Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Phosphine-catalyzed [5+1] annulation of β′-acetoxy allenoates: A straightforward access to tetrahydroquinoline derivatives

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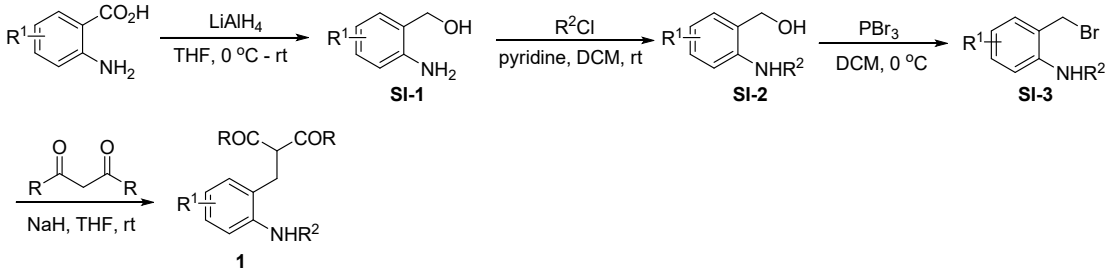
Table of Contents

1. General information

All the solvents were used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded on a Bruker AV 400 (400 MHz) spectrometer with $CDCl_3$ as solvent. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane as an internal reference. All shifts are reported in ppm as downfield from TMS as standard. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants J are reported in Hz. HRMS were obtained on an VG ZAB-HS mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Column chromatography was performed on silica gel 200-300 mesh. The dinucleophiles **1**[1] were prepared according to a previous procedure reported in the literature with slight modification. The allenoates **2** were synthesized according to the literature procedure[2].

2. General procedures

2.1 Preparation of the dinucleophiles 1



The synthesis of **SI-1**: Anthranilic acid (20 mmol) was dissolve in THF (80 mL) in a dried 250 mL round-bottomed flask, the solution was cooled in an ice bath, and $LiAlH_4$ (40 mmol, 2.0 equiv.) was added slowly in portions, then the mixture was stirred for 1 h at room temperature. After that, the reaction mixture was quenched carefully with 1.5 mL water, 1.5 mL 15% NaOH solution and 4.5 mL water successively, after stirring for 15 min, the resulting heterogeneous mixture was filtered through a Celite pad, and concentrated through rotary evaporation. The obtained crude product **SI-1** was used for the next step without further purification.

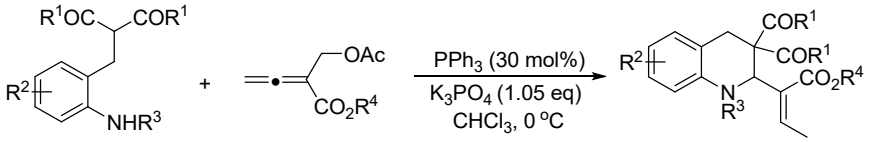
The synthesis of **SI-2**: The crude product **SI-1** (20 mmol)**)** was dissolve in CH_2Cl_2 (80 mL) in a dried 250 mL round-bottomed flask, then pyridine (40 mmol, 2.0 equiv.) was added in one portion at room temperature. To the solution was added TsCl (24 mmol, 1.2 equiv.) in portions, and then the mixture was stirred for 4 h at room temperature. The reaction was washed with 1N HCl and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated. The obtained crude product **SI-2** was used for the next step without further purification.

The synthesis of **SI-3**: **SI-2** (10 mmol) was dissolve in CH_2Cl_2 (75 mL) in a dried 250 mL round-bottomed flask, the solution was cooled in an ice bath, and PBr_3 (15 mmol, 1.5 equiv.) was added dropwise, the mixture was stirred for 1 h at this temperature. Water (15 mL) was added and the organic layer was separated, washed with water (2 × 30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo to give the residue. The residue was purified by recrystallization from CH_2Cl_2/n-hexane to afford **SI-3**.

The synthesis of dinucleophiles **1**: 1, 3-dicarbonyl compound (6.0 mmol, 1.2 equiv.) was dissolve in THF (30 mL) in a dried 100 mL round-bottomed flask, and NaH (7.5 mmol, 1.5 equiv.) was added in portions, the mixture was stirred for 5 min at room temperature, then the THF (8 mL) solution of **SI-3**

(5.0 mmol) was added dropwise, the mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with saturated NH_4Cl (15 mL), and the resulting residue was extracted with CH_2Cl_2, the organic phase was washed with brine, then dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc (2:1), giving the corresponding product **1**.

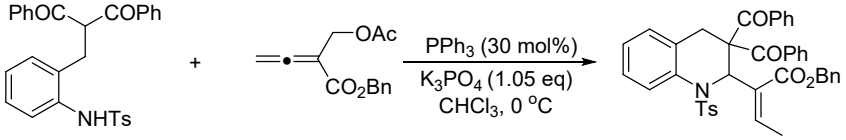
2.2 General procedure for the synthesis of tetrahydroquinolines 3:



1 **2** **3**

Dinucleophiles **1** (0.10 mmol), PPh_3 (0.03 mmol, 30 mol%), K_3PO_4 (0.105 mmol, 1.05 equiv) and $CHCl_3$ (1.0 mL) were added to a dry flask at 0 ° C. Then β'-acetoxy allenoates **2** (0.15 mmol, 1.5 equiv) was added. This solution was stirred at 0 ° C until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (PE: EA = 4:1) to afford products **3**.

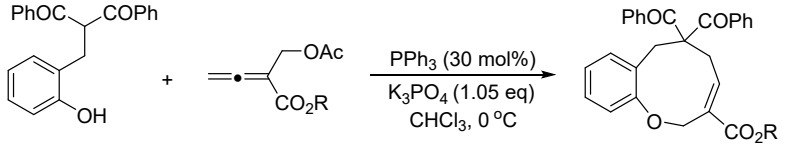
2.3 Procedure for the gram-scale synthesis of tetrahydroquinoline 3aa:



1a, 3 mmol **2a**, 4.5 mmol **3aa**, 1.38 g, 79% yield

Dinucleophiles **1a** (1.45 g, 3.0 mmol), PPh_3 (30 mol%, 236 mg, 0.9 mmol) and $CHCl_3$ (30 mL) were added to a dry 100 mL flask at 0 ℃. Then β'-acetoxy allenoate **2a** (1.5 equiv., 1.05 g, 4.5 mmol) was added. This solution was stirred at 0 ℃ until the complete consumption of **1a** monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (PE: EA = 4:1) on silica gel to afford product **3aa** as white solid (1.38 g, 79% yield).

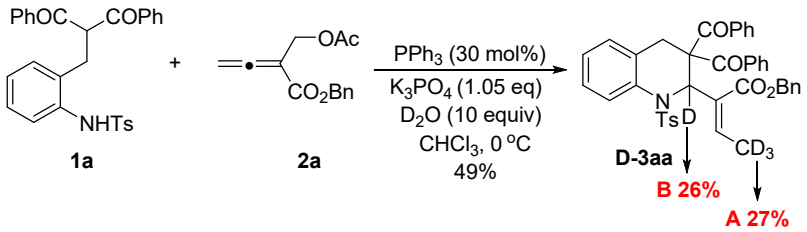
2.4 General procedure for the synthesis of 2,5,6,7-tetrahydrobenzo[b]oxonines 5:



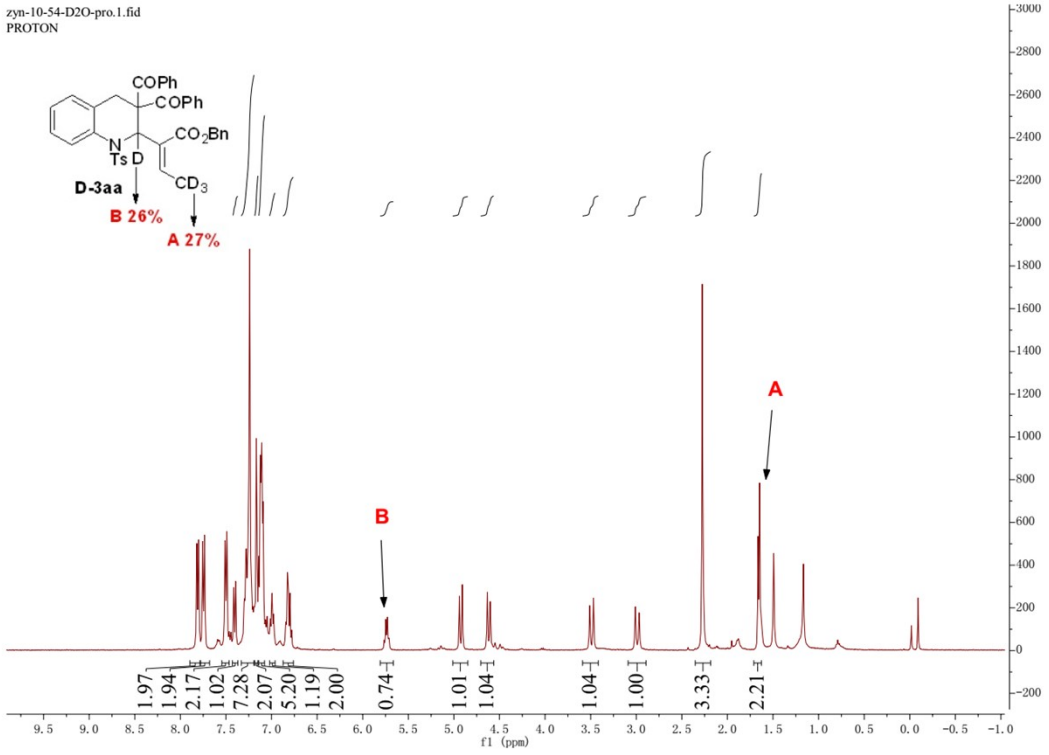
4a **2** **5**

Dinucleophile **4a** (0.10 mmol), PPh_3 (0.03 mmol, 30 mol%), K_3PO_4 (0.105 mmol, 1.05 equiv) and $CHCl_3$ (1.0 mL) were added to a dry flask at 0 ° C. Then β'-acetoxy allenoates **2** (0.15 mmol, 1.5 equiv) was added. This solution was stirred at 0 ° C until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (PE: EA = 4:1) to afford products **5**.

2.5 General procedure for the deuterium labeling experiment:

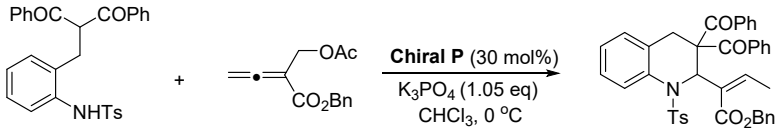


Dinucleophile **1a** (0.10 mmol), PPh_3 (0.03 mmol, 30 mol %), K_3PO_4 (0.105 mmol, 1.05 equiv) and $CHCl_3$ (2.0 mL) were added to a dry flask at 0 ° C. Then D_2O (10 equiv) and β'-acetoxy allenoate **2a** (0.15 mmol, 1.5 equiv) were added successively. This solution was stirred at 0 ° C until the complete consumption of the starting materials monitored by TLC. After the removal of the solvent, the residue was purified by flash column chromatography (PE: EA = 4:1) to afford products **D-3aa** (49% yield).

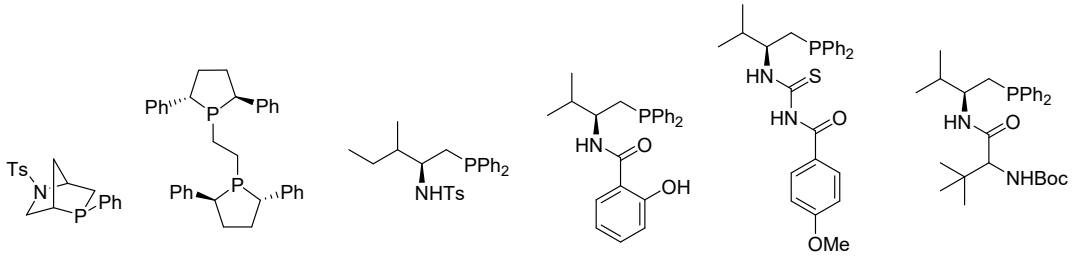


3. Asymmetric study

Table S1. Asymmetric study of the [5+1] annulation reactions[a]



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



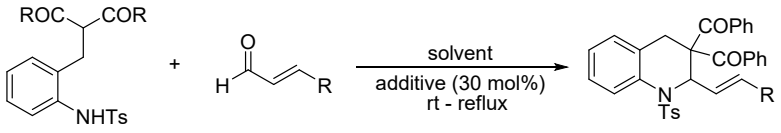
P1 **P2** **P3** **P4** **P5** **P6**

entry	cat.	yield (%)[b]	ee (%)[c]
1	**P1**	48	<5
2	**P2**	27	<5
3	**P3**	52	<5
4	**P4**	35	12
5	**P5**	44	43
6	**P6**	17	50

[a]Reactions were carried out with: **1a** (0.1 mmol), **2a** (0.15 mmol), chiral phosphorus catalysts (30 mol%), K_3PO_4 (0.105 mmol) and 1.0 mL $CHCl_3$ at 0 °C. [b]Isolated yield. [c]Determined by HPLC.

4. Mannich reactions study

Table S2. Mannich reactions of 1,5-dinucleophiles 1a with aldehydes 4[a]



1a, R = Ph
1b, R = Me

4a, R = CH_3
4b, R = Ph

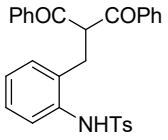
5

Entry[b]	**1**	**4**	Solvent	Additive	Yield of **5** (%)
1	**1a**	**4a**	EtOH	-	NR
2	**1a**	**4a**	EtOH	CF_3CO_2H	NR
3	**1a**	**4b**	toluene	-	NR
4	**1a**	**4b**	toluene	CF_3CO_2H	NR
5	**1b**	**4a**	EtOH	-	NR
6	**1b**	**4a**	EtOH	CF_3CO_2H	NR
7	**1b**	**4b**	toluene	-	NR
8	**1b**	**4b**	toluene	CF_3CO_2H	NR

[a]Reactions were carried out with: **1** (0.1 mmol), **4** (0.2 mmol), additive (30 mol%) and 1.0 mL solvent. [b]Each reaction was performed in a pair of parallel experiments at room temperature and reflux, respectively.

5. Characterization Data

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)phenyl)-4-methylbenzenesulfonamide (**1a**)



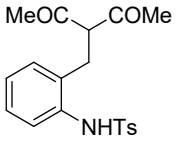
76% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 4H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 4H), 5.57 (t, *J* = 6.6 Hz, 1H), 2.89 (d, *J* = 6.6 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.5, 137.0, 135.2, 135.0, 134.1, 133.1, 130.6, 129.6, 129.1, 128.8, 127.9, 127.1, 126.6, 126.2, 58.6, 29.3, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{26}NO_4S$ 484.1577; Found 484.1574.

N-(2-(2-acetyl-3-oxobutyl)phenyl)-4-methylbenzenesulfonamide (**1b**)



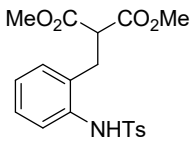
64% yield; Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.30 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 7.14 – 7.07 (m, 1H), 7.08 – 6.91 (m, 1H), 3.49 (s, 1H), 2.73 (d, *J* = 7.2 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 192.2, 144.1, 143.7, 137.1, 136.8, 134.9, 134.5, 134.1, 132.9, 130.2, 129.8, 129.7, 127.9, 127.5, 127.3, 127.3, 127.2, 127.2, 126.8, 126.4, 126.3, 106.4, 69.5, 29.6, 28.5, 28.1, 22.8, 21.6, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_4S$ 382.1083; Found 382.1081.

dimethyl 2-(2-(4-methylphenylsulfonamido)benzyl)malonate (**1c**)



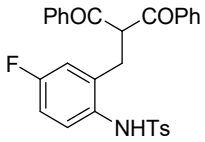
36% yield; Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.16 – 7.04 (m, 2H), 3.70 (s, 6H), 3.53 (t, *J* = 7.3 Hz, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 143.5, 137.1, 134.9, 132.0, 130.4, 129.6, 128.1, 127.1, 126.6, 126.2, 53.2, 53.0, 29.0, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_6S$ 392.1162; Found 392.1161.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4-fluorophenyl)-4-methylbenzenesulfonamide (**1d**)



58% yield; White solid

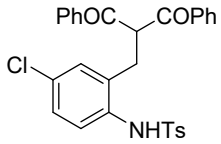
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.96 (s, 4H), 7.72 – 7.29 (m, 8H), 7.36 – 6.99 (m, 3H), 7.08 – 6.65 (m, 2H), 5.64 (s, 1H), 2.89 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 162.1, 159.7, 143.7, 136.6, 135.1, 134.2, 130.8, 129.7, 129.1, 128.7, 127.2, 117.1 (d, J = 22.0 Hz), 114.8 (d, J = 21.8 Hz), 58.1, 29.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.38 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}FNO_4S$ 502.1483; Found 502.1483.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4-chlorophenyl)-4-methylbenzenesulfonamide (**1e**)



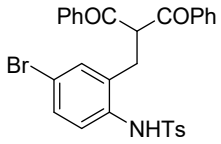
61% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.03 – 7.82 (m, 4H), 7.72 – 7.52 (m, 4H), 7.50 – 7.29 (m, 4H), 7.20 – 6.96 (m, 5H), 5.51 (s, 1H), 2.81 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 143.7, 136.8, 135.0, 134.9, 134.3, 133.7, 131.8, 130.2, 129.7, 129.2, 128.8, 128.1, 127.8, 127.1, 58.4, 29.1, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}ClNO_4S$ 518.1187; Found 518.1187.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4-bromophenyl)-4-methylbenzenesulfonamide (**1f**)



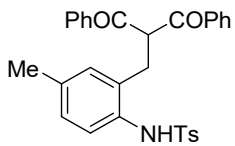
60% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.95 (d, J = 7.7 Hz, 4H), 7.65 (d, J = 7.9 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.6 Hz, 4H), 7.35 (s, 1H), 7.25 (s, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.59 (t, J = 6.7 Hz, 1H), 2.86 (d, J = 6.7 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 143.8, 136.7, 135.2, 135.0, 134.3, 133.3, 131.0, 129.8, 129.2, 128.8, 127.9, 127.1, 119.7, 58.3, 29.2, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}BrNO_4S$ 562.0682; Found 562.0679.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4-methylphenyl)-4-methylbenzenesulfonamide (**1g**)



65% yield; White solid

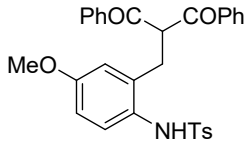
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.83 – 7.66 (m, 4H), 7.43 (d, J = 8.0 Hz, 2H), 7.40 – 7.33

(m, 2H), 7.24 (t, *J* = 7.7 Hz, 4H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.35 (t, *J* = 6.7 Hz, 1H), 2.64 (d, *J* = 6.7 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 143.3, 137.1, 136.5, 135.3, 134.0, 133.3, 132.2, 131.0, 129.5, 129.0, 128.7, 128.6, 127.1, 126.8, 58.8, 29.4, 21.5, 20.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{28}NO_4S$ 498.1734; Found 498.1730.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (**1h**)



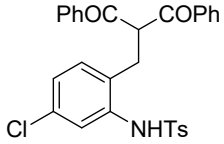
84% yield; White solid

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (d, *J* = 3.8 Hz, 1H), 8.13 – 7.92 (m, 4H), 7.72 – 7.55 (m, 4H), 7.50 (t, *J* = 7.6 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 6.55 (s, 2H), 6.16 (td, *J* = 7.2, 2.6 Hz, 1H), 3.53 (s, 3H), 3.26 (dd, *J* = 7.3, 3.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 196.5, 158.1, 143.5, 138.6, 138.0, 136.1, 134.3, 130.1, 129.5, 129.3, 128.9, 127.7, 127.3, 116.8, 112.6, 55.5, 31.7, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{28}NO_5S$ 514.1683; Found 514.1680.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-5-chlorophenyl)-4-methylbenzenesulfonamide (**1i**)



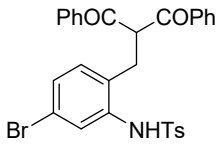
62% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.11 – 7.83 (m, 4H), 7.79 – 7.54 (m, 4H), 7.53 – 7.35 (m, 5H), 7.27 – 6.98 (m, 4H), 5.46 (s, 1H), 2.85 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 143.7, 136.8, 136.3, 135.0, 134.3, 133.3, 131.4, 130.7, 129.7, 129.2, 128.8, 127.1, 126.3, 125.5, 58.7, 28.8, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}ClNO_4S$ 518.1187; Found 518.1186.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-5-bromophenyl)-4-methylbenzenesulfonamide (**1j**)



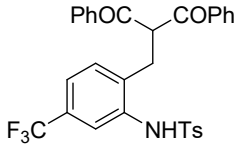
57% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 4H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.64 – 7.55 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.14 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.50 (t, *J* = 6.7 Hz, 1H), 2.86 (d, *J* = 6.6 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 143.8, 136.8, 136.5, 135.0, 134.3, 131.7, 131.4, 129.7, 129.3, 129.2, 128.8, 128.5, 127.1, 121.1, 58.6, 28.9, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{25}BrNO_4S$ 562.0682; Found 562.0677.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (**1k**)



58% yield; White solid

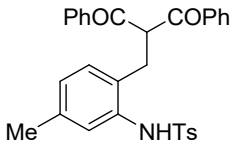
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.78 – 7.66 (m, 4H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.24 (t, *J* = 7.7 Hz, 4H), 7.14 – 7.07 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 5.33 (t, *J* = 6.7 Hz, 1H), 2.77 (d, *J* = 6.6 Hz, 2H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 144.0, 136.6, 136.5, 135.8, 135.0, 134.3, 131.2, 129.7, 129.2, 128.8, 127.2, 123.5 (q, *J* = 272.3 Hz), 122.7 (q, *J* = 3.6 Hz), 122.6 (q, *J* = 3.8 Hz), 58.4, 29.3, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74 (s, 3F).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{25}F_3NO_4S$ 552.1451; Found 552.1447.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-5-methylphenyl)-4-methylbenzenesulfonamide (**1l**)



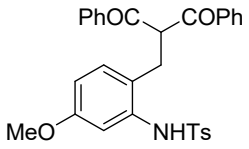
67% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 4H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.24 (s, 1H), 7.19 – 7.06 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.55 (d, *J* = 6.9 Hz, 1H), 2.83 (d, *J* = 6.6 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 143.4, 137.8, 137.1, 135.2, 134.7, 134.1, 130.2, 129.9, 129.5, 129.1, 128.8, 127.5, 127.1, 126.9, 58.9, 28.9, 21.5, 21.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{28}NO_4S$ 498.1734; Found 498.1732.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-5-methoxyphenyl)-4-methylbenzenesulfonamide (**1m**)



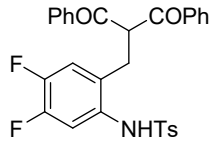
71% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 4H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 4H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.81 – 6.68 (m, 1H), 6.45 (dd, *J* = 8.4, 2.7 Hz, 1H), 5.24 (t, *J* = 8.1 Hz, 1H), 3.50 (s, 3H), 2.61 (d, *J* = 6.6 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 158.9, 143.4, 137.1, 136.0, 135.2, 134.1, 131.0, 129.6, 129.1, 128.8, 127.2, 124.2, 113.0, 110.2, 59.1, 55.4, 28.6, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{27}NNaO_5S$ 536.1502; Found 536.1499.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4,5-difluorophenyl)-4-methylbenzenesulfonamide (**1n**)



54% yield; White solid

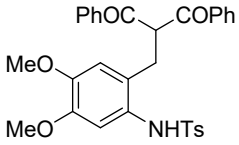
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 4H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.27 – 7.12 (m, 3H), 6.99 (t, *J* = 9.6 Hz, 1H), 5.51 (t, *J* = 6.7 Hz, 1H), 2.80 (d, *J* = 6.7 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 150.1 (d, *J* = 13.2 Hz), 149.6 (d, *J* = 13.1 Hz), 147.6 (d, *J* = 13.4 Hz), 147.2 (d, *J* = 12.9 Hz), 144.0, 136.5, 135.0, 134.3, 131.4 (d, *J* = 3.2 Hz), 131.3 (d, *J* = 3.2 Hz), 129.8, 129.2, 128.7, 127.1, 118.4 (d, *J* = 17.7 Hz), 115.7 (d, *J* = 19.5 Hz), 58.3, 28.9, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.69 (dt, *J* = 21.2, 10.0 Hz, 1F), -139.03 (dt, *J* = 19.1, 9.0 Hz, 1F).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{24}F_2NO_4S$ 520.1389; Found 520.1385.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (**1o**)



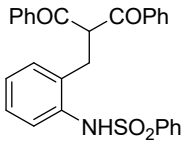
65% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 4H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.73 (s, 1H), 6.57 (s, 1H), 5.51 (t, *J* = 6.7 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 2.84 (d, *J* = 6.7 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 148.0, 147.7, 143.5, 136.8, 135.5, 134.0, 129.5, 129.0, 128.8, 127.3, 127.3, 126.4, 112.9, 111.0, 58.8, 56.0, 55.8, 29.6, 21.5.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{29}NNaO_6S$ 566.1608; Found 566.1604.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)phenyl)benzenesulfonamide (**1p**)



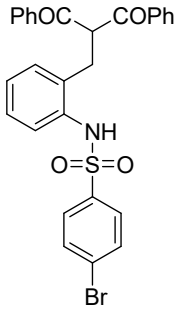
43% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 4H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.09 (m, 8H), 7.04 – 6.84 (m, 3H), 5.29 (t, *J* = 6.6 Hz, 1H), 2.63 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 140.0, 135.2, 134.9, 134.1, 133.0, 132.7, 130.3, 129.1, 129.0, 128.8, 128.0, 127.1, 126.6, 126.4, 58.9, 29.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{24}NO_4S$ 470.1421; Found 470.1416.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)phenyl)-4-bromobenzenesulfonamide (**1q**)



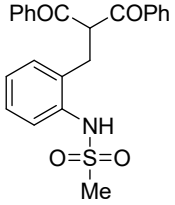
51% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 8.08 – 7.79 (m, 4H), 7.68 – 7.55 (m, 4H), 7.55 – 7.29 (m, 6H), 7.29 – 6.98 (m, 4H), 5.51 (s, 1H), 2.87 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 139.1, 135.0, 134.6, 134.3, 132.7, 132.2, 130.5, 129.2, 128.8, 128.7, 128.1, 127.6, 126.7, 126.1, 58.9, 29.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{23}BrNO_4S$ 548.0526; Found 548.0525.

