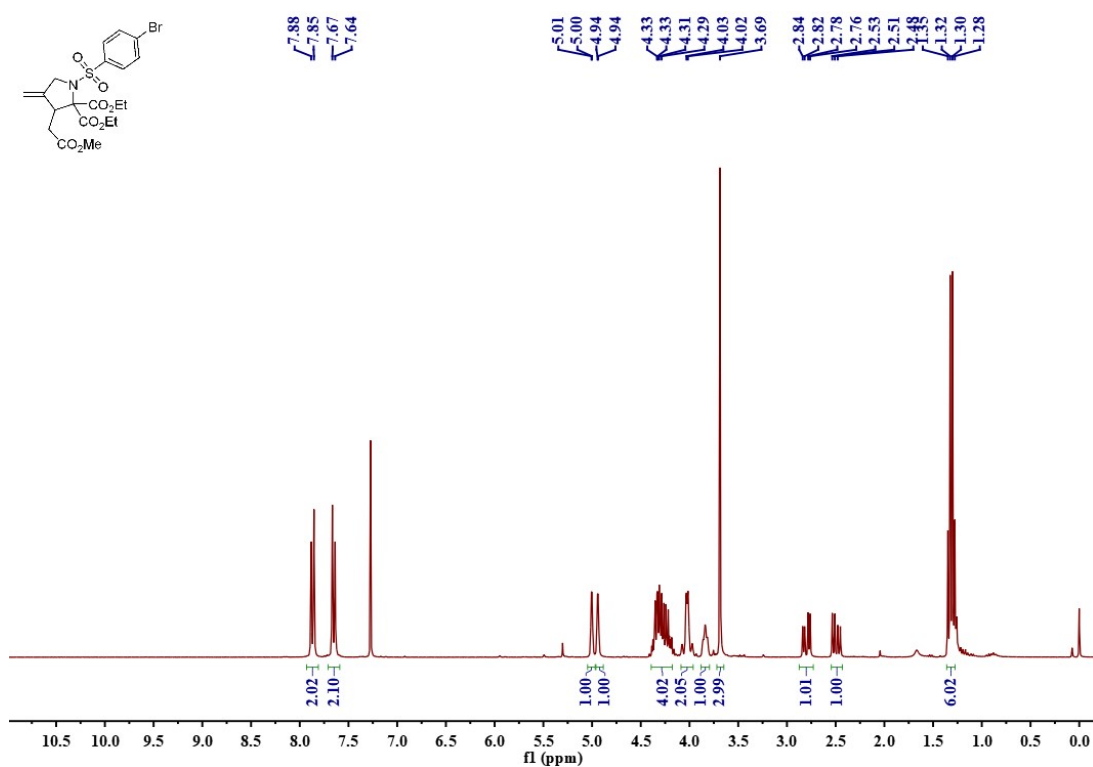
¹³C NMR (CDCl₃, 75 MHz) NMR of 3al



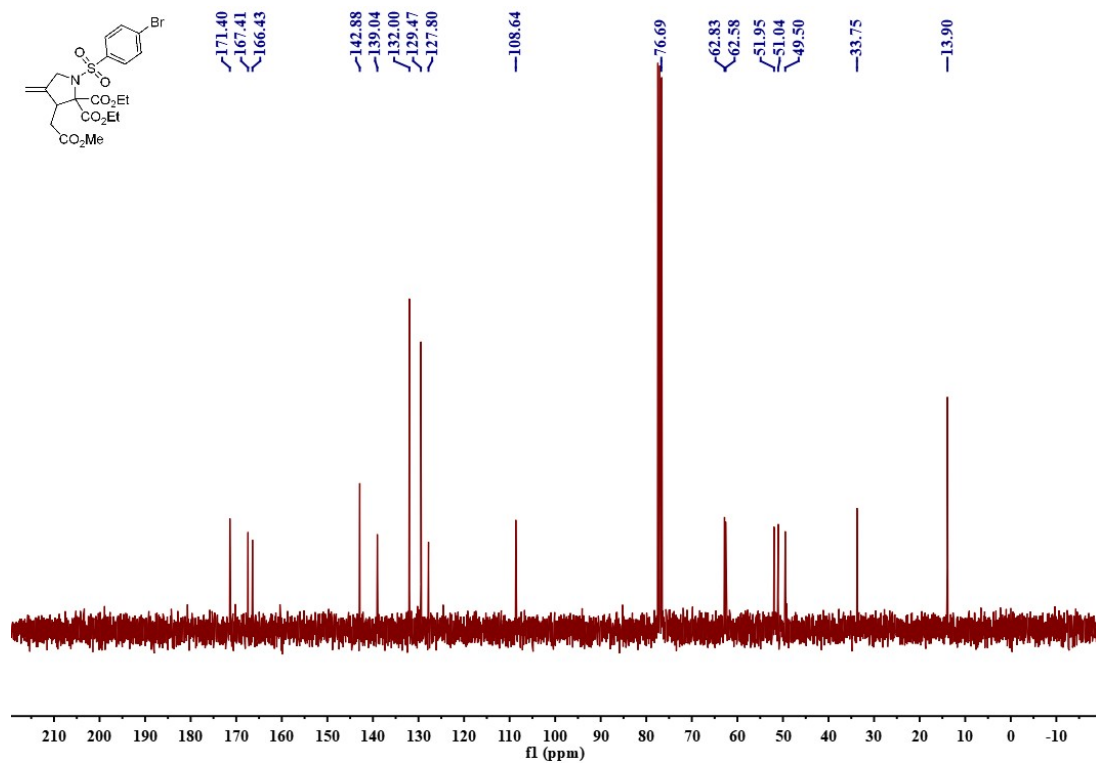
¹H NMR (CDCl₃, 300 MHz) NMR of 3bg



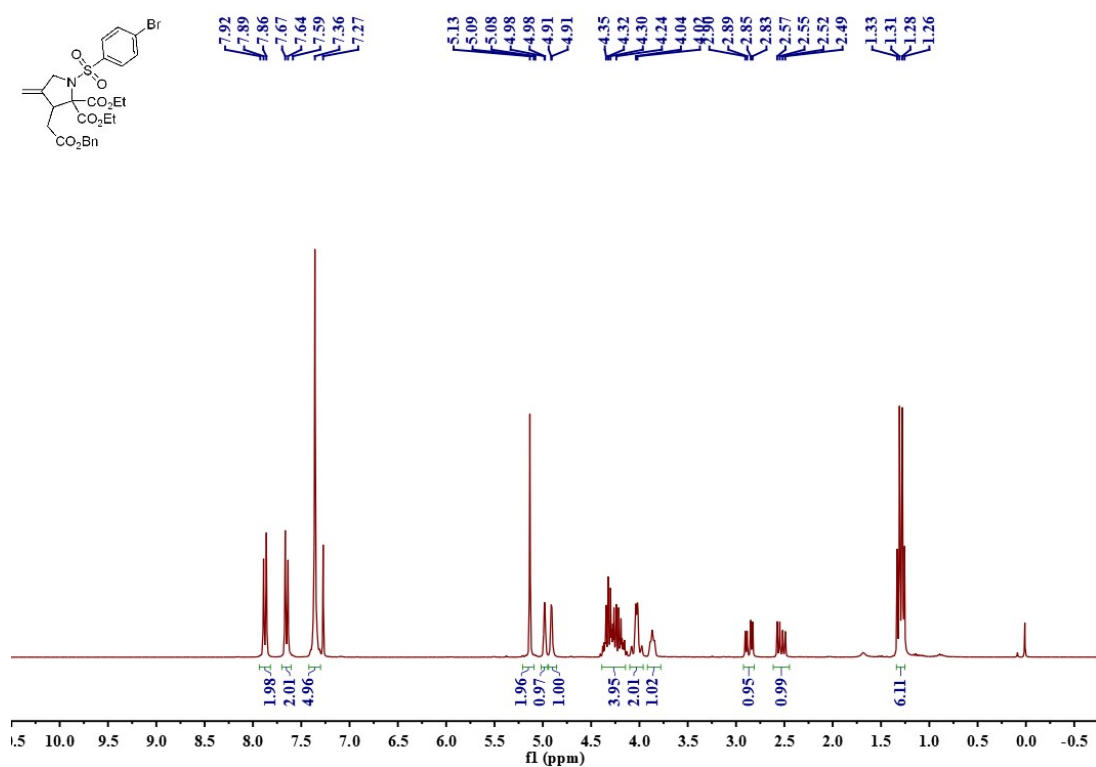
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3bg**



