Supporting Information

Pd(II) Auxiliaries Assembling and Diverse Transformations *via* Inert C(sp^3)–H Bond Activation

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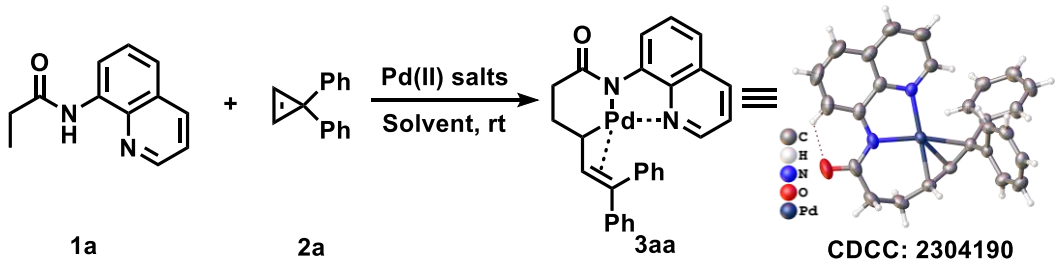
General methods:

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 - 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at RT on 400 or 500 MHz Bruker spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for **^{1}H NMR** spectra and 77.0 ppm for **^{13}C NMR** spectra in $CDCl_3$). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. **HRMS (ESI)** spectra were recorded on a Waters Q-Tof premier TM mass spectrometer.

Table S1. Optimization of reaction conditions[a,b]

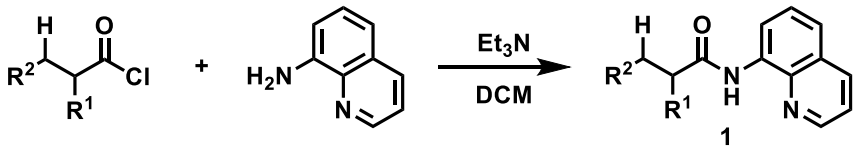


Entry	Pd salt	Solvent	Yield(%)[b]
1	PdI_2	DCM	0
2	$PdCl_2$	DCM	20
3	$Pd(acac)_2$	DCM	0
4	$PdCl_2(PPh_3)_2$	DCM	0
5	$Pd(TFA)_2$	DCM	45
6	$Pd(OAc)_2$	DCM	81
7	$Pd(OAc)_2$	DCE	75
8	$Pd(OAc)_2$	TCE	40
9	$Pd(OAc)_2$	$CHCl_3$	52
10	$Pd(OAc)_2$	THF	12
11	$Pd(OAc)_2$	ACN	10
12	$Pd(OAc)_2$	Tol.	65
13	$Pd(OAc)_2$	PhCl	35
14[c]	$Pd(OAc)_2$	DCM	90
15[d]	$Pd(OAc)_2$	DCM	91

[a]Unless otherwise noted, reactions were carried out using **1a** (0.20 mmol), **2a** (0.60 mmol), $Pd(OAc)_2$ (0.20 mmol) in DCM (0.05 M, 4 mL) at room temperature. [b]Isolated yields. [c]$Pd(OAc)_2$-loading: 130 mol %. [d]$Pd(OAc)_2$-loading: 150 mol %. DCM = dichloromethane, DCE = 1,2-Dichloroethane, TCE = 1,1,2,2-Tetrachloroethane, ACN = Acetonitrile, Tol. = toluene, THF = tetrahydrofuran.

General procedure for amide compounds and their spectral data:

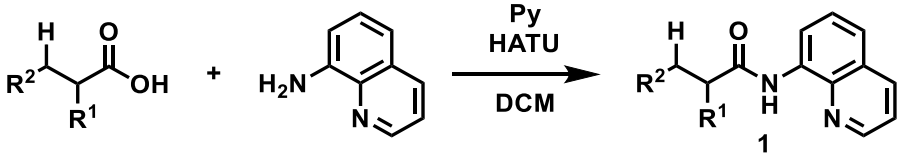
General procedure A for the synthesis of amide compounds:



A mixture of acyl chloride (7.5 mmol, 1.5 equiv.), 8-aminoquinoline (5 mmol, 1.0 equiv.), and triethylamine (10 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) was

stirred at room temperature overnight. The reaction mixture was then washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give desired amide compounds **1**.

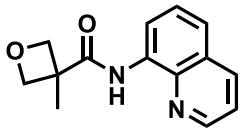
General procedure B for the synthesis of amide compounds:



A mixture of carboxylic acid (6.0 mmol, 1.2 equiv.), 8-aminoquinoline (5 mmol, 1.0 equiv.), 2-(7-azabenzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate (6.0 mmol, 1.2 equiv.) and pyridine (10 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The reaction mixture was then washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography to give desired amide compounds **1**.

Amide compounds 1a-1d, 1f, 1h-1m, 1o-1s were prepared to the known literatures[1-6]

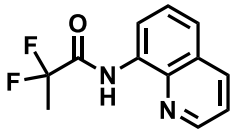
3-Methyl-*N*-(quinolin-8-yl)oxetane-3-carboxamide (1e):



The title compound was prepared according to the general procedure B. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (2:3) as the eluent

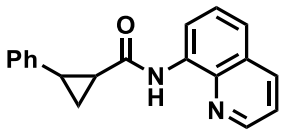
the desired product **1e** as white solid in 82% yield (992.0 mg), Mp. 86 - 87 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.2 (s, 1H), 8.85 – 8.75 (m, 2H), 8.22 – 8.15 (m, 1H), 7.62 – 7.51 (m, 2H), 7.51 – 7.48 (m, 1H), 5.16 (d, *J* = 6.0 Hz, 2H), 4.60 (d, *J* = 6.0 Hz, 2H), 1.85 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.8, 148.4, 138.5, 136.2, 134.0, 127.9, 127.4, 121.8, 121.7, 116.5, 80.0, 46.6, 22.4; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{14}H_{15}N_2O_2$: 243.1134. Found: 243.1136.

2,2-Difluoro-*N*-(quinolin-8-yl)propenamide (1g):



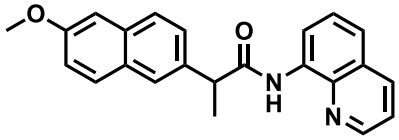
The title compound was prepared according to the general procedure B. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (1:4) as the eluent the desired product **1g** as white solid in 75% yield (883.8mg), Mp. 57 - 58 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.73 (s, 1H), 8.88 – 8.82 (m, 1H), 8.79 – 8.71 (m, 1H), 8.82 – 8.14 (m, 1H), 7.63 – 7.52 (m, 2H), 7.52 – 7.45 (m, 1H), 1.98 (t, *J* = 19.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.6 (t, *J* = 29.0 Hz), 148.7, 138.6, 136.3, 132.8, 127.9, 127.1, 123.0, 121.9, 117.3 (t, *J* = 250.9 Hz), 117.1, 21.1 (t, *J* = 25.5 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -66.19; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{12}H_{10}F_2N_2O$: 237.0839. Found: 237.0838.

2-Phenyl-*N*-(quinolin-8-yl)cyclopropane-1-carboxamide (1n):



The title compound was prepared according to the general procedure B. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (1:4) as the eluent the desired product **1n** as white solid in 70% yield (1006.3 mg), Mp. 80 - 81 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 8.82 – 8.71 (m, 2H), 8.20 – 8.10 (m, 1H), 7.57 – 7.47 (m, 2H), 7.47 – 7.41 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.14 (m, 3H), 2.72 – 2.63 (m, 1H), 2.10 – 2.02 (m, 1H), 1.84 – 1.76 (m, 1H), 1.48 – 1.39 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.5, 148.0, 140.6, 138.1, 136.4, 134.5, 128.5, 127.9, 127.4, 126.4, 126.1, 121.6, 121.4, 116.4, 28.2, 26.1, 16.6; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{19}H_{17}N_2O$: 289.1341. Found: 289.1340.

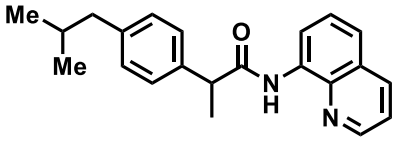
2-(6-Methoxynaphthalen-2-yl)-*N*-(quinolin-8-yl)propenamide (1t):



The title compound was prepared according to the general procedure B. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (1:4) as the eluent the desired product **1t** as white solid in 60% yield (1067.4 mg), Mp. 77 - 78 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.95 (s, 1H), 8.83 – 8.74 (m, 1H), 8.52 – 8.45 (m, 1H), 7.92 – 7.80 (m, 2H), 7.72 – 7.66 (m, 2H), 7.57 – 7.51 (m, 1H), 7.44 – 7.36 (m, 1H), 7.32 – 7.24 (m, 1H), 7.18 – 7.08 (m, 2H), 7.06 – 7.01 (m, 1H), 4.01 (q, J = 7.2 Hz, 1H), 3.78 (s, 3H), 1.73 (t, J = 7.1 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.6, 157.4,

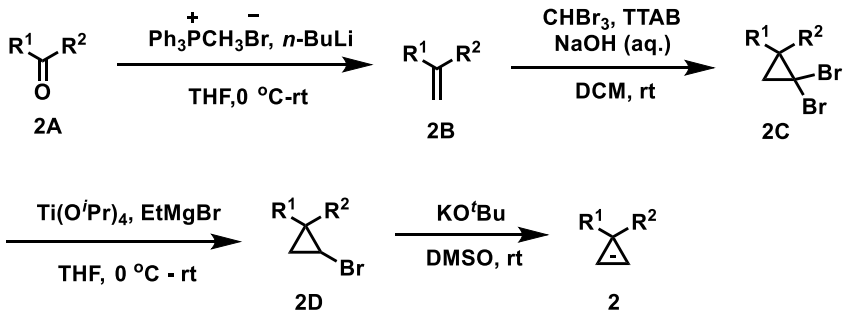
147.8, 138.0, 136.1, 135.9, 134.2, 133.6, 129.1, 128.9, 127.5, 127.4, 127.0, 126.0, 126.0, 121.2, 121.2, 118.8, 115.9, 105.3, 55.0, 48.3, 18.5; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{23}H_{21}N_2O_2$: 357.1603. Found: 357.1602.

2-(4-Isobutylphenyl)-N-(quinolin-8-yl)propenamide (1u):



The title compound was prepared according to the general procedure B. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (1:4) as the eluent the desired product **1u** as white solid in 65% yield (1076.5 mg), Mp. 50 - 51 ºC; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 8.81 – 8.73 (m, 1H), 8.69 – 8.61 (m, 1H), 8.12 – 8.04 (m, 1H), 7.53 – 7.41 (m, 2H), 7.41 – 7.33 (m, 3H), 7.19 – 7.13 (m, 2H), 3.90 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.93 – 1.78 (m, 1H), 1.68 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.7, 147.7, 140.4, 138.0, 137.6, 135.8, 134.2, 129.4, 129.1, 127.4, 127.2, 126.9, 121.1, 115.9, 47.9, 44.7, 29.9, 22.1, 18.3; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{22}H_{25}N_2O$: 333.1967. Found: 333.1968.

General procedure for cyclopropenes and their spectral data:



To a stirred solution of Ph_3PCH_3Br (100 mmol) in THF (150 mL) at 0 °C was added 1.6 M *n*-butyllitium (90 mmol) dropwise over 60 minutes. The reaction mixture was stirred for 2 hours at room temperature. Ketone **2A** (50 mmol) in THF (15 mL) was added dropwise to the cooled reaction mixture at 0 °C via cannular. The reaction was then stirred at room temperature for 48 hours, quenched with saturated NH_4Cl (40 mL), diluted with water (30 mL) and extracted with EtOAc (3 x 30 mL). The combined organic extracts were washed with brine (2 x 30 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was dissolved in hexane and triphenylphosphine oxide was filtered off. The filtrate solution was then concentrated under reduced pressure. The product **2B** was isolated by flash column chromatography (eluent: EA/PE = 5%).

A solution of 10 M aqueous sodium hydroxide (200 mmol) was added to alkyltrimethylammonium bromide (2.0 g). To the stirring reaction mixture was added a solution of alkene **2B** (50 mmol) in DCM (2 mL). Bromoform (100 mmol) in DCM (10 mL) was added dropwise over 1 hour. The reaction was allowed to stir vigorously at 25 °C for 24 hours, after which the mixture was extracted with DCM (3 x 100 mL). The combined organic layers were washed with brine (2 x 100 mL), dried over $MgSO_4$

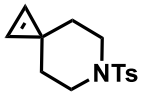
and concentrated under reduced pressure. The product 2**C** was purified by flash column chromatography (eluent: EA/PE = 5%)

A solution of ethylmagnesium bromide (75 mmol) was added dropwise over an hour to a stirring solution of 2, 2-dibromocyclopropane **2C** (50 mmol), $Ti(O^iPr)_4$ (5.0 mmol) and Et_2O (50 mL) and the resulting mixture was stirred for 3 hours at 25 °C. The reaction was quenched by slow addition of water (20 mL) and 1 M HCl (30 mL), stirred for a further few minutes followed by the addition of Et_2O (30 mL). The aqueous layer was washed with Et_2O (3 x 20 mL), combined organic layers washed with saturated sodium bicarbonate (10 mL), brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude oil was purified by flash column chromatography to afford **2D** (eluent: EA/PE = 5%).

Potassium *tert*-butoxide (10 mmol) and dimethyl sulfoxide (10 mL) were heated to 55 °C and allowed to stir for 30 minutes at this temperature until the mixture was homogenous. The solution was then cooled to 25 °C. 2-Bromocyclopropane **2D** (5 mmol) in DMSO (5 mL) was added to the reaction mixture over 3 hours and allowed to stir at 25 °C for 20 hours. The reaction was quenched with brine (50 mL) and PE (50 mL) and layers partitioned. The aqueous layer was washed with PE (3 x 50 mL) and combined organic layers washed with brine (2 x 50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified by flash column chromatography (eluent: EA/PE = 5%) to afford cyclopropenes **2**.

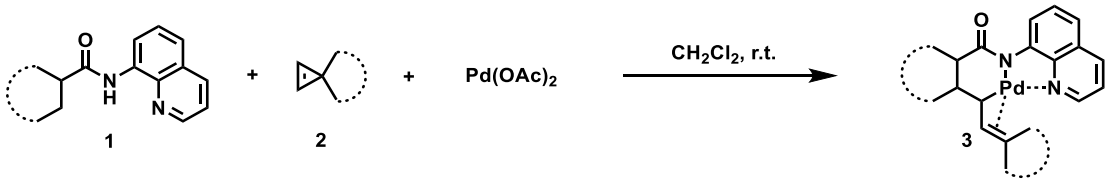
Cyclopropenes 2a-2g[7], 2h-2m[8] were prepared according to the known literature.

6-Tosyl-6-azaspiro[2.5]oct-1-ene (2b):



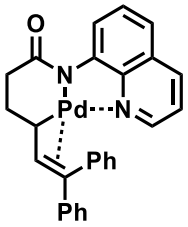
The title compound was prepared according to the general procedure. The product was purified by flash column chromatography (PE:EtOAc = 19:1) to give **2b** as a withe solid (790 mg, 60% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 – 7.60 (m, 2H), 7.42 (s, 2H), 7.37 – 7.29 (m, 2H), 3.17 – 2.96 (m, 4H), 2.45 (s, 3H), 1.65 – 1.52 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.3, 132.9, 129.6, 127.7, 122.1, 46.7, 37.9, 21.5, 20.8; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{14}H_{18}NSO_3$: 264.1058. Found: 264.1056.

General procedure for Pd-complexs and their spectral data:



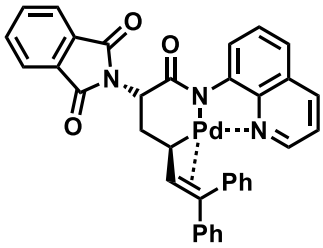
A mixture of amide **1** (0.2 mmol, 1.0 equiv.) and $Pd(OAc)_2$ (0.26 mmol, 1.3 equiv.) was dissolved in CH_2Cl_2 (2.0 mL) in a Schlenk tube. To the stirring reaction mixture was added a solution of cyclopropene **2** (0.6 mmol, 3.0 equiv.) in CH_2Cl_2 (2 mL). The mixture was allowed to stir at room temperature until the **1** was consumed (determined by TLC). Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **3**.

Pd-complex 3aa:



The Pd-complex **3aa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (4:1) as the eluent to give the desired product **3aa** as yellow solid in 90% yield (89.4 mg); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.27 (d, J = 8.0 Hz, 1H), 8.18 – 8.13 (m, 1H), 7.74 – 7.70 (m, 1H), 7.52 – 7.46 (m, 1H), 7.39 – 7.35 (m, 2H), 7.26 – 7.15 (m, 10H), 5.90 (d, J = 11.2 Hz, 1H), 3.92 – 3.84 (m, 1H), 2.89 – 2.83 (m, 2H), 2.27 – 2.10 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.5, 148.5, 147.5, 143.8, 143.5, 139.2, 138.8, 130.7, 129.7, 129.7, 128.8, 128.7, 128.0, 127.3, 127.2, 122.6, 120.7, 118.6, 109.4, 90.2, 79.4, 45.4, 30.6; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{27}H_{23}N_2OPd$: 497.0845. Found: 497.0828.

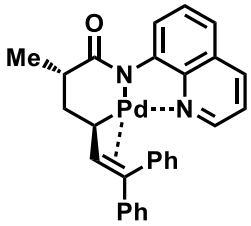
Pd-complex 3ba:



The Pd-complex **3ba** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ba** as yellow solid in 85% yield (111.5 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.70 (d, J = 4.4 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.42 – 7.34 (m, 3H), 7.29

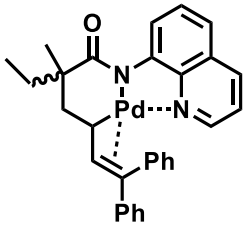
– 7.16 (m, 10H), 5.91 (d, J = 10.8 Hz, 1H), 5.15 – 5.06 (m, 1H), 3.81 – 3.71 (m, 1H), 3.43 – 3.30 (m, 1H), 2.54 (d, *J* = 13.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.3, 148.2, 147.5, 143.8, 143.0, 139.0, 138.8, 133.7, 132.4, 130.6, 129.6, 129.5, 128.9, 128.9, 128.0, 127.5, 127.5, 123.4, 123.1, 120.7, 119.3, 109.2, 92.9, 70.4, 58.5, 35.8; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{35}H_{26}N_3O_3Pd$: 642.1009. Found: 642.1016.

Pd-complex 3ca:



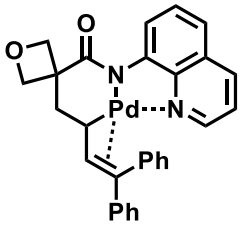
The Pd-complex **3ca** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ca** as yellow solid in 80% yield (83.9 mg, *d.r.*> 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.33 (d, *J* = 8.0 Hz, 1H), 8.26 – 8.21 (m, 1H), 7.83 – 7.78 (m, 1H), 7.60 – 7.54 (m, 1H), 7.48 – 7.42 (m, 2H), 7.34 – 7.23 (m, 10H), 6.00 (d, *J* = 11.2 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.20 – 3.14 (m, 1H), 2.49 – 2.39 (m, 1H), 2.23 – 2.14 (m, 1H), 1.39 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.7, 149.0, 147.5, 143.9, 143.6, 139.3, 138.8, 130.7, 129.7, 128.8, 128.7, 128.0, 127.2, 127.2, 122.8, 120.7, 118.5, 110.3, 90.1, 75.8, 50.4, 36.5, 18.7; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{28}H_{25}N_2OPd$: 511.1002. Found: 511.1001.

Pd-complex 3da:



The Pd-complex **3da** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3da** as yellow solid in 84% yield (90.3 mg, *d.r.* = 1.17:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.29 & 9.03 (d, *J* = 8.0 Hz & 8.0 Hz, 1H), 8.27 – 8.16 (m, 1H), 7.84 – 7.76 (m, 1H), 7.59 – 7.38 (m, 3H), 7.37 – 7.15 (m, 11H), 5.96 & 5.88 (d, *J* = 10.8 Hz & 10.8 Hz, 1H), 3.96 – 3.83 (m, 1H), 2.61 – 2.40 (m, 1H), 2.37 – 2.19 (m, 1H), 2.18 – 2.02 (m, 1H), 1.64 – 1.40 (m, 2H), 1.36 & 1.34 (s, 3H), 0.98 & 0.91 (t, *J* = 7.2 Hz & 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 184.2, 181.4, 149.4, 149.0, 147.4, 144.3, 144.0, 143.7, 139.4, 139.3, 138.8, 138.8, 130.7, 129.8, 129.6, 129.5, 128.8, 128.7, 128.0, 128.0, 127.2, 127.1, 123.2, 122.8, 120.6, 120.6, 118.5, 118.0, 109.9, 109.4, 91.6, 90.8, 73.4, 73.0, 52.8, 52.7, 42.4, 39.8, 36.3, 33.1, 26.9, 24.4, 9.8, 9.2; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{30}H_{29}N_2OPd$: 539.1315. Found: 539.1317.

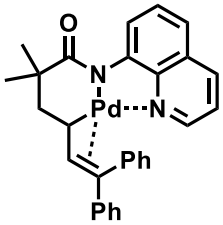
Pd-complex 3ea:



The Pd-complex **3ea** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ea** as yellow solid in 77% yield (85.3 mg). **^{1}H NMR (400**

MHz, $CDCl_3$) δ 9.17 (d, J = 8.0 Hz, 1H), 8.20 – 8.13 (m, 1H), 7.76 – 7.70 (m, 1H), 7.55 – 7.47 (m, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.17 (m, 10H), 5.87 (d, J = 11.2 Hz, 1H), 5.51 (d, J = 5.2 Hz, 1H), 4.80 (d, J = 5.6 Hz, 1H), 4.49 (d, J = 6.0 Hz, 1H), 4.31 (d, J = 5.2 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.13 – 3.04 (m, 1H), 2.62 – 2.52 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.6, 148.5, 147.6, 144.1, 143.3, 139.0, 138.9, 130.5, 129.7, 129.5, 128.9, 128.8, 128.1, 127.5, 127.4, 123.1, 120.8, 119.0, 109.6, 92.0, 81.3, 78.8, 70.8, 55.3, 39.8; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{25}N_2O_2Pd$: 539.0951. Found: 539.0945.

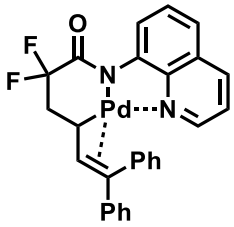
Pd-complex 3fa:



The Pd-complex **3fa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3fa** as yellow solid in 84% yield (90.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (d, J = 8.0 Hz, 1H), 8.25 – 8.19 (m, 1H), 7.82 – 7.79 (m, 1H), 7.58 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 7.32 – 7.23 (m, 10H), 5.92 (d, J = 10.8 Hz, 1H), 3.94 – 3.83 (m, 1H), 2.51 – 2.40 (m, 1H), 2.25 – 2.18 (m, 1H), 1.44 (s, 3H), 1.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.9, 149.4, 147.4, 144.1, 143.7, 139.3, 138.8, 130.7, 129.8, 129.6, 128.8, 128.7, 128.0, 127.2, 127.1, 123.0, 120.6, 118.3, 109.6, 91.3,

73.4, 49.5, 44.1, 30.2, 27.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{27}N_2OPd$: 525.1158. Found: 525.1156.

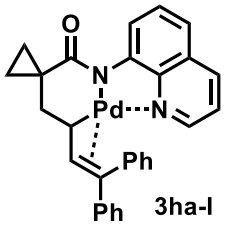
Pd-complex 3ga:



The Pd-complex **3ga** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ga** as yellow solid in 74% yield (81.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.32 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.38 – 7.25 (m, 10H), 5.91 (d, J = 11.2 Hz, 1H), 3.79 – 3.68 (m, 1H), 3.14 – 3.01 (m, 1H), 2.82 – 2.62 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.4 (dd, J_1 = 31.0 Hz, J_2 = 27.0 Hz), 147.9, 147.2, 147.2, 144.0, 142.8, 139.2, 138.3, 130.5, 129.6, 129.0, 128.9, 128.1, 127.9, 127.7, 123.9, 121.0, 120.3, 118.7 (dd, J_1 = 245.0 Hz, J_2 = 248.0 Hz), 110.1, 94.3, 64.2 (dd, J_1 = 13.0 Hz, J_2 = 5.0 Hz), 39.8 (dd , J_1 = 31.0 Hz, J_2 = 24.0 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -86.37 (dd, J_1 = 267.0 Hz, J_2 = 11.3 Hz), -98.2 (ddd, J_1 = 263.2 Hz, J_2 = 30.1 Hz, J_3 = 7.5 Hz); **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{27}H_{21}F_2N_2OPd$: 533.0657. Found: 533.0656.

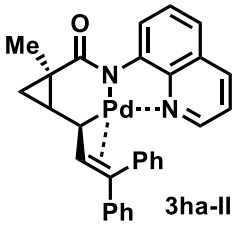
Pd-complex 3ha:

The Pd-complex **3ha-1** and **3ha-2** were prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ha-1** (TLC R_f = 0.5) as yellow solid in 50% yield (53.8 mg) and **3ha-2** (TLC R_f = 0.3) as yellow solid in 37% yield (39.7 mg, *d.r.* > 20:1).



3ha-I

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 – 9.23 (m, 1H), 8.25 – 8.21 (m, 1H), 7.84 – 7.80 (m, 1H), 7.58 – 7.51 (m, 1H), 7.49 – 7.44 (m, 2H), 7.33 – 7.24 (m, 10H), 5.96 (d, *J* = 11.2 Hz, 1H), 4.04 – 3.94 (m, 1H), 2.90 – 2.77 (m, 1H), 1.73 – 1.66 (m, 1H), 1.61 – 1.55 (m, 1H), 1.11 – 1.04 (m, 1H), 0.75 – 0.69 (m, 1H), 0.67 – 0.60 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.0, 148.9, 147.5, 144.4, 143.7, 139.3, 138.9, 130.8, 129.9, 129.68, 128.9, 128.8, 128.1, 127.3, 127.2, 123.0, 120.7, 118.5, 109.1, 92.0, 76.0, 39.7, 30.0, 16.6, 16.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{25}N_2OPd$: 523.1002. Found: 523.1000.

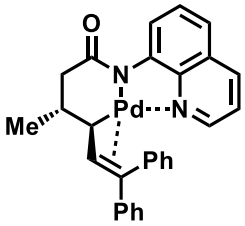


3ha-II

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 – 9.30 & 9.29 – 9.23 (m, 1H), 7.88 – 7.83 & 7.77 – 7.74 (m, 1H), 7.64 – 7.58 (m, 2H), 7.58 – 7.52 (m, 1H), 7.35 – 7.26 (m, 5H), 7.18 – 7.06 (m, 5H), 6.18 & 5.96 (d, *J* = 11.6 & 10.8 Hz, 1H), 4.50 – 4.45 & 4.28 – 4.20 (m,

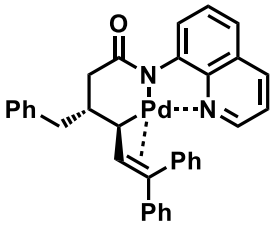
1H), 1.54 – 1.48 (m, 1H), 1.47 & 1.44 (s, 3H); 1.34 – 1.25 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.2, 149.2, 148.1, 147.5, 146.8, 145.0, 144.2, 143.7, 139.4, 139.2, 138.9, 130.6, 130.4, 129.7, 128.8, 128.7, 128.3, 128.1, 127.3, 127.0, 122.5, 122.1, 120.8, 120.6, 118.5, 117.6, 111.4, 110.8, 80.2, 41.9, 31.7, 29.7, 28.6, 26.5, 24.9, 24.0, 22.5; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{29}H_{25}N_2OPd$: 523.1002. Found: 523.0994.

Pd-complex 3ia:



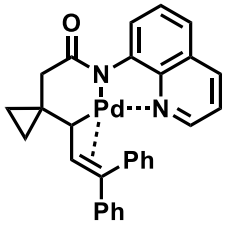
The Pd-complex **3ia** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ia** as yellow solid in 79% yield (83.1 mg, *d.r.*> 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 (d, J = 8.0 Hz, 1H), 8.26 – 8.22 (m, 1H), 7.83 – 7.79 (m, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 – 7.23 (m, 10H), 5.94 (d, J = 10.8 Hz, 1H), 3.80 (t, J = 10.8 Hz, 1H), 2.95 – 2.86 (m, 1H), 2.76 – 2.69 (m, 1H), 2.64 – 2.51 (m, 1H), 1.29 (d, J = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.4, 148.3, 147.5, 144.3, 143.6, 139.2, 138.8, 132.4, 130.7, 129.7, 128.9, 128.8, 128.1, 127.3, 127.2, 122.7, 120.7, 118.6, 108.6, 90.7, 84.2, 54.3, 37.4, 22.4; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{28}H_{25}N_2OPd$: 511.1002. Found: 511.1005.

Pd-complex 3ja:



The Pd-complex **3ia** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ia** as yellow solid in 60% yield (70.3 mg, *d.r.*> 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 – 9.26 (m, 1H), 8.24 – 8.20 (m, 1H), 7.69 – 7.65 (m, 1H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.38 – 7.18 (m, 17H), 5.38 (d, *J* = 10.8 Hz, 1H), 3.66 – 3.58 (m, 1H), 3.08 – 2.84 (m, 3H), 2.71 – 2.61 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.1, 148.1, 147.5, 144.3, 143.3, 139.2, 138.8, 130.8, 129.7, 129.5, 128.8, 128.7, 128.4, 128.0, 127.3, 127.2, 126.5, 122.7, 120.7, 118.7, 109.5, 90.4, 81.3, 52.8, 44.6, 42.4; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{34}H_{29}N_2OPd$: 587.1315. Found: 587.1316.

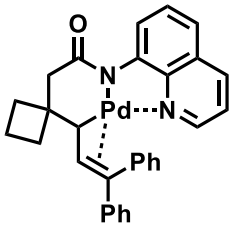
Pd-complex 3ka:



The Pd-complex **3ka** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ka** as yellow solid in 88% yield (91.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.36 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 4.8 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.24 (m, 10H), 5.72 (d, *J* =

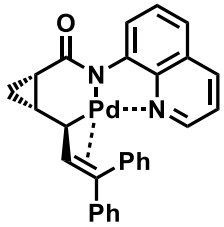
10.8 Hz, 1H), 4.33 (d, *J* = 11.2 Hz, 1H), 3.51 (d, *J* = 15.6 Hz, 1H), 2.14 (d, *J* = 16.0 Hz, 1H), 1.09 – 1.03 (m, 1H), 0.92 – 0.76 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.7, 148.5, 147.5, 144.2, 143.7, 139.3, 138.8, 130.6, 129.7, 128.8, 128.8, 128.1, 127.4, 127.2, 122.5, 120.7, 118.6, 106.4, 90.7, 80.9, 55.7, 21.7, 16.9, 8.9; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{29}H_{25}N_2OPd$: 523.1002. Found: 523.1003.

Pd-complex 3la:



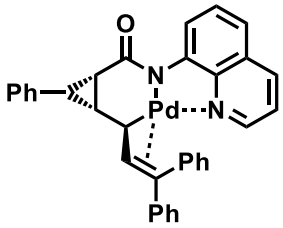
The Pd-complex **3la** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3la** as yellow solid in 86% yield (92.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.36 – 9.31 (m, 1H), 8.24 – 8.18 (m, 1H), 7.82 – 7.79 (m, 1H), 7.58 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 7.34 – 7.22 (m, 10H), 6.04 (d, *J* = 11.2 Hz, 1H), 4.00 (d, *J* = 11.6 Hz, 1H), 3.15 – 3.01 (m, 2H), 2.41 – 2.32 (m, 1H), 2.20 – 2.05 (m, 4H), 2.01 – 1.92 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.5, 148.3, 147.4, 144.3, 143.9, 139.4, 138.8, 130.7, 129.7, 129.7, 128.9, 128.8, 128.2, 127.3, 127.2, 122.5, 120.7, 118.5, 106.0, 90.9, 84.9, 58.6, 44.1, 34.5, 26.5, 14.6; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{30}H_{27}N_2OPd$: 537.1158. Found: 537.1157.

Pd-complex 3ma:



The Pd-complex **3ma** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ma** as yellow solid in 82% yield (83.3 mg, *d.r.*= 19:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.11 & 9.01 (d, *J* = 8.0 Hz & 8.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.79 (m, 1H), 7.66 – 7.50 (m, 3H), 7.40 – 7.12 & 6.98 – 6.76 (m, 10H), 6.39 & 6.27 (d, *J* = 15.2 Hz & 11.6 Hz, 1H), 5.53 – 5.42 & 4.49 – 4.32 (m, 1H), 4.25 – 4.18 & 3.99 – 3.90 (m, 1H), 2.47 – 2.18 (m, 1H), 1.71 - 1.50 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.1, 147.9, 147.7, 144.6, 144.1, 139.4, 138.9, 130.5, 129.6, 128.8, 128.8, 128.2, 127.3, 127.1, 123.1, 120.8, 118.7, 111.5, 87.7, 81.5, 37.2, 20.7, 16.5; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{28}H_{23}N_2OPd$: 509.0845. Found: 509.0850.

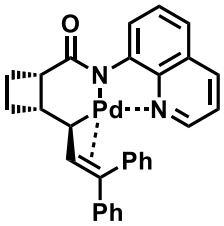
Pd-complex 3na:



The Pd-complex **3na** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3na** as yellow solid in 78% yield (91.1 mg, *d.r.* = 19:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.39 – 9.34 & 9.14 – 9.09 (m, 1H), 8.29 – 8.22 (m, 1H),

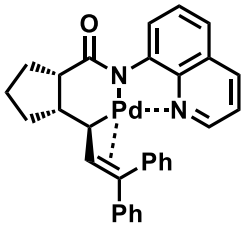
7.88 – 7.78 (m, 1H), 7.63 – 7.48 (m, 3H), 7.37 – 7.11 (m, 15H), 6.32 & 6.14 (d, J = 11.6 Hz & 11.2 Hz, 1H), 4.61 & 4.52 (dd, J_1 = 11.2 Hz & 11.6 Hz, J_2 = 2.8 Hz & 4.4 Hz, 1H), 3.10 – 3.05 & 2.77 – 2.72 (m, 1H), 2.72 – 2.65 & 2.44 – 2.39 (m, 1H), 2.07 – 1.96 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.5, 148.0, 147.7, 144.6, 143.9, 141.3, 139.3, 138.9, 130.5, 129.6, 129.6, 128.8, 128.8, 128.3, 128.2, 127.3, 127.1, 126.1, 123.3, 120.9, 118.8, 111.3, 88.0, 80.4, 47.3, 33.9, 30.4; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{34}H_{27}N_2OPd$: 585.1158. Found: 585.1155.

Pd-complex 3oa:



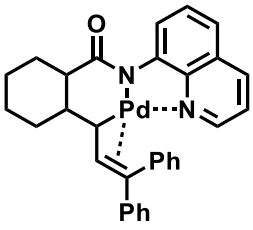
The Pd-complex **3oa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3oa** as yellow solid in 79% yield (82.4 mg, *d.r.* = 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.29 – 9.22 & 9.19 – 9.13 (m, 1H), 8.27 – 8.20 (m, 1H), 7.83 – 7.77 (m, 1H), 7.57 – 7.49 (m, 3H), 7.37 – 7.14 (m, 10H), 5.92 & 5.80 (d, J = 10.8 Hz & 11.6 Hz, 1H), 4.75 – 4.65 (m, 1H), 3.95 – 3.85 (m, 1H), 3.16 – 3.06 (m, 1H), 2.68 – 2.45 (m, 2H), 2.31 – 2.18 (m, 1H), 1.77 – 1.69 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.1, 148.0, 147.2, 144.6, 143.7, 139.2, 138.8, 130.4, 129.8, 129.7, 128.8, 128.2, 127.3, 127.2, 122.1, 120.7, 118.4, 110.0, 89.3, 81.9, 53.2, 43.5, 26.1, 22.6; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{25}N_2OPd$: 523.1002. Found: 523.1003.

Pd-complex 3pa:



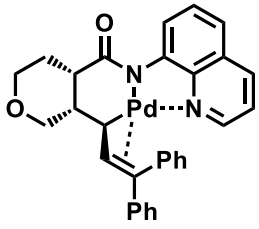
The Pd-complex **3pa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3pa** as yellow solid in 74% yield (79.3 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.39 – 9.36 & 9.18 – 9.16 (m, 1H), 8.27 – 8.20 (m, 1H), 7.88 – 7.79 (m, 1H), 7.61 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 7.36 – 7.20 & 7.13 – 7.07 (m, 10H), 6.59 & 5.93 (d, *J* = 7.6 Hz & 11.2 Hz, 1H), 4.59 – 4.55 & 4.20 – 4.08 (m, 1H), 3.30 – 3.13 (m, 1H), 2.93 – 2.79 (m, 1H), 2.42 – 2.28 (m, 1H), 2.10 – 1.70 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.8, 148.4, 147.4, 144.7, 143.8, 139.3, 138.8, 130.5, 129.7, 129.7, 128.8, 128.7, 128.1, 127.3, 127.1, 123.0, 120.7, 118.6, 109.1, 90.2, 80.0, 61.8, 45.8, 33.2, 29.7, 21.2; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{30}H_{27}N_2OPd$: 537.1158. Found: 537.1159.

Pd-complex 3qa:



The Pd-complex **3qa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3qa** as yellow solid in 70% yield (77.0 mg, *d.r.* = 11.5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.33 & 9.17 (d, *J* = 8.0 Hz & 3.2 Hz, 1H), 8.29 – 8.20 (m, 1H), 7.92 – 7.84 & 7.78 – 7.74 (m, 1H), 7.62 – 7.52 (m, 1H), 7.52 – 7.34 (m, 2H), 7.36 – 7.20 & 7.18 – 7.05 (m, 10H), 6.48 & 5.92 (d, *J* = 7.6 Hz & 10.8 Hz, 1H), 4.68 – 4.59 & 4.50 – 4.34 (m, 1H), 3.38 – 3.30 & 3.00 – 2.89 (m, 1H), 2.88 – 2.67 (m, 1H), 2.42 – 2.28 (m, 1H), 2.16 – 1.98 (m, 1H), 1.95 – 1.67 & 1.57 – 1.48 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.5, 148.8, 147.5, 144.5, 143.8, 139.5, 138.8, 130.5, 129.7, 129.7, 128.8, 128.7, 128.2, 127.3, 127.1, 126.4, 123.2, 120.7, 118.6, 109.7, 90.9, 78.2, 59.8, 40.9, 33.1, 27.1, 20.7; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{31}H_{29}N_2OPd$: 551.1315. Found: 551.1313.

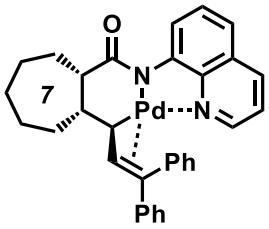
Pd-complex 3ra:



The Pd-complex **3ra** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3ra** as yellow solid in 60% yield (66.2 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.35 – 9.31 (m, 1H), 8.28 – 8.22 (m, 1H), 7.89 – 7.85 (m, 1H), 7.61 – 7.54 (m, 1H), 7.49 – 7.46 (m, 2H), 7.37 – 7.26 (m, 10H), 5.95 (d, *J* = 11.2

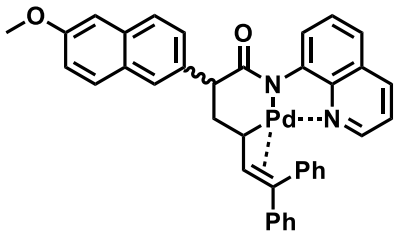
Hz, 1H), 4.52 (t, *J* = 10.8 Hz, 1H), 4.15 – 4.09 (m, 1H), 4.06 – 4.01 (m, 1H), 3.72 – 3.66 (m, 1H), 3.64 – 3.56 (m, 1H), 3.18 – 3.09 (m, 1H), 2.59 – 2.51 (m, 1H), 2.17 – 1.98 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.6, 148.4, 147.6, 144.5, 143.7, 139.0, 138.9, 130.5, 129.7, 129.6, 129.0, 128.8, 128.2, 127.4, 127.2, 123.3, 120.8, 119.1, 109.6, 91.5, 76.5, 72.6, 69.6, 57.0, 42.6, 27.8; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{30}H_{27}N_2O_2Pd$: 553.1107. Found: 553.1105.

Pd-complex 3sa:



The Pd-complex **3sa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3sa** as yellow solid in 60% yield (66.2 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.25 (d, *J* = 8.0 Hz, 1H), 8.25 – 8.20 (m, 1H), 7.86 – 7.82 (m, 1H), 7.59 – 7.52 (m, 1H), 7.48 – 7.43 (m, 2H), 7.34 – 7.23 (m, 10H), 5.93 (d, *J* = 11.2 Hz, 1H), 4.13 (t, *J* = 11.8 Hz, 1H), 3.02 – 2.95 (m, 1H), 2.90 – 2.81 (m, 1H), 2.22 – 2.11 (m, 0H), 2.01 – 1.70 (m, 6H), 1.59 – 1.44 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.9, 148.8, 147.5, 144.3, 143.6, 139.5, 138.8, 130.4, 129.8, 129.7, 128.8, 128.7, 128.1, 127.3, 127.2, 122.8, 120.7, 118.5, 109.9, 91.0, 78.8, 61.8, 44.6, 44.2, 34.9, 30.7, 30.4, 28.3, 27.2, 27.2, 26.3, 25.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{32}H_{31}N_2OPd$: 565.1471. Found: 565.1476.

Pd-complex 3ta:



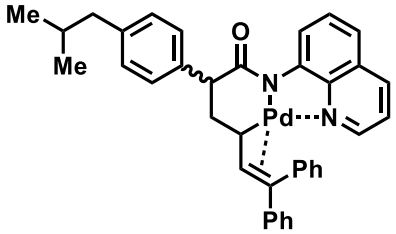
The Pd-complex **3ta** was prepared according to the general procedure. Purification by column chromatography (TLC major: R_f = 0.4, minor: R_f = 0.7) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ta** as yellow solid in 90% yield (117.3 mg, *d.r.*= 2:1).

Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 – 9.46 (m, 1H), 8.30 – 8.23 (m, 1H), 7.84 – 7.82 (m, 1H), 7.80 (s, 1H), 7.61 – 7.52 (m, 2H), 7.50 – 7.35 (m, 5H), 7.32 – 7.26 (m, 4H), 7.20 – 7.16 (m, 2H), 7.13 – 7.08 (m, 3H), 7.01 – 6.97 (m, 2H), 6.06 (d, J = 10.8 Hz, 1H), 4.59 (t, J = 3.6 Hz, 1H), 3.86 (s, 3H), 3.79 – 3.72 (m, 1H), 2.77 – 2.67 (m, 1H), 2.53 – 2.45 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.3, 157.1, 148.7, 147.6, 144.3, 143.3, 138.9, 138.9, 136.5, 133.3, 130.4, 129.8, 129.8, 129.3, 128.9, 128.8, 128.6, 128.0, 127.4, 127.3, 127.1, 126.7, 126.6, 123.1, 120.8, 119.0, 118.2, 109.6, 105.3, 91.0, 76.4, 62.0, 55.2, 37.5; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{38}H_{31}N_2O_2Pd$: 653.1420. Found: 653.1422.

Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.17 (m, 1H), 8.26 – 8.21 (m, 1H), 7.86 – 7.82 (m, 1H), 7.75 – 7.65 (m, 2H), 7.63 (s, 1H), 7.53 – 7.43 (m, 4H), 7.35 – 7.24 (m, 10H), 7.13 – 7.05 (m, 2H), 5.96 (d, J = 10.8 Hz, 1H), 4.24 (dd, J_1 = 12.0, J_2 = 2.8 Hz, 1H), 4.07 – 3.99 (m, 1H), 3.91 (s, 3H), 2.91 – 2.78 (m, 1H), 2.64 – 2.58 (m, 1H).; **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 177.8, 157.2, 148.7, 147.5, 144.1, 143.5, 139.7, 139.2, 138.9, 133.3, 130.8, 129.8, 129.7, 129.3, 129.1, 128.9, 128.8, 128.1, 127.7, 127.4, 127.3, 126.7, 126.3, 123.1, 120.6, 118.6, 118.2, 109.0, 105.7, 91.6, 75.0, 59.6, 55.3, 39.5; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{38}H_{31}N_2O_2Pd$: 653.1420. Found: 653.1418.

Pd-complex 3ua:

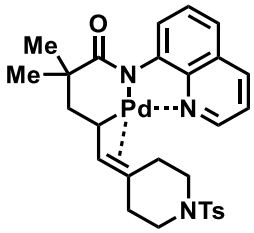


The Pd-complex **3ua** was prepared according to the general procedure. Purification by column chromatography (TLC major: R_f = 0.6, minor: R_f = 0.8) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ua** as yellow solid in 84% yield (105.5 mg, *d.r.*= 1.8:1).

Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 – 9.48 (m, 1H), 8.29 – 8.23 (m, 1H), 7.83 – 7.79 (m, 1H), 7.62 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.39 – 7.25 (m, 7H), 7.20 – 7.10 (m, 5H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.04 (d, *J* = 11.2 Hz, 1H), 4.44 (t, *J* = 3.6 Hz, 1H), 3.68 – 3.58 (m, 1H), 2.68 – 2.59 (m, 1H), 2.47 – 2.39 (m, 1H), 2.37 – 2.25 (m, 2H), 1.75 – 1.65 (m, 1H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.5, 148.6, 147.5, 144.2, 143.4, 139.4, 138.9, 138.9, 138.3, 130.4, 129.8, 129.8, 128.8, 128.8, 128.5, 127.9, 127.8, 127.2, 127.0, 123.0, 120.7, 118.9, 109.6, 90.7, 76.6, 61.4, 44.9, 37.4, 30.1, 22.4, 22.2; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{37}H_{35}N_2OPd$: 629.1784. Found: 629.1788.

Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, J = 8.0 Hz, 1H), 8.28 – 8.21 (m, 1H), 7.85 – 7.80 (m, 1H), 7.53 – 7.42 (m, 3H), 7.34 – 7.25 (m, 10H), 7.21 – 7.18 (m, 2H), 7.13 – 7.08 (m, 2H), 5.94 (d, J = 11.2 Hz, 1H), 4.07 (dd, J_1 = 12.4, J_2 = 3.2 Hz, 1H), 4.02 – 3.94 (m, 1H), 2.82 – 2.69 (m, 1H), 2.60 – 2.53 (m, 1H), 2.48 – 2.43 (m, 2H), 1.93 – 1.81 (m, 1H), 0.92 (d, J = 6.8 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.9, 148.8, 147.5, 144.1, 143.5, 141.7, 139.3, 139.2, 138.9, 130.7, 129.8, 129.6, 129.0, 128.8, 128.8, 128.0, 128.0, 127.3, 127.3, 123.1, 120.6, 118.5, 108.9, 91.5, 75.1, 59.2, 45.2, 39.5, 30.1, 22.5, 22.5; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{37}H_{35}N_2OPd$: 629.1784. Found: 629.1783.

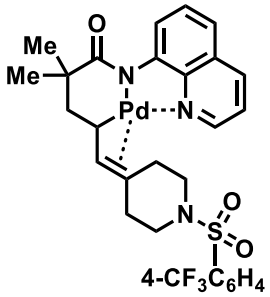
Pd-complex 3eb:



The Pd-complex **3eb** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (3:2) as the eluent to give the desired product **3eb** as yellow solid in 74% yield (87.9 mg,). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.27 (d, J = 8.0 Hz, 1H), 8.49 – 8.46 (m, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.45 (m, 1H), 7.39 – 7.30 (m, 3H), 5.06 (d, J = 11.2 Hz, 1H), 4.12 – 4.08 (m, 1H), 3.93 – 3.82 (m, 2H), 2.51 – 2.41 (m, 5H), 2.31 – 2.20 (m, 2H), 2.15 – 2.03 (m, 3H), 1.75 (d, J = 13.2 Hz, 1H), 1.52 (s, 3H), 1.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.7, 149.4, 147.1, 143.8, 139.3, 133.1,

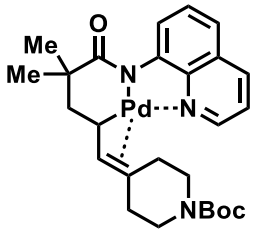
129.9, 129.8, 127.6, 122.8, 120.5, 118.3, 107.8, 81.8, 71.9, 49.9, 49.6, 49.3, 43.5, 36.6, 32.2, 30.2, 27.3, 21.6; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{28}H_{32}N_3O_3PdS$: 596.1199. Found: 596.1198.

Pd-complex 3ec:



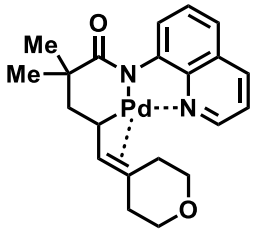
The Pd-complex **3ec** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ec** as yellow solid in 74% yield (77.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.21 – 9.16 (m, 1H), 8.42 – 8.37 (m, 1H), 8.27 – 8.21 (m, 1H), 7.87 – 7.82 (m, 2H), 7.79 – 7.74 (m, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.38 (m, 1H), 7.27 – 7.21 (m, 1H), 5.01 (d, *J* = 11.2 Hz, 1H), 4.07 (d, *J* = 7.2 Hz, 1H), 3.87 – 3.79 (m, 2H), 2.49 – 2.35 (m, 2H), 2.25 – 2.15 (m, 2H), 2.15 – 2.05 (m, 2H), 2.04 – 1.96 (m, 1H), 1.75 – 1.68 (m, 1H), 1.45 (s, 3H), 1.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.6, 149.5, 147.1, 144.1, 140.0, 139.3, 134.8, 130.0, 128.0, 126.4(q, *J* = 4.0 Hz), 122.9, 120.5, 118.4, 107.8, 81.0, 72.2, 49.8, 49.6, 49.2, 43.5, 36.6, 32.3, 30.2, 27.3; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{28}H_{29}F_3N_3O_3PdS$: 650.0911. Found:.650.0909.

Pd-complex 3ed:



The Pd-complex **3ed** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ed** as yellow solid in 75% yield (81.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.20 (d, J = 8.0 Hz, 1H), 8.43 – 8.37 (m, 1H), 8.22 – 8.19 (m, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.25 – 7.20 (m, 1H), 5.14 (d, J = 11.2 Hz, 1H), 4.34 (s, 1H), 4.06 (s, 1H), 3.92 – 3.83 (m, 1H), 2.91 – 2.80 (m, 2H), 2.58 – 2.47 (m, 2H), 2.30 – 2.14 (m, 2H), 2.11 – 2.04 (m, 1H), 2.00 – 1.93 (m, 2H), 1.67 – 1.60 (m, 1H), 1.49 (s, 3H), 1.44 (s, 9H), 1.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.9, 154.5, 149.5, 147.0, 144.1, 139.1, 129.9, 129.7, 122.8, 120.4, 118.2, 107.7, 84.7, 78.0, 77.3, 71.6, 49.6, 43.7, 37.4, 33.3, 30.3, 28.4, 27.3; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{26}H_{34}N_3O_3Pd$: 542.1629. Found:542.1631.

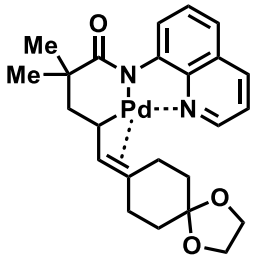
Pd-complex 3ee:



The Pd-complex **3ee** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (1:3) as the eluent

to give the desired product **3ee** as yellow solid in 67% yield (59.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.21 (dd, J_1 = 8.4, J_2 = 1.2 Hz, 1H), 8.48 (dd, J_1 = 4.4, J_2 = 1.6 Hz, 1H), 8.22 (dd, J_1 = 8.4, J_2 = 1.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.38 (dd, J_1 = 8.0, J_2 = 4.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 5.16 (d, J = 11.2 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.93 – 3.83 (m, 2H), 3.62 – 3.53 (m, 1H), 3.27 – 3.19 (m, 1H), 2.46 – 2.37 (m, 1H), 2.30 – 2.16 (m, 2H), 2.11 – 2.03 (m, 1H), 1.96 – 1.88 (m, 1H), 1.61 – 1.54 (m, 1H), 1.49 (s, 3H), 1.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.9, 149.5, 146.8, 144.1, 139.1, 129.9, 129.7, 122.8, 120.4, 118.2, 107.6, 84.0, 71.6, 71.4, 71.0, 49.6, 43.7, 38.6, 34.9, 30.3, 27.3; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{21}H_{25}N_2O_2Pd$: 443.0945. Found:443.0947.

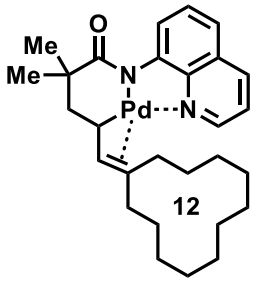
Pd-complex 3ef:



The Pd-complex **3ef** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **3ee** as yellow solid in 79% yield (78.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.23 – 9.19 (m, 1H), 8.49 – 8.44 (m, 1H), 8.23 – 8.18 (m, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.25 – 7.21 (m, 1H), 5.10 (d, J = 11.2 Hz, 1H), 4.00 – 3.93 (m, 3H), 3.91 – 3.83 (m, 2H), 2.34 – 2.22 (m, 2H), 2.10 – 1.95 (m, 4H), 1.83 – 1.70 (m, 4H), 1.50 (s, 3H), 1.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.0,

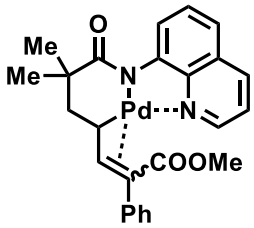
149.6, 147.2, 144.2, 139.0, 129.9, 129.6, 122.8, 120.4, 118. 2, 108.5, 108.1, 86.6, 71.0, 64.5, 64.4, 49.6, 43.7, 38.6, 38.0, 34.6, 30.3, 29.5, 27.3; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{24}H_{29}N_2O_3Pd$: 499.1208. Found: 499.1205.

Pd-complex 3eg:



The Pd-complex **3eg** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **3eg** as yellow solid in 65% yield (68.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.30 – 9.24 (m, 1H), 8.53 – 8.50 (m, 1H), 8.30 – 8.26 (m, 1H), 7.59 – 7.53 (m, 1H), 7.49 – 7.44 (m, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 3.85 – 3.75 (m, 1H), 2.37 – 2.29 (m, 2H), 2.11 – 2.05 (m, 1H), 1.83 – 1.62 (m, 6H), 1.57 (s, 3H), 1.54 – 1.47 (m, 4H), 1.44 (s, 3H), 1.42 – 1.24 (m, 11H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.3, 149.7, 148.1, 138.7, 129.9, 129.5, 122.9, 120.4, 118.2, 110.0, 91.3, 69.4, 49.4, 43.9, 32.6, 30.3, 28.4, 27.3, 26.0, 25.8, 25.7, 24.7, 24.3, 22.7, 22.6, 22.5, 22.1; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{28}H_{39}N_2OPd$: 525.2092. Found: 525.2093.

Pd-complex 3eh:

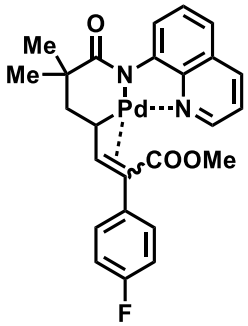


The Pd-complex **3eh** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3eh** as yellow solid in 91% yield (92.0 mg, *E/Z* = 67:33).

3eh-*E*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 – 9.04 (m, 1H), 8.09 – 8.01 (m, 2H), 7.42 – 7.32 (m, 3H), 7.16 – 7.04 (m, 5H), 5.31 (d, *J* = 11.6 Hz, 1H), 4.75 – 4.64 (m, 1H), 3.55 (s, 3H), 2.15 – 2.11 (m, 2H), 1.41 (s, 3H), 1.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.5, 168.6, 149.4, 148.6, 143.8, 139.5, 139.1, 129.7, 129.6, 129.2, 128.5, 127.7, 122.8, 120.8, 118.5, 112.0, 79.5, 78.1, 52.1, 49.6, 44.2, 30.1, 27.3; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{25}N_2O_3Pd$: 507.0900. Found: 507.0901.

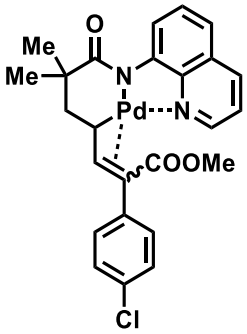
3eh-*Z*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 – 9.15 (m, 1H), 8.80 – 8.75 (m, 1H), 8.32 – 8.26 (m, 1H), 7.51 – 7.46 (m, 2H), 7.32 – 7.24 (m, 3H), 7.20 – 7.14 (m, 4H), 6.37 (d, *J* = 11.6 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.69 (s, 3H), 2.38 – 2.29 (m, 1H), 2.24 – 2.17 (m, 1H), 1.35 (s, 3H), 1.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.4, 171.1, 149.5, 147.6, 144.1, 139.5, 135.1, 130.7, 130.0, 129.7, 128.3, 127.4, 123.2, 120.9, 118.7, 109.7, 78.6, 77.10, 52.4, 49.2, 43.4, 30.1, 27.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{25}N_2O_3Pd$: 507.0900. Found: 507.0899.

Pd-complex 3ei:



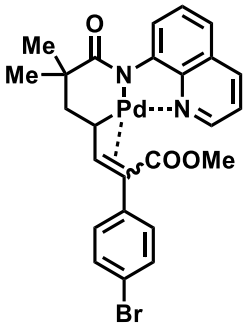
The Pd-complex **3ei** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ei** as yellow solid in 89% yield (93.1 mg, *E/Z* = 67:33). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 – 9.22 (m, 1H), 8.84 – 8.77 & 8.29 – 8.23 (m, 1H), 8.41 – 8.34 & 8.29 – 8.23 (m, 1H), 7.61 – 7.51 & 7.39 – 7.28 (m, 5H), 7.02 – 6.89 (m, 2H), 6.44 & 5.49 (d, *J* = 11.6 Hz & 11.6 Hz, 1H), 4.96 – 4.86 & 4.14 – 4.04 (m, 1H), 3.77 & 3.75 (s, 3H), 2.48 – 2.23 (m, 2H), 1.61 & 1.43 (s, 3H), 1.47 & 1.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.5, 181.3, 171.3, 171.0, 171.0, 168.5, 167.7, 161.9 (d, *J* = 261.0 Hz), 161.8 (d, *J* = 253.0 Hz), 149.5, 149.4, 148.4, 147.4, 144.2, 143.8, 139.6, 139.3, 132.4, 132.3, 131.1 (d, *J* = 4.0 Hz), 131.0 (d, *J* = 8.0 Hz), 130.1, 129.8, 129.7, 129.6, 123.3, 122.9, 120.9, 120.9, 118.7, 118.6, 115.5 (d, *J* = 22.0 Hz), 115.3 (d, *J* = 22.0 Hz), 111.9, 109.8, 78.7, 78.4, 78.3, 76.0, 52.5, 52.1, 49.7, 49.1, 44.2, 43.4, 30.1, 29.7, 27.3, 27.1; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -113.66, -114.02; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{24}FN_2O_3Pd$: 525.0806. Found: 525.0808.

Pd-complex 3ej:



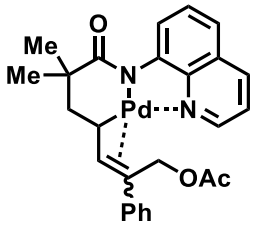
The Pd-complex **3ej** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ej** as yellow solid in 88% yield (95.0 mg, *E/Z* = 69:31). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 – 9.21 (m, 1H), 8.84 – 8.77 & 8.29 – 8.23 (m, 1H), 8.40 – 8.34 & 8.29 – 8.23 (m, 1H), 7.61 – 7.50 & 7.39 – 7.27 (m, 5H), 7.02 – 6.88 (m, 2H), 6.44 & 5.49 (d, *J* = 11.6 Hz & 11.6 Hz, 1H), 4.97 – 4.86 & 4.15 – 4.04 (m, 1H), 3.77 & 3.75 (s, 3H), 2.47 – 2.23 (m, 2H), 1.61 & 1.43 (s, 3H), 1.47 & 1.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.5, 181.3, 171.0, 168.5, 163.2, 163.1, 149.4, 149.4, 148.4, 147.4, 144.1, 143.8, 139.6, 139.2, 132.4, 132.3, 131.1, 131.0, 131.0, 130.9, 130.0, 129.8, 123.2, 122.8, 120.9, 120.9, 118.7, 118.6, 115.6, 115.4, 115.4, 115.2, 111.9, 109.8, 78.7, 78.4, 78.3, 76.0, 52.5, 52.1, 49.6, 49.1, 44.2, 43.4, 30.1, 27.3, 27.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{24}ClN_2O_3Pd$: 541.0510. Found: 541.0510.

Pd-complex 3ek:



The Pd-complex **3ek** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **3ek** as yellow solid in 90% yield (105.0 mg, *E/Z* = 62:38). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.31 – 9.19 (m, 1H), 8.83 – 8.77 & 8.26 – 8.23 (m, 1H), 8.40 – 8.34 & 8.30 – 8.23 (m, 1H), 7.62 – 7.54 & 7.48 – 7.39 (m, 3H), 7.39 – 7.30 & 7.26 – 7.20 (m, 4H), 6.42 & 5.49 (d, *J* = 12.0 Hz & 11.6 Hz, 1H), 4.98 – 4.88 & 4.15 – 4.05 (m, 1H), 3.77 & 3.75 (s, 3H), 2.47 – 2.24 (m, 2H), 1.61 & 1.43 (s, 3H), 1.47 & 1.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.4, 181.2, 170.7, 168.2, 149.6, 148.5, 147.4, 144.1, 143.8, 139.6, 139.3, 138.7, 134.3, 132.3, 131.6, 131.5, 130.9, 130.1, 129.8, 129.7, 123.3, 122.9, 121.5, 120.9, 118.7, 118.6, 111.8, 109.5, 78.8, 78.7, 78.1, 75.9, 52.5, 52.1, 49.6, 49.1, 44.2, 43.4, 30.1, 27.3, 27.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{24}BrN_2O_3Pd$: 585.0005. Found: 585.0006.

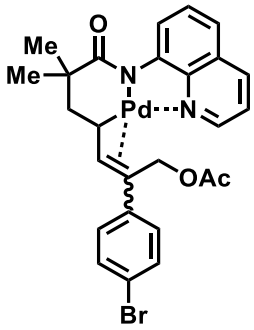
Pd-complex 3ej:



The Pd-complex **3ej** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ej** as yellow solid in 95% yield (98.6 mg, *E/Z* > 99:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.28 – 9.17 (m, 1H), 8.96 – 8.88 (m, 1H), 8.39 – 8.31 (m, 1H), 7.60 – 7.51 (m, 2H), 7.37– 7.28 (m, 3H), 7.25 – 7.20 (m, 3H), 5.59 (d, *J* = 11.2

Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 4.70 (d, *J* = 12.4 Hz, 1H), 4.05 – 3.95 (m, 1H), 2.39 – 2.29 (m, 1H), 2.21 – 2.13 (m, 1H), 1.99 (s, 3H), 1.42 (s, 3H), 1.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.9, 170.9, 149.7, 149.0, 144.1, 139.3, 138.4, 130.0, 129.7, 129.0, 128.8, 127.2, 123.1, 120.7, 118.5, 108.4, 83.2, 75.9, 69.1, 49.1, 43.5, 30.2, 27.0, 20.8; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{26}H_{27}N_2O_3Pd$: 521.1057. Found: 521.1058.

Pd-complex 3ek:

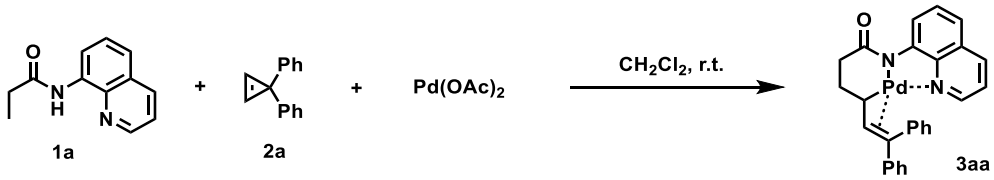


The Pd-complex **3ek** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (2:3) as the eluent to give the desired product **3ek** as yellow solid in 93% yield (111.1 mg, *E*/*Z* > 99:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.27 – 9.20 (m, 1H), 8.91 – 8.85 (m, 1H), 8.40 – 8.33 (m, 1H), 7.61 – 7.52 (m, 2H), 7.39 – 7.31 (m, 3H), 7.22 – 7.13 (m, 2H), 5.57 (d, *J* = 11.6 Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 4.70 (d, *J* = 12.4 Hz, 1H), 4.04 – 3.92 (m, 1H), 2.40 – 2.27 (m, 1H), 2.23 – 2.12 (m, 1H), 2.00 (s, 3H), 1.41 (d, *J* = 4.0 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.7, 170.8, 149.7, 148.9, 144.0, 139.5, 137.5, 132.0, 130.6, 130.1, 129.8, 123.2, 121.1, 120.7, 118.5, 108.6, 81.7, 76.2, 68.9, 49.1, 43.5, 30.1, 27.1,

20.8; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{26}H_{26}BrN_2O_3Pd$: 599.0162. Found: 599.0160.

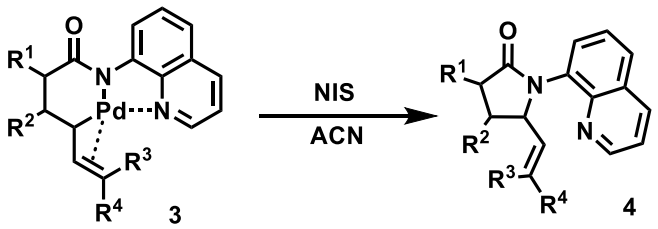
Late-stage modification and their spectral data:

Large-scale reaction of 3aa:



A mixture of amide **1a** (5.0 mmol, 1.0 equiv.) and $Pd(OAc)_2$ (0.26 mmol, 1.3 equiv.) was dissolved in CH_2Cl_2 (50.0 mL) in a Schlenk tube. To the stirring reaction mixture was added a solution of cyclopropene **2a** (15 mmol, 3.0 equiv.) in CH_2Cl_2 (50.0 mL). The mixture was allowed to stir at room temperature until the **1** was consumed (determined by TLC). Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **3aa** (2.236g, 90% yield).

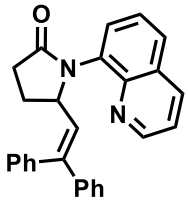
General procedure for lactam and their spectral data[9]:



A flame-dried test tube was charged with **3** (0.20 mmol, 1.0 equiv.) and *N*-Iodosuccinimide (0.30 mmol, 1.5 equiv.) followed by CH_3CN (2.0 mL). After being

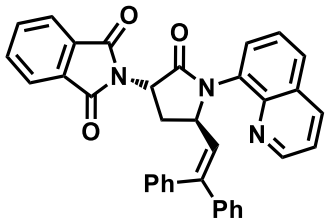
stirred at room temperature for 1 hour, it concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **4**.

5-(2,2-Diphenylvinyl)-1-(quinolin-8-yl)pyrrolidin-2-one (4aa):



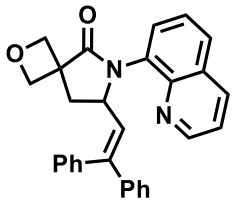
The **4aa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (2:1) as the eluent to give the desired product **4aa** as white solid in 98% yield (76.5 mg). M.p. 209 - 210 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.55 – 8.48 (m, 1H), 8.09 – 8.02 (m, 1H), 7.74 – 7.67 (m, 1H), 7.58 – 7.44 (m, 2H), 7.30 – 7.22 (m, 1H), 7.11 – 7.02 (m, 4H), 6.96 – 6.88 (m, 2H), 6.86 – 6.79 (m, 2H), 6.35 – 6.27 (m, 2H), 5.94 (d, *J* = 9.6 Hz, 1H), 5.16 – 5.06 (m, 1H), 2.72 – 2.64 (m, 2H), 2.52 – 2.39 (m, 1H), 2.16 – 2.01 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.7, 149.8, 145.0, 144.2, 141.0, 138.4, 136.1, 135.1, 130.2, 129.2, 129.0, 128.5, 128.0, 127.9, 127.7, 127.6, 127.1, 127.0, 126.2, 121.2, 60.3, 31.1, 26.8; **HRMS (ESI) m/z $[M+H]^+$**: Calcd for $C_{27}H_{23}N_2O$: 391.1805. Found: 391.1801.

2-(5-(2,2-Diphenylvinyl)-2-oxo-1-(quinolin-8-yl)pyrrolidin-3-yl)isoindoline-1,3-dione (4ba):



The **4ba** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.2) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4ba** as white solid in 97% yield (103.9 mg, *d.r.* > 20:1). M.p. 220 - 221 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 – 8.43 (m, 1H), 8.15 – 8.08 (m, 1H), 7.95 – 7.84 (m, 3H), 7.84 – 7.77 (m, 1H), 7.78 – 7.69 (m, 2H), 7.66 – 7.58 (m, 1H), 7.35 – 7.27 (m, 1H), 7.25 – 7.09 (m, 4H), 7.10 – 7.02 (m, 2H), 6.93 – 6.84 (m, 2H), 6.43 – 6.35 (m, 2H), 6.10 (d, *J* = 10.0 Hz, 1H), 5.47 – 5.36 (m, 1H), 5.35 (t, *J* = 10.0 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.61 – 2.48 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.8, 167.6, 149.9, 145.8, 144.1, 140.9, 138.3, 135.9, 134.6, 134.1, 132.1, 130.9, 129.1, 129.0, 128.1, 128.0, 127.8, 127.7, 127.2, 127.2, 126.2, 123.5, 121.2, 56.4, 50.2, 31.9; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{35}H_{26}N_3O_3$: 536.1969. Found: 536.1963.

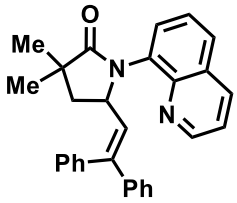
7-(2,2-Diphenylvinyl)-6-(quinolin-8-yl)-2-oxa-6-azaspiro[3.4]octan-5-one (4ea):



The **4ea** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.2) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **4ea** as colorless oil in 87% yield (75.3 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.59 – 8.50 (m, 1H), 8.19 – 8.07 (m, 1H), 7.84 – 7.77 (m, 1H), 7.63 – 7.50

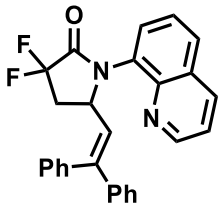
(m, 2H), 7.37 – 7.30 (m, 1H), 7.20 – 7.08 (m, 4H), 7.01 – 6.87 (m, 4H)., 6.38 – 6.28 (m, 2H), 5.85 (d, J = 10.0 Hz, 1H), 5.27 (d, J = 5.6 Hz, 1H), 5.11 (d, J = 5.8 Hz, 1H), 5.07 – 4.99 (m, 1H), 4.68 (dd, J_1 = 5.6 Hz, J_2 = 3.6 Hz, 2H), 3.01 – 2.92 (m, 1H), 2.52 – 2.43 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.3, 150.0, 145.8, 144.1, 140.9, 138.2, 136.0, 135.0, 130.0, 129.2, 128.9, 128.1, 127.9, 127.8, 127.8, 127.1, 127.1, 126.1, 121.4, 79.9, 78.6, 57.5, 46.8, 38.7; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{25}N_2O_2$: 433.1911. Found: 433.1906.

5-(2,2-Diphenylvinyl)-3,3-dimethyl-1-(quinolin-8-yl)pyrrolidin-2-one (4fa):



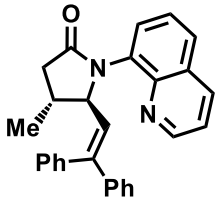
The **4fa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4fa** as colorless oil in 91% yield (76.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 8.18 – 8.11 (m, 1H), 7.83 – 7.76 (m, 1H), 7.67 – 7.60 (m, 1H), 7.61 – 7.53 (m, 1H), 7.38 – 7.30 (m, 1H), 7.22 – 7.13 (m, 4H), 7.08 – 7.00 (m, 2H), 6.95 – 6.88 (m, 2H), 6.44 – 6.38 (m, 2H), 5.97 (d, J = 10.0 Hz, 1H), 5.24 – 5.13 (m, 1H), 2.37 – 2.30 (m, 1H), 2.10 – 2.01 (m, 1H), 1.43 (s, 3H), 1.39 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.6, 145.1, 141.2, 138.5, 131.3, 130.4, 129.6, 129.1, 128.0, 127.8, 127.7, 127.5, 127.1, 127.0, 126.3, 121.2, 56.9, 42.9, 41.3, 25.7, 25.3; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{29}H_{27}N_2O$: 419.2118. Found: 419.2118.

