Supporting Information

Chiral phosphoric acid catalyzed enantioselective synthesis of functionalized pyrrolinones containing a geminal diamine core via aza-Friedel-Crafts reaction of newly developed pyrrolinone ketimines

Tong Zhang,[a] Zhen-Hua Wang,[a]* Yong Li,[b] Jian-Qiang Zhao,[a] Yong You,[a] Yan-Ping Zhang,[a] Jun-Qing Yin,[a] and Wei-Cheng Yuan[a]*

[a]Innovation Research Center of Chiral Drugs, Institute for Advanced Study, Chengdu University, Chengdu 610106, China

[b]College of Pharmacy, National & Local Joint Engineering Research Center of Targeted and Innovative Therapeutics, IATTI, Chongqing University of Arts and Sciences, Chongqing 402160, China

wangzhenhua@cdu.edu.cn

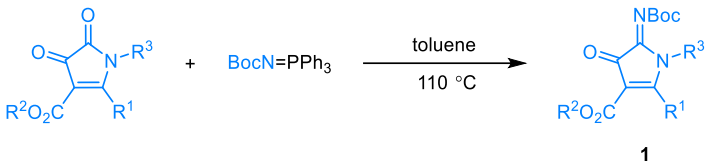
yuanwc@cioc.ac.cn

Table of Contents

1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Flash column chromatography was performed over silica gel (H, purchased from Qingdao Ocean Chemical Co., Ltd. Qingdao, China). Analytical thin layer chromatography (TLC) was performed on silica gel HSGF254 glass plates (purchased from Yantai Xinuo Chemical Co., Ltd. Yantai, China) containing a 254 nm fluorescent indicator. The enantiomeric excesses were determined by chiral HPLC analysis that was performed by Agilent HPLC systems using chiral columns described below in detail. Optical rotations were measured with a polarimeter. ^{1}H NMR spectra were measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of 400 MHz. Proton chemical shifts are reported in parts per million (δ scale) and referenced using tetramethylsilane (TMS) as an internal standard or residual protium in the NMR solvent [$CDCl_3$: δ 7.26 ($CHCl_3$) or DMSO-d_6: δ 2.50 (CD_2HSOCD_3)]. Data are reported as follows: chemical shift [multi-plicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets,brs = broad singlet), coupling constant(s) (Hz), integration]. ^{13}C NMR spectra were also measured on a Bruker AVANCE NEO 400 MHz spectrometer at the ambient temperature of ^{13}C at 101MHz. Carbon chemical shifts are reported in parts per million (δ scale), and referenced using the carbon resonances of the solvent [δ 77.16 ($CDCl_3$) or δ 39.52 (DMSO-d_6)]. The melting points of products were recorded on a Büchi Melting Point B-545 and temperatures were not corrected. High-resolution mass spectra (HRMS) were recorded by Agilent 6545 LC/Q-TOF mass spectrometer by using an electrospray ionization (ESI) ionization source analyzed by quadrupole time-of-flight (Q-TOF). It should be particularly noted that, in most of the ^{1}H NMR spectra, partial protons such as BocN-H, O-H, and PhCH-H appear incompletely. This may be due to a certain degree of steric hindrance resulting from the attachment of the 1-naphthol group to the chiral tetra-substituted carbon, which restricts the fast free rotation of the C-C bond.

2. General experimental procedure for the synthesis of pyrrolinone ketimines 1



1

The 1*H*-pyrrole-2,3-diones (1.0 equiv), BocN=PPh_3 (1.2 equiv) in a flask, and toluene (0.5 M) was added at room temperature. The mixture was stirred at 110 °C for 5 h. After the removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether as the eluent to give the pyrrolinone ketimines **1**.

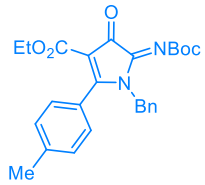
Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1a)

Yellow solid, m.p. 137.2 – 138.1 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.58 – 7.51 (m, 1H), 7.47 – 7.41 (m, 2H), 7.23 – 7.18 (m, 5H), 6.90 (dd, *J* = 7.0, 2.5 Hz, 2H), 4.71 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.63 (s, 9H), 1.05 (t, *J* = 7.1 Hz, 3H).

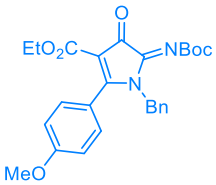
^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 179.4, 174.1, 161.1, 158.5, 146.3, 135.5, 131.4, 128.8, 128.5, 128.1, 127.8, 127.5, 104.5, 83.7, 60.2, 46.2, 28.1, 14.1.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{26}N_2O_5Na$: 457.1734; found: 457.1744.

Ethyl 1-benzyl-5-((tert-butoxycarbonyl)imino)-4-oxo-2-(p-tolyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (1b)



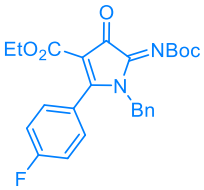
Yellow solid, m.p. 154.8 – 155.2 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 5H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.88 (m, 2H), 4.72 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.62 (s, 9H), 1.11 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 174.1, 161.3, 158.5, 146.5, 142.3, 135.6, 129.2, 128.8, 128.0, 127.4, 125.5, 104.4, 83.6, 60.3, 46.2, 28.1, 21.8, 14.2.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{26}H_{28}N_2O_5Na$: 471.1890; found: 471.1904.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1c)



Yellow solid, m.p. 161.9 – 162.3 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.28 – 7.18 (m, 6H), 6.99 – 6.90 (m, 4H), 4.76 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.62 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 174.1, 162.5, 161.5, 158.6, 146.8, 135.7, 130.4, 128.8, 128.0, 127.3, 120.2, 113.9, 104.2, 83.5, 60.3, 55.6, 46.4, 28.1, 14.3.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{26}H_{28}N_2O_6Na$: 487.1840; found: 487.1850.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(4-fluorophenyl)-4-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (1d)

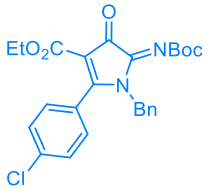


Yellow solid, m.p. 133.7 – 134.2 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.25 – 7.17 (m, 5H), 7.16 – 7.11 (m, 2H), 6.91 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.71 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.62 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 178.4, 173.9, 164.5 (d, *J* = 254.5 Hz, 1C),161.1, 158.4, 146.2, 135.5, 130.4 (d, *J* = 9.1 Hz, 2C), 128.9, 128.2, 127.3, 124.5 (d, *J* = 3.0 Hz, 1C), 115.9 (d, *J* = 22.2 Hz, 2C), 104.7, 83.8, 60.4, 46.3, 28.1, 14.2.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{25}FN_2O_5Na$: 475.1640; found: 475.1666.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(4-chlorophenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1e)



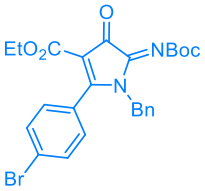
Yellow solid, m.p. 149.2 – 149.8 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.44 – 7.38 (m, 2H), 7.26 – 7.20 (m, 3H), 7.16 – 7.10 (m, 2H), 6.97 – 6.87 (m, 2H), 4.70 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.62 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 178.3, 173.8, 161.0, 158.3, 146.1, 137.9, 135.4, 129.4, 129.0, 128.9, 128.2, 127.3, 104.7, 83.8, 60.5, 46.3, 28.1, 14.2.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{25}ClN_2O_5Na$: 491.1344, 493.1327; found: 491.1359, 493.1339.

Ethyl 1-benzyl-2-(4-bromophenyl)-5-((*tert*-butoxycarbonyl)imino)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1f)



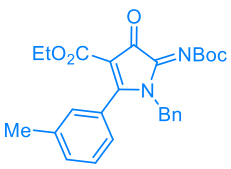
Yellow solid, m.p. 161.0 – 162.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.61 – 7.55 (m, 2H), 7.25 (dd, *J* = 6.2, 3.4 Hz, 3H), 7.10 – 7.03 (m, 2H), 6.96 – 6.87 (m, 2H), 4.70 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.62 (s, 9H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 178.3, 173.8, 161.0, 158.3, 146.1, 135.4, 131.9, 129.5, 129.0, 128.2, 127.3, 126.2, 104.6, 83.8, 60.5, 46.3, 28.1, 14.2.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{25}BrN_2O_5Na$: 535.0839, 537.0822; found: 535.0856, 535.0842.

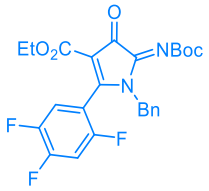
Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-4-oxo-2-(m-tolyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (1g)



Yellow solid, m.p. 115.8 – 116.7 °C

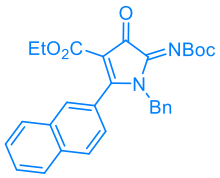
^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.32 (d, *J* = 5.1 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.04 – 6.98 (m, 1H), 6.94 – 6.88 (m, 3H), 4.68 (s, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.62 (s, 9H), 1.06 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 179.8, 174.1, 161.1, 158.5, 146.4, 138.3, 135.7, 132.2, 128.7, 128.5, 128.4, 128.2, 128.0, 127.5, 124.9, 104.4, 83.6, 60.2, 46.3, 28.1, 21.4, 14.1.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{26}H_{28}BrN_2O_5Na$: 471.1890; found: 471.1909.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-4-oxo-2-(2,4,5-trifluorophenyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1h)



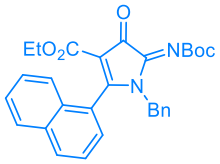
Yellow solid, m.p. 65.1 – 66.5 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ major isomer: 7.25 – 7.20 (m, 3H), 7.05 – 6.97 (m, 1H), 6.93 – 6.87 (m, 2H), 6.87 – 6.80 (m, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.57 (d, *J* = 15.7 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.63 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ major isomer: 173.4, 171.4, 160.5, 158.1, 155.6 – 147.9 (m, 3C), 145.5, 134.9, 129.0, 128.5, 127.2, 117.7 – 117.4 (m, 1C), 113.2 –112.9 (m, 1C), 106.9 – 106.4 (m, 1C), 105.8, 84.0, 60.6, 46.4, 28.1, 14.1.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{25}H_{23}F_3N_2O_5Na$: 511.1451; found: 511.1473.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(naphthalen-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1i)



Yellow solid, m.p. 171.5 – 172.6 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.64 – 7.52 (m, 2H), 7.26 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24 – 7.16 (m, 3H), 6.90 (dd, *J* = 7.9, 1.4 Hz, 2H), 4.75 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.64 (s, 10H), 1.00 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 174.1, 161.2, 158.5, 146.5, 135.7, 134.4, 132.1, 128.9, 128.8, 128.4, 128.3, 128.3, 128.1, 128.1, 127.5, 127.3, 125.8, 124.5, 104.7, 83.7, 77.5, 77.2, 76.8, 60.3, 46.5, 28.1, 14.1.
HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{29}H_{28}N_2O_5Na$: 507.1890; found: 507.1898.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(naphthalen-1-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1j)



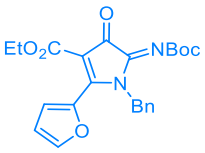
Yellow solid, m.p. 70.2 – 71.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.37 (m, 4H), 7.22 – 7.16 (m, 1H), 7.14 – 6.97 (m, 3H), 6.70 – 6.60 (m, 2H), 4.74 (d, *J* = 15.3 Hz, 1H), 4.38 (d, *J* = 15.3 Hz, 1H), 3.86 (q, *J* = 7.1 Hz, 2H), 1.67 (s, 9H), 0.73 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 174.2, 160.7, 158.6, 146.2, 135.3, 133.1, 131.4, 129.6, 128.7, 128.5, 128.0, 127.8, 127.8, 126.9, 126.6, 125.9, 124.7, 124.3, 105.7, 83.8, 77.5, 77.2, 76.8, 60.0, 46.3, 28.1, 13.7.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{29}H_{28}N_2O_5Na$: 507.1890; found: 507.1908.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-2-(furan-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1k)



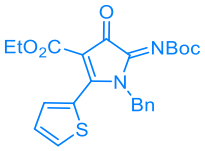
Brown solid, m.p. 44.8 – 45.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 1.6, 0.5 Hz, 1H), 7.61 (dd, *J* = 3.8, 0.5 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.08 (dd, *J* = 7.7, 1.5 Hz, 2H), 6.62 (dd, *J* = 3.8, 1.7 Hz, 1H), 5.17 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.61 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 162.7, 162.0, 158.8, 147.8, 147.1, 141.4, 136.0, 128.8, 127.9, 126.6, 125.7, 113.7, 102.6, 83.4, 60.8, 47.6, 28.1, 14.4.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{23}H_{24}N_2O_6Na$: 447.1527; found: 447.1535.

Ethyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-4-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1l)



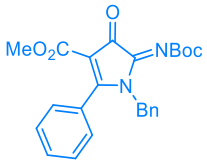
Yellow solid, m.p. 125.2 – 125.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.31 – 7.24 (m, 4H), 7.15 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.9 Hz, 2H), 4.91 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.61 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 171.6, 161.4, 158.5, 146.5, 135.7, 133.2, 132.6, 129.0, 128.0, 127.8, 127.2, 126.9, 105.4, 83.6, 60.6, 46.6, 28.1, 14.2.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{23}H_{24}N_2O_5SNa$: 463.1298; found: 463.1306.

Methyl 1-benzyl-5-((*tert*-butoxycarbonyl)imino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1m)



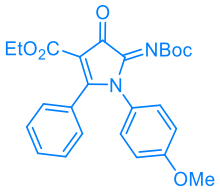
Yellow solid, m.p. 165.7 – 166.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.48 – 7.39 (m, 2H), 7.25 – 7.18 (m, 5H), 6.93 – 6.85 (m, 2H), 4.72 (s, 2H), 3.64 (s, 3H), 1.63 (s, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 173.9, 161.7, 158.4, 146.3, 135.4, 131.6, 128.8, 128.5, 128.3, 128.1, 127.8, 127.5, 104.0, 83.7, 51.5, 46.2, 28.1.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{24}H_{24}N_2O_5Na$: 443.1577; found: 443.1581.

Ethyl 5-((*tert*-butoxycarbonyl)imino)-1-(4-methoxyphenyl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (1n)



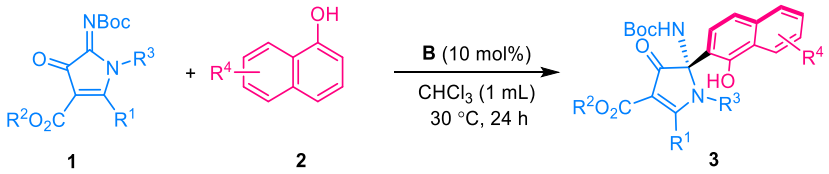
Yellow solid, m.p. 180.7 – 182.2 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 2H), 7.00 – 6.94 (m, 2H), 6.80 – 6.74 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 1.58 (s, 9H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 174.1, 161.4, 159.5, 158.6, 146.9, 131.5, 129.7, 129.1, 128.4, 128.1, 126.2, 114.5, 104.6, 83.6, 60.5, 55.5, 28.1, 14.2.

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{26}H_{29}N_2O_6$: 465.2020; found: 465.2016.

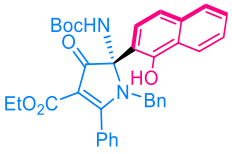
3. General experimental procedure for the asymmetric synthesis of compounds 3



1 2 3

In a reaction tube equipped with a magnetic stirring bar was charged with pyrrolinone ketimines **1** (0.10 mmol), naphthols **2** (0.15 mmol), and 9-anthryl-substituted chiral phosphoric acid **B** (0.01 mmol). $CHCl_3$ (1.0 mL) was added to the tube via syringe. Then the mixture was stirred for indicated time at 30 °C. After completion, the reaction mixture was directly purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate) to give the corresponding product **3**.

Ethyl (*S*)-1-benzyl-4-((tert-butoxycarbonyl)amino)-4-(1-hydroxynaphthalen-2-yl)-5-oxo-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (3aa).



It was purified by flash chromatography (petroleum ether/EtOAc = 3:1) as white solid (51.5 mg, 89% yield); 98% *ee*; $[\alpha]_D^{20}$ = -524.2 (*c* 2.57, CH_2Cl_2); m.p. 129.7 – 130.9 °C.

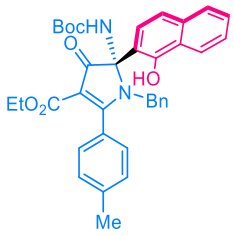
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.55 – 8.32 (m, 1H), 7.87 – 7.67 (m, 1H), 7.39 (d, *J* = 69.0 Hz, 8H), 7.22 – 6.62 (m, 6H), 5.97 (s, 1H), 4.95 (d, *J* = 15.9 Hz, 1H), 4.65 (d, *J* = 15.7 Hz, 1H), 4.10 – 3.90 (m, 2H), 1.37 (s, 9H), 1.04 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.5, 162.7, 154.5, 153.3, 135.6, 135.0, 130.6, 130.4, 128.5, 127.9, 127.7, 127.2, 126.1, 123.3, 121.5, 120.5, 113.4, 100.8, 82.9, 81.6, 59.6, 48.9, 28.3, 14.2.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.29 min (major), 8.98 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{35}N_2O_6$: 579.2490; found: 579.2507.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-2-(*p*-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ba)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (57.9 mg, 98% yield); 97% *ee*; $[\alpha]_D^{20}$ = -820.4 (*c* 1.45, CH_2Cl_2); m.p. 124.0 – 125.1 °C.

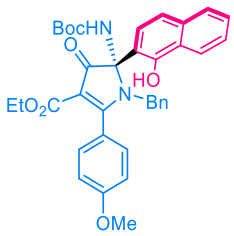
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 – 10.07 (m, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.29 (m, 7H), 7.22 – 7.09 (m, 3H), 7.09 – 6.76 (m, 3H), 6.04 – 5.48 (m, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.60 (d, *J* = 15.5 Hz, 1H), 4.08 – 3.83 (m, 2H), 2.59 (s, 3H), 1.38 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.5, 162.8, 153.4, 152.7, 135.4, 133.9, 130.7, 130.5, 128.6, 128.5, 128.2, 128.1, 127.8, 127.6, 126.6, 125.8, 123.8, 123.7, 122.0, 112.7, 101.0, 82.9, 81.6, 59.7, 48.9, 28.3, 19.6, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.86 min (major), 9.55 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_6$: 593.2646; found: 593.2669.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-2-(4-methoxyphenyl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ca)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (55.1 mg, 90% yield); 97% *ee*; $[\alpha]_D^{20}$ = -684.8 (*c* 1.38, CH_2Cl_2); m.p. 111.2 – 111.8 °C.

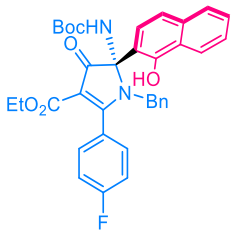
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.89 – 10.46 (m, 1H), 8.39 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.30 (m, 8H), 7.22 – 6.71 (m, 5H), 6.05 – 5.62 (m, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 15.4 Hz, 1H), 4.12 – 3.91 (m, 2H), 1.39 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 181.0, 162.6, 154.1, 153.2, 135.0, 133.1, 130.6, 130.5, 129.1, 128.9, 128.7, 128.6, 128.2, 128.0, 126.8, 126.7, 125.5, 123.7, 114.1, 113.5, 101.2, 82.2, 81.9, 59.8, 48.8, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.94 min (major), 10.06 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{36}N_2O_7Na$: 631.2415; found: 631.2313.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-2-(4-fluorophenyl)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate (3da)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (58.8 mg, 98% yield); 98% *ee*; $[\alpha]_D^{20}$ = -593.1 (*c* 1.47, CH_2Cl_2); m.p. 119.7 – 120.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.67 (s, 1H), 8.40 (d, *J* = 6.8 Hz, 1H), 7.91 – 7.65 (m, 1H), 7.63 – 7.27 (m, 5H), 7.22 – 6.62 (m, 8H), 6.04 (s, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 4.11 – 3.92 (m, 2H), 1.39 (s, 9H), 1.07 (t, *J* = 6.8 Hz, 3H).

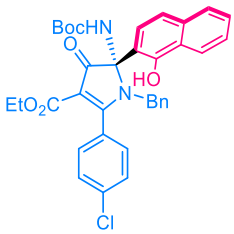
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 179.6, 163.8 (d, *J* = 252.7 Hz, 1C), 162.7, 154.5, 153.4, 135.5, 135.0, 128.5, 127.9, 127.8 (2C), 127.2, 126.5, 126.1, 123.3, 121.3, 120.5, 115.8 (d, *J* = 23.2 Hz, 1C), 113.3, 100.9, 83.0, 81.7, 59.7, 49.0, 28.2, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) *δ* -109.0

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.63 min (major), 9.12 (minor).

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{35}H_{33}FN_2O_6Na$: 619.2215; found: 619.2227.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-2-(4-chlorophenyl)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ea)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (60.5 mg, 99% yield); 97% *ee*; $[\alpha]_D^{20}$ = -642.2 (*c* 1.51, CH_2Cl_2); m.p. 125.4 – 126.1 °C.

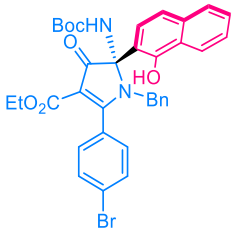
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.39 (d, *J* = 7.0 Hz, 1H), 7.97 – 7.67 (m, 1H), 7.64 – 7.24 (m, 7H), 7.19 – 6.62 (m, 6H), 6.02 (s, 1H), 4.89 (d, *J* = 15.8 Hz, 1H), 4.68 (d, *J* = 15.7 Hz, 1H), 4.14 – 3.93 (m, 2H), 1.39 (s, 9H), 1.07 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 179.4, 162.7, 154.5, 153.4, 136.7, 135.4, 135.0, 128.8, 128.6, 127.9, 127.8, 127.2, 126.2, 123.2, 121.3, 120.6, 113.2, 100.9, 83.1, 81.7, 59.8, 49.0, 28.2, 14.3.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.64 min (major), 9.27 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}ClN_2O_6$: 613.2100, 615.2090; found: 613.2120, 615.2122.

Ethyl (*R*)-1-benzyl-2-(4-bromophenyl)-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3fa)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (64.5 mg, 98% yield); 97% *ee*; $[\alpha]_D^{20}$ = -666.0 (*c* 1.61, CH_2Cl_2); m.p. 128.8 – 129.4 °C.

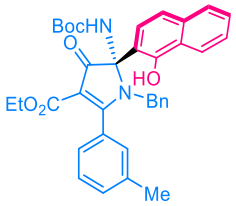
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.53 – 8.31 (m, 1H), 7.90 – 7.23 (m, 8H), 7.20 – 6.62 (m, 6H), 6.05 (s, 1H), 4.90 (d, *J* = 16.2 Hz, 1H), 4.69 (d, *J* = 15.9 Hz, 1H), 4.14 – 3.82 (m, 2H), 1.39 (s, 9H), 1.07 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 179.3, 162.7, 154.5, 153.4, 135.4, 134.9, 131.7, 129.4, 128.5, 127.8, 127.7, 127.1, 126.1, 125.0, 123.2, 121.3, 120.5, 113.1, 100.9, 83.1, 81.7, 59.8, 49.0, 28.2, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.69 min (major), 9.51 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}BrN_2O_6$: 657.1595, 659.1581; found: 657.1604, 659.1594.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-2-(*m*-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ga)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (44.3 mg, 75% yield); 98% *ee*; $[\alpha]_D^{20}$ = -847.9 (*c* 1.11, CH_2Cl_2); m.p. 117.5 – 118.2 °C.

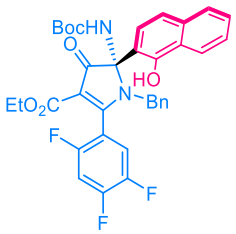
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.42 (t, *J* = 11.5 Hz, 1H), 7.92 – 7.66 (m, 1H), 7.65 – 7.23 (m, 6H), 7.22 – 6.60 (m, 7H), 6.01 (s, 1H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.64 (d, *J* = 15.6 Hz, 1H), 4.15 – 3.87 (m, 2H), 2.37 (s, 3H), 1.38 (s, 9H), 1.05 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.8, 162.7, 154.5, 153.3, 138.3, 135.6, 135.0, 131.2, 130.5, 128.4, 128.0, 127.9, 127.8, 127.6, 127.1, 126.0, 123.3, 121.5, 120.4, 113.4, 100.7, 82.9, 81.5, 59.6, 49.0, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.69 min (major), 9.51 (minor).

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{36}H_{36}N_2O_6Na$: 615.2466; found: 615.2475.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-2-(2,4,5-trifluorophenyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ha)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (52.5 mg, 83% yield); 98% *ee*; $[\alpha]_D^{20}$ = -695.3 (*c* 1.31, CH_2Cl_2); m.p. 124.1 – 124.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 – 10.19 (m, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.63 (m, 1H), 7.50 (d, *J* = 13.7, 6.2 Hz, 2H), 7.39 – 7.27 (m, 1H), 7.25 – 6.72 (m, 8H), 6.09 (s, 1H), 4.79 (q, *J* = 16.1 Hz, 2H), 4.16 – 3.93 (m, 2H), 1.48 – 1.38 (m, 9H), 1.12 (t, *J* = 7.1 Hz, 3H).

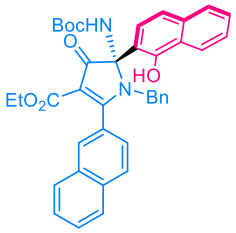
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 172.9, 162.4, 154.2, 153.6, 135.2, 135.1, 128.7, 128.1, 127.9, 127.8, 127.7, 127.2, 126.1, 123.3, 123.2, 121.8, 121.8, 120.7, 120.7, 113.1, 107.1 – 105.6 (1C),101.3, 83.8, 82.1, 60.0, 49.7, 28.3, 14.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.6 (dd, *J* = 14.0, 4.6 Hz), -127.9 (dd, *J* = 21.4, 4.6 Hz), -141.0 (dd, *J* = 21.3, 14.3 Hz).

HPLC (IA, ethanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 20.43 min (major), 29.48 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{32}F_3N_2O_6$: 633.2207; found: 633.2224.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-2-(naphthalen-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ia)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (62.1 mg, 99% yield); 64% *ee*; $[\alpha]_D^{20}$ = -697.7 (*c* 1.55, CH_2Cl_2); m.p. 129.3 – 130.5 °C.

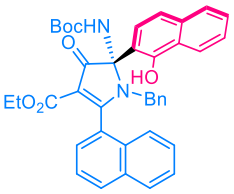
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 8.43 (d, *J* = 6.9 Hz, 1H), 8.15 – 7.68 (m, 5H), 7.66 – 7.30 (m, 6H), 7.24 – 6.58 (m, 6H), 6.02 (s, 1H), 5.02 (d, *J* = 13.1 Hz, 1H), 4.84 – 4.17 (m, 1H), 4.13 – 3.84 (m, 2H), 1.39 (s, 9H), 1.06 – 0.92 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.6, 162.8, 154.6, 153.4, 135.5, 135.0, 133.9, 132.5, 128.6, 128.4, 128.1, 127.9, 127.7, 127.2, 127.0, 126.1, 123.3, 121.6, 120.5, 113.4, 101.0, 83.0, 81.5, 59.7, 49.0, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.40 min (major), 10.34 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{37}N_2O_6$: 629.2646; found: 629.2669.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-2-(naphthalen-1-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ja)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (33.9 mg, 54% yield); 64% *ee*; $[\alpha]_D^{20}$ = -493.9 (*c* 0.85, CH_2Cl_2); m.p. 129.8 – 130.5 °C.

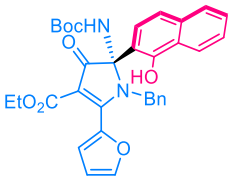
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.43 (d, *J* = 7.5 Hz, 1H), 7.97 (dd, *J* = 19.3, 8.1 Hz, 2H), 7.86 – 7.72 (m, 2H), 7.72 – 7.61 (m, 2H), 7.58 – 7.50 (m, 2H), 7.48 – 7.32 (m, 3H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 2H), 6.64 (d, *J* = 7.4 Hz, 2H), 6.10 (d, *J* = 11.5 Hz, 1H), 4.78 (dd, *J* = 15.0, 3.0 Hz, 1H), 4.59 (dd, *J* = 15.0, 4.0 Hz, 1H), 3.92 – 3.61 (m, 2H), 1.51 (s, 9H), 0.64 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 180.3, 162.3, 154.3, 153.3, 135.0, 134.0, 133.1, 131.1, 130.7, 129.6, 129.4, 128.0, 127.9, 127.8, 127.7, 127.3, 127.2, 126.7, 126.1, 126.0, 124.6, 123.9, 123.2, 121.9, 120.4, 113.3, 102.1, 83.1, 81.7, 59.3, 49.6, 28.4, 13.6.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.83 min (major), 6.09 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{37}N_2O_6$: 629.2646; found: 629.2653.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-2-(furan-2-yl)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ka)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (49.1 mg, 86% yield); 95% *ee*; $[\alpha]_D^{20}$ = -630.3 (*c* 1.64, CH_2Cl_2); m.p. 72.2 – 72.7 °C.

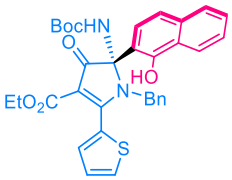
^{1}H NMR (400 MHz, $CDCl_3$) δ10.82 (s, 1H), 8.56 – 8.24 (m, 1H), 7.86 – 7.43 (m, 5H), 7.38 – 7.29 (m, 1H), 7.24 – 6.98 (m, 6H), 6.49 (s, 1H), 5.95 (s, 1H), 5.50 (d, *J* = 16.2 Hz, 1H), 4.78 (d, *J* = 16.1 Hz, 1H), 4.29 – 4.11 (m, 2H), 1.34 – 1.23 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 165.0, 163.3, 154.3, 153.4, 145.8, 141.5, 135.9, 135.1, 128.4, 127.8, 127.4, 127.2, 126.9, 126.0, 123.8, 123.2, 122.1, 120.5, 113.9, 112.7, 98.4, 83.2, 81.6, 60.1, 50.2, 28.2, 14.5.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.89 min (major), 7.75 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{33}H_{33}N_2O_7$: 569.2282; found: 569.2292

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3la)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (52.6 mg, 90% yield); 96% *ee*; $[\alpha]_D^{20}$ = -606.9 (*c* 1.75, CH_2Cl_2); m.p. 117.3 – 118.0 °C.

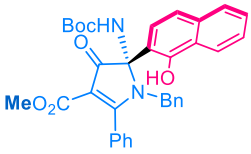
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.40 (s, 1H), 7.87 – 7.45 (m, 4H), 7.43 – 7.28 (m, 2H), 7.25 – 6.64 (m, 7H), 5.92 (s, 1H), 5.17 (d, *J* = 16.1 Hz, 1H), 4.69 (d, *J* = 15.7 Hz, 1H), 4.19 – 3.93 (m, 2H), 1.33 (s, 9H), 1.13 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 173.4, 162.7, 154.5, 153.3, 135.7, 135.0, 131.5, 130.1, 128.6, 127.9, 127.6, 127.5, 127.2, 126.1, 123.2, 121.5, 120.6, 113.3, 101.7, 83.1, 81.6, 59.9, 49.2, 28.2, 14.3.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.93 min (major), 5.54 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{33}H_{33}N_2O_6S$: 585.2054; found: 585.2069.

Methyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ma)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (54.5 mg, 97% yield); 98% *ee*; $[\alpha]_D^{20}$ = -501.5 (*c* 1.00, CH_2Cl_2); m.p. 126.9 – 127.5 °C.

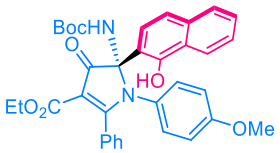
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 8.39 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 6.7 Hz, 1H), 7.63 – 7.28 (m, 8H), 7.20 – 6.63 (m, 6H), 5.98 (s, 1H), 4.97 (d, *J* = 15.8 Hz, 1H), 4.64 (d, *J* = 15.8 Hz, 1H), 3.58 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 180.9, 163.3, 154.5, 153.4, 135.4, 135.0, 130.6, 130.2, 128.6, 128.5, 127.9, 127.7, 127.2, 126.1, 123.3, 121.4, 120.6, 113.2, 100.5, 83.0, 81.6, 51.1, 49.0, 28.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.94 min (major), 7.73 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{33}N_2O_6$: 565.2333; found: 565.2332.

Ethyl (*R*)-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxynaphthalen-2-yl)-1-(4-methoxyphenyl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3na)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (24.5 mg, 41% yield); 14% *ee*; $[\alpha]_D^{20}$ = -96.4 (*c* 0.61, CH_2Cl_2); m.p. 104.9 – 105.8 °C.

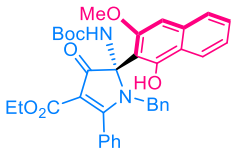
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.39 (d, *J* = 7.5 Hz, 1H), 7.78 (dd, *J* = 6.9, 2.1 Hz, 2H), 7.69 – 7.56 (m, 2H), 7.56 – 7.48 (m, 3H), 7.47 – 7.32 (m, 3H), 7.05 – 6.81 (m, 2H), 6.65 – 6.53 (m, 2H), 5.69 (s, 1H), 4.19 – 4.05 (m, 2H), 3.67 (s, 3H), 1.26 (s, 9H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 179.1, 163.1, 158.3, 154.1, 153.0, 135.2, 131.2, 130.3, 129.9, 128.7, 128.2, 127.8, 127.7, 127.2, 126.1, 123.2, 123.0, 120.3, 114.0, 113.7, 102.8, 84.2, 81.2, 60.0, 55.4, 28.1, 14.3.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.93 min (major), 5.95 (minor).

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{35}H_{34}N_2O_7Na$: 617.2258; found: 617.2276.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxy-3-methoxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ab).



It was purified by flash chromatography (petroleum ether/EtOAc = 8:1) as white solid (36.3 mg, 60% yield); 99% *ee*; $[\alpha]_D^{20}$ = 78.6 (*c* 0.91, CH_2Cl_2); m.p. 95.0 – 95.6 °C.

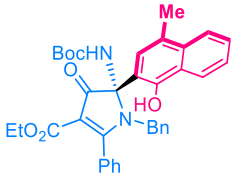
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.00 (m, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.39 (m, 3H), 7.38 – 7.23 (m, 3H), 7.16 – 6.98 (m, 2H), 6.94 – 6.79 (m, 3H), 6.60 (d, *J* = 7.4 Hz, 2H), 6.40 (s, 1H), 6.15 – 5.69 (m, 1H), 4.85 (d, *J* = 17.0 Hz, 1H), 4.29 (d, *J* = 16.6 Hz, 1H), 4.02 – 3.92 (m, 2H), 3.53 (s, 3H), 1.52 (s, 9H), 0.85 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 157.4, 154.0, 138.7, 136.4, 131.4, 129.0, 128.6, 128.3, 127.9, 127.7, 127.5, 126.6, 126.2, 125.9, 123.4, 123.3, 117.7, 117.0, 108.6, 98.3, 88.2, 59.2, 55.2, 46.6, 28.4, 14.3, 13.8.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.94 min (major), 5.51 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_7$: 609.2597; found: 609.2613.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(1-hydroxy-4-methylnaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ac)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (51.9 mg, 88% yield); 97% *ee*; $[\alpha]_D^{20}$ = -692.1 (*c* 1.30, CH_2Cl_2); m.p. 119.5 – 120.3 °C.

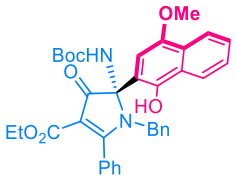
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.30 (m, 7H), 7.22 – 7.10 (m, 3H), 7.09 – 6.76 (m, 3H), 5.91 (s, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 4.61 (d, *J* = 15.5 Hz, 1H), 4.08 – 3.90 (m, 2H), 2.60 (s, 3H), 1.39 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.5, 162.8, 153.4, 152.7, 135.4, 133.9, 130.7, 130.5, 128.6, 128.5, 128.1, 128.1, 127.8, 127.6, 126.6, 125.8, 123.8, 123.7, 122.0, 112.7, 101.0, 82.9, 81.6, 59.7, 48.9, 28.3, 19.6, 14.2.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.41 min (major), 9.68 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_6$: 593.2646; found: 593.2657.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(1-hydroxy-4-methoxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ad)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (52.8 mg, 87% yield); 97% *ee*; $[\alpha]_D^{20}$ = -715.8 (*c* 1.32, CH_2Cl_2); m.p. 181.2 – 182.2 °C.

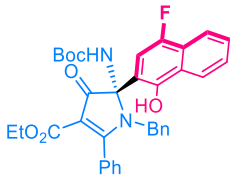
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 8.35 (s, 1H), 8.21 – 8.04 (m, 1H), 7.73 – 7.29 (m, 7H), 7.22 – 7.10 (m, 3H), 7.08 – 6.77 (m, 2H), 6.40 (s, 1H), 6.15 – 5.70 (m, 1H), 4.86 (d, *J* = 15.5 Hz, 1H), 4.62 (d, *J* = 15.6 Hz, 1H), 4.17 – 3.97 (m, 2H), 3.90 (s, 3H), 1.40 (s, 9H), 1.05 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.6, 162.8, 153.5, 149.7, 147.8, 135.4, 130.8, 130.5, 128.8, 128.7, 128.5, 128.3, 127.9, 127.2, 126.9, 126.7, 123.0, 121.6, 112.6, 101.2, 100.0, 82.9, 81.6, 59.7, 55.8, 48.9, 28.3, 14.2.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.84 min (major), 8.95 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_7$: 609.2595; found: 609.2615.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(4-fluoro-1-hydroxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ae)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (47.2 mg, 79% yield); 96% *ee*; $[\alpha]_D^{20}$ = -727.5 (*c* 1.18, CH_2Cl_2); m.p. 120.7 – 121.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.37 (d, *J* = 6.7 Hz, 1H), 8.02 – 7.91 (m, 1H), 7.79 – 7.27 (m, 7H), 7.23 – 7.10 (m, 3H), 7.10 – 6.67 (m, 3H), 6.04 – 5.63 (m, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 4.62 (d, *J* = 15.6 Hz, 1H), 4.11 – 3.92 (m, 2H), 1.38 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

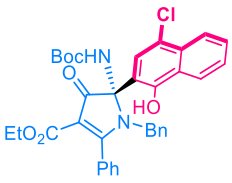
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 180.8, 162.5, 153.3, 153.0 (d, *J* = 246.4 Hz, 1C), 150.4, 135.3, 130.5 (d, *J* = 11.1 Hz, 1C), 128.7 (d, *J* = 4.0 Hz, 1C), 128.5, 128.1, 128.0, 127.8, 127.1, 124.8 (d, *J* = 18.2 Hz, 1C), 123.4, 120.1 (d, *J* = 3.0 Hz, 1C), 112.6, 105.3 (d, *J* = 24.2 Hz, 1C), 101.1, 82.3, 81.8, 59.7, 48.9, 28.2, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) *δ* -130.9.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.12 min (major), 7.42 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}FN_2O_6$: 597.2395; found: 597.2421.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(4-chloro-1-hydroxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3af)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (49.6 mg, 81% yield); 93% *ee*; $[\alpha]_D^{20}$ = -745.5 (*c* 2.48, CH_2Cl_2); m.p. 157.6 – 158.3 °C.

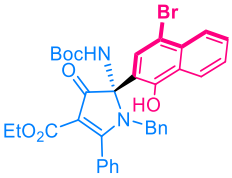
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.31 (m, 7H), 7.23 – 7.11 (m, 4H), 7.10 – 6.72 (m, 2H), 6.01 – 5.57 (m, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 15.4 Hz, 1H), 4.13 – 3.89 (m, 2H), 1.38 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 181.0, 162.6, 153.5, 153.3, 135.1, 131.9, 130.6, 130.5, 128.9, 128.7, 128.6, 128.2, 128.0, 126.8, 124.1, 123.7, 123.6, 121.9, 113.6, 101.1, 82.3, 81.9, 59.8, 48.9, 28.3, 14.2.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.01 min (major), 6.50 (minor).

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{35}H_{33}ClN_2O_6Na$: 635.1919; found: 635.1931.

Ethyl (*R*)-1-benzyl-5-(4-bromo-1-hydroxynaphthalen-2-yl)-5-((*tert*-butoxycarbonyl)amino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ag)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (51.5 mg, 78% yield); 94% *ee*; $[\alpha]_D^{20}$ = -631.9 (*c* 1.29, CH_2Cl_2); m.p. 123.1 – 123.8 °C.

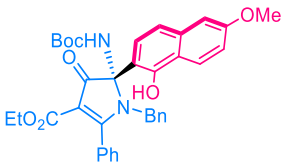
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.39 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.29 (m, 8H), 7.21 – 7.11 (m, 3H), 7.10 – 6.74 (m, 2H), 5.91 (s, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 15.4 Hz, 1H), 4.13 – 3.88 (m, 2H), 1.39 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 181.0, 162.6, 154.1, 153.2, 135.0, 133.1, 130.6, 130.5, 129.1, 128.9, 128.7, 128.6, 128.2, 128.0, 126.8, 126.7, 125.5, 123.7, 114.1, 113.5, 101.2, 82.2, 81.9, 59.8, 48.8, 28.3, 14.2.

HPLC (IA, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.12 min (major), 6.52 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}BrN_2O_6$: 657.1595, 659.1581; found: 657.1608, 659.1593.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(1-hydroxy-6-methoxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ah)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (51.0 mg, 84% yield); 98% *ee*; $[\alpha]_D^{20}$ = -666.9 (*c* 1.27, CH_2Cl_2); m.p. 128.9 – 129.5 °C.

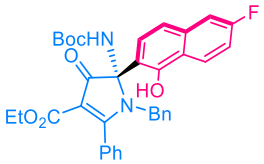
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.46 (s, 5H), 7.25 – 6.67 (m, 9H), 5.91 (s, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 4.16 – 3.96 (m, 2H), 3.92 (s, 3H), 1.36 (s, 9H), 1.04 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 180.4, 162.8, 159.2, 154.6, 153.3, 136.7, 135.6, 130.6, 130.4, 128.5, 127.9, 127.6, 125.1, 123.1, 122.3, 119.4, 118.5, 111.5, 105.3, 100.8, 82.9, 81.5, 59.6, 55.4, 48.9, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 4.21 min (major), 18.75 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_7$: 609.2595; found: 609.2616.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(6-fluoro-1-hydroxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ai)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (50.4 mg, 85% yield); 96% *ee*; $[\alpha]_D^{20}$ = -699.0 (*c* 1.26, CH_2Cl_2); m.p. 126.4 – 127.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.39 (s, 1H), 7.84 – 7.20 (m, 8H), 7.19 – 6.62 (m, 6H), 6.12 – 5.30 (m, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.77 – 4.17 (m, 1H), 4.00 (s, 2H), 1.36 (s, 9H), 1.02 (t, *J* = 7.0 Hz, 3H).

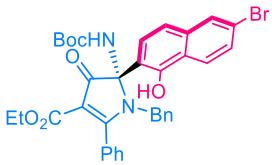
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 180.6, 162.6, 162.1 (d, *J* = 248.5 Hz, 1C), 154.8, 153.3, 136.2 (d, *J* = 9.1 Hz, 1C), 135.5, 130.5, 128.5, 127.9, 127.7, 126.3 (d, *J* = 9.1 Hz, 1C), 124.9, 123.0, 119.7 (d, *J* = 5.0 Hz, 1C), 116.2 (d, *J* = 24.2 Hz, 1C), 112.9, 110.3 (d, *J* = 21.2 Hz, 1C), 100.9, 82.8, 81.6, 59.7, 48.9, 28.2, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) *δ* -112.6.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 3.52 min (major), 6.04 (minor).

HRMS (ESI) m/z $[M+Na]^+$ Calcd. for $C_{35}H_{33}FN_2O_6$: 619.2215; found: 619.2229.

Ethyl (*R*)-1-benzyl-5-(6-bromo-1-hydroxynaphthalen-2-yl)-5-((*tert*-butoxycarbonyl)amino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3aj)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (53.4 mg, 81% yield); 96% *ee*; $[\alpha]_D^{20}$ = -629.3 (*c* 1.33, CH_2Cl_2); m.p. 127.4 – 127.9 °C.

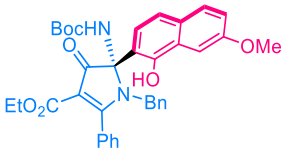
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 7.72 – 7.31 (m, 6H), 7.26 – 6.62 (m, 7H), 6.02 – 5.39 (m, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 4.76 – 4.20 (m, 1H), 4.00 (s, 2H), 1.36 (s, 9H), 1.02 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.7, 162.6, 154.7, 153.3, 136.1, 135.4, 130.5, 129.4, 129.2, 128.5, 127.9, 127.8, 126.4, 125.3, 122.9, 122.3, 119.4, 114.0, 100.9, 82.8, 81.7, 59.7, 49.0, 28.2, 14.2.

HPLC (IC, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.11 min (major), 20.08 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}BrN_2O_6$: 657.1595, 659.1581; found: 657.1611, 659.1594.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(1-hydroxy-7-methoxynaphthalen-2-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ak)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (48.2 mg, 79% yield); 97% *ee*; $[\alpha]_D^{20}$ = -716.3 (*c* 1.20, CH_2Cl_2); m.p. 126.0 – 126.7 °C.

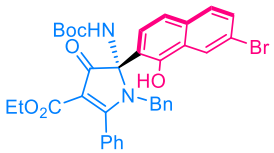
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.75 – 7.22 (m, 8H), 7.19 – 6.67 (m, 7H), 6.11 – 5.23 (m, 1H), 5.01 – 4.78 (m, 1H), 4.73 – 4.13 (m, 1H), 4.12 – 3.96 (m, 2H), 3.90 (s, 3H), 1.37 (s, 9H), 1.03 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.4, 162.7, 158.0, 153.3, 153.2, 135.7, 130.6, 130.5, 130.4, 129.0, 128.7, 128.5, 127.9, 127.6, 120.8, 120.3, 119.1, 114.1, 101.0, 100.8, 83.0, 81.5, 77.5, 77.2, 76.8, 59.6, 55.5, 49.0, 28.3.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 4.03 min (major), 7.67 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{37}N_2O_7$: 609.2595; found: 609.2619.

Ethyl (*R*)-1-benzyl-5-(7-bromo-1-hydroxynaphthalen-2-yl)-5-((*tert*-butoxycarbonyl)amino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3al)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (50.2 mg, 76% yield); 96% *ee*; $[\alpha]_D^{20}$ = -726.1 (*c* 1.25, CH_2Cl_2); m.p. 139.6 – 140.1 °C.

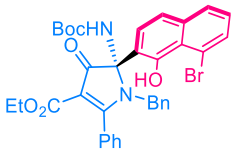
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 8.52 (s, 1H), 7.65 – 7.27 (m, 8H), 7.19 – 6.70 (m, 6H), 6.09 – 5.49 (m, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.73 – 4.32 (m, 1H), 4.08 – 3.90 (m, 2H), 1.37 (s, 9H), 1.03 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.7, 162.6, 153.6, 153.3, 135.4, 133.3, 131.1, 130.5, 130.5, 128.9, 128.8, 128.5, 127.9, 127.8, 125.7, 122.1, 120.3, 114.6, 100.9, 82.8, 81.7, 59.7, 49.0, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.58 min (major), 10.08 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}BrN_2O_6$: 657.1595, 659.1581; found: 657.1612, 659.1597.

Ethyl (*R*)-1-benzyl-5-(8-bromo-1-hydroxynaphthalen-2-yl)-5-((*tert*-butoxycarbonyl)amino)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3am)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (43.6 mg, 66% yield); 98% *ee*; $[\alpha]_D^{20}$ = -704.5 (*c* 1.09, CH_2Cl_2); m.p. 122.1 – 122.9 °C.

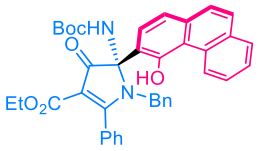
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.78 (d, *J* = 6.3 Hz, 1H), 7.72 – 7.20 (m, 8H), 7.18 – 6.62 (m, 6H), 6.28 – 5.33 (m, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 4.71 – 4.22 (m, 1H), 4.01 (d, *J* = 6.6 Hz, 2H), 1.37 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ196.5, 180.6, 162.7, 155.1, 153.3, 137.5, 135.4, 133.9, 130.5, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 125.4, 122.7, 121.2, 117.8, 115.4, 100.8, 83.0, 81.7, 59.7, 48.9, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 40/60, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 4.05 min (major), 13.79 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{35}H_{34}BrN_2O_6$: 657.1595, 659.1581; found: 657.1609, 659.1595.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(4-hydroxyphenanthren-3-yl)-4-oxo-2-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (3an)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (53.5 mg, 85% yield); 96% *ee*; $[\alpha]_D^{20}$ = -589.9 (*c* 0.89, CH_2Cl_2); m.p. 138.7 – 139.5 °C.

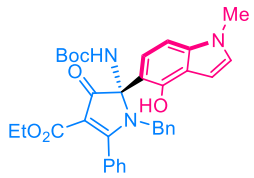
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.35 (d, *J* = 22.3 Hz, 1H), 9.97 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.83 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.32 (m, 9H), 7.25 – 6.71 (m, 6H), 5.85 (s, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.68 – 4.30 (m, 1H), 4.15 – 3.88 (m, 2H), 1.40 (s, 9H), 1.04 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 180.7, 162.7, 157.6, 153.5, 135.8, 135.5, 132.9, 130.8, 130.6, 130.5, 129.7, 129.4, 128.6, 128.5, 128.4, 128.0, 127.7, 127.0, 126.5, 126.3, 123.5, 122.4, 121.1, 116.9, 100.7, 83.5, 81.7, 59.7, 48.9, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.99 min (major), 12.04 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{39}H_{37}N_2O_6$: 629.2646; found: 629.2644.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(4-hydroxy-1-methyl-1*H*-indol-5-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ao)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (46.8 mg, 80% yield); 96% *ee*; $[\alpha]_D^{20}$ = -476.3 (*c* 0.78, CH_2Cl_2); m.p. 140.8 – 141.3 °C.

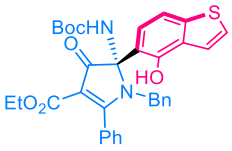
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.72 – 7.28 (m, 5H), 7.22 – 7.09 (m, 3H), 7.08 – 6.75 (m, 5H), 6.69 (s, 1H), 5.67 (s, 1H), 4.92 (d, *J* = 15.8 Hz, 1H), 4.64 (d, *J* = 15.8 Hz, 1H), 4.11 – 3.93 (m, 2H), 3.75 (s, 3H), 1.35 (s, 9H), 1.05 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 180.0, 163.0, 153.4, 151.4, 139.1, 135.9, 130.8, 130.2, 128.7, 128.4, 127.8, 127.5, 122.4, 118.4, 109.0, 102.5, 100.5, 99.6, 83.1, 81.3, 59.5, 48.8, 33.1, 28.3, 14.3.

HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 13.45 min (major), 38.81 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{34}H_{36}N_3O_6$: 582.2599; found: 582.2595.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-5-(4-hydroxybenzo[*b*]thiophen-5-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3ap)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (46.0 mg, 79% yield); 94% *ee*; $[\alpha]_D^{20}$ = -341.6 (*c* 0.77, CH_2Cl_2); m.p. 132.4 – 132.9 °C.

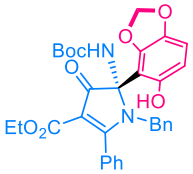
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.66 – 7.31 (m, 8H), 7.22 – 7.09 (m, 3H), 7.09 – 6.71 (m, 3H), 5.64 (s, 1H), 4.92 (d, *J* = 15.8 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 4.11 – 3.91 (m, 2H), 1.36 (s, 9H), 1.04 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 180.5, 162.7, 153.2, 153.1, 143.0, 135.6, 134.1, 130.5, 130.4, 128.5, 127.9, 127.7, 126.1, 121.5, 121.0, 114.9, 114.2, 100.8, 82.8, 81.6, 59.7, 48.9, 28.3, 14.2.

HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 5.84 min (major), 12.02 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{33}H_{33}N_2O_6S$: 585.2054; found: 585.2052.

Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-5-(5-hydroxybenzo[*d*][1,3]dioxol-4-yl)-4-oxo-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3aq)



It was purified by flash chromatography (petroleum ether/EtOAc = 4:1) as white solid (46.8 mg, 82% yield); 85% *ee*; $[\alpha]_D^{20}$ = -346.1 (*c* 0.78, CH_2Cl_2); m.p. 131.4 – 132.1 °C.

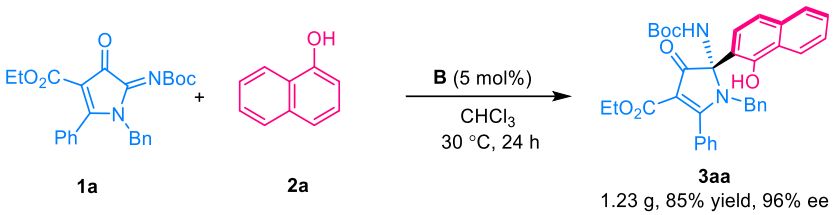
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.91 – 7.26 (m, 5H), 7.21 – 7.08 (m, 3H), 6.93 (s, 2H), 6.59 (s, 1H), 6.50 (s, 1H), 5.94 (dd, *J* = 15.9, 1.4 Hz, 2H), 5.84 (s, 1H), 4.79 (d, *J* = 15.8 Hz, 1H), 4.53 (d, *J* = 15.7 Hz, 1H), 4.10 – 3.90 (m, 2H), 1.34 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 180.4, 162.7, 153.3, 153.1, 149.6, 142.1, 135.5, 130.5, 128.5, 127.8, 127.7, 112.0, 104.3, 103.3, 101.8, 100.8, 82.3, 81.6, 59.6, 48.7, 28.2, 14.2.

HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.42 min (major), 15.72 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{32}H_{33}N_2O_8$: 573.2231; found: 573.2231.

