Supporting Information

Catalytic Asymmetric de novo Construction of Dihydroquinazolinone Scaffolds via Enantioselective Decarboxylative [4+2] Cycloadditions

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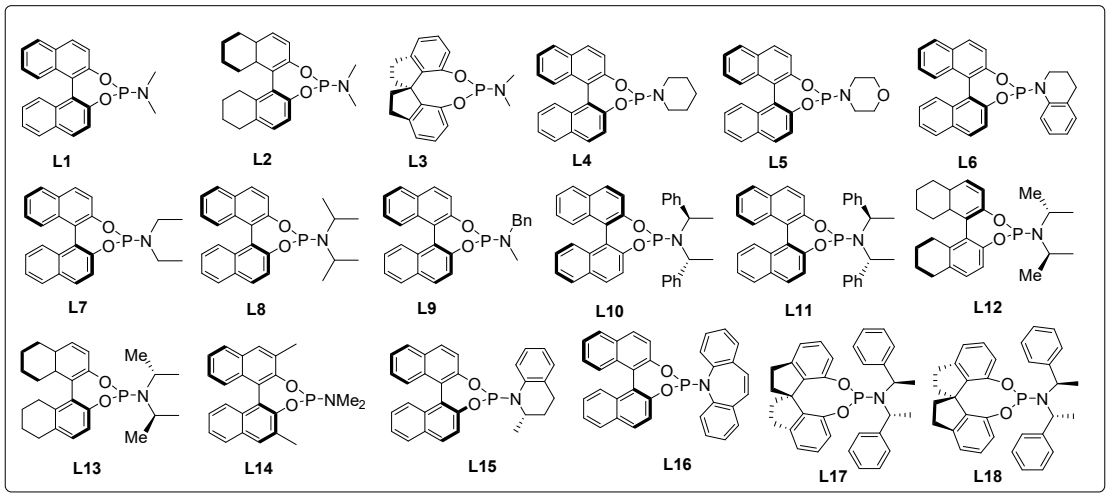
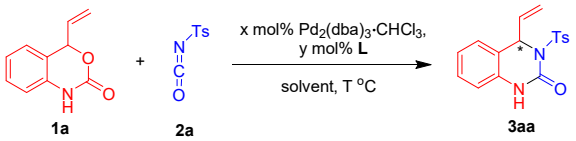
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Enantiomeric ratios (*er*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of Enantiomeric ratios by chiral HPLC were Chiralpak columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The X-ray source used for the single crystal X-ray diffraction analysis of compound **3ja** was MoKα (λ = 0.71073), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography were distilled before use. All starting materials commercially available were used directly. Substrates **1** were synthesized according to the literature method.[1]

2. Screening of ligands and condition optimization

Table 1. Screening of ligands and optimization of reaction conditions[a]





entry	L	solvent	1a:2a	x	y	T (°C)	yield (%)[b]	er[c]
1	**L1**	$PhCH_3$ (2mL)	1:1	3	8	30	38	72:28
2	**L2**	$PhCH_3$ (2mL)	1:1	3	8	30	38	80:20

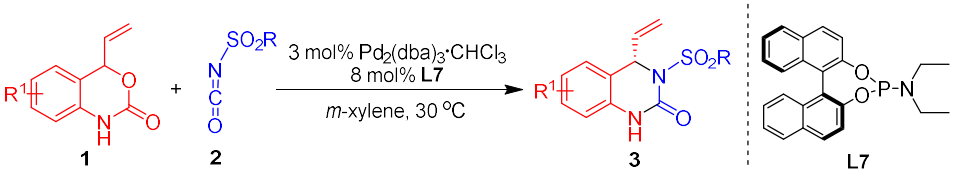
1. Mei, G.-J.; Bian, C.-Y.; Li, G.-H.; Xu, S.-L.; Zheng, W.-Q.; Shi, F. *Org. Lett.* **2017**, *19*, 3219.

3	**L3**	$PhCH_3$ (2mL)	1:1	3	8	30	69	57:43
4	**L4**	$PhCH_3$ (2mL)	1:1	3	8	30	49	76:24
5	**L5**	$PhCH_3$ (2mL)	1:1	3	8	30	33	60:40
6	**L6**	$PhCH_3$ (2mL)	1:1	3	8	30	62	66:34
7	**L7**	$PhCH_3$ (2mL)	1:1	3	8	30	48	92:8
8	**L8**	$PhCH_3$ (2mL)	1:1	3	8	30	23	56:44
9	**L9**	$PhCH_3$ (2mL)	1:1	3	8	30	26	58:42
10	**L10**	$PhCH_3$ (2mL)	1:1	3	8	30	99	52:48
11	**L11**	$PhCH_3$ (2mL)	1:1	3	8	30	35	77:23
12	**L12**	$PhCH_3$ (2mL)	1:1	3	8	30	33	58:42
13	**L13**	$PhCH_3$ (2mL)	1:1	3	8	30	59	77:23
14	**L14**	$PhCH_3$ (2mL)	1:1	3	8	30	56	40:60
15	**L15**	$PhCH_3$ (2mL)	1:1	3	8	30	22	49:51
16	**L16**	$PhCH_3$ (2mL)	1:1	3	8	30	18	65:35
17	**L17**	$PhCH_3$ (2mL)	1:1	3	8	30	9	70:30
18	**L18**	$PhCH_3$ (2mL)	1:1	3	8	30	10	36:64
19	**L7**	EtOAc (2mL)	1:1	3	8	30	7	79:21
20	**L7**	CH_3CN (2mL)	1:1	3	8	30	45	69:31
21	**L7**	THF (2mL)	1:1	3	8	30	16	79:21
22	**L7**	dichloromethane (2mL)	1:1	3	8	30	49	86:14
23	**L7**	acetone (2mL)	1:1	3	8	30	trace	-
24	**L7**	$PhCH_3$ (2mL)	1:2	3	8	30	57	93:7
25	**L7**	$PhCH_3$ (2mL)	1:3	3	8	30	69	94:6
26	**L7**	$PhCH_3$ (2mL)	1.2:1	3	8	30	75	90:10
27	**L7**	$PhCH_3$ (2mL)	2:1	3	8	30	45	88:12
28	**L7**	$PhCH_3$ (2mL)	3:1	3	8	30	21	92:8
29	**L7**	FPh (2mL)	1:3	3	8	30	90	92:8
30	**L7**	ClPh (2mL)	1:3	3	8	30	89	93:7
31	**L7**	BrPh (2mL)	1:3	3	8	30	85	91:9
32	**L7**	*o*-xylene (2mL)	1:3	3	8	30	92	95:5
33	**L7**	*m*-xylene (2mL)	1:3	3	8	30	98	96:4
34	**L7**	*p*-xylene (2mL)	1:3	3	8	30	74	93:7
35	**L7**	*m*-xylene (2mL)	1:3	3	8	50	61	94:6
36	**L7**	*m*-xylene (2mL)	1:3	3	8	40	65	93:7
37	**L7**	*m*-xylene (2mL)	1:3	3	8	20	60	94:6
38	**L7**	*m*-xylene (2mL)	1:3	3	8	10	54	93:7
39	**L7**	*m*-xylene (2mL)	1:3	3	8	0	30	93:7
40	**L7**	*m*-xylene (2mL)	1:3	3	8	-10	trace	-
41	**L7**	*m*-xylene (2mL)	1:3	3	8	-20	trace	-
42	**L7**	*m*-xylene (0.5mL)	1:3	3	8	30	66	92:8
43	**L7**	*m*-xylene (1mL)	1:3	3	8	30	90	93:7
44	**L7**	*m*-xylene (4mL)	1:3	3	8	30	69	94:6
45	**L7**	*m*-xylene (2mL)	1:3	3	10	30	92	93:7

46	**L7**	*m*-xylene (2mL)	1:3	3	15	30	83	93:7
47	**L7**	*m*-xylene (2mL)	1:3	3	20	30	92	93:7
48	**L7**	*m*-xylene (2mL)	1:3	5	8	30	61	92:8
49	**L7**	*m*-xylene (2mL)	1:3	1	3	30	97	94:6
50	**L7**	*m*-xylene (2mL)	1:3	2.5	7.5	30	93	93:7
51	**L7**	*m*-xylene (2mL)	1:3	5	15	30	90	93:7

[a] Unless otherwise indicated, the reaction was carried out at 0.1 mmol scale in a solvent for 12 h. [b] Isolated yield. [c] The *er* value was determined by HPLC.

3. General procedure for the synthesis of products 3



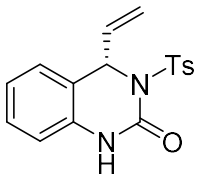
Under argon atmosphere, to the mixture of vinyl benzoxazinone **1** (0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2** (0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified by preparative thin layer chromatography to afford pure product **3**.

4. Characterization data of products 3

(*S*)-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3aa):

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (17.5 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3aa**

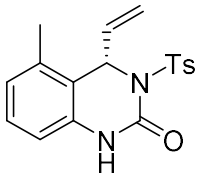
(32.2 mg) in 98% yield as yellow solid.



m.p. 59-60 °C; $[\alpha]_D^{20}$ = +56.3 (c 0.4, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.76 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (m, 2H), 7.10 – 7.05 (m, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.08 (d, *J* = 6.2 Hz, 1H), 5.86 (ddd, *J* = 16.4, 10.0, 6.1 Hz, 1H), 5.20 (d, *J* = 16.4 Hz, 1H), 5.14 (d, *J* = 9.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.1, 144.7, 136.3, 135.2, 134.5, 129.3, 129.2, 128.9, 126.3, 123.5, 121.1, 117.1, 117.0, 114.9, 114.8, 60.5, 21.7; IR (KBr): 3503, 2360, 1697, 1616, 1362, 1275, 1260, 1170, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{15}N_2O_3S$ 327.0804, Found 327.0802; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 21.570 min (major), t_R = 27.250 min (minor).

(*S*)-5-methyl-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ba) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1b** (18.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 40 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ba** (17.5 mg) in 51% yield as white solid.

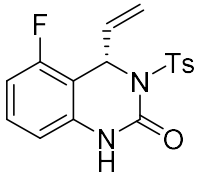


m.p. 94-95 °C; $[\alpha]_D^{20}$ = +26.0 (c 0.29, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.17 –

7.10 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.19 (d, *J* = 6.5 Hz, 1H), 5.82 (ddd, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.25 – 5.10 (m, 2H), 2.42 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.9, 144.7, 136.4, 134.8, 134.7, 133.1, 129.3, 129.2, 128.7, 125.4, 119.7, 117.7, 112.7, 57.5, 21.7, 18.4; IR (KBr): 3157, 2359, 1692, 1636, 1558, 1399, 1275, 1111, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0960, Found 341.0978; Enantiomeric ratio: 99:1, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.647 min (major), t_R = 20.690 min (minor).

(*S*)-5-fluoro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ca):

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1c** (19.3 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ca** (27.0 mg) in 78% yield as white solid.

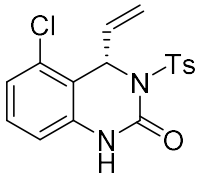


m.p. 138-139 °C; $[\alpha]_D^{20}$ = +37.4 (c 0.54, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.41 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.16 (m, 1H), 6.83 – 6.77 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 6.3 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.4 (d, *J* = 246 Hz), 150.5, 144.9, 136.2 (d, *J* = 6.3 Hz), 136.1, 133.4, 130.2 (d, *J* = 9.3 Hz), 129.4, 129.2, 117.6, 110.3 (d, *J* =

20.6 Hz), 110.2 (d, J = 3.4 Hz), 109.4 (d, J = 20.3 Hz), 54.9 (d, J = 2.4 Hz), 21.7; IR (KBr): 3446, 2359, 1716, 1697, 1635, 1558, 1362, 1275, 1170, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{17}H_{14}FN_2O_3S$ 345.0709, Found 345.0711; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 9.130 min (major), t_R = 10.853 min (minor).

(*S*)-5-chloro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3da):

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1d** (20.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^oC for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3da** (16.3 mg) in 45% yield as white solid.

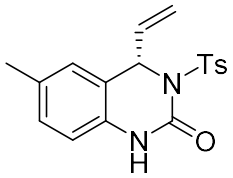


m.p. 167-168 ^oC; $[\alpha]_D^{20}$ = +30.0 (c 0.21, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.90 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.21 – 7.16 (m, 1H), 7.11 (d, J = 7.4 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 6.42 (d, J = 5.9 Hz, 1H), 5.82 (ddd, J = 16.6, 10.2, 6.1 Hz, 1H), 5.25 (d, J = 18.3 Hz, 1H), 5.20 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.1, 144.9, 136.1, 136.0, 132.2, 131.6, 129.8, 129.3, 129.2, 124.2, 119.5, 117.9, 113.5, 57.7, 21.7; IR (KBr): 3446, 3005, 2359, 1716, 1636, 1521, 1275, 749, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{17}H_{14}ClN_2O_3S$ 361.0414, Found 361.0431; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak IC,

hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.867 min (major), t_R = 11.647 min (minor).

(*S*)-6-methyl-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ea) :

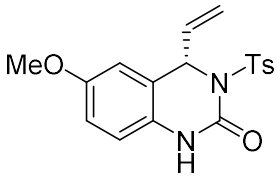
Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1e** (18.9 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ea** (28.4 mg) in 83% yield as white solid.



m.p. 55-56 °C; $[\alpha]_D^{20}$ = +26.9 (c 0.32, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.08 – 6.98 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.13 (d, *J* = 9.6 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.7, 144.6, 136.4, 135.3, 133.2, 132.0, 129.5, 129.3, 129.1, 126.7, 121.1, 116.9, 114.6, 60.6, 21.7, 20.8; IR (KBr): 3447, 2359, 1696, 1576, 1507, 1362, 1260, 1169, 1111, 749, 669 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0960, Found 341.0972; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.820 min (major), t_R = 25.470 min (minor).

(*S*)-6-methoxy-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3fa) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1f** (20.5 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3fa** (30.4 mg) in 85% yield as white solid.

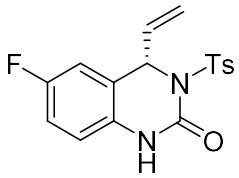


m.p. 154-155 °C; $[\alpha]_D^{20}$ = +9.3 (c 0.49, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.83 – 6.72 (m, 2H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.03 (d, *J* = 6.2 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.9, 150.6, 144.7, 136.4, 134.9, 129.3, 129.1, 128.0, 122.3, 117.2, 115.7, 114.6, 111.5, 60.6, 55.7, 21.7; IR (KBr): 3447, 3005, 2360, 1716, 1684, 1558, 1507, 1275, 1169, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{18}H_{17}N_2O_4S$ 357.0909, Found 357.0908; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 20.700 min (major), t_R = 30.530 min (minor).

(*S*)-6-fluoro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ga) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1g** (19.3 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2

mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ga** (31.5 mg) in 91% yield as white solid.

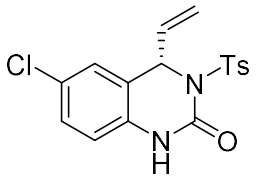


m.p. 173-174 °C; $[\alpha]_D^{20}$ = +44.5 (c 0.33, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.89 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.01 – 6.91 (m, 2H), 6.76 – 6.65 (m, 1H), 6.04 (d, *J* = 6.4 Hz, 1H), 5.83 (ddd, *J* = 16.7, 10.1, 6.3 Hz, 1H), 5.27 – 5.10 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 158.8 (d, *J* = 242.1 Hz), 150.9, 144.9, 136.2, 134.5, 130.8 (d, *J* = 2.5 Hz), 129.3, 129.2, 122.7 (d, *J* = 7.5 Hz), 117.6, 116.1 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 22.3 Hz), 113.3 (d, *J* = 23.8 Hz), 60.2 (d, *J* = 1.7Hz), 21.7; IR (KBr): 3446, 3005, 2359, 1716, 1683, 1558, 1507, 1275, 764, 749, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{14}FN_2O_3S$ 345.0709, Found 345.0719; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.623 min (major), t_R = 17.680 min (minor).

(*S*)-6-chloro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ha) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1h** (20.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ha**

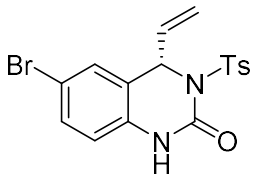
(34.8 mg) in 96% yield as white solid.



m.p. 101-102 °C; $[\alpha]_D^{20}$ = +16.3 (c 0.48, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.74 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.04 (d, *J* = 6.4 Hz, 1H), 5.82 (ddd, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.25 – 5.15 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.7, 145.0, 136.1, 134.5, 133.2, 129.3, 129.2, 129.0, 128.6, 126.3, 122.7, 117.7, 116.0, 60.1, 21.7; IR (KBr): 2988, 1696, 1597, 1359, 1275, 1260, 1187, 1005, 764, 750, 672 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{14}ClN_2O_3S$ 361.0414, Found 361.0418; Enantiomeric ratio: 94:6, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.050 min (major), t_R = 17.237 min (minor).

(*S*)-6-bromo-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ia) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1i** (25.3 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ia** (37.4 mg) in 92% yield as white solid.

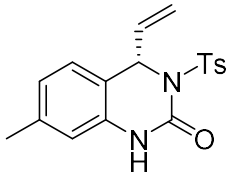


m.p. 175-176 °C; $[\alpha]_D^{20}$ = +9.6 (c 0.58, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.61 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.33 (m,

2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.03 (d, *J* = 6.4 Hz, 1H), 5.82 (ddd, *J* = 16.6, 10.1, 6.4 Hz, 1H), 5.26 – 5.14 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.6, 145.0, 136.0, 134.5, 133.7, 131.9, 129.3, 129.2, 129.1, 123.1, 117.7, 116.4, 115.9, 60.0, 21.7; IR (KBr): 3446, 2360, 1697, 1521, 1472, 1275, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{17}H_{14}BrN_2O_3S$ 404.9909, Found 404.9917; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 14.957 min (major), t_R = 17.403 min (minor).

(*S*)-7-methyl-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ja) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1j** (18.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ja** (33.6 mg) in 98% yield as white solid.

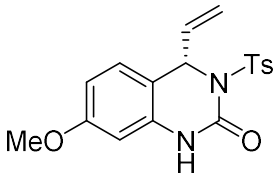


m.p. 165-166 ^{o}C; $[\alpha]_D^{20}$ = +25.2 (c 0.53, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.72 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.59 (s, 1H), 6.05 (d, *J* = 6.5 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 5.12 (d, *J* = 10.1 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.1, 144.6, 139.1, 136.4, 135.5, 134.4, 129.3, 129.1, 126.1, 124.3, 118.3, 116.8, 115.3, 60.4, 21.7, 21.3; IR (KBr): 2988, 2359, 1716, 1696, 1521, 1275, 1169, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$

Calcd for $C_{18}H_{17}N_2O_3S$ 341.0960, Found 341.0974; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 20.940 min (major), t_R = 32.253 min (minor).

(*S*)-7-methoxy-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ka) :

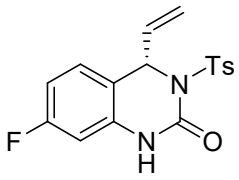
Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1k** (20.5 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^oC for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ka** (30.1 mg) in 84% yield as yellow solid.



m.p. 49-50 ^oC; $[\alpha]_D^{20}$ = +19.8 (c 0.52, Acetone); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.82 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.64 – 6.57 (m, 1H), 6.38 – 6.31 (m, 1H), 6.02 (d, *J* = 6.4 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.17 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 160.3, 151.2, 144.7, 136.3, 135.7, 135.6, 129.3, 129.2, 127.2, 116.6, 113.5, 109.0, 100.8, 60.2, 55.5, 21.7; IR (KBr): 3355, 2360, 1696, 1601, 1518, 1361, 1187, 1118, 764, 669, 641 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{18}H_{17}N_2O_4S$ 357.0909, Found 357.0914; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 28.150 min (major), t_R = 56.000 min (minor).

(*S*)-7-fluoro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3la) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1l** (19.3 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3la** (30.5 mg) in 88% yield as yellow solid.

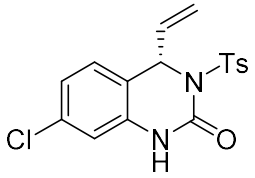


m.p. 145-146 °C; $[\alpha]_D^{20}$ = +24.2 (c 0.55, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.30 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.12 (m, 1H), 6.82 – 6.74 (m, 1H), 6.47 – 6.39 (m, 1H), 6.06 (d, *J* = 6.4 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.23 – 5.10 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.8 (d, *J* = 245.3 Hz), 151.2, 145.1, 136.1 (d, *J* = 11.1 Hz), 135.1, 129.3, 129.2, 127.8 (d, *J* = 9.7 Hz), 117.3, 116.9 (d, *J* = 3.1 Hz), 110.4 (d, *J* = 22.2 Hz), 102.4 (d, *J* = 25.9 Hz), 59.9, 21.7; IR (KBr): 3566, 2988, 2359, 1716, 1697, 1616, 1507, 1170, 764, 749, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{14}FN_2O_3S$ 345.0709, Found 345.0706; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 22.370 min (major), t_R = 32.593 min (minor).

(*S*)-7-chloro-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ma) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1m** (20.9 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg,

0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ma** (31.5 mg) in 87% yield as white solid.

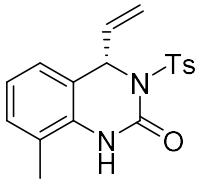


m.p. 163-164 ^{o}C; $[\alpha]_D^{20}$ = +48.7 (c 0.32, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.43 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.06 (d, *J* = 6.3 Hz, 1H), 5.84 (ddd, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.26 – 5.15 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.2, 145.1, 136.0, 135.8, 134.9, 134.6, 129.4, 129.3, 127.5, 123.6, 119.6, 117.5, 115.0, 60.0, 21.7; IR (KBr): 3447, 3005, 2359, 1696, 1521, 1275, 1169, 1005, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{14}ClN_2O_3S$ 361.0414, Found 361.0420; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 20.263 min (major), t_R = 29.707 min (minor).

(*S*)-8-methyl-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3na) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1n** (18.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 40 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3na**

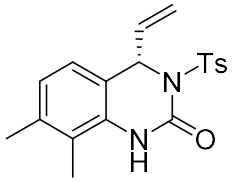
(19.8 mg) in 58% yield as yellow solid.



m.p. 104-105 °C; $[\alpha]_D^{20}$ = +27.3 (c 0.19, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.04 (m, 3H), 7.01 – 6.96 (m, 1H), 6.07 (d, *J* = 6.1 Hz, 1H), 5.85 (ddd, *J* = 16.6, 10.2, 6.1 Hz, 1H), 5.19 (d, *J* = 16.9 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 2.42 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.1, 144.7, 136.2, 135.2, 132.8, 130.3, 129.3, 129.2, 124.2, 123.3, 122.4, 121.1, 116.9, 100.0, 60.5, 21.7, 16.5; IR (KBr): 3447, 1684, 1558, 1398, 1275, 1170, 1088, 764, 750,671 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{18}H_{17}N_2O_3S$ 341.0960, Found 341.0967; Enantiomeric ratio: 91:9, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.597 min (minor), t_R = 31.527 min (major).

(*S*)-7,8-dimethyl-3-tosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3oa) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1o** (20.3 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2a** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3oa** (31.0 mg) in 87% yield as white solid.

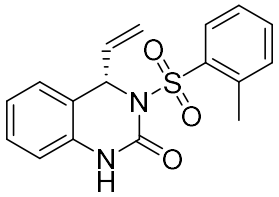


m.p. 78-79 °C; $[\alpha]_D^{20}$ = +19.8 (c 0.57, Acetone); ^{1}H NMR (400 MHz,

$CDCl_3$) δ (ppm): 7.95 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.02 (d, *J* = 6.2 Hz, 1H), 5.84 (ddd, *J* = 16.6, 10.1, 6.2 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.5, 144.6, 137.5, 136.3, 135.4, 132.8, 129.2, 129.1, 124.9, 123.4, 121.1, 119.1, 116.7, 60.5, 21.7, 20.4, 12.5; IR (KBr): 3446, 2360, 1716, 1684, 1576, 1521, 1275, 1169, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{19}H1_9N_2O_3S$ 355.1117, Found 355.1116; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.837 min (minor), t_R = 24.537 min (major).

(*S*)-3-(*o*-tolylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ab) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (17.5 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2b** (59.1 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ab** (16.4 mg) in 50% yield as yellow solid.

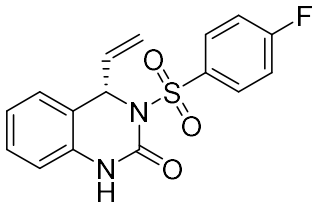


m.p. 63-64 °C; $[\alpha]_D^{20}$ = +93.5 (c 0.12, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.49 – 7.44 (m, 1H), 7.40 – 7.34 (m, 1H), 7.26 – 7.18 (m, 3H), 7.12 – 7.06 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.08 (d, *J* = 5.5 Hz, 1H), 6.01 (ddd, *J* = 16.0, 10.1, 5.3 Hz, 1H), 5.35 –

5.21 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.2, 137.5, 137.1, 135.5, 134.5, 133.7, 132.3, 132.1, 129.0, 126.4, 126.0, 123.6, 120.4, 117.1, 114.6, 59.7, 19.9; IR (KBr): 2918, 2360, 2342, 1718, 1498, 1261, 1172, 804, 763, 696 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{15}N_2O_3S$ 327.0804, Found 327.0802; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.323 min (major), t_R = 12.867 min (minor).

(*S*)-3-((4-fluorophenyl)sulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ac) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (17.5 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2c** (60.3 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ac** (27.2 mg) in 82% yield as yellow solid.

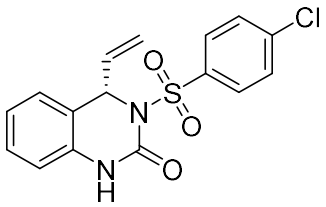


m.p. 50-51 °C; $[\alpha]_D^{20}$ = +11.9 (c 0.52, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.62 (s, 1H), 8.13 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.31 – 7.21 (m, 1H), 7.24 – 7.13 (m, 3H), 7.12 – 7.06 (m, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.07 (d, *J* = 6.5 Hz, 1H), 5.85 (ddd, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.7 (d, *J* = 255.0 Hz), 150.9, 135.2 (d, *J* = 3.2 Hz), 135.0, 134.3, 132.3 (d, *J* = 9.6 Hz), 129.1, 126.3, 123.8, 121.1, 117.2, 115.8 (d, *J* = 22.6 Hz), 114.8, 60.7; IR (KBr): 3006, 2359, 2341, 1275, 1260, 764,

749,668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_{12}FN_2O_3S$ 331.0553, Found 331.0557; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.860 min (major), t_R = 21.577 min (minor).

(*S*)-3-((4-chlorophenyl)sulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ad) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (17.5 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2d** (65.3 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 24 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ad** (22.6 mg) in 65% yield as yellow solid.

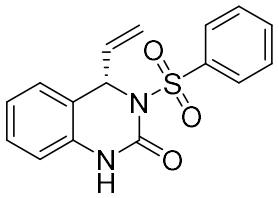


m.p. 54-55 °C; $[\alpha]_D^{20}$ = +46.0 (c 0.05, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.60 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.23 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.06 (d, *J* = 6.5 Hz, 1H), 5.85 (ddd, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.21 (d, *J* = 16.9 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.9, 140.4, 137.7, 135.0, 134.3, 130.8, 129.1, 128.9, 126.4, 123.8, 121.1, 121.0, 117.3, 114.9, 60.7; IR (KBr): 3446, 2359, 1772, 1646, 1507, 1275, 1260, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_{12}ClN_2O_3S$ 347.0257, Found 347.0273; Enantiomeric ratio: 85:15, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow

rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 17.927 min (major), t_R = 31.357 min (minor).

(*S*)-3-(phenylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ae) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (17.5 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2e** (54.9 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ae** (18.8 mg) in 60% yield as yellow solid.

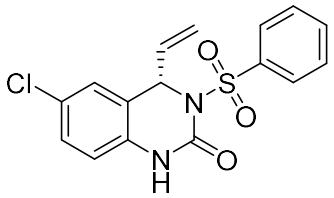


m.p. 85-86 °C; $[\alpha]_D^{20}$ = +39.8 (c 0.13, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63 (s, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.57 (m, 1H), 7.55 – 7.47 (m, 2H), 7.27 – 7.17 (m, 2H), 7.12 – 7.03 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.09 (d, *J* = 6.3 Hz, 1H), 5.87 (ddd, *J* = 16.7, 10.2, 6.3 Hz, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.9, 139.3, 135.1, 134.4, 133.7, 129.2, 129.0, 128.6, 126.3, 123.6, 121.1, 117.1, 114.8, 60.5; IR (KBr): 3446, 2359, 1792, 1684, 1507, 1275, 1260, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{16}H_{13}N_2O_3S$ 313.0647, Found 313.0648; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.737 min (major), t_R = 12.770 min (minor).

(*S*)-6-chloro-3-(phenylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3he) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1h** (20.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg,

0.008 mmol) was added the solution of sulfonyl isocyanate **2e** (54.9 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3he** (18.5 mg) in 53% yield as white solid.

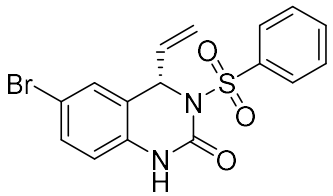


m.p. 88-89 ^{o}C; $[\alpha]_D^{20}$ = +22.0 (c 0.22, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.20 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.56 – 7.47 (m, 2H), 7.23 – 7.18 (m, 2H), 6.64 (d, *J* = 8.7 Hz, 1H), 6.04 (d, *J* = 6.4 Hz, 1H), 5.83 (ddd, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.26 – 5.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.1, 139.1, 134.5, 133.9, 133.1, 129.2, 129.1, 128.7, 128.6, 126.3, 122.6, 117.8, 116.3, 60.1; IR (KBr): 3065, 2918, 1697, 1600, 1496, 1200, 1086, 1011, 753, 726, 685 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{16}H_{12}ClN_2O_3S$ 347.0257, Found 347.0276; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 12.603 min (major), t_R = 16.083 min (minor).

(*S*)-6-bromo-3-(phenylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3ie) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1i** (25.3 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2e** (54.9 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3ie**

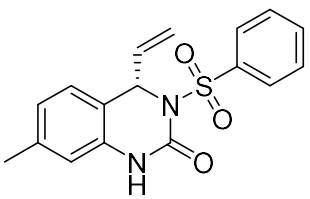
(23.9 mg) in 61% yield as yellow solid.



m.p. 95-96 °C; $[\alpha]_D^{20}$ = +20.5 (c 0.4, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.92 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 7.35 (d, *J* = 6.9 Hz, 2H), 6.59 (d, *J* = 9.1 Hz, 1H), 6.04 (d, *J* = 6.3 Hz, 1H), 5.82 (ddd, *J* = 16.7, 10.1, 6.3 Hz, 1H), 5.26 – 5.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.9, 139.1, 134.5, 133.9, 133.6, 131.9, 129.2, 129.1, 128.6, 123.0, 117.8, 116.5, 115.9, 60.0; IR (KBr): 3397, 3100, 2917, 1699, 1374, 1172, 1009, 727, 691, 659 cm^{-1}; HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{16}H_{12}BrN_2O_3S$ 390.9752, Found 390.9757; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.517 min (major), t_R = 9.983 min (minor).

(*S*)-7-methyl-3-(phenylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3je) :

Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1j** (18.9 mg, 0.1 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2e** (54.9 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3je** (18.4 mg) in 56% yield as yellow solid.

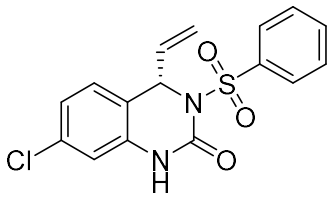


m.p. 126-127 °C; $[\alpha]_D^{20}$ = +17.4 (c 0.37, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.34 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.57 (m, 1H), 7.54 – 7.45 (m,

2H), 7.09 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.57 (s, 1H), 6.06 (d, *J* = 6.4 Hz, 1H), 5.85 (ddd, *J* = 16.7, 10.1, 6.3 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.8, 139.4, 139.2, 135.4, 134.3, 133.6, 129.2, 128.5, 126.1, 124.4, 118.3, 116.8, 115.3, 60.4, 21.3; IR (KBr): 3212, 2923, 1693, 1598, 1372, 1297, 1172, 1085, 1019, 773, 731, 683 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{17}H_{15}N_2O_3S$ 327.0804, Found 327.0808; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.710 min (major), t_R = 14.333 min (minor).

(*S*)-7-chloro-3-(phenylsulfonyl)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3me) :

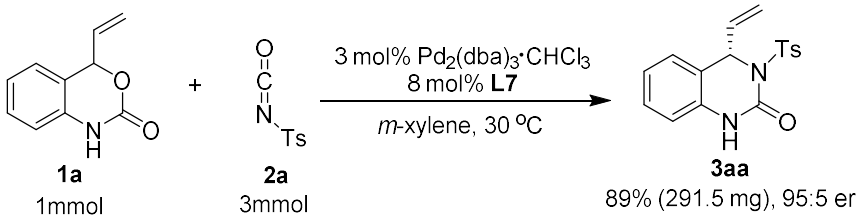
Following the general procedure, under argon atmosphere, to the mixture of vinyl benzoxazinone **1m** (20.9 mg, 0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (3.0 mg, 0.003 mmol) and **L7** (3.0 mg, 0.008 mmol) was added the solution of sulfonyl isocyanate **2e** (54.9 mg, 0.3 mmol) in *m*-xylene (2 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 3:2) to afford pure products **3me** (20.2 mg) in 58% yield as yellow solid.



m.p. 201-202 °C; $[\alpha]_D^{20}$ = +33.1 (c 0.15, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.91 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.68 – 7.59 (m, 1H), 7.59 – 7.51 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.73 (d, *J* = 1.9 Hz, 1H), 6.07 (d, *J* = 6.3 Hz, 1H), 5.85 (ddd, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.27 – 5.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 150.8, 139.0, 135.6, 134.8, 134.7, 134.0, 129.2, 128.7, 127.5, 123.7, 119.5, 117.5, 114.9, 59.9; IR (KBr): 2918, 1697,

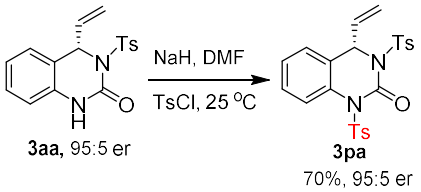
1595, 1491, 1362, 1197, 1087, 1010, 751, 725, 685 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{16}H_{12}ClN_2O_3S$ 347.0257, Found 347.0271; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.190 min (major), t_R = 19.973 min (minor).

5. Procedure for one-mmol scale synthesis of product 3aa



Under argon atmosphere, to the mixture of vinyl benzoxazinone **1a** (175 mg, 1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (30.0 mg, 0.03 mmol) and **L7** (30.0 mg, 0.08 mmol) was added the solution of sulfonyl isocyanate **2a** (591 mg, 3 mmol) in *m*-xylene (20 mL). Then, the reaction mixture was stirred at 30 °C for 12 hours. After the completion of the reaction which was indicated by TLC, the resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography (PE:EA = 20:1) to afford pure products **3aa** (291.5 mg) in 89% yield as yellow solid.

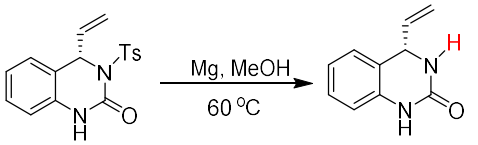
6. Procedure for the derivation of product 3aa



(*S*)-1,3-ditosyl-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3pa):

To the suspension of NaH (4.8 mg, 0.2 mmol) in DMF (0.5 mL) was added the solution of **3aa** (32.8 mg, 0.1 mmol) in DMF (0.5 mL), which was stirred at 25 ^{o}C for 30 min. Then, 4-methylbenzenesulfonyl chloride (28.7 mg, 0.15 mmol) was added to the reaction mixture, which was stirred at 25 ^{o}C for 12 hours. After the completion of the reaction which was indicated by TLC, the reaction mixture was quenched by saturated aqueous solution of ammonia chloride, which was extracted by dichloromethane for several times. The organic layer was combined together and concentrated under reduced pressure to give a residue, which was purified by preparative thin layer chromatography to afford pure product **3pa** (33.7 mg) in 70% yield as yellow solid.

Preparative thin layer chromatography, petroleum ether /ethyl acetate = 2/1; reaction time = 12 h; yield: 70% (33.7 mg); yellow solid; m.p. 56-57 ^{o}C; $[\alpha]_D^{20}$ = +83.5 (c 0.26, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.06 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.36 – 7.26 (m, 4H), 7.30 – 7.23 (m, 1H), 5.94 (d, *J* = 5.6 Hz, 1H), 5.82 (ddd, *J* = 16.8, 10.2, 5.5 Hz, 1H), 5.21 – 5.13 (m, 1H), 5.12 – 5.02 (m, 1H), 2.45 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.3, 145.3, 145.2, 136.3, 135.1, 134.0, 133.6, 129.7, 129.4, 129.2, 128.8, 128.6, 128.2, 126.4, 126.2, 121.7, 118.3, 60.2, 21.8, 21.7; IR (KBr): 3005, 2359, 1717, 1684, 1558, 1275, 1260, 1172, 1084, 764, 750, 668 cm^{-1}; HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{24}H_{21}N_2O_5S_2$ 481.0892, Found 481.0890; Enantiomeric ratio: 95:5, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 13.373 min (major), t_R = 17.633 min (minor).