5-(2,2-Diphenylvinyl)-3,3-difluoro-1-(quinolin-8-yl)pyrrolidin-2-one (4ga):



The **4ga** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.7) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4ga** as white oil in 94% yield (80.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 – 8.52 (m, 1H), 8.18 – 8.11 (m, 1H), 7.88 – 7.81 (m, 1H), 7.71 – 7.64 (m, 1H), 7.62 – 7.54 (m, 1H), 7.39 – 7.32 (m, 1H), 7.21 – 7.09 (m, 4H), 7.02 – 6.93 (m, 2H), 6.94 – 6.86 (m, 2H), 6.36 – 6.29 (m, 2H), 5.97 (d, *J* = 10.0 Hz, 1H), 5.43 – 5.35 (m, 1H), 3.12 – 2.97 (m, 1H), 2.69 – 2.54 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.6 (t, *J* = 31.3 Hz), 150.3, 147.3, 143.7, 140.3, 137.6, 136.0, 132.8, 129.4, 129.1, 128.1, 128.1 (t, *J* = 93.8 Hz), 127.9 (t, *J* = 100.0 Hz), 126.0, 125.6, 121.6, 117.9 (t, *J* = 248.8 Hz), 54.7, 54.7, 54.7, 36.7 (t, *J* = 21.3 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -101.1 (d, *J* = 269.2 Hz), -105.4 (d, *J* = 269.2 Hz); **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{27}H_{21}N_2F_2O$: 427.1617. Found: 427.1616.

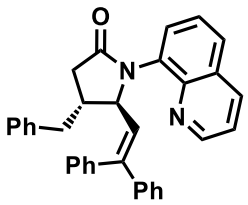
5-(2,2-Diphenylvinyl)-4-methyl-1-(quinolin-8-yl)pyrrolidin-2-one (4ia):



The **4ia** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.2) on silica gel using EtOAc/PE (1:1) as the eluent to give

the desired product **4ia** as colorless oil in 87% yield (70.4 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (s, 1H), 8.18 – 8.01 (m, 1H), 7.77 – 7.69 (m, 1H), 7.52 – 7.43 (m, 2H), 7.34 – 7.28 (m, 1H), 7.13 – 7.02 (m, 4H), 6.94 – 6.83 (m, 4H), 6.30 – 6.21 (m, 2H), 5.95 (d, J = 10.0 Hz, 1H), 4.57 (dd, J_1 = 10.0, J_2 = 7.2 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.41 – 2.30 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.7, 146.4, 141.0, 138.4, 130.4, 129.3, 129.1, 128.1, 127.7, 127.7, 127.6, 127.1, 126.9, 126.3, 121.3, 67.30, 39.3, 35.8, 17.6; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{28}H_{25}N_2O$: 405.1961. Found: 405.1958.

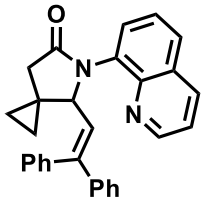
4-Benzyl-5-(2,2-diphenylvinyl)-1-(quinolin-8-yl)pyrrolidin-2-one (4ja):



The **4ja** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.2) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4ja** as colorless oil in 93% yield (89.3 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 – 8.63 (m, 1H), 8.16 – 8.08 (m, 1H), 7.82 – 7.75 (m, 1H), 7.61 – 7.49 (m, 2H), 7.39 – 7.27 (m, 3H), 7.27 – 7.21 (m, 2H), 7.22 – 7.13 (m, 3H), 7.03 – 6.92 (m, 3H), 6.81 – 6.73 (m, 2H), 6.11 – 6.03 (m, 1H), 6.06 – 6.01 (m, 1H), 4.91 (dd, J_1 = 10.4, J_2 = 4.8 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.91 – 2.78 (m, 1H), 2.81 – 2.72 (m, 1H), 2.56 – 2.46 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.9, 145.0, 145.9, 144.6, 141.1, 139.7, 138.1, 135.9, 135.0, 130.2, 129.2, 129.1, 128.8, 128.5, 128.1, 128.0,

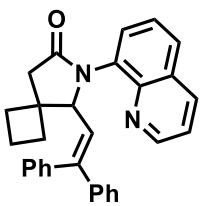
127.7, 127.6, 127.1, 126.6, 126.3, 126.1, 121.3, 64.9, 41.9, 39.4, 37.2; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{34}H_{29}N_2O$: 481.2274. Found: 481.2271.

4-(2,2-Diphenylvinyl)-5-(quinolin-8-yl)-5-azaspiro[2.4]heptan-6-one (4ka):



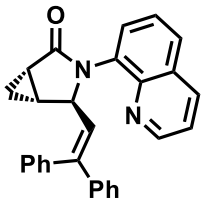
The **4ka** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4ka** as colorless oil in 95% yield (71.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 – 8.62 (m, 1H), 8.18 – 8.11 (m, 1H), 7.83 – 7.76 (m, 1H), 7.68 – 7.62 (m, 1H), 7.59 – 7.51 (m, 1H), 7.39 – 7.32 (m, 1H), 7.20 – 7.12 (m, 3H), 7.12 – 7.04 (m, 1H), 6.97 – 6.86 (m, 4H), 6.17 – 6.10 (m, 2H), 6.03 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 2.89 – 2.72 (m, 2H), 0.96 – 0.90 (m, 1H), 0.84 – 0.78 (m, 1H), 0.77 – 0.67 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.5, 150.1, 140.9, 138.1, 136.0, 130.2, 129.2, 128.9, 128.1, 128.0, 127.7, 127.6, 127.0, 126.8, 126.2, 125.9, 121.3, 65.6, 40.5, 19.8, 11.8, 10.0; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{29}H_{25}N_2O$: 417.1691. Found: 417.1689.

5-(2,2-Diphenylvinyl)-6-(quinolin-8-yl)-6-azaspiro[3.4]octan-7-one (4la):



The **4la** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4la** as colorless oil in 94% yield (80.9 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 – 8.62 (m, 1H), 8.15 – 8.10 (m, 1H), 7.80 – 7.75 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.50 (m, 1H), 7.37 – 7.30 (m, 1H), 7.21 – 7.16 (m, 3H), 7.11 – 6.98 (m, 3H), 6.92 – 6.86 (m, 2H), 6.30 – 6.25 (m, 2H), 6.07 (d, *J* = 10.8 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 2.99 – 2.75 (m, 2H), 2.39 – 2.28 (m, 2H), 2.20 – 2.03 (m, 2H), 2.01 – 1.82 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.4, 149.9, 146.5, 144.5, 141.1, 138.4, 135.8, 135.0, 129.8, 129.2, 129.0 128.1, 127.7, 127.7, 127.6, 127.1, 126.8, 126.2, 125.0, 121.3, 69.4, 44.7, 44.0, 34.8, 28.9, 16.4; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{30}H_{27}N_2O$: 431.2118. Found: 431.2116.

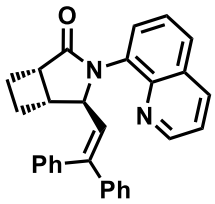
4-(2,2-Diphenylvinyl)-3-(quinolin-8-yl)-3-azabicyclo[3.1.0]hexan-2-one (4ma):



The **4ma** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4ma** as colorless oil in 91% yield (75.8 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.60 – 8.54 (m, 1H), 8.12 – 8.05 (m, 1H), 7.78 – 7.71 (m, 1H), 7.69 – 7.62 (m, 1H), 7.56 – 7.48 (m, 1H), 7.33 – 7.25 (m, 1H), 7.25 – 7.17 (m, 3H), 7.13 – 7.05 (m, 2H), 7.06 – 6.97 (m, 1H), 6.89 – 6.80 (m, 2H), 6.35 – 6.28 (m, 2H), 6.19 (d, *J* = 10.4 Hz, 1H), 5.04 – 4.96 (m, 1H), 2.27 – 2.17 (m, 1H), 2.02 – 1.93 (m,

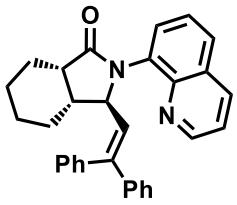
1H), 1.45 (q, *J* = 4.2 Hz, 1H), 1.28 – 1.17 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.1, 149. 8, 145.1, 144.4, 141.0, 138.2, 135.7, 134.0, 131.0, 129.1, 128.9, 128.1, 128.1, 127.7, 127.7, 127.6, 127.2, 126.8, 126.1, 121.1, 61.5, 20.2, 18.4, 12.0; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{28}H_{23}N_2O$: 403.1805. Found: 403.1805.

4-(2,2-Diphenylvinyl)-3-(quinolin-8-yl)-3-azabicyclo[3.2.0]heptan-2-one (4oa):



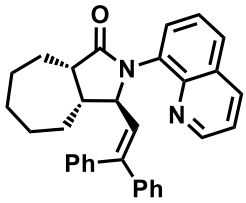
The **4oa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4oa** as colorless oil in 96% yield (80.0 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 – 8.61 (m, 1H), 8.16 – 8.09 (m, 1H), 7.82 – 7.75 (m, 1H), 7.68 – 7.61 (m, 1H), 7.59 – 7.51 (m, 1H), 7.37 – 7.29 (m, 1H), 7.24 – 7.14 (m, 3H), 7.05 – 6.97 (m, 3H), 6.89 – 6.80 (m, 2H), 6.30 – 6.23 (m, 2H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 3.45 – 3.35 (m, 1H), 3.06 – 2.96 (m, 1H), 2.72 – 2.50 (m, 2H), 2.49 – 2.28 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.9, 149.9, 144.6, 143.8, 141. 1, 138.3, 135.8, 135.0, 130.0, 129.2, 128.9, 128.1, 127.9, 127.8, 127.54, 127.1, 126.7, 126.2, 121.2, 66.3, 41.4, 38.0, 25.2, 24.6; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{29}H_{25}N_2O$: 417.1961. Found: 417.1961.

3-(2,2-Diphenylvinyl)-2-(quinolin-8-yl)octahydro-1H-isoindol-1-one (4qa):



The **4qa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.6) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4qa** as colorless oil in 82% yield (72.9 mg, *d.r.* > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 – 8.60 (m, 1H), 8.15 – 8.08 (m, 1H), 7.79 – 7.72 (m, 1H), 7.61 – 7.49 (m, 2H), 7.37 – 7.31 (m, 1H), 7.20 – 7.08 (m, 4H), 7.01 – 6.92 (m, 4H), 6.37 – 6.31 (m, 2H), 6.09 (d, *J* = 10.0 Hz, 1H), 4.97 – 4.85 (m, 1H), 2.89 – 2.80 (m, 1H), 2.54 – 2.45 (m, 1H), 2.13 – 2.03 (m, 1H), 1.90 – 1.80 (m, 2H), 1.75 – 1.64 (m, 1H), 1.59 – 1.53 (m, 1H), 1.48 – 1.29 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.7, 149.9, 145.8, 144.9, 141.1, 138.6, 135.8, 135.5, 130.0, 129.2, 129.1, 128.1, 127.7, 127.7, 127.5, 127.5, 127.0, 126.8, 126.1, 121.2, 62.8, 42.0, 40.4, 25.2, 24.5, 23.6, 22.8; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{31}H_{29}N_2O$: 455.2274. Found: 455.2271.

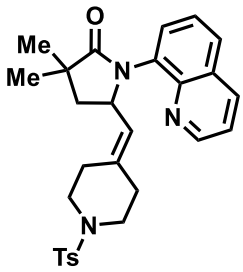
3-(2,2-Diphenylvinyl)-2-(quinolin-8-yl)octahydrocyclohepta[c]pyrrol-1(2H)-one (4sa):



The **4sa** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.5) on silica gel using EtOAc/PE (1:1) as the eluent to give the desired product **4sa** as colorless oil in 94% yield (86.2 mg, *d.r.* > 20:1). **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 8.67 – 8.58 (m, 1H), 8.16 – 8.07 (m, 1H), 7.81 – 7.73 (m, 1H), 7.58 – 7.49 (m, 2H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.20 – 7.12 (m, 3H), 7.11 – 7.05 (m, 1H), 6.99 – 6.85 (m, 4H), 6.25 – 6.18 (m, 2H), 6.03 (d, *J* = 10.0 Hz, 1H), 4.66 – 4.56 (m, 1H), 2.99 – 2.87 (m, 1H), 2.73 – 2.61 (m, 1H), 2.14 – 1.77 (m, 6H), 1.55 – 1.25 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.5, 150.1, 145.6, 144.6, 141.1, 138.5, 135.8, 135.7, 130.2, 129.2, 129.0, 128.8, 128.0, 127.9, 127.6, 127.5, 127.0, 126.7, 126.1, 121.3, 65.5, 48.1, 45.0, 31.5, 30.4, 30.0, 27.9, 27.5; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{32}H_{31}N_2O$: 459.2431. Found: 459.2430.

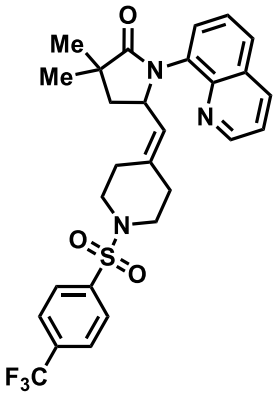
3,3-Dimethyl-1-(quinolin-8-yl)-5-((1-tosylpiperidin-4-ylidene)methyl)pyrrolidin-2-one (4eb):



The **4eb** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.3) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **4eb** as colorless oil in 82% yield (80.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78 – 8.72 (m, 1H), 7.96 – 7.89 (m, 1H), 7.42 – 7.31 (m, 4H), 7.32 – 7.24 (m, 3H), 7.25 – 7.18 (m, 1H), 5.35 – 5.24 (m, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.68 – 2.61 (m, 1H), 2.46 (s, 3H), 2.21 – 2.13 (m, 1H), 2.06 – 1.90 (m, 2H), 1.88 – 1.63 (m, 5H), 1.36 (s, 3H), 1.26 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.5, 150.0, 143.3, 139.2, 136.0, 135.2, 133.3, 131.1, 129.5, 128.9, 127.5, 127.3, 125.8, 125.5,

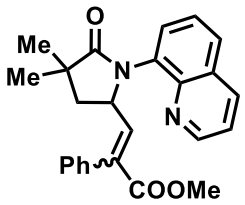
121.3, 54.6, 47.7, 46.3, 43.0, 41.3, 35.1, 27.7, 25.5, 25.1, 21.6; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{28}H_{32}N_3O_3S$: 490.2159. Found: 490.2160.

3,3-Dimethyl-1-(quinolin-8-yl)-5-((1-((4-(trifluoromethyl)phenyl)sulfonyl)piperidin-4-ylidene)methyl)pyrrolidin-2-one (4ec):



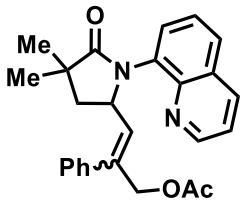
The **4ec** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **4ec** as colorless oil in 82% yield (80.3 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.79 – 8.73 (m, 1H), 7.98 – 7.90 (m, 1H), 7.77 – 7.71 (m, 2H), 7.62 – 7.57 (m, 2H), 7.43 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.26 – 7.20 (m, 1H), 5.38 – 5.30 (m, 1H), 4.97 (d, *J* = 9.6 Hz, 1H), 3.20 – 3.14 (m, 1H), 2.79 – 2.70 (m, 1H), 2.21 – 2.14 (m, 1H), 2.08 – 1.67 (m, 7H), 1.35 (s, 3H), 1.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 181.1, 150.4, 145.1, 143.5, 143.0, 139.0, 135.7, 135.2, 133.2, 131.1, 129.72 (d, *J* = 9.0 Hz), 128.1, 127.4, 125.3, 122.3, 120.9, 53.8, 47.6, 46.2, 42.6, 40.7, 34.0, 27.8, 25.4, 24.5, 21.7; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.9; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{28}H_{29}N_3O_3F_3S$: 544.1876. Found: 544.1879.

Methyl-3-(4,4-dimethyl-5-oxo-1-(quinolin-8-yl)pyrrolidin-2-yl)-2-phenylacrylate (4eh):



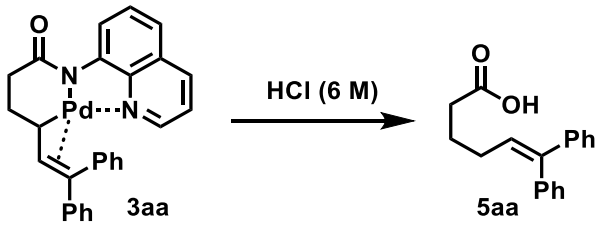
The **4eh** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.4) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **4eh** as colorless oil in 62% yield (49.7 mg, *E/Z* = 77:23). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80– 8.74 & 8.43 – 8.39 (m, 1H), 8.30 – 8.25 (m, 1H), 8.10 – 8.04 (m, 1H), 7.43 – 7.38 & 7.35 – 7.31 (m, 1H), 7.34 – 7.32 & 7.31 – 7.28 (m, 2H), 7.17 – 7.14 & 6.94 – 6.89 (m, 1H), 7.14 – 7.09 & 7.02 – 6.96 (m, 2H), 6.77 & 6.03 (d, *J* = 10.0 Hz, 1H), 6.94 – 6.92 & 6.42 – 6.37 (m, 2H), 5.60 – 5.70 & 5.21 – 5.10 (m, 1H), 3.54 & 3.44 (s, 3H), 2.44 – 2.51 & 2.19 – 2.12 (m, 1H), 1.94 – 1.87 (m, 1H), 1.39 & 1.30 (s, 3H), 1.32 & 1.24 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.7, 180.4, 167.4, 166.7, 150.4, 144.6, 143.2, 140.5, 139.0, 137.3, 136.4, 135.9, 133.7, 131.4, 131.1, 130.9, 128.8, 128.3, 128.2, 127.7, 127.6, 127.1, 123.0, 122.9, 98.1, 57.3, 56.1, 52.2, 51.7, 42.3, 41.9, 41.1, 41.0, 25.6, 25.6, 25.2, 25.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{25}H_{25}N_2O_3$: 401.1860. Found: 401.1861.

(*E*)-3-(4,4-Dimethyl-5-oxo-1-(quinolin-8-yl)pyrrolidin-2-yl)-2-phenylallyl acetate (4el):



The **4el** was prepared according to the general procedure. Purification by column chromatography (TLC R_f = 0.2) on silica gel using EtOAc/PE (1:2) as the eluent to give the desired product **4el** as colorless oil in 67% yield (55.5 mg, *E/Z* > 99:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 – 8.82 (m, 1H), 8.12 – 8.06 (m, 1H), 7.73 – 7.66 (m, 1H), 7.61 – 7.54 (m, 1H), 7.52 – 7.44 (m, 1H), 7.38 – 7.31 (m, 1H), 7.16 – 7.09 (m, 3H), 7.01 – 6.94 (m, 2H), 5.82 – 5.68 (m, 2H), 4.72 (d, *J* = 12.4 Hz, 1H), 4.45 (d, *J* = 12.4 Hz, 1H), 2.33 (dd, J_1 = 12.8 Hz, J_2 = 6.4 Hz, 1H), 1.73 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.5, 170.6, 139.4, 137.6, 134.9, 134.4, 130.5, 130.1, 129.2, 128.3, 127.7, 127.7, 126.3, 126.1, 121.4, 60.6, 55.9, 42.9, 41.2, 25.5, 25.1, 20.7; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{26}H_{27}N_2O_3$: 415.2016. Found: 415.2018.

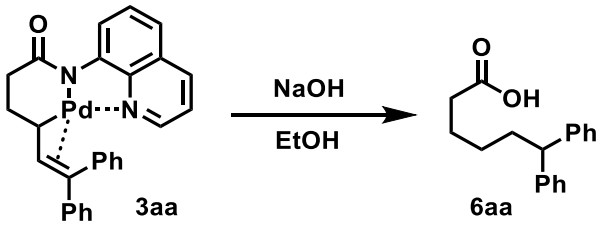
6,6-Diphenylhex-5-enoic acid(5aa)[10]



To a 10 mL round-bottom flask was added compound **3aa** (0.20 mmol, 64.8 mg), followed by HCl (6 M, 2 mL). After being stirred at 120 ºC for 24 h, the reaction mixture was cooled to room temperature, washed with HCl (1 M, 20 mL) and extracted with ethyl acetate (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash

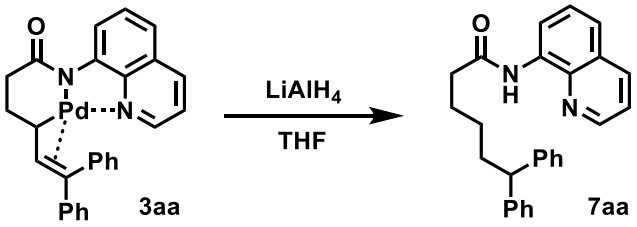
column chromatography to afford **5aa** as yellow oil in 74% yield (39.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 – 7.07 (m, 10H), 5.98 (d, J = 7.2 Hz, 1H), 2.27 (d, J = 7.6 Hz, 2H), 2.10 (q, J_1 = 14.8, J_2 = 7.6 Hz, 2H), 1.76 – 1.66 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.2, 142.5, 140.0, 129.8, 128.1, 127.2, 127.0, 33.3, 29.0, 24.8; **HRMS (ESI) m/z [M+Na]$^+$**: Calcd for $C_{18}H_{18}NaO_2$: 289.1199. Found: 289.1194.

6,6-Diphenylhexanoic acid (6aa) [11]



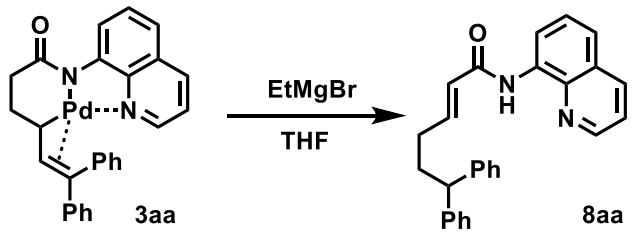
Under air atmosphere, **3aa** (0.20 mmol, 1.0 equiv.), NaOH (3.0 mmol, 15.0 equiv.) was dissolved in 2.0 mL of EtOH at room temperature. The reaction system stirred at 100 ^{o}C for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **6aa** as yellow oil in 81% yield (43.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.23 – 7.07 (m, 10H), 3.82 (t, J = 7.6 Hz, 1H), 2.24 (t, J = 7.6 Hz, 2H), 1.99 (q, J = 8.0 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.29 – 1.19 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.0, 144.9, 128.4, 127.8, 126.1, 51.1, 35.3, 33.7, 27.4, 24.6; **HRMS (ESI) m/z [M+Na]$^+$**: Calcd for $C_{18}H_{21}O_2Na$: 291.1356. Found: 291.1347.

6,6-Diphenyl-*N*-(quinolin-8-yl)hexanamide (7aa) [12]



To a 10 mL round-bottom flask was added compound **3aa** (0.20 mmol, 1.0 equiv.), $LiAlH_4$ (0.8 mmol, 4.0 equiv.) were dissolved in 2.0 mL of THF. After being stirred at 25 ºC for 24 h, washed with H_2O (20 mL), extracted with ethyl acetate (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **7aa** as yellow oil in 80% yield (63.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.76 (s, 1H), 8.82 – 8.73 (m, 2H), 8.19 – 8.12 (m, 1H), 7.57 – 7.41 (m, 3H), 7.29 – 7.20 (m, 8H), 7.19 – 7.10 (m, 2H), 3.92 (d, *J* = 8.0 Hz, 1H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.35 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 148.1, 145.0, 138.3, 136.4, 134.5, 128.4, 127.9, 127.8, 127.4, 126.1, 121.6, 121.3, 116.4, 51.2, 38.1, 35.5, 27.7, 25.6; **HRMS (ESI) m/z [M+Na]$^+$**: Calcd for $C_{27}H_{27}N_2ONa$: 417.1937. Found: 417.1929.

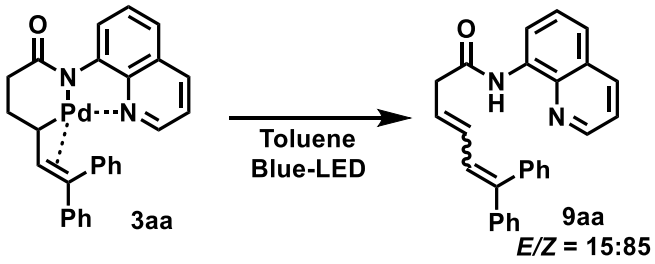
(*E*)-6,6-Diphenyl-*N*-(quinolin-8-yl)hex-2-enamide (8aa) [13]



To a 10 mL round-bottom flask was added compound **3aa** (0.20 mmol, 1.0 equiv.), EtMgBr (1 M in THF, 0.8 mmol, 4.0 equiv.) were dissolved in 2.0 mL of THF. After

being stirred at 50 °C for 24 h, the reaction mixture was cooled to room temperature, washed with H_2O (20 mL), extracted with ethyl acetate (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **8aa** as colorless oil in 60% yield (47.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 8.76 – 8.67 (m, 2H), 8.14 – 8.07 (m, 1H), 7.53 – 7.41 (m, 2H), 7.42 – 7.34 (m, 1H), 7.14 – 7.01 (m, 10H), 6.03 – 5.93 (m, 1H), 5.52 – 5.40 (m, 1H), 4.60 (d, J = 7.6 Hz, 1H), 2.64 – 2.48 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 147.8, 143.8, 139.6, 136.8, 134.3, 134.1, 130.1, 128.5, 128.2, 128.0, 127.6, 126.1, 121.5, 121.5, 117.0, 53.9, 37.9, 28.6; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{27}H_{25}N_2O$: 393.1961. Found: 393.1960.

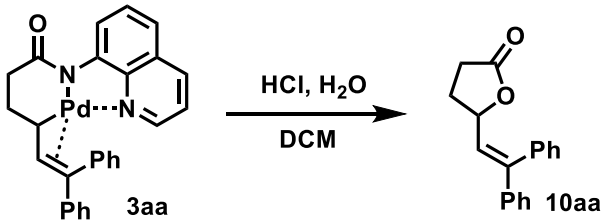
6,6-Diphenyl-*N*-(quinolin-8-yl)hexa-3,5-dienamide (9aa) [14]



To a 10 mL round-bottom flask was added compound **3aa** (0.20 mmol, 1.0 equiv.) were dissolved in 2.0 mL of Toluene (2 mL). Then the tube was stirred at 0 °C under 24 W Blue LEDs for 12 h until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the mixture was extracted three times with EtOAc. The organic layer was dried over Na_2SO_4, filtration and evaporation of the solvent. And the resulting residue was purified by silica gel column chromatography to obtain the desired products **9aa** as yellow oil in 78% yield (60.9 mg, *E/Z* = 15:85). **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.76 – 8.72 (m, 1H), 8.71 – 8.67 (m, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 7.33 – 7.26 (m, 3H), 7.23 – 7.18 (m, 7H), 6.73 (d, J = 11.2 Hz, 1H), 6.42 – 6.33 (m, 1H), 6.14 – 6.05 (m, 1H), 3.30 (d, J = 7.6 Hz, 2H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.3, 148.2, 142.8, 142.1, 139.6, 138.4, 136.3, 134.3, 133.2, 130.5, 128.2, 127.9, 127.6, 127.5, 127.4, 127.4, 127.2, 127.2, 121.6, 116.4, 42.4.; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{27}H_{23}N_2O$: 391.1805. Found: 391.1800.

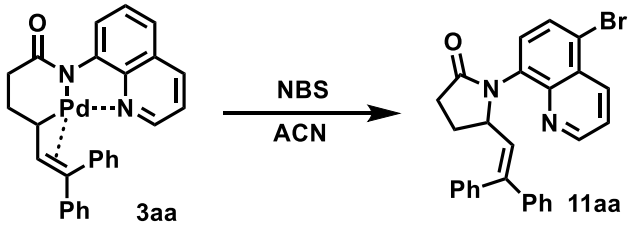
5-(2,2-Diphenylvinyl)dihydrofuran-2(3*H*)-one (10aa) [15]



To a 25 mL round-bottom flask was added compound **3aa** (0.20 mmol, 1.0 equiv.), HCl (12 M, 760 μL) and H_2O (2.0 mL) were dissolved in 2.0 mL of CH_2Cl_2. After being stirred at 120 ^{o}C for 36 h, washed with H_2O (20 mL), extracted with dichloromethane (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **10aa** as yellow oil in 60% yield (31.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.28 (m, 3H), 7.25 – 7.12 (m, 7H), 5.99 (d, J = 9.2 Hz, 1H), 4.93 – 4.85 (m, 1H), 2.58 – 2.38 (m, 2H), 2.34 – 2.24 (m, 1H), 2.11 – 1.96 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.0, 147.3, 140.9, 138.4, 129.7, 128.4, 128.3, 128.3, 128.0, 127.7, 125.4, 78.5, 29.5, 29.1; **HRMS (ESI) m/z [M+H]$^+$**: Calcd for $C_{18}H_{17}O_2$:

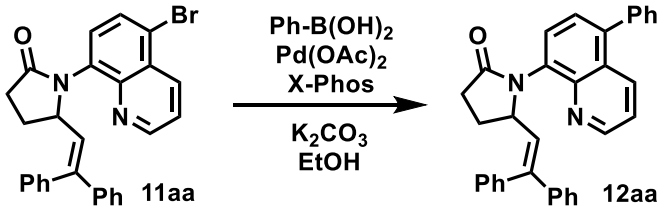
265.1223. Found: 265.1221.

1-(5-Bromoquinolin-8-yl)-5-(2,2-diphenylvinyl)pyrrolidin-2-one (11aa) [9]



To a 10 mL round-bottom flask was added compound **3aa** (0.20 mmol, 1.0 equiv.), *N*-Bromosuccinimide (0.30 mmol, 1.5 equiv.) were dissolved in 2.0 mL of CH_3CN. After being stirred at 25 ºC for 2 h, washed with H_2O (20 mL), extracted with ethyl acetate (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **11aa** as colorless oil in 81% yield (76.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 – 8.51 (m, 1H), 8.47 – 8.41 (m, 1H), 7.80 – 7.75 (m, 1H), 7.44 – 7.34 (m, 2H), 7.13 – 7.03 (m, 4H), 6.98 – 6.89 (m, 2H), 6.88 – 6.82 (m, 2H), 6.38 – 6.31 (m, 2H), 5.94 (d, J = 10.0 Hz, 1H), 5.17 – 5.09 (m, 1H), 2.70 – 2.64 (m, 2H), 2.52 – 2.40 (m, 1H), 2.15 – 2.03 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.8, 150.4, 148.9, 145.4, 144.8, 140.9, 138.3, 135.9, 135.1, 130.4, 129.9, 129.0, 128.4, 128.1, 127.8, 127.7, 127.1, 127.1, 122.4, 121.5, 60.2, 31.1, 26.9; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{27}H_{23}N_2O$: 469.0910. Found: 469.0912.

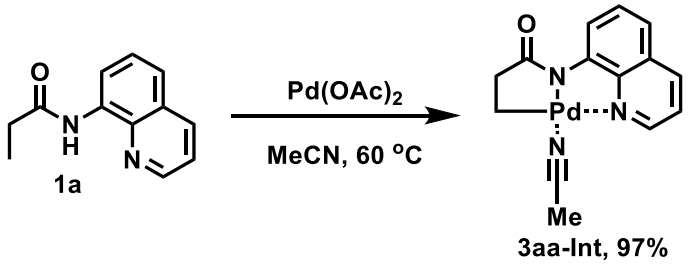
5-(2,2-Diphenylvinyl)-1-(5-phenylquinolin-8-yl)pyrrolidin-2-one (12aa) [16]



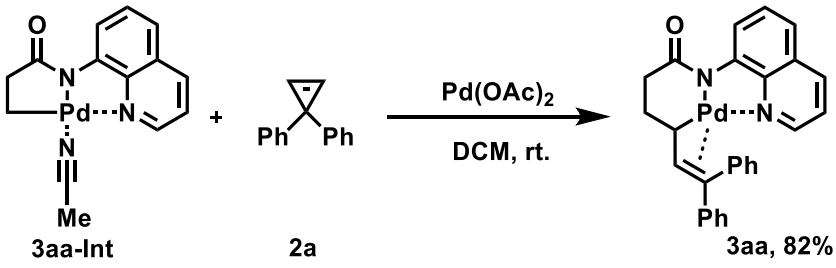
To a 10 mL round-bottom flask was added compound **11aa** (0.2 mmol, 93.9 mg), $Pd(OAc)_2$ (0.02 mmol, 14.0 mg), 2-(Dicyclohexylphosphino)-2',4',6'-tri-i-propyl-1,1'-biphenyl (0.03 mmol, 14.0 mg) and K_2CO_3 (0.6 mmol, 82.8 mg) followed by EtOH (2.0 mL) and phenylboronic acid (0.4 mmol, 48.8 mg). After being stirred at 80 °C for 12 h, the reaction mixture was cooled to room temperature, washed with H_2O (20 mL), extracted with ethyl acetate (30 mL × 3). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford **12aa** as yellow oil in 79% yield (73.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 – 8.51 (m, 1H), 8.15 – 8.09 (m, 1H), 7.61 – 7.55 (m, 1H), 7.48 – 7.34 (m, 6H), 7.25 – 7.18 (m, 1H), 7.13 – 7.02 (m, 4H), 6.98 – 6.90 (m, 2H), 6.92 – 6.85 (m, 2H), 6.40 – 6.34 (m, 2H), 6.01 (d, J = 10.0 Hz, 1H), 5.20 – 5.09 (m, 1H), 2.75 – 2.66 (m, 2H), 2.54 – 2.41 (m, 1H), 2.18 – 2.04 (m, 1H).; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.9, 149.6, 145.1, 141.1, 140.6, 139.0, 138.4, 134.7, 134.6, 134.4, 130.0, 129.6, 129.0, 128.6, 128.5, 128.1, 127.8, 127.8, 127.6, 127.6, 127.1, 127.0, 126.8, 121.2, 60.4, 31.2, 26.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{33}H_{27}N_2O$: 467.2118. Found: 467.2117.

Mechanism studies and their NMR spectra:

Control Experiment for scheme 3-A-I[17]:



A mixture of **1a** (0.2 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.2 mmol, 1.0 equiv.) was dissolved in CH_3CN (2.0 mL) in a Schlenk tube. The mixture was allowed to stir at 60 °C for 4 hours after the **1a** was consumed (determined by TLC). The solvent was removed and the crude residue was purified by flash column chromatography (DCM: MeCN = 5:1) to afford desired product **3aa-Int** (67.1 mg, 97% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 9.04 (dd, J_1 = 4.8, J_2 = 1.6 Hz, 1H), 8.87 (dd, J_1 = 8.0, J_2 = 1.4 Hz, 1H), 8.52 (dd, J_1 = 8.4, J_2 = 1.6 Hz, 1H), 7.67 (dd, J_1 = 8.4, J_2 = 4.8 Hz, 1H), 7.56 – 7.41 (m, 2H), 2.65 (t, J = 7.2 Hz, 2H), 1.91 (s, 3H), 1.51 (t, J = 7.2 Hz, 2H); **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 13C NMR (101 MHz, DMSO) δ 184.4, 172.0, 149.4, 145.5, 144.8, 138.9, 129.6, 128.5, 121.6, 119.0, 118.7, 21.1, 8.1; **HRMS (ESI) m/z [M+H]$^+$:** Calcd for $C_{14}H_{14}N_3OPd$: 346.0166. Found: 346.0165.

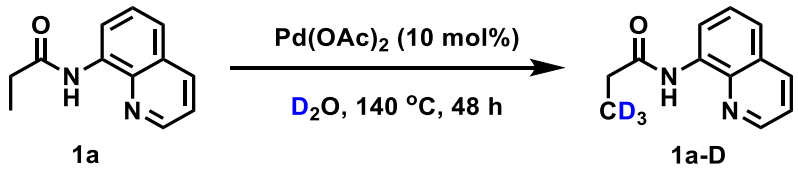


A mixture of **3aa-Int** (0.2 mmol, 1.0 equiv.) and **2a** (0.6 mmol, 3.0 equiv.) was dissolved in DCM (4.0 mL) in a Schlenk tube. The mixture was allowed to stir at room temperature until the **3aa-Int** was consumed (determined by TLC). Then the reaction

mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **3aa** (81.5 mg, 82%).

Kinetic isotopic effects for scheme 3-A-||:

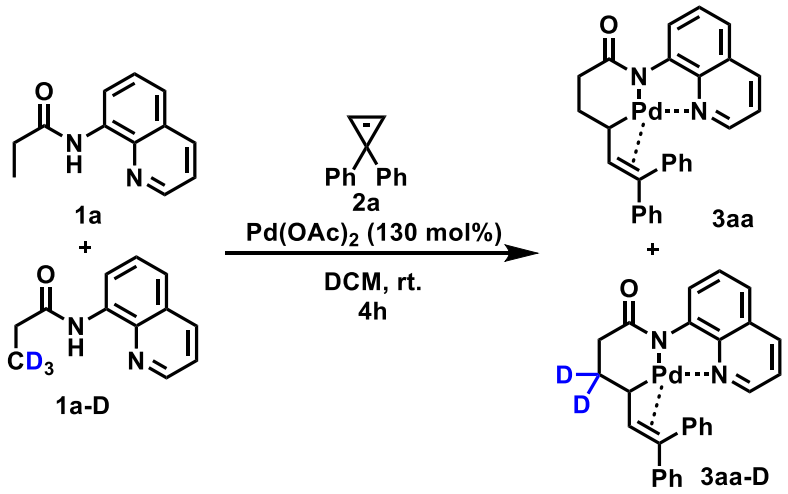
(1) Preparation of 1a-D[18]



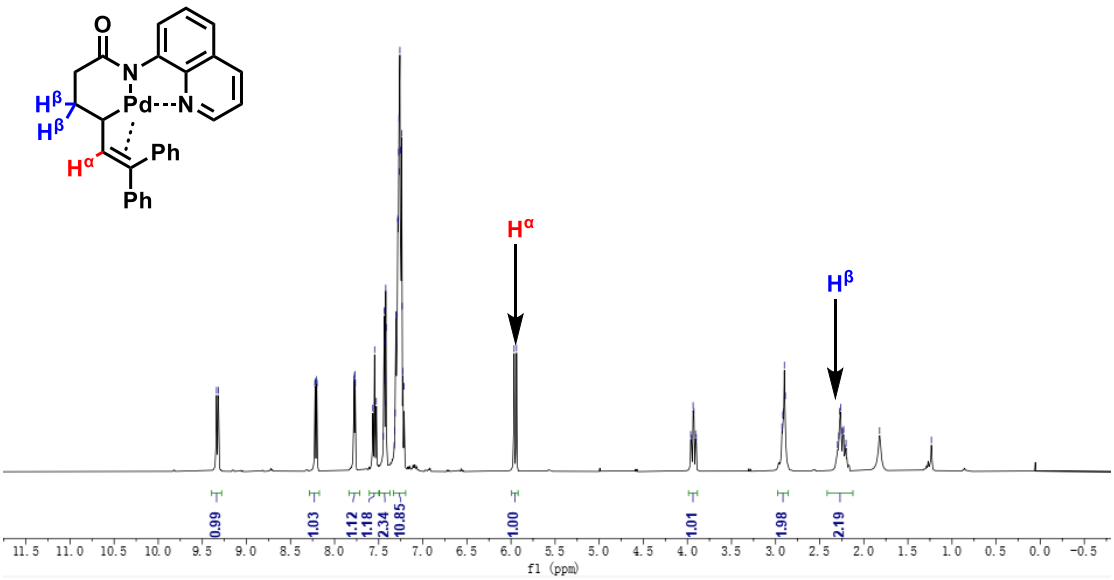
1a **1a-D**

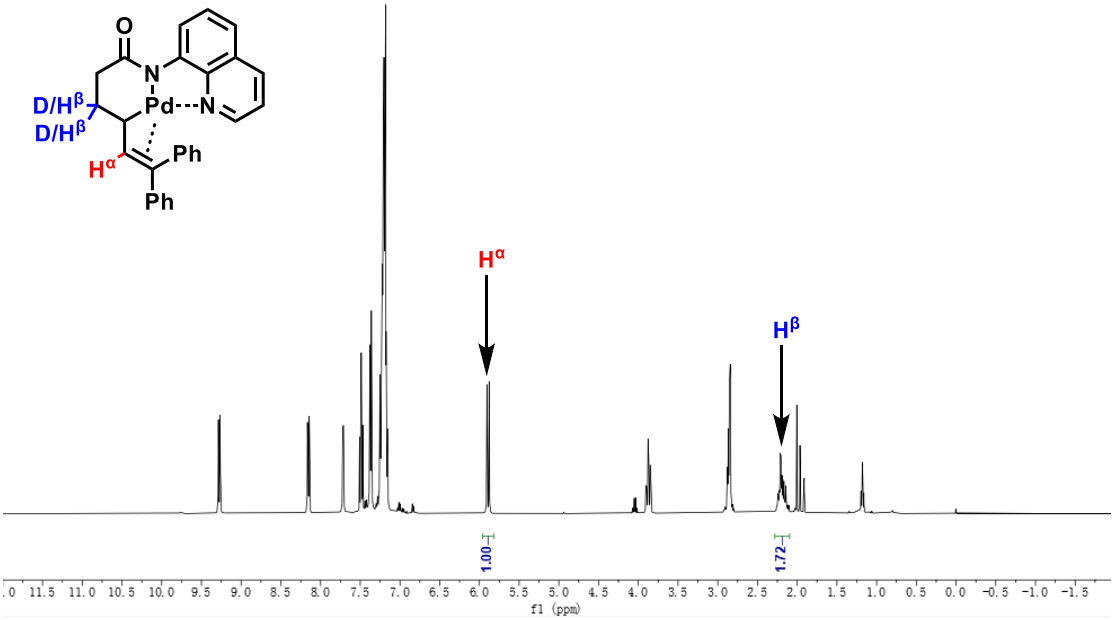
A mixture of **1a** (200 mg, 1 mmol, 1.0 equiv), $Pd(OAc)_2$ (15 mol%, 45 mg, 0.15 mol), and D_2O (2.0 mL) in a 10 mL pressure tube was stirred at 140 °C nitrogen atmosphere for 48 h. After cooling to room temperature, the mixture was filtered through a layer of celite. The layer of celite was washed with EtOAc (5.0 mL). The product was purified by flash column chromatography over silica gel (Hexane/EtOAc = 20/1) to give **1a-D** as a colorless oil (92 mg, 95% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 8.84 – 8.77 (m, 1H), 8.22 – 8.16 (m, 1H), 7.59 – 7.43 (m, 3H), 2.59 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.6, 147.9, 138.1, 136.7, 134.3, 128.0, 127.6, 127.5, 121.5, 121.4, 31.0; **HRMS (ESI) m/z $[M+H]^+$:** Calcd for $C_{12}H_{10}D_3N_2O$: 204.1211. Found: 204.1209.

(2) Determination of kinetic isotopic effect (KIE)

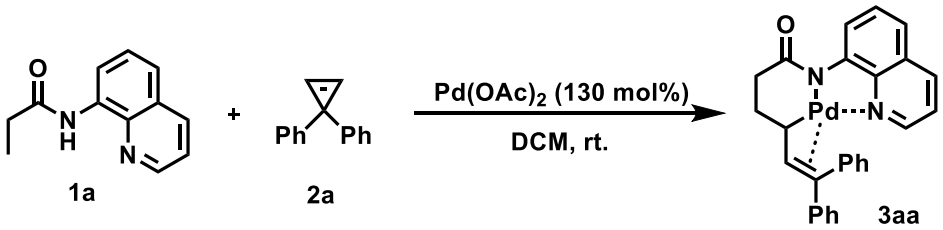


A mixture of amide **1a** (0.1 mmol, 0.5 equiv.), **1a-D** (0.1 mmol, 0.5 equiv.) and $Pd(OAc)_2$ (0.26 mmol, 1.3 equiv.) was dissolved in DCM (2.0 mL) in a Schlenk tube. To the stirring reaction mixture was added a solution of cyclopropene **2a** (0.6 mmol, 3.0 equiv.) in DCM (2 mL). The mixture was allowed to stir at room temperature for 4 h. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **3aa** and **3aa-D**. The KIE value by competitive experiments was determined to be k_H/k_D =1.72/(2.19−1.72), the value is 3.66 on the basis of ^{1}H NMR spectroscopy.

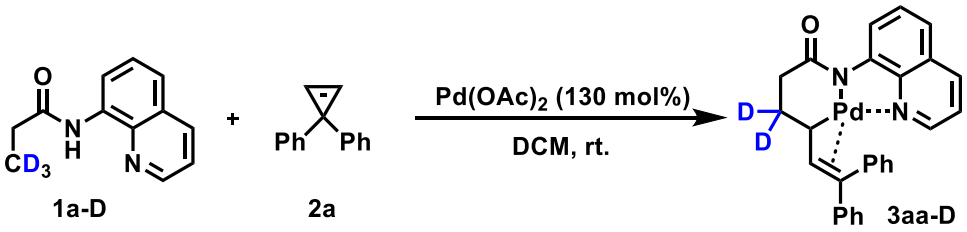




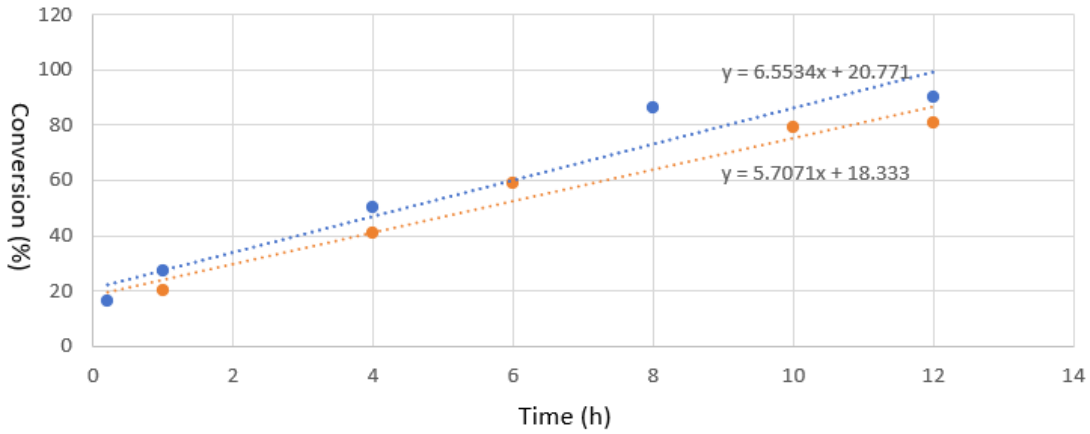
(3) KIE by parallel experiments



Time (h)	Convesion (%)
0.2	16
1	27
4	50
8	86
12	90



Time (h)	Convesion (%)
1	20
4	41
6	59
10	79
12	81

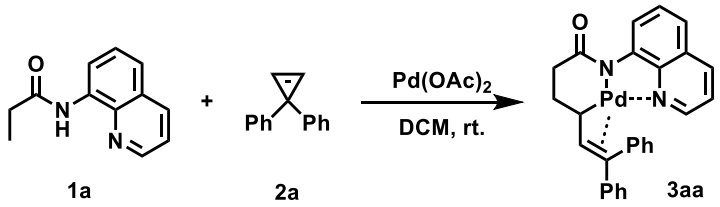


KIE=k_H/k_D=6.5534/5.7071=1.15

A mixture of amide **1a** (0.1 mmol, 1.0 equiv.) and $Pd(OAc)_2$ (0.13 mmol, 1.3 equiv.) was dissolved in DCM (1.0 mL) in a Schlenk tube. To the stirring reaction mixture was added a solution of cyclopropene **2a** (0.3 mmol, 3.0 equiv.) in DCM (1.0 mL). The mixture was allowed to stir at room temperature. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography to give the desired product **3aa**.

In another reaction pressure tube, **1a-D** was used instead of **1a**. The kinetic isotope effect (KIE) is determined as 1.15.

Real-time tracing experiments for scheme 3-B:



1a 2a 3aa

Entry	Detection time (h)	Solvent	conversion (%)	
			1a[b]	3aa[b]
1	0.2	DCM	83	16
2	0.5	DCM	80	19
3	1	DCM	71	27
4	2	DCM	70	29
5	3	DCM	56	42
6	4	DCM	49	50
7	5	DCM	35	63
8	6	DCM	31	68
9	8	DCM	13	86
10	10	DCM	9	89
11	12	DCM	8	90
12	15	DCM	8	90
13	24	DCM	7	90

[a]Unless otherwise noted, reactions were carried out using **1a** (0.20 mmol), **2a** (0.60 mmol), $Pd(OAc)_2$ (0.26 mmol) in DCM (0.05 M, 4 mL) at room temperature. [b]Isolated yields.

A mixture of amide **1a** (0.2 mmol, 1.0 equiv.) and $Pd(OAc)_2$ (0.26 mmol, 1.3 equiv.)was dissolved in CH_2Cl_2 (2.0 m)in a Schlenk tube. To the stirring reaction mixture was added a solution of cvclopropene **2a** (0.6 mmol, 3.0 equiv.) in CH_2Cl_2 (2.0 ml). The mixture was allowed to stir at room temperature. Then, the reaction mixture was concentrated under reduced pressure and purified by column chromatography to afford the unreacted starting material **1a** and the desired product **3aa**.

DFT calculation results

Computational Details

Density functional theory (DFT) calculations were performed by Gaussian 16[19]program. All the geometrical structures involved in the selected reaction model were optimized at the B3LYP-D3[20-22]/def2-SVP[23]/IEF-PCM$_{CH2Cl2}$[24,25] level, and then the single point energies of the obtained stationary points were refined at the B3LYP/def2-TZVP[26]/IEF-PCM$_{CH2Cl2}$ level. Subsequently, frequency calculations were performed to determine whether the stationary point is a local minima or transition structure to afford the zero-point and thermochemical corrections for the enthalpies and free energies. In addition, CYLview[27] software was used for the optimized 3D structure drawing.

2a

Zero-point correction= 0.218144

Thermal correction to Energy= 0.230032

Thermal correction to Enthalpy= 0.230976

Thermal correction to Gibbs Free Energy= 0.178628

Sum of electronic and zero-point Energies= -578.126033

Sum of electronic and thermal Energies= -578.114145

Sum of electronic and thermal Enthalpies= -578.113201

Sum of electronic and thermal Free Energies= -578.165549

Cartesian coordinates

C	-0.000025	1.063387	-0.000027
C	0.002161	2.434896	0.648451
C	-0.002262	2.434846	-0.648614
H	-0.000326	2.963209	1.599460
H	0.000144	2.963043	-1.599686
C	-1.283585	0.259261	0.041614

C	-1.388279	-0.881097	0.858237
C	-2.411158	0.650884	-0.697034
C	-2.582252	-1.603009	0.935499
H	-0.520887	-1.207246	1.437496
C	-3.606495	-0.072220	-0.627941
H	-2.353260	1.537755	-1.334206
C	-3.697849	-1.202612	0.190604
H	-2.642339	-2.483495	1.580980
H	-4.469348	0.248782	-1.217737
H	-4.631249	-1.768527	0.247601
C	1.283576	0.259330	-0.041589
C	2.410904	0.650634	0.697589
C	1.388531	-0.880632	-0.858727
C	3.606285	-0.072405	0.628499
H	2.352778	1.537200	1.335167
C	2.582544	-1.602475	-0.935985
H	0.521303	-1.206516	-1.438388
C	3.697909	-1.202396	-0.190567
H	4.468958	0.248340	1.218699
H	2.642852	-2.482647	-1.581874
H	4.631340	-1.768259	-0.247564

Vibrational frequencies

21.5530	44.2609	79.1103
117.4814	210.2557	215.7929
291.7041	295.1717	339.4573

418.3345	423.5391	437.1687
445.2426	559.2809	559.7847
588.0416	631.3047	631.9087
665.1191	709.6388	722.7111
723.9619	772.5808	791.5026
866.1089	866.1696	878.6448
879.9320	917.5754	919.8355
950.4476	957.9373	1006.2030
1006.4204	1010.7850	1011.1919
1017.5648	1028.9284	1029.1298
1047.8494	1052.7677	1100.8090
1104.4464	1131.0317	1171.5388
1171.9565	1195.0629	1195.3220
1250.4498	1274.6775	1326.8794
1334.7122	1359.2288	1363.1758
1471.1442	1476.0992	1521.9521
1525.0873	1630.2819	1634.0990
1656.1628	1657.0004	1734.1663
3165.4690	3165.6096	3171.2906
3171.6023	3179.8867	3180.0075
3186.6251	3186.7216	3195.4486
3195.5782	3239.8796	3288.4123

A

Zero-point correction= 0.196688

Thermal correction to Energy= 0.209418

Thermal correction to Enthalpy= 0.210363

Thermal correction to Gibbs Free Energy= 0.156671

Sum of electronic and zero-point Energies= -775.361776

Sum of electronic and thermal Energies= -775.349045

Sum of electronic and thermal Enthalpies= -775.348101

Sum of electronic and thermal Free Energies= -775.401792

Cartesian coordinates

C	1.981773	1.615922	0.050997
O	1.927159	2.839910	-0.005132
C	3.286486	0.845811	0.228685
H	3.526047	0.925923	1.304533
H	4.085145	1.392802	-0.300567
C	3.164129	-0.625763	-0.184452
H	3.791795	-1.294382	0.430577
H	3.426605	-0.769552	-1.248494
N	0.888394	0.773096	0.020105
C	-0.450220	1.153674	-0.010503
C	-1.415292	0.080262	0.010260
C	-0.937555	2.464318	-0.044872
C	-2.817952	0.357893	0.000523
C	-2.327060	2.722725	-0.053526
H	-0.224256	3.283175	-0.062908
C	-1.803279	-2.221110	0.061085
C	-3.704722	-0.752555	0.022655
C	-3.261571	1.706136	-0.031573

H	-2.659917	3.763774	-0.079793
C	-3.204417	-2.036978	0.052711
H	-1.373281	-3.226733	0.086244
H	-4.782829	-0.571915	0.015344
H	-4.333114	1.917390	-0.040279
H	-3.862778	-2.907055	0.070482
Pd	1.225223	-1.174743	-0.025362
N	-0.950232	-1.209743	0.039984

Vibrational frequencies

50.2658	76.3268	112.3681
149.8097	168.6372	176.0730
209.3554	256.7767	262.9840
295.6572	349.0070	451.0946
456.7435	461.5031	490.3216
523.6877	543.5374	551.8954
565.2266	608.8166	633.4155
667.0210	681.6008	696.8828
783.0570	810.4382	816.0117
822.1362	872.6498	881.8113
928.9784	941.2176	967.5481
968.9404	1006.4624	1020.4472
1028.4009	1067.1057	1082.9647
1100.3854	1106.4701	1131.7093
1155.4135	1191.3363	1232.3816
1242.1636	1256.3325	1275.1537

1306.0682	1354.2733	1363.9707
1411.0291	1416.8901	1420.2794
1430.6033	1452.6333	1495.4435
1544.2783	1619.3392	1637.8234
1654.1412	1722.4087	3001.8128
3024.5101	3060.2930	3075.1826
3177.8816	3181.0182	3186.8557
3196.1657	3213.8573	3260.5751

B

Zero-point correction= 0.417860

Thermal correction to Energy= 0.443518

Thermal correction to Enthalpy= 0.444462

Thermal correction to Gibbs Free Energy= 0.360830

Sum of electronic and zero-point Energies= -1353.523958

Sum of electronic and thermal Energies= -1353.498300

Sum of electronic and thermal Enthalpies= -1353.497356

Sum of electronic and thermal Free Energies= -1353.580988

Cartesian coordinates

C	-2.521420	-2.652700	-0.171564
O	-3.534222	-3.339303	-0.072663
C	-1.151093	-3.240240	-0.478187
H	-1.133530	-3.386602	-1.573736
H	-1.092936	-4.249932	-0.036812
C	0.007127	-2.339173	-0.046593

H	0.899054	-2.481794	-0.664492
H	0.284465	-2.503672	1.006524
N	-2.463816	-1.277742	-0.087299
C	-3.561048	-0.428323	0.038046
C	-3.269616	0.984975	0.039000
C	-4.901262	-0.811558	0.146478
C	-4.321685	1.950004	0.130932
C	-5.931297	0.152627	0.242897
H	-5.138143	-1.871577	0.152878
C	-1.654424	2.665725	-0.070501
C	-3.956542	3.322417	0.112692
C	-5.667257	1.507320	0.234969
H	-6.963617	-0.197755	0.325280
C	-2.629603	3.683832	0.009483
H	-0.593582	2.919466	-0.149965
H	-4.739839	4.081985	0.180031
H	-6.469353	2.244918	0.308769
H	-2.320567	4.730119	-0.009459
Pd	-0.645079	-0.402124	-0.096340
N	-1.959788	1.379511	-0.053503
C	2.374703	0.350178	-0.021413
C	1.105560	0.717094	-0.773548
C	1.054317	0.783882	0.581661
H	0.884322	1.298641	-1.671091
H	0.764724	1.447089	1.399428

C	3.446103	1.425420	-0.019183
C	4.805792	1.104485	0.154435
C	3.107787	2.784930	-0.179287
C	5.786761	2.099580	0.164468
H	5.102172	0.063193	0.284217
C	4.089281	3.779849	-0.171930
H	2.066123	3.081116	-0.311030
C	5.435256	3.443181	-0.000104
H	6.834636	1.820279	0.301962
H	3.797273	4.825319	-0.300660
H	6.203145	4.220733	0.006531
C	2.891129	-1.058083	0.078408
C	3.352183	-1.724554	-1.066176
C	2.967406	-1.703135	1.318168
C	3.856029	-3.024855	-0.976703
H	3.298491	-1.221371	-2.035471
C	3.472069	-3.004130	1.413333
H	2.609011	-1.185070	2.211642
C	3.914272	-3.669553	0.265147
H	4.199944	-3.539712	-1.877558
H	3.514298	-3.502318	2.385393
H	4.303408	-4.688444	0.336593

Vibrational frequencies

17.4444	28.2466	43.9549
50.1392	58.4171	62.2279

69.7830 84.7515 91.2127

104.4104 134.0672 141.2634

163.6010 181.1076 189.4841

204.9172 208.8182 236.7495

250.0167 258.7785 275.1384

305.8144 306.8599 344.1465

399.9439 419.1285 423.9254

450.0951 451.5820 456.0725

456.4563 462.9017 492.0110

504.1238 524.9813 546.5258

549.4747 560.2332 567.7548

575.7990 610.6091 629.7438

630.6020 632.2476 643.2969

672.4876 690.8335 694.7000

712.6674 717.1453 724.1359

724.8712 777.3705 783.7761

787.2131 811.9546 818.8393

827.6006 861.2635 866.8411

869.4094 874.7406 889.1209

899.2009 928.8938 931.0841

946.3510 951.4953 960.5601

976.7013 977.6388 982.1470

1006.5187 1008.3750 1010.9567

1014.1311 1017.0375 1022.3233

1030.6407 1030.9064 1032.4707

1034.5213	1048.5289	1056.2086
1073.5116	1092.9320	1098.4593
1102.1161	1112.3180	1118.1210
1135.4219	1140.9905	1153.7987
1171.6838	1175.8422	1187.3850
1191.1670	1210.9224	1227.6299
1232.4606	1242.9241	1259.5648
1272.0600	1300.2876	1312.9082
1324.6191	1342.3981	1358.3162
1359.3966	1365.1702	1365.5453
1413.9803	1419.3999	1423.2360
1441.1402	1451.2145	1470.7016
1474.0397	1499.4652	1505.6802
1523.4505	1535.0229	1545.6360
1620.6616	1630.1855	1635.9994
1638.2604	1655.0435	1655.2586
1660.7316	1721.4836	3019.5619
3056.9298	3069.5594	3168.0196
3168.9077	3172.4479	3172.5724
3177.8434	3180.5269	3180.8745
3182.0214	3185.9571	3186.6557
3187.7846	3193.7580	3195.8562
3197.2768	3202.1506	3211.3457
3214.5355	3215.0676	3260.6659

TS-1

Zero-point correction= 0.414821

Thermal correction to Energy= 0.440976

Thermal correction to Enthalpy= 0.441921

Thermal correction to Gibbs Free Energy= 0.356073

Sum of electronic and zero-point Energies= -1353.492109

Sum of electronic and thermal Energies= -1353.465953

Sum of electronic and thermal Enthalpies= -1353.465009

Sum of electronic and thermal Free Energies= -1353.550857

Cartesian coordinates

C	2.974900	-2.723488	0.668843
O	4.119417	-3.081648	0.944577
C	1.771205	-3.644561	0.835681
H	1.502148	-3.585704	1.906411
H	2.099970	-4.684393	0.663394
C	0.575573	-3.240298	-0.030909
H	-0.370858	-3.618657	0.383807
H	0.676222	-3.631911	-1.059240
N	2.600109	-1.473829	0.237319
C	3.435515	-0.372303	0.124159
C	2.812638	0.850514	-0.326047
C	4.805880	-0.337374	0.410501
C	3.587376	2.045562	-0.476702
C	5.553014	0.852080	0.264488
H	5.285251	-1.252171	0.746704

C	0.884148	1.941381	-1.042235
C	2.918815	3.210644	-0.938274
C	4.973587	2.027603	-0.169876
H	6.620295	0.828343	0.501150
C	1.573034	3.160179	-1.226693
H	-0.185442	1.891817	-1.245421
H	3.486133	4.137215	-1.060242
H	5.558590	2.942684	-0.286093
H	1.026933	4.035251	-1.582346
Pd	0.652367	-1.212185	-0.275556
N	1.468058	0.836516	-0.607073
C	-1.466243	-1.240799	-0.413750
H	-1.914042	-1.944929	0.278713
C	-1.754713	-0.402367	-1.422178
H	-1.264740	-0.075516	-2.343025
C	-2.603924	0.150729	-0.406041
C	-2.207735	1.426573	0.274384
C	-2.677894	2.656200	-0.216092
C	-1.348311	1.414070	1.381683
C	-2.276279	3.854077	0.381624
H	-3.354227	2.670695	-1.074688
C	-0.952628	2.612018	1.983643
H	-0.971238	0.461086	1.760749
C	-1.409889	3.834497	1.481073
H	-2.639133	4.806210	-0.013581

H	-0.277552	2.589063	2.842551
H	-1.091920	4.771434	1.944926
C	-3.998793	-0.343444	-0.227431
C	-4.608223	-1.181819	-1.182464
C	-4.740682	0.029429	0.909872
C	-5.911512	-1.645543	-0.995451
H	-4.058249	-1.466714	-2.082474
C	-6.046565	-0.431232	1.091087
H	-4.287647	0.682722	1.658194
C	-6.637147	-1.273211	0.142252
H	-6.368013	-2.291895	-1.749393
H	-6.605239	-0.132620	1.981746
H	-7.659519	-1.631825	0.284509

Vibrational frequencies

-561.7446	13.8962	21.0866
35.6054	40.4184	50.2898
60.0331	68.8426	74.2530
81.4631	102.5791	119.0413
128.7772	146.6103	167.8499
179.2461	193.3815	211.4130
221.6186	244.9150	254.2833
259.0529	290.6259	301.6135
334.1524	354.0882	386.8344
416.0565	421.3103	440.0141
448.3801	456.2867	458.3633

463.7009	493.2207	524.0112
536.9282	548.2892	565.7844
568.4237	580.6249	608.3338
618.5762	629.6979	631.6284
639.8361	671.7252	687.0950
713.6126	714.9829	721.7093
723.1530	727.4014	773.6292
781.5754	788.7410	811.3444
813.2833	817.2044	827.1436
835.1041	862.3965	867.6778
872.4660	896.5495	928.5873
932.9091	940.2566	949.0307
956.9815	970.7593	971.6653
1007.1723	1007.9676	1009.5089
1012.6520	1015.3038	1019.5026
1027.7106	1032.8585	1033.3541
1046.7575	1051.6516	1073.7163
1090.5340	1093.2885	1101.0022
1101.8643	1110.2502	1118.6721
1151.6246	1154.8523	1173.6553
1174.3888	1184.5897	1191.2030
1191.4682	1199.0991	1230.4820
1240.6700	1256.6269	1275.2850
1302.5924	1313.2459	1316.7062
1325.2336	1356.0360	1358.7387

1360.1077	1363.5645	1368.3089
1411.4791	1417.1673	1423.3502
1438.0147	1452.5619	1470.4997
1477.7277	1497.6174	1516.7936
1524.8403	1537.2994	1545.7694
1617.7057	1627.8621	1630.6825
1638.7673	1651.9988	1654.7138
1654.9139	1708.4681	3013.4767
3018.9096	3058.5787	3091.8361
3172.7520	3174.1181	3174.6381
3176.6373	3181.0373	3183.6506
3184.3978	3189.2069	3192.0027
3192.2362	3193.3511	3196.6002
3201.2324	3202.3981	3210.6951
3229.5993	3258.2883	3300.8150

C

Zero-point correction= 0.418987

Thermal correction to Energy= 0.444861

Thermal correction to Enthalpy= 0.445806

Thermal correction to Gibbs Free Energy= 0.360071

Sum of electronic and zero-point Energies= -1353.546232

Sum of electronic and thermal Energies= -1353.520358

Sum of electronic and thermal Enthalpies= -1353.519414

Sum of electronic and thermal Free Energies= -1353.605148

Cartesian coordinates

C	3.584209	-2.427137	-0.476988
O	4.716540	-2.755240	-0.832062
C	2.477925	-3.456083	-0.227898
H	2.646620	-3.819228	0.802836
H	2.662479	-4.322988	-0.886657
C	1.052820	-2.893376	-0.358586
H	0.327017	-3.468748	0.236829
H	0.715717	-2.917329	-1.409510
N	3.154212	-1.153890	-0.201946
C	3.926033	-0.008139	-0.221971
C	3.246552	1.197072	0.200022
C	5.275329	0.099715	-0.579817
C	3.942482	2.445345	0.262709
C	5.946410	1.341671	-0.522249
H	5.796860	-0.799268	-0.898192
C	1.275211	2.184414	0.966591
C	3.212326	3.581578	0.703034
C	5.311695	2.498784	-0.112027
H	7.000178	1.377861	-0.812181
C	1.885732	3.454746	1.057855
H	0.228201	2.049913	1.248514
H	3.716879	4.549801	0.759381
H	5.840264	3.453818	-0.071520
H	1.302350	4.308738	1.406160

Pd	1.154470	-0.912579	0.185724
N	1.921571	1.107555	0.547257
C	-0.766067	-0.815978	0.401451
H	-1.312576	-1.632574	0.898455
C	-1.594652	0.227485	-0.061209
H	-1.109360	1.130048	-0.445759
C	-2.992061	0.221499	-0.075187
C	-3.734354	1.462160	-0.355590
C	-4.976054	1.423884	-1.029755
C	-3.218312	2.721109	0.028805
C	-5.666544	2.600218	-1.319914
H	-5.385557	0.464346	-1.349548
C	-3.918159	3.893060	-0.249522
H	-2.278156	2.775884	0.580067
C	-5.142153	3.837264	-0.928845
H	-6.617371	2.552137	-1.855630
H	-3.512330	4.855584	0.070250
H	-5.687641	4.757952	-1.149758
C	-3.759368	-1.017259	0.149104
C	-3.385038	-2.227185	-0.475228
C	-4.889240	-1.013782	0.996657
C	-4.108797	-3.398211	-0.245382
H	-2.545122	-2.233186	-1.172340
C	-5.596565	-2.189969	1.238818
H	-5.191297	-0.084928	1.484584

C	-5.209727	-3.384584	0.617272
H	-3.815067	-4.323078	-0.747061
H	-6.454969	-2.176865	1.914472
H	-5.773317	-4.302812	0.799698

Vibrational frequencies

13.1916	21.4409	22.1704
46.7829	58.8608	59.5128
71.7764	74.6854	79.9114
90.6153	124.1371	142.3650
158.8791	169.1422	184.6463
207.5086	217.7211	222.9352
250.3367	260.7316	268.2257
298.6751	307.2752	334.8015
345.5707	365.6263	419.9768
431.1586	450.7292	455.4834
464.2692	465.1777	470.8371
493.9210	521.7587	534.7874
547.8105	564.6102	589.6772
607.9403	617.3462	626.6619
628.7163	641.9476	670.6257
676.0290	693.8085	713.8151
715.3164	723.4024	727.4912
754.1857	781.0793	794.6775
807.6410	810.5806	817.6533
828.5380	865.3568	872.0851

873.4569 889.0155 903.3062

931.0956 938.4659 941.1920

960.7677 967.7414 968.5439

972.4993 979.2282 1008.0418

1008.9086 1009.5386 1015.3208

1016.0243 1020.0716 1027.3365

1040.2009 1041.6500 1049.3784

1053.3331 1069.1943 1092.5578

1100.1927 1110.1131 1112.9250

1118.8472 1139.1376 1154.0284

1160.4736 1177.6025 1179.0084

1188.9062 1200.3965 1204.5935

1226.2351 1236.1765 1240.1711

1255.4310 1271.7921 1273.7937

1310.1845 1314.7995 1326.2279

1343.1332 1356.6346 1365.1945

1367.3972 1370.7681 1403.3204

1412.3214 1417.2351 1424.7515

1439.9538 1451.2647 1468.4161

1475.8176 1495.2687 1516.3662

1520.0278 1523.7132 1542.9224

1616.9686 1618.9592 1622.1393

1635.0749 1647.1990 1650.6416

1652.0913 1704.5413 3011.4228

3024.6996 3055.1649 3088.6624

3093.3947	3154.8532	3174.3405
3181.4212	3182.5036	3183.9001
3189.6227	3191.2612	3193.2408
3194.7127	3196.6644	3199.7402
3203.3158	3207.6042	3207.9432
3210.7231	3213.5567	3252.7958

TS-2

Zero-point correction= 0.418495

Thermal correction to Energy= 0.443802

Thermal correction to Enthalpy= 0.444746

Thermal correction to Gibbs Free Energy= 0.360215

Sum of electronic and zero-point Energies= -1353.517295

Sum of electronic and thermal Energies= -1353.491988

Sum of electronic and thermal Enthalpies= -1353.491044

Sum of electronic and thermal Free Energies= -1353.575575

Cartesian coordinates

C	2.896497	-2.153099	-1.440859
O	3.853902	-2.774667	-1.897105
C	1.476973	-2.777699	-1.437483
H	1.436872	-3.411180	-0.534265
H	1.423219	-3.469645	-2.293623
C	0.193891	-1.859212	-1.487104
H	-0.634711	-2.583803	-1.496534
H	0.147145	-1.306817	-2.436964

N	2.939479	-0.945427	-0.817580
C	4.010544	-0.208136	-0.376829
C	3.635020	0.885025	0.486335
C	5.365606	-0.404606	-0.649841
C	4.624155	1.759367	1.026589
C	6.337150	0.463326	-0.100087
H	5.650705	-1.236605	-1.291609
C	1.911021	2.052576	1.555605
C	4.174256	2.821578	1.855808
C	5.991793	1.526758	0.714358
H	7.389943	0.285231	-0.335180
C	2.827705	2.970610	2.115266
H	0.840749	2.136961	1.754305
H	4.905835	3.512840	2.282234
H	6.751641	2.195068	1.124980
H	2.454075	3.777325	2.747764
Pd	1.094035	-0.374812	-0.191109
N	2.296290	1.050532	0.776944
C	-0.789856	-0.937534	-0.234653
H	-1.094592	-1.630393	0.559788
C	-1.868138	-0.210577	-0.858850
H	-1.620273	0.326887	-1.779892
C	-3.120268	-0.022221	-0.329571
C	-4.028756	1.006478	-0.886158
C	-5.429759	0.835641	-0.824030

C	-3.535723	2.176319	-1.505118
C	-6.296035	1.777781	-1.380291
H	-5.839748	-0.056210	-0.345872
C	-4.403776	3.118738	-2.059445
H	-2.460007	2.363002	-1.526416
C	-5.788598	2.924180	-2.003106
H	-7.375784	1.615395	-1.328248
H	-3.995847	4.019151	-2.526151
H	-6.467587	3.665082	-2.432500
C	-3.610066	-0.819710	0.831357
C	-3.646014	-2.225838	0.775929
C	-4.068597	-0.183175	1.999510
C	-4.112778	-2.973078	1.860418
H	-3.312895	-2.730941	-0.134224
C	-4.529657	-0.929818	3.086876
H	-4.059002	0.908336	2.051521
C	-4.552650	-2.327568	3.021634
H	-4.138957	-4.063934	1.796162
H	-4.873930	-0.417871	3.989217
H	-4.917685	-2.911556	3.870265

Vibrational frequencies

-175.2490	14.9981	18.7851
25.7450	38.4860	56.9576
60.4373	62.7572	69.8947
93.3647	103.5403	141.2913

158.7982 166.2118 177.5112

200.3065 212.5970 228.9389

242.8857 267.0651 276.2568

287.5843 300.3130 313.3597

344.5996 385.7992 421.1384

424.9303 431.1653 458.2630

460.3330 477.0255 479.1870

491.8684 502.0944 513.9675

547.3327 555.3608 591.9956

605.9178 611.4365 625.8324

629.1731 630.5500 658.8265

665.2337 683.0780 704.9504

715.4831 719.1595 726.4967

748.4014 779.5397 794.4061

800.3254 806.8210 813.5048

825.7162 863.5102 870.9807

871.9349 899.0361 916.0170

931.5401 934.2003 940.7332

947.8999 954.2650 963.5713

969.0729 982.7804 1003.2994

1006.5853 1009.6139 1010.8082

1011.4840 1020.4008 1025.9781

1031.1953 1032.7468 1047.9629

1053.2072 1063.5761 1090.9086

1099.6994 1106.8580 1108.0271

1144.6535	1153.1994	1157.0234
1170.9502	1172.8843	1174.2241
1191.7043	1195.3258	1200.7400
1215.8747	1228.9799	1233.6216
1253.4138	1277.6362	1282.9878
1307.7504	1323.3506	1328.1085
1328.9605	1355.9899	1357.3293
1361.6539	1387.0073	1396.5776
1397.9022	1413.9525	1419.7224
1437.8067	1453.9866	1469.7918
1473.6173	1500.0799	1519.5276
1524.3854	1539.6605	1586.7426
1622.1522	1622.6642	1628.5050
1634.6163	1650.1351	1651.1058
1654.6598	1710.0985	3037.9901
3058.9167	3087.3551	3118.8329
3130.2355	3151.2089	3171.0463
3172.0539	3176.7308	3178.1416
3179.6810	3184.8758	3187.9004
3190.3480	3190.8723	3196.3836
3196.6689	3199.0920	3201.1218
3206.1446	3218.9224	3236.5128

3aa

Zero-point correction= 0.422527

Thermal correction to Energy= 0.447334

Thermal correction to Enthalpy= 0.448279

Thermal correction to Gibbs Free Energy= 0.367101

Sum of electronic and zero-point Energies= -1353.619497

Sum of electronic and thermal Energies= -1353.594690

Sum of electronic and thermal Enthalpies= -1353.593746

Sum of electronic and thermal Free Energies= -1353.674923

Cartesian coordinates

C	2.686527	-2.344867	-0.729426
O	3.878277	-2.637935	-0.876942
C	1.662284	-3.460143	-1.026315
H	1.380185	-3.895407	-0.049449
H	2.239217	-4.233474	-1.552010
C	0.375597	-3.147820	-1.812238
H	-0.074438	-4.112147	-2.112342
H	0.613238	-2.604727	-2.741710
N	2.224702	-1.142458	-0.264499
C	3.068511	-0.113249	0.157728
C	2.433198	1.137140	0.513883
C	4.463264	-0.165816	0.289792
C	3.197940	2.256179	0.975304
C	5.206686	0.942210	0.755029
H	4.970656	-1.086038	0.020203
C	0.444412	2.365478	0.678661
C	2.495712	3.449906	1.290404

C	4.606783	2.137520	1.095141
H	6.291644	0.836879	0.841319
C	1.126085	3.510653	1.141235
H	-0.638062	2.379746	0.527791
H	3.058221	4.317007	1.646492
H	5.189423	2.990520	1.449799
H	0.563510	4.417523	1.368246
C	-0.601195	-2.367330	-0.973858
H	-0.901184	-2.864659	-0.043326
Pd	0.216121	-0.569639	-0.298438
C	-1.404363	-1.299385	-1.459924
H	-1.345819	-1.022660	-2.518000
C	-1.993699	-0.380255	-0.532666
C	-2.497437	0.939391	-1.032254
C	-3.663537	1.521891	-0.498072
C	-1.819998	1.645059	-2.050665
C	-4.136935	2.751837	-0.965593
H	-4.214368	1.002755	0.287417
C	-2.294291	2.870215	-2.519522
H	-0.891634	1.243059	-2.462423
C	-3.456659	3.433105	-1.978467
H	-5.046797	3.176882	-0.533932
H	-1.744208	3.395822	-3.304251
H	-3.823786	4.396685	-2.340329
C	-2.561891	-0.879344	0.766790

C	-3.360999	-2.035097	0.798392
C	-2.342912	-0.186230	1.972602
C	-3.908843	-2.496373	2.000217
H	-3.557573	-2.573774	-0.131350
C	-2.891778	-0.642555	3.171954
H	-1.727165	0.715594	1.965849
C	-3.675228	-1.803435	3.191463
H	-4.526328	-3.398329	2.002136
H	-2.703173	-0.092531	4.097379
H	-4.103041	-2.162654	4.130746
N	1.072481	1.235131	0.389909

Vibrational frequencies

22.1676	34.2033	37.8583
49.3328	57.0123	64.7065
74.0168	88.7861	102.1487
137.5404	154.2266	173.6930
191.6475	198.5381	205.5326
223.3889	243.7515	248.5309
265.1459	268.4541	304.1904
309.0827	319.4027	347.7788
400.8227	420.8865	426.2326
441.3275	455.4088	461.3237
469.2349	493.2944	499.9562
504.0799	514.1164	535.1382
549.9073	565.6647	600.8881

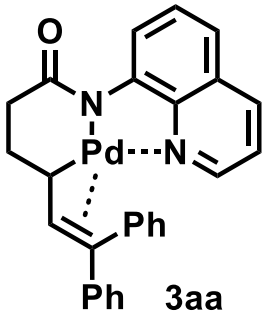
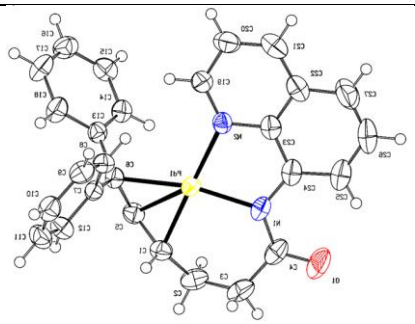
611.4512	623.3360	631.9849
642.2800	647.8011	658.2241
674.1390	713.3422	722.5911
724.4790	744.5829	781.9830
784.7705	791.2848	794.8288
814.0282	816.8929	867.2408
867.8839	871.4352	877.3305
887.6004	922.6317	932.1223
942.5350	949.7259	951.9776
956.8211	971.0484	974.4318
993.2380	1008.5523	1009.1130
1012.1509	1012.3125	1020.8450
1030.2275	1031.7741	1032.6170
1046.9681	1050.3252	1055.7061
1074.2465	1095.5919	1099.9532
1104.4403	1108.9242	1116.6415
1145.2357	1154.6645	1173.0945
1174.5900	1180.5245	1187.3058
1196.5818	1207.5208	1230.0963
1244.4194	1247.8102	1255.5926
1264.5529	1277.6552	1309.5655
1316.9137	1331.7830	1344.9288
1354.7407	1358.8589	1359.3831
1362.8679	1364.7393	1395.1227
1411.7088	1417.7196	1438.5492

1451.3070	1453.7888	1471.0878
1477.8879	1491.9601	1522.4302
1524.4394	1540.0737	1545.3424
1615.0962	1625.4008	1628.8898
1637.1804	1652.2644	1652.4836
1655.2438	1677.3130	3010.4277
3021.9576	3072.9857	3112.9865
3131.0688	3157.6770	3172.4872
3172.8691	3175.1513	3179.9672
3180.2490	3185.4473	3188.9844
3189.3214	3191.4172	3194.9730
3195.4368	3197.6418	3201.5548
3206.6711	3215.6728	3270.4811

X-ray crystallography of compound 3aa and 4aa:

X-ray crystallography of compound 3aa:

Good quality crystal of **3aa** (colourless block crystal) was obtained by vaporization of a petroleum ether/ethyl acetate solution of compound **3aa** (~20 mg). Single colourless plate crystals of **3aa** were used as supplied. A suitable crystal with dimensions 0.10 × 0.10 × 0.10 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 273.15 K during data collection. CCDC: 2304190 contains the supplementary crystallographic data for this paper. The ellipsoid contour % probability level is 50%. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.