4. Scale-up experiment

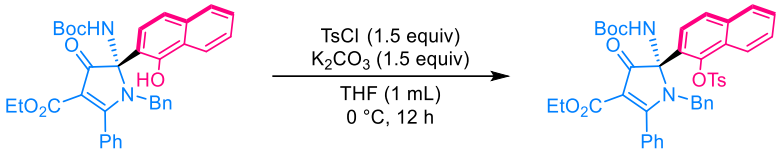


1a **2a** **3aa**

1.23 g, 85% yield, 96% ee

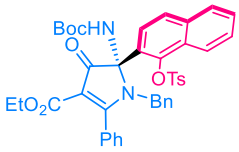
To an ordinary vial charged with a magnetic stirring bar were added **1a** (1.086 g, 2.5 mmol), **2a** (0.540 g, 3.75 mmol), catalyst **B** (87.5 mg), and $CHCl_3$ (25 mL). Then the mixture was stirred at 30 °C for 24 h. Product **3aa** was isolated by flash chromatography on silica gel as a solid (1.23 g, 85% yield, 96% *ee*).

5. Procedure for the synthesis of product 4



3aa **4**

The compound **3aa** (57.8 mg, 0.1 mmol, 1.0 equiv) was suspended in THF (1 mL) and then cooled to 0 °C. Then K_2CO_3 (1.5 equiv, 20.7 mg, 0.15 mmol), TsCl (1.5 equiv, 28.5 mg, 0.15 mmol) was added slowly and the solution was stirred for 12 h at 0 °C. The reaction was quenched with H_2O and extracted with EA (10 mL × 3), dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by chromatography over silica gel eluting with PE/EA to provide the desired product **4**.



Ethyl (*R*)-1-benzyl-5-((*tert*-butoxycarbonyl)amino)-4-oxo-2-phenyl-5-(1-(tosyloxy)naphthalen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (4)

It was purified by flash chromatography (petroleum ether/EtOAc = 1:1) as white solid (66.8 mg, 91% yield); 96% *ee*; $[\alpha]_D^{20}$ = -124.7 (*c* 1.11, CH_2Cl_2); m.p. 201.5 – 201.8 °C.

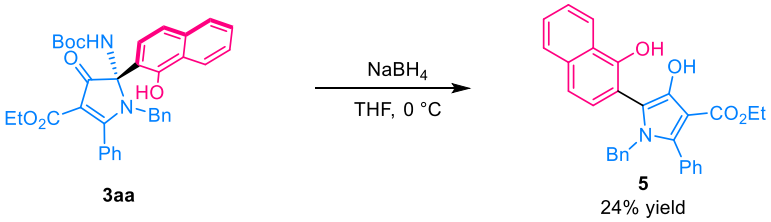
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.3 – 7.9 (m, 3H), 7.7 (dd, *J* = 23.8, 8.5 Hz, 3H), 7.6 – 7.3 (m, 10H), 7.1 – 7.0 (m, 3H), 7.0 – 6.8 (m, 2H), 4.7 – 4.4 (m, 2H), 4.1 – 3.8 (m, 2H), 2.5 (s, 3H), 1.4 (s, 9H), 1.0 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 153.2, 146.1, 143.7, 135.8, 135.0, 132.6, 131.4, 130.2, 130.0, 129.1, 128.4, 128.3, 128.2, 127.8, 127.5, 127.1, 126.7, 124.5, 124.1, 123.8, 81.7, 80.6, 59.4, 48.3, 28.4, 22.0, 14.2.

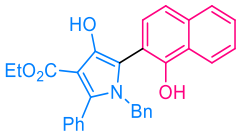
HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 9.80 min (major), 27.4 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{42}H_{41}N_2O_8S$: 733.2578; found: 733.2578.

6. Procedure for the synthesis of product 5



To the substrate **3aa** (173.7 mg, 0.3 mmol) in a dry reactor was added anhydrous THF (3.0 mL), and the mixture was stirred at 0 °C for 10 min. Then $NaBH_4$ (56.8 mg, 1.5 mmol) was added in one portion. Upon reaction completion, water (10 mL) was added and the mixture was extracted with DCM, washed with water and brine, dried over Mg_2SO_4, filtered, and concentrated to afford the crude product. The product was purified by flash chromatography with PE/EA to provide the desired compound **5** in 24% yield (32.7 mg) as a white solid.



Ethyl 1-benzyl-4-hydroxy-5-(1-hydroxynaphthalen-2-yl)-2-phenyl-1H-pyrrole-3-carboxylate (5)

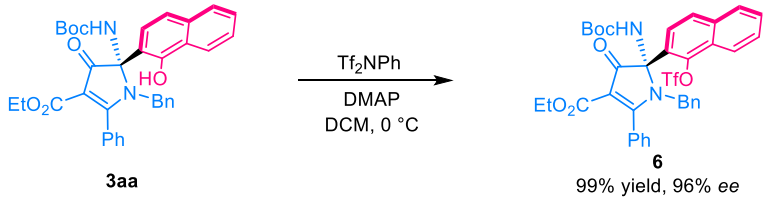
It was purified by flash chromatography (petroleum ether/EtOAc = 10:1) as white solid (32.7 mg, 24% yield); m.p. 49.7 – 50.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.37 – 8.27 (m, 1H), 7.79 – 7.70 (m, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.31 (m, 4H), 7.29 – 7.23 (m, 3H), 7.07 – 7.00 (m, 3H), 6.64 (s, 1H), 6.51 (dd, *J* = 7.4, 1.8 Hz, 2H), 4.98 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 150.3, 144.1, 137.6, 137.5, 134.4, 131.3, 130.9, 128.7, 128.4, 127.9, 127.4, 127.3, 126.8, 126.2, 125.5, 125.5, 123.1, 120.2, 111.8, 110.2, 101.8, 60.2, 48.9, 13.9.

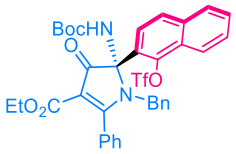
HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{30}H_{25}NO_4$: 464.1856; found: 464.1872.

7. Procedure for the synthesis of product 6



Compound **3aa** (57.9 mg, 0.1 mmol), DMAP (36.7 mg, 0.3 mmol), were successively added to a tube, followed by the addition of DCM (1 mL). Then Tf_2NPh (71.5 mg, 0.2 mmol) was added in one portion. The resulting mixture was stirred at room temperture for 10 min until almost full consumption of **3aa** (monitored by thin layer chromatography), and then DCM (10 mL) was added to the reaction mixture. The organic layer was washed with water and brine, dried over Mg_2SO_4, filtered, and concentrated to afford the crude product. The product was purified by flash chromatography with PE/EA to provide the desired compound **6** in 99% yield (70.0 mg) as a white solid.

Ethyl (*R*)-1-benzyl-5-((tert-butoxycarbonyl)amino)-4-oxo-2-phenyl-5-(1-(((trifluoromethyl) sulfonyl)oxy)naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-3-carboxylate (6)



It was purified by flash chromatography (petroleum ether/EtOAc = 5:1) as white solid (70.0 mg, 99% yield); 96% *ee*; $[\alpha]_D^{20}$ = -258.5 (*c* 1.87, CH_2Cl_2); m.p. 175.1 – 175.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.66 – 7.55 (m, 2H), 7.48 (s, 5H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.09 – 7.03 (m, 3H), 6.97 – 6.89 (m, 2H), 6.74 (s, 1H), 4.66 – 4.48 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 1.43 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

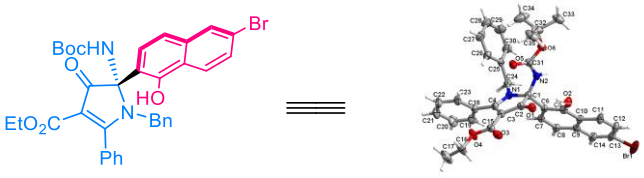
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 181.4, 163.2, 153.2, 142.4, 135.5, 135.2, 130.9, 130.2, 129.5, 128.7, 128.6, 128.4, 128.4, 127.9, 127.9, 127.7, 127.5, 127.2, 124.5, 123.6, 123.0, 118.8 (d, *J* = 322.2 Hz, 1C), 116.0, 101.9, 81.2, 59.6, 48.5, 28.2, 14.2.

HPLC (IC, ethanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.50 min (major), 11.17 (minor).

HRMS (ESI) m/z $[M+H]^+$ Calcd. for $C_{36}H_{34}F_3N_2O_8S$: 711.1982; found: 711.2006.

8. Crystal data

Single crystals of compound **3aj** was prepared through dissolving the sample in mixture solvent of EtOH/DCM (1/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on a 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



3aj CCDC: 2291492

ORTEP of **3aj** (at the 50% probability level)

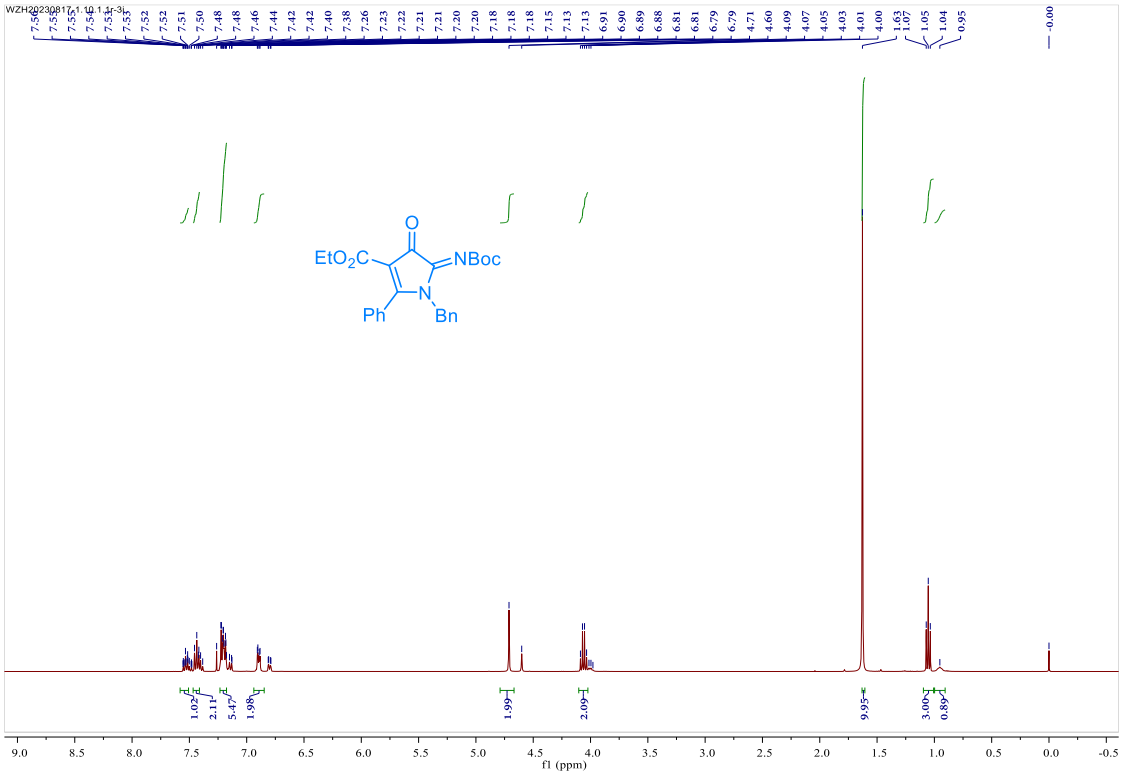
Identification code	**3aj**
Empirical formula	$C_{35}H_{33}BrN_2O_6$
Formula weight	657.54
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.4143(4)
b/Å	13.9129(3)
c/Å	11.8361(2)
α/°	90
β/°	99.402(3)
γ/°	90
Volume/Å^3	1691.94(8)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	2.026
F(000)	680.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.57 to 140.922
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-14 \le l \le 8$
Reflections collected	12241
Independent reflections	6341 [R_{int} = 0.0263, R_{sigma} = 0.0434]
Data/restraints/parameters	6341/2/406
Goodness-of-fit on F^2	1.044

Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1141
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.1233
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.33
Flack parameter	-0.024(12)

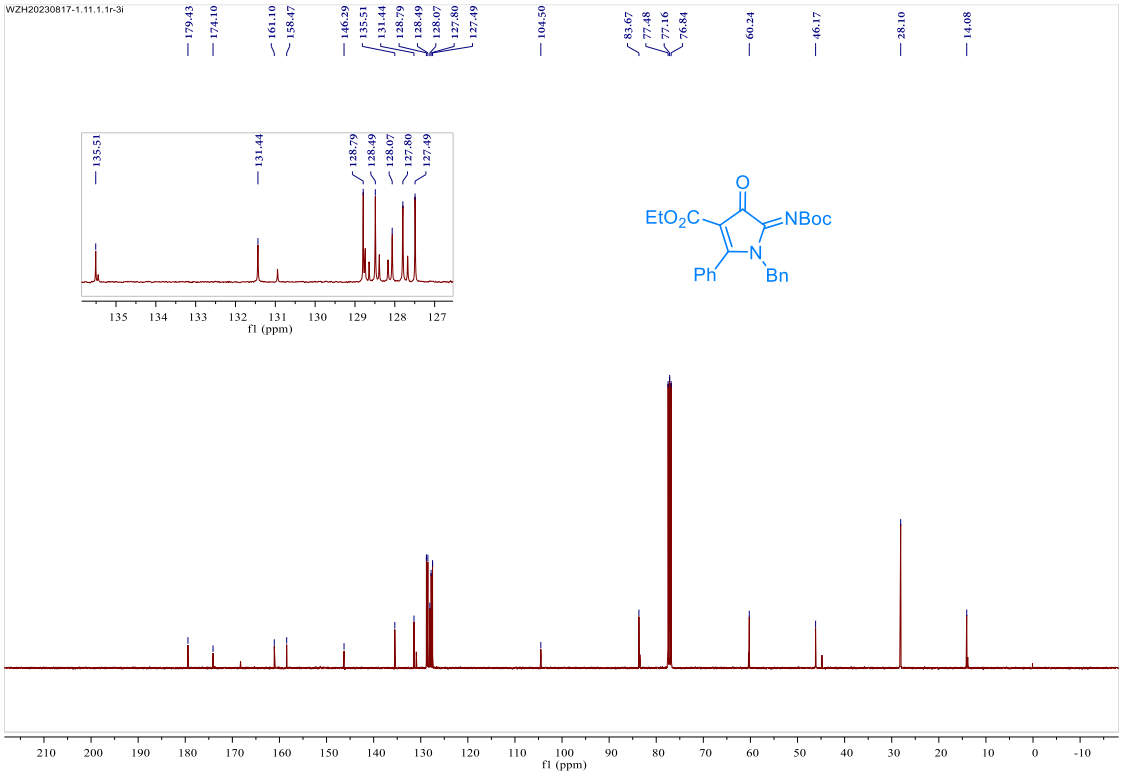
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K; Puschmann, H. *J. Appl. Cryst.*, 2009, **42**, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* 2015, **A71**, 3-8.
3. Sheldrick, G. M. *Acta Cryst.* 2015, **C71**, 3-8.

9. ^{1}H, ^{13}C NMR spectra for pyrrolinone ketimines

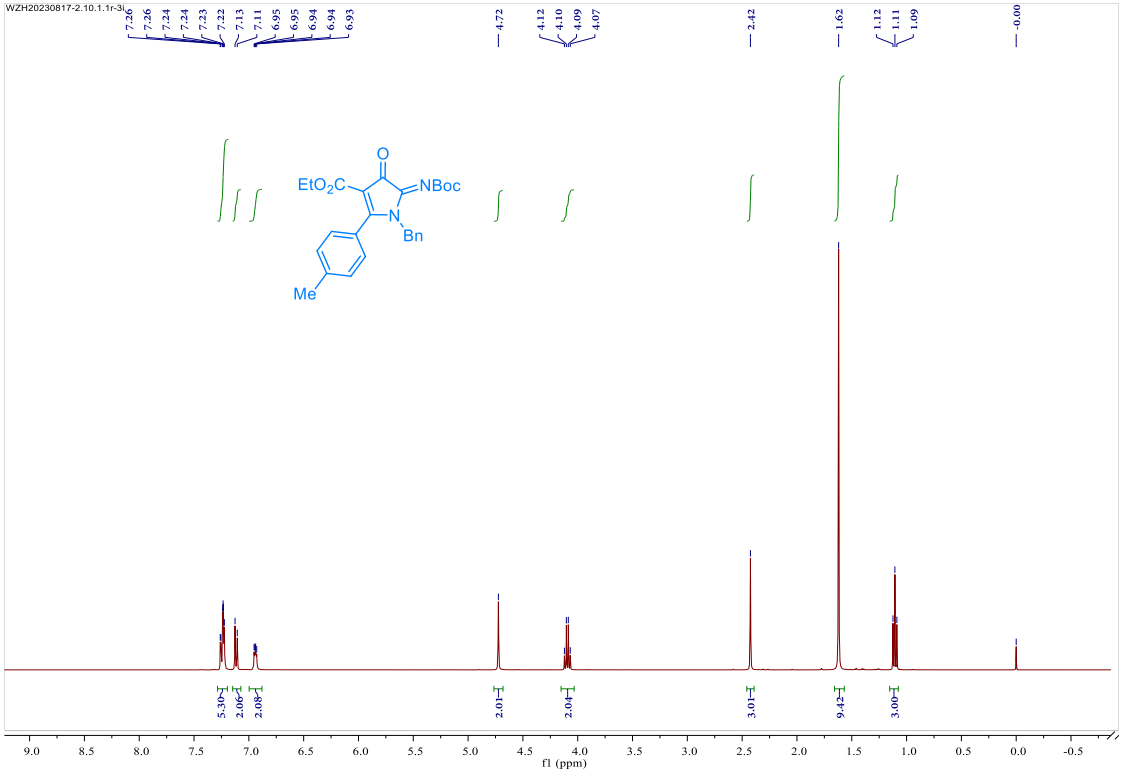
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



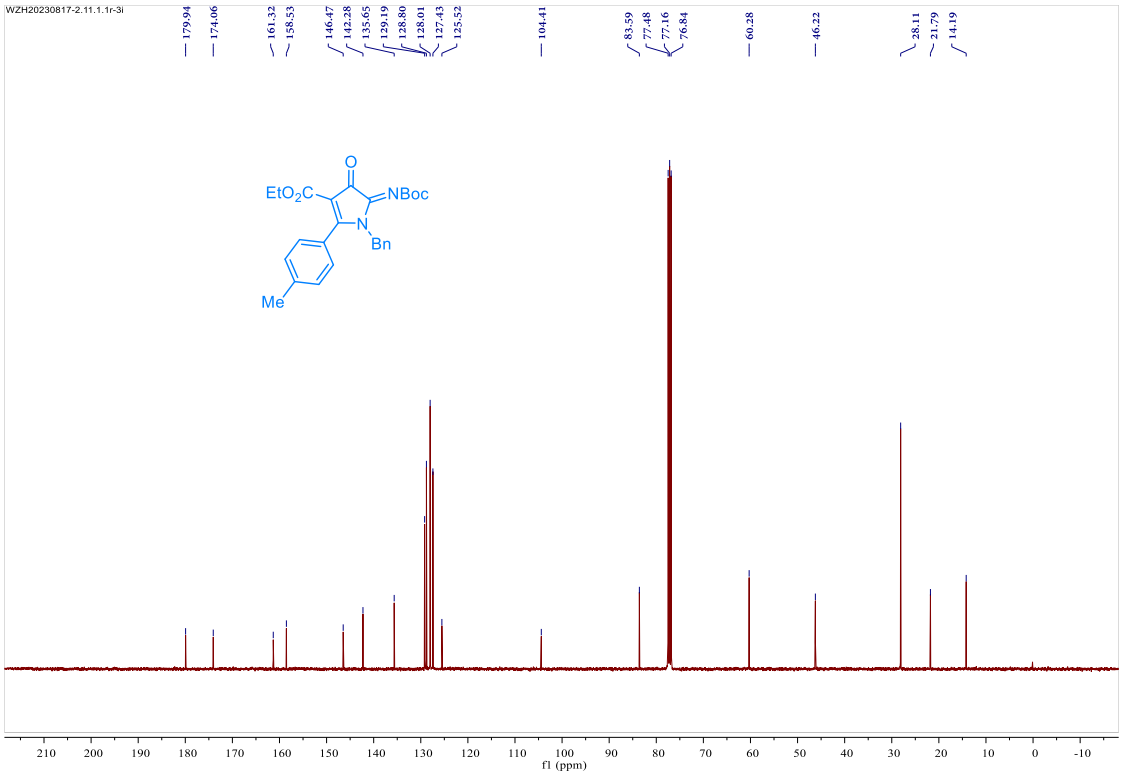
^{13}C NMR (101 MHz, $CDCl_3$) of **1a**



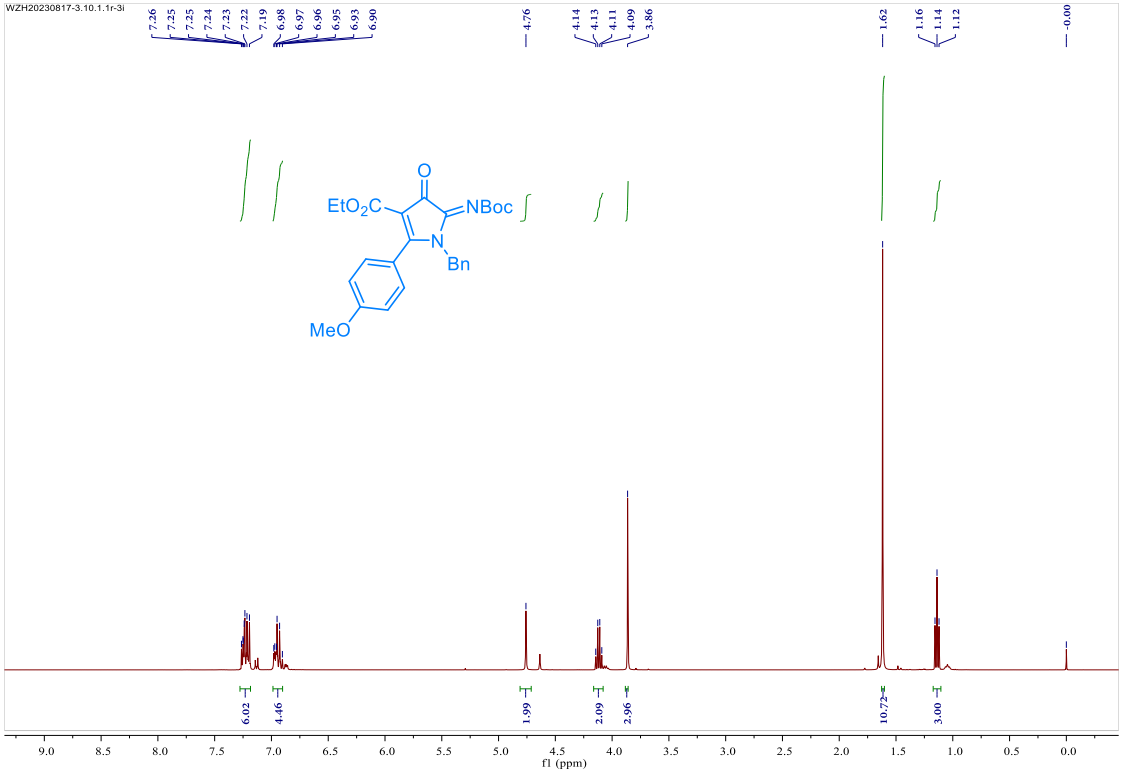
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



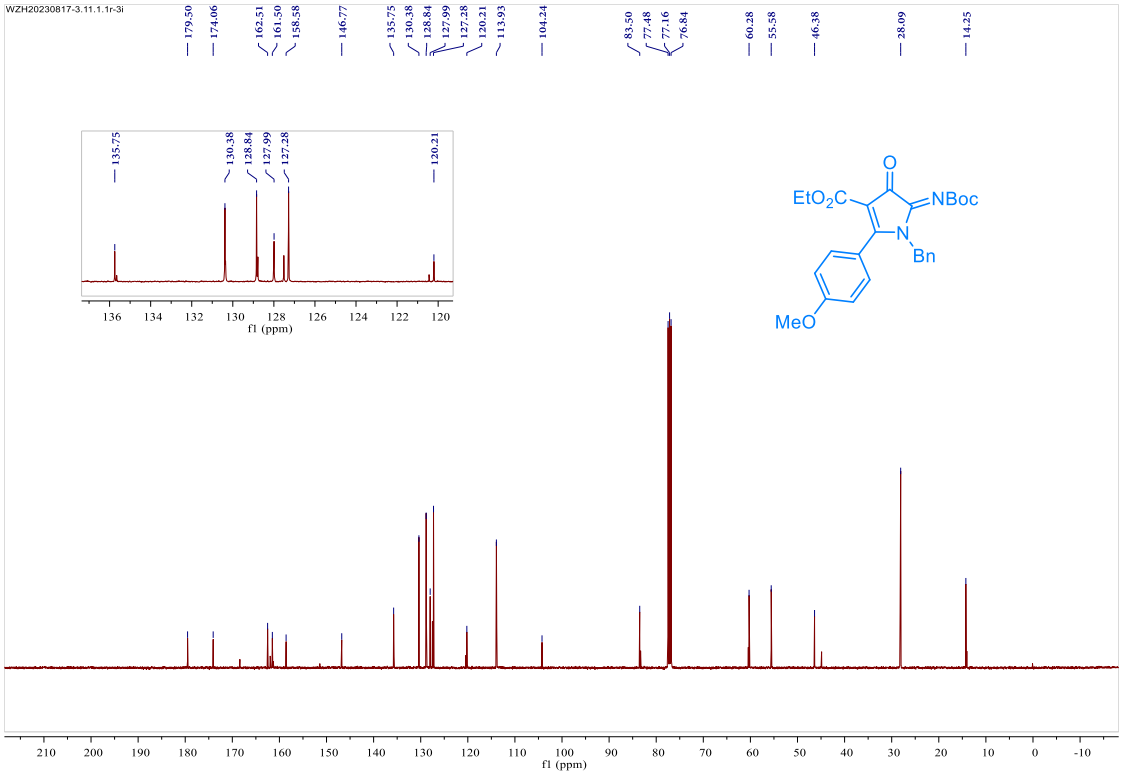
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



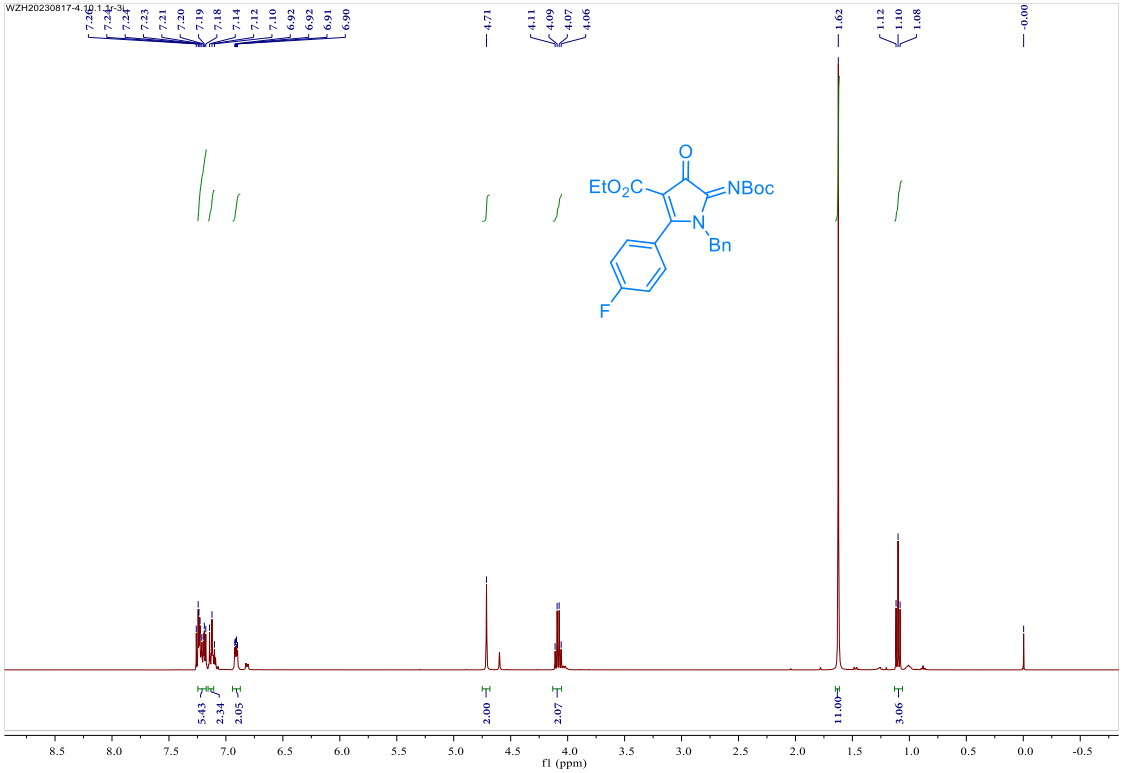
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



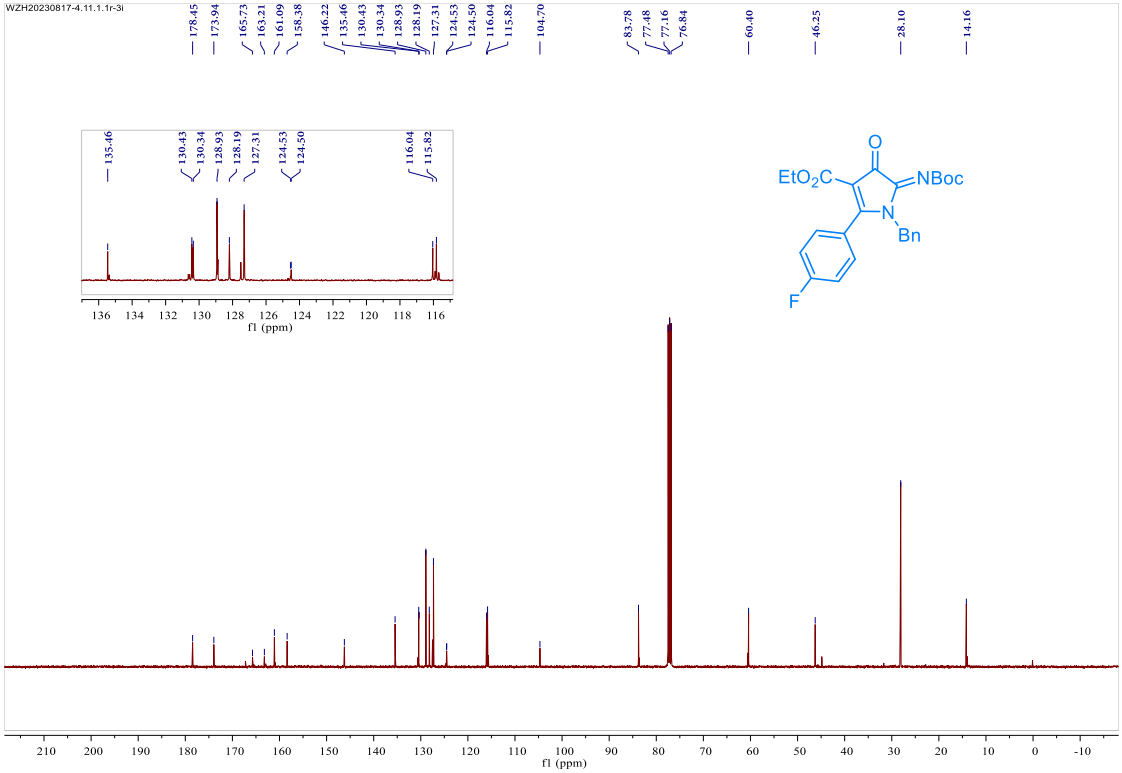
^{13}C NMR (101 MHz, $CDCl_3$) of **1c**



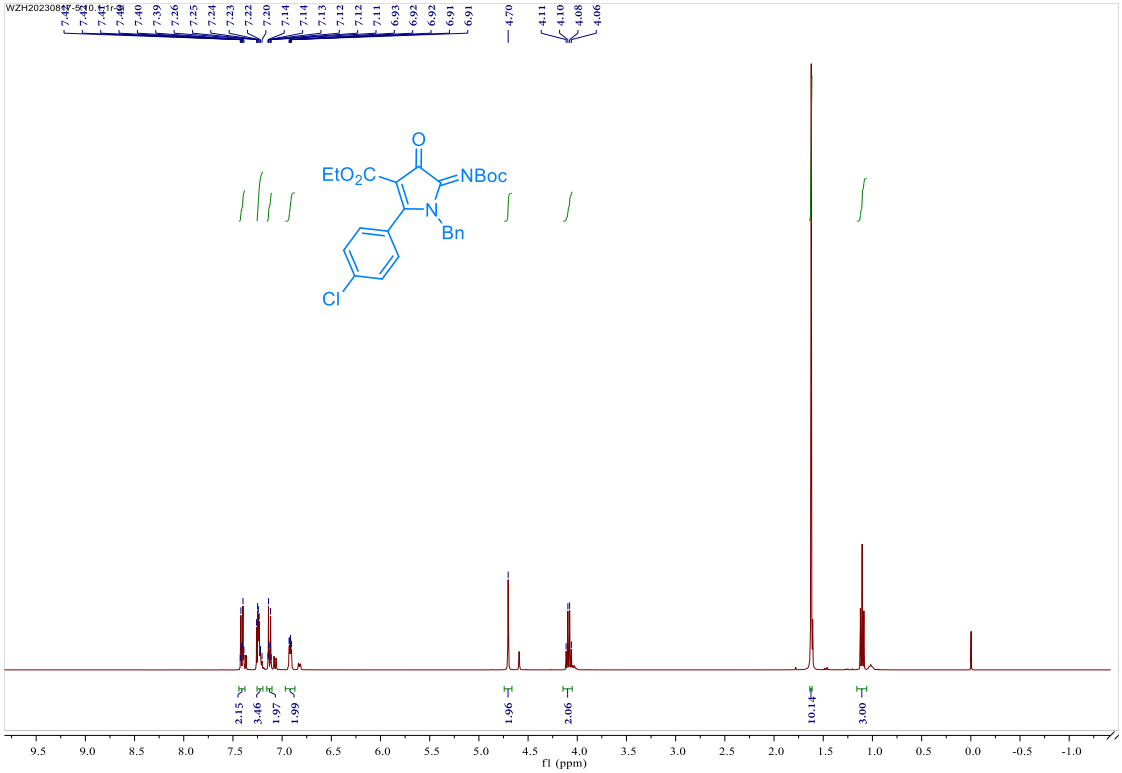
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



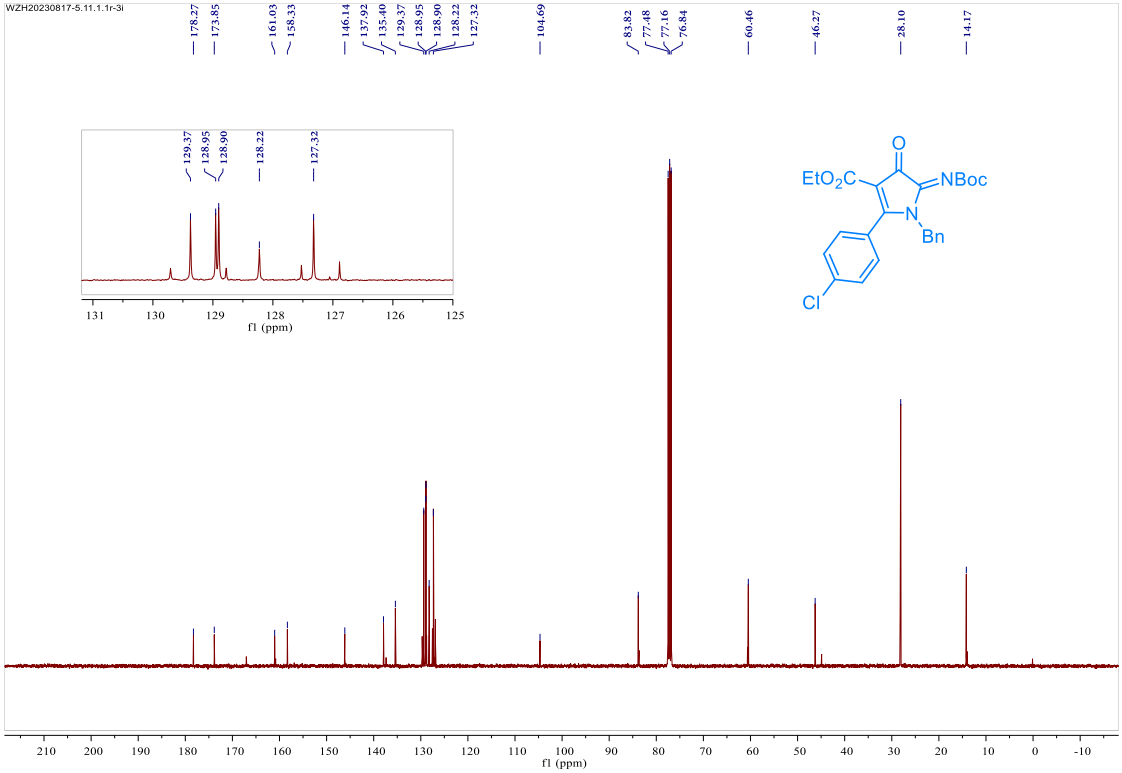
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**



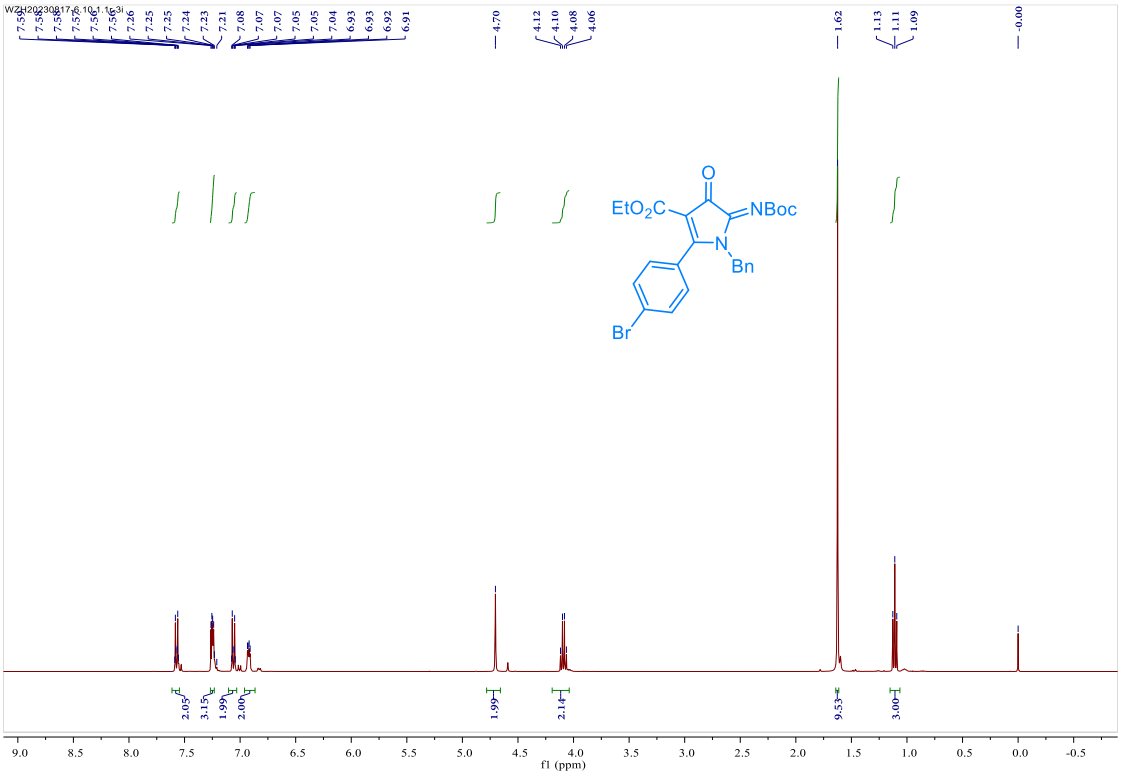
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



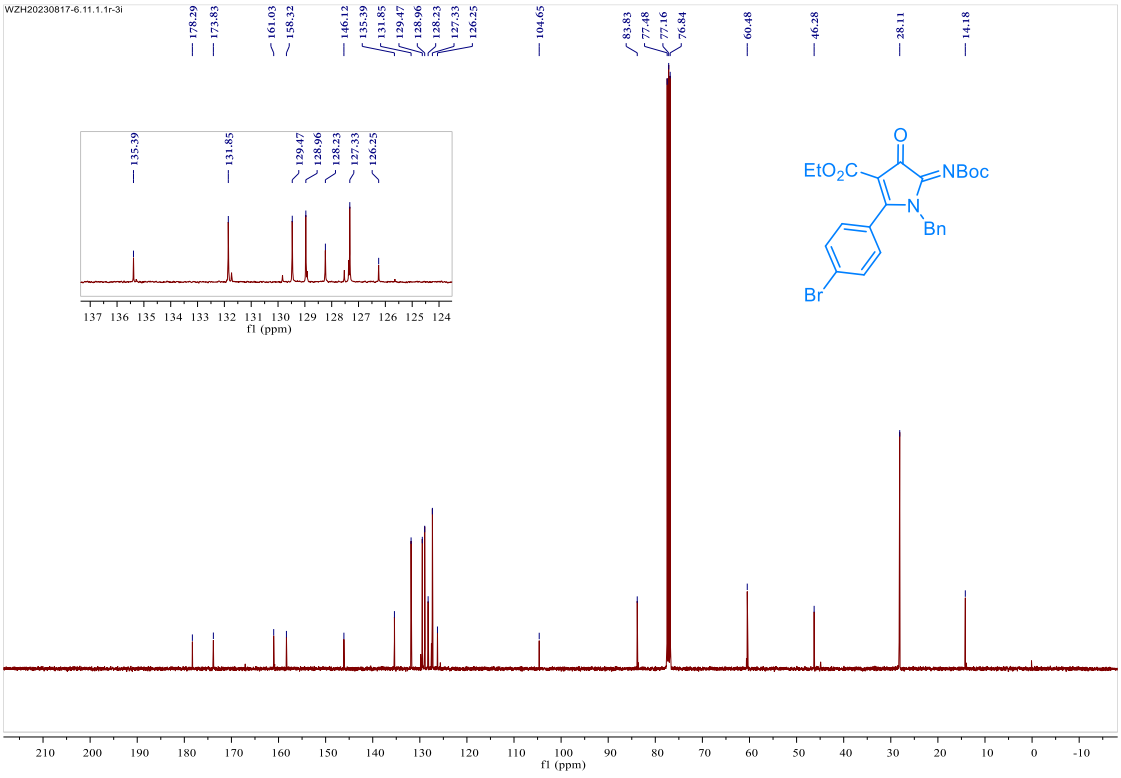
^{13}C NMR (101 MHz, $CDCl_3$) of **1e**



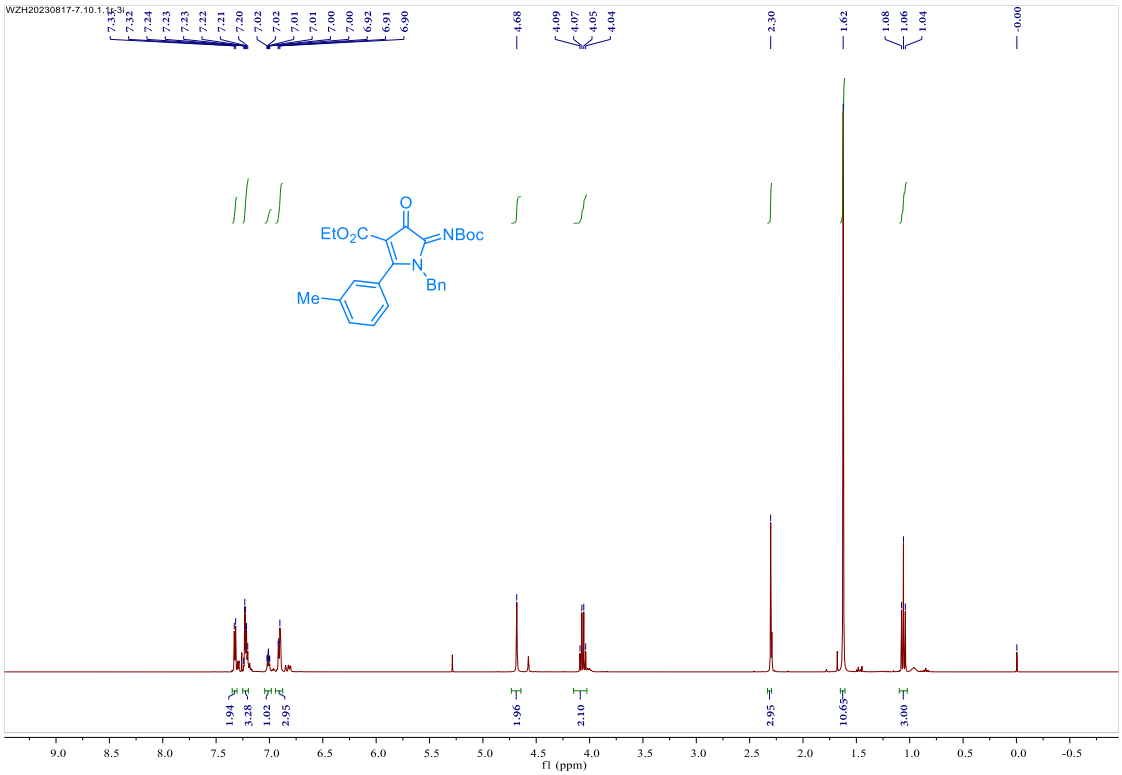
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



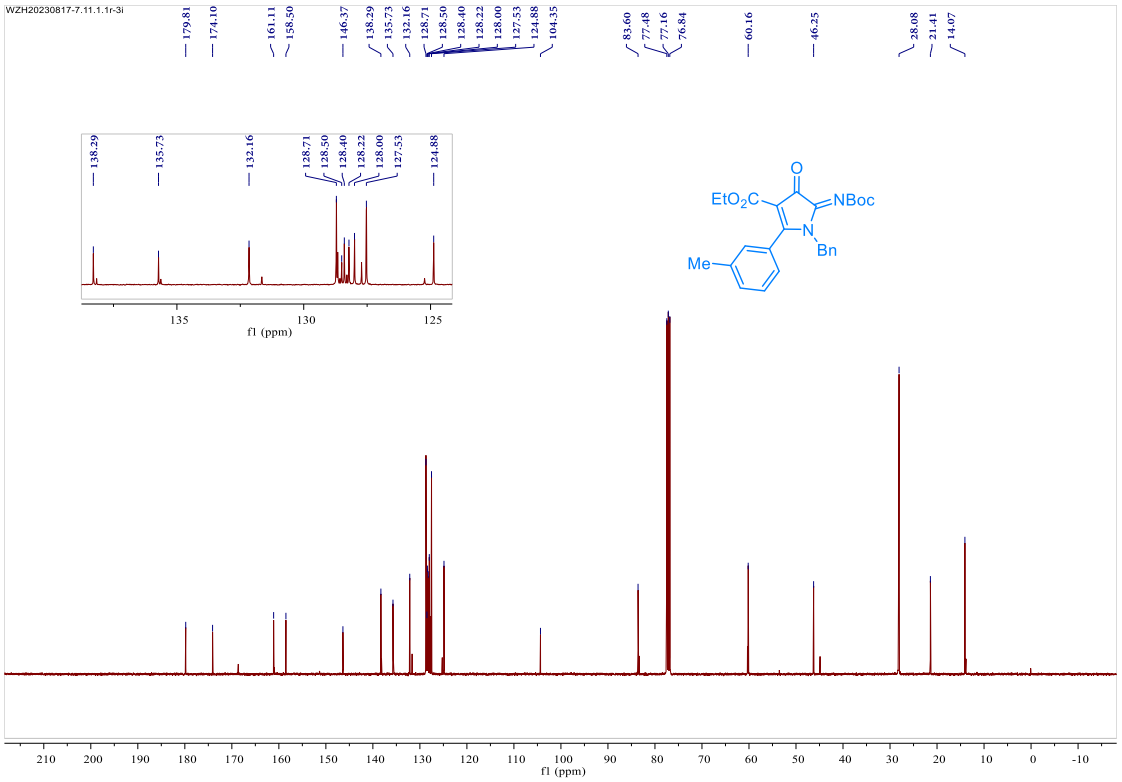
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



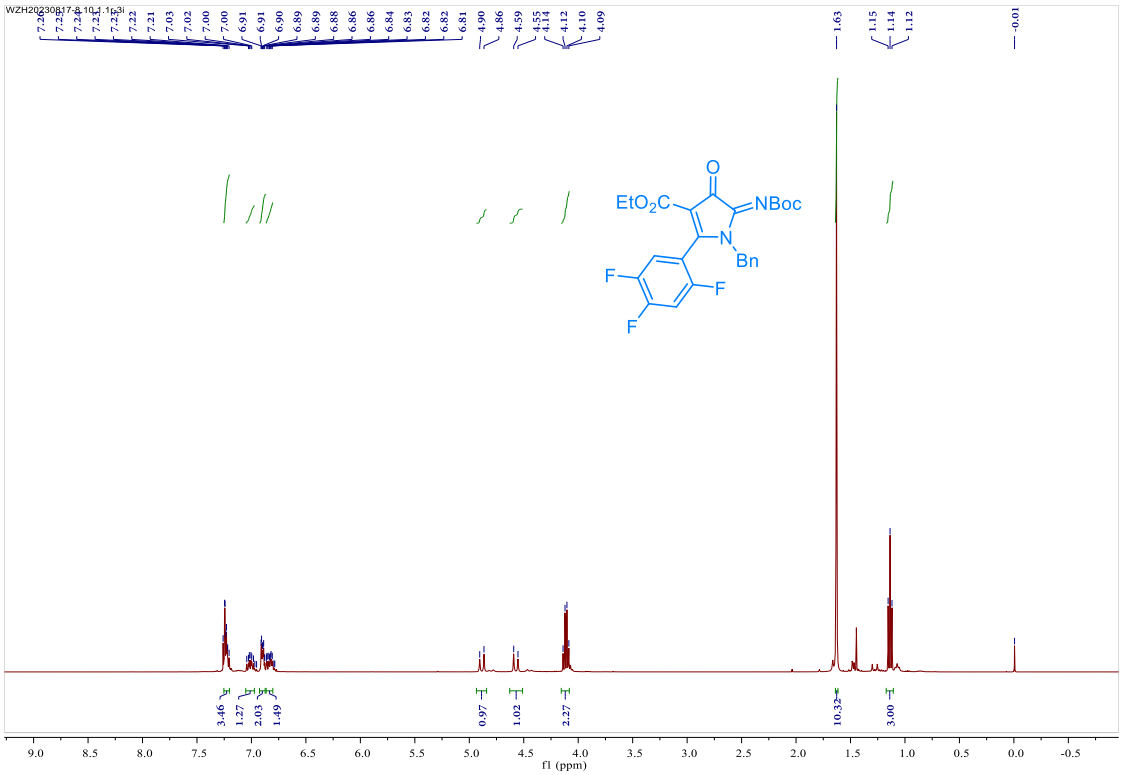
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



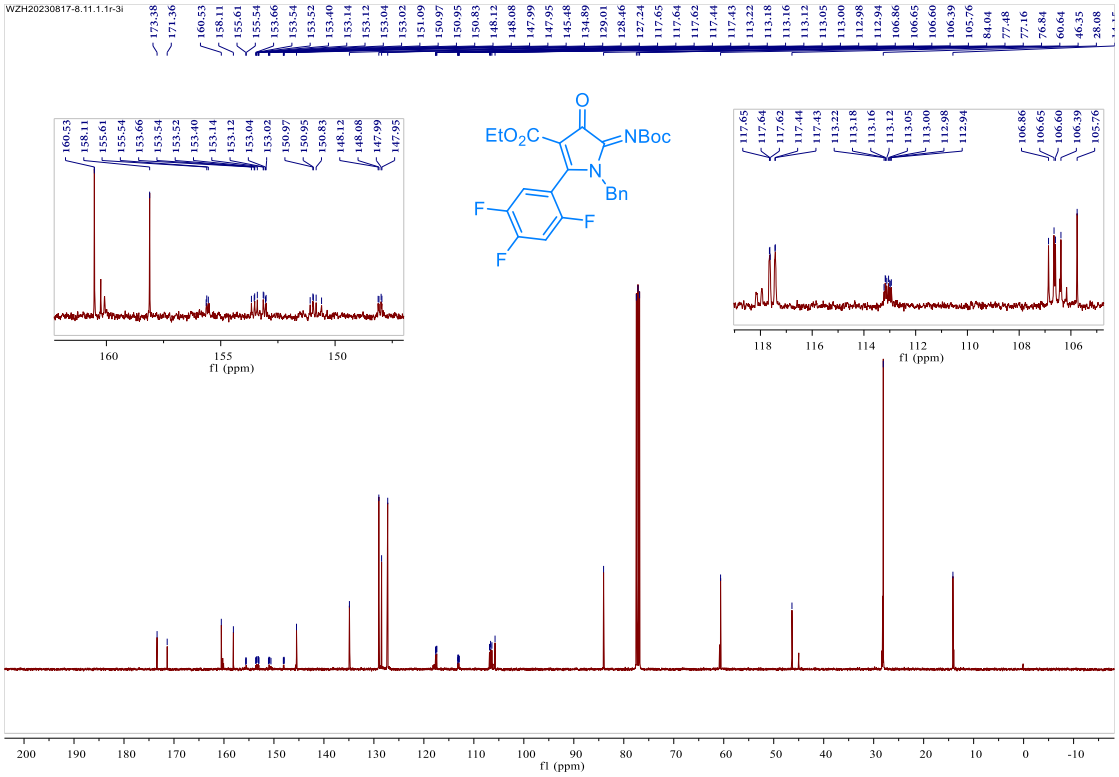
^{13}C NMR (101 MHz, $CDCl_3$) of **1g**