3aa, 95:5 er

3qa
90%, 93:7 er

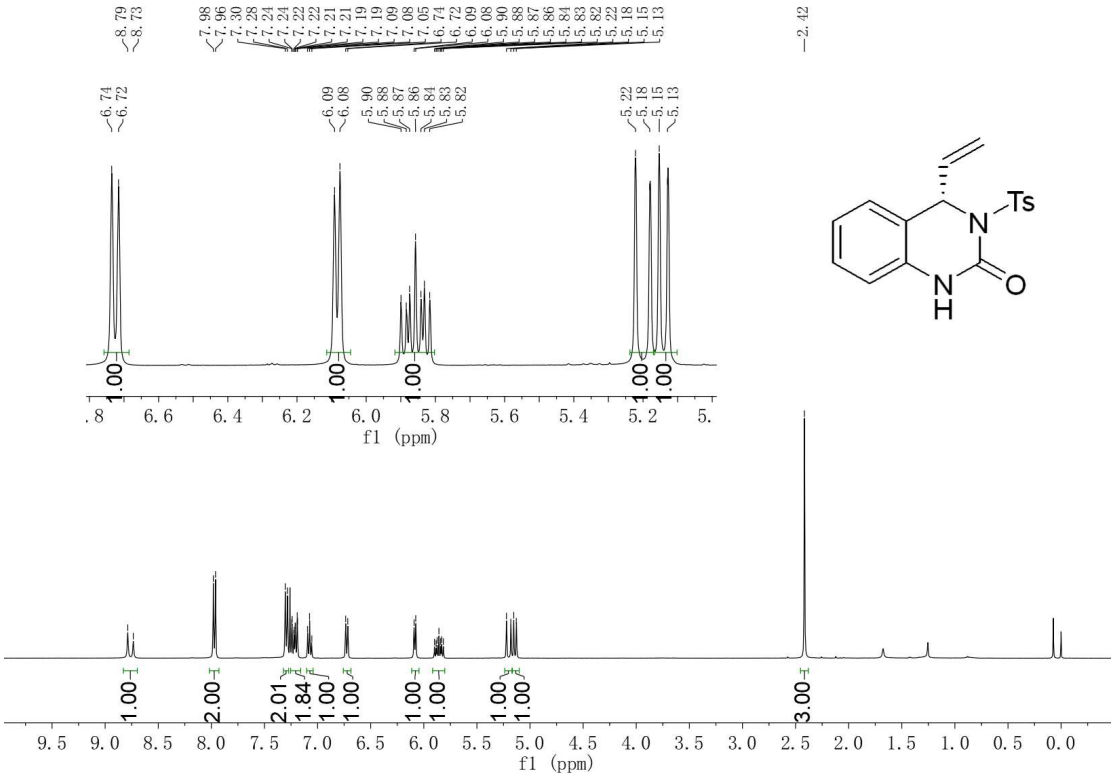
(*S*)-4-vinyl-3,4-dihydroquinazolin-2(1*H*)-one (3qa):

Under argon atmosphere, to the mixture of **3aa** (32.8 mg, 0.1 mmol) and Mg (240mg) was added dried methanol (3.4 mL). Then, the reaction mixture was stirred at 60 °C for one hour. After the completion of the reaction which was indicated by TLC, the reaction mixture was quenched by saturated aqueous solution of ammonia chloride, which was extracted by ethyl acetate for several times. The organic layer was combined together and concentrated under reduced pressure to give a residue, which was purified by preparative thin layer chromatography to afford pure product **3qa** (15.7 mg) in 90% yield as white solid.

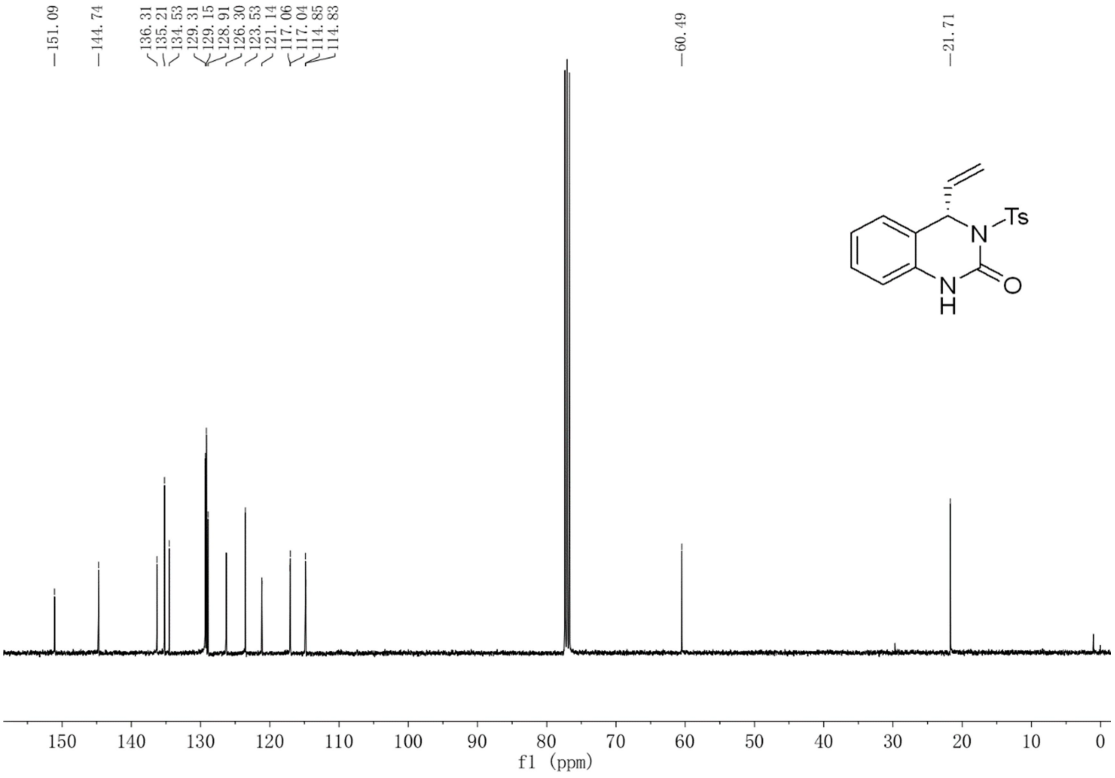
Preparative thin layer chromatography, petroleum ether /ethyl acetate = 1/1; reaction time = 1 h; yield: 90% (15.7 mg); white solid; m.p. 90-91 °C; $[\alpha]_D^{20}$ = -88.1 (c 0.29, Acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (s, 1H), 7.20 – 7.13 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.96 (ddd, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.57 (s, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.8, 138.2, 135.8, 128.5, 126.4, 122.4, 119.6, 116.5, 114.5, 57.3; IR (KBr): 3084, 2919, 2282, 1855, 1688, 1493, 1256, 751 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}N_2O$ 175.0871, Found 175.0860; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.513 min (minor), t_R = 12.227 min (major).

7. NMR spectra of products 3

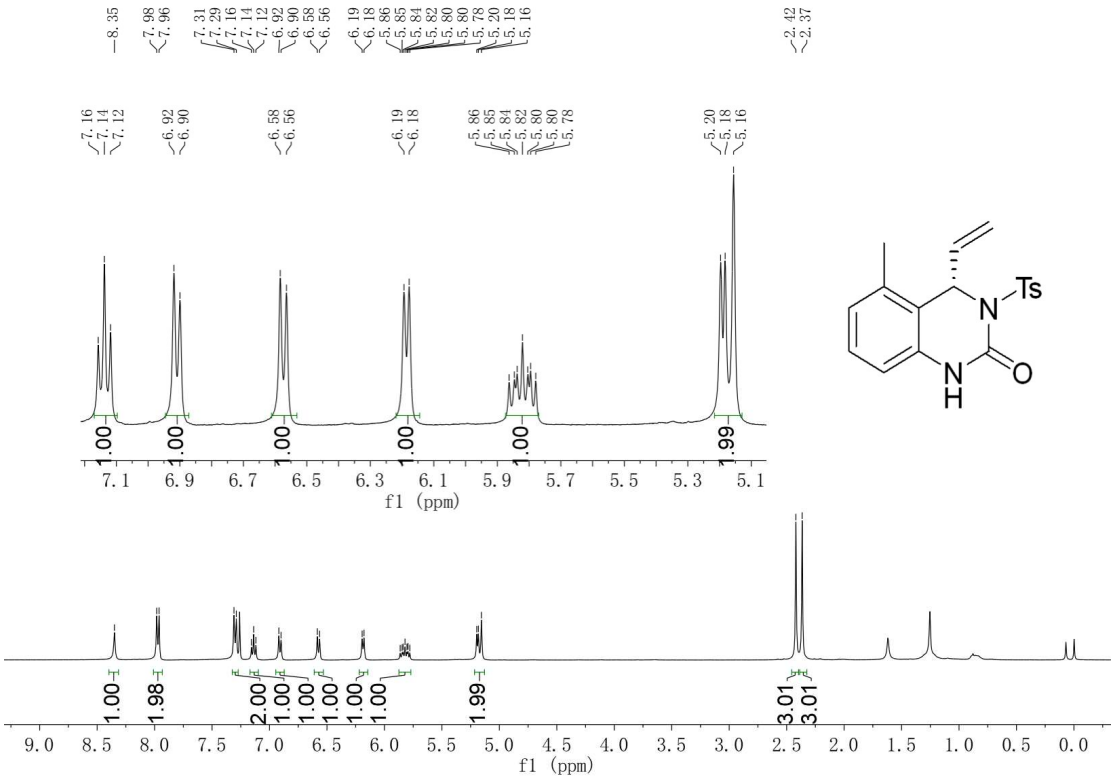
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**



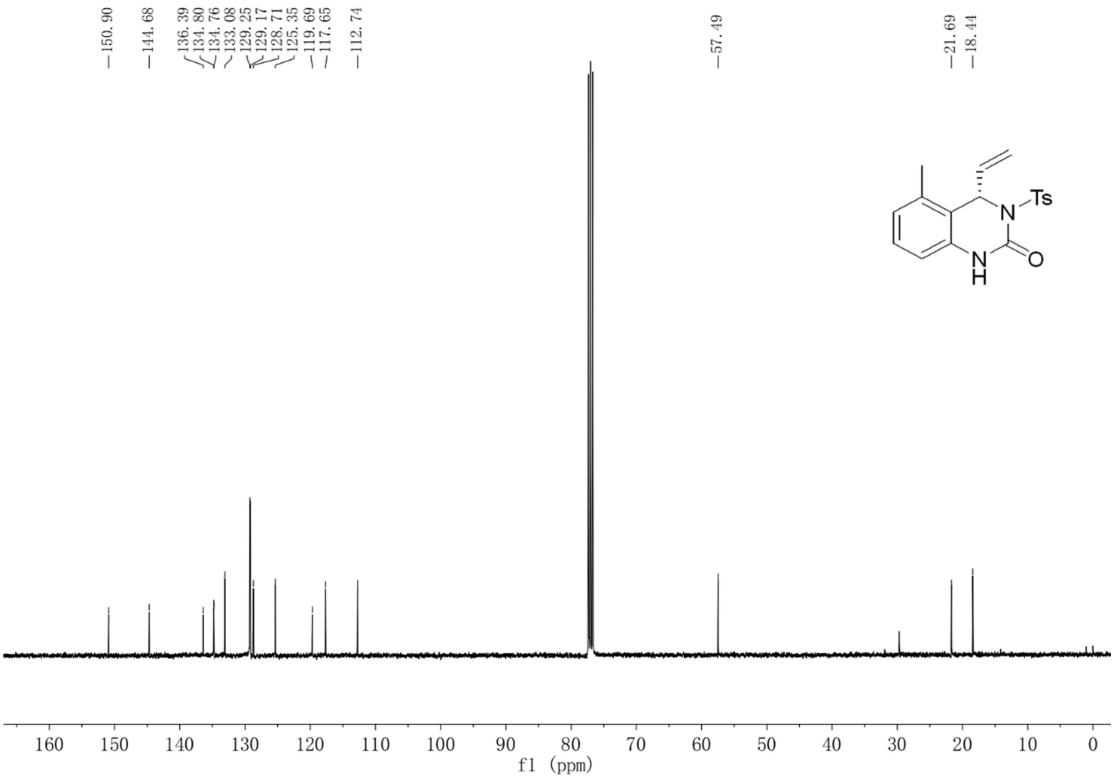
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**



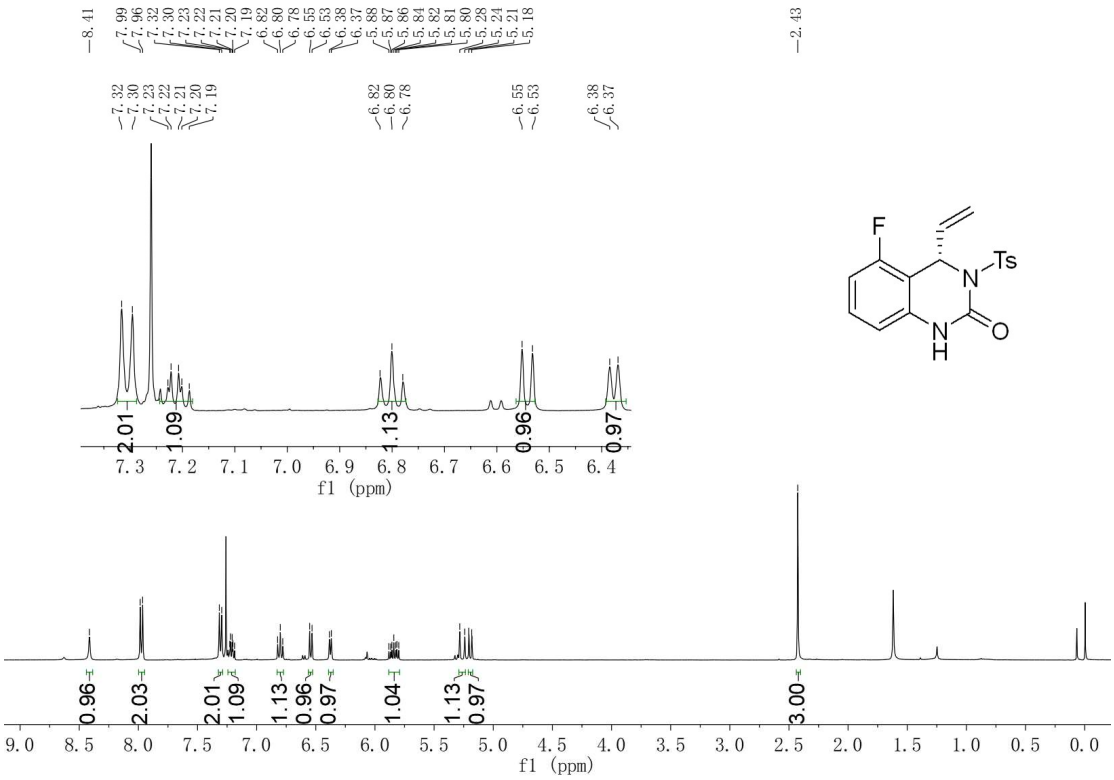
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba**



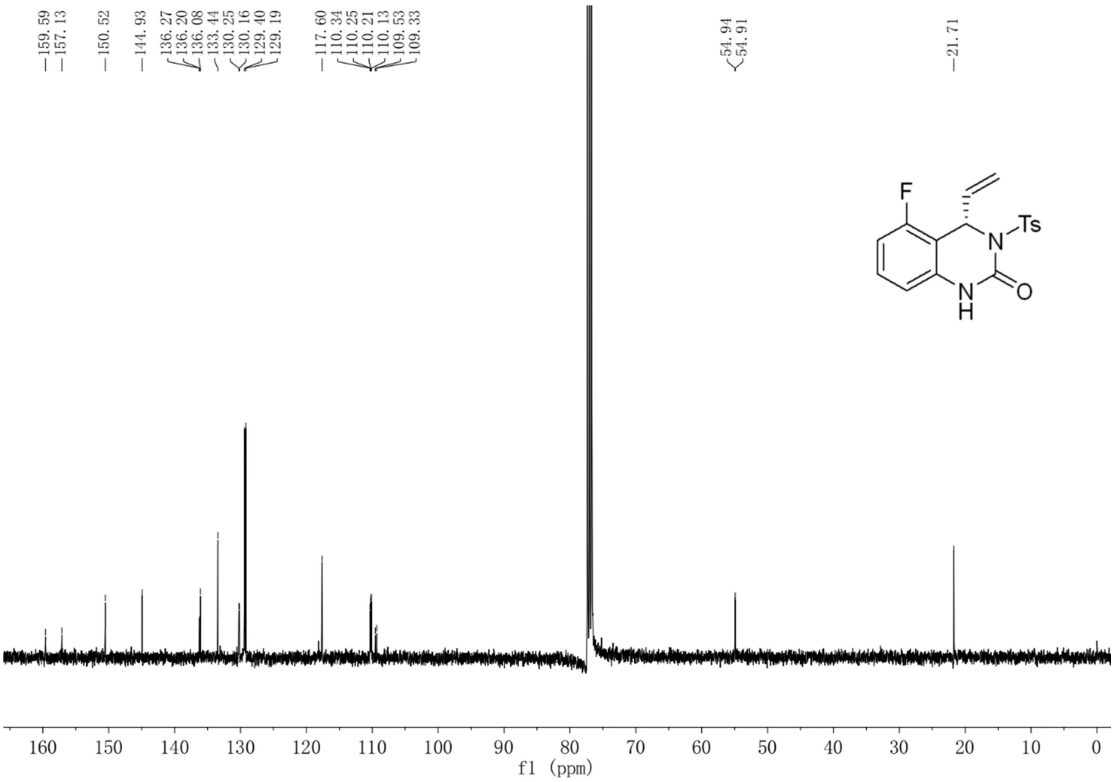
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba**



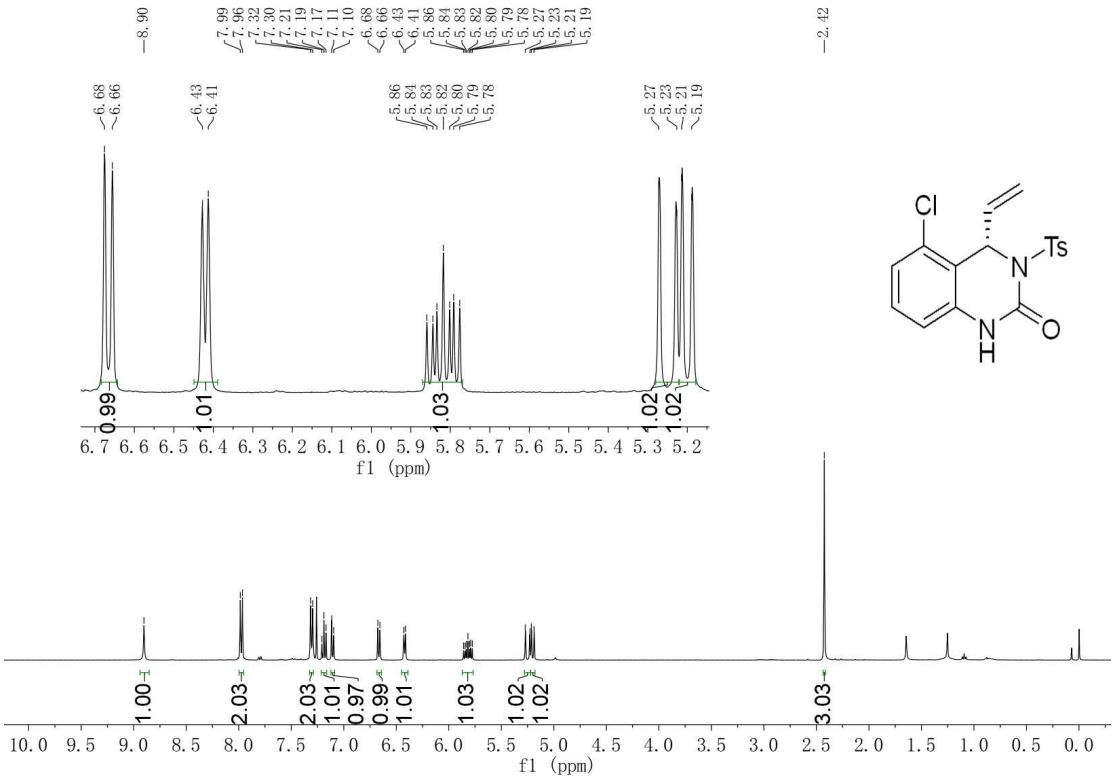
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ca**



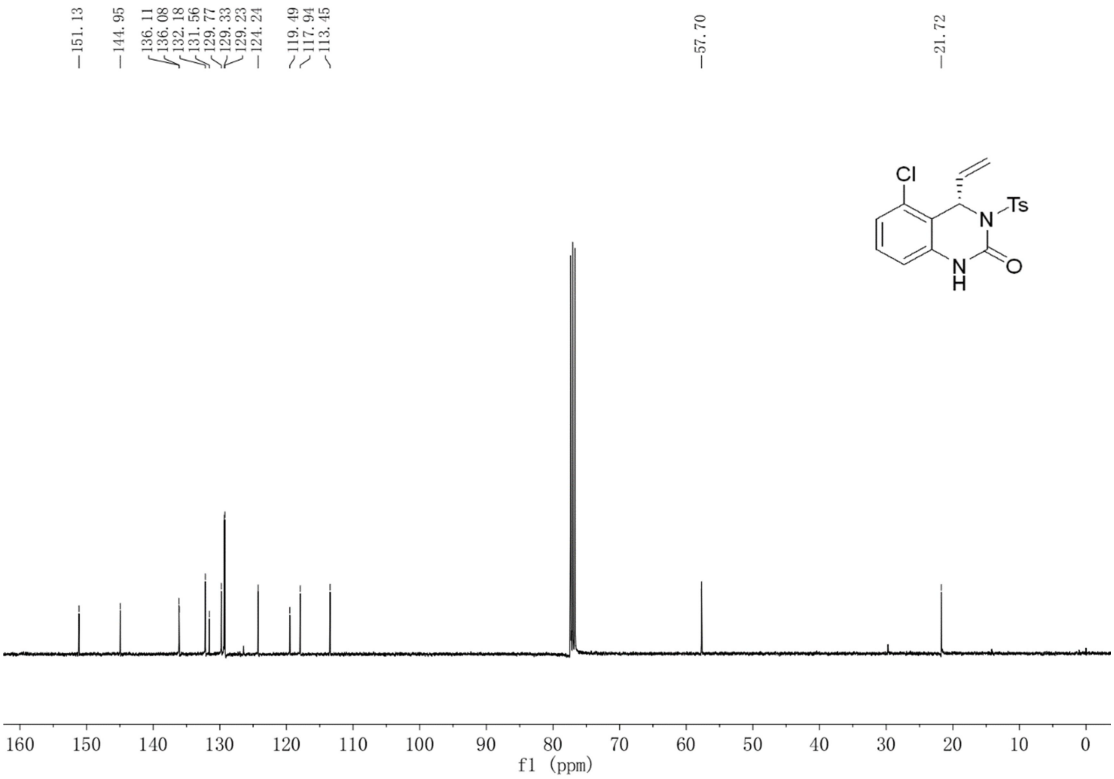
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ca**



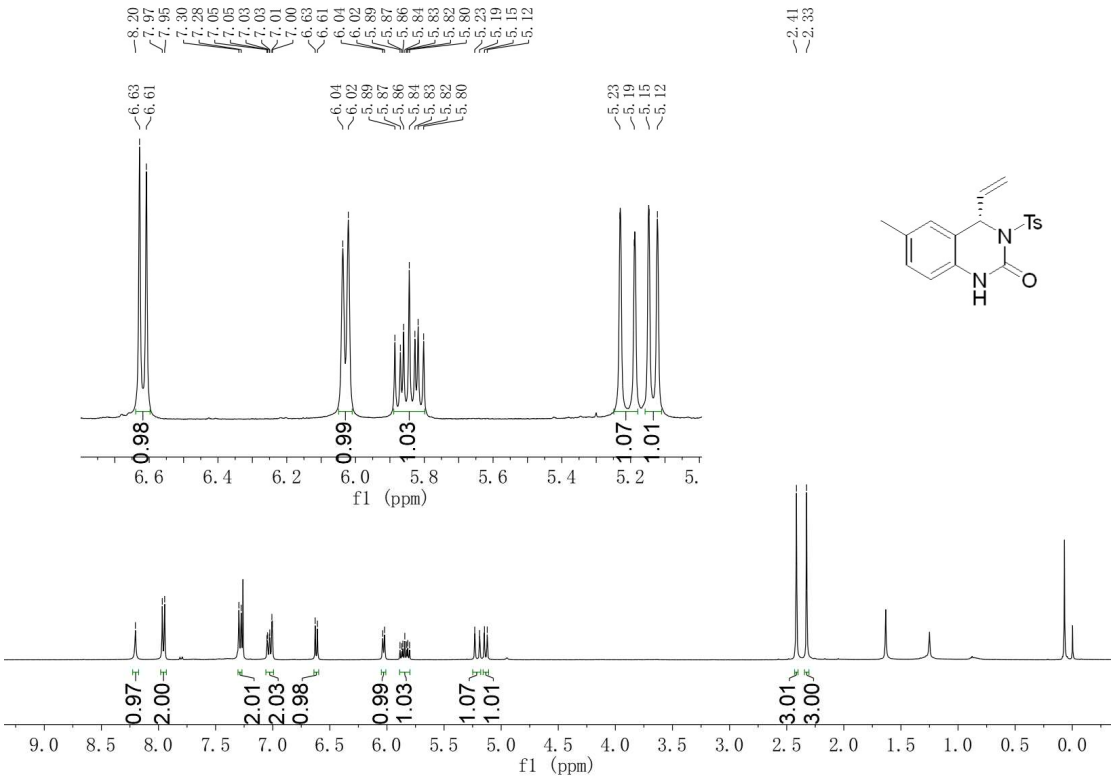
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da**



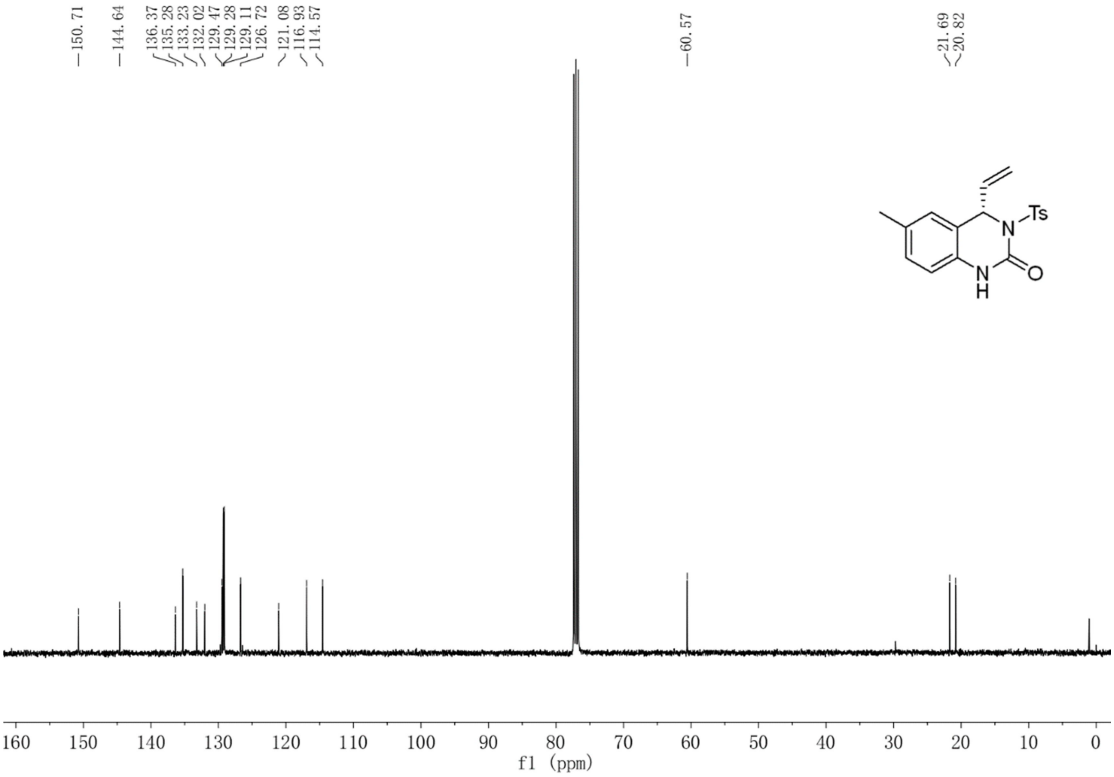
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da**



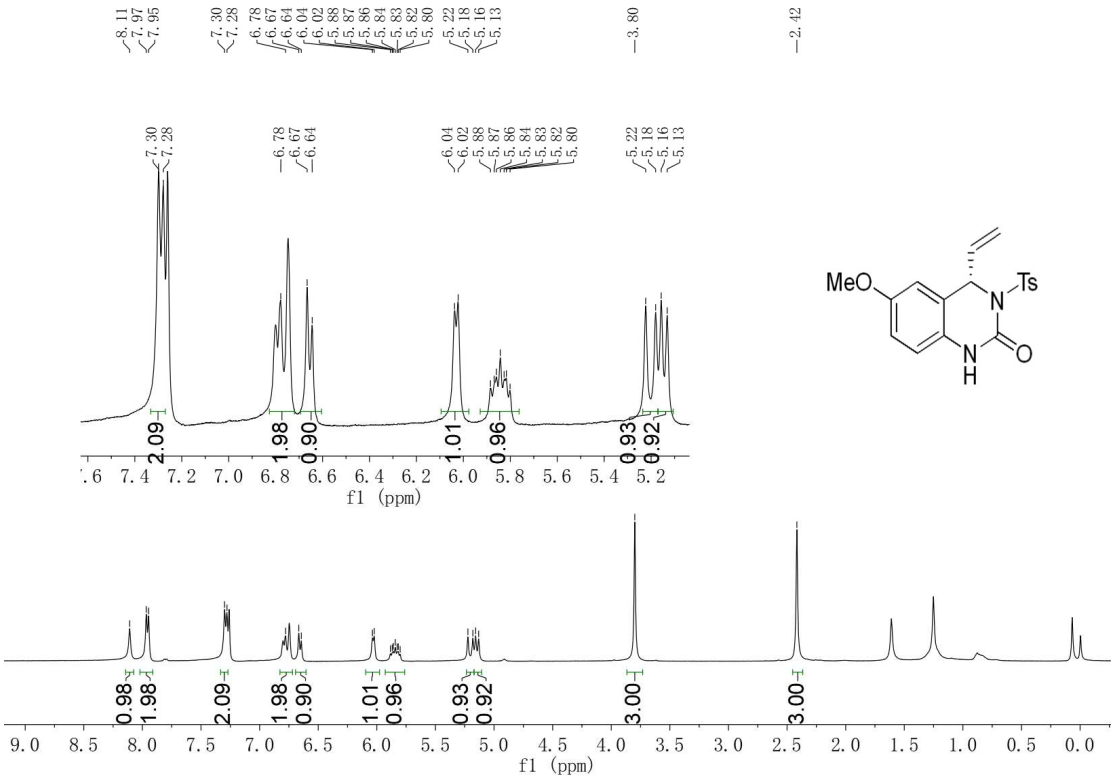
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ea**



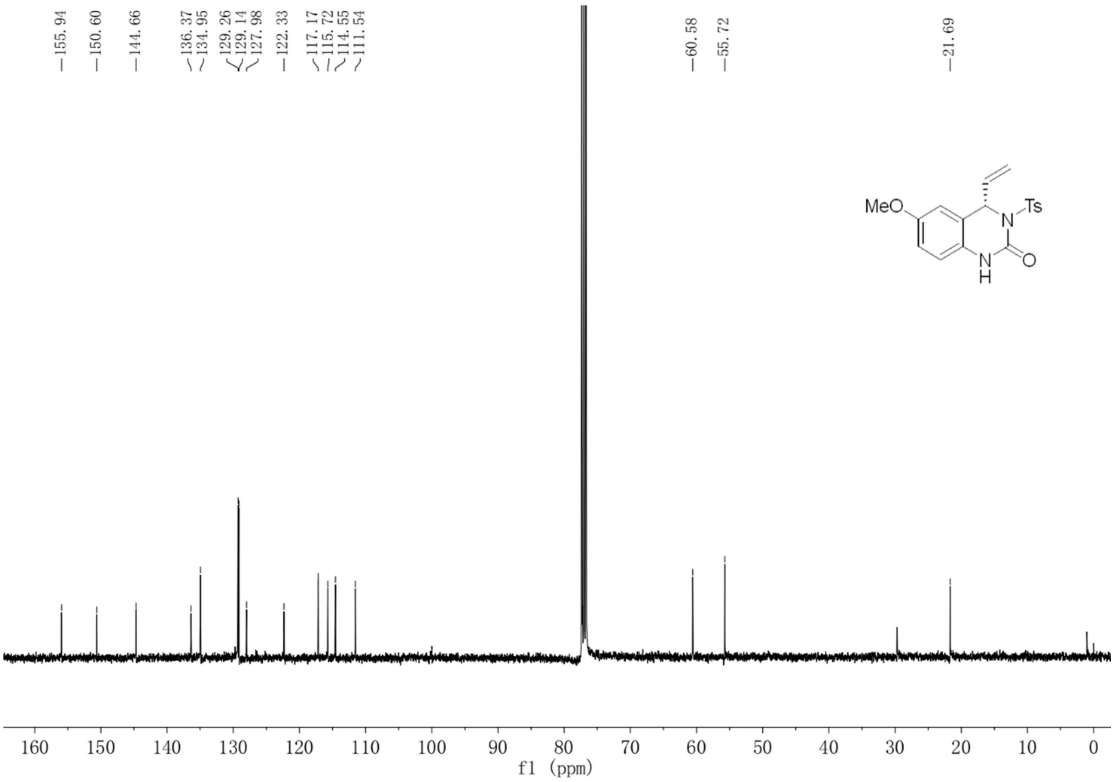
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea**



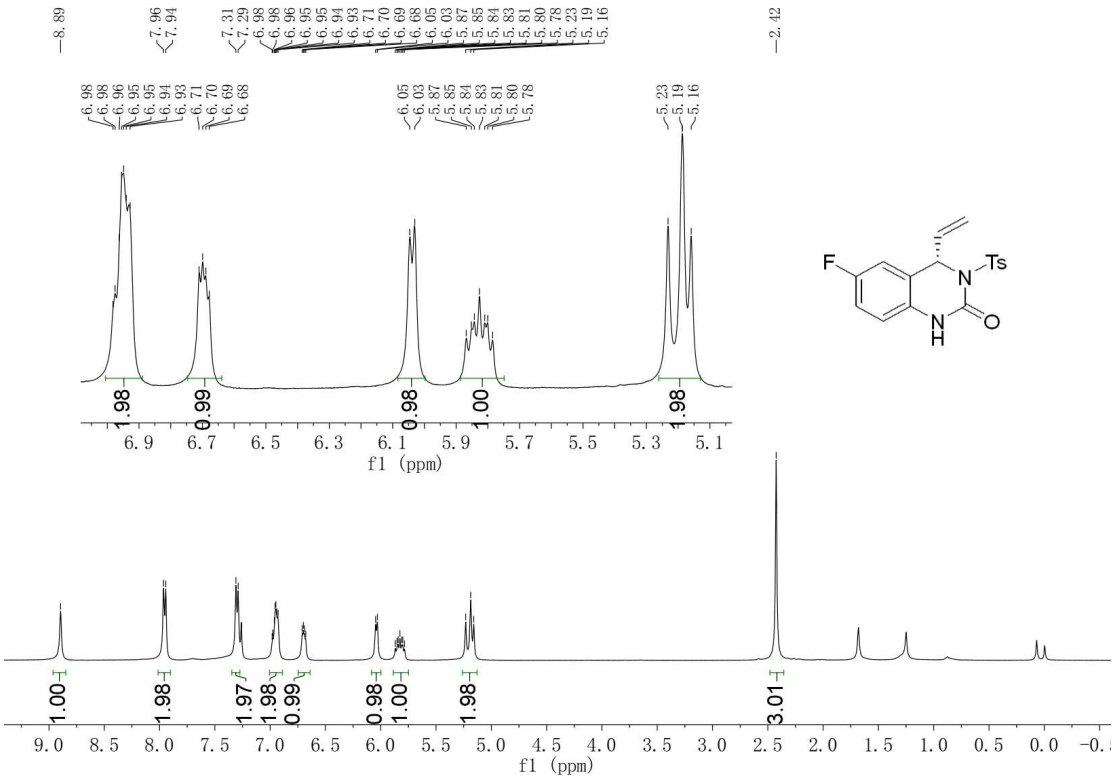
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3fa**



