Supporting Information for

Enantioselective Direct Vinylogous Michael Addition for Constructing Enantioenriched γ,γ-Dialkyl Substituted Butyrolactams and Octahydroindoles†

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1. General Information

All commercially available reagents were used without further purification unless otherwise noted. All solvents were dried and distilled as follow: THF and Et_2O were distilled from sodium; CH_2Cl_2 and toluene ware distilled from calcium hydride; $CHCl_3$ was distilled from P_2O_5, anhydrous 1,2-dichloroethane (Aladdin, 99.8%, with molecular sieves), acetonitrile, 1,4-dioxane, 2-Methylfuran, and other solvents were commercially available. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal 200-400 mesh silica gel. All new compounds gave satisfactory spectroscopic analyses (^{1}H NMR, ^{13}C NMR, HRMS). NMR spectra were recorded on Bruker AVANCE III 500MHz NMR spectrometer. HRMS spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI). Chiral HPLC analyses were performed on Waters 2487 Series using Daicel Chiralpak (AD-H, OD-H, IC and IB-3) column with hexane/*i*PrOH/MeOH as the eluent. Optical rotations were measured on Anton Paar MCP 300 polarimeter.

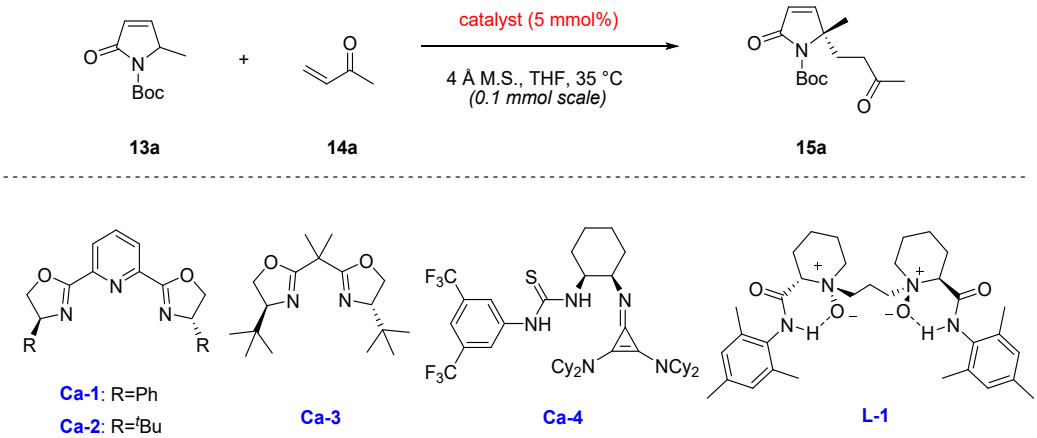
2. Reaction Conditions Optimization

2.1 General Procedure

Unless noted otherwise, reactions were carried out for the following procedure. Metal salt (5 mol% or 10 mol%), *N*, *N*′-dioxide ligand (6 mol% or 12 mol %), base (1.0 equiv.), and 4Å molecular sieves (20.0 mg) were stirred in anhydrous solvent (0.2 M) under argon atmosphere at 35 °C for 1 hour. Then a mixture of *α*, *β*-Unsaturated *γ*-butyrolactam **13** and *α*, *β*-unsaturated ketones **14** or **16** in the solvent was added to the above solution. The mixture was stirred at 35 °C until TLC showed the staring material was no longer consumed. The reaction mixture was filtered through Celite® and washed with EtOAc. The filtrate was then concentrated under reduced pressure to give a residue which was purified by silica gel chromatography to afford the addition product **15** or **17**.

2.2 Screening Details for the Model Reaction

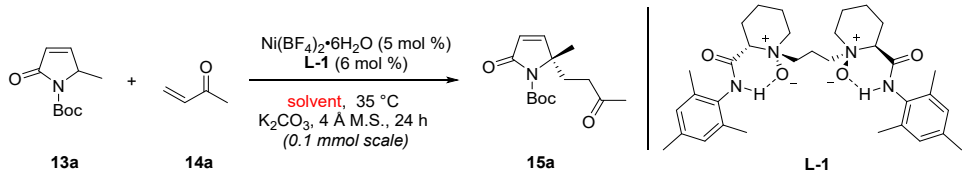
Table S1. The screening of catalysts[a]



Entry	Catalyst	Yield (%)	*ee* (%)
1	——	NR	——
2	**Ca-1**/$Ni(BF_4)_2·6H_2O$ (1.2:1)	NR	——
3	**Ca-2**/$Ni(BF_4)_2·6H_2O$ (1.2:1)	Trace	——
4	**Ca-3**/$Ni(BF_4)_2·6H_2O$ (1.2:1)	NR	——
5	**Ca-4**	5	6
6	**L-1**/$Ni(BF_4)_2·6H_2O$ (1.2:1)	41	67

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **14a**, 1.0 equiv of K_2CO_3, 5 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC in THF for 24 h.

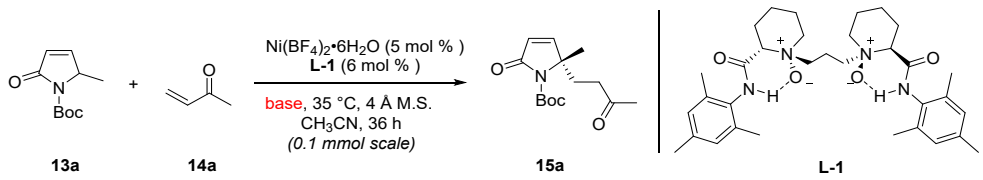
Table S2. The screening of solvents[a]



Entry	Solvent	Yield (%)	*ee* (%)
1	THF	41	67
2	1,4-dioxane	56	54
3	$CHCl_3$	33	69
4	EtOAc	37	65
5	2-methylfuran	30	62
6	DCM	41	52
7	1,2-DCE	59	84
8	CH_3CN	61	84
9	Acetone	19	83
10	*i*-PrOH	30	67

[a] Reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **14a**, 1.0 equiv of K_2CO_3, 5 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC for 24 h.

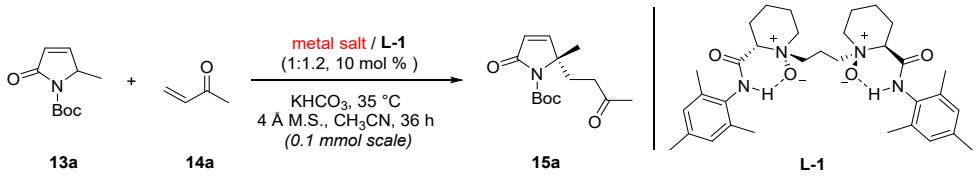
Table S3. The screening of bases[a]



Entry	Base	Yield (%)	*ee* (%)
1	$KHCO_3$	68	84
2	$NaHCO_3$	32	84
3	DBU	30	14
4	2,6-Lutidine	15	81
5	pyridine	NR	——
6	Quinine	56	78
7	Quinidine	63	80

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **14a**, 1.0 equiv of base, 5 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC in CH_3CN for 36 h.

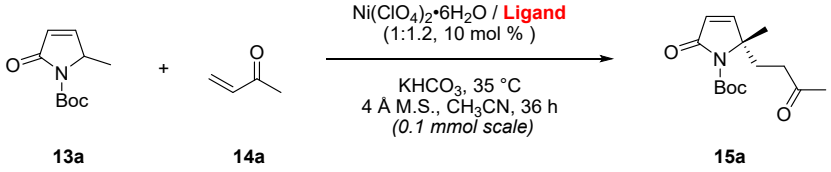
Table S4. The screening of metal salts[a]

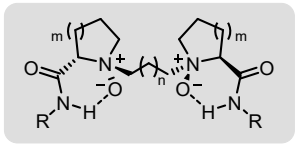


Entry	Metal salt	Yield (%)	*ee* (%)
1	$Ni(OTf)_2$	70	84
2	$Ni(acac)_2$	11	41
3	$NiCl_2$	Trace	——
4	$NiCl_2·6H_2O$	Trace	——
5	$Ni(BF_4)_2·6H_2O$	75	84
6	$Ni(ClO_4)_2·6H_2O$	84	84

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **14a**, 1.0 equiv of $KHCO_3$, 10 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC in CH_3CN for 36 h.

Table S5. The screening of *N, N'*-dioxide ligands[a]





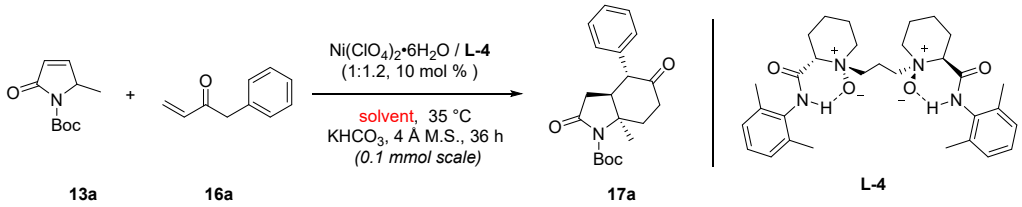
L-1: R=2,4,6-$Me_3C_6H_2$, m=2, n=1
L-2: R=2,4,6-$Me_3C_6H_2$, m=1, n=1
L-3: R=2,4,6-$Me_3C_6H_2$, m=2, n=0
L-4: R=2,6-$Me_2C_6H_3$, m=2, n=1
L-5: R=2,6-Et_2-4-MeC_6H_2, m=2, n=1
L-6: R=2,6-Et_2-4-MeC_6H_2, m=2, n=0
L-7: R=2,6-$Me_2C_6H_3$, m=2, n=0
L-8: R=2,6-^{i}Pr$_2$C$_6$H$_3$, m=2, n=1
L-9: R=2,6-*i*Pr$_2$C$_6$H$_3$, m=1, n=1

Entry	Ligand (1.2x mol%)	Yield (%)	*ee* (%)
1	**L-1**	84	84
2	**L-2**	33	66
3	**L-3**	44	31
4	**L-4**	63	83
5	**L-5**	48	80
6	**L-6**	44	26
7	**L-7**	NR	——
8	**L-8**	61	78
9	**L-9**	11	69

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **14a**, 1.0 equiv of $KHCO_3$, 10 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC in CH_3CN for 36 h.

2.3 Screening Details for the Tandem-Michael Reaction

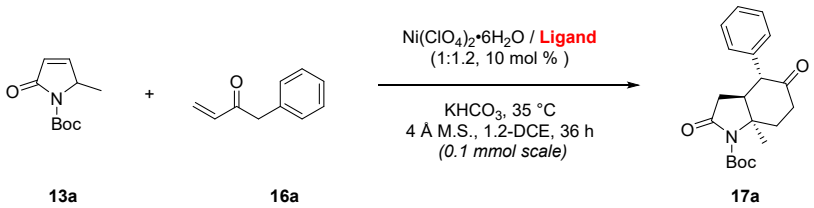
Table S6. The screening of solvents[a]



Entry	Solvent	Yield (%)	*ee* (%)
1	CH_3CN	71	65
2	DCM	68	36
3	CH_3Cl	56	72
4	1,2-DCE	50	82
5	THF	68	73
6	1,4-dioxane	32	54
7	EtOAc	47	82
8	Acetone	65	69

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **16a**, 1.0 equiv of $KHCO_3$, 10 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC for 36 h.

Table S7. The screening of *N, N'*-dioxide ligands[a]



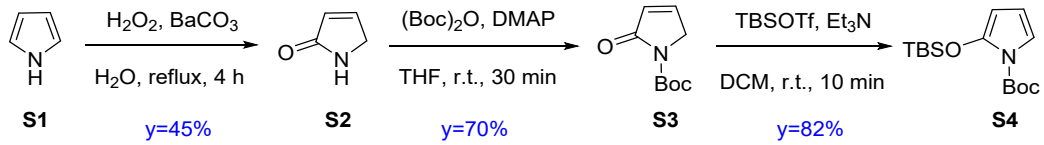
Entry	Ligand	Yield (%)	*ee* (%)
1	**L-1**	83	83
2	**L-2**	29	84
3	**L-3**	38	35
4	**L-4**	50	82
5	**L-5**	65	74
6	**L-6**	38	35
7	**L-7**	24	35
8	**L-8**	47	83
9	**L-9**	Trace	——

[a] Unless noted otherwise, reactions performed using 1.0 equiv of **13a** (0.1 mmol, 0.2 M), 1.2 equiv of **16a**, 1.0 equiv of $KHCO_3$, 10 mmol % catalyst, and 20 mg 4 A M.S. at 35 ºC in 1,2-DCE for 36 h.

3. Preparation of Substrates

3.1 Preparation of Unsaturated *N*-Boc-γ-lactam

The starting substrate **S4** was prepared from pyrrole **S1** following the reported literature[1] procedure in a three steps sequence:

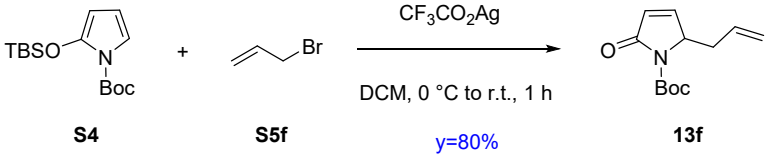


General procedure A (Preparation of **13a-13c**, **13e):**

The unsaturated *N*-Boc-γ-lactams **13a-13c**, **13e** were prepared from **S4** with the corresponding iodide **S5** by the following procedure:

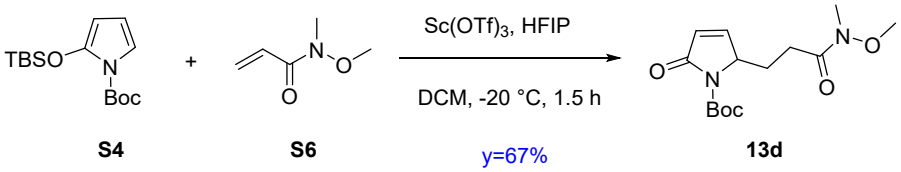
To a solution of **S4** (1.0 equiv.) in anhydrous CH_2Cl_2 (0.25 M) cooled to 0 ºC in an ice-bath, the corresponding iodide **S5** (1.5 equiv.) was added under argon atmosphere. After 10 min, CF_3CO_2Ag (1.5 equiv.) was added in one portion, and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. After reaction completion, the mixture was filtered through Celite® and washed with EtOAc. The filtrate was then concentrated under reduced pressure to give a residue which was purified by silica gel chromatography.

Preparation of **13f**:



Similar to general procedure A, **13f** was prepared from **S4** with allyl bromide **S5f** in 10.0 mmol scale. The crude residue was purified by silica gel chromatography (PE/EA=8/1) to afford the pure product as a brown oil (1.78 g, 80% yield).

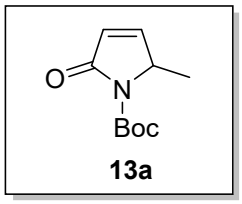
Preparation of **13d**:



[1] (a) Bocchi, V.; Chierici, L.; Gardini, G. P.; Mondelli, R. *Tetrahedron* **1970**, *26*, 4073-4082.
(b) Casiraghi, G.; Rassu, G.; Spanu, P.; Pinna, L. *J. Org. Chem.* **1992**, *57*, 3760-3763.

To a stirring solution of **S6** (1.38 g, 12.0 mmol) in anhydrous CH_2Cl_2 (40 mL) was sequentially added $Sc(OTf)_3$ (492 mg, 1.0 mmol) and HFIP (1,1,1,3,3,3-Hexafluoro-2-propanol, 5.2 mL, 50.0 mmol) at room temperature. The solution was cooled to -20 ºC under argon atmosphere and then a solution of **S4** (2.97 g, 10.0 mmol) in 10 mL of dry DCM was added slowly dropwise over 10 min via syringe. After being stirred at the same temperature for 1.5 h, the reaction was quenched with H_2O and extracted with DCM. The combined organic layers were washed with brine, dried, filtrated and concentrated. The residue was purified by silica gel chromatography (PE/EA=1/1) to give **13d** as a white solid (2.00 g, 67% yield).

***tert*-butyl 2-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13a)**



13a

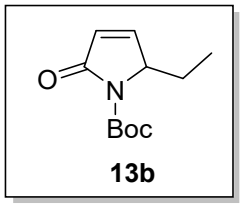
R_f = 0.5 (hexanes:EtOAc, 1:1), white solid (985 mg, 50% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.09 (dd, *J* = 6.1, 1.9 Hz, 1H), 6.06 (dd, *J* = 6.1, 1.5 Hz, 1H), 4.64 – 4.58 (m, 1H), 1.55 (s, 9H), 1.43 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.9, 151.7, 149.4, 125.9, 82.8, 58.4, 28.2, 18.1.

HRMS (ESI): $C_{10}H_{16}NO_3$ $[M+H]^+$ calcd: 198.1125, found: 198.1122.

***tert*-butyl 2-ethyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13b)**



13b

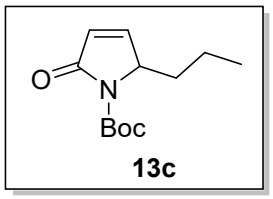
R_f = 0.3 (hexanes:EtOAc, 2:1), white solid (1.29 g, 61% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (dd, *J* = 6.1, 2.0 Hz, 1H), 6.08 (dd, *J* = 6.1, 1.7 Hz, 1H), 4.60 – 4.53 (m, 1H), 2.06 – 1.96 (m, 1H), 1.86 – 1.78 (m, 1H), 1.53 (s, 9H), 0.82 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.52, 150.2, 149.5, 126.8, 82.8, 63.1, 28.1, 24.3, 7.9.

HRMS (ESI): $C_{11}H_{18}NO_3$ $[M+H]^+$ calcd: 212.1281, found: 212.1276.

***tert*-butyl 2-oxo-5-propyl-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13c)**



13c

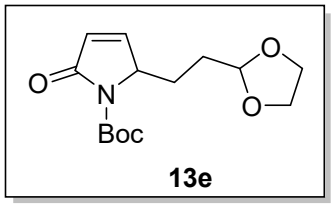
R_f = 0.3 (hexanes:EtOAc, 2:1), white solid (1.35 g, 60% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (dd, *J* = 6.1, 2.0 Hz, 1H), 6.09 (dd, *J* = 6.1, 1.7 Hz, 1H), 4.63 – 4.57 (m, 1H), 2.05 – 1.97 (m, 1H), 1.75 – 1.66 (m, 1H), 1.56 (s, 9H), 1.37 – 1.24 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.4, 150.5, 149.4, 126.5, 82.9, 62.3, 33.6, 28.2, 17.5, 14.1.

HRMS (ESI): $C_{12}H_{20}NO_3$ $[M+H]^+$ calcd: 226.1438, found: 226.1438.

***tert*-butyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13e)**



13e

R_f = 0.4 (hexanes:EtOAc, 2:1), yellow oil (1.75 g, 62% yield in 10.0 mmol scale).

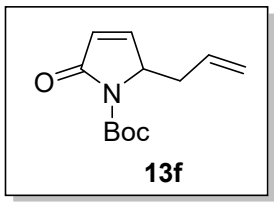
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.13 (d, *J* = 6.2 Hz, 1H), 6.07 (d, *J* = 5.7 Hz, 1H), 4.87 – 4.80 (m, 1H), 4.69 – 4.61 (m, 1H), 3.96 –

3.88 (m, 2H), 3.85 – 3.78 (m, 2H), 2.17 – 2.07 (m, 1H), 1.96 – 1.82 (m, 1H), 1.67 – 1.54 (m, 2H), 1.54 – 1.51 (m, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.3, 150.1, 149.3, 126.9, 103.7, 82.9, 65.0, 64.9, 61.8, 28.1, 25.5.

HRMS (ESI): $C_{14}H_{21}NNaO_5$ $[M+Na]^+$ calcd: 306.1312, found: 306.1307.

***tert*-butyl 2-allyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13f)**



13f

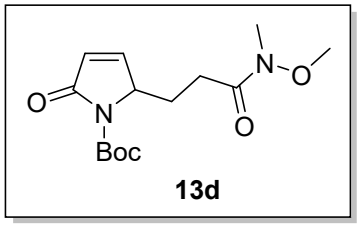
R_f = 0.3 (hexanes:EtOAc, 4:1), brown oil (1.78 g, 80% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (dd, *J* = 6.1, 2.1 Hz, 1H), 6.08 (dd, *J* = 6.3, 1.7 Hz, 1H), 5.69 – 5.55 (m, 1H), 5.16 – 5.04 (m, 2H), 4.66 – 4.57 (m, 1H), 2.81 – 2.73 (m, 1H), 2.51 – 2.42 (m, 1H), 1.55 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 150.0, 149.4, 131.1, 126.8, 119.6, 82.9, 61.7, 35.7, 28.1.

HRMS (ESI): $C_{12}H_{18}NO_3$ $[M+H]^+$ calcd: 224.1281, found: 224.1278.

***tert*-butyl 2-(3-(methoxy(methyl)amino)-3-oxopropyl)-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13d)**



13d

R_f = 0.1 (hexanes:EtOAc, 1:1), white solid (2.00 g, 67% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (dd, *J* = 6.0, 2.1 Hz, 1H), 6.07 (dd, *J* = 6.2, 1.8 Hz, 1H), 4.80 – 4.67 (m, 1H), 3.62 (s, 3H), 3.13 (s, 3H), 2.39 – 2.20 (m, 4H), 1.54 (s, 9H).

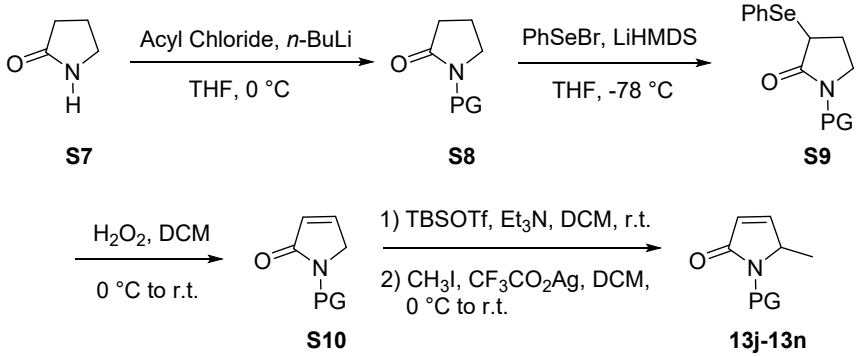
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.1, 169.3, 150.1, 149.4, 126.7, 83.1, 61.6, 61.3, 32.3, 28.1, 25.7, 25.7.

HRMS (ESI): $C_{14}H_{23}N_2O_5$ $[M+H]^+$ calcd: 299.1601, found: 299.1599.

3.2 Preparation of other unsaturated *N*-protecting-γ-lactam

General procedure B (Preparation of **13j-13n**)

The unsaturated *N*-protecting-γ-lactams **13j-13n** were prepared from pyrrolidone **S7** for four steps by the following procedure [2]:



S7 **S8** **S9** **S10** **13j-13n**

[2] Curti C, Ranieri B, Battistini L, et al. *Adv. Synth. Catal.* **2010**, *352*, 2011-2022.

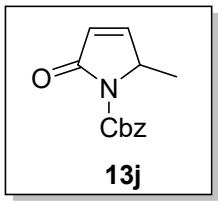
To a solution of **S7** (1.0 equiv.) in anhydrous THF (0.25 M), *n*-BuLi (1.1 equiv.) was added under argon atmosphere at 0 ºC. The resulting solution was stirred at the same temperature for 1 h, then the corresponding Acyl Chloride (1.1 equiv.) was added. The reaction mixture was stirred for 1 h, then allowed to warm to room temperature until reaction completion as monitored by TLC. The mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried, filtrated and concentrated. The crude material was purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **S8**.

To a solution of **S8** (1.0 equiv.) and PhSeBr (1.1 equiv.) in anhydrous THF (0.10 M), LiHMDS (1.1 equiv.) was added slowly dropwise over 10 min via syringe under argon atmosphere at -78 ºC. After being stirred for 1.5 h, the reaction was quenched with aqueous 1.0 M HCl at the same temperature and then warmed to room temperature extracted with EtOAc. The combined organic layers were washed with brine, dried, filtrated and concentrated. The crude material was purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **S9**.

30% aqueous H_2O_2 (4.0 equiv.) was added to a solution of **S9** (1.0 equiv.) in DCM (0.20 M) in an ice-bath. The resulting solution was stirred at room temperature for 1 h, then quenched with a saturated aqueous solution of $Na_2S_2O_3$ and extracted with DCM. The combined organic layers were washed with brine, dried, filtrated and concentrated. The crude material was purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **S10**.

To a solution of **S10** (1.0 equiv.) and Et_3N (1.2 equiv.) in anhydrous DCM (0.10 M), TBSOTf (1.05 equiv.) was added at 0 ºC in an ice-bath. After being stirred for 30 min, the reaction mixture was directly concentrated under reduced pressure and pumped for another 2 h on the vacuum pump. The crude silyl dienol ether product was directly used to the next step without further purification. To a solution of the resulting crude residue in anhydrous CH_2Cl_2 (0.25 M) cooled to 0 ºC in an ice-bath, CH_3I (2.0 equiv.) was added under argon atmosphere. After 10 min, CF_3CO_2Ag (2.0 equiv.) was added in one portion, and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. After reaction completion, the mixture was filtered through Celite® and washed with EtOAc. The filtrate was concentrated under reduced pressure to give a residue and then purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **13j-13n**.

benzyl 2-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13j)



13j

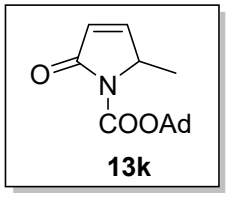
R_f = 0.3 (hexanes:EtOAc, 2:1), white solid (356 mg, 22% yield in 7.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 6.8 Hz, 2H), 7.36 (t, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.13 (dd, *J* = 6.1, 2.1 Hz, 1H), 6.06 (dd, *J* = 6.1, 1.7 Hz, 1H), 5.37 – 5.28 (m, 2H), 4.72 – 4.61 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.5, 152.4, 150.9, 135.4, 128.6, 128.3, 128.1, 125.7, 67.9, 58.5, 18.1.

HRMS (ESI): $C_{13}H_{14}NO_3$ $[M+H]^+$ calcd: 232.0968, found: 232.0968.

(3*r*)-adamantan-1-yl 2-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13k)

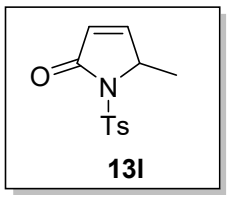


13k

R_f = 0.5 (hexanes:EtOAc, 2:1), white solid (701 mg, 51% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 (dd, *J* = 5.9, 1.9 Hz, 1H), 6.08 – 6.03 (m, 1H), 4.65 – 4.58 (m, 1H), 2.23 – 2.19 (m, 9H), 1.71 – 1.67 (m, 6H), 1.44 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 151.8, 148.9, 125.9, 82.9, 58.5, 41.4, 36.1, 31.0, 18.2.
HRMS (ESI): $C_{16}H_{21}NNaO_3$ $[M+Na]^+$ calcd: 298.1414, found: 298.1413.

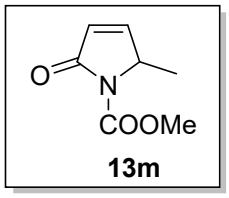
5-methyl-1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (13l)



13l

R_f = 0.6 (hexanes:EtOAc, 2:1), white solid (138 mg, 11% yield in 5.0 mmol scale).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 6.0, 2.1 Hz, 1H), 5.97 (dd, *J* = 6.0, 1.7 Hz, 1H), 4.87 (qt, *J* = 6.8, 1.8 Hz, 1H), 2.42 (s, 3H), 1.57 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.6, 153.2, 145.0, 136.2, 129.6, 128.0, 125.1, 60.5, 21.7, 19.1.
HRMS (ESI): $C_{12}H_{14}NO_3S$ $[M+H]^+$ calcd: 252.0689, found: 252.0691.

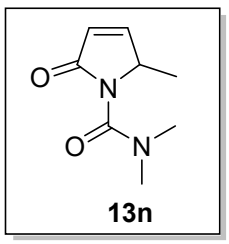
methyl 2-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (13m)



13m

R_f = 0.3 (hexanes:EtOAc, 1:1), white solid (240 mg, 31% yield in 5.0 mmol scale).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (dd, *J* = 6.1, 2.0 Hz, 1H), 6.06 (dd, *J* = 6.0, 1.7 Hz, 1H), 4.67 (qt, *J* = 6.8, 1.9 Hz, 1H), 3.89 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.6, 152.6, 151.7, 125.7, 58.6, 53.5, 18.0.
HRMS (ESI): $C_7H_{10}NO_3$ $[M+H]^+$ calcd: 156.0655, found: 156.0658.

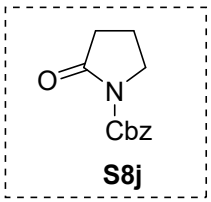
***N,N*,2-trimethyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxamide (13n)**



13n

R_f = 0.1 (hexanes:EtOAc, 1:1), white solid (294 mg, 35% yield in 5.0 mmol scale).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (dd, *J* = 5.9, 1.8 Hz, 1H), 5.96 (dd, *J* = 5.9, 1.8 Hz, 1H), 4.93 (qt, *J* = 7.0, 1.8 Hz, 1H), 3.01 (s, 6H), 1.30 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.2, 153.4, 152.0, 125.2, 58.3, 38.6, 36.9, 17.3.
HRMS (ESI): $C_8H_{13}N_2O_2$ $[M+H]^+$ calcd: 169.0972, found: 169.0969.

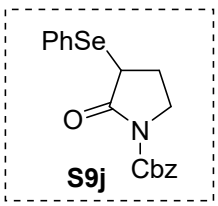
benzyl 2-oxopyrrolidine-1-carboxylate (S8j)



S8j

R_f = 0.5 (hexanes:EtOAc, 1:1), white solid (6.13 g, 56% yield in 50.0 mmol scale).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 6.7 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.27 (s, 2H), 3.80 (t, *J* = 7.2 Hz, 2H), 2.57 – 2.45 (m, 2H), 2.07 – 1.95 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 151.5, 135.4, 128.6, 128.4, 128.2, 68.0, 46.4, 32.8, 17.6.
HRMS (ESI): $C_{12}H_{14}NO_3$ $[M+H]^+$ calcd: 220.0968, found: 220.0965.

benzyl 2-oxo-3-(phenylselanyl)pyrrolidine-1-carboxylate (S9j)



S9j

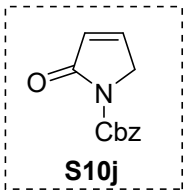
R_f = 0.3 (hexanes:EtOAc, 4:1), yellow oil (4.21 g, 45% yield in 25.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.30 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.25 (s, 2H), 3.96 – 3.90 (m, 1H), 3.71 – 3.65 (m, 1H), 3.50 – 3.44 (m, 1H), 2.52 – 2.43 (m, 1H), 2.11 – 2.04 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.3, 151.4, 135.9, 135.3, 129.3, 129.0, 128.6, 128.4, 128.2, 126.7, 68.1, 44.8, 41.6, 26.1.

HRMS (ESI): $C_{18}H_{18}NO_3Se$ $[M+H]^+$ calcd: 376.0446, found: 376.0449.

benzyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (S10j)



S10j

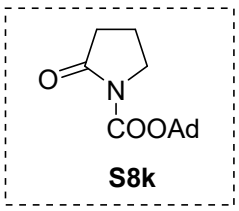
R_f = 0.2 (hexanes:EtOAc, 2:1), white solid (1.87 g, 86% yield in 10.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 6.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.23 (dt, *J* = 6.2, 2.1 Hz, 1H), 6.18 (dt, *J* = 6.1, 2.0 Hz, 1H), 5.33 (s, 2H), 4.41 (t, *J* = 2.1 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.7, 150.9, 145.7, 135.3, 128.6, 128.5, 128.3, 127.7, 68.1, 51.6.

HRMS (ESI): $C_{12}H_{12}NO_3$ $[M+H]^+$ calcd: 218.0812, found: 218.0809.

(3*r*)-adamantan-1-yl 2-oxopyrrolidine-1-carboxylate (S8k)



S8k

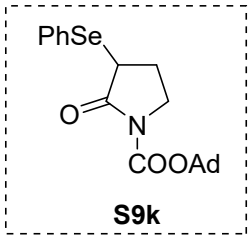
R_f = 0.3 (hexanes:EtOAc, 2:1), white solid (9.07 g, 69% yield in 50.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.77 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 8.1 Hz, 2H), 2.25 – 2.17 (m, 9H), 2.06 – 1.97 (m, 2H), 1.73 – 1.67 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.3, 149.8, 82.7, 46.5, 41.3, 36.1, 33.0, 31.0, 17.4.

HRMS (ESI): $C_{15}H_{22}NO_3$ $[M+H]^+$ calcd: 264.1594, found: 264.1588.

(3*r*)-adamantan-1-yl 2-oxo-3-(phenylselanyl)pyrrolidine-1-carboxylate (S9k)



S9k

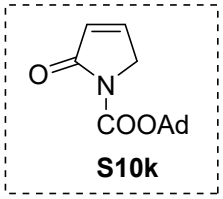
R_f = 0.5 (hexanes:EtOAc, 3:1), colorless oil (15.88 g, 76% yield in 30.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.35 (t, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 3.96 – 3.91 (m, 1H), 3.64 – 3.58 (m, 1H), 3.45 – 3.39 (m, 1H), 2.50 – 2.40 (m, 1H), 2.21 – 2.17 (m, 2H), 2.16 – 2.13 (m, 6H), 2.11 – 2.00 (m, 2H), 1.68 – 1.64 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 149.5, 135.8, 129.2, 128.8, 127.0, 83.0, 44.8, 42.1, 41.3, 36.1, 31.0, 26.1.

HRMS (ESI): $C_{21}H_{26}NO_3Se$ $[M+H]^+$ calcd: 420.1072, found: 420.1069.

(3*r*)-adamantan-1-yl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (S10k)



S10k

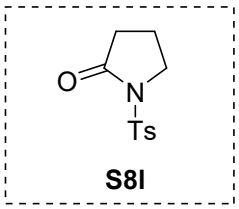
R_f = 0.2 (hexanes:EtOAc, 2:1), white solid (4.70 g, 90% yield in 20.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (dt, *J* = 6.2 Hz, 1H), 6.15 (dt, *J* = 6.2 Hz, 1H), 4.36 – 4.33 (m, 2H), 2.23 – 2.19 (m, 9H), 1.70 – 1.66 (m, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 149.1, 145.1, 128.0, 82.9, 51.7, 41.4, 36.1, 31.0.

HRMS (ESI): $C_{15}H_{20}NO_3$ $[M+H]^+$ calcd: 262.1438, found: 262.1435.

1-tosylpyrrolidin-2-one (S8l)



S8l

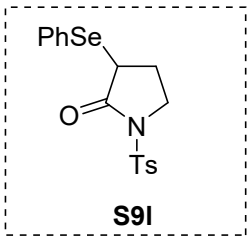
R_f = 0.1 (hexanes:EtOAc, 4:1), white solid (9.44 g, 79% yield in 50.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.88 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.42 – 2.38 (m, 2H), 2.06 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.4, 145.2, 135.2, 129.7, 128.1, 47.3, 32.3, 21.7, 18.2.

HRMS (ESI): $C_{11}H_{14}NO_3S$ $[M+H]^+$ calcd: 240.0689, found: 240.0690.

3-(phenylselanyl)-1-tosylpyrrolidin-2-one (S9l)



S9l

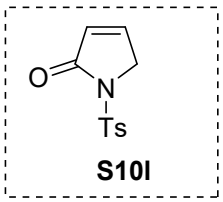
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (4.49 g, 38% yield in 30.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 6.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 3.85 – 3.78 (m, 2H), 3.61 – 3.53 (m, 1H), 2.54 – 2.47 (m, 1H), 2.46 (s, 3H), 2.08 – 2.01 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.6, 145.3, 136.1, 134.8, 129.7, 129.3, 129.1, 128.3, 126.1, 45.7, 40.7, 26.3, 21.8.

HRMS (ESI): $C_{17}H_{18}NO_3SSe$ $[M+H]^+$ calcd: 396.0167, found: 396.0160.

1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (S10l)



S10l

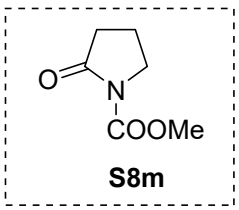
R_f = 0.3 (hexanes:EtOAc, 2:1), white solid (4.46 g, 94% yield in 20.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 (dt, *J* = 6.1, 2.0 Hz, 1H), 6.05 (dt, *J* = 6.1, 2.0 Hz, 1H), 4.48 (t, *J* = 2.1 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 146.6, 145.2, 135.3, 129.8, 128.0, 127.1, 52.4, 21.7.

HRMS (ESI): $C_{11}H_{12}NO_3S$ $[M+H]^+$ calcd: 238.0532, found: 238.0529.

methyl 2-oxopyrrolidine-1-carboxylate (S8m)



S8m

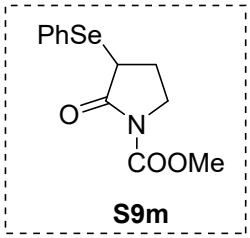
R_f = 0.3 (hexanes:EtOAc, 1:1), white solid (4.08 g, 57% yield in 50.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.83 – 3.79 (m, 3H), 3.77 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 2.01 (p, *J* = 7.9 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 152.3, 53.5, 46.5, 32.8, 17.6.

HRMS (ESI): $C_6H_{10}NO_3$ $[M+H]^+$ calcd: 144.0655, found: 144.0658.

methyl 2-oxo-3-(phenylselanyl)pyrrolidine-1-carboxylate (S9m)



S9m

R_f = 0.1 (hexanes:EtOAc, 4:1), colorless oil (4.29 g, 48% yield in 30.0 mmol scale).

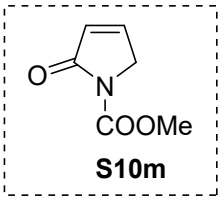
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 6.8 Hz, 2H), 3.96 – 3.87 (m, 1H), 3.78 (s, 3H), 3.68

– 3.62 (m, 1H), 3.51 – 3.44 (m, 1H), 2.48 – 2.39 (m, 1H), 2.07 – 1.99 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.3, 152.1, 135.9, 135.8, 129.3, 129.0, 126.8, 53.6, 44.8, 41.6, 26.0.

HRMS (ESI): $C_{12}H_{14}NO_3Se$ $[M+H]^+$ calcd: 300.0133, found: 300.0130.

methyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (S10m)



S10m

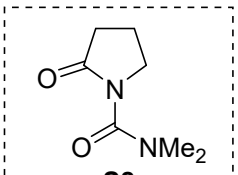
R_f = 0.1 (hexanes:EtOAc, 1:1), white solid (1.47 g, 52% yield in 20.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 6.1 Hz, 1H), 6.18 (d, *J* = 6.1 Hz, 1H), 4.41 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.6, 151.7, 145.8, 127.7, 53.6, 51.6.

HRMS (ESI): $C_6H_8NO_3$ $[M+H]^+$ calcd: 142.0499, found: 142.0503.

***N,N*-dimethyl-2-oxopyrrolidine-1-carboxamide (S8n)**



S8n

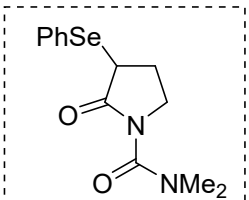
R_f = 0.1 (hexanes:EtOAc, 1:1), white solid (3.35 g, 43% yield in 50.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.70 (t, *J* = 7.0 Hz, 2H), 2.96 (s, 6H), 2.42 (t, *J* = 8.0 Hz, 2H), 2.04 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.3, 154.7, 46.9, 38.4, 36.7, 32.1, 18.5.

HRMS (ESI): $C_7H_{13}N_2O_2$ $[M+H]^+$ calcd: 157.0972, found: 157.0976.

***N,N*-dimethyl-2-oxo-3-(phenylselanyl)pyrrolidine-1-carboxamide (S9n)**



S9n

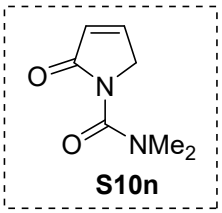
R_f = 0.3 (hexanes:EtOAc, 1:1), yellow solid (7.09 g, 76% yield in 30.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.36 – 7.27 (m, 3H), 3.94 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.62 – 3.55 (m, 1H), 2.94 (s, 6H), 2.59 – 2.48 (m, 1H), 2.17 – 2.07 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 154.3, 135.7, 129.3, 128.7, 127.2, 45.2, 41.4, 38.5, 37.0, 26.9.

HRMS (ESI): $C_{13}H_{17}N_2O_2Se$ $[M+H]^+$ calcd: 313.0450, found: 313.0453.

***N,N*-dimethyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxamide (S10n)**



S10n

R_f = 0.1 (hexanes:EtOAc, 1:1), white solid (2.65 g, 86% yield in 20.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (dt, *J* = 5.9, 1.4 Hz, 1H), 6.06 (dt, *J* = 6.0, 2.0 Hz, 1H), 4.45 (t, *J* = 1.9 Hz, 2H), 3.02 (s, 6H).

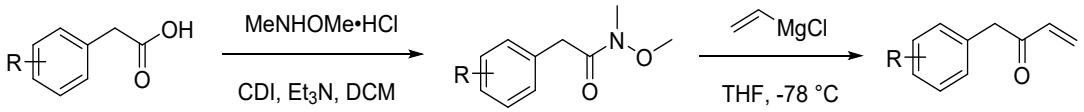
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 154.0, 146.4, 126.6, 51.9, 38.3, 37.7.

HRMS (ESI): $C_7H_{11}N_2O_2$ $[M+H]^+$ calcd: 155.0815, found: 155.0811.

3.3 Preparation of benzyl vinyl ketones

General procedure C (Preparation of **16**)

The benzyl vinyl ketones **16** were prepared from phenylacetic acid **S11** for two steps by the following procedure:

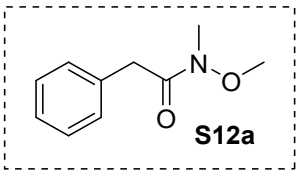


S11 **S12** **16**

A solution of **S11** (1.0 equiv.) in CH_2Cl_2 (0.25 M) was cooled to 0 ºC and treated with CDI (1.1 equiv.). After being stirred for 30 min, *N,O*-dimethylhydroxylamine hydrochloride (1.2 equiv.) and TEA (3.2 equiv.) were added subsequently and the mixture was stirred overnight at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried, filtrated and concentrated. The crude material was purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **S12**.

To a solution of **S12** (1.0 equiv.) in anhydrous THF (0.25 M), vinylmagnesium chloride (1.5 equiv.) was added slowly via syringe under argon atmosphere at -78 ºC. After being stirred overnight, the reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried, filtrated and concentrated. The crude material was purified by silica gel chromatography eluted with petroleum ether/EtOAc to afford product **16**.

***N*-methoxy-*N*-methyl-2-phenylacetamide (S12a)**



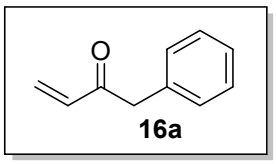
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (797 mg, 89% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 3.77 (s, 2H), 3.60 (s, 3H), 3.19 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.0, 129.3, 128.5, 126.8, 61.3, 39.4, 32.3.

HRMS (ESI): $C_{10}H_{14}NO_2$ $[M+H]^+$ calcd: 180.1019, found: 180.1015.

1-phenylbut-3-en-2-one (16a)



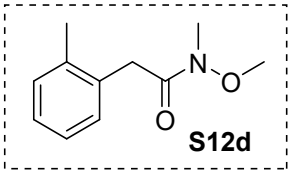
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (225 mg, 77% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 6.9 Hz, 2H), 6.43 – 6.35 (m, 1H), 6.28 (d, *J* = 16.3 Hz, 1H), 5.79 (d, *J* = 10.4 Hz, 1H), 3.85 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.7, 135.7, 134.1, 129.5, 129.0, 128.8, 127.0, 47.2.

HRMS (ESI): $C_{10}H_{11}O$ $[M+H]^+$ calcd: 147.0804, found: 147.0801.

***N*-methoxy-*N*-methyl-2-(*o*-tolyl)acetamide (S12d)**



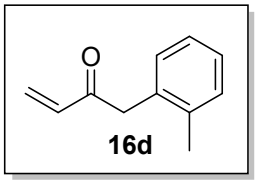
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (907 mg, 94% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 4H), 3.78 (s, 2H), 3.61 (s, 3H), 3.21 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.6, 136.8, 133.6, 130.2, 129.9, 127.0, 126.0, 61.2, 37.2, 32.4, 19.7.

HRMS (ESI): $C_{11}H_{16}NO_2$ $[M+H]^+$ calcd: 194.1176, found: 194.1175.

1-(*o*-tolyl)but-3-en-2-one (16d)



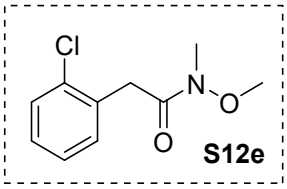
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (179 mg, 56% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 – 7.08 (m, 4H), 6.48 – 6.37 (m, 1H), 6.31 (d, *J* = 17.4 Hz, 1H), 5.79 (d, *J* = 9.1 Hz, 1H), 3.87 (s, 2H), 2.23 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.6, 137.0, 135.4, 132.9, 130.5, 130.5, 128.6, 127.4, 126.2, 45.6, 19.7.

HRMS (ESI): $C_{11}H_{13}NO$ $[M+H]^+$ calcd: 161.0961, found: 161.0959.

2-(2-chlorophenyl)-*N*-methoxy-*N*-methylacetamide (S12e)



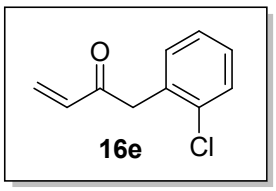
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (1.05 g, 98% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 3.91 (s, 2H), 3.69 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.4, 134.4, 133.2, 131.4, 129.4, 128.4, 126.9, 61.4, 37.0, 32.4.

HRMS (ESI): $C_{10}H_{13}ClNO_2$ $[M+H]^+$ calcd: 214.0629, found: 214.0629.

1-(2-chlorophenyl)but-3-en-2-one (16e)



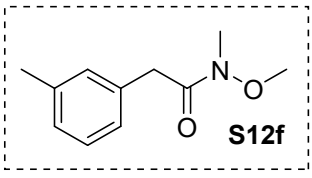
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (170 mg, 47% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 1H), 7.25 – 7.19 (m, 3H), 6.50 – 6.39 (m, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 5.86 (d, *J* = 10.4 Hz, 1H), 4.03 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.5, 135.6, 134.5, 132.7, 131.7, 129.6, 129.0, 128.7, 127.0, 44.7.

HRMS (ESI): $C_{10}H_{10}ClO$ $[M+H]^+$ calcd:181.0415, found: 181.0409.

***N*-methoxy-*N*-methyl-2-(*m*-tolyl)acetamide (S12f)**



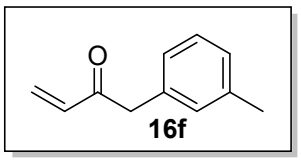
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (753 mg, 78% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 7.10 – 7.03 (m, 2H), 3.74 (s, 2H), 3.61 (s, 3H), 3.19 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.6, 138.1, 134.8, 130.0, 128.4, 127.6, 126.4, 61.3, 39.3, 32.3, 21.4.

HRMS (ESI): $C_{11}H_{16}NO_2$ $[M+H]^+$ calcd: 194.1176, found: 194.1177.

1-(*m*-tolyl)but-3-en-2-one (16f)



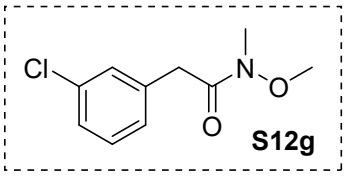
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (227 mg, 71% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.45 – 6.38 (m, 1H), 6.31 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.82 (dd, *J* = 10.4, 1.3 Hz, 1H), 3.84 (s, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.9, 138.4, 135.6, 134.0, 130.2, 129.0, 128.7, 127.8, 126.5, 47.2, 21.4.

HRMS (ESI): $C_{11}H_{13}O$ $[M+H]^+$ calcd: 161.0961, found: 161.0957.

2-(3-chlorophenyl)-*N*-methoxy-*N*-methylacetamide (S12g)



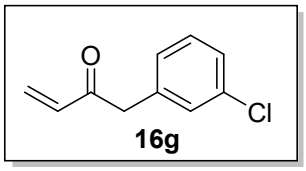
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (931 mg, 87% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 6.8 Hz, 1H), 3.74 (s, 2H), 3.63 (s, 3H), 3.19 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.6, 136.9, 134.2, 129.7, 129.5, 127.6, 127.0, 61.4, 38.9, 32.3.

HRMS (ESI): $C_{10}H_{13}ClNO_2$ $[M+H]^+$ calcd: 214.0629, found: 214.0628.

1-(3-chlorophenyl)but-3-en-2-one (16g)



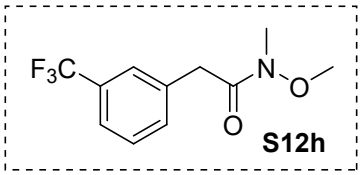
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (206 mg, 57% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 – 7.24 (m, 2H), 7.21 (s, 1H), 7.11 – 7.07 (m, 1H), 6.45 – 6.36 (m, 1H), 6.31 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.87 (dd, *J* = 10.2 Hz, 1H), 3.85 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.9, 135.9, 135.6, 134.5, 129.9, 129.7, 129.4, 127.7, 127.3, 46.4.

HRMS (ESI): $C_{10}H_{10}ClO$ $[M+H]^+$ calcd: 181.0415, found: 181.0411.

***N*-methoxy-*N*-methyl-2-(3-(trifluoromethyl)phenyl)acetamide (S12h)**



R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (1.12 g, 91% yield in 5.0 mmol scale).

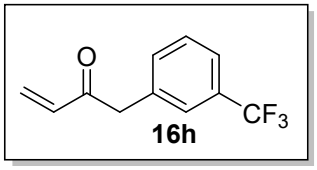
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 7.50 (t, *J* = 8.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 3.82 (s, 2H), 3.65 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.5, 135.8, 132.9, 130.8 (q, *J* = 31.8 Hz), 128.9, 126.3 (q, *J* = 4.0 Hz), 124.1 (q, *J* = 270.6 Hz), 123.7 (q, *J* = 4.3 Hz), 61.3, 39.0, 32.3.

HRMS (ESI): $C_{11}H_{13}F_3NO_2$ $[M+H]^+$ calcd:248.0893, found: 248.0892.

1-(3-(trifluoromethyl)phenyl)but-3-en-2-one (16h)

R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (244 mg, 57% yield in 2.0 mmol scale).

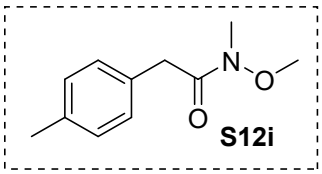


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 6.47 – 6.38 (m, 1H), 6.33 (d, *J* = 17.5 Hz, 1H), 5.89 (d, *J* = 10.3 Hz, 1H), 3.95 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 196.7, 135.7, 134.9, 133.0, 131.1 (q, *J* = 31.1 Hz), 129.4, 129.1, 126.3 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 270.6 Hz), 123.9 (q, *J* = 3.9 Hz), 46.4.

HRMS (ESI): $C_{11}H_9F_3NaO$ $[M+Na]^+$ calcd: 237.0498, found: 237.0497.

***N*-methoxy-*N*-methyl-2-(*p*-tolyl)acetamide (S12i)**



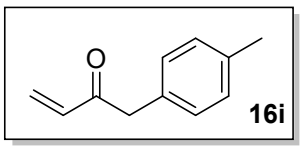
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (917 mg, 95% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.72 (s, 2H), 3.59 (s, 3H), 3.17 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.6, 136.3, 131.9, 129.2, 129.2, 61.3, 39.0, 32.3, 21.1.

HRMS (ESI): $C_{11}H_{16}NO_2$ $[M+H]^+$ calcd: 194.1176, found: 194.1179.

1-(*p*-tolyl)but-3-en-2-one (16i)



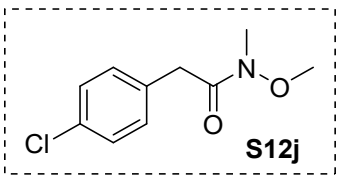
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (189 mg, 59% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.45 – 6.35 (m, 1H), 6.29 (d, *J* = 17.5 Hz, 1H), 5.80 (d, *J* = 10.3 Hz, 1H), 3.83 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.9, 136.7, 135.6, 131.0, 129.5, 129.4, 128.9, 46.9, 21.1.

HRMS (ESI): $C_{11}H_{13}O$ $[M+H]^+$ calcd: 161.0961, found: 161.0958.

2-(4-chlorophenyl)-*N*-methoxy-*N*-methylacetamide (S12j)



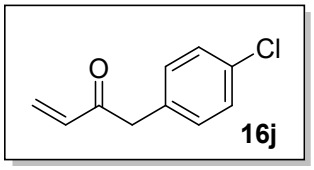
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (995 mg, 93% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 3.73 (s, 2H), 3.63 (s, 3H), 3.19 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.9, 133.4, 132.7, 130.7, 128.6, 61.3, 38.6, 32.3.

HRMS (ESI): $C_{10}H_{13}ClNO_2$ $[M+H]^+$ calcd: 214.0629, found: 214.0625.

1-(4-chlorophenyl)but-3-en-2-one (16j)



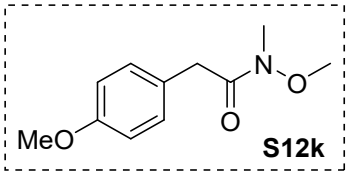
R_f = 0.2 (hexanes:EtOAc, 20:1), white solid (188 mg, 52% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.49 – 6.36 (m, 1H), 6.30 (d, *J* = 17.5 Hz, 1H), 5.85 (d, *J* = 10.5 Hz, 1H), 3.85 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.1, 135.6, 133.0, 132.5, 130.9, 129.2, 128.9, 46.2.

HRMS (ESI): $C_{10}H_{10}ClO$ $[M+H]^+$ calcd: 181.0415, found: 181.0413.

***N*-methoxy-2-(4-methoxyphenyl)-*N*-methylacetamide (S12k)**



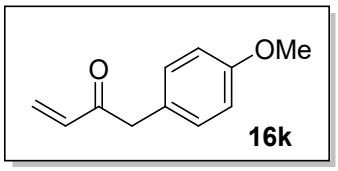
R_f = 0.2 (hexanes:EtOAc, 2:1), colorless oil (993 mg, 95% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.71 (s, 2H), 3.61 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.8, 158.5, 130.3, 127.0, 114.0, 61.3, 55.3, 38.5, 32.3.

HRMS (ESI): $C_{11}H_{16}NO_3$ $[M+H]^+$ calcd: 210.1125, found: 210.1127.

1-(4-methoxyphenyl)but-3-en-2-one (16k)



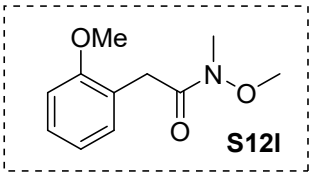
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (225 mg, 64% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.44 – 6.35 (m, 1H), 6.33 – 6.26 (m, 1H), 5.81 (dd, *J* = 10.3, 1.3 Hz, 1H), 3.81 (s, 2H), 3.78 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.1, 158.7, 135.6, 130.5, 128.9, 126.0, 114.2, 55.3, 46.4.

HRMS (ESI): $C_{11}H_{13}O_2$ $[M+H]^+$ calcd: 177.0910, found: 177.0907.

***N*-methoxy-2-(2-methoxyphenyl)-*N*-methylacetamide (S12l)**



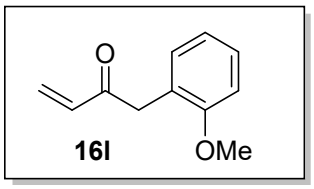
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (972 mg, 93% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.17 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 2H), 3.66 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.4, 130.9, 128.2, 123.8, 120.6, 110.5, 61.2, 55.5, 33.5.

HRMS (ESI): $C_{11}H_{16}NO_3$ $[M+H]^+$ calcd: 210.1125, found: 210.1122.

1-(2-methoxyphenyl)but-3-en-2-one (16l)



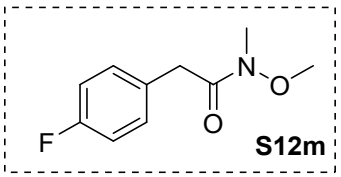
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (162 mg, 46% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.46 – 6.36 (m, 1H), 6.34 – 6.26 (m, 1H), 5.76 (d, *J* = 10.1 Hz, 1H), 3.85 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.1, 157.4, 135.7, 131.1, 128.5, 128.2, 123.3, 120.7, 110.6, 55.4, 41.8.

HRMS (ESI): $C_{11}H_{13}O_2$ $[M+H]^+$ calcd: 177.0910, found: 177.0905.

2-(4-fluorophenyl)-N-methoxy-N-methylacetamide (S12m)



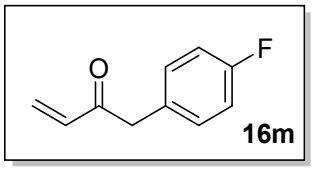
R_f = 0.2 (hexanes:EtOAc, 4:1), colorless oil (896 mg, 91% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (t, *J* = 7.2 Hz, 2H), 6.99 (t, 2H), 3.73 (s, 2H), 3.63 (s, 3H), 3.18 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 162.8, 160.9, 130.9, 130.8, 115.4, 115.2, 61.3, 38.4, 32.3.

HRMS (ESI): $C_{10}H_{13}FNO_2$ $[M+H]^+$ calcd: 198.0925, found: 198.0924.

1-(4-fluorophenyl)but-3-en-2-one (16m)



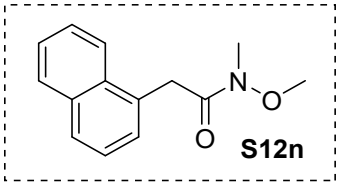
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (180 mg, 55% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.13 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.41 (dd, *J* = 17.6, 10.4 Hz, 1H), 6.31 (dd, *J* = 17.6, 1.3 Hz, 1H), 5.85 (dd, *J* = 10.4, 1.3 Hz, 1H), 3.85 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.4, 163.0, 161.0, 135.6, 131.0, 131.0, 129.0, 115.7, 115.5, 46.1.

HRMS (ESI): $C_{10}H_{10}FO$ $[M+H]^+$ calcd: 165.0710, found: 165.0711.

***N*-methoxy-*N*-methyl-2-(naphthalen-1-yl)acetamide (S12n)**



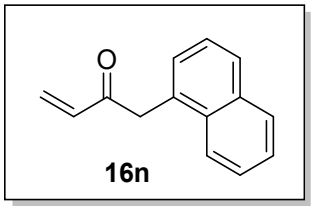
R_f = 0.2 (hexanes:EtOAc, 20:1), colorless oil (1.12 g, 98% yield in 5.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.46 – 7.40 (m, 2H), 4.23 (s, 2H), 3.61 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 133.9, 132.4, 131.4, 128.7, 127.7, 126.2, 125.7, 125.4, 124.0, 61.4, 37.1.

HRMS (ESI): $C_{14}H_{16}NO_2$ $[M+H]^+$ calcd: 230.1176, found: 230.1173.

1-(naphthalen-1-yl)but-3-en-2-one (16n)



R_f = 0.8 (hexanes:EtOAc, 20:1), colorless oil (172 mg, 44% yield in 2.0 mmol scale).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.84 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 1H), 6.47 (dd, *J* = 17.5, 10.4 Hz, 1H), 6.36 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.76 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.30 (s, 2H).

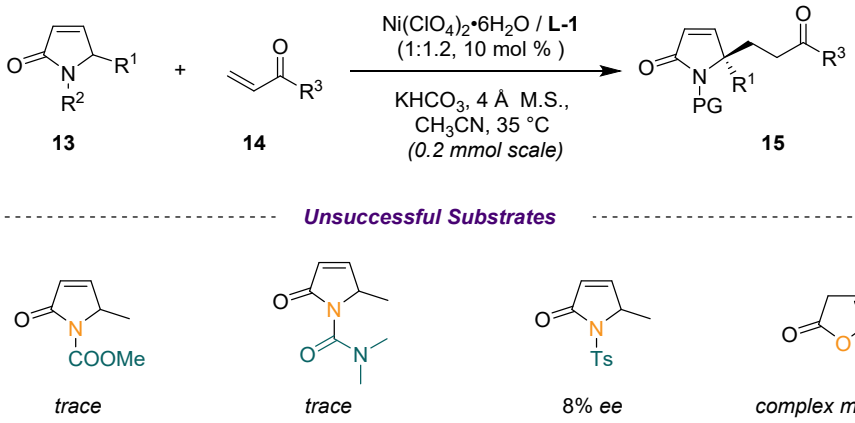
^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.7, 134.9, 134.0, 132.3, 130.7, 128.9, 128.8, 128.3, 128.1, 126.5, 125.9, 125.5, 123.9, 45.7.

HRMS (ESI): $C_{14}H_{13}O$ $[M+H]^+$ calcd: 197.0961, found: 197.0966.

4. Substrate Scope of the Michael Addition Reaction

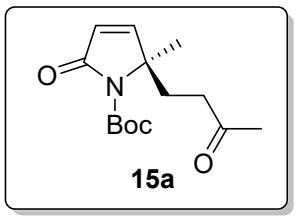
4.1 Preparation of 15

General procedure: $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 10 mmol%, 0.02 mmol), **L-1** (13.6 mg, 12 mmol%, 0.024 mmol), $KHCO_3$ (20.0 mg, 0.2 mmol), and 4Å molecular sieves (20.0 mg) were stirred in anhydrous CH_3CN (0.2 M) under argon atmosphere at 35 °C for 1 hour. Then a mixture of *α*, *β*-unsaturated *γ*-butyrolactam **13** (0.2 mmol) and *α*, *β*-unsaturated ketones **14** (0.24mmol) in the acetonitrile was added to the above solution. The mixture was stirred at 35 °C until TLC showed the staring material was no longer consumed. The reaction mixture was filtered through Celite® and washed with EtOAc. The filtrate was then concentrated under reduced pressure to give a residue which was purified by silica gel chromatography to afford the addition product **15**.



Scheme S1. Unsuccessful substrates for the Michael addition reactions.

***tert*-butyl 2-methyl-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15a)**



R_f = 0.3 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -10.99 (*c* = 0.335, $CHCl_3$).

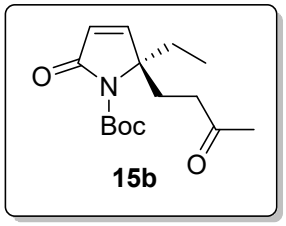
HPLC analysis: 84% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 12.00 min, t_r(minor) = 11.15 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.89 (d, *J* = 6.1 Hz, 1H), 6.01 (d, *J* = 6.0 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.25 – 2.17 (m, 1H), 2.13 – 2.08 (m, 1H), 2.07 (s, 3H), 2.06 – 1.99 (m, 1H), 1.55 (s, 9H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.0, 169.5, 156.1, 149.3, 124.7, 83.1, 67.8, 37.4, 30.1, 29.2, 28.2, 23.9.

HRMS (ESI): $C_{14}H_{21}NNaO_4$ $[M+Na]^+$ calcd: 290.1363, found: 290.1358.

***tert*-butyl 2-ethyl-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15b)**



R_f = 0.3 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -4.88 (*c* = 0.355, $CHCl_3$).

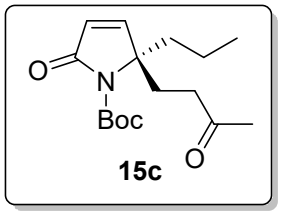
HPLC analysis: 75% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 0.4 mL/min, λ = 214 nm; Major isomer: t_r(major) = 24.14 min, t_r(minor) = 25.67 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.79 (d, *J* = 6.1 Hz, 1H), 6.09 (d, *J* = 6.1 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.28 – 2.20 (m, 2H), 2.18 – 2.09 (m, 2H), 2.08 (s, 3H), 1.83 – 1.75 (m, 1H), 1.55 (s, 9H), 0.70 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.3, 170.1, 154.7, 149.3, 126.0, 83.1, 71.4, 37.1, 30.2, 29.1, 28.8, 28.2, 7.4.

HRMS (ESI): $C_{15}H_{23}NNaO_4$ $[M+Na]^+$ calcd: 304.1519, found: 304.1512.

***tert*-butyl 5-oxo-2-(3-oxobutyl)-2-propyl-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15c)**



R_f = 0.3 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -15.03 (*c* = 0.173, $CHCl_3$).

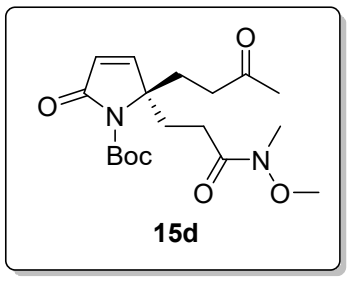
HPLC analysis: 73% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 90/10, flow rate = 0.6 mL/min, λ = 214 nm; Major isomer: t_r(major) = 14.47 min, t_r(minor) = 15.75 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.81 (d, *J* = 6.1 Hz, 1H), 6.05 (d, *J* = 6.0 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.25 – 2.14 (m, 2H), 2.14 – 2.06 (m, 2H), 2.06 (s, 3H), 1.74 – 1.67 (m, 1H), 1.53 (s, 9H), 1.10 – 1.02 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.3, 170.1, 155.0, 149.3, 125.6, 83.1, 71.1, 38.4, 37.0, 30.2, 29.0, 28.2, 16.5, 14.0.

HRMS (ESI): $C_{16}H_{25}NNaO_4$ $[M+Na]^+$ calcd: 318.1676, found: 318.1674.

***tert*-butyl 2-(3-(methoxy(methyl)amino)-3-oxopropyl)-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15d)**



R_f = 0.2 (hexanes:EtOAc, 0:1), white solid.

$[\alpha]_D^{20}$ = +11.65 (*c* = 0.105, $CHCl_3$).

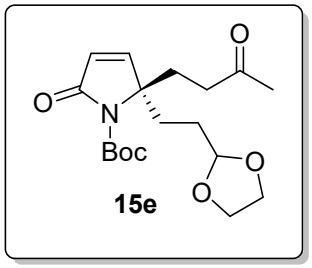
HPLC analysis: 68% ee, Chiralpak AD-H, Hexane/*i*-PrOH/MeOH = 90/05/05, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 24.94 min, t_r(minor) = 28.89 min. The enantiomeric excess can be enhanced to >99% by recrystallization from 10% EtOAc in *n*-hexane.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.83 (d, *J* = 6.1 Hz, 1H), 6.04 (d, *J* = 6.1 Hz, 1H), 3.57 (s, 3H), 3.09 (s, 3H), 2.57 – 2.44 (m, 2H), 2.23 – 2.05 (m, 6H), 2.04 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.9, 173.0, 170.0, 154.7, 149.2, 125.7, 83.5, 70.6, 61.3, 37.0, 32.2, 30.4, 30.1, 29.2, 28.1, 25.5.

HRMS (ESI): $C_{18}H_{28}N_2NaO_6$ $[M+Na]^+$ calcd: 391.1840, found: 391.1838.

***tert*-butyl 2-(2-(1,3-dioxolan-2-yl)ethyl)-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15e)**



R_f = 0.2 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -0.44 (*c* = 0.450, $CHCl_3$).

HPLC analysis: 71% ee, Chiralpak AD-H, Hexane/*i*-PrOH = 85/15, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 18.55 min, t_r(minor) = 15.84 min.

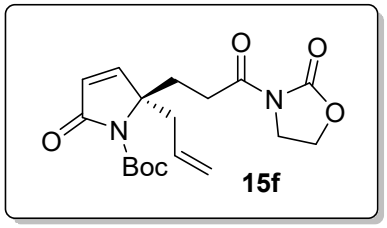
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.80 (d, *J* = 6.1 Hz, 1H), 6.07 (d, *J* = 6.0 Hz, 1H), 4.80 (t, *J* = 4.4 Hz, 1H), 3.94 – 3.87 (m, 2H), 3.83 –

3.78 (m, 2H), 2.52 – 2.44 (m, 1H), 2.42 – 2.34 (m, 1H), 2.25 – 2.18 (m, 1H), 2.16 – 2.07 (m, 2H), 2.06 (s, 3H), 1.87 – 1.81 (m, 1H), 1.54 (s, 9H), 1.43 – 1.33 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.0, 169.8, 154.5, 149.1, 126.0, 103.5, 83.3, 70.5, 65.0, 37.0, 30.2, 29.8, 29.1, 28.1, 27.6.

HRMS (ESI): $C_{18}H_{27}NNaO_6$ $[M+Na]^+$ calcd: 376.1731, found: 376.1726.

***tert*-butyl 2-allyl-5-oxo-2-(3-oxo-3-(2-oxooxazolidin-3-yl)propyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15f)**



15f

R_f = 0.1 (hexanes:EtOAc, 2:1), white solid.

$[\alpha]_D^{20}$ = -16.50 (*c* = 0.208, $CHCl_3$).

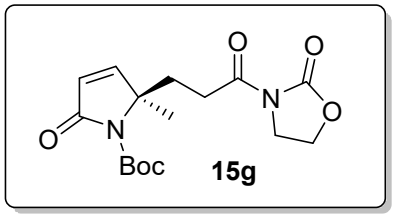
HPLC analysis: 73% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 60/40, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 18.44 min, t_r(minor) = 25.61 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 6.1 Hz, 1H), 6.09 (d, *J* = 6.1 Hz, 1H), 5.51 – 5.38 (m, 1H), 5.09 – 5.02 (m, 2H), 4.42 – 4.36 (m, 2H), 4.02 – 3.91 (m, 2H), 2.99 – 2.90 (m, 1H), 2.75 – 2.65 (m, 3H), 2.57 – 2.50 (m, 1H), 2.16 – 2.10 (m, 1H), 1.56 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.3, 169.5, 153.9, 153.3, 149.3, 130.6, 126.3, 120.1, 83.2, 70.5, 62.1, 42.6, 40.4, 30.0, 29.2, 28.2.

HRMS (ESI): $C_{18}H_{24}N_2NaO_6$ $[M+Na]^+$ calcd: 387.1527, found: 387.1521.

***tert*-butyl 2-methyl-5-oxo-2-(3-oxo-3-(2-oxooxazolidin-3-yl)propyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15g)**



15g

R_f = 0.2 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -12.03 (*c* = 0.453, $CHCl_3$).

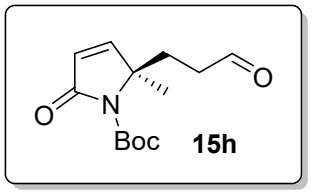
HPLC analysis: 77% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 47.32 min, t_r(minor) = 69.71 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 6.0 Hz, 1H), 4.43 (t, *J* = 8.3 Hz, 2H), 4.07 – 3.95 (m, 2H), 2.76 – 2.68 (m, 3H), 2.15 (s, 1H), 1.61 (s, 9H), 1.60 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.2, 169.4, 155.8, 153.3, 149.3, 125.0, 83.2, 67.8, 62.1, 42.6, 30.8, 29.6, 28.2, 24.0.

HRMS (ESI): $C_{16}H_{22}N_2NaO_6$ $[M+Na]^+$ calcd: 361.1370, found: 361.1368.

***tert*-butyl 2-methyl-5-oxo-2-(3-oxopropyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15h)**



15h

R_f = 0.3 (hexanes:EtOAc, 1:1), colorless oil.

$[\alpha]_D^{20}$ = -0.23 (*c* = 0.383, $CHCl_3$).

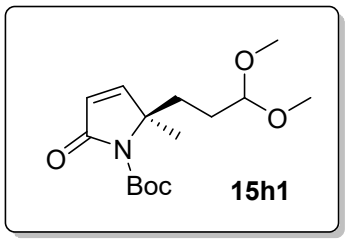
HPLC analysis: 80% ee was obtained by its derivative **15h1**.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 6.94 (d, *J* = 6.0 Hz, 1H), 6.08 (d, *J* = 6.0 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.36 – 2.26 (m, 1H), 2.25 – 2.17 (m, 1H), 2.15 – 2.07 (m, 1H), 1.61 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 200.3, 169.2, 155.7, 149.3, 125.1, 83.3, 67.5, 38.1, 28.2, 27.8, 23.9.

HRMS (ESI): $C_{13}H_{19}NNaO_4$ $[M+Na]^+$ calcd: 276.1206, found: 276.1204.

***tert*-butyl 2-(3,3-dimethoxypropyl)-2-methyl-5-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15h1)**



R_f = 0.4 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = +3.92 (*c* = 0.393, $CHCl_3$).

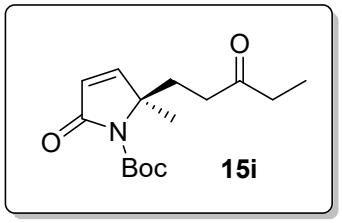
HPLC analysis: 80% ee, Chiralpak IC, Hexane/*i*-PrOH = 85/15, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 26.10 min, t_r(minor) = 20.93 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.91 (d, *J* = 6.1 Hz, 1H), 6.04 (d, *J* = 6.0 Hz, 1H), 4.28 (t, *J* = 5.4 Hz, 1H), 3.28 (s, 3H), 3.26 (s, 3H), 2.33 (d, *J* = 31.2 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.56 (s, 9H), 1.53 (s, 3H), 1.38 – 1.32 (m, 1H), 1.30 – 1.25 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.5, 156.1, 149.4, 124.9, 104.1, 82.9, 68.0, 53.3, 52.7, 30.9, 28.2, 26.8, 24.0.

HRMS (ESI): $C_{15}H_{25}NNaO_5$ $[M+Na]^+$ calcd: 322.1625, found: 322.1619.

***tert*-butyl 2-methyl-5-oxo-2-(3-oxopentyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15i)**



R_f = 0.2 (hexanes:EtOAc, 1:1), white solid.

$[\alpha]_D^{20}$ = -0.30 (*c* = 0.380, $CHCl_3$).

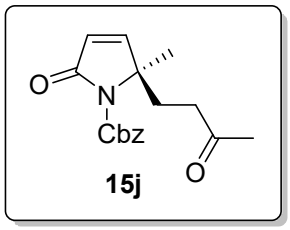
HPLC analysis: 83% ee, Chiralpak OD-H, Hexane/*i*-PrOH/MeOH = 90/05/05, flow rate = 0.3 mL/min, λ = 214 nm; Major isomer: t_r(major) = 25.05 min, t_r(minor) = 27.22 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 6.0 Hz, 1H), 6.05 (d, *J* = 6.1 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.43 – 2.33 (m, 2H), 2.27 – 2.18 (m, 1H), 2.14 – 2.07 (m, 2H), 1.60 (s, 9H), 1.59 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 210.0, 169.6, 156.2, 149.3, 124.6, 83.1, 67.9, 36.2, 36.0, 29.4, 28.2, 24.0, 7.8.

HRMS (ESI): $C_{15}H_{23}NNaO_4$ $[M+Na]^+$ calcd: 304.1519, found: 304.1514.

benzyl 2-methyl-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15j)



R_f = 0.2 (hexanes:EtOAc, 2:1), colorless oil.

$[\alpha]_D^{20}$ = -3.82 (*c* = 0.433, $CHCl_3$).

