

Supporting Information

Iridium and Brønsted Acid Cooperatively Catalyzed Chemodivergent and Stereoselective Reactions of Vinyl Benzoxazinones with Azlactones

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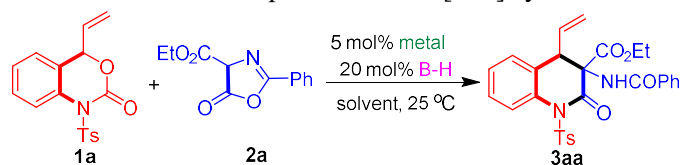
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1. General information

^1H and ^{13}C NMR spectra were measured 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 $\lambda = 589$ 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 compounds **3aa** and chiral **3aa** was a $\text{MoK}\alpha$ ($\lambda = 0.71073$), 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 catalysts and condition optimization

Table S1. Condition optimization for [4+2] cycloaddition^a



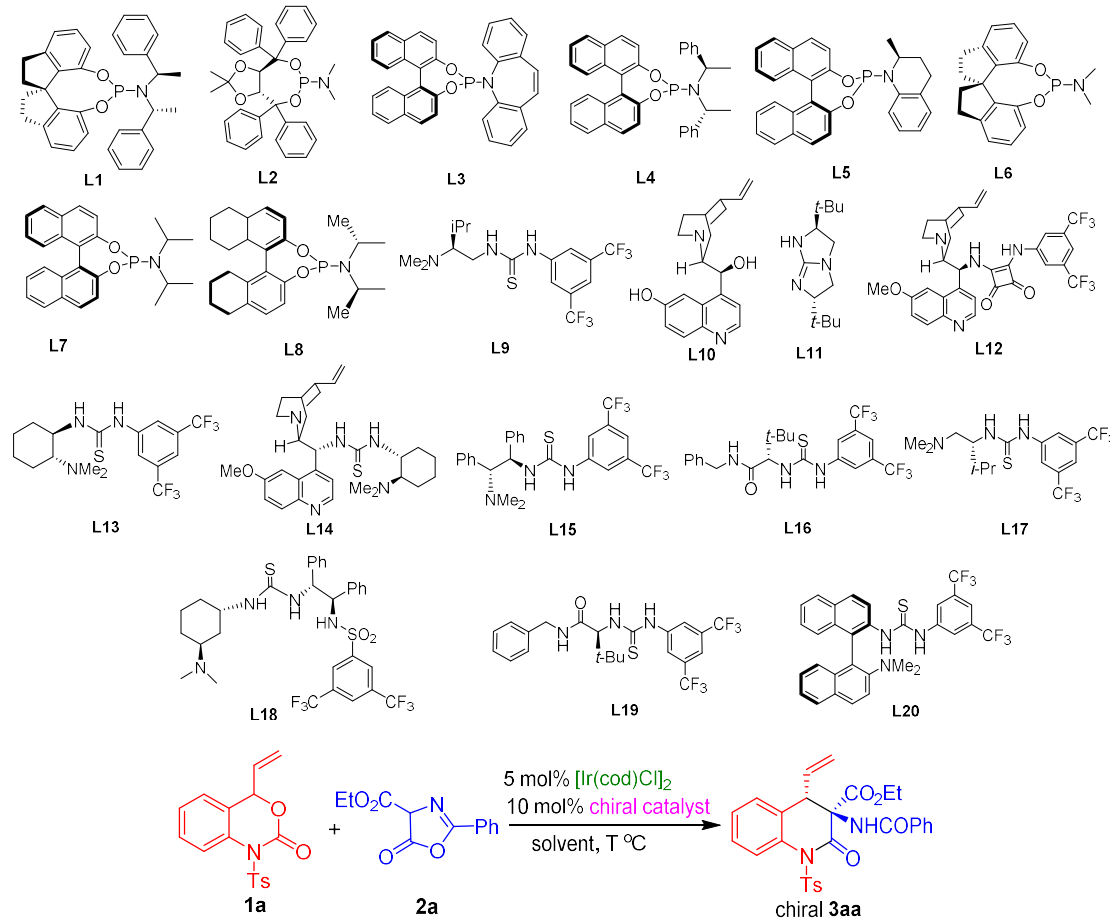
entry	metal	B-H	solvent	1a:2a	dr ^b	yield (%) ^c
1	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	toluene (0.1 M)	1:1	64:36	84
2	$\text{Pd}(\text{PPh}_3)_4$	-	toluene (0.1 M)	1:1	>95:5	20
3	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	THF (0.1 M)	1:1	72:28	85
4	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	acetone (0.1 M)	1:1	75:25	92
5	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	EtOAc (0.1 M)	1:1	72:28	89
6	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	CH_2Cl_2 (0.1 M)	1:1	60:40	60
7	$[\text{Ir}(\text{cod})\text{Cl}]_2$	-	MeCN (0.1 M)	1:1	75:25	82
8	$[\text{Ir}(\text{cod})\text{Cl}]_2$	TFA	acetone (0.1 M)	1:1	91:9	72
9	$[\text{Ir}(\text{cod})\text{Cl}]_2$	TfOH	acetone (0.1 M)	1:1	75:25	30
10	$[\text{Ir}(\text{cod})\text{Cl}]_2$	AcOH	acetone (0.1 M)	1:1	72:28	80
11	$[\text{Ir}(\text{cod})\text{Cl}]_2$	PhCO_2H	acetone (0.1 M)	1:1	80:20	75
12	$[\text{Ir}(\text{cod})\text{Cl}]_2$	$\text{TsOH}\cdot\text{H}_2\text{O}$	acetone (0.1 M)	1:1	94:6	67
13	$[\text{Ir}(\text{cod})\text{Cl}]_2$	$\text{TsOH}\cdot\text{H}_2\text{O}$	acetone (0.05 M)	1:1	94:6	67
14	$[\text{Ir}(\text{cod})\text{Cl}]_2$	$\text{TsOH}\cdot\text{H}_2\text{O}$	acetone (0.025 M)	1:1	94:6	80
15	$[\text{Ir}(\text{cod})\text{Cl}]_2$	$\text{TsOH}\cdot\text{H}_2\text{O}$	acetone (0.013 M)	1:1	94:6	70

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

16	[Ir(cod)Cl] ₂	TsOH·H ₂ O	acetone (0.025 M)	1:1.5	94:6	94
17	[Ir(cod)Cl] ₂	TsOH·H ₂ O	acetone (0.025 M)	1:2	94:6	85
18	[Ir(cod)Cl] ₂	TsOH·H ₂ O	acetone (0.025 M)	2:1	94:6	73

^aThe reaction was conducted at the 0.05 mmol scale in a solvent at 25 °C for 1.5 h. ^bThe dr value was determined by ¹H NMR spectroscopy. ^cIsolated yield.

Table S2. Condition optimization for catalytic asymmetric [4+2] cycloaddition^a



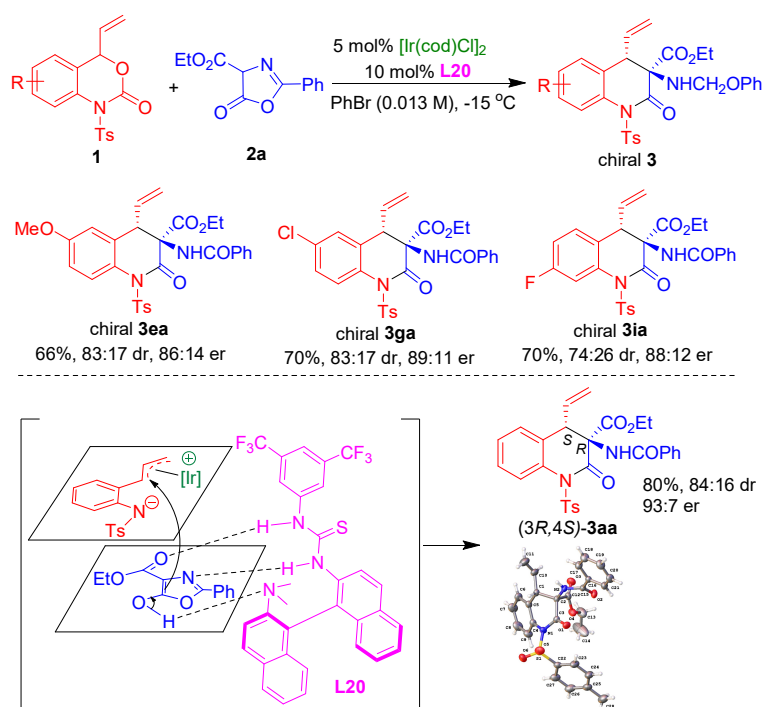
entry	chiral catalyst	solvent	T (°C)	1a:2a	yield (%) ^b	dr ^c	er ^d
1	L1	PhMe (0.5 mL)	25	1:1.5	78	67:33	54:46
2	L2	PhMe (0.5 mL)	25	1:1.5	83	85:15	51:49
3	L3	PhMe (0.5 mL)	25	1:1.5	74	50:50	50:50
4	L4	PhMe (0.5 mL)	25	1:1.5	89	70:30	51:49
5	L5	PhMe (0.5 mL)	25	1:1.5	86	86:14	52:48
6	L6	PhMe (0.5 mL)	25	1:1.5	75	84:16	50:50
7	L7	PhMe (0.5 mL)	25	1:1.5	87	85:15	51:49
8	L8	PhMe (0.5 mL)	25	1:1.5	83	81:19	51:49
9	L9	PhMe (0.5 mL)	25	1:1.5	85	82:18	50:50
10	L10	PhMe (0.5 mL)	25	1:1.5	82	84:16	50:50
11	L11	PhMe (0.5 mL)	25	1:1.5	86	81:19	50:50

12	L12	PhMe (0.5 mL)	25	1:1.5	89	83:17	50:50
13	L13	PhMe (0.5 mL)	25	1:1.5	60	79:21	75:25
14	L14	PhMe (0.5 mL)	25	1:1.5	75	80:20	54:46
15	L15	PhMe (0.5 mL)	25	1:1.5	63	79:21	53:47
16	L16	PhMe (0.5 mL)	25	1:1.5	69	75:25	54:46
17	L17	PhMe (0.5 mL)	25	1:1.5	83	77:23	57:43
18	L18	PhMe (0.5 mL)	25	1:1.5	86	79:21	57:43
19	L19	PhMe (0.5 mL)	25	1:1.5	45	78:22	51:49
20	L20	PhMe (0.5 mL)	25	1:1.5	85	88:12	76:24
21	L20	1,4-dioxane (0.5 mL)	25	1:1.5	90	75:25	55:45
22	L20	acetone (0.5 mL)	25	1:1.5	93	81:19	64:36
23	L20	EtOAc (0.5 mL)	25	1:1.5	85	77:23	70:30
24	L20	DCE (0.5 mL)	25	1:1.5	94	82:18	69:31
25	L20	MeCN (0.5 mL)	25	1:1.5	98	80:20	55:45
26	L20	<i>p</i> -xylene (0.5 mL)	25	1:1.5	84	88:12	72:28
27	L20	<i>o</i> -xylene (0.5 mL)	25	1:1.5	60	87:13	69:31
28	L20	<i>m</i> -xylene (0.5 mL)	25	1:1.5	82	87:13	71:29
29	L20	FPh (0.5 mL)	25	1:1.5	83	86:14	73:27
30	L20	ClPh (0.5 mL)	25	1:1.5	86	87:13	77:23
31	L20	BrPh (0.5 mL)	25	1:1.5	78	86:14	79:21
32	L20	BrPh (1 mL)	25	1:1.5	80	84:16	79:21
33	L20	BrPh (2 mL)	25	1:1.5	79	79:21	81:19
34	L20	BrPh (4 mL)	25	1:1.5	83	88:12	83:17
35	L20	BrPh (8 mL)	25	1:1.5	82	86:14	81:19
36	L20	BrPh (4 mL)	-30	1:1.5	80	81:19	85:15
37	L20	BrPh (4 mL)	-20	1:1.5	81	87:13	87:13
38	L20	BrPh (4 mL)	-15	1:1.5	83	88:12	89:11
39	L20	BrPh (4 mL)	0	1:1.5	82	85:15	86:14
40	L20	BrPh (4 mL)	50	1:1.5	90	87:13	83:17
41	L20	BrPh (4 mL)	-15	1:1	81	81:19	89:11
42	L20	BrPh (4 mL)	-15	1:2	83	85:15	88:12
43	L20	BrPh (4 mL)	-15	1:3	83	83:17	88:12
44	L20	BrPh (4 mL)	-15	2:1	80	84:16	93:7
45	L20	BrPh (4 mL)	-15	4:1	75	84:16	90:10

^aThe reaction was carried out at the 0.05 mmol scale in a solvent at T °C for 1.5 h. ^bIsolated yield. ^cThe dr value was determined by ¹H NMR spectroscopy. ^dThe er value was determined by HPLC and referred to that of the major diastereomer.

We performed a preliminary investigation on the catalytic asymmetric version of the formal [4+2] cycloaddition (Scheme S1). After condition optimization (Table S2), we found that the cooperative catalytic system of iridium and chiral thiourea-tertiary amine **L20** could promote the

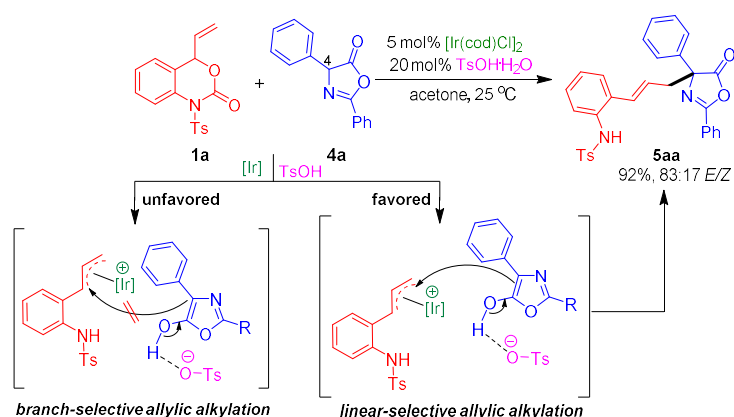
reaction to provide a chiral **3aa** in a high yield (80%), a considerable diastereoselectivity of 84:16 dr and a high enantioselectivity of 93:7 er. Under the optimal conditions, several chiral products of **3** were synthesized in moderate to good diastereo- and enantioselectivities. A possible activation mode of the cooperative catalysis was suggested to explain the generation of chiral **3aa** with the observed (3*R*,4*S*)-configuration. The iridium catalyst and chiral thiourea-tertiary amine catalyst simultaneously activated the two reaction partners, and the enantioselectivity was achieved by the stereocontrol of the chiral thiourea-tertiary amine on the azlactones via hydrogen-bonding interactions. Therefore, the catalytic asymmetric version also provided a cooperative catalysis-enabled reaction for vinyl benzoxazinones. Notably, this reaction has established a scarcely reported cooperative catalysis of iridium and chiral H-bonding catalyst.



Scheme S1. Investigation on the catalytic asymmetric version.

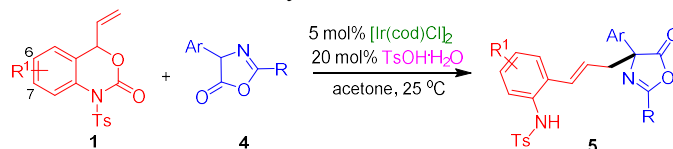
3. Effect of the C4-substituent of azlactones on the chemoselectivity and the generality of the substitution reactions

As suggested in Scheme S2, when azlactone **4a** attacked the π -allyl-Ir intermediate, the branch-selective allylic alkylation was disfavored due to the existence of the bulky C4-phenyl group. In contrast, the linear-selective allylic alkylation was favored because there was less steric hindrance when azlactone **4a** attacked the π -allyl-Ir intermediate from the terminal position. Thus, the favored linear-selective allylic alkylation resulted in the formation of **5aa**. However, apart from steric effect, the softness/hardness of azlactones **4** bearing different C4-substituents should also account for the observed chemoselectivity.



Scheme S2. Effect of the C4-substituent of azlactones on the chemoselectivity.

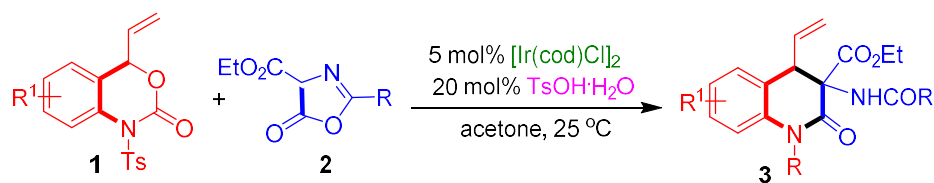
Table S3. Generality of the substitution reactions^a



entry	5	R ¹ (1)	R/Ar (4)	E/Z ^b	yield (%) ^c
1	5aa	H (1a)	Ph/Ph (4a)	83:17	92
2	5ab	H (1a)	<i>o</i> -ClC ₆ H ₄ /Ph (4b)	95:5	95
3	5ac	H (1a)	<i>m</i> -ClC ₆ H ₄ /Ph (4c)	91:9	51
4	5ad	H (1a)	<i>p</i> -MeC ₆ H ₄ /Ph (4d)	91:9	87
5	5ae	H (1a)	Ph/ <i>m</i> -ClC ₆ H ₄ (4e)	83:17	95
6	5af	H (1a)	Ph/ <i>p</i> -FC ₆ H ₄ (4f)	83:17	83
7	5da	6-Me (1d)	Ph/Ph (4a)	>95:5	80
8	5ea	6-OMe (1e)	Ph/Ph (4a)	93:7	83
9	5fa	6-F (1f)	Ph/Ph (4a)	89:11	51
10	5ga	6-Cl (1g)	Ph/Ph (4a)	87:13	70
11	5ha	6-Br (1h)	Ph/Ph (4a)	83:17	82
12	5ia	7-F (1i)	Ph/Ph (4a)	>95:5	93

^aThe reaction was carried out at the 0.1 mmol scale in acetone (0.025 M) at 25 °C for 1.5 h, and the molar ratio of **1**:**4** was 1:1.5. ^bThe E/Z value was determined by ¹H NMR spectroscopy. ^cIsolated yield.

4. Procedure for the synthesis of products 3 and characterization data



Under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1** (0.1 mmol), azlactone **2** (0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure product **3**.

ethyl 3-benzamido-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3aa):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3aa** (48.7 mg) in 94% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr= 94:6); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.40 – 7.34 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 5.82 – 5.69 (m, 1H), 5.47 (d, *J* = 10.1 Hz, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 4.97 (d, *J* = 9.5 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.4, 145.1, 135.6, 135.1, 133.4, 131.9, 130.9, 129.7, 129.3, 128.5, 128.3, 127.6, 126.9, 126.2, 126.1, 123.7, 122.2, 68.3, 62.9, 45.5, 21.8, 13.2; IR (KBr): 2986, 1733, 1669, 1506, 1265, 1159, 933, 740 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₅N₂O₆S 517.1434, found 517.1422.

ethyl 3-benzamido-5-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ba):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to

the mixture of vinyl benzoxazinanone **1b** (34.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ba** (45.8 mg) in 86% yield as light yellow solid.

m.p. 85-86 °C; inseparable diastereomers (dr > 95:5); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.2 Hz, 1H), 7.49 – 7.26 (m, 7H), 7.22 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.68 (s, 1H), 6.11 – 5.98 (m, 1H), 5.12 – 4.94 (m, 2H), 4.43 (d, J = 7.5 Hz, 1H), 4.32 – 4.13 (m, 2H), 2.45 (s, 3H), 2.25 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7, 161.7, 160.4, 140.5, 131.6, 131.3, 130.6, 128.6, 128.5, 127.2, 124.7, 124.6, 123.8, 122.7, 122.5, 122.1, 116.0, 113.7, 100.0, 63.0, 57.9, 43.2, 17.0, 14.3, 9.1; IR (KBr): 2962, 1735, 1654, 1473, 1260, 1085, 798, 668 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_6\text{S}$ 531.1590, found 531.1598.

ethyl 3-benzamido-5-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ca): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1c** (36.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ca** (44.2mg) in 80% yield as light yellow solid.

m.p. 74-75 °C; inseparable diastereomers (dr > 95:5); ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, J = 8.1 Hz, 2H), 7.55 – 7.41 (m, 4H), 7.41 – 7.30 (m, 4H), 7.25 – 7.15 (m, 2H), 6.99 (s, 1H), 6.07 – 5.92 (m, 1H), 5.21 (d, J = 16.9 Hz, 1H), 5.11 (d, J = 10.1 Hz, 1H), 4.40 (d, J = 8.8 Hz, 1H), 4.32 – 4.14 (m, 2H), 2.46 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 161.3, 160.6, 140.5, 132.6, 131.6, 128.3, 128.1, 127.7, 127.3, 124.9, 124.2, 123.8, 122.3, 116.1, 114.0, 62.9, 58.4, 46.1, 17.0, 9.0; IR (KBr): 2917, 1738, 1651, 1454, 1259, 1169, 992, 749 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{24}\text{ClN}_2\text{O}_6\text{S}$ 551.1044, found 551.1041.

ethyl 3-benzamido-6-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3da): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinane **1d** (34.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3da** (44.2 mg) in 83% yield as light yellow solid.

m.p. 80-81 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.57 (m, 3H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.00 (s, 1H), 6.94 (s, 1H), 5.84 – 5.70 (m, 1H), 5.47 (d, *J* = 10.1 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.90 (d, *J* = 9.4 Hz, 1H), 4.04 – 3.91 (m, 1H), 3.84 – 3.74 (m, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 0.73 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 165.9, 165.4, 145.0, 135.9, 135.7, 133.4, 132.6, 131.9, 131.1, 129.6, 129.2, 128.5, 128.1, 128.0, 127.0, 126.7, 123.5, 122.1, 68.3, 62.9, 45.6, 21.7, 21.0, 13.2; IR (KBr): 3126, 1733, 1669, 1399, 1172, 1086, 811, 668 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1600.

ethyl

3-benzamido-6-methoxy-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ea): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinane **1e** (35.9 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ea** (46.1 mg) in 84% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.01 (s, 1H), 6.92 – 6.85 (m, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 5.82 – 5.68 (m, 1H), 5.46 (d,

$J = 10.1$ Hz, 1H), 5.31 (d, $J = 16.8$ Hz, 1H), 4.89 (d, $J = 8.9$ Hz, 1H), 4.04 – 3.93 (m, 1H), 3.90 – 3.81 (m, 1H), 3.80 (s, 3H), 2.47 (s, 3H), 0.78 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 165.9, 165.3, 157.7, 145.0, 135.6, 133.4, 131.9, 130.8, 130.0, 129.6, 129.2, 128.5, 128.1, 127.0, 123.8, 123.5, 112.5, 111.8, 68.3, 62.9, 55.6, 45.7, 21.7, 13.3; IR (KBr): 2982, 1733, 1670, 1489, 1219, 1152, 936, 710 cm^{-1} ; HRMS (ESI-TOF) m/z : [M - H]⁻ Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_7\text{S}$ 547.1539, found 547.1536;

ethyl 3-benzamido-6-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3fa):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1f** (34.7 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3fa** (49.8 mg) in 93% yield as light yellow solid.

m.p. 83-84 °C; inseparable diastereomers (dr =95:5); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.3$ Hz, 2H), 7.75 – 7.69 (m, 1H), 7.58 (d, $J = 7.4$ Hz, 2H), 7.52 – 7.46 (t, $J = 7.3$ Hz, 1H), 7.42 – 7.35 (m, 4H), 7.12 – 7.03 (m, 2H), 6.93 – 6.85 (m, 1H), 5.75 – 5.59 (m, 1H), 5.48 (d, $J = 10.1$ Hz, 1H), 5.33 (d, $J = 16.8$ Hz, 1H), 4.98 (d, $J = 9.5$ Hz, 1H), 4.08 – 3.95 (m, 1H), 3.91 – 3.81 (m, 1H), 2.48 (s, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 165.0, 160.6 ($J = 250$ Hz), 145.3, 135.3, 133.2, 132.0, 131.0, 130.2, 129.8, 129.3, 128.5, 127.0, 124.3, 123.9 ($J = 10$ Hz), 114.2, 114.0, 113.5 ($J = 20$ Hz), 68.2, 63.2, 45.3, 21.8, 13.3; IR (KBr): 2978, 1744, 1671, 1487, 1367, 1173, 931, 708 cm^{-1} ; HRMS (ESI-TOF) m/z : [M - H]⁻ Calcd for $\text{C}_{28}\text{H}_{24}\text{FN}_2\text{O}_6\text{S}$ 535.1339, found 535.1330.

ethyl 3-benzamido-6-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ga): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1g** (36.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction

mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ga** (45.8 mg) in 83% yield as light yellow solid.

m.p. 74-75 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.43 – 7.31 (m, 5H), 7.13 (s, 1H), 7.09 (s, 1H), 5.73 – 5.59 (m, 1H), 5.49 (d, *J* = 10.0 Hz, 1H), 5.33 (d, *J* = 16.7 Hz, 1H), 4.99 (d, *J* = 9.6 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.91 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 165.8, 164.9, 145.4, 135.1, 133.6, 133.2, 132.0, 131.7, 130.5, 130.1, 129.9, 129.3, 128.5, 127.4, 126.9, 126.3, 124.5, 123.4, 68.1, 63.3, 45.2, 21.8, 13.3; IR (KBr): 3124, 1734, 1670, 1479, 1399, 1154, 935, 810 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1040.

ethyl 3-benzamido-6-bromo-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ha): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1h** (40.6 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ha** (54.8 mg) in 92% yield as light yellow solid.

m.p. 80-81 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.36 (m, 4H), 7.27 (s, 1H), 7.09 (s, 1H), 5.73 – 5.58 (m, 1H), 5.49 (d, *J* = 10.0 Hz, 1H), 5.33 (d, *J* = 16.7 Hz, 1H), 4.99 (d, *J* = 9.5 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.91 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 164.8, 145.4, 135.1, 134.1, 133.2, 132.0, 130.7, 130.4, 130.0, 129.9, 129.3, 129.2, 128.5, 126.9, 124.5, 123.7, 119.5, 68.2, 63.3, 45.1, 21.8, 13.3; IR (KBr): 2983, 1733, 1669, 1476, 1362, 1155, 1085, 933, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄BrN₂O₆S 595.0539, found 595.0544.

ethyl 3-benzamido-7-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ia): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1i** (34.7 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ia** (48.2 mg) in 90% yield as light yellow solid.

m.p. 129-130 °C; inseparable diastereomers (dr = 92:8); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 4H), 7.13 – 7.07 (m, 1H), 7.05 (s, 1H), 6.97 – 6.90 (m, 1H), 5.78 – 5.63 (m, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.92 (d, *J* = 9.5 Hz, 1H), 4.07 – 3.96 (m, 1H), 3.89 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 165.9, 165.1, 161.7 (*J* = 240 Hz), 145.4, 136.1, 135.3, 133.2, 132.0, 130.6 (*J* = 10 Hz), 129.7, 129.4, 128.5, 127.3 (*J* = 10 Hz), 126.7, 124.1, 124.0, 112.6 (*J* = 20 Hz), 110.2 (*J* = 30 Hz), 68.2, 63.1, 45.0, 21.8, 13.3; IR (KBr): 2988, 1748, 1670, 1507, 1275, 1177, 847, 750 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄FN₂O₆S 535.1339, found 535.1351.

ethyl 3-benzamido-7-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ja): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1j** (36.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ja** (44.7 mg) in 81% yield as light yellow solid.

m.p. 72-73 °C; inseparable diastereomers (dr = 91:9); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 4H), 7.23 – 7.18 (m, 1H), 7.13 – 7.01 (m, 2H), 5.76 – 5.62 (m, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.06 – 3.95 (m, 1H), 3.90 – 3.81 (m, 1H), 2.49

(s, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 165.8, 165.0, 145.4, 135.9, 135.2, 133.3, 133.2, 132.0, 130.4, 129.8, 129.3, 128.5, 127.2, 127.0, 126.9, 125.9, 124.2, 122.3, 68.2, 63.2, 45.0, 21.8, 13.3; IR (KBr): 2963, 1743, 1649, 1482, 1366, 1158, 941, 807 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{24}\text{ClN}_2\text{O}_6\text{S}$ 551.1044, found 551.1062.

ethyl 3-benzamido-8-methyl-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ka): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1k** (34.3 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 $^\circ\text{C}$ for 1.5 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 = 20:1) to afford pure product **3ka** (46.8 mg) in 88% yield as light yellow solid.

m.p. 79-80 $^\circ\text{C}$; inseparable diastereomers (dr = 95:5); ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 7.4$ Hz, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.32 (m, 4H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.57 (s, 1H), 6.08 – 5.91 (m, 1H), 5.48 (d, $J = 10.1$ Hz, 1H), 5.30 (d, $J = 16.9$ Hz, 1H), 4.41 (s, 1H), 3.88 – 3.73 (m, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 166.0, 165.9, 145.3, 135.8, 135.4, 134.7, 133.6, 131.9, 131.4, 131.1, 130.6, 130.1, 129.3, 128.5, 127.3, 126.9, 123.6, 123.2, 68.4, 62.6, 47.0, 21.8, 20.9, 13.1; IR (KBr): 2987, 1733, 1670, 1507, 1275, 1158, 936, 749 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_6\text{S}$ 531.1590, found 531.1589.

ethyl

3-benzamido-2-oxo-1-tosyl-6-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3la): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1l** (39.7 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.01 mmol) Then, the reaction mixture was stirred at 25 $^\circ\text{C}$ for 1.5 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 = 20:1) to afford pure product **3la** (49.8 mg) in 85% yield as light yellow solid.

m.p. 89-90 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.46 (m, 1H), 7.44 – 7.34 (m, 5H), 7.14 (s, 1H), 5.74 – 5.60 (m, 1H), 5.53 (dd, *J* = 10.0, 1.3 Hz, 1H), 5.42 – 5.31 (m, 1H), 5.09 (d, *J* = 9.6 Hz, 1H), 4.11 – 3.99 (m, 1H), 3.88 – 3.75 (m, 1H), 2.50 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 165.8, 164.9, 145.7, 138.0, 135.0, 133.2, 132.2, 130.2, 129.8, 129.6, 129.4, 128.7, 128.2 (*J* = 33 Hz), 127.0, 125.0, 124.7 (*J* = 4 Hz), 123.7 (*J* = 265 Hz), 123.4 (*J* = 4 Hz), 122.4, 68.2, 63.4, 45.2, 21.9, 13.2; IR (KBr): 2959, 1748, 1671, 1506, 1335, 1154, 935, 662 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₄F₃N₂O₆S 585.1307, found 585.1321.

ethyl

3-benzamido-2-oxo-1-tosyl-7-(trifluoromethyl)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ma): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1m** (39.7 mg, 0.1 mmol), azlactone **2a** (35 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.01 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ma** (55.7 mg) in 95% yield as light yellow solid.

m.p. 131-132 °C; inseparable diastereomers (dr = 93:7); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 8.02 (s, 1H), 7.62 – 7.56 (m, 2H), 7.53 – 7.46 (m, 2H), 7.43 – 7.35 (m, 4H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.12 (s, 1H), 5.75 – 5.61 (m, 1H), 5.50 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.40 – 5.30 (m, 1H), 5.08 (d, *J* = 9.4 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.88 – 3.77 (m, 1H), 2.49 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 165.8, 164.7, 145.6, 135.6, 135.0, 132.6 (*J* = 9 Hz), 133.1, 130.3, 130.0, 129.9, 129.4, 128.7, 128.6, 127.2, 127.0, 125.7 (*J* = 222 Hz), 122.6 (*J* = 37 Hz), 119.2 (*J* = 39 Hz), 68.2, 63.3, 45.3, 21.8, 13.0; IR (KBr): 2963, 1748, 1669, 1507, 1330, 1155, 942, 668 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₄F₃N₂O₆S 585.1307, found 585.1313.

ethyl

3-(2-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ab): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2b** (37.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ab** (50.5 mg) in 95% yield as light yellow solid.