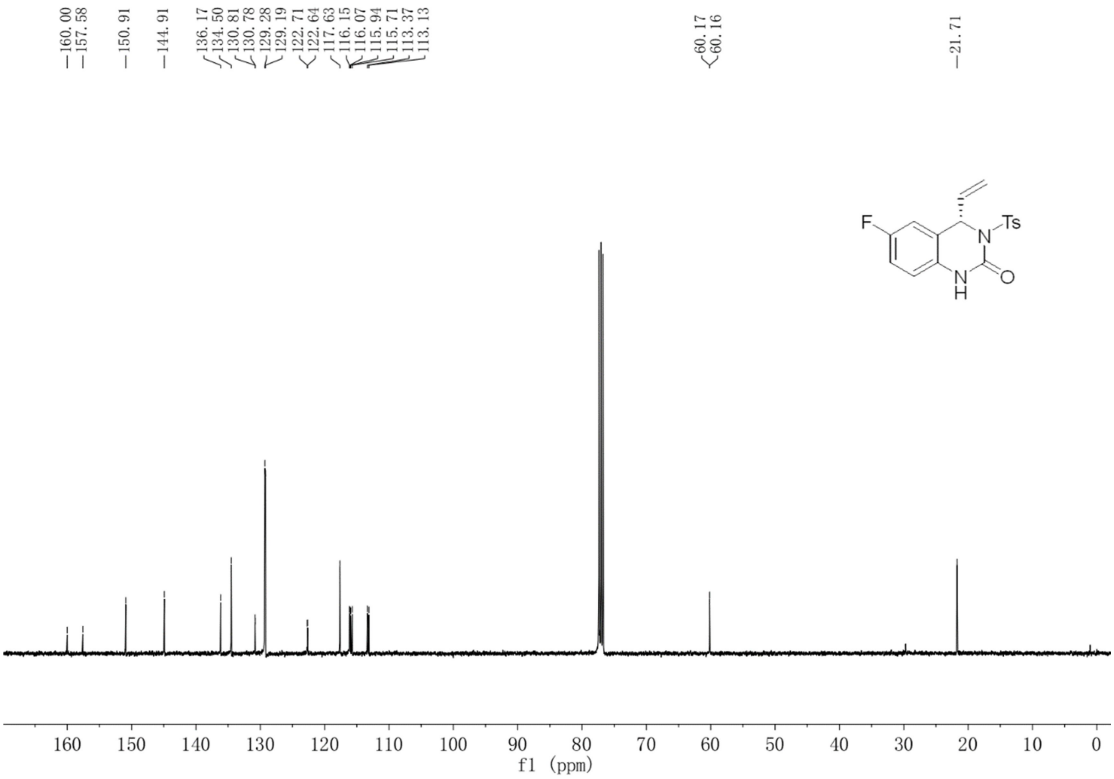
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3fa**



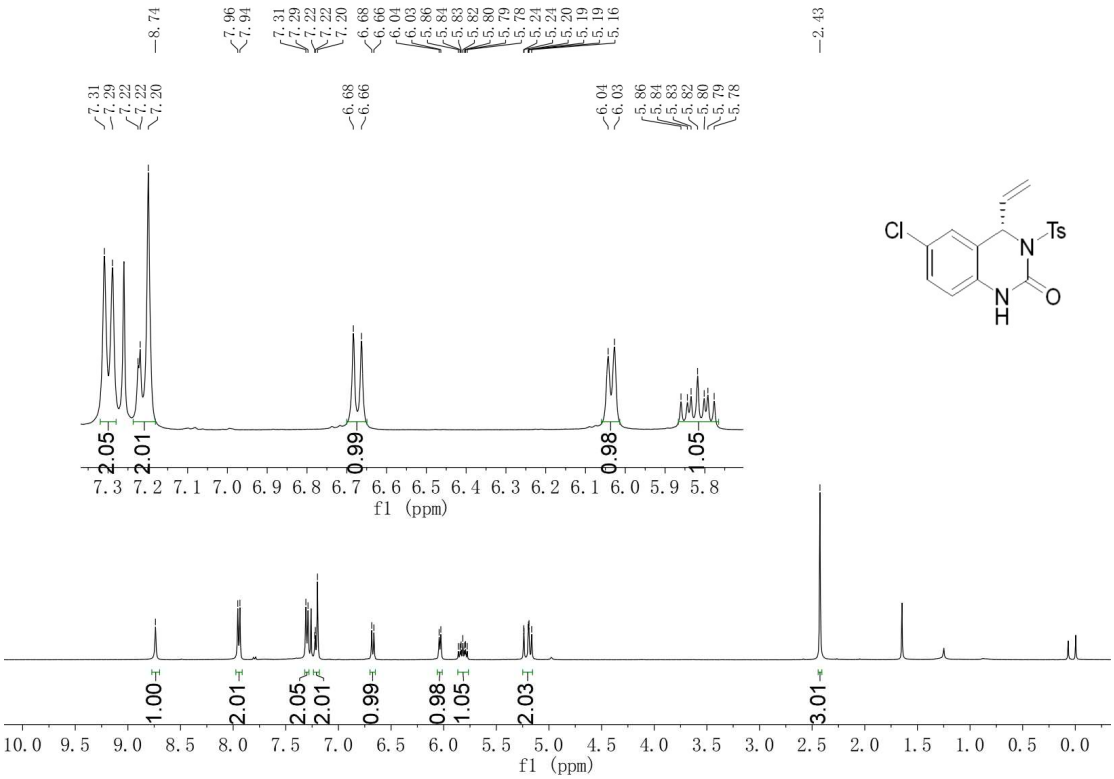
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ga**



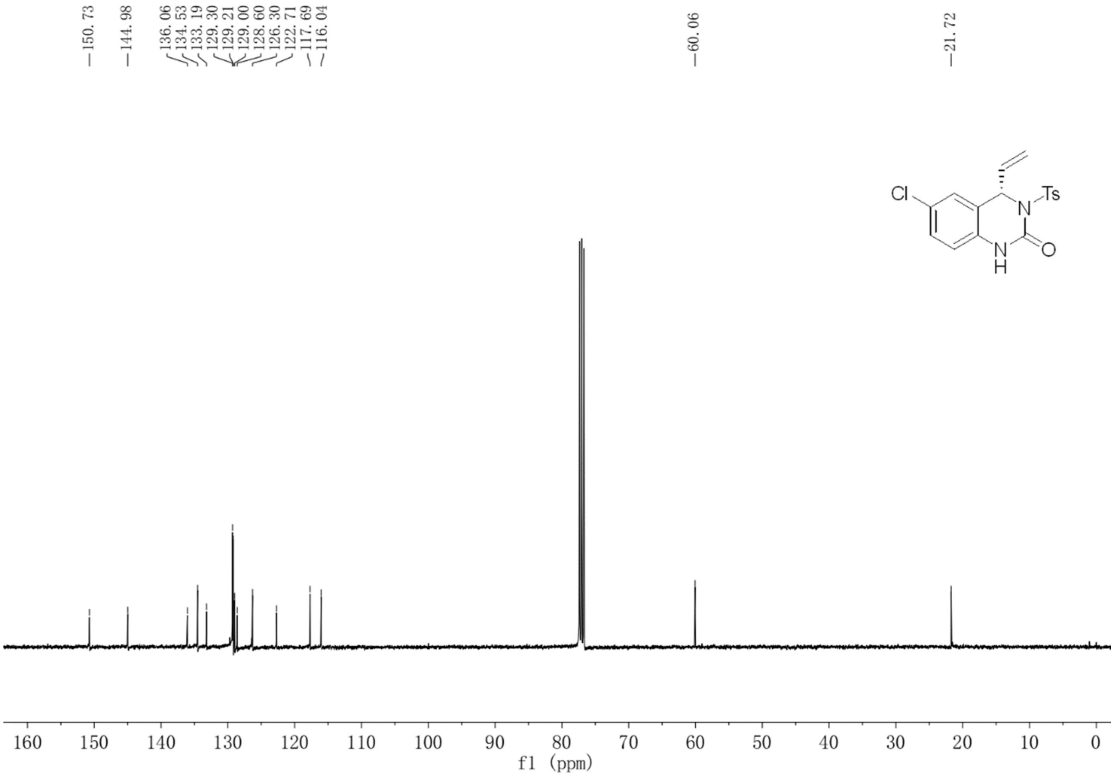
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**



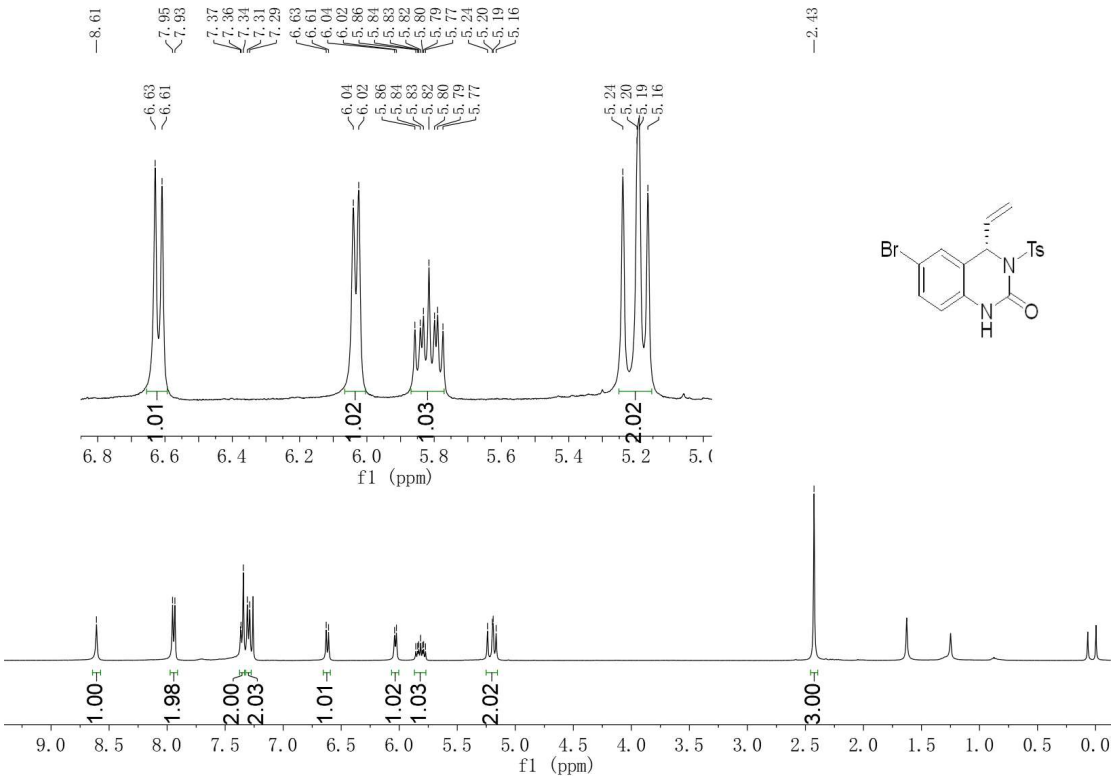
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ha**



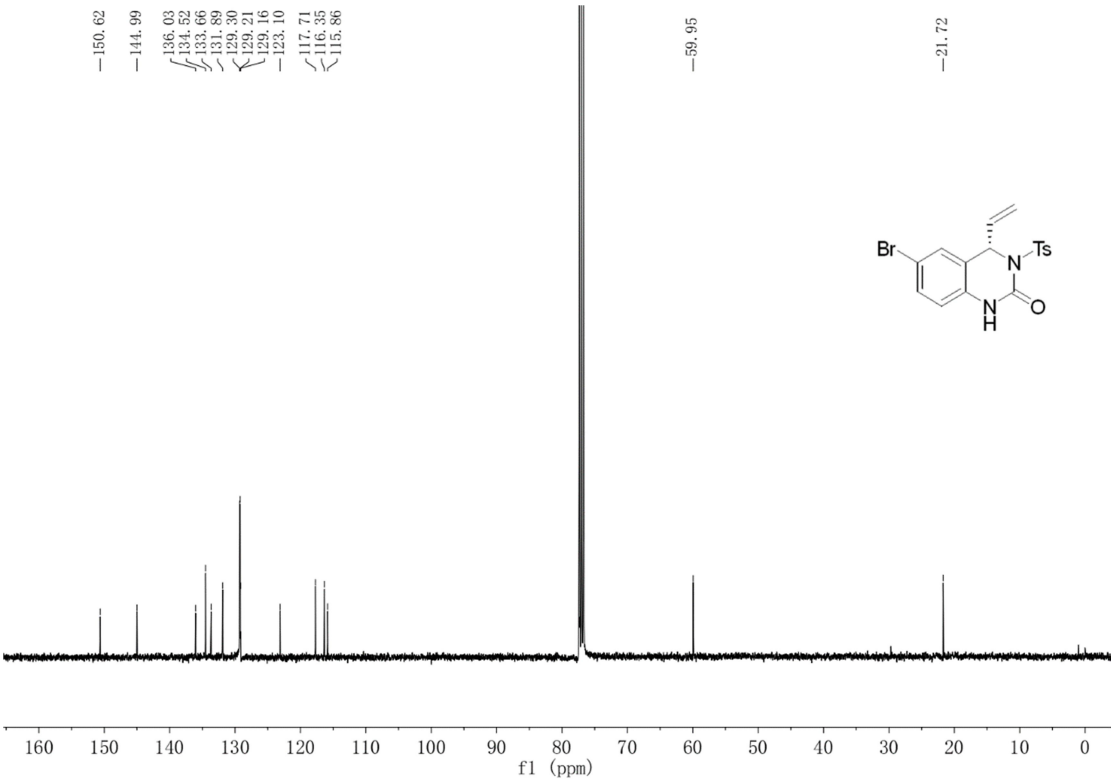
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha**



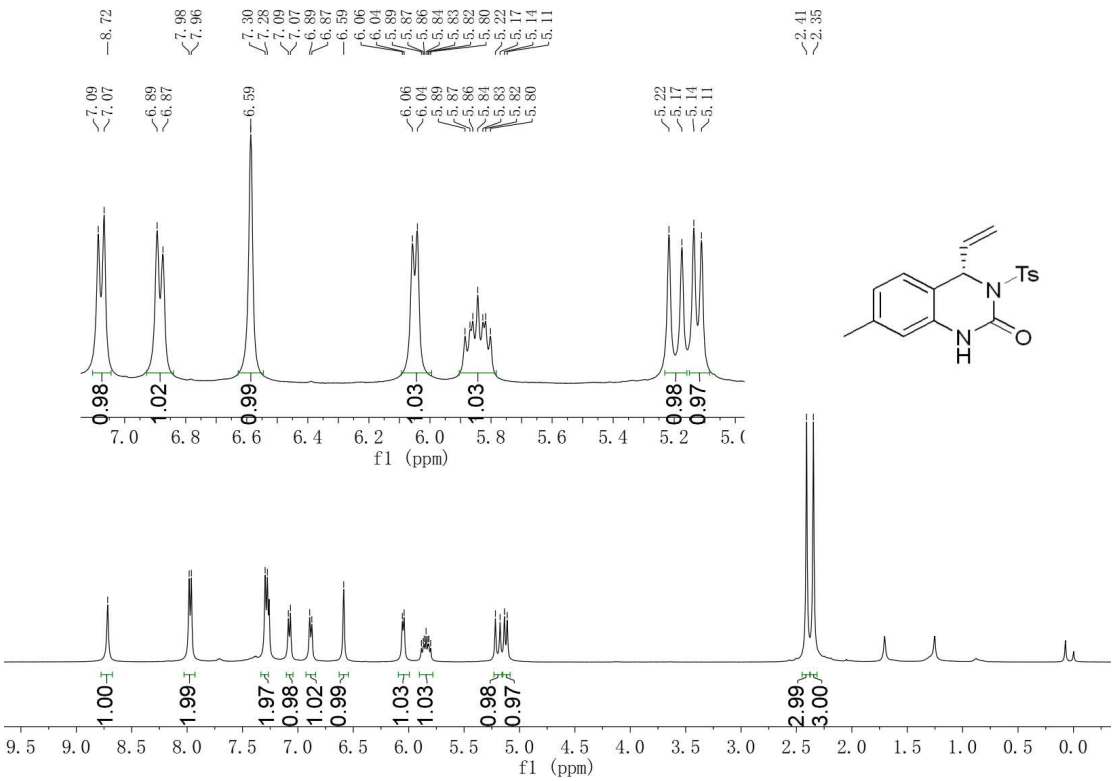
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ia**



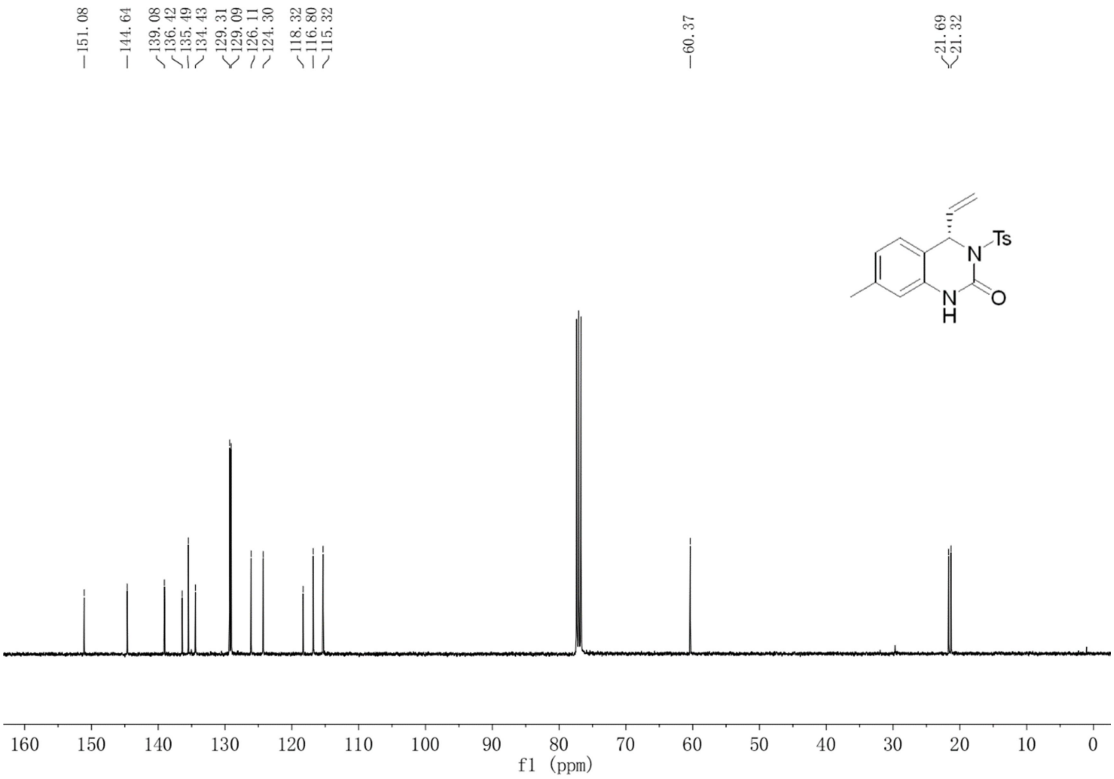
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ia**



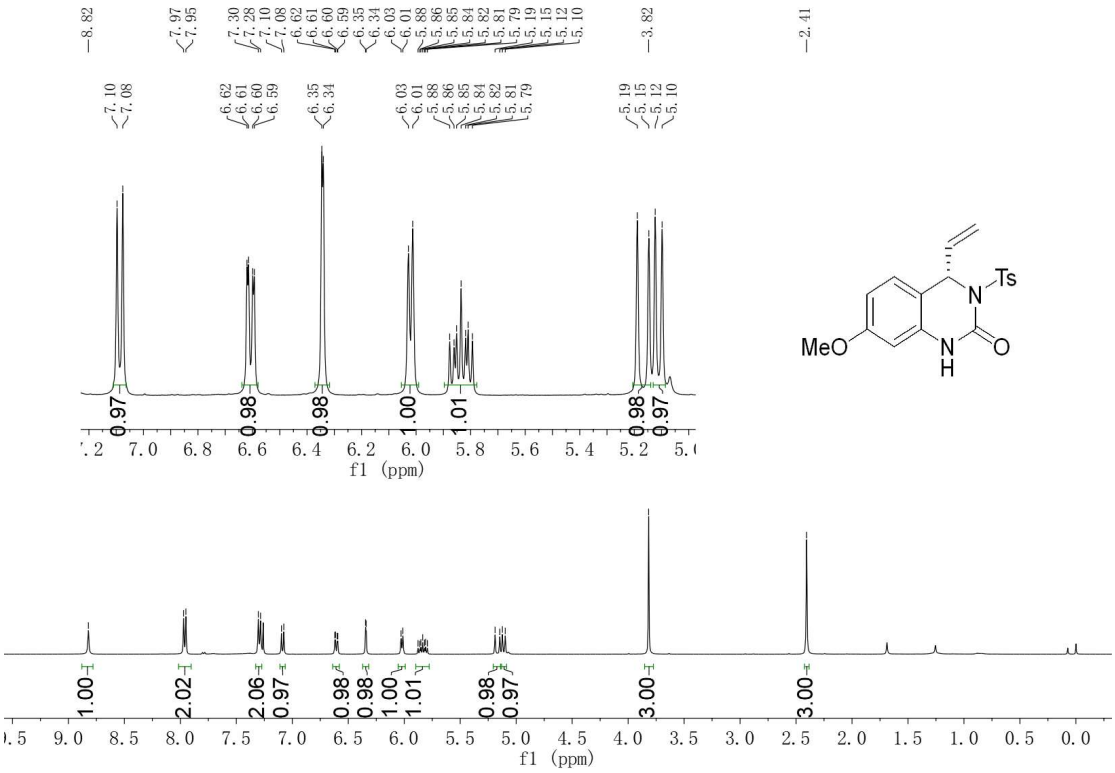
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ja**



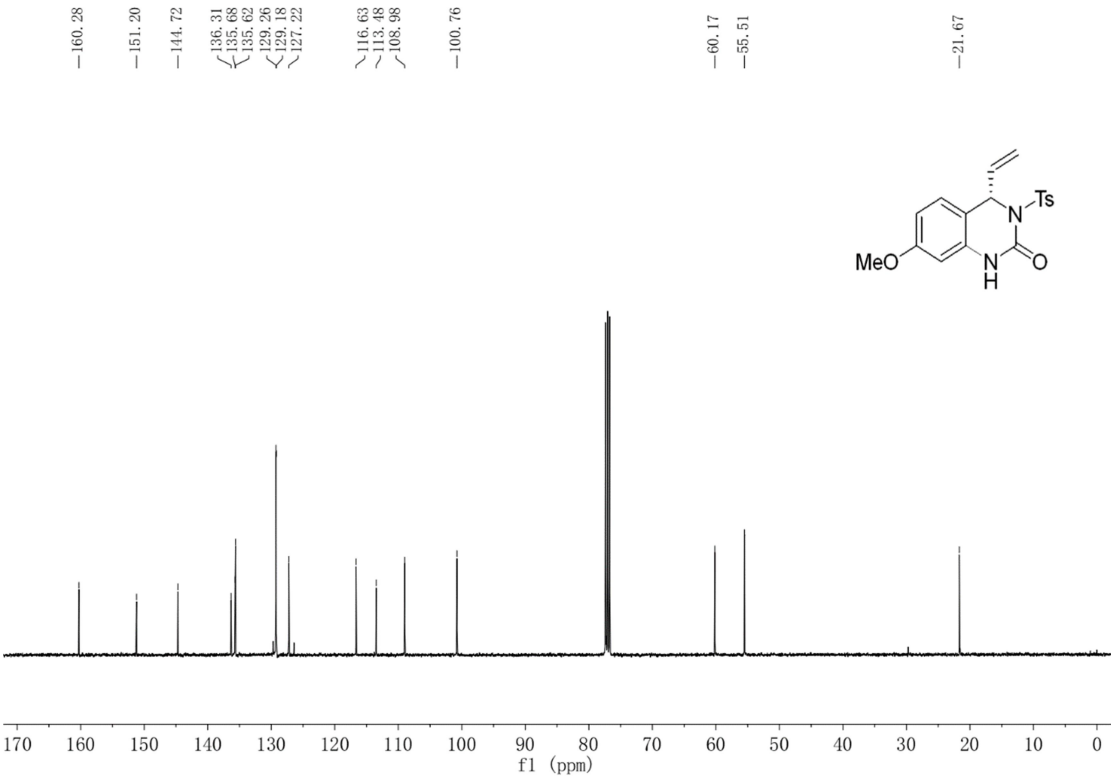
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ja**



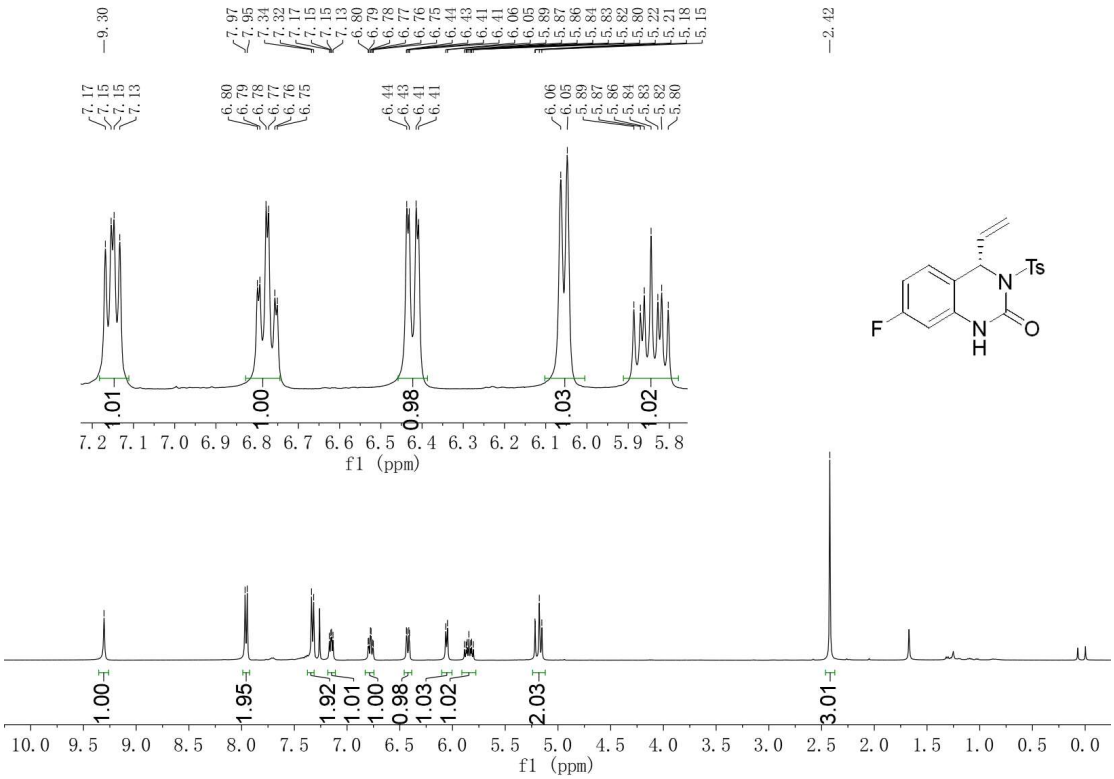
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ka**



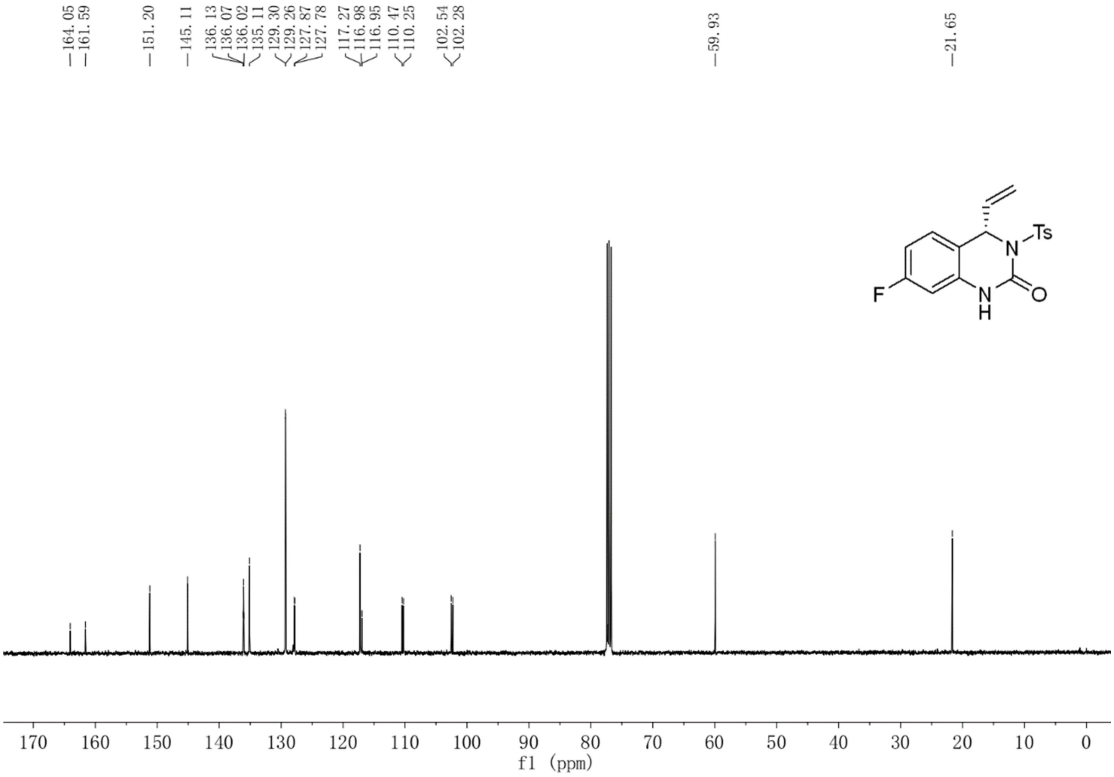
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ka**



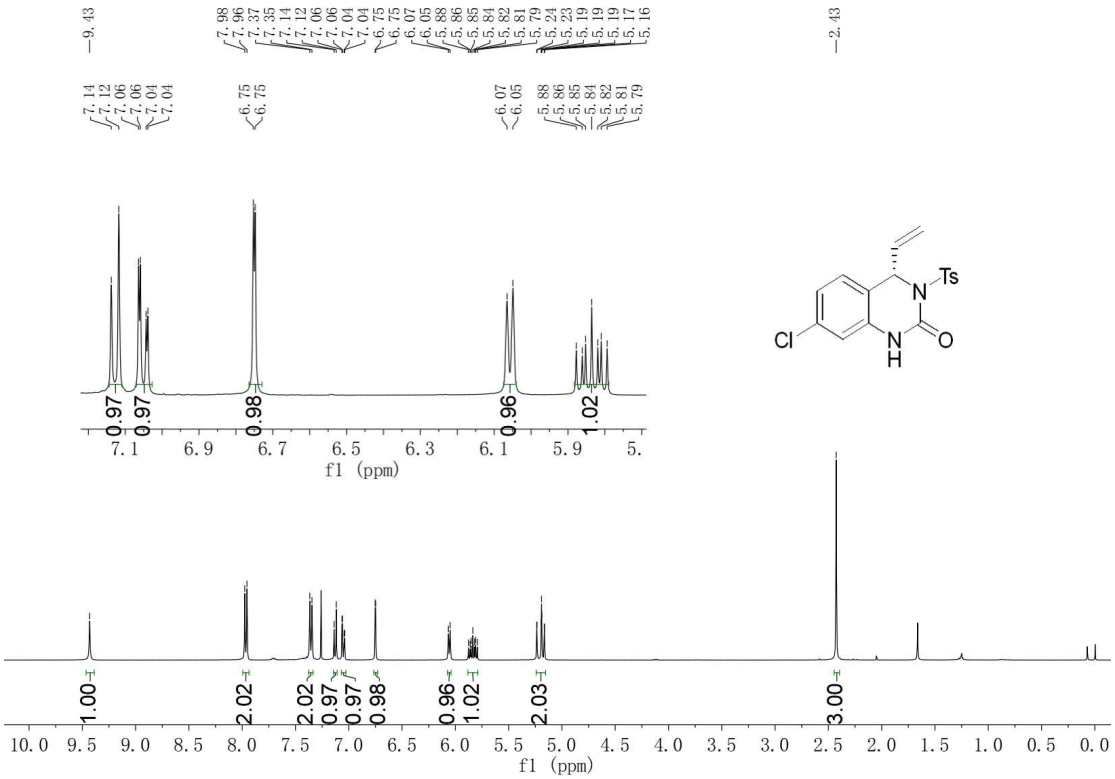
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3la**



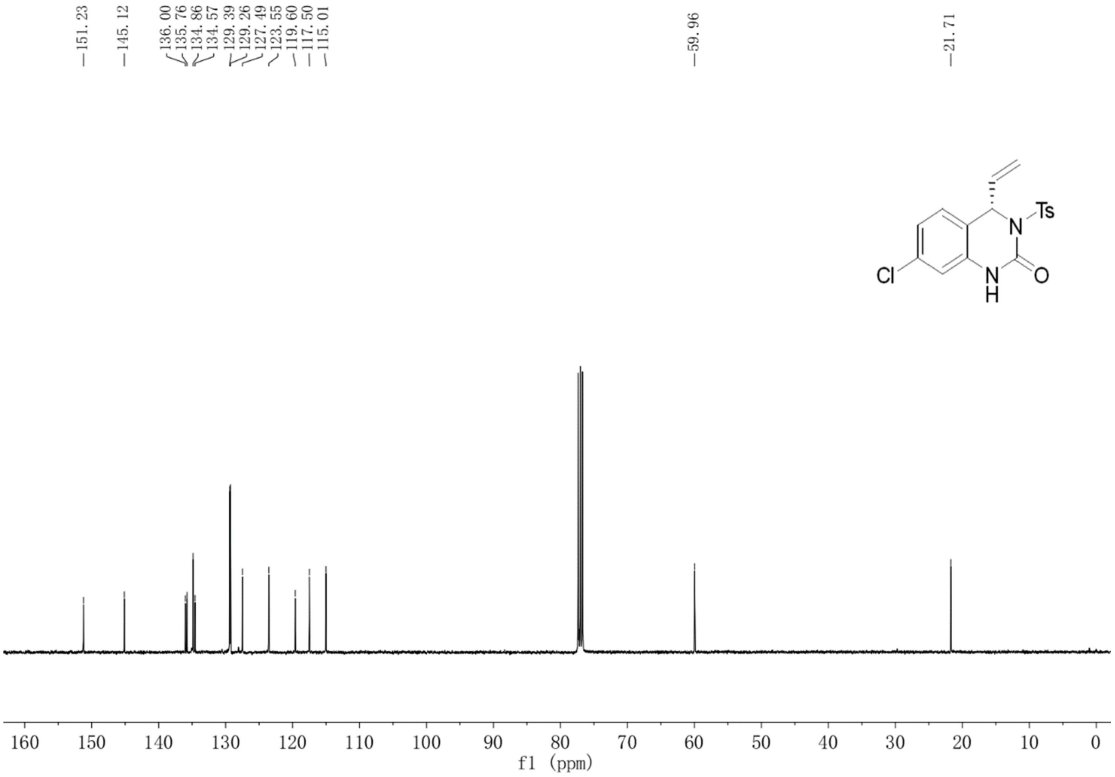
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3la**



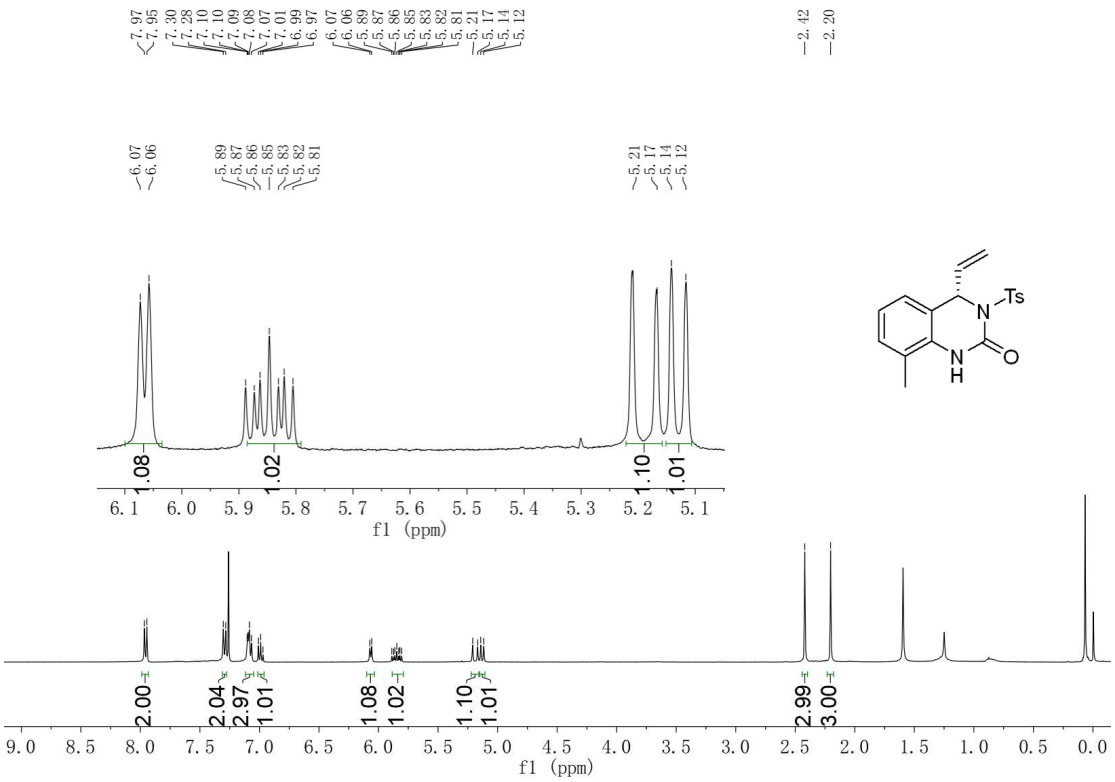
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ma**