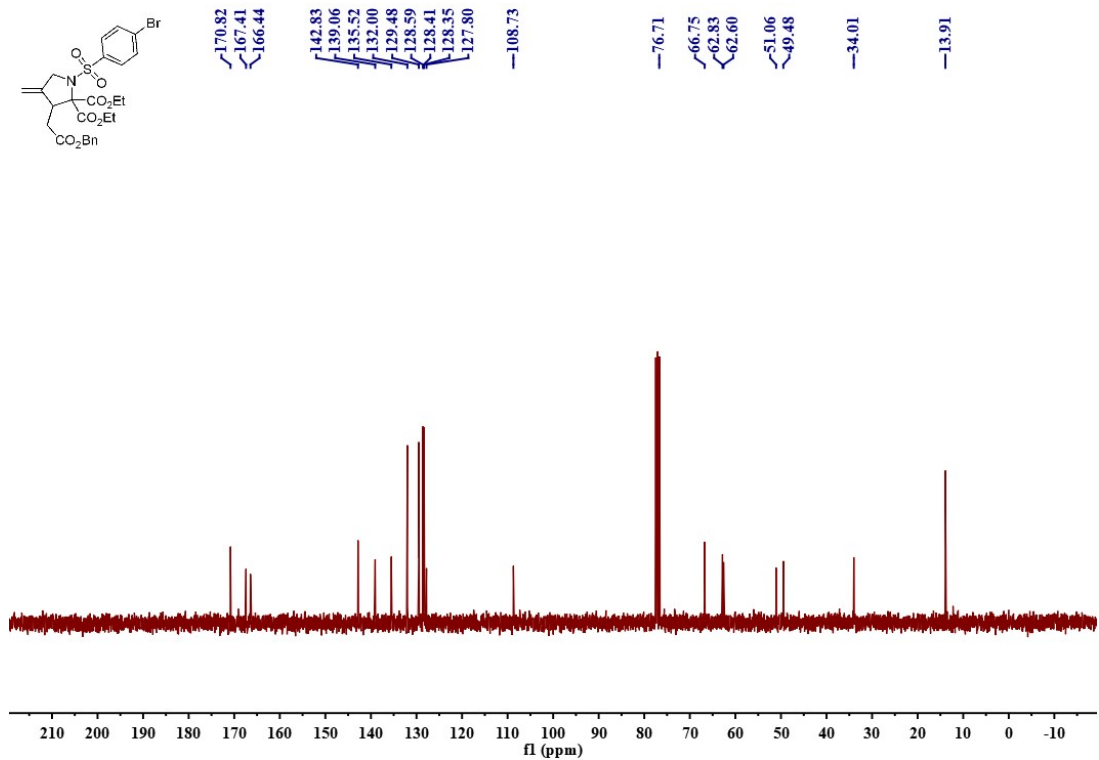
^1H NMR (CDCl₃, 300 MHz) NMR of **3cg**



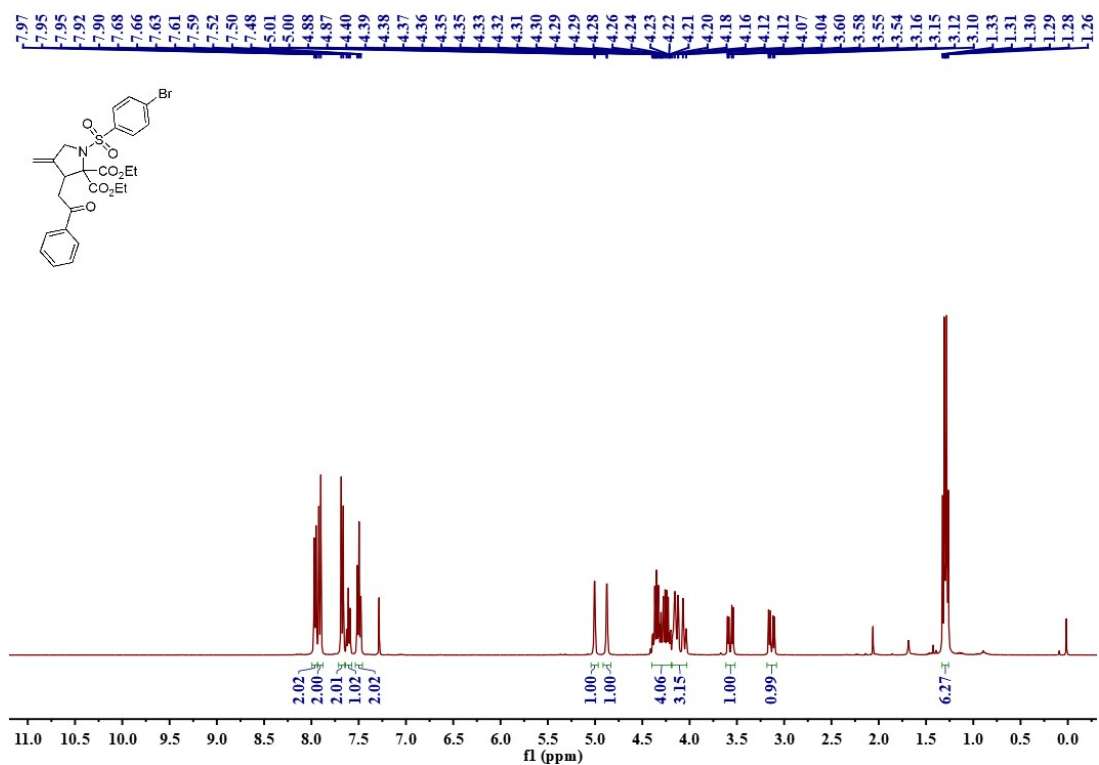
¹³C NMR (CDCl₃, 75 MHz) NMR of 3cg



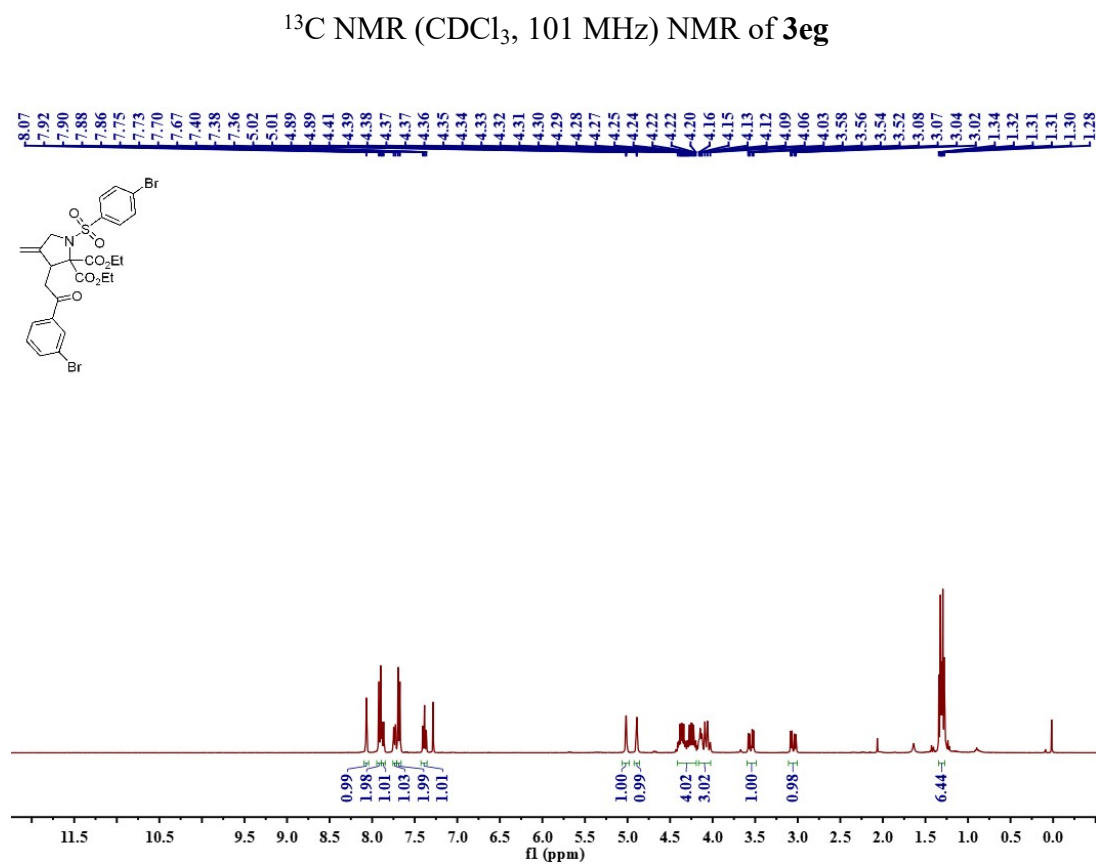
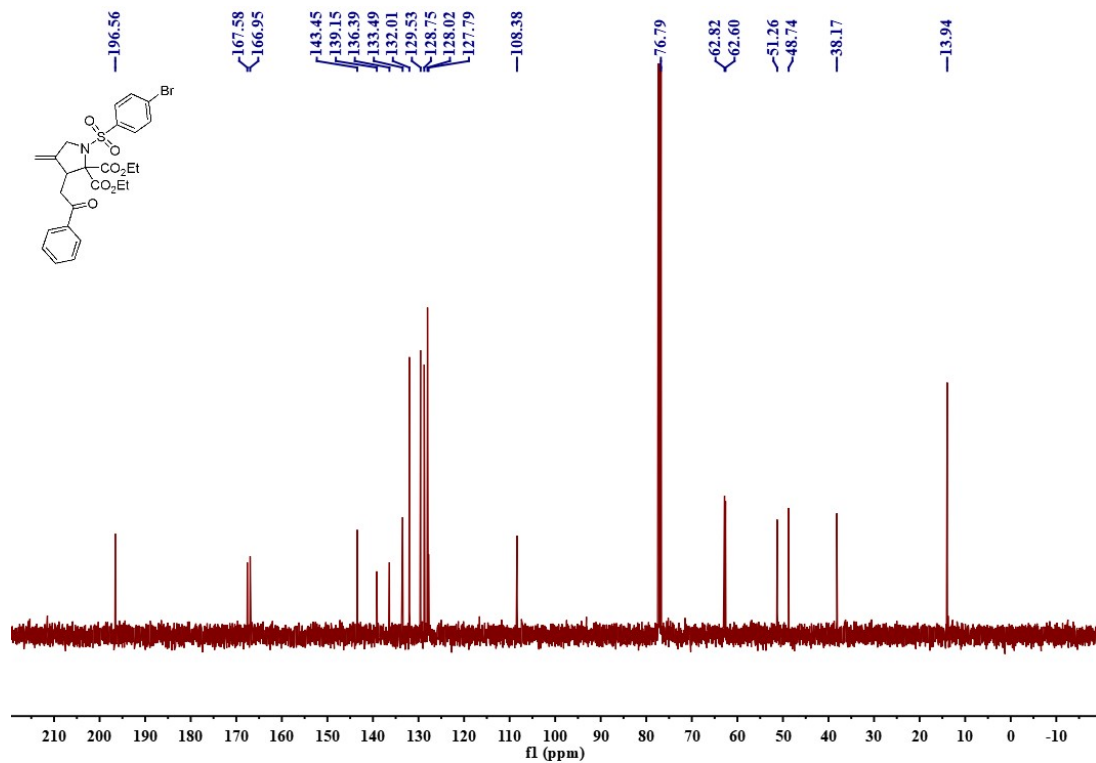
¹H NMR (CDCl₃, 300 MHz) NMR of 3dg



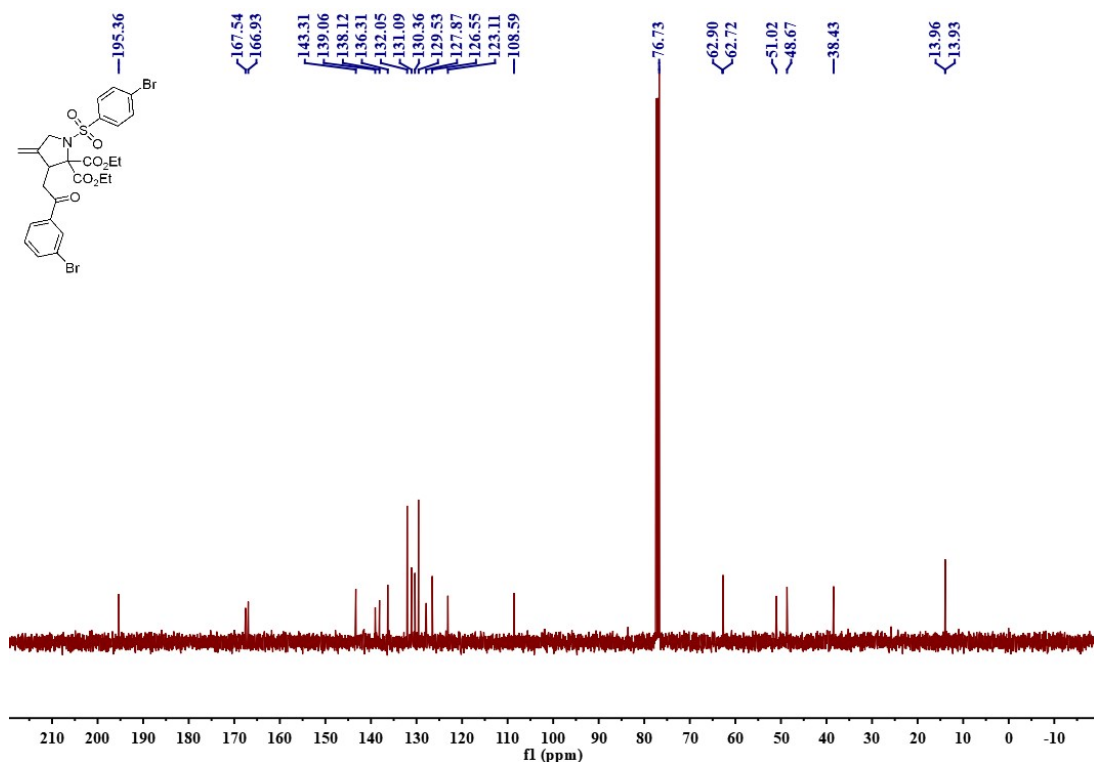
^{13}C NMR (CDCl₃, 75 MHz) NMR of **3dg**



