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Supporting Information

Gold-catalyzed formal (3+2) and (4+2) cycloadditions of alkynes to highly functionalized dihydropyrroles and tetrahydropyridines

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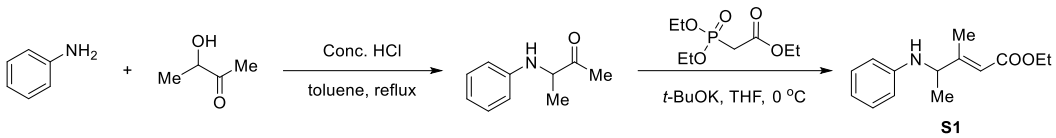
General

NMR spectra were recorded on a Bruker-400 MHz. ^{1}H NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shift in ppm using residue solvent peak as internal standard ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration. ^{13}C NMR spectra were recorded at 101 MHz and data are reported as follows: chemical shift in ppm using solvent residue peak as internal indicator ($CDCl_3$ δ 77.16 ppm). High resolution mass spectra were performed on a WATERS I-Class VION IMS QTof at the Instrumental Analysis Center of Xi'an Jiaotong University and are given in m/z. GCMS were performed on Agilent 8860 GC/5977B GC/MSD System and are given in m/z. All reactions were carried out in glassware dried overnight in an oven at 110 °C. All reactions were performed under air. Commercial reagents and solvents were used without further purification unless stated otherwise. TLC was performed on pre-coated glass plates visualized either with a UV lamp (254 nm), or using solutions of $KMnO_4$–K_2CO_3 in water followed by heating. Flash chromatography was performed on silica gel (230-400 mesh).

Preparation of the Unknown Substrates

Ethyl (*E*)-3-methyl-4-(phenylamino)pent-2-enoate（S1）



Aniline (931.3 mg, 10 mmol) and acetoin (1.76 g, 20 mmol) were dissolved in toluene (30 mL), and then 0.035 mL of conc. HCl was added. The formed water from the reaction was removed by using Dean-Stark apparatus for 18 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to obtain the target compound (1.33 g, 81%) as grey solid.

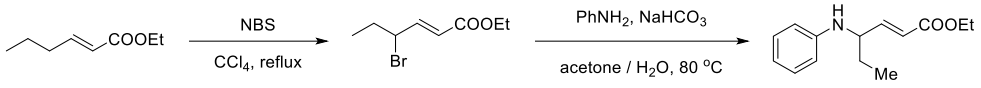
To a magnetically stirred suspension of *t*-BuOK (516 mg, 4.6 mmol) in 5 mL of anhydrous tetrahydrofuran (THF), was added dropwise ethyl 2-(diethoxyphosphoryl)acetate (1.03 g, 4.6 mmol) under N_2 at 0 °C. Then the reaction mixture was allowed to stir for 30 min at 0 °C. 3-(phenylamino)butan-2-one (500 mg, 3.06 mmol) in THF (5 mL) was then added dropwise, and the mixture was stirred for 2.5 h at room temperature. Quenched by saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Then the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give the desired product **S1** (400 mg, 56%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 2H), 6.70 (tt, J = 7.4, 1.2 Hz, 1H), 6.55 – 6.42 (m, 2H), 5.99 (d, J = 1.4 Hz, 1H), 4.13 (qd, J = 7.1, 1.7 Hz, 2H), 3.85 (q, J = 10.5, 8.7 Hz, 2H), 2.17 (d, J = 1.4 Hz, 3H), 1.36 (d, J = 6.7 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 161.1, 146.7, 129.3, 117.8, 115.2, 113.3, 59.8, 56.7, 21.3, 15.3, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{14}H_{20}NO_2^+$ 234.14886; found: 234.14874.

Ethyl (*E*)-4-(phenylamino)hex-2-enoate (S2)



To a solution of ethyl (*E*)-hex-2-enoate (568 mg, 4 mmol) in CCl_4 (6 mL) was added N-succinbromoimide (854 mg, 4.8 mmol) at room temperature, then the reaction mixture was allowed to reflux until the reaction was completed. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 40/1) to give ethyl (*E*)-4-bromohex-2-enoate (720 mg, 81%) as colorless oil.

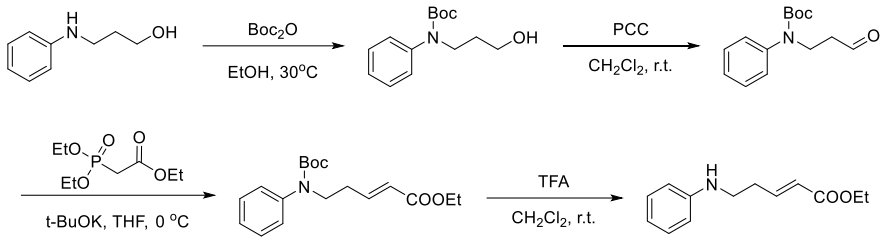
To a stirred solution of aniline (139 mg, 1.5 mmol) in 4 mL acetone was added ethyl (*E*)-4-bromohex-2-enoate (221 mg, 1 mmol), $NaHCO_3$ (311 mg, 3.7 mmol), and water (1 mL) in sequential way. The reaction contents were refluxed at 80 °C in an oil bath for 3 h. Upon completion, the solution was then cooled to room temperature, diluted with water, and extracted with EtOAc. The crude product was purified with silica-gel flash chromatography (petroleum ether/ethyl acetate = 12/1) to obtain the pure product **S2** (120 mg, 51%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 2H), 6.90 (dd, J = 15.6, 5.5 Hz, 1H), 6.70 (td, J = 7.3, 1.1 Hz, 1H), 6.63 – 6.50 (m, 2H), 5.99 (dt, J = 15.6, 1.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.05 – 3.82 (m, 1H), 3.70 (s, 1H), 1.70 (dtd, J = 17.8, 13.9, 6.9 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 149.7, 147.1, 129.4, 121.6, 117.9, 113.4, 60.6, 56.1, 28.3, 14.4, 10.6 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{14}H_{20}NO_2^+$ 234.14886; found: 234.14875.

Ethyl (*E*)-5-(phenylamino)pent-2-enoate (S3)



To a solution of 3-(phenylamino)propan-1-ol (500 mg, 3.31 mmol) in EtOH (5 mL) was added tert-butyldicarbonate (1.08 g, 4.97 mmol) at 30 °C and stirred overnight. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 1.5/1) to give *tert*-butyl (3-hydroxypropyl)(phenyl)carbamate (780 mg, 94%) as yellow oil.

To a solution of *tert*-butyl (3-hydroxypropyl)(phenyl)carbamate (740 mg, 2.94 mmol) in anhydrous CH_2Cl_2 (15 mL) was added PCC (1.27 g, 5.89 mmol) and celite (1.27 g). The mixture was stirred at room temperature until the reaction was completed. The solid was removed by filtration through celite. The filtrate was evaporated under reduced pressure and the residual was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), get the aldehyde (458 mg, 62%) as colorless oil.

To a magnetically stirred suspension of *t*-BuOK (206 mg, 1.84 mmol) in 2 mL of anhydrous tetrahydrofuran (THF), was added dropwise ethyl 2-(diethoxyphosphoryl)acetate (412 mg, 1.84 mmol) under N_2 at 0 °C. Then the reaction mixture was allowed to stir for 30 min at 0 °C. The aldehyde (458 mg, 1.84 mmol) in THF (2 mL) was then added dropwise, and the mixture was stirred for 2.5 h at room temperature. Quenched by saturated aq. NH_4Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Then the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the product ethyl (*E*)-5-((*tert*-butoxycarbonyl)(phenyl)amino)pent-2-enoate (394 mg, 67%) as colorless oil.

To a solution of ethyl (*E*)-5-((*tert*-butoxycarbonyl)(phenyl)amino)pent-2-enoate (394 mg, 1.23 mmol) in CH_2Cl_2 (5 mL) was added CF_3COOH (0.94 mL, 12.3 mmol) dropwise at 0 °C

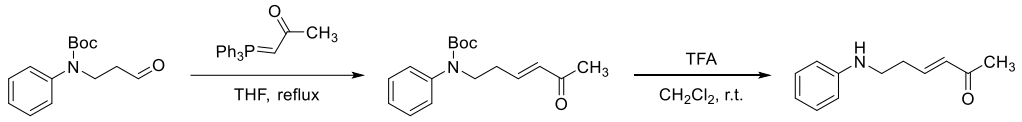
and the reaction was stirred at room temperature for 2 h. It was quenched by saturated aqueous Na_2CO_3 until pH was 7-8. Then separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated to give the desired product **S3** as colorless oil (235 mg, 87%) after purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.97 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.68 – 6.54 (m, 2H), 5.92 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.54 (qd, *J* = 6.9, 1.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 147.8, 145.9, 129.5, 123.5, 117.9, 113.1, 60.5, 42.4, 32.2, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{13}H_{18}NO_2^+$ 220.13321; found: 220.13306.

(*E*)-6-(phenylamino)hex-3-en-2-one (S4)



To a solution of the aldehyde (498 mg, 2 mmol) in THF (8 mL) was added methyl (triphenylphosphoranylidene)methyl ketone (955 mg, 3 mmol) at room temperature, then the reaction mixture was allowed to reflux until the reaction was completed. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give *tert*-butyl (*E*)-(5-oxohex-3-en-1-yl)(phenyl)carbamate (404 mg, 70%) as yellow oil.

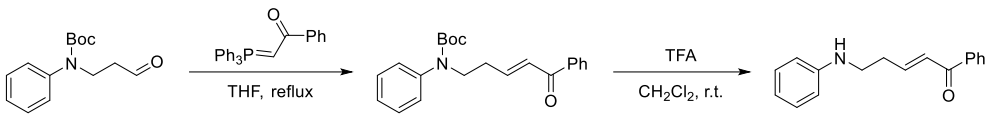
To a solution of *tert*-butyl (*E*)-(5-oxohex-3-en-1-yl)(phenyl)carbamate (404 mg, 1.4 mmol) in CH_2Cl_2 (5 mL) was added CF_3COOH (1.07 mL, 14 mmol) dropwise at 0 °C and the reaction was stirred at room temperature for 2 h. It was quenched by saturated aqueous Na_2CO_3 until pH was 7-8. Then separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated to give the desired product **S4** as yellow oil (167 mg, 63%) after purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.82 (dt, *J* = 15.9, 7.0 Hz, 1H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.67 – 6.57 (m, 2H), 6.17 (dt, *J* = 16.0, 1.5 Hz, 1H), 3.65 (s, 1H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.56 (qd, *J* = 6.8, 1.5 Hz, 2H), 2.26 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 147.7, 145.0, 133.0, 129.5, 117.9, 113.0, 42.4, 32.5, 27.1 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{12}H_{16}NO^+$ 190.12264; found: 190.12260.

(*E*)-1-phenyl-5-(phenylamino)pent-2-en-1-one (S5)



To a solution of the aldehyde (1 g, 4 mmol) in THF (15 mL) was added 2-(triphenylphosphoranylidene)-acetophenon (1.83 g, 4.8 mmol) at room temperature, then the reaction mixture was allowed to reflux until the reaction was completed. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give *tert*-butyl (*E*)-(5-oxo-5-phenylpent-3-en-1-yl)(phenyl)carbamate (893 mg, 64%) as yellow oil.

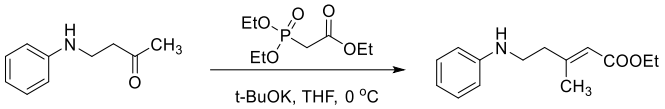
To a solution of *tert*-butyl (*E*)-(5-oxo-5-phenylpent-3-en-1-yl)(phenyl)carbamate (893 mg, 2.54 mmol) in CH_2Cl_2 (10 mL) was added CF_3COOH (1.95 mL, 25.4 mmol) dropwise at 0 ^oC and the reaction was stirred at room temperature for 2 h. It was quenched by saturated aqueous Na_2CO_3 until pH was 7-8. Then separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated to give the desired product **S5** as yellow solid (340 mg, 53%) after purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.62 – 7.53 (m, 1H), 7.53 – 7.42 (m, 2H), 7.25 – 7.16 (m, 2H), 7.08 (dt, *J* = 15.4, 6.7 Hz, 1H), 7.02 – 6.90 (m, 1H), 6.73 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.69 – 6.56 (m, 2H), 3.72 (s, 1H), 3.37 (t, *J* = 6.7 Hz, 2H), 2.66 (qd, *J* = 6.8, 1.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 147.6, 146.2, 137.7, 133.0, 129.5, 128.7, 127.8, 117.9, 113.2, 42.5, 32.7 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{17}H_{18}NO^+$ 252.13829; found: 252.13831.

Ethyl (*E*)-3-methyl-5-(phenylamino)pent-2-enoate (S6)



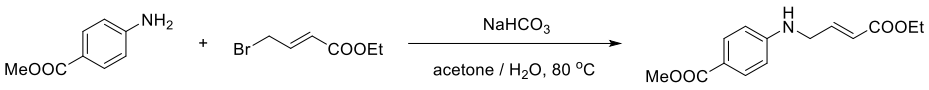
To a magnetically stirred suspension of *t*-BuOK (227 mg, 2.02 mmol) in 3 mL of anhydrous tetrahydrofuran (THF), was added dropwise ethyl 2-(diethoxyphosphoryl)acetate (453 mg, 2.02 mmol) under N_2 at 0 °C. Then the reaction mixture was allowed to stir for 30 min at 0 °C. 4-(phenylamino)butan-2-one (220 mg, 1.35 mmol) in THF (2 mL) was then added dropwise, and the mixture was stirred for 15 h at room temperature. Quenched by saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Then the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the product **S6** (150 mg, 48%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 2H), 6.79 – 6.67 (m, 1H), 6.61 (dd, J = 8.6, 1.1 Hz, 2H), 5.74 (q, J = 1.3 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.30 (t, J = 6.9 Hz, 2H), 2.46 (td, J = 6.9, 1.1 Hz, 2H), 2.21 (d, J = 1.3 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 156.6, 147.7, 129.5, 118.0, 117.6, 113.2, 59.9, 41.6, 40.4, 18.7, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{14}H_{20}NO_2^+$ 234.14886; found: 234.14878.

Methyl (*E*)-4-((4-ethoxy-4-oxobut-2-en-1-yl)amino)benzoate (S7)



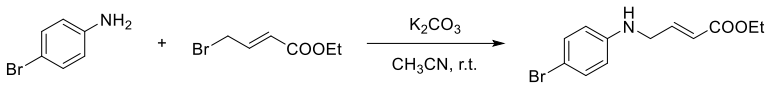
To a stirred solution of methyl 4-aminobenzoate (500 mg, 3.31 mmol) in 8 mL acetone was added ethyl (*E*)-4-bromobut-2-enoate (958 mg, 4.96 mmol), $NaHCO_3$ (1.03 g, 12.25 mmol), and water (2 mL) in sequential way. The reaction contents were refluxed at 80 °C in an oil bath for 3 h. Upon completion, the solution was then cooled to room temperature, diluted with water, and extracted with EtOAc. The crude product was purified with silica-gel flash chromatography (petroleum ether/ethyl acetate = 3/1) to obtain the pure product **S7** (557 mg, 64%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.75 (m, 2H), 6.98 (dt, J = 15.7, 4.5 Hz, 1H), 6.60 – 6.43 (m, 2H), 5.99 (dt, J = 15.7, 1.9 Hz, 1H), 4.48 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.00 (dd, J = 4.5, 2.0 Hz, 2H), 3.84 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 166.2, 151.1, 144.3, 131.7, 122.3, 119.3, 111.9, 60.6, 51.7, 44.3, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{14}H_{18}NO_4^+$ 264.12303; found: 264.12297.

Ethyl (*E*)-4-((4-bromophenyl)amino)but-2-enoate (S8)



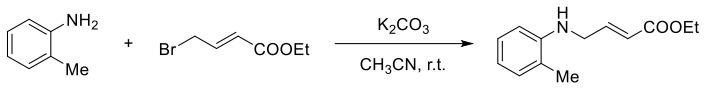
Ethyl (*E*)-4-bromobut-2-enoate (500 mg, 2.59 mmol), 4-bromoaniline (668 mg, 3.88 mmol) and K_2CO_3 (72 mg, 0.52 mmol) were dissolved in CH_3CN (5 mL), and the mixture was stirred at room temperature for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the desired product **S8** (400 mg, 54%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 2H), 6.99 (dt, J = 15.7, 4.5 Hz, 1H), 6.53 – 6.38 (m, 2H), 6.01 (dt, J = 15.7, 1.9 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.93 (dd, J = 4.5, 2.0 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 146.2, 144.8, 132.1, 122.2, 114.7, 109.8, 60.6, 44.9, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{12}H_{15}BrNO_2^+$ 284.02807; found: 284.02788.

Ethyl (*E*)-4-(o-tolylamino)but-2-enoate (*S*9)



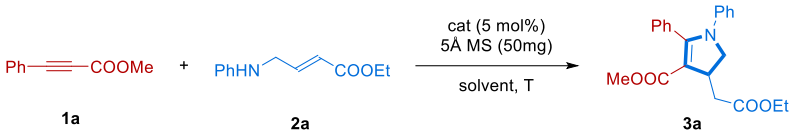
Ethyl (*E*)-4-bromobut-2-enoate (965.2 mg, 5 mmol), *o*-toluidine (803 mg, 7.5 mmol) and K_2CO_3 (138 mg, 1 mmol) were dissolved in CH_3CN (10 mL), and the mixture was stirred at room temperature for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the desired product **S9** (700 mg, 64%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.01 (m, 3H), 6.70 (td, J = 7.4, 1.2 Hz, 1H), 6.53 (dd, J = 7.9, 1.2 Hz, 1H), 6.04 (dt, J = 15.7, 2.0 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.02 (dd, J = 4.6, 2.0 Hz, 2H), 2.18 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 145.6, 145.2, 130.3, 127.3, 122.3, 121.9, 117.8, 110.1, 60.5, 44.9, 17.6, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{13}H_{18}NO_2^+$ 220.13321; found: 220.13307.

Reaction condition optimizations



entry [b]	cat	solvent	T(°C)	1:2 (eq)	conc.(M)	t (h)	yield (%)[c]
1	$BrettPhosAuNTf_2$	DCE	110	1:1.5	0.05	18	53
2	PPh_3AuNTf_2	DCE	110	1:1.5	0.05	18	37
3	$IPrAuNTf_2$	DCE	110	1:1.5	0.05	18	51
4	$JohnPhosAuNTf_2$	DCE	110	1:1.5	0.05	5	55
5	$[((2,4\text{-}{}^tBu_2C_6H_3O)_3P)AuNTf_2$	DCE	110	1:1.5	0.05	18	31
6	$AuCl_3$	DCE	110	1:1.5	0.05	24	11
7	$PicAuCl_2$	DCE	110	1:1.5	0.05	24	13
8	no catalyst	DCE	110	1:2	0.05	4	NR
9	$Sc(OTf)_3$	DCE	110	1:1.5	0.05	5	NR
10	$Cu(OTf)_3$	DCE	110	1:1.5	0.05	5	NR
11	$Zn(OTf)_3$	DCE	110	1:1.5	0.05	5	NR
12	$In(OTf)_3$	DCE	110	1:1.5	0.05	5	NR
13	$AgNTf_2$	DCE	110	1:1.5	0.05	5	NR
14	K_2CO_3 (50 mol %)	DCE	110	1:1.5	0.05	3.5	NR
15	K_3PO_4 (50 mol %)	DCE	110	1:1.5	0.05	3.5	NR
16	*t*-BuOK (50 mol %)	DCE	110	1:1.5	0.05	3.5	NR
17	TMG (50 mol %)	DCE	110	1:1.5	0.05	3.5	NR
18	DBU (50 mol %)	DCE	110	1:1.5	0.05	3.5	NR
19	$JohnPhosAuNTf_2$	DCE	70	1:1.5	0.05	40	57

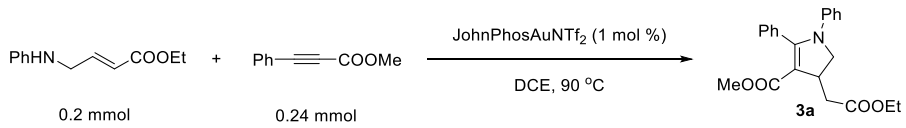
20	JohnPhosAuNTf$_2$	DCE	90	1:1.5	0.05	18	64
21	JohnPhosAuNTf$_2$	DCE	90	1:1	0.05	18	57
22	JohnPhosAuNTf$_2$	DCE	90	1:2	0.05	18	64
23	JohnPhosAuNTf$_2$	DCE	90	2:1	0.05	18	72
24	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.05	18	74
25	JohnPhosAuNTf$_2$	DCE	90	1.2:1	0.05	18	66
26	JohnPhosAuCl+AgBF$_4$	DCE	90	1.5:1	0.05	36	41
27	JohnPhosAuCl+AgOTf	DCE	90	1.5:1	0.05	18	58
28	JohnPhosAuCl+AgSbF$_6$	DCE	90	1.5:1	0.05	18	58
29	JohnPhosAuCl+NaBArF	DCE	90	1.5:1	0.05	18	53
30	JohnPhosAuNTf$_2$	toluene	90	1.5:1	0.05	24	40
31	JohnPhosAuNTf$_2$	PhCl	90	1.5:1	0.05	24	57
32	JohnPhosAuNTf$_2$	(CHCl$_2$)$_2$	90	1.5:1	0.05	14	68
33	JohnPhosAuNTf$_2$	CH$_3$CN	90	1.5:1	0.05	14	57
34	JohnPhosAuNTf$_2$	THF	90	1.5:1	0.05	24	32
35 [d]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.05	24	68
36 [d]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.10	20	66
37 [e, f]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.05	36	50
38 [e, f]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.10	36	54
39 [e]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.20	24	76
40 [e]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.40	24	83
41 [e, g]	JohnPhosAuNTf$_2$	DCE	90	1.5:1	0.50	24	82
42 [e, g]	JohnPhosAuNTf$_2$	DCE	90	1.2:1	0.50	24	80
43 [g, h]	JohnPhosAuNTf$_2$	DCE	90	1.0:1	1.0	36	75
44 [g, h]	JohnPhosAuNTf$_2$	DCE	90	1.2:1	1.0	36	80

[*a*] Unless otherwise specified, all reactions were carried out in 0.05 mmol scale, using 5 mol % catalyst, 50 mg 5Å molecular sieves and 1.0 mL solvent. [*b*] Entries 35-40 were carried out in 0.1 mmol scale, entries 41 and 42 were carried out in 0.2 mmol scale. [*c*] NMR yield of **3a**. [*d*] 2.5 mol % catalyst was used. [*e*] 1 mol % catalyst. [*f*] 100 mg 5Å molecular sieves were used. [*g*] Without molecular sieves. [*h*] 0.5 mol % catalyst was used.

DCE = 1,2-dichloroethane THF = Tetrahydrofuran
TMG = N,N'-Tetramethylguanidine DBU = 1,8-Diazabicyclo[5.4.]undec-7-ene

Scope of the Substrates

Methyl 4-(2-ethoxy-2-oxoethyl)-1,2-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3a)



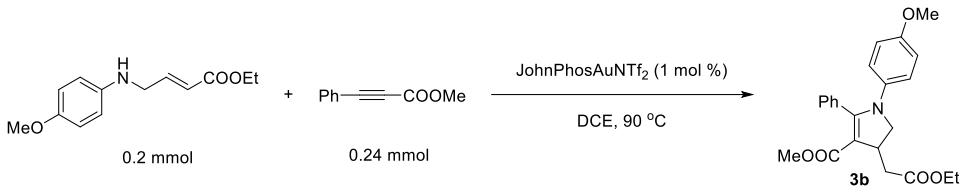
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3a** (64.2 mg, 88%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 7.16 – 6.98 (m, 2H), 6.93 – 6.84 (m, 1H), 6.71 – 6.57 (m, 2H), 4.46 (t, *J* = 10.5 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.78 (dd, *J* = 10.7, 3.9 Hz, 1H), 3.67 (tt, *J* = 11.3, 4.1 Hz, 1H), 3.56 (s, 3H), 2.98 (dd, *J* = 16.0, 3.3 Hz, 1H), 2.57 (dd, *J* = 16.1, 10.3 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.1, 158.2, 142.2, 131.5, 129.6, 129.2, 128.5, 127.8, 123.1, 121.9, 105.6, 60.4, 59.2, 50.4, 38.9, 37.1, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{22}H_{24}NO_4^+$ 366.16998; found: 366.17007.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3b)



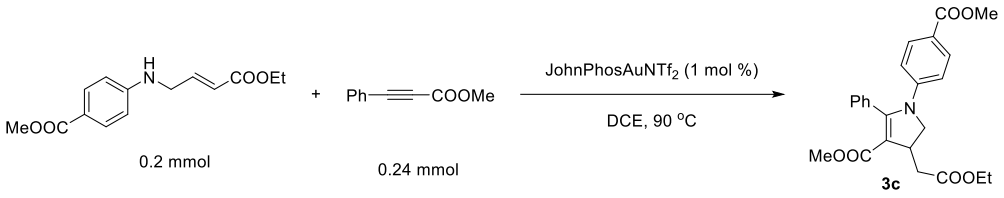
Ethyl (*E*)-4-((4-methoxyphenyl)amino)but-2-enoate (47.06 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 30 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product **3b** (43 mg, 54%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 5H), 6.68 – 6.55 (m, 4H), 4.47 – 4.28 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.75 – 3.69 (m, 1H), 3.68 (s, 3H), 3.67 – 3.61 (m, 1H), 3.54 (s, 3H), 2.98 (dd, J = 16.1, 3.1 Hz, 1H), 2.55 (dd, J = 15.9, 10.1 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 166.3, 159.4, 156.0, 135.6, 131.6, 129.7, 129.0, 127.8, 124.4, 113.9, 104.0, 60.5, 60.0, 55.4, 50.4, 39.1, 37.2, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_5^+$ 396.18055; found: 396.18062.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-(4-(methoxycarbonyl)phenyl)-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3c)



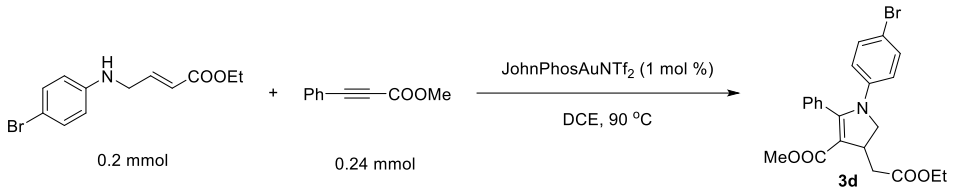
Methyl (*E*)-4-((4-ethoxy-4-oxobut-2-en-1-yl)amino)benzoate (52.66 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 48 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product **3c** (61 mg, 72%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 2H), 7.43 – 7.29 (m, 3H), 7.29 – 7.21 (m, 2H), 6.60 – 6.48 (m, 2H), 4.48 (t, J = 10.4 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.81 (m, 4H), 3.71 – 3.60 (m, 1H), 3.55 (s, 3H), 2.95 (dd, J = 16.0, 3.3 Hz, 1H), 2.54 (dd, J = 16.1, 10.2 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 166.7, 165.9, 156.6, 146.2, 131.2, 130.2, 129.7, 129.5, 128.3, 123.4, 119.7, 108.6, 60.6, 58.7, 52.0, 50.8, 38.7, 37.1, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{24}H_{26}NO_6^+$ 424.17546; found: 424.17569.

Methyl 1-(4-bromophenyl)-4-(2-ethoxy-2-oxoethyl)-2-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3d)



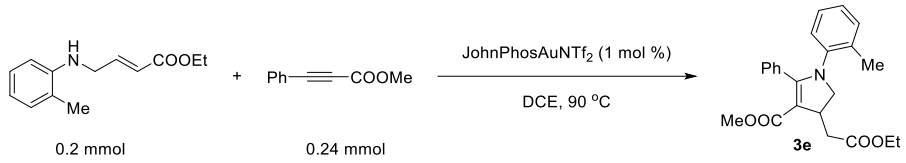
Ethyl (*E*)-4-((4-bromophenyl)amino)but-2-enoate (56.8 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 48 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product **3c** (65 mg, 73%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 7.18 – 7.13 (m, 2H), 6.48 (d, *J* = 8.6 Hz, 2H), 4.41 (t, *J* = 10.5 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.69 – 3.60 (m, 1H), 3.55 (s, 3H), 2.96 (dd, *J* = 16.0, 3.3 Hz, 1H), 2.54 (dd, *J* = 16.1, 10.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.1, 157.4, 141.4, 131.6, 131.2, 129.6, 129.5, 128.1, 123.1, 115.8, 106.3, 60.6, 59.2, 50.6, 38.8, 37.1, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{22}H_{23}BrNO_4^+$ 444.08050; found: 444.07963.

Methyl 4-(2-ethoxy-2-oxoethyl)-2-phenyl-1-(o-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3e)



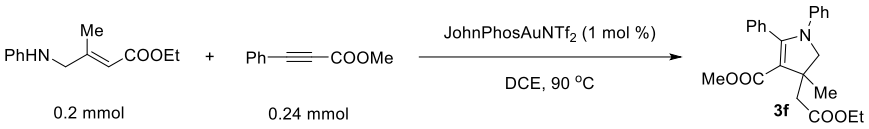
Ethyl (*E*)-4-(*o*-tolylamino)but-2-enoate (43.9 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 33 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3e** (64.4 mg, 85%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 5H), 7.07 (d, J = 7.4 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.80 (s, 1H), 4.28 – 3.65 (m, 5H), 3.56 (s, 3H), 3.06 (s, 1H), 2.59 (dt, J = 16.3, 6.1 Hz, 1H), 2.26 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 166.4, 161.8, 141.8, 135.5, 131.4, 130.9, 129.5, 129.0, 127.9, 127.4, 126.6, 103.1, 60.5, 60.1, 50.4, 40.0, 38.1, 18.2, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_4^+$ 380.18563; found: 380.18570.

Methyl 4-(2-ethoxy-2-oxoethyl)-4-methyl-1,2-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3f)



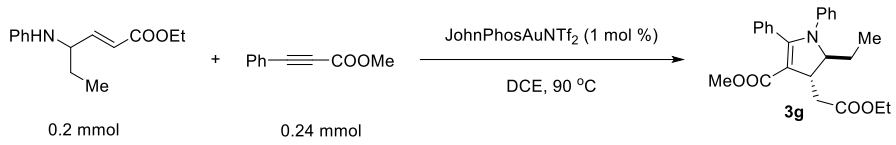
Ethyl (E)-3-methyl-4-(phenylamino)but-2-enoate (43.9 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 10 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3f** (75.1 mg, 99%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 3H), 7.22 (dq, J = 6.4, 2.2 Hz, 2H), 7.11 – 7.00 (m, 2H), 6.94 – 6.83 (m, 1H), 6.72 – 6.55 (m, 2H), 4.28 (d, J = 10.3 Hz, 1H), 4.18 – 3.99 (m, 2H), 3.90 (d, J = 10.4 Hz, 1H), 3.50 (s, 3H), 2.86 (d, J = 1.1 Hz, 2H), 1.53 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 166.4, 157.5, 142.2, 132.3, 129.4, 128.9, 128.5, 127.9, 123.1, 122.1, 109.8, 65.5, 60.3, 50.1, 43.9, 43.2, 25.5, 14.2 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_4^+$ 380.18563; found: 380.18568.

Methyl -4-(2-ethoxy-2-oxoethyl)-5-ethyl-1,2-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (3g)



Ethyl (*E*)-4-(phenylamino)hex-2-enoate (46.7 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 20 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the product **3g** (57.8 mg, 73%, 3/1 dr) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 5H), 7.13 – 7.04 (m, 2H), 6.97 – 6.89 (m, 1H), 6.82 – 6.72 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.89 (dd, *J* = 7.7, 3.2 Hz, 1H), 3.56 (s, 3H), 3.34 (dt, *J* = 9.7, 3.0 Hz, 1H), 2.89 (dd, *J* = 15.4, 3.4 Hz, 1H), 2.54 (dd, *J* = 15.5, 9.8 Hz, 1H), 1.94 – 1.73 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 166.4, 158.3, 142.5, 132.0, 129.7, 129.1, 128.7, 127.7, 124.2, 124.1, 104.4, 71.8, 60.4, 50.5, 42.7, 39.5, 26.7, 14.4, 8.6 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{24}H_{28}NO_4^+$ 394.20128; found: 394.20170.

Methyl 4-(2-ethoxy-2-oxoethyl)-4,5-dimethyl-1,2-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (3h)

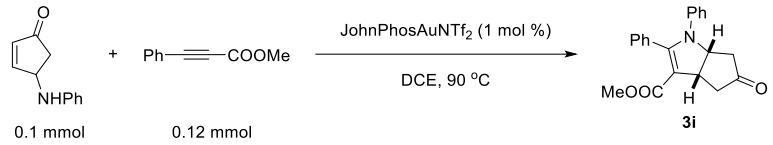
Ethyl (*E*)-3-methyl-4-(phenylamino)pent-2-enoate (46.7 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 20 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to give the product **3h** (69.5 mg, 88%, 1/1 dr) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 10H), 7.12 – 7.03 (m, 4H), 7.01 – 6.90 (m, 2H), 6.86 – 6.74 (m, 4H), 4.38 (q, *J* = 6.6 Hz, 1H), 4.25 – 3.99 (m, 5H), 3.47 (d, *J* = 2.1 Hz, 6H), 2.96 (dd, *J* = 18.3, 14.7 Hz, 2H), 2.68 (dd, *J* = 23.9, 14.7 Hz, 2H), 1.52 (s, 3H), 1.39 (s, 3H), 1.31 – 1.18 (m, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 172.0, 166.7, 166.6, 158.5, 158.0, 141.6, 141.5, 132.8, 132.7, 129.4, 129.3, 128.6, 128.4, 127.5, 127.5, 126.0, 125.2, 124.8, 124.5, 109.1, 108.6, 70.9, 67.8, 60.2, 60.1, 50.1, 50.0, 47.5, 47.1, 43.5, 38.3, 25.4, 19.4, 14.3, 14.2, 14.0, 13.7 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{24}H_{28}NO_4^+$ 394.20128; found: 394.20140.

Methyl -5-oxo-1,2-diphenyl-1,3a,4,5,6,6a-hexahydrocyclopenta[*b*]pyrrole-3-carboxylate (3i)



4-(phenylamino)cyclopent-2-en-1-one (17.3 mg, 0.1 mmol), methyl 3-phenylpropiolate (19.22 mg, 0.12 mmol) and JohnPhosAuNTf$_2$ (0.8 mg, 0.001 mmol) was dissolved in DCE (0.2 mL), and the mixture was stirred at 90 °C for 12 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 3/1) to give the product **3i** (26 mg, 78%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 3H), 7.22 – 7.17 (m, 2H), 7.14 – 7.06 (m, 2H), 7.00 – 6.94 (m, 1H), 6.72 – 6.66 (m, 2H), 5.02 (ddd, *J* = 10.3, 7.3, 2.8 Hz, 1H), 4.04 (td, *J* = 9.8, 5.5 Hz, 1H), 3.55 (s, 3H), 2.87 (ddd, *J* = 19.7, 9.7, 1.7 Hz, 1H), 2.69 (ddd, *J* = 19.3, 7.2, 1.6 Hz, 1H), 2.63 – 2.48 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.2, 166.3, 158.7, 140.5, 131.2, 129.6, 129.2, 129.0, 127.8, 124.8, 124.7, 107.0, 65.8, 50.7, 44.6, 43.6, 41.9 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{21}H_{20}NO_3^+$ 334.14377; found: 334.14337.

Methyl 4-(2-ethoxy-2-oxoethyl)-1,2-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (3j)

Ethyl (*E*)-5-(phenylamino)pent-2-enoate (43.86 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 16 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3j** (52 mg, 69%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, J = 2.0 Hz, 5H), 7.06 (dd, J = 8.3, 7.3 Hz, 2H), 6.94 – 6.87 (m, 1H), 6.85 – 6.80 (m, 2H), 4.17 (qd, J = 7.2, 1.3 Hz, 2H), 3.67 (td, J = 5.7, 5.1, 2.2 Hz, 2H), 3.48 (ddt, J = 11.1, 5.8, 2.9 Hz, 1H), 3.37 (s, 3H), 2.76 (ddd, J = 15.2, 3.4, 1.0 Hz, 1H), 2.35 (dd, J = 15.3, 10.7 Hz, 1H), 2.03 – 1.92 (m, 1H), 1.92 – 1.83 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 169.7, 154.1, 146.9, 137.7, 129.7, 128.6, 127.9, 127.5, 126.9, 124.6, 106.7, 60.4, 50.8, 49.1, 40.1, 30.5, 26.1, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_4^+$ 380.18563; found: 380.18569.

Methyl 4-(2-ethoxy-2-oxoethyl)-4-methyl-1,2-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (3k)

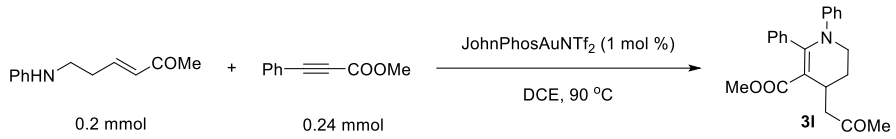
Ethyl (*E*)-3-methyl-5-(phenylamino)pent-2-enoate (46.6 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 36 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the product **3k** (76.2 mg, 96%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 7.3, 2.4 Hz, 2H), 7.14 – 7.03 (m, 5H), 6.95 – 6.82 (m, 3H), 4.15 (q, J = 7.1 Hz, 2H), 3.69 (dd, J = 7.0, 4.0 Hz, 2H), 3.20 (s, 3H), 3.17 (d, J = 14.5 Hz, 1H), 2.80 (d, J = 14.6 Hz, 1H), 2.20 (dt, J = 13.7, 6.9 Hz, 1H), 1.70 (dt, J = 13.6, 3.9 Hz, 1H), 1.35 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 171.0, 152.3, 147.1, 138.6, 129.6, 128.6, 128.1, 127.7, 126.1, 123.8, 114.8, 60.0, 50.5, 50.2, 44.7, 35.6, 27.6, 14.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{24}H_{28}NO_4^+$ 394.20128; found: 394.20128.

Methyl 4-(2-oxopropyl)-1,2-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (3l)



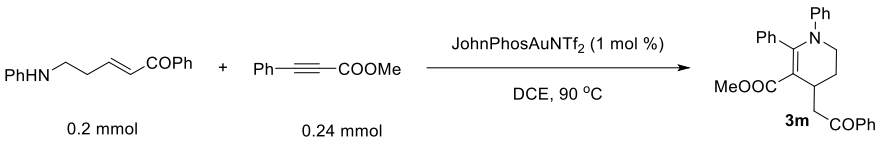
(*E*)-6-(phenylamino)hex-3-en-2-one (37.8 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give the product **3l** (65 mg, 93%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (m, 5H), 7.05 (t, J = 7.8 Hz, 2H), 6.93 – 6.86 (m, 1H), 6.84 – 6.79 (m, 2H), 3.69 – 3.59 (m, 2H), 3.48 (ddt, J = 10.8, 5.5, 2.6 Hz, 1H), 3.35 (s, 3H), 2.85 (dd, J = 15.9, 2.9 Hz, 1H), 2.44 (dd, J = 15.8, 10.3 Hz, 1H), 2.21 (s, 3H), 2.02 – 1.89 (m, 1H), 1.83 – 1.73 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 169.8, 154.1, 146.8, 137.7, 129.7, 128.6, 127.9, 127.5, 126.8, 124.6, 106.9, 50.7, 49.6, 49.1, 30.1, 29.6, 26.1 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{22}H_{24}NO_3^+$ 350.17507; found: 350.17526.

Methyl 4-(2-oxo-2-phenylethyl)-1,2-diphenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (3m)



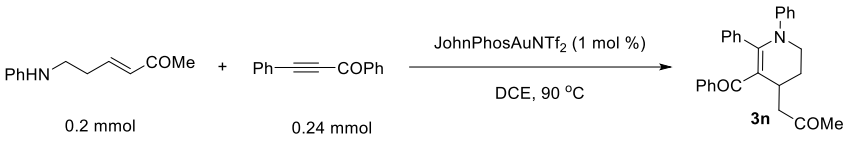
(*E*)-1-phenyl-5-(phenylamino)pent-2-en-1-one (50.3 mg, 0.2 mmol), methyl 3-phenylpropiolate (38.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 36 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3m** (67 mg, 81%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.63 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.14 (ddd, *J* = 7.8, 5.6, 3.2 Hz, 5H), 7.10 – 7.03 (m, 2H), 6.94 – 6.88 (m, 1H), 6.88 – 6.82 (m, 2H), 3.76 (ddd, *J* = 12.6, 11.1, 3.3 Hz, 1H), 3.68 (ddd, *J* = 8.6, 5.5, 3.1 Hz, 2H), 3.55 (ddd, *J* = 15.3, 2.9, 1.1 Hz, 1H), 3.39 (s, 3H), 2.89 (dd, *J* = 15.3, 11.0 Hz, 1H), 2.03 – 1.84 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 169.9, 154.4, 146.8, 137.7, 136.9, 133.2, 129.7, 128.7, 128.6, 128.5, 127.9, 127.5, 126.9, 124.6, 106.8, 50.8, 49.1, 44.7, 30.5, 25.6 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{27}H_{26}NO_3^+$ 412.19072; found: 412.19097.