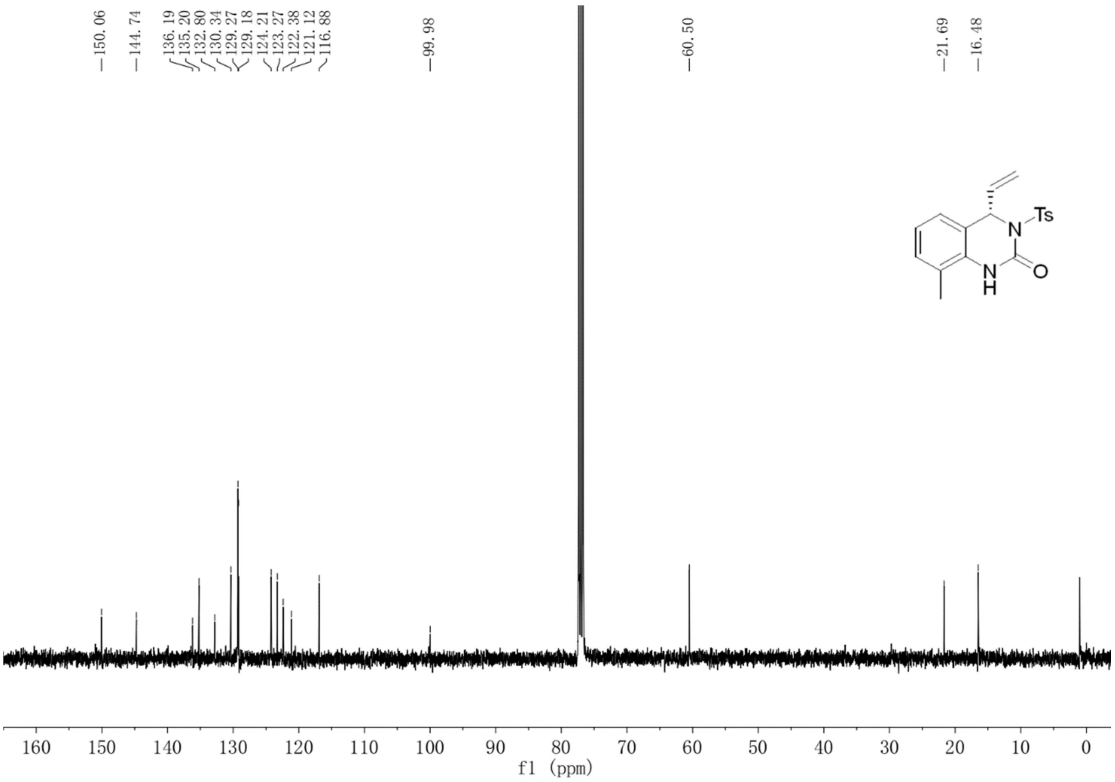
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ma**



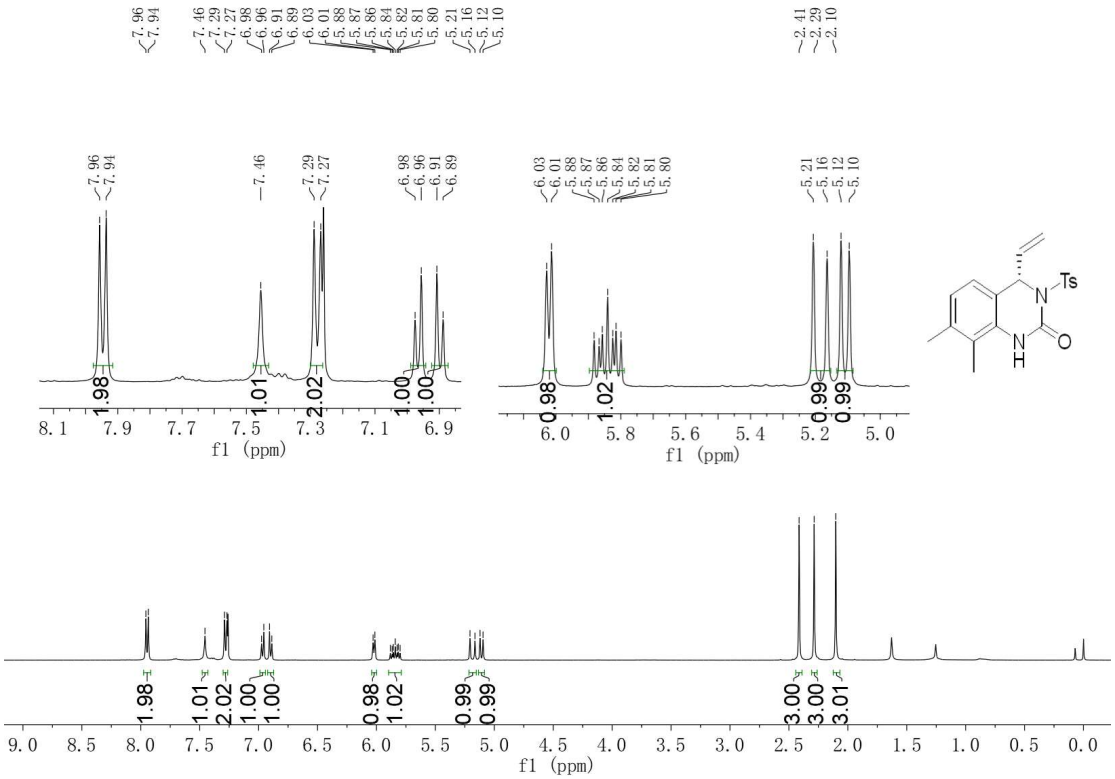
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3na**



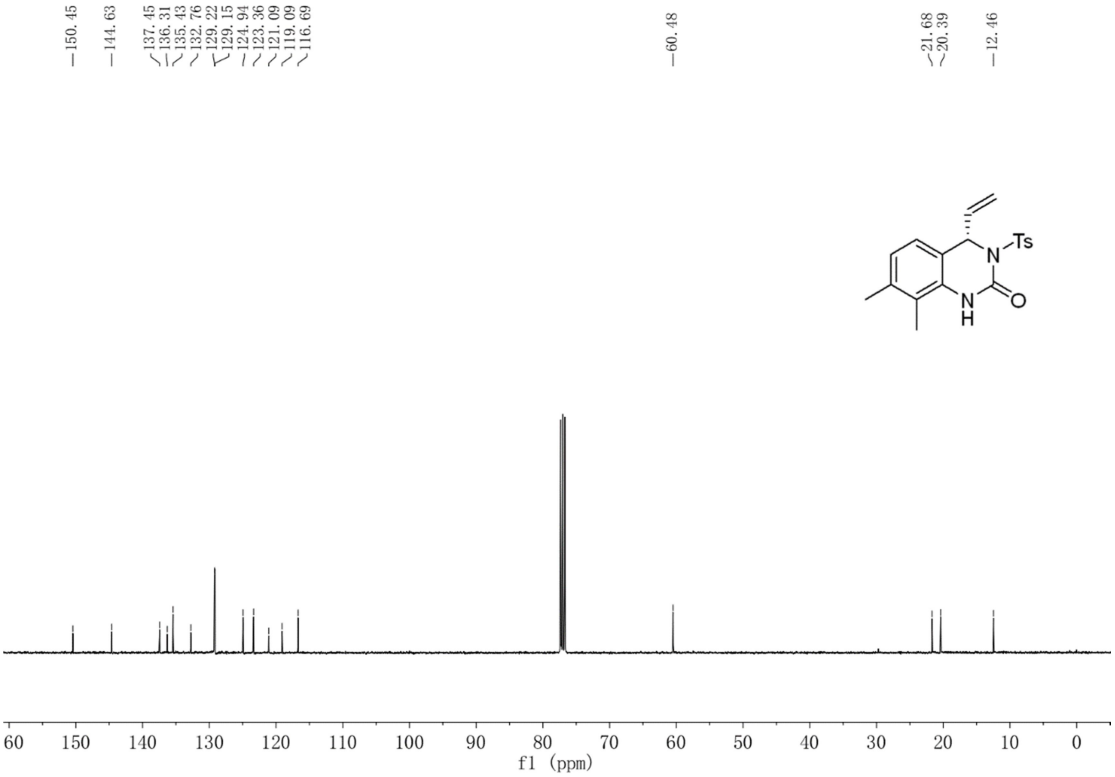
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3na**



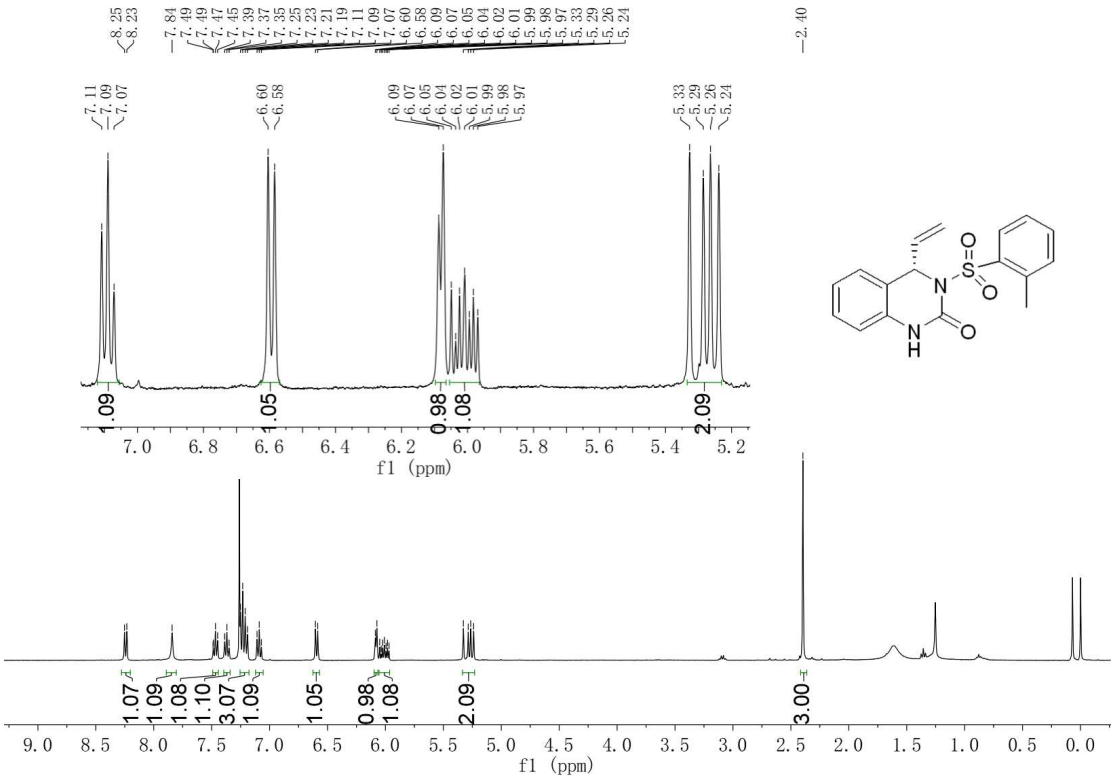
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3oa**



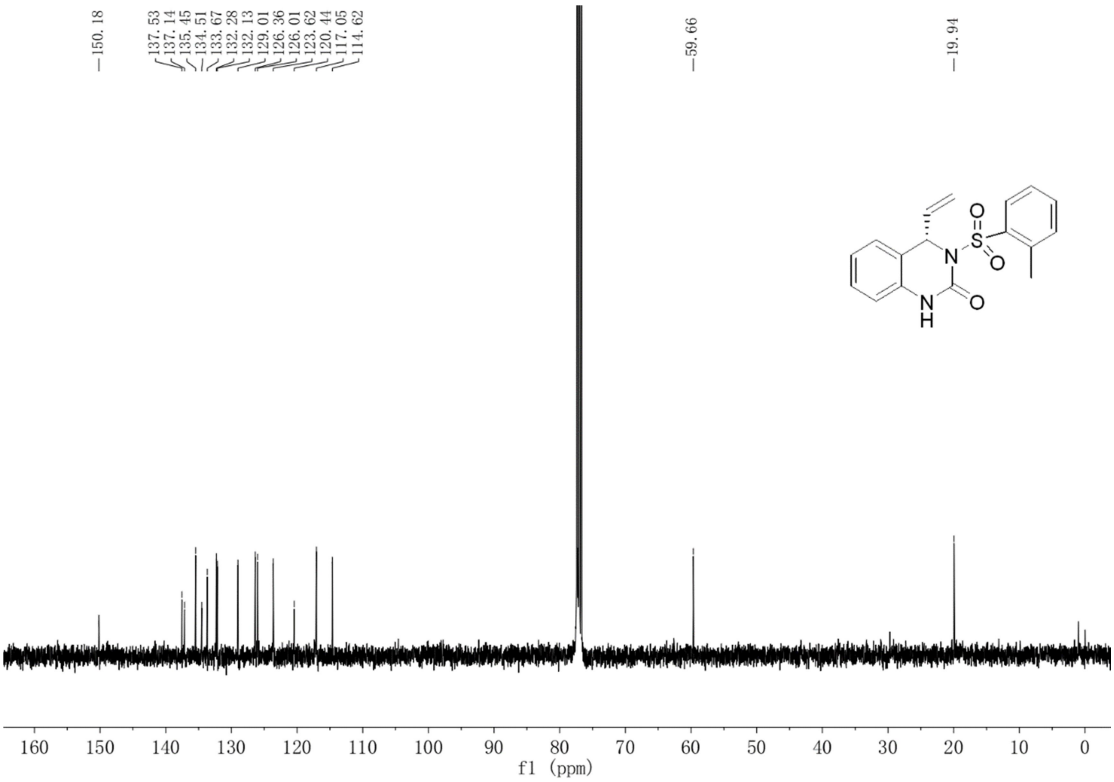
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3oa**



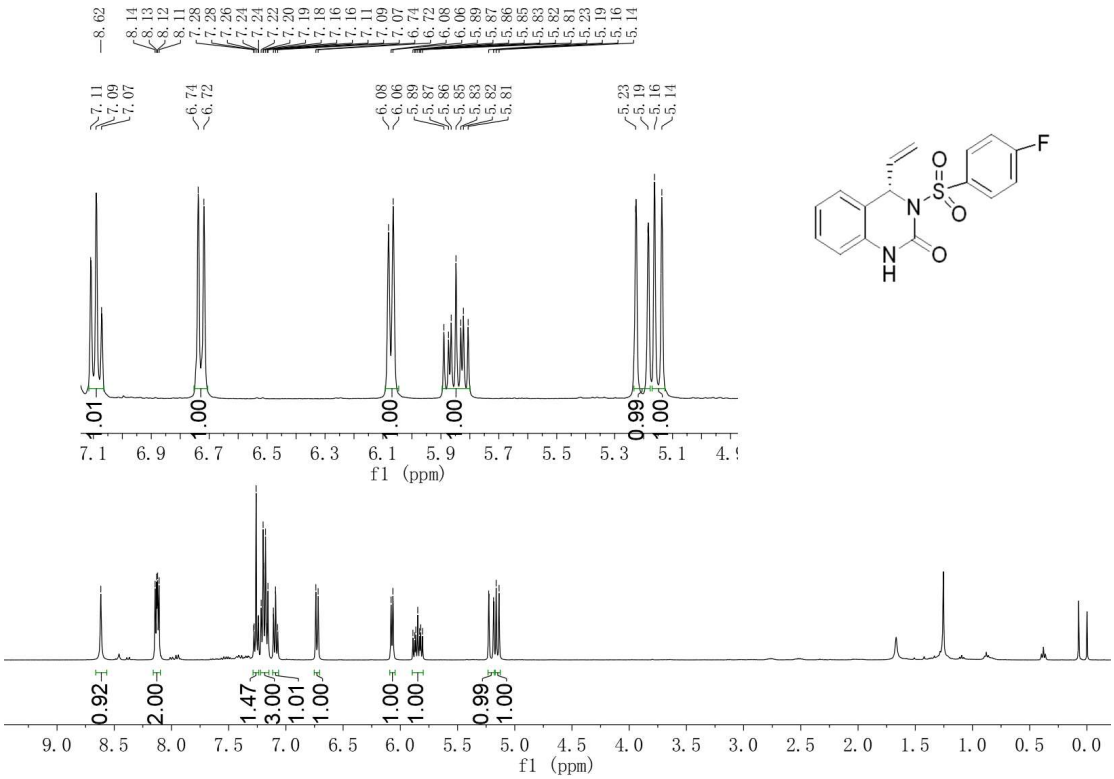
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab**



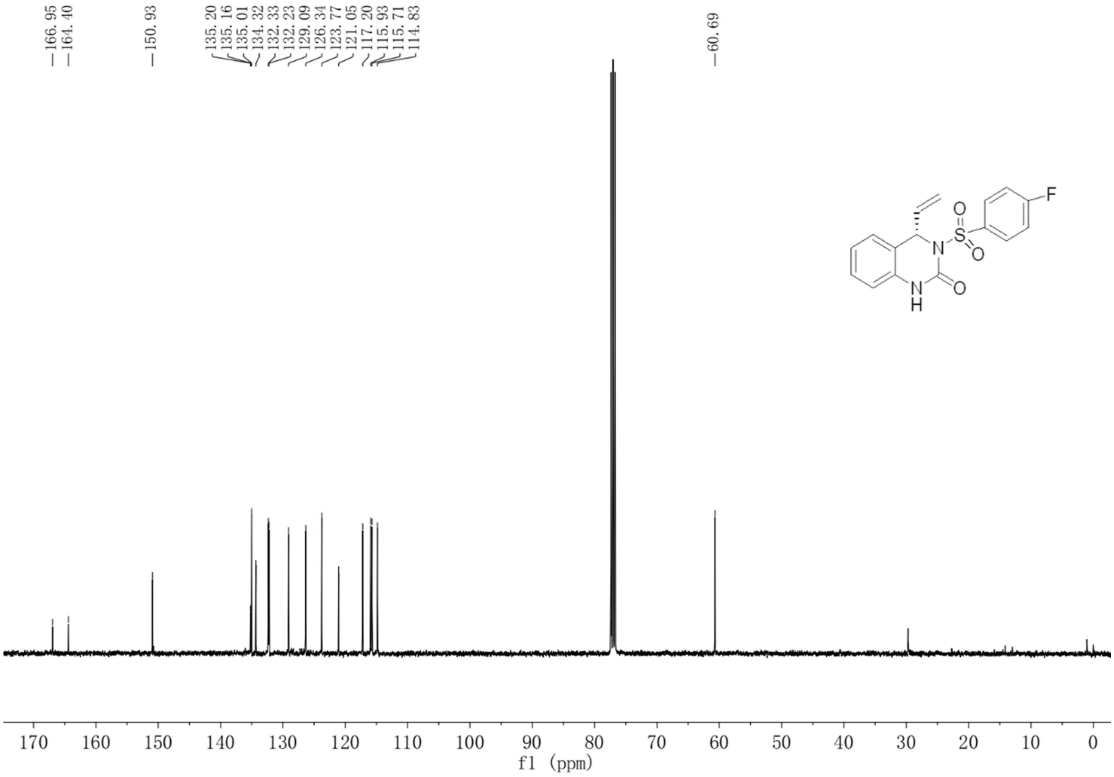
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ab**



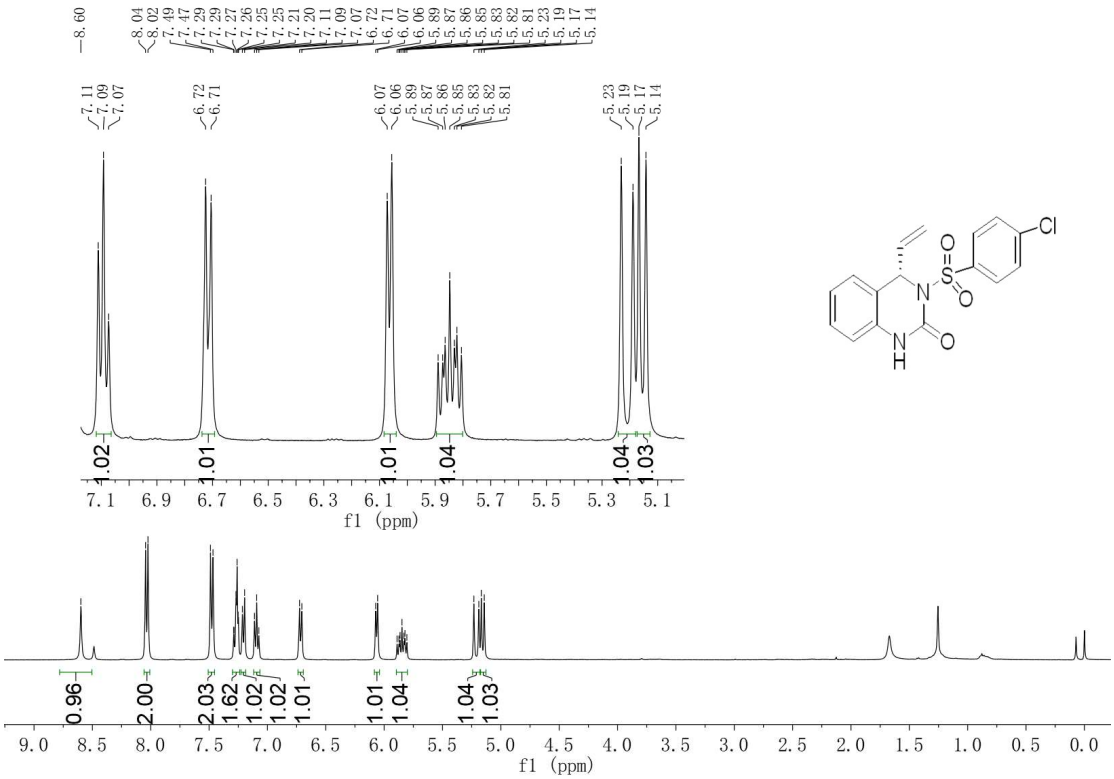
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac**



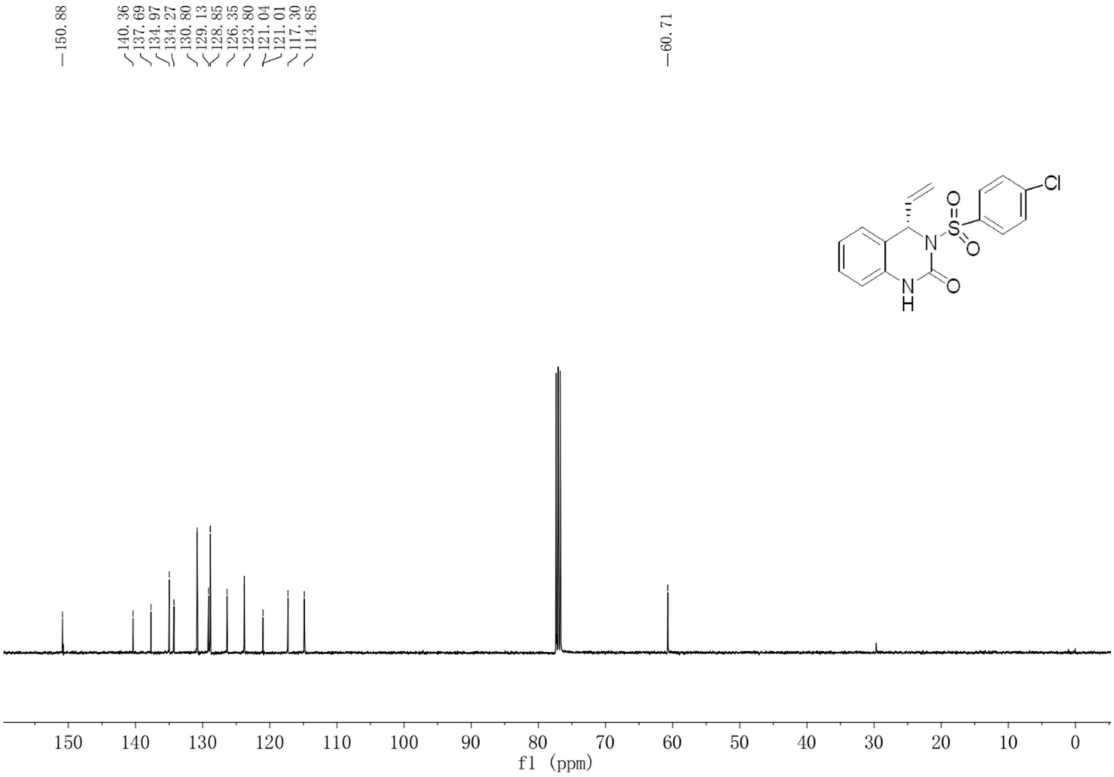
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ac**



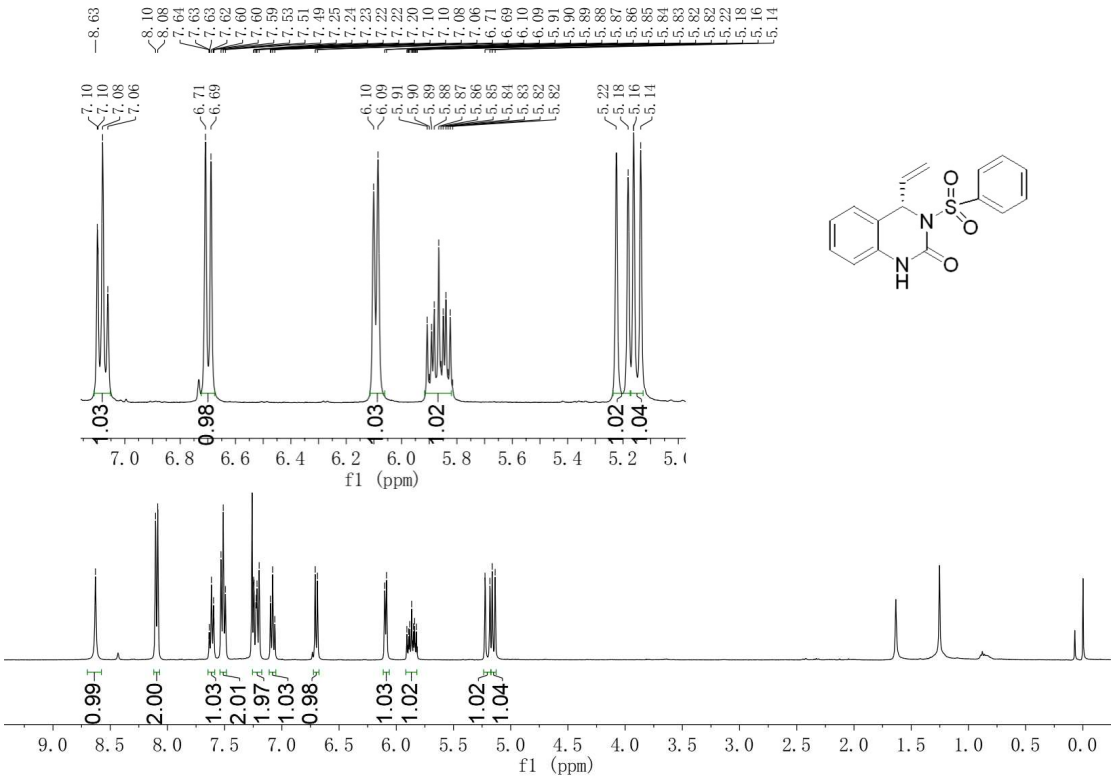
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad**



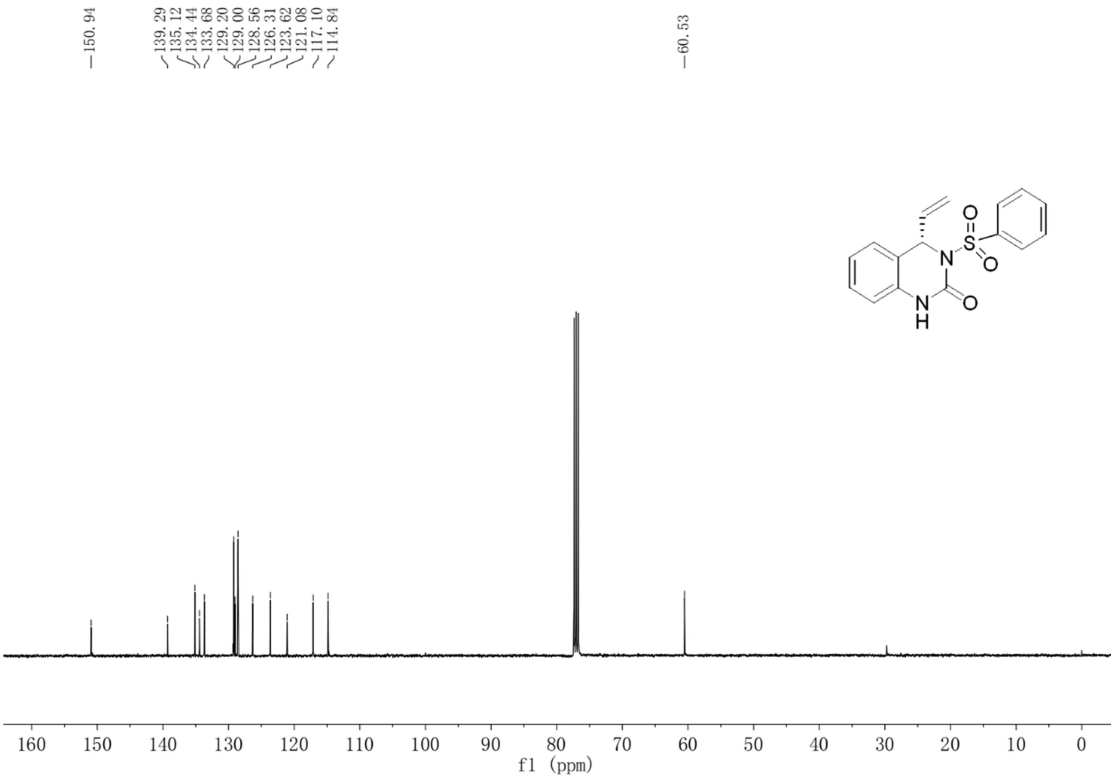
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ad**



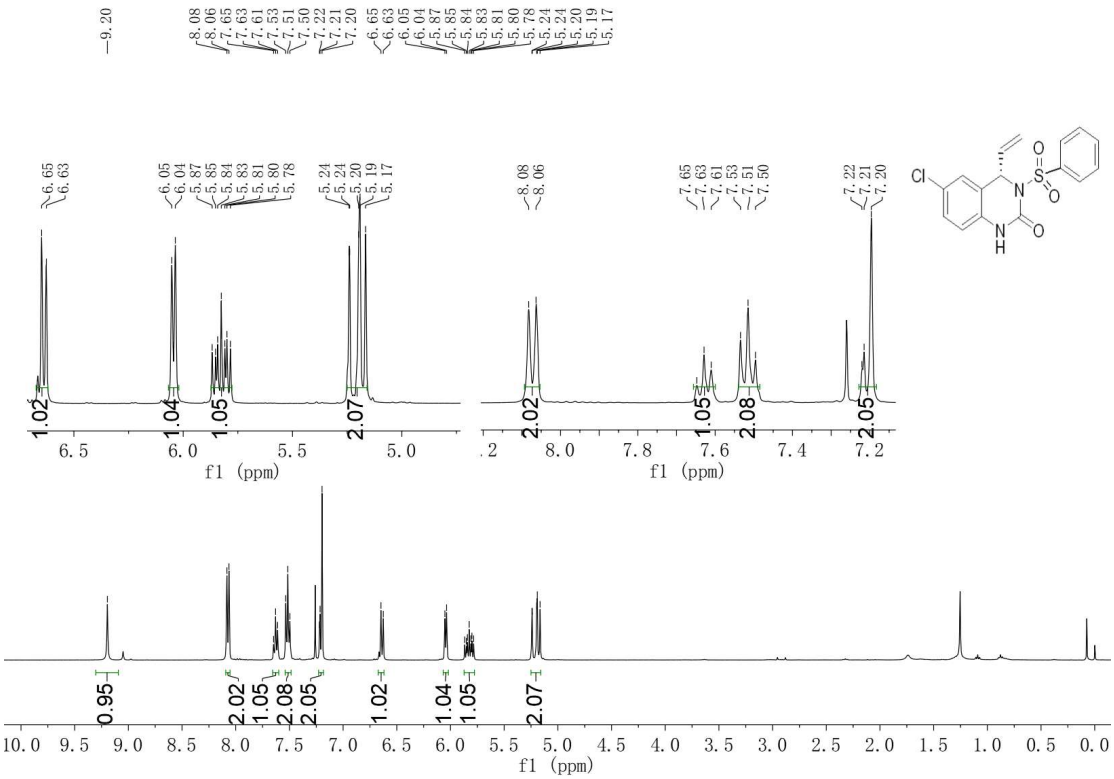
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ae**



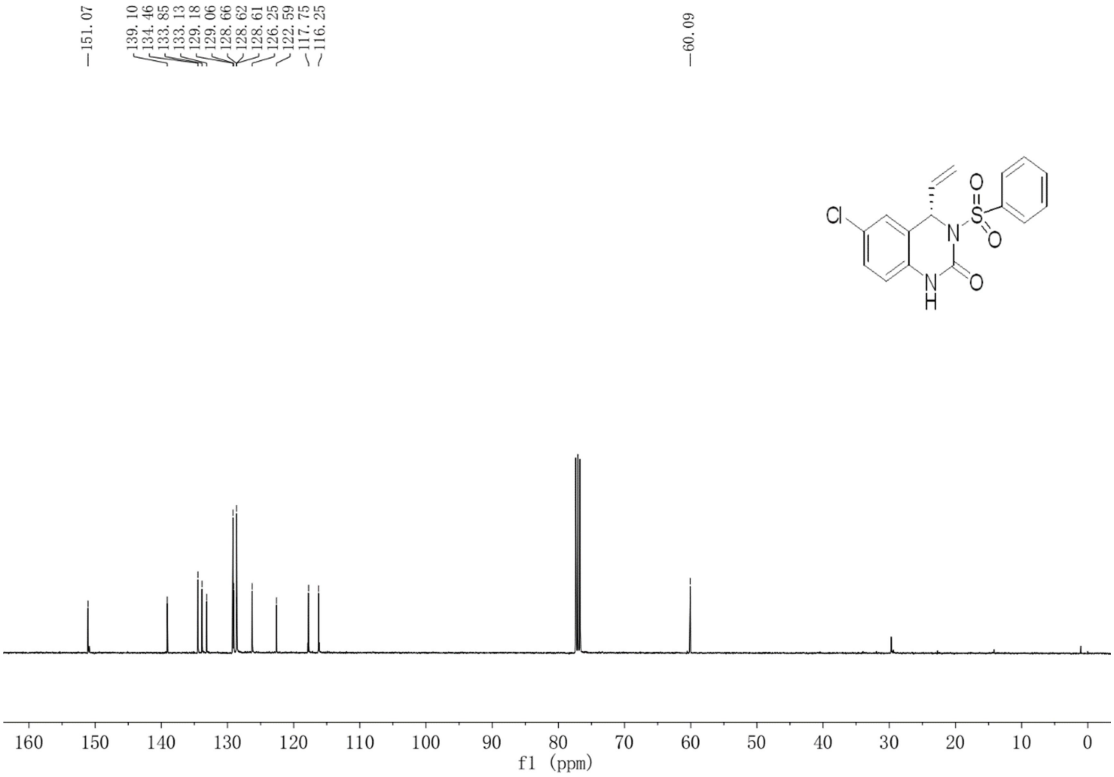
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ae**



