Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Diverse Synthesis of Functionalized Hydroquinoline Derivatives from α-Aryl Vinylsulfonium Salts

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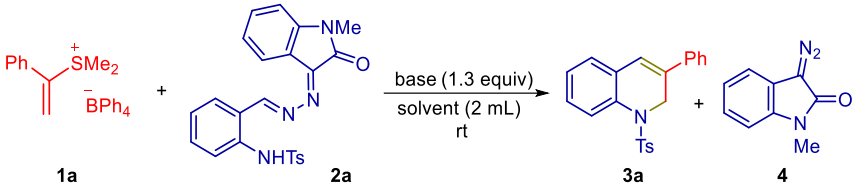
1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. The NMR spectrum were recorded by Bruker Avance NEO 400 or 300. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). The melting points of the products were determined by the OptiMelt melting point apparatus. The HRMS were recorded by Agilent 6545 LC/Q-TOF mass spectrometer.

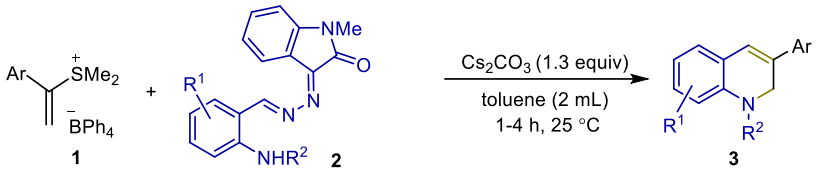
2. Table S1 Optimization of conditions for the synthesis of 3a



entry	base	solvent	temp. (°C)	time (h)	yield (%)[b]
1	Et_3N	DCM	25	28	34
2	DABCO	DCM	25	28	7
3	DBU	DCM	25	1.0	95
4	TMG	DCM	25	2.5	66
5	K_2CO_3	DCM	25	10	97
6	Cs_2CO_3	DCM	25	1.0	98
7	*t*-BuOK	DCM	25	2.5	63
8	$K_3PO_4{\cdot}7H_2O$	DCM	25	1.5	93
9	Cs_2CO_3	THF	25	1.0	91
10	Cs_2CO_3	CH_3CN	25	1.0	90
11	Cs_2CO_3	toluene	25	1.0	99
12	Cs_2CO_3	MTBE	25	9.0	85
13	Cs_2CO_3	EtOAc	25	0.5	62
14	Cs_2CO_3	MeOH	25	1.0	n.p.
15[c]	Cs_2CO_3	toluene	25	1.0	97
16[d]	Cs_2CO_3	toluene	25	1.0	98
17[e]	Cs_2CO_3	toluene	25	1.5	98
18[f]	Cs_2CO_3	toluene	40	1.0	98

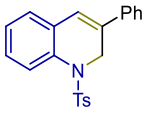
[a]Unless otherwise noted, the reactions were carried out with **1a** (0.24 mmol), **2** (0.18 mmol) and base (0.24 mmol) in 2 mL specified solvent at room temperature for the indicated time; [b] Isolated yield; [c] 1.6 equiv Cs_2CO_3 was used. [d]2.1 equiv Cs_2CO_3 was used. [e]1.1 equiv Cs_2CO_3 was used. [f]The reaction was conducted at 40 °C. n.p. = no product.

3. General procedure for the synthesis of the product 3



Substrate **1** (0.24 mmol), substrate **2** (0.18 mmol), Cs_2CO_3 (0.24 mmol) and 2.0 mL of toluene were successively added to a vial. The resulting mixture was stirred at room temperature for indicated time. After completion of the reaction (monitored by TLC), the reaction mixture was directly subjected to flash column chromatography (petroleum ether/ethyl acetate/dichloromethane (10:1:1)) on silica gel to afford the corresponding product **3**.

3-phenyl-1-tosyl-1,2-dihydroquinoline (3a)



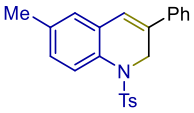
White solid, 66.7 mg, 99% yield; m.p. 186.1 − 186.5 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 1H), 7.44 − 7.33 (m, 3H), 7.33 – 7.29 (m, 2H), 7.28 – 7.21 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.10-7.01 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.33 (s, 1H), 4.82 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 137.5, 135.8, 134.6, 134.4, 130.6, 129.0, 128.8, 128.3, 128.0, 127.2, 127.1, 127.0, 126.9, 125.2, 121.4, 47.7, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{19}NO_2SNa$ 384.1029; found: 384.1022.

6-methyl-3-phenyl-1-tosyl-1,2-dihydroquinoline (3b)



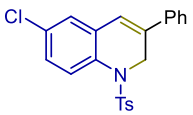
White solid, 69.3 mg, 98% yield; m.p. 139.5 – 104.7 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.29 (m, 3H), 7.28 – 7.21 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.26 (s, 1H), 4.77 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.6, 136.8, 135.7, 134.4, 131.8, 130.3, 128.9, 128.7, 128.2, 127.5, 127.2, 126.6, 125.2, 121.4, 47.7, 21.5, 21.1.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{21}NO_2SNa$ 398.1185; found: 398.1204

6-chloro-3-phenyl-1-tosyl-1,2-dihydroquinoline (3c)



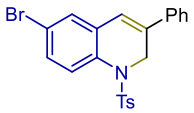
White solid, 73.0 mg, 98% yield; m.p. 108.1 – 109.0 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.30 (m, 3H), 7.29 – 7.21 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.24 (s, 1H), 4.78 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 137.0, 136.1, 135.5, 132.8, 132.4, 131.9, 129.1, 128.8, 128.7, 128.1, 127.7, 127.1, 126.6, 125.3, 120.2, 47.6, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}ClNO_2SNa$ 418.0639, 420.0616; found: 418.0650, 420.0628.

6-bromo-3-phenyl-1-tosyl-1,2-dihydroquinoline (3d)



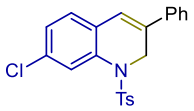
White solid, 82.9 mg, 99% yield; m.p. 119.0 – 119.9 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.24 (s, 1H), 4.78 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 137.0, 136.1, 135.5, 133.3, 132.2, 130.6, 129.6, 129.1, 128.8, 128.7, 128.4, 127.1, 125.3, 120.4, 120.0, 47.5, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}BrNO_2SNa$ 462.0134, 464.0115; found: 462.0132, 464.0115.

7-chloro-3-phenyl-1-tosyl-1,2-dihydroquinoline (3e)



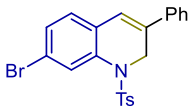
White solid, 73.4 mg, 99% yield; m.p. 186.0 – 186.9 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.6 Hz, 1H), 7.44 – 7.30 (m, 3H), 7.29 – 7.12 (m, 5H), 6.95 (t, *J* = 7.3 Hz, 3H), 6.29 (s, 1H), 4.78 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 137.1, 135.6, 135.3, 134.8, 133.0, 129.1, 128.9, 128.8, 128.6, 127.8, 127.1, 126.8, 125.2, 120.4, 47.5, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}ClNO_2SNa$ 418.0639, 420.0616; found: 418.0661, 420.0639.

7-bromo-3-phenyl-1-tosyl-1,2-dihydroquinoline (3f)



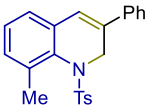
White solid, 83.0 mg, 99% yield; m.p. 265.7 – 166.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.43 – 7.33 (m, 4H), 7.30 – 7.26 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.30 (s, 1H), 4.79 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 137.1, 135.6, 135.5, 135.1, 130.1, 129.6, 129.4, 129.1, 128.8, 128.6, 128.1, 127.1, 125.2, 120.8, 120.4, 47.5, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}BrNO_2SNa$ 462.0134, 464.0115; found: 462.0156, 464.0140.

8-methyl-3-phenyl-1-tosyl-1,2-dihydroquinoline (3g)



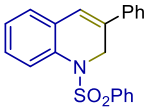
White solid, 68.6 mg, 97% yield; m.p. 147.9 – 148.7 °C

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 – 7.28 (m, 3H), 7.27 – 7.21 (m, 1H), 7.21 – 7.11 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.88 – 6.83 (m, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 17.6 Hz, 1H), 4.23 (dd, *J* = 17.6, 2.4 Hz, 1H), 2.65 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 143.4, 137.7, 137.4, 135.7, 135.1, 133.2, 131.9, 130.9, 128.8, 128.6, 128.2, 127.7, 127.4, 124.9, 124.6, 122.1, 48.5, 21.5, 19.6.

HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for $C_{23}H_{21}NO_2SNa$ 398.1185; found: 398.1202.

3-phenyl-1-(phenylsulfonyl)-1,2-dihydroquinoline (3h)



White solid, 64.2 mg, 99% yield; m.p. 141.4 – 142.1 °C

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.37 – 7.30 (m, 3H), 7.29 – 7.23 (m, 4H), 7.15 (t, *J* = 7.9 Hz, 2H), 7.05 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.30 (s, 1H), 4.83 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 138.5, 137.4, 134.6, 134.2, 132.7, 130.6, 128.8, 128.4, 128.3, 128.0, 127.2, 127.1, 127.0, 126.9, 125.2, 121.2, 47.7.

HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for $C_{21}H_{17}NO_2SNa$ 370.0872; found: 370.0878.

1-(methylsulfonyl)-3-phenyl-1,2-dihydroquinoline (3i)

White solid, 43.2 mg, 82% yield; m.p. 129.1 – 130.0 ºC

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.71 – 7.61 (m, 1H), 7.60 – 7.53 (m, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.34 (m, 1H), 7.33 – 7.27 (m, 3H), 6.95 (s, 1H), 4.78 (s, 2H), 2.64 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 137.1, 135.7, 134.5, 129.9, 129.1, 128.7, 128.4, 127.4, 127.2, 126.4, 125.4, 122.0, 47.4, 37.6.

HRMS (ESI) m/z: [M+Na]$^+$ Calcd. for $C_{16}H_{15}N_2O_2SNa$ 308.0716; found: 308.0719.

3-phenyl-1-(propylsulfonyl)-1,2-dihydroquinoline (3j)

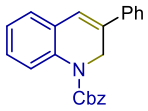
White solid, 51.0 mg, 88% yield; m.p. 86.2 – 87.0 °C

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.75 – 7.69 (m, 1H), 7.61 – 7.55 (m, 2H), 7.51 – 7.44 (m, 2H), 7.42 – 7.36 (m, 1H), 7.33 – 7.27 (m, 3H), 6.96 (s, 1H), 4.79 (s, 2H), 2.81 – 2.73 (m, 2H), 1.76 – 1.65 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) *δ* 137.1, 136.1, 134.7, 129.8, 129.1, 128.7, 128.3, 127.4, 126.7, 125.6, 125.4, 122.0, 52.9, 47.3, 17.0, 13.1.

HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for $C_{18}H_{19}NO_2SNa$ 336.1029; found: 336.1030

benzyl 3-phenylquinoline-1(2H)-carboxylate (3k)



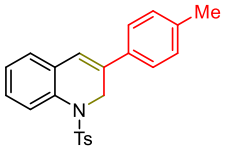
Colorless oil, 49.9 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 1H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.35 (m, 8H), 7.31 – 7.21 (m, 2H), 7.21 – 7.14 (m, 1H), 6.90 (s, 1H), 5.32 (s, 2H), 4.87 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 177.0, 154.2, 137.6, 136.2, 135.7, 128.9, 128.8, 128.7, 128.3, 128.2, 128.1, 127.4, 127.0, 125.3, 124.8, 123.6, 122.1, 68.0, 45.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{19}NO_2Na$ 364.1308; found: 364.1310.

3-(*p*-tolyl)-1-tosyl-1,2-dihydroquinoline (3l)



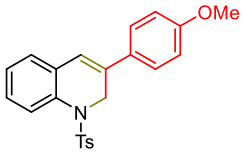
White solid, 69.4 mg, 99% yield; m.p. 149.0 – 149.8 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.25 (m, 1H), 7.25 – 7.20 (m, 1H), 7.20 – 7.13 (m, 6H), 7.07 – 6.99 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 4.78 (s, 2H), 2.38 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 138.3, 135.7, 134.6, 134.2, 130.7, 129.5, 128.9, 127.7, 127.1, 127.0, 126.9, 126.8, 125.1, 120.5, 47.6, 21.5, 21.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{21}NO_2SNa$ 398.1185; found: 398.1191.

3-(4-methoxyphenyl)-1-tosyl-1,2-dihydroquinoline (3m)



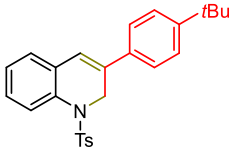
White solid, 68.9 mg, 94% yield; m.p. 132.0 – 132.9 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.19 (m, 4H), 7.18 – 7.12 (m, 2H), 7.00 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.95 – 6.86 (m, 4H), 6.21 (s, 1H), 4.75 (s, 2H), 3.84 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 143.4, 135.7, 134.2, 134.0, 130.8, 130.0, 128.9, 127.5, 127.1, 127.0, 126.8, 126.5, 119.5, 114.1, 55.4, 47.6, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{21}NO_3SNa$ 414.1134; found: 414.1143.

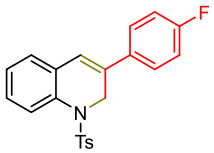
3-(4-(tert-butyl)phenyl)-1-tosyl-1,2-dihydroquinoline (3n)



White solid, 77.2 mg, 99% yield; m.p. 174.0 – 174.8 °C

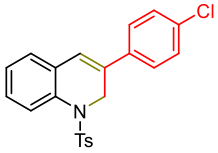
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.16 (m, 6H), 7.06 – 6.98 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.30 (s, 1H), 4.80 (s, 2H), 2.29 (s, 3H), 1.37 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 143.4, 135.7, 134.7, 134.6, 134.2, 130.7, 128.9, 127.7, 127.2, 127.0, 126.7, 125.7, 125.0, 120.6, 47.7, 34.8, 31.4, 21.6.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{27}NO_2SNa$ 440.1655; found: 440.1664.

3-(4-fluorophenyl)-1-tosyl-1,2-dihydroquinoline (3o)



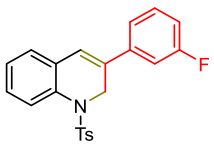
White solid, 70.4 mg, 99% yield; m.p. 141.1 – 142.0 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.18 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.10 – 6.99 (m, 3H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.25 (s, 1H), 4.75 (s, 2H), 2.28 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, *J* = 246.9 Hz), 143.5, 135.7, 134.2, 133.7 (d, *J* = 3.2 Hz), 133.4, 130.4, 128.9, 128.0, 127.1, 127.0, 126.9, 126.8, 121.2, 115.8 (d, *J* = 21.5 Hz), 47.6, 21.6.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}FNO_2SNa$ 402.0934; found: 402.0938.

3-(4-chlorophenyl)-1-tosyl-1,2-dihydroquinoline (3p)



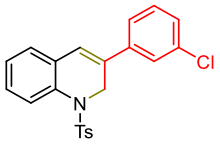
White solid, 71.6 mg, 96% yield; m.p. 189.9 – 190.9 °C
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.38-7.27 (m, 3H), 7.25 – 7.09 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.29 (s, 1H), 4.74 (s, 2H), 2.28 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 135.9, 135.6, 134.3, 134.1, 133.2, 130.2, 129.0, 128.2, 127.2, 127.1, 127.0, 126.9, 126.4, 121.8, 47.4, 21.5.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}ClNO_2SNa$ 418.0639, 420.0616; found: 418.0644, 420.0622.

3-(3-fluorophenyl)-1-tosyl-1,2-dihydroquinoline (3q)



White solid, 70.3 mg, 98% yield; m.p. 167.2 – 167.9 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.09 – 6.97 (m, 3H), 6.96 – 6.84 (m, 3H), 6.32 (s, 1H), 4.75 (s, 2H), 2.29 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.2 Hz), 143.7, 139.7 (d, *J* = 7.7 Hz), 135.7, 134.5, 133.2, 133.2, 130.3 (d, *J* = 8.5 Hz), 130.1, 129.0, 128.4, 127.3, 127.1, 126.9, 122.4, 120.8 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 21.4 Hz), 112.0 (d, *J* = 22.3 Hz), 47.5, 21.5.
HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}FNO_2SNa$ 402.0934; found: 402.0939.

3-(3-chlorophenyl)-1-tosyl-1,2-dihydroquinoline (3r)



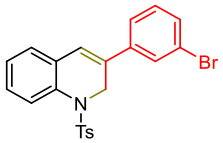
White solid, 74.0 mg, 99% yield; m.p. 153.4 – 154.1 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 1H), 7.37 – 7.20 (m, 4H), 7.18 – 7.09 (m, 4H), 7.07 – 7.02 (m, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.31 (s, 1H), 4.73 (d, J = 1.3 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 139.3, 135.7, 134.7, 134.5, 133.0, 130.0, 129.0, 128.4, 128.2, 127.3, 127.2, 127.1, 127.0, 125.4, 123.2, 122.5, 47.4, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}ClNO_2SNa$ 418.0639, 420.0616; found: 418.0646, 420.0623.

3-(3-bromophenyl)-1-tosyl-1,2-dihydroquinoline (3s)



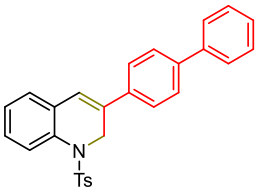
White solid, 81.6 mg, 99% yield; m.p. 139.5 – 140.3 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.28 – 7.20 (m, 3H), 7.19 – 7.09 (m, 3H), 7.04 (d, J = 7.4 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 4.72 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 139.6, 135.7, 134.4, 132.9, 131.1, 130.3, 130.0, 129.0, 128.4, 128.3, 127.3, 127.1, 127.0, 126.9, 123.7, 122.9, 122.5, 47.4, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{18}BrNO_2SNa$ 462.0134, 464.0115; found: 462.0137, 464.0118.

3-([1,1'-biphenyl]-4-yl)-1-tosyl-1,2-dihydroquinoline (3t)



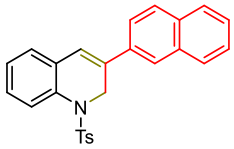
White solid, 73.7 mg, 90% yield; m.p. 185.2 – 186.1 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.5 Hz, 4H), 7.50 (t, J = 7.5 Hz, 2H), 7.45 – 7.30 (m, 4H), 7.30 – 7.19 (m, 3H), 7.08 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.40 (s, 1H), 4.86 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 141.0, 140.3, 136.3, 135.7, 134.3, 134.1, 130.5, 129.0, 128.9, 128.0, 127.7, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 125.6, 121.2, 47.5, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{23}NO_2SNa$ 460.1342; found: 460.1347.

3-(naphthalen-2-yl)-1-tosyl-1,2-dihydroquinoline (3u)



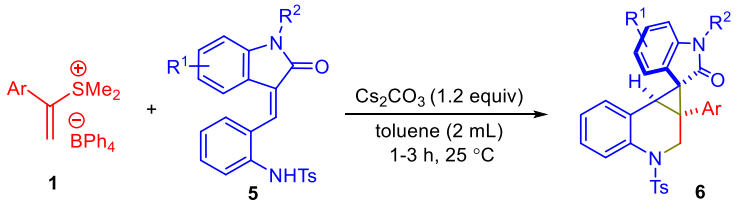
White solid, 76.8 mg, 99% yield; m.p. 144.0 – 144.9 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.75 (m, 4H), 7.71 (s, 1H), 7.56 – 7.44 (m, 2H), 7.37 – 7.26 (m, 2H), 7.26 – 7.19 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.09 – 7.02 (m, 1H), 6.85 (d, *J* = 8.1 Hz, 2H), 6.44 (s, 1H), 4.90 (s, 2H), 2.24 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 135.7, 134.5, 134.4, 134.2, 133.4, 133.1, 130.5, 128.9, 128.4, 128.3, 128.0, 127.7, 127.2, 127.1, 126.9, 126.7, 126.5, 124.2, 123.0, 121.7, 47.5, 21.5.

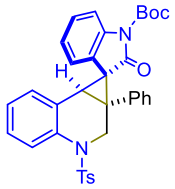
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{21}NO_2SNa$ 434.1185; found: 434.1193.

4. Procedure for the synthesis of spiro-cyclopropane-oxindole-fused tetrahydroquinolines 6



Substrate **1** (0.24 mmol), substrate **5** (0.20 mmol), Cs_2CO_3 (0.24 mmol) and 2.0 mL of toluene were successively added to a vial. The resulting mixture was stirred at room temperature for indicated time. After completion of the reaction (monitored by TLC), the reaction mixture was directly subjected to flash column chromatography (petroleum ether/ethyl acetate/dichloromethane (10:1:1)) on silica gel to afford the corresponding product **6**.

***Tert*-butyl 2'-oxo-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6a)**



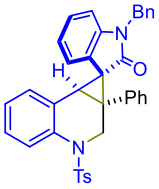
White solid, 117.1 mg, 99% yield; m.p. 195.6 – 196.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.24 – 7.09 (m, 8H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.68 (s, 2H), 5.91 (d, *J* = 7.6 Hz, 1H), 4.89 (d, *J* = 16.2 Hz, 1H), 4.23 (d, *J* = 16.2 Hz, 1H), 3.64 (s, 1H), 2.41 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 148.9, 143.6, 140.5, 138.5, 137.0, 136.8, 131.0, 129.8, 128.7, 128.1, 127.5, 127.4, 127.3, 126.6, 126.2, 125.3, 123.4, 123.3, 122.2, 114.8, 84.1, 49.6, 43.1, 39.8, 31.5, 28.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{35}H_{32}N_2O_5SNa$ 615.1924; found: 615.1930.

1'-Benzyl-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indolin]-2'-one (6b)



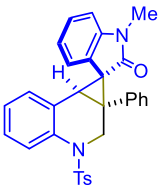
White solid, 108.0 mg, 93% yield; m.p. 262.2 – 263.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.32 (m, 1H), 7.31 – 7.12 (m, 10H), 7.11 – 6.99 (m, 5H), 6.92 – 6.29 (m, 4H), 5.93 (d, *J* = 7.5 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.43 (d, *J* = 15.6 Hz, 1H), 4.31 (d, *J* = 16.1 Hz, 1H), 3.68 (s, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 143.8, 143.6, 139.2, 136.9, 136.9, 136.1, 130.9, 129.8, 128.8, 128.7, 128.5, 128.0, 127.6, 127.4, 127.3, 127.3, 127.2, 126.7, 126.3, 126.0, 124.3, 122.6, 121.4, 109.1, 50.3, 43.8, 43.1, 38.5, 30.8, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{37}H_{30}N_2O_3SNa$ 605.1869; found: 605.1876.

1'-Methyl-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indolin]-2'-one (6c)



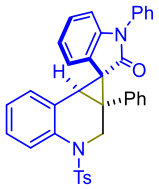
White solid, 117.1 mg, 70% yield; m.p. 231.2 – 232.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.10 (m, 8H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 – 6.46 (m, 3H), 5.97 (d, *J* = 7.5 Hz, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.35 (d, *J* = 16.2 Hz, 1H), 3.60 (s, 1H), 3.07 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 144.8, 143.5, 139.2, 137.0, 136.9, 130.9, 129.8, 128.7, 128.5, 128.0, 127.4, 127.3, 127.2, 126.7, 126.3, 126.0, 124.4, 122.6, 121.4, 108.3, 50.3, 43.1, 38.1, 31.0, 26.6, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{31}H_{26}N_2O_3SNa$ 529.1556; found: 529.1566.

1a,1'-Diphenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[c]quinoline-1,3'-indolin]-2'-one (6d)



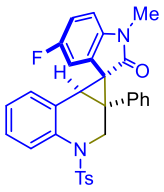
White solid, 113.0 mg, 99% yield; m.p. 259.0 – 259.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.31 – 7.24 (m, 2H), 7.23 – 7.07 (m, 9H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.87 – 6.48 (m, 4H), 6.01 (d, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 16.1 Hz, 1H), 4.37 (d, *J* = 16.1 Hz, 1H), 3.70 (s, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 144.5, 143.5, 139.0, 137.0, 136.9, 134.5, 131.0, 129.8, 129.5, 128.6, 128.5, 128.0, 127.9, 127.4, 127.2, 127.1, 126.7, 126.6, 126.2, 125.8, 124.1, 122.7, 121.8, 109.5, 50.2, 43.1, 38.7, 31.1, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{36}H_{28}N_2O_3SNa$ 591.1713; found: 591.1713.

5'-Fluoro-1'-methyl-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indolin]-2'-one (6e)



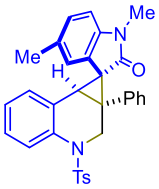
White solid, 104.2 mg, 99% yield; m.p. 245.0 – 245.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.10 (m, 7H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.89 (t, *J* = 8.7 Hz, 1H), 6.81 – 6.47 (m, 3H), 5.68 (d, *J* = 8.9 Hz, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.26 (d, *J* = 16.2 Hz, 1H), 3.62 (s, 1H), 3.04 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 158.0 (d, *J* = 239.3 Hz) 143.6, 140.8, 140.7, 138.9, 136.8 (d, *J* = 3.4 Hz), 130.8, 129.8, 128.8, 128.7, 128.1, 127.4, 126.8, 126.4, 125.9 (d, *J* = 8.9 Hz), 125.5, 113.4 (d, *J* = 23.4 Hz), 110.8 (d, *J* = 26.9 Hz), 108.4 (d, *J* = 8.4 Hz), 50.1, 43.2, 38.7, 31.3, 26.7, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{31}H_{25}FN_2O_3SNa$ 547.1462; found: 547.1476.

1',5'-Dimethyl-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[c]quinoline-1,3'-indolin]-2'-one (6f)



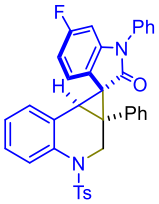
White solid, 101.6 mg, 98% yield; m.p. 238.8 – 239.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.11 (m, 7H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.85 – 6.38 (m, 3H), 5.76 (s, 1H), 4.92 (d, *J* = 16.1 Hz, 1H), 4.37 (d, *J* = 16.1 Hz, 1H), 3.59 (s, 1H), 3.04 (s, 3H), 2.44 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 143.5, 142.4, 139.3, 136.9, 136.8, 130.9, 130.7, 129.8, 128.6, 128.3, 128.0, 127.5, 127.4, 127.1, 126.6, 126.2, 126.1, 124.3, 123.5, 107.9, 50.3, 43.1, 37.9, 30.8, 26.6, 21.6, 21.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{32}H_{28}N_2O_3SNa$ 543.1713; found: 543.1715.

6'-Fluoro-1a,1'-diphenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[c]quinoline-1,3'-indolin]-2'-one (6g)



White solid, 113.8 mg, 97% yield; m.p. 249.3 – 250.1 °C

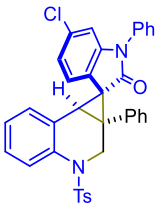
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.34 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.09 (m, 7H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.71 (s, 2H), 6.57 (d, *J* = 9.0 Hz, 1H),

6.45 (t, *J* = 8.8 Hz, 1H), 5.95 – 5.86 (m, 1H), 4.96 (d, *J* = 16.2 Hz, 1H), 4.30 (d, *J* = 16.2 Hz, 1H), 3.67 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 162.5 (d, *J* = 245.9 Hz), 145.9 (d, *J* = 11.3 Hz), 143.6, 138.8, 136.9, 136.8, 134.1, 130.9, 129.8, 129.6, 128.7, 128.6, 128.2, 128.1, 127.4, 127.3, 126.7, 126.6, 126.3, 125.6, 123.6(d, *J* = 9.4 Hz), 119.4, 119.4, 108.1 (d, *J* = 22.2 Hz), 98.4 (d, *J* = 27.9 Hz), 50.2, 42.8, 38.6, 31.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{36}H_{27}FN_2O_3SNa$ 609.1619; found: 609.1623.

6'-Chloro-1a,1'-diphenyl-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indolin]-2'-one (6h)



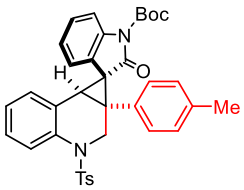
White solid, 118.9 mg, 99% yield; m.p. 266.3 – 267.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 3H), 7.35 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 7.21 – 7.09 (m, 7H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.91 – 6.38 (m, 4H), 5.89 (d, *J* = 8.1 Hz, 1H), 4.96 (d, *J* = 16.2 Hz, 1H), 4.29 (d, *J* = 16.2 Hz, 1H), 3.69 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 145.7, 143.7, 138.7, 137.0, 136.8, 134.0, 133.5, 131.0, 129.9, 129.7, 128.8, 128.6, 128.3, 128.2, 127.5, 127.4, 126.8, 126.7, 126.4, 125.5, 123.4, 122.5, 121.7, 110.1, 50.1, 42.9, 39.2, 31.3, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{36}H_{27}ClN_2O_3SNa$ 625.1323, 627.1310; found: 625.1332, 627.1320.

***Tert*-butyl 2'-oxo-1a-(*p*-tolyl)-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6i)**



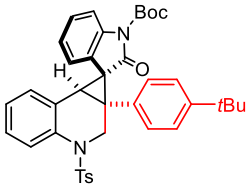
White solid, 118.4 mg, 98% yield; m.p. 179.4 – 180.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.25 – 7.14 (m, 5H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.3 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.60 (s, 2H), 5.91 (d, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 16.2 Hz, 1H), 4.21 (d, *J* = 16.1 Hz, 1H), 3.63 (s, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 148.9, 143.6, 140.5, 137.1, 136.8, 136.8, 135.4, 131.0, 129.7, 128.8, 128.7, 128.6, 127.4, 127.4, 126.5, 126.0, 125.3, 123.6, 123.3, 122.3, 114.7, 84.1, 49.8, 43.1, 39.8, 31.6, 28.0, 21.6, 21.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{36}H_{34}N_2O_5SNa$ 629.2081; found: 629.2086.

***Tert*-butyl 1a-(4-(tert-butyl)phenyl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*] quinoline-1,3'-indoline]-1'-carboxylate (6j)**



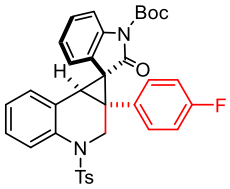
White solid, 126.5 mg, 98% yield; m.p. 109.8 – 110.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.24 – 7.18 (m, 3H), 7.17 – 7.08 (m, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 2H), 5.90 (d, *J* = 7.7 Hz, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.22 (d, *J* = 16.2 Hz, 1H), 3.65 (s, 1H), 2.43 (s, 3H), 1.47 (s, 9H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 149.8, 149.0, 143.3, 140.5, 137.0, 136.9, 135.1, 130.9, 129.7, 128.6, 128.3, 127.4, 127.3, 126.6, 126.4, 125.4, 124.8, 123.6, 123.3, 122.2, 114.7, 83.9, 49.7, 43.2, 39.5, 34.5, 31.4, 31.2, 28.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{39}H_{40}N_2O_5SNa$ 671.2550; found: 671.2559.

***Tert*-butyl 1a-(4-fluorophenyl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro [cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6k)**



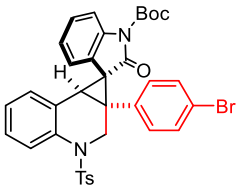
White solid, 121.9 mg, 99% yield; m.p. 181.0 – 182.1 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.15 (m, 5H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 3H), 6.68 (s, 2H), 5.91 (d, *J* = 7.7 Hz, 1H), 4.84 (d, *J* = 16.2 Hz, 1H), 4.22 (d, *J* = 16.2 Hz, 1H), 3.61 (s, 1H), 2.43 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 161.8 (d, *J* = 246.4 Hz, 1C) 148.8, 143.7, 140.5, 137.0, 137.0, 134.3 (d, *J* = 3.2 Hz, 1C), 131.0, 130.4 (d, *J* = 7.2 Hz, 1C) 129.8, 128.8, 127.6, 127.3, 126.7, 126.2, 125.1, 123.4, 123.2, 122.3, 115.0 (d, *J* = 21.9 Hz, 1C), 114.8, 84.3, 49.6, 43.0, 39.1, 31.8, 28.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{35}H_{31}FN_2O_5SNa$ 633.1830; found: 633.1837.

***Tert*-butyl 1a-(4-bromophenyl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro [cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6l)**



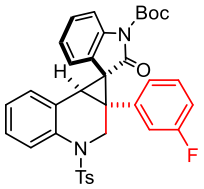
White solid, 134.0 mg, 99% yield; m.p. 131.7 – 132.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.14 (m, 7H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.60 (s, 2H), 5.91 (d, *J* = 7.7 Hz, 1H), 4.80 (d, *J* = 16.2 Hz, 1H), 4.21 (d, *J* = 16.2 Hz, 1H), 3.60 (s, 1H), 2.44 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 148.8, 143.9, 140.5, 137.5, 137.0, 136.9, 131.2, 130.9, 130.4, 129.8, 128.8, 127.7, 127.3, 126.7, 126.2, 124.8, 123.4, 123.1, 122.3, 121.2, 114.9, 84.4, 49.3, 43.0, 39.0, 31.5, 28.0, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{35}H_{31}BrN_2O_5SNa$ 693.1029, 695.1014; found: 693.1034, 695.1020.

***Tert*-butyl 1a-(3-fluorophenyl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro [cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6m)**



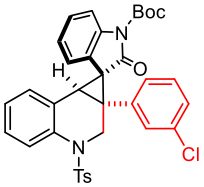
White solid, 119.6 mg, 98% yield; m.p. 176.9 – 178.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.05 (m, 8H), 6.94 – 6.77 (m, 2H), 6.59 (s, 1H), 6.12 (s, 1H), 5.91 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 16.3 Hz, 1H), 4.23 (d, *J* = 16.3 Hz, 1H), 3.58 (s, 1H), 2.43 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 162.2 (d, *J* = 244.9 Hz), 148.8, 144.2, 141.1 (d, *J* = 7.6 Hz), 140.6, 136.9 (d, *J* = 22.7 Hz), 130.9, 129.9, 128.9, 127.7, 127.3, 126.8, 126.5, 124.9, 124.3, 123.4, 123.1, 122.3, 116.0 (d, *J* = 22.4 Hz), 114.9, 114.3 (d, *J* = 21.1 Hz), 84.3, 49.4, 43.1, 39.0, 31.6, 28.0, 21.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{35}H_{31}FN_2O_5SNa$ 633.1830; found: 633.1828.

***Tert*-butyl 1a-(3-chlorophenyl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro [cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6n)**



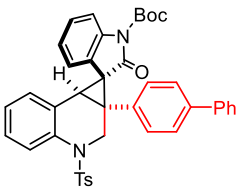
White solid, 124.9 mg, 99% yield; m.p. 181.8 – 182.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.06 (m, 9H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.79 – 6.27 (m, 2H), 5.91 (d, *J* = 7.6 Hz, 1H), 4.89 (d, *J* = 16.3 Hz, 1H), 4.23 (d, *J* = 16.3 Hz, 1H), 3.59 (s, 1H), 2.44 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 148.8, 144.0, 140.7, 140.6, 136.9, 136.6, 133.8, 131.0, 129.9, 129.6, 129.0, 128.9, 127.7, 127.6, 127.3, 127.0, 126.8, 126.4, 124.9, 123.4, 123.0, 122.4, 114.9, 84.4, 49.3, 43.1, 39.0, 31.5, 28.0, 21.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{35}H_{31}ClN_2O_5SNa$ 649.1534, 651.1521; found: 649.1534, 651.1525.

***Tert*-butyl 1a-([1,1'-biphenyl]-4-yl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro[cyclopropa[*c*] quinoline-1,3'-indoline]-1'-carboxylate (6o)**



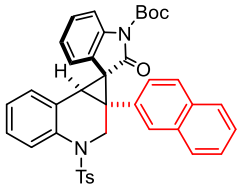
White solid, 130.1 mg, 97% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.32 (m, 4H), 7.25 – 7.16 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.92 – 6.63 (m, 3H), 5.94 (d, *J* = 7.6 Hz, 1H), 4.95 (d, *J* = 16.2 Hz, 1H), 4.27 (d, *J* = 16.2 Hz, 1H), 3.69 (s, 1H), 2.40 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 149.0, 143.7, 140.8, 140.6, 140.0, 137.5, 137.1, 136.9, 131.1, 129.8, 129.2, 128.9, 128.8, 127.6, 127.5, 127.1, 126.8, 126.7, 126.3, 125.3, 123.5, 123.4, 122.4, 114.9, 84.3, 49.7, 43.3, 39.6, 31.7, 28.1, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{41}H_{36}N_2O_5SNa$ 691.2237; found: 691.2242.

***Tert*-butyl 1a-(naphthalen-2-yl)-2'-oxo-3-tosyl-1a,2,3,7b-tetrahydrospiro [cyclopropa[*c*]quinoline-1,3'-indoline]-1'-carboxylate (6p)**



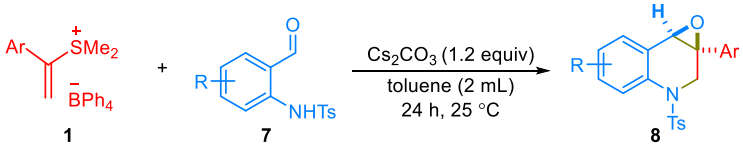
White solid, 128.0 mg, 99% yield; m.p. 197.0 – 198.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.73 – 7.51 (m, 2H), 7.51 – 7.35 (m, 3H), 7.30 – 7.16 (m, 3H), 7.15 – 6.60 (m, 7H), 5.97 (d, *J* = 7.7 Hz, 1H), 5.04 (d, *J* = 16.2 Hz, 1H), 4.32 (d, *J* = 16.2 Hz, 1H), 3.79 (s, 1H), 2.33 (s, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 148.8, 143.5, 140.6, 137.1, 136.8, 132.8, 132.7, 131.1, 129.7, 128.8, 128.3, 127.7, 127.5, 127.3, 126.7, 126.2, 126.1, 126.0, 125.2, 123.5, 123.4, 122.4, 114.8, 84.2, 49.6, 40.0, 31.7, 28.0, 21.7.

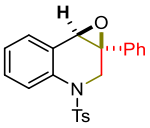
HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{39}H_{34}N_2O_5SNa$ 665.2081; found: 665.2087.

5. Procedure for the synthesis of epoxypropane-fused tetrahydroquinolines 8



Substrate **1** (0.24 mmol), substrate **5** (0.20 mmol), Cs_2CO_3 (0.24 mmol) and 2.0 mL of toluene were successively added to a vial. The resulting mixture was stirred at room temperature for indicated time. After completion of the reaction (monitored by TLC), the reaction mixture was directly subjected to flash column chromatography (petroleum ether/ethyl acetate (20:1)) on silica gel to afford the corresponding product **6**.

1a-Phenyl-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8a)



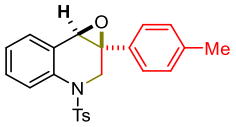
White solid, 46.0 mg, 61% yield; m.p. 164.3 – 165.5 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.16 (m, 7H), 7.15 – 7.07 (m, 3H), 4.74 (d, *J* = 15.2 Hz, 1H), 3.79 (d, *J* = 15.3 Hz, 1H), 3.57 (s, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.1, 135.6, 135.5, 129.8, 129.6, 129.1, 128.9, 128.7, 128.1, 127.2, 126.3, 126.0, 125.5, 69.0, 59.0, 46.5, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{19}NO_3SNa$ 400.0978; found: 400.0976.

1a-(*p*-Tolyl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8b)



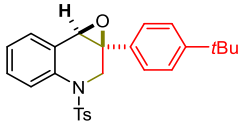
White solid, 24.2 mg, 31% yield; m.p. 149.5 – 150.3 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.15 – 7.01 (m, 7H), 4.72 (d, *J* = 15.2 Hz, 1H), 3.75 (d, *J* = 15.2 Hz, 1H), 3.55 (s, 1H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.6, 135.7, 135.5, 133.1, 129.8, 129.5, 129.4, 129.1, 128.1, 127.3, 126.3, 126.0, 125.5, 69.0, 59.0, 46.5, 21.8, 21.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}NO_3SNa$ 414.1134; found: 414.1127.

1a-(4-(*Tert*-butyl)phenyl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8c)



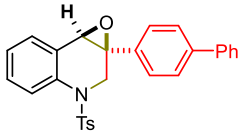
White solid, 28.0 mg, 33% yield; m.p. 159.4 – 198.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.27 (m, 3H), 7.23 – 7.15 (m, 3H), 7.14 – 7.06 (m, 3H), 4.74 (d, *J* = 15.3 Hz, 1H), 3.78 (d, *J* = 15.2 Hz, 1H), 3.57 (s, 1H), 2.29 (s, 3H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 143.5, 135.7, 135.5, 133.2, 129.7, 129.5, 129.1, 128.1, 127.3, 126.3, 126.0, 125.8, 125.3, 68.9, 59.1, 46.4, 34.8, 31.4, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_3SNa$ 456.1604; found: 456.1612.

1a-([1,1'-Biphenyl]-4-yl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8d)



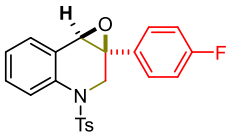
White solid, 42.2 mg, 47% yield; m.p. 173.0 – 173.6 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.60 (t, *J* = 8.2 Hz, 4H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.35 (m, 6H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.16 (m, 3H), 4.87 (d, *J* = 15.2 Hz, 1H), 3.92 (d, *J* = 15.2 Hz, 1H), 3.70 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 141.7, 140.5, 135.7, 135.5, 135.1, 129.8, 129.6, 129.2, 129.0, 128.1, 127.8, 127.6, 127.2, 127.1, 126.3, 126.0, 126.0, 68.8, 59.2, 46.4, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{23}NO_3SNa$ 476.1291; found: 476.1297.

1a-(4-Fluorophenyl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-c]quinoline (8e)



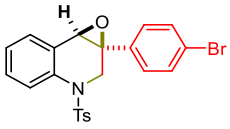
White solid, 32.5 mg, 41% yield; m.p. 190.0 – 190.7 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.23 – 7.13 (m, 3H), 7.06 (t, *J* = 8.3 Hz, 2H), 4.78 (d, *J* = 15.2 Hz, 1H), 3.82 (d, *J* = 15.2 Hz, 1H), 3.62 (s, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.9 Hz, 1C), 143.6, 135.6, 135.4, 132.0, 132.0, 129.7 (d, *J* = 10.4 Hz, 1C), 129.2, 128.0, 127.5 (d, *J* = 8.4 Hz, 1C), 126.9, 126.3, 126.1, 115.9 (d, *J* = 21.7 Hz, 1C), 68.6, 59.0, 46.5, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}FNO_3SNa$ 418.0884; found: 418.0892.

