Electronic supplementary information

Iridium-Catalyzed Asymmetric Cascade Dearomative Allylation/Acyl Transfer Rearrangement: Access to Chiral N-Substituted 2-Pyridones

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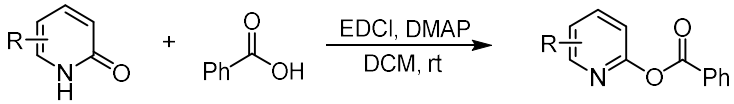
1. General remarks

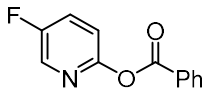
^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple or unresolved, br s = broad single, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Bruker 101 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal CF_3COOH signal at -76.55 ppm. High resolution mass spectra (HR-MS) were recorded on a LTQ-Orbitrap Elite mass spectrometer with CH_3CN/MeOH as solvent mixture for the measurements. Commercially obtained reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Enantiomeric excess was determined by chiral-phase HPLC analysis in comparison with authentic racemic materials. Optical rotations were measured on a Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]_D$ values reported in degrees; concentration (*c*) is in g/100 mL. Chiral ligands,[4,5] dbcot,[6] and [Ir*]-**1-4** complexes[7,8] were prepared according to the literature procedure. The absolute configuration of product **7** was determined by comparison of optical rotation data with the literature,[9] the absolute configurations of others were assigned by analogy.

2. Preparation of aryl 2- pyridyl esters[1,2]



To a round-bottomed flask with the carboxylic acid (1.0 equiv., 10 mmol) were added pyridine 2-ol (1.0 equiv., 10 mmol), DMAP (0.2 equiv.), EDC·HCl (1.3 equiv.) and DCM (10 mL), The reaction mixture was monitored by TLC. When the starting material was consumed, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted three times with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4, and then filtered. The filtrate was concentrated in vacuo and the residue was purified by column chromatography to afford the corresponding aryl 2-pyridyl esters.

The characterization data of new compounds are given as following:



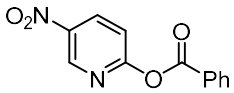
5-fluoropyridin-2-yl benzoate (1b): yield (92%); colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.25 (m, 1H), 8.22 – 8.18 (m, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.46 (m, 3H), 7.22 – 7.16 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6, 157.9 (d, *J* = 253.7 Hz), 153.7 (d, *J* = 2.2 Hz), 135.9 (d, *J* = 26.4 Hz), 133.9, 130.2, 128.6, 128.5, 126.4 (d, *J* = 21.0 Hz), 117.4 (d, *J* = 5.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -130.40 - -130.43 (m).

HRMS (ESI+) Calcd. For $C_{12}H_9FNO_2^+$ ([M+H]$^+$): 218.0612, found: 218.0613.

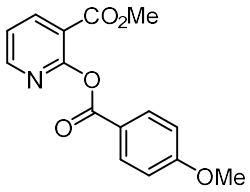


5-nitropyridin-2-yl benzoate (1c): yield (35%); white solid; m.p. 122 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (d, *J* = 2.8 Hz, 1H), 8.67 – 8.54 (m, 1H), 8.29 – 8.18 (m, 2H), 7.73 – 7.66 (m, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.42 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.8, 161.7, 145.0, 142.7, 134.9, 134.5, 130.5, 128.8, 128.0, 116.9.

HRMS (ESI+) Calcd. For $C_{12}H_8N_2O_4Na^+$ ([M+Na]$^+$): 267.0376, found: 267.0377.

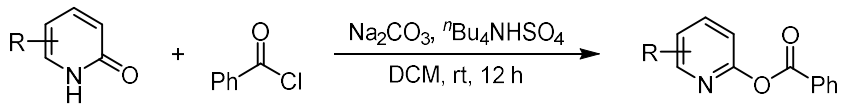


methyl 2-((4-methoxybenzoyl)oxy) nicotinate (1d): yield (90%); colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.61 (dd, *J* = 4.7, 1.5 Hz, 1H), 8.45 (d, *J* = 7.8, 1.4 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.77 (s, 3H).

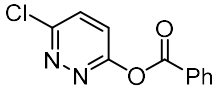
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 164.0, 163.9, 157.1, 152.2, 141.7, 132.5, 122.2, 121.2, 119.3, 113.8, 55.4, 52.5.

HRMS (ESI+) Calcd. For $C_{15}H_{13}NO_5Na^+$ ([M+Na]$^+$): 310.0686, found: 310.0684.



To a solution of pyridine 2-ol (4 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added $^nBu_4NHSO_4$ (0.04 mmol, 1.0 mol %) and Na_2CO_3 (10 mmol, 2.5 equiv.), then stirred for 10 min at room temperature. Acid chloride (6 mmol, 1.5 equiv.) was added dropwise, the resulting mixture was stirred for 12 hours at room temperature. The reaction mixture was filtered and extracted with CH_2Cl_2, the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. the residue was purified by column chromatography to give desired product.

The characterization data of new compounds are given as following:

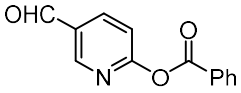


6-chloropyridazin-3-yl benzoate (1e): yield (26%); white solid; m.p. 91.5 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 – 8.22 (m, 2H), 7.74 – 7.64 (m, 2H), 7.60 – 7.48 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.0, 161.1, 155.3, 134.7, 131.2, 130.7, 128.9, 127.8, 124.4.

HRMS (ESI+) Calcd. For $C_{11}H_7ClN_2O_2Na^+$ ([M+Na]$^+$): 257.0088, found: 257.0088.



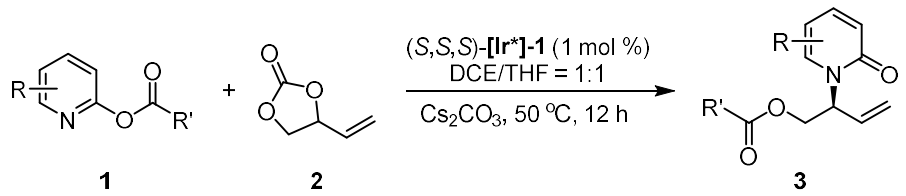
5-formylpyridin-2-yl benzoate (1f): yield (79%); white solid; m.p. 72 ºC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.14 (s, 1H), 8.95 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.27 – 8.22 (m, 2H), 7.73 – 7.65 (m, 1H), 7.58 – 7.50 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.2, 164.1, 161.9, 152.0, 139.3, 134.3, 130.5, 130.3, 128.7, 128.4, 117.2.

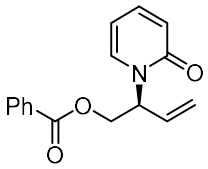
HRMS (ESI+) Calcd. For $C_{13}H_9NO_3Na^+$ ([M+Na]$^+$): 250.0475, found: 250.0477.

3. General procedure for chiral N-substituted 2-pyridones[3]



A flame dried Schlenk tube was cooled to rt and evacuated and backfilled with argon for three times. To this Schlenk tube were added (*S*,*S*,*S*)-[Ir*]-**1** (0.002 mmol, 1 mol%), pyridin-2-yl benzoates **1** (0.20 mmol, 1.0 equiv.), VEC **2** (0.60 mmol, 3.0 equiv.), Cs_2CO_3 (0.2 mmol, 1.0 equiv.) and DCM:THF = 1:1 (2 mL). The reaction was stirred at 50 °C for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess.

4. Spectral characterization data for the products



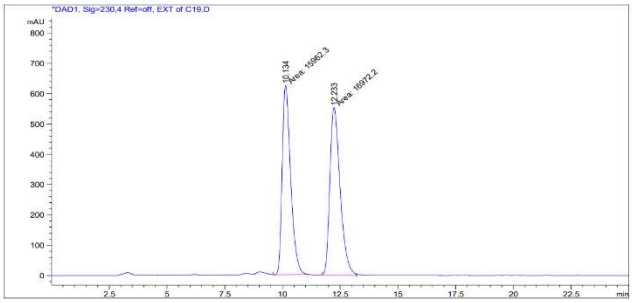
(*S*)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3a): yield (80%); colorless oil; $[\alpha]^{15}_{D}$ = -188.1 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 10.20 and 12.14 min.

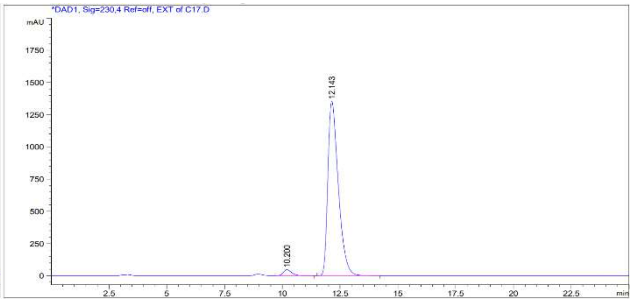
^{1}H NMR (400 MHz, Chloroform-d) δ 7.95 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.38 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.61 (dd, *J* = 9.2, 1.3 Hz, 1H), 6.23 – 6.18 (m, 1H), 6.11 – 5.99 (m, 2H), 5.50 – 5.35 (m, 2H), 4.75 – 4.63 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 162.4, 139.3, 134.8, 133.2, 132.5, 129.5, 129.4, 128.4, 120.8, 120.2, 106.1, 64.0, 55.2.

HRMS (ESI+) Calcd. For $C_{16}H_{16}NO_3^+$ ($[M+H]^+$): 270.1125, found: 270.1125.

HPLC chromatogram of compound 3a





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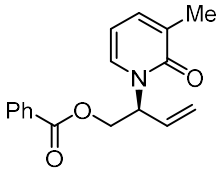
1	10.134	MM	0.4261	1.59623e4	624.41016	48.4669
2	12.233	MM	0.5122	1.69722e4	552.23590	51.5331

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.200	BB	0.3908	1221.76953	47.70282	2.7920
2	12.143	BB	0.4742	4.25373e4	1355.04028	97.2080



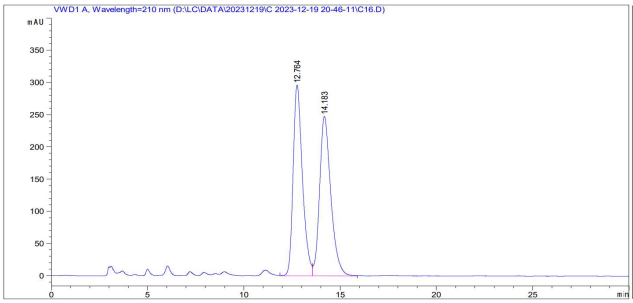
(*S*)-2-(3-methyl-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3b): yield (75%); colorless oil; $[\alpha]^{15}_{D}$ = -158.8 (*c* 0.22, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 210 nm); t_r = 12.72 and 14.27 min.

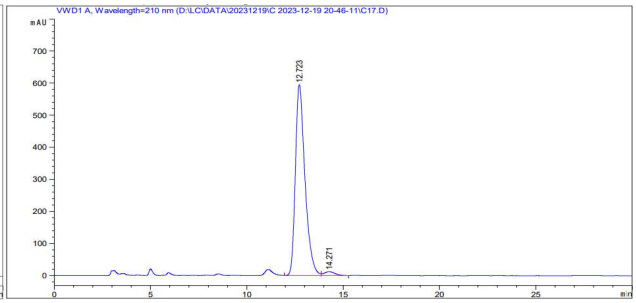
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.59 – 7.51 (m, 1H), 7.45 – 7.38 (m, 2H), 7.29 – 7.22 (m, 1H), 7.18 (d, *J* = 6.6 Hz, 1H), 6.17 – 6.10 (m, 1H), 6.09 – 5.99 (m, 2H), 5.47 – 5.33 (m, 2H), 4.76 – 4.63 (m, 2H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 162.7, 136.5, 133.2, 132.8, 132.2, 129.8, 129.6, 129.5, 128.4, 119.9, 105.7, 64.1, 55.6, 17.4.

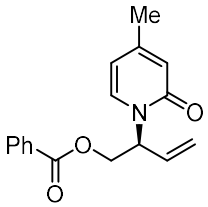
HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_3^+$ ($[M+H]^+$): 284.1281, found: 284.1281.

HPLC chromatogram of compound 3b





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.764	VV	0.5070	9958.22754	296.37408	49.7663	1	12.723	VV	0.5202	2.06043e4	595.39166	97.5652
2	14.183	VB	0.6158	1.00517e4	247.85780	50.2337	2	14.271	VV	0.5795	514.19867	12.63891	2.4348



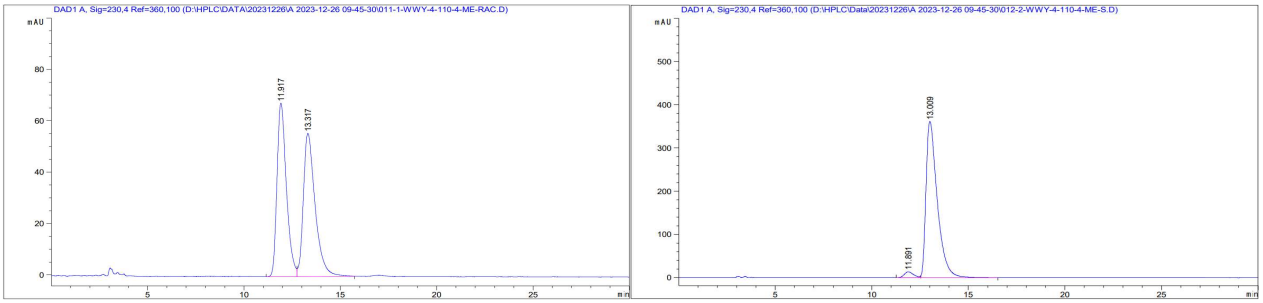
(*S*)-2-(4-methyl-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3c): yield (74%); colorless oil; $[\alpha]^{15}_{D}$ = -141.5 (*c* 0.29, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OD-H, *i*-propanol/hexane = 15/85, flow rate 1.0 mL/min, λ = 230 nm); t_r = 11.89 and 13 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 7.29 – 7.22 (m, 1H), 6.41 (s, 1H), 6.09 – 5.94 (m, 3H), 5.46 – 5.35 (m, 2H), 4.75 – 4.61 (m, 2H), 2.17 (s, 3H).

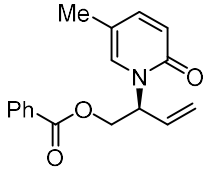
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 162.3, 150.9, 133.7, 133.2, 132.7, 129.6, 129.4, 128.4, 119.9, 119.1, 108.7, 64.1, 54.7, 21.1.

HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_3^+$ ([M+H]$^+$): 284.1281, found: 284.1279.

HPLC chromatogram of compound 3c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.917	BV	0.5125	2284.79028	67.57712	49.1002	1	11.891	BV E	0.4833	440.20004	13.60984	2.9152
2	13.317	VB	0.6222	2368.53516	55.68481	50.8998	2	13.009	VB R	0.6074	1.46601e4	361.27127	97.0848



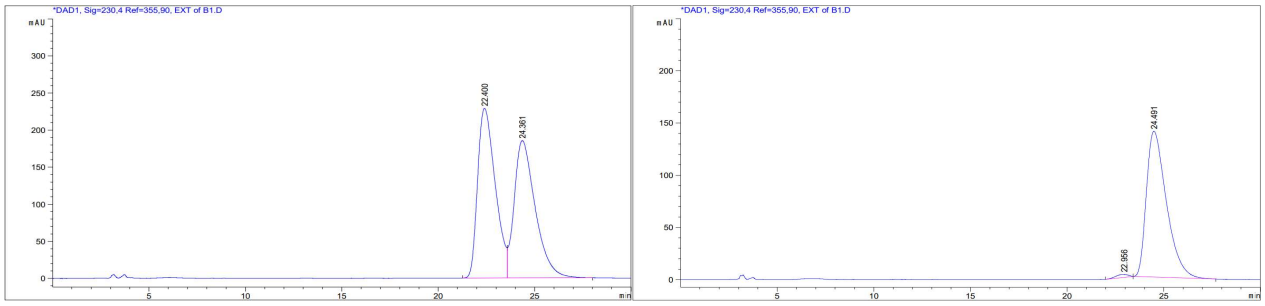
(*S*)-2-(5-methyl-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3d): yield (72%); colorless oil; $[\alpha]^{15}_{D}$ = -124.14 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralpak OD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 22.96 and 24.49 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.61 – 7.52 (m, 1H), 7.47 – 7.38 (m, 2H), 7.17 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.56 (d, *J* = 9.2 Hz, 1H), 6.11 – 5.97 (m, 2H), 5.50 – 5.34 (m, 2H), 4.67 (d, *J* = 5.5 Hz, 2H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 161.6, 141.9, 133.2, 132.8, 132.0, 129.5, 129.4, 128.4, 120.4, 120.0, 115.0, 64.1, 54.9, 17.2.

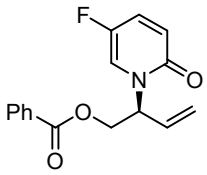
HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_3^+$ ($[M+H]^+$): 284.1281, found: 284.1281.

HPLC chromatogram of compound 3d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.400	BV	0.9553	1.45421e4	228.87624	50.8653
2	24.361	VB	1.1134	1.40473e4	185.09550	49.1347

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.956	BB	0.5546	125.50831	2.72862	1.2339
2	24.491	BB	1.0804	1.00461e4	139.80003	98.7661



(*S*)-2-(5-fluoro-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3e): yield (66%); colorless oil; m.p. 69.8 °C. $[\alpha]^{15}_{D}$ = -209.9 (*c* 0.28, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 12.55 and 14.22 min.

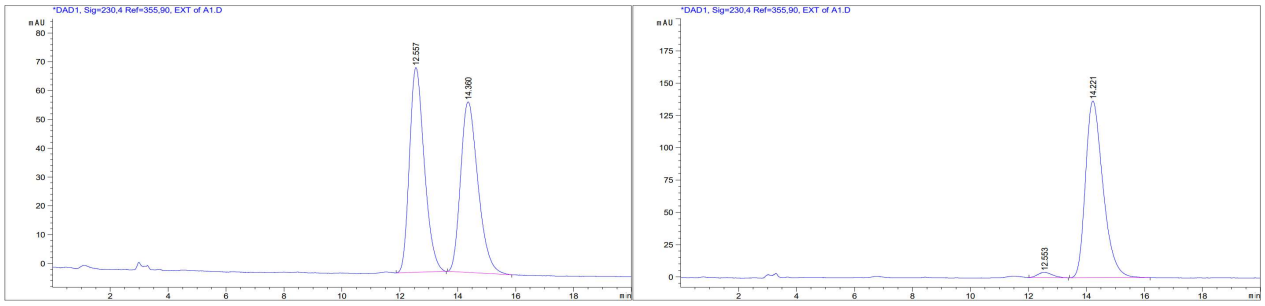
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.62 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 7.35 – 7.23 (m, 2H), 6.59 (dd, *J* = 10.0, 5.4 Hz, 1H), 6.07 – 5.94 (m, 2H), 5.56 – 5.38 (m, 2H), 4.74 – 4.60 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 160.5, 147.2 (d, *J* = 232.0 Hz), 133.3, 132.0, 131.3 (d, *J* = 24.1 Hz), 129.5, 129.2, 128.5, 121.4 (d, *J* = 7.2 Hz), 120.8, 120.1 (d, *J* = 37.5 Hz), 63.8, 55.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -147.45 - -147.49 (m).

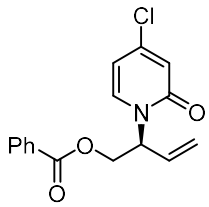
HRMS (ESI+) Calcd. For $C_{16}H_{15}FNO_3^+$ ($[M+H]^+$): 288.1030, found: 288.1027.

HPLC chromatogram of compound 3e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.557	BB	0.5479	2534.42700	71.09342	50.5747
2	14.360	BB	0.6377	2476.82983	59.25523	49.4253

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.553	BB	0.4080	137.76189	3.99837	2.3409
2	14.221	BB	0.6378	5747.14697	136.89003	97.6591



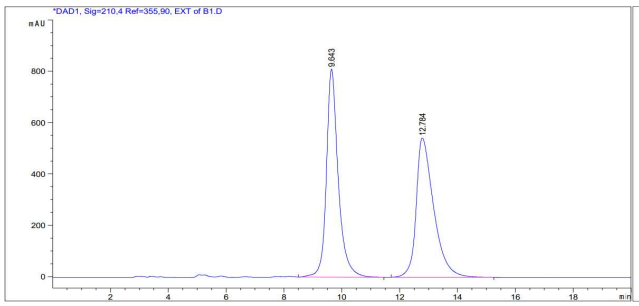
(*S*)-2-(4-chloro-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3f): yield (82%); colorless oil; $[\alpha]^{15}_D$ = -102.0 (*c* 0.26, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak IA, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 210 nm); t_r = 9.62 and 12.78 min.

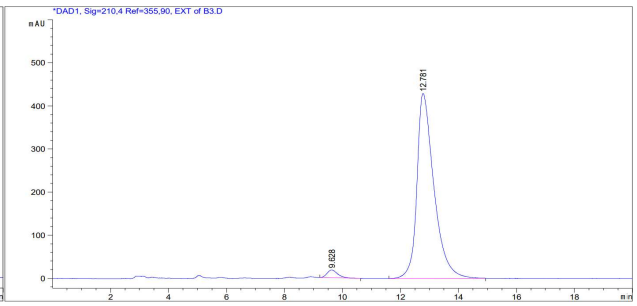
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 2H), 7.63 – 7.52 (m, 1H), 7.47 – 7.41 (m, 2H), 7.33 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 6.23 (dd, *J* = 7.5, 2.3 Hz, 1H), 6.08 – 5.90 (m, 2H), 5.57 – 5.36 (m, 2H), 4.74 – 4.60 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 161.3, 146.6, 135.2, 133.3, 132.1, 129.5, 129.2, 128.5, 120.6, 119.2, 107.9, 63.8, 55.3.

HRMS (ESI+) Calcd. For $C_{16}H_{15}ClNO_3^+$ ($[M+H]^+$): 304.0735, found: 304.0734.

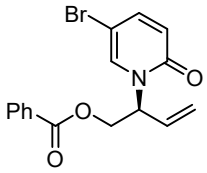
HPLC chromatogram of compound 3f





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.643	BB	0.4172	2.29891e4	809.75348	50.2269
2	12.784	BB	0.6102	2.27814e4	542.17444	49.7731

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.628	BB	0.3605	463.17865	18.22665	2.5820
2	12.781	BB	0.6033	1.74752e4	428.95956	97.4180



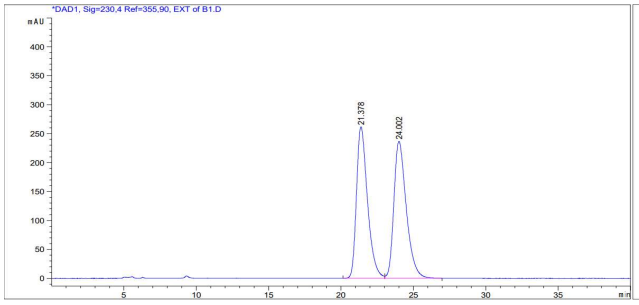
(*S*)-2-(5-bromo-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3g): yield (75%); colorless oil; $[\alpha]^{15}_{D}$ = -83.1 (*c* 0.41, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 21.58 and 24.01 min.

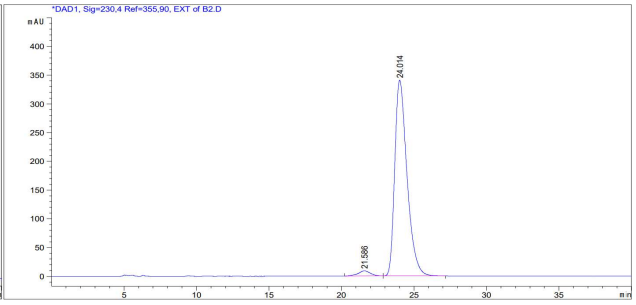
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.61 – 7.54 (m, 1H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.44 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.34 (dd, *J* = 9.7, 2.7 Hz, 1H), 6.53 (d, *J* = 9.7 Hz, 1H), 6.16 – 5.87 (m, 2H), 5.61 – 5.37 (m, 2H), 4.80 – 4.37 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 160.7, 142.4, 135.1, 133.3, 132.0, 129.6, 129.2, 128.5, 122.0, 121.0, 98.0, 63.7, 55.5.

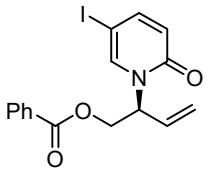
HRMS (ESI+) Calcd. For $C_{16}H_{15}BrNO_3^+$ ($[M+H]^+$): 348.0230, found: 348.0229.

HPLC chromatogram of compound 3g





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.378	BV	0.8063	1.38235e4	261.68234	49.5396	1	21.586	BB	0.6987	535.37653	9.01685	2.6042
2	24.002	VB	0.9014	1.40804e4	236.21667	50.4604	2	24.014	BB	0.8898	2.00228e4	340.64465	97.3958



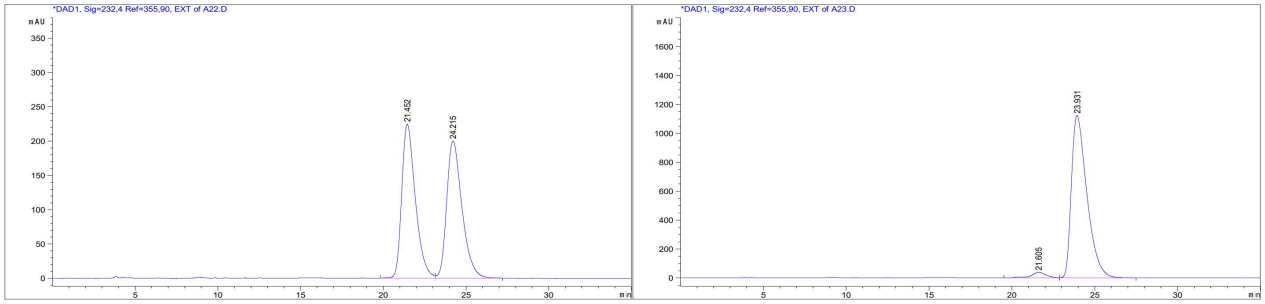
(*S*)-2-(5-iodo-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3h): yield (80%); yellow oil; $[\alpha]^{15}_{D}$ = -58.7 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak OD-H, i-propanol/hexane = 15/85, flow rate 0.8 mL/min, λ = 232 nm); t_r = 21.6 and 23.93 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.65 – 7.54 (m, 2H), 7.49 – 7.38 (m, 3H), 6.43 (d, *J* = 9.5 Hz, 1H), 6.07 – 5.97 (m, 1H), 5.96 – 5.89 (m, 1H), 5.55 – 5.40 (m, 2H), 4.74 – 4.68 (m, 1H), 4.66 – 4.58 (m, 1H).

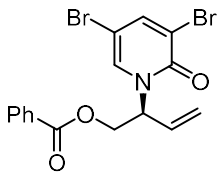
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 160.7, 146.7, 140.3, 133.3, 132.1, 129.6, 129.2, 128.5, 122.6, 121.0, 64.3, 63.7, 55.4.

HRMS (ESI+) Calcd. For $C_{16}H_{15}INO_3^+$ ([M+H]$^+$): 396.0091, found: 396.0089.

HPLC chromatogram of compound 3h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.452	BV	0.8559	1.28093e4	224.40665	49.9704	1	21.605	BV	0.8854	2567.93188	38.34113	3.3941
2	24.215	VB	0.9577	1.28245e4	200.11703	50.0296	2	23.931	VB	0.9777	7.30901e4	1122.39563	96.6059



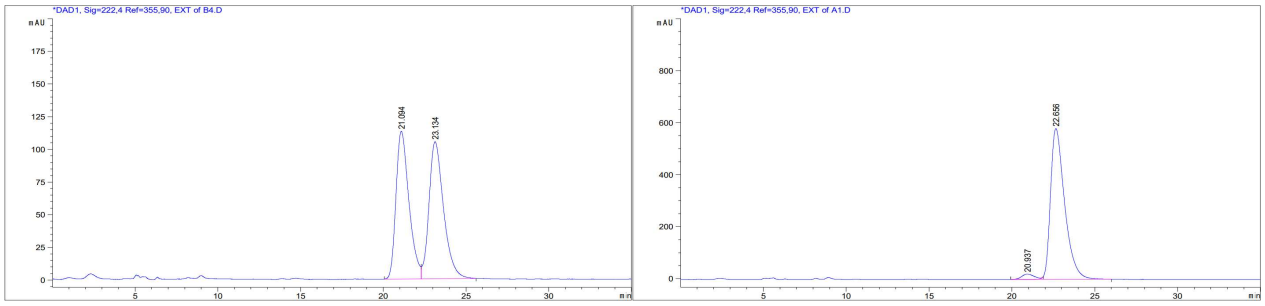
(*S*)-2-(3,5-dibromo-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3i): yield (72%); colorless oil; $[\alpha]^{15}_D$ = -107.0 (*c* 0.23, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 0.6 mL/min, λ = 222 nm); t_r = 20.93 and 22.65 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 2H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 (d, *J* = 2.6 Hz, 1H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.11 – 5.87 (m, 2H), 5.67 – 5.32 (m, 2H), 4.78 – 4.49 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 157.5, 143.7, 134.6, 133.4, 131.5, 129.6, 129.1, 128.5, 121.6, 117.5, 96.9, 63.5, 57.6.

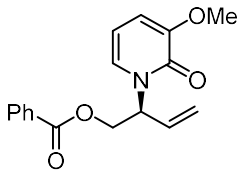
HRMS (ESI+) Calcd. For $C_{16}H_{14}Br_2NO_3^+$ ($[M+Na]^+$): 447.9154, found: 447.9153.

HPLC chromatogram of compound 3i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.094	BV	0.8080	6158.46143	112.96193	48.9654
2	23.134	VB	0.8728	6418.71582	104.76714	51.0346

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.937	BV E	0.7111	1048.80835	20.42382	2.9740
2	22.656	VB R	0.8965	3.42173e4	579.80096	97.0260



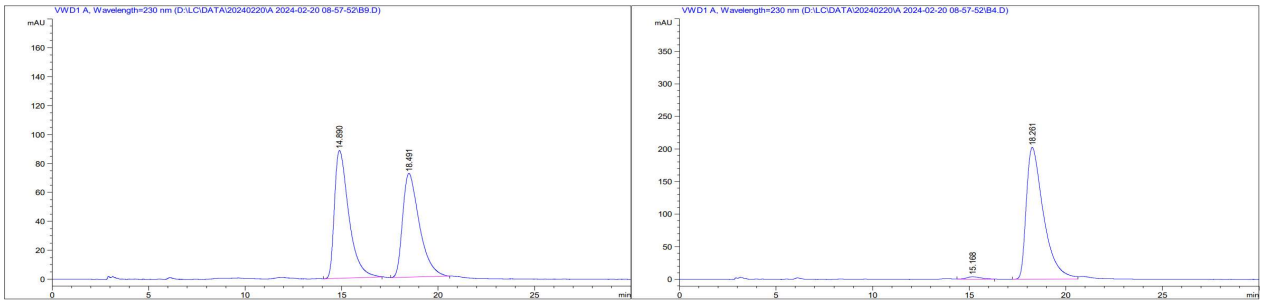
(*S*)-2-(3-methoxy-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3j): yield (76%); colorless oil; $[\alpha]^{15}_D$ = -84.9 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 15.17 and 18.26 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 – 7.39 (m, 2H), 7.03 – 6.97 (m, 1H), 6.63 – 6.56 (m, 1H), 6.17 – 6.11 (m, 1H), 6.11 – 6.00 (m, 2H), 5.46 – 5.33 (m, 2H), 4.78 – 4.62 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 158.0, 149.9, 133.2, 132.6, 129.6, 129.4, 128.4, 125.5, 120.0, 111.8, 104.9, 64.1, 55.8, 55.5.

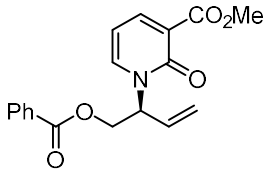
HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_4^+$ ([M+H]$^+$): 300.1230, found: 300.1229.

HPLC chromatogram of compound 3j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.890	VB	0.7743	4568.55029	88.25942	51.3922
2	18.491	BB	0.8788	4321.03467	71.74884	48.6078

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.168	VV	0.6387	203.11038	3.83255	1.5991
2	18.261	VB	0.9233	1.24984e4	202.25999	98.4009



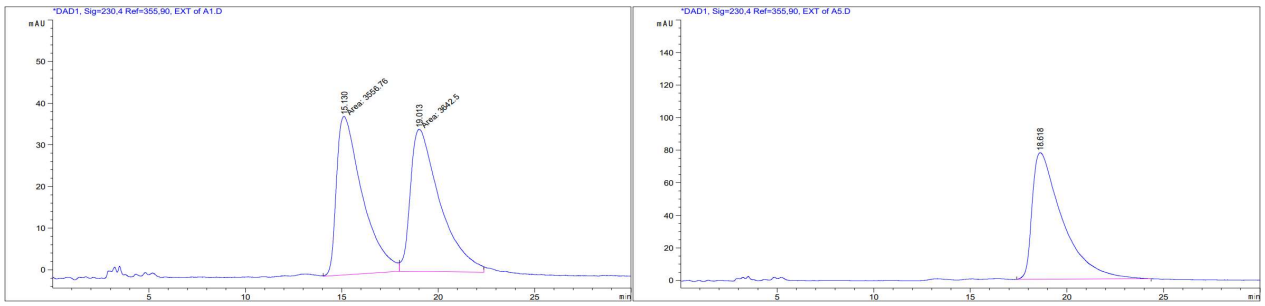
methyl (*S*)-1-(1-(benzoyloxy)but-3-en-2-yl)-2-oxo-1,2-dihydropyridine-3-carboxylate (3k): yield (60%); colorless oil; $[\alpha]^{15}_D$ = -103.0 (*c* 0.21, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: > 99% ee (Chiralpak IA, i-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 230 nm); t_r = 15.13, 19.01 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.63 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.47 – 7.39 (m, 2H), 6.33 – 6.23 (m, 1H), 6.14 – 5.96 (m, 2H), 5.56 – 5.37 (m, 2H), 4.86 – 4.61 (m, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 165.7, 159.1, 144.8, 140.2, 133.3, 132.2, 129.6, 129.2, 128.5, 120.9, 120.8, 104.8, 63.6, 56.4, 52.4.

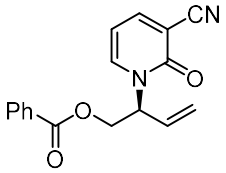
HRMS (ESI+) Calcd. For $C_{18}H_{18}NO_5^+$ ([M+H]$^+$): 328.1179, found: 328.1181.

HPLC chromatogram of compound 3k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.130	MM	1.5565	3556.75879	38.08603	49.4045
2	19.013	MM	1.7784	3642.50146	34.13724	50.5955

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.618	BB	1.4341	8446.05957	77.70387	100.0000



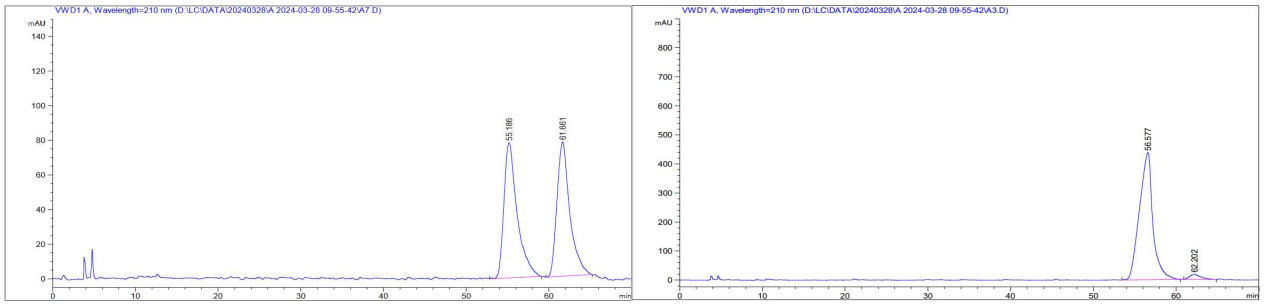
(*S*)-2-(3-cyano-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3l): yield (90%); colorless oil; $[\alpha]^{15}_{D}$ = -255.4 (*c* 0.30, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AD-H, i-propanol/hexane = 10/90, flow rate 0.8 mL/min, λ = 210 nm); t_r = 56.57 and 62.20 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.81 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.70 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.47 – 7.40 (m, 2H), 6.37 – 6.31 (m, 1H), 6.13 – 6.01 (m, 1H), 5.98 – 5.91 (m, 1H), 5.59 – 5.42 (m, 2H), 4.82 – 4.66 (m, 2H).

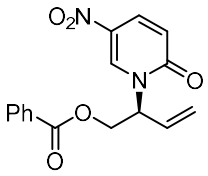
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 159.4, 147.0, 140.5, 133.4, 131.2, 129.4, 129.0, 128.5, 121.6, 115.4, 105.54, 105.45, 63.3, 56.9.

HRMS (ESI+) Calcd. For $C_{17}H_{15}N_2O_3^+$ ([M+H]$^+$): 295.1077, found: 295.1078.