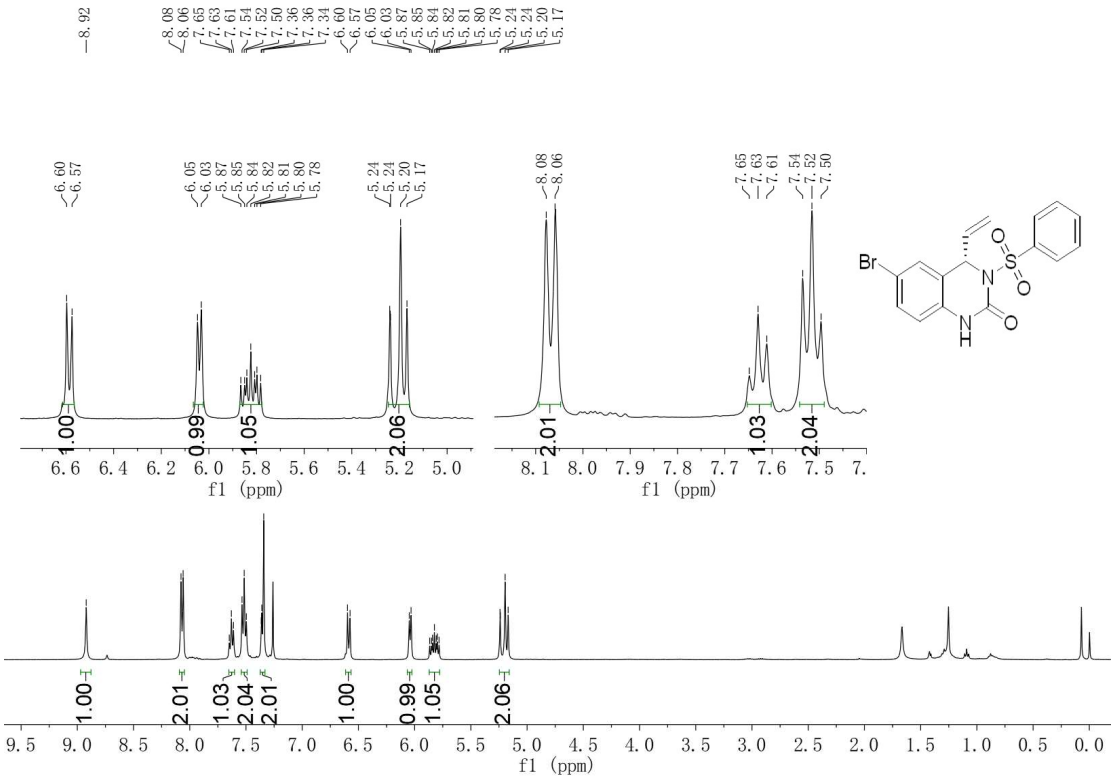
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3he**



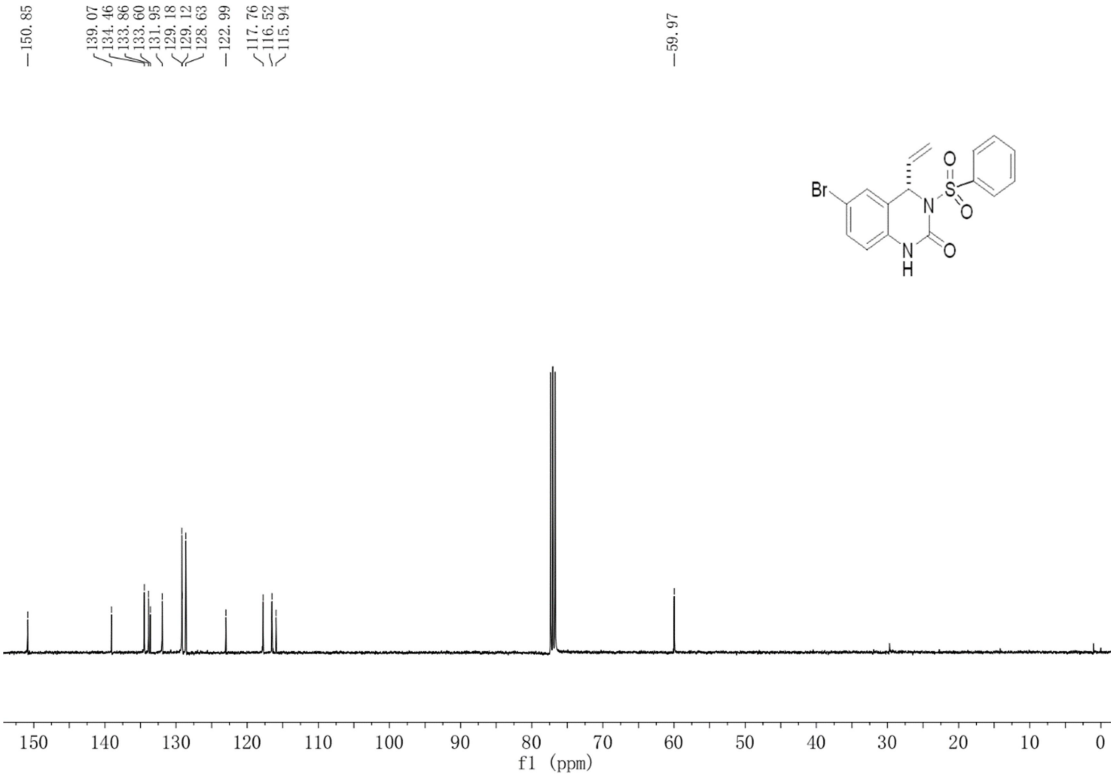
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3he**



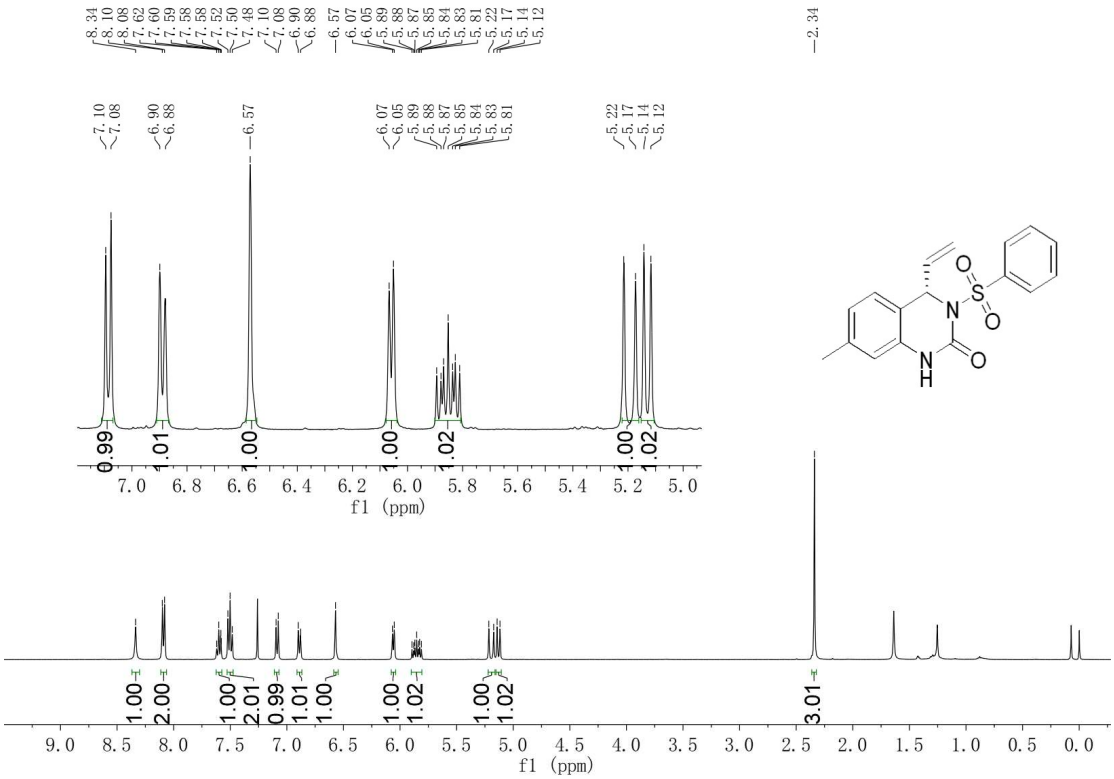
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ie**



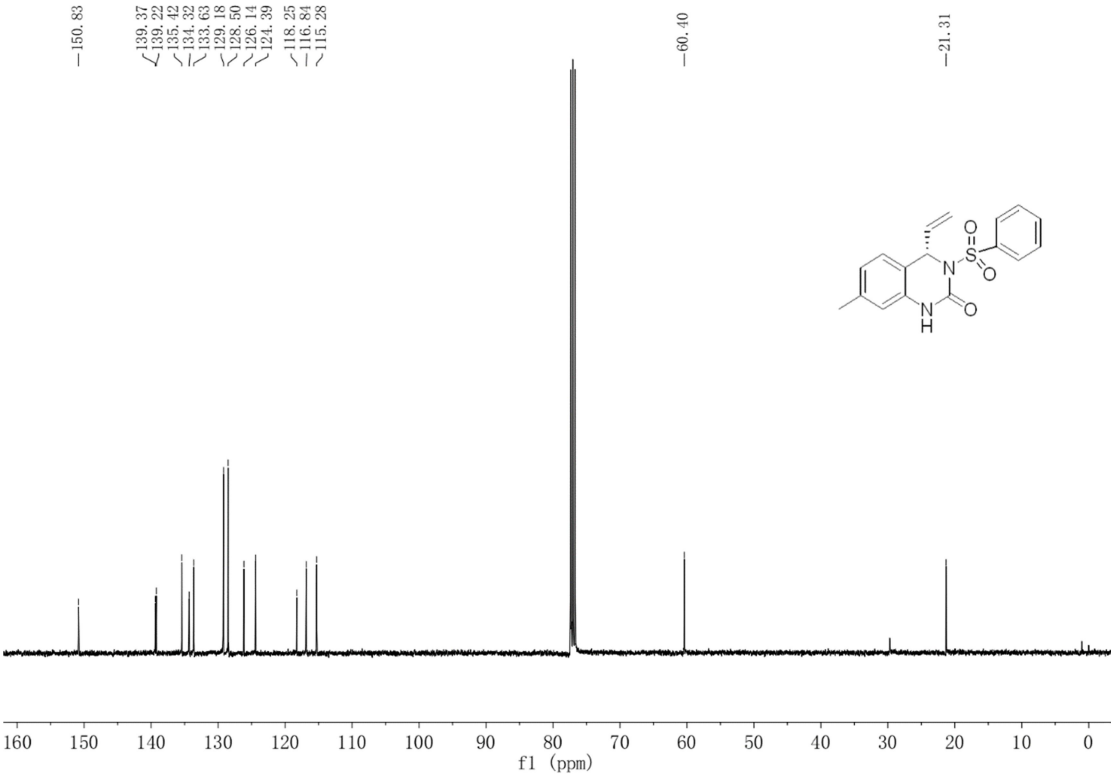
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ie**



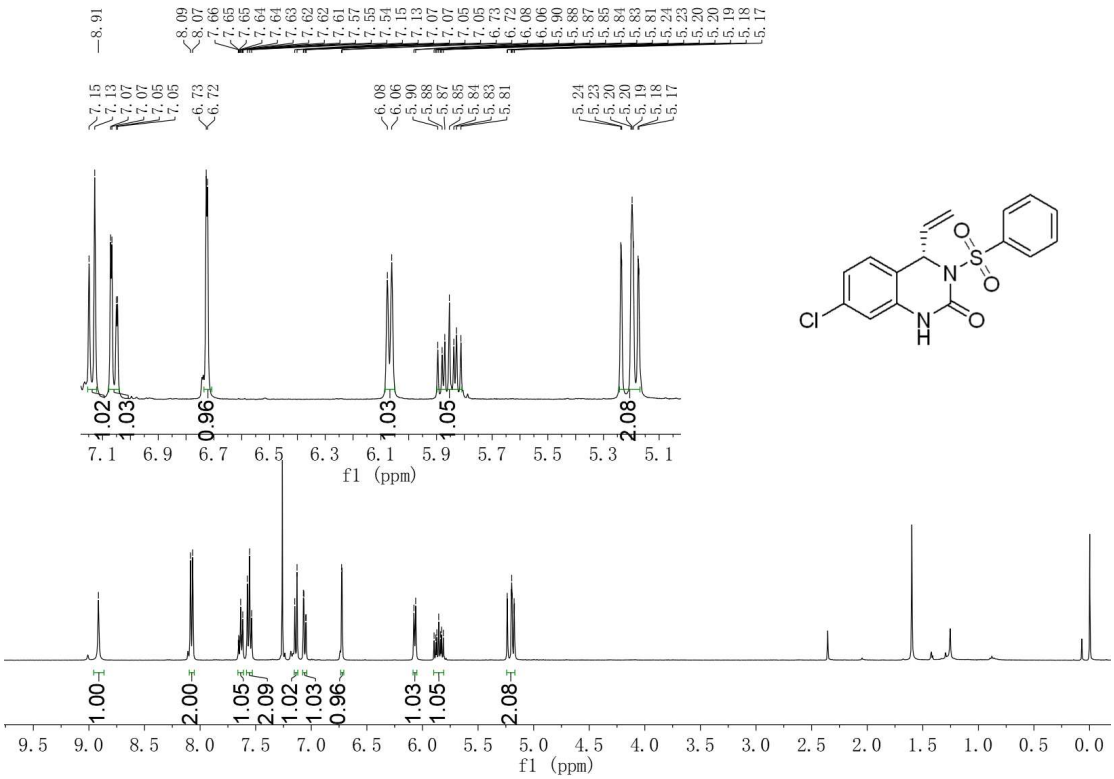
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3je**



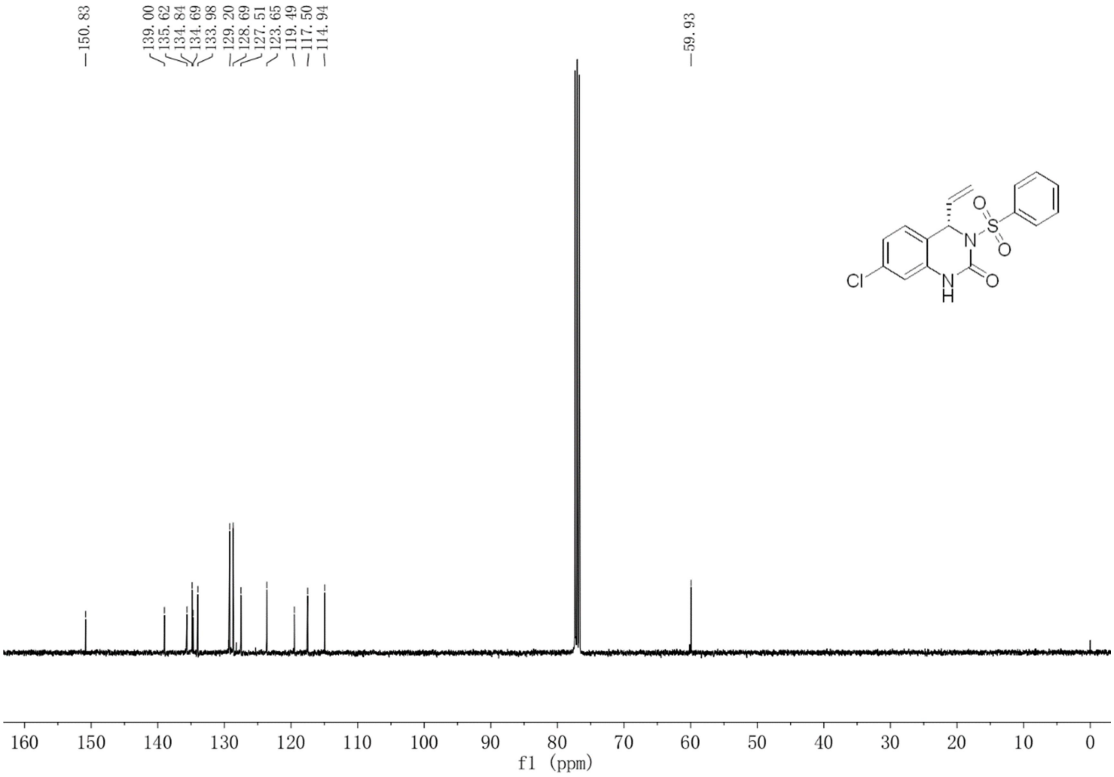
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3je**



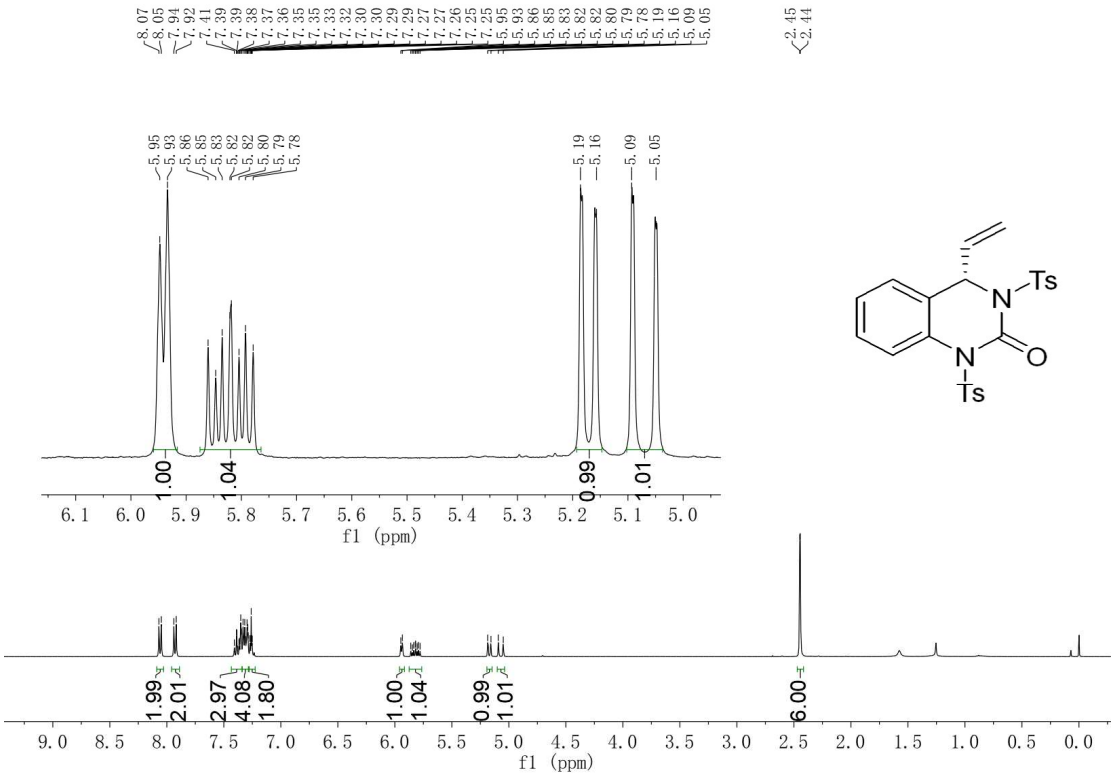
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3me**



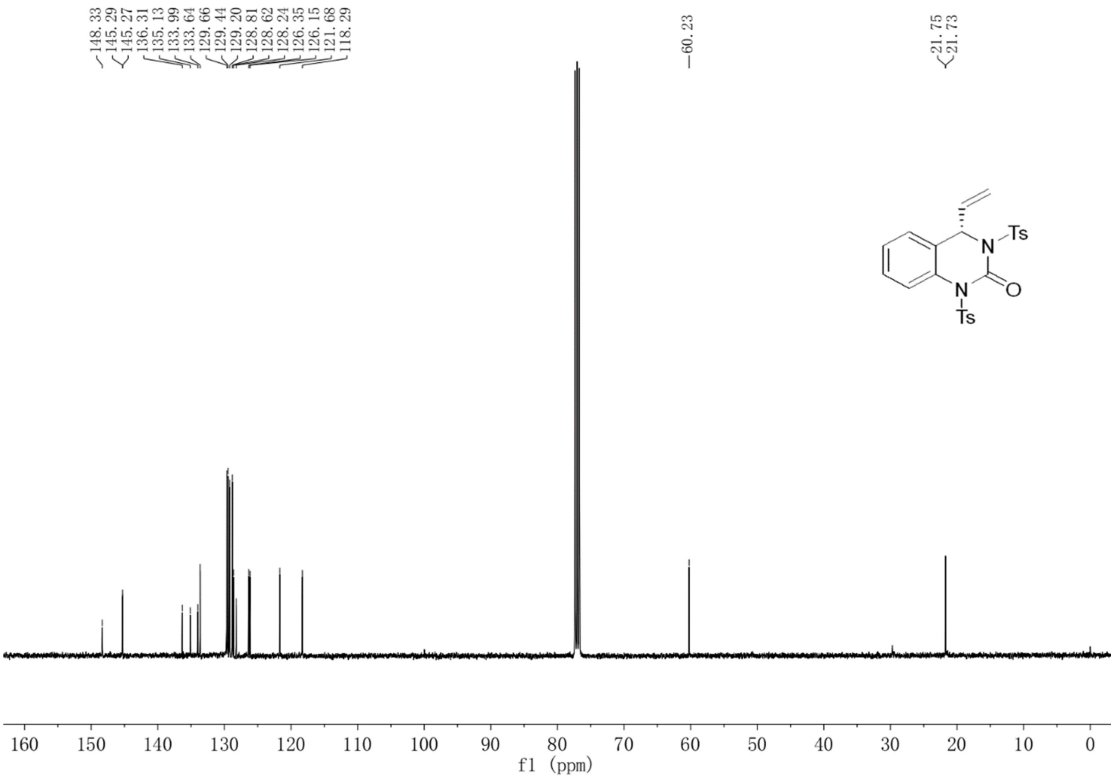
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3me**



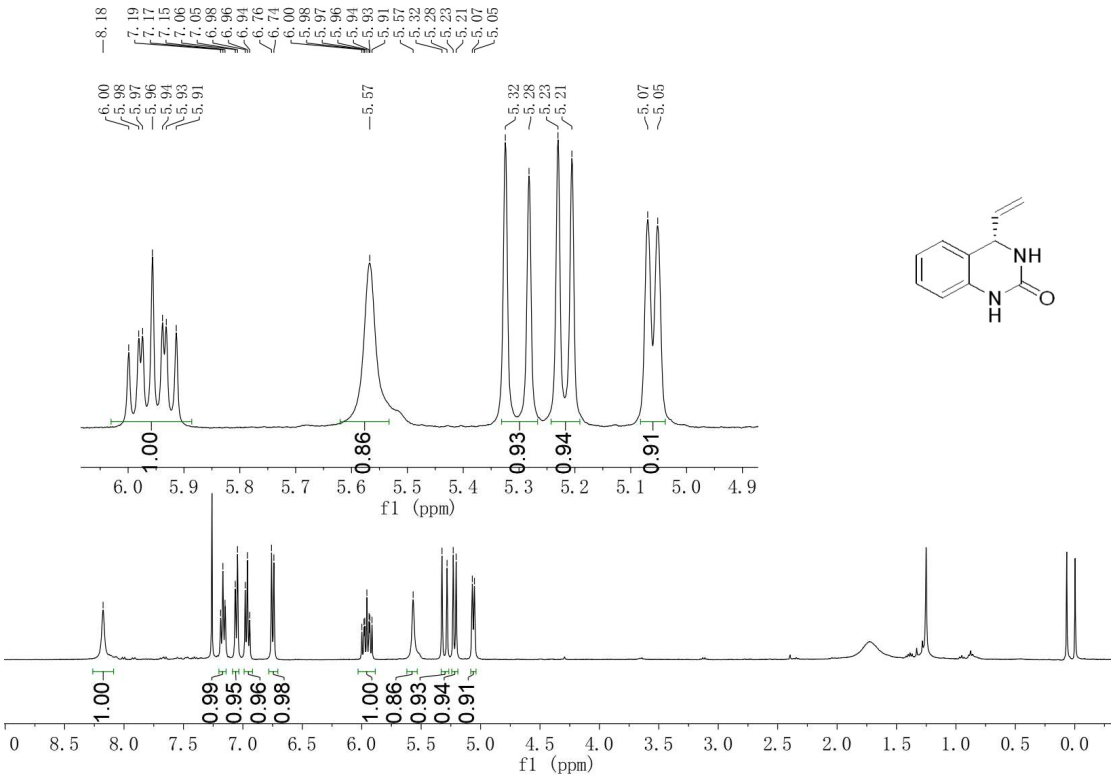
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3pa**



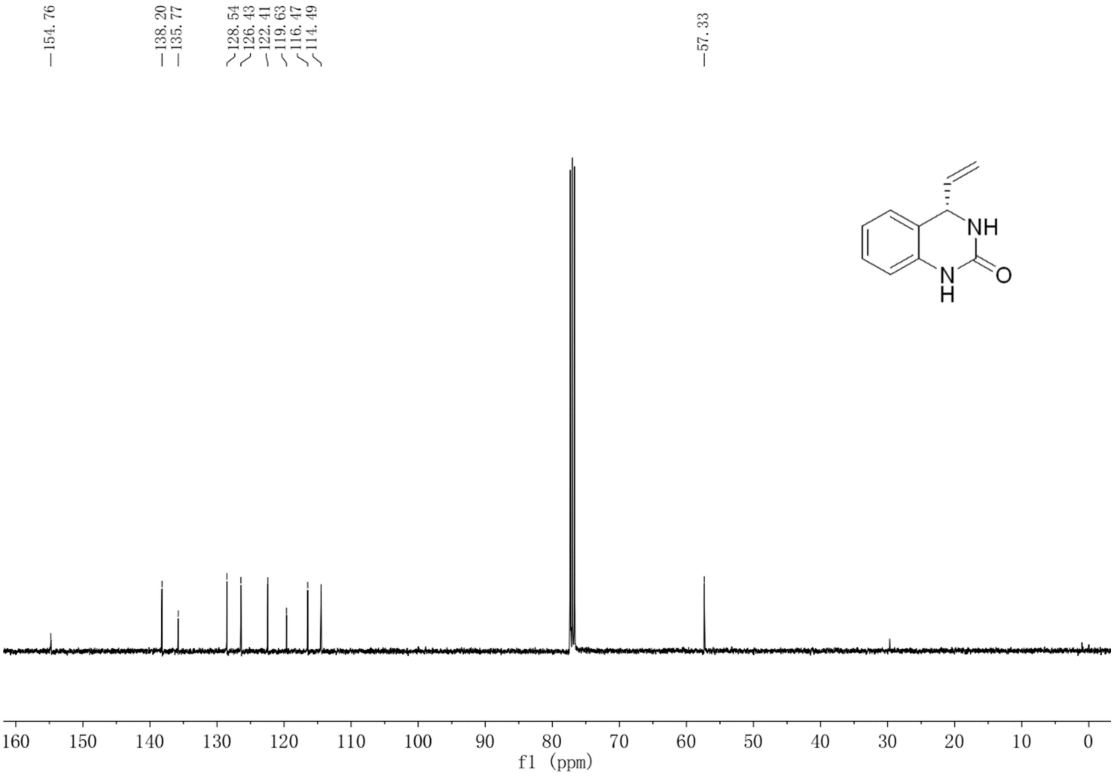
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3pa**



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

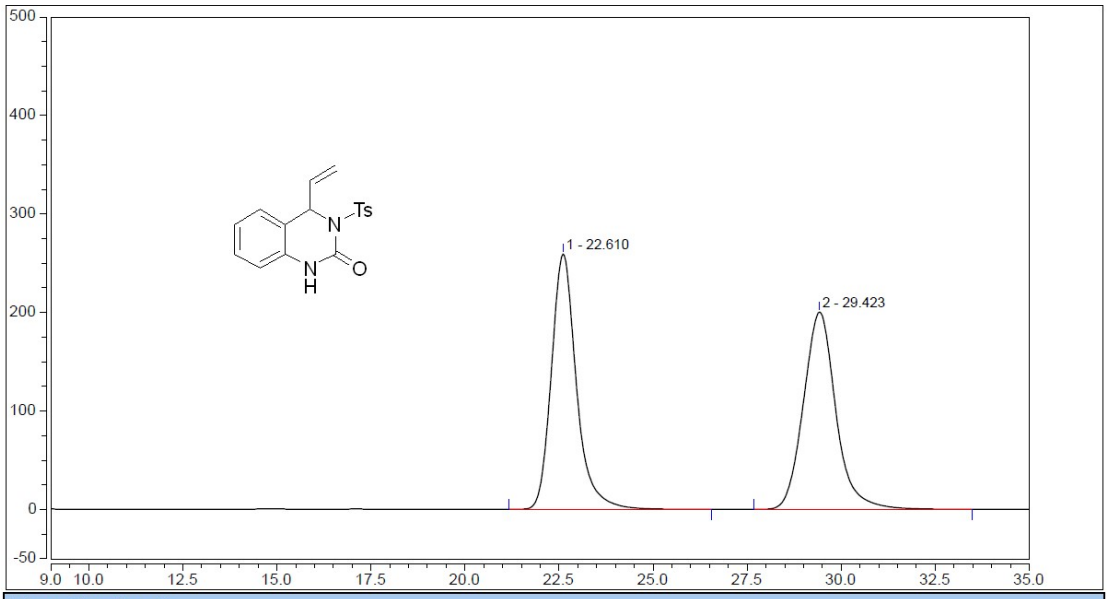


^{13}C NMR (100 MHz, $CDCl_3$) of compound **3qa**

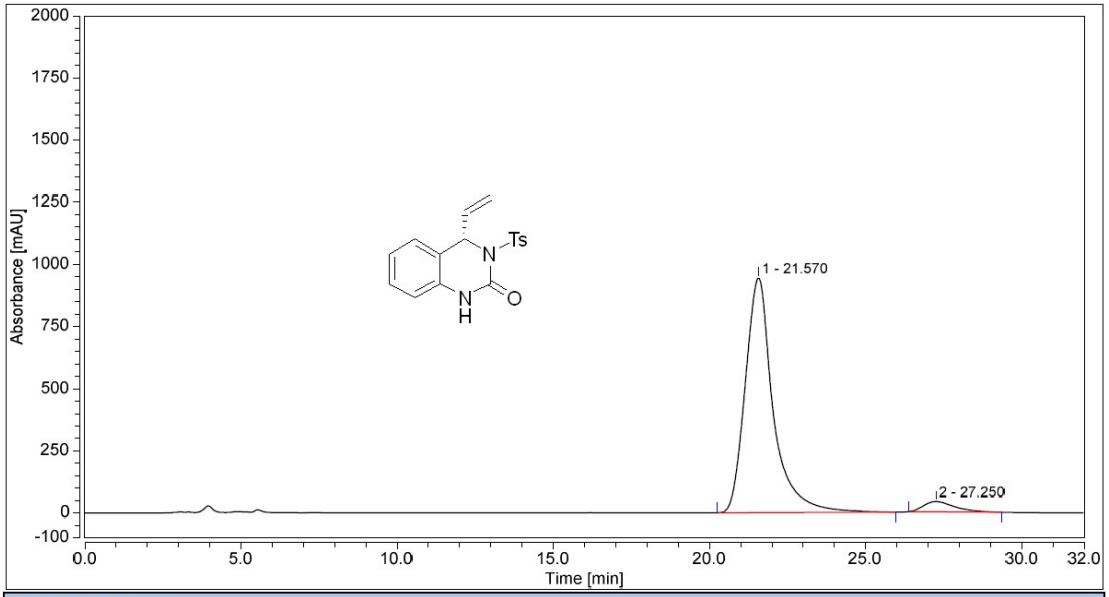


8. HPLC spectra of products 3

3aa

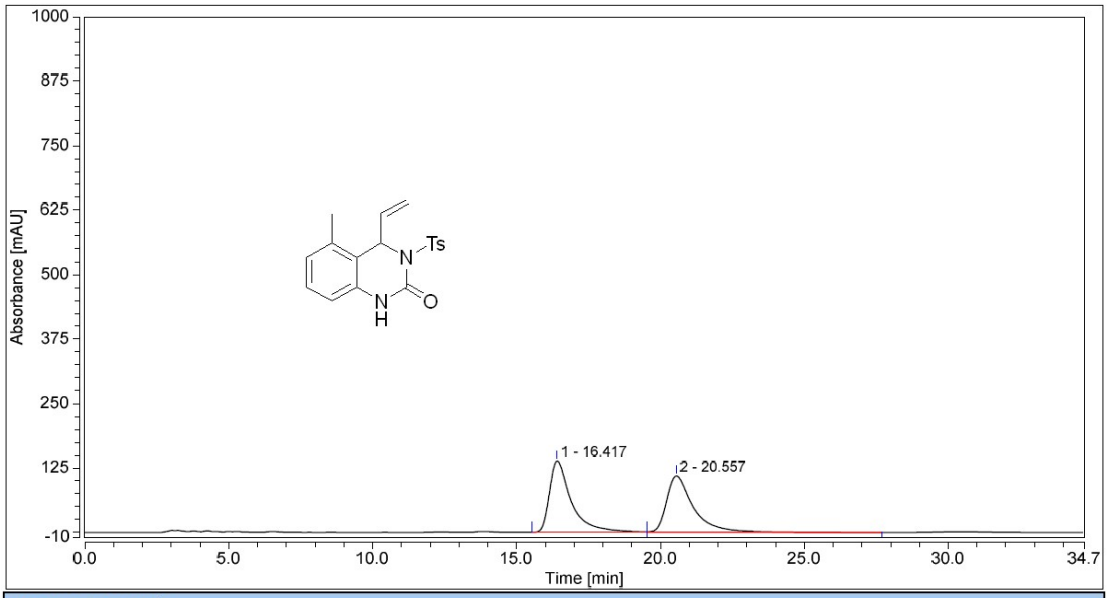


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.610	199.984	259.120	49.99	56.42	n.a.
2		29.423	200.062	200.184	50.01	43.58	n.a.
Total:			**400.046**	**459.304**	**100.00**	**100.00**	

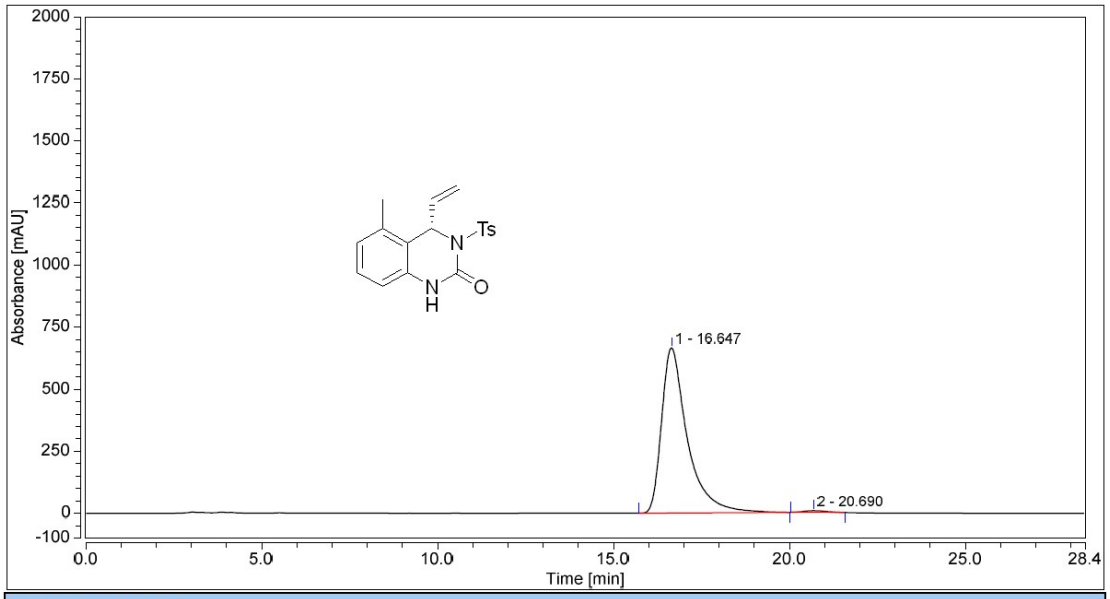


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.570	977.241	944.438	95.35	95.79	n.a.
2		27.250	47.678	41.516	4.65	4.21	n.a.
Total:			**1024.919**	**985.954**	**100.00**	**100.00**	

3ba

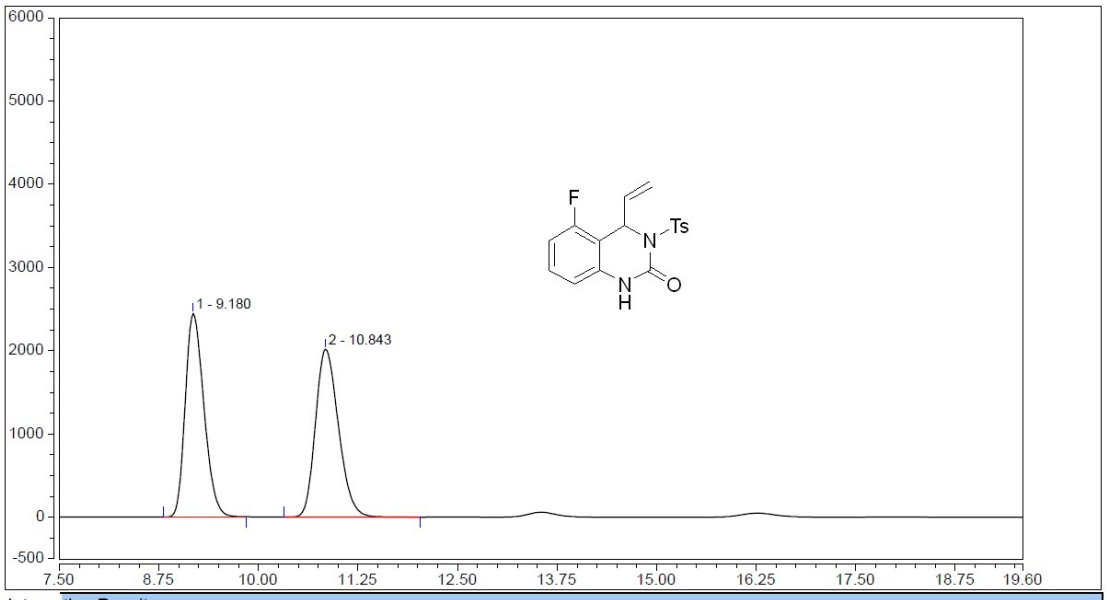


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.417	121.865	138.302	50.61	55.88	n.a.
2		20.557	118.934	109.190	49.39	44.12	n.a.
Total:			**240.799**	**247.491**	**100.00**	**100.00**	