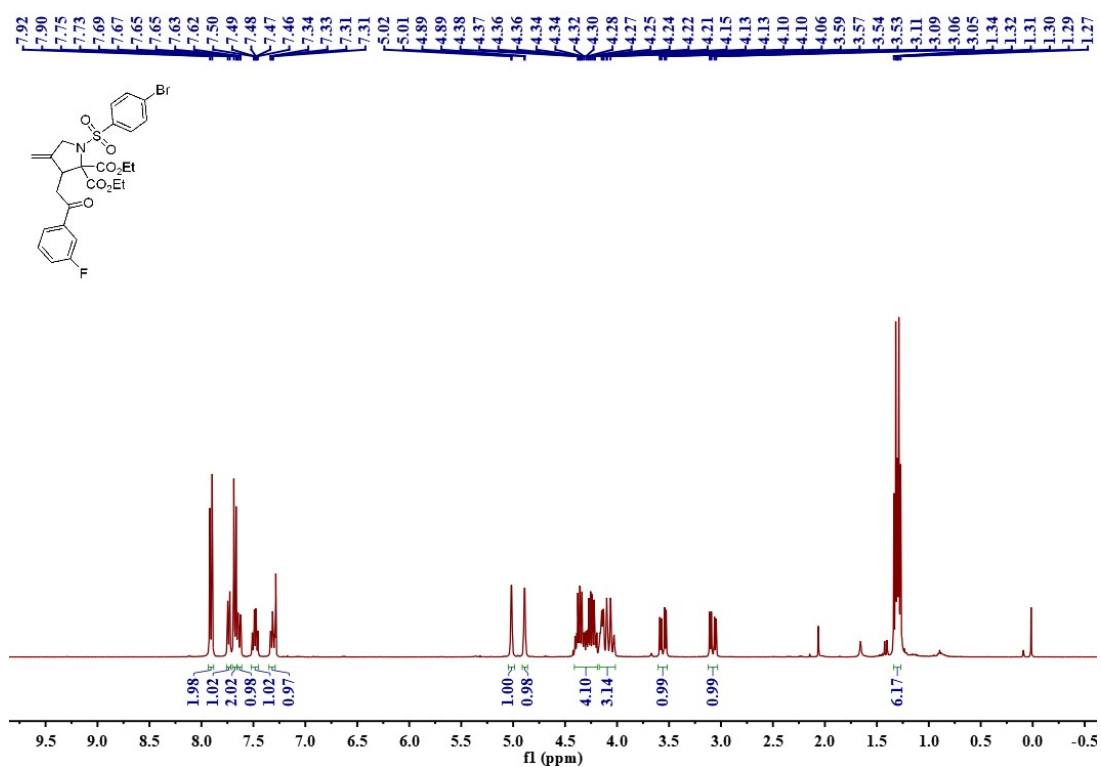
^1H NMR (CDCl₃, 400MHz) NMR of **3eg**



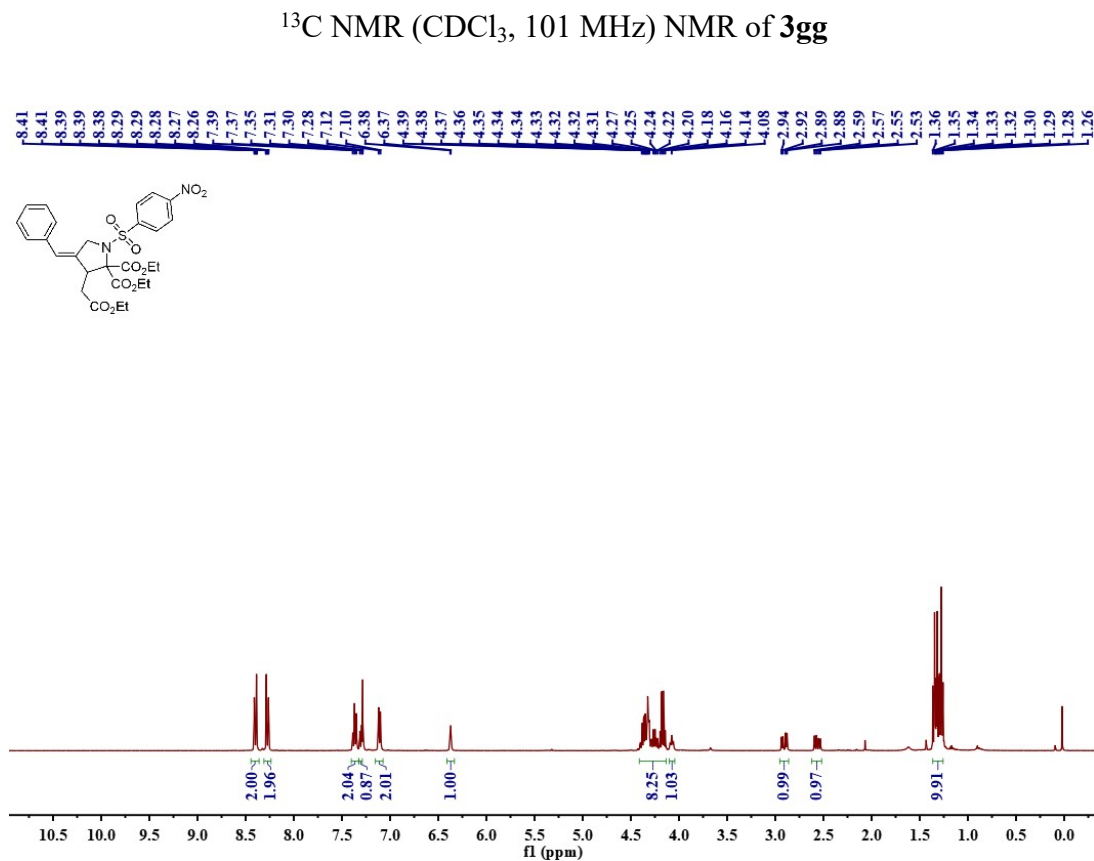
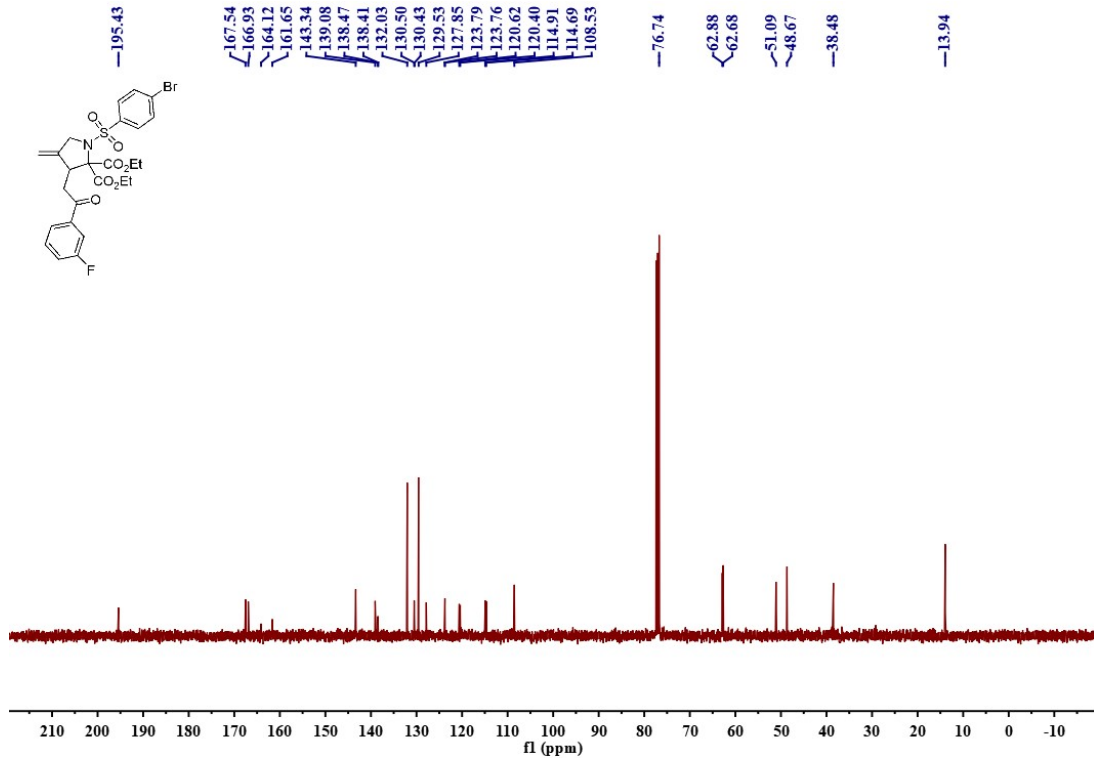
^1H NMR (CDCl₃, 400 MHz) NMR of **3fg**

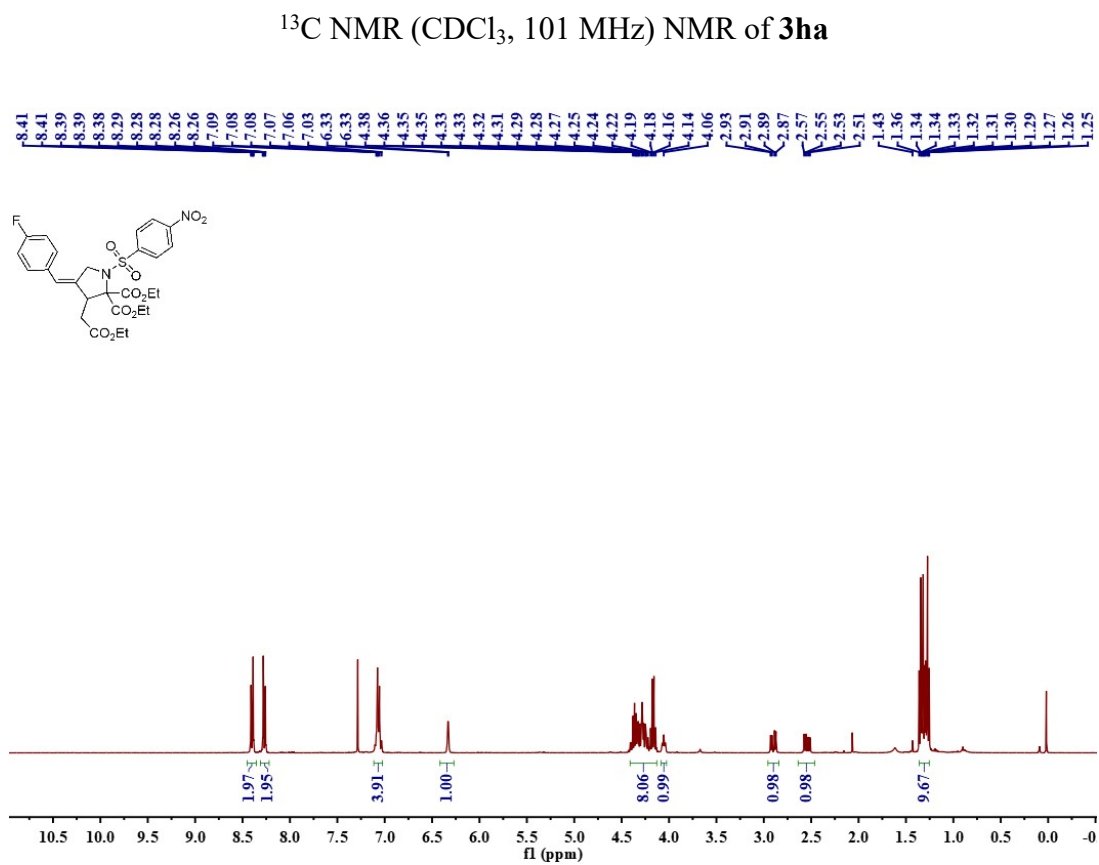
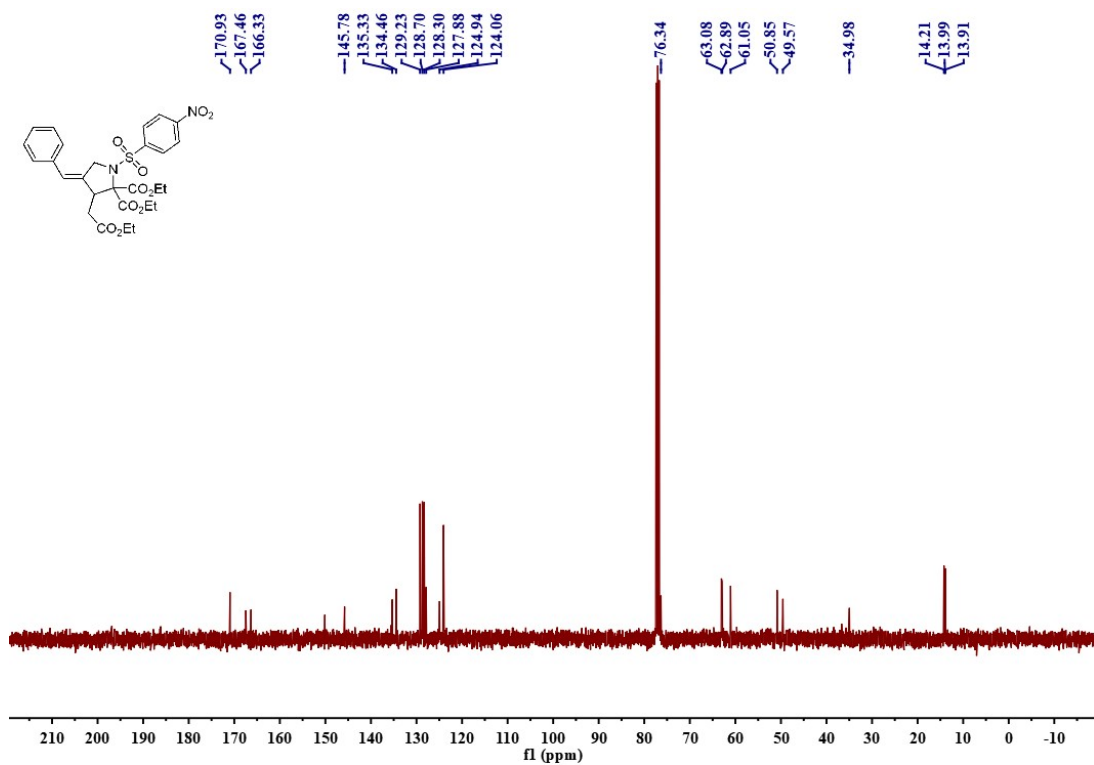