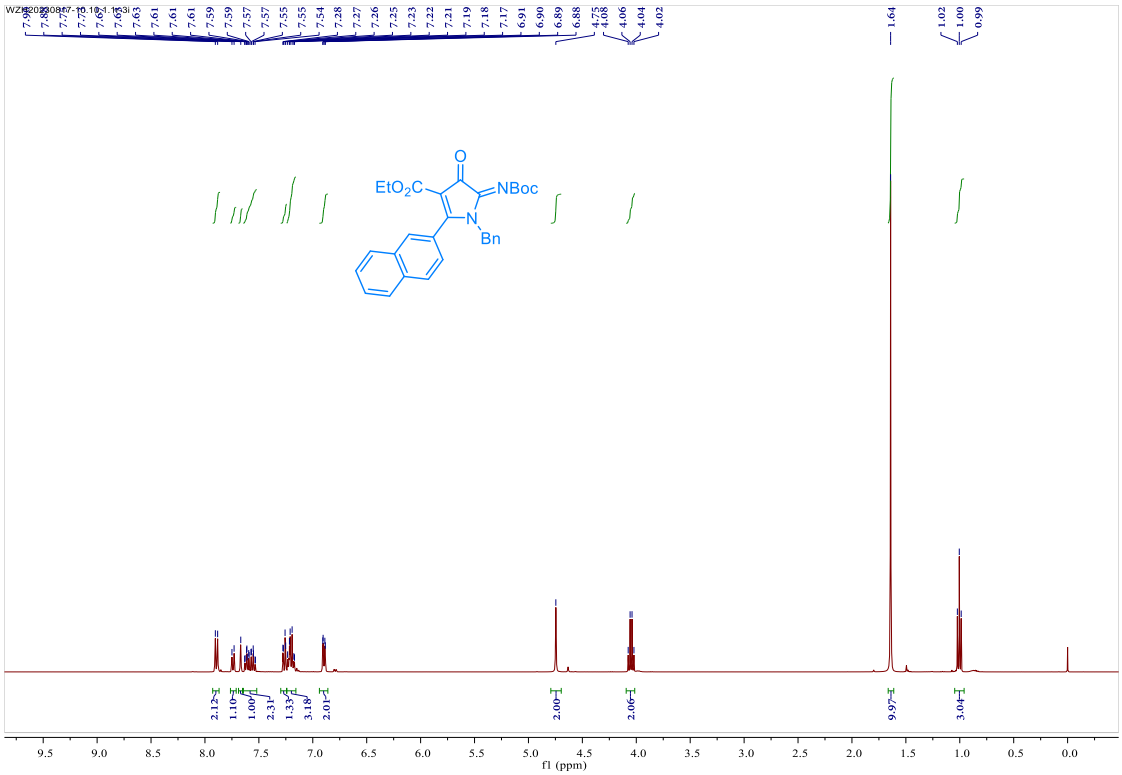
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



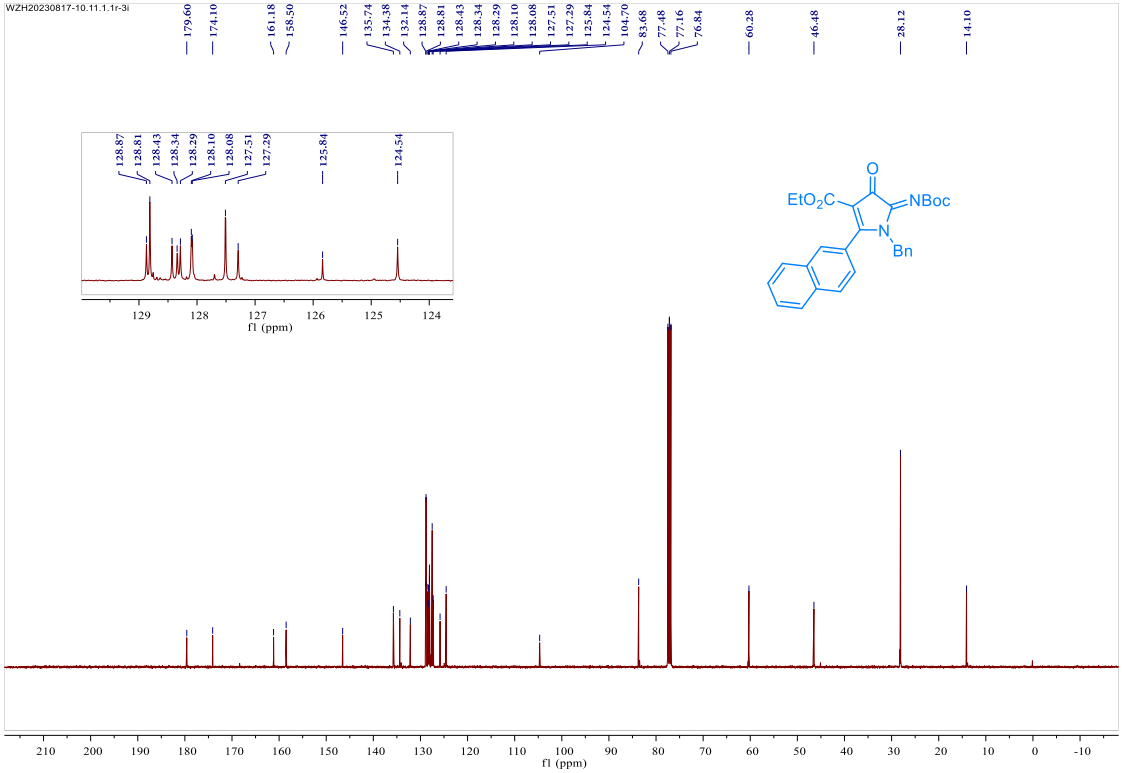
^{13}C NMR (101 MHz, $CDCl_3$) of **1h**



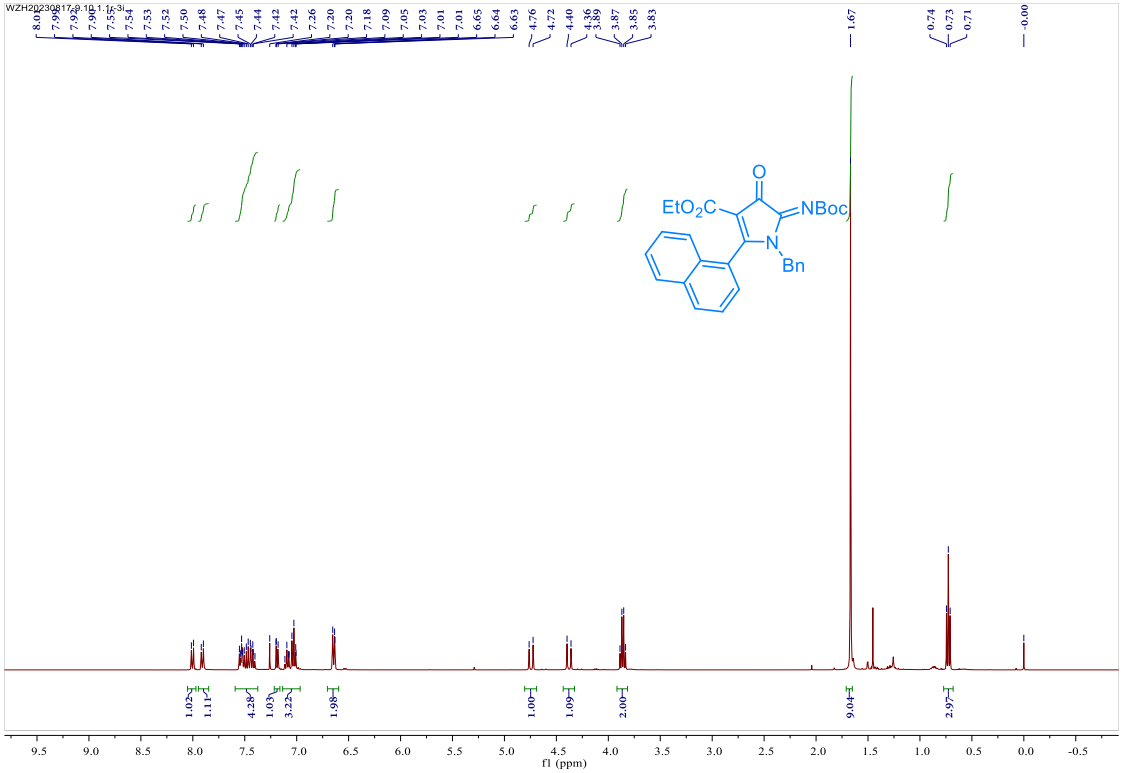
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



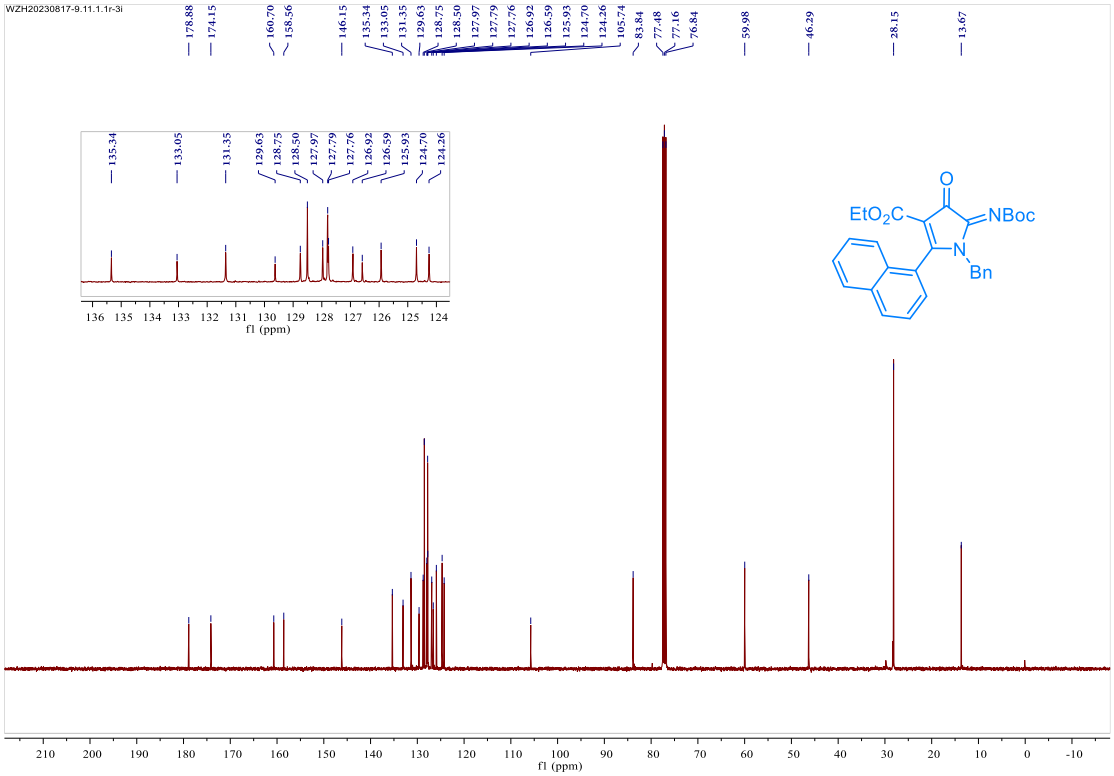
^{13}C NMR (101 MHz, $CDCl_3$) of **1i**



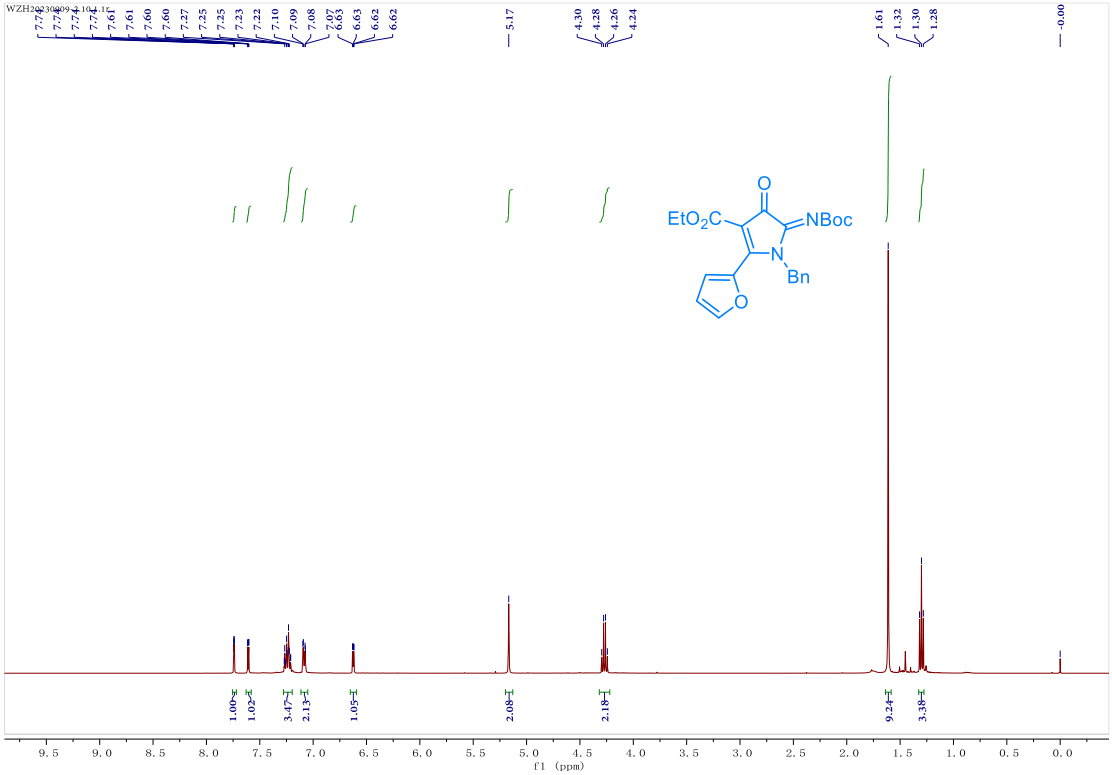
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**



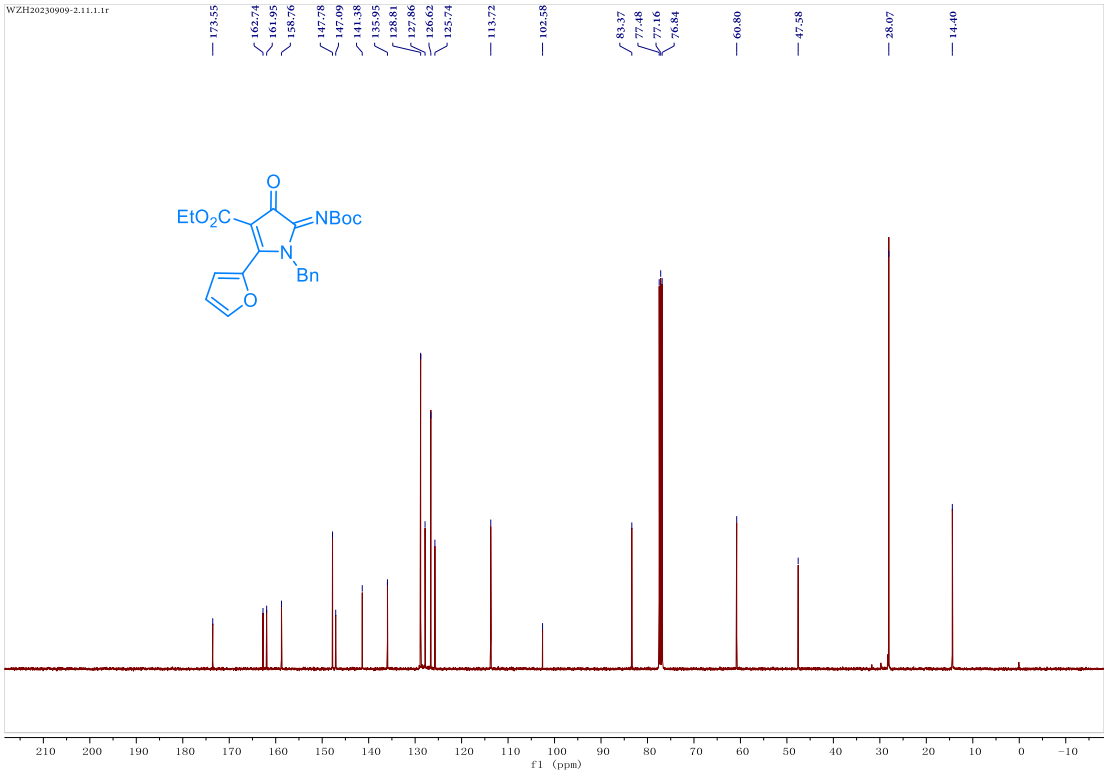
^{13}C NMR (101 MHz, $CDCl_3$) of **1j**



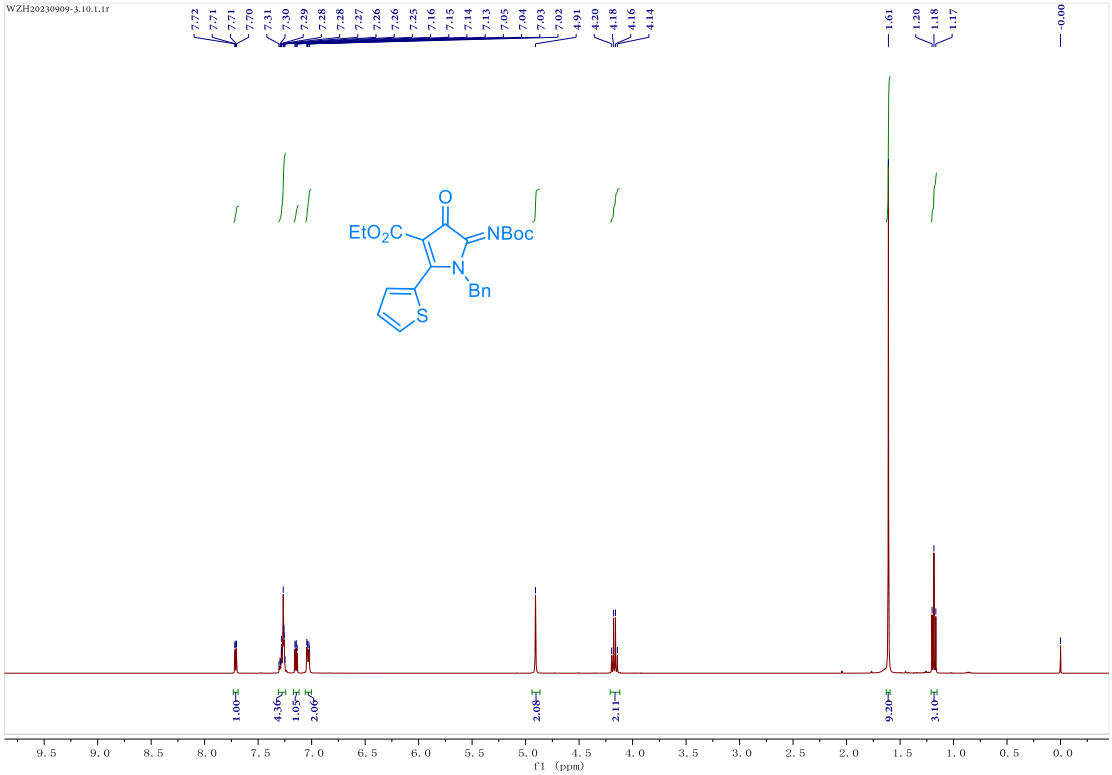
^{1}H NMR (400 MHz, $CDCl_3$) of **1k**



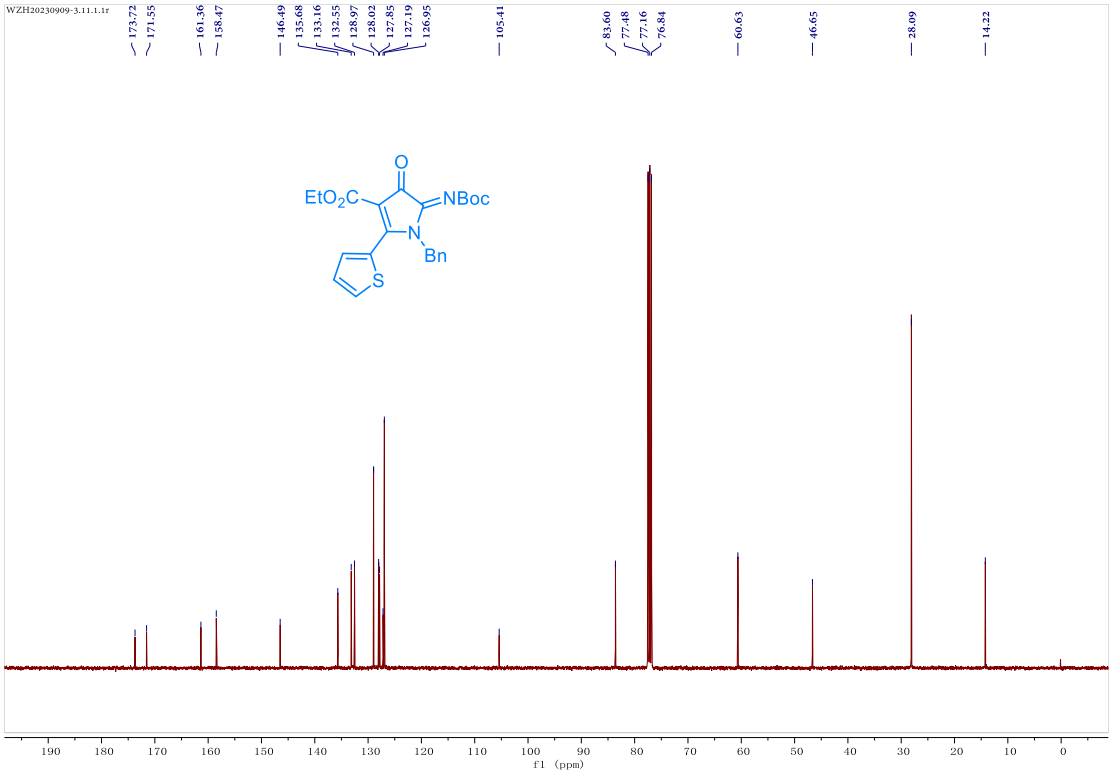
^{13}C NMR (101 MHz, $CDCl_3$) of **1k**



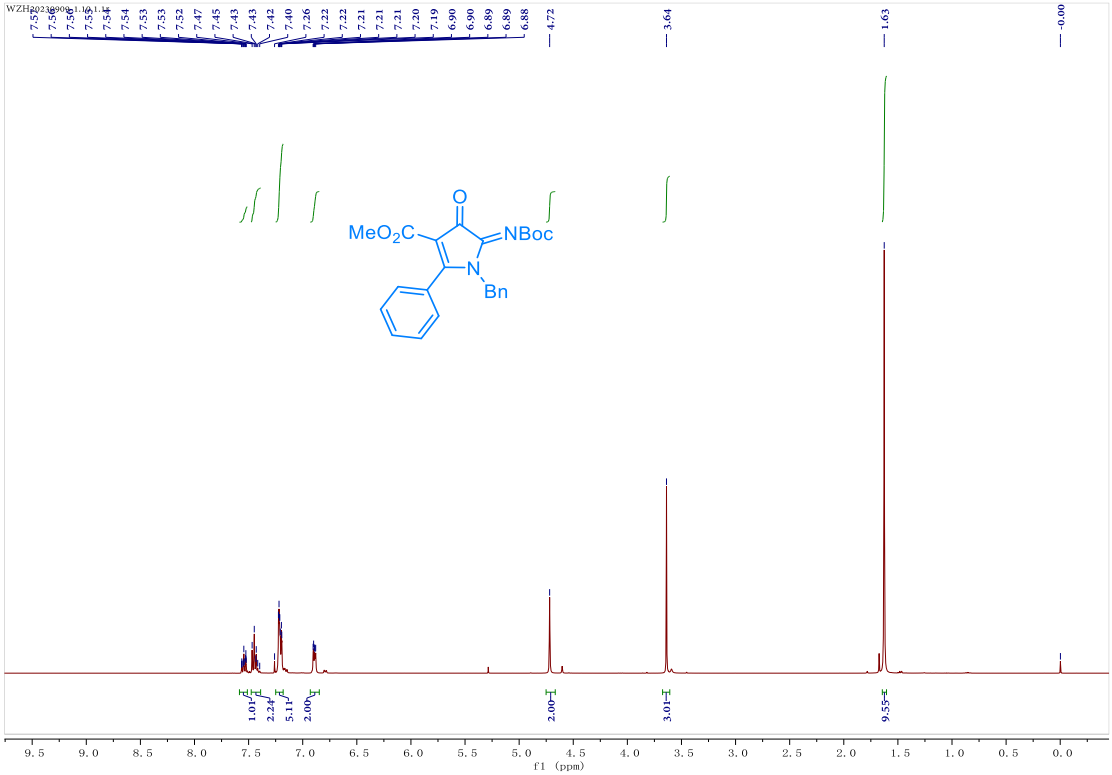
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



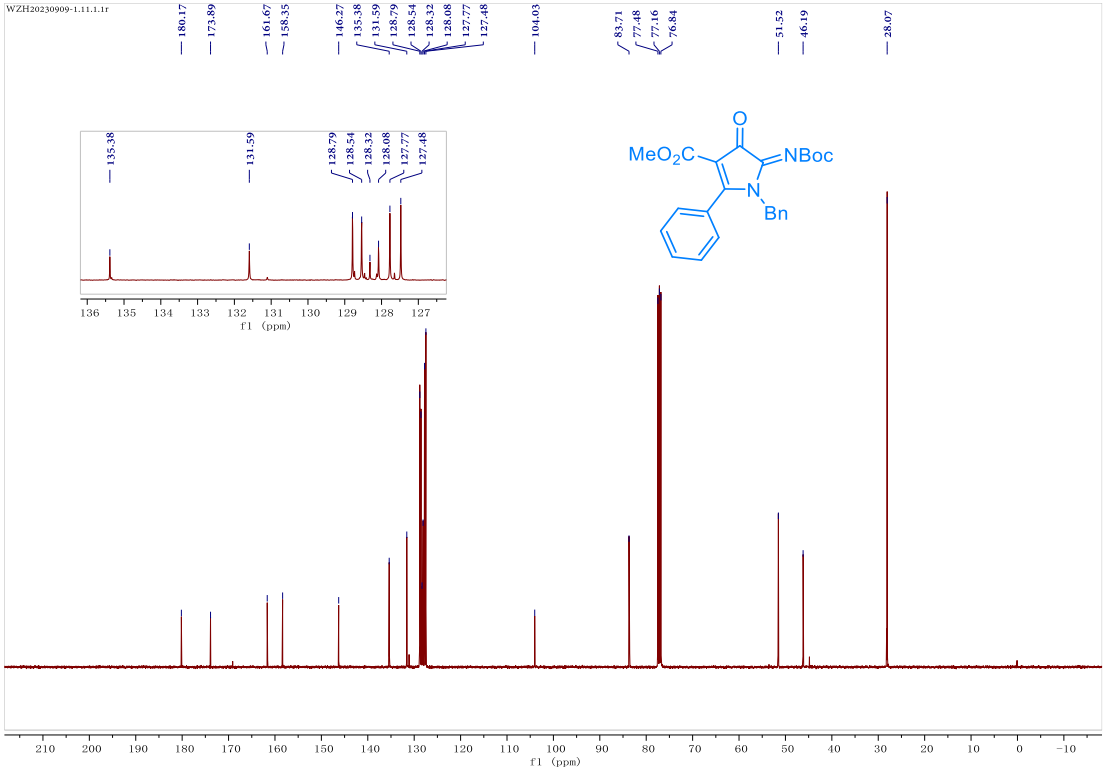
^{13}C NMR (101 MHz, $CDCl_3$) of **1l**



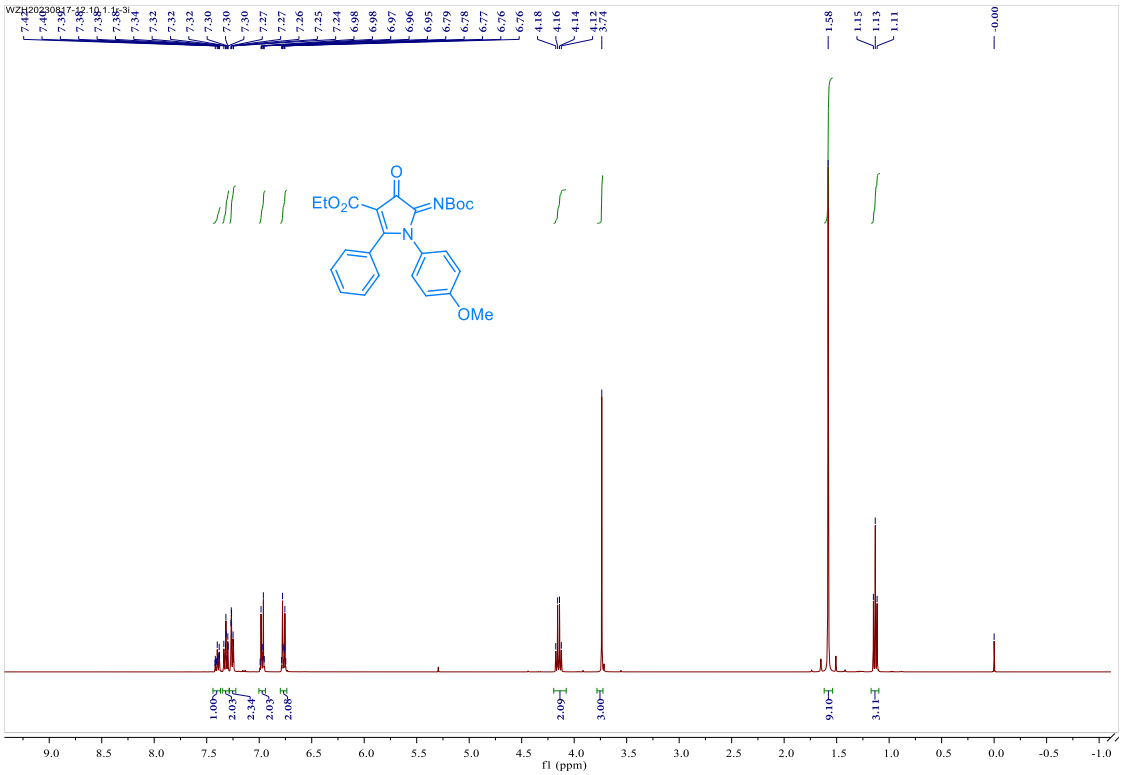
^{1}H NMR (400 MHz, $CDCl_3$) of **1m**



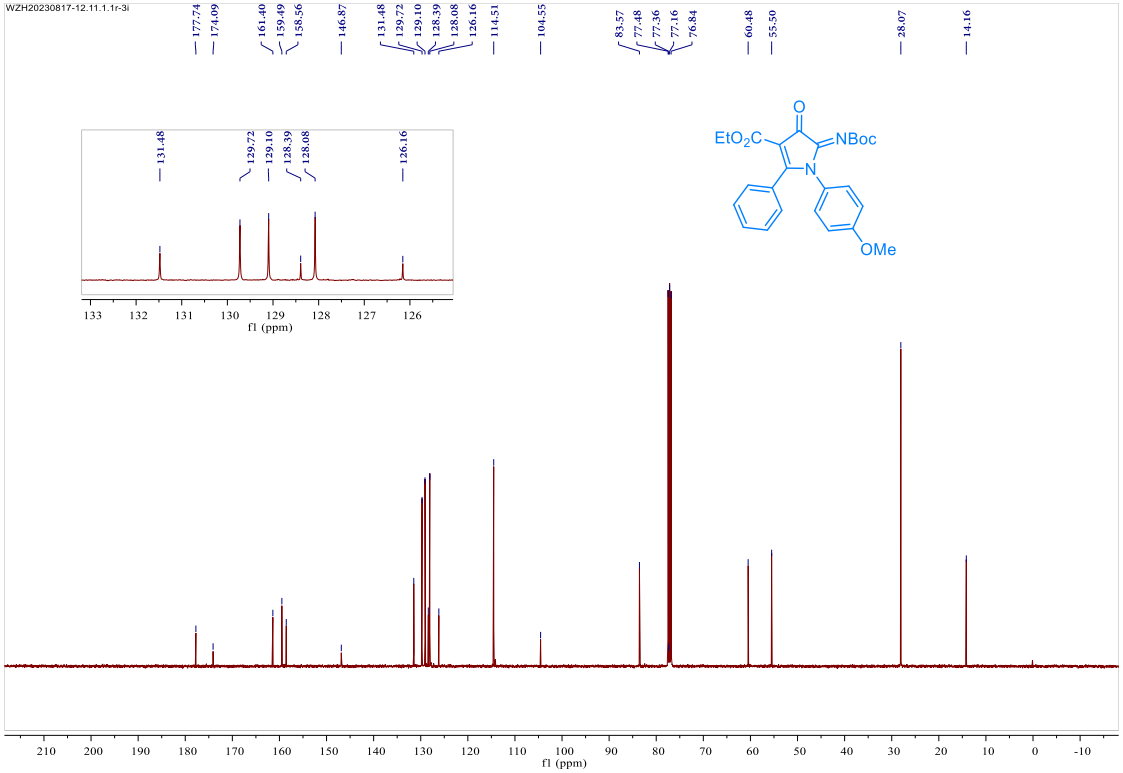
^{13}C NMR (101 MHz, $CDCl_3$) of **1m**



^{1}H NMR (400 MHz, $CDCl_3$) of **1n**

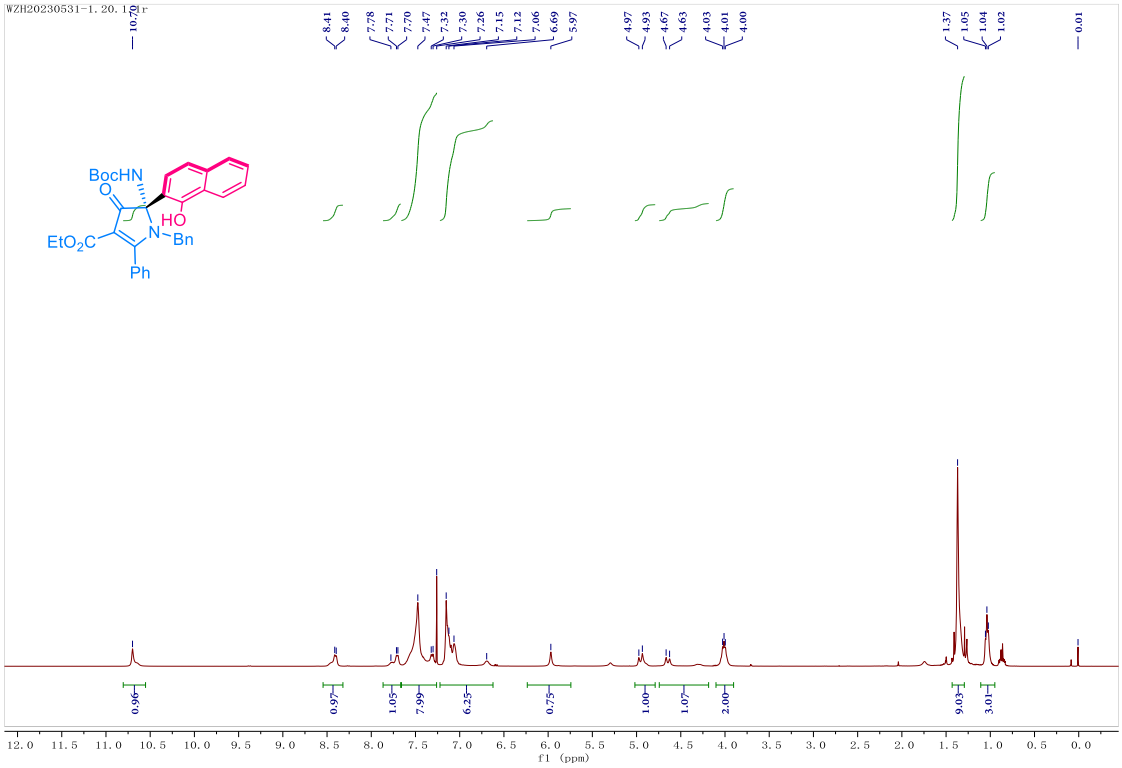


^{13}C NMR (101 MHz, $CDCl_3$) of **1n**

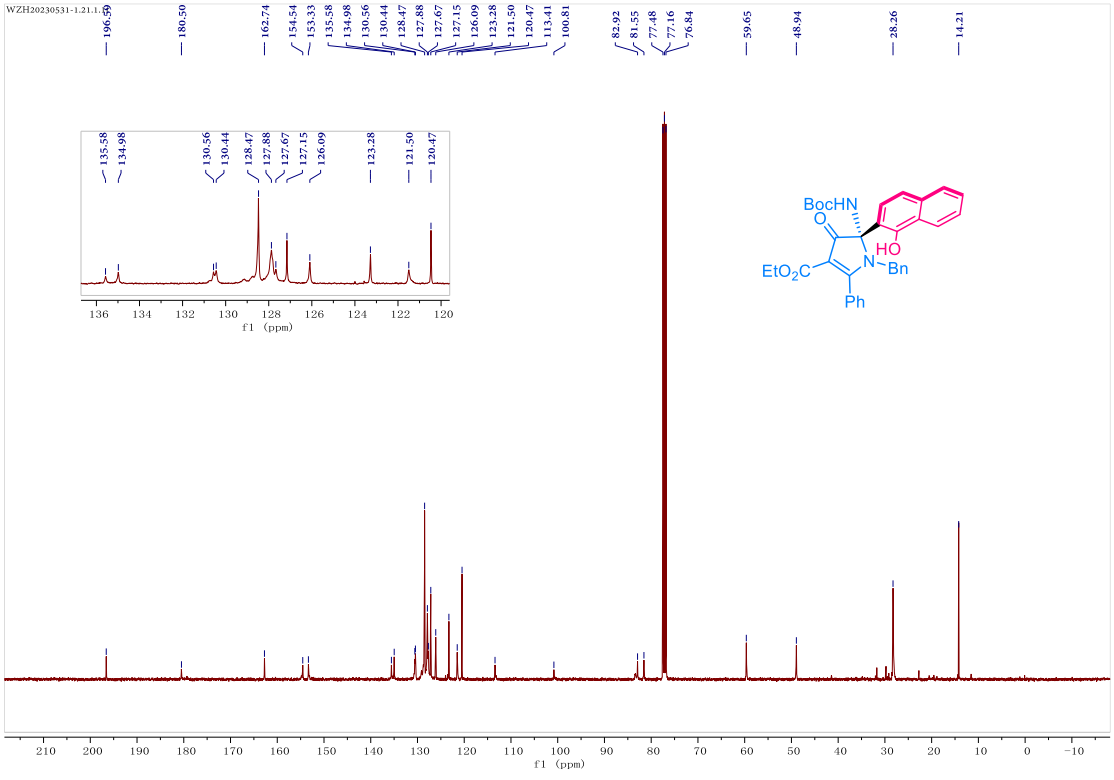


10. ^{1}H, ^{13}C NMR, and HPLC spectra for compounds 3 and 4-6

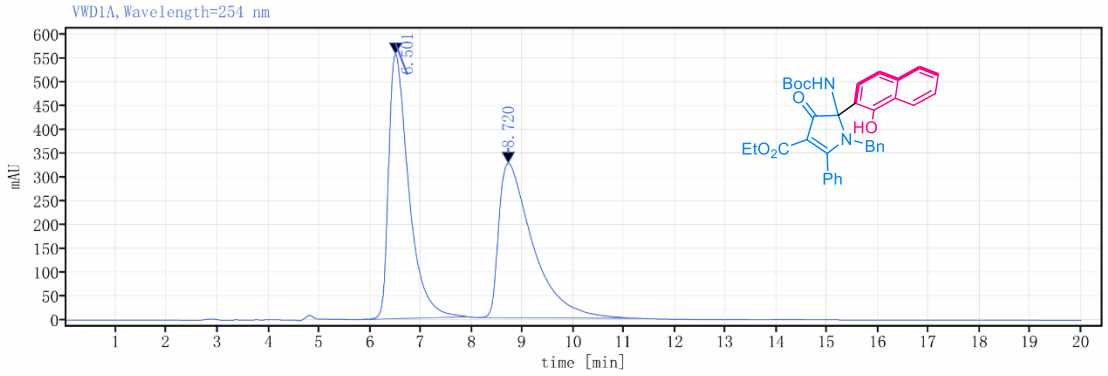
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**

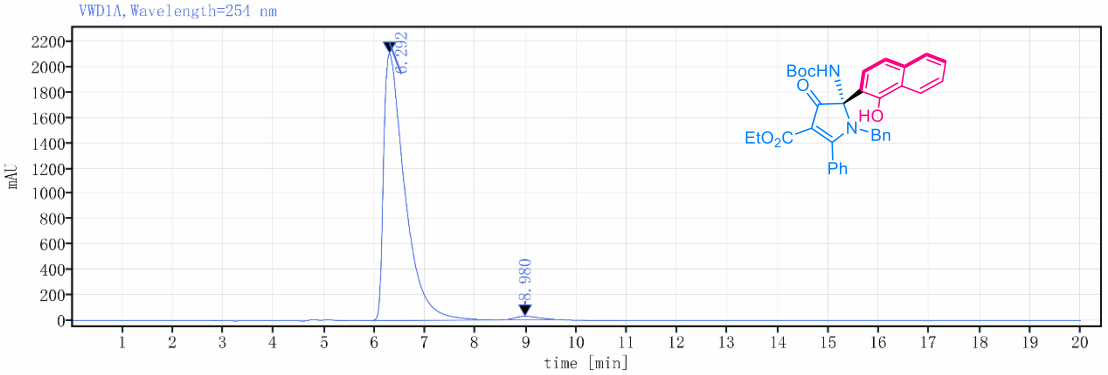


HPLC spectra of **3aa**



Detector VWD1A, Wavelength=254 nm

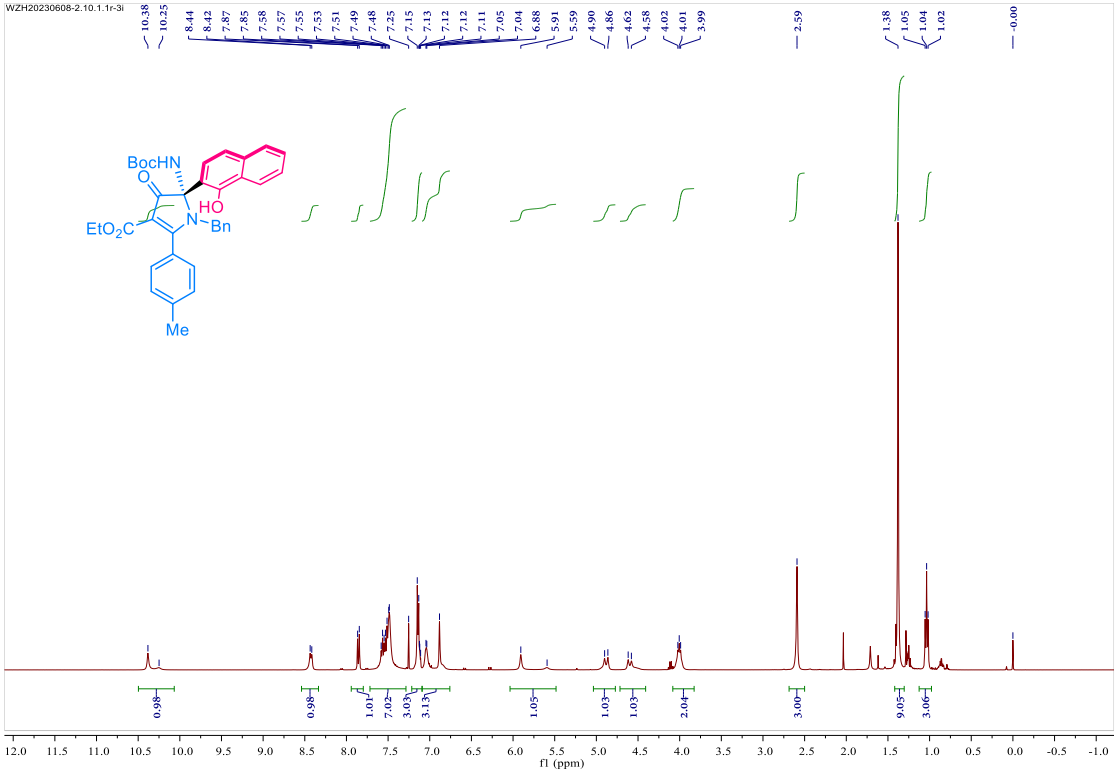
Peak	Ret.Time [min]	Area	Height	Area%
	6.501	15306.82	554.90	50.37
	8.720	15082.18	323.92	49.63
		30388.99		100.00



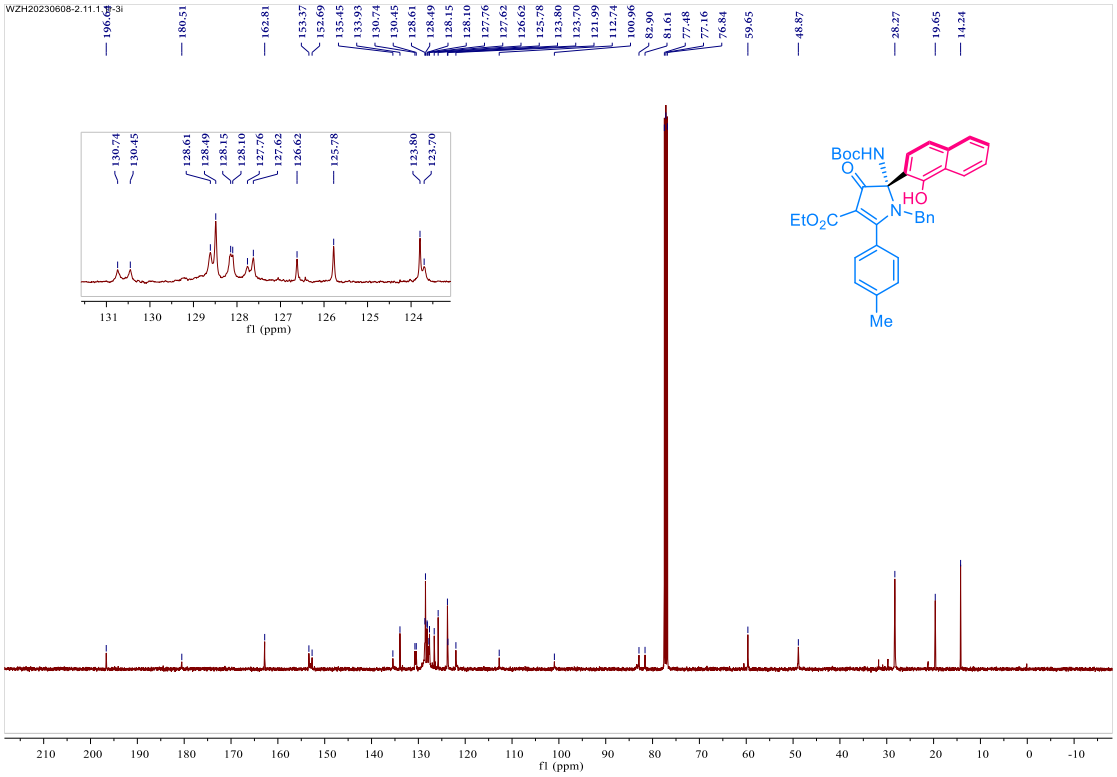
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.292	61281.61	2104.76	98.79
	8.980	749.45	24.65	1.21
		62031.06		100.00

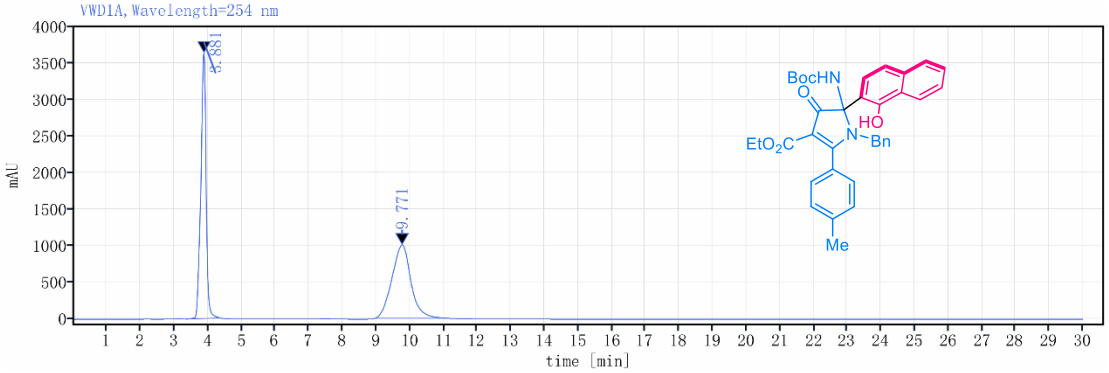
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**

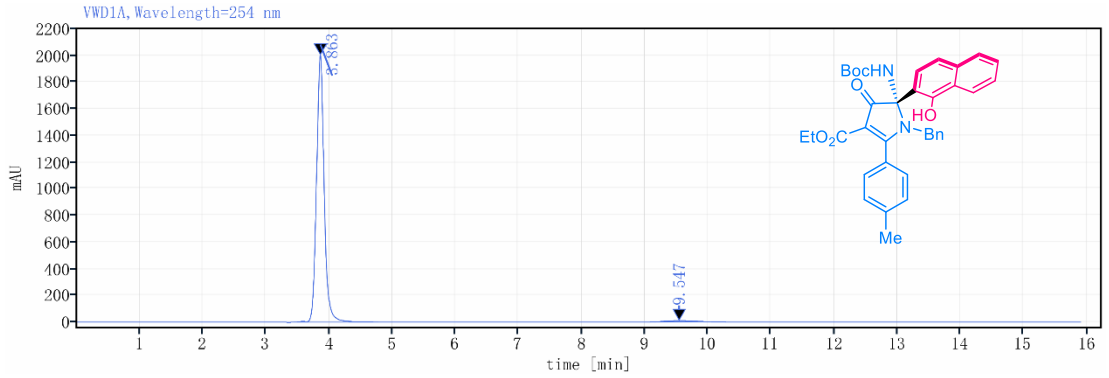


HPLC spectra of **3ba**



Detector VWD1A, Wavelength=254 nm

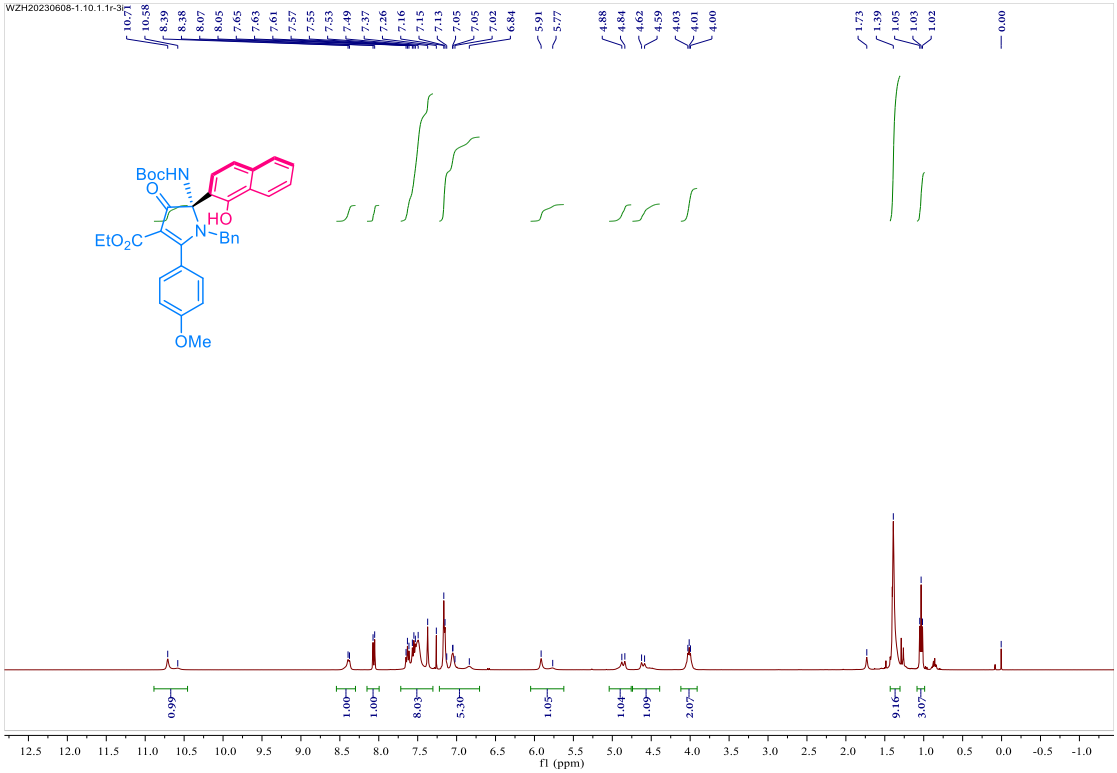
Peak	Ret.Time [min]	Area	Height	Area%
	3.881	40055.50	3641.43	50.40
	9.771	39424.26	1006.10	49.60
		79479.76		100.00