N-(2-(2-benzoyl-3-oxo-3-phenylpropyl)phenyl)methanesulfonamide (**1r**)



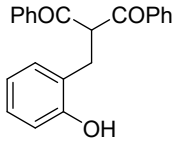
56% yield; White solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 4H), 7.69 – 7.54 (m, 2H), 7.53 – 7.34 (m, 6H), 7.17 (p, *J* = 7.5 Hz, 2H), 5.81 (t, *J* = 6.8 Hz, 1H), 3.42 (d, *J* = 6.9 Hz, 2H), 3.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 135.3, 135.2, 134.2, 132.4, 131.0, 129.2, 128.8, 128.2, 126.5, 125.0, 58.2, 39.9, 30.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}NO_4S$ 408.1264; Found 408.1262.

2-(2-hydroxybenzyl)-1,3-diphenylpropane-1,3-dione (**4a**)

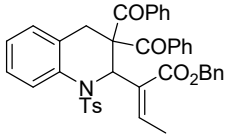


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.39 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.93 – 6.82 (m, 2H), 5.82 – 5.53 (m, 1H), 3.34 (d, *J* = 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 154.5, 135.4, 134.1, 131.1, 129.1, 128.8, 128.6, 125.1, 120.9, 117.5, 117.4, 58.2, 29.4.

HRMS (ESI): m/z calcd for $C_{34}H_{28}NaO_5$ ($[M+Na]^+$): 539.1829; found: 539.1824.

(Z)-benzyl 2-(3,3-dibenzoyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3aa**)



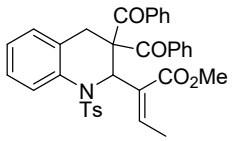
51 mg, 76% yield; white solid; mp 139-141°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.25 (d, *J* = 3.6 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 6H), 7.09 (d, *J* = 6.7 Hz, 1H), 6.97 – 6.82 (m, 2H), 5.83 (q, *J* = 7.2 Hz, 1H), 5.02 (d, *J* = 12.7 Hz, 1H), 4.71 (d, *J* = 12.7 Hz, 1H), 3.59 (d, *J* = 16.5 Hz, 1H), 3.09 (d, *J* = 16.5 Hz, 1H), 2.36 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 196.1, 165.8, 143.6, 141.3, 137.8, 136.8, 136.3, 136.0, 135.9, 133.4, 132.9, 132.1, 129.5, 129.4, 129.4, 128.9, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 127.4, 124.4, 123.2, 119.8, 66.9, 66.1, 58.6, 33.2, 21.6, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{36}NO_6S$ 670.2258; Found 670.2255.

(Z)-methyl 2-(3,3-dibenzoyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ab**)



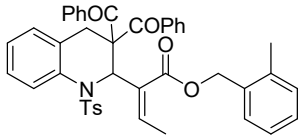
48 mg, 80% yield; white solid; mp 154-157°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.9 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.45 (dd, *J* = 10.2, 7.9 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.31 – 7.25 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.13 – 7.01 (m, 1H), 6.84 (d, *J* = 5.8 Hz, 2H), 5.92 (q, *J* = 7.2 Hz, 1H), 3.67 (d, *J* = 16.6 Hz, 1H), 3.24 (s, 3H), 3.06 (d, *J* = 4.2 Hz, 1H), 2.40 (s, 3H), 1.84 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 195.8, 165.9, 143.8, 142.0, 137.8, 137.1, 136.3, 136.2, 133.4, 132.8, 131.8, 129.7, 129.5, 128.7, 128.6, 128.3, 128.1, 127.4, 123.4, 122.9, 119.1, 66.3, 58.9, 50.9, 33.0, 21.6, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{32}NO_6S$ 594.1945; Found 594.1941.

(Z)-2-methylbenzyl 2-(3,3-dibenzoyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ac**)



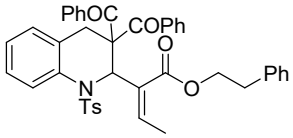
47 mg, 69% yield; white solid; mp 110-113°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.29 (d, *J* = 4.2 Hz, 2H), 7.26 – 7.15 (m, 8H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.97 – 6.87 (m, 2H), 5.84 (q, *J* = 7.1 Hz, 1H), 5.08 (d, *J* = 12.8 Hz, 1H), 4.74 (d, *J* = 12.7 Hz, 1H), 3.62 (d, *J* = 16.5 Hz, 1H), 3.12 (d, *J* = 16.5 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 196.1, 165.8, 143.6, 141.1, 137.8, 136.9, 136.6, 136.3, 136.0, 133.9, 133.3, 132.9, 132.1, 130.1, 129.5, 129.4, 129.4, 129.0, 128.9, 128.5, 128.4, 128.1, 127.9, 127.4, 126.0, 124.4, 123.2, 119.7, 66.9, 64.4, 58.6, 33.2, 21.6, 18.9, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{38}NO_6S$ 684.2414; Found 684.2410.

(Z)-phenethyl 2-(3,3-dibenzoyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ad**)



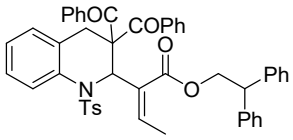
55 mg, 80% yield; white solid; mp 122-124°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 8.8 Hz, 2H), 7.24 (q, *J* = 15.7, 12.1 Hz, 12H), 7.14 – 7.06 (m, 1H), 6.97 – 6.84 (m, 2H), 5.76 (q, *J* = 7.3 Hz, 1H), 4.16 (q, *J* = 8.4 Hz, 1H), 3.79 (q, *J* = 8.8, 8.4 Hz, 1H), 3.64 (d, *J* = 16.5 Hz, 1H), 2.99 (d, *J* = 16.5 Hz, 1H), 2.78 (h, *J* = 6.4 Hz, 2H), 2.37 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 196.0, 165.8, 143.6, 141.5, 138.0, 137.9, 137.0, 136.4, 136.2, 133.4, 132.8, 131.9, 129.6, 129.4, 129.1, 128.8, 128.6, 128.5, 128.4, 128.0, 127.4, 126.5, 124.6, 123.3, 120.1, 67.2, 65.2, 58.7, 34.8, 33.2, 21.6, 15.9.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{37}NNaO_6S$ 706.2234; Found 706.2229.

(Z)-2,2-diphenylethyl 2-(3,3-dibenzoyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ae**)



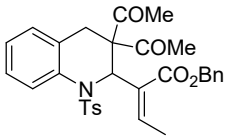
57 mg, 75% yield; white solid; mp 153-155°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.42 (q, *J* = 6.5 Hz, 2H), 7.36 – 7.25 (m, 13H), 7.25 – 7.20 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.85 (m, 2H), 5.65 (q, *J* = 7.2 Hz, 1H), 4.58 (dd, *J* = 10.4, 7.1 Hz, 1H), 4.45 – 4.09 (m, 2H), 3.60 (d, *J* = 16.5 Hz, 1H), 3.03 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H), 1.43 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 196.1, 166.2, 143.5, 141.4, 141.3, 140.9, 137.8, 136.9, 136.3, 136.1, 133.4, 132.9, 131.7, 129.6, 129.3, 129.3, 128.9, 128.6 (2C), 128.4 (2C), 128.3, 127.9, 127.4, 126.7 (2C), 124.7, 123.4, 120.2, 67.2, 67.1, 58.7, 49.6, 33.2, 21.6, 15.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{41}NNaO_6S$ 782.2547; Found 782.2542.

(Z)-benzyl 2-(3,3-diacetyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ba**)



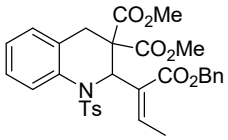
38 mg, 71% yield; white solid; mp 106-108°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.29 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.66 (s, 1H), 5.85 (q, *J* = 7.2 Hz, 1H), 5.16 (d, *J* = 5.6 Hz, 2H), 3.43 – 3.08 (m, 2H), 2.37 (s, 3H), 2.15 (s, 3H), 2.09 (s, 3H), 1.71 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 202.9, 166.7, 144.0, 138.5, 137.3, 136.2, 135.6, 131.6, 129.8, 129.5, 128.5, 128.4, 128.2, 128.1, 127.5, 123.0 (d, *J* = 5.1 Hz), 118.5, 69.5, 66.8, 58.0, 28.8, 28.1, 26.4, 21.6, 15.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{32}NO_6S$ 546.1945; Found 546.1941.

(Z)-dimethyl 2-(1-(benzyloxy)-1-oxobut-2-en-2-yl)-1-tosyl-1,2-dihydroquinoline-3,3(4H)-dicarboxylate (**3ca**)



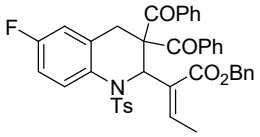
40 mg, 68% yield; white solid; mp 128-131°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28 – 7.13 (m, 5H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.00 – 6.91 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 6.05 (q, *J* = 7.2 Hz, 1H), 5.01 (d, *J* = 2.6 Hz, 2H), 3.50 (s, 3H), 3.33 (s, 3H), 3.02 (d, *J* = 16.1 Hz, 1H), 2.65 (d, *J* = 16.1 Hz, 1H), 2.22 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 168.7, 166.2, 143.8, 140.5, 137.3, 136.0, 135.8, 131.6, 129.5, 129.3, 128.5, 128.3, 128.1, 127.7, 127.4, 125.3, 123.8, 120.9, 66.4, 58.7, 57.9, 53.1, 52.7, 31.1, 21.5, 16.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{32}NO_8S$ 578.1843; Found 578.1840.

(Z)-benzyl 2-(3,3-dibenzoyl-6-fluoro-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3da**)



52 mg, 75% yield; white solid; mp 138-141°C.

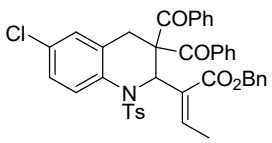
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.41 – 7.29 (m, 5H), 7.27 – 7.09 (m, 8H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.76 (q, *J* = 7.4 Hz, 1H), 5.02 (d, *J* = 12.5 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 3.50 (d, *J* = 16.3 Hz, 1H), 2.78 (d, *J* = 16.3 Hz, 1H), 2.35 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0 (d, *J* = 3.5 Hz), 165.8, 159.0 (d, *J* = 244.2 Hz), 143.8, 141.8, 137.3, 136.6, 135.8, 133.4, 133.1, 132.3, 131.8, 129.4, 129.1, 128.5, 128.4, 128.2, 128.0, 127.8, 123.0 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 22.8 Hz), 114.4 (d, *J* = 22.1 Hz), 68.3, 66.3, 58.5, 33.8, 21.6, 16.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.84 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{35}FNO_6S$ 688.2164; Found 688.2158.

(Z)-benzyl 2-(3,3-dibenzoyl-6-chloro-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ea**)

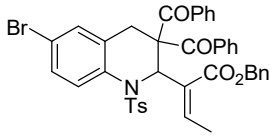


46 mg, 65% yield; white solid; mp 118-120°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.20 (m, 7H), 7.18 – 7.06 (m, 7H), 6.95 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.84 (d, *J* = 2.6 Hz, 1H), 5.71 (q, *J* = 7.1 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.67 (d, *J* = 12.6 Hz, 1H), 3.44 (d, *J* = 16.7 Hz, 1H), 2.96 (d, *J* = 16.7 Hz, 1H), 2.28 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).

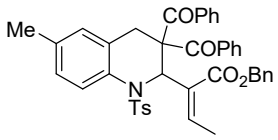
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 195.8, 165.7, 143.9, 141.2, 137.4, 136.7, 135.7, 135.7, 134.9, 133.5, 133.2, 132.0, 129.5, 129.0, 128.9, 128.6, 128.5, 128.4, 128.4, 128.1, 128.0, 127.4, 126.3, 120.9, 66.6, 66.3, 58.7, 33.0, 21.6, 16.0.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{34}ClNNaO_6S$ 726.1688; Found 726.1682.

(Z)-benzyl 2-(3,3-dibenzoyl-6-bromo-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3fa**)



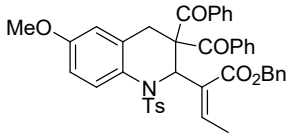
54 mg, 72% yield; white solid; mp 131-133°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.30 (dd, *J* = 11.0, 6.2 Hz, 3H), 7.26 – 7.22 (m, 4H), 7.19 – 7.05 (m, 9H), 6.98 (s, 1H), 5.72 (q, *J* = 7.1 Hz, 1H), 4.94 (d, *J* = 12.6 Hz, 1H), 4.66 (d, *J* = 12.8 Hz, 1H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.00 (d, *J* = 16.7 Hz, 1H), 2.28 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 195.8, 165.7, 144.0, 141.1, 137.4, 136.7, 135.7, 135.6, 135.5, 133.5, 133.2, 132.0, 131.8, 130.3, 129.5, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 126.5, 121.1, 115.9, 66.4, 66.3, 58.7, 32.8, 21.6, 16.0.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{35}BrNO_6S$ 748.1363; Found 748.1361.

(Z)-benzyl 2-(3,3-dibenzoyl-6-methyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ga**)



54 mg, 79% yield; white solid; mp 111-114°C.
1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.9 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.43 – 7.28 (m, 9H), 7.19 (q, J = 7.4 Hz, 6H), 6.89 (d, J = 8.7 Hz, 1H), 6.77 (s, 1H), 5.80 (q, J = 7.0 Hz, 1H), 5.05 (d, J = 12.6 Hz, 1H), 4.77 (d, J = 12.5 Hz, 1H), 3.51 (d, J = 16.3 Hz, 1H), 3.01 (d, J = 16.4 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H), 1.72 (d, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 165.9, 143.5, 141.1, 137.8, 136.8, 136.0, 135.9, 133.7, 133.3, 133.0, 132.9, 132.1, 129.7, 129.5, 129.3, 129.0, 128.5, 128.4, 128.4, 128.1, 128.1, 127.9, 124.7, 120.0, 67.3, 66.2, 58.3, 33.2, 21.6, 20.5, 16.0.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{38}NO_6S$ 684.2414; Found 684.2411.

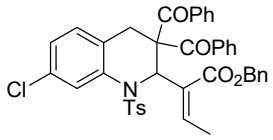
(Z)-benzyl 2-(3,3-dibenzoyl-6-methoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ha**)



49 mg, 71% yield; white solid; mp 135-138°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.9 Hz, 2H), 7.43 – 7.10 (m, 9H), 7.07 (d, *J* = 7.6 Hz, 4H), 6.62 (d, *J* = 9.3 Hz, 1H), 6.49 (s, 1H), 5.64 (q, *J* = 7.4 Hz, 1H), 4.96 (d, *J* = 12.6 Hz, 1H), 4.79 (d, *J* = 12.1 Hz, 1H), 3.63 (s, 3H),

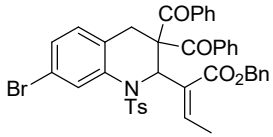
3.38 (d, *J* = 14.6 Hz, 1H), 2.57 (d, *J* = 16.0 Hz, 1H), 2.25 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 196.2, 165.9, 156.3, 143.4, 142.1, 137.5, 136.7, 136.0, 135.9, 133.3, 133.0, 131.8, 129.4, 129.3, 129.3, 129.1, 128.5, 128.2, 127.9, 127.7, 123.7, 113.9, 113.1, 69.3, 66.3, 58.1, 55.4, 34.2, 21.5, 16.1.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{38}NO_7S$ 700.2363; Found 700.2360.

(Z)-benzyl 2-(3,3-dibenzoyl-7-chloro-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ia**)



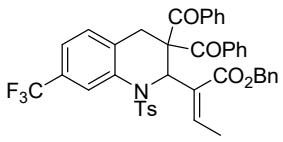
55 mg, 77% yield; white solid; mp 140-143°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.53 (m, 3H), 7.42 – 7.28 (m, 5H), 7.29 – 7.08 (m, 9H), 6.82 (s, 2H), 5.83 (q, *J* = 8.7, 8.0 Hz, 1H), 5.01 (d, *J* = 12.6 Hz, 1H), 4.68 (d, *J* = 13.0 Hz, 1H), 3.55 (d, *J* = 16.8 Hz, 1H), 3.18 (d, *J* = 16.8 Hz, 1H), 2.37 (s, 3H), 1.77 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.34, 195.75, 165.68, 144.16, 141.07, 137.17, 137.15, 136.77, 135.74, 135.70, 133.52, 133.07, 132.82, 131.98, 130.29, 129.55, 128.88, 128.64, 128.49, 128.45, 128.16, 128.02, 127.97, 122.88, 121.78, 118.93, 66.23, 65.87, 58.73, 32.47, 21.61, 16.00.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{34}ClNNaO_6S$ 726.1688; Found 726.1683.

(Z)-benzyl 2-(3,3-dibenzoyl-7-bromo-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ja**)



52 mg, 71% yield; white solid; mp 141-143°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.72 – 7.67 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.37 – 7.32 (m, 4H), 7.31 – 7.16 (m, 6H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.86 (q, *J* = 7.3 Hz, 1H), 5.05 (d, *J* = 12.7 Hz, 1H), 4.71 (d, *J* = 12.9 Hz, 1H), 3.56 (d, *J* = 16.8 Hz, 1H), 3.20 (d, *J* = 16.8 Hz, 1H), 2.41 (s, 3H), 1.81 (d, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 195.7, 165.7, 144.2, 141.1, 137.4, 137.1, 136.7, 135.7, 133.5, 133.1, 132.0, 130.6, 129.6, 129.5, 128.9, 128.7, 128.5, 128.5, 128.2, 128.0, 128.0, 125.7, 122.3, 121.7, 120.7, 66.2, 65.8, 58.7, 32.5, 21.6, 16.0.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{41}H_{35}BrNO_6S$ 748.1363; Found 748.1360.

(Z)-benzyl 2-(3,3-dibenzoyl-1-tosyl-7-(trifluoromethyl)-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ka**)



57 mg, 78% yield; white solid; mp 149-151°C.

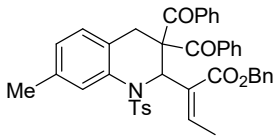
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.81 (m, 3H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.28 – 7.16 (m, 7H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 5.79 (q, *J* = 7.1 Hz, 1H), 5.01 (d, *J* = 12.8 Hz, 1H), 4.71 (d, *J* = 12.4 Hz, 1H), 3.63 (d, *J* = 17.2 Hz, 1H), 3.31 (d, *J* = 17.1 Hz, 1H), 2.38 (s, 3H), 1.77 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 195.6, 165.7, 144.3, 140.9, 136.9, 136.7, 136.5, 135.6, 135.5, 133.6, 133.2, 132.0, 129.9, 129.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.3, 128.0, 128.0, 127.0, 127.8 – 120.2 (m), 119.1 (q, *J* = 3.7 Hz), 115.4 (q, *J* = 4.5, 4.0 Hz), 66.3, 65.6, 58.8, 32.8, 21.6, 16.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.52 (s, 1F).

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}F_3NO_6S$ 738.2132; Found 738.2127.

(Z)-benzyl 2-(3,3-dibenzoyl-7-methyl-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3la**)



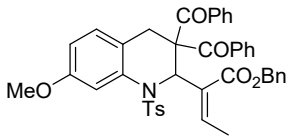
45 mg, 65% yield; white solid; mp 175-178°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.55 (m, 2H), 7.42 – 7.29 (m, 8H), 7.25 – 7.10 (m, 7H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.69 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.85 (q, *J* = 7.1 Hz, 1H), 5.01 (d, *J* = 12.7 Hz, 1H), 4.69 (d, *J* = 12.7 Hz, 1H), 3.54 (d, *J* = 16.5 Hz, 1H), 3.06 (d, *J* = 16.5 Hz, 1H), 2.37 (s, 3H), 2.22 (s, 3H), 1.76 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 196.2, 165.8, 143.6, 141.3, 137.9, 137.0, 136.9, 136.1, 136.0, 135.9, 133.3, 132.8, 132.1, 129.5, 129.3, 129.1, 128.9, 128.5, 128.4, 128.3, 128.0, 128.0, 127.8, 124.1, 121.1, 120.3, 66.8, 66.1, 58.5, 32.8, 21.6, 21.5, 16.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{38}NO_6S$ 684.2414; Found 684.2410.

(Z)-benzyl 2-(3,3-dibenzoyl-7-methoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ma**)



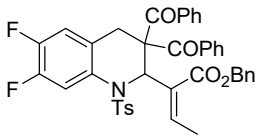
40 mg, 57% yield; white solid; mp 178-181°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 13.4, 7.9 Hz, 4H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.42 – 7.28 (m, 7H), 7.29 – 7.11 (m, 7H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.42 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.90 (q, *J* = 7.1 Hz, 1H), 5.00 (d, *J* = 12.7 Hz, 1H), 4.63 (d, *J* = 12.7 Hz, 1H), 3.66 (s, 3H), 3.54 (d, *J* = 16.5 Hz, 1H), 3.13 (d, *J* = 16.5 Hz, 1H), 2.38 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 196.0, 165.7, 158.6, 143.8, 141.3, 138.0, 136.9, 136.9, 136.1, 135.8, 133.3, 132.8, 132.1, 129.9, 129.6, 129.4, 128.8, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 115.2, 109.4, 104.6, 66.2, 66.1, 58.6, 55.2, 32.1, 21.6, 16.0.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{38}NO_7S$ 700.2363; Found 700.2360.

(Z)-benzyl 2-(3,3-dibenzoyl-6,7-difluoro-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3na**)



49 mg, 70% yield; white solid; mp 134-137°C.

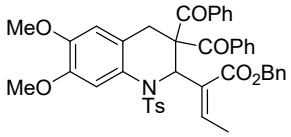
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.36 (m, 3H), 7.32 (d, *J* = 2.5 Hz, 5H), 7.28 – 7.08 (m, 7H), 6.73 (t, *J* = 9.3 Hz, 1H), 5.81 (q, *J* = 7.2 Hz, 1H), 5.02 (d, *J* = 12.6 Hz, 1H), 4.74 (d, *J* = 12.6 Hz, 1H), 3.49 (d, *J* = 16.6 Hz, 1H), 2.98 (d, *J* = 16.5 Hz, 1H), 2.38 (s, 3H), 1.75 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 195.7, 165.7, 149.9 (d, *J* = 13.1 Hz), 147.5 (d, *J* = 8.2 Hz), 147.4 (d, *J* = 7.9 Hz), 145.0 (d, *J* = 12.9 Hz), 144.2, 141.4, 136.9, 136.6, 135.6 (d, *J* = 3.7 Hz), 133.6, 133.3, 132.3 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 2.7 Hz), 131.8, 129.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 120.9 (d, *J* = 3.8 Hz), 120.8 (d, *J* = 3.3 Hz), 117.1 (d, *J* = 17.9 Hz), 109.5 (d, *J* = 23.0 Hz), 66.6, 66.3, 58.6, 32.6, 21.6, 16.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.95 (ddd, *J* = 21.6, 12.6, 8.2 Hz, 1F), -144.05 (dt, *J* = 22.7, 9.0 Hz, 1F).

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{34}F_2NO_6S$ 706.2069; Found 706.2065.