1a-(4-Bromophenyl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8f)



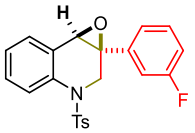
White solid, 62.0 mg, 68% yield; m.p. 145.2 – 146.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.43 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.14 (m, 5H), 4.76 (d, *J* = 15.2 Hz, 1H), 3.82 (d, *J* = 15.2 Hz, 1H), 3.60 (s, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 135.6, 135.4, 135.1, 132.0, 129.8, 129.7, 129.1, 128.0, 127.2, 126.8, 126.3, 126.1, 122.8, 68.5, 59.1, 46.2, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}BrNO_3SNa$ 478.0083, 480.0064; found: 478.0084, 480.0065.

1a-(3-Fluorophenyl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8g)

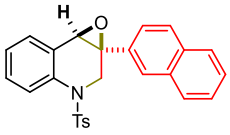


White solid, 48.1 mg, 61% yield; m.p. 143.4 – 143.9 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.32 (m, 2H), 7.31 – 7.24 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 3H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.08 – 6.97 (m, 2H), 4.79 (d, *J* = 15.2 Hz, 1H), 3.86 (d, *J* = 15.2 Hz, 1H), 3.62 (s, 1H), 2.38 (s, 3H).

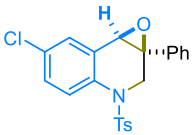
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.3 Hz), 143.6, 138.7, 138.6, 135.6, 135.4, 130.6 (d, *J* = 8.3 Hz), 129.8, 129.7, 129.2, 128.0, 126.7, 126.3, 126.1, 121.2 (d, *J* = 3.0 Hz), 115.7 (d, *J* = 21.1 Hz), 112.6 (d, *J* = 22.9 Hz), 68.4 (d, *J* = 2.0 Hz), 59.3, 46.2, 21.7.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}FNO_3SNa$ 418.0884; found: 418.0888.

1a-(Naphthalen-2-yl)-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8h)



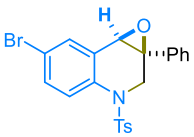
White solid, 47.8 mg, 56% yield; m.p. 165.8 – 166.2 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.79 (m, 4H), 7.52 (d, *J* = 7.2 Hz, 4H), 7.46 – 7.37 (m, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.16 (m, 3H), 4.93 (d, *J* = 15.2 Hz, 1H), 3.99 (d, *J* = 15.2 Hz, 1H), 3.75 (s, 1H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 135.7, 135.5, 133.5, 133.3, 133.1, 129.8, 129.7, 129.2, 128.8, 128.1, 127.9, 127.1, 126.8, 126.7, 126.3, 126.0, 125.1, 122.9, 69.2, 59.2, 46.6, 21.8.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{21}NO_3SNa$ 450.1134; found: 450.1127.

6-Chloro-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-c]quinoline (8i)



White solid, 47.2 mg, 57% yield; m.p. 153.6 – 154.2 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 7.25 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.78 (d, *J* = 15.3 Hz, 1H), 3.83 (d, *J* = 15.3 Hz, 1H), 3.57 (s, 1H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 135.5, 135.2, 134.0, 131.2, 129.5, 129.2, 128.9, 128.0, 127.6, 125.5, 69.0, 58.3, 46.3, 21.7.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}ClNO_3SNa$ 434.0588, 436.0565; found: 434.0591, 436.0570.

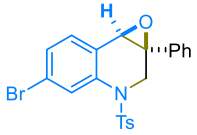
6-Bromo-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8j)



White solid, 42.3 mg, 46% yield; m.p. 162.5 – 163.3 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.42 – 7.34 (m, 4H), 7.33 – 7.27 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.79 (d, *J* = 15.3 Hz, 1H), 3.83 (d, *J* = 15.3 Hz, 1H), 3.57 (s, 1H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 135.6, 135.2, 134.6, 132.5, 132.4, 129.3, 129.2, 128.9, 128.0, 127.9, 125.5, 119.0, 69.1, 58.2, 46.4, 21.7.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}BrNO_3SNa$ 478.0083, 480.0064; found: 478.0088, 480.0069.

7-Bromo-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8k)



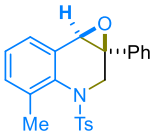
White solid, 30.3 mg, 33% yield; m.p. 166.4 – 166.9 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.79 (d, *J* = 15.3 Hz, 1H), 3.84 (d, *J* = 15.3 Hz, 1H), 3.62 (s, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.6, 135.7, 135.2, 130.8, 129.3, 129.1, 129.0, 128.9, 128.1, 126.1, 125.5, 123.1, 69.0, 58.5, 46.3, 21.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{18}BrNO_3SNa$ 478.0083, 480.0064; found: 478.0084, 480.0065.

4-methyl-1a-phenyl-3-tosyl-1a,2,3,7b-tetrahydrooxireno[2,3-*c*]quinoline (8l)



White solid, 43.2 mg, 55% yield; m.p. 148.5 – 148.8 °C

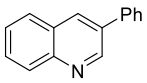
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.26 – 7.11 (m, 6H), 4.56 (d, *J* = 15.4 Hz, 1H), 3.73 (d, *J* = 15.4 Hz, 1H), 3.61 (s, 1H), 2.51 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.4, 136.6, 136.1, 134.3, 132.7, 129.2, 129.0, 128.8, 128.6, 128.5, 127.3, 126.9, 125.6, 66.9, 58.8, 47.4, 21.7, 20.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{21}NO_3SNa$ 414.1134; found: 414.1136.

6. Procedure for the synthesis of 3-phenylquinoline 9

In a dry round-bottom flask, the 1-(methylsulfonyl)-3-phenyl-1,2-dihydroquinoline **3i** (57.1 mg, 0.2 mmol) was added under Ar atmosphere, followed by anhydrous THF (3.5 mL) and *t*-BuOH (90 μL), *t*-BuOK (45 mg) at 25 °C The mixture was stirred at room temperature for 16 h. Upon reaction completion, 10% NaOH (10 mL) was added and the mixture was extracted with EtOAc, washed with water and brine, dried over Mg_2SO_4, filtered, and concentrated to afford the crude product. The product was purified by flash chromatography with MTBE/PE to provide the desired compound in 99% yield (42.2 mg) as a white solid.



White solid, 42.2 mg, 99% yield; m.p. 51.7 – 52.4 °C

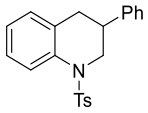
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.28 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.66 (m, 3H), 7.62 – 7.48 (m, 3H), 7.47 – 7.38 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 147.4, 137.9, 133.9, 133.3, 129.5, 129.3, 129.2, 128.2, 128.1, 127.5, 127.1.

HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}N$ 206.0964; found: 206.0970.

7. Procedure for the synthesis of 3-phenyl-1-tosyl-1,2,3,4-tetrahydroquinoline 10

To the substrate **3a** (108.5 mg, 0.3 mmol) in a dry hydrogenation reactor was added anhydrous THF (3.0 mL) and 10% Pd/C (32.4 mg). The mixture was stirred at room temperature under a H_2 atmosphere (0.8 MPa) for 18 h. Filtered with diatomite, and concentrated to afford the crude product. The product was purified by flash chromatography with MTBE/PE to provide the title compound in 99% yield (107.8 mg) as a white solid.



White solid, 107.8 mg, 99% yield; m.p. 127.0 – 127.6 °C

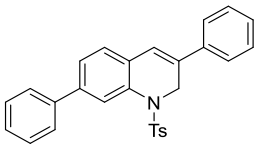
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.17 (m, 4H), 7.15 – 7.00 (m, 4H), 4.39 – 4.28 (m, 1H), 3.47 – 3.34 (m, 1H), 2.81 – 2.62 (m, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 141.9, 136.7, 136.4, 130.1, 129.8, 129.3, 128.9, 127.3, 127.0, 126.8, 125.1, 124.7, 52.3, 38.2, 34.5, 21.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{21}NO_2SNa$ 386.1185; found: 386.1189.

8. Procedure for the synthesis of 3,7-diphenyl-1-tosyl-1,2,3,4-tetrahydroquinoline 11

Under Ar nitrogen atmosphere, compound **3f** (88.0 mg, 0.2 mmol), phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.20 equiv), and butyl di-1-adamantylphosphine (0.24 equiv) were successively added to a dried sealedtube, followed by the addition of 2.0 mL of DME. The resulting mixture was stirred at 80 °C for 38 h until almost full consumption of **3f** (monitored by thin layer chromatography), and then the reaction mixture was directly subjected to flash column chromatography on silica gel to afford the corresponding product **6** in 96% yield (84.1 mg) as a white solid.



White solid, 84.1 mg, 96% yield; m.p. 152.0 – 152.9 °C

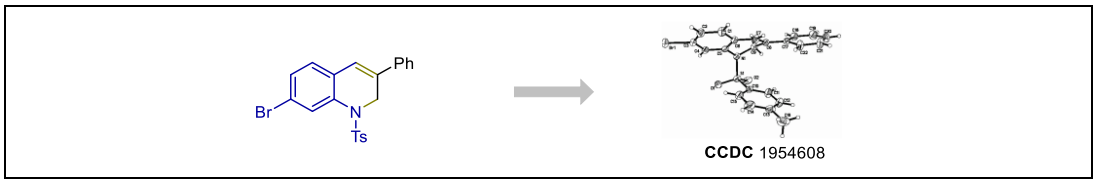
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.05 (m, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.43 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.37 (s, 1H), 4.85 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.8, 140.1, 137.5, 135.8, 134.8, 134.5, 129.5, 129.1, 129.0, 128.8, 128.4, 127.8, 127.4, 127.3, 127.1, 125.5, 125.4, 125.2, 121.1, 47.8, 21.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{23}NO_2SNa$ 460.1342; found: 460.1343.

9. Crystal data and structure refinement

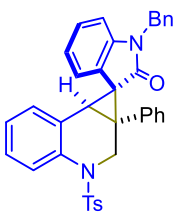
Single crystals of compound **3f** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (5/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on a 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



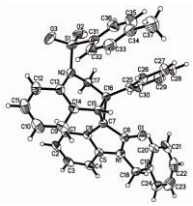
Identification code	**3f**
Empirical formula	$C_{22}H_{18}BrNO_2S$
Formula weight	440.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.8433(6)
b/Å	14.8254(6)
c/Å	9.4672(4)
α/°	90
β/°	90.436(4)
γ/°	90
Volume/Å^3	1942.93(14)
Z	4
ρ_{calc}g/cm^3	1.505
μ/mm^{-1}	4.023
F(000)	896.0
Crystal size/mm^3	0.13 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.74 to 134.158
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 12, -11 ≤ l ≤ 9
Reflections collected	7440
Independent reflections	3462 [R_{int} = 0.0361, R_{sigma} = 0.0489]
Data/restraints/parameters	3462/0/233
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1235
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1389
Largest diff. peak/hole / e Å^{-3}	0.37/-0.42

1. Dolomanov, O. V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* **2008**. *A64*, 112-122.
3. Sheldrick, G. M. *Acta Cryst.* **2015**. *C71*, 3-8

Single crystals of compound **6b** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (4/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on a 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



6b

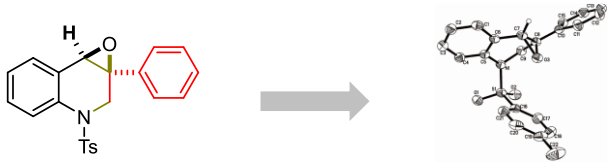


CCDC: 2255452

Identification code	**6b**
Empirical formula	$C_{37}H_{30}N_2O_3S$
Formula weight	582.69
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5153(3)
b/Å	7.31558(19)
c/Å	30.8108(7)
α/°	90
β/°	98.412(2)
γ/°	90
Volume/Å^3	3013.55(12)
Z	4
ρ_{calc}g/cm^3	1.284
μ/mm^{-1}	1.271
F(000)	1224.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.82 to 134.156
Index ranges	-16 ≤ h ≤ 13, -8 ≤ k ≤ 5, -34 ≤ l ≤ 36
Reflections collected	10849
Independent reflections	5374 [R_{int} = 0.0289, R_{sigma} = 0.0414]
Data/restraints/parameters	5374/0/389
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1361
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1571
Largest diff. peak/hole / e Å^{-3}	0.18/-0.27

1. Dolomanov, O. V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* **2008**. *A64*, 112-122.
3. Sheldrick, G. M. *Acta Cryst.* **2015**. *C71*, 3-8

Single crystals of compound **8a** were prepared through dissolving the sample in mixture solvent of EtOH/DCM (1/1) at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on a 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



8a

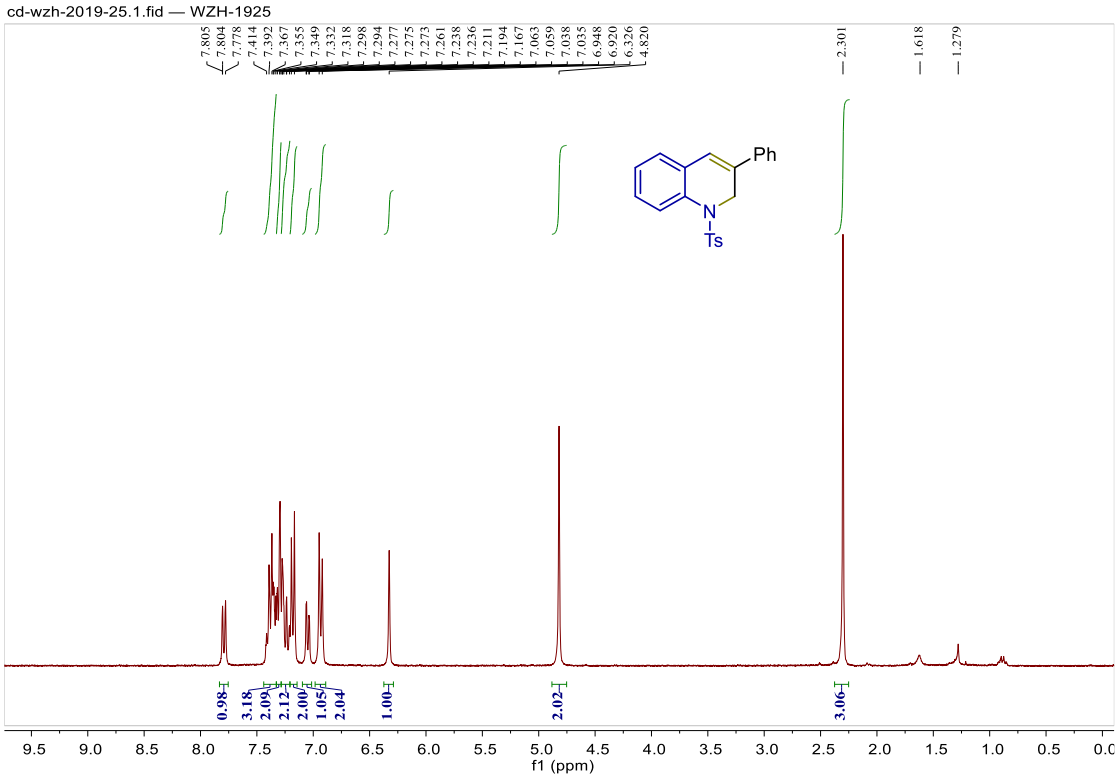
CCDC: 2255453

Identification code	**8a**
Empirical formula	$C_{22}H_{19}NO_3S$
Formula weight	377.44
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.3137(4)
b/Å	10.2800(9)
c/Å	11.9158(9)
α/°	67.229(8)
β/°	81.908(5)
γ/°	89.234(5)
Volume/Å^3	928.71(13)
Z	2
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	1.733
F(000)	396.0
Crystal size/mm^3	0.18 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.136 to 134.14
Index ranges	-5 ≤ h ≤ 9, -12 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	6490
Independent reflections	3313 [R_{int} = 0.0222, R_{sigma} = 0.0323]
Data/restraints/parameters	3313/0/246
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1236
Final R indexes [all data]	R_1 = 0.0533, wR_2 = 0.1340
Largest diff. peak/hole / e Å^{-3}	0.20/-0.25

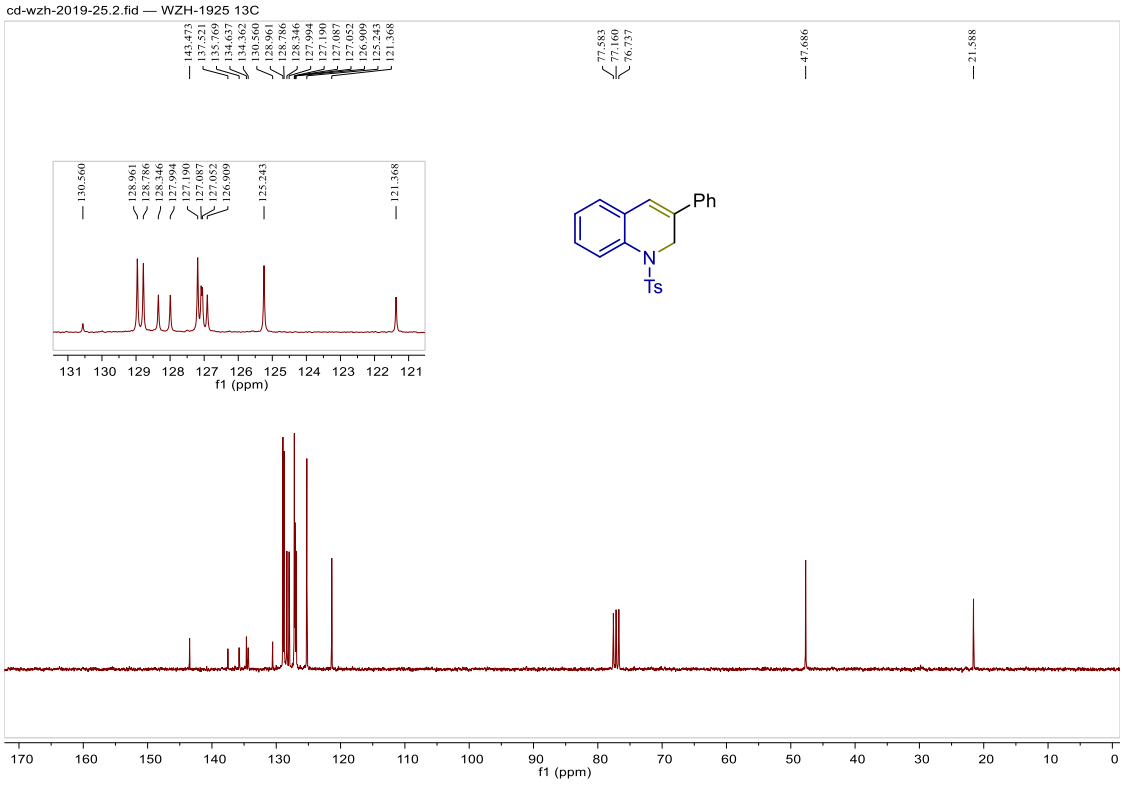
1. Dolomanov, O. V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* **2008**. *A64*, 112-122.
3. Sheldrick, G. M. *Acta Cryst.* **2015**. *C71*, 3-8