 **3aa**	 **CCDC 2304190**

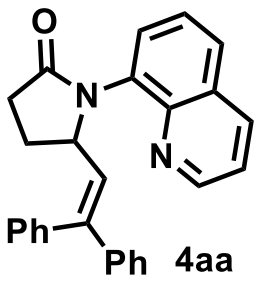
$C_{27}H_{22}N_2OPd$ (M =496.86 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.993(3) Å, b =22.743(6) Å, c =10.981(4) Å, β =109.413(14)°, V = 2118.1(11) Å^3, Z = 4, T = 273.15 K, μ(MoKα) = 0.898 mm^{-1}, *Dcalc* = 1.558 g/cm^3, 20985 reflections measured (6.232° ≤ 2Θ ≤ 50°), 3525 unique (R_{int} = 0.0294, R_{sigma} = 0.0199) which were used in all calculations. The final R_1 was 0.0302 (I > 2σ(I)) and wR_2 was 0.0717 (all data).

Compound	**3aa**
Empirical formula	$C_{27}H_{22}N_2OPd$
Formula weight	496.86
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8993(3)
b/Å	22.743(6)
c/Å	10.981(4)
α/°	90
β/°	109.413(14)
γ/°	90
Volume/Å^3	2118.1(11)
Z	4
ρ_{calc}g/cm^3	1.558
μ/mm^{-1}	0.898
F(000)	1008.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	Mo Kα (λ = 0.71076)
2Θ range for data collection/°	6.232 to 50

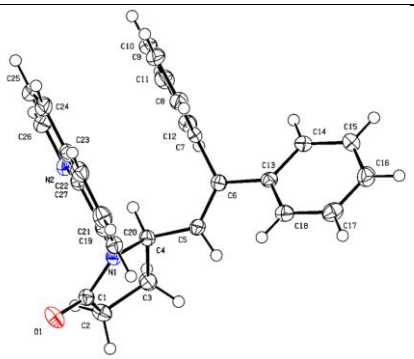
Index ranges	$-10 \leq h \leq 10, -27 \leq k \leq 27, -13 \leq l \leq 11$
Reflections collected	20985
Independent reflections	3525[R_{int} = 0.0294, R_{sigma} = 0.0199]
Data/restraints/parameters	3525/0/281
Goodness-of-fit on F^2	1.297
Final R indexes [I>=2σ (I)]	R_1 = 0.0302, wR_2 = 0.0708
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0717
Largest diff. peak/hole / e $Å^{-3}$	0.32/-0.33

X-ray crystallography of compound 4aa:

Good quality crystal of **4aa** (colourless block crystal) was obtained by vaporization of a petroleum ether/ethyl acetate solution of compound **4aa** (~20 mg). Single colourless plate crystals of **4aa** were used as supplied. A suitable crystal with dimensions 0.10 × 0.10 × 0.10 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. CCDC: 2358373 contains the supplementary crystallographic data for this paper. The ellipsoid contour % probability level is 50%. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.



4aa



CCDC 2358373

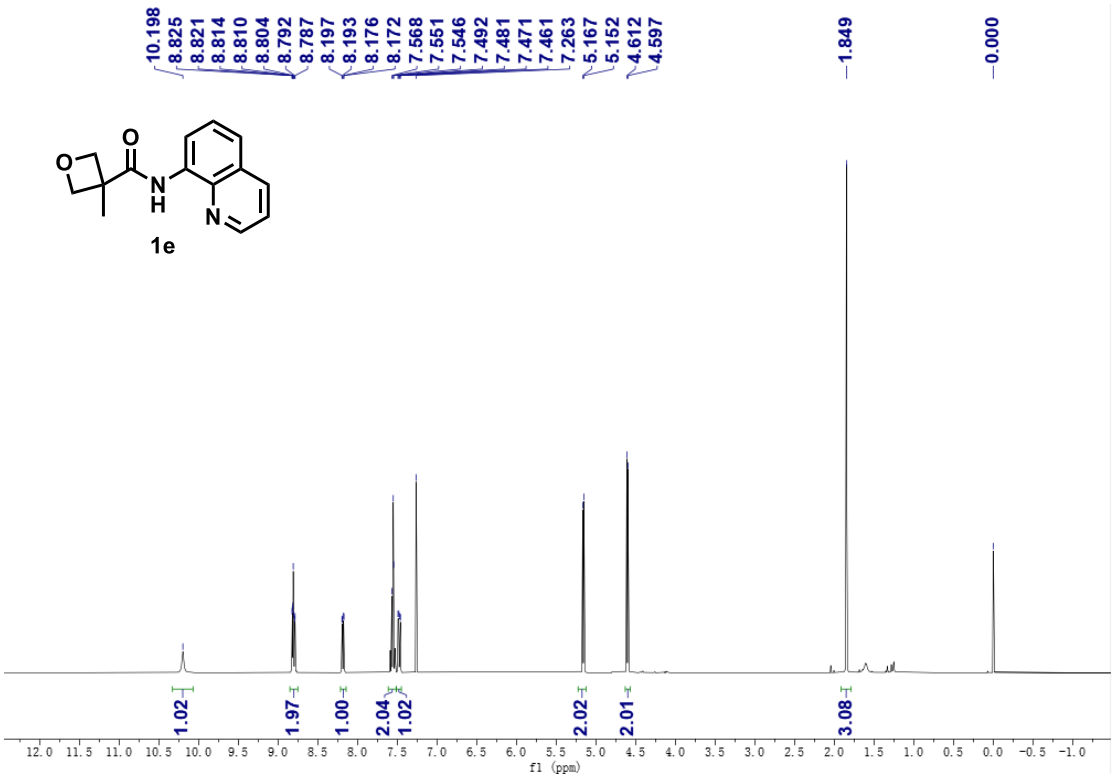
$C_{27}H_{22}N_2O$ (M =390.46 g/mol): orthorhombic, space group Pbca (no. 61), a = 12.94530(13) Å, b = 11.28159(12) Å, c = 27.8952(3) Å, V = 4073.91(7) $Å^3$, Z = 8, T =

100.00(10) K, μ(Cu Kα) = 0.607 mm^{-1}, *Dcalc* = 1.273 g/cm^3, 24443 reflections measured (6.338° ≤ 2Θ ≤ 146.668°), 4013 unique (R_{int} = 0.0360, R_{sigma} = 0.0235) which were used in all calculations. The final R_1 was 0.0378 (I > 2σ(I)) and wR_2 was 0.0943 (all data).

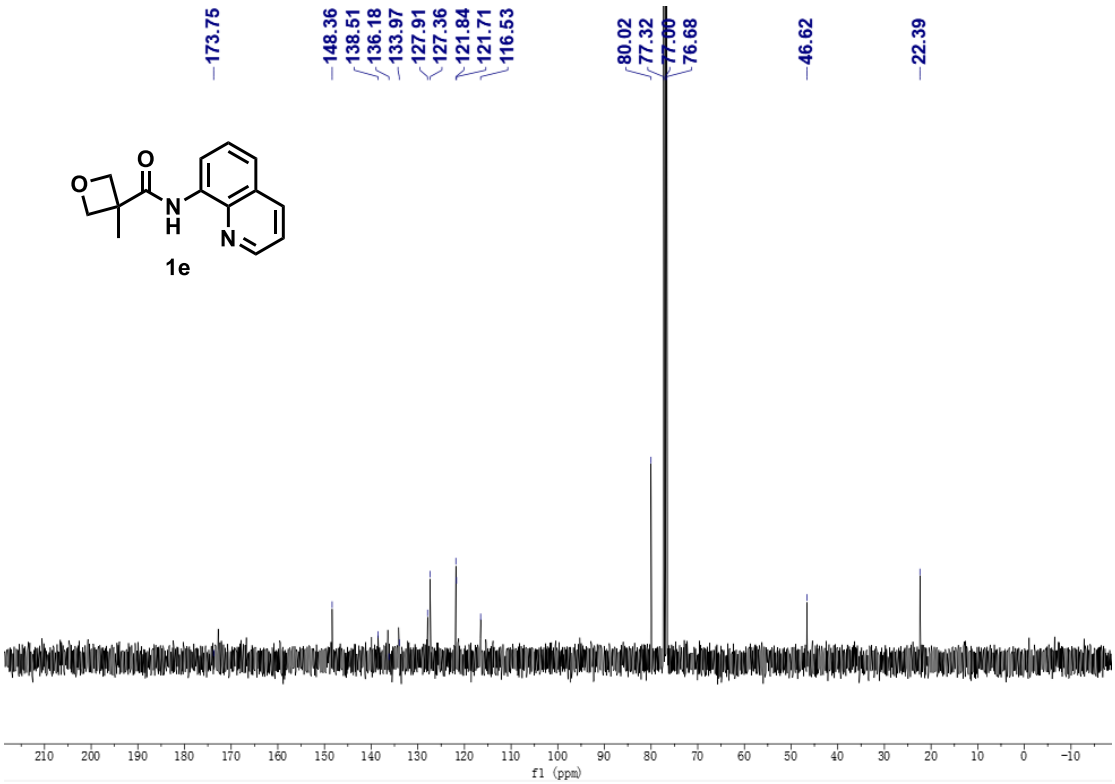
Empirical formula	$C_{27}H_{22}N_2O$
Formula weight	390.46
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.94530(13)
b/Å	11.28159(12)
c/Å	27.8952(3)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	4073.91(7)
Z	8
$\rho_{calc}g/cm^3$	1.273
μ/mm^{-1}	0.607
F(000)	1648.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.338 to 146.668
Index ranges	-15 ≤ h ≤ 16, -13 ≤ k ≤ 12, -34 ≤ l ≤ 20
Reflections collected	24443
Independent reflections	4013 [R_{int} = 0.0360, R_{sigma} = 0.0235]
Data/restraints/parameters	4013/0/271
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0920
Final R indexes [all data]	R_1 = 0.0410, wR_2 = 0.0943
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.21

NMR spectra for amide compounds:

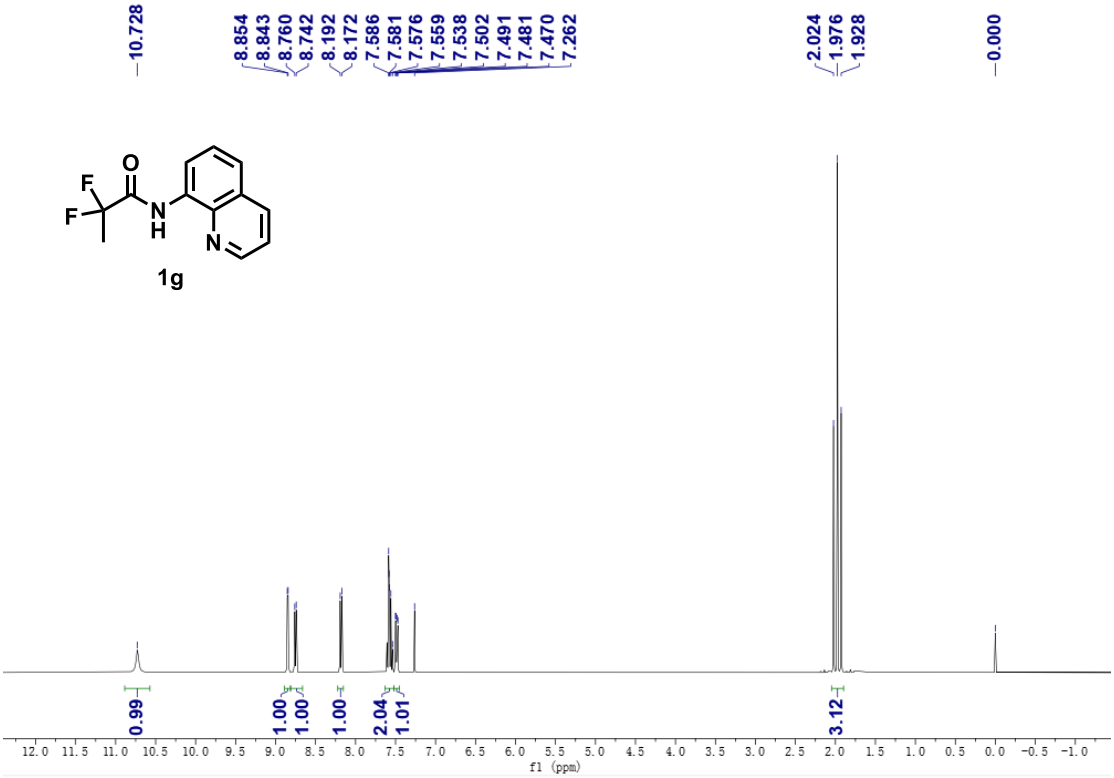
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



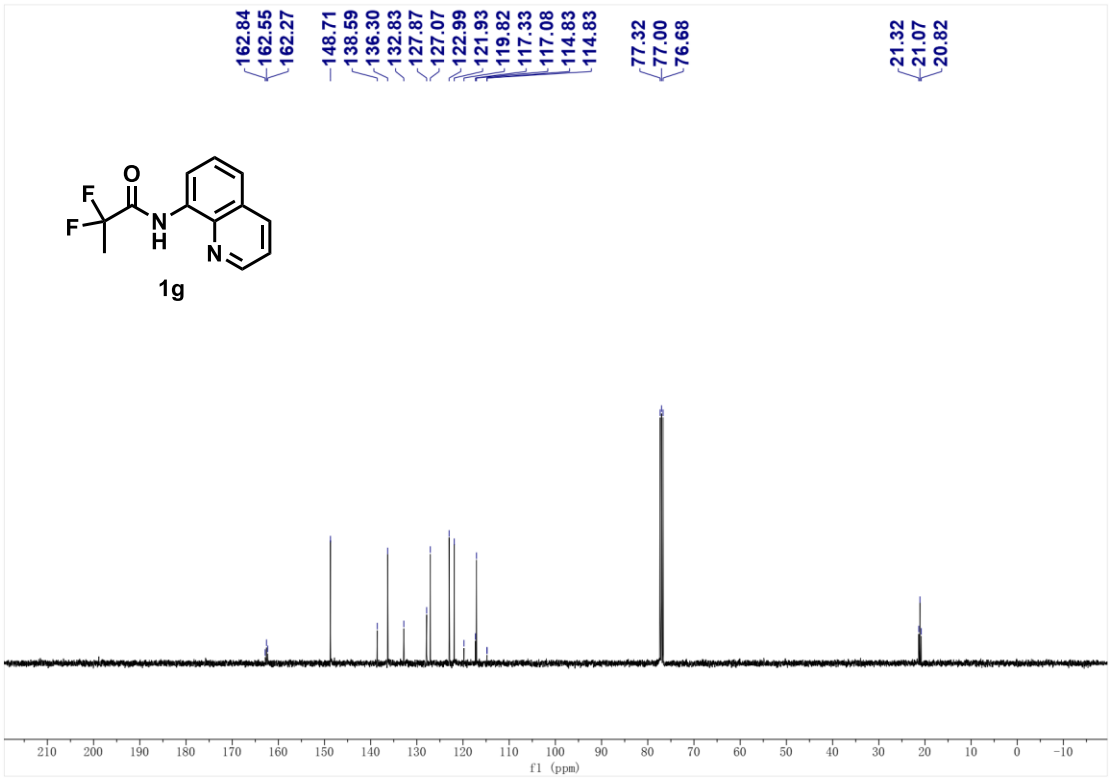
^{13}C NMR (100 MHz, $CDCl_3$) of **1e**



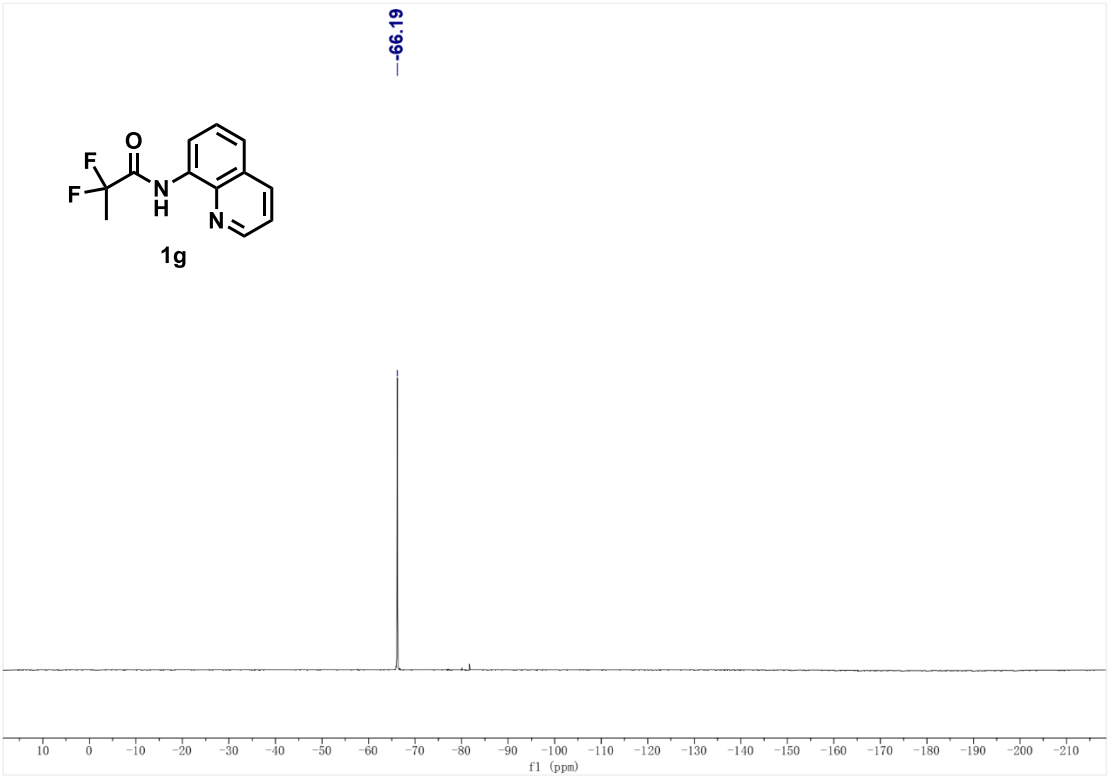
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**



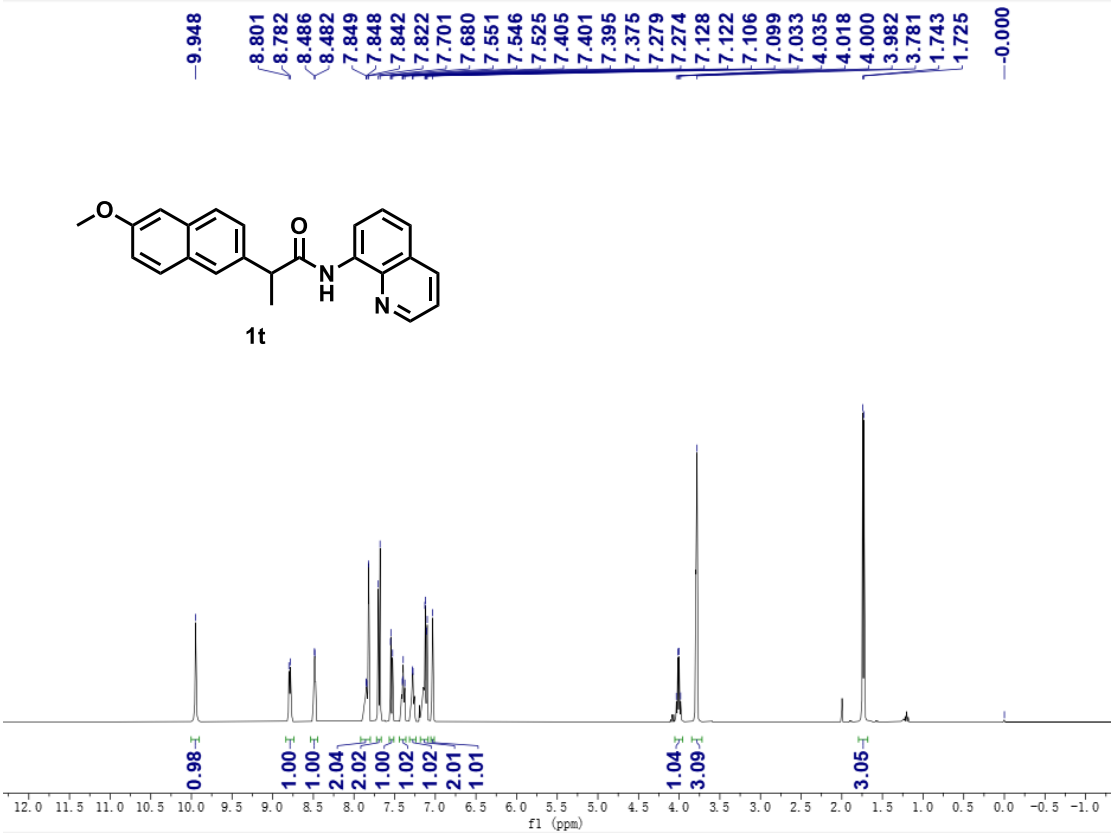
^{13}C NMR (100 MHz, $CDCl_3$) of **1g**



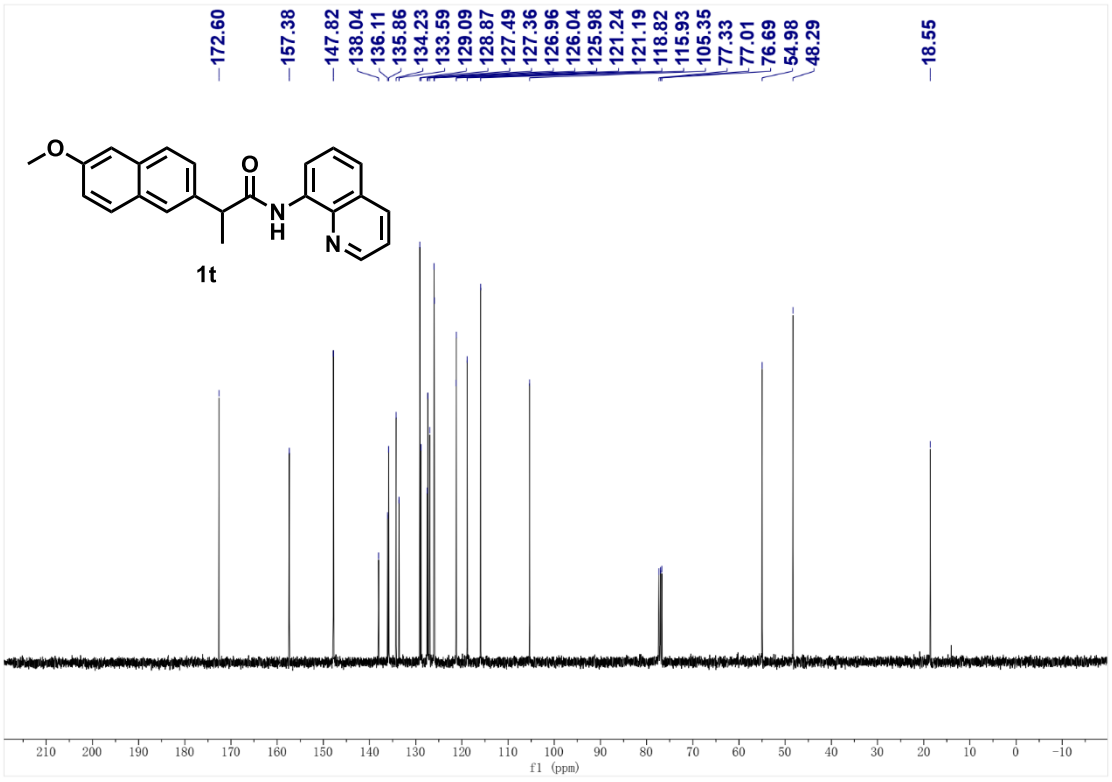
^{19}F NMR (376 MHz, $CDCl_3$) of **1g**



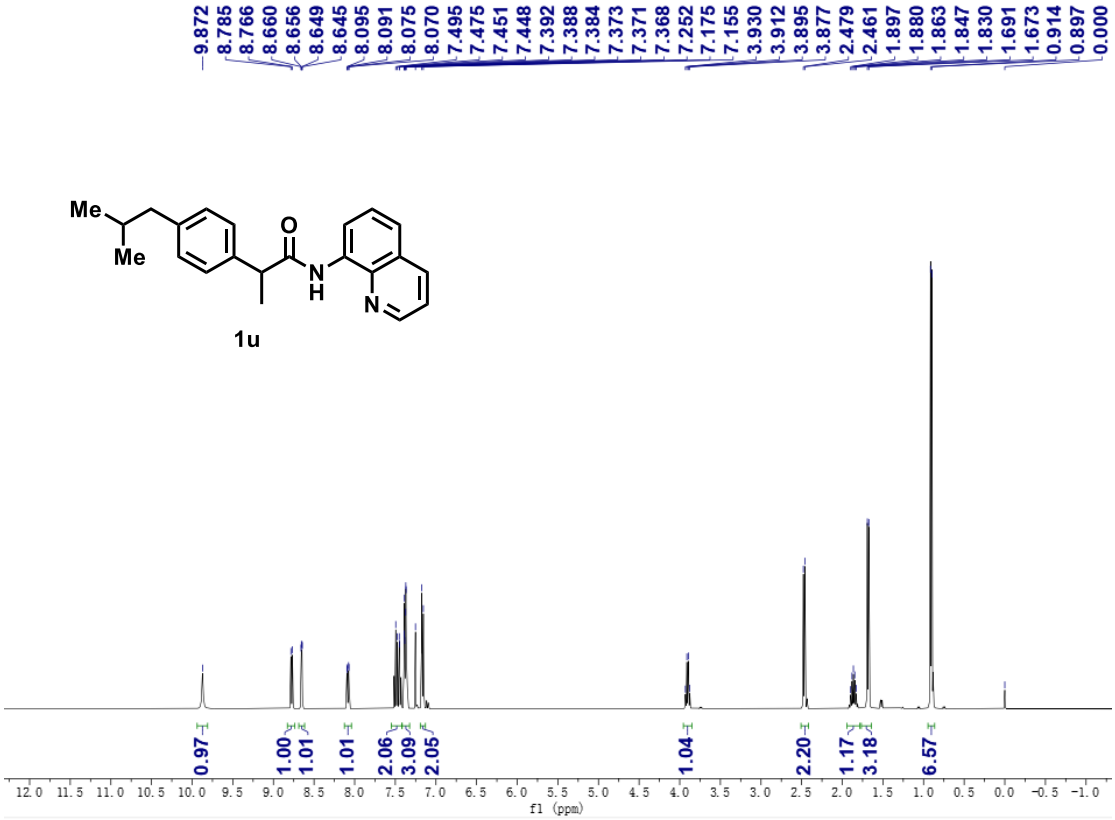
^{1}H NMR (400 MHz, $CDCl_3$) of **1t**



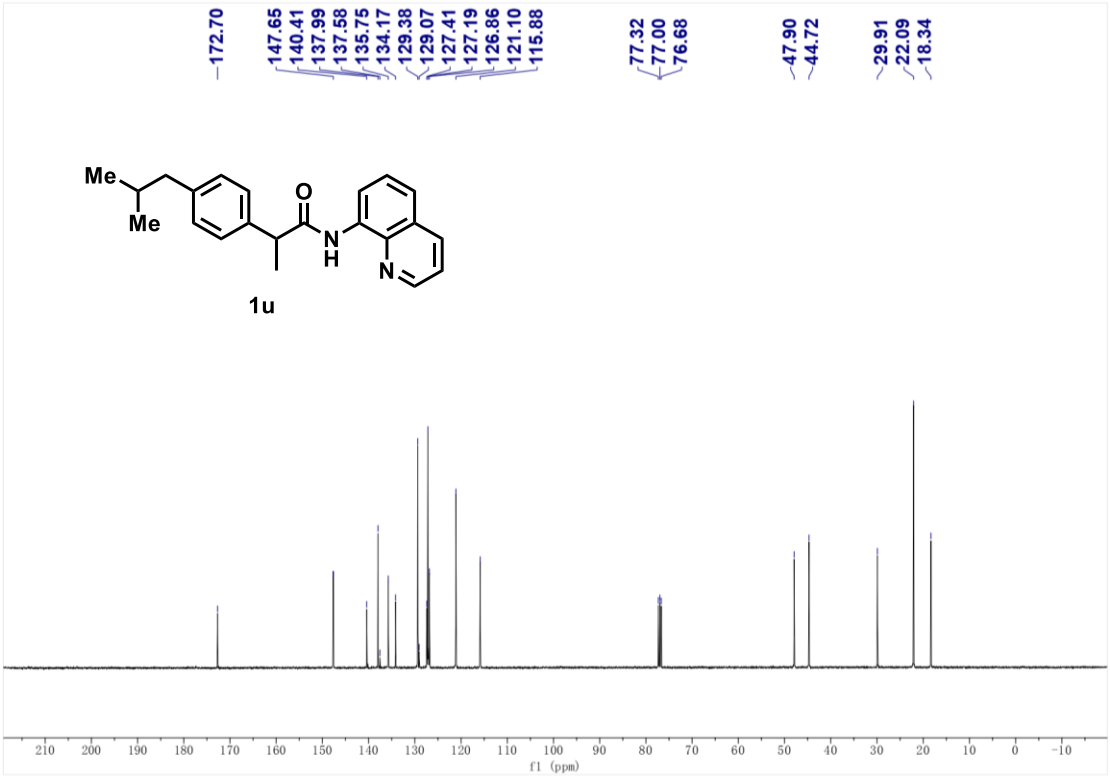
^{13}C NMR (100 MHz, $CDCl_3$) of **1t**



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

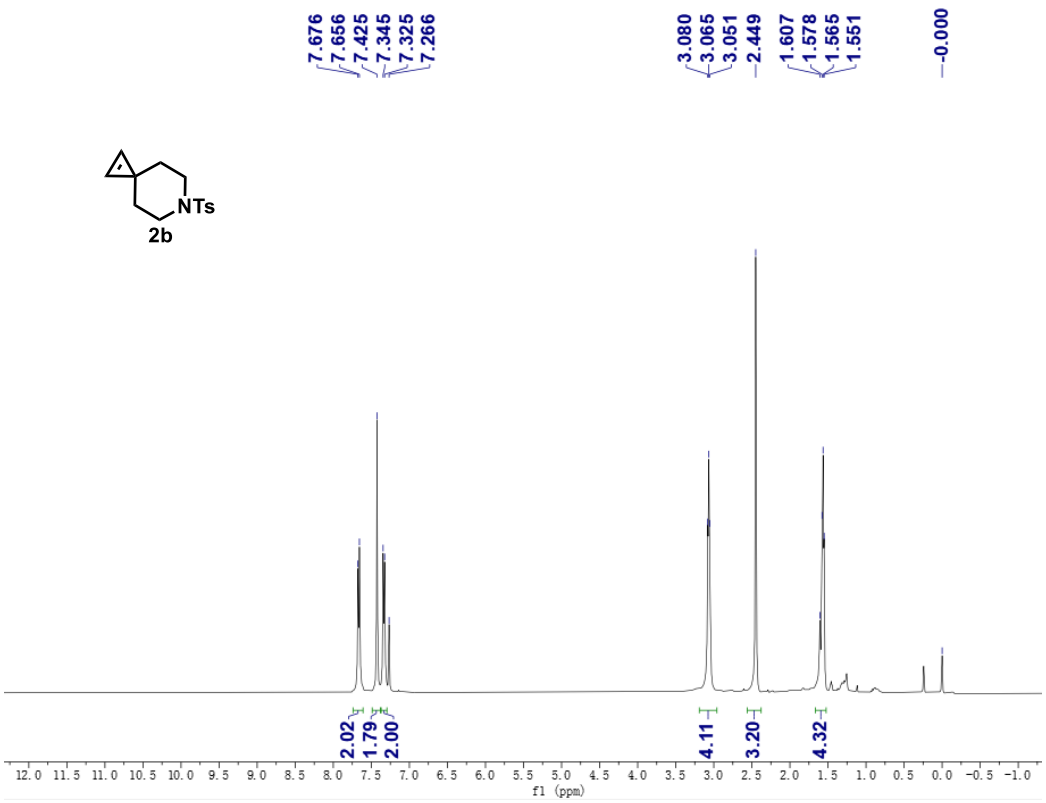


^{13}C NMR (100 MHz, $CDCl_3$) of **1u**

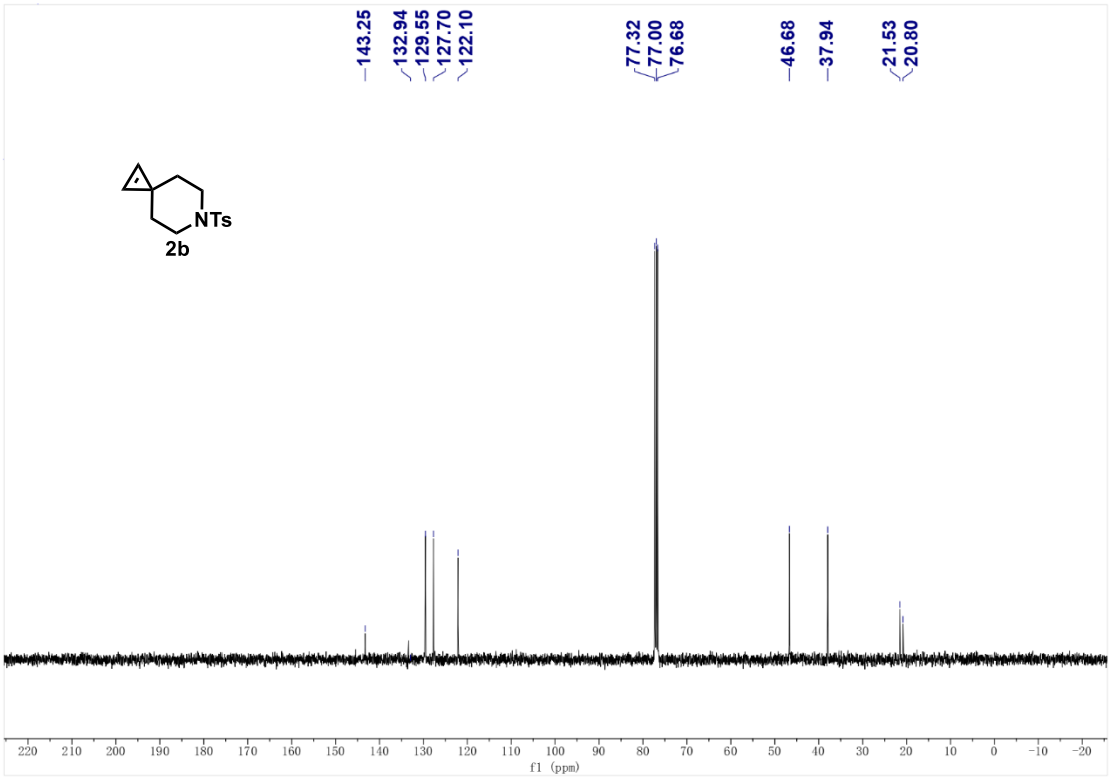


NMR spectra for cyclopropenes:

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

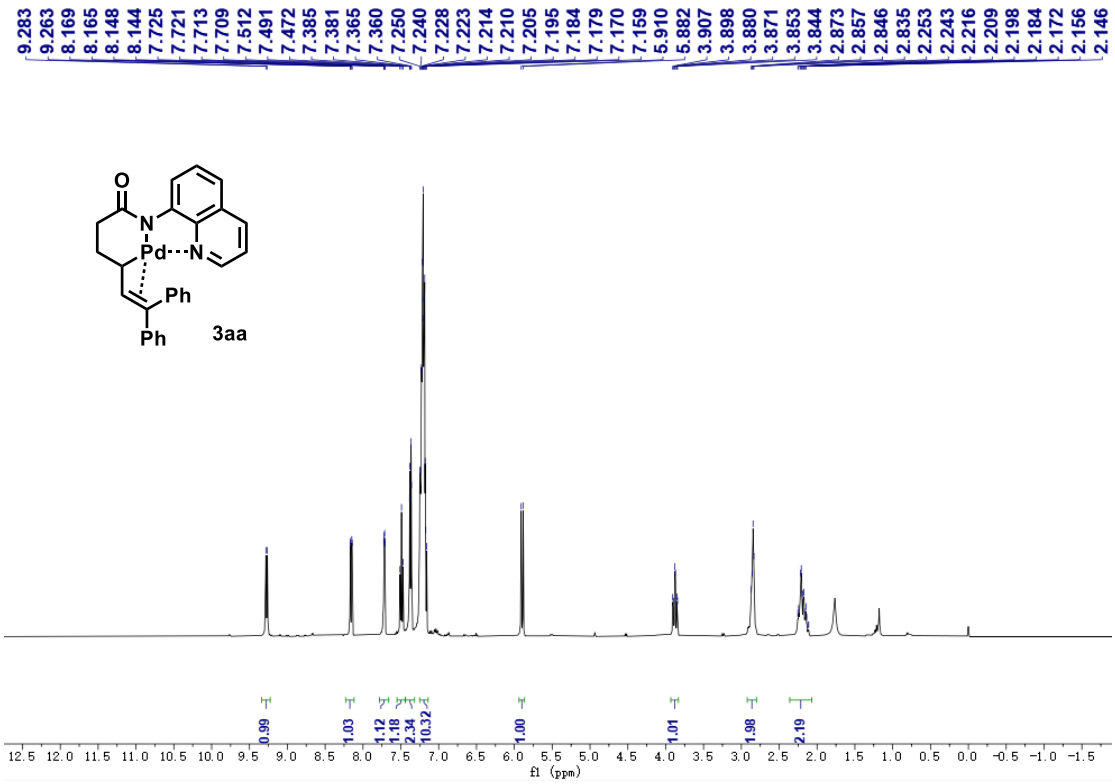


^{13}C NMR (100 MHz, $CDCl_3$) of **2b**

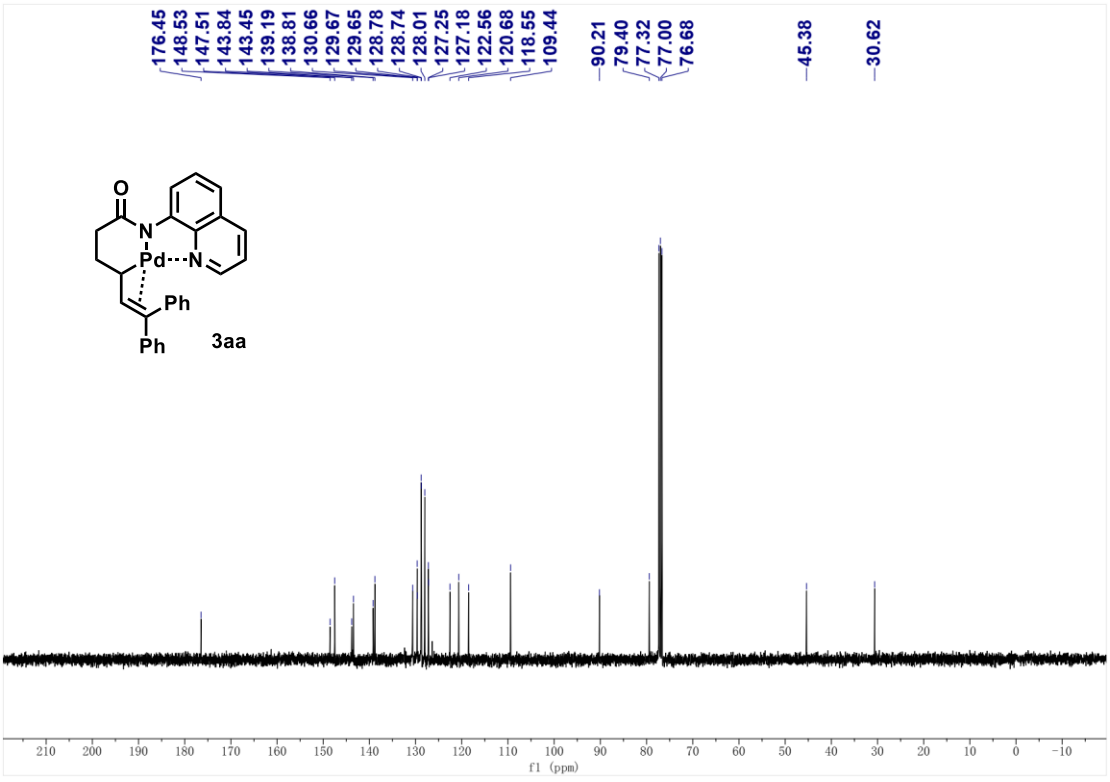


Spectra of complex-Pd:

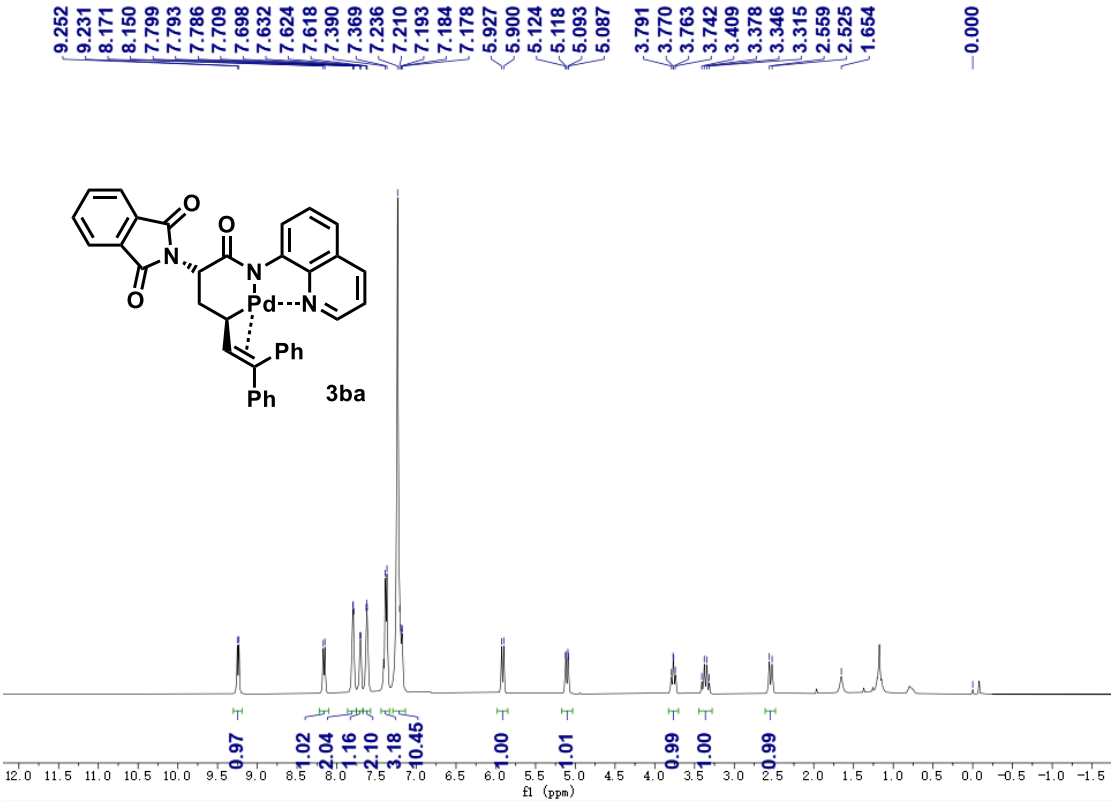
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



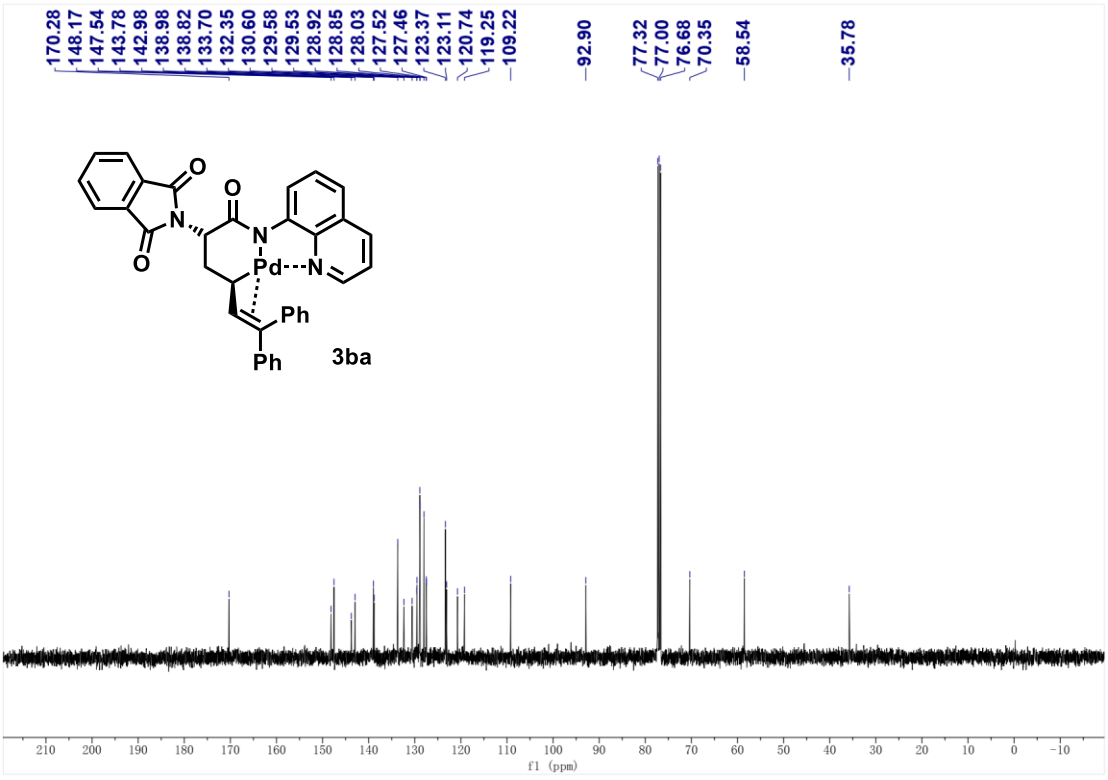
^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**



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

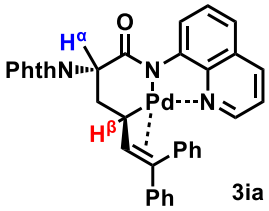


^{13}C NMR (100 MHz, $CDCl_3$) of **3ba**



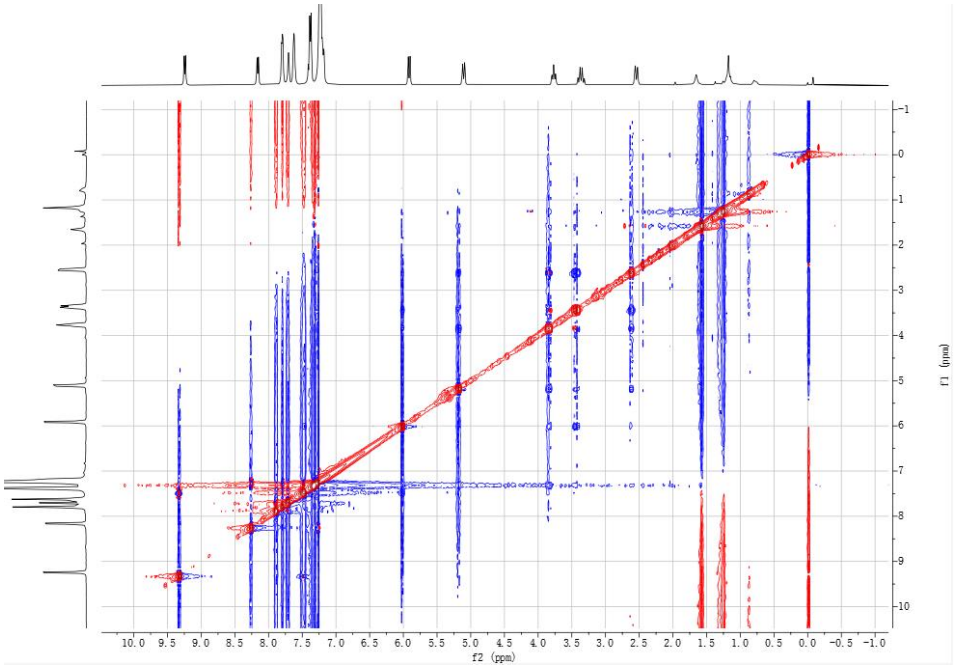
No NOE was observed between H^{α} and H^{β}

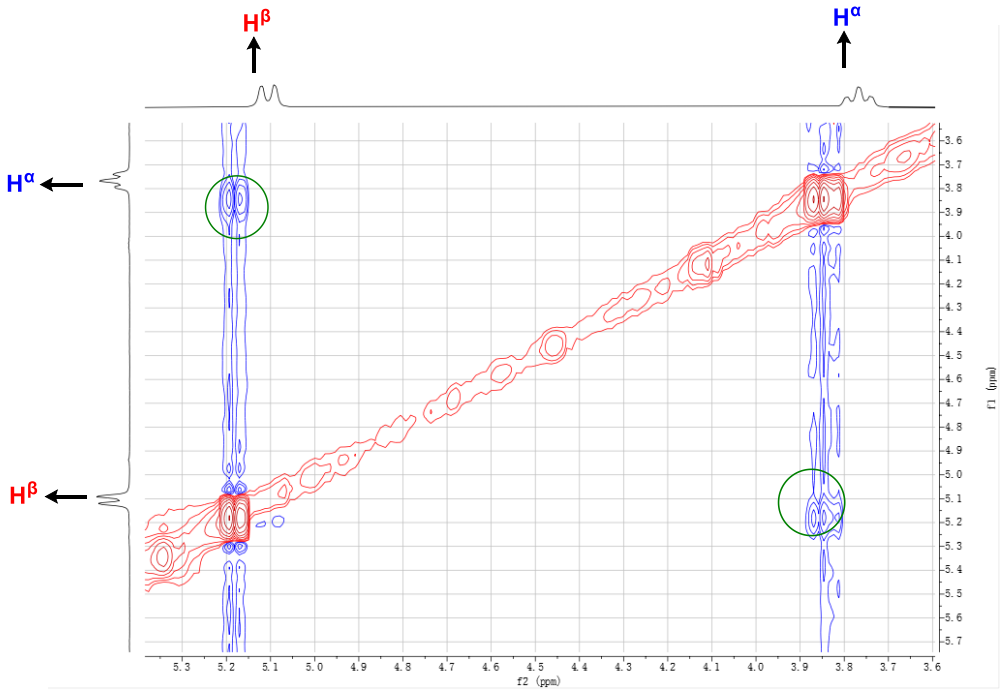
.



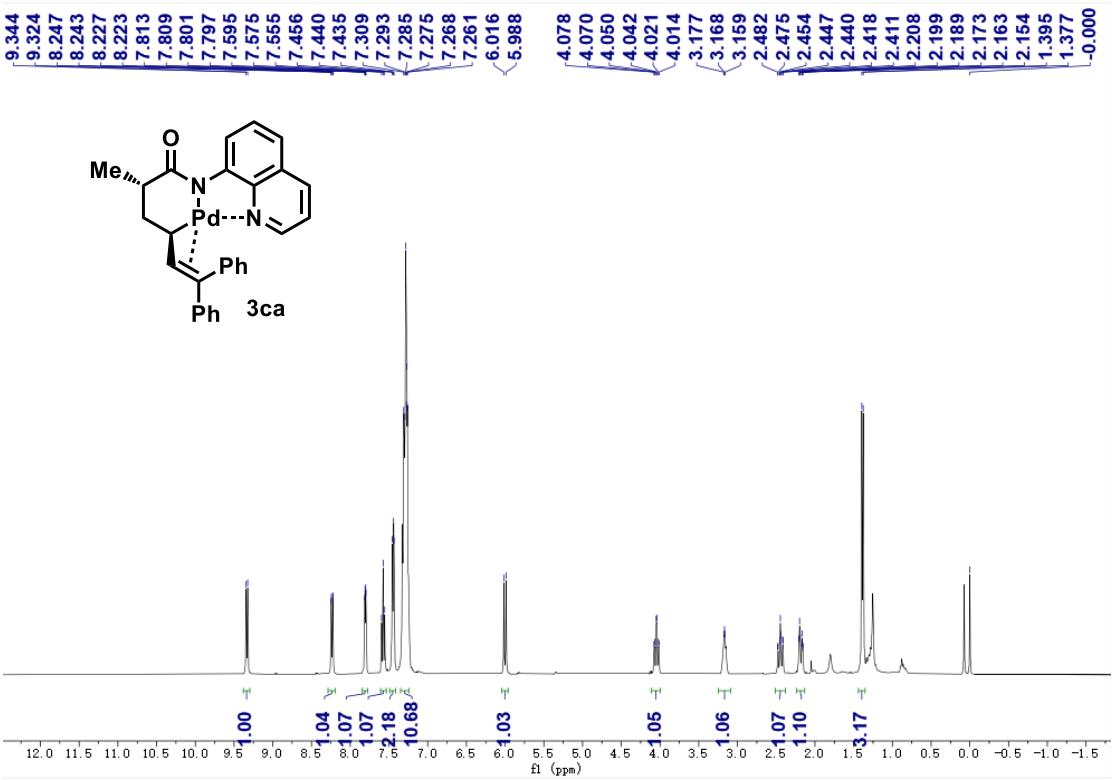
3ia

NOESY:

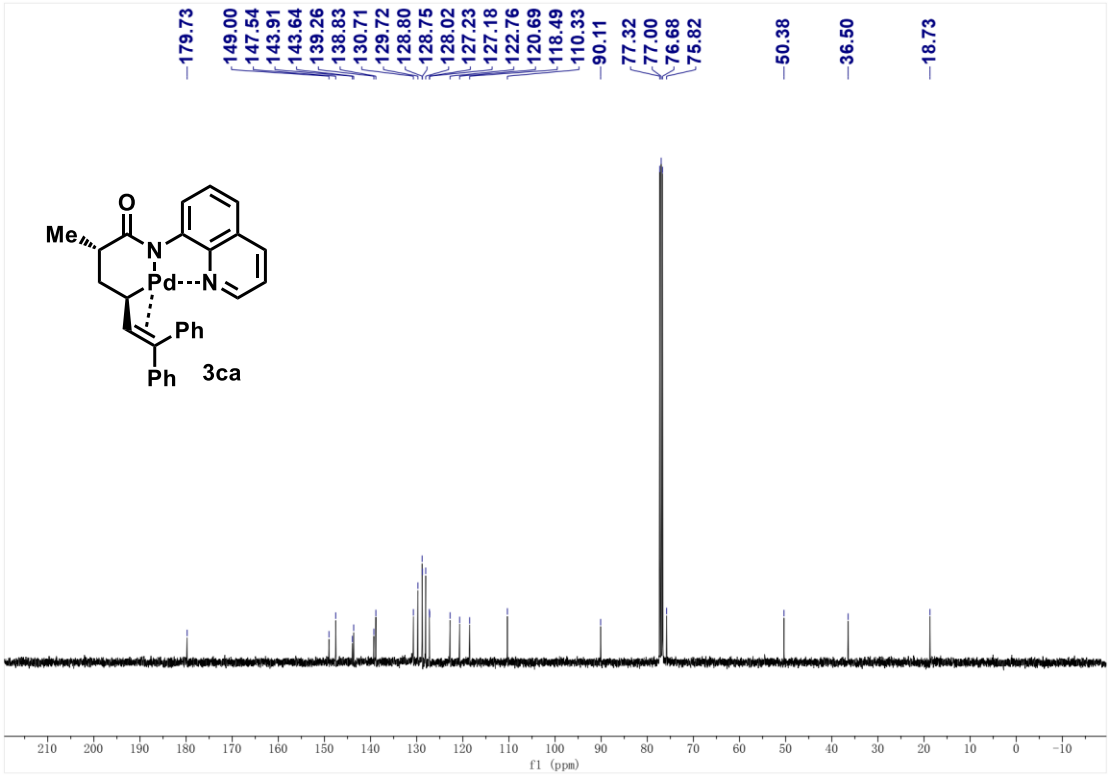




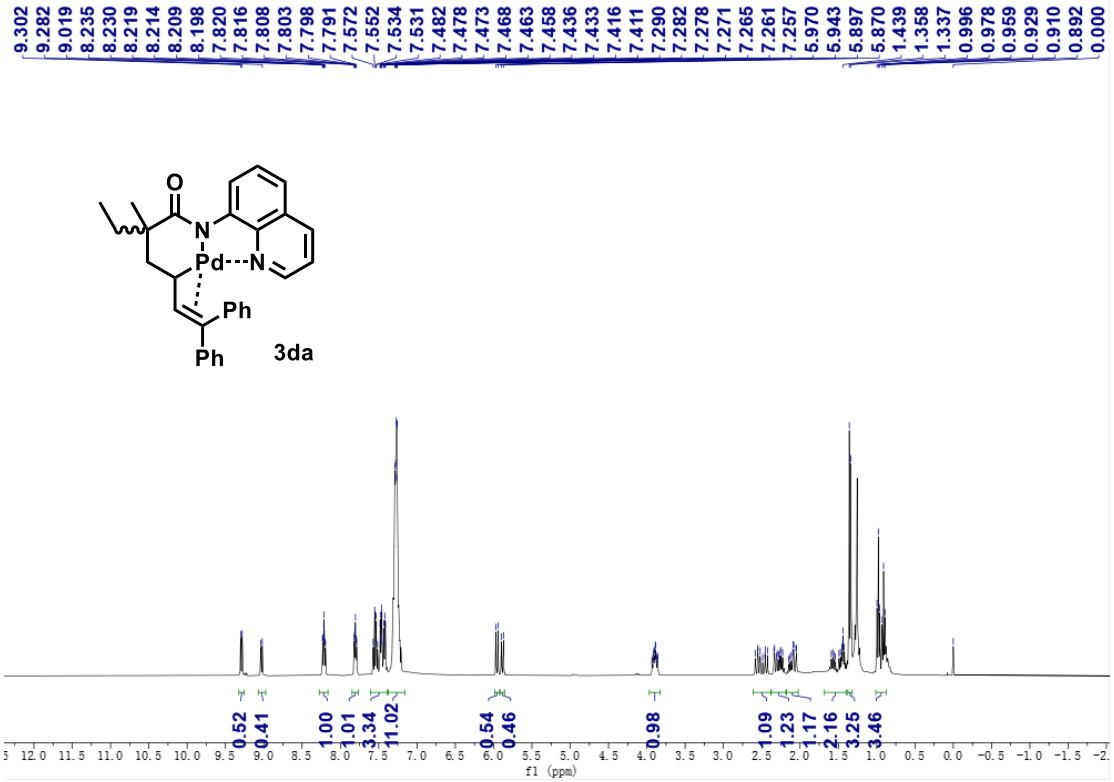
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



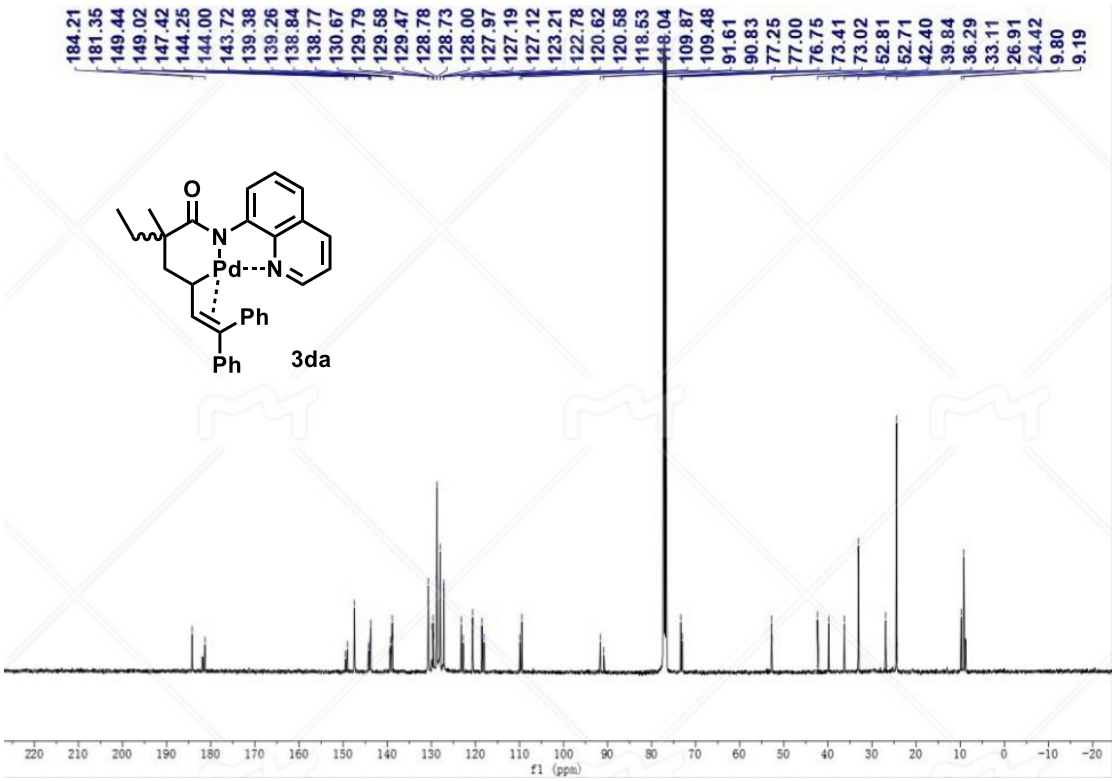
^{13}C NMR (100 MHz, $CDCl_3$) of **3ca**



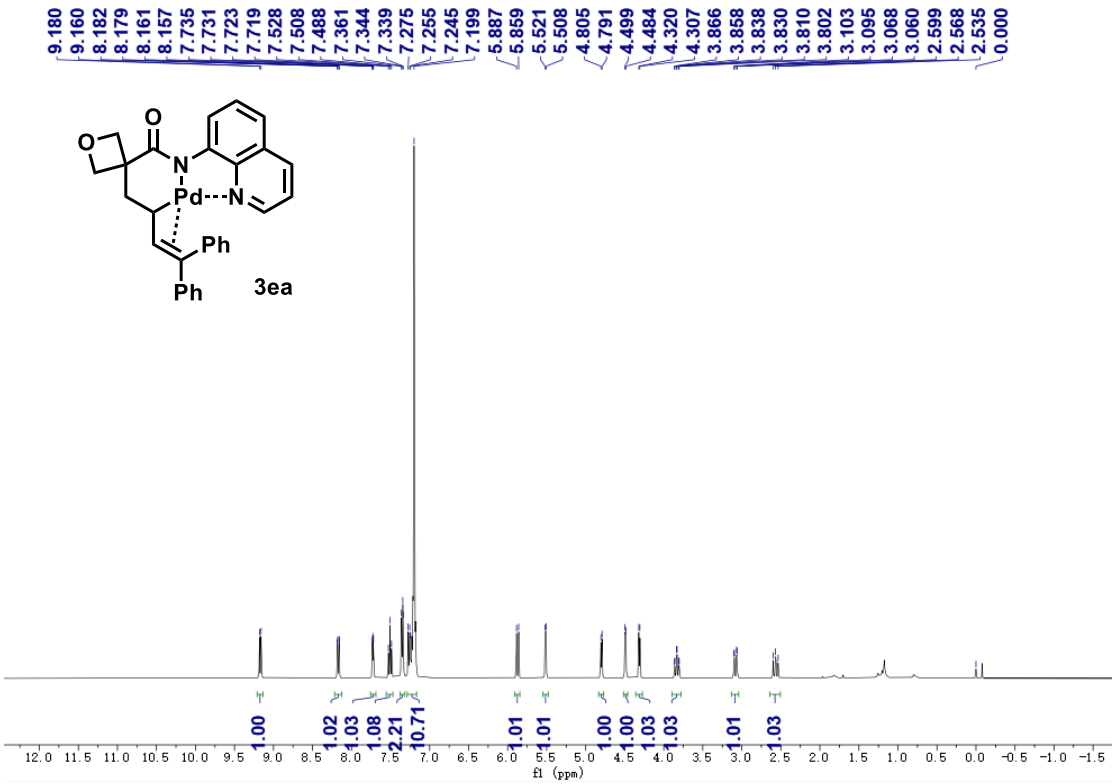
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



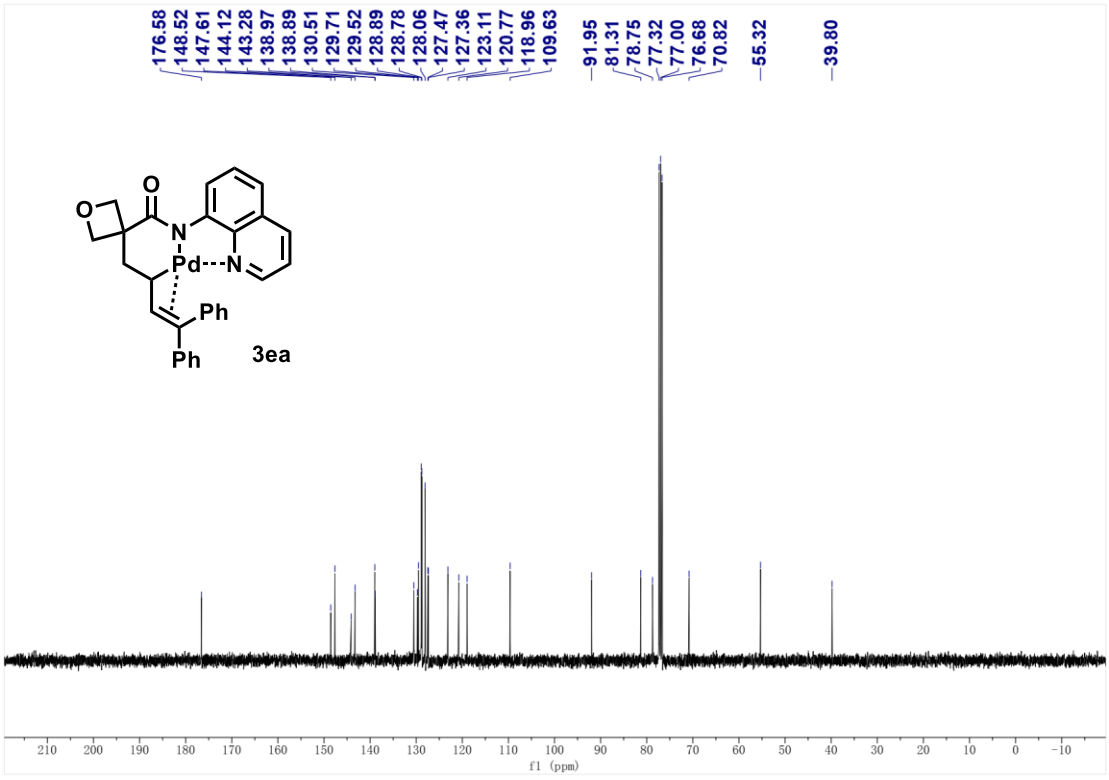
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