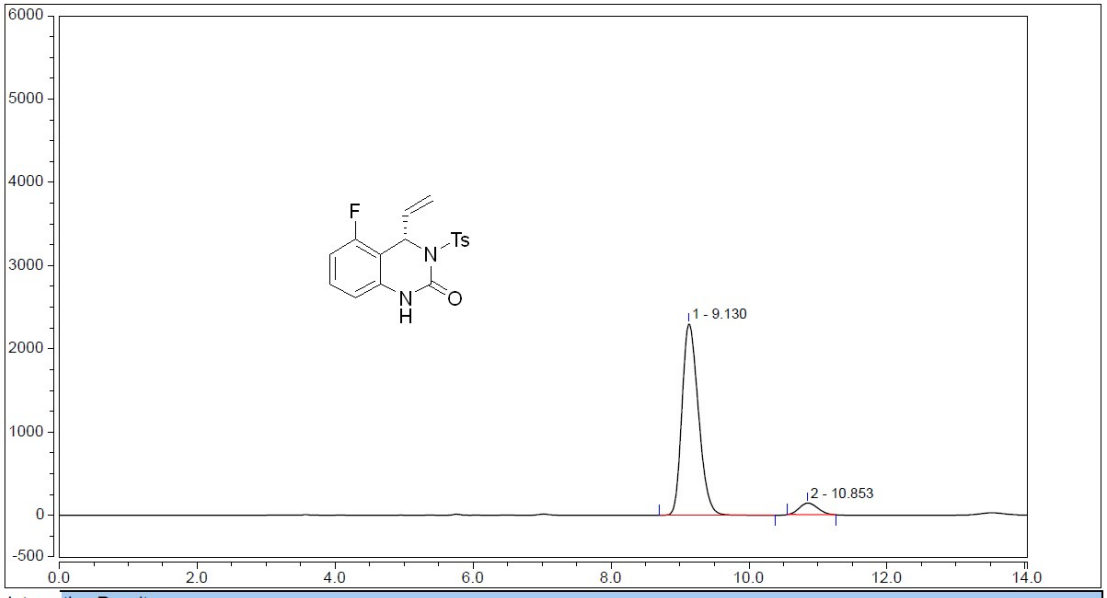
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.647	563.617	664.835	99.11	99.02	n.a.
2		20.690	5.055	6.554	0.89	0.98	n.a.
Total:			**568.672**	**671.389**	**100.00**	**100.00**	

3ca



Integration Results

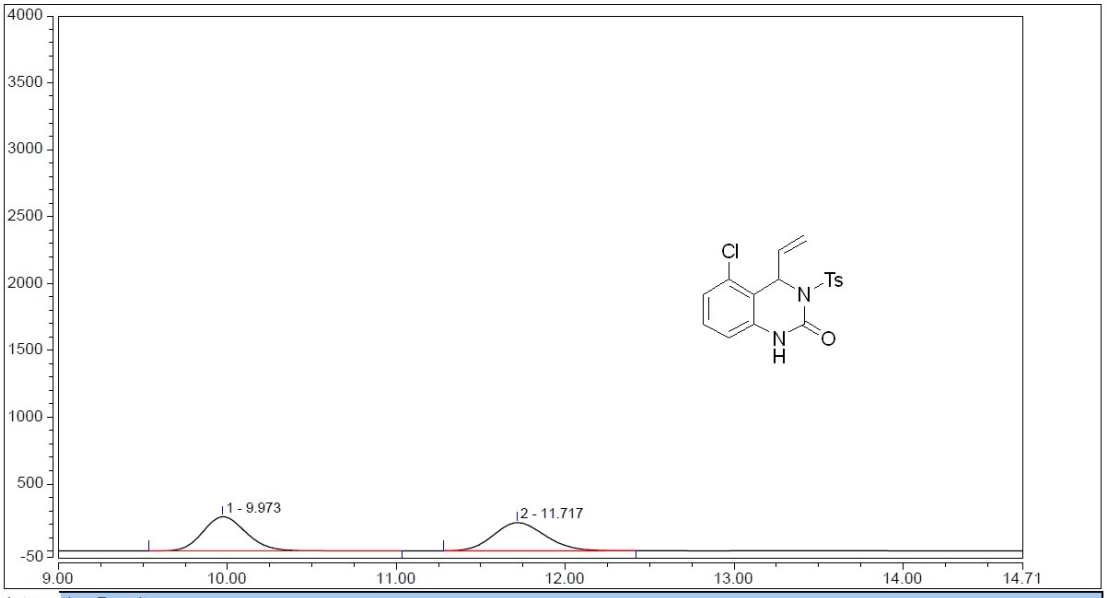
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.180	667.000	2444.652	49.69	54.79	n.a.
2		10.843	675.398	2017.195	50.31	45.21	n.a.
Total:			**1342.398**	**4461.846**	**100.00**	**100.00**	



Integration Results

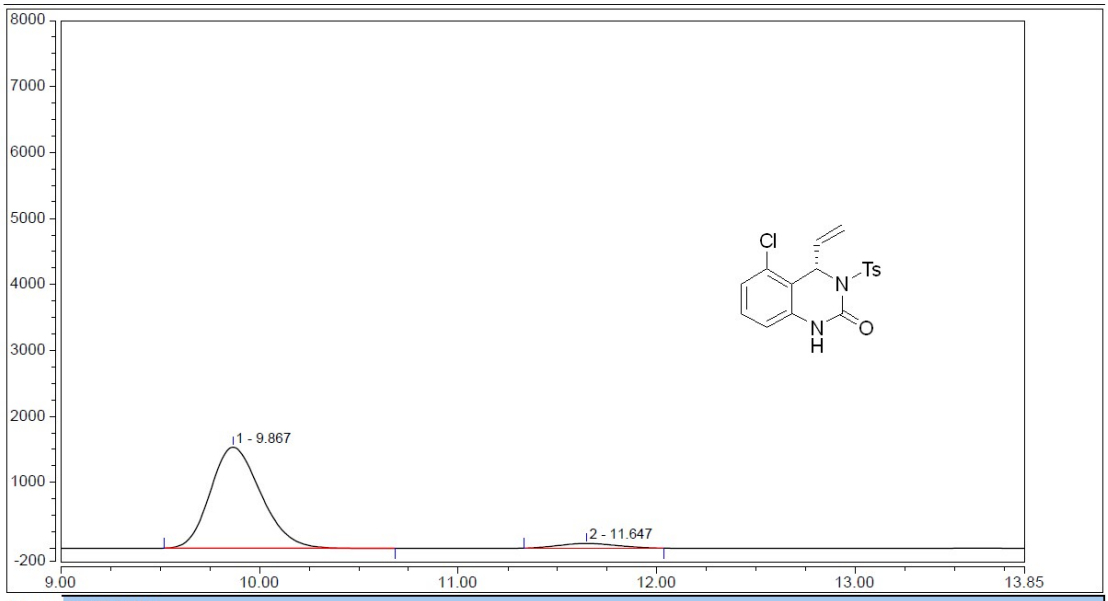
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.130	635.719	2302.345	93.59	94.27	n.a.
2		10.853	43.537	140.063	6.41	5.73	n.a.
Total:			**679.256**	**2442.409**	**100.00**	**100.00**	

3da



Integration Results

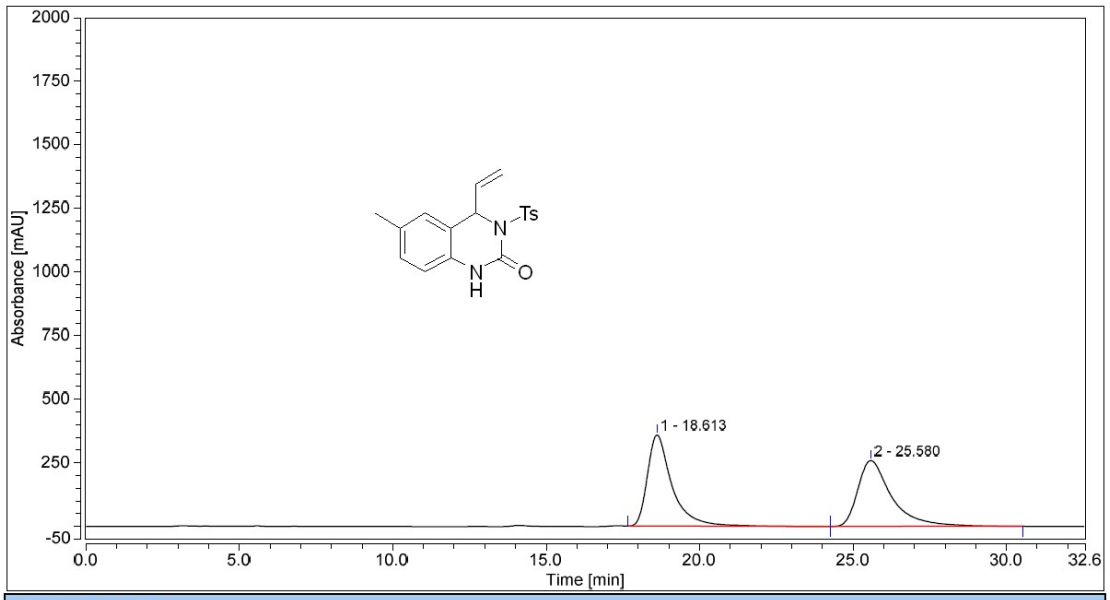
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.973	75.840	254.987	50.44	54.82	n.a.
2		11.717	74.526	210.139	49.56	45.18	n.a.
Total:			**150.366**	**465.126**	**100.00**	**100.00**	



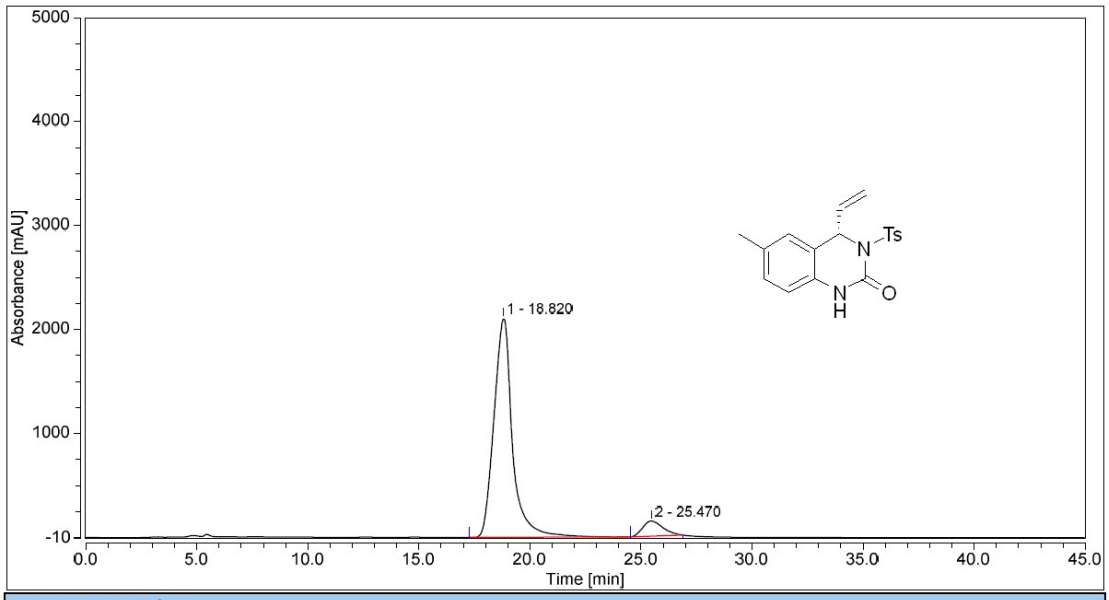
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.867	452.257	1530.634	95.08	95.61	n.a.
2		11.647	23.396	70.219	4.92	4.39	n.a.
Total:			**475.654**	**1600.853**	**100.00**	**100.00**	

3ea

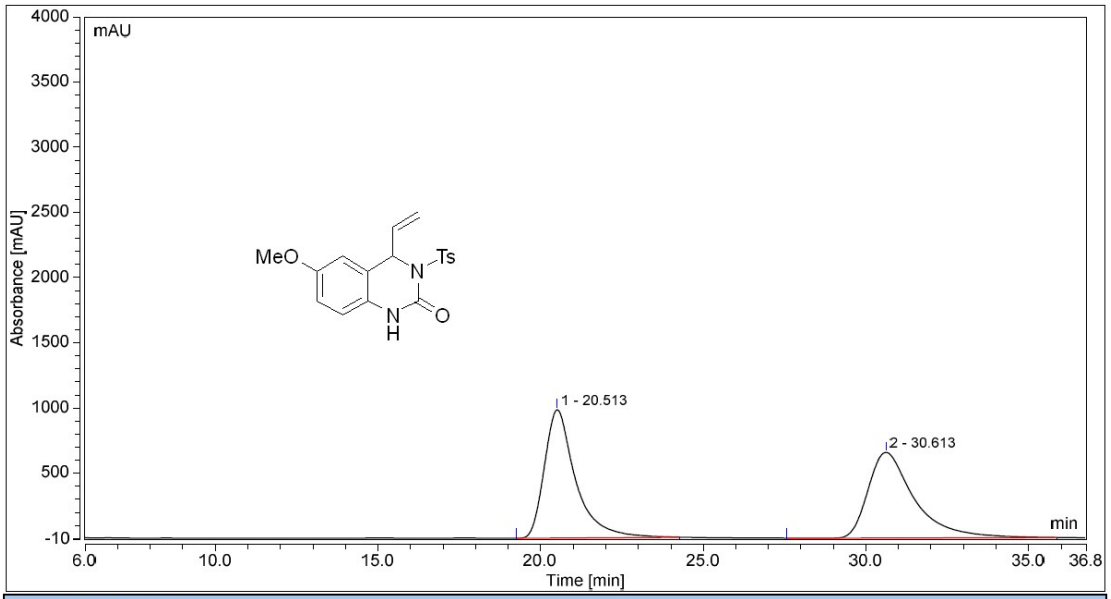


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.613	332.630	358.382	49.97	58.01	n.a.
2		25.580	333.005	259.434	50.03	41.99	n.a.
Total:			**665.635**	**617.815**	**100.00**	**100.00**	

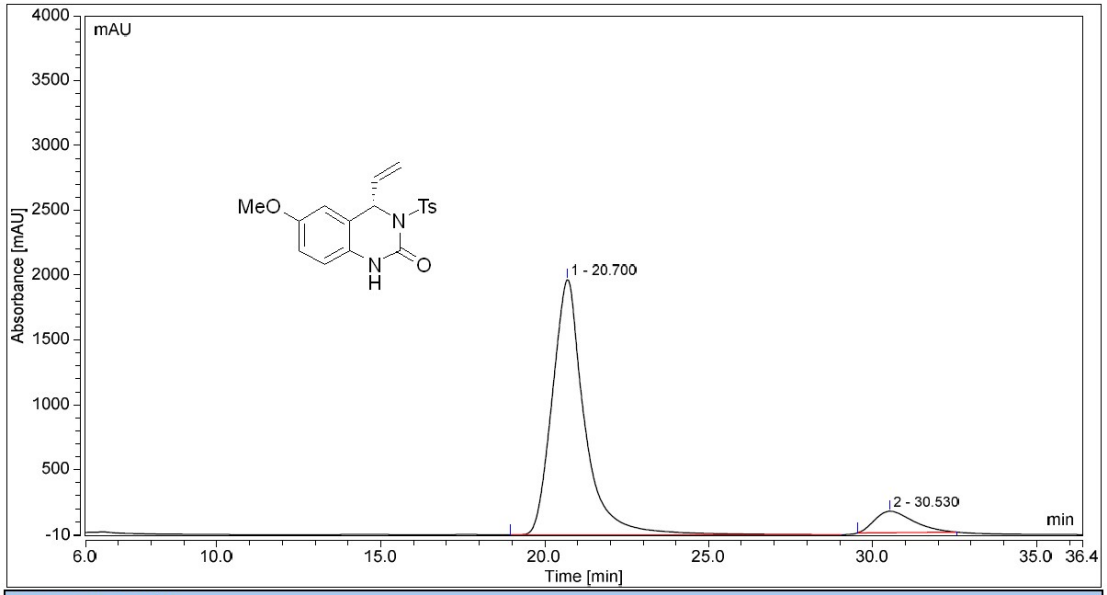


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.820	2024.928	2105.349	92.94	93.53	n.a.
2		25.470	153.841	145.642	7.06	6.47	n.a.
Total:			**2178.769**	**2250.992**	**100.00**	**100.00**	

3fa

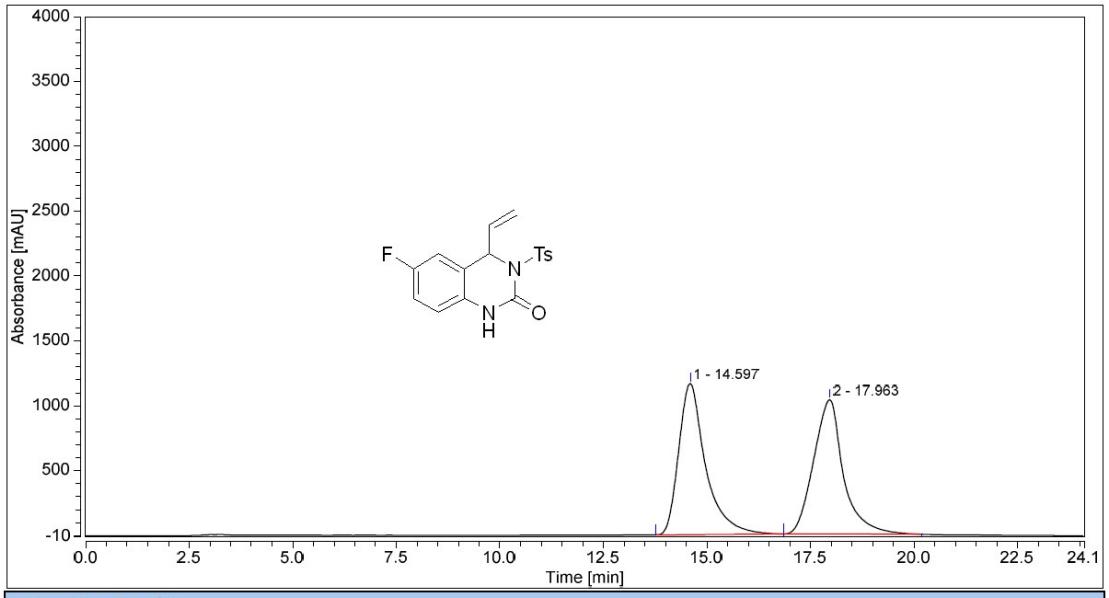


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.513	1094.677	984.303	50.44	59.97	n.a.
2		30.613	1075.694	656.918	49.56	40.03	n.a.
Total:			**2170.371**	**1641.220**	**100.00**	**100.00**	



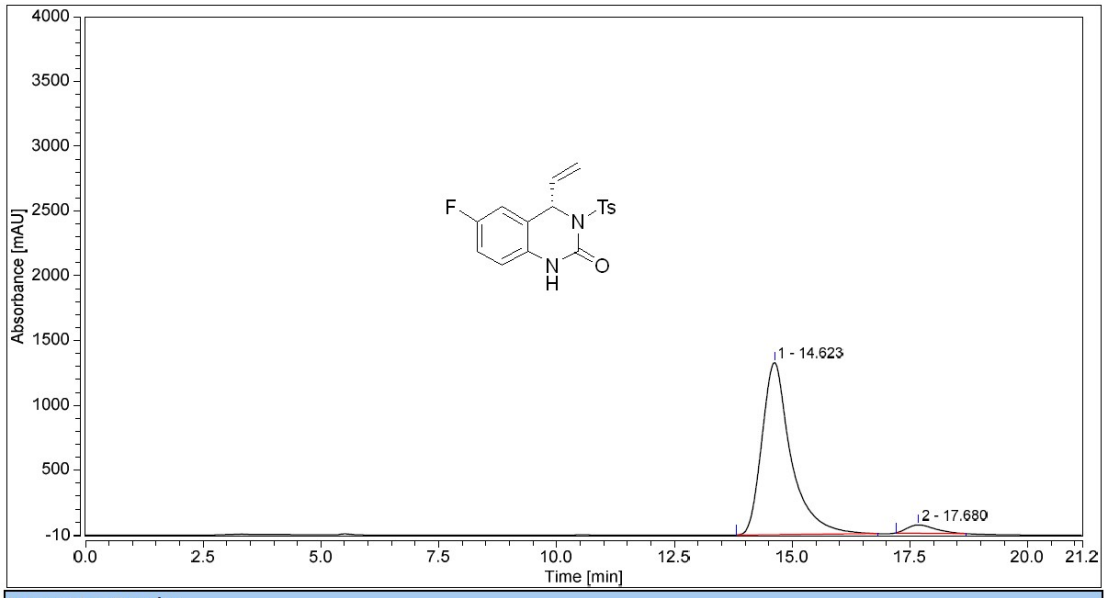
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.700	2236.139	1967.686	90.83	92.24	n.a.
2		30.530	225.891	165.489	9.17	7.76	n.a.
Total:			**2462.030**	**2133.175**	**100.00**	**100.00**	

3ga



Integration Results

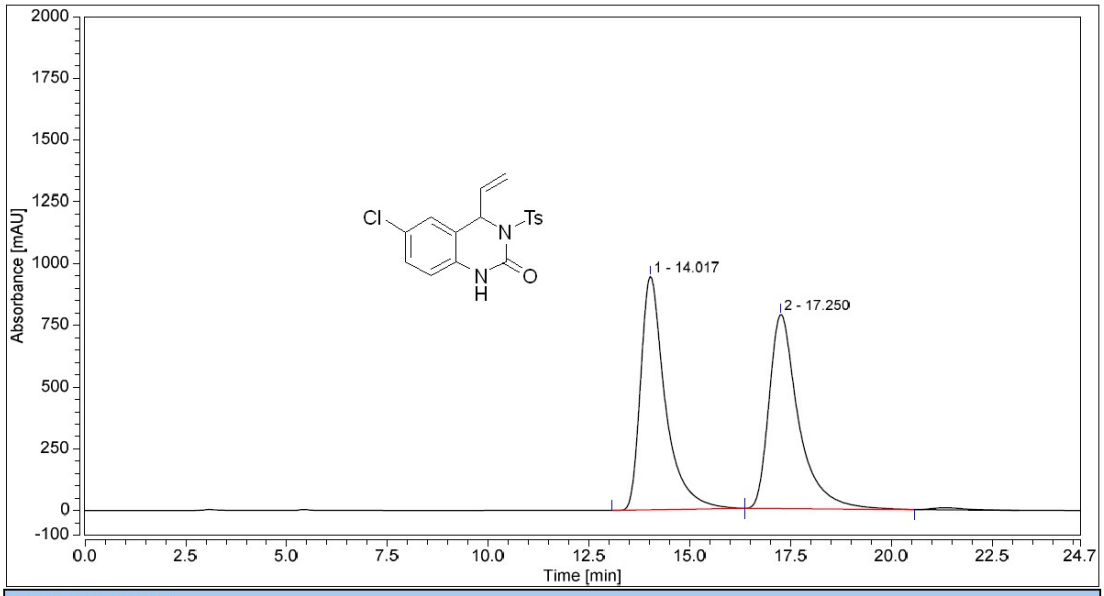
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.597	875.110	1164.567	50.33	52.93	n.a.
2		17.963	863.464	1035.542	49.67	47.07	n.a.
Total:			**1738.573**	**2200.109**	**100.00**	**100.00**	



Integration Results

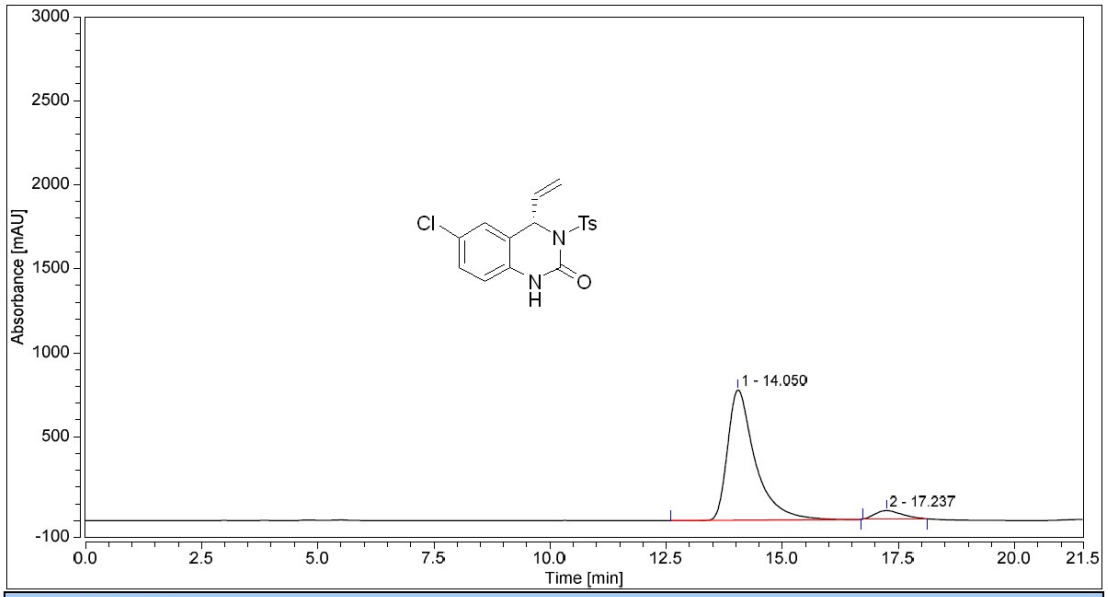
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.623	951.444	1328.035	95.60	95.42	n.a.
2		17.680	43.797	63.812	4.40	4.58	n.a.
Total:			**995.240**	**1391.846**	**100.00**	**100.00**	

3ha



Integration Results

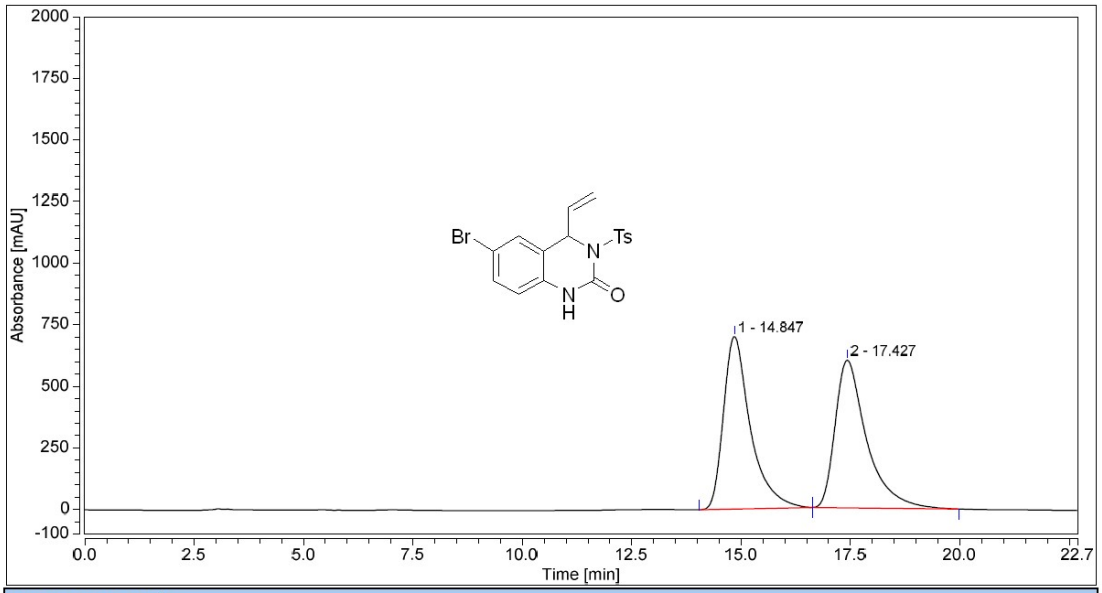
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.017	669.961	944.725	50.08	54.59	n.a.
2		17.250	667.911	786.011	49.92	45.41	n.a.
Total:			**1337.871**	**1730.736**	**100.00**	**100.00**	



Integration Results

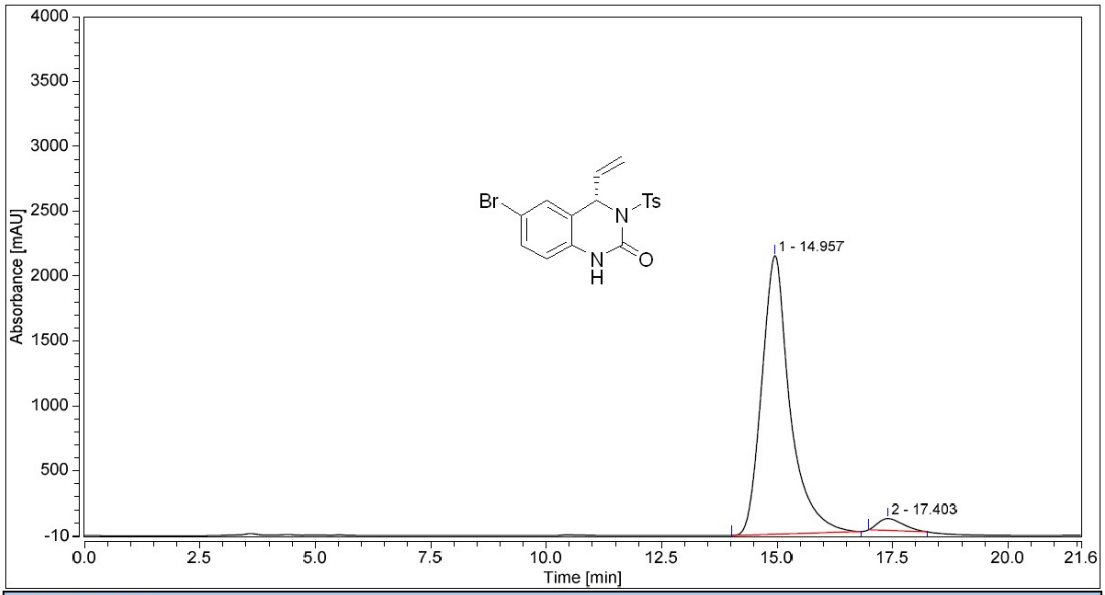
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.050	531.155	775.960	94.12	93.99	n.a.
2		17.237	33.196	49.590	5.88	6.01	n.a.
Total:			**564.352**	**825.550**	**100.00**	**100.00**	

3ia



Integration Results

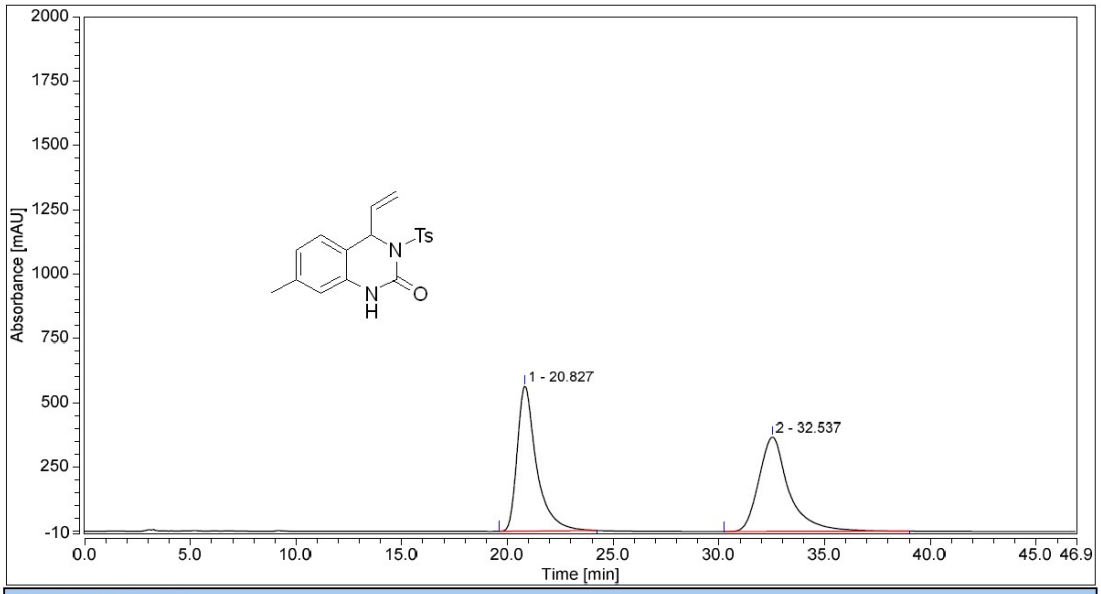
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.847	499.250	700.527	49.97	53.89	n.a.
2		17.427	499.801	599.402	50.03	46.11	n.a.
Total:			**999.051**	**1299.929**	**100.00**	**100.00**	



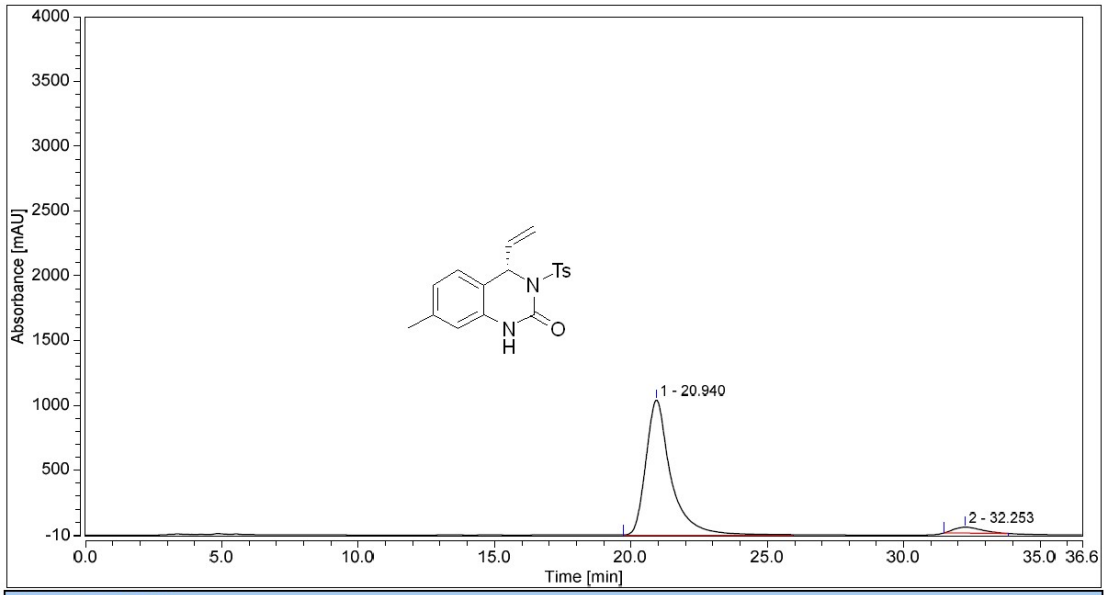
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.957	1517.572	2145.934	96.34	95.90	n.a.
2		17.403	57.714	91.702	3.66	4.10	n.a.
Total:			**1575.287**	**2237.636**	**100.00**	**100.00**	

3ja

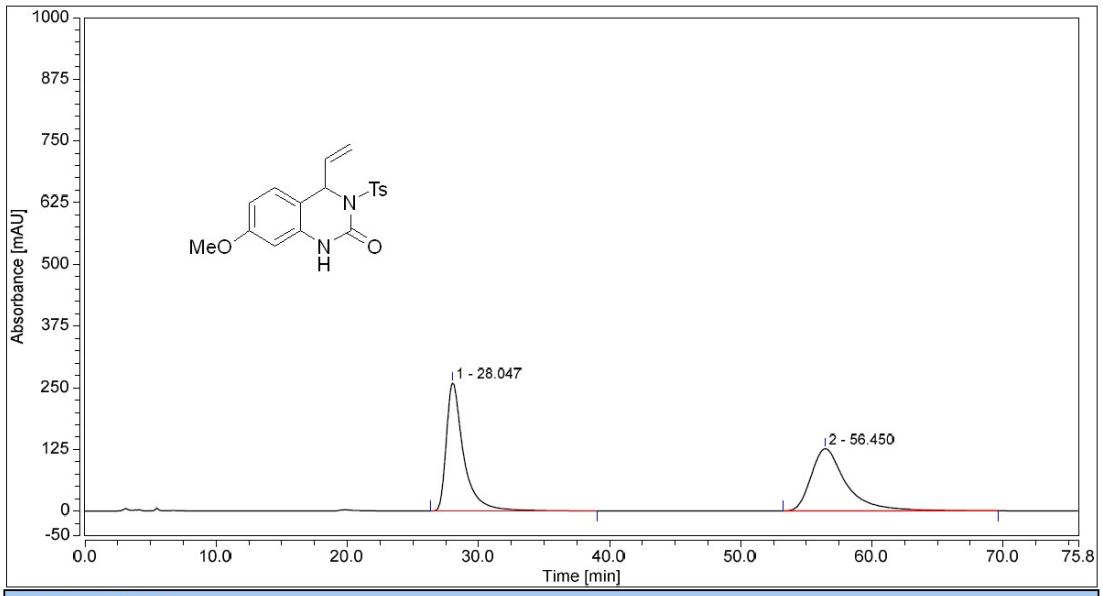


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.827	596.078	563.779	49.73	60.59	n.a.
2		32.537	602.461	366.739	50.27	39.41	n.a.
Total:			**1198.539**	**930.519**	**100.00**	**100.00**	