10. ^{1}H, ^{13}C NMR spectra for compounds 3, 6, 8, 9, 10, and 11

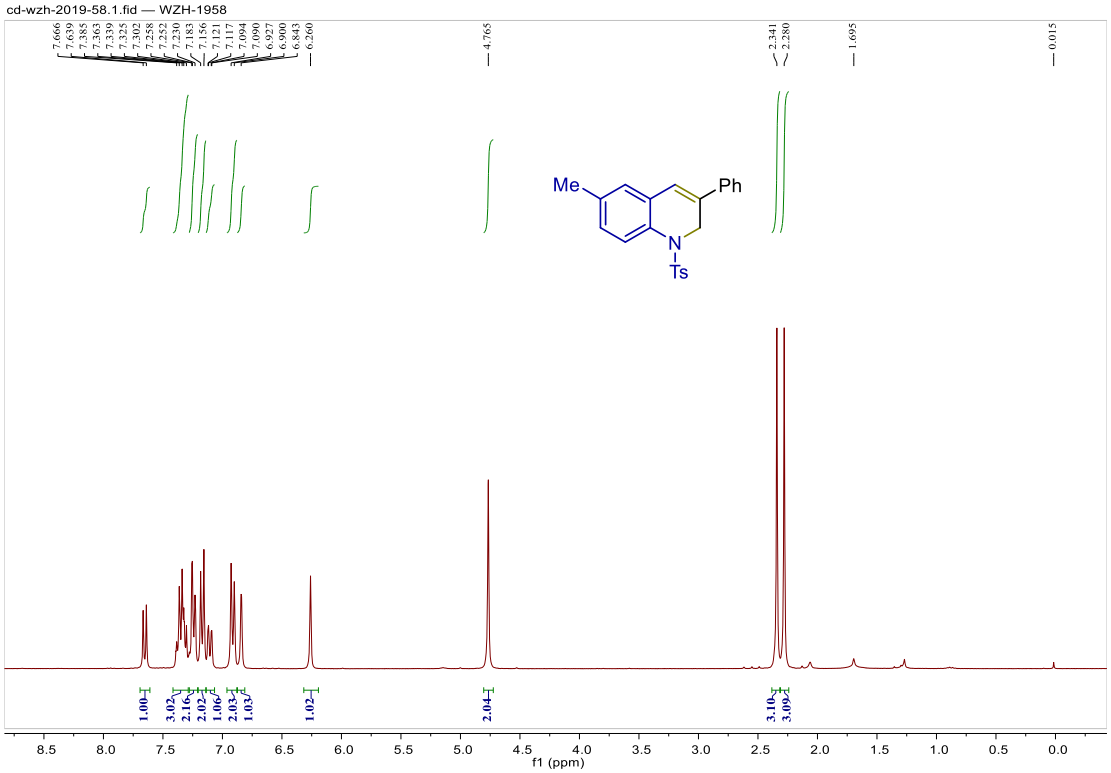
^{1}H NMR (300 MHz, $CDCl_3$) of **3a**



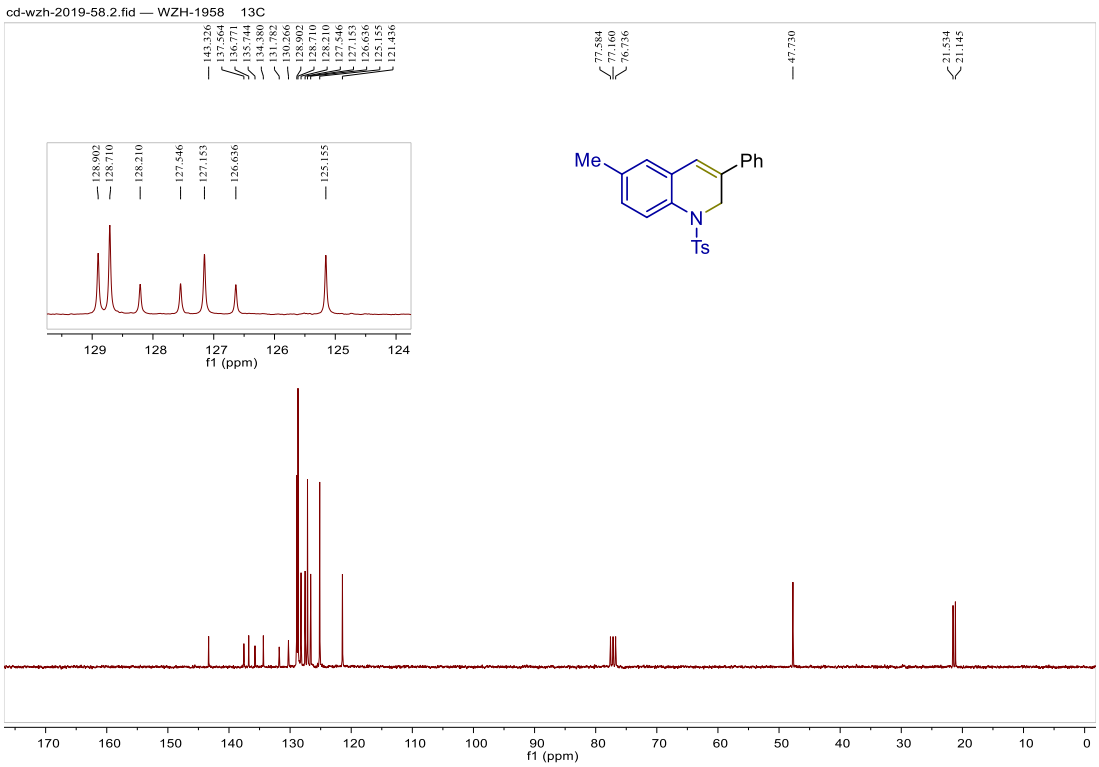
^{13}C NMR (75 MHz, $CDCl_3$) of **3a**



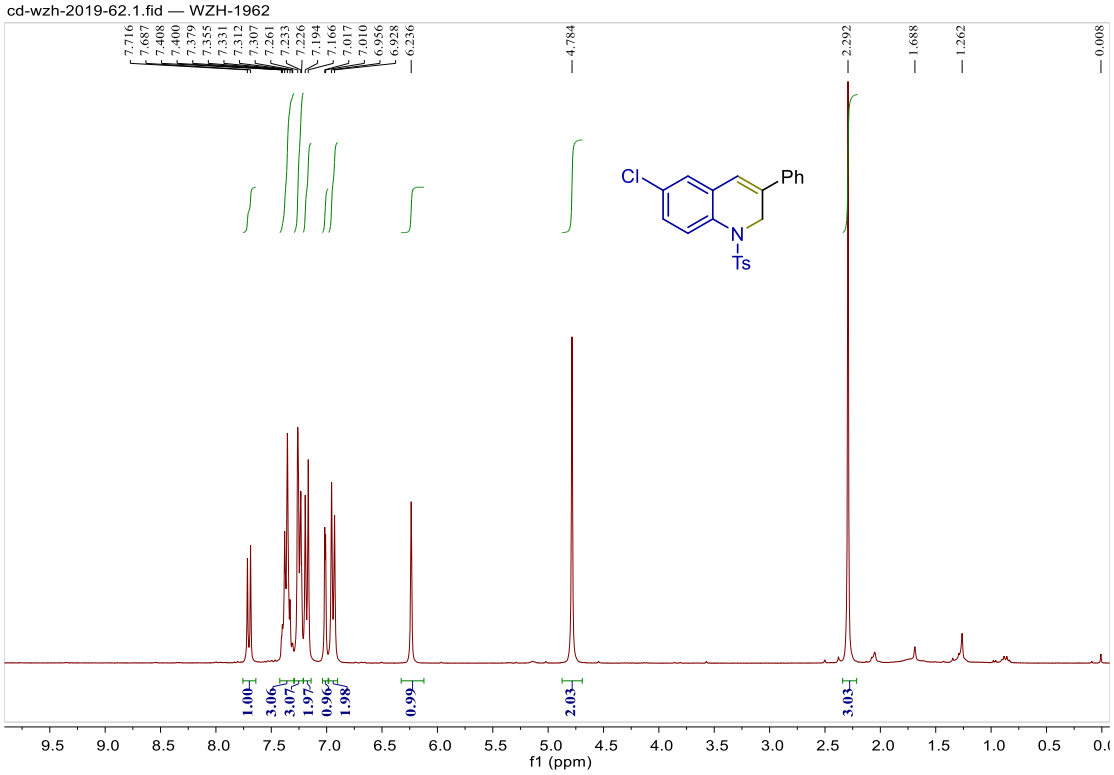
^{1}H NMR (300 MHz, $CDCl_3$) of **3b**



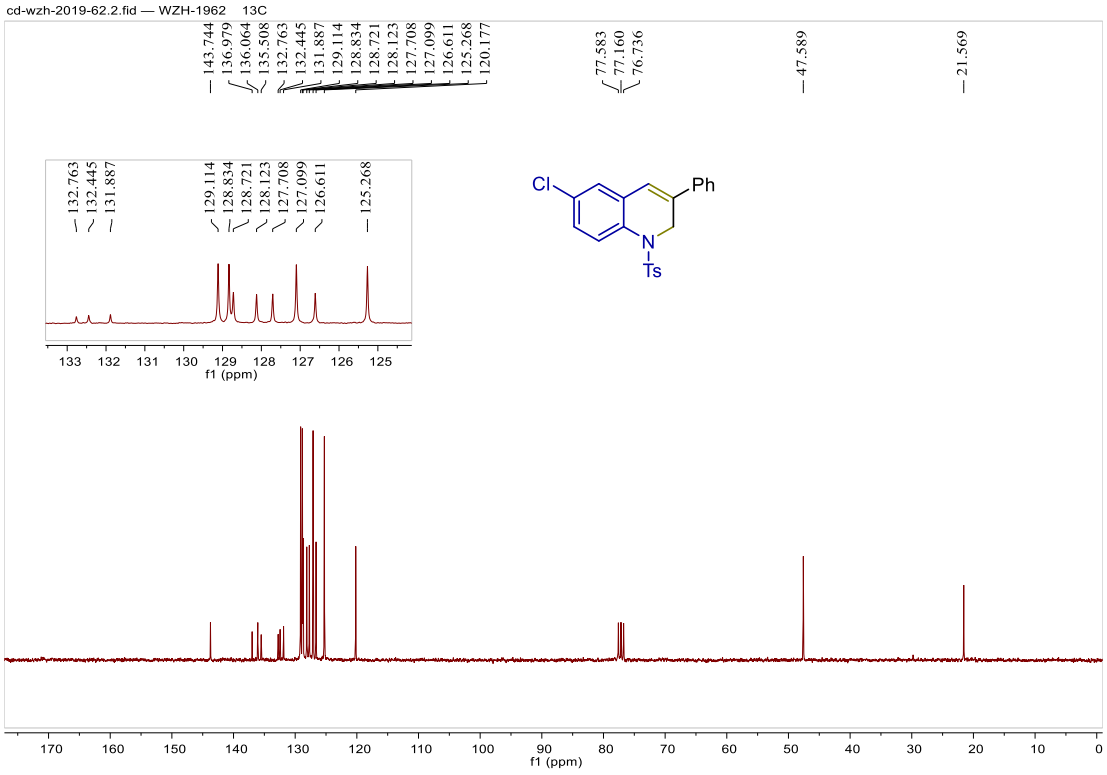
^{13}C NMR (75 MHz, $CDCl_3$) of **3b**



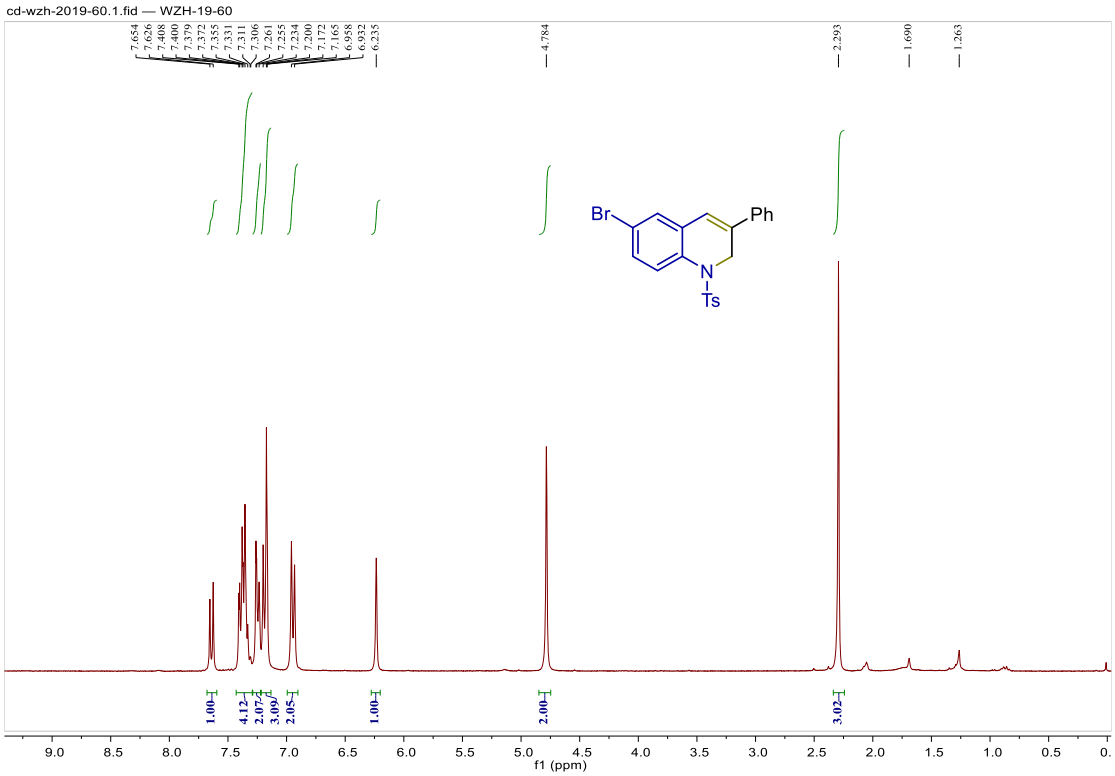
^{1}H NMR (300 MHz, $CDCl_3$) of **3c**



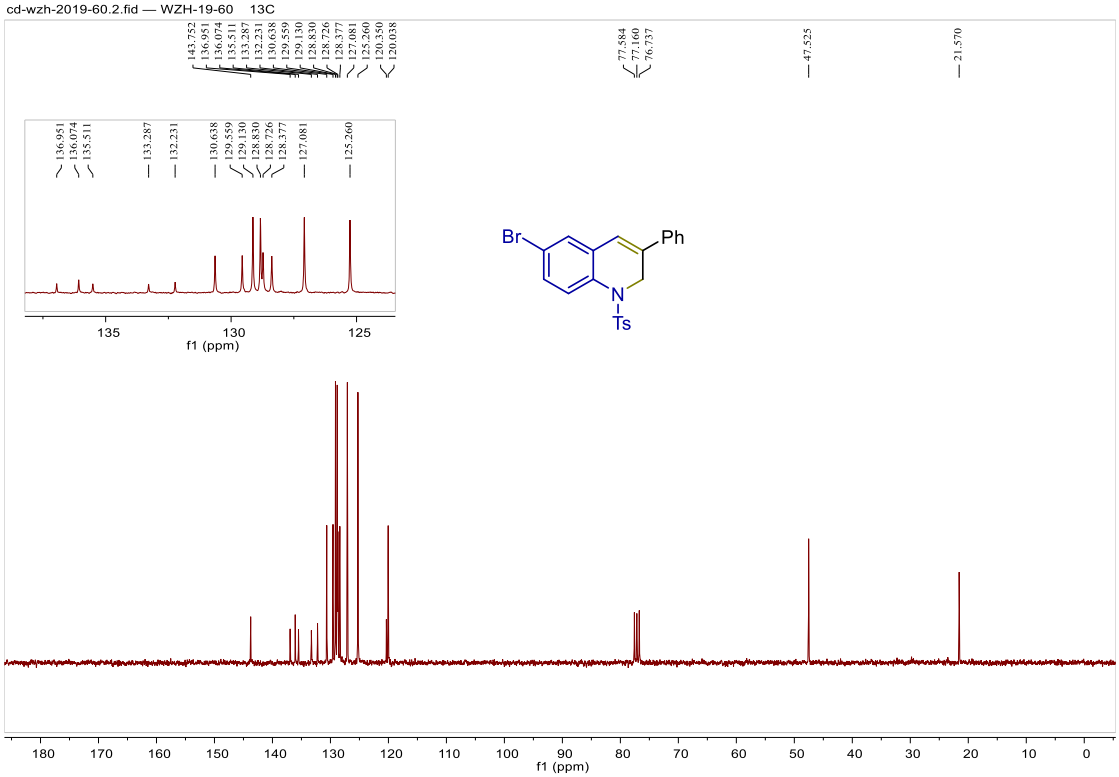
^{13}C NMR (75 MHz, $CDCl_3$) of **3c**



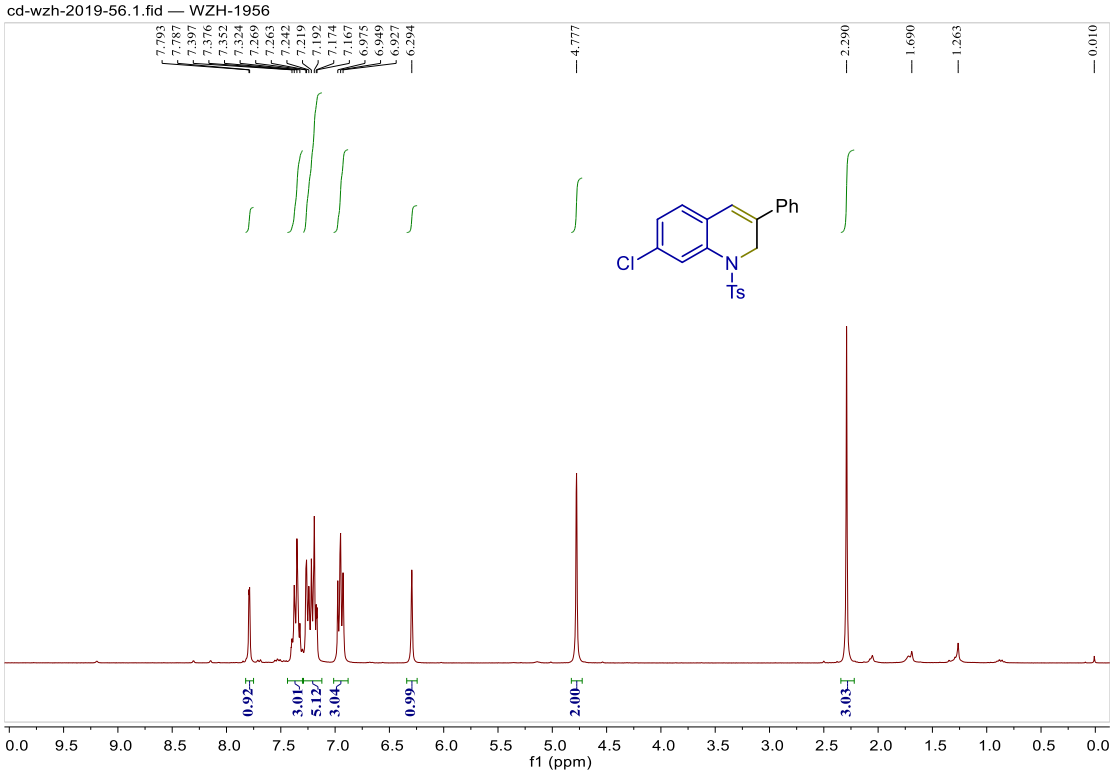
^{1}H NMR (300 MHz, $CDCl_3$) of **3d**



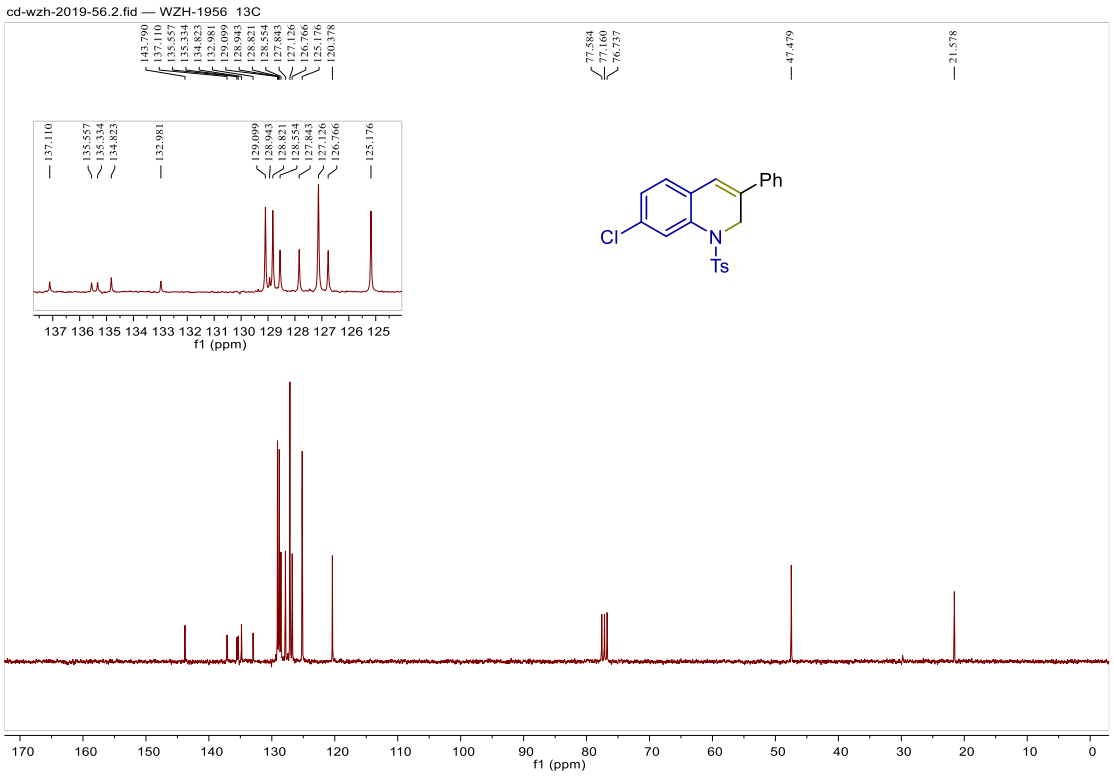
^{13}C NMR (75 MHz, $CDCl_3$) of **3d**



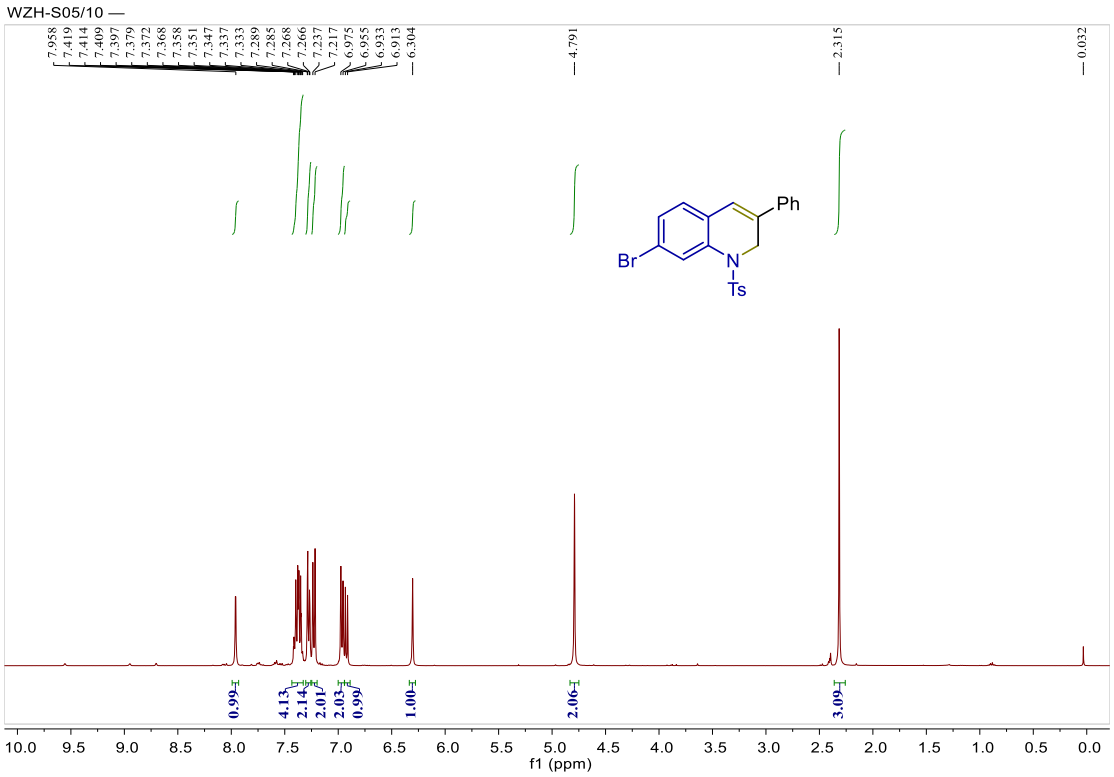
^{1}H NMR (300 MHz, $CDCl_3$) of **3e**



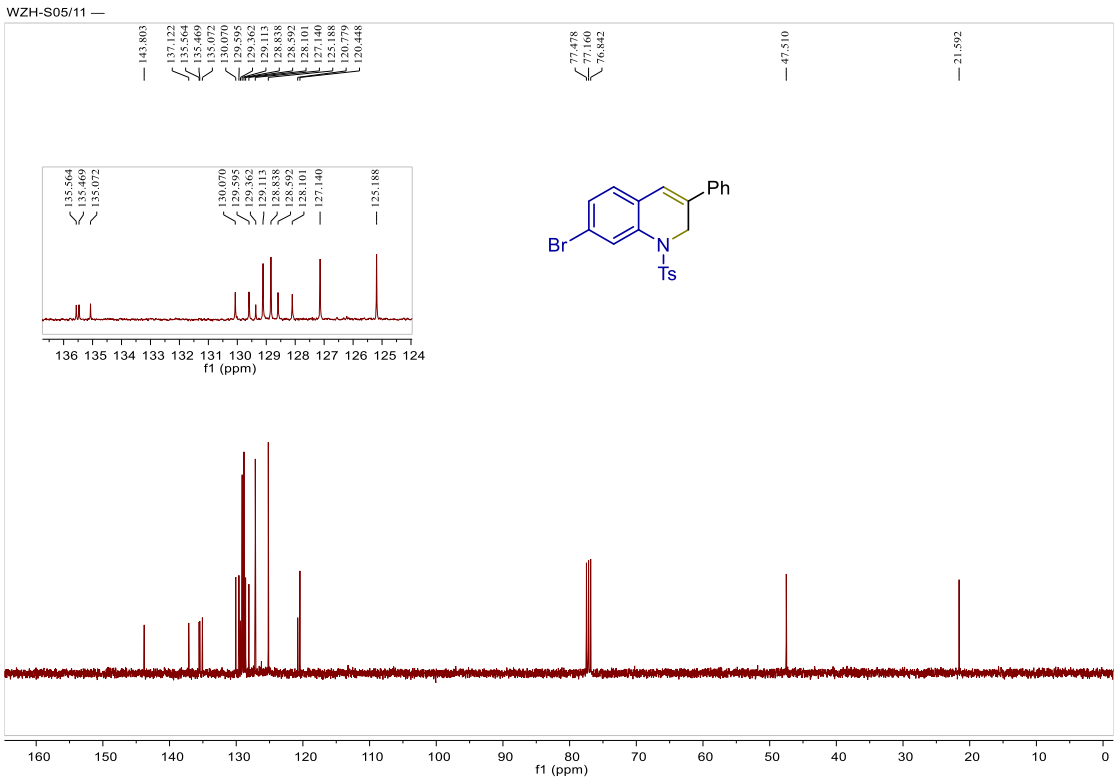
^{13}C NMR (75 MHz, $CDCl_3$) of **3e**



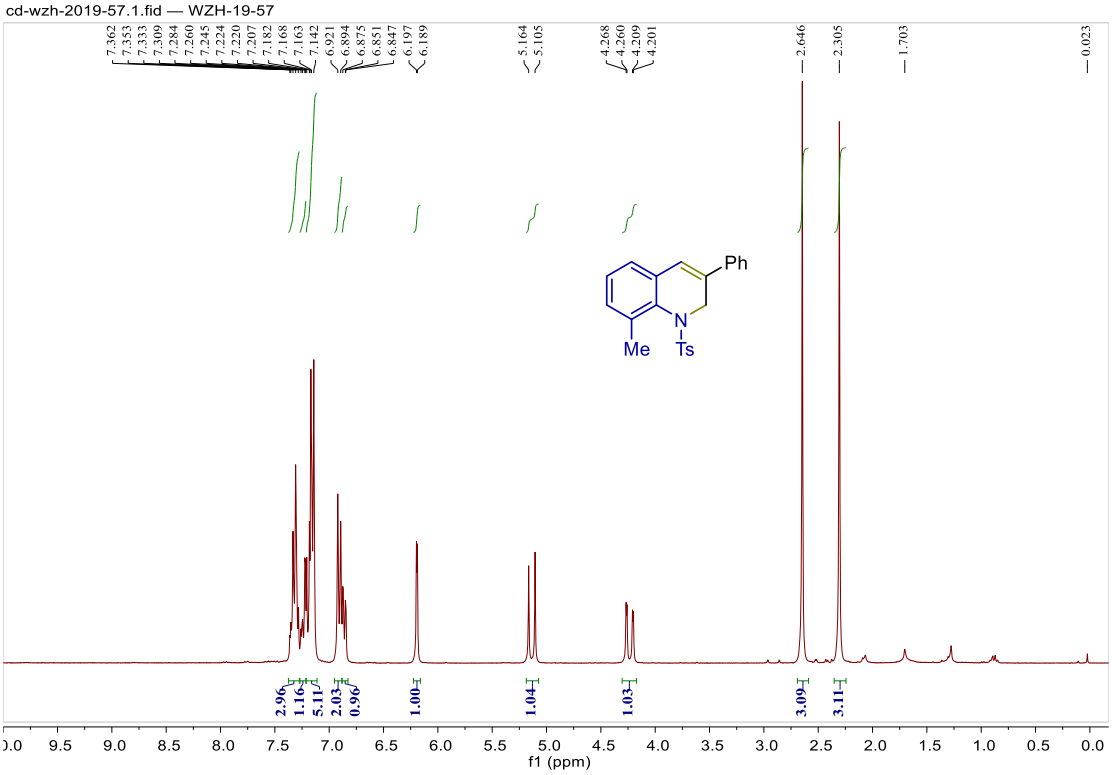
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



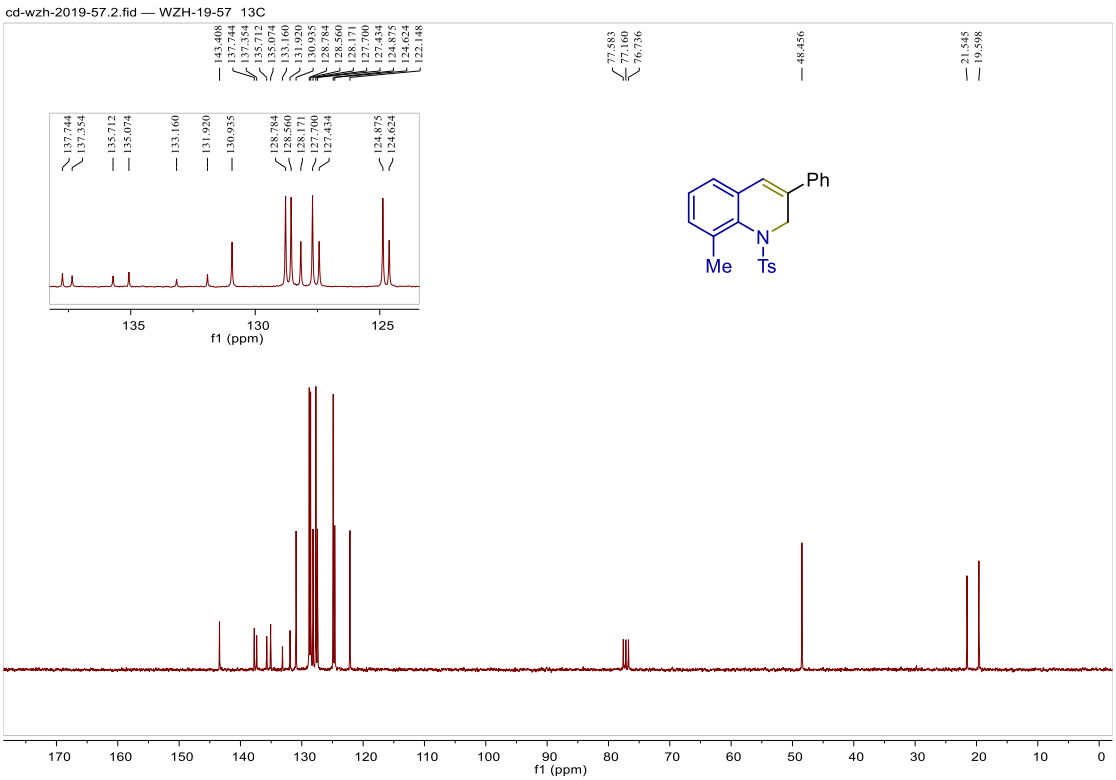
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



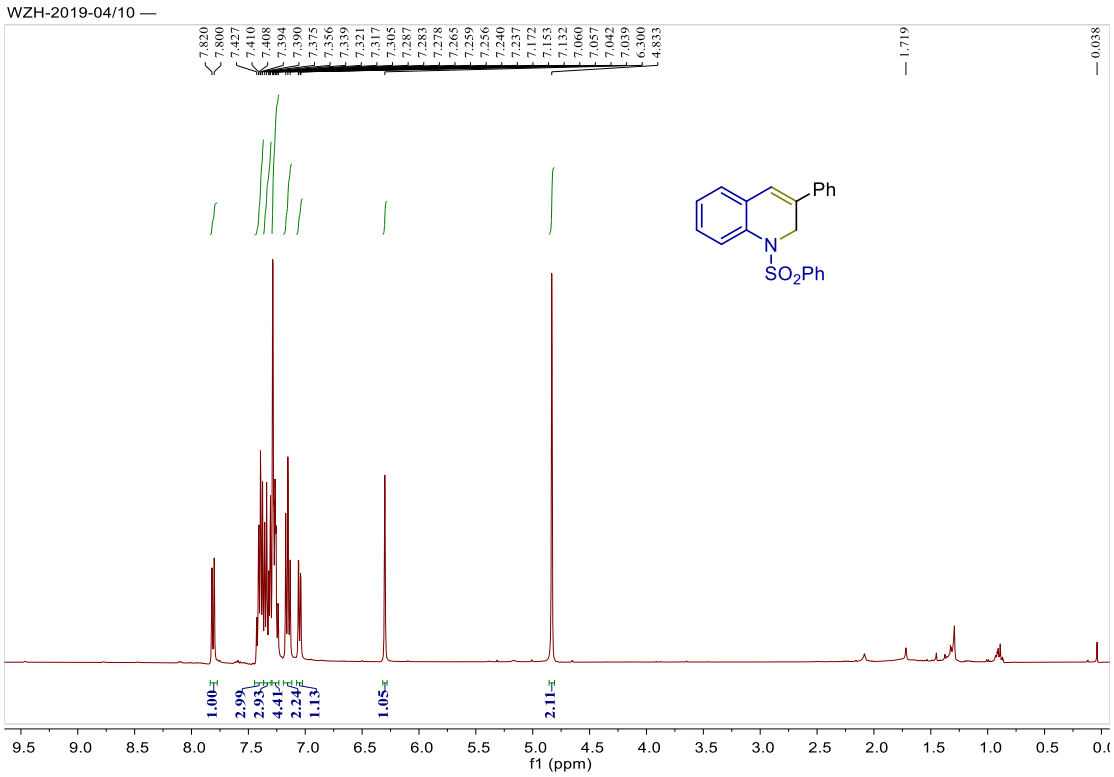
^{1}H NMR (300 MHz, $CDCl_3$) of **3g**



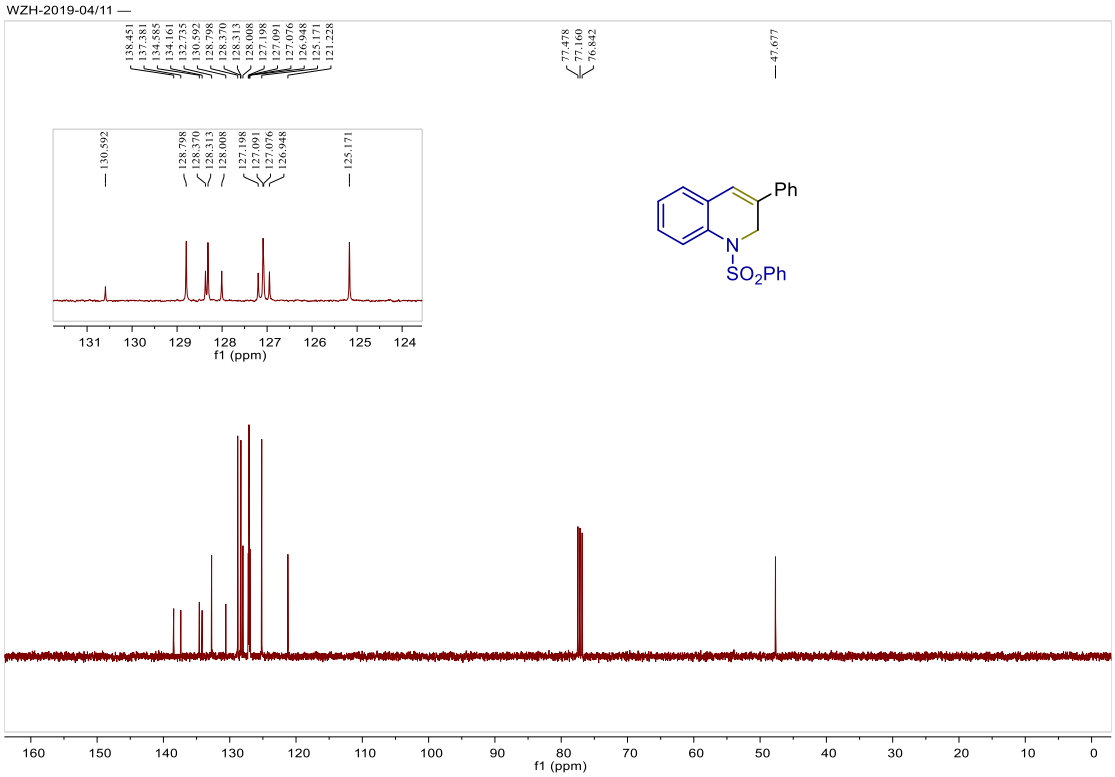
^{13}C NMR (75 MHz, $CDCl_3$) of **3g**



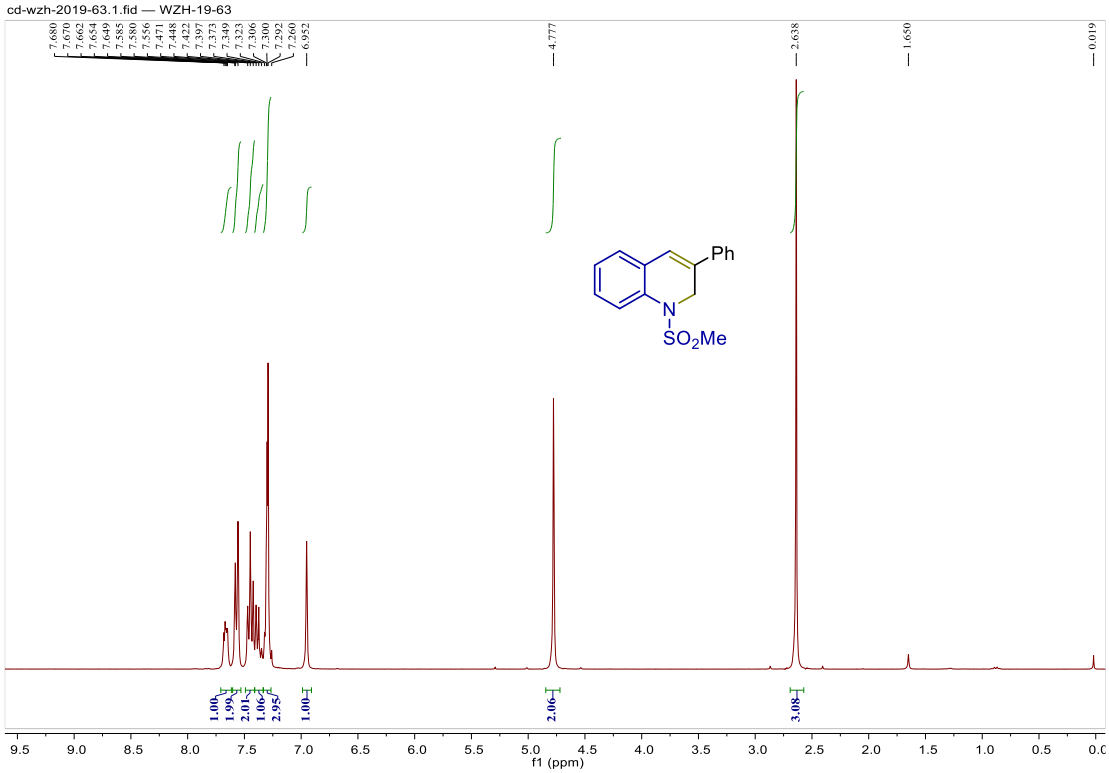
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



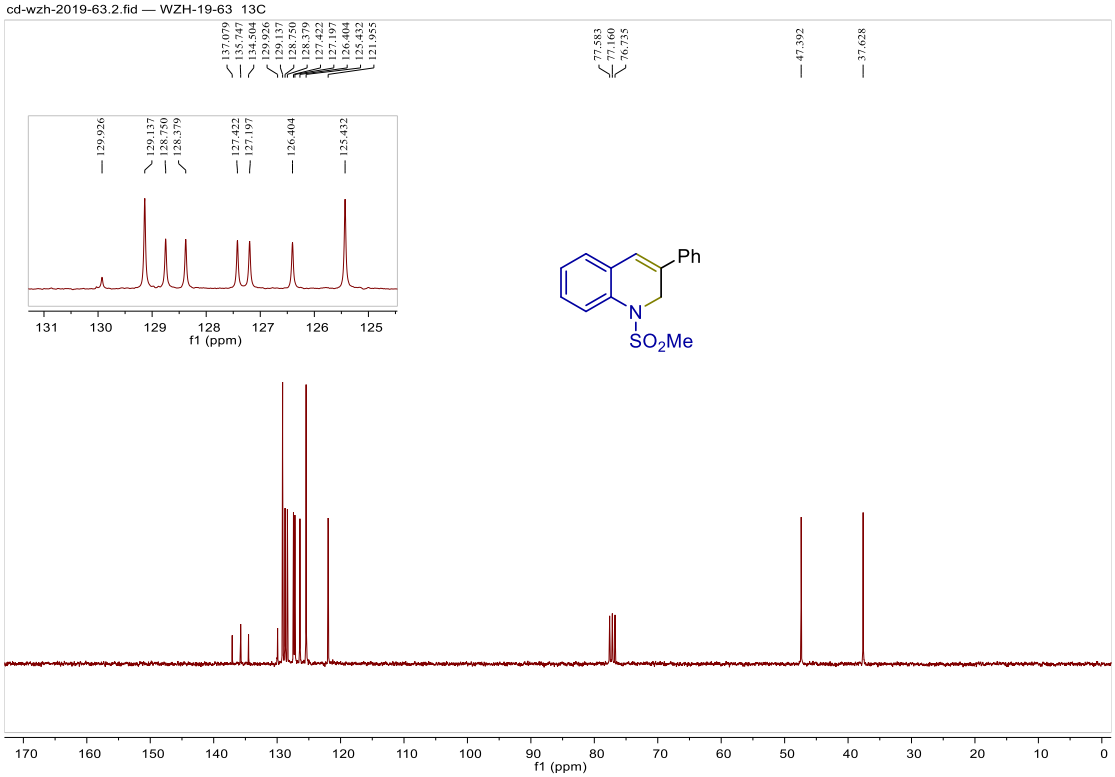
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



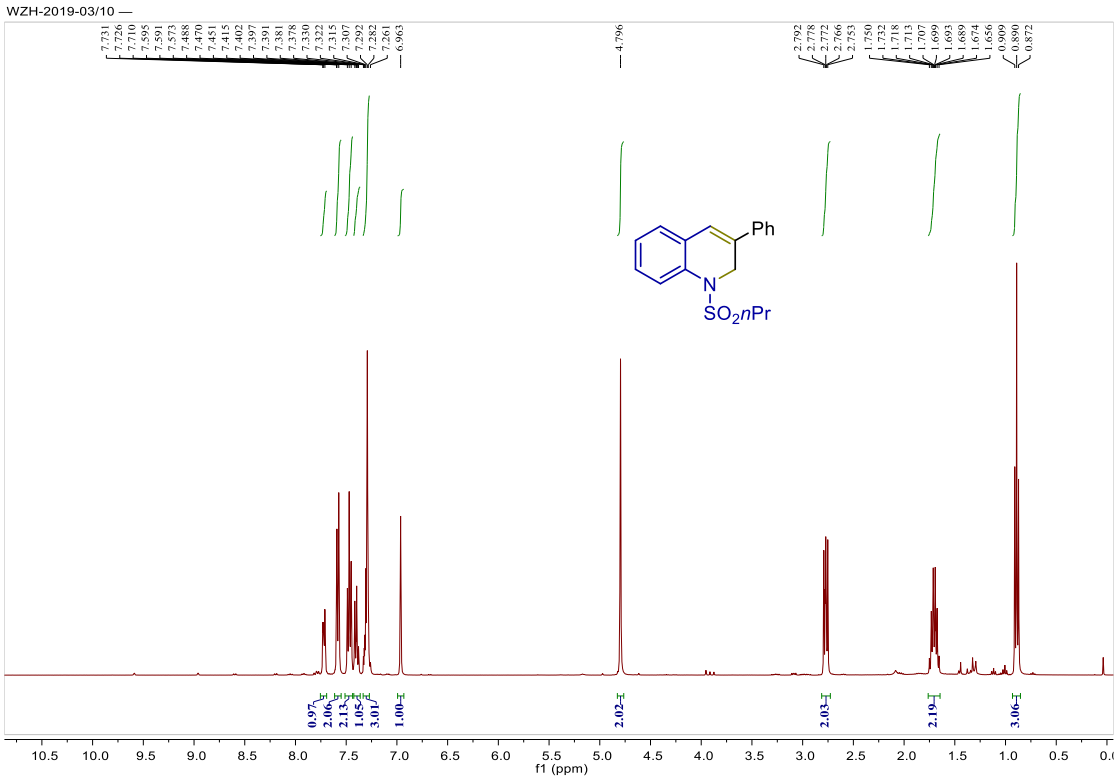
^{1}H NMR (300 MHz, $CDCl_3$) of **3i**



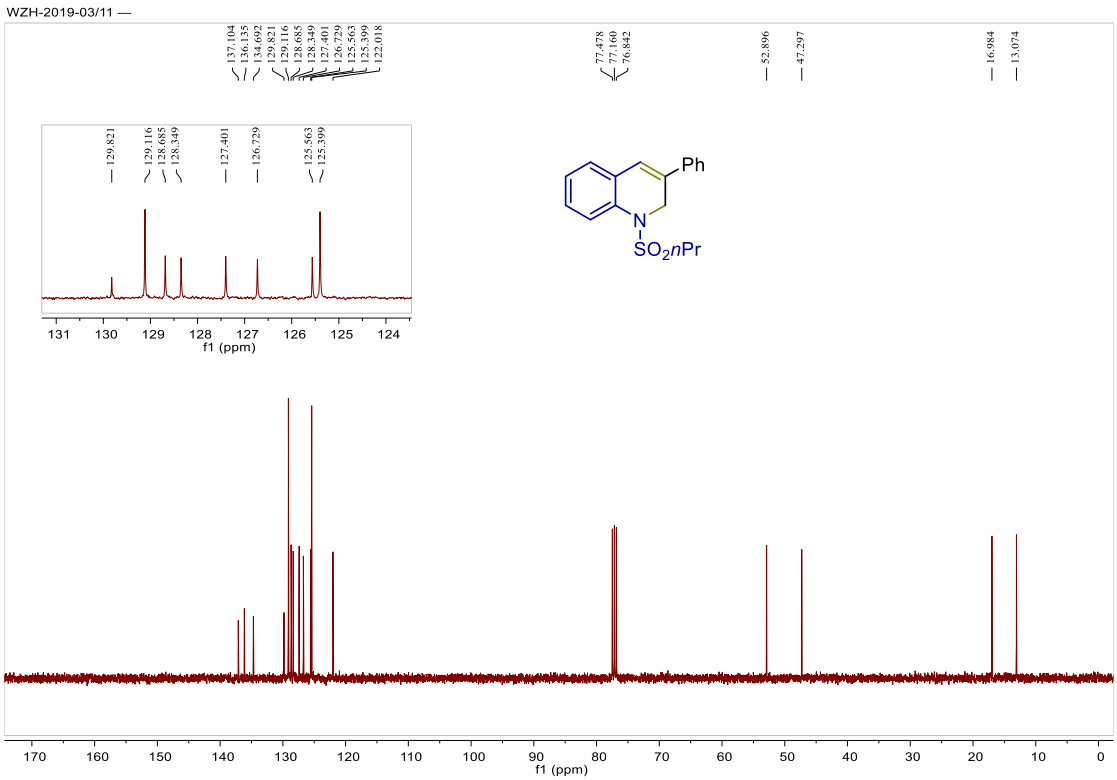
^{13}C NMR (75 MHz, $CDCl_3$) of **3i**



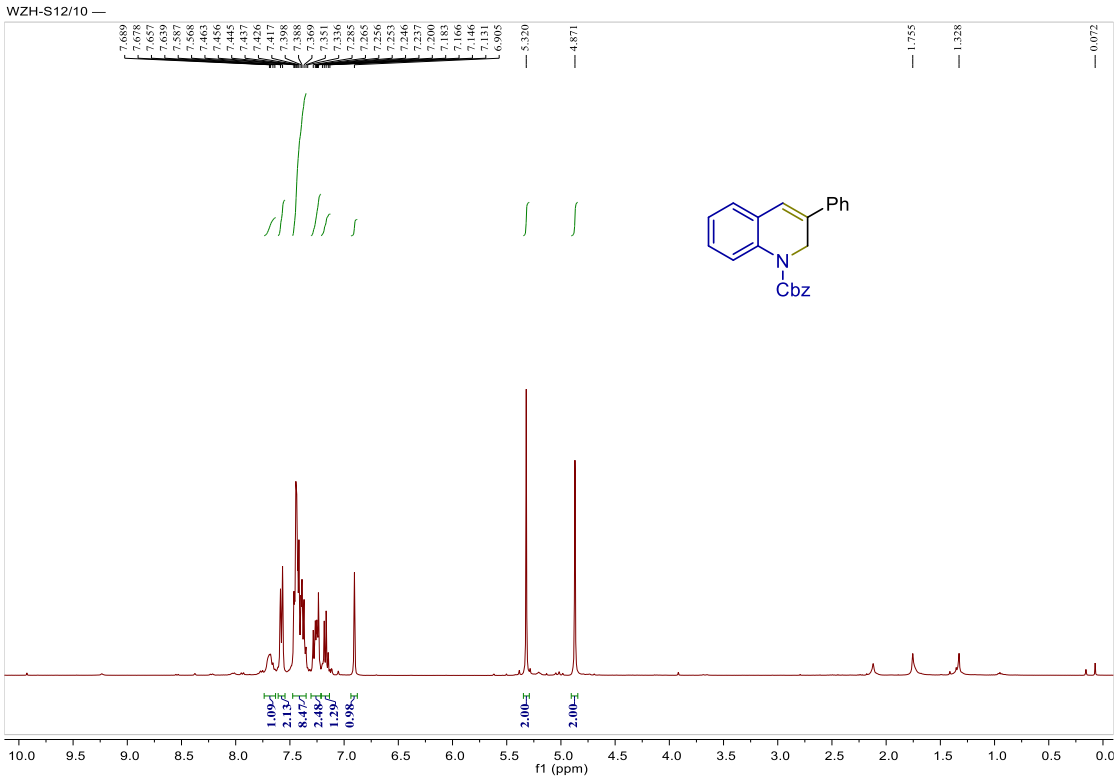
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



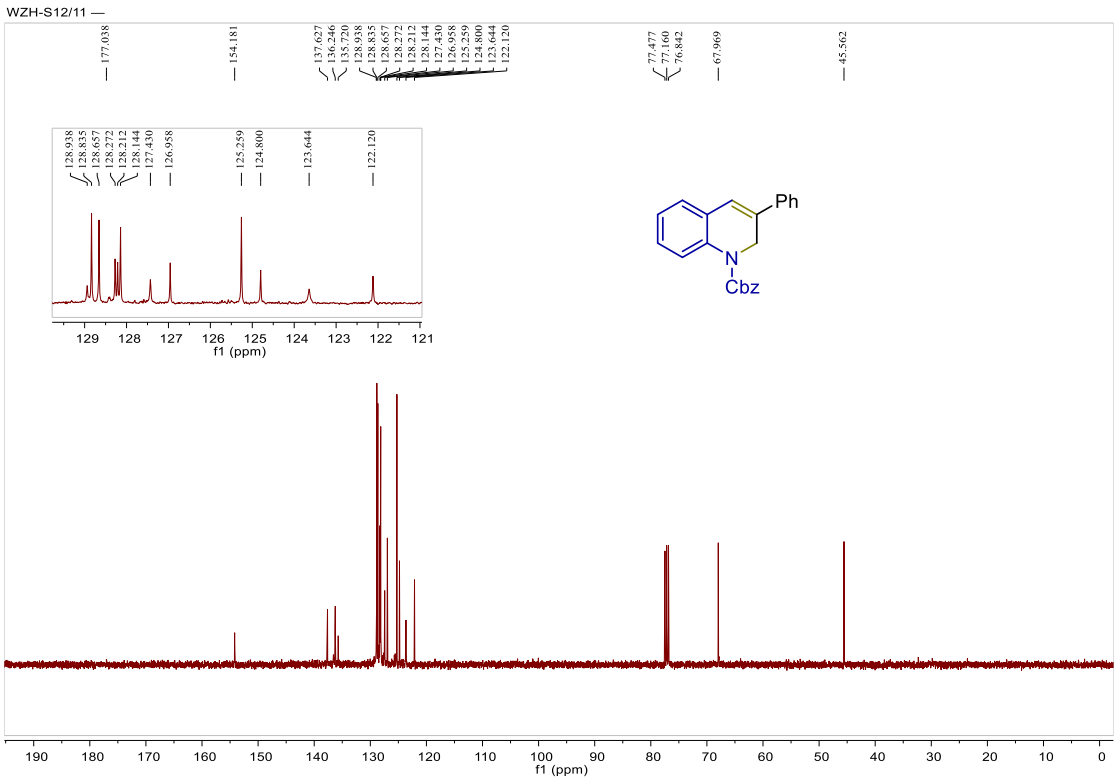
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



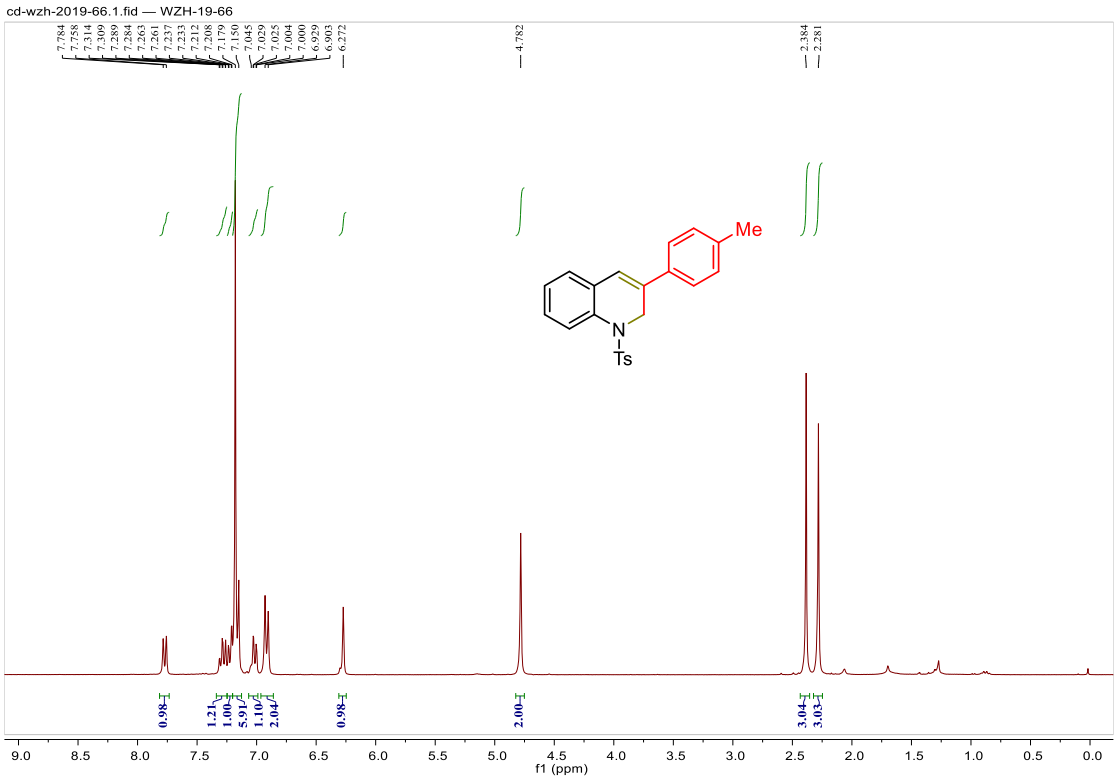
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



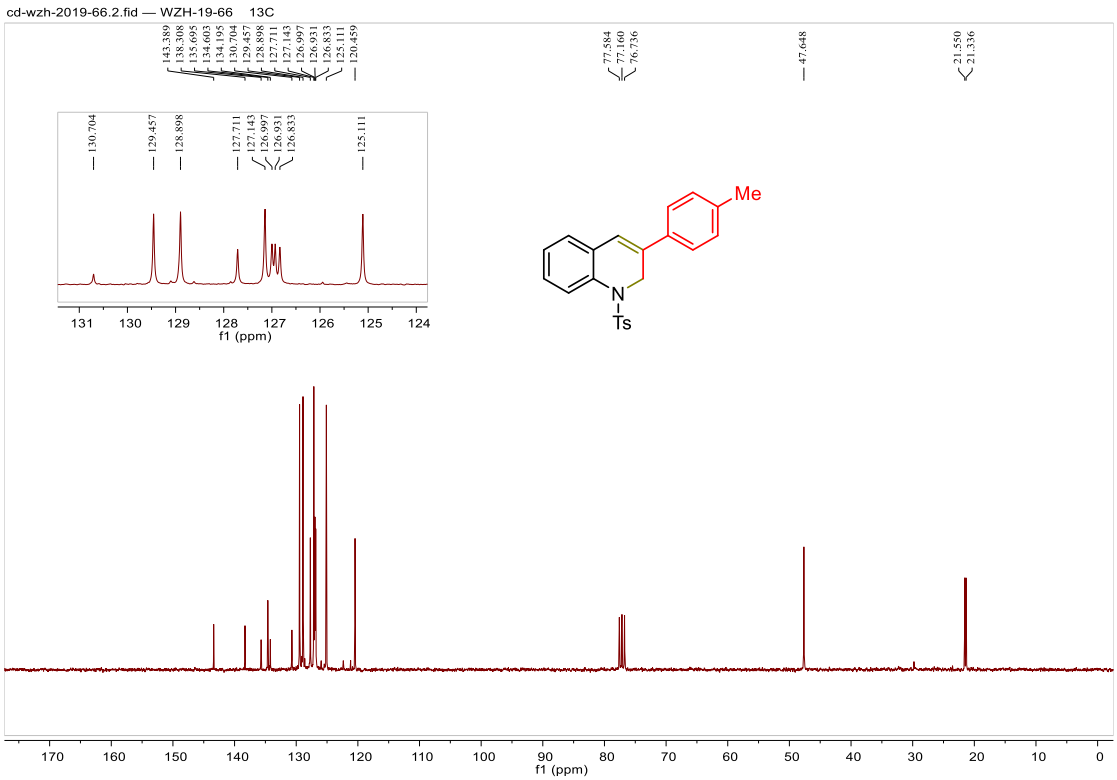
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