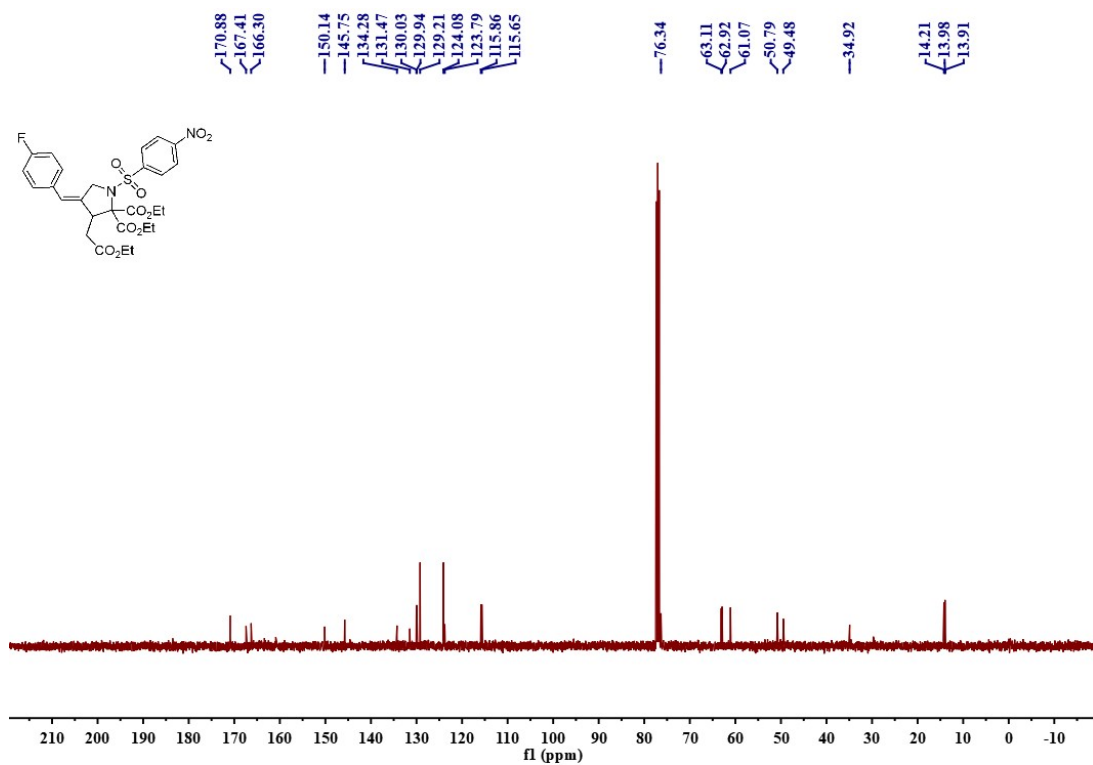
¹³C NMR (CDCl₃, 101 MHz) NMR of **3fg**



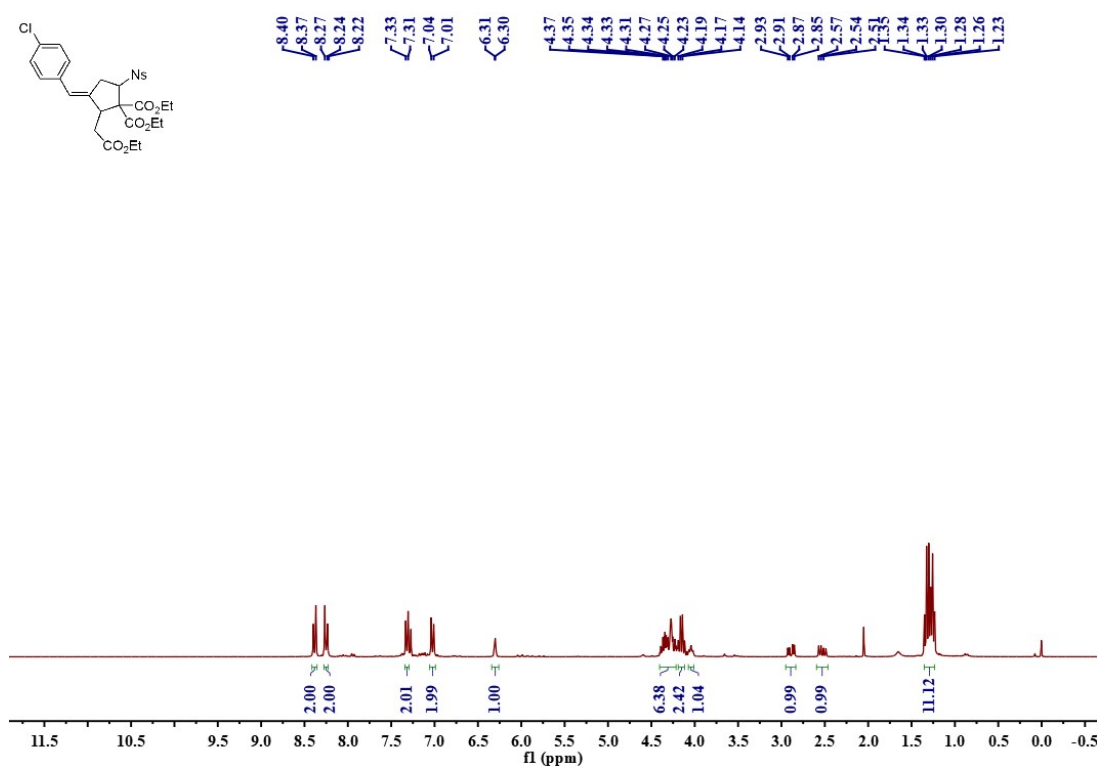
¹H NMR (CDCl₃, 400 MHz) NMR of **3gg**



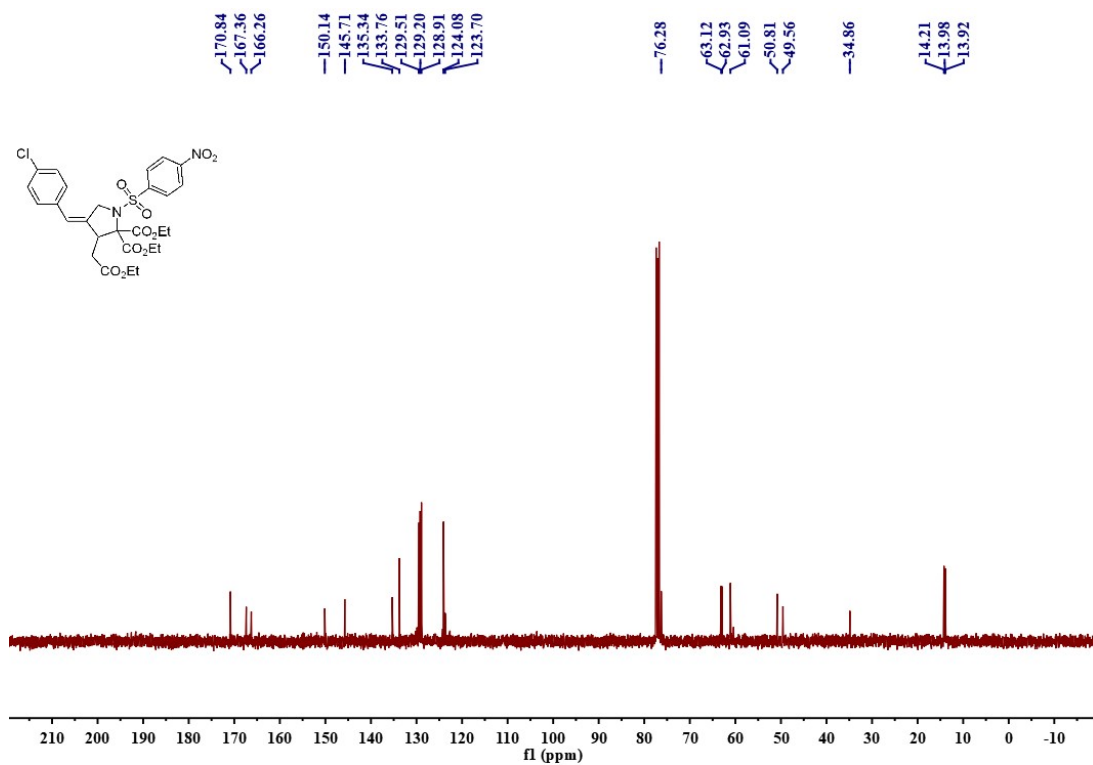