1-(5-benzoyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-4-yl)propan-2-one (3n)



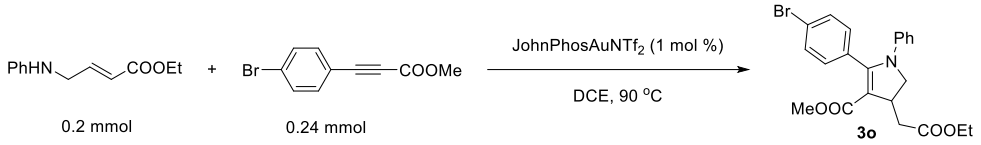
(*E*)-6-(phenylamino)hex-3-en-2-one (37.8 mg, 0.2 mmol), 1,3-diphenylprop-2-yn-1-one (49.5 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 14 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product **3n** (60.7 mg, 76%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.11 – 6.94 (m, 7H), 6.89 – 6.79 (m, 3H), 6.77 – 6.72 (m, 3H), 3.87 – 3.65 (m, 3H), 2.76 (dd, *J* = 15.4, 2.7 Hz, 1H), 2.41 (dd, *J* = 15.5, 10.8 Hz, 1H), 2.17 (s, 3H), 1.99 – 1.76 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 199.6, 153.3, 147.4, 141.6, 137.1, 131.4, 130.6, 128.8, 128.7, 128.5, 127.6, 127.4, 126.2, 124.1, 120.2, 49.9, 48.8, 30.8, 29.8, 26.0 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{27}H_{26}NO_2^+$ 396.19581; found: 396.19566.

Methyl 2-(4-bromophenyl)-4-(2-ethoxy-2-oxoethyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3o)



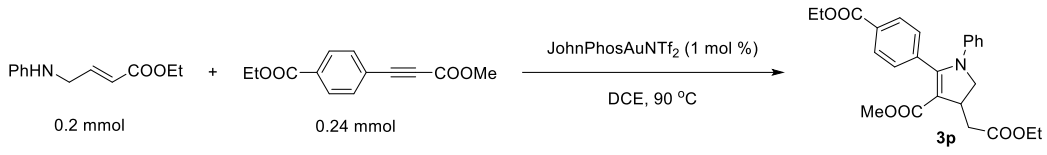
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(4-bromophenyl)propiolate (57.4 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 30 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3o** (69.5 mg, 78%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.18 – 7.04 (m, 4H), 6.96 – 6.89 (m, 1H), 6.66 – 6.59 (m, 2H), 4.44 (t, *J* = 10.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.74 (dd, *J* = 10.7, 3.9 Hz, 1H), 3.69 – 3.60 (m, 1H), 3.57 (s, 3H), 2.94 (dd, *J* = 16.1, 3.4 Hz, 1H), 2.53 (dd, *J* = 16.0, 10.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.1, 157.1, 142.2, 131.5, 131.2, 130.4, 128.8, 123.6, 123.6, 122.3, 106.1, 60.6, 59.5, 50.6, 39.0, 37.2, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{22}H_{23}BrNO_4^+$ 444.08050; found: 444.08086.

Methyl 4-(2-ethoxy-2-oxoethyl)-2-(4-(ethoxycarbonyl)phenyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3p)



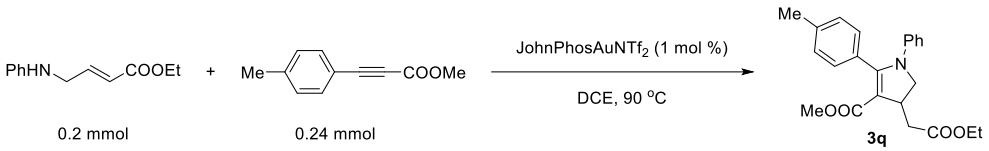
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate (55.8 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 48 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give the product **3p** (68.4 mg, 78%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 8.6, 7.2 Hz, 2H), 6.96 – 6.86 (m, 1H), 6.70 – 6.58 (m, 2H), 4.45 (t, J = 10.6 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.78 (dd, J = 10.7, 4.1 Hz, 1H), 3.67 (ddt, J = 10.3, 6.6, 3.6 Hz, 1H), 3.53 (s, 3H), 2.97 (dd, J = 16.0, 3.3 Hz, 1H), 2.56 (dd, J = 16.1, 10.2 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.2, 166.0, 157.3, 142.0, 136.2, 131.0, 129.8, 129.1, 128.8, 123.6, 122.1, 106.3, 61.2, 60.6, 59.6, 50.6, 38.9, 37.2, 14.4, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{25}H_{28}NO_6^+$ 438.19111; found: 438.19106.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-phenyl-2-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3q)



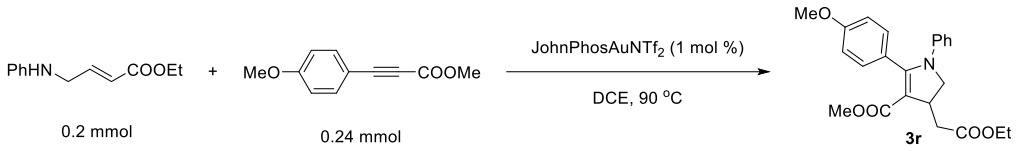
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(*p*-tolyl)propiolate (41.8 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 6/1) to give the product **3q** (73 mg, 96%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 7.9 Hz, 2H), 7.12 – 7.03 (m, 4H), 6.89 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H), 4.45 (t, J = 10.5 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.80 – 3.71 (m, 1H), 3.70 – 3.59 (m, 1H), 3.57 (s, 3H), 2.95 (dd, J = 16.1, 3.3 Hz, 1H), 2.54 (dd, J = 16.1, 10.3 Hz, 1H), 2.33 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.3, 158.5, 142.5, 139.2, 129.6, 128.6, 128.6, 128.4, 123.0, 121.9, 105.3, 60.5, 59.3, 50.4, 39.0, 37.1, 21.5, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_4^+$ 380.18563; found: 380.18542.

Methyl 4-(2-ethoxy-2-oxoethyl)-2-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3r)



Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(4-methoxyphenyl)propiolate (45.6 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to give the product **3r** (71.9 mg, 91%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.3 Hz, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.85 – 6.75 (m, 2H), 6.64 (d, J = 8.0 Hz, 2H), 4.44 (t, J = 10.5 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.76 – 3.70 (m, 1H), 3.66 – 3.59 (m, 1H), 3.57 (s, 3H), 2.93 (dd, J = 16.0, 3.3 Hz, 1H), 2.52 (dd, J = 16.0, 10.3 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.3, 160.2, 158.0, 142.6, 131.3, 128.5, 123.3, 122.9, 122.0, 113.3, 104.9, 60.4, 59.2, 55.1, 50.4, 39.0, 37.0, 14.2 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{23}H_{26}NO_5^+$ 396.18055; found: 396.18069.

Methyl 2-(3,4-dimethoxyphenyl)-4-(2-ethoxy-2-oxoethyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3s)

0.2 mmol 0.24 mmol

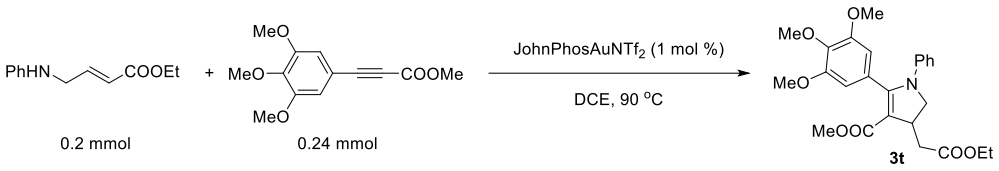
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(3,4-dimethoxyphenyl)propiolate (52.8 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 22 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 2/1) to give the product **3s** (74 mg, 87%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 7.7 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.3 Hz, 1H), 6.66 (dd, J = 26.6, 4.9 Hz, 3H), 4.43 (t, J = 10.4 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.78 – 3.69 (m, 1H), 3.66 (s, 3H), 3.64 – 3.60 (m, 1H), 3.57 (s, 3H), 2.94 (dd, J = 16.0, 3.3 Hz, 1H), 2.67 – 2.43 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.3, 157.9, 149.7, 148.2, 142.6, 128.6, 123.2, 122.0, 113.0, 110.3, 104.9, 60.5, 59.1, 55.8, 55.8, 50.5, 38.9, 37.1, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{24}H_{28}NO_6^+$ 426.19111; found: 426.19150.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-phenyl-2-(3,4,5-trimethoxyphenyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3t)



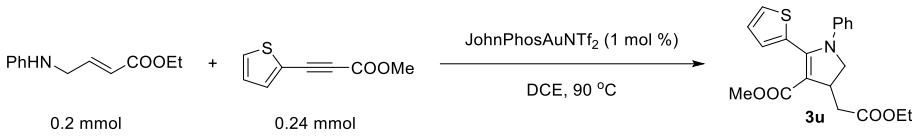
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(3,4,5-trimethoxyphenyl)propiolate (60.06 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 22 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 2/1) to give the product **3t** (75.7 mg, 83%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 7.7 Hz, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 6.46 (s, 2H), 4.42 (t, J = 10.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 3.77 – 3.69 (m, 1H), 3.65 (s, 6H), 3.64 – 3.59 (m, 1H), 3.58 (s, 3H), 2.95 (dd, J = 16.0, 3.4 Hz, 1H), 2.64 – 2.44 (m, 1H), 1.22 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.2, 157.8, 152.7, 142.5, 138.8, 128.7, 126.2, 123.3, 121.9, 107.5, 105.1, 61.0, 60.5, 59.1, 56.2, 50.6, 38.9, 37.2, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{25}H_{30}NO_7^+$ 456.20168; found: 456.20179.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-phenyl-2-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3u)



Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(thiophen-2-yl)propiolate (39.89 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3u** (71.6 mg, 96%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 5.1 Hz, 1H), 7.18 – 7.07 (m, 3H), 7.01 – 6.90 (m, 2H), 6.73 (d, J = 7.9 Hz, 2H), 4.41 (t, J = 10.5 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.74 – 3.57 (m, 5H), 2.92 (dd, J = 16.1, 3.3 Hz, 1H), 2.51 (dd, J = 16.1, 10.3 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 165.9, 150.8, 143.2, 131.3, 131.3, 128.7, 128.3, 126.6, 123.6, 122.3, 107.0, 60.5, 59.5, 50.6, 38.9, 37.4, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{20}H_{22}NO_4S^+$ 372.12641; found: 372.12651.

Methyl 4-(2-ethoxy-2-oxoethyl)-1-phenyl-2-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3v)

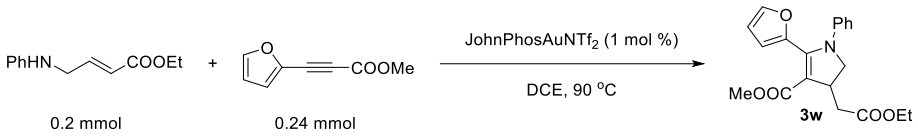
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(thiophen-3-yl)propiolate (39.89 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3v** (70.9 mg, 95%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.19 (dd, J = 5.0, 2.9 Hz, 1H), 7.09 (t, J = 7.8 Hz, 2H), 6.96 (dd, J = 5.0, 1.3 Hz, 1H), 6.92 (t, J = 7.7 Hz, 1H), 6.64 (d, J = 7.9 Hz, 2H), 4.40 (t, J = 10.5 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.75 – 3.61 (m, 2H), 3.60 (s, 3H), 2.93 (dd, J = 16.0, 3.3 Hz, 1H), 2.50 (dd, J = 16.1, 10.4 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.1, 152.9, 142.8, 131.0, 129.0, 128.7, 128.0, 124.5, 123.3, 122.0, 105.6, 60.5, 59.2, 50.6, 38.9, 37.1, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{20}H_{22}NO_4S^+$ 372.12641; found: 372.12677.

Methyl 4-(2-ethoxy-2-oxoethyl)-2-(furan-2-yl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3w)



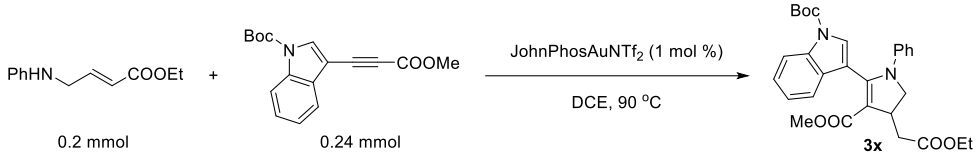
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-(furan-2-yl)propiolate (36.03 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 22 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3w** (53.8 mg, 76%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 1.7 Hz, 1H), 7.15 (dd, J = 8.6, 7.3 Hz, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 3.4 Hz, 1H), 6.67 – 6.57 (m, 2H), 6.44 (dd, J = 3.4, 1.8 Hz, 1H), 4.42 (t, J = 10.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.78 – 3.55 (m, 5H), 2.89 (dd, J = 16.2, 3.2 Hz, 1H), 2.47 (dd, J = 16.2, 10.4 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 165.6, 146.2, 143.6, 143.5, 143.2, 128.7, 123.0, 120.6, 115.7, 111.4, 106.9, 60.5, 59.1, 50.8, 38.8, 37.3, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{20}H_{22}NO_5^+$ 356.14925; found: 356.14912.

Tert-butyl 3-(4-(2-ethoxy-2-oxoethyl)-3-(methoxycarbonyl)-1-phenyl-4,5-dihydro-1*H*-pyrrol-2-yl)-1*H*-indole-1-carboxylate (3x)



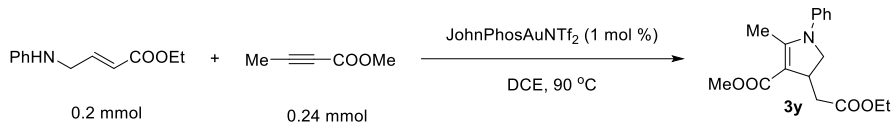
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), *tert*-butyl 3-(3-methoxy-3-oxoprop-1-yn-1-yl)-1*H*-indole-1-carboxylate (71.8 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3x** (56.7 mg, 53%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.3 Hz, 1H), 7.41 – 6.99 (m, 6H), 6.97 – 6.66 (m, 3H), 4.50 (t, J = 10.6 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.86 – 3.62 (m, 2H), 3.51 (s, 3H), 3.00 (dd, J = 16.0, 3.4 Hz, 1H), 2.59 (dd, J = 16.0, 10.3 Hz, 1H), 1.64 (s, 9H), 1.24 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 166.0, 150.2, 149.4, 143.0, 134.8, 128.7, 124.5, 123.4, 123.0, 121.5, 120.6, 115.2, 111.7, 107.3, 84.3, 60.5, 59.3, 50.5, 39.1, 37.4, 28.2, 14.3 ppm.

HRMS: $[M+Na]^+$ *calcd*. For $C_{29}H_{32}N_2NaO_6^+$ 527.21526; found: 527.21583.

Methyl 4-(2-ethoxy-2-oxoethyl)-2-methyl-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3y)



Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl but-2-ynoate (33.6 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 36 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3y** (44.4 mg, 73%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.16 – 7.10 (m, 1H), 7.07 – 6.97 (m, 2H), 4.21 – 4.03 (m, 3H), 3.68 (s, 3H), 3.59 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.54 – 3.42 (m, 1H), 2.84 (dd, *J* = 16.1, 3.3 Hz, 1H), 2.43 – 2.31 (m, 1H), 2.24 (d, *J* = 1.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 167.2, 159.0, 141.5, 129.2, 124.9, 123.6, 103.1, 60.3, 59.2, 50.3, 38.6, 36.1, 14.2, 14.2 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{17}H_{22}NO_4^+$ 304.15433; found: 304.15399.

Methyl 2-butyl-4-(2-ethoxy-2-oxoethyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3z)

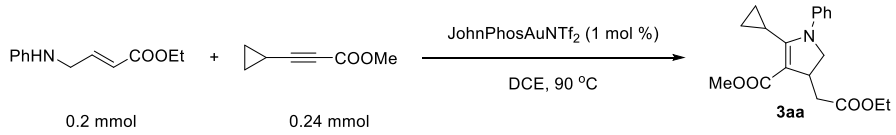
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl hept-2-ynoate (33.6 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 12/1) to give the product **3z** (60.2 mg, 87%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.22 – 7.15 (m, 1H), 7.10 – 7.05 (m, 2H), 4.14 – 4.06 (m, 3H), 3.69 (s, 3H), 3.61 – 3.53 (m, 1H), 3.46 (tt, *J* = 10.4, 3.4 Hz, 1H), 2.83 (dd, *J* = 16.0, 3.3 Hz, 1H), 2.65 (qdd, *J* = 12.9, 9.1, 6.5 Hz, 2H), 2.37 (dd, *J* = 16.0, 10.4 Hz, 1H), 1.45 – 1.31 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 5H), 0.76 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 166.9, 164.3, 142.0, 129.4, 125.7, 124.8, 102.1, 60.3, 59.9, 50.3, 38.7, 36.2, 30.3, 25.8, 22.6, 14.3, 13.7 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{20}H_{28}NO_4^+$ 346.20128; found: 346.20135.

Methyl 2-cyclopropyl-4-(2-ethoxy-2-oxoethyl)-1-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3aa)



Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), methyl 3-cyclopropylpropiolate (29.8 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to give the product **3aa** (46.1 mg, 70%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.14 – 7.03 (m, 3H), 4.21 – 4.01 (m, 3H), 3.71 (s, 3H), 3.57 (dd, *J* = 10.7, 4.1 Hz, 1H), 3.50 – 3.38 (m, 1H), 2.83 (dd, *J* = 16.1, 3.3 Hz, 1H), 2.33 (dd, *J* = 16.1, 10.4 Hz, 1H), 1.92 – 1.75 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.93 (tdd, *J* = 8.8, 6.4, 4.7 Hz, 1H), 0.73 (tdd, *J* = 8.8, 6.3, 4.8 Hz, 1H), 0.45 (dtd, *J* = 9.5, 6.0, 4.7 Hz, 1H), 0.34 (dtd, *J* = 9.3, 6.2, 4.9 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 166.4, 162.3, 143.3, 128.8, 124.0, 123.0, 106.6, 60.4, 59.7, 50.4, 38.9, 36.5, 14.3, 10.4, 10.3, 9.4 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{19}H_{24}NO_4^+$ 330.16998; found: 330.16965.

Ethyl 2-(4-benzoyl-1,5-diphenyl-2,3-dihydro-1*H*-pyrrol-3-yl)acetate (3ab)

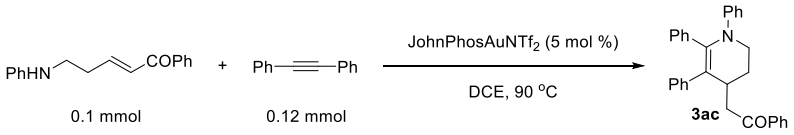
Ethyl (*E*)-4-(phenylamino)but-2-enoate (41.05 mg, 0.2 mmol), 1,3-diphenylprop-2-yn-1-one (49.5 mg, 0.24 mmol) and JohnPhosAuNTf$_2$ (1.6 mg, 0.002 mmol) was dissolved in DCE (0.4 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product **3aa** (62.7 mg, 76%) as red oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 7.06 (t, J = 7.8 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.94 – 6.82 (m, 7H), 6.68 – 6.60 (m, 2H), 4.47 (t, J = 9.5 Hz, 1H), 4.22 – 4.05 (m, 2H), 4.04 – 3.88 (m, 2H), 3.28 (dd, J = 16.4, 3.1 Hz, 1H), 2.64 (dd, J = 16.2, 9.7 Hz, 1H), 1.22 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 172.8, 158.9, 141.9, 140.6, 130.6, 130.3, 129.5, 129.1, 128.6, 128.5, 127.7, 127.1, 123.8, 122.6, 117.4, 60.4, 59.6, 39.5, 37.8, 14.3 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{27}H_{26}NO_3^+$ 412.19072; found: 412.19116.

1-phenyl-2-(1,5,6-triphenyl-1,2,3,4-tetrahydropyridin-4-yl)ethan-1-one (3ac)



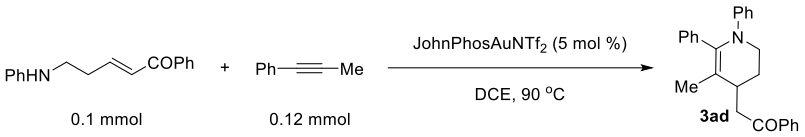
(*E*)-1-phenyl-5-(phenylamino)pent-2-en-1-one (25.1 mg, 0.1 mmol), 1,2-diphenylethyne (21.4 mg, 0.12 mmol) and JohnPhosAuNTf$_2$ (3.9 mg, 0.005 mmol) was dissolved in DCE (0.2 mL), and the mixture was stirred at 90 °C for 12 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 40/1) to give the product **3ac** (39 mg, 90%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.59 – 7.47 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.19 – 7.02 (m, 9H), 6.97 – 6.86 (m, 5H), 6.85 – 6.76 (m, 1H), 3.83 (dt, J = 12.6, 3.4 Hz, 1H), 3.76 – 3.60 (m, 2H), 3.02 – 2.84 (m, 2H), 2.04 (ddq, J = 12.7, 9.3, 3.4 Hz, 1H), 1.75 (ddt, J = 13.6, 3.2, 1.7 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 148.7, 141.9, 141.3, 138.1, 137.1, 133.1, 131.4, 130.7, 128.6, 128.4, 128.3, 127.9, 127.3, 126.6, 125.6, 124.9, 123.3, 122.1, 49.3, 43.0, 33.7, 25.9 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{31}H_{28}NO^+$ 430.21654; found: 430.21695.

2-(5-methyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-4-yl)-1-phenylethan-1-one (3ad)



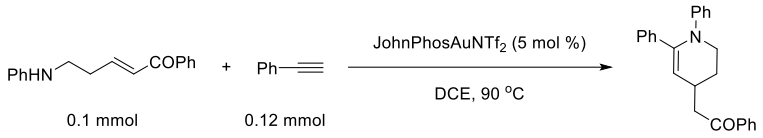
(*E*)-1-phenyl-5-(phenylamino)pent-2-en-1-one (25.1 mg, 0.1 mmol), prop-1-yn-1-ylbenzene (13.9 mg, 0.12 mmol) and JohnPhosAuNTf$_2$ (3.9 mg, 0.005 mmol) was dissolved in DCE (0.2 mL), and the mixture was stirred at 90 °C for 22 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 30/1) to give the product **3ad** (19.1 mg, 52%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.56 – 7.46 (m, 1H), 7.42 – 7.26 (m, 8H), 7.25 – 7.19 (m, 1H), 7.08 – 7.00 (m, 3H), 3.55 (dd, *J* = 7.1, 3.6 Hz, 2H), 3.26 (dddd, *J* = 10.3, 5.9, 4.0, 2.1 Hz, 1H), 2.95 (dd, *J* = 16.2, 2.7 Hz, 1H), 2.78 (dd, *J* = 16.1, 10.9 Hz, 1H), 2.05 – 1.92 (m, 1H), 1.67 – 1.60 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 148.7, 142.3, 137.1, 136.2, 133.0, 130.2, 128.9, 128.6, 128.3, 128.2, 126.2, 125.0, 123.1, 121.1, 50.0, 43.5, 34.6, 26.3, 18.8 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{26}H_{26}NO^+$ 368.20089; found: 368.20097.

2-(1,6-diphenyl-1,2,3,4-tetrahydropyridin-4-yl)-1-phenylethan-1-one (3ae)



(*E*)-1-phenyl-5-(phenylamino)pent-2-en-1-one (25.1 mg, 0.1 mmol), ethynylbenzene (12.2 mg, 0.12 mmol) and JohnPhosAuNTf$_2$ (3.9 mg, 0.005 mmol) was dissolved in DCE (0.2 mL), and the mixture was stirred at 90 °C for 22 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 30/1) to give the product **3ae** (11 mg, 31%) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.62 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 7.40 – 7.31 (m, 2H), 7.21 – 7.05 (m, 5H), 6.90 – 6.76 (m, 3H), 5.42 (d, *J* = 3.2 Hz, 1H), 3.75 (dd, *J* = 6.2, 4.3 Hz, 2H), 3.21 – 3.12 (m, 2H), 3.06 (dd, *J* = 17.6, 9.5 Hz, 1H), 2.02 – 1.90 (m, 1H), 1.55 – 1.48 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 148.7, 143.6, 139.0, 137.3, 133.3, 128.8, 128.6, 128.3, 128.2, 127.4, 127.0, 123.5, 121.5, 115.0, 51.5, 45.2, 30.7, 27.5 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{25}H_{24}NO^+$ 354.18524; found: 354.18535.

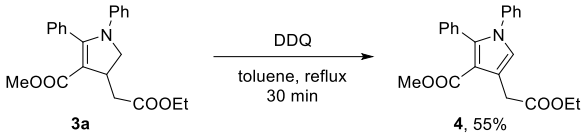
1 mmol Scale

Methyl 4-(2-ethoxy-2-oxoethyl)-1,2-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (3a)

Ethyl (*E*)-4-(phenylamino)but-2-enoate (205.26 mg, 1 mmol), methyl 3-phenylpropiolate (192.2 mg, 1.2 mmol) and JohnPhosAuNTf$_2$ (7.8 mg, 0.01 mmol) was dissolved in DCE (2 mL), and the mixture was stirred at 90 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **3a** (338 mg, 92%) as yellow oil.

Synthetic Transformations

Methyl 4-(2-ethoxy-2-oxoethyl)-1,2-diphenyl-1*H*-pyrrole-3-carboxylate (4)



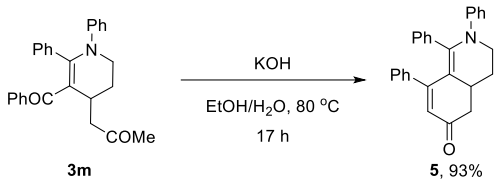
Methyl 4-(2-ethoxy-2-oxoethyl)-1,2-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate **3a** (36.5 mg, 0.1 mmol) and DDQ (45.4 mg, 0.2 mmol) was dissolved in toluene (1 mL)，and the mixture was allowed to reflux for 30 min. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the product **4** (20 mg, 55%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (ttd, J = 8.2, 4.0, 3.5, 1.7 Hz, 8H), 7.07 – 7.00 (m, 2H), 6.87 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.82 (s, 2H), 3.62 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 165.5, 139.3, 138.8, 131.7, 131.3, 128.9, 128.0, 127.6, 127.3, 126.2, 123.1, 118.4, 113.3, 60.7, 50.7, 32.9, 14.4 ppm.

HRMS: $[M+Na]^+$ *calcd*. For $C_{22}H_{21}NNaO_4^+$ 386.13628; found: 386.13648.

1,2,8-triphenyl-3,4,4a,5-tetrahydroisoquinolin-6(2*H*)-one (5)



3m **5**, 93%

To a solution of 1-(5-benzoyl-1,6-diphenyl-1,2,3,4-tetrahydropyridin-4-yl)propan-2-one **3m** (19.8 mg, 0.05 mmol) in 0.5 mL ethanol and 0.5 mL water was added KOH (16.8 mg, 0.3 mmol). The reaction contents were refluxed at 80 °C for 17 h. Upon completion, the solution was then cooled to room temperature, diluted with water, and extracted with EtOAc. The crude product was purified with silica-gel flash chromatography (petroleum ether/ethyl acetate = 5/1) to obtain the pure product **5** (17.5 mg, 93%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.01 (m, 5H), 6.97 – 6.80 (m, 7H), 6.73 (q, *J* = 4.8 Hz, 3H), 6.03 (s, 1H), 3.95 (dt, *J* = 12.3, 3.1 Hz, 1H), 3.73 (td, *J* = 12.4, 1.7 Hz, 1H), 3.12 (dddd, *J* = 15.1, 11.3, 7.2, 4.1 Hz, 1H), 2.94 (dd, *J* = 16.2, 4.1 Hz, 1H), 2.33 (dd, *J* = 16.3, 14.4 Hz, 1H), 2.19 (dddd, *J* = 12.5, 7.3, 3.2, 1.7 Hz, 1H), 1.71 (qd, *J* = 12.6, 3.1 Hz, 1H) ppm.

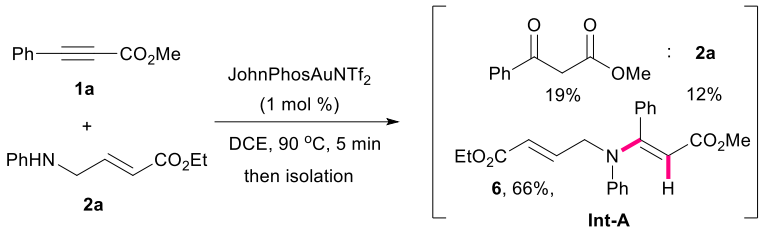
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 162.6, 150.0, 147.8, 140.8, 137.0, 128.7, 128.5, 128.1, 128.1, 127.5, 127.3, 126.2, 124.9, 123.7, 117.1, 53.4, 45.9, 39.2, 31.1 ppm.

HRMS: $[M+H]^+$ *calcd*. For $C_{27}H_{24}NO^+$ 378.18524; found: 378.18561.

Mechanism Explorations

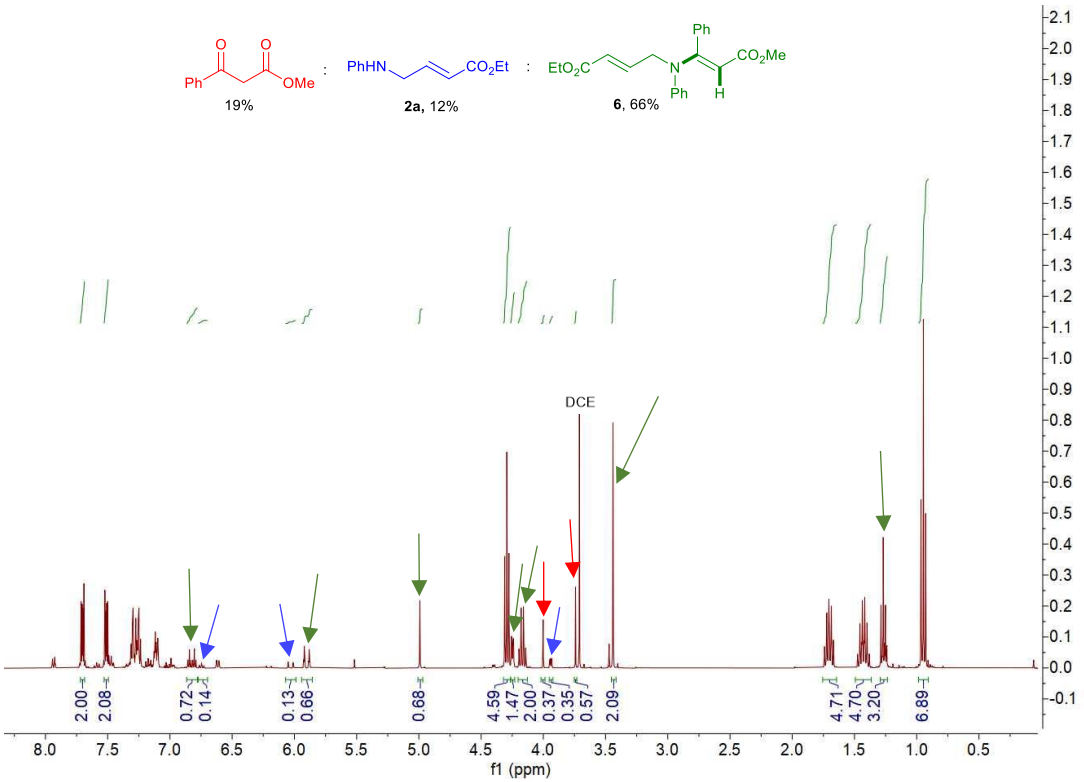
1) Capture of the reaction intermediate

Ethyl (E)-4-(((E)-3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)(phenyl)amino)but-2-enoate (6)

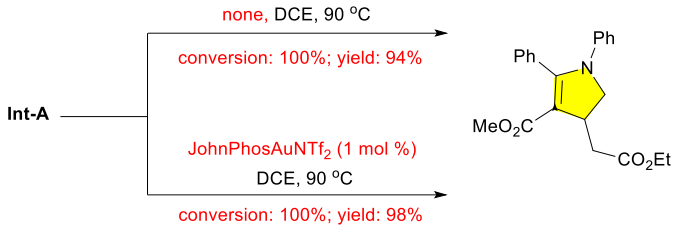


Ethyl (*E*)-4-(phenylamino)but-2-enoate (82.12 mg, 0.4 mmol), methyl 3-phenylpropiolate (76.88 mg, 0.48 mmol) and JohnPhosAuNTf$_2$ (3.2 mg, 0.004 mmol) was dissolved in DCE (0.8 mL), and the mixture was stirred at 90 ^{o}C for 5 min. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 7/1) to give the intermediate product **Int-A** (86 mg) as yellow oil. The enamine **6** was partially hydrolysed into **2a** and methyl 3-oxo-3-phenylpropanoate during purification. The H^{1}-NMR of **Int-A** showed that it contained 66 % product **6**, 19% methyl 3-oxo-3-phenylpropanoate and 12% starting material **2a** (dibutyl phthalate used as internal standard).

HRMS for 6: $[M+H]^+$ *calcd*. For $C_{22}H_{24}NO_4^+$ 366.16998; found: 366.16979.

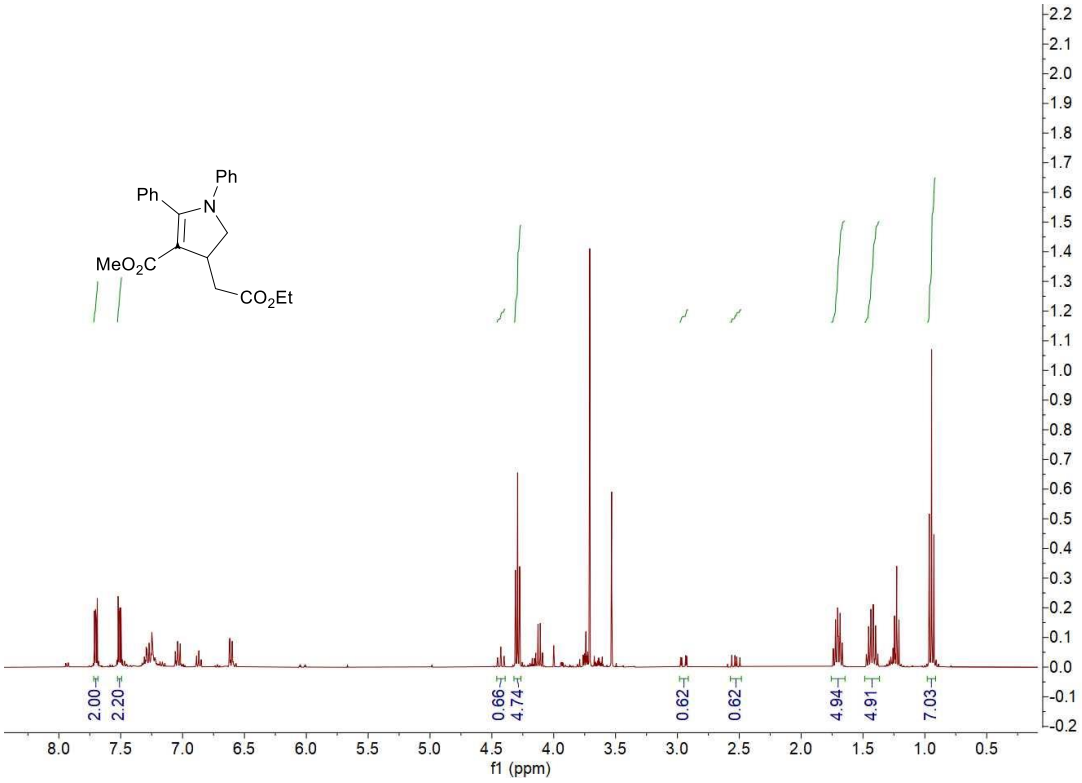

Ph
O
O
OMe
19%
:
PhHN
CO2Et
2a, 12%
:
EtO2C
N
Ph
Ph
CO2Me
H
6, 66%
DCE
2.00
2.08
0.72
0.14
0.13
0.66
0.68
4.59
1.47
2.00
0.37
0.35
0.57
2.09
4.71
4.70
3.20
6.89
f1 (ppm)

2) The role of Au (I) catalyst in the second step

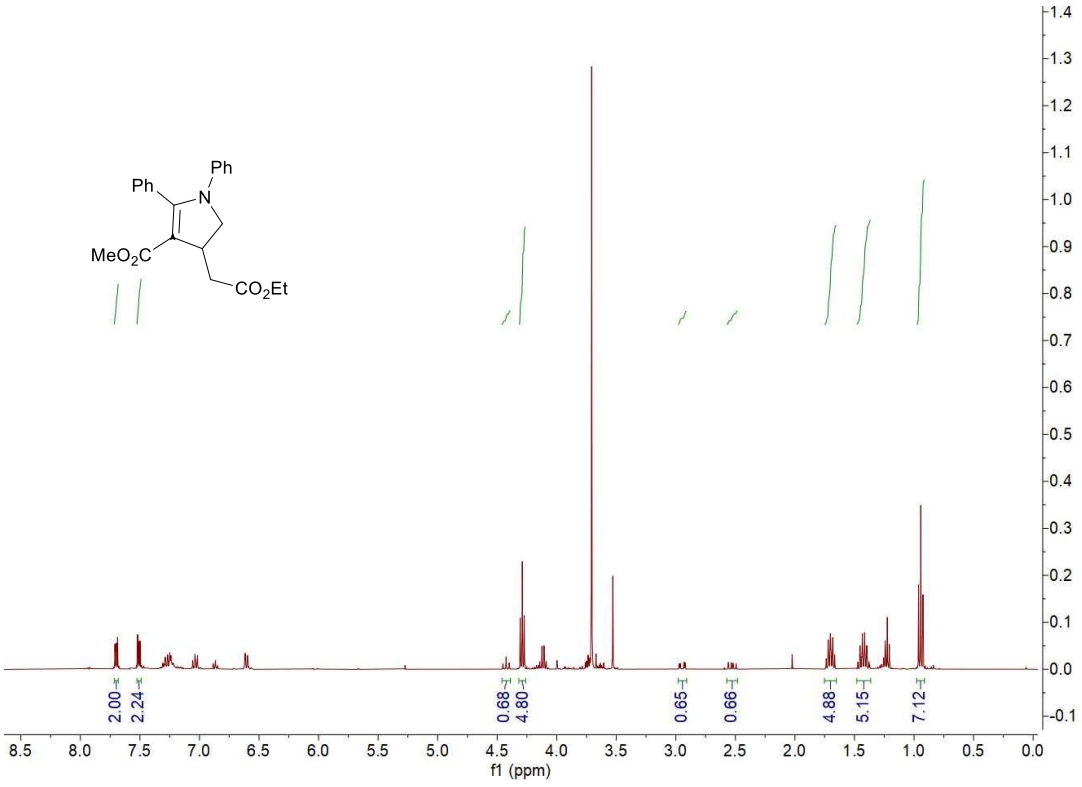


Then the **Int-A** (0.05 mmol，66% **6**) was dissolved in DCE (0.1 mL). One was directly allowed to stir at 90 °C , another was allowed to stir at 90 °C after adding JohnPhosAuNTf$_2$ (1 mol %). After 24 h, 1 mL dibutyl phthalate (0.05 M in DCE) was added as internal standard for NMR yield. The crude H^1-NMR showed that the cyclization of the **InA** with or without the gold catalyst afforded full conversion and similar yield, indicating the gold catalyst was not critical to the cyclization step.