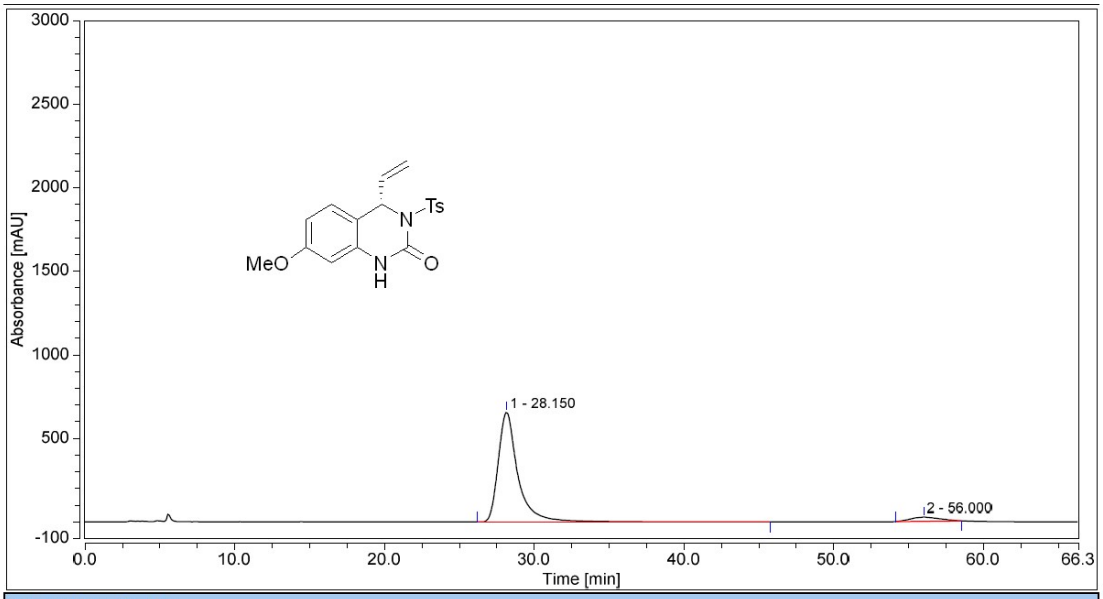


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.940	1097.876	1040.732	95.30	95.79	n.a.
2		32.253	54.102	45.711	4.70	4.21	n.a.
Total:			**1151.978**	**1086.443**	**100.00**	**100.00**	

3ka

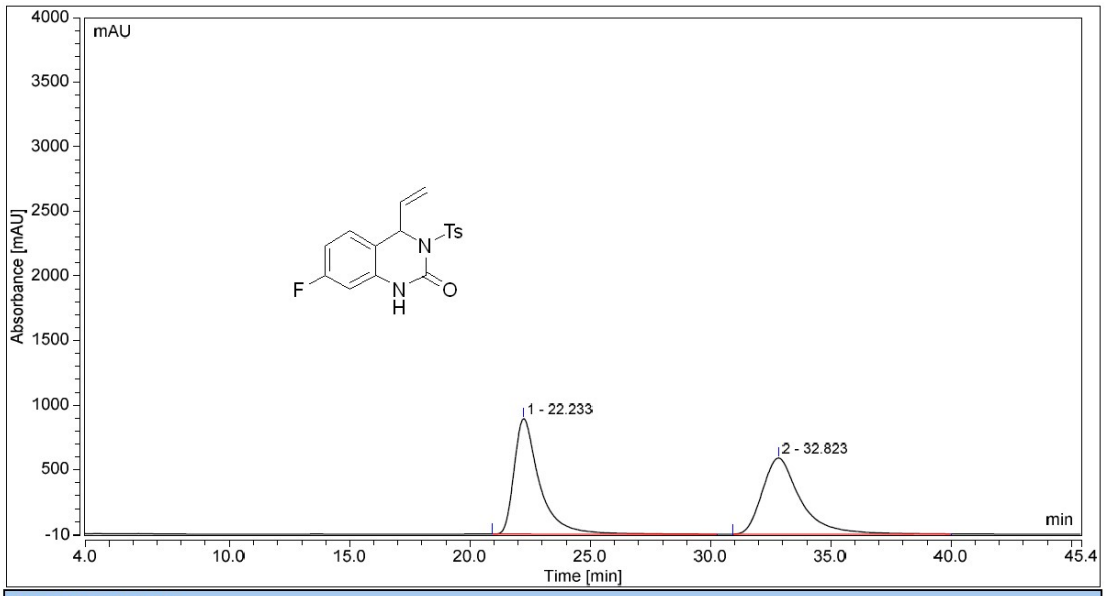


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.047	399.496	259.724	50.49	67.32	n.a.
2		56.450	391.728	126.054	49.51	32.68	n.a.
Total:			**791.224**	**385.778**	**100.00**	**100.00**	



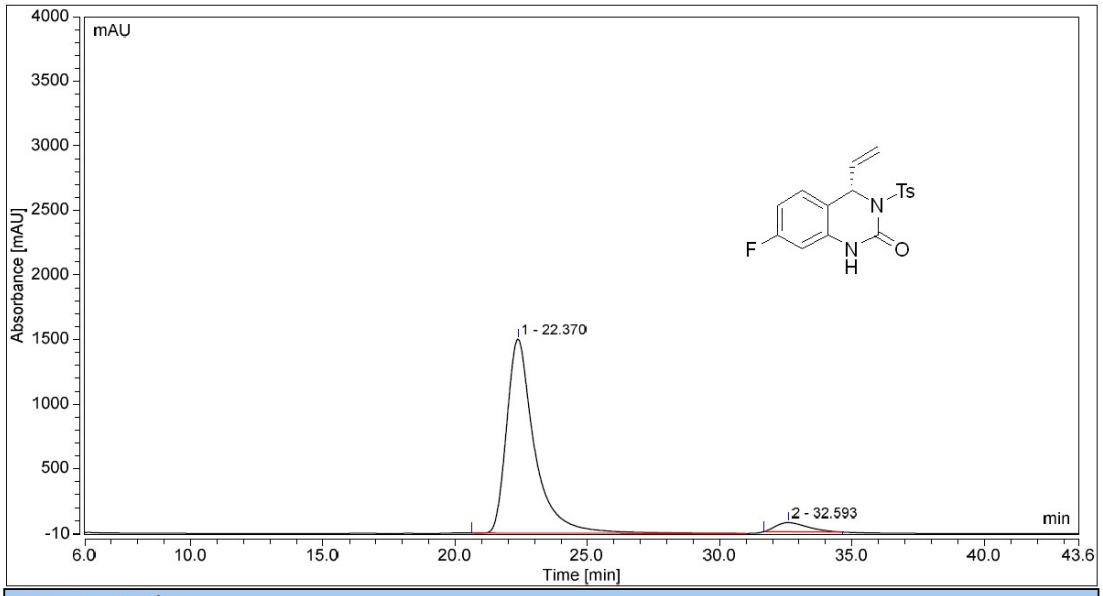
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.150	1001.206	655.300	94.88	96.45	n.a.
2		56.000	54.034	24.106	5.12	3.55	n.a.
Total:			**1055.241**	**679.406**	**100.00**	**100.00**	

3la



Integration Results

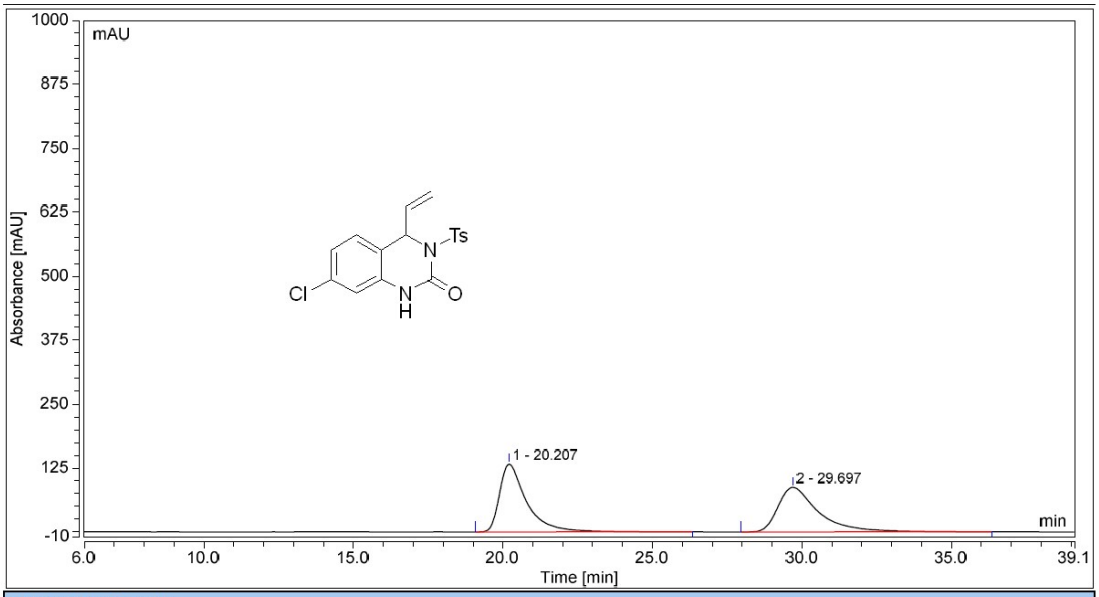
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.233	1099.434	894.078	50.39	60.25	n.a.
2		32.823	1082.449	589.829	49.61	39.75	n.a.
Total:			**2181.883**	**1483.908**	**100.00**	**100.00**	



Integration Results

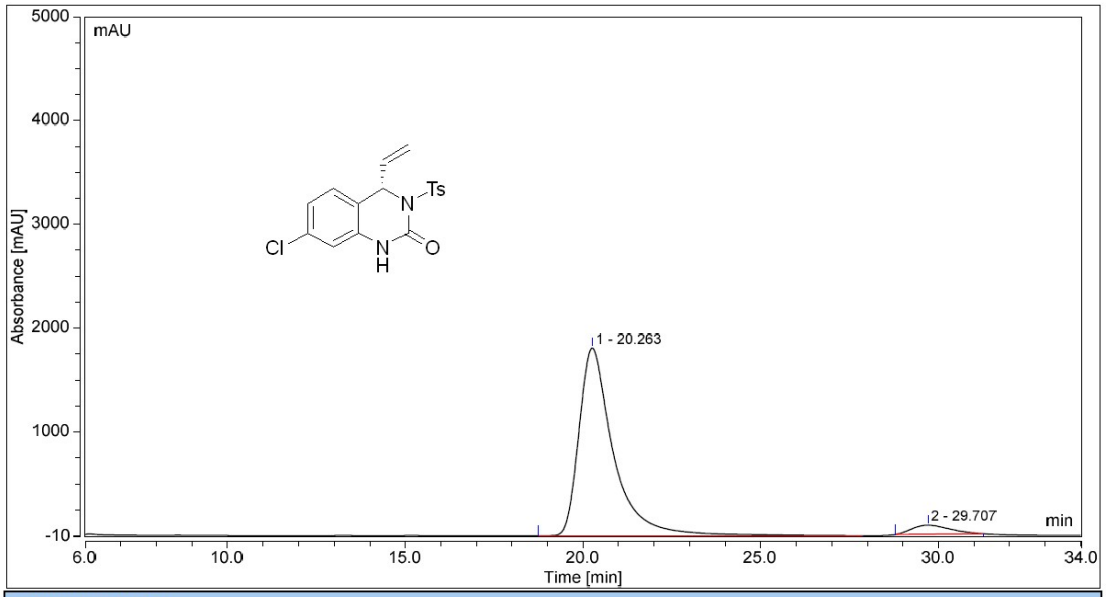
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.370	1833.963	1502.689	94.90	95.48	n.a.
2		32.593	98.517	71.066	5.10	4.52	n.a.
Total:			**1932.480**	**1573.755**	**100.00**	**100.00**	

3ma



Integration Results

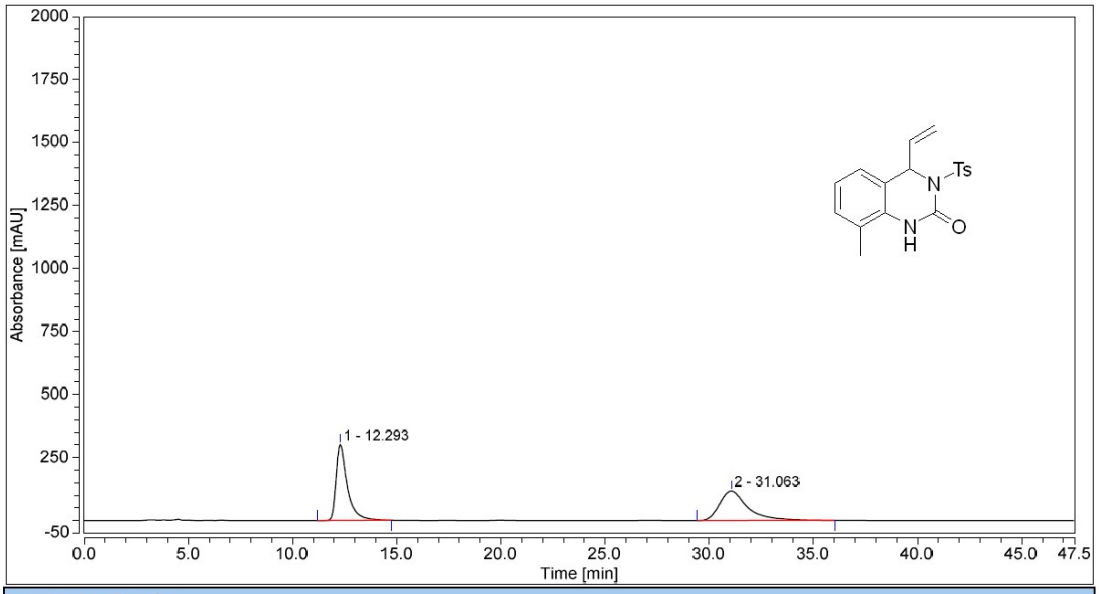
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.207	139.448	132.444	50.45	60.33	n.a.
2		29.697	136.959	87.075	49.55	39.67	n.a.
Total:			**276.408**	**219.520**	**100.00**	**100.00**	



Integration Results

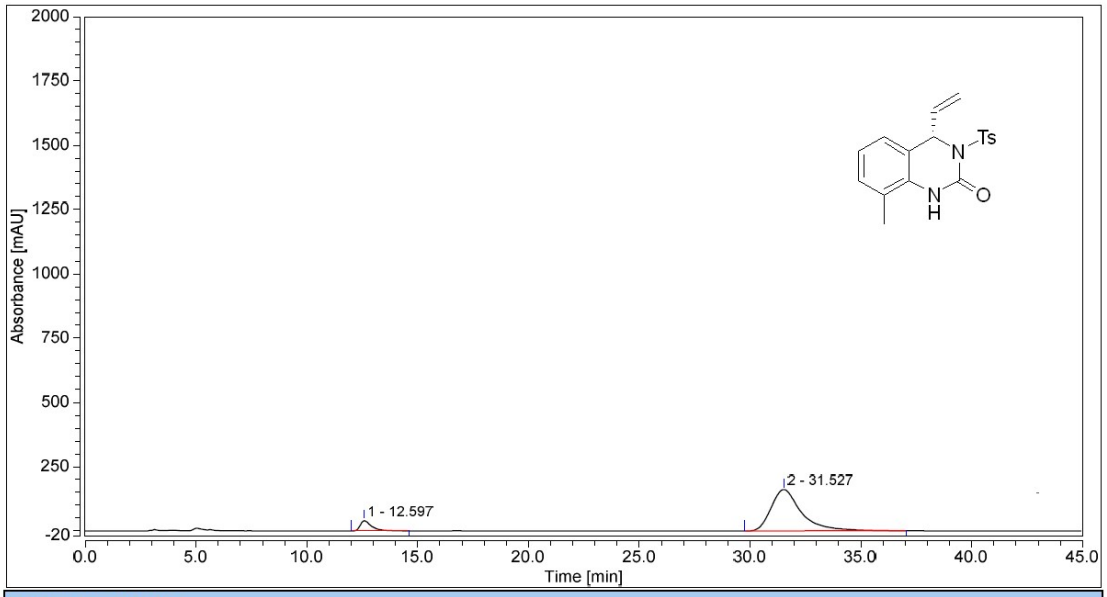
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.263	2027.295	1806.440	94.98	95.41	n.a.
2		29.707	107.227	86.901	5.02	4.59	n.a.
Total:			**2134.521**	**1893.341**	**100.00**	**100.00**	

3na



Integration Results

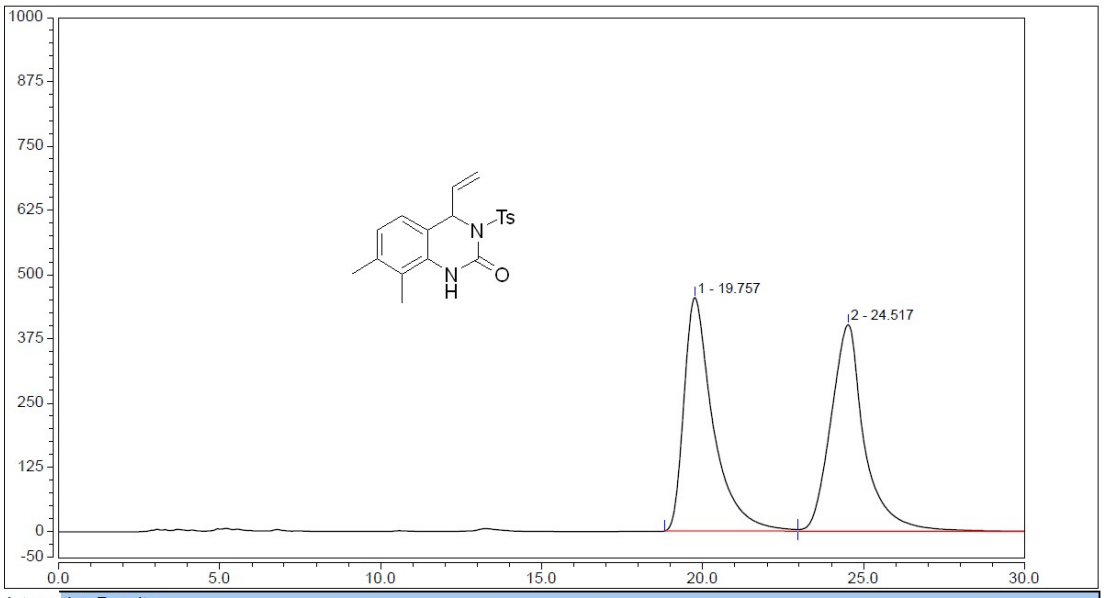
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.293	187.981	300.772	50.66	71.98	n.a.
2		31.063	183.079	117.106	49.34	28.02	n.a.
Total:			**371.060**	**417.878**	**100.00**	**100.00**	



Integration Results

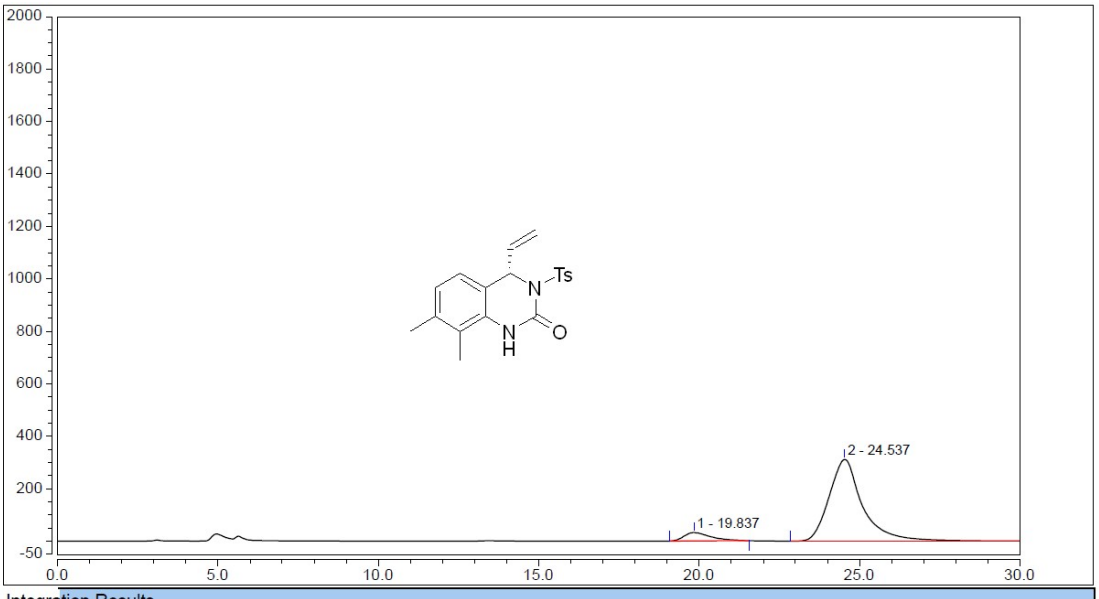
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.597	24.042	39.857	8.55	19.79	n.a.
2		31.527	257.253	161.521	91.45	80.21	n.a.
Total:			**281.296**	**201.379**	**100.00**	**100.00**	

3oa



Integration Results

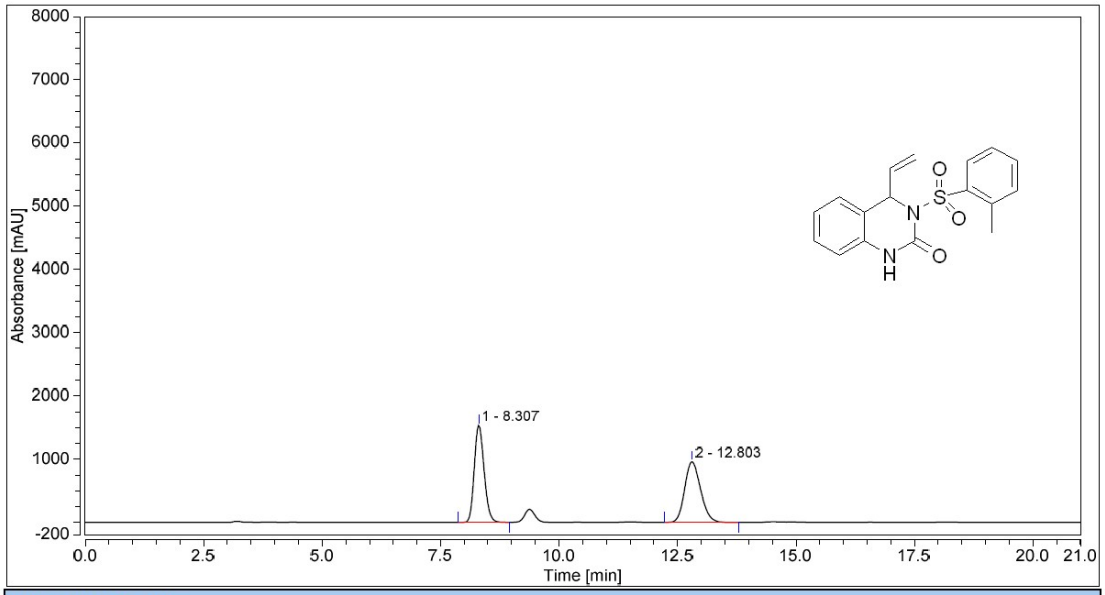
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.757	476.844	454.097	49.70	53.06	n.a.
2		24.517	482.678	401.725	50.30	46.94	n.a.
Total:			**959.522**	**855.822**	**100.00**	**100.00**	



Integration Results

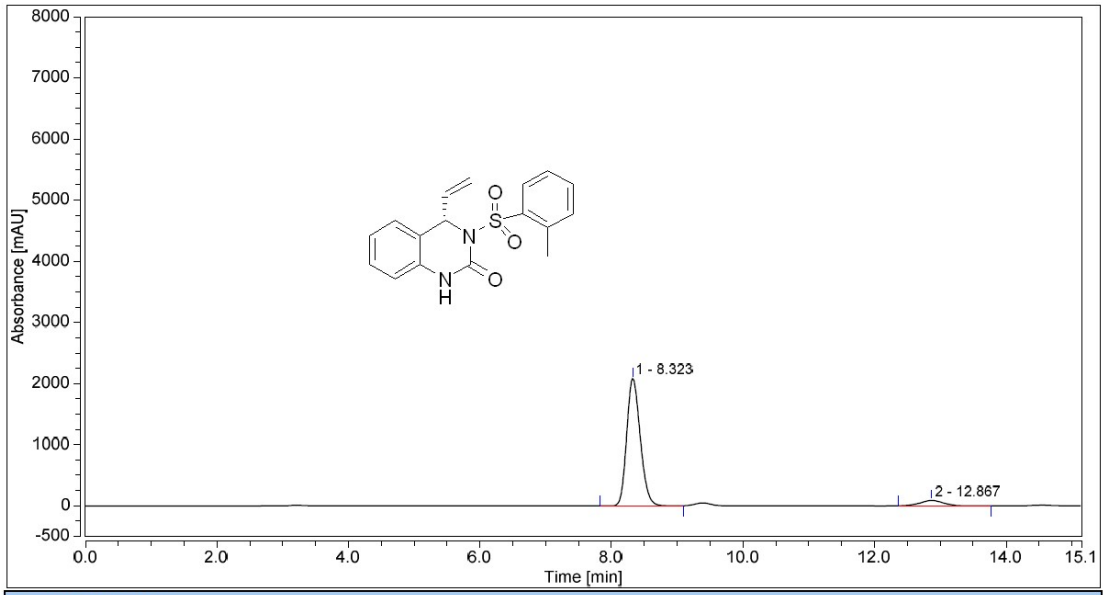
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.837	30.195	31.675	7.43	9.23	n.a.
2		24.537	376.389	311.365	92.57	90.77	n.a.
Total:			**406.584**	**343.040**	**100.00**	**100.00**	

3ab



Integration Results

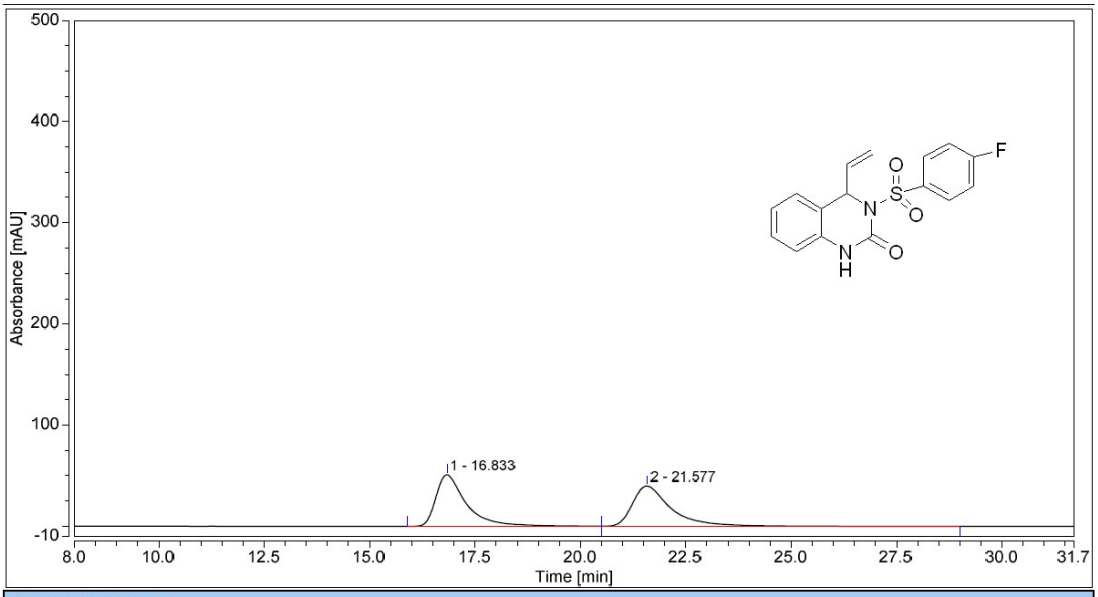
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.307	368.293	1532.778	49.61	61.48	n.a.
2		12.803	374.154	960.491	50.39	38.52	n.a.
Total:			**742.447**	**2493.270**	**100.00**	**100.00**	



Integration Results

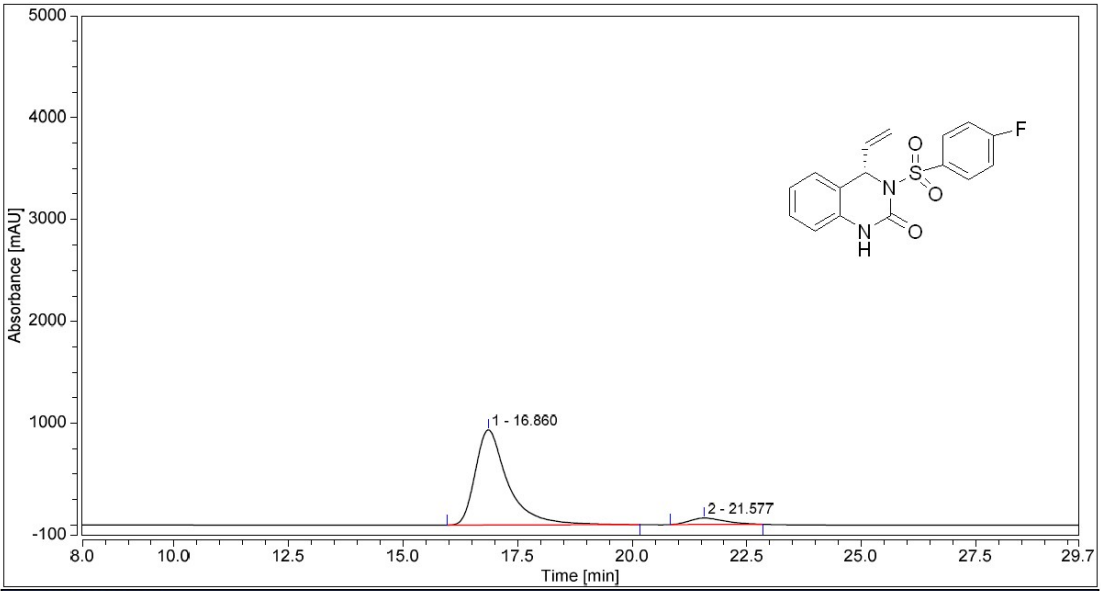
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.323	495.515	2080.582	93.38	95.99	n.a.
2		12.867	35.141	86.885	6.62	4.01	n.a.
Total:			**530.656**	**2167.467**	**100.00**	**100.00**	

3ac



Integration Results

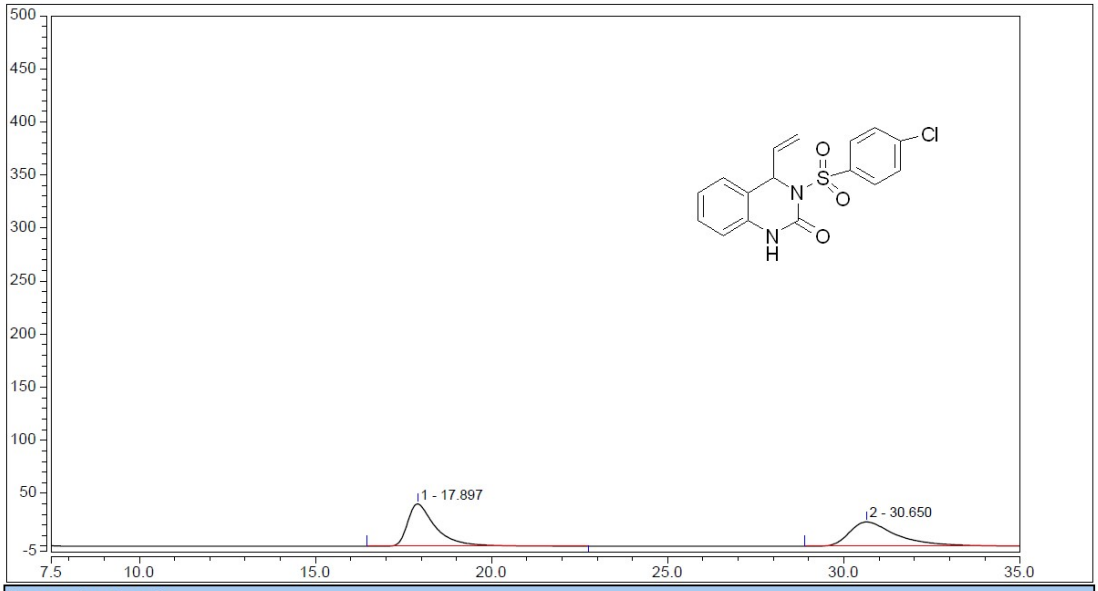
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.833	42.864	50.954	49.91	56.11	n.a.
2		21.577	43.023	39.849	50.09	43.89	n.a.
Total:			**85.887**	**90.803**	**100.00**	**100.00**	



Integration Results

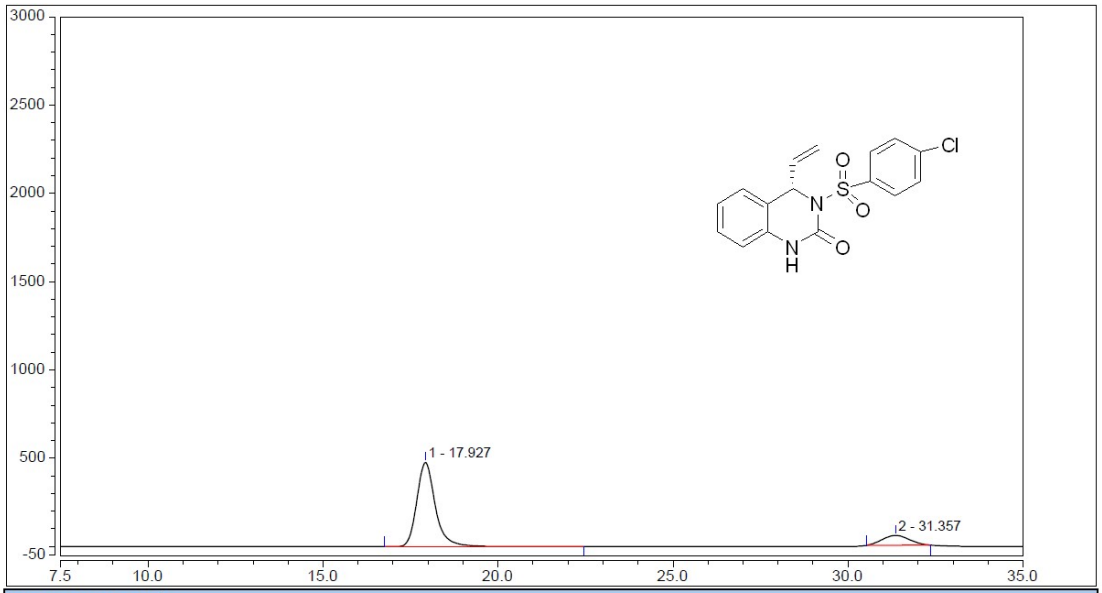
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.860	768.772	933.277	93.28	93.70	n.a.
2		21.577	55.341	62.737	6.72	6.30	n.a.
Total:			**824.113**	**996.014**	**100.00**	**100.00**	

3ad



Integration Results

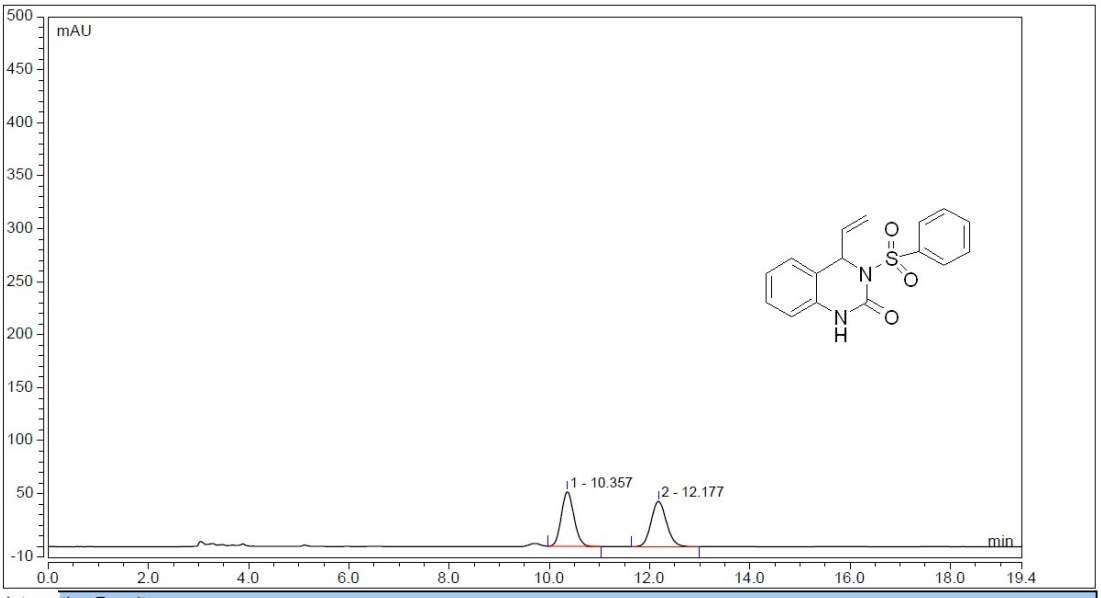
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.897	36.814	39.845	50.43	63.52	n.a.
2		30.650	36.188	22.886	49.57	36.48	n.a.
Total:			**73.002**	**62.731**	**100.00**	**100.00**	