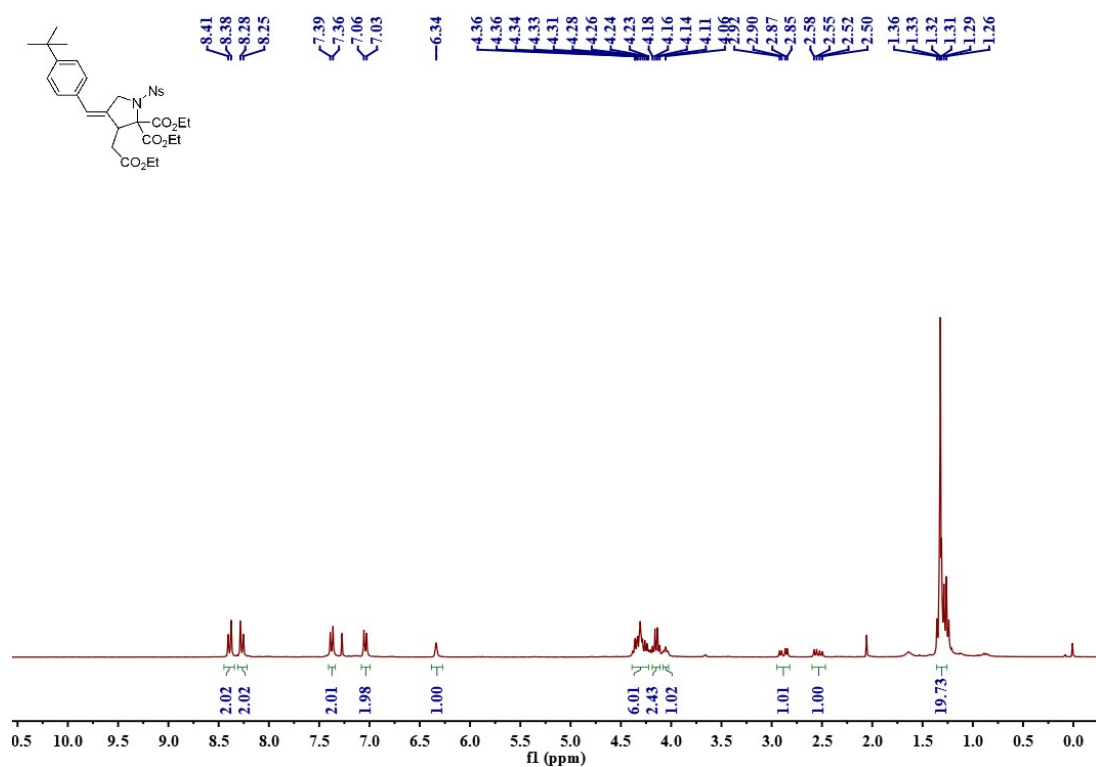
¹³C NMR (CDCl₃, 101 MHz) NMR of **3ia**



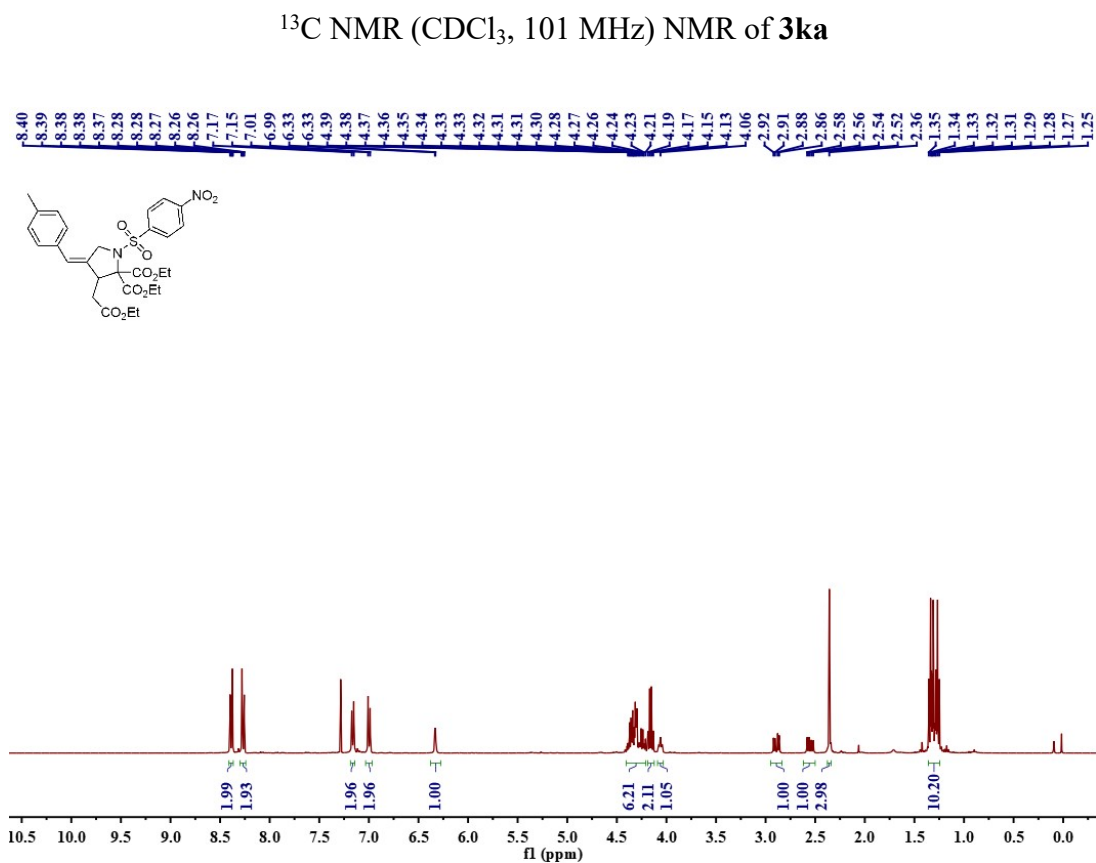
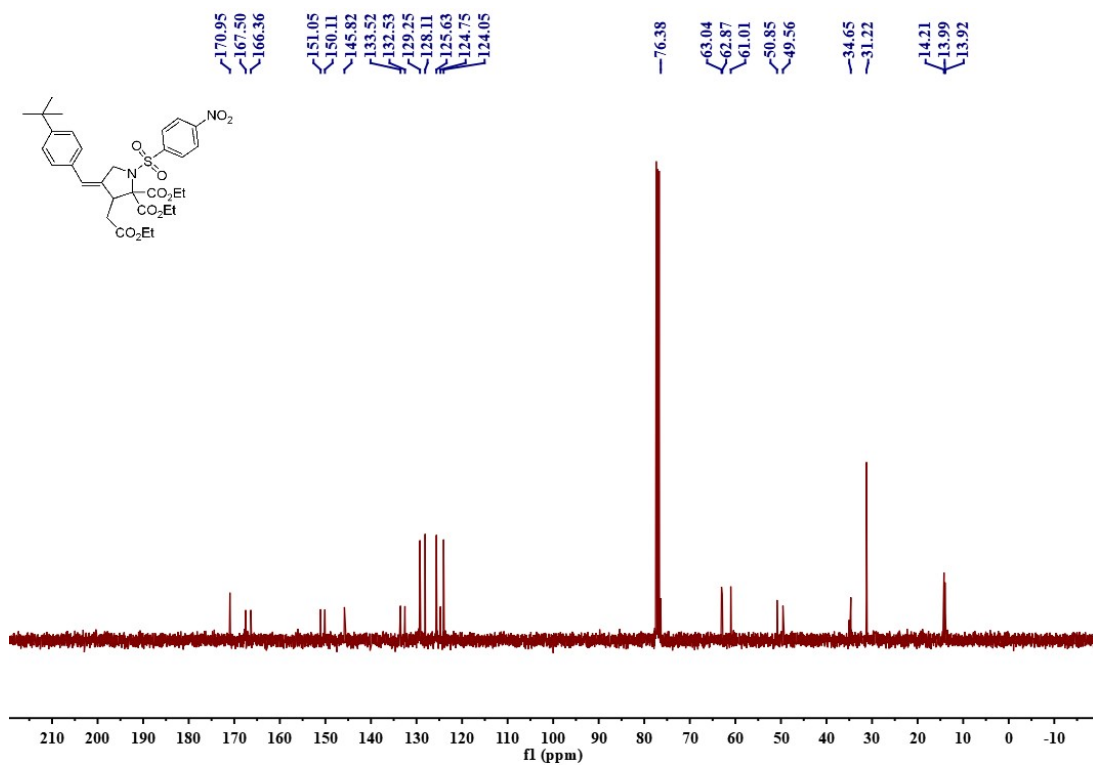
¹H NMR (CDCl₃, 300 MHz) NMR of **3ja**