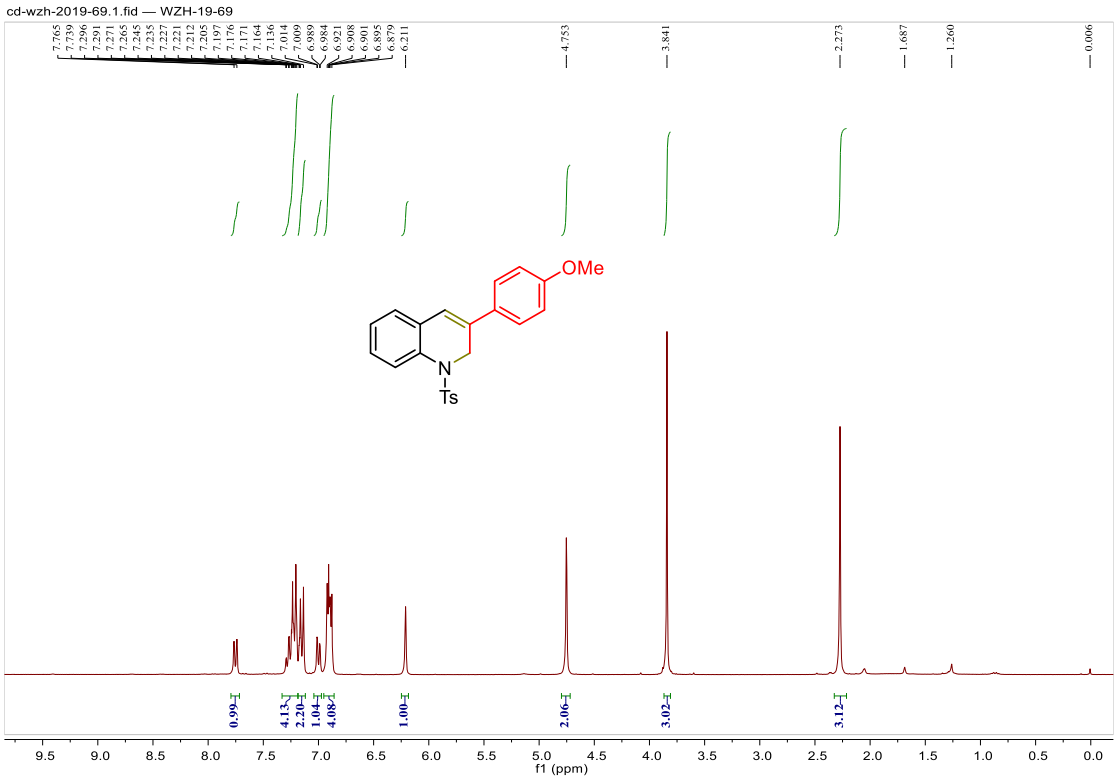
^{1}H NMR (300 MHz, $CDCl_3$) of **3l**



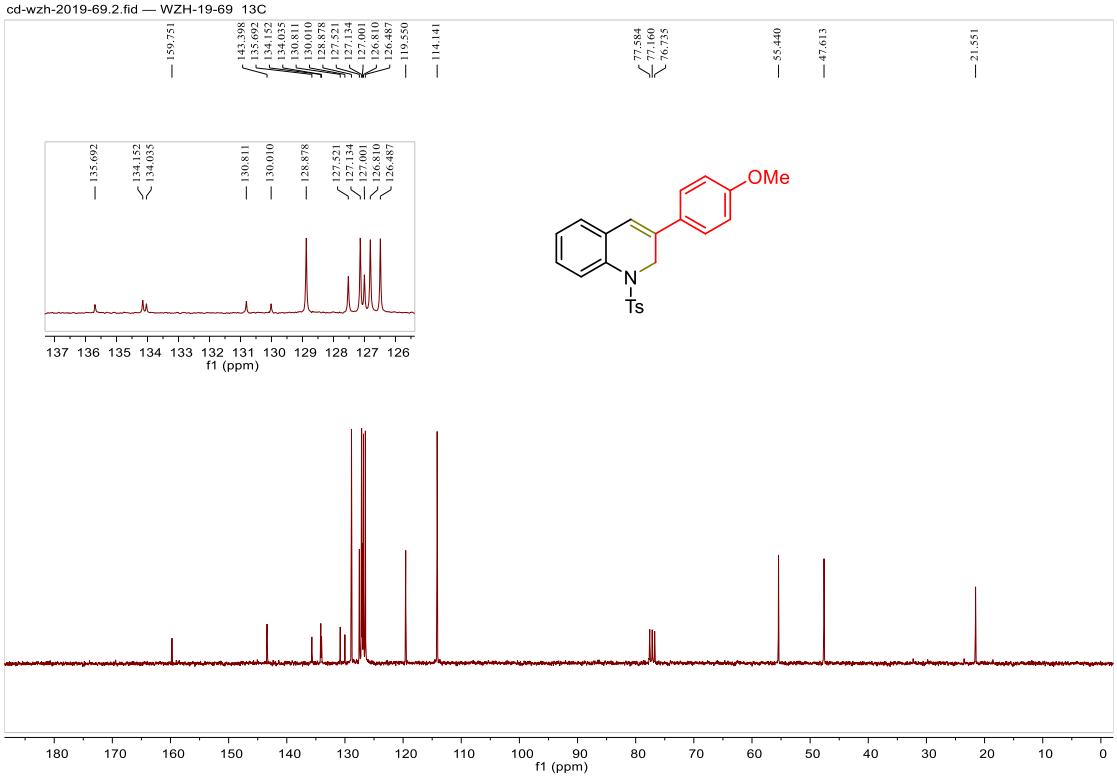
^{13}C NMR (75 MHz, $CDCl_3$) of **3l**



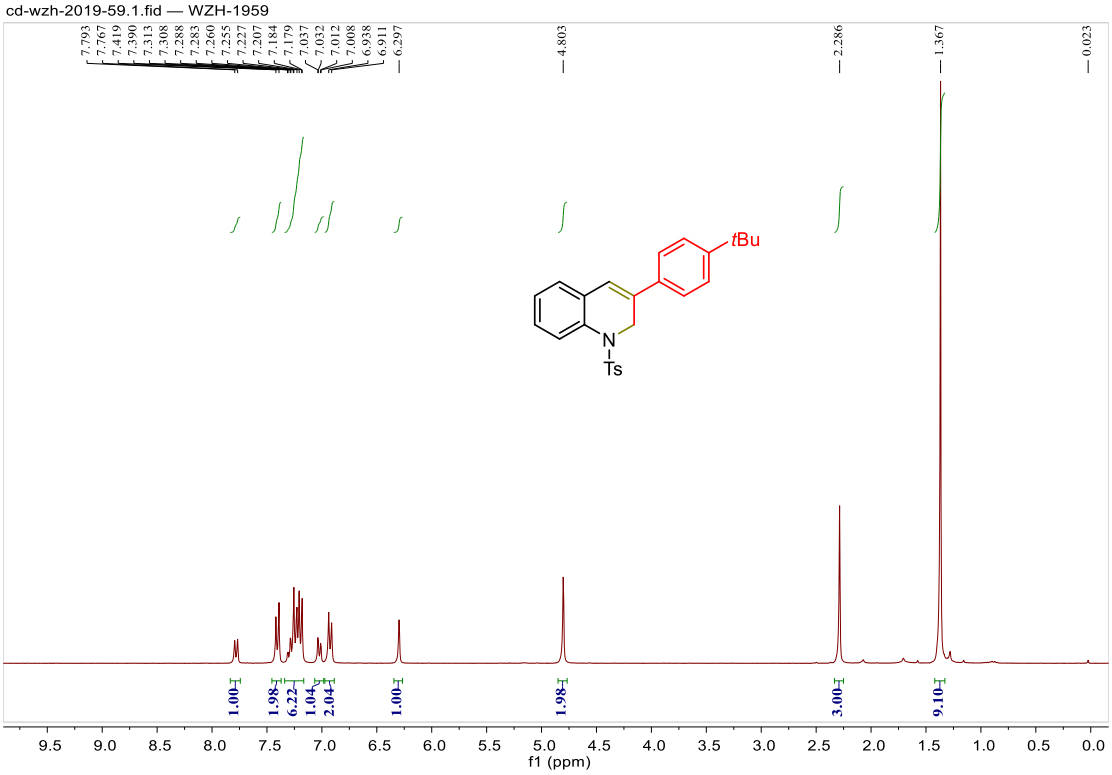
^{1}H NMR (300 MHz, $CDCl_3$) of **3m**



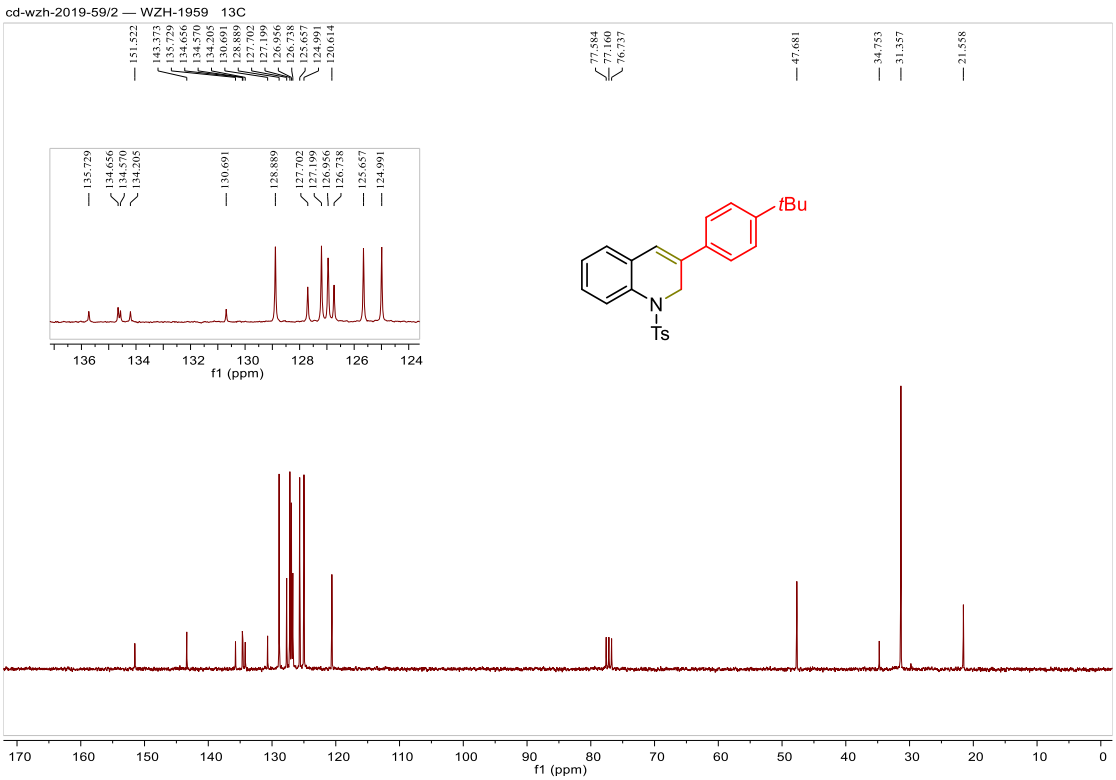
^{13}C NMR (75 MHz, $CDCl_3$) of **3m**



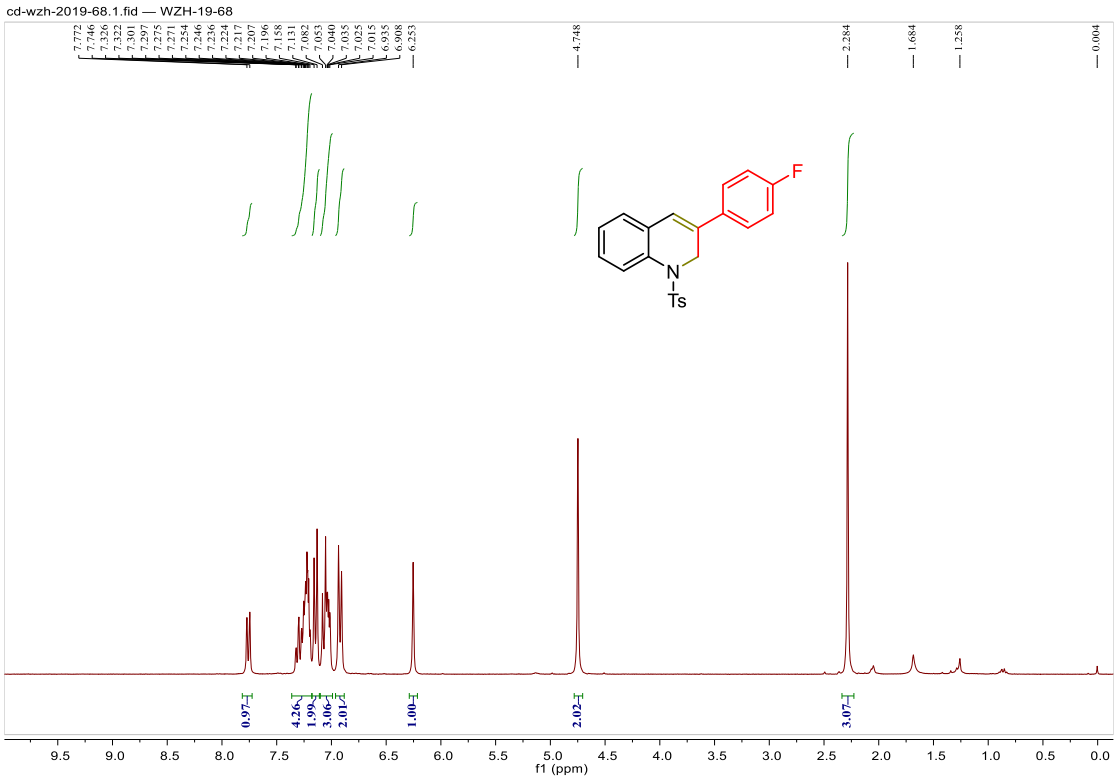
^{1}H NMR (300 MHz, $CDCl_3$) of **3n**



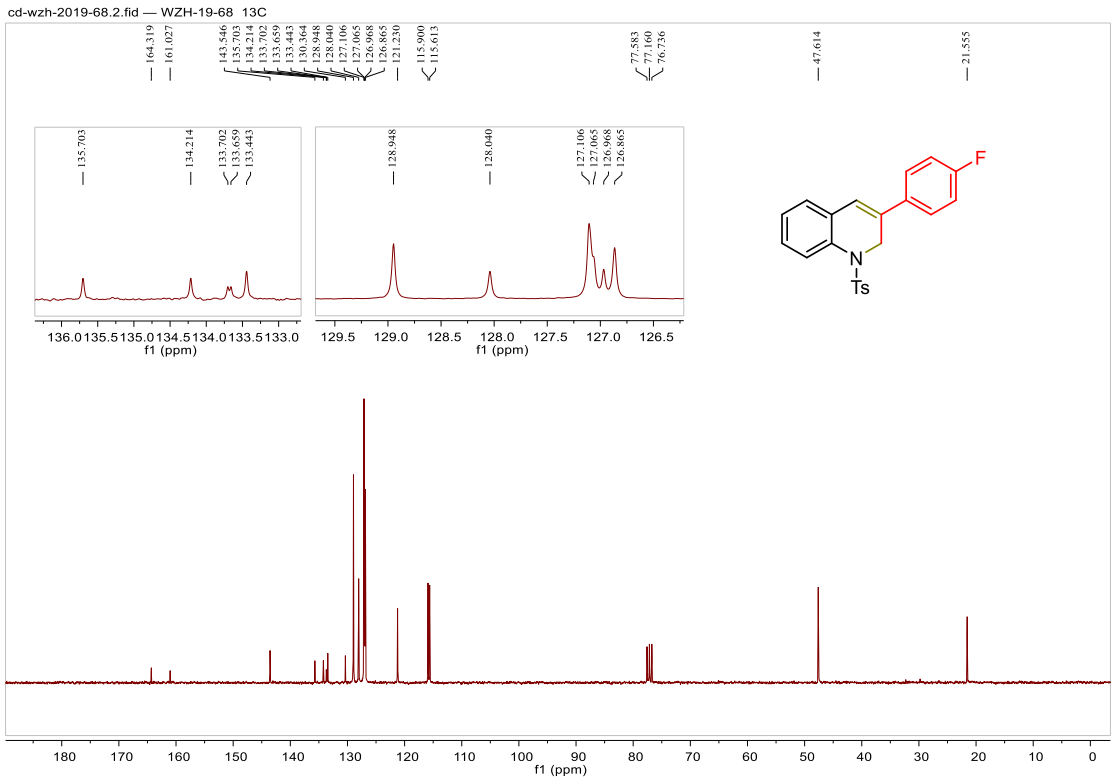
^{13}C NMR (75 MHz, $CDCl_3$) of **3n**



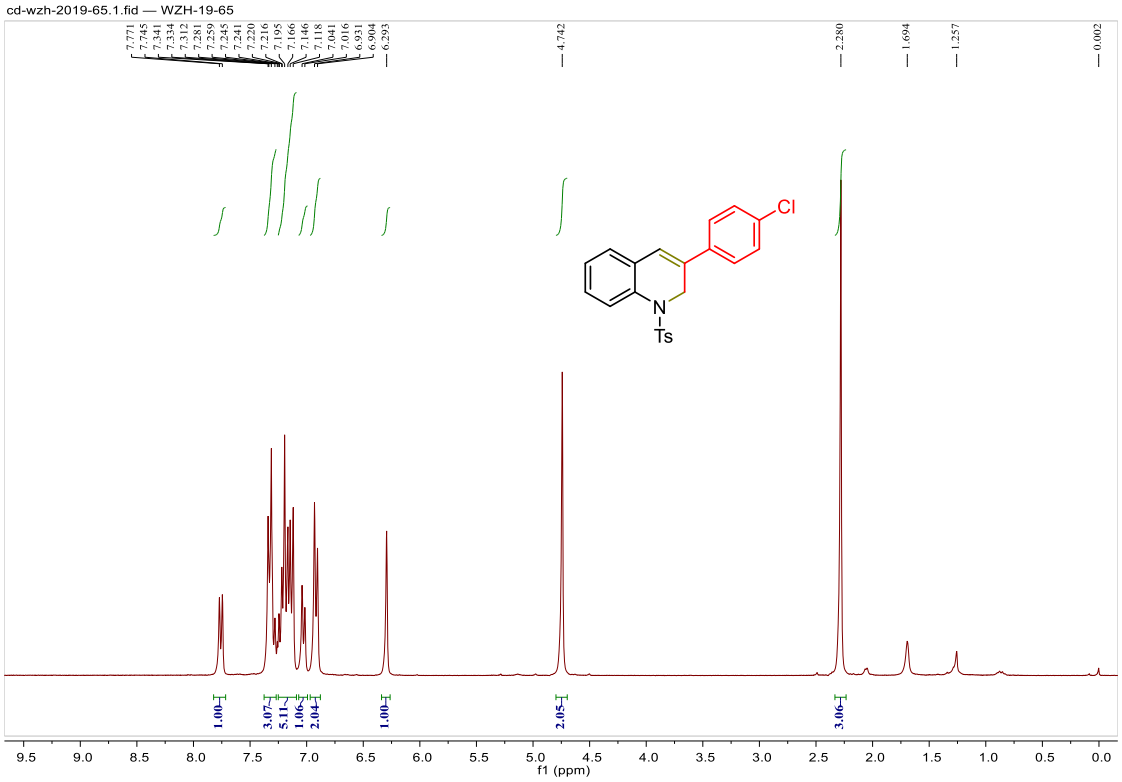
^{1}H NMR (300 MHz, $CDCl_3$) of **3o**



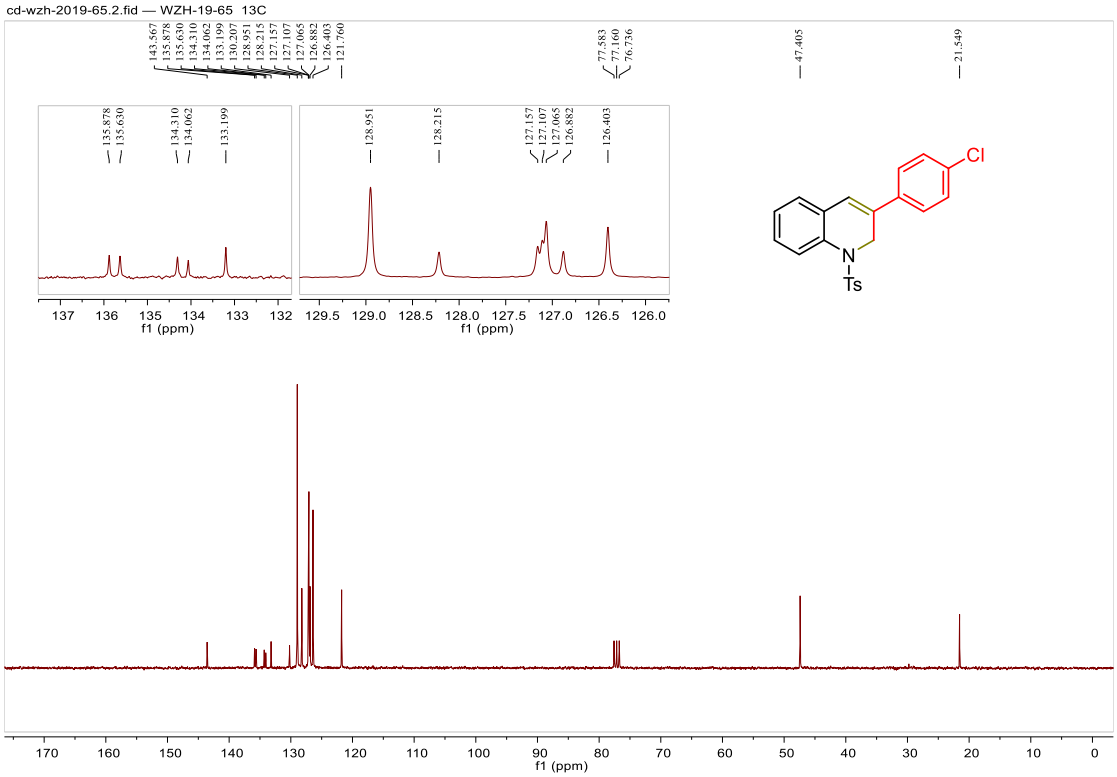
^{13}C NMR (75 MHz, $CDCl_3$) of **3o**



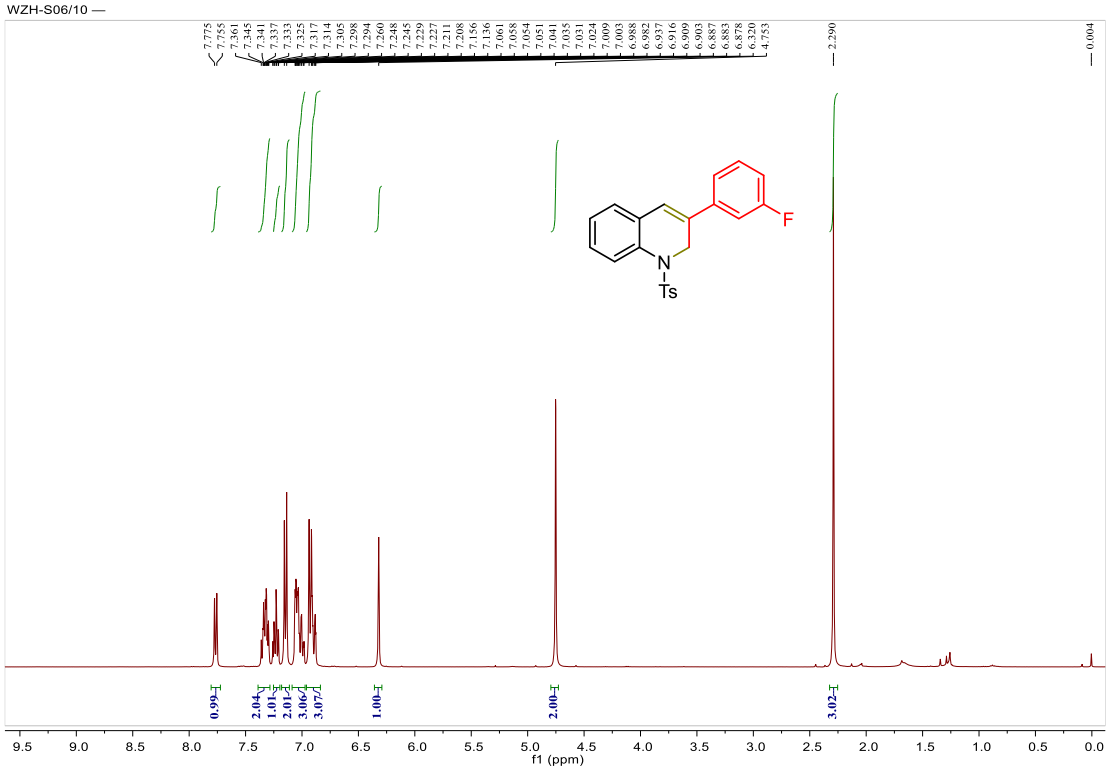
^{1}H NMR (300 MHz, $CDCl_3$) of **3p**



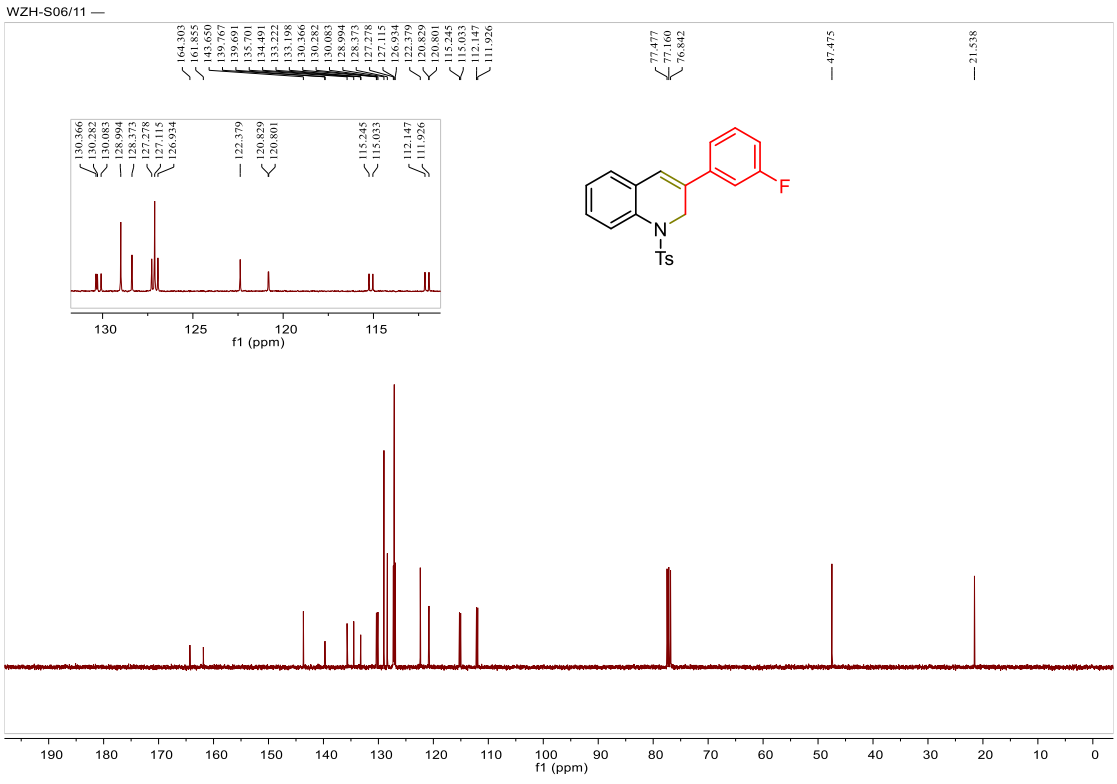
^{13}C NMR (75 MHz, $CDCl_3$) of **3p**



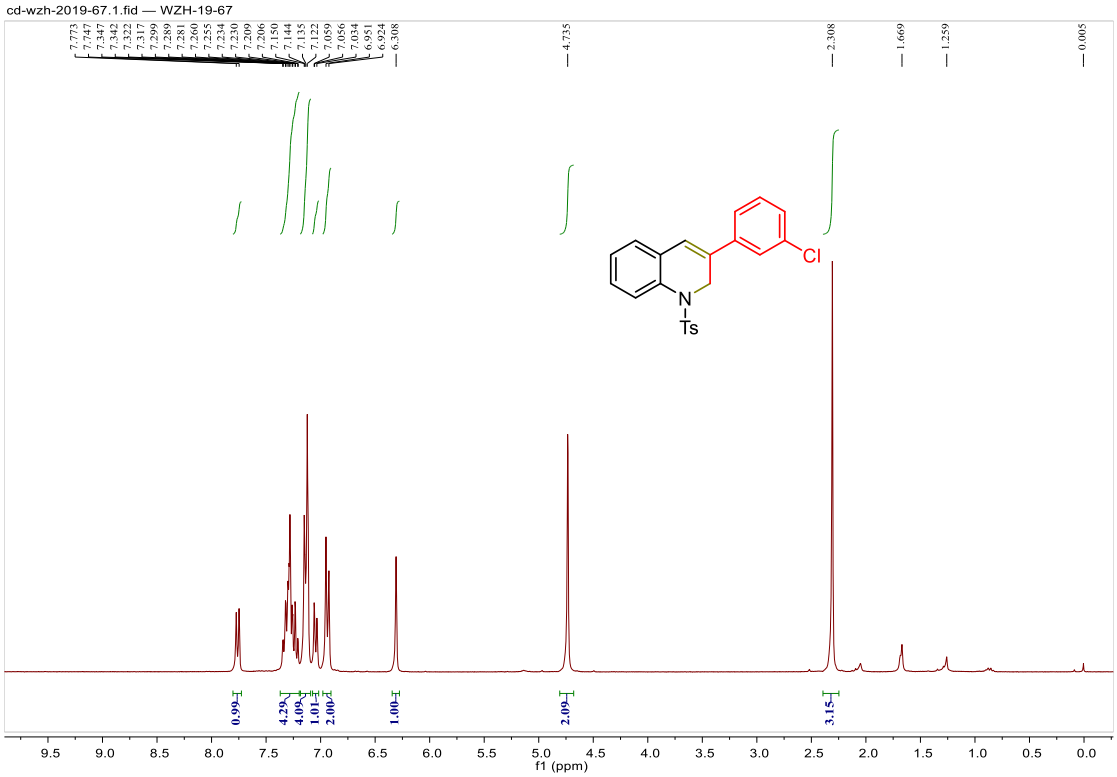
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



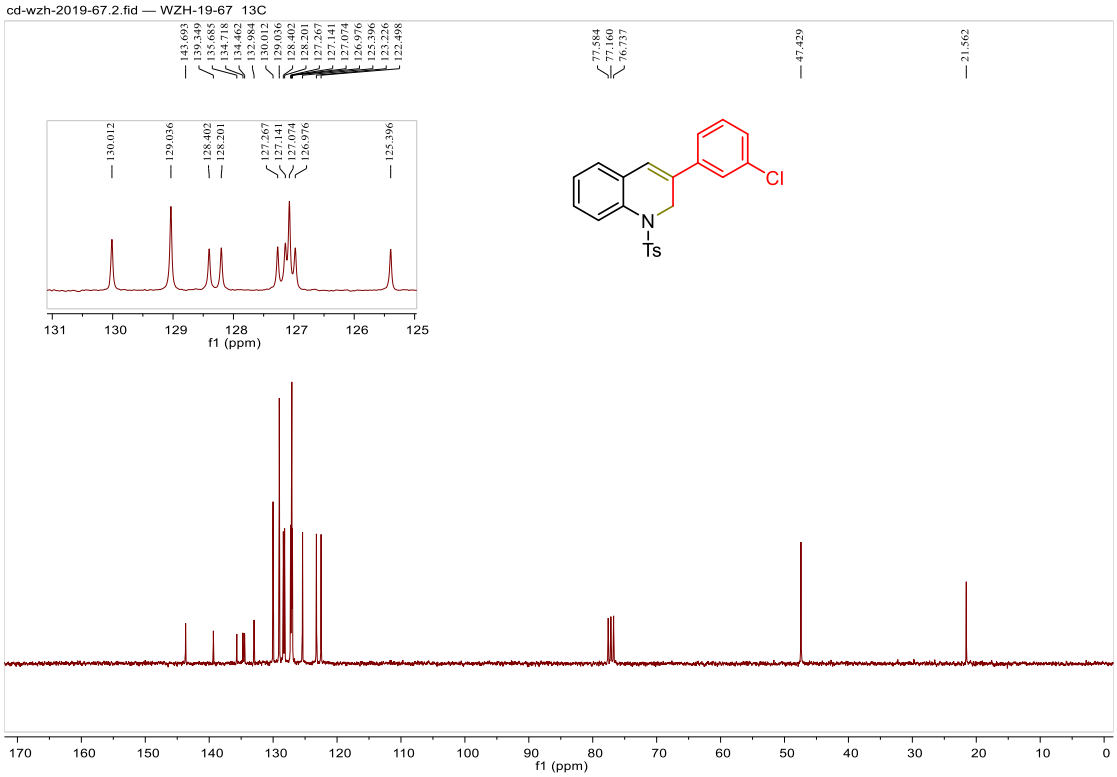
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