m.p. 82-83 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.26 (m, 5H), 7.24 – 7.09 (m, 4H), 6.71 (s, 1H), 5.85 – 5.69 (m, 1H), 5.57 (d, *J* = 9.9 Hz, 1H), 5.43 (d, *J* = 16.8 Hz, 1H), 5.08 (d, *J* = 8.6 Hz, 1H), 4.04 – 3.90 (m, 1H), 3.87 – 3.72 (m, 1H), 2.44 (s, 3H), 2.10 (s, 3H), 0.72 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.2, 160.3, 140.4, 132.2, 130.7, 130.3, 129.9, 126.4, 126.2, 125.5, 125.3, 124.3, 123.5, 122.8, 122.0, 121.3, 120.8, 118.8, 117.5, 63.4, 58.3, 40.5, 17.0, 14.7, 8.4; IR (KBr): 2978, 1742, 1671, 1476, 1363, 1159, 933, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1592.

ethyl 3-(2-fluorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ac): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (37.7 mg, 0.1 mmol), azlactone **2c** (37.7 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ac** (48.2 mg) in 90% yield as light yellow solid.

m.p. 71-72 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.82 – 7.76 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.25 – 7.13 (m, 3H), 7.12 – 7.04 (m, 1H), 5.92 – 5.71 (m, 1H), 5.48 (d, *J*

= 10.1 Hz, 1H), 5.34 (d, $J = 17.0$ Hz, 1H), 4.88 (s, 1H), 4.00 – 3.90 (m, 1H), 3.85 – 3.75 (m, 1H), 2.47 (s, 3H), 0.72 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 165.3, 161.9, 160.9 ($J = 250$ Hz), 145.0, 135.8, 135.2, 133.8 ($J = 10$ Hz), 131.9, 130.6, 129.5, 129.3, 128.2, 127.7, 126.1, 124.6, 123.7, 122.2, 120.0 ($J = 10$ Hz), 116.1 ($J = 20$ Hz), 68.7, 62.8, 45.8, 21.7, 13.2; IR (KBr): 2983, 1744, 1669, 1479, 1314, 1159, 1085, 755 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{24}\text{FN}_2\text{O}_6\text{S}$ 535.1339, found 535.1339.

ethyl 3-(2-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ad): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2d** (40.1 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ad** (45.3 mg) in 82% yield as light yellow solid.

m.p. 77-78 °C; inseparable diastereomers (dr = 88:12); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.41 – 7.27 (m, 7H), 7.24 – 7.19 (m, 1H), 7.16 (d, $J = 7.6$ Hz, 1H), 5.81 – 5.67 (m, 1H), 5.53 (d, $J = 10.0$ Hz, 1H), 5.41 (d, $J = 16.8$ Hz, 1H), 5.02 (d, $J = 9.5$ Hz, 1H), 4.02 – 3.91 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 (s, 3H), 0.72 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 165.0, 164.7, 145.2, 135.5, 135.0, 133.3, 131.8, 131.2, 130.6, 130.5, 130.4, 129.9, 129.2, 128.2, 127.6, 126.9, 126.2, 126.1, 123.9, 122.2, 68.9, 63.0, 45.4, 21.7, 13.1; IR (KBr): 2984, 1733, 1683, 1558, 1362, 1160, 933, 747 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{24}\text{ClN}_2\text{O}_6\text{S}$ 551.1044, found 551.1035.

ethyl 3-(2-bromobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ae): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2e** (46.8 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ae** (56.6 mg) in 95% yield as light yellow solid.

m.p. 70-71 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 5.83 – 5.67 (m, 1H), 5.55 (d, *J* = 9.8 Hz, 1H), 5.45 (d, *J* = 16.8 Hz, 1H), 5.03 (d, *J* = 9.3 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.85 – 3.74 (m, 1H), 2.44 (s, 3H), 0.72 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 165.7, 164.9, 145.2, 135.9, 135.6, 135.0, 133.6, 131.7, 130.7, 130.0, 129.8, 129.2, 128.2, 127.6, 127.3, 126.2, 126.1, 124.0, 122.2, 119.6, 68.7, 63.0, 45.4, 21.8, 13.2; IR (KBr): 2981, 1734, 1653, 1507, 1159, 1085, 933, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄BrN₂O₆S 595.0539, found 595.0540.

ethyl

3-(3-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3af):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2f** (37.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3af** (44.1 mg) in 83% yield as light yellow solid.

m.p. 102-103 °C; inseparable diastereomers (dr > 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.31 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 5.81 – 5.67 (m, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.98 (d, *J* = 9.6 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.87 – 3.74 (m, 1H), 2.49 (s, 3H), 2.36 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 166.0, 165.4, 145.0, 138.3, 135.6, 135.1, 133.3, 132.7, 130.9, 129.8, 129.2, 128.4, 127.8, 127.5, 126.2, 126.0, 123.9, 123.6, 122.2, 68.4, 62.9, 45.5, 21.8, 21.3, 13.2; IR (KBr): 2984, 1771, 1698, 1576, 1175, 1086, 935, 740 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₇N₂O₆S 531.1590, found 531.1597.

ethyl 3-(3-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ag): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2g** (40.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ag** (52.4 mg) in 95% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 3H), 7.34 – 7.28 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 5.81 – 5.66 (m, 1H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.84 – 3.74 (m, 1H), 2.49 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 165.2, 164.6, 145.2, 135.5, 135.1, 135.0, 134.8, 132.0, 130.8, 129.8, 129.2, 128.2, 127.6, 126.2, 126.1, 124.8, 123.7, 122.2, 68.5, 63.1, 45.4, 21.8, 13.1; IR (KBr): 2982, 1733, 1674, 1558, 1368, 1161, 933, 750 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1041.

ethyl

3-(4-methylbenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ah): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2h** (37.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ah** (45.2 mg) in 85% yield as light yellow solid.

m.p. 88-89 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.23 – 7.13

(m, 4H), 6.99 (s, 1H), 5.84 – 5.67 (m, 1H), 5.45 (d, $J = 10.1$ Hz, 1H), 5.31 (d, $J = 16.9$ Hz, 1H), 4.97 (d, $J = 9.4$ Hz, 1H), 4.01 – 3.90 (m, 1H), 3.86 – 3.74 (m, 1H), 2.47 (s, 3H), 2.37 (s, 3H), 0.71 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.4, 161.0, 160.7, 140.3, 137.7, 130.9, 130.4, 126.1, 125.8, 124.9, 124.5, 124.4, 123.6, 122.8, 122.3, 121.4, 121.3, 118.9, 117.4, 63.6, 58.1, 40.8, 17.0, 16.8, 8.4; IR (KBr): 2986, 1742, 1667, 1500, 1364, 1177, 803, 668 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_6\text{S}$ 531.1590, found 531.1596.

ethyl

3-(4-methoxybenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3ai): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2i** (39.5 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ai** (51 mg) in 93% yield as light yellow solid.

m.p. 87-88 °C; inseparable diastereomers (dr = 92:8); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 2H), 7.38 – 7.34 (m, 3H), 7.23 – 7.18 (m, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 6.94 (s, 1H), 6.87 (d, $J = 8.7$ Hz, 2H), 5.85 – 5.66 (m, 1H), 5.45 (d, $J = 10.1$ Hz, 1H), 5.31 (d, $J = 16.8$ Hz, 1H), 4.95 (d, $J = 8.8$ Hz, 1H), 4.01 – 3.89 (m, 1H), 3.85 – 3.77 (m, 4H), 2.47 (s, 3H), 0.70 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 165.6, 165.3, 162.5, 145.0, 135.7, 135.2, 130.9, 129.6, 129.3, 128.9, 128.4, 127.5, 126.1, 126.0, 125.6, 123.6, 122.1, 113.7, 68.3, 62.8, 55.4, 45.6, 21.7, 13.2; IR (KBr): 2985, 1732, 1667, 1487, 1263, 1176, 933, 747 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_7\text{S}$ 547.1539, found 547.1548.

ethyl 3-(4-fluorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3aj): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2j** (37.7 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction

mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3aj** (49.3 mg) in 92% yield as light yellow solid.

m.p. 79-80 °C; inseparable diastereomers (dr = 91:9); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.36 (d, *J* = 7.9 Hz, 3H), 7.23 – 7.19 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.98 (s, 1H), 5.85 – 5.70 (m, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 5.32 (d, *J* = 16.7 Hz, 1H), 4.94 (d, *J* = 9.1 Hz, 1H), 4.00 – 3.88 (m, 1H), 3.86 – 3.74 (m, 1H), 2.47 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.4, 164.8, 145.1, 135.7, 135.1, 130.9, 129.6, 129.5, 129.4 (*J* = 10 Hz), 129.3, 128.2, 127.6, 126.2, 126.1, 123.7, 122.2, 115.6 (*J* = 20 Hz), 68.4, 63.0, 45.5, 21.7, 13.2; IR (KBr): 2987, 1734, 1653, 1489, 1233, 1158, 850, 762 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄FN₂O₆S 535.1339, found 535.1339.

ethyl 3-(4-chlorobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3ak): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2k** (40.1 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3ak** (48.6 mg) in 88% yield as light yellow solid.

m.p. 87-88 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 5H), 7.25 – 7.19 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 5.83 – 5.67 (m, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 4.94 (d, *J* = 9.4 Hz, 1H), 4.02 – 3.89 (m, 1H), 3.84 – 3.74 (m, 1H), 2.47 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.3, 164.8, 145.1, 138.2, 135.7, 135.1, 131.7, 130.8, 129.6, 129.3, 128.8, 128.4, 128.2, 127.6, 126.1, 123.7, 122.2, 68.4, 63.0, 45.5, 21.7, 13.1; IR (KBr): 2981, 1733, 1670, 1481, 1363, 1160, 933, 755 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄ClN₂O₆S 551.1044, found 551.1055.

ethyl 3-(4-bromobenzamido)-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate

(3al): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **2l** (46.8 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3al** (50.7 mg) in 85% yield as light yellow solid.

m.p. 78-79 °C; inseparable diastereomers (dr = 95:5); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.23 – 7.18 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 5.83 – 5.67 (m, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 4.94 (d, *J* = 9.4 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.84 – 3.74 (m, 1H), 2.46 (s, 3H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 165.3, 164.9, 145.1, 135.7, 135.1, 132.2, 131.8, 130.8, 129.6, 129.3, 128.6, 128.2, 127.6, 126.7, 126.1, 123.7, 122.2, 68.4, 63.0, 45.5, 21.7, 13.1; IR (KBr):2981, 1733, 1670, 1479, 1367, 1160, 1010, 844 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₄BrN₂O₆S 595.0539, found 595.0532.

ethyl

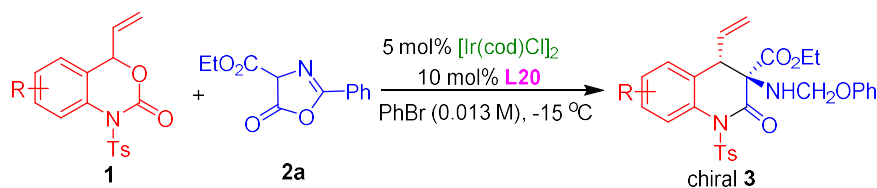
2-oxo-1-tosyl-3-(4-(trifluoromethyl)benzamido)-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (3am):

Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **2m** (45.2 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **3am** (48.6 mg) in 83% yield as light yellow solid.

m.p. 104-105 °C; inseparable diastereomers (dr = 94:6); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.76 – 7.70 (m, 3H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.25 – 7.20 (m,

1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.08 (s, 1H), 5.83 – 5.68 (m, 1H), 5.47 (d, $J = 10.6$ Hz, 1H), 5.33 (d, $J = 16.8$ Hz, 1H), 4.96 (d, $J = 9.7$ Hz, 1H), 4.00 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 165.1, 164.6, 145.2, 136.6, 135.4 ($J = 60$ Hz), 133.6 ($J = 40$ Hz), 130.8, 129.6, 129.3, 128.1, 127.7, 127.5, 126.2, 125.6 ($J = 3$ Hz), 123.7, 122.2, 68.5, 63.1, 45.4, 21.7, 13.1; IR (KBr): 2984, 1734, 1670, 1522, 1325, 1162, 933, 856 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{29}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_6\text{S}$ 585.1307, found 585.1325.

5. Procedure for the synthesis of chiral 3 and characterization data



Under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinone **1** (0.1 mmol), azlactone **2a** (0.05 mmol), [Ir(COD)Cl]₂ (0.0025 mmol) and **L20** (0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure product **chiral 3**.

ethyl (3R,4S)-3-benzamido-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3aa): Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **2a** (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and **L20** (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 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 = 15:1) to afford pure product chiral **3aa** (20.7 mg) in 80% yield as light yellow solid.

m.p. 75-77 °C; [α]_D²⁰ = +11.1 (c 0.38, Acetone); inseparable diastereomers (dr = 84:16); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.40 – 7.34 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 5.82 – 5.69 (m, 1H), 5.47 (d, *J* = 10.1 Hz, 1H), 5.33 (d, *J* = 16.9 Hz, 1H), 4.97 (d, *J* = 9.5 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.47 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.4, 145.1, 135.6, 135.1, 133.4, 131.9, 130.9, 129.7, 129.2, 128.5, 128.3, 127.6, 127.0, 126.2, 126.1, 123.7, 122.2, 68.3, 62.9, 45.5, 21.8, 13.2; IR (KBr): 2986, 1733, 1669, 1506, 1265, 1159, 933, 740 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₈H₂₆N₂O₆S 517.1434, found 517.1422; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AS-H, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 41.560 min (minor), *t*_R = 20.360 min (major).

ethyl

(3R,4S)-3-benzamido-6-methoxy-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3ea): Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone **1e** (35.9 mg, 0.1 mmol), azlactone **2a** (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and **L20** (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 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 = 15:1) to afford pure product chiral **3ea** (18.2 mg) in 66% yield as light yellow solid.

m.p. 77-79 °C; [α]_D²⁰ = +9.9 (c 0.36, Acetone); inseparable diastereomers (dr = 83:17); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.42 – 7.33 (m, 4H), 7.00 (s, 1H), 6.91 – 6.86 (m, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 5.82 – 5.68 (m, 1H), 5.46 (d, *J* = 10.1 Hz, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 4.89 (d, *J* = 8.9 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.89 – 3.81 (m, 1H), 3.80 (s, 3H), 2.48 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.9, 165.3, 157.7, 145.0, 135.6, 133.4, 131.9, 130.8, 130.0, 129.6, 129.2, 128.5, 128.2, 127.0, 123.7, 123.6, 112.5, 111.8, 68.3, 62.9, 55.6, 45.7, 21.7, 13.3; IR (KBr): 2982, 1733, 1670, 1489, 1219, 1152, 936, 710 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M - H]⁻ Calcd for C₂₉H₂₈N₂O₇S 547.1539, found 547.1536; Enantiomeric excess: 86:14, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 36.187 min (minor), *t*_R = 25.073 min (major).

ethyl

(3R,4S)-3-benzamido-6-chloro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral 3ga): Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinanone **1g** (36.3 mg, 0.1 mmol), azlactone **2a** (11.2 mg, 0.05 mmol), [Ir(COD)Cl]₂ (1.7 mg, 0.0025 mmol) and **L20** (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 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 = 15:1) to afford pure product chiral **3ga** (19.2mg) in 70% yield as light yellow solid.

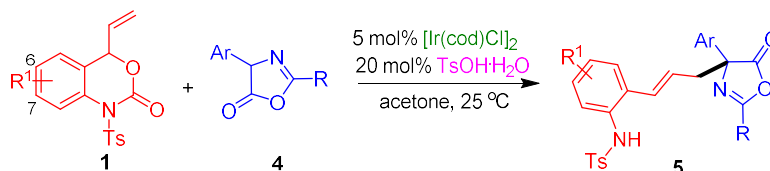
m.p. 74-76 °C; $[\alpha]_D^{20} = +14.1$ (c 0.38, Acetone); inseparable diastereomers (dr = 83:17); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.57 (d, $J = 7.3$ Hz, 2H), 7.53 – 7.47 (m, 1H), 7.43 – 7.33 (m, 5H), 7.13 (s, 1H), 7.08 (s, 1H), 5.73 – 5.61 (m, 1H), 5.49 (d, $J = 10.0$ Hz, 1H), 5.33 (d, $J = 16.7$ Hz, 1H), 4.99 (d, $J = 9.6$ Hz, 1H), 4.07 – 4.00 (m, 1H), 3.91 – 3.82 (m, 1H), 2.49 (s, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 165.8, 164.9, 145.4, 135.1, 133.6, 133.2, 132.0, 131.7, 130.5, 130.1, 129.9, 129.3, 128.5, 127.4, 127.0, 126.3, 124.5, 123.4, 68.1, 63.3, 45.2, 21.8, 13.3; IR (KBr): 3124, 1734, 1670, 1479, 1399, 1154, 935, 810 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{25}\text{ClN}_2\text{O}_6\text{S}$ 551.1044, found 551.1040; Enantiomeric excess: 89:11, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 11.963$ min (minor), $t_R = 17.737$ min (major).

ethyl

(3*R*,4*S*)-3-benzamido-7-fluoro-2-oxo-1-tosyl-4-vinyl-1,2,3,4-tetrahydroquinoline-3-carboxylate (chiral **3ia):** Following the general procedure, under an argon atmosphere, bromobenzene (4 mL) was added to the mixture of vinyl benzoxazinone **1i** (34.7 mg, 0.1 mmol), azlactone **2a** (11.2 mg, 0.05 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (1.7 mg, 0.0025 mmol) and **L20** (3.0 mg, 0.005 mmol). Then, the reaction mixture was stirred at -15 °C for 1.5 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 = 15:1) to afford pure product chiral **3ia** (18.7 mg) in 70% yield as light yellow solid. m.p. 127-129 °C; $[\alpha]_D^{20} = +10.7$ (c 0.37, Acetone); inseparable diastereomers (dr = 74:26); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 7.5$ Hz, 2H), 7.57 – 7.52 (m, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.42 – 7.36 (m, 4H), 7.13 – 7.07 (m, 1H), 7.05 (s, 1H), 6.97 – 6.90 (m, 1H), 5.78 – 5.63 (m, 1H), 5.47 (d, $J = 10.0$ Hz, 1H), 5.32 (d, $J = 16.8$ Hz, 1H), 4.92 (d, $J = 9.5$ Hz, 1H), 4.07 – 3.96 (m, 1H), 3.89 – 3.80 (m, 1H), 2.48 (s, 3H), 0.79 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 165.8, 165.1, 145.4, 136.1, 135.3, 133.2, 132.0, 130.6, 129.7, 129.3, 128.5, 127.0, 124.0, 112.6 ($J = 20$ Hz), 110.2 ($J = 30$ Hz), 68.2, 63.1, 45.0, 21.8, 13.3; IR (KBr): 2988, 1748, 1670, 1507, 1275, 1177, 847, 750 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{28}\text{H}_{25}\text{FN}_2\text{O}_6\text{S}$ 535.1339, found 535.1351; Enantiomeric

excess: 88:12, determined by HPLC (Daicel Chiralpak OD-H, hexane/ isopropanol = 95/ 5, flow rate 1.0 mL/min, T = 30 °C, 254 nm): $t_R = 19.283$ min (minor), $t_R = 27.760$ min (major).

6. Procedure for the synthesis of product 5 and characterization data



Under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinones **1** (0.1 mmol), azlactones **4** (0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure products **5**.

(E)-4-methyl-N-(2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide (5aa) :Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5aa** (48 mg) in 92% yield as light yellow solid.

m.p. 60-61 °C ; *E/Z* = 83:17; ^1H NMR (400 MHz, CDCl_3) δ 8.45 – 8.35 (m, 2H), 7.67 – 7.61 (m, 2H), 7.61 – 7.53 (m, 3H), 7.53 – 7.38 (m, 4H), 7.34 (s, 1H), 7.28 – 7.25 (m, 1H), 7.22 (d, $J = 6.2$ Hz, 2H), 7.19 – 7.12 (m, 1H), 7.12 – 7.02 (m, 2H), 6.26 (s, 1H), 6.09 (d, $J = 15.7$ Hz, 1H), 5.77 – 5.64 (m, 1H), 3.07 – 2.88 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 156.2, 143.9, 138.2, 136.6, 133.1, 132.7, 131.6, 131.2, 129.6, 129.2, 128.9, 128.8, 128.7, 128.6, 128.3, 127.3, 127.2, 126.3, 126.0, 125.7, 124.7, 106.0, 45.3, 21.6; IR (KBr): 2923, 1772, 1338, 1161, 963, 750 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$ 523.1692, found 523.1693.

(E)-N-(2-(3-(2-(2-chlorophenyl)-5-oxo-4-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ab): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **4b** (40.7mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ab** (52.8 mg) in 95% yield as light yellow solid.

m.p. 70-71 °C; *E/Z* = 95:5; ¹H NMR (400 MHz, CDCl₃) δ 8.50 – 8.39 (m, 2H), 7.67 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.63 – 7.46 (m, 6H), 7.40 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.08 – 7.00 (m, 2H), 6.13 (s, 1H), 6.03 (d, *J* = 15.7 Hz, 1H), 5.75 – 5.61 (m, 1H), 3.36 – 3.13 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.6, 143.9, 136.6, 135.2, 133.1, 132.9, 132.3, 132.0, 131.7, 131.3, 130.7, 129.7, 129.2, 128.9, 128.6, 128.2, 127.3, 127.1, 127.0, 126.4, 125.9, 125.0, 105.3, 41.5, 21.6; IR (KBr): 2963, 1778, 1337, 1162, 961, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₂₆ClN₂O₄S 557.1302, found 557.1320.

(E)-N-(2-(3-(2-(3-chlorophenyl)-5-oxo-4-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ac): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **4c** (40.7mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ac** (28.1 mg) in 51% yield as light yellow solid.

m.p. 63-64 °C; *E/Z* = 91:9; ¹H NMR (400 MHz, CDCl₃) δ 8.48 – 8.33 (m, 2H), 7.68 – 7.63 (m, 1H), 7.62 – 7.44 (m, 6H), 7.42 – 7.35 (m, 2H), 7.25 – 7.19 (m, 3H), 7.19 – 7.03 (m, 3H), 6.28 (s, 1H), 6.18 (d, *J* = 15.7 Hz, 1H), 5.75 – 5.61 (m, 1H), 3.08 – 2.87 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 156.5, 143.9, 140.2, 136.6, 134.7, 133.1, 133.0, 131.7, 130.0, 129.7, 129.3, 128.9, 128.8, 128.7, 128.1, 127.3, 127.2, 126.4, 124.9, 124.8, 124.2, 105.1, 45.1, 21.6; IR

(KBr): 2922, 1779, 1337, 1160, 965, 751 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{26}\text{ClN}_2\text{O}_4\text{S}$ 557.1302, found 557.1318.

(E)-4-methyl-N-(2-(3-(5-oxo-4-phenyl-2-(p-tolyl)-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide (5ad): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **4d** (37.7mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ad** (46.6 mg) in 87% yield as light yellow solid.

m.p. 68-69 °C; E/Z = 91:9; ^1H NMR (400 MHz, CDCl_3) δ 8.45 – 8.35 (m, 2H), 7.60 – 7.54 (m, 3H), 7.53 – 7.45 (m, 4H), 7.31 – 7.26 (m, 2H), 7.25 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.18 – 7.14 (m, 1H), 7.11 – 7.03 (m, 2H), 6.25 (s, 1H), 6.04 (d, J = 15.7 Hz, 1H), 5.76 – 5.65 (m, 1H), 3.03 – 2.87 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 156.1, 143.9, 139.2, 136.6, 135.3, 133.1, 132.7, 131.6, 131.1, 129.6, 129.3, 128.8, 128.7, 128.6, 128.4, 127.3, 127.2, 126.3, 126.0, 125.9, 124.8, 106.1, 45.2, 21.6, 21.2; IR (KBr): 2925, 1774, 1338, 1162, 967, 753 cm^{-1} ; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}_4\text{S}$ 537.1848, found 537.1835.

(E)-N-(2-(3-(4-(3-chlorophenyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ae): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinanone **1a** (32.9 mg, 0.1 mmol), azlactone **4e** (40.7mg, 0.15 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ae** (52.8 mg) in 95% yield as light yellow solid.

m.p. 65-66 °C; E/Z = 83:17; ^1H NMR (400 MHz, CDCl_3) δ 8.43 – 8.37 (m, 1H), 8.36 – 8.29 (m, 1H), 7.67 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.50 (m, 1H), 7.49 – 7.39 (m, 4H), 7.26 – 7.18 (m, 3H), 7.18 – 7.12 (m, 1H), 7.12 – 7.03 (m, 2H), 6.36 (s, 1H), 6.15 (d, J = 15.7 Hz, 1H),

5.77 – 5.62 (m, 1H), 3.08 – 2.89 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 155.2, 143.9, 137.9, 136.6, 135.0, 133.1, 132.8, 131.6, 131.4, 130.2, 129.9, 129.6, 129.3, 128.7, 128.6, 127.2, 126.9, 126.4, 126.0, 125.2, 124.8, 106.2, 45.2, 21.6; IR (KBr): 2923, 1777, 1333, 1162, 967, 756 cm⁻¹; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₂₆ClN₂O₄S 5557.1302, found 557.1313.

(E)-N-(2-(3-(4-(4-fluorophenyl)-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5af): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1a** (32.9 mg, 0.1 mmol), azlactone **4f** (38.3mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5af** (44.8 mg) in 83% yield as light yellow solid.

m.p. 60-61 °C; *E/Z* = 83:17; ¹H NMR (400 MHz, CDCl₃) δ 8.55 – 8.37 (m, 2H), 7.66 – 7.55 (m, 4H), 7.49 – 7.39 (m, 3H), 7.26 – 7.13 (m, 6H), 7.11 – 7.03 (m, 2H), 6.30 (s, 1H), 6.13 (d, *J* = 15.8 Hz, 1H), 5.76 – 5.64 (m, 1H), 3.04 – 2.92 (m, 2H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.6(*J* = 253 Hz), 163.9, 155.1, 143.9, 138.2, 136.6, 133.1, 131.6, 131.3, 131.2, 129.6, 129.2, 128.7, 128.6, 127.3, 127.2, 126.3, 126.0, 125.5, 124.7, 124.6, 116.1(*J* = 21.8 Hz), 45.3, 21.6; IR (KBr): 2923, 1774, 1509, 1333, 1157, 964, 753 cm⁻¹; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₂₆FN₂O₄S 541.1597, found 541.1599.

(E)-4-methyl-N-(4-methyl-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)benzenesulfonamide (5da) : Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1d**(34.3 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5da** (42.9 mg) in 80% yield as light yellow solid.

m.p. 45-49 °C; *E/Z* > 95:5; ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 6.7 Hz, 2H), 7.60 – 7.53 (m, 3H), 7.53 – 7.32 (m, 5H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.89 (s, 1H), 6.14 (s, 1H), 6.04 (d, *J* = 15.8 Hz, 1H), 5.76 – 5.59 (m, 1H), 3.10 – 2.84 (m, 2H), 2.39 (s, 3H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 156.2, 143.7, 138.3, 136.7, 136.4, 132.7, 132.1, 131.5, 130.4, 129.6, 129.3, 129.1, 128.8, 128.7, 128.4, 127.7, 126.0, 125.6, 124.5, 106.0, 45.2, 21.6, 20.9; IR (KBr): 2923, 1773, 1396, 1162, 962, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₂H₂₉N₂O₄S 537.1848, found 537.1848.

(*E*)-*N*-(4-methoxy-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ea) : Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1e** (35.9 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ea** (45.8 mg) in 83% yield as light yellow solid.

m.p. 79-80 °C; inseparable *E/Z*-isomers (*E/Z* = 93:7); ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.28 (m, 2H), 7.63 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.59 – 7.41 (m, 8H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.69 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.03 (d, *J* = 15.8 Hz, 1H), 5.97 (s, 1H), 5.73 – 5.61 (m, 1H), 3.66 (s, 3H), 3.02 – 2.83 (m, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 158.4, 156.2, 143.7, 138.3, 136.7, 134.8, 132.7, 131.6, 129.6, 129.1, 128.9, 128.8, 128.7, 128.4, 127.3, 126.0, 125.9, 125.0, 114.2, 111.5, 105.9, 55.3, 45.1, 21.9; IR (KBr): 2962, 1773, 1494, 1160, 803, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₂H₂₉N₂O₅S 553.1797, found 553.1805.

(*E*)-*N*-(4-fluoro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5fa): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1f** (34.7 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol) Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5fa** (27.5 mg) in 51% yield as light yellow solid.

m.p. 67-68 °C; inseparable *E/Z*-isomers (*E/Z* = 89:11); ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 7.4 Hz, 2H), 7.65 – 7.40 (m, 10H), 7.25 – 7.15 (m, 3H), 6.92 – 6.77 (m, 2H), 6.06 (s, 1H), 6.01 (d, *J* = 15.8 Hz, 1H), 5.78 – 5.66 (m, 1H), 3.02 – 2.86 (m, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 161.1 (*J* = 245 Hz), 159.9, 156.3, 144.0, 138.1, 136.4, 134.9 (*J* = 8.3 Hz), 132.8, 129.7, 129.2, 128.9, 128.8, 128.7, 127.2, 126.4, 126.0, 115.4 (*J* = 22.6 Hz), 113.4 (*J* = 23.3 Hz), 105.8, 45.1, 21.6; IR (KBr): 2916, 1773, 1507, 1261, 1161, 962, 750 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₂₆FN₂O₄S 541.1597, found 541.1591.

(*E*)-*N*-(4-chloro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ga): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1g** (36.3 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ga** (38.9 mg) in 70% yield as light yellow solid.

m.p. 72-73 °C; inseparable *E/Z*-isomers (*E/Z* = 87:13); ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.31 (m, 2H), 7.67 – 7.61 (m, 2H), 7.60 – 7.41 (m, 8H), 7.25 – 7.17 (m, 3H), 7.15 – 7.08 (m, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.22 (s, 1H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.79 – 5.65 (m, 1H), 3.05 – 2.86 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 156.3, 144.1, 138.1, 136.3, 133.3, 132.8, 132.0, 131.7, 130.1, 130.0, 129.7, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.3, 126.0, 105.8, 45.2, 21.6; IR (KBr): 2918, 1776, 1333, 1163, 963, 748 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₂₆ClN₂O₄S 557.1302, found 557.1304.

(*E*)-*N*-(4-bromo-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ha): Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1h** (40.6 mg, 0.1 mmol),

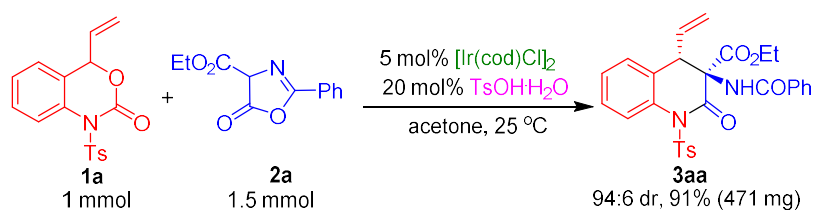
azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography (toluene/ethyl acetate = 20:1) to afford pure product **5ha** (49.2 mg) in 82% yield as light yellow solid.

m.p. 81-82 °C; inseparable *E/Z*-isomers (*E/Z* = 83:17); ¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.26 (m, 2H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.59 – 7.43 (m, 8H), 7.26 – 7.19 (m, 4H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.27 (s, 1H), 5.98 (d, *J* = 15.8 Hz, 1H), 5.80 – 5.63 (m, 1H), 3.07 – 2.84 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 156.3, 144.1, 138.1, 136.3, 133.5, 132.8, 132.2, 131.5, 130.1, 129.8, 129.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.2, 126.9, 126.8, 126.3, 126.0, 119.7, 105.8, 45.2, 21.6; IR (KBr): 2925, 1776, 1478, 1275, 1163, 962, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₂₆BrN₂O₄S 601.0797, found 601.0792.