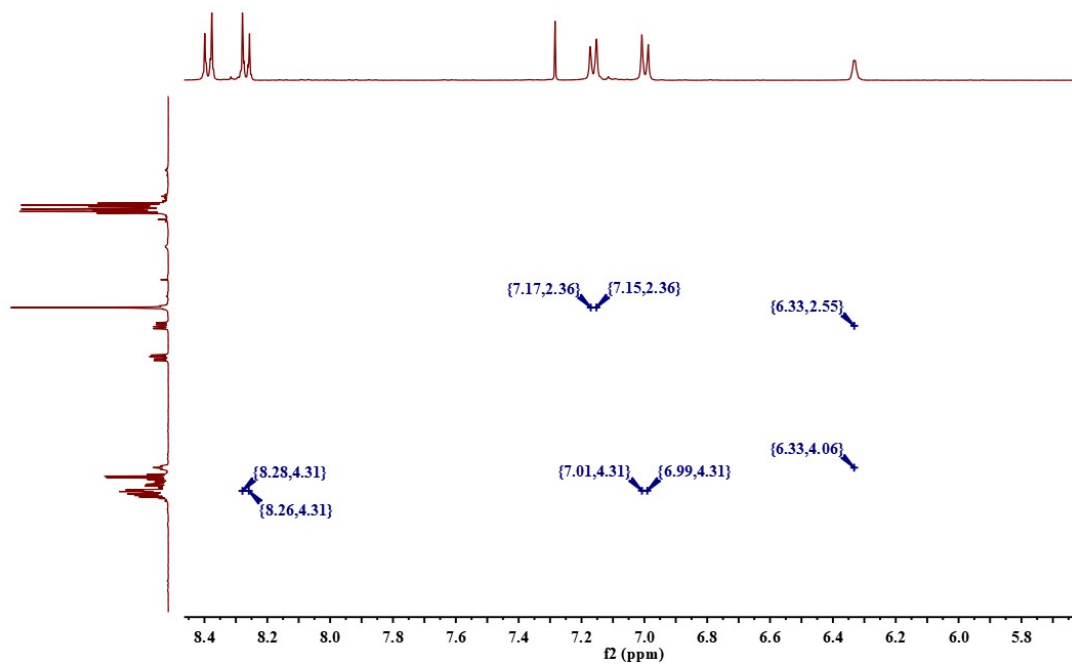


¹³C NMR (CDCl₃, 101 MHz) NMR of **3ja**

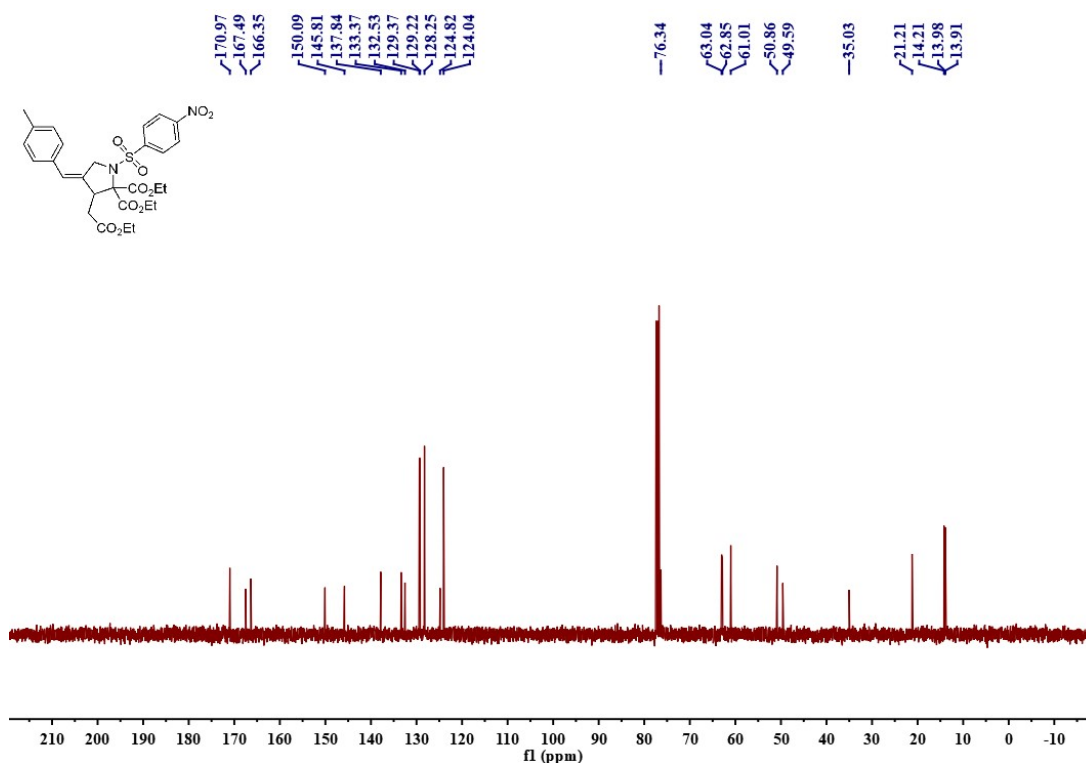


¹H NMR (CDCl₃, 300 MHz) NMR of **3ka**

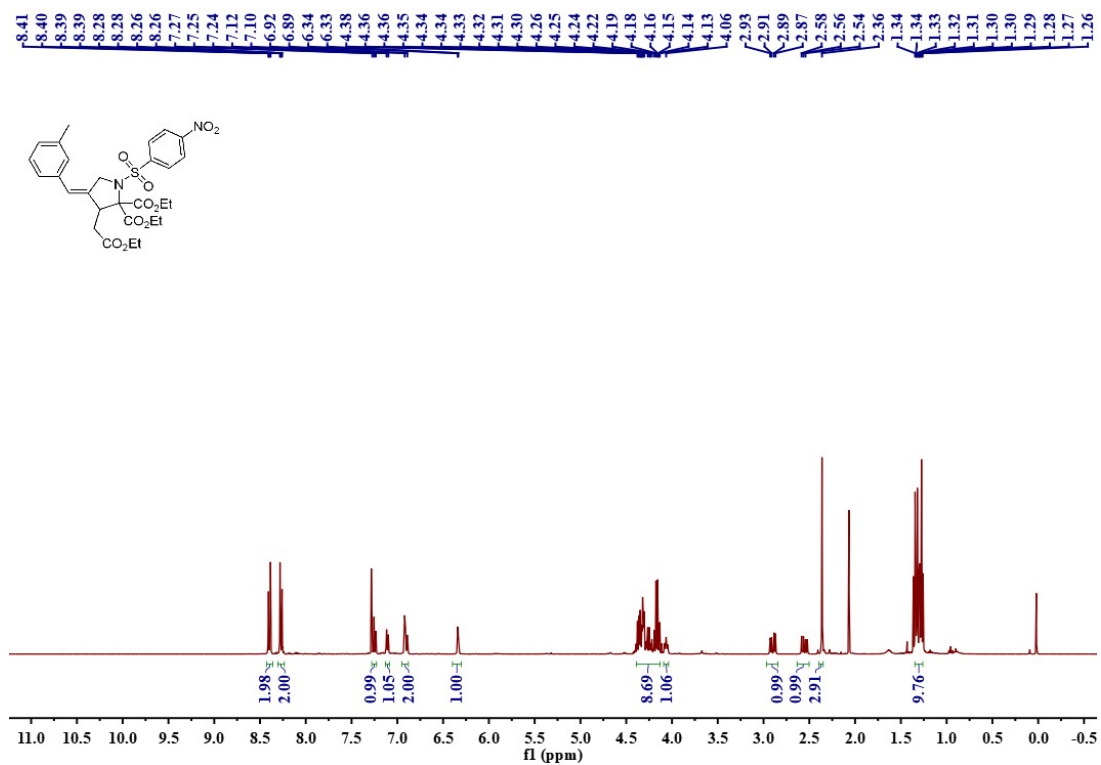




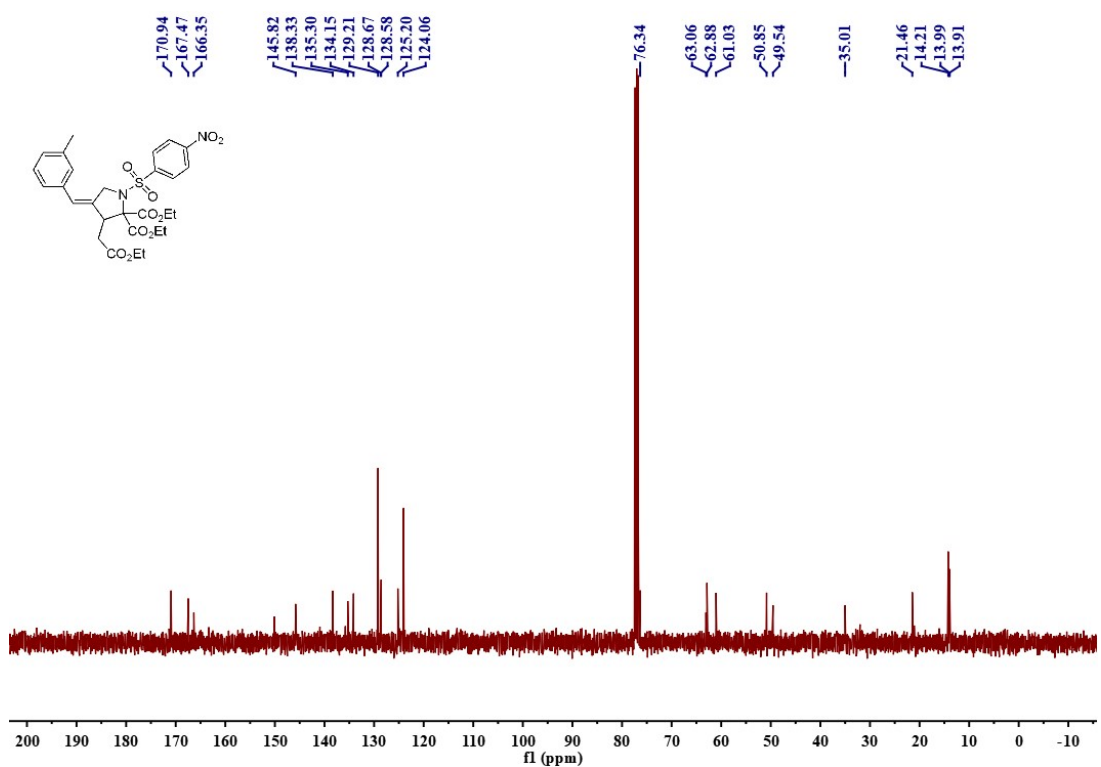
NOESY (CDCl₃, 400 MHz) of **3a**



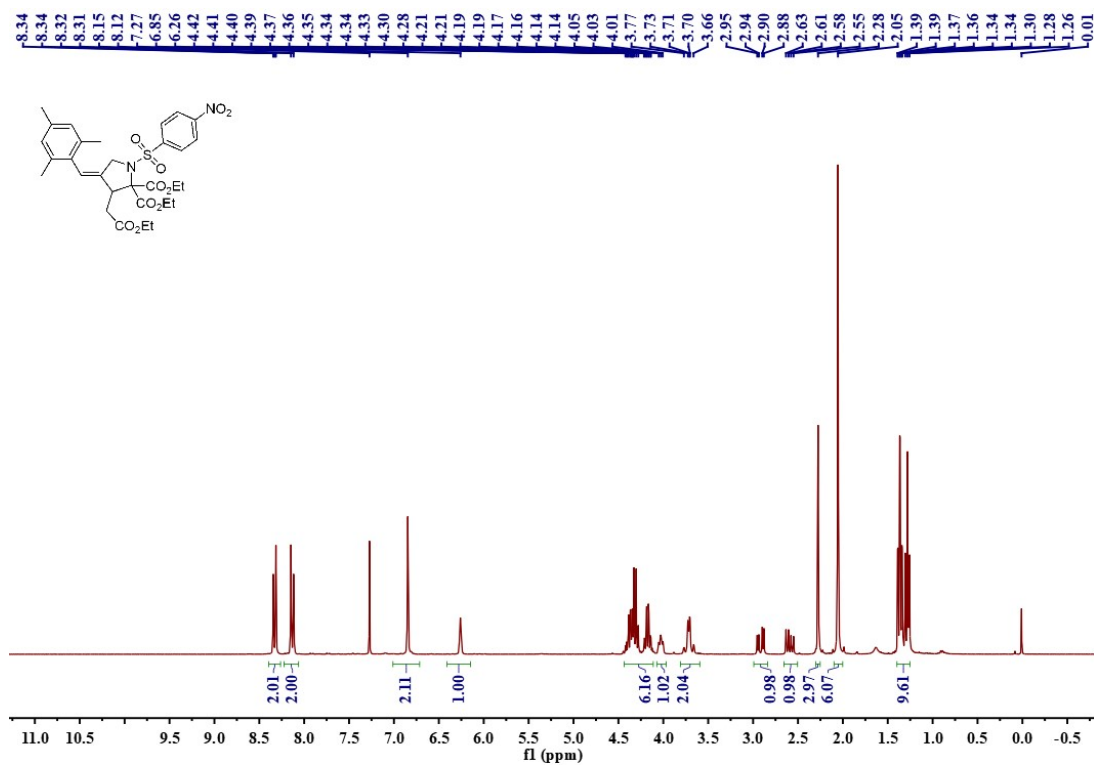
¹³C NMR (CDCl₃, 101 MHz) NMR of **3a**



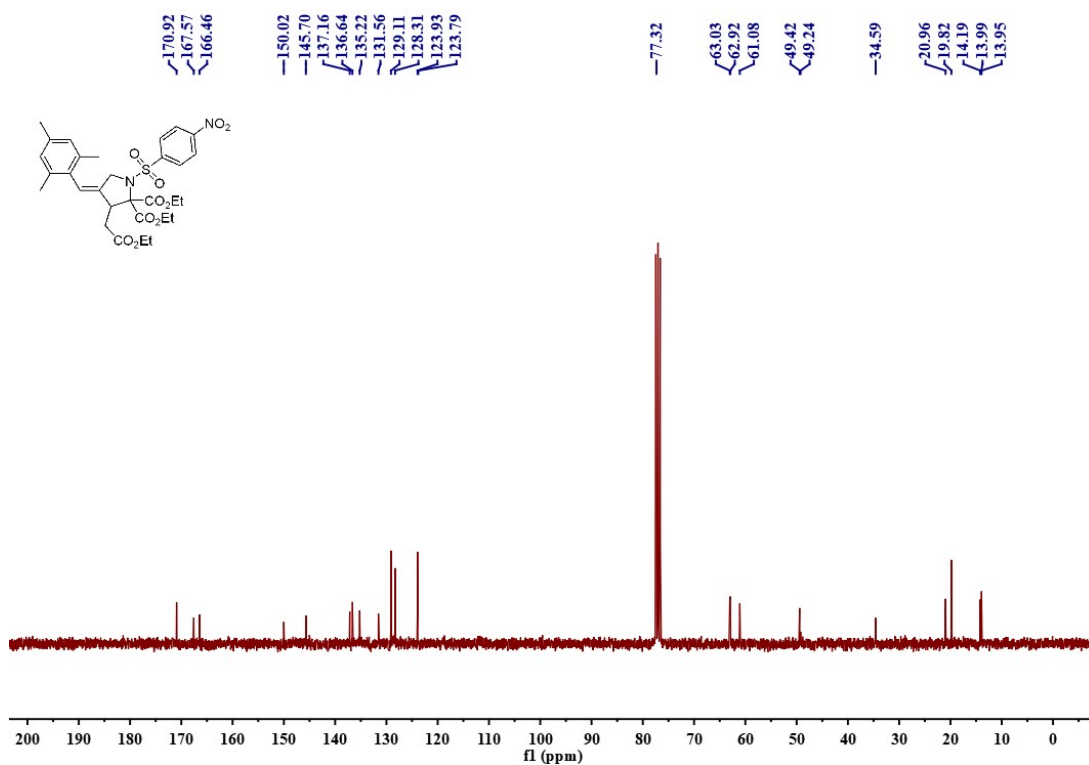
¹H NMR (CDCl₃, 400 MHz) NMR of **3ma**



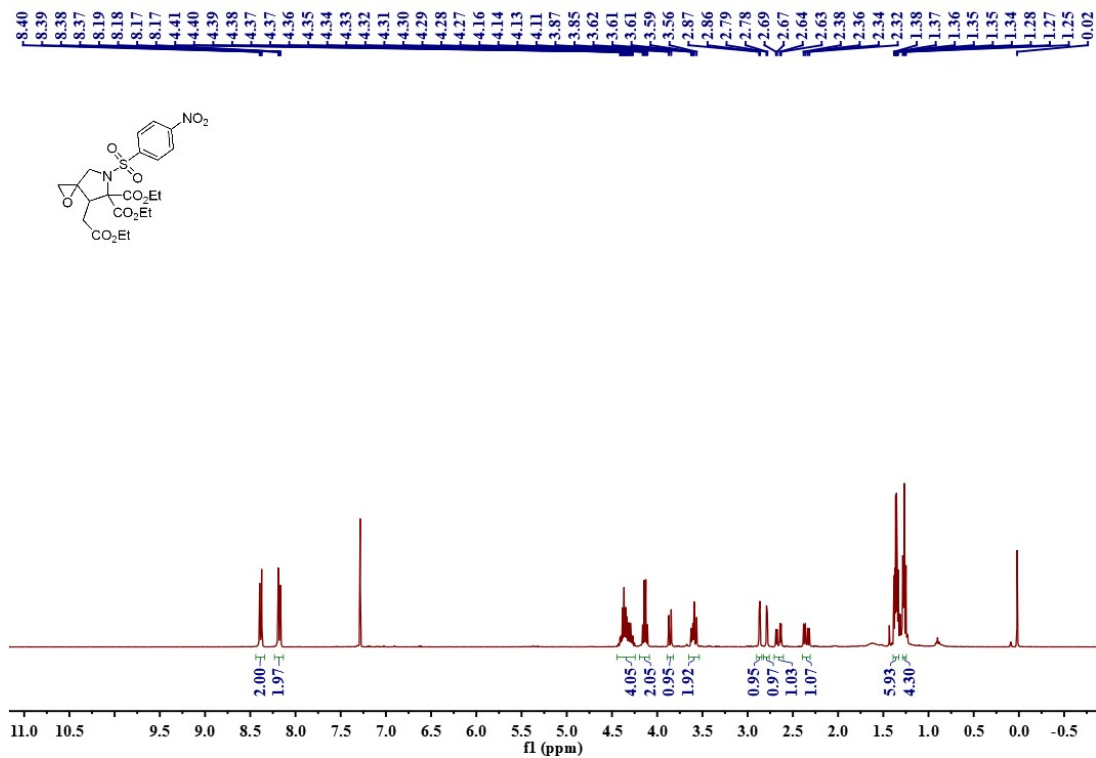
¹³C NMR (CDCl₃, 101 MHz) NMR of **3ma**



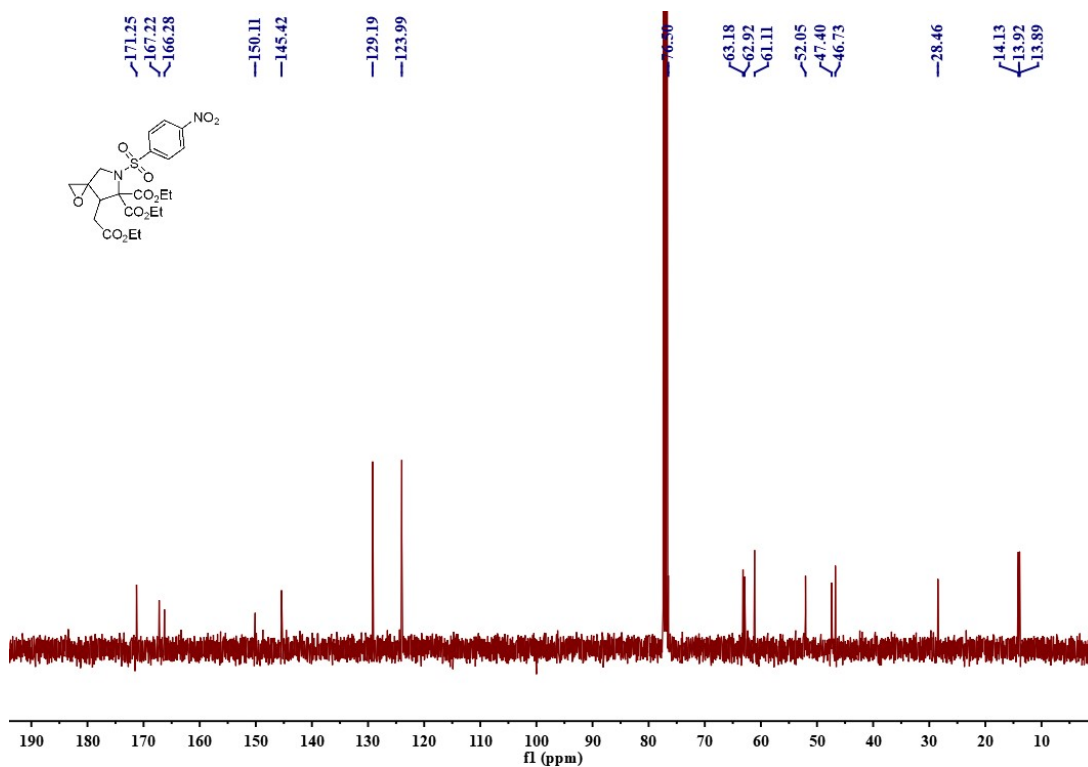
¹H NMR (CDCl₃, 300 MHz) NMR of **3na**



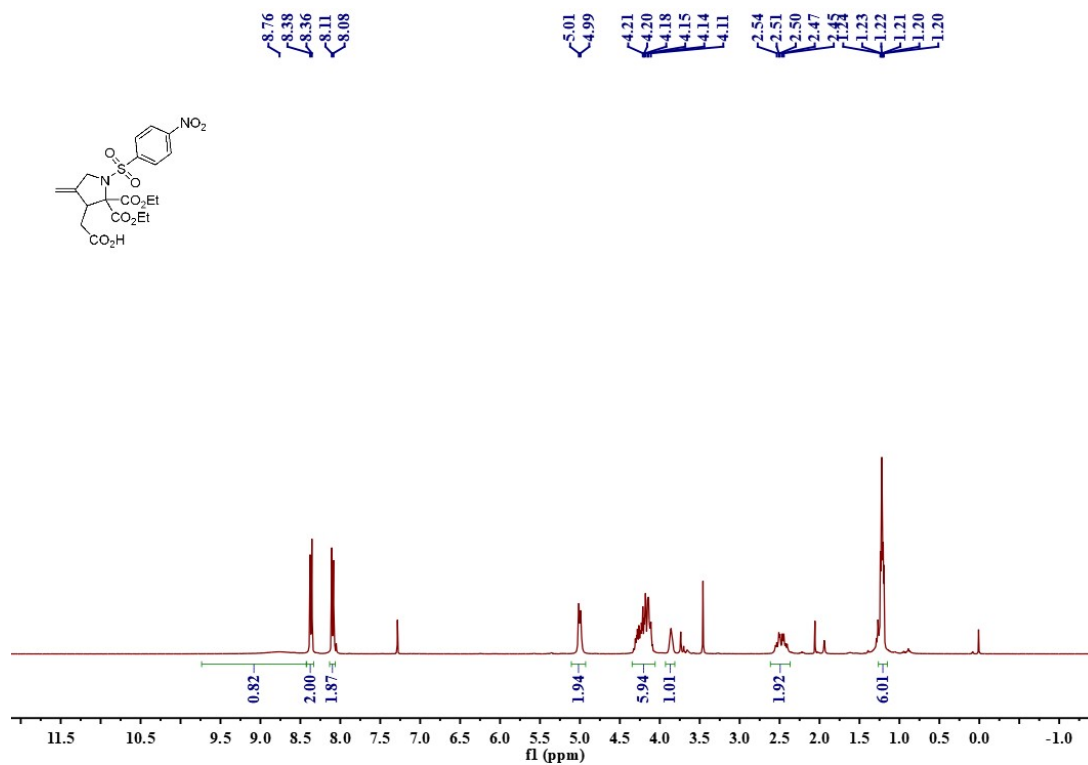
¹³C NMR (CDCl₃, 75 MHz) NMR of **3na**



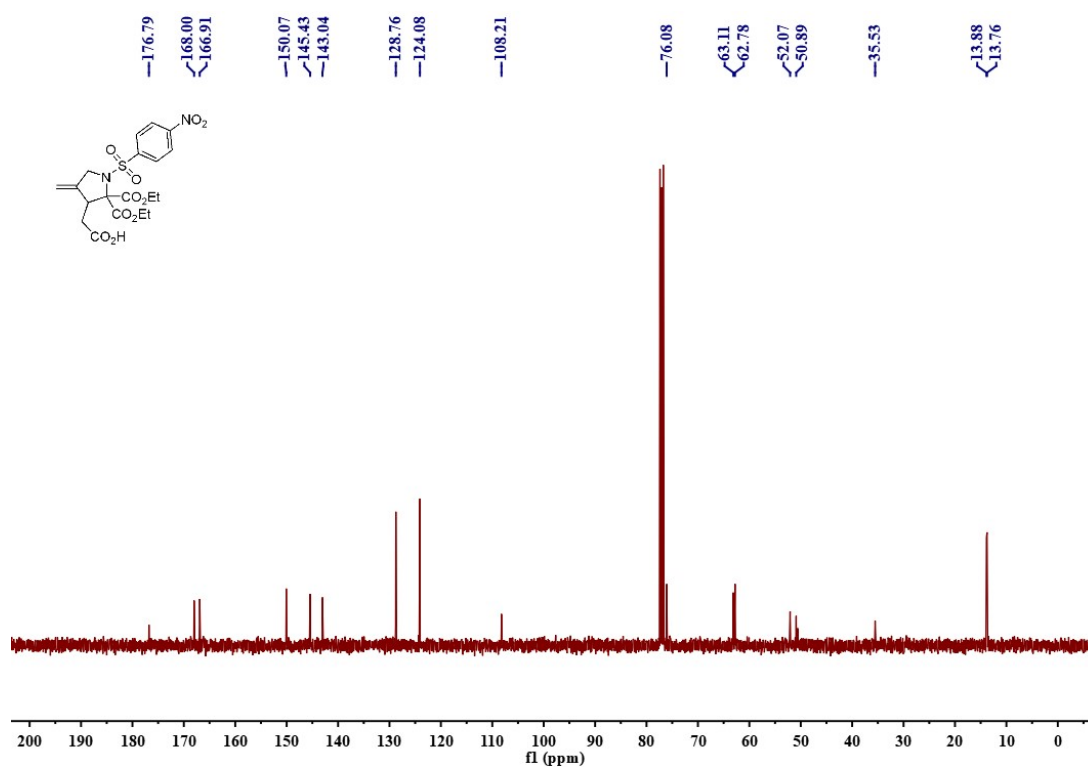
¹H NMR (CDCl₃, 400 MHz) NMR of 4



¹³C NMR (CDCl₃, 101 MHz) NMR of 4



¹H NMR (CDCl₃, 400 MHz) NMR of **5**



¹³C NMR (CDCl₃, 101 MHz) NMR of **5**

6. Copies of HPLC Chromatograms

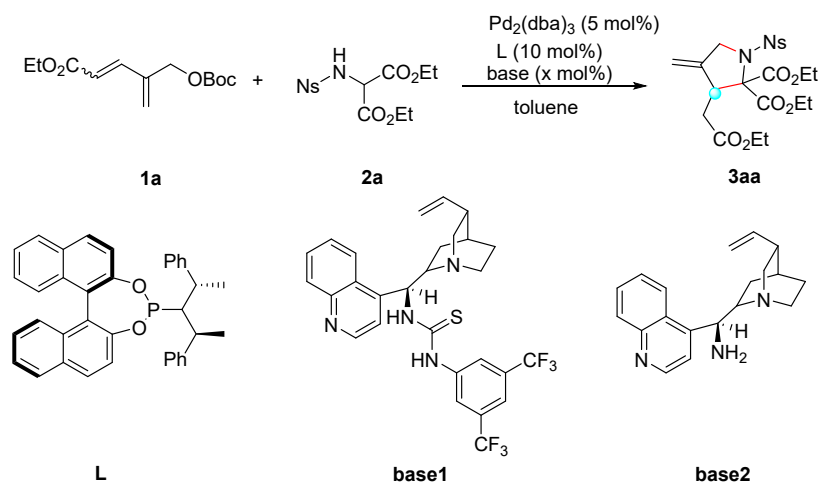


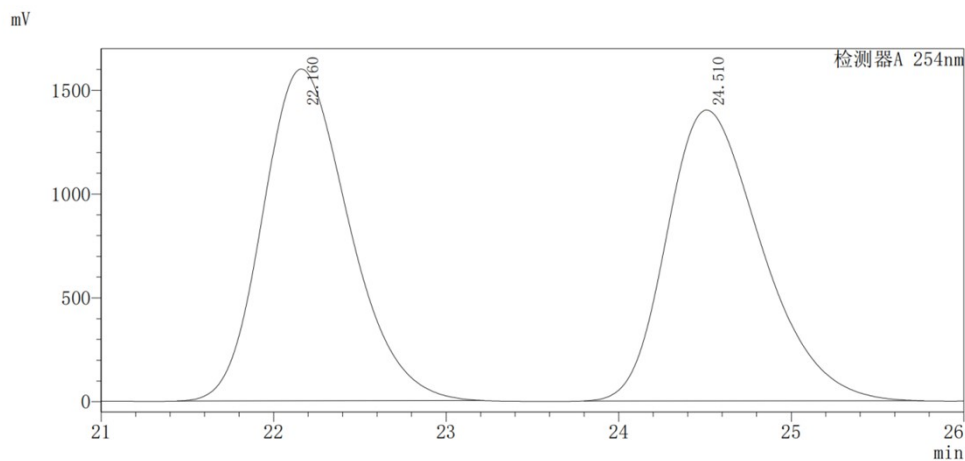
Table S2 Asymmetric [3+2] cyclization

Entry	1a	Cat	L	Base	equiv	Yields (%) ^b	ee(%) ^c
1	<i>trans</i> -1a	$\text{Pd}_2(\text{dba})_3$	L	base1	0.2	20	Rac ^e
2	<i>trans</i> -1a	$\text{Pd}_2(\text{dba})_3$	L	base1	0.5	73	35
3	<i>trans</i> -1a	$\text{Pd}_2(\text{dba})_3$	L	base1	0.75	49	33
4	<i>trans</i> -1a	$\text{Pd}_2(\text{dba})_3$	L	base1	1	ND ^d	-