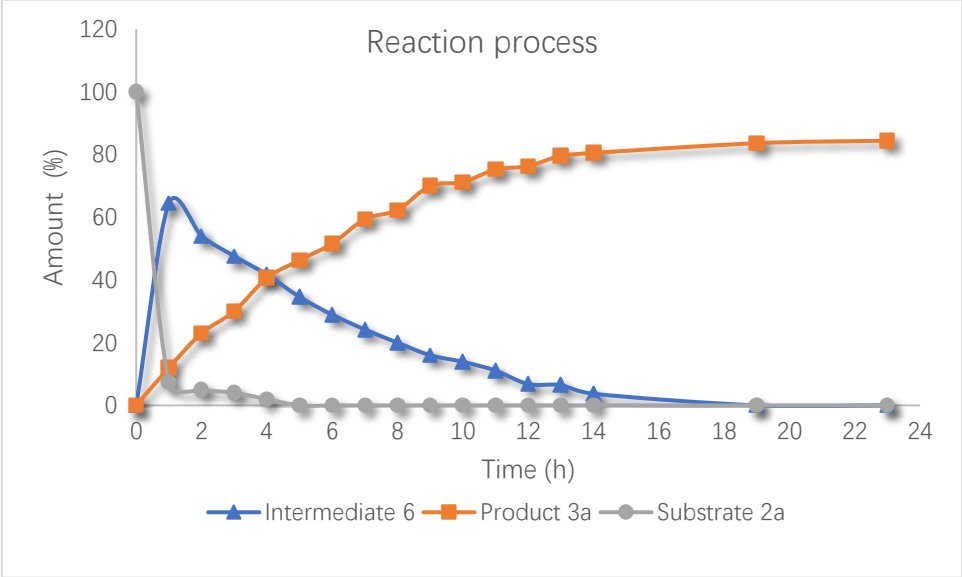
a) Without the gold catalyst



b) With the gold catalyst



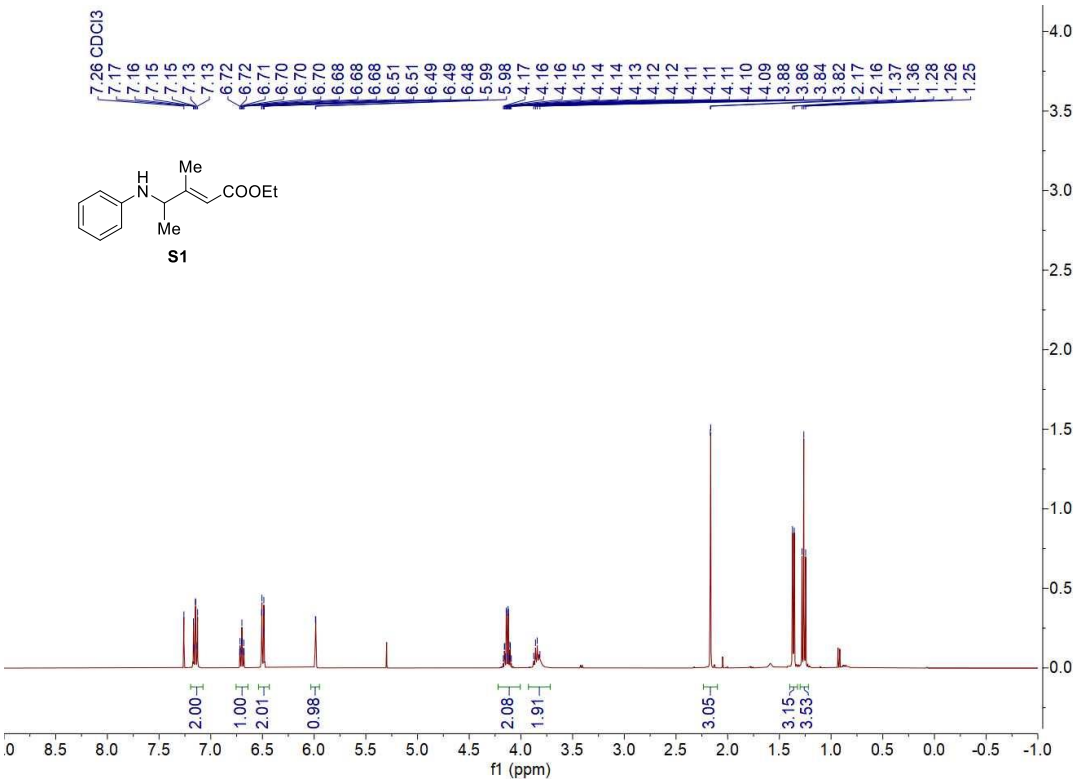
3) Reaction process monitoring using NMR



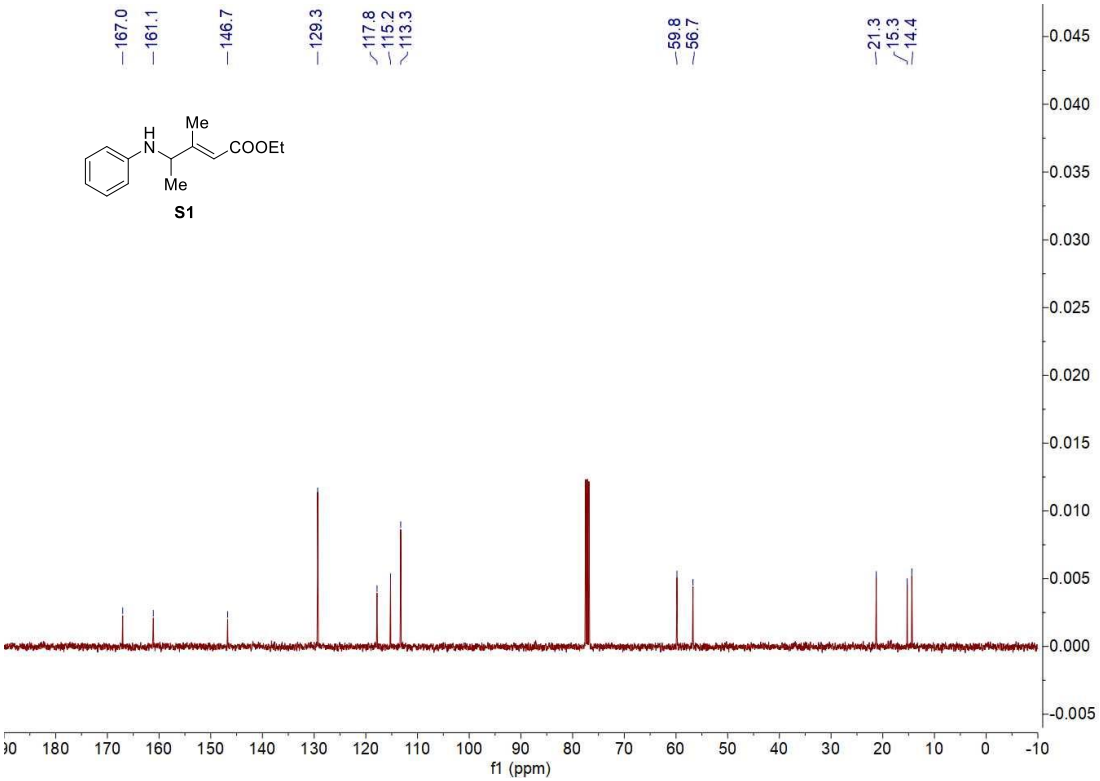
As the reaction progressed, the intermediate first increased then decreased and the product **3a** gradually accumulated. After 5 hours, **2a** was fully consumed and the intermediate **6** was gradually converted into **3a**, clearly indicating the reaction was stepwise not synergistic.

NMR Spectra

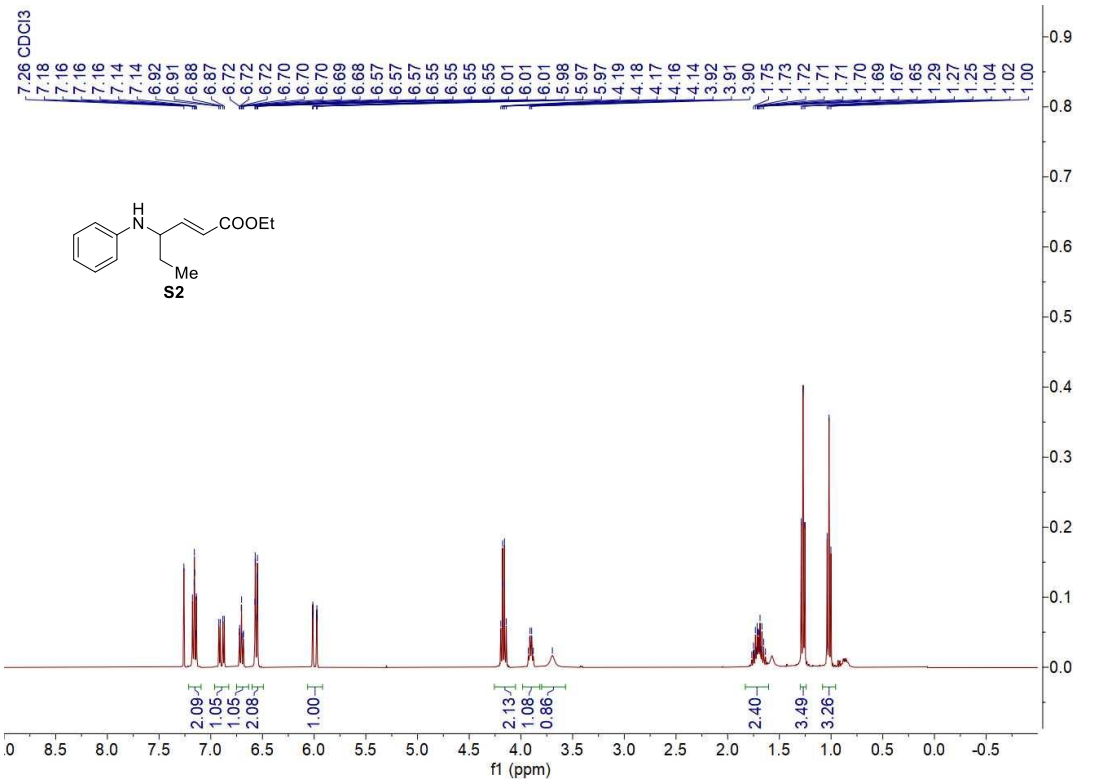
The ^{1}H NMR spectrum of S1 (400 MHz, $CDCl_3$)



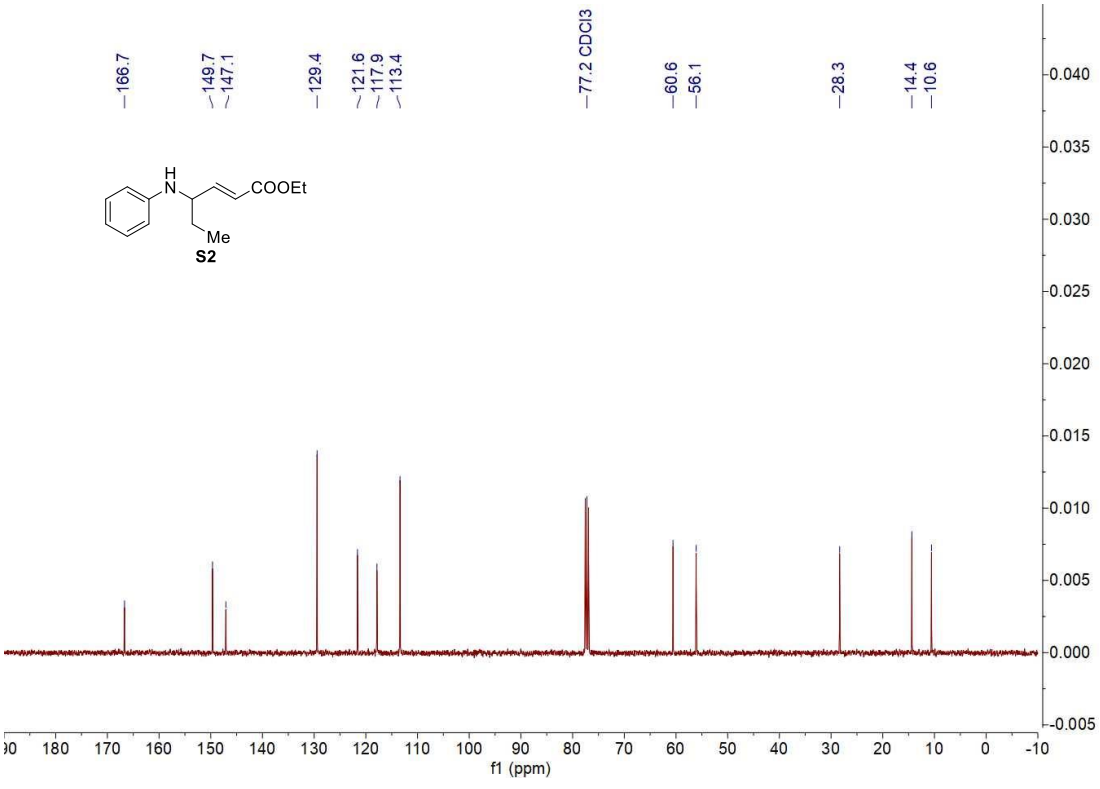
The ^{13}C NMR spectrum of S1 (101 MHz, $CDCl_3$)



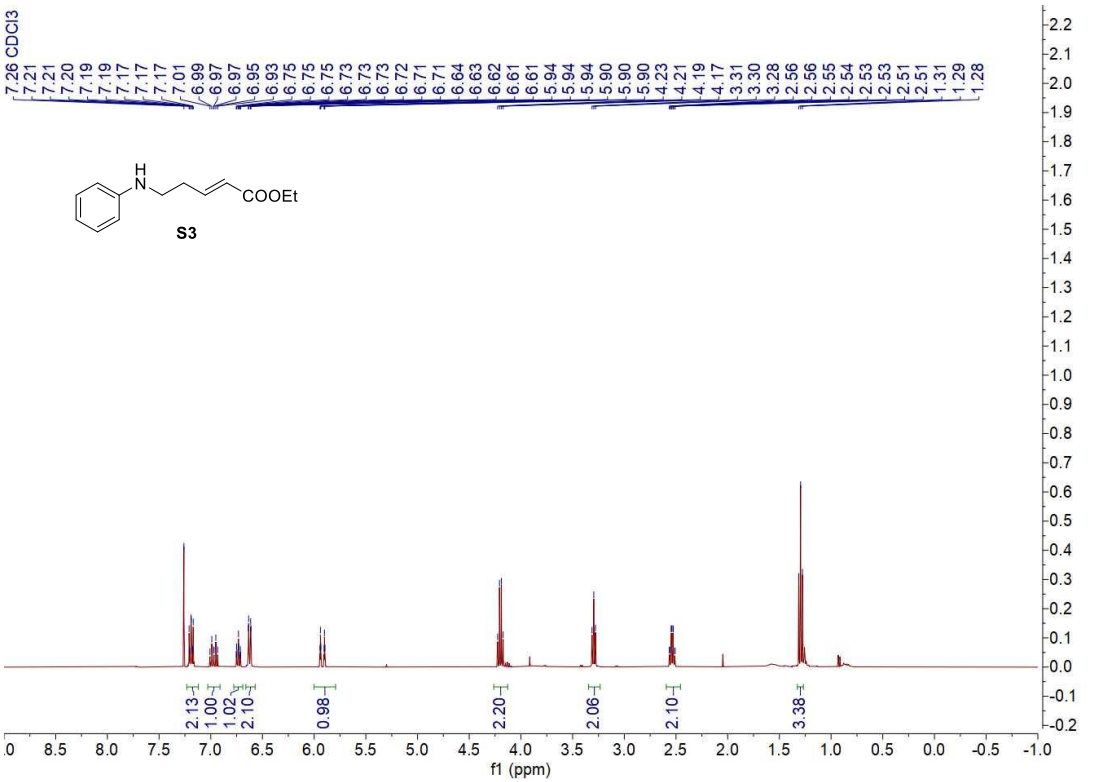
The ^{1}H NMR spectrum of S2 (400 MHz, $CDCl_3$)



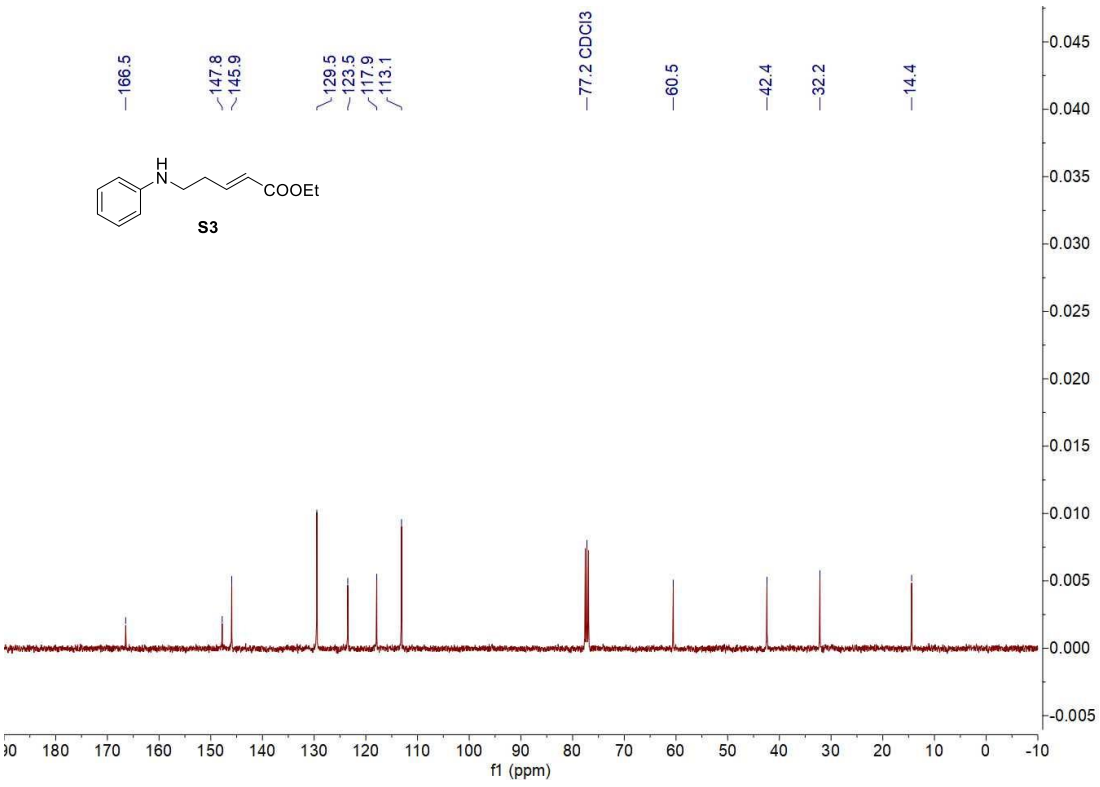
The ^{13}C NMR spectrum of S2 (101 MHz, $CDCl_3$)



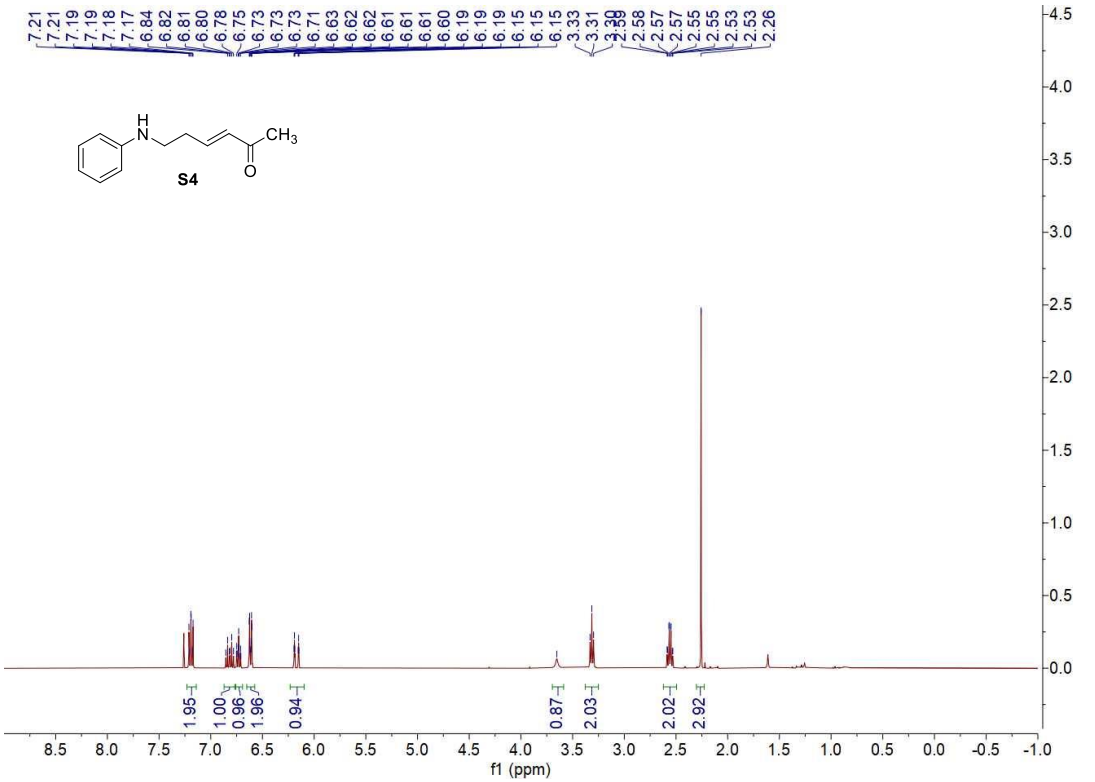
The ^{1}H NMR spectrum of S3 (400 MHz, $CDCl_3$)



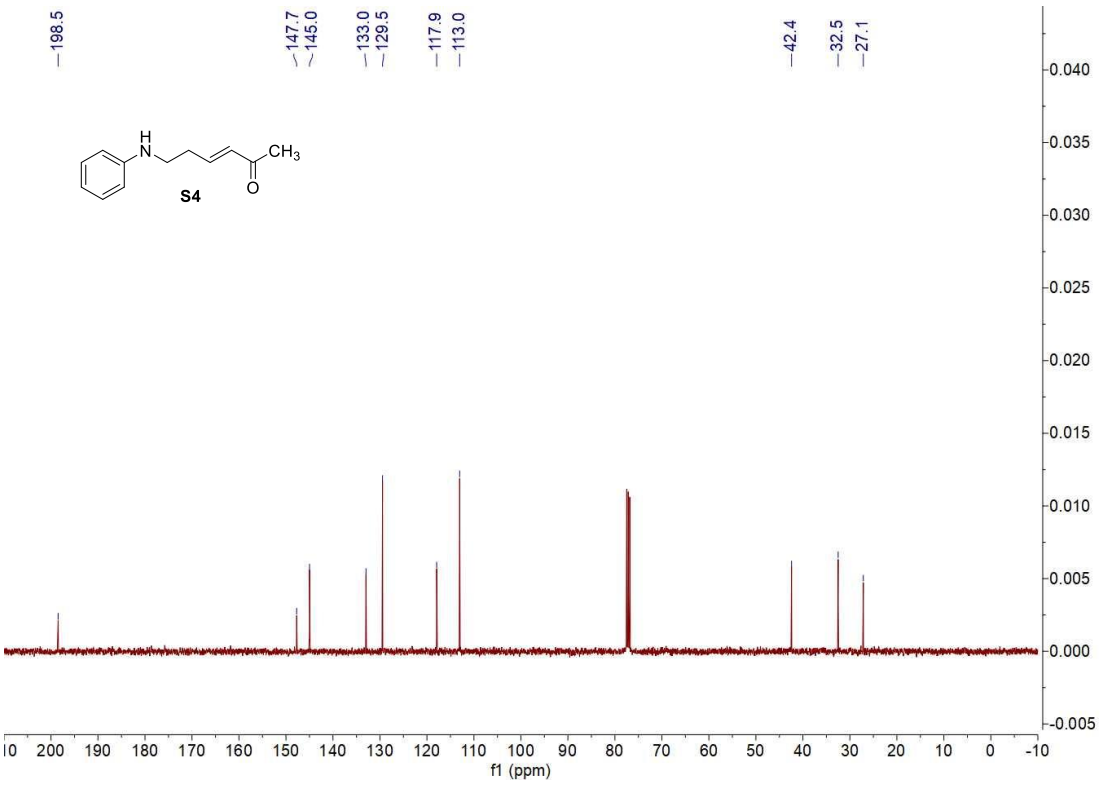
The ^{13}C NMR spectrum of S3 (101 MHz, $CDCl_3$)



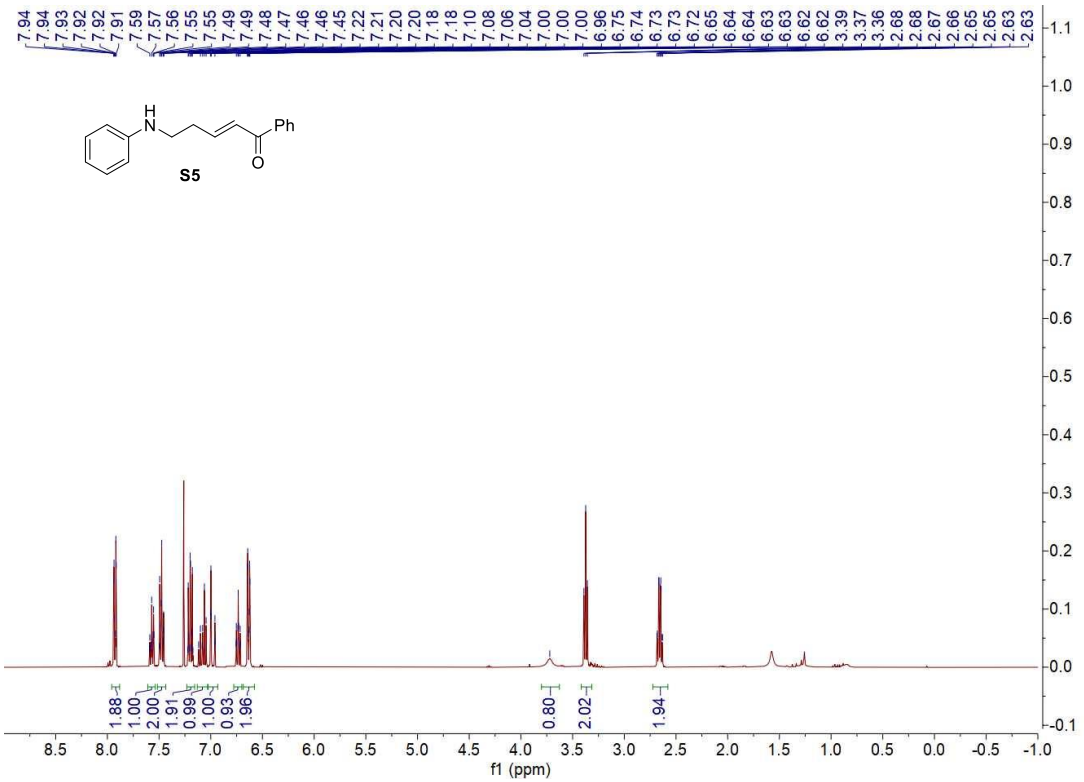
The ^{1}H NMR spectrum of S4 (400 MHz, $CDCl_3$)



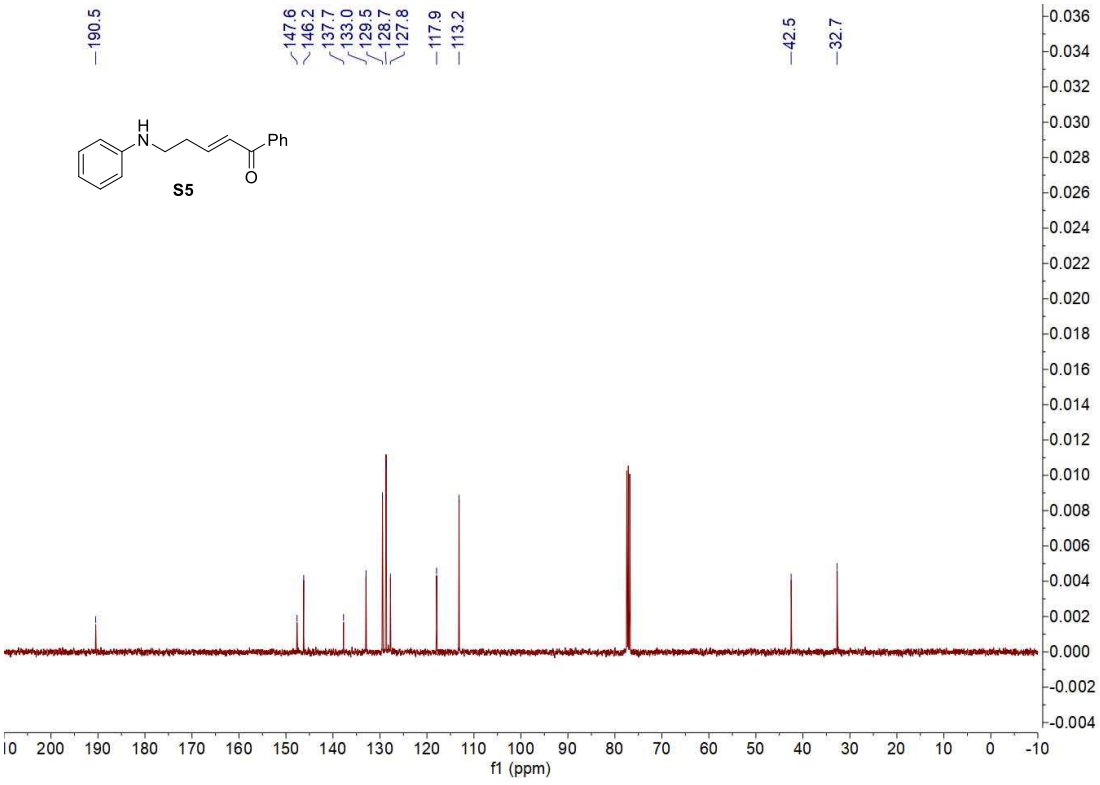
The ^{13}C NMR spectrum of S4 (101 MHz, $CDCl_3$)



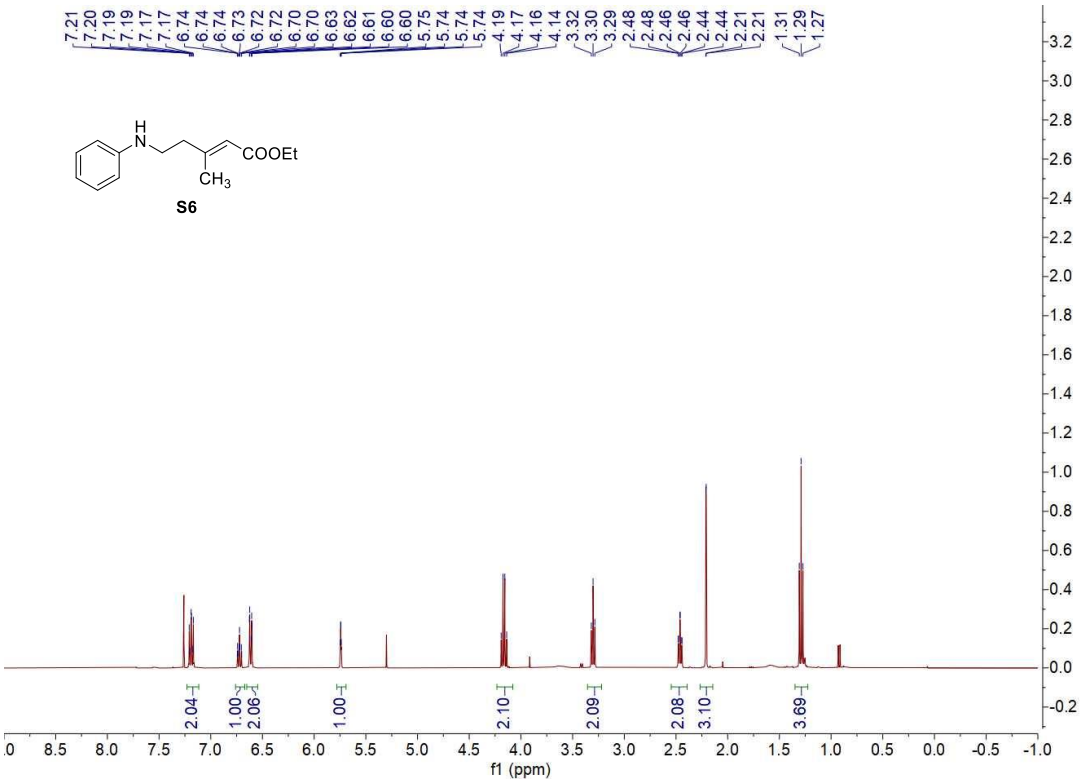
The ^{1}H NMR spectrum of S5 (400 MHz, $CDCl_3$)



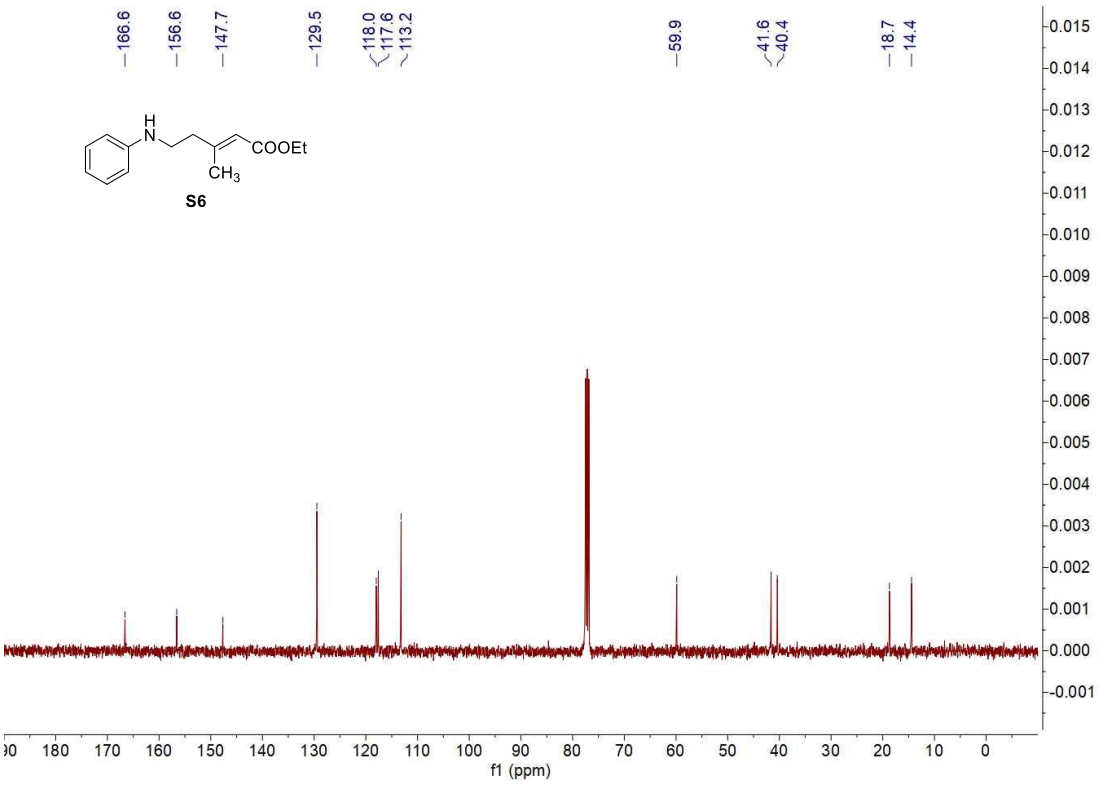
The ^{13}C NMR spectrum of S5 (101 MHz, $CDCl_3$)



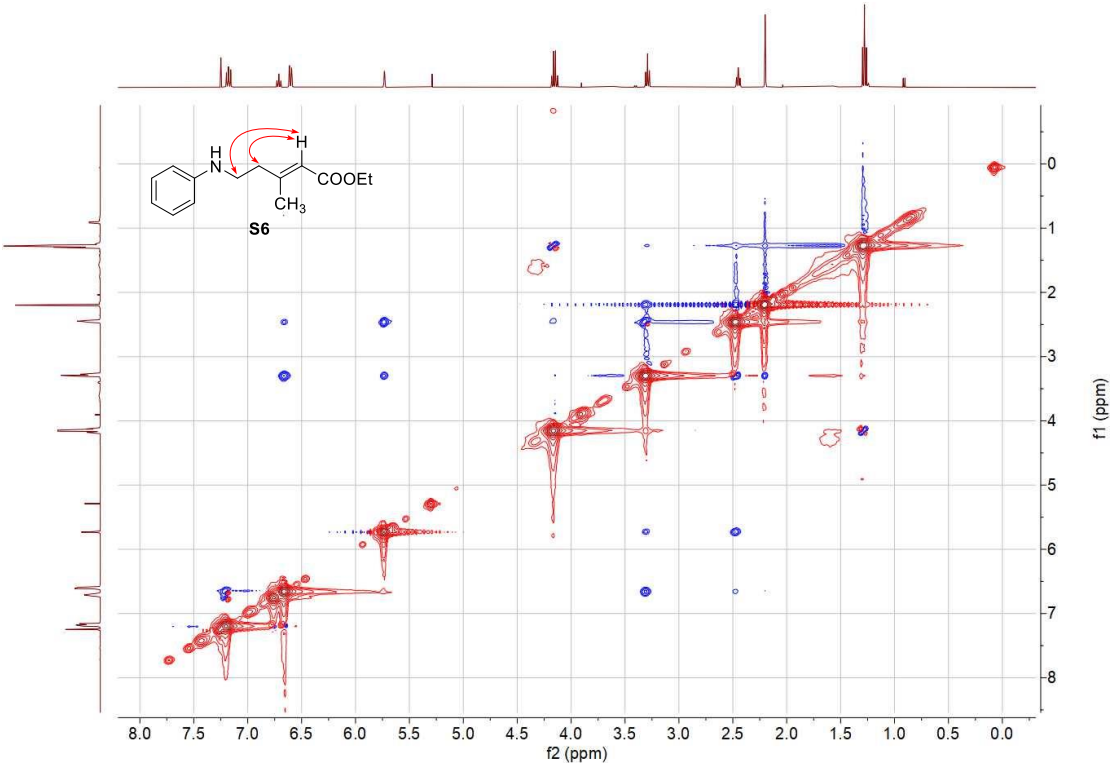
The ^{1}H NMR spectrum of S6 (400 MHz, $CDCl_3$)



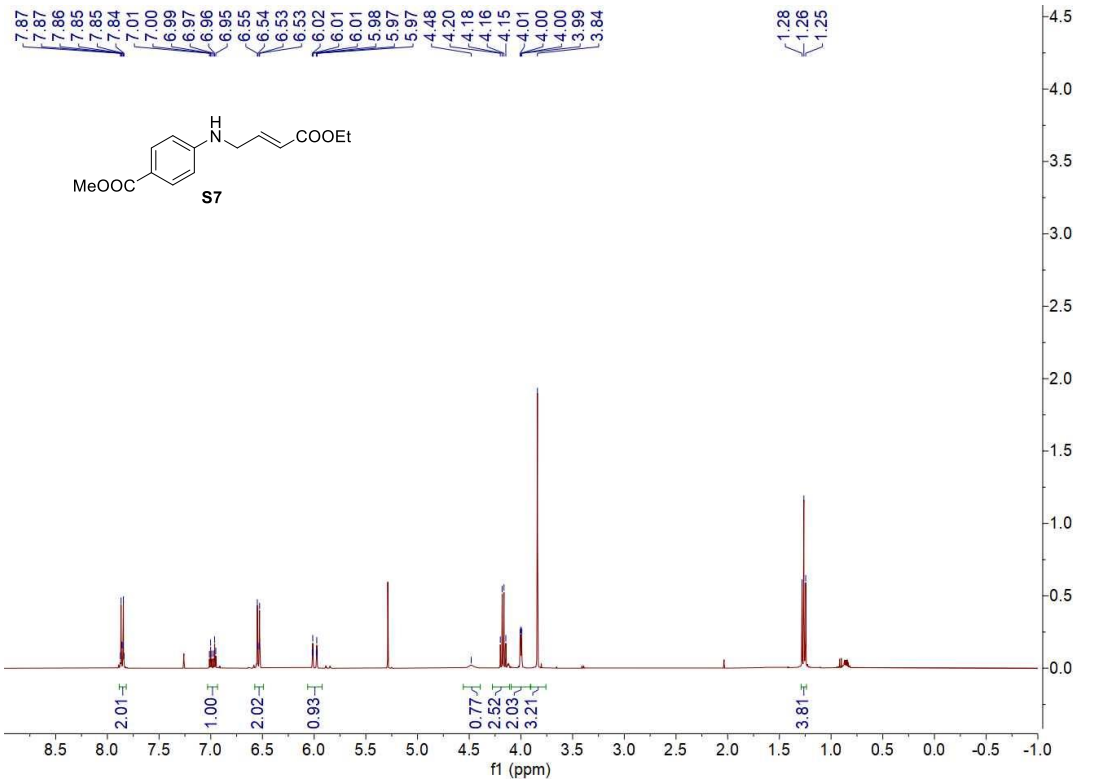
The ^{13}C NMR spectrum of S6 (101 MHz, $CDCl_3$)



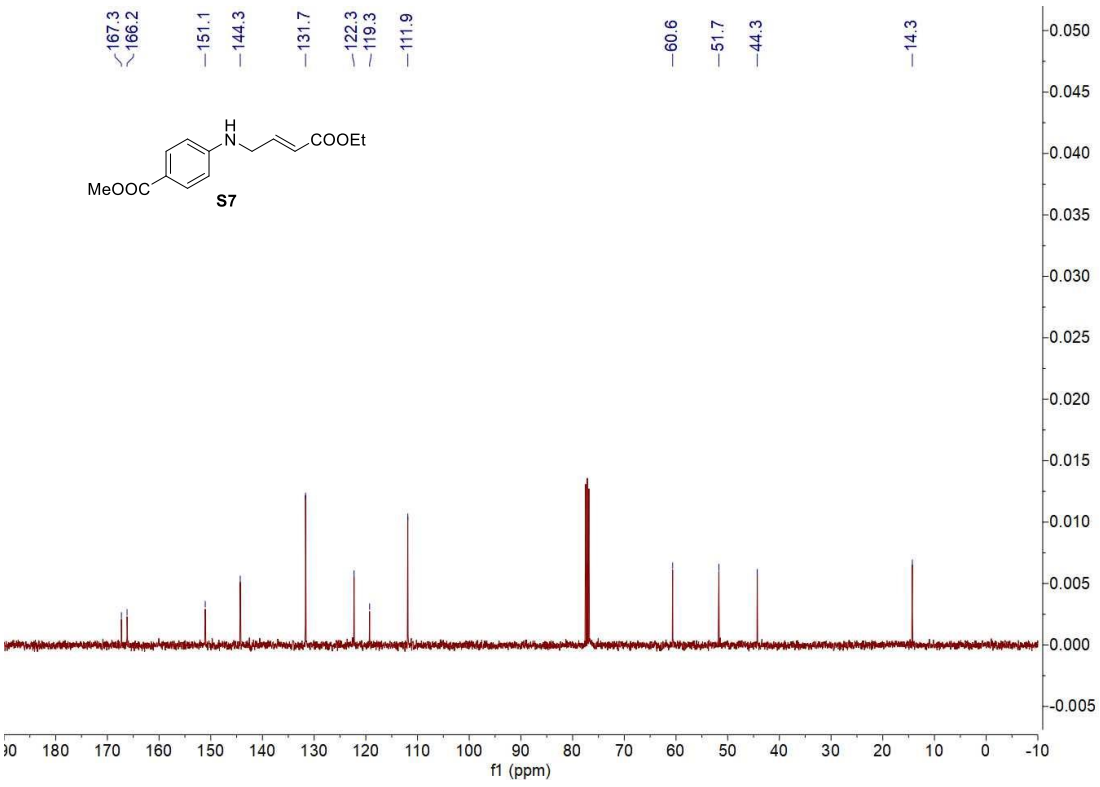
The NOESY spectrum of S6 (400 MHz, $CDCl_3$)