HPLC chromatogram of compound 3l



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.186	VB R	1.5071	8655.49902	78.00778	50.7385	1	56.577	VB R	1.5477	4.92125e4	437.67819	96.7731
2	61.661	BV R	1.3637	8403.52832	77.61050	49.2615	2	62.202	BB	1.1698	1641.00391	16.65577	3.2269



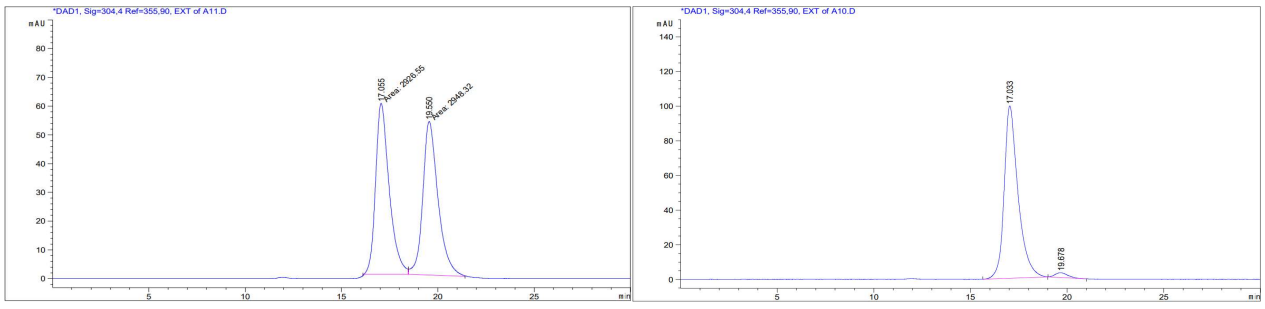
(*S*)-2-(5-nitro-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate 3m: yield (80%); colorless oil; $[\alpha]^{15}_{D}$ = -41.5 (*c* 0.28, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak IA, i-propanol/hexane = 15/85, flow rate 1.0 mL/min, λ = 304 nm); t_r = 17.03 and 19.67 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 3.0 Hz, 1H), 8.08 (dd, *J* = 10.1, 3.1 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.63 – 7.54 (m, 1H), 7.49 – 7.41 (m, 2H), 6.60 (d, *J* = 10.0 Hz, 1H), 6.15 – 6.04 (m, 1H), 6.01 – 5.93 (m, 1H), 5.68 – 5.50 (m, 2H), 4.79 (dd, *J* = 12.1, 5.4 Hz, 1H), 4.66 (dd, *J* = 12.1, 4.0 Hz, 1H).

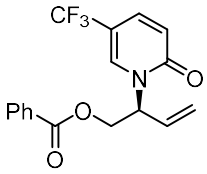
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 161.0, 137.6, 133.6, 133.0, 131.0, 130.8, 129.5, 128.8, 128.6, 122.4, 119.5, 63.5, 56.5.

HRMS (ESI+) Calcd. For $C_{16}H_{15}N_2O_5^+$ ($[M+H]^+$): 315.0975, found: 315.0977.

HPLC chromatogram of compound 3m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.055	MM	0.8205	2926.54956	59.44670	49.8147	1	17.033	BB	0.7326	4969.93701	99.52761	97.5272
2	19.550	MM	0.9205	2948.31812	53.38530	50.1853	2	19.678	BB	0.5424	126.01509	2.77192	2.4728



(*S*)-2-(2-oxo-5-(trifluoromethyl)pyridin-1(2H)-yl)but-3-en-1-yl benzoate (3n): yield (78%); colorless oil; $[\alpha]^{15}_{D}$ = -106.7 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 10.53 and 11.91 min.

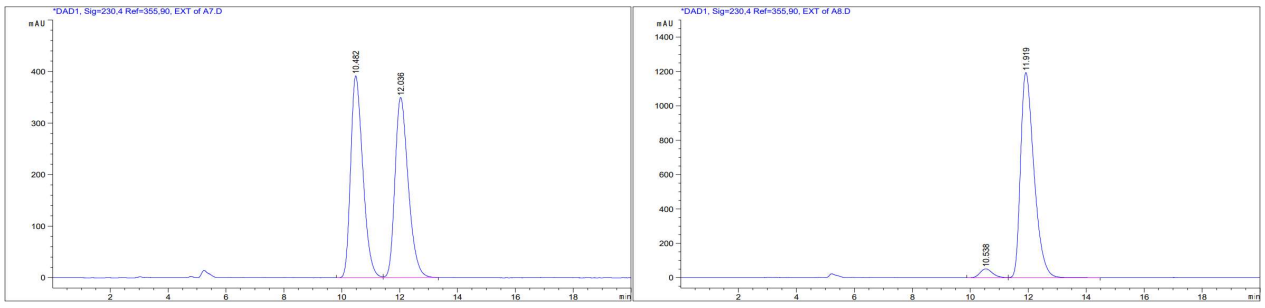
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.89 (m, 2H), 7.85 – 7.81 (m, 1H), 7.60 – 7.54 (m, 1H), 7.48 – 7.39 (m, 3H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.11 – 6.00 (m, 1H), 6.00 – 5.94 (m, 1H), 5.60 – 5.45 (m, 2H), 4.81 – 4.73 (m, 1H), 4.68 – 4.59 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 161.5, 135.2 (q, *J* = 5.28 Hz), 134.9 (q, *J* = 2.34 Hz), 133.4, 131.6, 129.5, 129.1, 128.5, 123.2 (q, *J* = 269.94 Hz), 121.5, 121.3, 109.6 (q, *J* = 34.96 Hz), 63.5, 55.9.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.47.

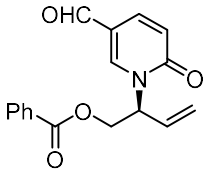
HRMS (ESI+) Calcd. For $C_{17}H_{15}F_3NO_3^+$ ([M+H]$^+$): 338.0999, found: 338.1002.

HPLC chromatogram of compound 3n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.482	BV	0.4594	1.14593e4	391.65677	50.7423
2	12.036	VB	0.4915	1.11240e4	349.31699	49.2577

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.538	BV	0.4569	1525.67761	51.30680	3.8233
2	11.919	VB	0.4892	3.83791e4	1193.37195	96.1767



(*S*)-2-(5-formyl-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (3o): yield (96%); yellow oil;

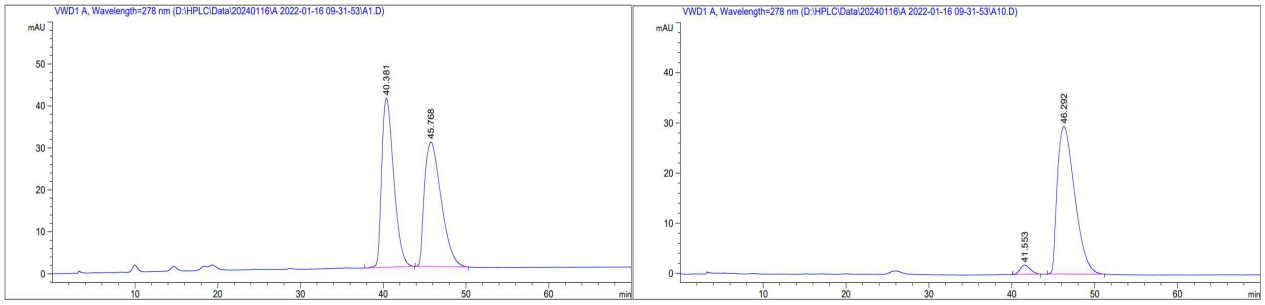
$[\alpha]^{15}_D$ = -69.5 (*c* 0.43, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak AD-H, i-propanol/hexane = 20/80, flow rate 0.6 mL/min, λ = 278 nm); t_r = 41.55 and 46.29 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.58 (s, 1H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.80 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.48 – 7.37 (m, 2H), 6.64 (d, *J* = 9.4 Hz, 1H), 6.16 – 6.04 (m, 1H), 6.04 – 5.96 (m, 1H), 5.57 – 5.48 (m, 2H), 4.82 – 4.67 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 186.0, 165.7, 162.1, 144.5, 135.5, 133.4, 131.5, 129.4, 129.0, 128.5, 121.6, 120.8, 118.3, 63.5, 56.0.

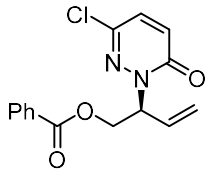
HRMS (ESI+) Calcd. For $C_{17}H_{16}NO_4^+$ ($[M+H]^+$): 298.1074, found: 298.1074.

HPLC chromatogram of compound 3o



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.381	BB	1.5056	4056.50366	40.32428	49.4177
2	45.768	BB	2.0327	4152.10840	29.66945	50.5823

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.553	BB	0.9962	156.26610	1.84678	3.5310
2	46.292	BB	1.8606	4269.29834	29.41059	96.4690



(*S*)-2-(3-chloro-6-oxopyridazin-1(6H)-yl)but-3-en-1-yl benzoate (3p): yield (40%); colorless oil; $[\alpha]^{15}_D$ = -14.7 (*c* 0.30, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OD-H, i-propanol/hexane = 15/85, flow rate 0.6 mL/min, λ = 210 nm); t_r = 26.44 and 29.23 min.

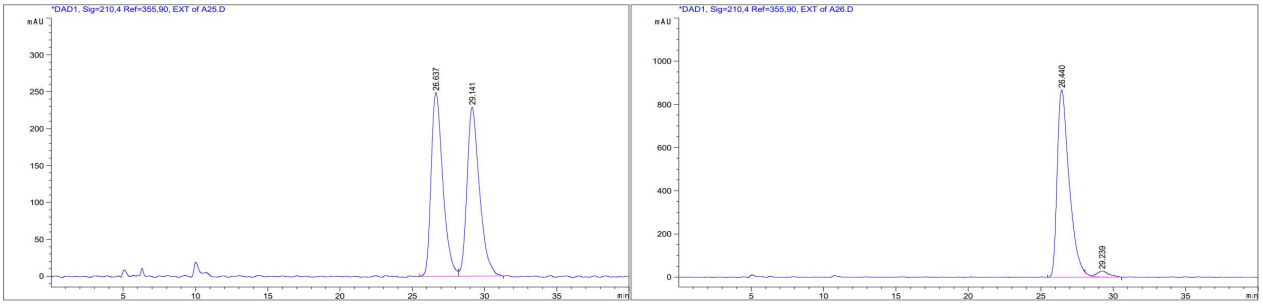
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 2H), 7.58 – 7.52 (m, 1H), 7.45 – 7.38 (m, 2H), 7.15 (d, *J* = 9.7 Hz, 1H), 6.92 (d, *J* = 9.7 Hz, 1H), 6.12 – 6.01 (m, 1H), 5.99 – 5.92 (m, 1H), 5.49 – 5.38 (m, 2H), 4.73 – 4.55 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 158.8, 137.8, 133.4, 133.1, 131.8, 131.8, 129.6, 129.5,

128.4, 120.9, 64.5, 58.8.

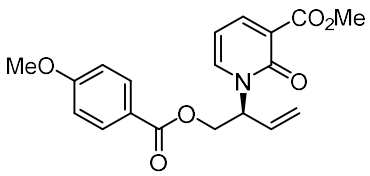
HRMS (ESI+) Calcd. For $C_{15}H_{14}ClN_2O_3^+$ ([M+H]$^+$): 305.0687, found: 305.0691.

HPLC chromatogram of compound 3p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.637	BV	0.8109	1.39839e4	249.09938	50.4208
2	29.141	VB	0.8480	1.37505e4	229.17809	49.5792

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.440	BV R	0.8296	5.01589e4	866.11938	96.8840
2	29.239	VB E	0.6943	1613.21887	27.74677	3.1160



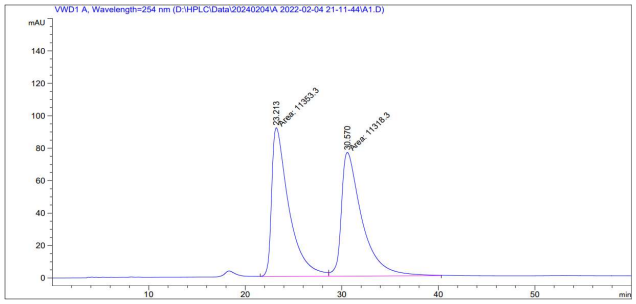
Methyl (*S*)-1-(1-((4-methoxybenzoyl)oxy)but-3-en-2-yl)-2-oxo-1,2-dihydropyridine-3 carboxylate (3q): yield (33%); colorless oil; $[\alpha]^{15}_D$ = -51.6 (*c* 0.51, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (Chiralpak IA, i-propanol/hexane = 30/70, flow rate 0.8 mL/min, λ = 254 nm); t_r = 23.82 and 28.55 min.

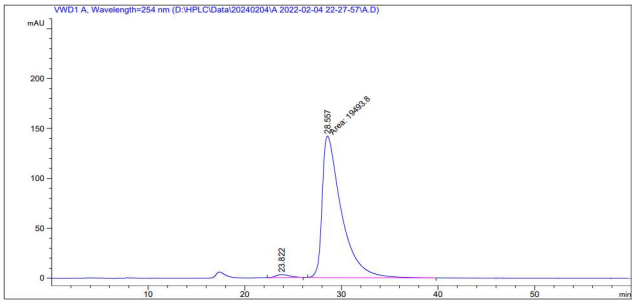
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.62 (dd, *J* = 6.8, 2.2 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.32 – 6.24 (m, 1H), 6.12 – 5.97 (m, 2H), 5.53 – 5.39 (m, 2H), 4.76 – 4.63 (m, 2H), 3.91 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 165.6, 163.6, 159.2, 144.8, 140.3, 132.2, 131.7, 121.6, 120.8, 120.7, 113.7, 104.7, 63.3, 56.4, 55.4, 52.4.

HRMS (ESI+) Calcd. For $C_{19}H_{19}NO_6Na^+$ ([M+Na]$^+$): 380.1105, found: 380.1108.

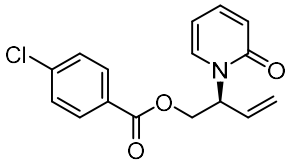
HPLC chromatogram of compound 3q





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.213	MF	2.0641	1.13533e4	91.67135	50.0772
2	30.570	FM	2.4735	1.13183e4	76.26447	49.9228

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.822	BB	1.1657	290.26810	2.93286	1.4672
2	28.557	MM	2.2920	1.94937e4	141.75130	98.5328



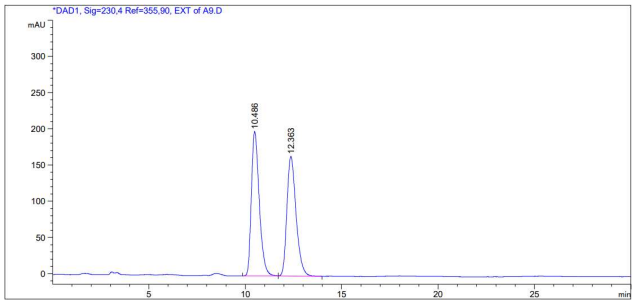
(*S*)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl 4-chlorobenzoate (3r): yield (90%); colorless oil; $[\alpha]^{15}_{D}$ = -131.7 (*c* 0.24, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 10.43 and 12.22 min.

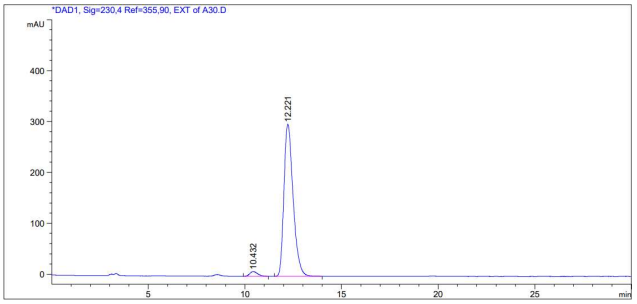
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 2H), 7.44 – 7.37 (m, 2H), 7.36 – 7.27 (m, 2H), 6.60 (d, *J* = 9.1 Hz, 1H), 6.24 – 6.17 (m, 1H), 6.10 – 5.97 (m, 2H), 5.49 – 5.38 (m, 2H), 4.69 – 4.67 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 162.4, 139.7, 139.3, 134.7, 132.4, 130.9, 128.8, 127.8, 120.9, 120.3, 106.2, 64.2, 55.2.

HRMS (ESI+) Calcd. For $C_{16}H_{14}ClNO_3Na^+$ ($[M+Na]^+$): 326.0554, found: 326.0555.

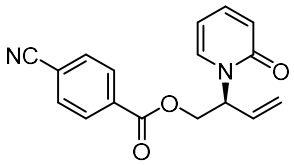
HPLC chromatogram of compound 3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.486	BB	0.4367	5651.32471	199.37723	50.9612
2	12.363	BB	0.5020	5438.13330	165.22981	49.0388

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.432	BB	0.4050	262.44678	9.36241	2.5934
2	12.221	BB	0.5033	9857.22852	298.50372	97.4066



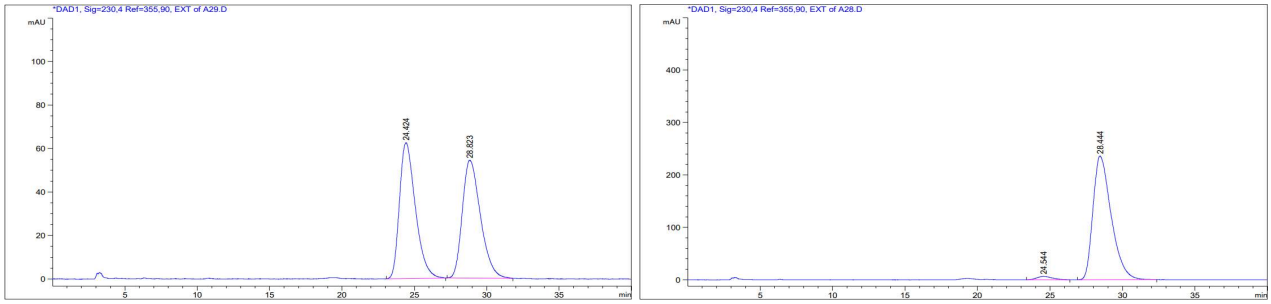
(*S*)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl 4-cyanobenzoate (3s): yield (92%); colorless oil; $[\alpha]^{15}_{D}$ = -92.9 (*c* 0.34, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 24.54 and 28.44 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.79 – 7.68 (m, 2H), 7.37 – 7.29 (m, 2H), 6.64 – 6.55 (m, 1H), 6.26 – 6.15 (m, 1H), 6.11 – 5.98 (m, 2H), 5.54 – 5.34 (m, 2H), 4.80 – 4.63 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 162.4, 139.4, 134.5, 133.2, 132.3, 132.3, 130.1, 121.0, 120.5, 117.8, 116.6, 106.3, 64.7, 55.0.

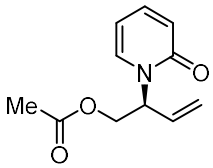
HRMS (ESI+) Calcd. For $C_{17}H_{15}N_2O_3^+$ ([M+H]$^+$): 295.1077, found: 295.1077.

HPLC chromatogram of compound 3s



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.424	BB	1.0029	4782.34277	62.48832	50.3239
2	28.823	BB	1.0455	4720.78320	54.23744	49.6761

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.544	BB	0.8719	481.17218	6.48311	2.2841
2	28.444	BB	1.2615	2.05850e4	236.01926	97.7159



(*S*)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl acetate(3t): yield (60%); colorless oil; $[\alpha]^{15}_{D}$ = -97.5 (*c* 0.31, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralpak OD-H, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 230 nm); t_r = 31.26 and 32.78 min.

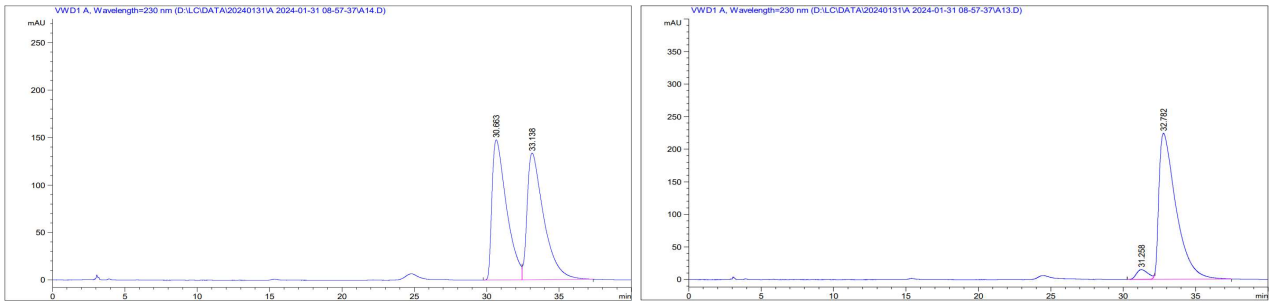
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 2H), 6.52 (d, *J* = 9.1 Hz, 1H), 6.15 – 6.10 (m,

1H), 5.95 – 5.84 (m, 1H), 5.83 – 5.77 (m, 1H), 5.35 (dd, *J* = 10.6, 1.7 Hz, 1H), 5.24 (dd, *J* = 17.4, 1.8 Hz, 1H), 4.44 – 4.31 (m, 2H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 162.3, 139.2, 134.8, 132.6, 120.8, 119.9, 106.0, 63.5, 55.0, 20.6.

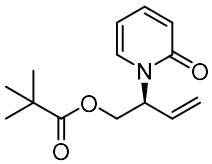
HRMS (ESI+) Calcd. For $C_{11}H_{14}NO_3^+$ ([M+H]$^+$): 208.0968, found: 208.0969.

HPLC chromatogram of compound 3t



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.663	VV R	1.0193	1.02873e4	147.70465	49.0748
2	33.138	VB	1.1295	1.06752e4	133.50294	50.9252

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.258	BV E	0.7475	845.57513	15.01123	4.4014
2	32.782	VB R	1.1545	1.83661e4	224.03165	95.5986



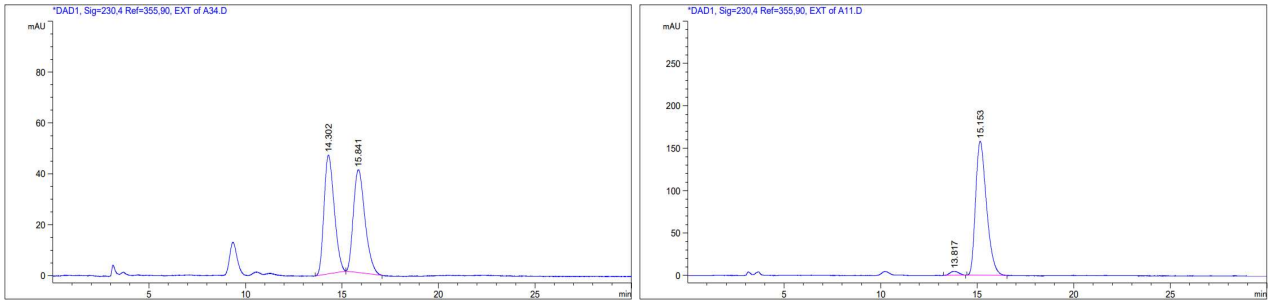
(S)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl pivalate (3u): yield (30%); white solid; m.p. 61.5 ºC. $[\alpha]^{15}_D$ = -84.6 (*c* 0.22, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralpak OD-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 230 nm); t_r = 13.81 and 15.15 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 6.58 (d, *J* = 9.0 Hz, 1H), 6.22 – 6.15 (m, 1H), 6.01 (ddd, *J* = 17.4, 10.7, 5.6 Hz, 1H), 5.85 – 5.77 (m, 1H), 5.45 – 5.29 (m, 2H), 4.45 (d, *J* = 5.2 Hz, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 153.0, 139.2, 135.3, 132.5, 120.9, 120.1, 105.9, 82.7, 66.0, 55.7, 27.6.

HRMS (ESI+) Calcd. For $C_{14}H_{19}NO_3Na^+$ ([M+Na]$^+$): 272.1257, found: 272.1261.

HPLC chromatogram of compound 3u

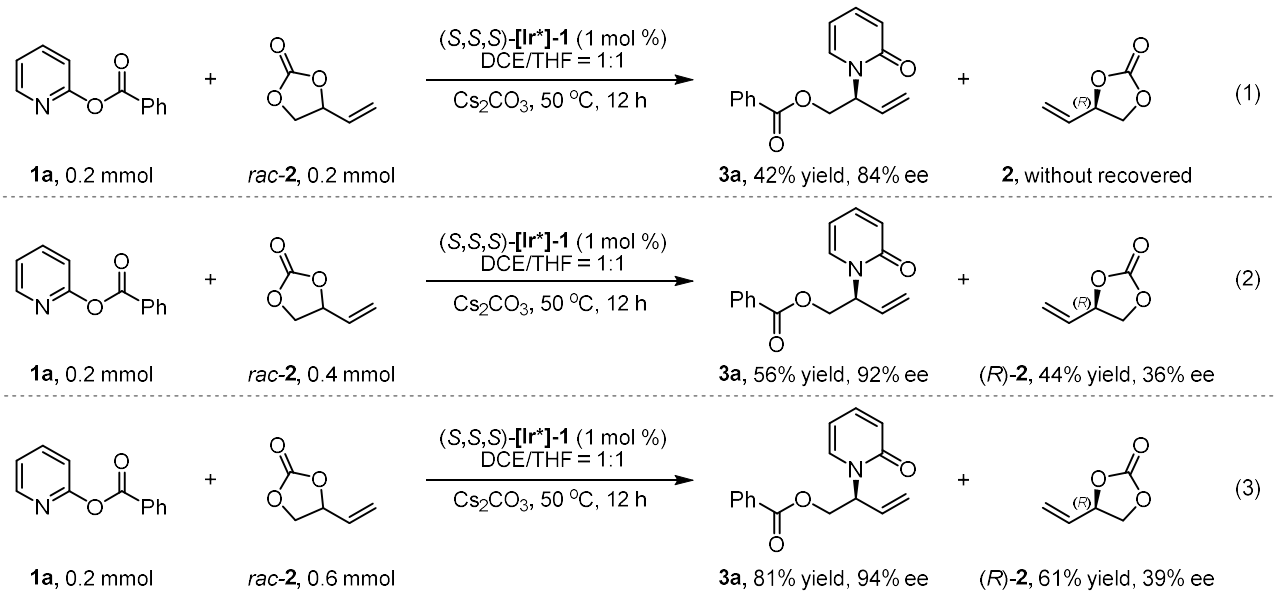


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.302	BB	0.4422	1714.24634	46.70810	50.3212
2	15.841	BB	0.4944	1692.36511	40.42622	49.6788

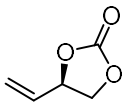
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.817	BB	0.3821	156.52882	4.81761	2.4573
2	15.153	BV R	0.5051	6213.51904	158.24599	97.5427

5. Control experiments and mechanistic investigations

a) Investigation of kinetic resolution



A flame dried Schlenk tube was cooled to rt, and it was then evacuated and backfilled with argon for three times. To this Schlenk tube was added (*S*,*S*,*S*)-**[Ir*]-1** (0.002 mmol, 1 mol%), pyridine **1a** (0.20 mmol, 1 equiv.), *rac*-**2** (0.2 mmol, 1 equiv.) and DCE:THF = 1:1 (2 mL). The reaction was stirred at 50 °C for 12 hours. Once starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography to give the desired product, which was then directly analyzed by HPLC to determine the enantiomeric excess. And recovered *rac*-**2** in Scheme (b and c) was then directly analyzed by GC to determine the enantiomeric excess.

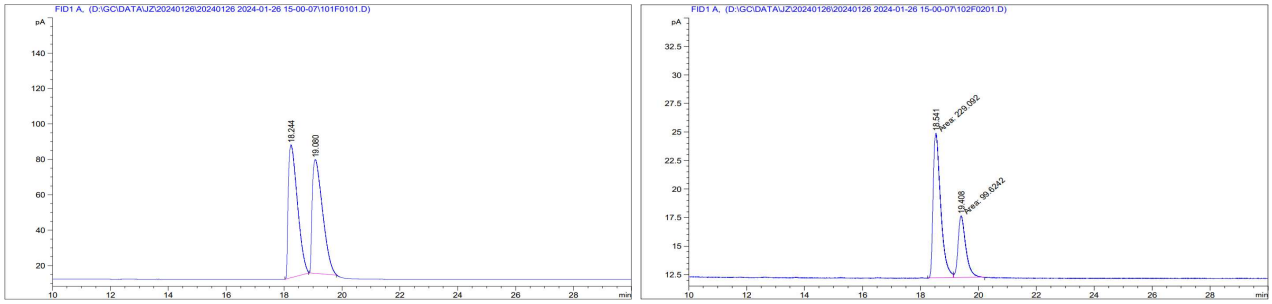


(*R*)-4-vinyl-1,3-dioxolan-2-one (2): yield (44%); colorless oil; $[\alpha]^{15}_{D}$ = 4.1 (*c* 0.72, CH_2Cl_2); The product was analyzed by GC to determine the enantiomeric excess: 39% ee (Beta DEX-390, N_2 flow rate 1.0 mL/min, 60 min at 150 °C); t_r = 18.54 and 19.41 min.

^{1}H NMR (400 MHz, Chloroform-d) δ 5.92 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.58 – 5.41 (m, 2H), 5.24 – 5.09 (m, 1H), 4.70 – 4.57 (m, 1H), 4.23 – 4.12 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.7, 132.0, 121.1, 77.3, 69.0.

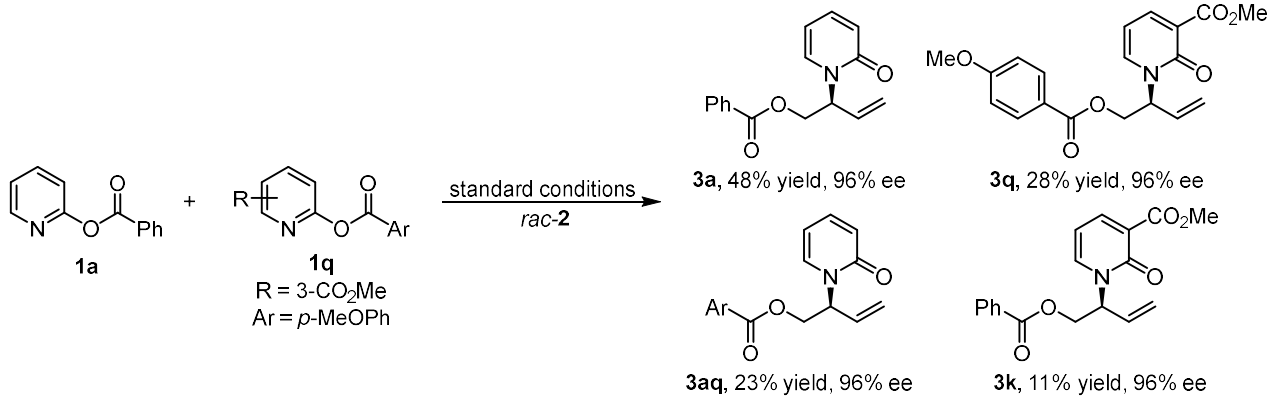
GC chromatogram of compound (*R*)-2



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.244	BB	0.2935	1643.62683	75.03956	50.67947
2	19.080	BB	0.2996	1599.55408	64.22037	49.32053

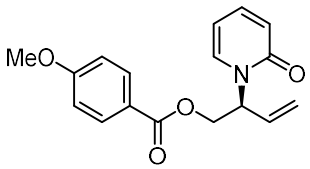
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.541	MF	0.3015	229.09244	12.66524	69.69300
2	19.408	FM	0.3072	99.62415	5.40478	30.30700

b) Cross-over experiments



A flame dried Schlenk tube was cooled to rt, and it was then evacuated and backfilled with argon for three times. To this Schlenk tube was added (*S*,*S*,*S*)-**[Ir*]-1** (0.002 mmol, 1 mol %), pyridine **1a** (0.20 mmol, 1.0 equiv.), **1q** (0.20 mmol, 1.0 equiv.), VEC **2** (1.2 mmol, 6 equiv.), Cs_2CO_3 (0.4 mmol, 2 equiv.) and DCE:THF = 1:1 (4 mL). The reaction was stirred at 50 ºC for 12 hours. Once

starting material was consumed (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by column chromatography to give the products **3a**, **3q**, **3aq** and **3k**, which were then directly analyzed by HPLC to determine the enantiomeric excess.



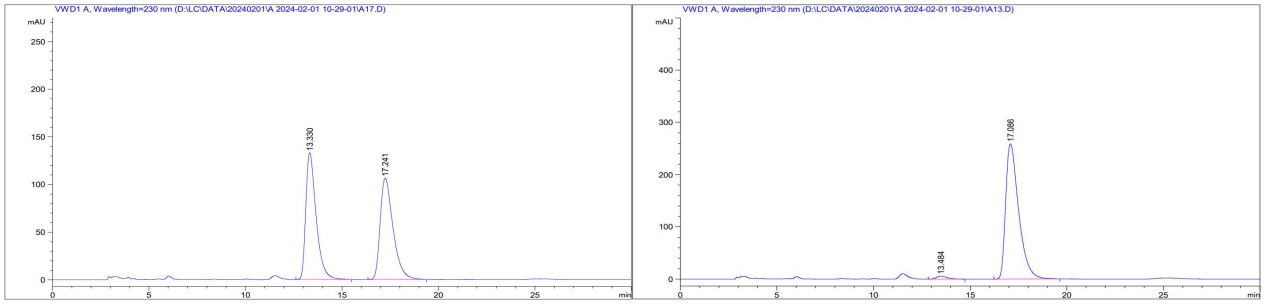
(*S*)-2-(2-oxopyridin-1(2H)-yl)but-3-en-1-yl 4-methoxybenzoate (3aq): yield (23%); colorless oil; $[\alpha]^{15}_{D}$ = -28.9 (*c* 0.20, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 96% ee (Chiralpak OD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 13.48 and 17.08 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.29 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 9.1 Hz, 1H), 6.23 – 6.16 (m, 1H), 6.10 – 5.98 (m, 2H), 5.50 – 5.32 (m, 2H), 4.73 – 4.59 (m, 2H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.7, 163.6, 162.4, 139.3, 134.9, 132.7, 131.7, 121.8, 120.9, 120.1, 113.7, 106.1, 63.8, 55.4, 55.2.

HRMS (ESI+) Calcd. For $C_{17}H_{17}NO_4Na^+$ ([M+Na]$^+$): 322.1050, found: 322.1052.

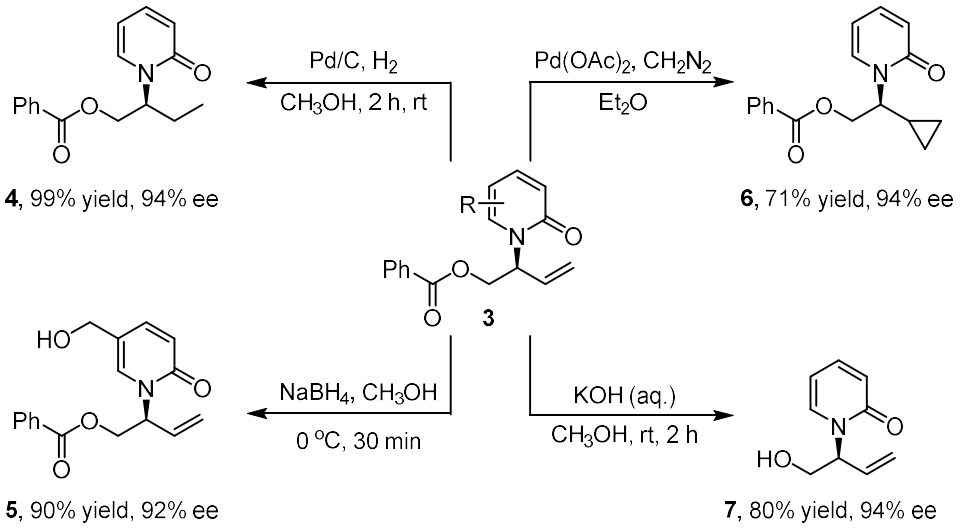
HPLC chromatogram of compound 3aq



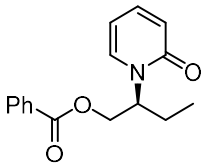
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.330	BV R	0.5673	4959.12451	133.07643	50.1606
2	17.241	BV R	0.6997	4927.36621	106.26189	49.8394

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.484	BB	0.4883	223.17181	5.65228	1.8132
2	17.086	BB	0.7122	1.20852e4	258.80353	98.1868

6. Synthetic transformation



(*S*)-2-(2-oxopyridin-1(2H)-yl)butyl benzoate (4)



A 10 mL dried Schlenk tube equipped with magnetic stirring bar. Then, (*S*)-**3a** (26.9 mg, 0.1 mmol), Pd/C (5.3 mg, 0.05 equiv.) and MeOH (2.0 mL) were added, respectively. The mixtures were degassed and stirred at room temperature under H_2 balloon pressure for 2 h. After completion, the solution was filtered via Kieselguhr and washed with DCM. The filtrate was concentrated in vacuo. The mixtures were purified by column chromatography to give the desired product **4**.