5	<i>cis</i> -1a	$\text{Pd}_2(\text{dba})_3$	xantphos	Base2	0.5	ND ^d	-

^a In N_2 atmosphere, **1a** (0.13 mmol), **2a** (0.1 mmol), [Pd] (5 mol %), and ligand (10 mol %) were performed in solvent (1.0 mL). ^b The yield of the separated products. ^c Chiral HPLC was used for the determination. The HPLC collection parameters were as follows :CHIRALCEL[®]AD-H, wavelength 254 nm, mobile phase :*i*PrOH:Hex=15:85, flow rate :1mL/min. ^d ND = Not detected. ^e Rac = racemic.

HPLC acquisition parameters: Chiral column: CHIRALCEL[®]AD-H, Wave length: 254 nm, Mobile phase: *i*PrOH:Hex = **15:85**, Flow rate: 1mL/min

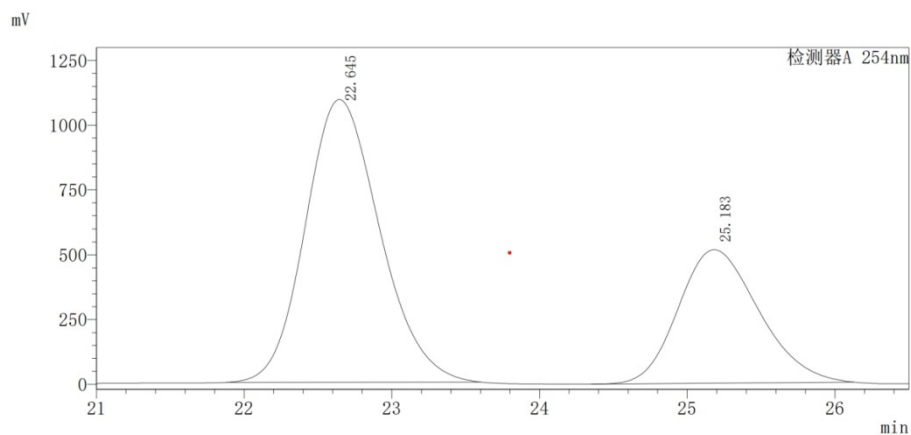
HPLC Spectra of racemic **3aa*** ($\text{Pd}(\text{PPh}_3)_4$)



Discloser A 254nm

Peak	Retent time(min)	Area(%)
1	22.160	50.853
2	24.510	49.147
total		100

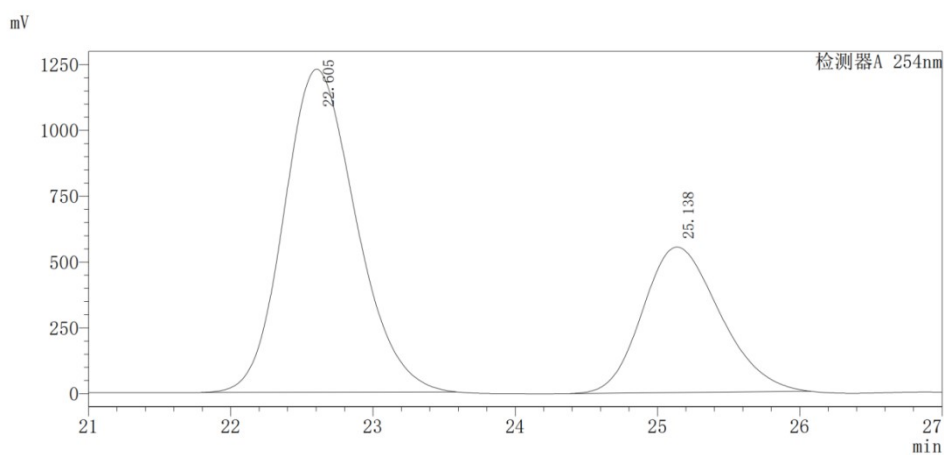
HPLC Spectra of enantiomeric **3aa*** (Table S2 entry 3)



Discloser A 254nm

Peak	Retent time(min)	Area(%)
1	22.645	66.210
2	25.183	33.790
total		100

HPLC Spectra of enantiomeric **3aa*** (Table S2 entry 2)

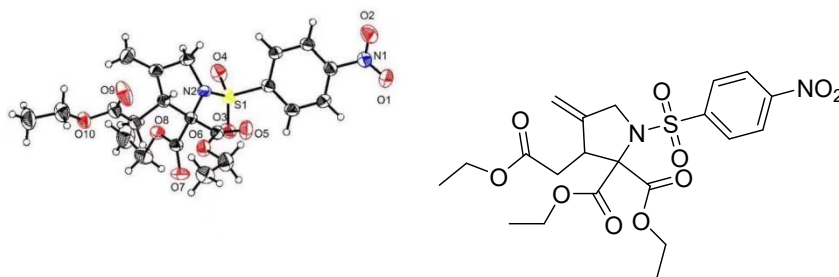


Discloser A 254nm

Peak	Retent time(min)	Area(%)
1	22.605	67.393
2	25.138	32.607
total		100

7. X-Ray single crystal data of product 3aa