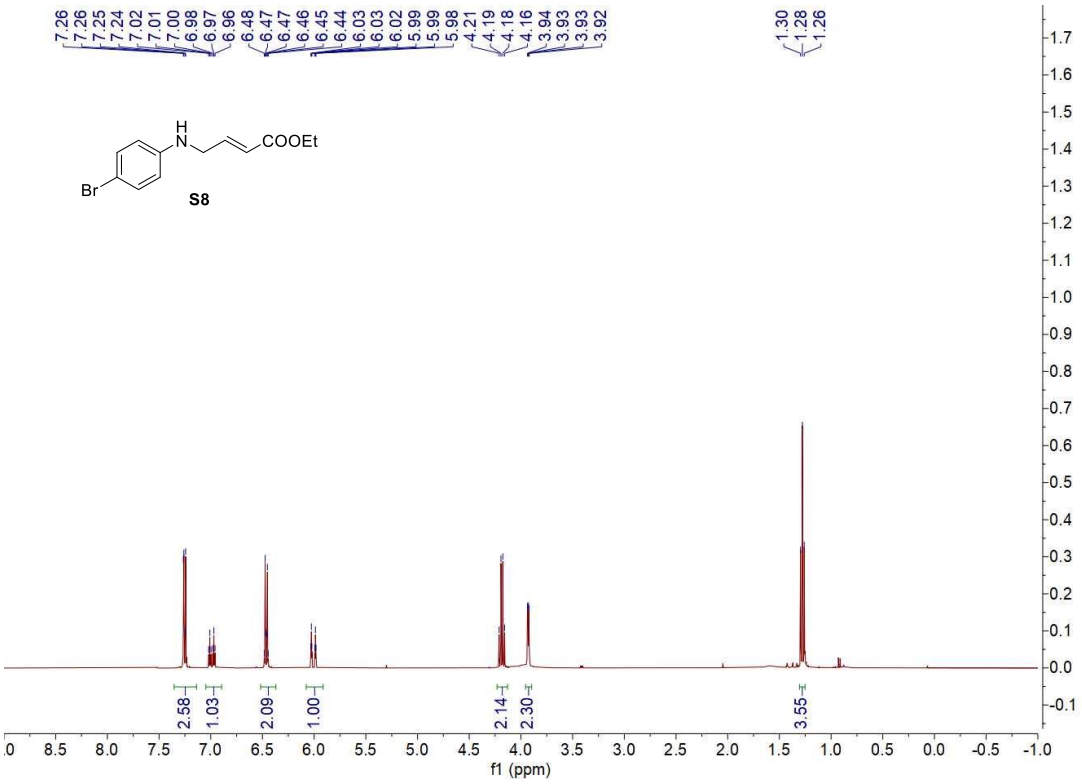
The ^{1}H NMR spectrum of S7 (400 MHz, $CDCl_3$)



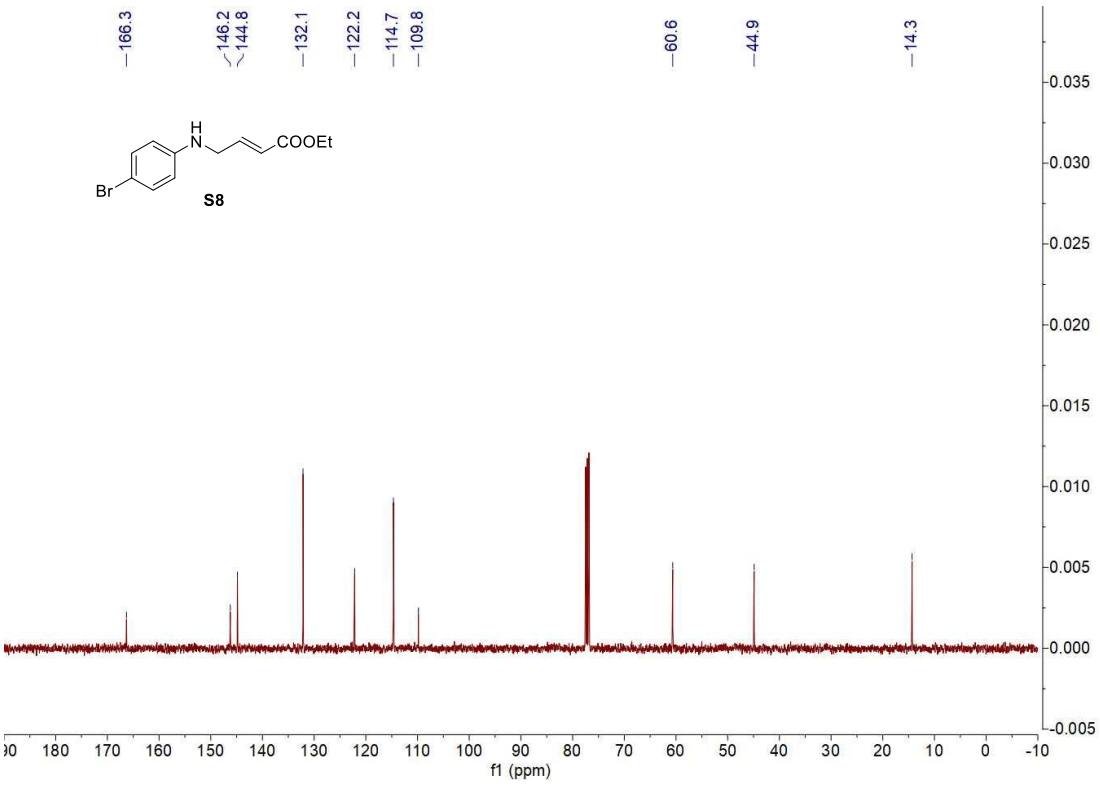
The ^{13}C NMR spectrum of S7 (101 MHz, $CDCl_3$)



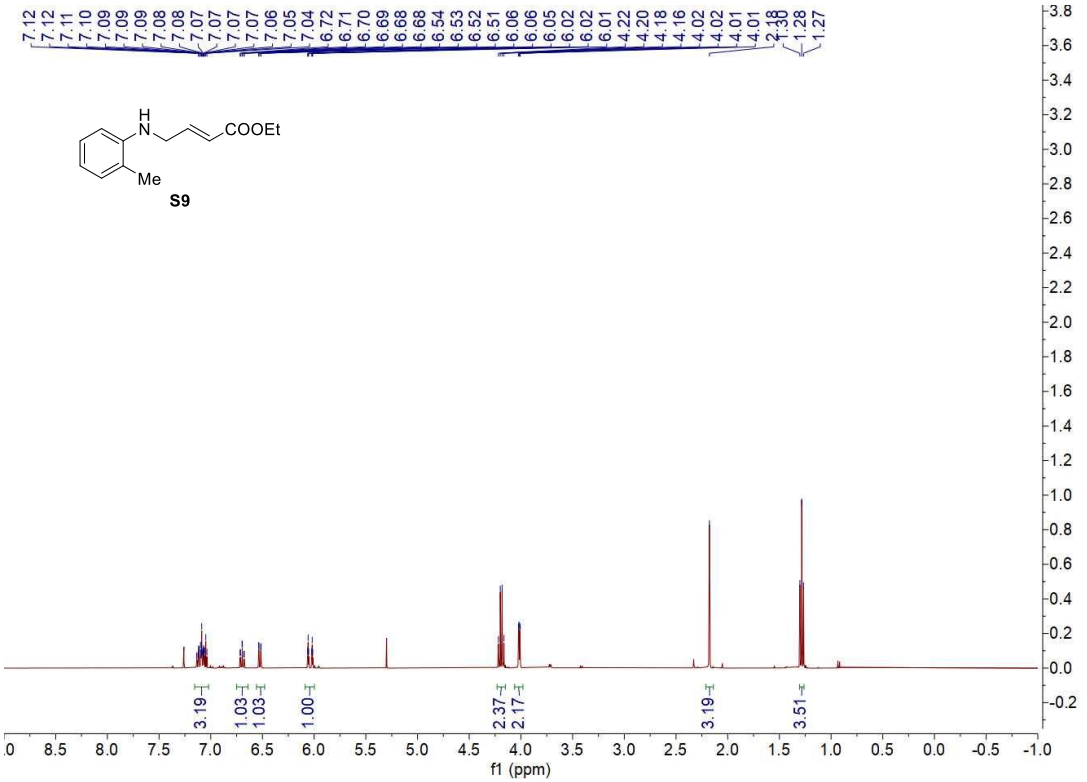
The ^{1}H NMR spectrum of S8 (400 MHz, $CDCl_3$)



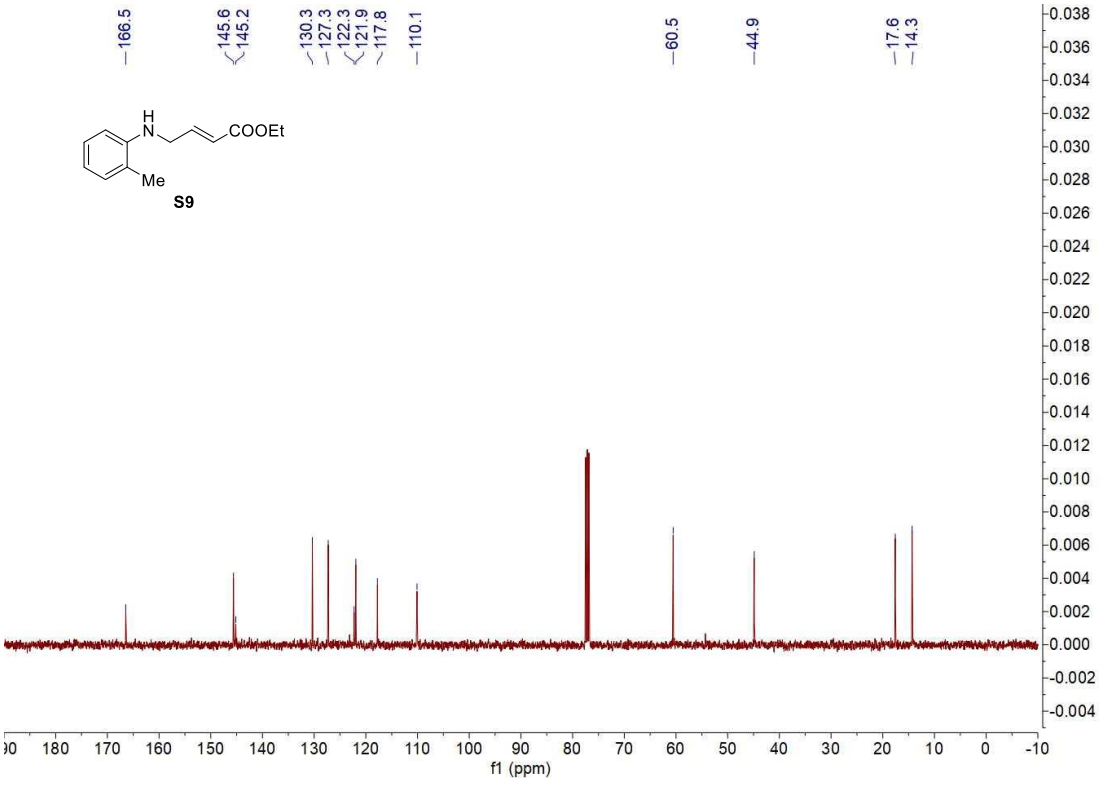
The ^{13}C NMR spectrum of S8 (101 MHz, $CDCl_3$)



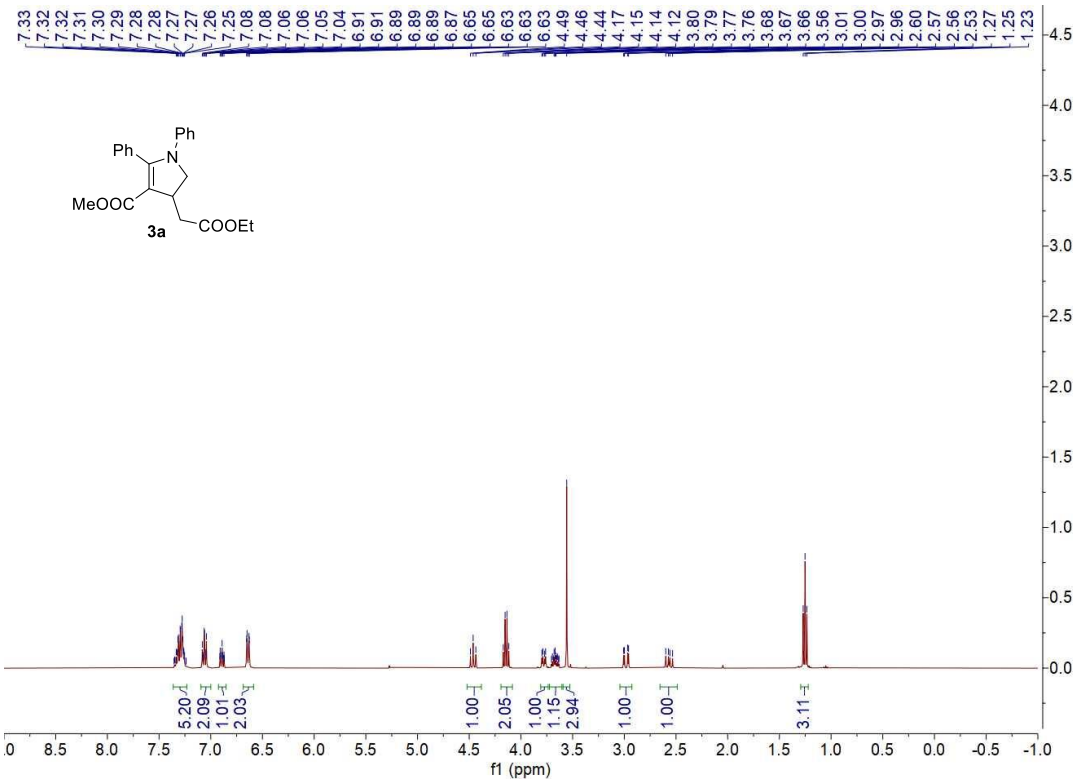
The ^{1}H NMR spectrum of S9 (400 MHz, $CDCl_3$)



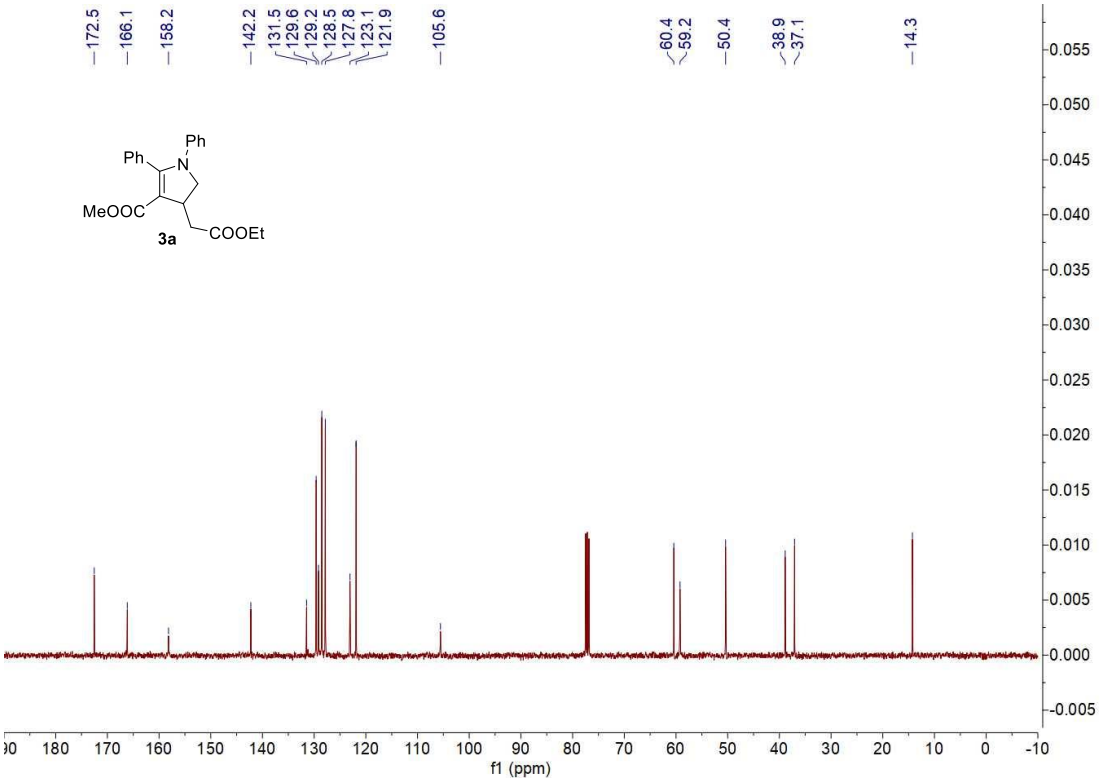
The ^{13}C NMR spectrum of S9 (101 MHz, $CDCl_3$)



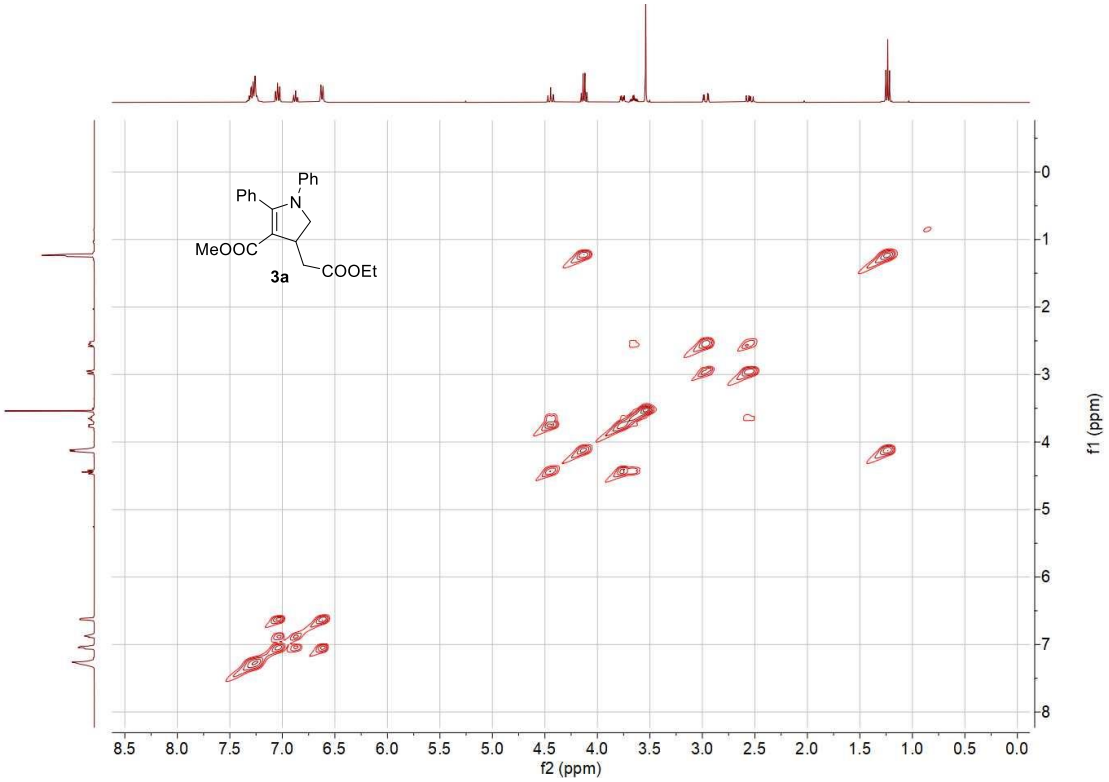
The ^{1}H NMR spectrum of 3a (400 MHz, $CDCl_3$)



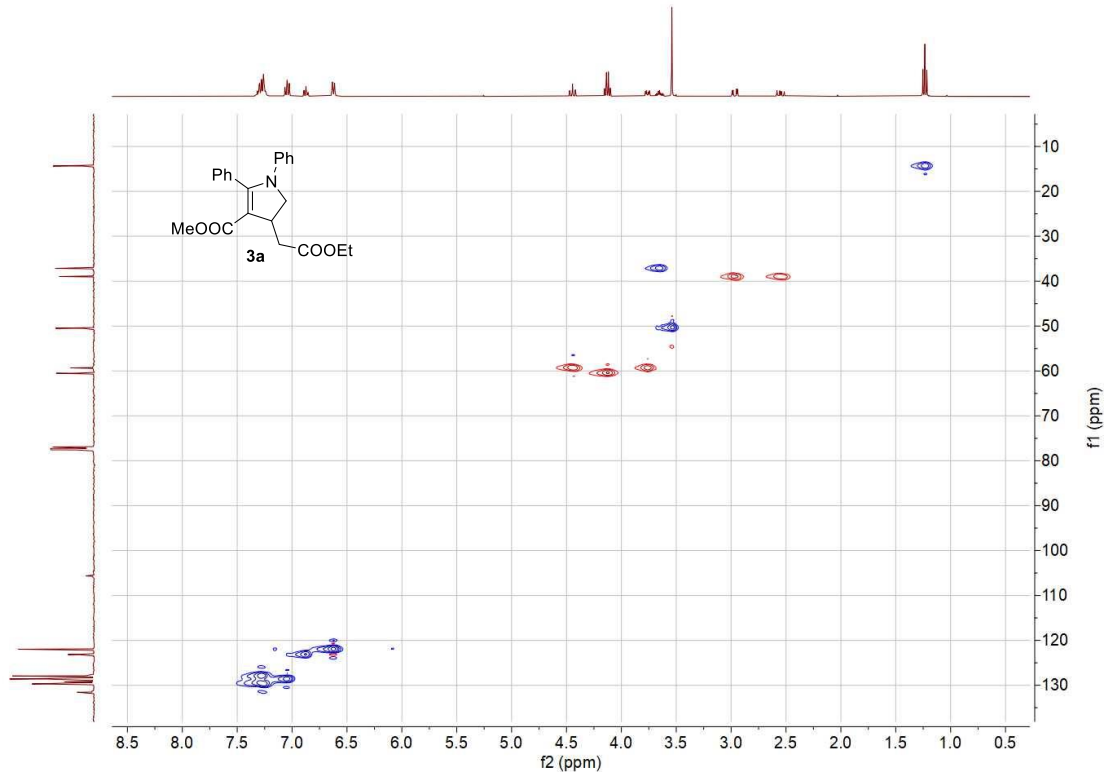
The ^{13}C NMR spectrum of 3a (101 MHz, $CDCl_3$)



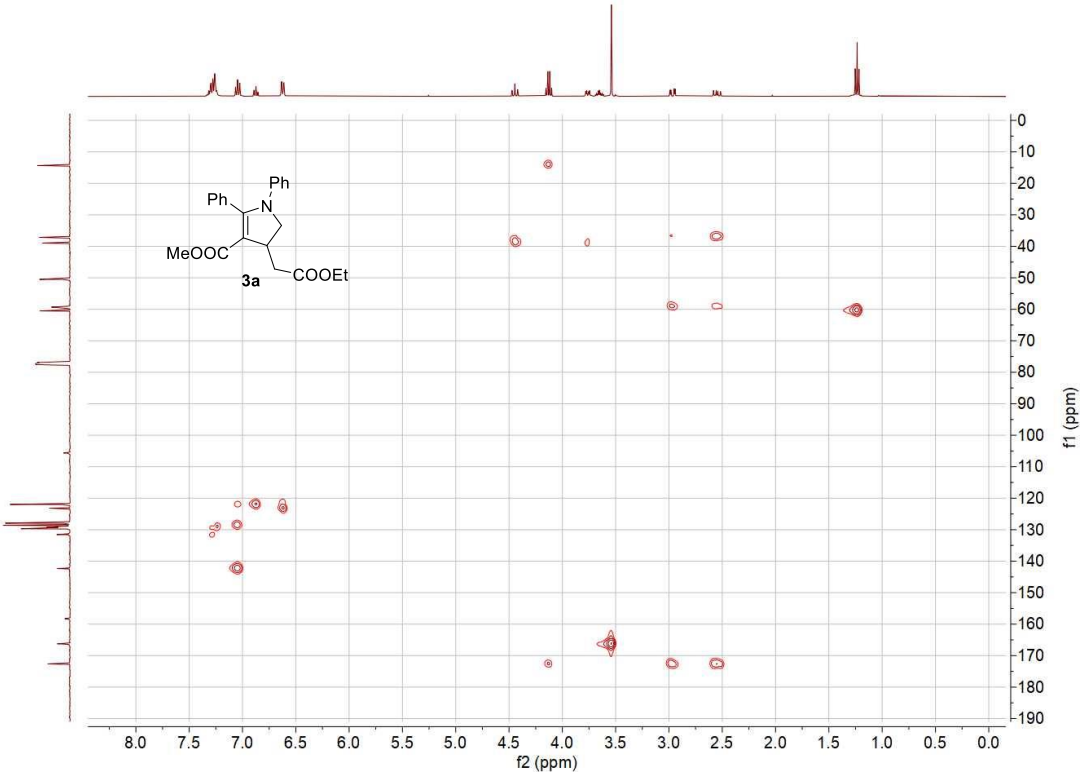
The COSY spectrum of 3a ($CDCl_3$)



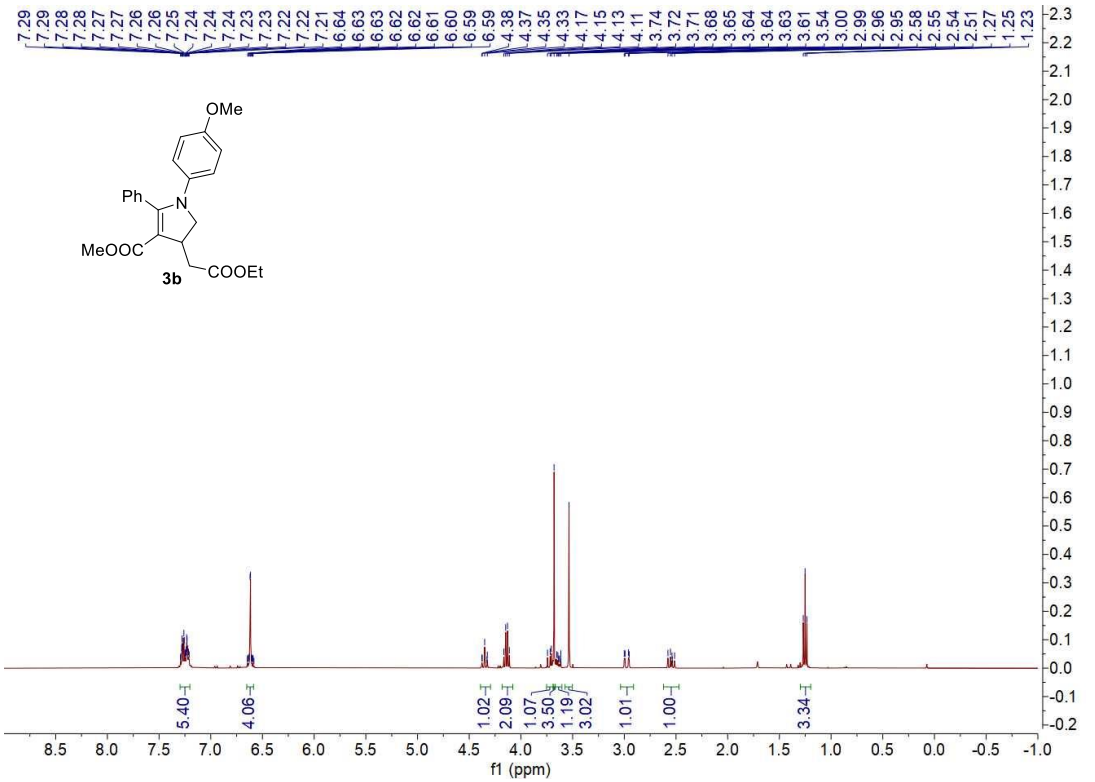
The HSQC spectrum of 3a ($CDCl_3$)



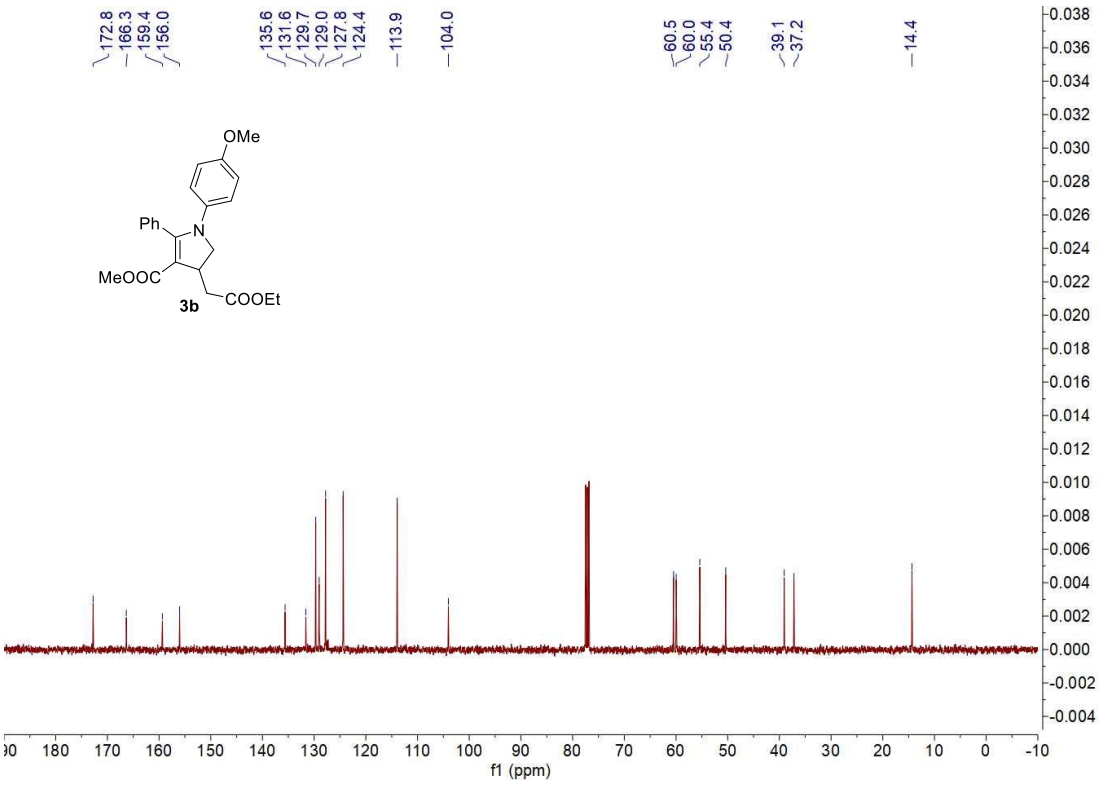
The HMBC spectrum of 3a ($CDCl_3$)



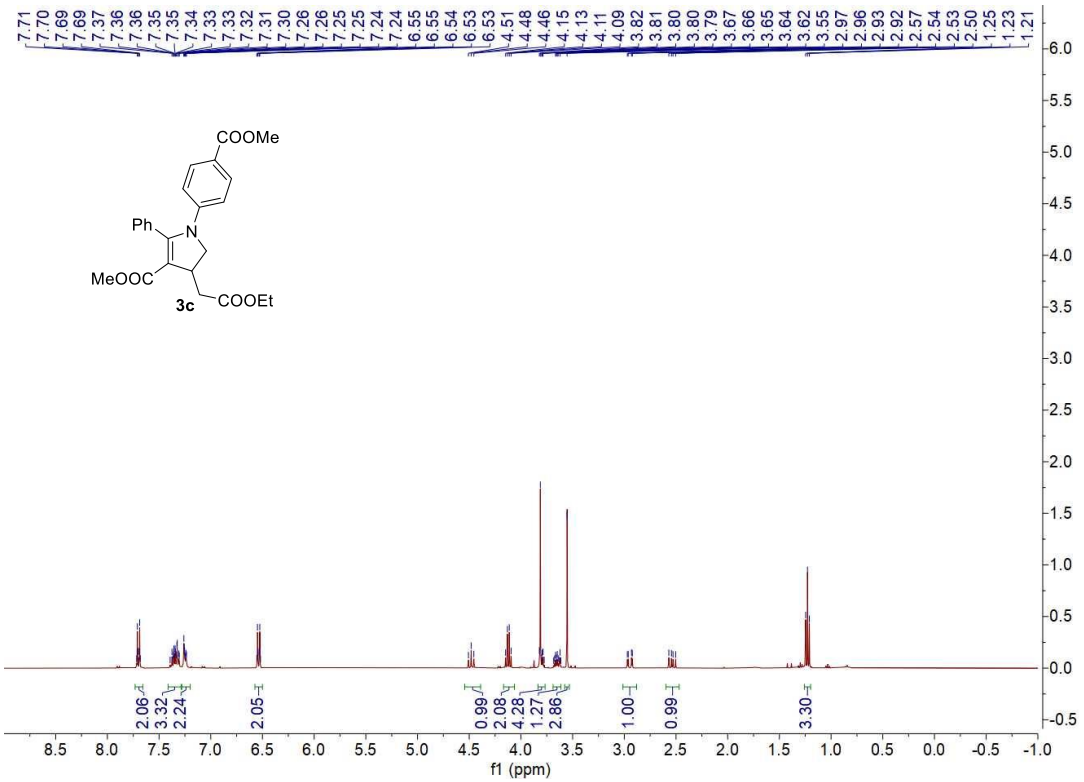
The ^{1}H NMR spectrum of 3b (400 MHz, $CDCl_3$)



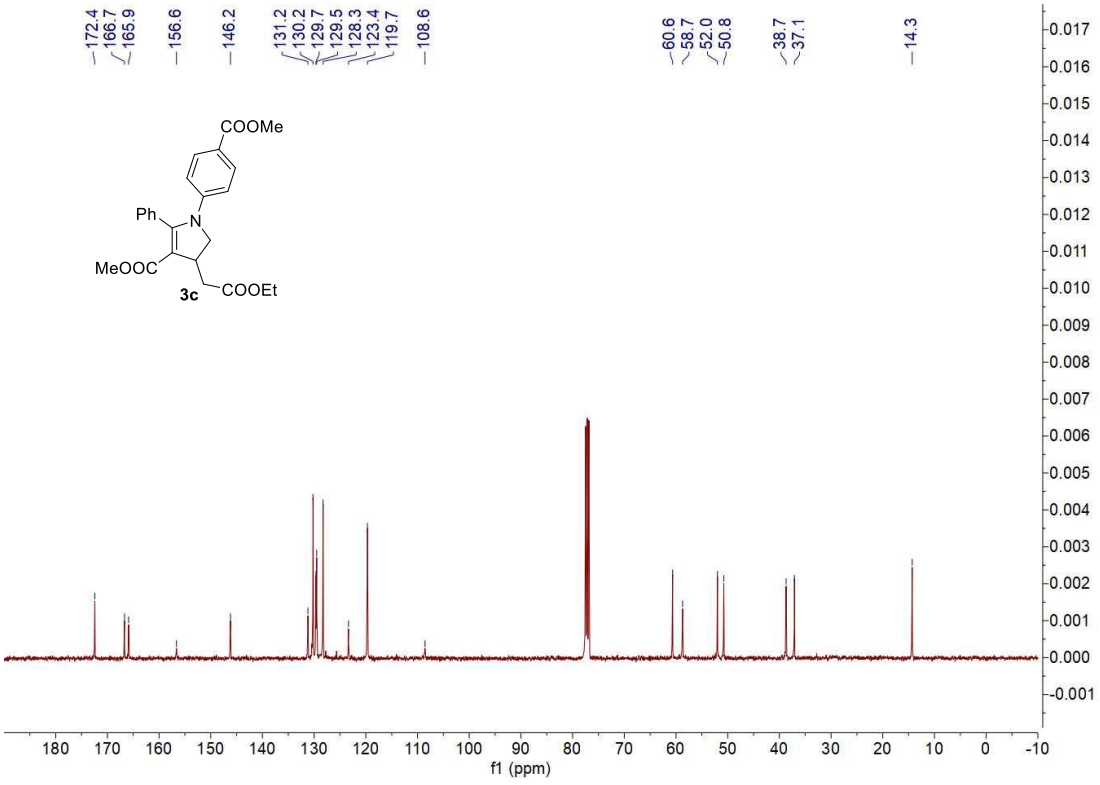
The ^{13}C NMR spectrum of 3b (101 MHz, $CDCl_3$)



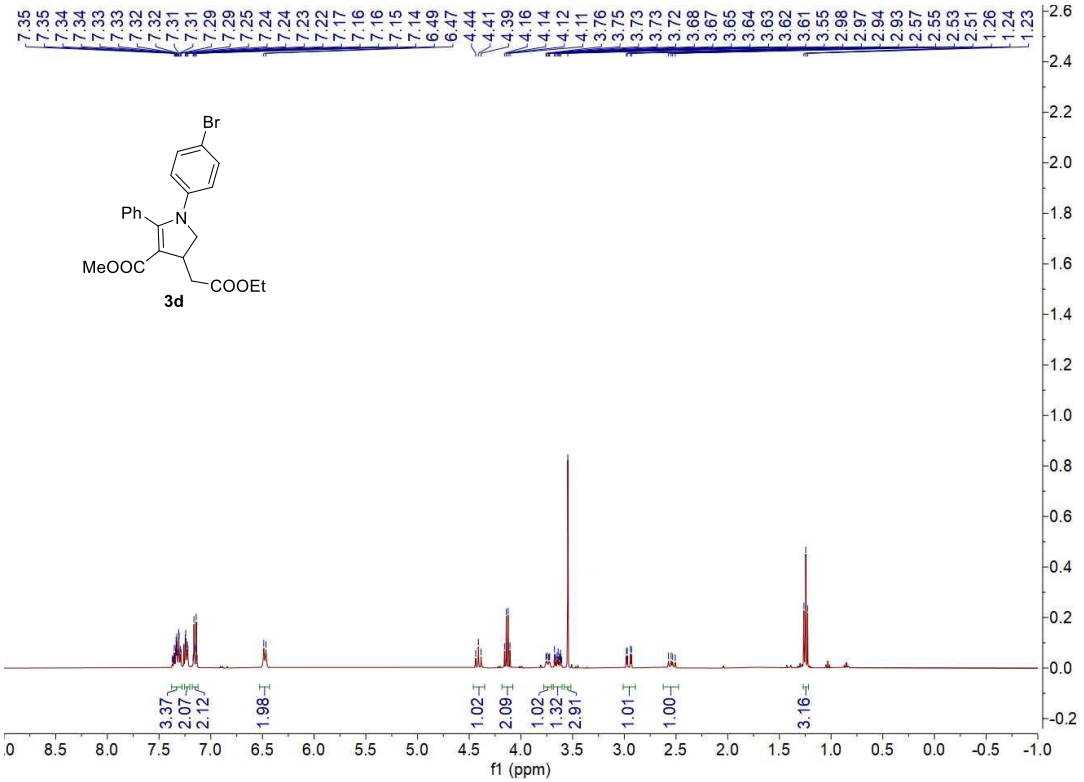
The ^{1}H NMR spectrum of 3c (400 MHz, $CDCl_3$)



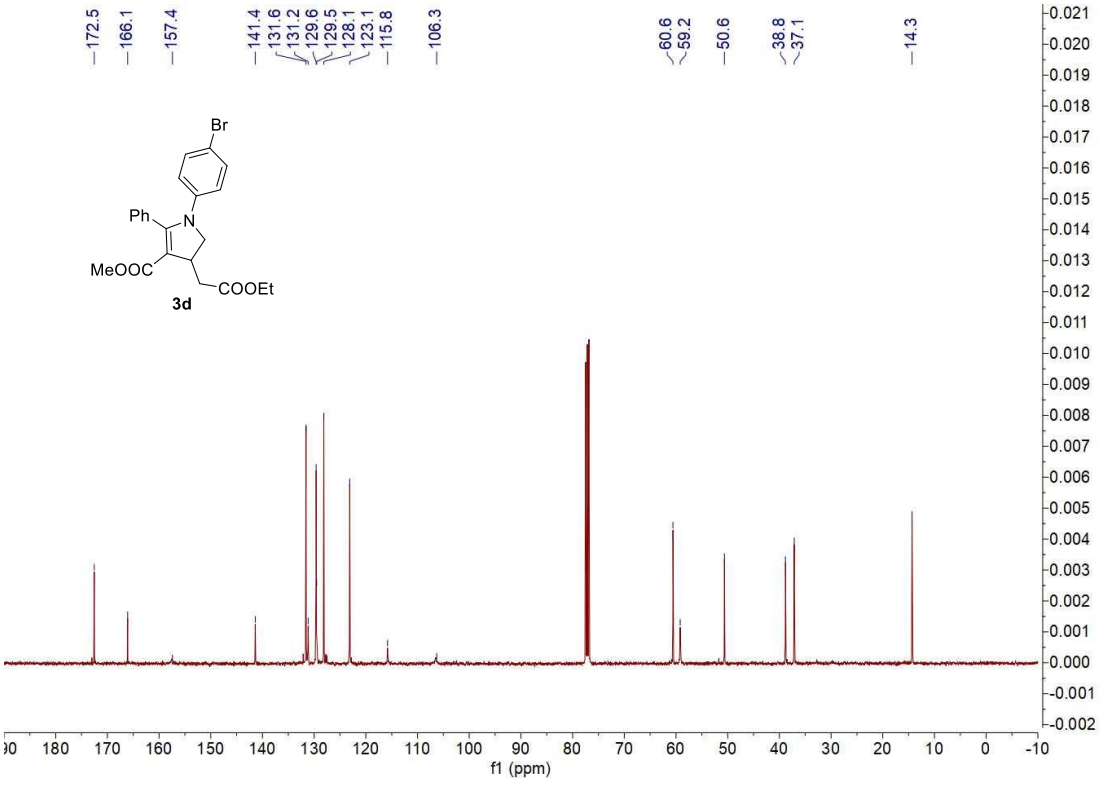
The ^{13}C NMR spectrum of 3c (101 MHz, $CDCl_3$)