(*E*)-*N*-(5-fluoro-2-(3-(5-oxo-2,4-diphenyl-4,5-dihydrooxazol-4-yl)prop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (5ia**):** Following the general procedure, under an argon atmosphere, acetone (4 mL) was added to the mixture of vinyl benzoxazinone **1i** (34.7 mg, 0.1 mmol), azlactone **4a** (35.6 mg, 0.15 mmol), [Ir(COD)Cl]₂ (3.4 mg, 0.005 mmol) and TsOH·H₂O (4.0 mg, 0.02 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 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 = 20:1) to afford pure product **5ia** (50.2 mg) in 93% yield as light yellow solid.

m.p. 66-67 °C; *E/Z* > 95:5; ¹H NMR (400 MHz, CDCl₃) δ 8.49 – 8.35 (m, 2H), 7.68 – 7.59 (m, 4H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.39 (m, 5H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.01 (dd, *J* = 8.6, 6.2 Hz, 1H), 6.78 – 6.66 (m, 1H), 6.45 (s, 1H), 6.04 (d, *J* = 15.7 Hz, 1H), 5.73 – 5.58 (m, 1H), 3.11 – 2.88 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 162.3 (*J* = 246 Hz), 156.3, 144.2, 138.2, 136.3, 134.7 (*J* = 10.7 Hz), 132.8, 130.2, 129.8, 129.2, 128.9, 128.8, 128.7, 128.3, 127.2, 126.5 (*J* = 3.3 Hz), 126.2, 126.0, 112.8 (*J* = 21.5 Hz), 110.3 (*J* = 25.3 Hz), 105.9, 45.2, 21.6; IR (KBr): 2918, 1774, 1497, 1335, 1168, 981, 749 cm⁻¹; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₃₁H₂₆FN₂O₄S 541.1597, found 541.1591.

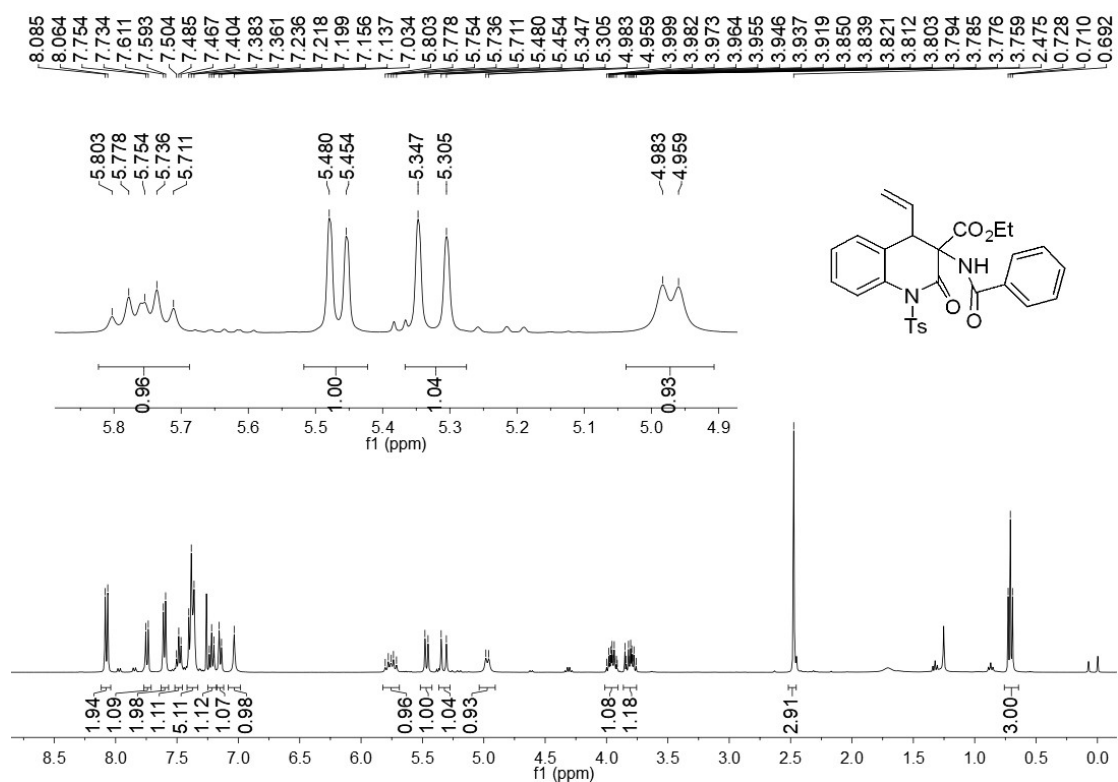
7. Procedure for one-mmol scale synthesis of product **3aa**



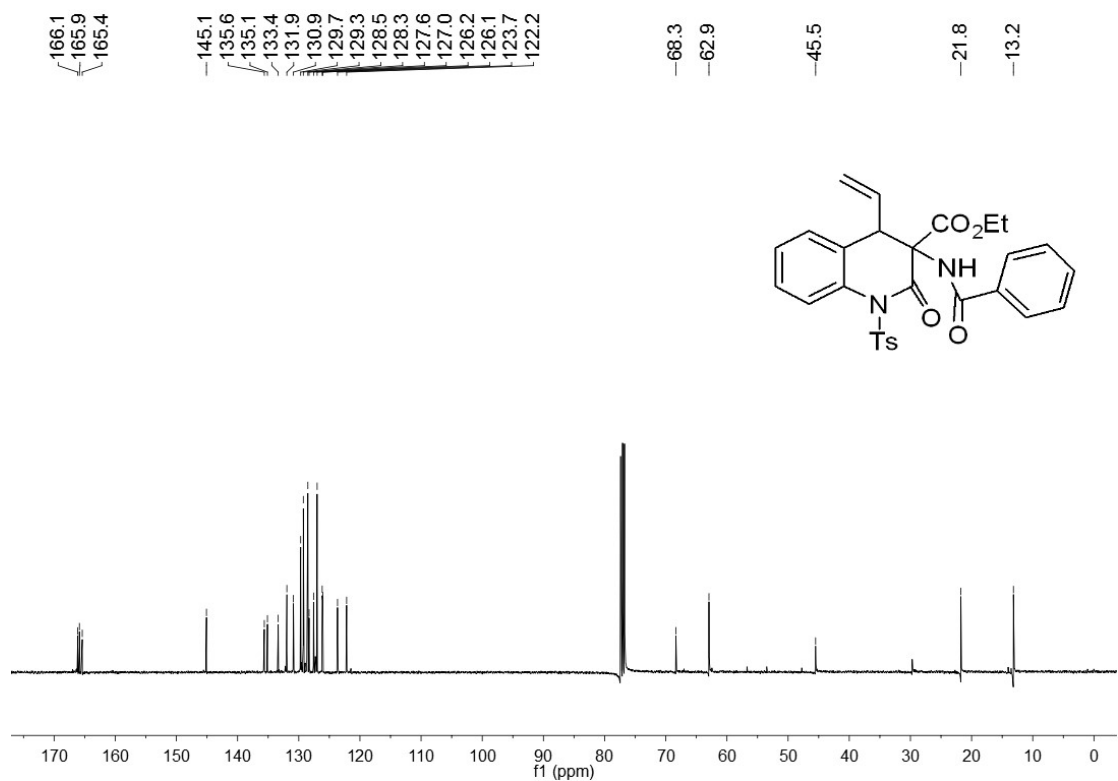
Under an argon atmosphere, acetone (40 mL) was added to the mixture of vinyl benzoxazinone **1a** (329 mg, 1 mmol), azlactone **2a** (350 mg, 1.5 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (34 mg, 0.05 mmol) and $\text{TsOH}\cdot\text{H}_2\text{O}$ (40 mg, 0.2 mmol). Then, the reaction mixture was stirred at 25 °C for 1.5 hours. After the completion of the reaction, which was indicated by TLC, the reaction mixture was directly purified through flash chromatography to afford pure product **3aa** (471 mg) in 91% yield as light yellow solid.

8. NMR spectra of products 3, 5 and chiral 3

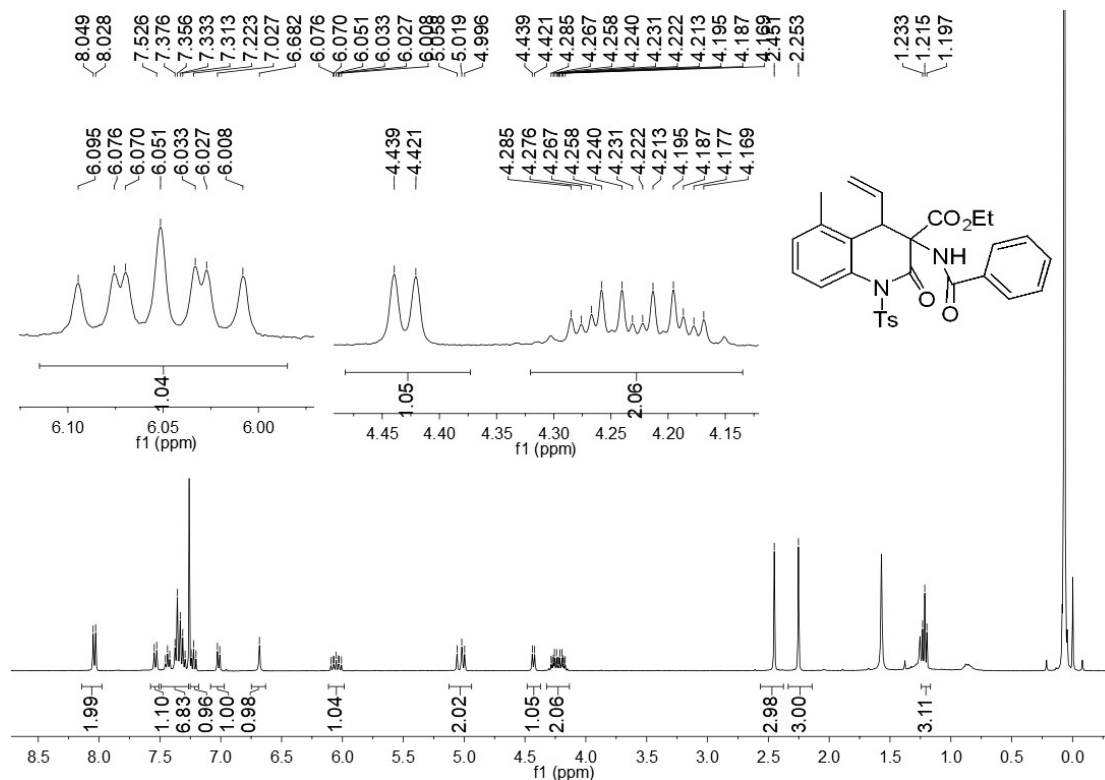
¹H NMR (400 MHz, CDCl₃) of compound **3aa**: inseparable diastereomers (dr = 94:6)



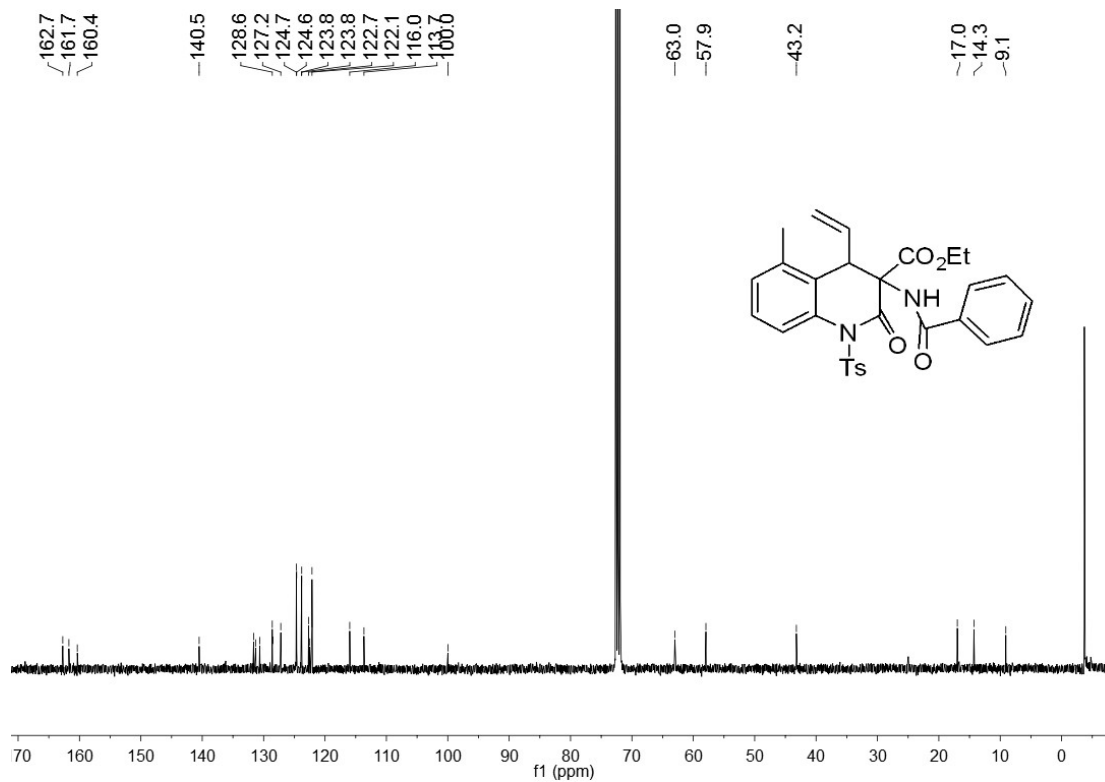
¹³C NMR (100 MHz, CDCl₃) of compound **3aa**: inseparable diastereomers (dr = 94:6)



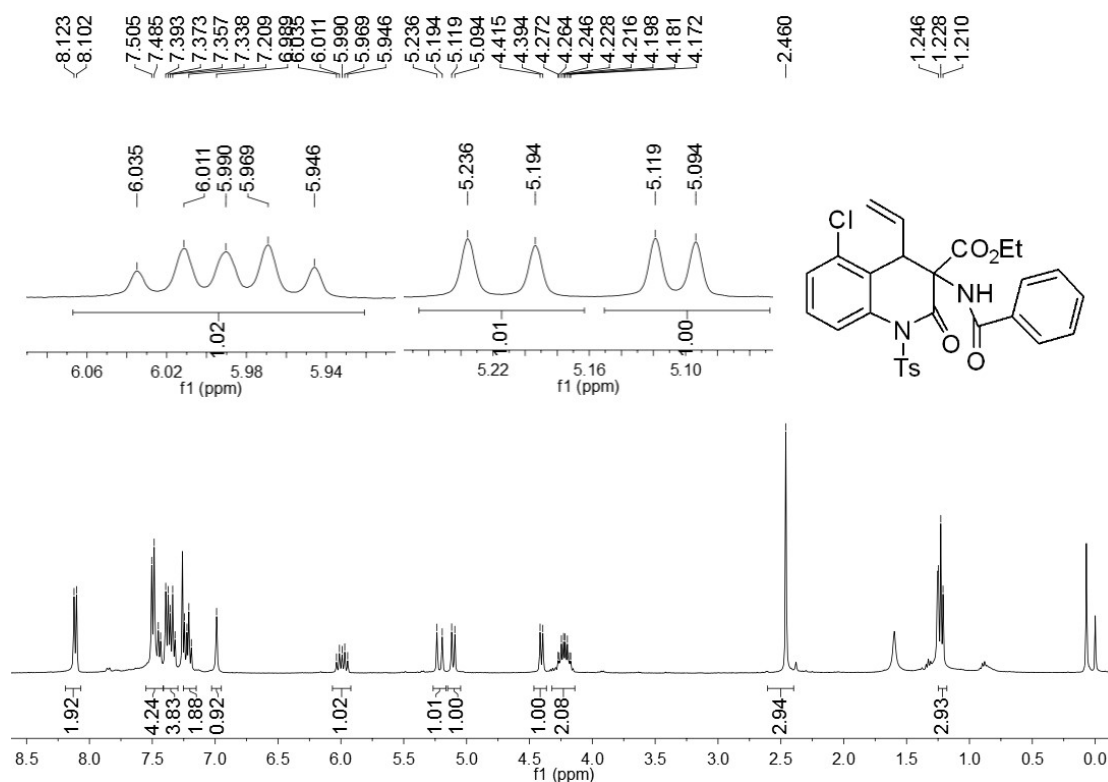
^1H NMR (400 MHz, CDCl_3) of compound **3ba**: inseparable diastereomers (dr > 95:5)



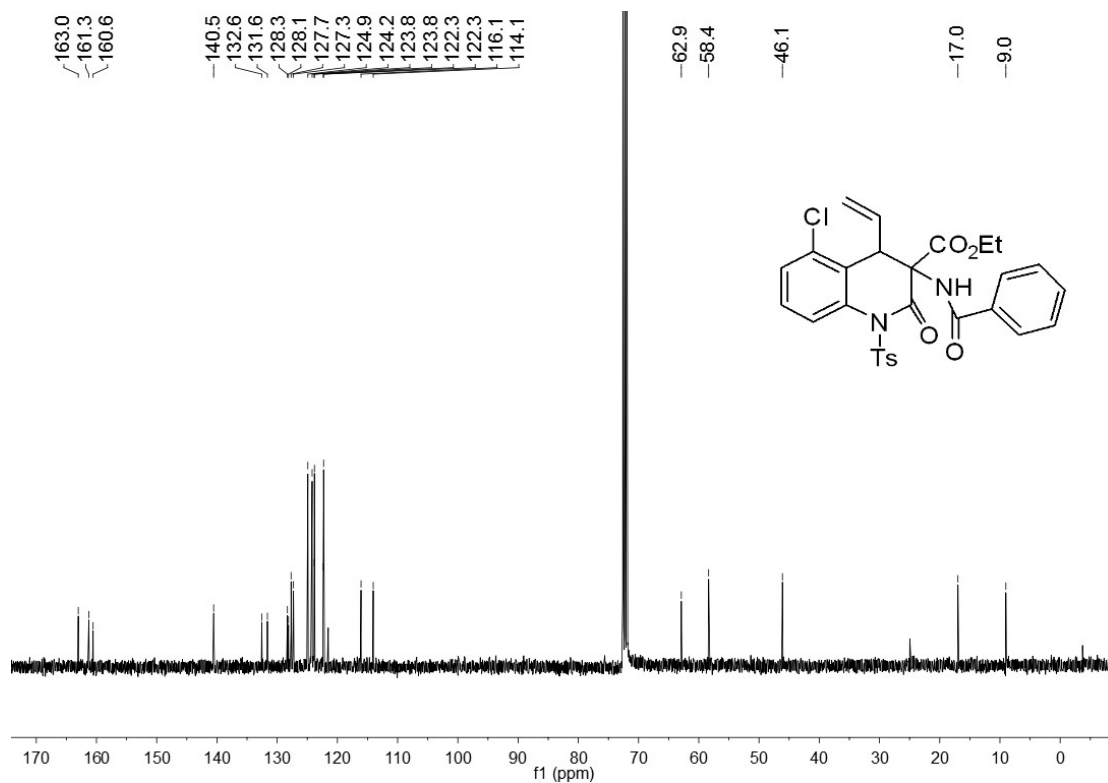
^{13}C NMR (100 MHz, CDCl_3) of compound **3ba**: inseparable diastereomers (dr > 95:5)



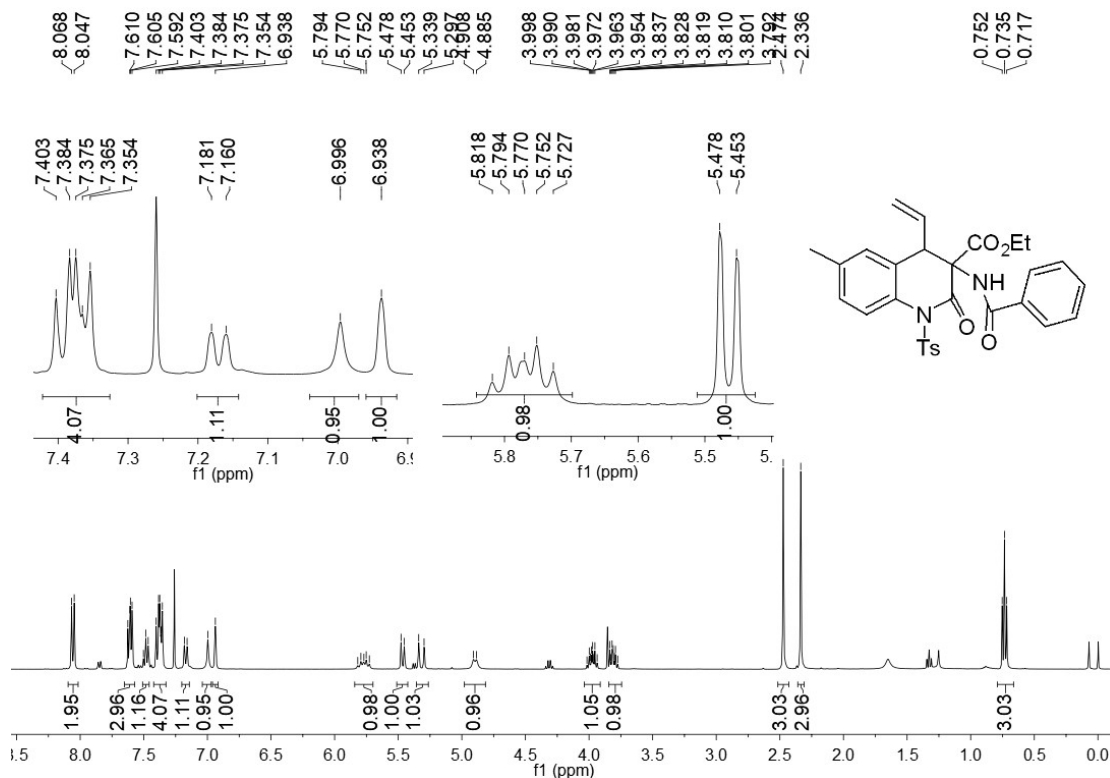
^1H NMR (400 MHz, CDCl_3) of compound **3ca**: inseparable diastereomers (dr > 95:5)



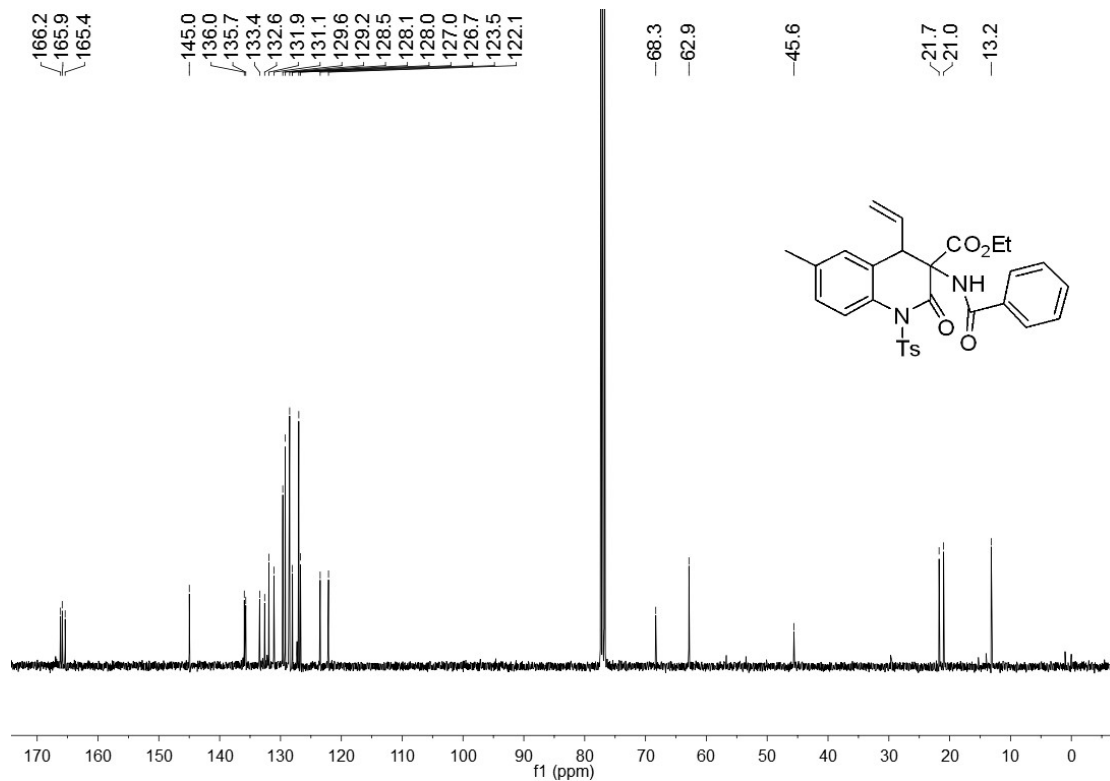
^{13}C NMR (100 MHz, CDCl_3) of compound **3ca**: inseparable diastereomers (dr > 95:5)



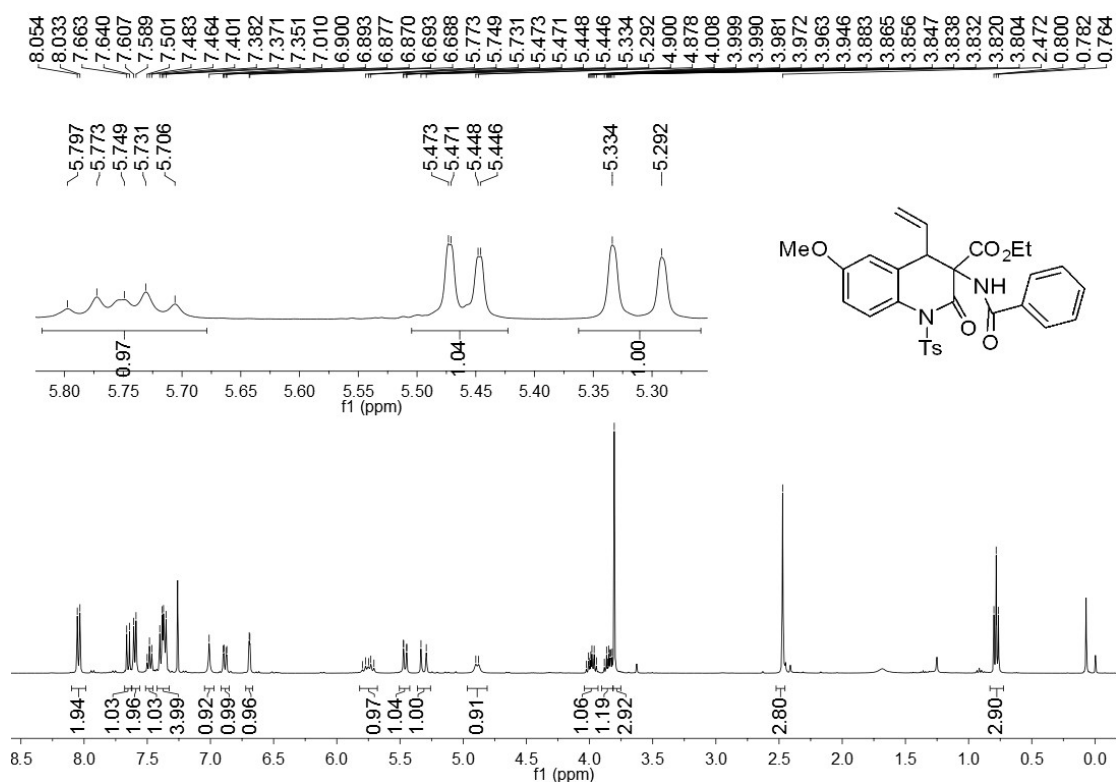
^1H NMR (400 MHz, CDCl_3) of compound **3da**: inseparable diastereomers (dr > 95:5)



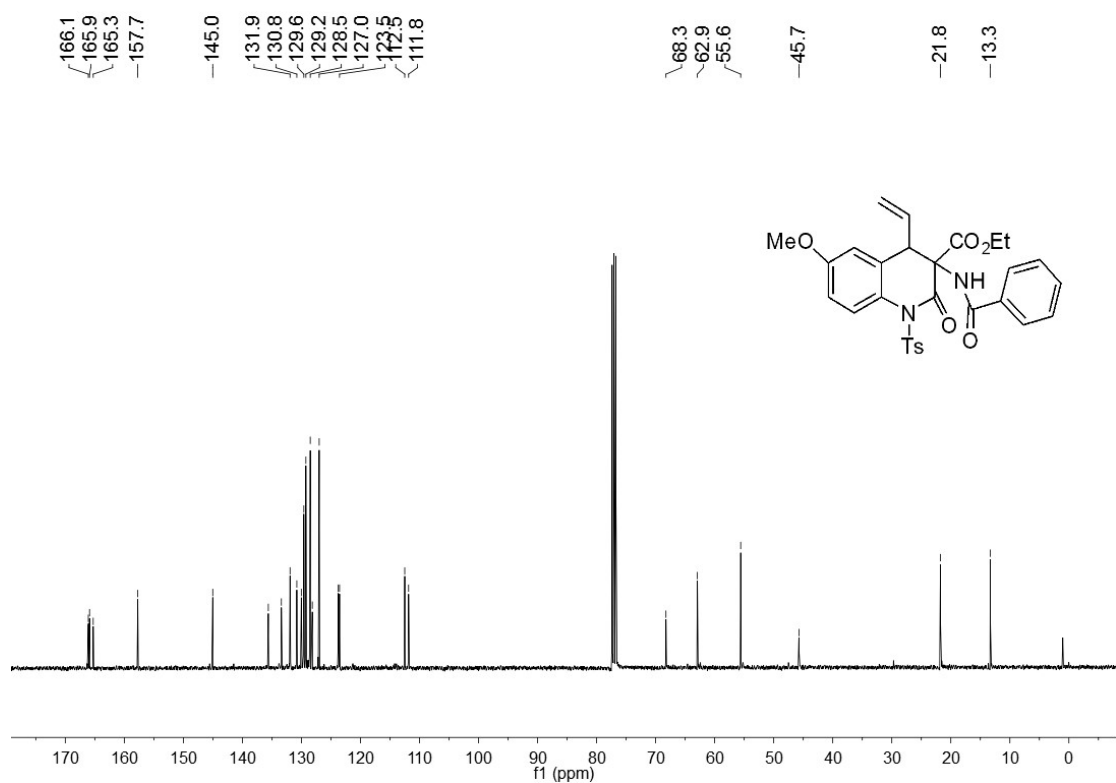
^{13}C NMR (100 MHz, CDCl_3) of compound **3da**: inseparable diastereomers (dr > 95:5)



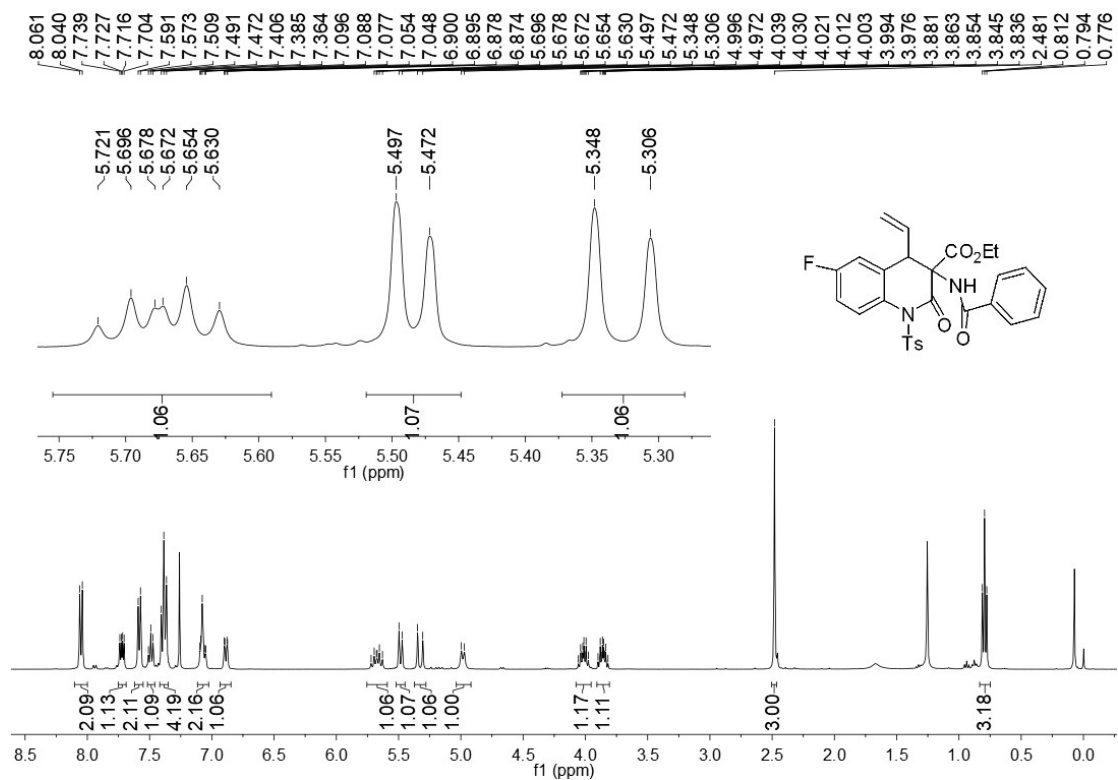
^1H NMR (400 MHz, CDCl_3) of compound **3ea**: inseparable diastereomers (dr > 95:5)