Integration Results

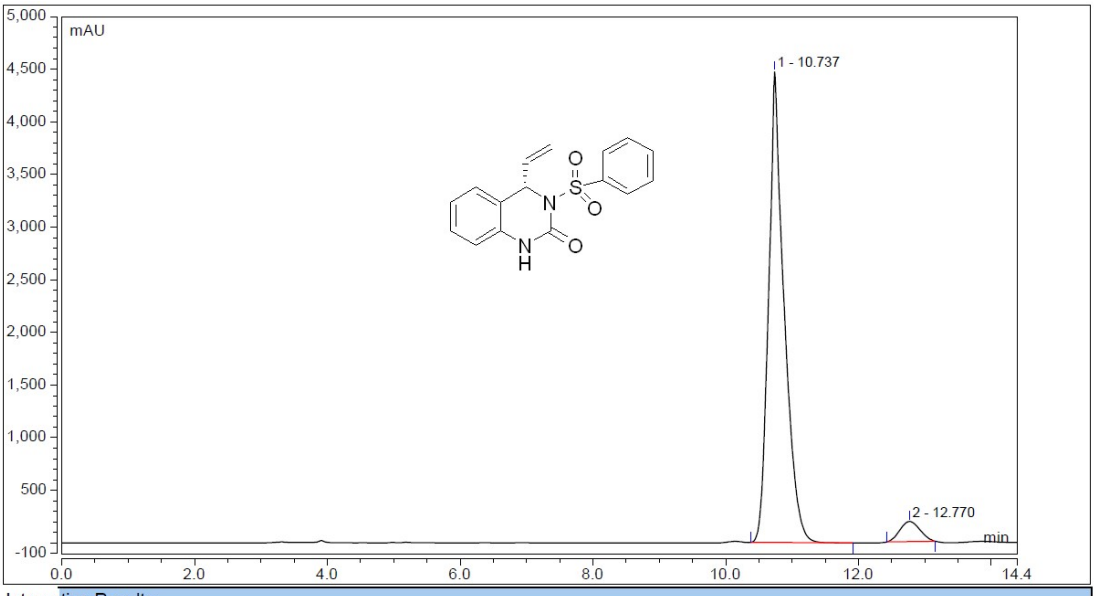
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.927	289.464	475.795	85.25	89.55	n.a.
2		31.357	50.064	55.536	14.75	10.45	n.a.
Total:			**339.528**	**531.331**	**100.00**	**100.00**	

3ae



Integration Results

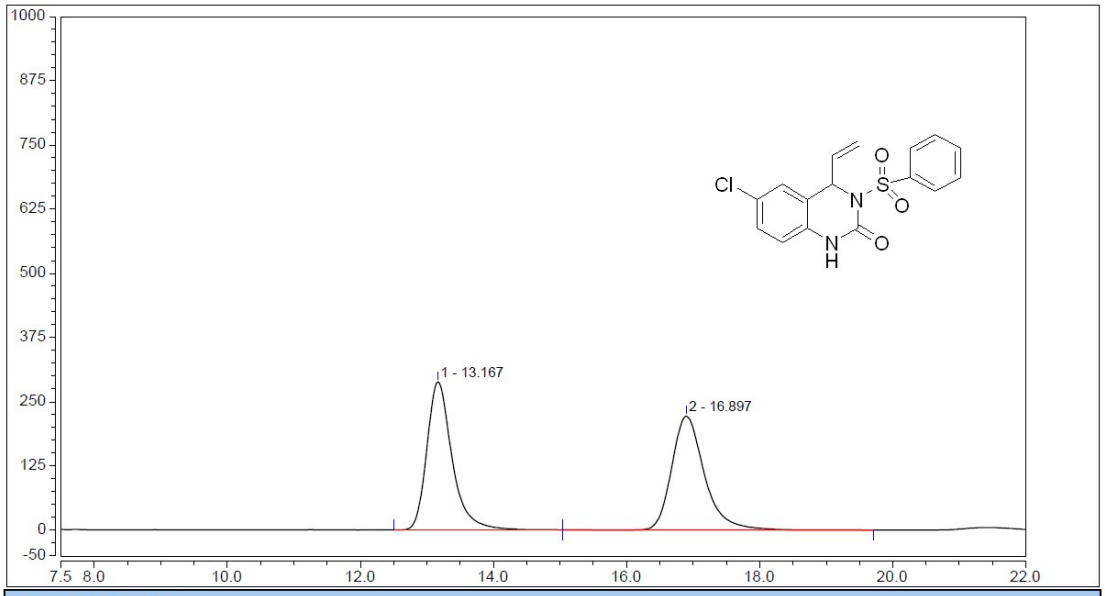
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.357	15.131	51.484	49.89	54.68	n.a.
2		12.177	15.198	42.663	50.11	45.32	n.a.
Total:			**30.329**	**94.146**	**100.00**	**100.00**	



Integration Results

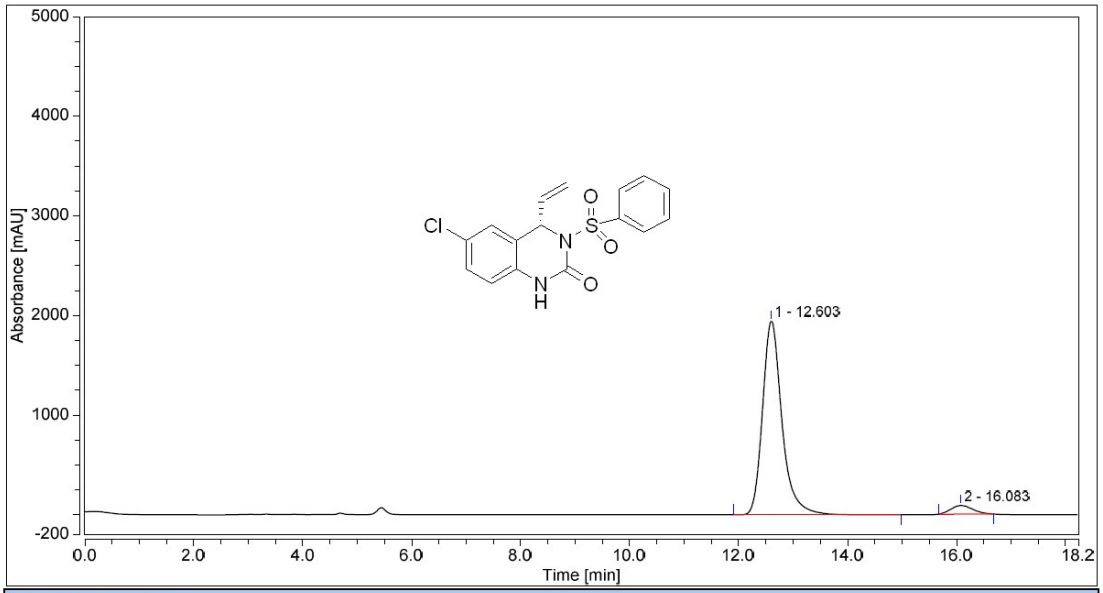
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.737	1205.752	4470.267	94.71	95.88	n.a.
2		12.770	67.363	192.100	5.29	4.12	n.a.
Total:			**1273.115**	**4662.367**	**100.00**	**100.00**	

3he



Integration Results

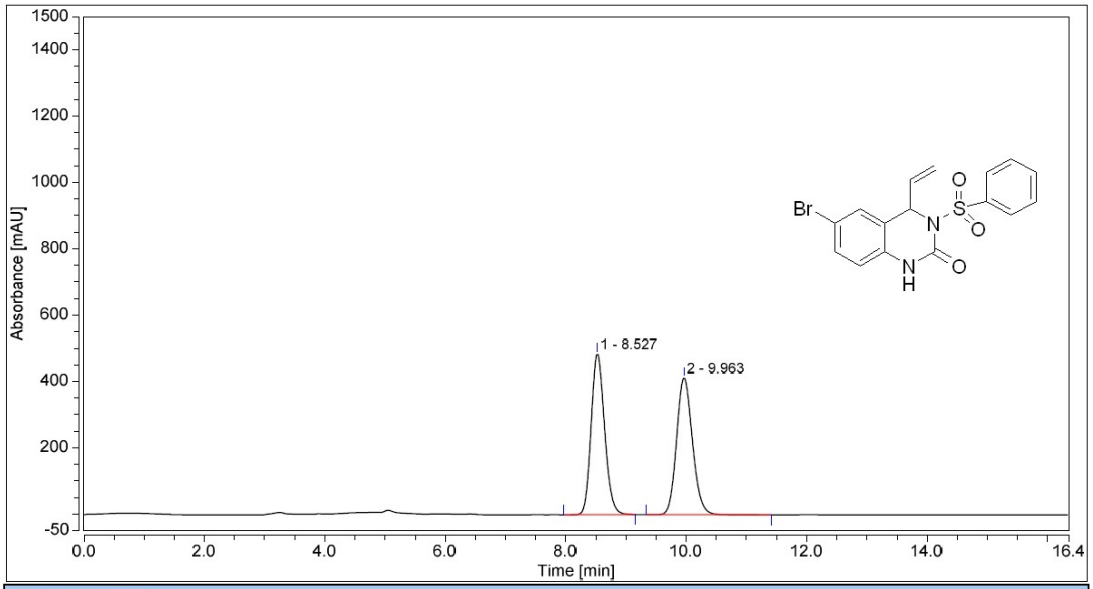
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.167	126.983	288.674	50.16	56.57	n.a.
2		16.897	126.176	221.580	49.84	43.43	n.a.
Total:			**253.159**	**510.254**	**100.00**	**100.00**	



Integration Results

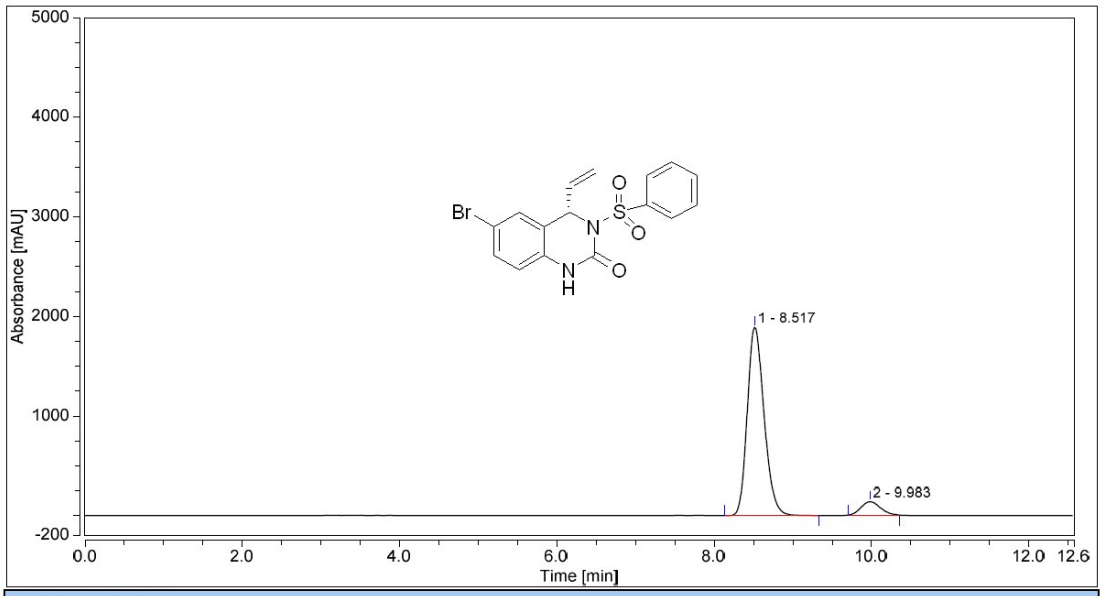
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.603	803.277	1946.321	95.24	95.75	n.a.
2		16.083	40.148	86.486	4.76	4.25	n.a.
Total:			**843.425**	**2032.808**	**100.00**	**100.00**	

3ie



Integration Results

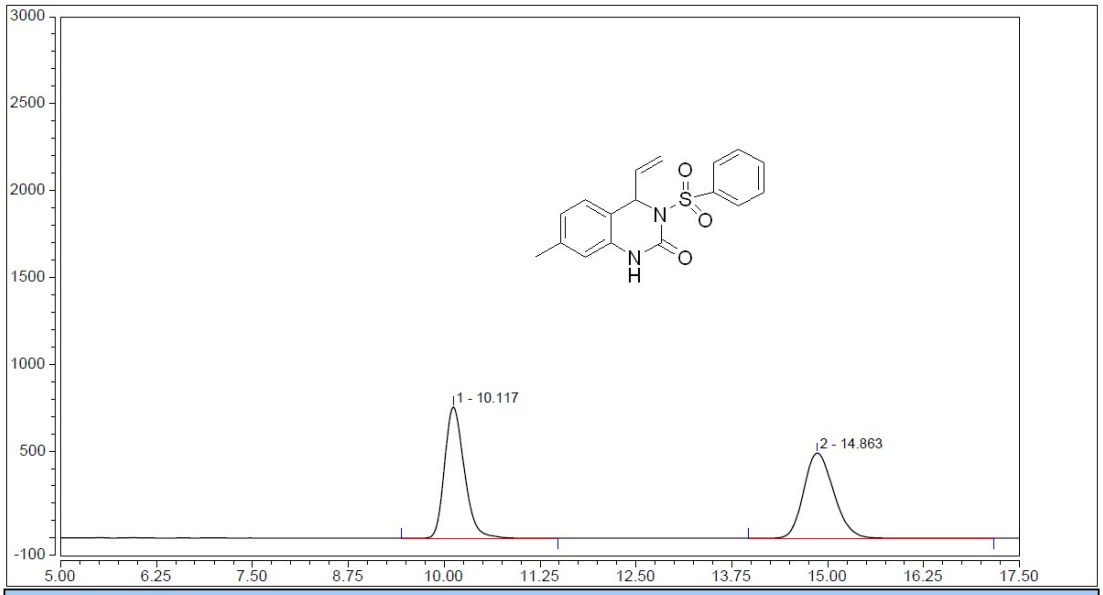
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.527	125.192	485.504	49.84	54.04	n.a.
2		9.963	125.972	412.831	50.16	45.96	n.a.
Total:			**251.164**	**898.334**	**100.00**	**100.00**	



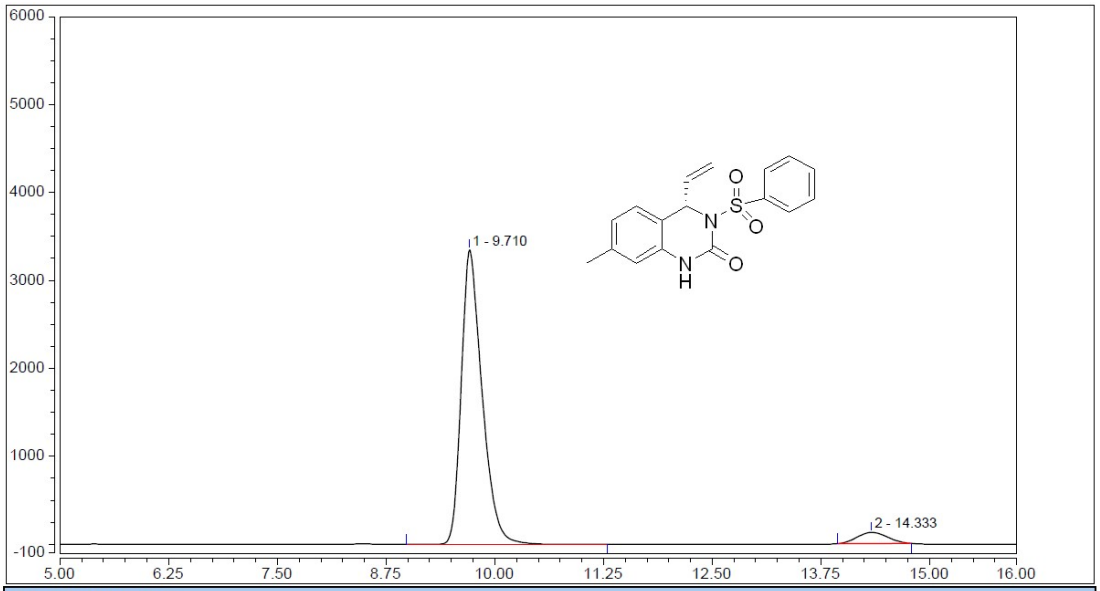
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.517	469.182	1893.151	92.51	93.40	n.a.
2		9.983	37.988	133.738	7.49	6.60	n.a.
Total:			**507.170**	**2026.890**	**100.00**	**100.00**	

3je

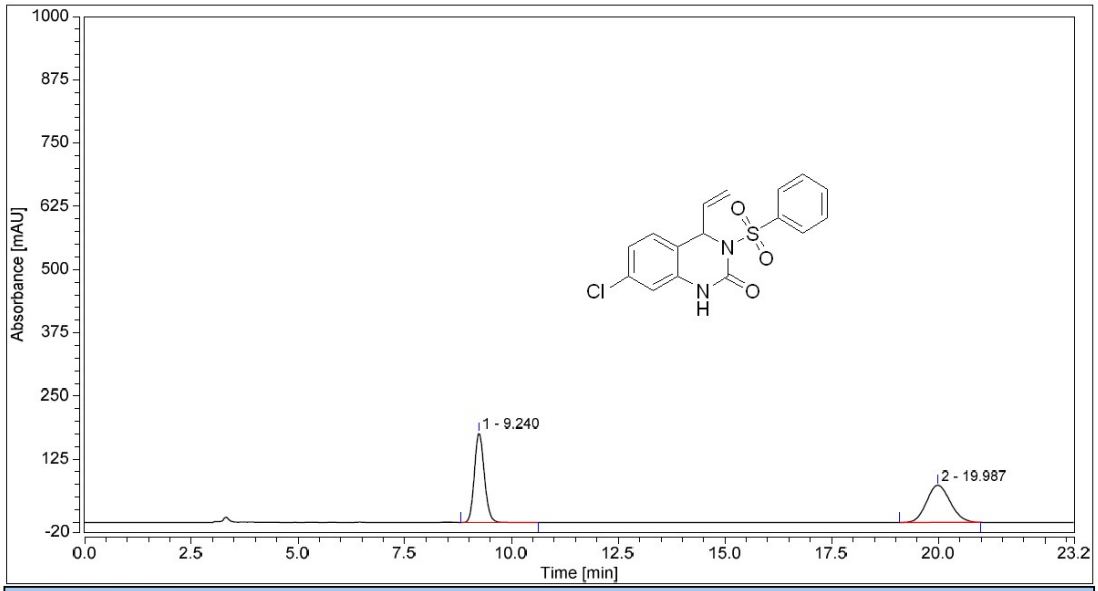


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.117	225.453	755.581	50.35	60.62	n.a.
2		14.863	222.350	490.914	49.65	39.38	n.a.
Total:			**447.803**	**1246.495**	**100.00**	**100.00**	

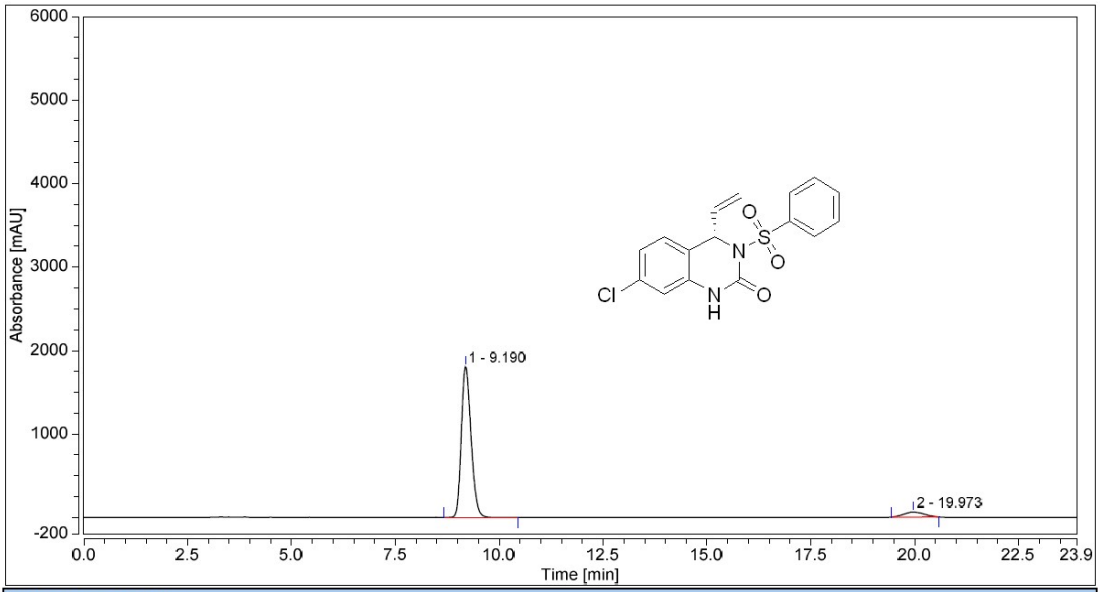


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.710	925.768	3346.744	94.71	96.33	n.a.
2		14.333	51.667	127.402	5.29	3.67	n.a.
Total:			**977.434**	**3474.146**	**100.00**	**100.00**	

3me

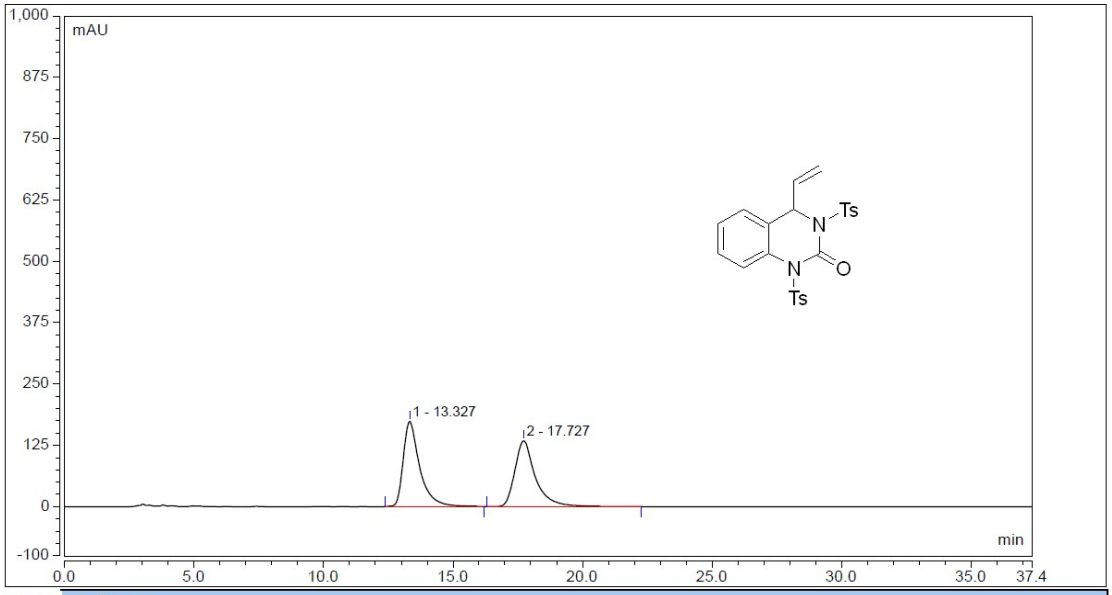


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.240	47.951	176.937	50.29	70.66	n.a.
2		19.987	47.396	73.464	49.71	29.34	n.a.
Total:			**95.347**	**250.401**	**100.00**	**100.00**	



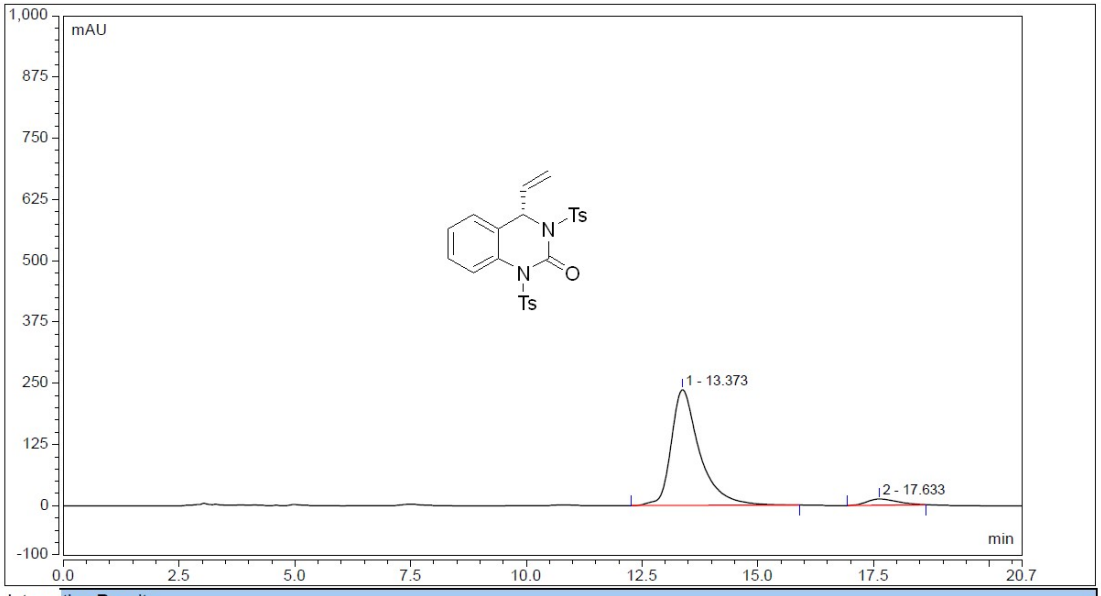
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.190	491.491	1808.924	93.47	96.82	n.a.
2		19.973	34.335	59.496	6.53	3.18	n.a.
Total:			**525.827**	**1868.420**	**100.00**	**100.00**	

3pa



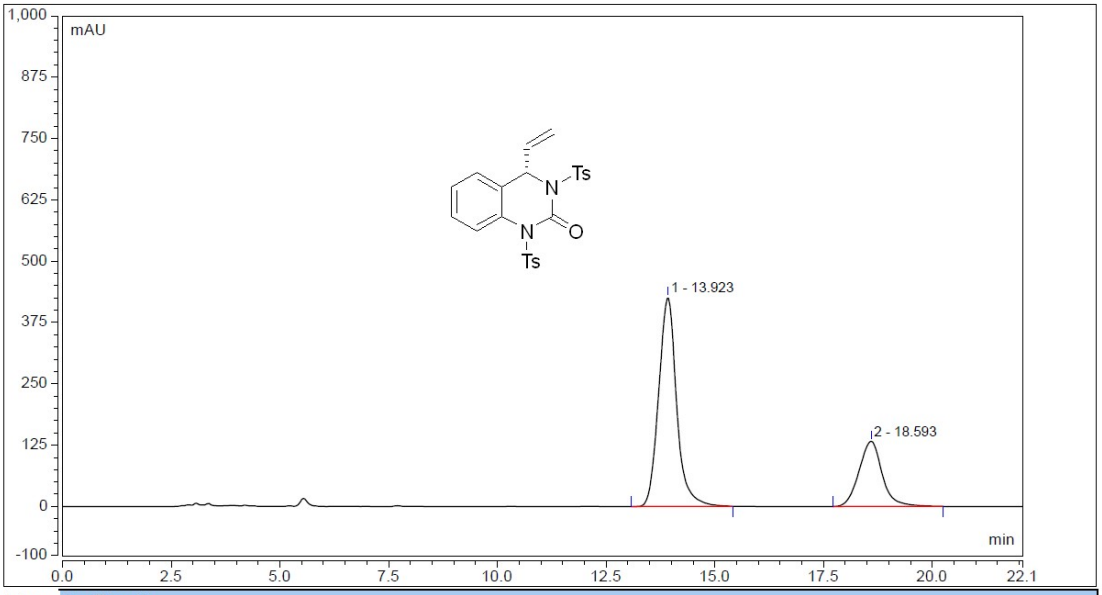
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.327	127.620	173.621	51.03	56.46	n.a.
2		17.727	122.460	133.886	48.97	43.54	n.a.
Total:			**250.080**	**307.507**	**100.00**	**100.00**	



Integration Results

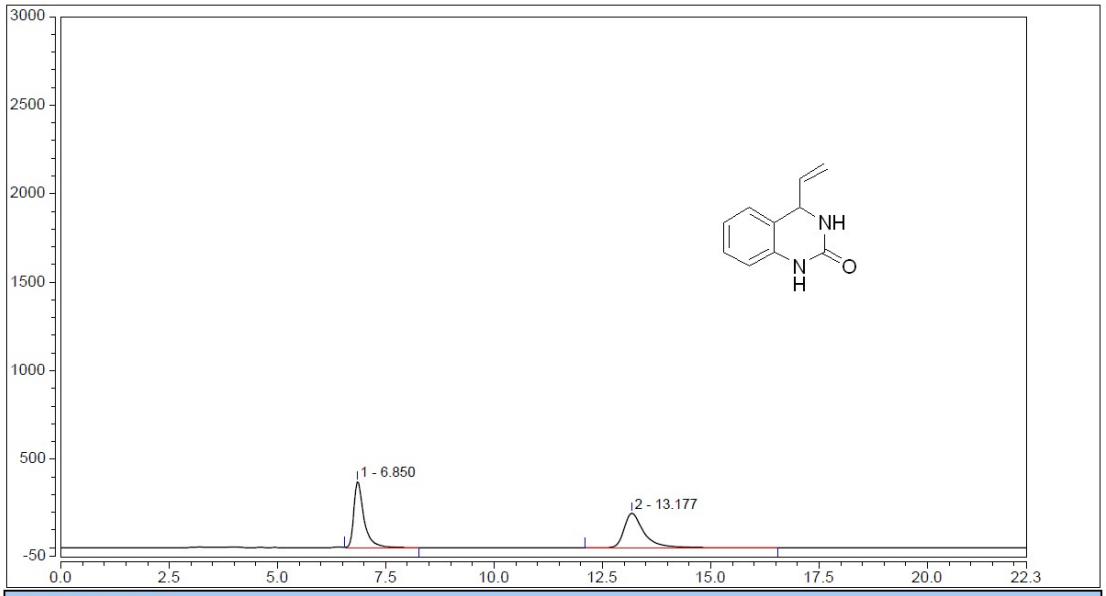
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.373	168.469	236.361	94.64	94.90	n.a.
2		17.633	9.540	12.699	5.36	5.10	n.a.
Total:			**178.009**	**249.060**	**100.00**	**100.00**	



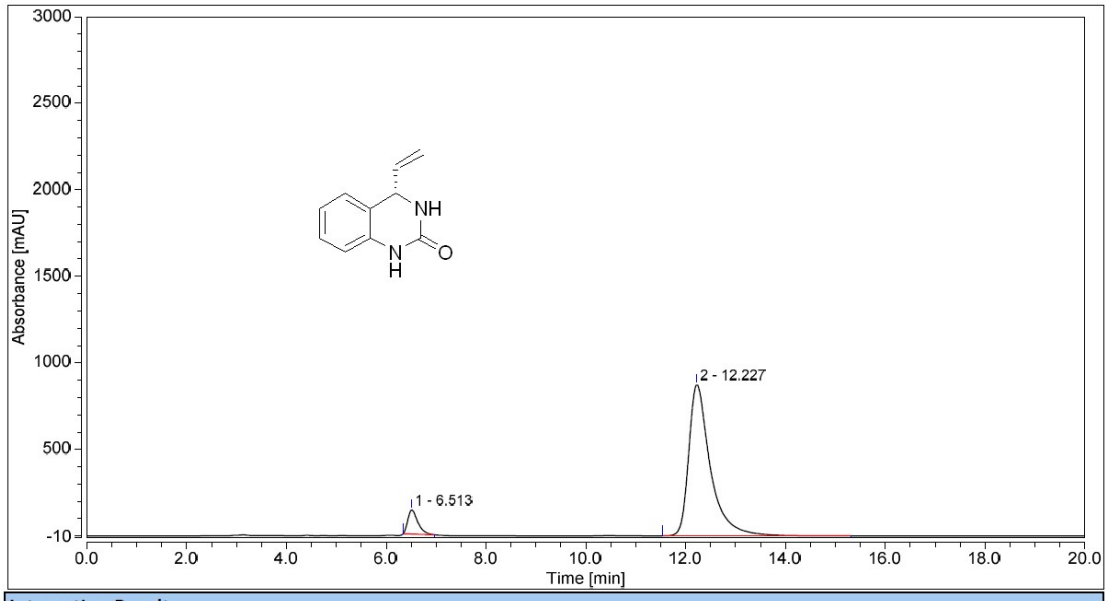
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.923	203.736	425.954	71.23	76.21	n.a.
2		18.593	82.307	132.988	28.77	23.79	n.a.
Total:			**286.043**	**558.942**	**100.00**	**100.00**	

3qa

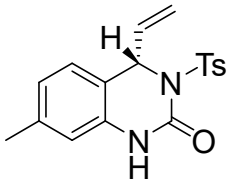


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.850	101.349	374.035	49.54	65.84	n.a.
2		13.177	103.225	194.027	50.46	34.16	n.a.
Total:			**204.573**	**568.062**	**100.00**	**100.00**	

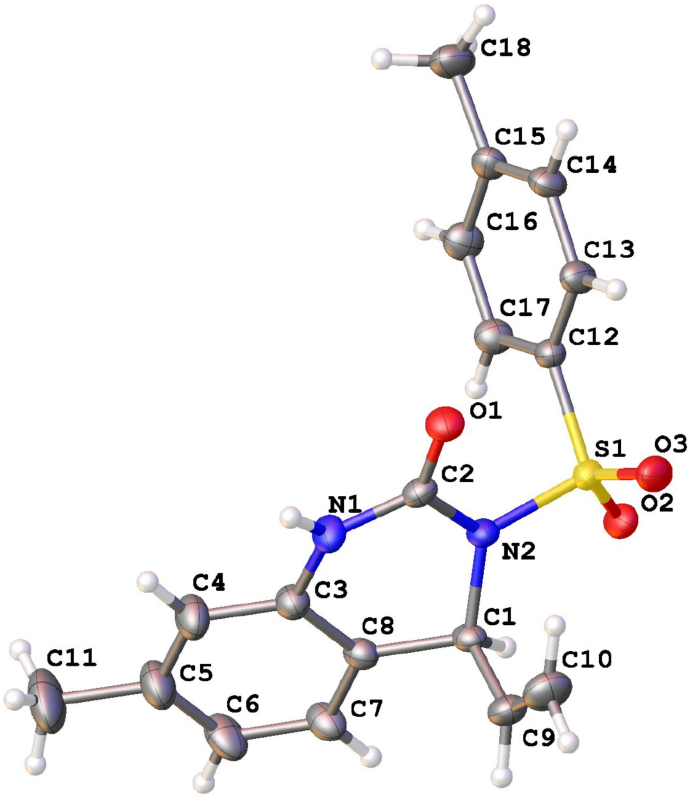


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.513	32.359	140.201	6.86	13.81	n.a.
2		12.227	439.353	874.856	93.14	86.19	n.a.
Total:			**471.712**	**1015.056**	**100.00**	**100.00**	

9. X-ray single crystal data for compound 3ja



(*S*)-3ja



The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C18 H18 N2 O3 S	
Formula weight	342.40	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.2292(12) Å	α= 90°.
	b = 12.3415(18) Å	β= 90°.
	c = 17.181(3) Å	γ = 90°.
Volume	1744.9(4) $Å^3$	
Z	4	
Density (calculated)	1.303 Mg/m^3	
Absorption coefficient	0.203 mm^{-1}	
F(000)	720	

Crystal size	0.5 x 0.3 x 0.2 mm^3
Theta range for data collection	2.744 to 28.638°.
Index ranges	-8<=h<=10, -15<=k<=14, -22<=l<=22
Reflections collected	10539
Independent reflections	4058 [R(int) = 0.0249]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6589
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4058 / 0 / 219
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0981
R indices (all data)	R1 = 0.0472, wR2 = 0.1025
Absolute structure parameter	0.00(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.248 and -0.269 $e.Å^{-3}$