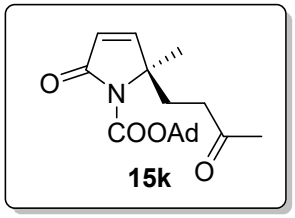
HPLC analysis: 70% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 95/5, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 79.57 min, t_r(minor) = 75.81 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 1H), 6.95 (d, *J* = 6.0 Hz, 1H), 6.03 (d, *J* = 6.0 Hz, 1H), 5.37 – 5.29 (m, 2H), 2.57 – 2.49 (m, 1H), 2.17 – 2.09 (m, 1H), 2.08 – 2.01 (m, 2H), 2.00 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.1, 169.0, 156.9, 150.7, 135.4, 128.7, 128.4, 128.1, 124.5, 68.2, 67.9, 37.3, 30.1, 28.9, 23.8.

HRMS (ESI): $C_{17}H_{19}NNaO_4$ $[M+Na]^+$ calcd: 324.1206, found: 324.1200.

(3*r*)-adamantan-1-yl 2-methyl-5-oxo-2-(3-oxobutyl)-2,5-dihydro-1*H*-pyrrole-1-carboxylate (15k)



R_f = 0.2 (hexanes:EtOAc, 2:1), colorless oil.

$[\alpha]_D^{20}$ = -42.15 (*c* = 0.138, $CHCl_3$).

HPLC analysis: 80% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 13.49 min, t_r(minor) = 12.12 min.

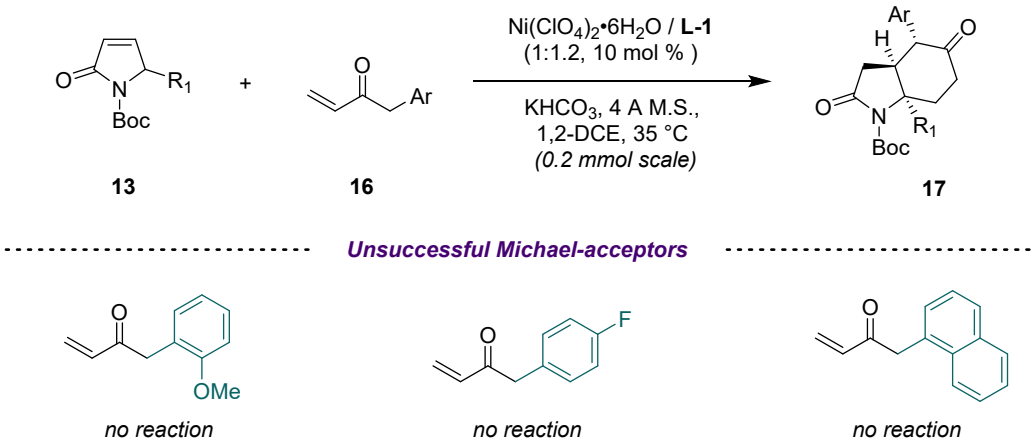
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.87 (d, *J* = 6.0 Hz, 1H), 6.00 (d, *J* = 6.0 Hz, 1H), 2.56 – 2.47 (m, 1H), 2.20 (s, 9H), 2.13 – 1.98 (m, 6H), 1.67 (s, 6H), 1.54 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.2, 169.6, 156.1, 148.8, 124.7, 83.2, 67.8, 41.5, 37.4, 36.1, 31.0, 30.2, 29.3, 24.0.

HRMS (ESI): $C_{20}H_{28}NO_4$ $[M+H]^+$ calcd: 346.2013, found: 346.2008.

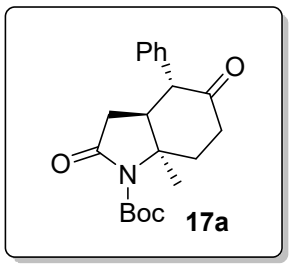
4.2 Preparation of 17

General procedure: $Ni(ClO_4)_2 \cdot 6H_2O$ (7.2 mg, 0.020 mmol), **L-1** (13.6 mg, 0.024 mmol), $KHCO_3$ (20.0 mg, 0.2 mmol), and 4Å molecular sieves (20.0 mg) were stirred in anhydrous 1,2-DCE (0.2 M) under argon atmosphere at 35 °C for 1 hour. Then a mixture of *α*, *β*-Unsaturated *γ*-butyrolactam **13** (0.2 mmol) and benzyl vinyl ketone **16** (0.24mmol) in 1,2-DCE was added to the above solution. The mixture was stirred at 35 °C until TLC showed the staring material was no longer consumed. The reaction mixture was filtered through Celite® and washed with EtOAc. The filtrate was then concentrated under reduced pressure to give a residue which was purified by silica gel chromatography to afford the addition product octahydroindoles **17**.



Scheme S2. Unsuccessful Michael-acceptors for the double Michael additions.

***tert*-butyl 7a-methyl-2,5-dioxo-4-phenyloctahydro-1*H*-indole-1-carboxylate (17a)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

[*α*]$_D^{20}$ = +6.92 (*c* = 0.535, $CHCl_3$).

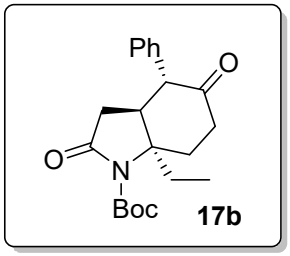
HPLC analysis: 83% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 24.38 min, t_r(minor) = 28.84 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.0 Hz, 2H), 3.49 (d, *J* = 12.6 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.60 – 2.54 (m, 2H), 2.49 – 2.41 (m, 2H), 2.37 – 2.30 (m, 1H), 2.15 – 2.09 (m, 1H), 1.62 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.1, 172.7, 150.1, 135.6, 129.5, 128.8, 127.7, 83.6, 63.7, 56.7, 43.3, 35.9, 35.7, 32.6, 28.2, 24.7.

HRMS (ESI): $C_{20}H_{25}NNaO_4$ $[M+Na]^+$ calcd: 366.1676, found: 366.1670.

***tert*-butyl 7a-ethyl-2,5-dioxo-4-phenyloctahydro-1*H*-indole-1-carboxylate (17b)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +60.45 (*c* = 0.118, $CHCl_3$).

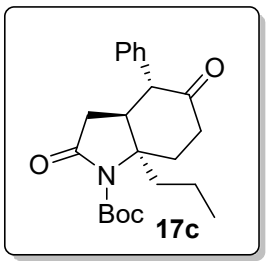
HPLC analysis: 73% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.4 mL/min, λ = 214 nm; Major isomer: t_r(major) = 44.07 min, t_r(minor) = 39.57 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 3.57 (d, *J* = 11.8 Hz, 1H), 2.68 – 2.45 (m, 5H), 2.38 – 2.31 (m, 1H), 2.26 – 2.19 (m, 1H), 2.19 – 2.14 (m, 1H), 1.93 – 1.85 (m, 1H), 1.57 (s, 9H), 0.98 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.2, 173.1, 150.3, 135.5, 129.4, 128.8, 127.8, 83.6, 66.8, 57.7, 40.2, 37.2, 35.9, 31.9, 31.1, 28.1, 8.3.

HRMS (ESI): $C_{21}H_{27}NNaO_4$ $[M+Na]^+$ calcd: 380.1832, found: 380.1827.

***tert*-butyl 2,5-dioxo-4-phenyl-7a-propyloctahydro-1*H*-indole-1-carboxylate (17c)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +4.32 (*c* = 0.445, $CHCl_3$).

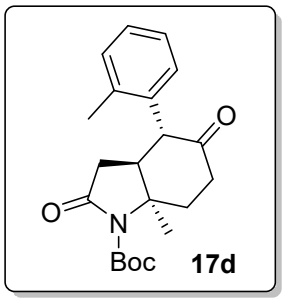
HPLC analysis: 64% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 24.23 min, t_r(minor) = 18.93 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 2H), 3.56 (d, *J* = 12.0 Hz, 1H), 2.66 (dt, J = 14.2, 4.2 Hz, 1H), 2.61 – 2.52 (m, 3H), 2.51 – 2.44 (m, 1H), 2.37 – 2.30 (m, 1H), 2.17 – 2.09 (m, 2H), 1.87 – 1.78 (m, 1H), 1.56 (s, 9H), 1.40 – 1.33 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.2, 173.1, 150.3, 135.5, 129.4, 128.8, 127.8, 83.5, 66.5, 57.7, 40.9, 40.6, 37.2, 35.9, 32.1, 28.1, 17.2, 14.4.

HRMS (ESI): $C_{22}H_{29}NNaO_4$ $[M+Na]^+$ calcd: 394.1989, found: 394.1989.

***tert*-butyl 7a-methyl-2,5-dioxo-4-(*o*-tolyl)octahydro-1*H*-indole-1-carboxylate (17d)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +62.49 (*c* = 0.123, $CHCl_3$).

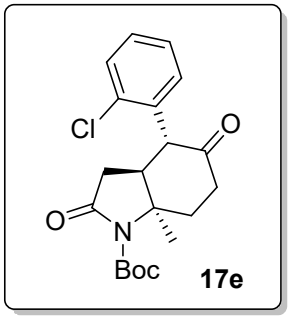
HPLC analysis: 93% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.6 mL/min, λ = 214 nm; Major isomer: t_r(major) = 18.96 min, t_r(minor) = 22.30 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.86 – 6.78 (m, 2H), 3.43 (d, *J* = 14.9 Hz, 1H), 2.69 – 2.62 (m, 1H), 2.61 – 2.54 (m, 2H), 2.49 – 2.41 (m, 2H), 2.34 – 2.30 (m, 4H), 2.14 (d, *J* = 18.2 Hz, 1H), 1.63 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.4, 172.8, 150.1, 138.5, 135.5, 130.3, 128.7, 128.5, 126.4, 83.6, 63.7, 56.6, 43.2, 35.9, 35.7, 32.7, 28.2, 24.7, 21.4.

HRMS (ESI): $C_{21}H_{27}NNaO_4$ $[M+Na]^+$ calcd: 380.1832, found: 380.1824.

***tert*-butyl 4-(2-chlorophenyl)-7a-methyl-2,5-dioxooctahydro-1*H*-indole-1-carboxylate (17e)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +70.31 (*c* = 0.245, $CHCl_3$).

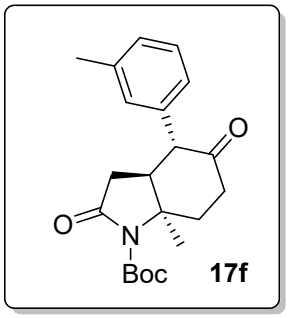
HPLC analysis: 75% ee, Chiralpak AD-H, Hexane/*i*-PrOH = 80/20, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 12.56 min, t_r(minor) = 18.35 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 1H), 7.27 – 7.23 (m, 2H), 7.09 – 7.01 (m, 1H), 3.84 (d, *J* = 10.0 Hz, 1H), 2.75 – 2.64 (m, 2H), 2.63 – 2.56 (m, 2H), 2.55 – 2.47 (m, 1H), 2.35 – 2.28 (m, 1H), 2.10 (d, *J* = 16.7 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 207.6, 172.6, 150.1, 134.6, 134.0, 131.6, 130.2, 129.2, 127.2, 83.6, 63.7, 54.7, 41.8, 35.8, 35.7, 32.6, 28.2, 24.8.

HRMS (ESI): $C_{20}H_{24}ClNNaO_4$ $[M+Na]^+$ calcd: 400.1286, found: 400.1278.

***tert*-butyl 7a-methyl-2,5-dioxo-4-(*m*-tolyl)octahydro-1*H*-indole-1-carboxylate (17f)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +55.04 (*c* = 0.185, $CHCl_3$).

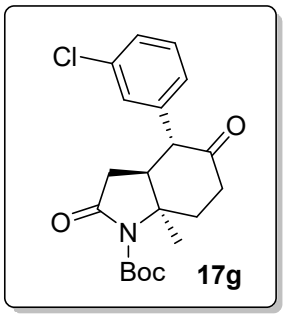
HPLC analysis: 81% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 24.48 min, t_r(minor) = 28.67 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.15 (m, 3H), 6.88 (d, *J* = 6.6 Hz, 1H), 3.71 (d, *J* = 12.9 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.62 – 2.55 (m, 2H), 2.55 – 2.41 (m, 2H), 2.35 – 2.29 (m, 1H), 2.21 (s, 3H), 2.04 (d, *J* = 18.0 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.1, 172.9, 150.1, 137.4, 134.3, 130.9, 128.5, 127.6, 126.4, 83.6, 63.7, 52.7, 42.7, 35.9, 35.8, 32.8, 28.2, 24.6, 20.2.

HRMS (ESI): $C_{21}H_{27}NNaO_4$ $[M+Na]^+$ calcd: 380.1832, found: 380.1823.

***tert*-butyl 4-(3-chlorophenyl)-7a-methyl-2,5-dioxooctahydro-1*H*-indole-1-carboxylate (17g)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +47.26 (*c* = 0.145, $CHCl_3$).

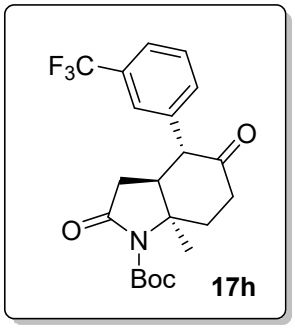
HPLC analysis: 78% ee, Chiralpak IB-3, Hexane/*i*-PrOH = 70/30, flow rate = 0.5 mL/min, λ = 214 nm; Major isomer: t_r(major) = 14.81 min, t_r(minor) = 17.57 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.02 (s, 1H), 6.91 (t, *J* = 4.6 Hz, 1H), 3.48 (d, *J* = 12.7 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.61 – 2.54 (m, 2H), 2.49 – 2.38 (m, 2H), 2.36 – 2.29 (m, 1H), 2.10 (d, *J* = 18.4 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.3, 172.3, 150.1, 137.6, 134.8, 130.0, 129.4, 128.0, 127.9, 83.7, 63.6, 56.4, 43.3, 35.8, 35.6, 32.6, 28.2, 24.7.

HRMS (ESI): $C_{20}H_{24}ClNNaO_4$ $[M+Na]^+$ calcd: 400.1286, found: 400.1284.

***tert*-butyl 7a-methyl-2,5-dioxo-4-(3-(trifluoromethyl)phenyl)octahydro-1*H*-indole-1-carboxylate (17h)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +47.08 (*c* = 0.160, $CHCl_3$).

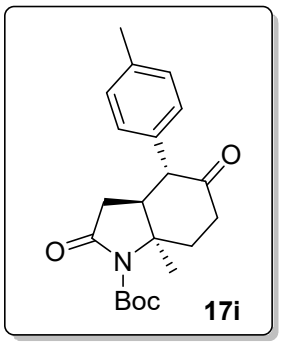
HPLC analysis: 71% ee, Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 14.97 min, t_r(minor) = 22.08 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 3.60 (d, *J* = 12.7 Hz, 1H), 2.74 – 2.66 (m, 1H), 2.64 – 2.56 (m, 2H), 2.53 – 2.42 (m, 2H), 2.40 – 2.33 (m, 1H), 2.06 (d, *J* = 19.9 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.1, 172.1, 150.1, 136.6, 133.1, 131.2 (q, *J* = 32.1 Hz), 129.3, 126.1 (q, *J* = 4.1 Hz), 124.7 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 271.1 Hz), 83.8, 63.6, 56.6, 43.3, 35.9, 35.6, 32.6, 28.1, 24.7.

HRMS (ESI): $C_{21}H_{24}F_3NNaO_4$ $[M+Na]^+$ calcd: 434.1550, found: 434.1546.

***tert*-butyl 7a-methyl-2,5-dioxo-4-(*p*-tolyl)octahydro-1*H*-indole-1-carboxylate (17i)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +31.44 (*c* = 0.148, $CHCl_3$).

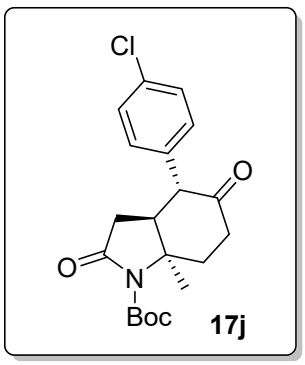
HPLC analysis: 86% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 36.65 min, t_r(minor) = 42.69 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 3.44 (d, *J* = 12.7 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.59 – 2.52 (m, 2H), 2.46 – 2.39 (m, 2H), 2.32 (s, 3H), 2.31 – 2.29 (m, 1H), 2.14 (d, *J* = 18.3 Hz, 1H), 1.61 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.4, 172.8, 150.2, 137.4, 132.5, 129.6, 129.3, 83.6, 63.7, 56.3, 43.3, 35.9, 35.7, 32.6, 28.2, 24.8, 21.1.

HRMS (ESI): $C_{21}H_{27}NNaO_4$ $[M+Na]^+$ calcd: 380.1832, found: 380.1826.

***tert*-butyl 4-(4-chlorophenyl)-7a-methyl-2,5-dioxooctahydro-1*H*-indole-1-carboxylate (17j)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +29.72 (*c* = 0.248, $CHCl_3$).

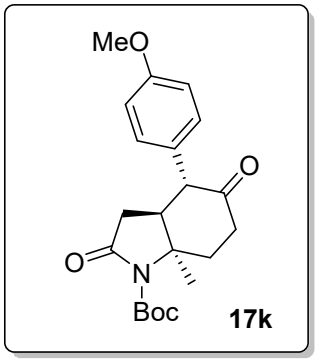
HPLC analysis: 92% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 17.70 min, t_r(minor) = 21.43 min.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.48 (d, *J* = 12.7 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.60 – 2.53 (m, 2H), 2.47 – 2.37 (m, 2H), 2.35 – 2.28 (m, 1H), 2.08 (d, *J* = 17.6 Hz, 1H), 1.61 (s, 3H), 1.56 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 208.7, 172.4, 150.1, 134.0, 133.7, 130.8, 129.1, 83.8, 63.7, 56.1, 43.3, 35.8, 35.6, 32.6, 28.2, 24.7.

HRMS (ESI): $C_{20}H_{24}ClNNaO_4$ $[M+Na]^+$ calcd: 400.1286, found: 400.1284.

***tert*-butyl 4-(4-methoxyphenyl)-7a-methyl-2,5-dioxooctahydro-1*H*-indole-1-carboxylate (17k)**



R_f = 0.2 (hexanes:EtOAc, 4:1), white solid.

$[\alpha]_D^{20}$ = +41.86 (*c* = 0.120, $CHCl_3$).

HPLC analysis: 75% ee, Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, flow rate = 0.7 mL/min, λ = 214 nm; Major isomer: t_r(major) = 48.27 min, t_r(minor) = 59.75 min.

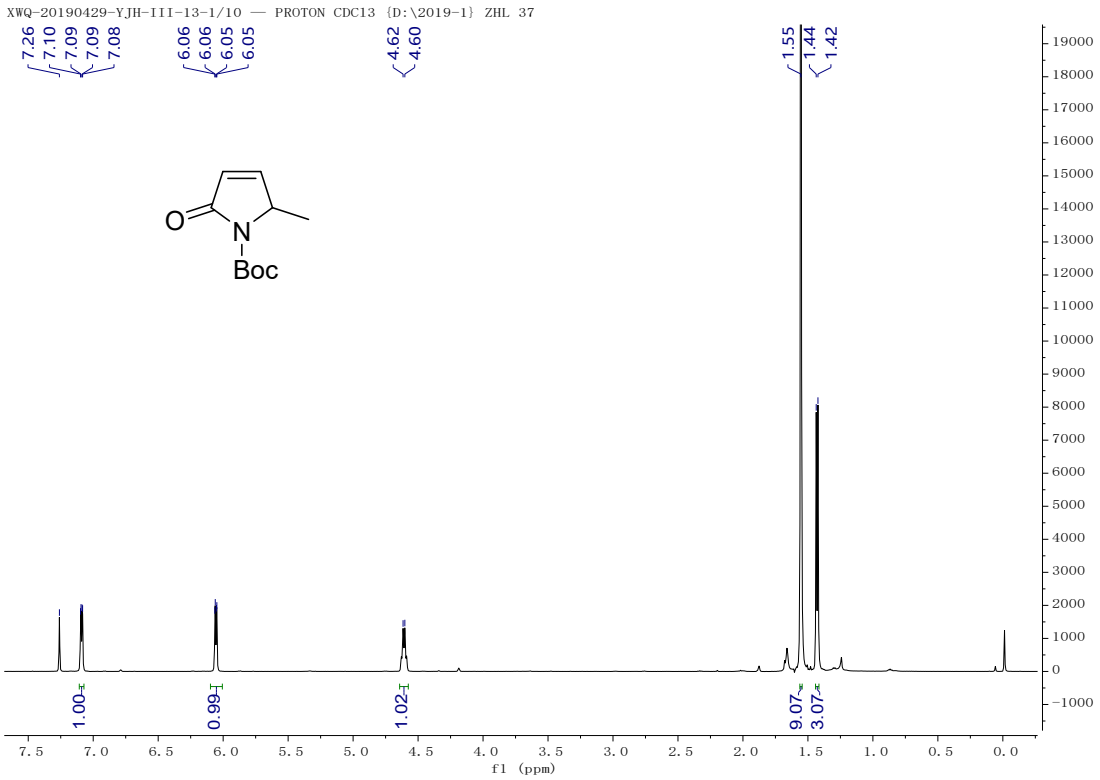
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 3.43 (d, *J* = 12.6 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.60 – 2.53 (m, 2H), 2.47 – 2.30 (m, 3H), 2.15 (d, *J* = 18.3 Hz, 1H), 1.62 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.5, 172.7, 159.1, 150.2, 130.4, 127.4, 114.4, 83.6, 63.7, 56.0, 55.3, 43.5, 35.9, 35.7, 32.6, 28.2, 24.8.

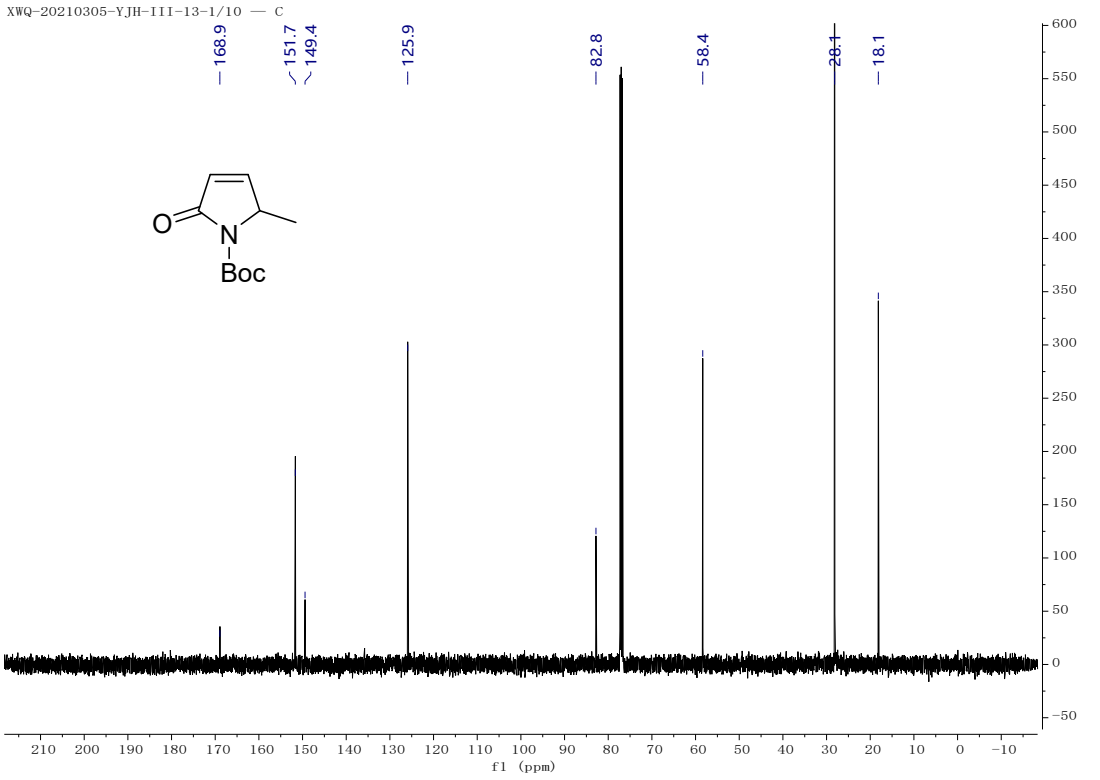
HRMS (ESI): $C_{21}H_{27}NNaO_5$ $[M+Na]^+$ calcd: 396.1781, found: 396.1781.

5. NMR Spectra

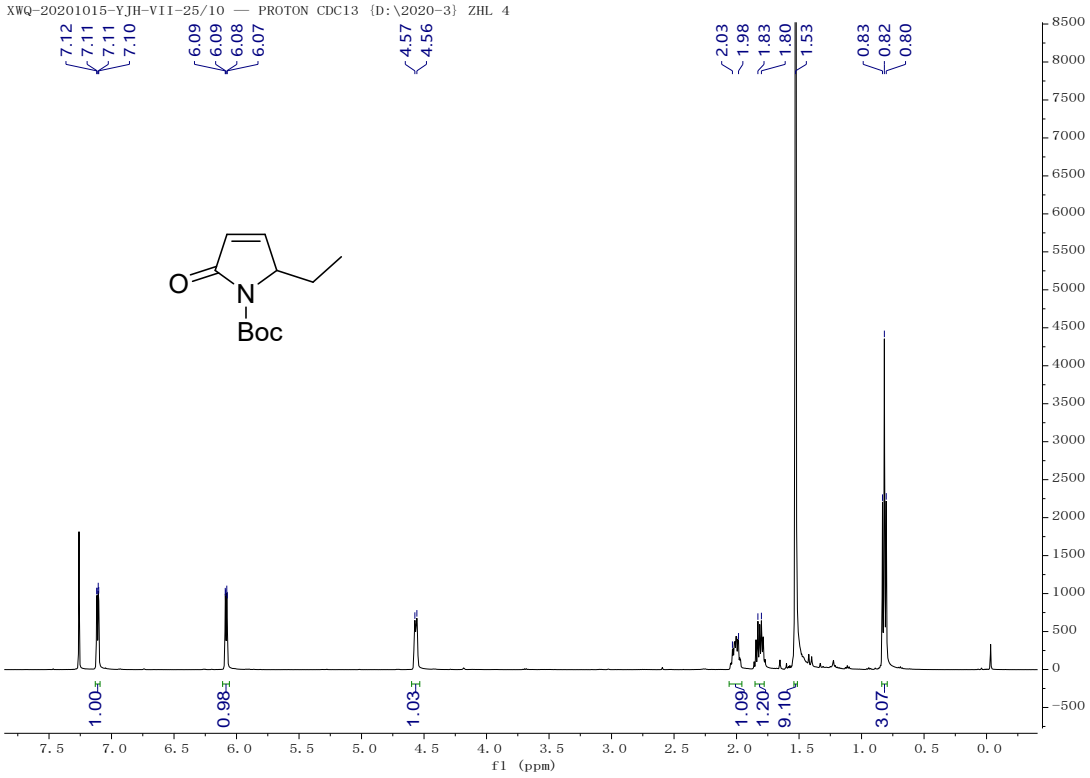
^{1}H NMR spectrum of compound 1**3a** (500 MHz, Chloroform-*d*)



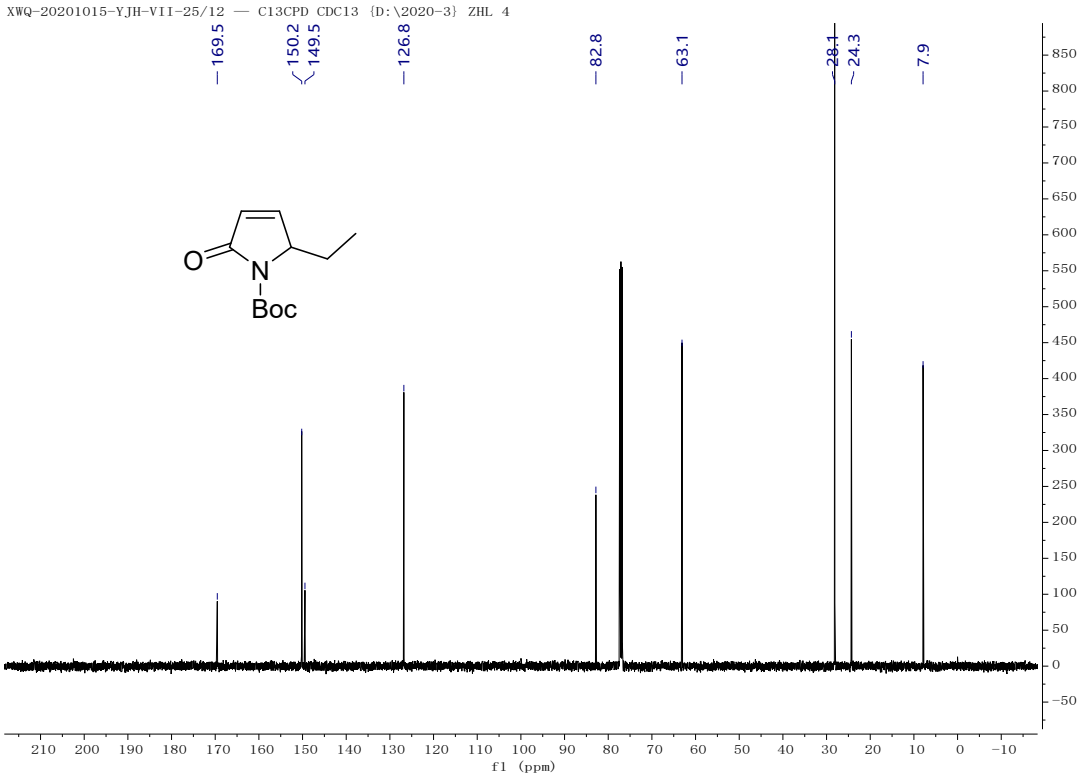
^{13}C NMR spectrum of compound 1**3a** (126 MHz, Chloroform-*d*)



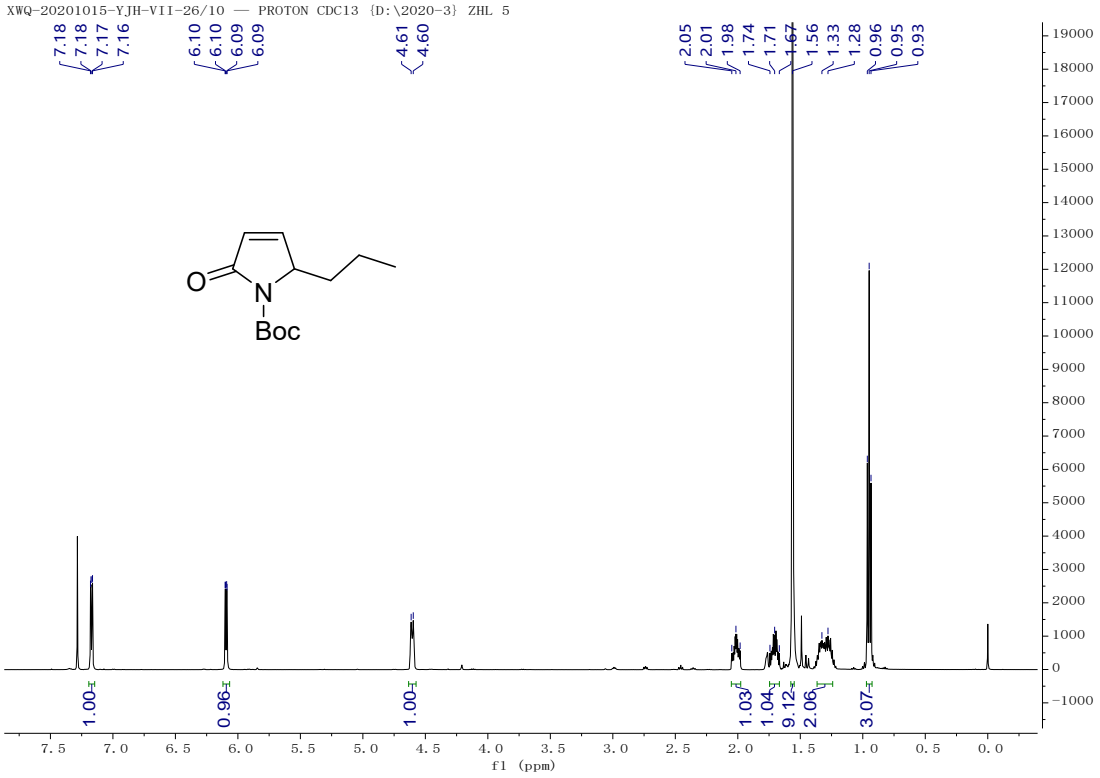
^{1}H NMR spectrum of compound **13b** (500 MHz, Chloroform-*d*)



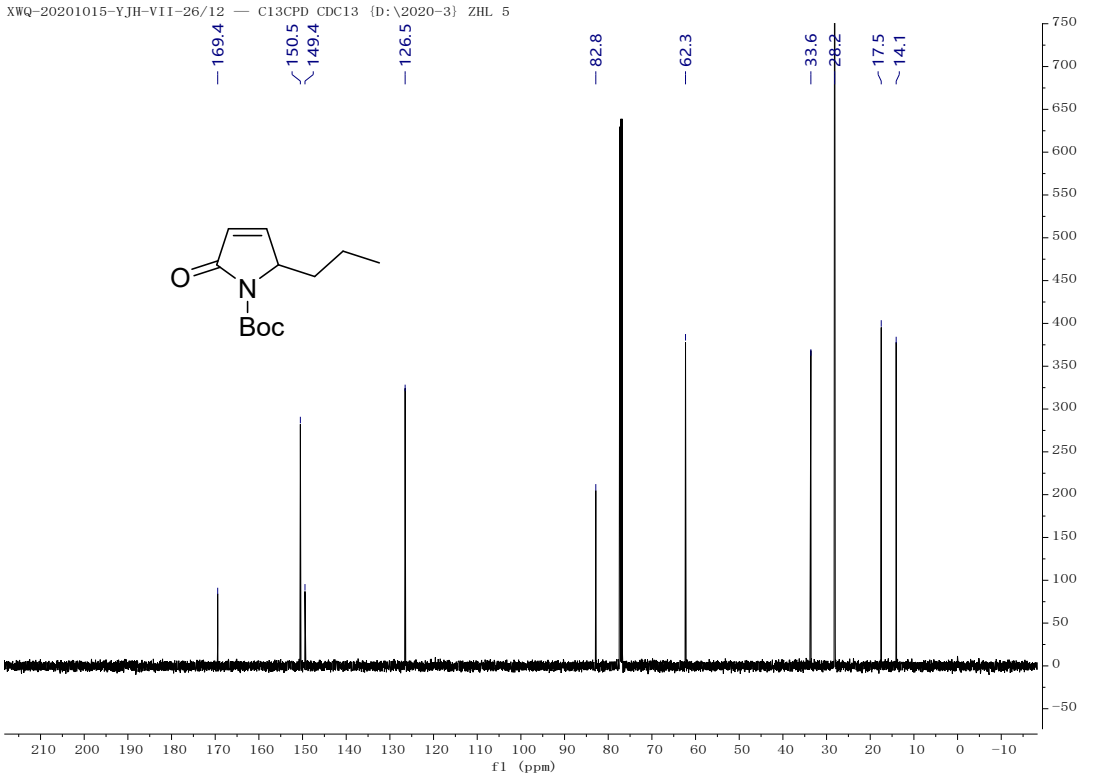
^{13}C NMR spectrum of compound **13b** (126 MHz, Chloroform-*d*)



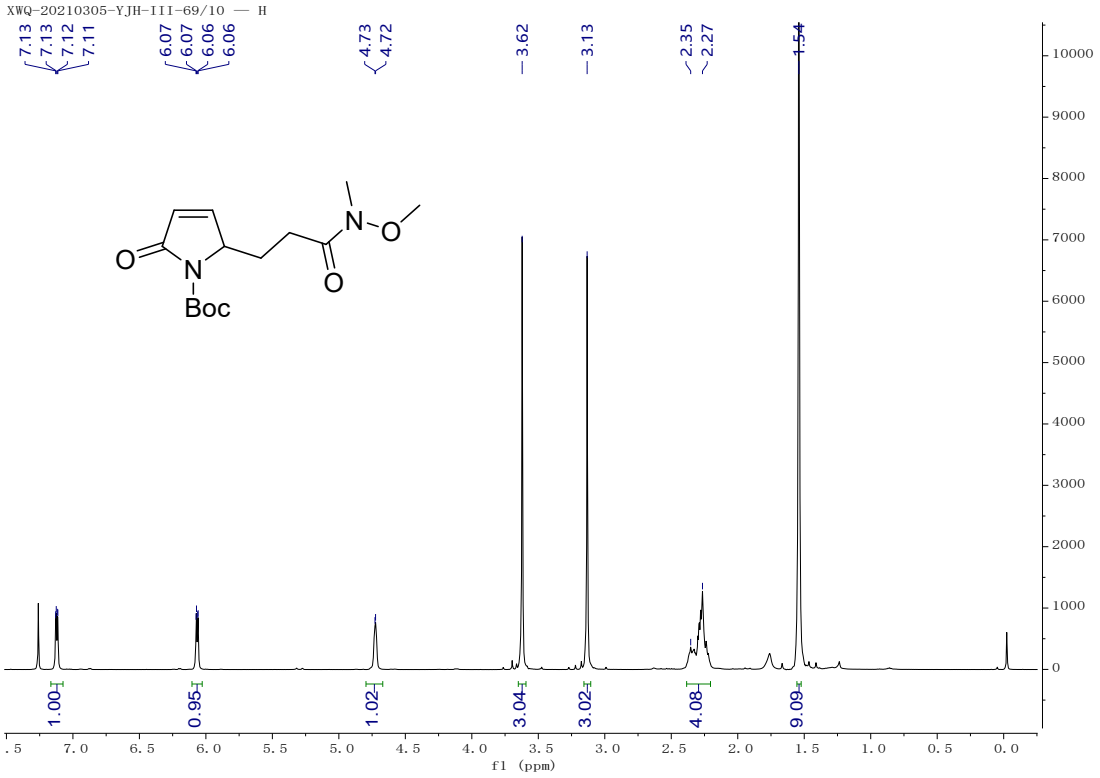
^{1}H NMR spectrum of compound **13c** (500 MHz, Chloroform-*d*)



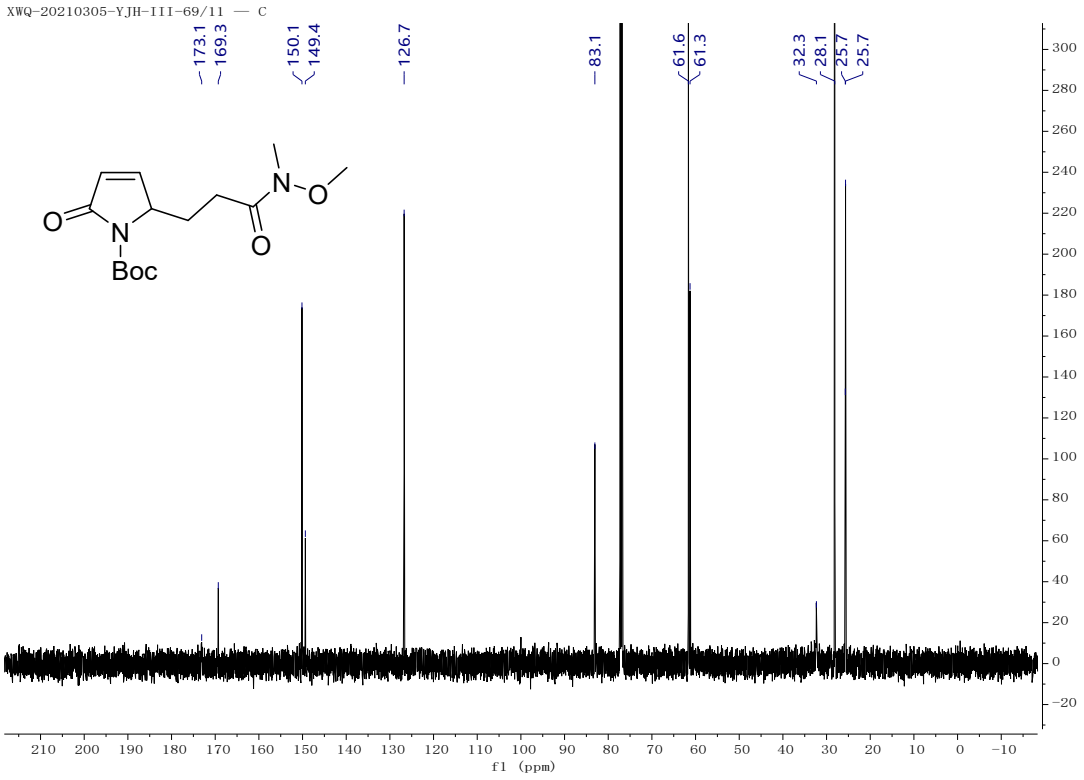
^{13}C NMR spectrum of compound **13c** (126 MHz, Chloroform-*d*)



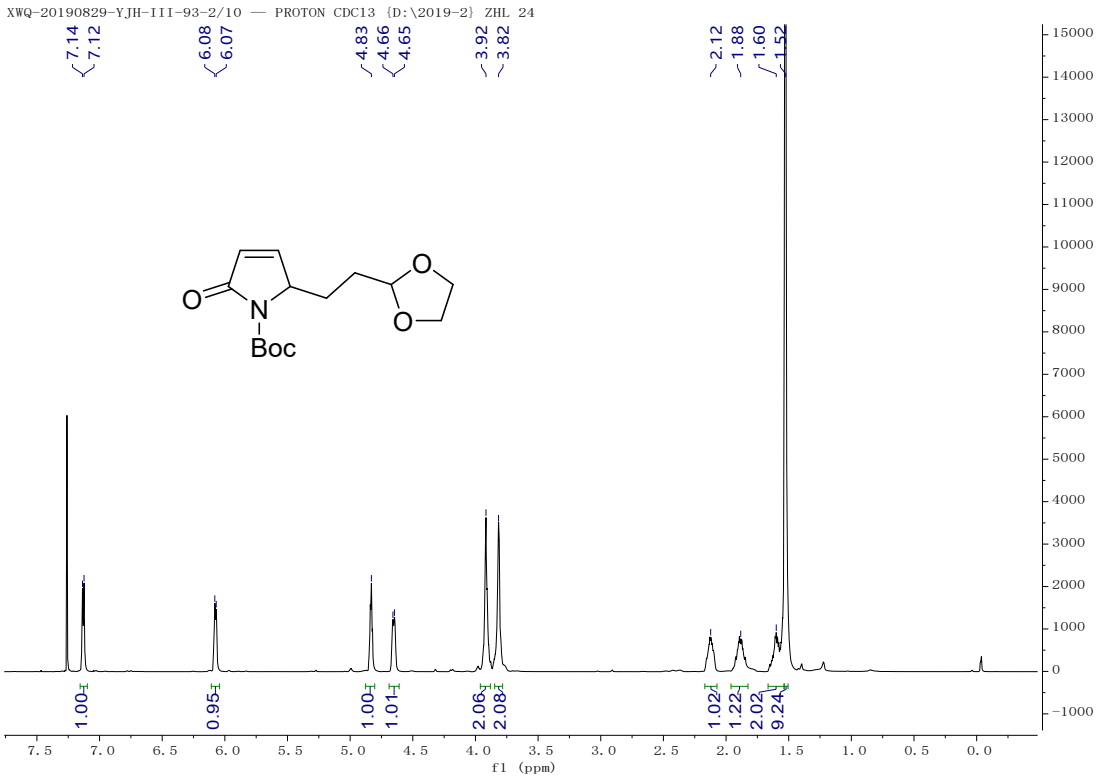
^{1}H NMR spectrum of compound **13d** (500 MHz, Chloroform-*d*)



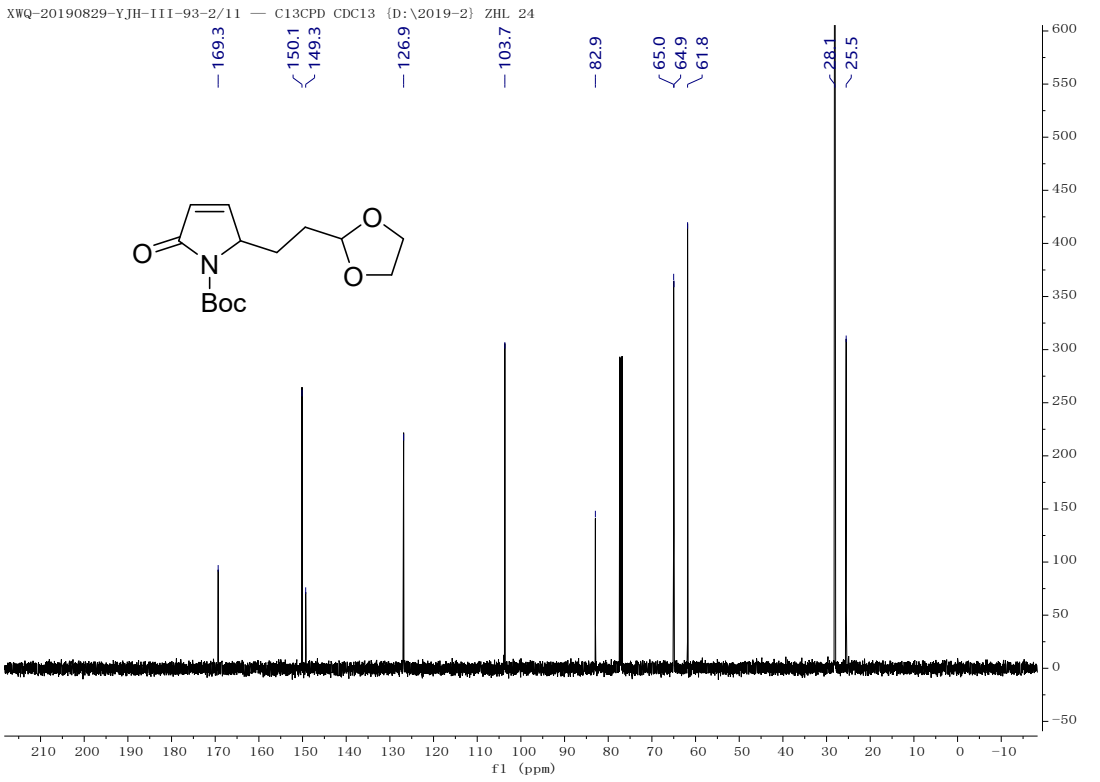
^{13}C NMR spectrum of compound **13d** (126 MHz, Chloroform-*d*)



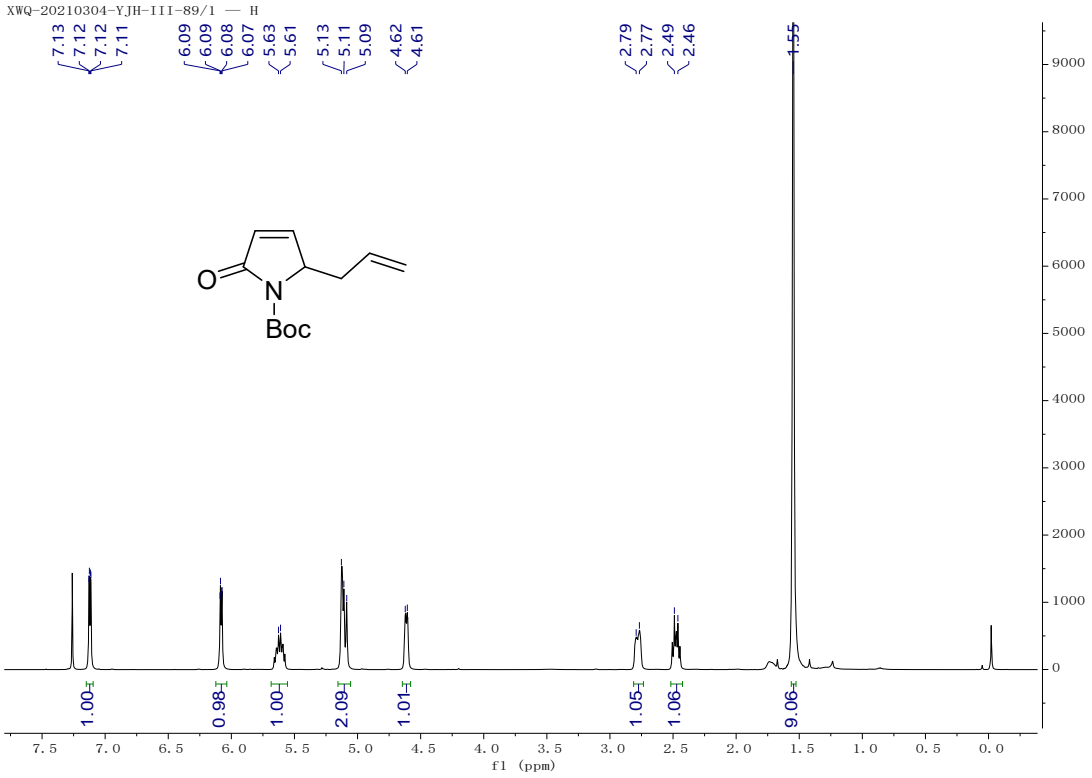
^{1}H NMR spectrum of compound **13e** (500 MHz, Chloroform-*d*)



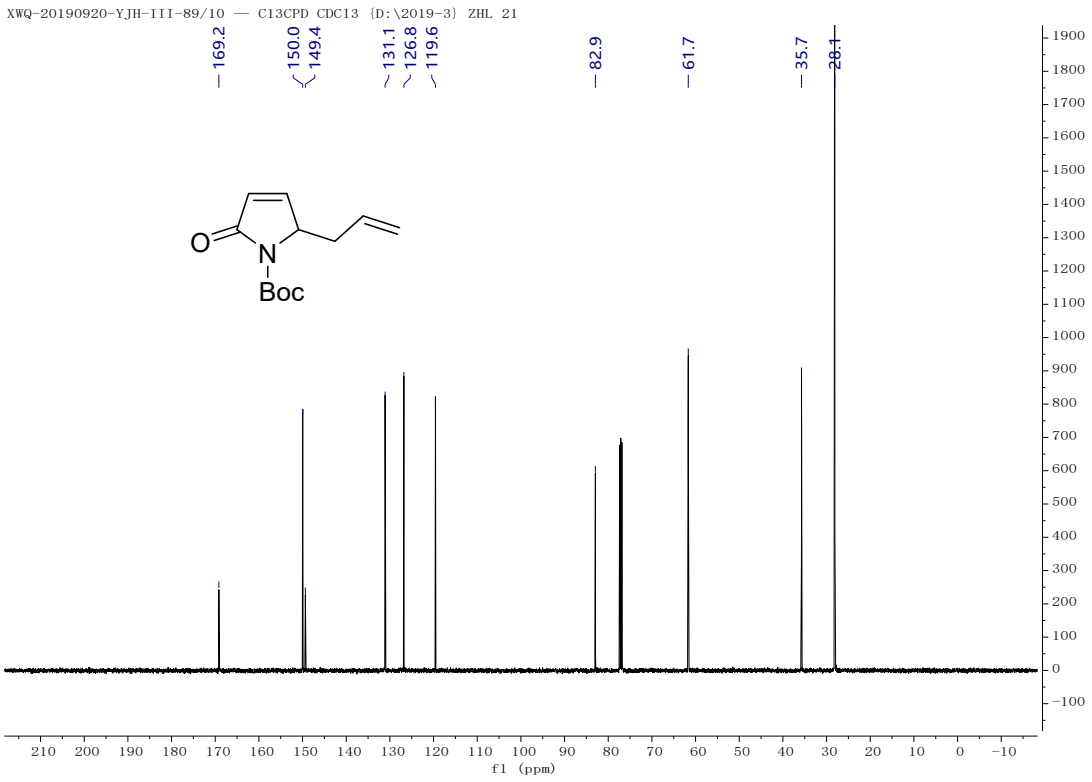
^{13}C NMR spectrum of compound **13e** (126 MHz, Chloroform-*d*)



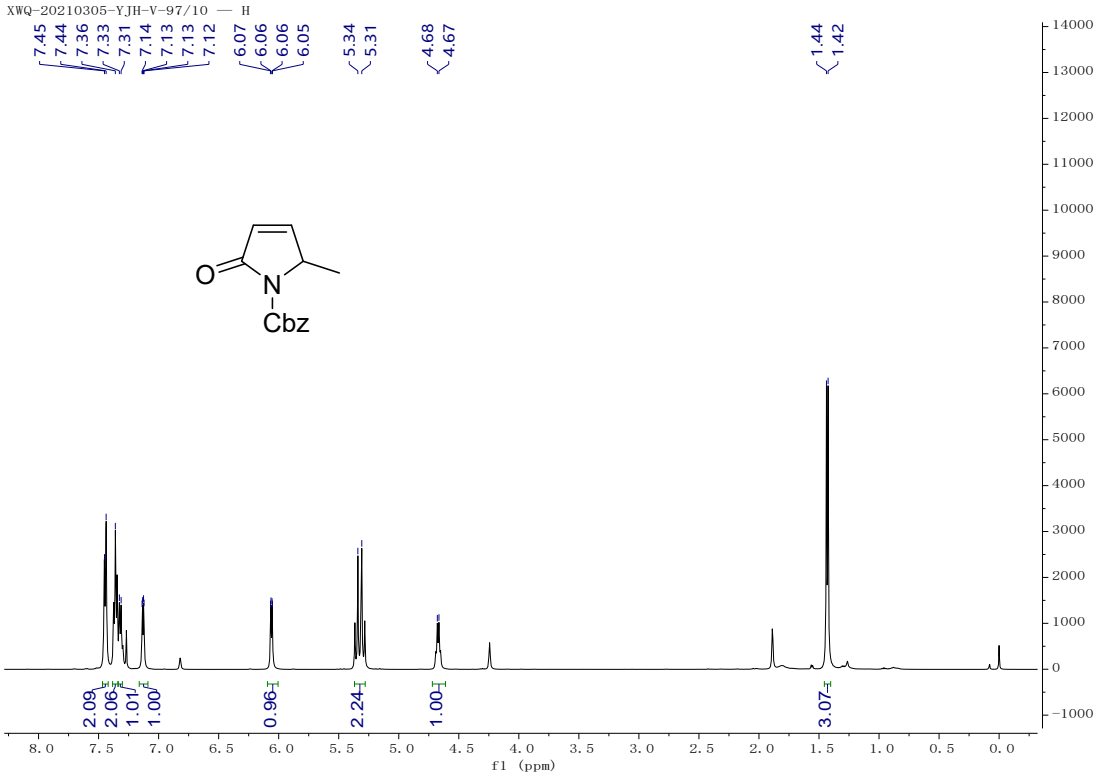
^{1}H NMR spectrum of compound **13f** (500 MHz, Chloroform-*d*)



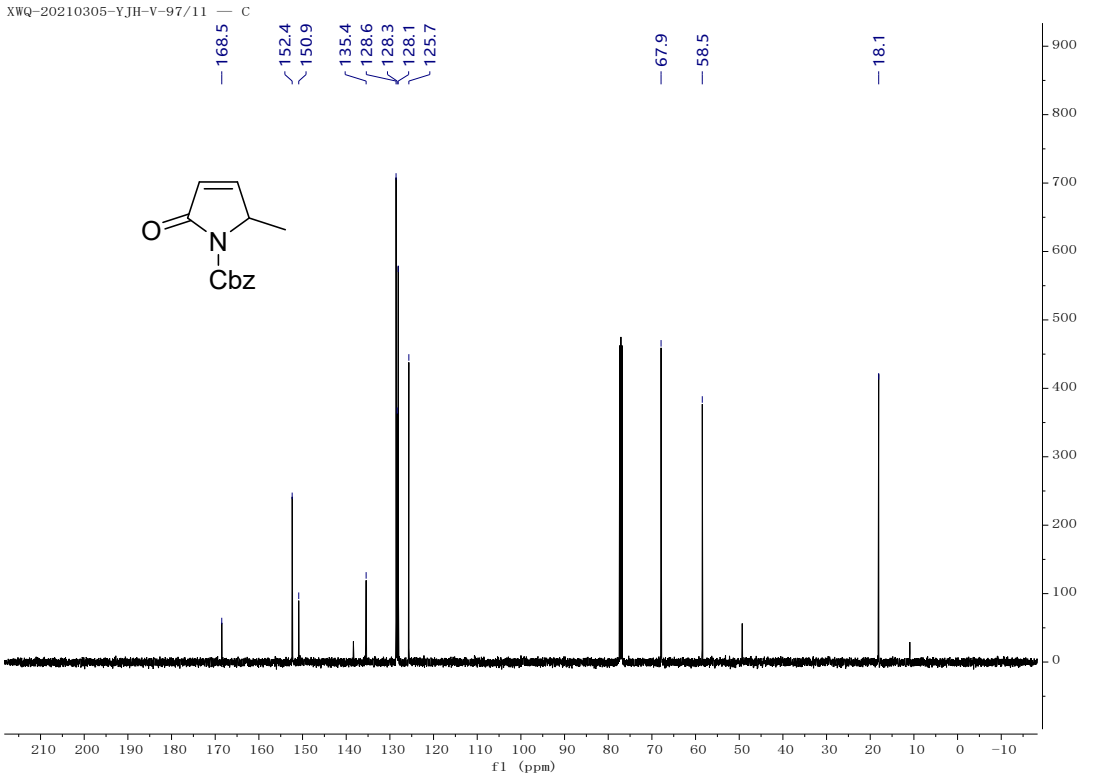
^{13}C NMR spectrum of compound **13f** (126 MHz, Chloroform-*d*)



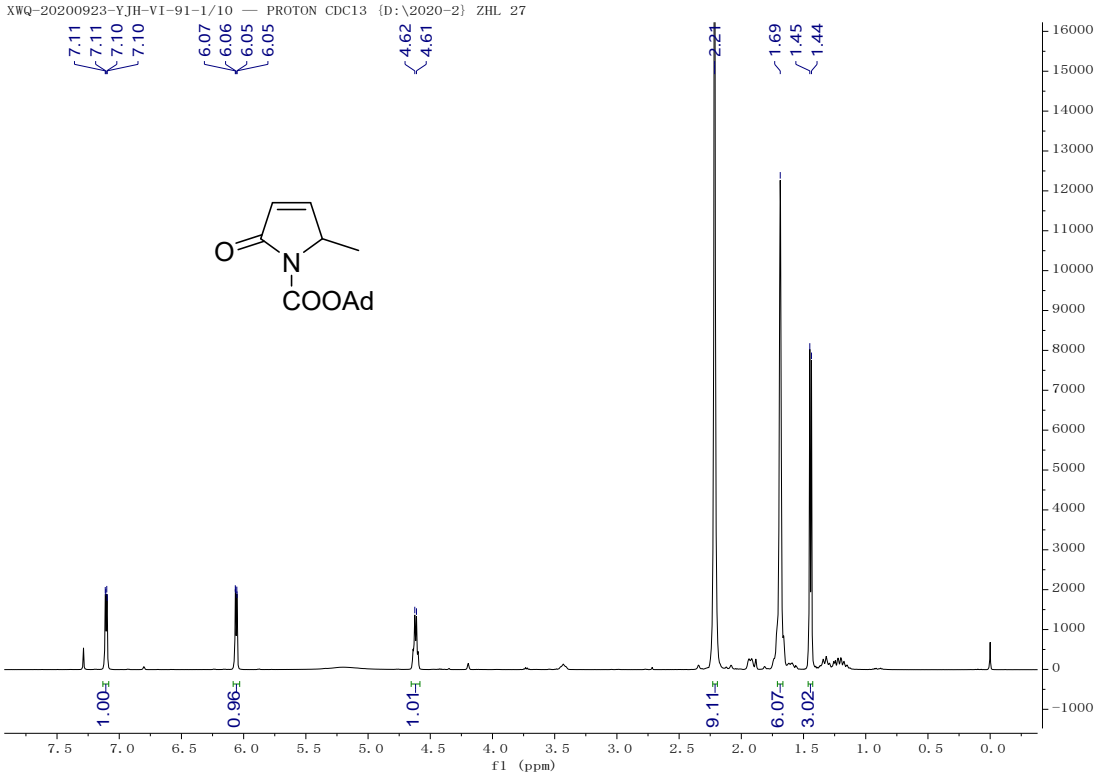
^{1}H NMR spectrum of compound **13j** (500 MHz, Chloroform-*d*)



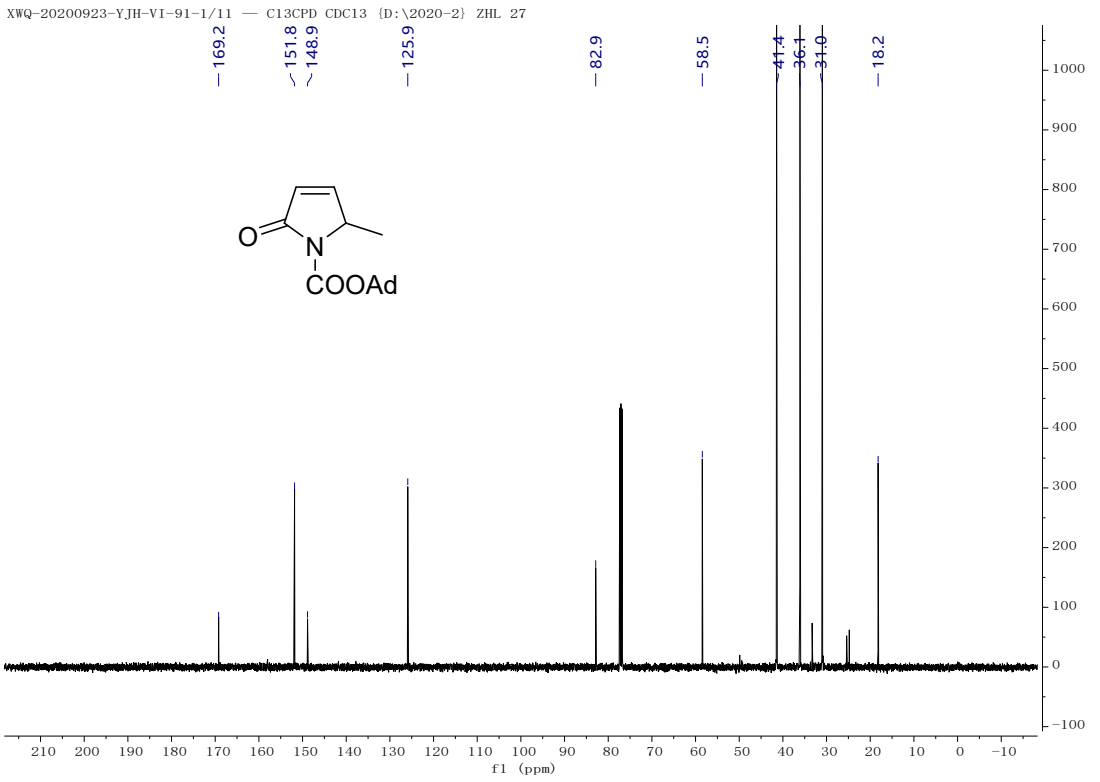
^{13}C NMR spectrum of compound **13j** (126 MHz, Chloroform-*d*)



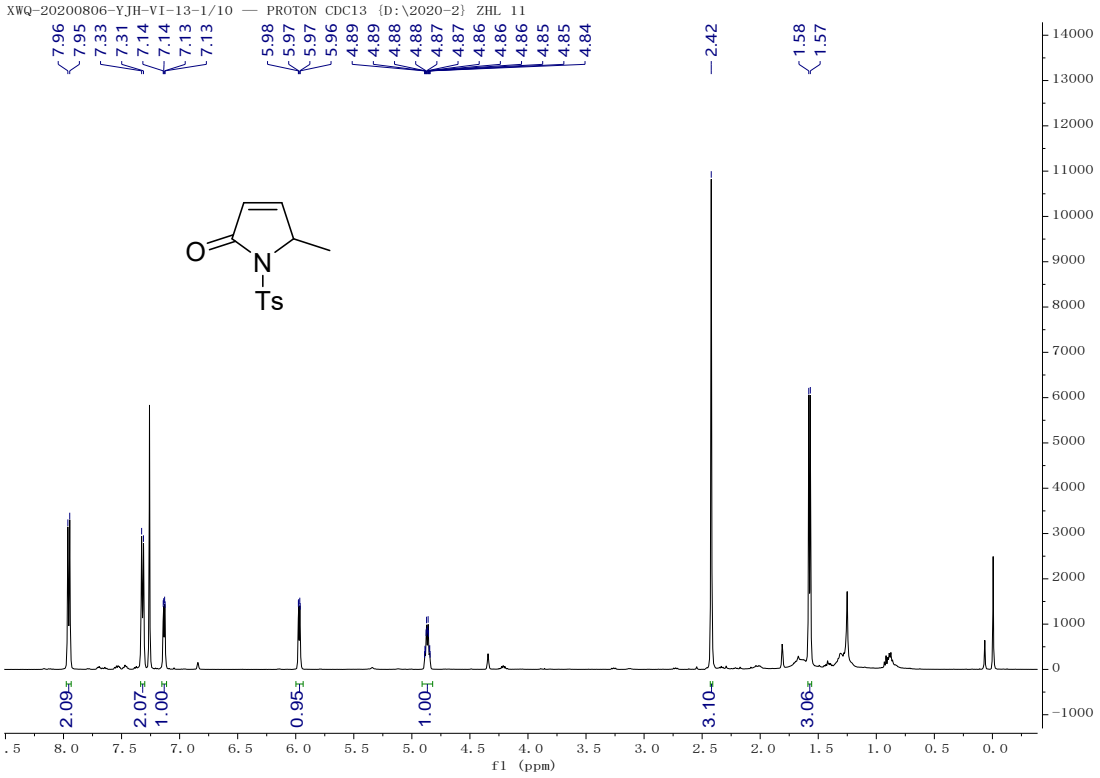
^{1}H NMR spectrum of compound **13k** (500 MHz, Chloroform-*d*)



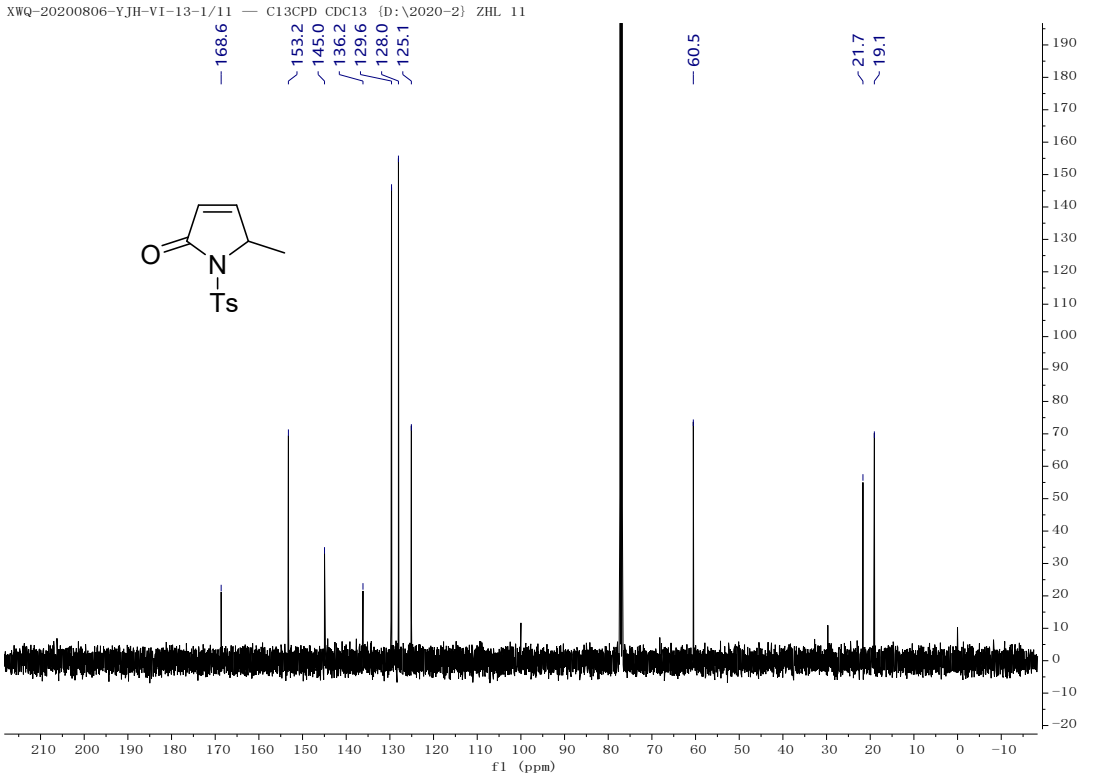
^{13}C NMR spectrum of compound **13k** (126 MHz, Chloroform-*d*)



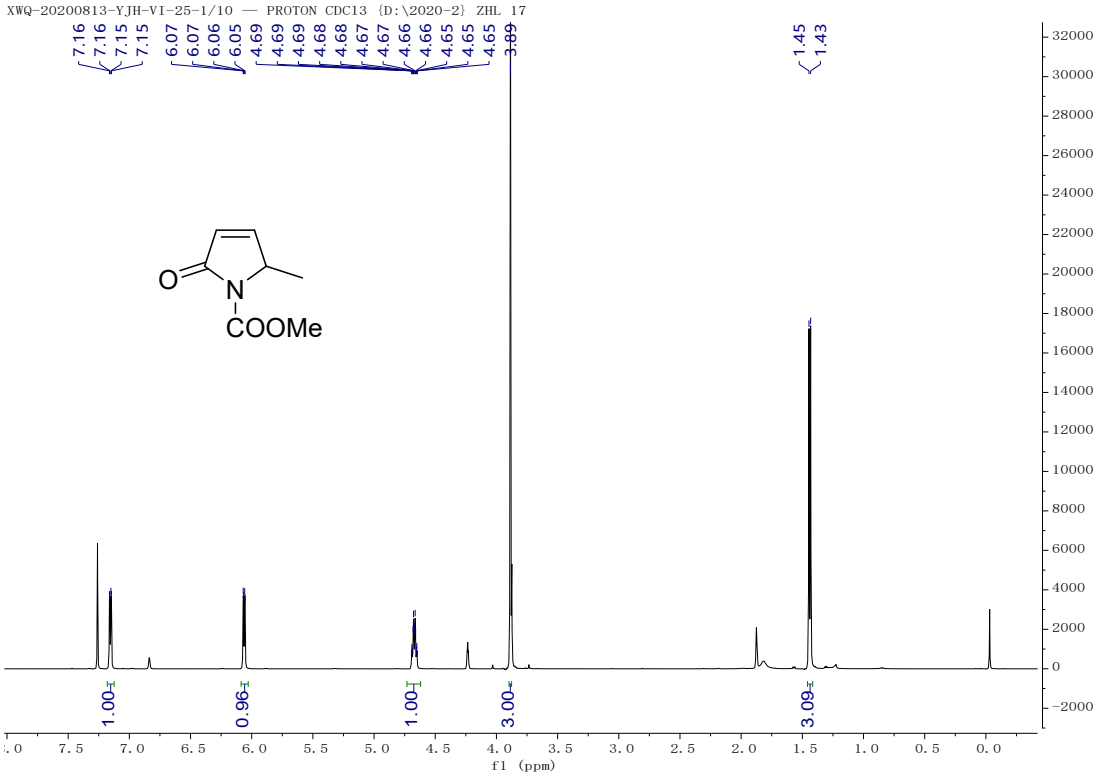
^{1}H NMR spectrum of compound **13l** (500 MHz, Chloroform-*d*)



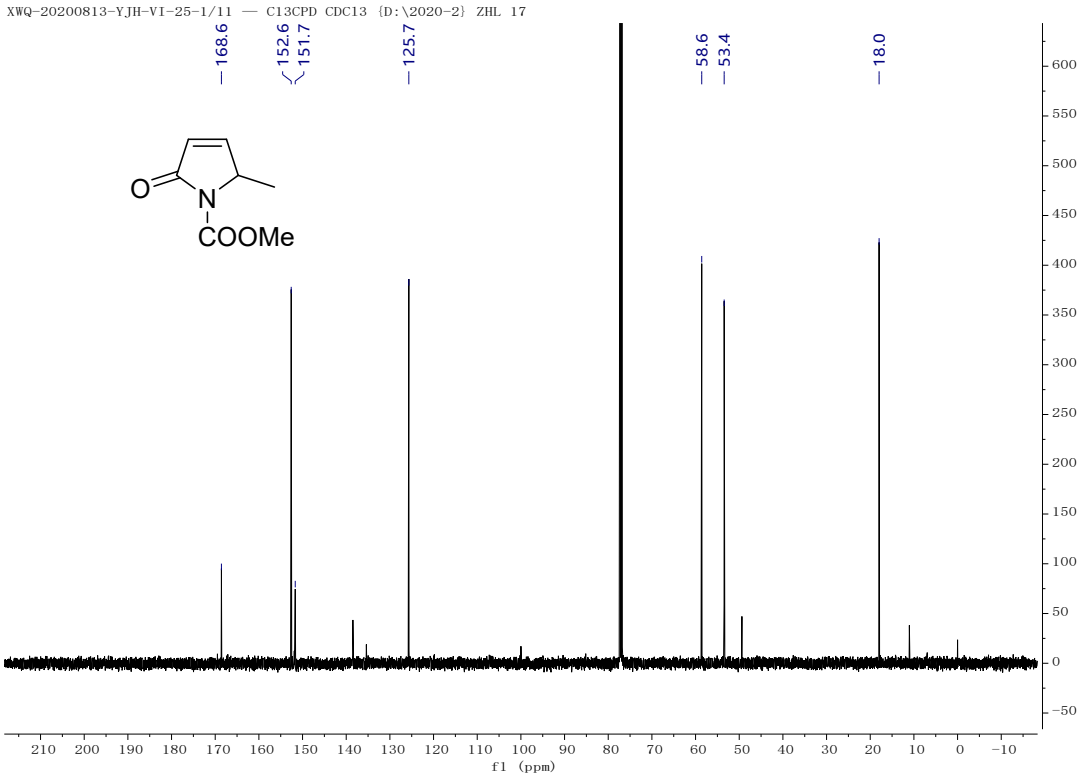
^{13}C NMR spectrum of compound **13l** (126 MHz, Chloroform-*d*)



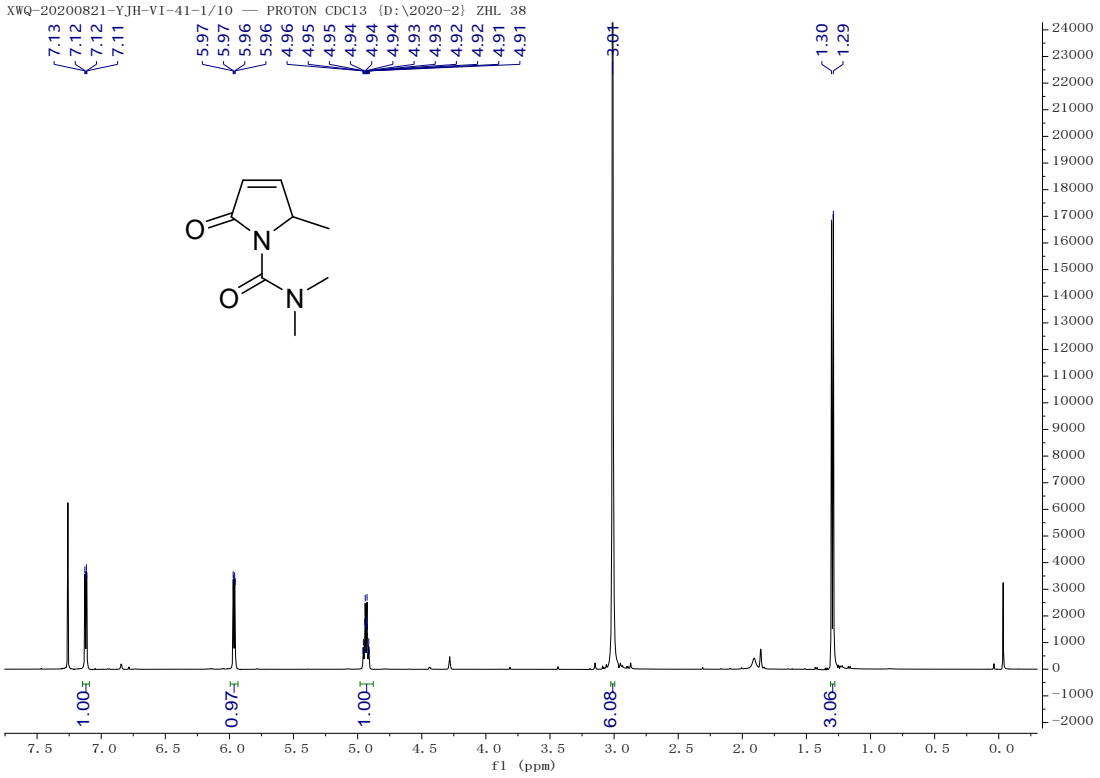
^{1}H NMR spectrum of compound **13m** (500 MHz, Chloroform-*d*)