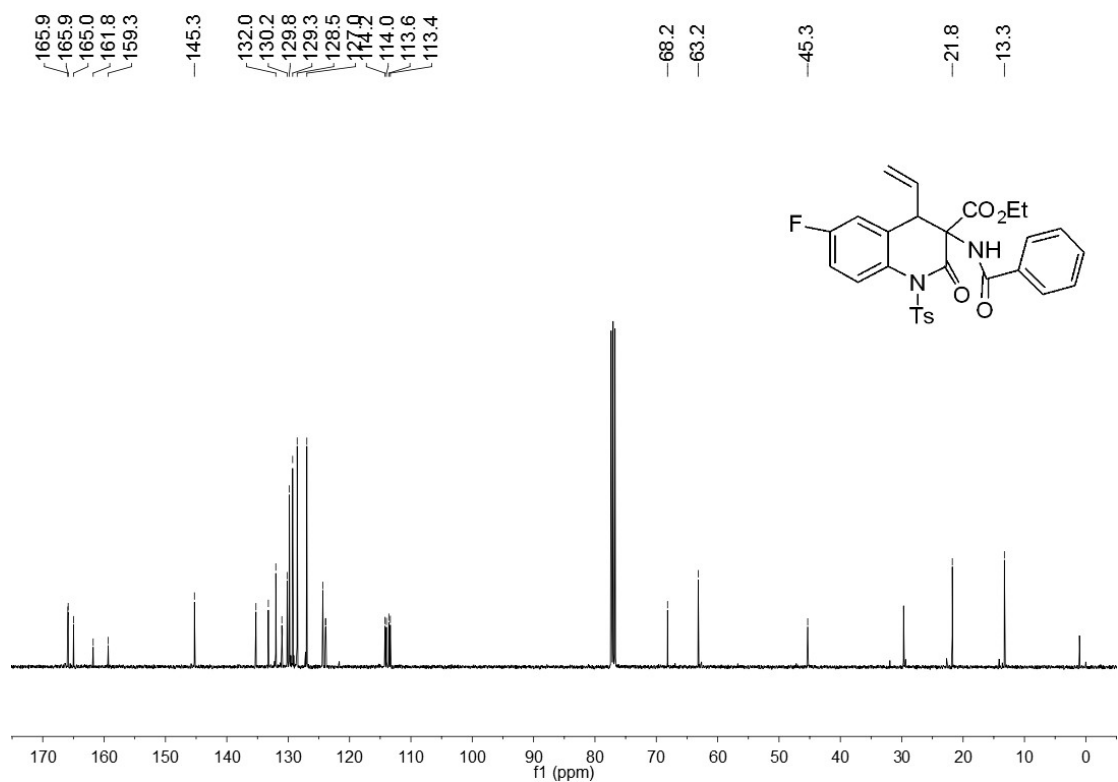
^{13}C NMR (100 MHz, CDCl_3) of compound **3ea**: inseparable diastereomers (dr > 95:5)



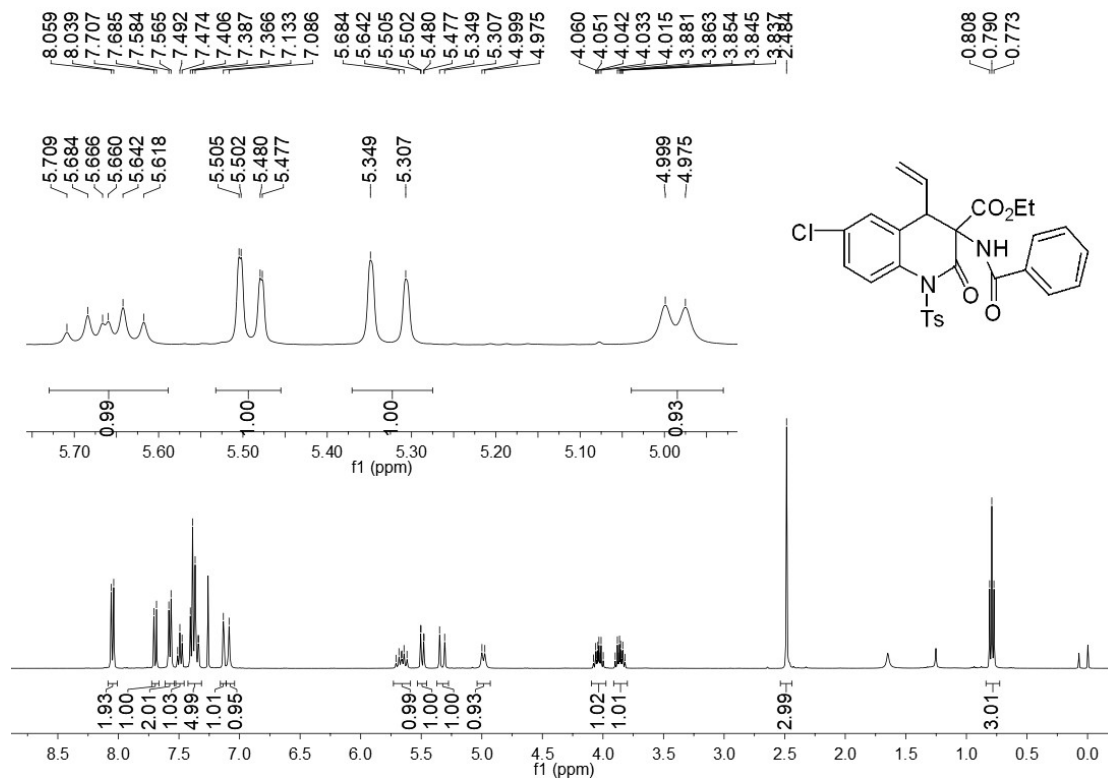
^1H NMR (400 MHz, CDCl_3) of compound **3fa**: inseparable diastereomers (dr = 95:5)



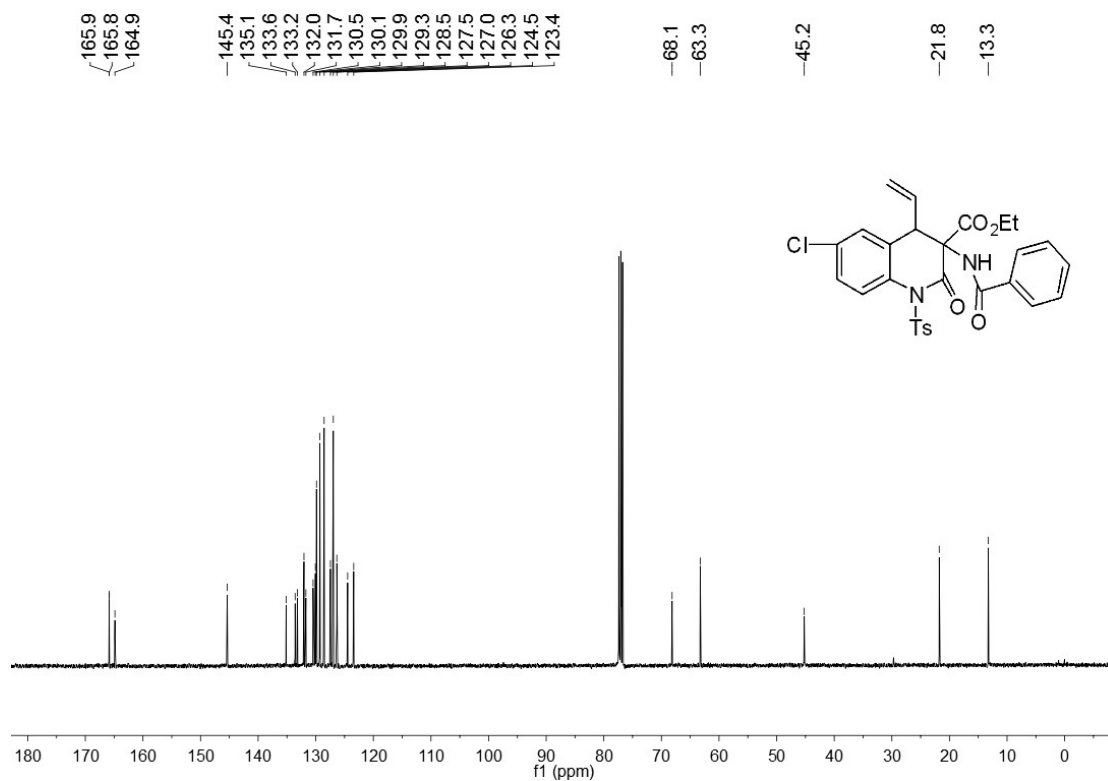
^{13}C NMR (100 MHz, CDCl_3) of compound **3fa**: inseparable diastereomers (dr = 95:5)



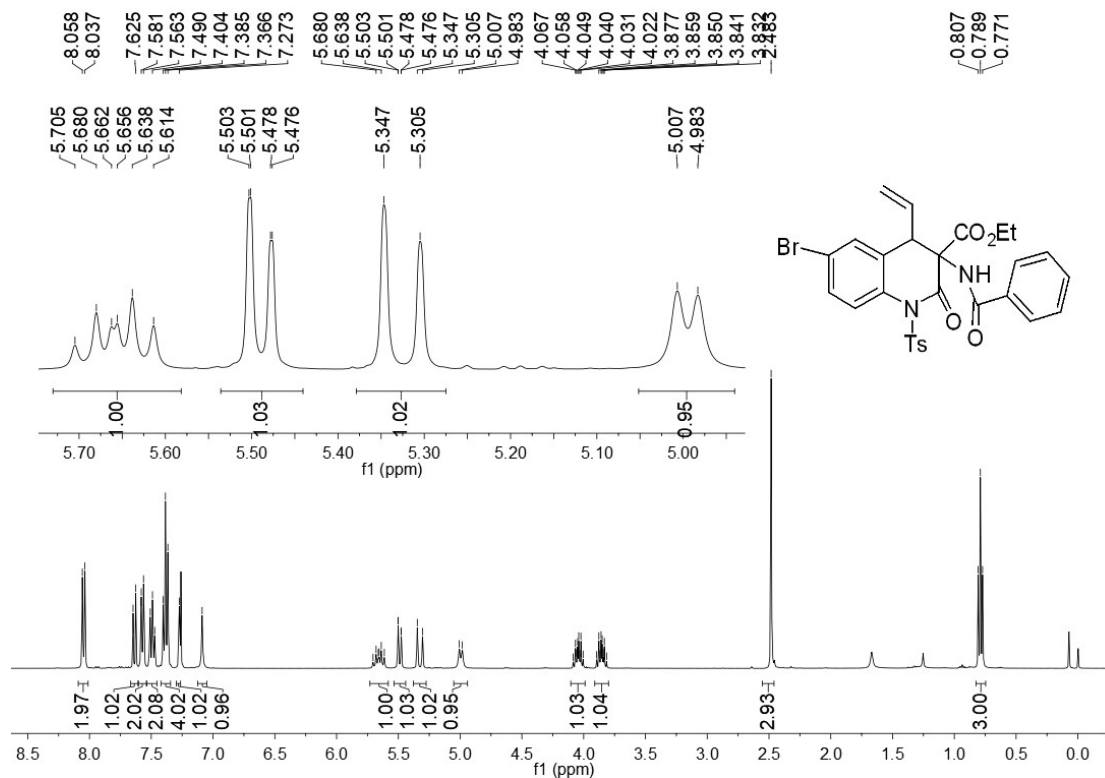
^1H NMR (400 MHz, CDCl_3) of compound **3ga**: inseparable diastereomers (dr > 95:5)



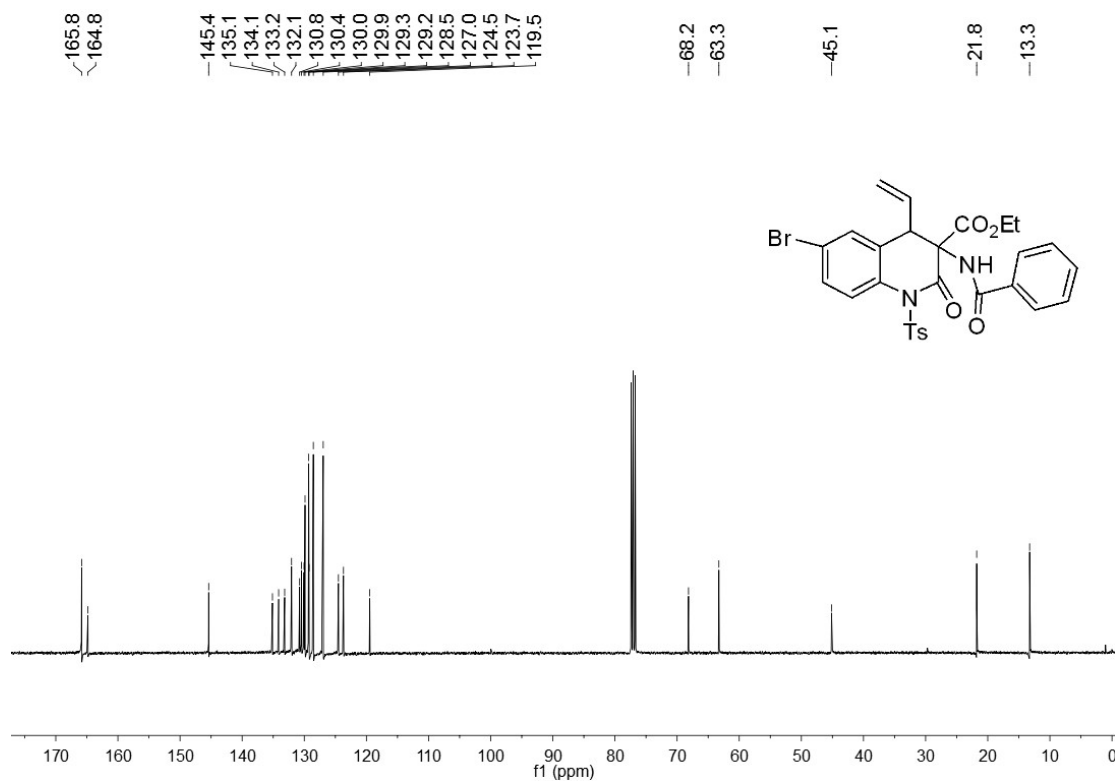
^{13}C NMR (100 MHz, CDCl_3) of compound **3ga**: inseparable diastereomers (dr > 95:5)



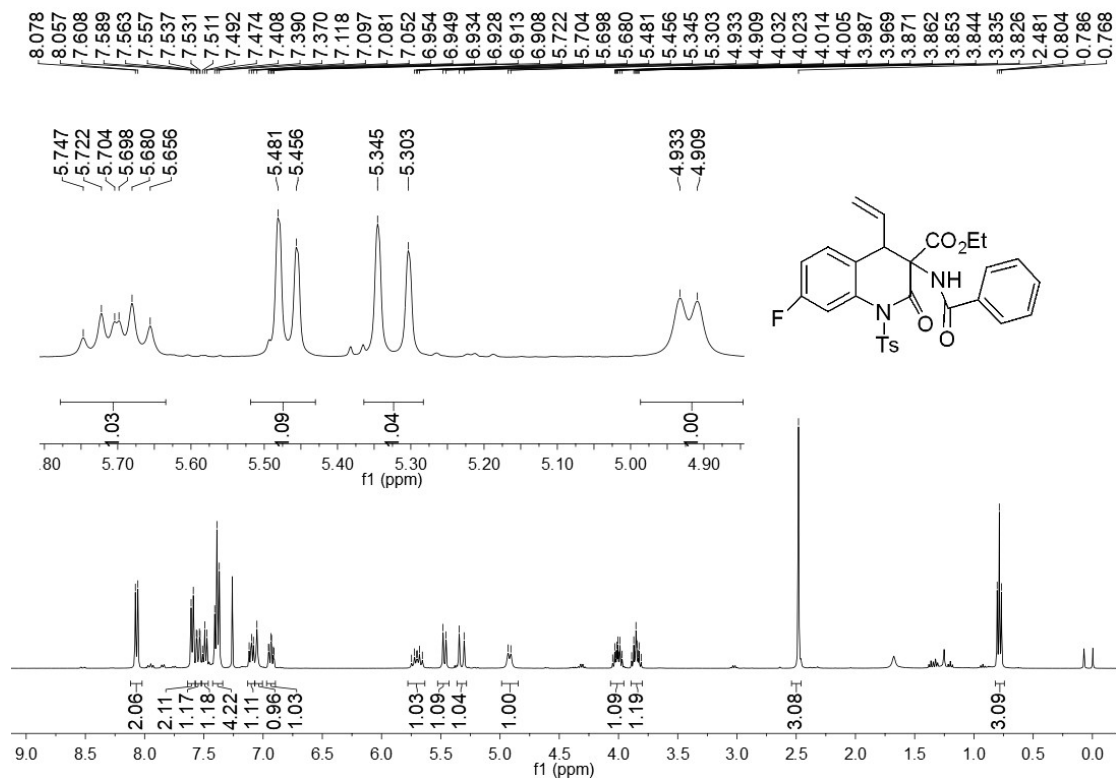
^1H NMR (400 MHz, CDCl_3) of compound **3ha**: inseparable diastereomers (dr > 95:5)



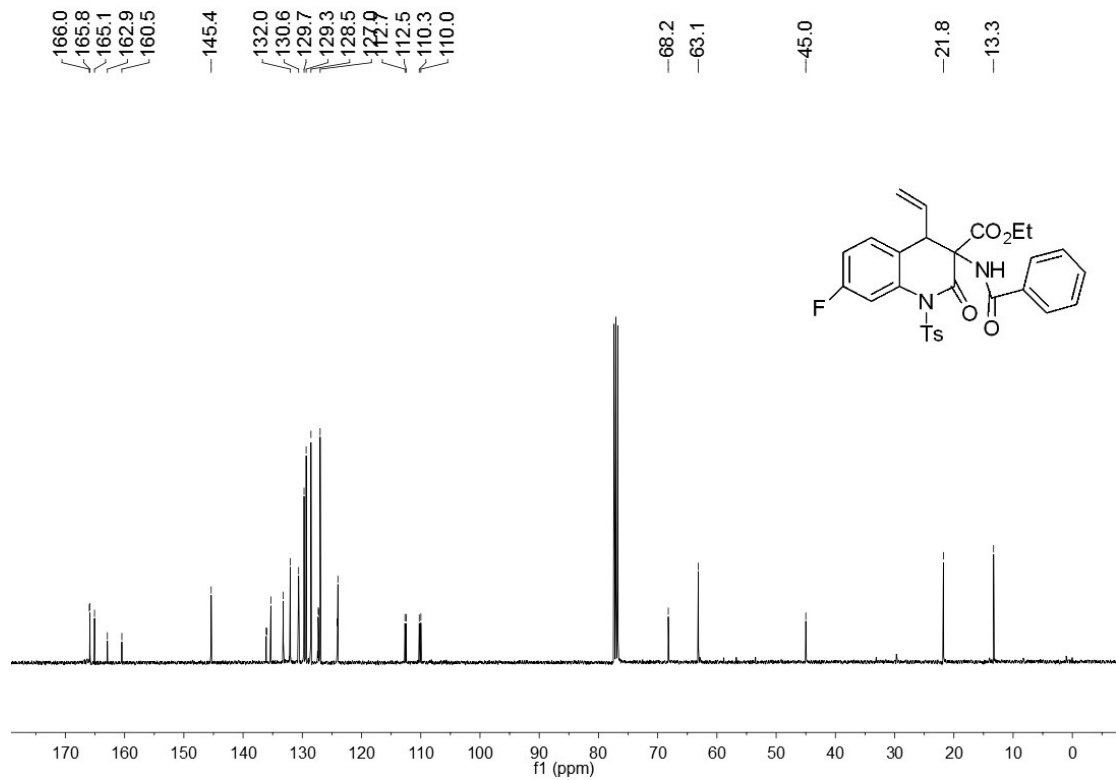
^{13}C NMR (100 MHz, CDCl_3) of compound **3ha**: inseparable diastereomers (dr > 95:5)



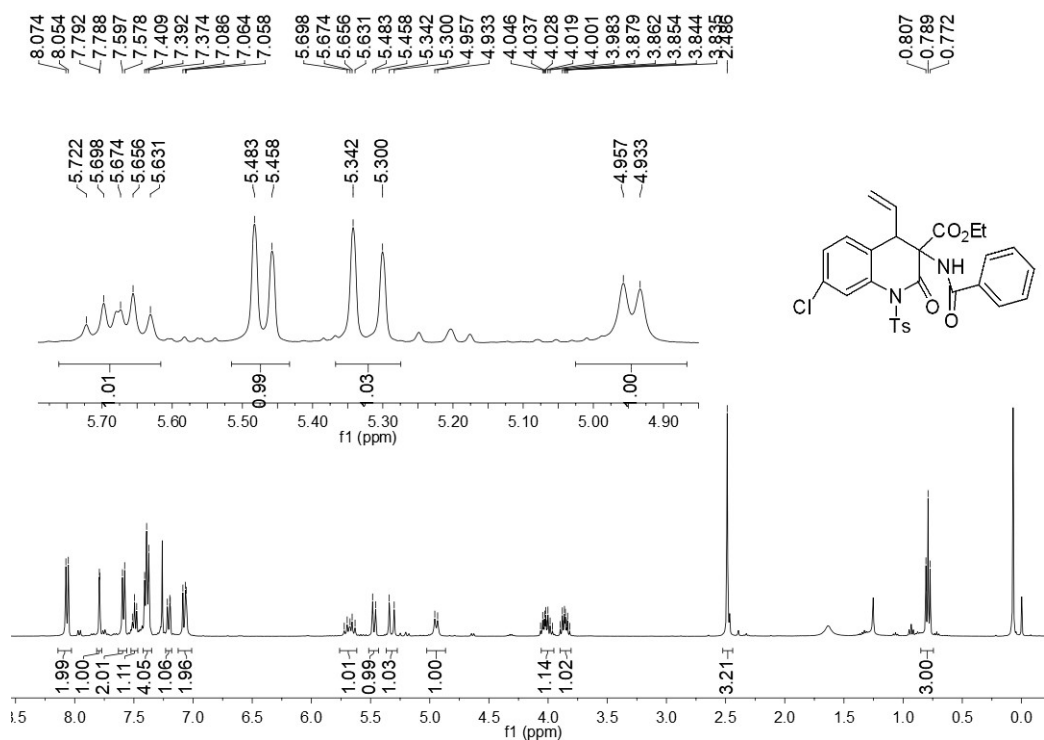
^1H NMR (400 MHz, CDCl_3) of compound **3ia**: inseparable diastereomers (dr = 92:8)



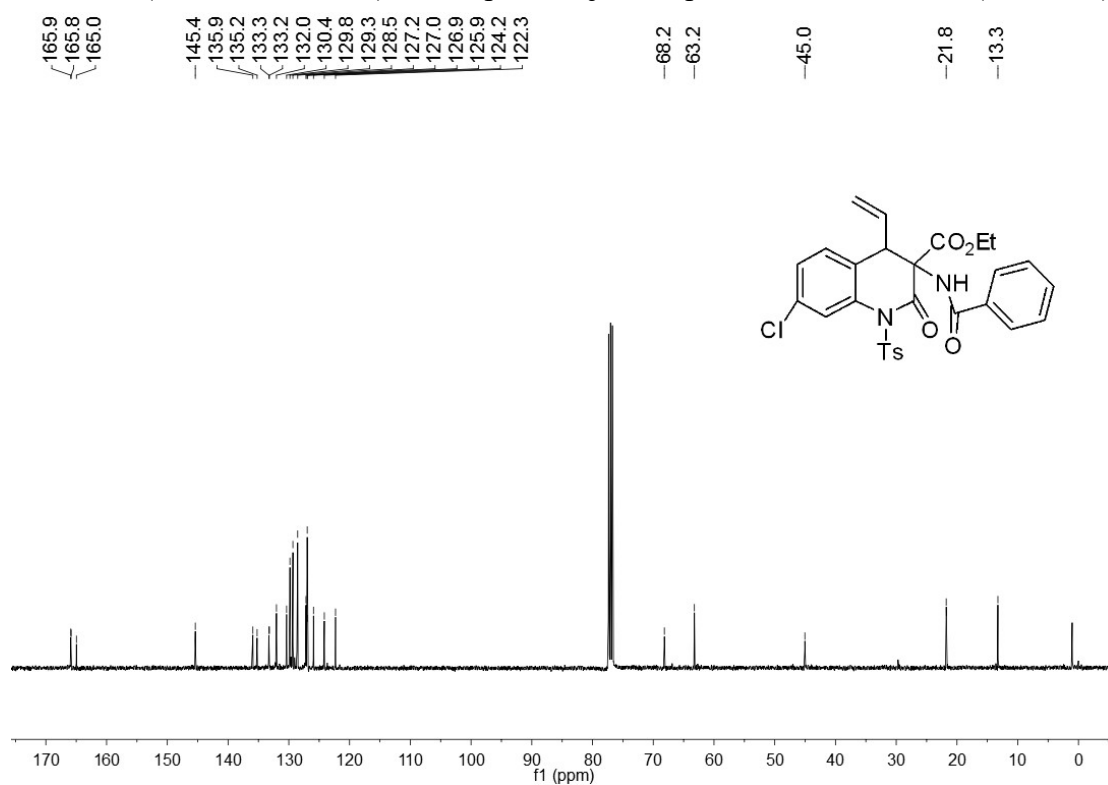
^{13}C NMR (100 MHz, CDCl_3) of compound **3ia**: inseparable diastereomers (dr = 92:8)



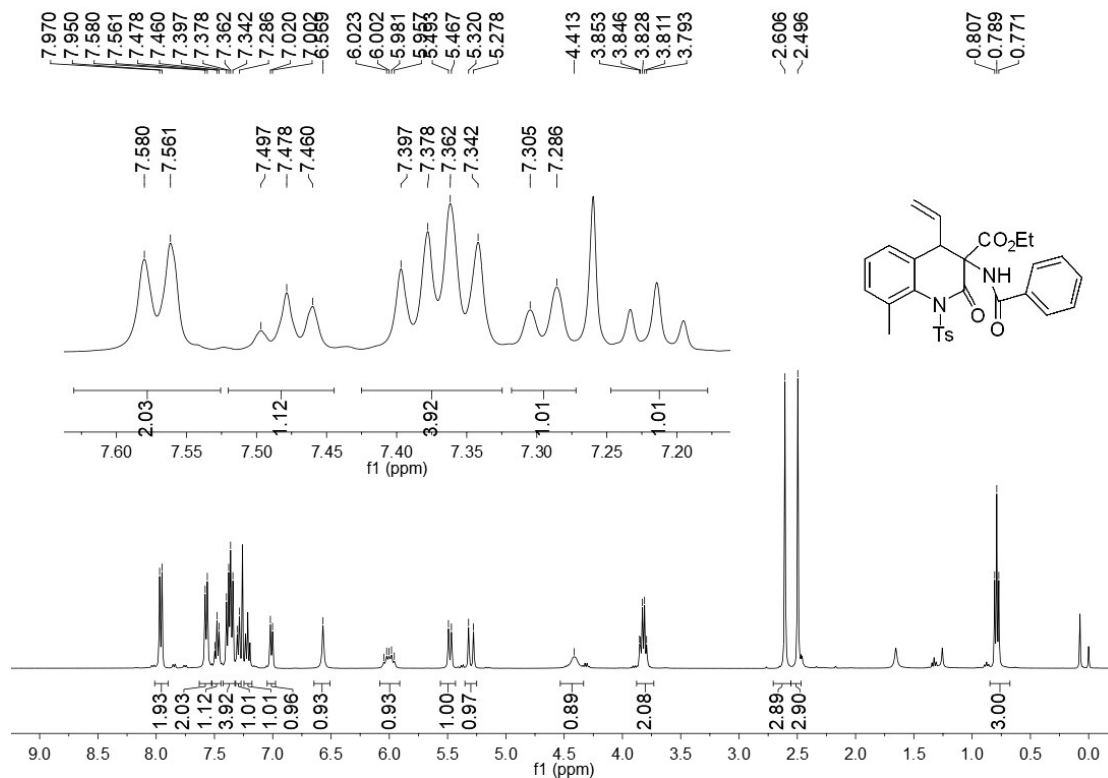
^1H NMR (400 MHz, CDCl_3) of compound **3ja**: inseparable diastereomers (dr = 91:9)



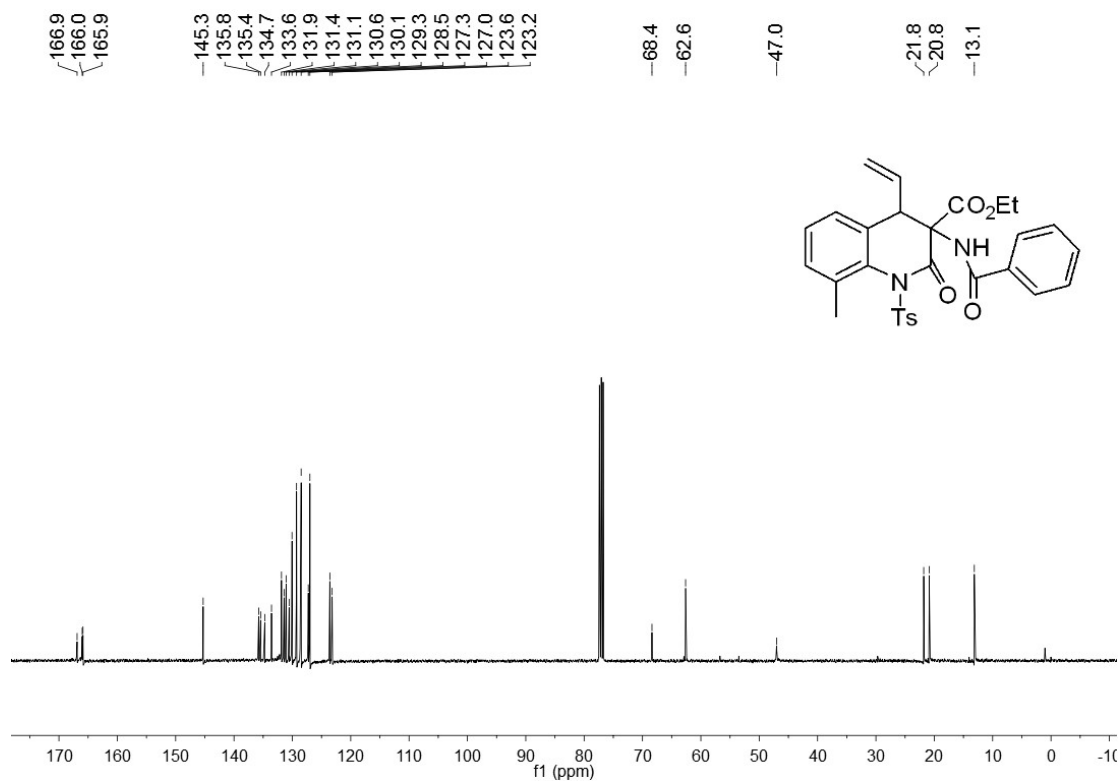
^{13}C NMR (100 MHz, CDCl_3) of compound **3ja**: inseparable diastereomers (dr = 91:9)