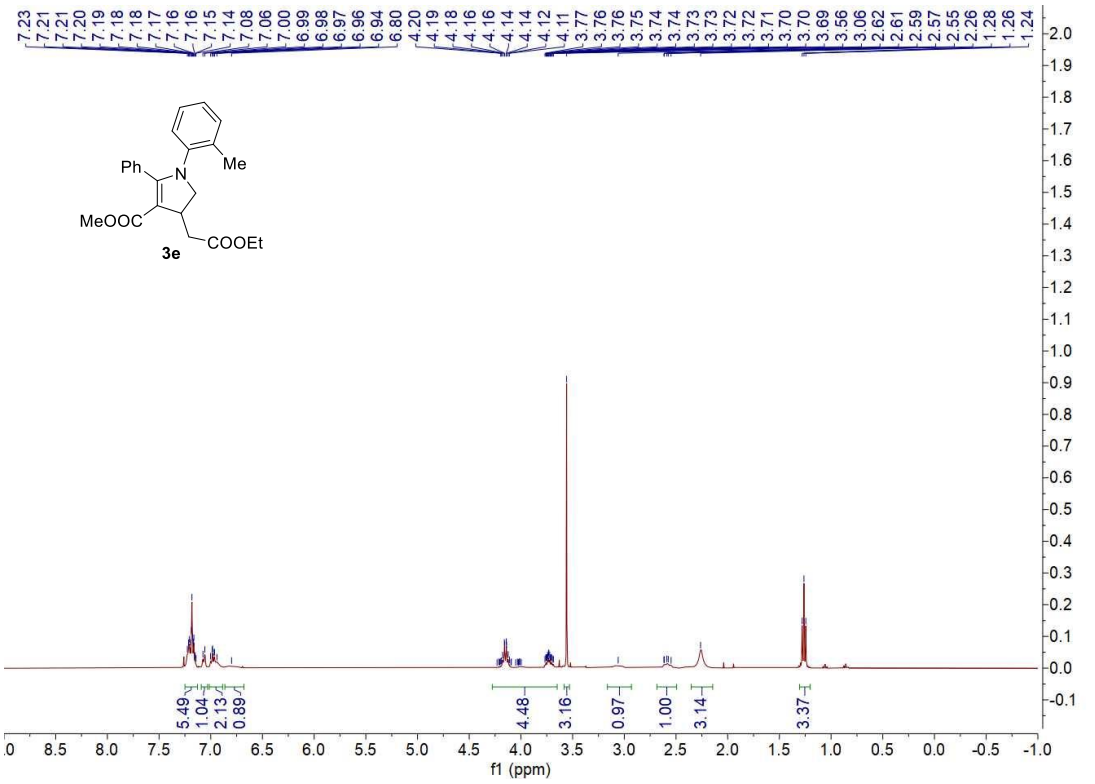
The ^{1}H NMR spectrum of 3d (400 MHz, $CDCl_3$)



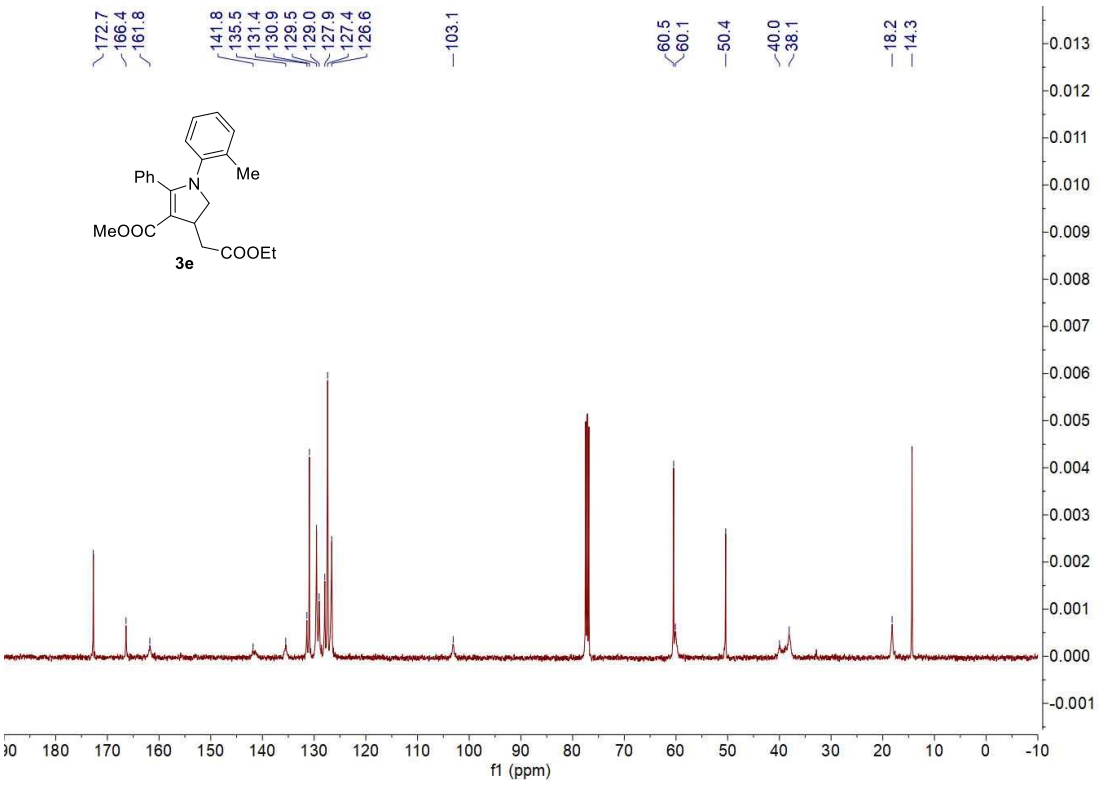
The ^{13}C NMR spectrum of 3d (101 MHz, $CDCl_3$)



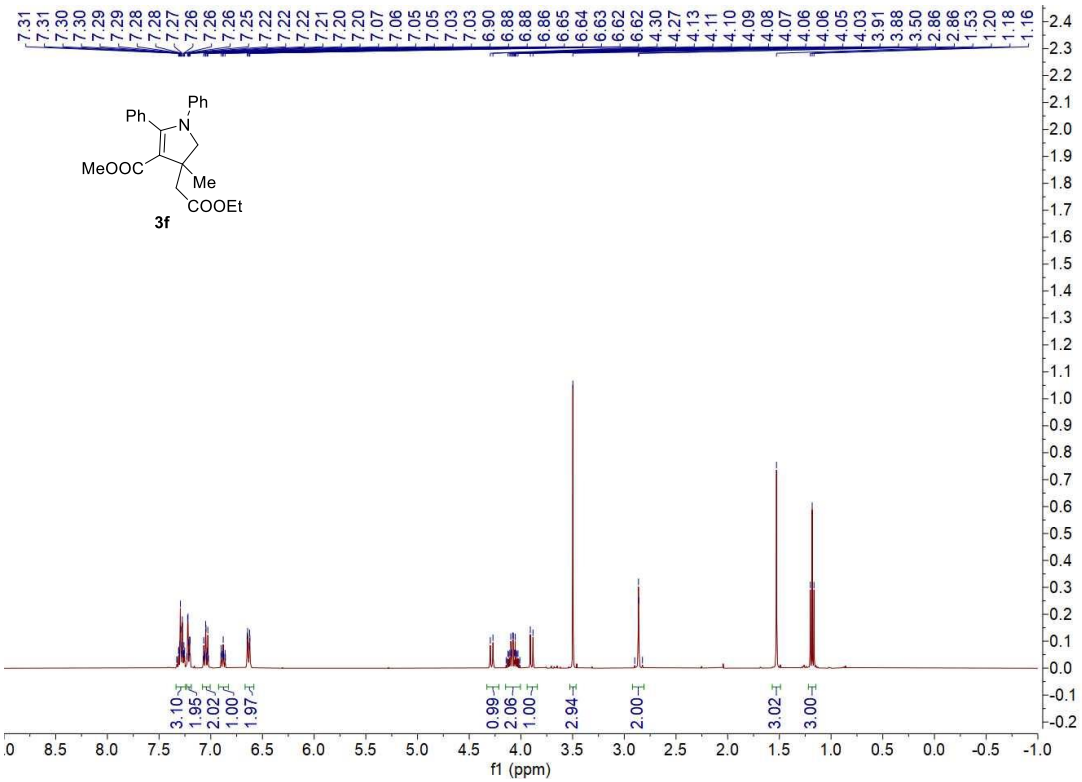
The ^{1}H NMR spectrum of 3e (400 MHz, $CDCl_3$)



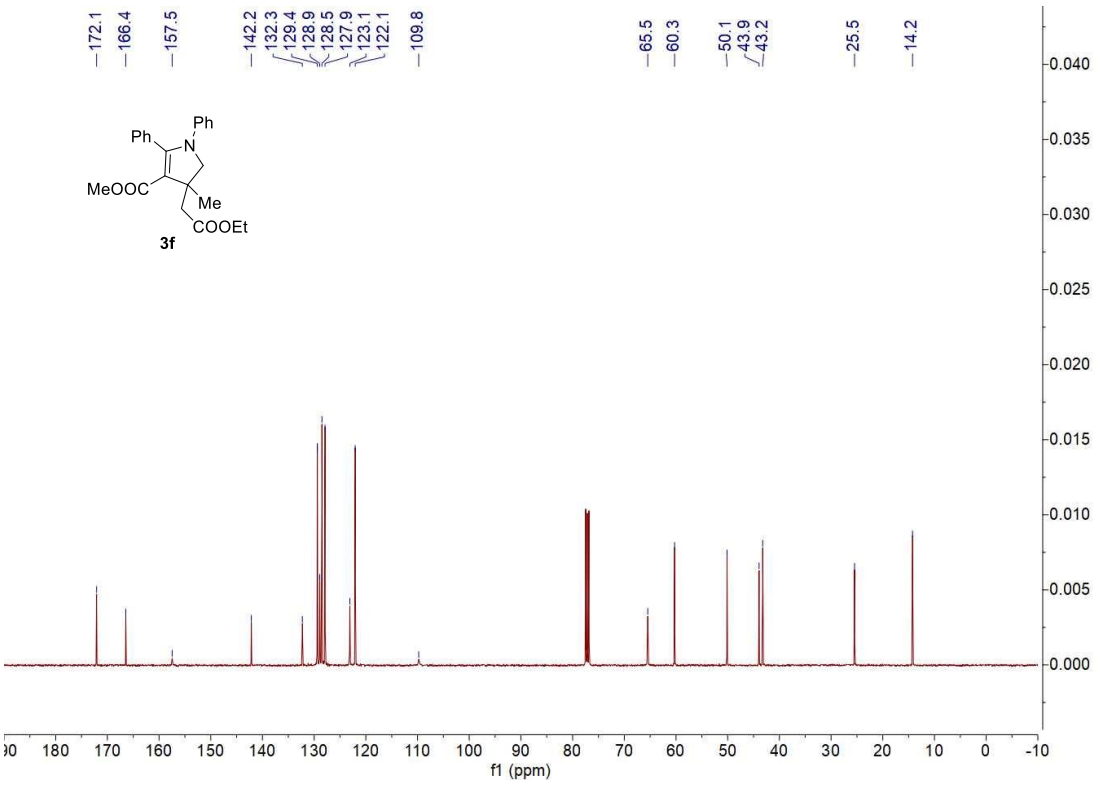
The ^{13}C NMR spectrum of 3e (101 MHz, $CDCl_3$)



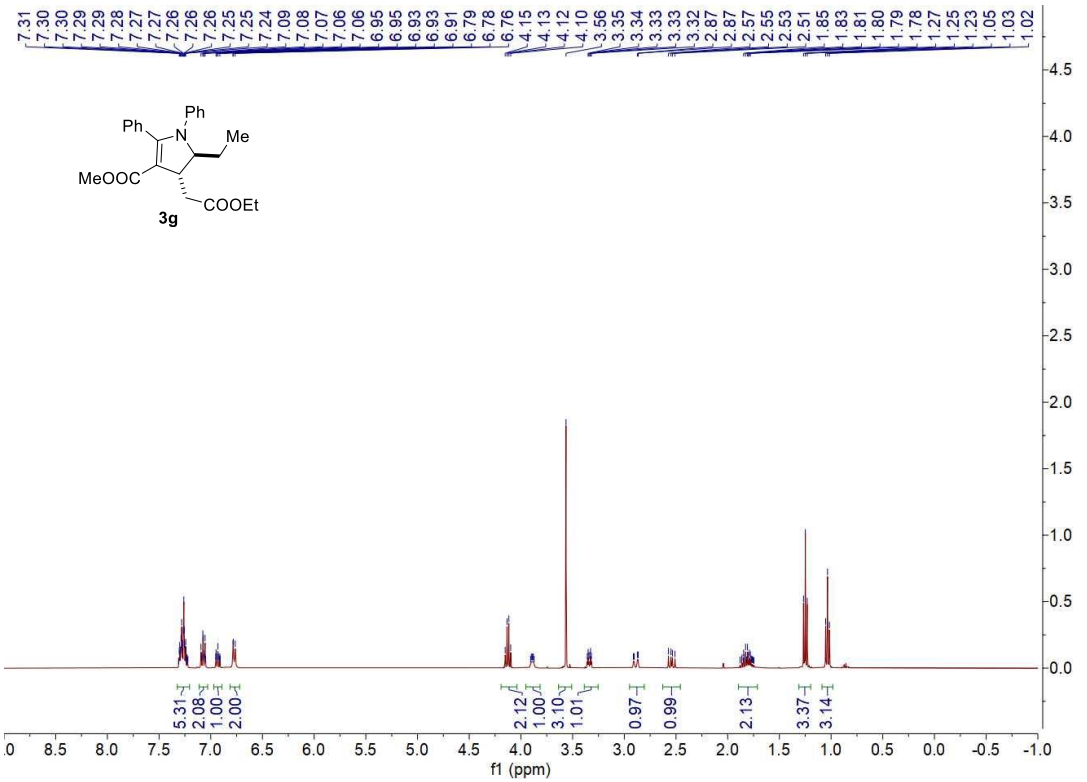
The ^{1}H NMR spectrum of 3f (400 MHz, $CDCl_3$)



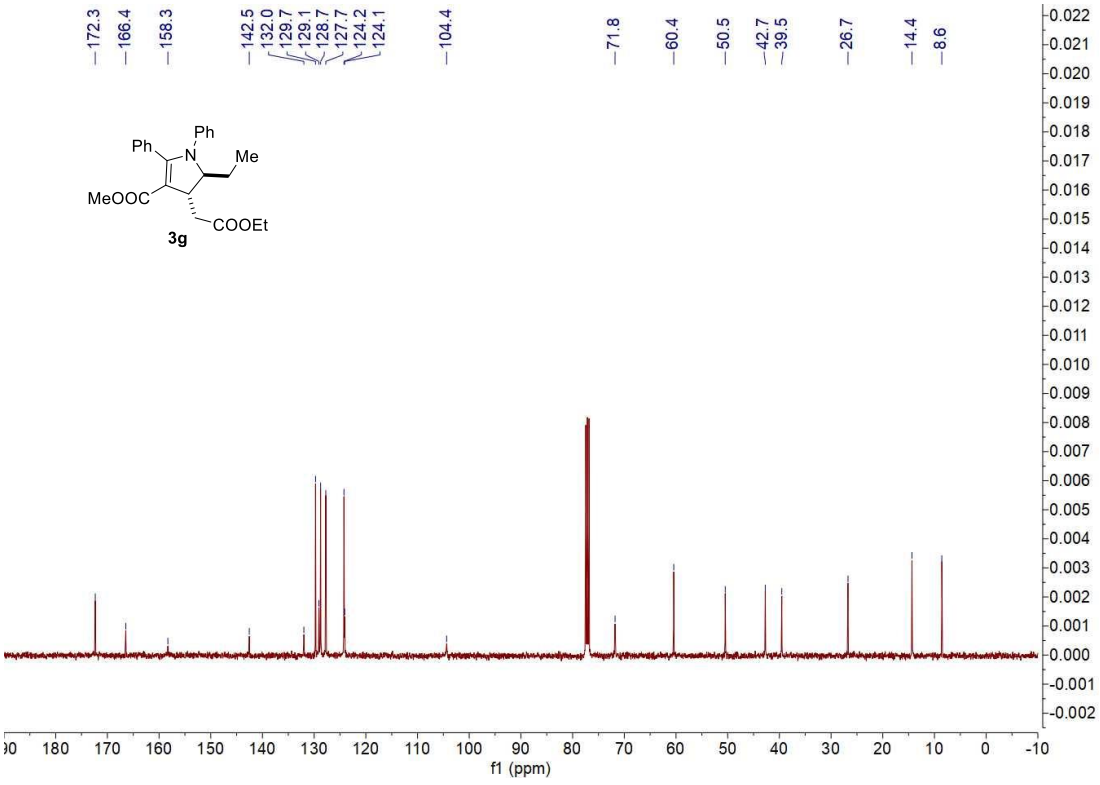
The ^{13}C NMR spectrum of 3f (101 MHz, $CDCl_3$)



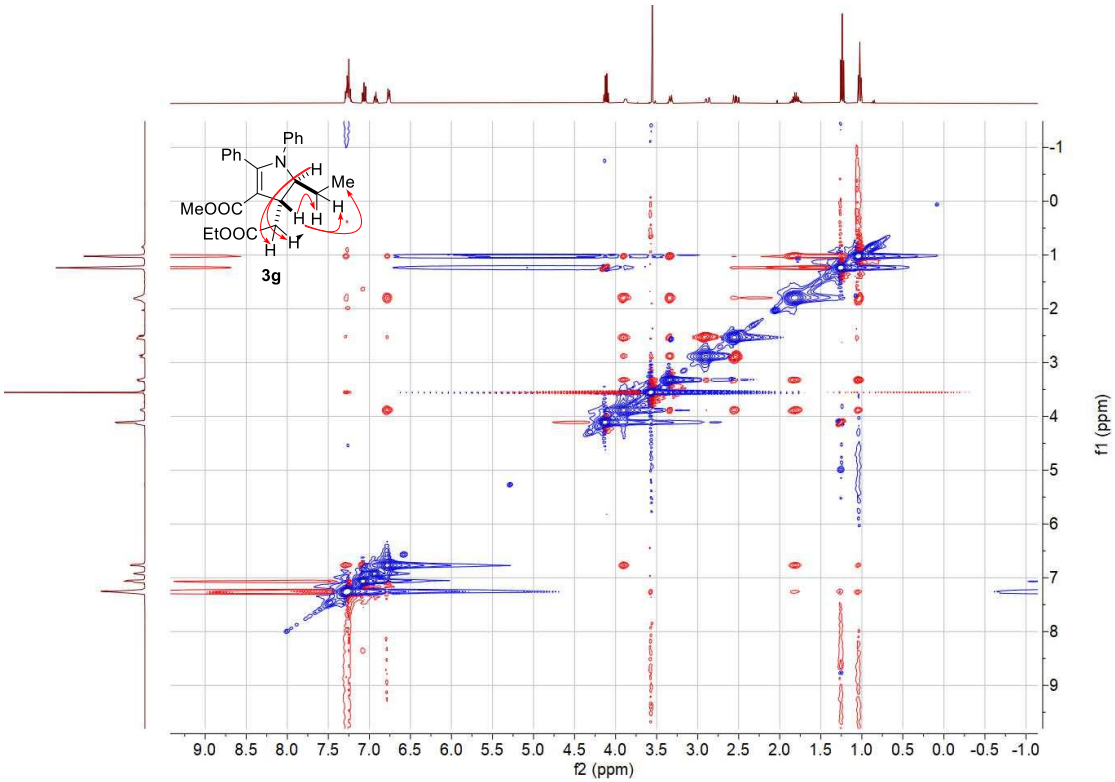
The ^{1}H NMR spectrum of 3g (400 MHz, $CDCl_3$)



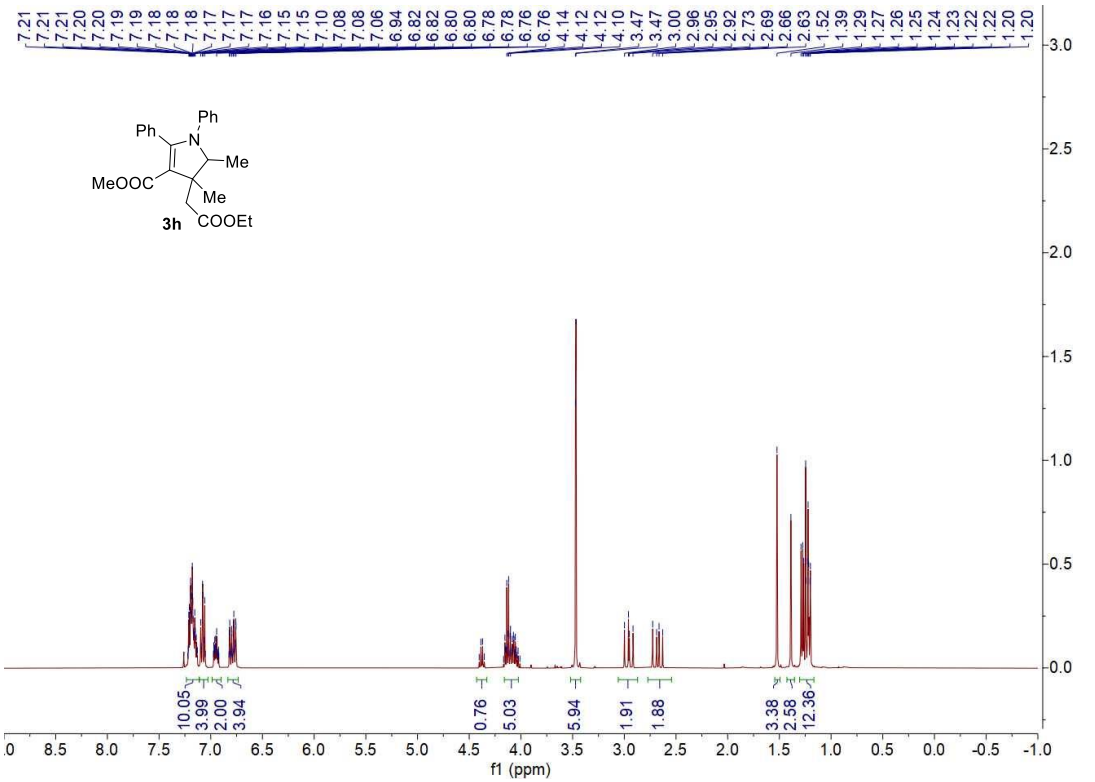
The ^{13}C NMR spectrum of 3g (101 MHz, $CDCl_3$)



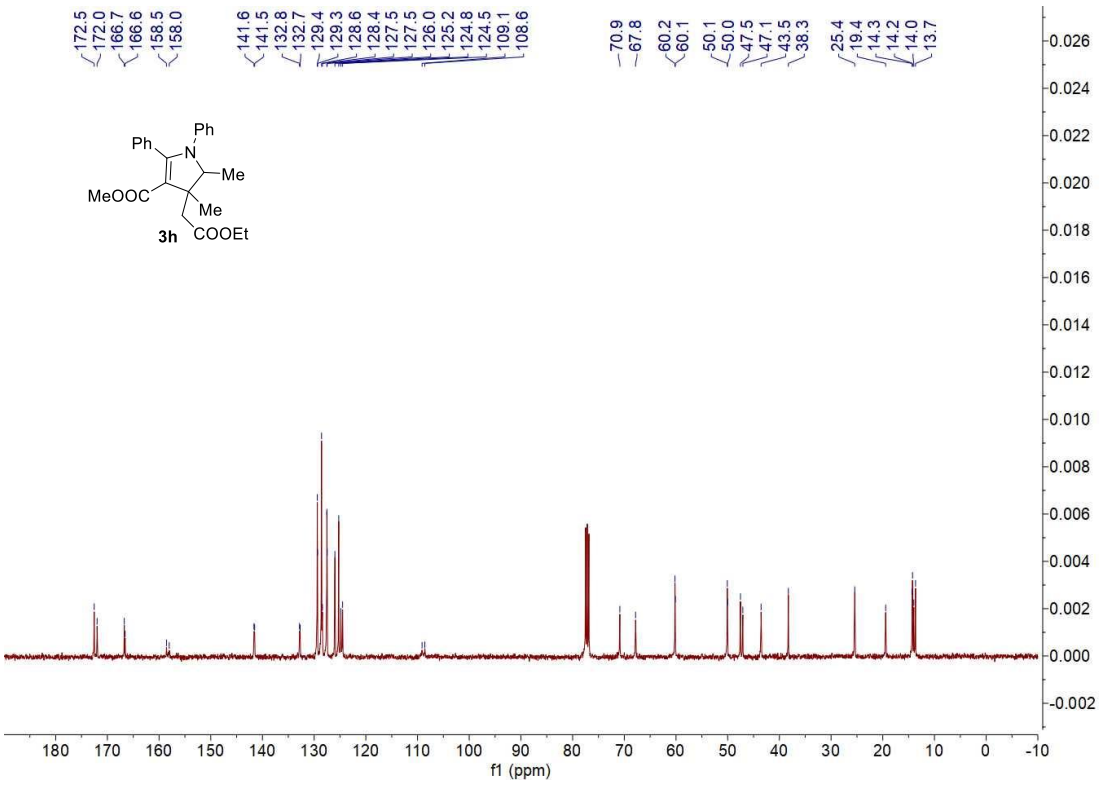
The NOESY spectrum of 3g (101 MHz, $CDCl_3$)



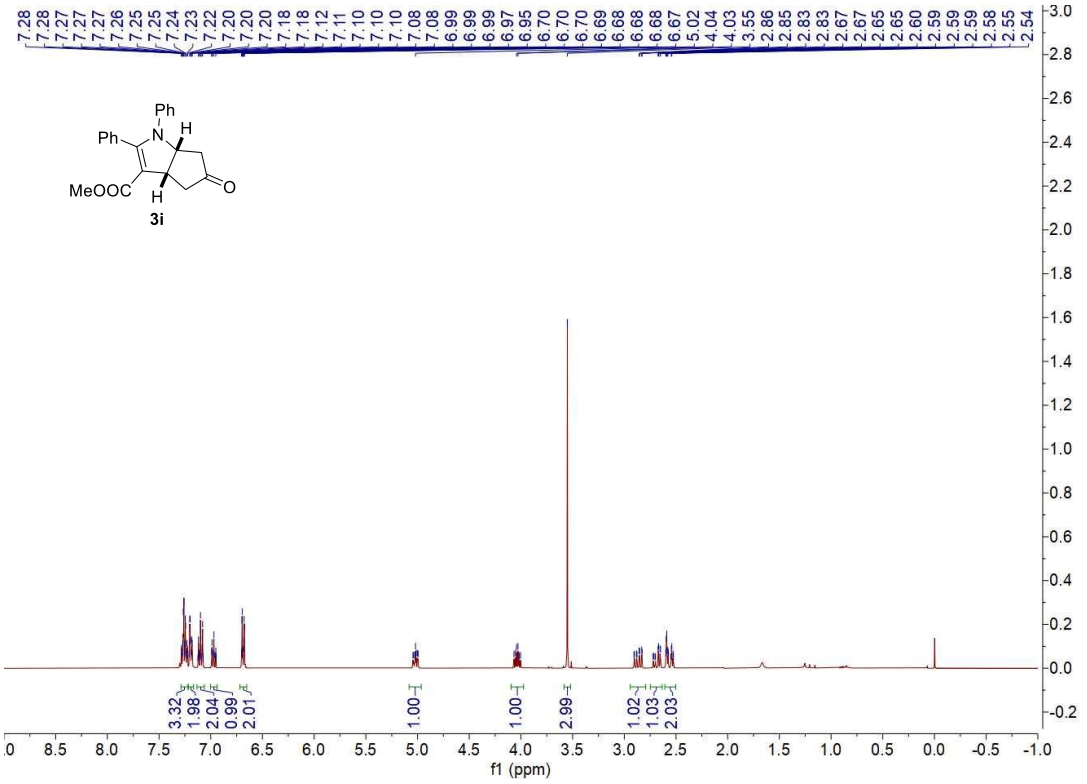
The ^{1}H NMR spectrum of 3h (400 MHz, $CDCl_3$)



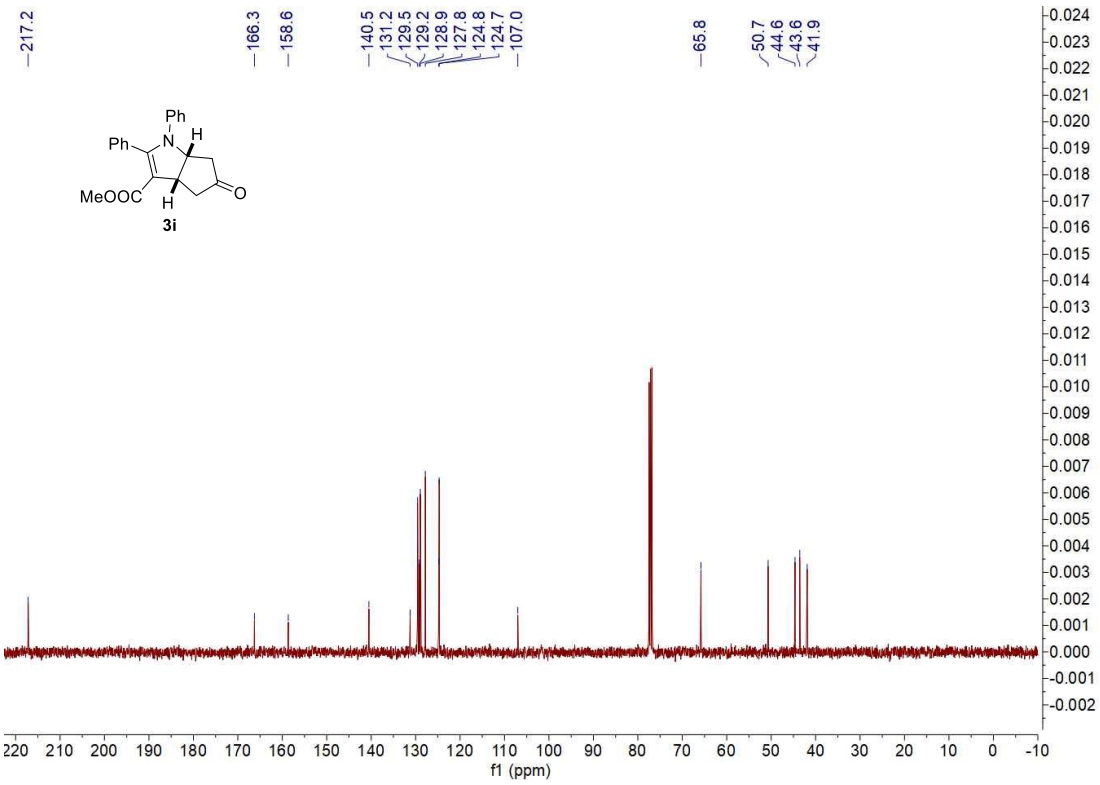
The ^{13}C NMR spectrum of 3h (101 MHz, $CDCl_3$)



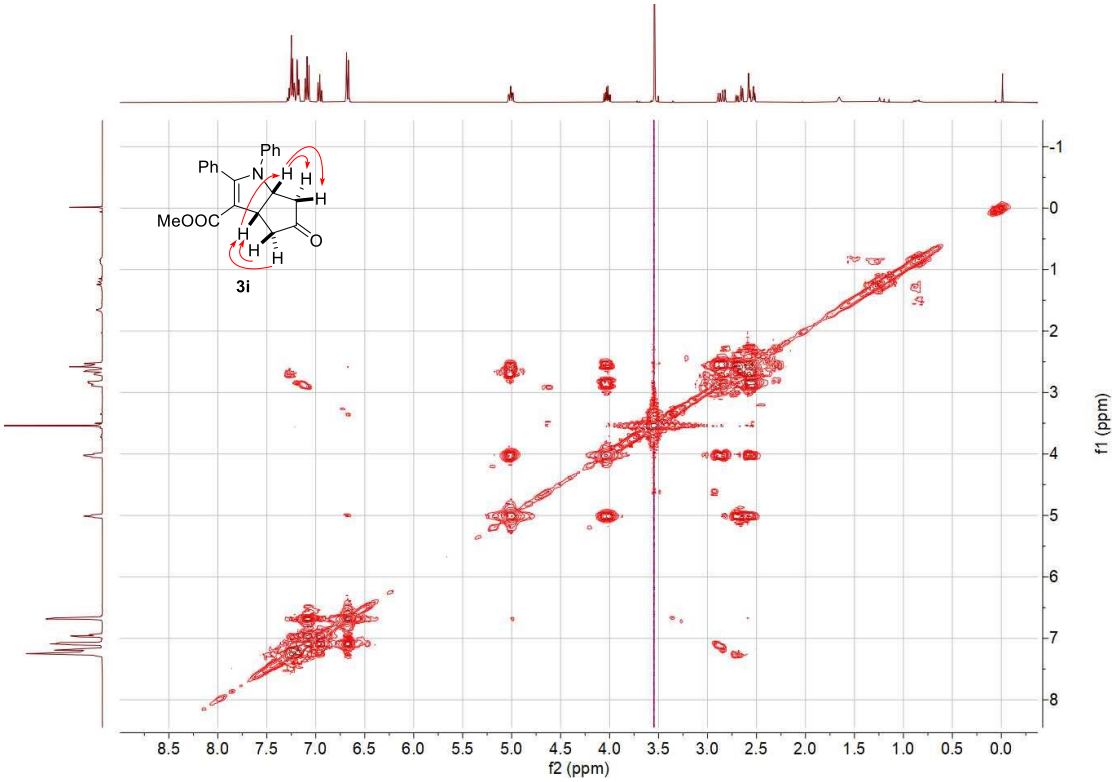
The ^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



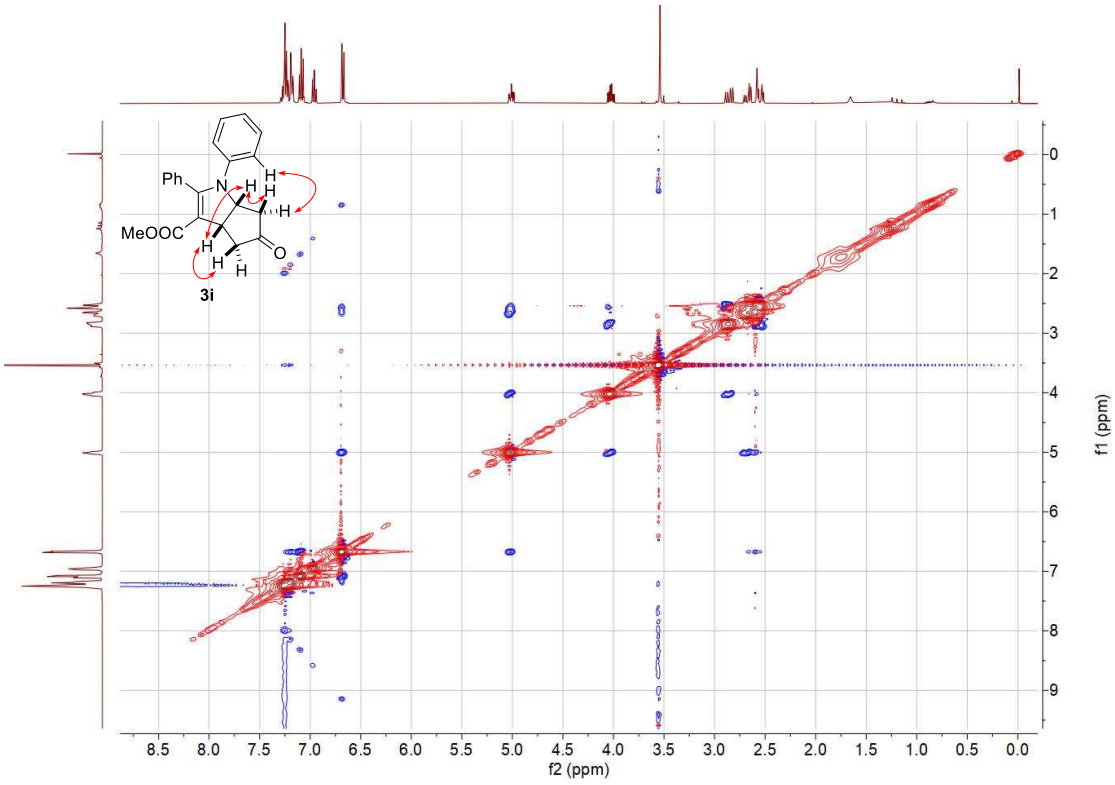
The ^{13}C NMR spectrum of 3i (101 MHz, $CDCl_3$)



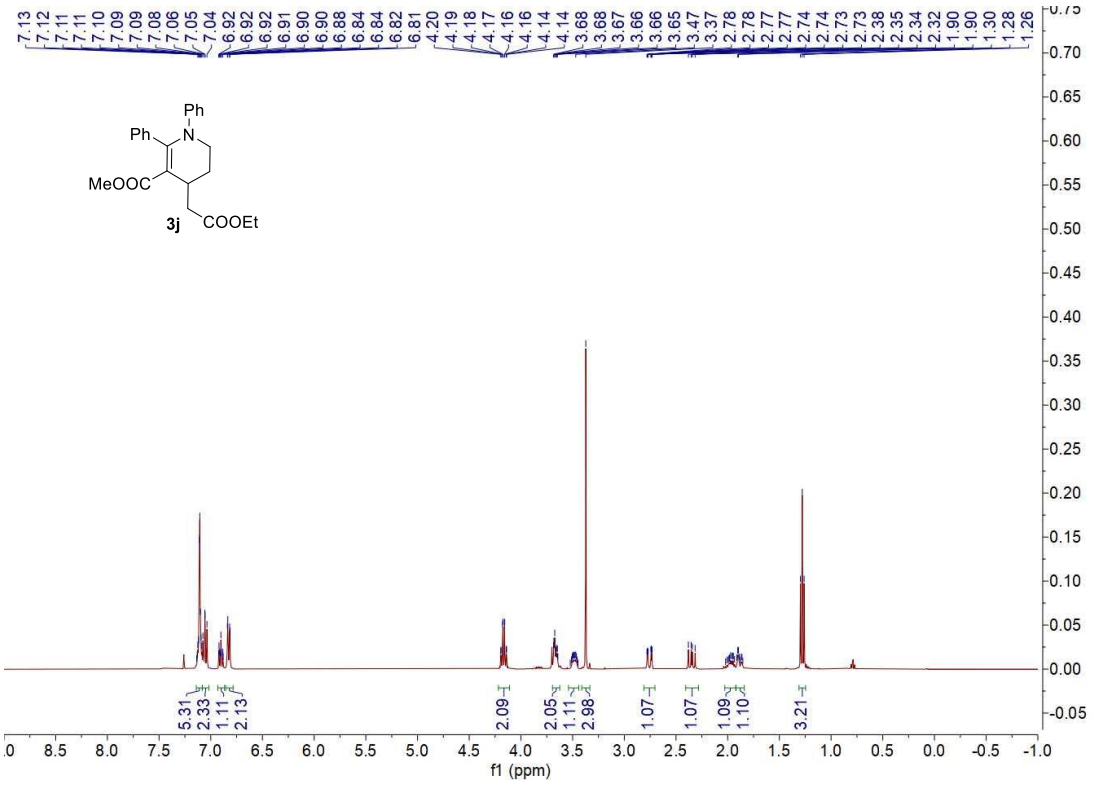
The COSY spectrum of 3i (400 MHz, $CDCl_3$)



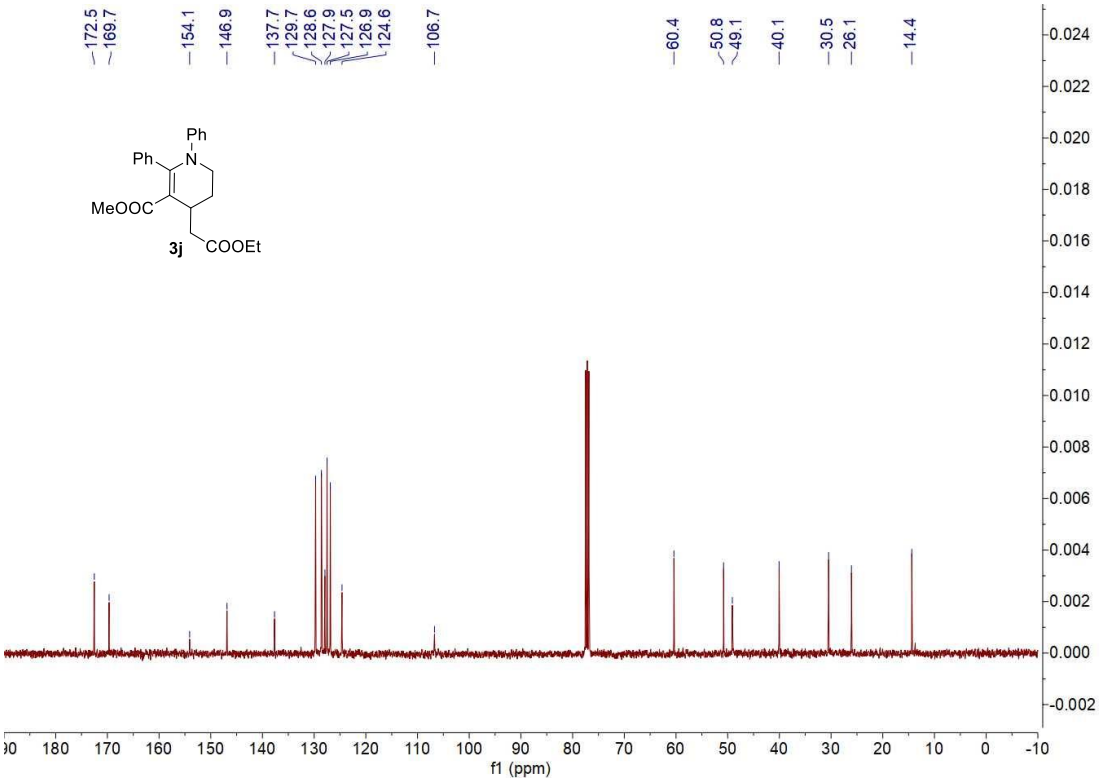
The NOESY spectrum of 3i (400 MHz, $CDCl_3$)