(Z)-benzyl 2-(3,3-dibenzoyl-6,7-dimethoxy-1-tosyl-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3oa**)



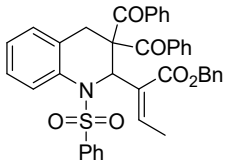
47 mg, 65% yield; white solid; mp 124-127°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.55 (m, 2H), 7.43 – 7.31 (m, 7H), 7.28 – 7.13 (m, 7H), 7.04 (s, 1H), 6.44 (s, 1H), 5.78 (q, *J* = 7.2 Hz, 1H), 5.02 (d, *J* = 12.6 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 3.51 – 3.41 (m, 1H), 2.74 (d, *J* = 16.1 Hz, 1H), 2.35 (s, 3H), 1.73 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 196.3, 165.9, 147.8, 145.6, 143.6, 141.7, 137.8, 136.8, 136.2, 135.9, 133.3, 132.8, 131.8, 129.4, 129.3, 129.0, 128.5, 128.4, 128.4, 128.1, 127.9, 127.8, 117.9, 111.4, 105.9, 68.6, 66.2, 58.2, 56.0, 55.9, 33.1, 21.5, 16.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{40}NO_8S$ 730.2469; Found 730.2466.

(Z)-benzyl 2-(3,3-dibenzoyl-1-(phenylsulfonyl)-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3pa**)



50 mg, 76% yield; white solid; mp 135-137°C.

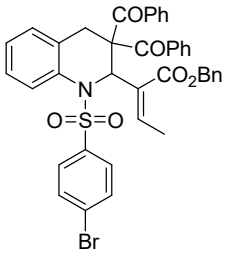
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.20 (m, 7H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.05 (m, 4H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.91 – 6.79 (m, 2H), 5.71 (q, *J* = 7.1 Hz, 1H), 4.93 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 12.7 Hz, 1H), 3.49 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 196.1, 165.8, 141.5, 140.7, 136.8, 136.2, 136.0, 135.8, 133.4,

132.9, 132.8, 132.0, 129.5, 129.4, 128.9, 128.8, 128.6, 128.4, 128.1, 127.9, 127.8, 127.5, 124.8, 123.5, 120.1, 67.2, 66.2, 58.6, 33.2, 16.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{34}NO_6S$ 656.2101; Found 656.2099.

(Z)-benzyl 2-(3,3-dibenzoyl-1-(4-bromophenylsulfonyl)-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3qa**)



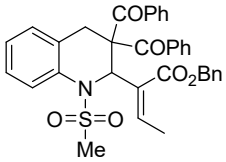
60 mg, 82% yield; white solid; mp 118-121°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.19 (m, 7H), 7.17 – 7.05 (m, 5H), 7.06 – 6.99 (m, 1H), 6.94 – 6.78 (m, 2H), 5.69 (q, *J* = 7.2 Hz, 1H), 4.91 (d, *J* = 12.6 Hz, 1H), 4.65 (d, *J* = 12.6 Hz, 1H), 3.54 (d, *J* = 16.6 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 195.9, 165.7, 141.5, 139.7, 136.8, 136.0, 135.8, 135.8, 133.4, 133.0, 132.0, 131.9, 129.5, 129.4, 128.9, 128.6, 128.5, 128.5, 128.1 (2C), 128.0, 127.9, 127.6, 125.0, 123.8, 120.2, 67.4, 66.3, 58.7, 33.3, 16.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{33}BrNO_6S$ 734.1206; Found 734.1205.

(Z)-benzyl 2-(3,3-dibenzoyl-1-(methylsulfonyl)-1,2,3,4-tetrahydroquinolin-2-yl)but-2-enoate (**3ra**)



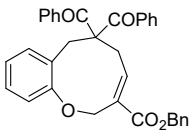
45 mg, 75% yield; white solid; mp 124-126°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.43 (dd, *J* = 17.3, 7.8 Hz, 4H), 7.37 – 7.12 (m, 10H), 7.01 (s, 1H), 6.93 – 6.75 (m, 2H), 6.13 (q, *J* = 7.1 Hz, 1H), 4.96 (d, *J* = 12.8 Hz, 1H), 4.34 (d, *J* = 12.8 Hz, 1H), 3.84 (d, *J* = 17.0 Hz, 1H), 3.44 (s, 3H), 3.34 (d, *J* = 17.0 Hz, 1H), 1.95 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 195.4, 165.3, 141.2, 137.3, 136.1, 135.8, 135.7, 133.5, 132.9, 132.3, 130.2, 129.7, 128.6, 128.4, 128.4, 128.2, 127.8, 127.7, 122.1, 120.7, 116.5, 65.8, 63.9, 59.2, 38.6, 32.7, 16.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{31}NNaO_6S$ 616.1764; Found 616.1759.

benzyl (E)-6,6-dibenzoyl-2,5,6,7-tetrahydrobenzo[b]oxonine-3-carboxylate (**5aa**)



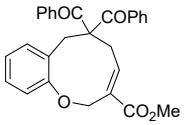
29 mg, 56% yield; pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.39 – 7.29 (m, 6H), 7.26 (t, *J* = 7.5 Hz, 3H), 7.16 – 7.00 (m, 3H), 6.66 (d, *J* = 2.8 Hz, 1H), 5.19 – 5.07 (m, 2H), 3.24 (s, 2H), 3.22 – 3.15 (m, 2H), 3.13 – 3.05 (m, 1H), 2.81 (dt, *J* = 19.3, 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 165.0, 164.3, 149.8, 141.4, 136.1, 136.0, 133.7, 133.4, 132.4, 131.6, 130.2, 129.3, 129.1, 129.0, 128.7, 128.6, 128.4, 128.2, 128.2, 128.1, 126.1, 122.7, 66.1, 59.2, 42.6, 41.7, 38.9.

HRMS (ESI): m/z calcd for $C_{34}H_{28}NaO_5$ ($[M+Na]^+$): 539.1829; found: 539.1824.

methyl (E)-6,6-dibenzoyl-2,5,6,7-tetrahydrobenzo[b]oxonine-3-carboxylate (**5ab**)



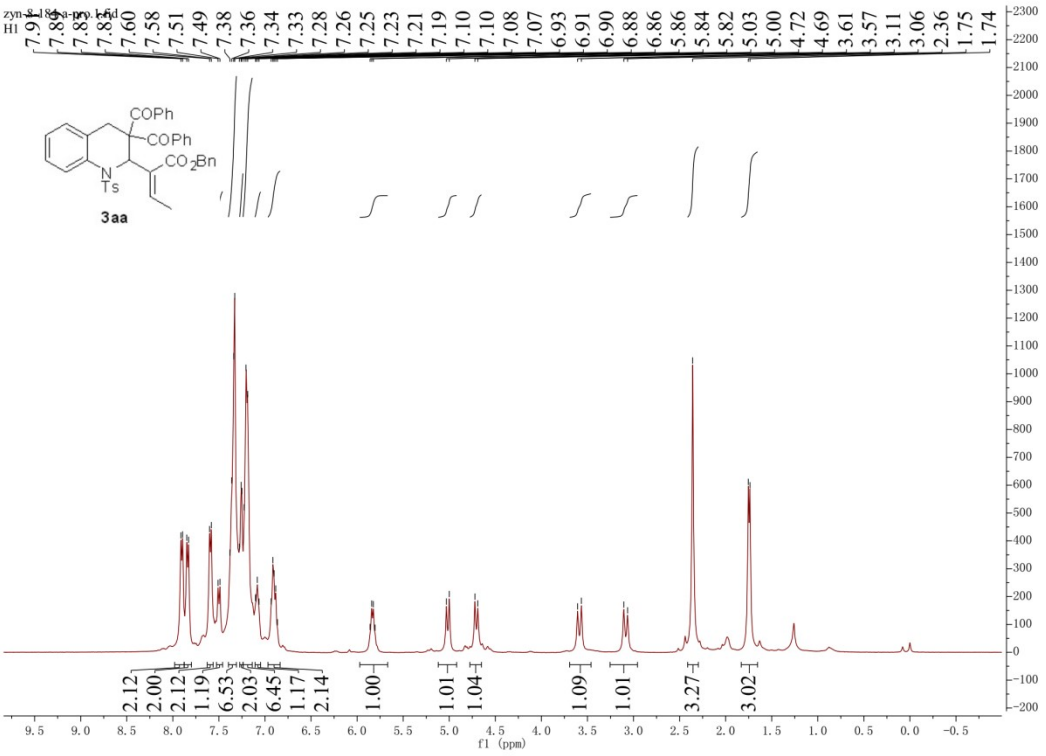
27 mg, 62% yield; pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 3H), 7.23 – 7.06 (m, 3H), 6.66 (s, 1H), 3.69 (s, 3H), 3.27 (d, *J* = 5.0 Hz, 2H), 3.22 (d, *J* = 21.4 Hz, 2H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.83 (d, *J* = 17.9 Hz, 1H).

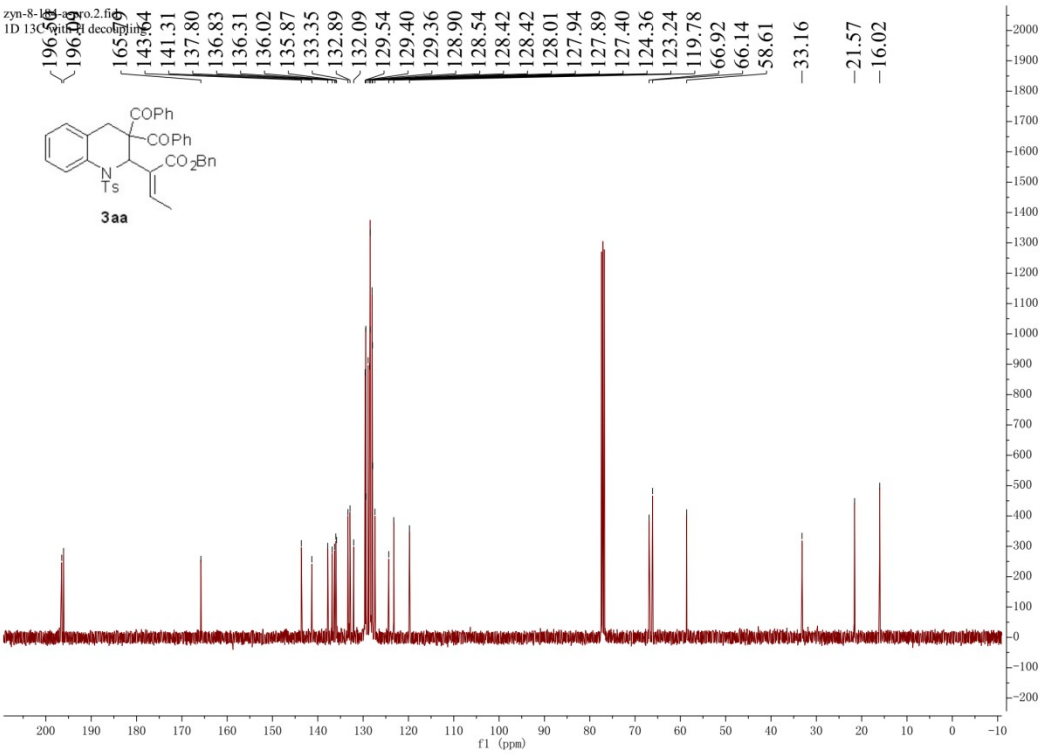
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 165.0, 164.9, 149.9, 141.0, 136.1, 133.7, 133.4, 132.4, 131.6, 130.2, 129.3, 129.1, 129.0, 128.6, 128.4, 128.2, 126.0, 122.7, 59.2, 51.5, 42.7, 41.7, 38.8.

HRMS (ESI): m/z calcd for $C_{28}H_{24}NaO_5$ ($[M+Na]^+$): 463.1516; found: 463.1511.

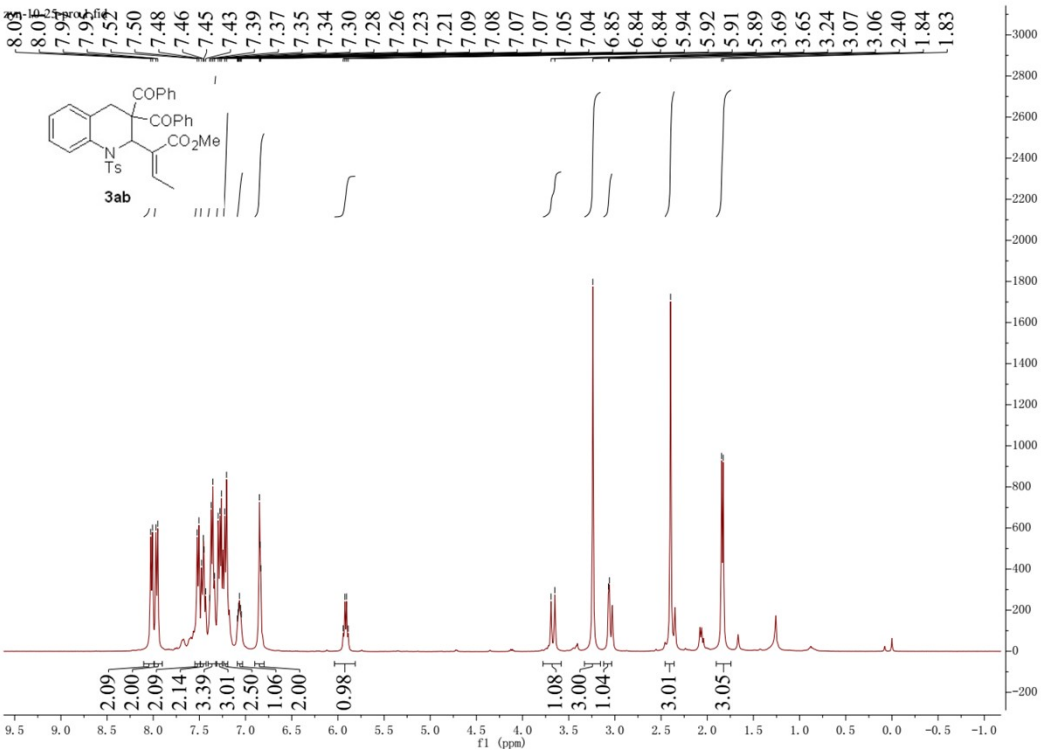
6. NMR data



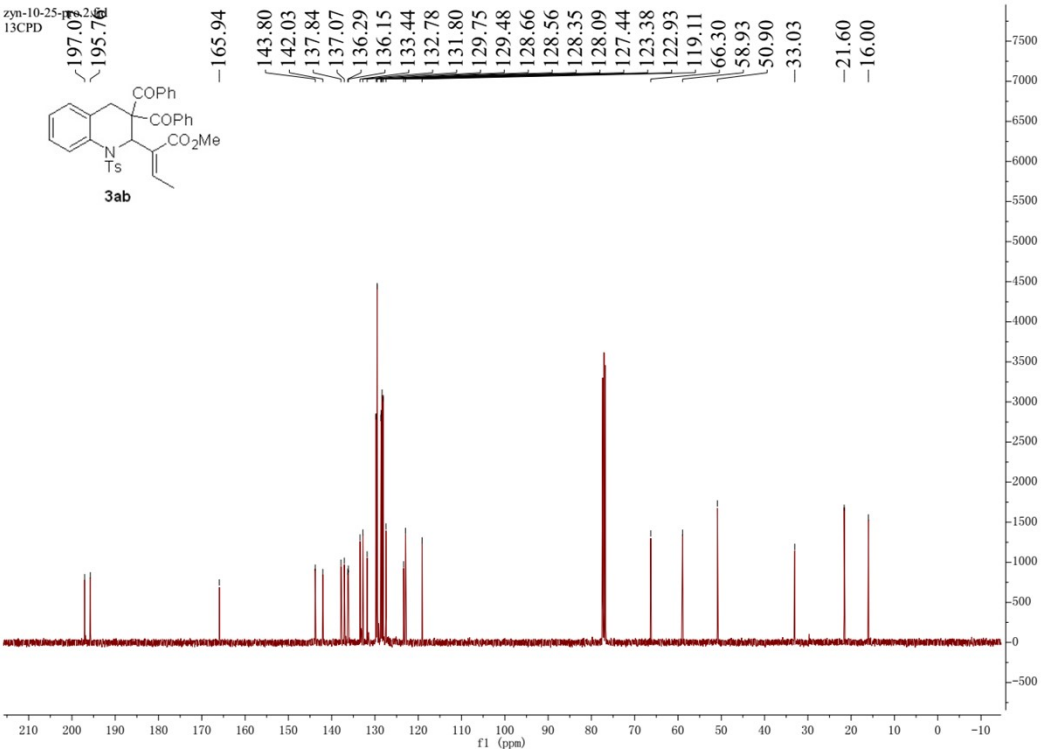
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3aa**



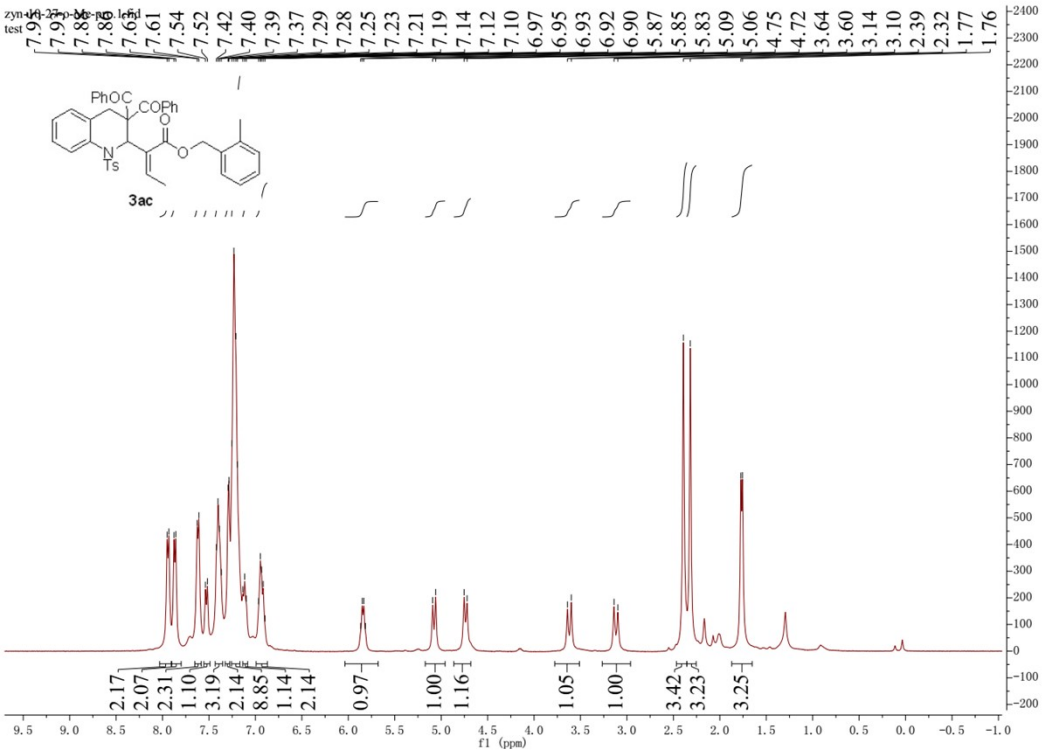
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3aa**



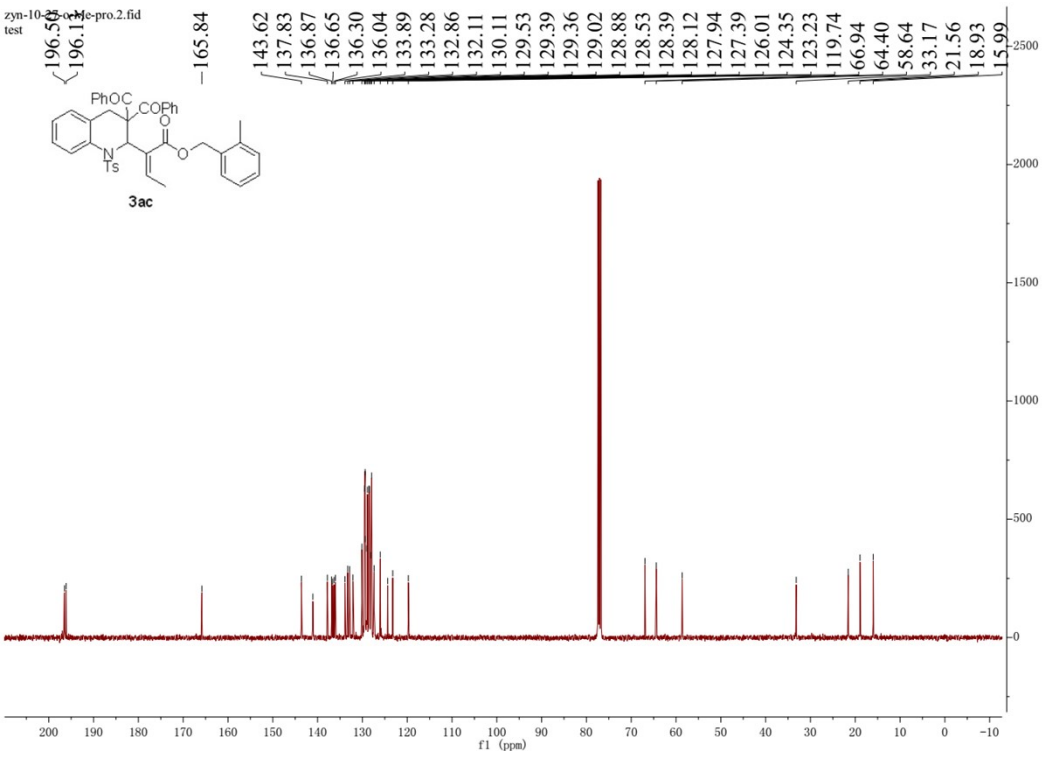
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ab**



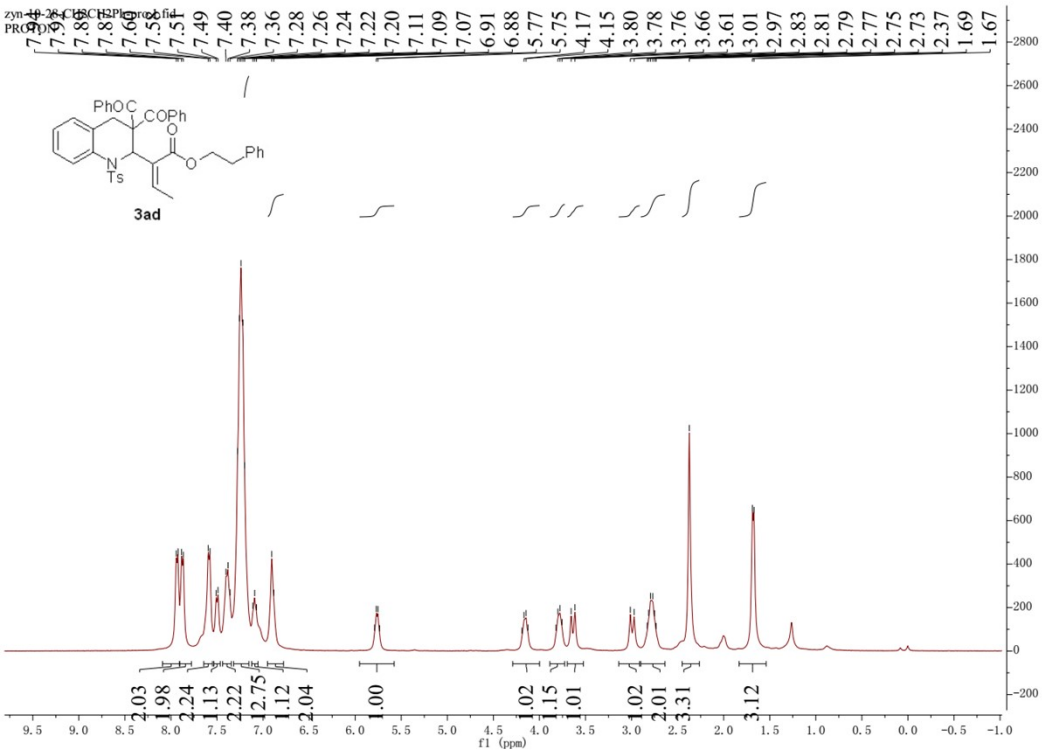
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ab**