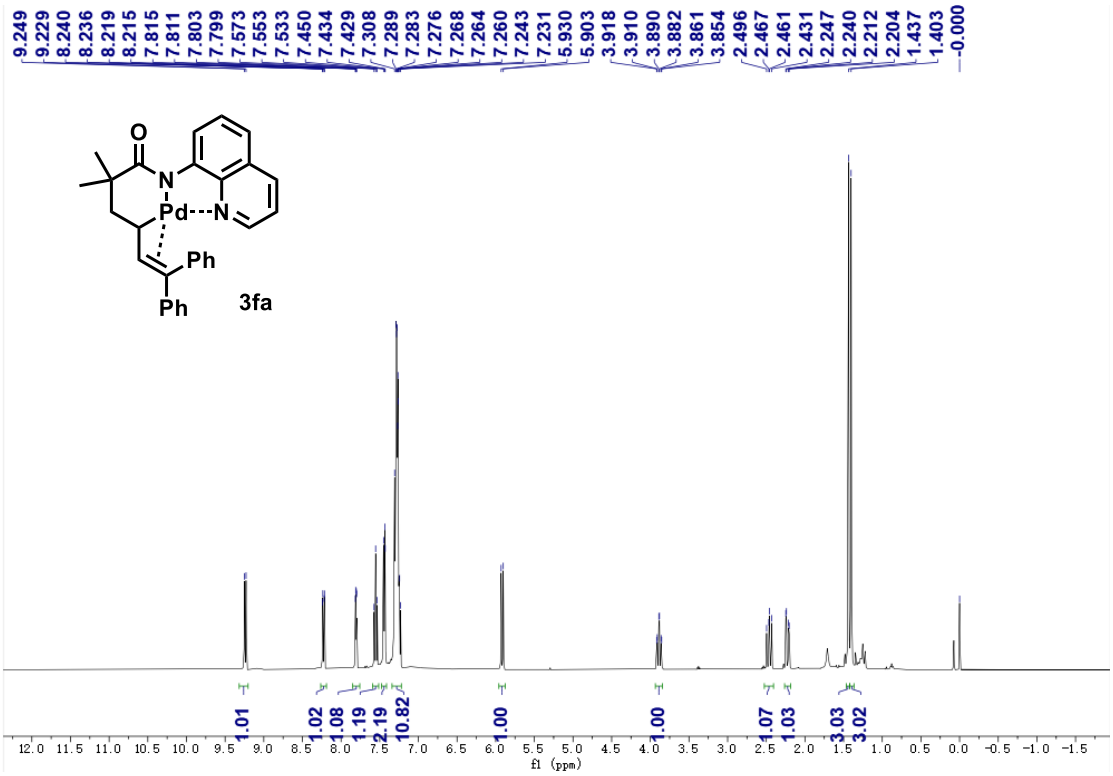
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



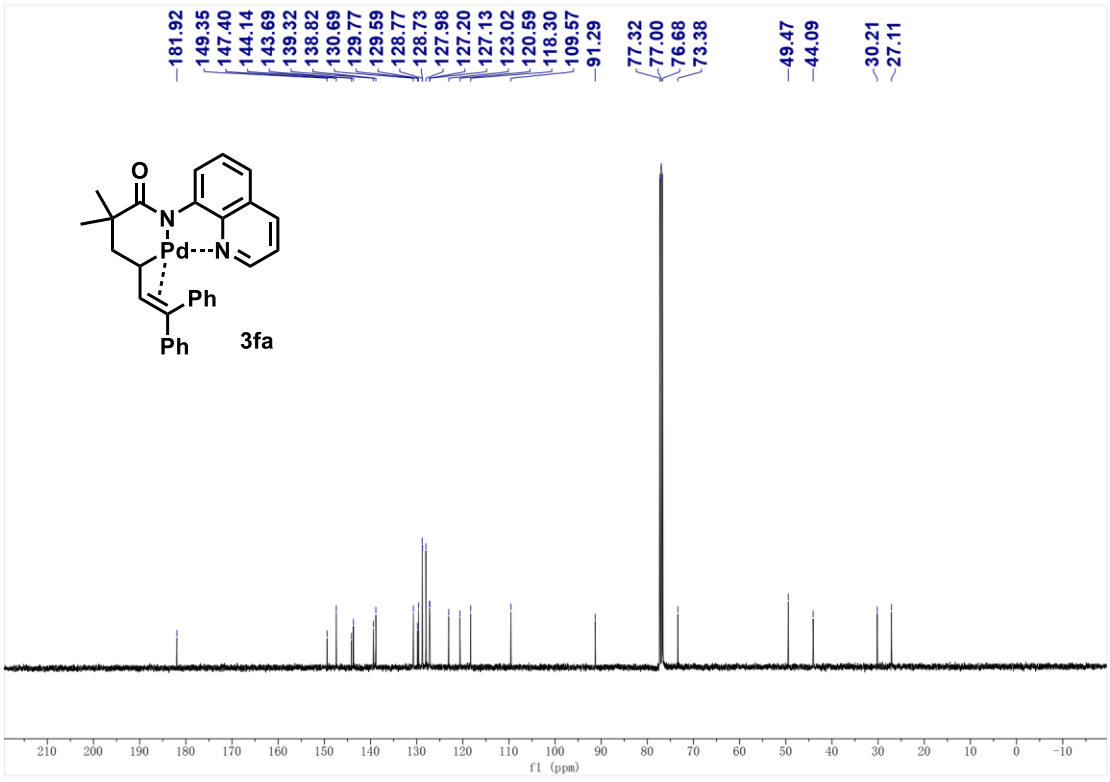
^{13}C NMR (100 MHz, $CDCl_3$) of **3ea**



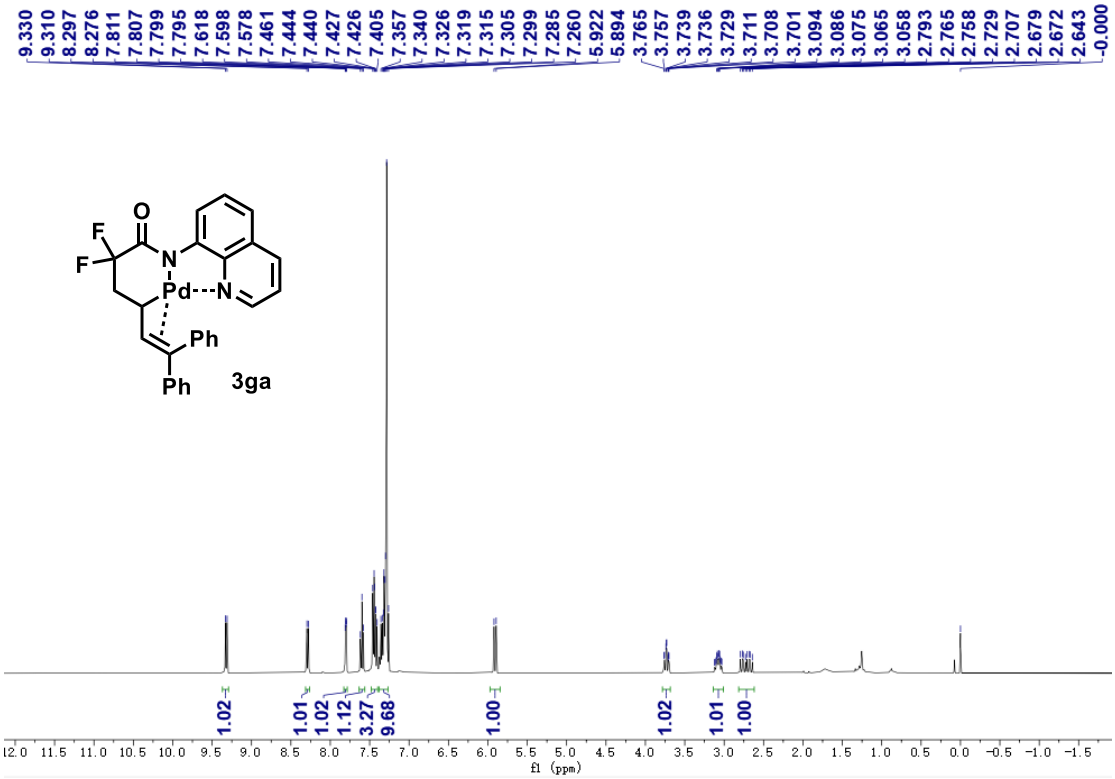
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



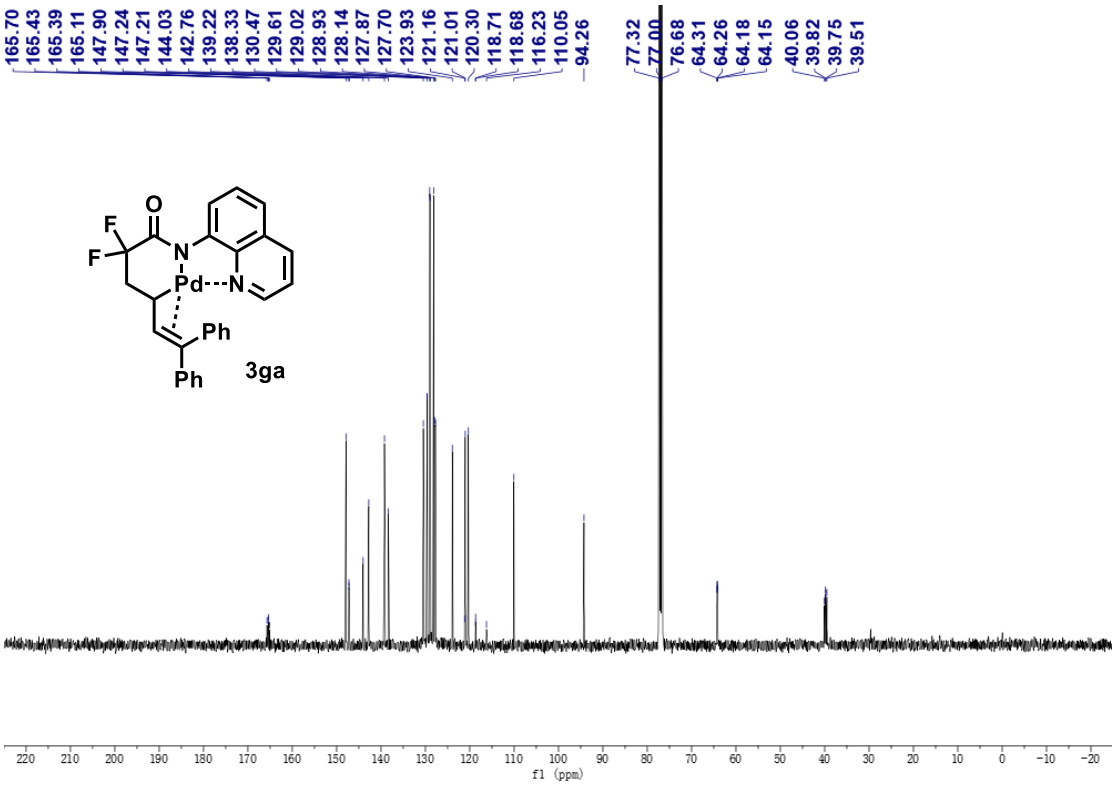
^{13}C NMR (100 MHz, $CDCl_3$) of **3fa**



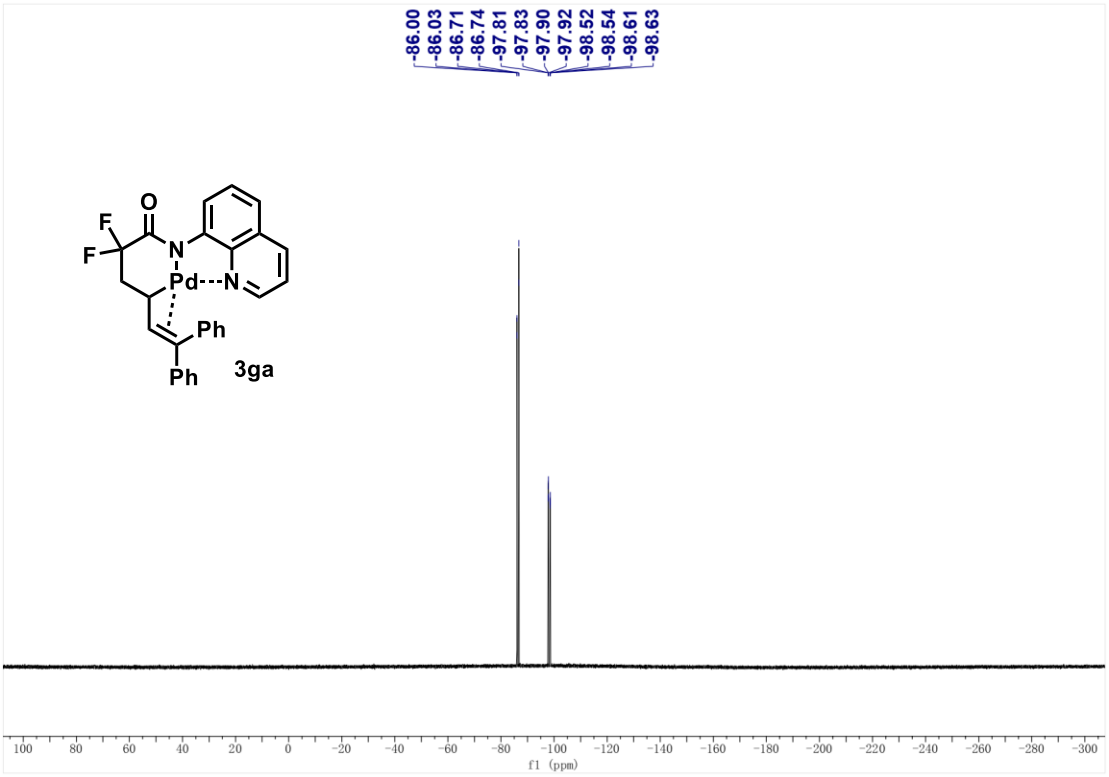
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



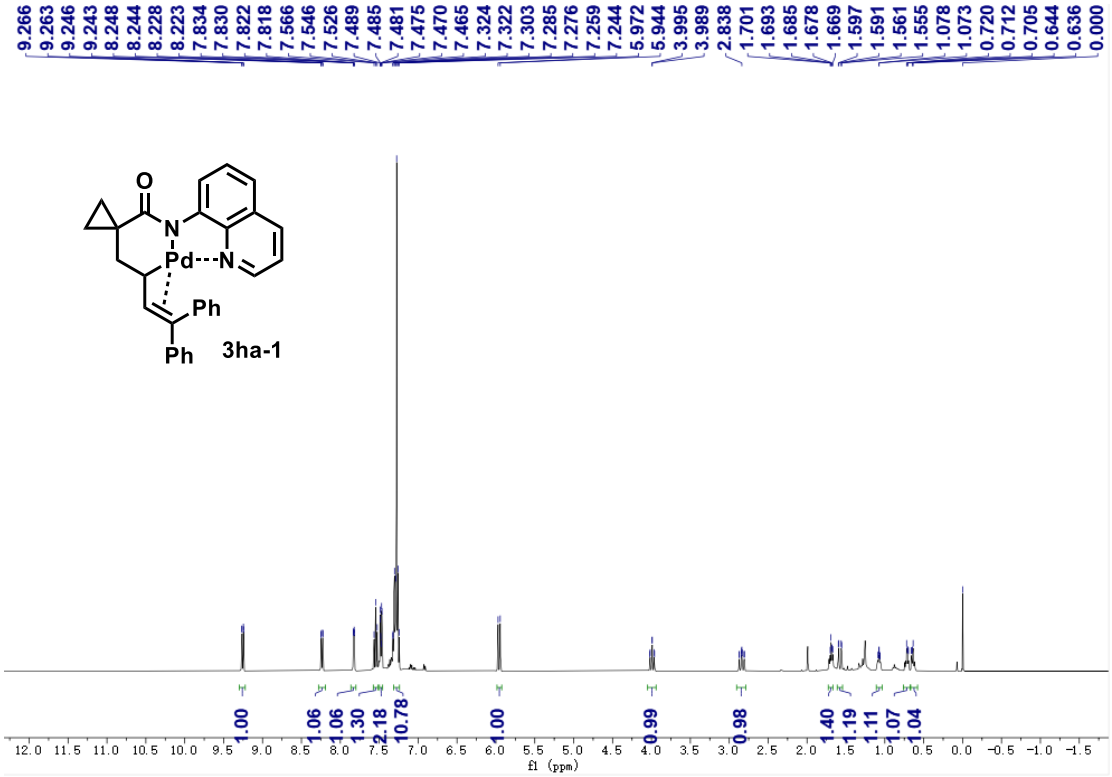
^{13}C NMR (100 MHz, $CDCl_3$) of **3ga**



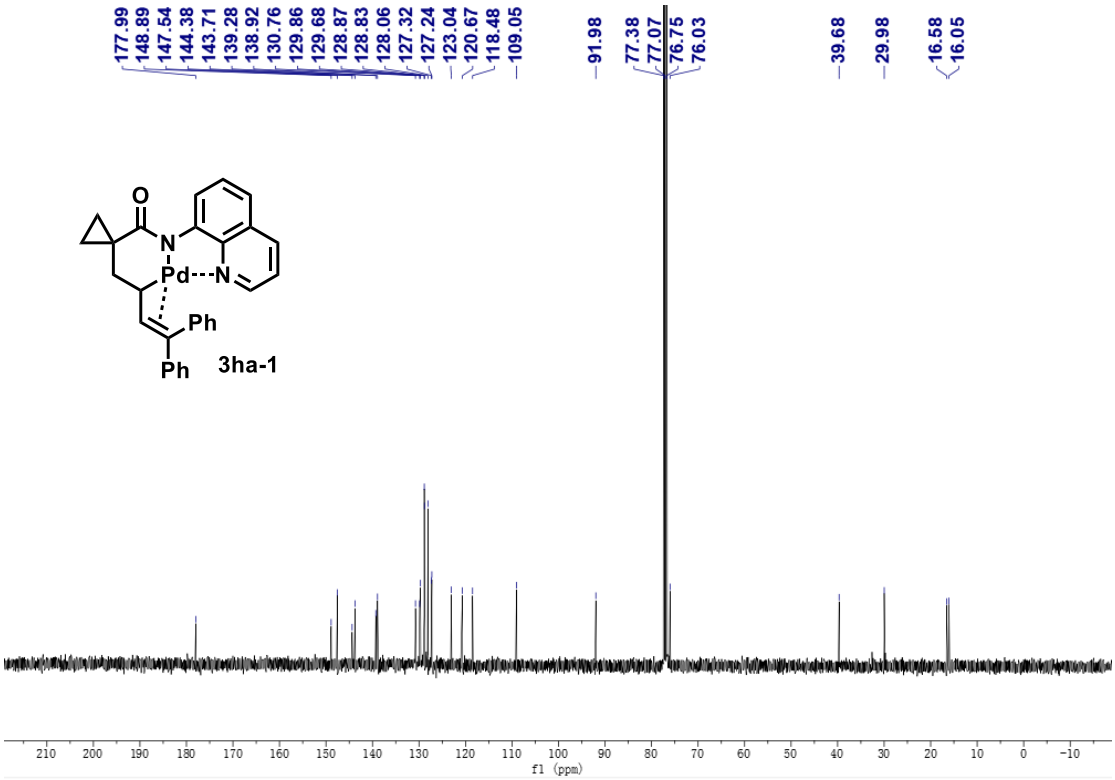
^{19}F NMR (376 MHz, $CDCl_3$) of **3ga**



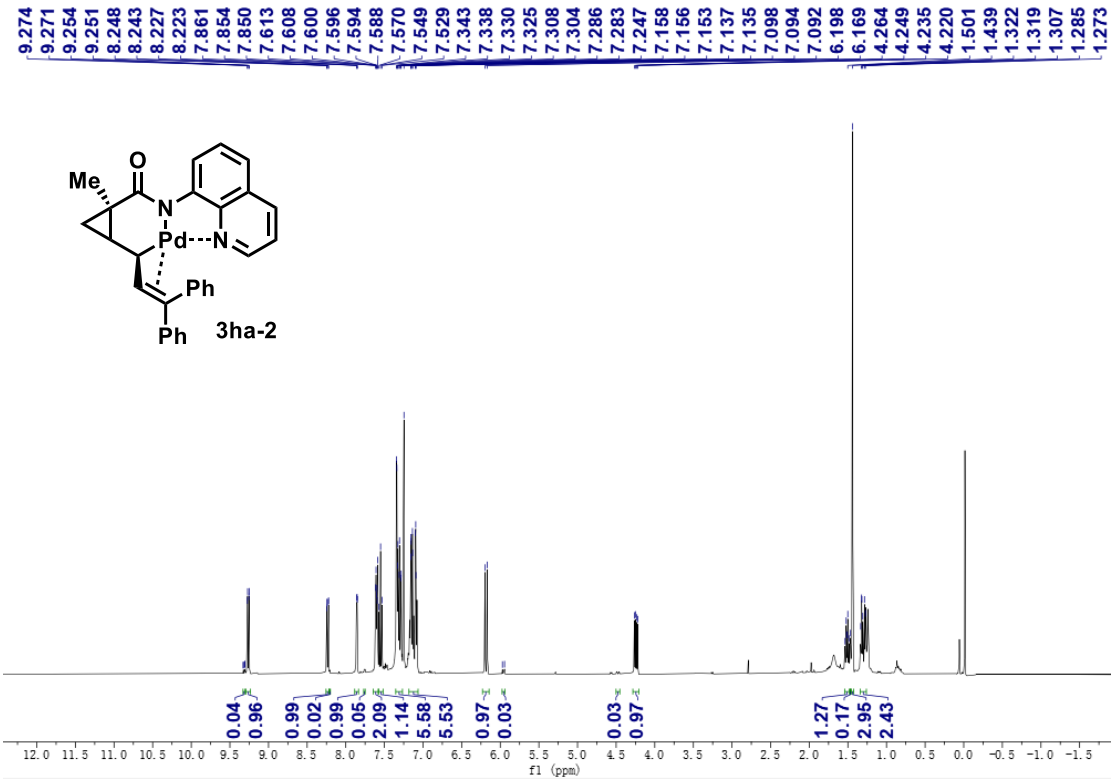
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha-1**



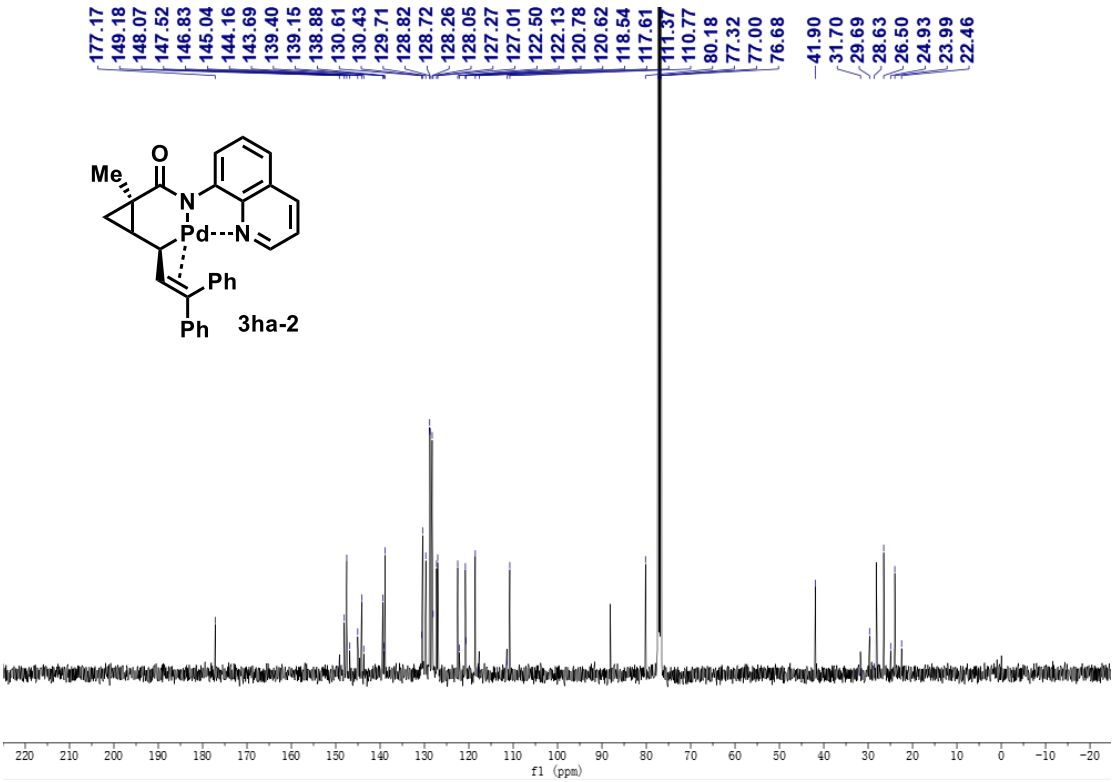
^{13}C NMR (100 MHz, $CDCl_3$) of **3ha-1**



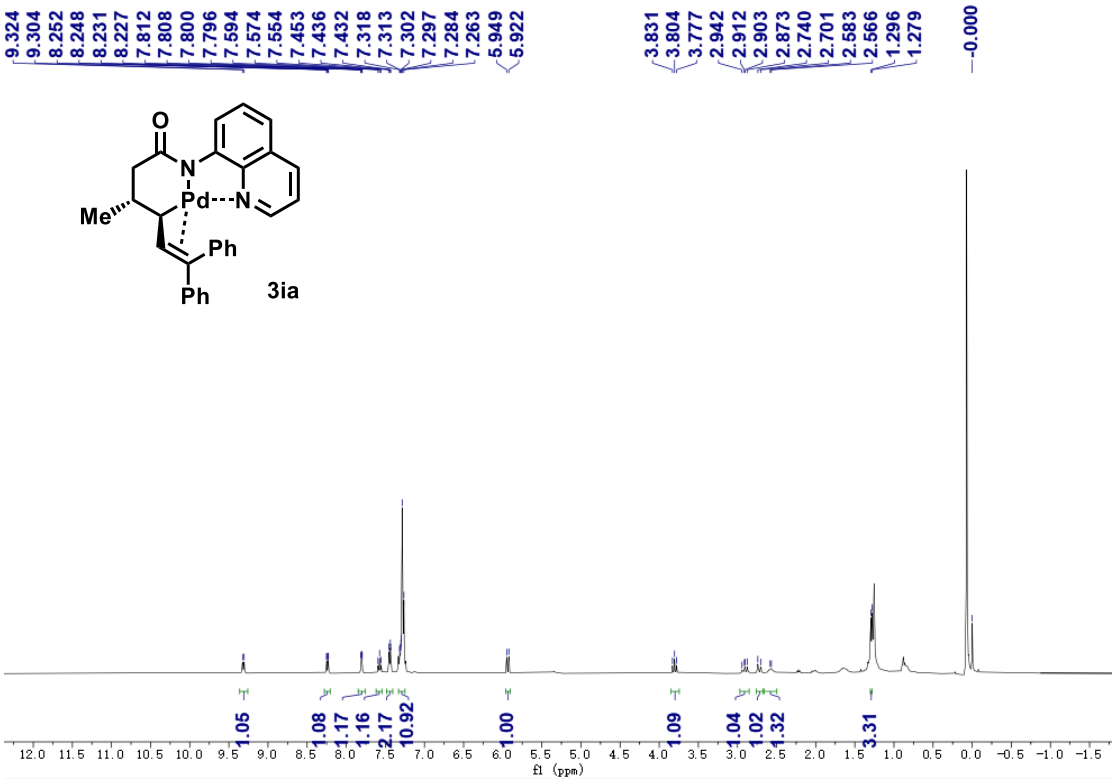
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha-2**



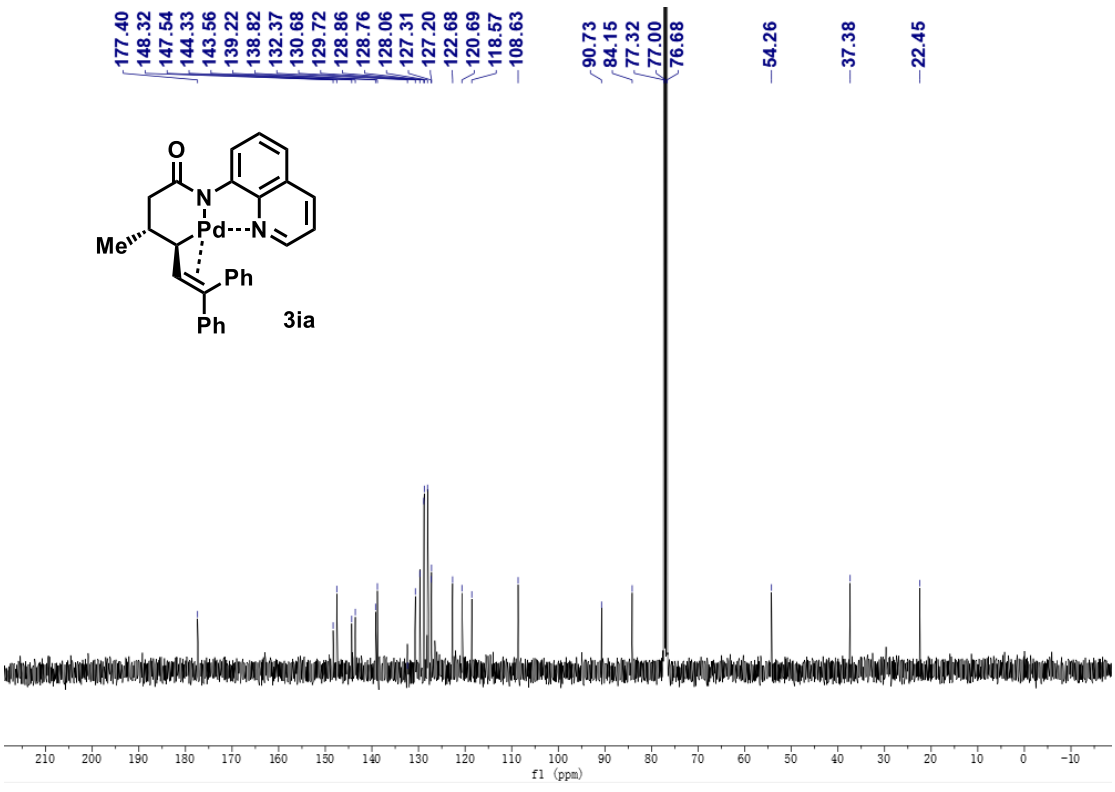
^{13}C NMR (100 MHz, $CDCl_3$) of **3ha-2**



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

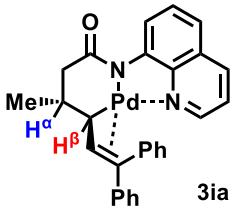


^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**



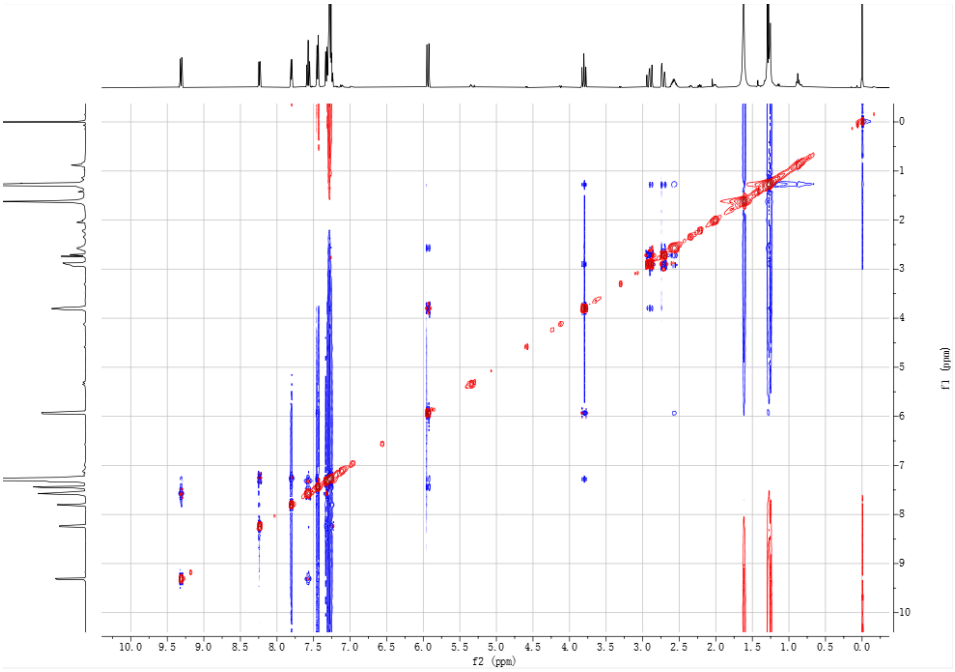
No NOE was observed between H^{α} and H^{β}

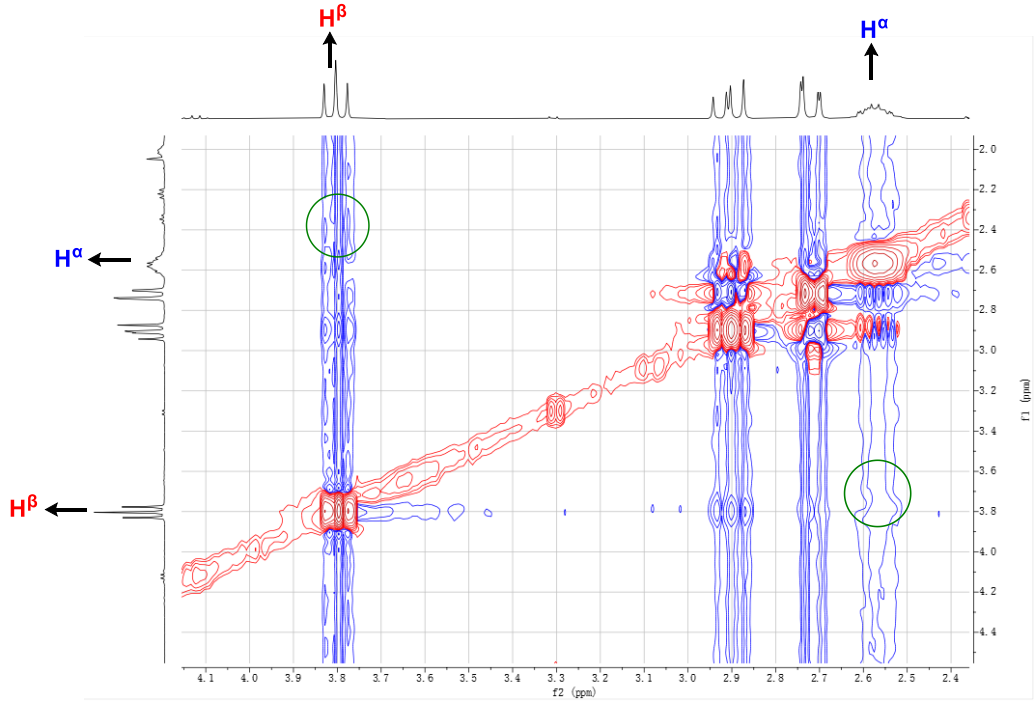
.



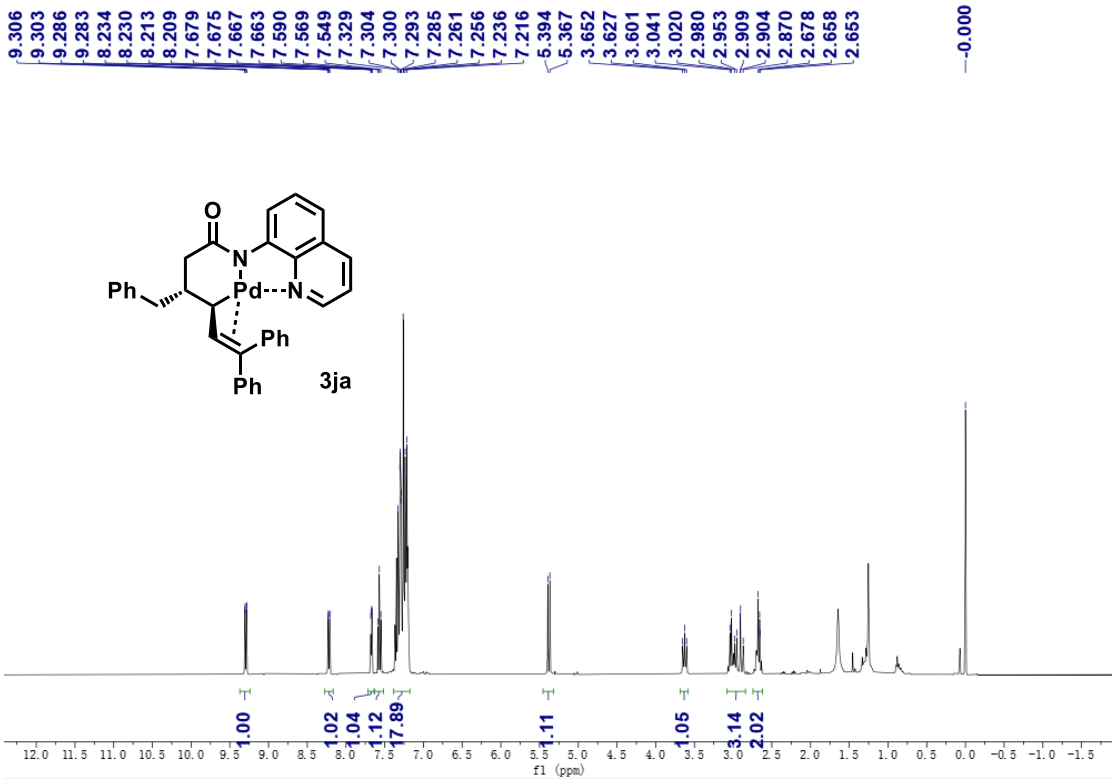
3ia

NOESY:

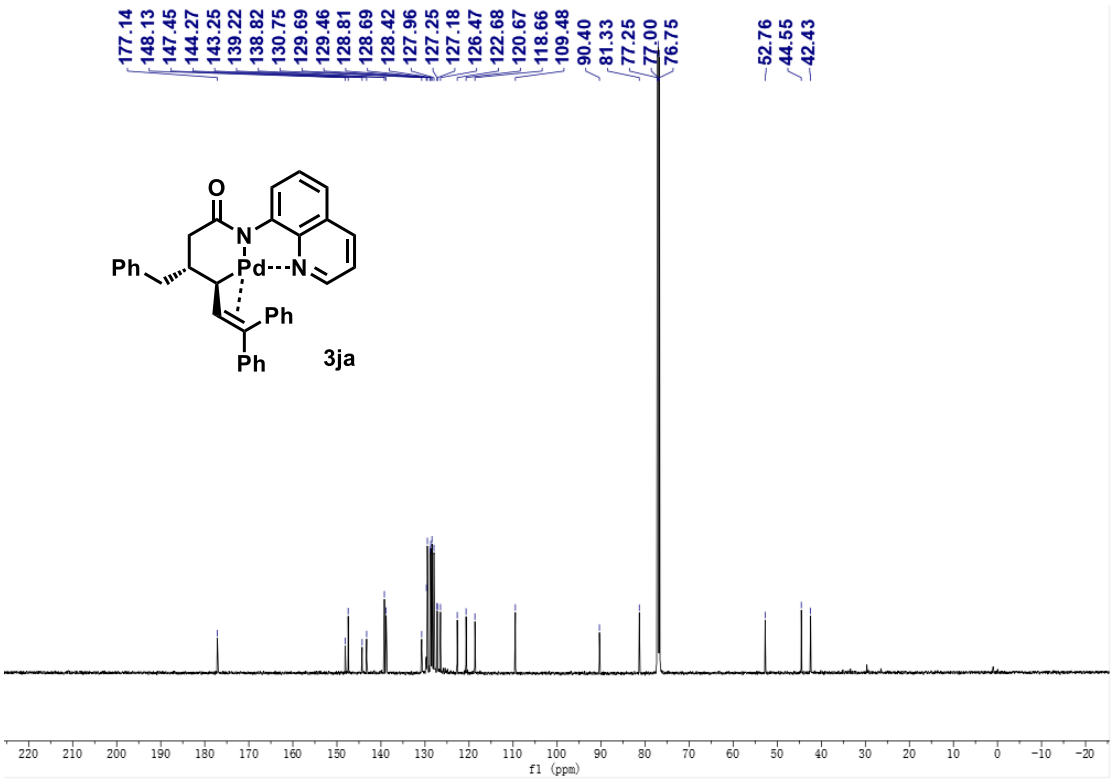




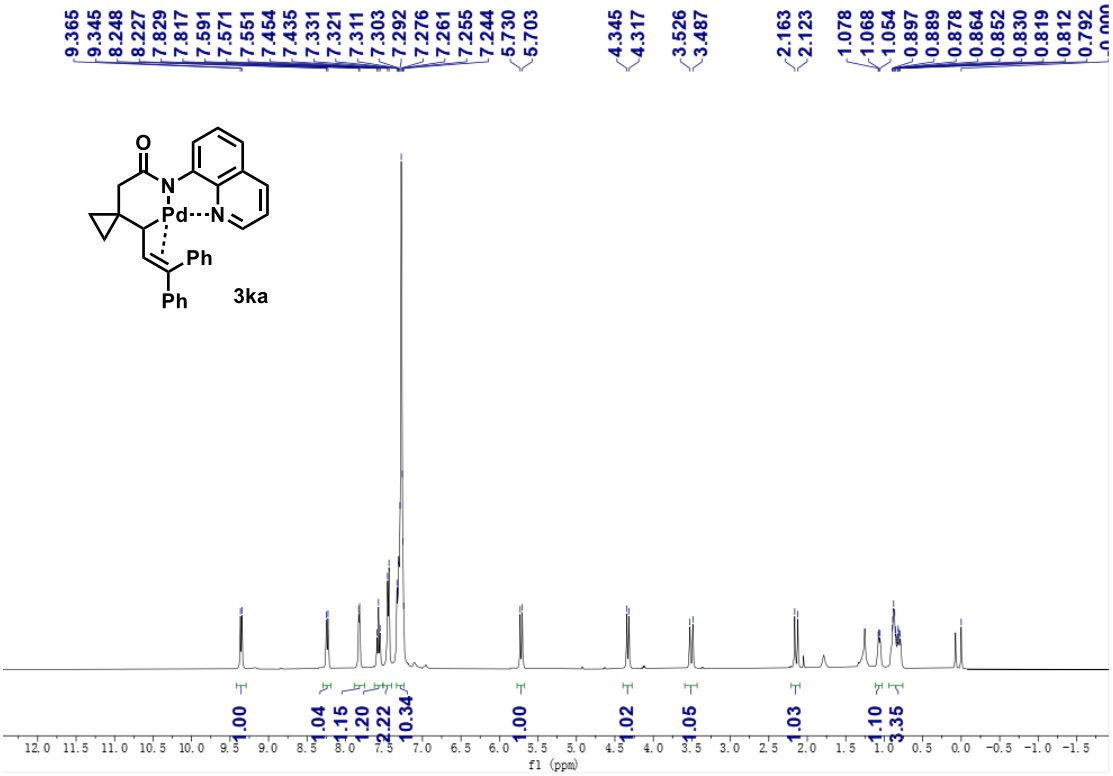
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



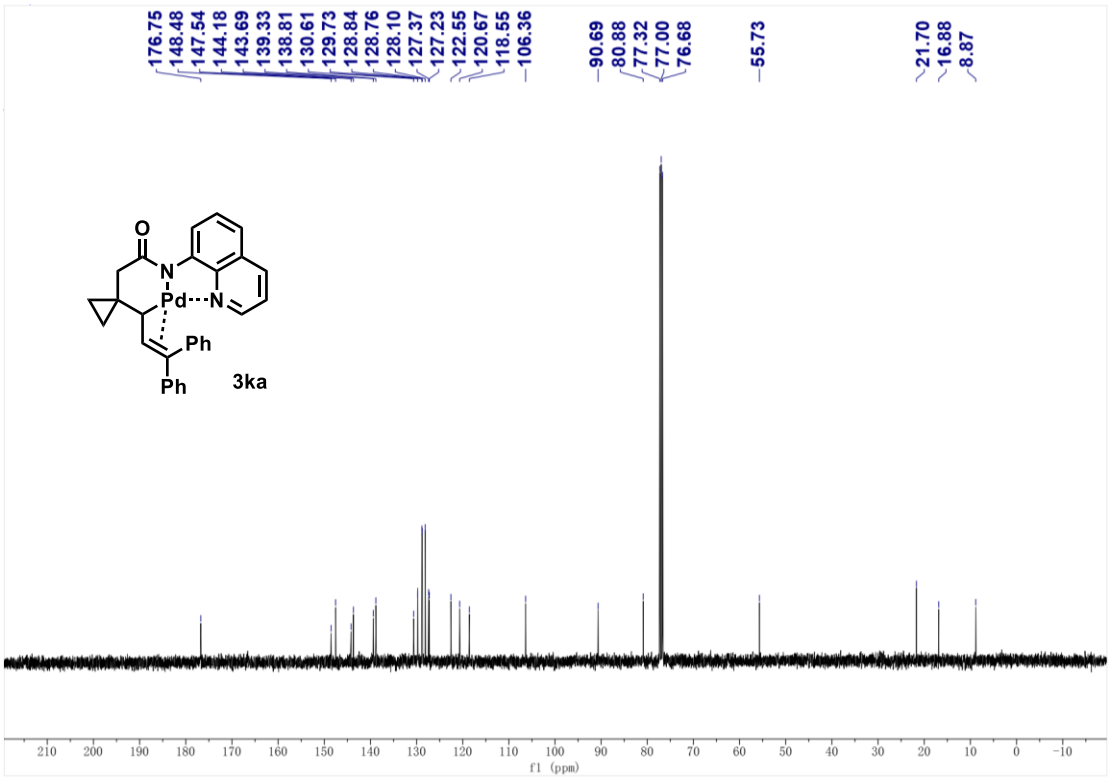
^{13}C NMR (100 MHz, $CDCl_3$) of **3ja**



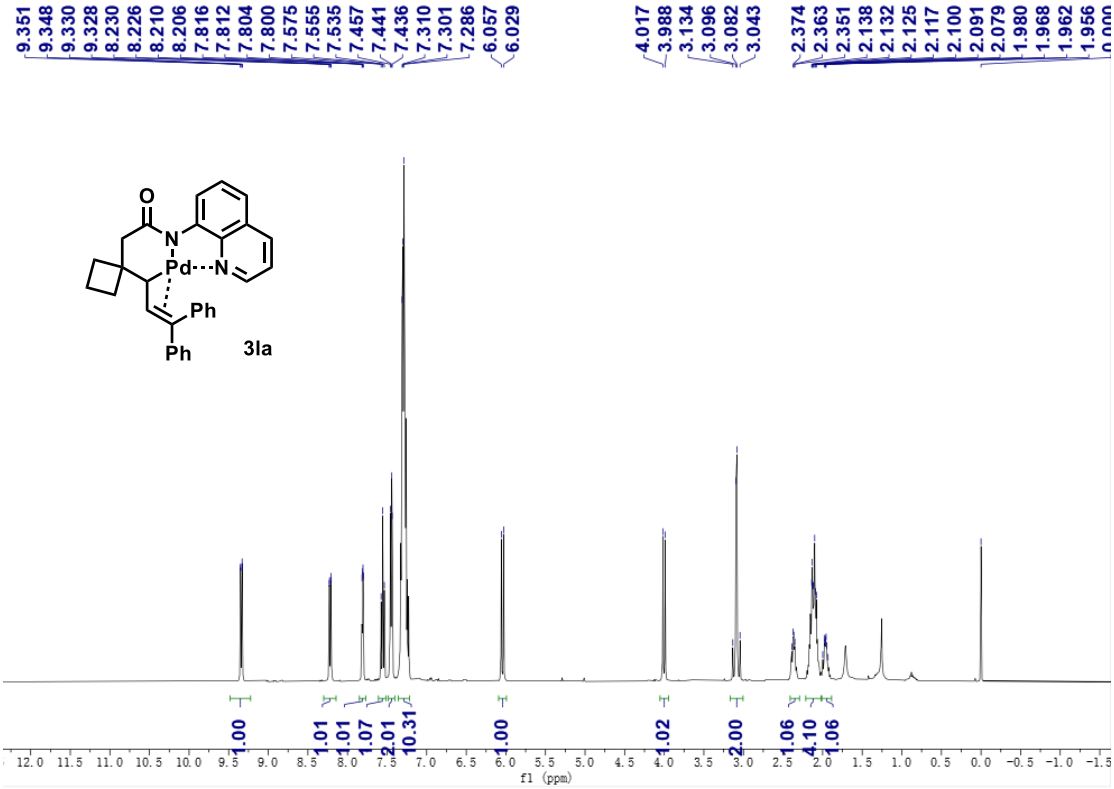
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**



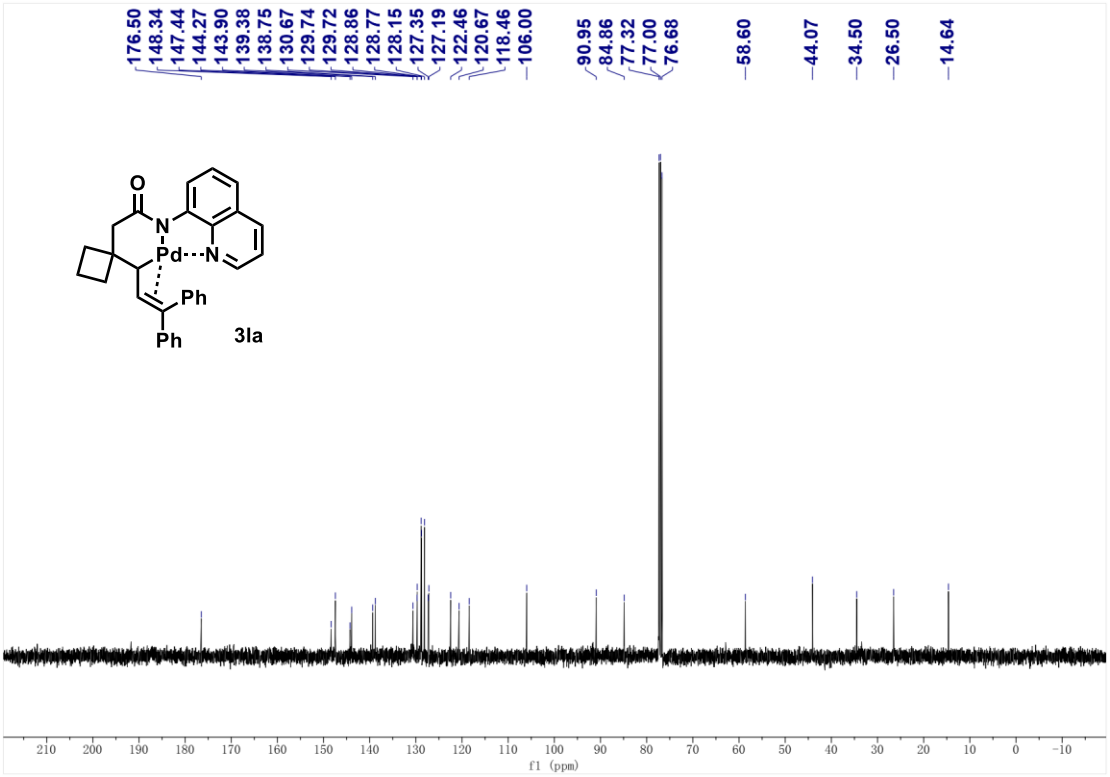
^{13}C NMR (100 MHz, $CDCl_3$) of **3ka**



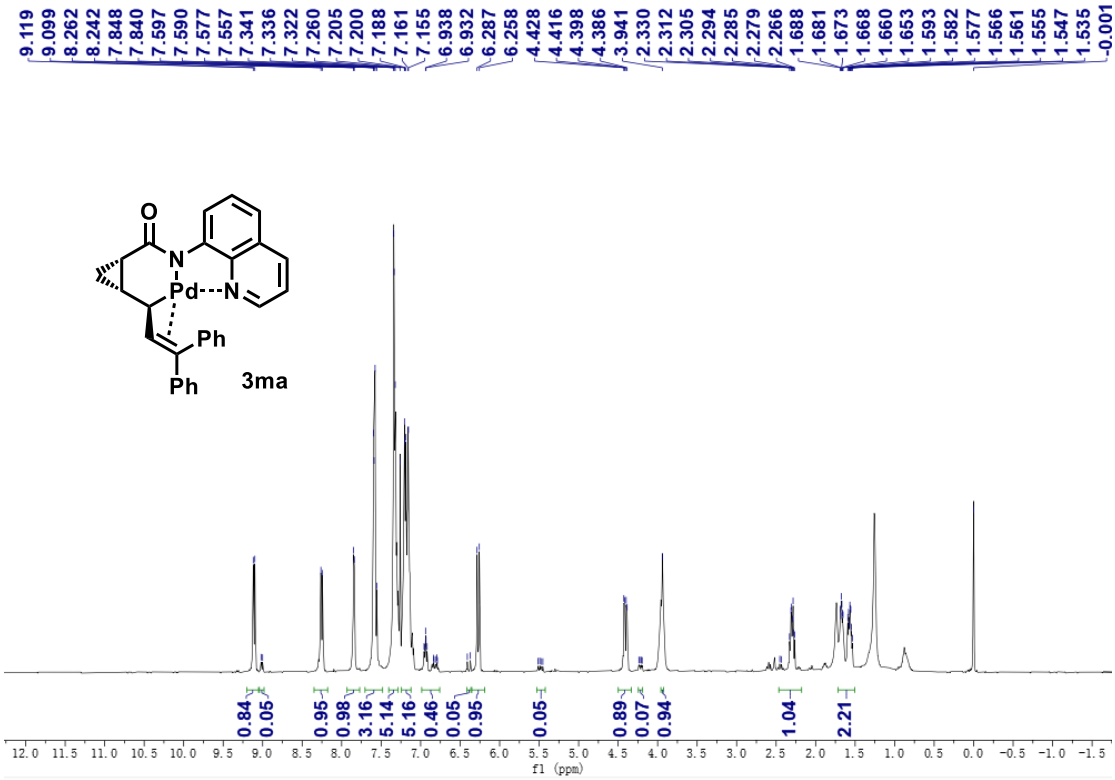
^{1}H NMR (400 MHz, $CDCl_3$) of **3la**



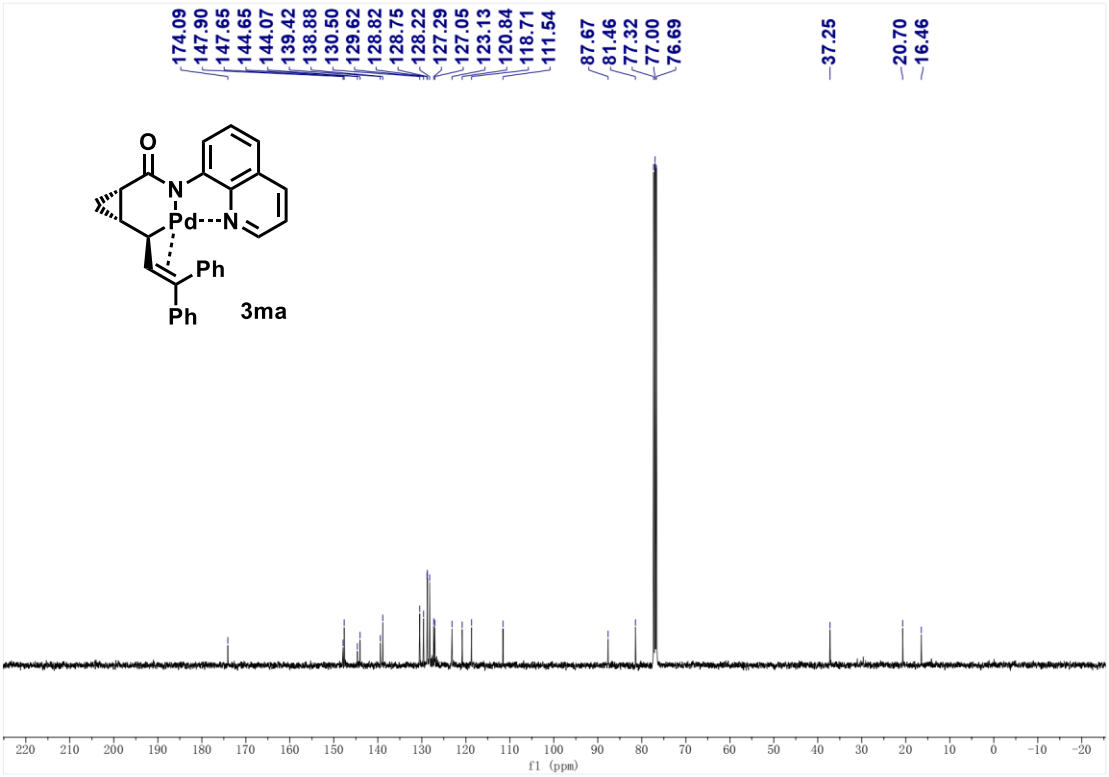
^{13}C NMR (100 MHz, $CDCl_3$) of **3la**



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

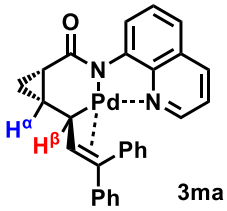


^{13}C NMR (100 MHz, $CDCl_3$) of **3ma**



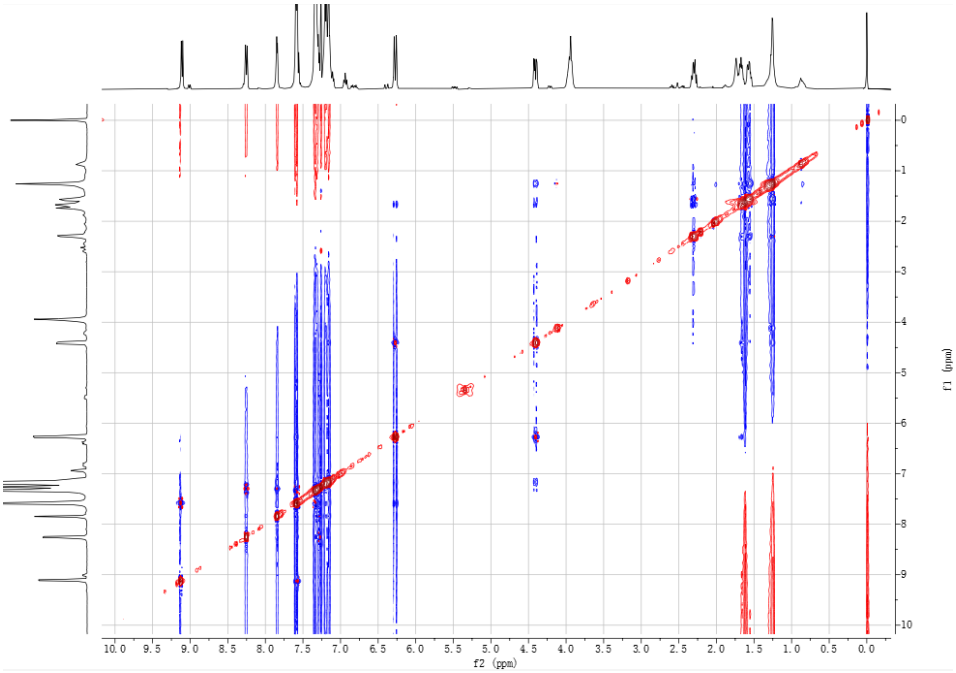
No NOE was observed between H^{α} and H^{β}

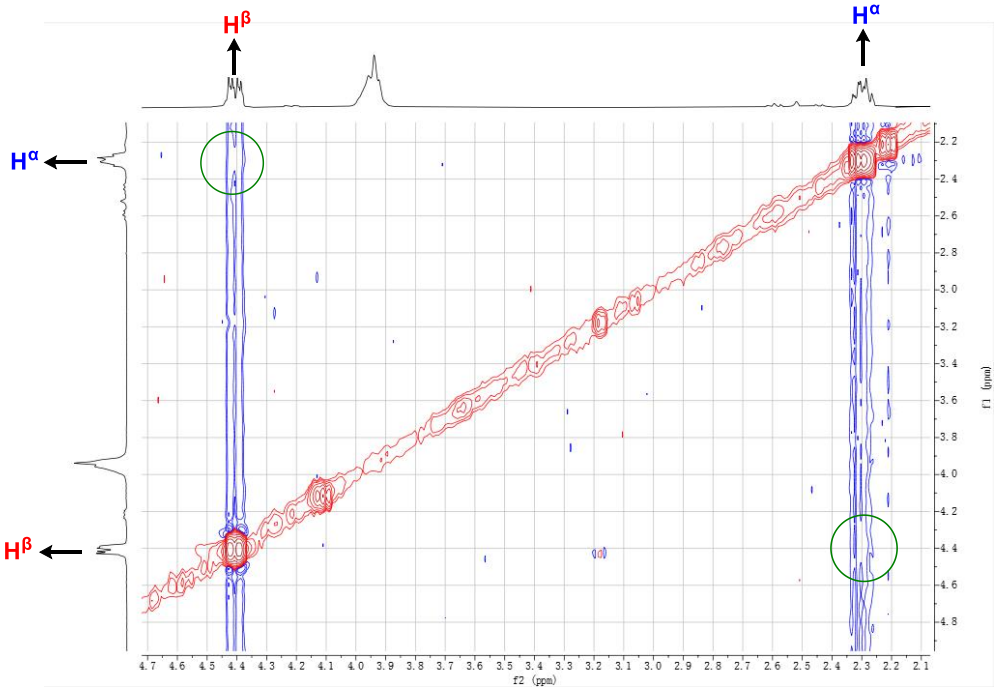
.