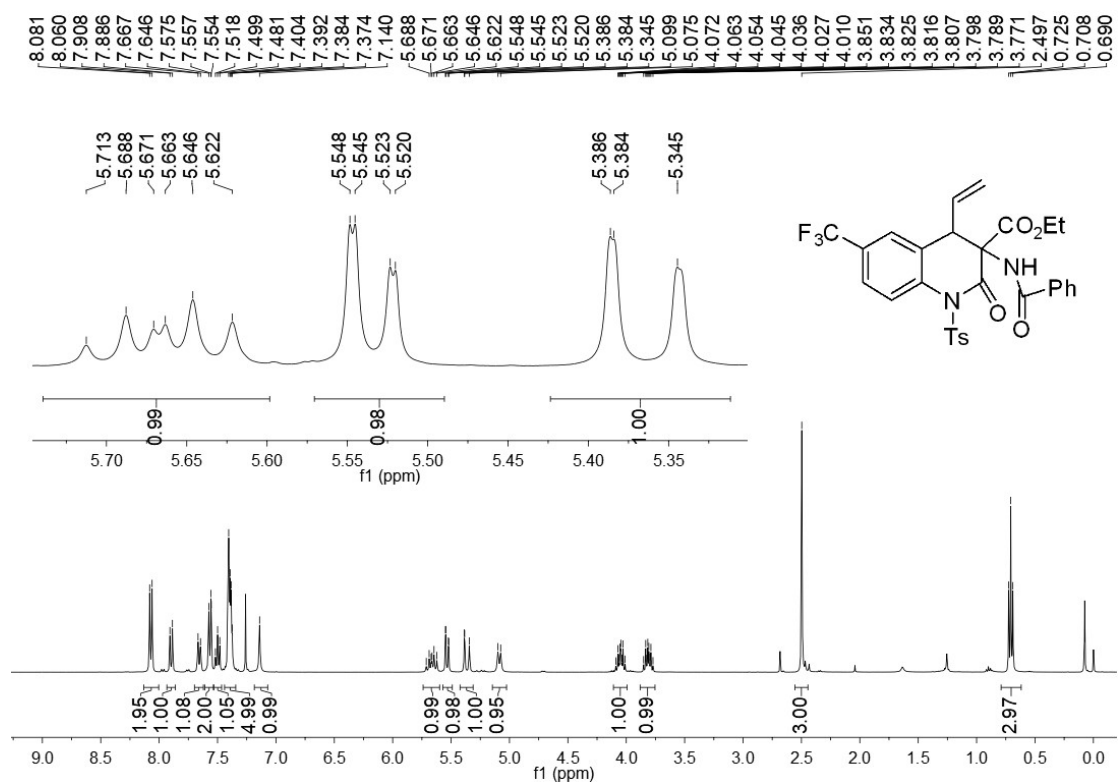
^1H NMR (400 MHz, CDCl_3) of compound **3ka**: inseparable diastereomers (dr = 95:5)



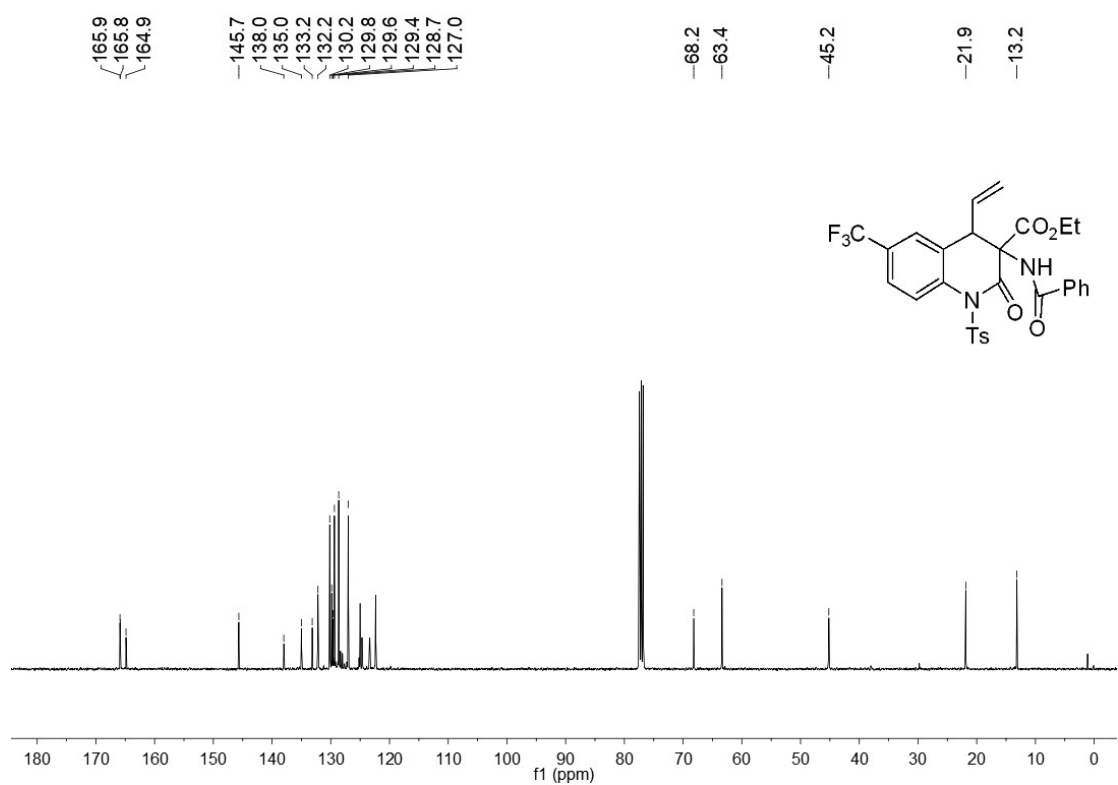
^{13}C NMR (100 MHz, CDCl_3) of compound **3ka**: inseparable diastereomers (dr= 95:5)



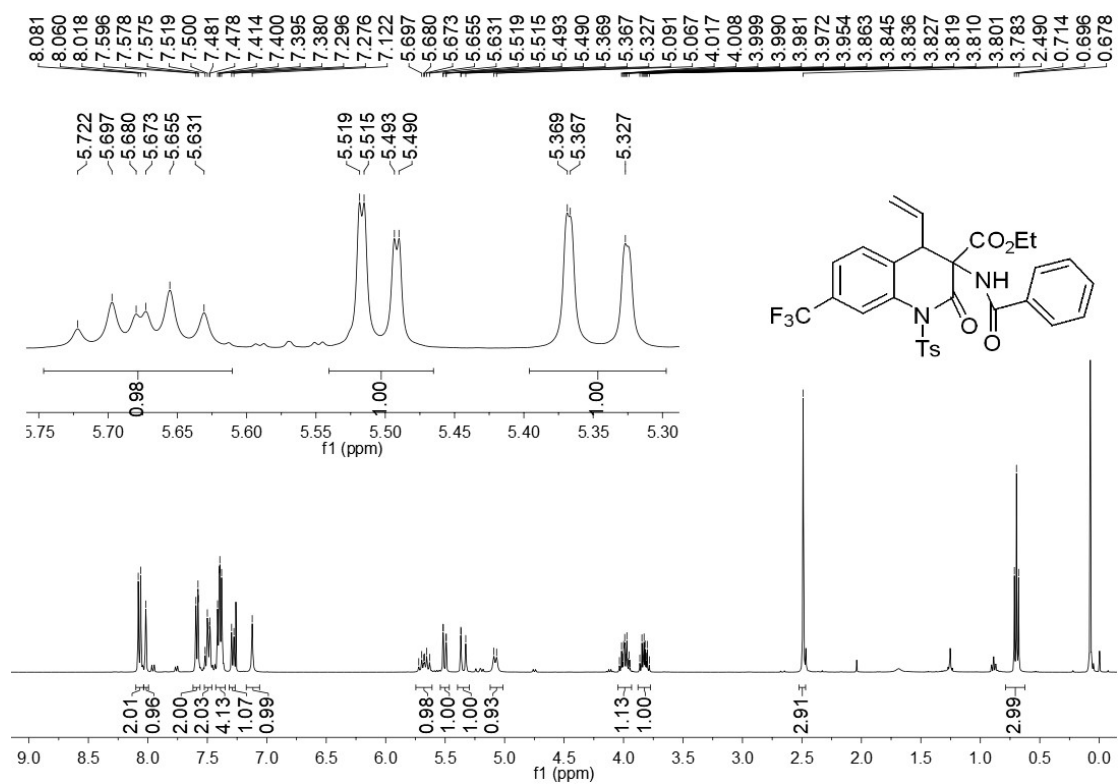
^1H NMR (400 MHz, CDCl_3) of compound **3la**: inseparable diastereomers (dr = 95:5)



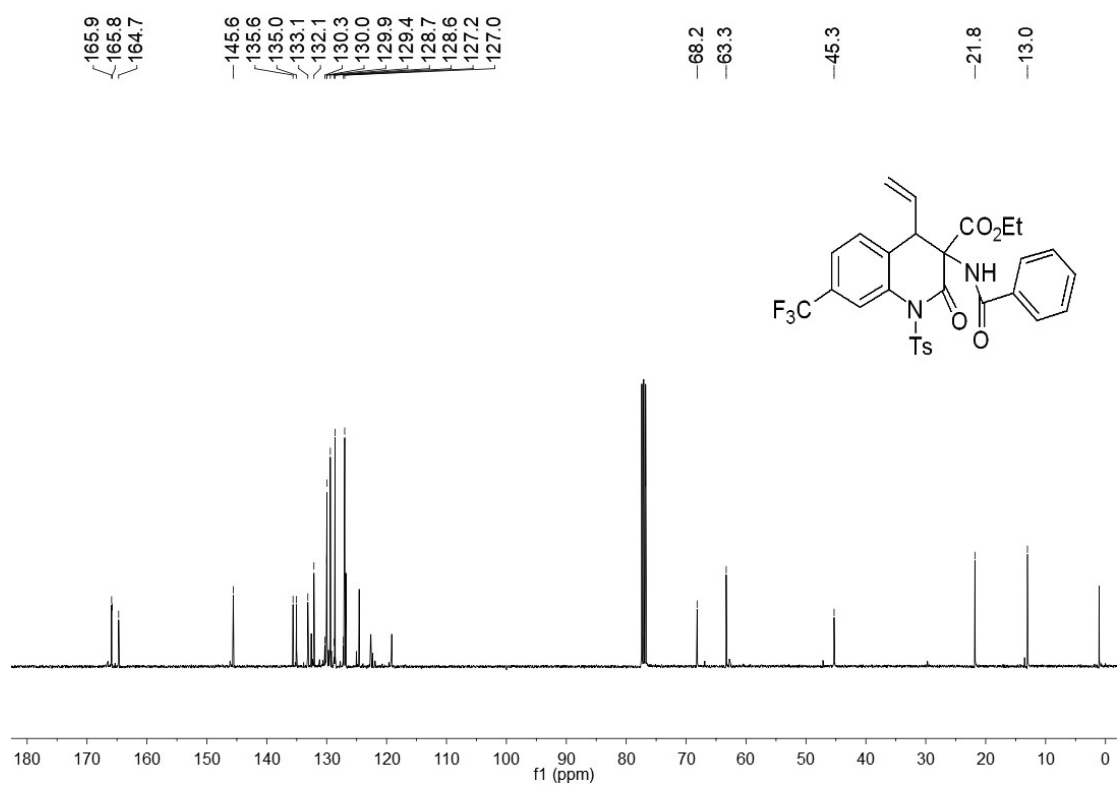
^{13}C NMR (100 MHz, CDCl_3) of compound **3la**: inseparable diastereomers (dr = 95:5)



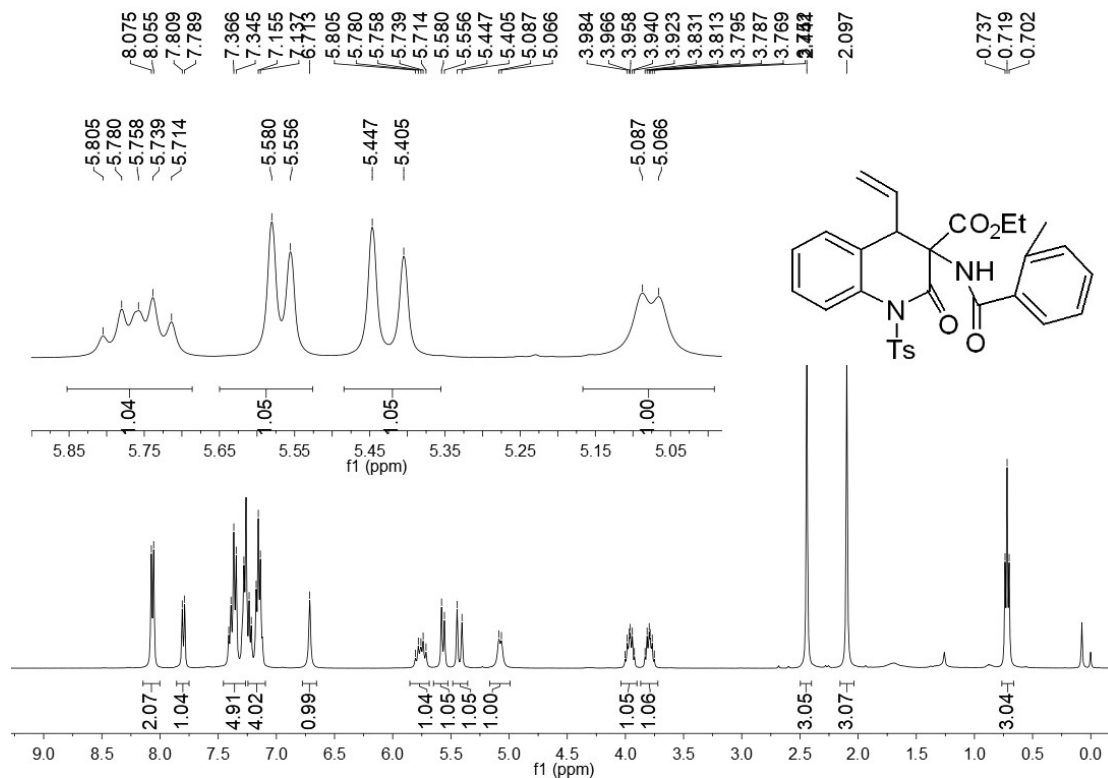
^1H NMR (400 MHz, CDCl_3) of compound **3ma**: inseparable diastereomers (dr = 93:7)



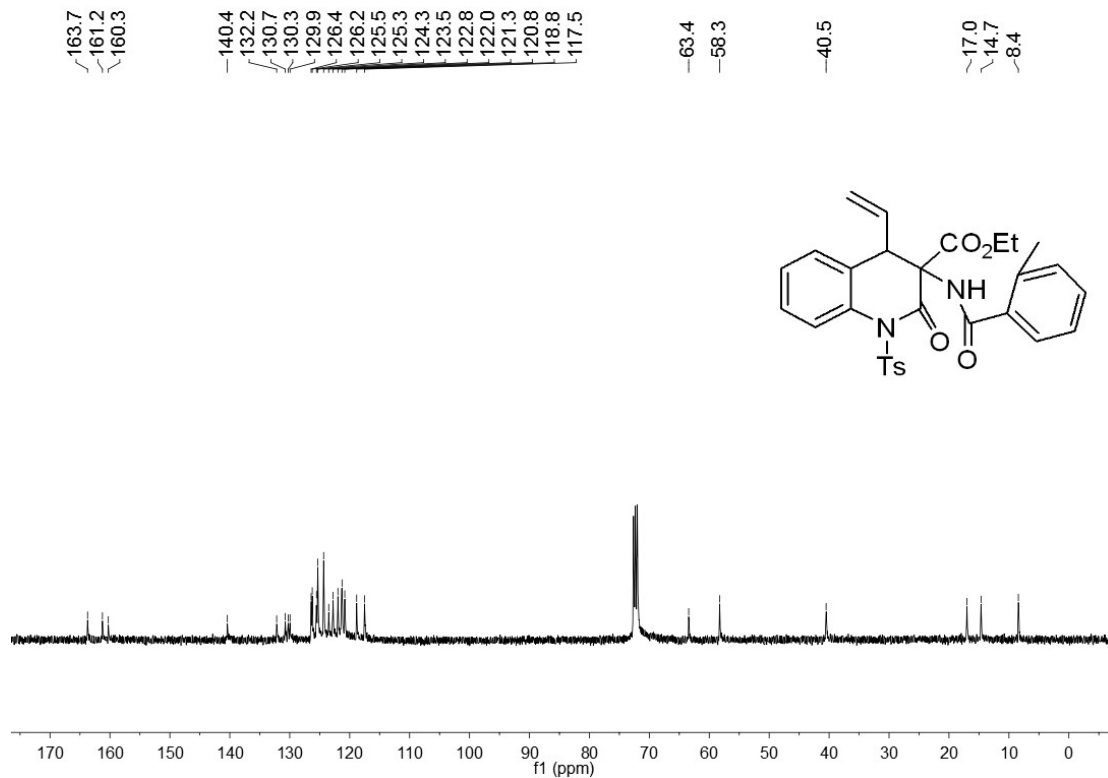
^{13}C NMR (100 MHz, CDCl_3) of compound **3ma**: inseparable diastereomers (dr = 93:7)



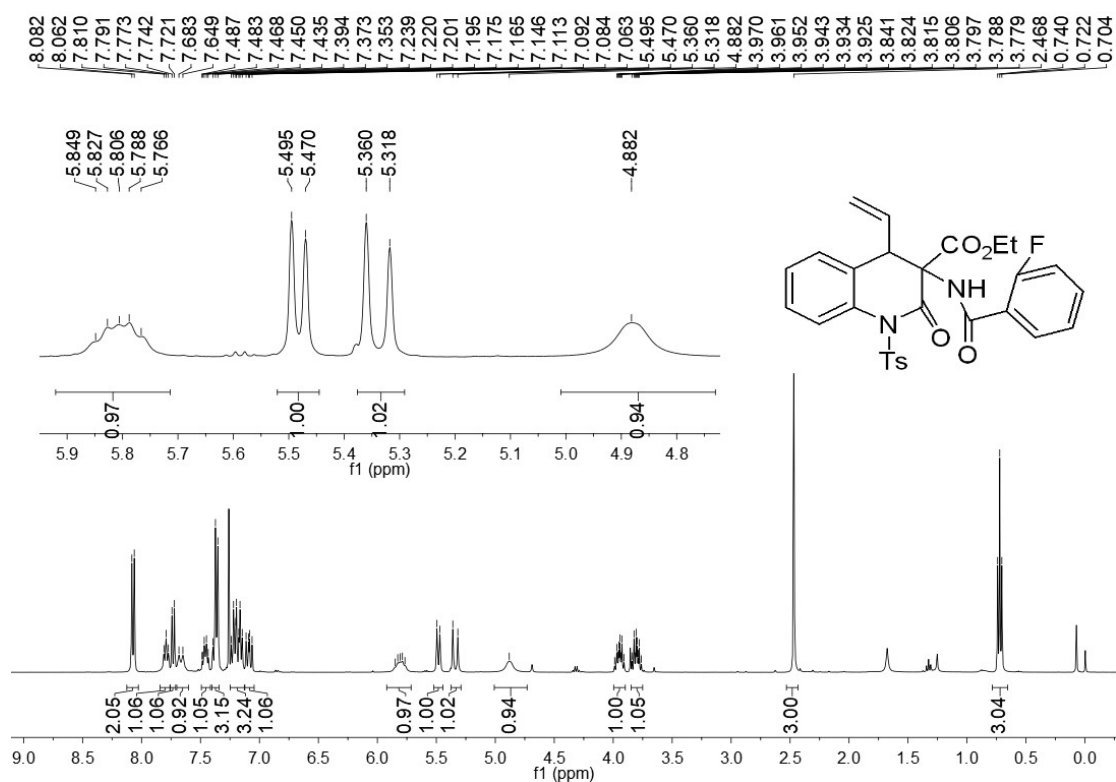
^1H NMR (400 MHz, CDCl_3) of compound **3ab**: inseparable diastereomers (dr > 95:5)



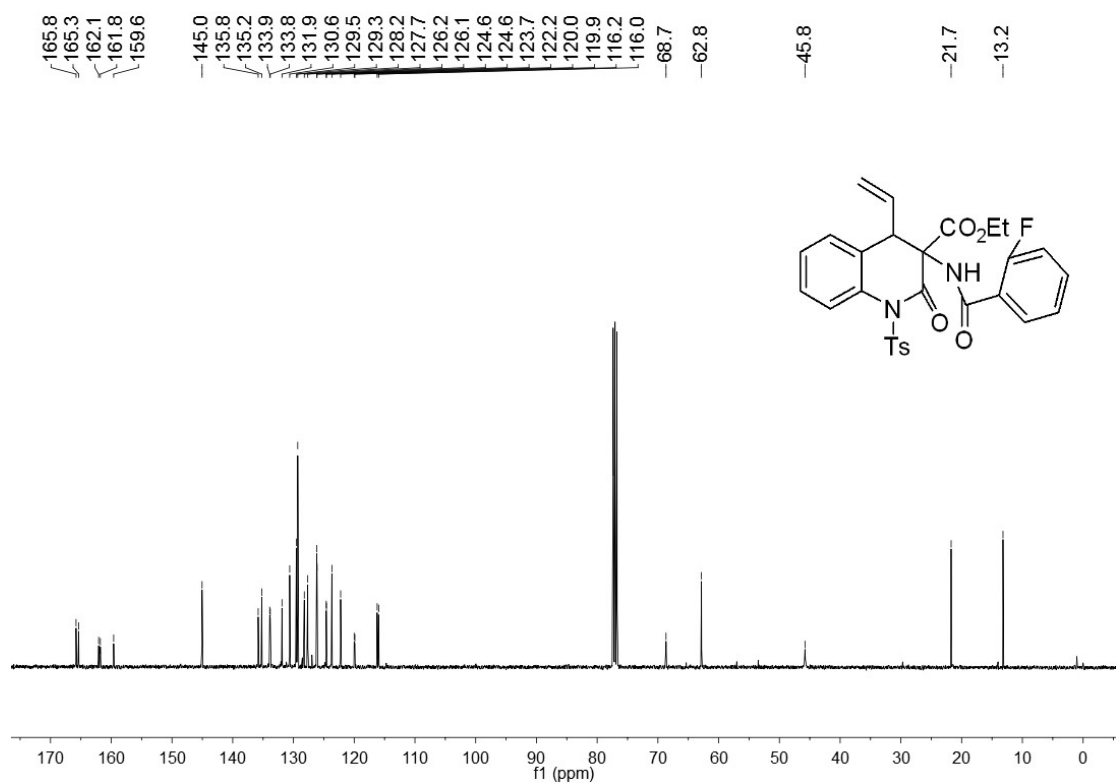
^{13}C NMR (100 MHz, CDCl_3) of compound **3ab**: inseparable diastereomers (dr > 95:5)



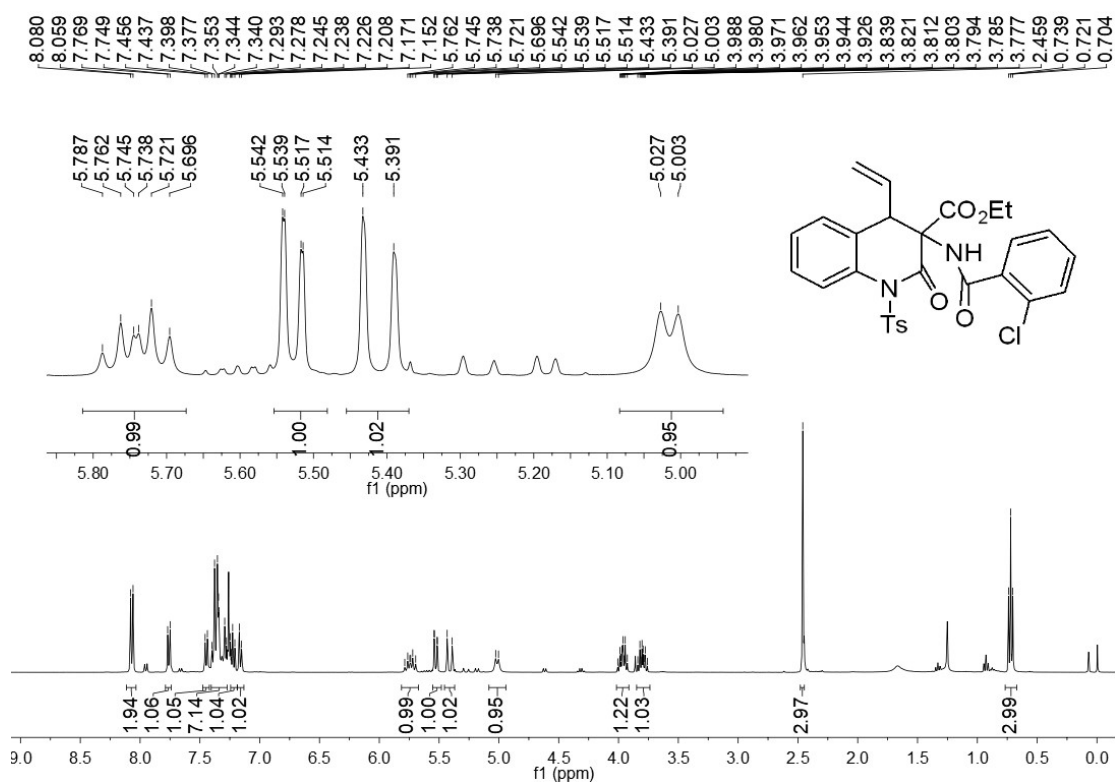
^1H NMR (400 MHz, CDCl_3) of compound **3ac**: inseparable diastereomers (dr = 95:5)



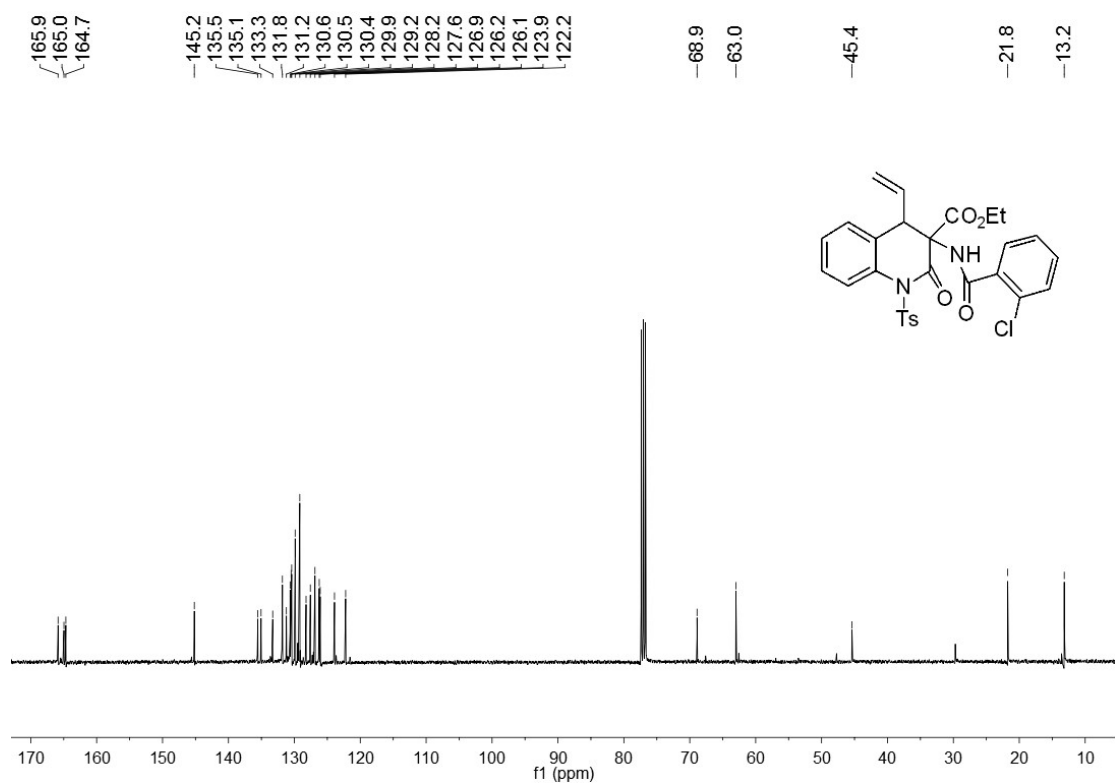
^{13}C NMR (100 MHz, CDCl_3) of compound **3ac**: inseparable diastereomers (dr = 95:5)



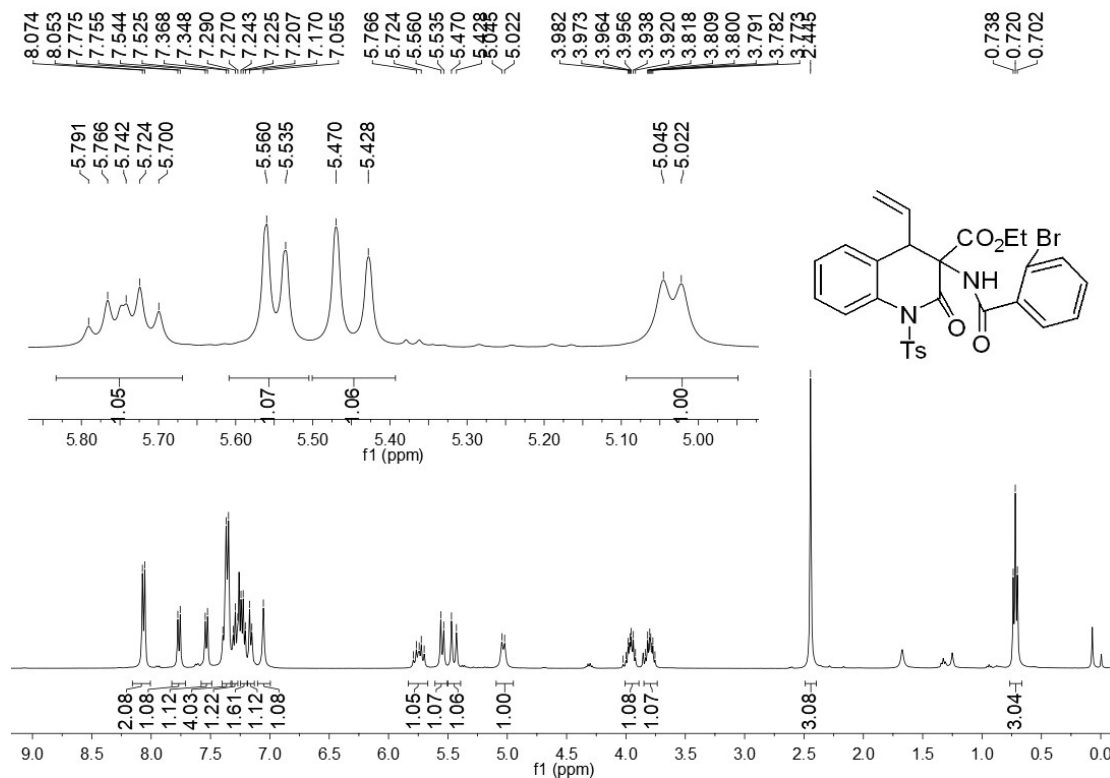
^1H NMR (400 MHz, CDCl_3) of compound **3ad**: inseparable diastereomers (dr=88:12)



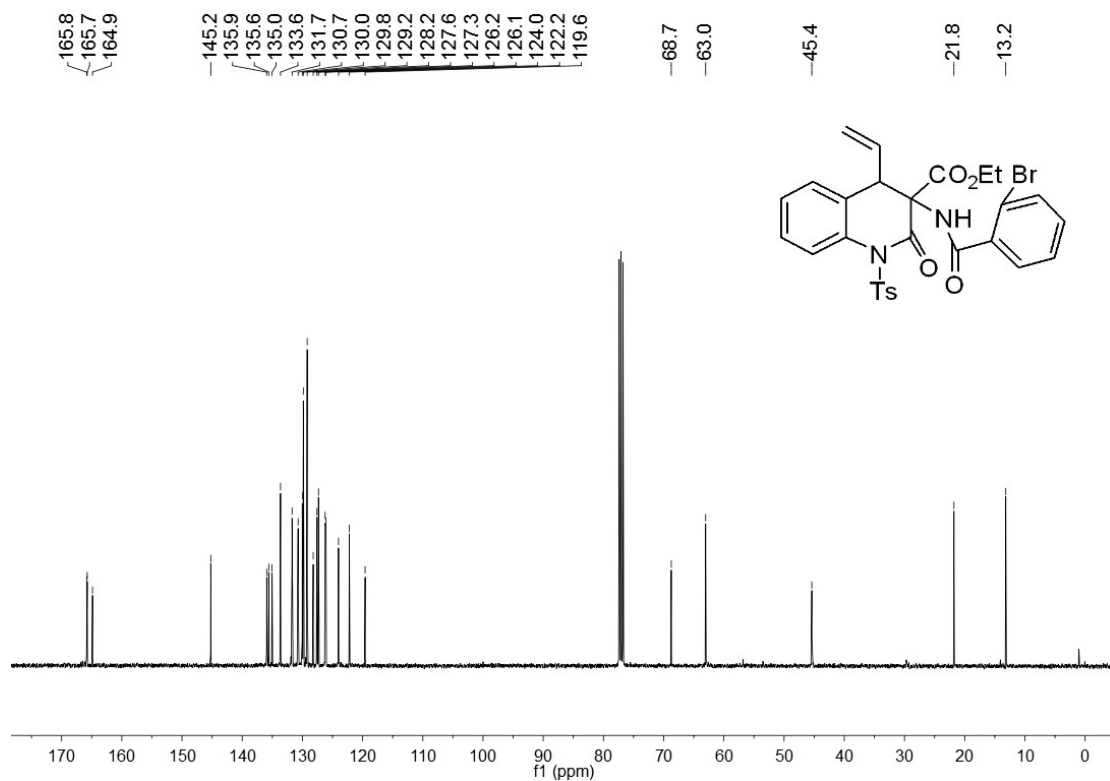
^{13}C NMR (100 MHz, CDCl_3) of compound **3ad**: inseparable diastereomers (dr= 88:12)