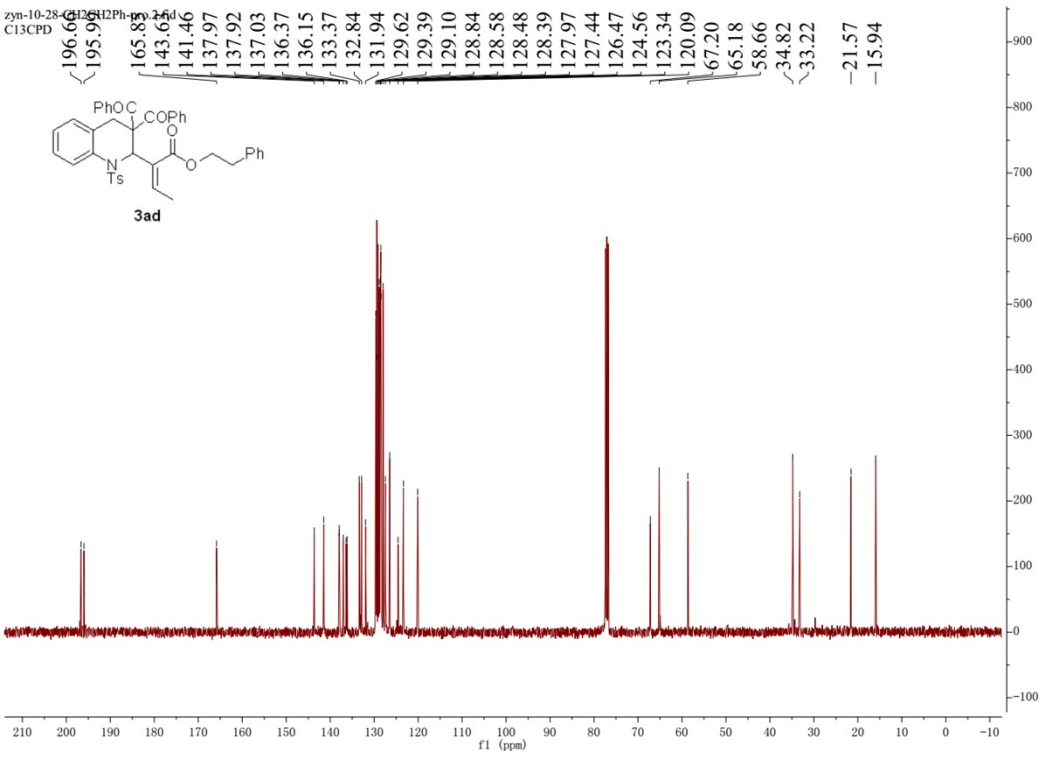
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ac**



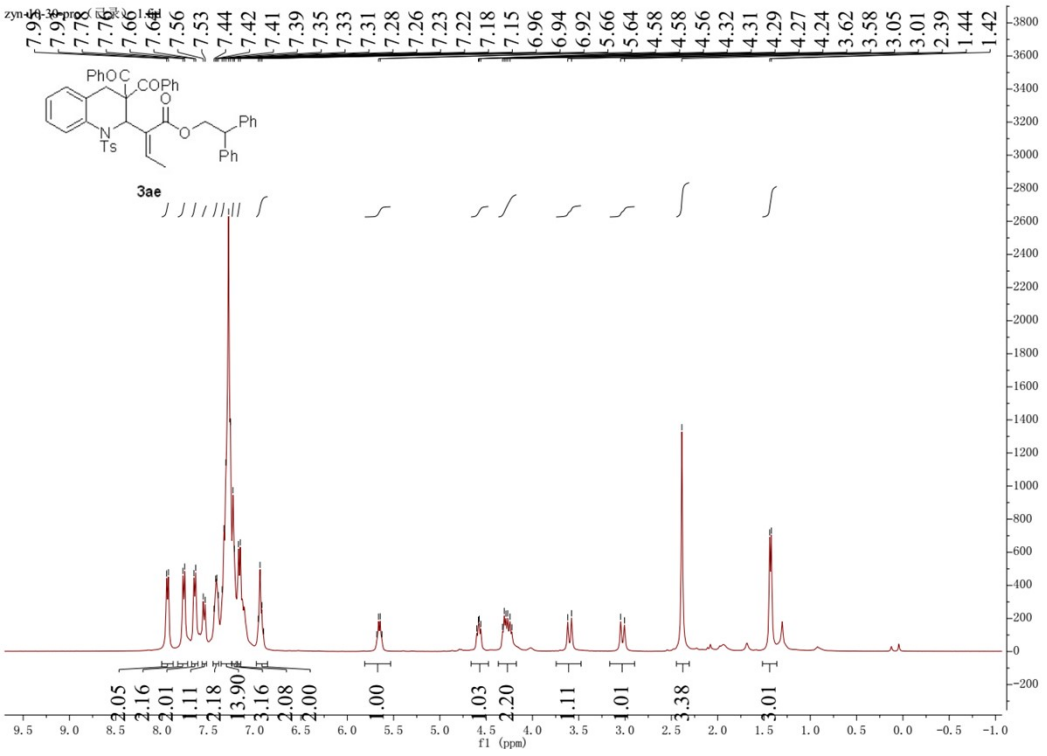
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ac**



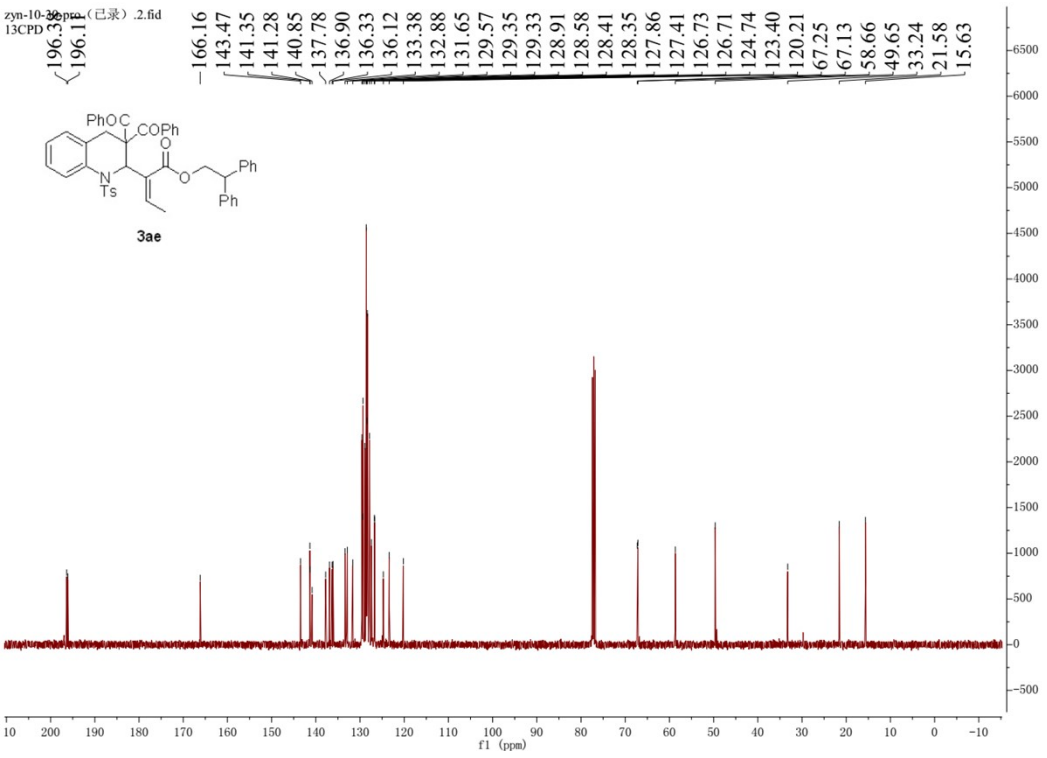
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ad**



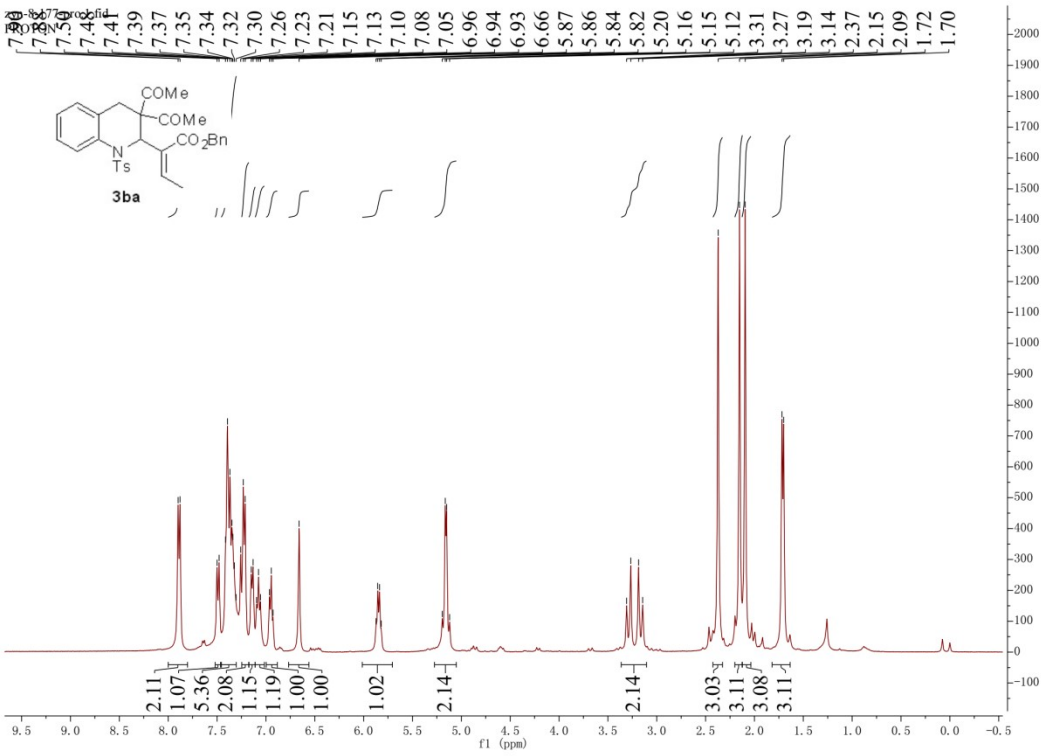
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ad**



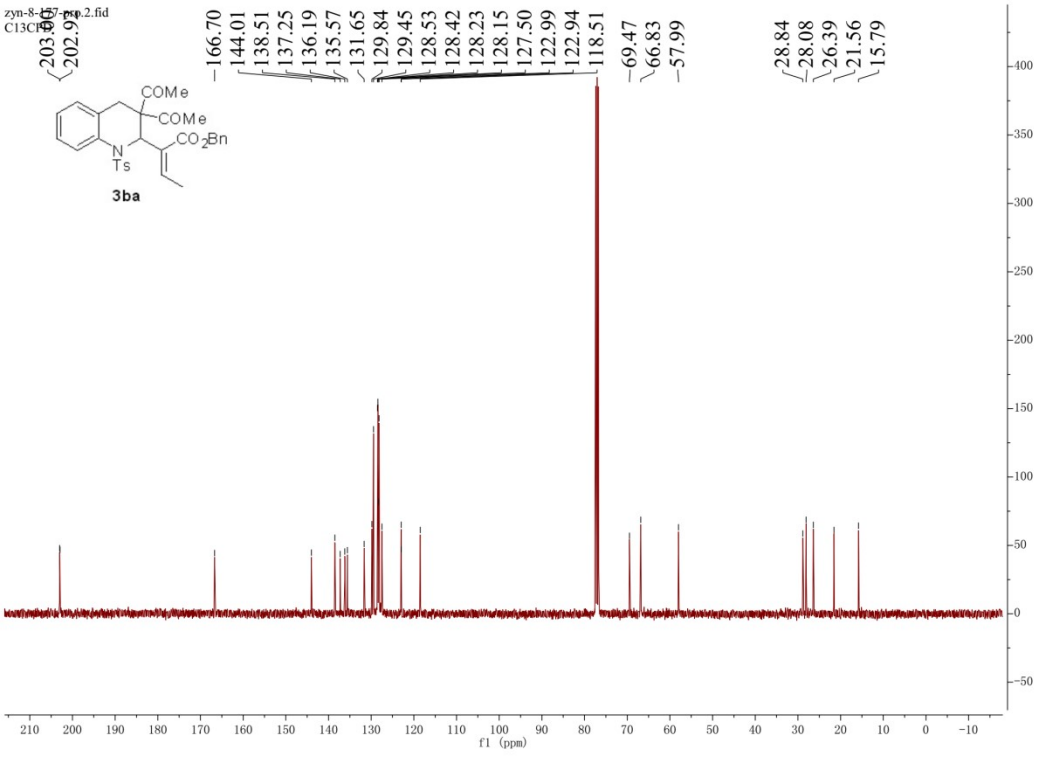
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ae**



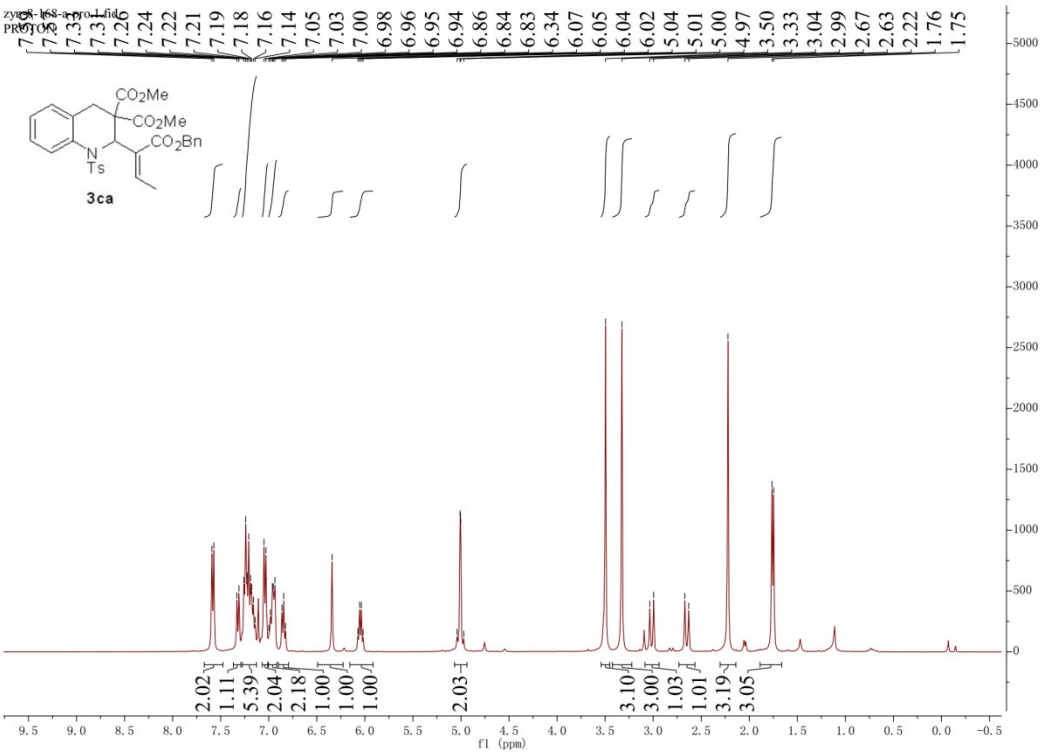
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ae**



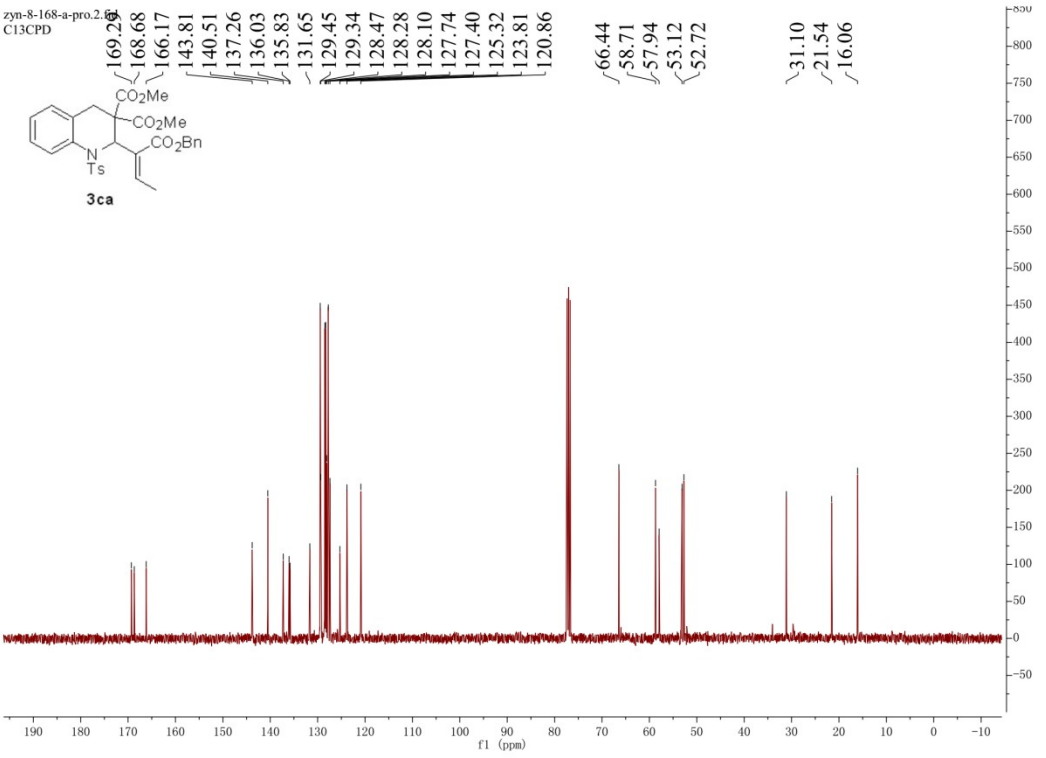
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ba**



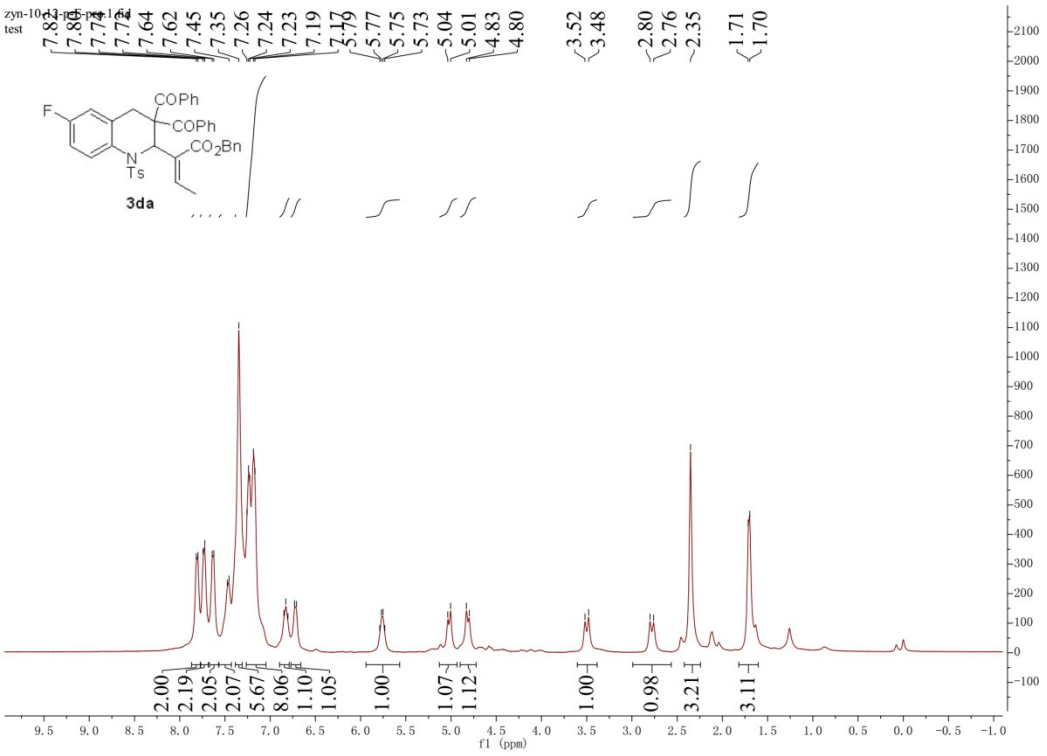
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ba**



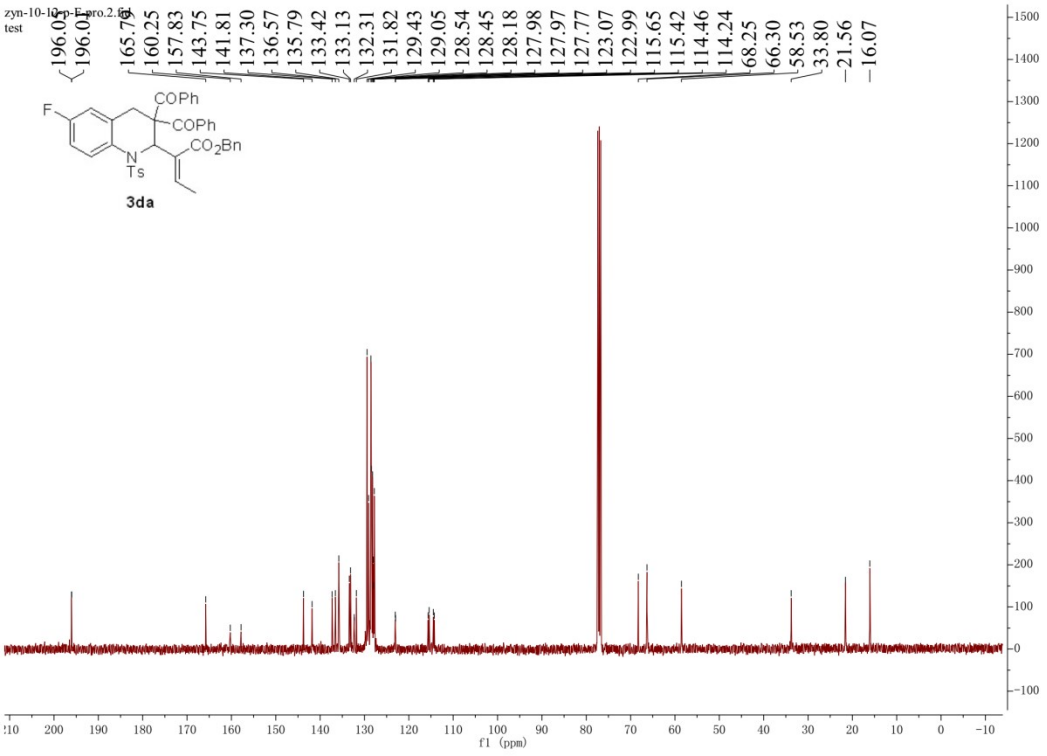
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ca**



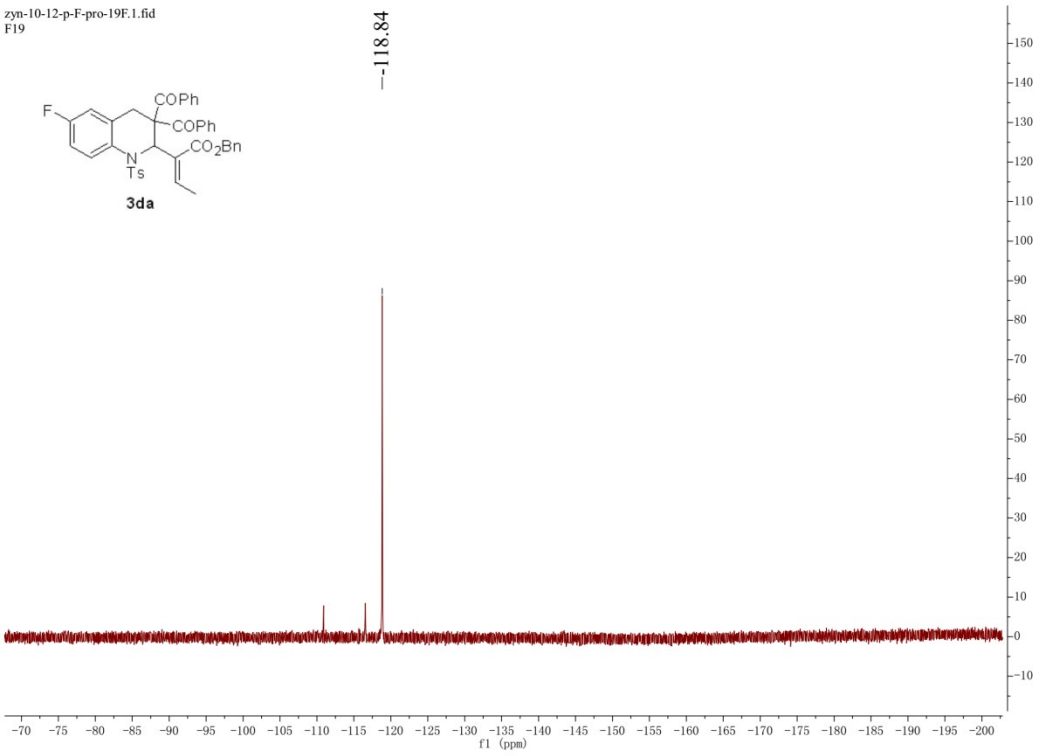
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ca**