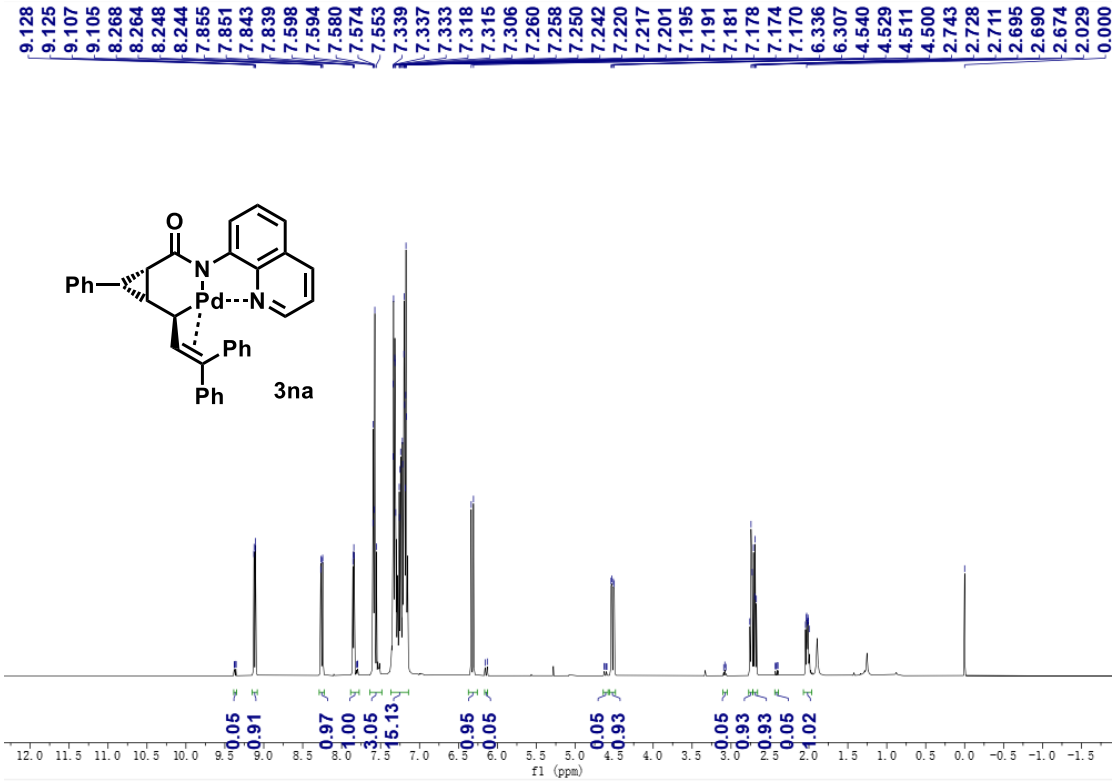
3ma

NOESY:

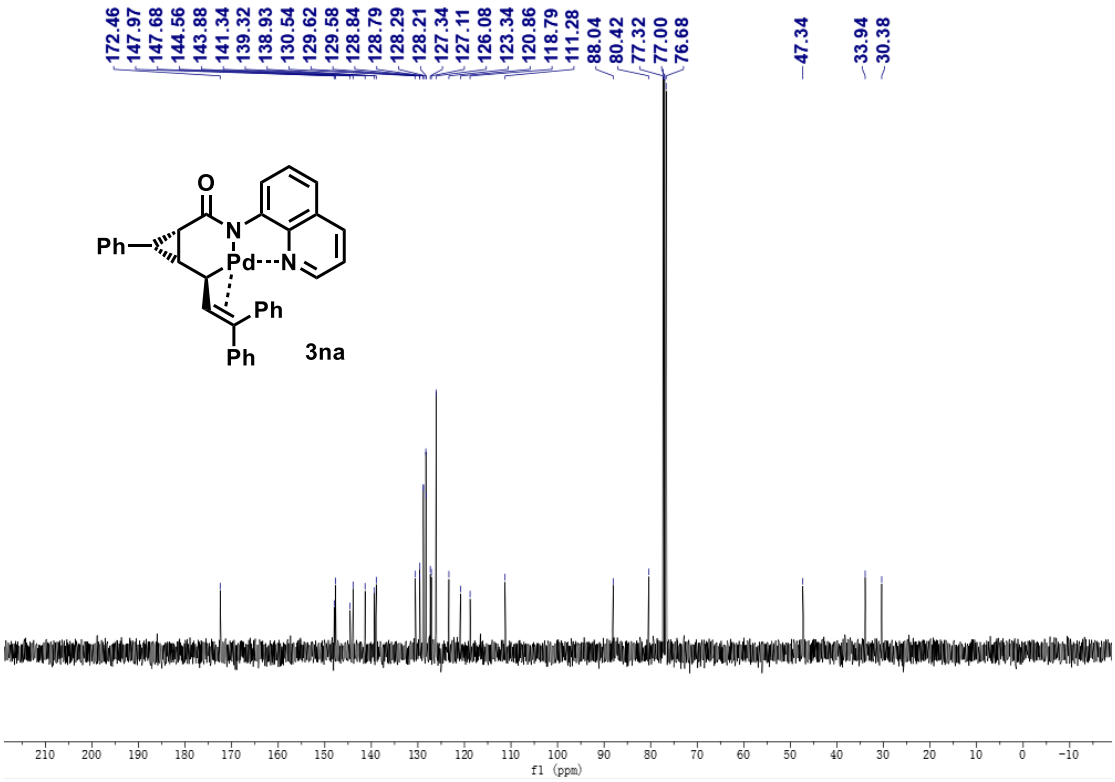




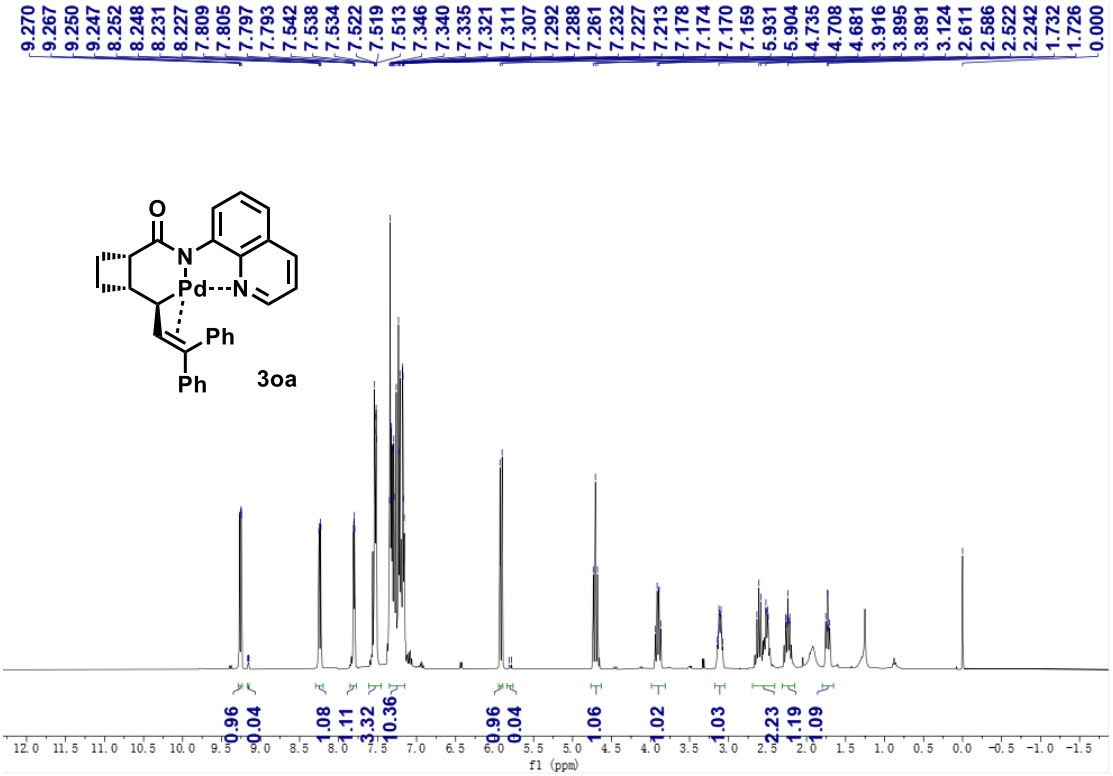
^{1}H NMR (400 MHz, $CDCl_3$) of **3na**



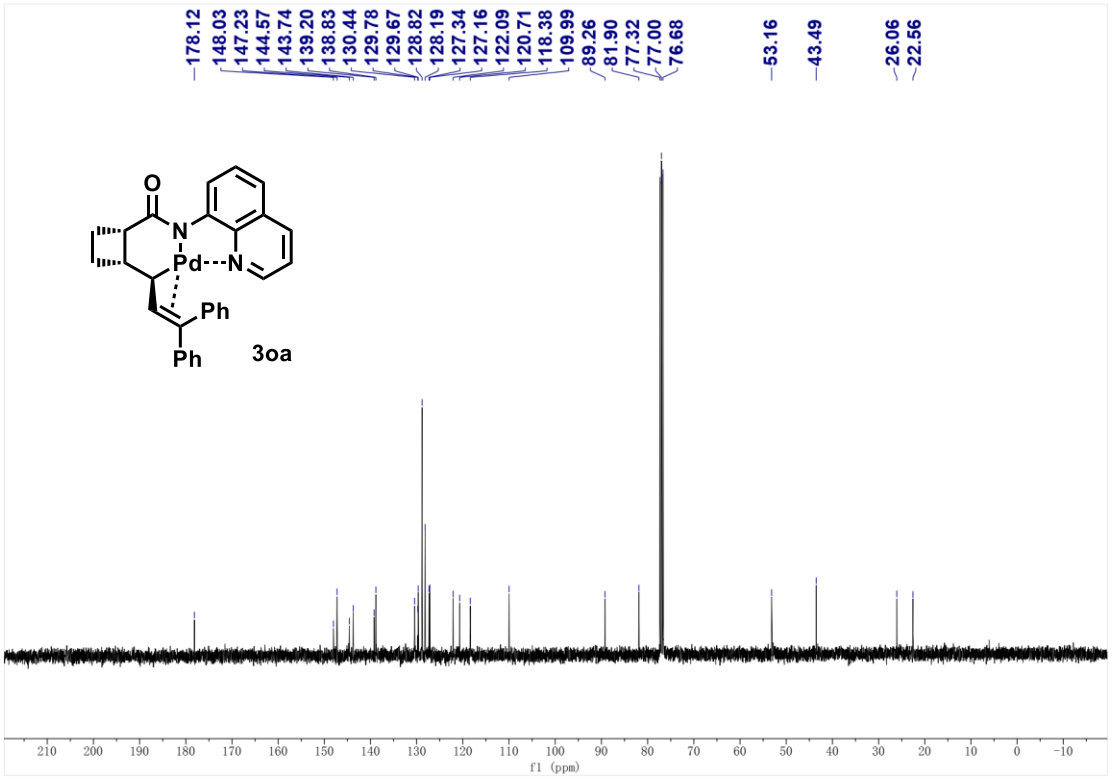
^{13}C NMR (100 MHz, $CDCl_3$) of **3na**



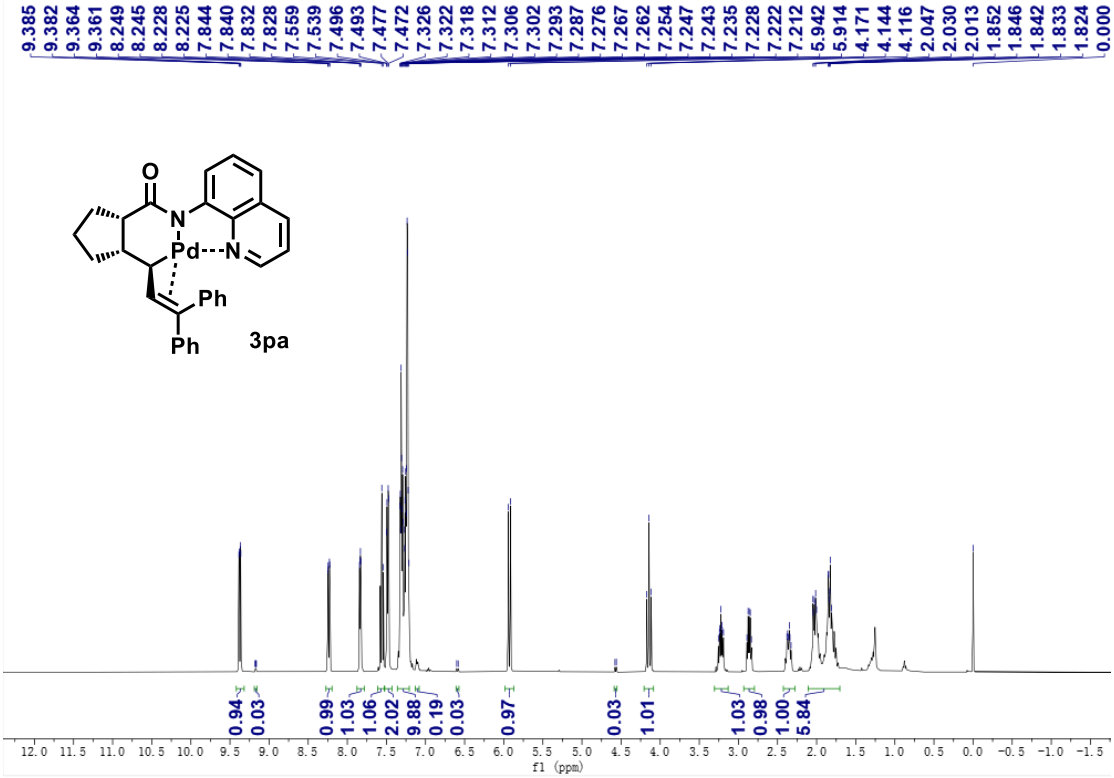
^{1}H NMR (400 MHz, $CDCl_3$) of **3oa**



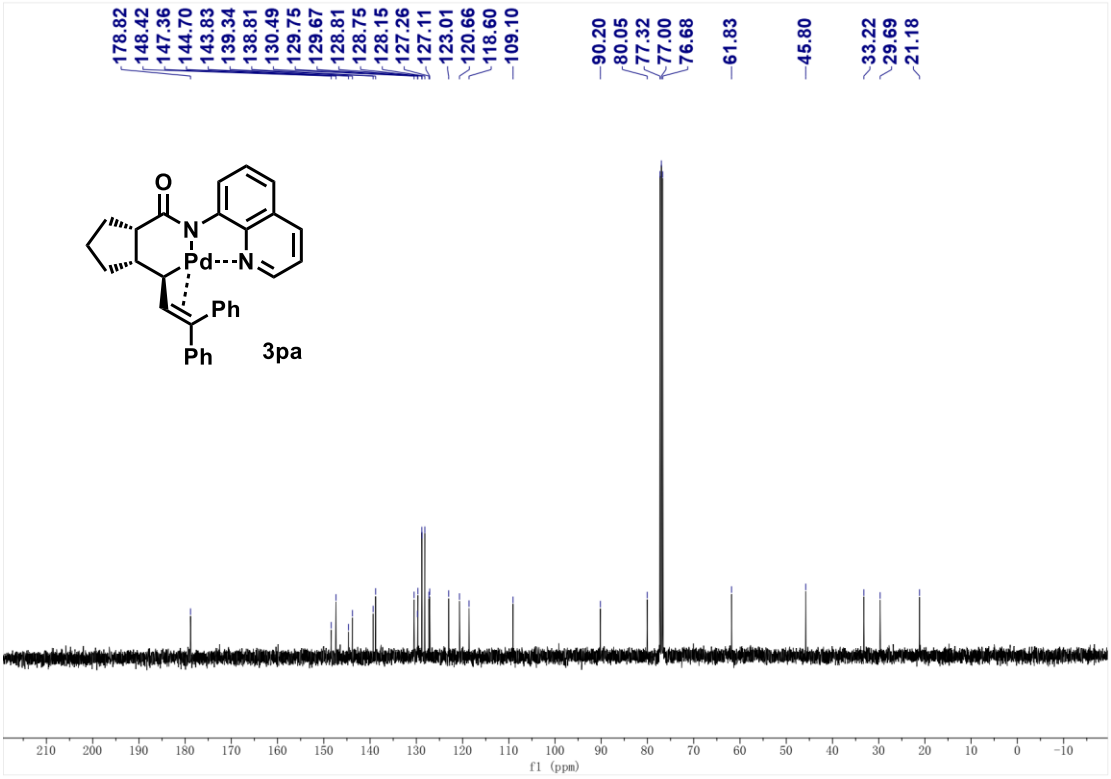
^{13}C NMR (100 MHz, $CDCl_3$) of **3oa**



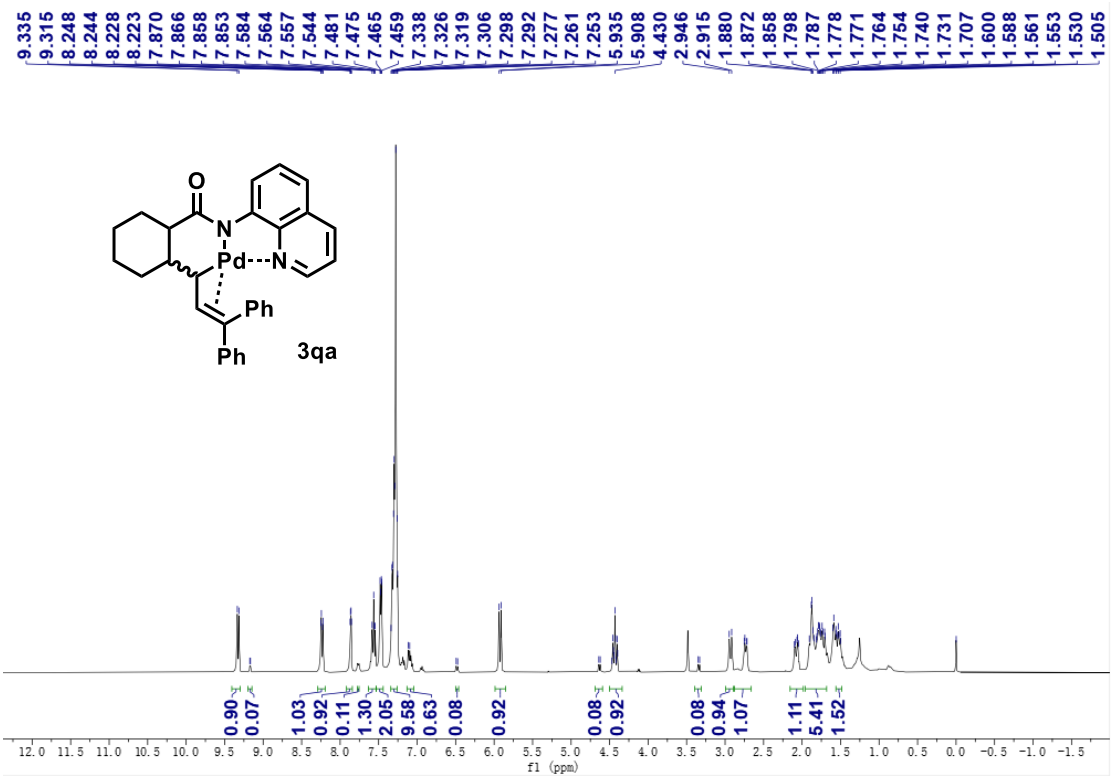
^{1}H NMR (400 MHz, $CDCl_3$) of **3pa**



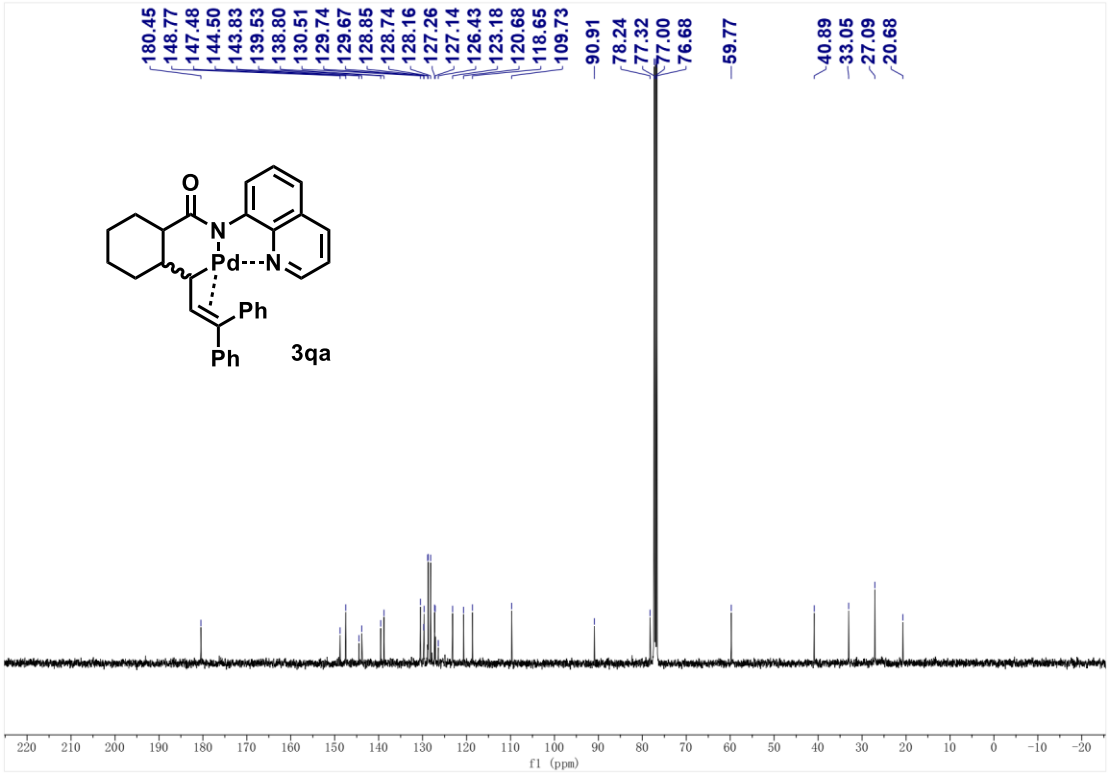
^{13}C NMR (100 MHz, $CDCl_3$) of **3pa**



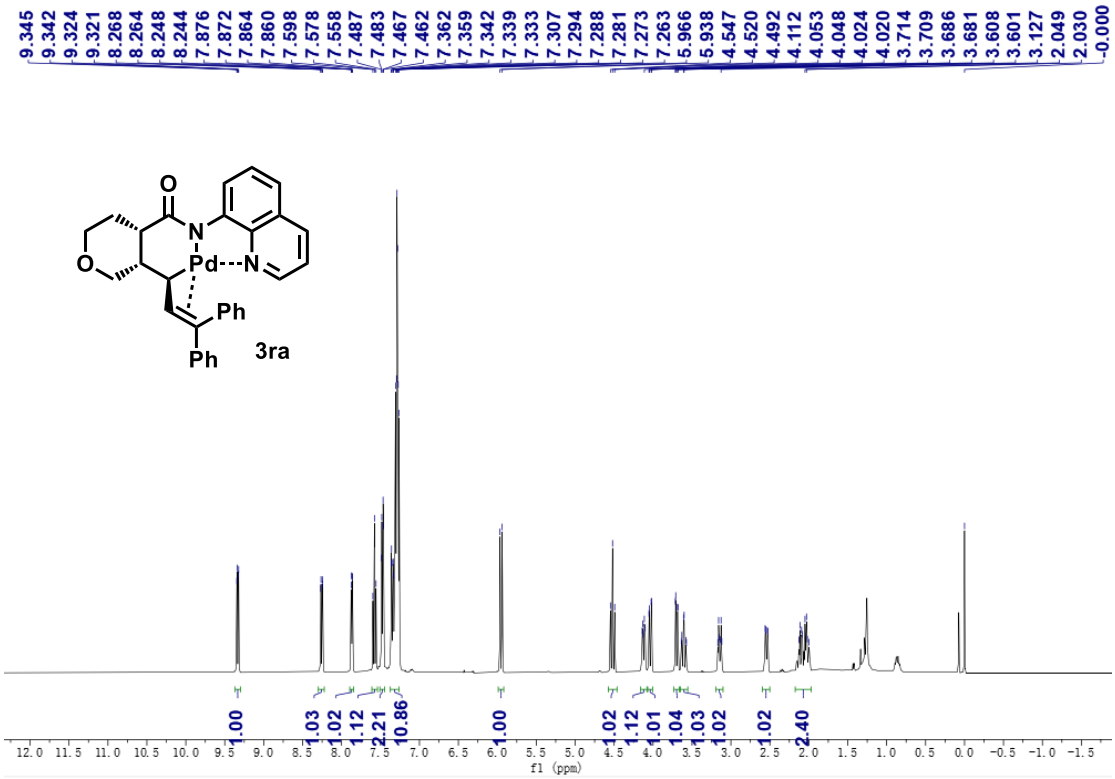
^{1}H NMR (400 MHz, $CDCl_3$) of **3qa**



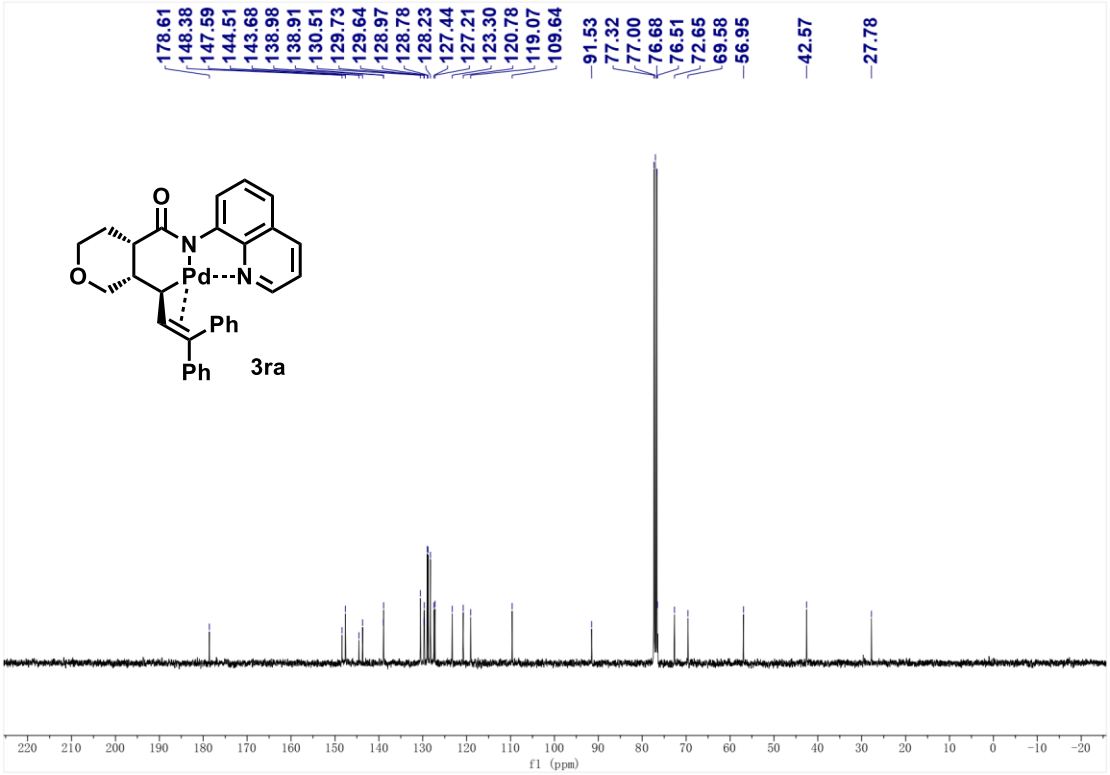
^{13}C NMR (100 MHz, $CDCl_3$) of **3qa**



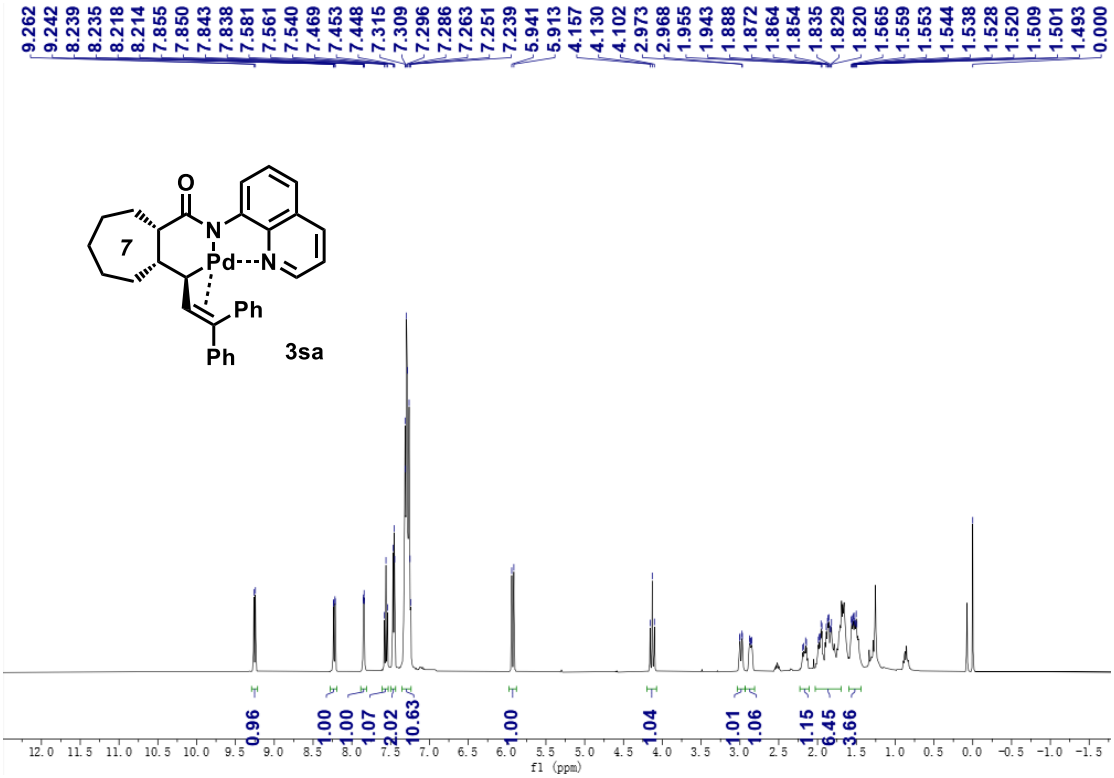
^{1}H NMR (400 MHz, $CDCl_3$) of **3ra**



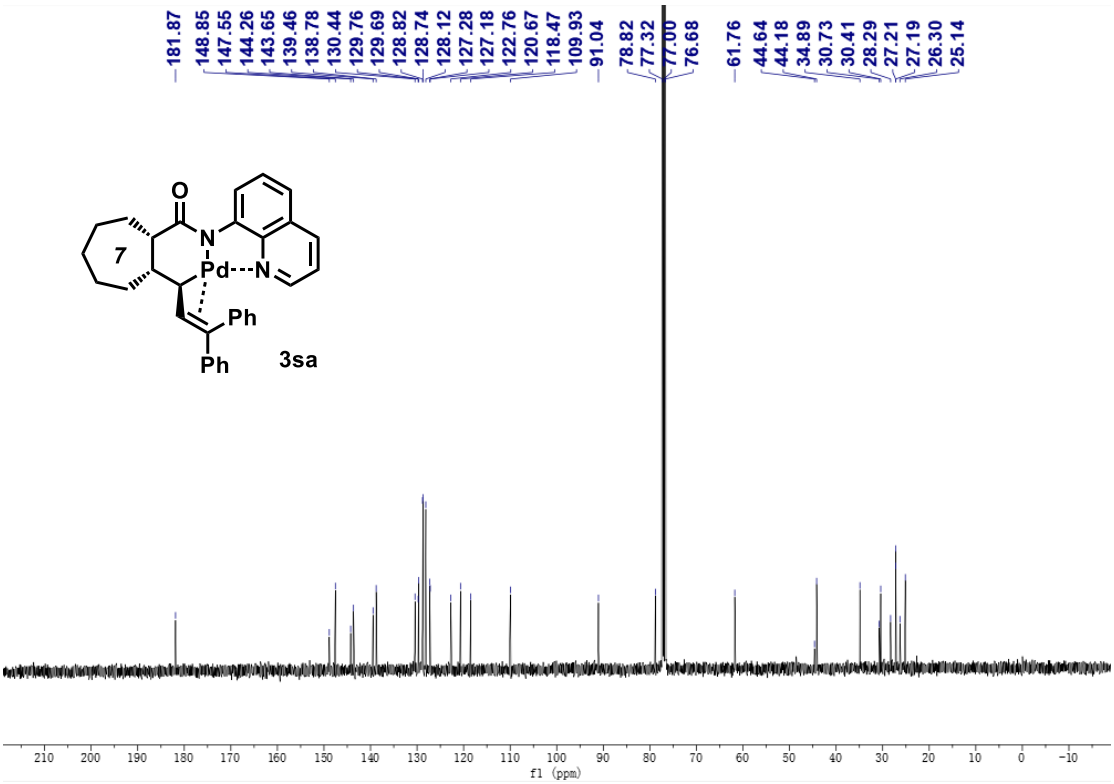
^{13}C NMR (100 MHz, $CDCl_3$) of **3ra**



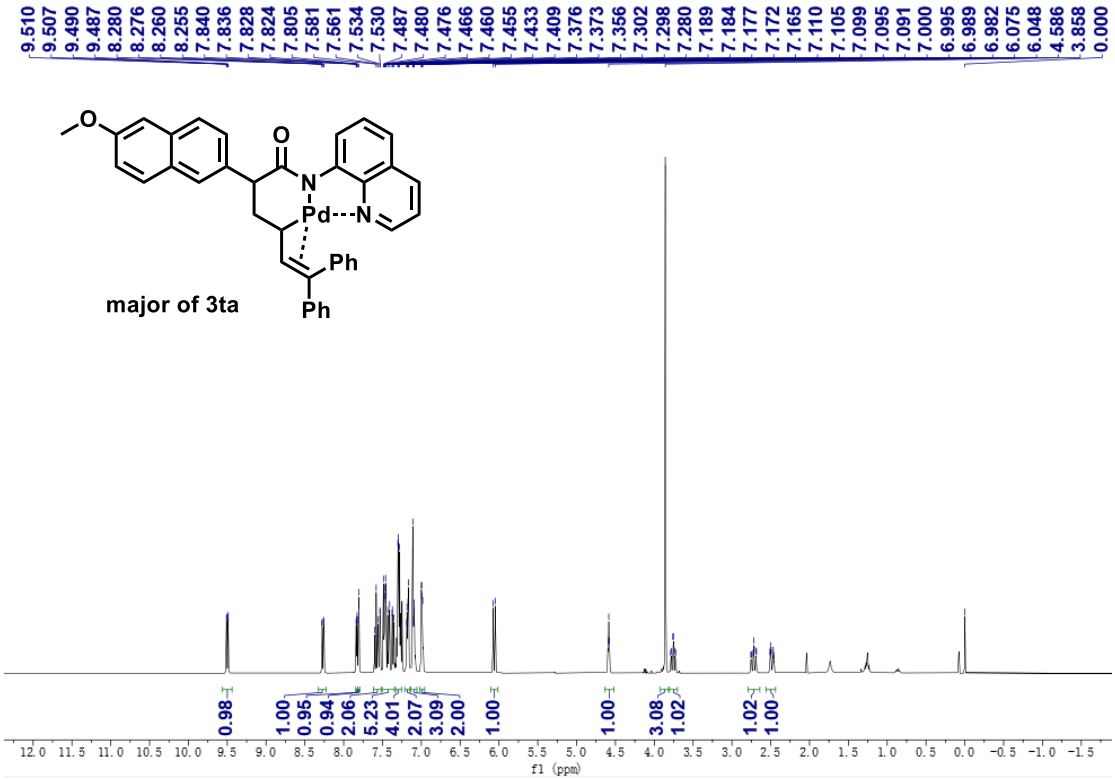
^{1}H NMR (400 MHz, $CDCl_3$) of **3sa**



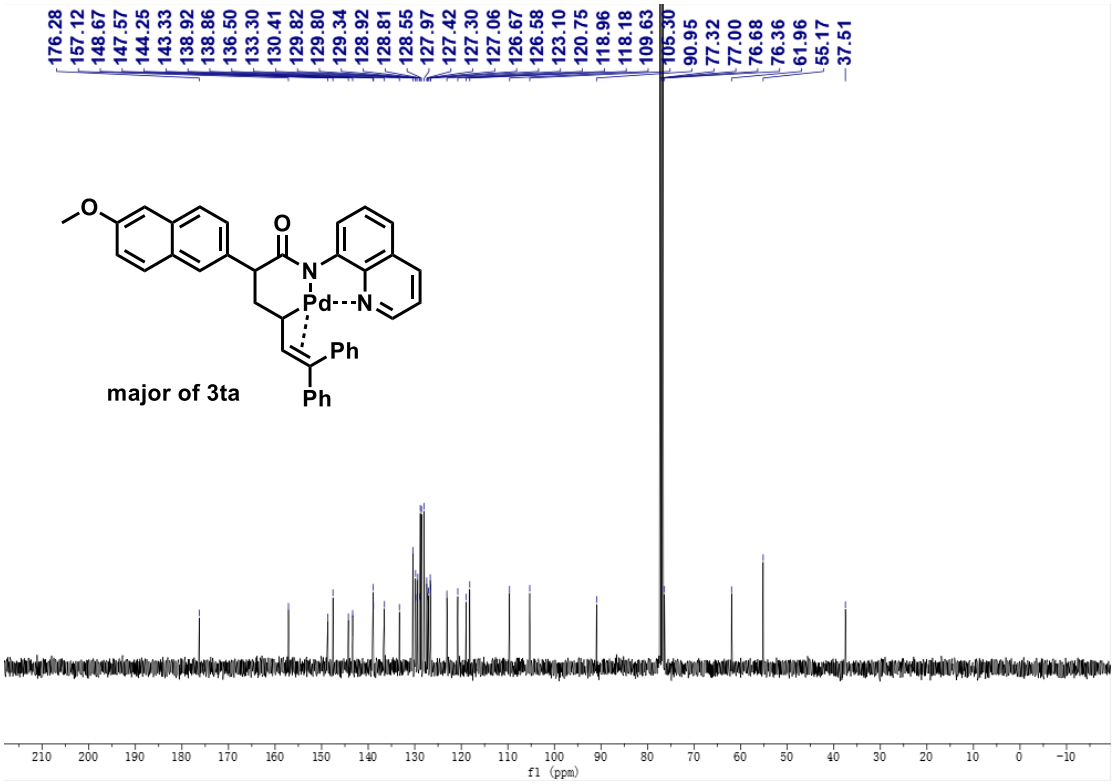
^{13}C NMR (100 MHz, $CDCl_3$) of **3sa**



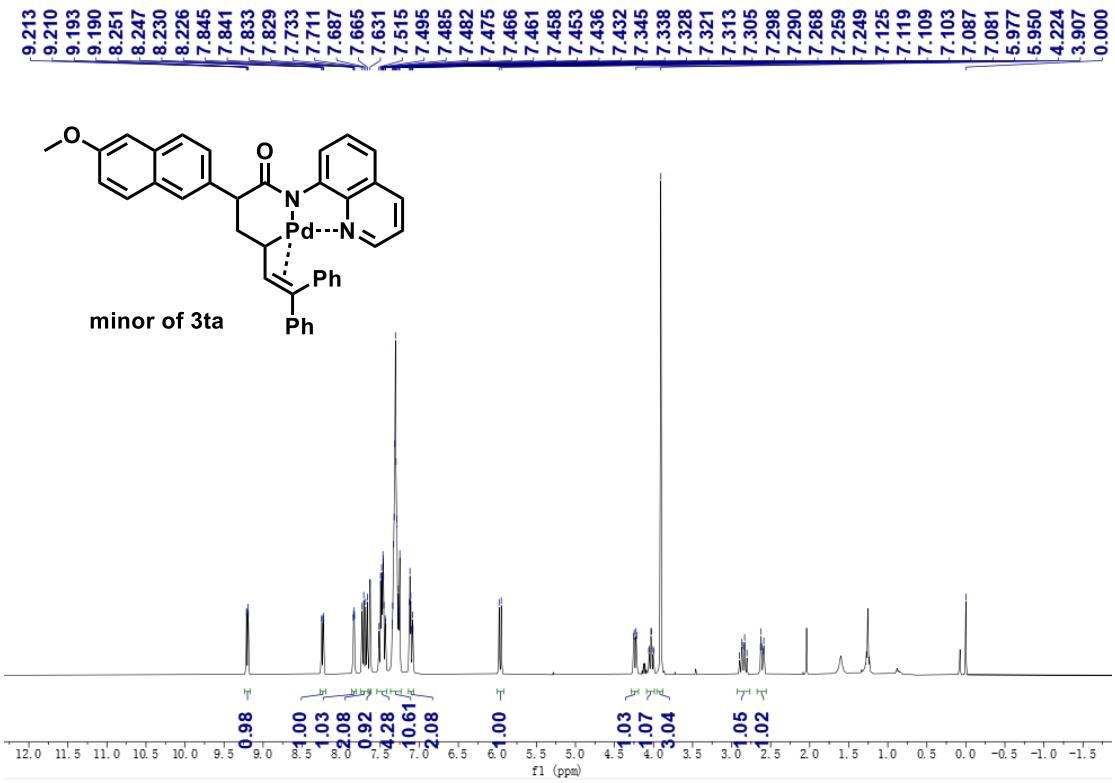
^{1}H NMR (400 MHz, $CDCl_3$) of **3ta-major**



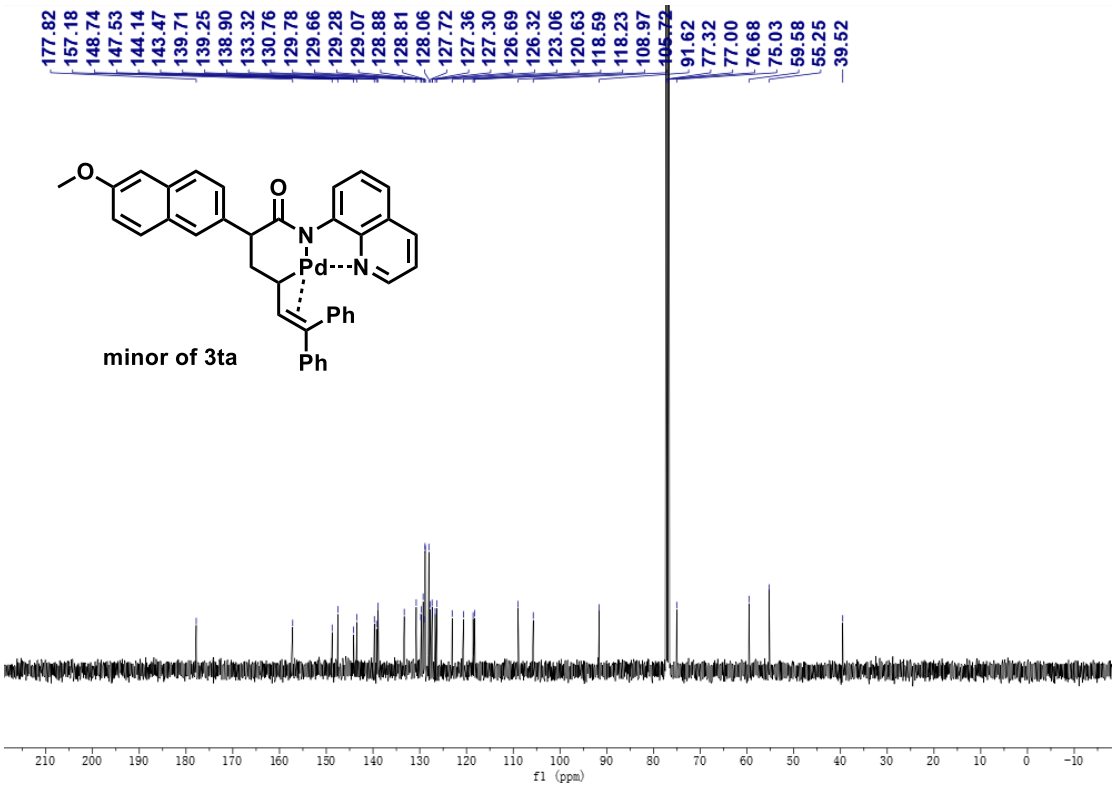
^{13}C NMR (100 MHz, $CDCl_3$) of **3ta-major**



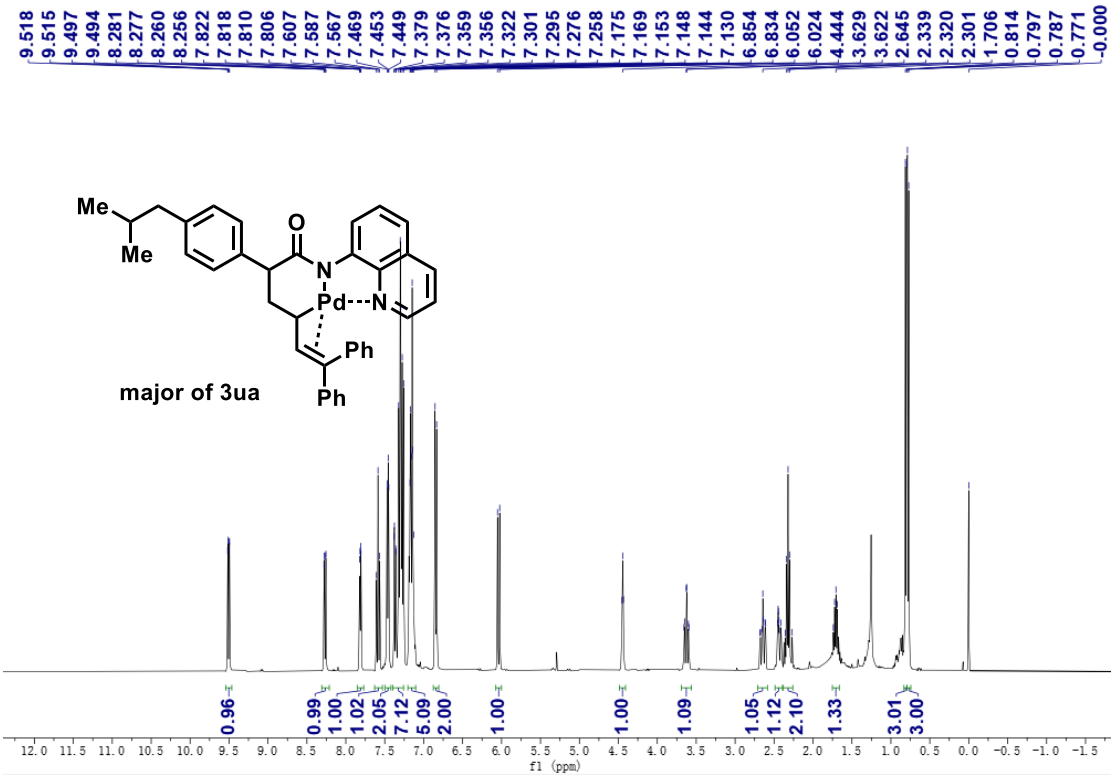
^{1}H NMR (400 MHz, $CDCl_3$) of **3ta-minor**



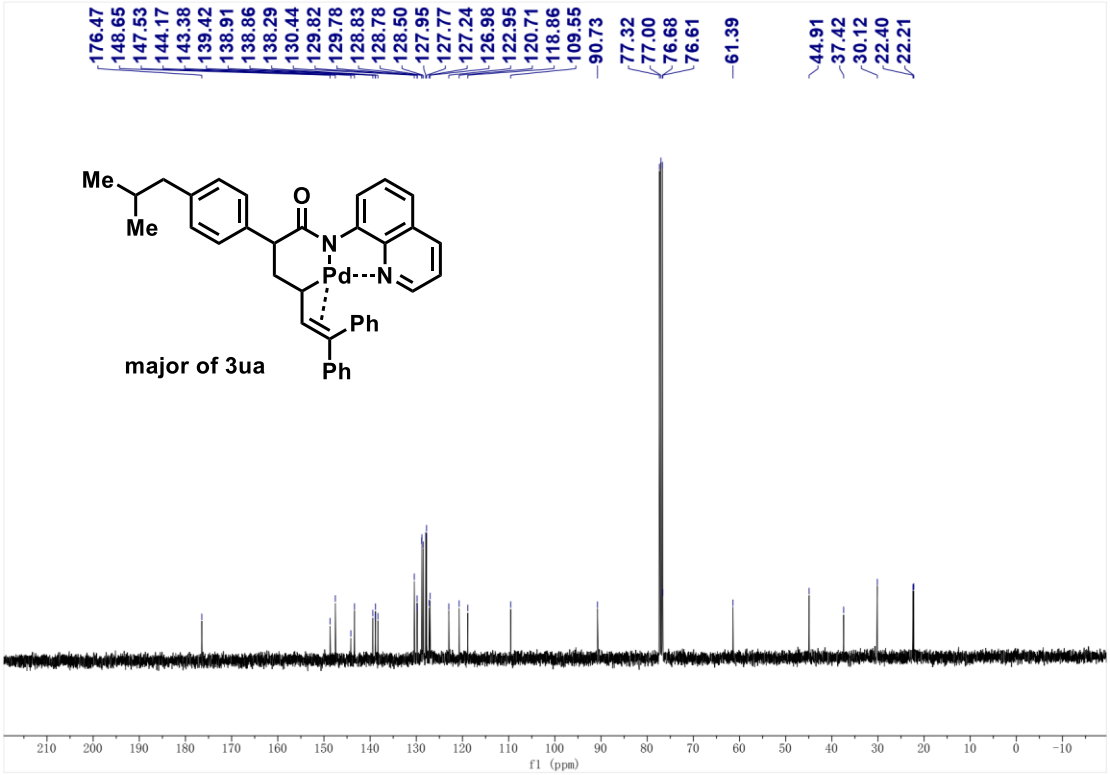
^{13}C NMR (100 MHz, $CDCl_3$) of **3ta-minor**



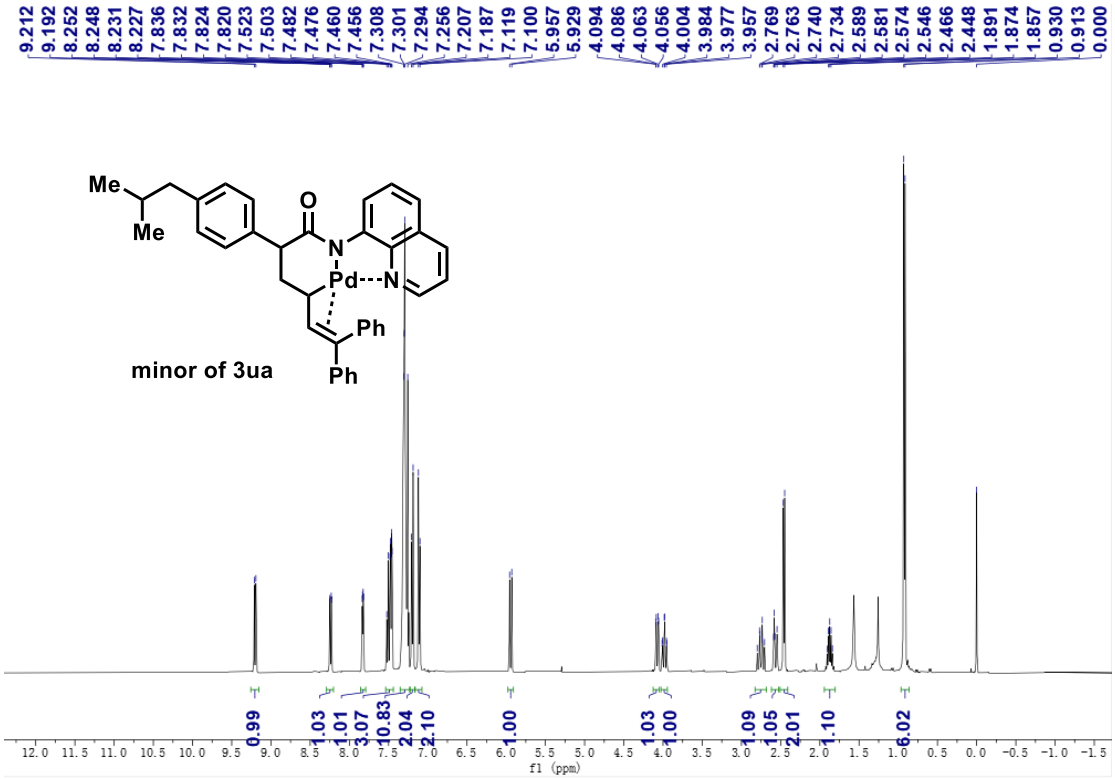
^{1}H NMR (400 MHz, $CDCl_3$) of **3ua-major**



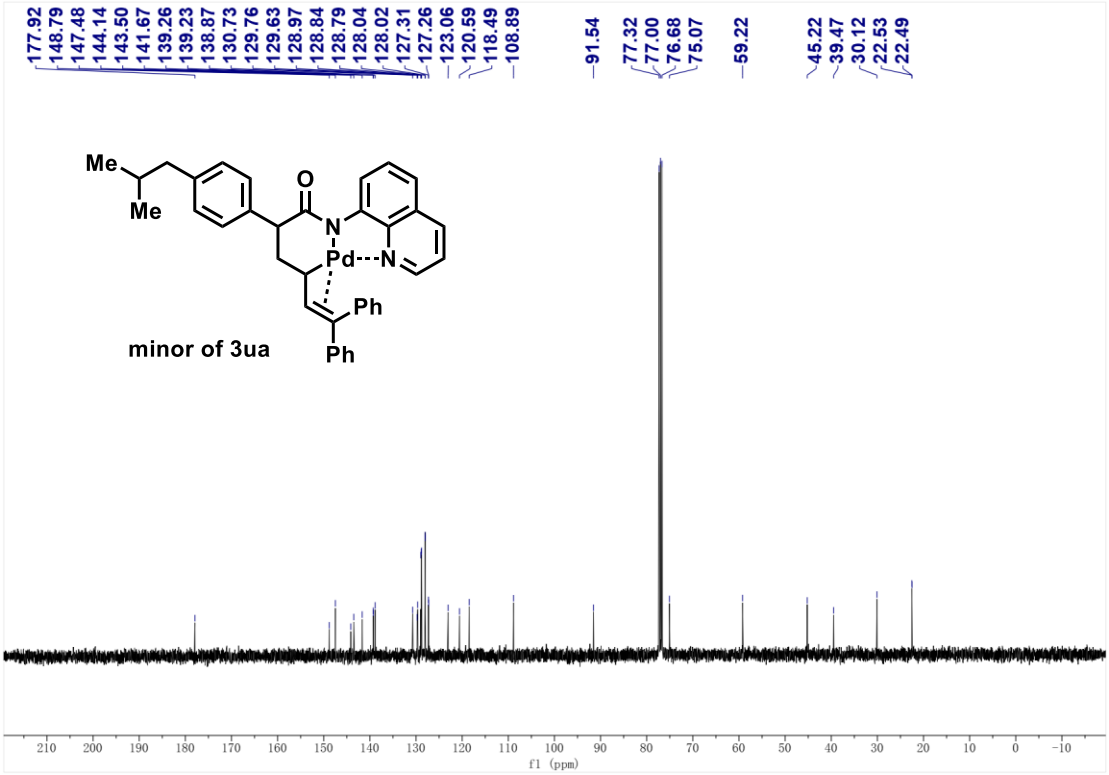
^{13}C NMR (100 MHz, $CDCl_3$) of **3ua-major**



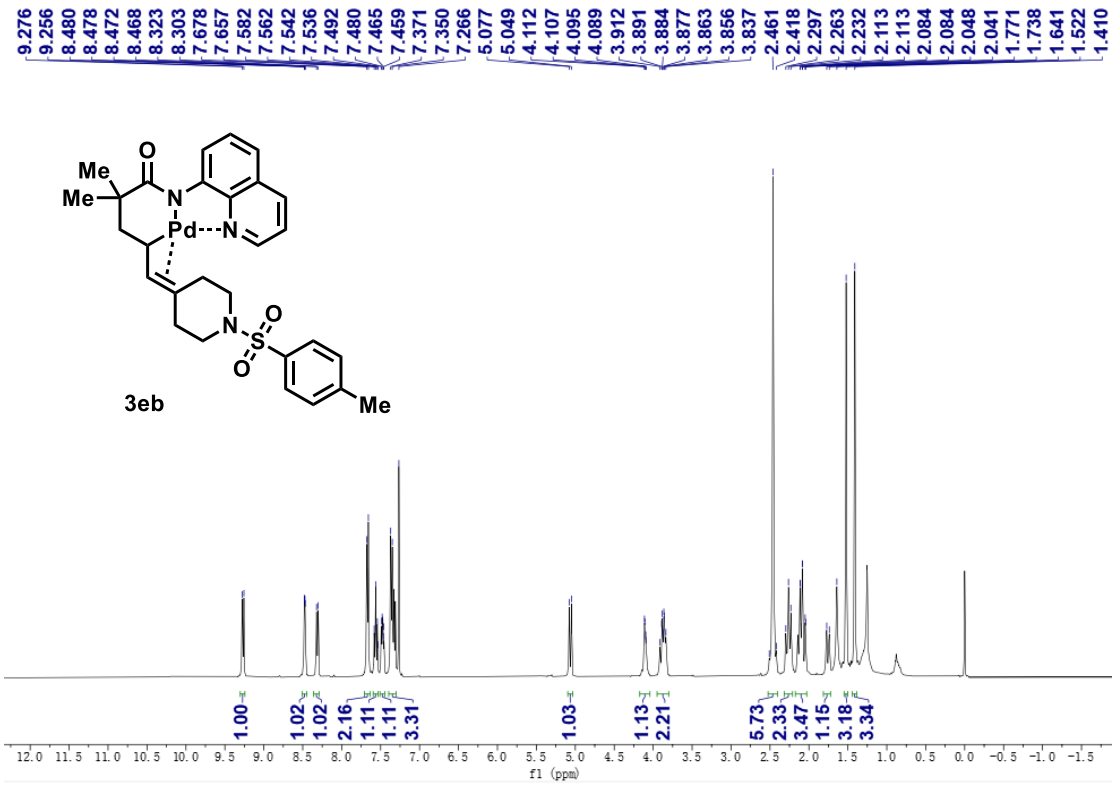
^{1}H NMR (400 MHz, $CDCl_3$) of **3ua-minor**



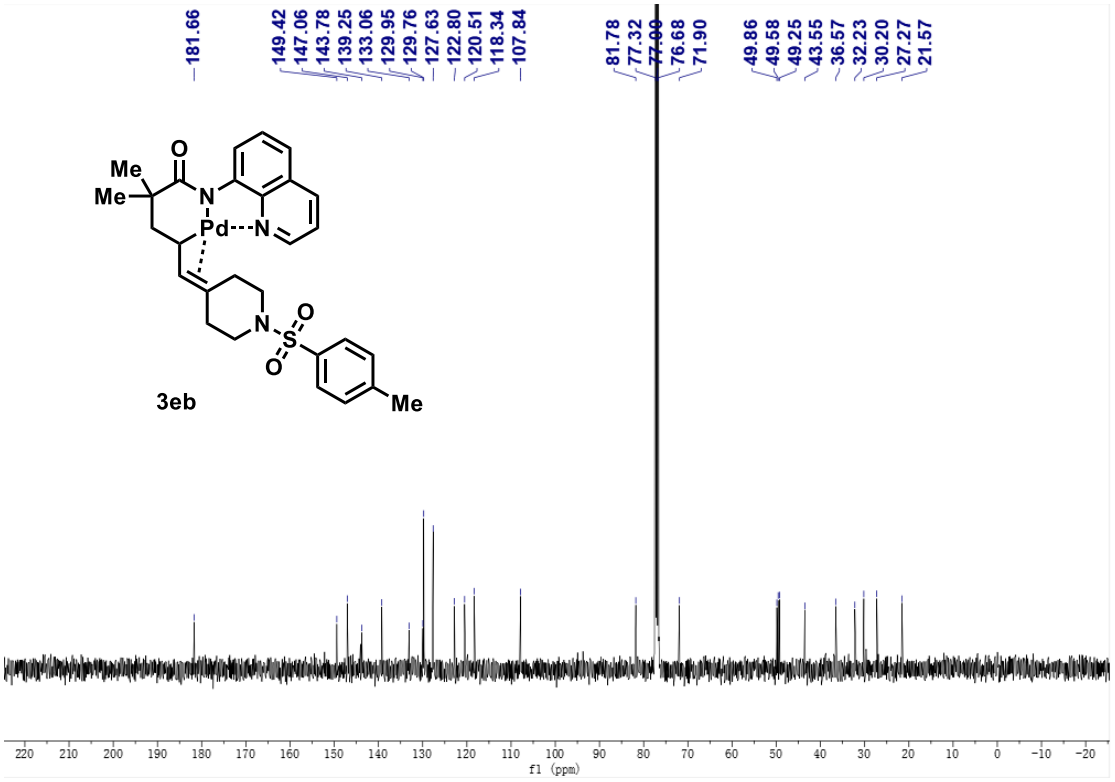
^{13}C NMR (100 MHz, $CDCl_3$) of **3ua-minor**



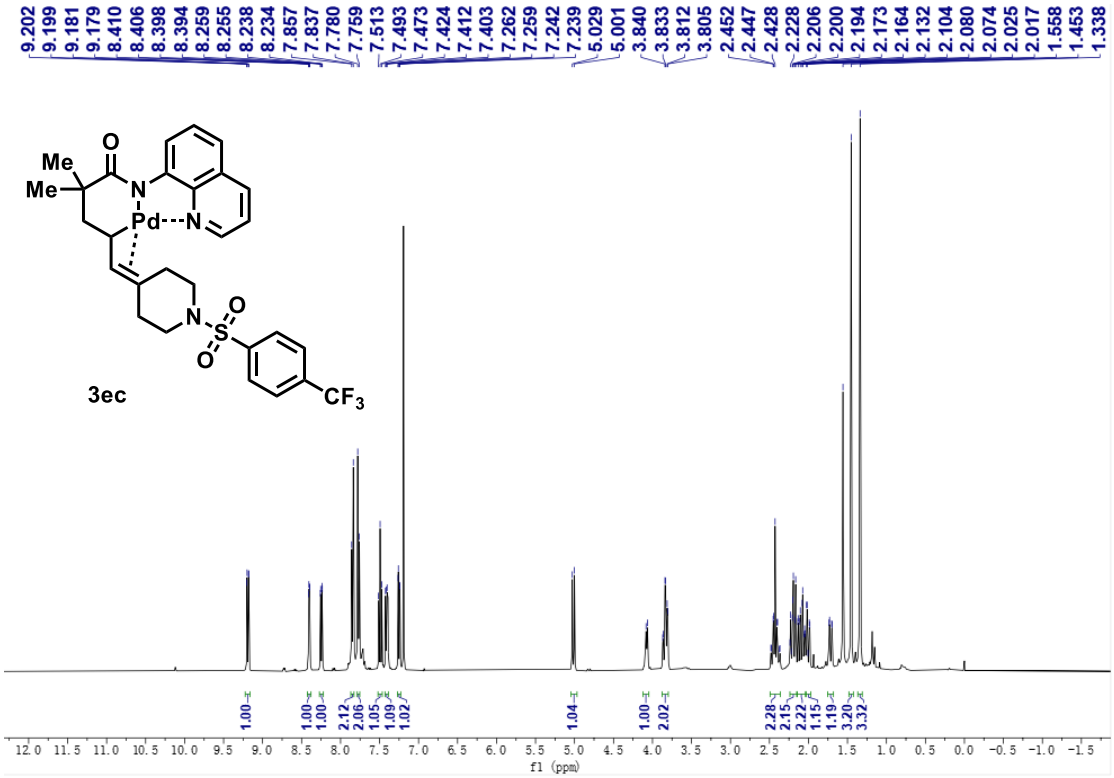
^{1}H NMR (400 MHz, $CDCl_3$) of **3eb**



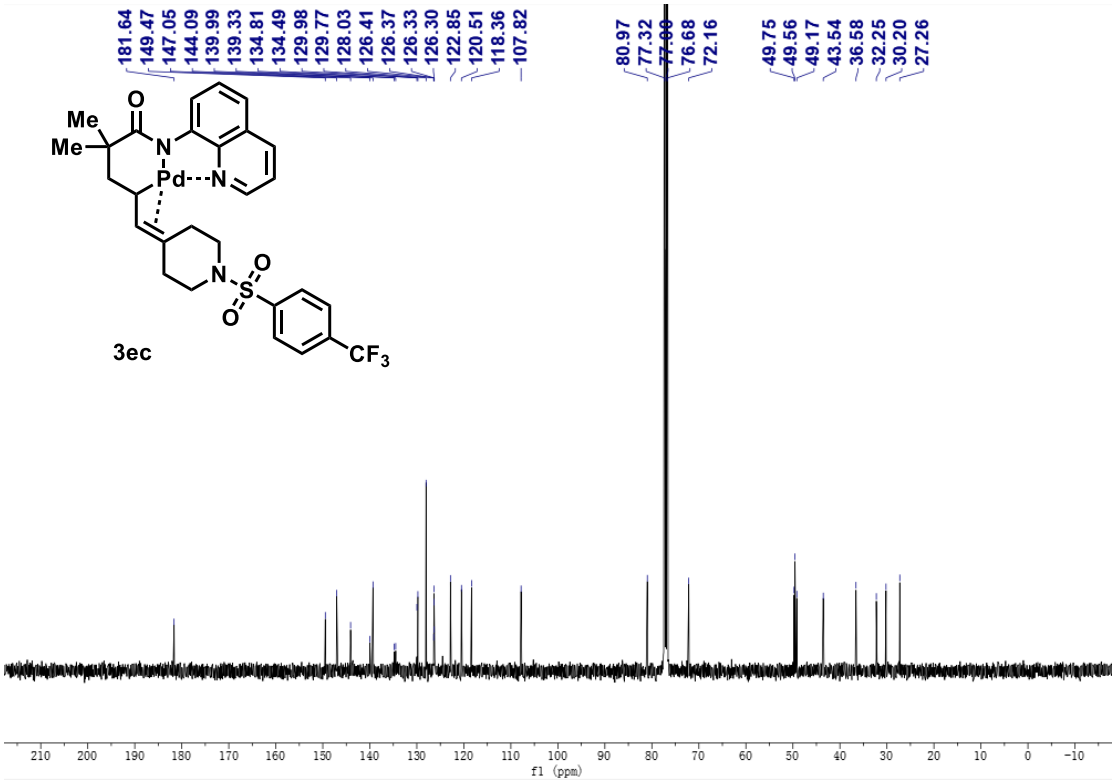
^{13}C NMR (100 MHz, $CDCl_3$) of **3eb**



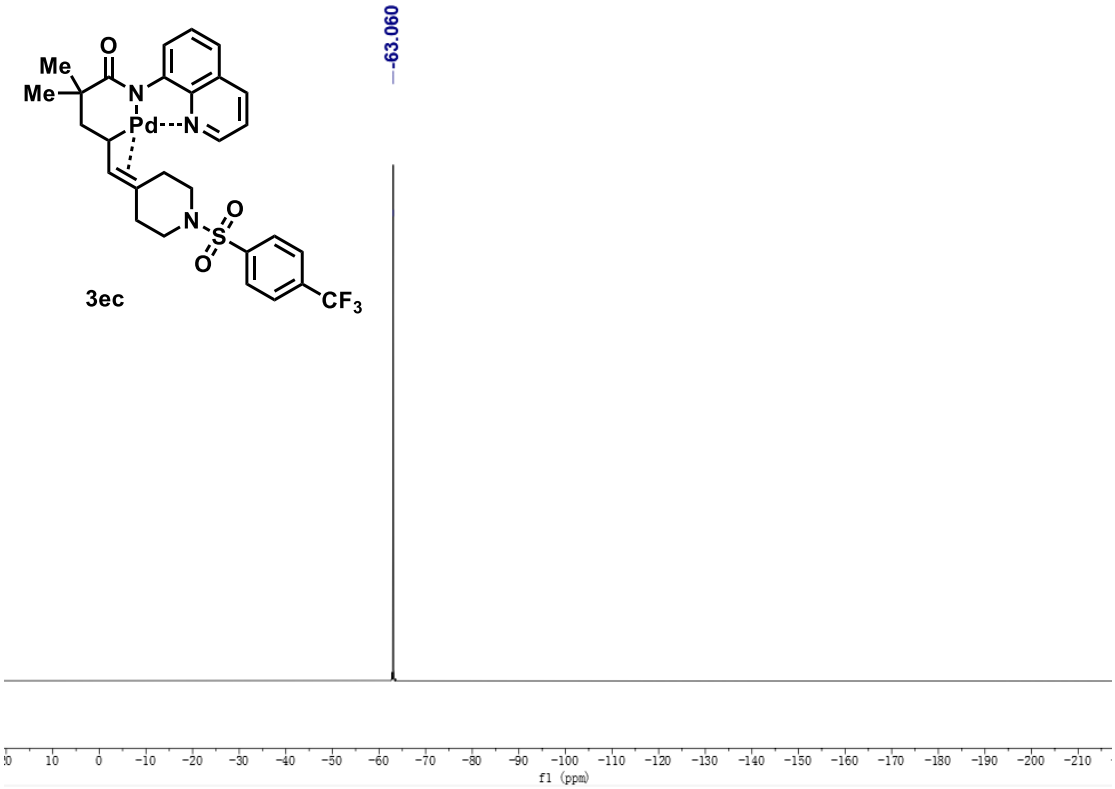
^{1}H NMR (400 MHz, $CDCl_3$) of **3ec**



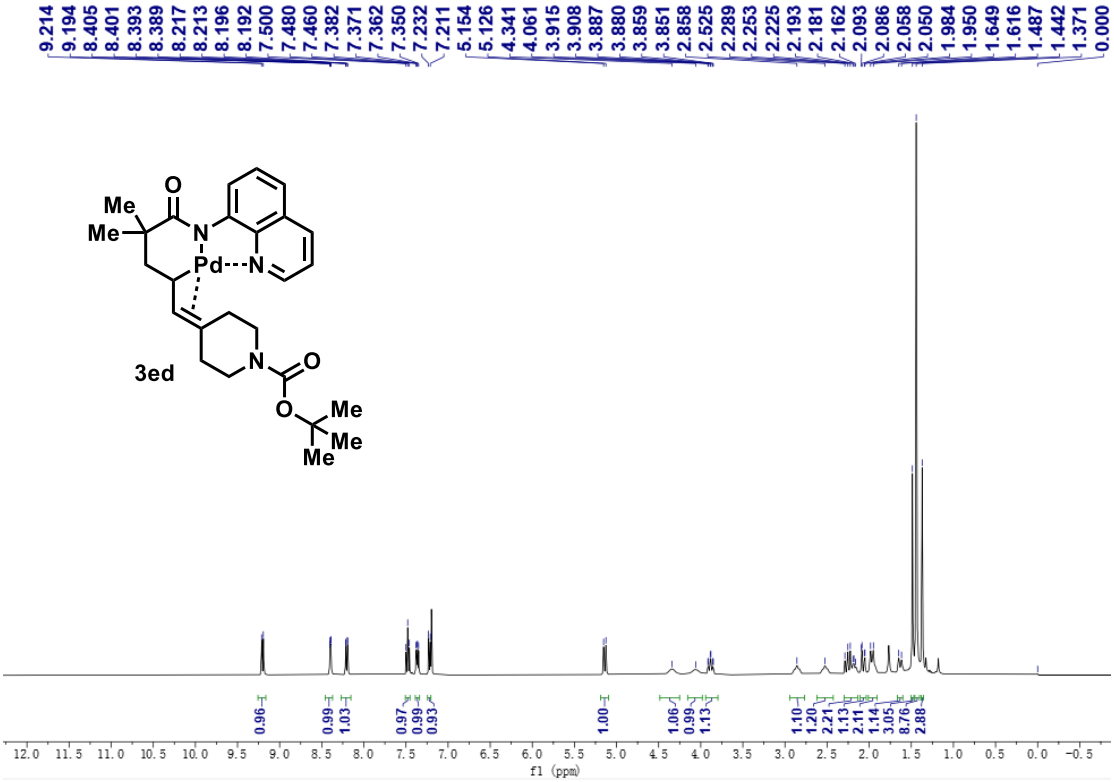
^{13}C NMR (100 MHz, $CDCl_3$) of **3ec**



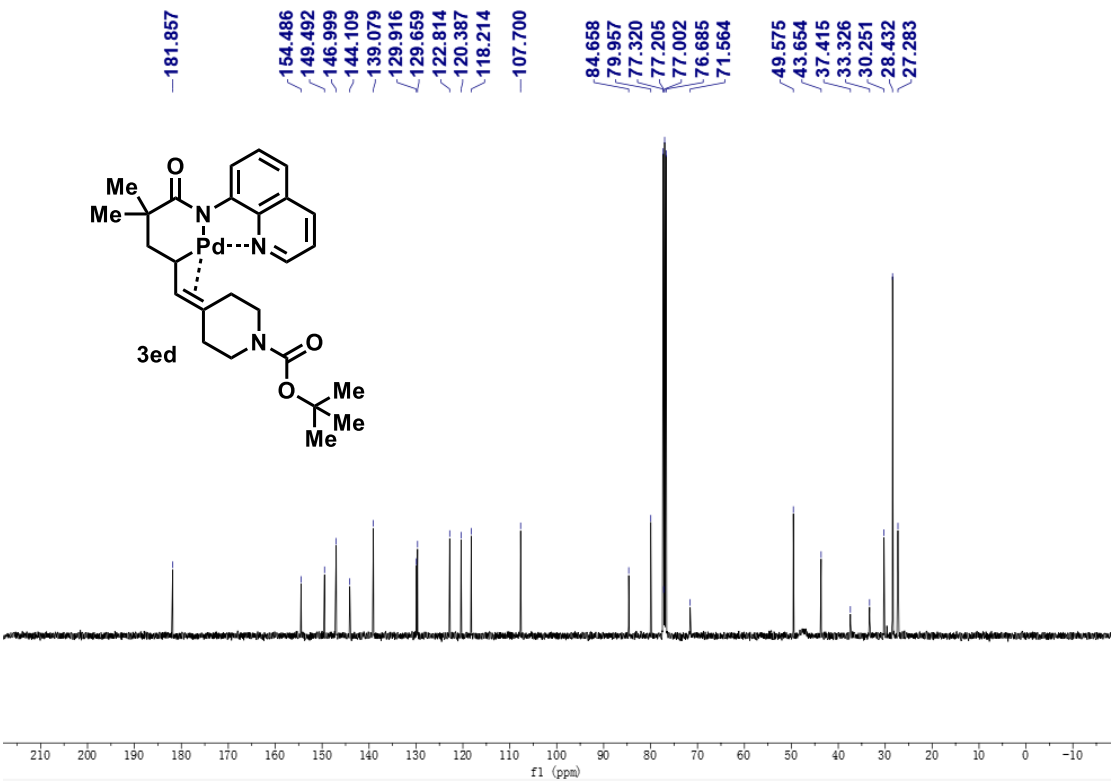
^{19}F NMR (376 MHz, $CDCl_3$) of **3ec**



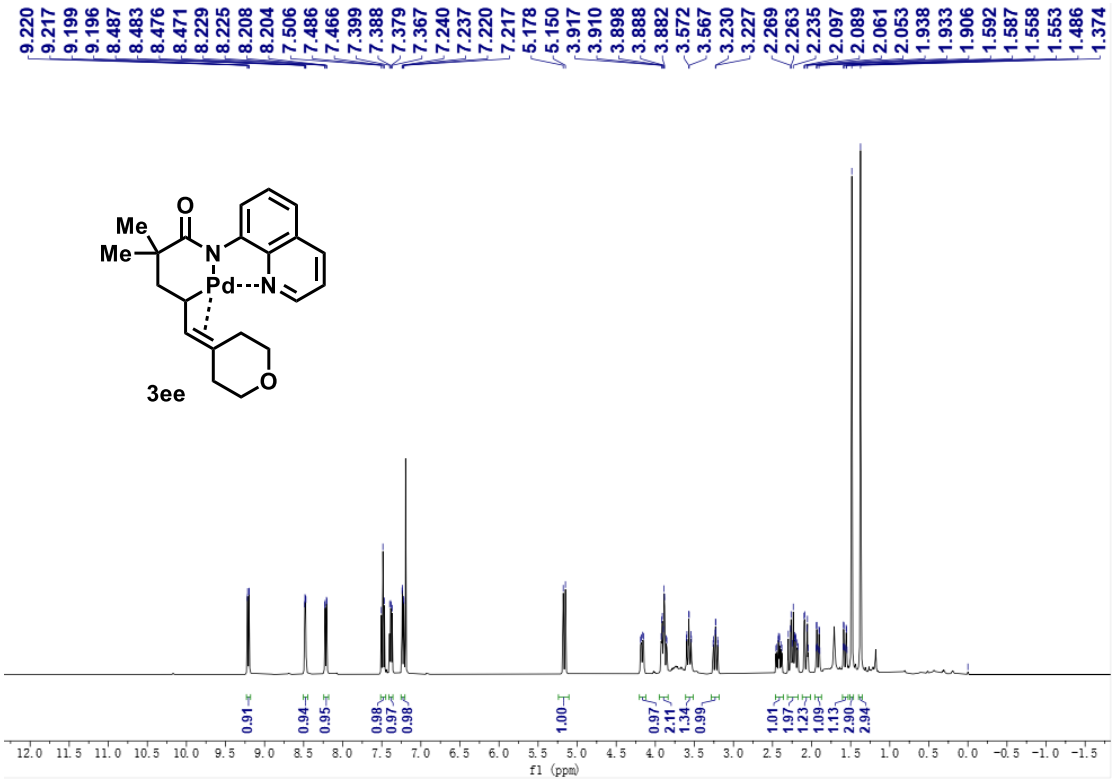
^{1}H NMR (400 MHz, $CDCl_3$) of **3ed**



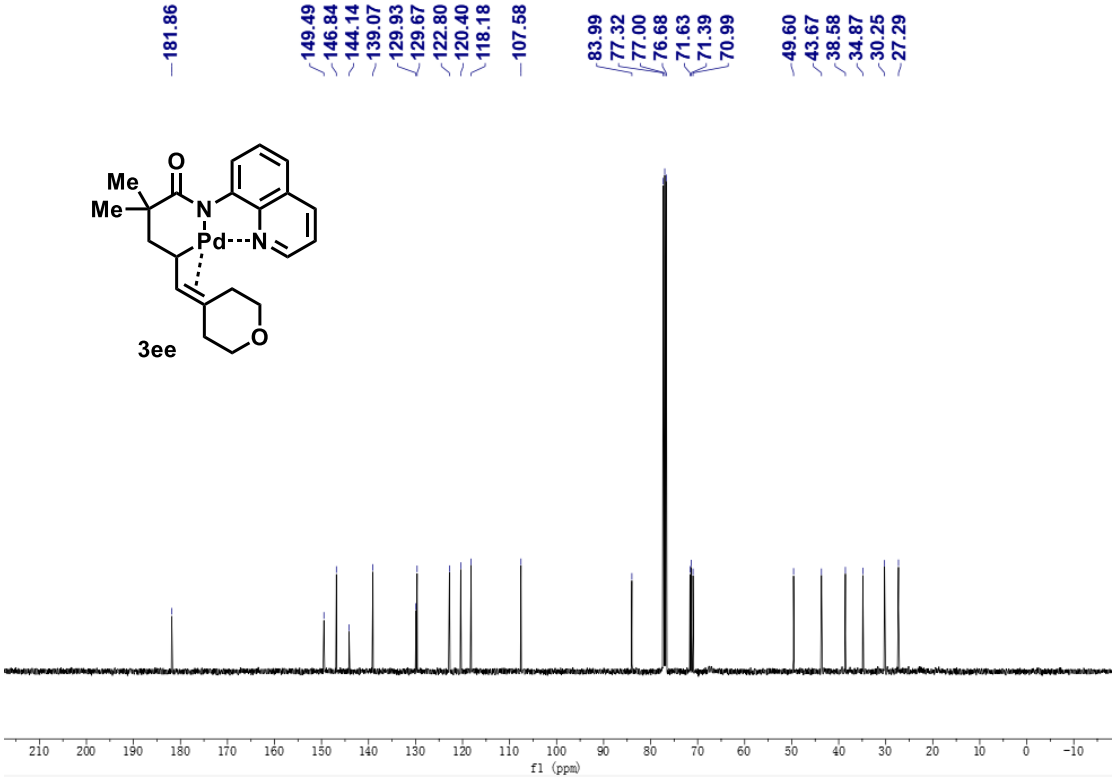
^{13}C NMR (100 MHz, $CDCl_3$) of **3ed**



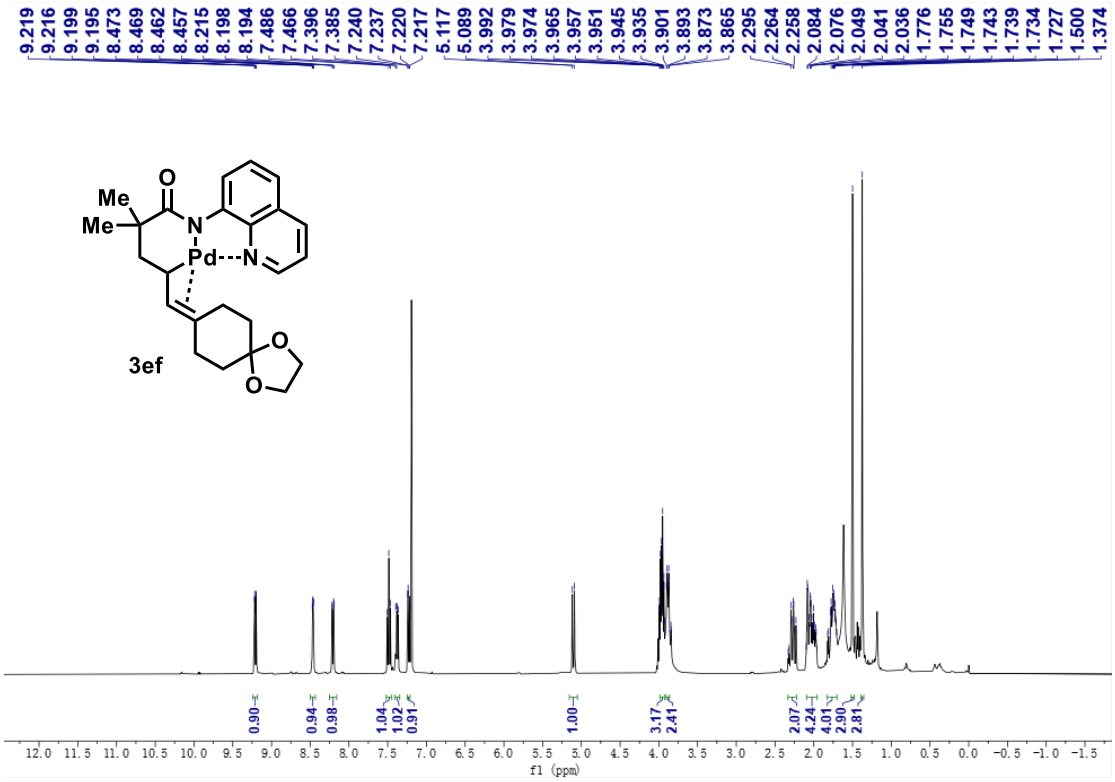
^{1}H NMR (400 MHz, $CDCl_3$) of **3ee**