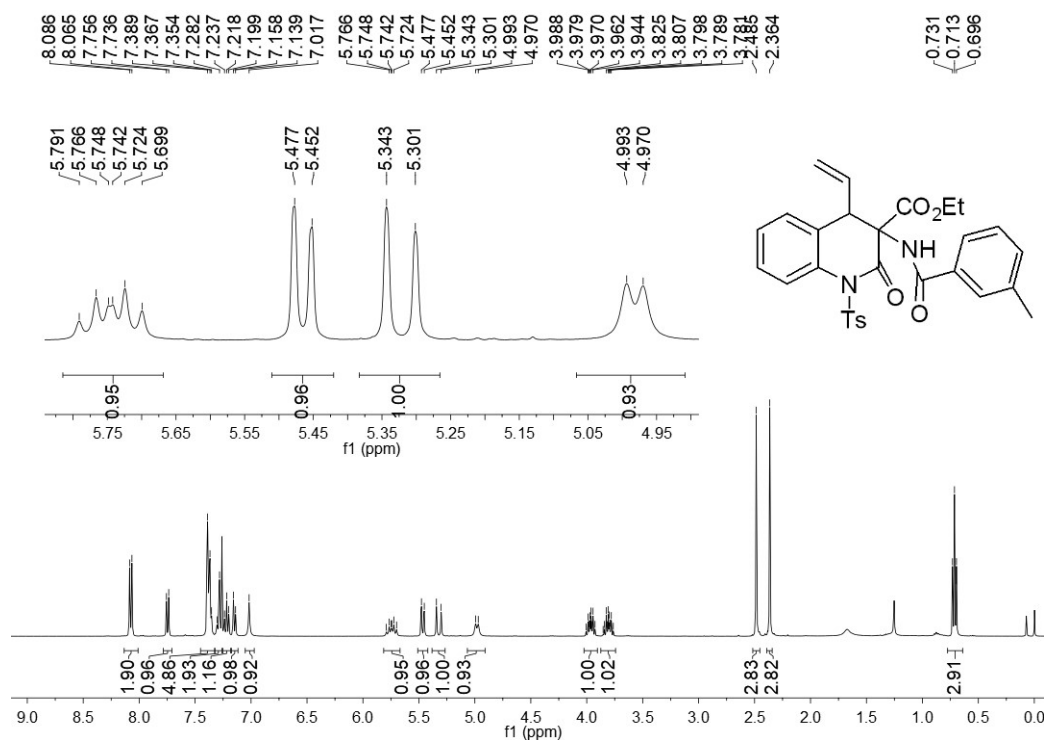
^1H NMR (400 MHz, CDCl_3) of compound **3ae**: inseparable diastereomers (dr = 95:5)



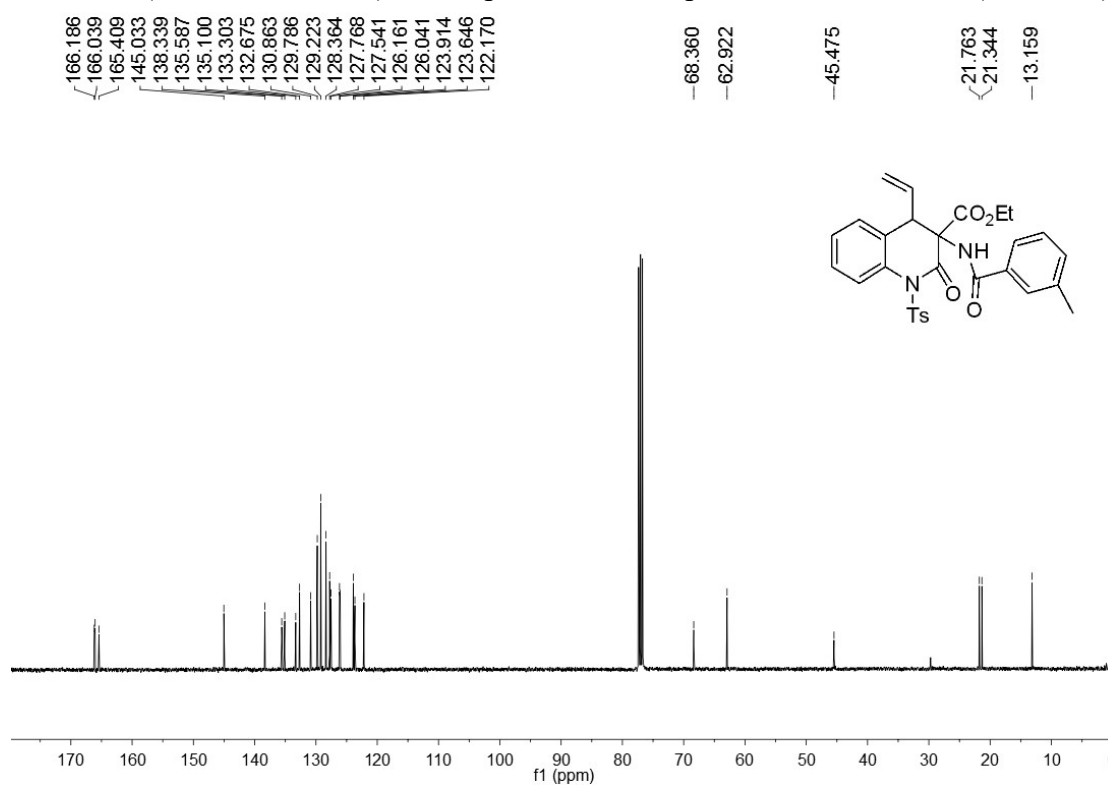
^{13}C NMR (100 MHz, CDCl_3) of compound **3ae**: inseparable diastereomers (dr = 95:5)



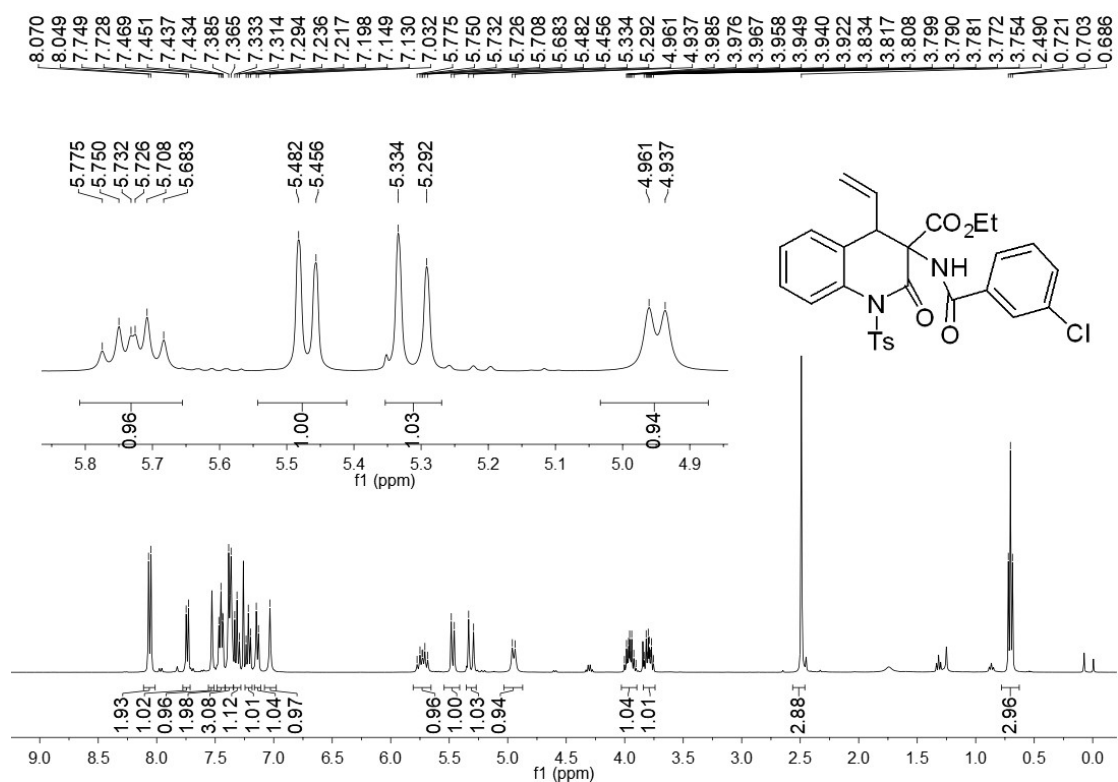
^1H NMR (400 MHz, CDCl_3) of compound **3af**: inseparable diastereomers (dr > 95:5)



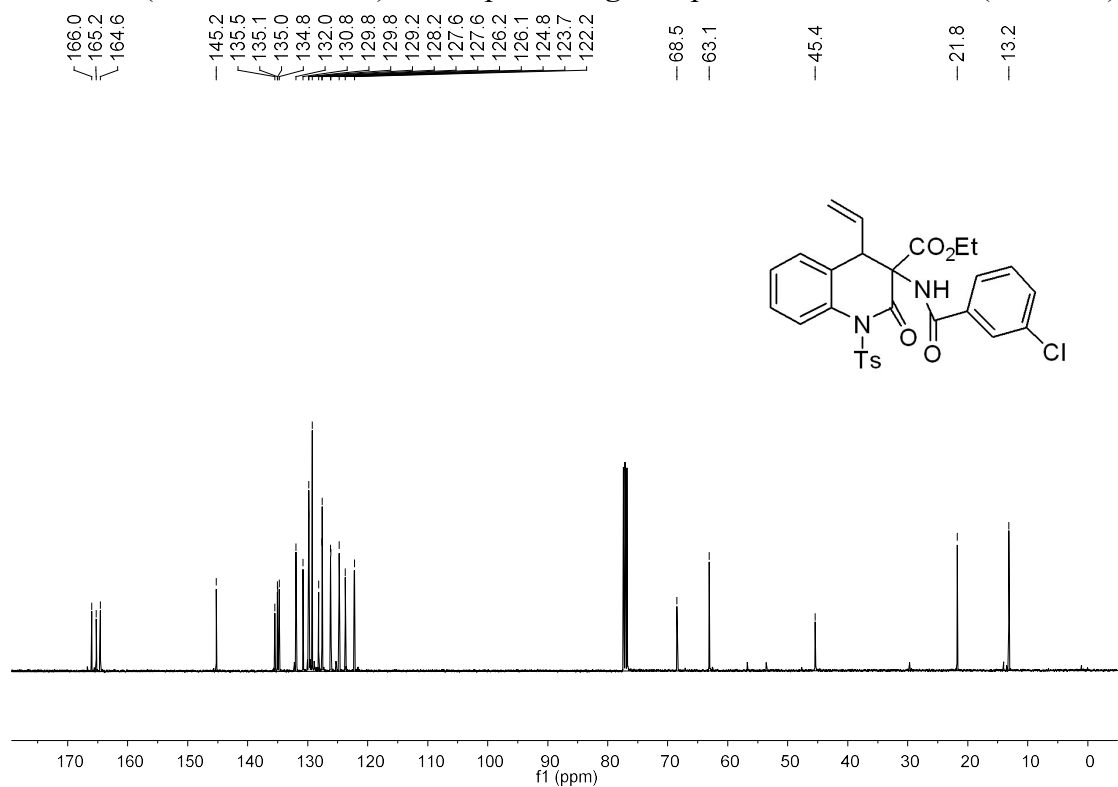
^{13}C NMR (100 MHz, CDCl_3) of compound **3af**: inseparable diastereomers (dr > 95:5)



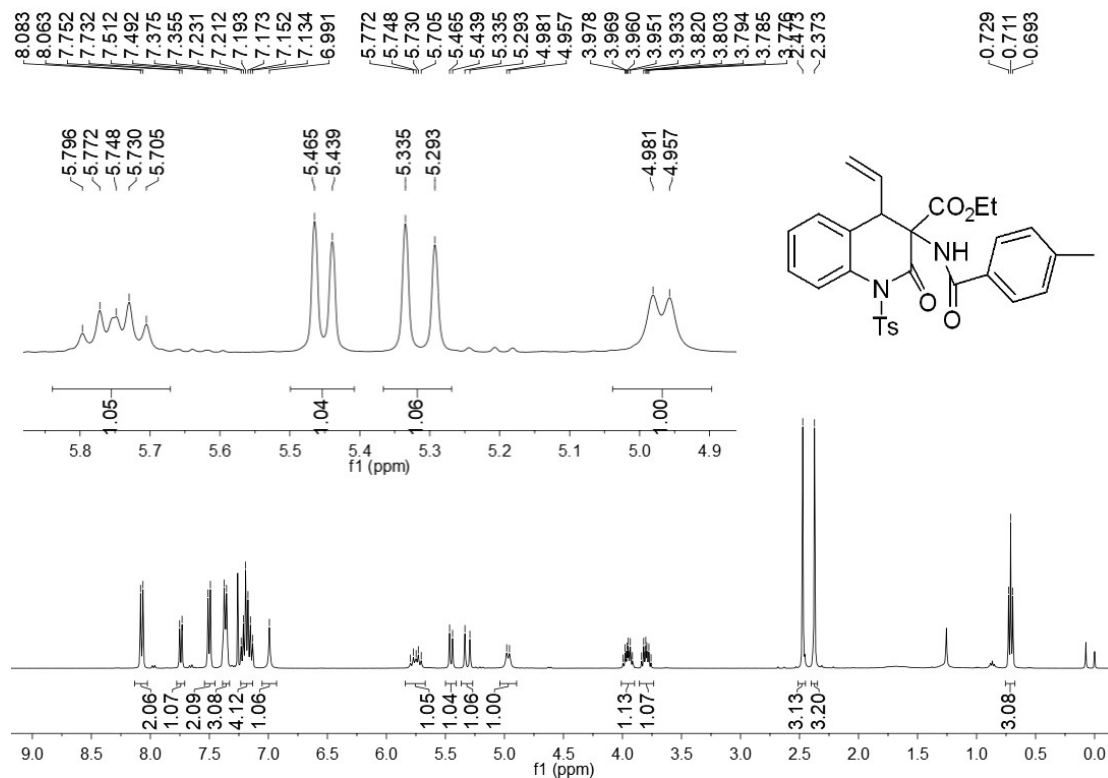
^1H NMR (400 MHz, CDCl_3) of compound **3ag**: inseparable diastereomers (dr = 95:5)



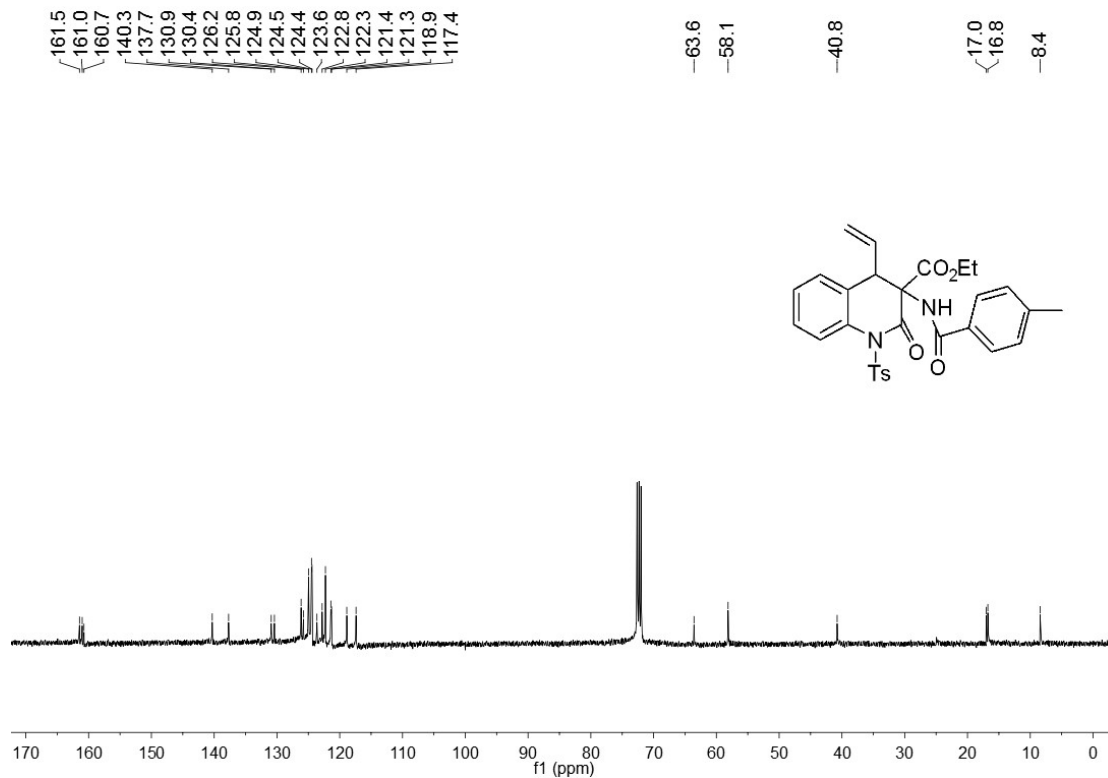
^{13}C NMR (100 MHz, CDCl_3) of compound **3ag**: inseparable diastereomers (dr = 95:5)



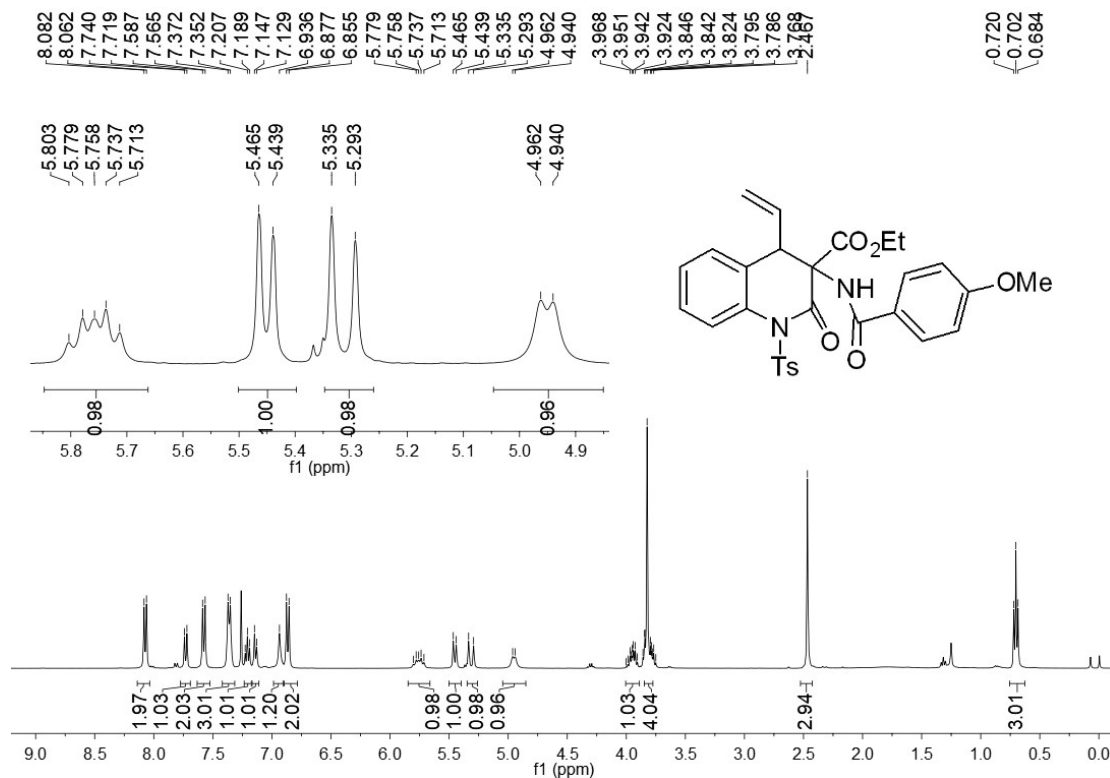
^1H NMR (400 MHz, CDCl_3) of compound **3ah**: inseparable diastereomers (dr = 95:5)



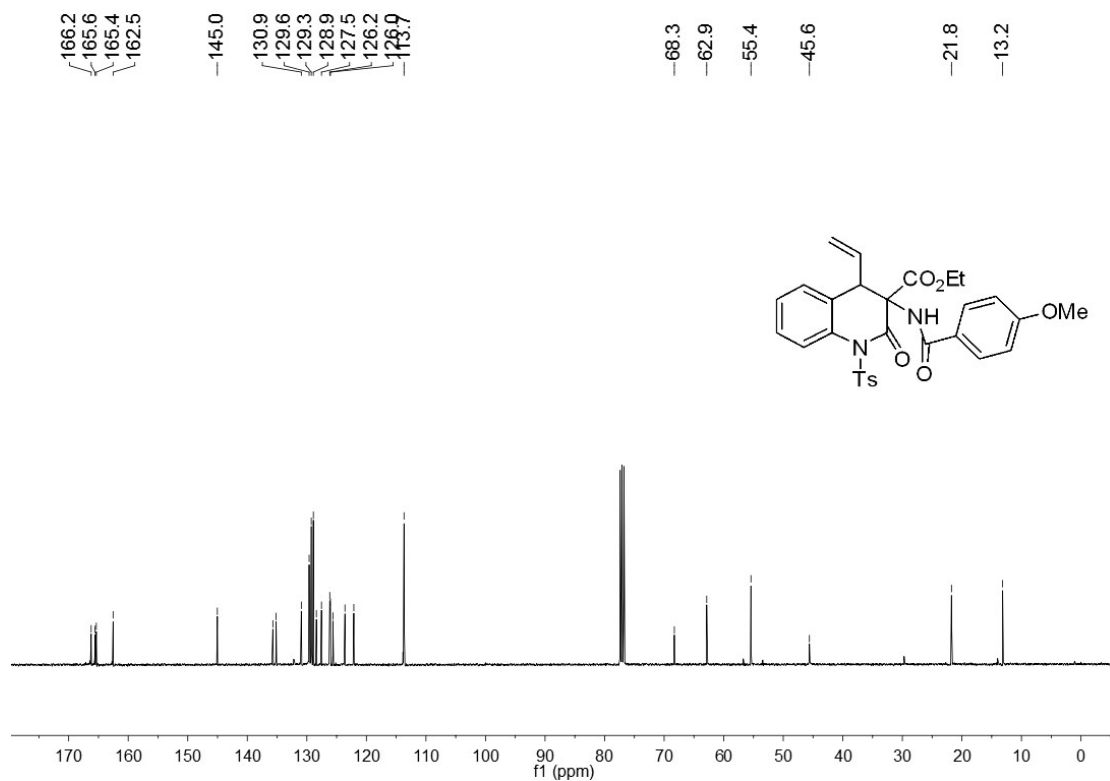
^{13}C NMR (100 MHz, CDCl_3) of compound **3ah**: inseparable diastereomers (dr= 95:5)



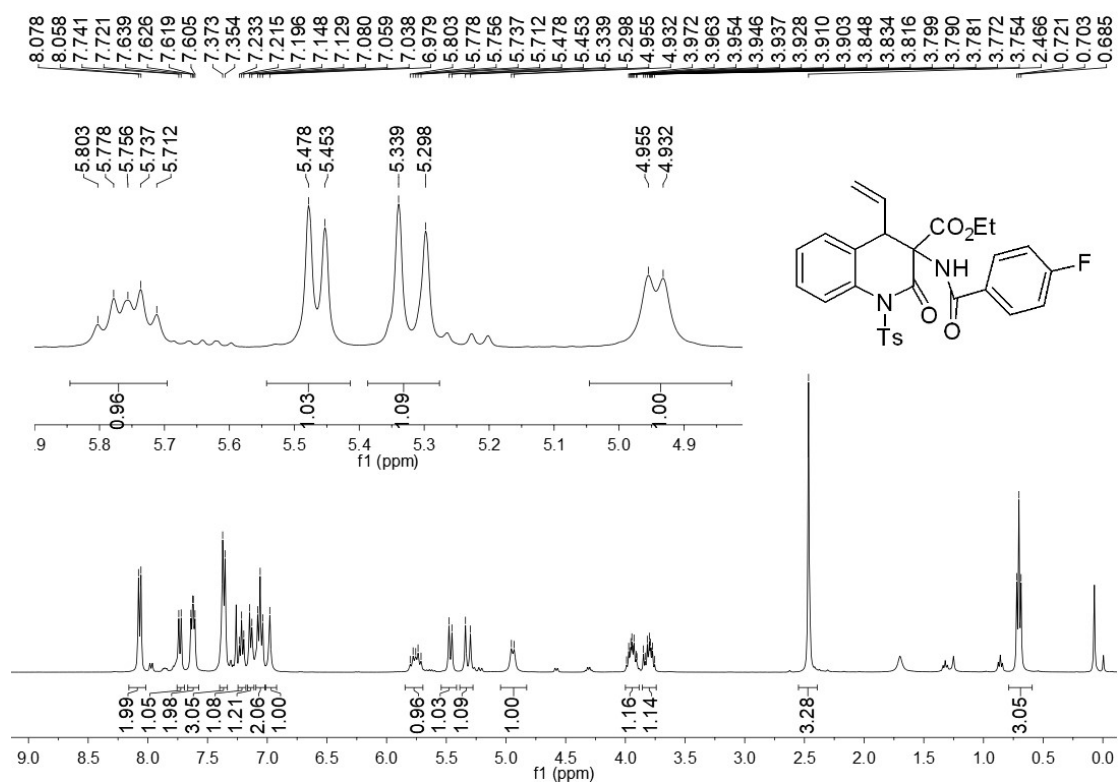
^1H NMR (400 MHz, CDCl_3) of compound **3ai**: inseparable diastereomers (dr = 92:8)



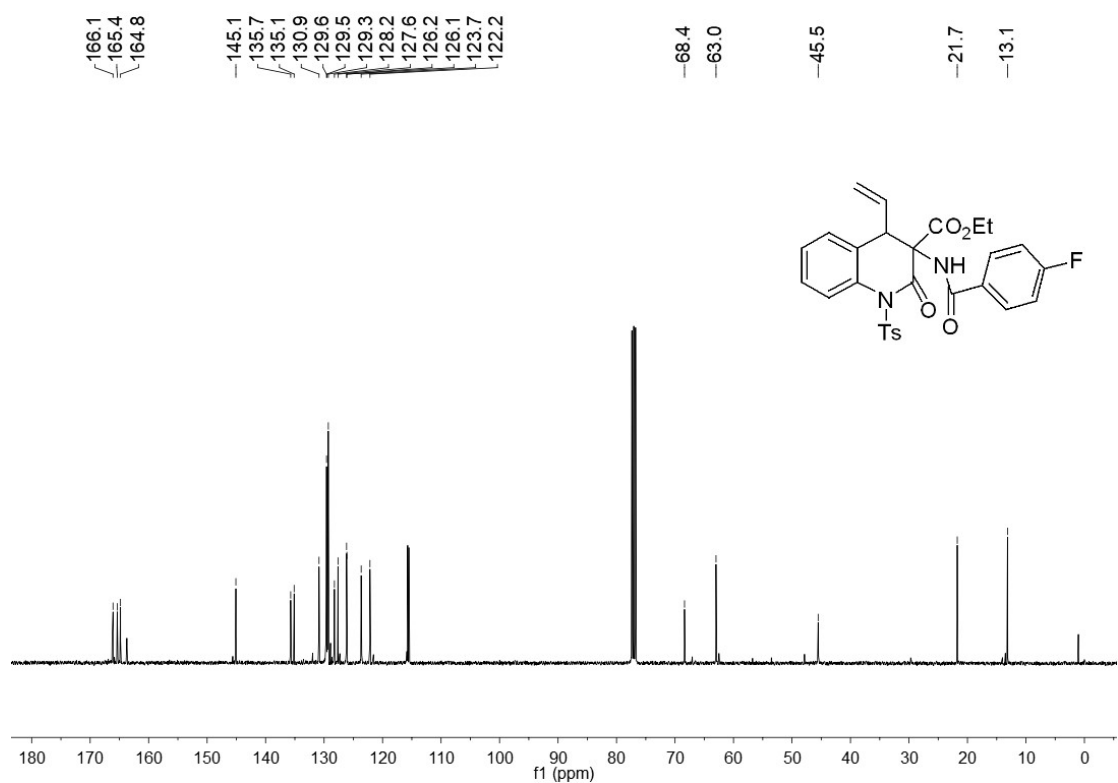
^{13}C NMR (100 MHz, CDCl_3) of compound **3ai**: inseparable diastereomers (dr = 92:8)



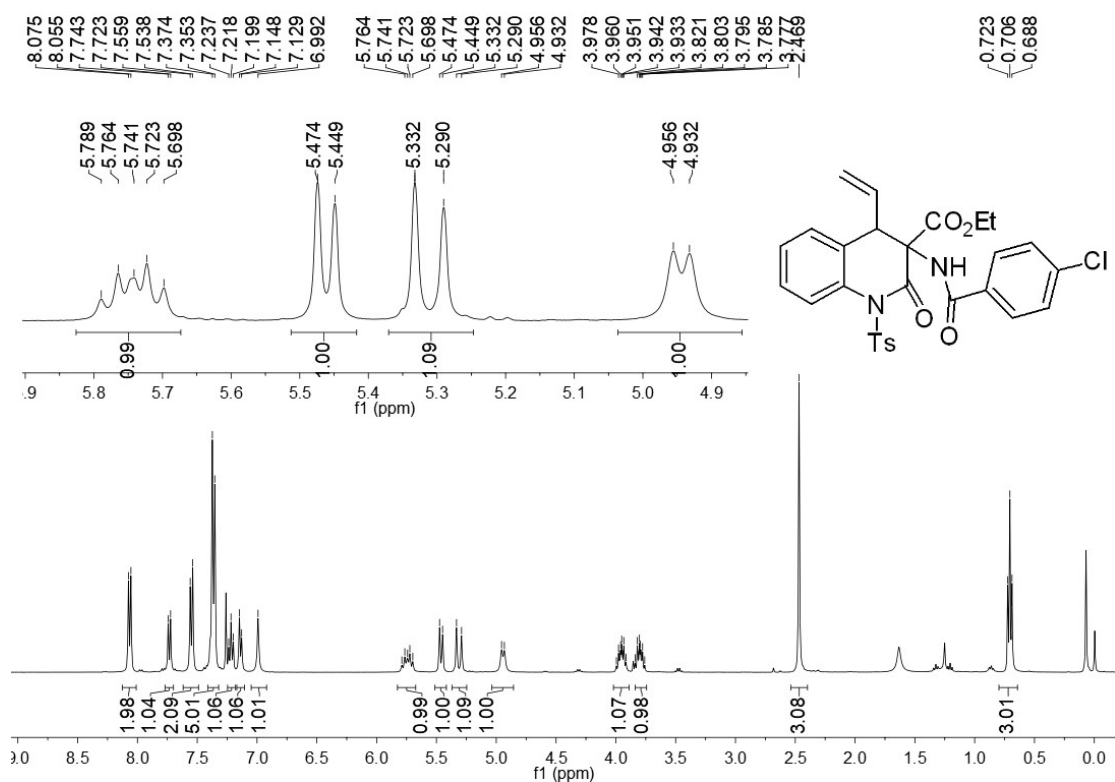
^1H NMR (400 MHz, CDCl_3) of compound **3aj**: inseparable diastereomers (dr = 91:9)