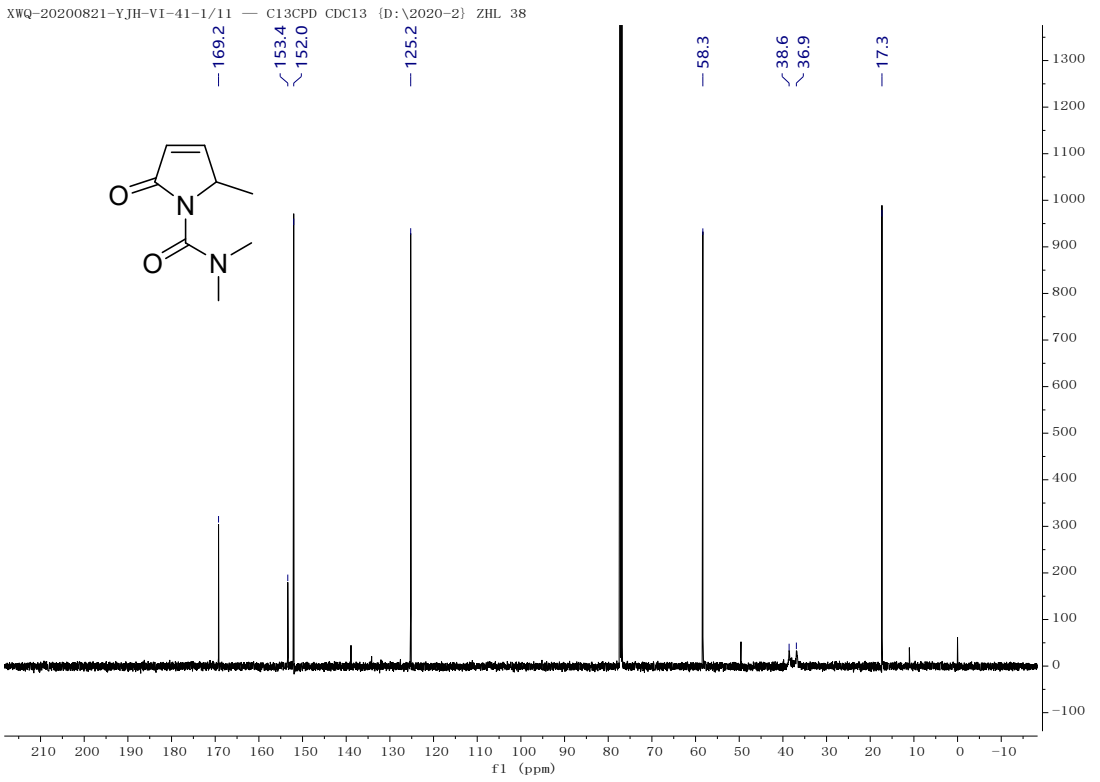
^{13}C NMR spectrum of compound **13m** (126 MHz, Chloroform-*d*)



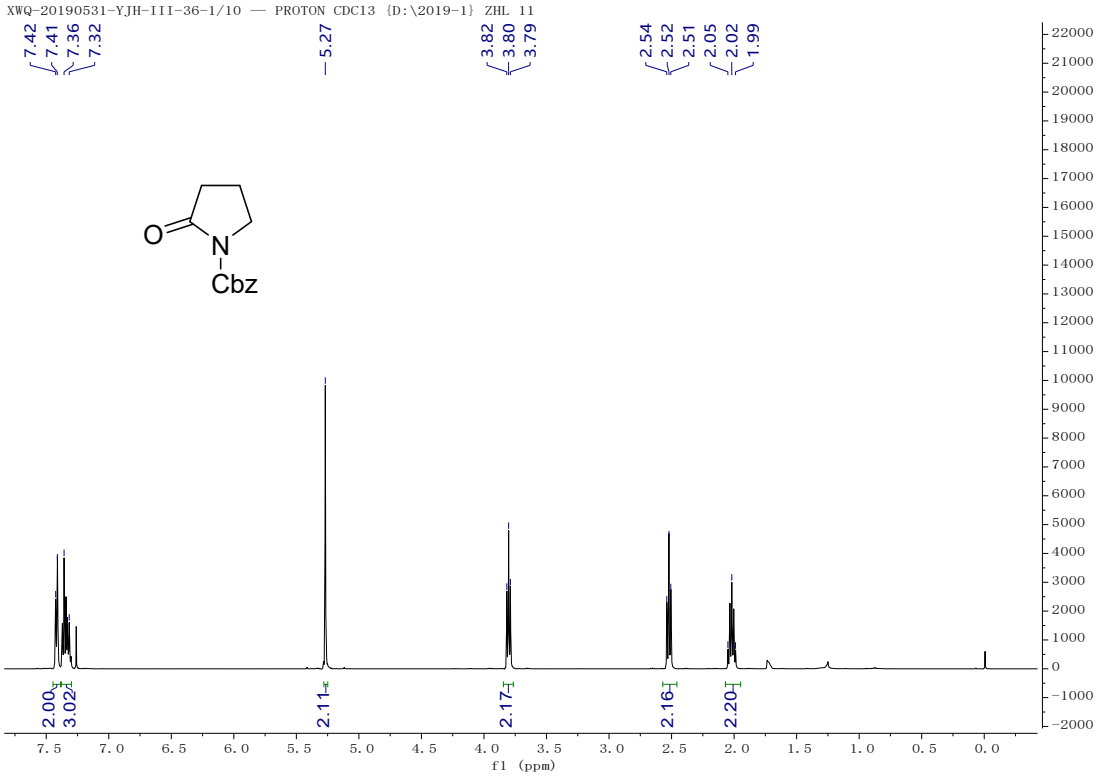
^{1}H NMR spectrum of compound **13n** (500 MHz, Chloroform-*d*)



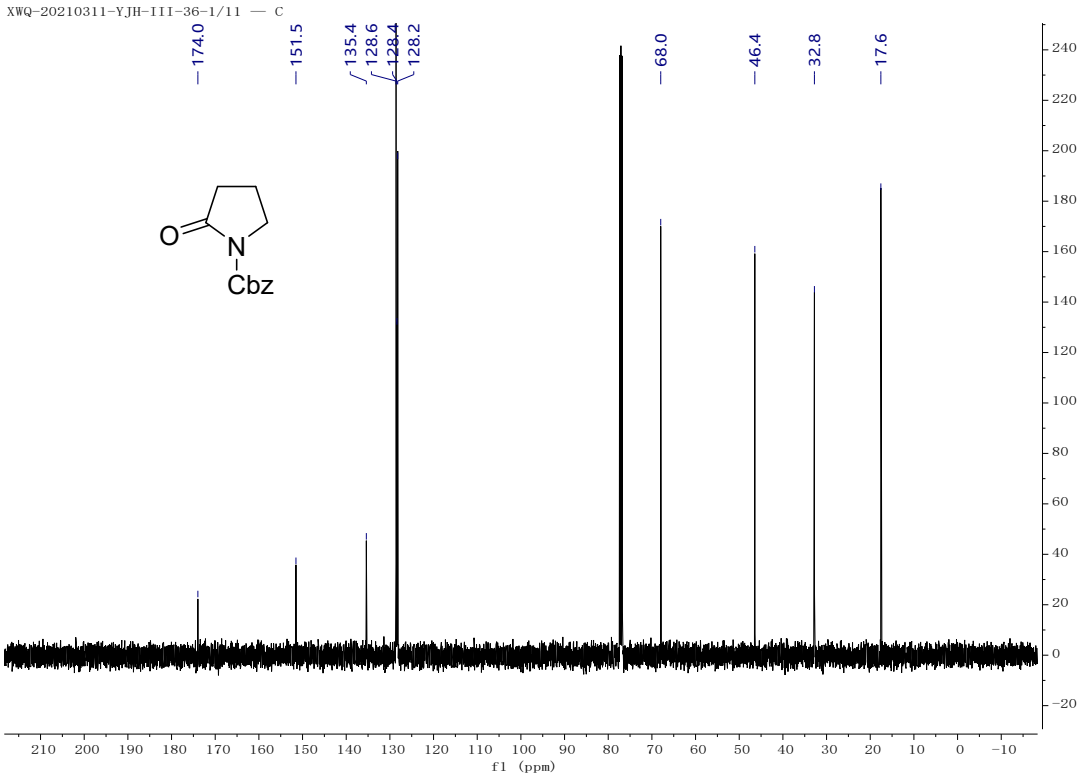
^{13}C NMR spectrum of compound **13n** (126 MHz, Chloroform-*d*)



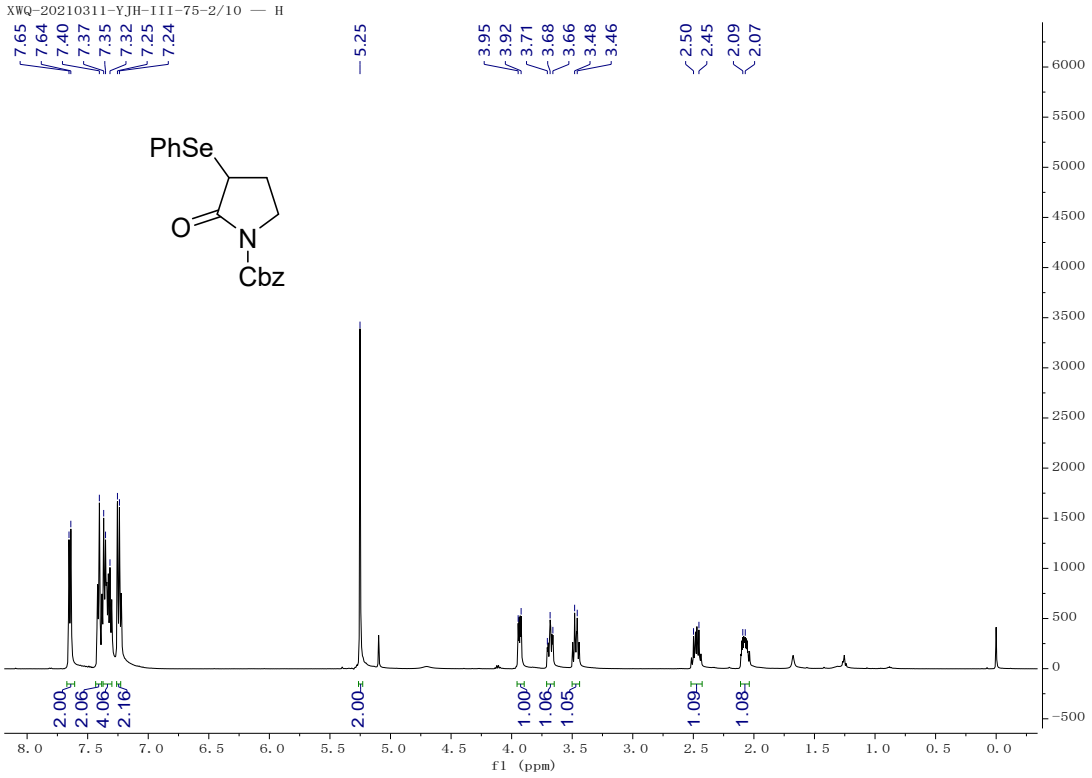
^{1}H NMR spectrum of compound **S8j** (500 MHz, Chloroform-*d*)



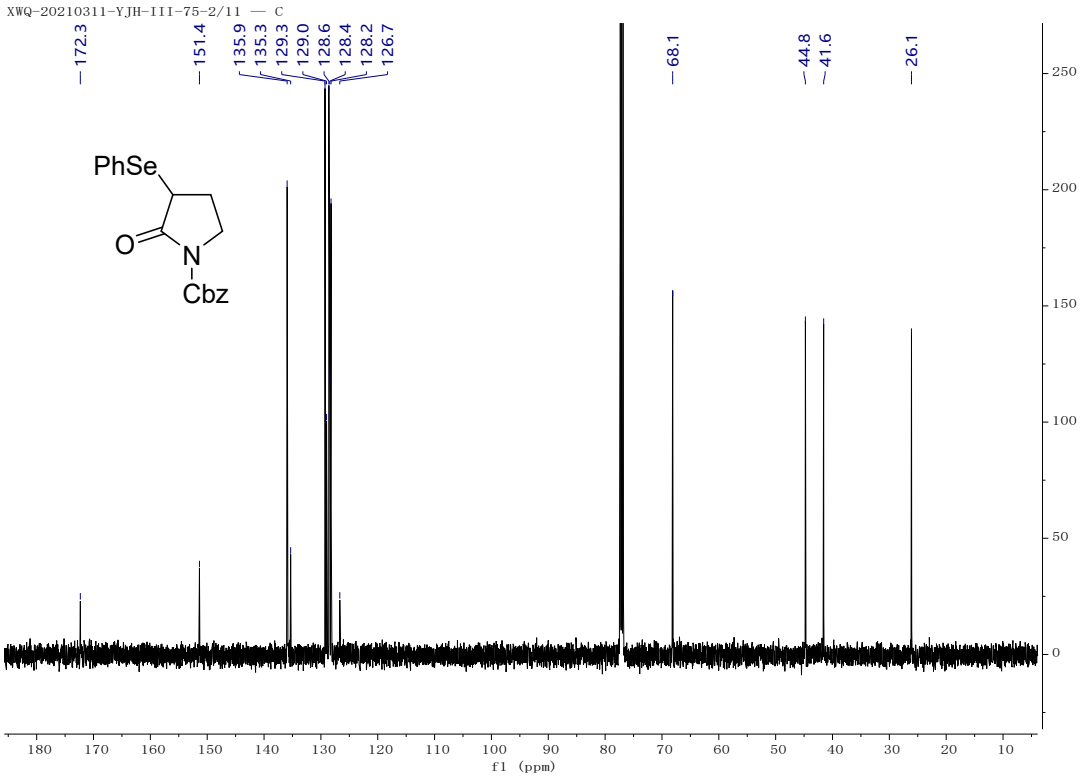
^{13}C NMR spectrum of compound **S8j** (126 MHz, Chloroform-*d*)



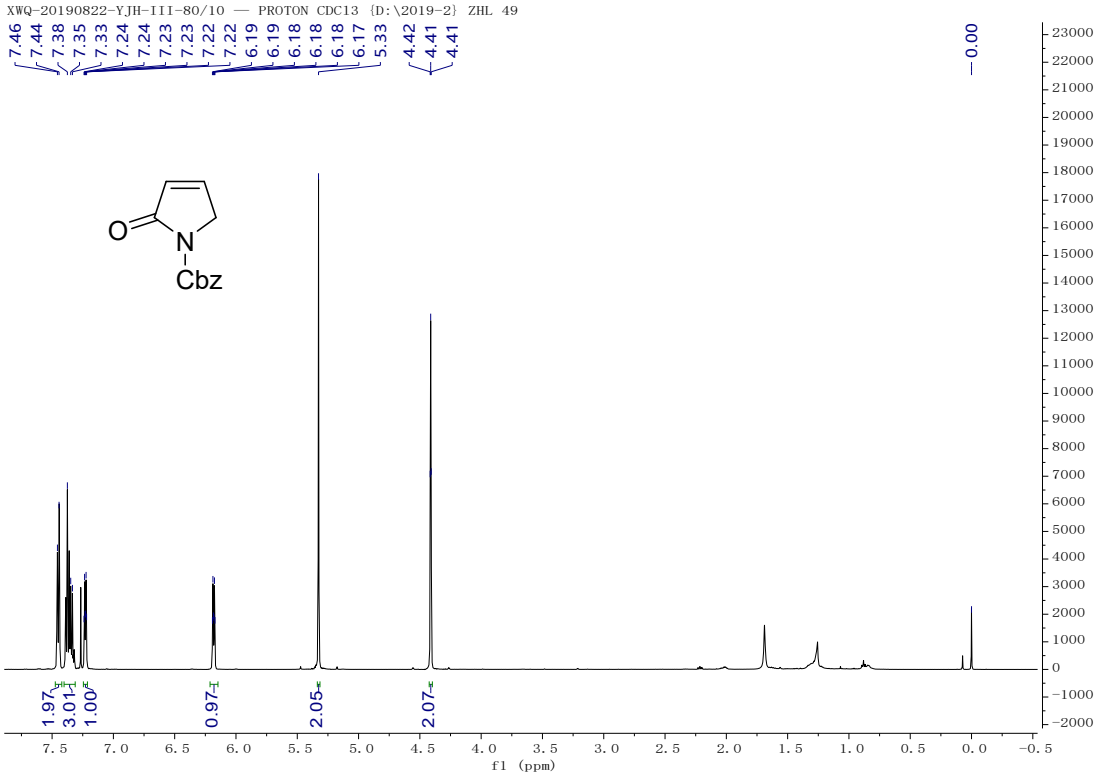
^{1}H NMR spectrum of compound **S9j** (500 MHz, Chloroform-*d*)



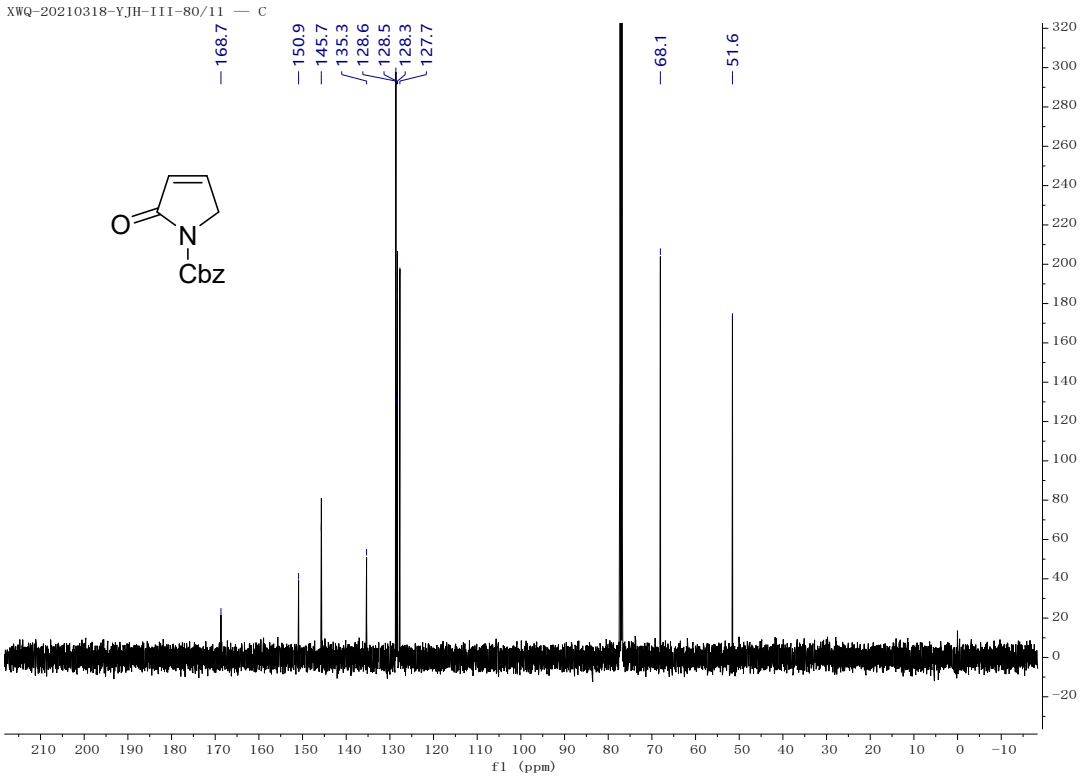
^{13}C NMR spectrum of compound **S9j** (126 MHz, Chloroform-*d*)



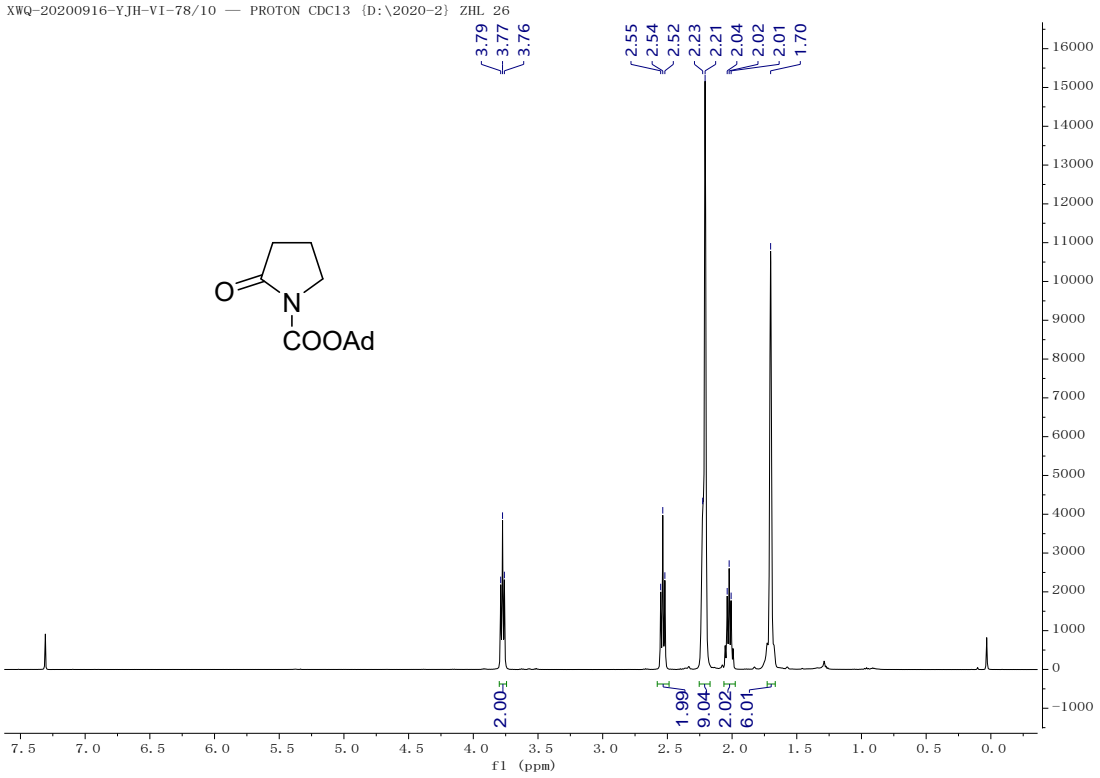
^{1}H NMR spectrum of compound **S10j** (500 MHz, Chloroform-*d*)



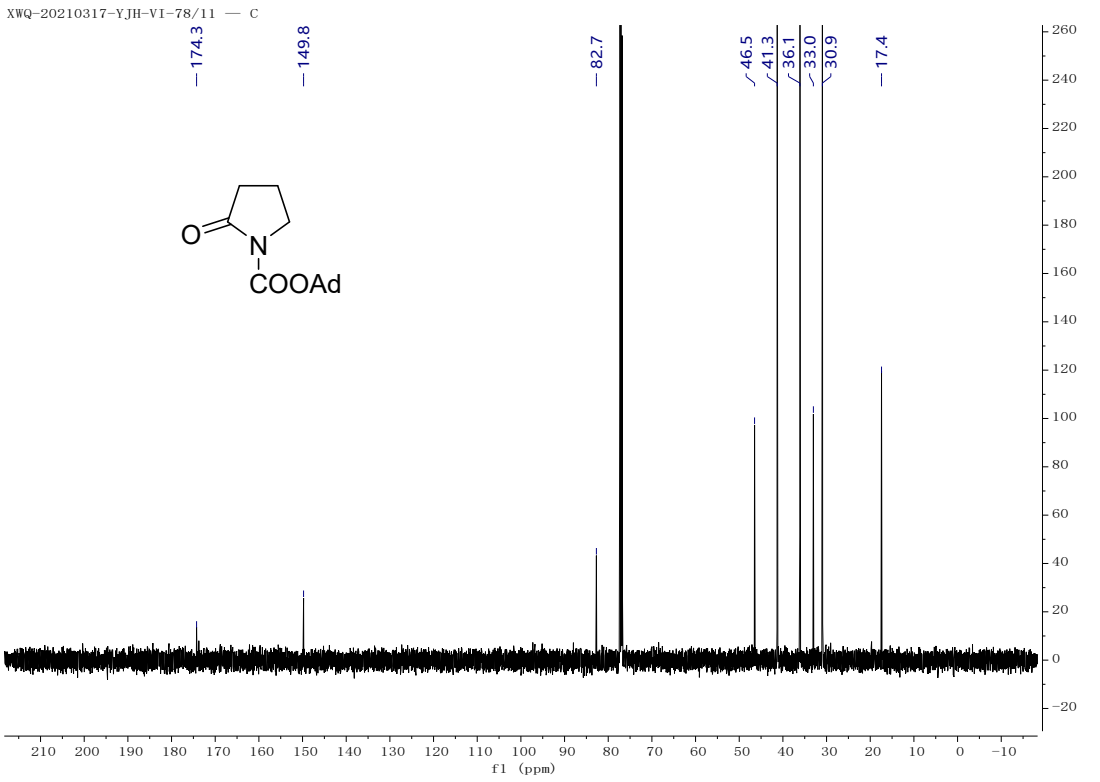
^{13}C NMR spectrum of compound **S10j** (126 MHz, Chloroform-*d*)



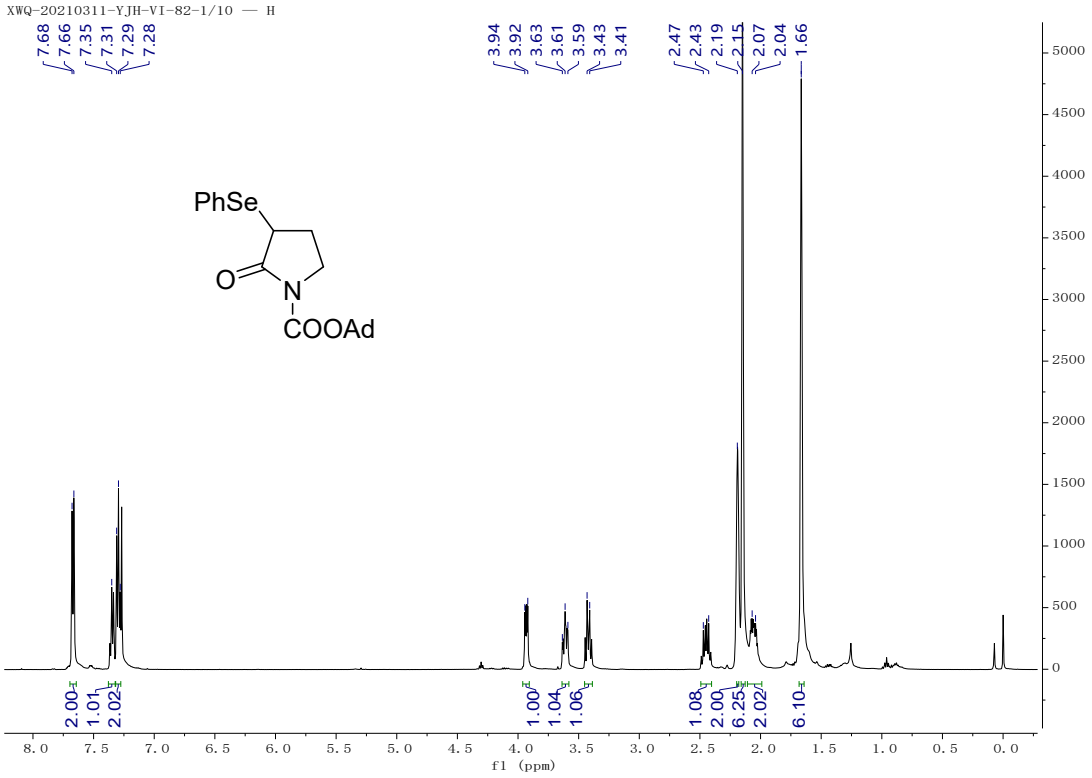
^{1}H NMR spectrum of compound **S8k** (500 MHz, Chloroform-*d*)



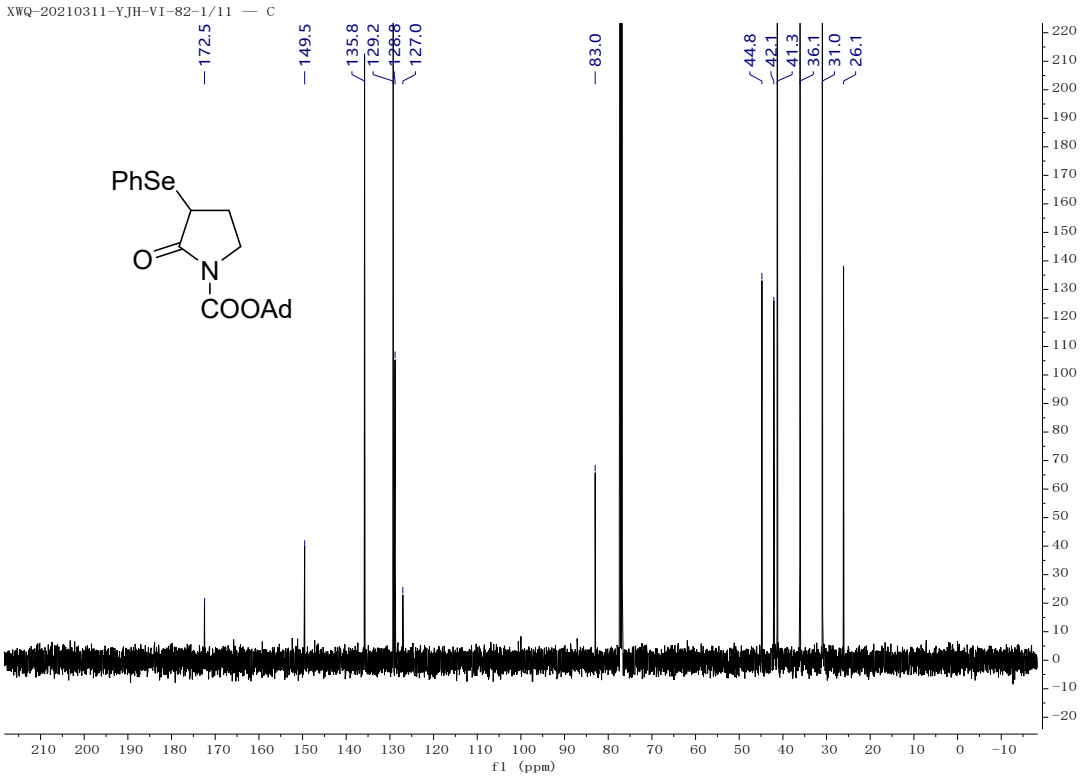
^{13}C NMR spectrum of compound **S8k** (126 MHz, Chloroform-*d*)



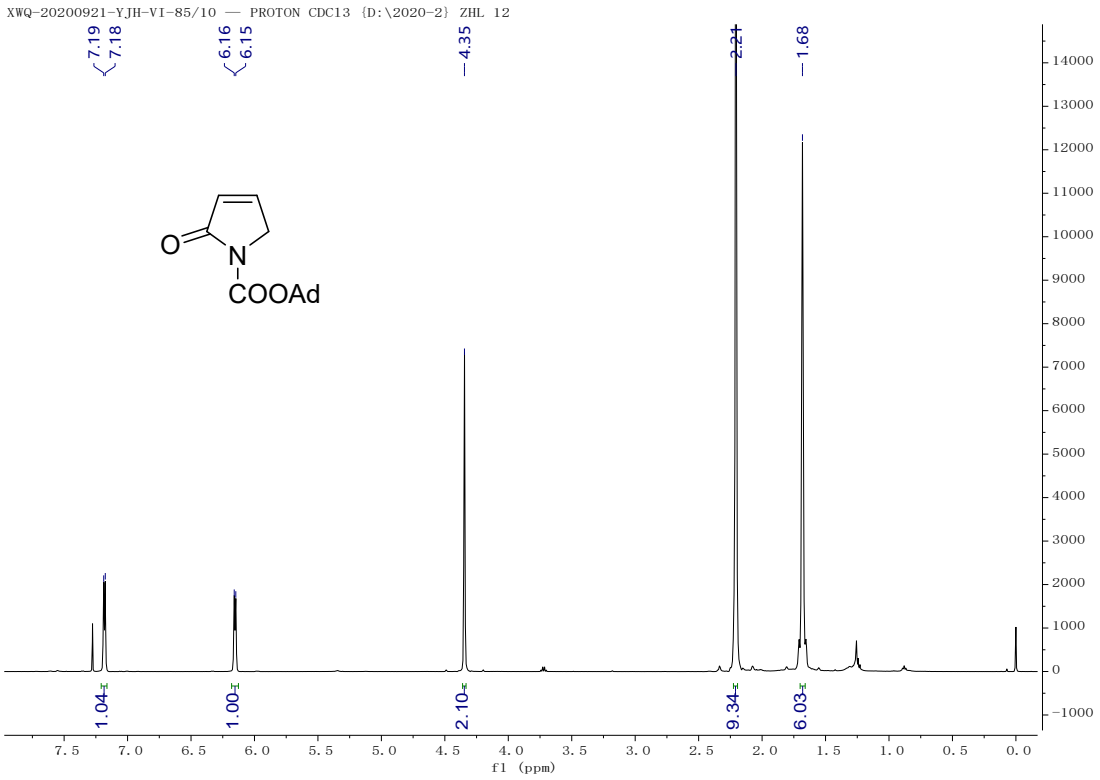
^{1}H NMR spectrum of compound **S9k** (500 MHz, Chloroform-*d*)



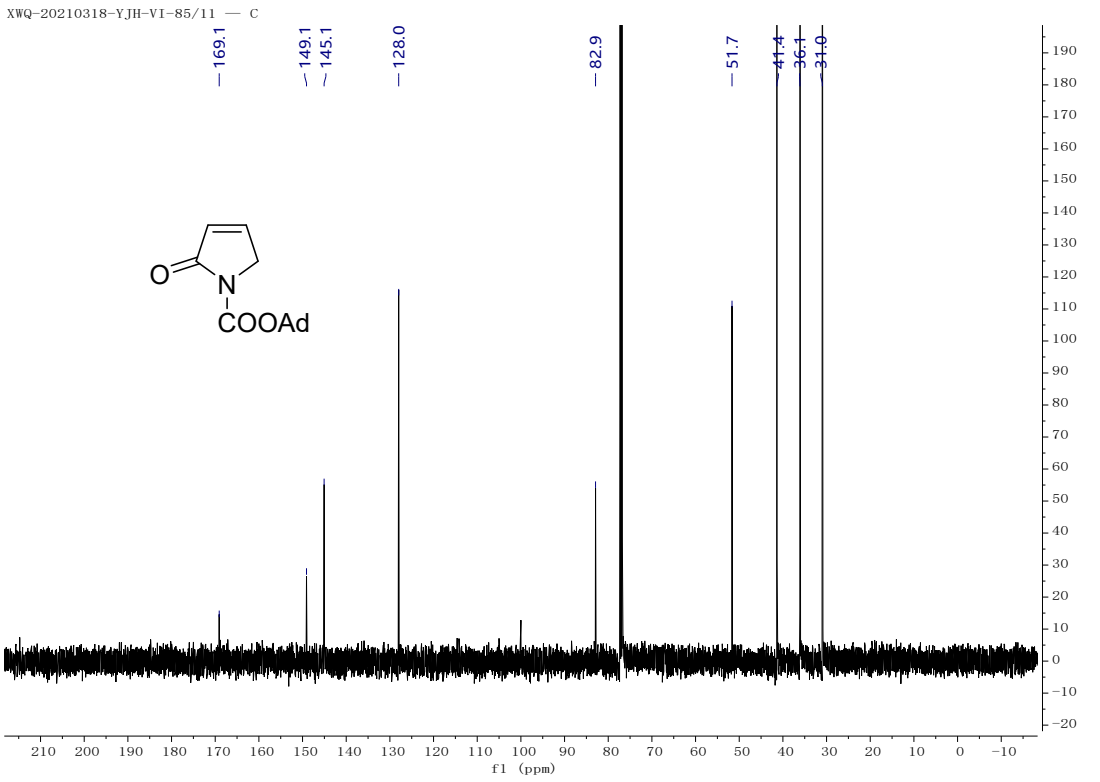
^{13}C NMR spectrum of compound **S9k** (126 MHz, Chloroform-*d*)



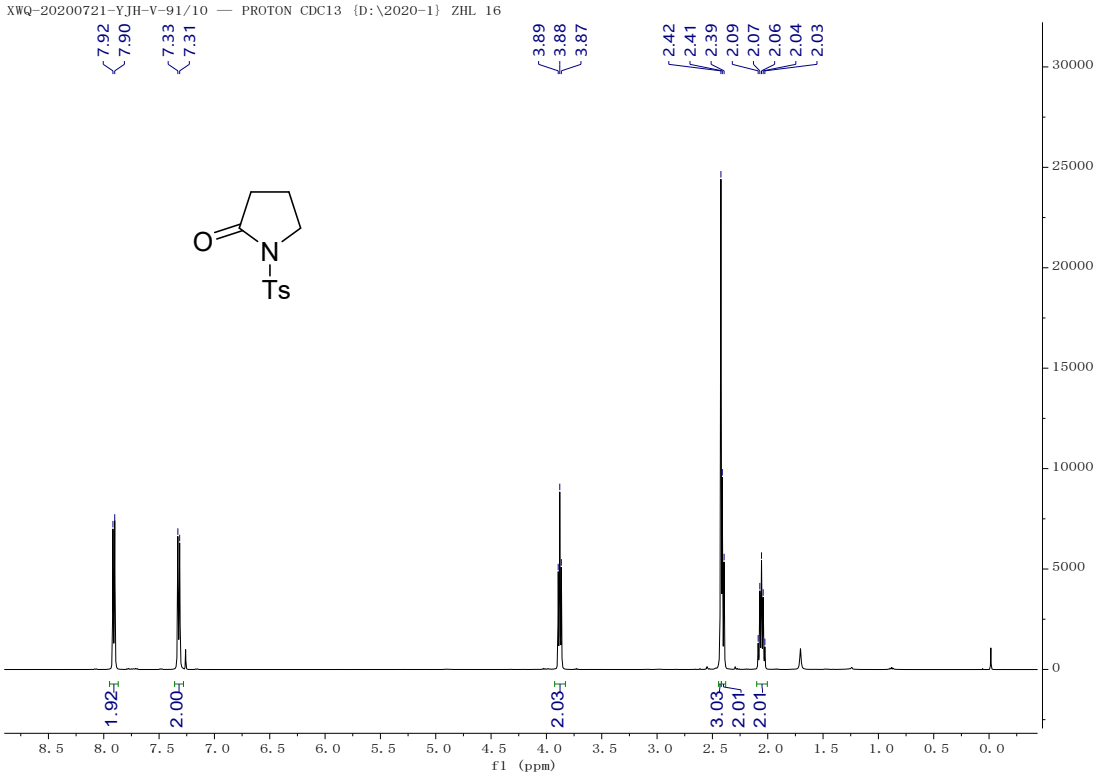
^{1}H NMR spectrum of compound **S10k** (500 MHz, Chloroform-*d*)



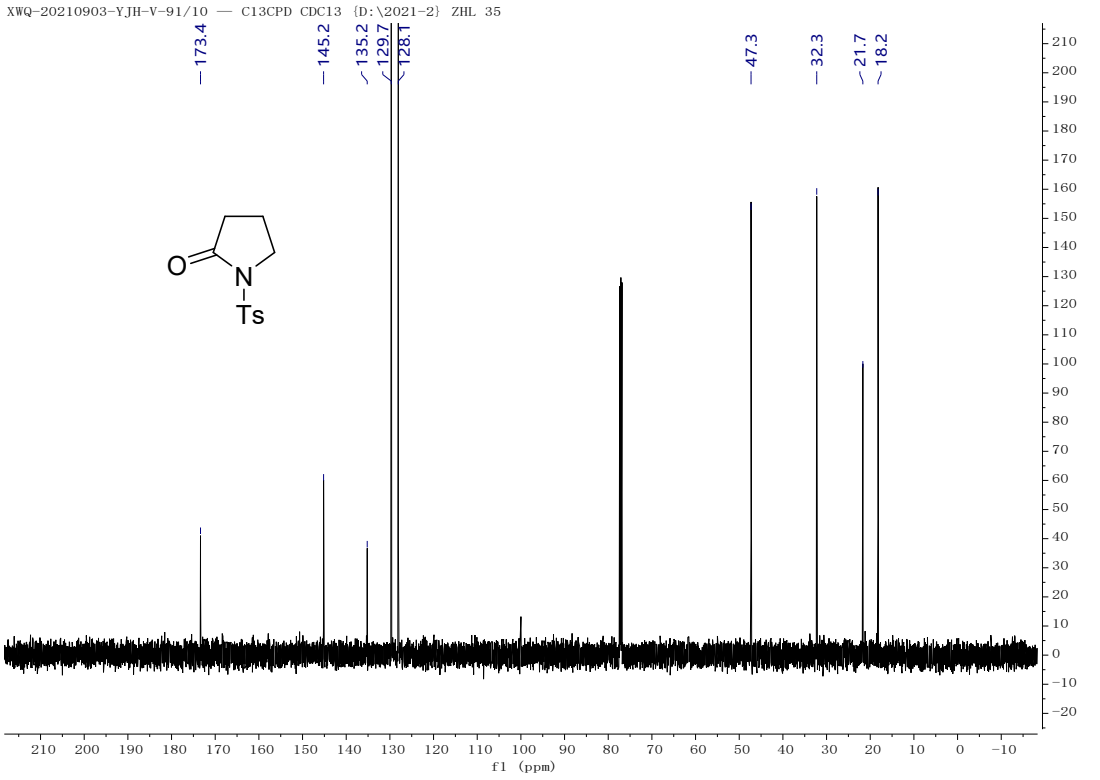
^{13}C NMR spectrum of compound **S10k** (126 MHz, Chloroform-*d*)



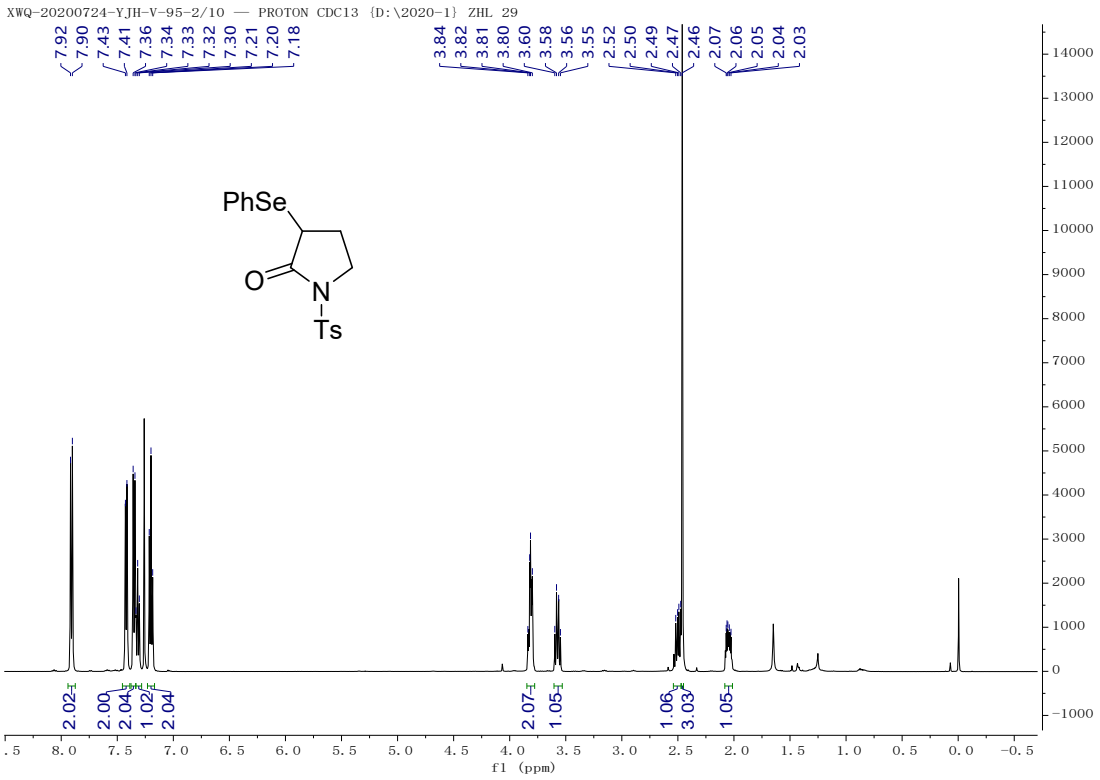
^{1}H NMR spectrum of compound **S8l** (500 MHz, Chloroform-*d*)



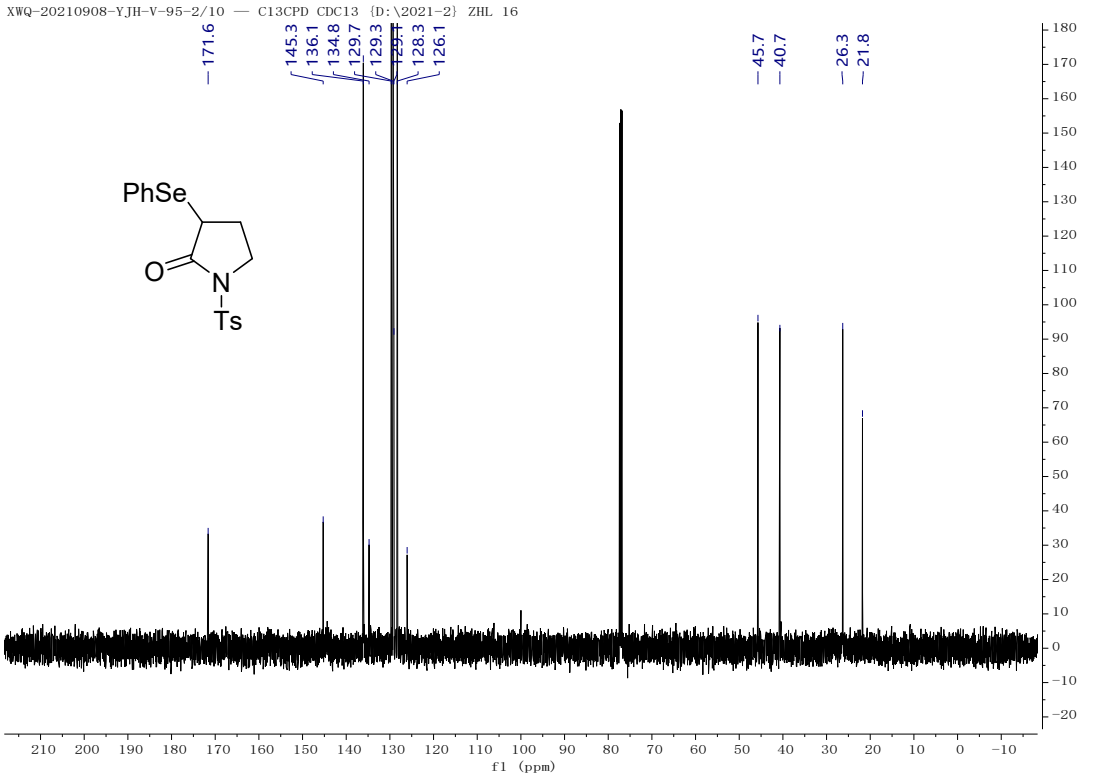
^{13}C NMR spectrum of compound **S8l** (126 MHz, Chloroform-*d*)



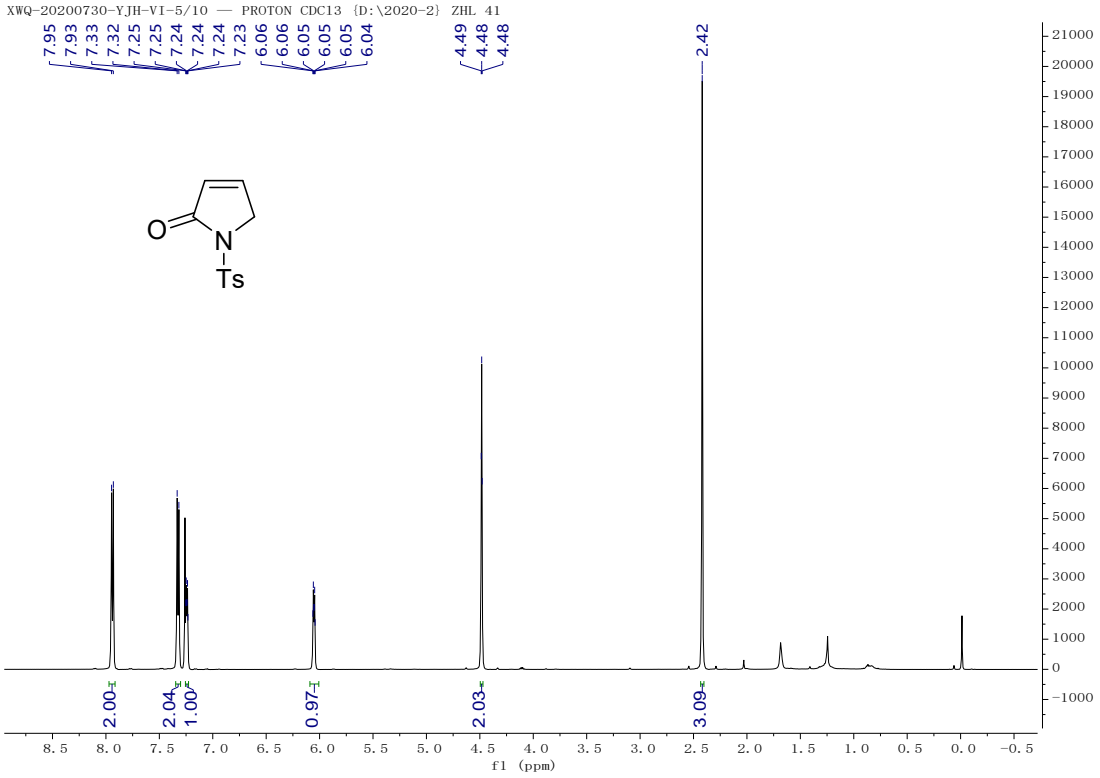
^{1}H NMR spectrum of compound **S9l** (500 MHz, Chloroform-*d*)



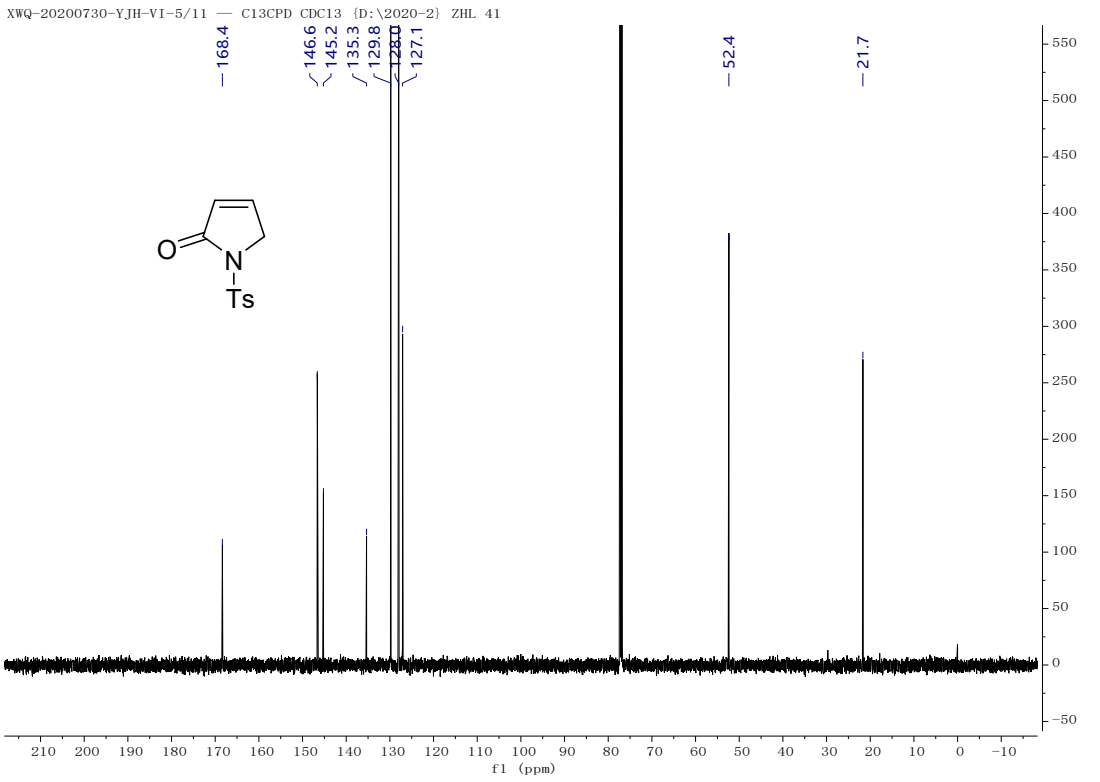
^{13}C NMR spectrum of compound **S9l** (126 MHz, Chloroform-*d*)



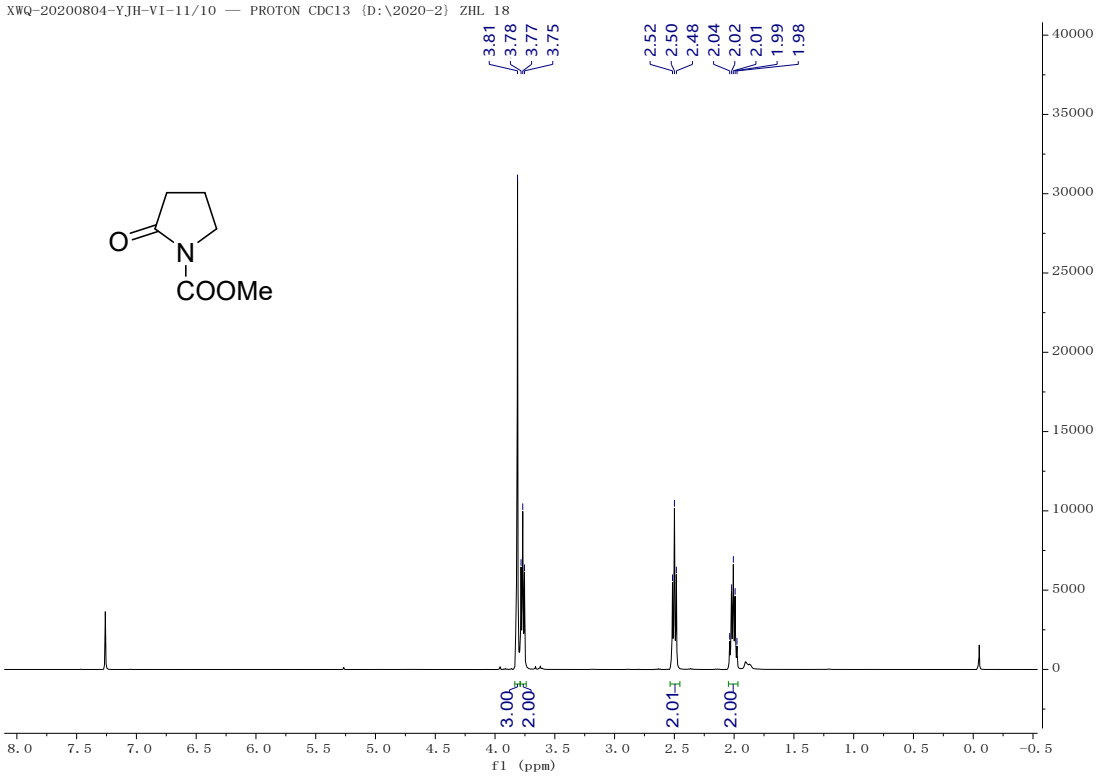
^{1}H NMR spectrum of compound **S10l** (500 MHz, Chloroform-*d*)



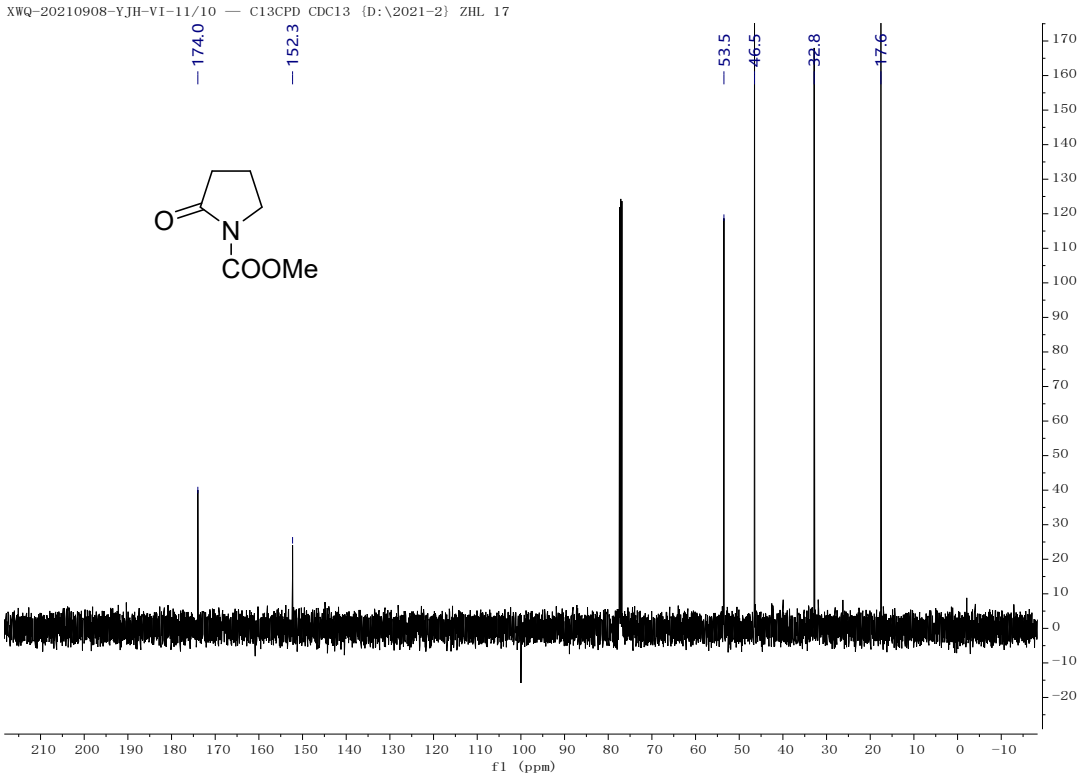
^{13}C NMR spectrum of compound **S10l** (126 MHz, Chloroform-*d*)



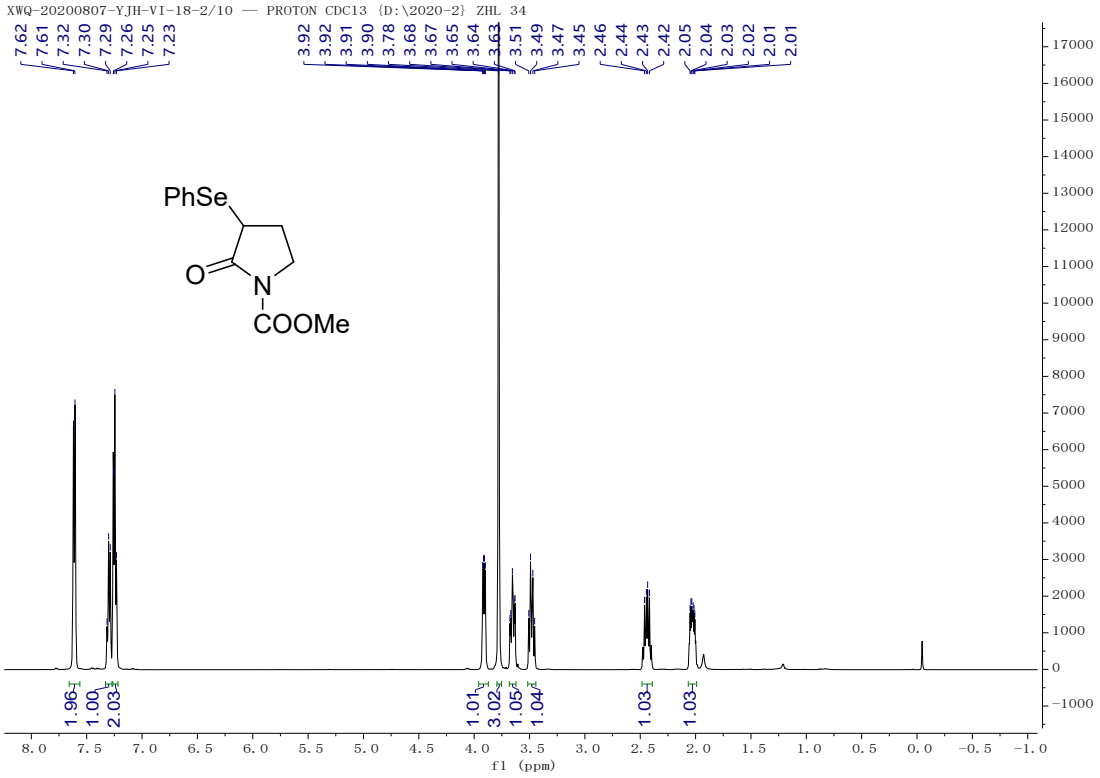
^{1}H NMR spectrum of compound **S8m** (500 MHz, Chloroform-*d*)



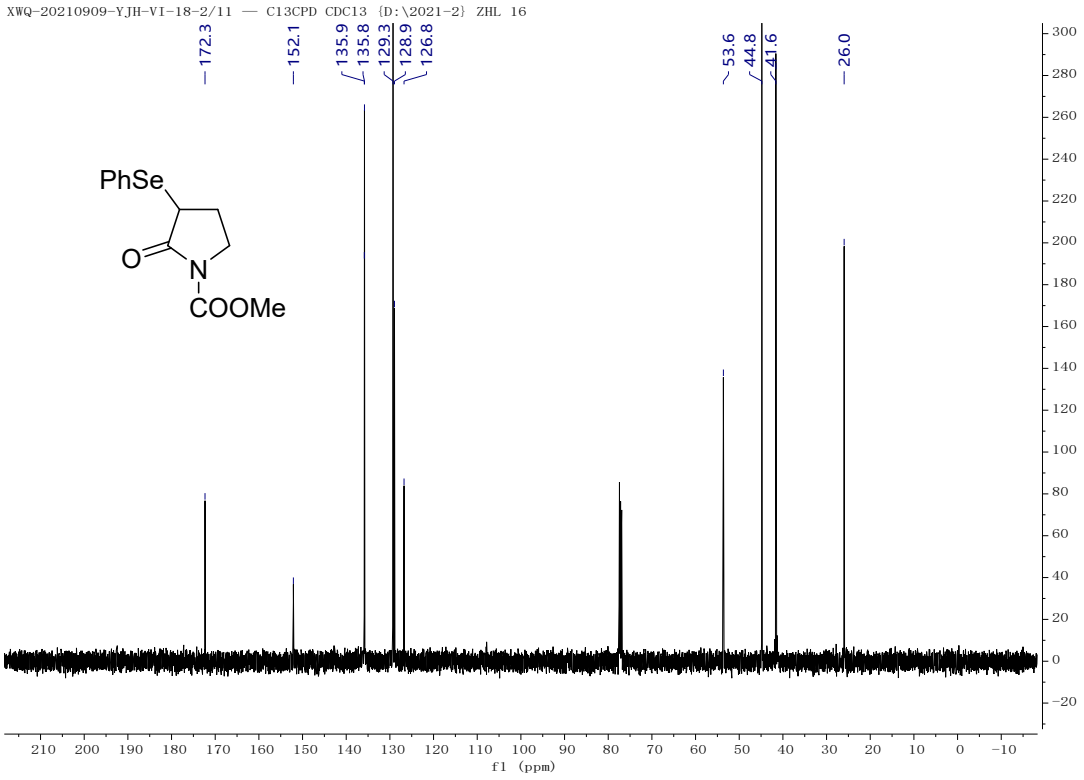
^{13}C NMR spectrum of compound **S8m** (126 MHz, Chloroform-*d*)



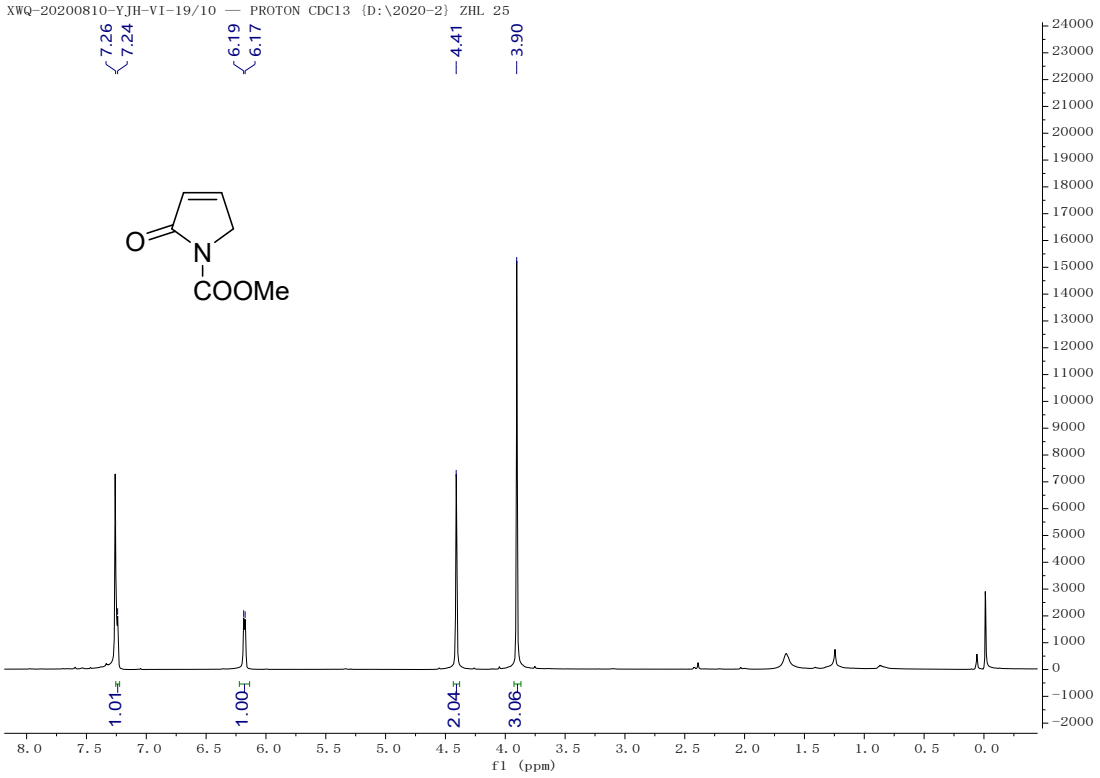
^{1}H NMR spectrum of compound **S9m** (500 MHz, Chloroform-*d*)



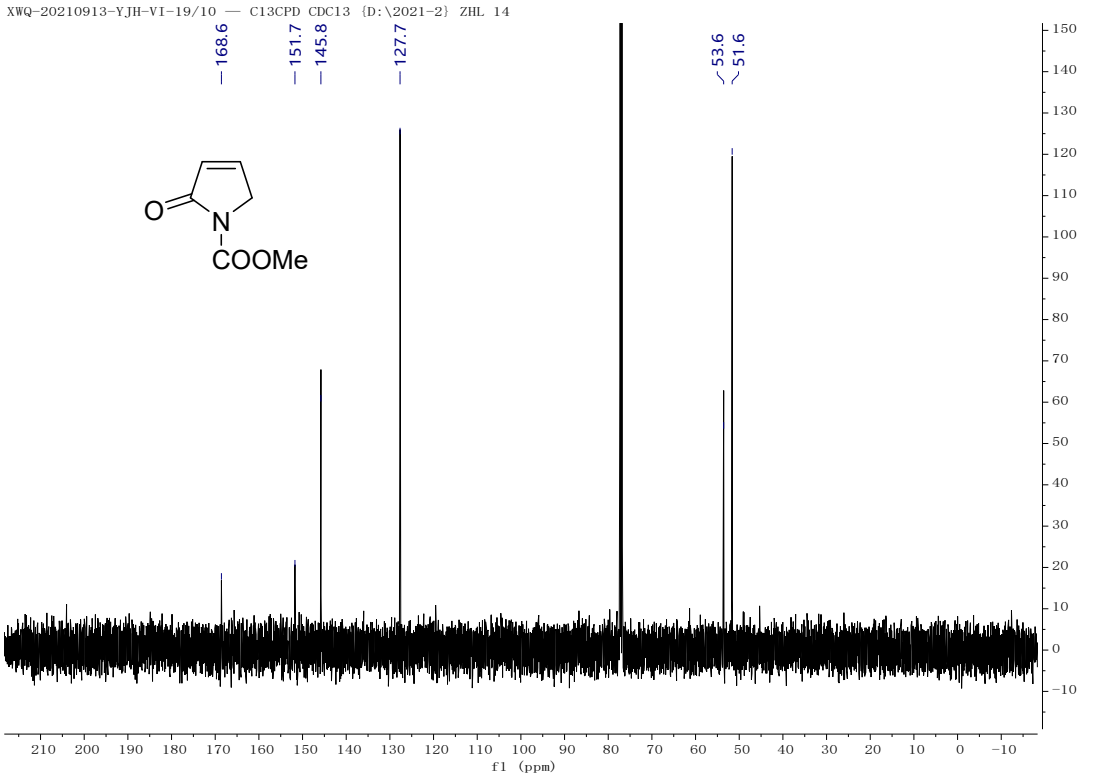
^{13}C NMR spectrum of compound **S9m** (126 MHz, Chloroform-*d*)



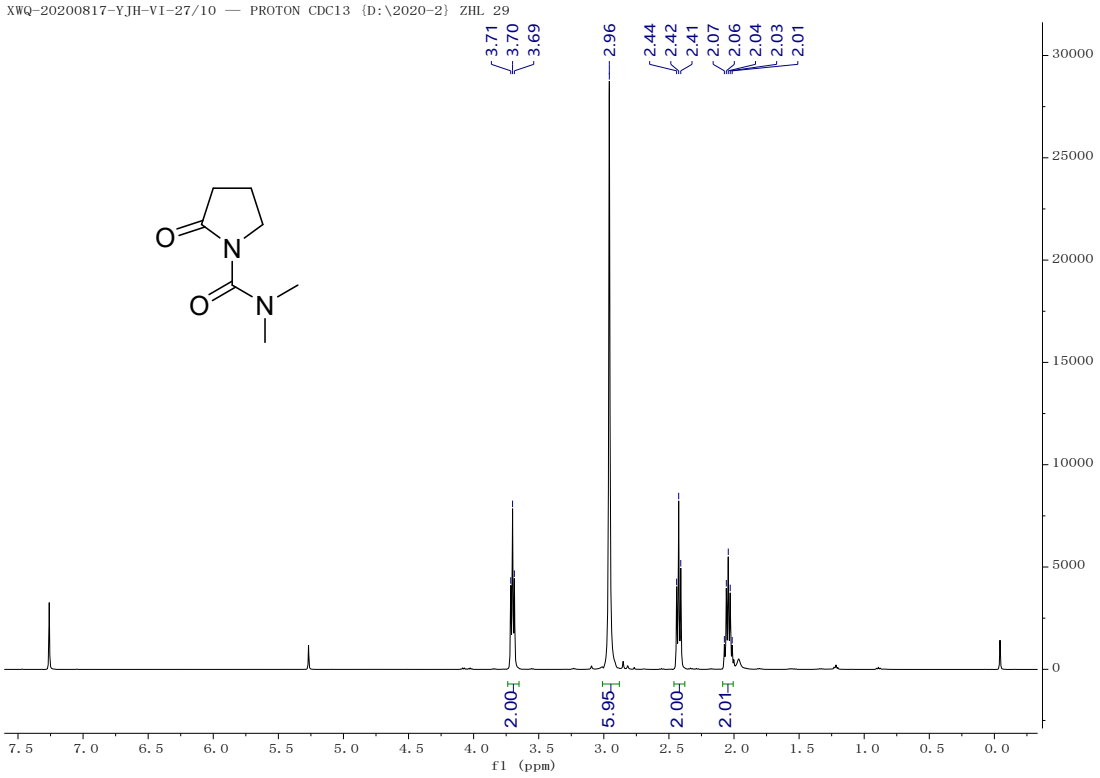
^{1}H NMR spectrum of compound **S10m** (500 MHz, Chloroform-*d*)



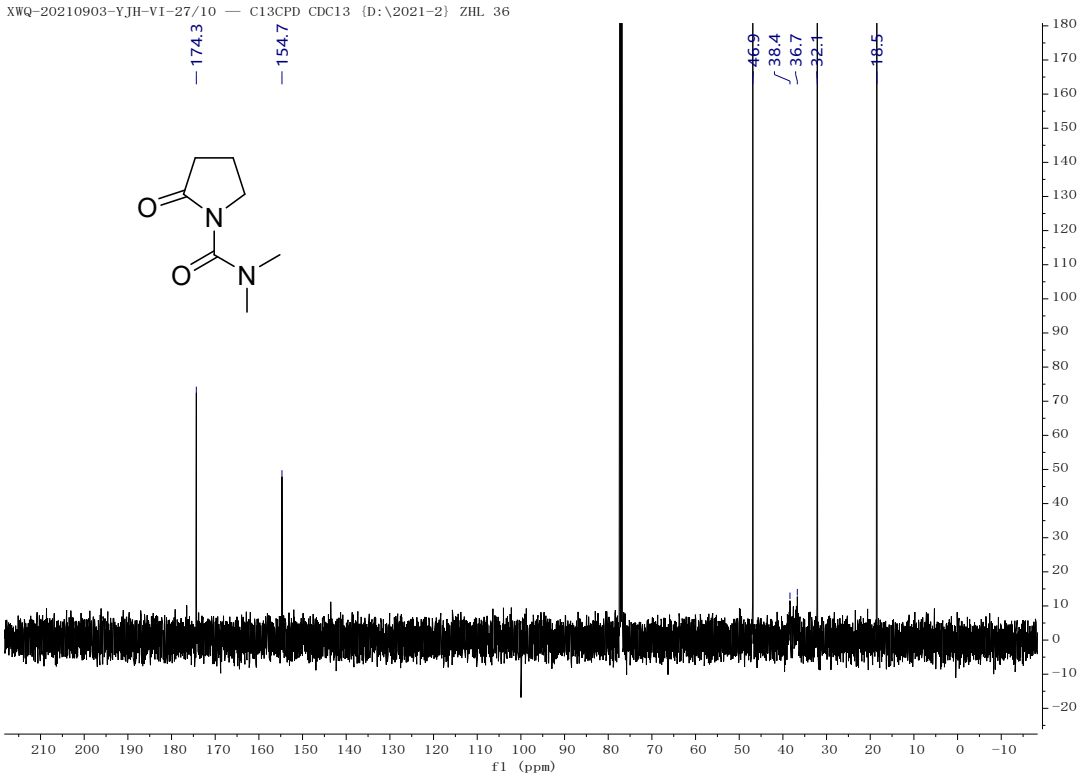
^{13}C NMR spectrum of compound **S10m** (126 MHz, Chloroform-*d*)