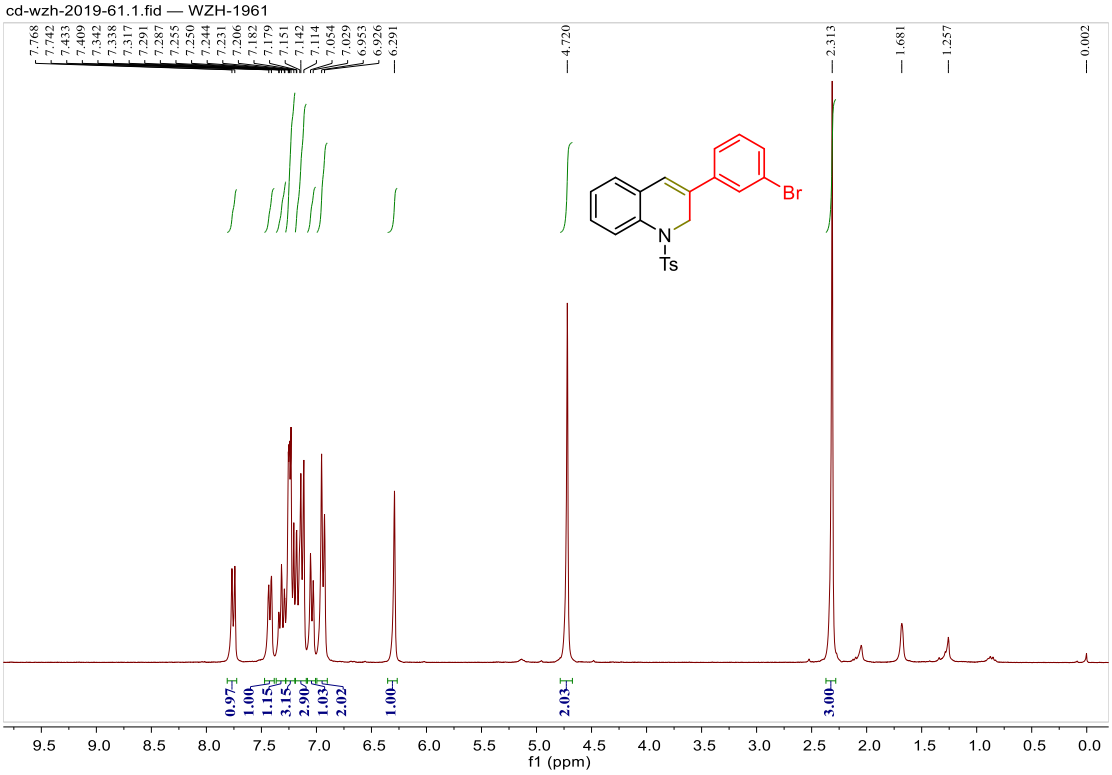
^{1}H NMR (300 MHz, $CDCl_3$) of **3r**



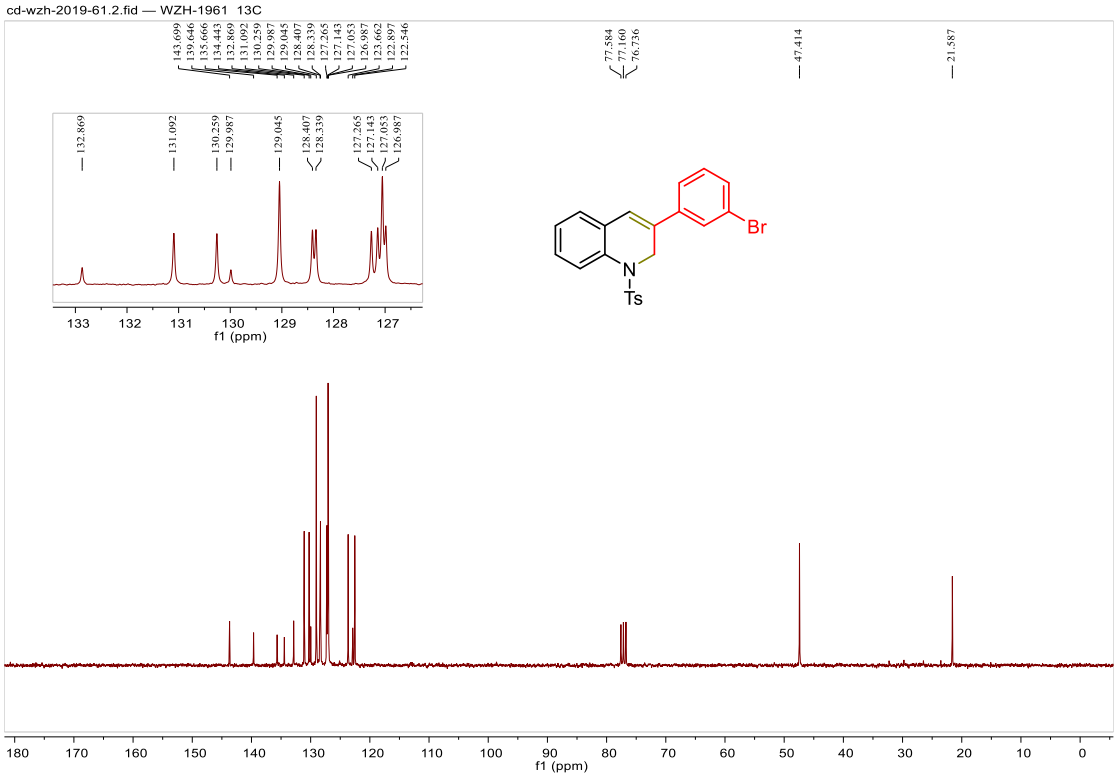
^{13}C NMR (75 MHz, $CDCl_3$) of **3r**



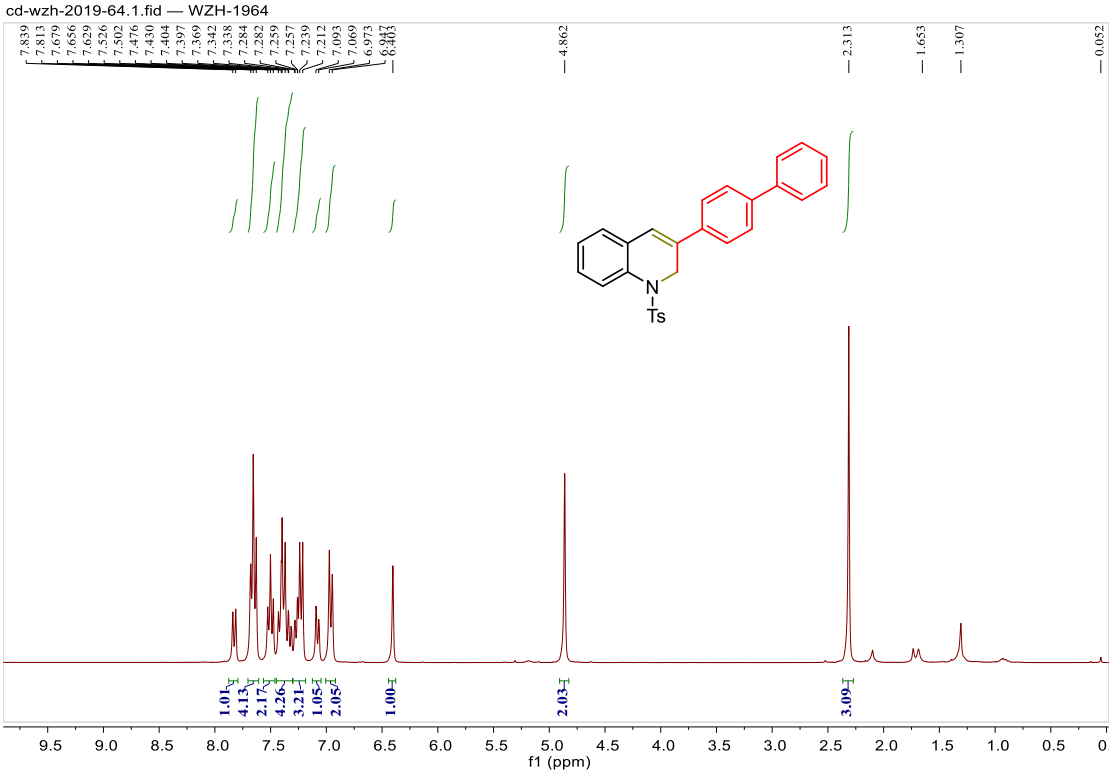
^{1}H NMR (300 MHz, $CDCl_3$) of **3s**



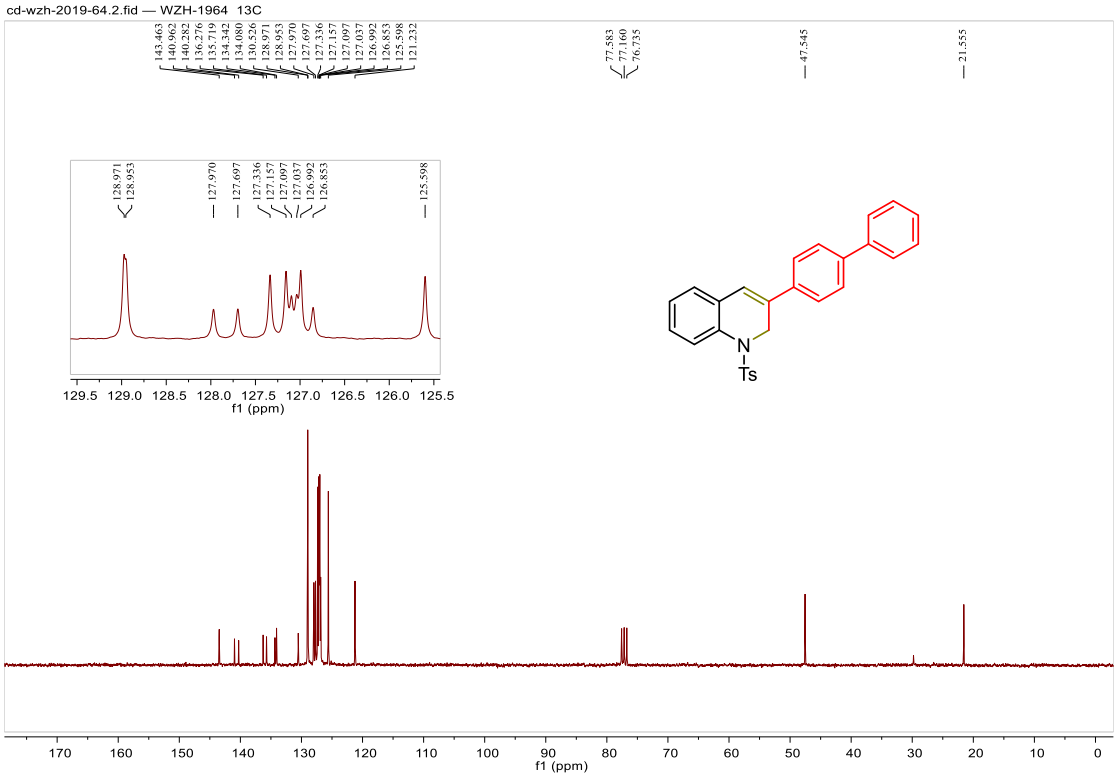
^{13}C NMR (75 MHz, $CDCl_3$) of **3s**



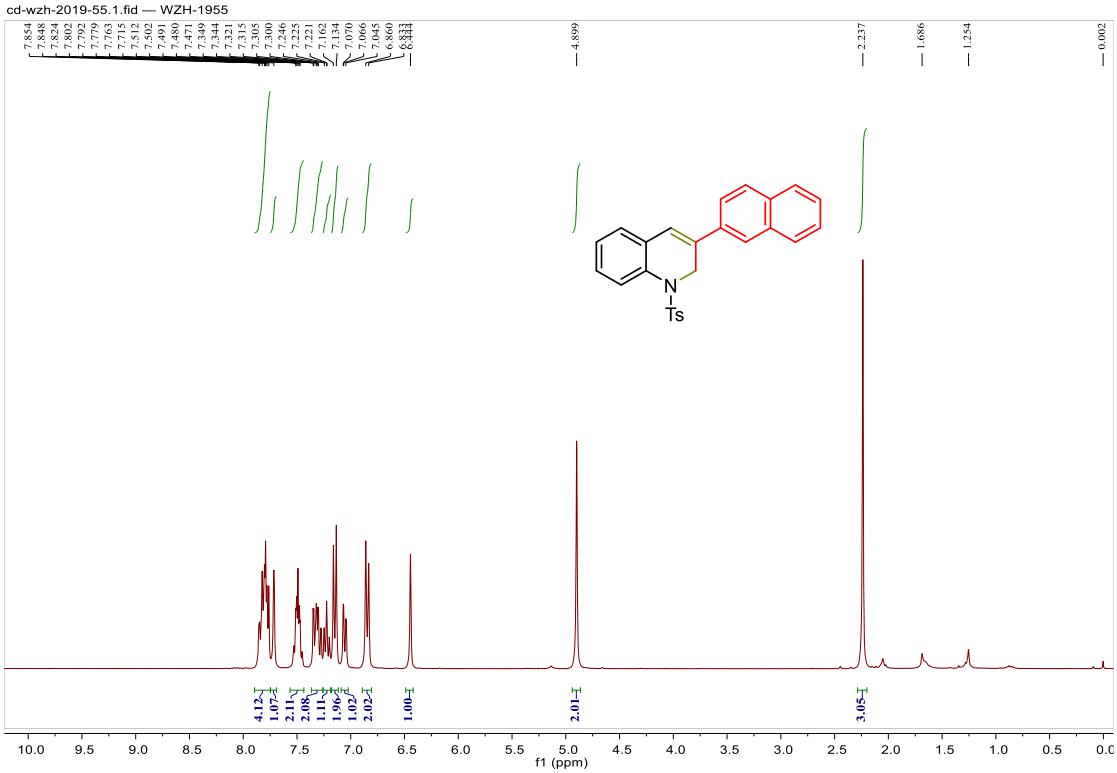
^{1}H NMR (300 MHz, $CDCl_3$) of **3t**



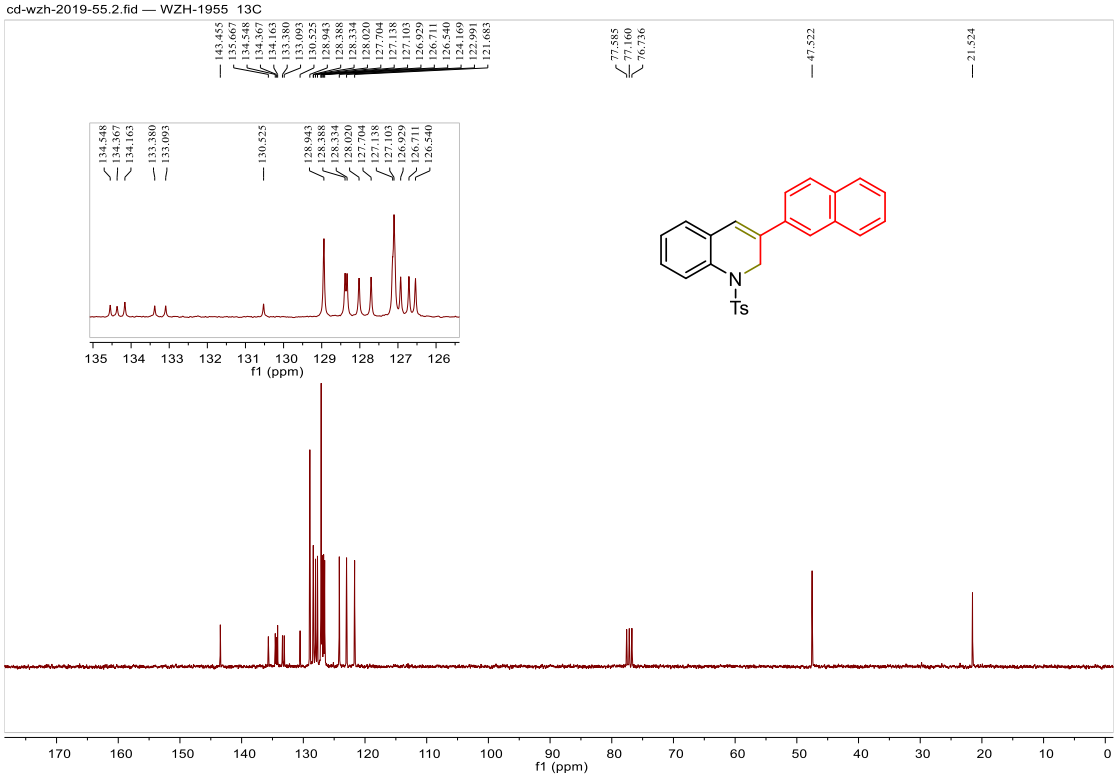
^{13}C NMR (75 MHz, $CDCl_3$) of **3t**



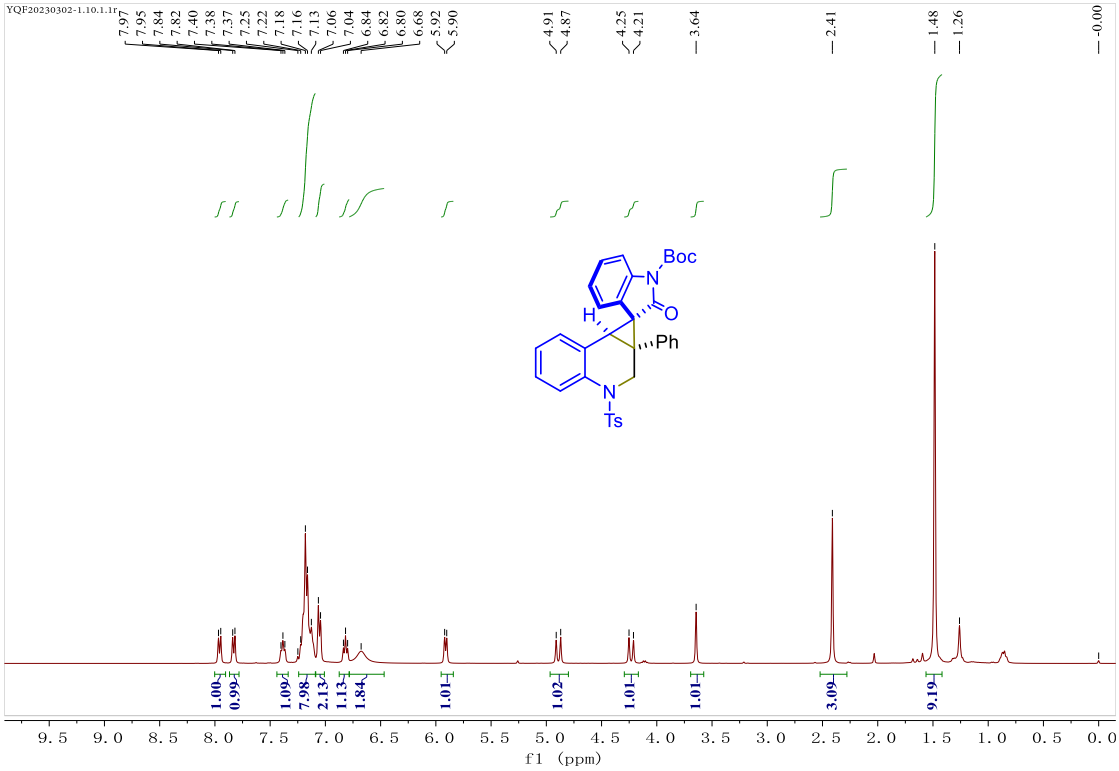
^{1}H NMR (300 MHz, $CDCl_3$) of **3u**



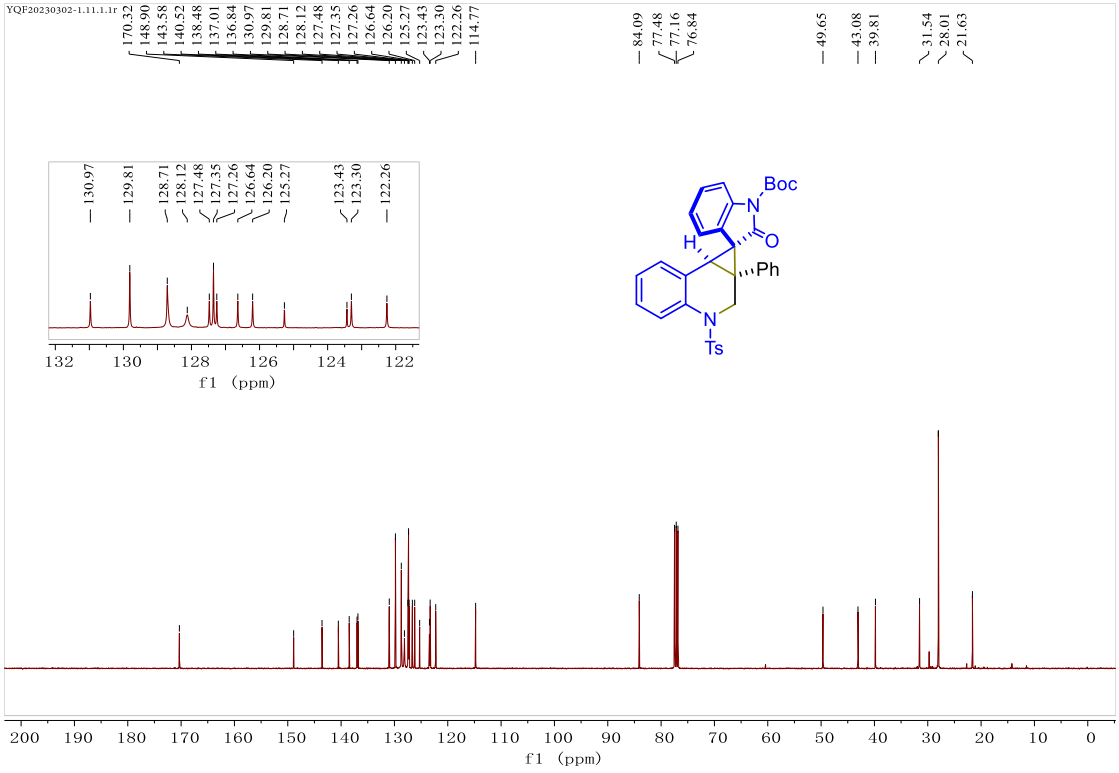
^{13}C NMR (75 MHz, $CDCl_3$) of **3u**



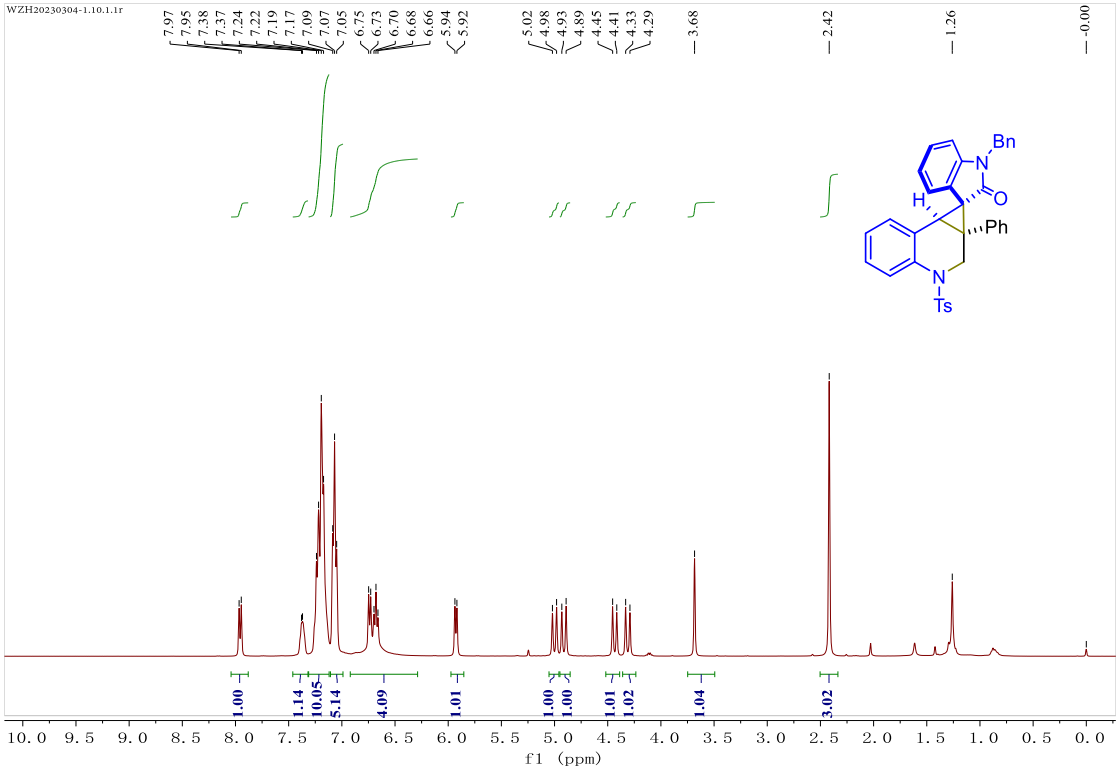
^{1}H NMR (400 MHz, $CDCl_3$) of **6a**



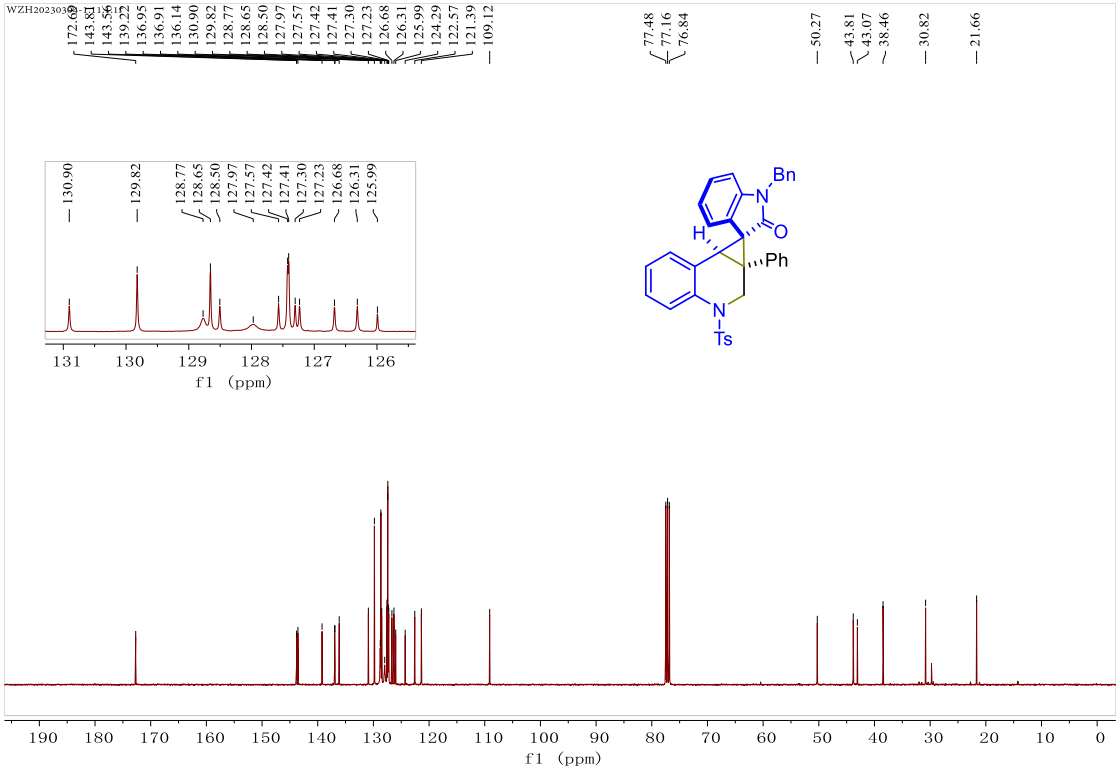
^{13}C NMR (101 MHz, $CDCl_3$) of **6a**



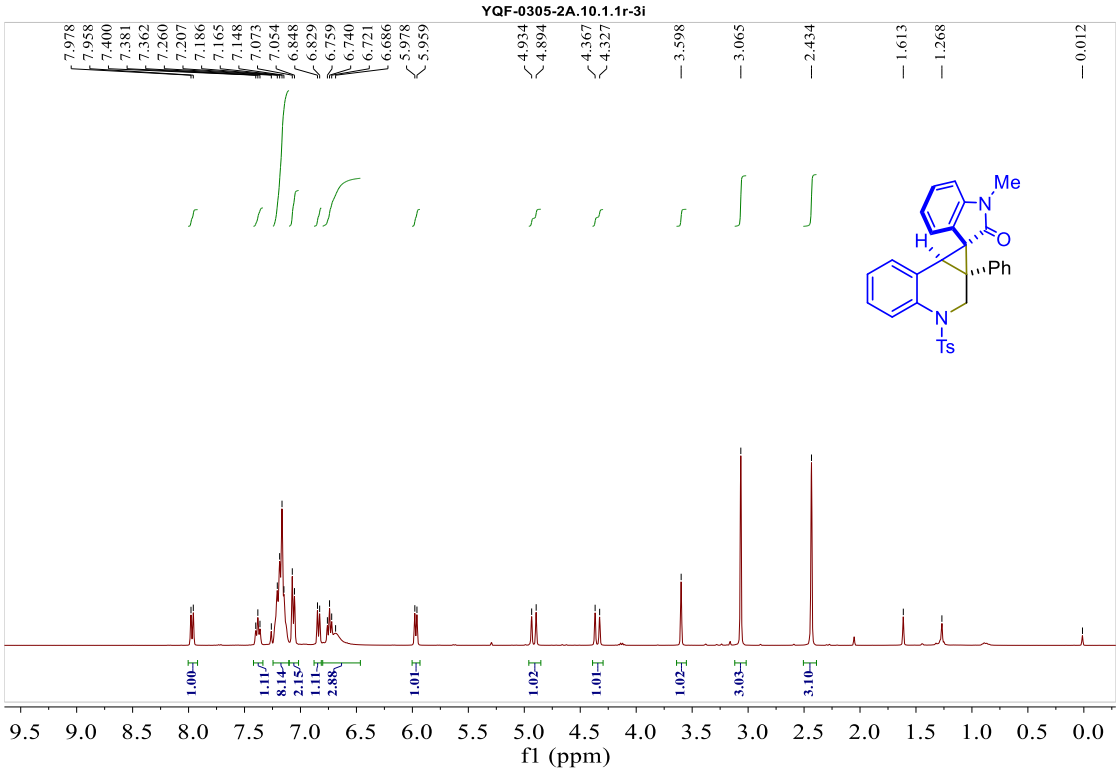
^{1}H NMR (400 MHz, $CDCl_3$) of **6b**



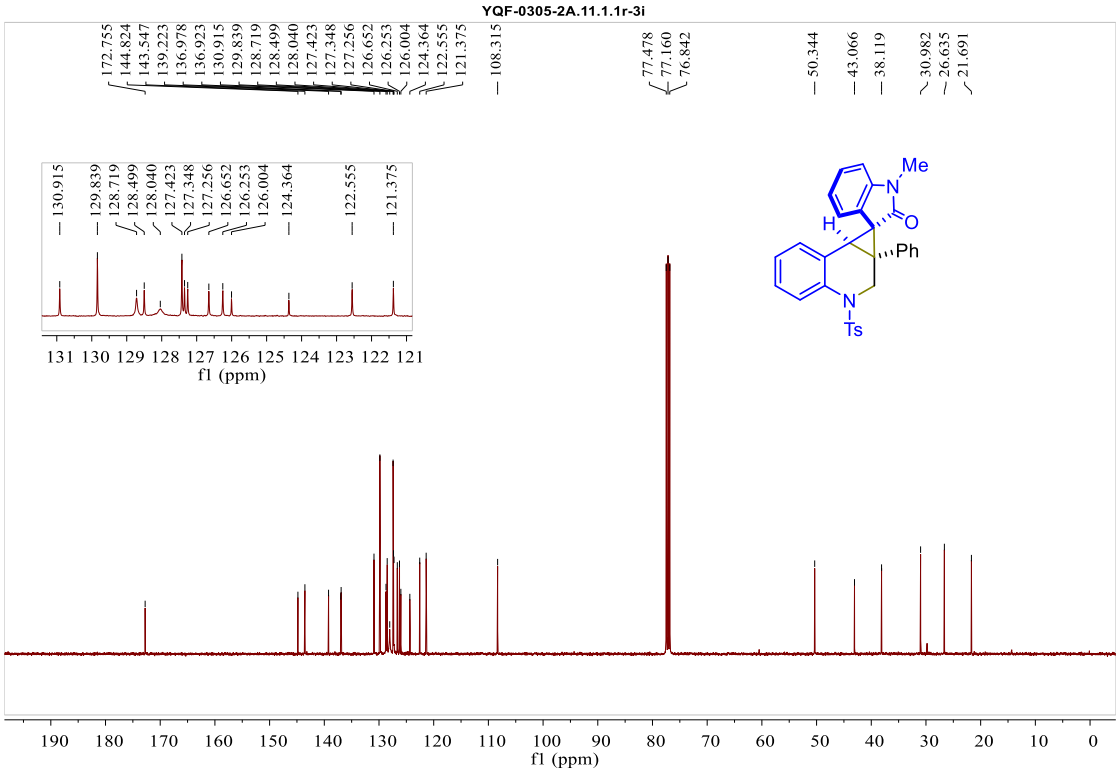
^{13}C NMR (101 MHz, $CDCl_3$) of **6b**



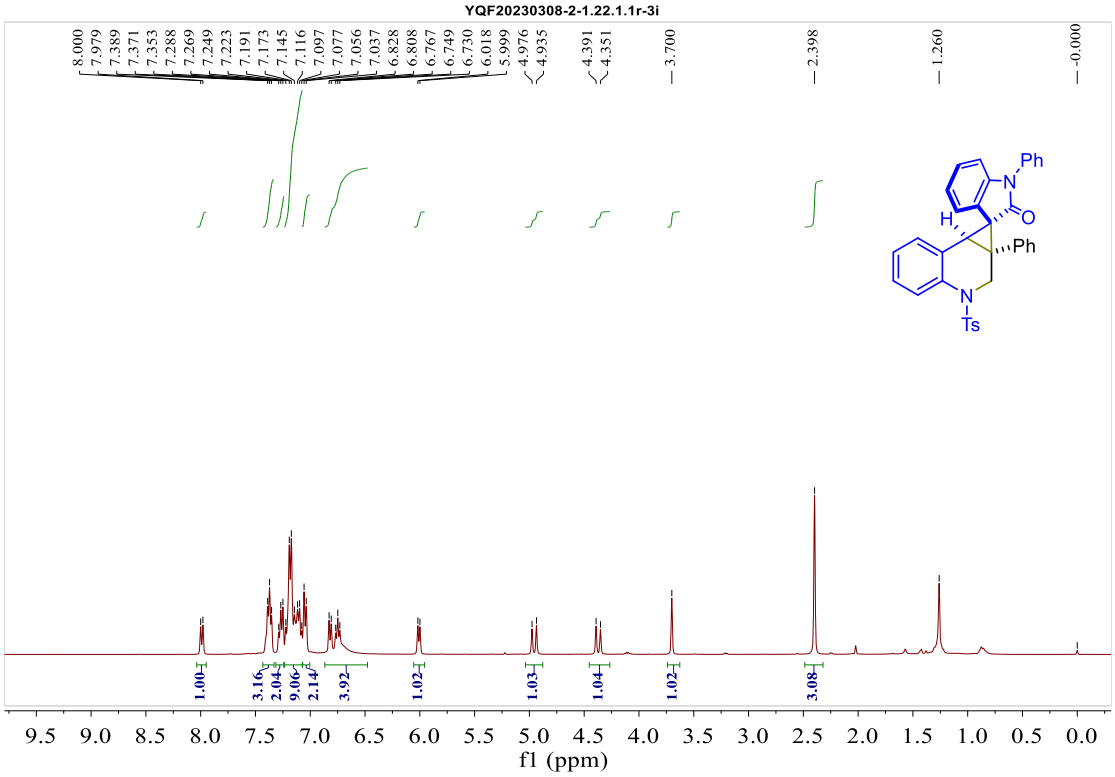
^{1}H NMR (400 MHz, $CDCl_3$) of **6c**



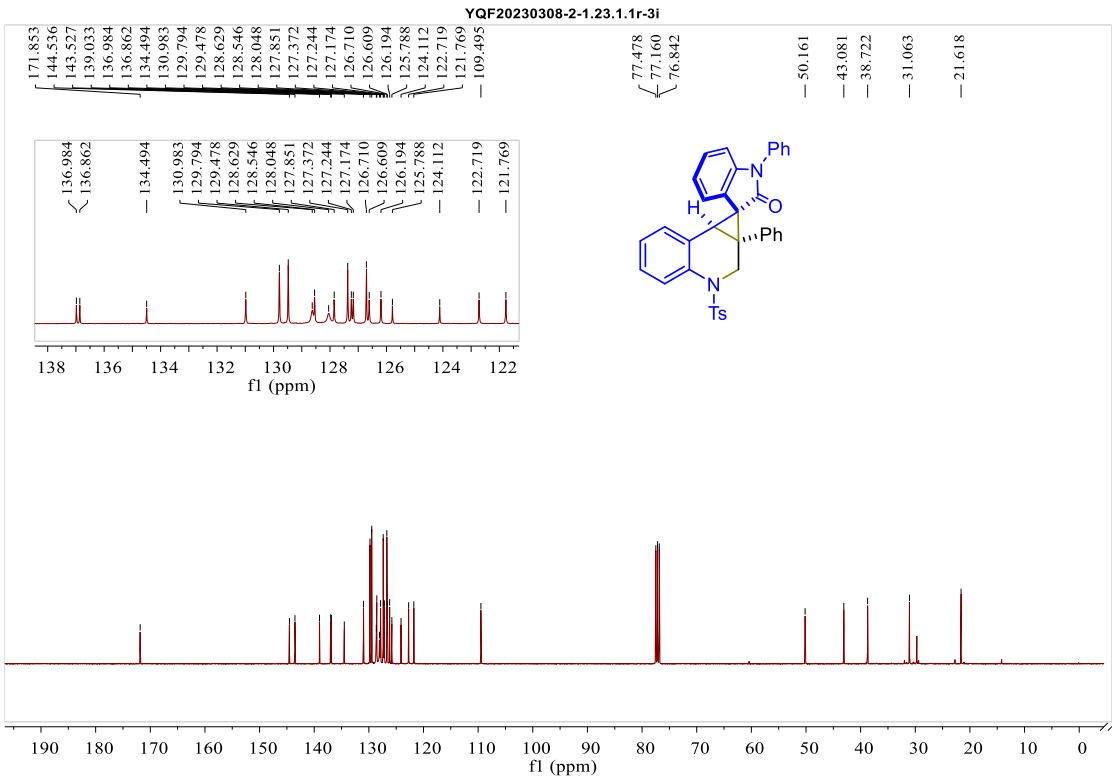
^{13}C NMR (101 MHz, $CDCl_3$) of **6c**



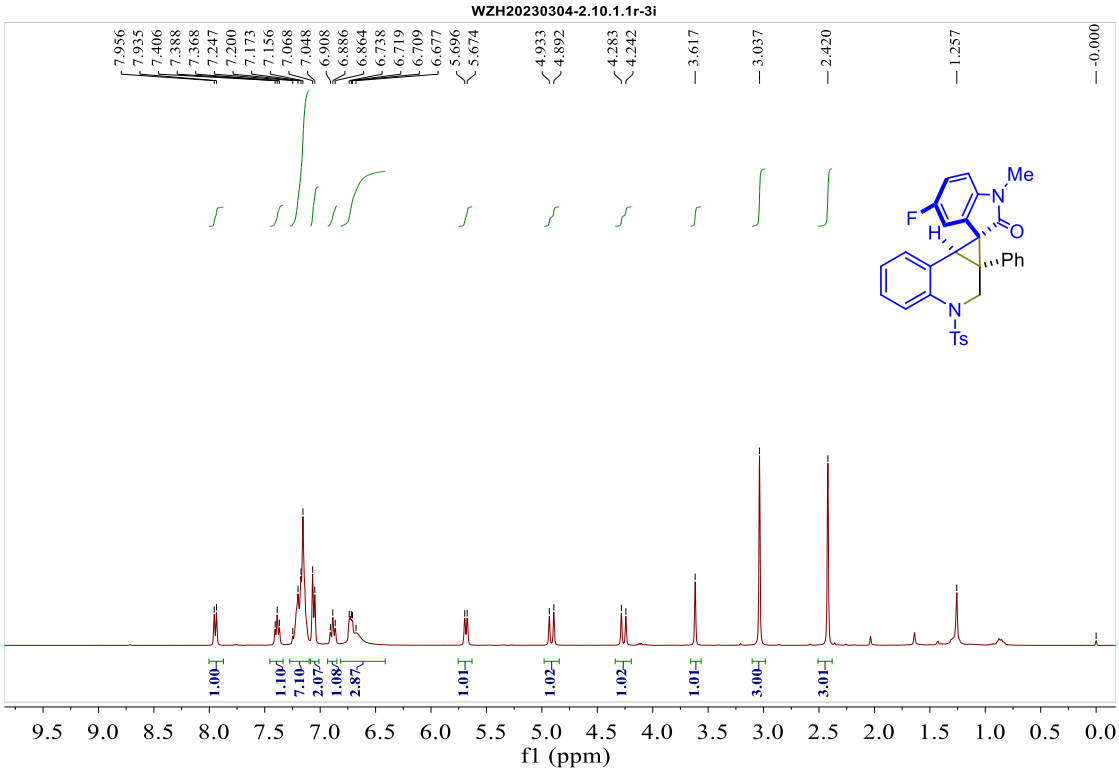
^{1}H NMR (400 MHz, $CDCl_3$) of **6d**



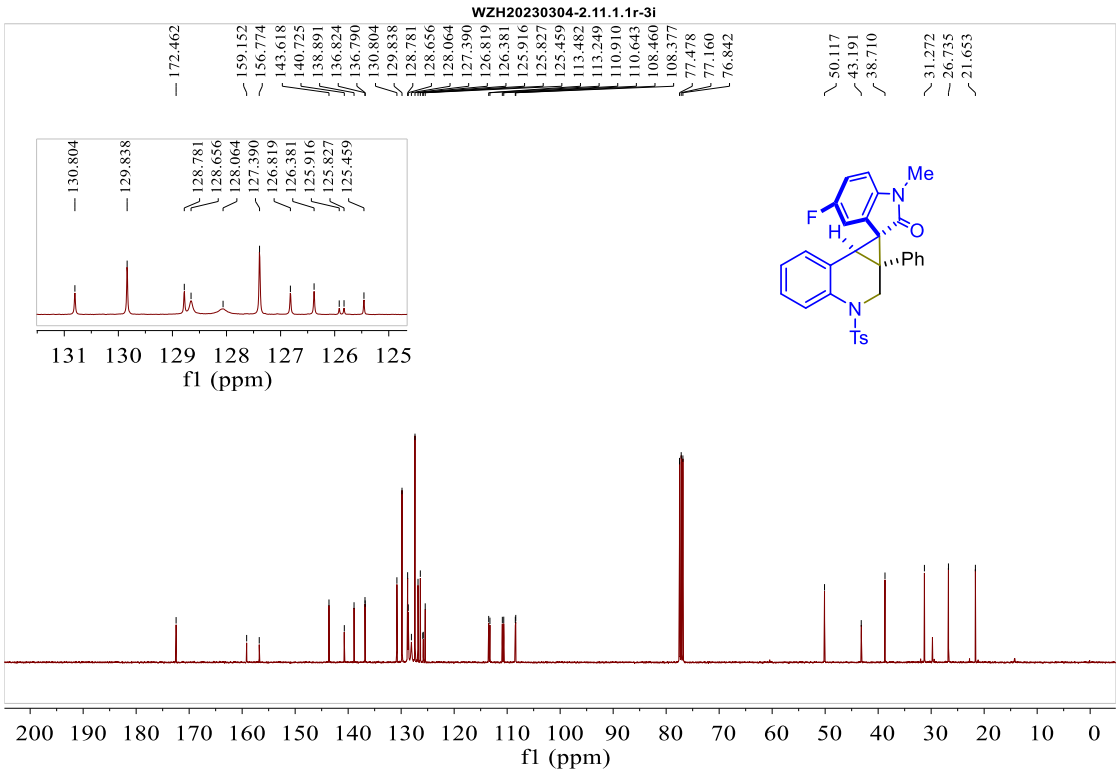
^{13}C NMR (101 MHz, $CDCl_3$) of **6d**



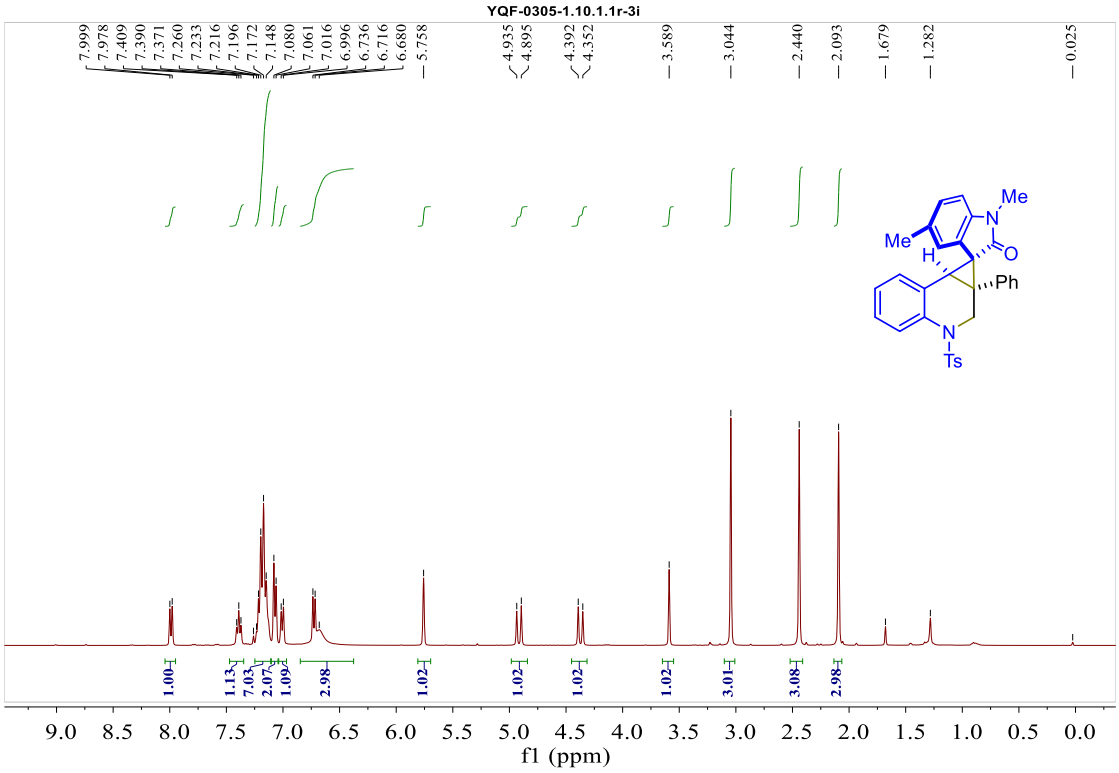
^{1}H NMR (400 MHz, $CDCl_3$) of **6e**



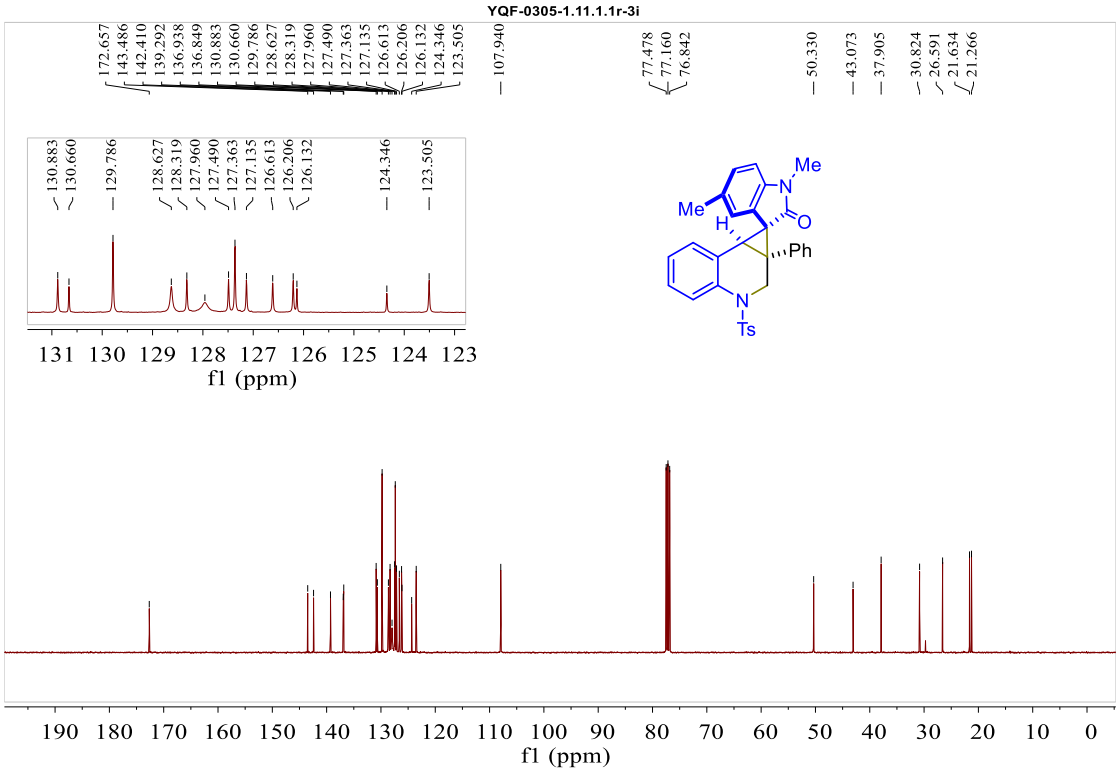
^{13}C NMR (101 MHz, $CDCl_3$) of **6e**



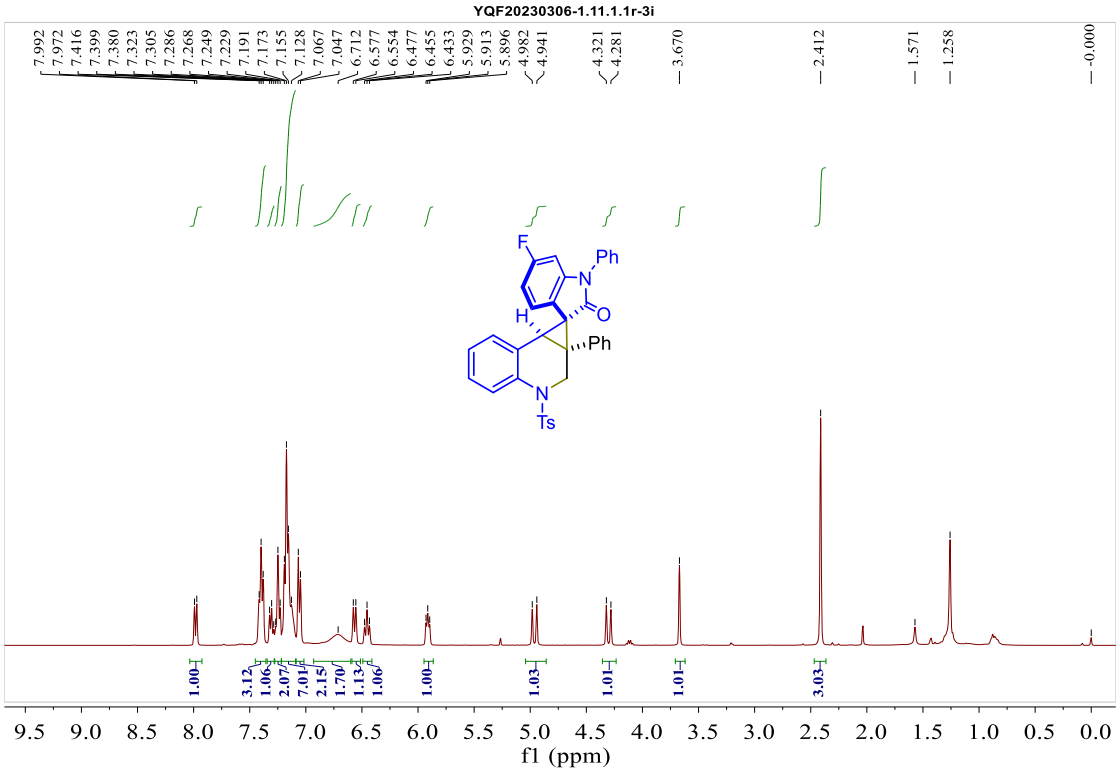
^{1}H NMR (400 MHz, $CDCl_3$) of **6f**



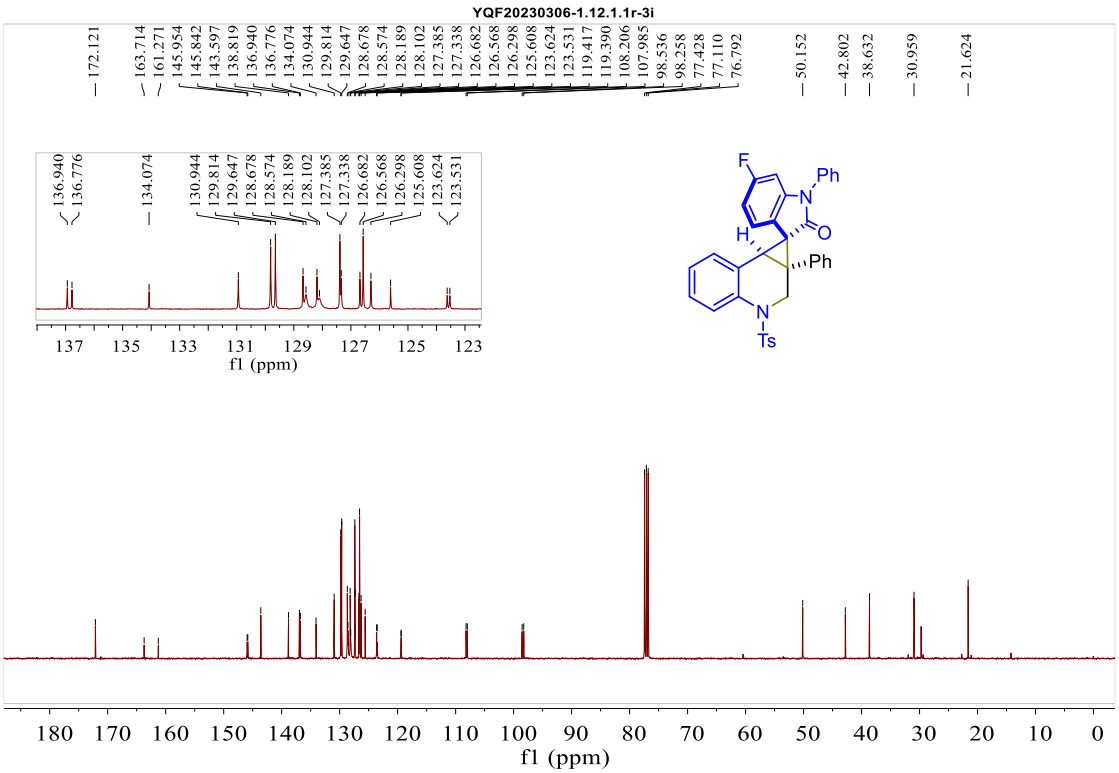
^{13}C NMR (101 MHz, $CDCl_3$) of **6f**