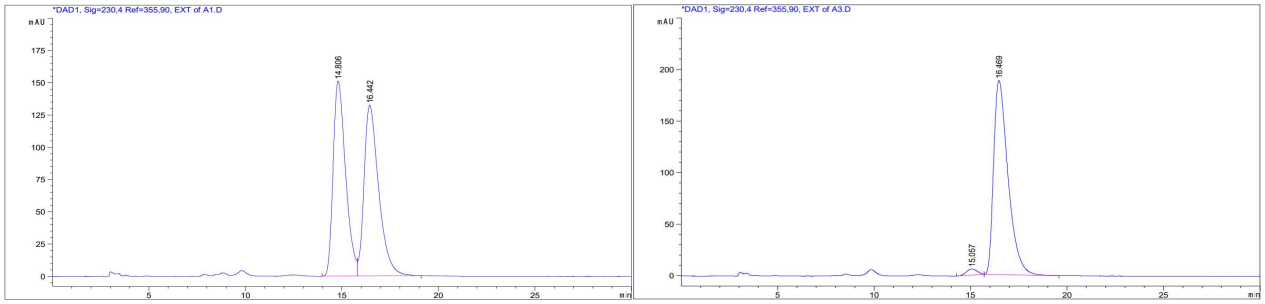
yield (99%); colorless oil; $[\alpha]^{15}_D$ = -122.6 (*c* 0.26, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak OD-H, i-propanol/hexane = 15/85, flow rate 1.0 mL/min, λ = 230 nm); t_r = 15.05 and 16.46 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.48 – 7.39 (m, 2H), 7.37 – 7.26 (m, 2H), 6.60 (dd, *J* = 9.2, 1.3 Hz, 1H), 6.28 – 6.17 (m, 1H), 5.42 – 5.22 (m, 1H), 4.63 (dd, *J* = 11.8, 6.6 Hz, 1H), 4.51 (dd, *J* = 11.8, 4.1 Hz, 1H), 2.05 – 1.80 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.0, 162.8, 138.8, 133.9, 133.1, 129.5, 129.4, 128.4, 120.9, 106.1, 65.1, 55.4, 23.3, 10.3.

HRMS (ESI+) Calcd. For $C_{16}H_{18}NO_3^+$ ($[M+H]^+$): 272.1281, found: 272.1279.

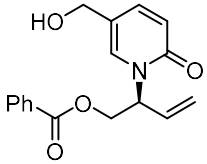
HPLC chromatogram of compound 4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.806	BV	0.6869	6776.12646	151.19736	49.2197
2	16.442	VB	0.7902	6990.96240	132.36012	50.7803

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.057	BB	0.4634	225.58276	5.85631	2.2619
2	16.469	BB	0.7691	9747.52441	187.93161	97.7381

(*S*)-2-(5-(hydroxymethyl)-2-oxopyridin-1(2H)-yl)but-3-en-1-yl benzoate (5)



A 10 mL dried flask equipped with magnetic stirring bar. Then, (*S*)-**3a** (53.8 mg, 0.2 mmol) and MeOH (2.0 mL) were added, respectively. Add sodium borodeuteride (15 mg, 0.4 mmol) to solution slowly at 0 °C. The mixture was allowed to react at this temperature and stir for 30 min. After completion, the solution was filtered via Kieselguhr and washed with ethyl acetate. The filtrate was concentrated in vacuo. The mixtures were purified by column chromatography to give the desired product **5**.

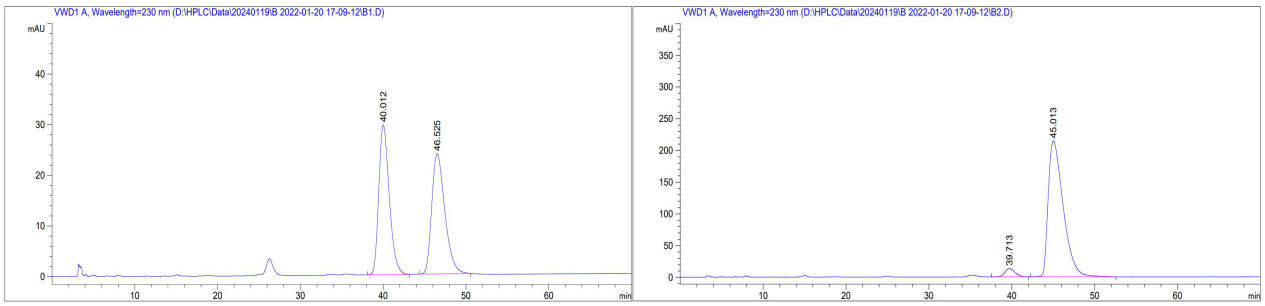
yield (75%); colorless oil; $[\alpha]^{15}_{D}$ = -96.3 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AD-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 230 nm); t_r = 39.71 and 45.01 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 2H), 7.59 – 7.50 (m, 1H), 7.44 – 7.38 (m, 3H), 7.37 – 7.31 (m, 1H), 6.56 (d, *J* = 9.2 Hz, 1H), 6.08 – 5.95 (m, 2H), 5.49 – 5.34 (m, 2H), 4.71 – 4.60 (m, 2H), 4.48 – 4.35 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 162.2, 139.7, 133.3, 132.8, 132.4, 129.6, 129.3, 128.4, 120.6, 120.4, 119.4, 64.0, 61.7, 55.2.

HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_4^+$ ($[M+H]^+$): 300.1230, found: 300.1231.

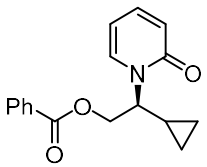
HPLC chromatogram of compound 5



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.012	BB	1.2920	2595.79199	29.54593	49.9451
2	46.525	BB	1.5654	2601.49658	23.72182	50.0549

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.713	BB	1.2452	1123.67834	13.14663	4.0157
2	45.013	BB	1.9401	2.68583e4	214.16632	95.9843

(*S*)-2-cyclopropyl-2-(2-oxopyridin-1(2H)-yl)ethyl benzoate (6)



To a Schlenk tube were added fresh prepared diazomethane solution (0.5 M in Et_2O, 2 mL) and (*S*)-**3a** (29.4 mg, 0.1 mmol) under a positive nitrogen pressure. The reaction mixture was cooled to -20 °C, and then $Pd(OAc)_2$ (1.5 mg, 2 mol %) was added in one portion with gas evolution. After stirring for 1 hour at -20 °C, the reaction was moved to room temperature and stirred overnight. While the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the product (*S*)-**6**.

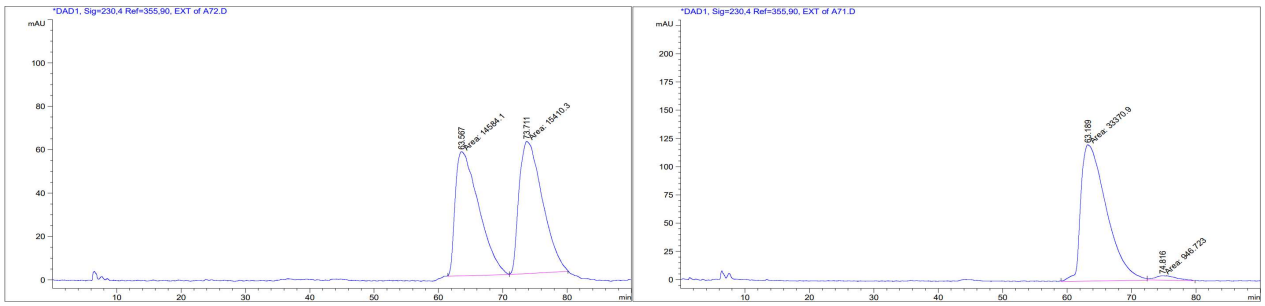
yield (71%); yellow oil; $[\alpha]^{15}_D$ = -151.4 (*c* 0.25, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralpak AS-H, i-propanol/hexane = 10/90, flow rate 0.5 mL/min, λ = 230 nm); t_r = 63.18 and 74.81 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.53 (m, 2H), 7.48 – 7.39 (m, 2H), 7.35 – 7.29 (m, 1H), 6.58 (d, *J* = 9.1 Hz, 1H), 6.26 – 6.21 (m, 1H), 4.74 – 4.62 (m, 2H), 4.57 – 4.47 (m, 1H), 1.44 – 1.32 (m, 1H), 0.91 – 0.78 (m, 1H), 0.68 – 0.58 (m, 2H), 0.44 – 0.35 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 162.6, 139.1, 134.7, 133.2, 129.62, 129.56, 128.4, 120.7, 105.9, 65.3, 59.9, 11.4, 6.3, 3.7.

HRMS (ESI+) Calcd. For $C_{17}H_{18}NO_3^+$ ($[M+H]^+$): 284.1281, found: 284.1282.

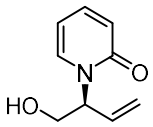
HPLC chromatogram of compound 6



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.567	MM	4.2441	1.45841e4	57.27205	48.6228
2	73.711	MM	4.2128	1.54103e4	60.96613	51.3772

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	63.189	MF	4.6054	3.33709e4	120.76711	97.2413
2	74.816	MM	3.9480	946.72284	3.99664	2.7587

(*S*)-1-(1-hydroxybut-3-en-2-yl)pyridin-2(1H)-one (7)



A 10 mL dried flask equipped with magnetic stirring bar. Then, (*S*)-**3a** (53.8 mg, 0.2 mmol) and MeOH (2.0 mL) were added, respectively. Add KOH (aq., 1 M) to solution slowly at room temperature. The mixture was allowed to react at this temperature and stir for 2 h. After completion, the aqueous phase was extracted with ethyl acetate. the combined organic layers were washed with brine, dried by Na_2SO_4 and concentrate in vacuo. The mixture was purified by column chromatography to give the desired product **7**.

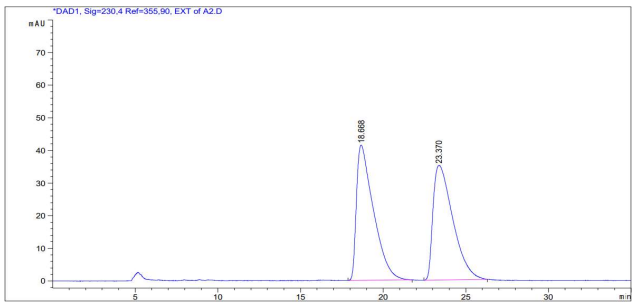
yield (80%); white solid; m.p. 89 ºC. $[\alpha]^{15}_{D}$ = -62.3 (*c* 0.23, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralpak AS-H, i-propanol/hexane = 25/75, flow rate 1.0 mL/min, λ = 230 nm); t_r = 18.58 and 23.79 min.

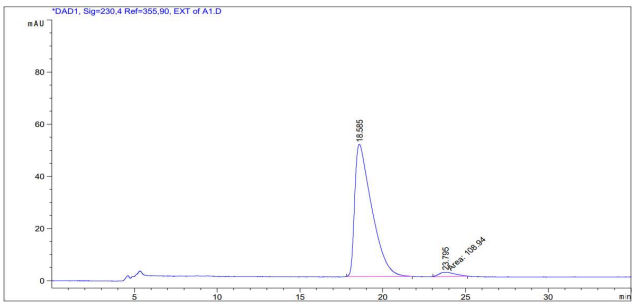
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 2H), 6.57 (d, *J* = 9.1 Hz, 1H), 6.29 – 6.21 (m, 1H), 6.07 – 5.96 (m, 1H), 5.64 – 5.55 (m, 1H), 5.41 (d, *J* = 10.6 Hz, 1H), 5.30 (dd, *J* = 17.4, 1.7 Hz, 1H), 4.08 – 4.00 (m, 1H), 3.98 – 3.90 (m, 1H), 3.72 – 3.64 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 139.5, 135.6, 133.0, 120.6, 119.6, 106.5, 63.5, 59.6.

HRMS (ESI+) Calcd. For $C_9H_{12}NO_2^+$ ($[M+H]^+$): 166.0863, found: 166.0863.

HPLC chromatogram of compound 7





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.668	BB	0.9670	2958.33472	41.43552	50.2938
2	23.370	BB	0.9826	2923.77417	35.14412	49.7062

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.585	BB	0.9600	3624.26050	50.69770	97.0819
2	23.795	MM	1.0831	108.93979	1.67630	2.9181

7. Reference

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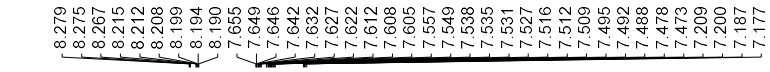
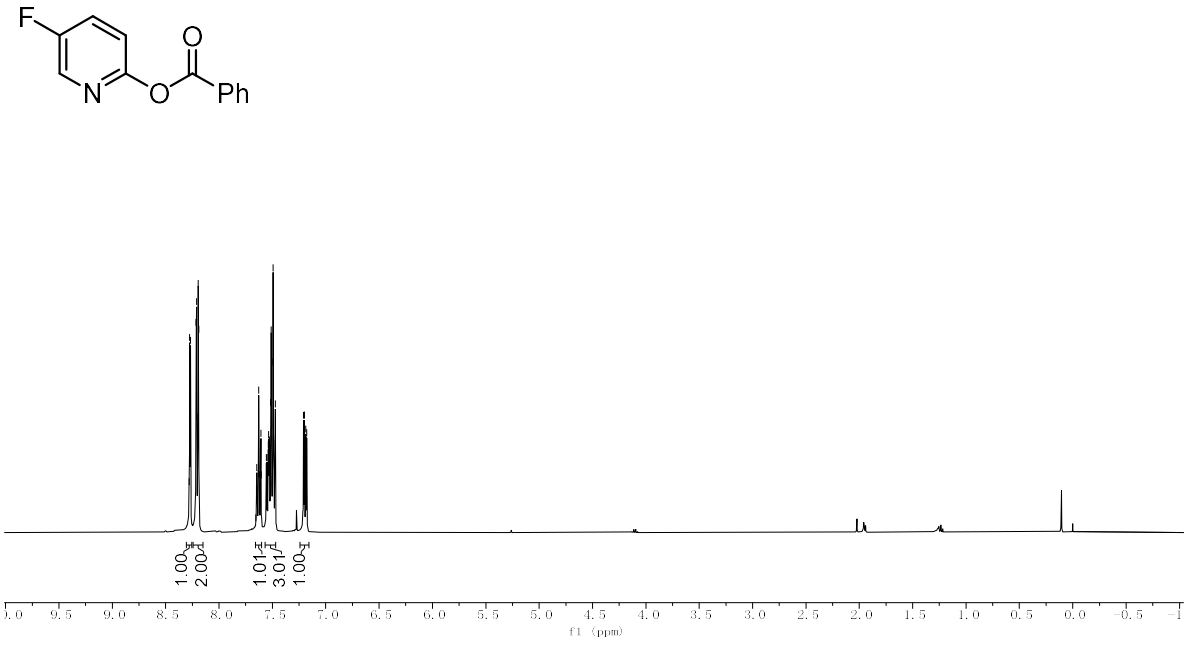
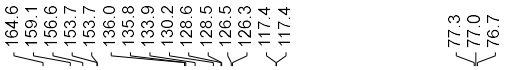
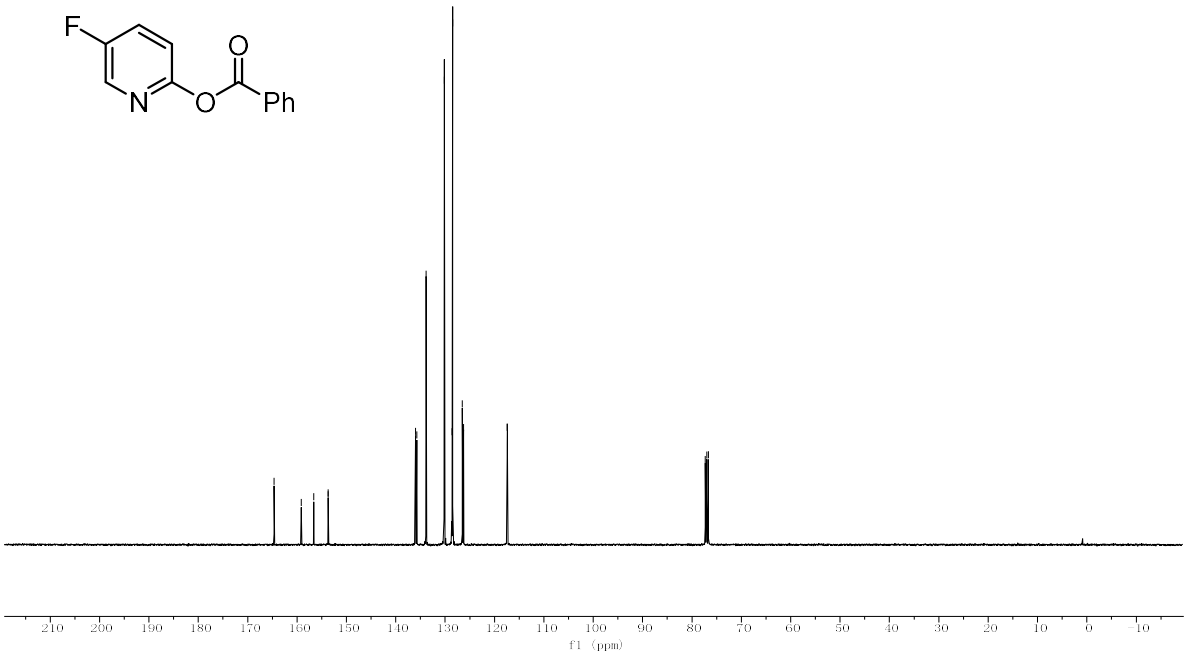
8. NMR spectra



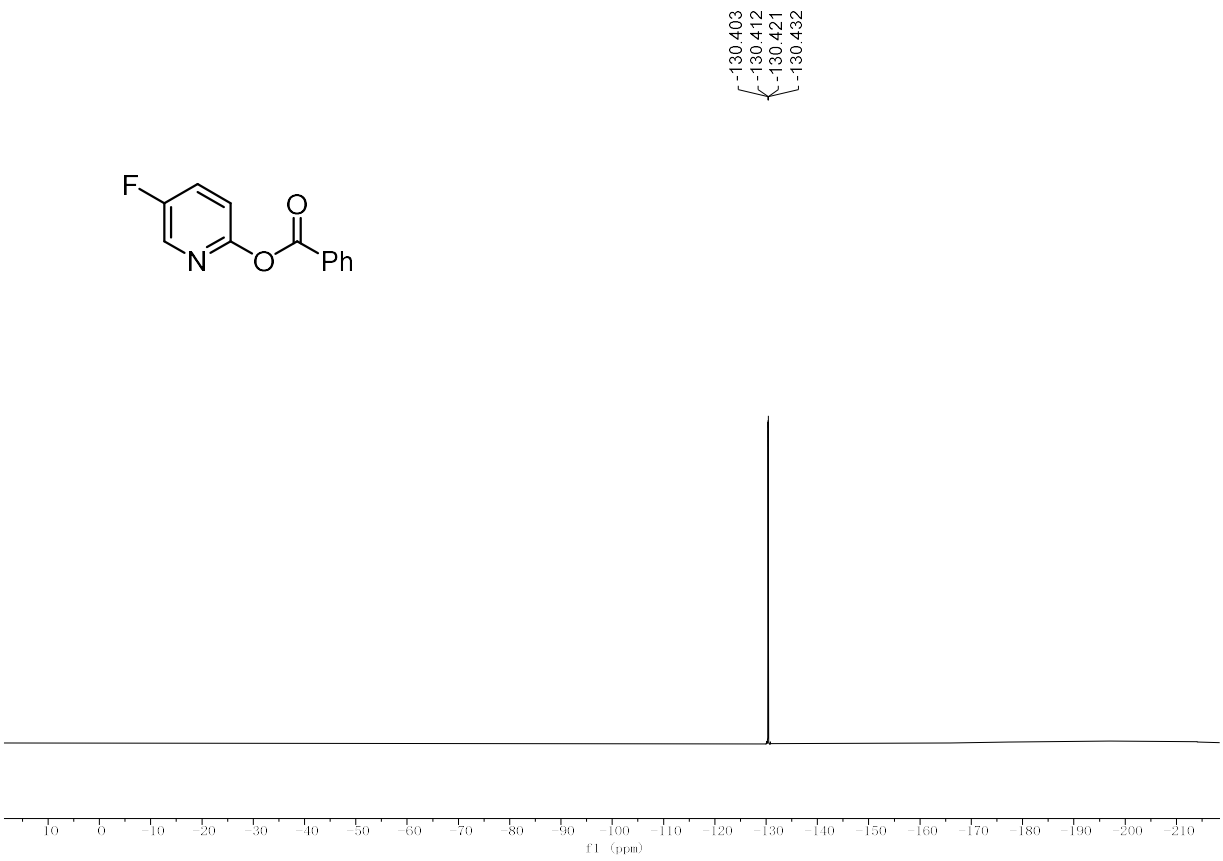


^{1}H NMR (400 MHz, $CDCl_3$) of **1b**

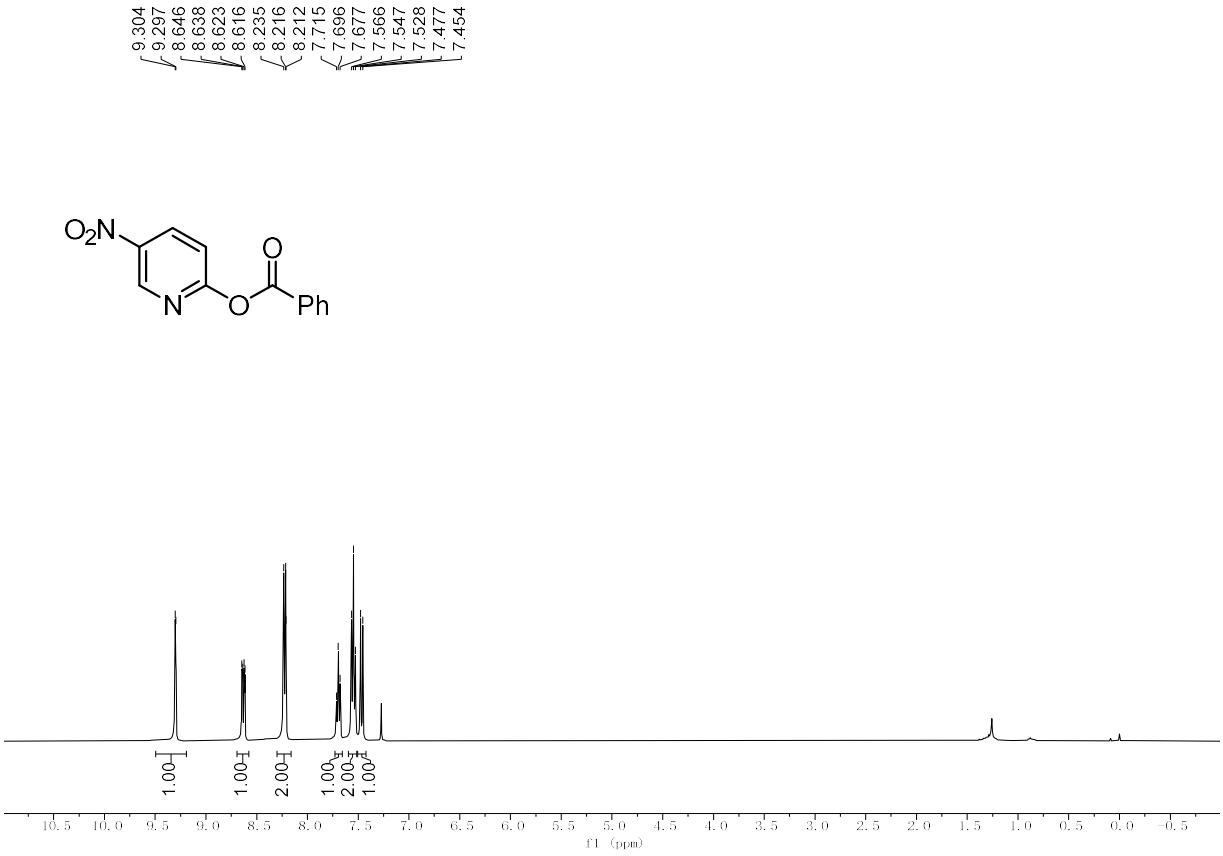




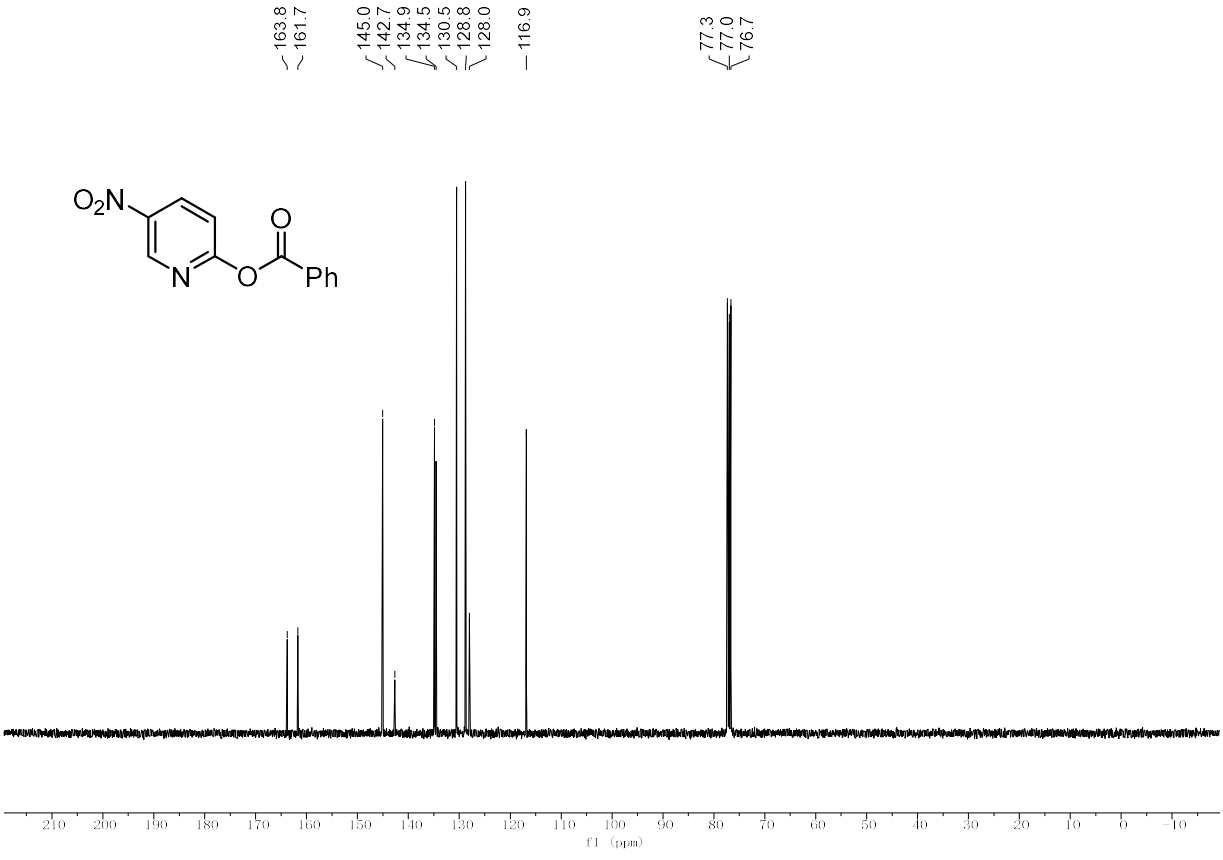
^{13}C NMR (101 MHz, $CDCl_3$) of **1b**



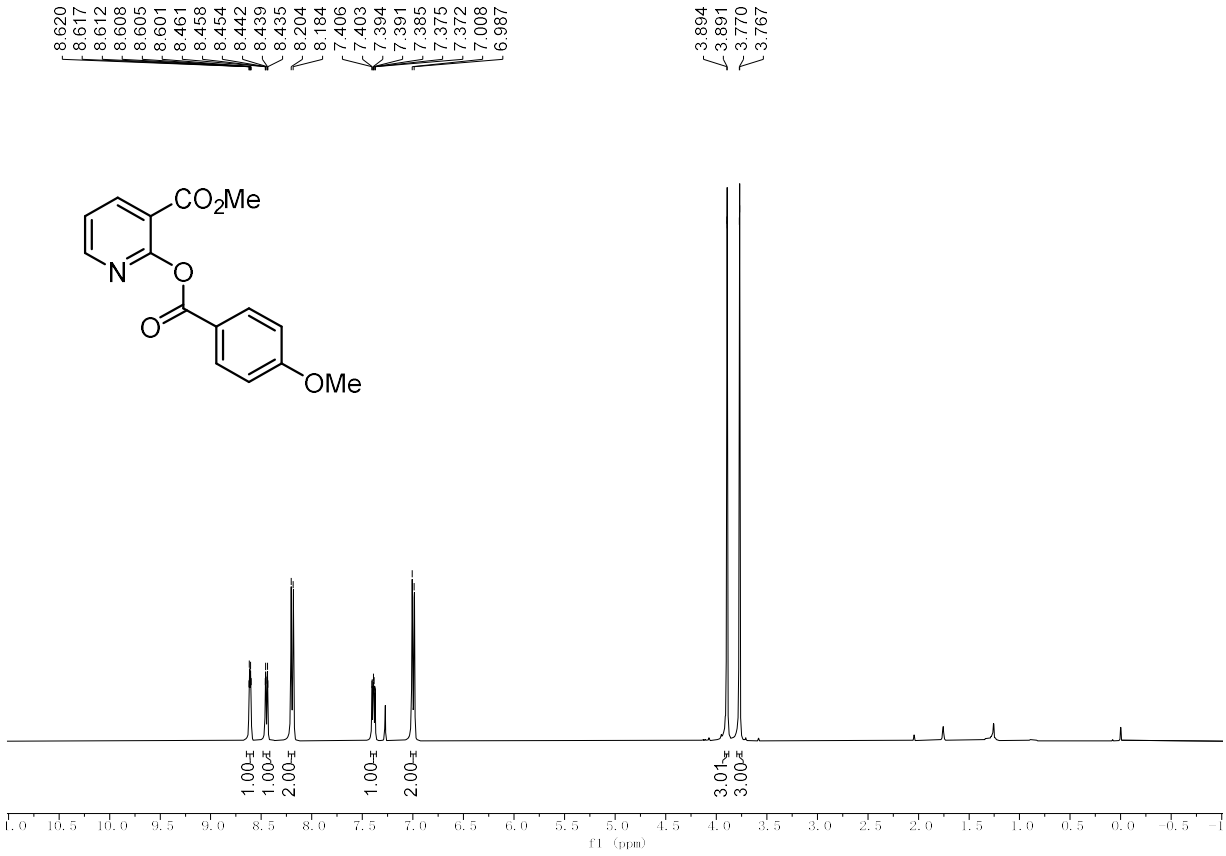
^{19}F NMR (376 MHz, $CDCl_3$) of **1b**



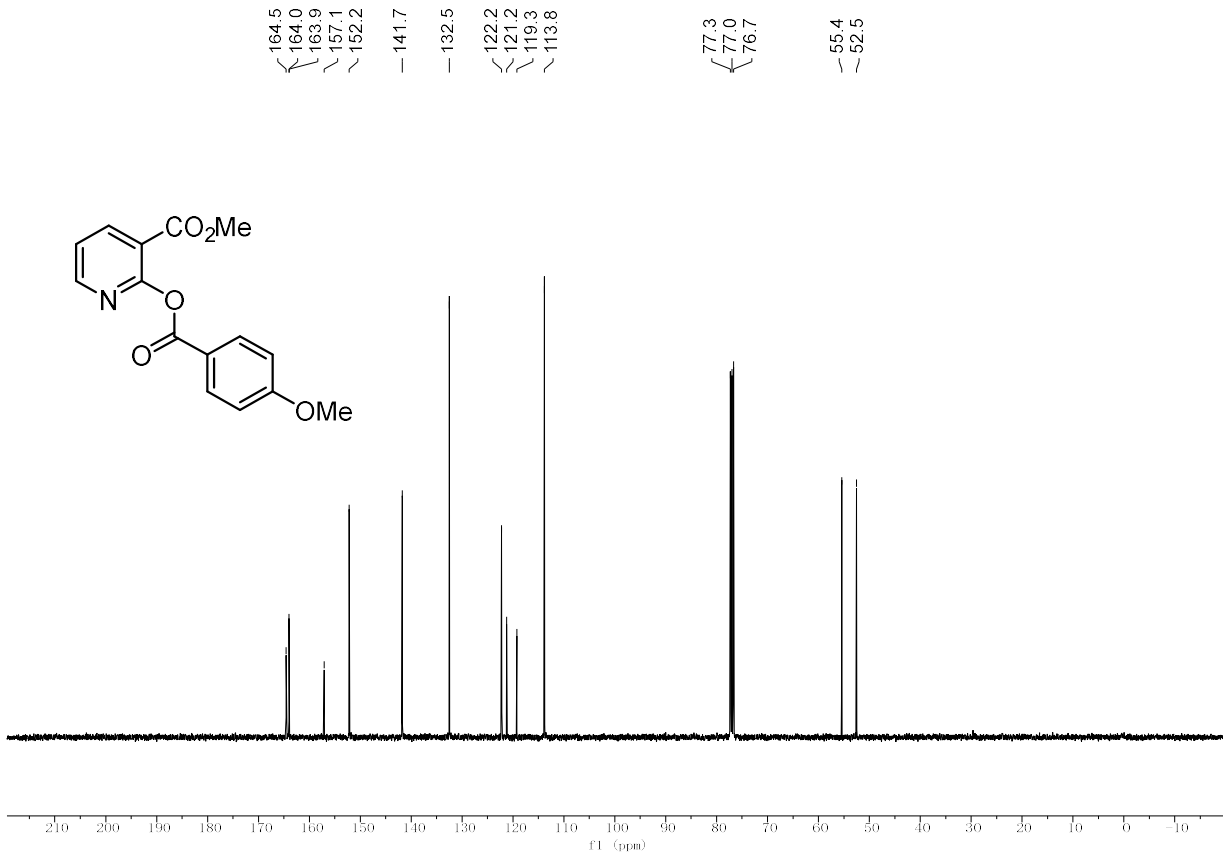
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



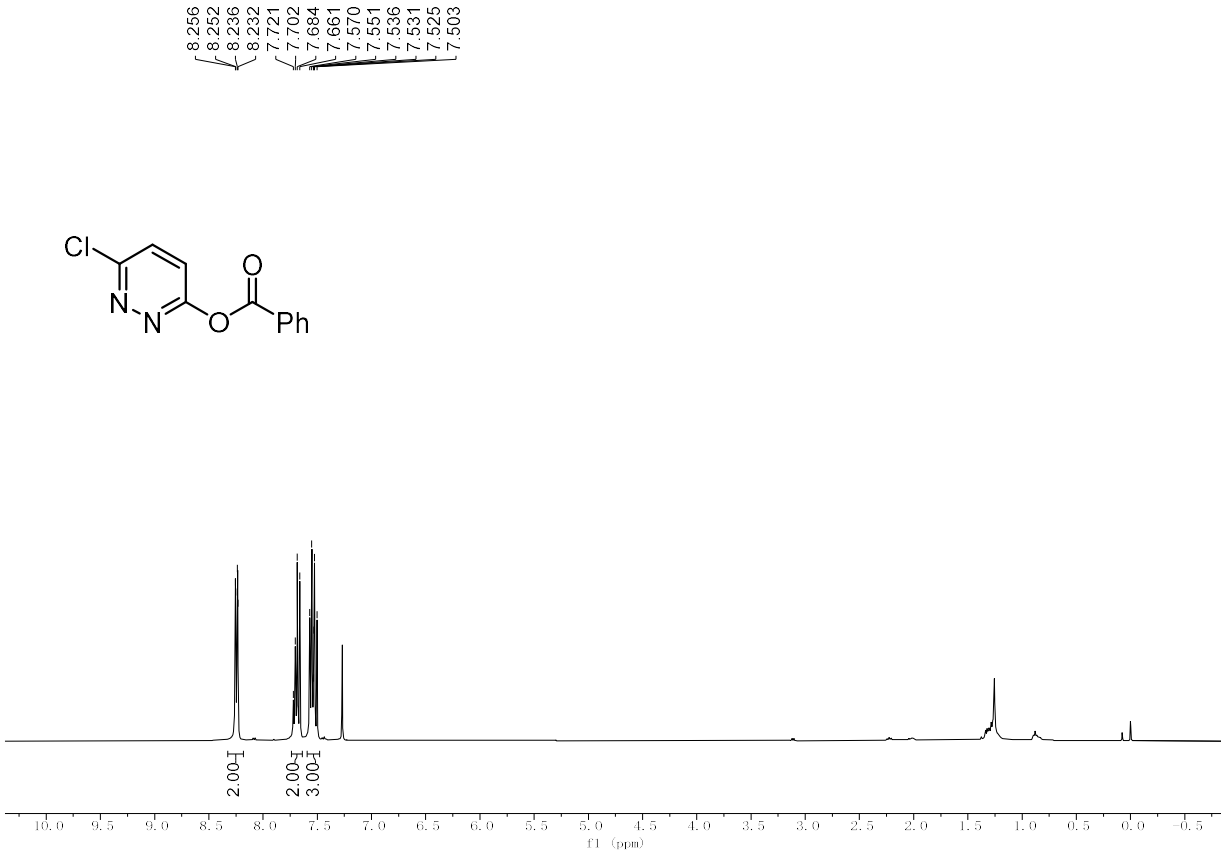
^{13}C NMR (101 MHz, $CDCl_3$) of **1c**