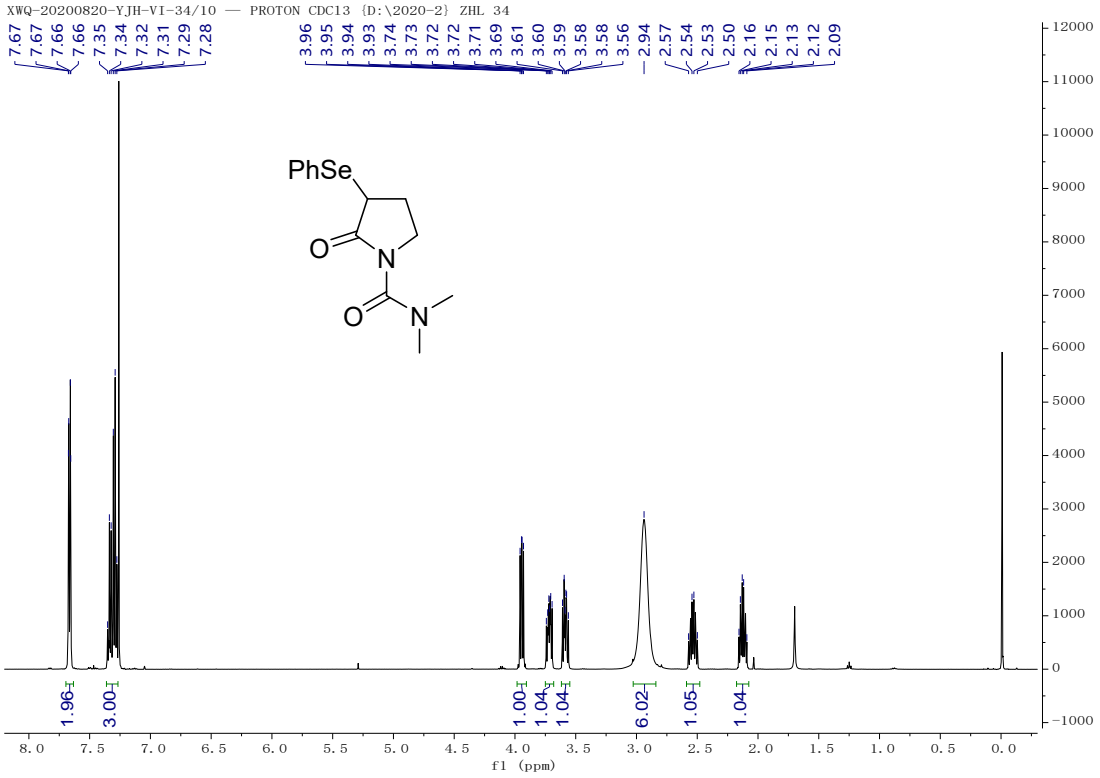
^{1}H NMR spectrum of compound **S8n** (500 MHz, Chloroform-*d*)



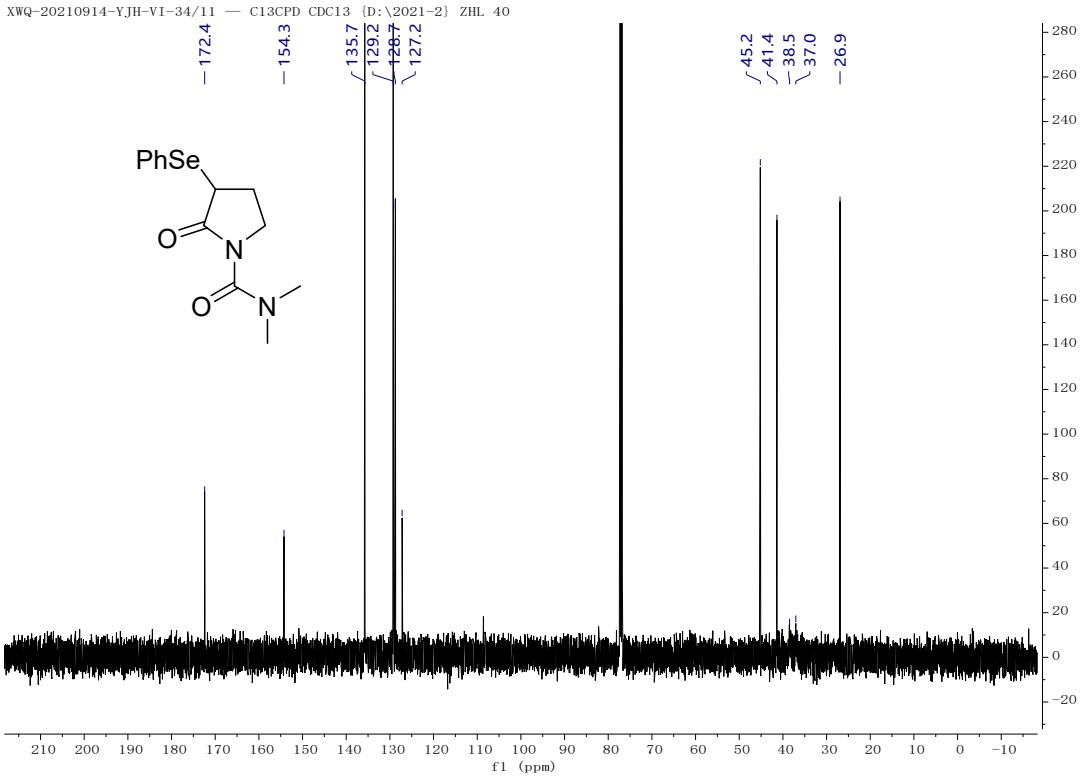
^{13}C NMR spectrum of compound **S8n** (126 MHz, Chloroform-*d*)



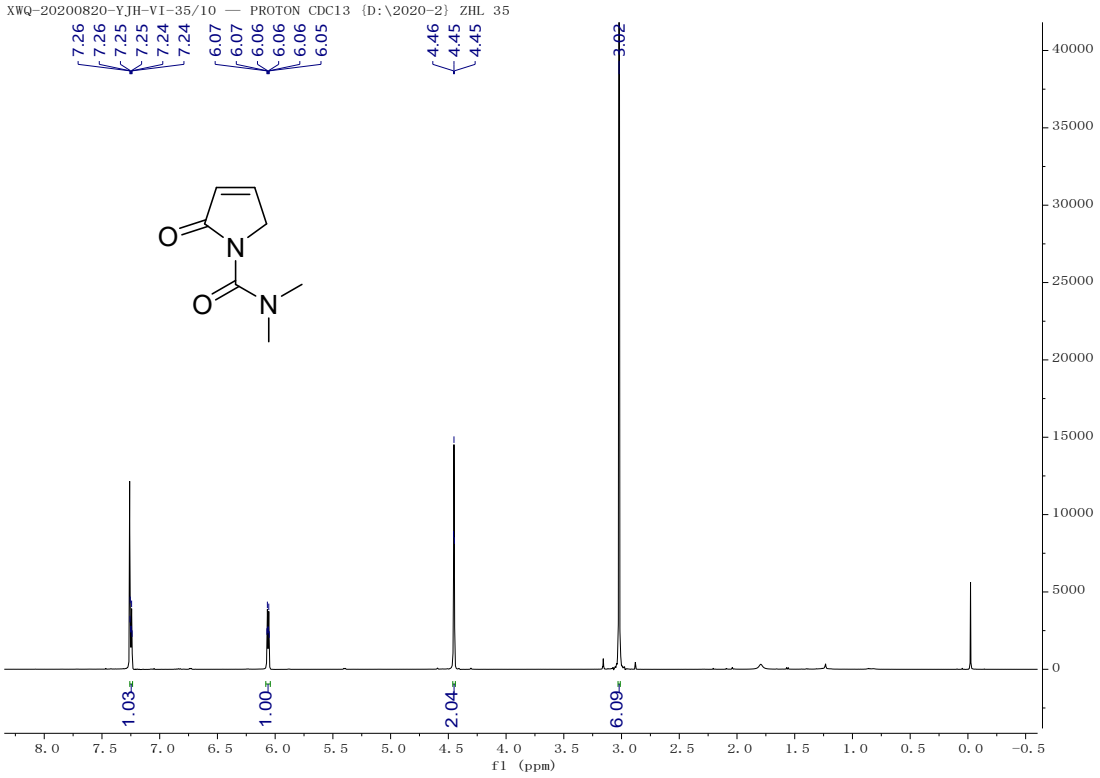
^{1}H NMR spectrum of compound **S9n** (500 MHz, Chloroform-*d*)



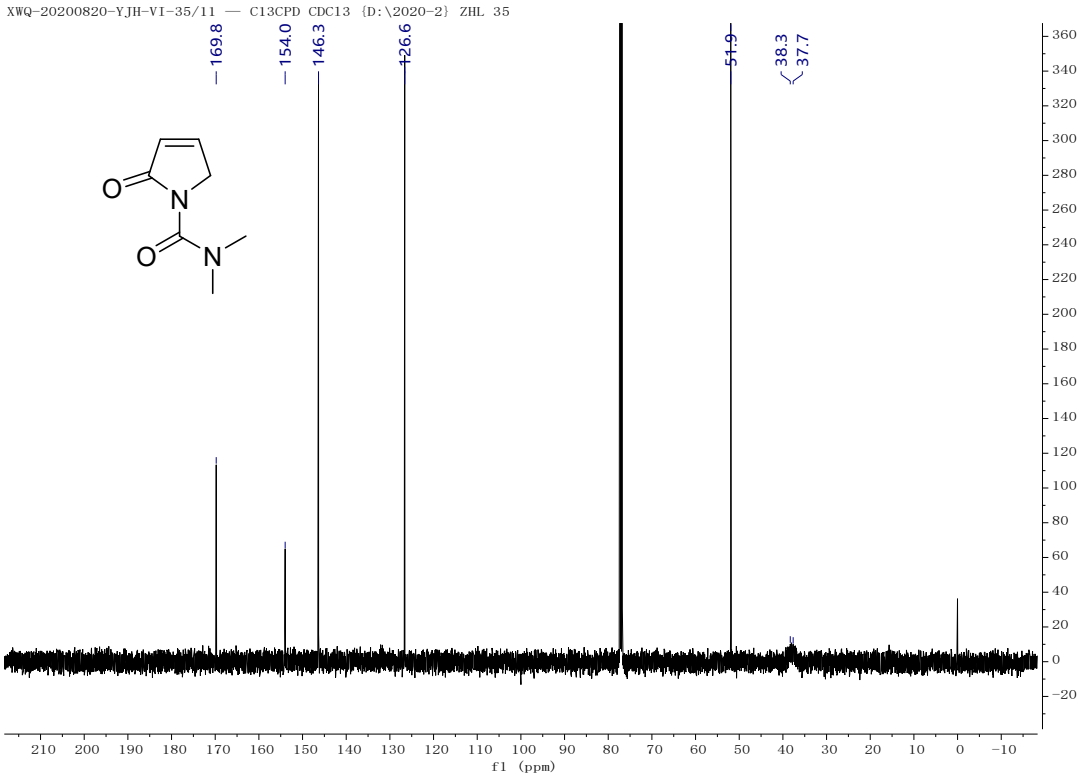
^{13}C NMR spectrum of compound **S9n** (126 MHz, Chloroform-*d*)



^{1}H NMR spectrum of compound **S10n** (500 MHz, Chloroform-*d*)

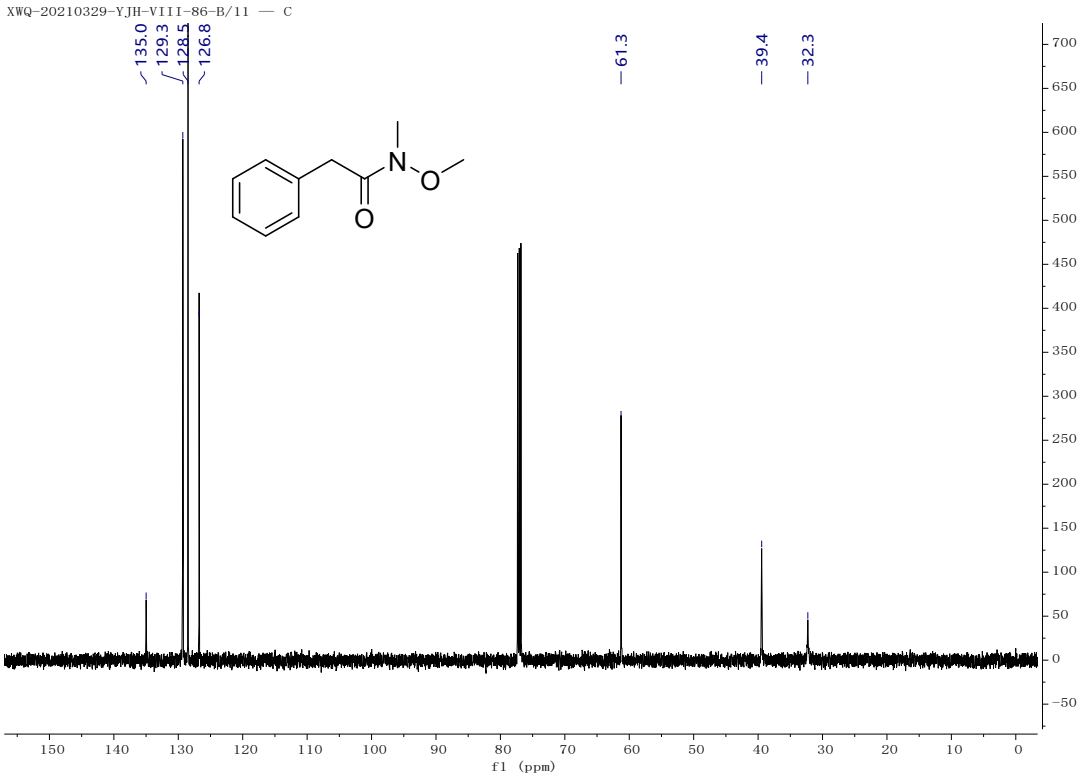


^{13}C NMR spectrum of compound **S10n** (126 MHz, Chloroform-*d*)

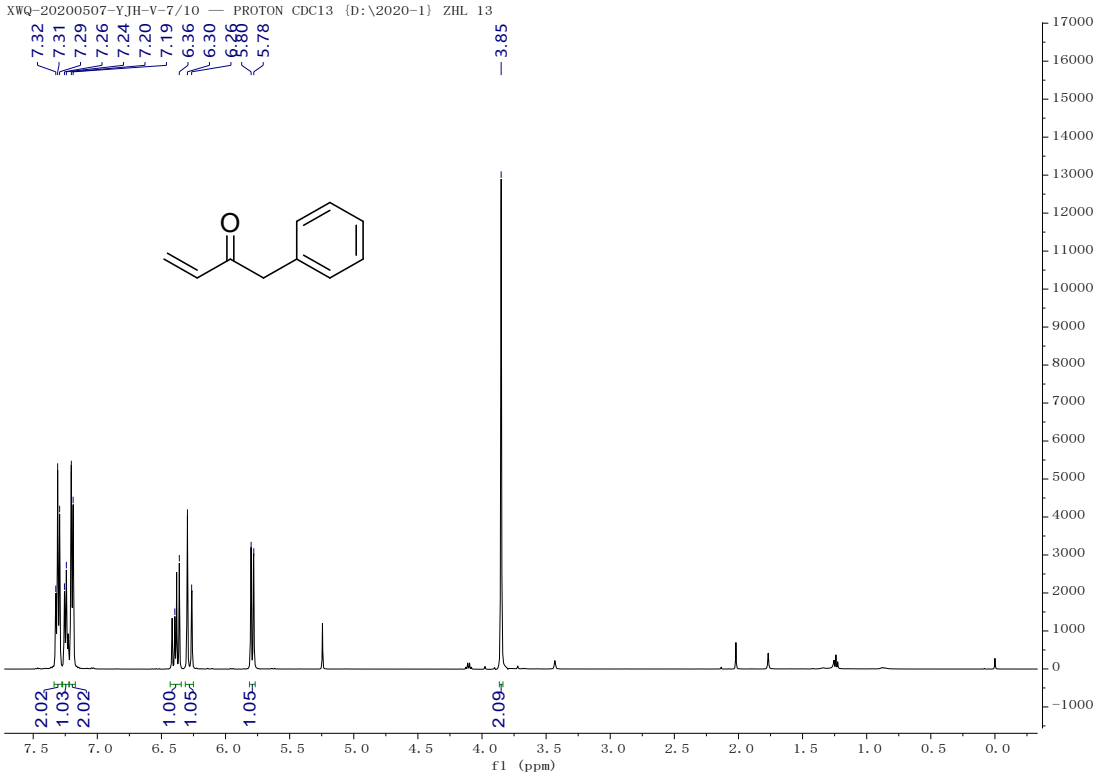


^{1}H NMR spectrum of compound **S12a** (500 MHz, Chloroform-*d*)

^{13}C NMR spectrum of compound **S12a** (126 MHz, Chloroform-*d*)

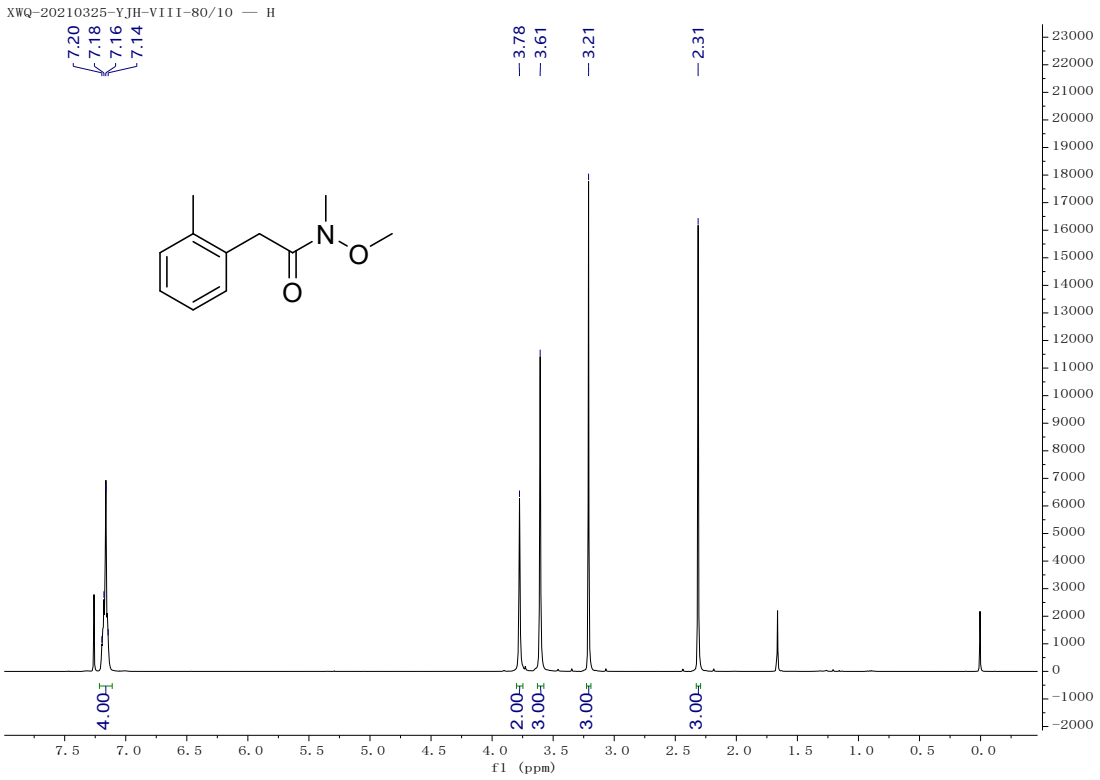


^{1}H NMR spectrum of compound **16a** (500 MHz, Chloroform-*d*)

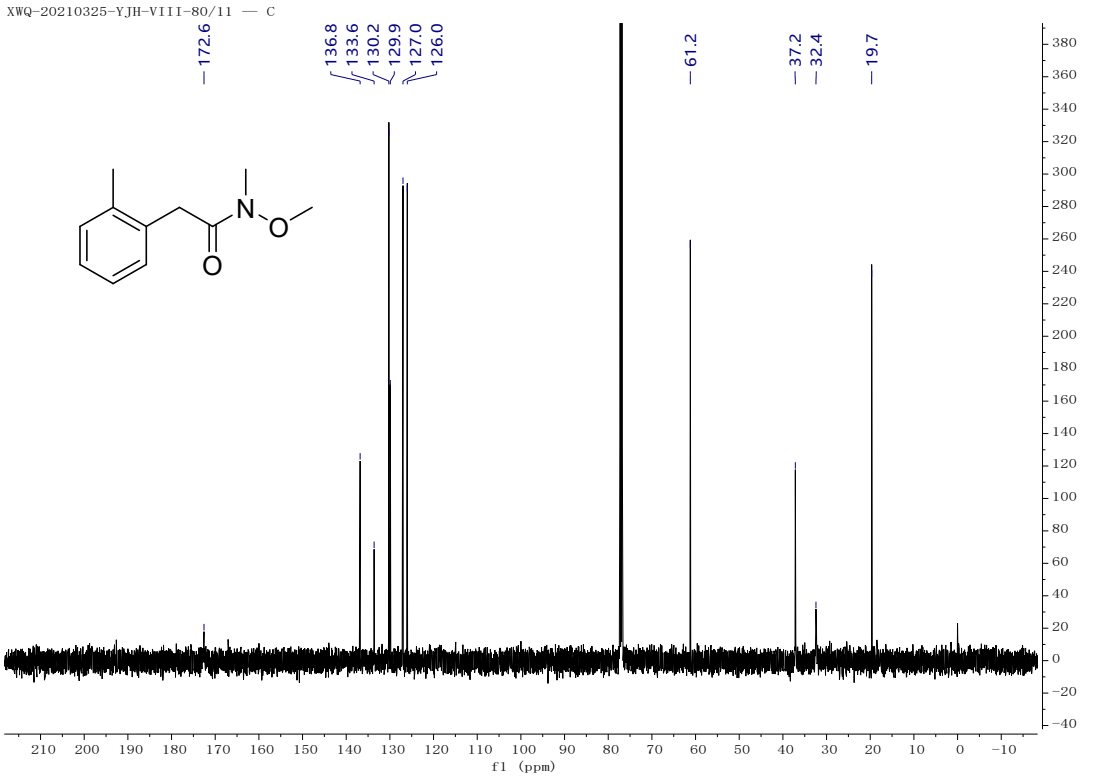


^{13}C NMR spectrum of compound **16a** (126 MHz, Chloroform-*d*)

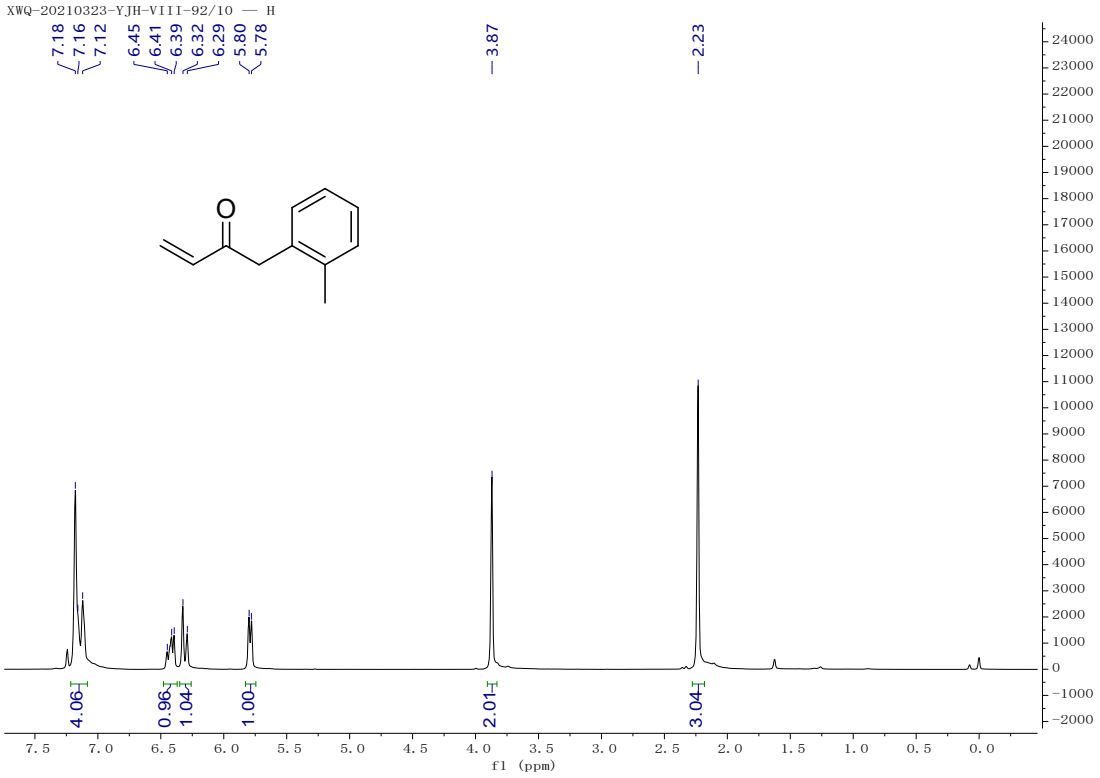
[1]H NMR spectrum of compound **S12d** (500 MHz, Chloroform-*d*)



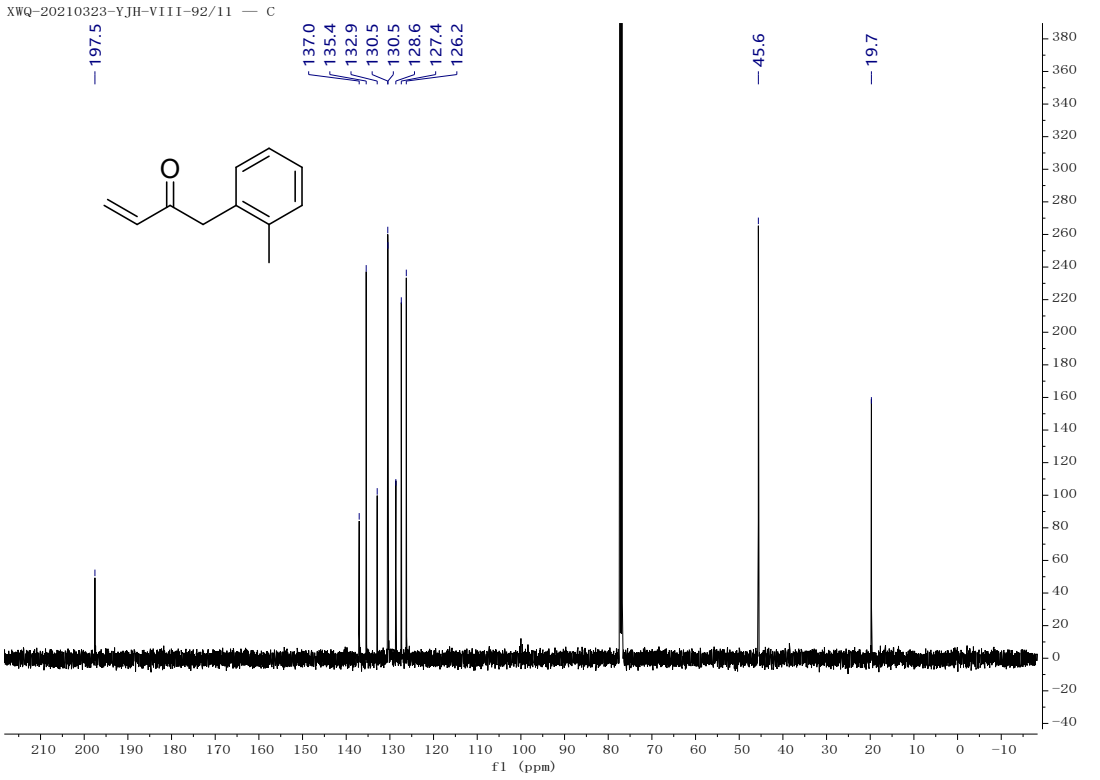
[13]C NMR spectrum of compound **S12d** (126 MHz, Chloroform-*d*)



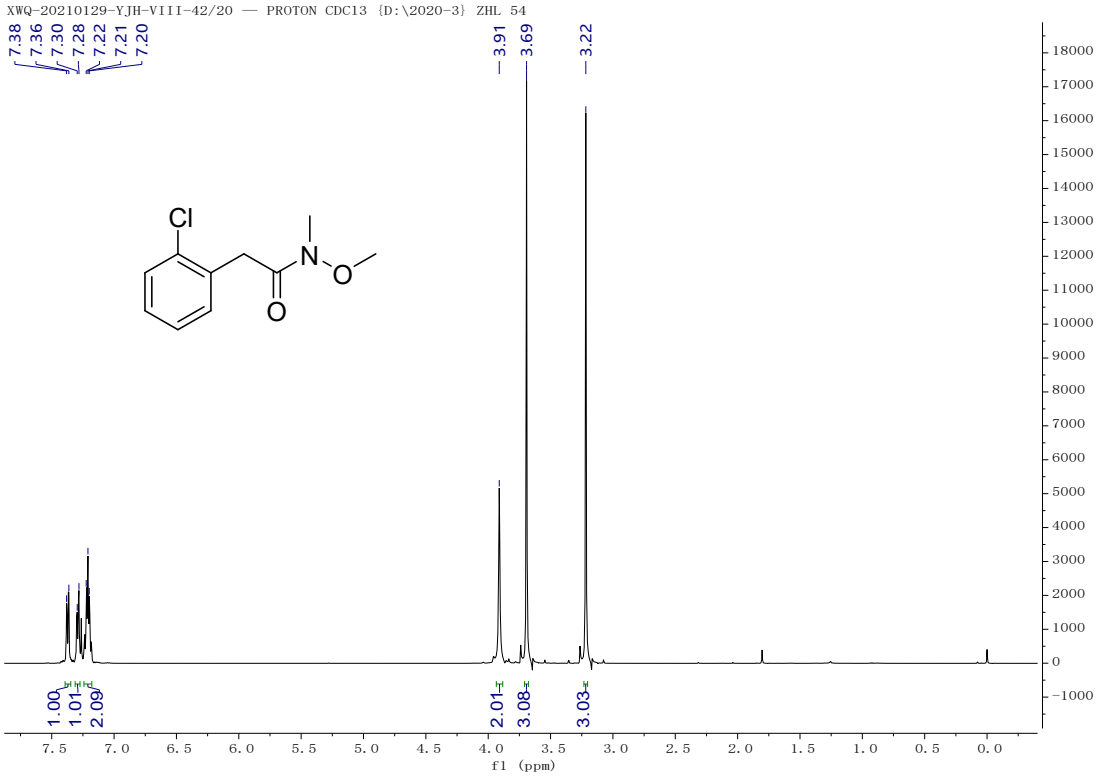
^{1}H NMR spectrum of compound **16d** (500 MHz, Chloroform-*d*)



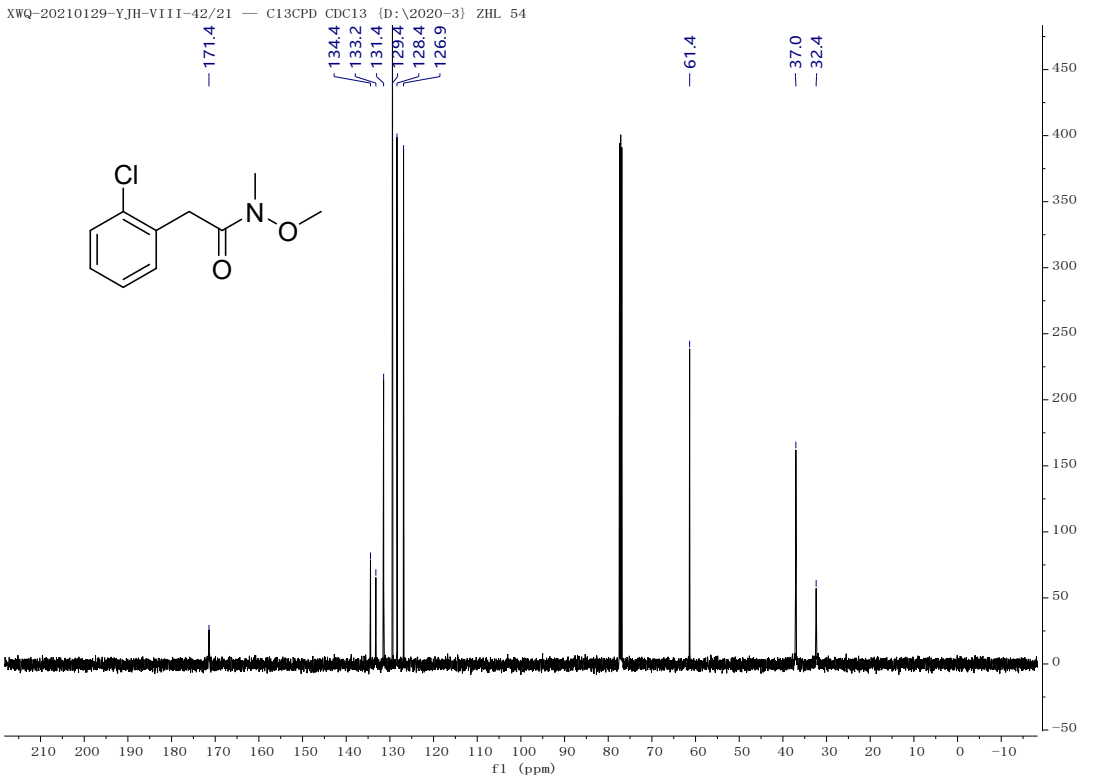
^{13}C NMR spectrum of compound **16d** (126 MHz, Chloroform-*d*)



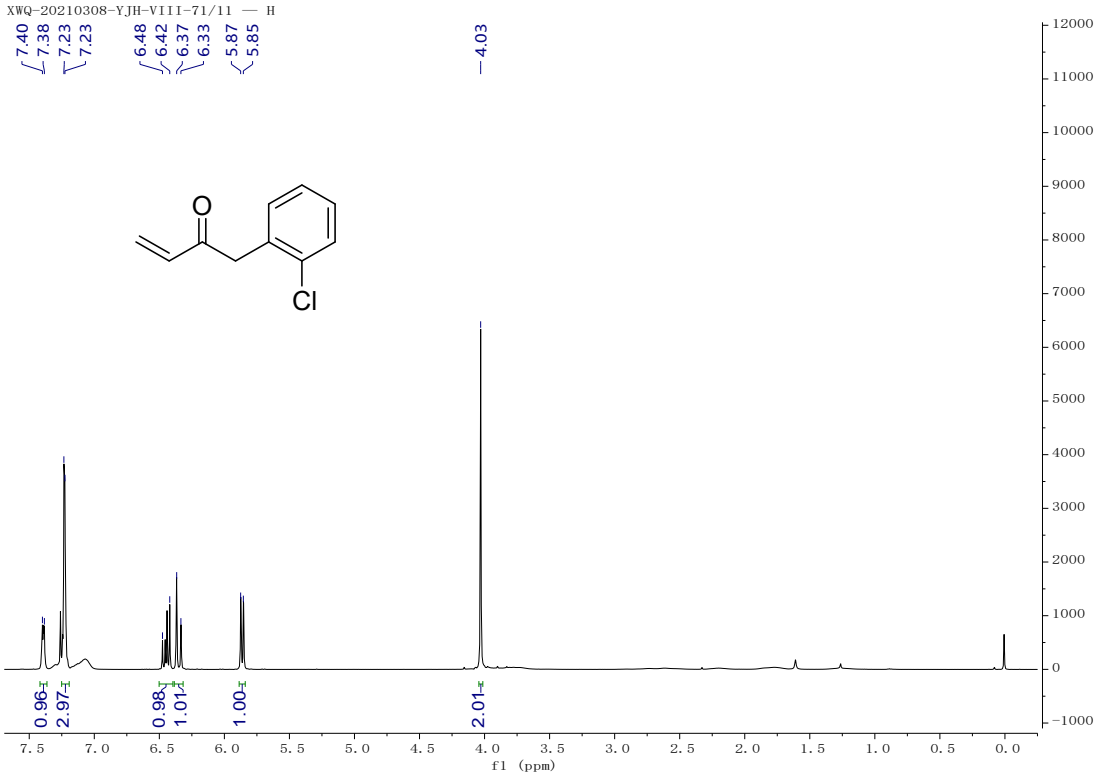
^{1}H NMR spectrum of compound **S12e** (500 MHz, Chloroform-*d*)



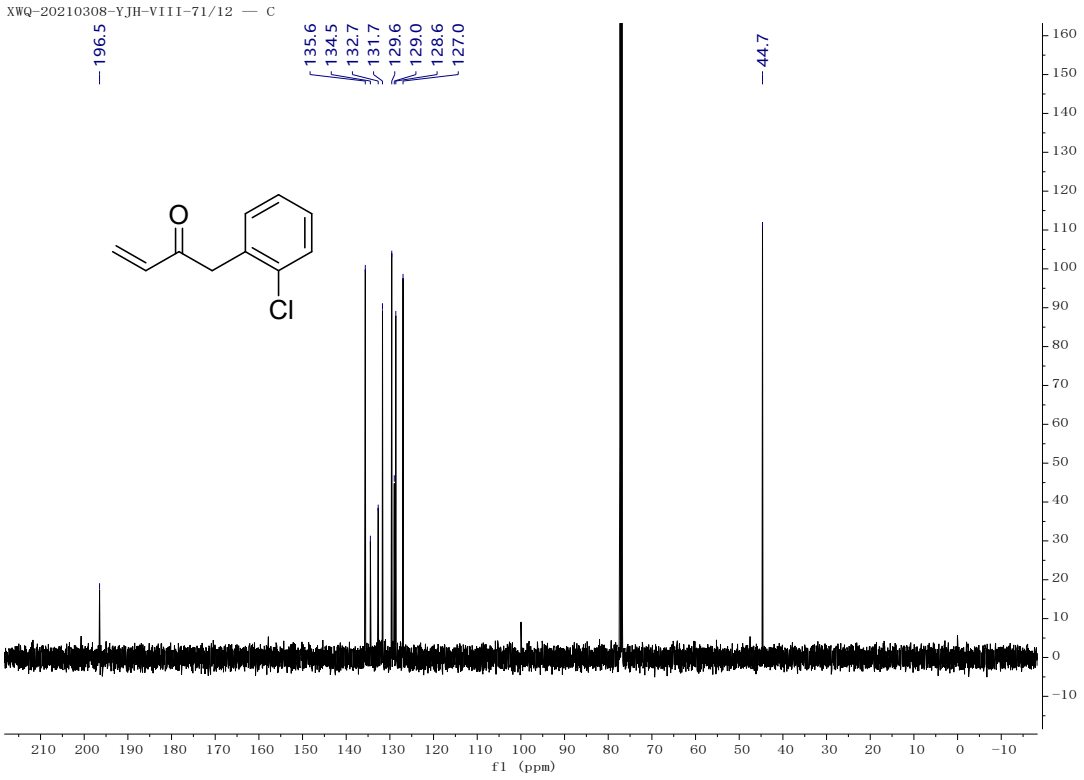
^{13}C NMR spectrum of compound **S12e** (126 MHz, Chloroform-*d*)



^{1}H NMR spectrum of compound **16e** (500 MHz, Chloroform-*d*)

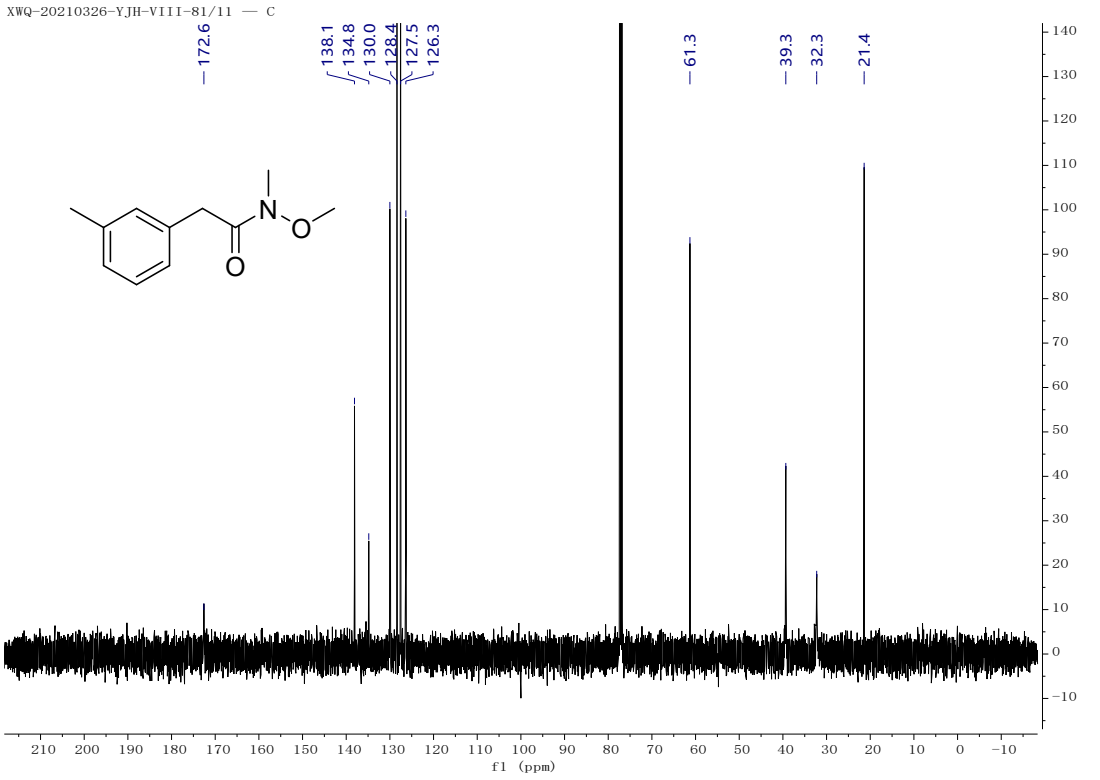


^{13}C NMR spectrum of compound **16e** (126 MHz, Chloroform-*d*)

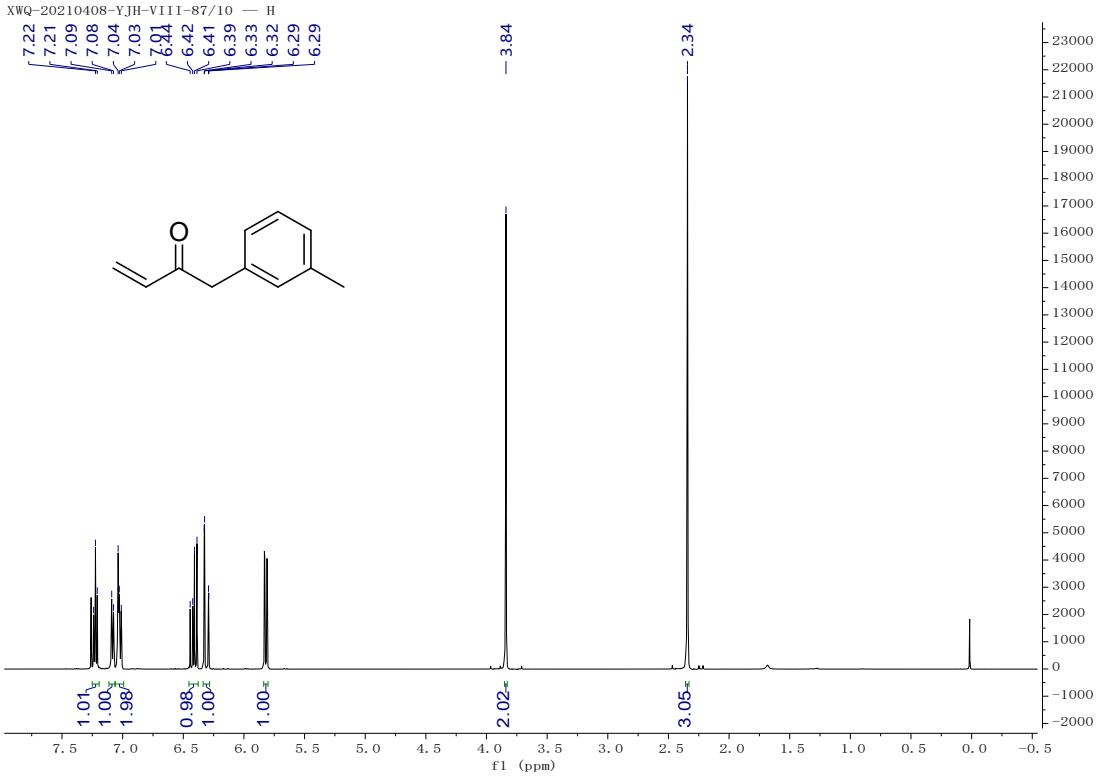


^{1}H NMR spectrum of compound **S12f** (500 MHz, Chloroform-*d*)

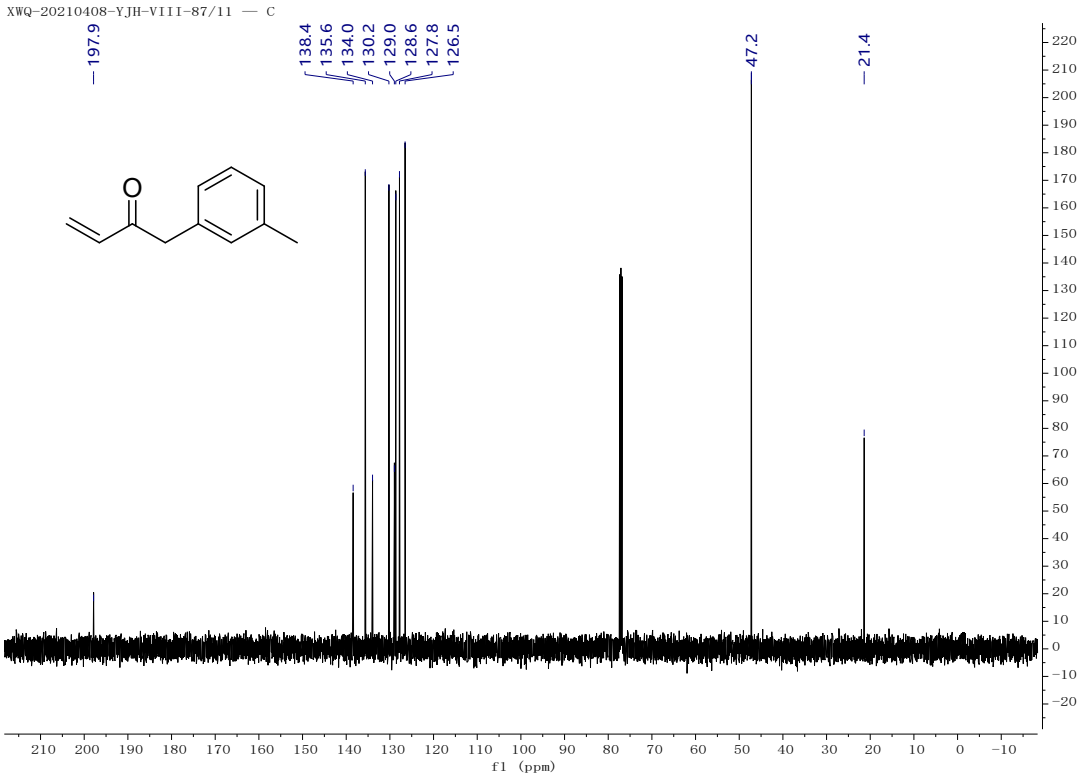
^{13}C NMR spectrum of compound **S12f** (126 MHz, Chloroform-*d*)



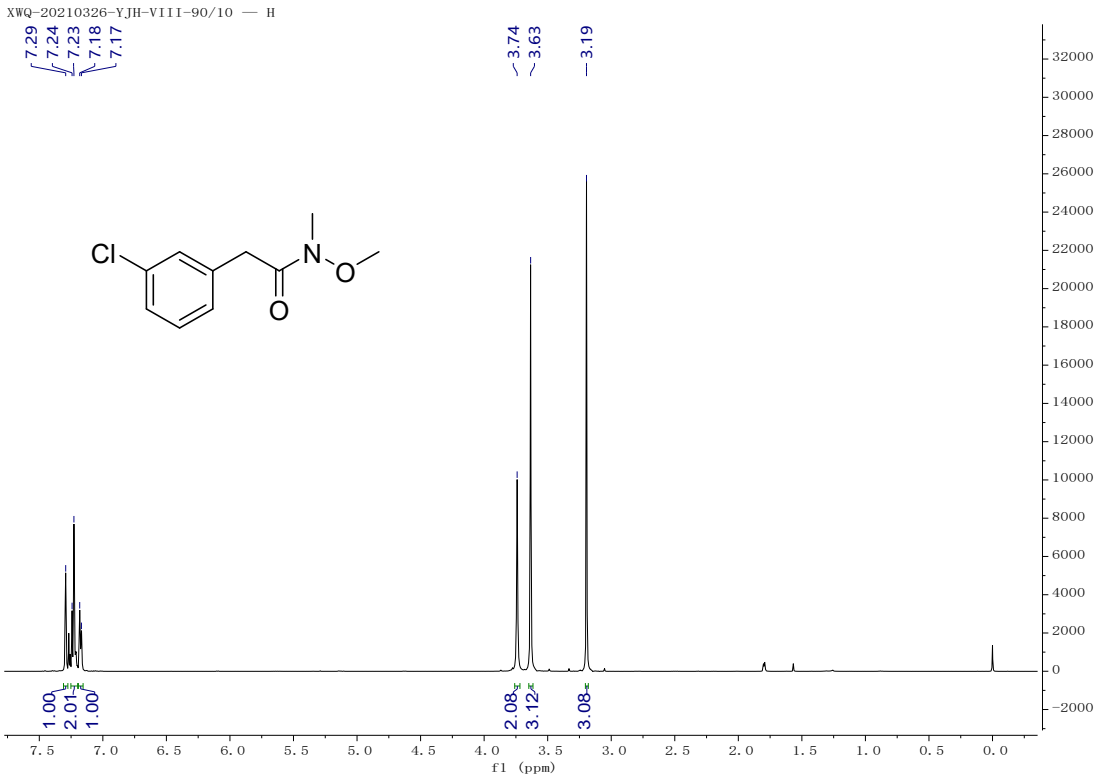
^{1}H NMR spectrum of compound **16f** (500 MHz, Chloroform-*d*)



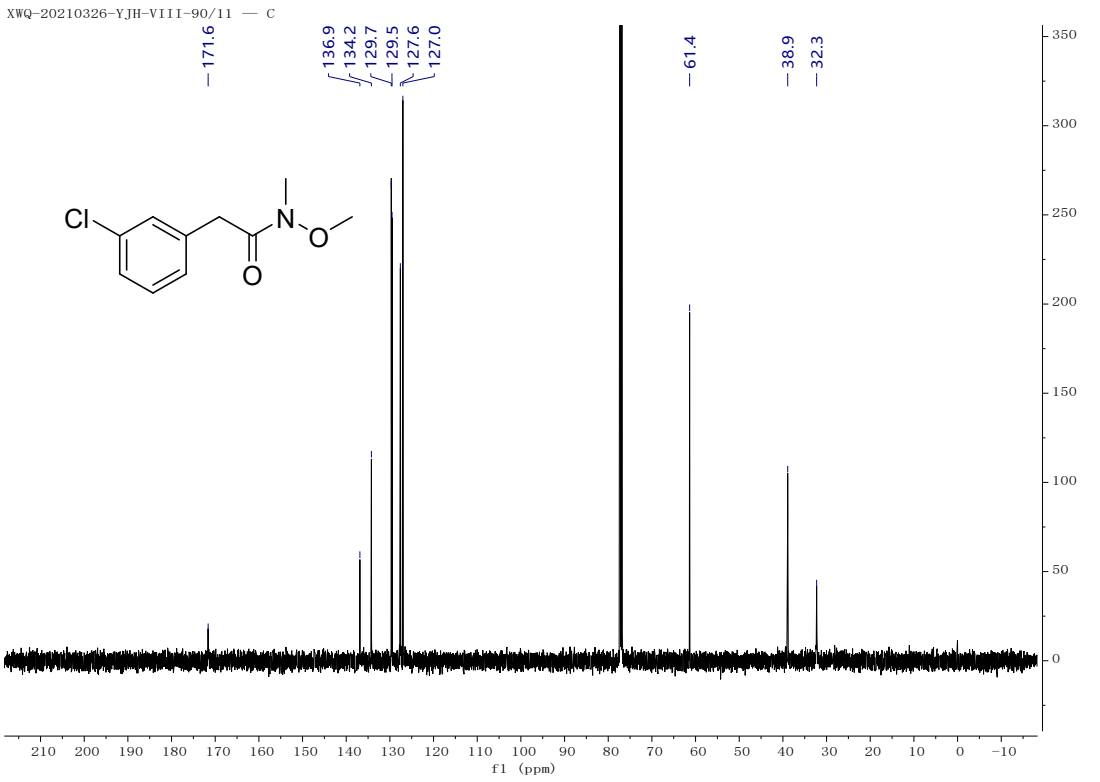
^{13}C NMR spectrum of compound **16f** (126 MHz, Chloroform-*d*)



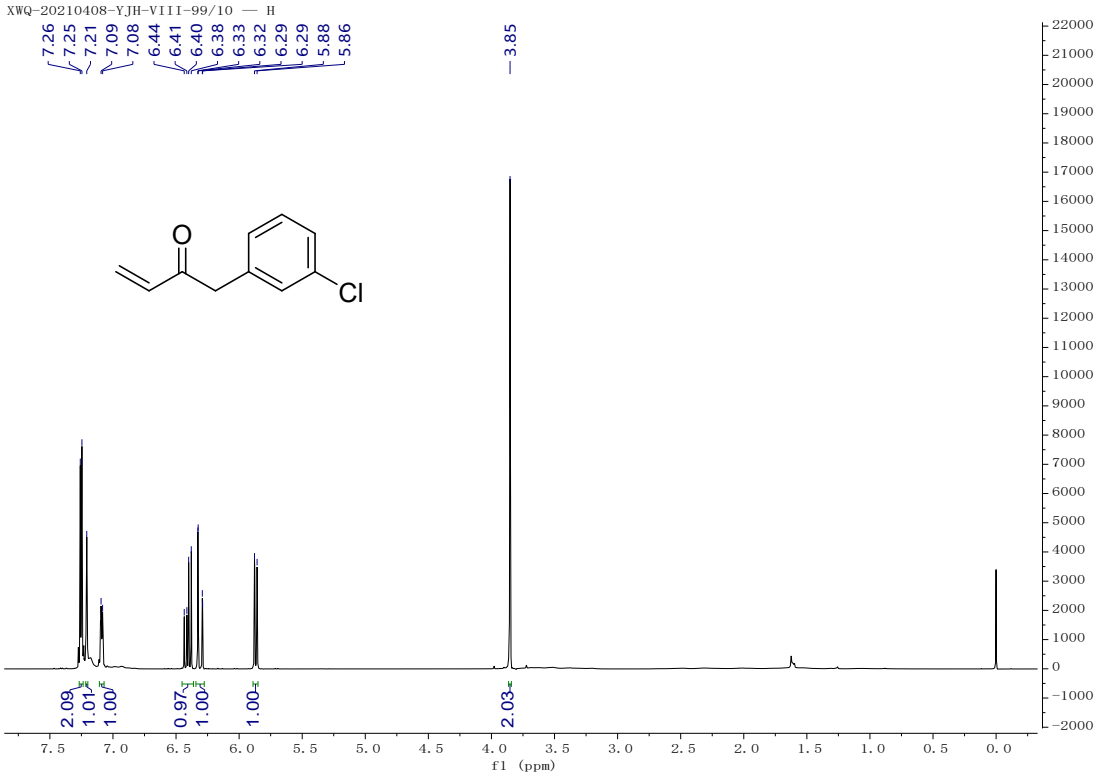
^{1}H NMR spectrum of compound **S12g** (500 MHz, Chloroform-*d*)



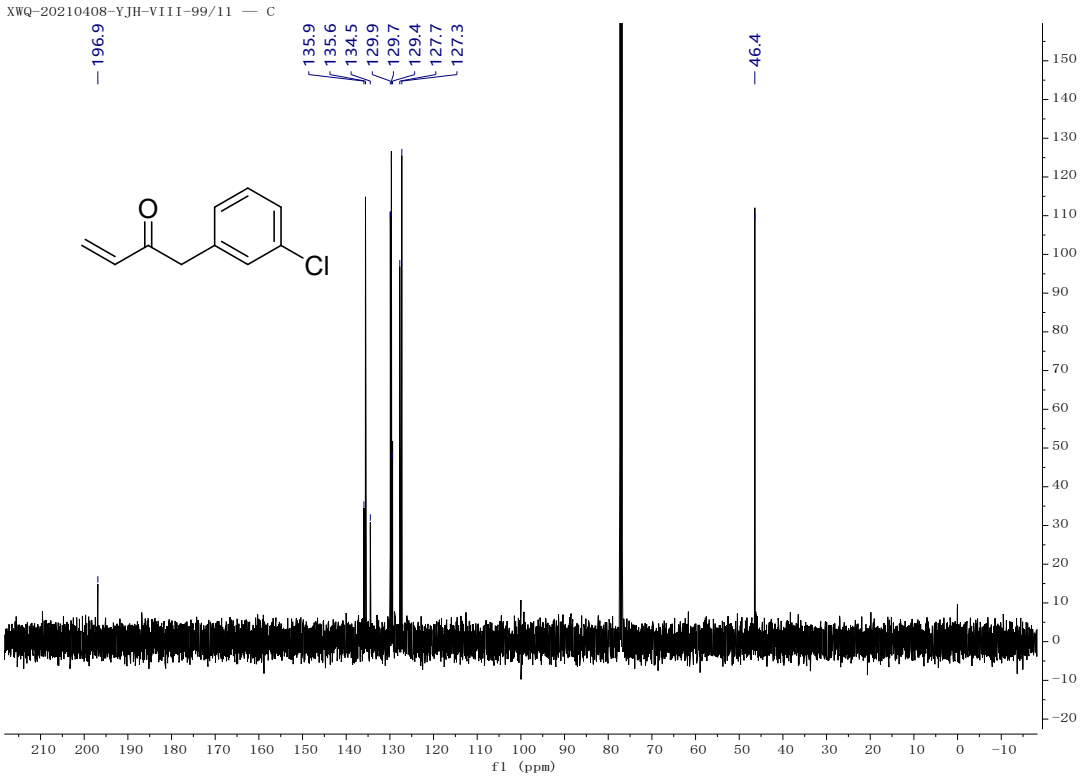
^{13}C NMR spectrum of compound **S12g** (126 MHz, Chloroform-*d*)



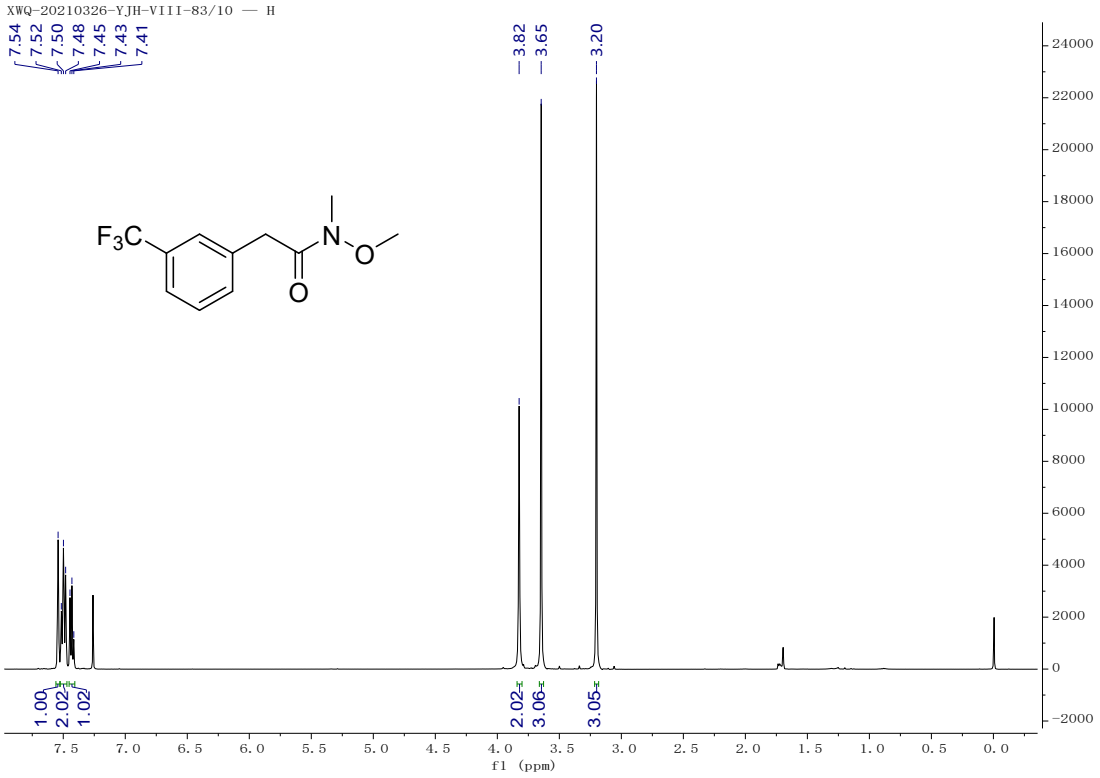
^{1}H NMR spectrum of compound **16g** (500 MHz, Chloroform-*d*)



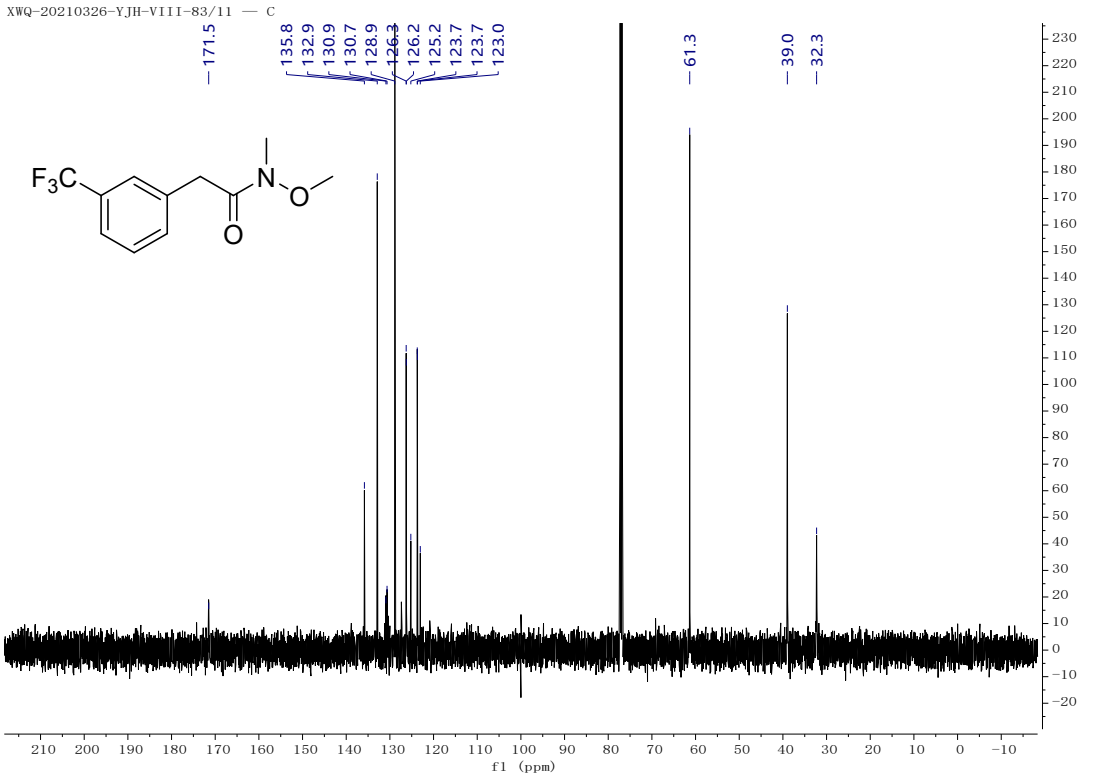
^{13}C NMR spectrum of compound **16g** (126 MHz, Chloroform-*d*)



[1]H NMR spectrum of compound **S12h** (500 MHz, Chloroform-*d*)

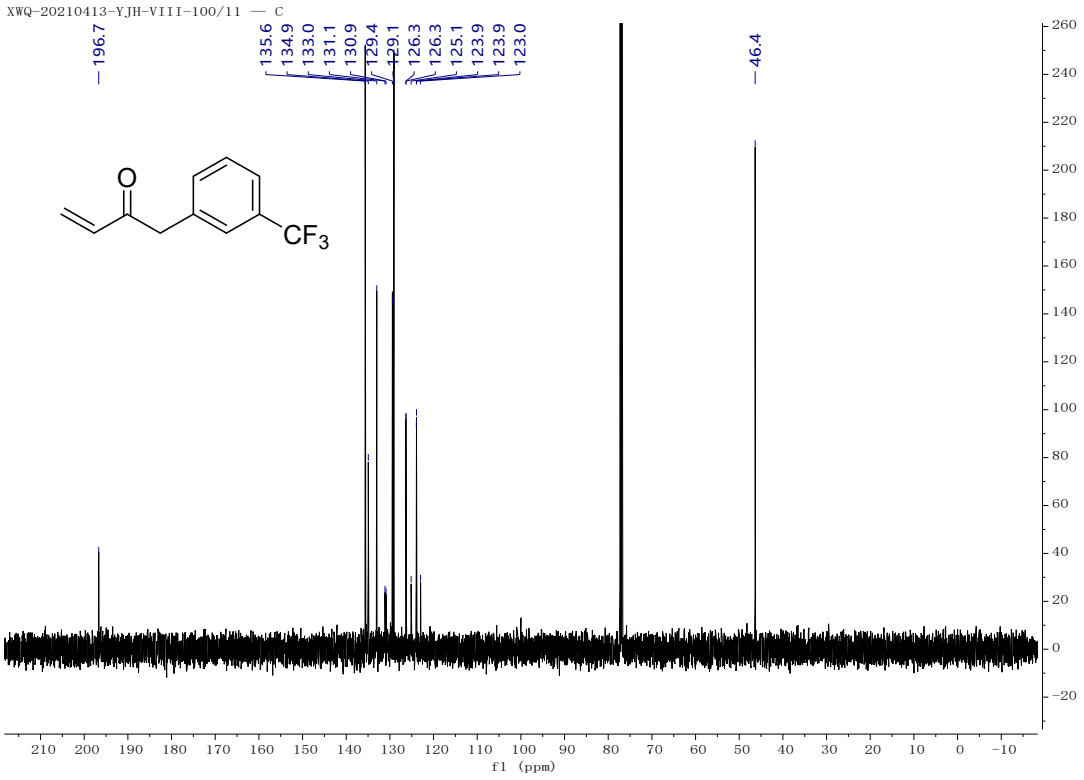


[13]C NMR spectrum of compound **S12h** (126 MHz, Chloroform-*d*)

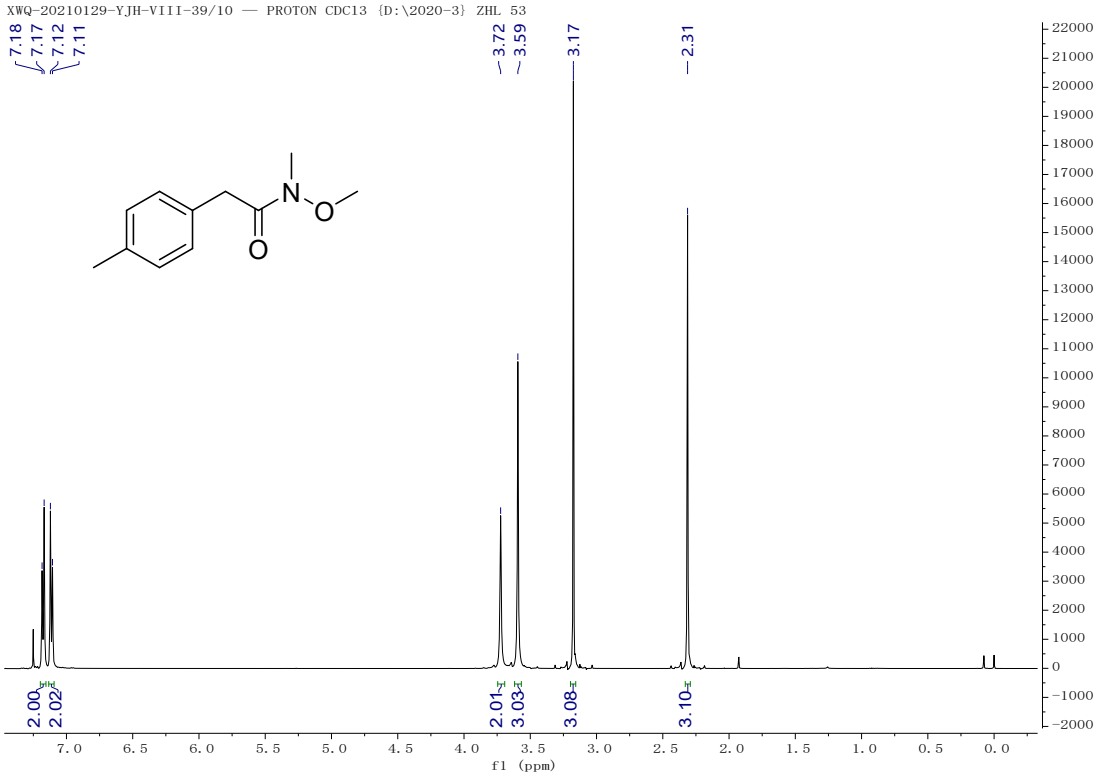


^{1}H NMR spectrum of compound **16h** (500 MHz, Chloroform-*d*)

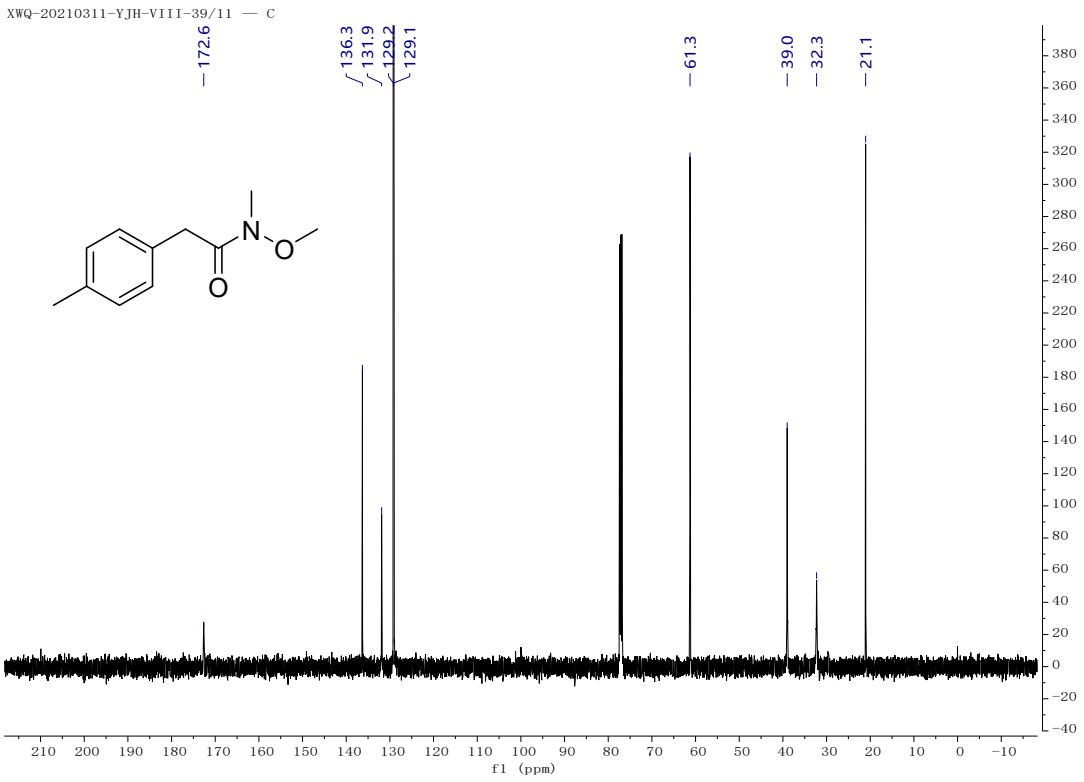
^{13}C NMR spectrum of compound **16h** (126 MHz, Chloroform-*d*)



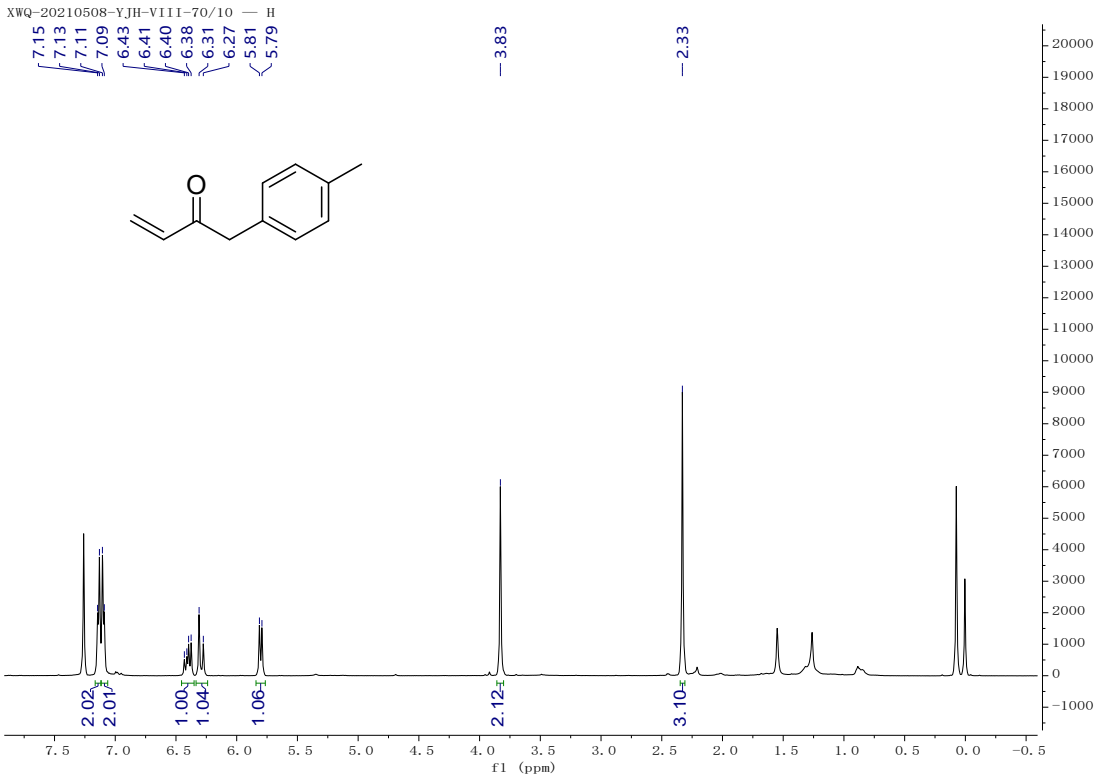
^{1}H NMR spectrum of compound **S12i** (500 MHz, Chloroform-*d*)