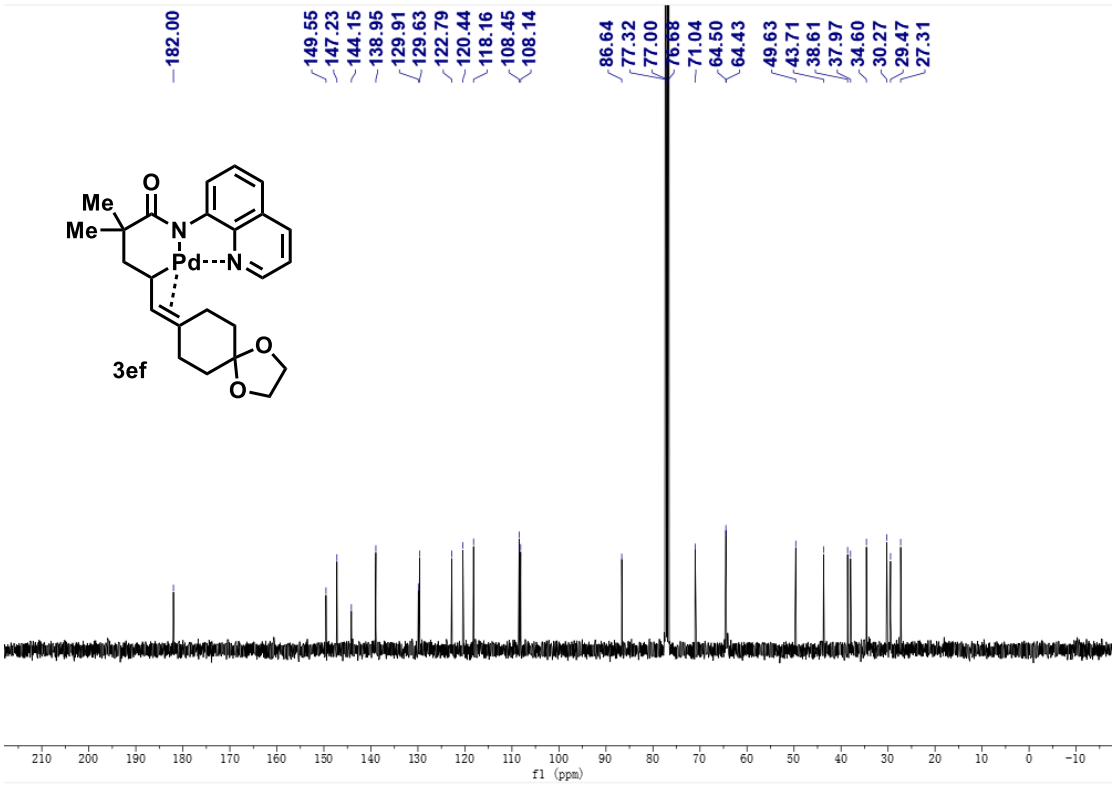
^{13}C NMR (100 MHz, $CDCl_3$) of **3ee**



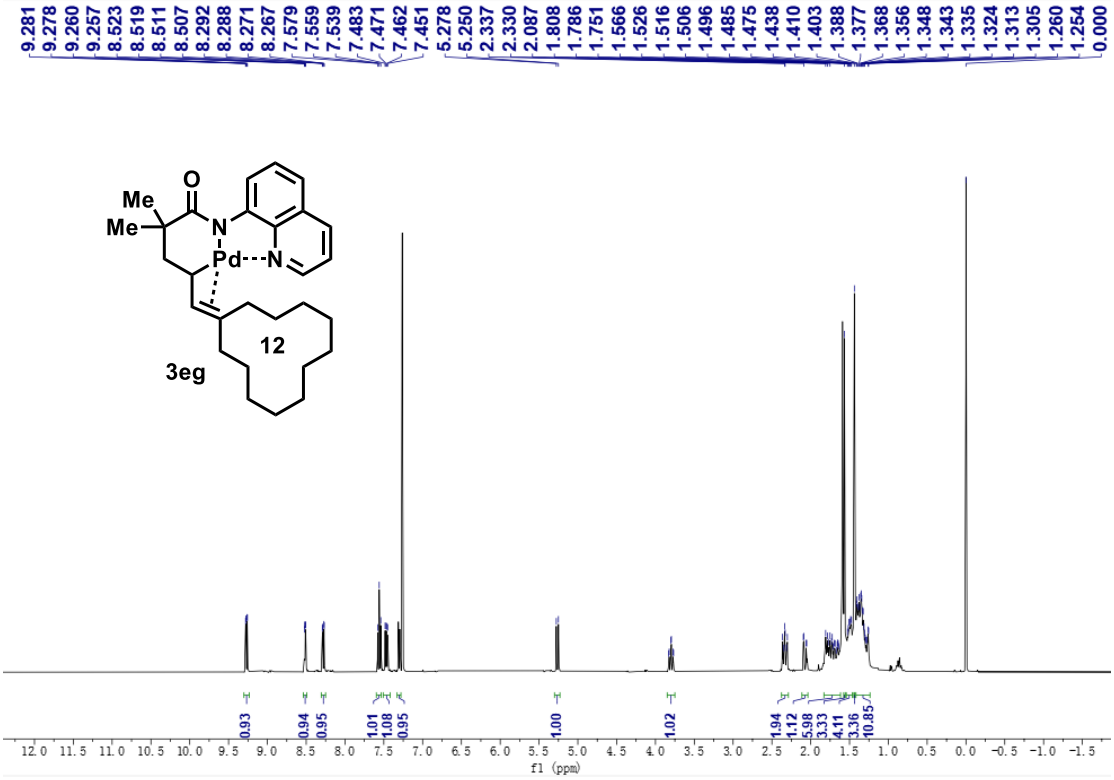
^{1}H NMR (400 MHz, $CDCl_3$) of **3ef**



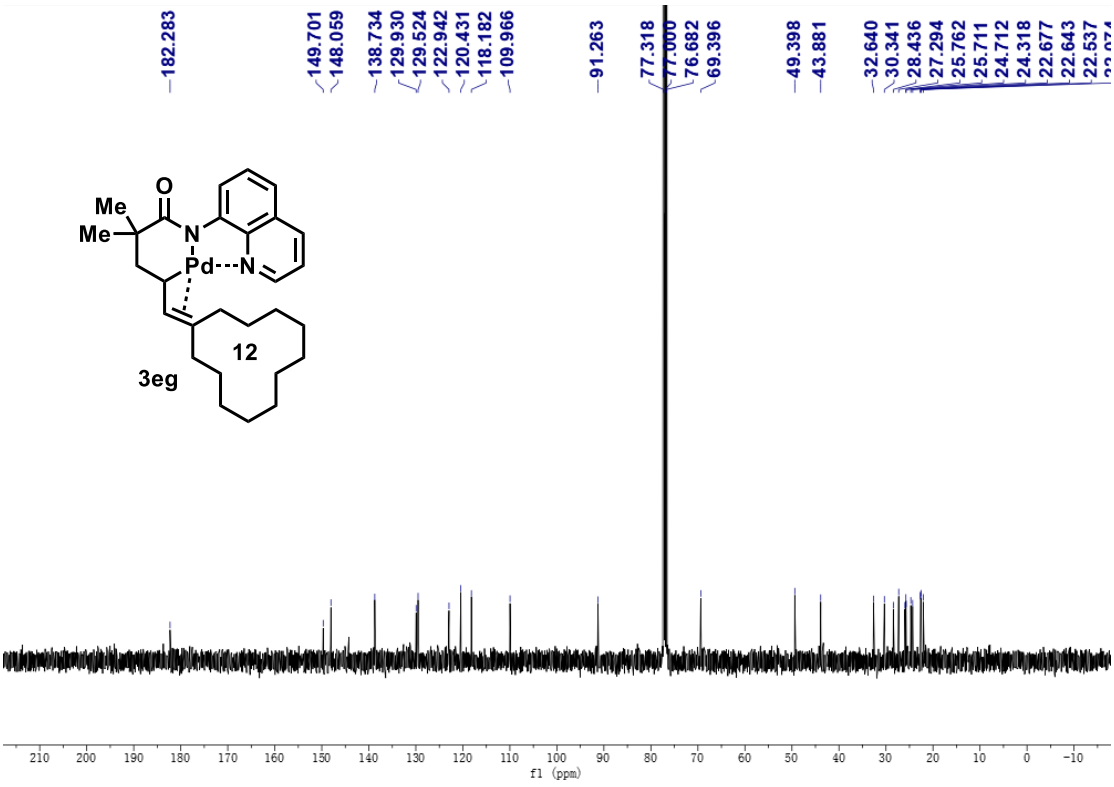
^{13}C NMR (100 MHz, $CDCl_3$) of **3ef**



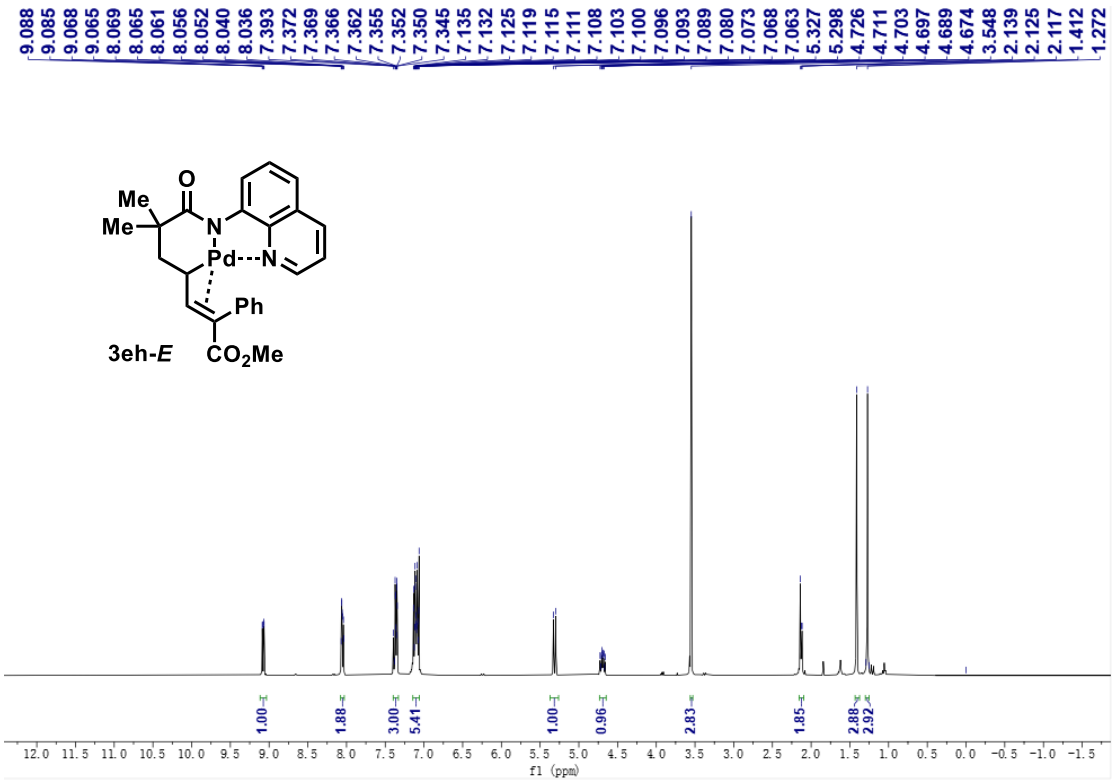
^{1}H NMR (400 MHz, $CDCl_3$) of **3eg**



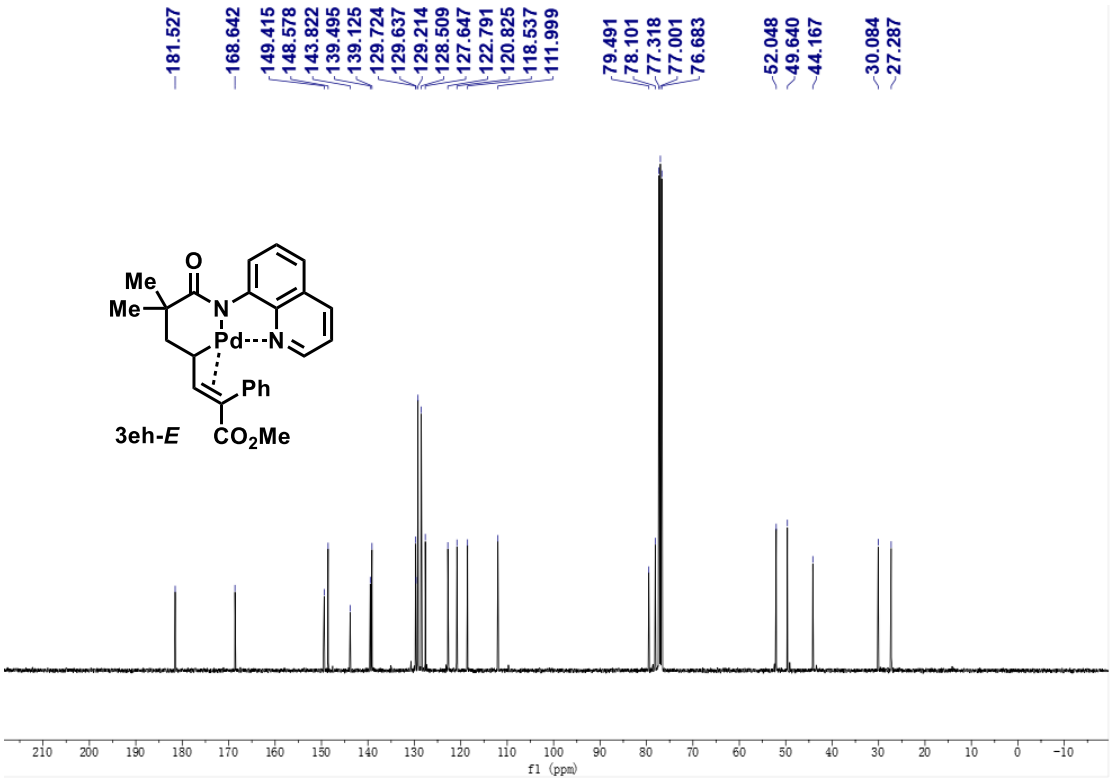
^{13}C NMR (100 MHz, $CDCl_3$) of **3eg**



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

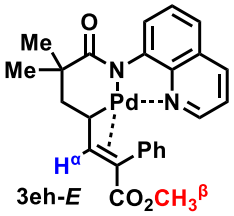


^{13}C NMR (100 MHz, $CDCl_3$) of **3eh-*E***

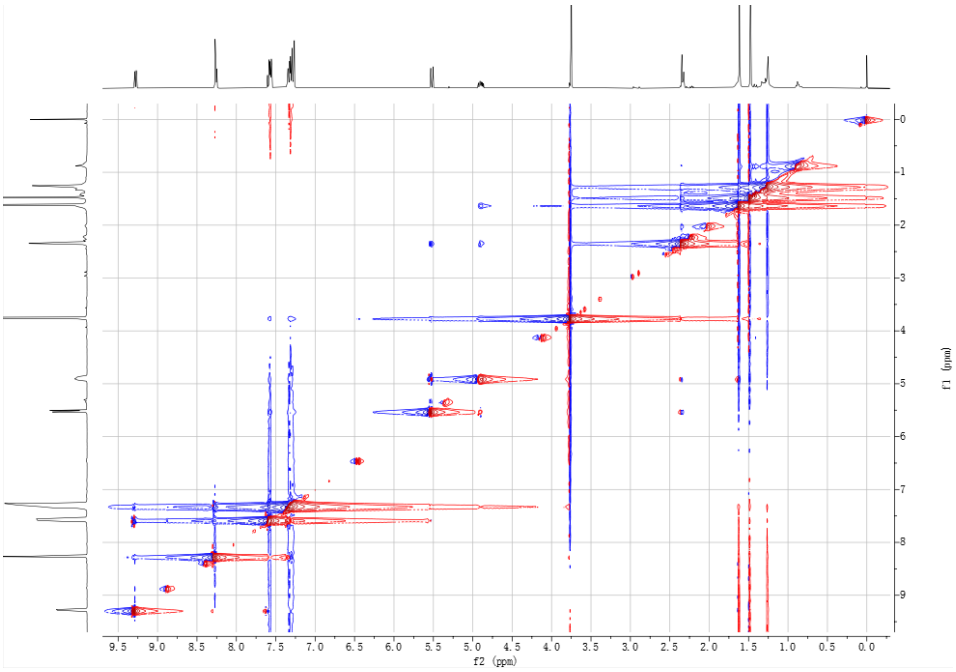


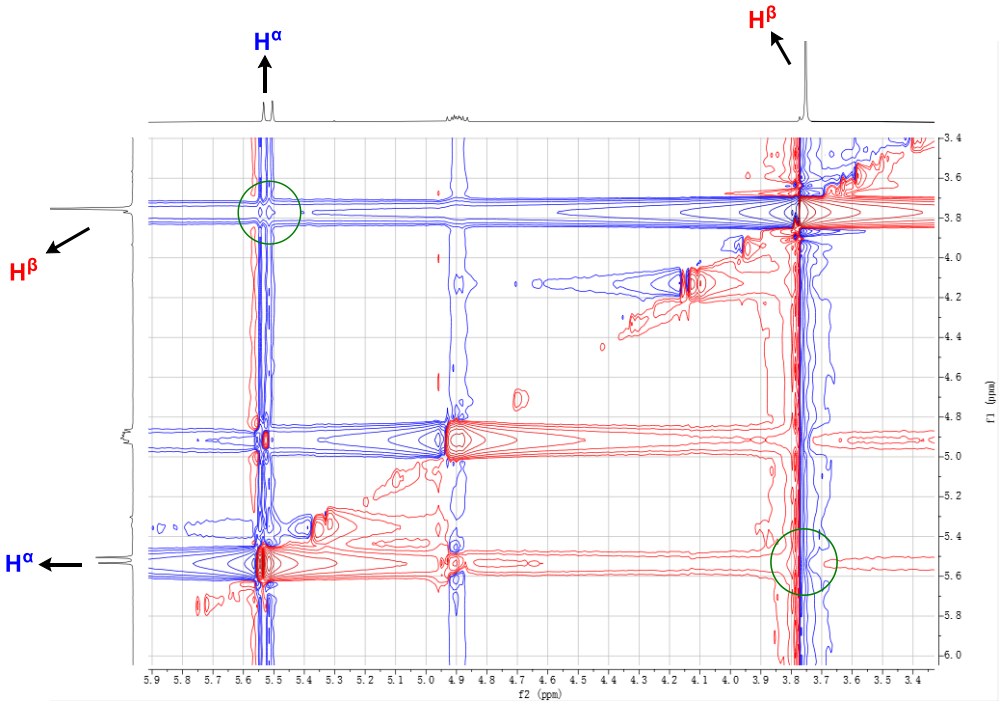
No NOE was observed between H^{α} and H^{β}

.

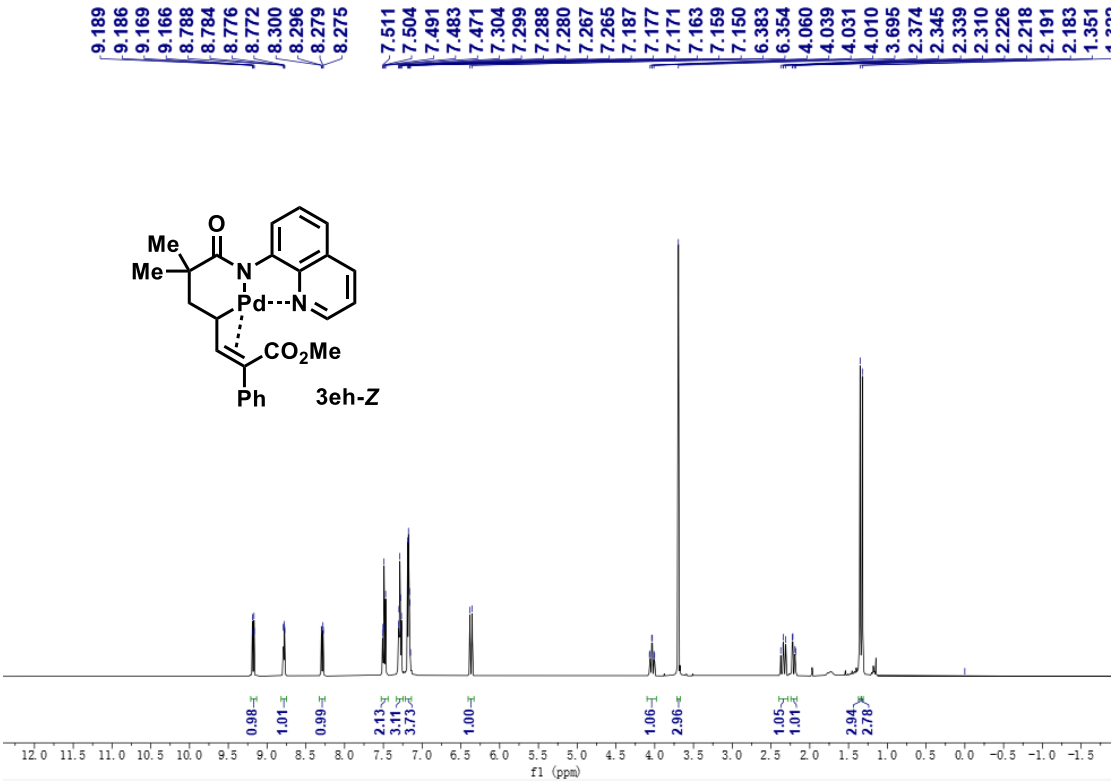


NOESY:

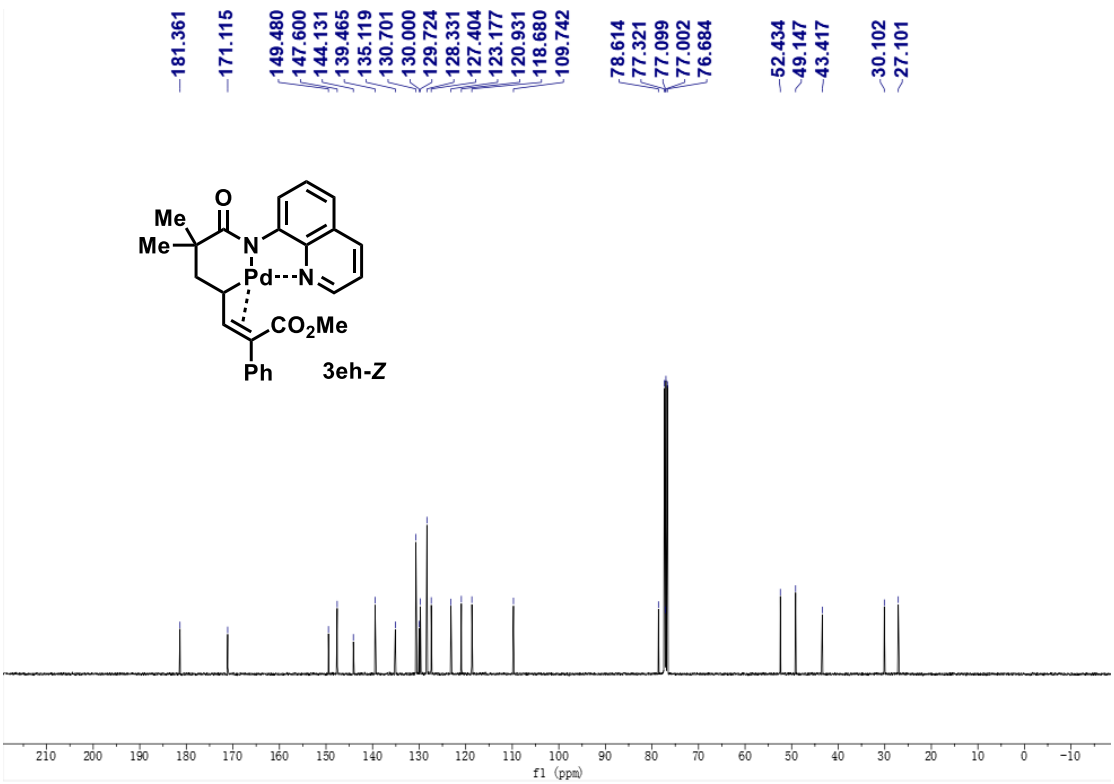




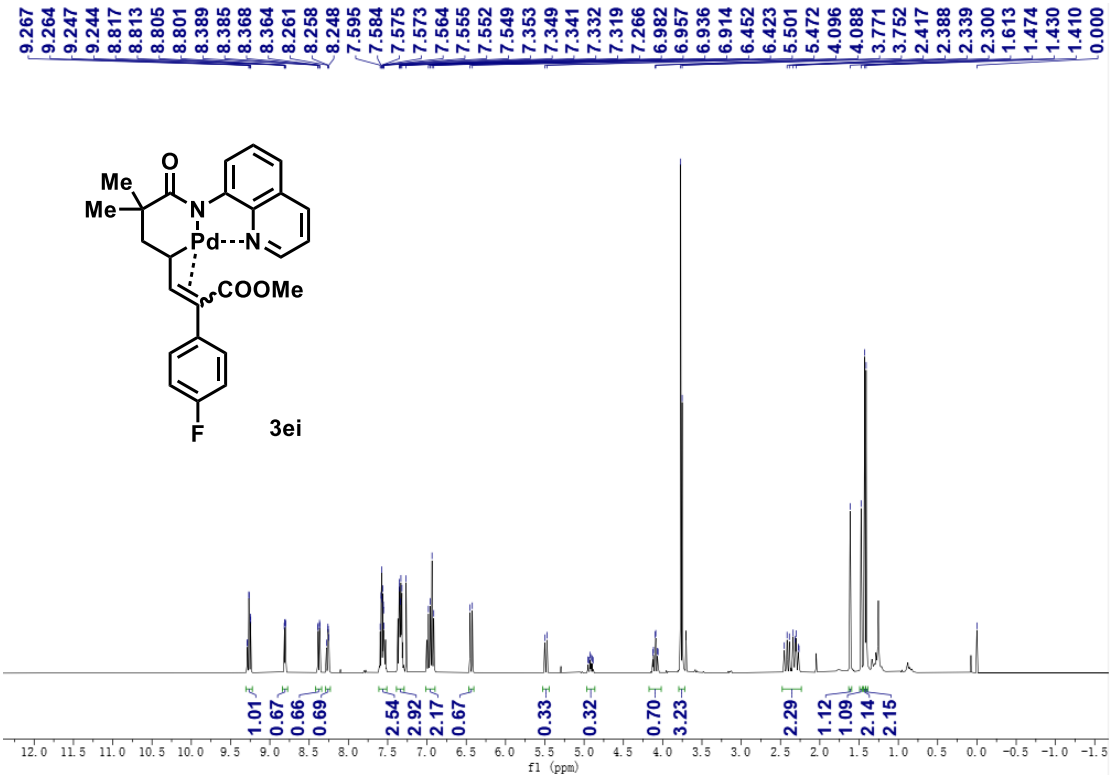
^{1}H NMR (400 MHz, $CDCl_3$) of **3eh-*Z***



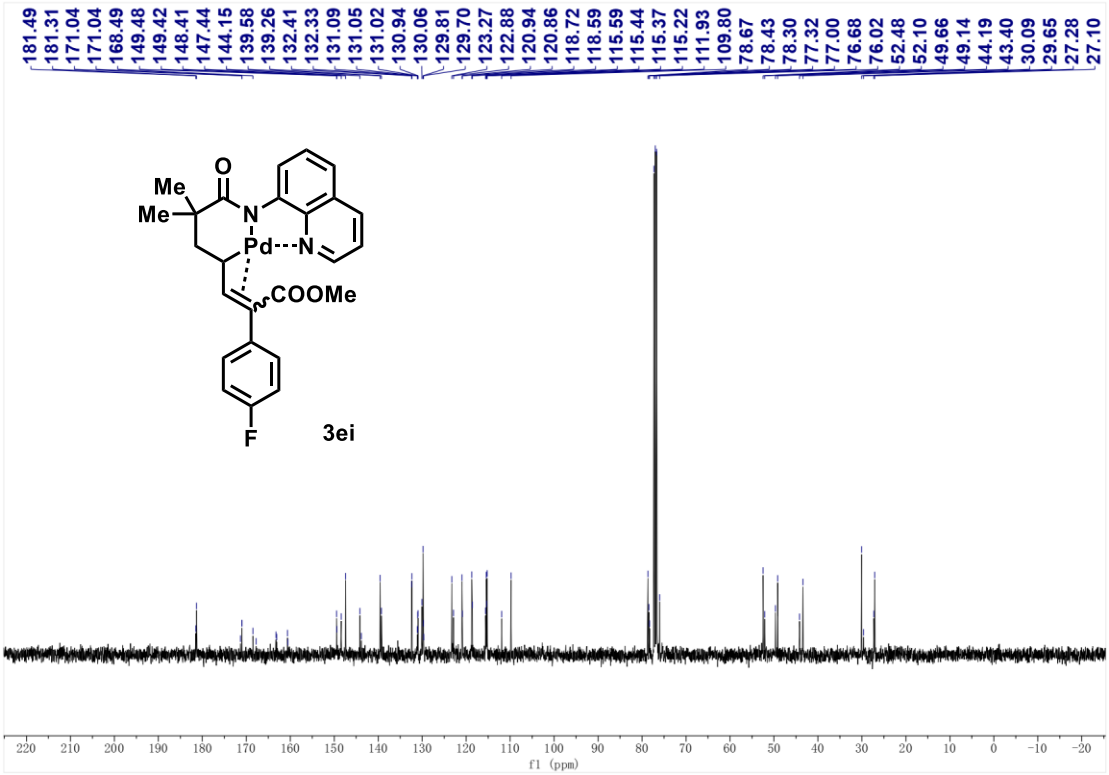
^{13}C NMR (100 MHz, $CDCl_3$) of **3eh-*Z***



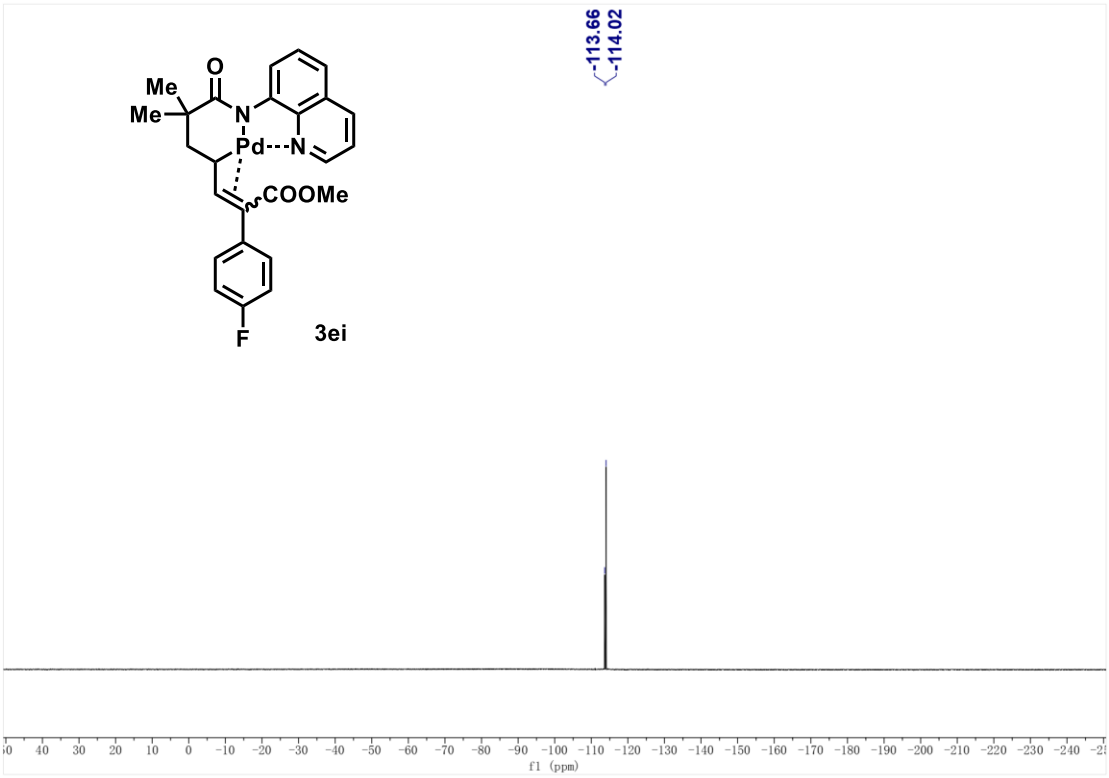
^{1}H NMR (400 MHz, $CDCl_3$) of **3ei**



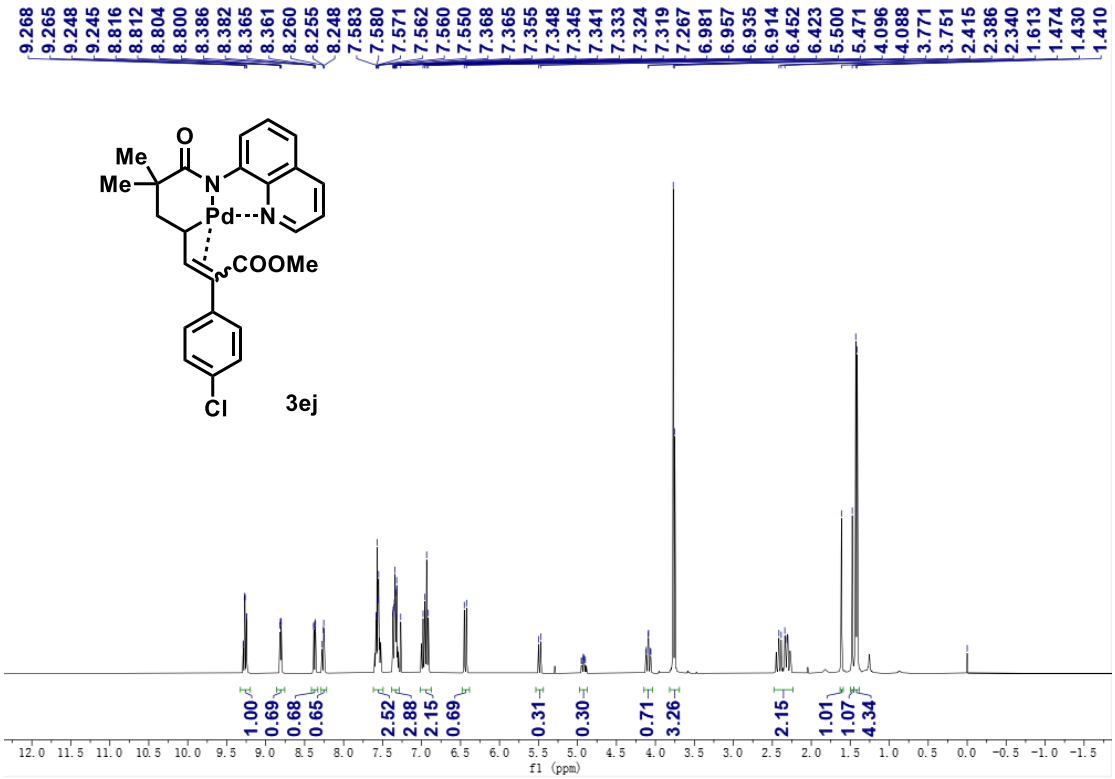
^{13}C NMR (100 MHz, $CDCl_3$) of **3ei**



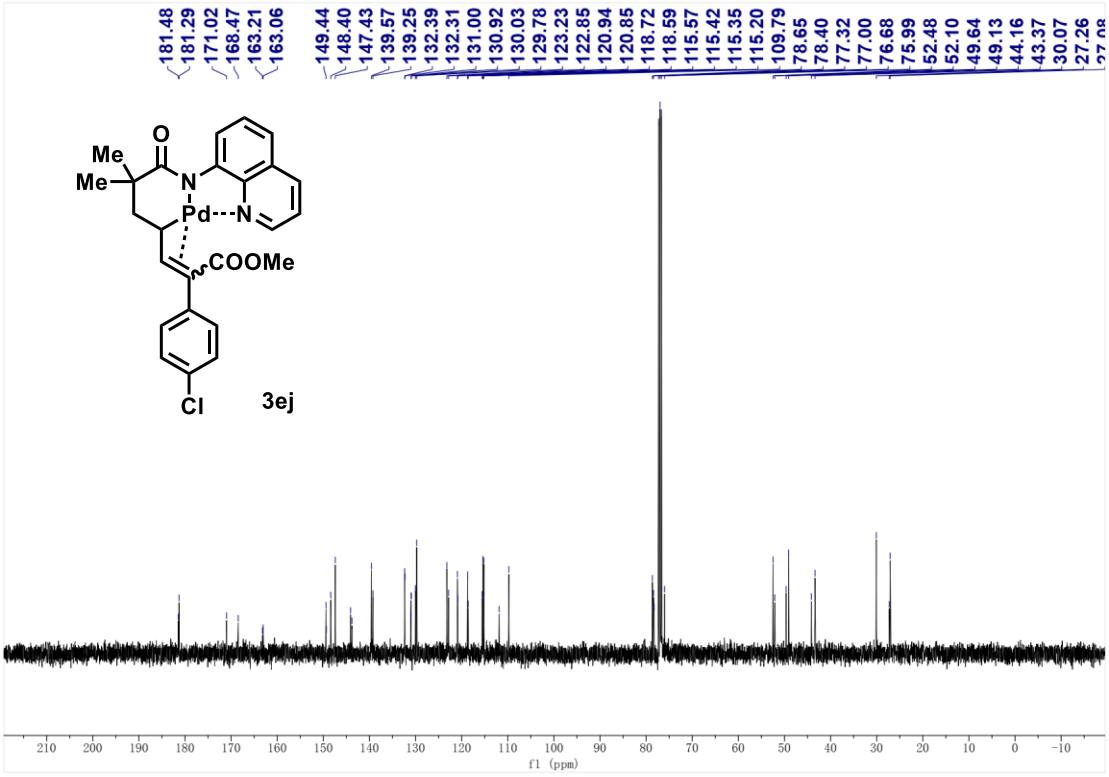
^{19}F NMR (376 MHz, $CDCl_3$) of **3ei**



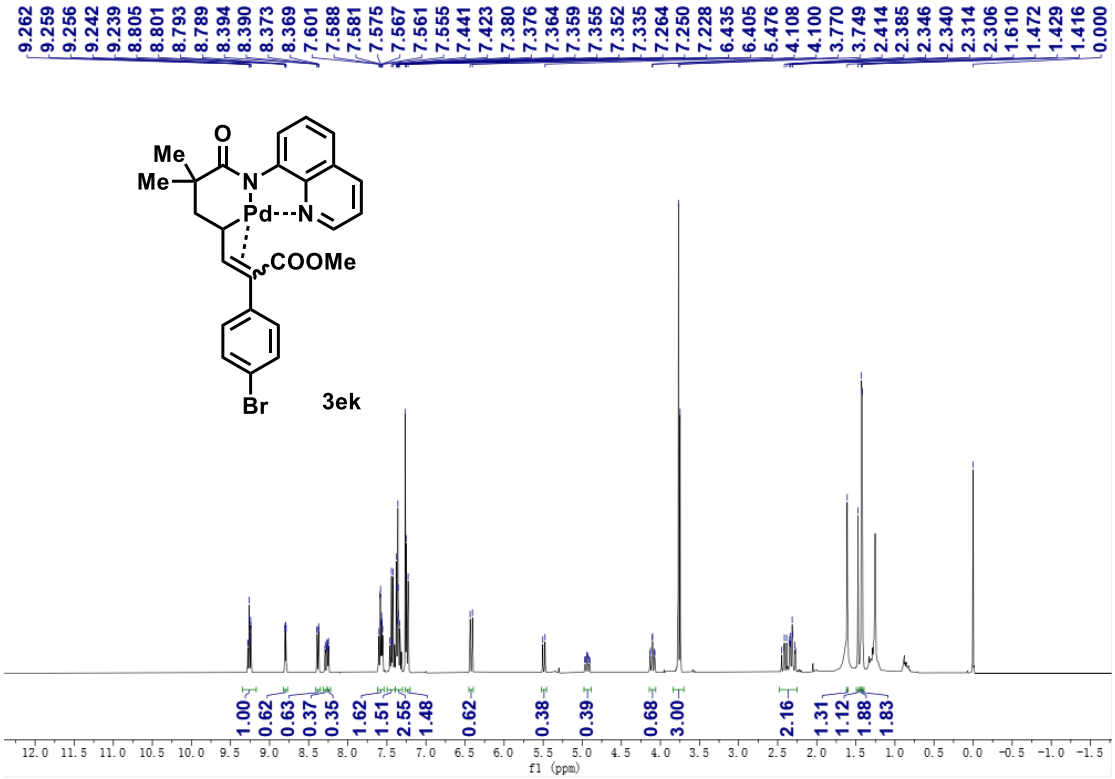
^{1}H NMR (400 MHz, $CDCl_3$) of **3ej**



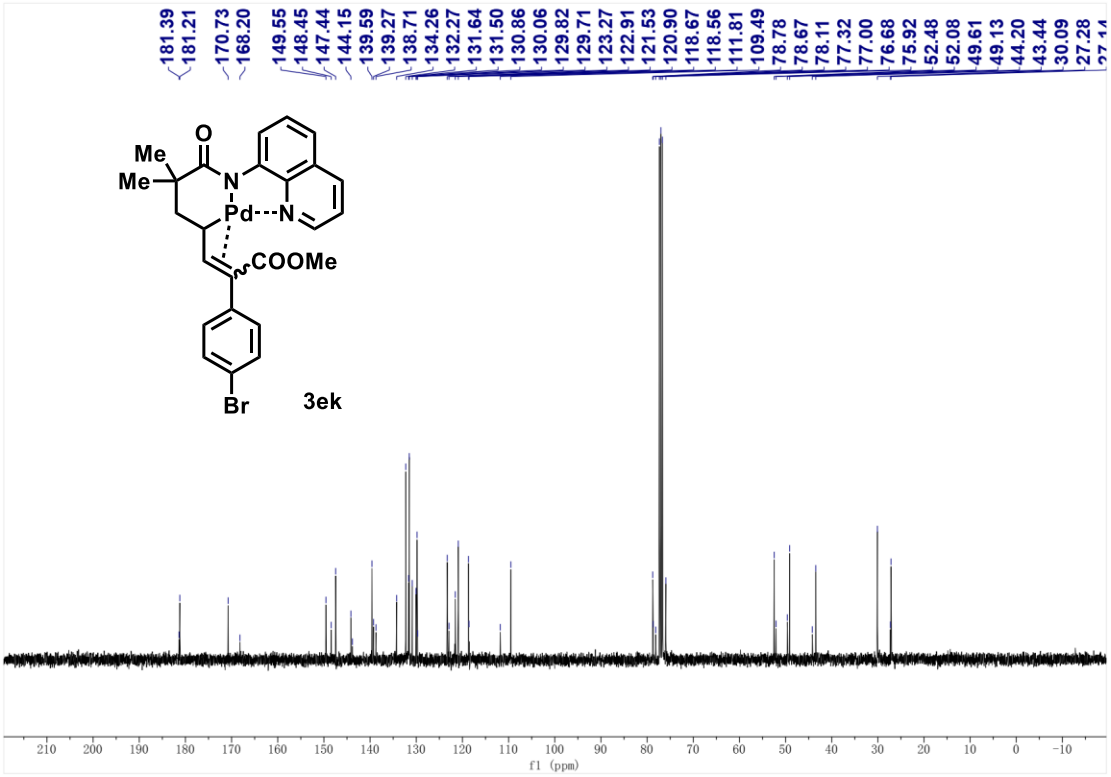
^{13}C NMR (100 MHz, $CDCl_3$) of **3ej**



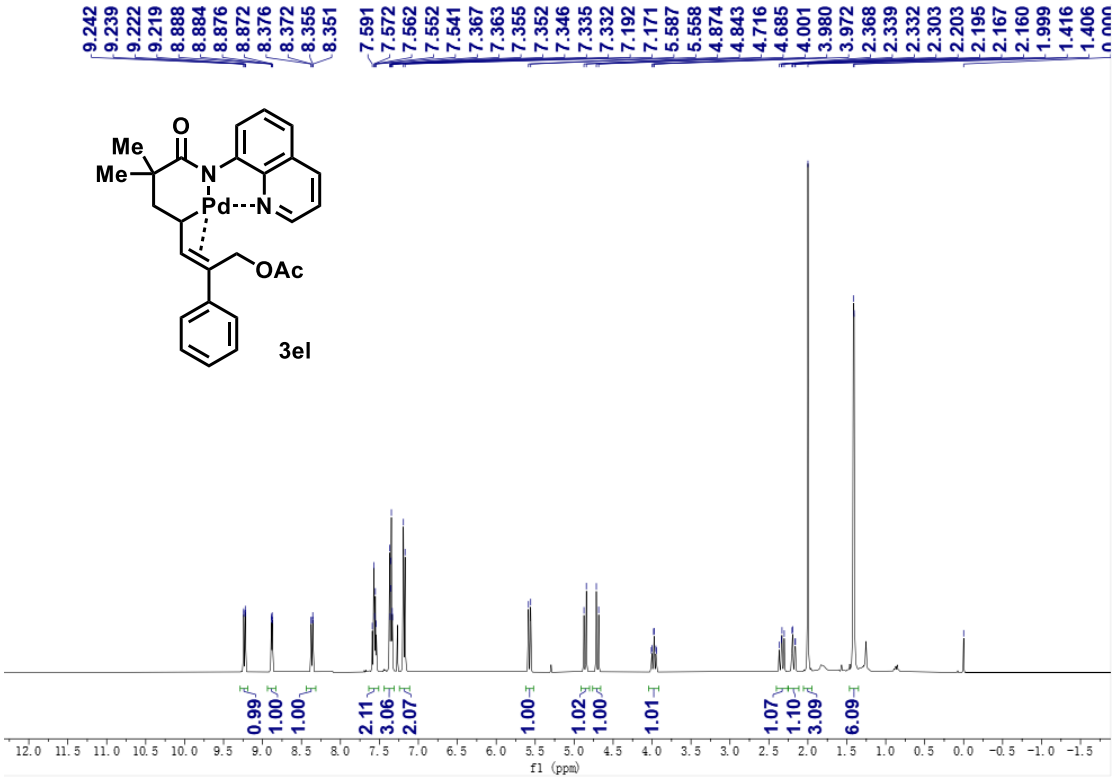
^{1}H NMR (400 MHz, $CDCl_3$) of **3ek**



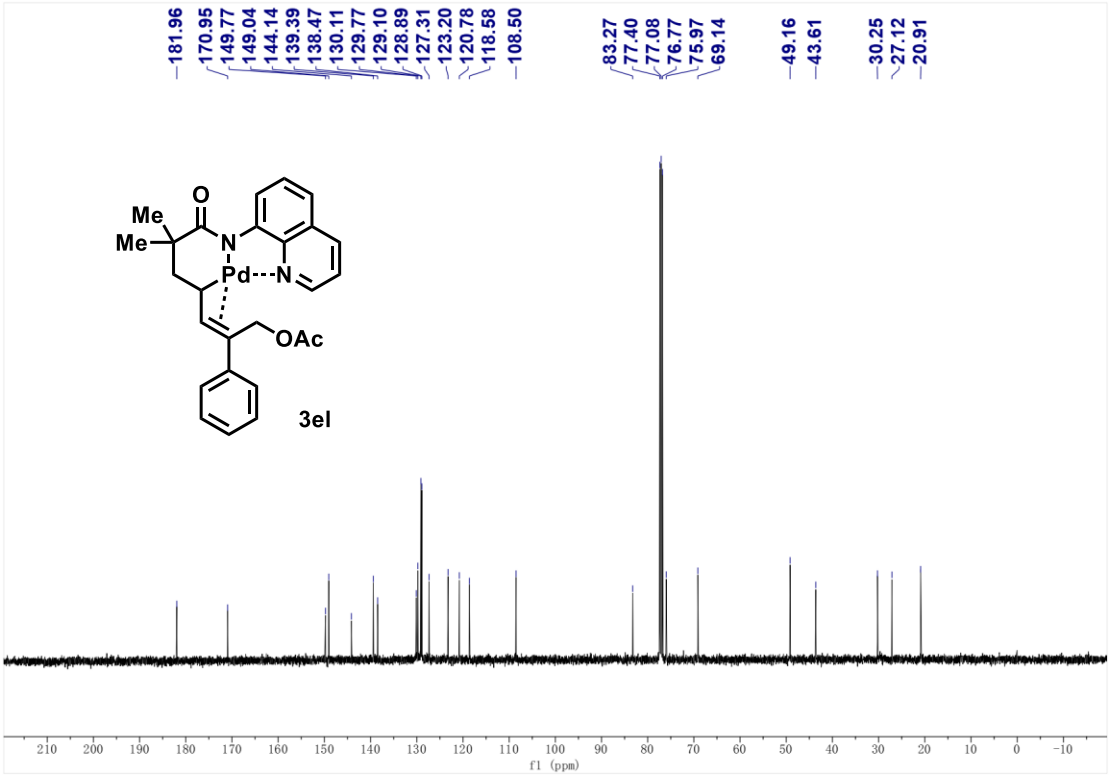
^{13}C NMR (100 MHz, $CDCl_3$) of **3ek**



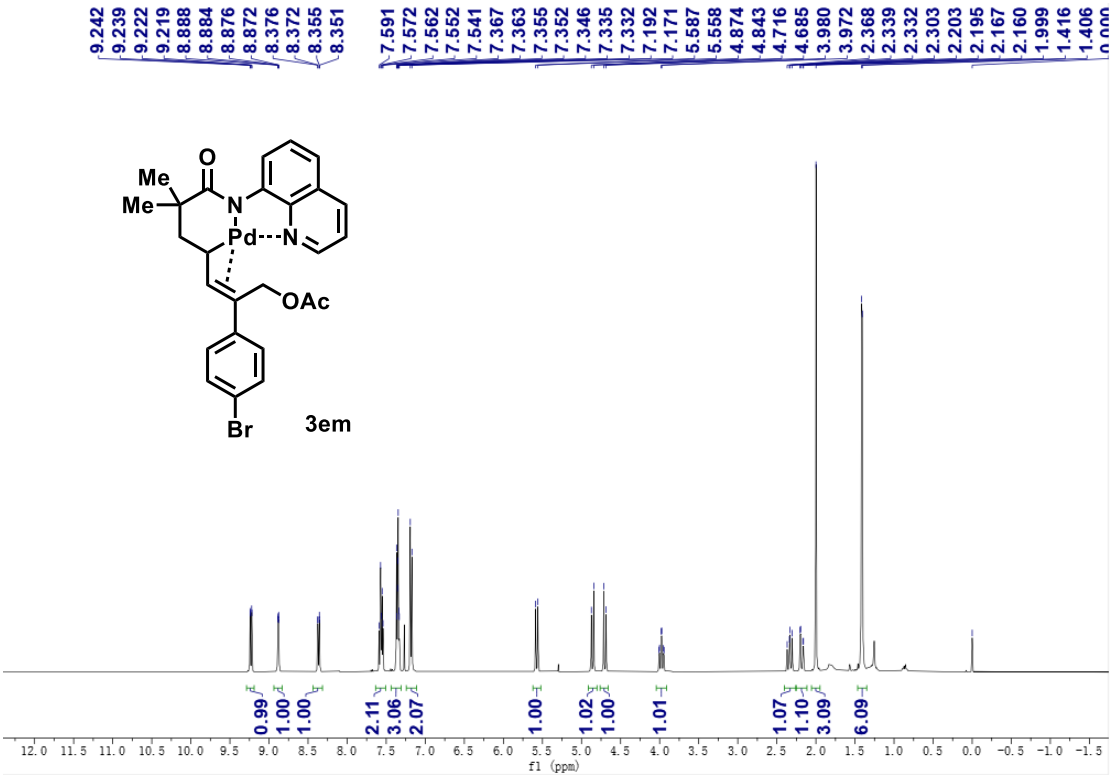
^{1}H NMR (400 MHz, $CDCl_3$) of **3el**



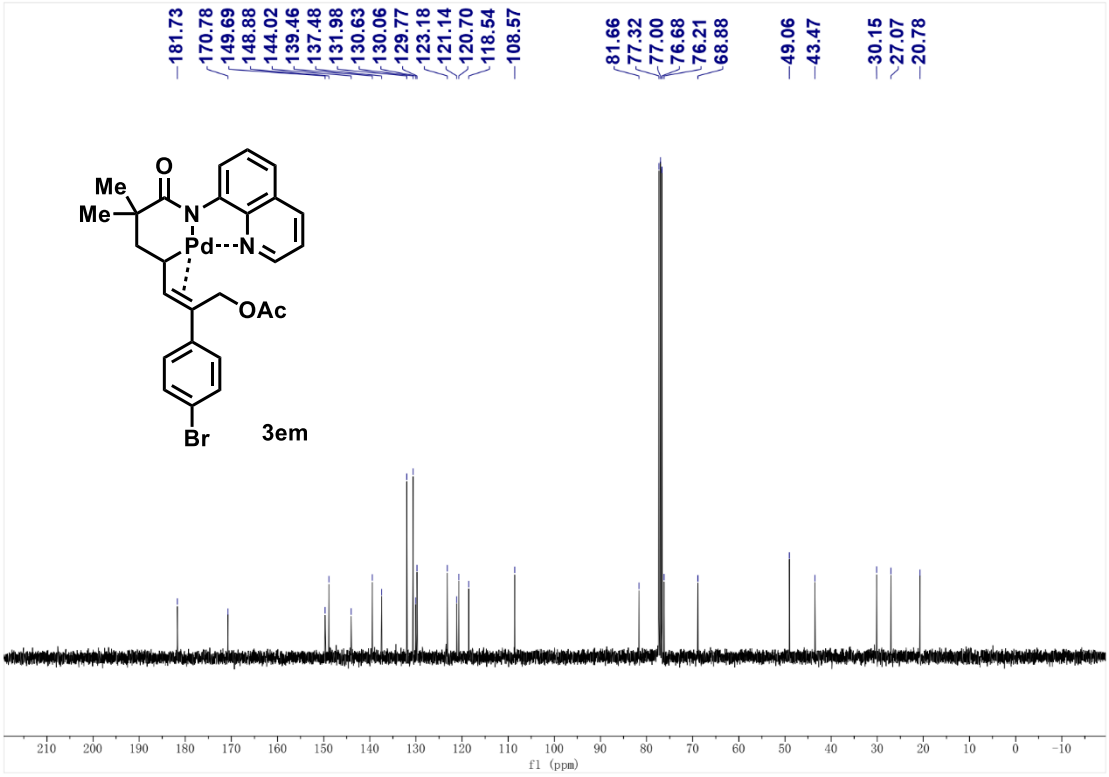
^{13}C NMR (100 MHz, $CDCl_3$) of **3el**



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

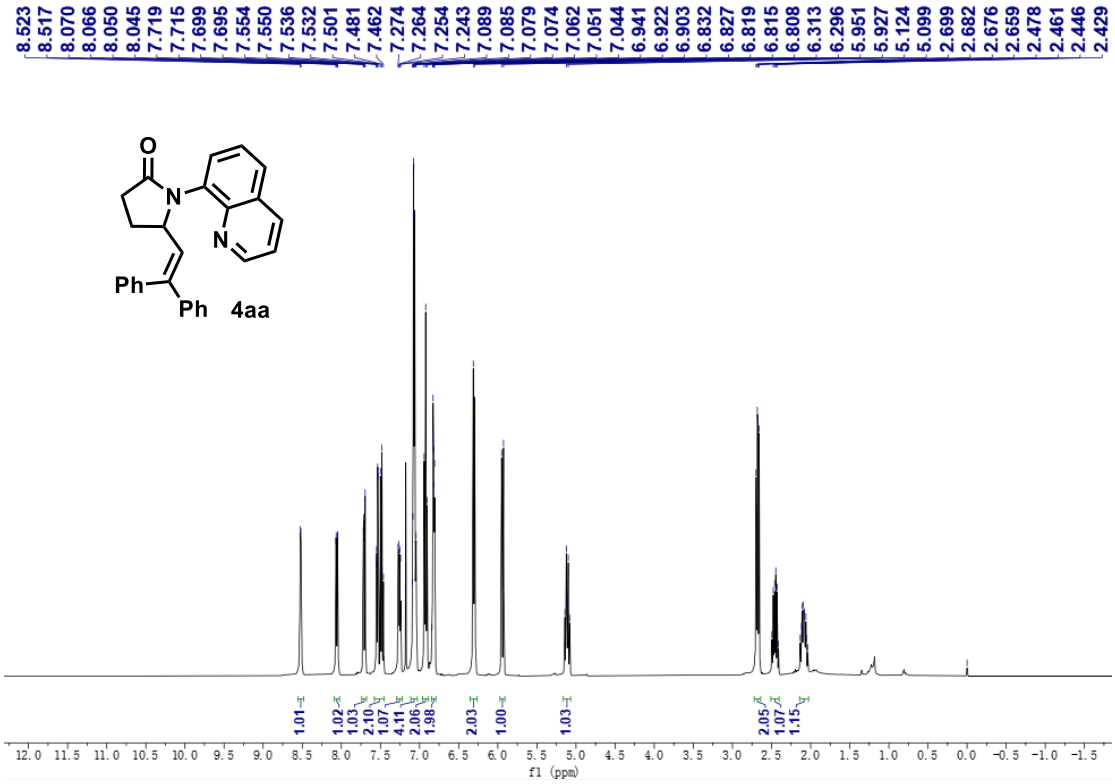


^{13}C NMR (100 MHz, $CDCl_3$) of **3em**

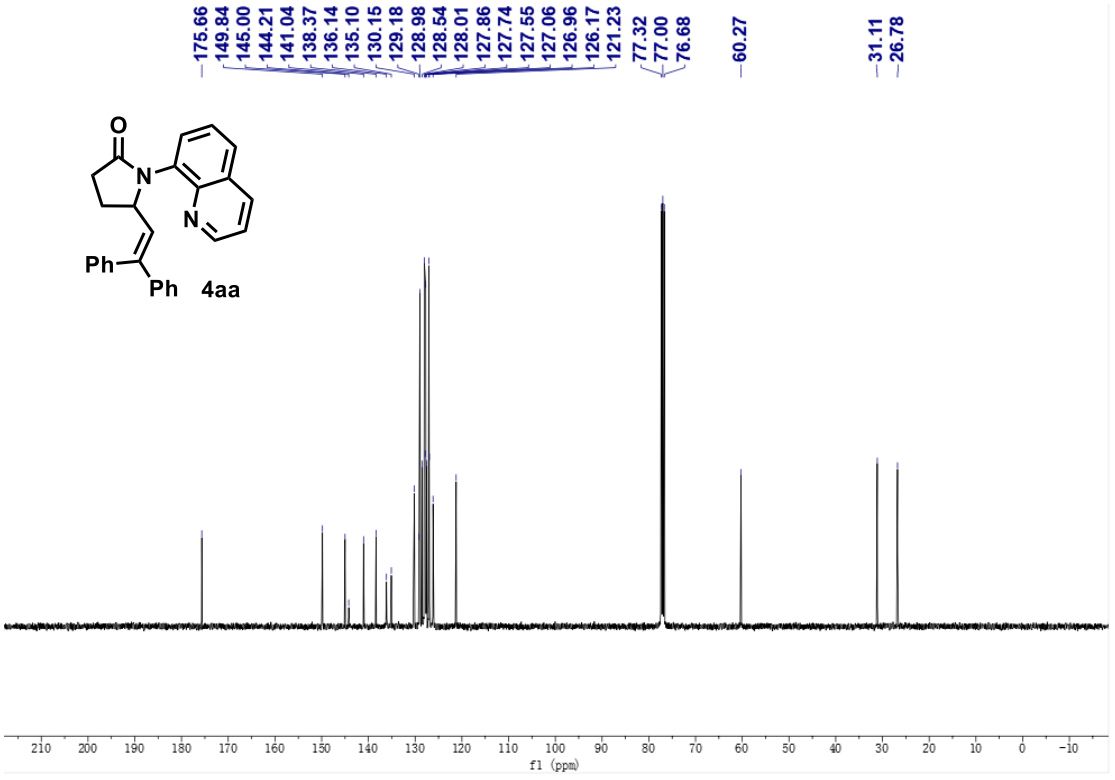


NMR spectra for late-stage modification products:

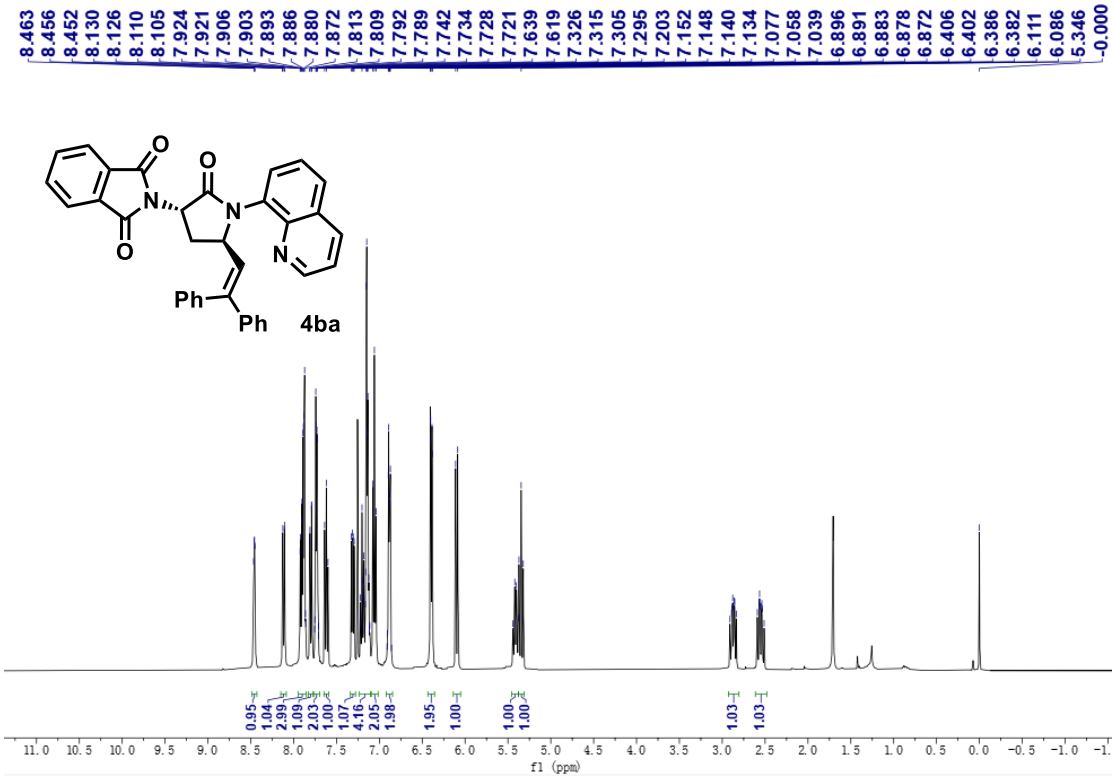
^{1}H NMR (400 MHz, $CDCl_3$) of **4aa**



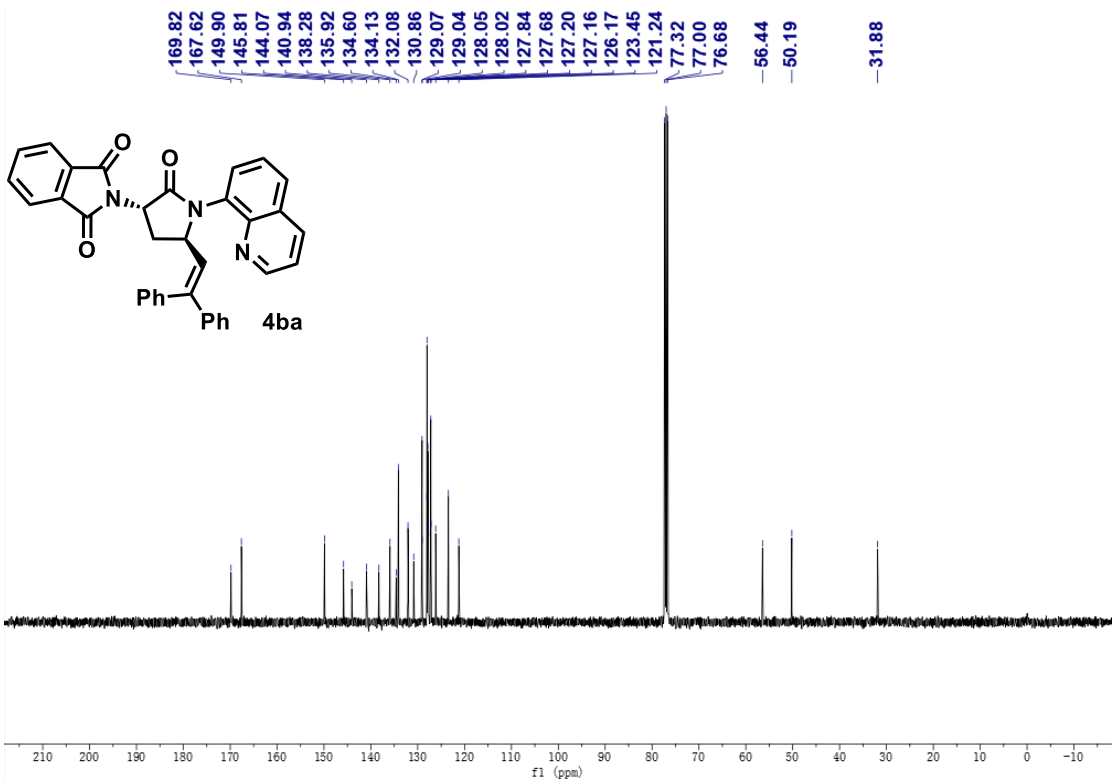
^{13}C NMR (100 MHz, $CDCl_3$) of **4aa**



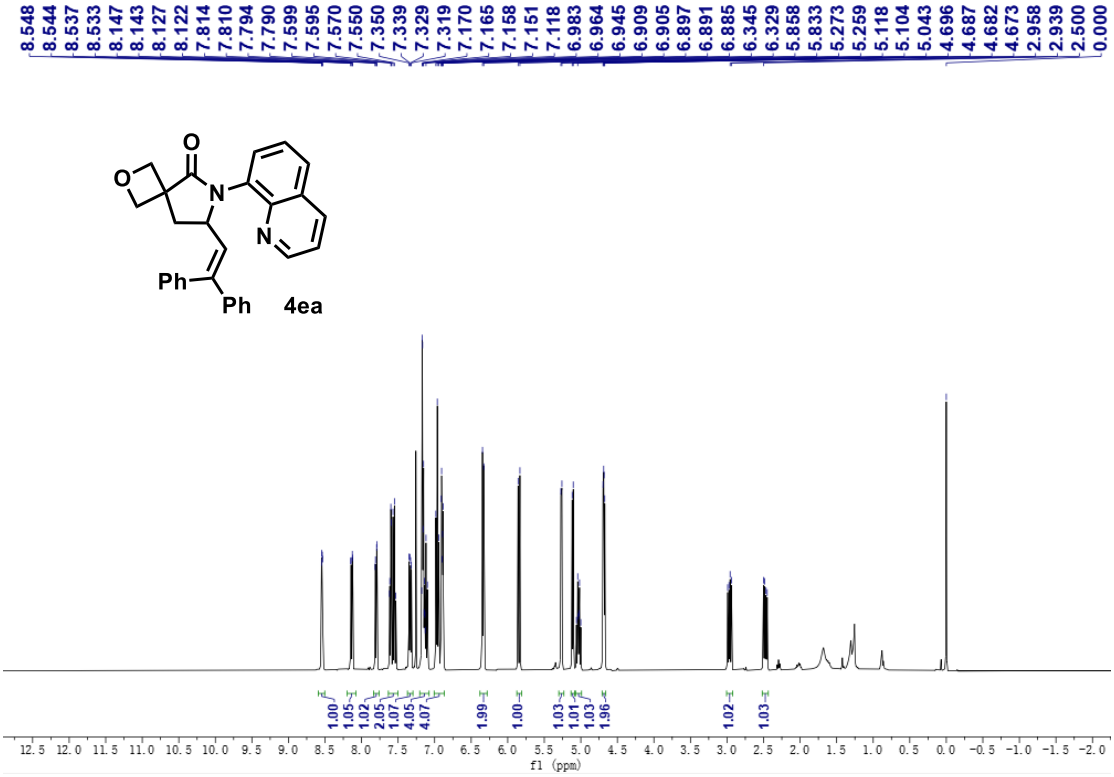
^{1}H NMR (400 MHz, $CDCl_3$) of **4ba**



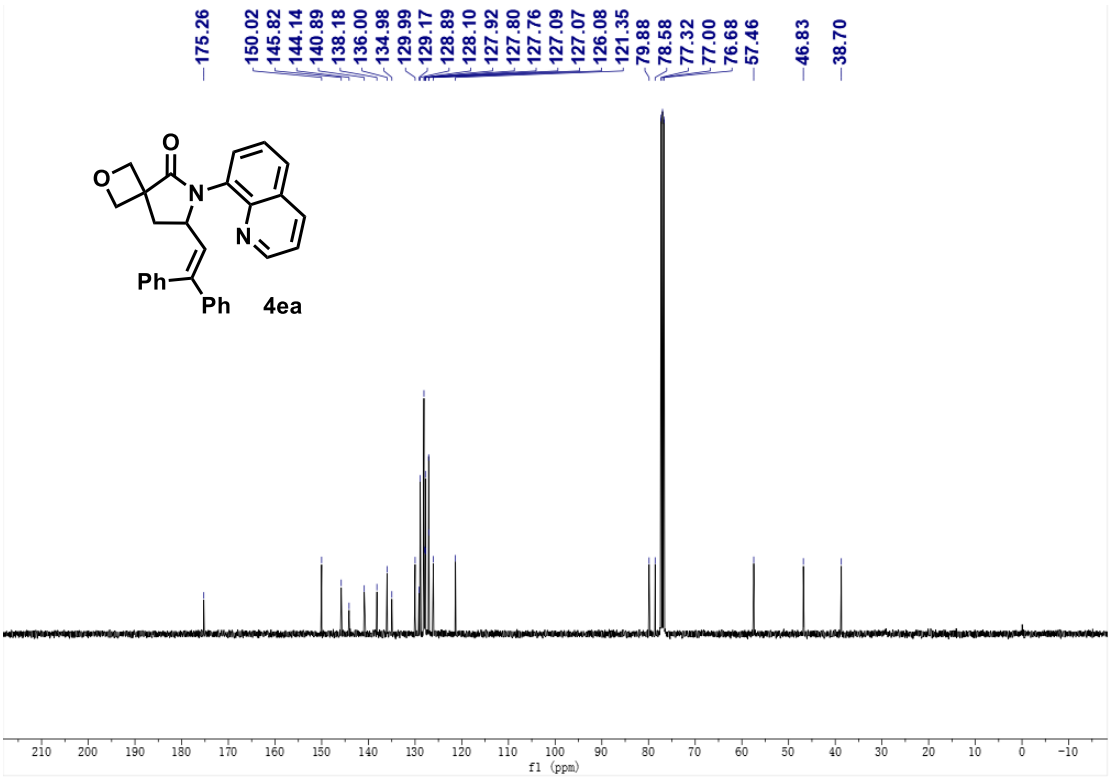
^{13}C NMR (100 MHz, $CDCl_3$) of **4ba**



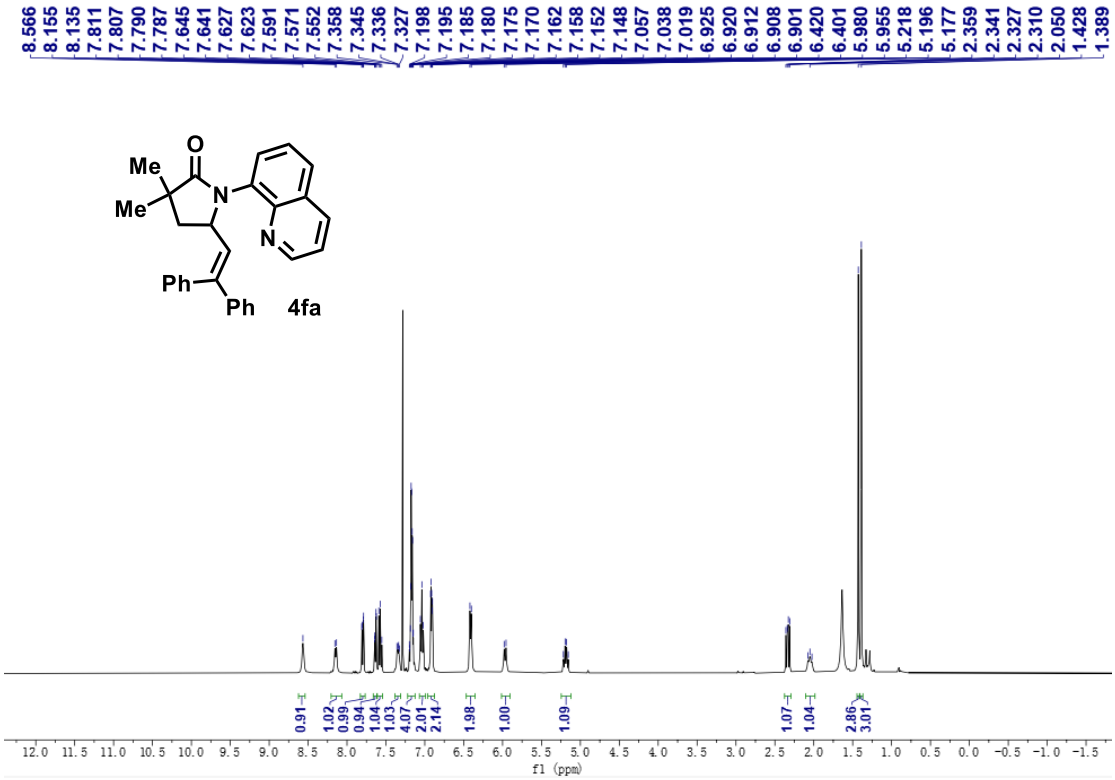
^{1}H NMR (400 MHz, $CDCl_3$) of **4ea**