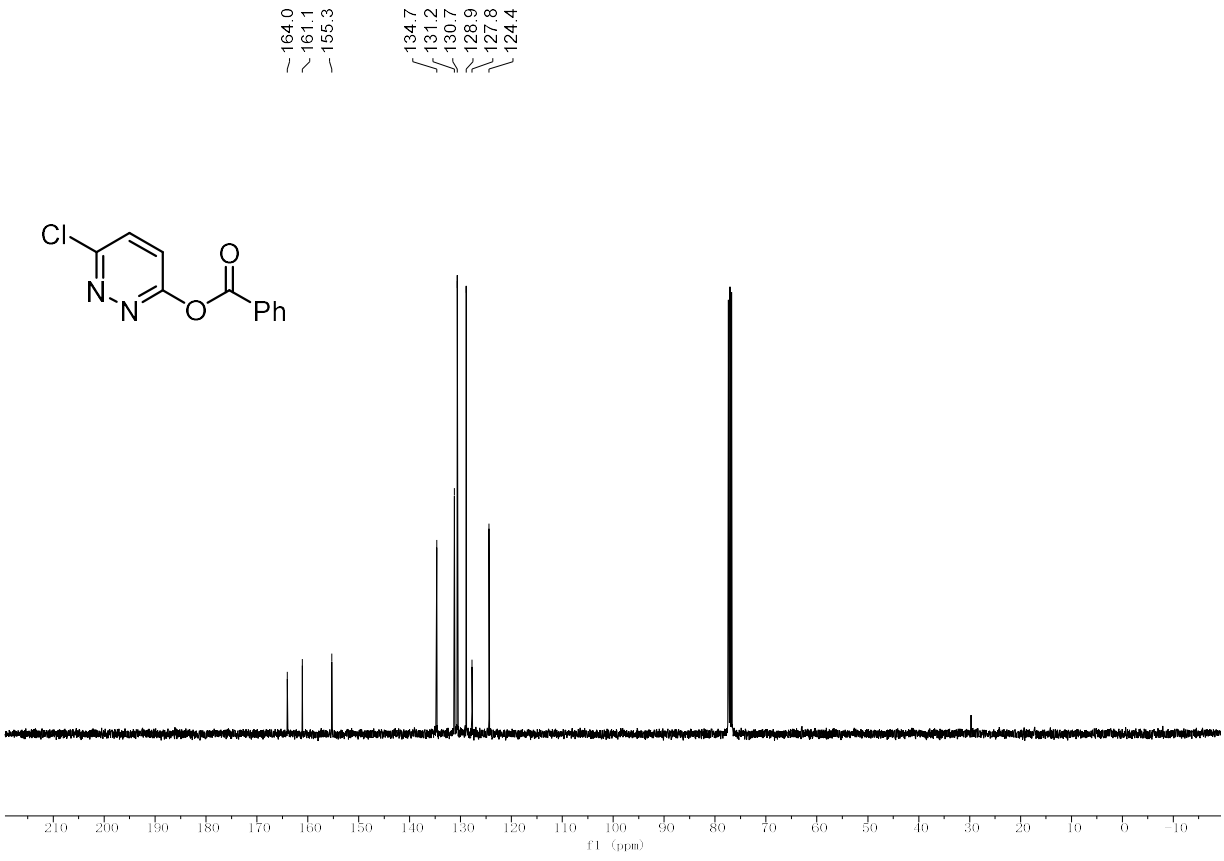
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



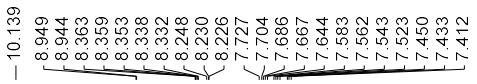
^{13}C NMR (101 MHz, $CDCl_3$) of **1d**

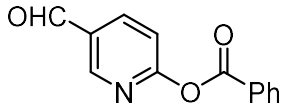


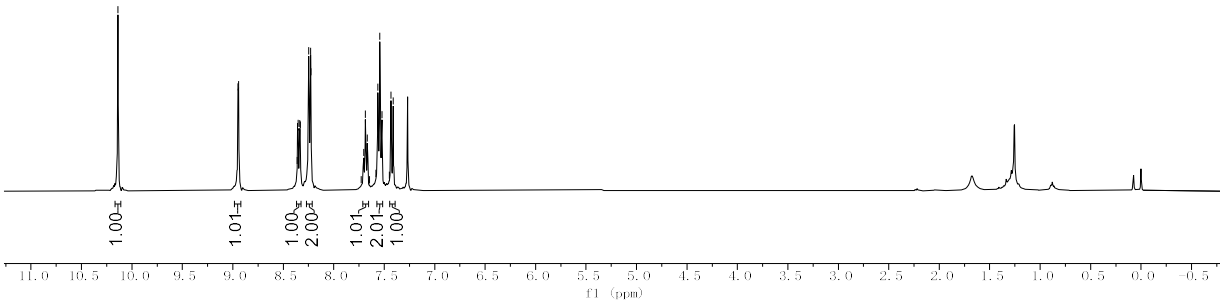
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



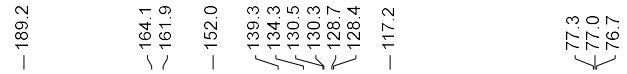
^{13}C NMR (101 MHz, $CDCl_3$) of **1e**

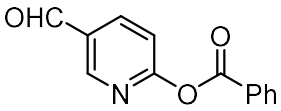


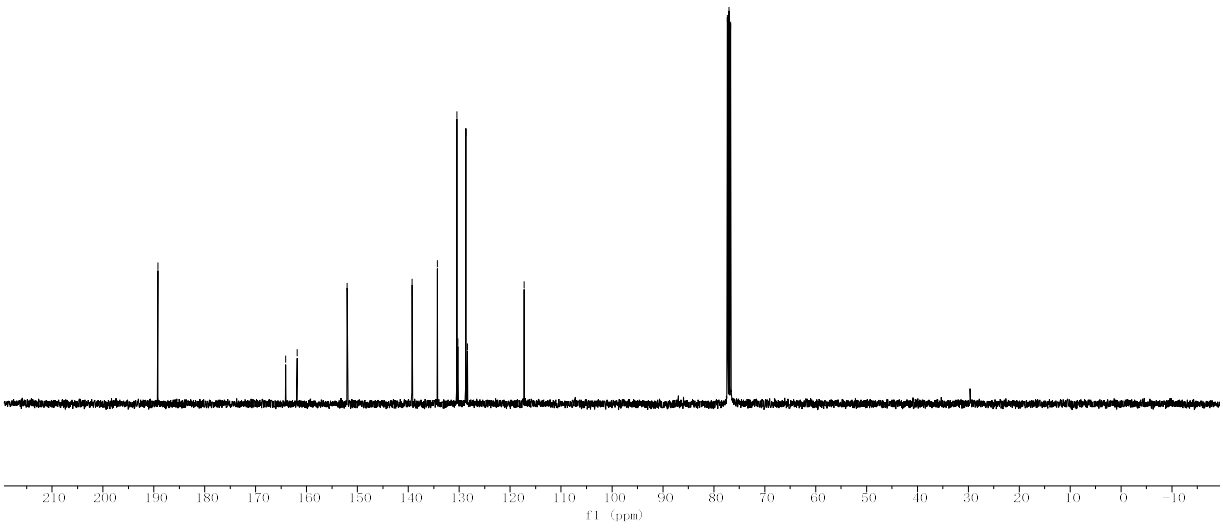




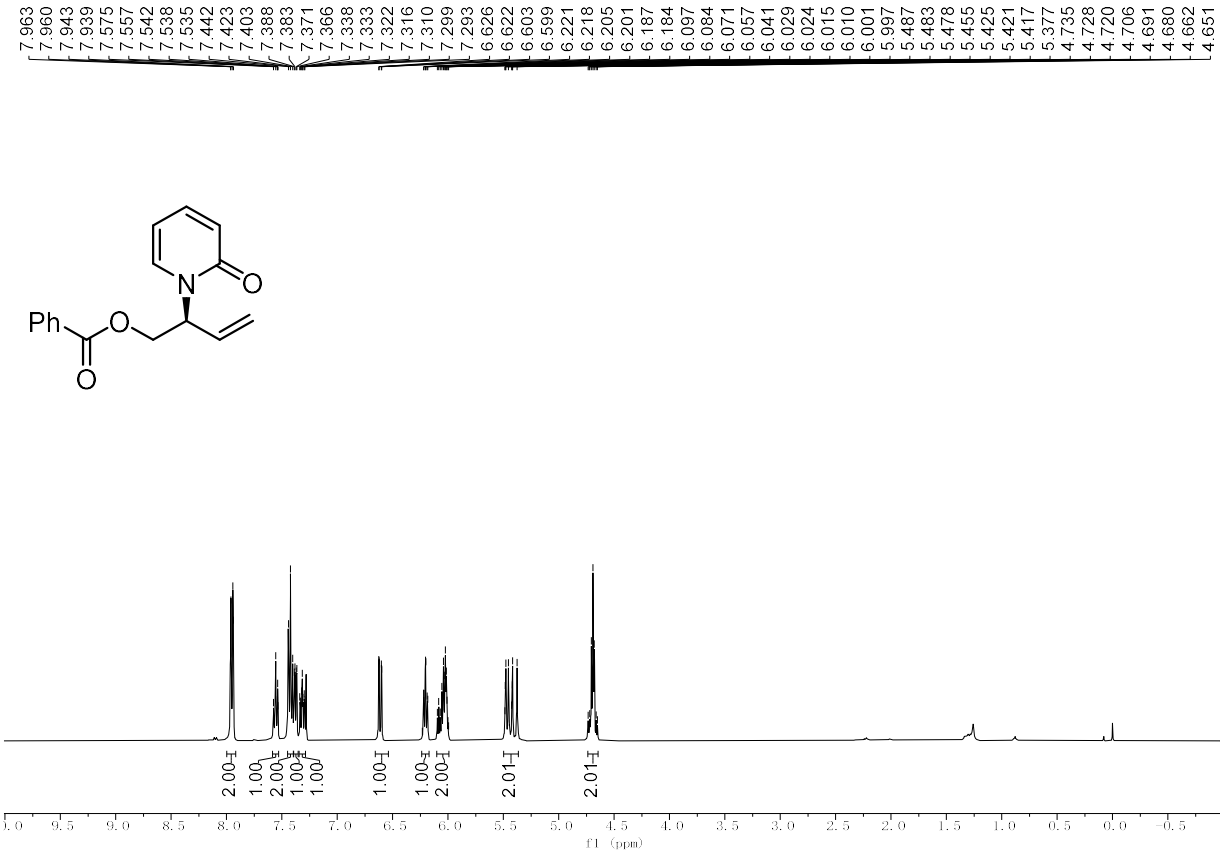
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



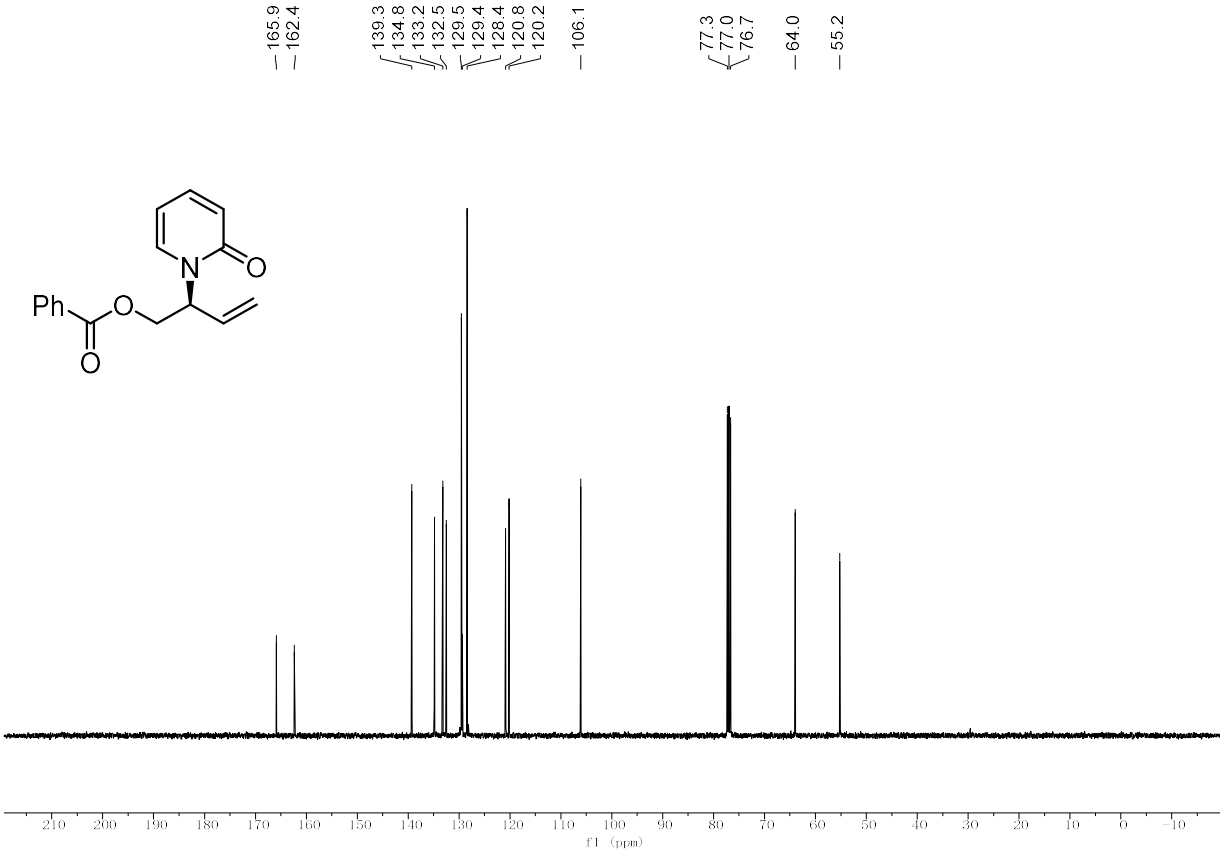




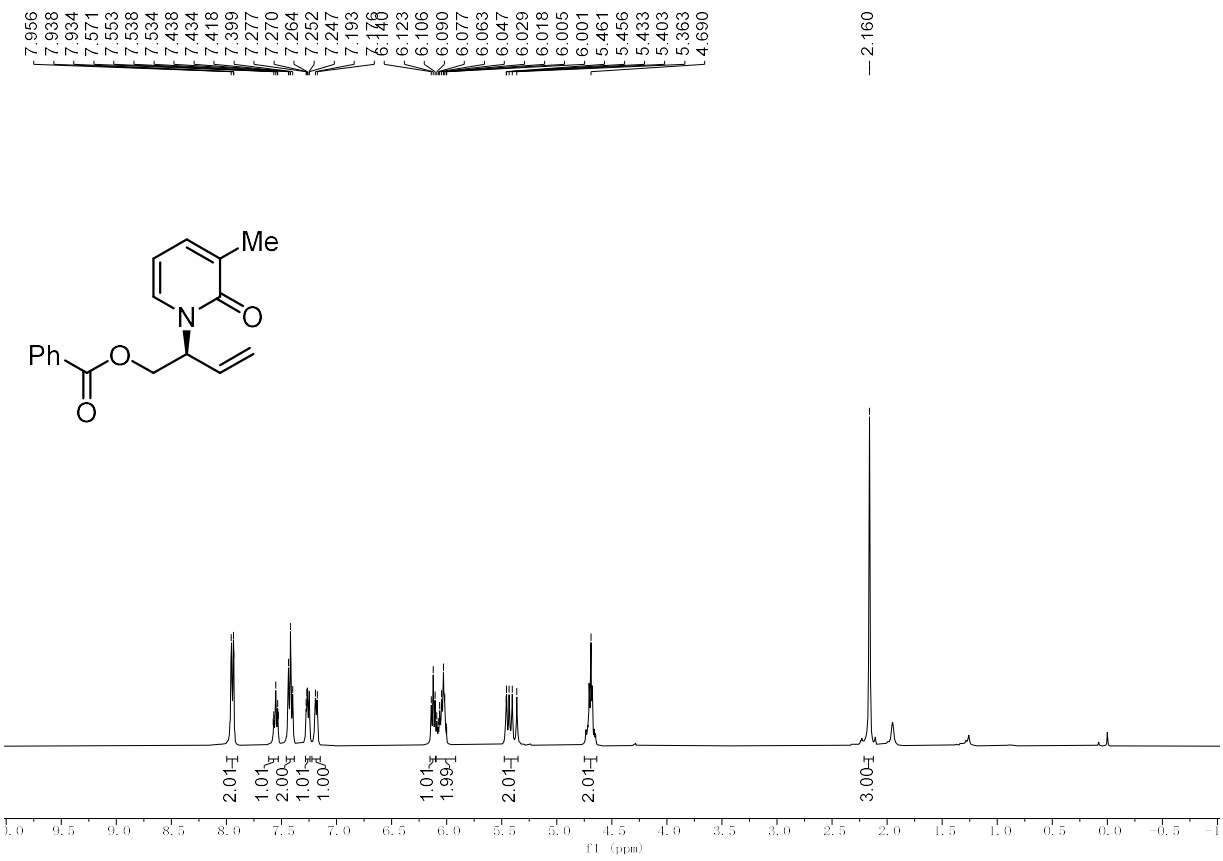
^{13}C NMR (101 MHz, $CDCl_3$) of **1f**



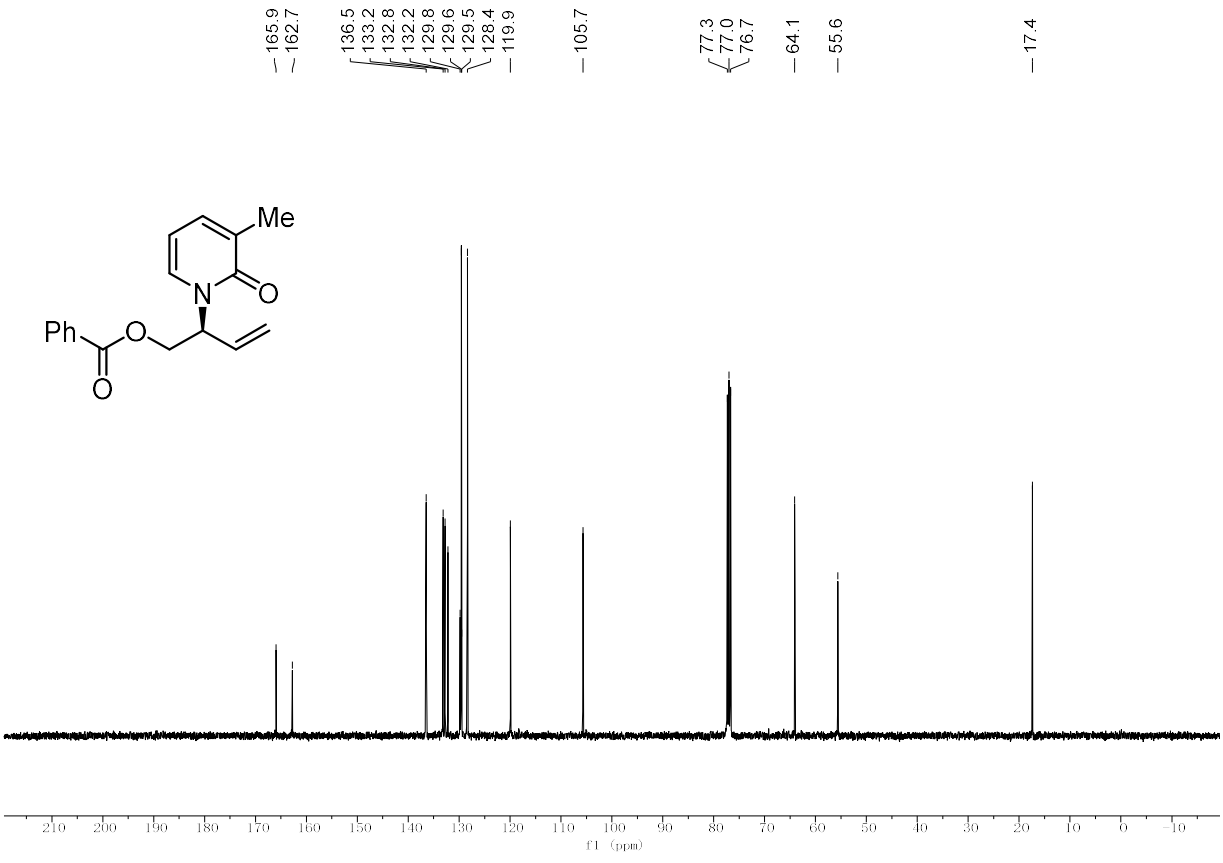
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



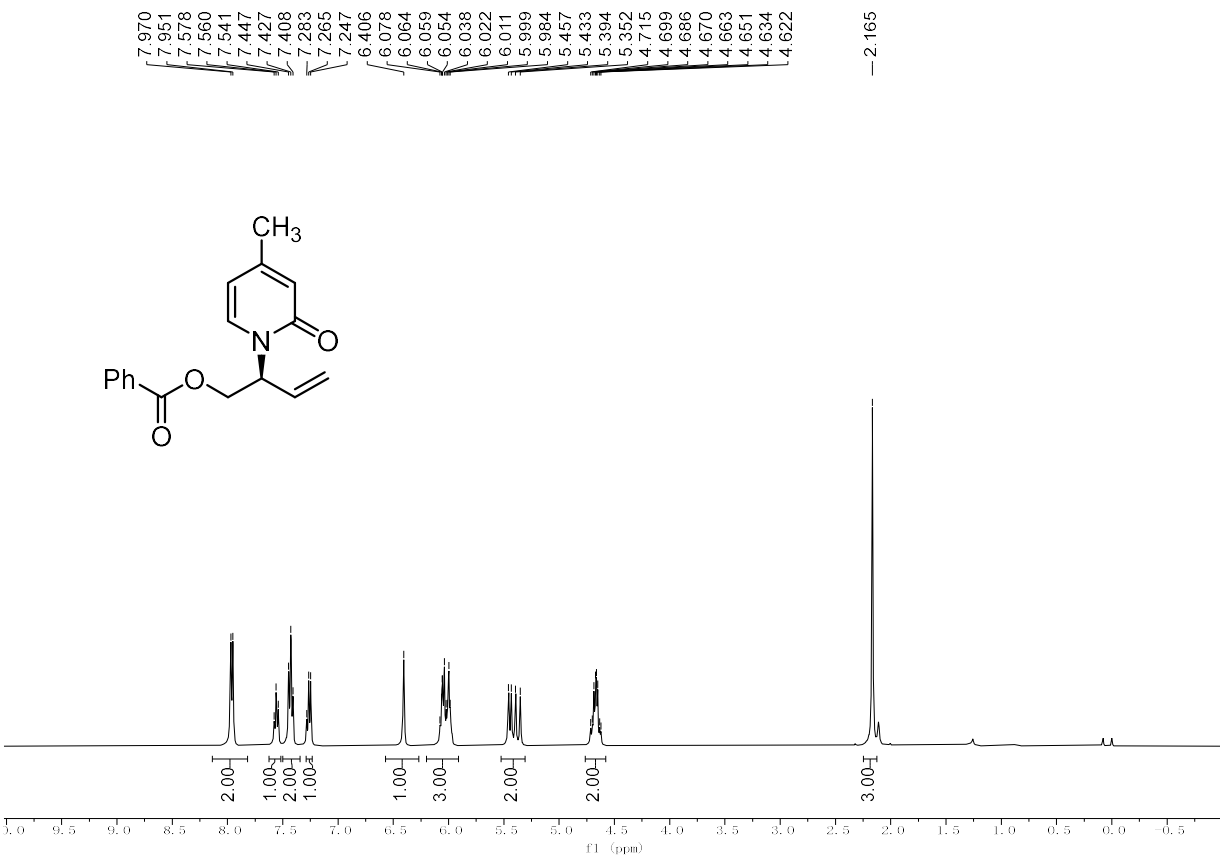
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



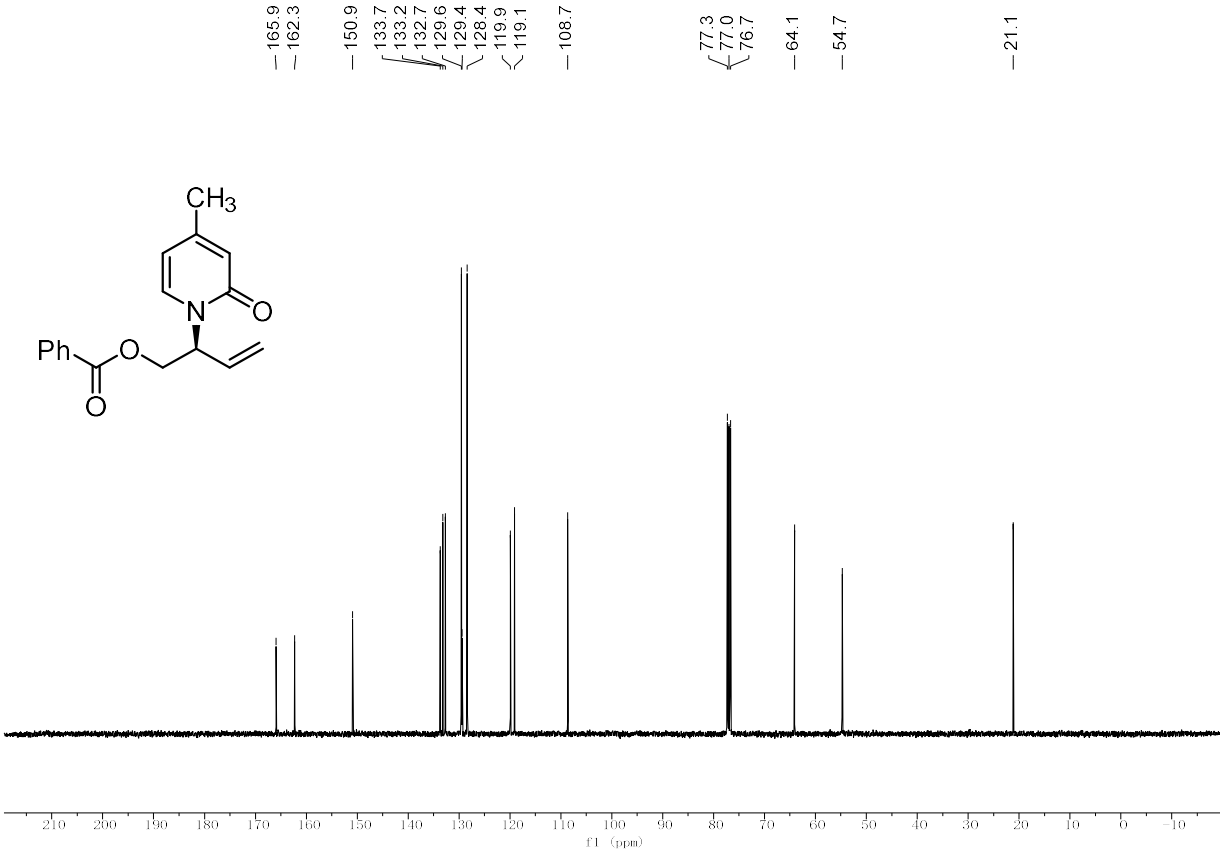
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



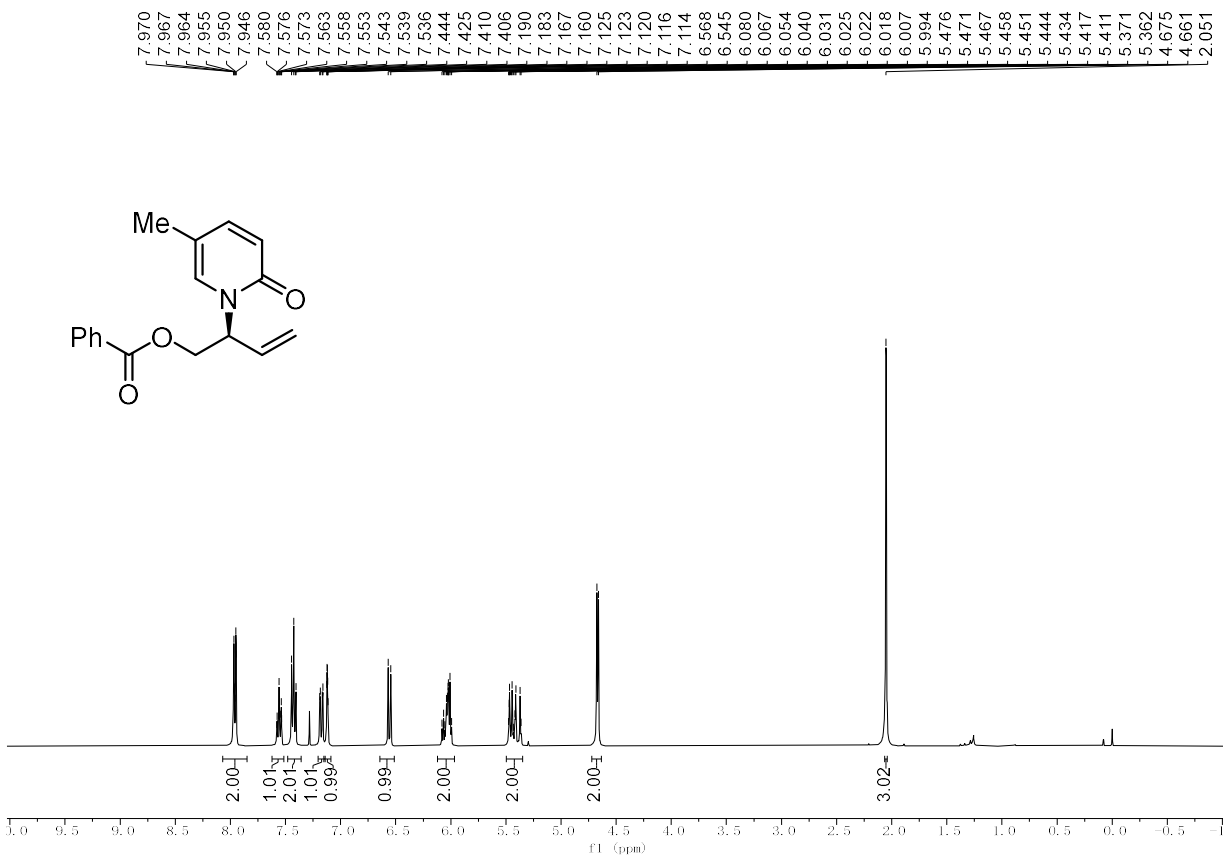
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



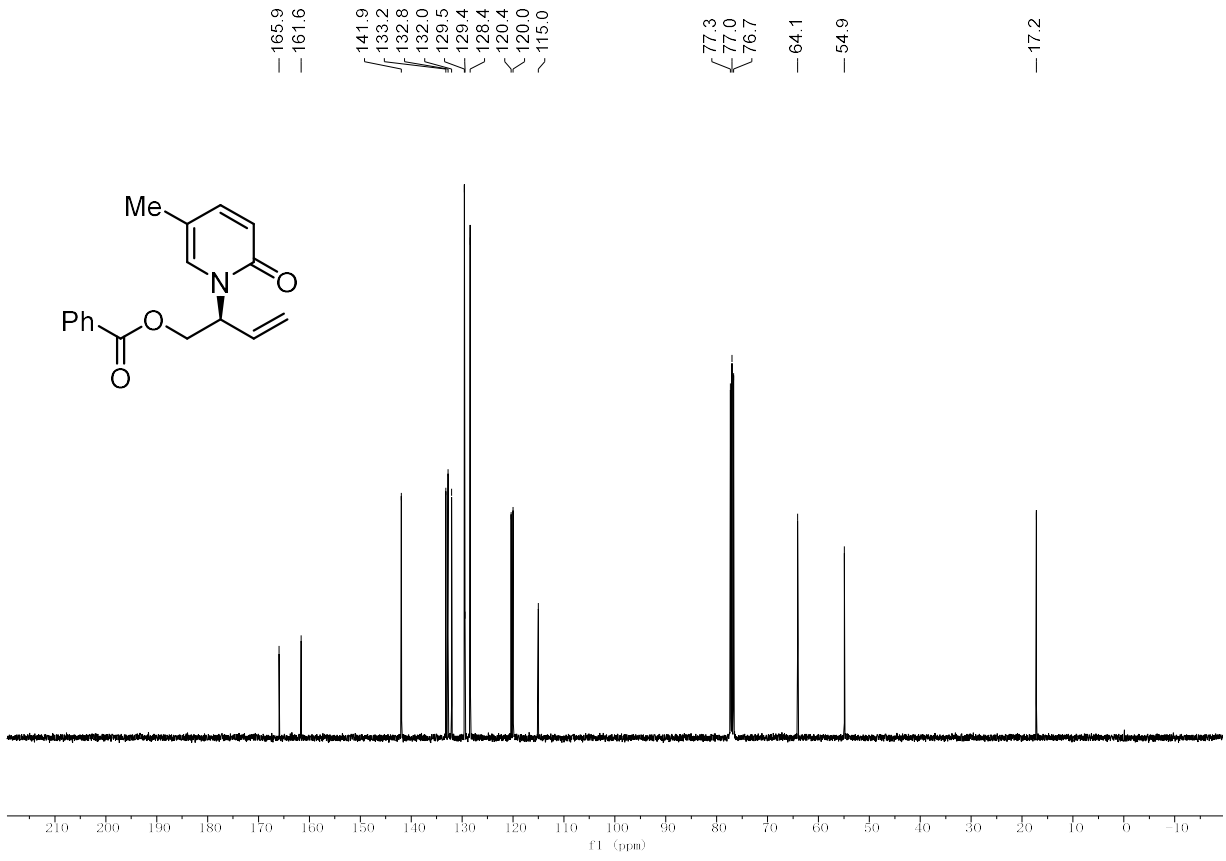
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



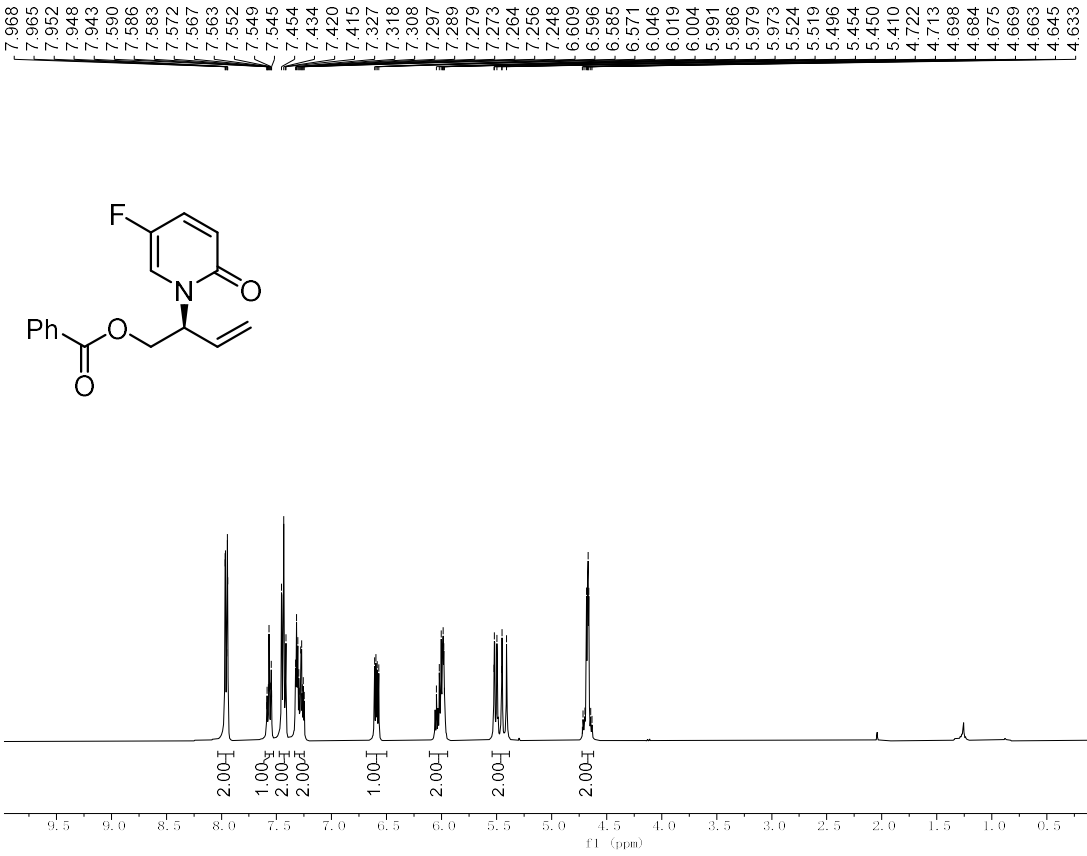
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