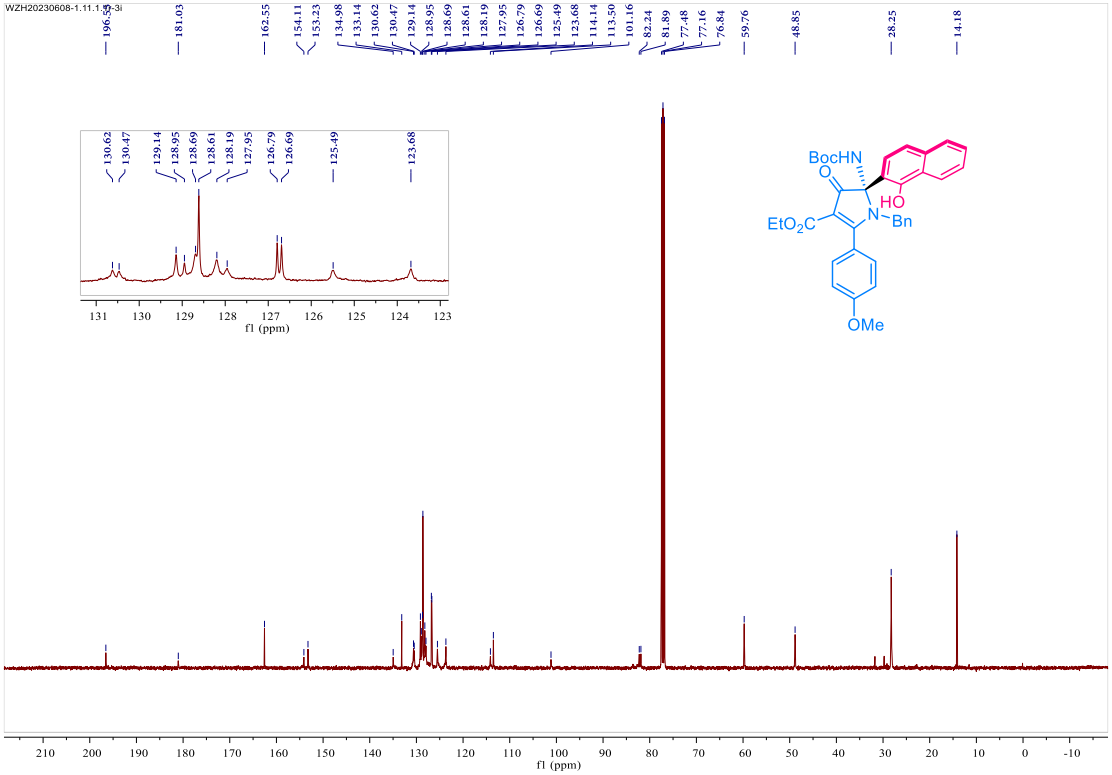
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.863	16901.72	2002.42	98.45
	9.547	266.84	8.85	1.55
		17168.56		100.00

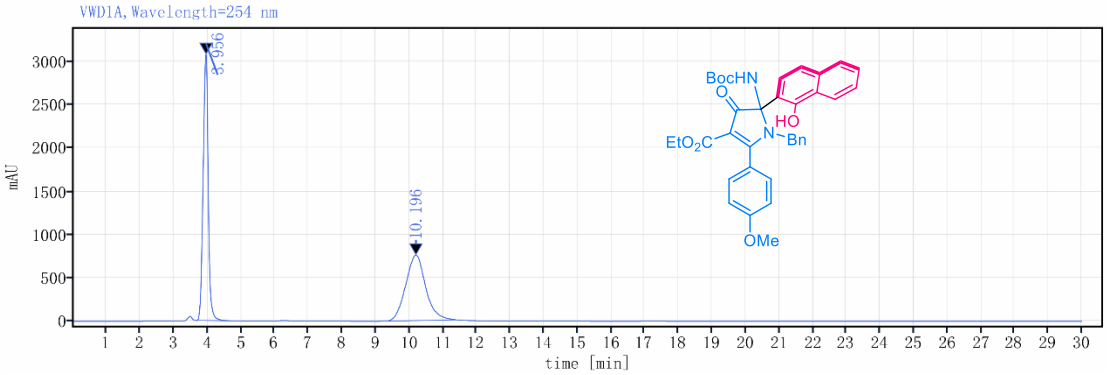
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**

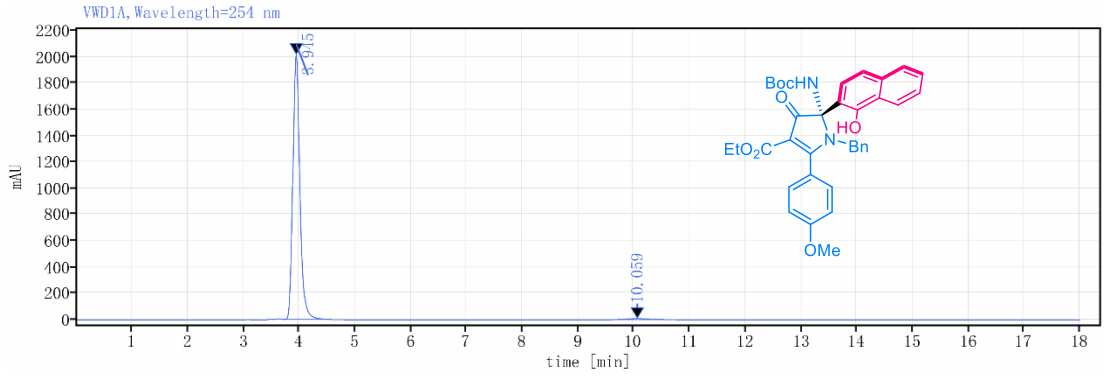


HPLC spectra of **3ca**



Detector VWD1A, Wavelength=254 nm

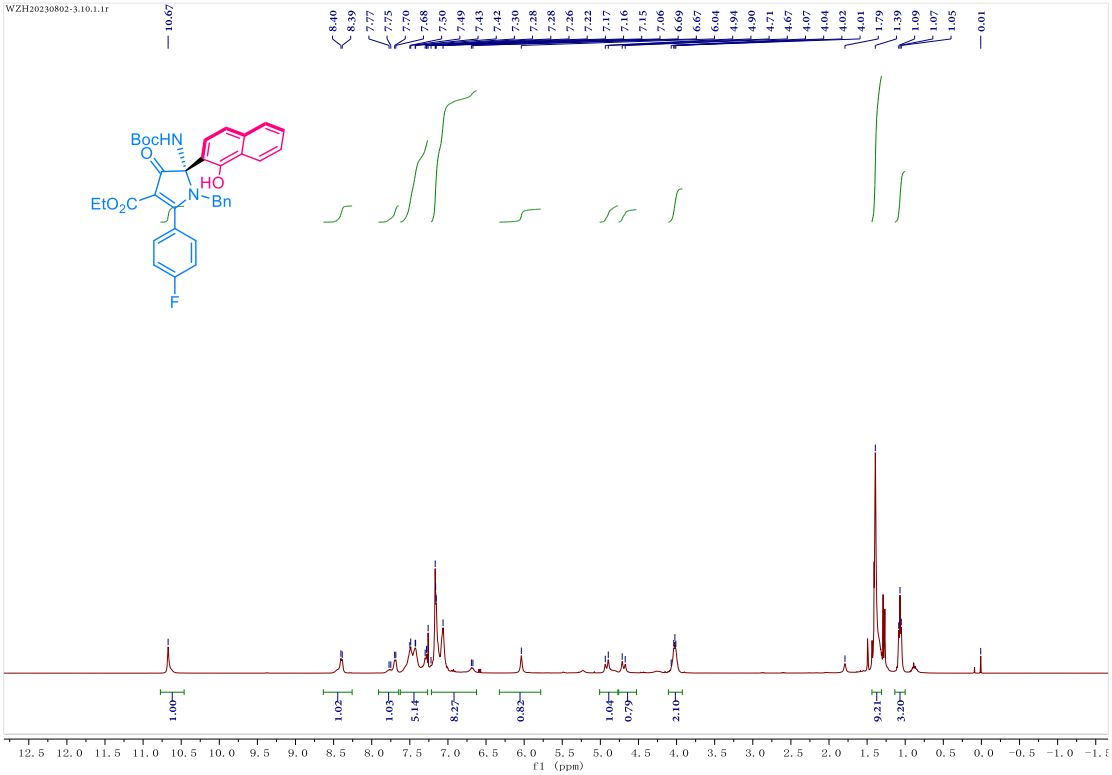
Peak	Ret.Time [min]	Area	Height	Area%
	3.956	32223.01	3081.76	50.76
	10.196	31254.47	758.46	49.24
		63477.49		100.00



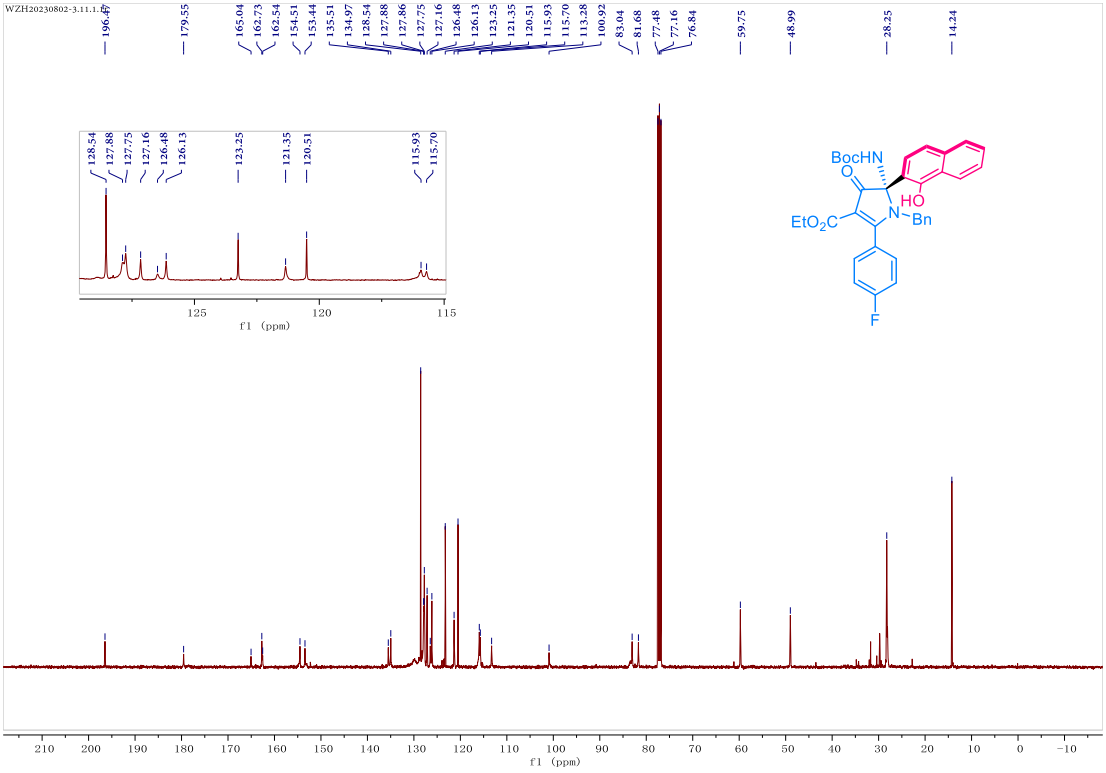
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.945	17627.98	2011.23	98.59
	10.059	251.60	7.43	1.41
		17879.59		100.00

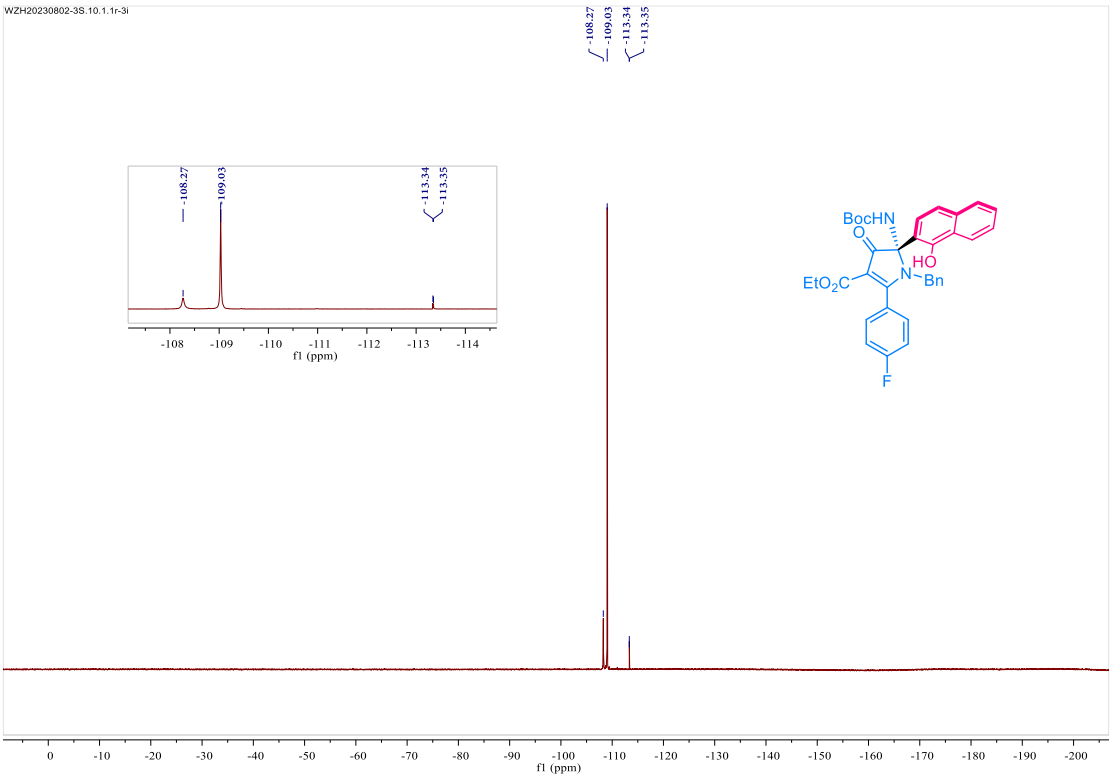
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



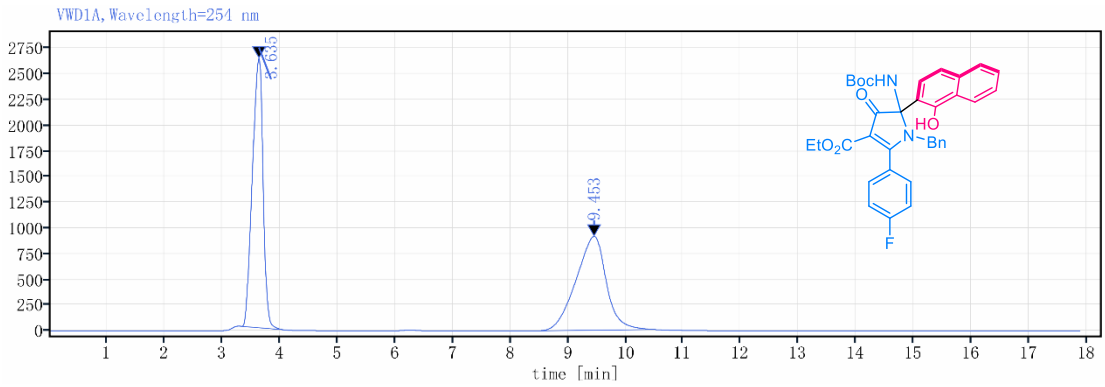
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



^{19}F NMR (377 MHz, $CDCl_3$) of **3da**

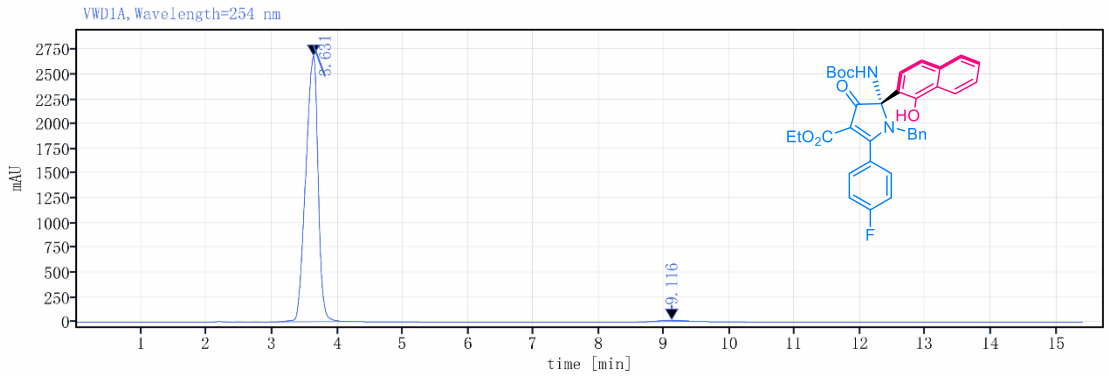


HPLC spectra of **3da**



Detector VWD1A, Wavelength=254 nm

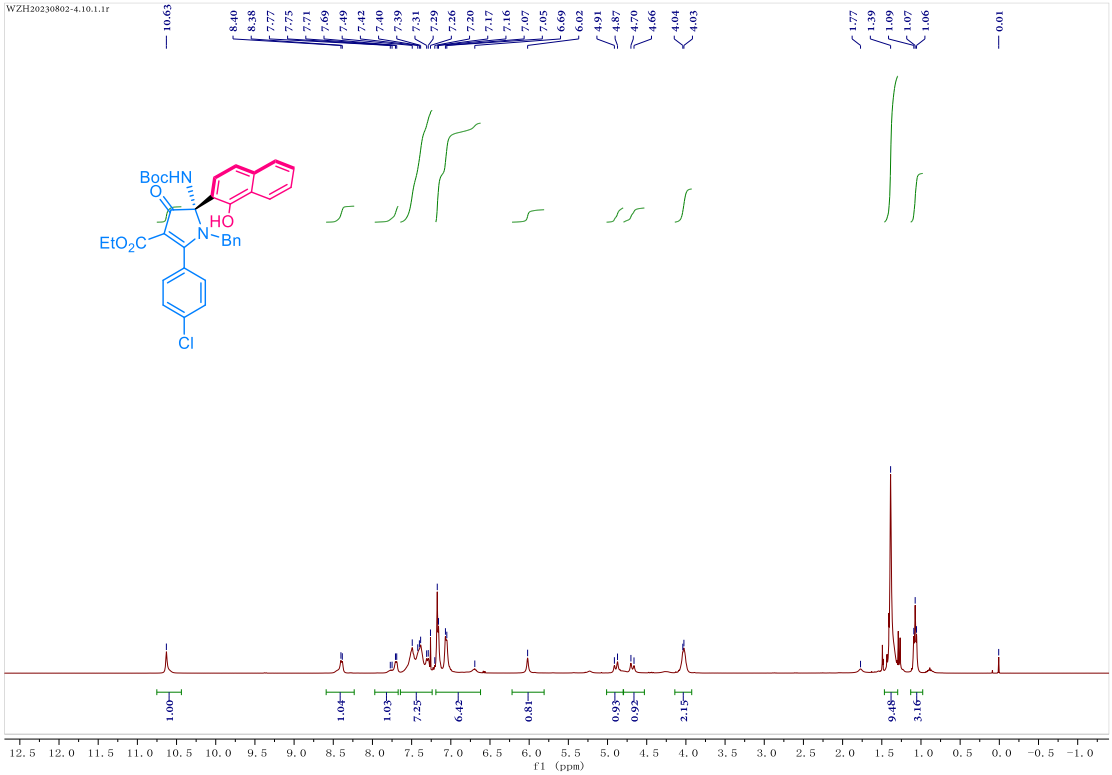
Peak	Ret.Time [min]	Area	Height	Area%
	3.635	33826.21	2624.06	50.32
	9.453	33397.08	914.22	49.68
		67223.29		100.00



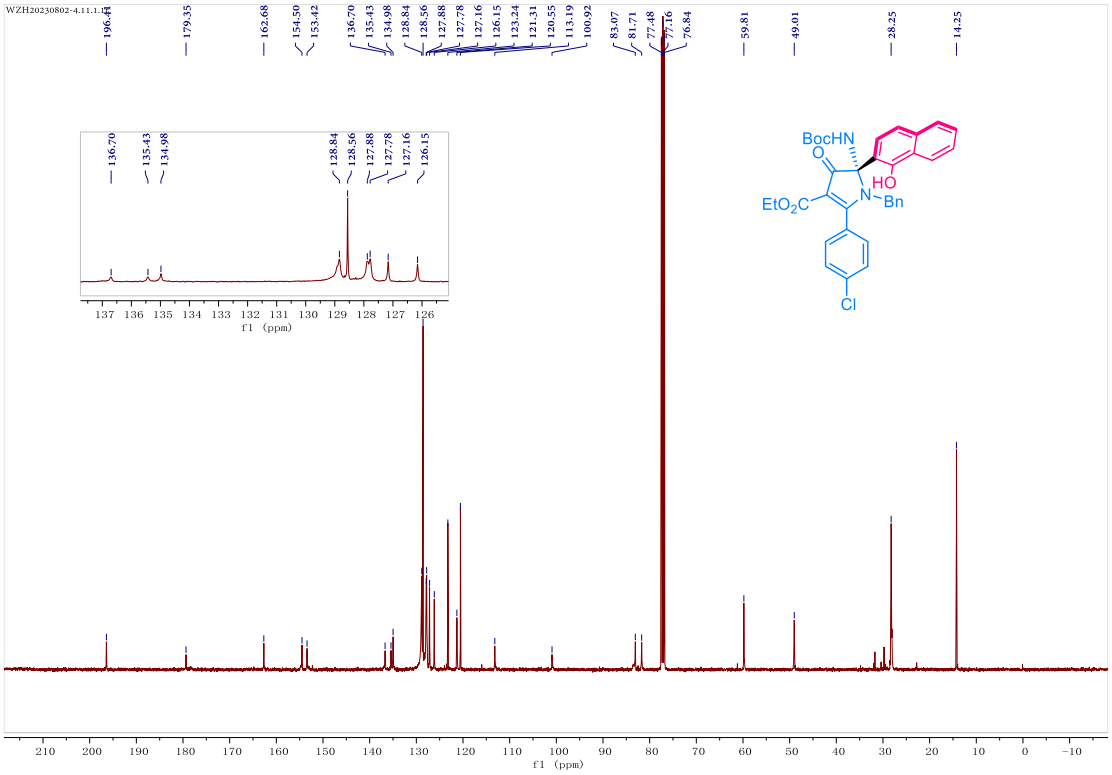
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.631	35218.32	2685.07	98.82
	9.116	419.75	14.79	1.18
		35638.07		100.00

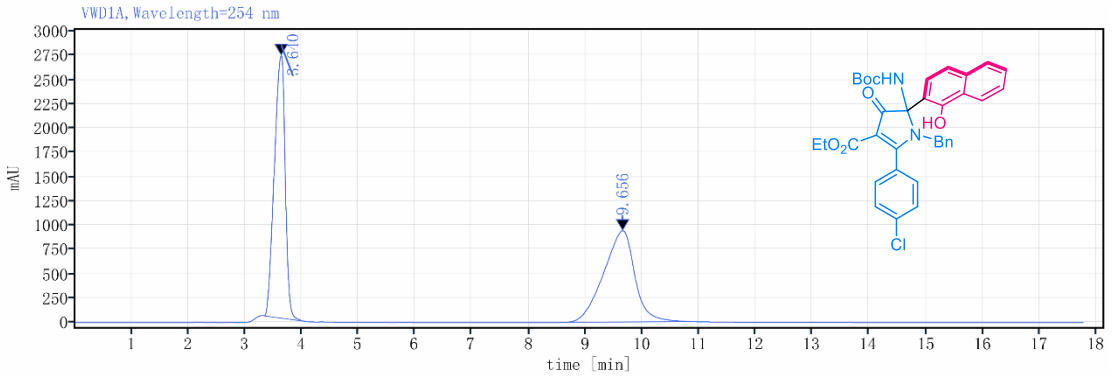
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**

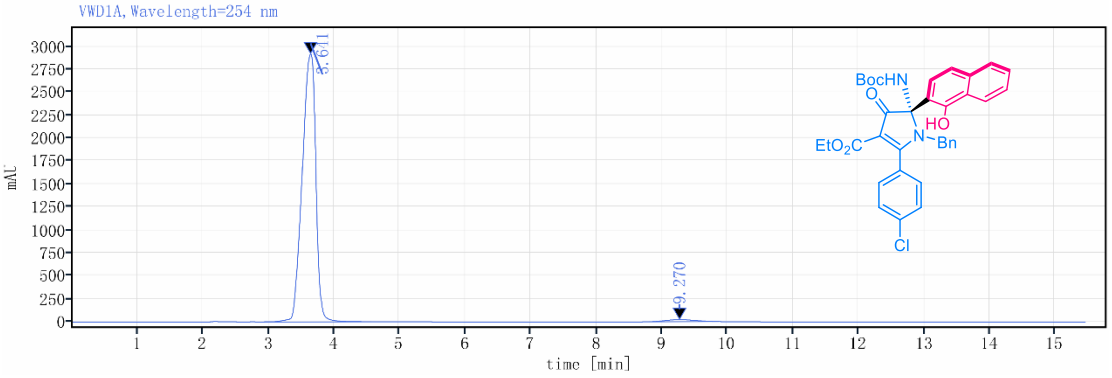


HPLC spectra of **3ea**



Detector VWD1A, Wavelength=254 nm

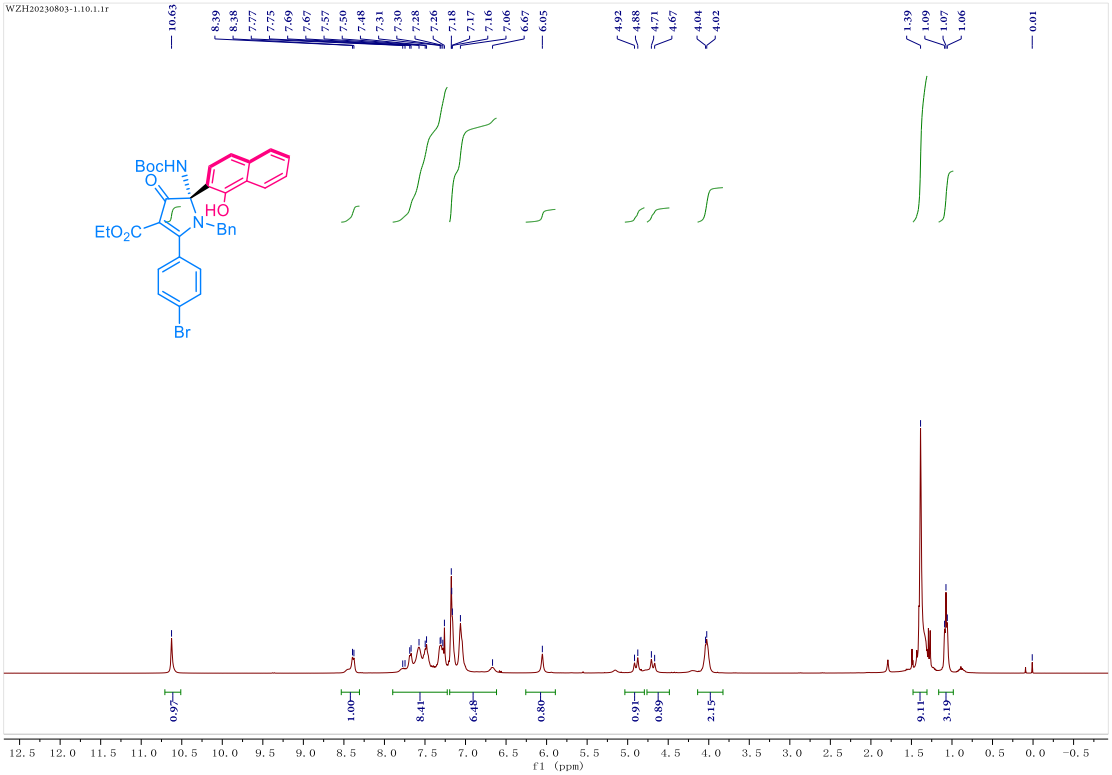
Peak	Ret.Time [min]	Area	Height	Area%
	3.640	36024.34	2704.67	50.04
	9.656	35967.64	941.03	49.96
		71991.97		100.00



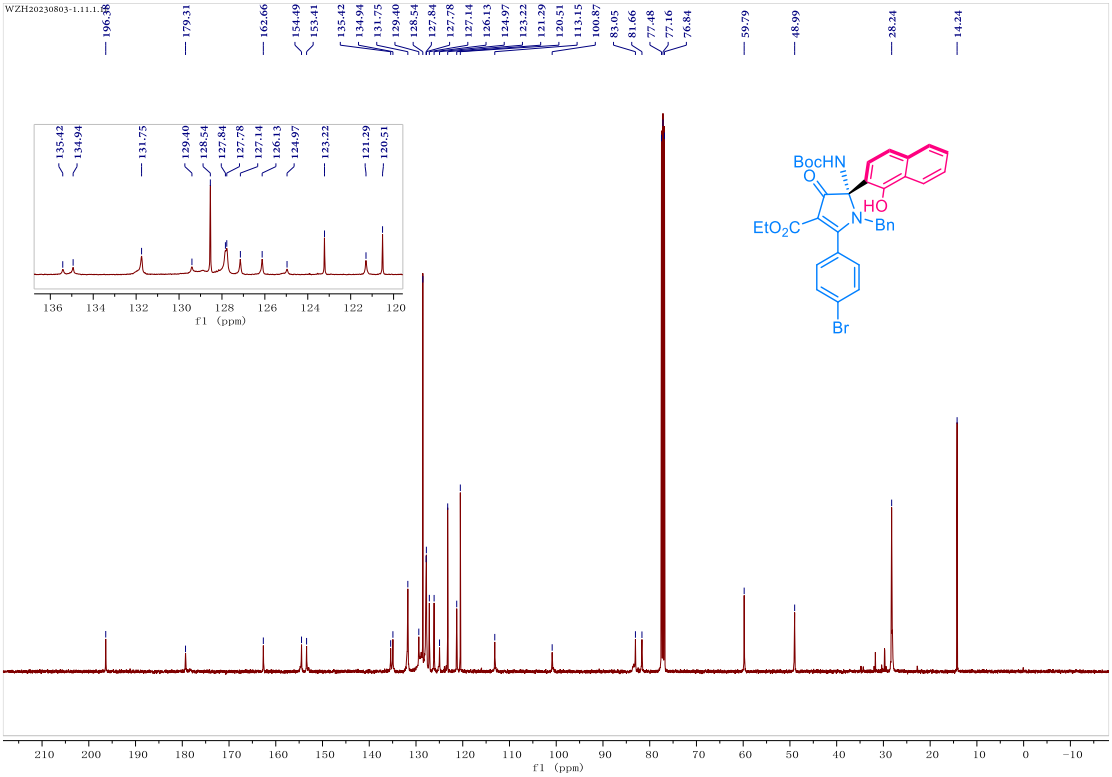
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.641	42066.33	2916.89	98.33
	9.270	713.21	22.44	1.67
		42779.54		100.00

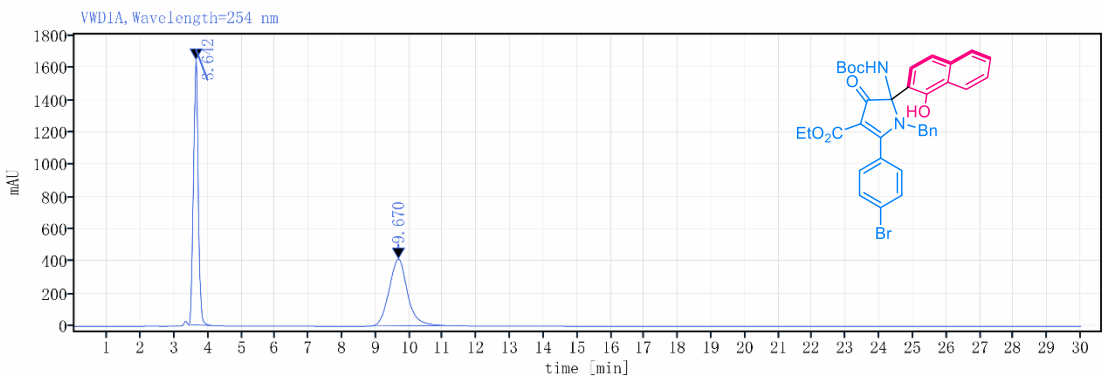
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**

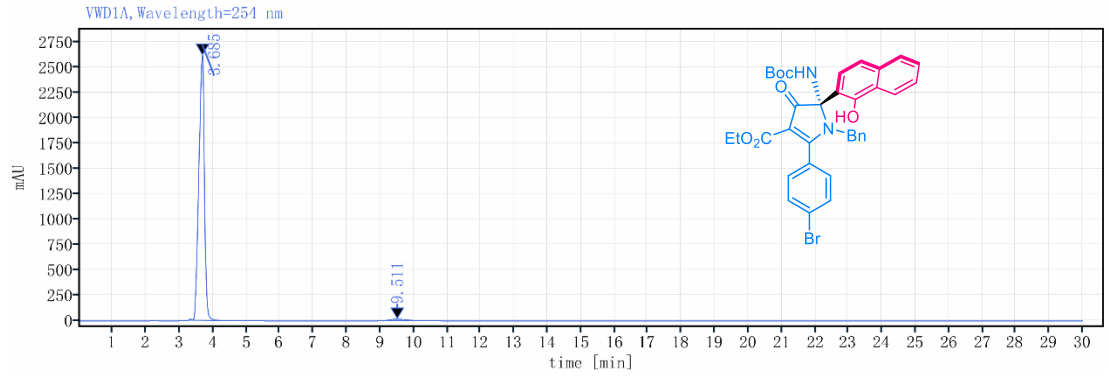


HPLC spectra of **3fa**



Detector VWD1A, Wavelength=254 nm

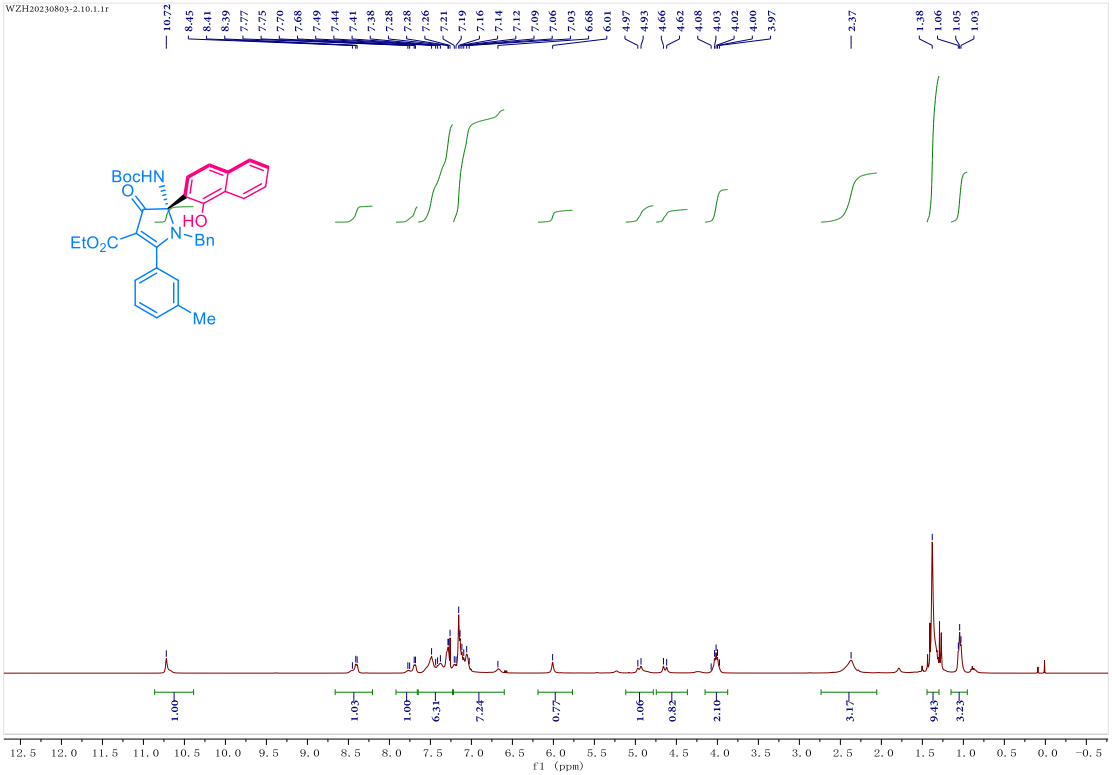
Peak	Ret.Time [min]	Area	Height	Area%
	3.642	16179.49	1639.90	50.79
	9.670	15673.39	413.93	49.21
		31852.88		100.00



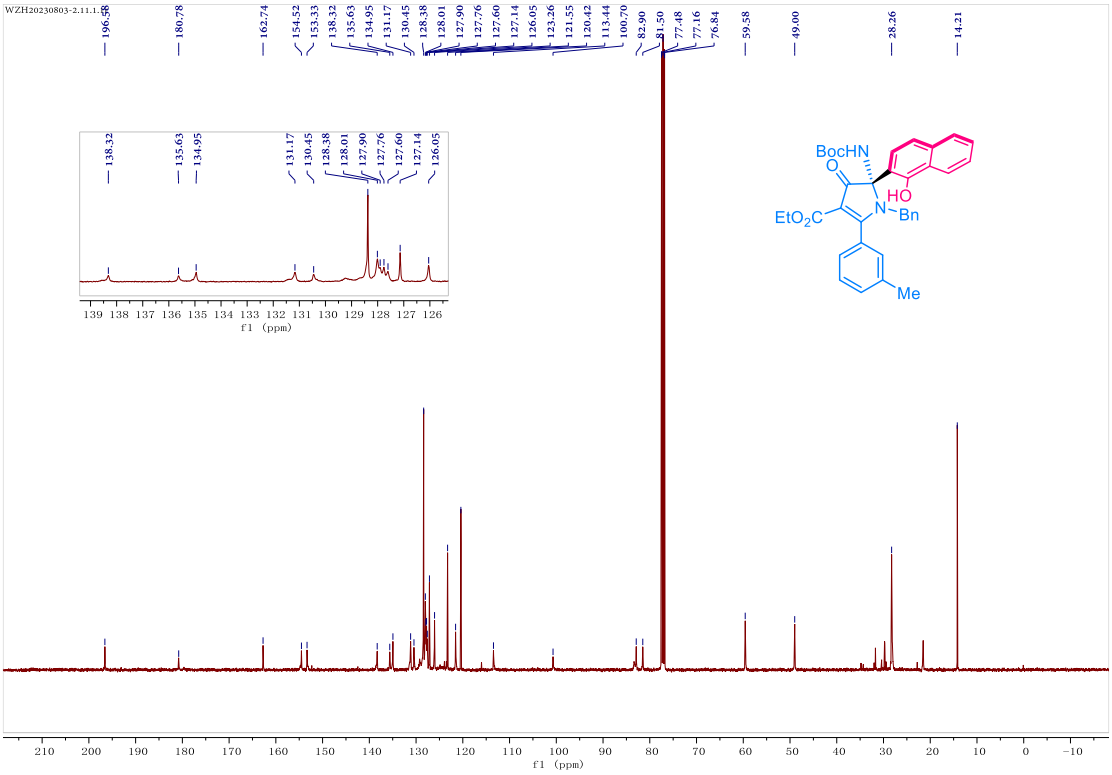
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.685	30434.72	2609.47	98.35
	9.511	509.55	15.54	1.65
		30944.28		100.00

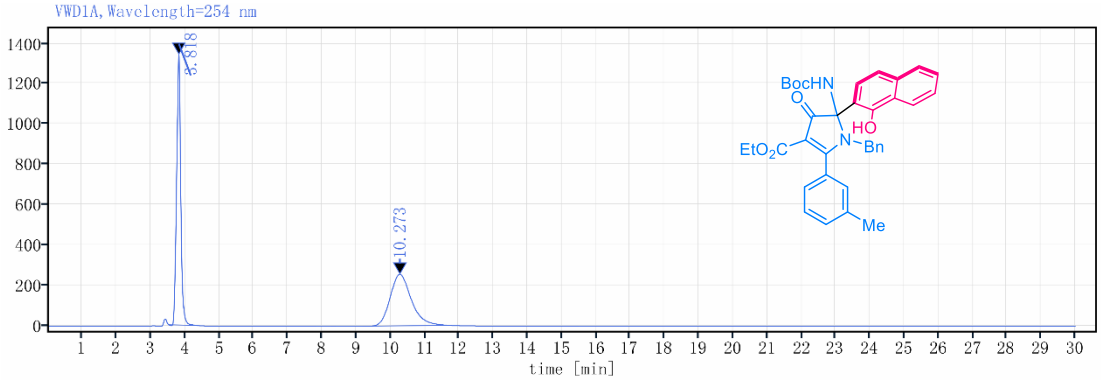
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**

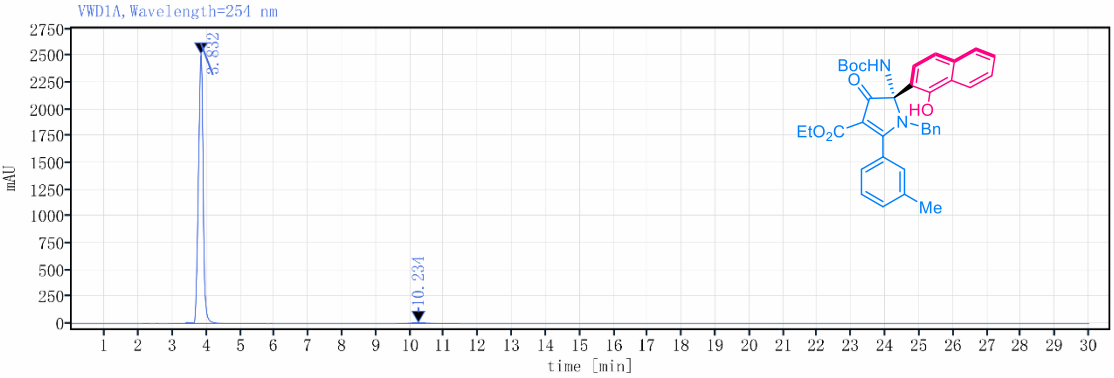


HPLC spectra of **3ga**



Detector VWD1A, Wavelength=254 nm

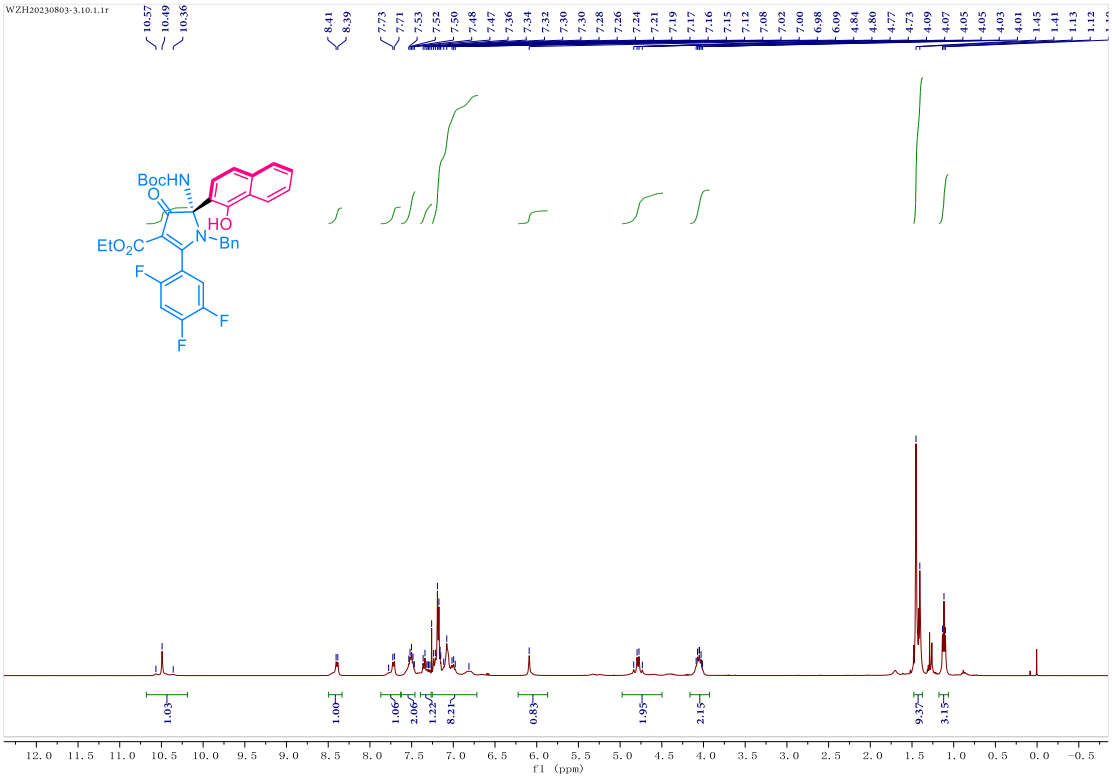
Peak	Ret.Time [min]	Area	Height	Area%
	3.818	11169.10	1339.40	50.40
	10.273	10991.92	255.34	49.60
		22161.03		100.00



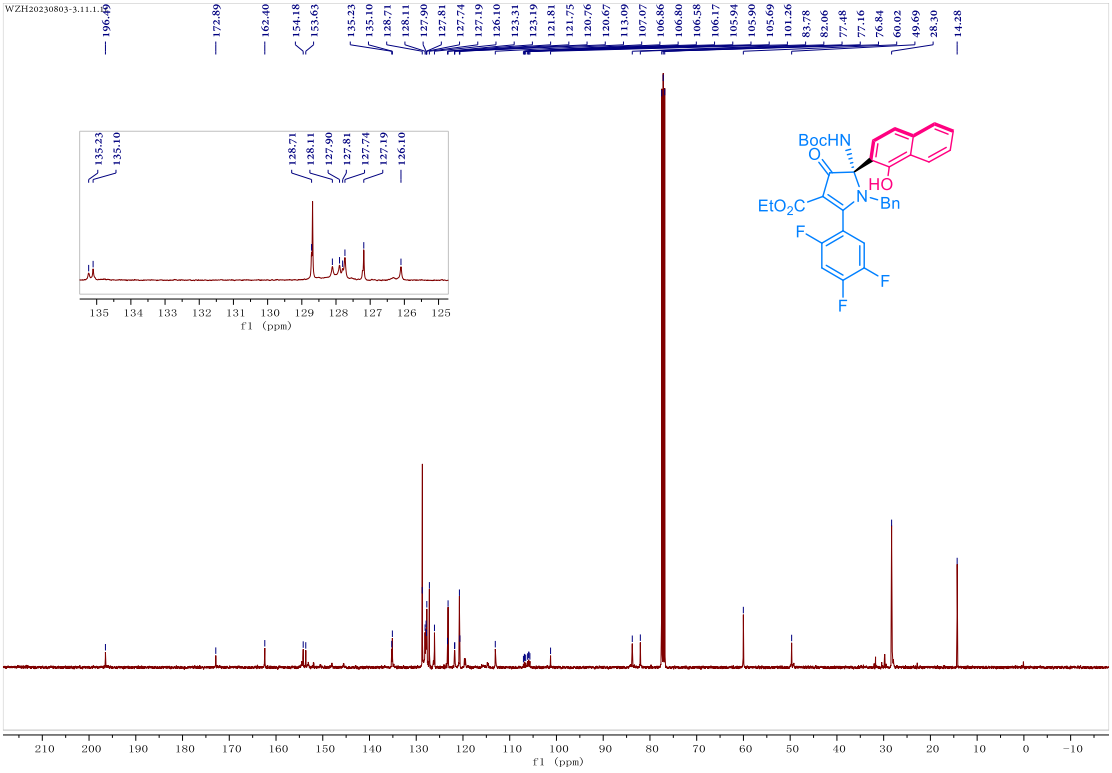
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.832	24519.22	2515.49	98.97
	10.234	255.14	7.48	1.03
		24774.35		100.00

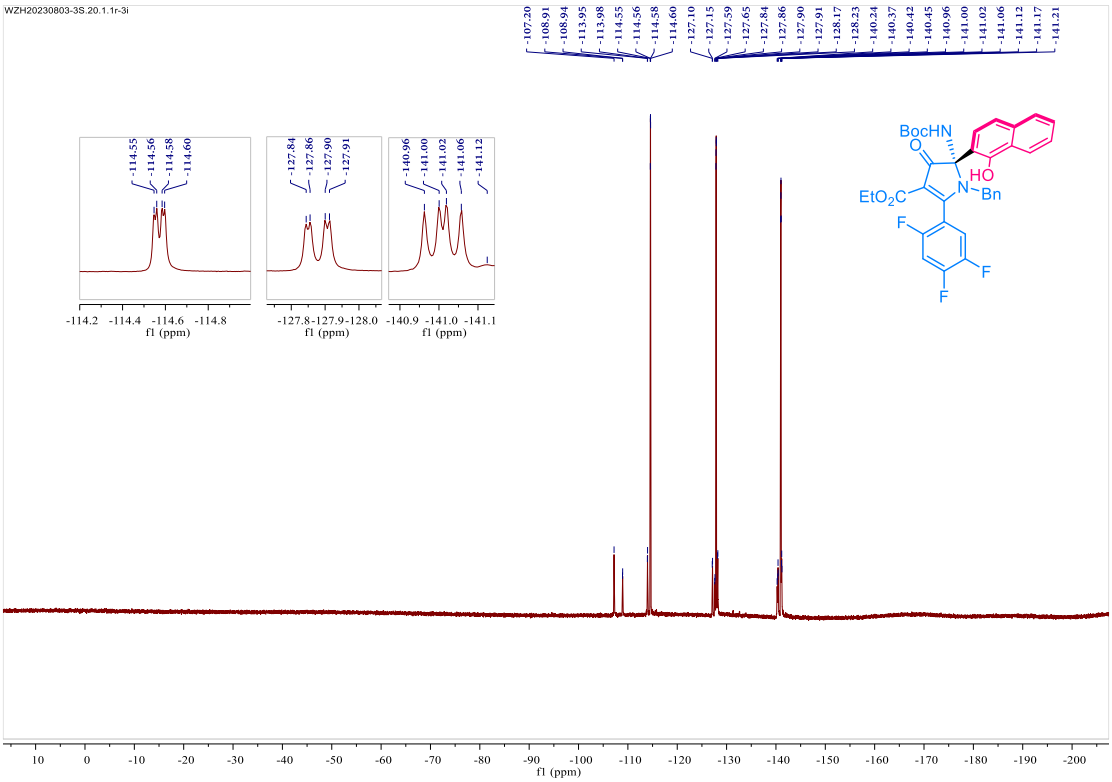
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



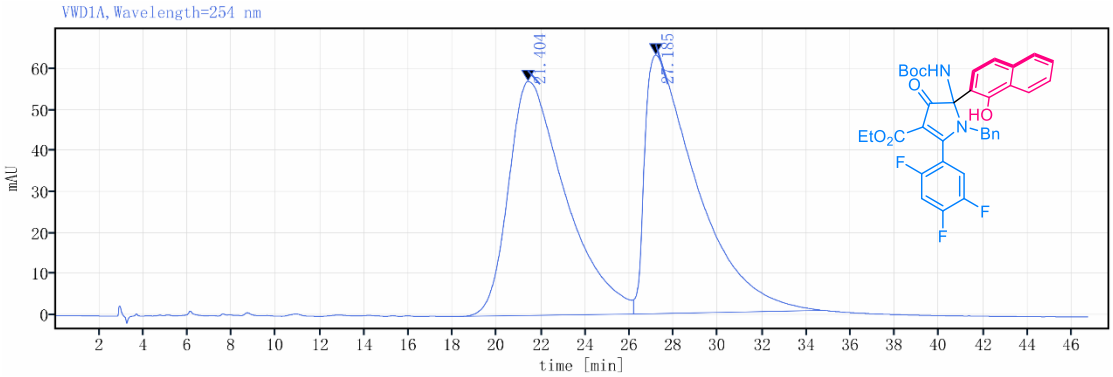
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