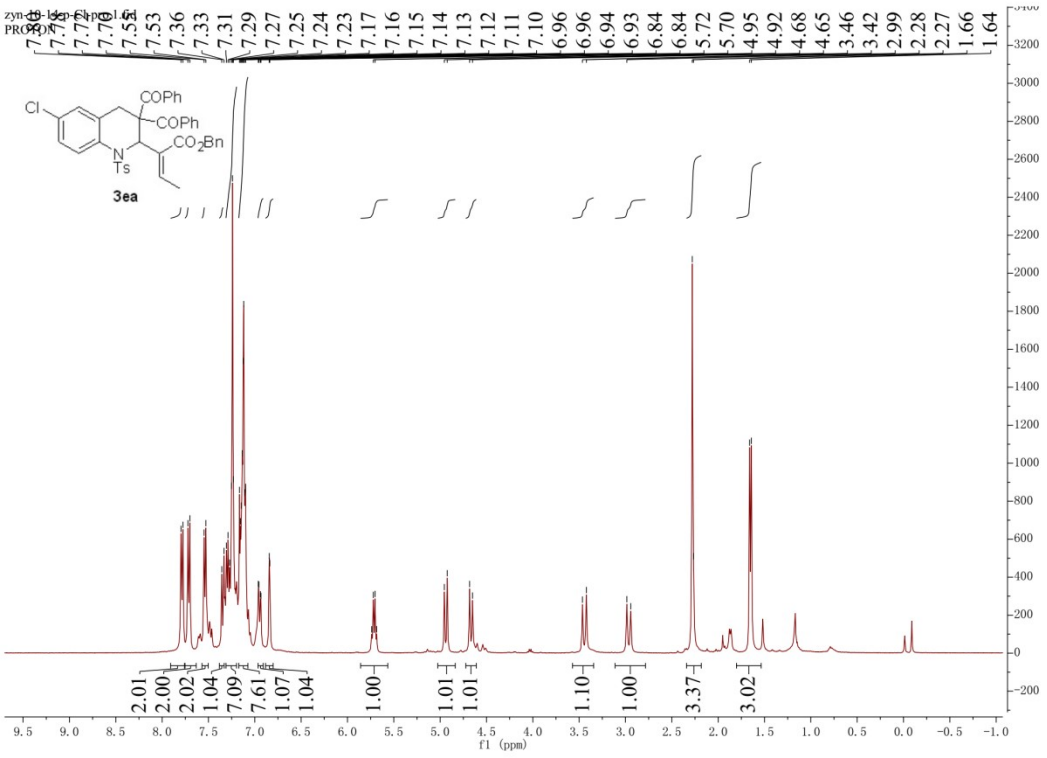
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3da**



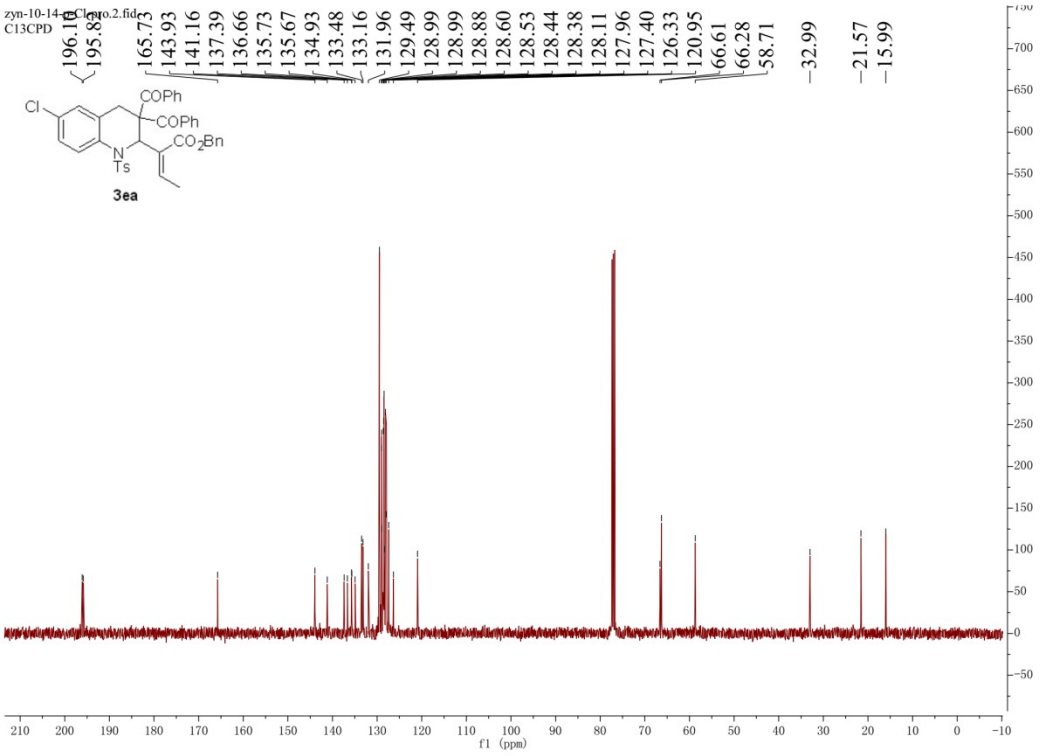
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3da**



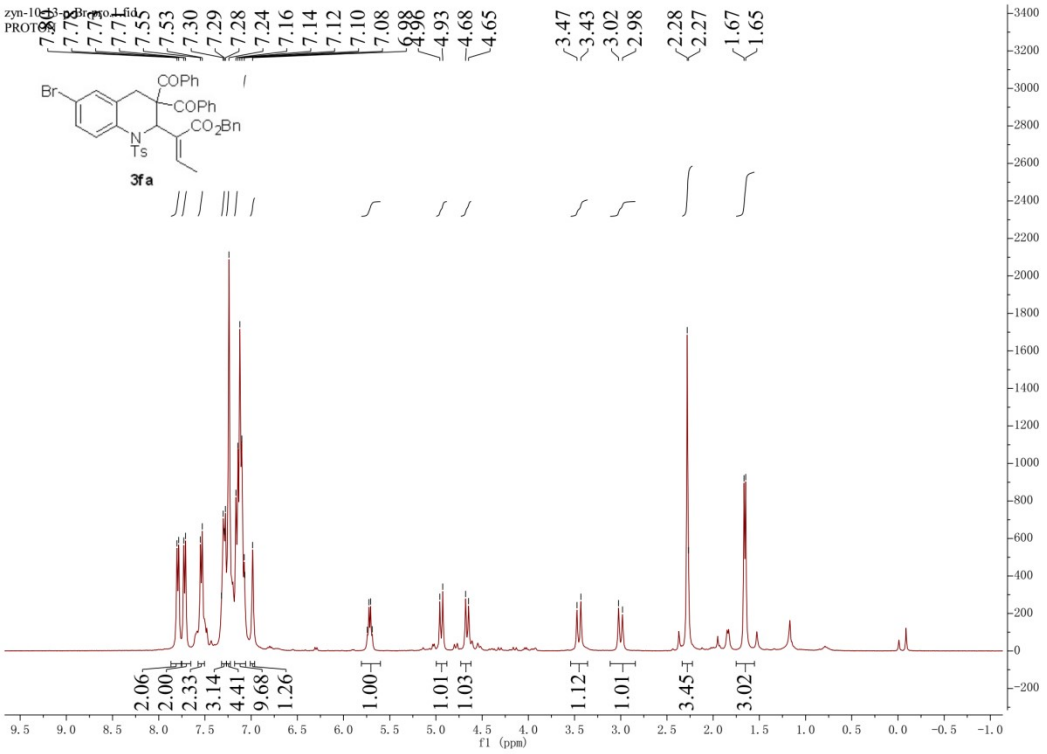
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3da**



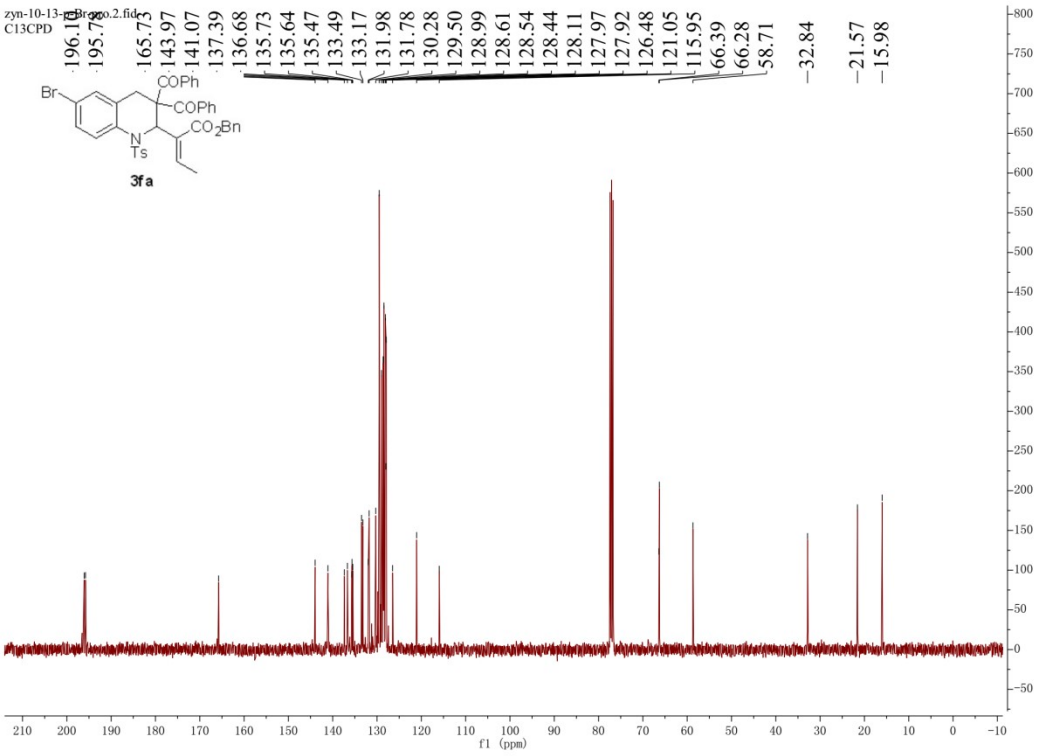
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ea**



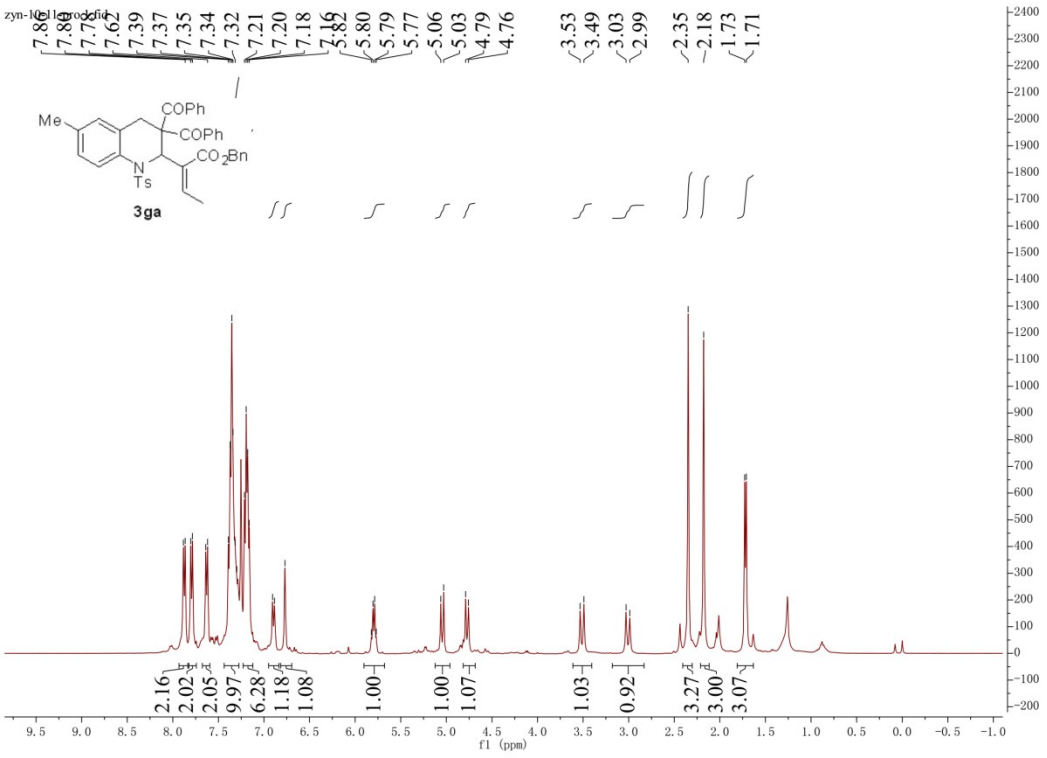
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ea**



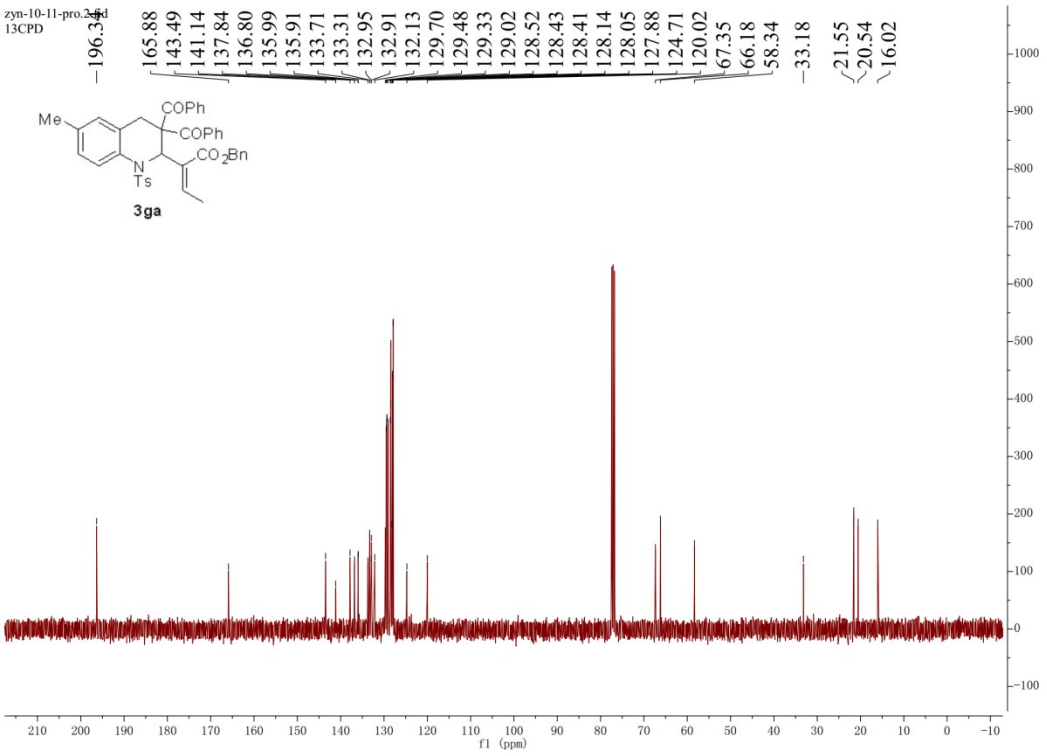
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3fa**



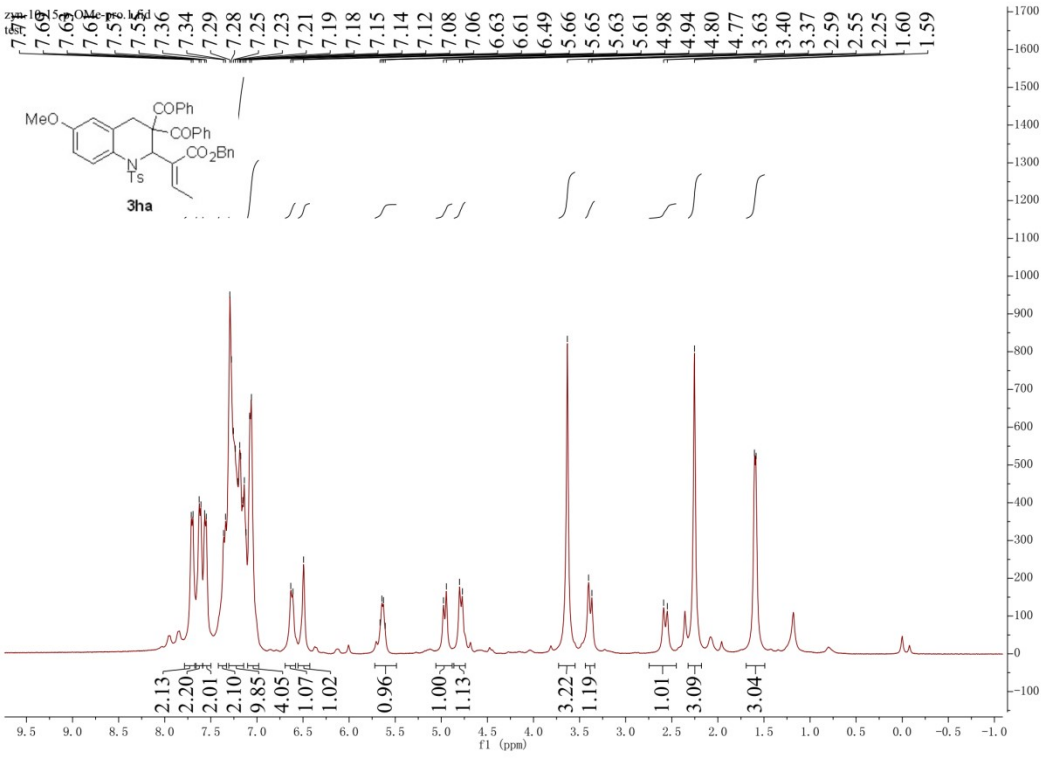
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3fa**



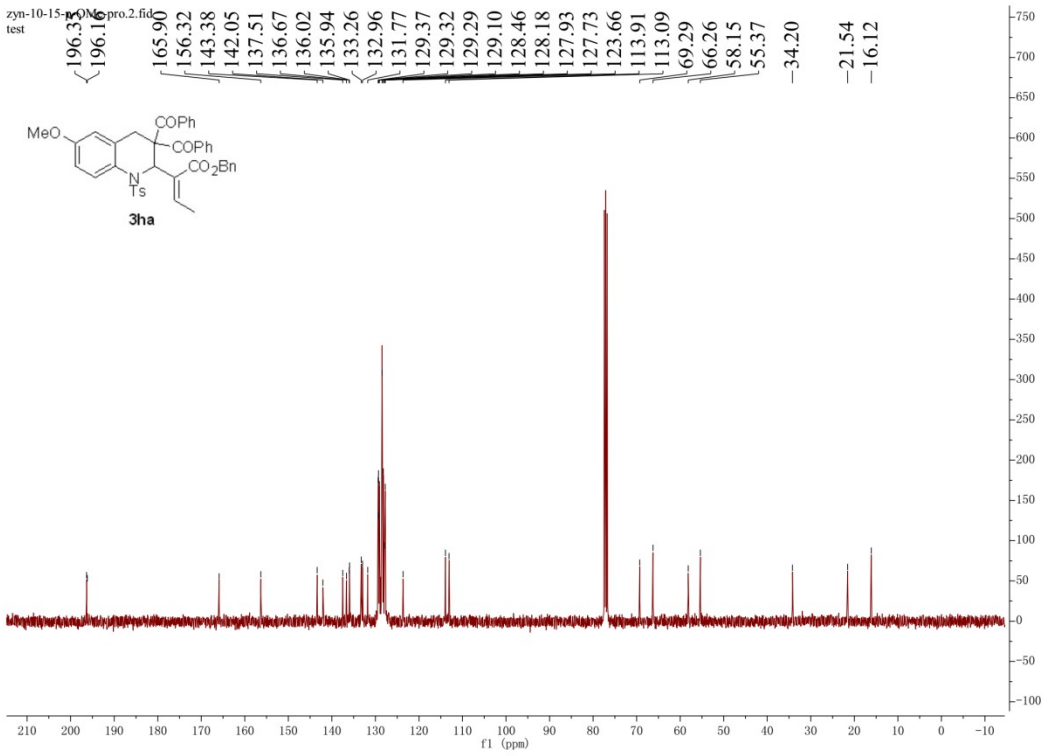
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ga**



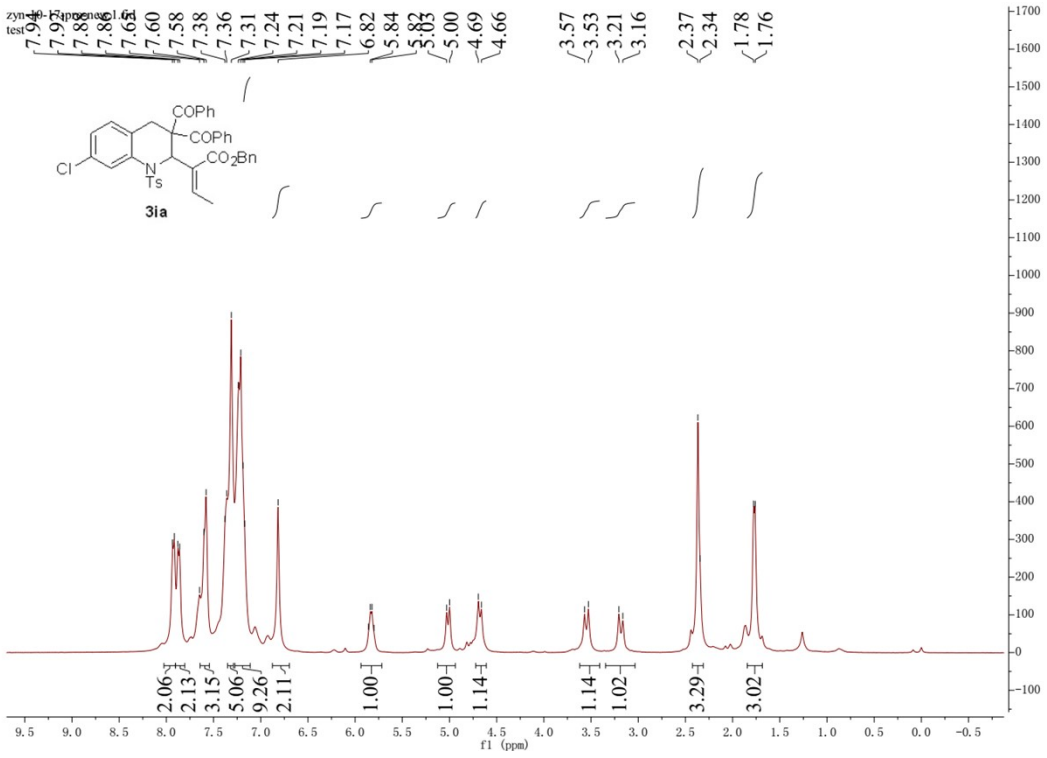
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ga**



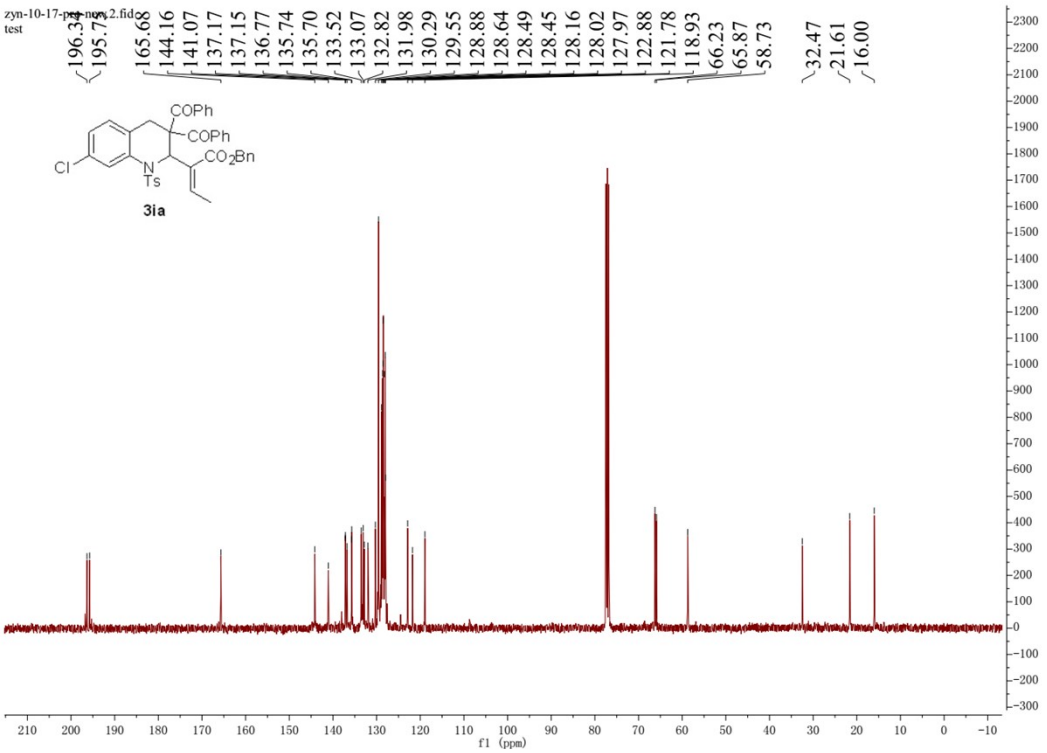
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ha**