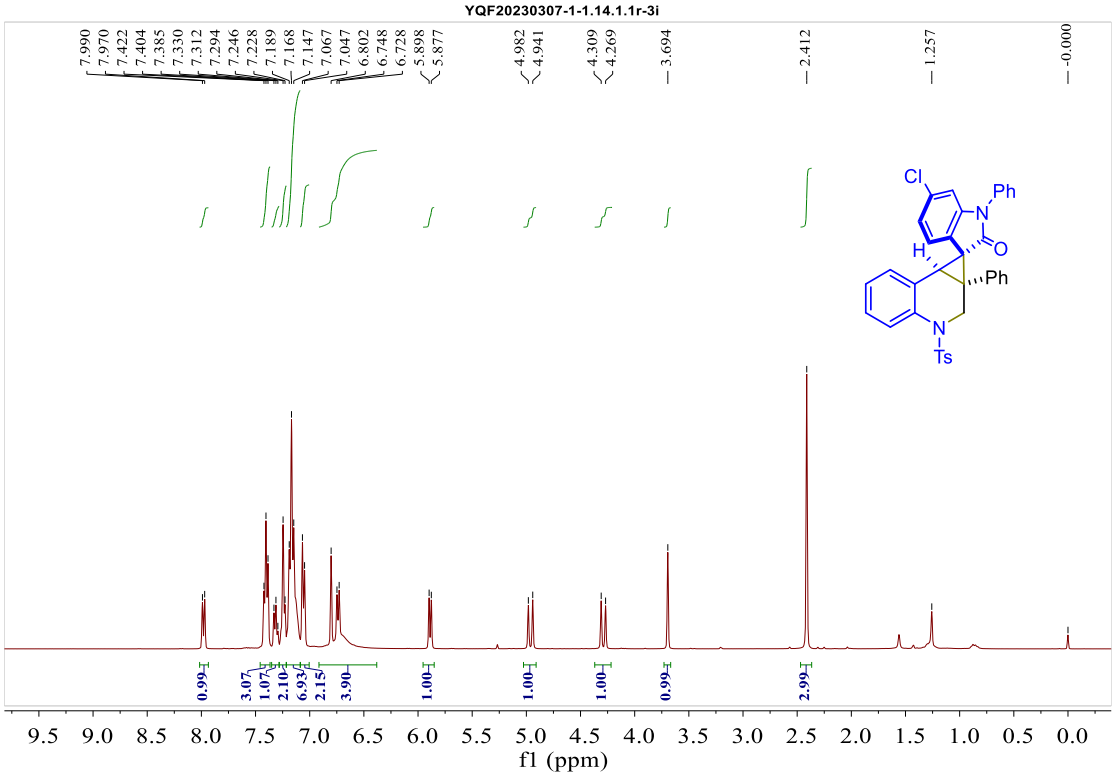
^{1}H NMR (400 MHz, $CDCl_3$) of **6g**



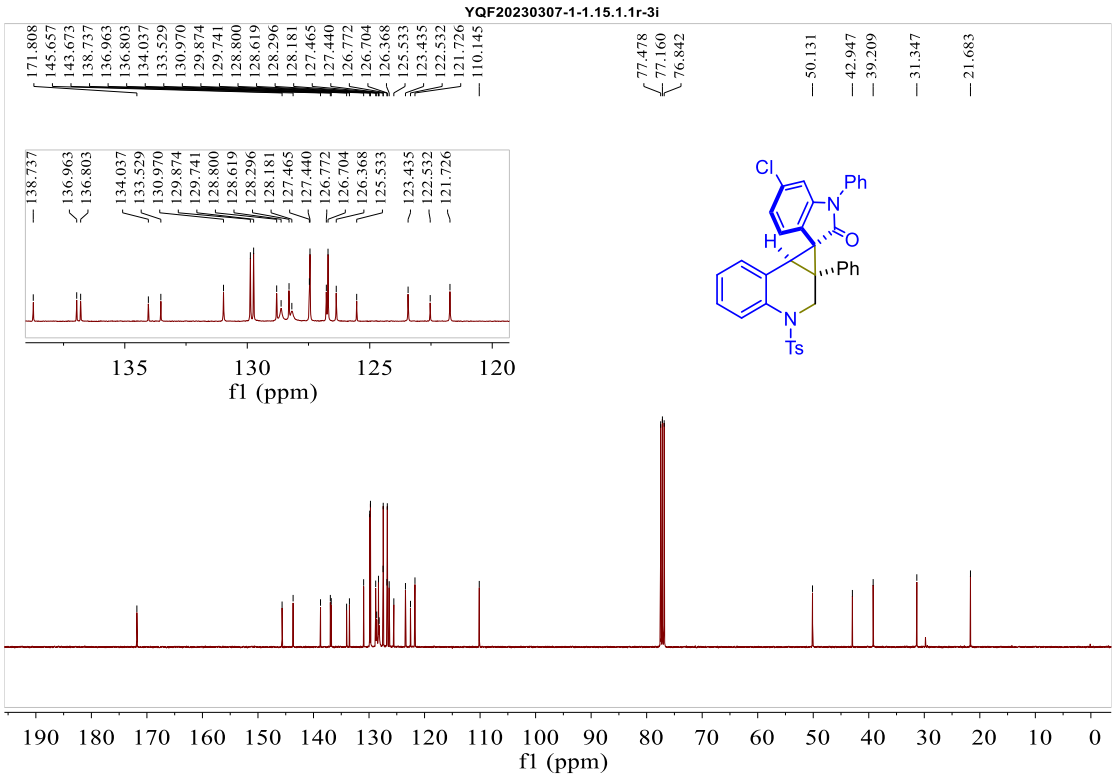
^{13}C NMR (101 MHz, $CDCl_3$) of **6g**



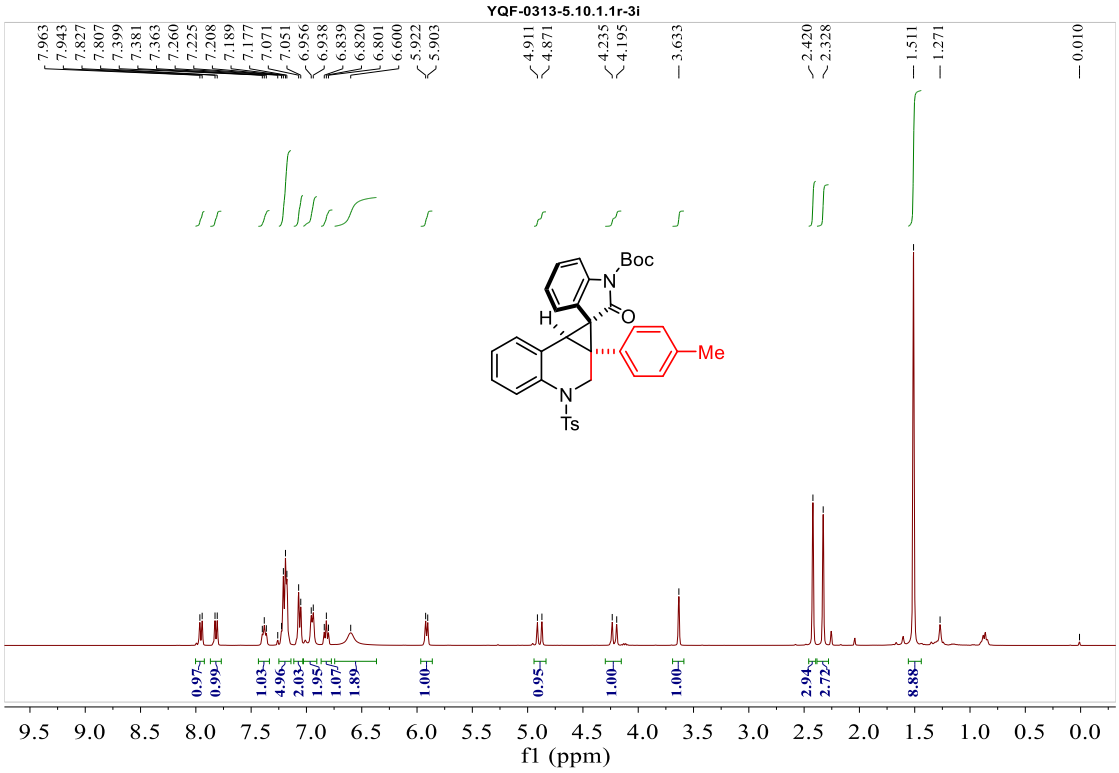
^{1}H NMR (400 MHz, $CDCl_3$) of **6h**



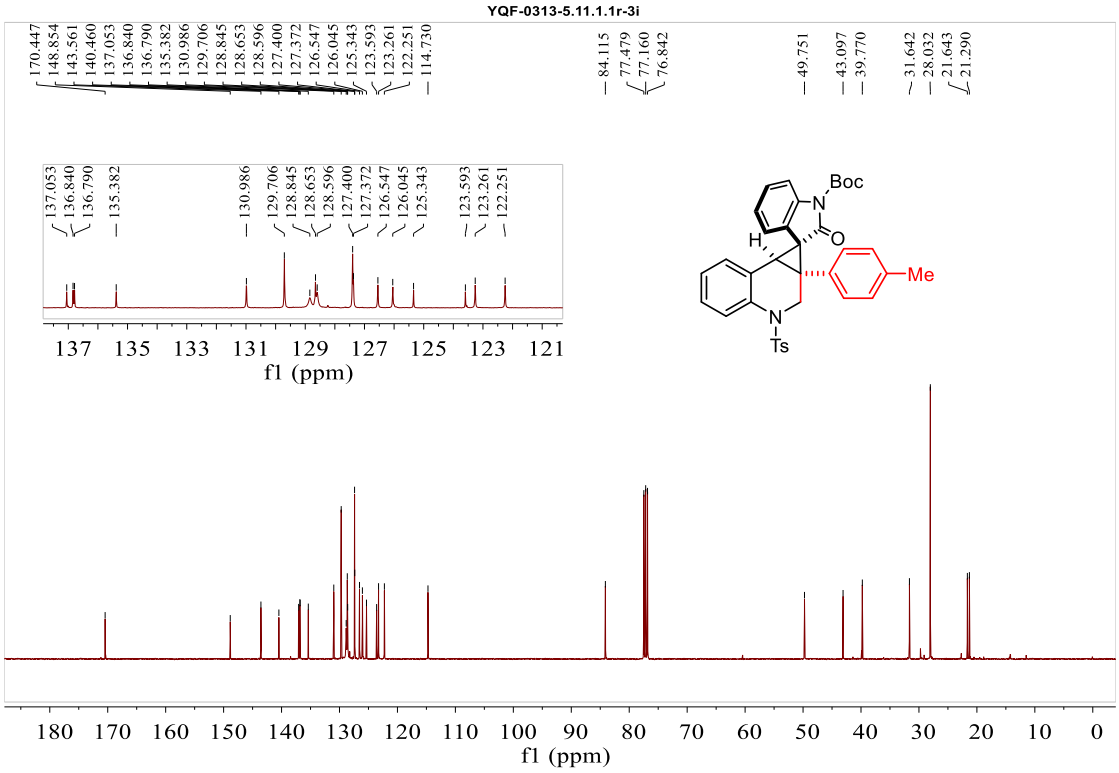
^{13}C NMR (101 MHz, $CDCl_3$) of **6h**



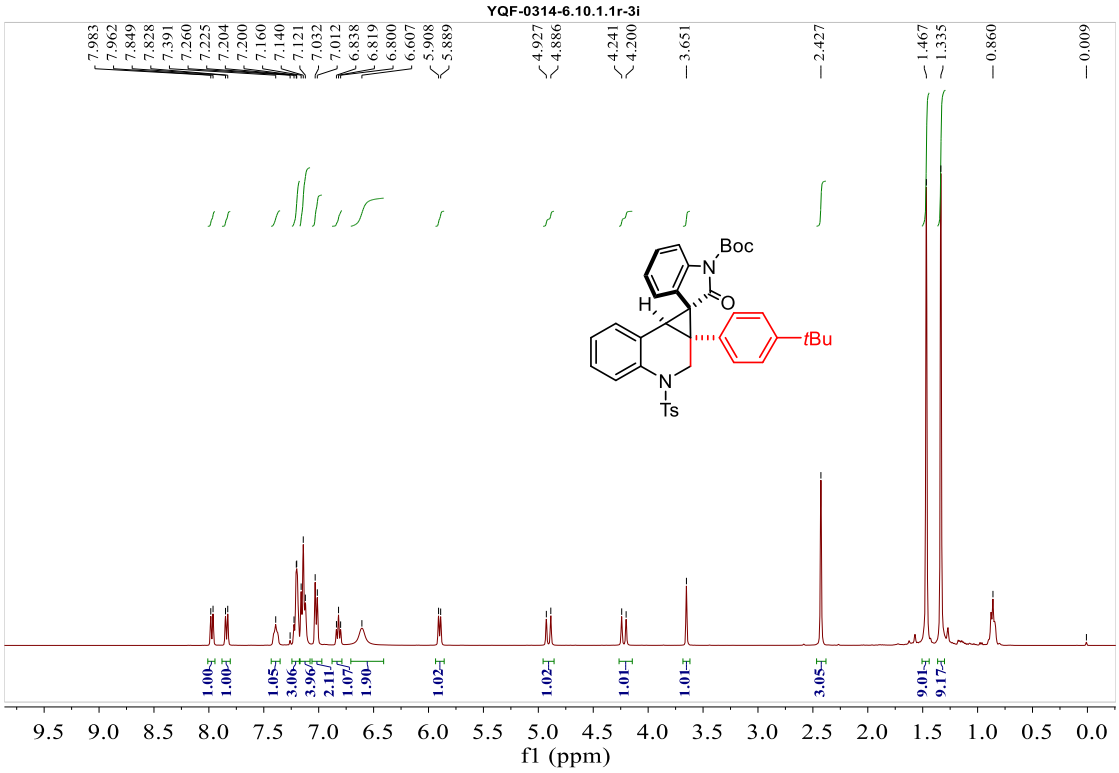
^{1}H NMR (400 MHz, $CDCl_3$) of **6i**



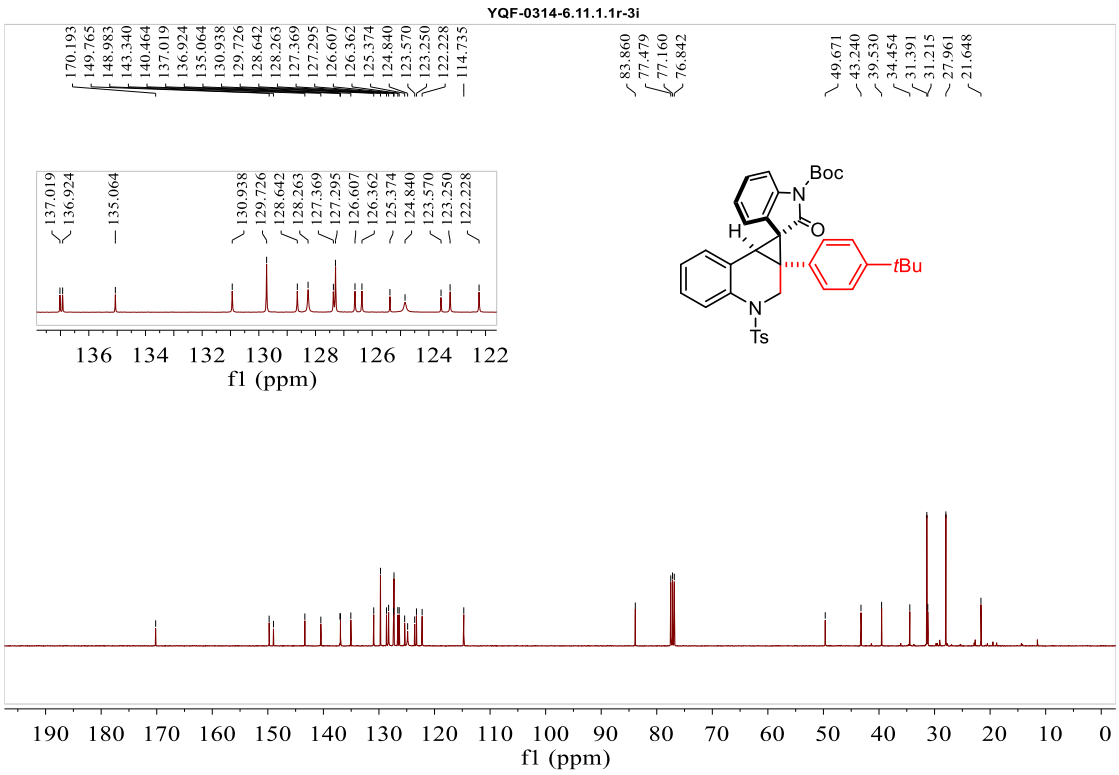
^{13}C NMR (101 MHz, $CDCl_3$) of **6i**



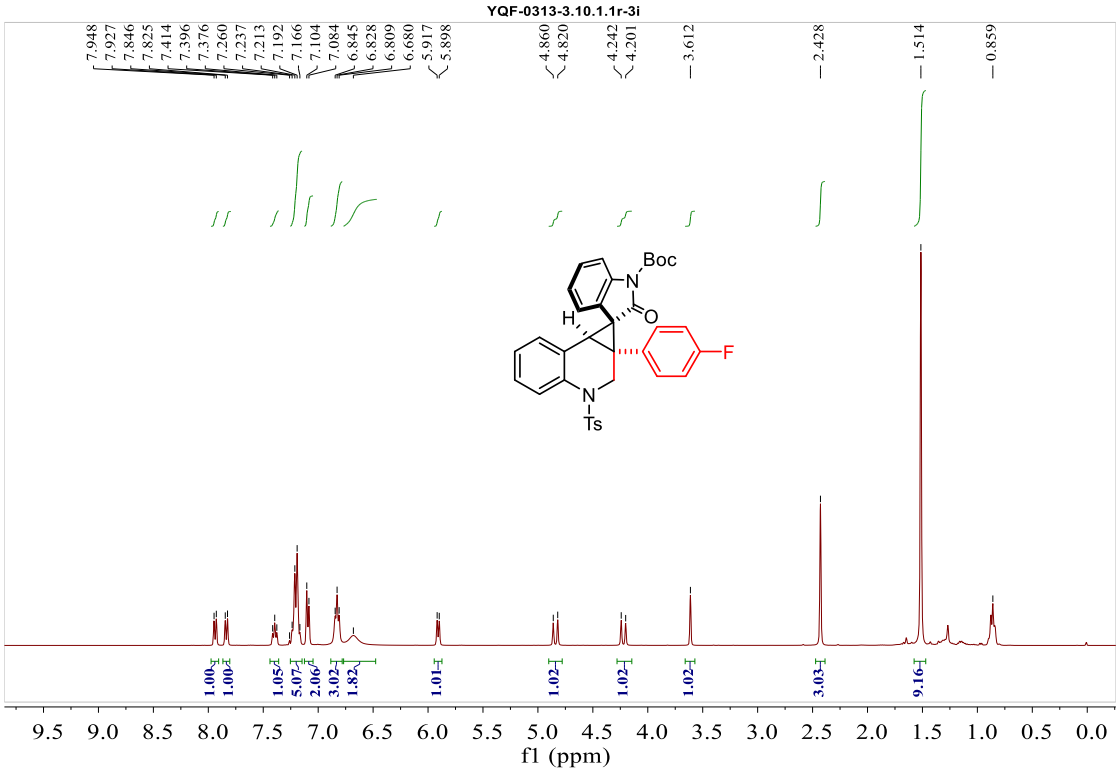
^{1}H NMR (400 MHz, $CDCl_3$) of **6j**



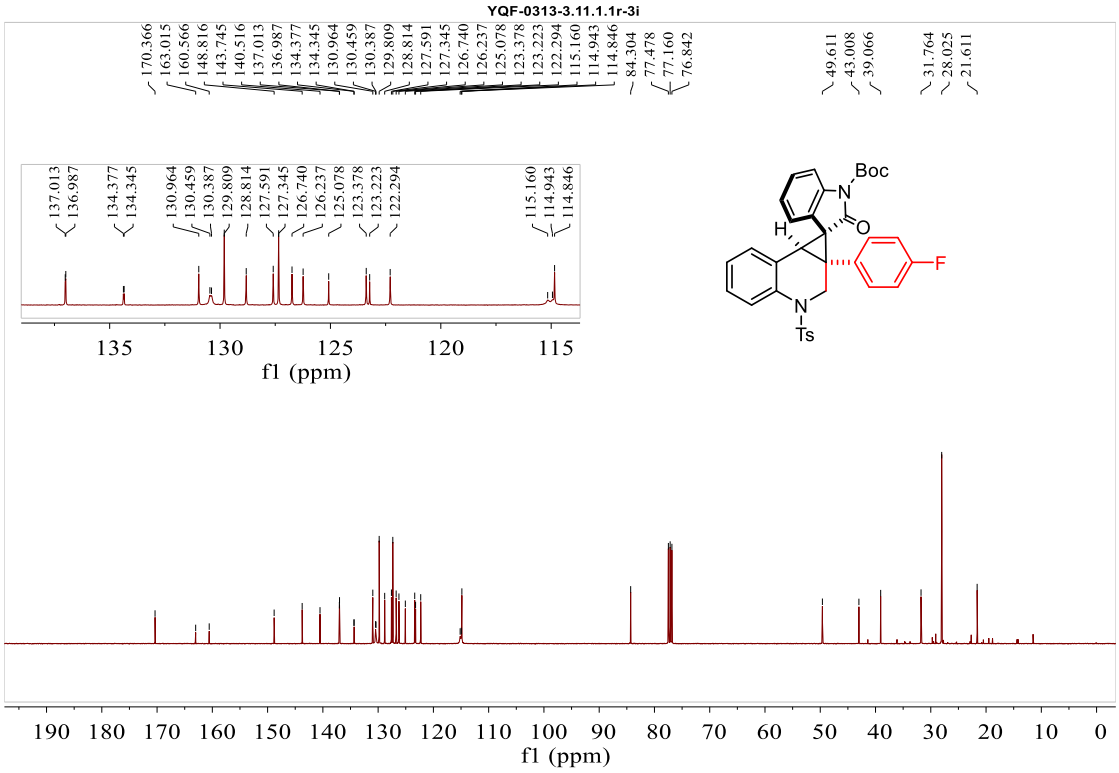
^{13}C NMR (101 MHz, $CDCl_3$) of **6j**



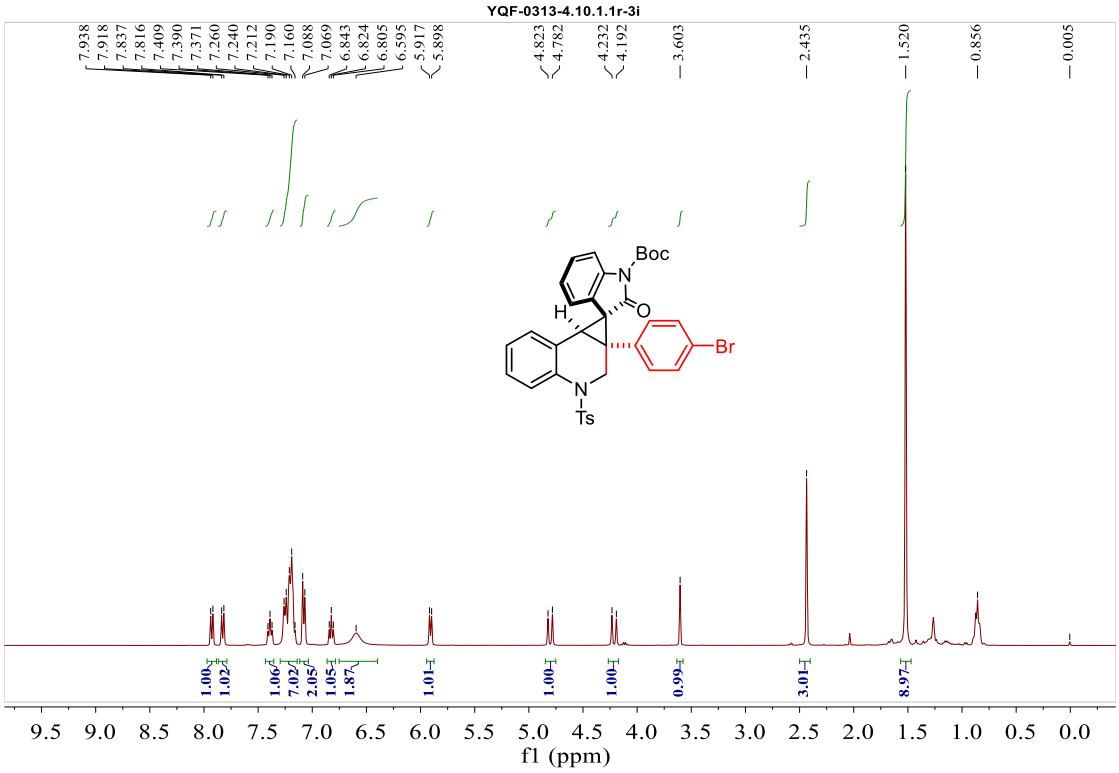
^{1}H NMR (400 MHz, $CDCl_3$) of **6k**



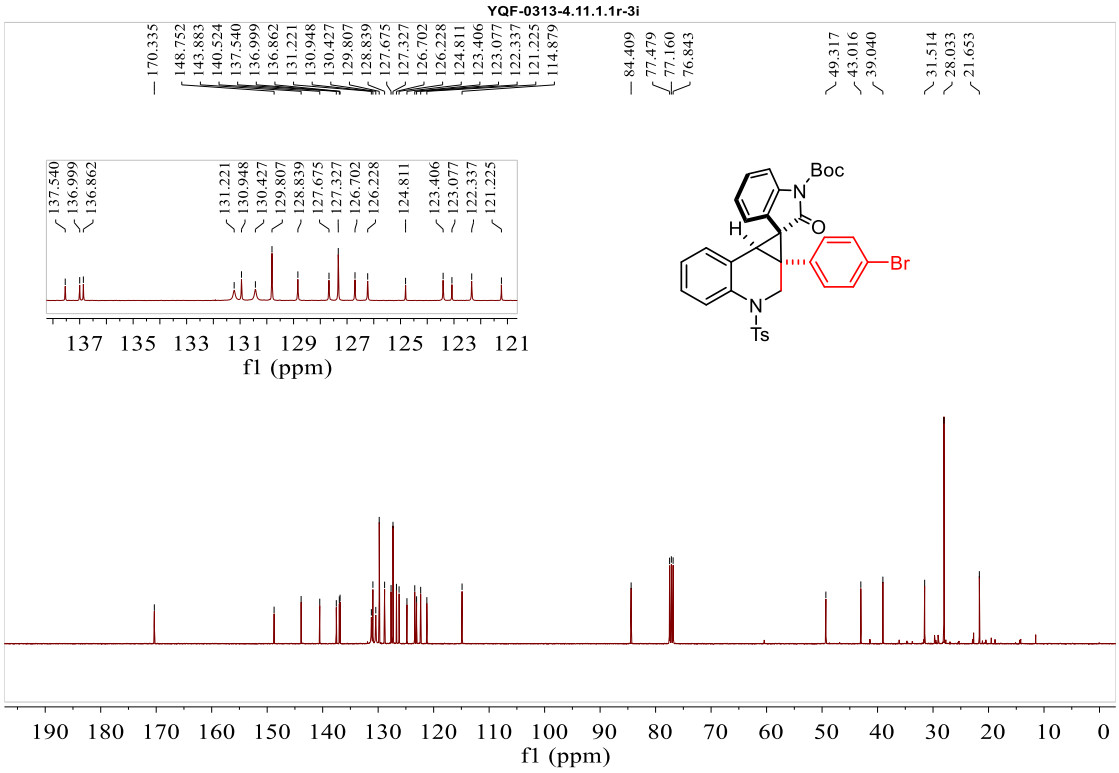
^{13}C NMR (101 MHz, $CDCl_3$) of **6k**



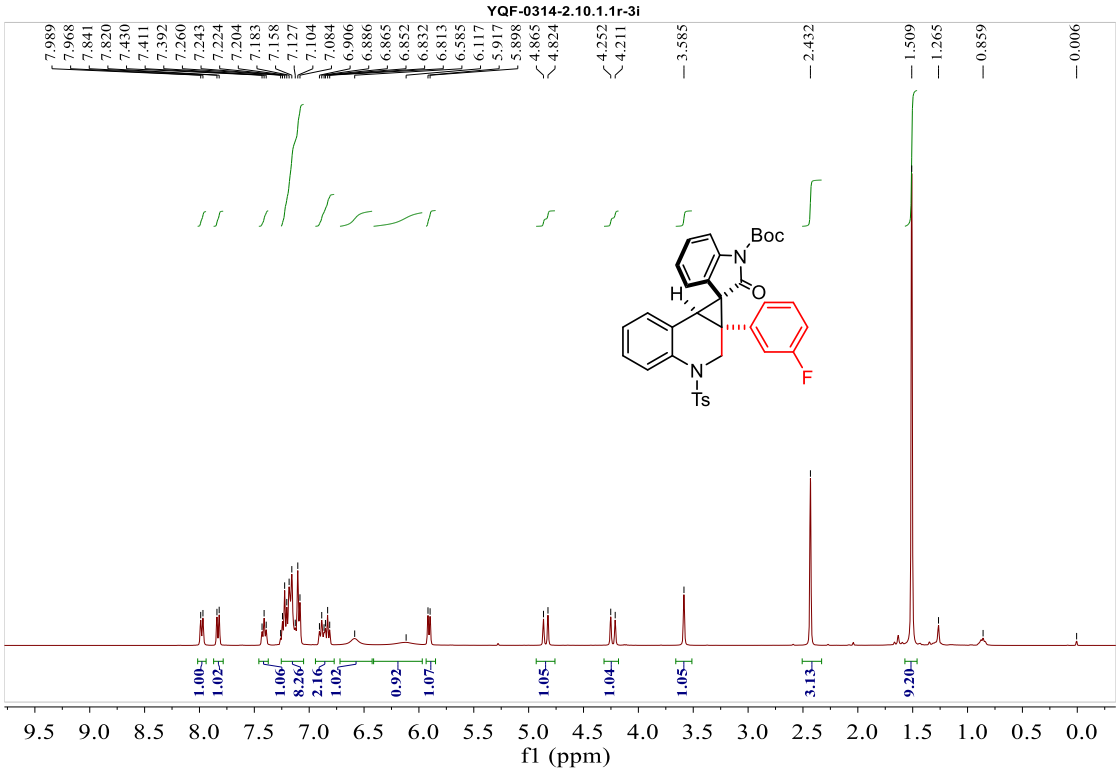
^{1}H NMR (400 MHz, $CDCl_3$) of **6l**



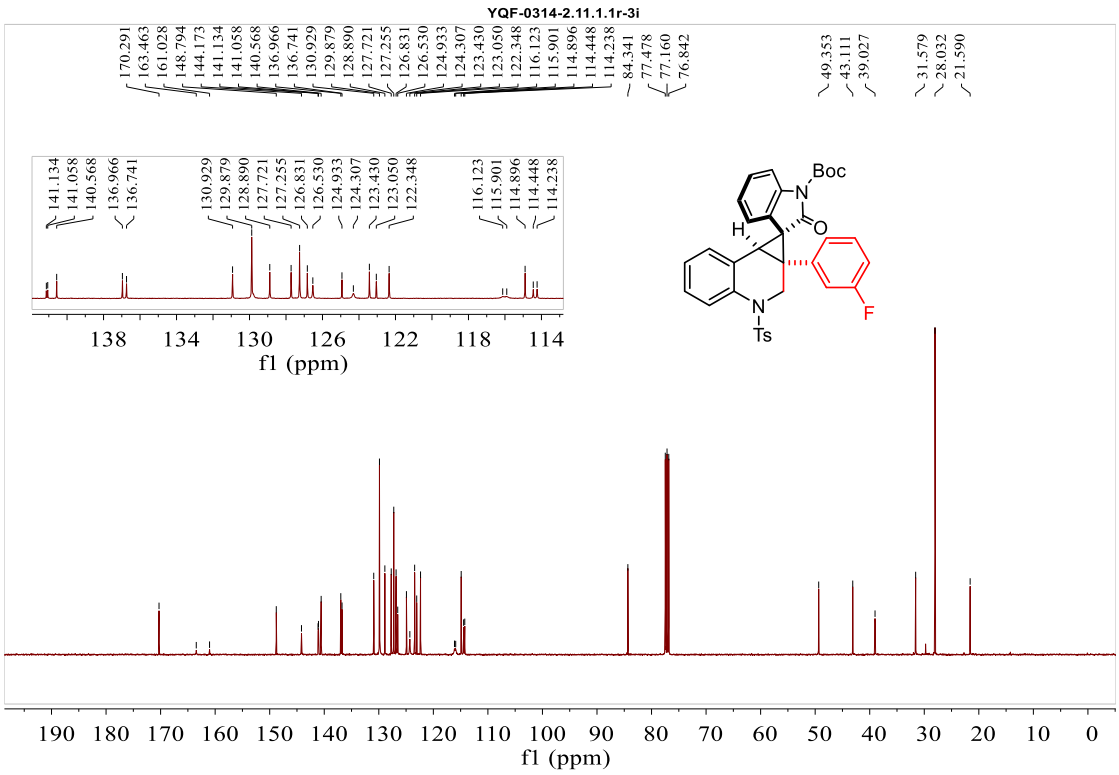
^{13}C NMR (101 MHz, $CDCl_3$) of **6l**



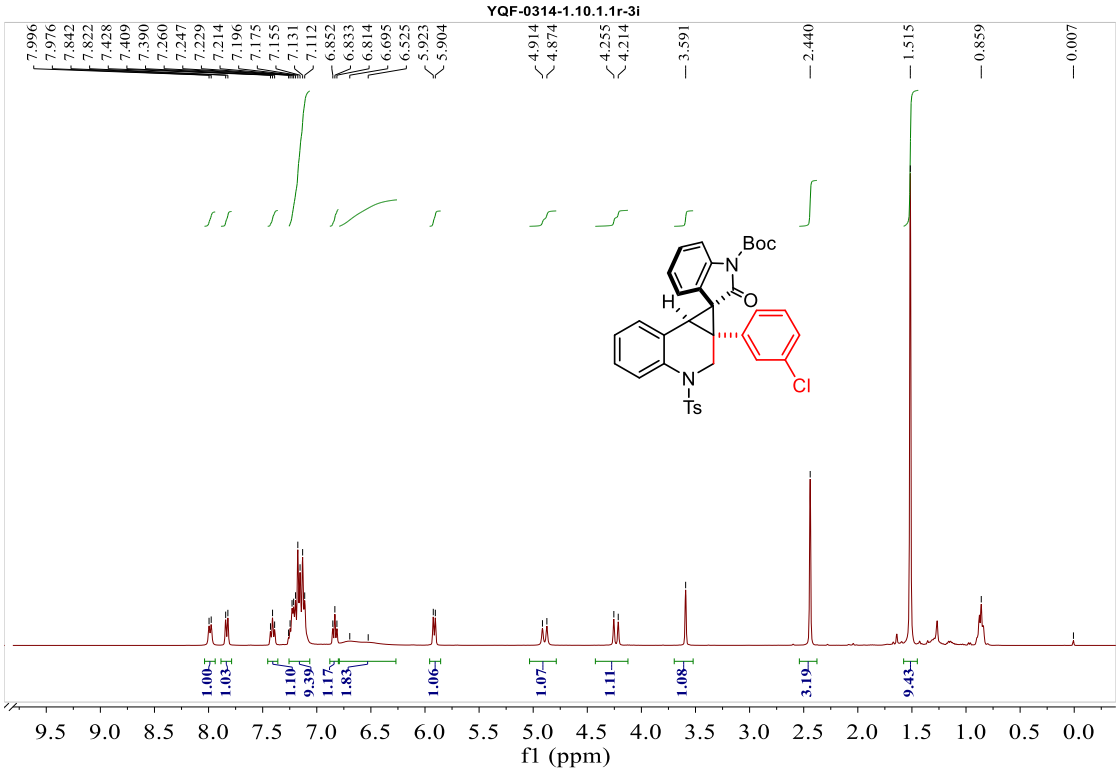
^{1}H NMR (400 MHz, $CDCl_3$) of **6m**



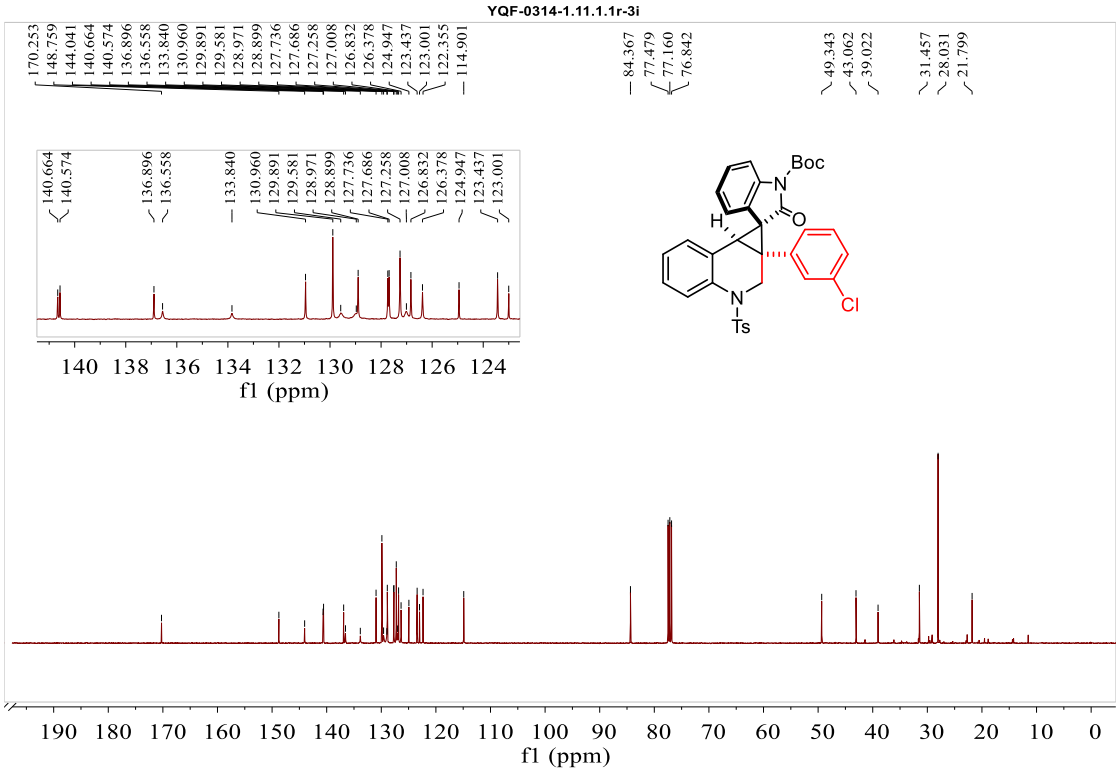
^{13}C NMR (101 MHz, $CDCl_3$) of **6m**



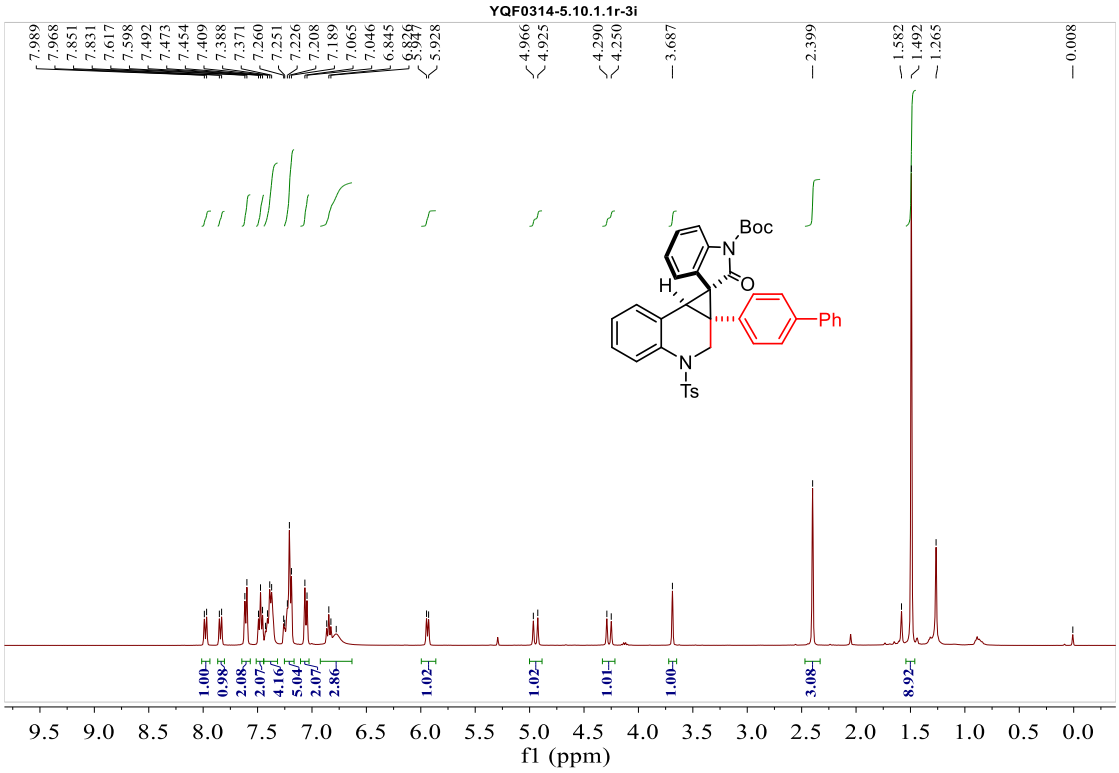
^{1}H NMR (400 MHz, $CDCl_3$) of **6n**



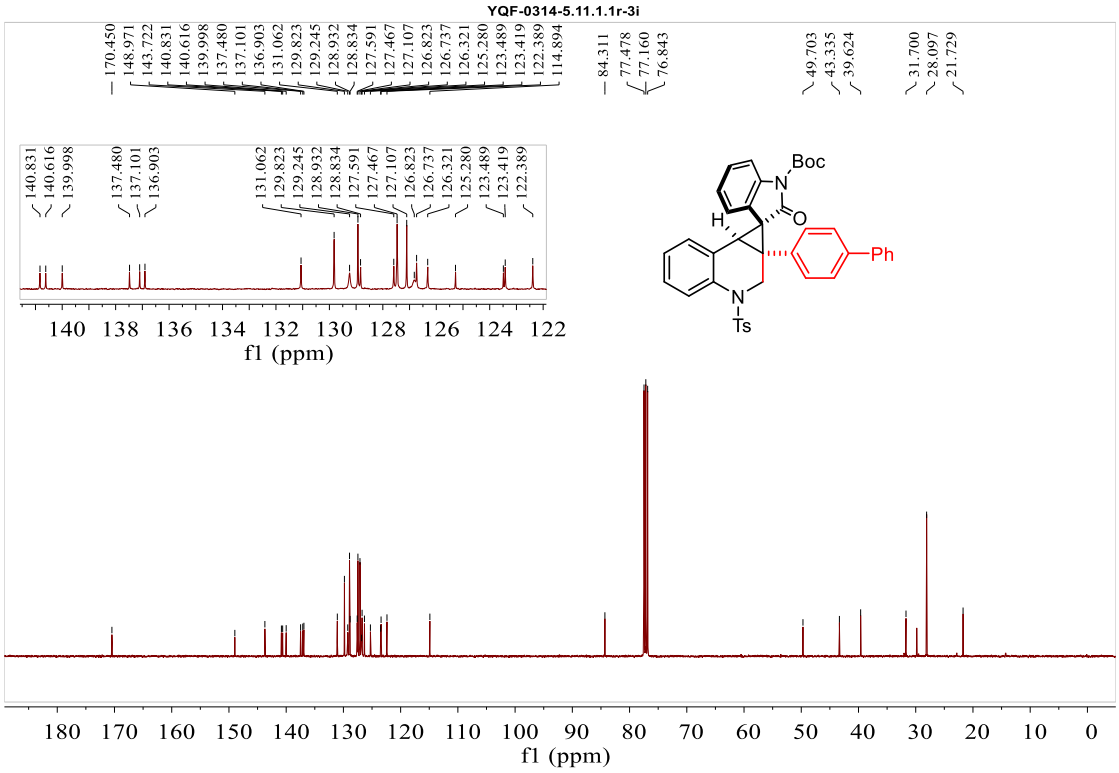
^{13}C NMR (101 MHz, $CDCl_3$) of **6n**