^{19}F NMR (377 MHz, $CDCl_3$) of **3ha**

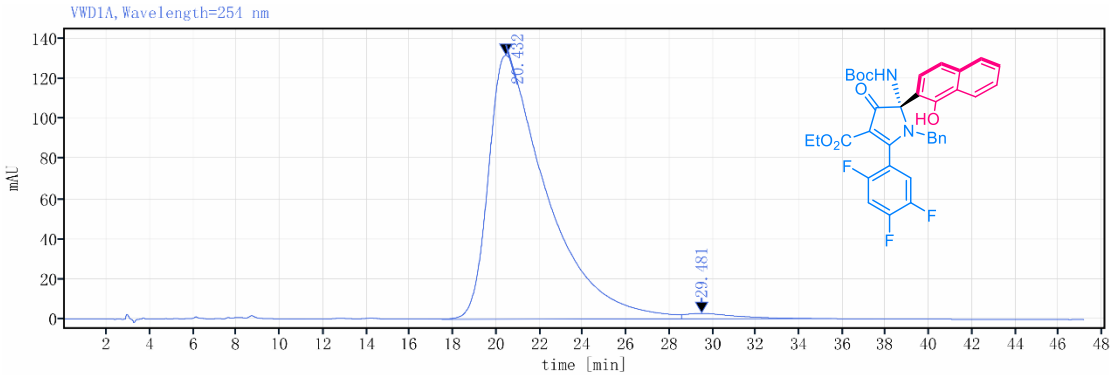


HPLC spectra of **3ha**



Detector VWD1A, Wavelength=254 nm

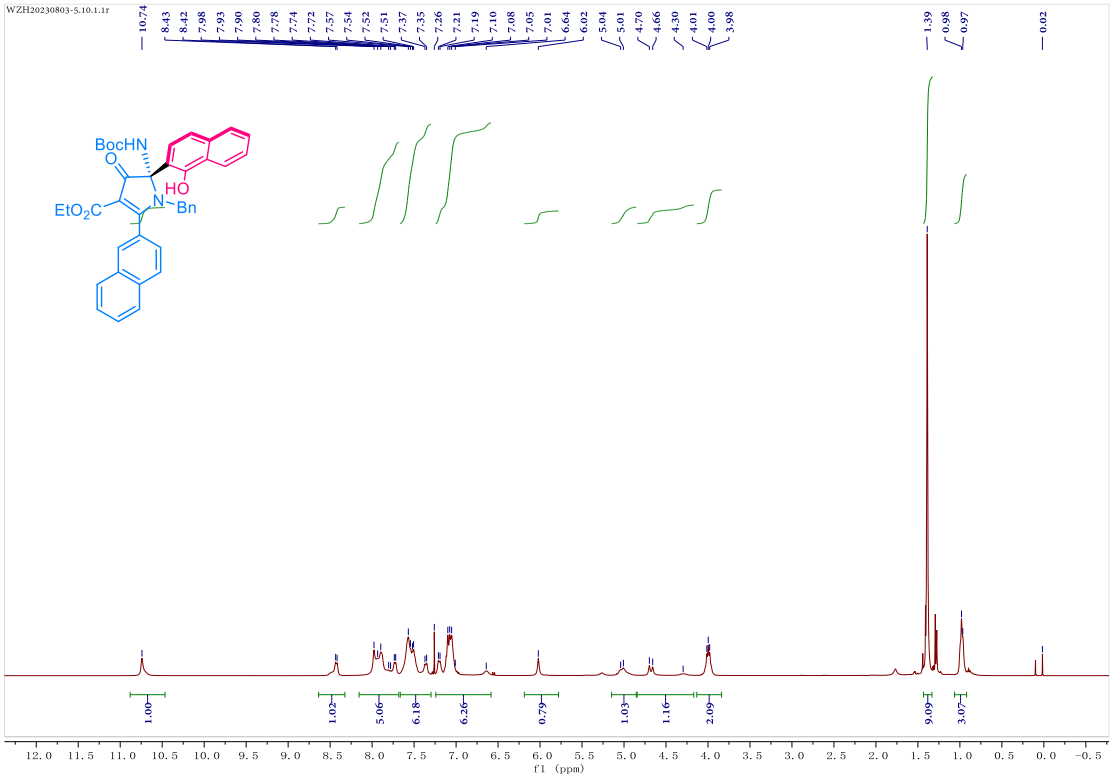
Peak	Ret.Time [min]	Area	Height	Area%
	21.404	10263.39	56.99	49.78
	27.185	10352.95	62.95	50.22
		20616.34		100.00



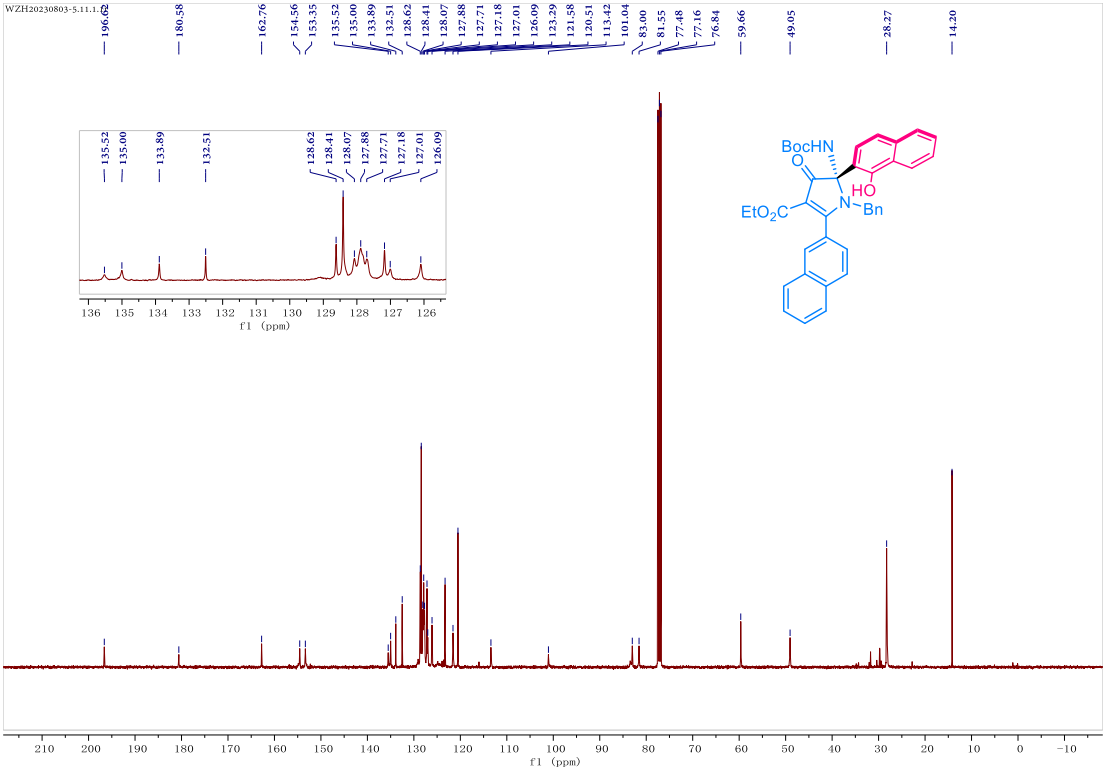
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	20.432	24750.74	131.94	98.19
	29.481	455.85	2.74	1.81
		25206.59		100.00

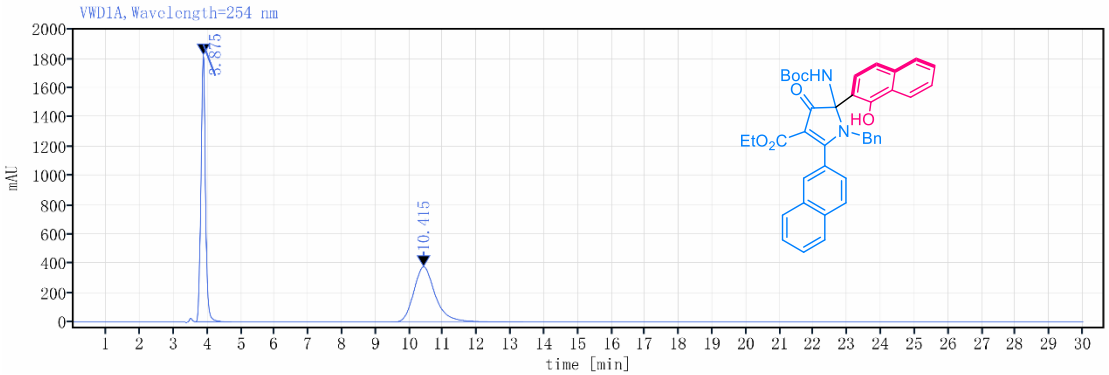
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**

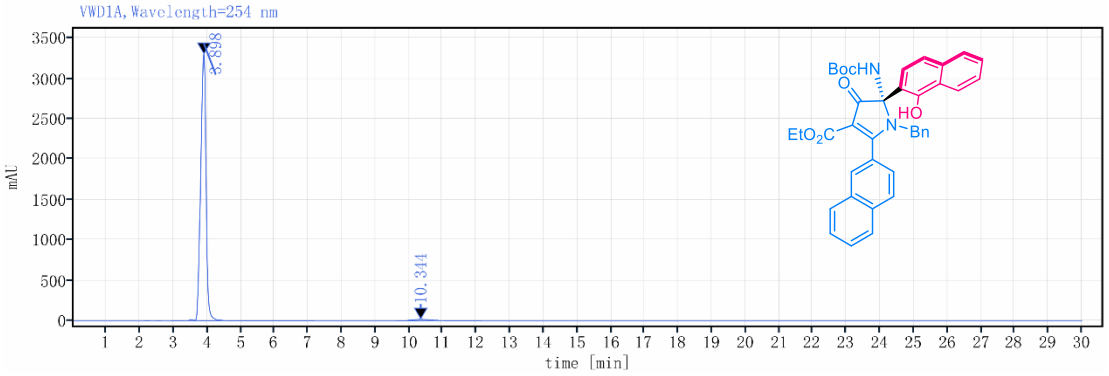


HPLC spectra of **3ia**



Detector VWD1A, Wavelength=254 nm

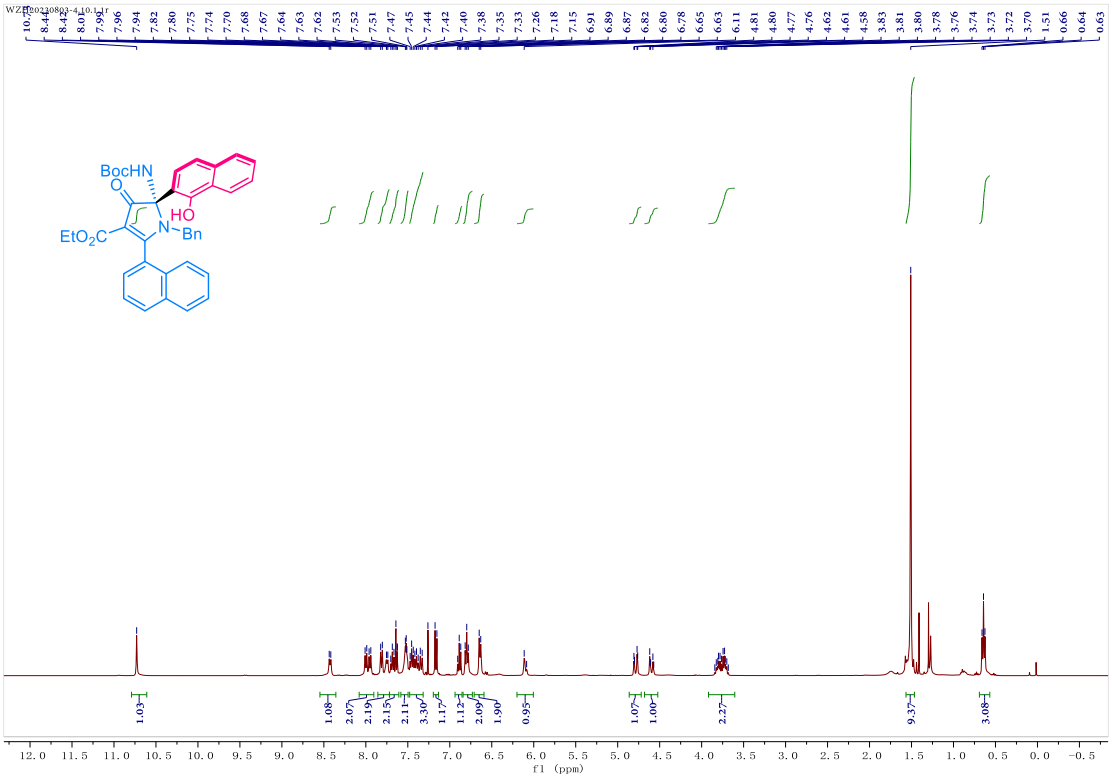
Peak	Ret.Time [min]	Area	Height	Area%
	3.875	16993.17	1822.24	49.96
	10.415	17020.76	378.24	50.04
		34013.94		100.00



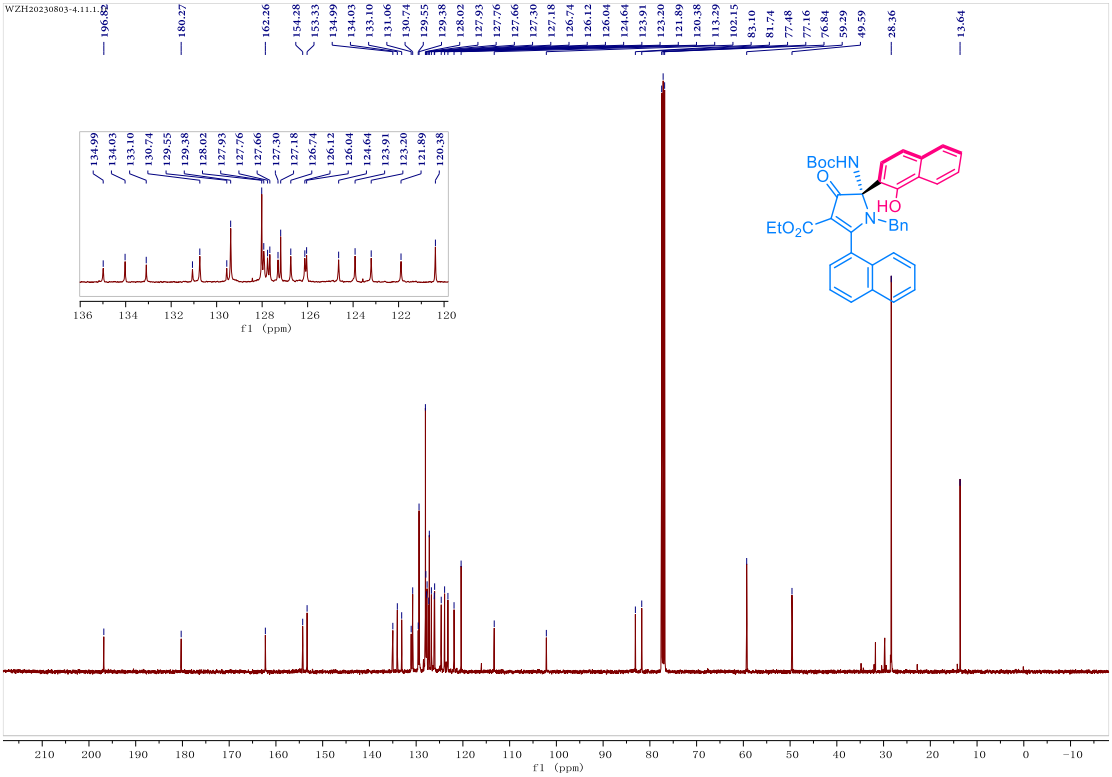
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.898	36751.58	3299.77	98.38
	10.344	604.84	16.56	1.62
		37356.42		100.00

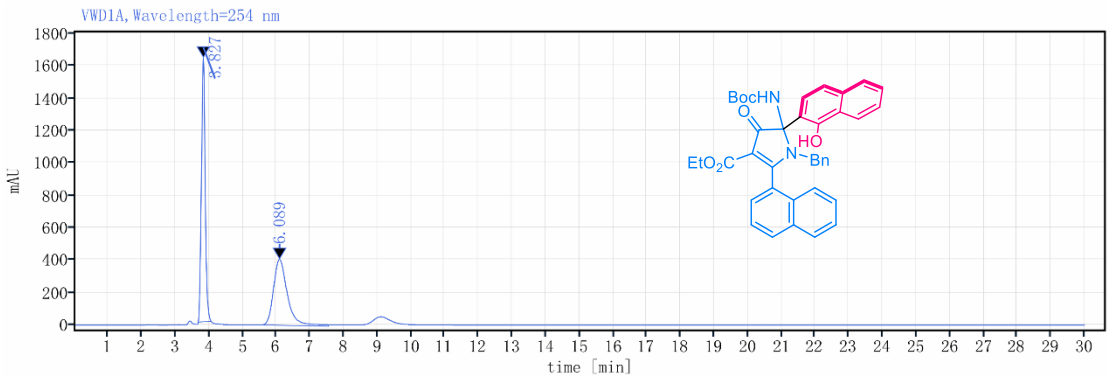
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ja**

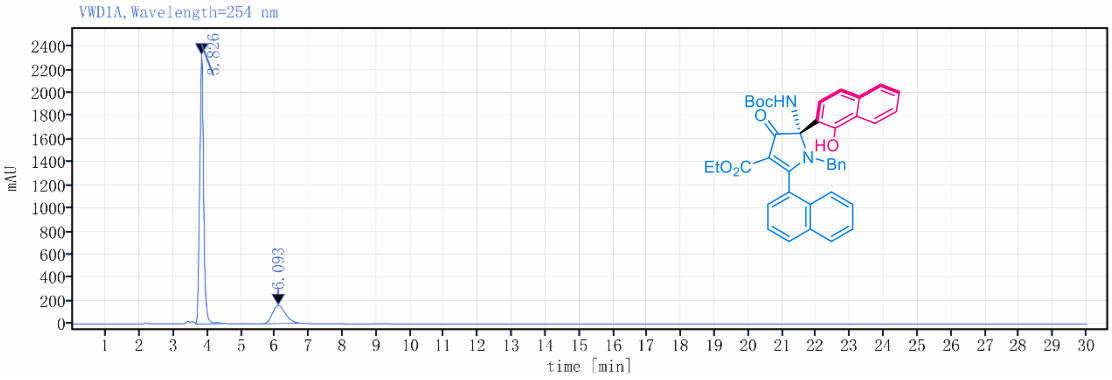


HPLC spectra of **3ja**



Detector VWD1A, Wavelength=254 nm

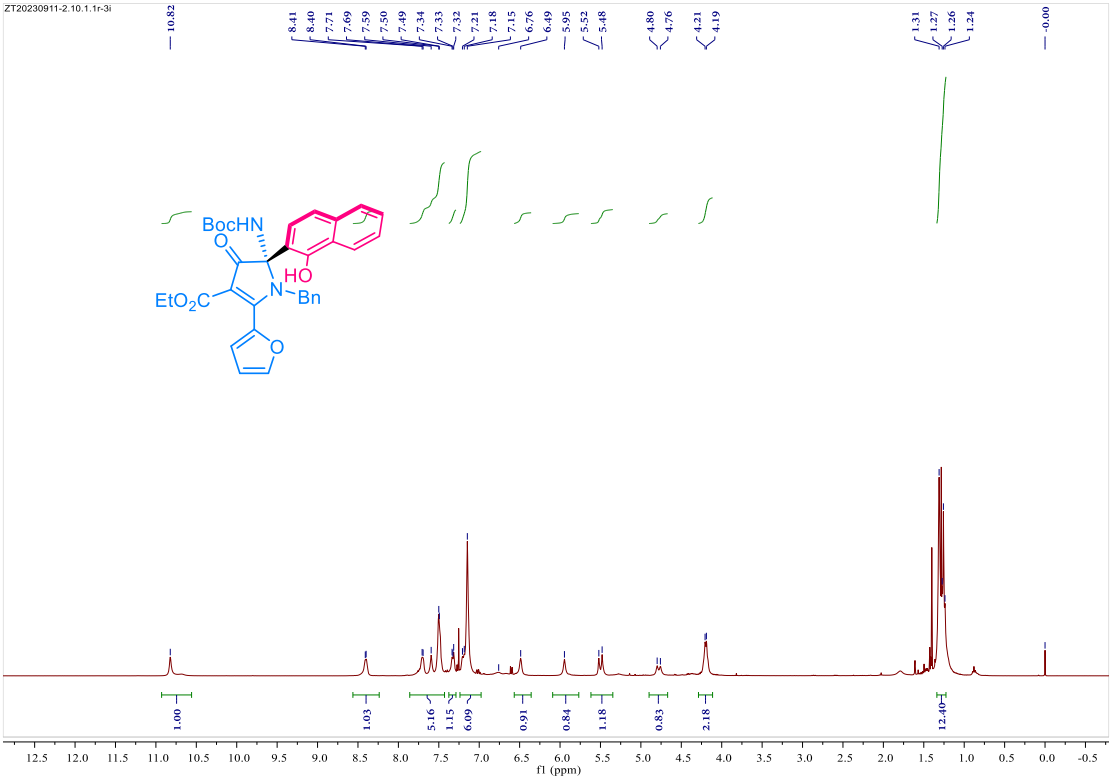
Peak	Ret.Time [min]	Area	Height	Area%
	3.827	12606.99	1628.08	51.85
	6.089	11707.80	406.57	48.15
		24314.79		100.00



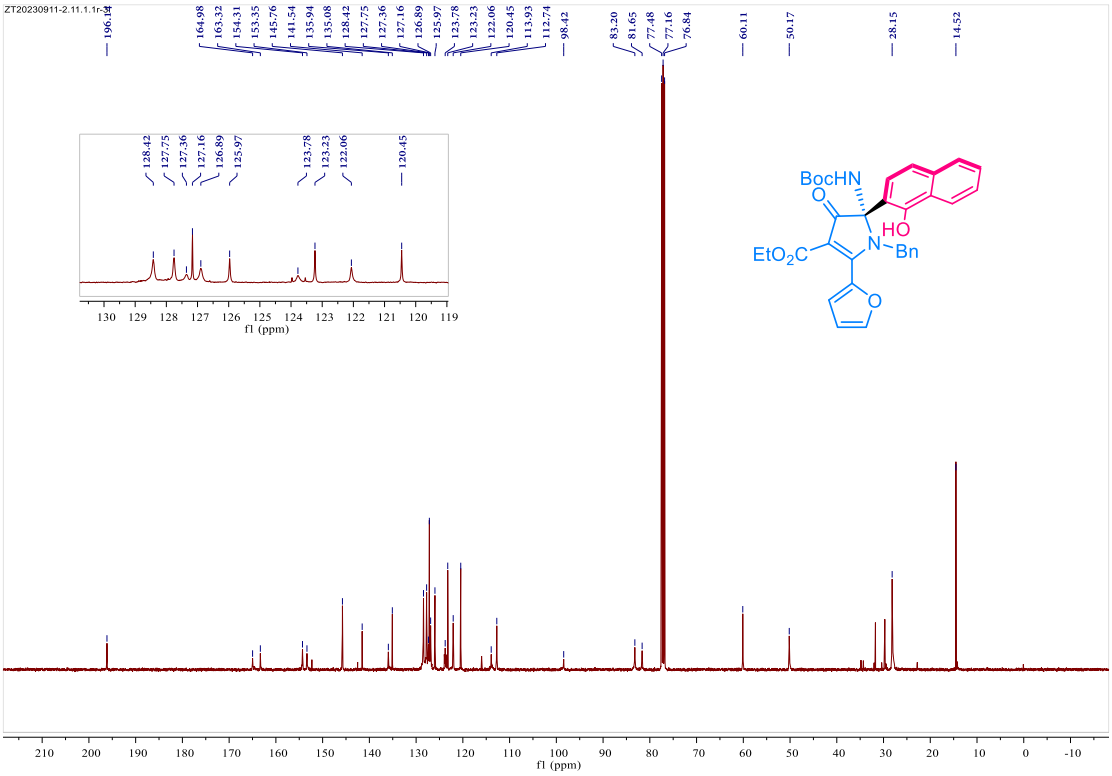
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.826	18914.77	2332.40	81.83
	6.093	4200.33	157.53	18.17
		23115.10		100.00

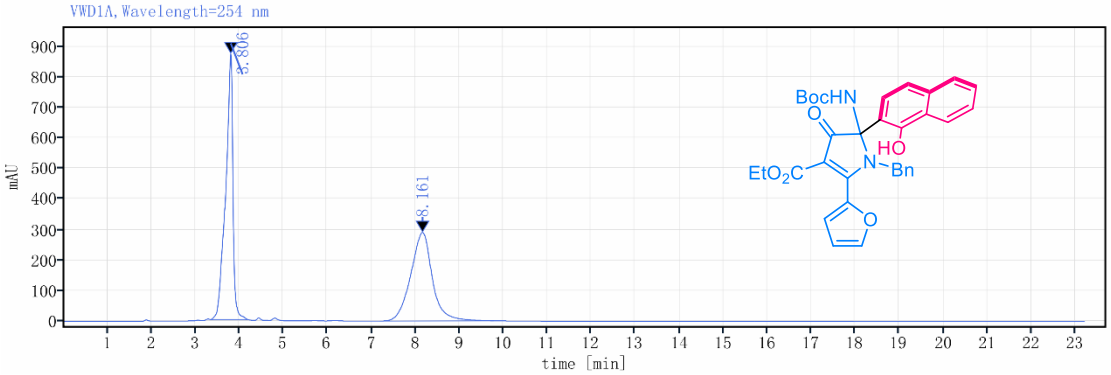
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ka**

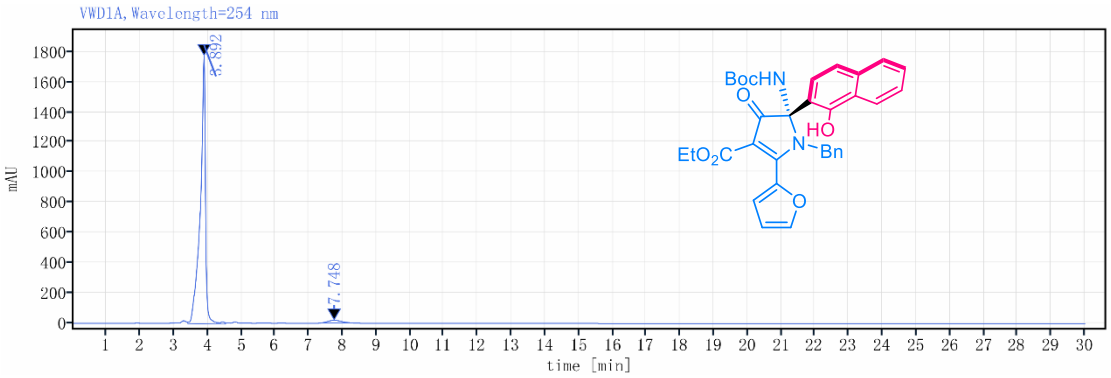


HPLC spectra of **3ka**



Detector VWD1A, Wavelength=254 nm

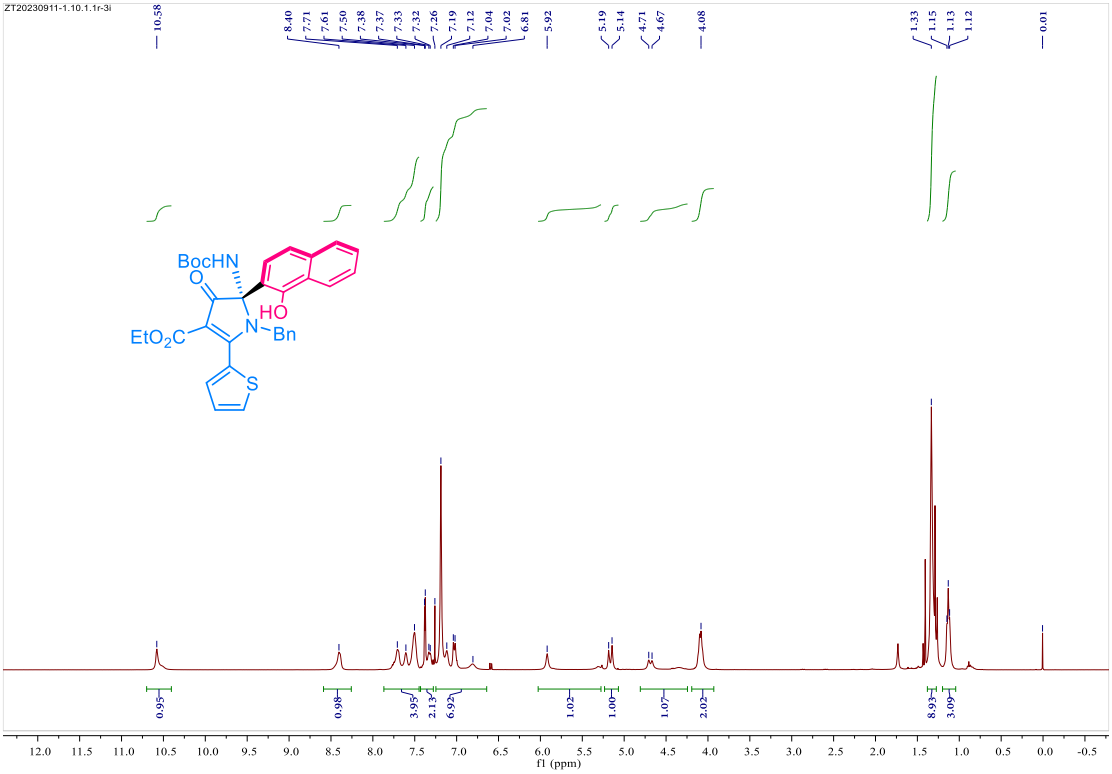
Peak	Ret.Time [min]	Area	Height	Area%
	3.806	9953.25	870.16	50.19
	8.161	9878.62	289.85	49.81
		19831.87		100.00



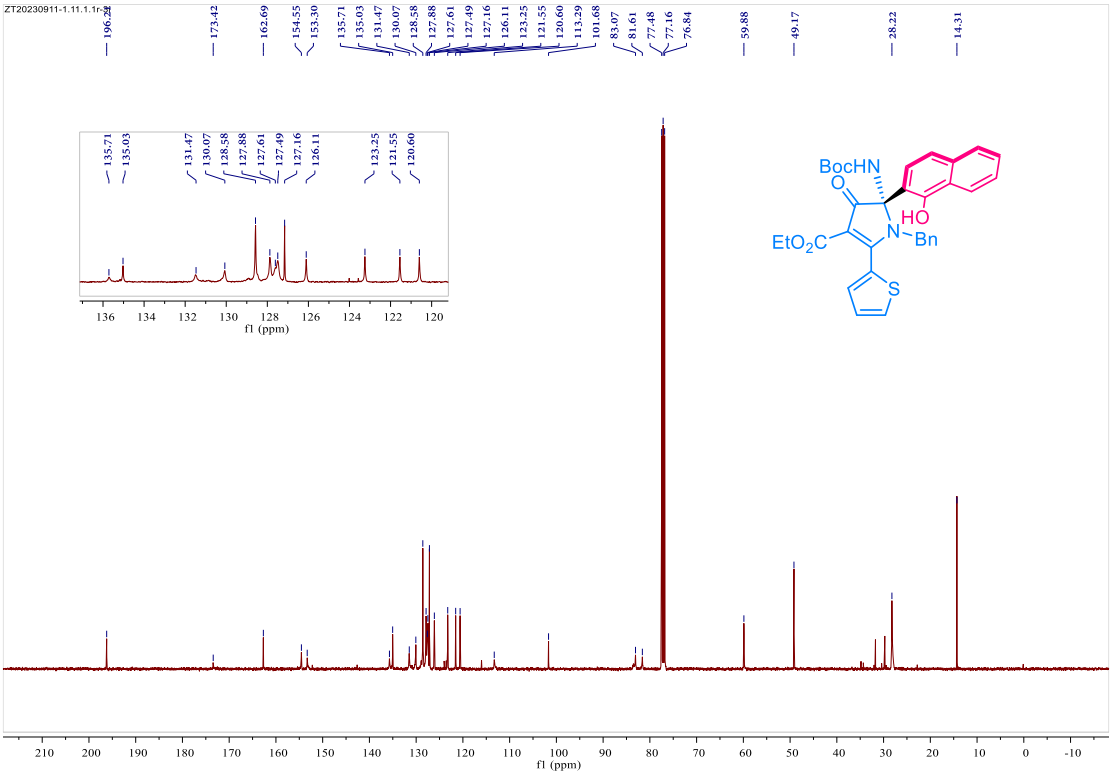
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.892	19308.95	1775.41	97.56
	7.748	482.41	17.54	2.44
		19791.36		100.00

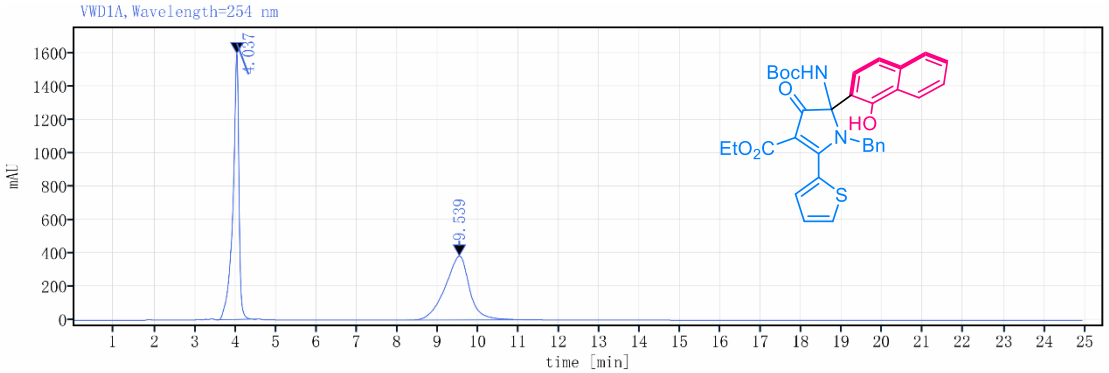
^{1}H NMR (400 MHz, $CDCl_3$) of **3la**



^{13}C NMR (101 MHz, $CDCl_3$) of **3la**

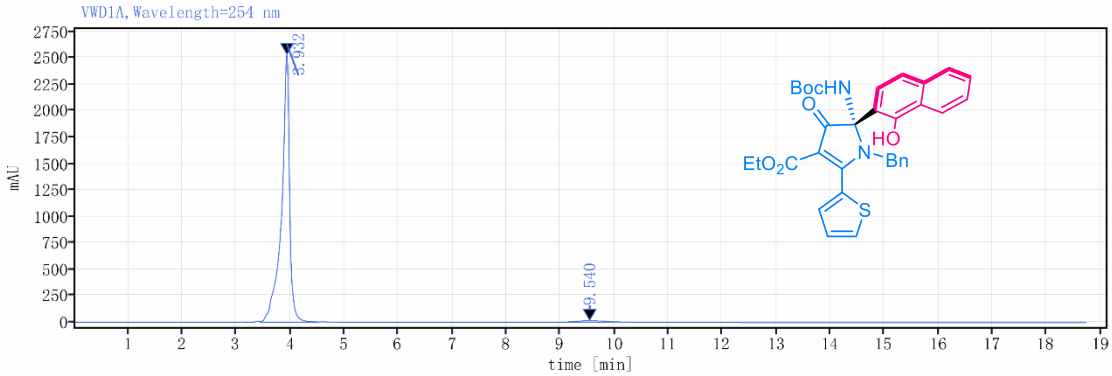


HPLC spectra of **3la**



Detector VWD1A, Wavelength=254 nm

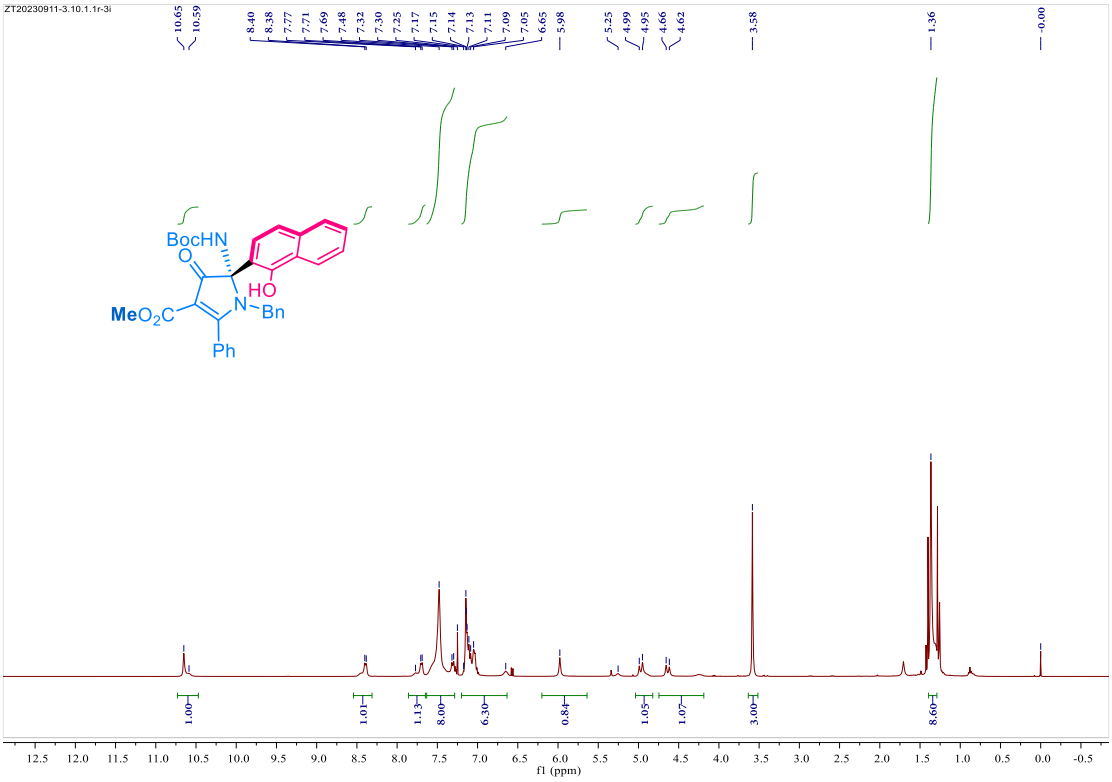
Peak	Ret.Time [min]	Area	Height	Area%
	4.037	16295.96	1588.68	50.25
	9.539	16135.76	382.38	49.75
		32431.72		100.00



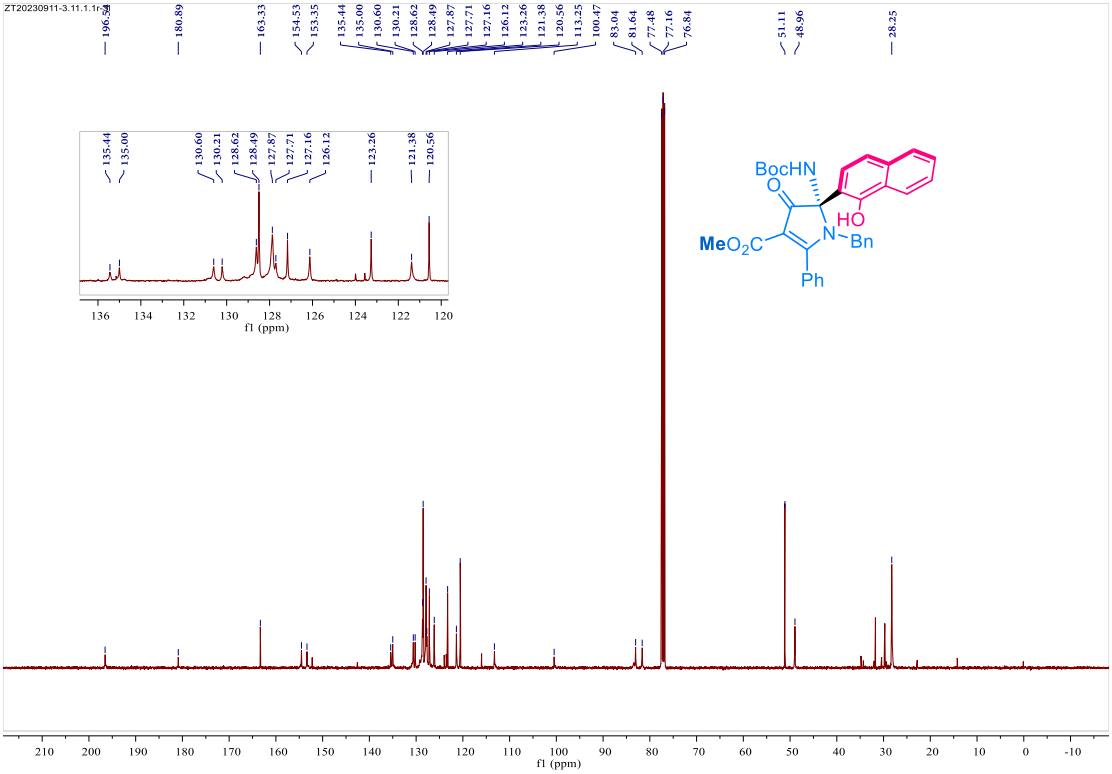
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.932	26463.85	2528.87	97.86
	9.540	577.96	14.85	2.14
		27041.80		100.00

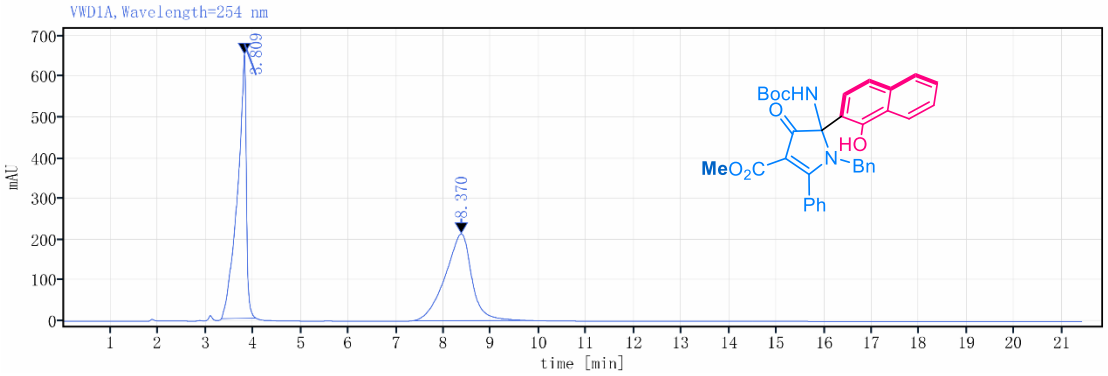
^{1}H NMR (400 MHz, $CDCl_3$) of **3ma**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ma**

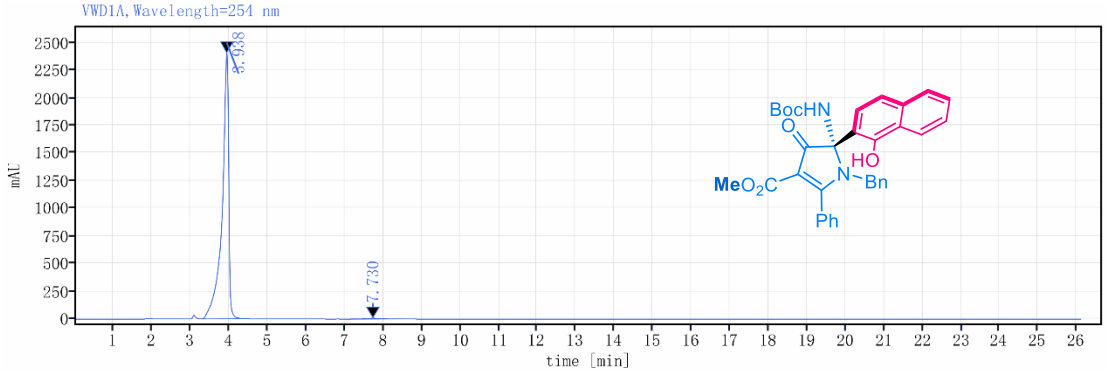


HPLC spectra of **3ma**



Detector VWD1A, Wavelength=254 nm

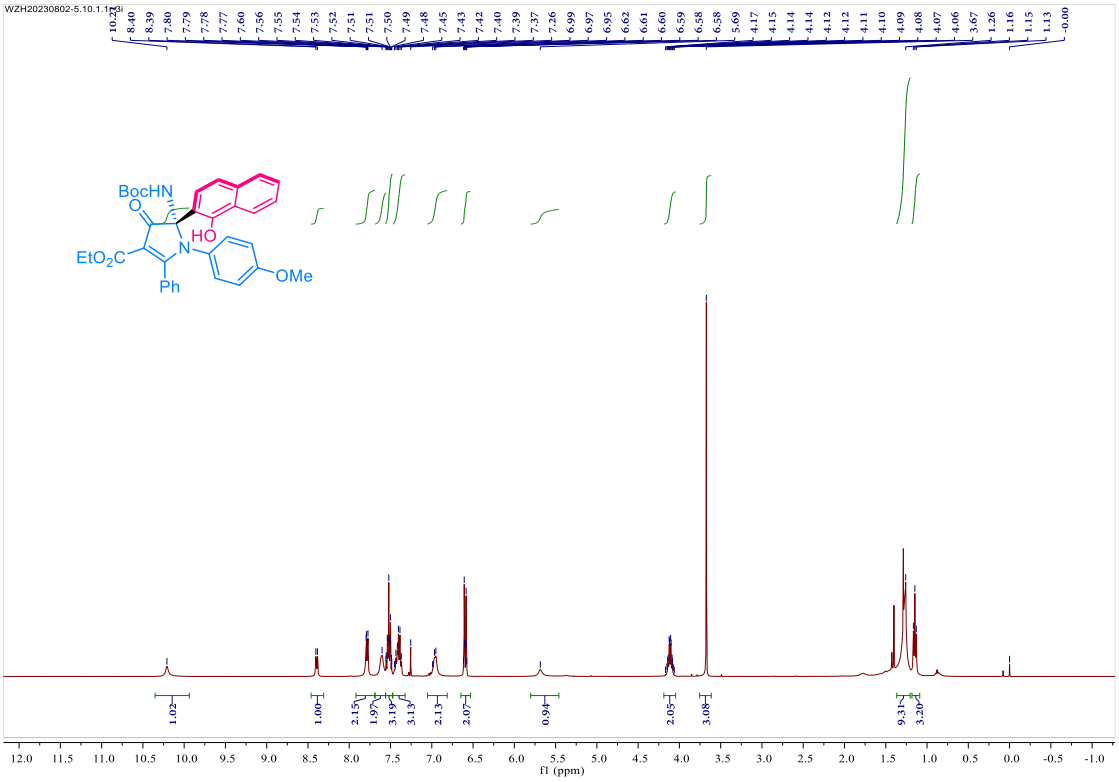
Peak	Ret.Time [min]	Area	Height	Area%
	3.809	8426.28	648.07	50.53
	8.370	8250.48	213.06	49.47
		16676.77		100.00



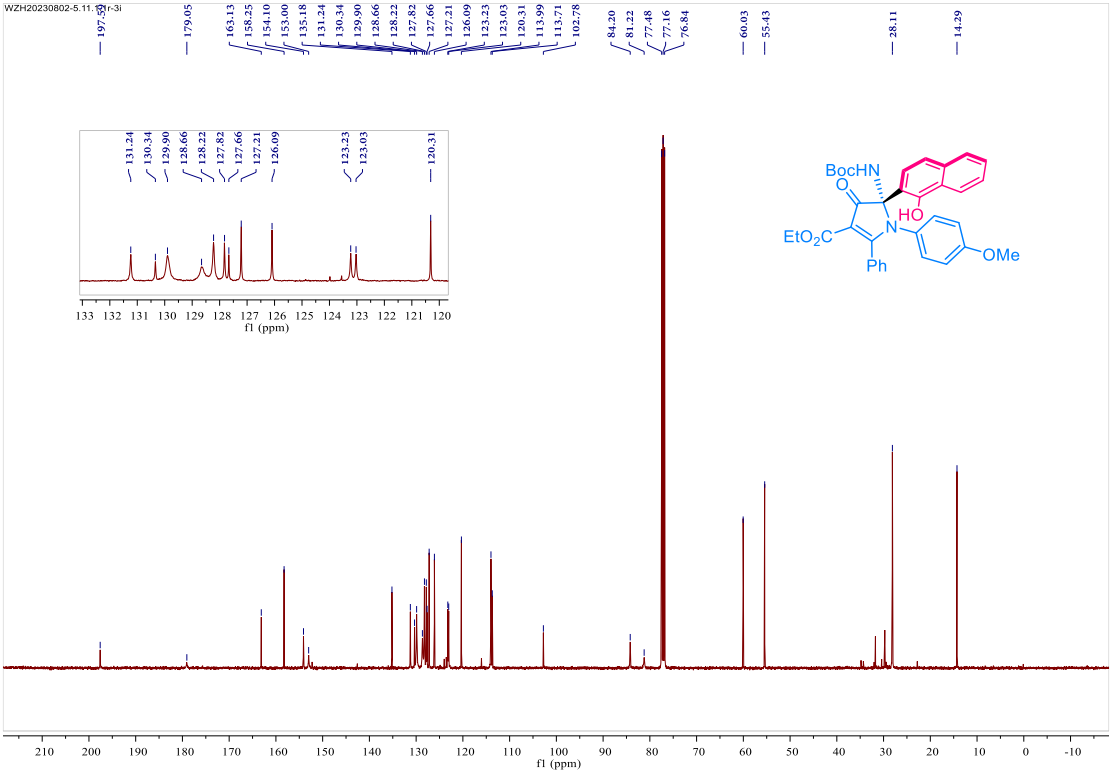
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.938	28457.14	2401.05	99.19
	7.730	233.06	7.09	0.81
		28690.21		100.00

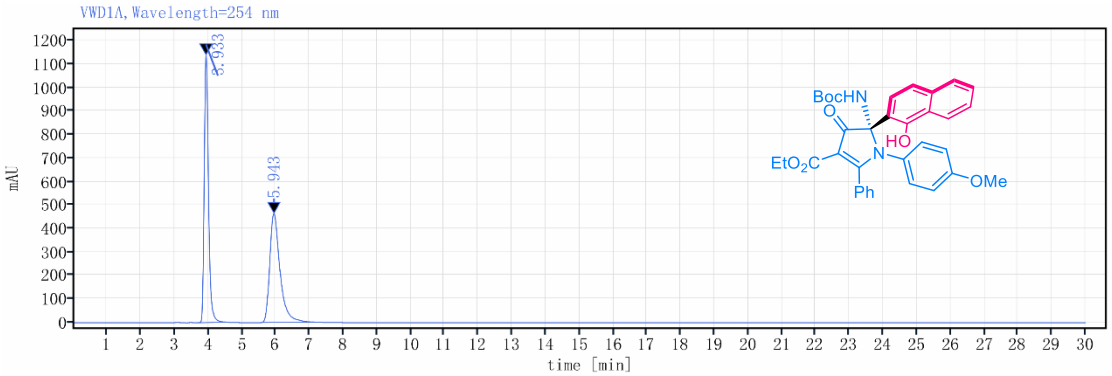
^{1}H NMR (400 MHz, $CDCl_3$) of **3na**



^{13}C NMR (101 MHz, $CDCl_3$) of **3na**

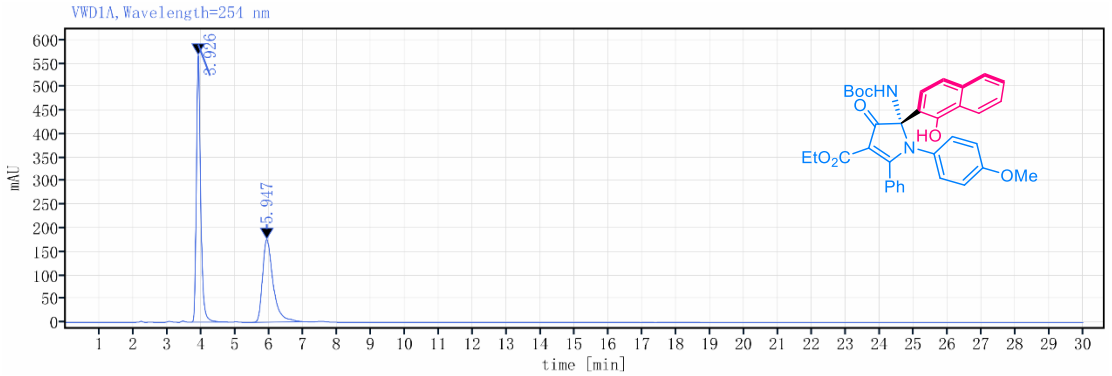


HPLC spectra of **3na**



Detector VWD1A, Wavelength=254 nm

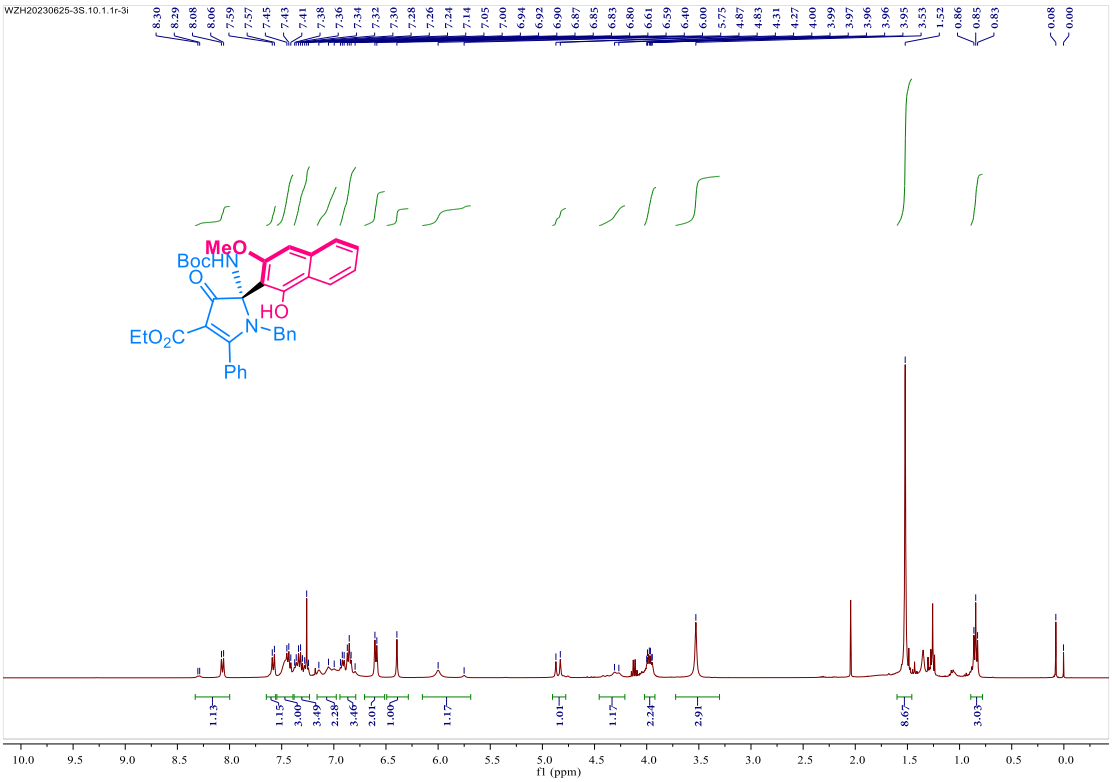
Peak	Ret.Time [min]	Area	Height	Area%
	3.933	9955.58	1139.08	50.31
	5.943	9832.24	463.13	49.69
		19787.82		100.00