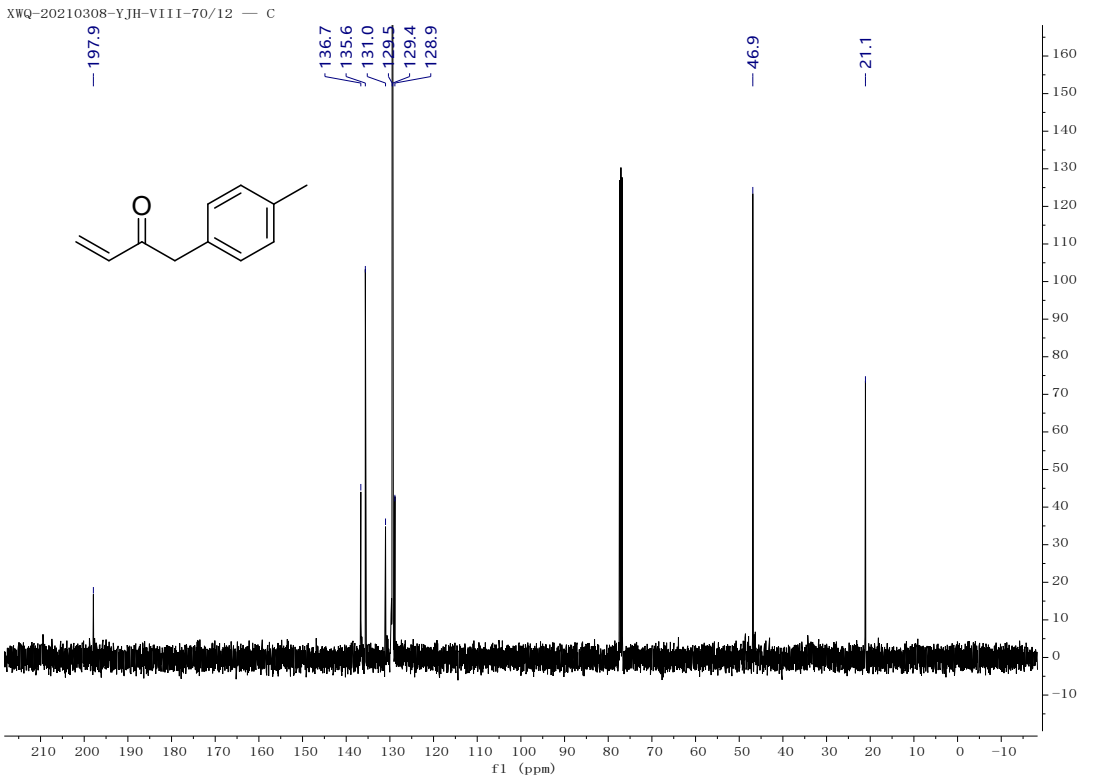
^{13}C NMR spectrum of compound **S12i** (126 MHz, Chloroform-*d*)



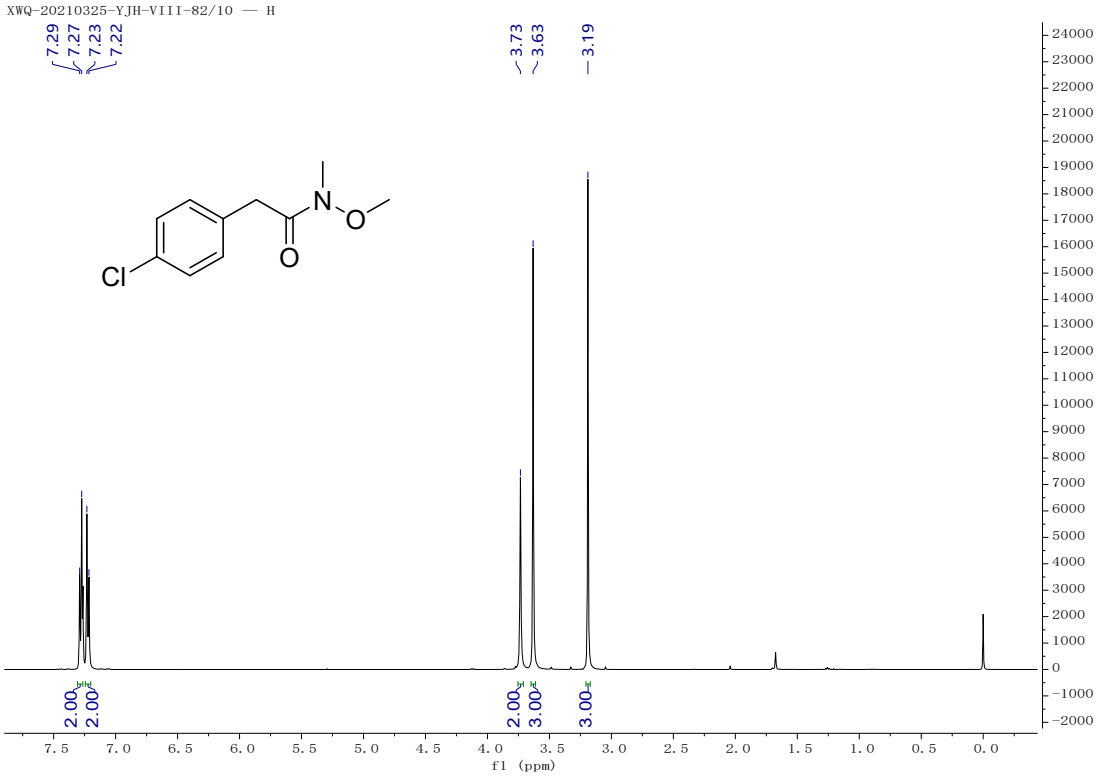
^{1}H NMR spectrum of compound **16i** (500 MHz, Chloroform-*d*)



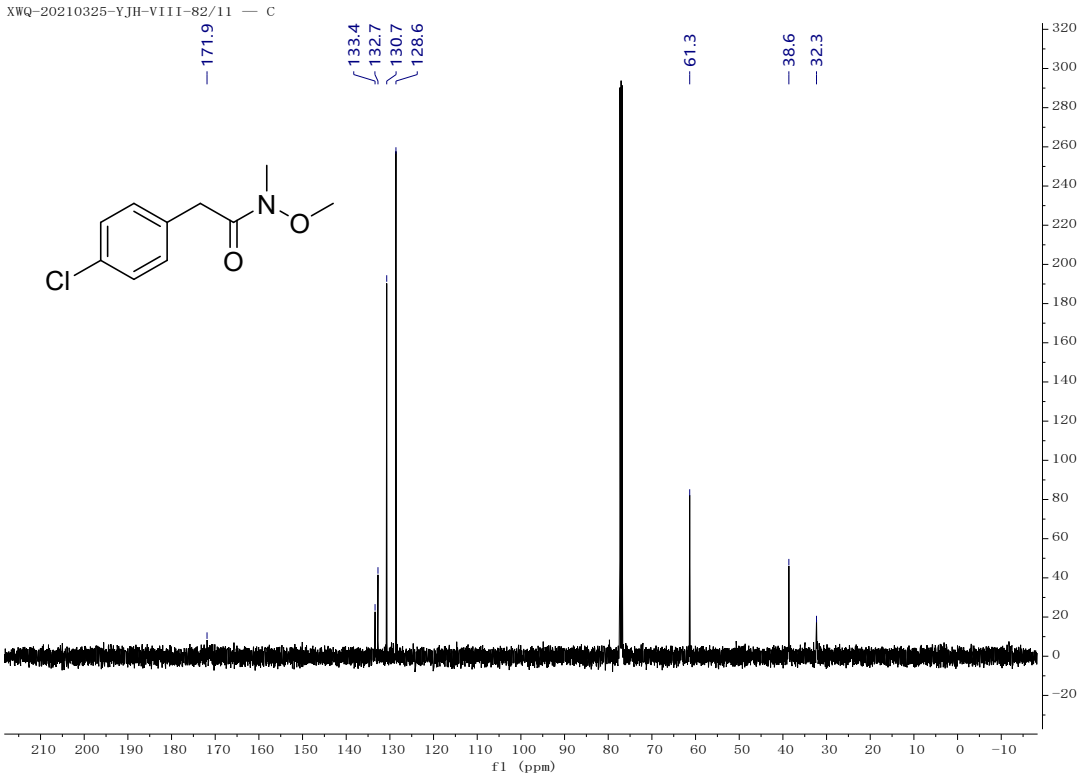
^{13}C NMR spectrum of compound **16i** (126 MHz, Chloroform-*d*)



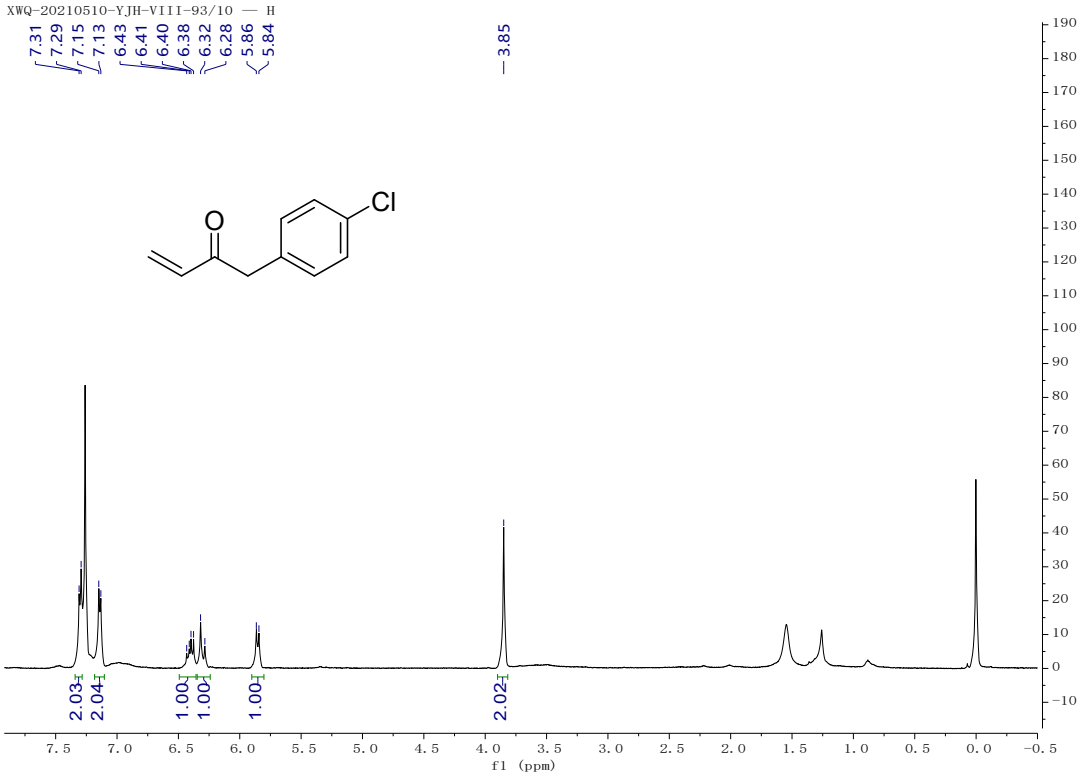
^{1}H NMR spectrum of compound **S12j** (500 MHz, Chloroform-*d*)



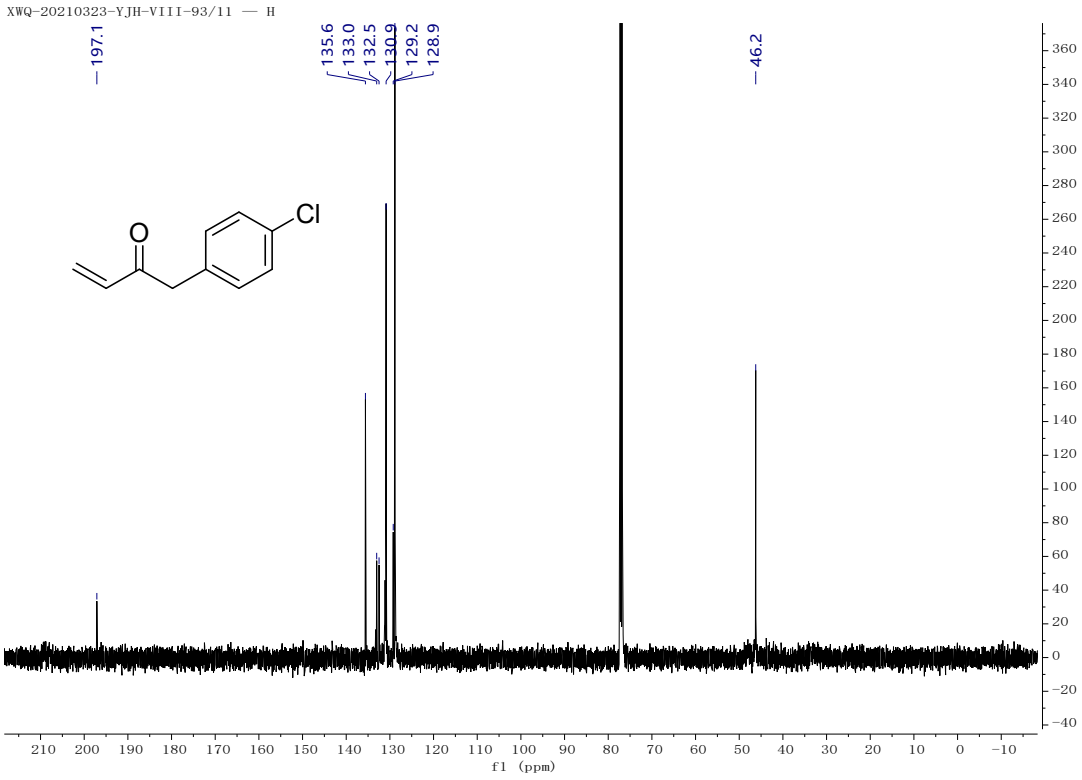
^{13}C NMR spectrum of compound **S12j** (126 MHz, Chloroform-*d*)



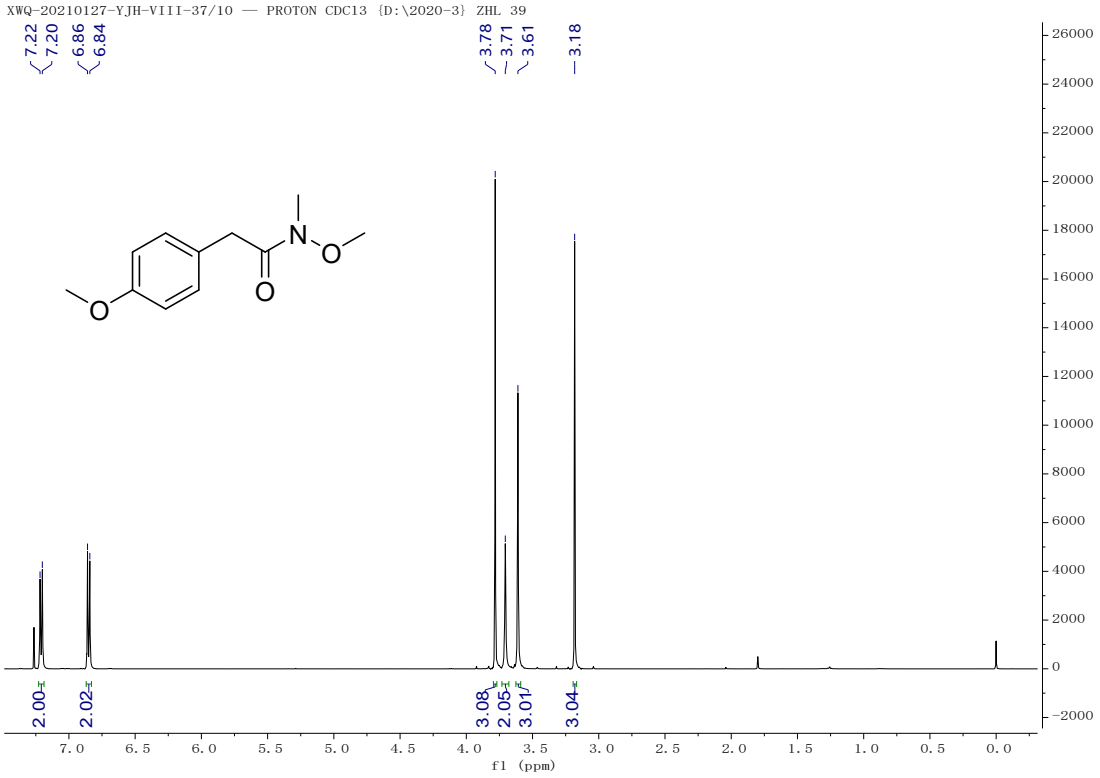
[1]H NMR spectrum of compound **16j** (500 MHz, Chloroform-*d*)



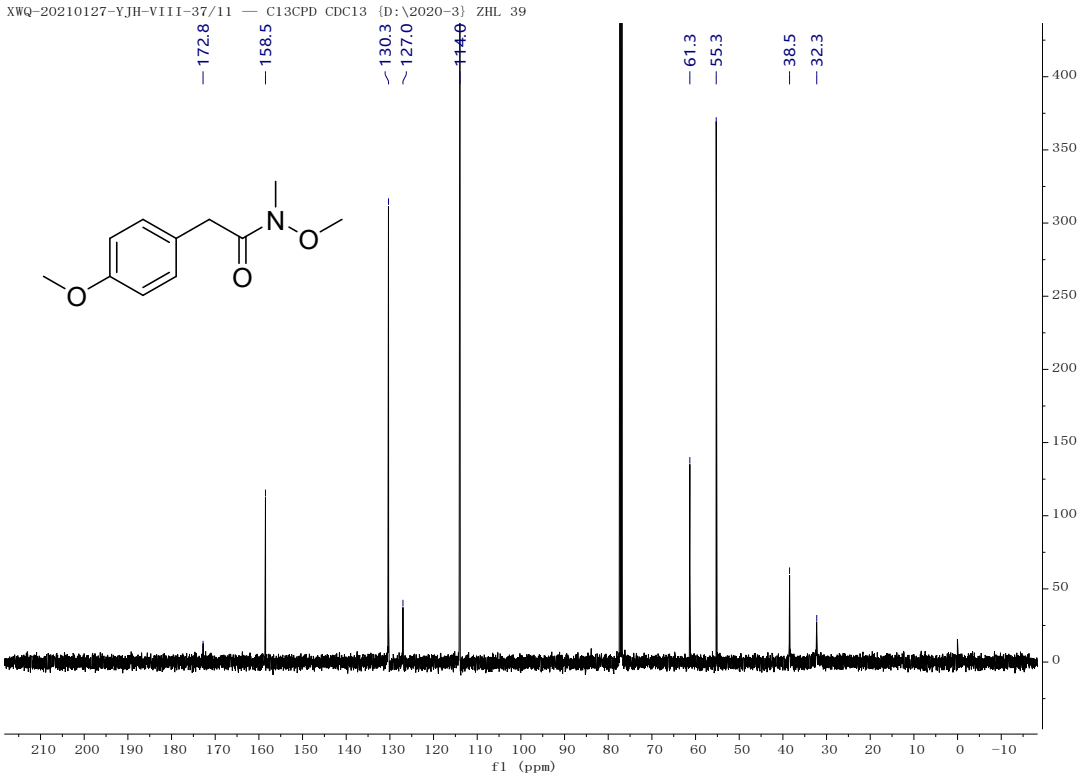
[13]C NMR spectrum of compound **16j** (126 MHz, Chloroform-*d*)



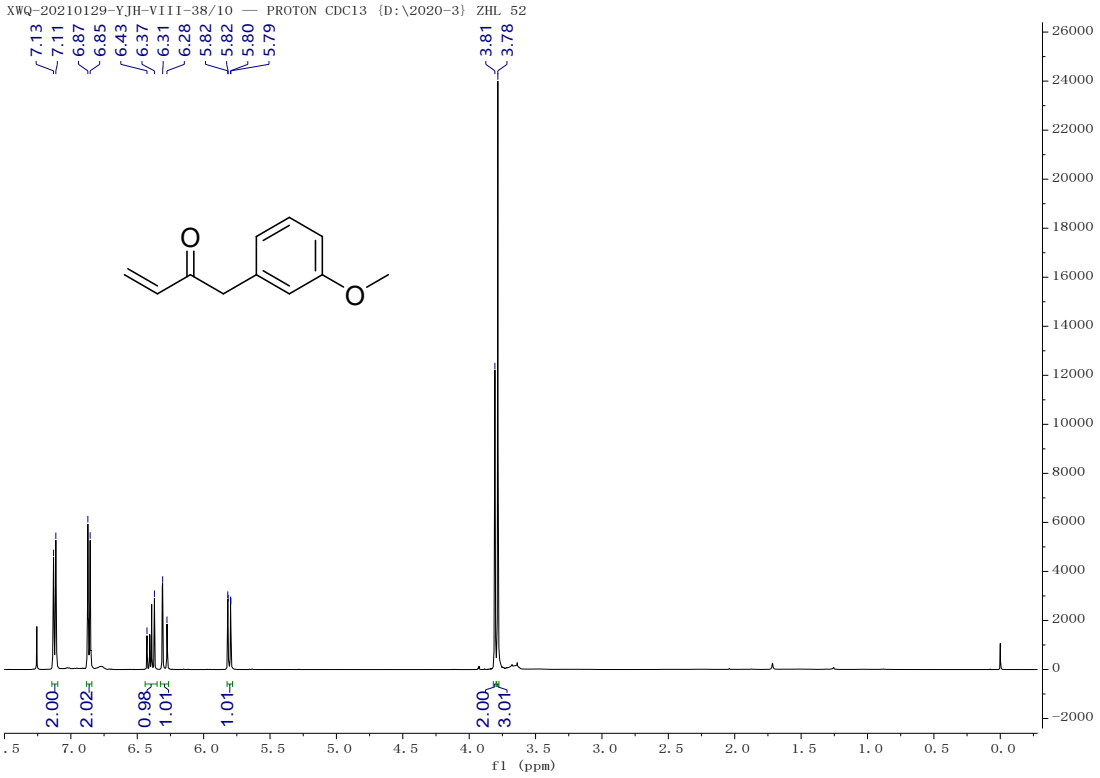
^{1}H NMR spectrum of compound **S12k** (500 MHz, Chloroform-*d*)



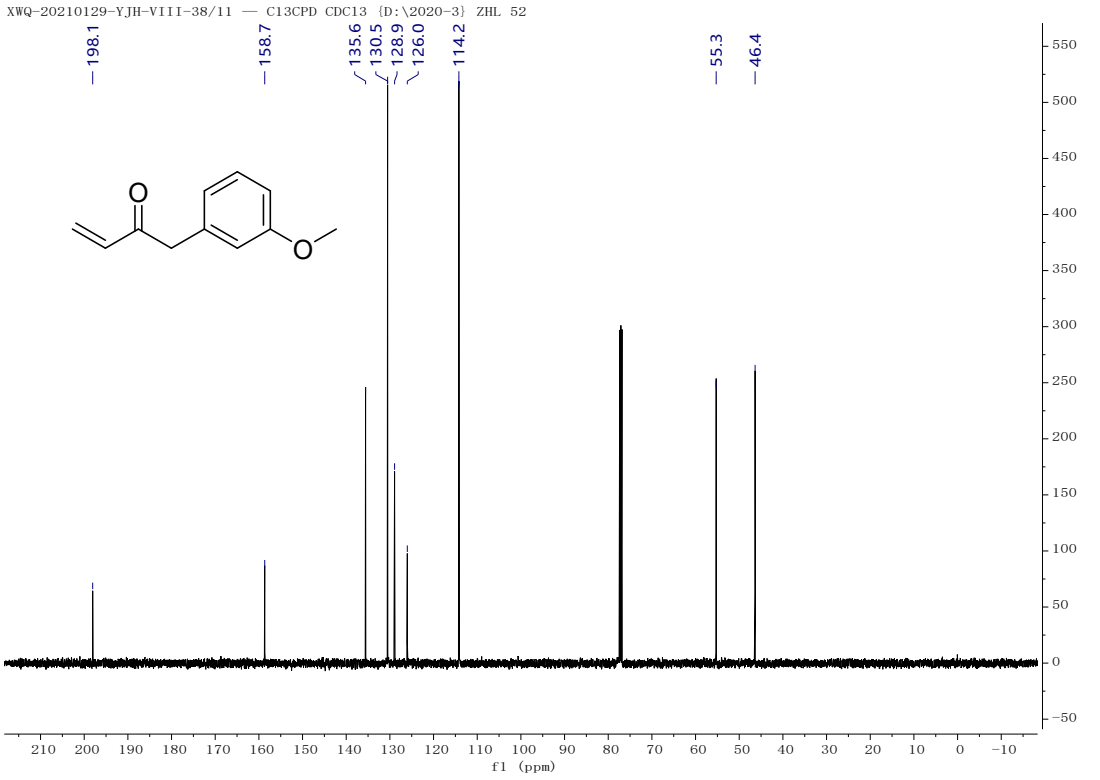
^{13}C NMR spectrum of compound **S12k** (126 MHz, Chloroform-*d*)



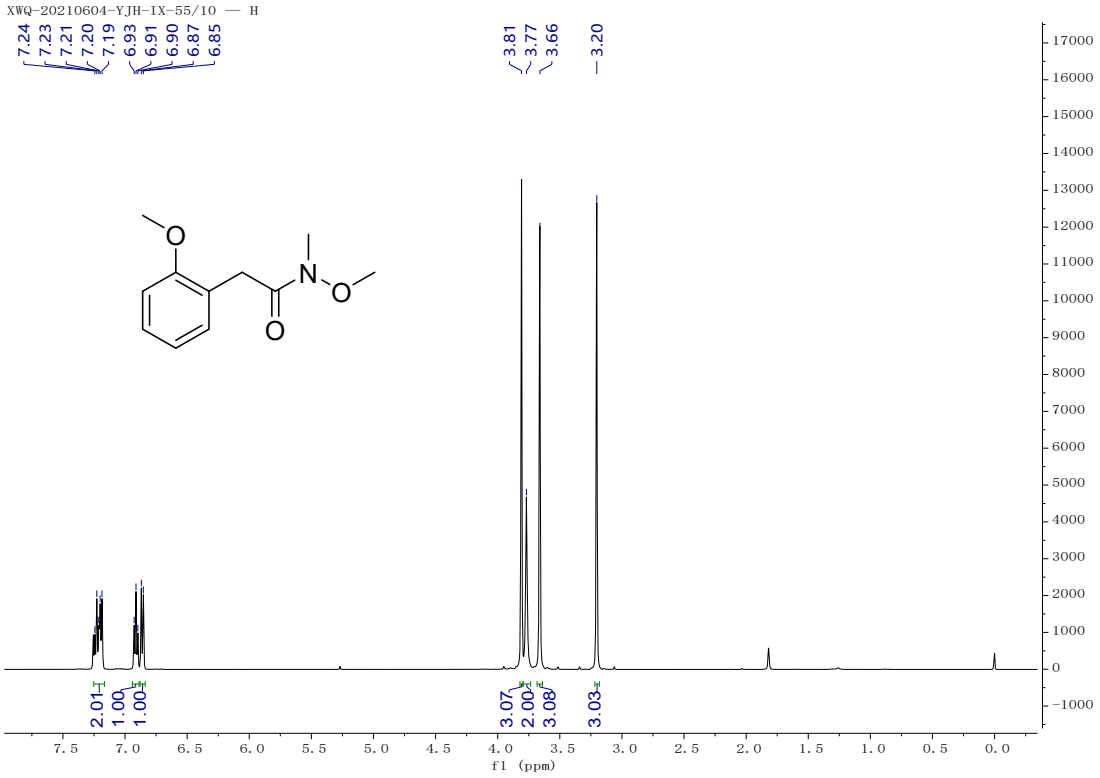
^{1}H NMR spectrum of compound **16k** (500 MHz, Chloroform-*d*)



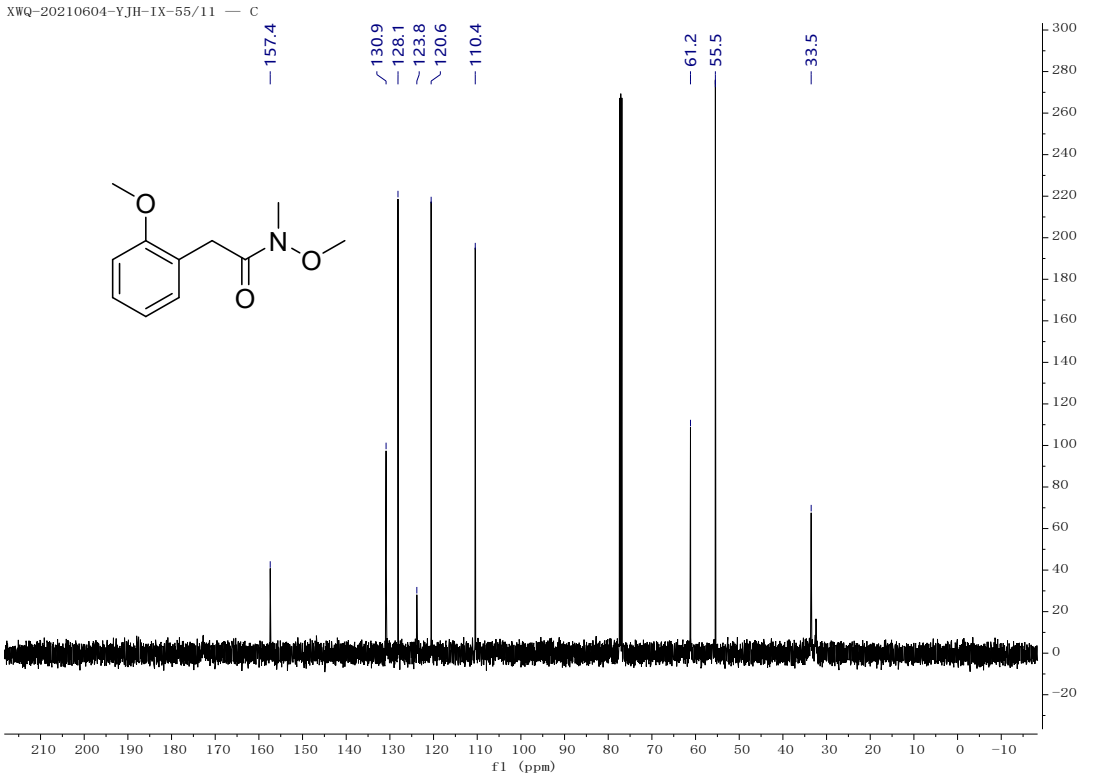
^{13}C NMR spectrum of compound **16k** (126 MHz, Chloroform-*d*)



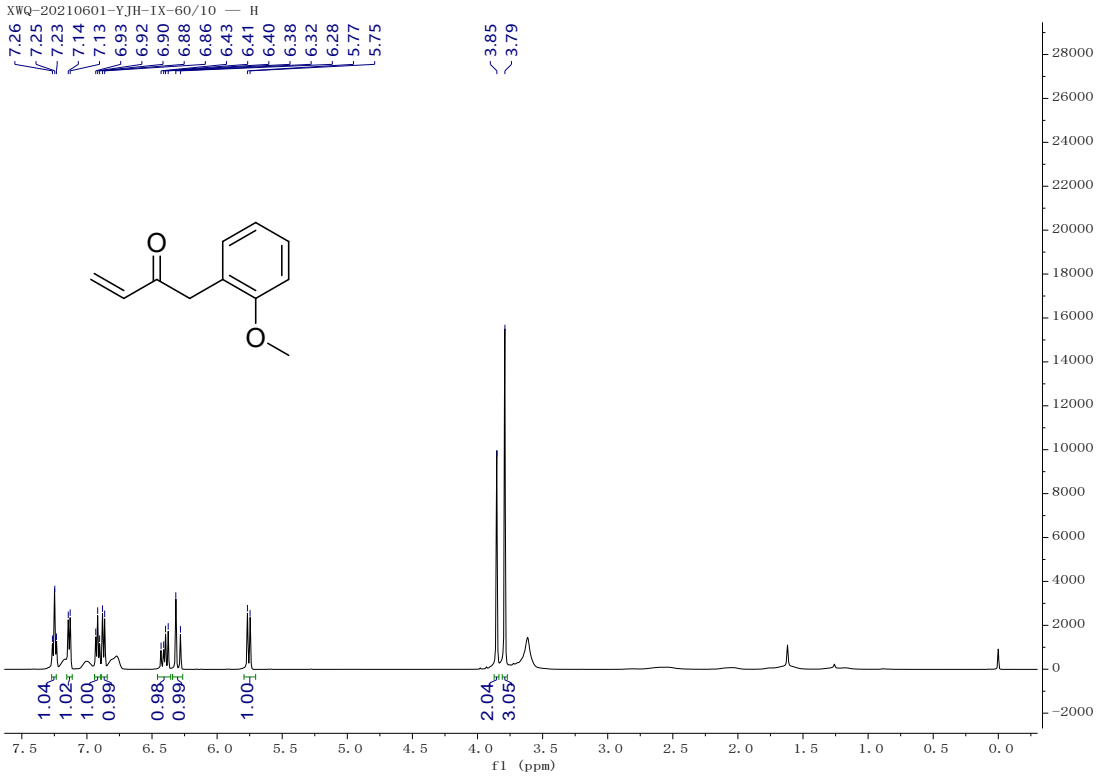
^{1}H NMR spectrum of compound **S12l** (500 MHz, Chloroform-*d*)



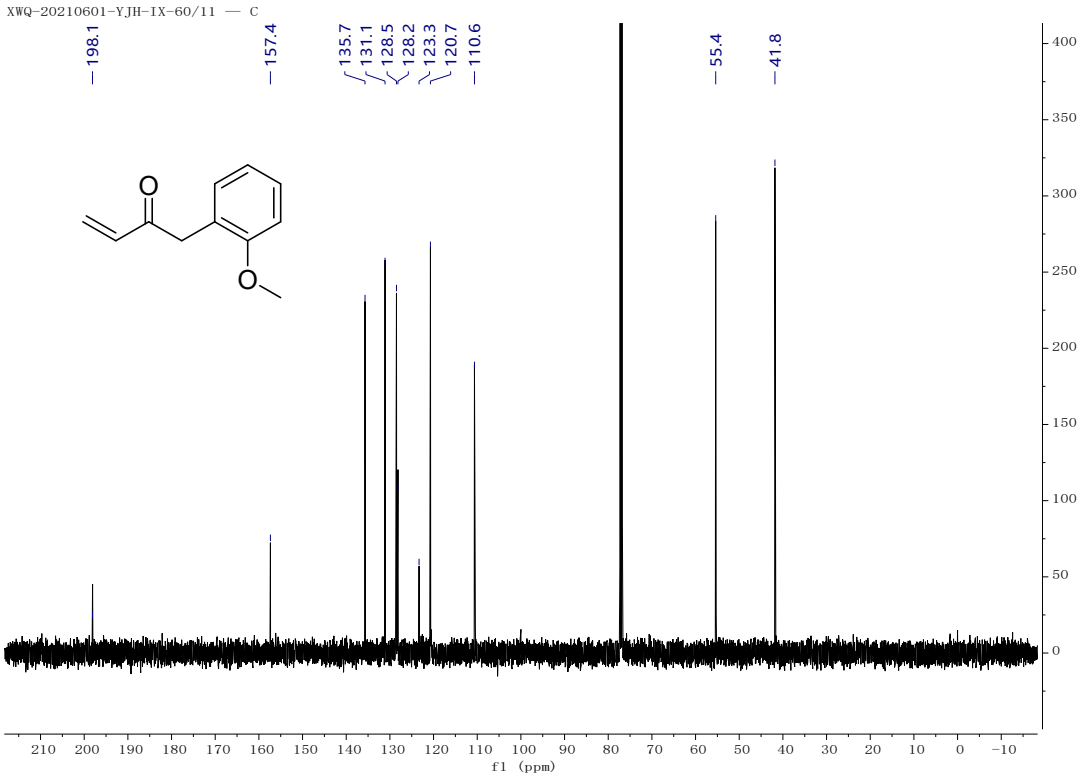
^{13}C NMR spectrum of compound **S12l** (126 MHz, Chloroform-*d*)



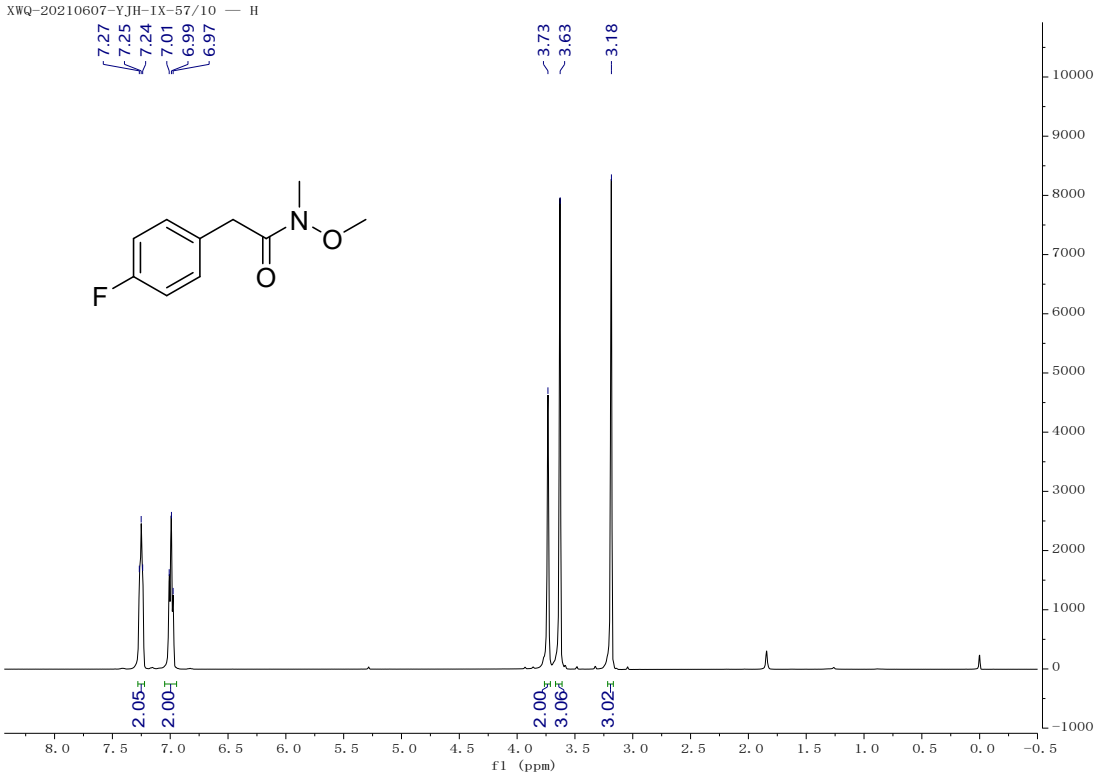
^{1}H NMR spectrum of compound **16l** (500 MHz, Chloroform-*d*)



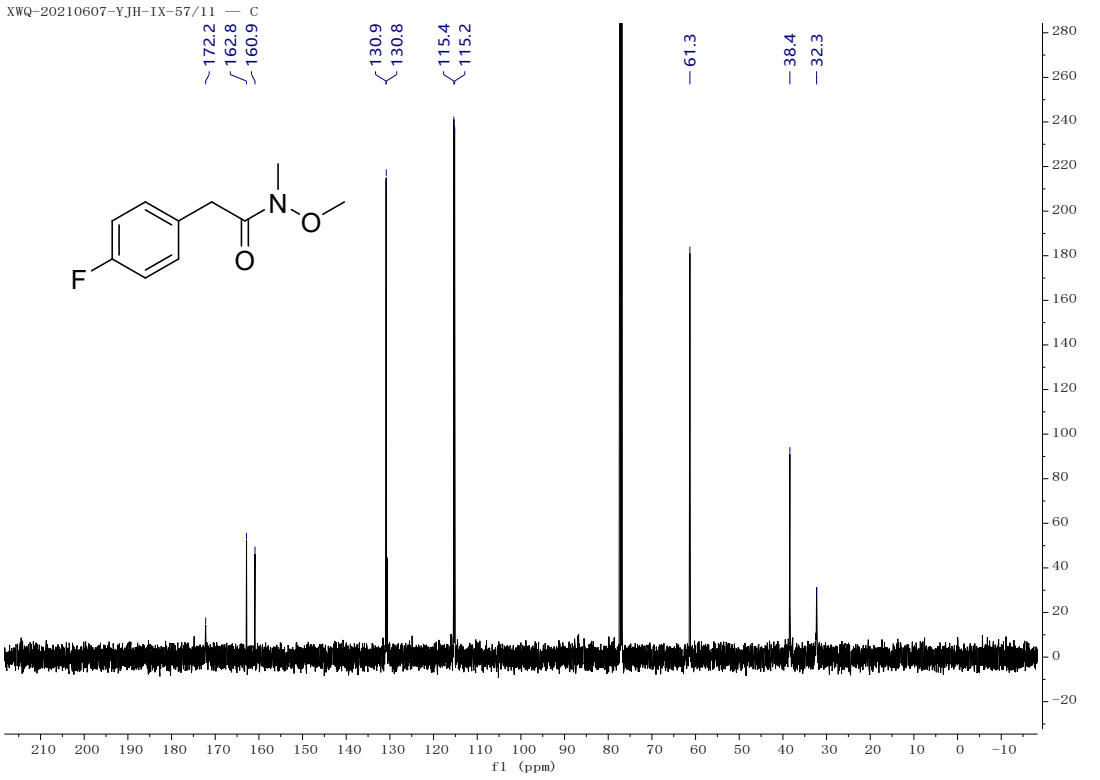
^{13}C NMR spectrum of compound **16l** (126 MHz, Chloroform-*d*)



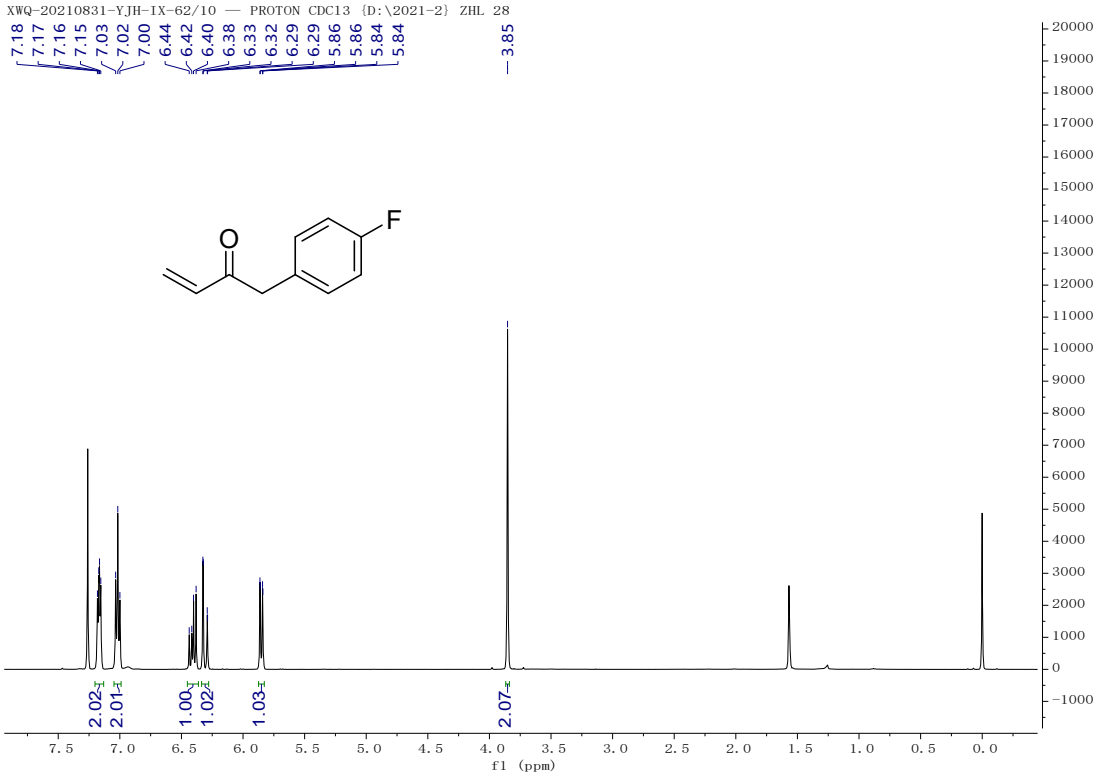
^{1}H NMR spectrum of compound **S12m** (500 MHz, Chloroform-*d*)



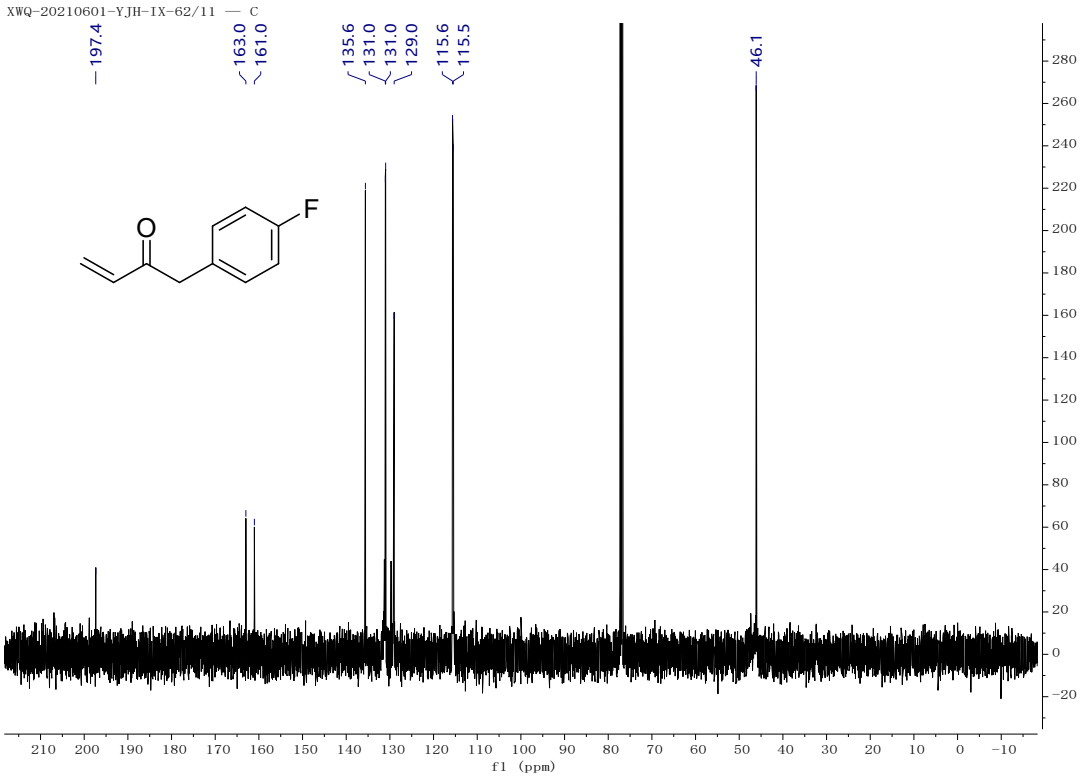
^{13}C NMR spectrum of compound **S12m** (126 MHz, Chloroform-*d*)



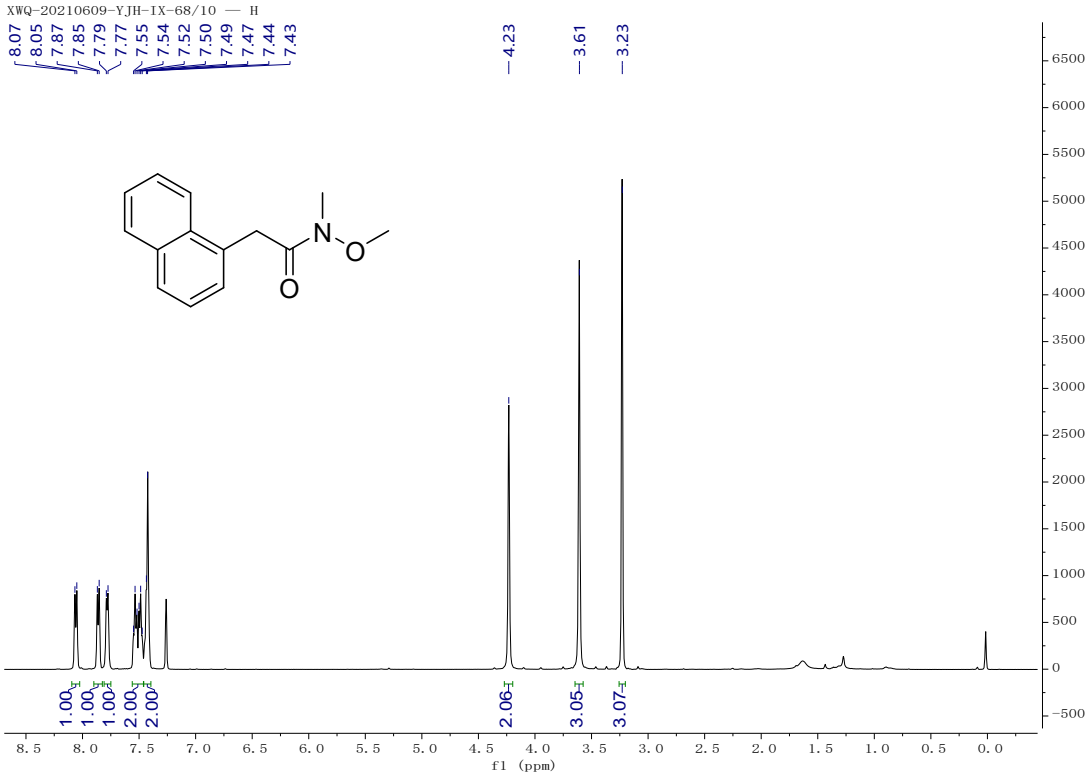
^{1}H NMR spectrum of compound **16m** (500 MHz, Chloroform-*d*)



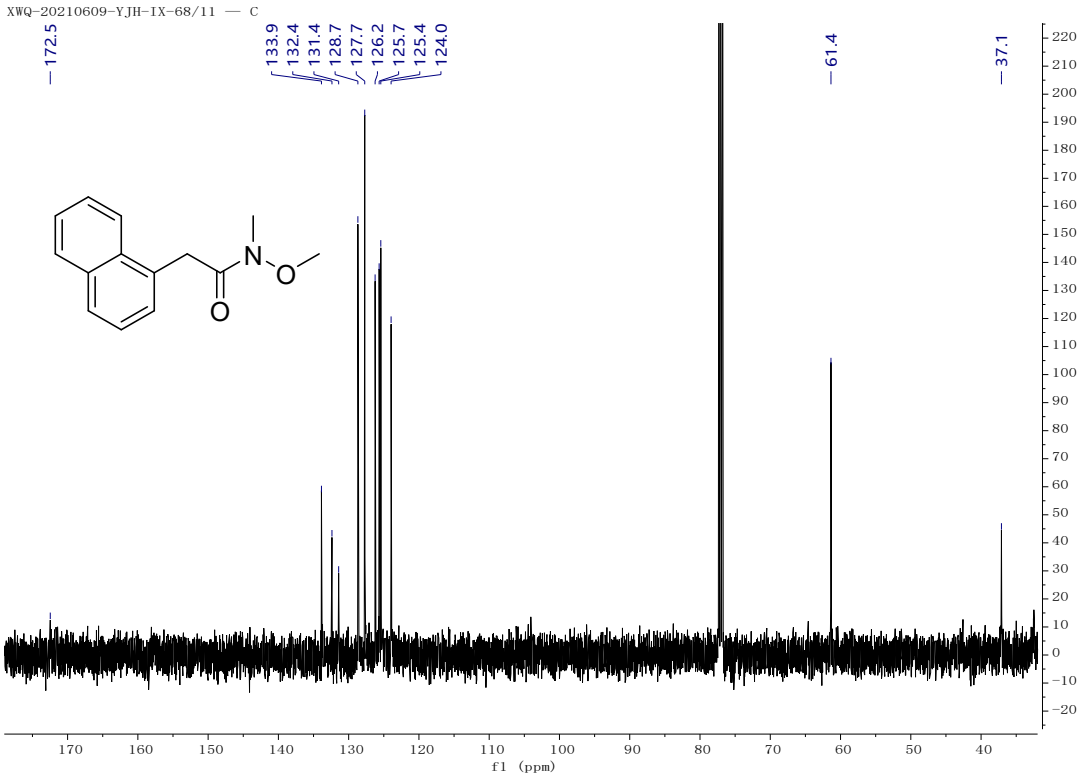
^{13}C NMR spectrum of compound **16m** (126 MHz, Chloroform-*d*)



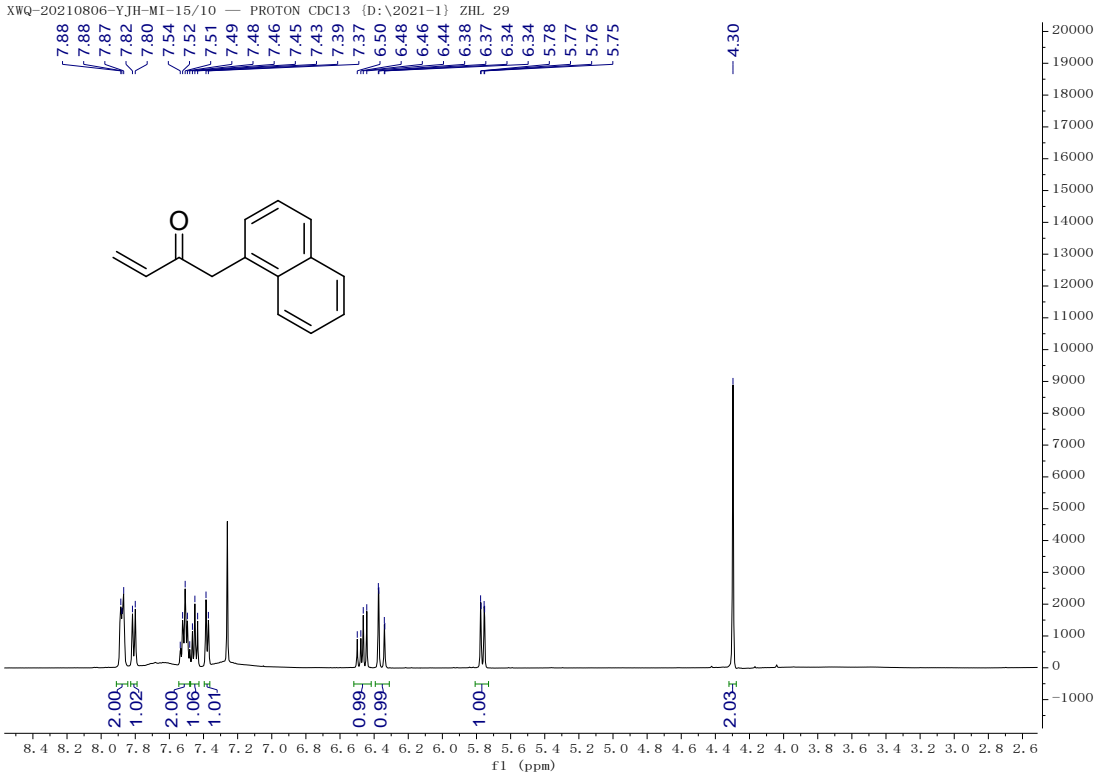
[1]H NMR spectrum of compound **S12n** (500 MHz, Chloroform-*d*)



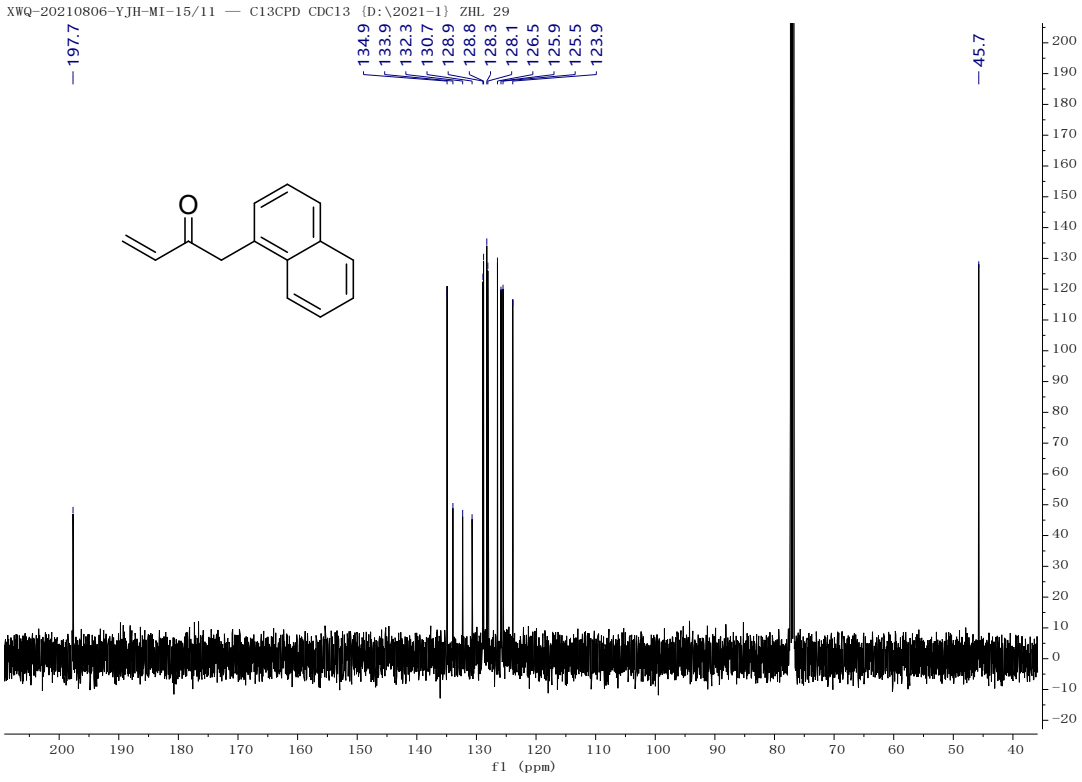
[13]C NMR spectrum of compound **S12n** (126 MHz, Chloroform-*d*)



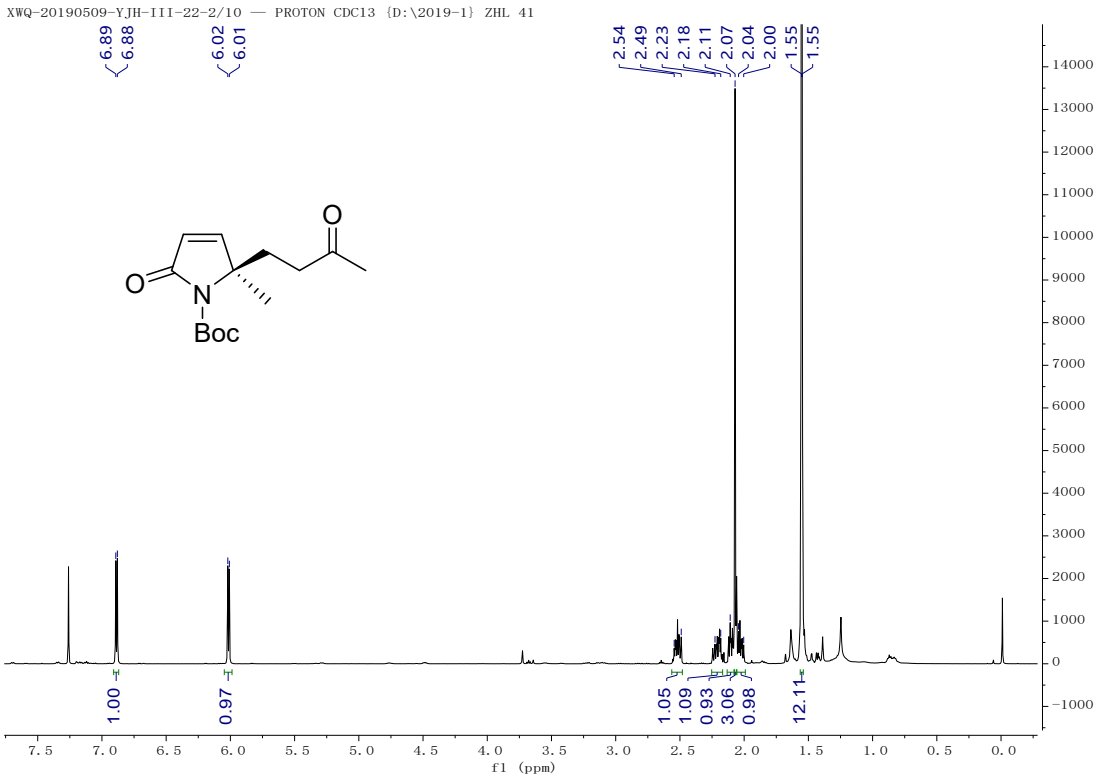
^{1}H NMR spectrum of compound **16n** (500 MHz, Chloroform-*d*)



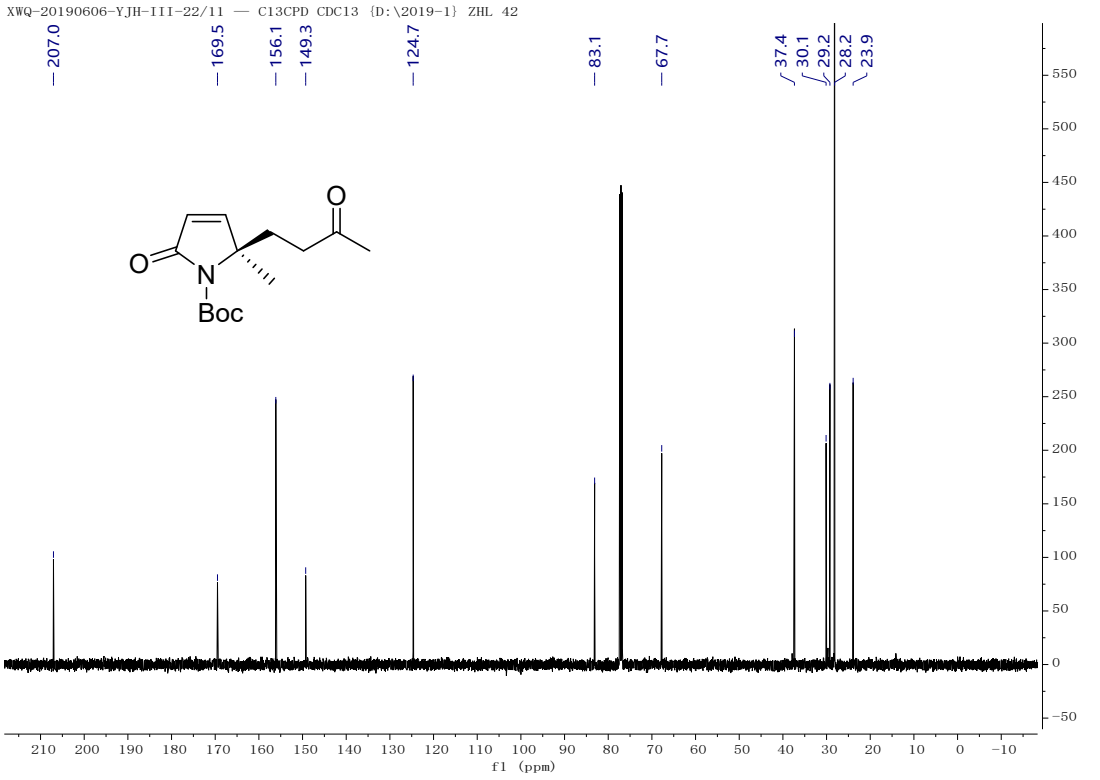
^{13}C NMR spectrum of compound **16n** (126 MHz, Chloroform-*d*)



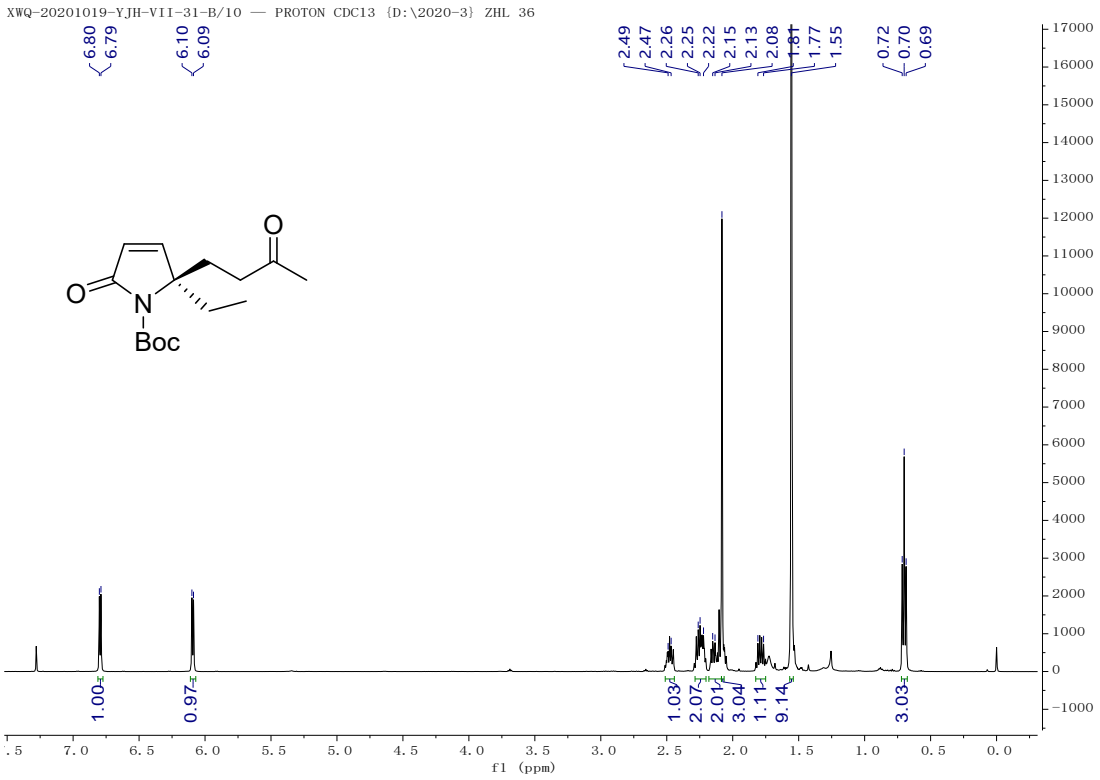
^{1}H NMR spectrum of compound **15a** (500 MHz, Chloroform-*d*)



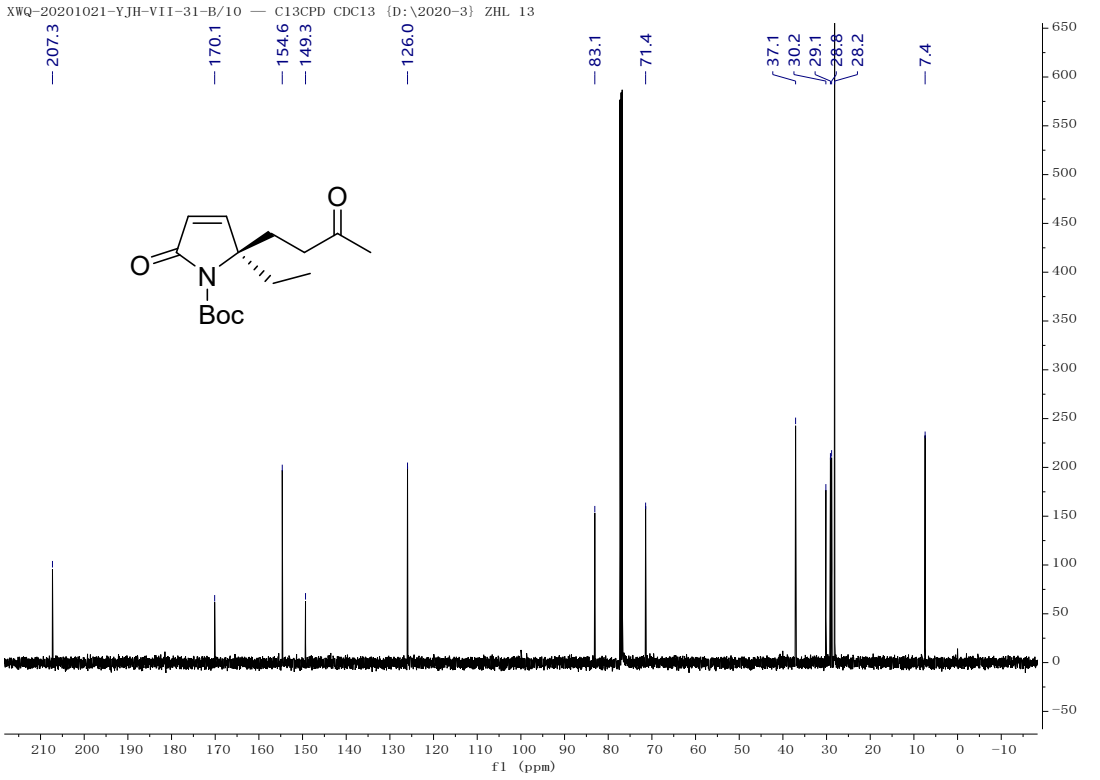
^{13}C NMR spectrum of compound **15a** (126 MHz, Chloroform-*d*)



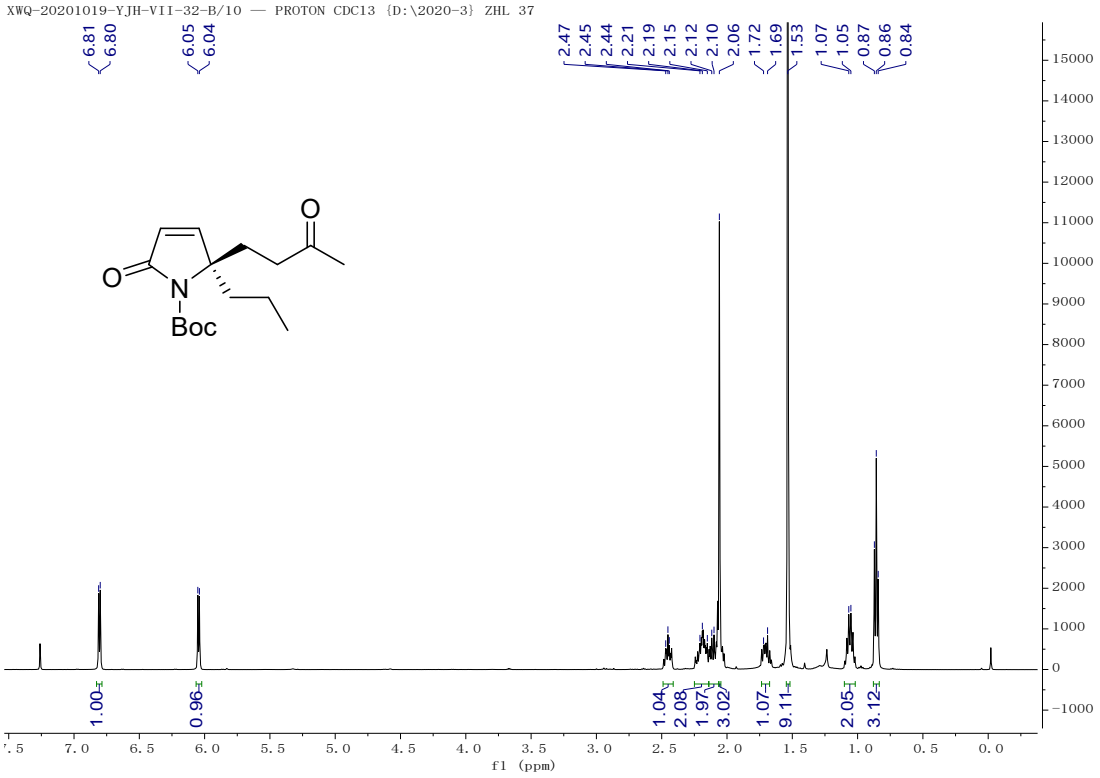
^{1}H NMR spectrum of compound **15b** (500 MHz, Chloroform-*d*)



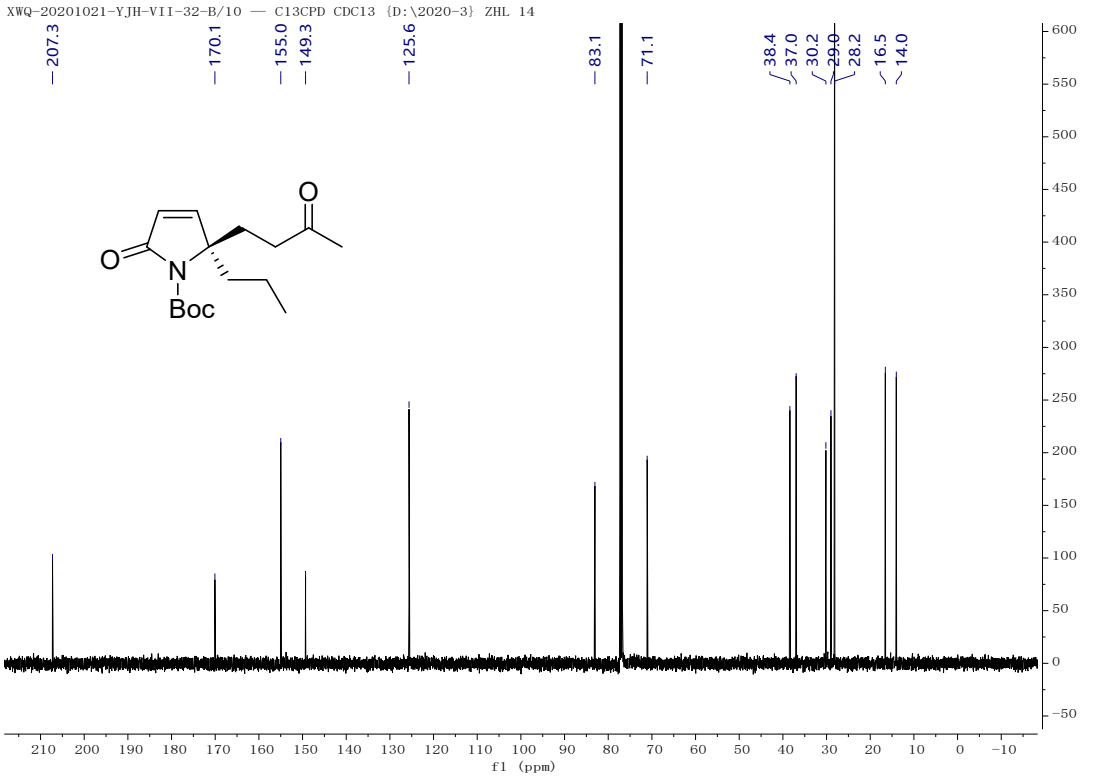
^{13}C NMR spectrum of compound **15b** (126 MHz, Chloroform-*d*)