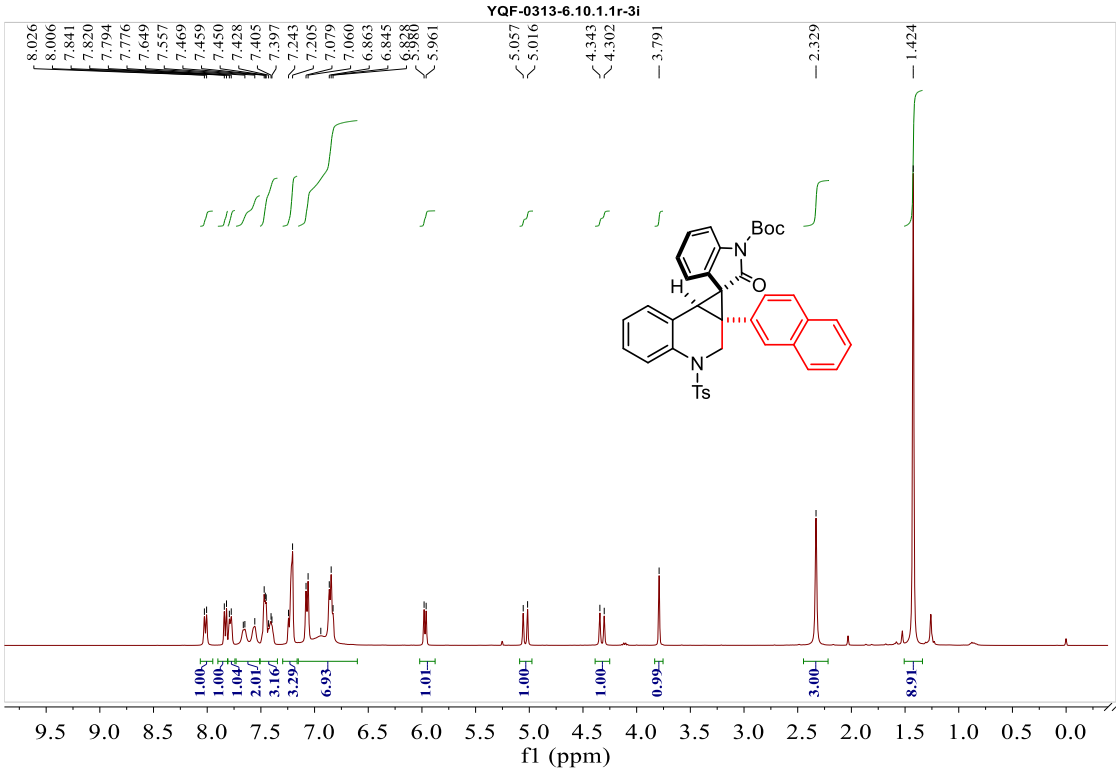
^{1}H NMR (400 MHz, $CDCl_3$) of **6o**



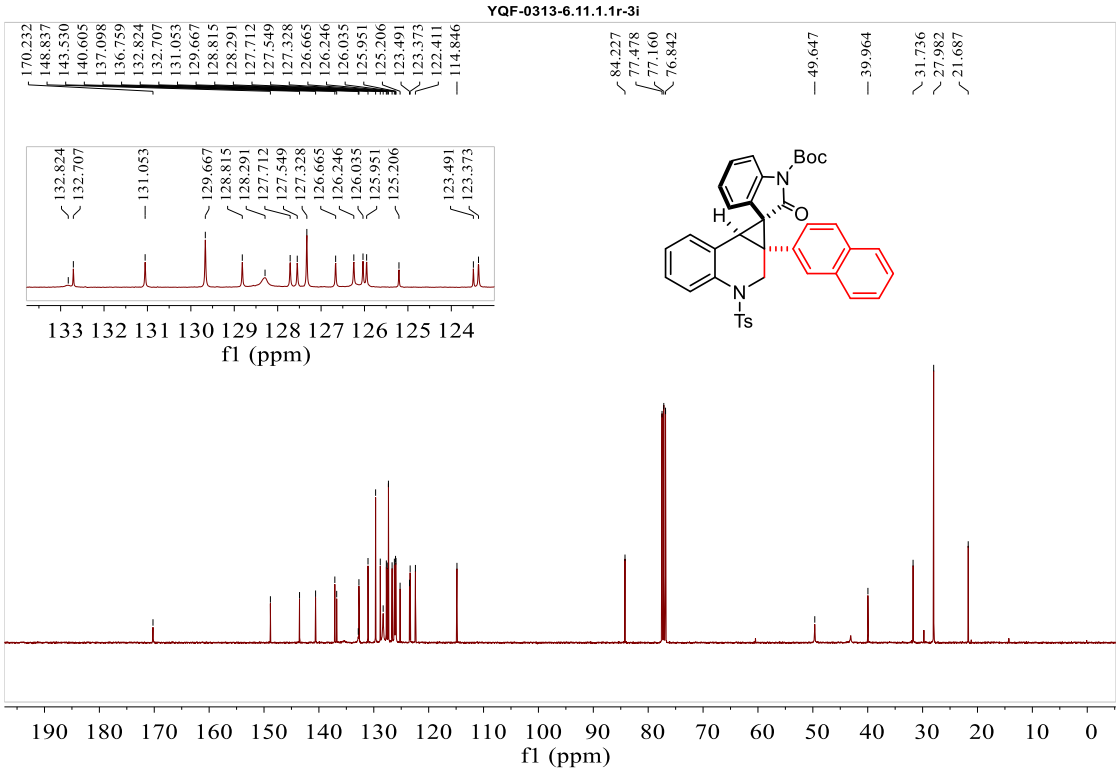
^{13}C NMR (101 MHz, $CDCl_3$) of **6o**



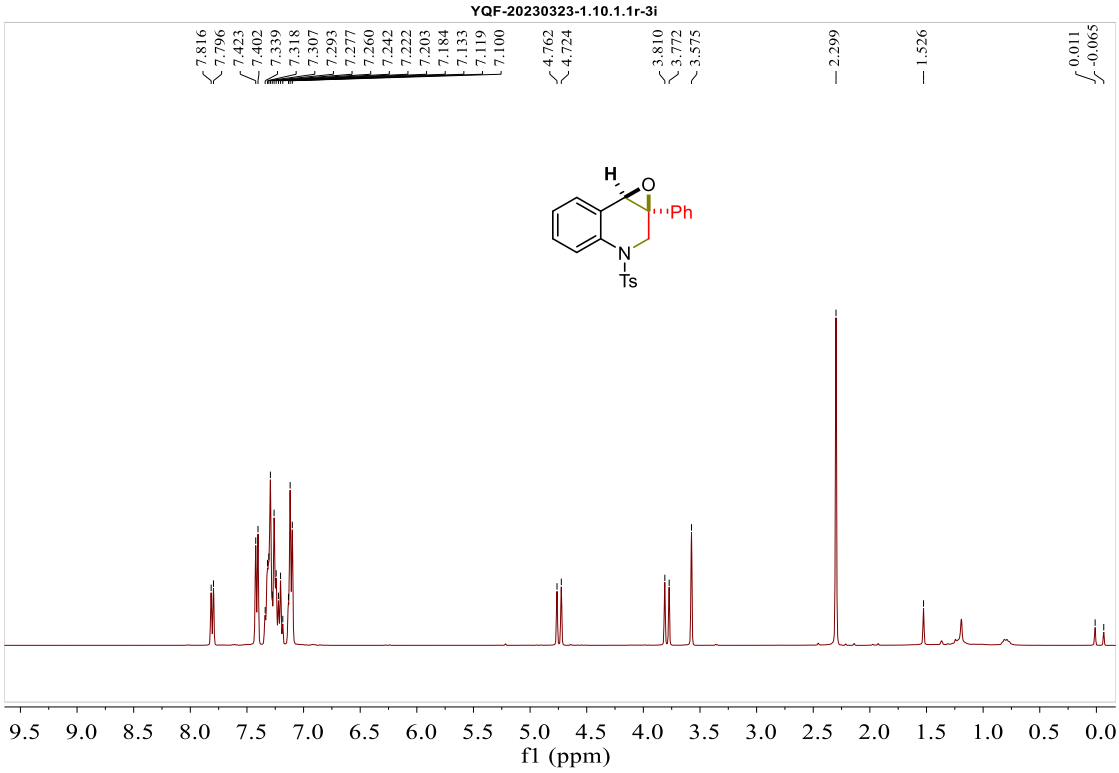
^{1}H NMR (400 MHz, $CDCl_3$) of **6p**



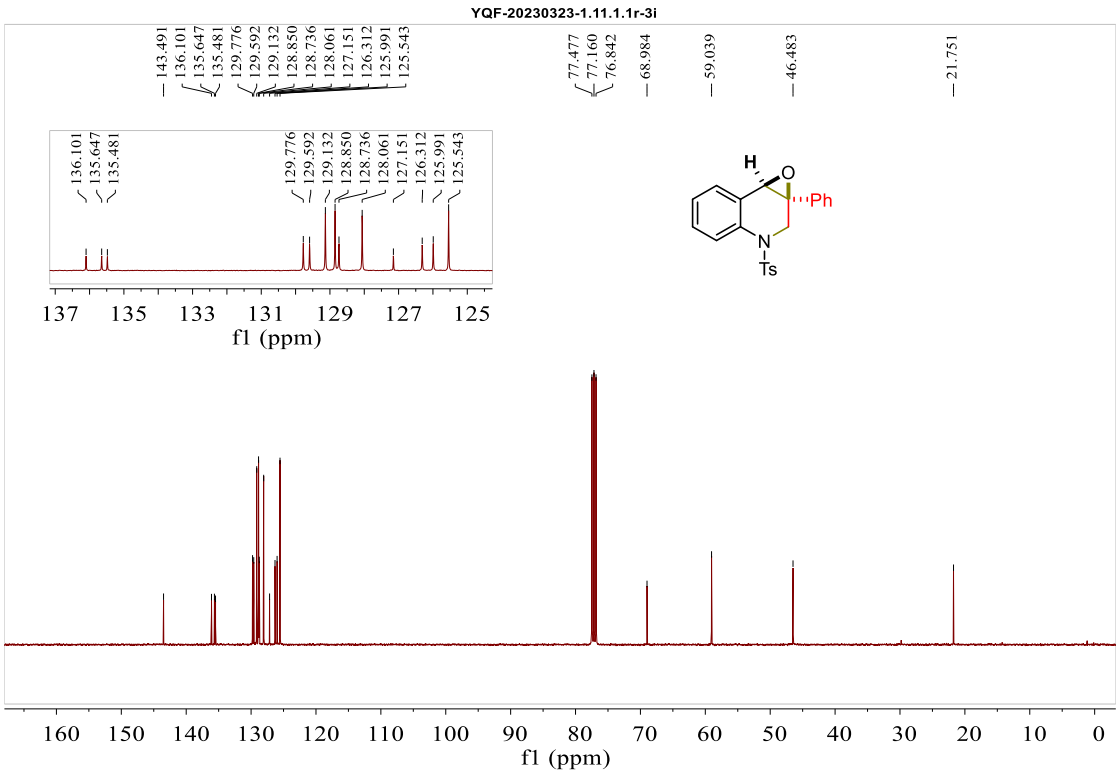
^{13}C NMR (101 MHz, $CDCl_3$) of **6p**



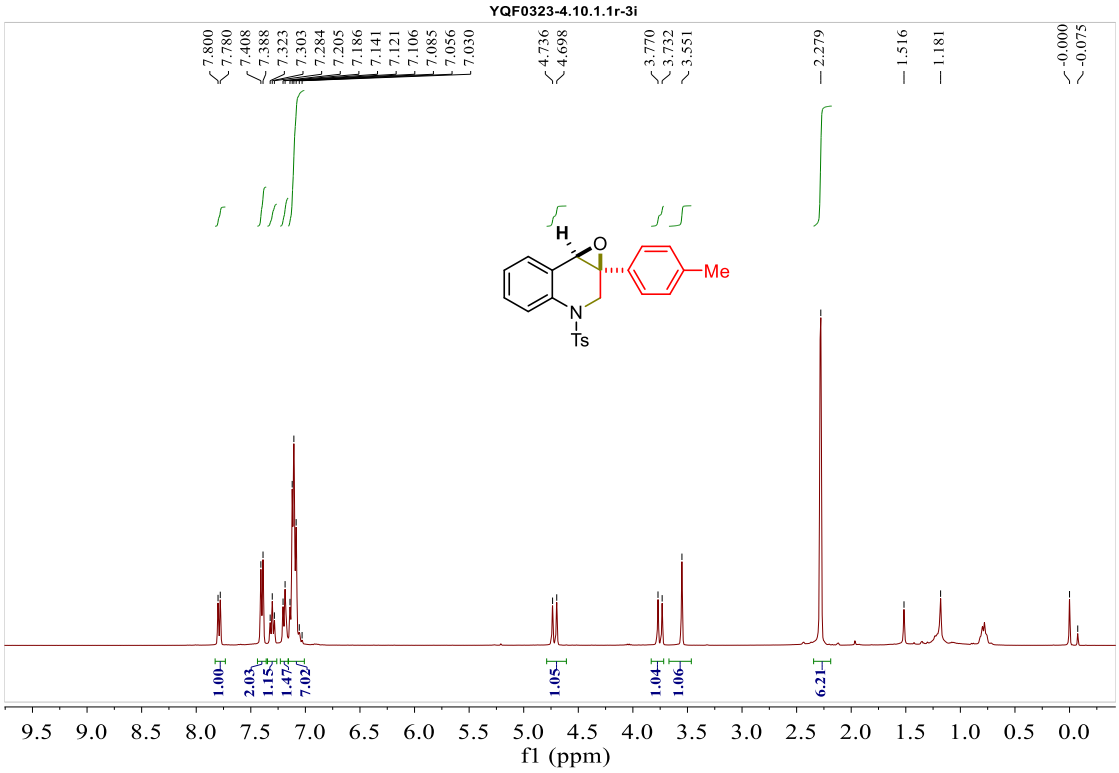
^{1}H NMR (400 MHz, $CDCl_3$) of **8a**



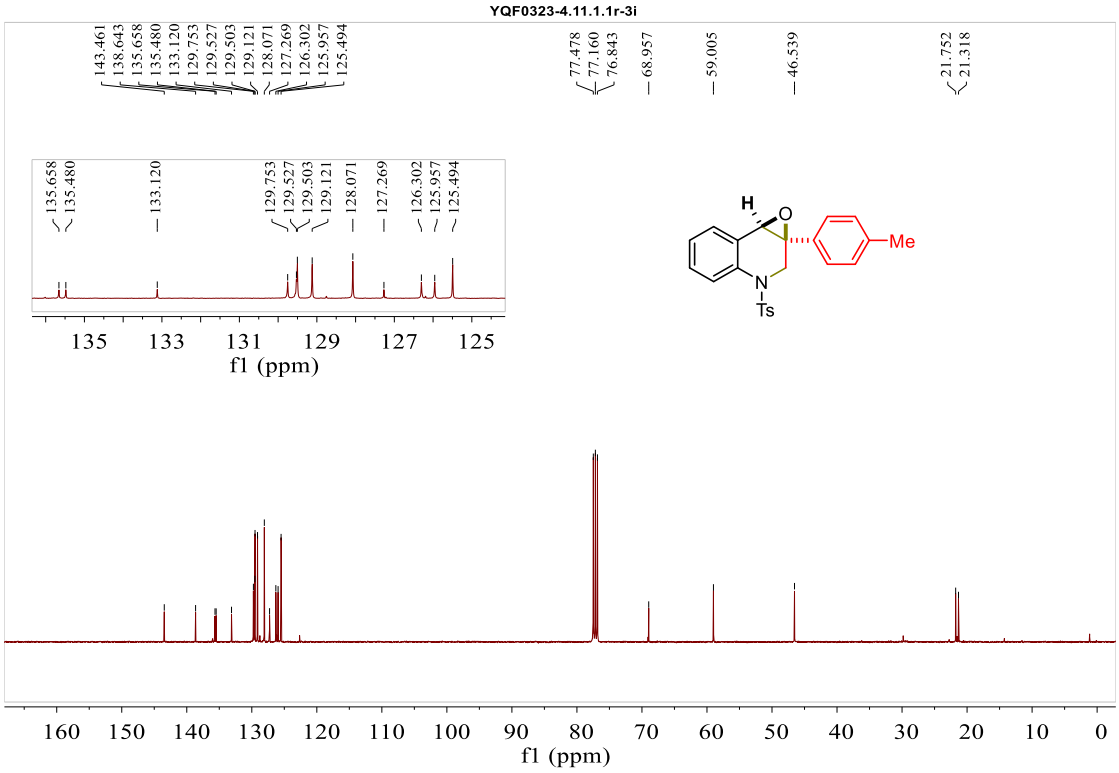
^{13}C NMR (101 MHz, $CDCl_3$) of **8a**



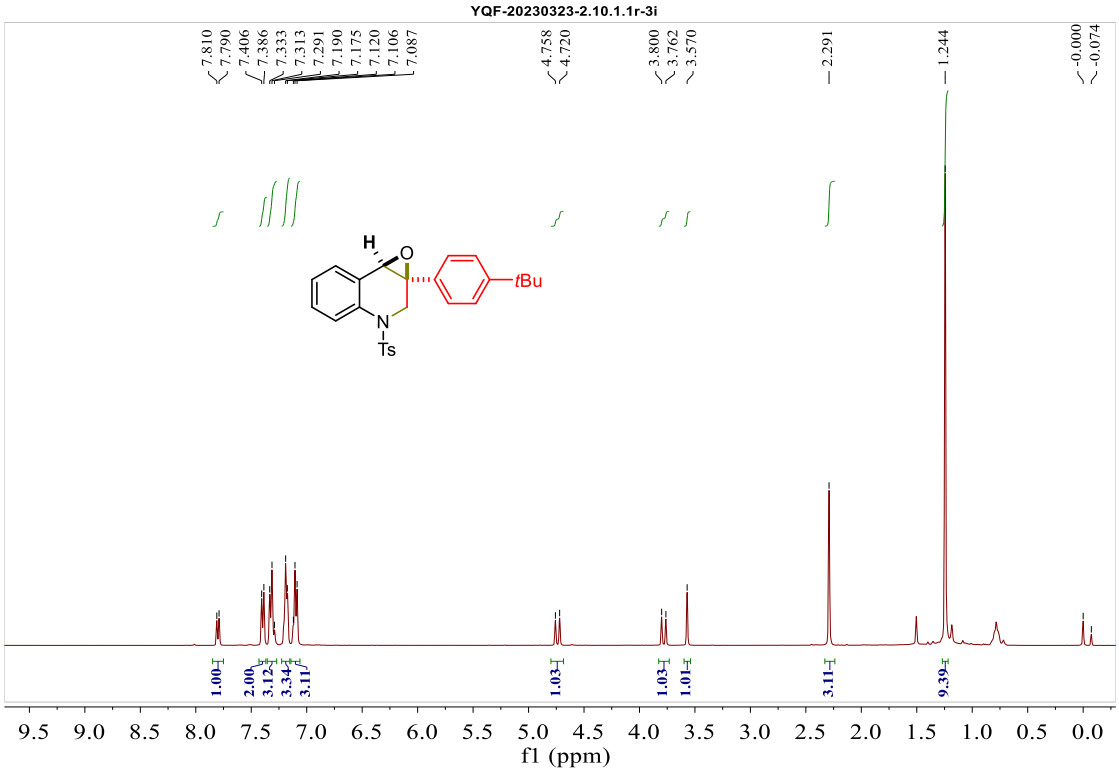
^{1}H NMR (400 MHz, $CDCl_3$) of **8b**



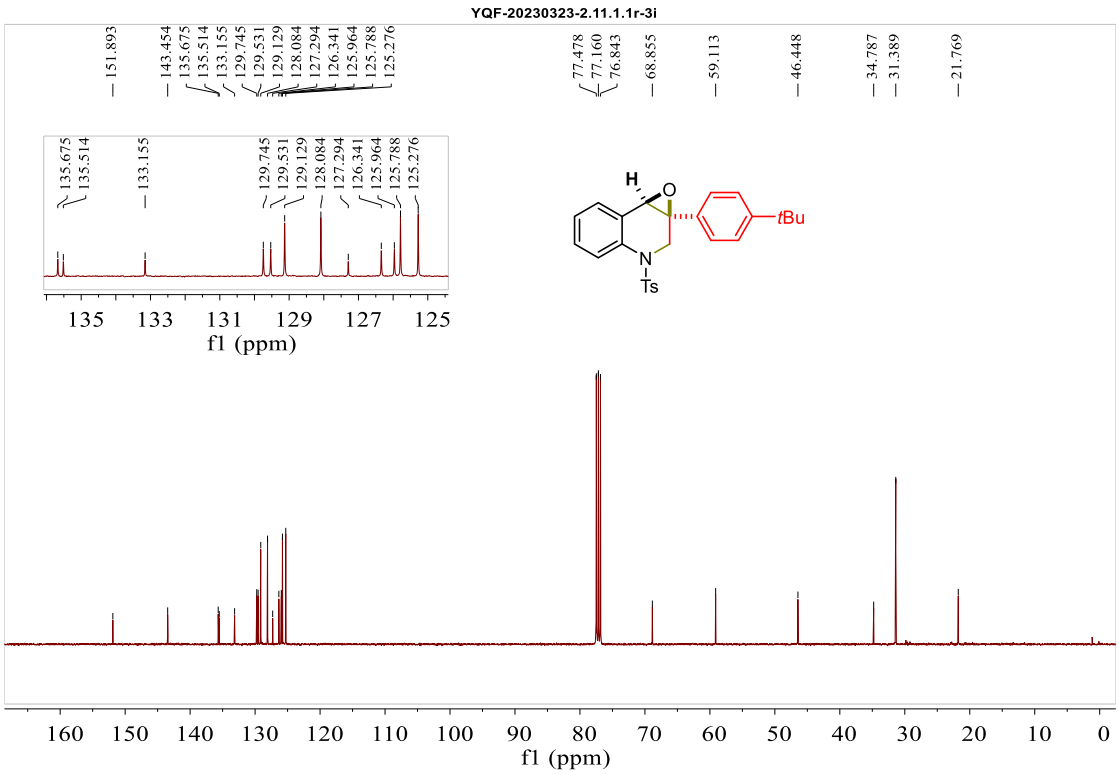
^{13}C NMR (101 MHz, $CDCl_3$) of **8b**



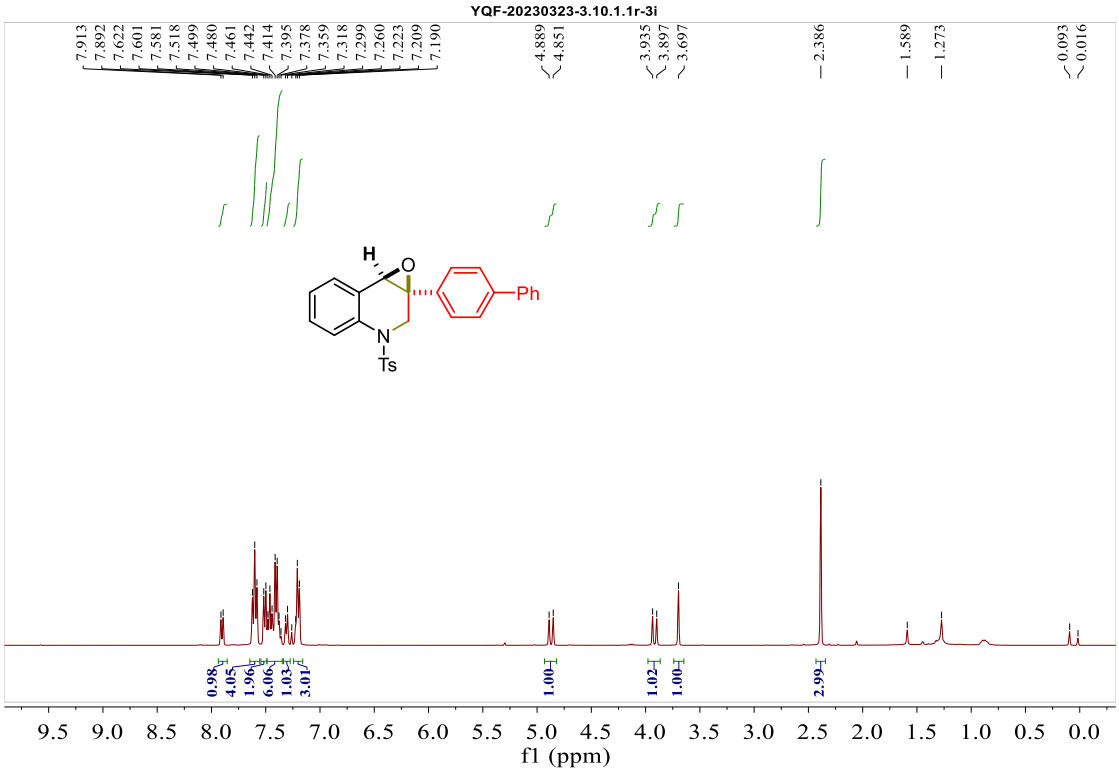
^{1}H NMR (400 MHz, $CDCl_3$) of **8c**



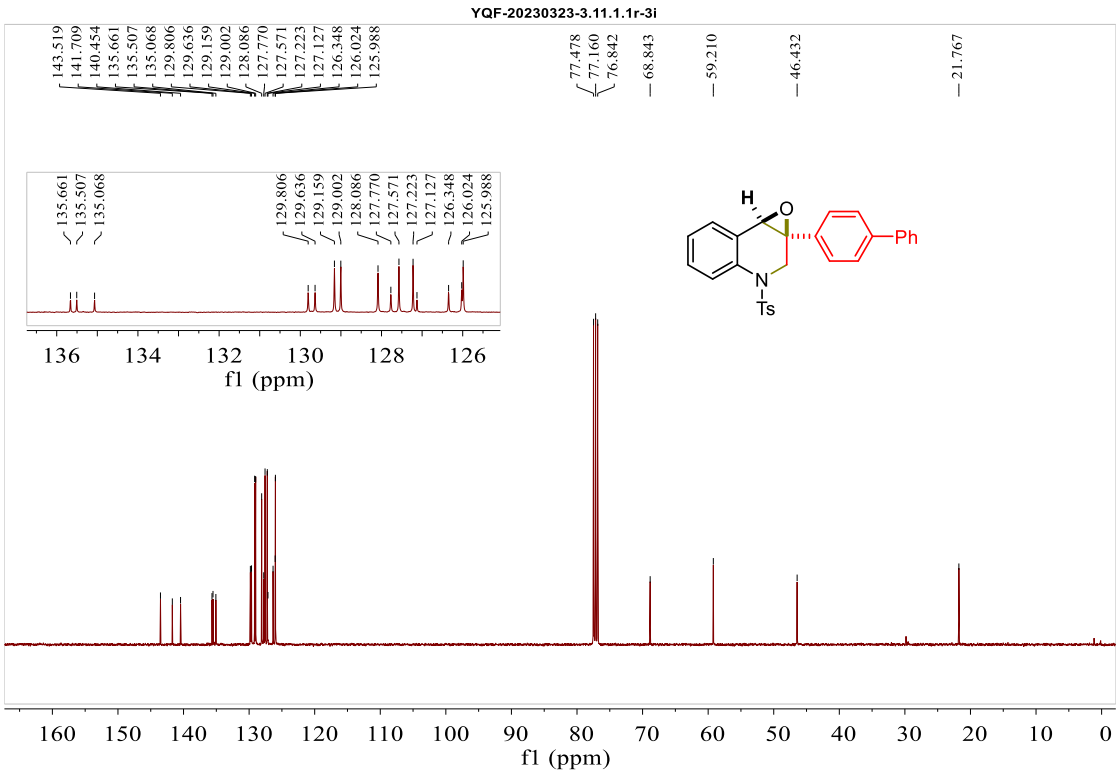
^{13}C NMR (101 MHz, $CDCl_3$) of **8c**



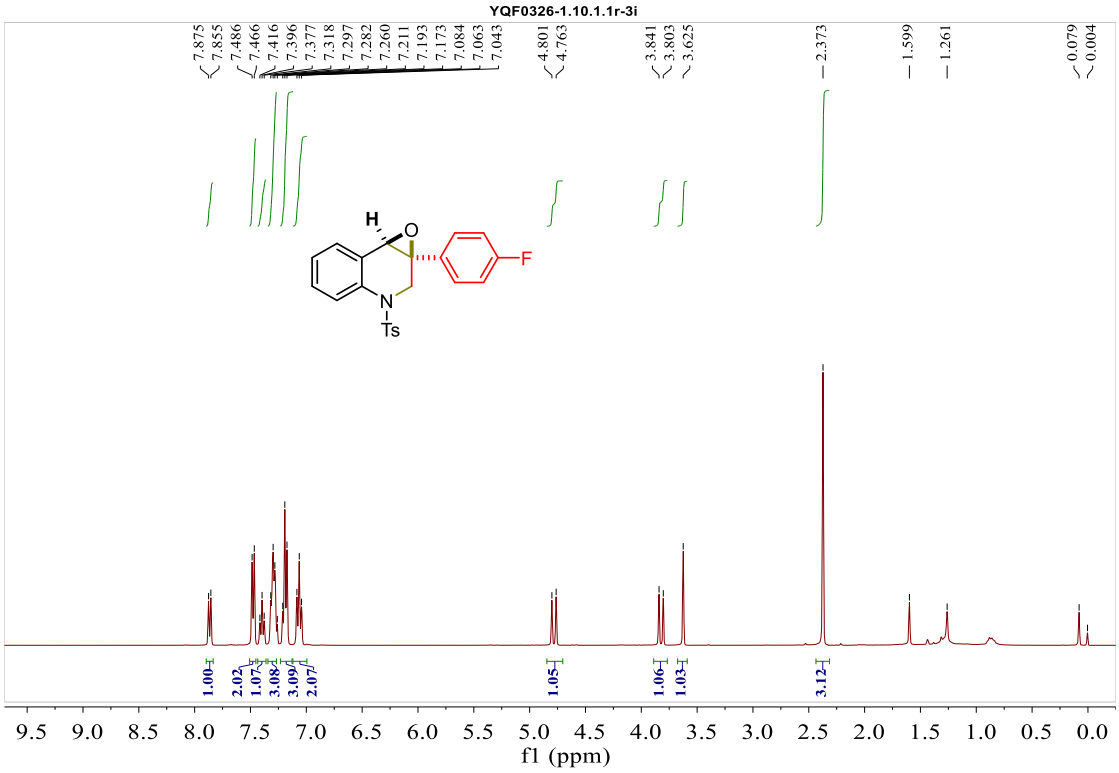
^{1}H NMR (400 MHz, $CDCl_3$) of **8d**



^{13}C NMR (101 MHz, $CDCl_3$) of **8d**



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



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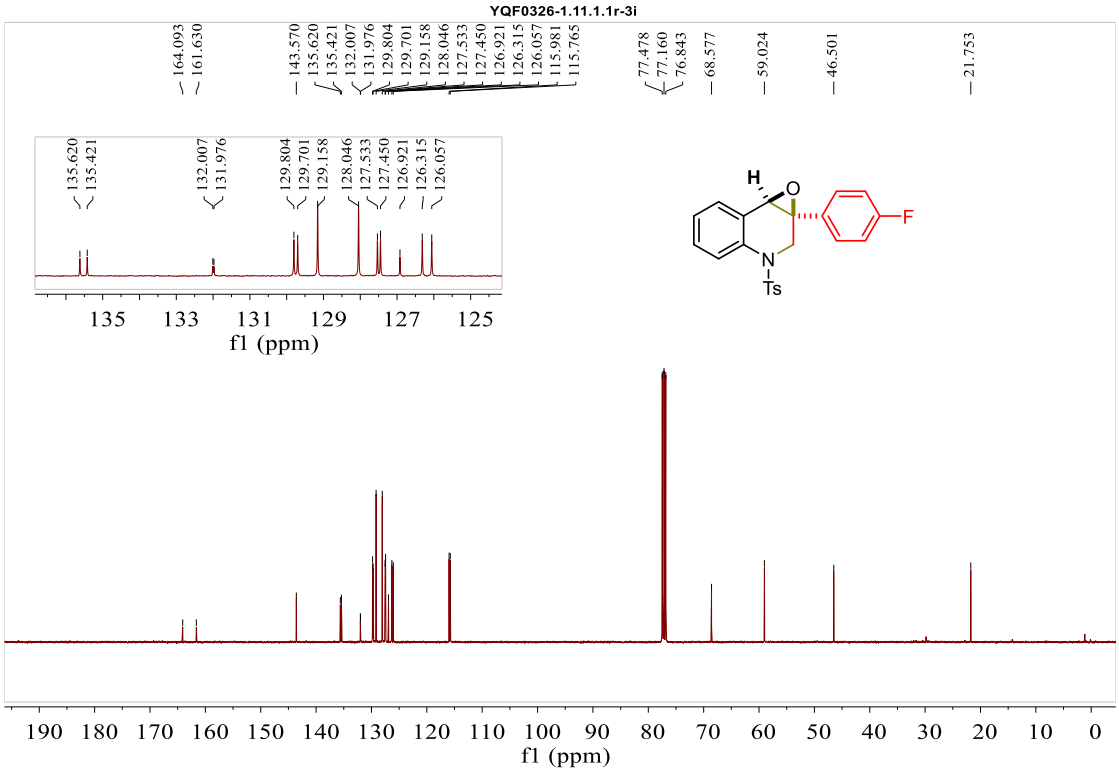
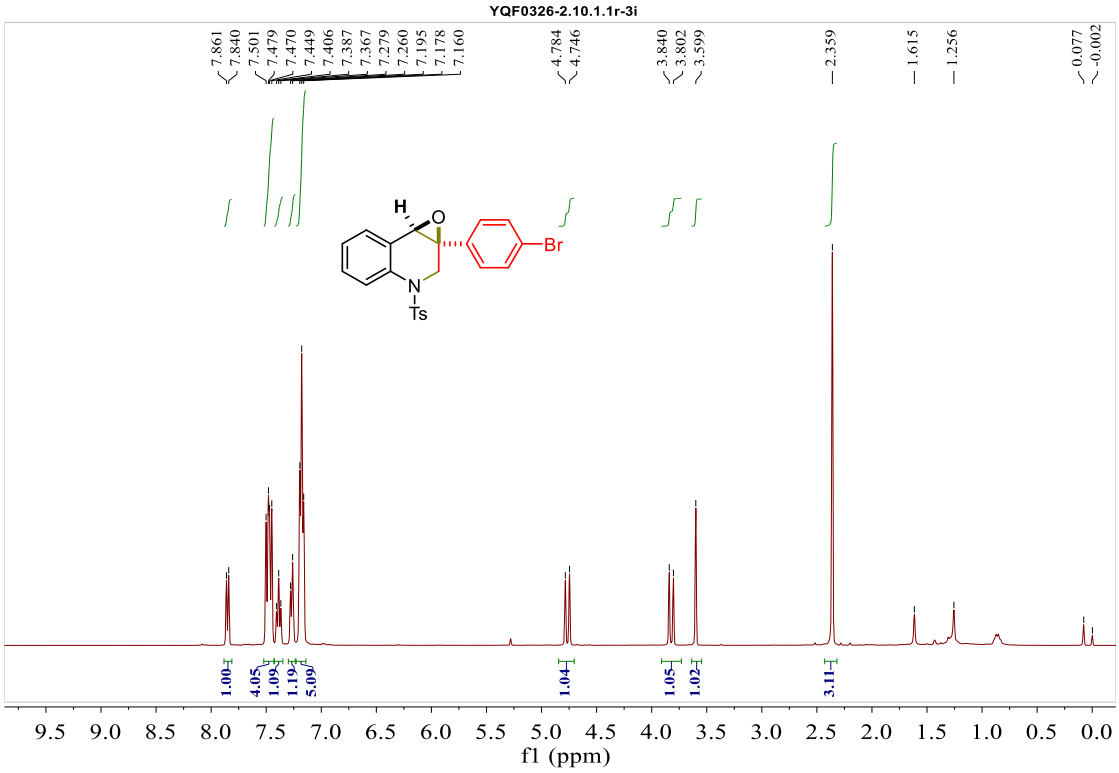
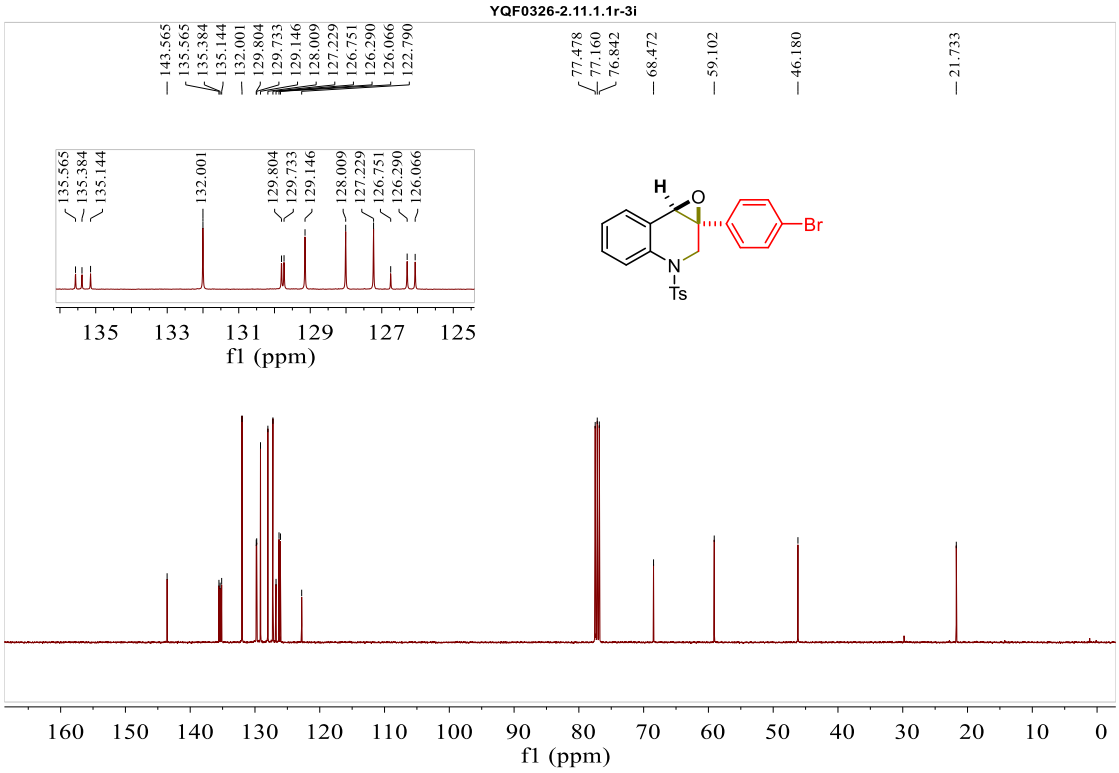


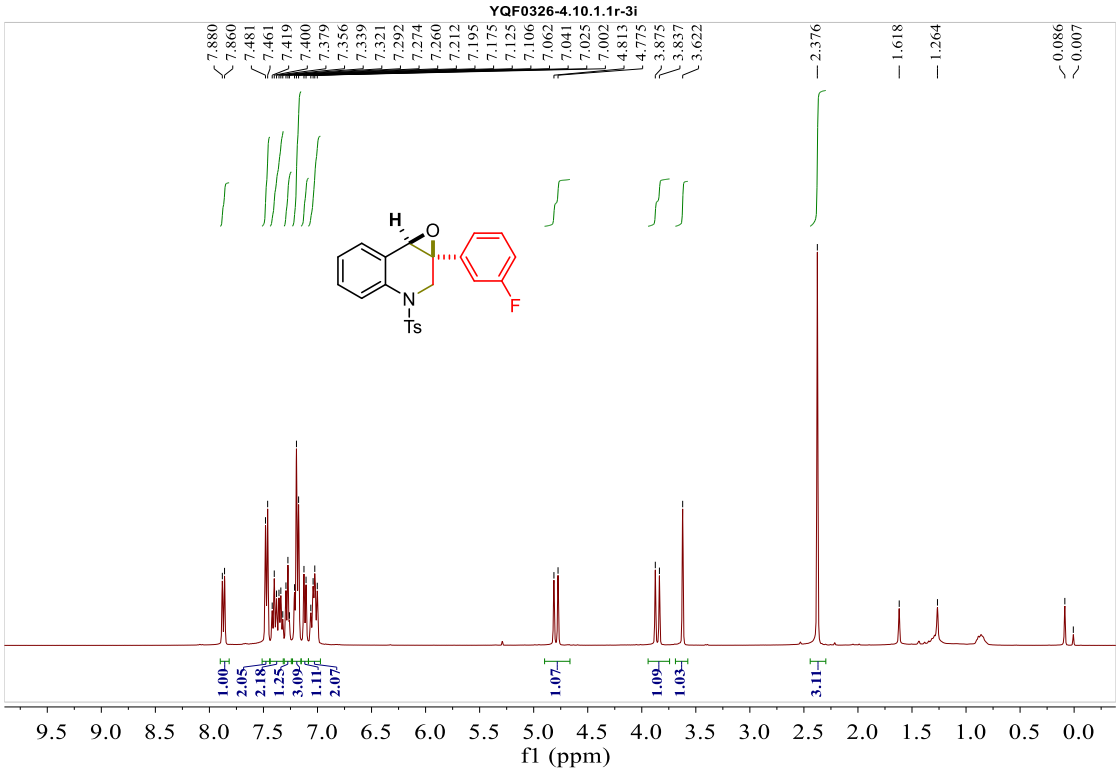
^{1}H NMR (400 MHz, $CDCl_3$) of **8f**



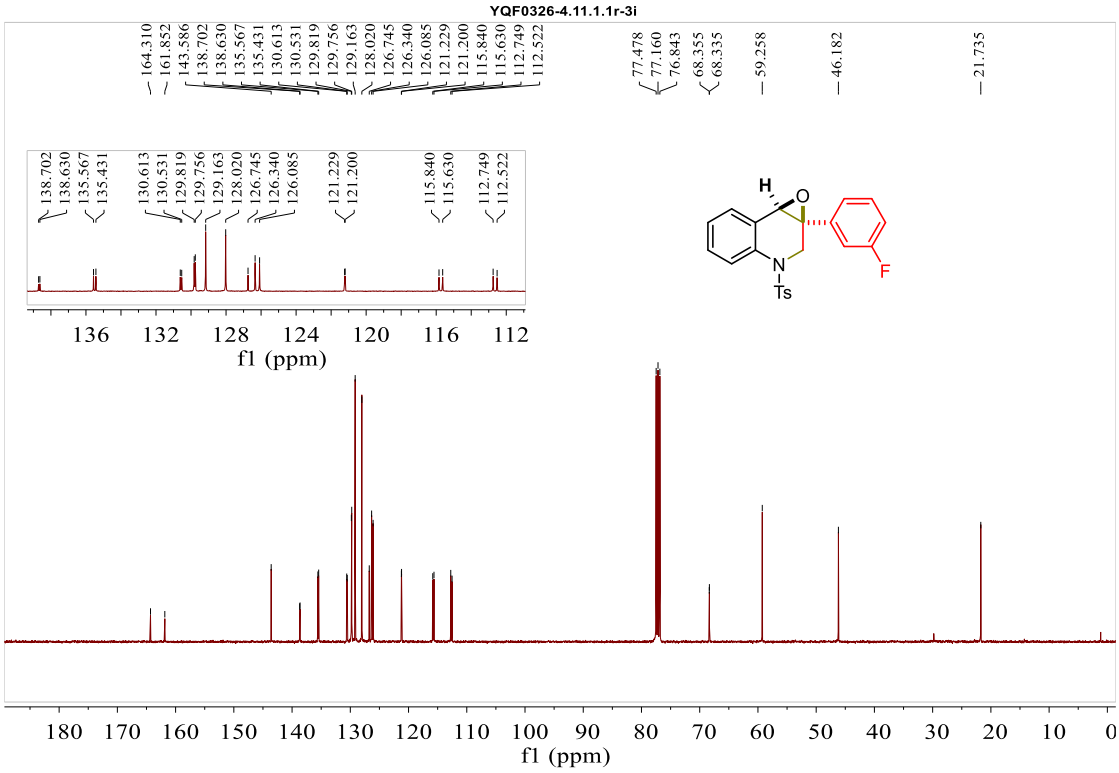
^{13}C NMR (101 MHz, $CDCl_3$) of **8f**