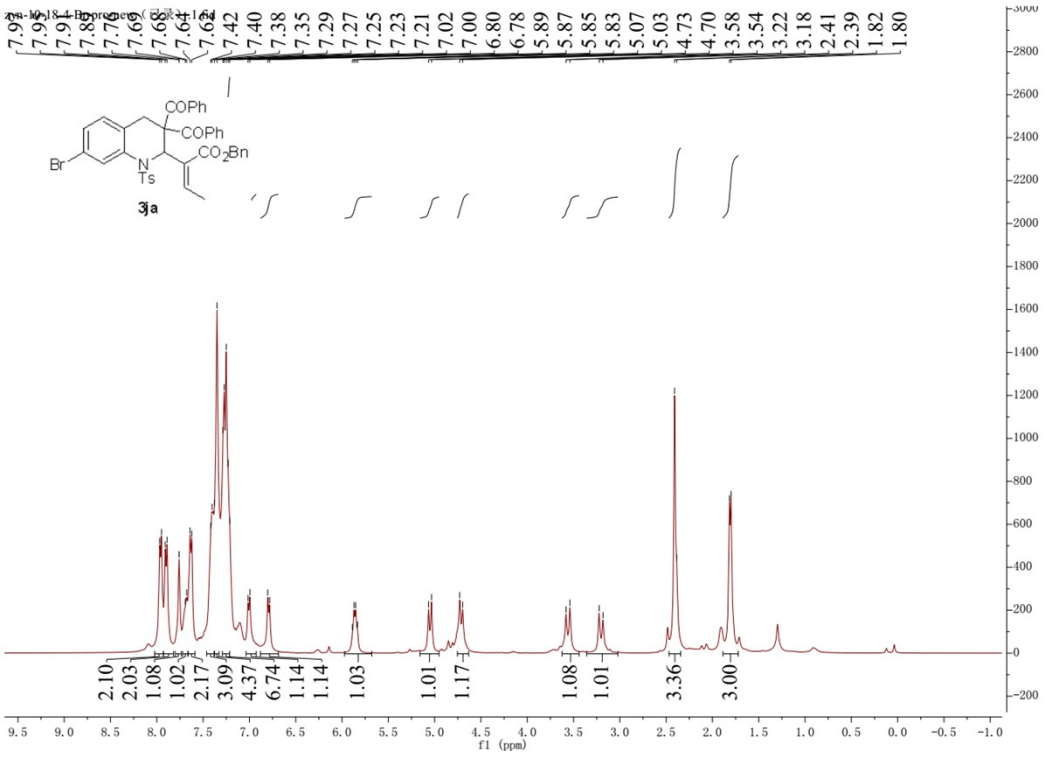
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ha**



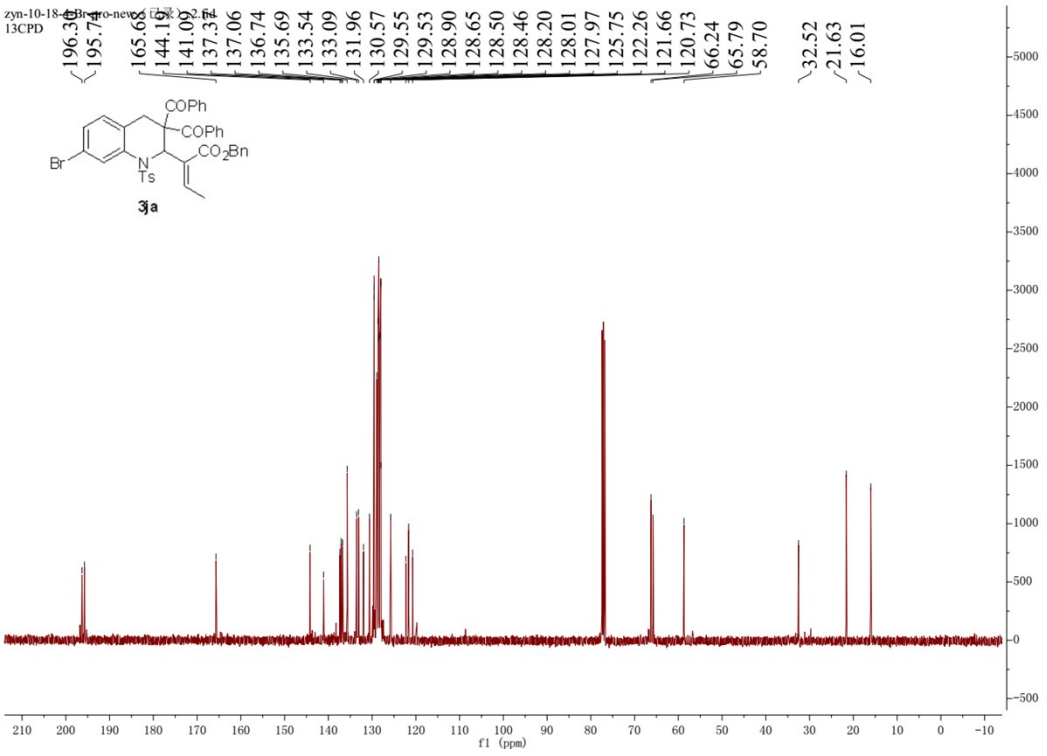
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ia**



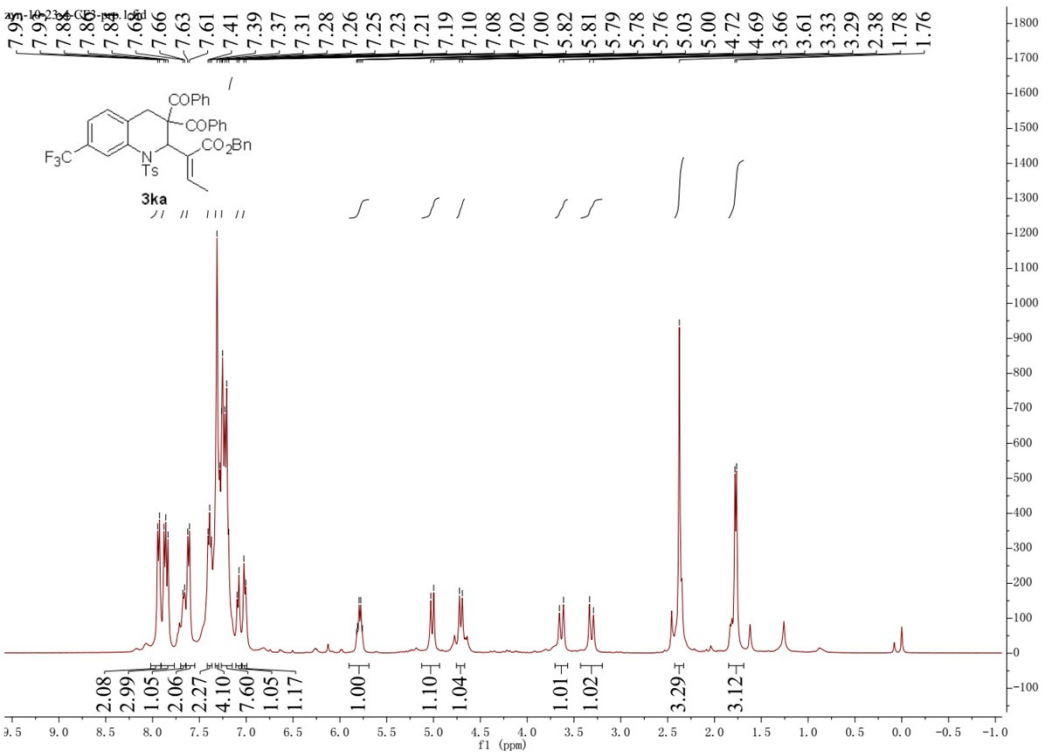
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ia**



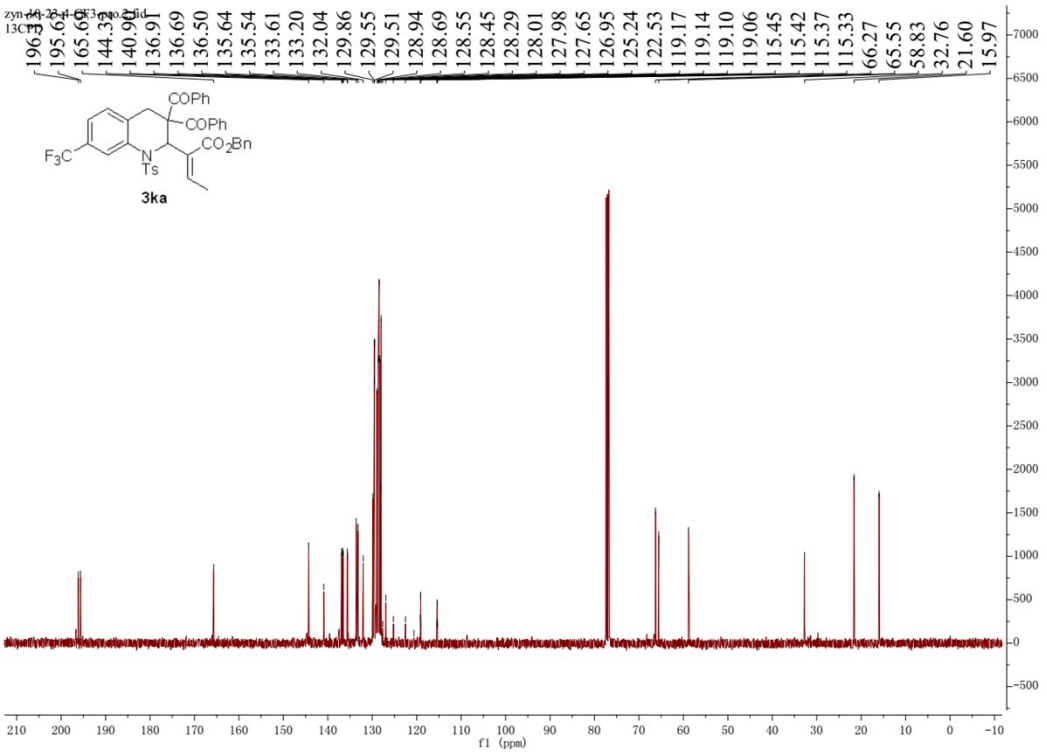
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ja**



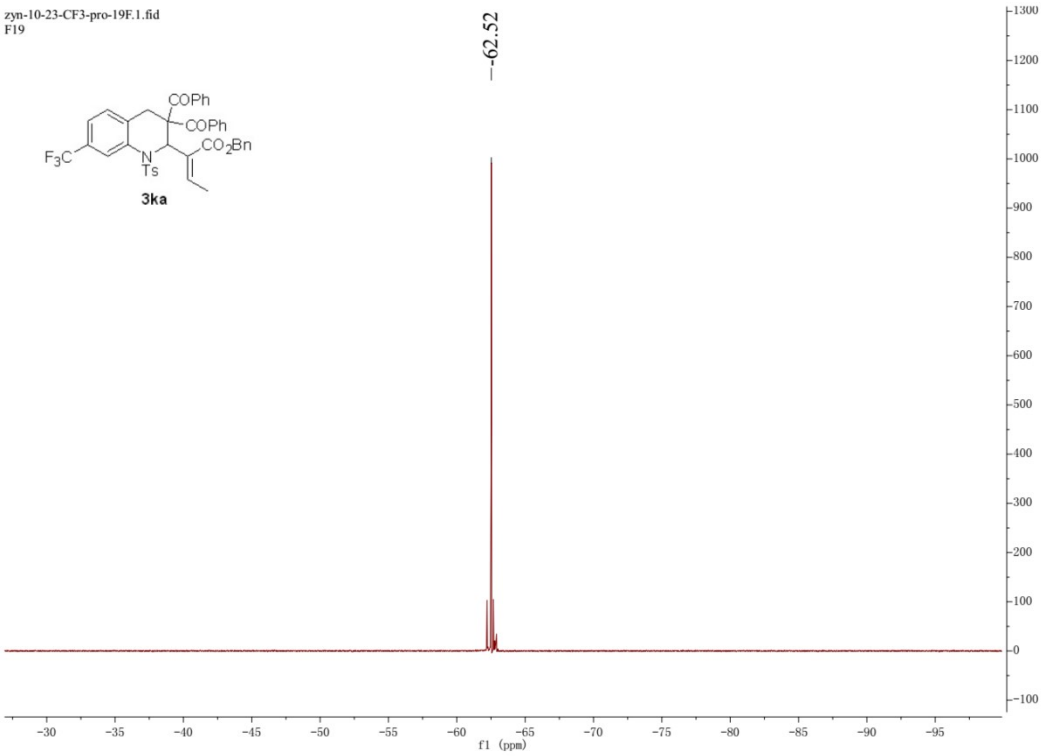
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ja**



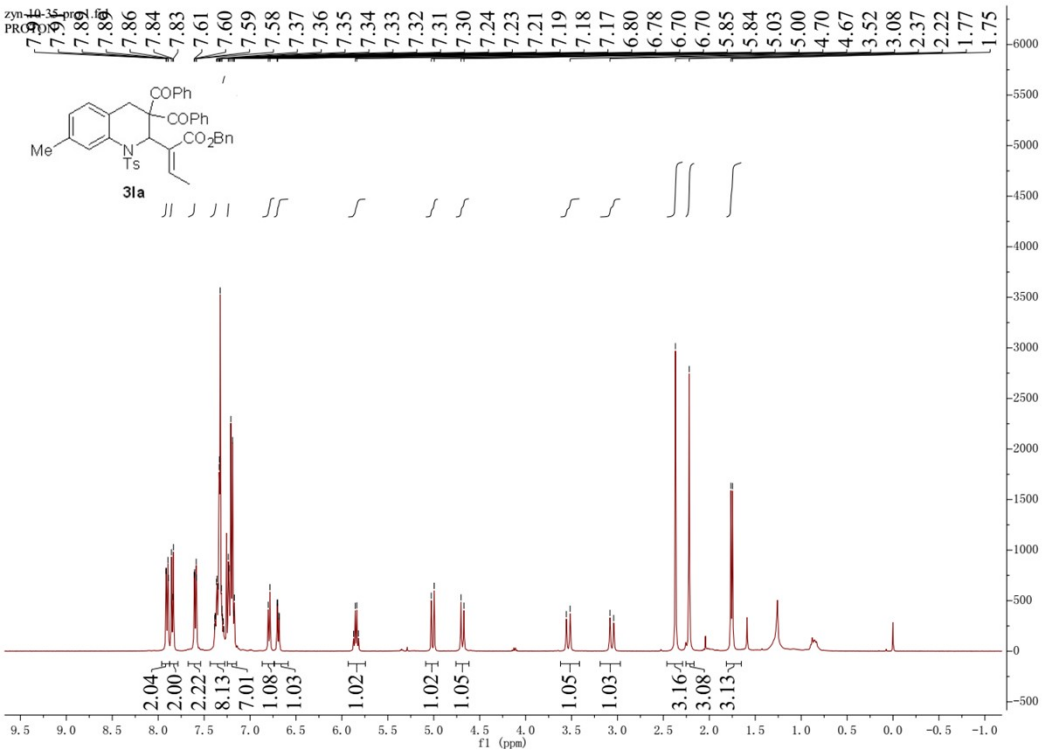
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ka**



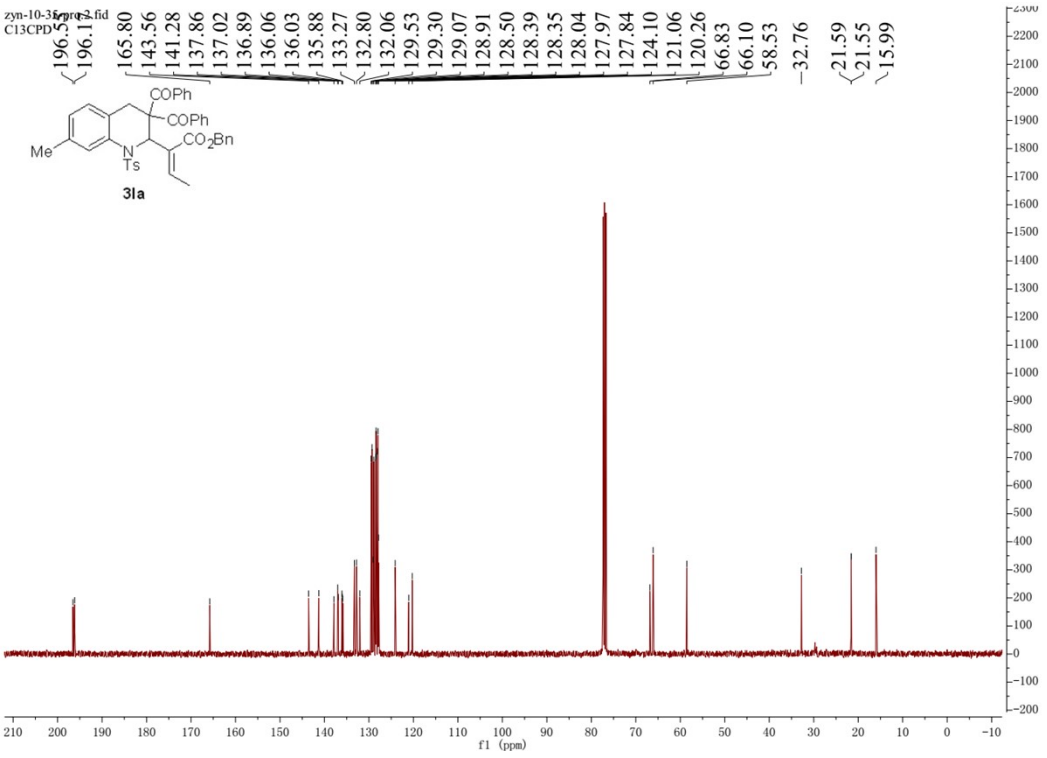
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ka**



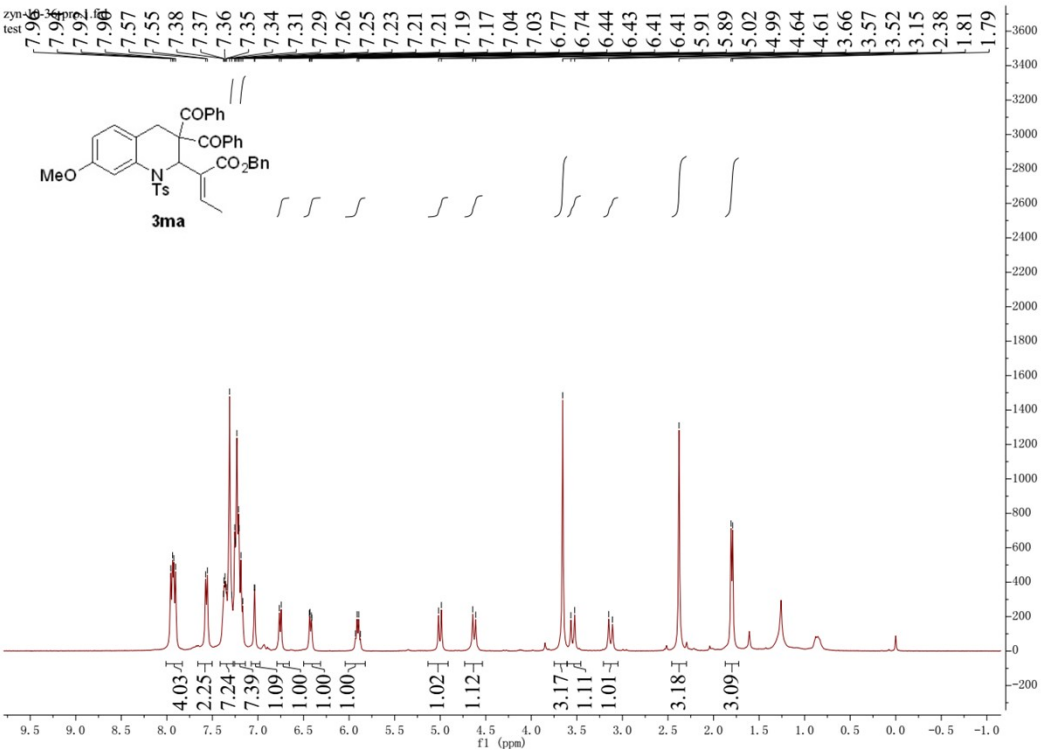
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3ka**



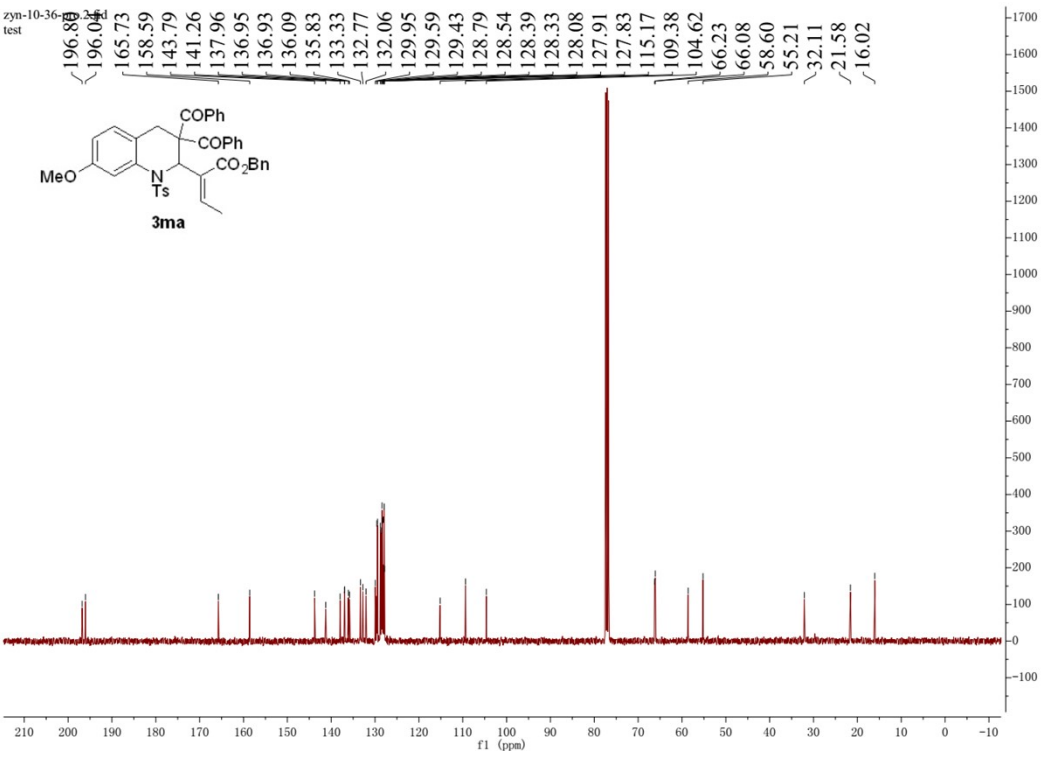
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3la**



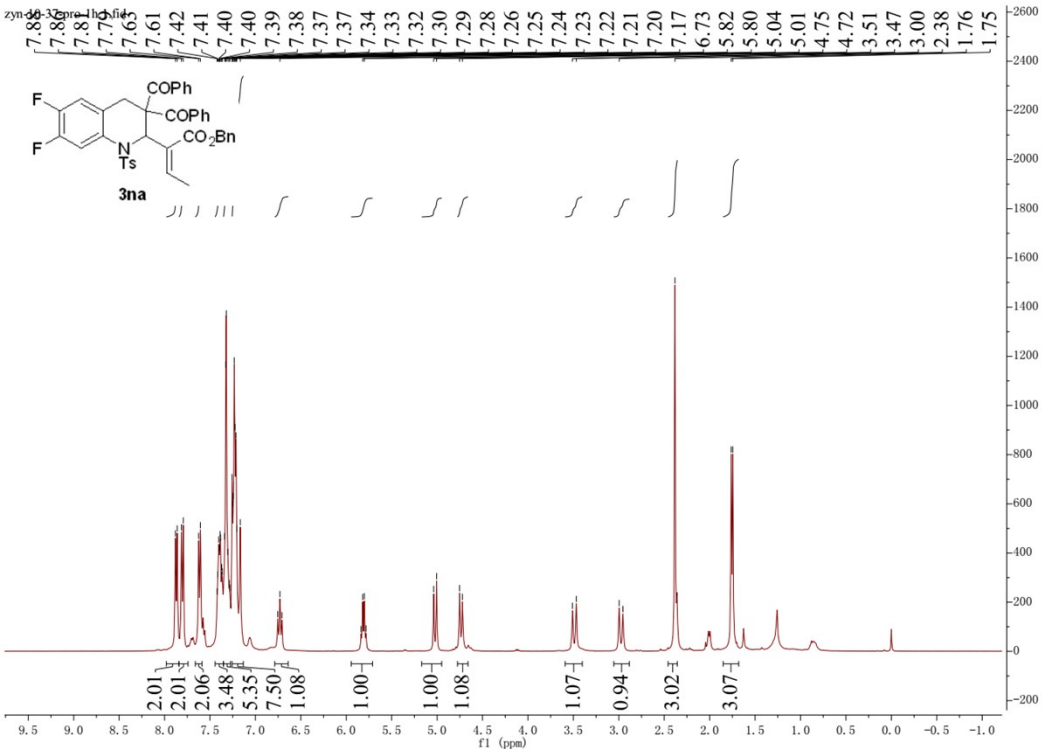
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3la**