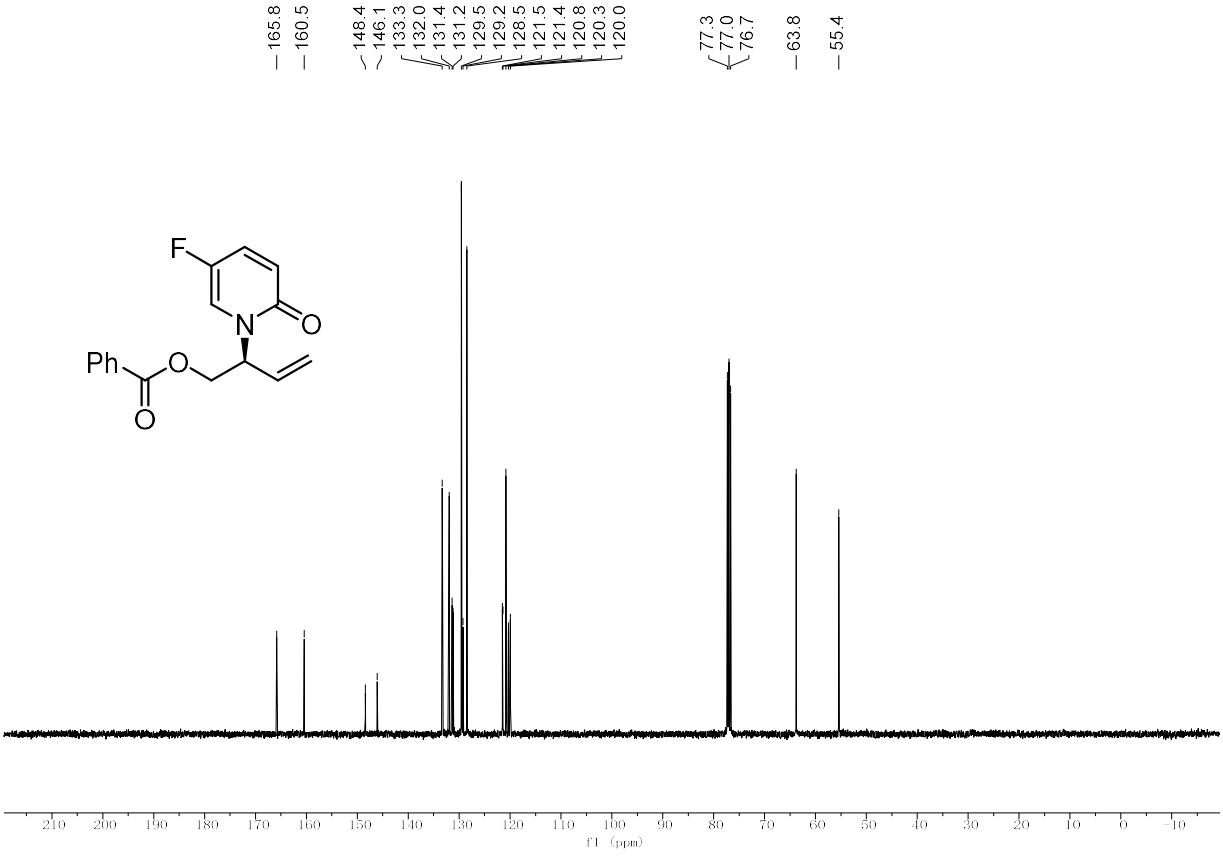
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



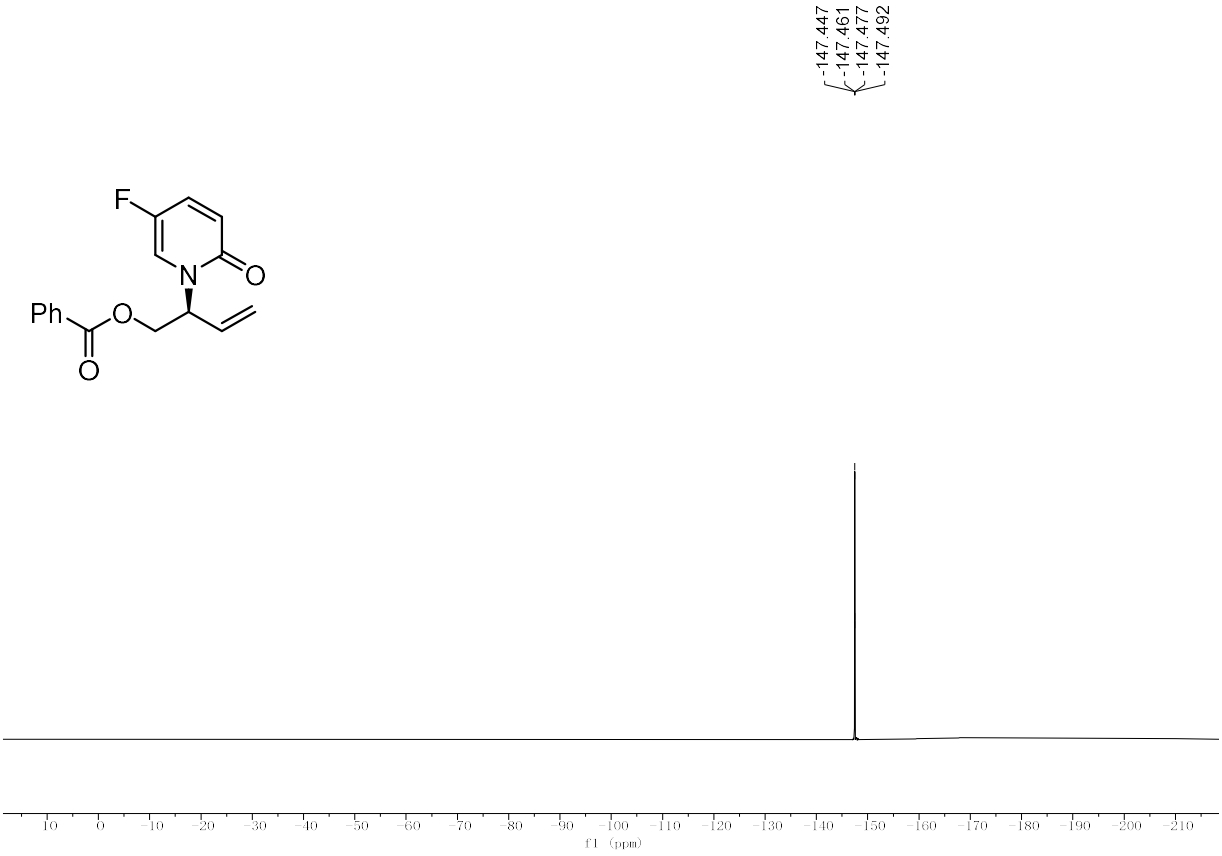
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



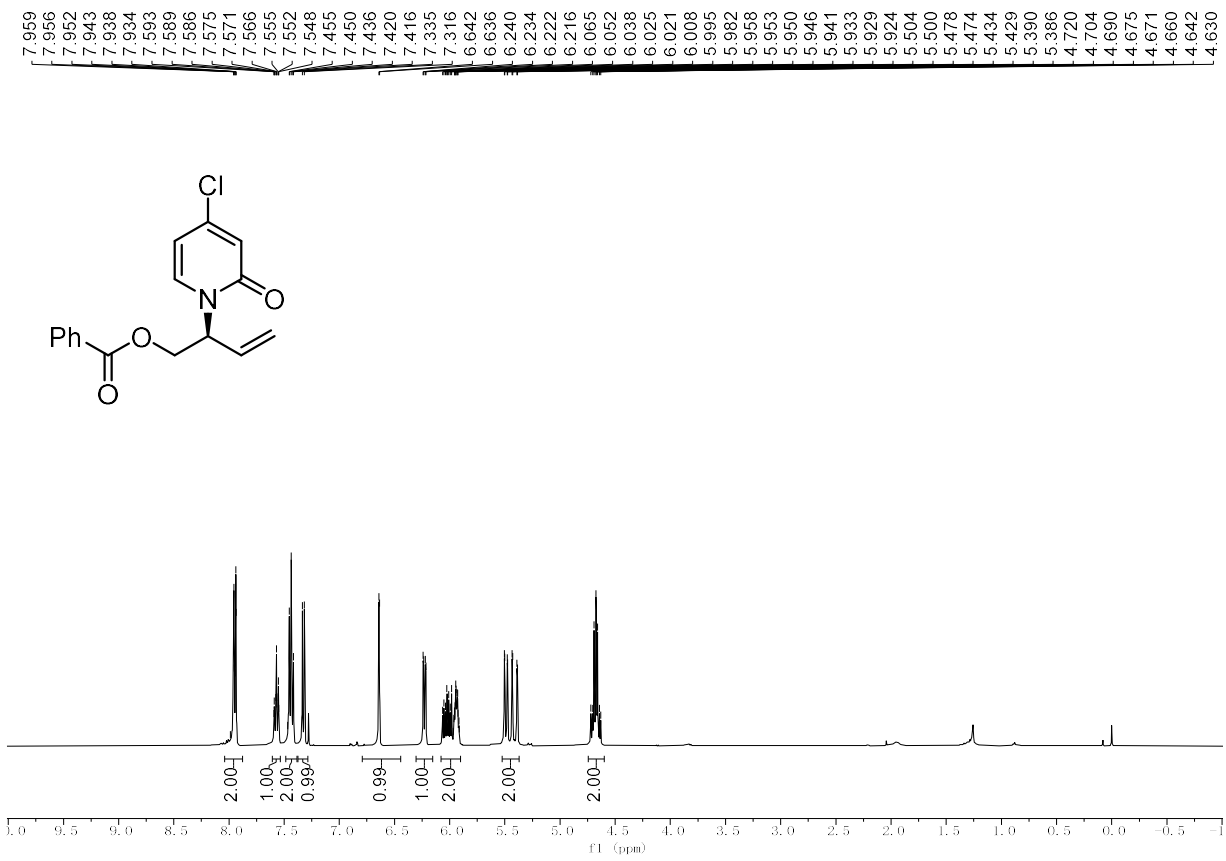
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



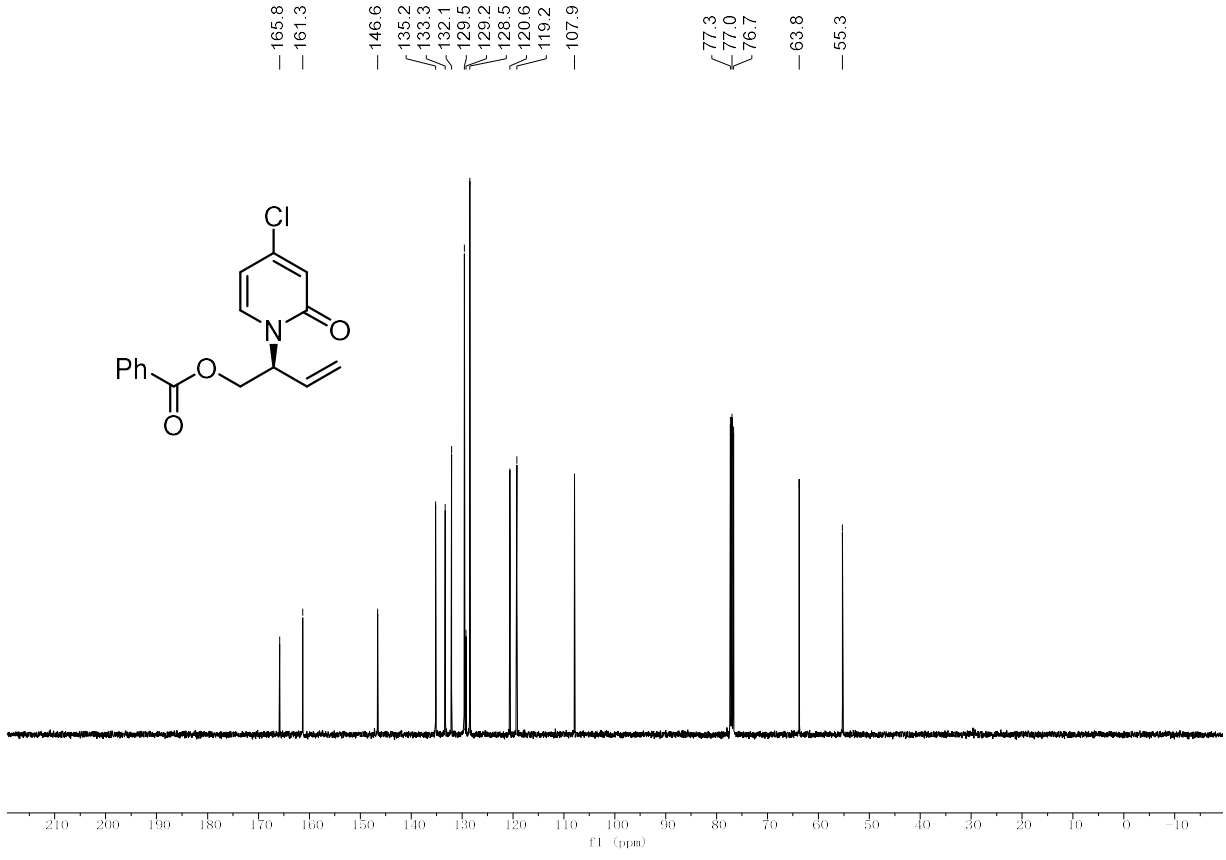
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



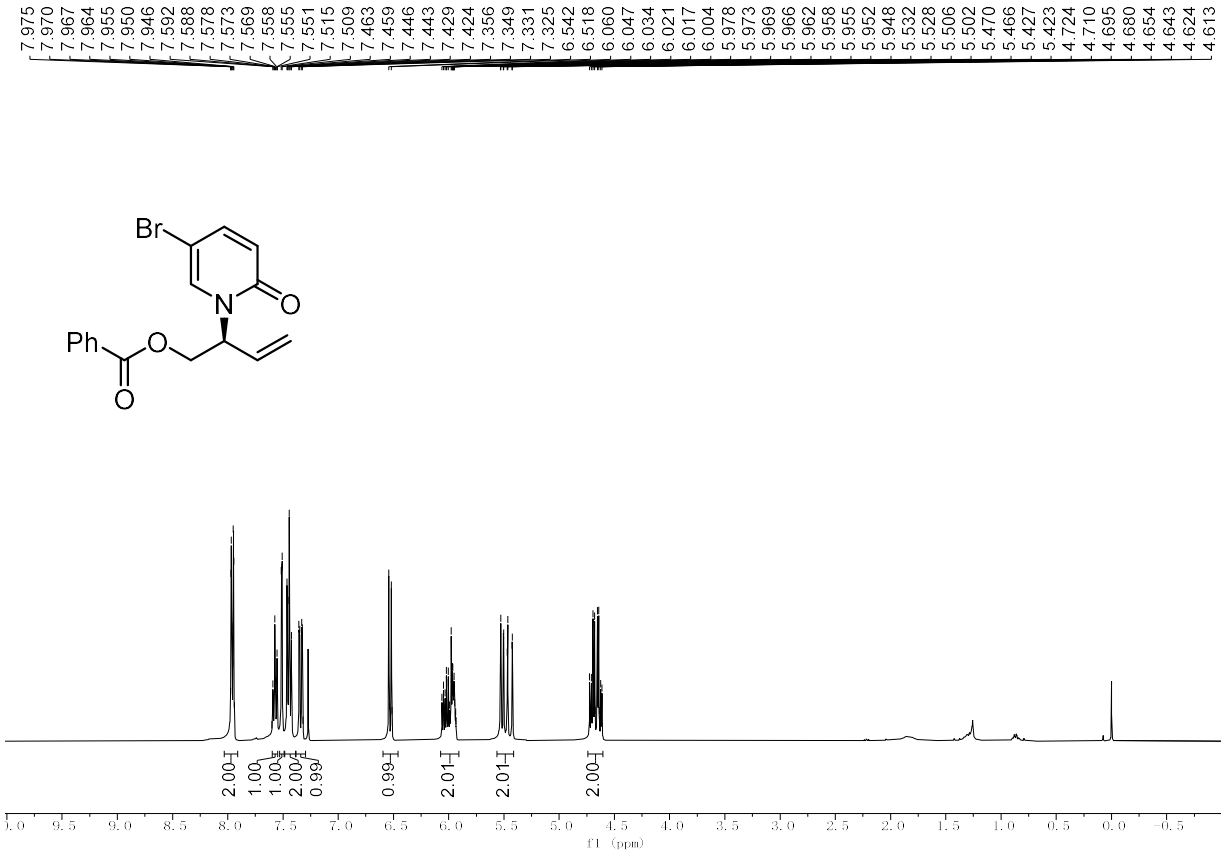
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



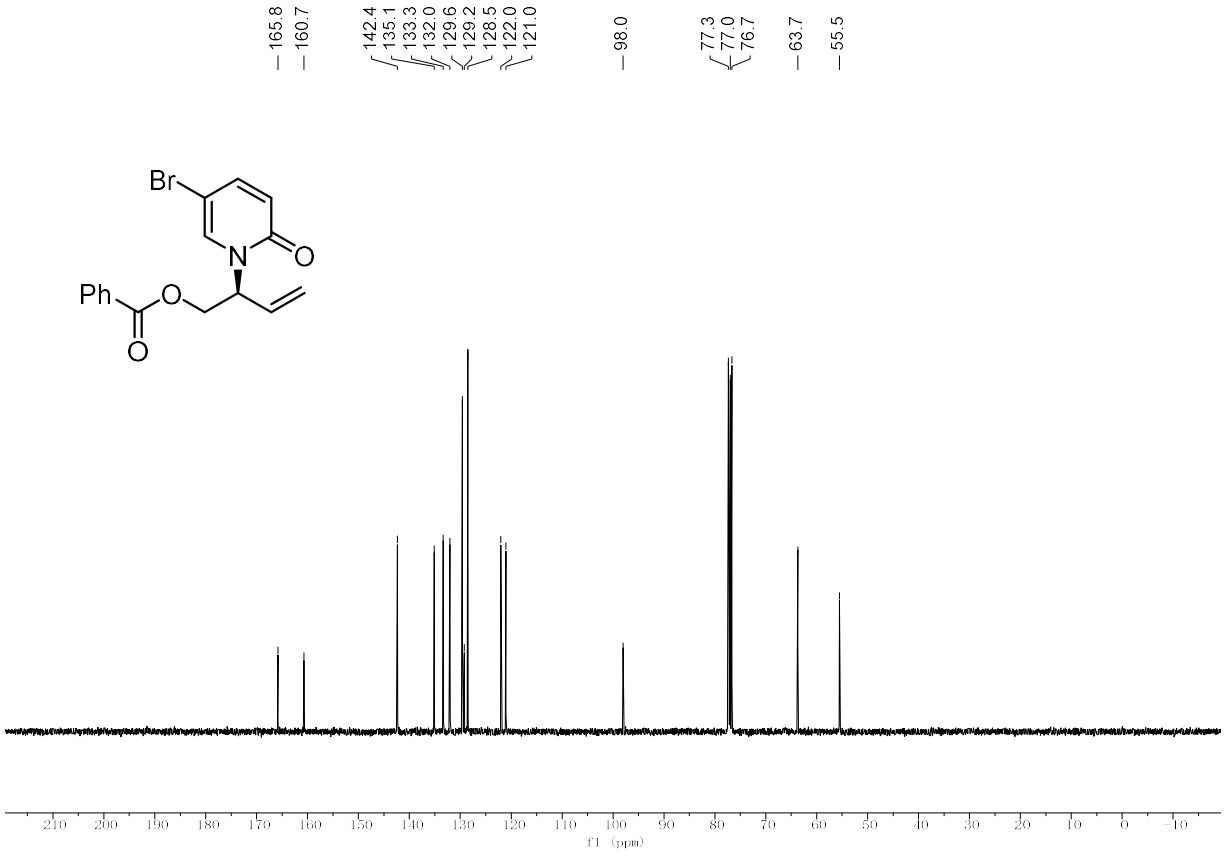
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



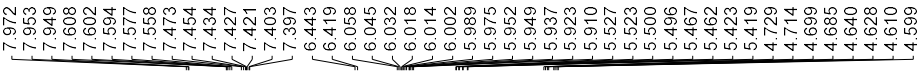
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**

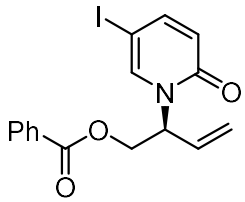


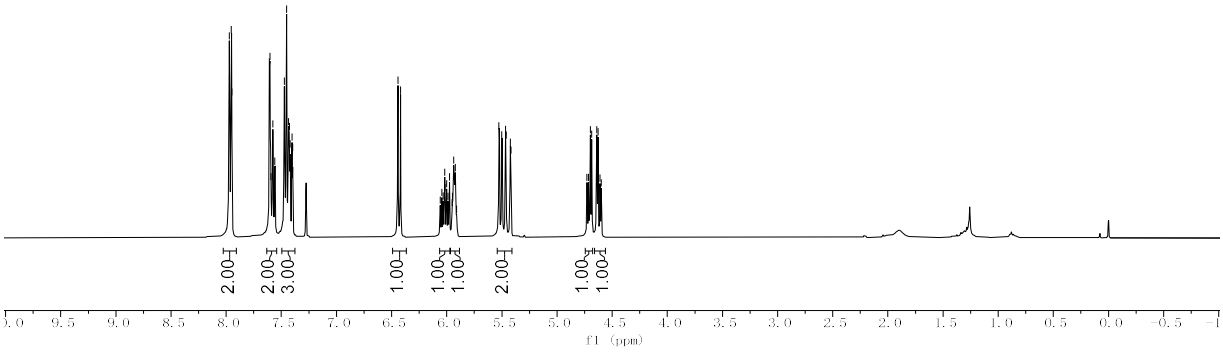
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



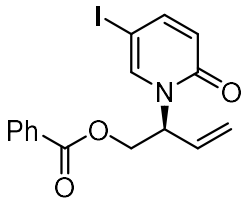
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**

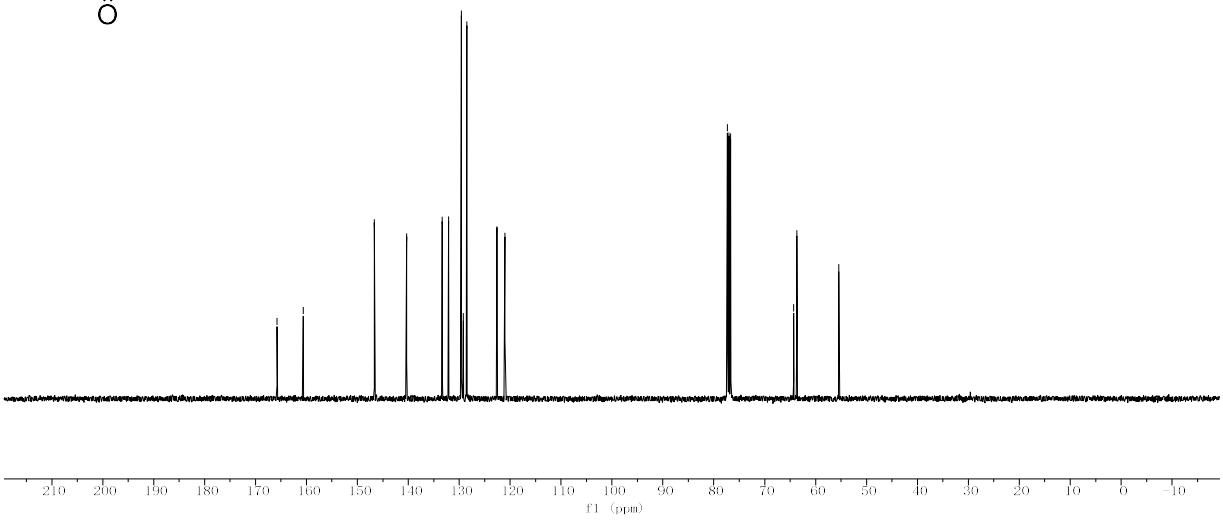




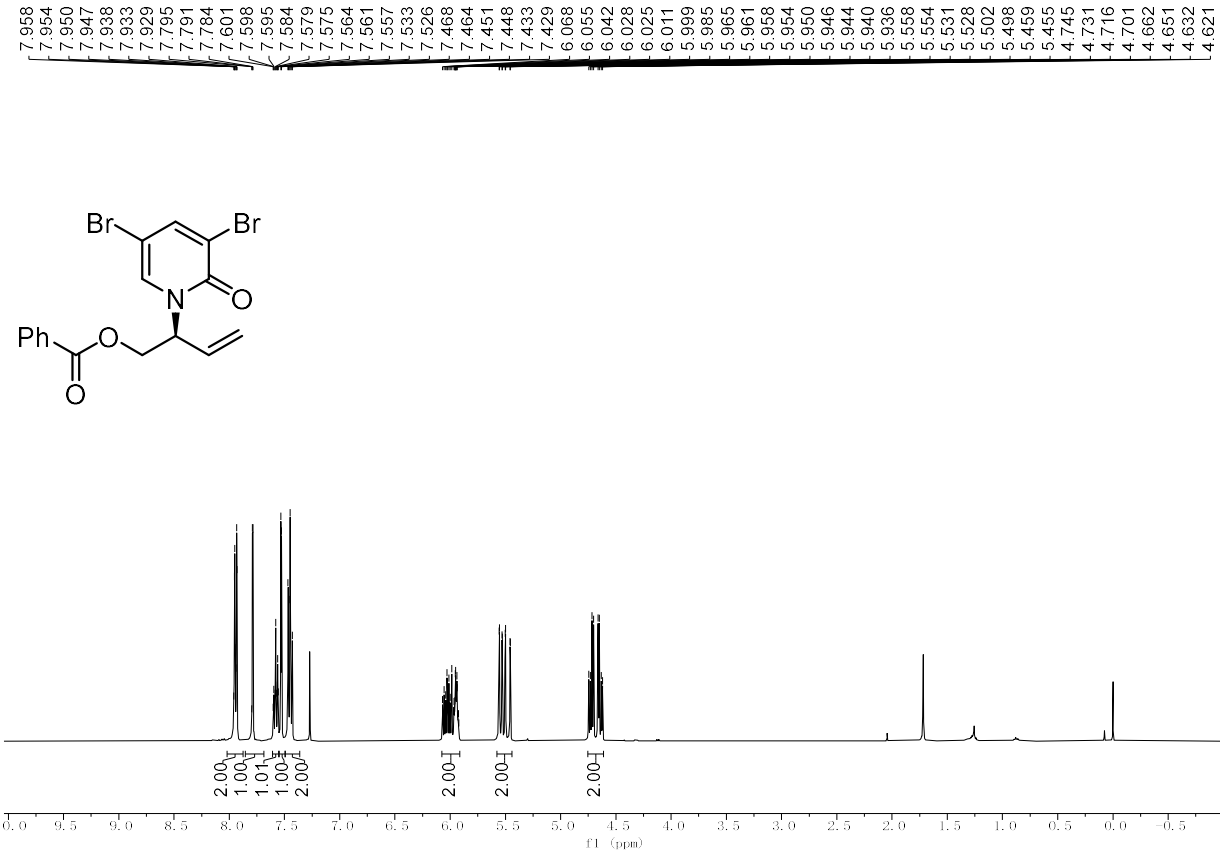


^{1}H NMR (400 MHz, $CDCl_3$) of **3h**

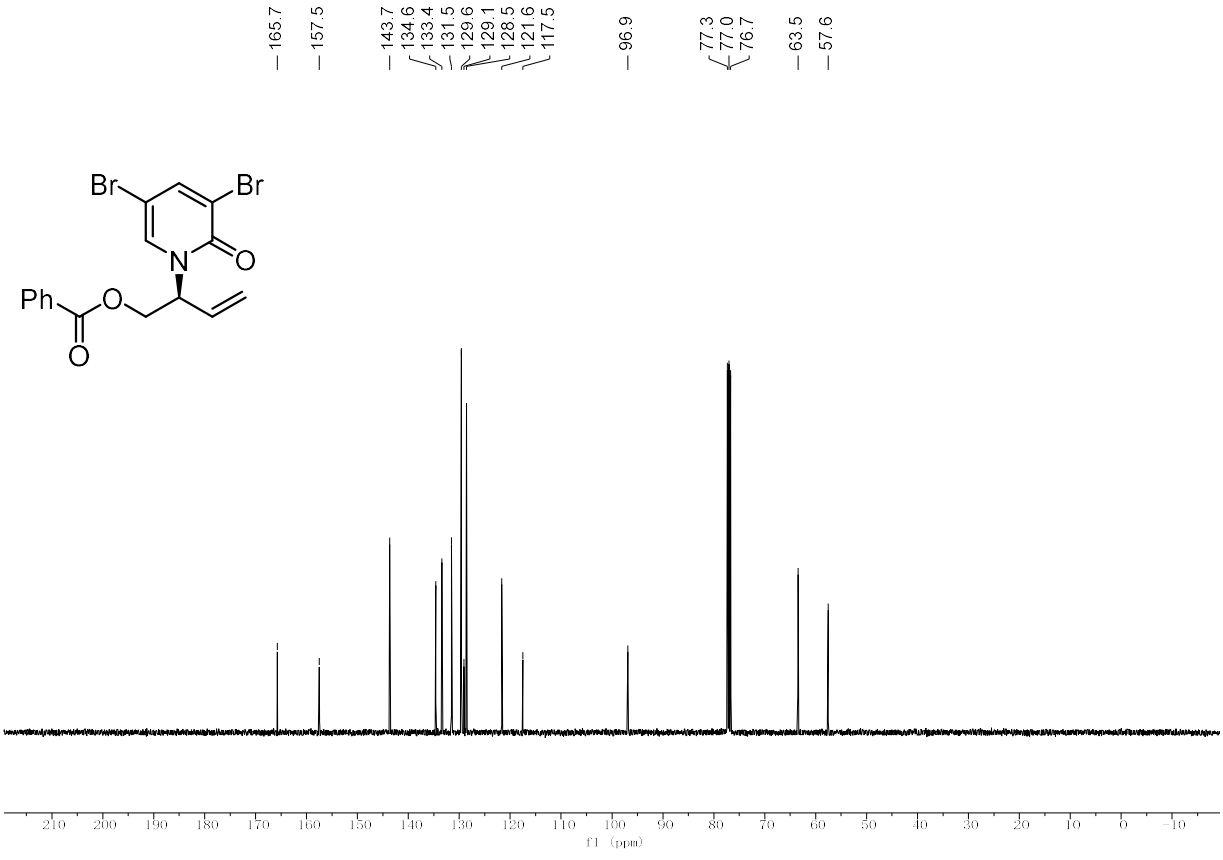




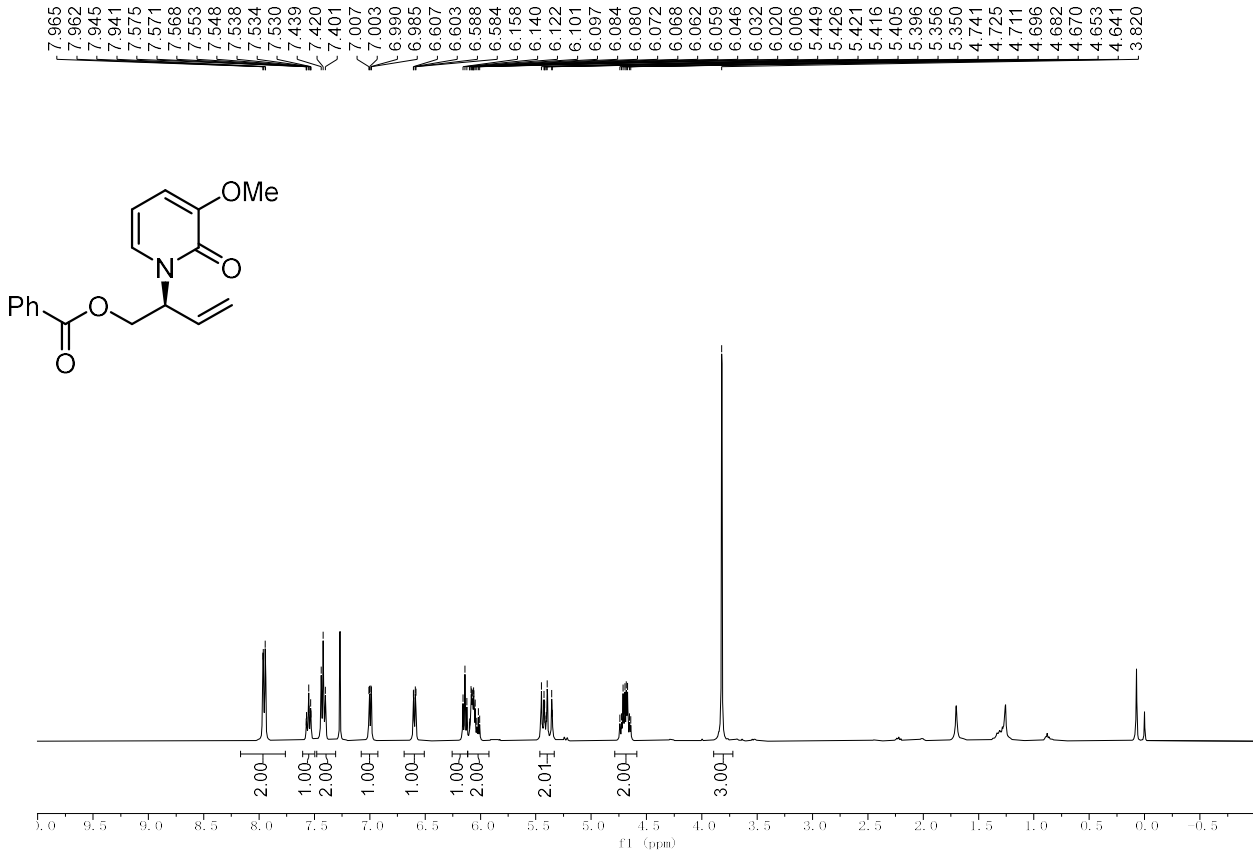
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



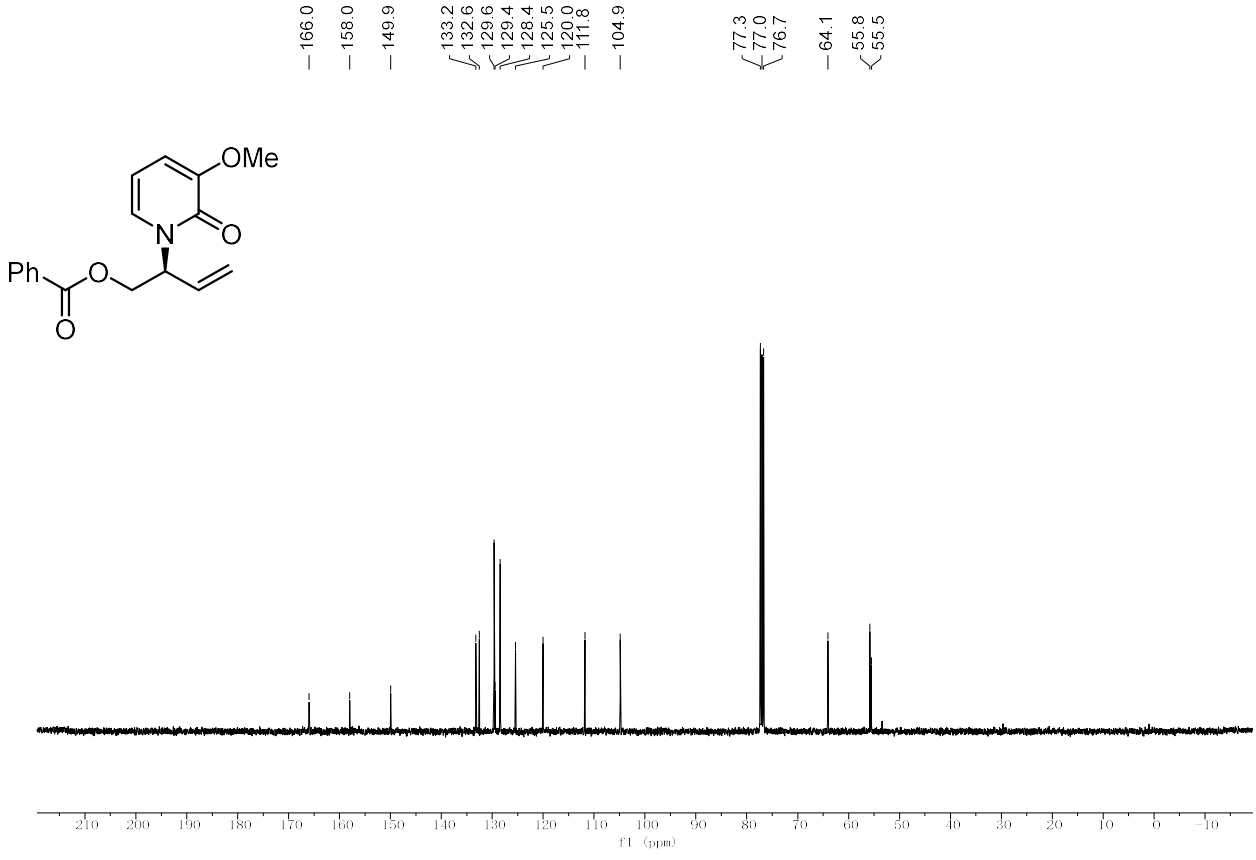
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