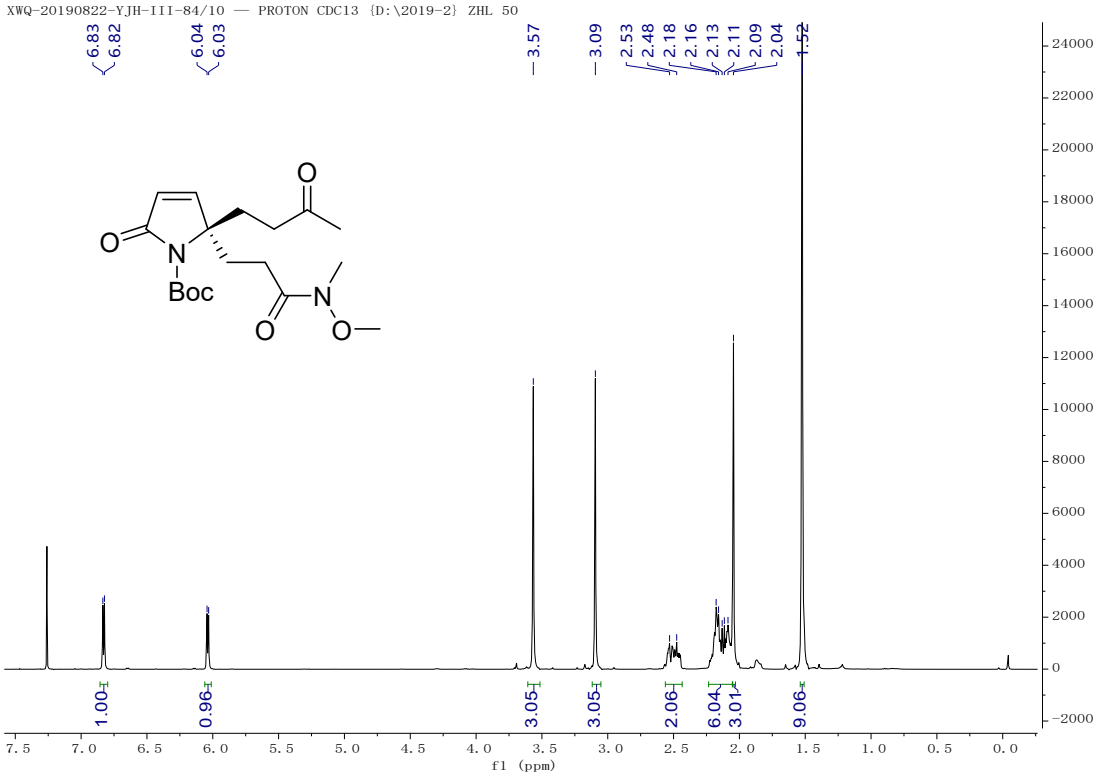
^{1}H NMR spectrum of compound **15c** (500 MHz, Chloroform-*d*)



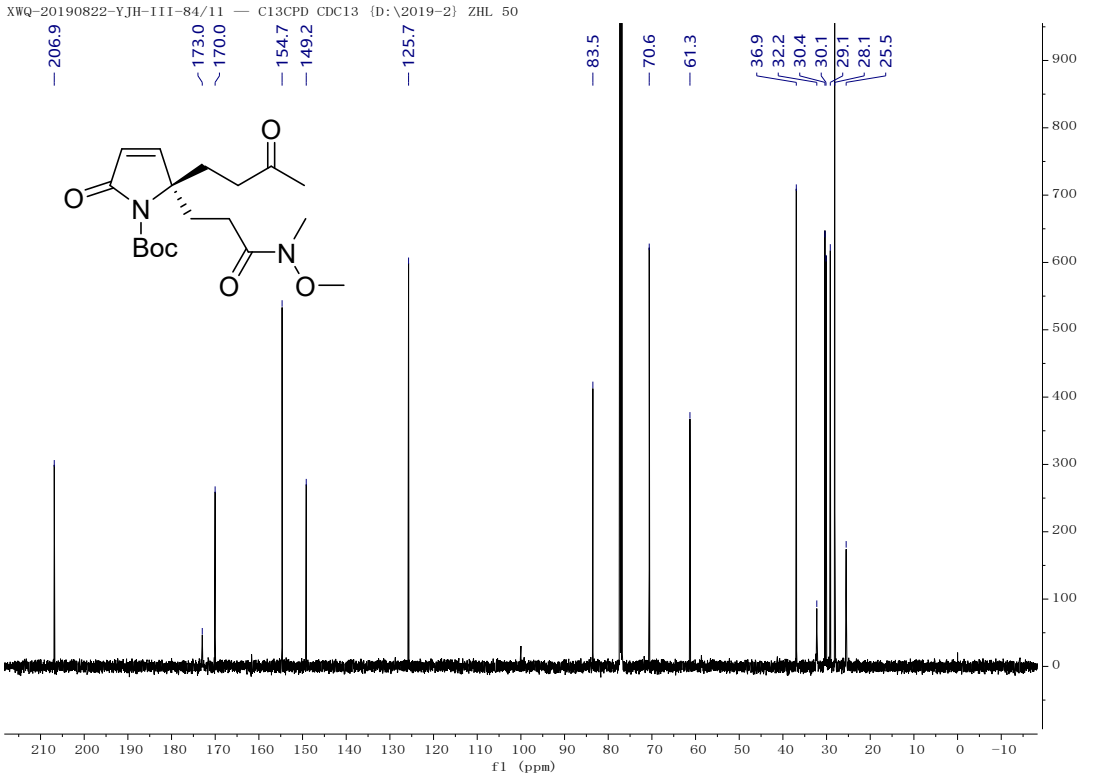
^{13}C NMR spectrum of compound **15c** (126 MHz, Chloroform-*d*)



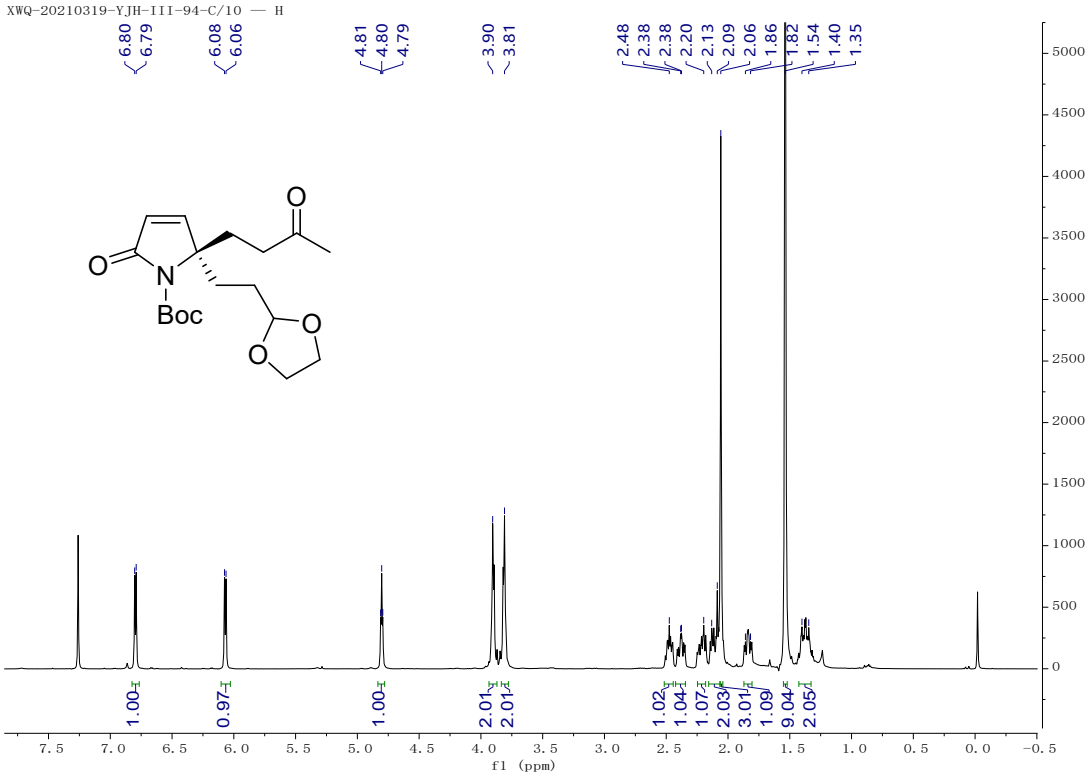
^{1}H NMR spectrum of compound **15d** (500 MHz, Chloroform-*d*)



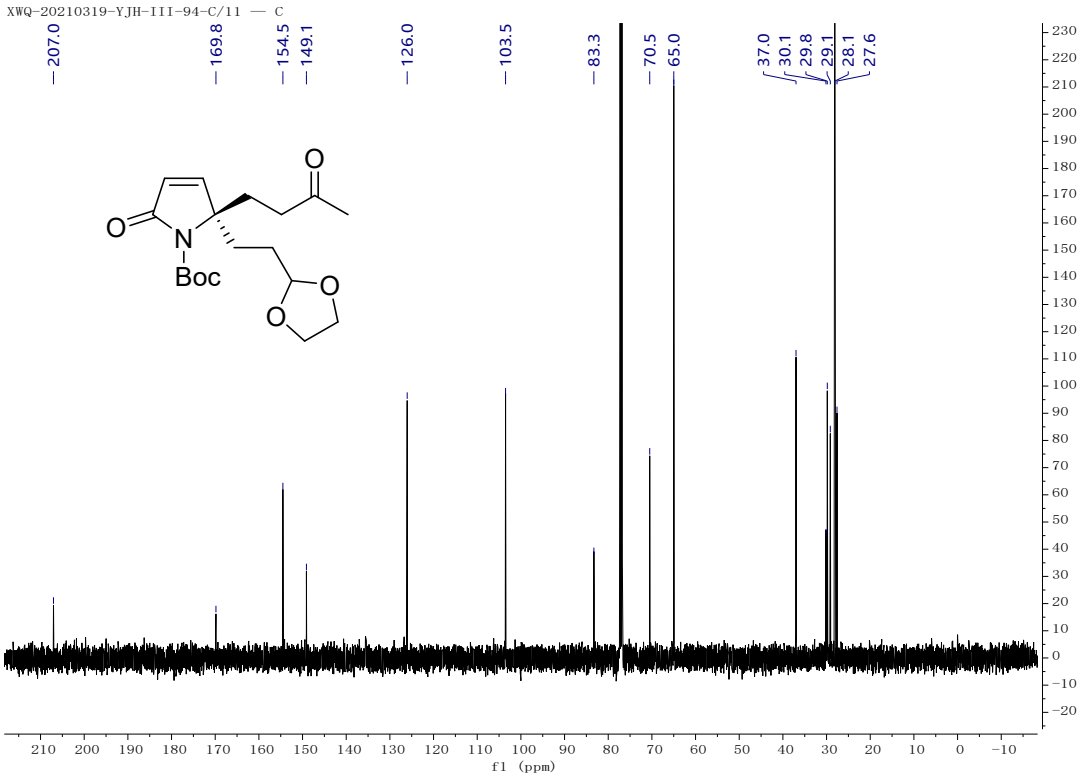
^{13}C NMR spectrum of compound **15d** (126 MHz, Chloroform-*d*)



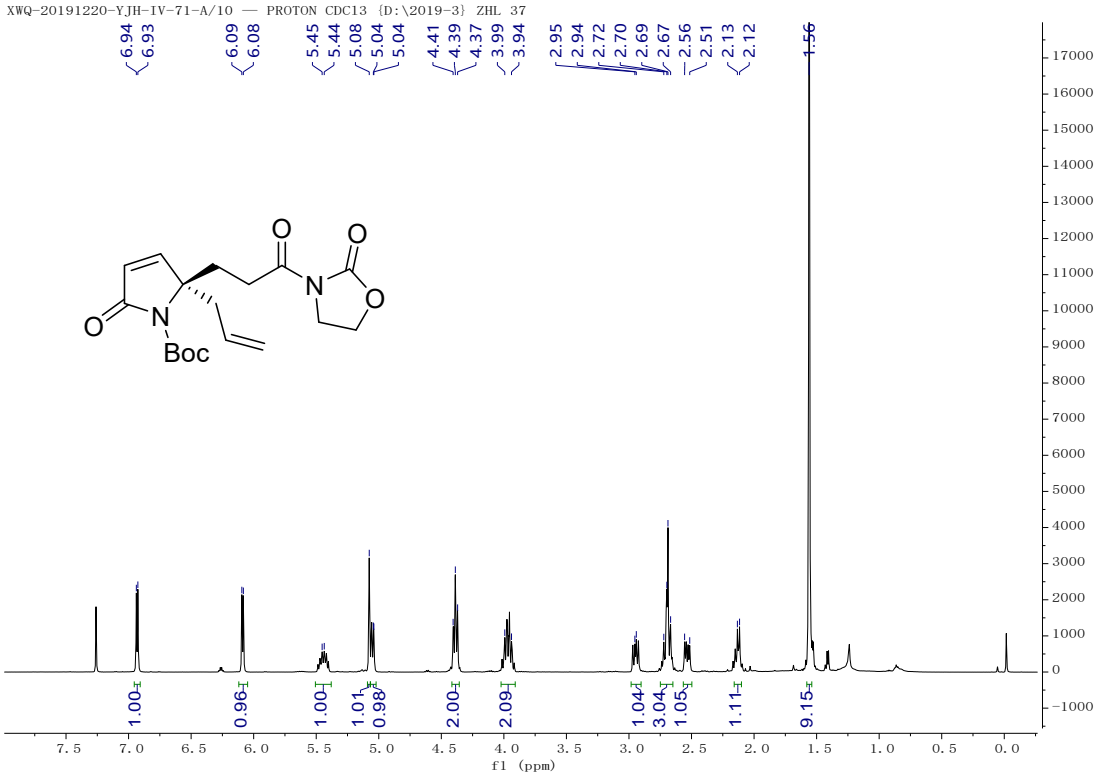
^{1}H NMR spectrum of compound **15e** (500 MHz, Chloroform-*d*)



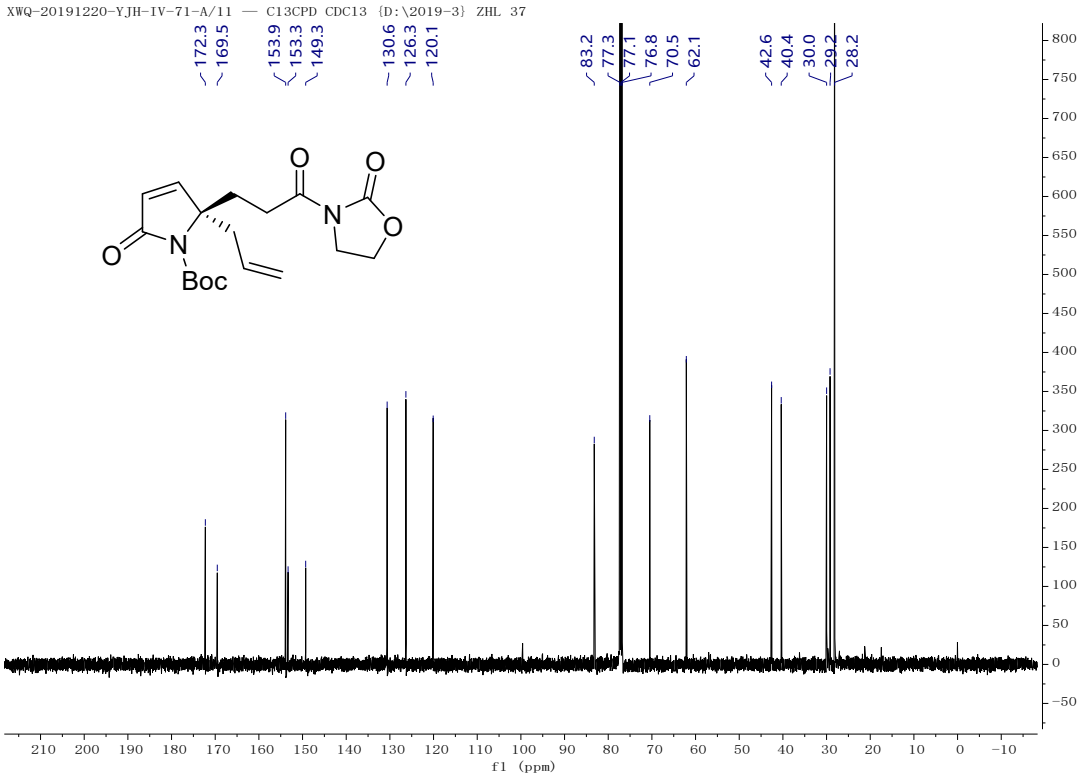
^{13}C NMR spectrum of compound **15e** (126 MHz, Chloroform-*d*)



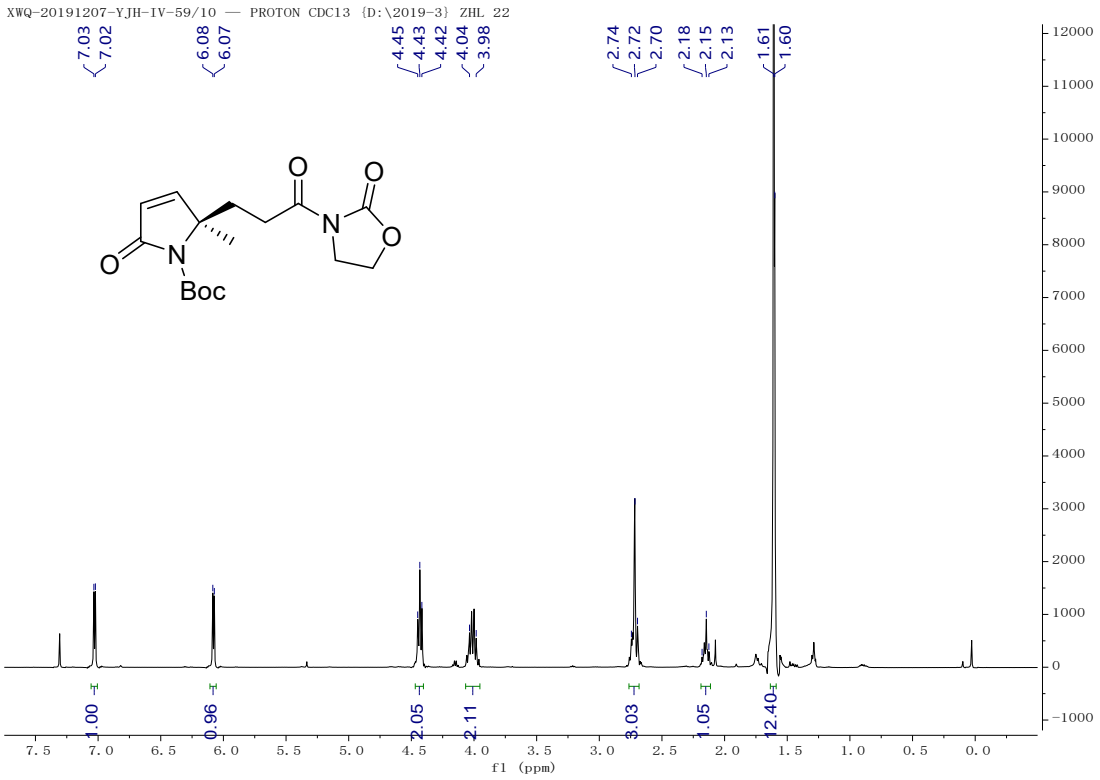
^{1}H NMR spectrum of compound **15f** (500 MHz, Chloroform-*d*)



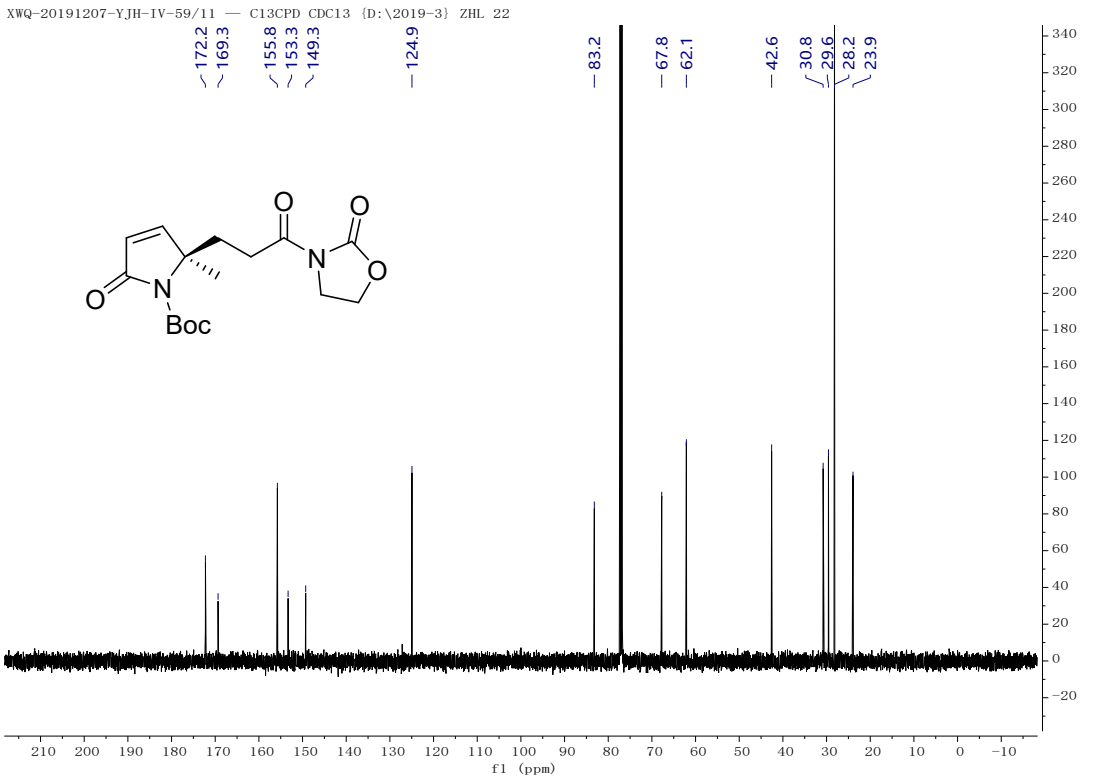
^{13}C NMR spectrum of compound **15f** (126 MHz, Chloroform-*d*)



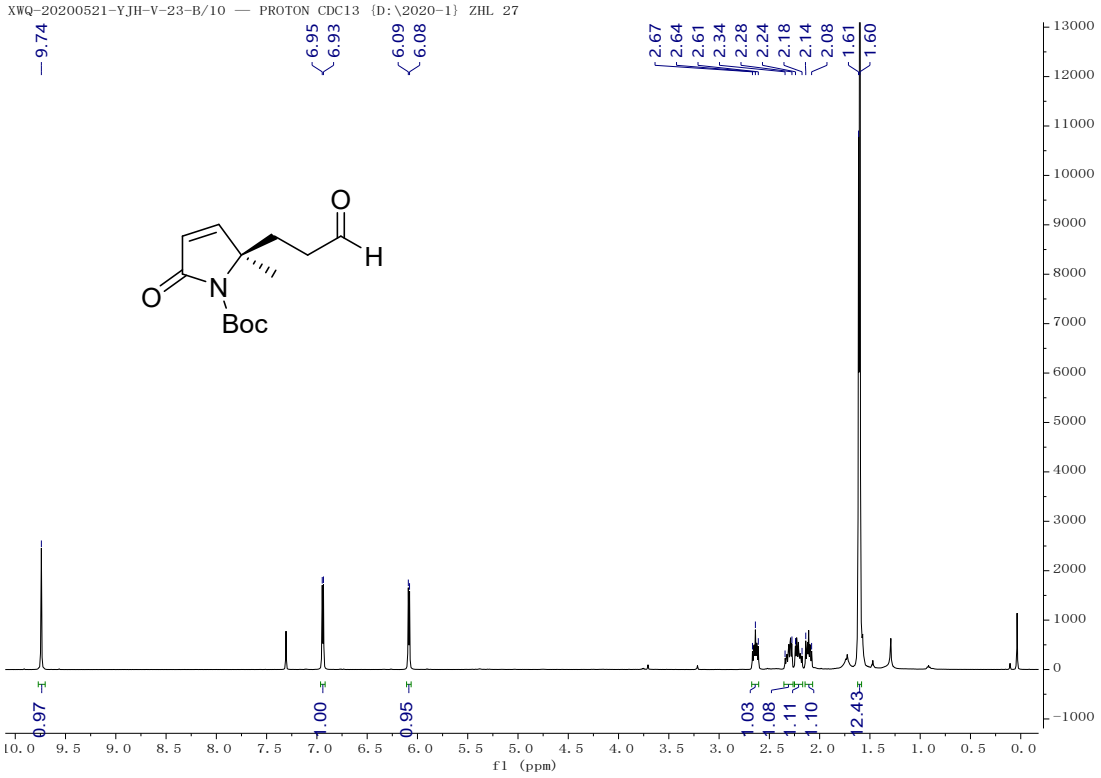
^{1}H NMR spectrum of compound **15g** (500 MHz, Chloroform-*d*)



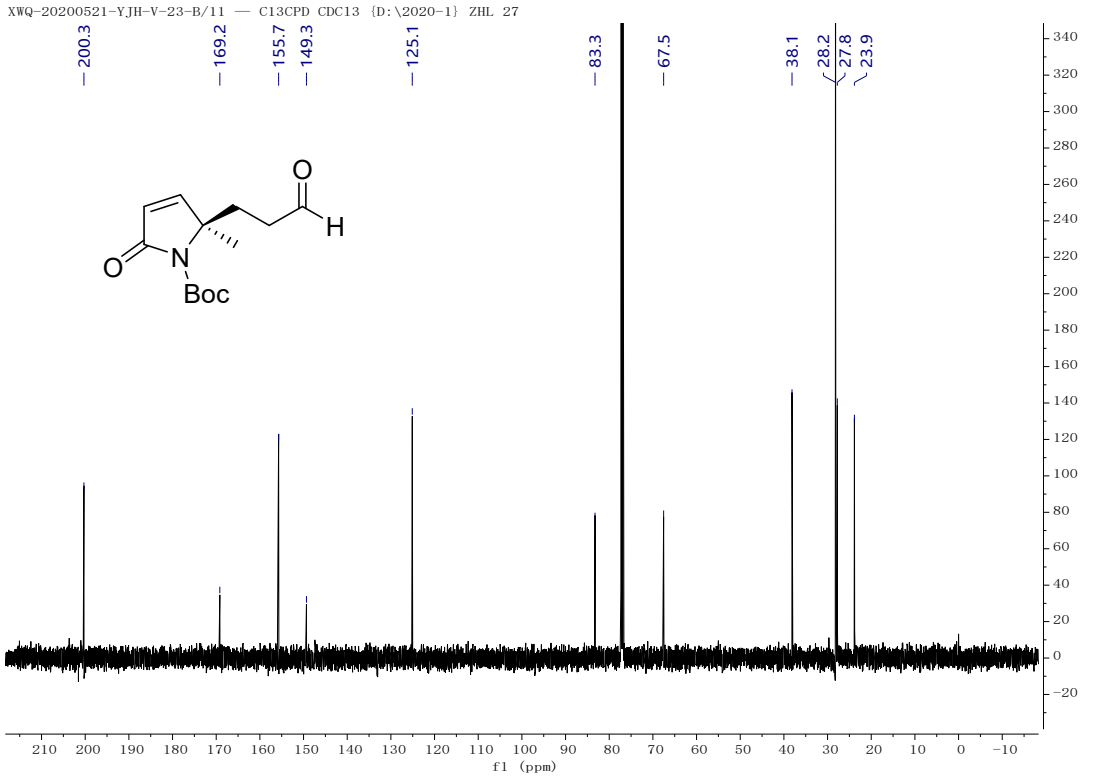
^{13}C NMR spectrum of compound **15g** (126 MHz, Chloroform-*d*)



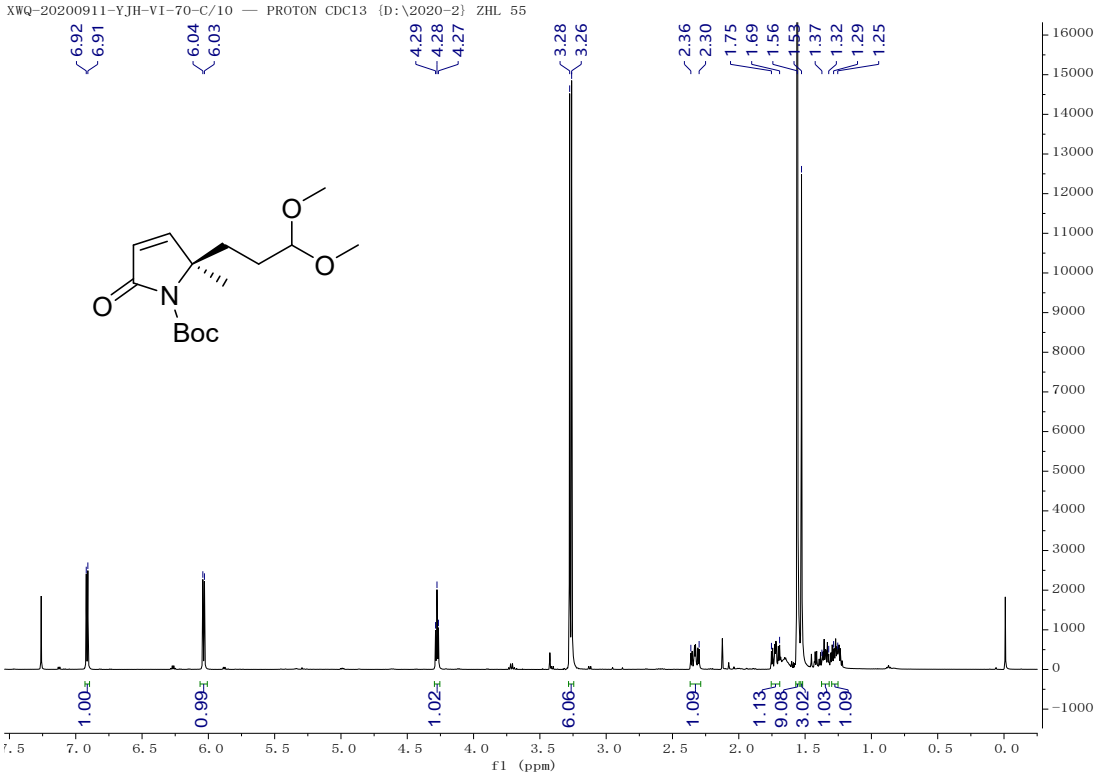
^{1}H NMR spectrum of compound **15h** (500 MHz, Chloroform-*d*)



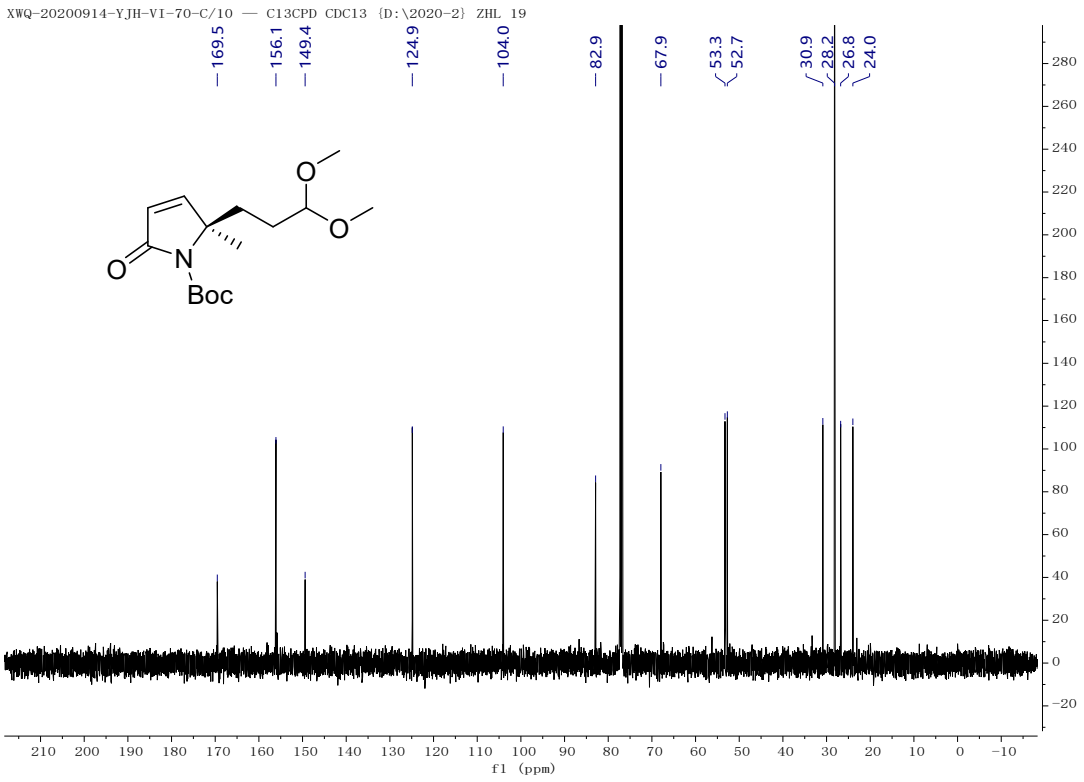
^{13}C NMR spectrum of compound **15h** (126 MHz, Chloroform-*d*)



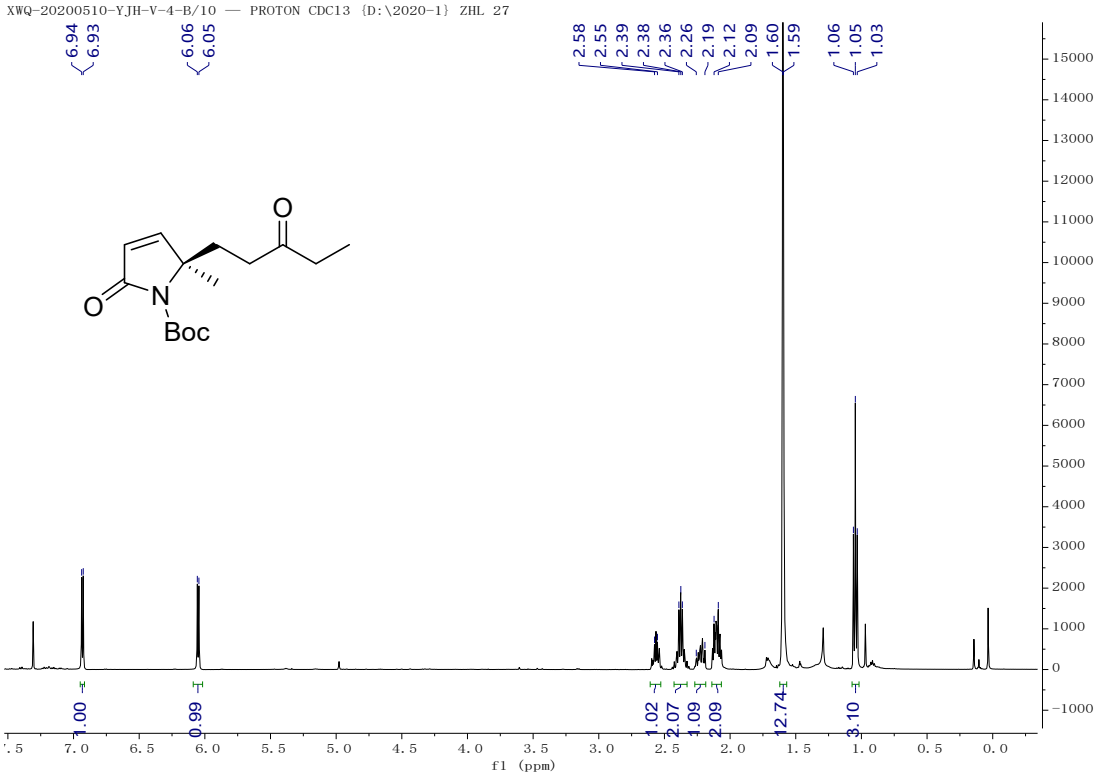
^{1}H NMR spectrum of compound **15h1** (500 MHz, Chloroform-*d*)



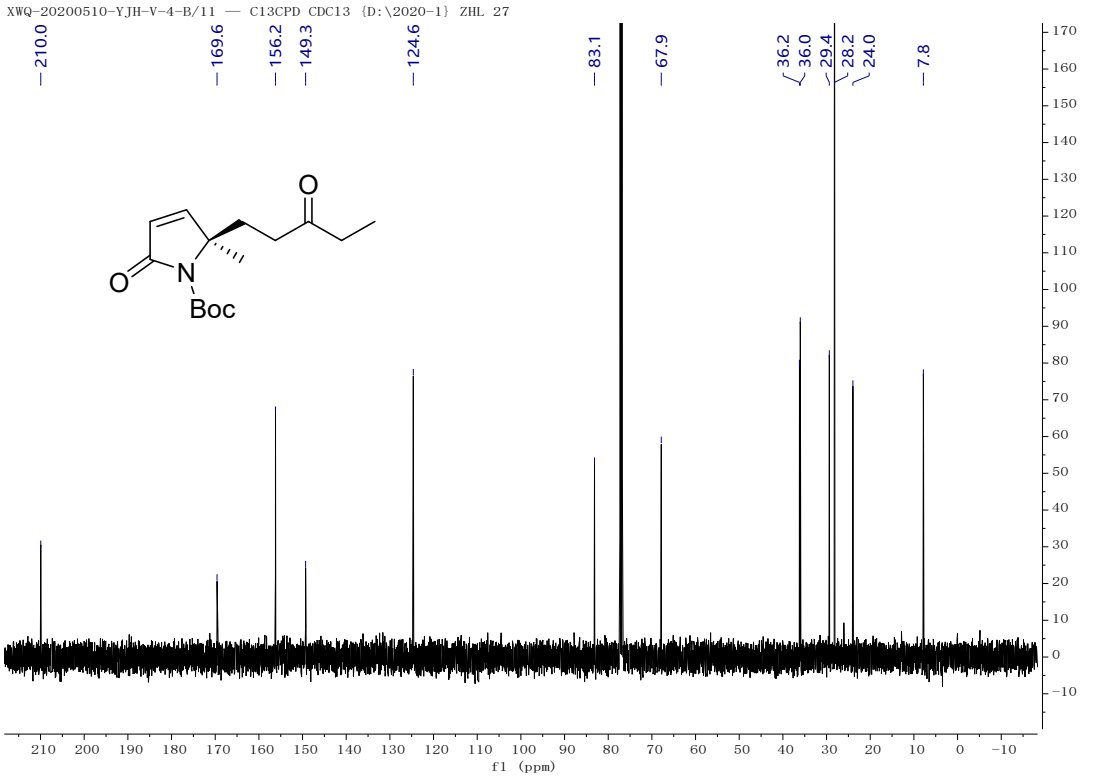
^{13}C NMR spectrum of compound **15h1** (126 MHz, Chloroform-*d*)



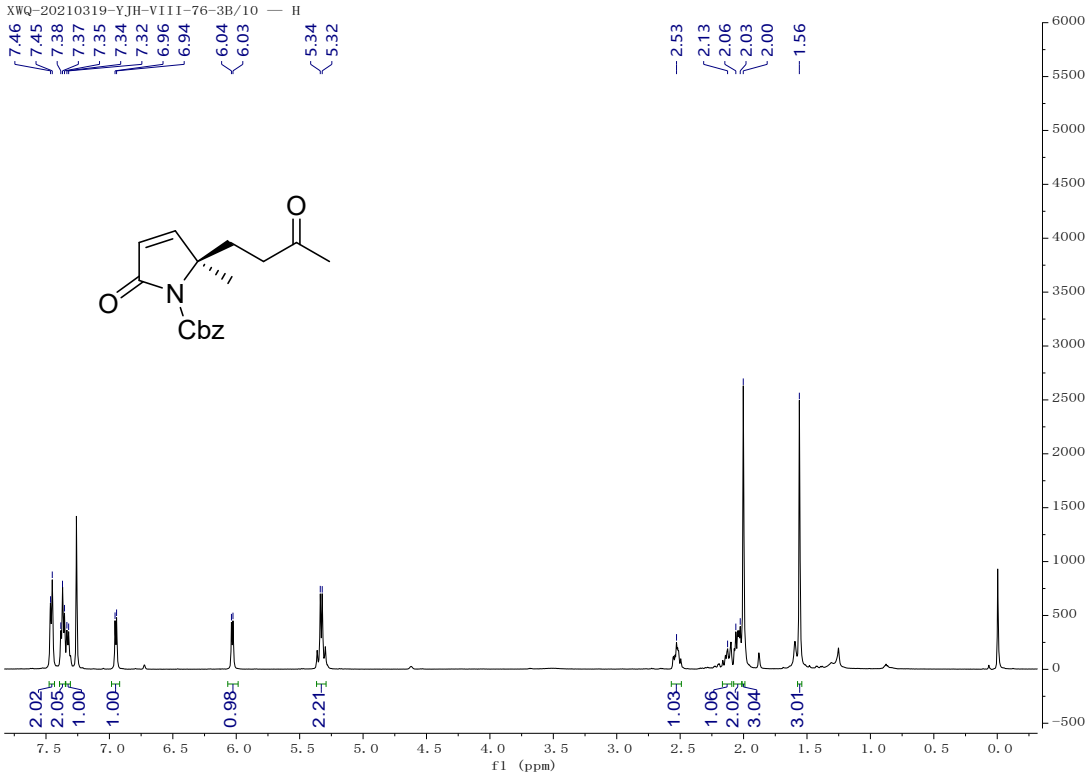
^{1}H NMR spectrum of compound **15i** (500 MHz, Chloroform-*d*)



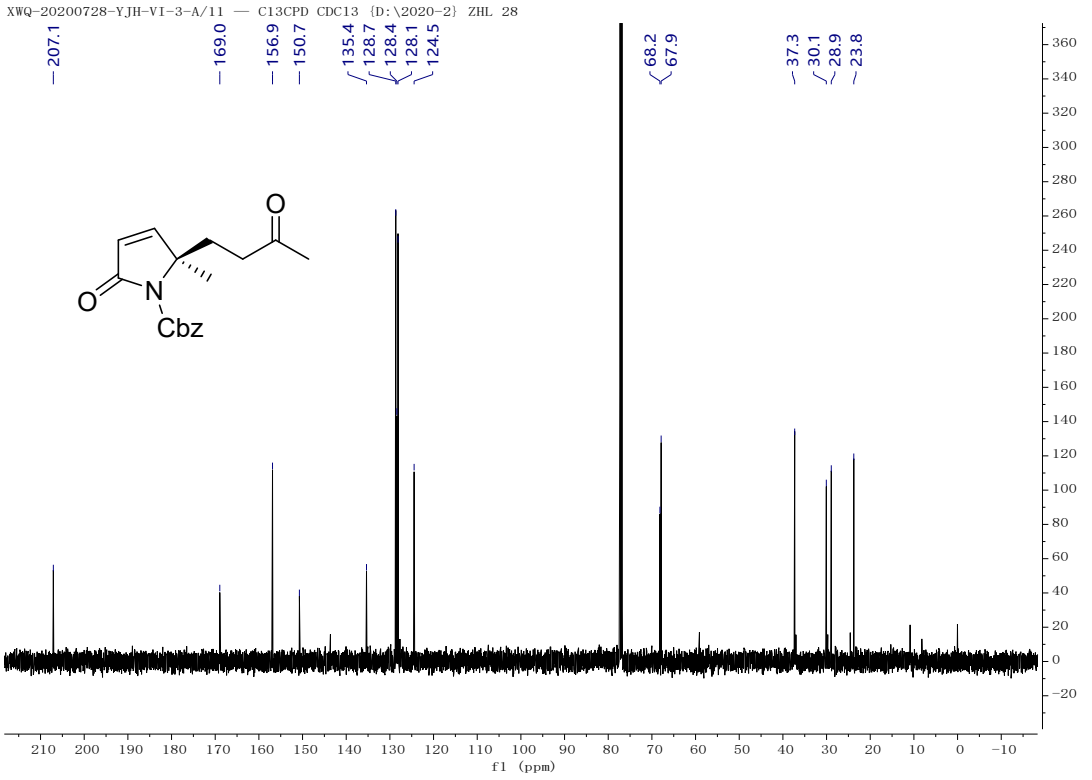
^{13}C NMR spectrum of compound **15i** (126 MHz, Chloroform-*d*)



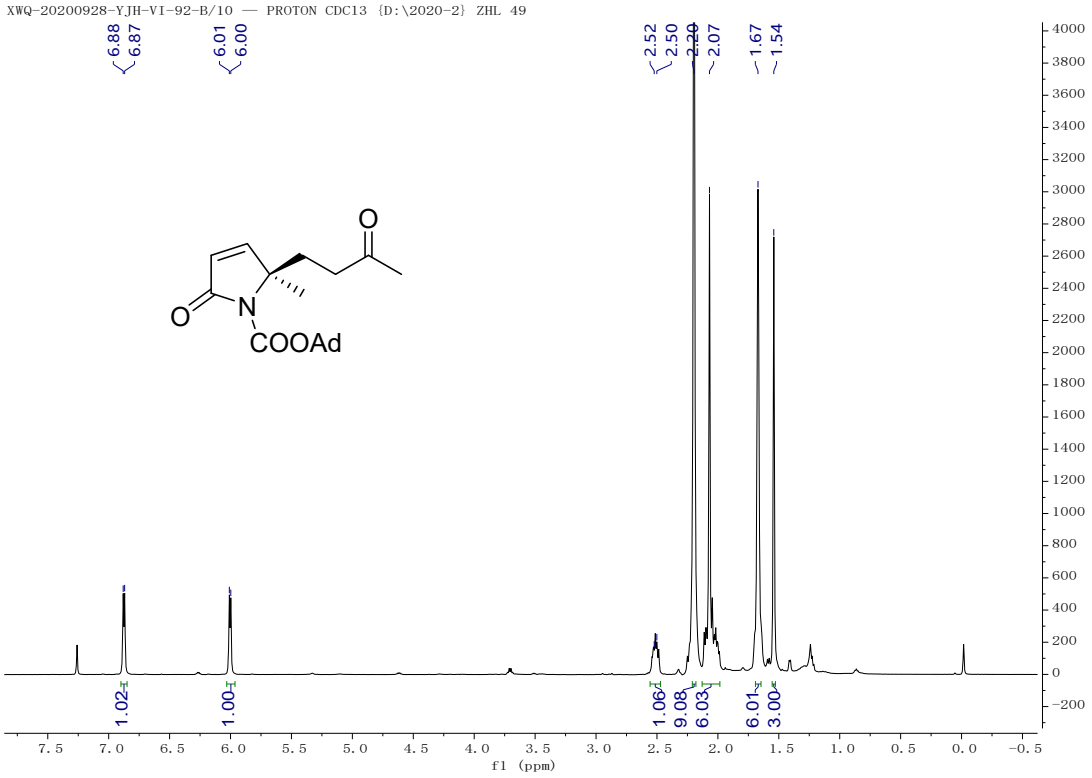
^{1}H NMR spectrum of compound **15j** (500 MHz, Chloroform-*d*)



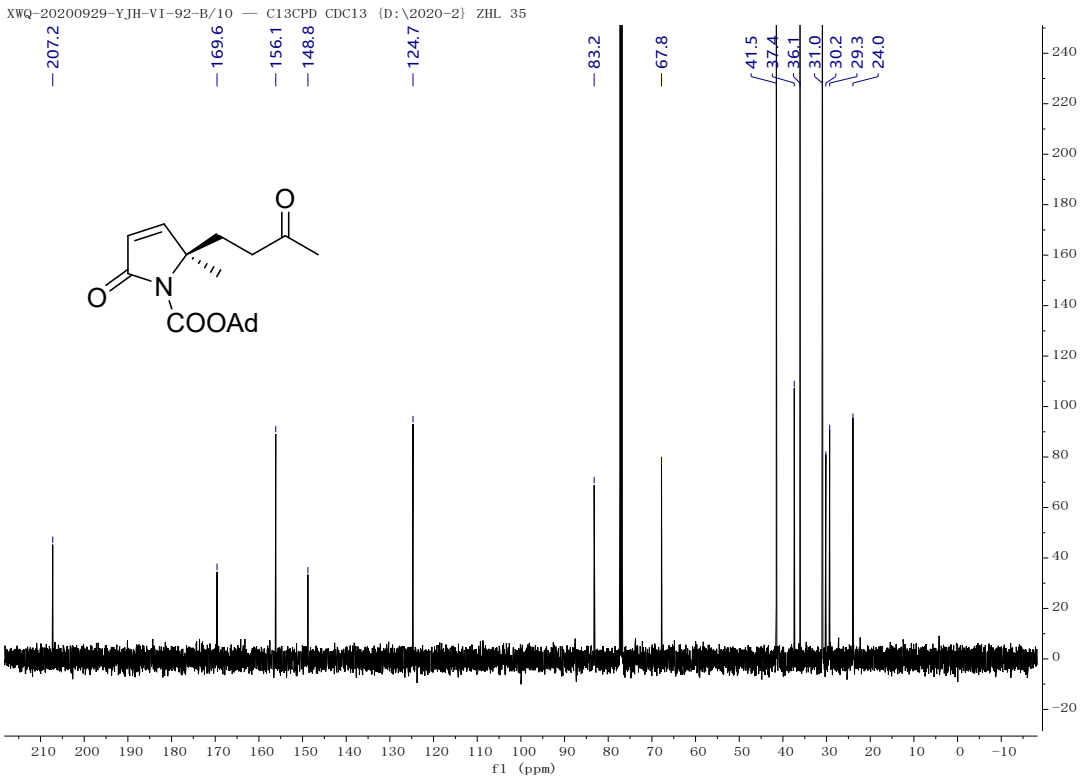
^{13}C NMR spectrum of compound **15j** (126 MHz, Chloroform-*d*)



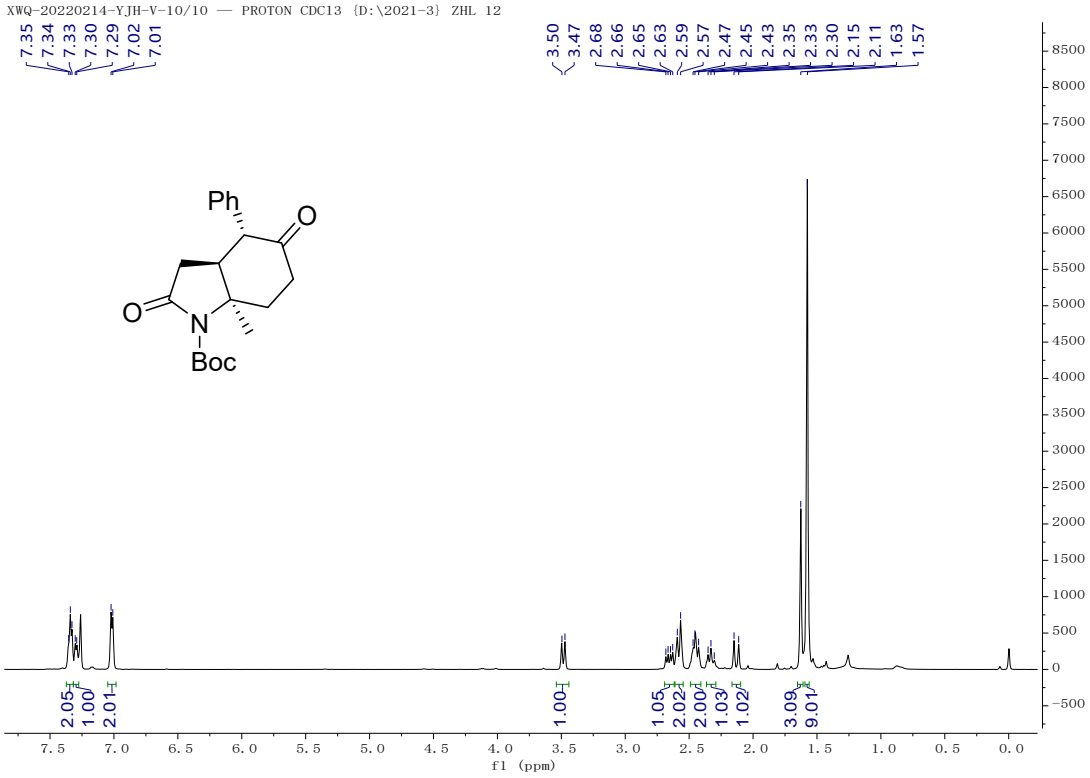
^{1}H NMR spectrum of compound **15k** (500 MHz, Chloroform-*d*)



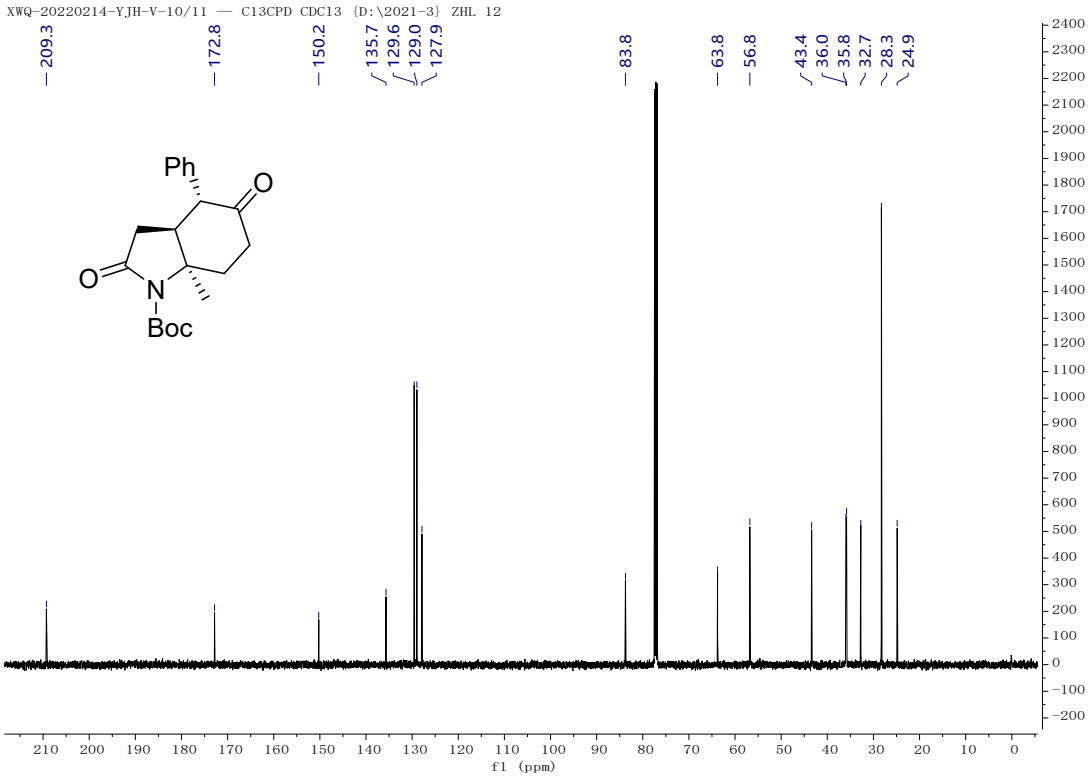
^{13}C NMR spectrum of compound **15k** (126 MHz, Chloroform-*d*)



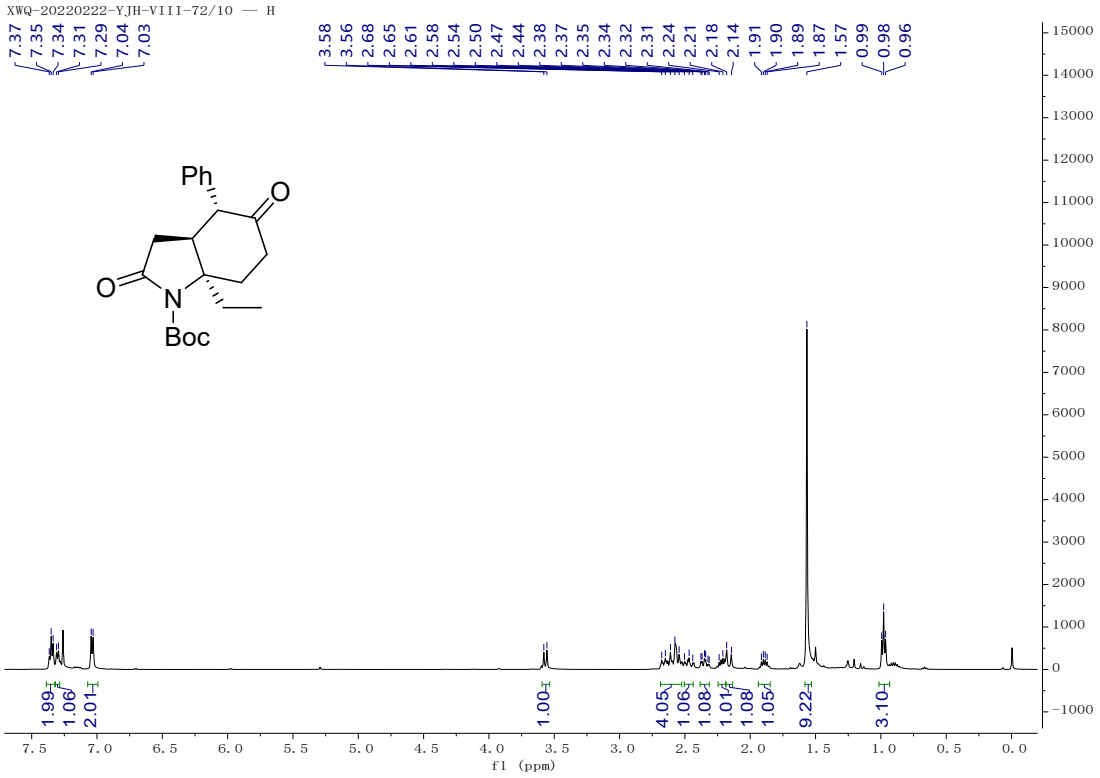
^{1}H NMR spectrum of compound **17a** (500 MHz, Chloroform-*d*)



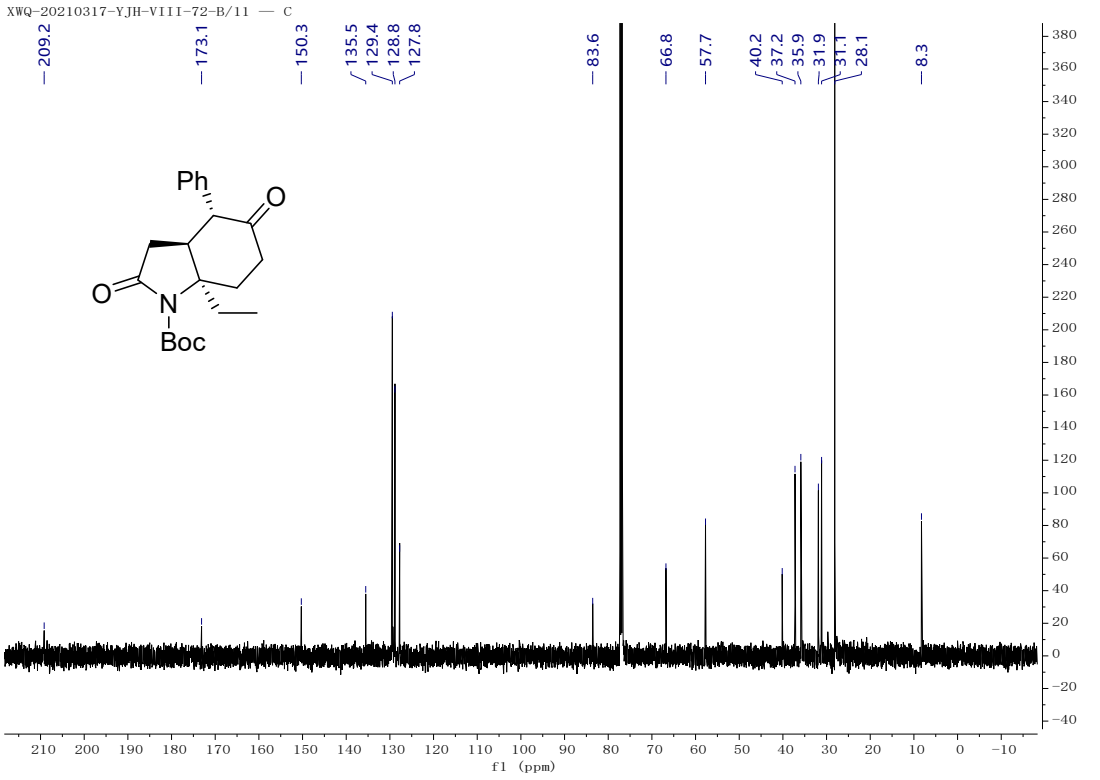
^{13}C NMR spectrum of compound **17a** (126 MHz, Chloroform-*d*)



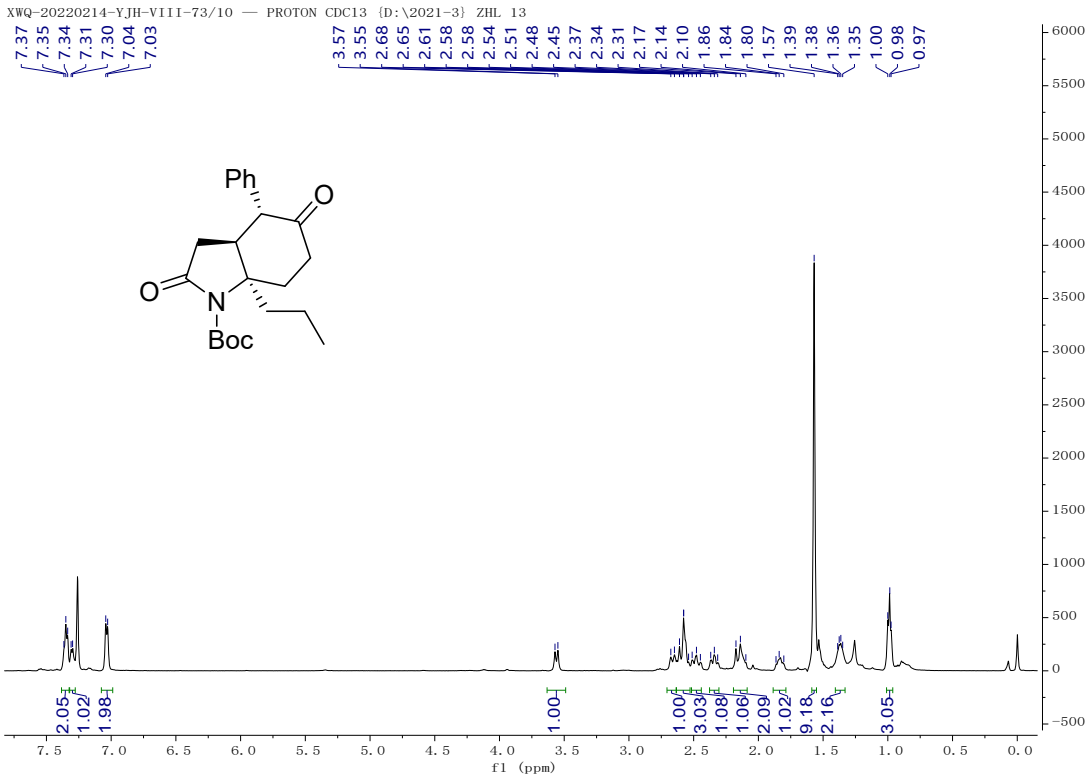
^{1}H NMR spectrum of compound **17b** (500 MHz, Chloroform-*d*)



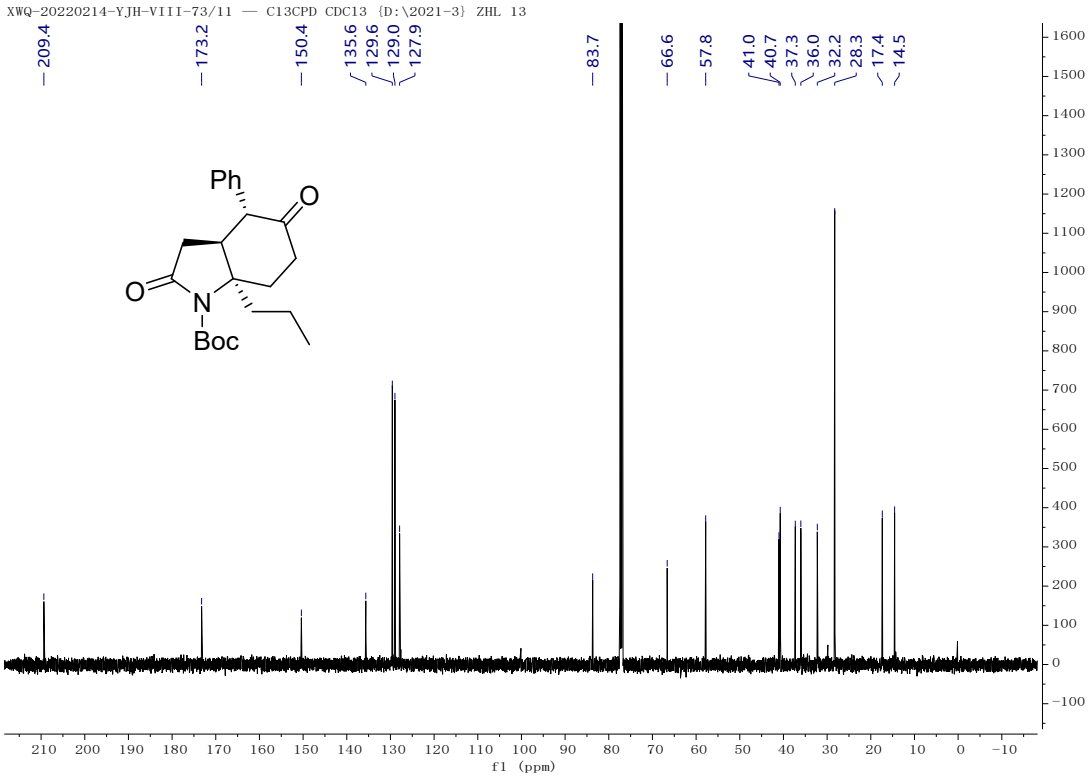
^{13}C NMR spectrum of compound **17b** (126 MHz, Chloroform-*d*)



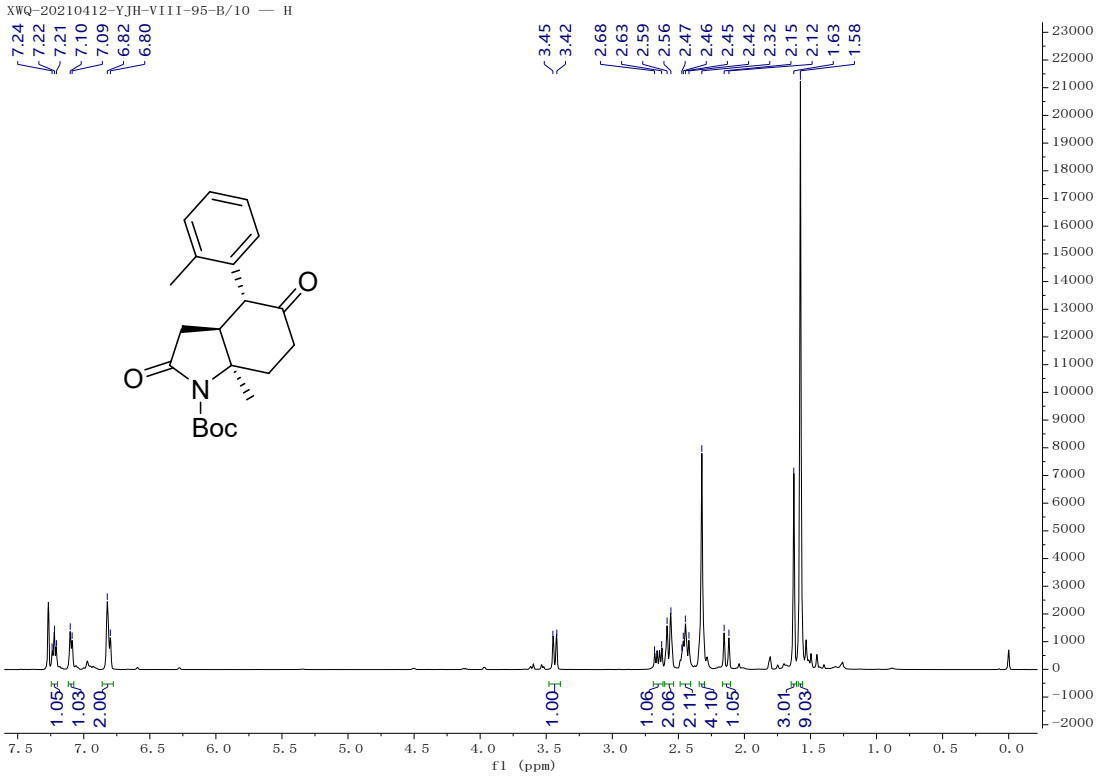
^{1}H NMR spectrum of compound **17c** (500 MHz, Chloroform-*d*)



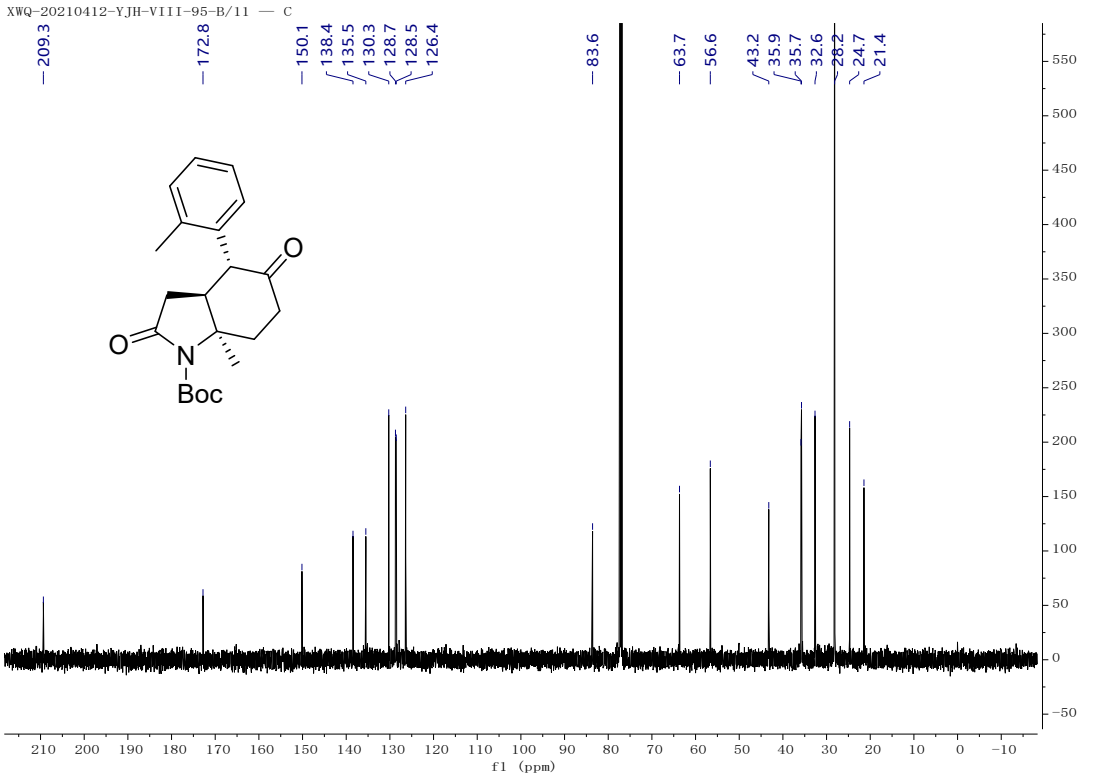
^{13}C NMR spectrum of compound **17c** (126 MHz, Chloroform-*d*)



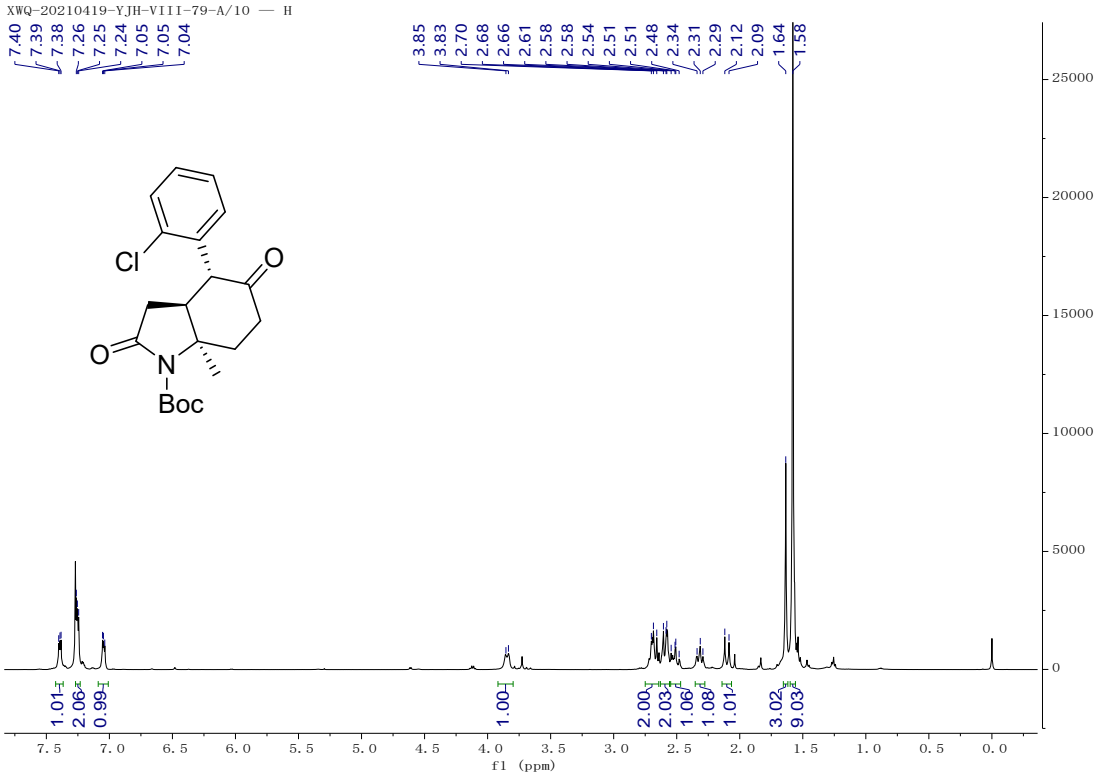
^{1}H NMR spectrum of compound **17d** (500 MHz, Chloroform-*d*)