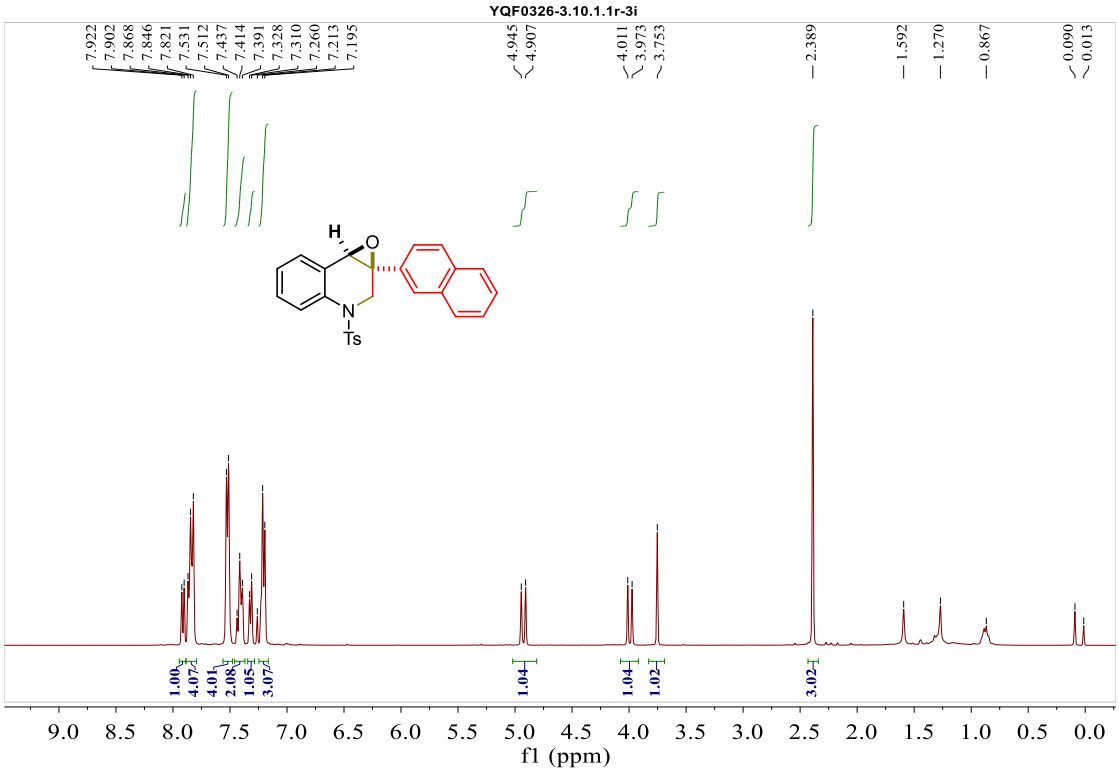
^{1}H NMR (400 MHz, $CDCl_3$) of **8g**



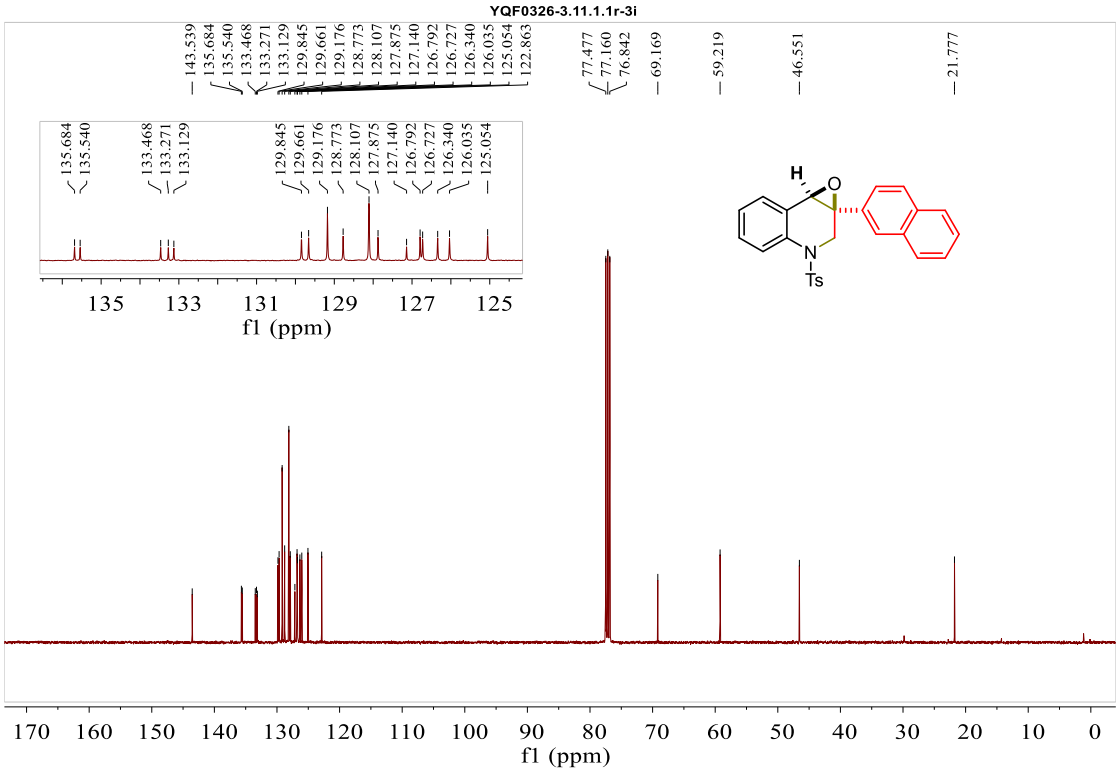
^{13}C NMR (101 MHz, $CDCl_3$) of **8g**



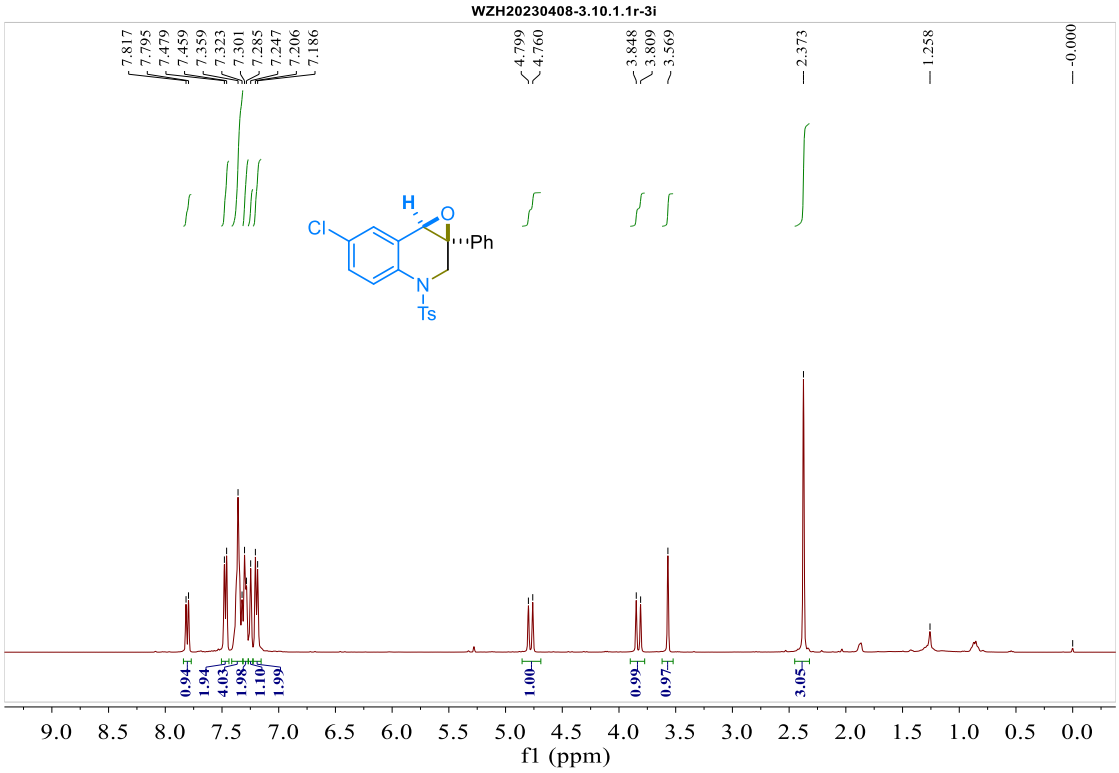
^{1}H NMR (400 MHz, $CDCl_3$) of **8h**



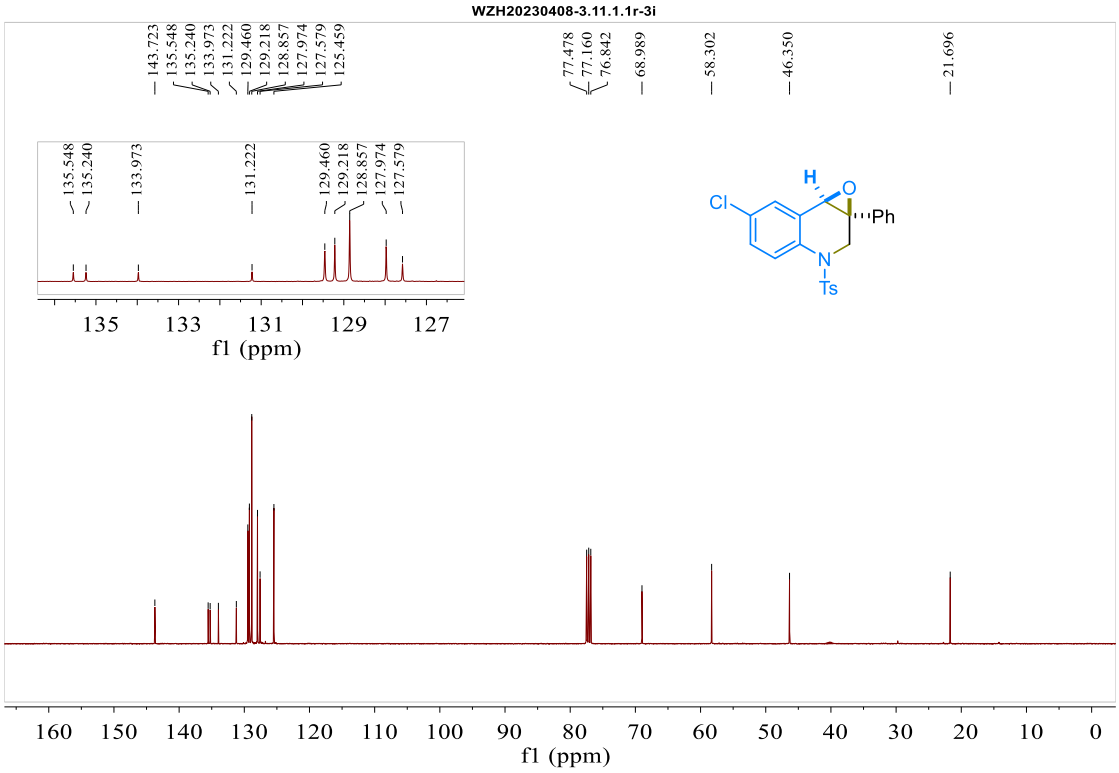
^{13}C NMR (101 MHz, $CDCl_3$) of **8h**



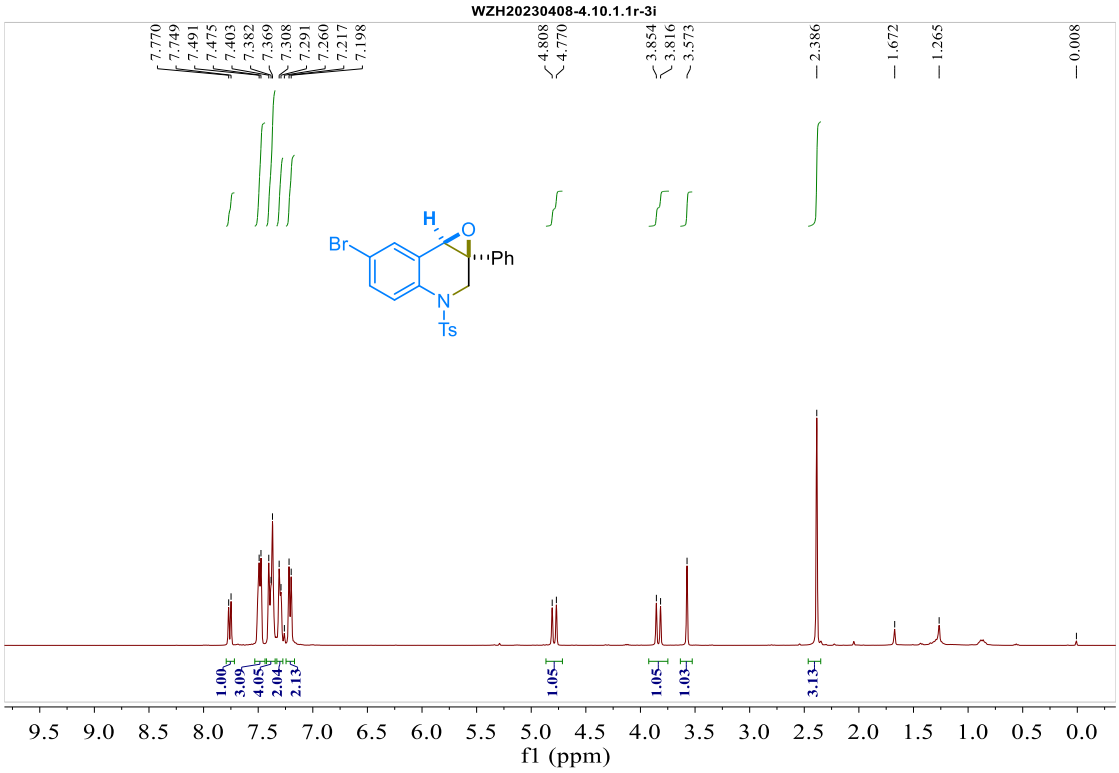
^{1}H NMR (400 MHz, $CDCl_3$) of **8i**



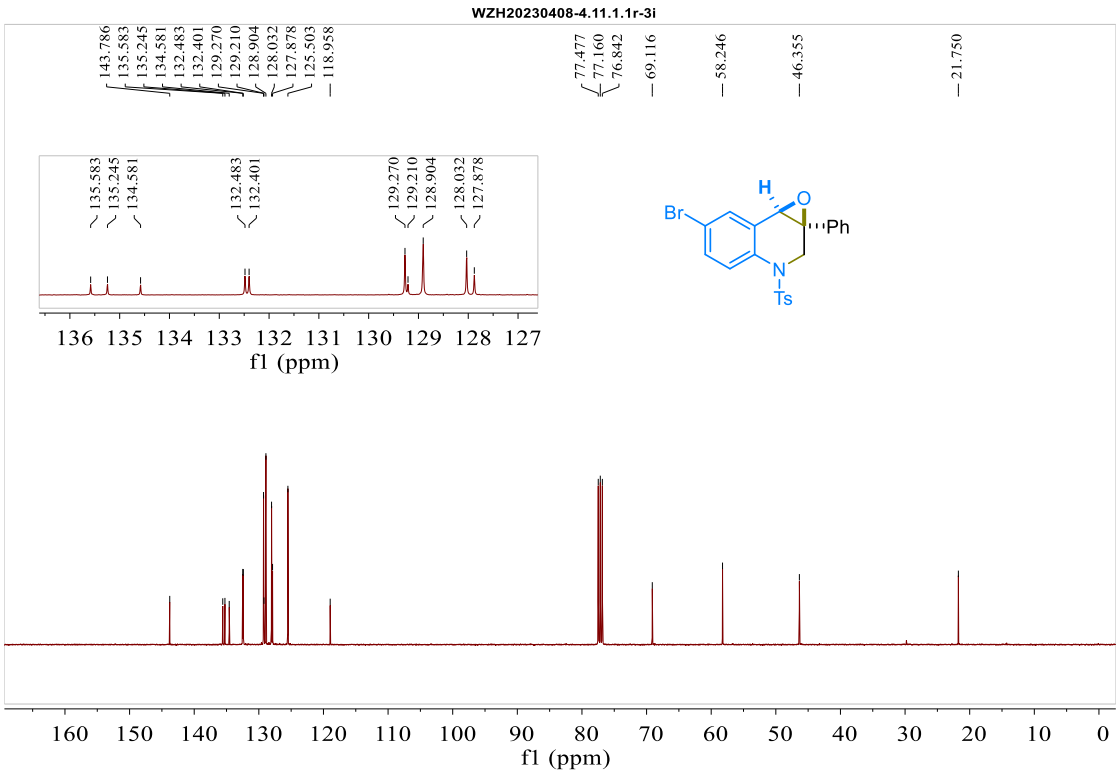
^{13}C NMR (101 MHz, $CDCl_3$) of **8i**



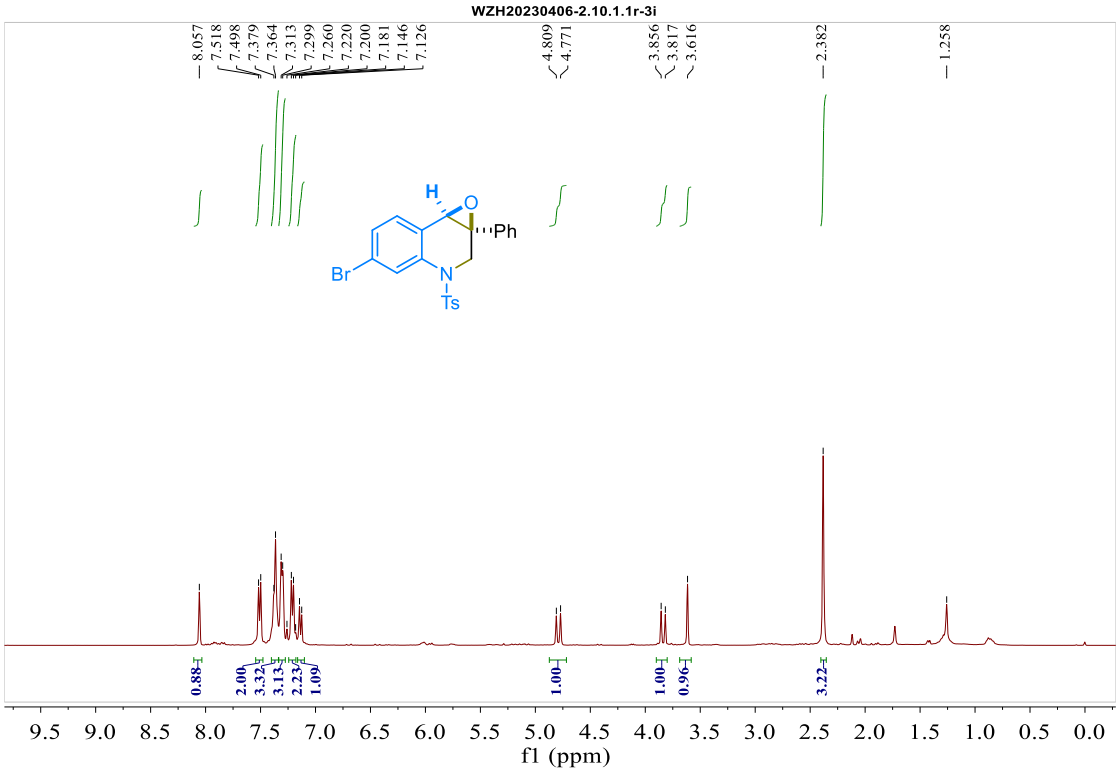
^{1}H NMR (400 MHz, $CDCl_3$) of **8j**



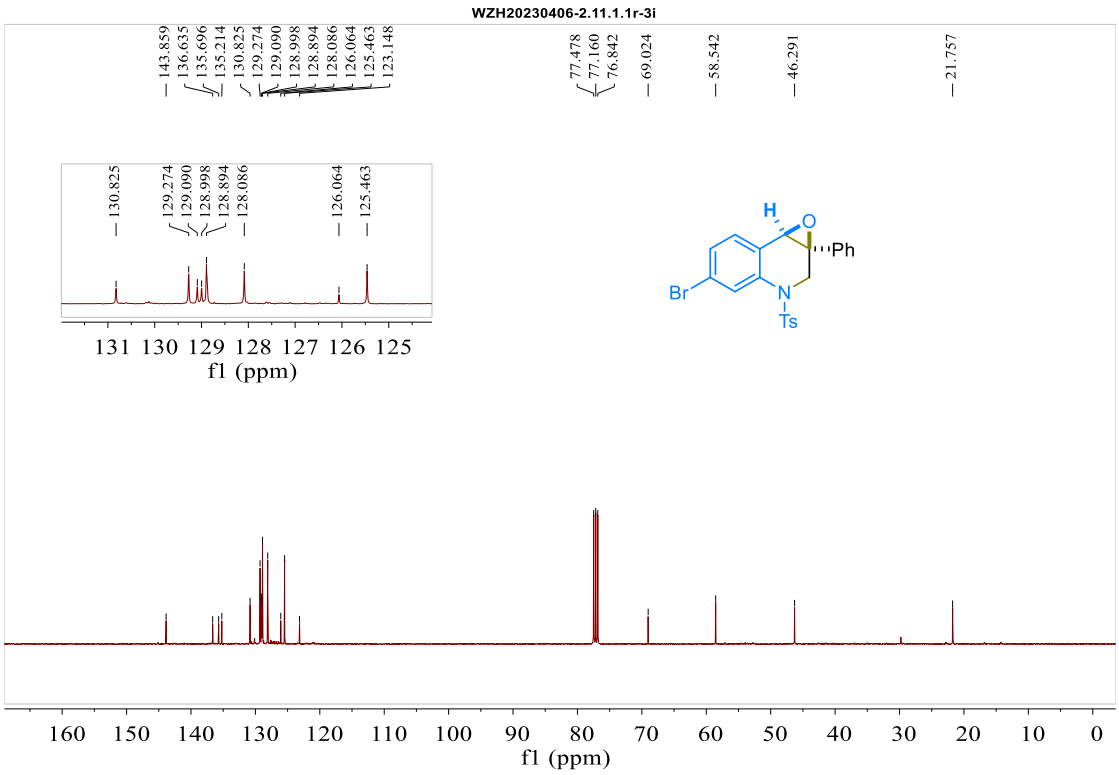
^{13}C NMR (101 MHz, $CDCl_3$) of **8j**



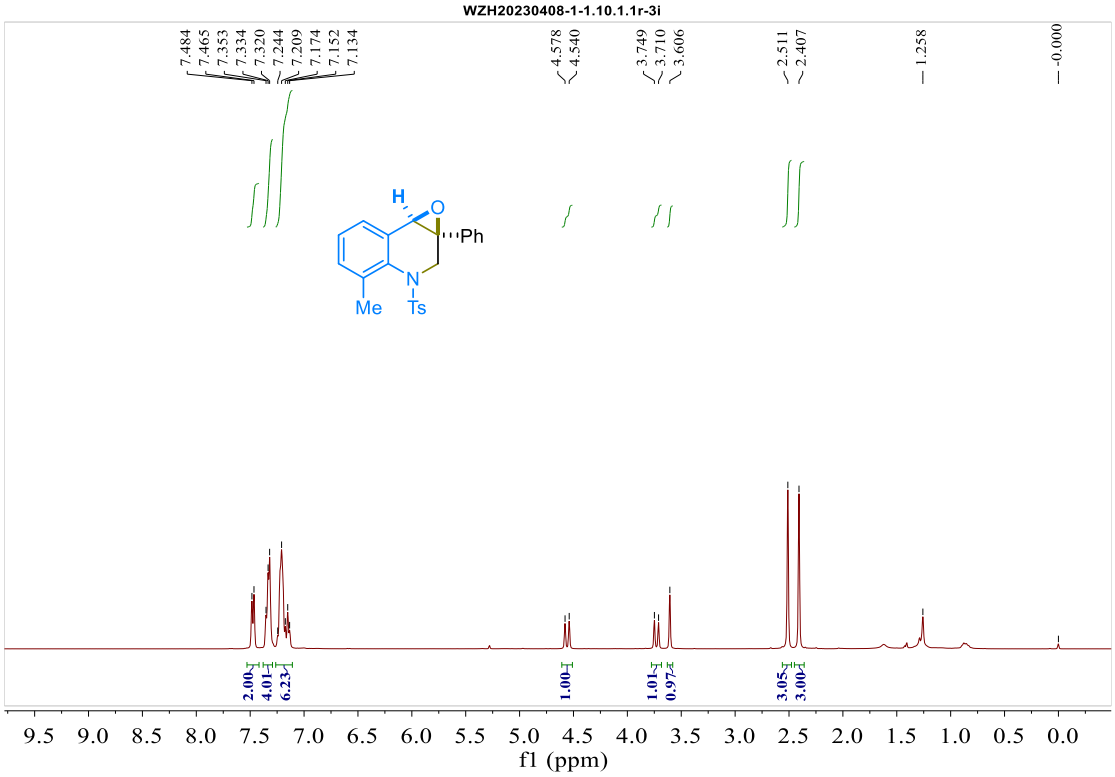
^{1}H NMR (400 MHz, $CDCl_3$) of **8k**



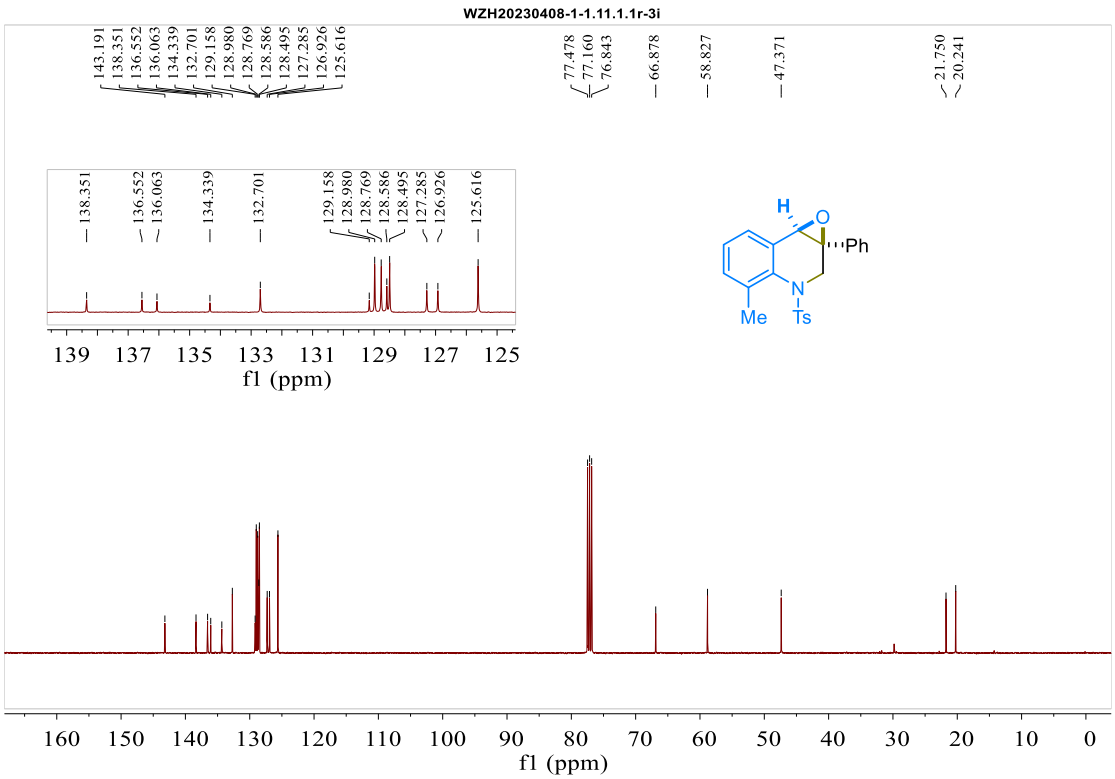
^{13}C NMR (101 MHz, $CDCl_3$) of **8k**



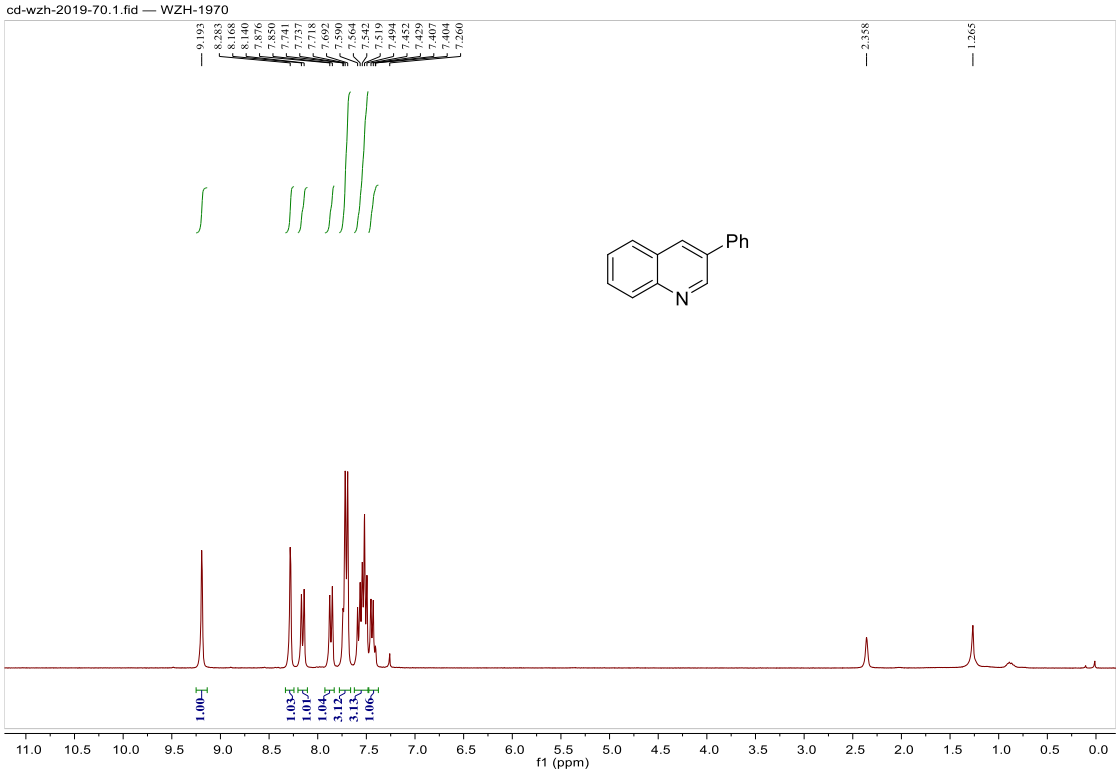
^{1}H NMR (400 MHz, $CDCl_3$) of **8l**



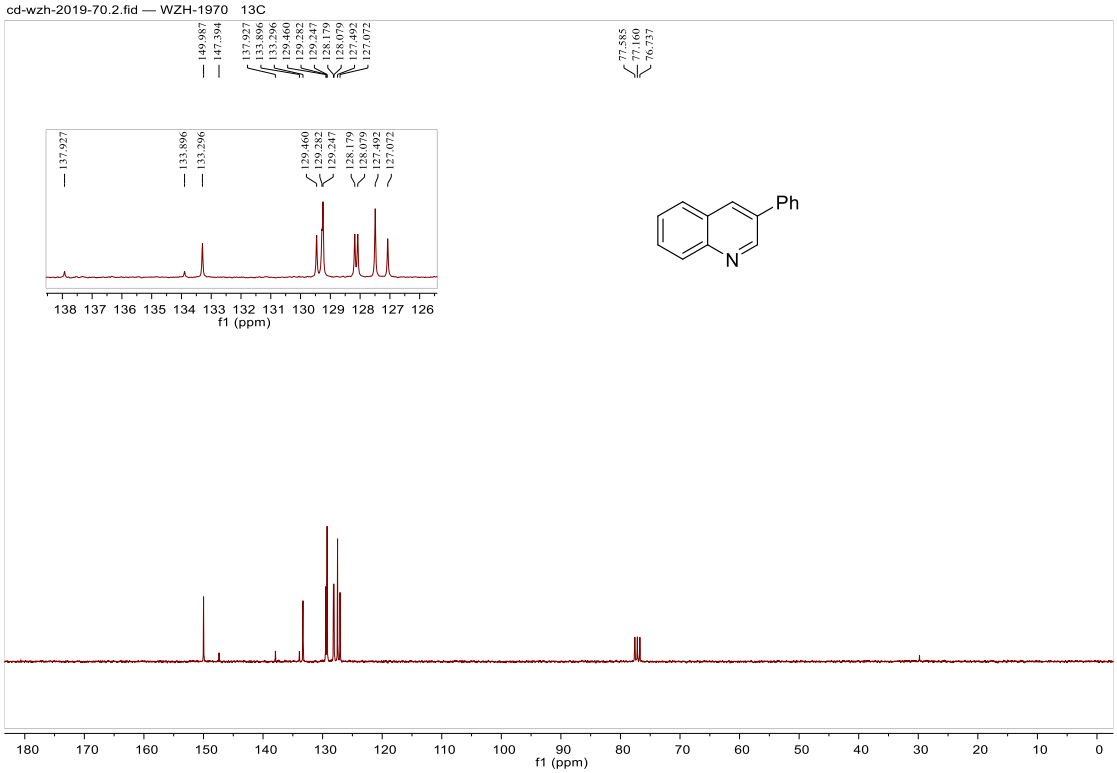
^{13}C NMR (101 MHz, $CDCl_3$) of **8l**



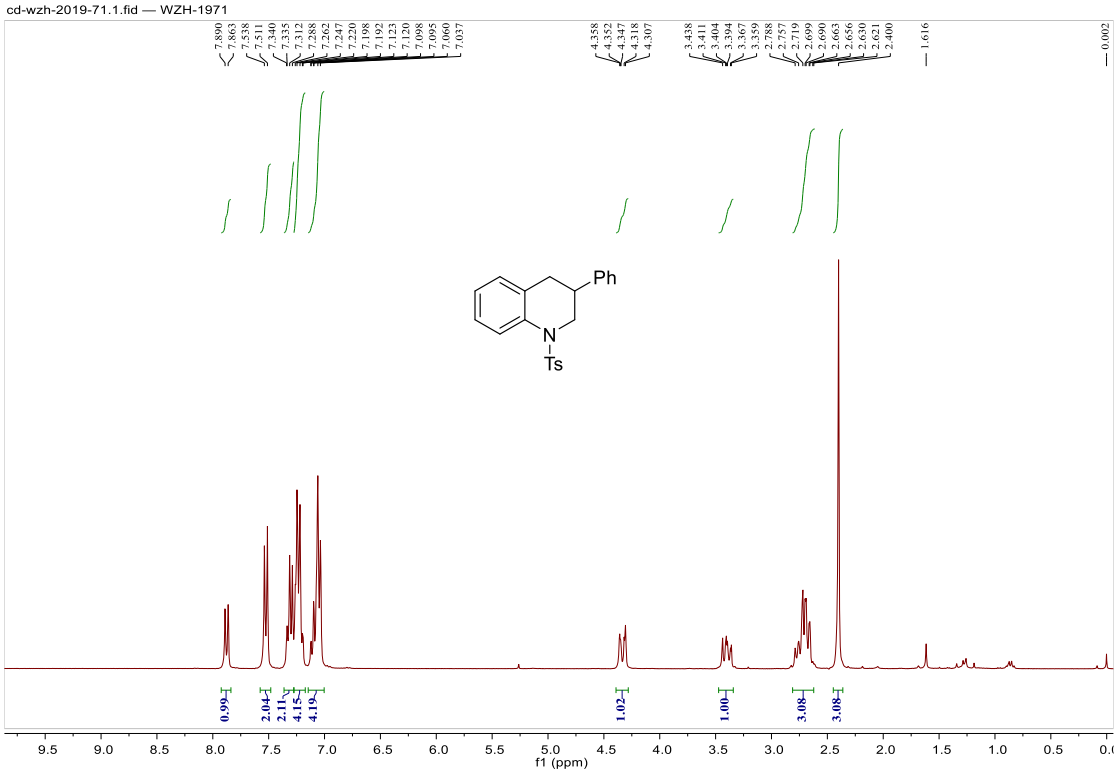
^{1}H NMR (300 MHz, $CDCl_3$) of **9**



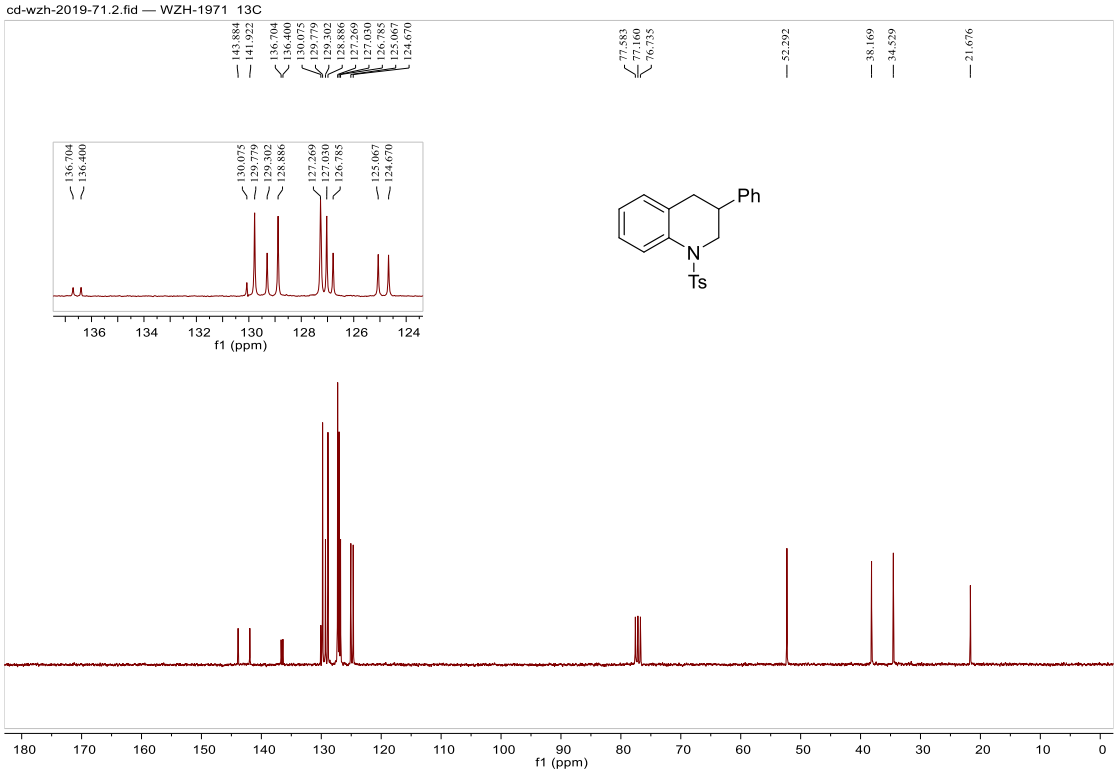
^{13}C NMR (75 MHz, $CDCl_3$) of **9**



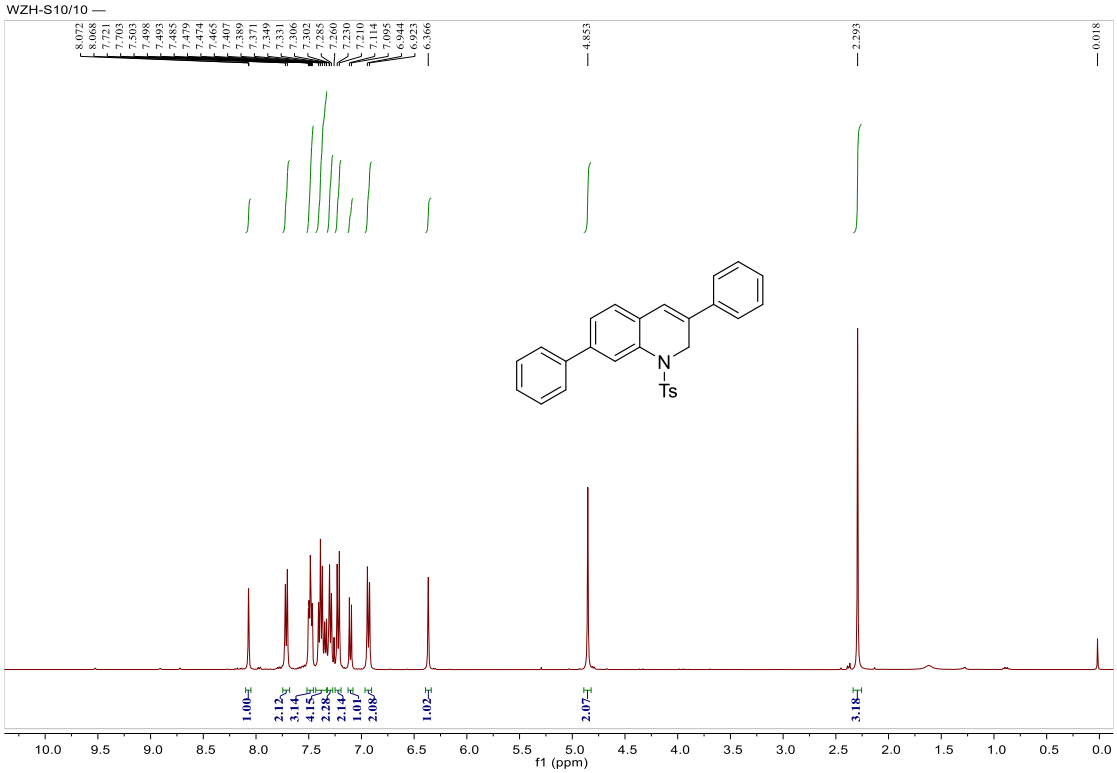
^{1}H NMR (300 MHz, $CDCl_3$) of **10**



^{13}C NMR (75 MHz, $CDCl_3$) of **10**



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



^{13}C NMR (101 MHz, $CDCl_3$) of **11**