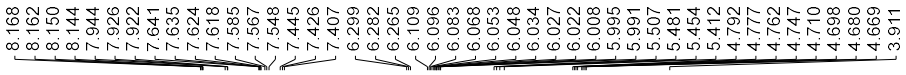
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**

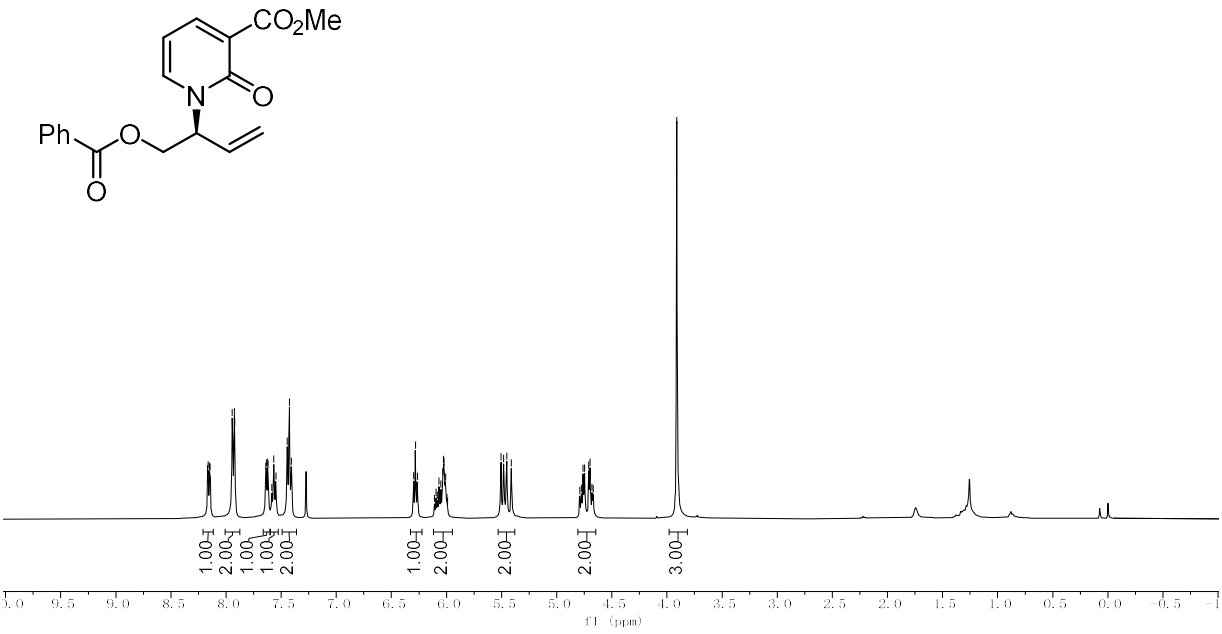


^{1}H NMR (400 MHz, $CDCl_3$) of **3j**

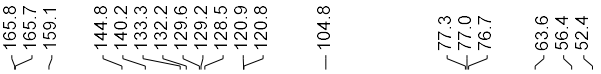


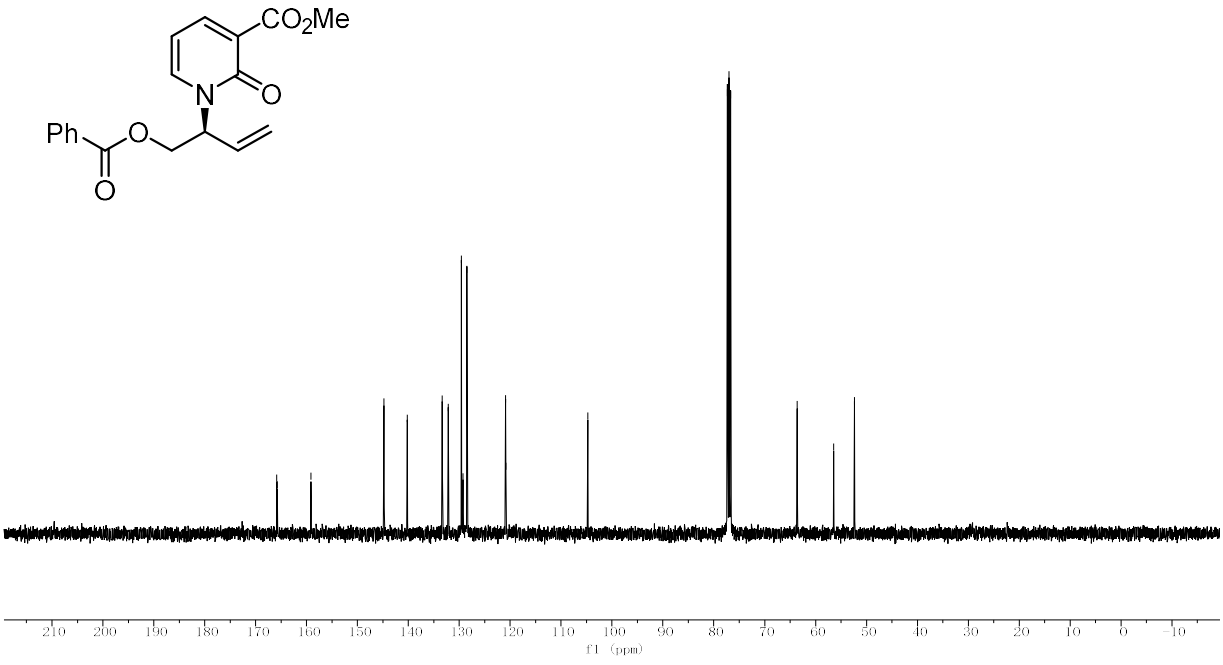
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



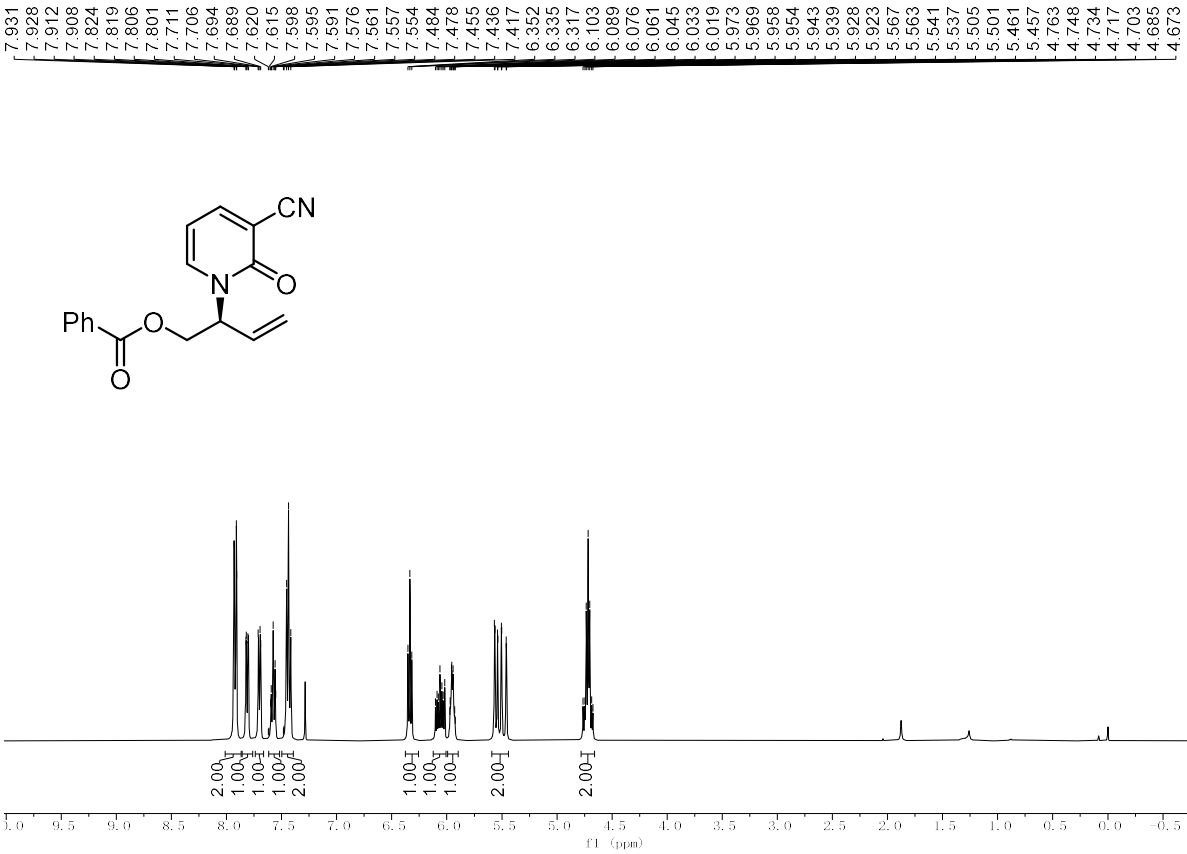


^{1}H NMR (400 MHz, $CDCl_3$) of **3k**

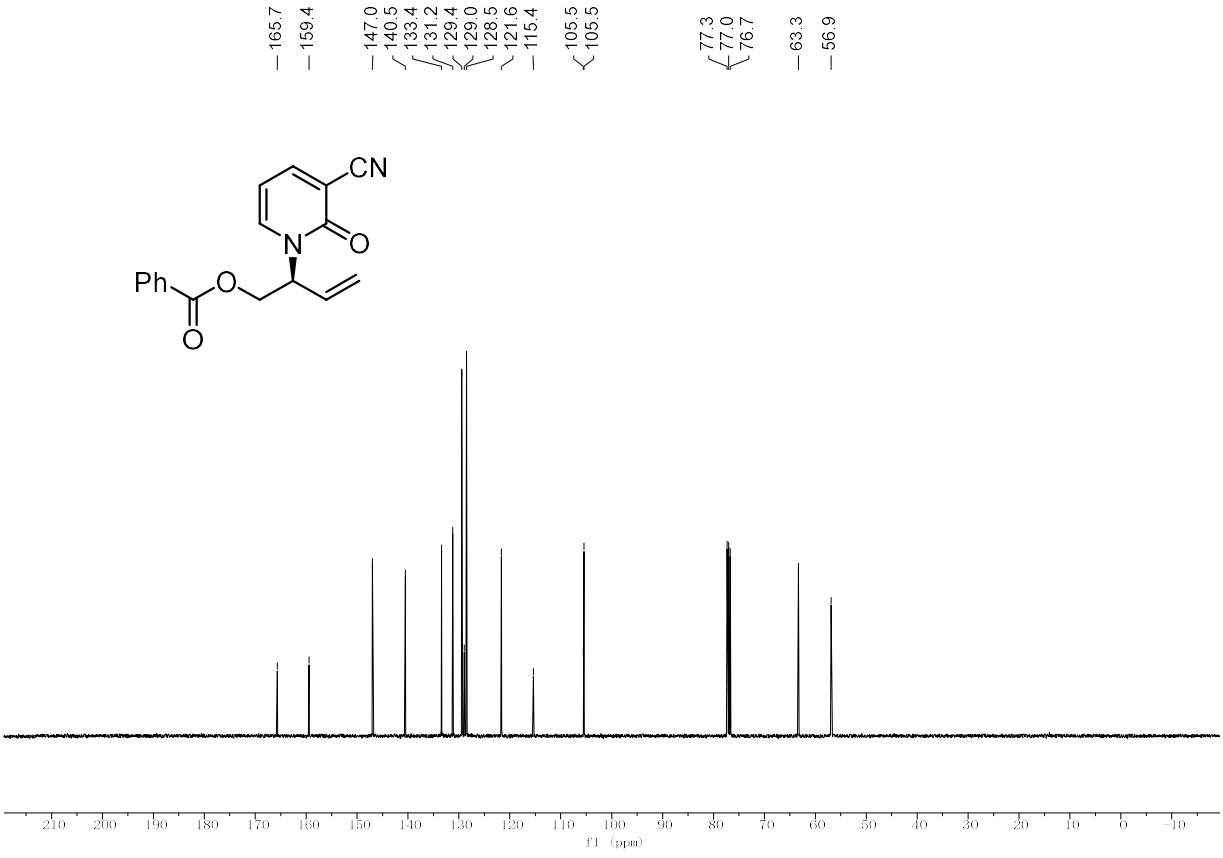




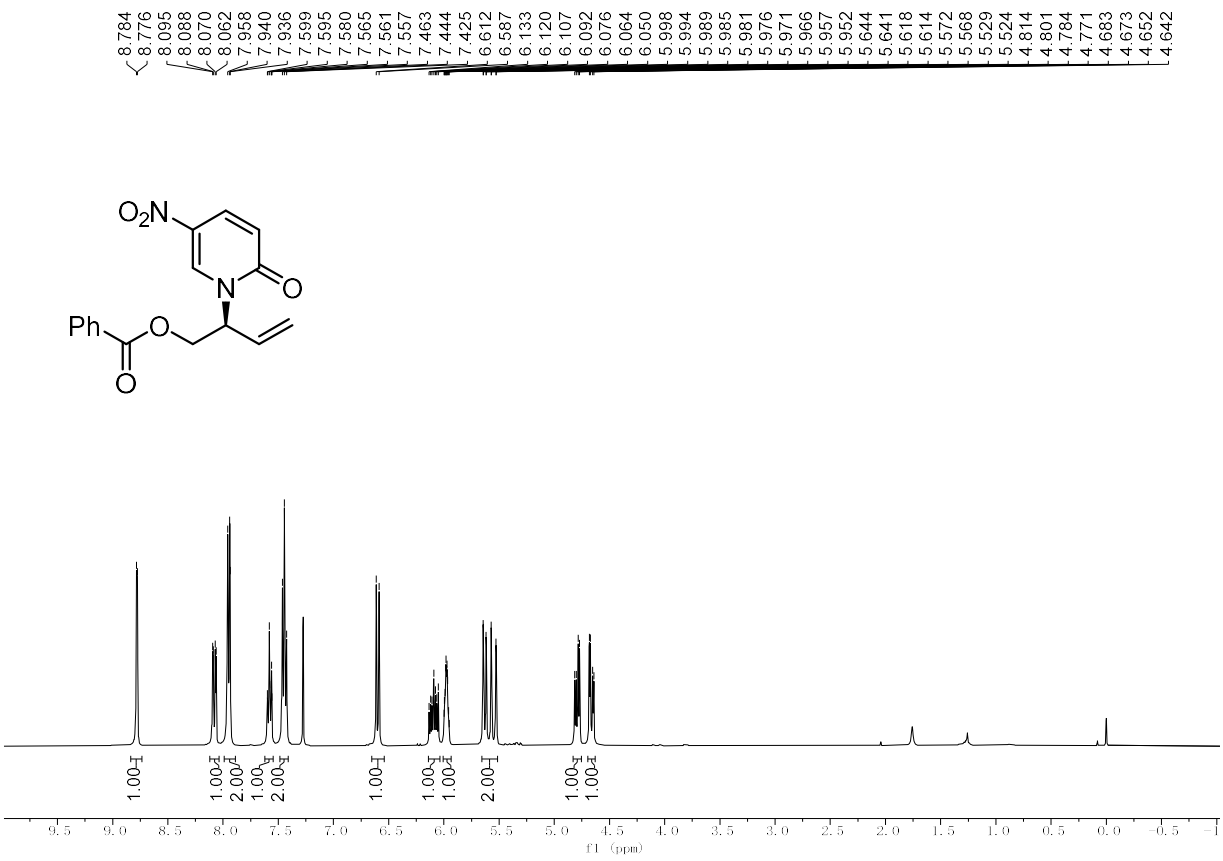
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



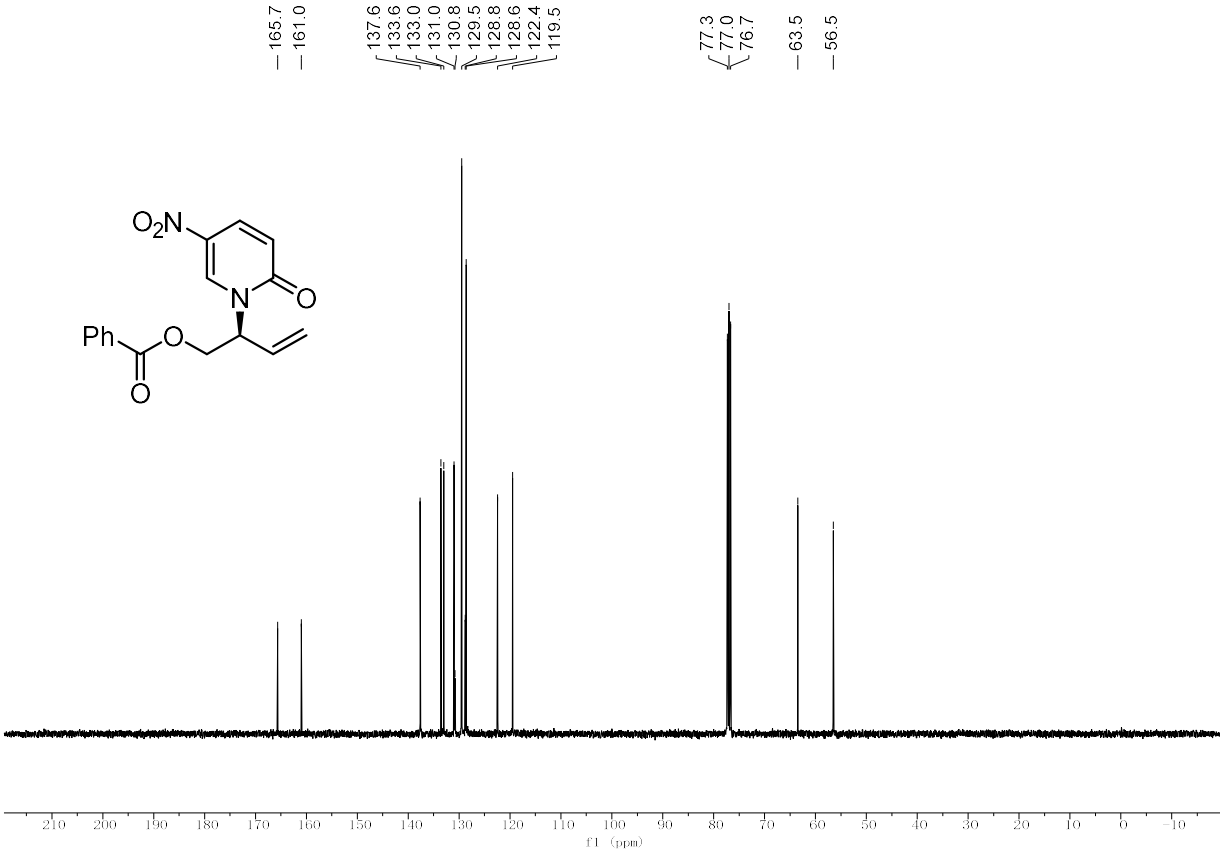
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



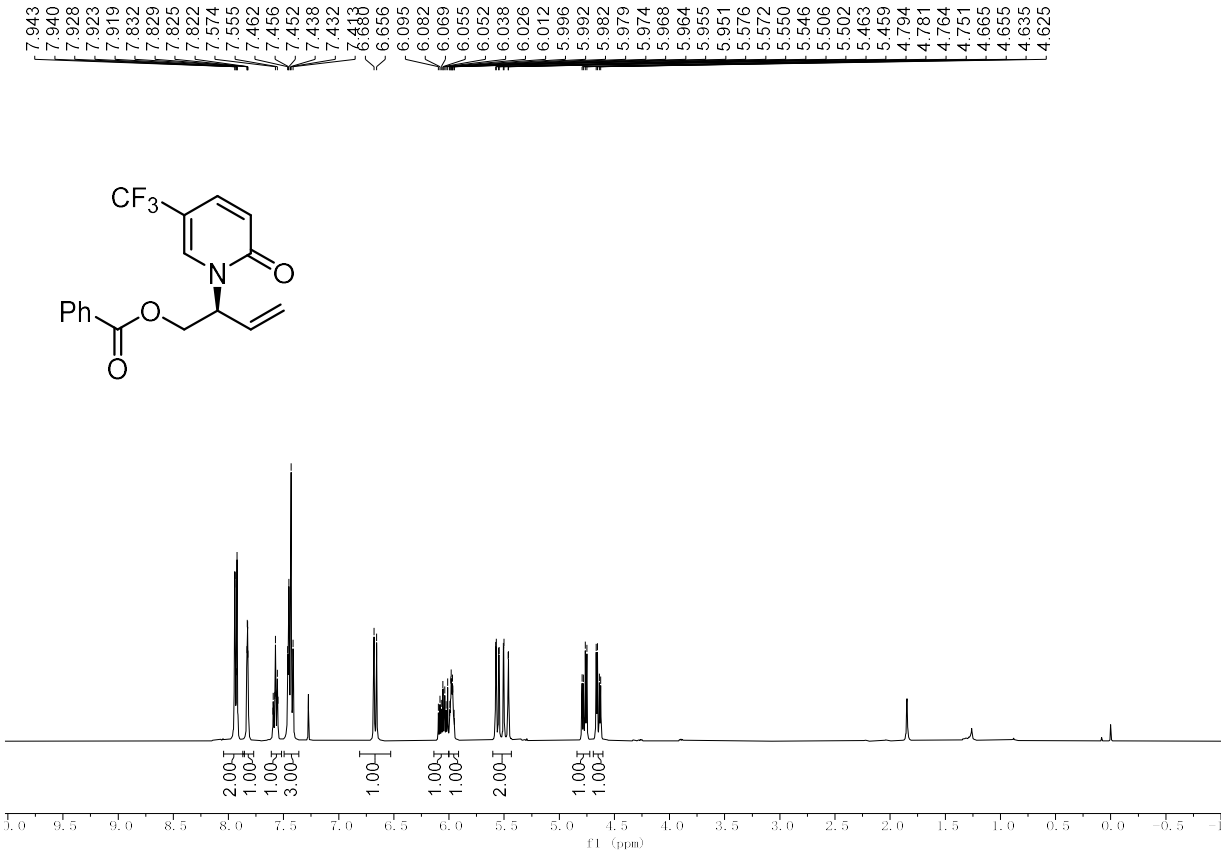
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



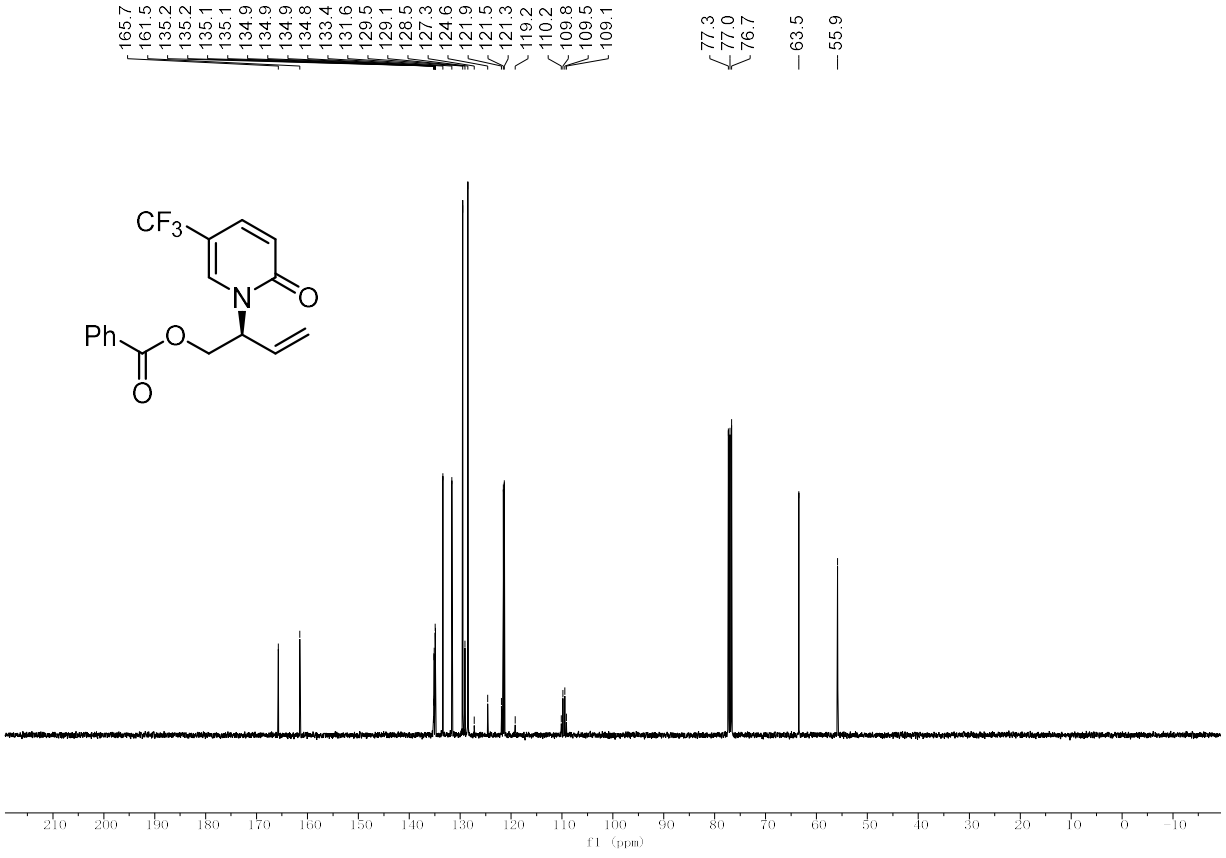
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



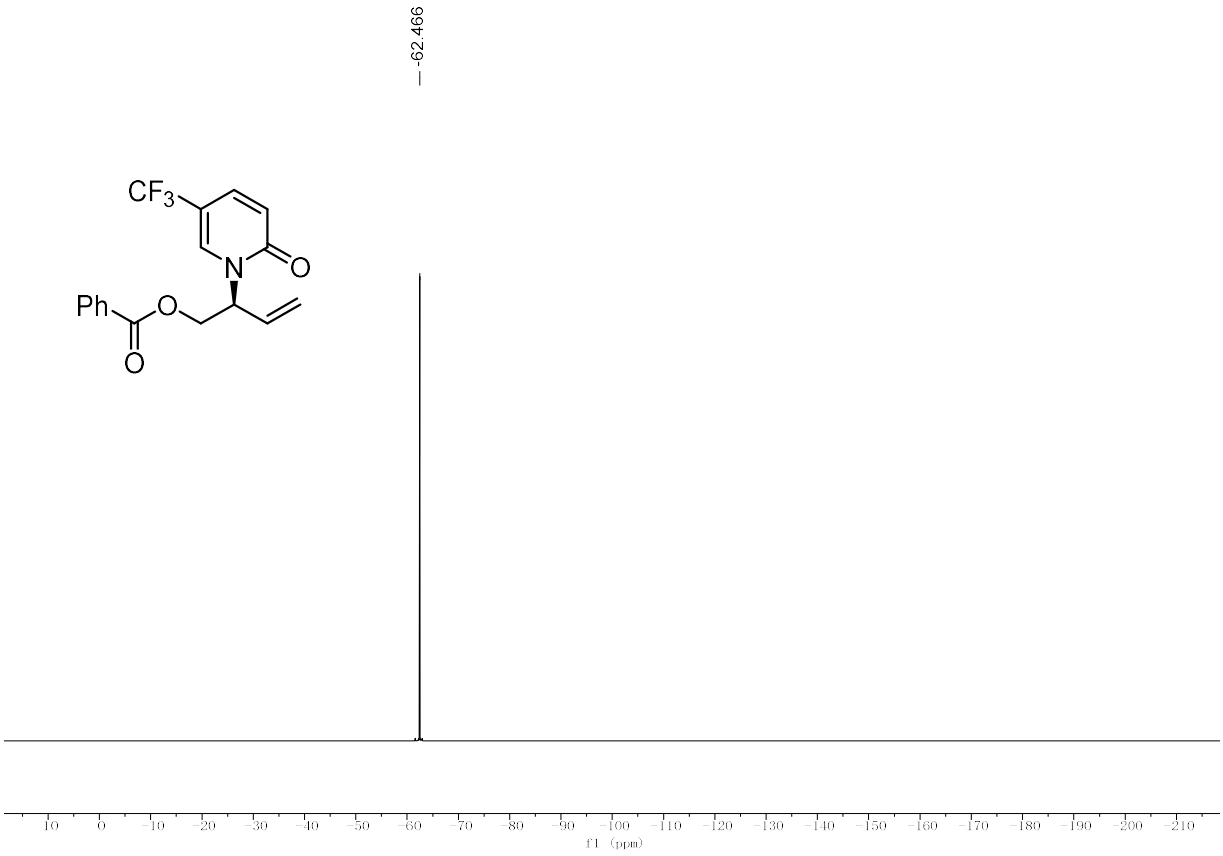
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



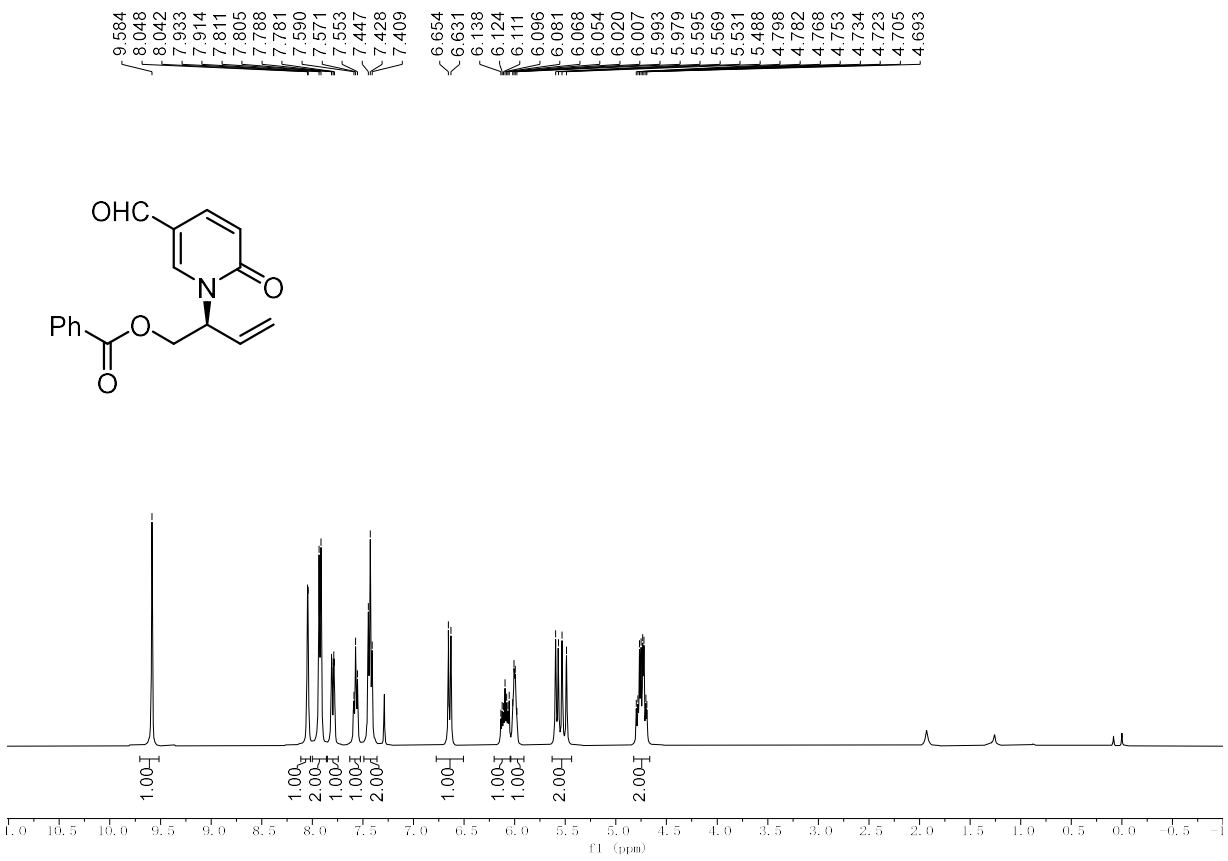
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



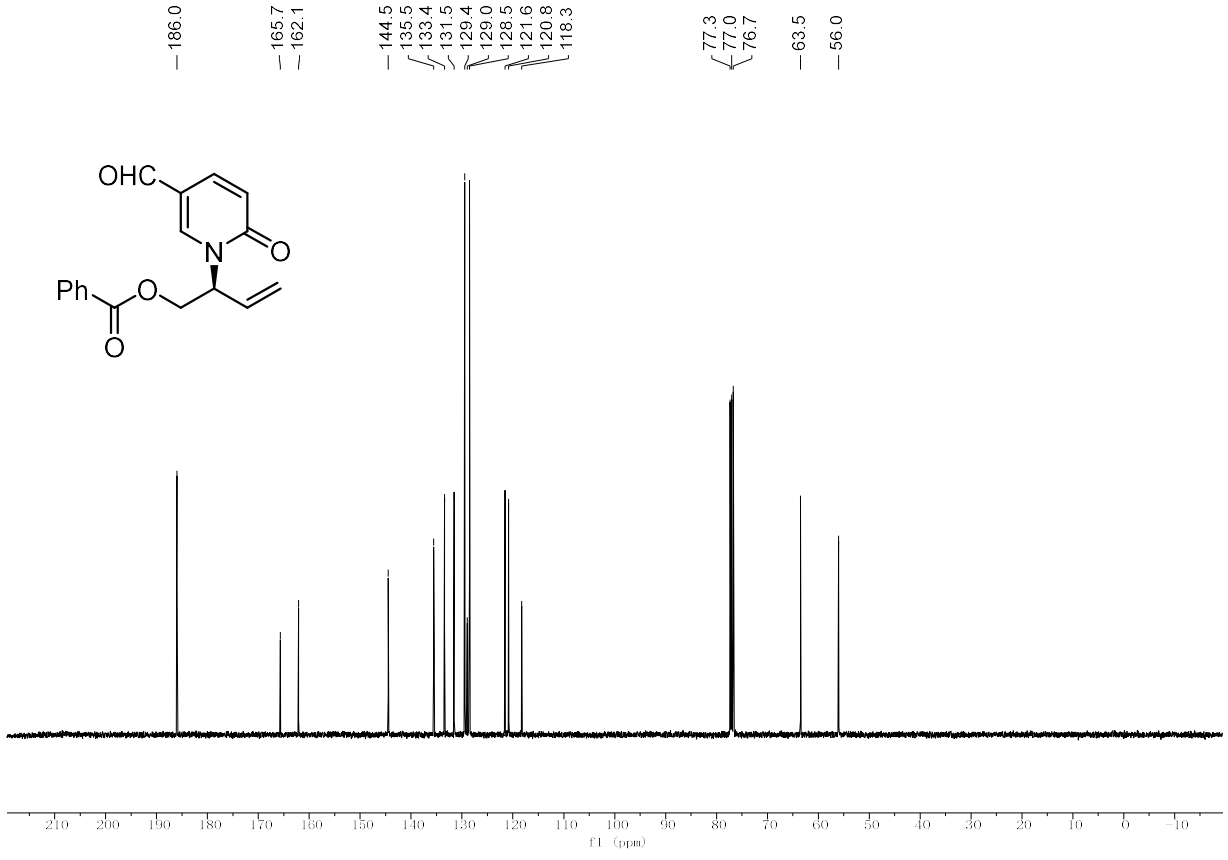
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



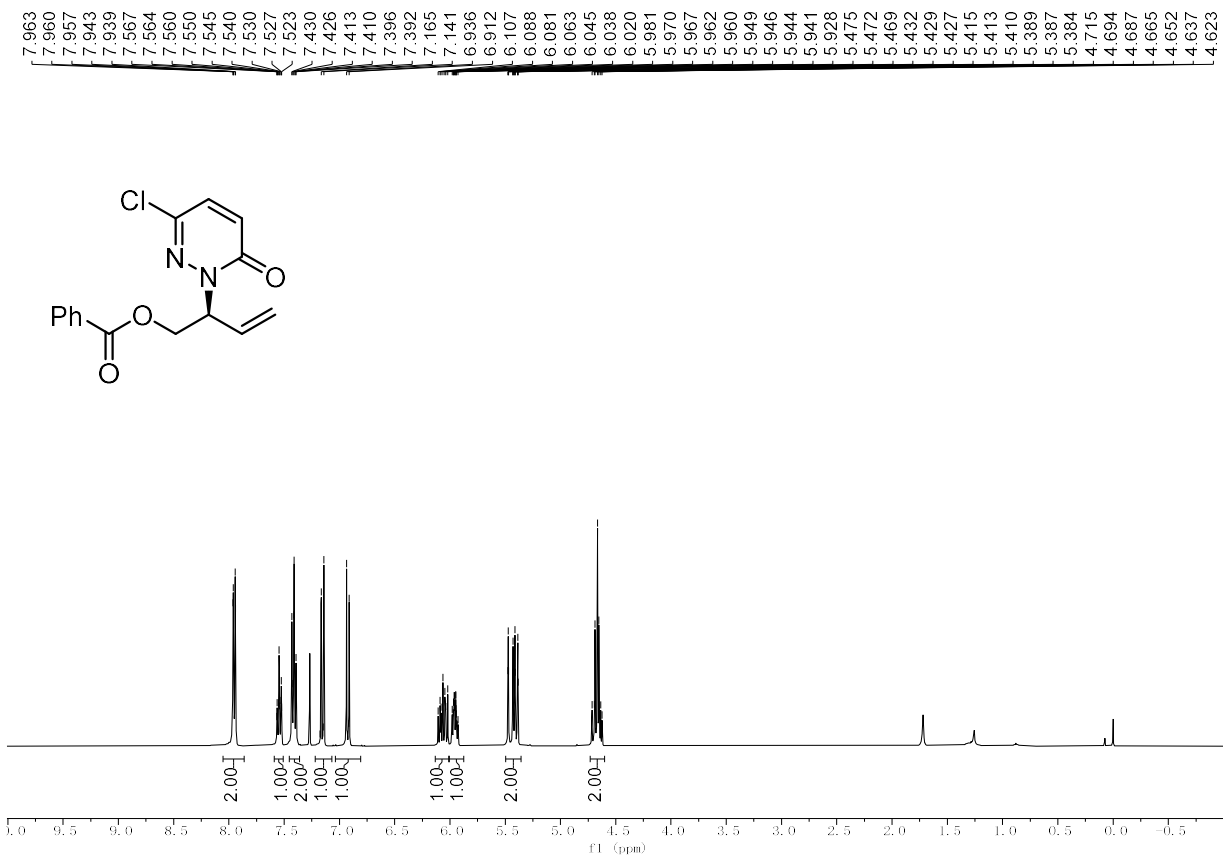
^{19}F NMR (376 MHz, $CDCl_3$) of **3n**