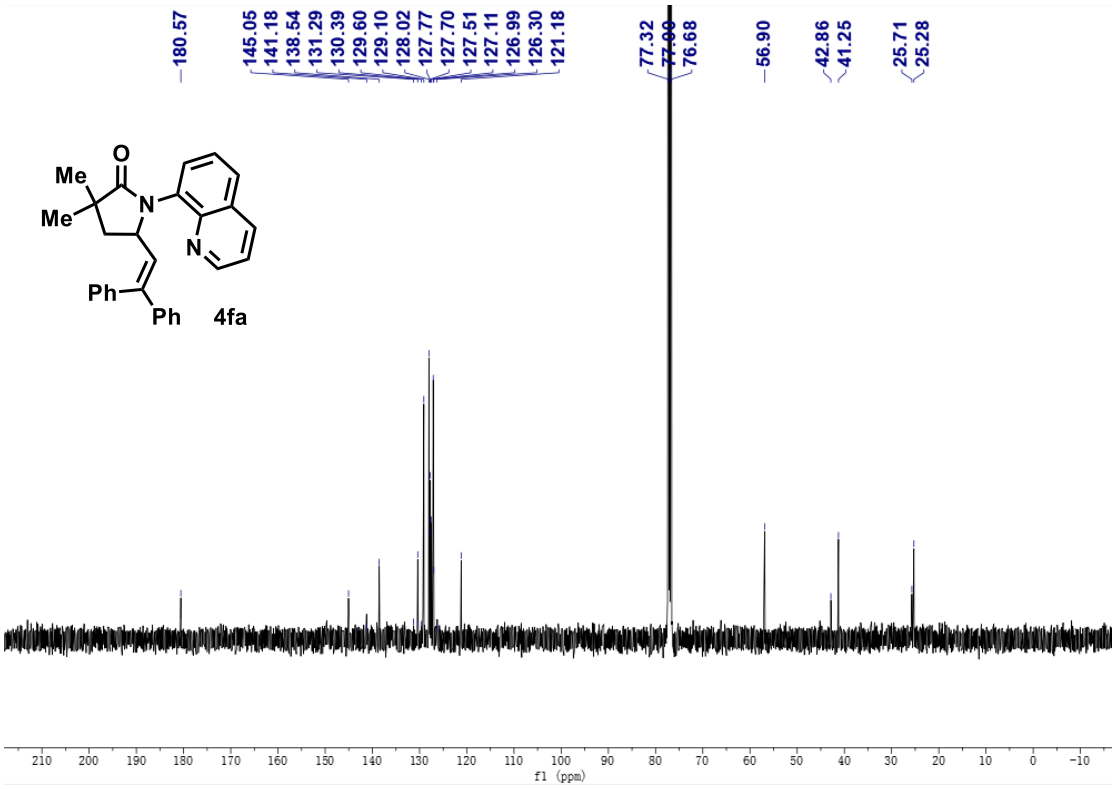
^{13}C NMR (100 MHz, $CDCl_3$) of **4ea**



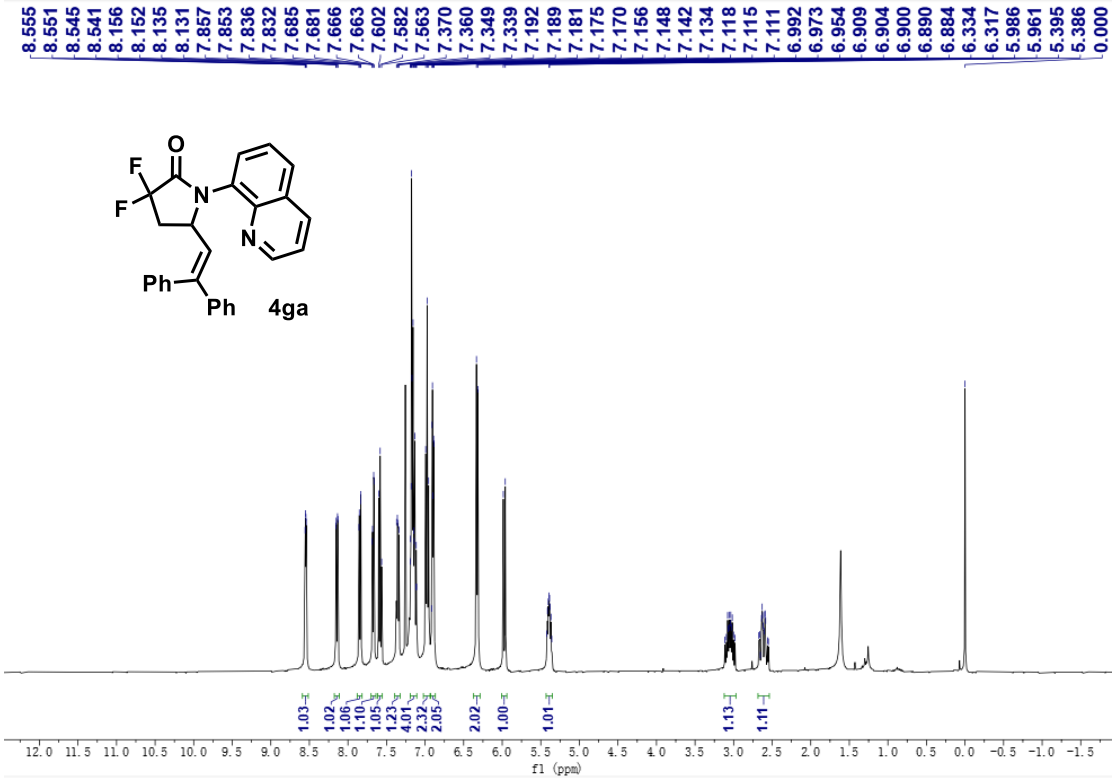
^{1}H NMR (400 MHz, $CDCl_3$) of **4fa**



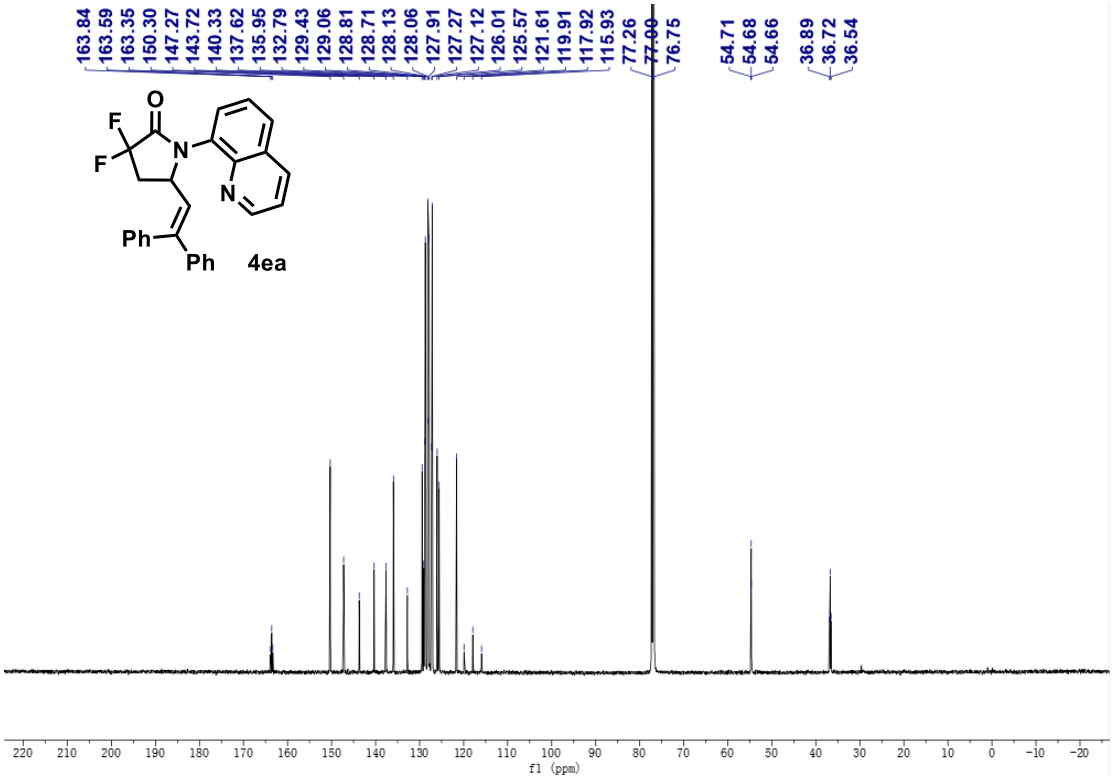
^{13}C NMR (100 MHz, $CDCl_3$) of **4fa**



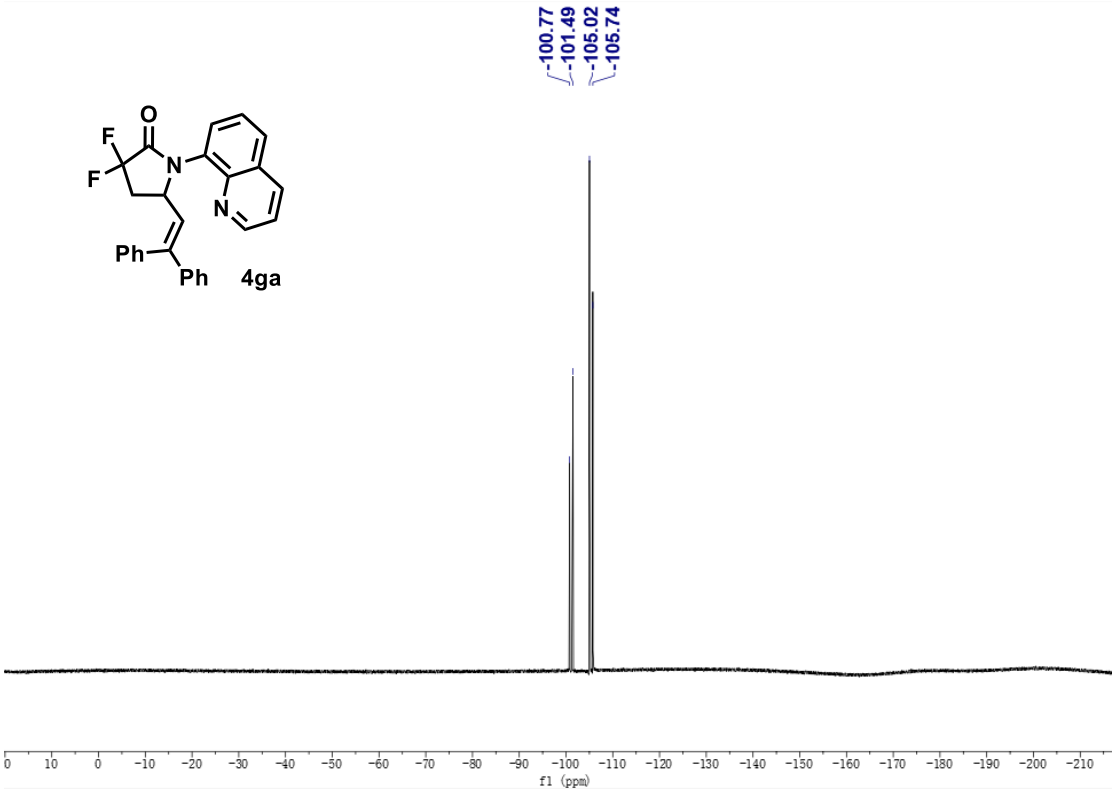
^{1}H NMR (400 MHz, $CDCl_3$) of **4ga**



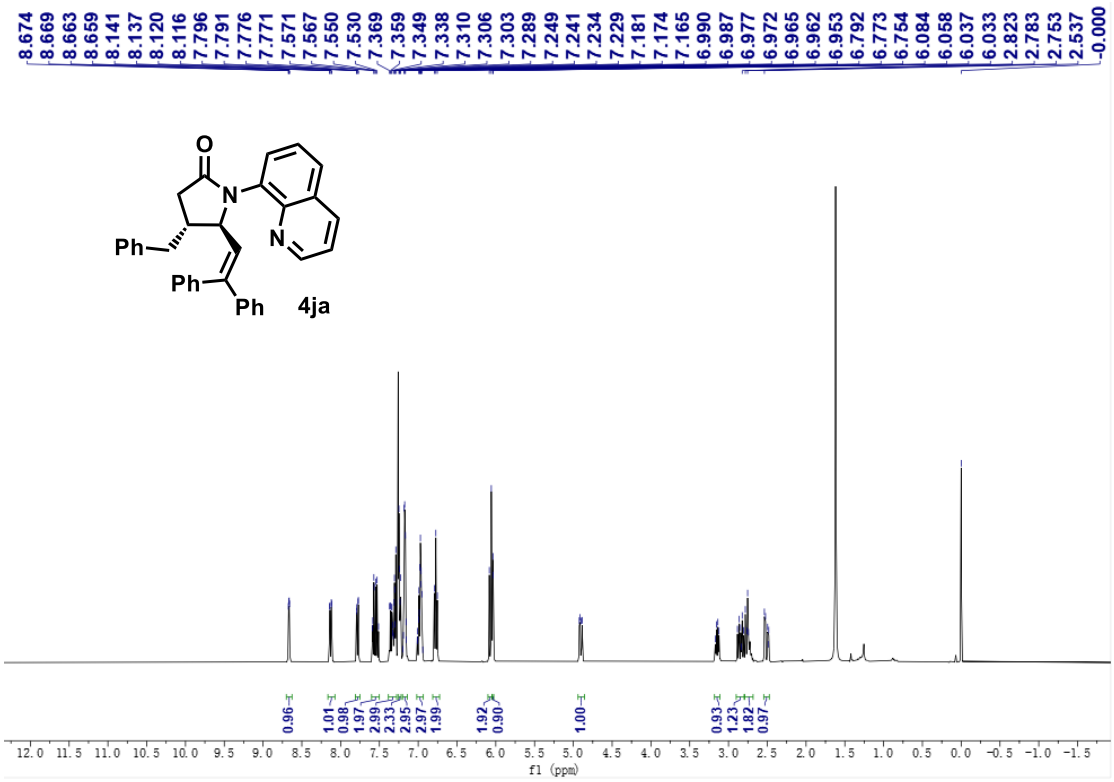
^{13}C NMR (100 MHz, $CDCl_3$) of **4ga**



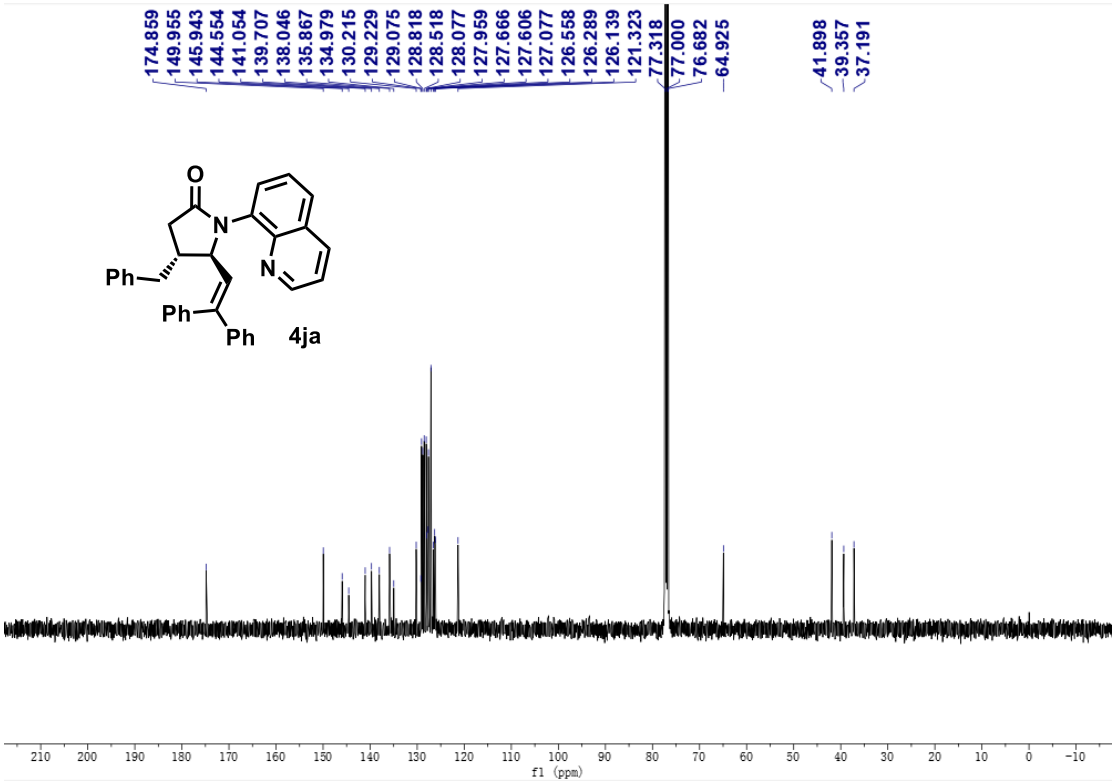
^{19}F NMR (376 MHz, $CDCl_3$) of **4ga**



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



^{13}C NMR (100 MHz, $CDCl_3$) of **4ja**



No NOE was observed between H^{α} and H^{β}

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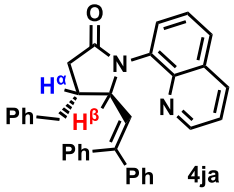

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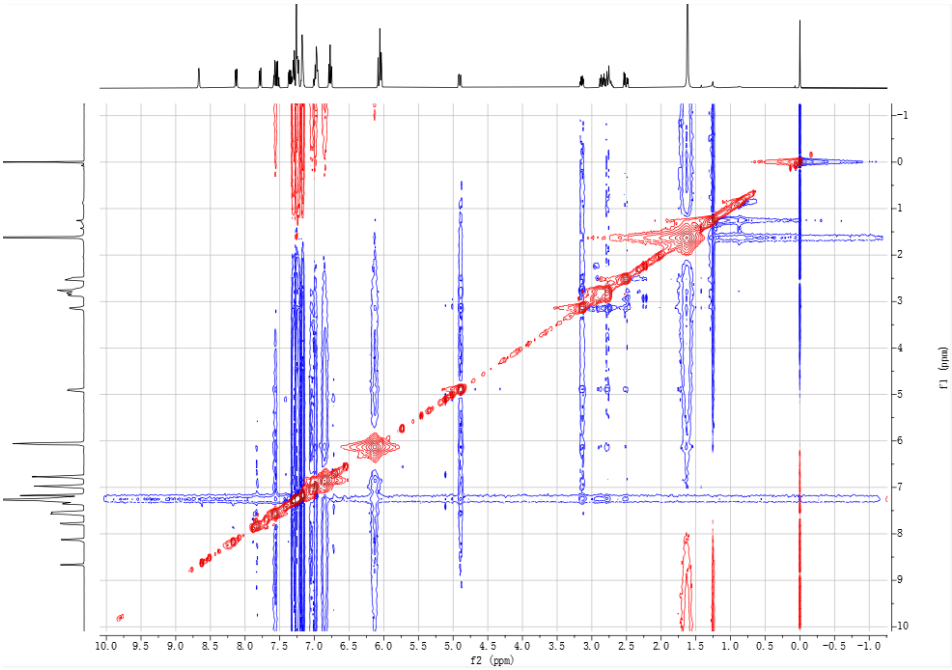
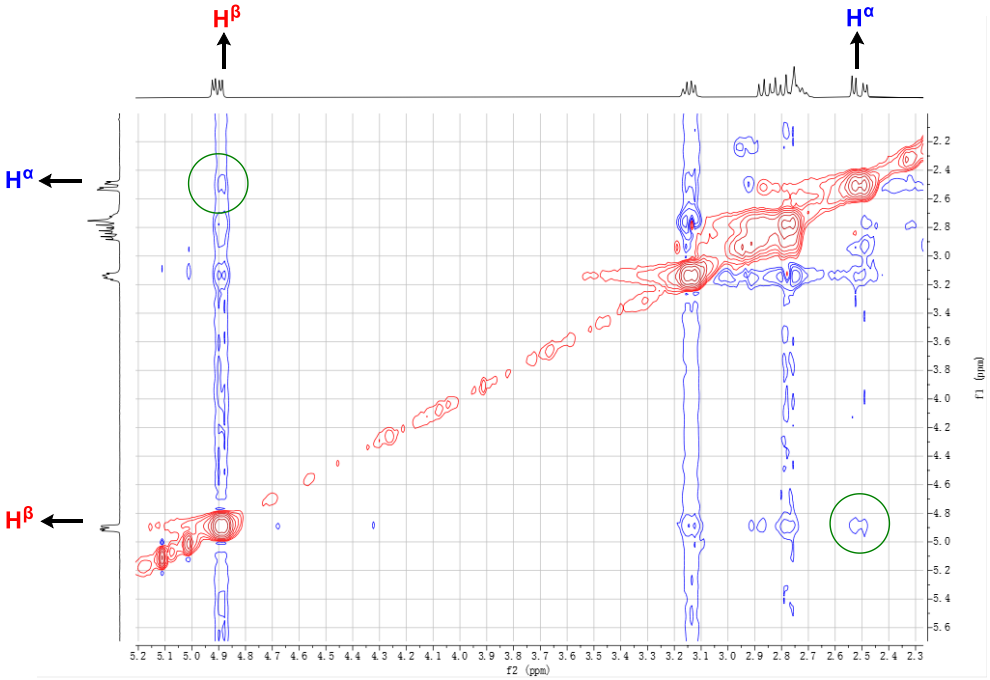
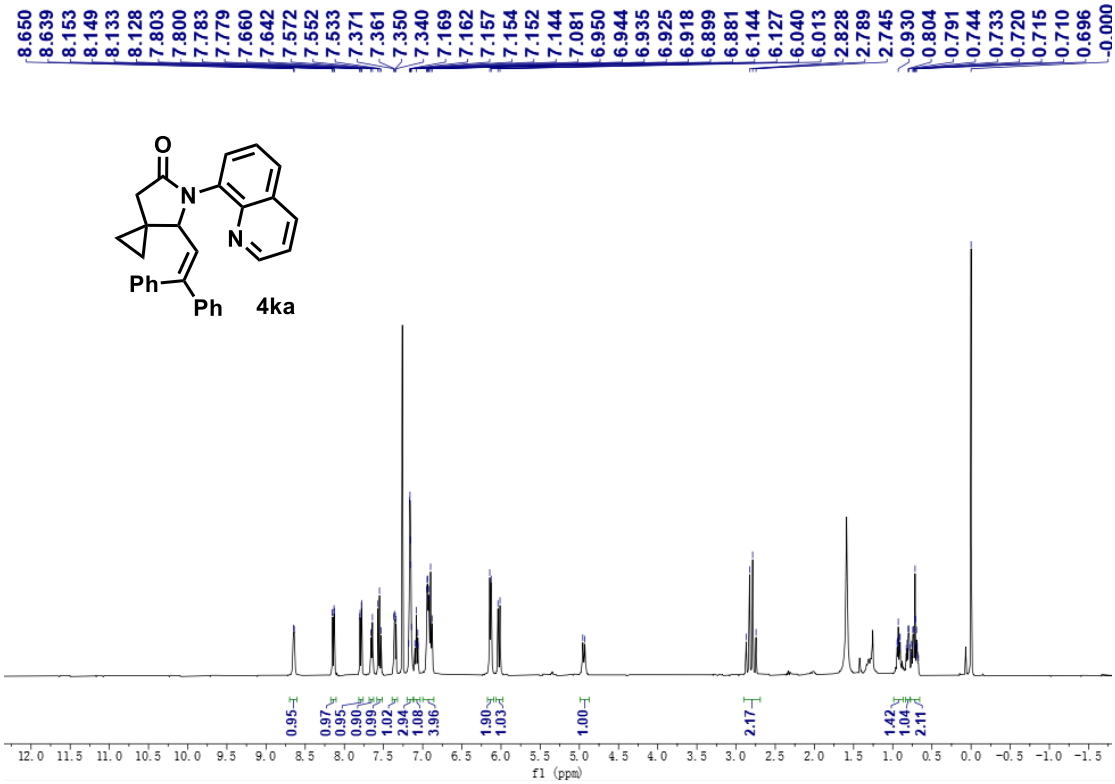
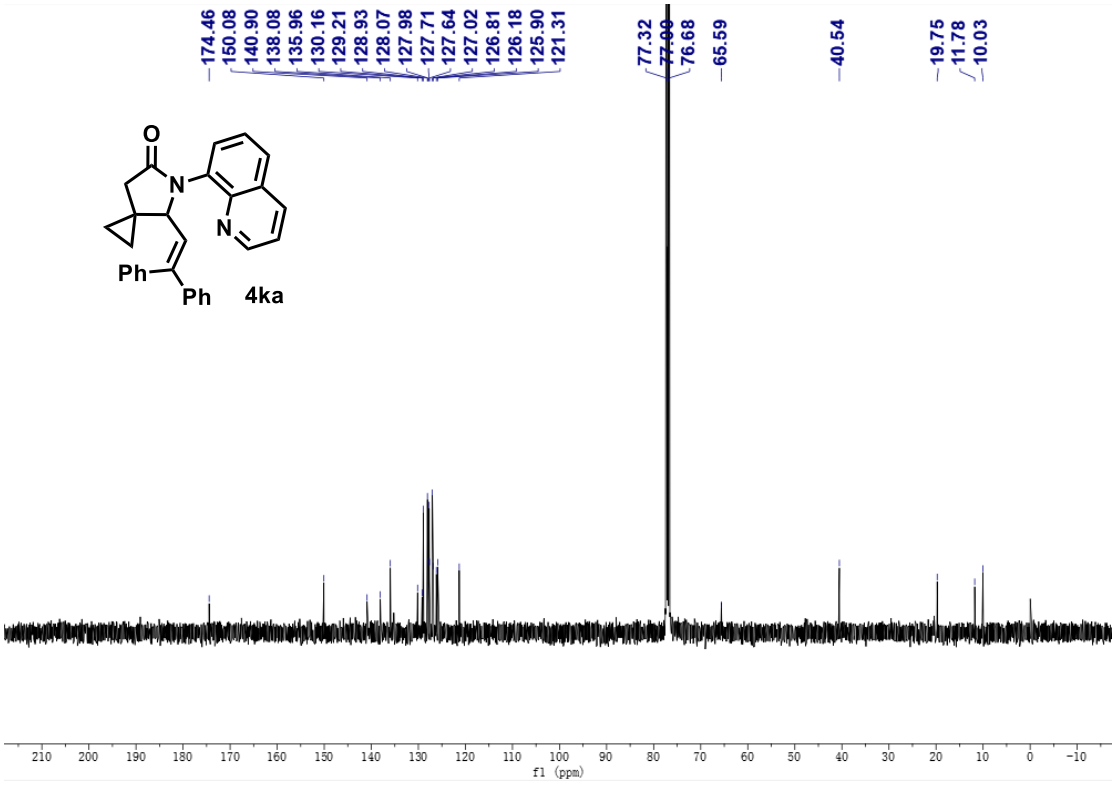




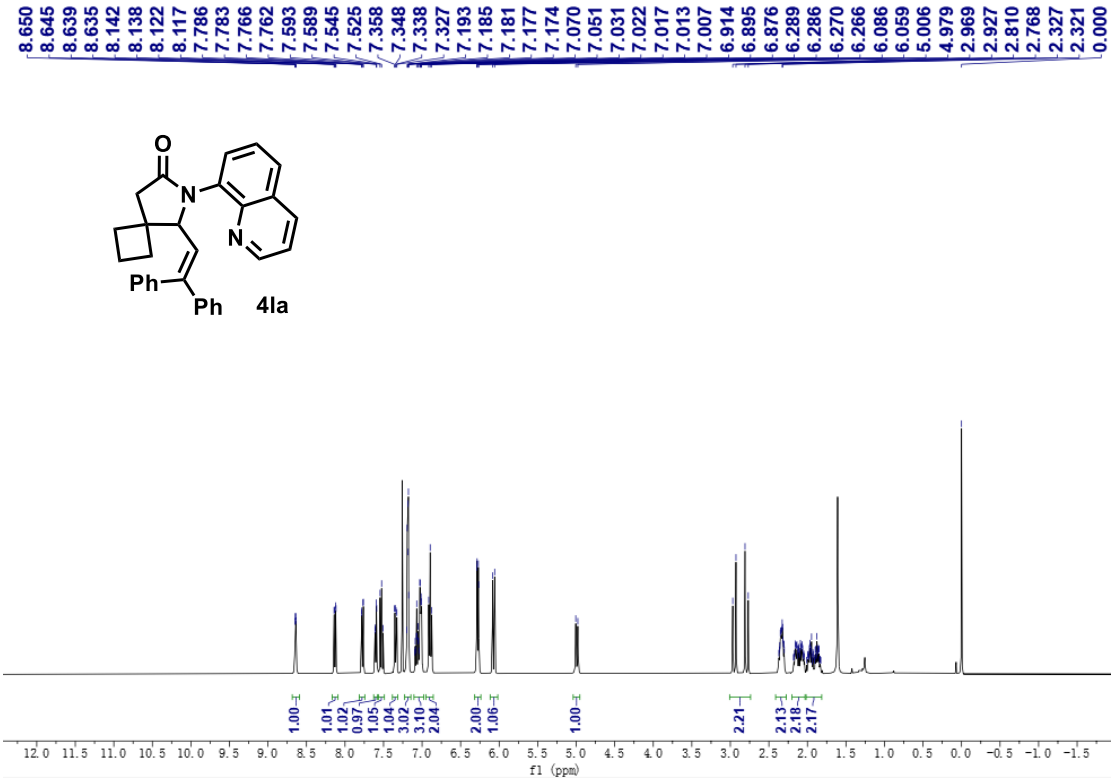
^{1}H NMR (400 MHz, $CDCl_3$) of **4ka**



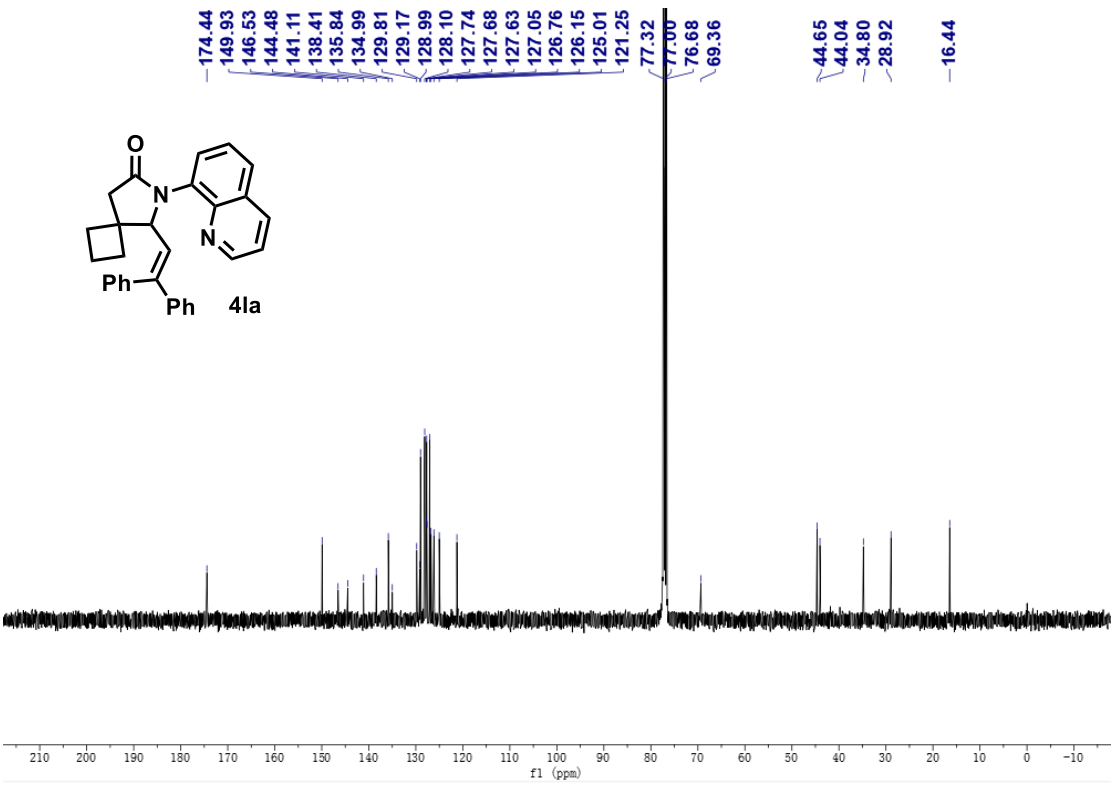
^{13}C NMR (100 MHz, $CDCl_3$) of **4ka**



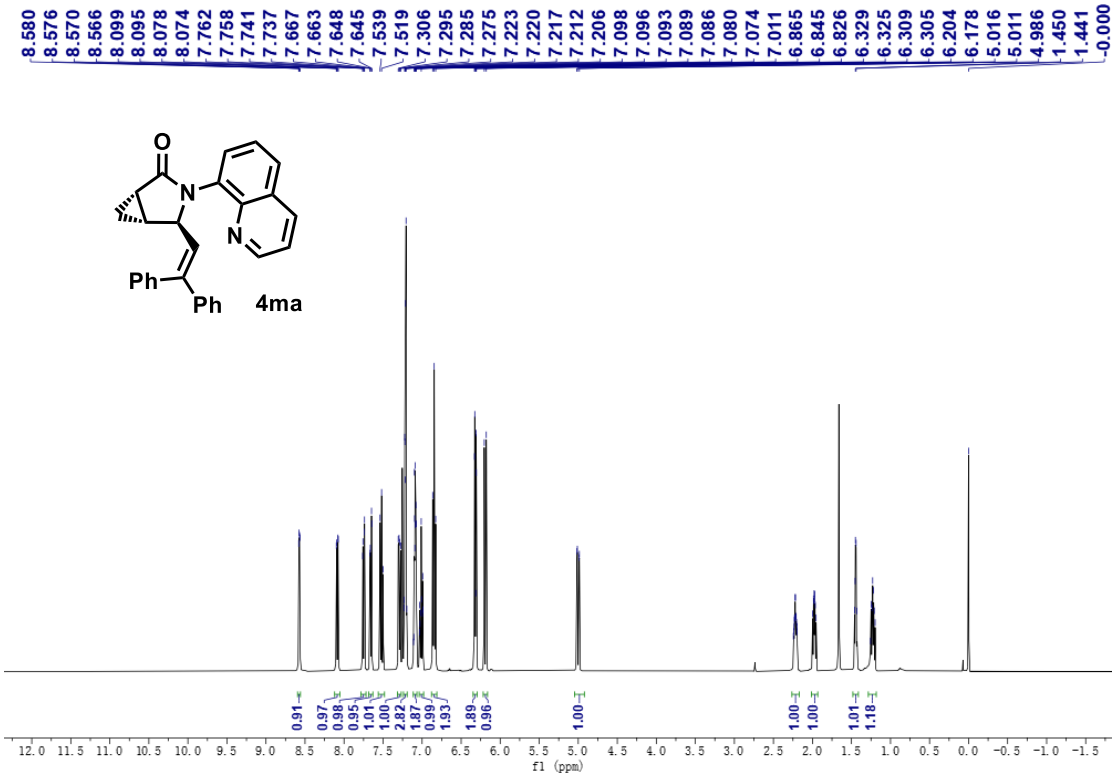
^{1}H NMR (400 MHz, $CDCl_3$) of **4la**



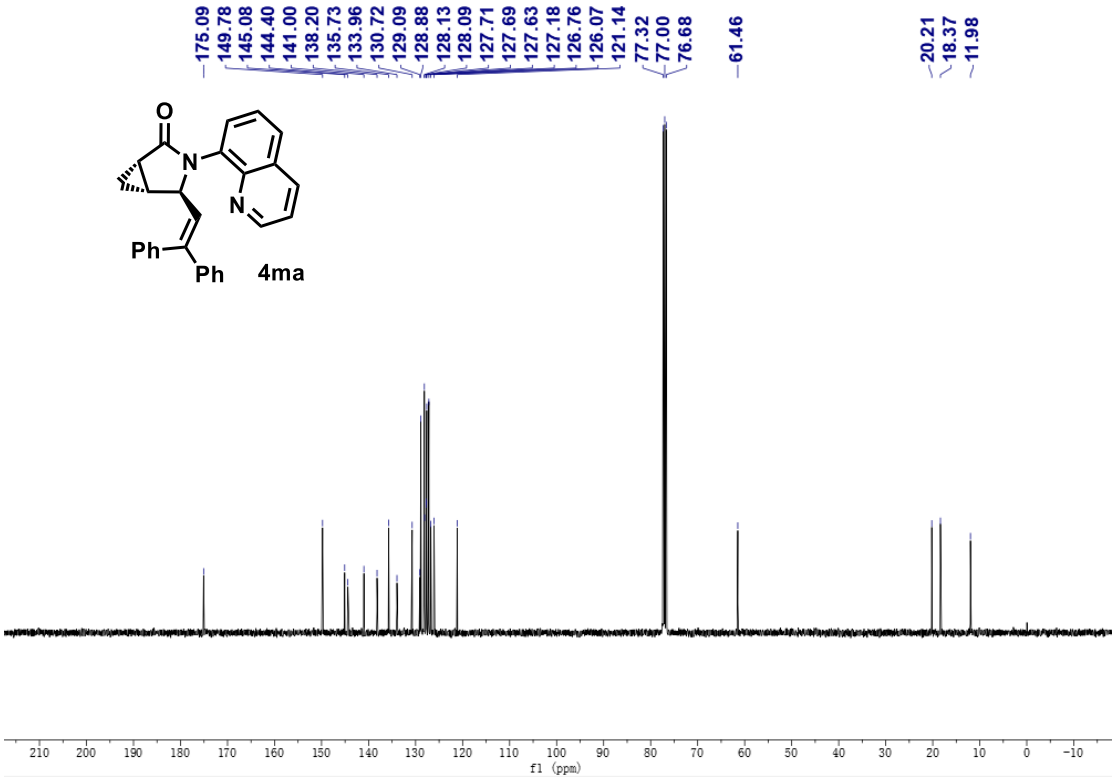
^{13}C NMR (100 MHz, $CDCl_3$) of **4la**



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



^{13}C NMR (100 MHz, $CDCl_3$) of **4ma**



No NOE was observed between H^{α} and H^{β}

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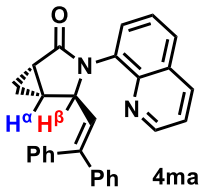

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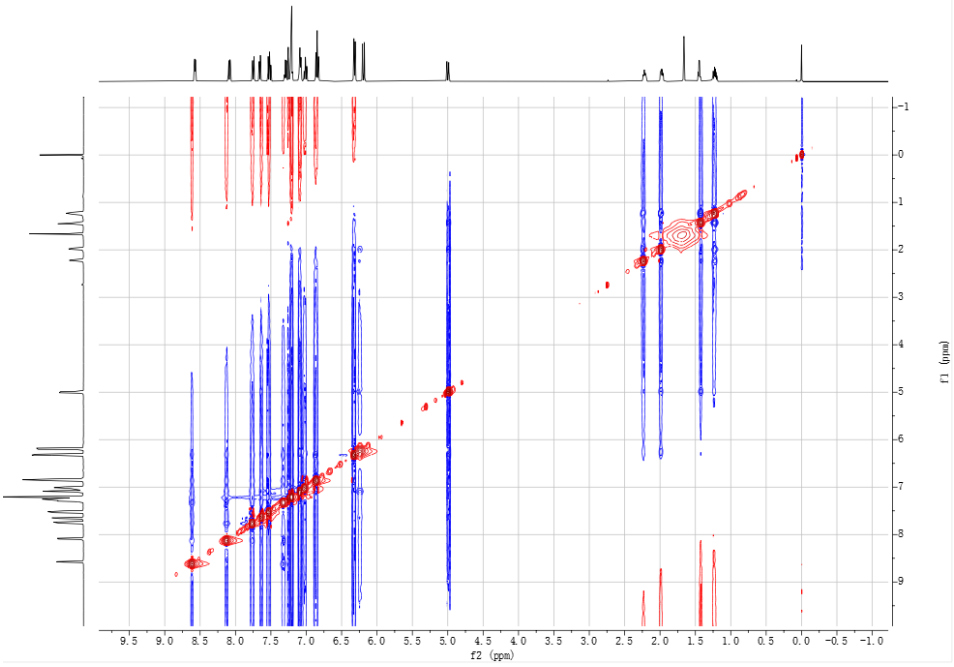
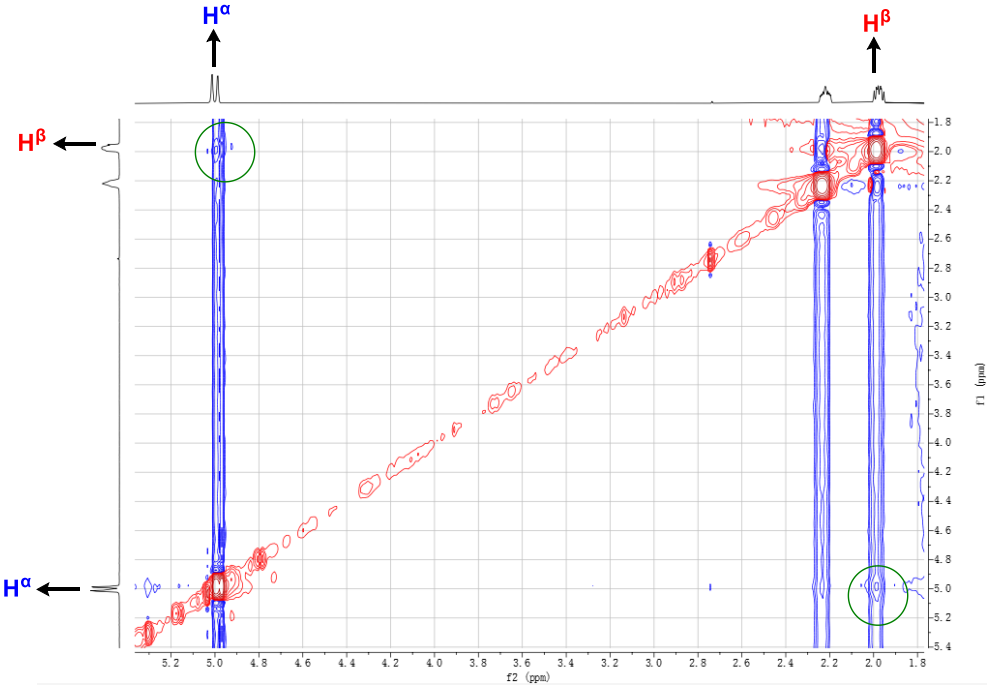
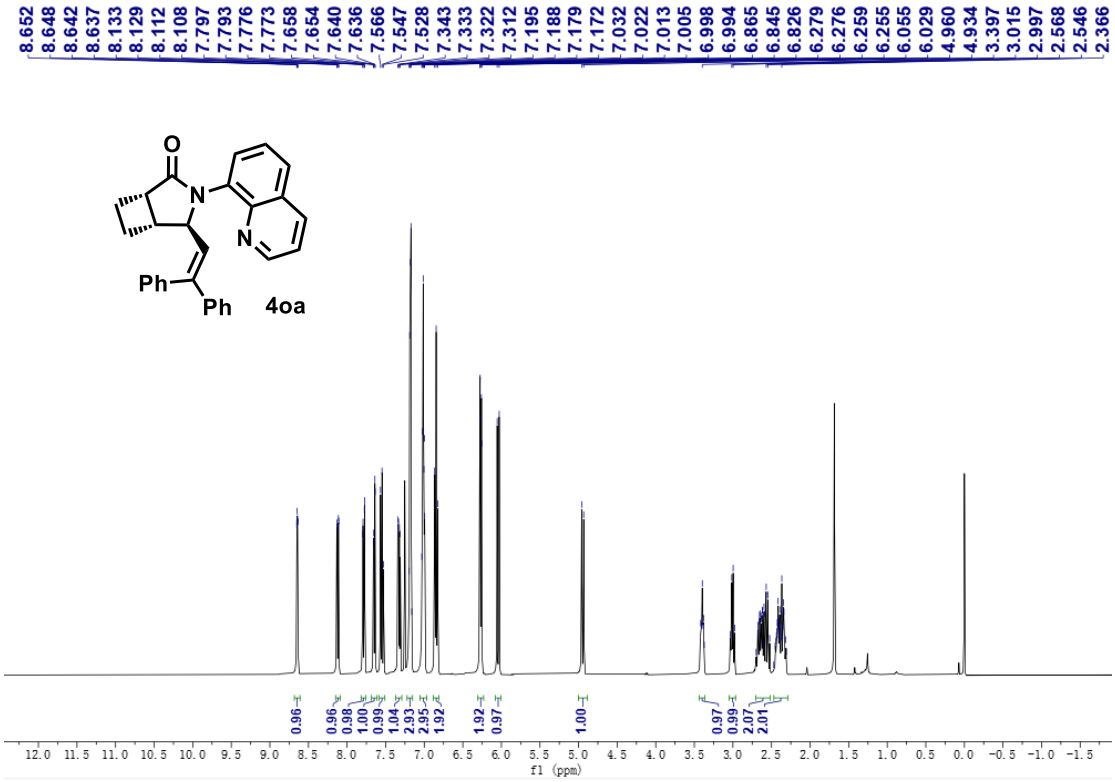
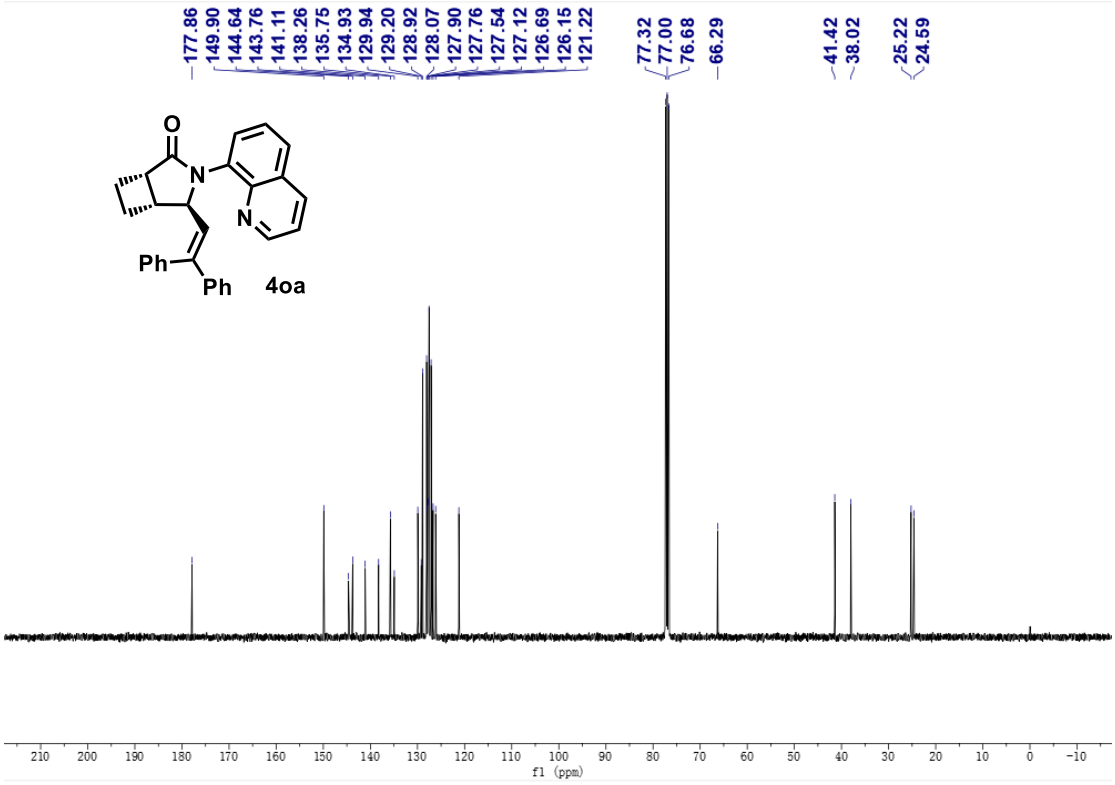




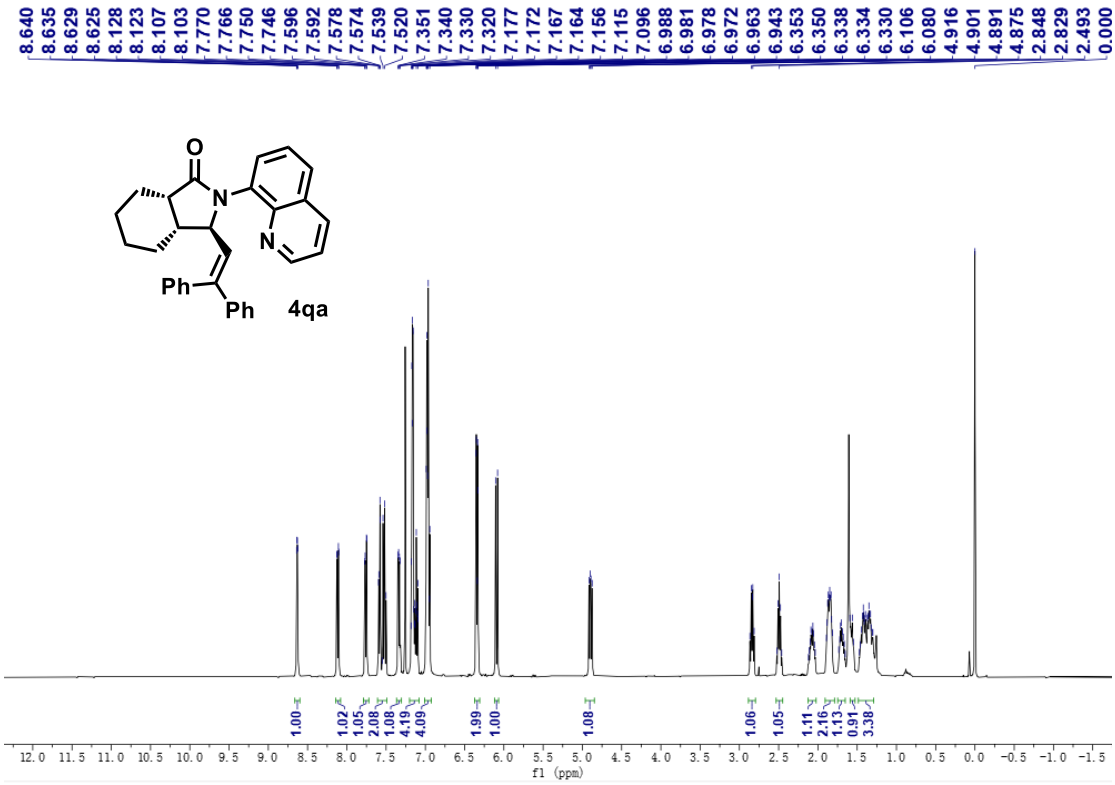
^{1}H NMR (400 MHz, $CDCl_3$) of **4oa**



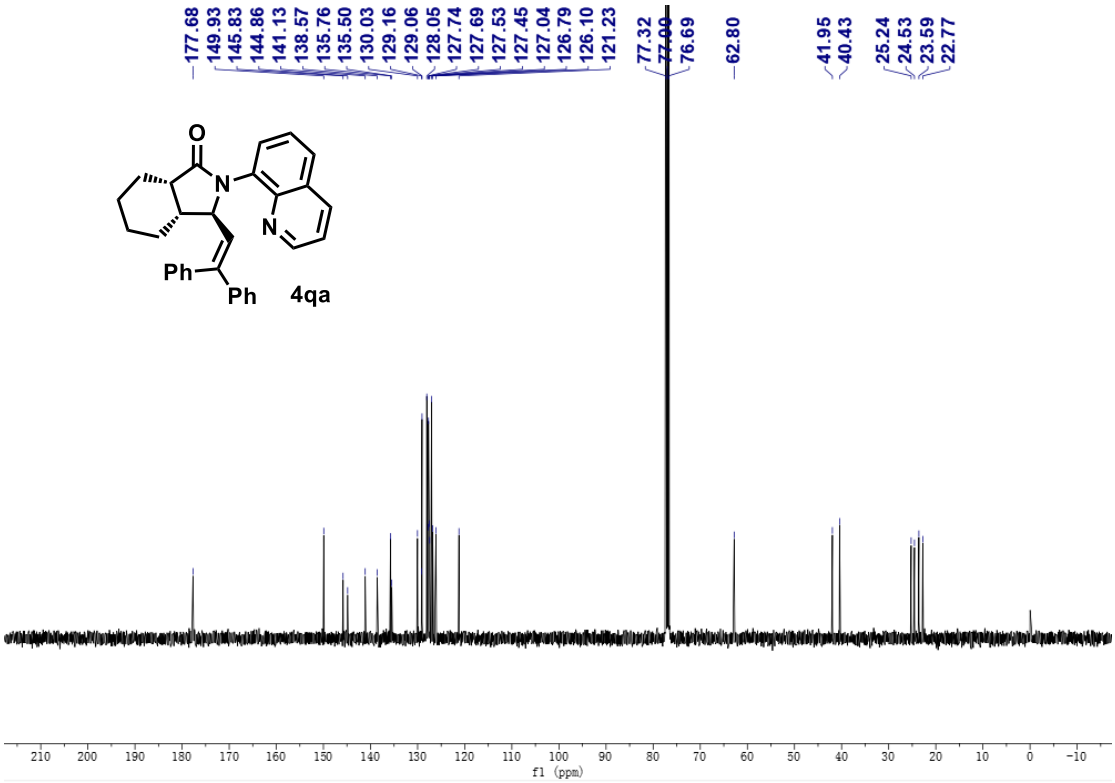
^{13}C NMR (100 MHz, $CDCl_3$) of **4oa**



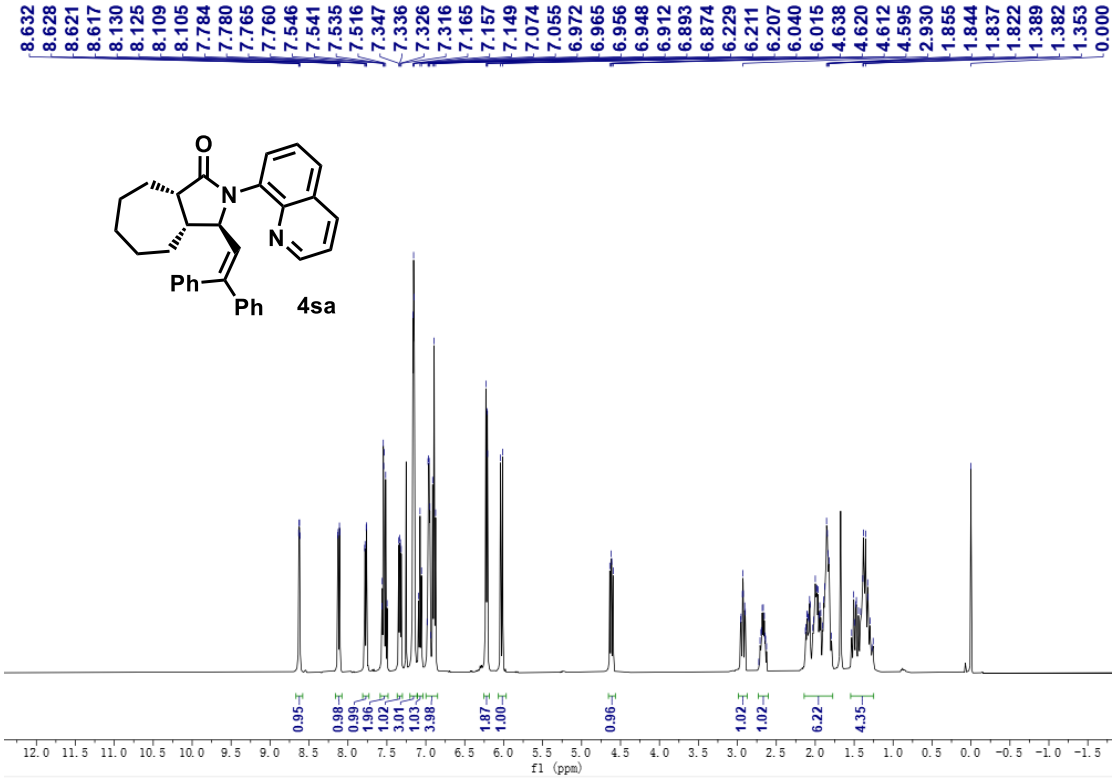
^{1}H NMR (400 MHz, $CDCl_3$) of **4qa**



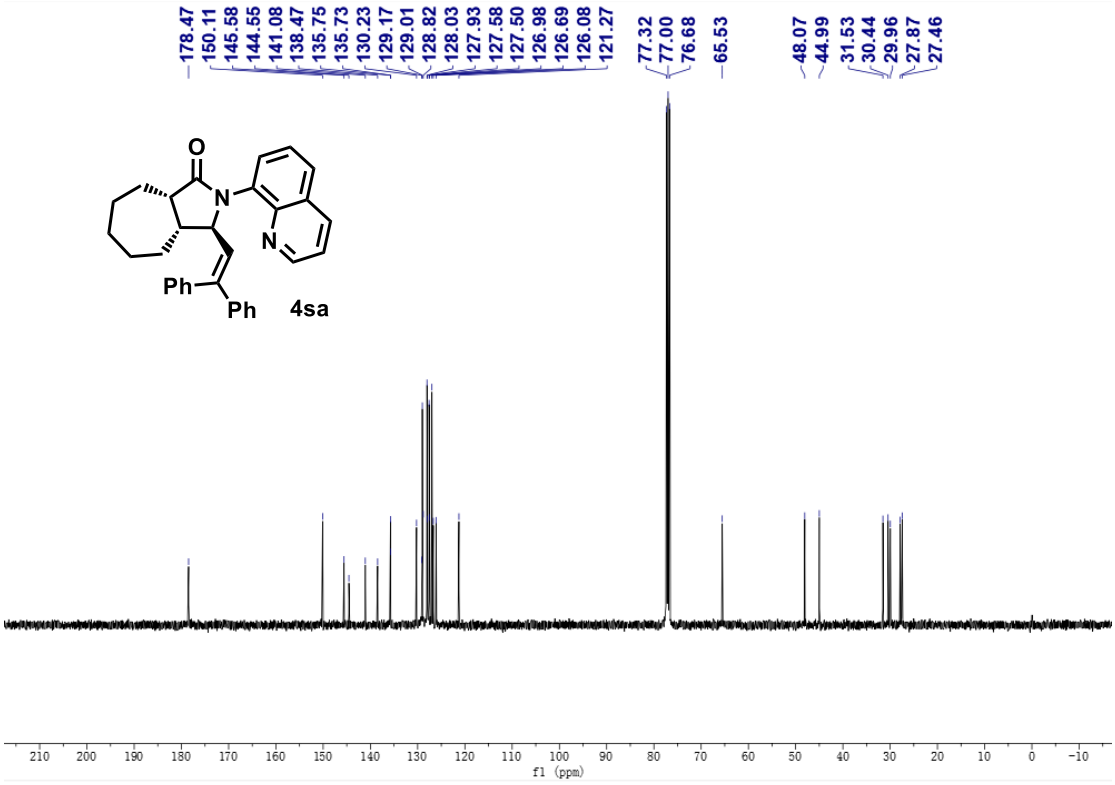
^{13}C NMR (100 MHz, $CDCl_3$) of **4qa**



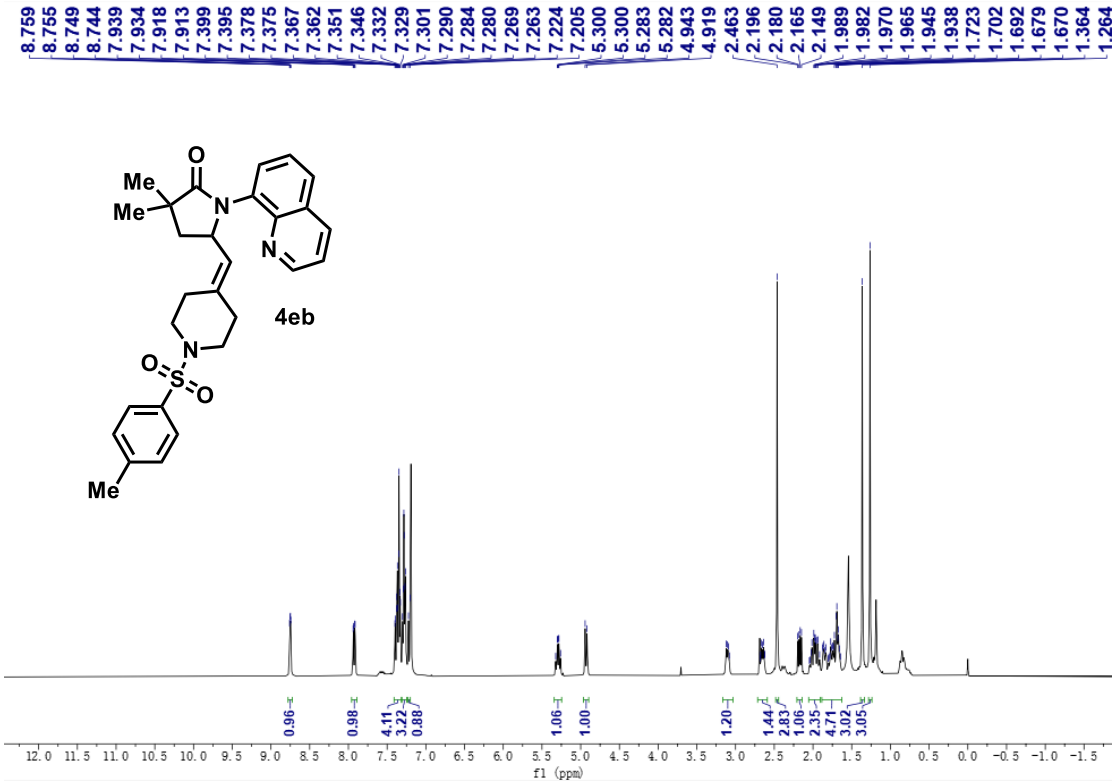
^{1}H NMR (400 MHz, $CDCl_3$) of **4sa**



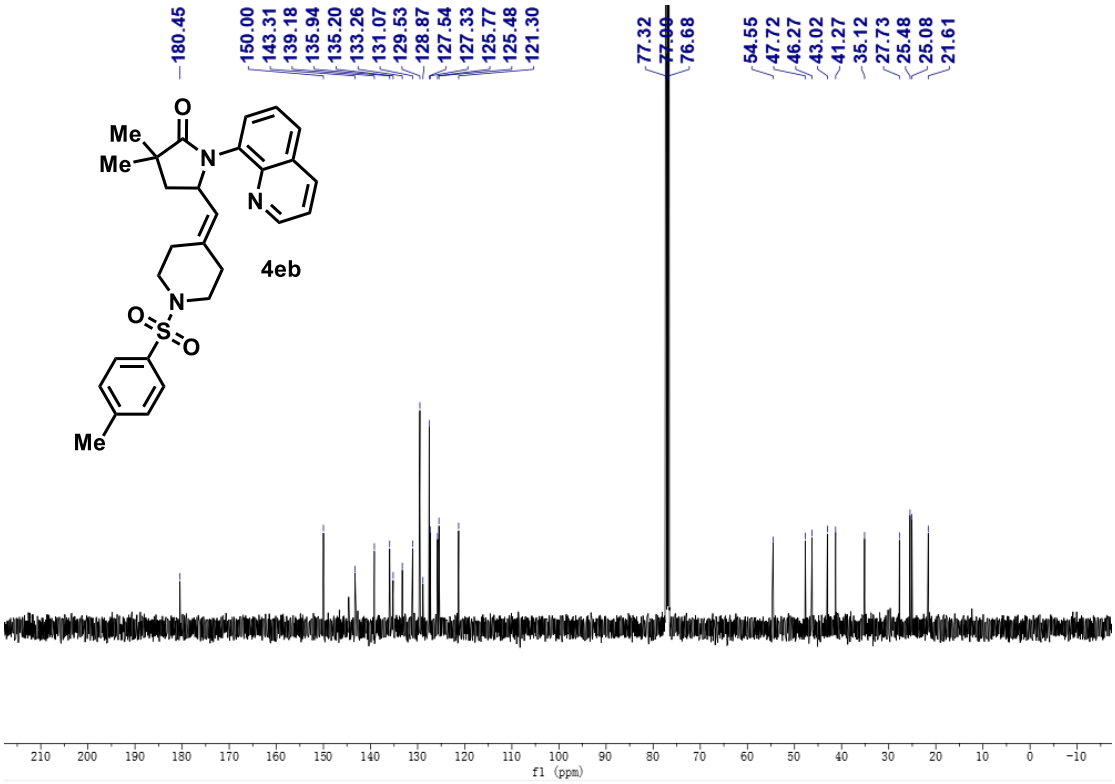
^{13}C NMR (100 MHz, $CDCl_3$) of **4sa**



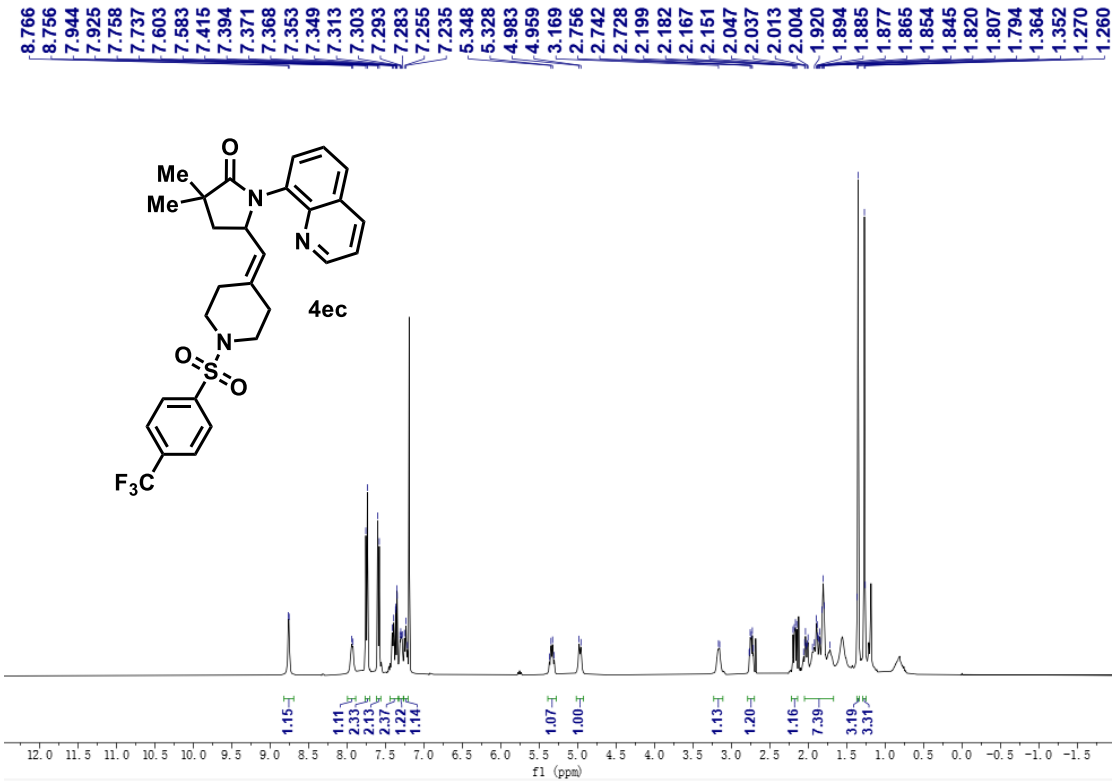
^{1}H NMR (400 MHz, $CDCl_3$) of **4eb**



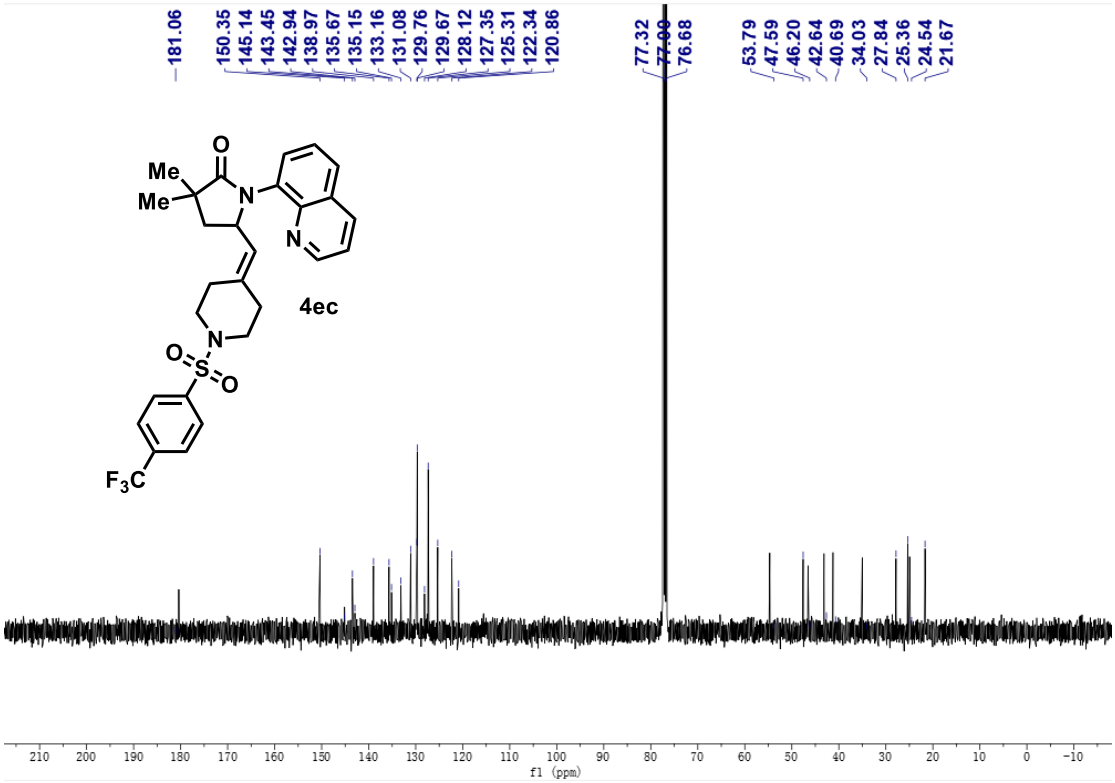
^{13}C NMR (100 MHz, $CDCl_3$) of **4eb**