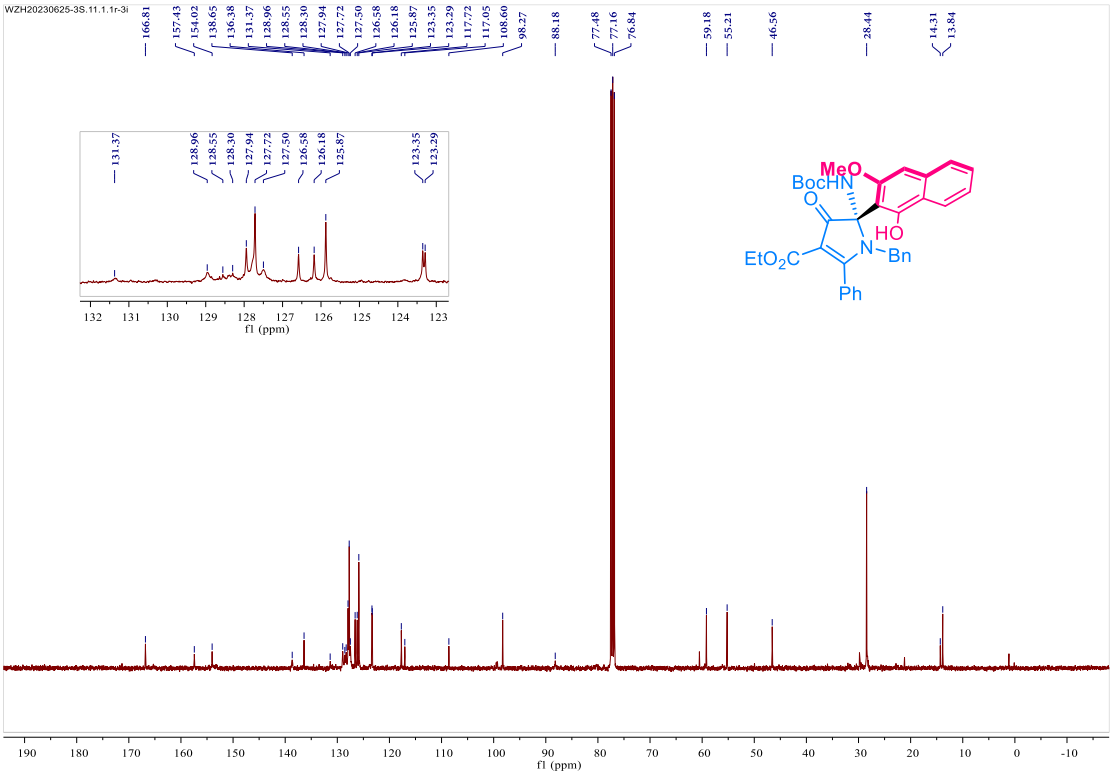
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.926	4996.40	566.90	56.74
	5.947	3809.18	175.47	43.26
		8805.58		100.00

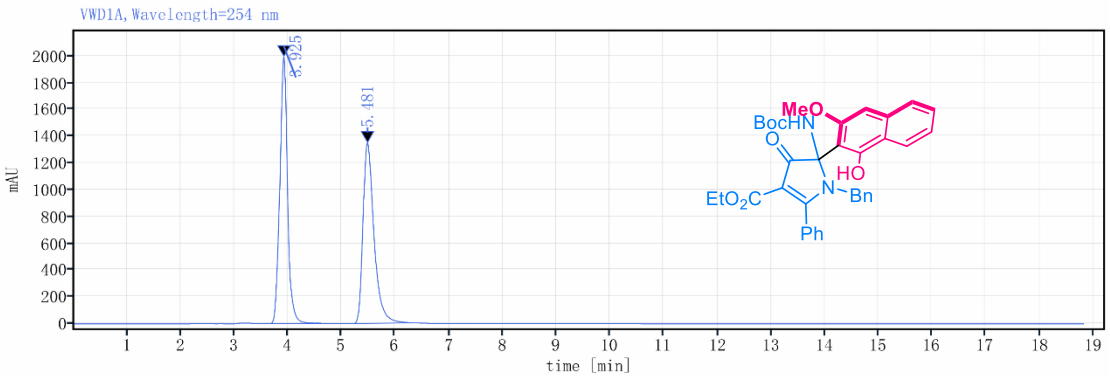
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**

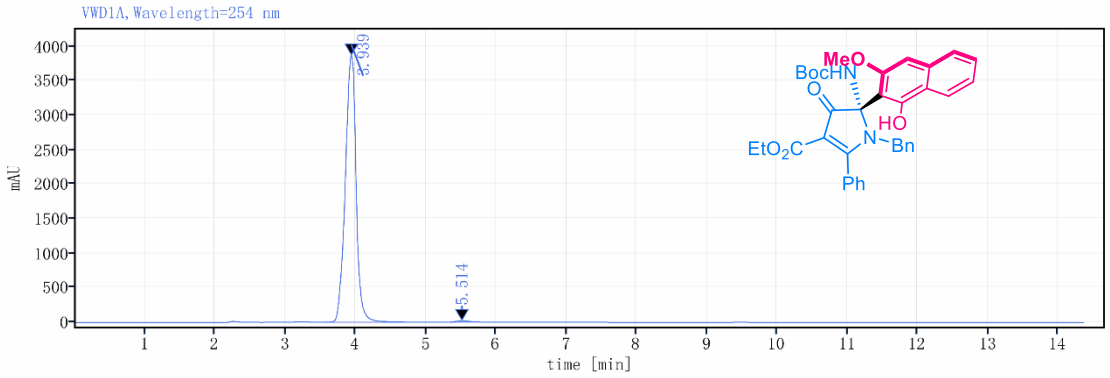


HPLC spectra of **3ab**



Detector VWD1A, Wavelength=254 nm

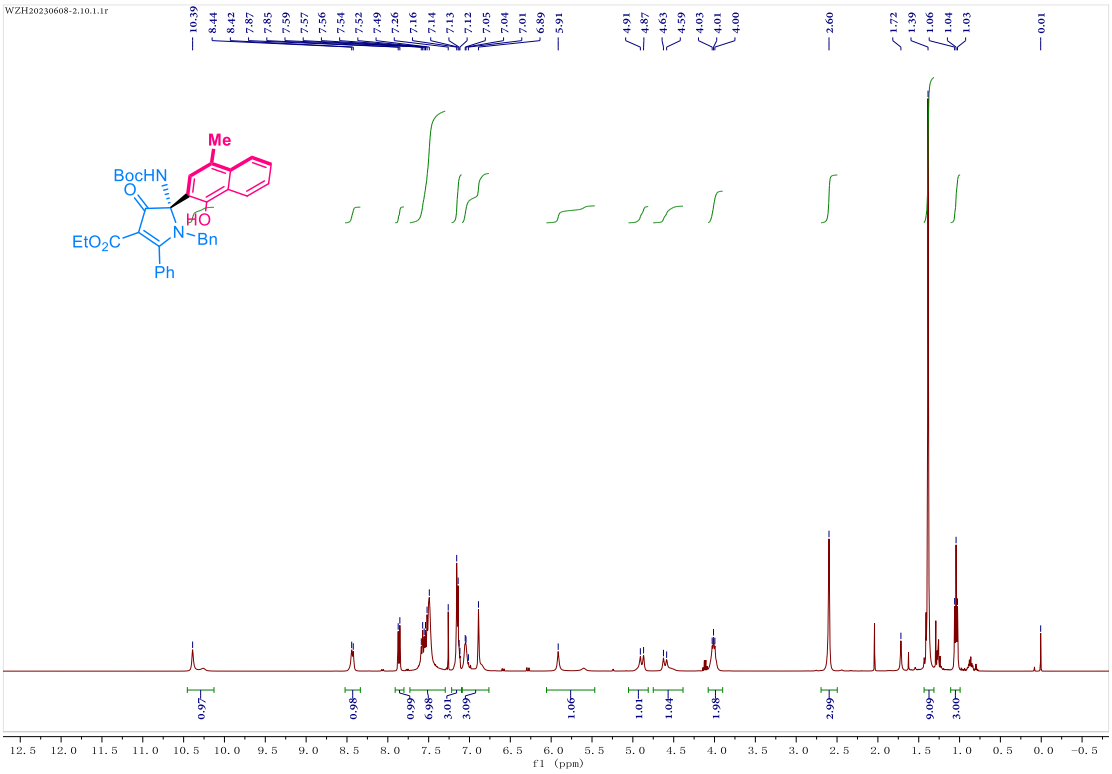
Peak	Ret.Time [min]	Area	Height	Area%
	3.925	19804.79	1992.30	50.66
	5.481	19285.33	1348.34	49.34
		39090.12		100.00



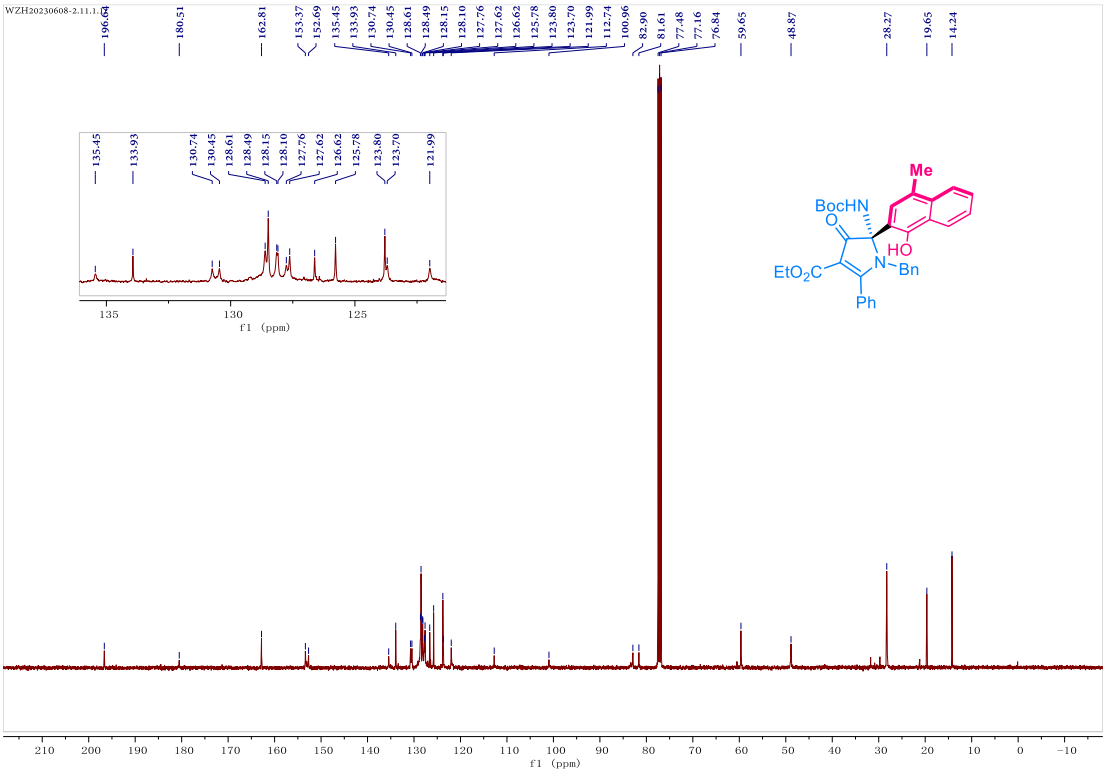
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.939	41369.92	3865.06	99.42
	5.514	239.59	19.46	0.58
		41609.51		100.00

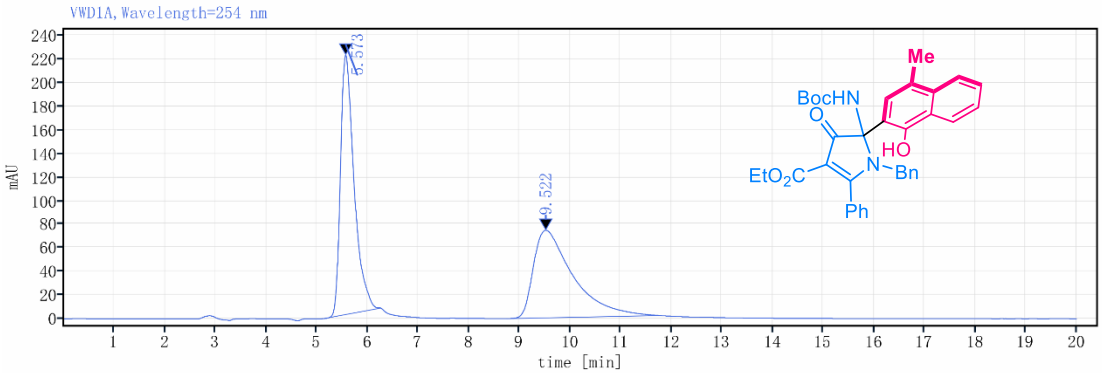
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**

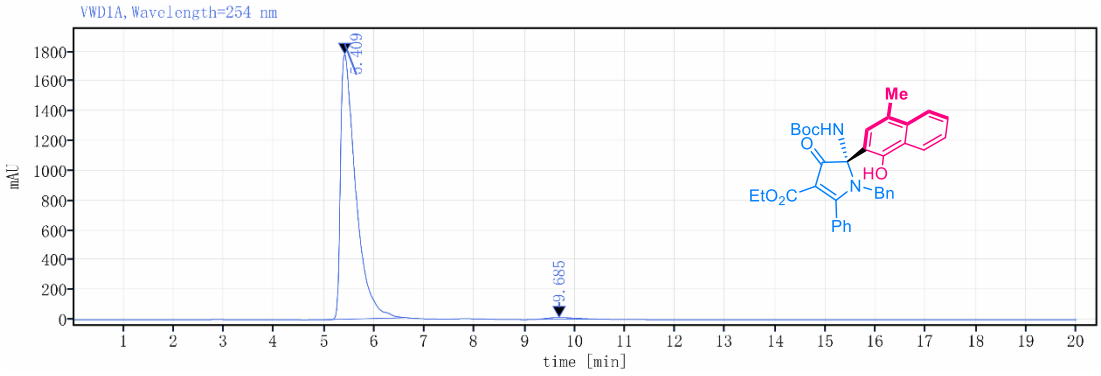


HPLC spectra of **3ac**



Detector VWD1A, Wavelength=254 nm

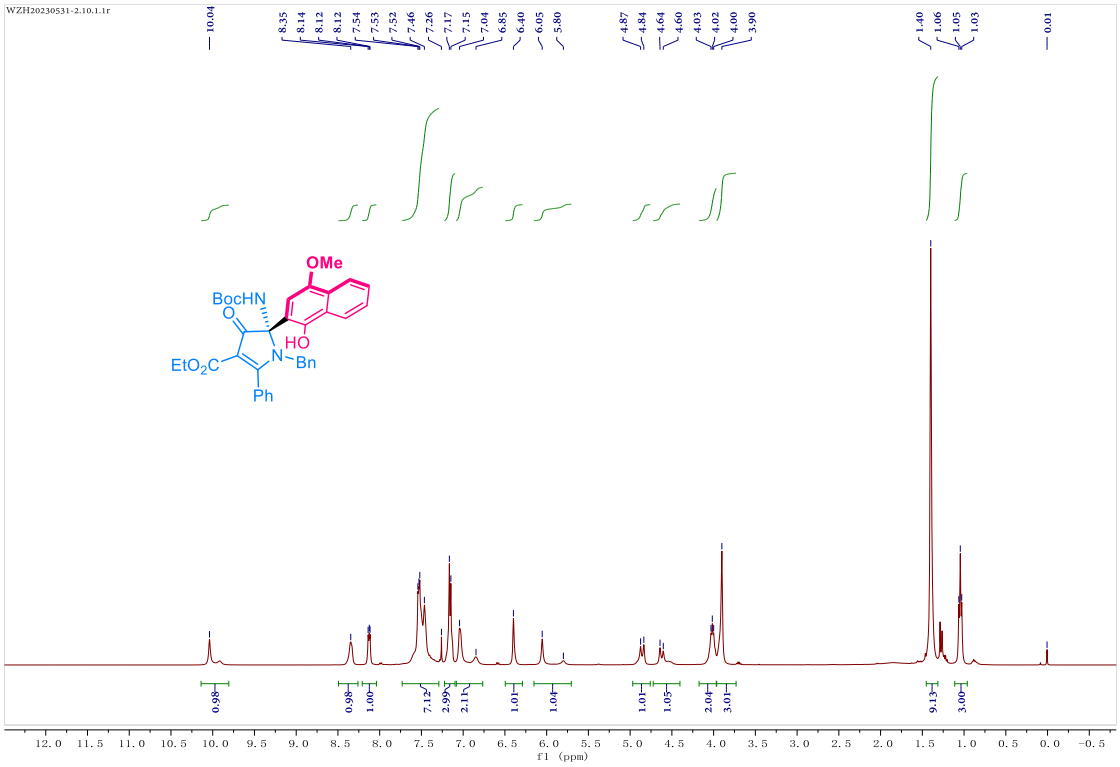
Peak	Ret.Time [min]	Area	Height	Area%
	5.573	4110.83	220.20	50.50
	9.522	4029.01	74.34	49.50
		8139.85		100.00



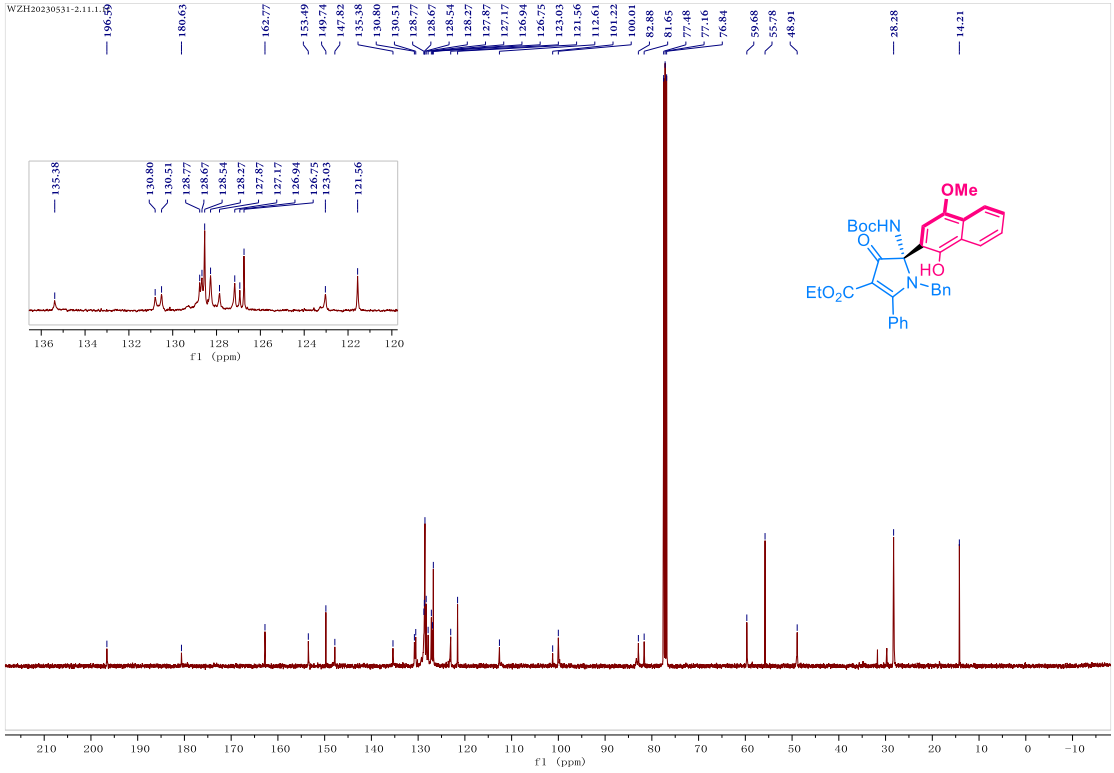
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.409	37610.51	1778.52	98.57
	9.685	546.18	12.51	1.43
		38156.69		100.00

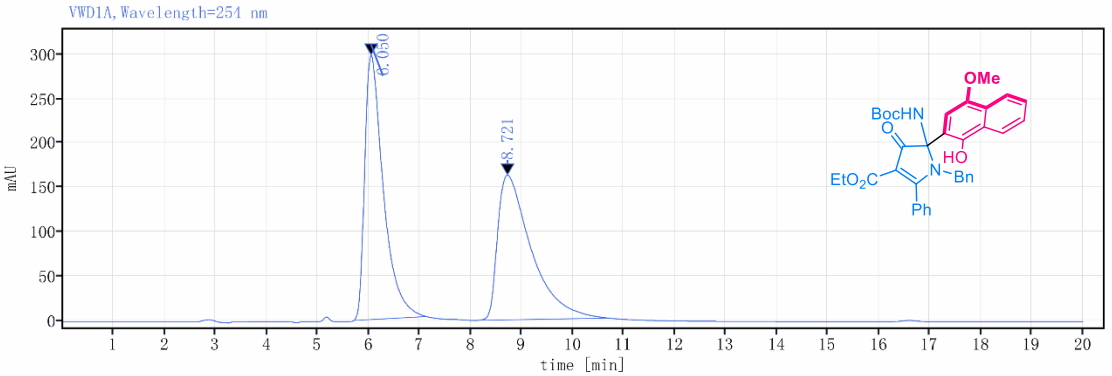
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**

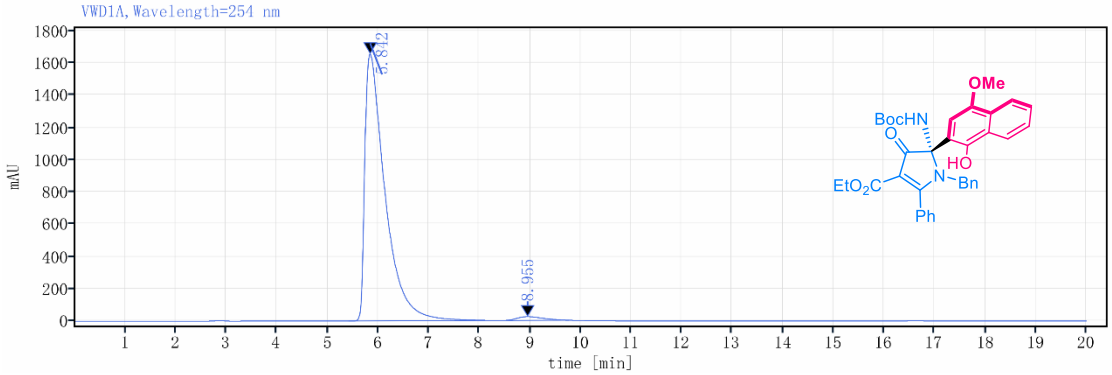


HPLC spectra of **3ad**



Detector VWD1A, Wavelength=254 nm

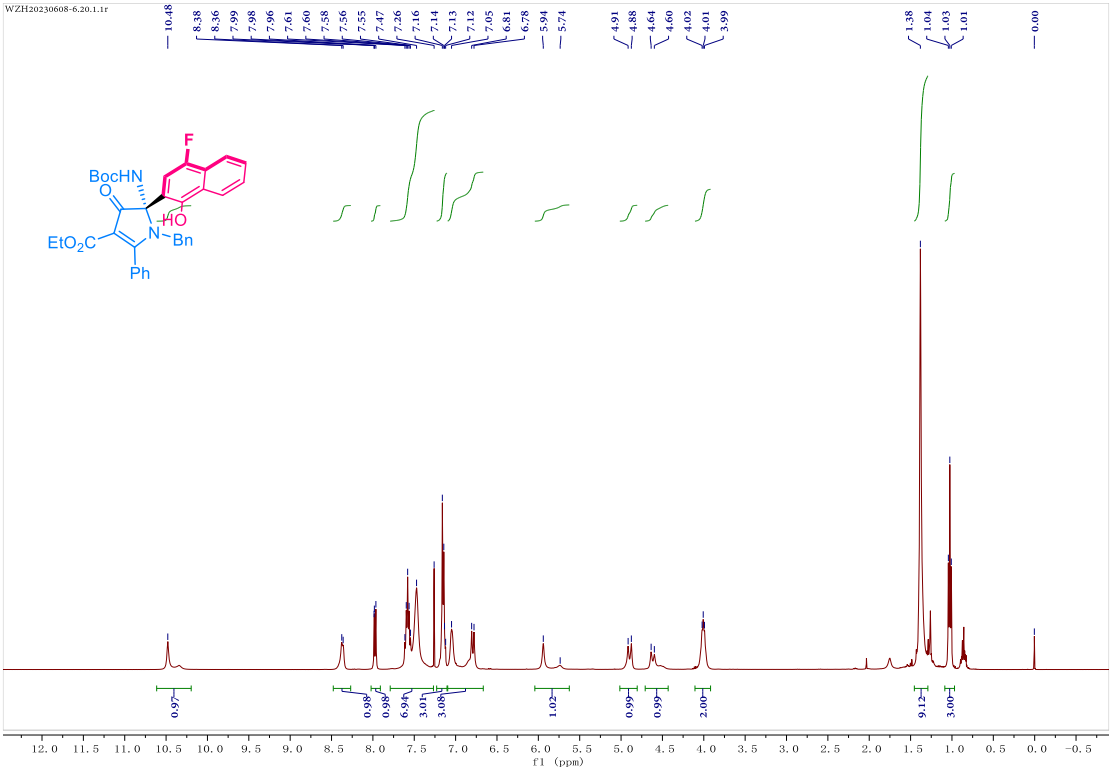
Peak	Ret.Time [min]	Area	Height	Area%
	6.050	7526.74	296.08	50.39
	8.721	7409.37	161.97	49.61
		14936.11		100.00



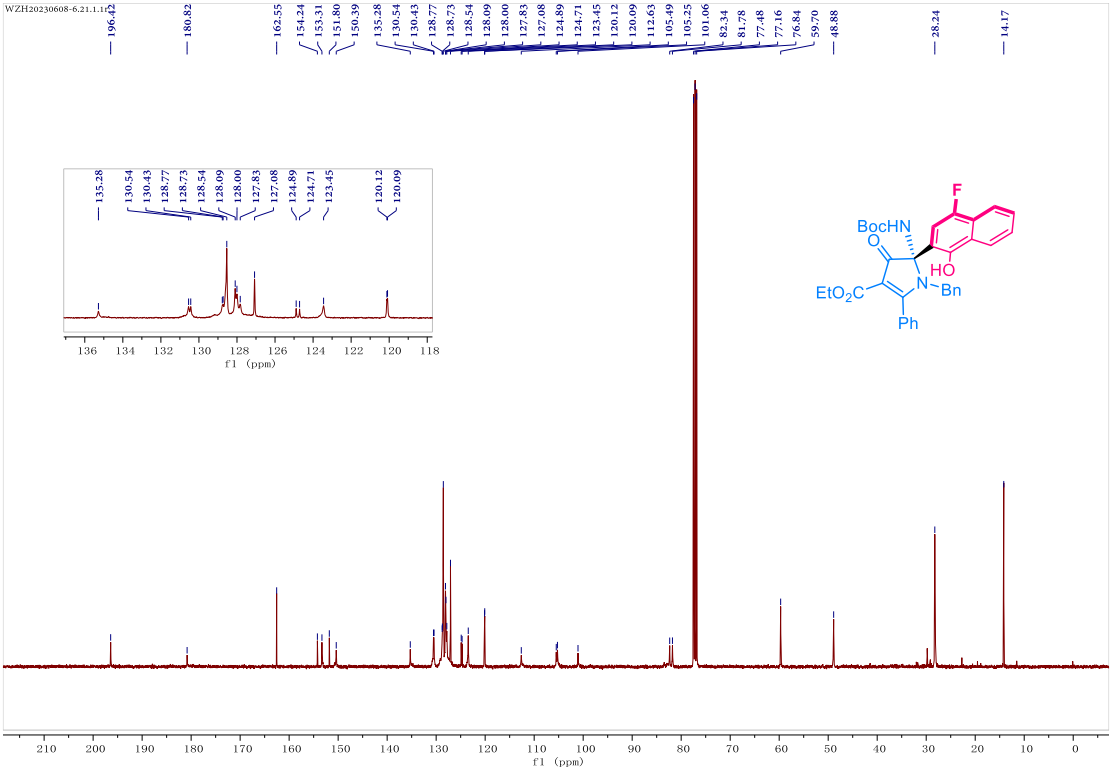
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.842	46044.29	1655.97	98.27
	8.955	812.97	22.88	1.73
		46857.26		100.00

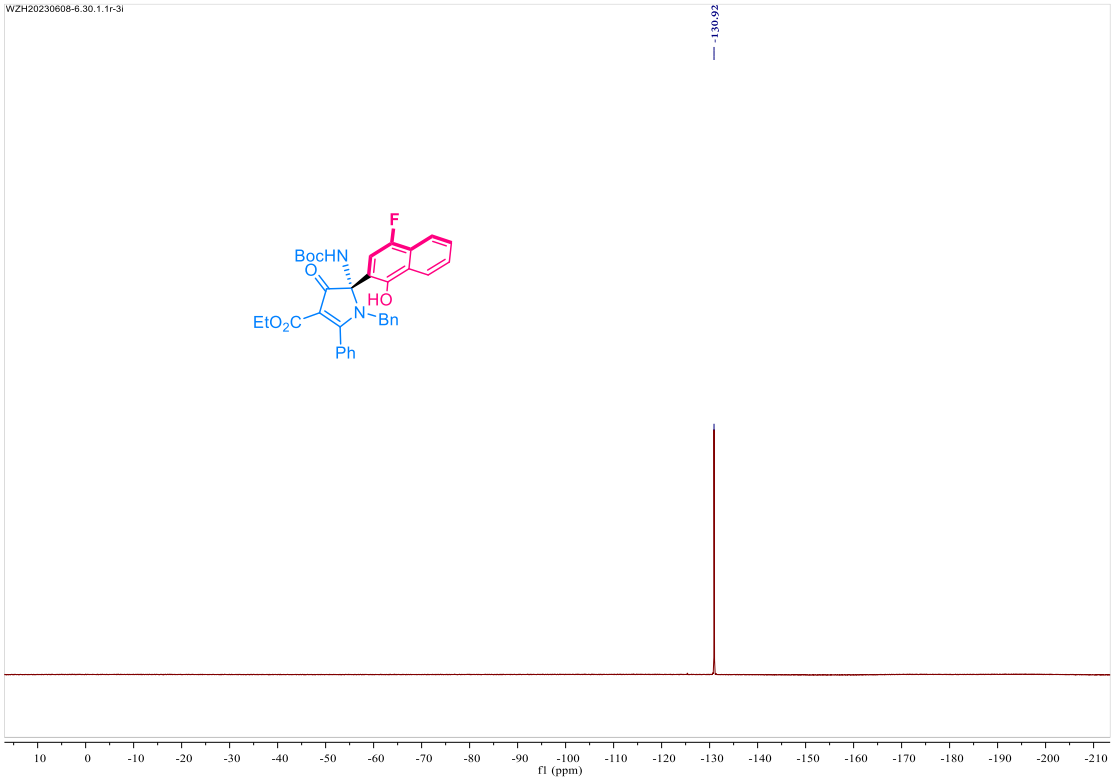
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



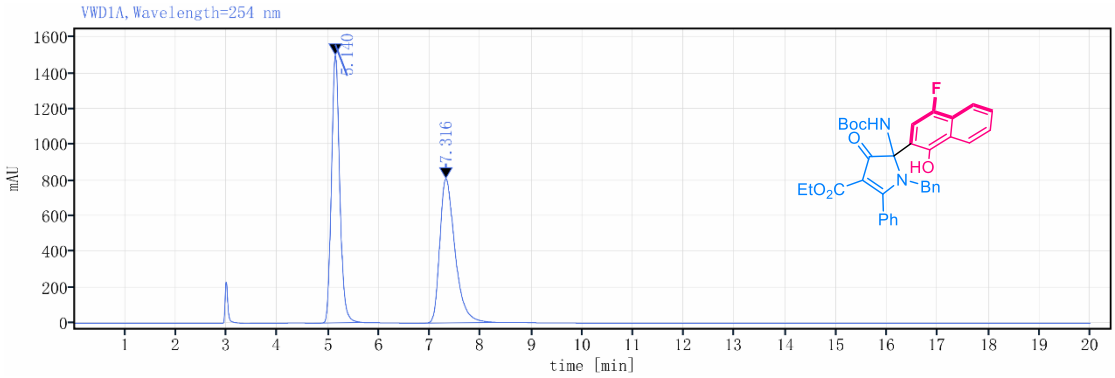
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



^{19}F NMR (377 MHz, $CDCl_3$) of **3ae**

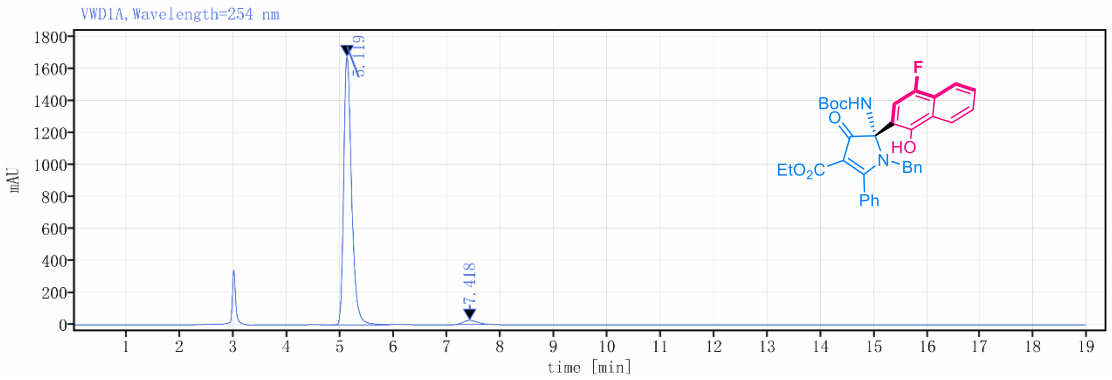


HPLC spectra of **3ae**



Detector VWD1A, Wavelength=254 nm

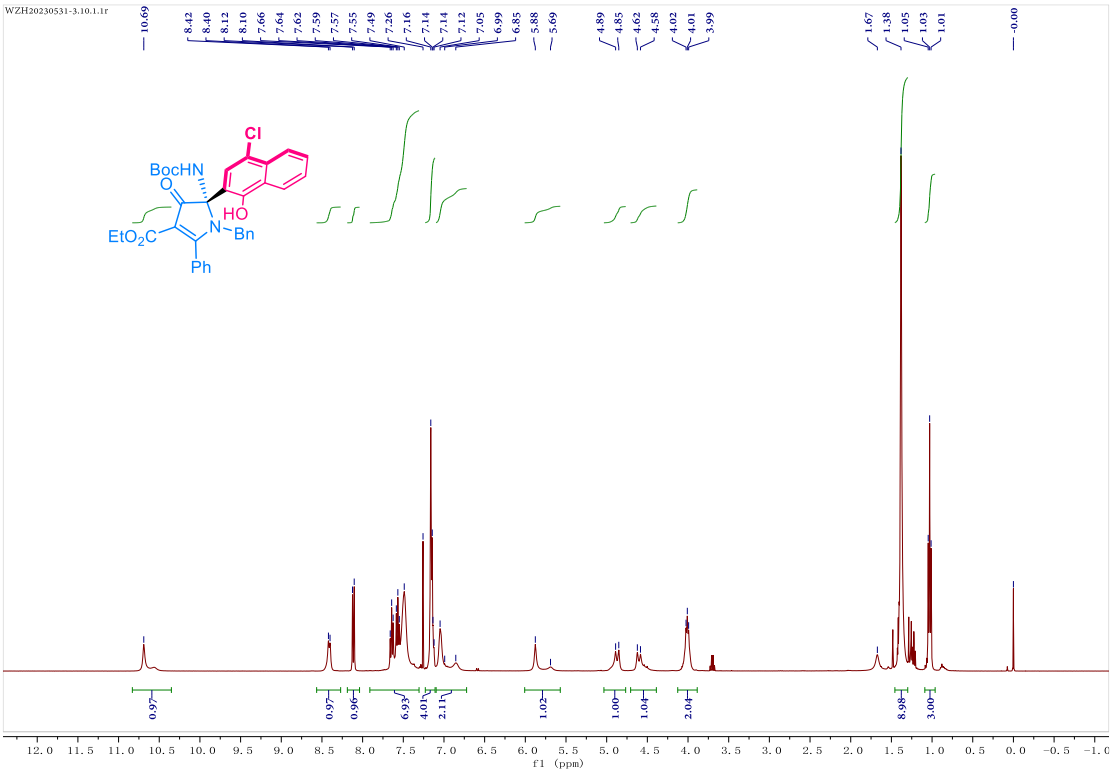
Peak	Ret.Time [min]	Area	Height	Area%
	5.140	16927.70	1499.32	50.25
	7.316	16761.96	806.76	49.75
		33689.66		100.00



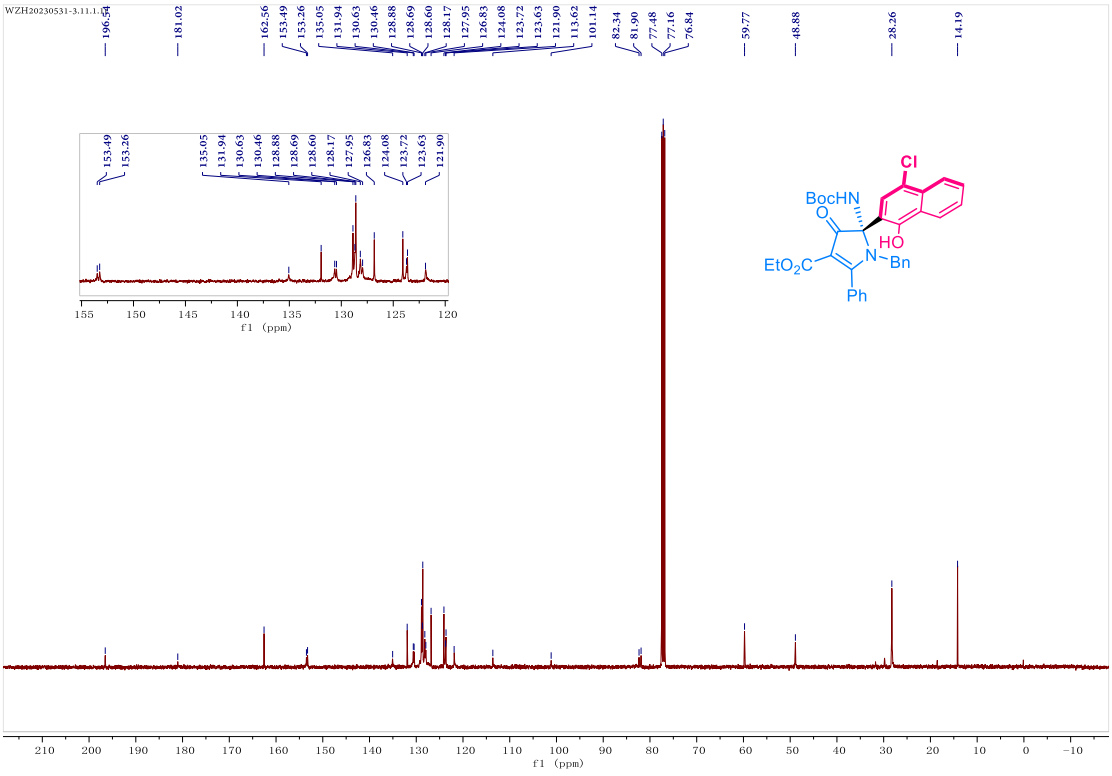
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.119	17258.25	1673.25	97.26
	7.418	486.70	26.47	2.74
		17744.95		100.00

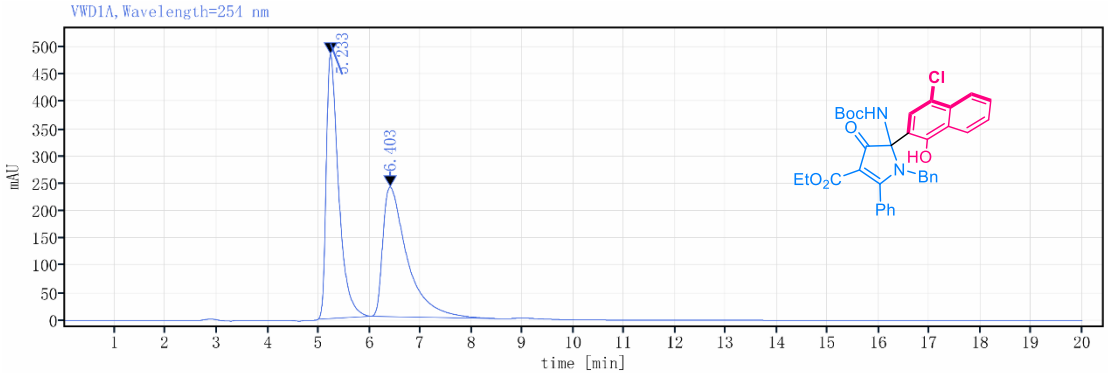
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



^{13}C NMR (101 MHz, $CDCl_3$) of **3af**

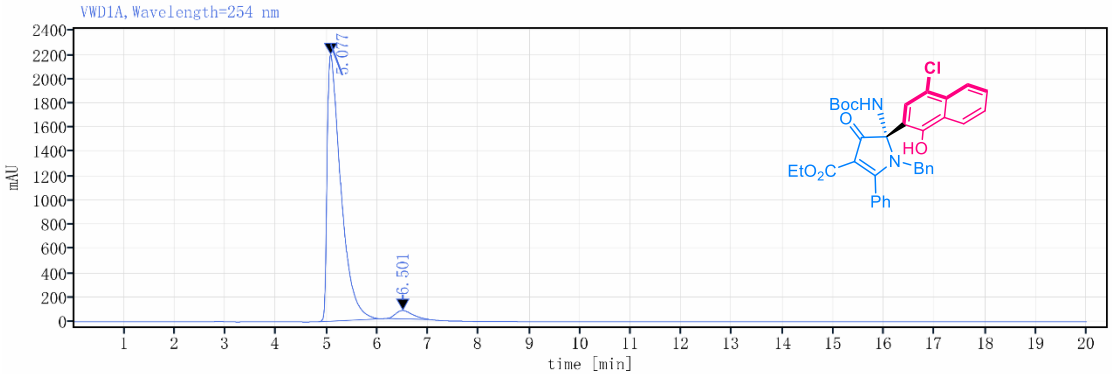


HPLC spectra of **3af**



Detector VWD1A, Wavelength=254 nm

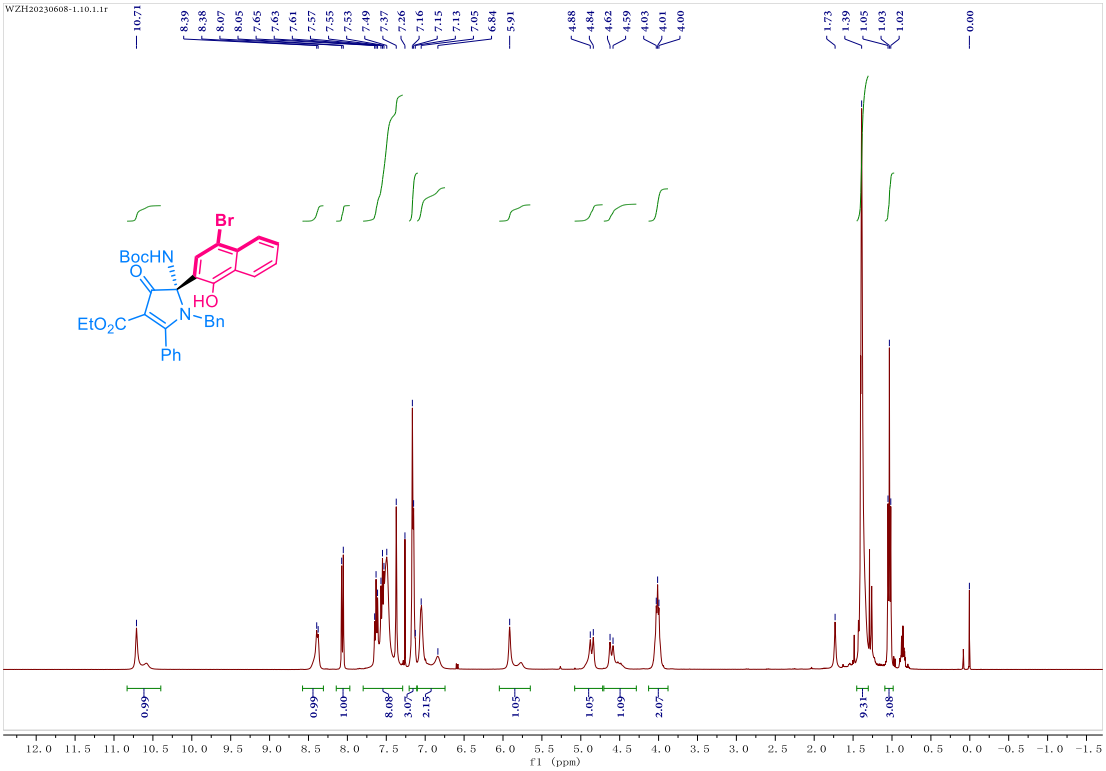
Peak	Ret.Time [min]	Area	Height	Area%
	5.233	8144.16	484.10	50.81
	6.403	7884.76	237.45	49.19
		16028.92		100.00



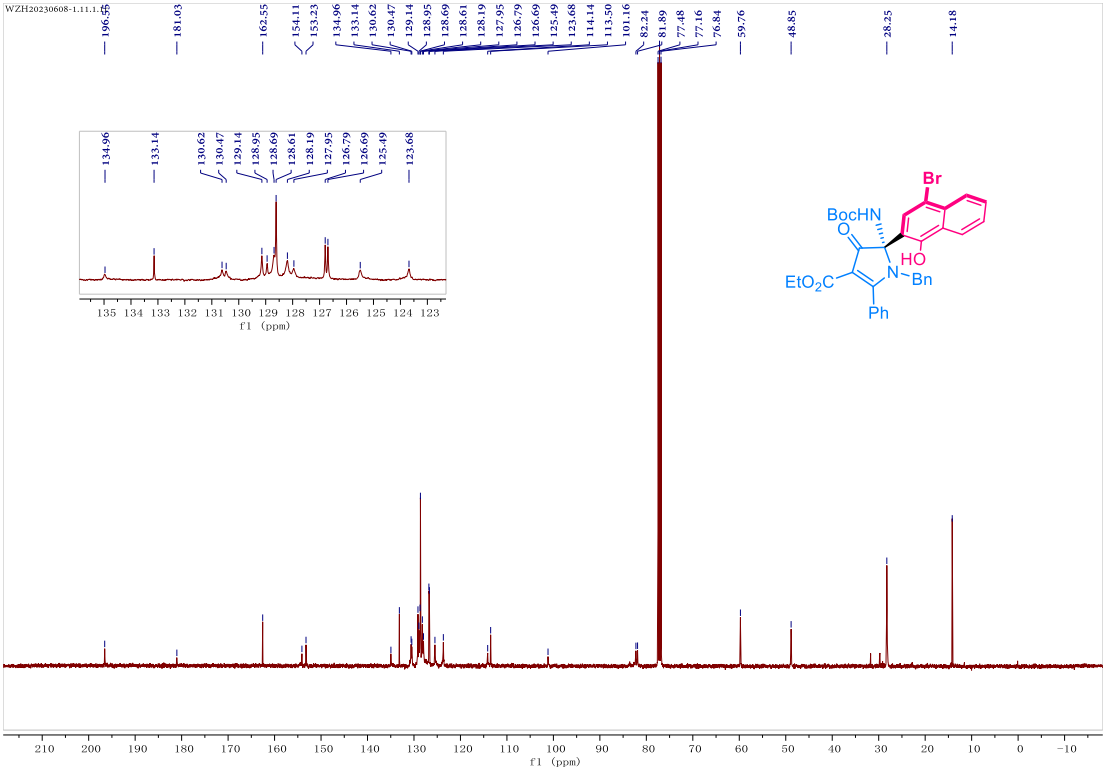
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.077	41423.25	2198.07	96.30
	6.501	1591.74	68.93	3.70
		43014.98		100.00

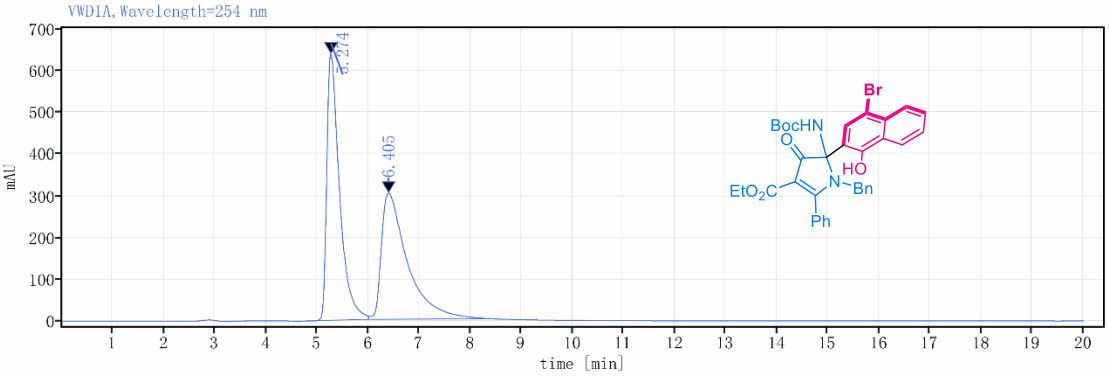
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**

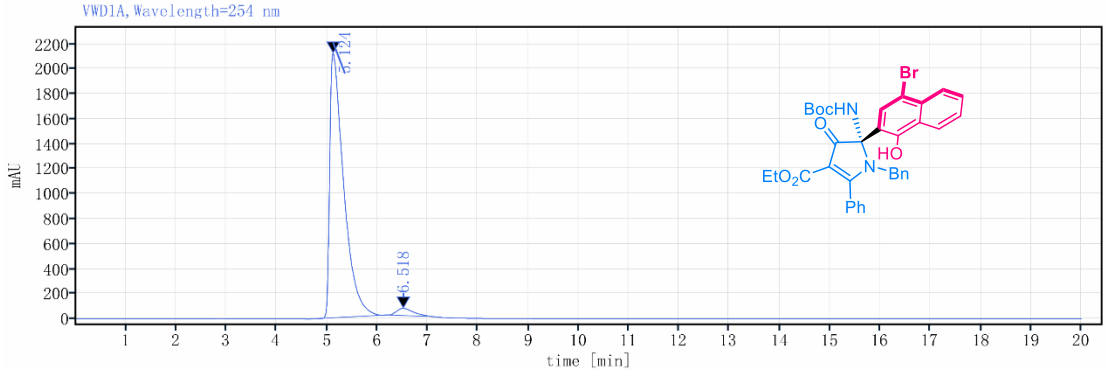


HPLC spectra of **3ag**



Detector VWD1A, Wavelength=254 nm

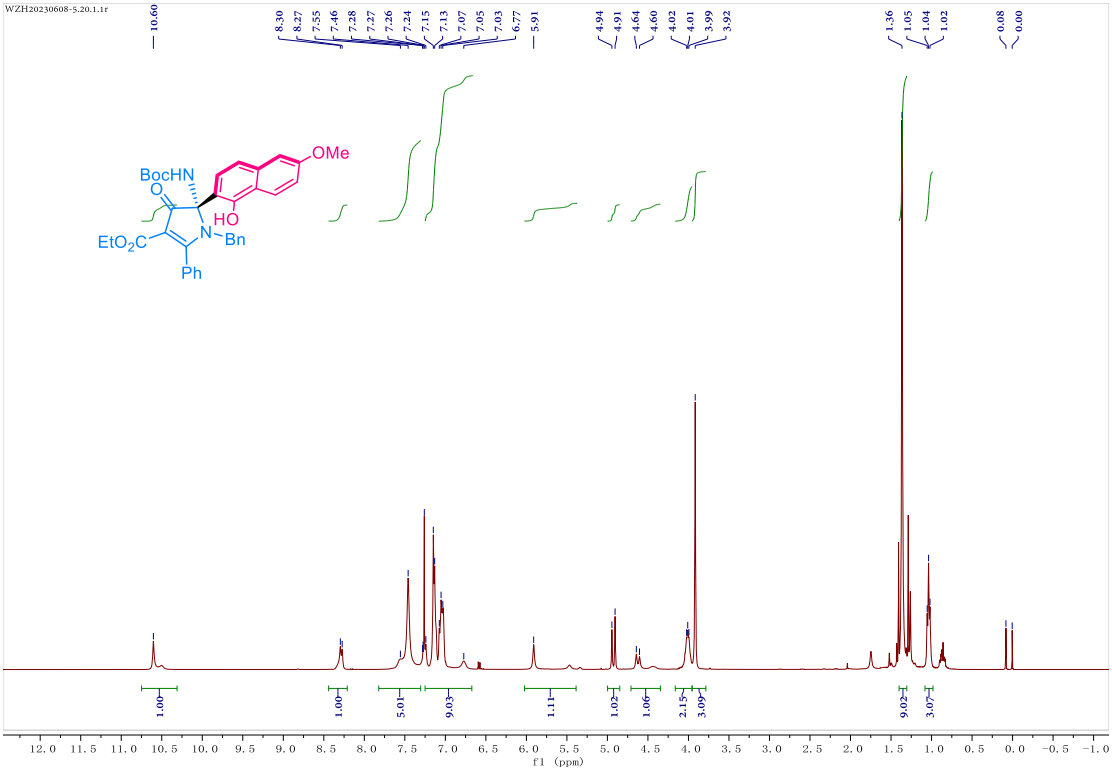
Peak	Ret.Time [min]	Area	Height	Area%
	5.274	11081.80	640.78	50.77
	6.405	10744.14	303.37	49.23
		21825.94		100.00