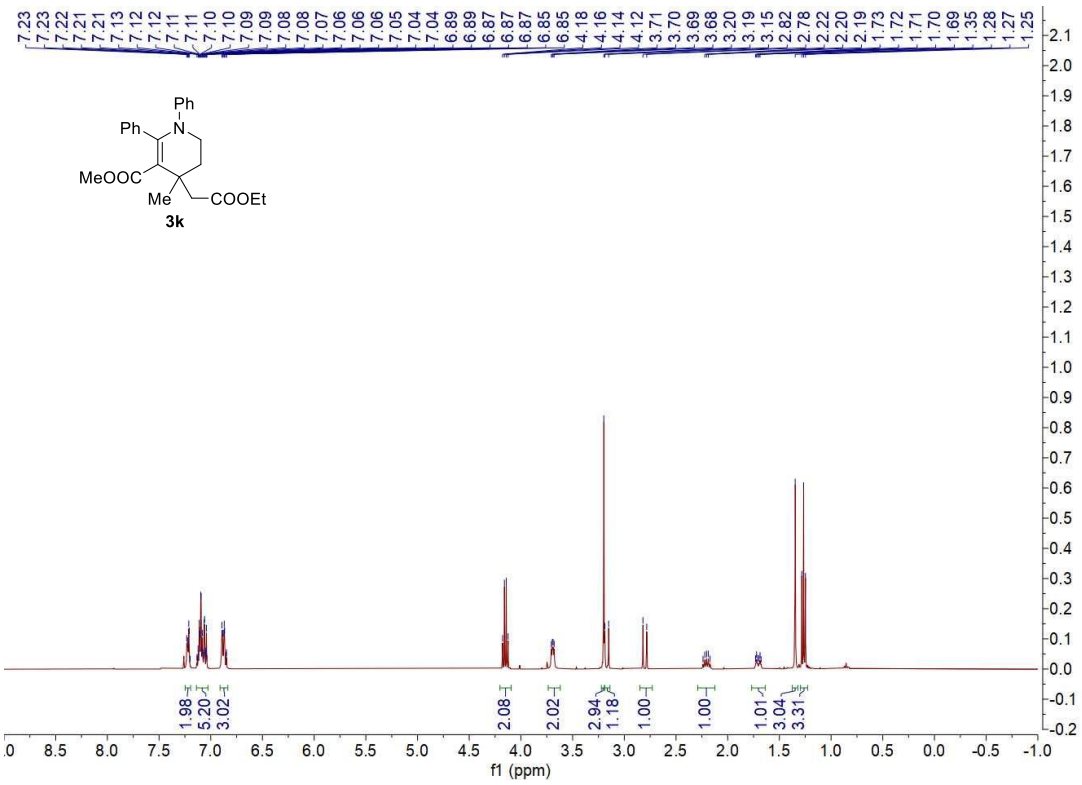
The ^{1}H NMR spectrum of 3j (400 MHz, $CDCl_3$)



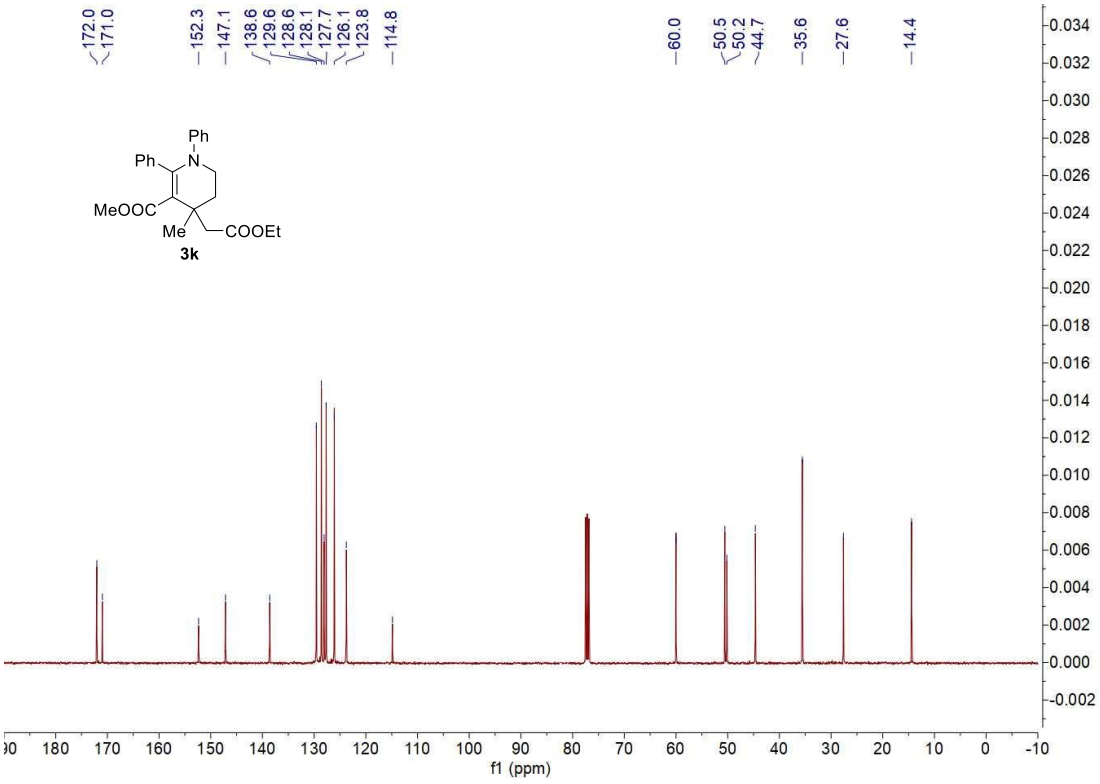
The ^{13}C NMR spectrum of 3j (101 MHz, $CDCl_3$)



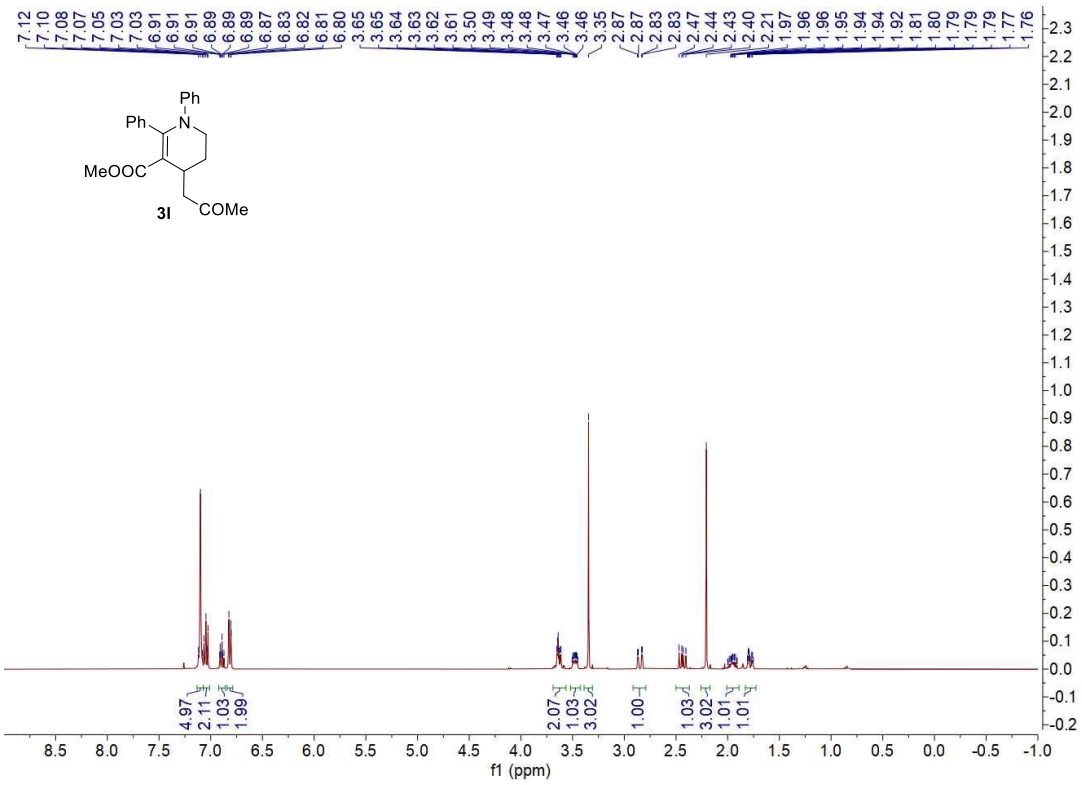
The ^{1}H NMR spectrum of 3k (400 MHz, $CDCl_3$)



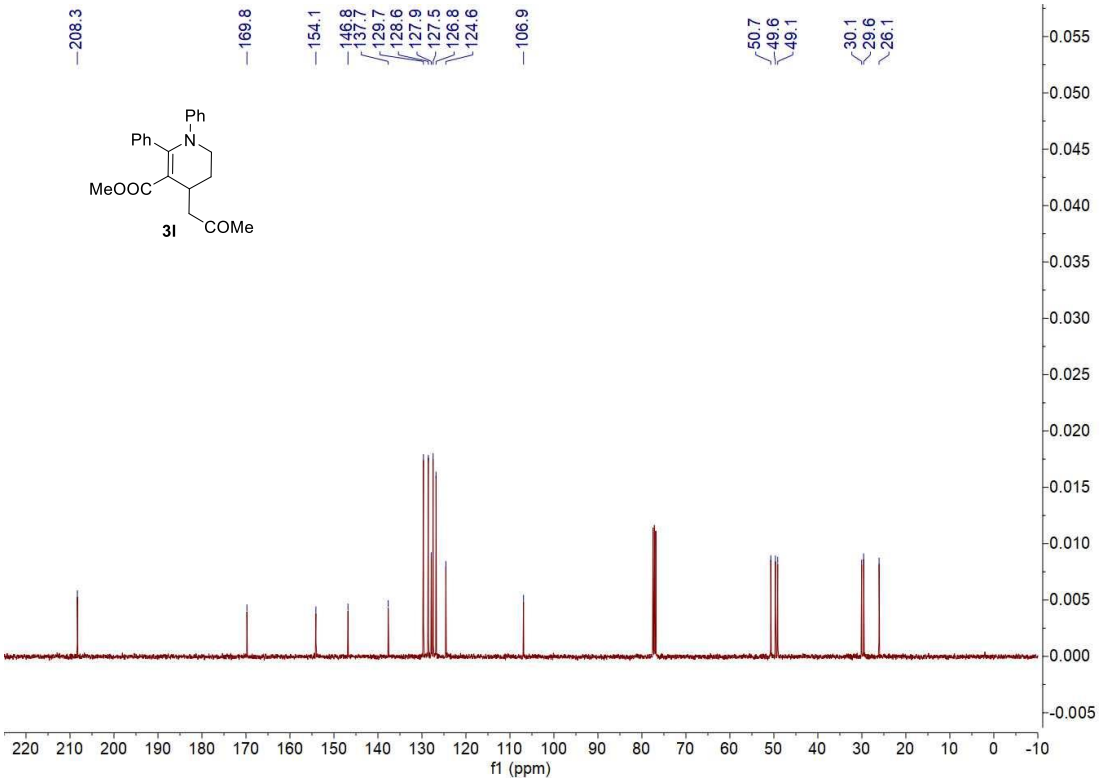
The ^{13}C NMR spectrum of 3k (101 MHz, $CDCl_3$)



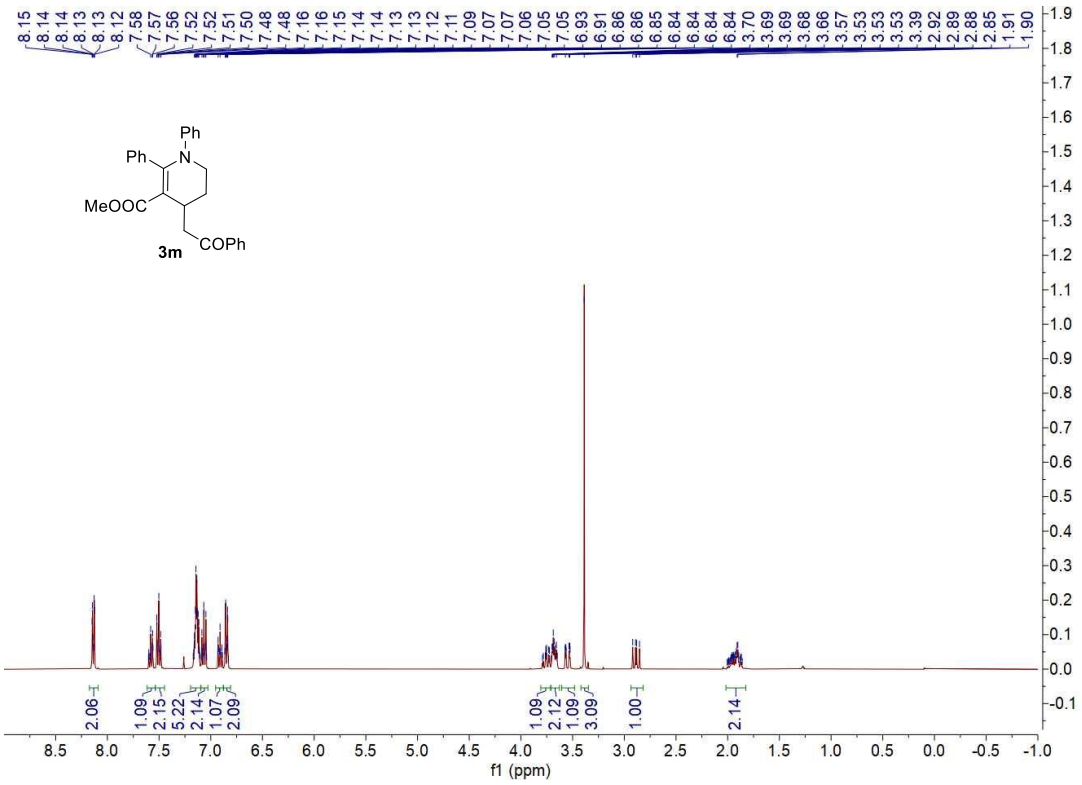
The ^{1}H NMR spectrum of 3l (400 MHz, $CDCl_3$)



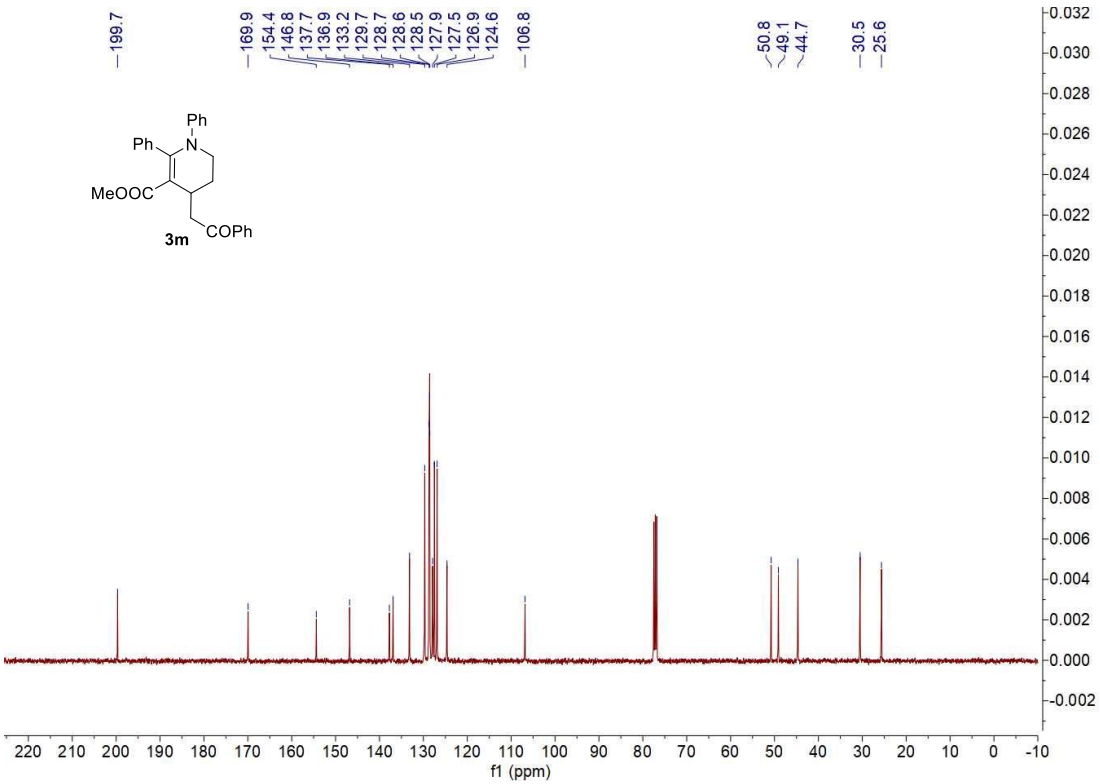
The ^{13}C NMR spectrum of 3l (101 MHz, $CDCl_3$)



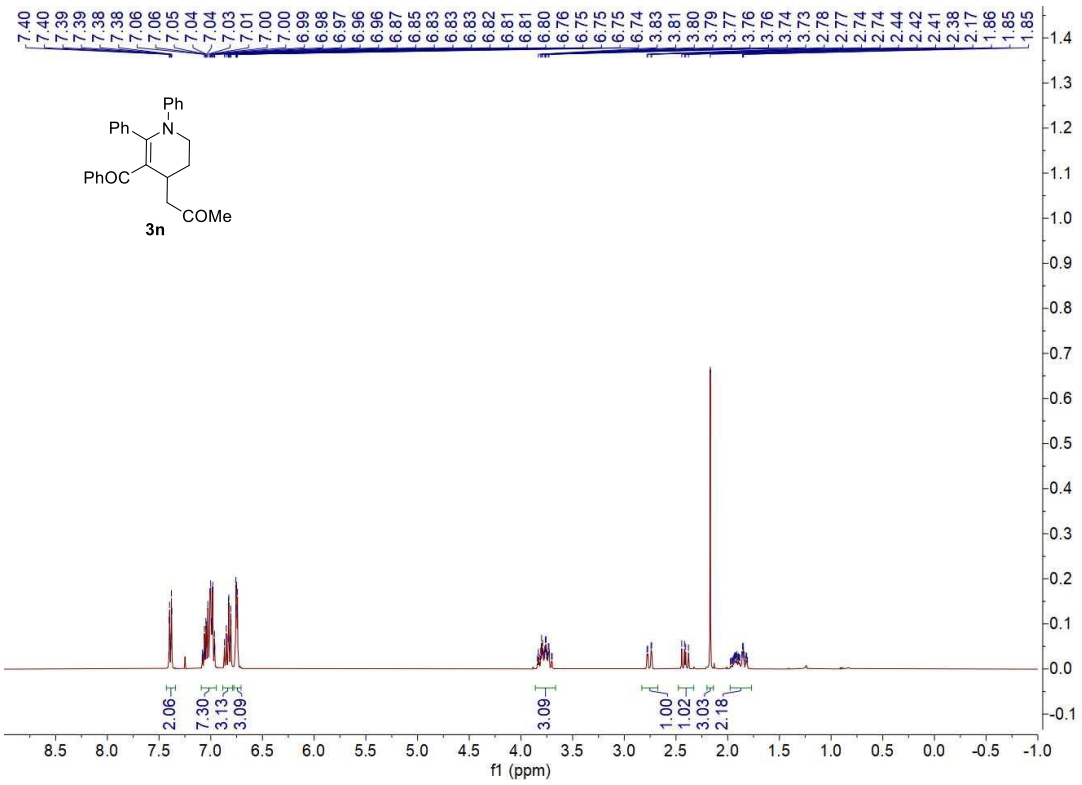
The ^{1}H NMR spectrum of 3m (400 MHz, $CDCl_3$)



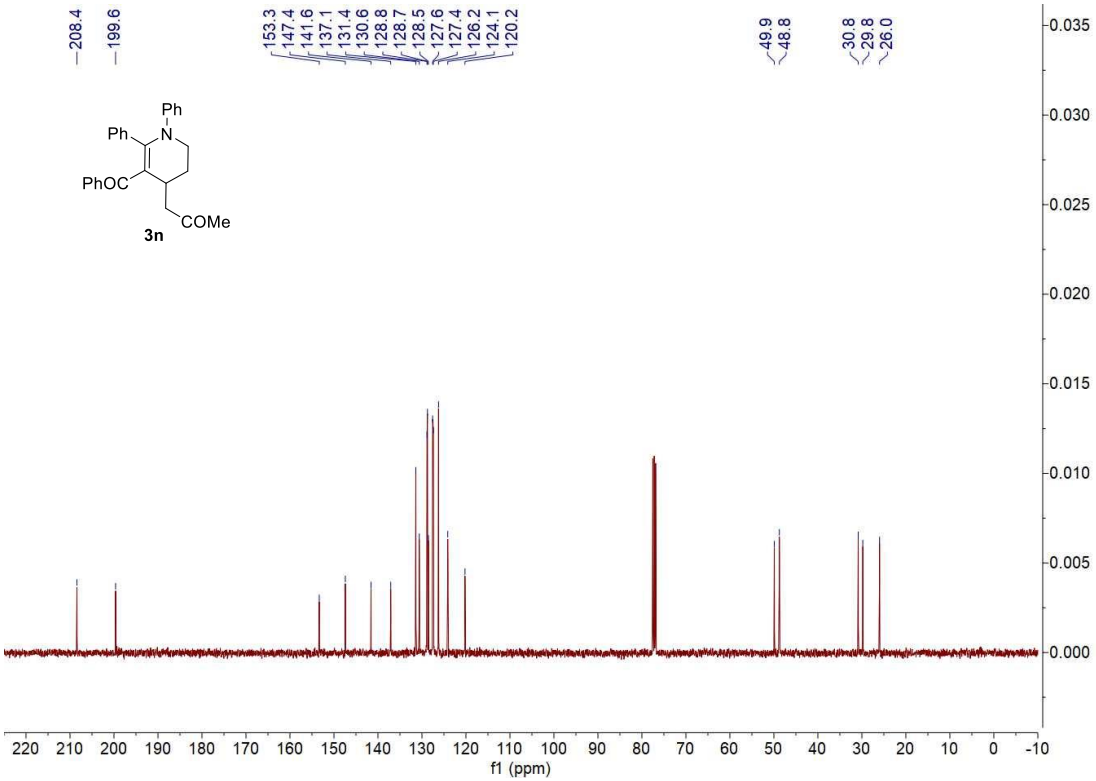
The ^{13}C NMR spectrum of 3m (101 MHz, $CDCl_3$)



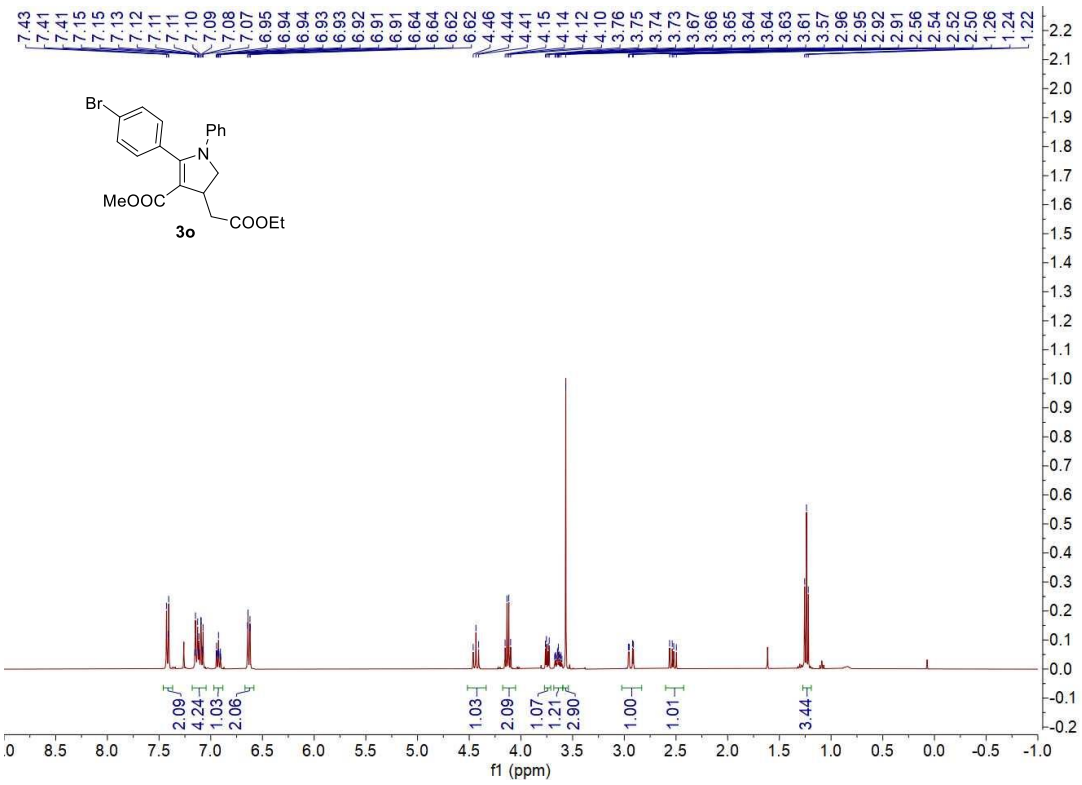
The ^{1}H NMR spectrum of 3n (400 MHz, $CDCl_3$)



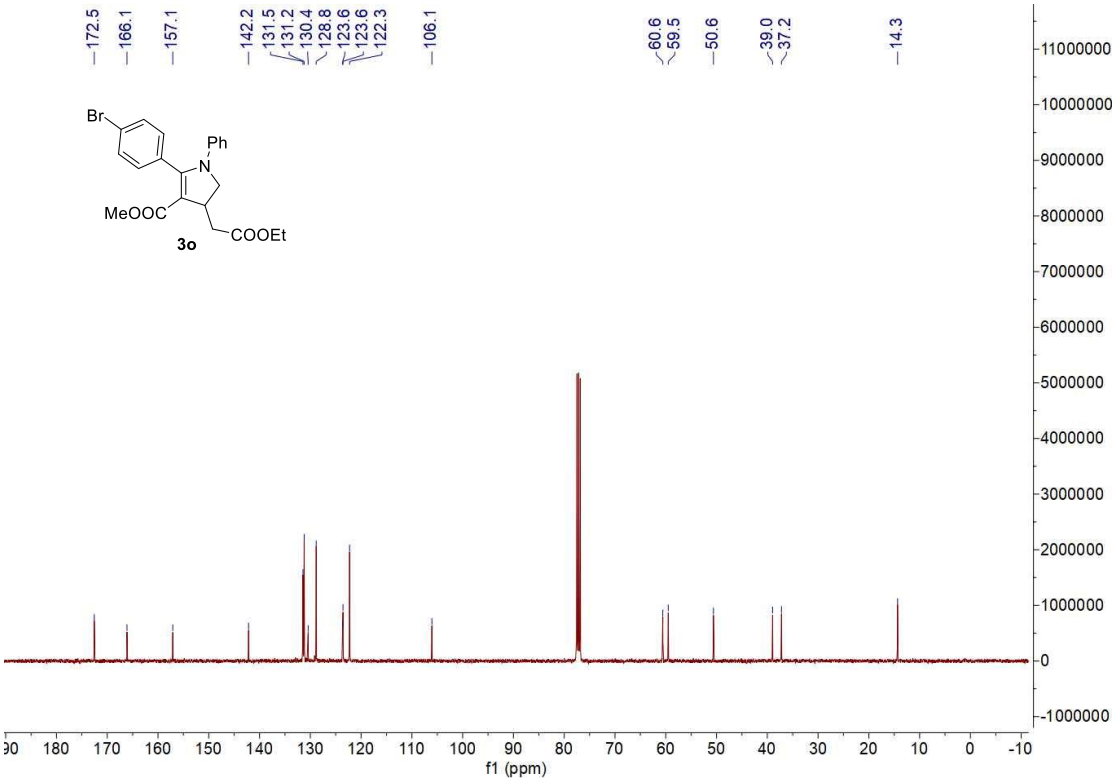
The ^{13}C NMR spectrum of 3n (101 MHz, $CDCl_3$)



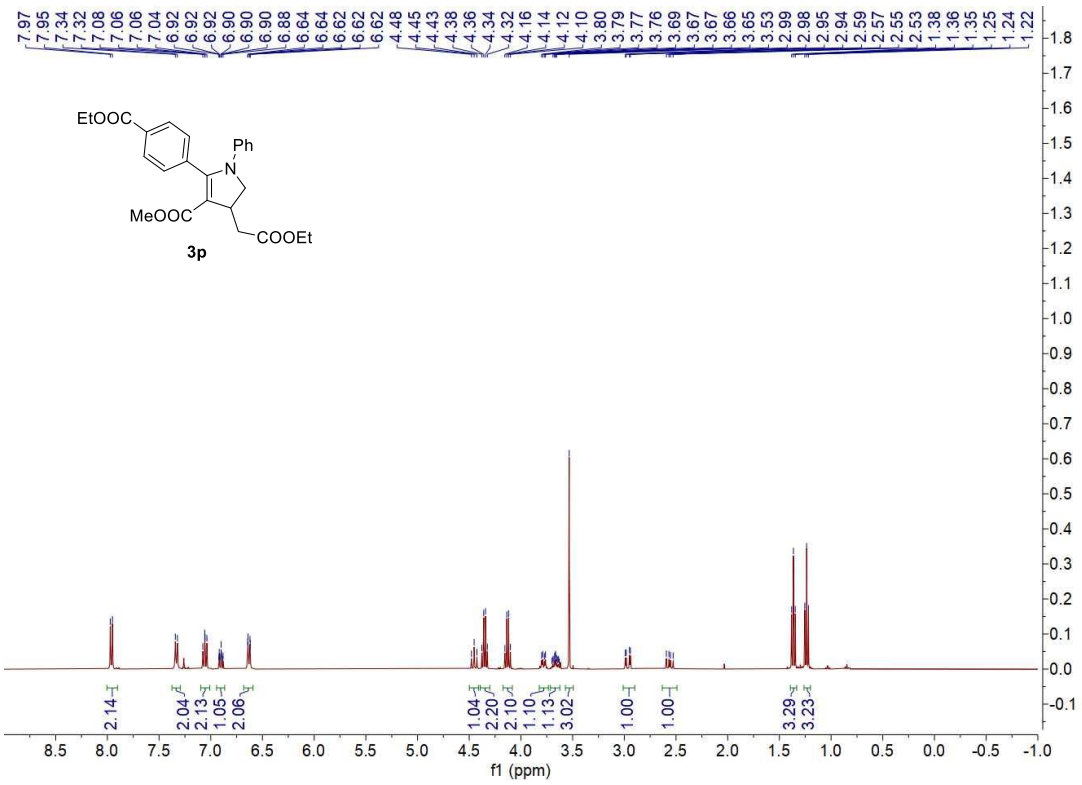
The ^{1}H NMR spectrum of 3o (400 MHz, $CDCl_3$)



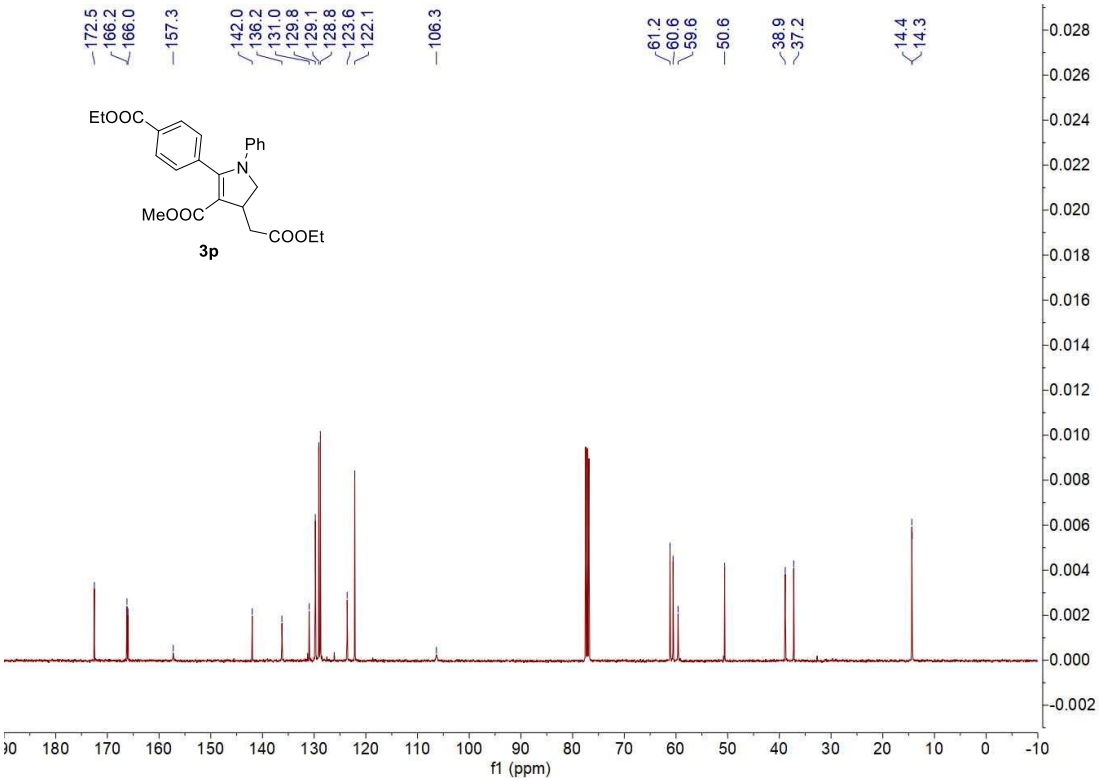
The ^{13}C NMR spectrum of 3o (101 MHz, $CDCl_3$)



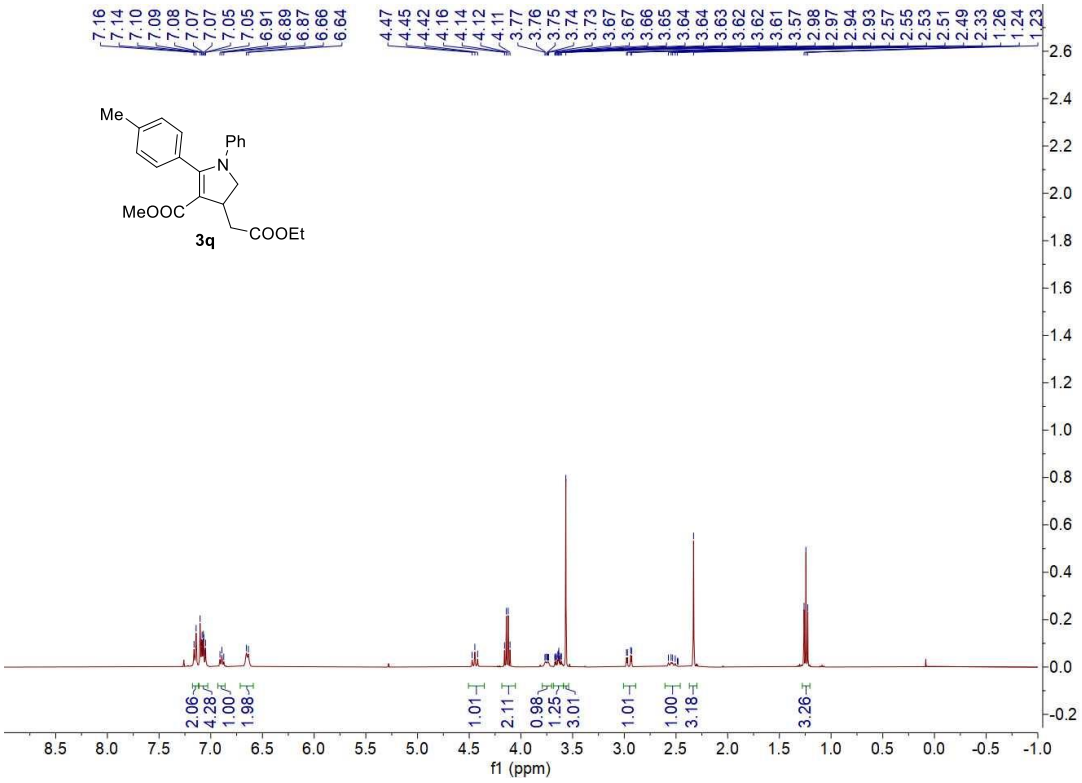
The ^{1}H NMR spectrum of 3p (400 MHz, $CDCl_3$)



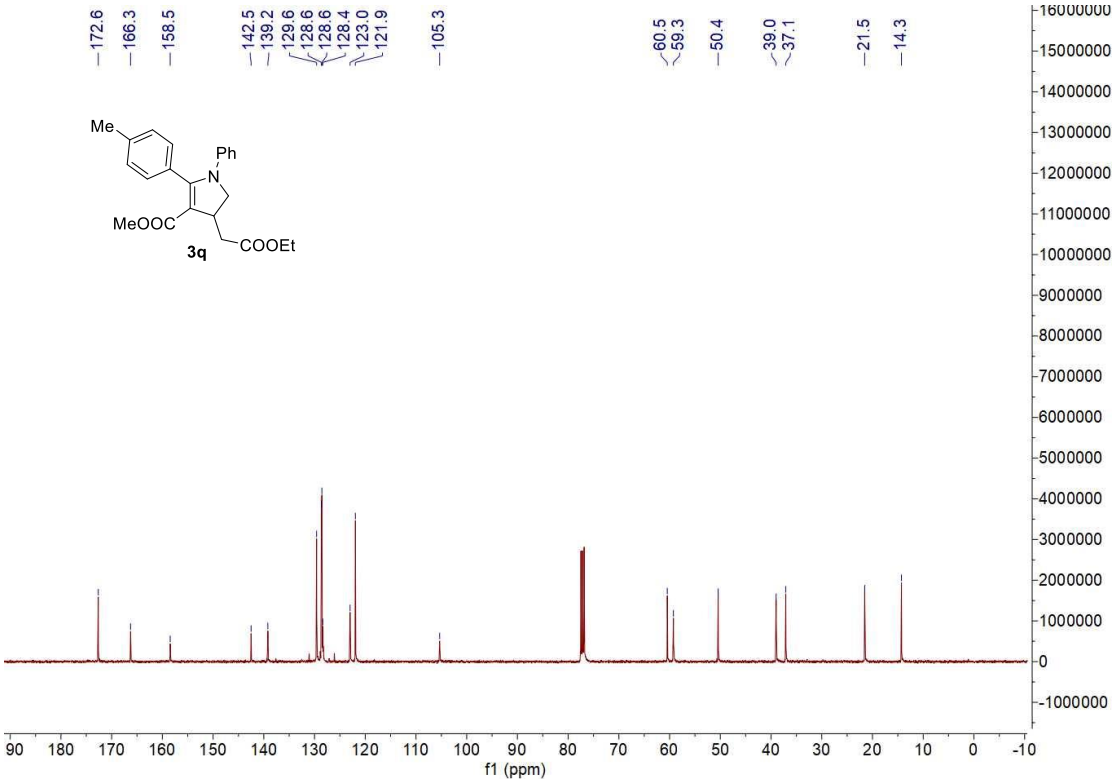
The ^{13}C NMR spectrum of 3p (101 MHz, $CDCl_3$)



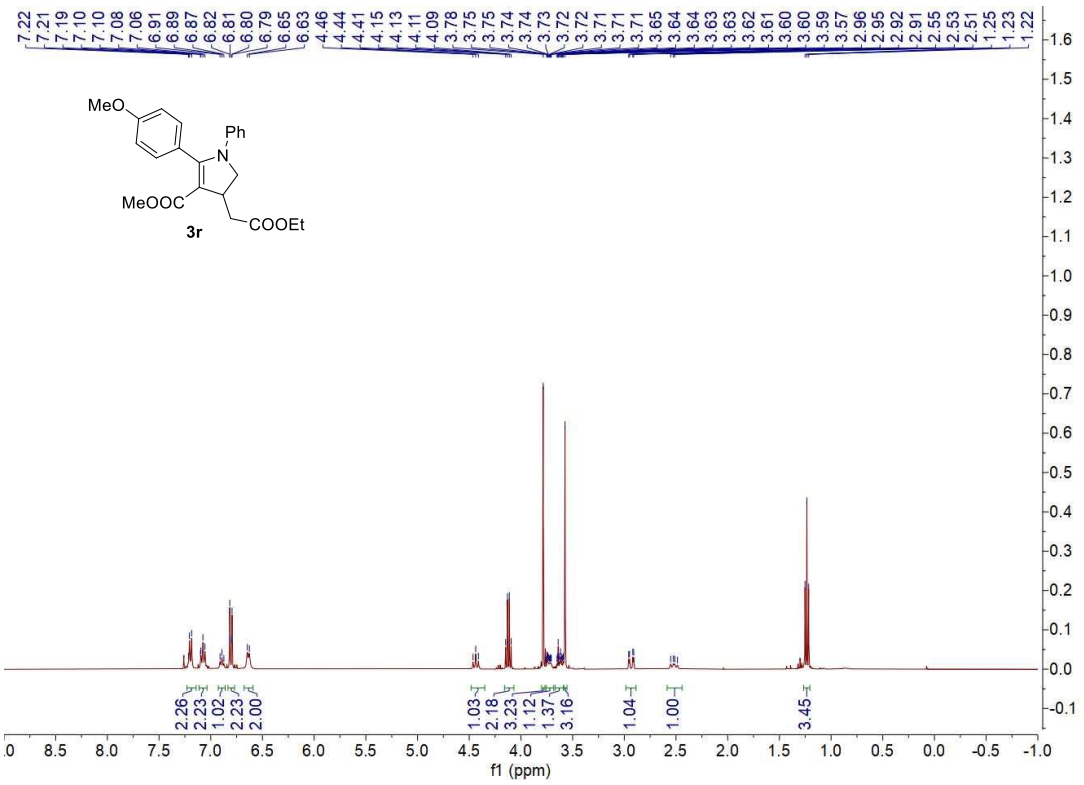
The ^{1}H NMR spectrum of 3q (400 MHz, $CDCl_3$)