The X-ray crystallographic structures for **3aa**. ORTEP view of the molecules of complex **3aa**, showing ellipsoids at 30% probability level. Crystal data have been deposited to CCDC, number **3aa (2223030)**. A summary of the fundamental crystal and refinement data are given in the Table 1 of the Supporting Information. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files. White crystals suitable for X-ray diffraction were grown by n-hexane/Ethyl acetate solution of **3aa** inside a penicillin bottle.



Crystal structure of 3aa (CCDC 2223030)

Table S3 Crystal data and structure refinement for 3aa

Identification code	3aa
Empirical formula	C ₂₁ H ₂₆ N ₂ O ₁₀ S
Formula weight	498.13
Temperature/K	199.99(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.44620(10)
b/Å	15.6061(2)
c/Å	15.3949(2)
α/°	90
β/°	107.3790(10)

$\gamma/^\circ$	90
Volume/ \AA^3	2395.17(5)
Z	34
$\rho_{\text{calc}}/\text{cm}^3$	1.770
μ/mm^{-1}	7.861
F(000)	1292.0
Crystal size/ mm^3	$0.2 \times 0.2 \times 0.2$
Radiation	CuK α ($\lambda = 1.54184$)
2 Θ range for data collection/ $^\circ$	9.112 to 147.586
Index ranges	$-12 \leq h \leq 12, -19 \leq k \leq 18, -15 \leq l \leq 18$
Reflections collected	14317
Independent reflections	4724 [$R_{\text{int}} = 0.0333, R_{\text{sigma}} = 0.0337$]
Data/restraints/parameters	4724/6/310
Goodness-of-fit on F^2	1.053
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0397, wR_2 = 0.1052$
Final R indexes [all data]	$R_1 = 0.0447, wR_2 = 0.1089$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.24/-0.49