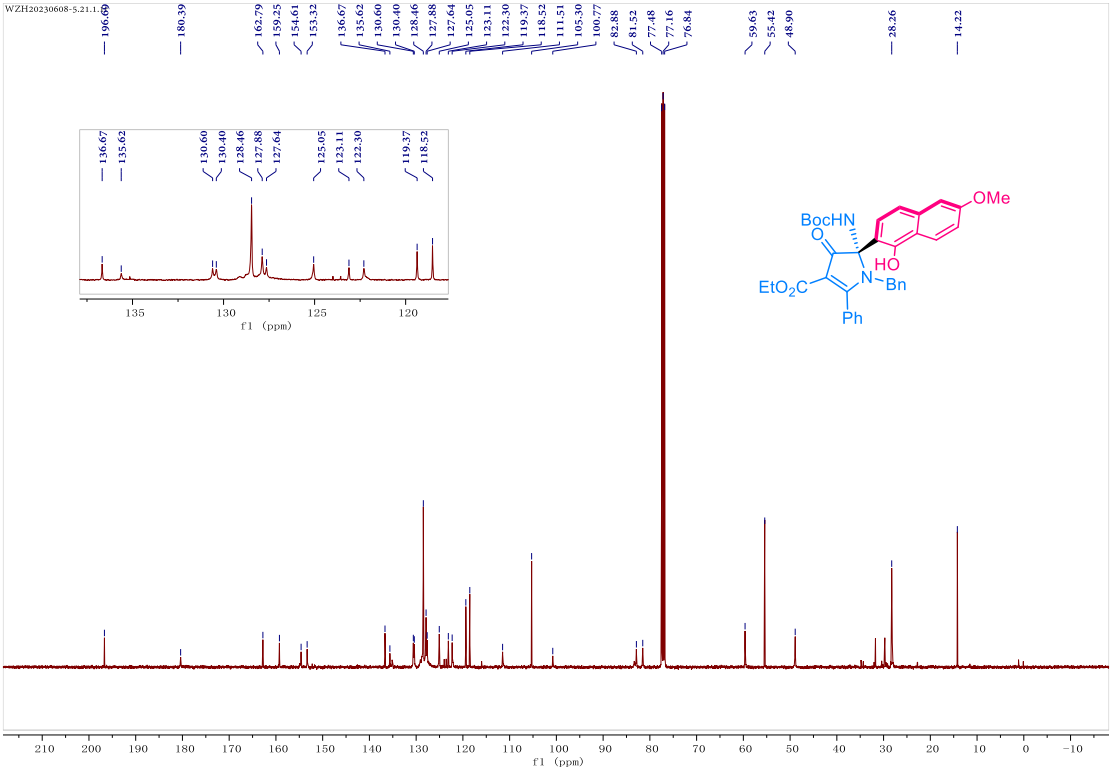
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.124	40886.46	2119.65	96.83
	6.518	1338.61	58.33	3.17
		42225.08		100.00

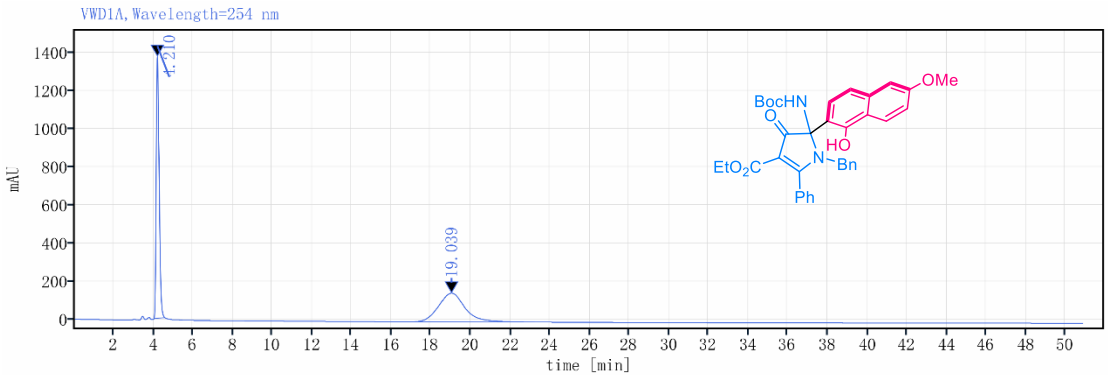
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**

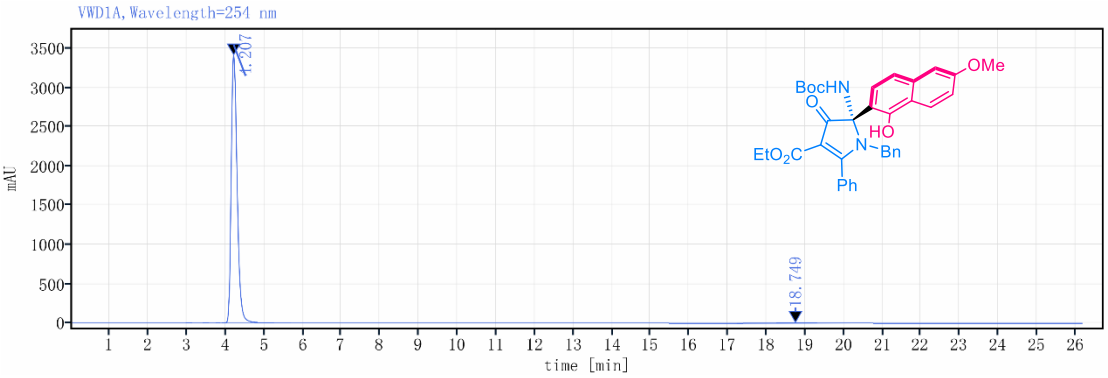


HPLC spectra of **3ah**



Detector VWD1A, Wavelength=254 nm

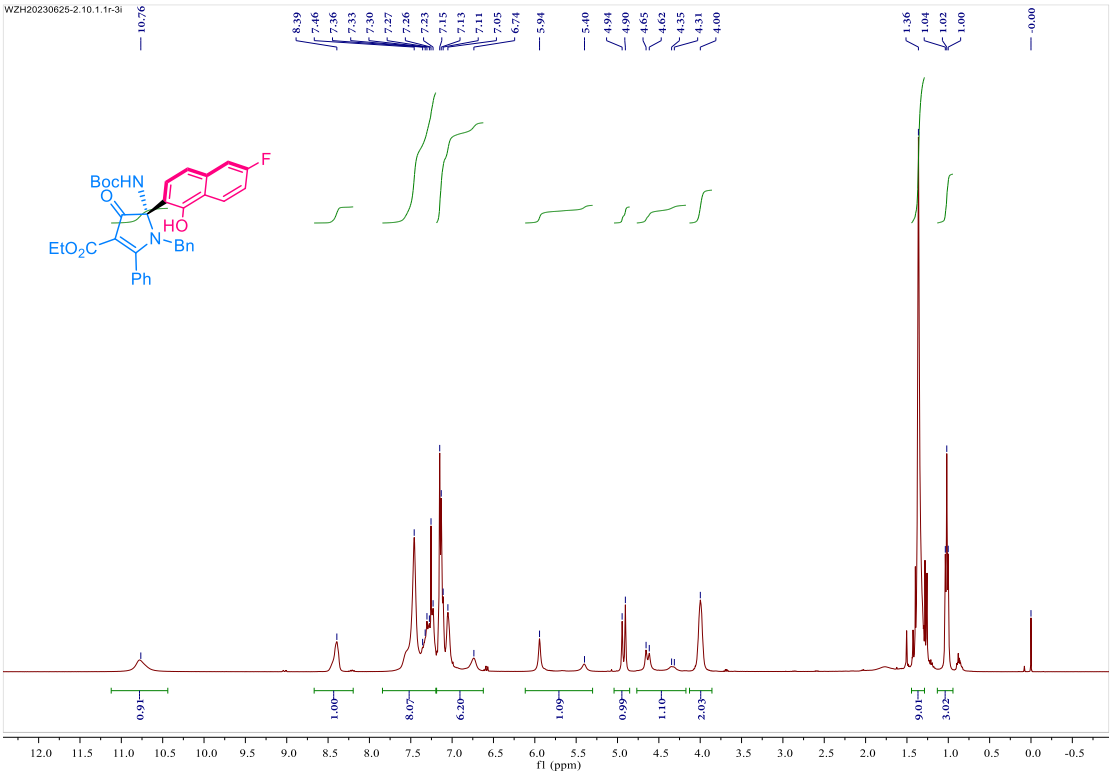
Peak	Ret.Time [min]	Area	Height	Area%
	4.210	14023.86	1376.05	50.07
	19.039	13983.85	150.68	49.93
		28007.72		100.00



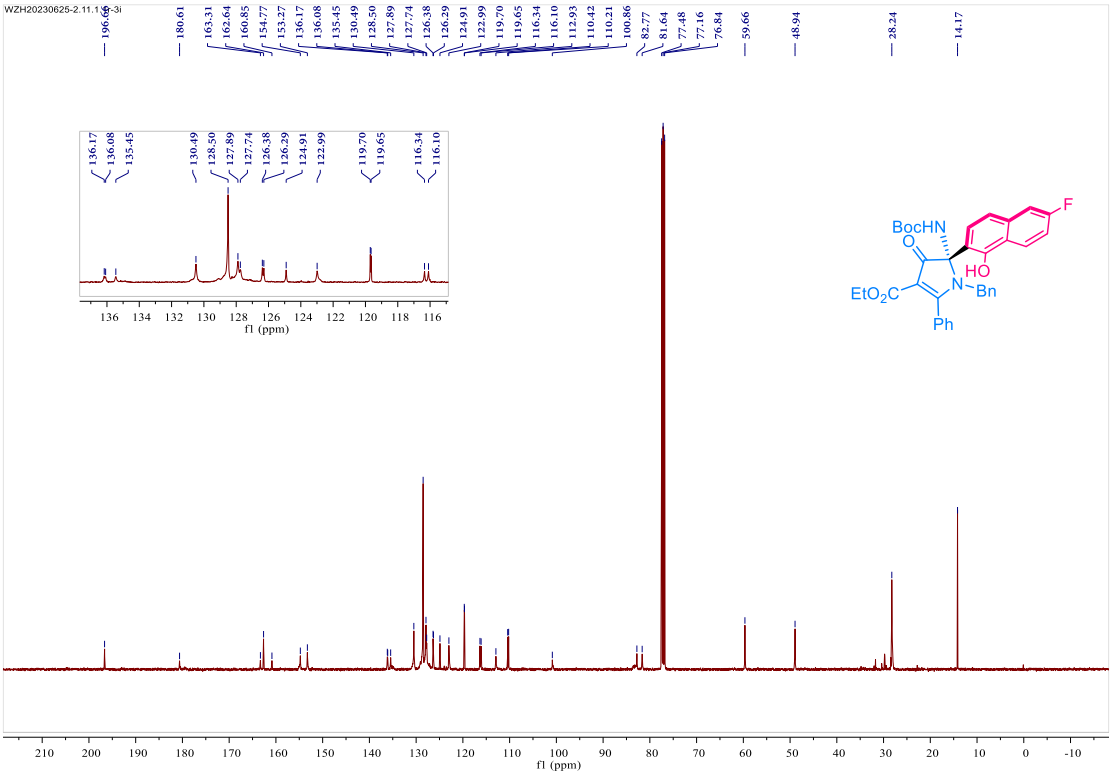
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	4.207	36766.47	3418.14	98.77
	18.749	459.29	5.12	1.23
		37225.77		100.00

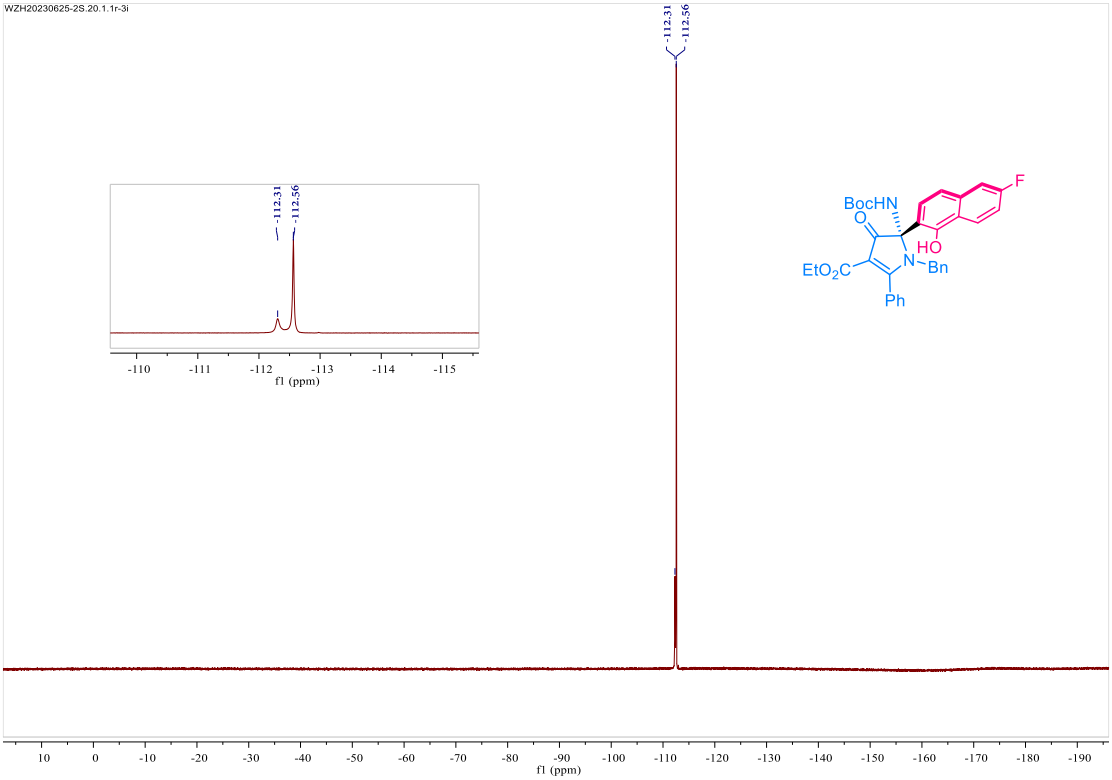
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



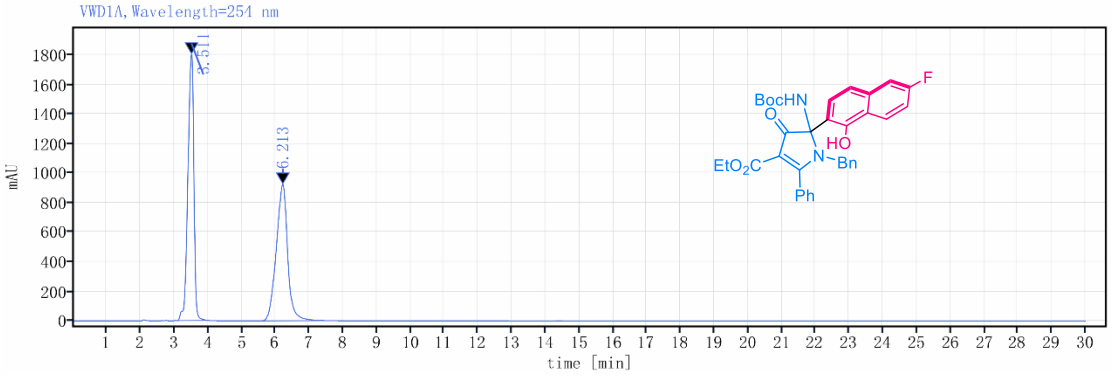
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



^{19}F NMR (377 MHz, $CDCl_3$) of **3ai**

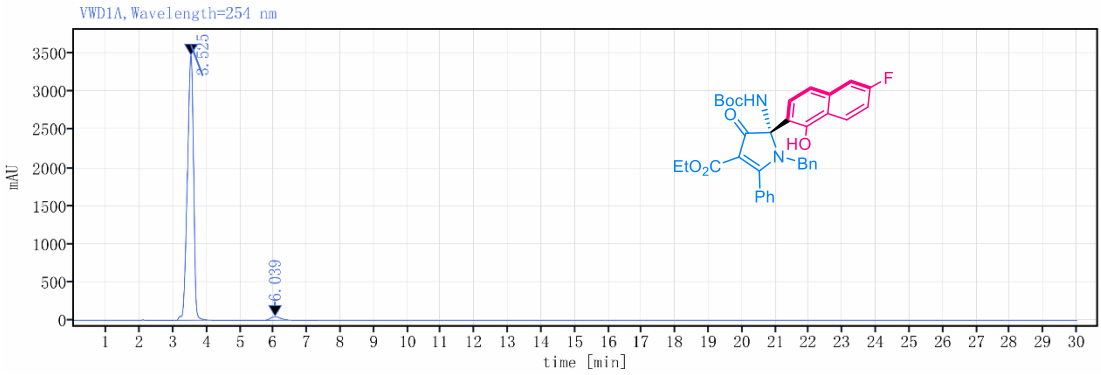


HPLC spectra of **3ai**



Detector VWD1A, Wavelength=254 nm

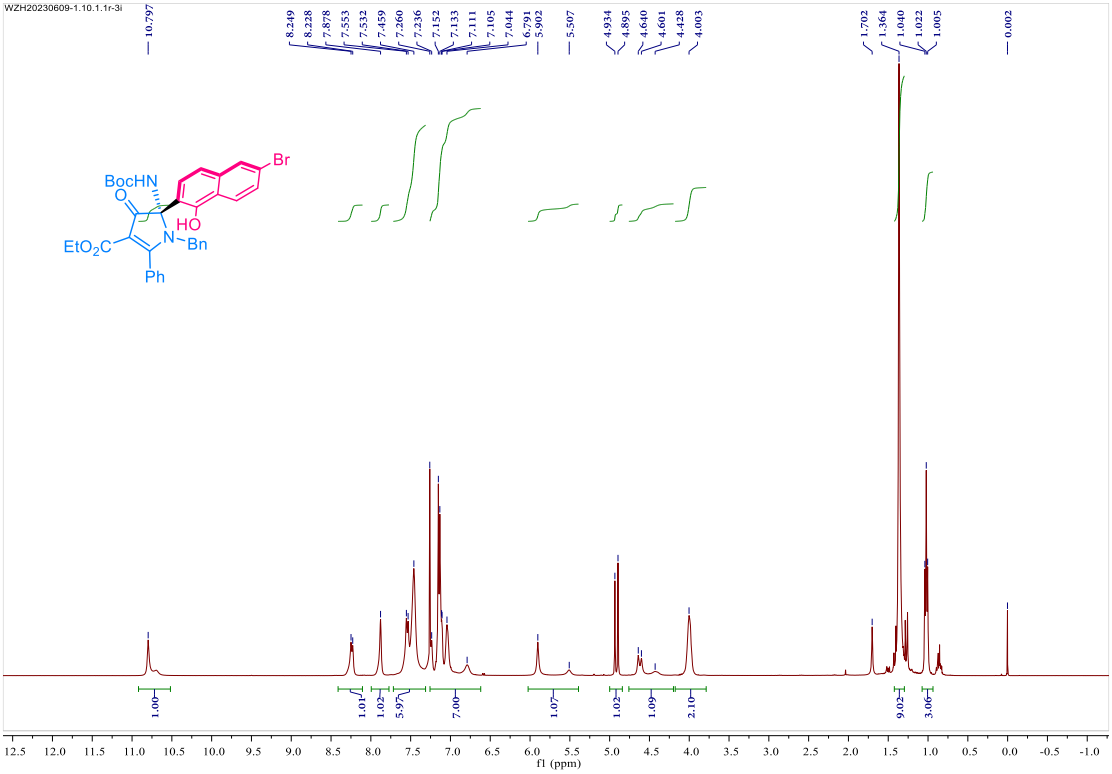
Peak	Ret.Time [min]	Area	Height	Area%
	3.511	22308.98	1804.44	50.85
	6.213	21565.70	925.02	49.15
		43874.69		100.00



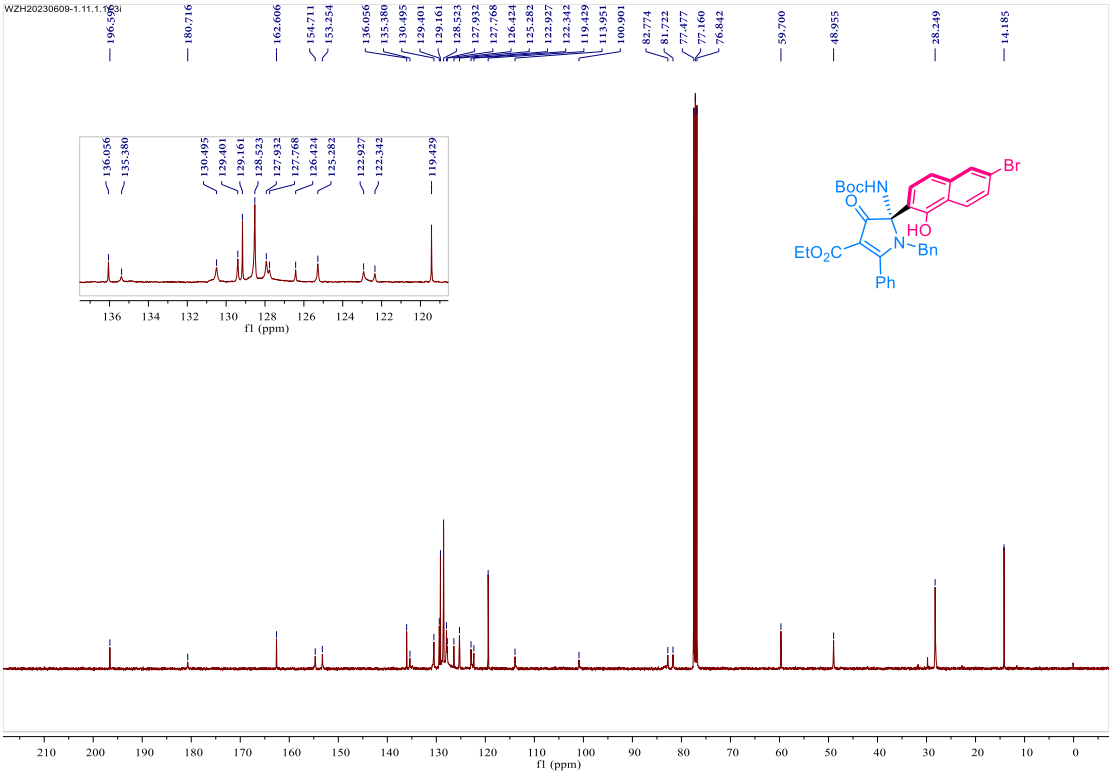
Detector VWD1A,Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	3.525	44708.17	3472.03	97.85
	6.039	983.84	47.49	2.15
		45692.01		100.00

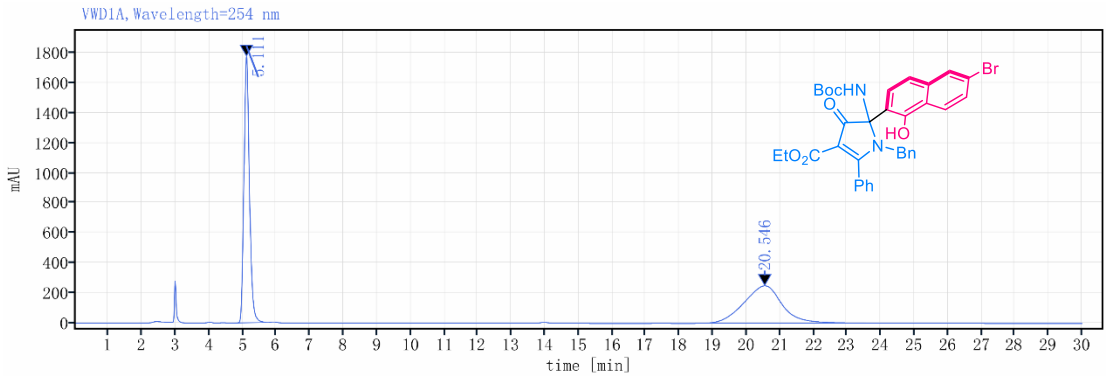
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**

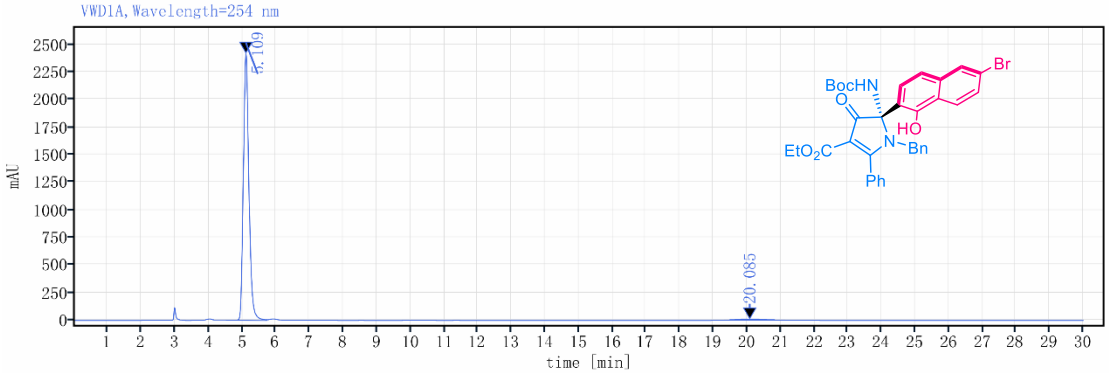


HPLC spectra of **3aj**



Detector VWD1A, Wavelength=254 nm

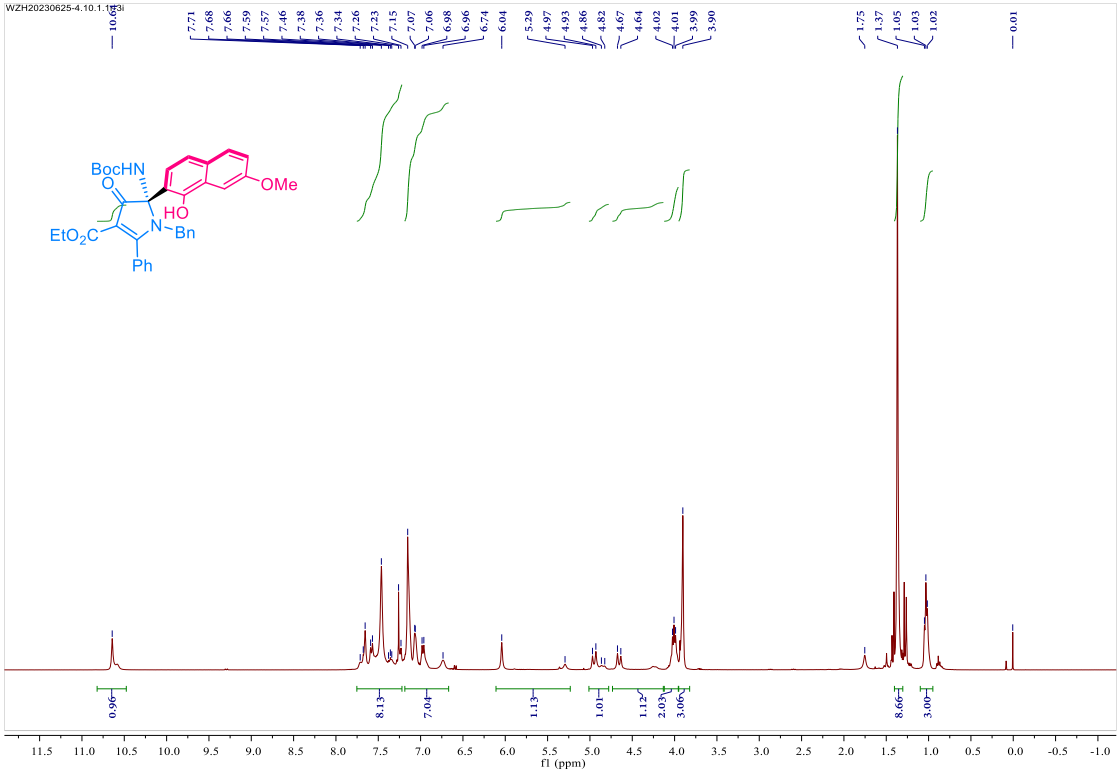
Peak	Ret.Time [min]	Area	Height	Area%
	5.111	20216.36	1772.52	50.41
	20.546	19890.87	249.28	49.59
		40107.23		100.00



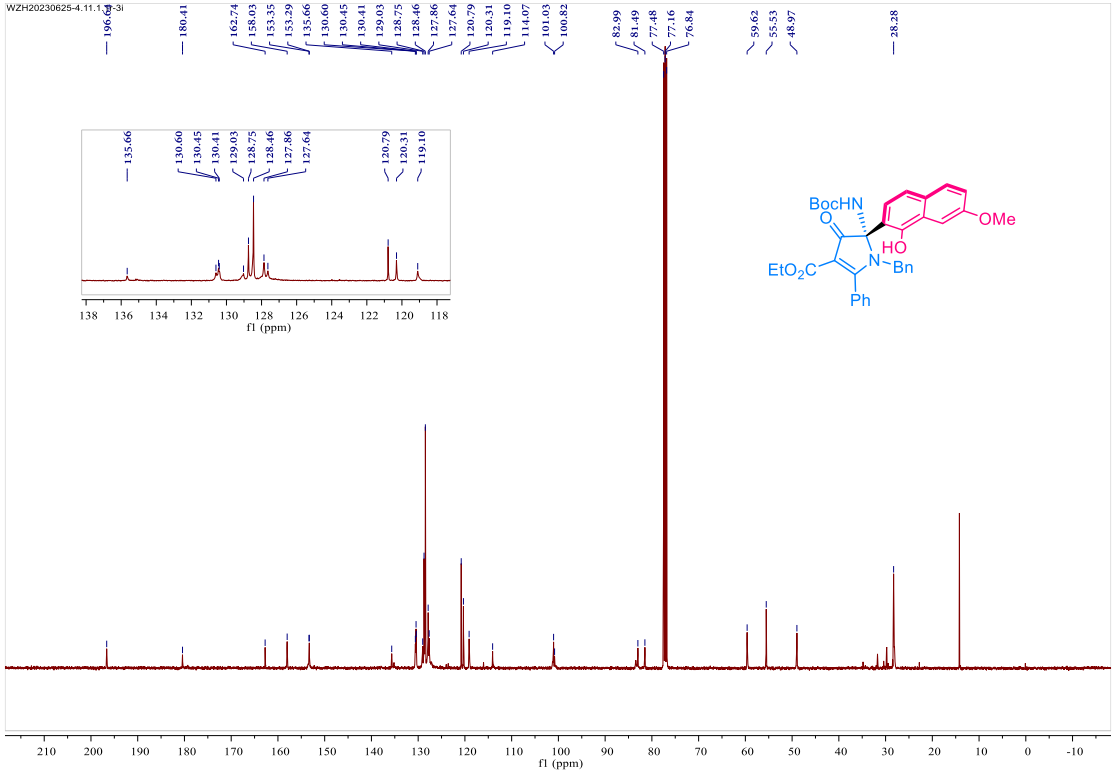
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.109	27671.52	2417.97	97.80
	20.085	621.03	9.43	2.20
		28292.55		100.00

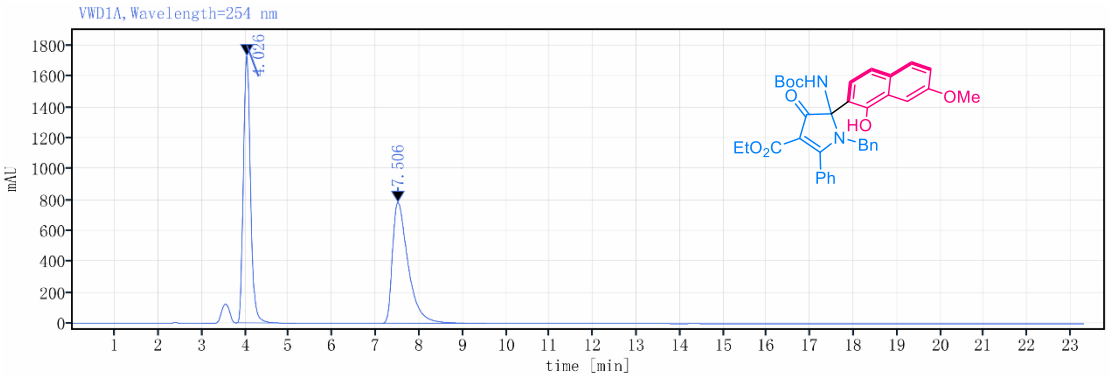
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**

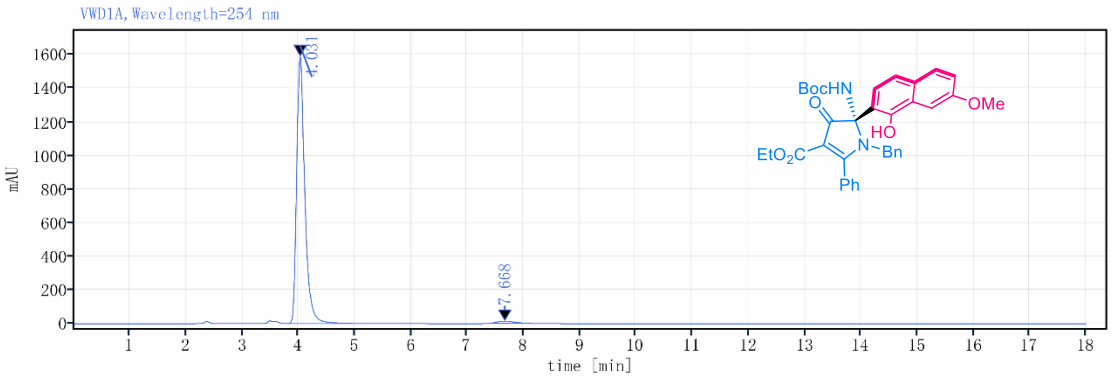


HPLC spectra of **3ak**



Detector VWD1A, Wavelength=254 nm

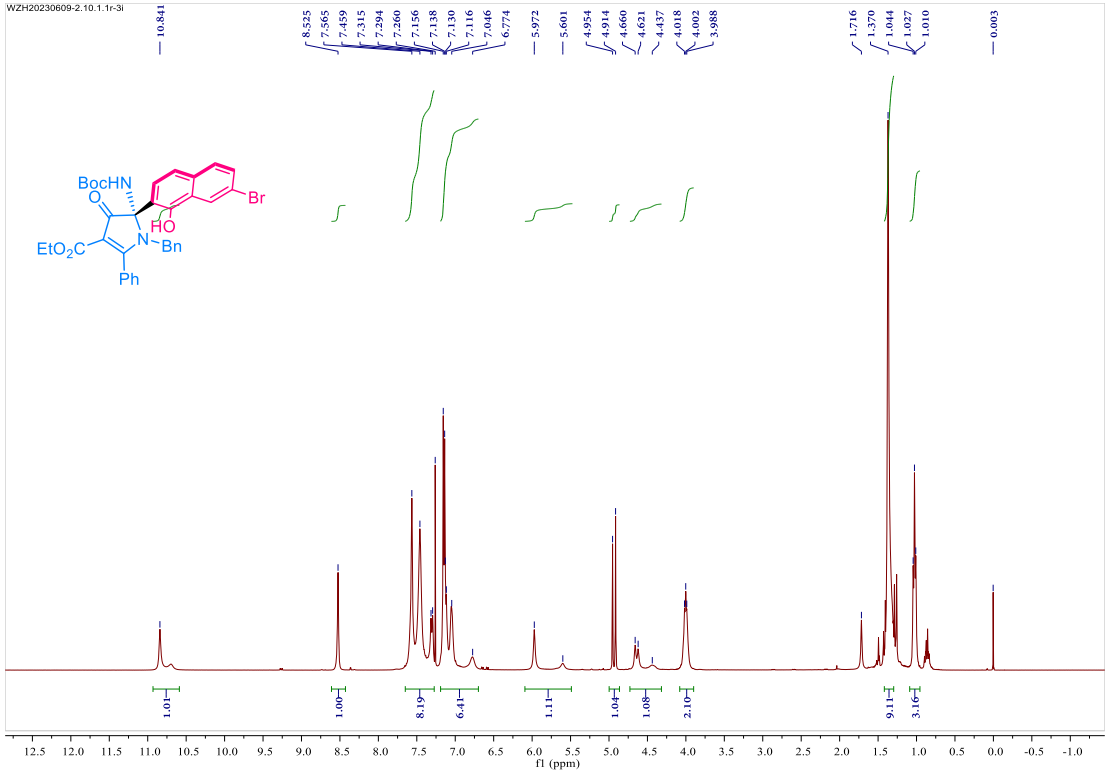
Peak	Ret.Time [min]	Area	Height	Area%
	4.026	19767.69	1730.05	50.08
	7.506	19705.24	784.78	49.92
		39472.92		100.00



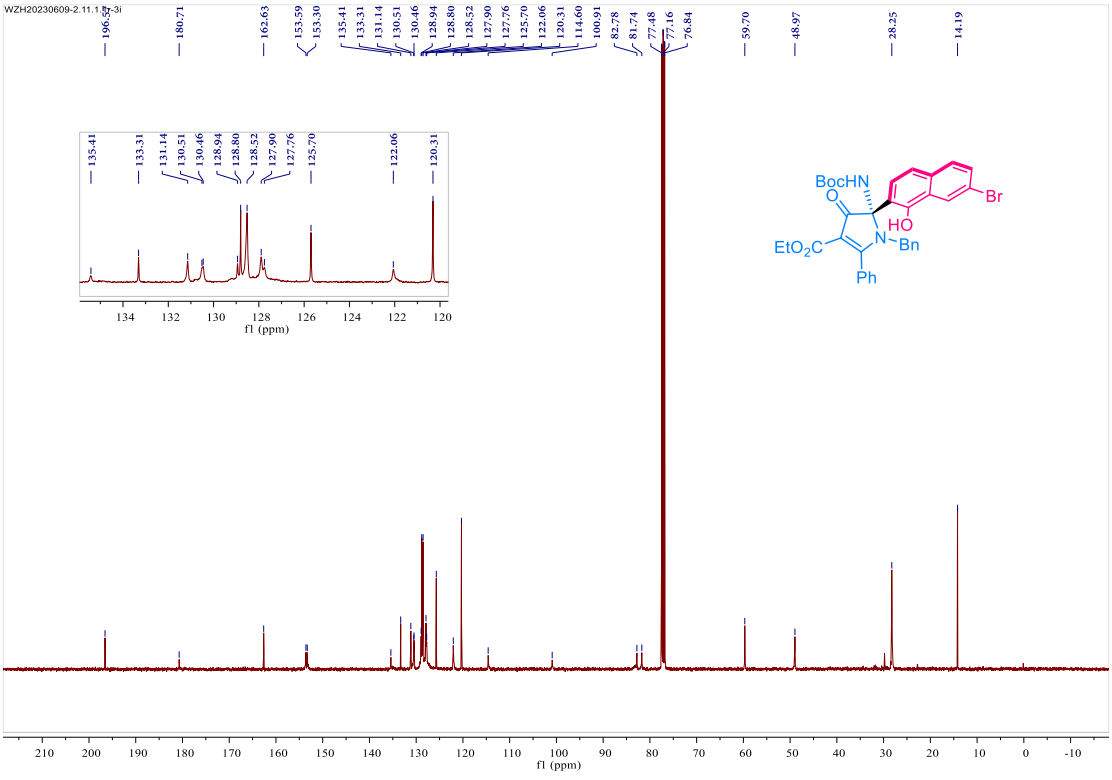
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	4.031	16008.26	1590.35	98.48
	7.668	246.33	12.48	1.52
		16254.59		100.00

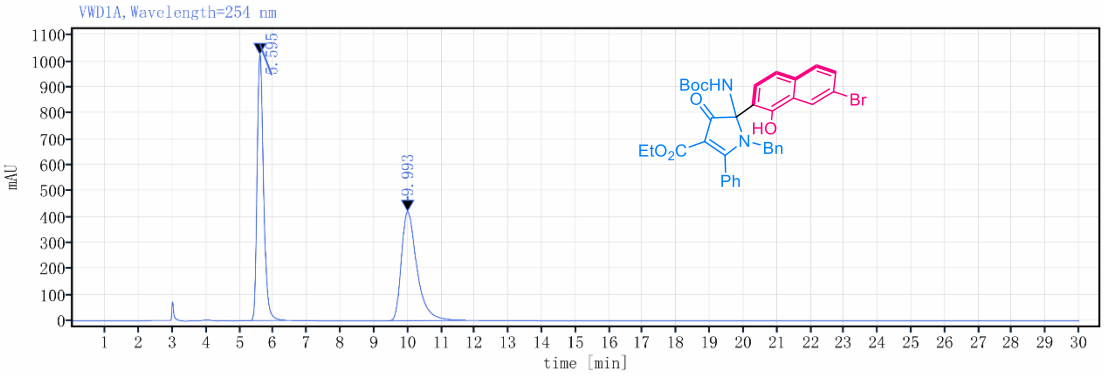
^{1}H NMR (400 MHz, $CDCl_3$) of **3al**



^{13}C NMR (101 MHz, $CDCl_3$) of **3al**

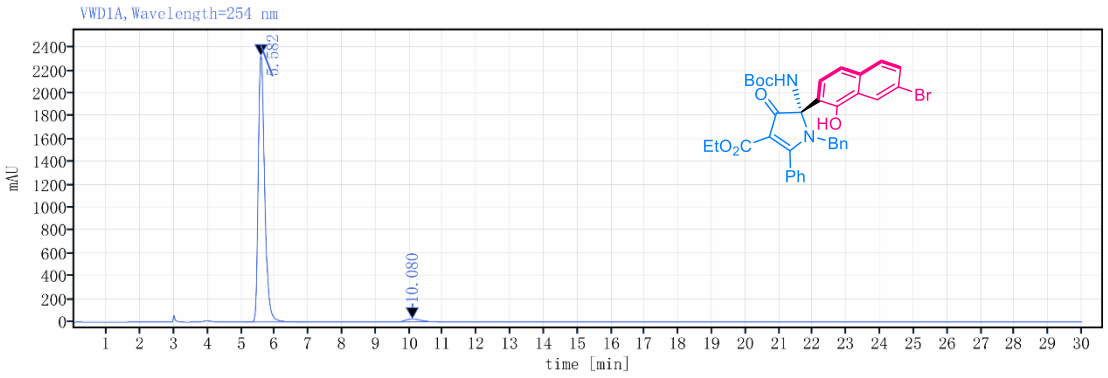


HPLC spectra of **3al**



Detector VWD1A, Wavelength=254 nm

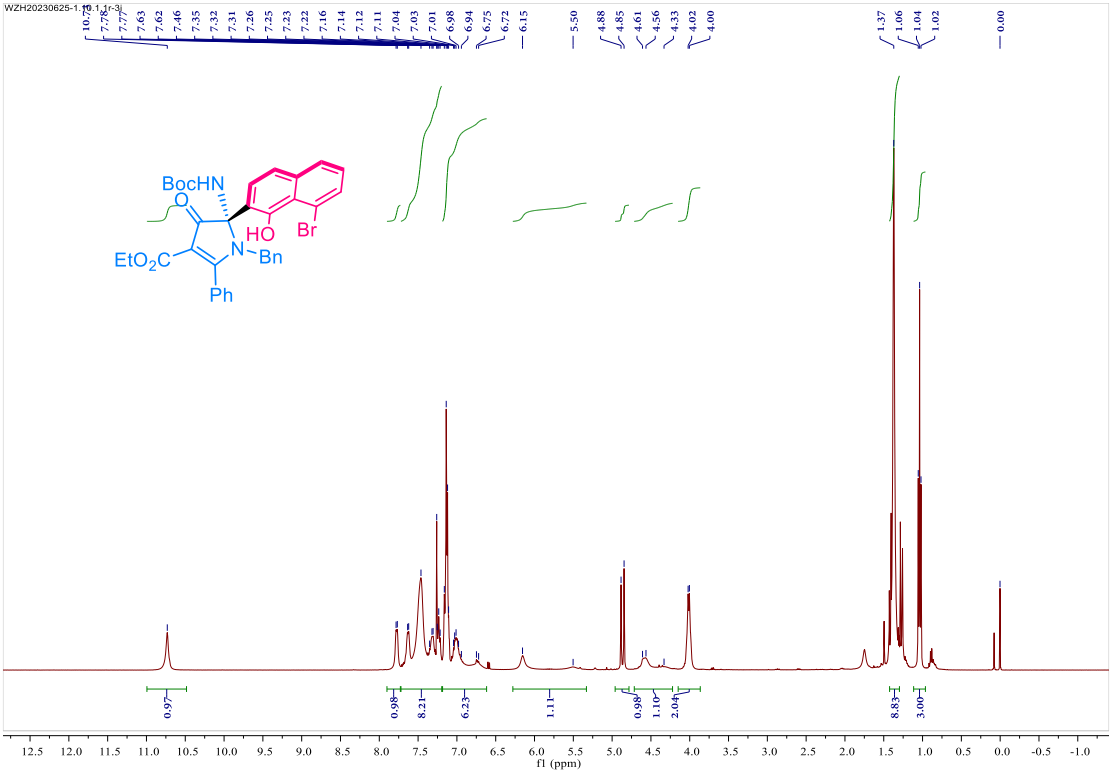
Peak	Ret.Time [min]	Area	Height	Area%
	5.595	13634.18	1026.47	50.11
	9.993	13572.04	421.15	49.89
		27206.21		100.00



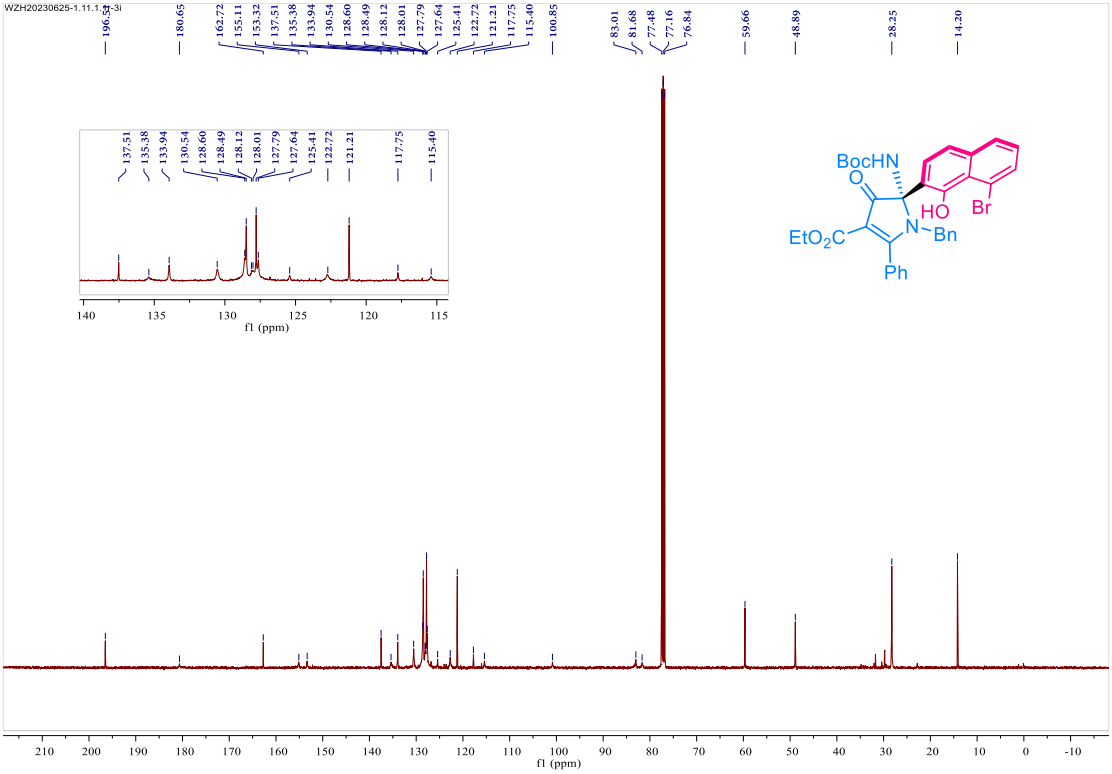
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.582	30832.68	2327.54	97.39
	10.080	827.34	26.86	2.61
		31660.03		100.00

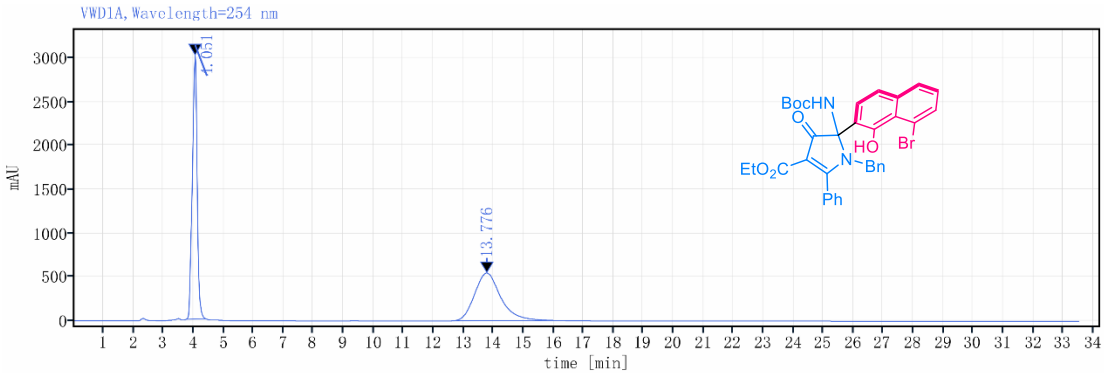
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



^{13}C NMR (101 MHz, $CDCl_3$) of **3am**

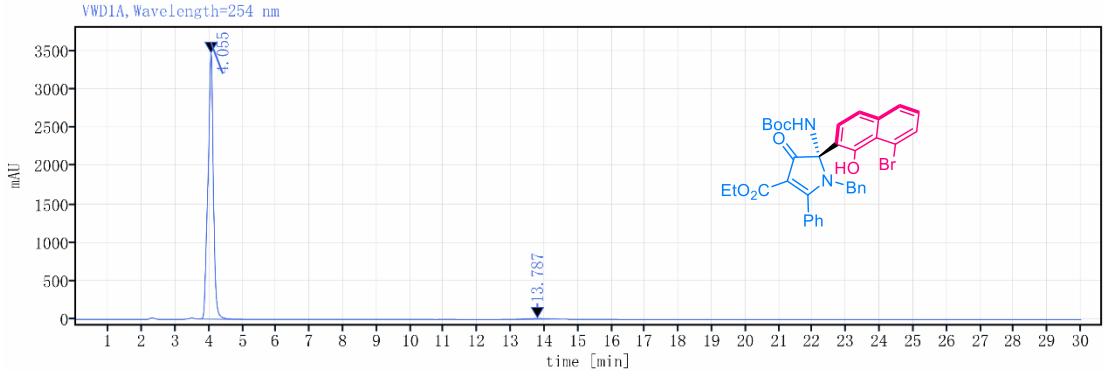


HPLC spectra of **3am**



Detector VWD1A, Wavelength=254 nm

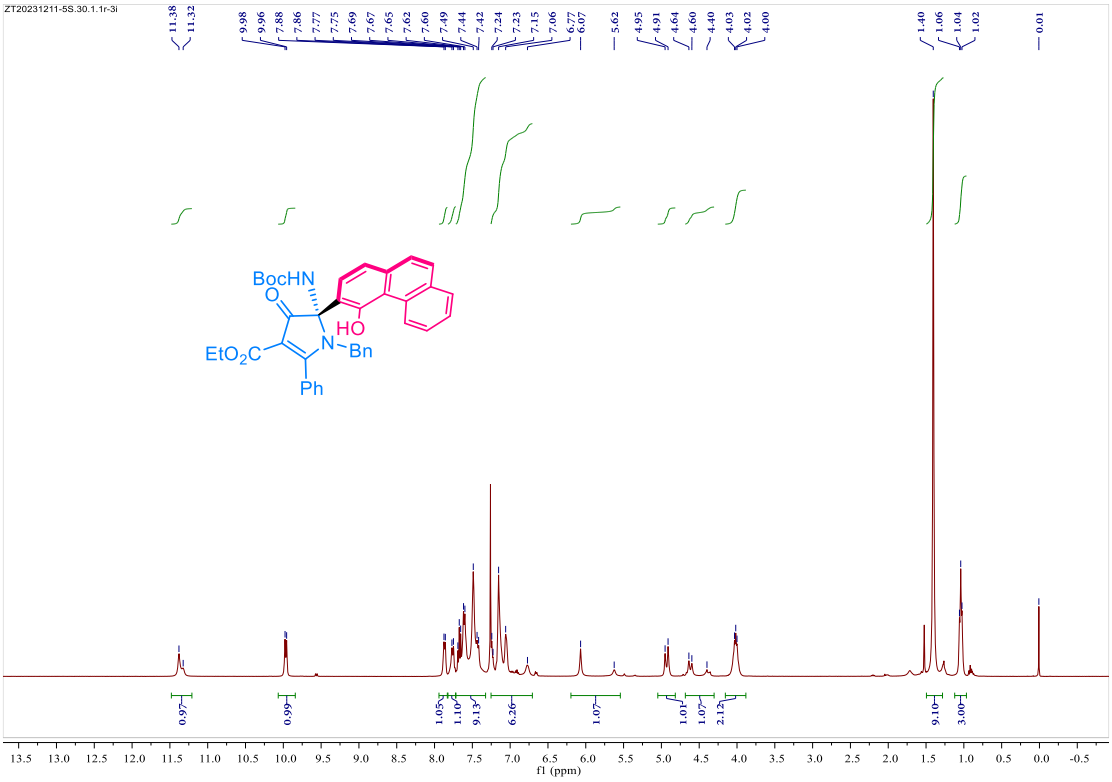
Peak	Ret.Time [min]	Area	Height	Area%
	4.051	33611.82	3015.48	50.42
	13.776	33058.31	544.89	49.58
		66670.13		100.00