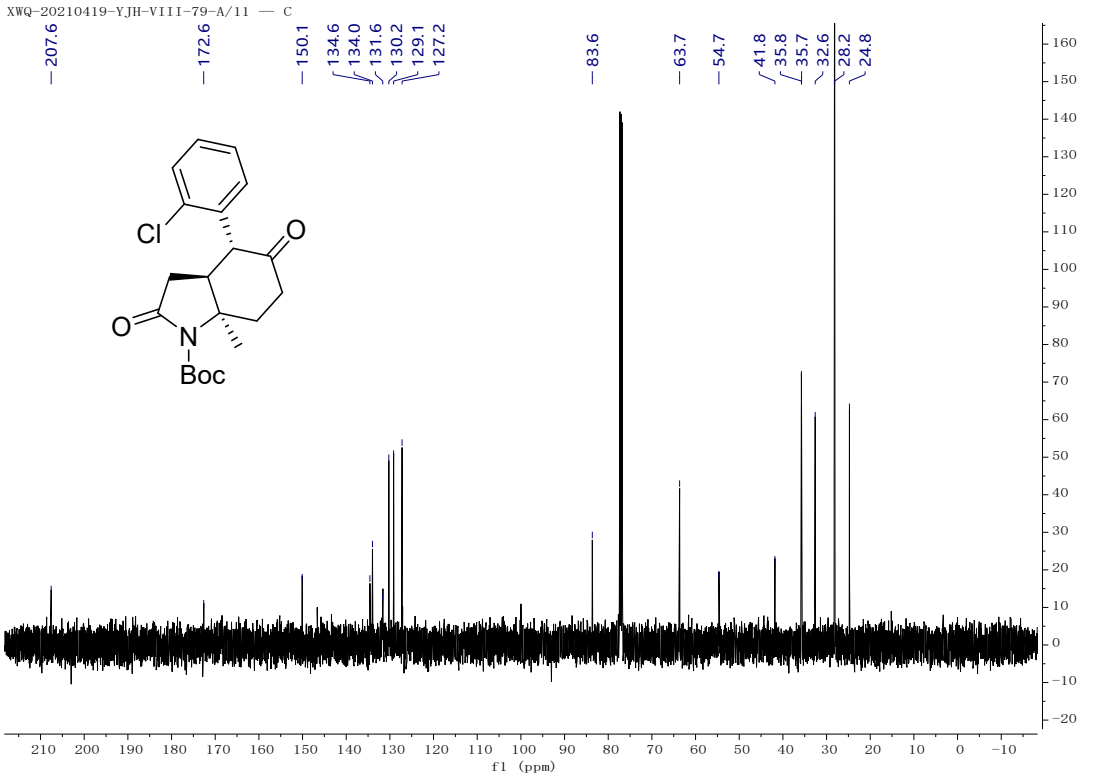
^{13}C NMR spectrum of compound **17d** (126 MHz, Chloroform-*d*)



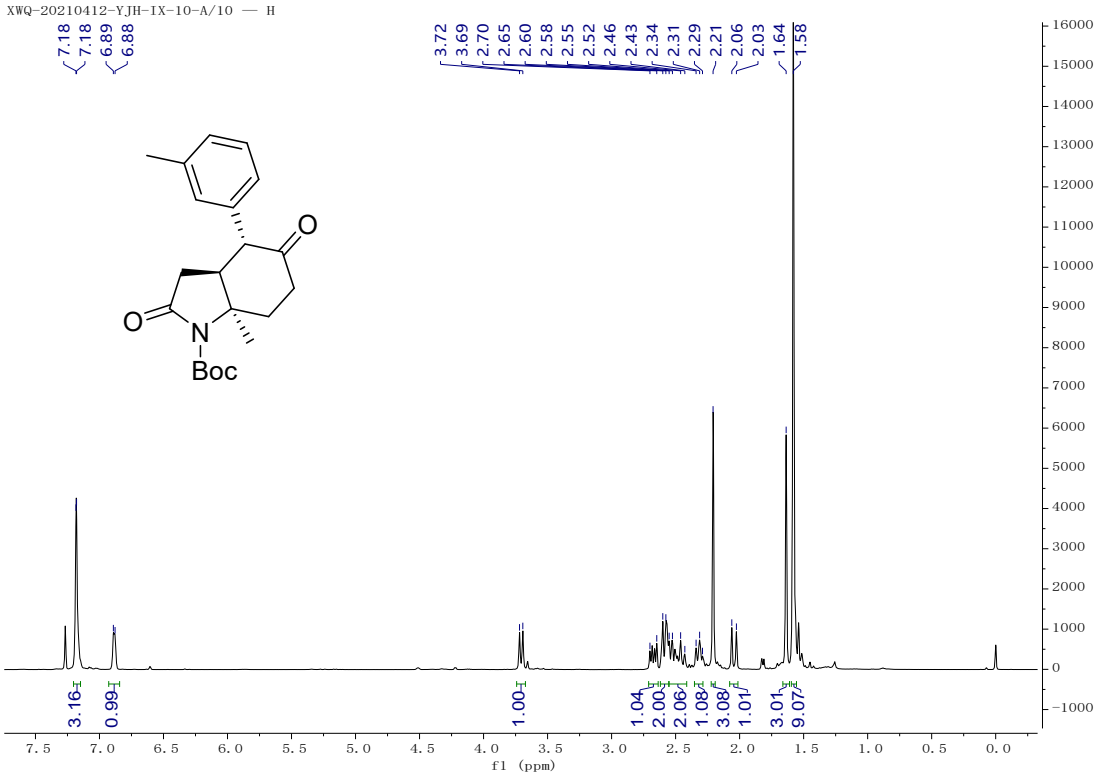
^{1}H NMR spectrum of compound **17e** (500 MHz, Chloroform-*d*)



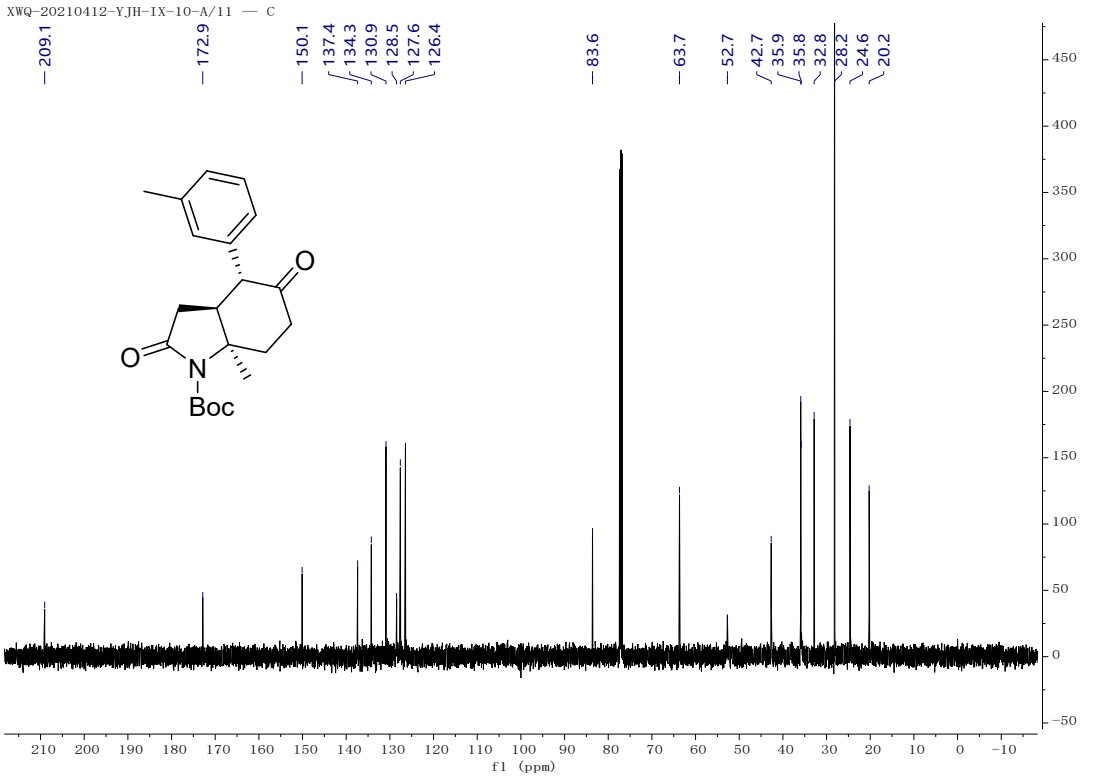
^{13}C NMR spectrum of compound **17e** (126 MHz, Chloroform-*d*)



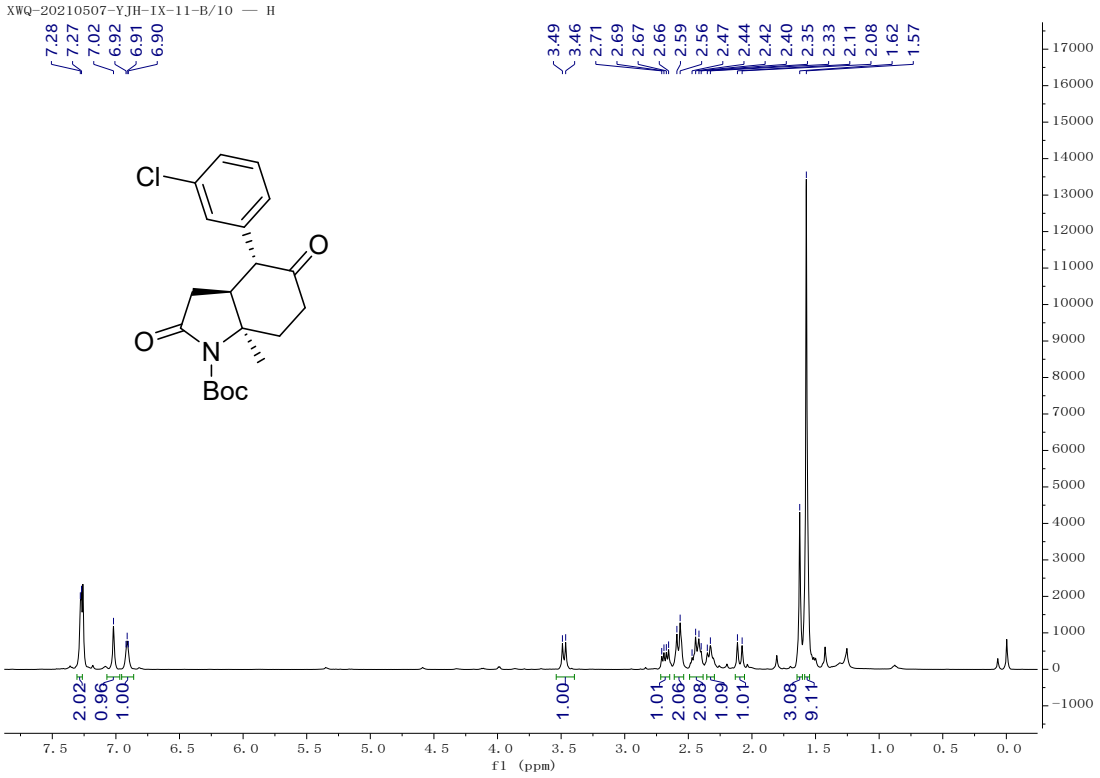
^{1}H NMR spectrum of compound **17f** (500 MHz, Chloroform-*d*)



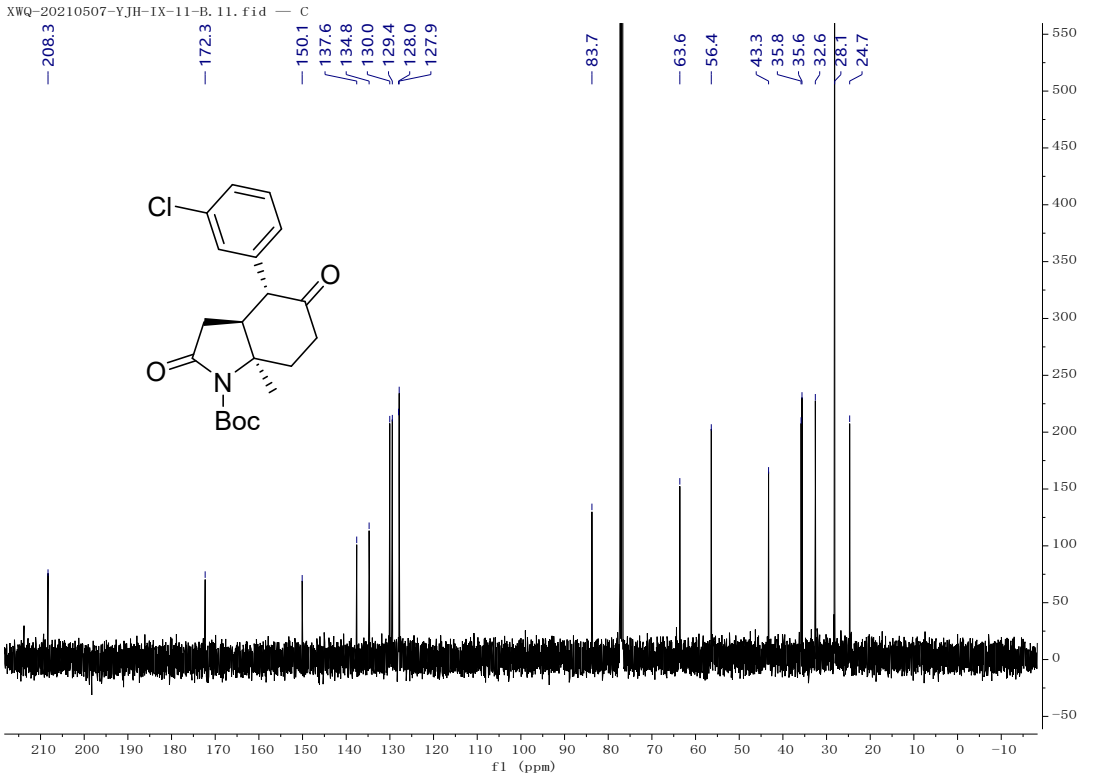
^{13}C NMR spectrum of compound **17f** (126 MHz, Chloroform-*d*)



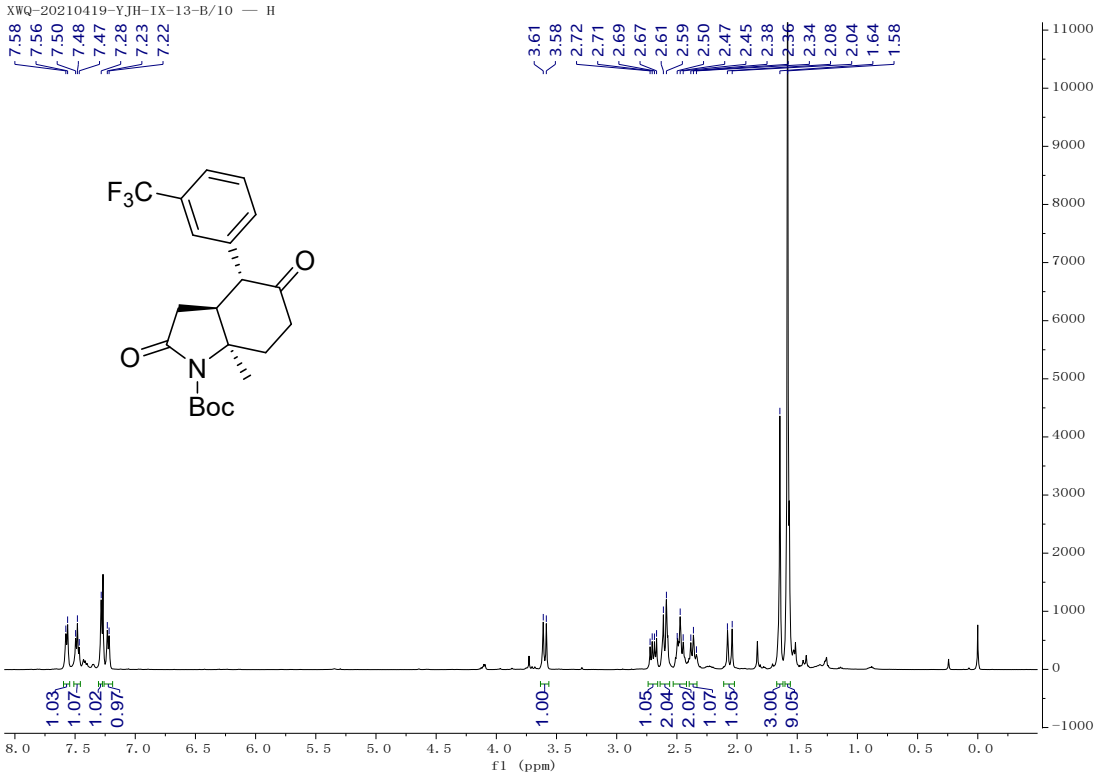
^{1}H NMR spectrum of compound **17g** (500 MHz, Chloroform-*d*)



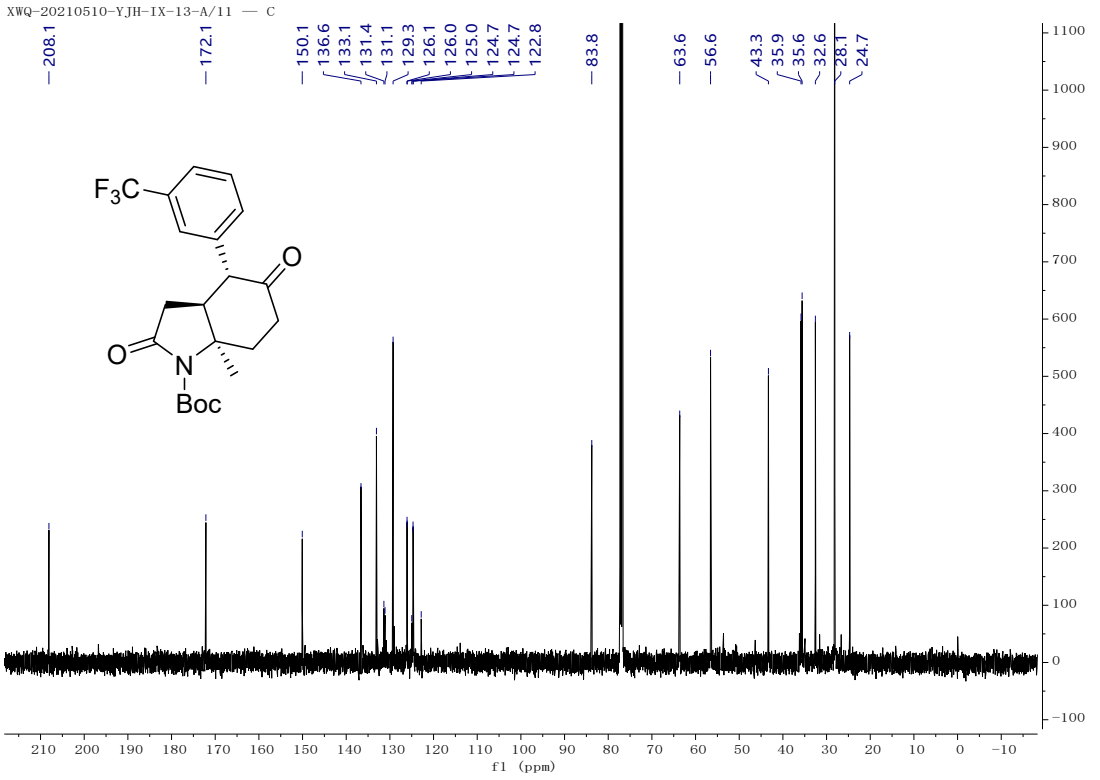
^{13}C NMR spectrum of compound **17g** (126 MHz, Chloroform-*d*)



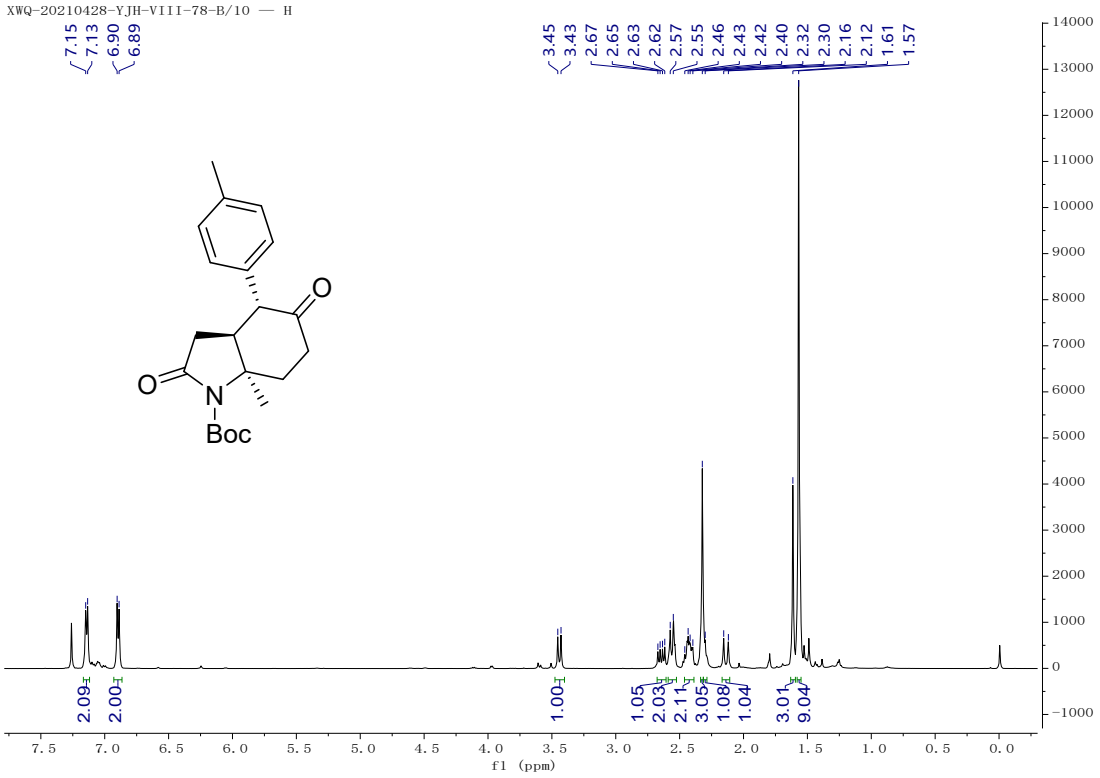
^{1}H NMR spectrum of compound **17h** (500 MHz, Chloroform-*d*)



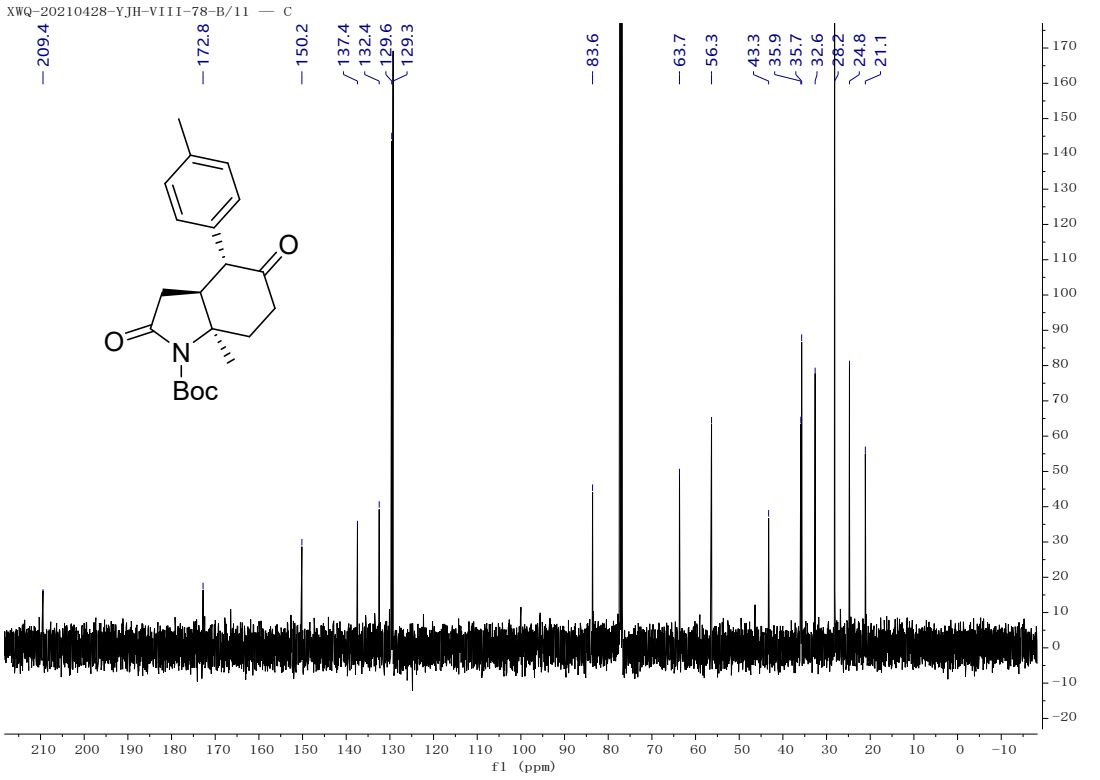
^{13}C NMR spectrum of compound **17h** (126 MHz, Chloroform-*d*)



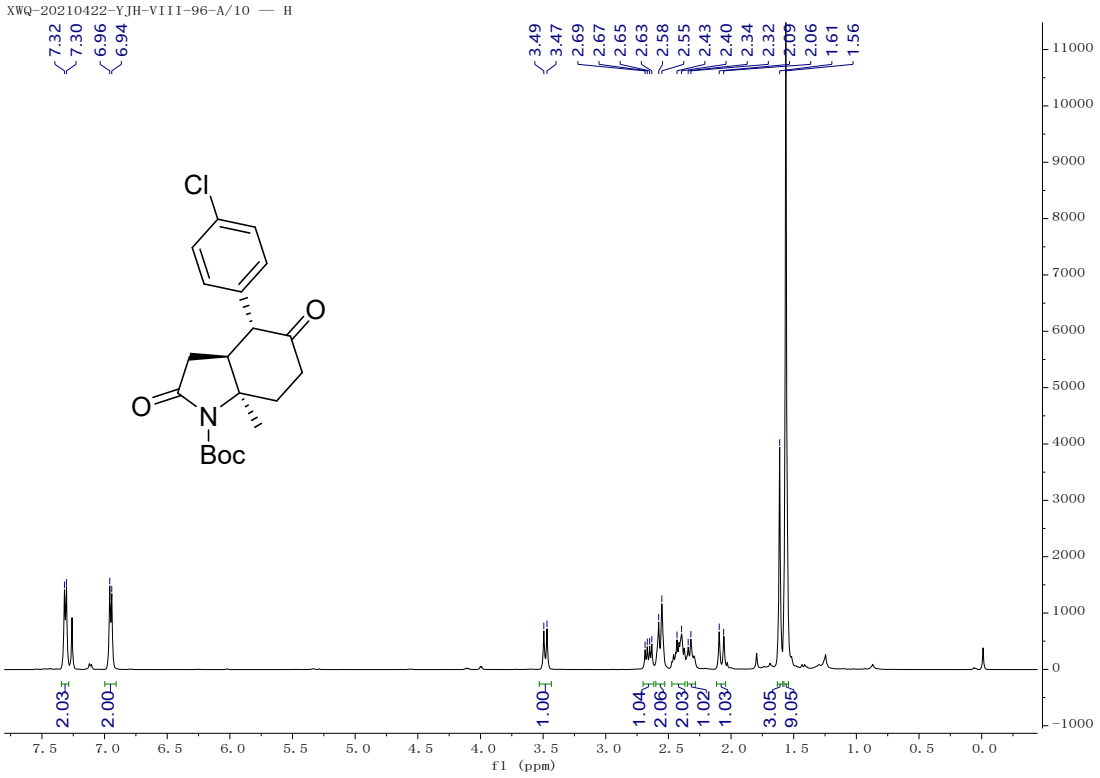
^{1}H NMR spectrum of compound **17i** (500 MHz, Chloroform-*d*)



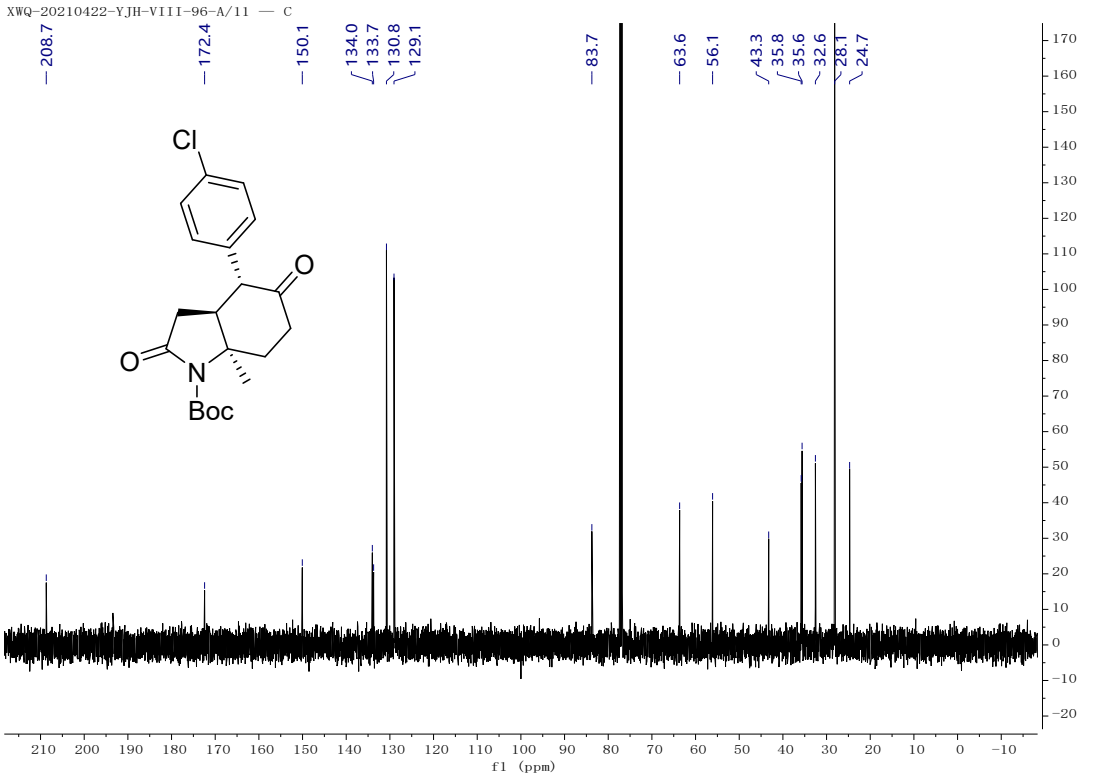
^{13}C NMR spectrum of compound **17i** (126 MHz, Chloroform-*d*)



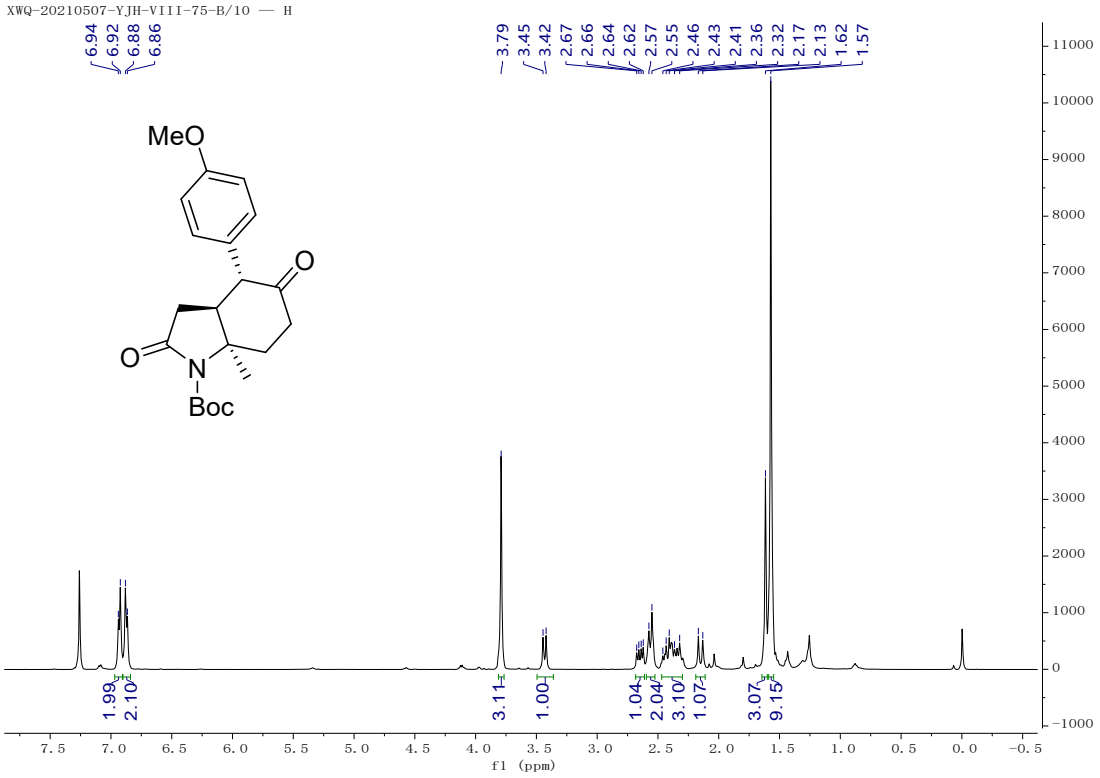
^{1}H NMR spectrum of compound **17j** (500 MHz, Chloroform-*d*)



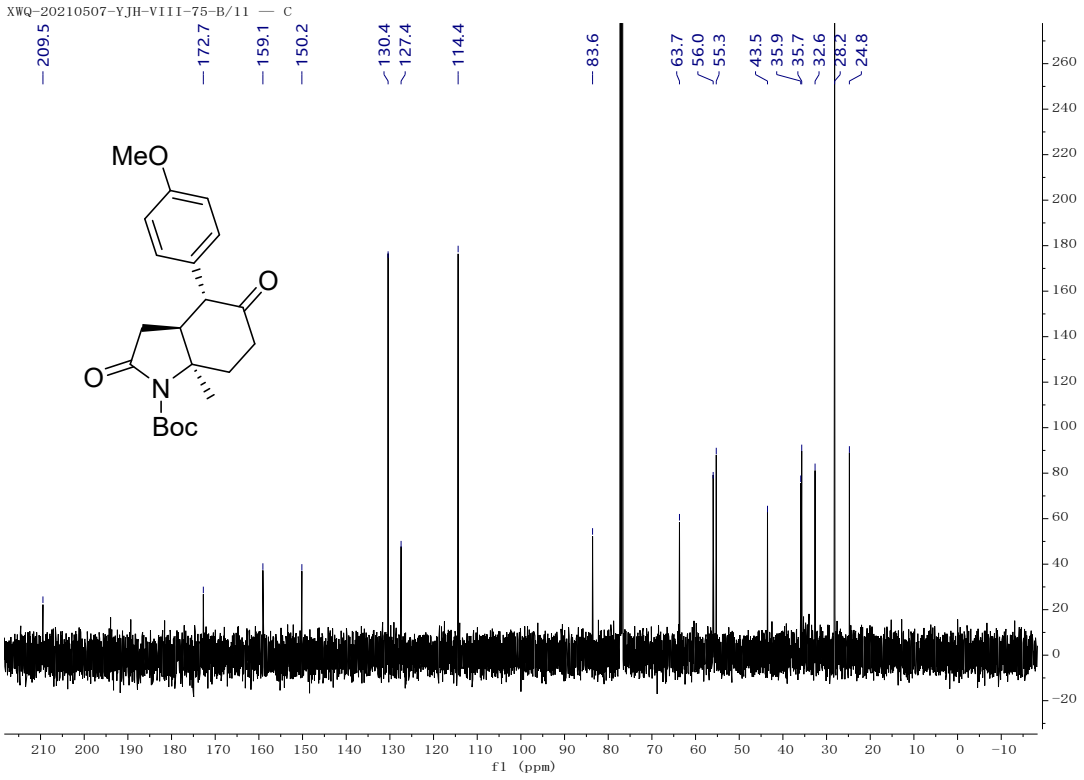
^{13}C NMR spectrum of compound **17j** (126 MHz, Chloroform-*d*)



^{1}H NMR spectrum of compound **17k** (500 MHz, Chloroform-*d*)



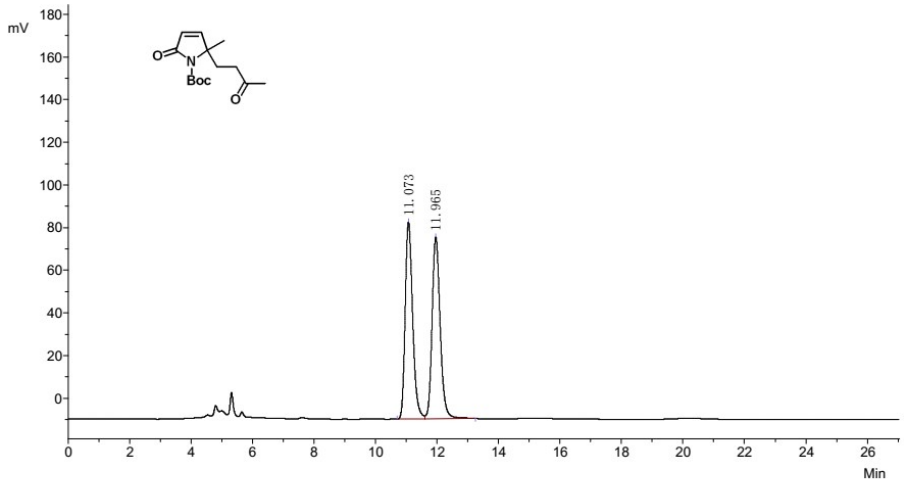
^{13}C NMR spectrum of compound **17k** (126 MHz, Chloroform-*d*)



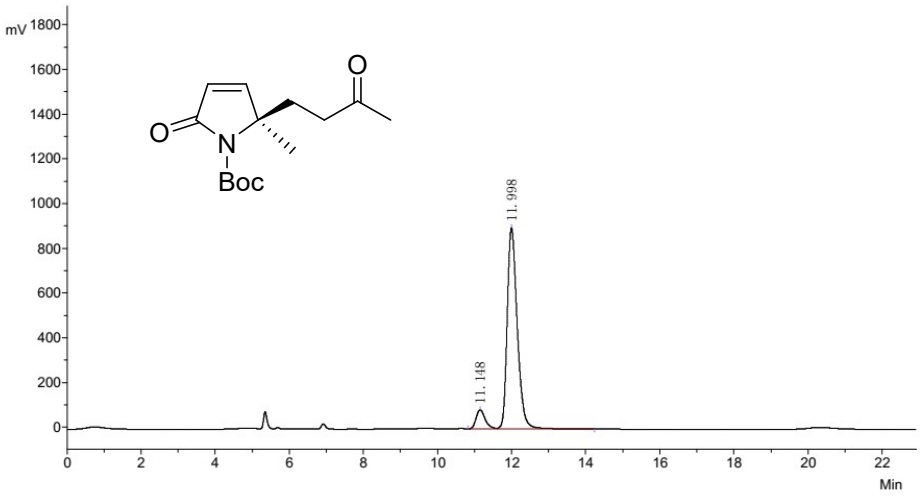
6. HPLC Data

HPLC data of compound **15a**

(Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, 0.7 mL/min, 214 nm)



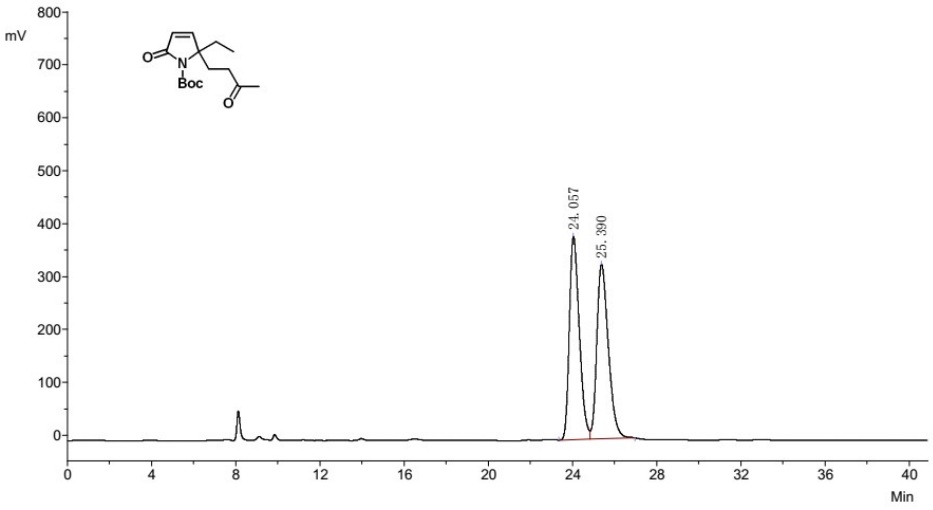
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.073	92349.5	1557412.1	50.0066	50.0066
2	11.965	85179.7	1557004.0	49.9934	49.9934
Total		177529.2	3114416.1	100.0000	100.0000



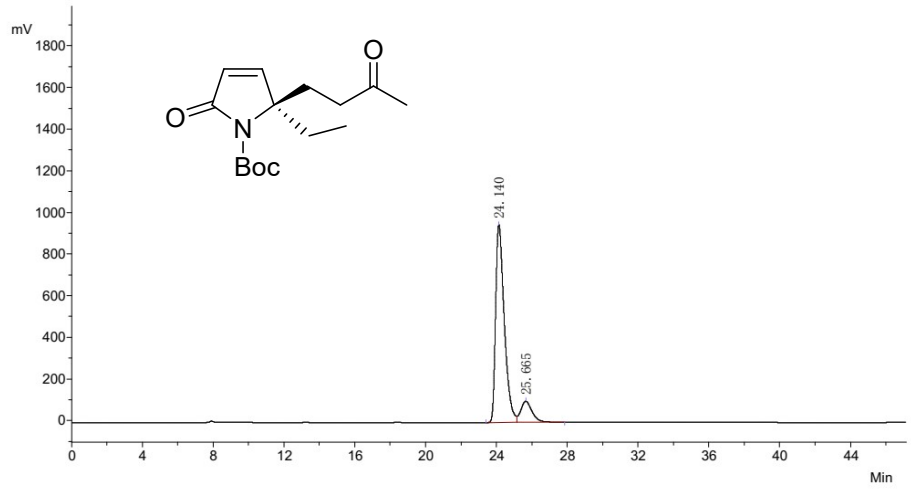
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.148	84924.0	1442450.3	7.8638	7.8638
2	11.998	898507.6	16900464.9	92.1362	92.1362
Total		983431.6	18342915.2	100.0000	100.0000

HPLC data of compound **15b**

(Chiralpak OD-H, Hexane/*i*-PrOH = 90/10, 0.4 mL/min, 214 nm)



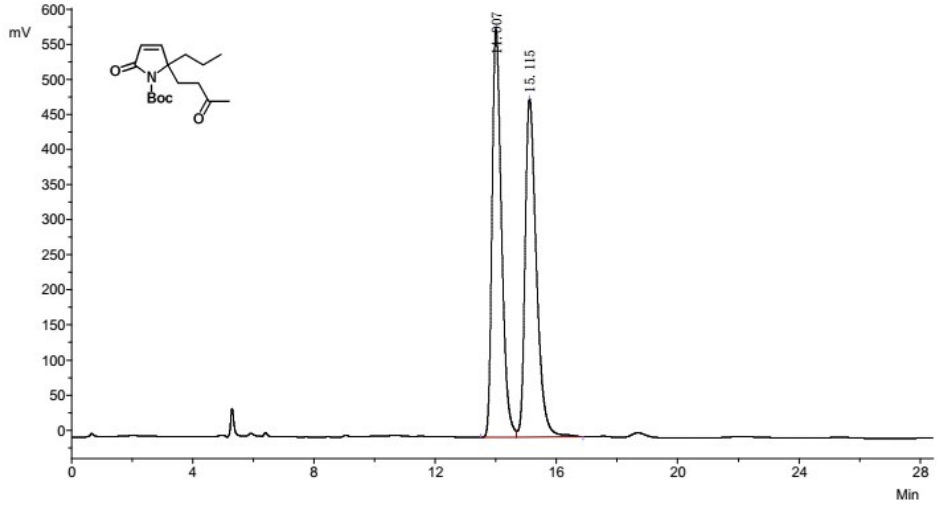
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.057	383633.0	12588310.7	50.0823	50.0823
2	25.390	329550.3	12546937.7	49.9177	49.9177
Total		713183.3	25135248.4	100.0000	100.0000



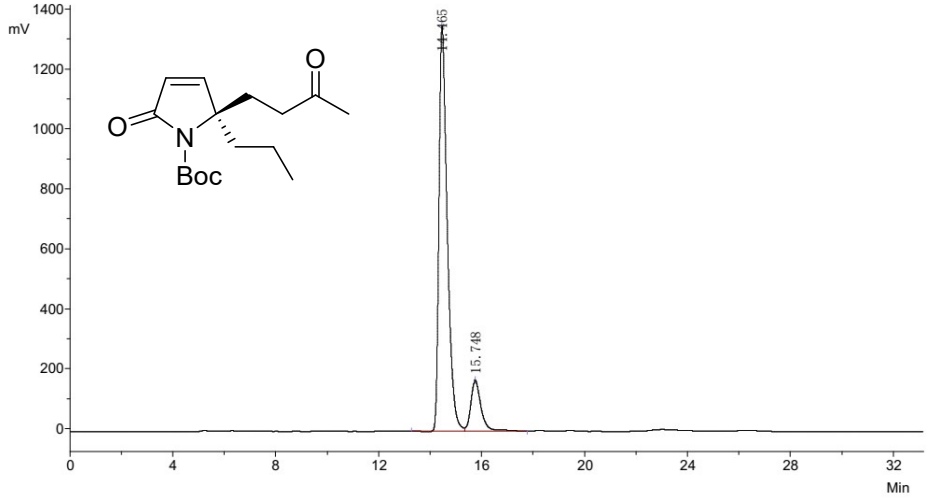
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.140	951362.8	32335220.9	87.4916	87.4916
2	25.665	101759.7	4622882.1	12.5084	12.5084
Total		1053122.4	36958103.0	100.0000	100.0000

HPLC data of compound **15c**

(Chiralpak OD-H, Hexane/*i*-PrOH = 90/10, 0.6 mL/min, 214 nm)



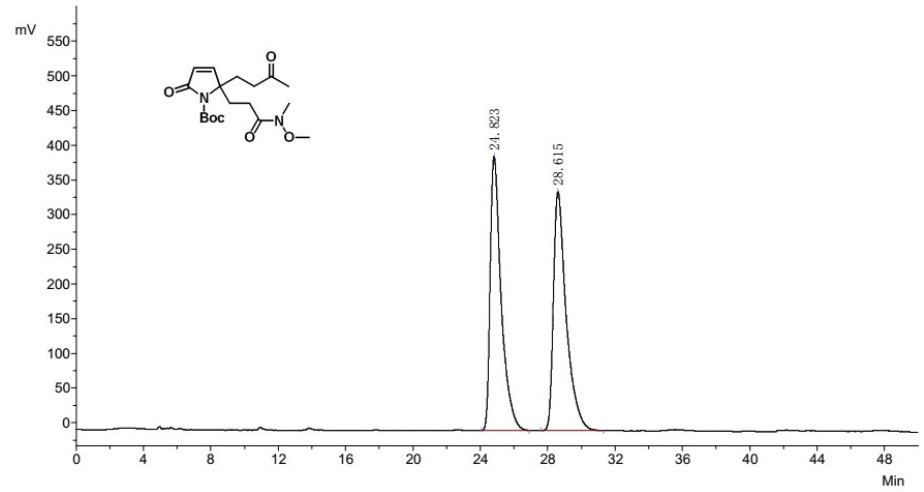
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.007	581937.7	12556589.6	50.1555	50.1555
2	15.115	482020.9	12478710.5	49.8445	49.8445
Total		1063958.6	25035300.1	100.0000	100.0000



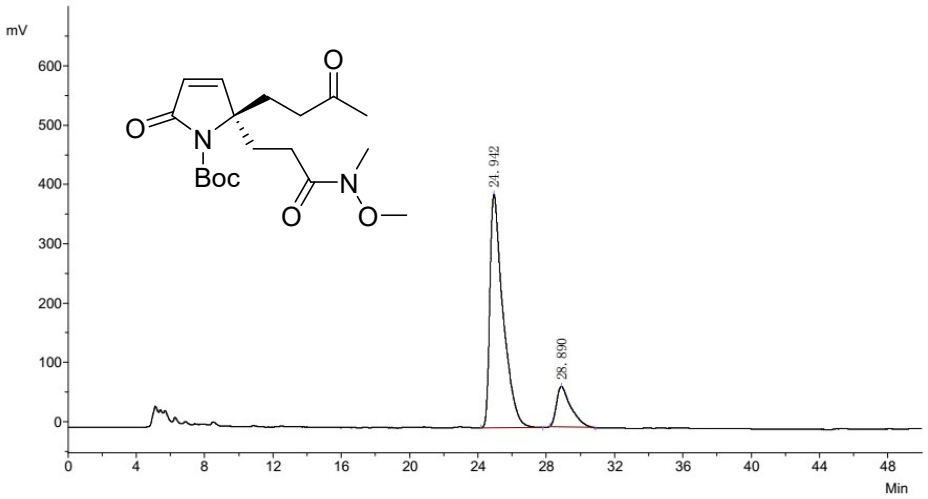
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.465	1352307.6	30155970.1	86.4906	86.4906
2	15.748	171866.9	4710192.0	13.5094	13.5094
Total		1524174.4	34866162.0	100.0000	100.0000

HPLC data of compound **15d**

(Chiralpak AD-H, Hexane/*i*-PrOH/MeOH = 95/5/5, 0.7 mL/min, 214 nm)



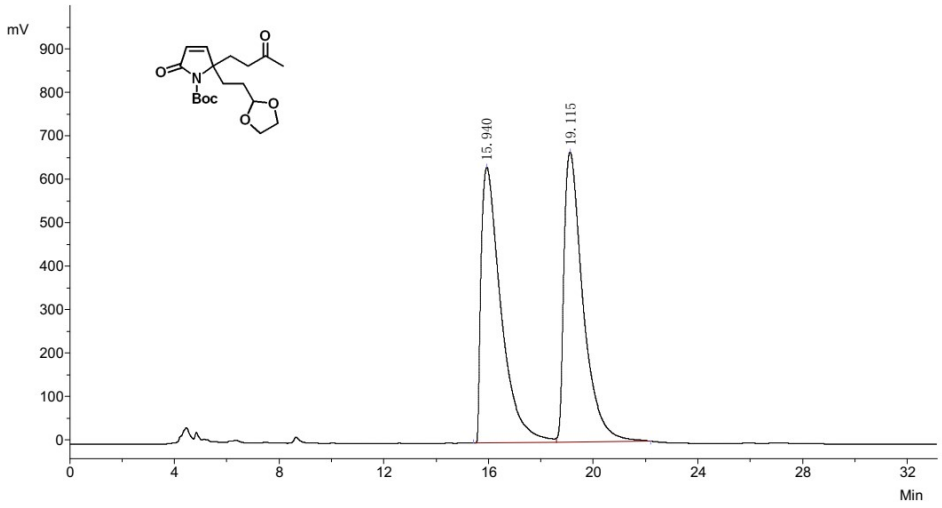
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.823	395280.2	17899970.2	49.7147	49.7147
2	28.615	343679.3	18105449.6	50.2853	50.2853
Total		738959.5	36005419.7	100.0000	100.0000



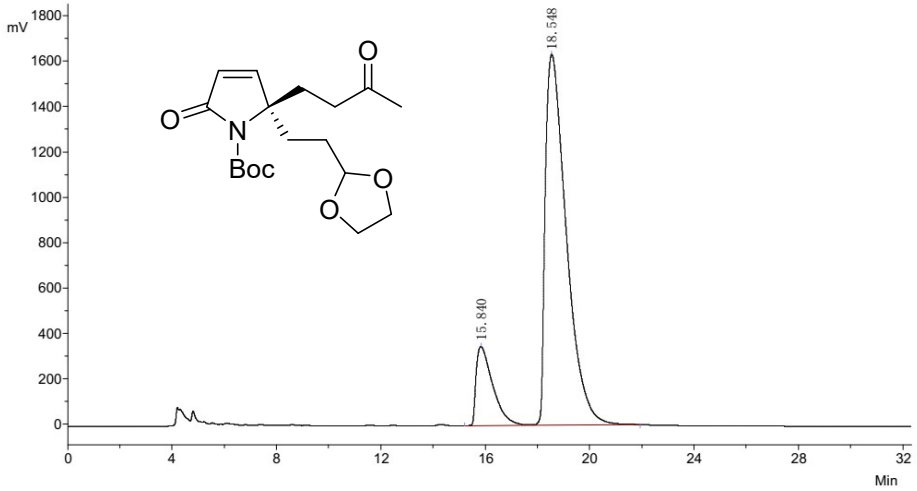
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.942	343875.9	20987880.2	84.0942	84.0942
2	28.890	68220.3	3969716.9	15.9058	15.9058
Total		412096.3	24957597.2	100.0000	100.0000

HPLC data of compound **15e**

(Chiralpak AD-H, Hexane/*i*-PrOH = 85/15, 0.7 mL/min, 214 nm)



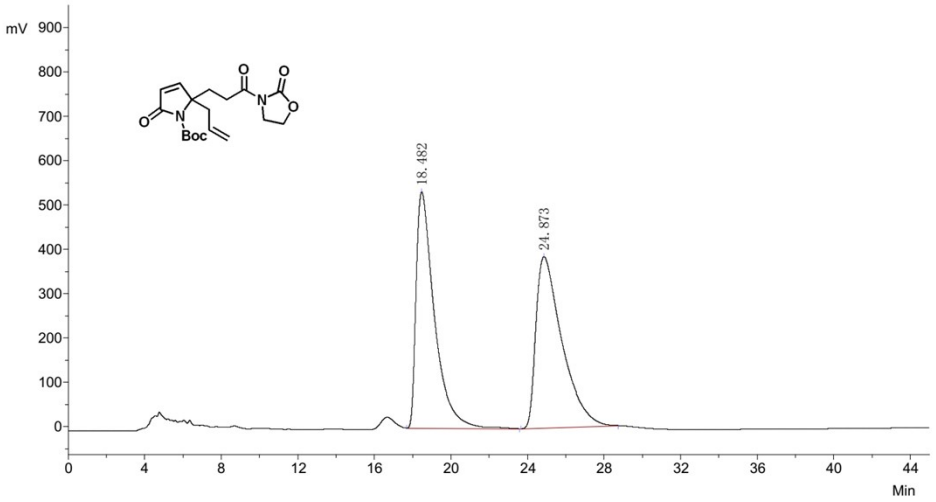
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	15.940	634986.8	33523169.1	49.7752	49.7752
2	19.115	668109.2	33825912.5	50.2248	50.2248
Total		1303096.0	67349081.6	100.0000	100.0000



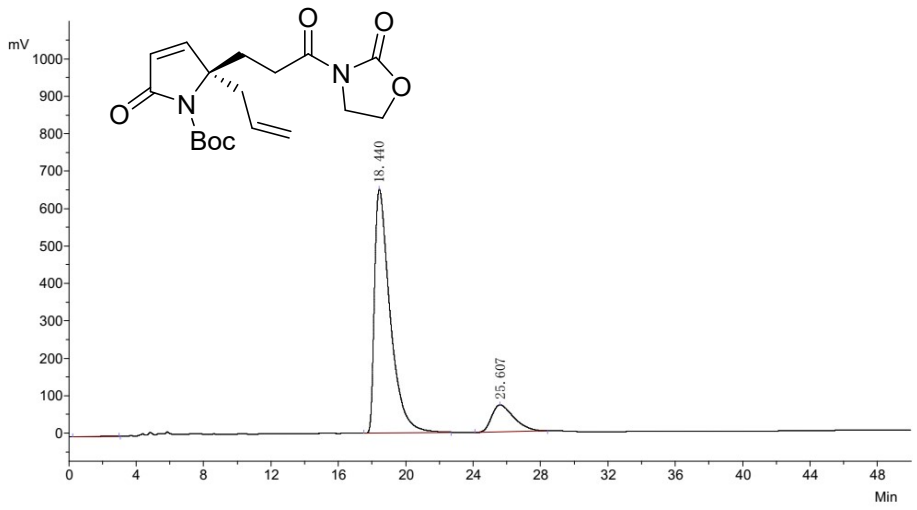
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	15.840	349887.6	15584830.3	14.5649	14.5649
2	18.548	1634019.8	91417477.2	85.4351	85.4351
Total		1983907.3	107002307.6	100.0000	100.0000

HPLC data of compound **15f**

(Chiralpak OD-H, Hexane/*i*-PrOH = 60/40, 0.7 mL/min, 214 nm)



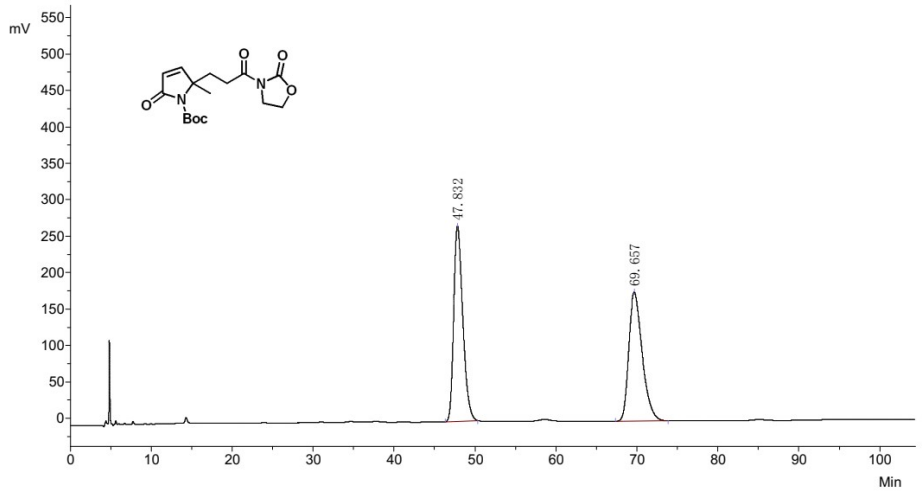
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.482	533211.1	35385340.9	49.2442	49.2442
2	24.873	386573.6	36471490.4	50.7558	50.7558
Total		919784.7	71856831.3	100.0000	100.0000



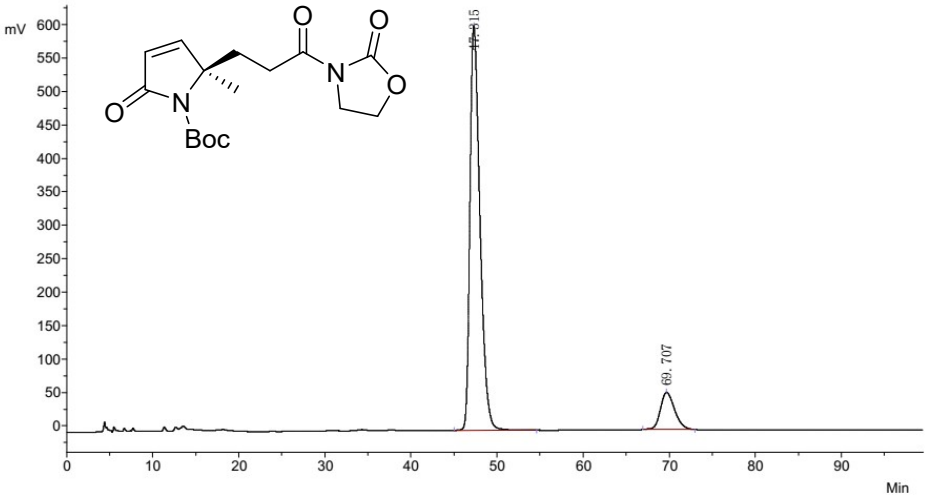
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.440	651941.7	41795722.2	86.2958	86.2958
2	25.607	71962.8	6637373.4	13.7042	13.7042
Total		723904.5	48433095.6	100.0000	100.0000

HPLC data of compound **15g**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



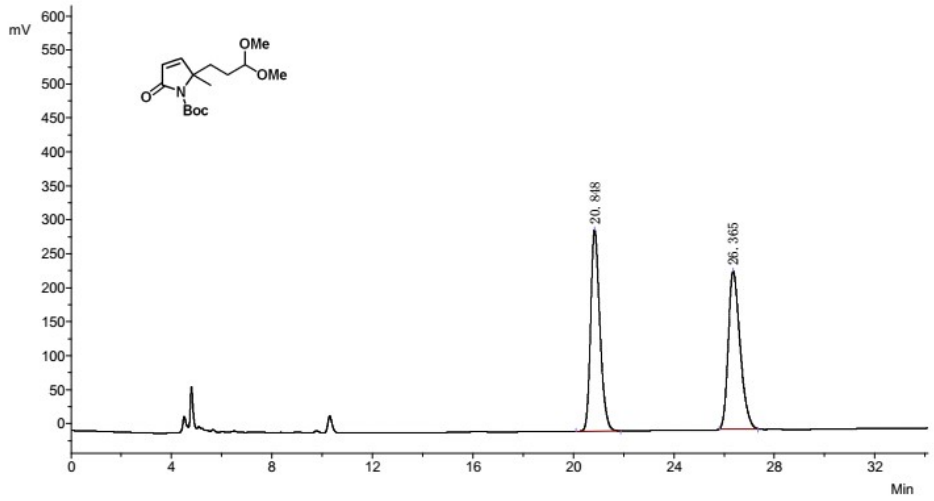
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	47.832	267761.6	20844289.5	50.6778	50.6778
2	69.657	176866.7	20286696.1	49.3222	49.3222
Total		444628.3	41130985.6	100.0000	100.0000



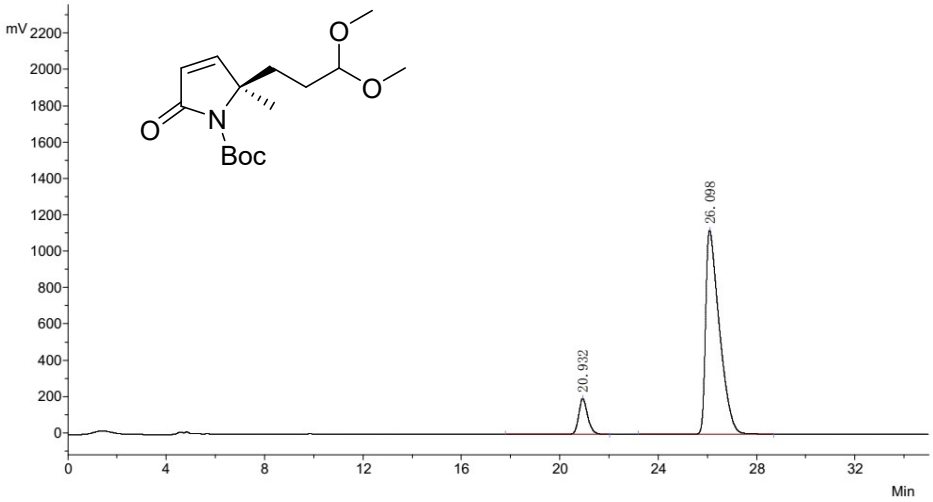
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	47.315	604800.2	48918545.6	88.4428	88.4428
2	69.707	55711.6	6392408.4	11.5572	11.5572
Total		660511.8	55310953.9	100.0000	100.0000

HPLC data of compound **15h1**

(Chiralpak IC, Hexane/*i*-PrOH = 85/15, 0.7 mL/min, 214 nm)



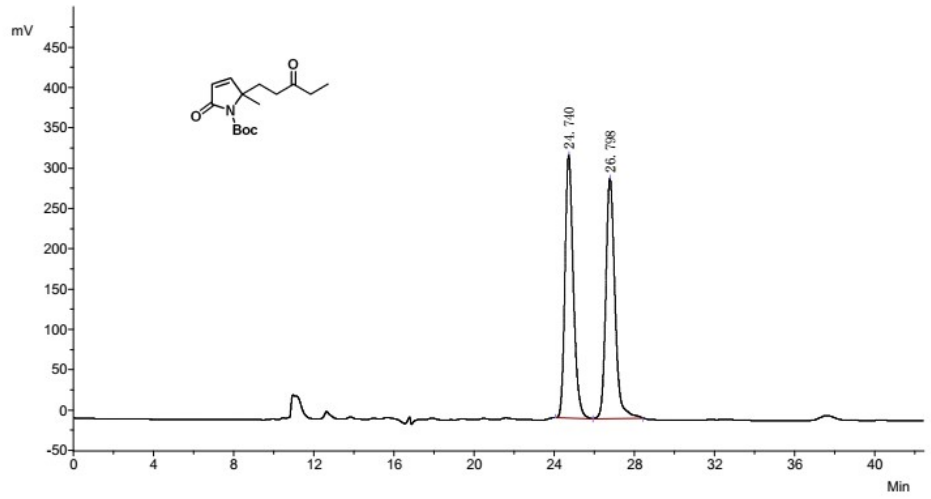
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	20.848	296279.6	7580544.1	49.9986	49.9986
2	26.365	232447.2	7580982.7	50.0014	50.0014
Total		528726.9	15161526.8	100.0000	100.0000



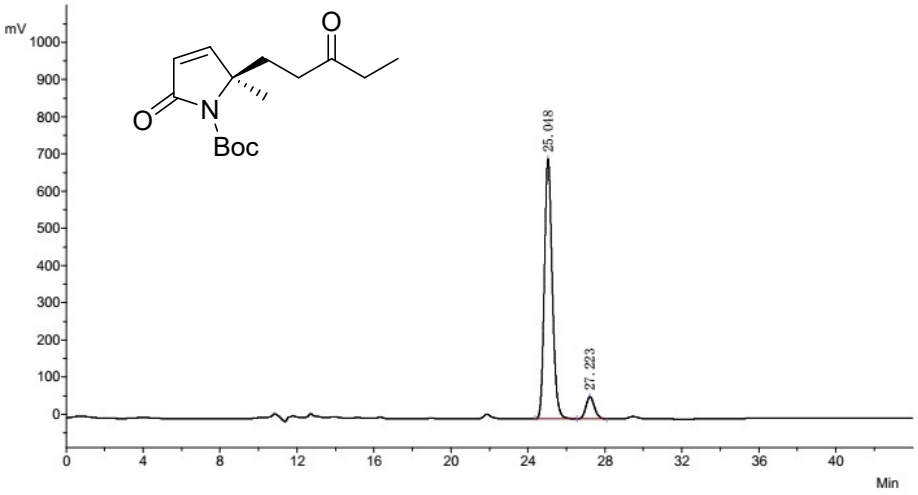
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	20.932	196207.1	4956944.8	10.2583	10.2583
2	26.098	1122417.3	43364548.6	89.7417	89.7417
Total		1318624.5	48321493.5	100.0000	100.0000

HPLC data of compound **15i**

(Chiralpak OD-H, Hexane/*i*-PrOH/MeOH = 95/5/5, 0.3 mL/min, 214 nm)



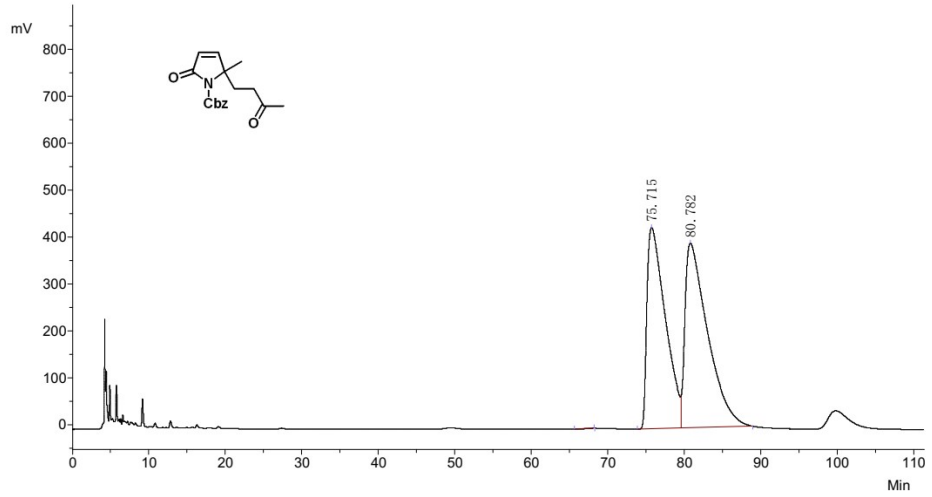
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.740	326543.0	9390811.2	49.9584	49.9584
2	26.798	298173.2	9406467.5	50.0416	50.0416
Total		624716.2	18797278.7	100.0000	100.0000



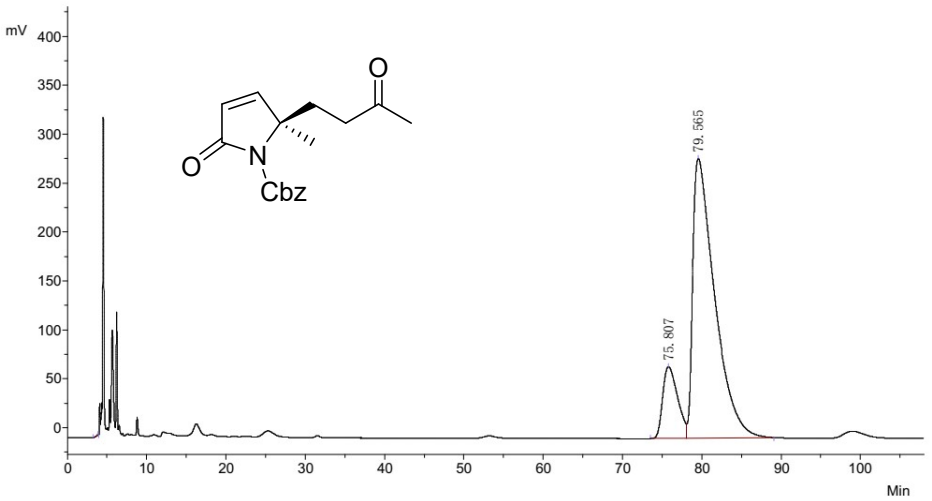
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	25.048	700172.4	19803886.2	91.6827	91.6827
2	27.223	59338.9	1796582.3	8.3173	8.3173
Total		759511.3	21600468.4	100.0000	100.0000

HPLC data of compound **15j**

(Chiralpak OD-H, Hexane/*i*-PrOH = 95/5, 0.7 mL/min, 214 nm)



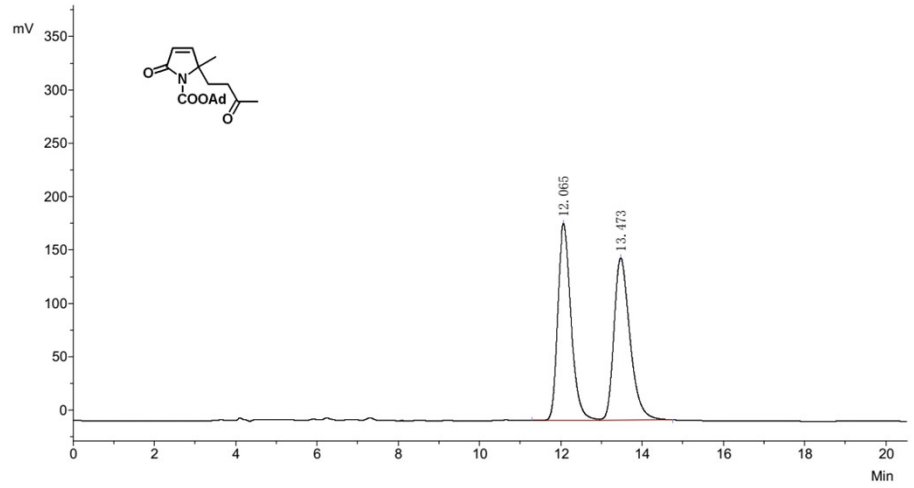
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	75.715	428670.1	71614938.4	46.9812	46.9812
2	80.782	393299.3	80818315.4	53.0188	53.0188
Total		821969.4	152433253.8	100.0000	100.0000



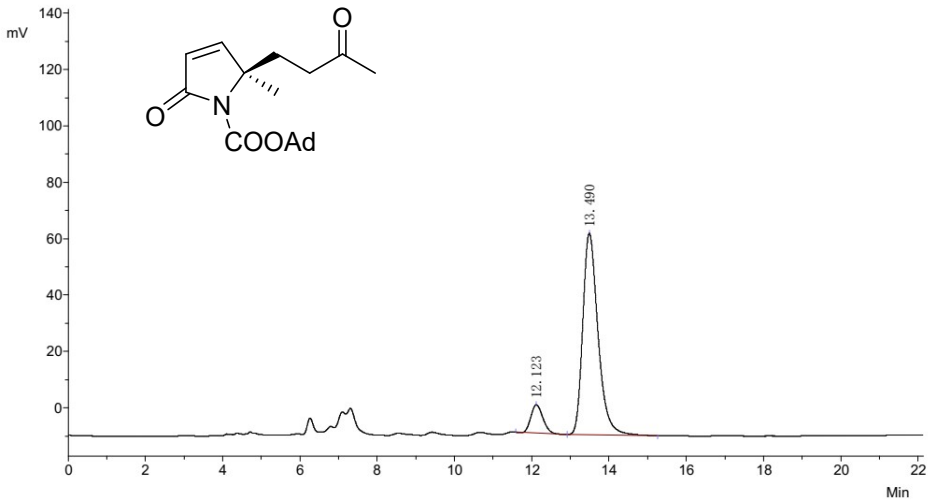
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	75.807	73443.4	9622823.1	14.9516	14.9516
2	79.565	285959.9	54737077.6	85.0484	85.0484
Total		359403.3	64359900.7	100.0000	100.0000

HPLC data of compound **15k**

(Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, 0.7 mL/min, 214 nm)



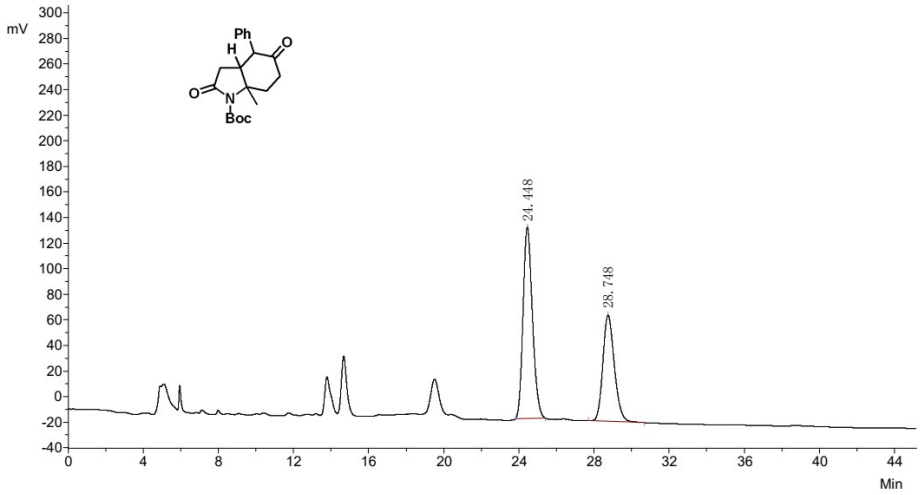
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.065	184543.1	4150436.3	49.9556	49.9556
2	13.473	152041.8	4157817.3	50.0444	50.0444
Total		336584.8	8308253.6	100.0000	100.0000



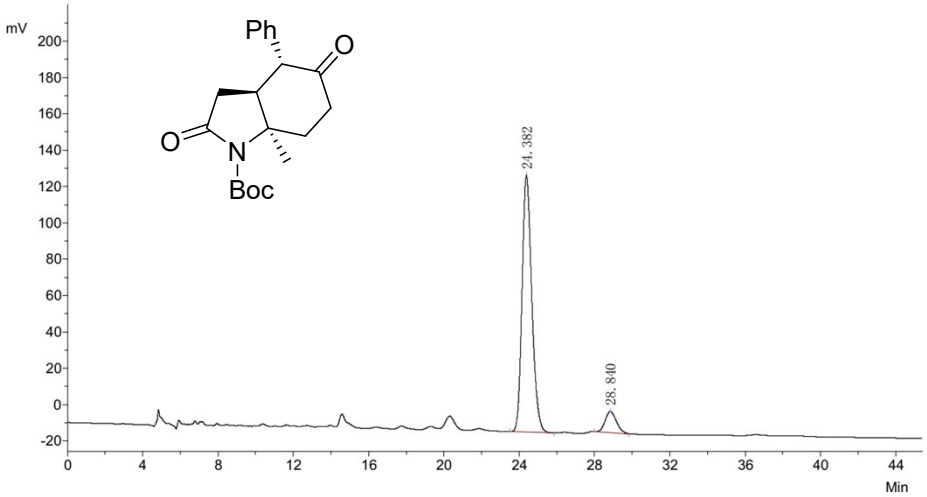
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.123	10047.8	215818.2	9.9112	9.9112
2	13.490	71602.8	1961690.3	90.0888	90.0888
Total		81650.6	2177508.5	100.0000	100.0000