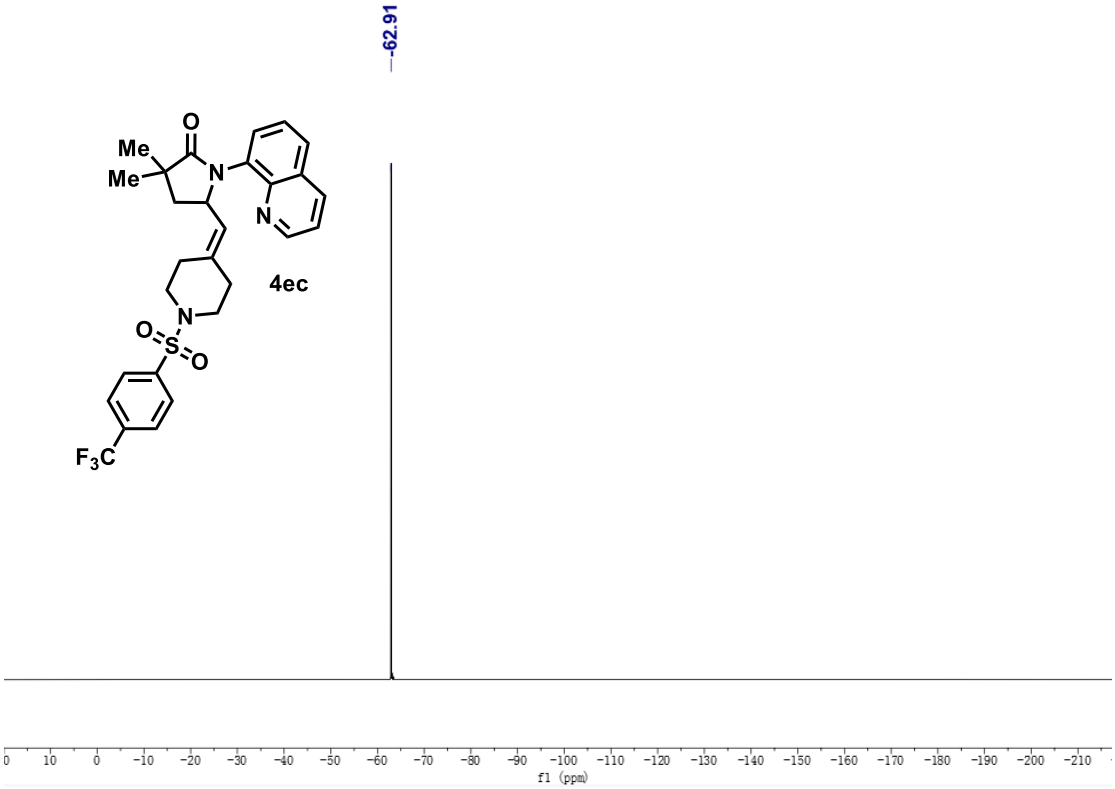
^{1}H NMR (400 MHz, $CDCl_3$) of **4ec**



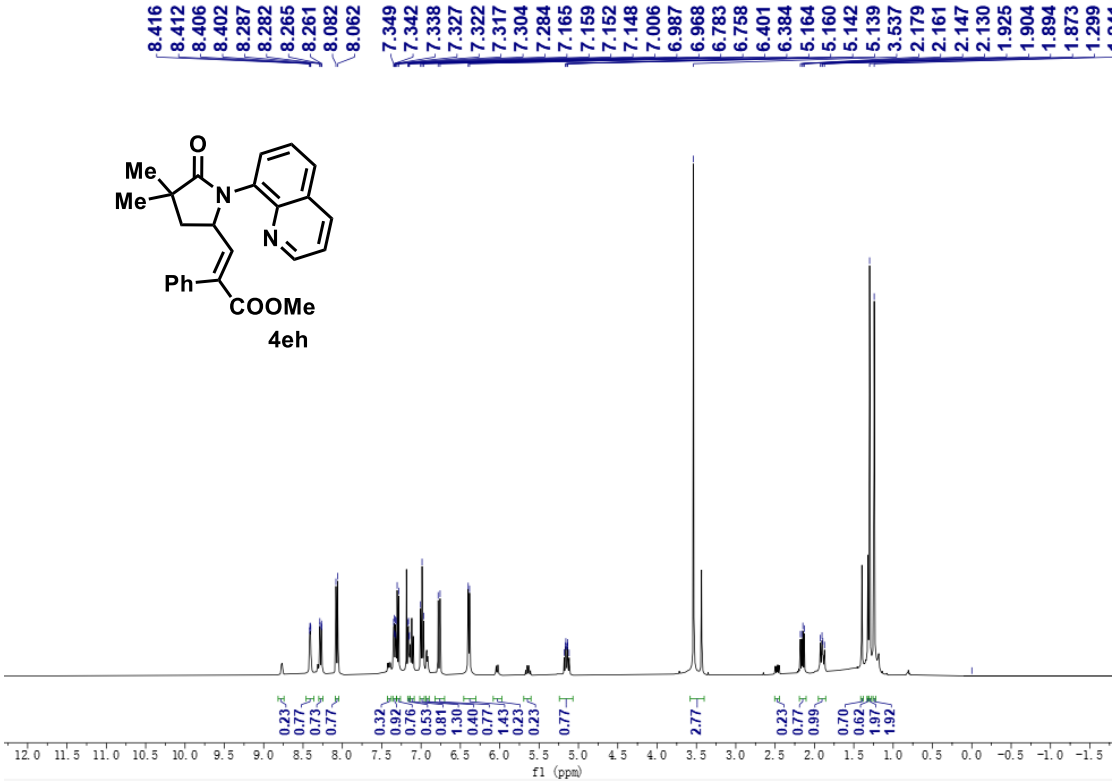
^{13}C NMR (100 MHz, $CDCl_3$) of **4ec**



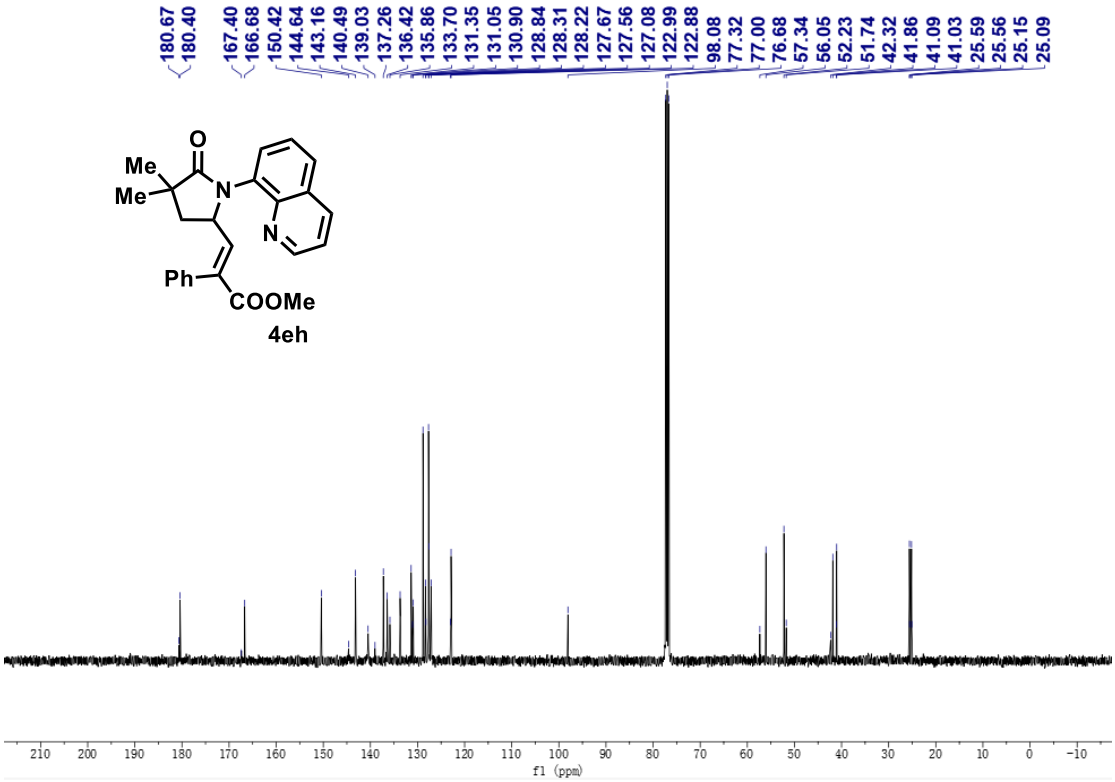
^{19}F NMR (376 MHz, $CDCl_3$) of **4ec**



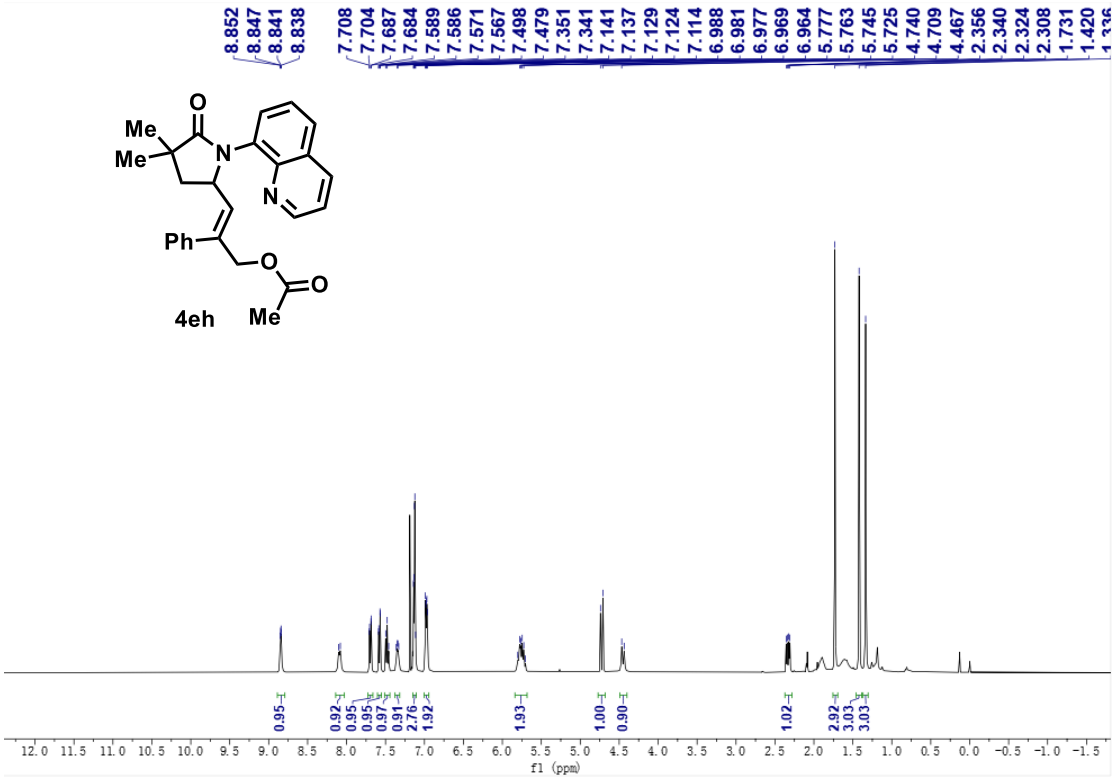
^{1}H NMR (400 MHz, $CDCl_3$) of **4eh**



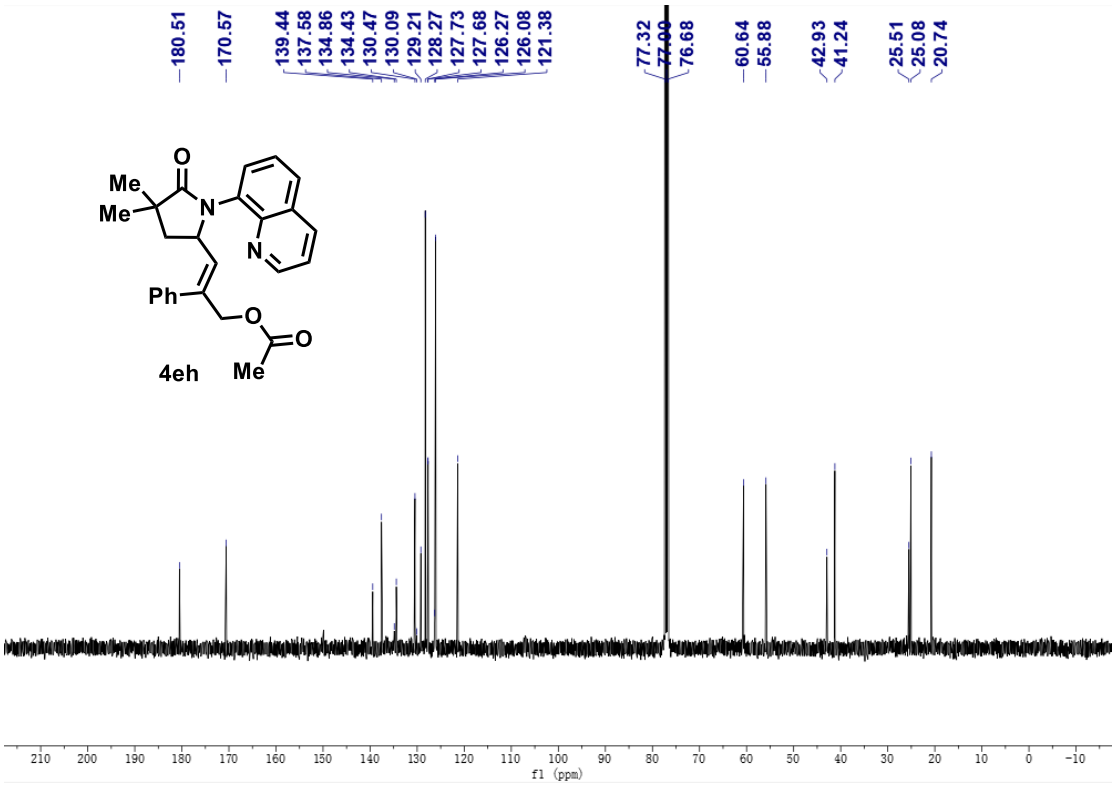
^{13}C NMR (100 MHz, $CDCl_3$) of **4eh**



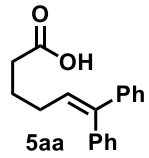
^{1}H NMR (400 MHz, $CDCl_3$) of **4el**

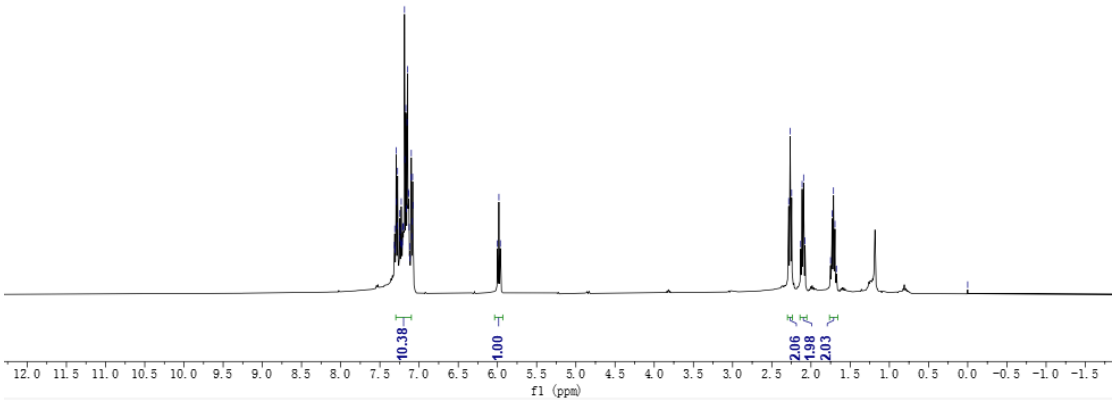


^{13}C NMR (100 MHz, $CDCl_3$) of **4el**

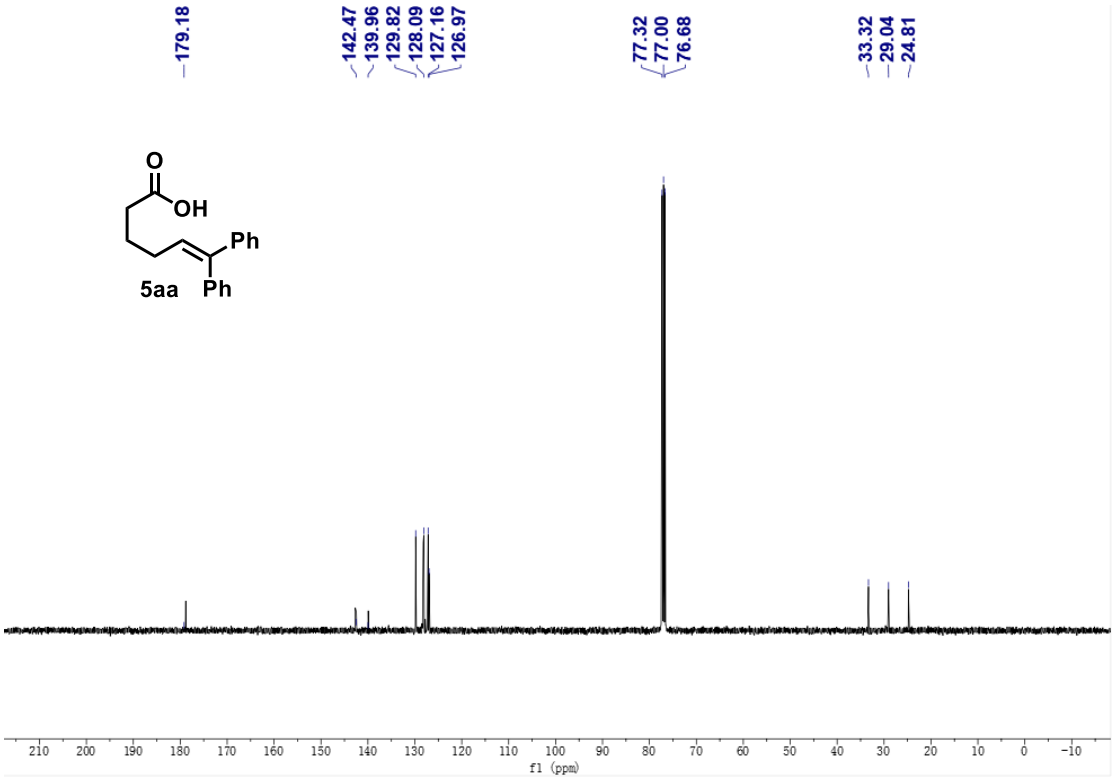


^{1}H NMR (400 MHz, $CDCl_3$) of **5aa**

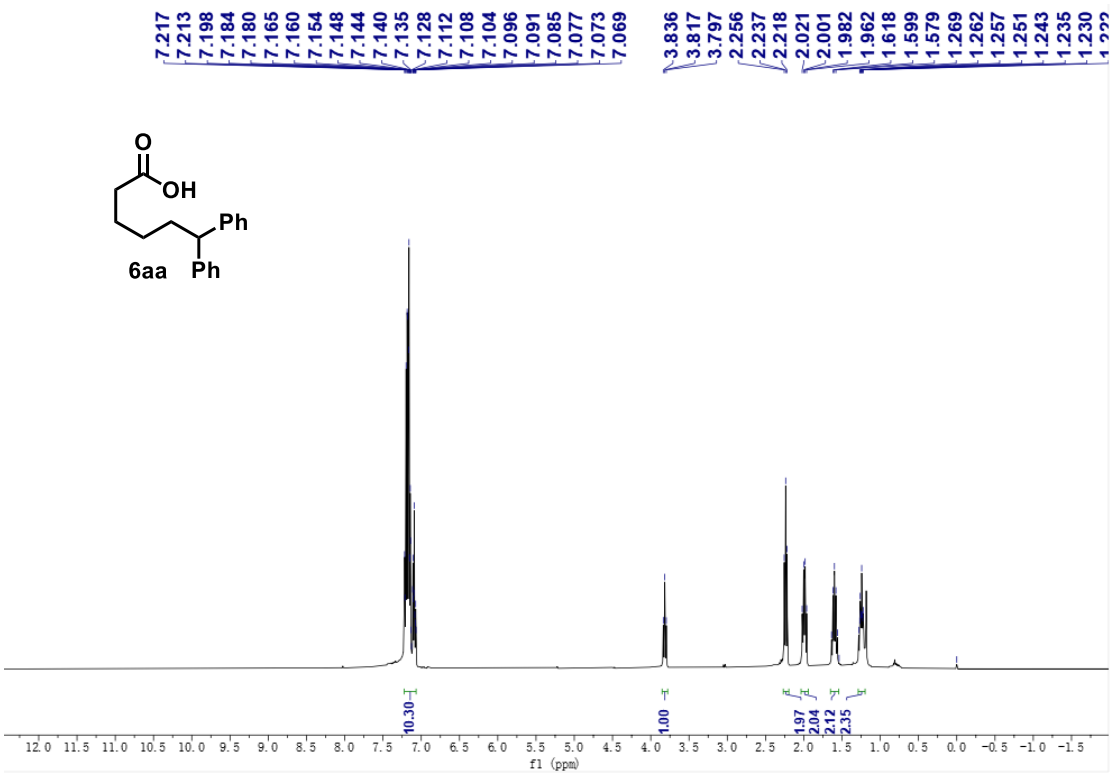




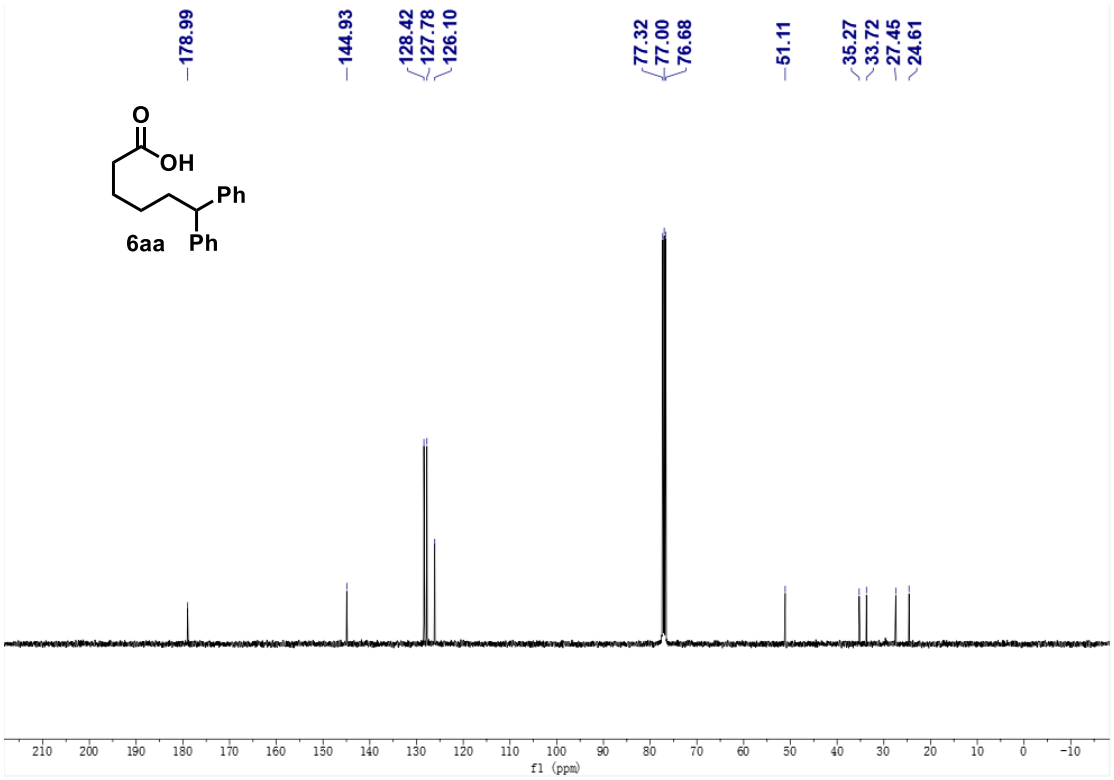
^{13}C NMR (100 MHz, $CDCl_3$) of **5aa**



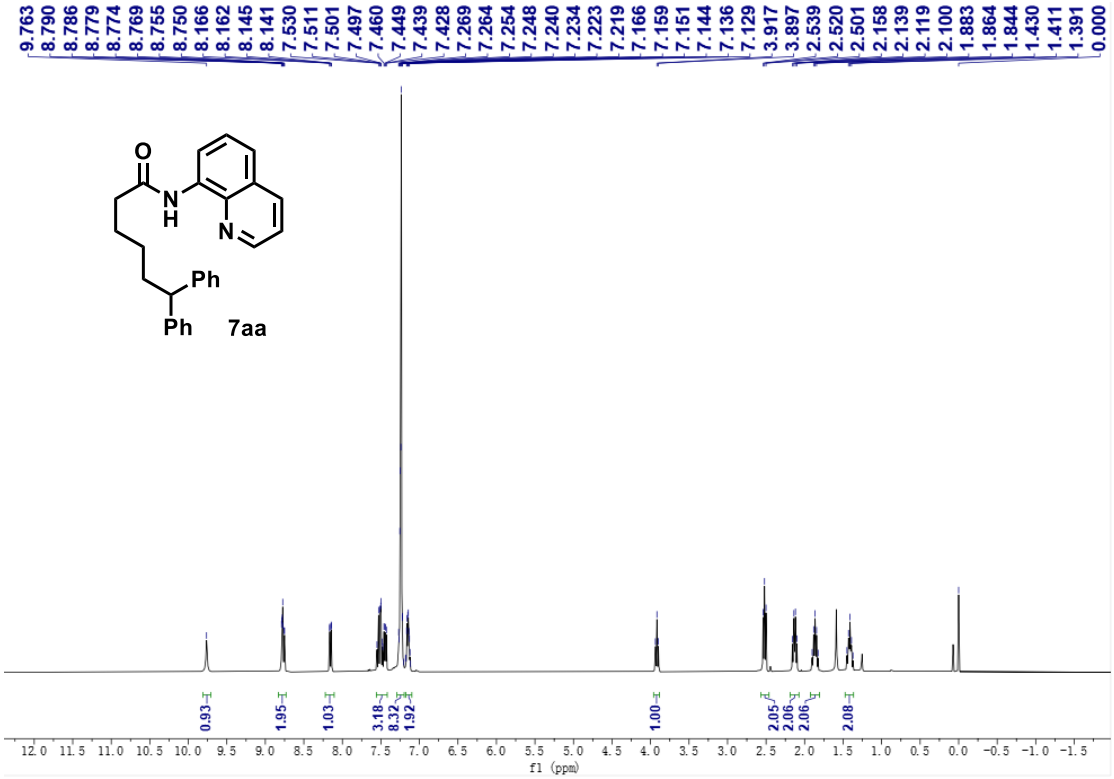
^{1}H NMR (400 MHz, $CDCl_3$) of 6**aa**



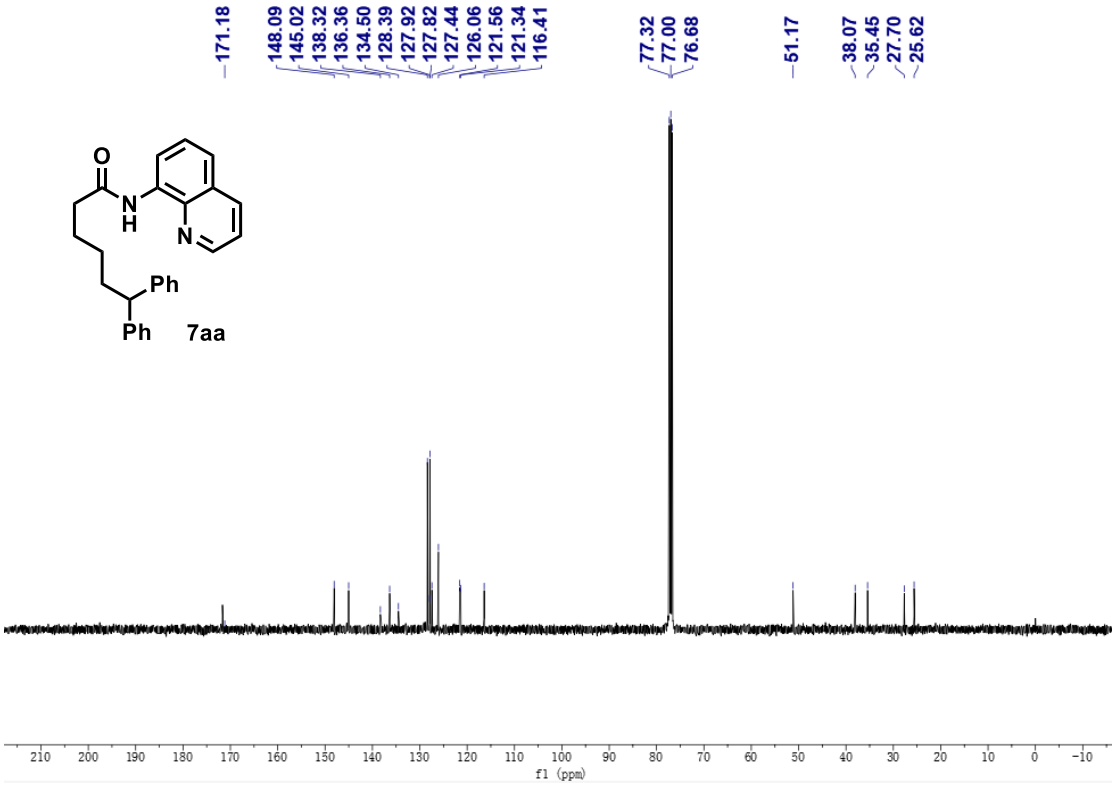
^{13}C NMR (100 MHz, $CDCl_3$) of **6aa**



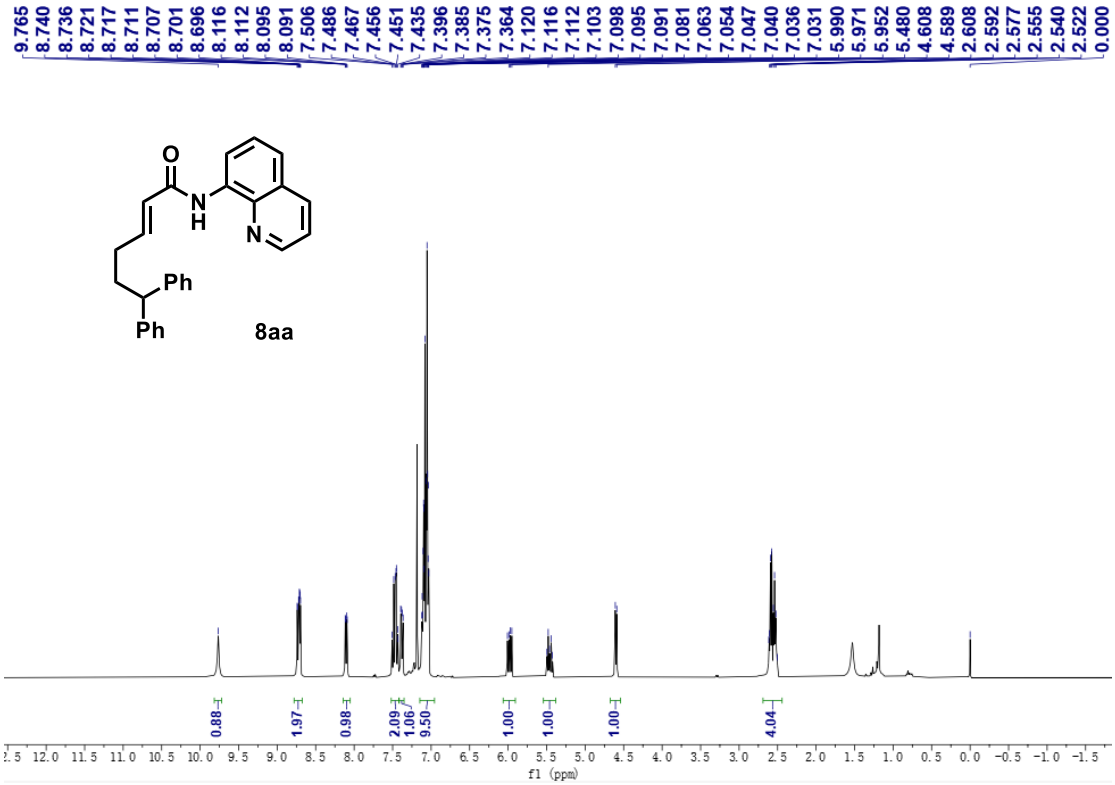
^{1}H NMR (400 MHz, $CDCl_3$) of 7**aa**



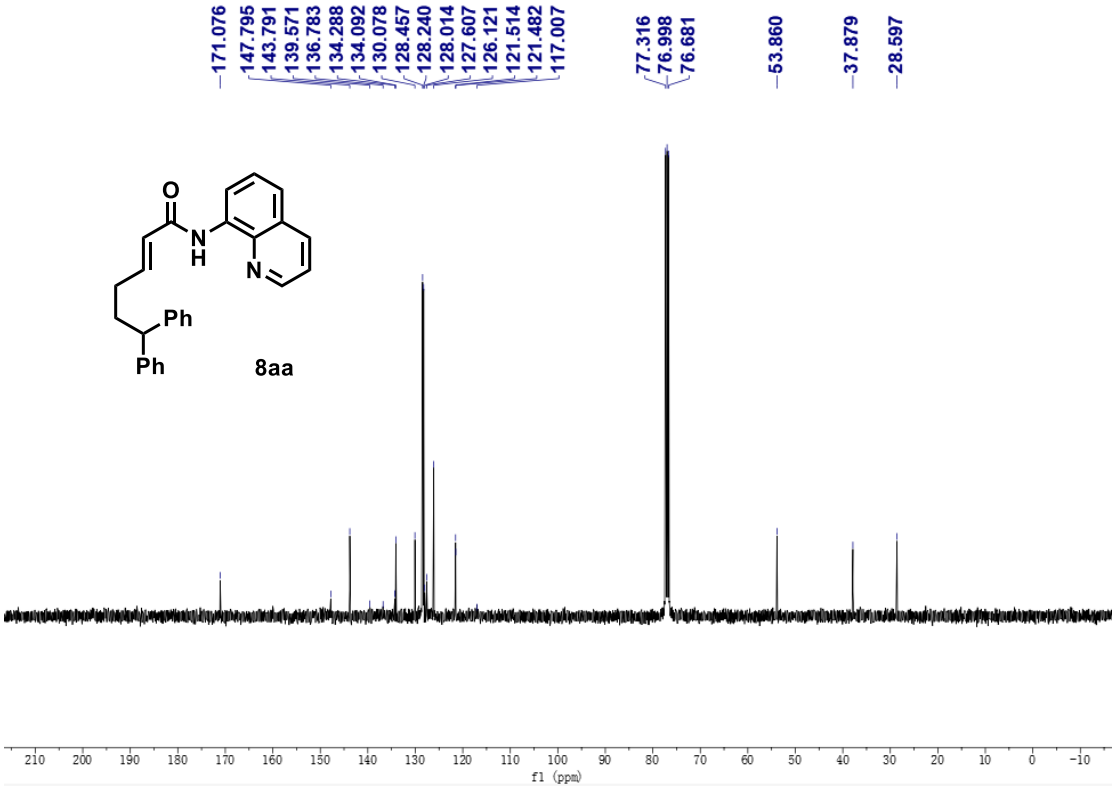
^{13}C NMR (100 MHz, $CDCl_3$) of **7aa**



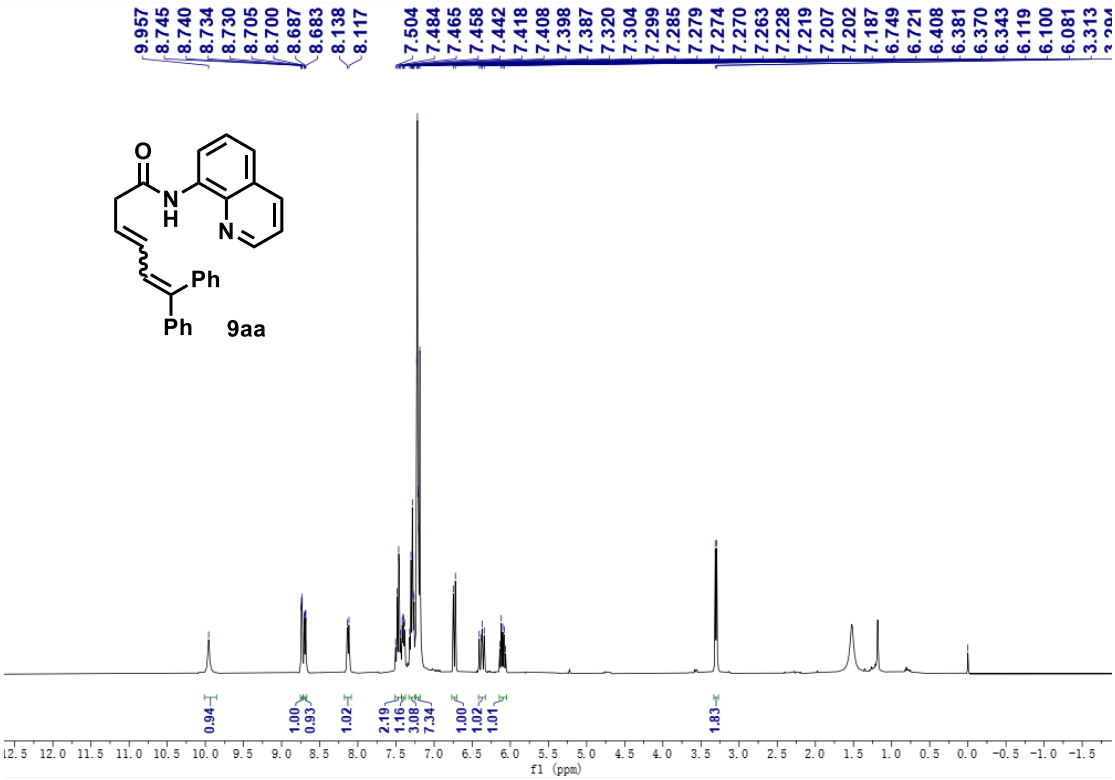
^{1}H NMR (400 MHz, $CDCl_3$) of 8**aa**



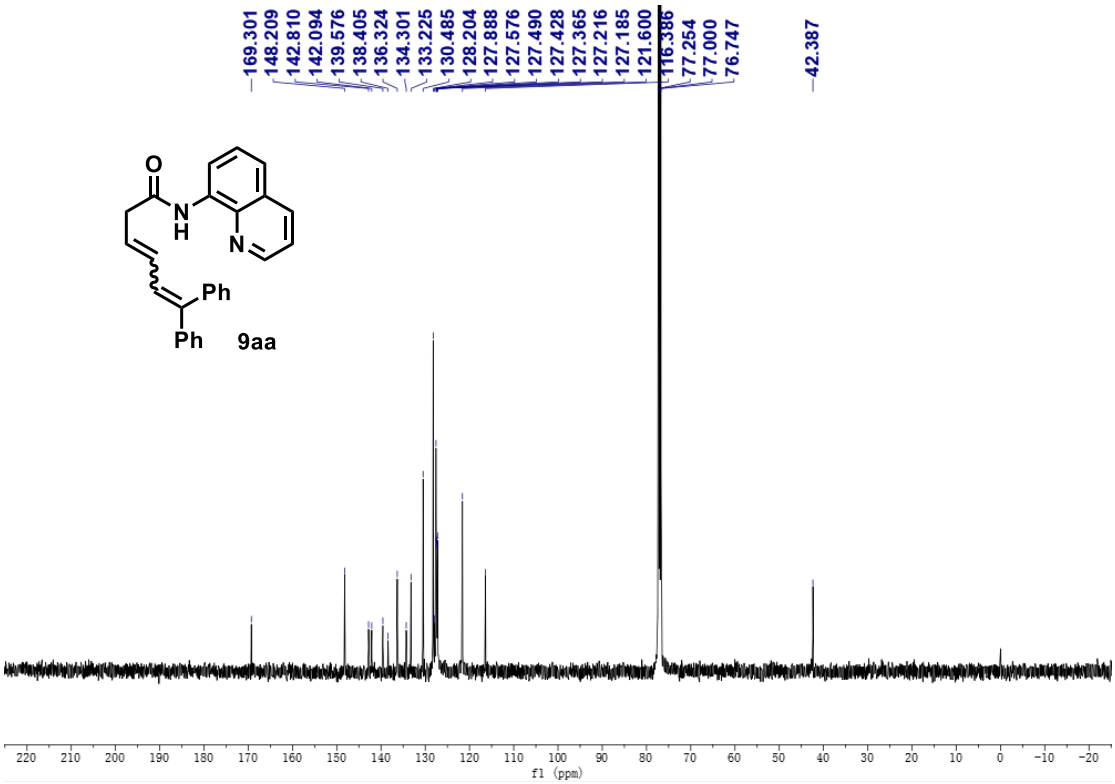
^{13}C NMR (100 MHz, $CDCl_3$) of **8aa**



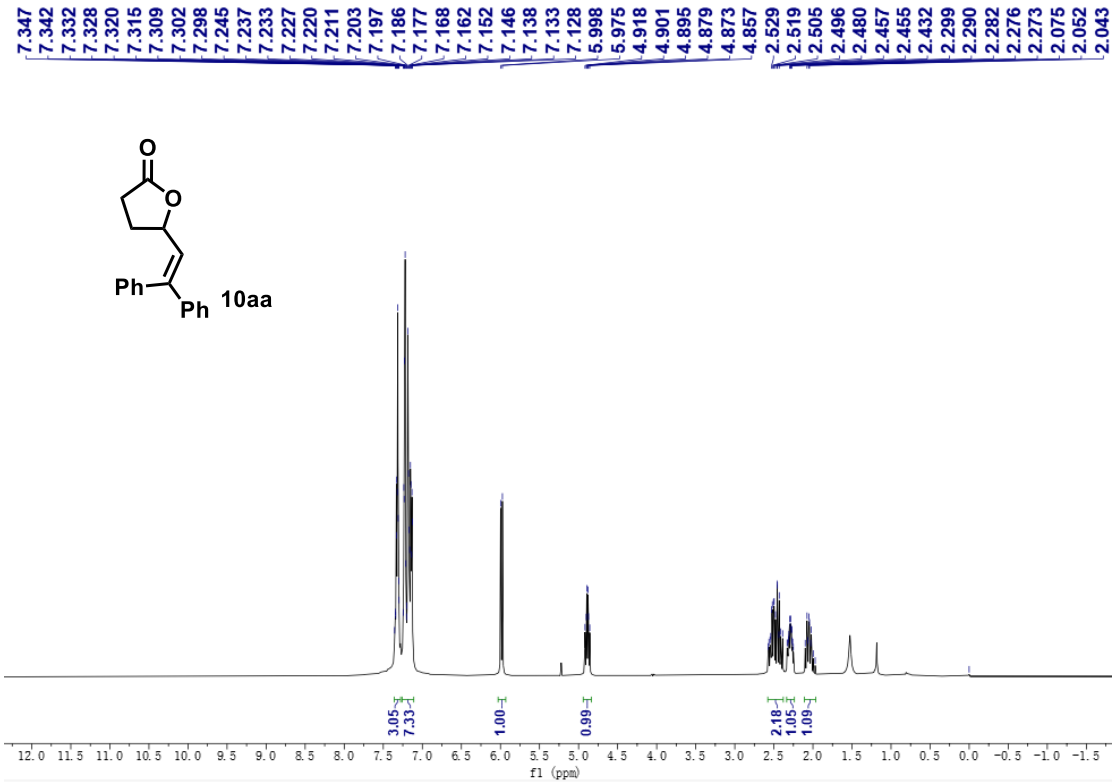
^{1}H NMR (400 MHz, $CDCl_3$) of **9aa**



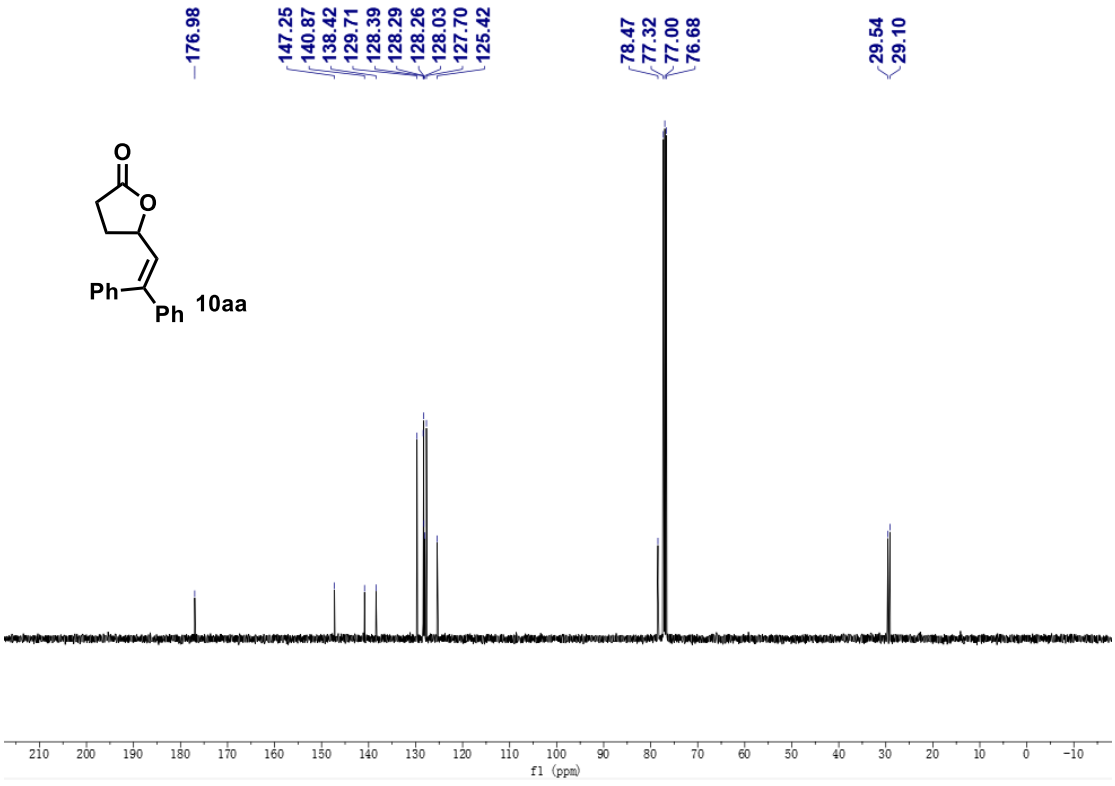
^{13}C NMR (100 MHz, $CDCl_3$) of **9aa**



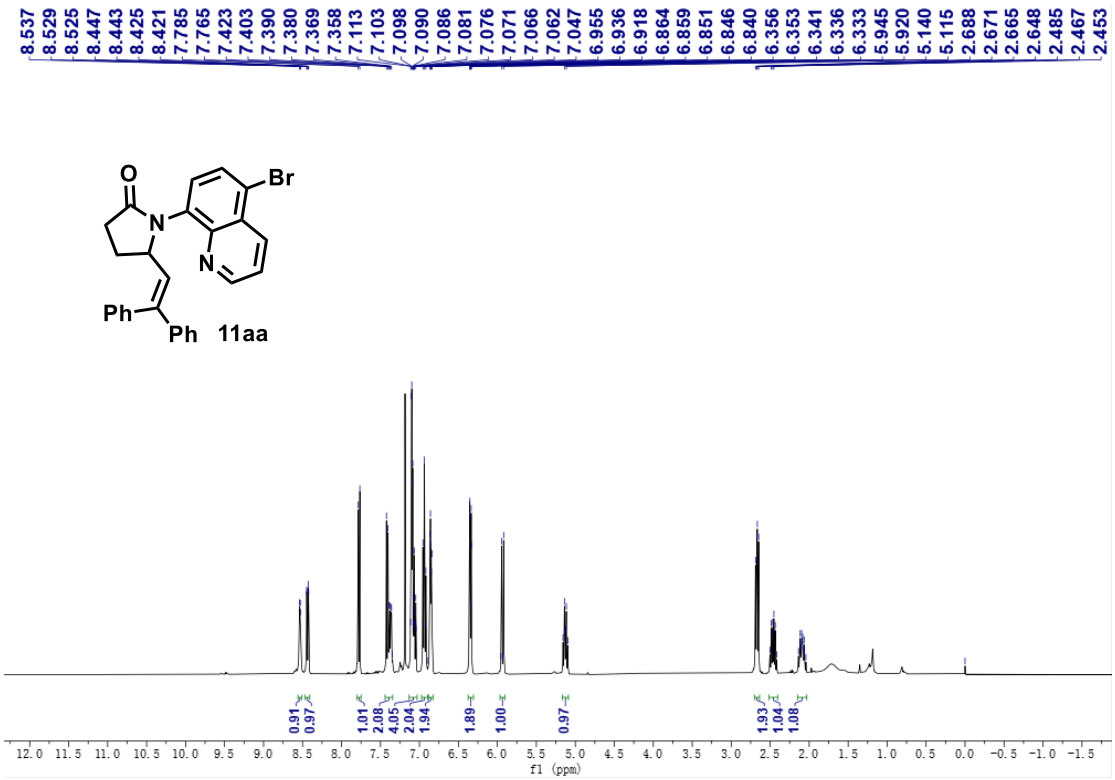
^{1}H NMR (400 MHz, $CDCl_3$) of 10**aa**



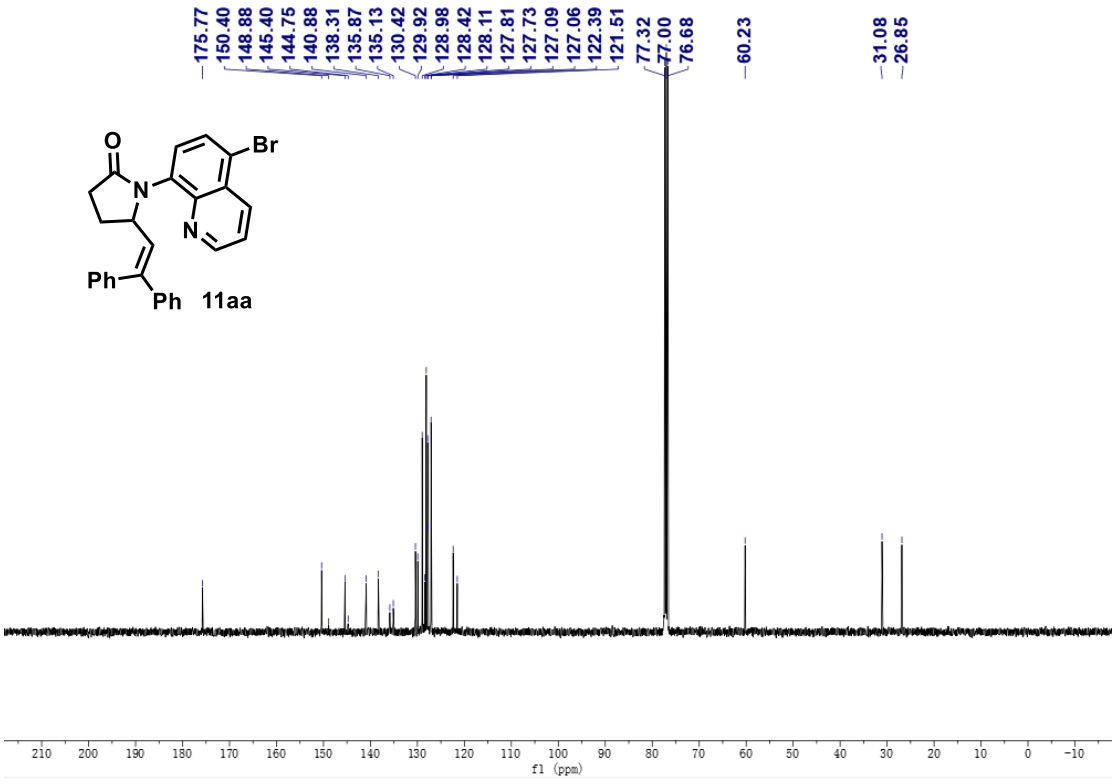
^{13}C NMR (100 MHz, $CDCl_3$) of **10aa**



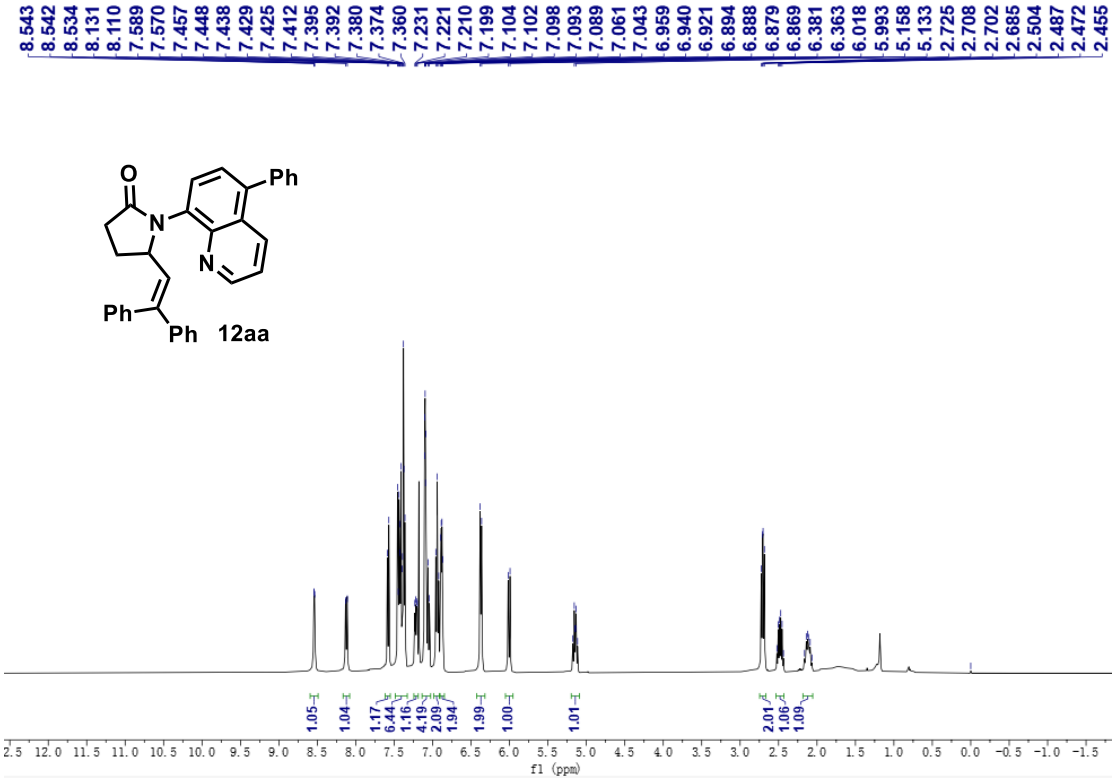
^{1}H NMR (400 MHz, $CDCl_3$) of 11**aa**



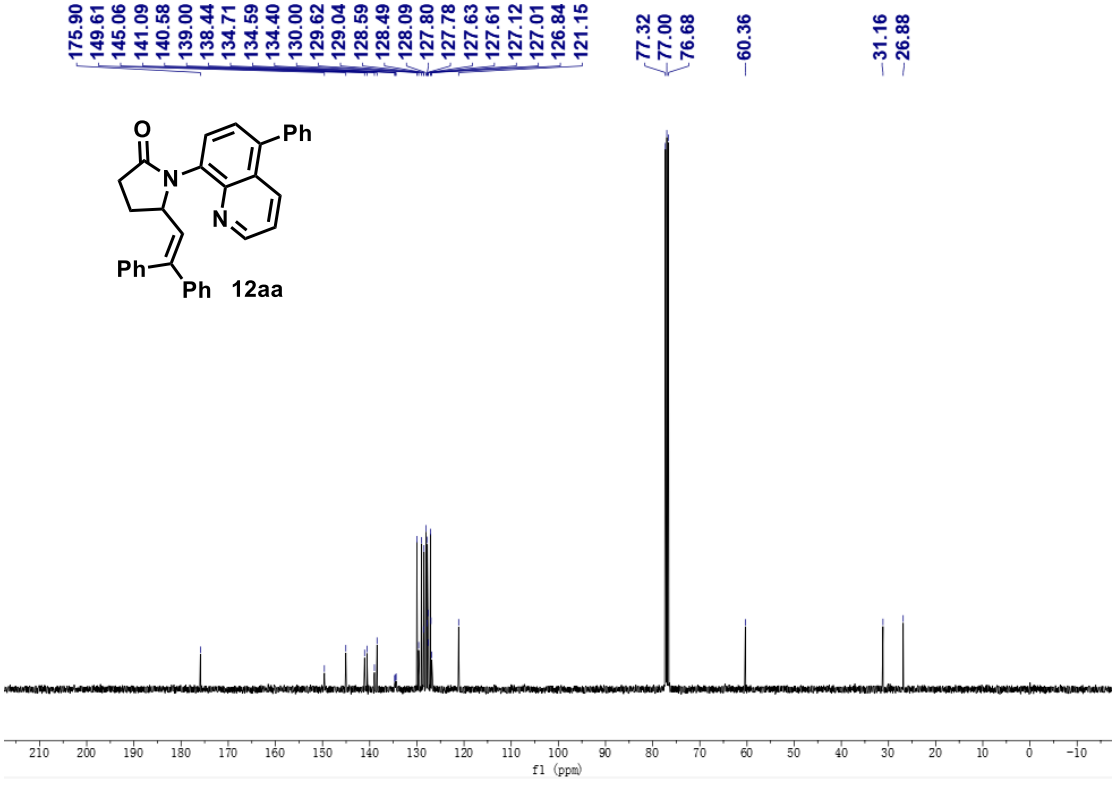
^{13}C NMR (100 MHz, $CDCl_3$) of **11aa**



^{1}H NMR (400 MHz, $CDCl_3$) of 12**aa**

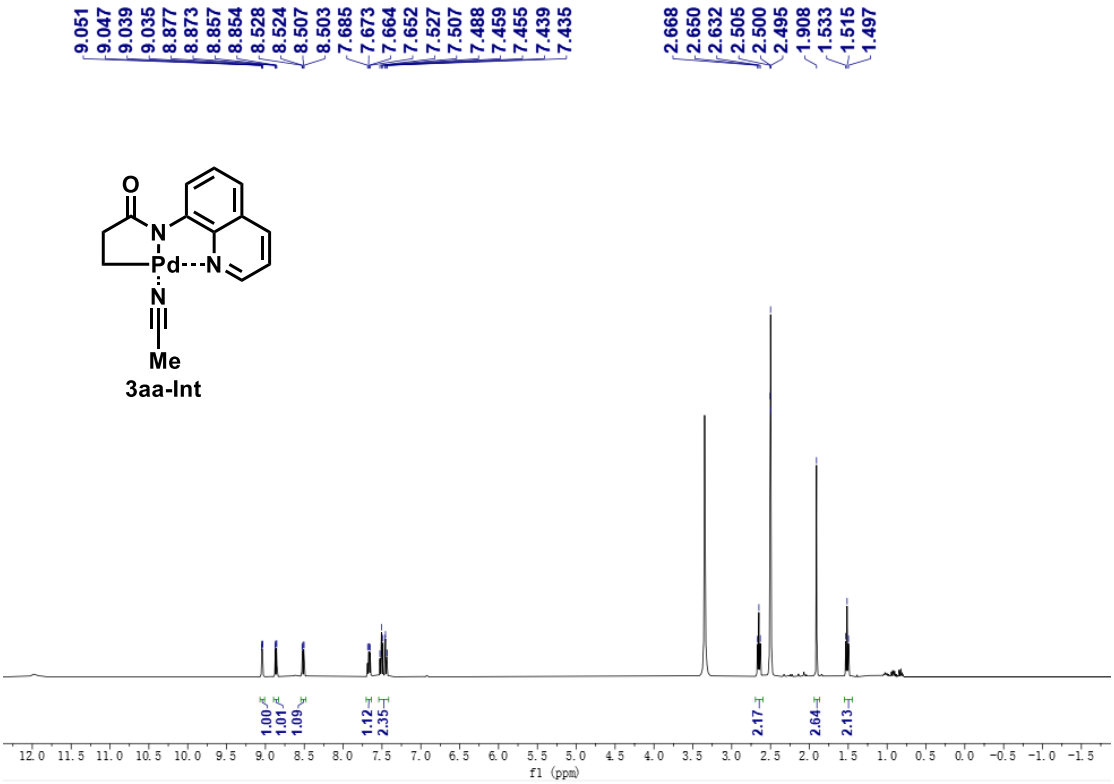


^{13}C NMR (100 MHz, $CDCl_3$) of **12aa**

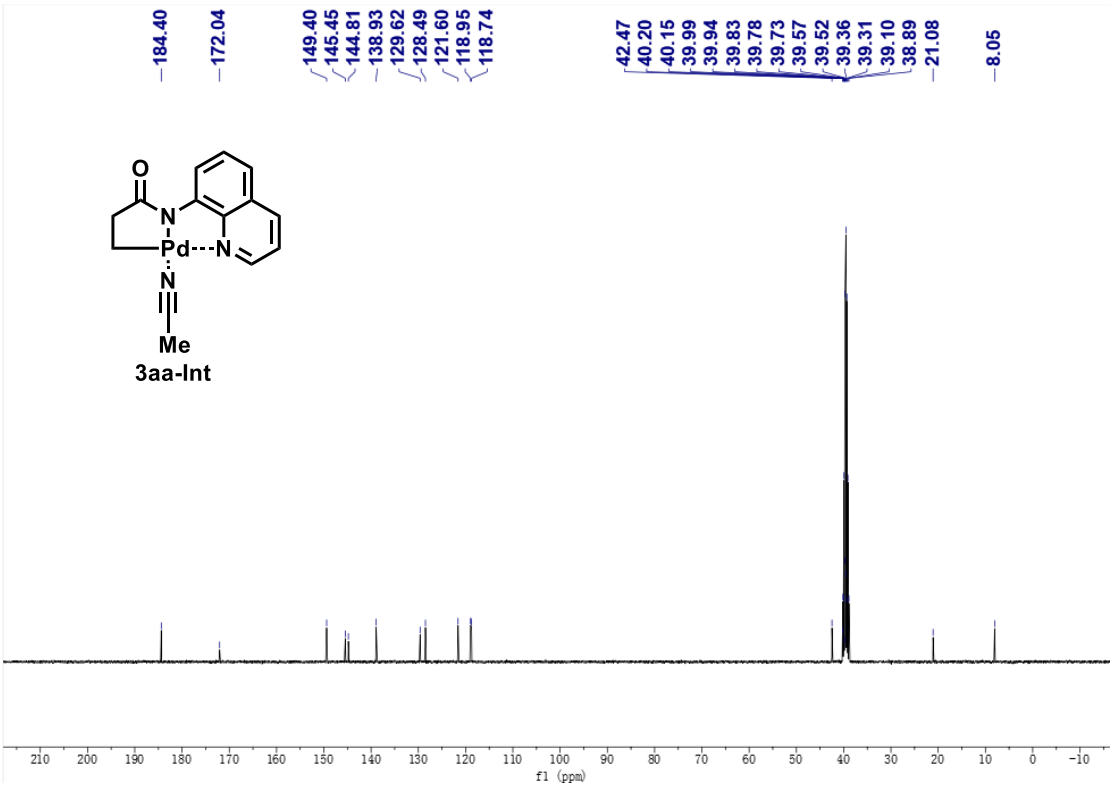


NMR spectra for mechanism studies：

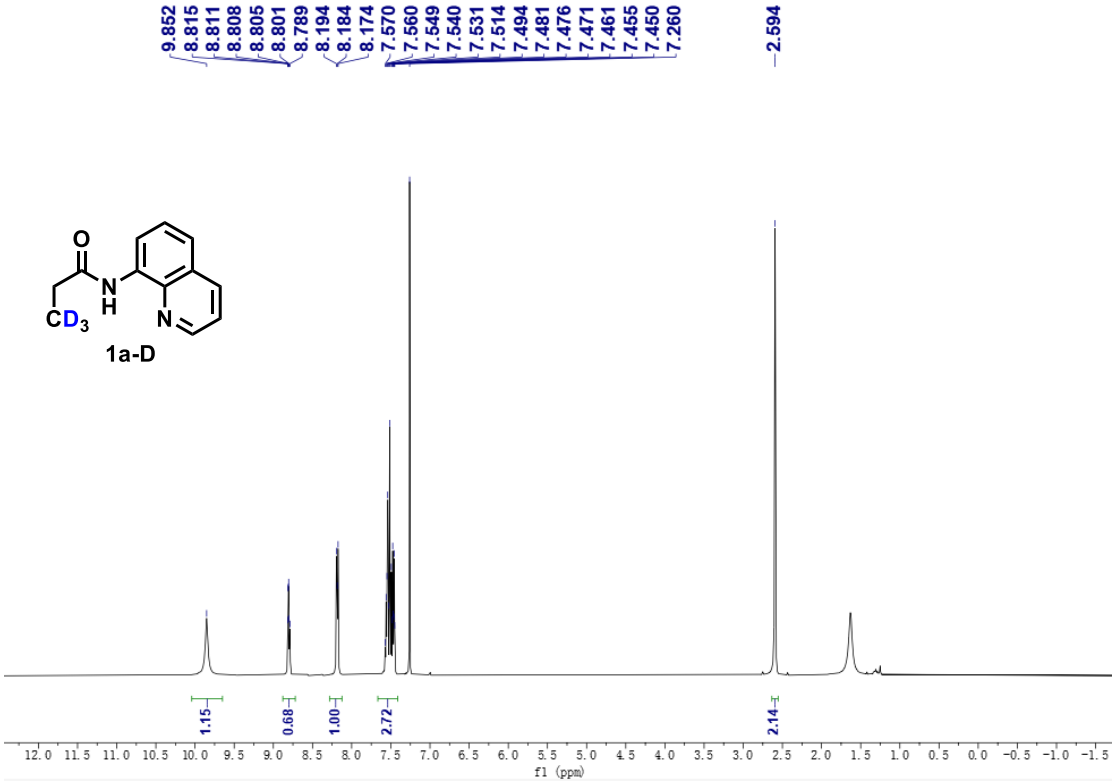
^{1}H NMR (DMSO-d_6 100 MHz) of **3aa-Int**



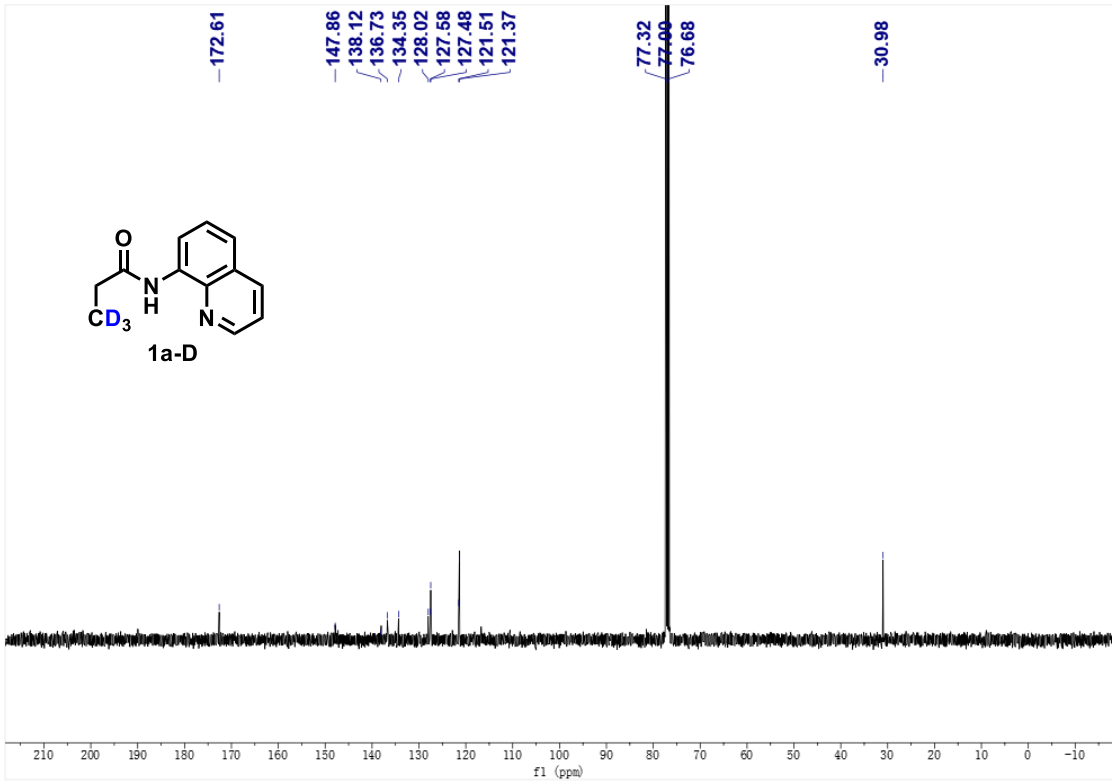
^{13}C NMR (DMSO-d_6 100 MHz) of **3aa-Int**



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



^{13}C NMR (100 MHz, $CDCl_3$) of **1a-D**



References and Notes

1. R. Shang, L. Ilies, A. Matsumoto and E. Nakamura, *J. Am. Chem. Soc.,* 2013, **135**, 6030–6032.
2. B. V. S. Reddy, L. R. Reddy and E. Corey, J. *Org. Lett*., 2006, **8**, 3391–3394.
3. S.-Y. Zhang, Q. Li, G. He, W. A. Nack and G. Chen, *J. Am. Chem. Soc*., 2013, **135**, 12135–12141.
4. S. Zhang, W. Sun, P. Cao, X. Dong, J. Liu and B. Wu, *J. Org. Chem*., 2016, **81**, 956–968.
5. N. Hoshiya, K. Takenaka, S. Shuto and J. Uenishi, *Org. Lett*., 2016, **18**, 48–51.
6. W.-W. Sun, P. Cao, R.-Q. Mei, Y. Li, Y.-L. Ma and B. Wu, *Org. Lett*., 2014, **16**, 480–483.
7. J. Chen, P. Guo, J. Zhang, J. Rong, W. Sun, Y. Jiang and T.-P. Loh, *Angew. Chem. Int. Ed*., 2019, **58**, 12674−12679.
8. C. Jiang, J. Wu, J. Han, K. Chen, Y. Qian, Z. Zhang and Y. Jiang, *Chem. Commun*., 2021, **57**, 5710−5713.
9. E. Y. Aguilera and M. S. Sanford, *Angew. Chem. Int. Ed*., 2021, **60**, 11227—11230.
10. H.-Q. Ni, M. K. Karunananda, T. Zeng, S. Yang, Z. Liu, K. N. Houk, P. Liu and K. M. Engle, *J. Am. Chem. Soc*., 2023, **145**, 12351–12359.
11. Y. Lv, W. Pu and L. Shi, *Org. Lett*., 2019, **21**, 6034–6039.
12. X. Ji, C. Shen, Y. Ni, Z.-Y. Si, Y. Wang, X. Zhi, Y. Zhao, H. Peng and L. Liu, *Angew. Chem. Int. Ed*. 2024, **63**, e202400805.
13. B. N. Babu and K. R. Chauhan, *Tetrahedron Lett*., 2009, **50**, 66-67.
14. M. L. Czyz, G. K. Weragoda, T. H. Horngren, T. U. Connell, D. Gomez, R. A. J. O'Hair and A. Polyzos, *Chem. Sci*., 2020, **11**, 2455-2463.
15. H. Lv, L.-J. Xiao, D. Zhao and Q.-L. Zhou, *Chem. Sci*., 2018, **9**, 6839-6843.
16. Y. Wang, Y. Wang, K. Jiang, Q. Zhang and D. Li, *Org. Biomol. Chem*. 2016, **14**, 10180-10184.
17. Y. Li, P. Zhang, Y.-J. Liu, Z.-X. Yu and B.-F. Shi, *ACS Catal*. 2020, **10**, 8212–8222.
18. D, Zhao, H. Luo, B. Chen, W. Chen, G. Zhang and Y. Yu, *J. Org. Chem*., 2018, **83**, 7860–7866.
19. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, ; M. A. Robb, J. R. C., G. Scalmani, V. Barone, ; G. A. Petersson, H. N., X. Li, M. Caricato, A. V. Marenich, ; J. Bloino, B. G. J., R. Gomperts, B. Mennucci, H. P. Hratchian, ; J. V. Ortiz, A. F. I., J. L. Sonnenberg, D. Williams-Young, ; F. Ding, F. L., F. Egidi, J. Goings, B. Peng, A. Petrone, ; T. Henderson, D. R., V. G. Zakrzewski, J. Gao, N. Rega, ; G. Zheng, W. L., M. Hada, M. Ehara, K. Toyota, R. Fukuda, ; J. Hasegawa, M. I., T. Nakajima, Y. Honda, O. Kitao, H. Nakai, ; T. Vreven, K. T., J. A. Montgomery, Jr., J. E. Peralta, ; F. Ogliaro, M. J. B., J. J. Heyd, E. N. Brothers, K. N. Kudin, ; V. N. Staroverov, T. A. K., R. Kobayashi, J. Normand, ; K. Raghavachari, A. P. R., J. C. Burant, S. S. Iyengar, ; J. Tomasi, M. C., J. M. Millam, M. Klene, C. Adamo, R. Cammi, ; J. W. Ochterski, R. L. M., K. Morokuma, O. Farkas, ; J. B. Foresman, D. J. Fox, Gaussian 16, Revision B.01. Gaussian, Inc., Wallingford, CT, 2016.
20. C. Lee, W. Yang and R. G. Parr, *Phys Rev B*., 1988, **37**, 785-789.
21. B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett*., 1989, **157**, 200-206.
22. A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648-5652.
23. E. Cancès, B. Mennucci and J. Tomasi, *J. Chem. Phys*., 1997, **107**, 3032-3041.
24. B. Mennucci and J. Tomasi, *J. Chem. Phys*. 1997, **106**, 5151-5158.
25. V. Barone and M. Cossi, *J. Phys. Chem. A*., 1998, **102**, 1995-2001.
26. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem*., Phys. 2005, **7**, 3297-3305.
27. C. Y. Legault, CYLview, 1.0b. Université de Sherbrooke, 2009, http://www.cylview.org