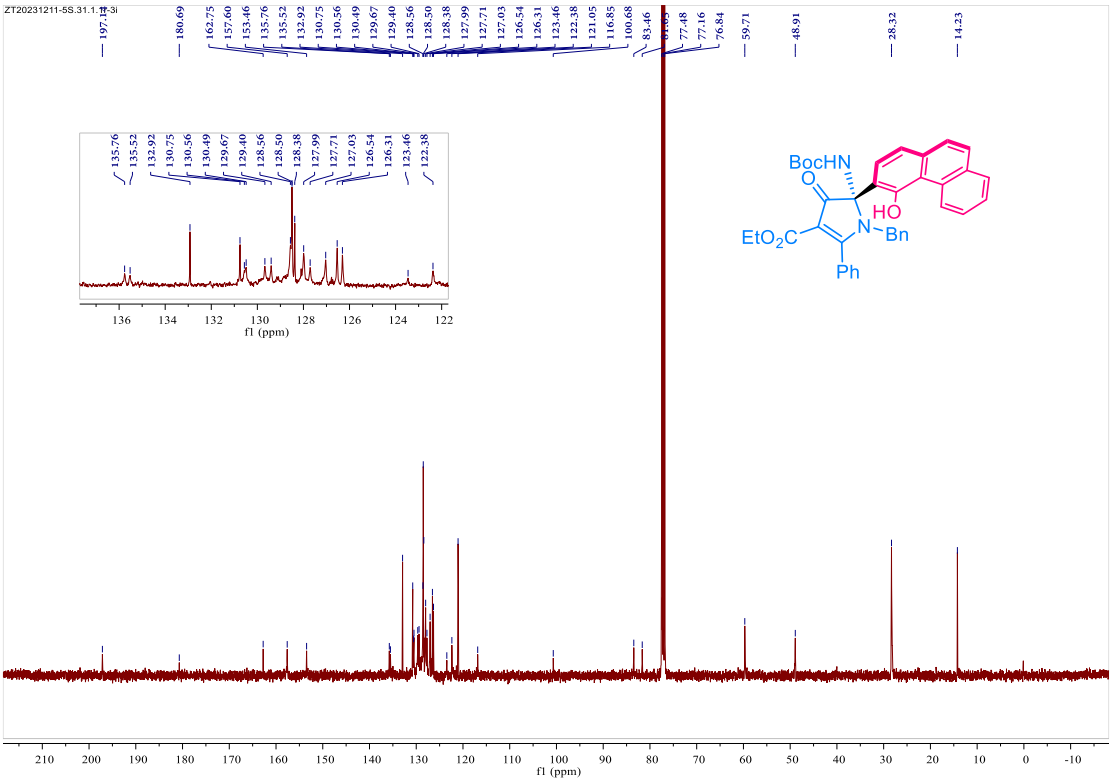
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	4.055	39118.22	3468.19	98.93
	13.787	423.69	9.29	1.07
		39541.91		100.00

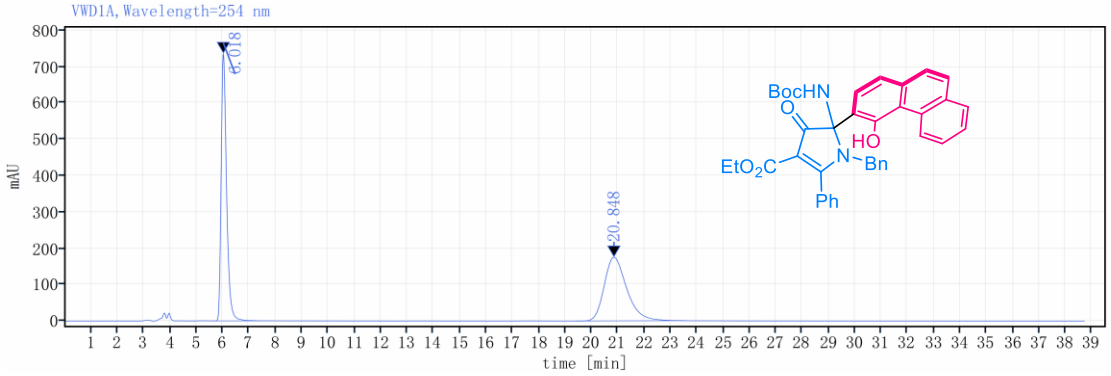
^{1}H NMR (400 MHz, $CDCl_3$) of **3an**



^{13}C NMR (101 MHz, $CDCl_3$) of **3an**

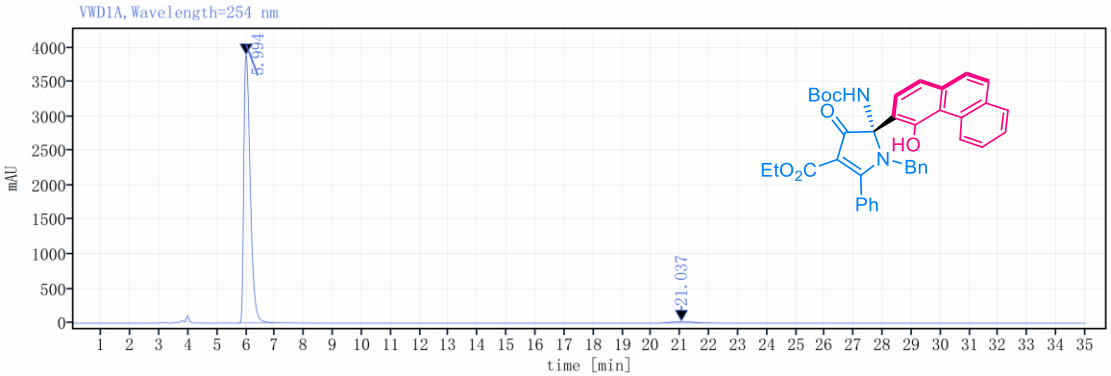


HPLC spectra of **3an**



Detector VWD1A, Wavelength=254 nm

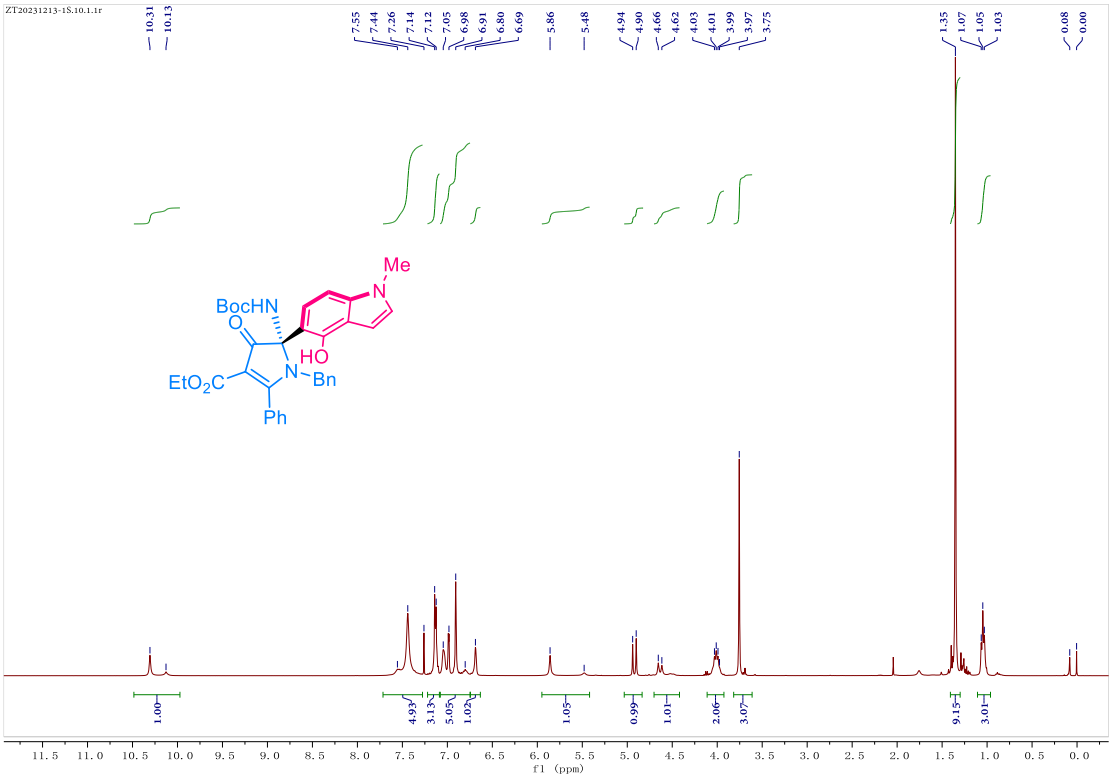
Peak	Ret.Time [min]	Area	Height	Area%
	6.018	10536.55	736.77	50.33
	20.848	10397.37	175.49	49.67
		20933.91		100.00



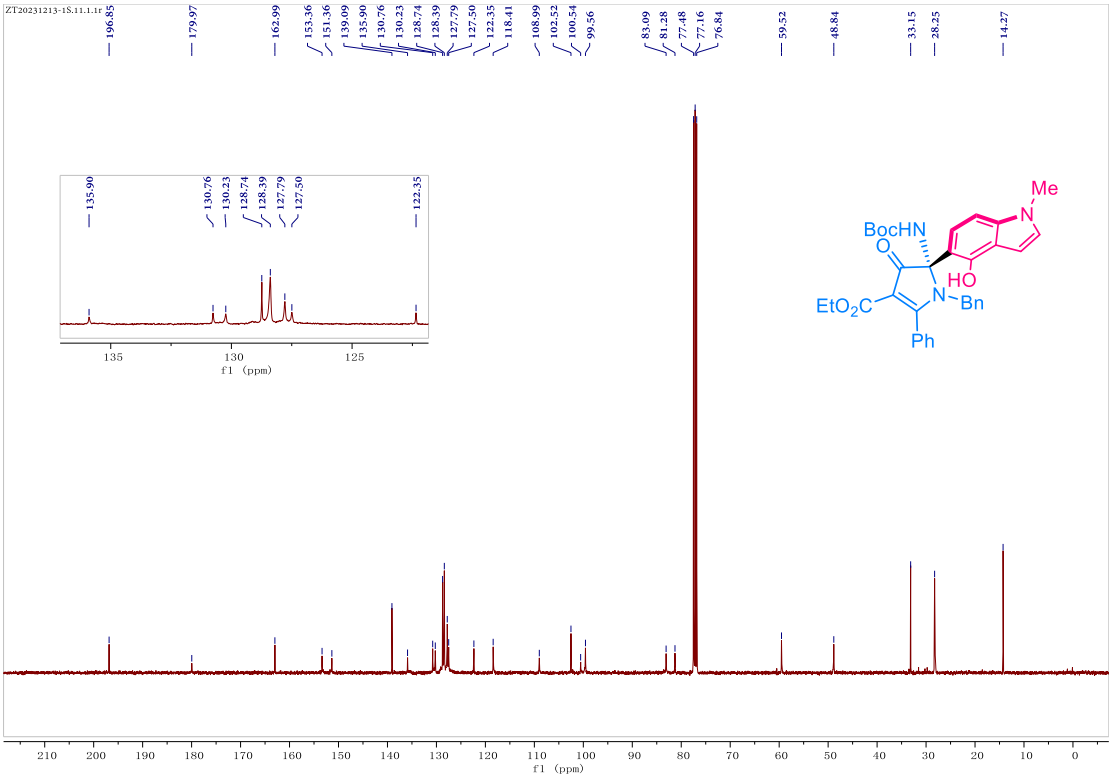
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.994	60372.05	3891.83	97.95
	21.037	1262.14	23.37	2.05
		61634.19		100.00

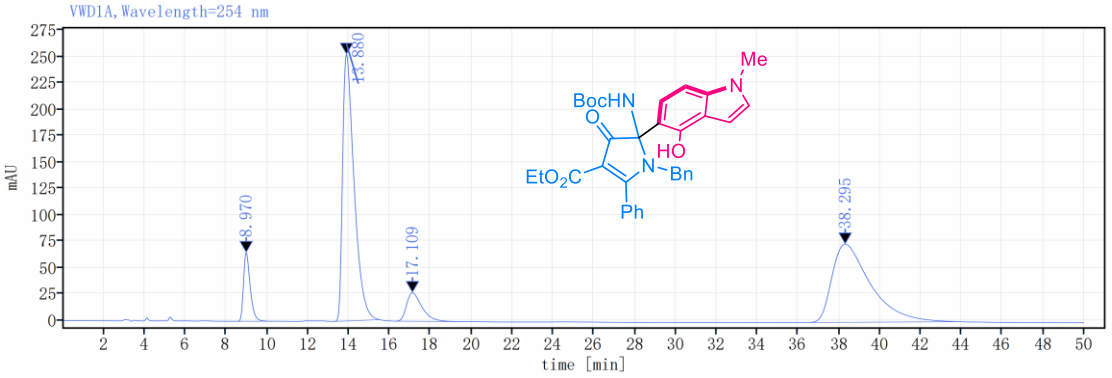
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ao**

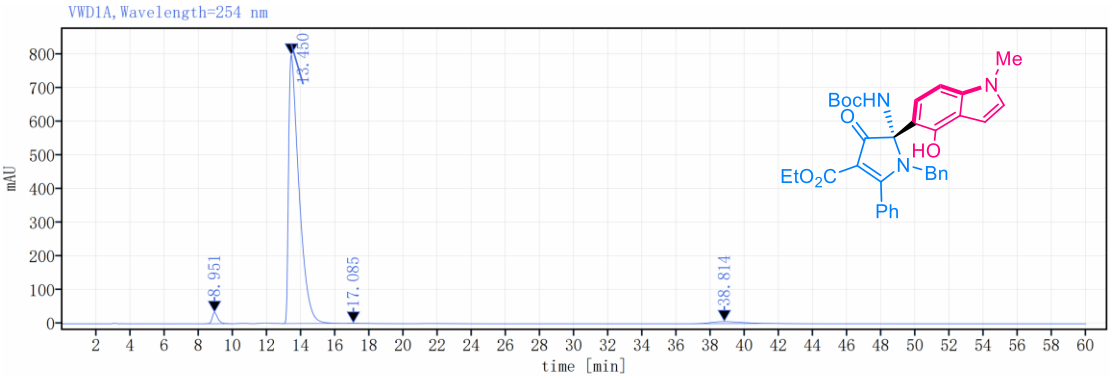


HPLC spectra of **3ao**



Detector VWD1A, Wavelength=254 nm

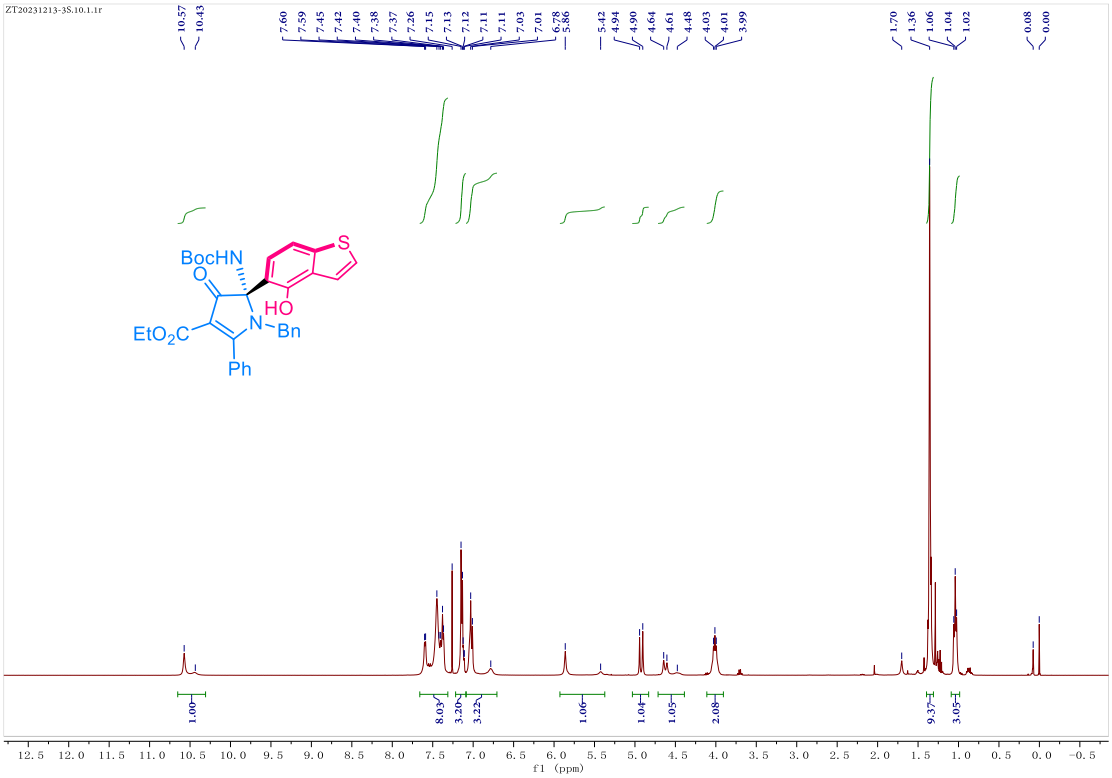
Peak	Ret.Time [min]	Area	Height	Area%
	8.970	1477.67	65.06	6.58
	13.880	9877.63	252.70	43.99
	17.109	1418.11	27.07	6.32
	38.295	9679.46	74.06	43.11
		22452.87		100.00



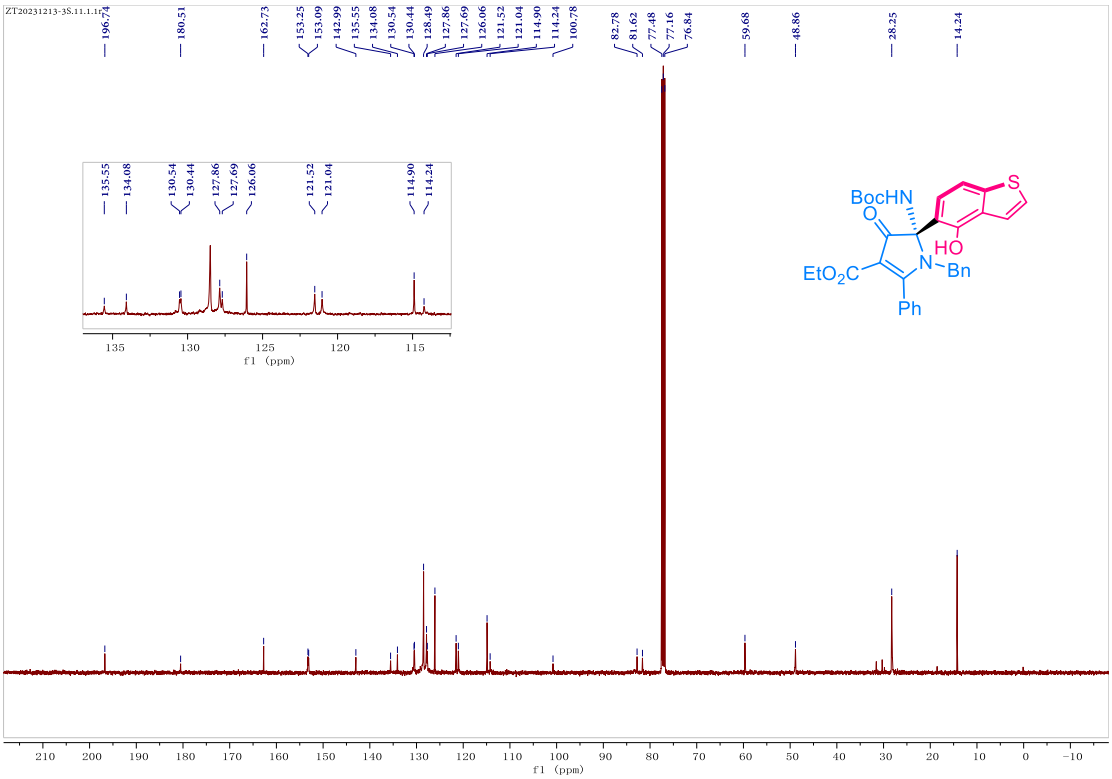
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	8.951	756.46	33.44	2.15
	13.450	33593.26	797.08	95.57
	17.085	33.56	0.76	0.10
	38.814	768.25	6.05	2.19
		35151.53		100.00

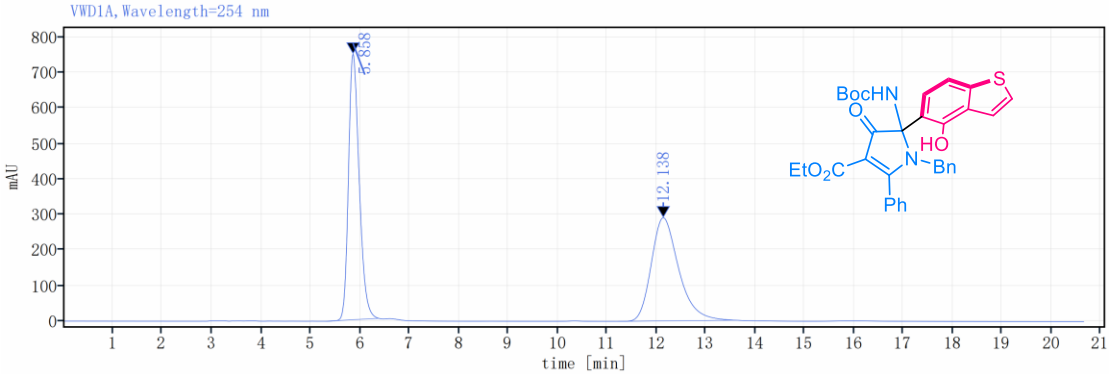
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ap**

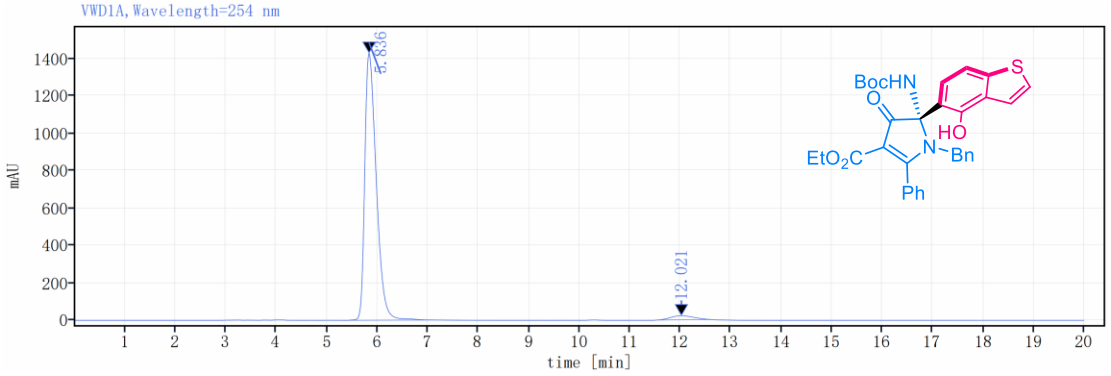


HPLC spectra of **3ap**



Detector VWD1A, Wavelength=254 nm

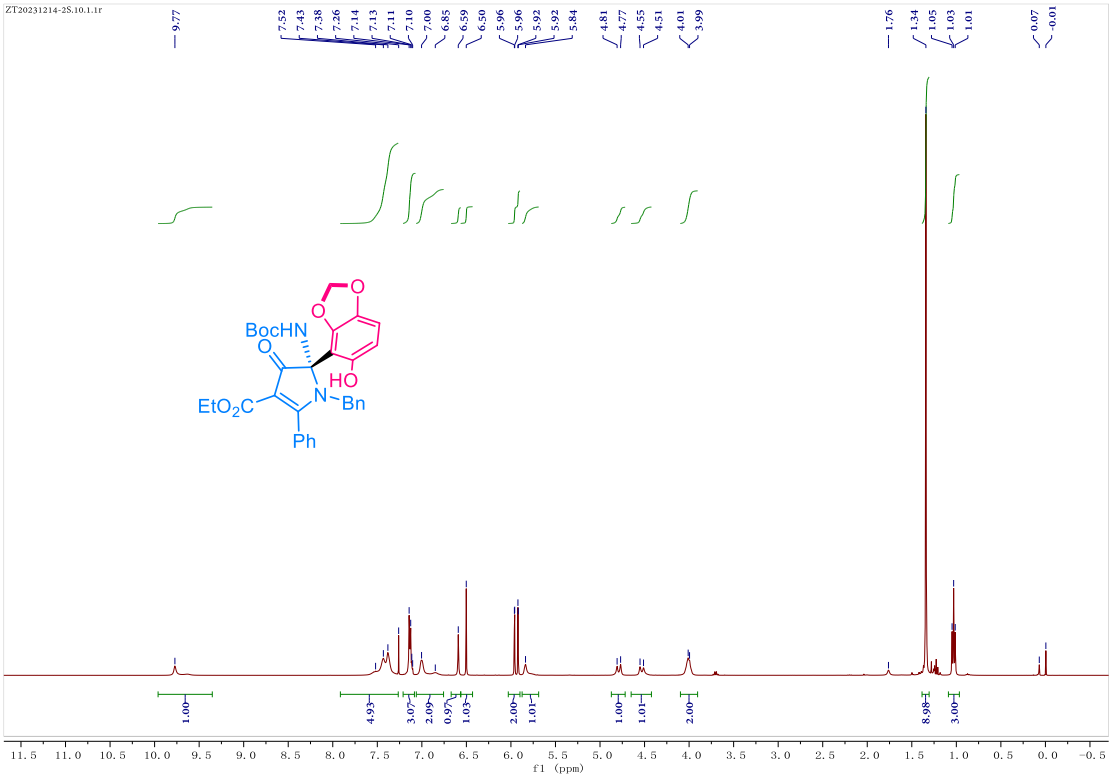
Peak	Ret.Time [min]	Area	Height	Area%
	5.858	11237.12	748.93	50.12
	12.138	11185.12	290.86	49.88
		22422.24		100.00



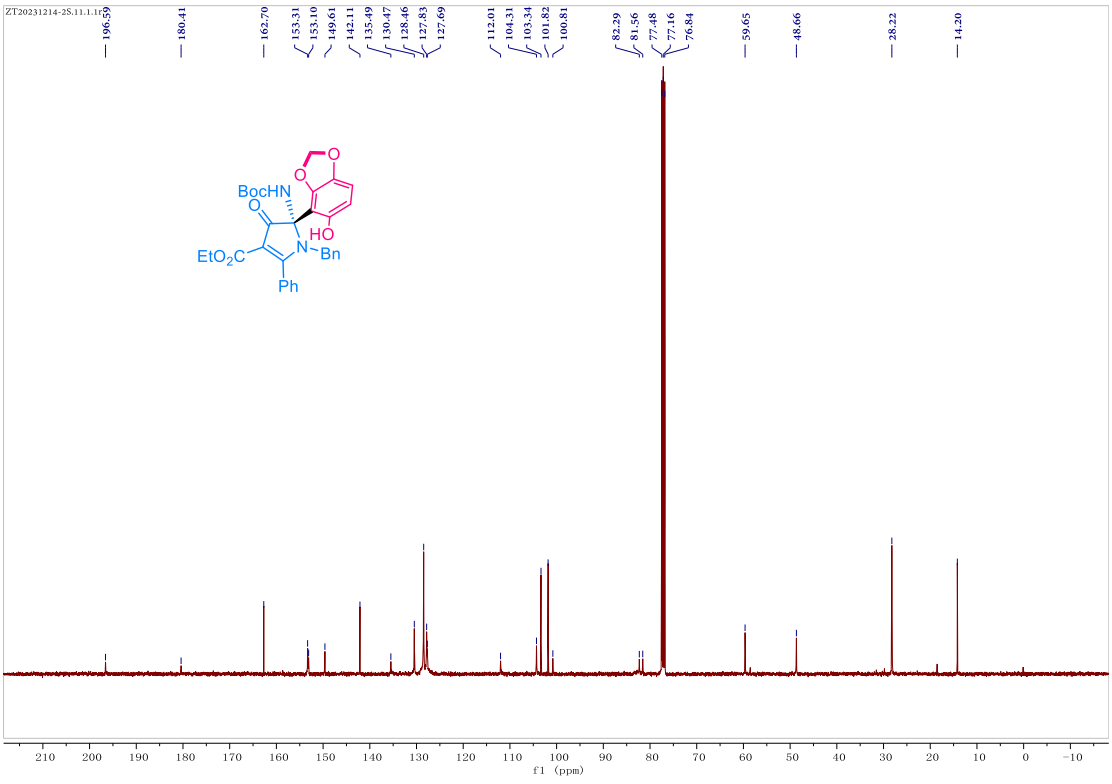
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.836	22582.28	1431.38	97.00
	12.021	699.11	21.69	3.00
		23281.39		100.00

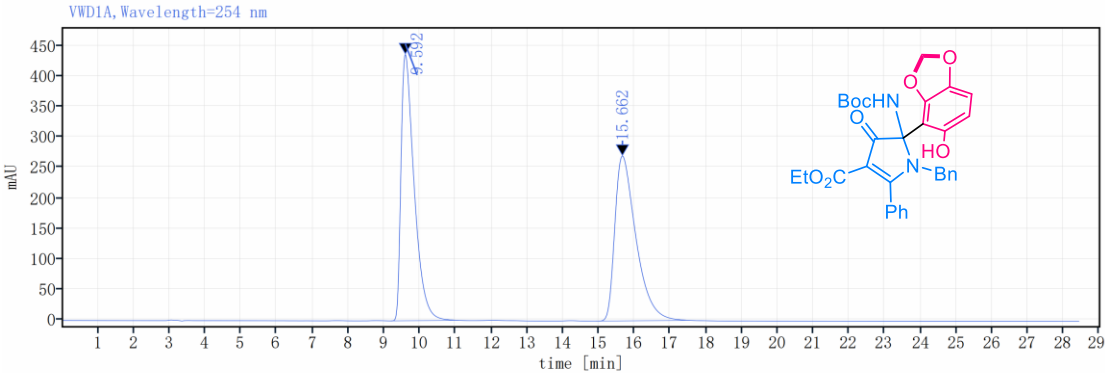
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq**



^{13}C NMR (101 MHz, $CDCl_3$) of **3aq**

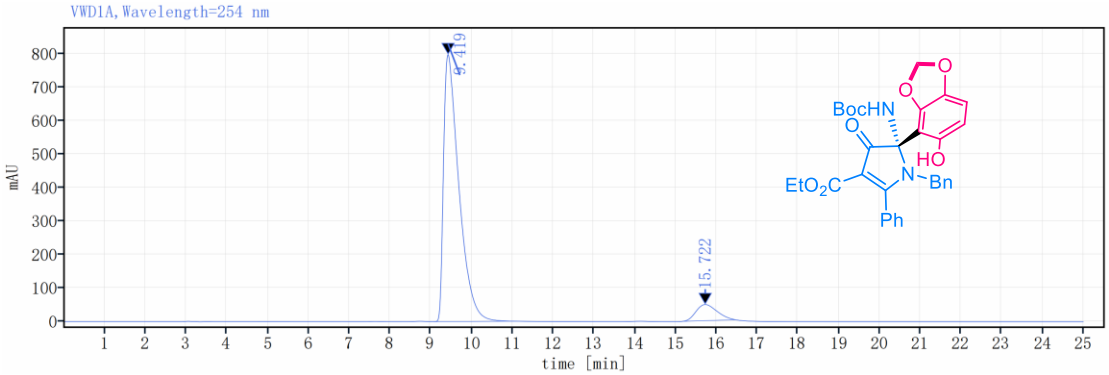


HPLC spectra of **3aq**



Detector VWD1A, Wavelength=254 nm

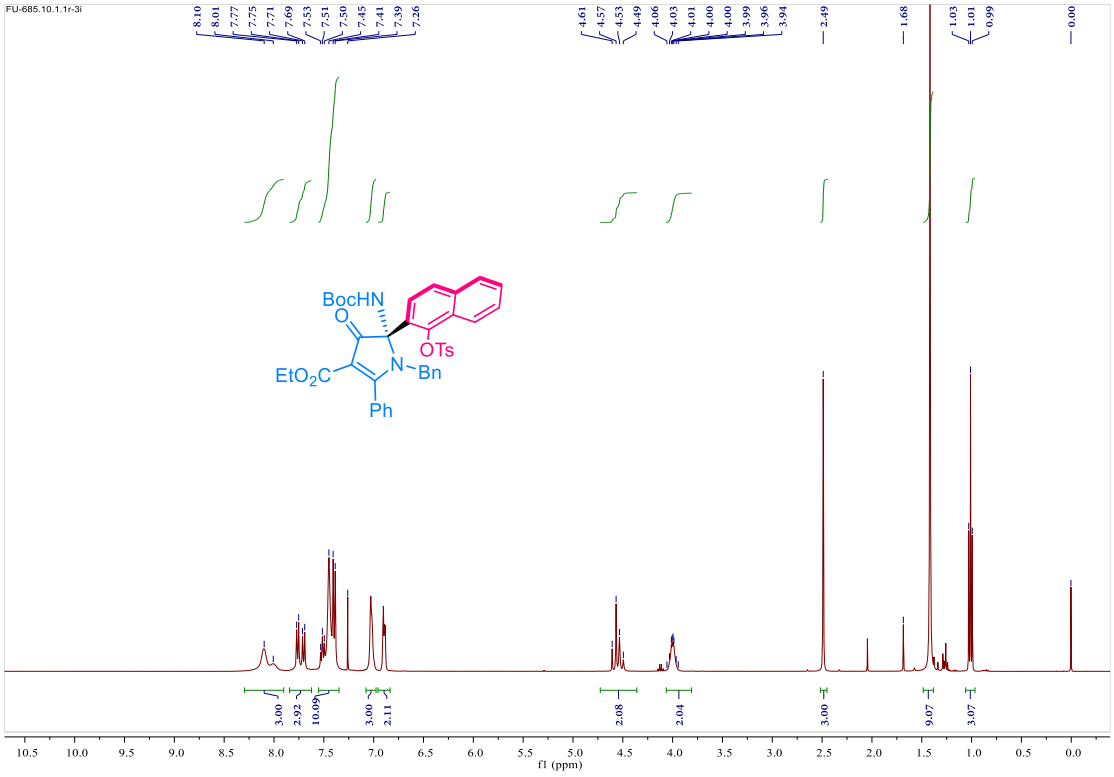
Peak	Ret.Time [min]	Area	Height	Area%
	9.592	11127.59	435.76	50.16
	15.662	11056.43	269.89	49.84
		22184.02		100.00



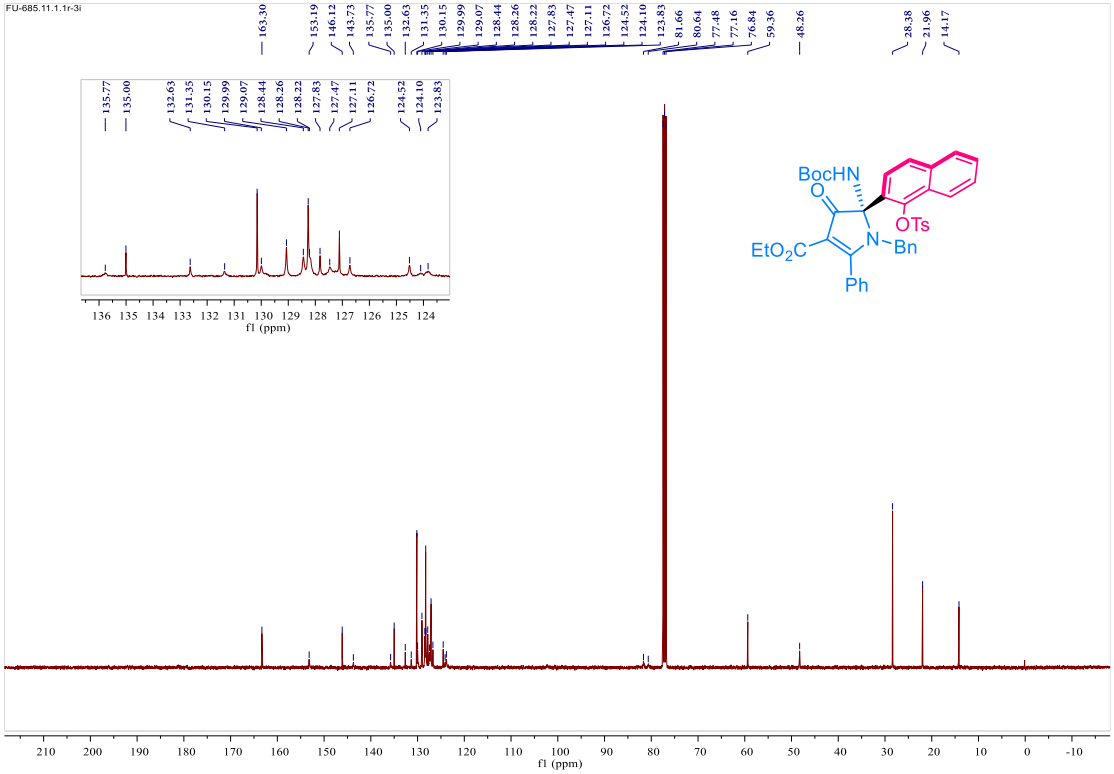
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	9.419	20776.71	796.52	92.32
	15.722	1727.57	48.20	7.68
		22504.28		100.00

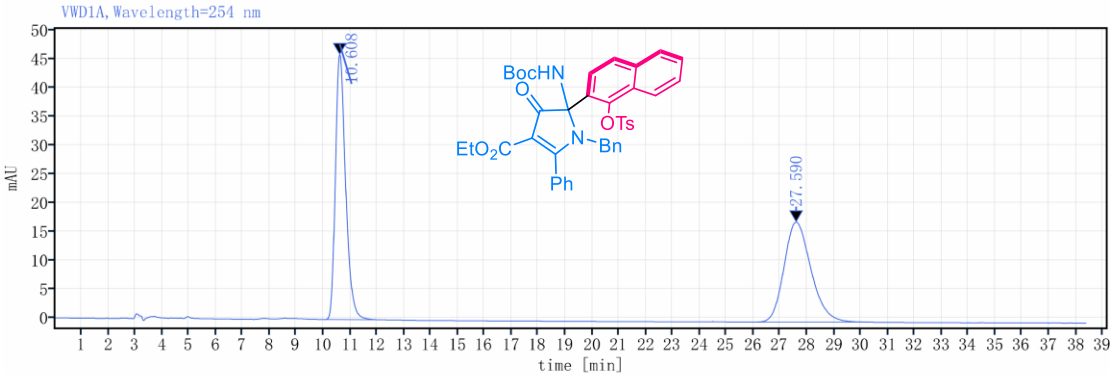
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



^{13}C NMR (101 MHz, $CDCl_3$) of **4**

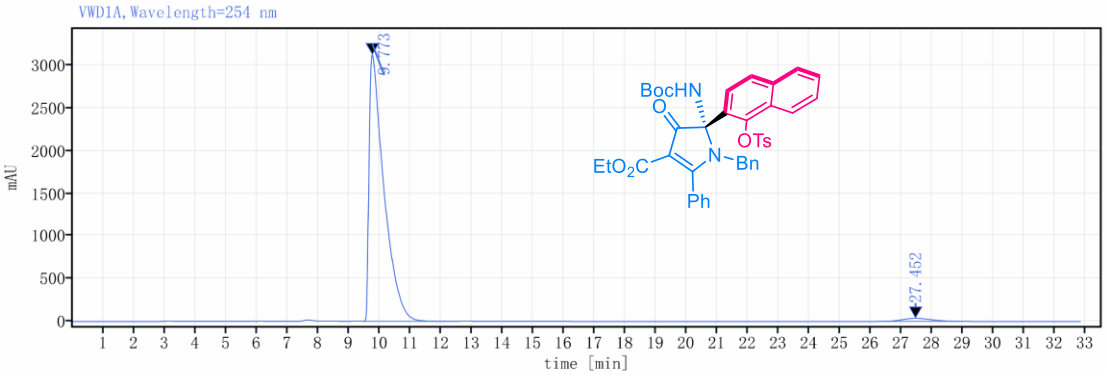


HPLC spectra of **4**



Detector VWD1A, Wavelength=254 nm

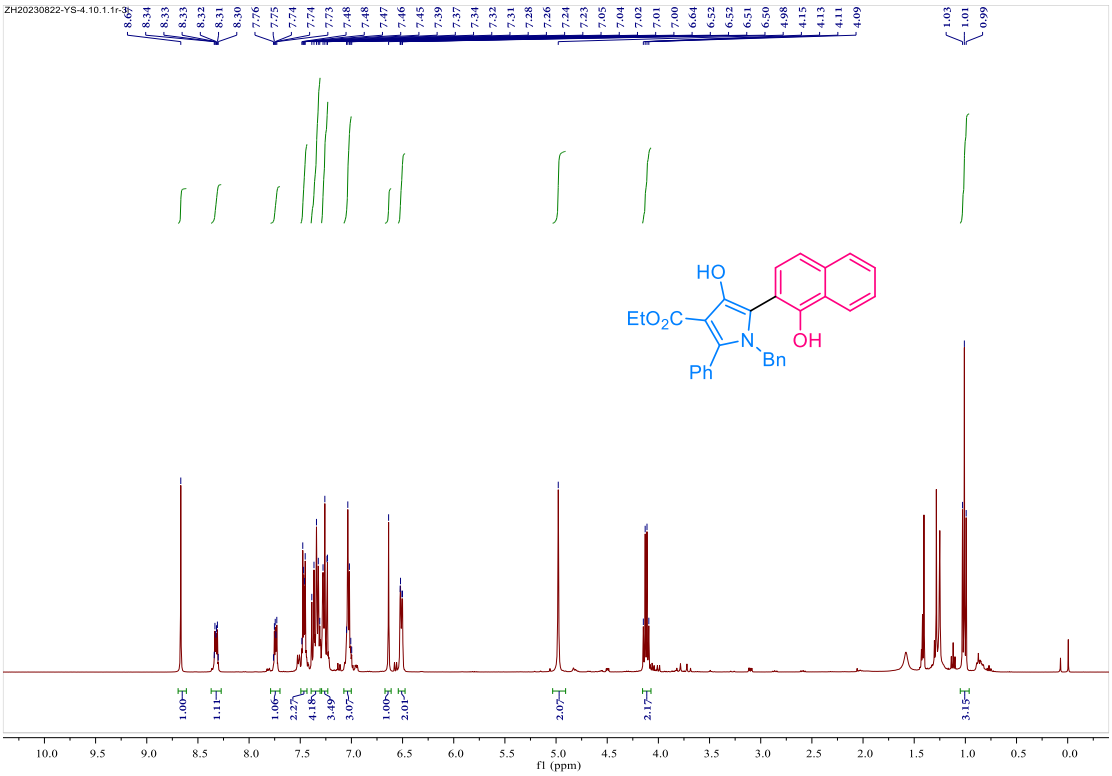
Peak	Ret.Time [min]	Area	Height	Area%
	10.608	1216.79	46.14	50.10
	27.590	1211.82	17.41	49.90
		2428.61		100.00



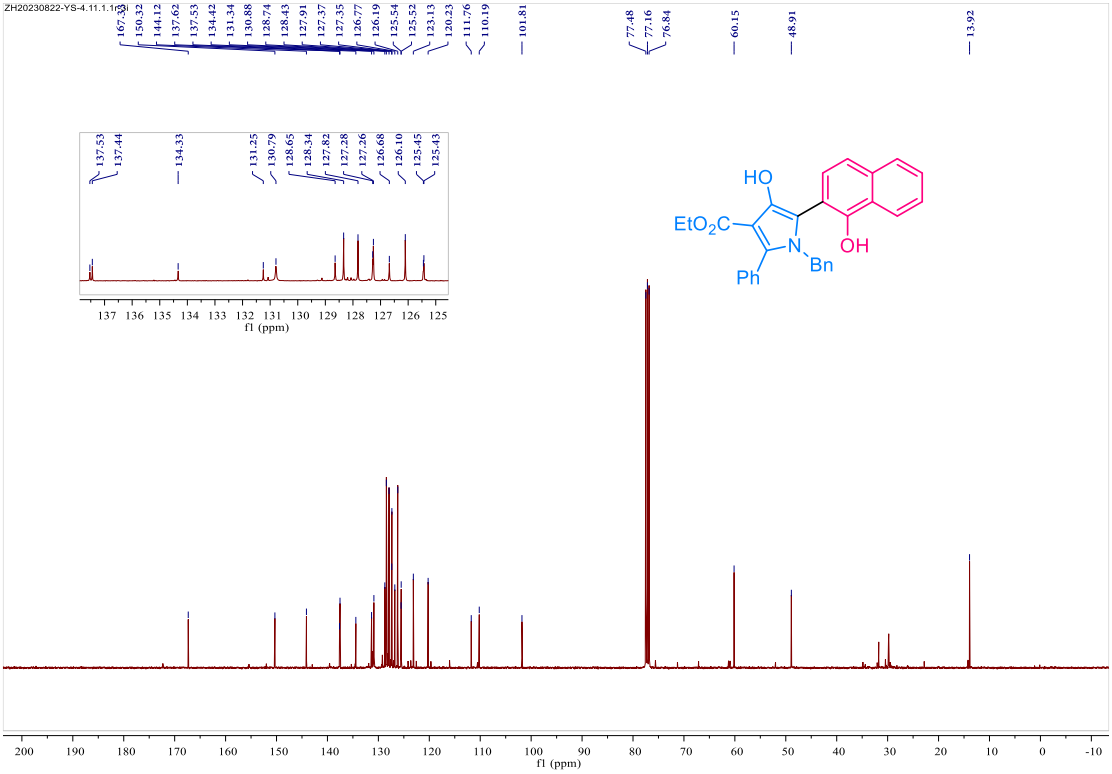
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	9.773	104756.40	3123.47	97.78
	27.452	2379.53	36.38	2.22
		107135.93		100.00

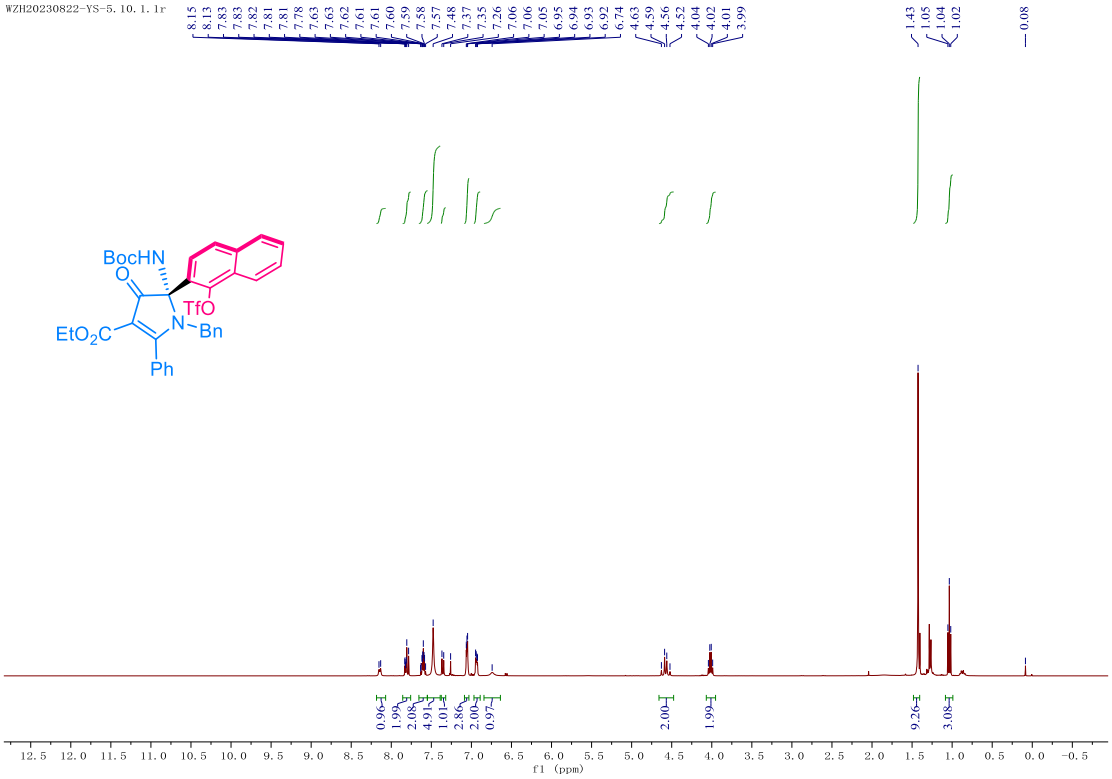
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



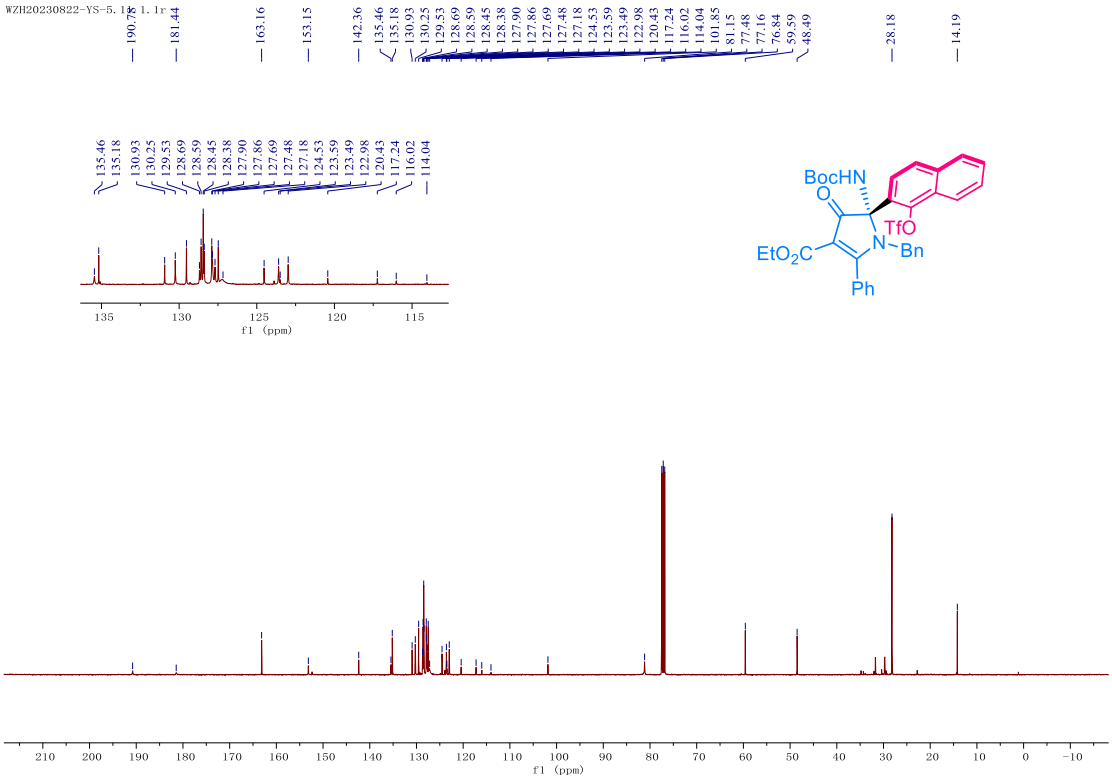
^{13}C NMR (101 MHz, $CDCl_3$) of **5**



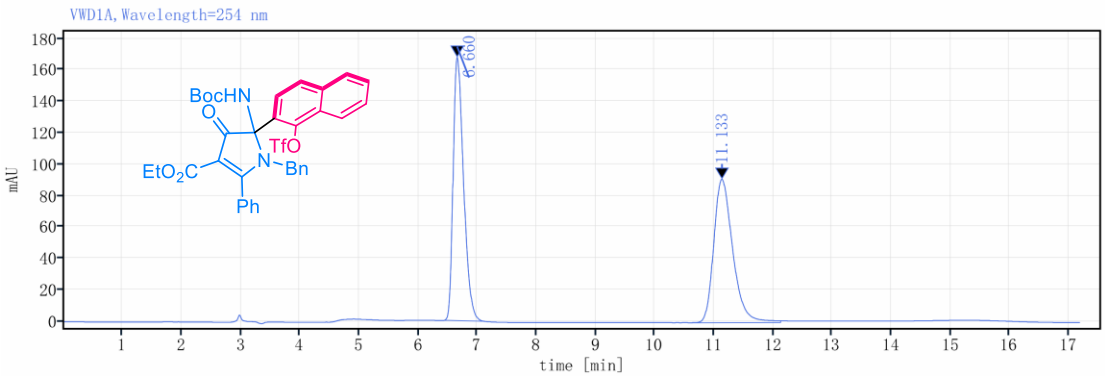
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



^{13}C NMR (101 MHz, $CDCl_3$) of **6**

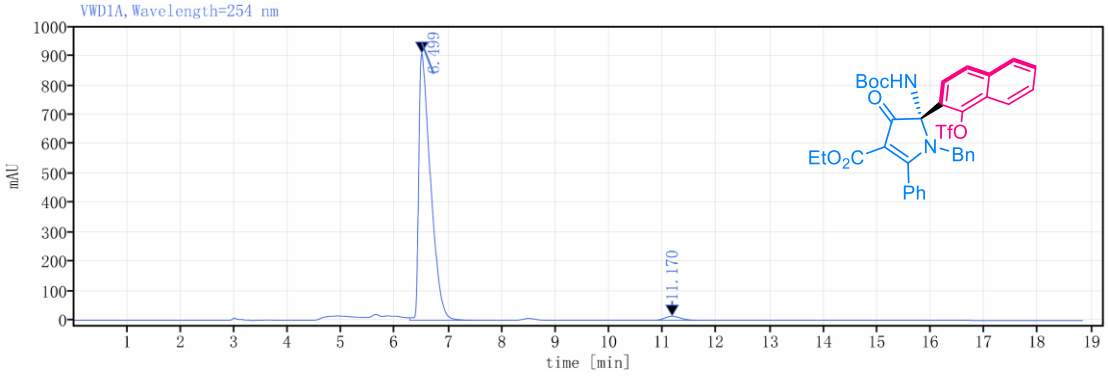


HPLC spectra of **6**



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.660	2058.30	167.61	50.30
	11.133	2033.58	91.25	49.70
		4091.88		100.00



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.499	13934.16	909.75	97.99
	11.170	286.27	13.81	2.01
		14220.43		100.00