HPLC data of compound **17a**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



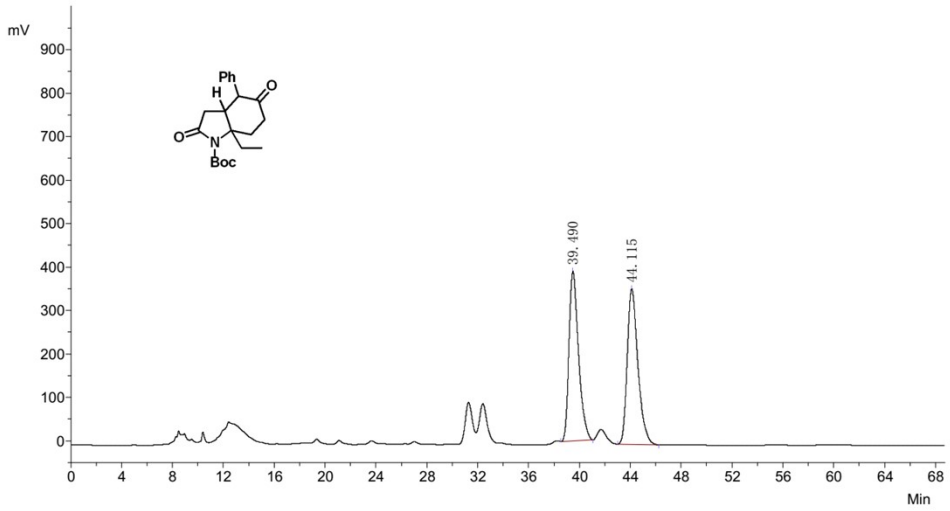
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.448	149567.6	5173692.6	59.3828	59.3828
2	28.748	83150.7	3538749.5	40.6172	40.6172
Total		232718.4	8712442.1	100.0000	100.0000



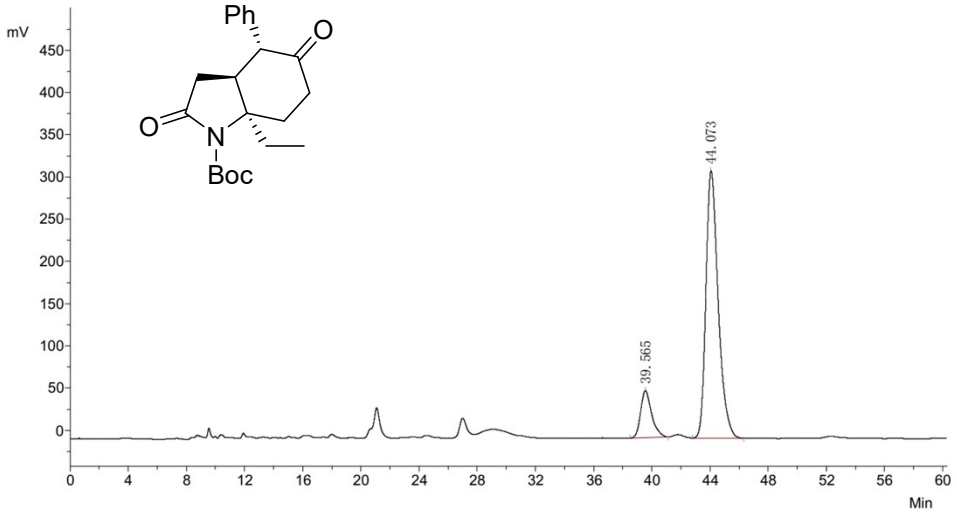
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.382	141316.6	5068045.5	91.4896	91.4896
2	28.840	11542.8	471428.7	8.5104	8.5104
Total		152859.5	5539474.2	100.0000	100.0000

HPLC data of compound **17b**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.4 mL/min, 214 nm)



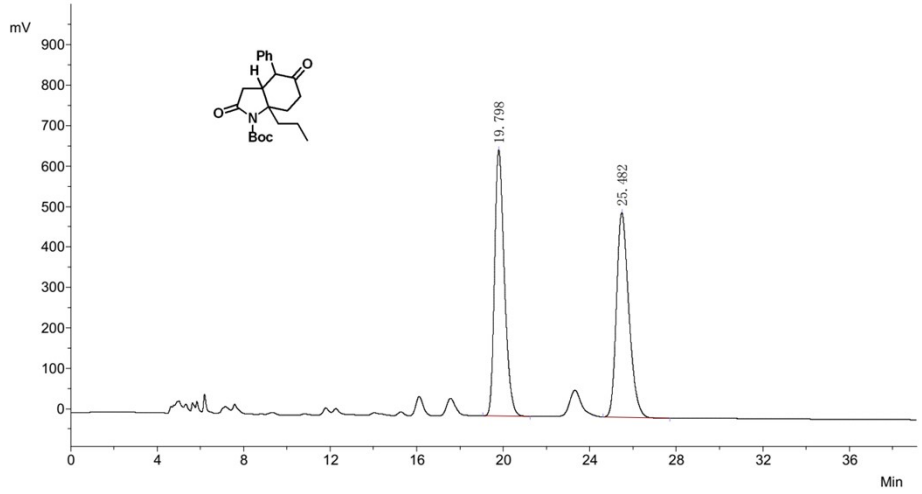
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	39.490	390503.1	20316300.0	49.2582	49.2582
2	44.115	357830.8	20928222.3	50.7418	50.7418
Total		748333.9	41244522.2	100.0000	100.0000



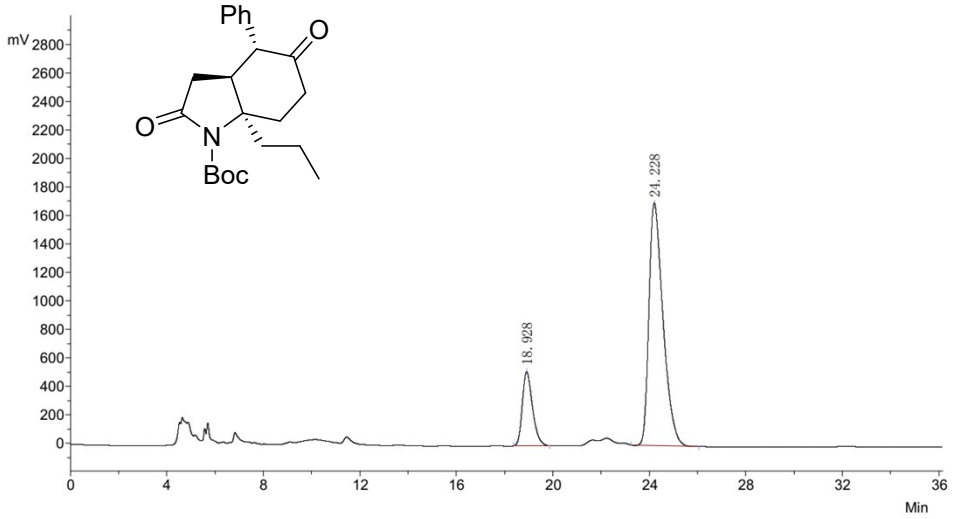
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	39.565	55571.6	2915313.0	13.6123	13.6123
2	44.073	316707.2	18501501.9	86.3877	86.3877
Total		372278.8	21416814.8	100.0000	100.0000

HPLC data of compound **17c**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



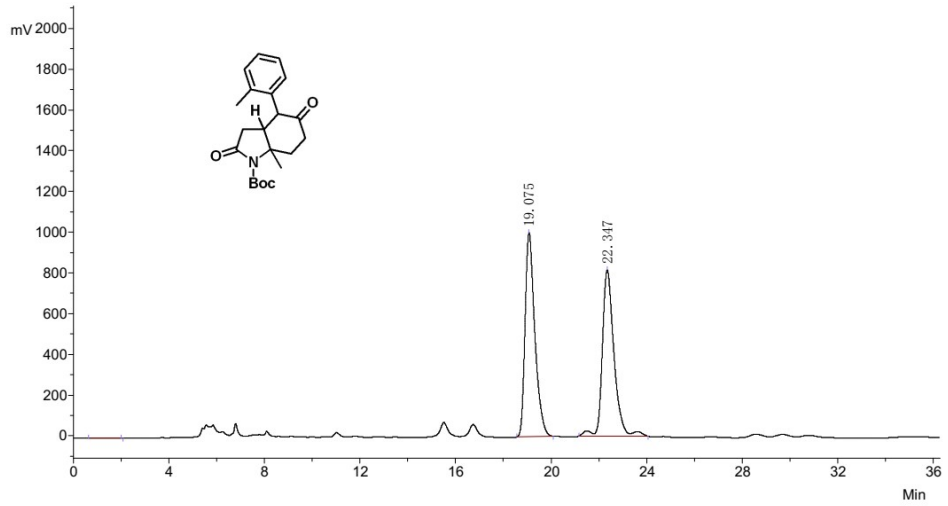
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	19.798	658600.9	20685417.8	50.6980	50.6980
2	25.482	506137.2	20115848.6	49.3020	49.3020
Total		1164738.0	40801266.4	100.0000	100.0000



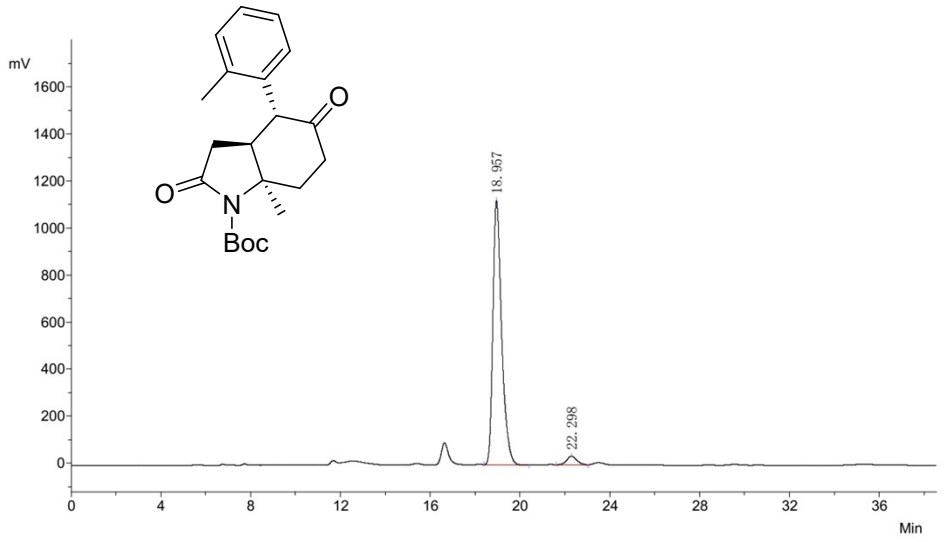
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.928	519109.0	15241702.3	18.0873	18.0873
2	24.228	1698240.5	69025520.8	81.9127	81.9127
Total		2217349.5	84267223.1	100.0000	100.0000

HPLC data of compound **17d**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.6 mL/min, 214 nm)



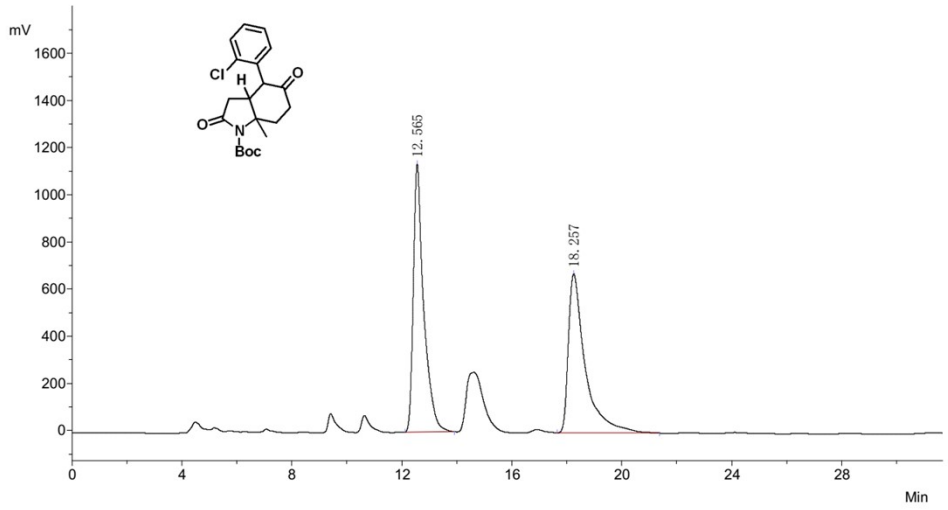
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	19.075	1003413.2	28329269.0	50.5142	50.5142
2	22.347	816221.9	27752534.8	49.4858	49.4858
Total		1819635.1	56081803.8	100.0000	100.0000



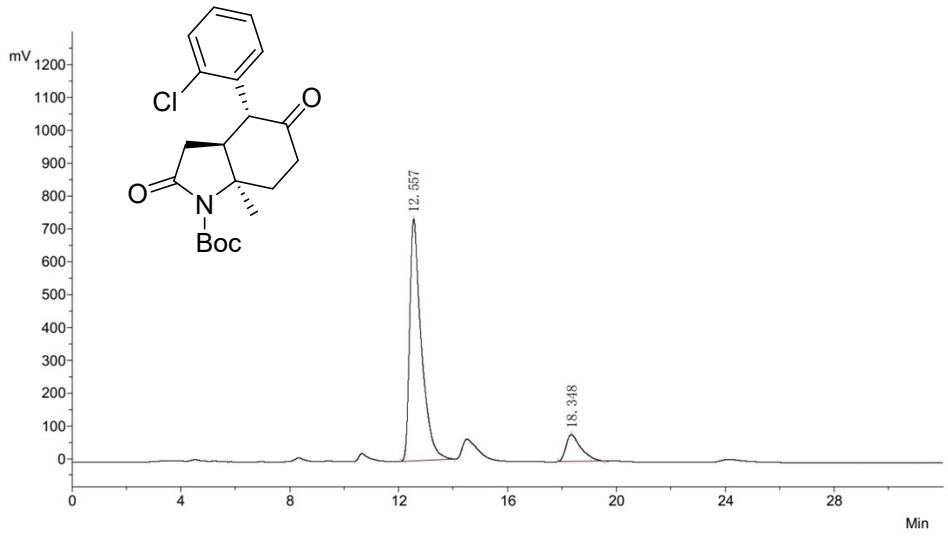
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.957	1123423.3	30416930.3	96.4601	96.4601
2	22.298	36041.5	1116251.5	3.5399	3.5399
Total		1159464.8	31533181.8	100.0000	100.0000

HPLC data of compound **17e**

(Chiralpak AD-H, Hexane/*i*-PrOH = 80/20, 0.7 mL/min, 214 nm)



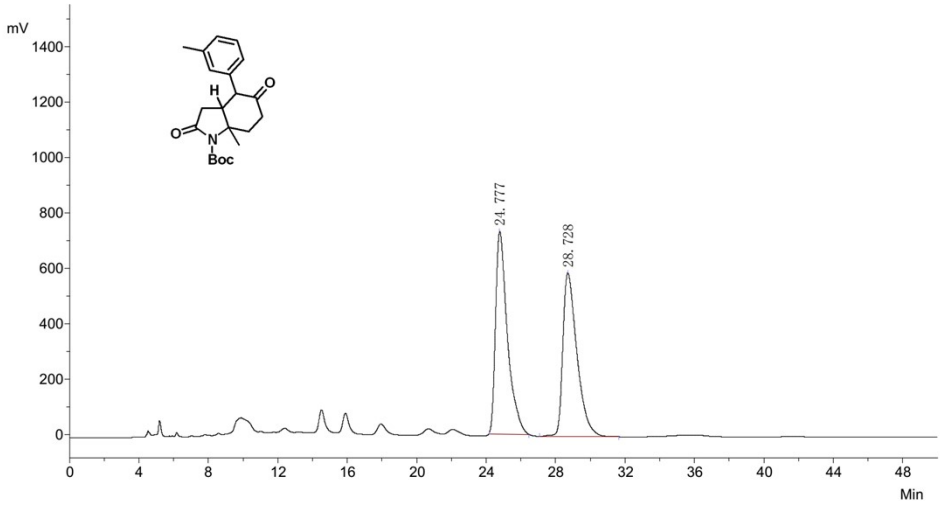
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.565	1137307.8	29745217.1	50.9320	50.9320
2	18.257	674134.9	28656560.5	49.0680	49.0680
Total		1811442.8	58401777.6	100.0000	100.0000



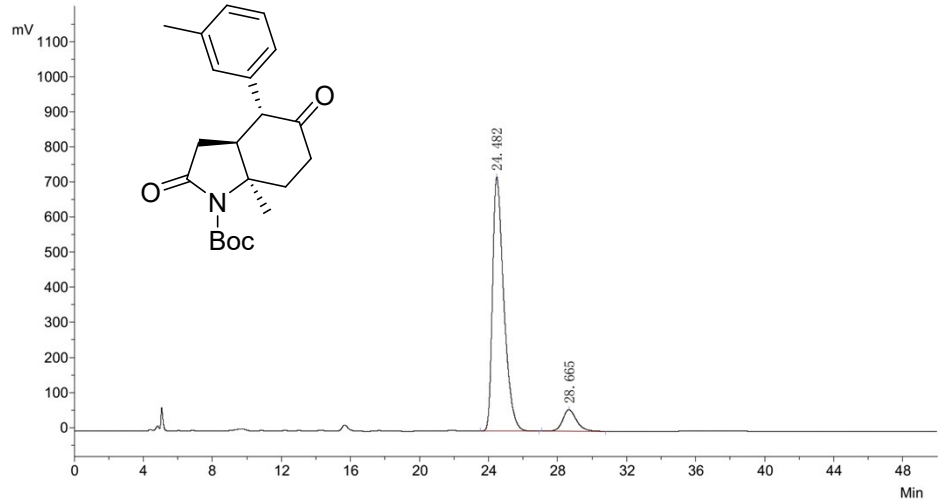
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.557	737847.0	21938123.4	87.4699	87.4699
2	18.348	81724.9	3142632.9	12.5301	12.5301
Total		819571.9	25080756.3	100.0000	100.0000

HPLC data of compound **17f**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



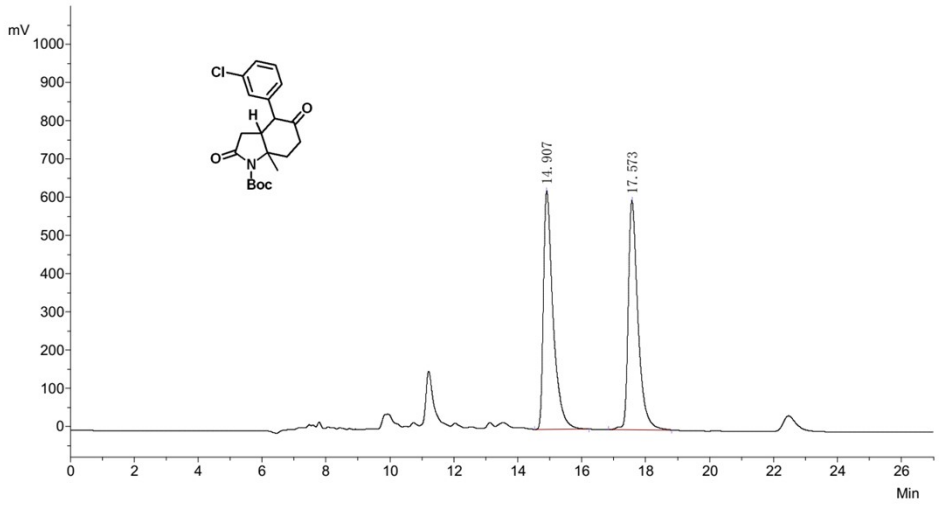
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.777	729469.7	34548838.9	50.9511	50.9511
2	28.728	589876.8	33258979.0	49.0489	49.0489
Total		1319346.4	67807817.9	100.0000	100.0000



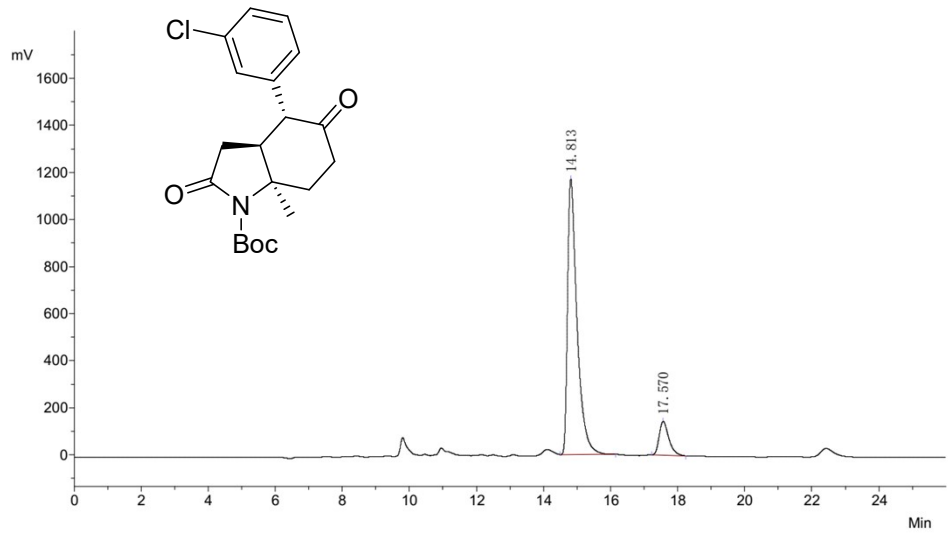
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	24.482	724036.9	33037058.7	90.5848	90.5848
2	28.665	61457.6	3433792.0	9.4152	9.4152
Total		785494.5	36470850.7	100.0000	100.0000

HPLC data of compound **17g**

(Chiralpak IB-3, Hexane/*i*-PrOH = 70/30, 0.5 mL/min, 214 nm)



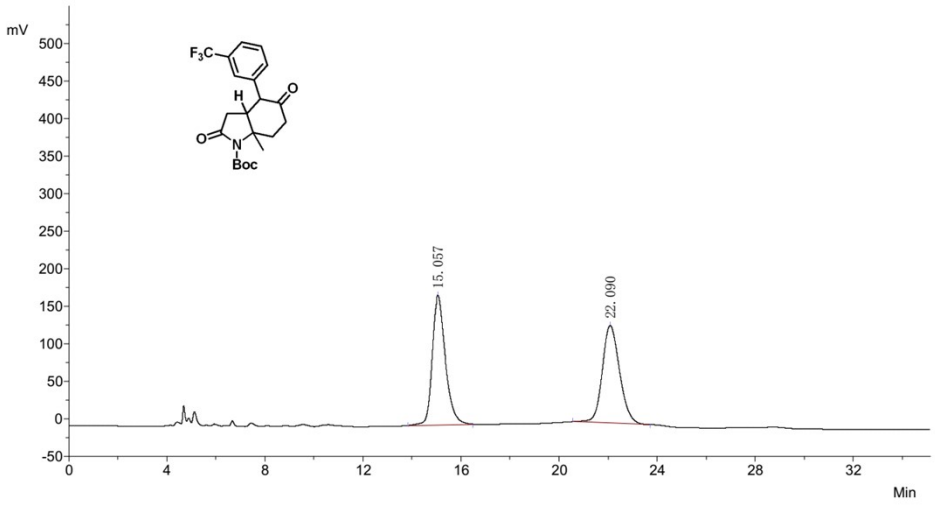
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.907	623878.9	13030137.1	50.6442	50.6442
2	17.573	600560.0	12698651.9	49.3558	49.3558
Total		1224438.9	25728789.0	100.0000	100.0000



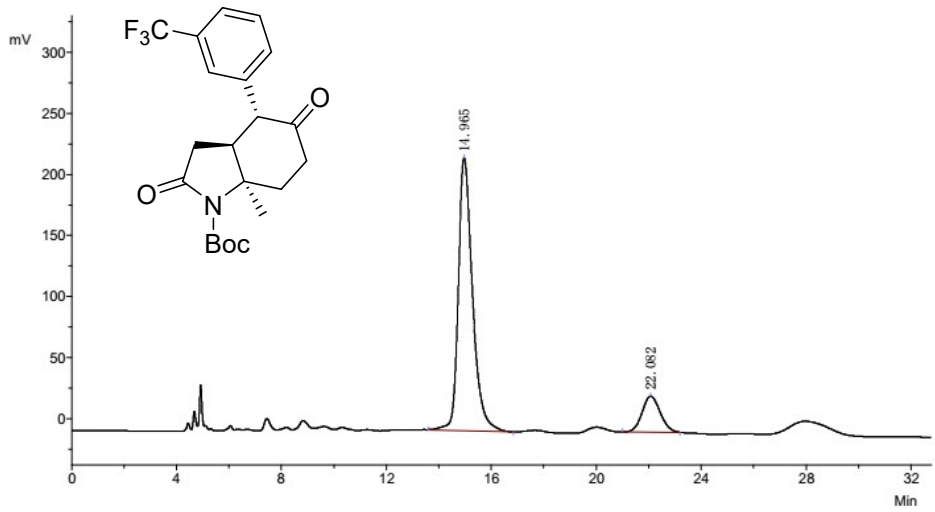
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.813	1171296.0	22886833.7	88.8373	88.8373
2	17.570	143761.3	2875793.6	11.1627	11.1627
Total		1315057.3	25762627.3	100.0000	100.0000

HPLC data of compound **17h**

(Chiralpak OD-H, Hexane/*i*-PrOH = 85/15, 0.7 mL/min, 214 nm)



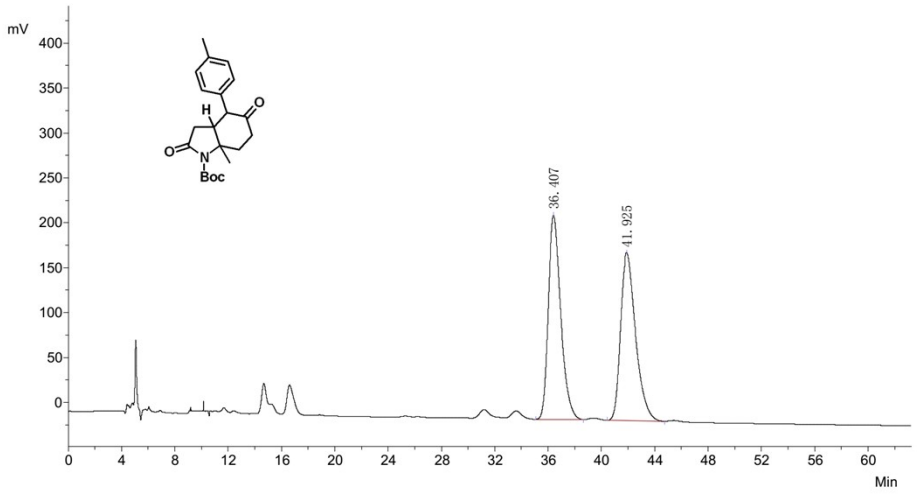
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	15.057	173375.6	6377674.7	49.9469	49.9469
2	22.090	130467.0	6391223.4	50.0531	50.0531
Total		303842.6	12768898.1	100.0000	100.0000



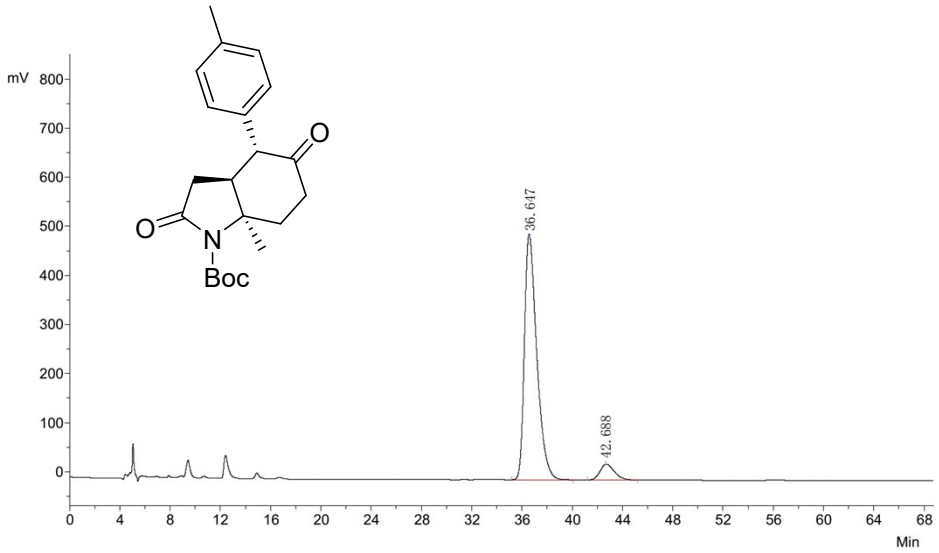
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.965	223375.3	8361081.1	85.5213	85.5213
2	22.082	29528.5	1415521.3	14.4787	14.4787
Total		252903.8	9776602.4	100.0000	100.0000

HPLC data of compound **17i**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



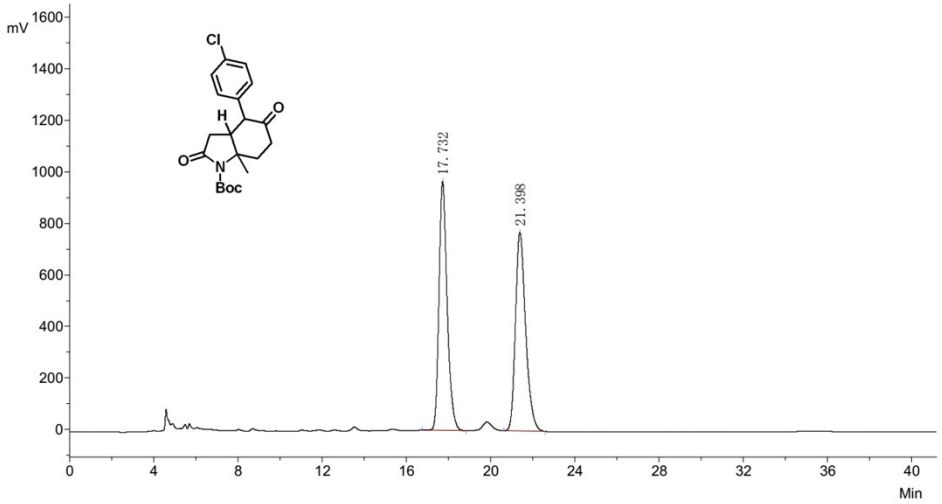
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	36.407	227338.8	14666994.5	50.2802	50.2802
2	41.925	187348.7	14503512.5	49.7198	49.7198
Total		414687.4	29170507.0	100.0000	100.0000



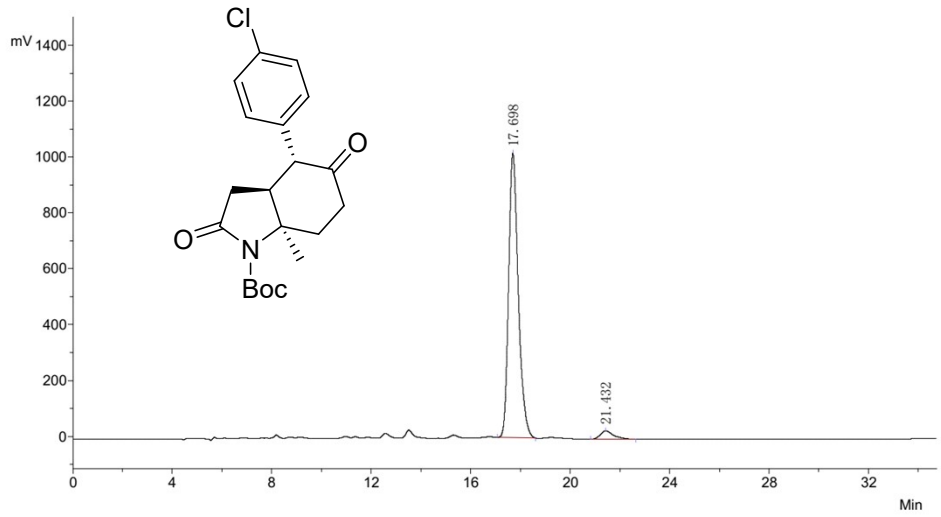
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	36.647	500306.0	33992709.2	93.0228	93.0228
2	42.688	32171.3	2549640.1	6.9772	6.9772
Total		532477.3	36542349.3	100.0000	100.0000

HPLC data of compound **17j**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



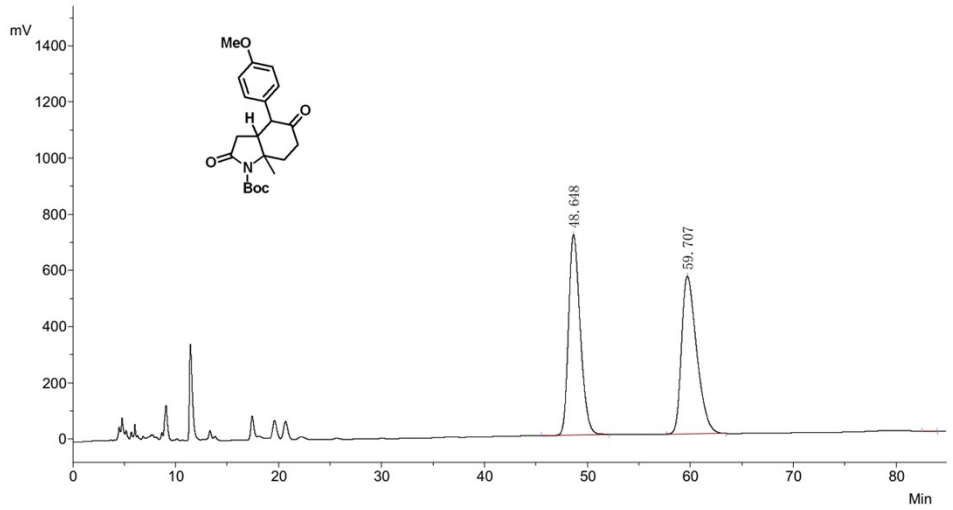
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	17.732	965375.8	25986962.9	50.0798	50.0798
2	21.398	771189.5	25904187.8	49.9202	49.9202
Total		1736565.3	51891150.7	100.0000	100.0000



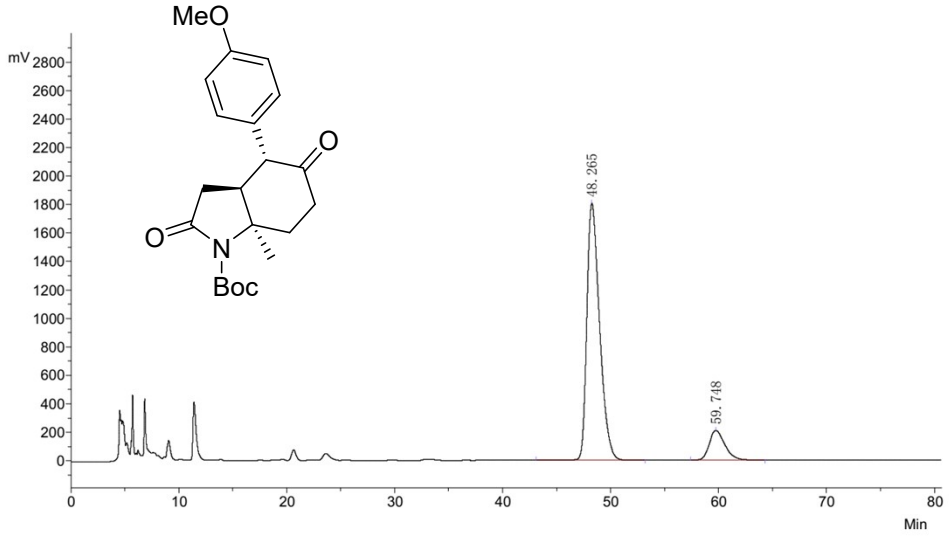
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	17.698	1018533.4	27416014.2	96.0948	96.0948
2	21.432	29905.1	1114165.6	3.9052	3.9052
Total		1048438.4	28530179.8	100.0000	100.0000

HPLC data of compound **17k**

(Chiralpak IC, Hexane/*i*-PrOH/MeOH = 70/20/10, 0.7 mL/min, 214 nm)



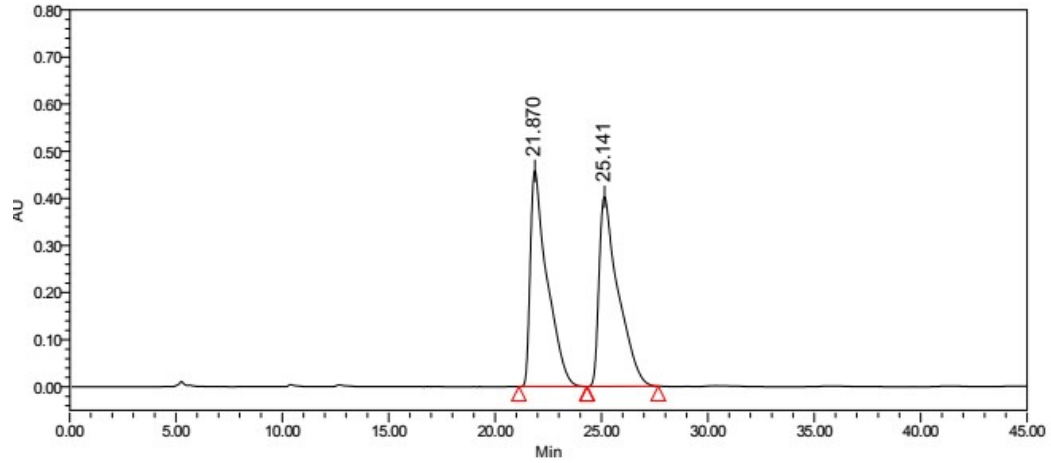
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	48.648	714136.0	56224439.3	49.4362	49.4362
2	59.707	561737.7	57506967.9	50.5638	50.5638
Total		1275873.7	113731407.1	100.0000	100.0000



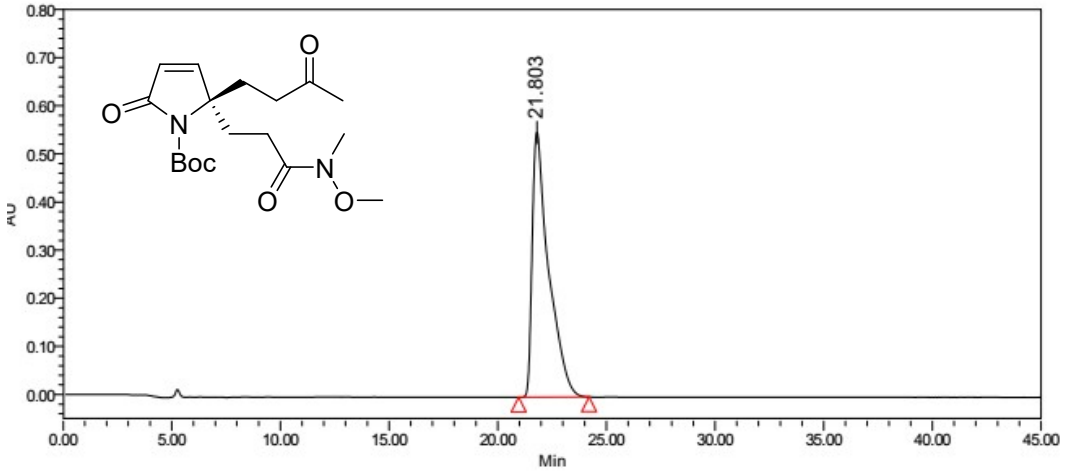
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	48.265	1803439.4	147155244.4	87.4855	87.4855
2	59.748	208520.6	21050124.2	12.5145	12.5145
Total		2011960.0	168205368.6	100.0000	100.0000

HPLC data of compound **15d** (Recrystallization)

(Chiralpak AD-H, Hexane/*i*-PrOH/MeOH = 95/5/5, 0.7 mL/min, 214 nm)



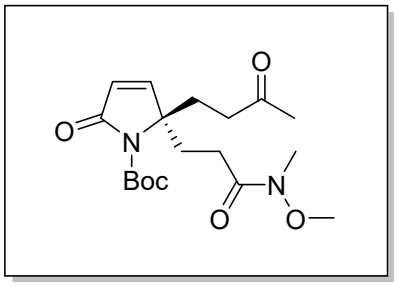
	R.Time (分钟)	PeakHeight (微伏)	PeakArea (微伏*秒)	PerCent (%)
1	21.870	458318	25304508	50.12
2	25.141	402644	25179134	49.88



	R.Time (分钟)	PeakHeight (微伏)	PeakArea (微伏*秒)	PerCent (%)
1	21.803	550054	29091798	100.00

7. X-Ray Single Crystal Diffraction Data

Compound **15d**



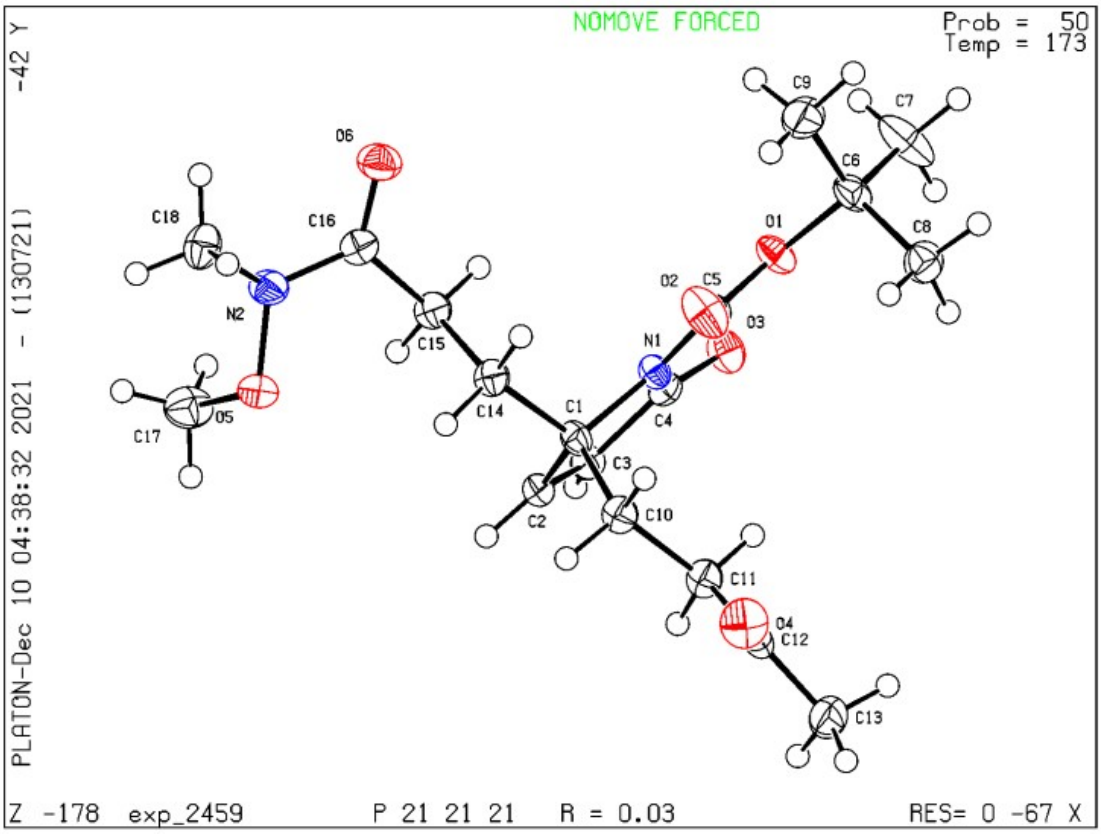


Figure S1. X-ray crystallographic structure of 15d

Table S8 Crystal data and structure refinement for 15d.

Identification code	15d
Empirical formula	$C_{18}H_{28}N_2O_6$
Formula weight	368.42
Temperature/K	173.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.53431(4)
b/Å	11.74547(7)
c/Å	21.92815(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1940.51(2)
Z	4
ρ_{calc}g/cm^3	1.261
μ/mm^{-1}	0.785
F(000)	792.0
Crystal size/mm^3	0.42 × 0.36 × 0.28
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.54 to 134.132
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-26 \le l \le 26$
Reflections collected	43698
Independent reflections	3438 [R_{int} = 0.0307, R_{sigma} = 0.0109]
Data/restraints/parameters	3438/0/241
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0686
Final R indexes [all data]	R_1 = 0.0272, wR_2 = 0.0687
Largest diff. peak/hole / e Å^{-3}	0.16/-0.17
Flack parameter	0.01(3)

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 15d. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	641.1(15)	2808.1(10)	6294.3(5)	26.3(3)
O2	-150.0(19)	4663.3(11)	6322.0(7)	36.7(3)
O3	3258.8(17)	2270.4(10)	5515.3(6)	27.9(3)
O4	-1950.5(19)	6415.3(12)	4680.0(7)	38.2(3)
O5	6476.8(16)	7694.8(10)	6379.7(5)	26.3(3)
O6	4715.8(19)	6041.6(11)	7547.9(5)	33.4(3)
N1	2285.2(18)	4103.6(11)	5783.1(6)	19.4(3)
N2	6197(2)	7307.2(13)	6979.9(6)	26.7(3)
C1	2760(2)	5286.0(13)	5597.6(7)	20.5(3)
C2	4327(2)	5062.0(14)	5191.5(7)	21.3(3)
C3	4667(2)	3963.3(14)	5130.0(7)	21.3(3)
C4	3377(2)	3297.9(14)	5486.7(7)	20.0(3)
C5	807(2)	3902.8(14)	6154.4(7)	23.2(3)
C6	-973(2)	2413.8(15)	6632.0(8)	26.4(4)
C7	-630(3)	1146.8(18)	6697.4(12)	48.0(6)

C8	-2595(2)	2615.8(17)	6240.9(8)	30.8(4)
C9	-1104(3)	2981(2)	7249.4(9)	44.7(5)
C10	1254(2)	5871.0(14)	5239.1(7)	23.1(3)
C11	599(2)	5215.0(14)	4686.5(8)	24.6(4)
C12	-1071(2)	5707.1(15)	4413.2(8)	25.8(4)
C13	-1625(3)	5243.4(17)	3808.1(9)	36.0(5)
C14	3299(2)	6028.8(14)	6146.5(7)	23.4(3)
C15	4967(2)	5613.4(14)	6480.3(8)	24.5(4)
C16	5276(2)	6324.7(14)	7045.3(8)	23.6(4)
C17	8337(3)	7645.0(19)	6240.8(9)	36.7(4)
C18	6182(3)	8198.7(16)	7439.7(8)	30.0(4)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 15d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	21.4(6)	25.2(6)	32.2(6)	7.1(5)	8.5(5)	0.5(5)
O2	35.2(7)	25.8(6)	49.1(8)	-3.4(6)	20.0(6)	1.7(6)
O3	29.5(6)	16.7(6)	37.5(7)	-1.0(5)	2.4(5)	1.8(5)
O4	31.9(8)	33.8(7)	48.8(8)	0.0(6)	-1.2(6)	10.3(6)
O5	29.1(6)	27.1(6)	22.6(6)	3.9(5)	1.3(5)	1.5(5)
O6	43.8(8)	32.5(7)	23.8(6)	1.1(5)	4.8(6)	-3.1(6)
N1	20.5(7)	15.8(6)	21.8(6)	-1.1(5)	3.0(5)	-0.2(5)
N2	37.0(8)	23.9(7)	19.2(6)	-3.2(6)	3.9(6)	-1.9(7)
C1	23.5(8)	14.4(7)	23.8(8)	-0.2(6)	2.5(7)	-2.1(6)
C2	20.6(8)	23.3(8)	20.2(8)	1.1(6)	0.6(7)	-3.6(6)
C3	17.8(8)	26.0(8)	20.1(7)	-1.2(7)	2.0(6)	1.3(7)
C4	20.1(8)	20.0(8)	20.1(7)	-1.7(6)	-2.5(6)	2.6(6)
C5	23.1(8)	22.9(8)	23.5(8)	0.0(6)	2.6(6)	-1.2(7)
C6	20.1(8)	29.8(9)	29.3(8)	6.6(7)	6.7(7)	-1.5(7)
C7	36.3(12)	36.6(11)	71.3(15)	26.8(11)	21.1(11)	4.5(9)
C8	25.0(9)	37.1(10)	30.5(9)	-1.7(8)	1.7(7)	-1.7(8)
C9	35.7(11)	73.6(15)	24.6(9)	-0.6(10)	4.7(8)	-18.8(11)
C10	25.2(9)	17.9(7)	26.3(8)	-1.9(6)	-0.1(7)	2.6(7)
C11	25.6(9)	20.0(8)	28.3(8)	-1.6(6)	-2.1(7)	2.3(7)
C12	23.3(8)	20.3(8)	33.8(9)	6.8(7)	0.2(7)	-3.9(7)
C13	37.0(11)	32.5(10)	38.3(10)	5.0(8)	-12.3(8)	-5.6(8)
C14	27.2(9)	18.3(7)	24.7(8)	-3.1(7)	-0.1(7)	0.9(7)
C15	31.2(9)	17.3(8)	25.1(8)	-2.0(6)	-1.7(7)	2.1(7)
C16	25.3(8)	21.6(8)	23.8(8)	-0.9(6)	-1.0(7)	4.9(7)
C17	31.5(10)	47.5(11)	31.2(9)	2.1(9)	6.5(8)	5.4(9)
C18	30.4(9)	28.6(9)	31.0(9)	-11.4(7)	0.2(8)	-0.4(7)

Table S11 Bond Lengths for 15d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C5	1.328(2)	C1	C2	1.502(2)
O1	C6	1.4971(19)	C1	C10	1.542(2)
O2	C5	1.205(2)	C1	C14	1.541(2)

O3	C4	1.212(2)	C2	C3	1.322(2)
O4	C12	1.214(2)	C3	C4	1.472(2)
O5	N2	1.4086(18)	C6	C7	1.517(3)
O5	C17	1.435(2)	C6	C8	1.512(2)
O6	C16	1.226(2)	C6	C9	1.512(3)
N1	C1	1.491(2)	C10	C11	1.518(2)
N1	C4	1.412(2)	C11	C12	1.509(2)
N1	C5	1.399(2)	C12	C13	1.494(3)
N2	C16	1.354(2)	C14	C15	1.534(2)
N2	C18	1.454(2)	C15	C16	1.512(2)

Table S12 Bond Angles for 15d.

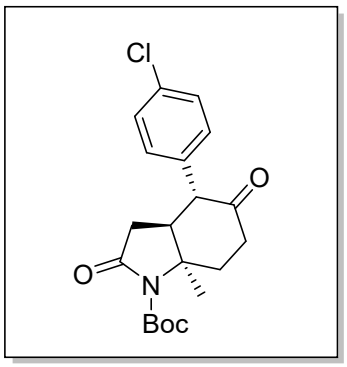
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O1	C6	119.37(13)	O1	C5	N1	111.88(14)
N2	O5	C17	109.36(13)	O2	C5	O1	126.21(16)
C4	N1	C1	111.04(13)	O2	C5	N1	121.91(15)
C5	N1	C1	120.44(13)	O1	C6	C7	102.24(14)
C5	N1	C4	128.18(14)	O1	C6	C8	109.12(13)
O5	N2	C18	114.60(14)	O1	C6	C9	111.07(15)
C16	N2	O5	116.82(13)	C8	C6	C7	110.18(17)
C16	N2	C18	122.46(15)	C8	C6	C9	112.69(16)
N1	C1	C2	100.79(13)	C9	C6	C7	111.04(18)
N1	C1	C10	112.19(13)	C11	C10	C1	114.82(14)
N1	C1	C14	112.18(13)	C12	C11	C10	113.16(14)
C2	C1	C10	110.75(13)	O4	C12	C11	121.77(16)
C2	C1	C14	110.77(14)	O4	C12	C13	121.69(17)
C14	C1	C10	109.88(13)	C13	C12	C11	116.50(16)
C3	C2	C1	112.54(14)	C15	C14	C1	114.13(14)
C2	C3	C4	109.64(15)	C16	C15	C14	109.95(14)
O3	C4	N1	126.94(16)	O6	C16	N2	120.17(16)
O3	C4	C3	127.20(16)	O6	C16	C15	122.25(16)
N1	C4	C3	105.86(13)	N2	C16	C15	117.58(15)

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 15d.

Atom	*x*	*y*	*z*	U(eq)
H2	4986.25	5632.83	5004.07	26
H3	5581.36	3657.56	4896.92	26
H7A	-512.06	810.79	6300.33	72
H7B	-1605.18	798.52	6908.6	72
H7C	443.67	1029.3	6924.49	72
H8A	-2805.26	3419.23	6205.48	46
H8B	-3606.71	2258.35	6426.01	46
H8C	-2404.31	2297.99	5842.94	46
H9A	-6.74	2883.34	7465.81	67
H9B	-2052.87	2642.1	7478.12	67
H9C	-1335.04	3778.98	7196.26	67

H10A	260.28	5993.24	5512.78	28
H10B	1666.25	6612.4	5105.37	28
H11A	1524.06	5210.75	4378.71	30
H11B	376.42	4431.95	4804.38	30
H13A	-2081.07	4486.3	3859.52	54
H13B	-619.81	5224.7	3539.22	54
H13C	-2530.24	5721.28	3636.58	54
H14A	3501.66	6800.53	6005.27	28
H14B	2320.85	6049.83	6433.76	28
H15A	4823.29	4820.69	6594.1	29
H15B	5986.27	5671.31	6211.81	29
H17A	8508.53	7767.59	5812.02	55
H17B	8793.91	6910.42	6351.17	55
H17C	8952.15	8223.77	6466.36	55
H18A	7136.15	8721.28	7362.87	45
H18B	6329.43	7865.23	7836.18	45
H18C	5071.84	8598.38	7423.64	45

Compound **17j**



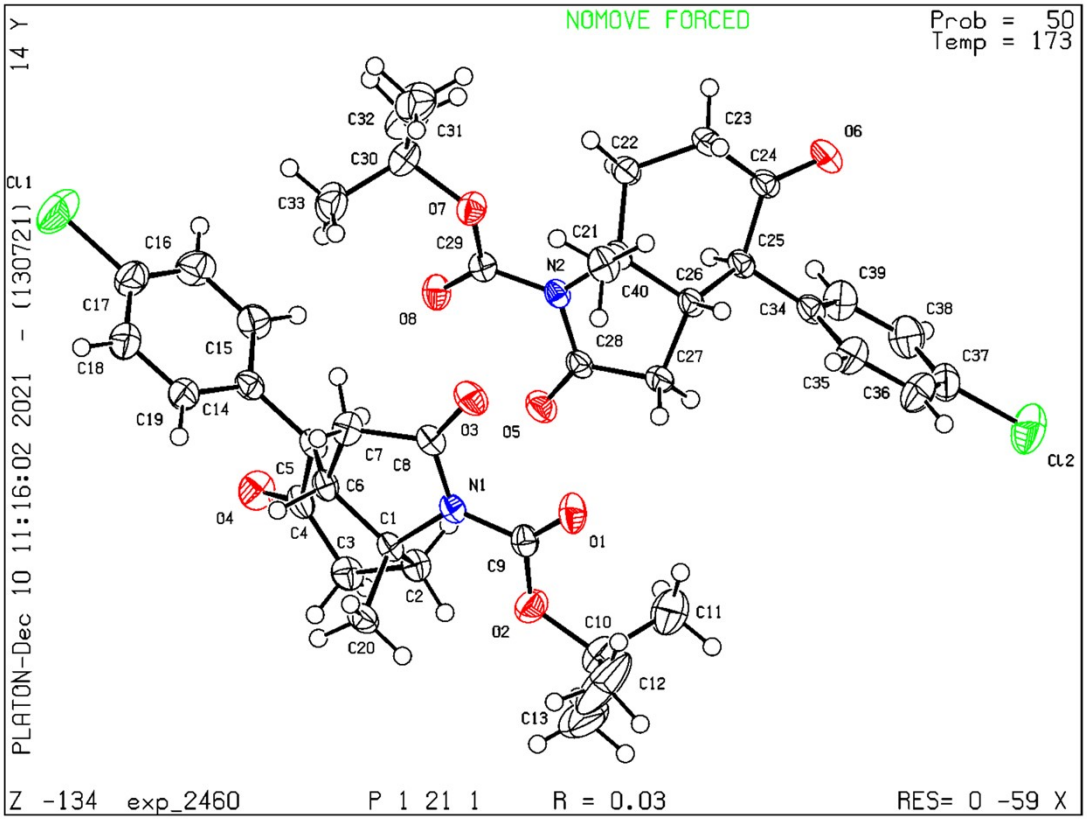


Figure S2. X-ray crystallographic structure of 17j

Table S14 Crystal data and structure refinement for 17j.

Identification code	17j
Empirical formula	$C_{20}H_{24}ClNO_4$
Formula weight	377.85
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.41290(10)
b/Å	6.44320(10)
c/Å	24.3361(3)
α/°	90
β/°	101.1400(10)
γ/°	90
Volume/Å^3	1909.70(4)
Z	4
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	1.978
F(000)	800.0
Crystal size/mm^3	0.36 × 0.28 × 0.22
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.258 to 134.12
Index ranges	$-14 \le h \le 14$, $-7 \le k \le 7$, $-29 \le l \le 29$
Reflections collected	42350
Independent reflections	6817 [R_{int} = 0.0504, R_{sigma} = 0.0305]
Data/restraints/parameters	6817/1/478
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0866
Final R indexes [all data]	R_1 = 0.0315, wR_2 = 0.0878
Largest diff. peak/hole / e Å^{-3}	0.18/-0.19
Flack parameter	0.008(5)

Table S15 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 17j. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	10056.9(6)	4090.3(13)	5522.8(4)	71.6(3)
O1	3632.9(12)	9110(3)	7733.3(6)	37.6(4)
O2	2527.3(12)	8866(3)	6883.3(6)	38.5(4)
O3	5783.2(12)	8593(3)	7704.5(6)	36.5(4)
O4	4910.4(13)	4272(3)	5117.4(6)	39.2(4)
N1	4340.0(13)	8598(2)	6936.4(6)	23.2(3)
C1	4174.5(15)	8528(3)	6310.7(7)	23.3(4)
C2	3384.1(16)	6775(3)	6068.4(8)	28.2(4)
C3	3561.5(16)	6129(3)	5488.8(8)	31.5(5)
C4	4692.7(16)	5313(3)	5493.8(8)	27.1(4)
C5	5552.8(15)	5885(3)	6011.8(7)	24.1(4)
C6	5363.9(16)	8115(3)	6208.2(8)	24.6(4)
C7	6128.5(15)	8612(3)	6762.5(8)	28.5(4)
C8	5438.5(16)	8589(3)	7206.1(7)	25.2(4)
C9	3497.9(16)	8886(3)	7236.9(8)	26.7(4)
C10	1504.2(18)	9283(4)	7084.6(10)	41.3(5)

C11	1337(2)	7703(6)	7511.8(12)	66.0(8)
C12	1533(2)	11465(5)	7298.9(19)	96.1(14)
C13	647(2)	8996(8)	6560.7(14)	88.4(14)
C14	6700.6(16)	5496(3)	5903.5(7)	26.6(4)
C15	7150.2(19)	3519(3)	5982.8(9)	35.6(5)
C16	8178(2)	3066(4)	5866.3(10)	43.4(6)
C17	8756.6(19)	4612(4)	5664.7(10)	41.8(6)
C18	8334.2(19)	6604(4)	5578.4(11)	44.8(6)
C19	7305.3(17)	7023(4)	5695.0(9)	36.4(5)
C20	3789.7(18)	10655(3)	6067.1(8)	33.2(5)
Cl2	-35.3(5)	-457.3(13)	9476.2(3)	63.3(2)
O5	4228.5(12)	3847(2)	7306.3(5)	32.9(3)
O6	5073.9(13)	-478(3)	9848.5(6)	41.3(4)
O7	7501.5(11)	4035(2)	8087.8(6)	31.5(3)
O8	6387.3(11)	3327(3)	7255.3(5)	31.6(3)
N2	5697.8(12)	3728(2)	8060.7(6)	22.3(3)
C21	5887.9(15)	3853(3)	8688.2(7)	23.7(4)
C22	6666.1(16)	2121(3)	8953.9(8)	28.6(4)
C23	6441.2(16)	1509(3)	9526.8(8)	31.5(5)
C24	5306.2(16)	658(3)	9494.8(7)	27.2(4)
C25	4462.6(15)	1315(3)	8978.0(7)	24.8(4)
C26	4700.2(15)	3552(3)	8804.6(7)	24.6(4)
C27	3947.4(16)	4192(3)	8258.3(8)	30.9(5)
C28	4594.7(15)	3884(3)	7802.9(7)	24.4(4)
C29	6529.9(15)	3664(3)	7749.5(8)	24.0(4)
C30	8538.2(16)	3603(4)	7899.7(10)	36.3(5)
C31	9387(2)	4233(6)	8407.8(11)	55.6(7)
C32	8592(2)	1305(4)	7780.0(13)	56.5(7)
C33	8647.9(18)	4946(4)	7405.2(9)	45.6(6)
C34	3310.1(16)	956(3)	9079.5(7)	26.4(4)
C35	2722.4(17)	2474(4)	9302.1(9)	35.5(5)
C36	1695.5(19)	2057(4)	9424.0(10)	42.9(6)
C37	1258.7(18)	85(4)	9326.4(9)	39.4(5)
C38	1818(2)	-1440(4)	9108.1(11)	45.4(6)
C39	2841.5(19)	-995(3)	8988.8(10)	39.3(5)
C40	6298.8(18)	6005(3)	8894.6(8)	32.3(5)

Table S16 Anisotropic Displacement Parameters ($Å^2×10^3$) for 17j. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	51.7(4)	80.7(7)	91.7(6)	1.8(4)	36.7(4)	22.3(4)
O1	42.9(8)	47.2(9)	25.7(7)	-5.1(7)	14.6(6)	-8.6(7)
O2	31.4(8)	51.8(10)	33.3(8)	-3.8(7)	8.5(6)	6.9(7)
O3	42.7(8)	43.2(9)	21.2(7)	1.0(6)	0.2(6)	-1.9(7)
O4	44.9(8)	42.8(9)	29.7(8)	-15.7(7)	6.8(6)	-2.1(7)
N1	30.7(8)	20.5(7)	18.5(7)	0.2(6)	5.4(6)	-0.7(6)
C1	31.0(9)	20.7(9)	18.6(8)	0.7(7)	5.4(7)	-0.7(7)
C2	31.6(10)	28.0(10)	25.0(10)	-2.5(8)	5.4(7)	-3.4(8)
C3	34.6(10)	36.3(11)	21.6(9)	-6.0(8)	0.4(8)	-5.7(9)

C4	35.6(10)	26.3(10)	19.6(9)	-0.7(8)	5.7(7)	-6.0(8)
C5	31.9(10)	20.7(9)	19.5(8)	0.3(7)	4.8(7)	-2.1(7)
C6	32.0(10)	20.6(9)	21.9(9)	-0.2(7)	7.2(7)	-4.0(7)
C7	29.3(10)	29.4(10)	26.7(10)	-8.7(8)	5.2(8)	-6.3(8)
C8	33.4(10)	20.2(9)	21.7(9)	-1.0(7)	4.1(8)	-2.3(8)
C9	32.4(10)	22.3(9)	27.0(10)	-0.7(8)	9.5(8)	-2.9(8)
C10	31.5(11)	42.7(13)	53.3(14)	-4.0(11)	17.0(10)	2.9(9)
C11	42.1(14)	76(2)	83(2)	16.7(18)	21.8(13)	-13.2(14)
C12	59.7(18)	43.7(17)	204(4)	-33(2)	73(2)	-5.0(14)
C13	37.4(14)	157(4)	67.6(19)	1(2)	0.8(13)	26(2)
C14	33.0(10)	27.0(10)	19.3(9)	-1.4(7)	3.8(7)	1.2(8)
C15	44.7(12)	26.4(10)	37.2(11)	-0.4(9)	11.5(9)	3.2(9)
C16	49.2(13)	36.2(13)	44.9(13)	-5.2(10)	9.4(10)	11.8(10)
C17	37.1(12)	51.5(14)	38.7(12)	-3.8(11)	12.0(10)	8.7(11)
C18	39.7(12)	48.0(15)	50.7(14)	10.8(12)	18.8(10)	3.1(11)
C19	36.5(11)	34.4(11)	40.7(12)	8.9(9)	13.4(9)	5.4(9)
C20	41.4(11)	28.2(11)	30.5(10)	8.8(9)	7.9(8)	4.7(9)
Cl2	47.1(4)	75.4(6)	74.2(5)	2.5(4)	28.3(3)	-17.6(3)
O5	36.6(8)	38.4(8)	22.6(7)	2.9(6)	3.0(6)	-0.5(6)
O6	45.1(8)	46.0(10)	32.7(8)	18.5(7)	7.6(7)	2.4(7)
O7	28.5(7)	38.2(8)	28.5(7)	-4.3(6)	7.5(6)	-2.6(6)
O8	36.7(7)	35.9(8)	23.8(7)	-5.1(6)	10.1(6)	-3.0(6)
N2	29.6(8)	19.3(7)	18.8(7)	-0.7(6)	6.6(6)	0.7(6)
C21	32.1(10)	22.2(10)	17.0(8)	-0.8(7)	5.7(7)	1.5(8)
C22	32.3(10)	29.2(10)	24.6(10)	3.1(8)	5.7(8)	4.5(8)
C23	35.1(10)	36.9(12)	21.3(9)	6.0(8)	2.5(8)	4.5(9)
C24	34.7(10)	26.8(10)	20.6(9)	1.5(8)	6.4(7)	6.8(8)
C25	32.4(10)	23.3(9)	19.3(9)	0.7(7)	6.4(7)	3.4(7)
C26	32.6(10)	22.6(9)	20.2(9)	0.8(7)	9.0(7)	5.0(8)
C27	34.5(10)	32.6(11)	27.3(10)	9.2(8)	10.3(8)	12.0(8)
C28	31.3(10)	19.1(9)	23.2(9)	4.4(7)	6.3(8)	1.8(7)
C29	29.2(10)	18.4(9)	24.7(9)	-2.0(7)	6.2(7)	-2.0(7)
C30	26.6(10)	40.9(12)	43.5(12)	-3.0(10)	11.5(9)	-1.7(9)
C31	33.6(12)	81(2)	49.9(14)	-3.8(15)	1.4(10)	-6.8(13)
C32	38.9(12)	41.5(14)	92(2)	-8.8(14)	19.9(12)	4.6(11)
C33	36.9(12)	55.4(15)	47.2(13)	1.4(12)	15.0(10)	-9.6(11)
C34	33.0(10)	27.6(10)	18.4(9)	1.1(7)	4.0(7)	1.5(8)
C35	34.8(10)	34.7(12)	38.4(11)	-10.9(9)	10.5(9)	-4.6(9)
C36	36.1(11)	50.1(14)	45.4(13)	-12.4(11)	15.1(9)	0.0(11)
C37	36.5(11)	50.0(14)	32.8(11)	2.2(10)	9.7(9)	-7.7(10)
C38	50.1(14)	38.0(13)	49.8(14)	0.9(11)	13.6(11)	-11.6(11)
C39	47.9(13)	28.7(12)	44.4(12)	-5.3(10)	16.8(10)	-3.6(10)
C40	44.3(11)	27.0(10)	26.3(10)	-6.6(8)	8.4(8)	-3.4(9)

Table S17 Bond Lengths for 17j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C17	1.747(2)	Cl2	C37	1.750(2)
O1	C9	1.196(2)	O5	C28	1.206(2)
O2	C9	1.338(2)	O6	C24	1.207(2)

O2	C10	1.472(2)	O7	C29	1.344(2)
O3	C8	1.206(2)	O7	C30	1.473(2)
O4	C4	1.208(2)	O8	C29	1.201(2)
N1	C1	1.497(2)	N2	C21	1.502(2)
N1	C8	1.394(2)	N2	C28	1.395(2)
N1	C9	1.399(2)	N2	C29	1.394(2)
C1	C2	1.537(3)	C21	C22	1.535(3)
C1	C6	1.567(3)	C21	C26	1.566(3)
C1	C20	1.533(3)	C21	C40	1.529(3)
C2	C3	1.527(3)	C22	C23	1.526(3)
C3	C4	1.497(3)	C23	C24	1.500(3)
C4	C5	1.531(2)	C24	C25	1.533(2)
C5	C6	1.546(3)	C25	C26	1.546(3)
C5	C14	1.519(3)	C25	C34	1.516(3)
C6	C7	1.526(2)	C26	C27	1.526(3)
C7	C8	1.502(3)	C27	C28	1.502(3)
C10	C11	1.498(4)	C30	C31	1.517(3)
C10	C12	1.498(4)	C30	C32	1.513(3)
C10	C13	1.506(4)	C30	C33	1.510(3)
C14	C15	1.389(3)	C34	C35	1.391(3)
C14	C19	1.392(3)	C34	C39	1.385(3)
C15	C16	1.391(3)	C35	C36	1.390(3)
C16	C17	1.373(4)	C36	C37	1.384(4)
C17	C18	1.387(4)	C37	C38	1.368(4)
C18	C19	1.387(3)	C38	C39	1.387(3)

Table S18 Bond Angles for 17j.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O2	C10	120.78(16)	C29	O7	C30	120.69(15)
C8	N1	C1	114.08(15)	C28	N2	C21	113.65(15)
C8	N1	C9	121.07(15)	C29	N2	C21	124.52(15)
C9	N1	C1	124.47(15)	C29	N2	C28	121.56(15)
N1	C1	C2	111.37(15)	N2	C21	C22	110.60(15)
N1	C1	C6	102.63(14)	N2	C21	C26	102.06(14)
N1	C1	C20	109.73(15)	N2	C21	C40	111.08(15)
C2	C1	C6	111.43(15)	C22	C21	C26	111.82(15)
C20	C1	C2	112.38(16)	C40	C21	C22	112.24(16)
C20	C1	C6	108.85(15)	C40	C21	C26	108.59(16)
C3	C2	C1	111.06(16)	C23	C22	C21	111.19(16)
C4	C3	C2	112.99(15)	C24	C23	C22	112.51(16)
O4	C4	C3	122.40(17)	O6	C24	C23	122.43(17)
O4	C4	C5	122.38(18)	O6	C24	C25	122.25(18)
C3	C4	C5	115.22(16)	C23	C24	C25	115.32(16)
C4	C5	C6	110.79(16)	C24	C25	C26	110.21(16)
C14	C5	C4	110.23(15)	C34	C25	C24	109.92(15)
C14	C5	C6	114.23(16)	C34	C25	C26	115.00(16)
C5	C6	C1	114.26(15)	C25	C26	C21	113.61(15)
C7	C6	C1	105.54(15)	C27	C26	C21	104.38(14)
C7	C6	C5	111.28(16)	C27	C26	C25	111.86(16)

C8	C7	C6	106.83(15)	C28	C27	C26	106.39(15)
O3	C8	N1	126.74(18)	O5	C28	N2	126.59(18)
O3	C8	C7	125.60(18)	O5	C28	C27	126.15(18)
N1	C8	C7	107.65(15)	N2	C28	C27	107.22(15)
O1	C9	O2	125.71(19)	O7	C29	N2	109.46(15)
O1	C9	N1	124.82(18)	O8	C29	O7	125.93(18)
O2	C9	N1	109.47(16)	O8	C29	N2	124.61(17)
O2	C10	C11	110.6(2)	O7	C30	C31	101.95(18)
O2	C10	C12	108.8(2)	O7	C30	C32	108.58(18)
O2	C10	C13	102.1(2)	O7	C30	C33	110.98(18)
C11	C10	C13	109.5(3)	C32	C30	C31	111.7(2)
C12	C10	C11	113.2(3)	C33	C30	C31	109.9(2)
C12	C10	C13	112.1(3)	C33	C30	C32	113.2(2)
C15	C14	C5	119.50(18)	C35	C34	C25	122.57(18)
C15	C14	C19	117.94(19)	C39	C34	C25	119.56(19)
C19	C14	C5	122.45(18)	C39	C34	C35	117.69(19)
C14	C15	C16	121.6(2)	C36	C35	C34	121.2(2)
C17	C16	C15	118.9(2)	C37	C36	C35	119.1(2)
C16	C17	Cl1	119.8(2)	C36	C37	Cl2	119.50(19)
C16	C17	C18	121.1(2)	C38	C37	Cl2	119.53(19)
C18	C17	Cl1	119.0(2)	C38	C37	C36	121.0(2)
C17	C18	C19	119.0(2)	C37	C38	C39	119.2(2)
C18	C19	C14	121.3(2)	C34	C39	C38	121.9(2)

Table S19 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 17j.

Atom	*x*	*y*	*z*	U(eq)
H2A	3500.67	5587.4	6317.88	34
H2B	2632.69	7239.54	6042.48	34
H3A	3029.92	5067.06	5341.08	38
H3B	3430.85	7316.49	5239.84	38
H5	5446.72	4943.65	6313.01	29
H6	5514.94	9092.56	5924.02	29
H7A	6707.51	7582.77	6844.56	34
H7B	6461.86	9966.29	6745.09	34
H11A	1418.99	6335.55	7368.74	99
H11B	612.58	7850.71	7591.22	99
H11C	1871.29	7910.22	7849.11	99
H12A	2037.36	11552.18	7650.98	144
H12B	813.12	11861.35	7348.96	144
H12C	1768.57	12380.88	7033.96	144
H13A	773.5	9971.71	6281.78	133
H13B	-68.4	9224.65	6644.15	133
H13C	690.13	7609.58	6422.23	133
H15	6754.05	2473.53	6117.14	43
H16	8469.34	1735.79	5923.99	52
H18	8734.94	7643.66	5444.47	54
H19	7013.87	8351.52	5632.5	44
H20A	3063.38	10927.75	6130.67	50

H20B	3782.4	10661.79	5671.88	50
H20C	4282.39	11708.89	6246.03	50
H22A	6572.56	917.35	8709.74	34
H22B	7419.81	2589.36	8993.83	34
H23A	6973.09	473.47	9692.34	38
H23B	6535.85	2716.79	9769.41	38
H25	4561.51	399.06	8670.15	30
H26	4591.35	4509.92	9101.94	30
H27A	3291.03	3339.42	8189.8	37
H27B	3731.42	5633.73	8275.22	37
H31A	9299.88	5677.16	8485.71	83
H31B	10109.89	4000.26	8334.18	83
H31C	9288.79	3419.87	8724.95	83
H32A	8430.58	530.4	8091.17	85
H32B	9315.58	957.06	7724.47	85
H32C	8065.07	970.32	7448.57	85
H33A	8140.08	4481.65	7079.61	68
H33B	9383.25	4848.41	7338.01	68
H33C	8489.99	6362.19	7483.42	68
H35	3022.48	3793.59	9370.65	43
H36	1307.15	3089.22	9569.15	51
H38	1515.7	-2757.25	9040.51	55
H39	3224.01	-2036.55	8843.88	47
H40A	7006.73	6247.15	8803.12	48
H40B	6356.2	6081.59	9293.14	48
H40C	5791.48	7039	8717.06	48