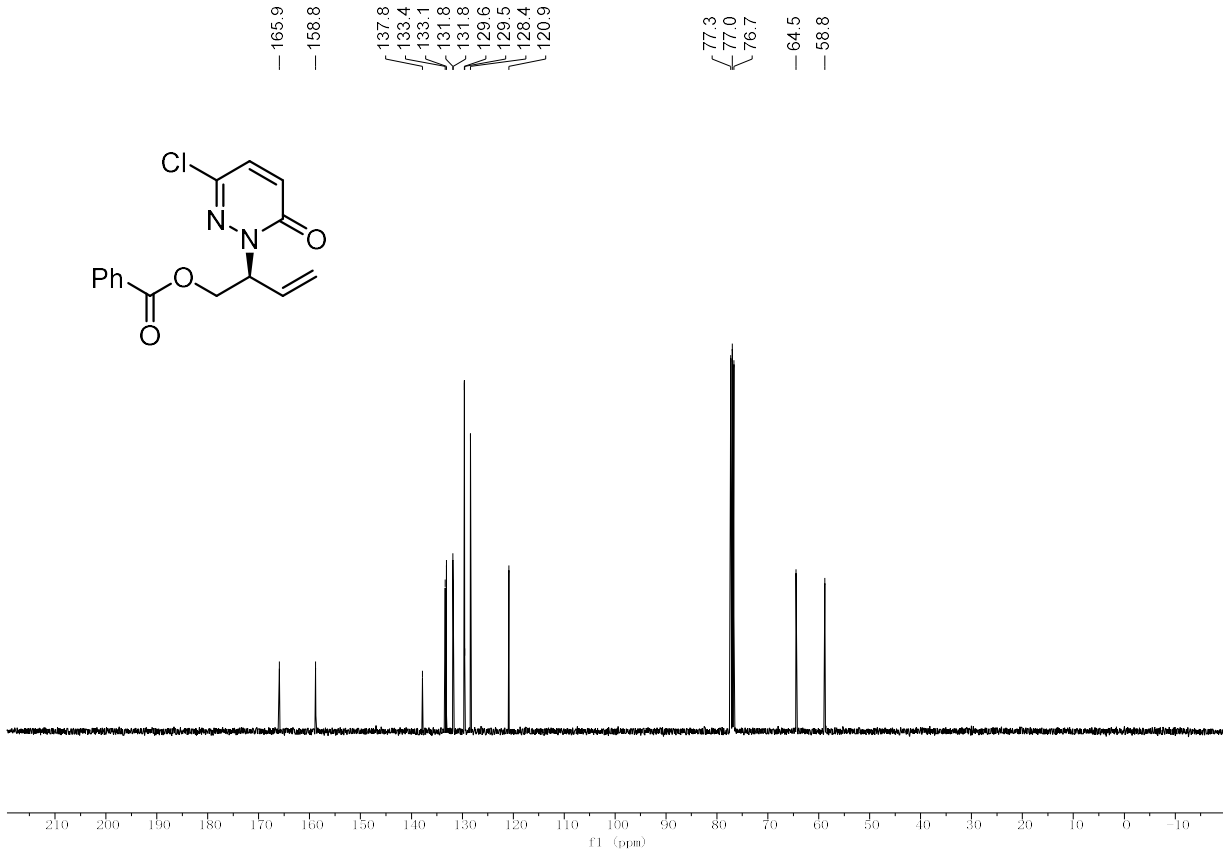
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



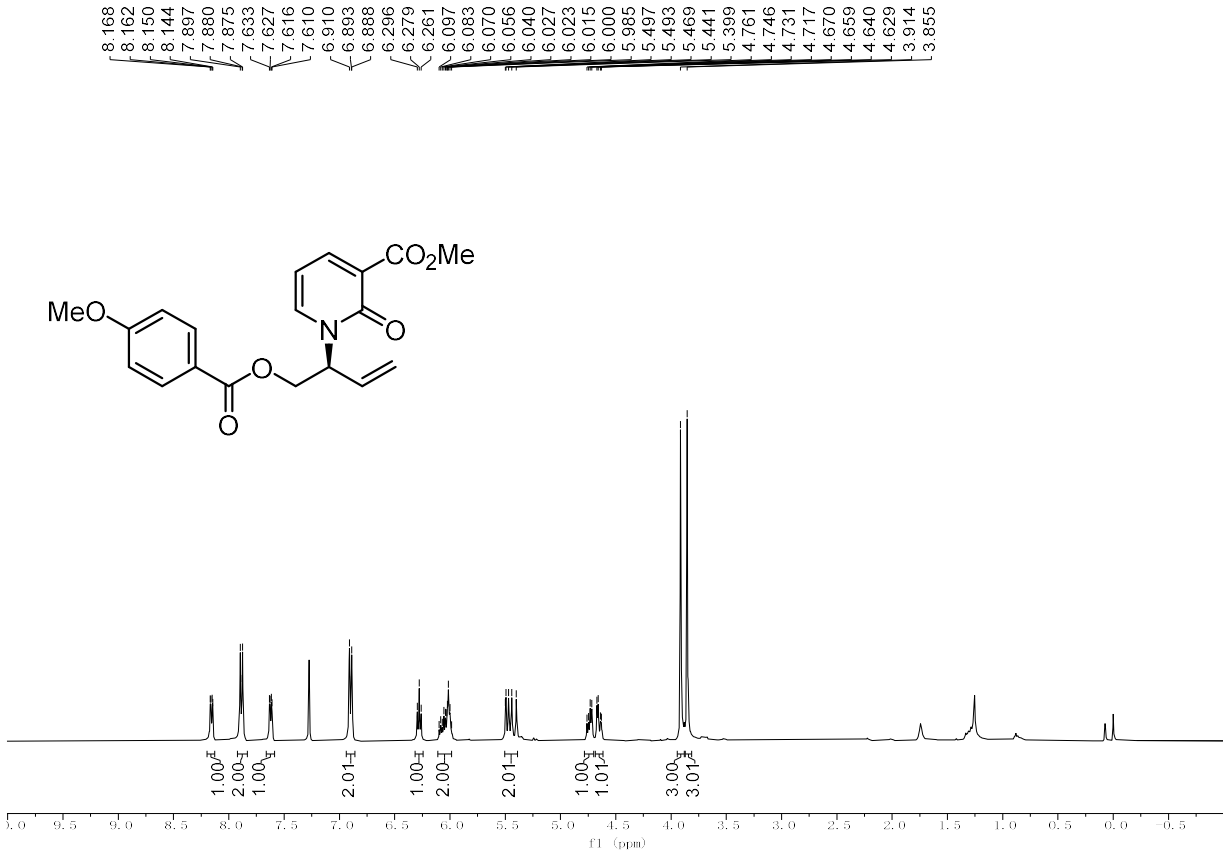
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



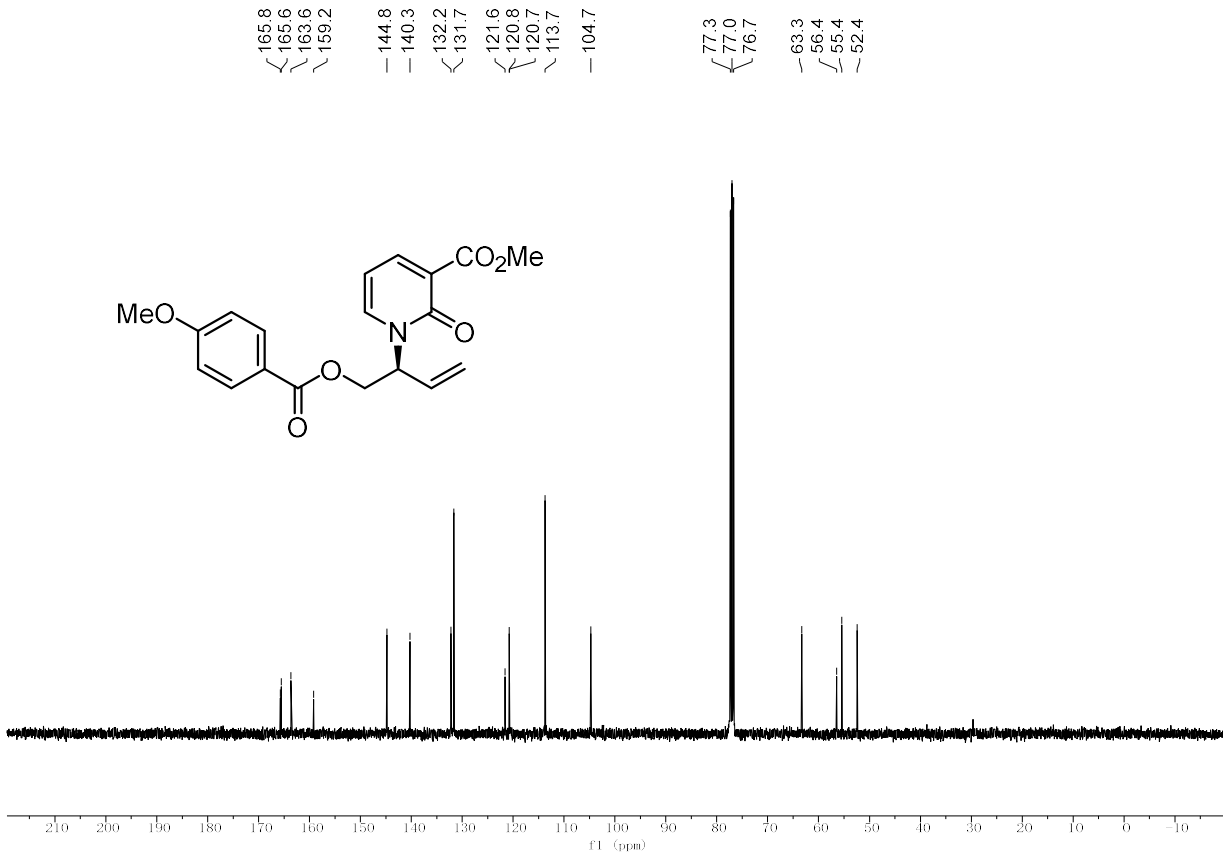
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



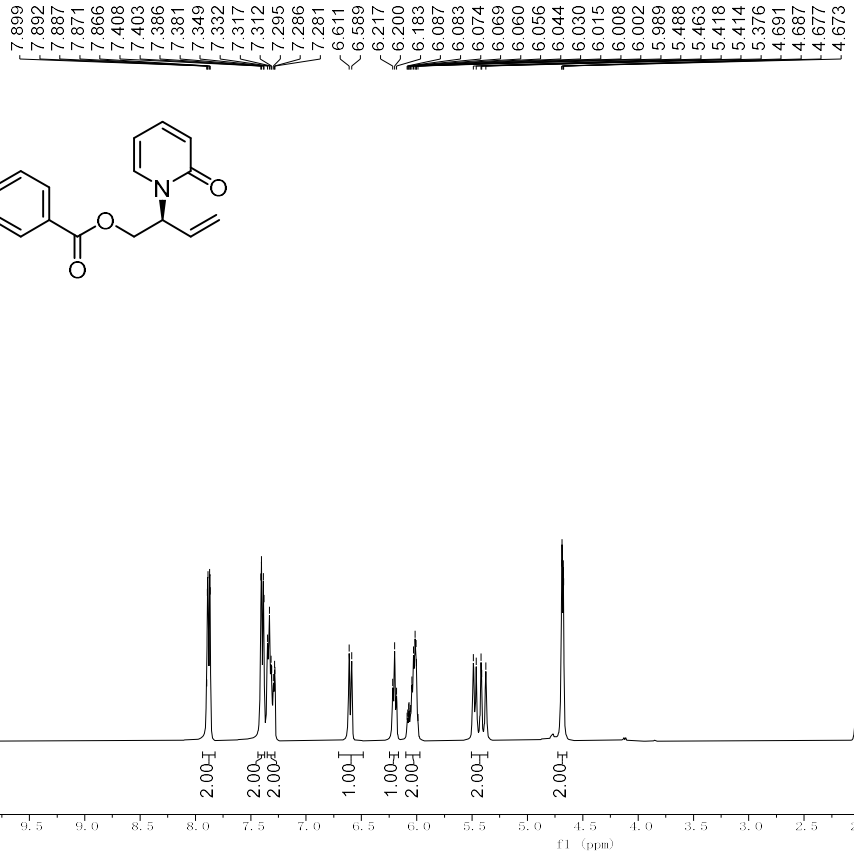
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



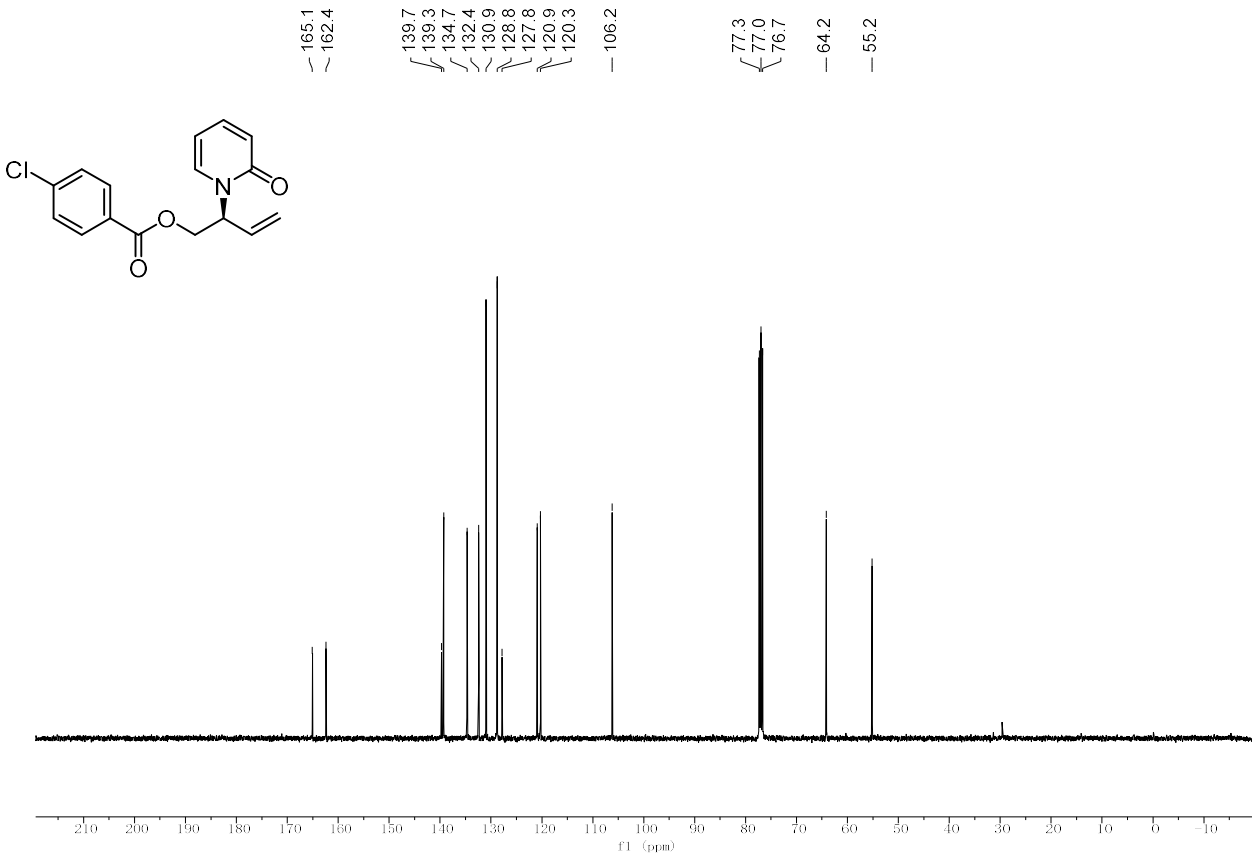
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



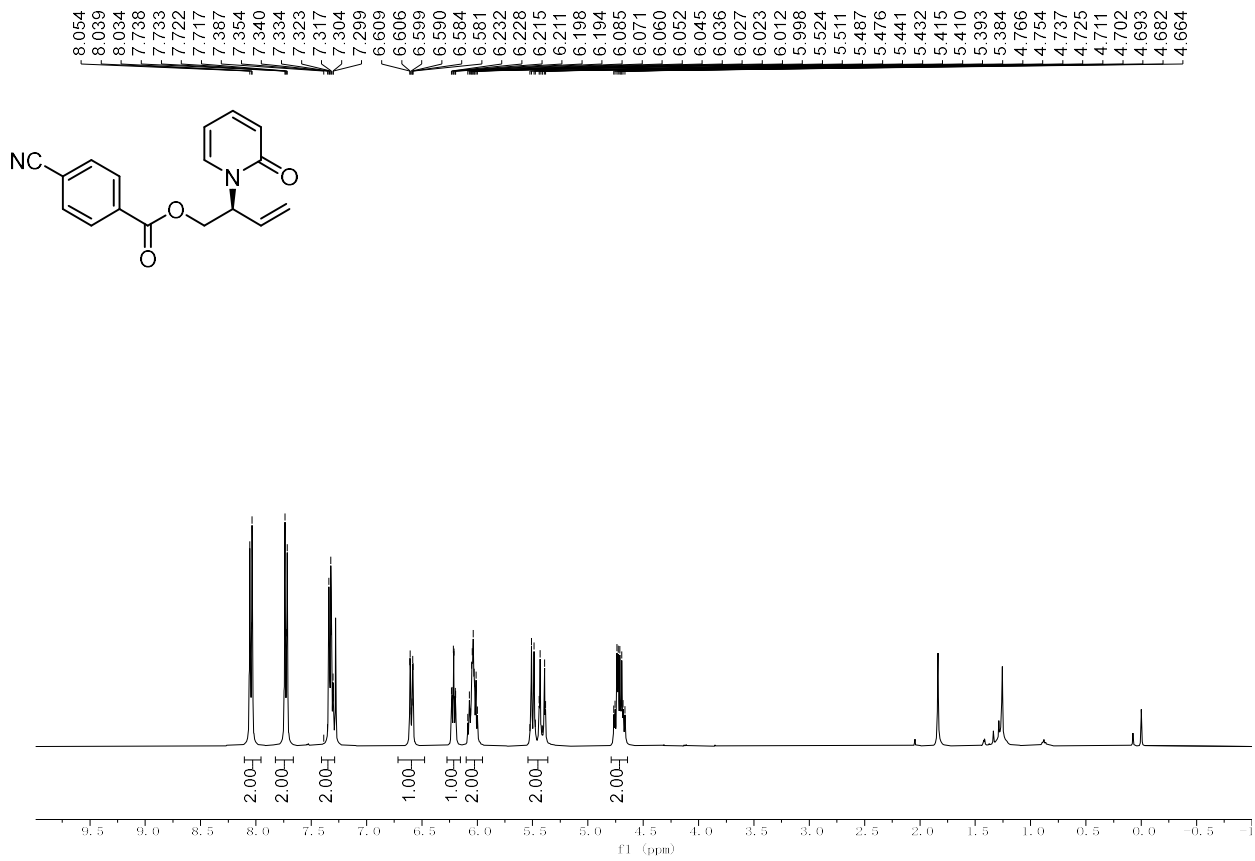
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



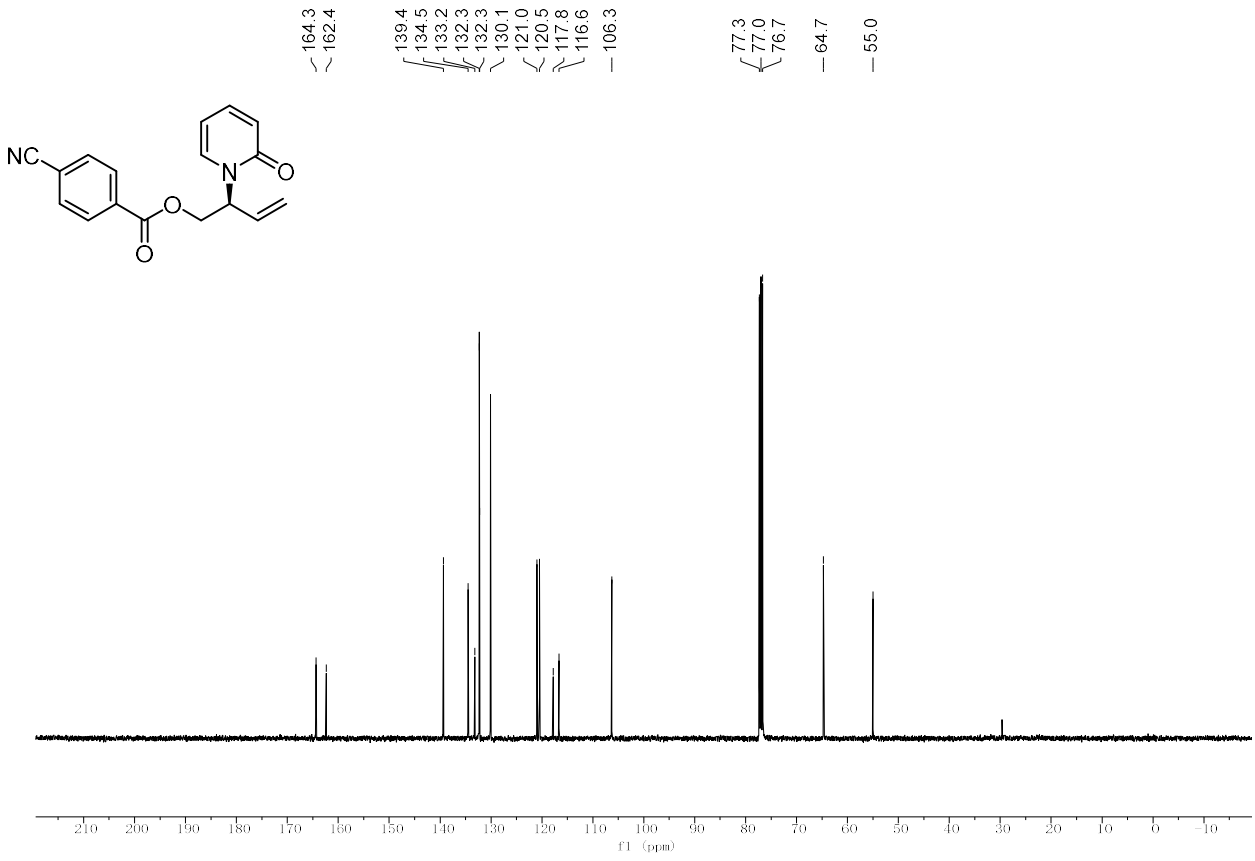
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



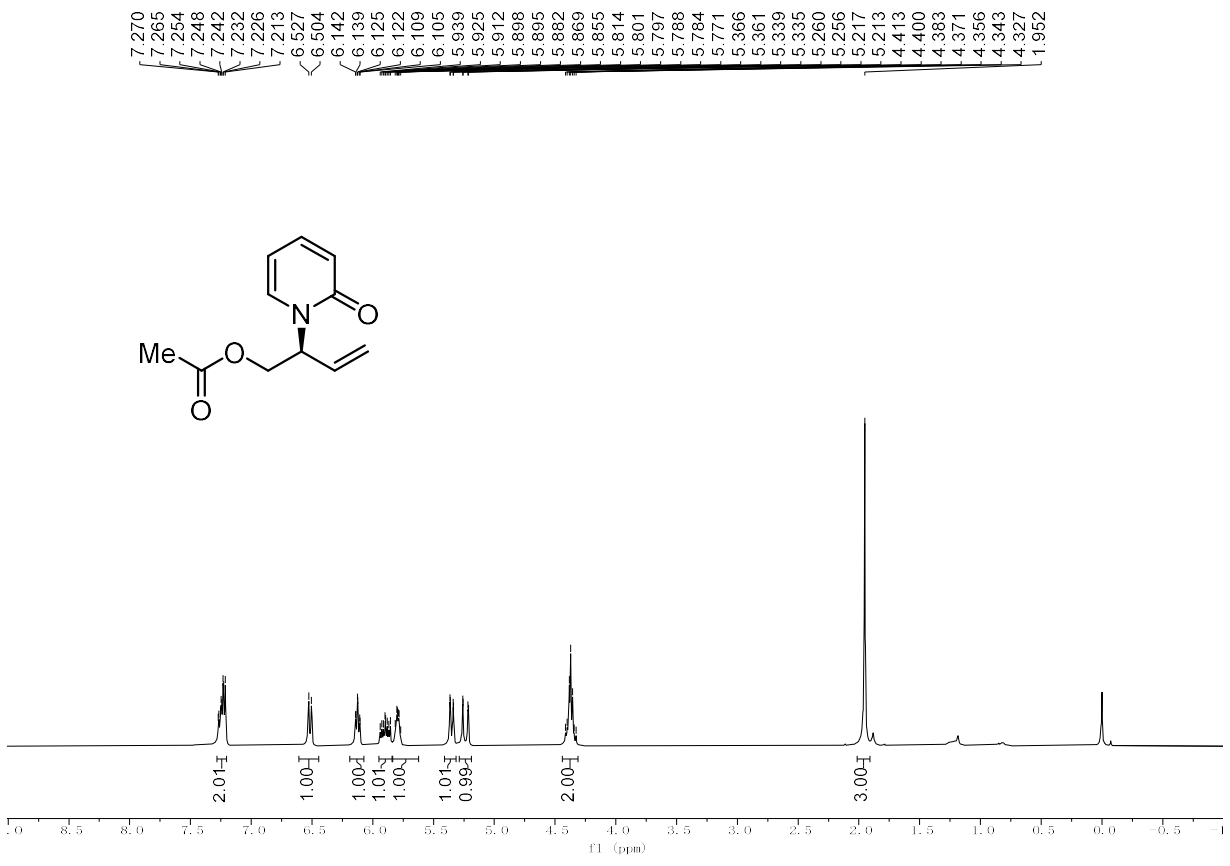
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



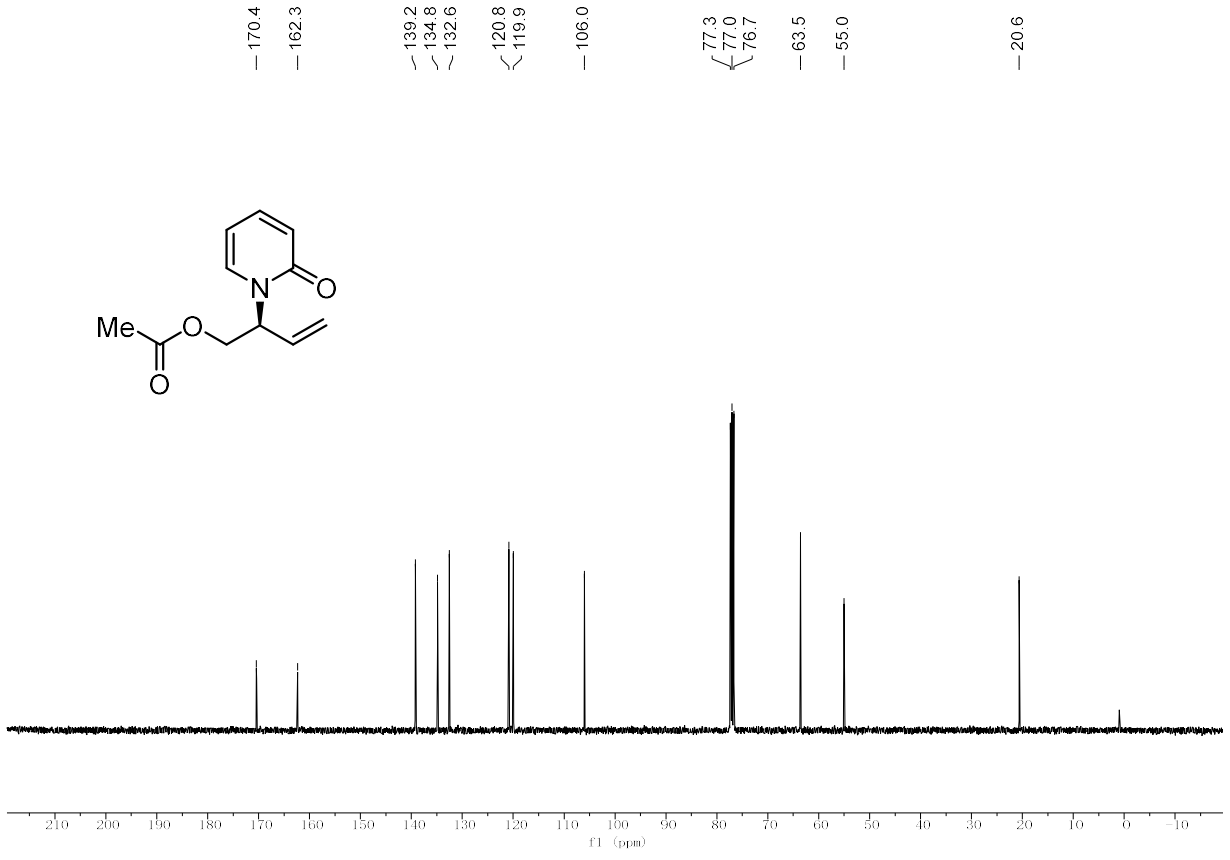
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



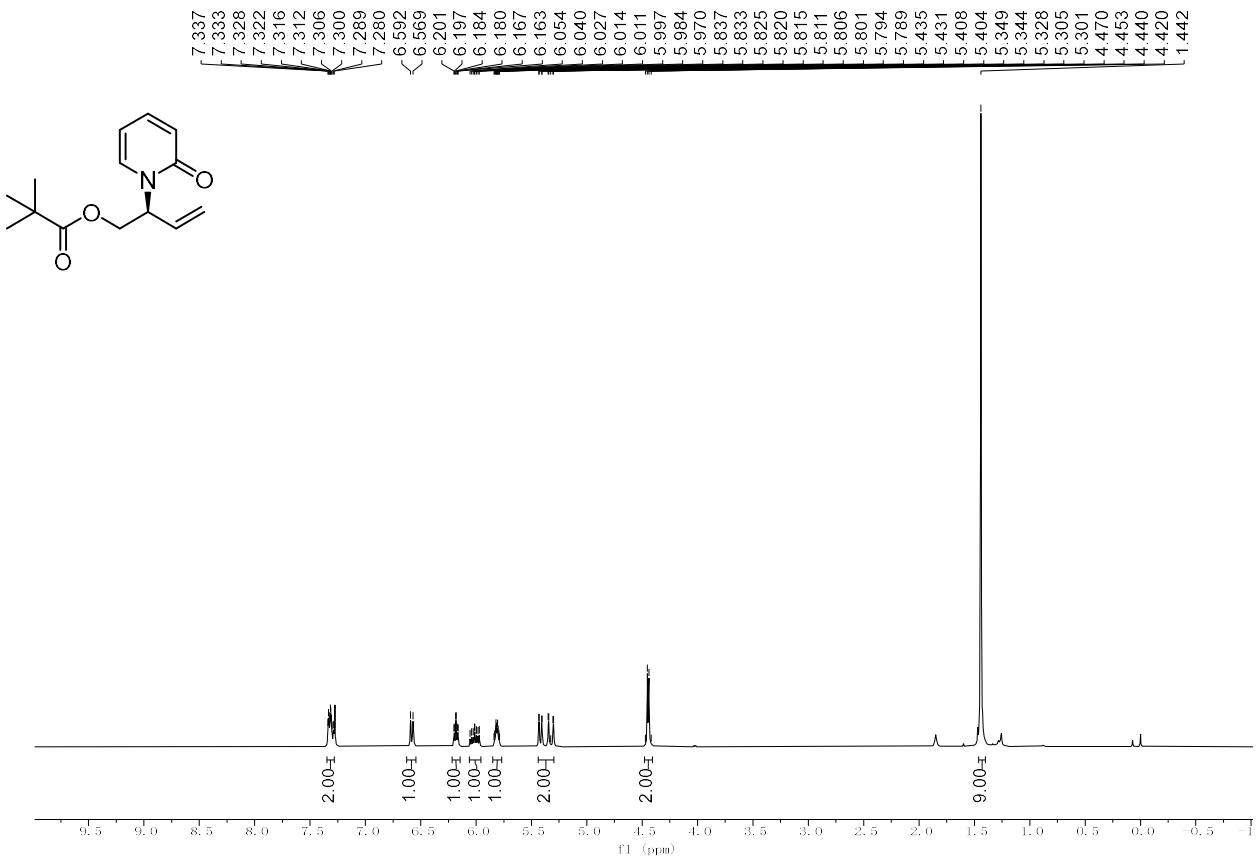
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



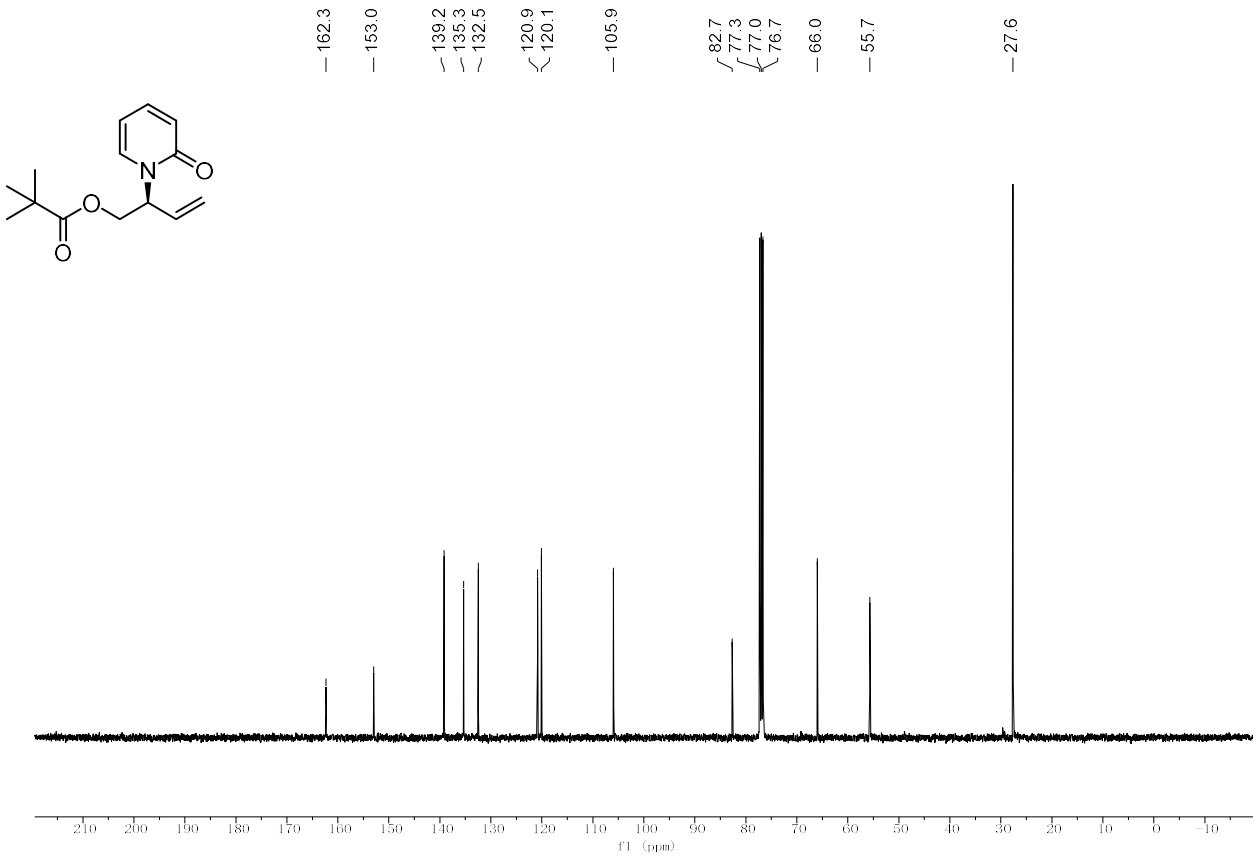
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