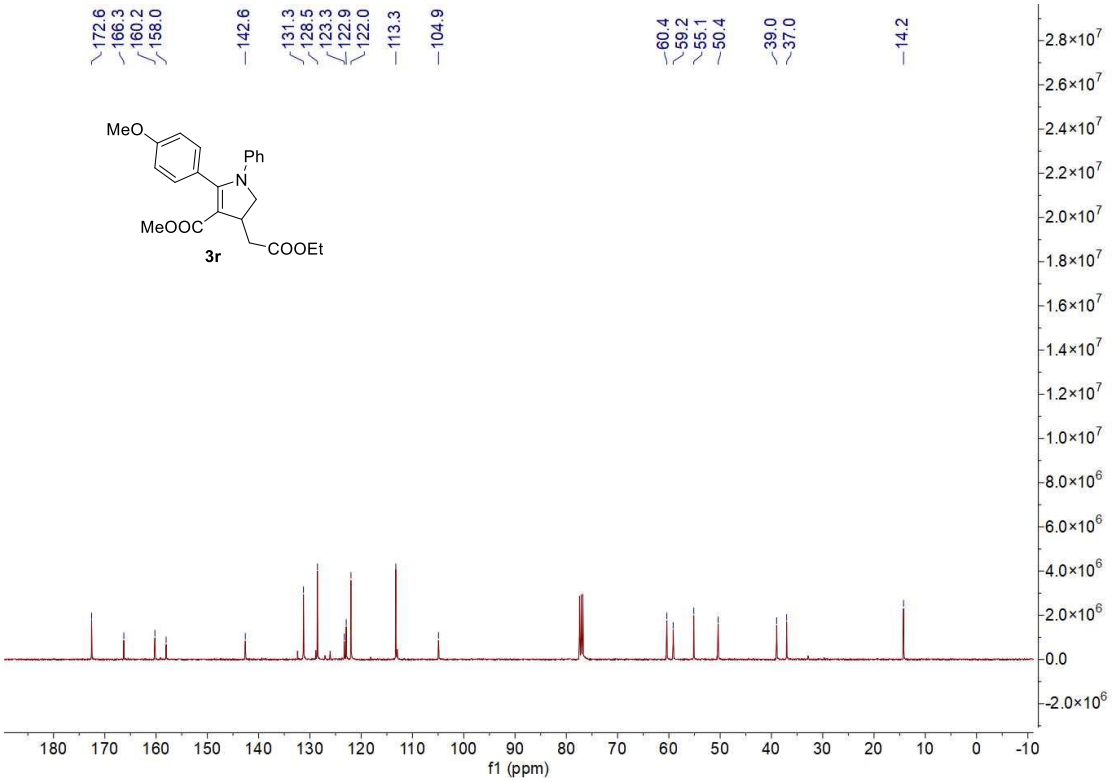
The ^{13}C NMR spectrum of 3q (101 MHz, $CDCl_3$)



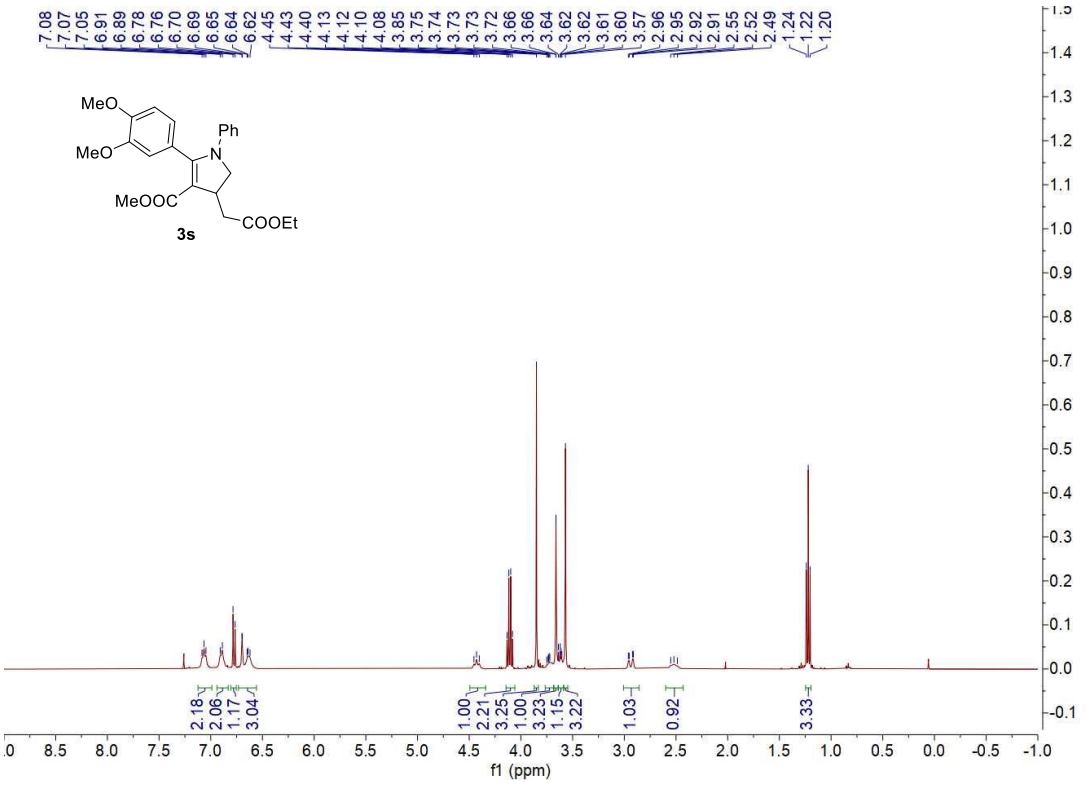
The ^{1}H NMR spectrum of 3r (400 MHz, $CDCl_3$)



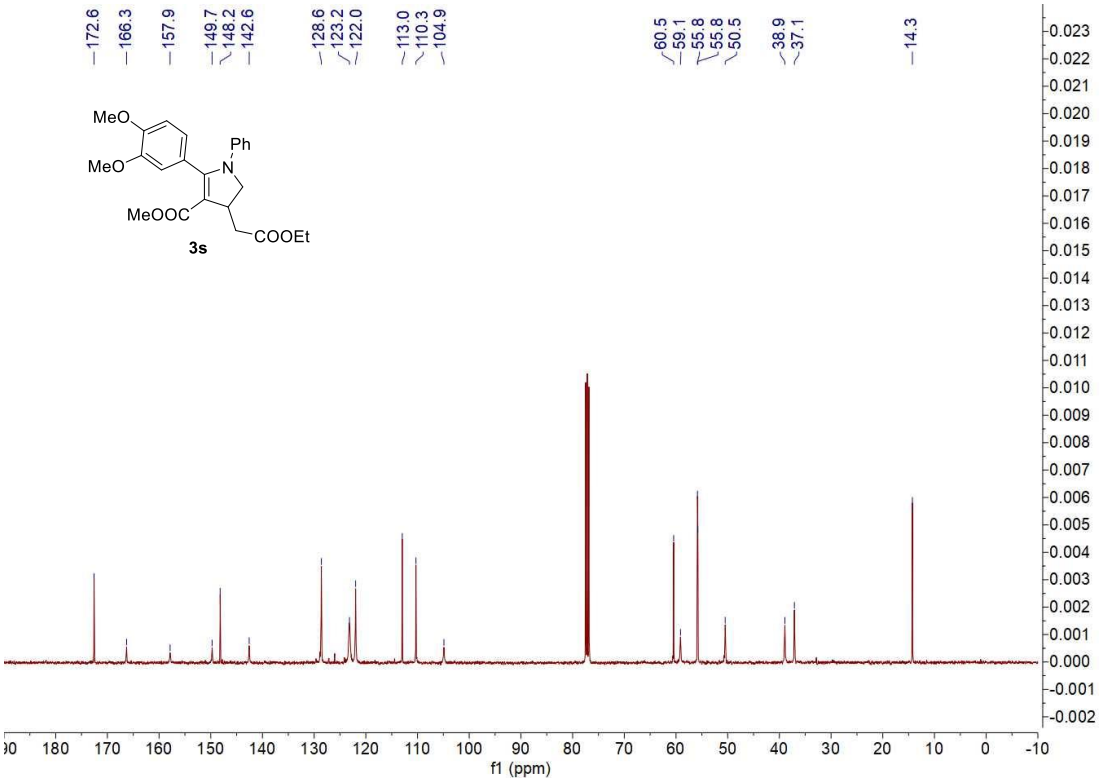
The ^{13}C NMR spectrum of 3r (101 MHz, $CDCl_3$)



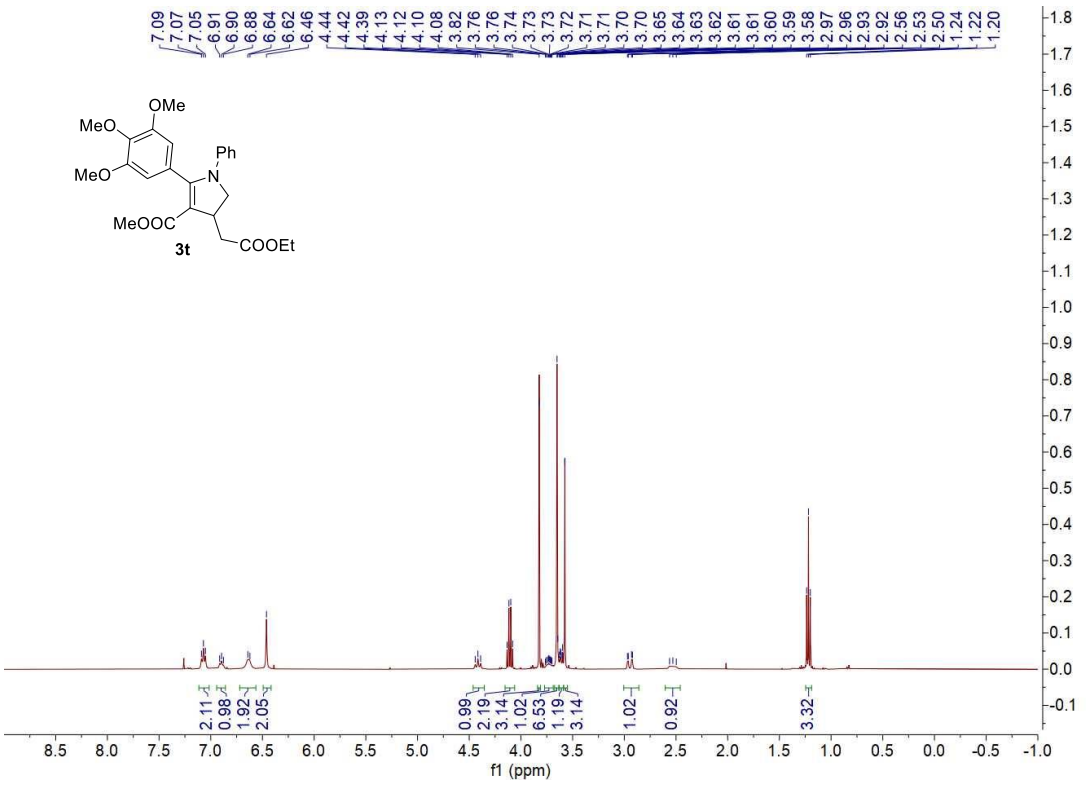
The ^{1}H NMR spectrum of 3s (400 MHz, $CDCl_3$)



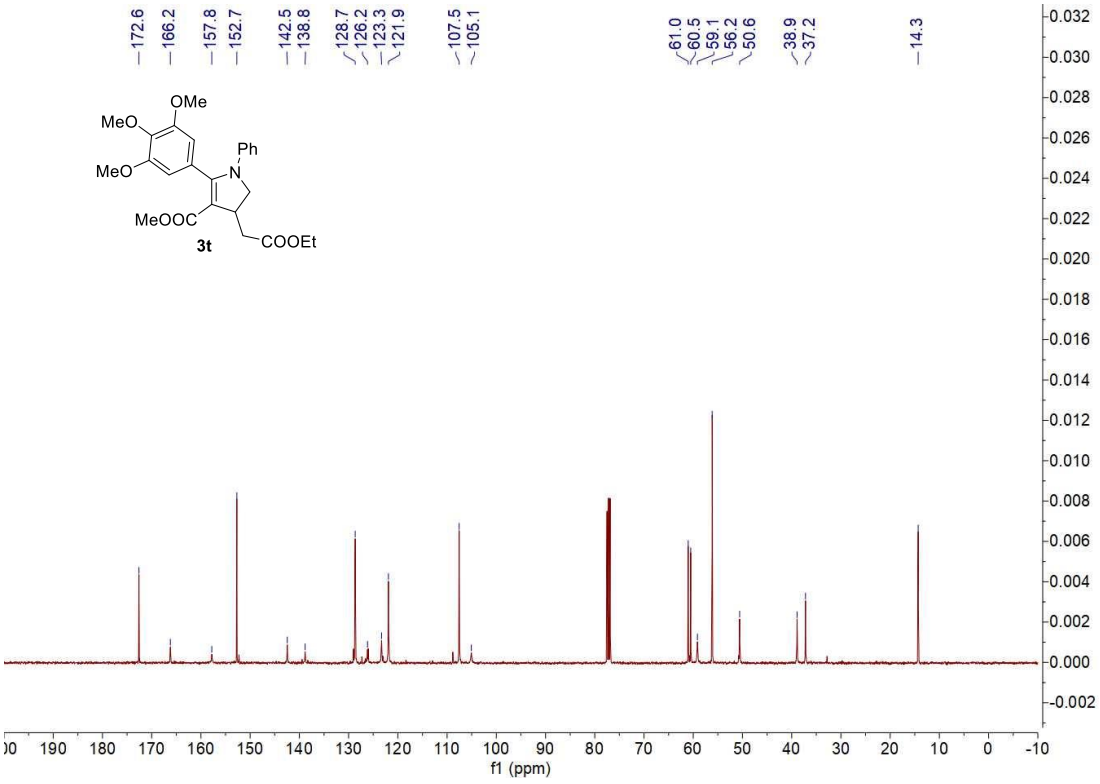
The ^{13}C NMR spectrum of 3s (101 MHz, $CDCl_3$)



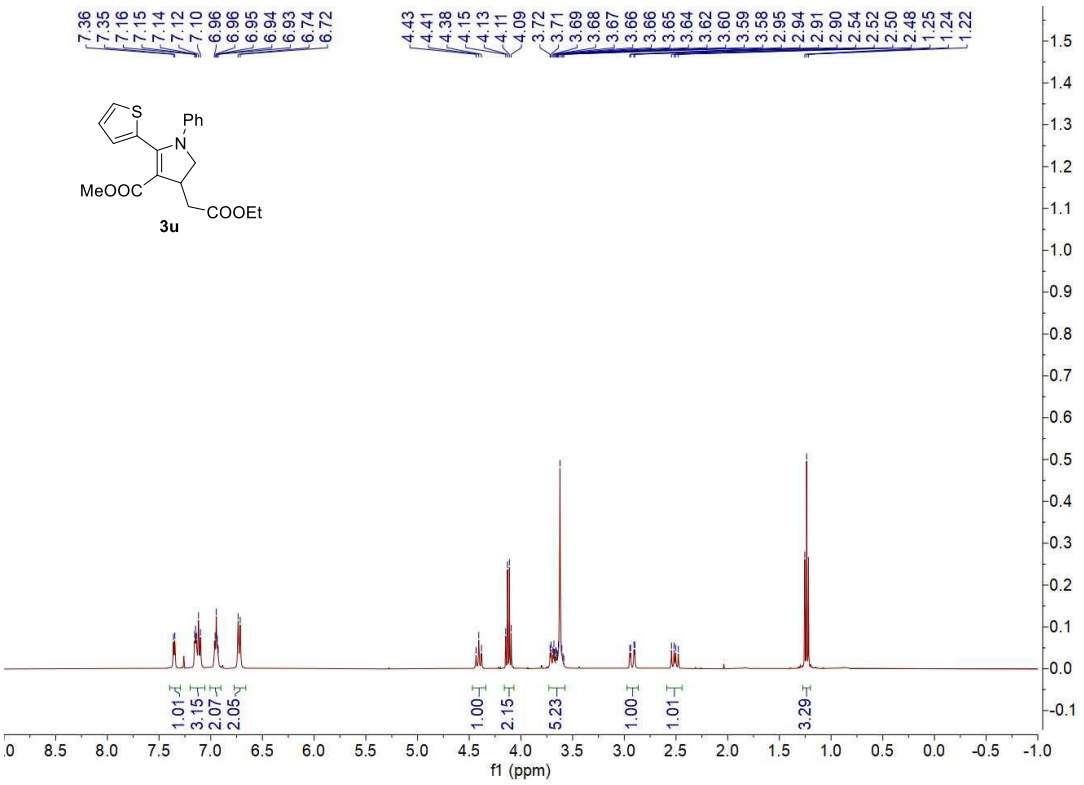
The ^{1}H NMR spectrum of 3t (400 MHz, $CDCl_3$)



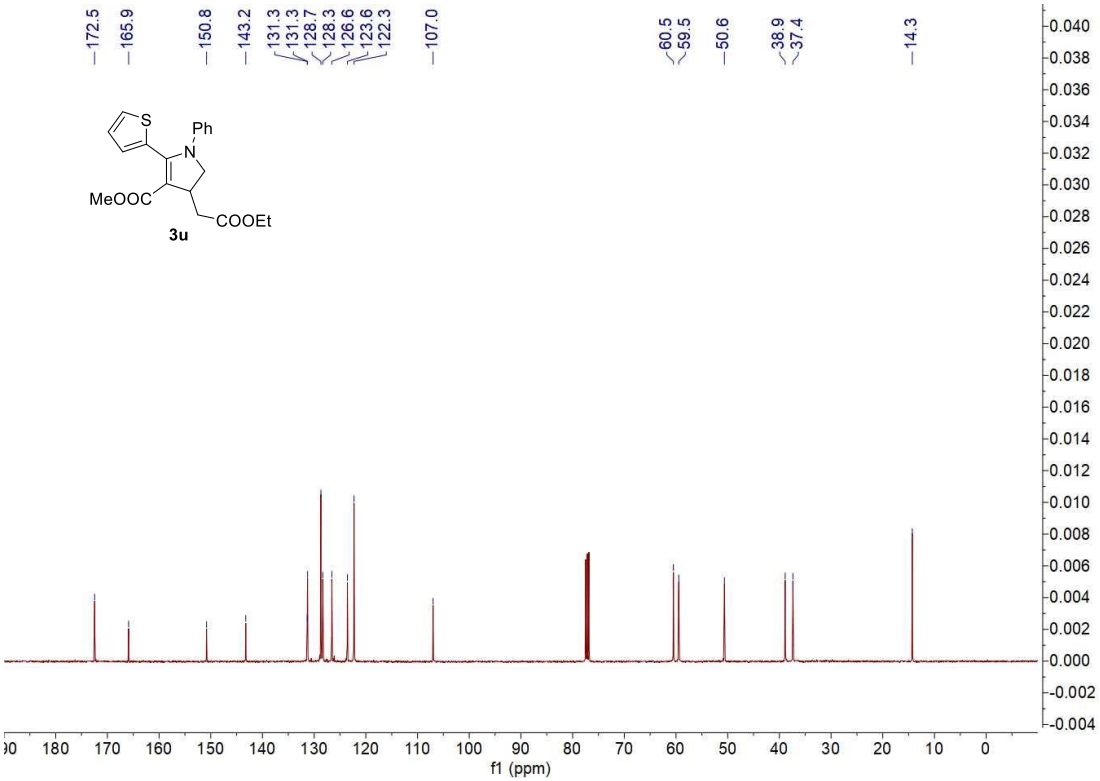
The ^{13}C NMR spectrum of 3t (101 MHz, $CDCl_3$)



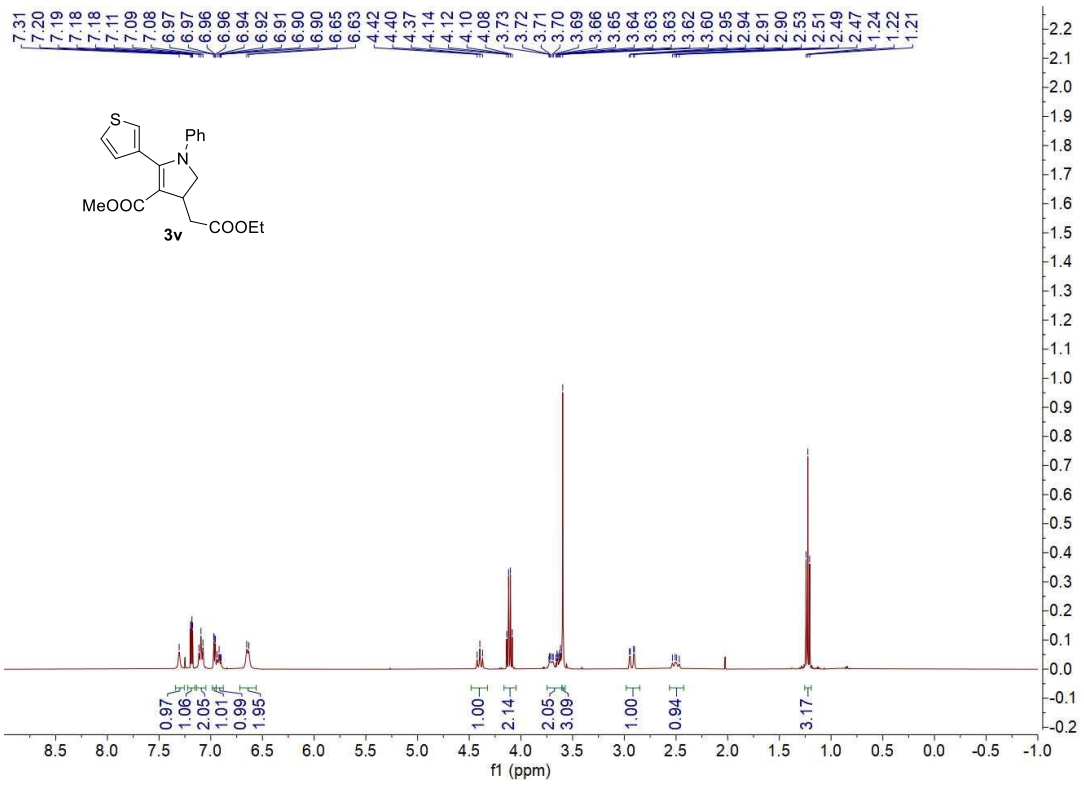
The ^{1}H NMR spectrum of 3u (400 MHz, $CDCl_3$)



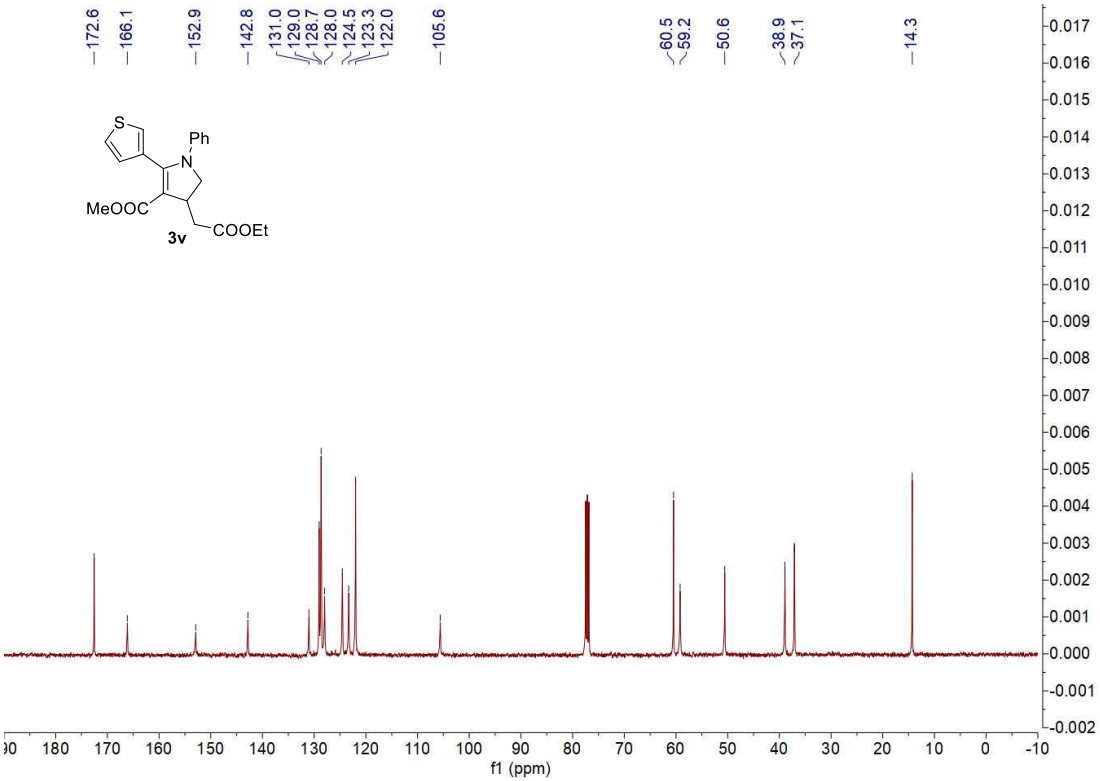
The ^{13}C NMR spectrum of 3u (101 MHz, $CDCl_3$)



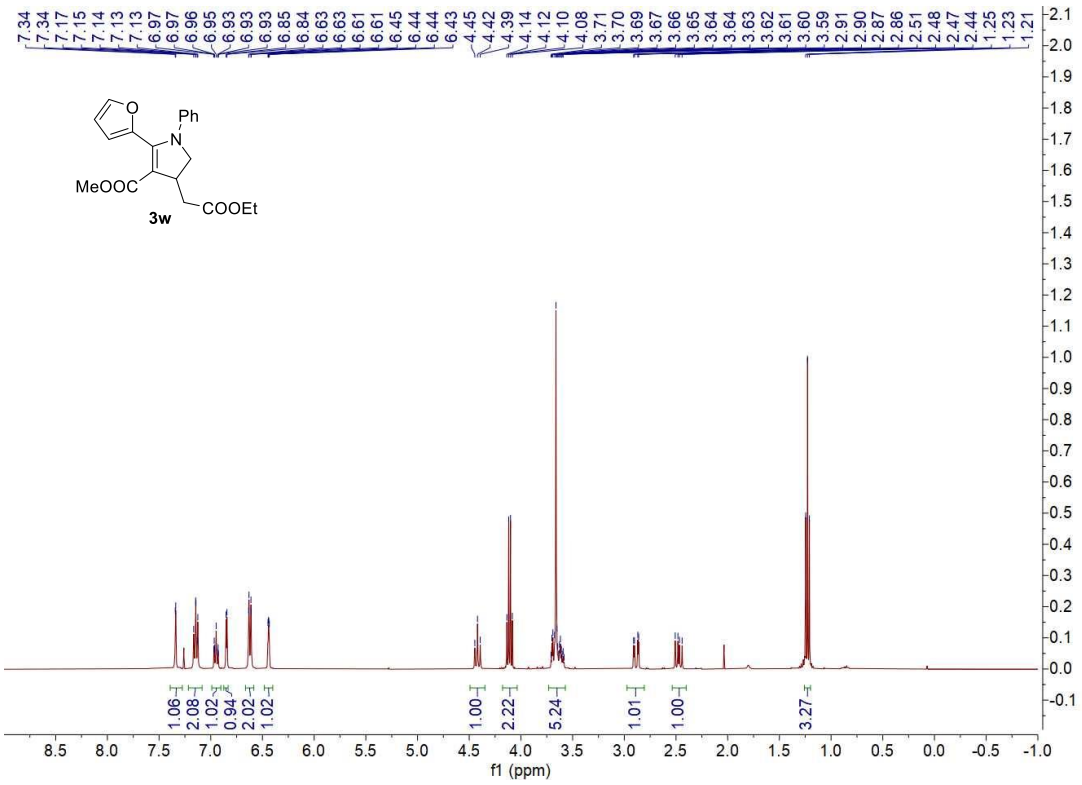
The ^{1}H NMR spectrum of 3v (400 MHz, $CDCl_3$)



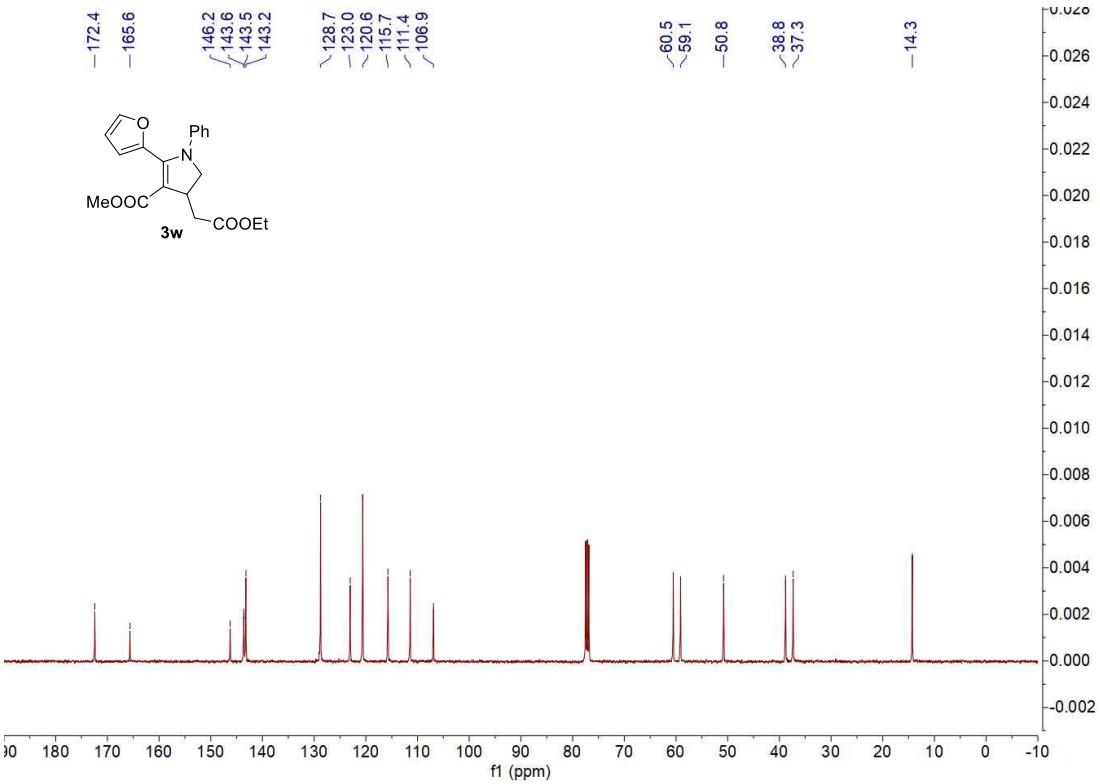
The ^{13}C NMR spectrum of 3v (101 MHz, $CDCl_3$)



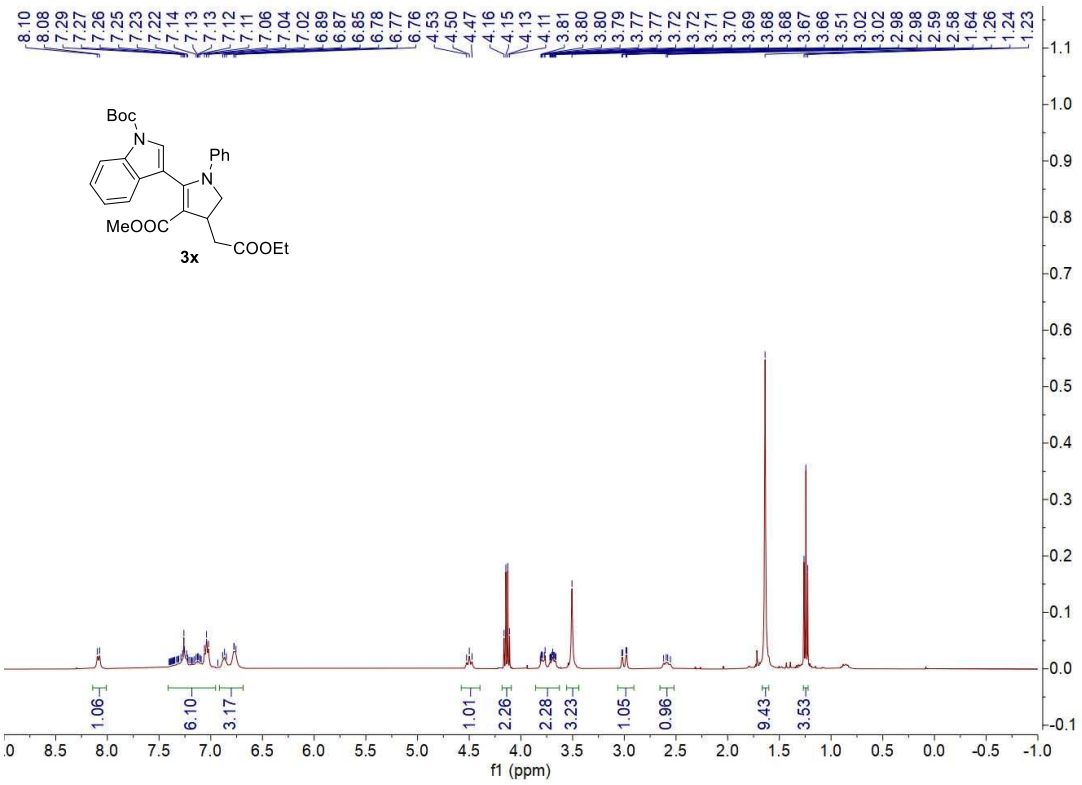
The ^{1}H NMR spectrum of 3w (400 MHz, $CDCl_3$)



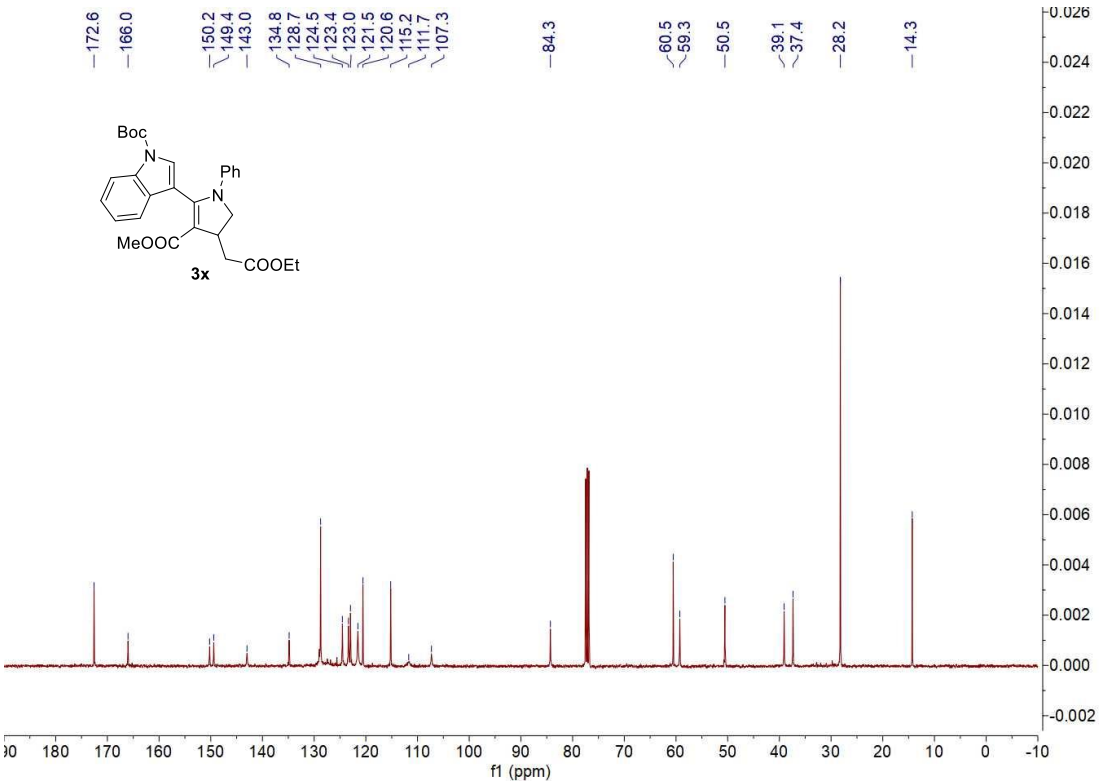
The ^{13}C NMR spectrum of 3w (101 MHz, $CDCl_3$)



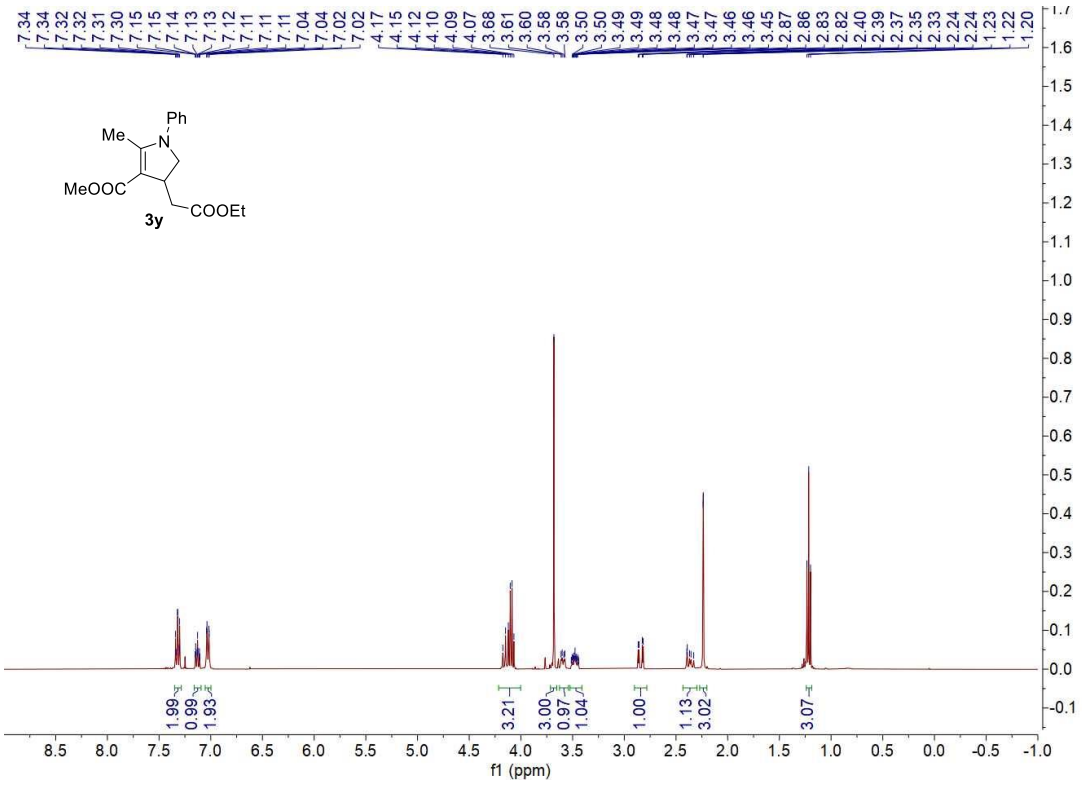
The ^{1}H NMR spectrum of 3x (400 MHz, $CDCl_3$)



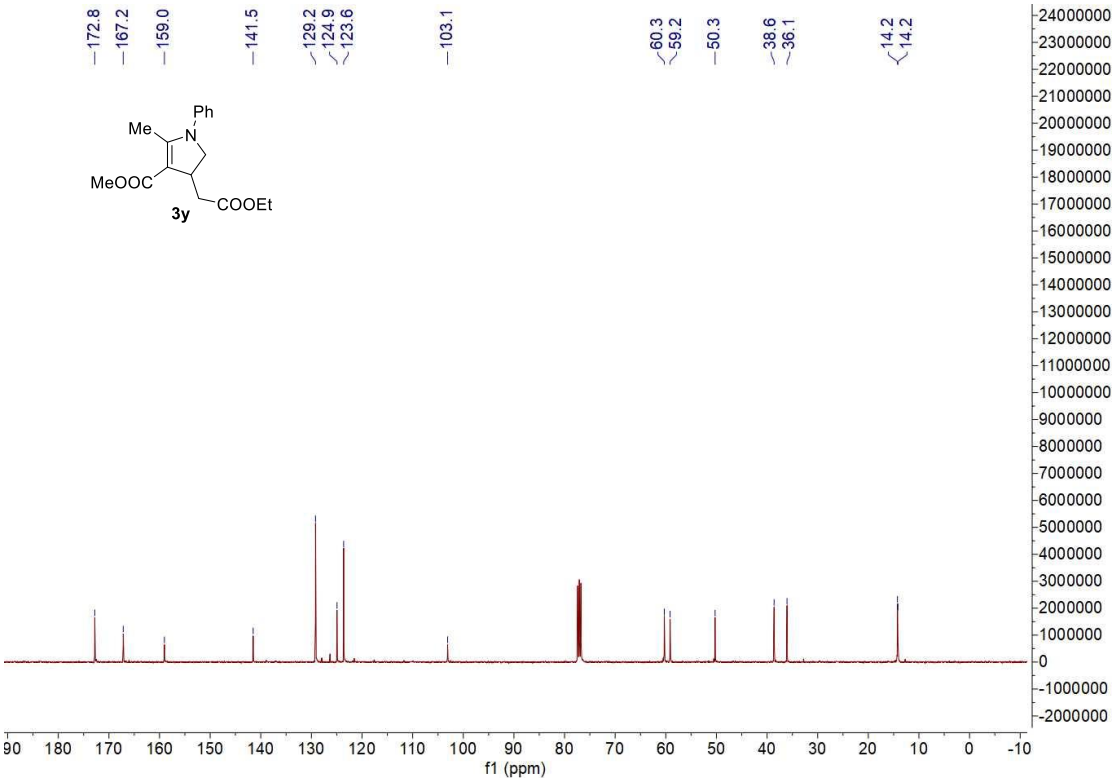
The ^{13}C NMR spectrum of 3x (101 MHz, $CDCl_3$)