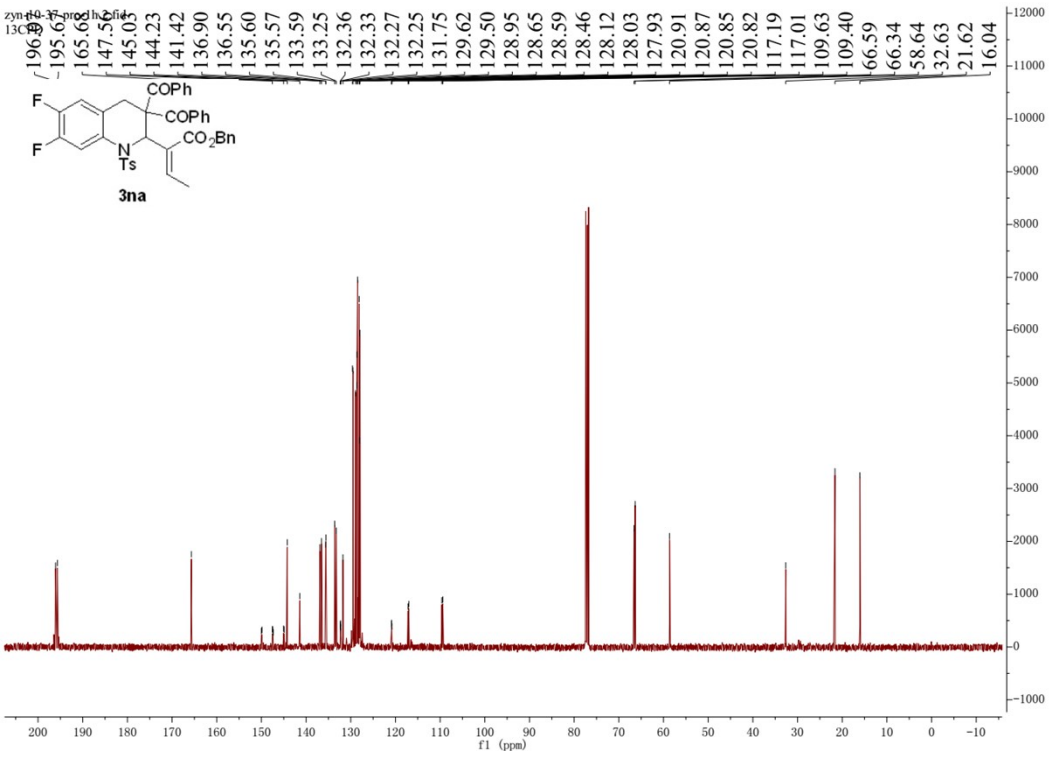
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ma**



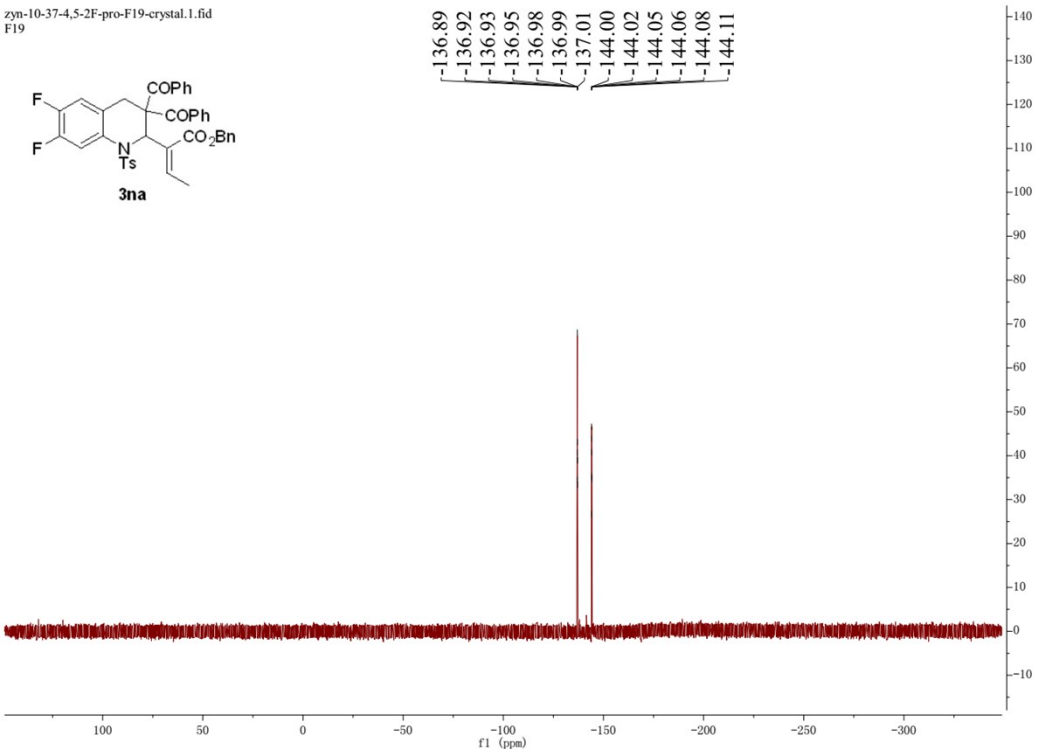
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ma**



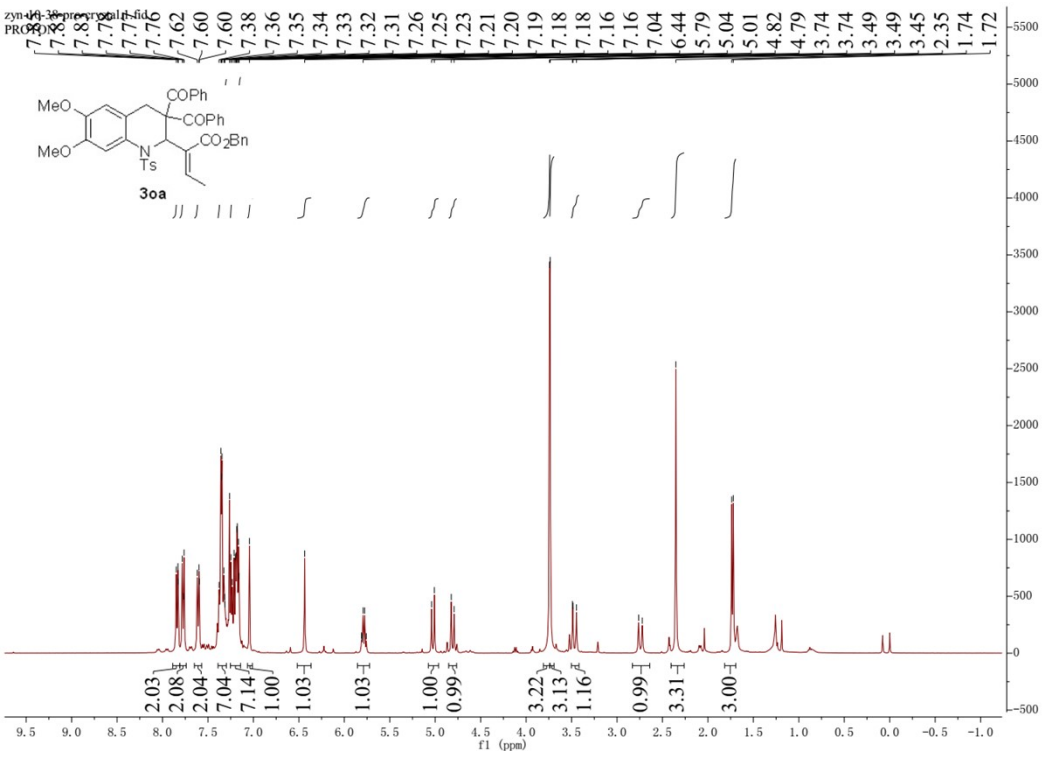
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3na**



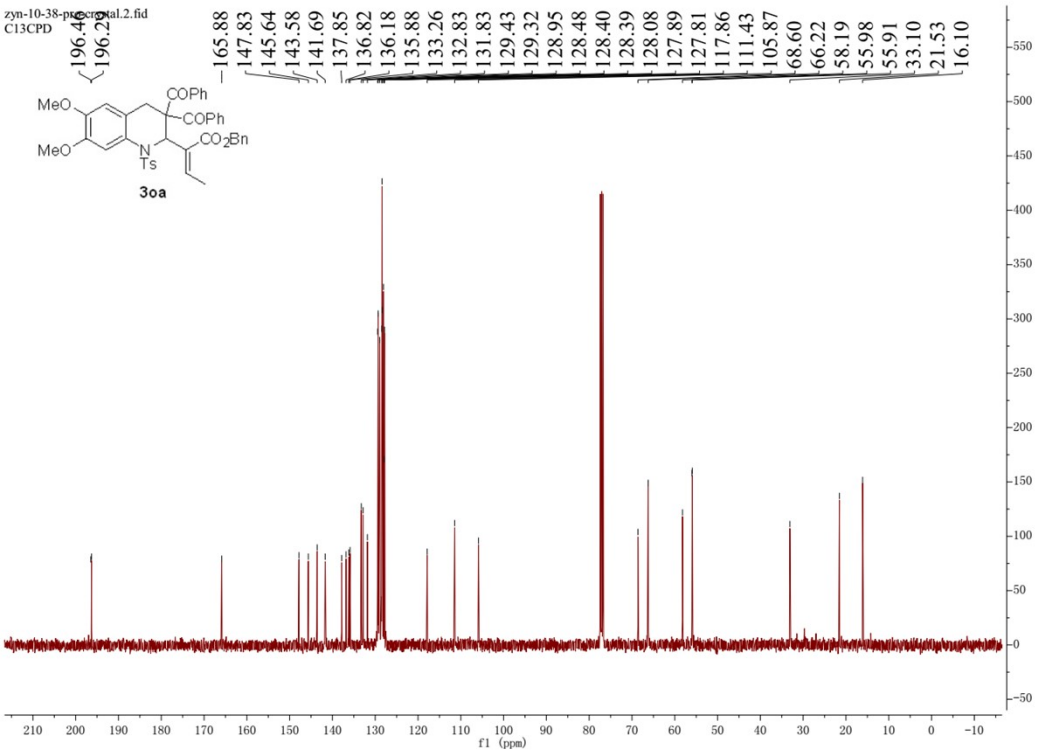
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3na**



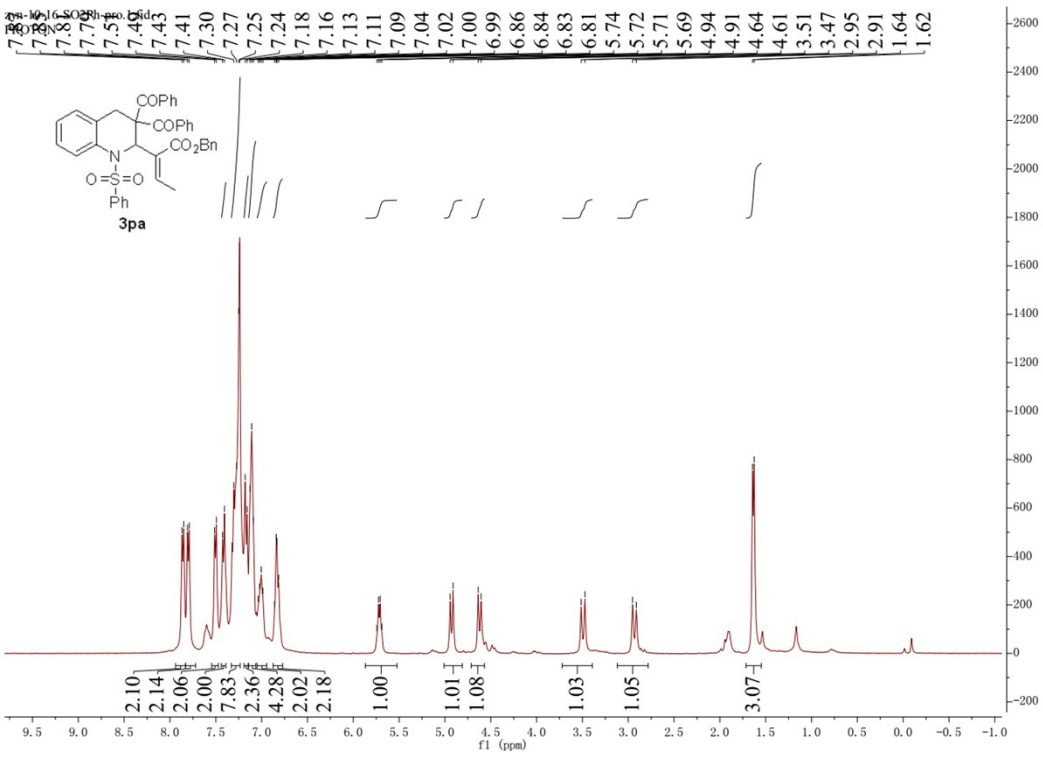
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3na**



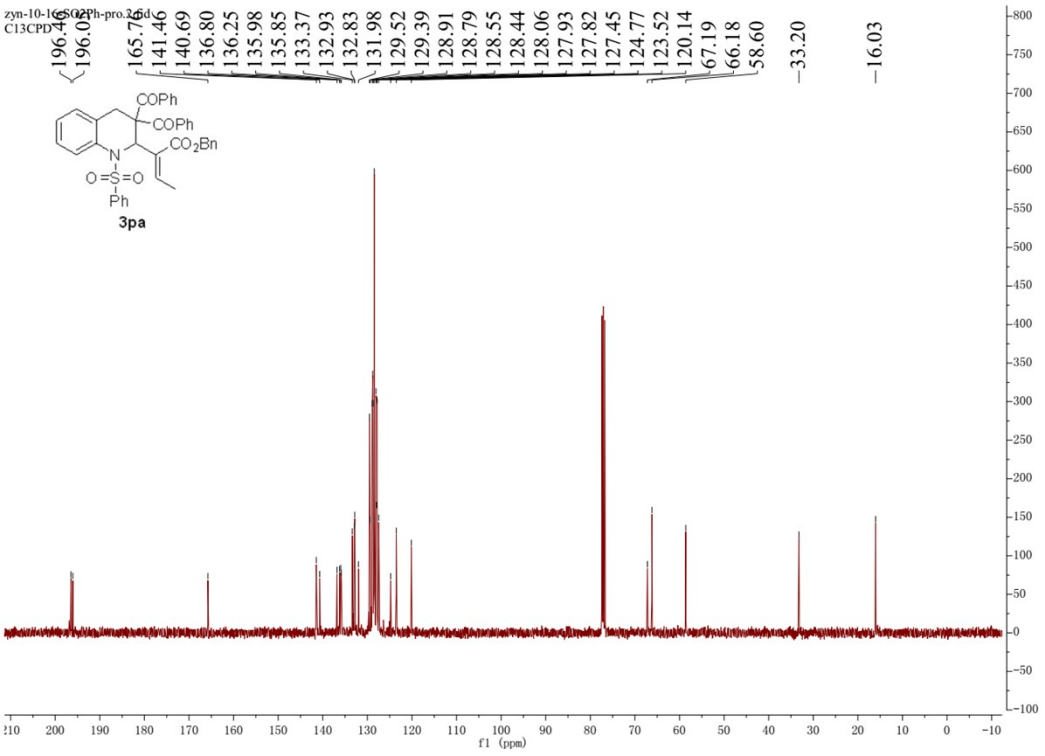
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3oa**



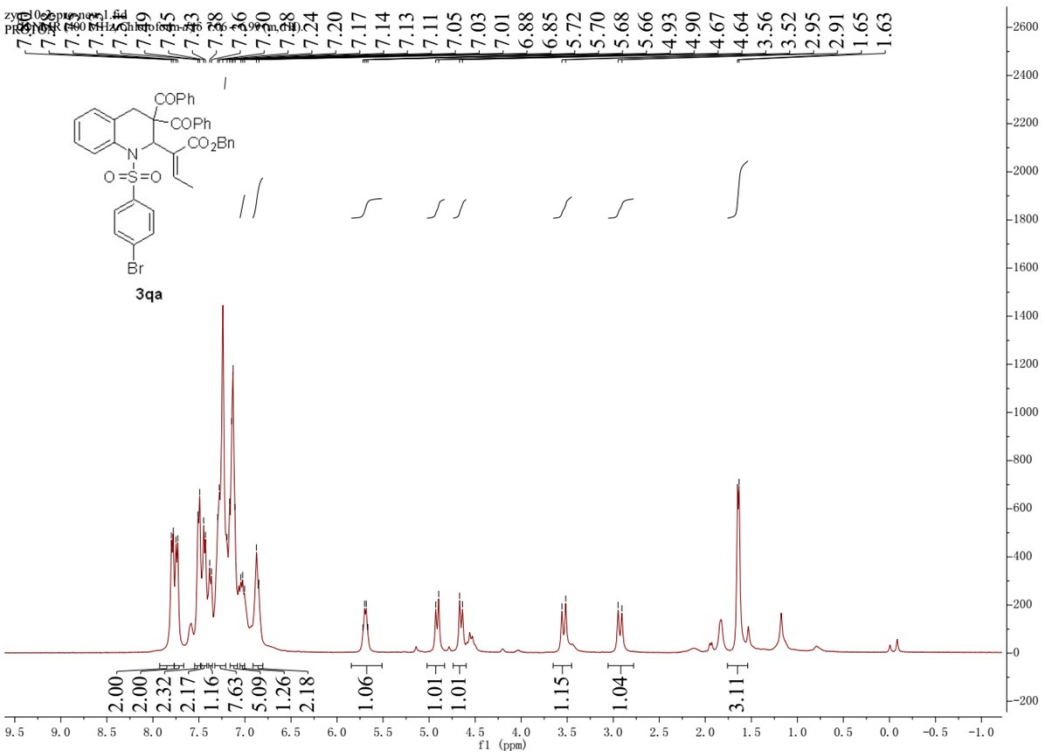
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3oa**



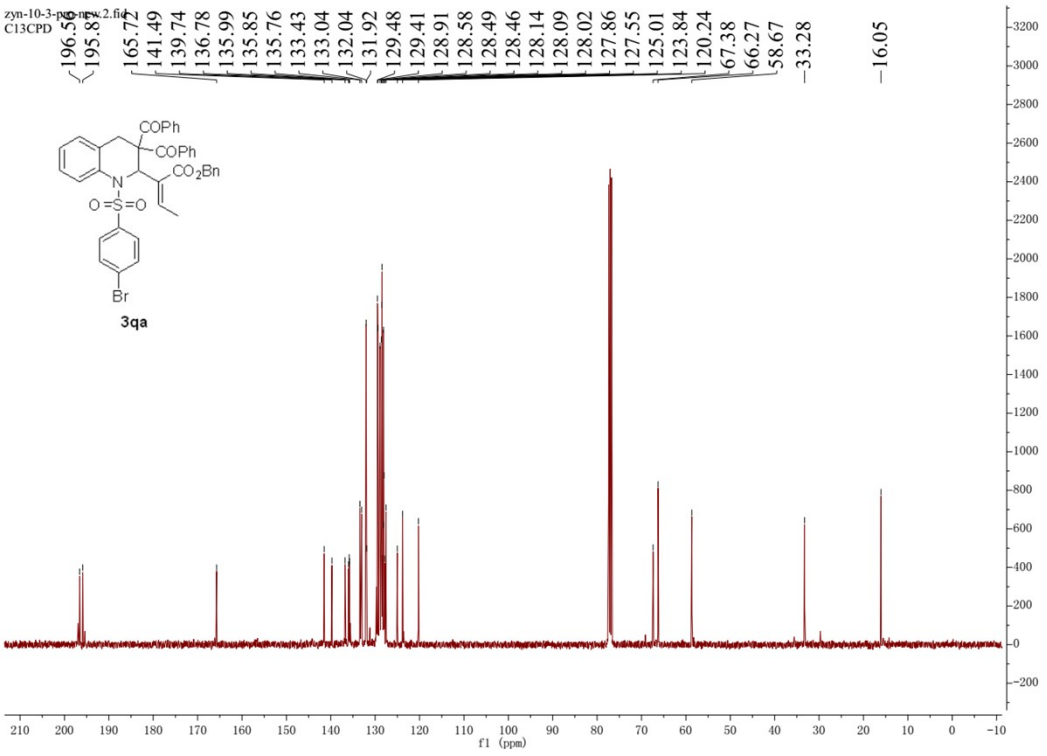
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3pa**



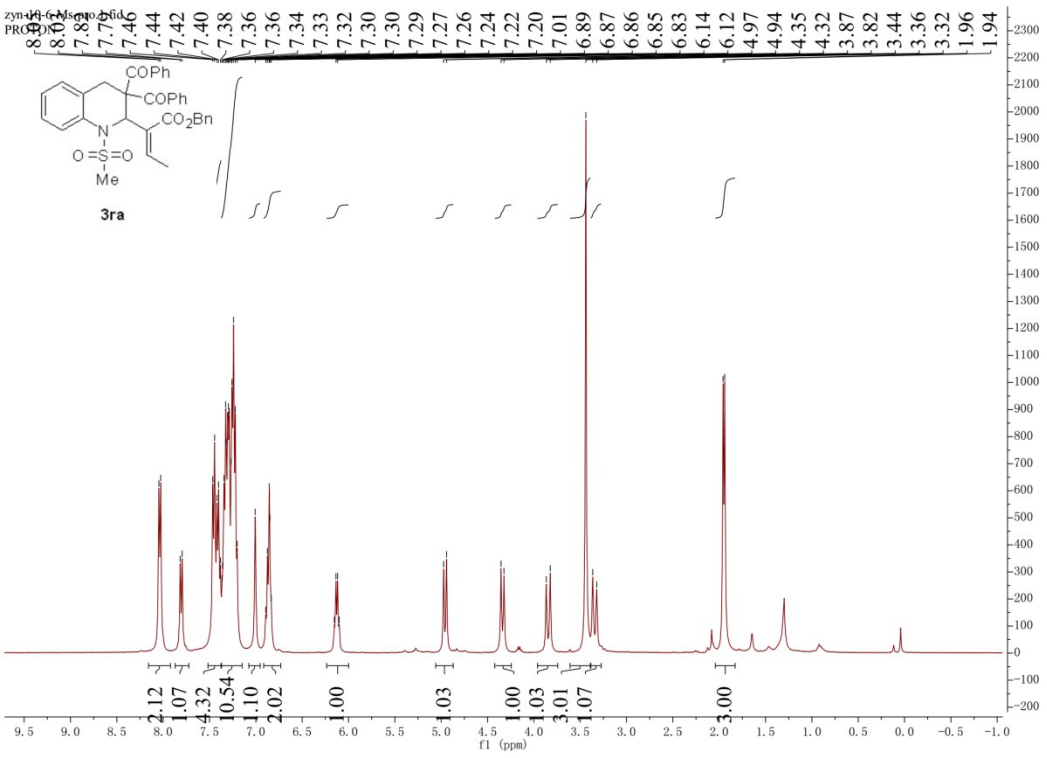
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3pa**