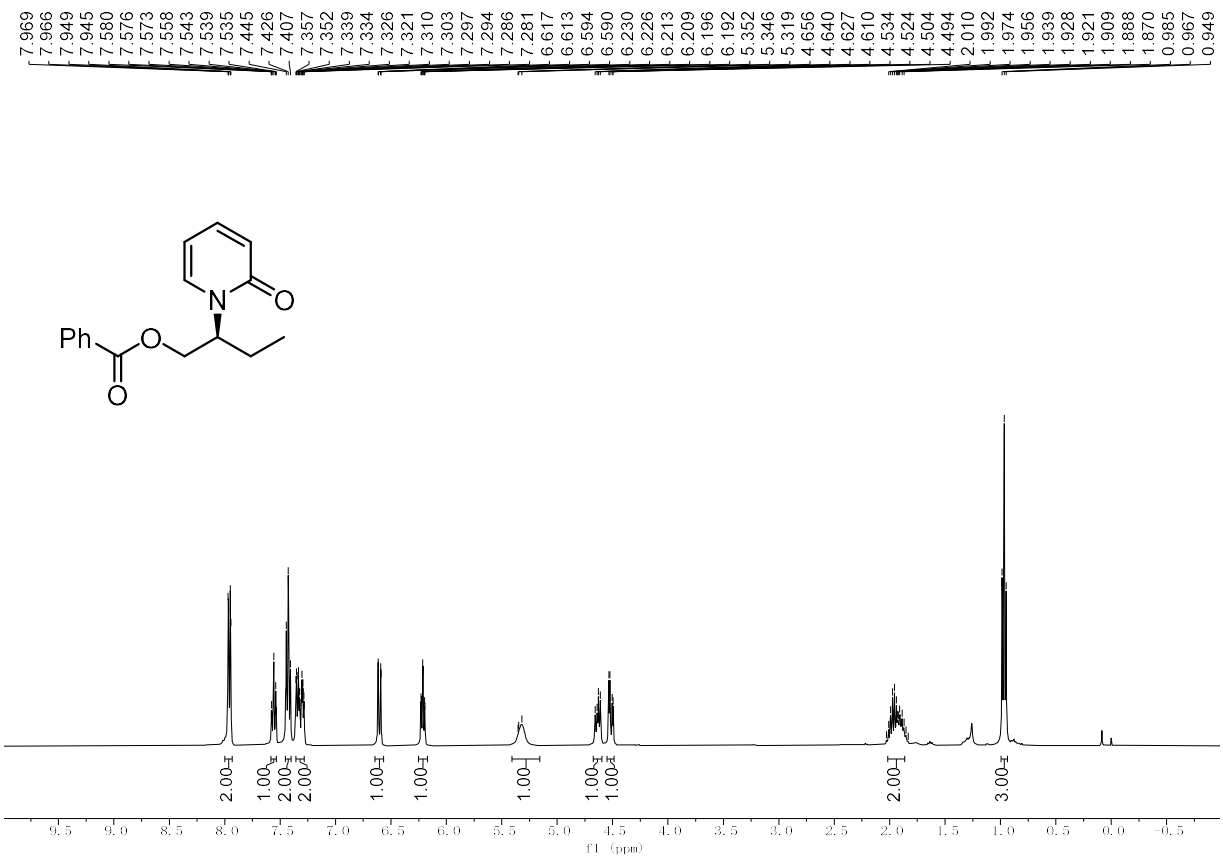
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



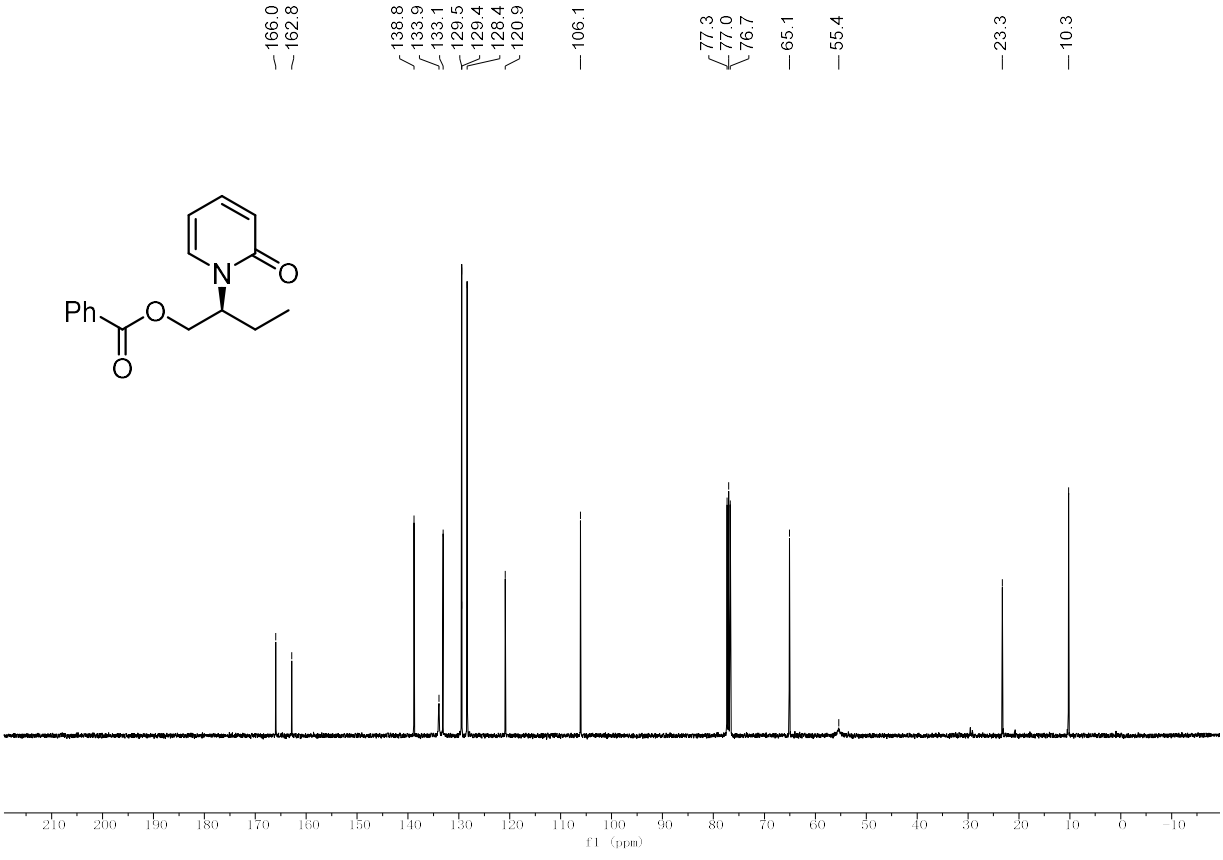
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



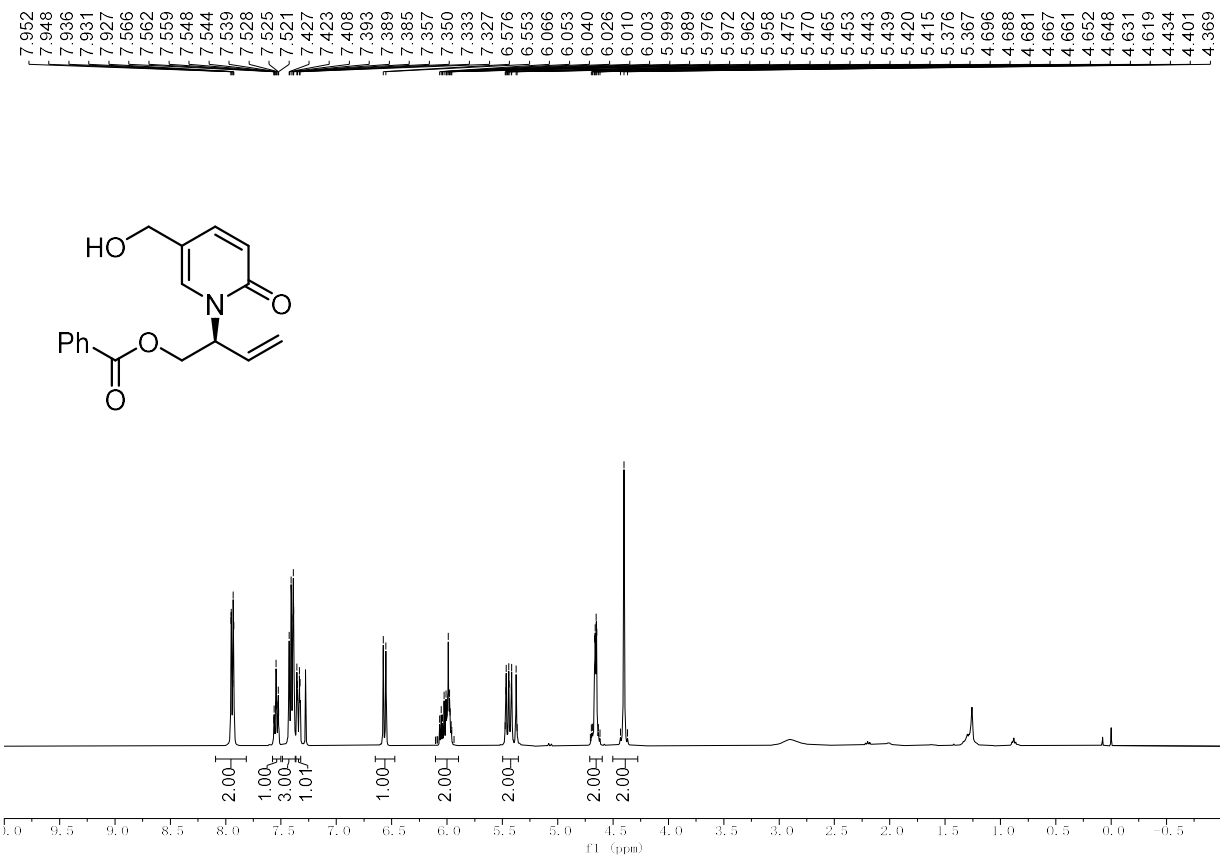
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



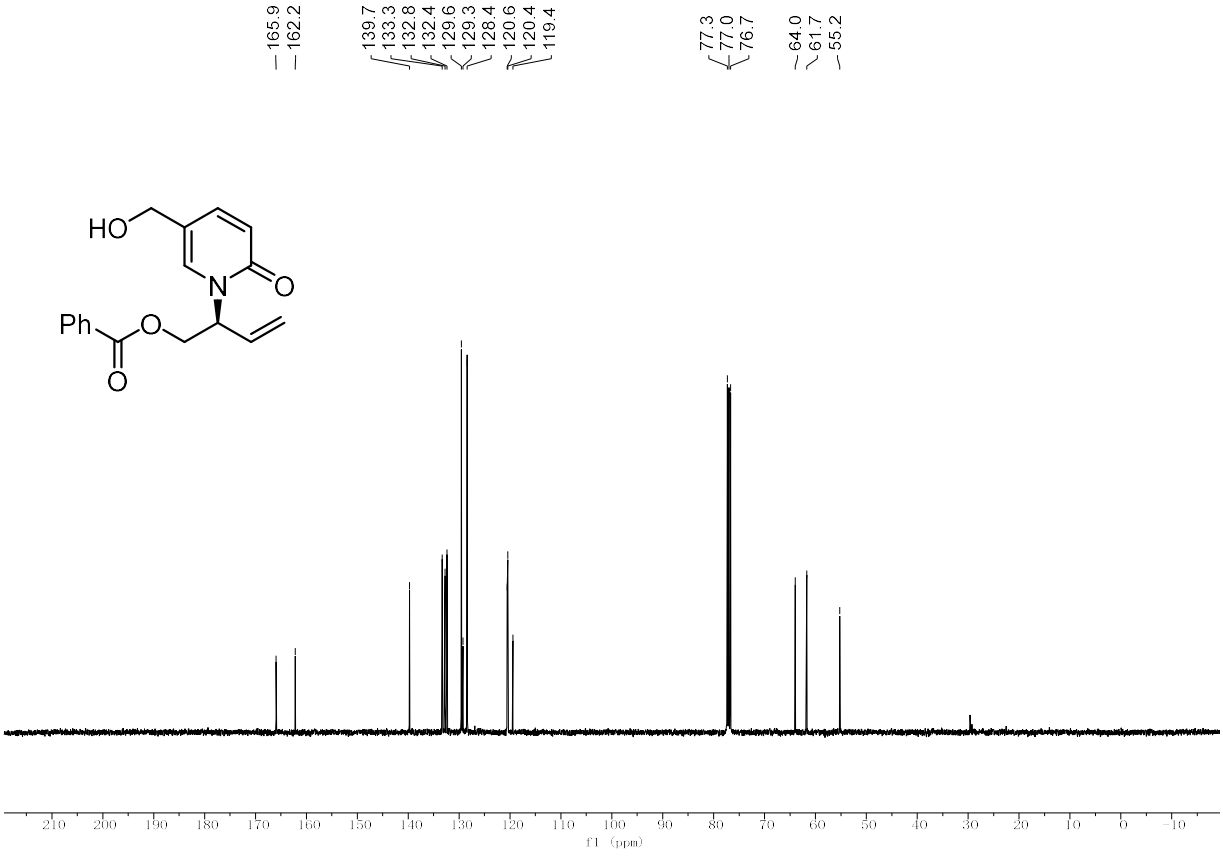
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



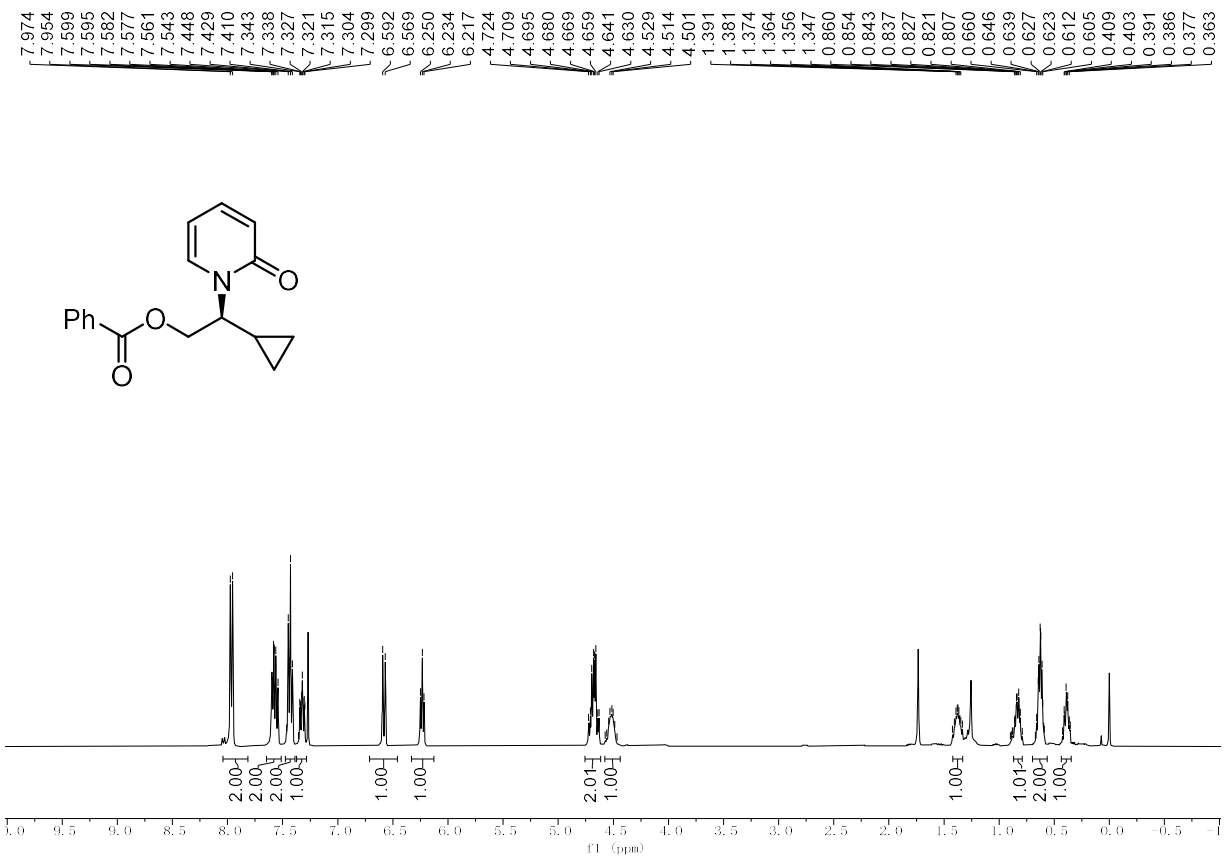
^{13}C NMR (101 MHz, $CDCl_3$) of **4**



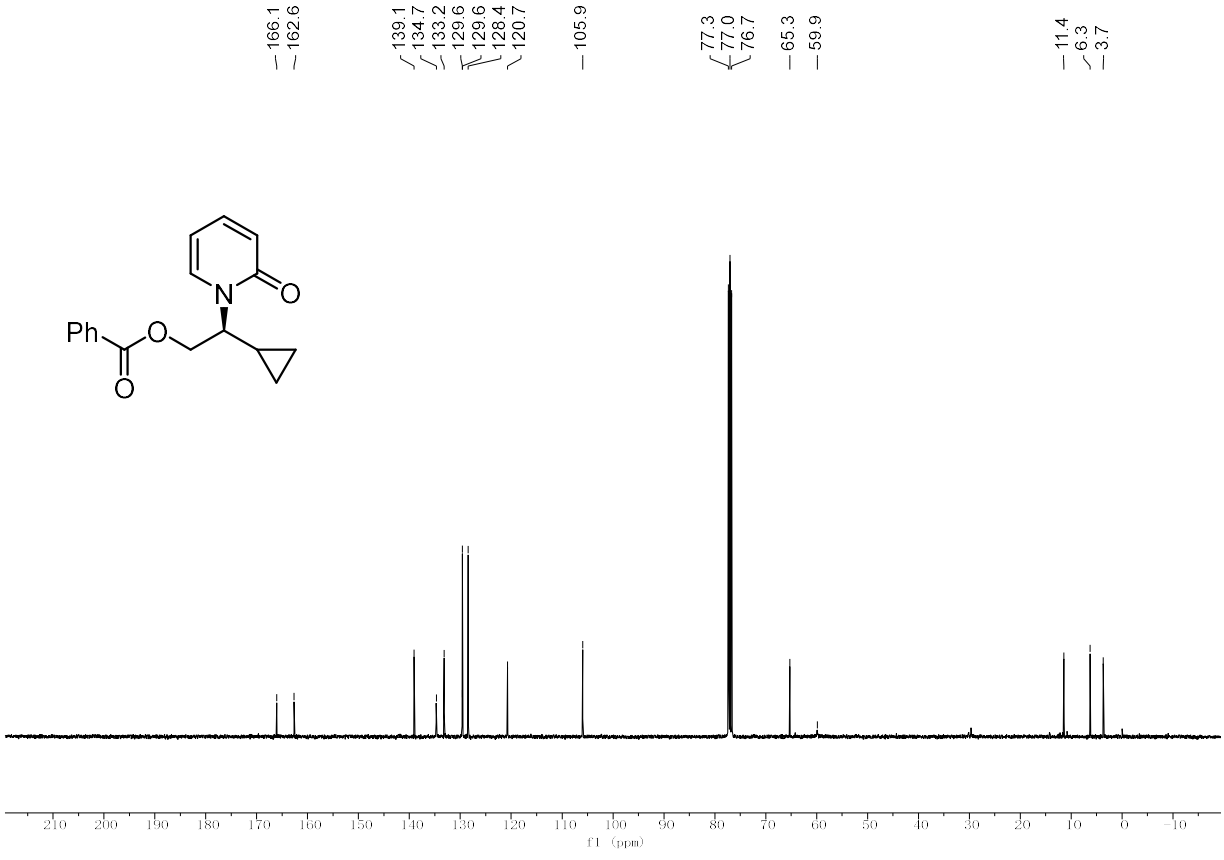
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



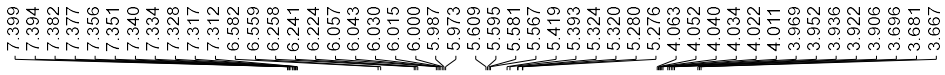
^{13}C NMR (101 MHz, $CDCl_3$) of **5**

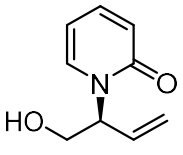


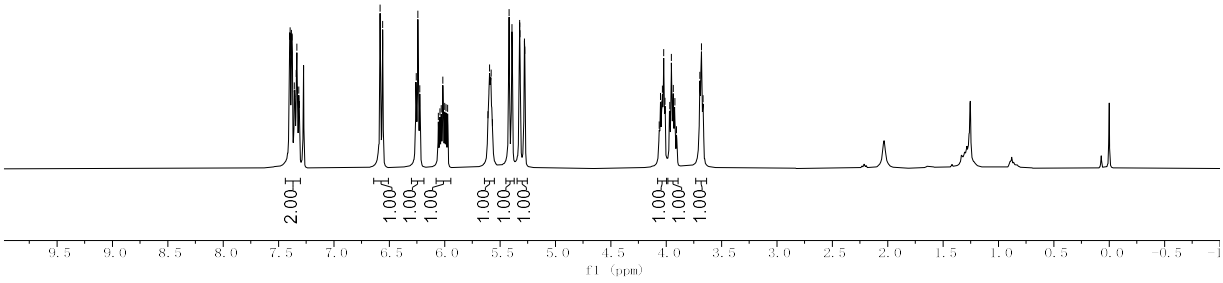
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



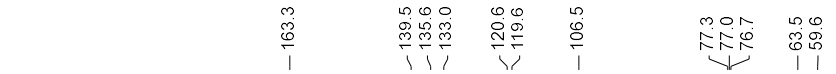
^{13}C NMR (101 MHz, $CDCl_3$) of **6**

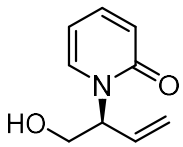


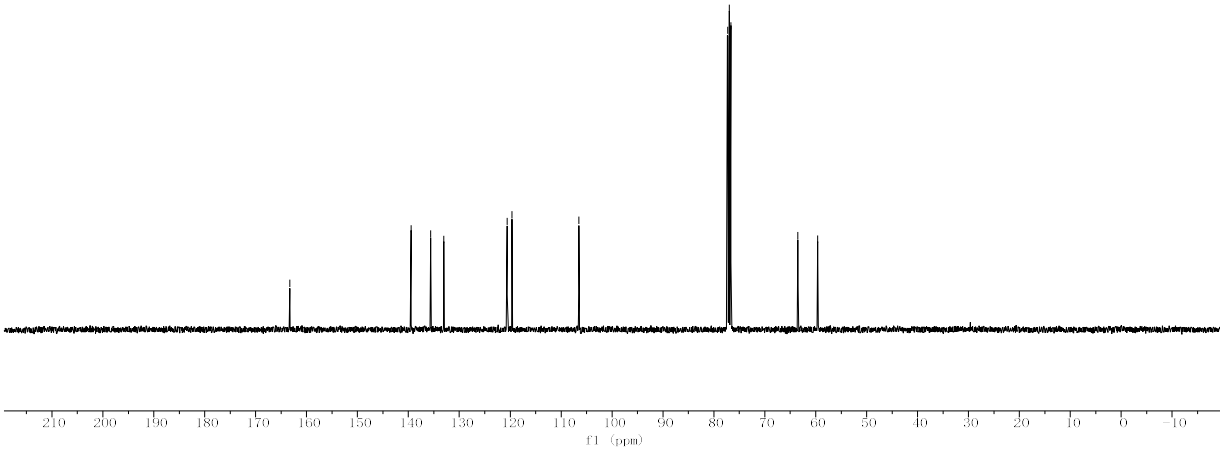




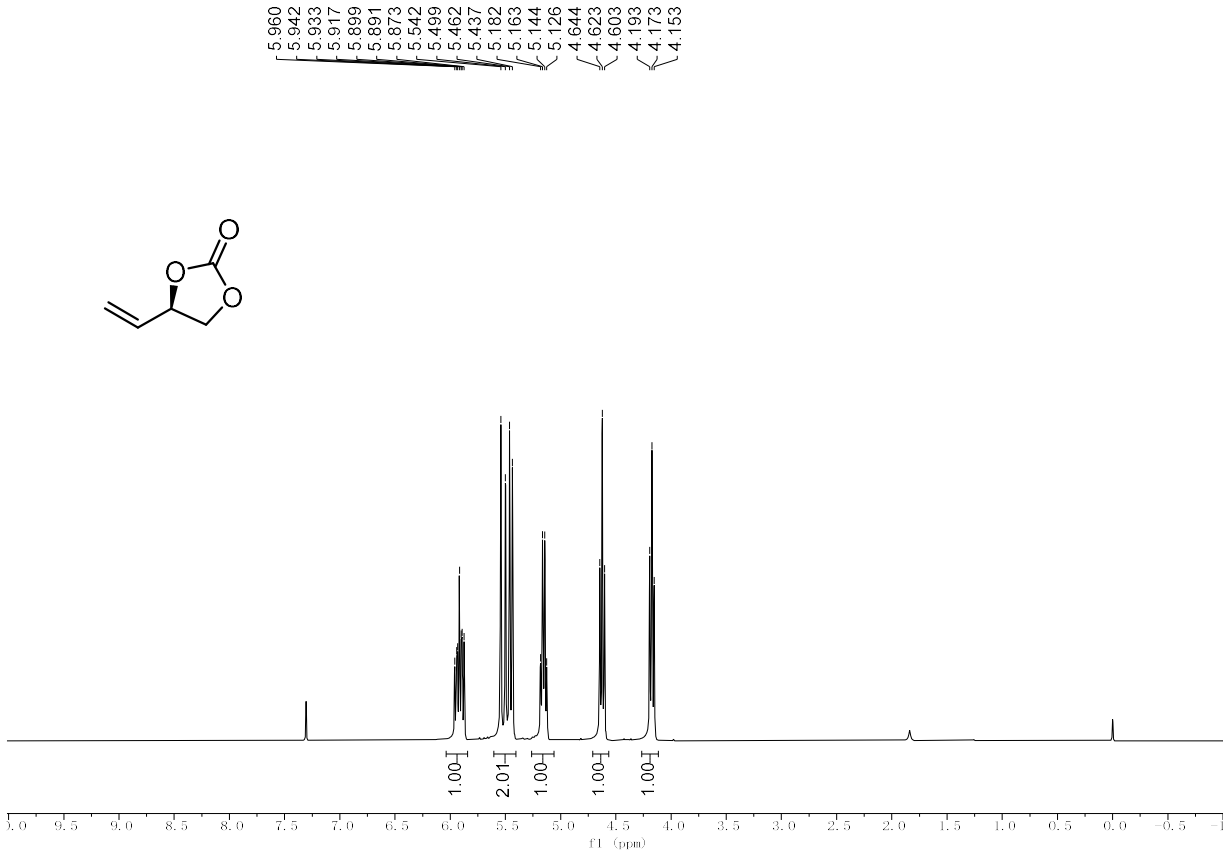
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



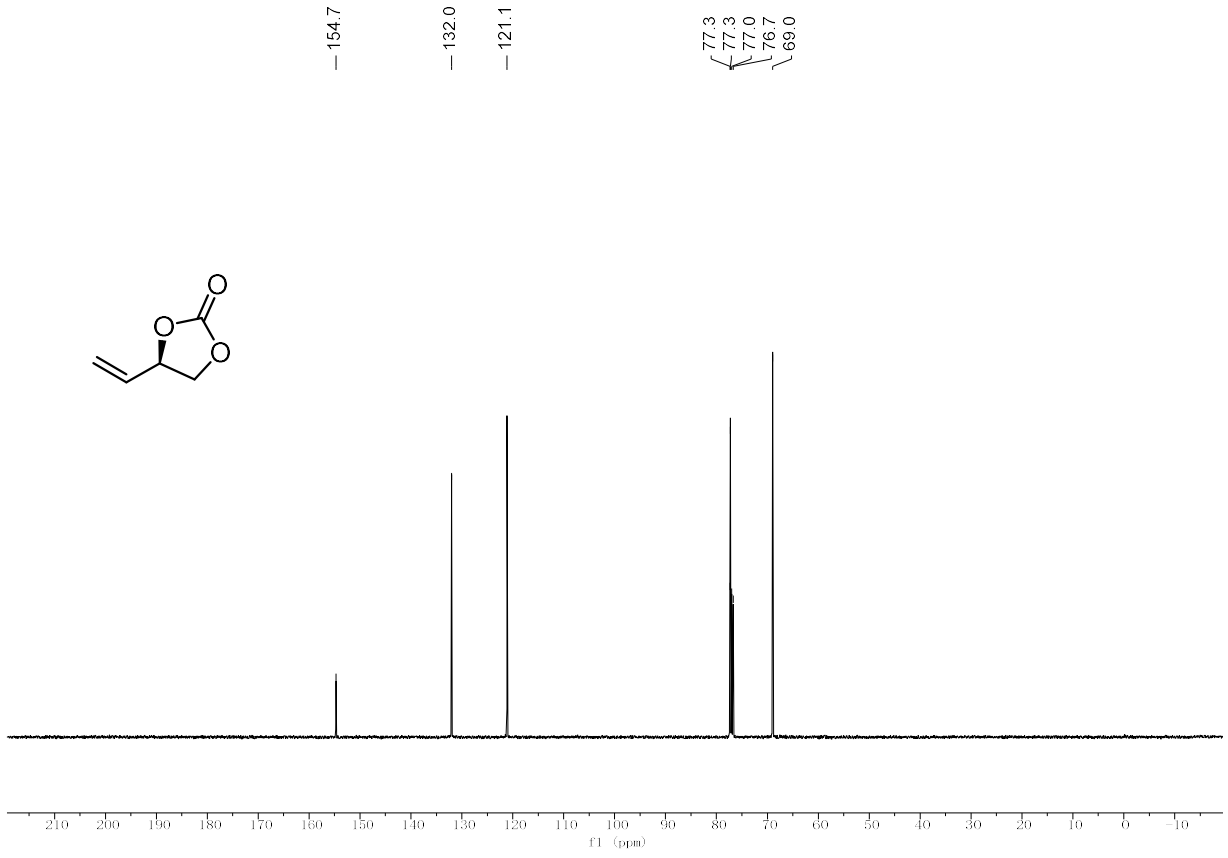




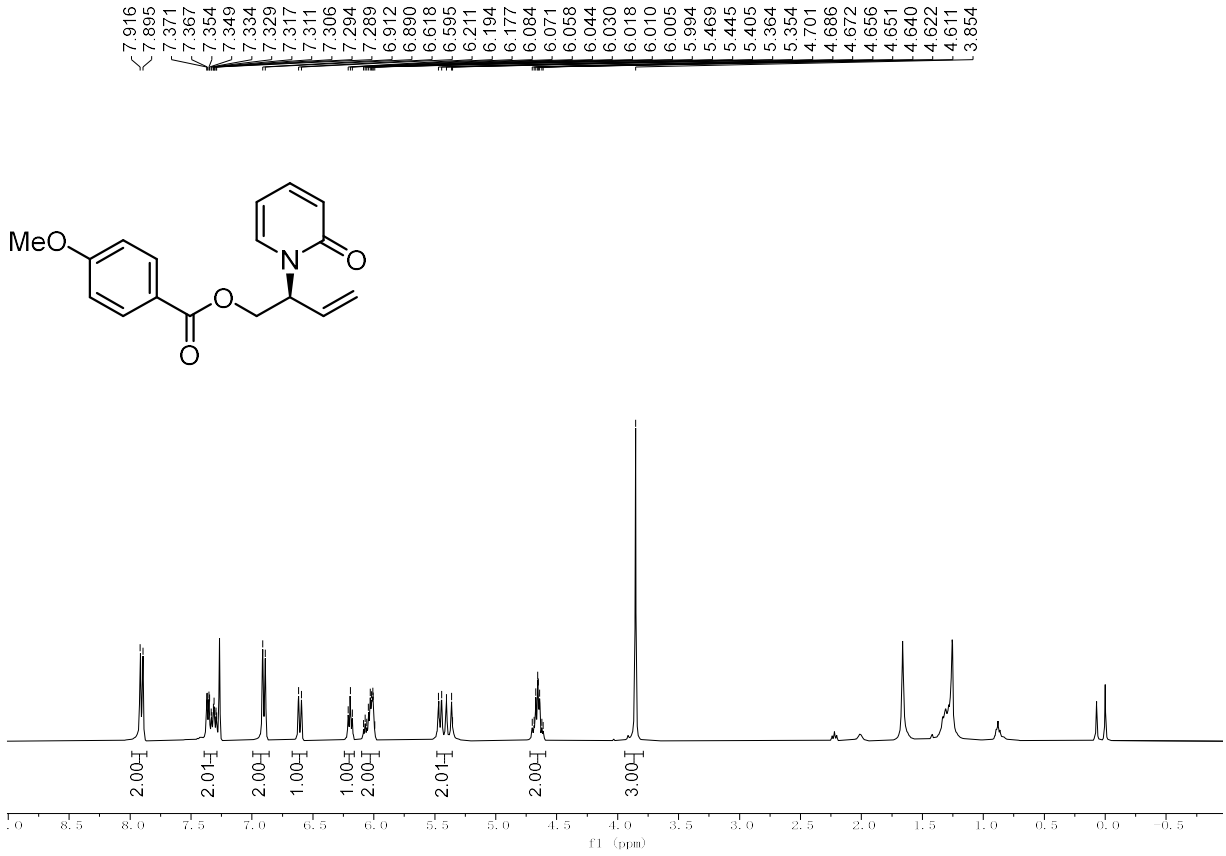
^{13}C NMR (101 MHz, $CDCl_3$) of **7**



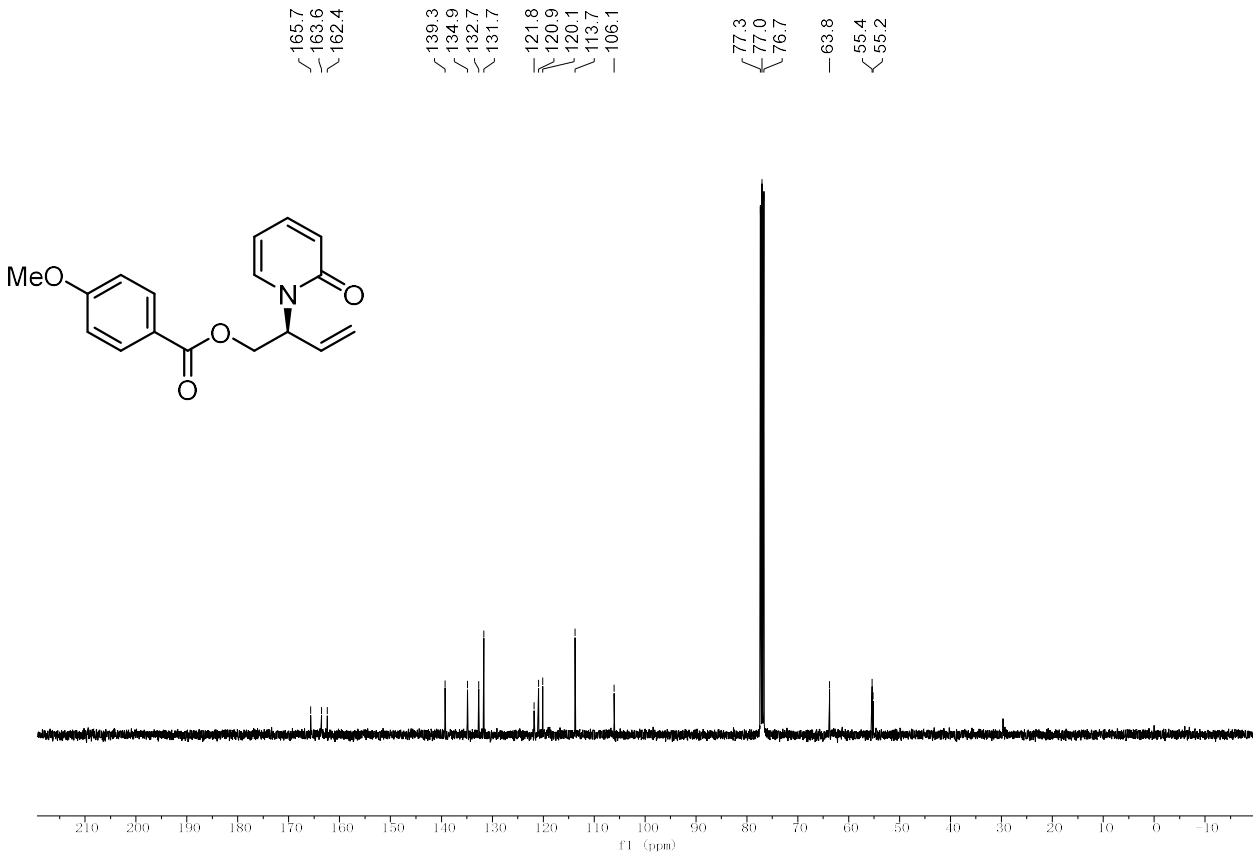
^{1}H NMR (400 MHz, $CDCl_3$) of (*R*)-**2**



^{13}C NMR (101 MHz, $CDCl_3$) of (*R*)-**2**



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



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