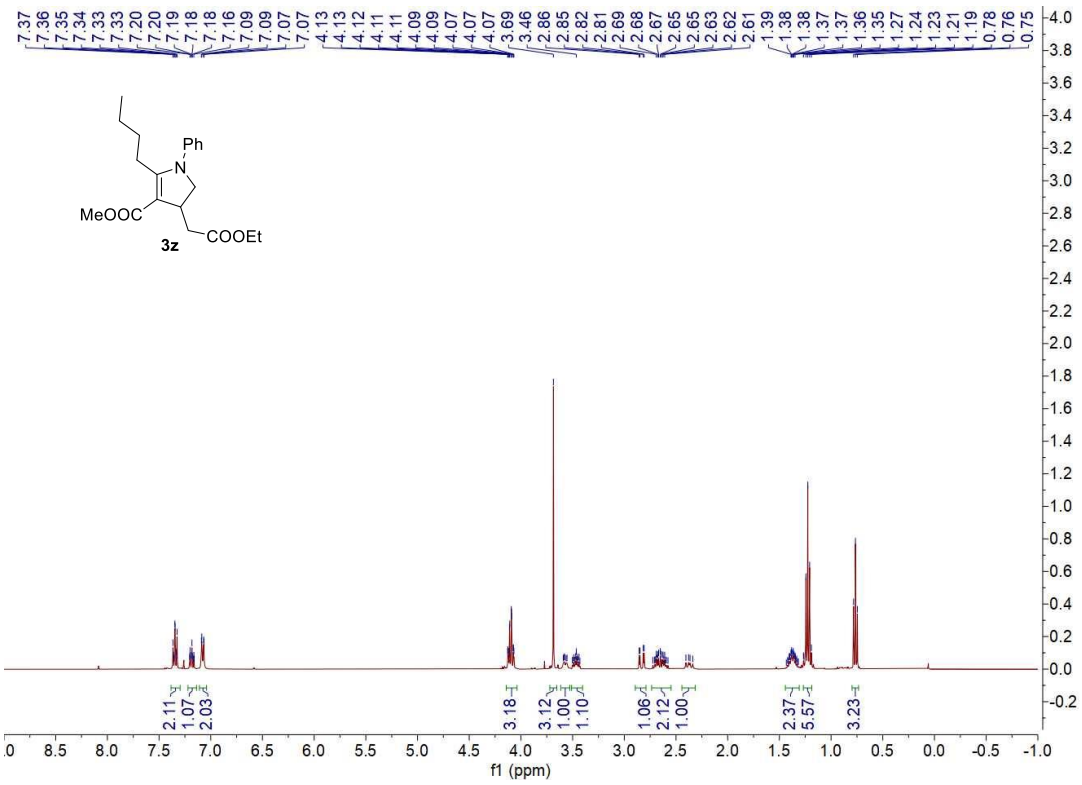
The ^{1}H NMR spectrum of 3y (400 MHz, $CDCl_3$)



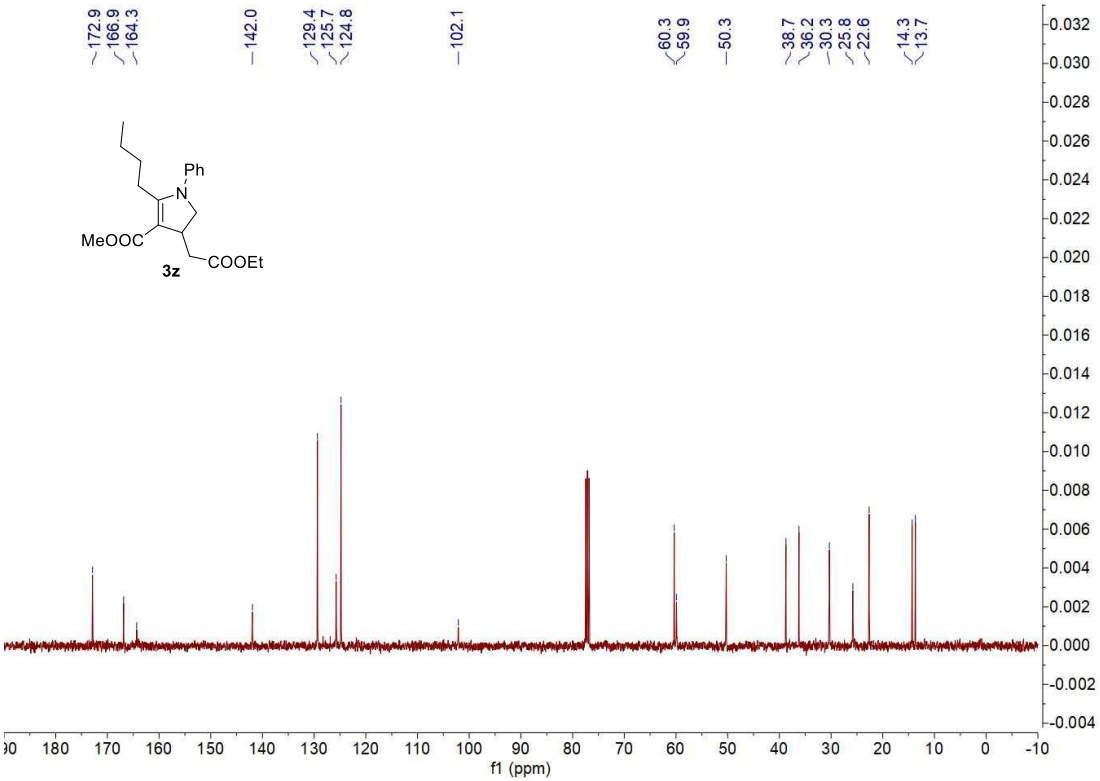
The ^{13}C NMR spectrum of 3y (101 MHz, $CDCl_3$)



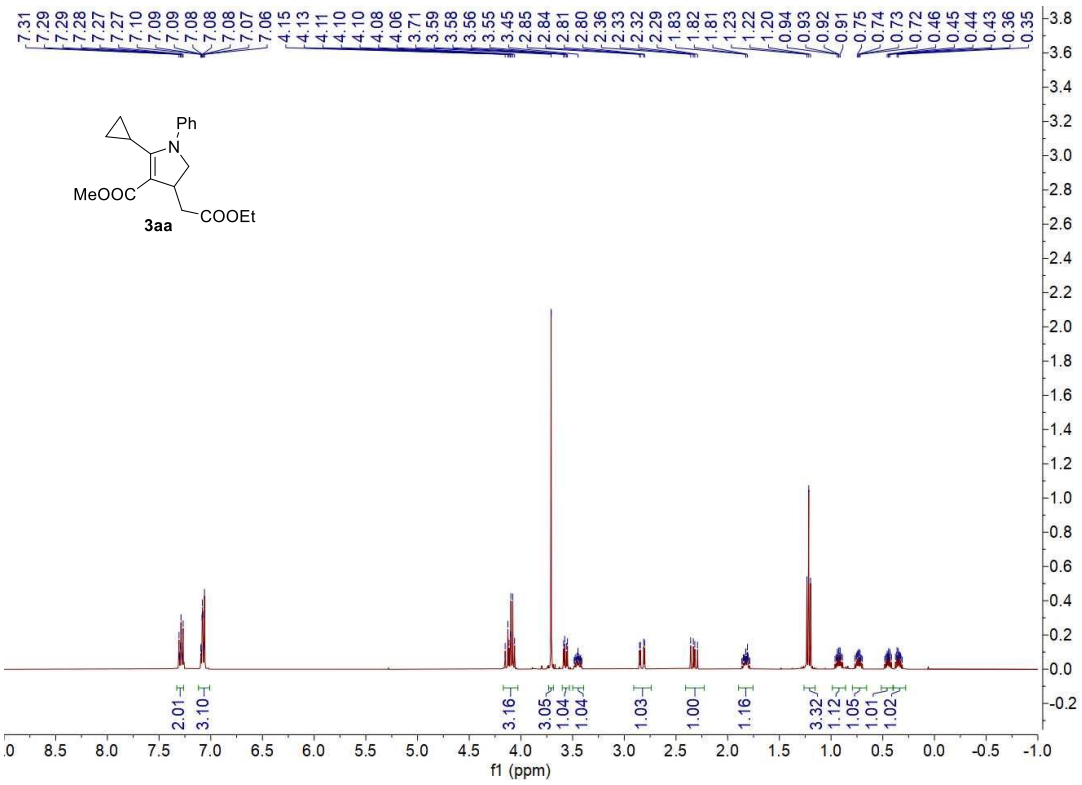
The ^{1}H NMR spectrum of 3z (400 MHz, $CDCl_3$)



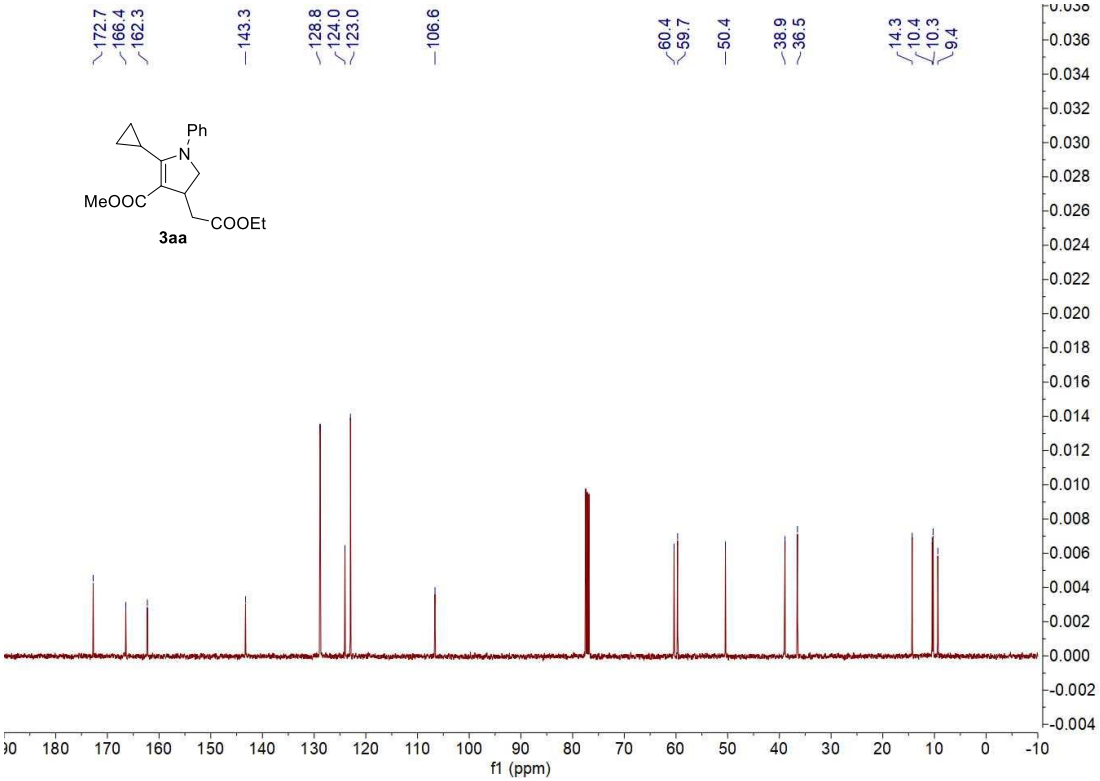
The ^{13}C NMR spectrum of 3z (101 MHz, $CDCl_3$)



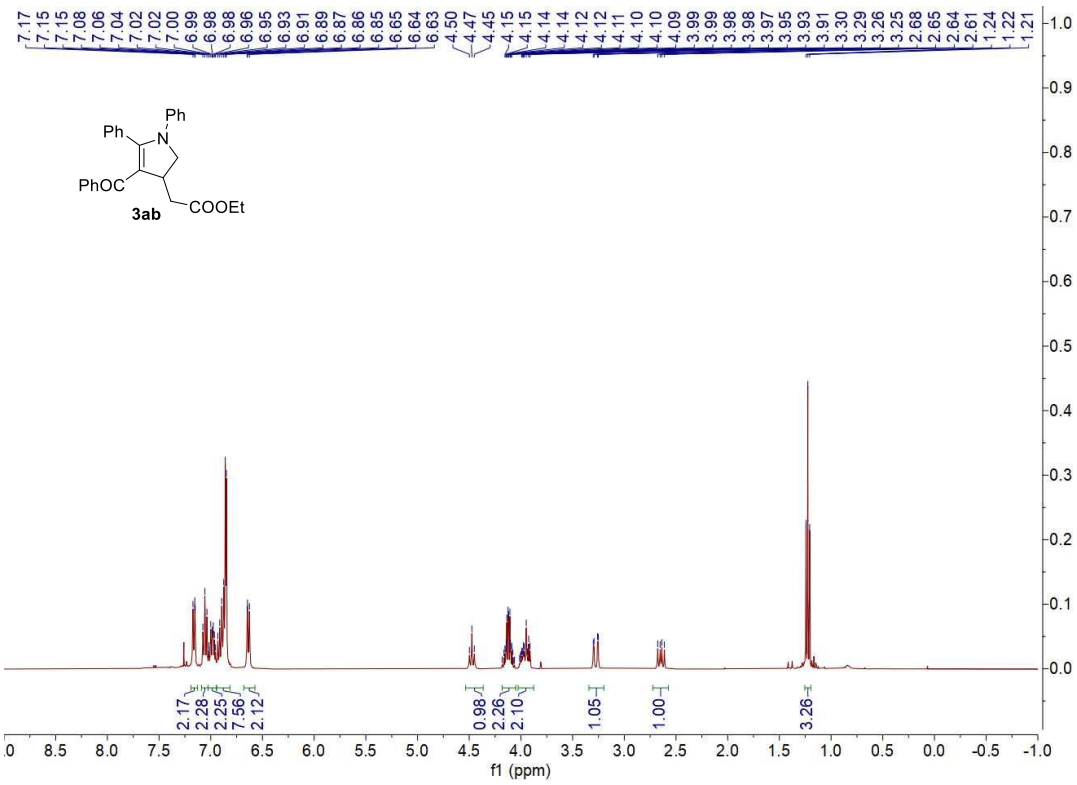
The ^{1}H NMR spectrum of 3aa (400 MHz, $CDCl_3$)



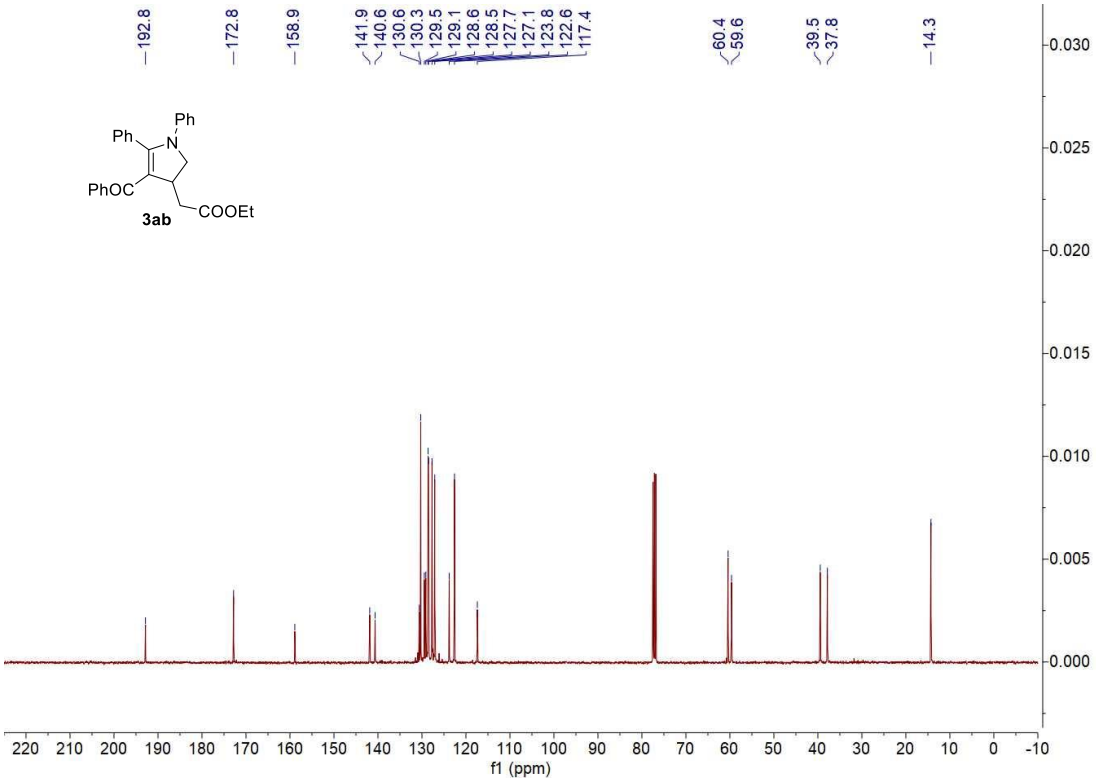
The ^{13}C NMR spectrum of 3aa (101 MHz, $CDCl_3$)



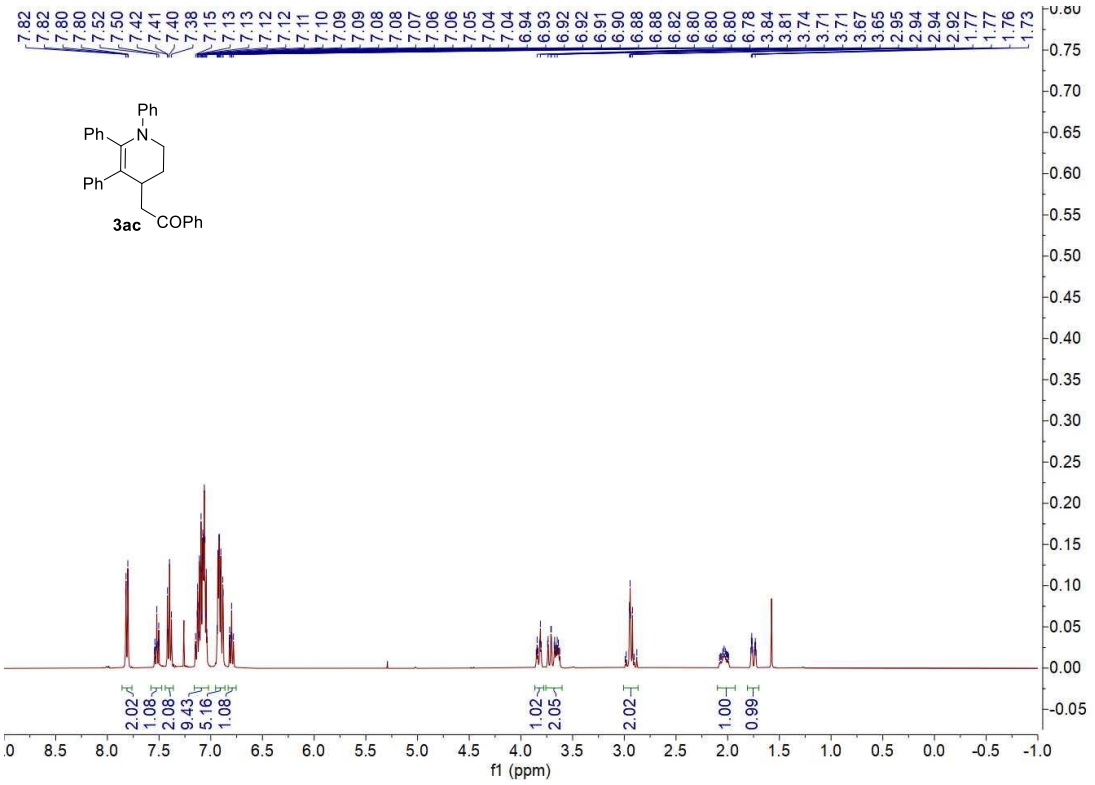
The ^{1}H NMR spectrum of 3ab (400 MHz, $CDCl_3$)



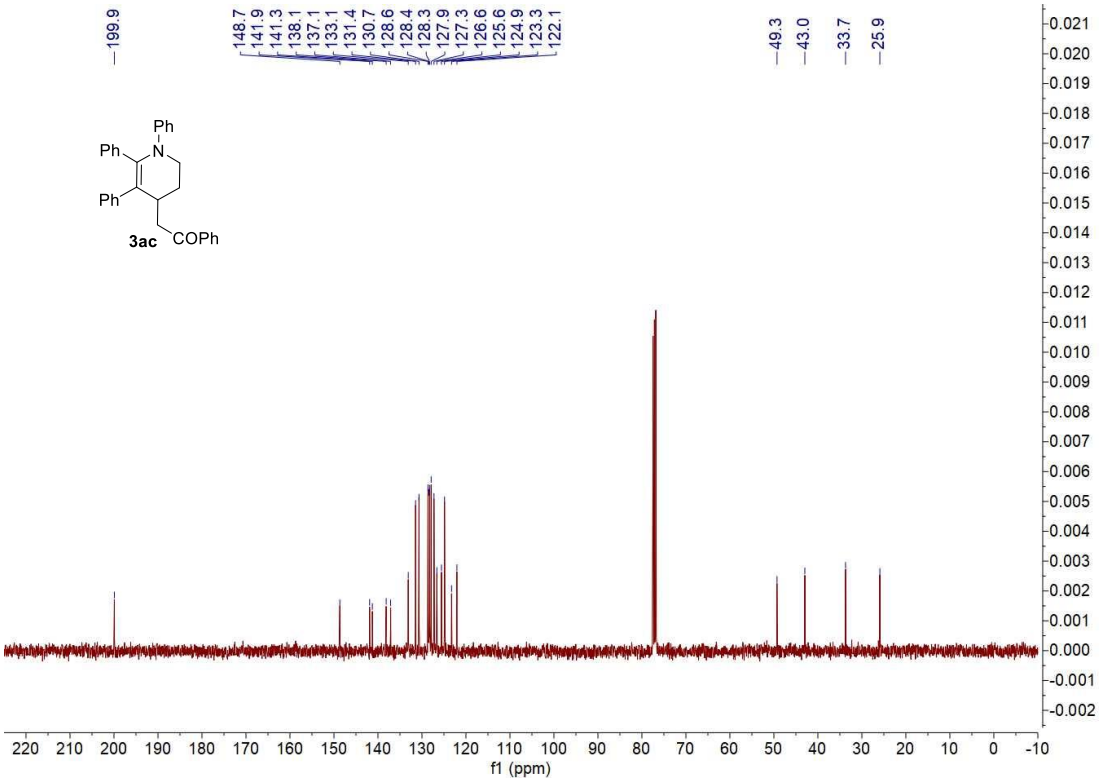
The ^{13}C NMR spectrum of 3ab (101 MHz, $CDCl_3$)



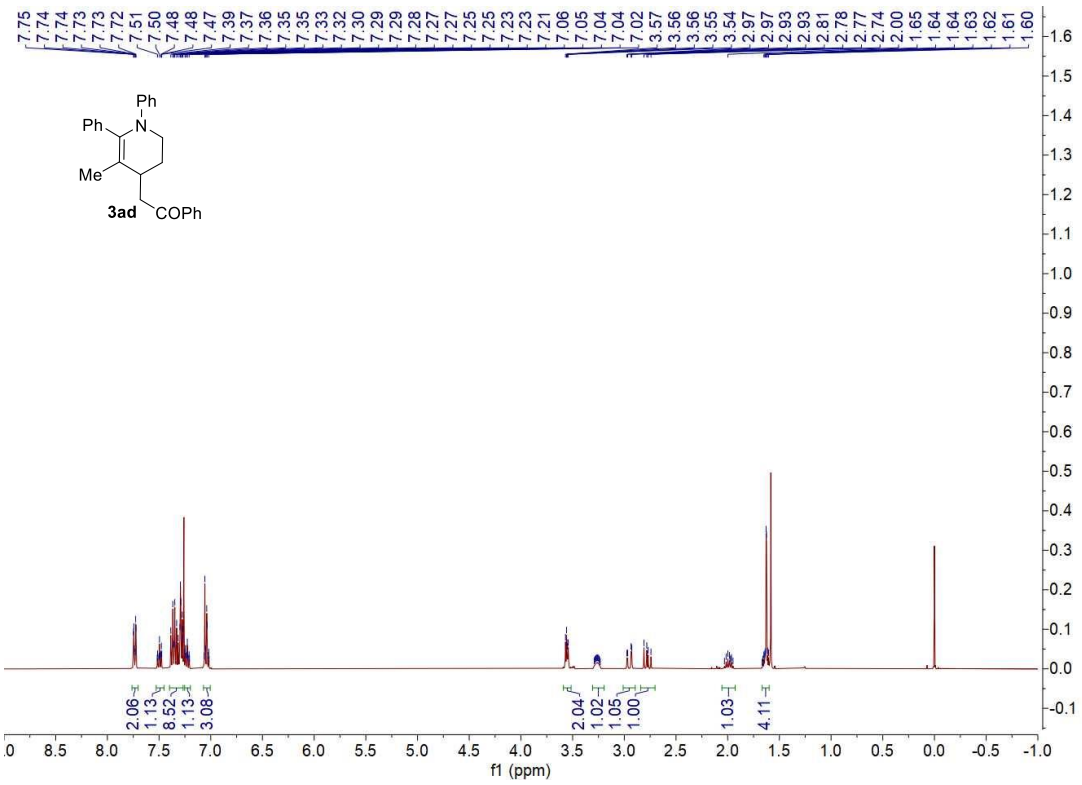
The ^{1}H NMR spectrum of 3ac (400 MHz, $CDCl_3$)



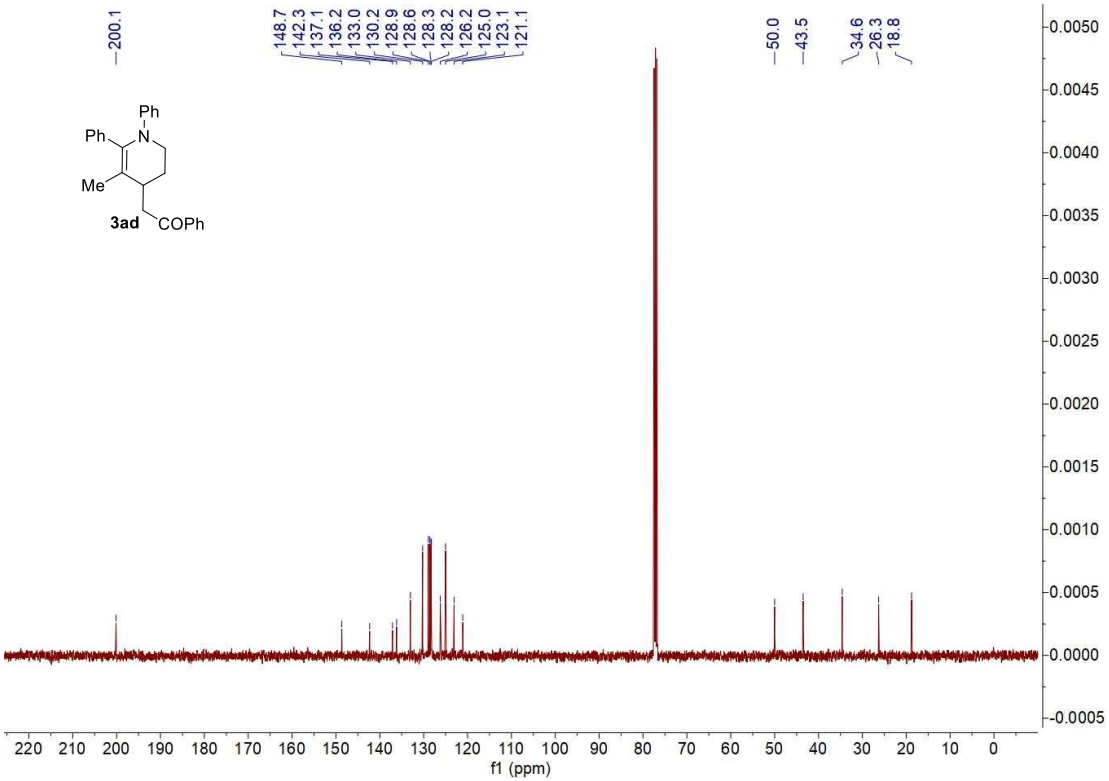
The ^{13}C NMR spectrum of 3ac (101 MHz, $CDCl_3$)



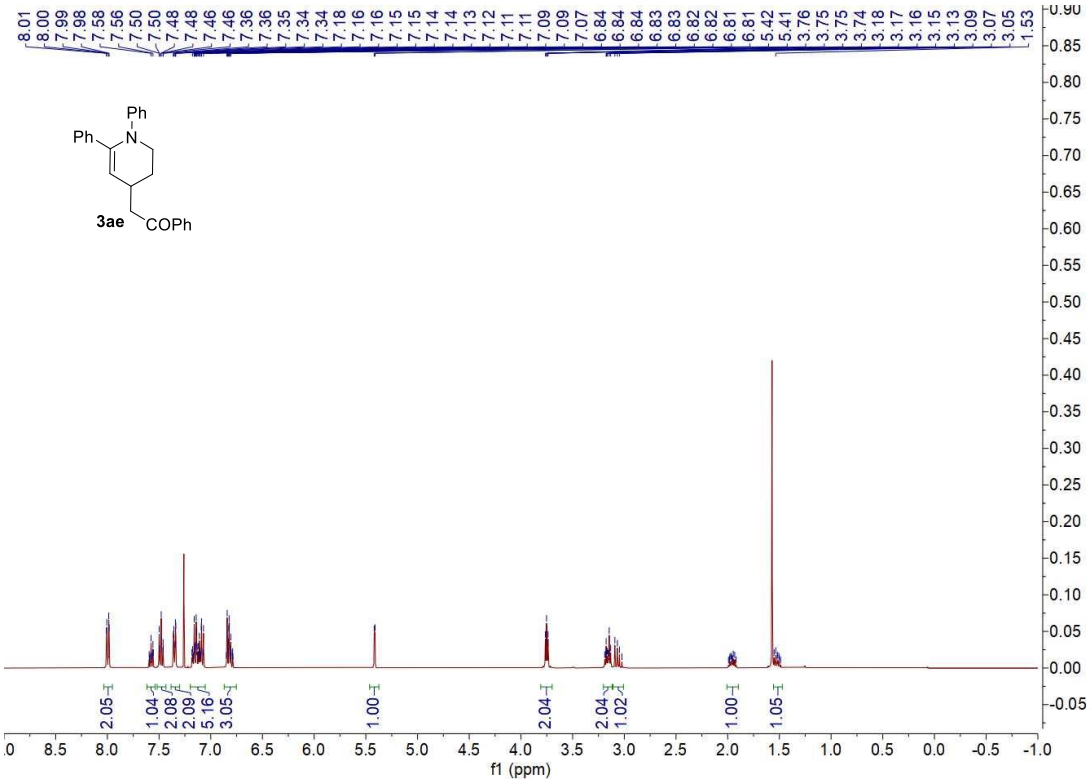
The ^{1}H NMR spectrum of 3ad (400 MHz, $CDCl_3$)



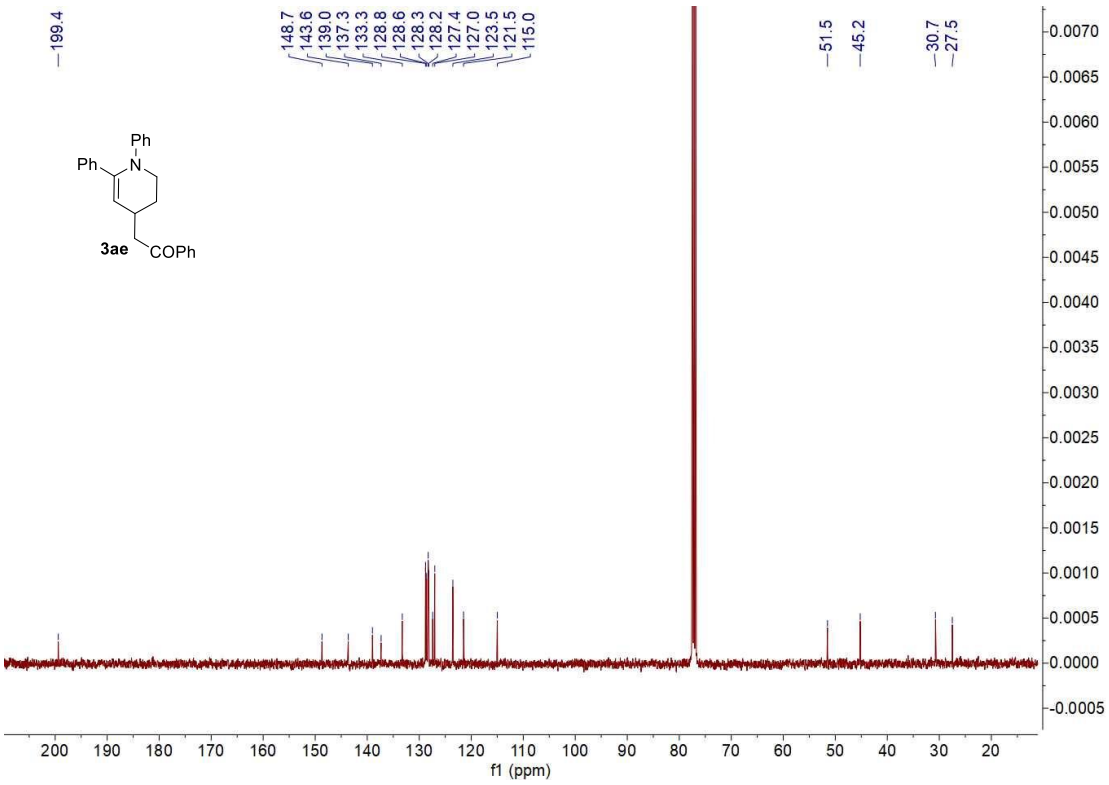
The ^{13}C NMR spectrum of 3ad (101 MHz, $CDCl_3$)



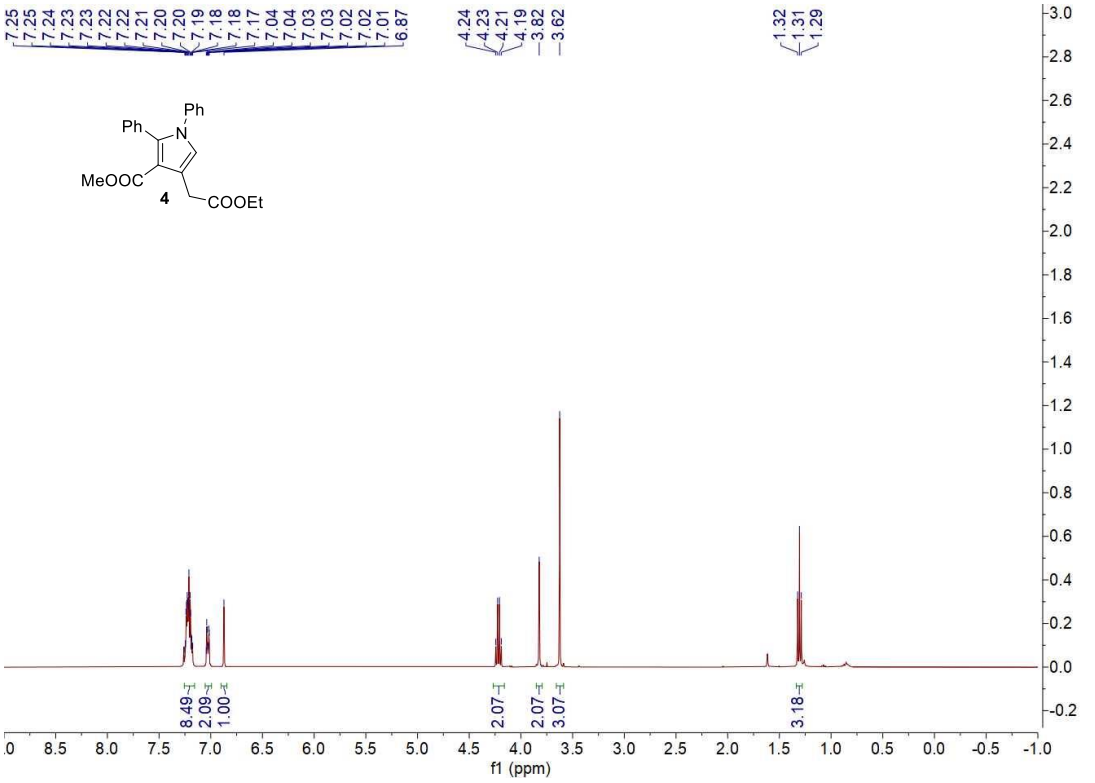
The ^{1}H NMR spectrum of 3ae (400 MHz, $CDCl_3$)



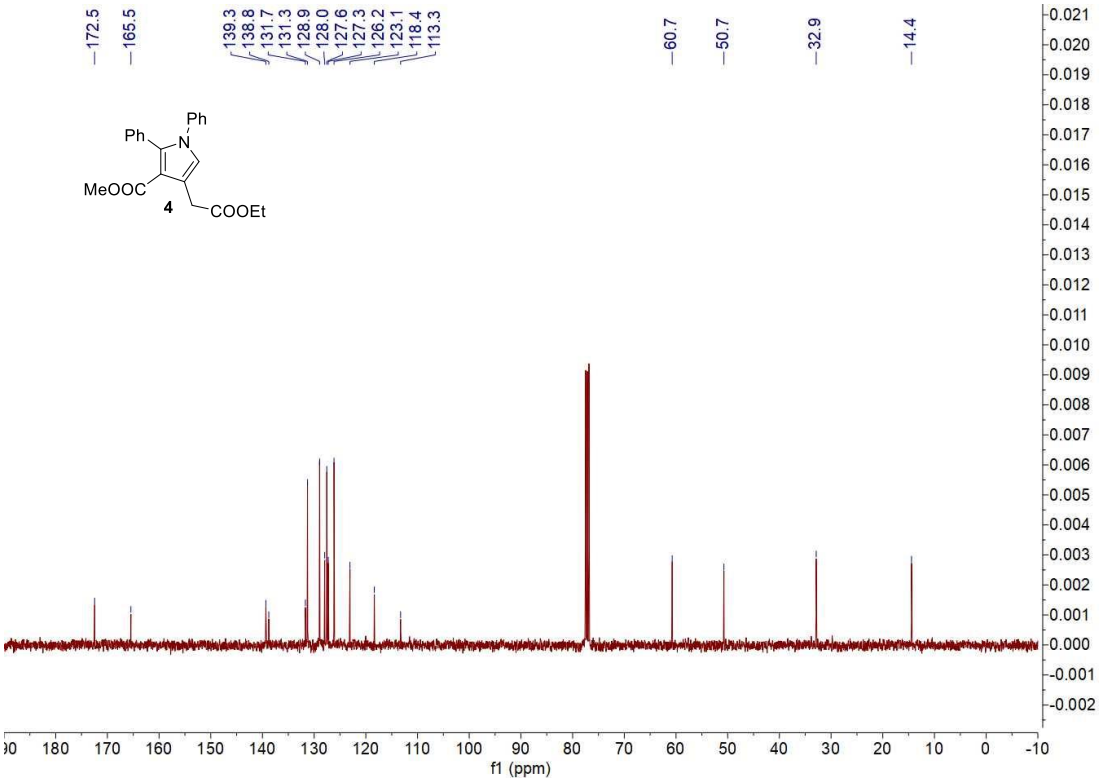
The ^{13}C NMR spectrum of 3ae (101 MHz, $CDCl_3$)



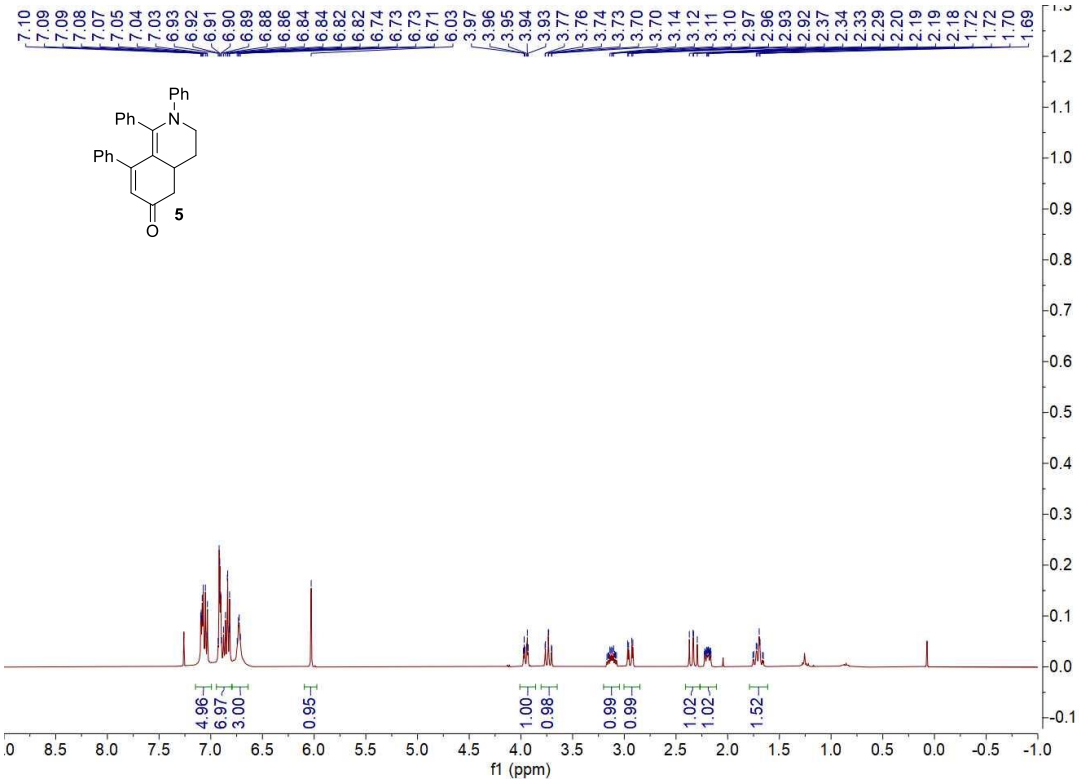
The ^{1}H NMR spectrum of 4 (400 MHz, $CDCl_3$)



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



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



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