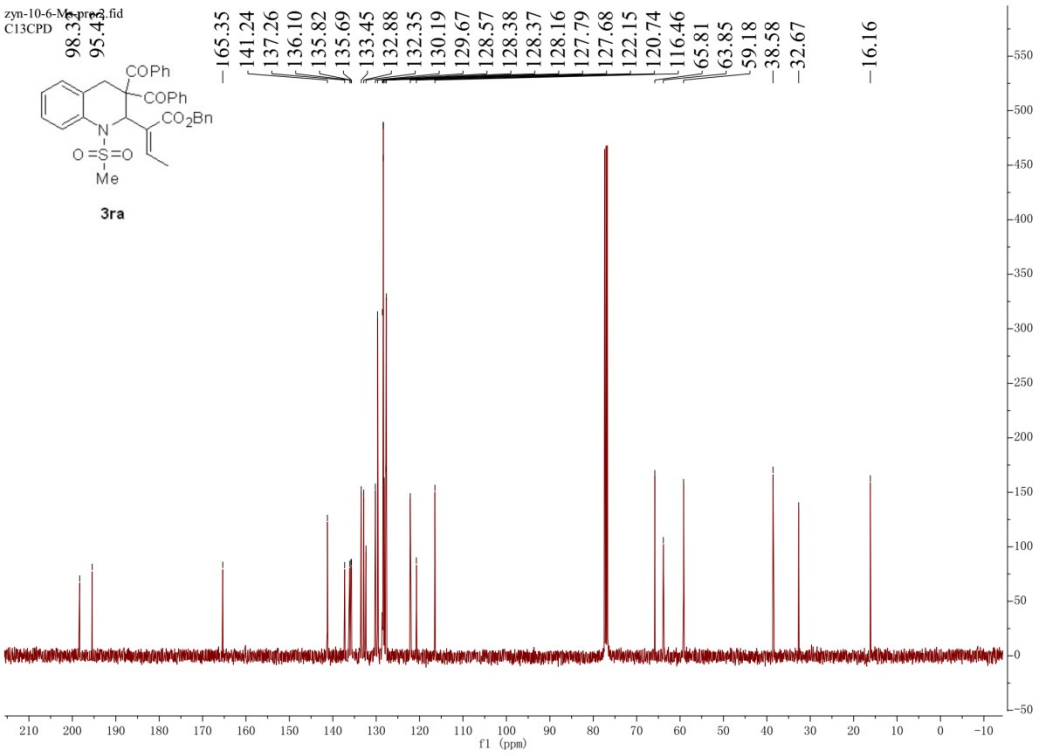
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3qa**



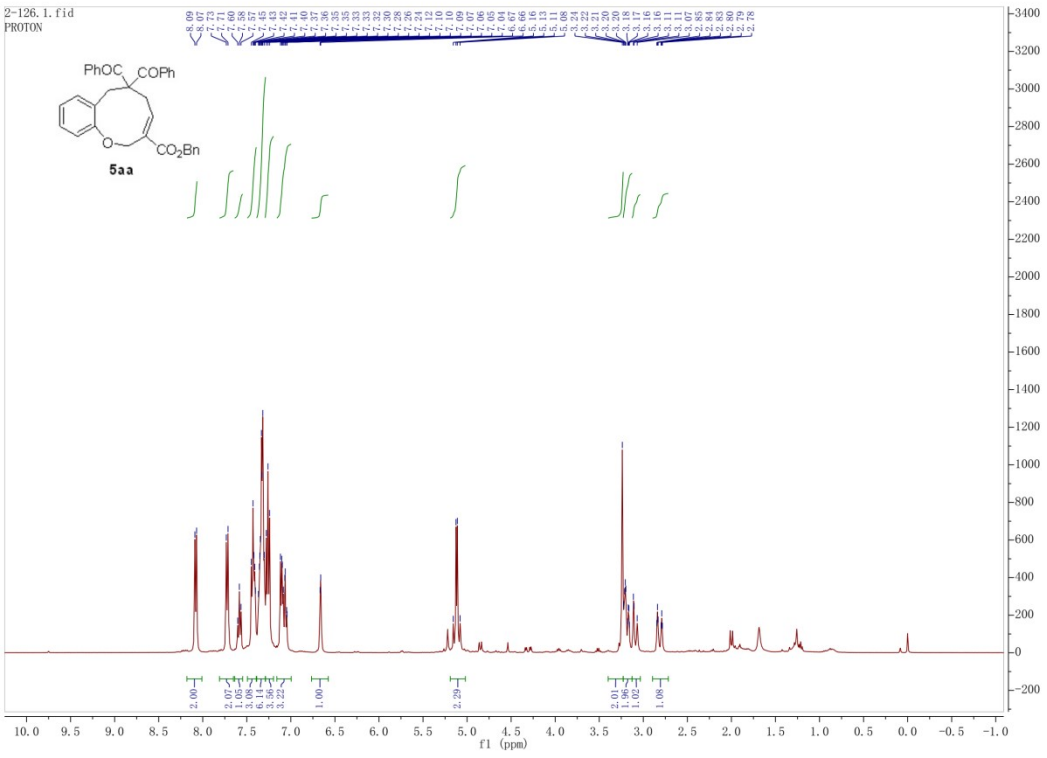
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3qa**



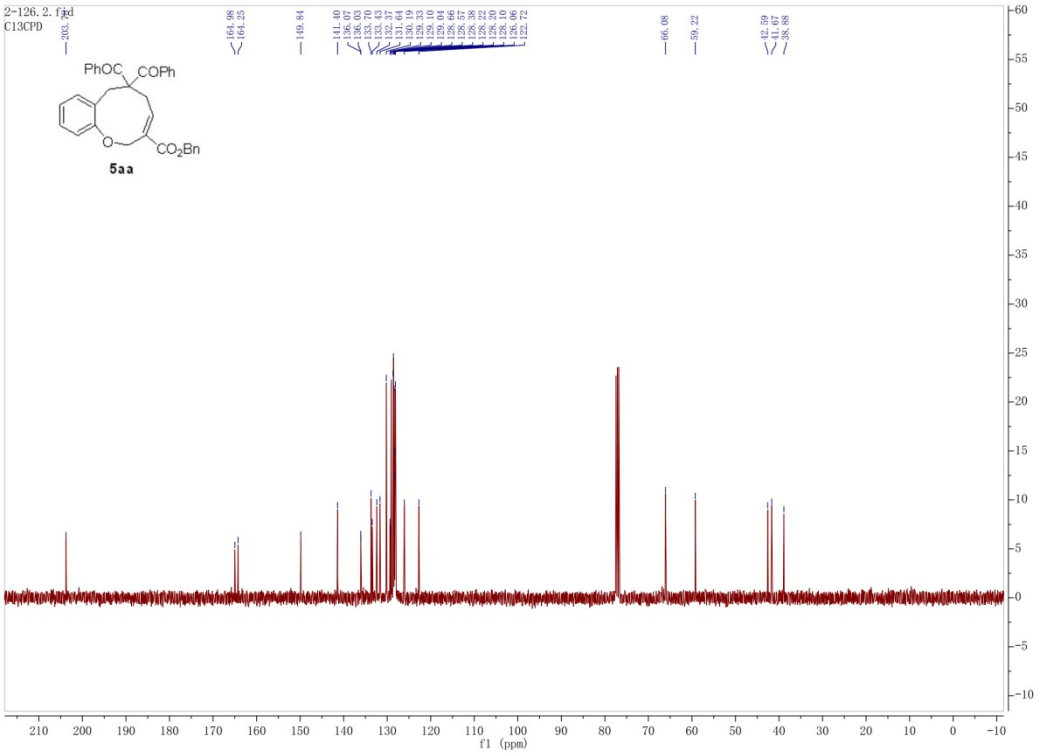
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ra**



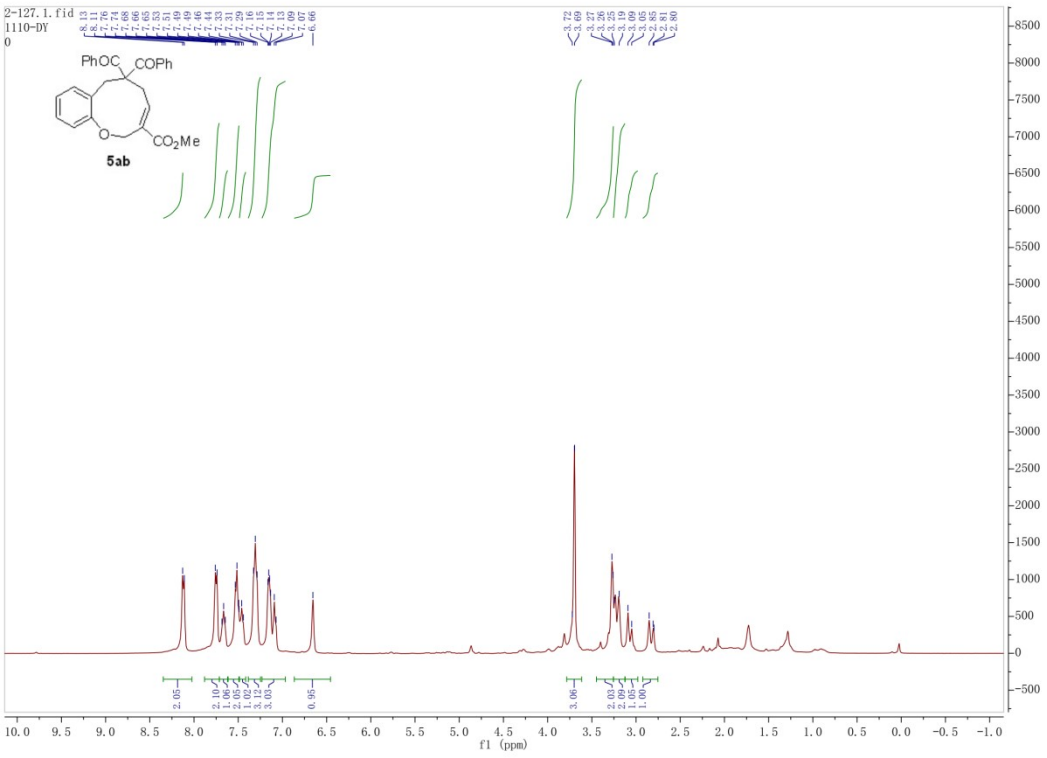
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ra**



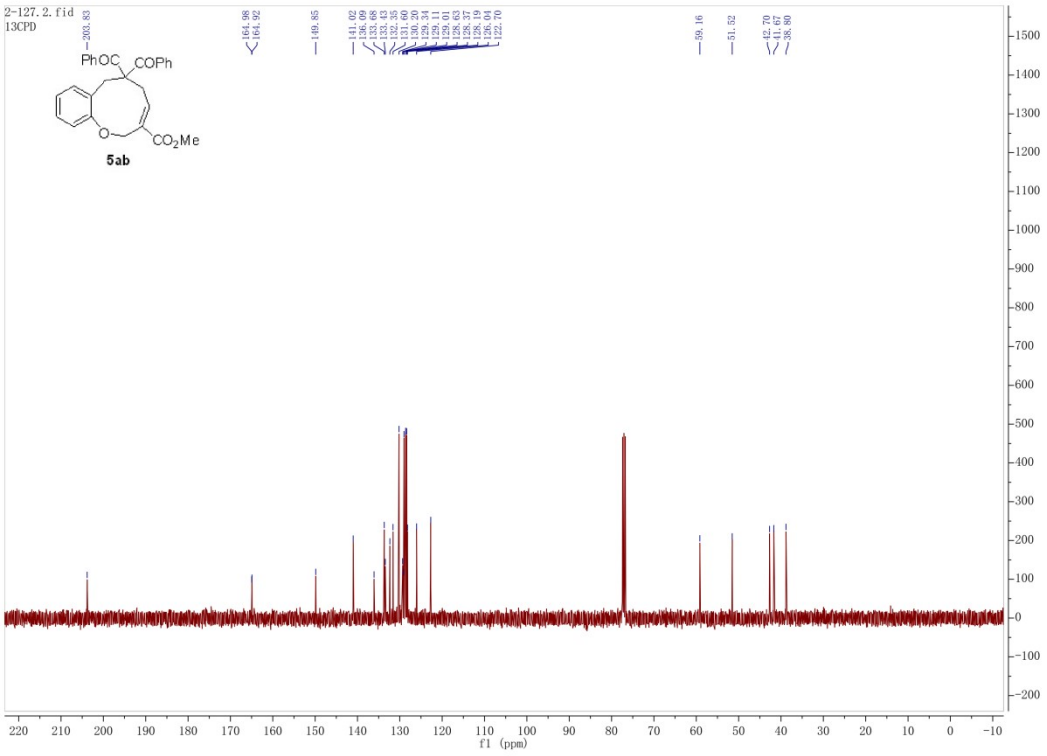
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **5aa**



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

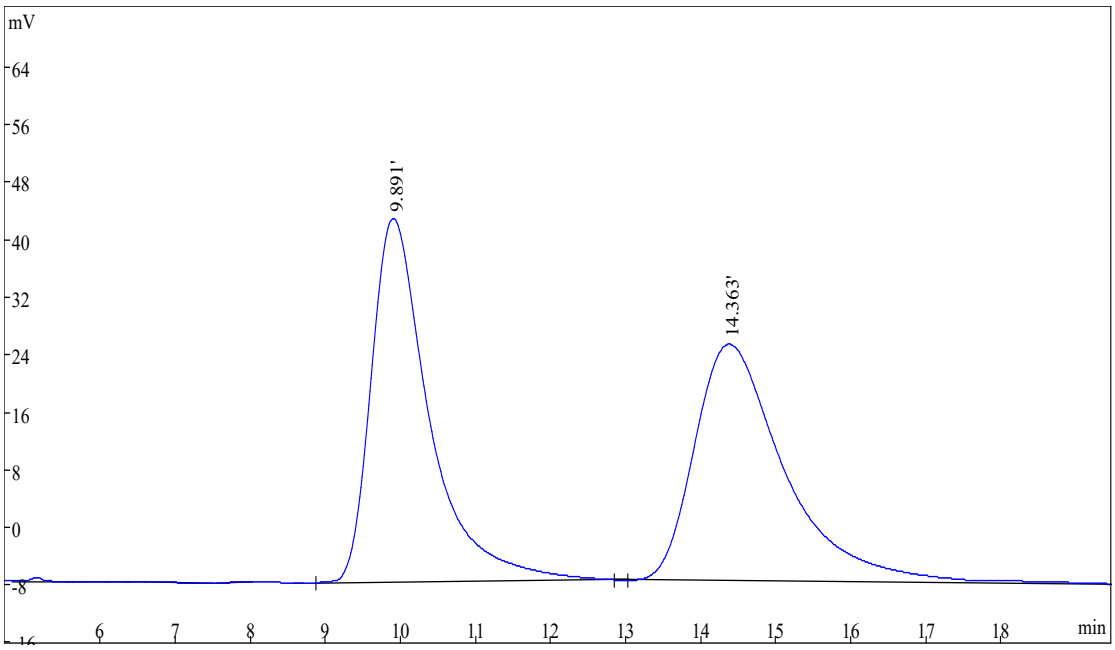


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **5ab**



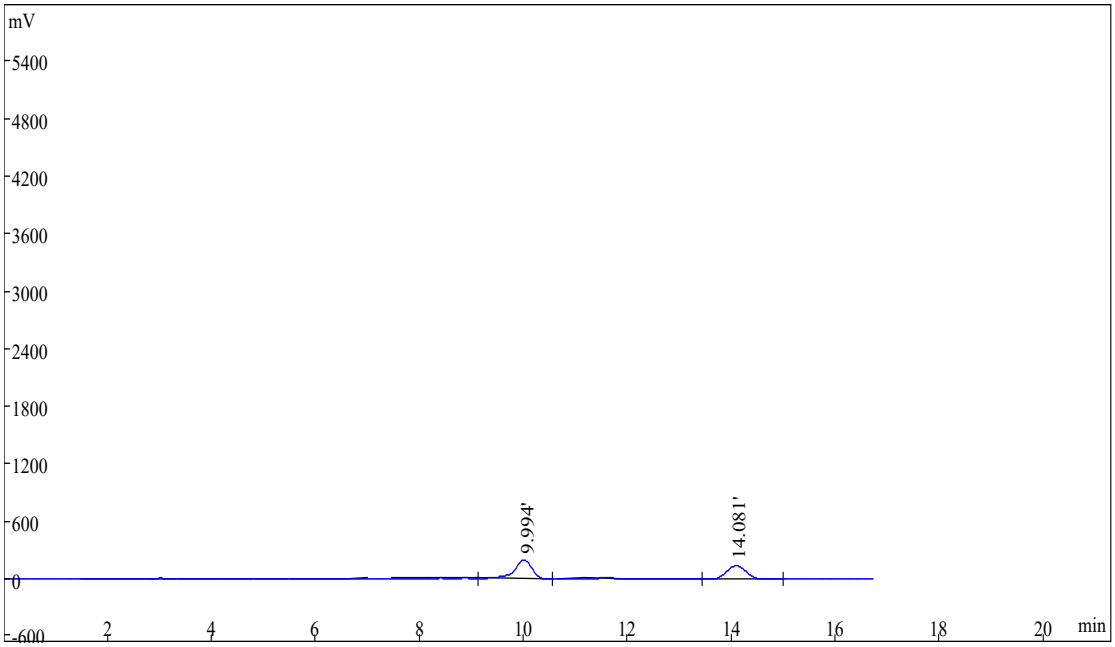
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **5ab**

7. Chiral HPLC analysis of 3aa



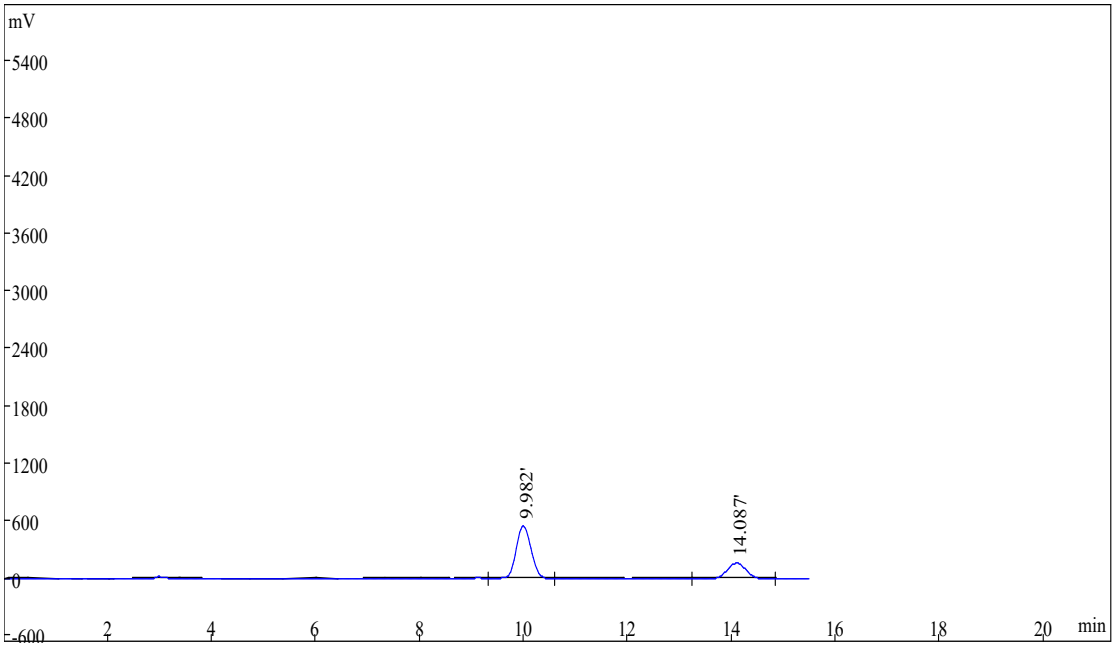
Rank	Time (min)	Area%	Area	Peak height
1	9.891	49.68	2746936	50679
2	14.363	50.32	2782152	32946
Total		100	5529088	83625

Racemic **3a**



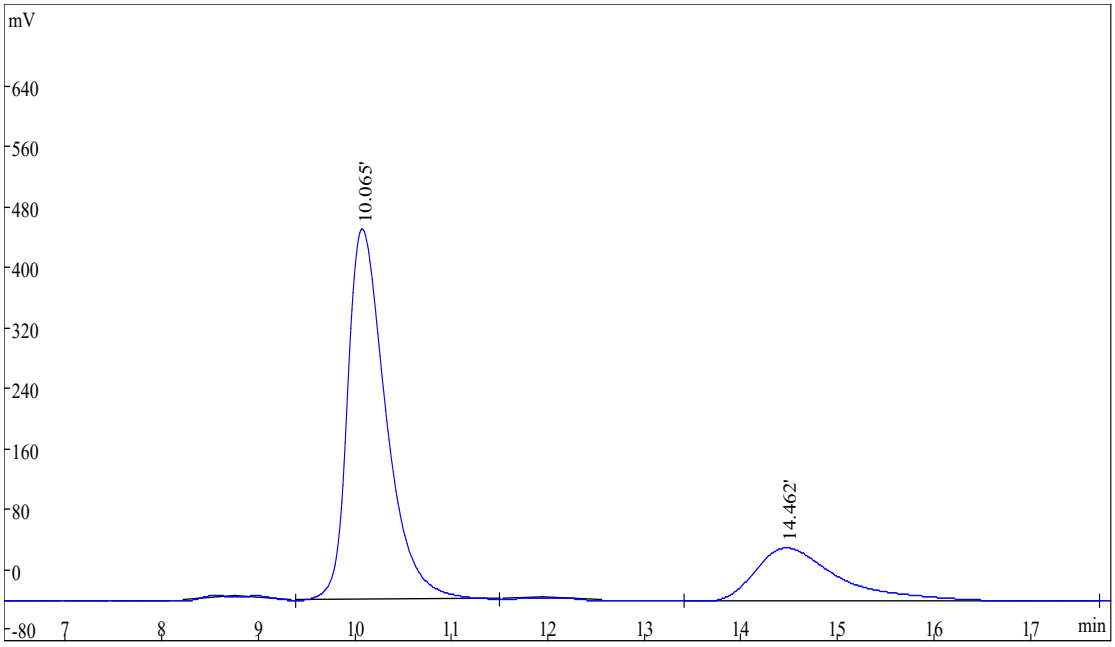
Rank	Time (min)	Area%	Area	Peak height
1	9.994	55.81	5017339	201497
2	14.081	44.19	3972932	146058
Total		100	5529088	83625

Enantiomerically enriched **3aa** (catalyst **P4**)



Rank	Time (min)	Area%	Area	Peak height
1	9.982	71.34	11039450	550929
2	14.087	28.66	4435391	168193
Total		100	5529088	83625

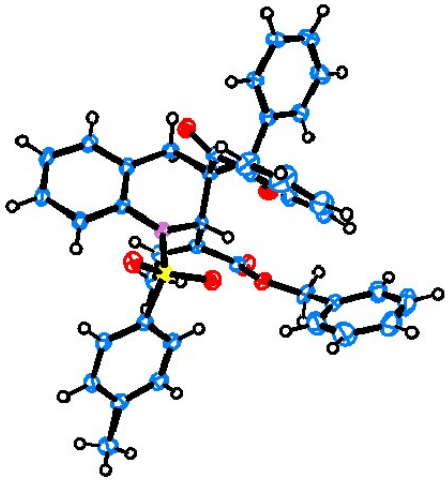
Enantiomerically enriched **3aa** (catalyst **P5**)

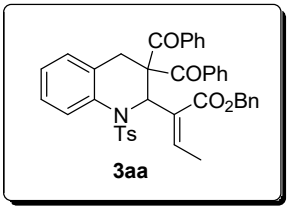


Rank	Time (min)	Area%	Area	Peak height
1	10.065	75.11	13582605	490648
2	14.462	24.89	4500252	71606
Total		100	5529088	83625

Enantiomerically enriched **3aa** (catalyst **P6**)

8. X-ray crystallography data





3aa

Figure S1. ORTEP diagram of **3aa**.[3] Thermal ellipsoids are shown at the 50% probability level.

Method of crystallization: A solution of **3aa** in n-hexane/CH_2Cl_2 (2:1) was added to a 10 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer.

Table S3. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**
Empirical formula	$C_{41}H_{35}NO_6S$
Formula weight	669.76
Temperature/K	113.15
Crystal system	triclinic
Space group	P-1
a/Å	9.1433(3)
b/Å	11.2038(4)
c/Å	17.4935(7)
α/°	87.493(3)
β/°	81.937(3)
γ/°	70.116(3)
Volume/Å^3	1668.52(11)
Z	2
ρ_{calc}g/cm^3	1.333
μ/mm^{-1}	0.149
F(000)	704.0
Crystal size/mm^3	0.32 × 0.28 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.516 to 56.566
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -23 ≤ l ≤ 23
Reflections collected	20347
Independent reflections	8241 [R_{int} = 0.0339, R_{sigma} = 0.0384]
Data/restraints/parameters	8241/0/445
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1164
Largest diff. peak/hole / e Å^{-3}	0.35/-0.41

9. References

1. V. Sriramurthy and O. Kwon, *Org. Lett.,* 2010, **12**, 1084–1087.

2. (a) Q. M. Zhang, L. Yang and X. F. Tong, *J. Am. Chem. Soc.,* 2010, **132**, 2550−2551; (b) D. T. Ziegler, L. Riesgo, T. Ikeda, Y. Fujiwara and G. C. Fu, *Angew. Chem. Int. Ed.,* 2014, **53**, 13183–13187.

3. For crystallographic data of **3aa** see the *CSD Communication*, DOI: 10.5517/ccdc.csd.cc27jql3.