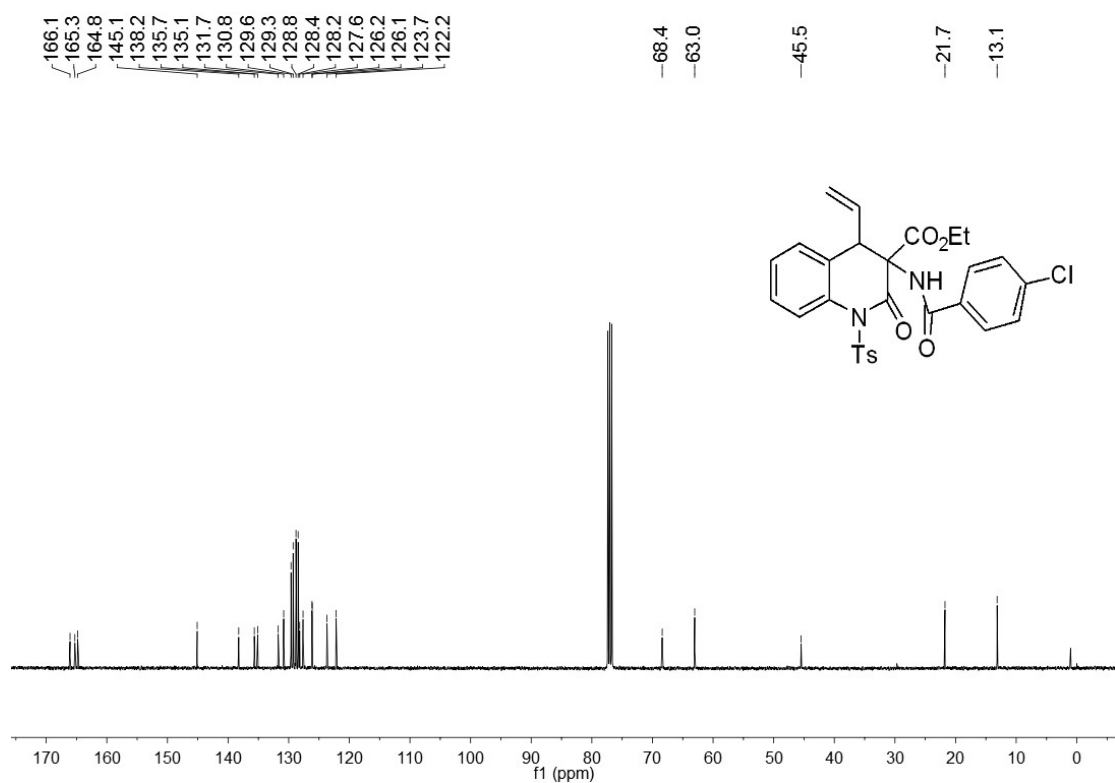
^{13}C NMR (100 MHz, CDCl_3) of compound **3aj**: inseparable diastereomers (dr = 91:9)



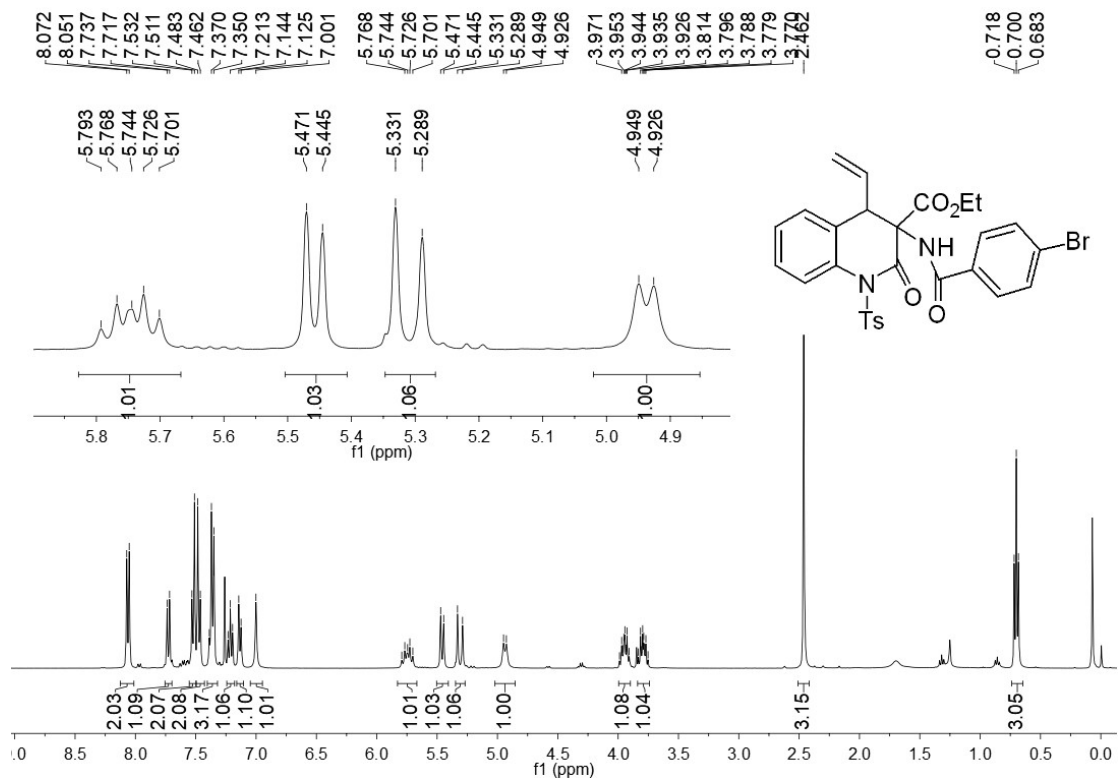
^1H NMR (400 MHz, CDCl_3) of compound **3ak**: inseparable diastereomers (dr = 95:5)



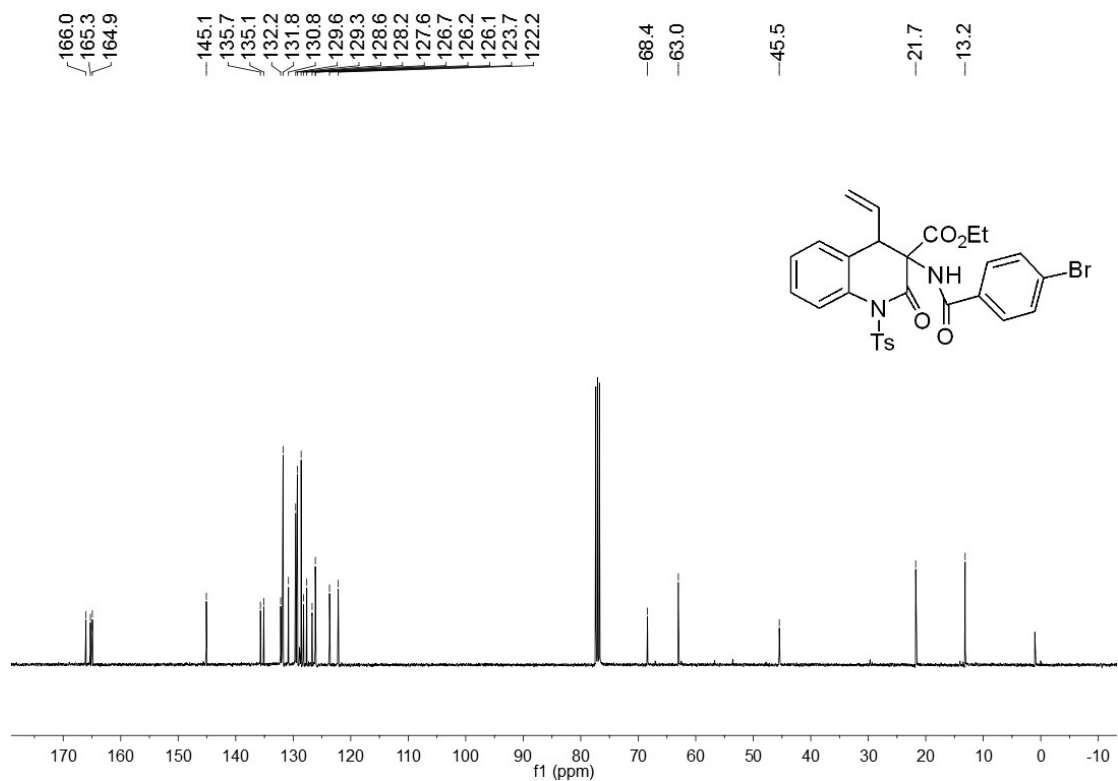
^{13}C NMR (100 MHz, CDCl_3) of compound **3ak**: inseparable diastereomers (dr= 95:5)



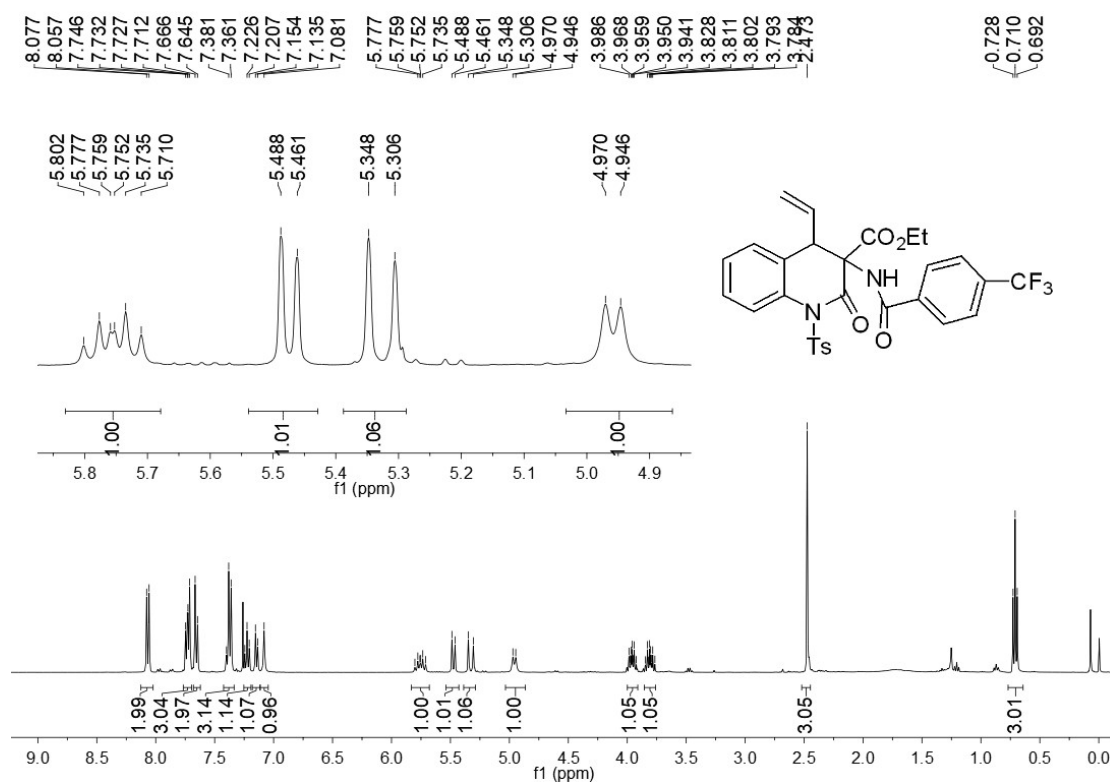
^1H NMR (400 MHz, CDCl_3) of compound **3al**: inseparable diastereomers (dr = 95:5)



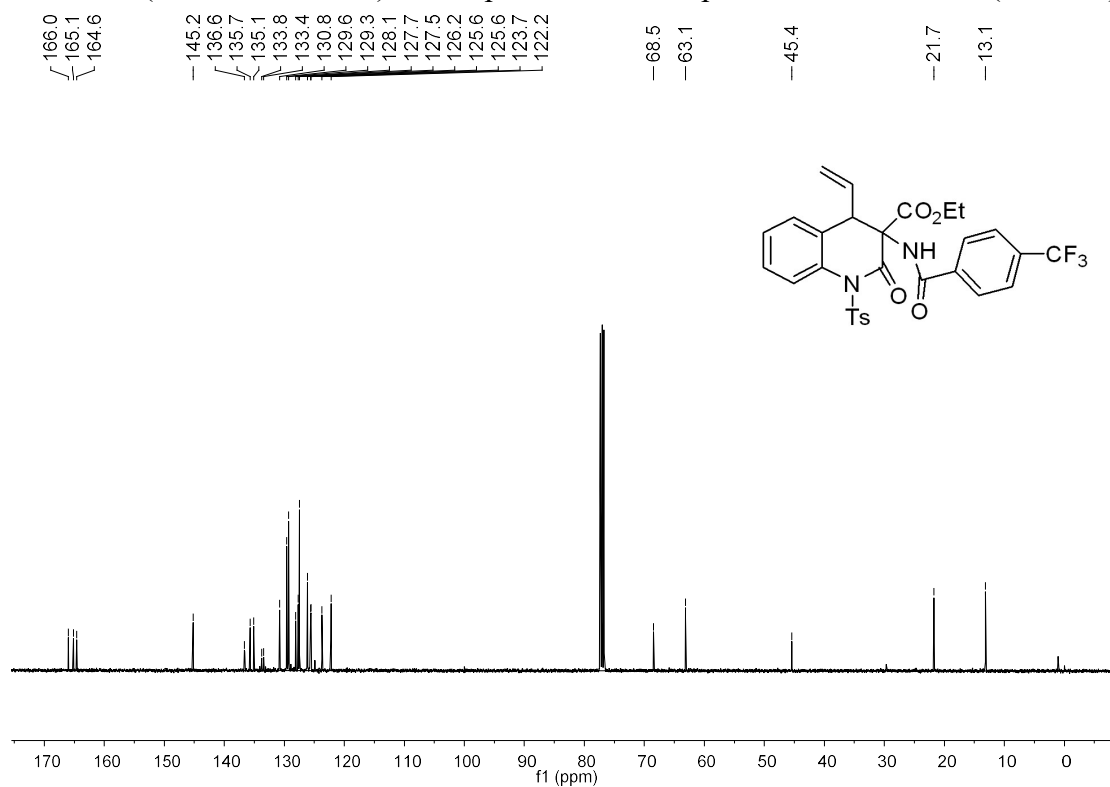
^{13}C NMR (100 MHz, CDCl_3) of compound **3al**: inseparable diastereomers (dr = 95:5)



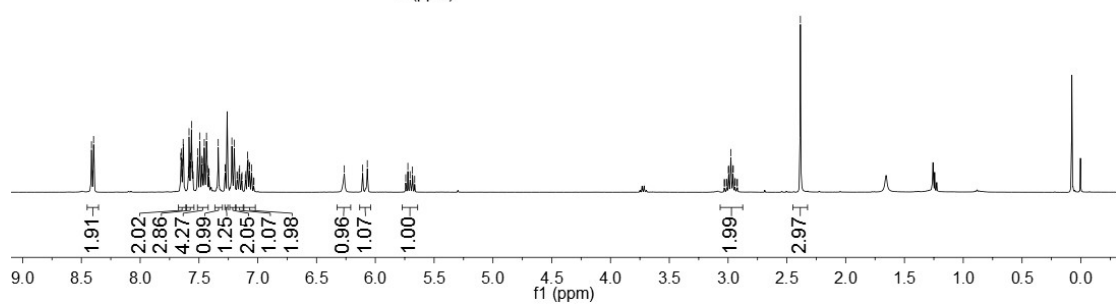
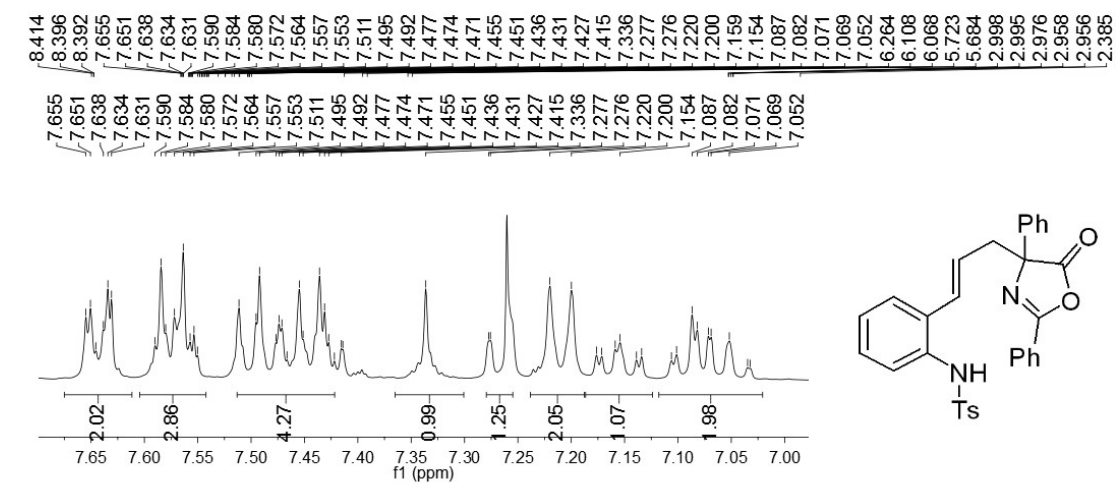
^1H NMR (400 MHz, CDCl_3) of compound **3am**: inseparable diastereomers (dr = 94:6)



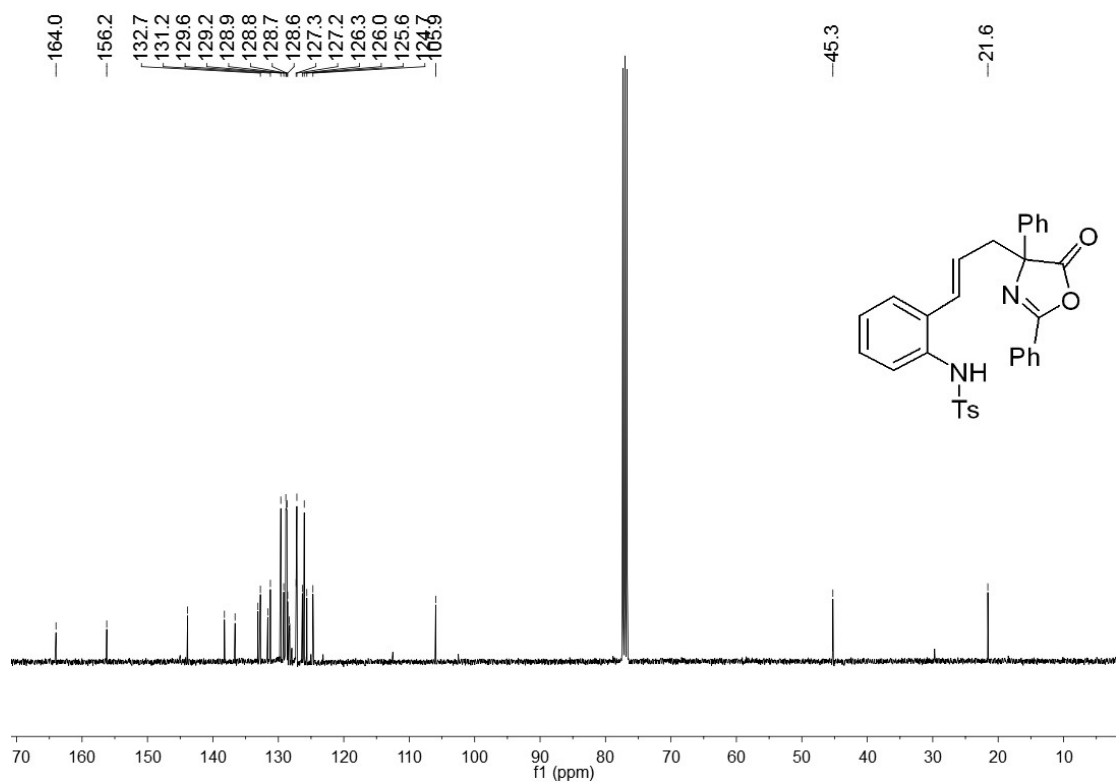
^{13}C NMR (100 MHz, CDCl_3) of compound **3am**: inseparable diastereomers (dr = 94:6)



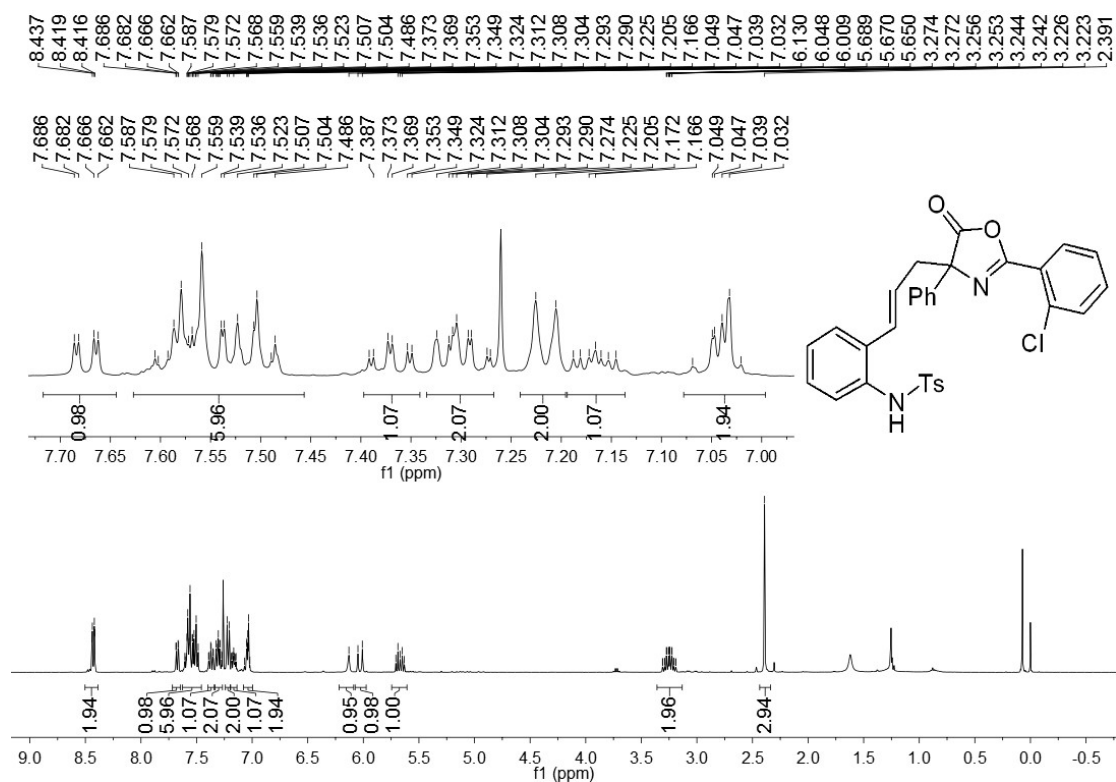
^1H NMR (400 MHz, CDCl_3) of compound **5aa**:



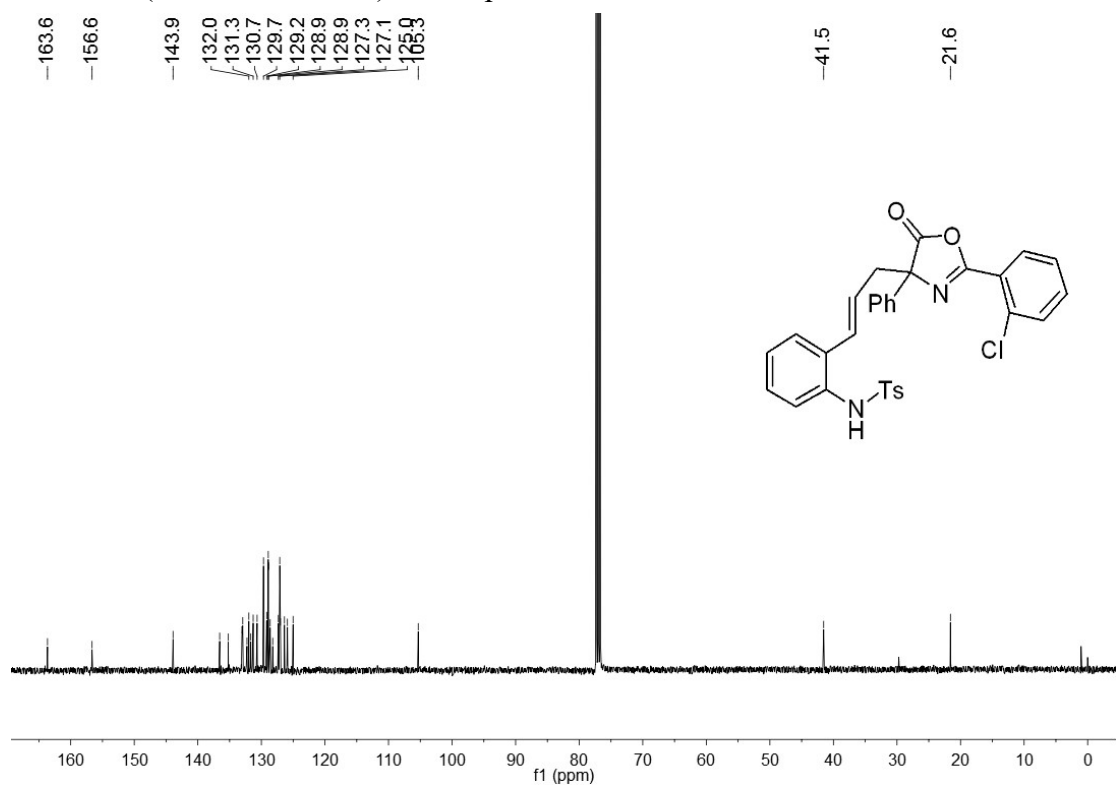
^{13}C NMR (100 MHz, CDCl_3) of compound **5aa**:



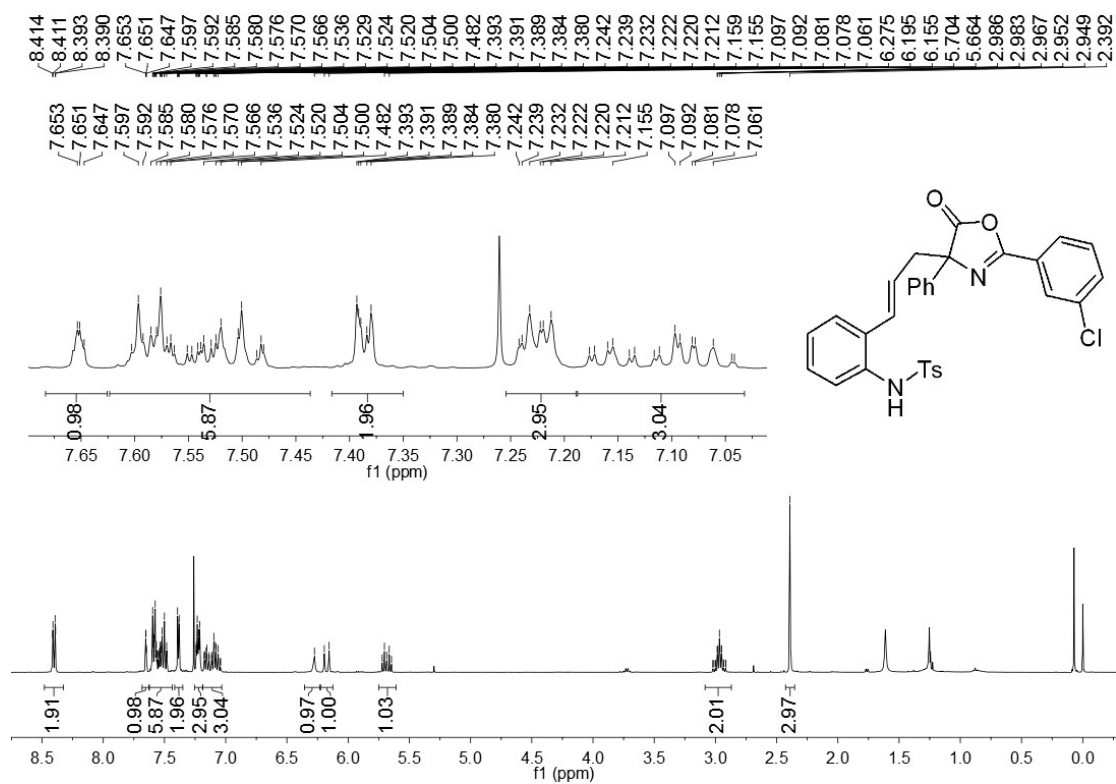
^1H NMR (400 MHz, CDCl_3) of compound **5ab**:



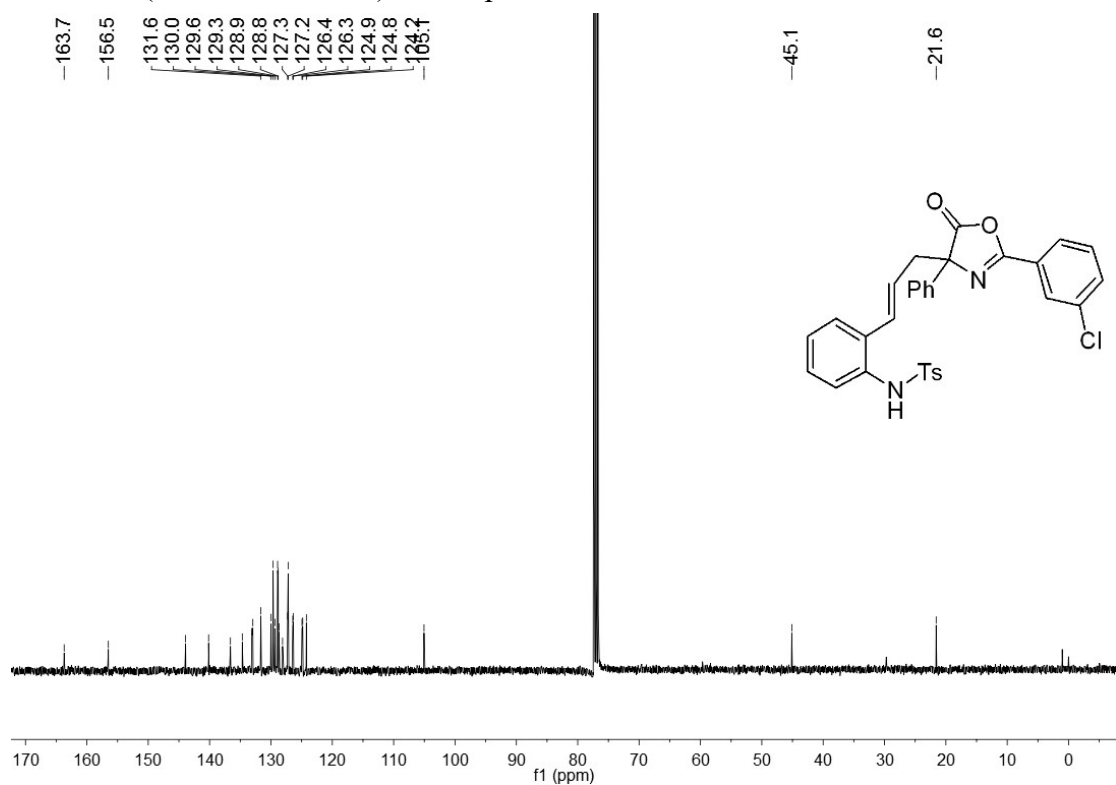
^{13}C NMR (100 MHz, CDCl_3) of compound **5ab**:



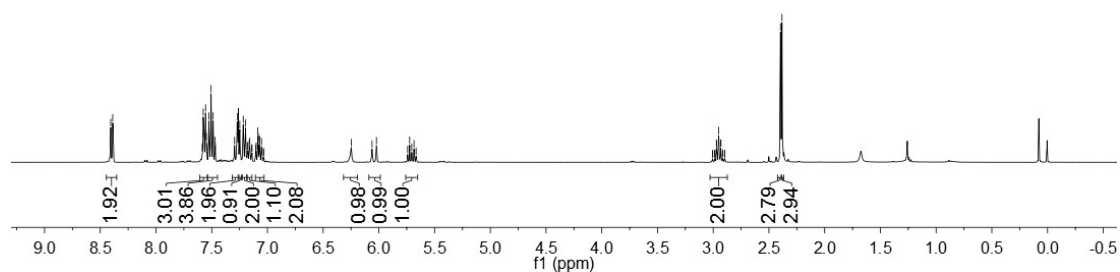
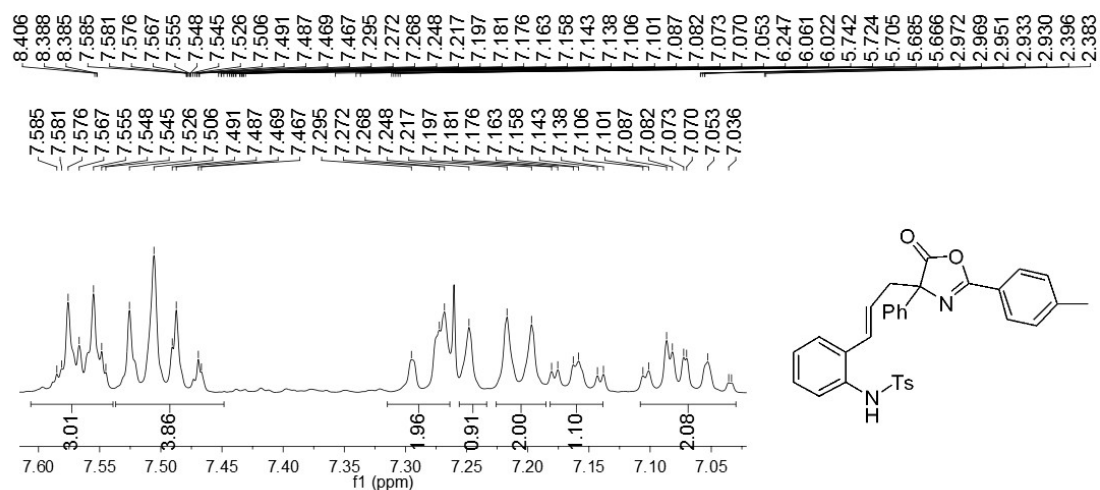
^1H NMR (400 MHz, CDCl_3) of compound **5ac**:



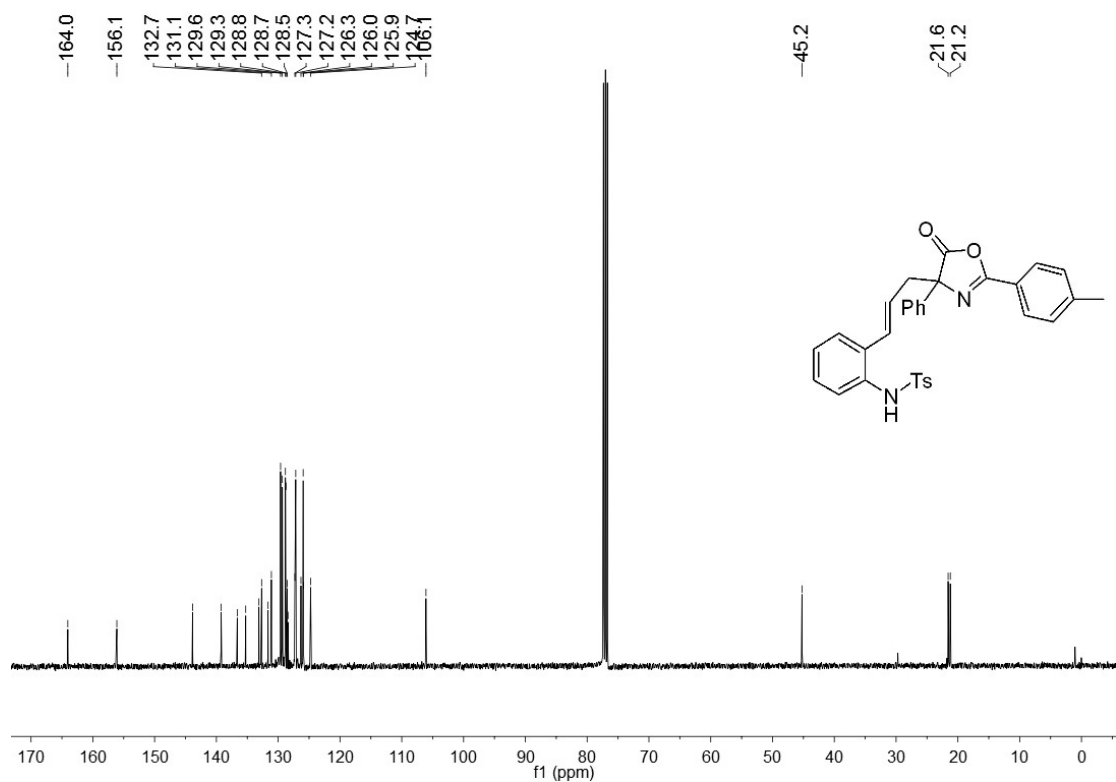
^{13}C NMR (100 MHz, CDCl_3) of compound **5ac**:



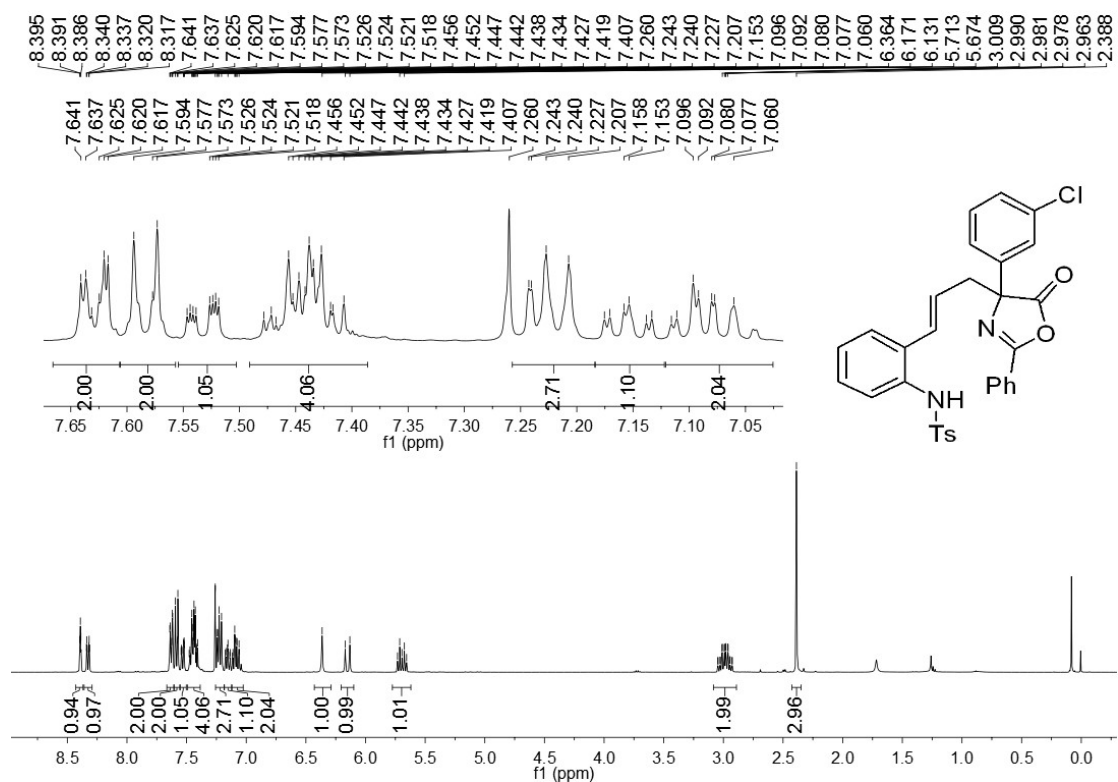
^1H NMR (400 MHz, CDCl_3) of compound **5ad**:



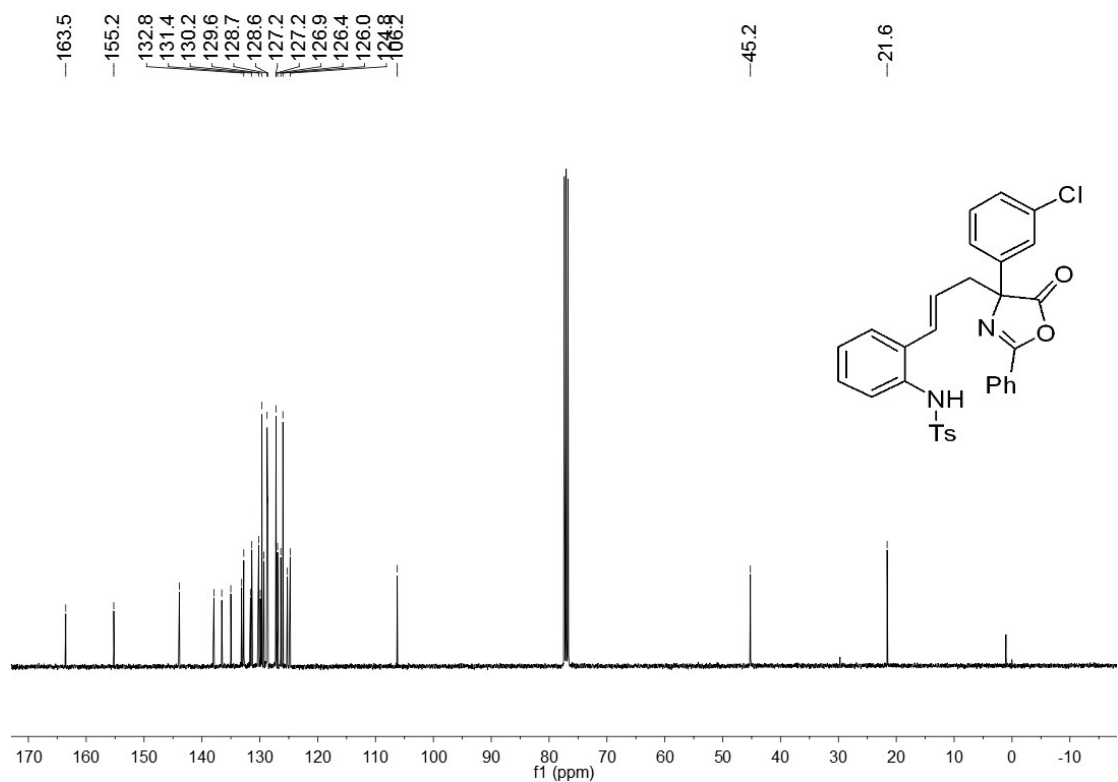
^{13}C NMR (100 MHz, CDCl_3) of compound **5ad**:



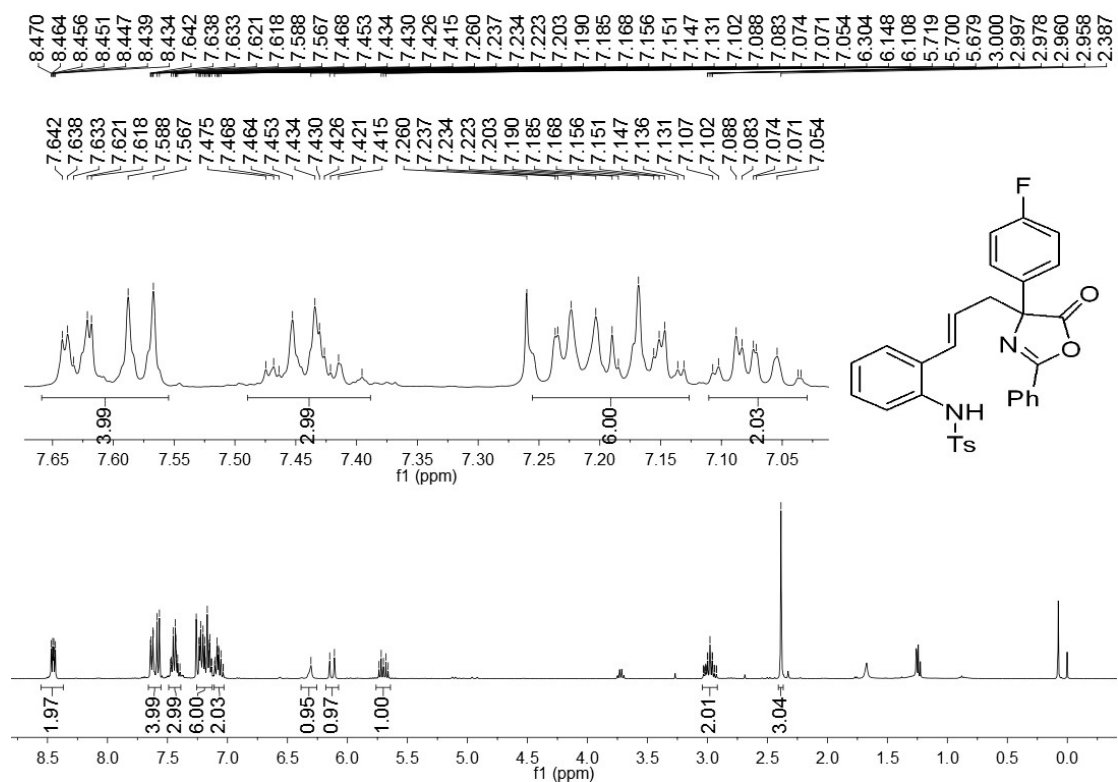
¹H NMR (400 MHz, CDCl₃) of compound **5ae**:



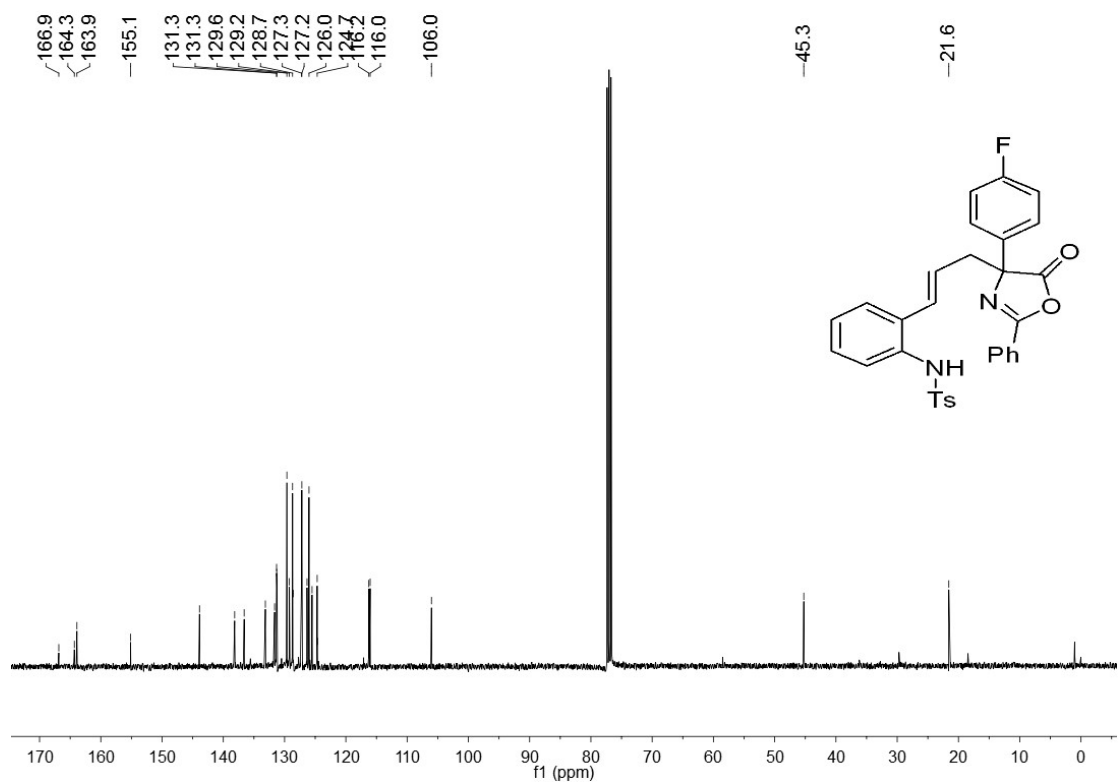
¹³C NMR (100 MHz, CDCl₃) of compound **5ae**:



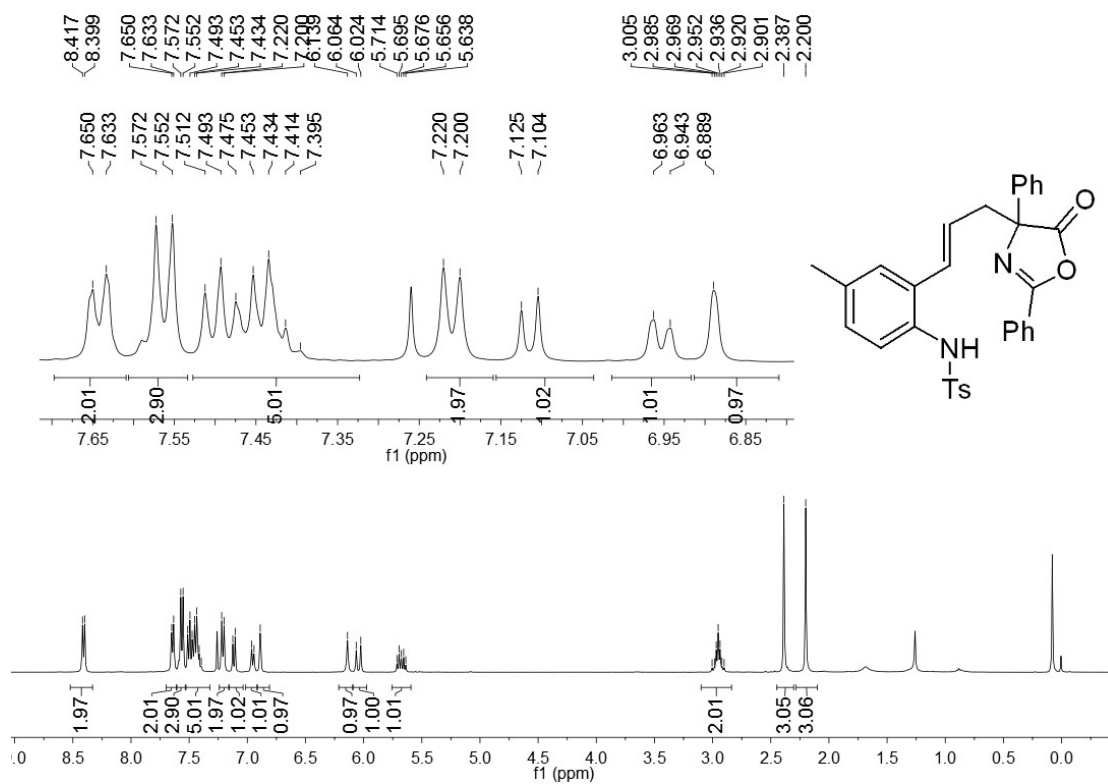
¹H NMR (400 MHz, CDCl₃) of compound **5af**:



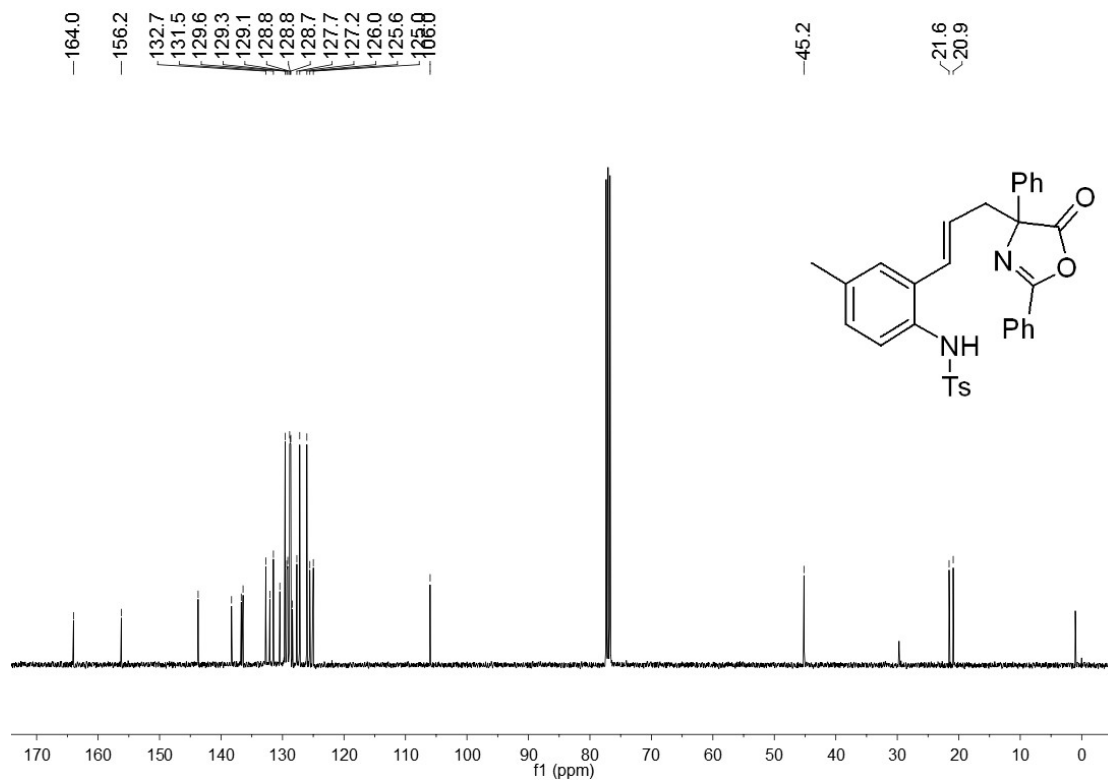
¹³C NMR (100 MHz, CDCl₃) of compound **5af**:



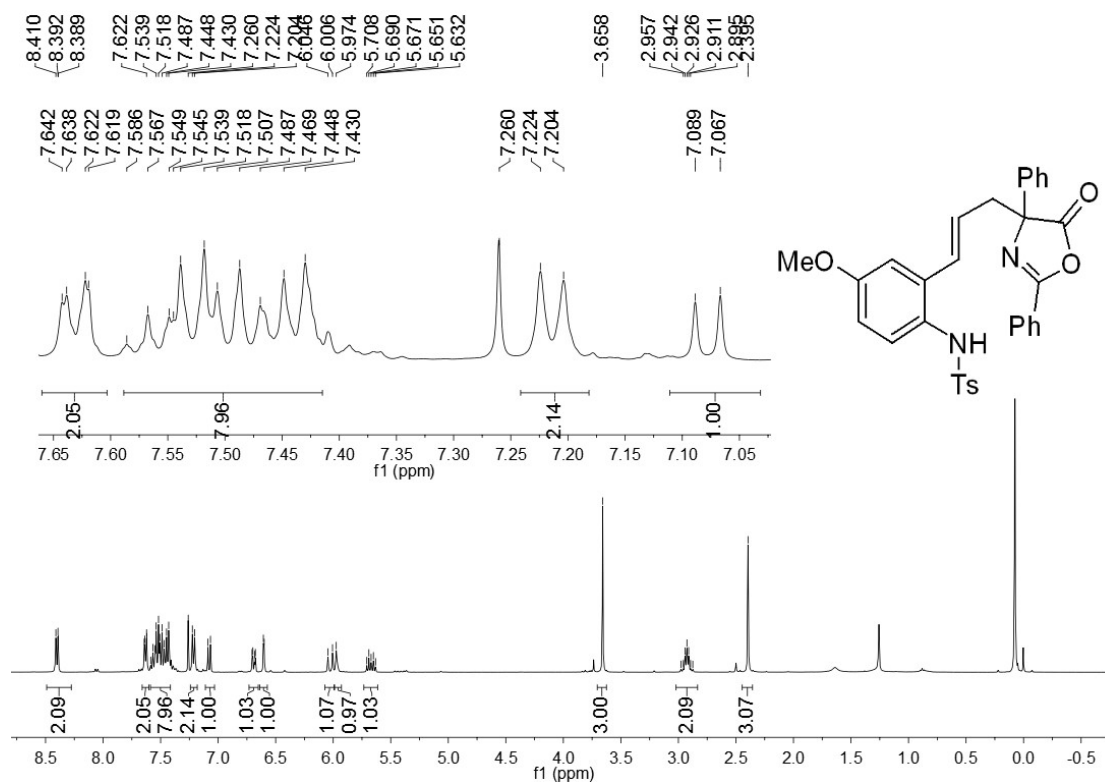
^1H NMR (400 MHz, CDCl_3) of compound **5da**:



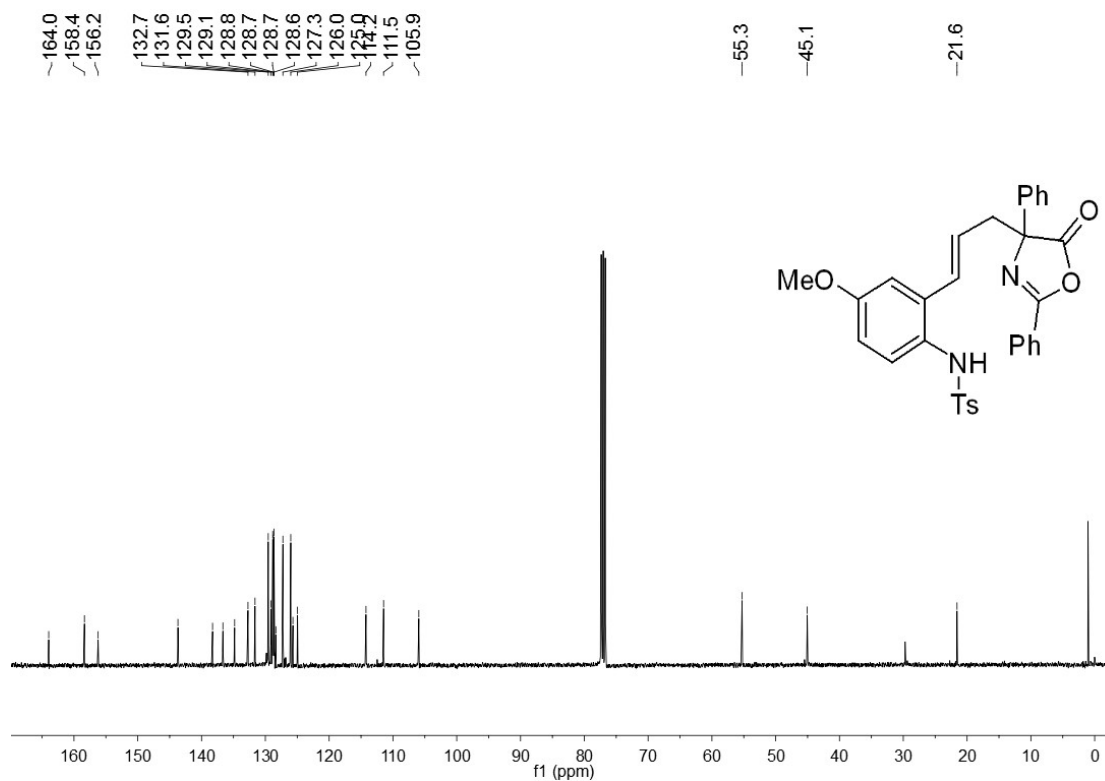
^{13}C NMR (100 MHz, CDCl_3) of compound **5da**:



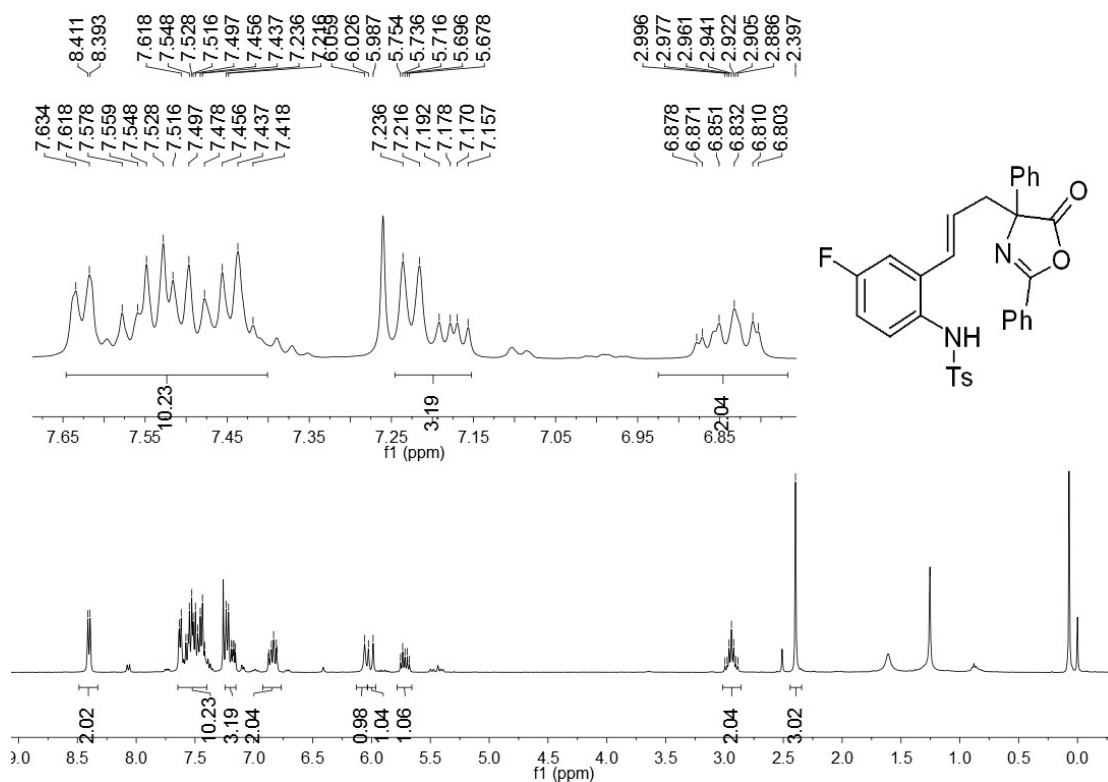
^1H NMR (400 MHz, CDCl_3) of compound **5ea**: inseparable *E/Z*-isomers (*E/Z*= 93:7)



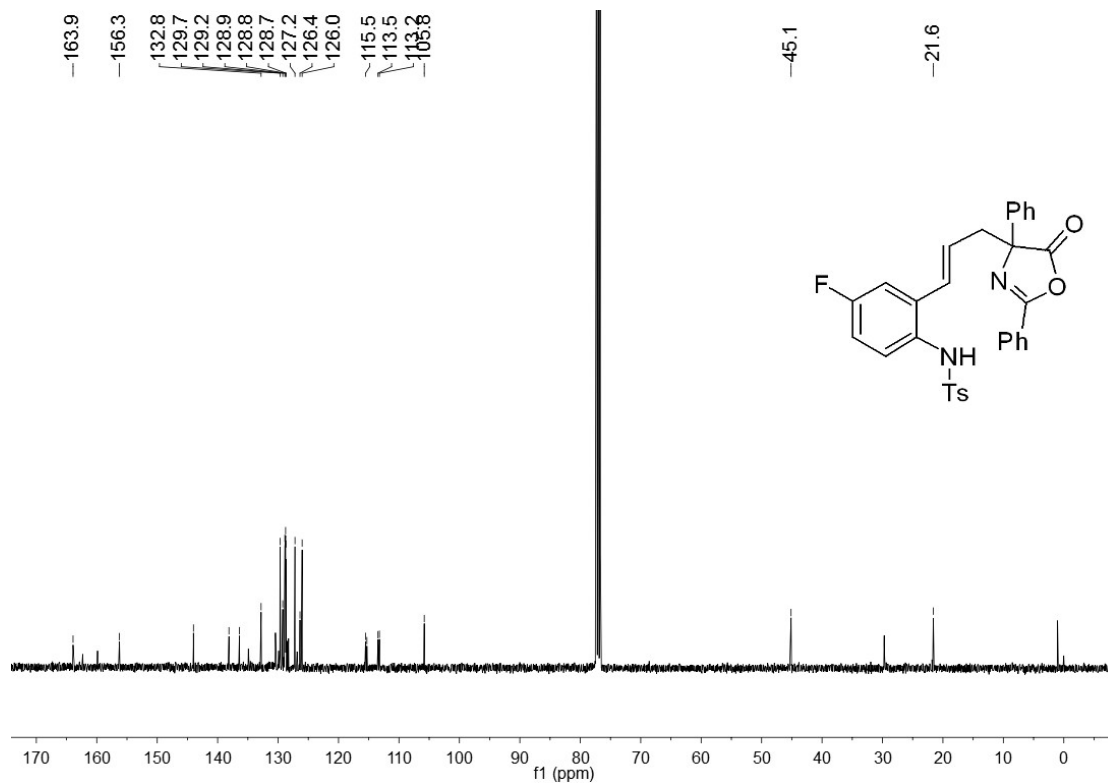
^{13}C NMR (100 MHz, CDCl_3) of compound **5ea**: inseparable *E/Z*-isomers (*E/Z*= 93:7)



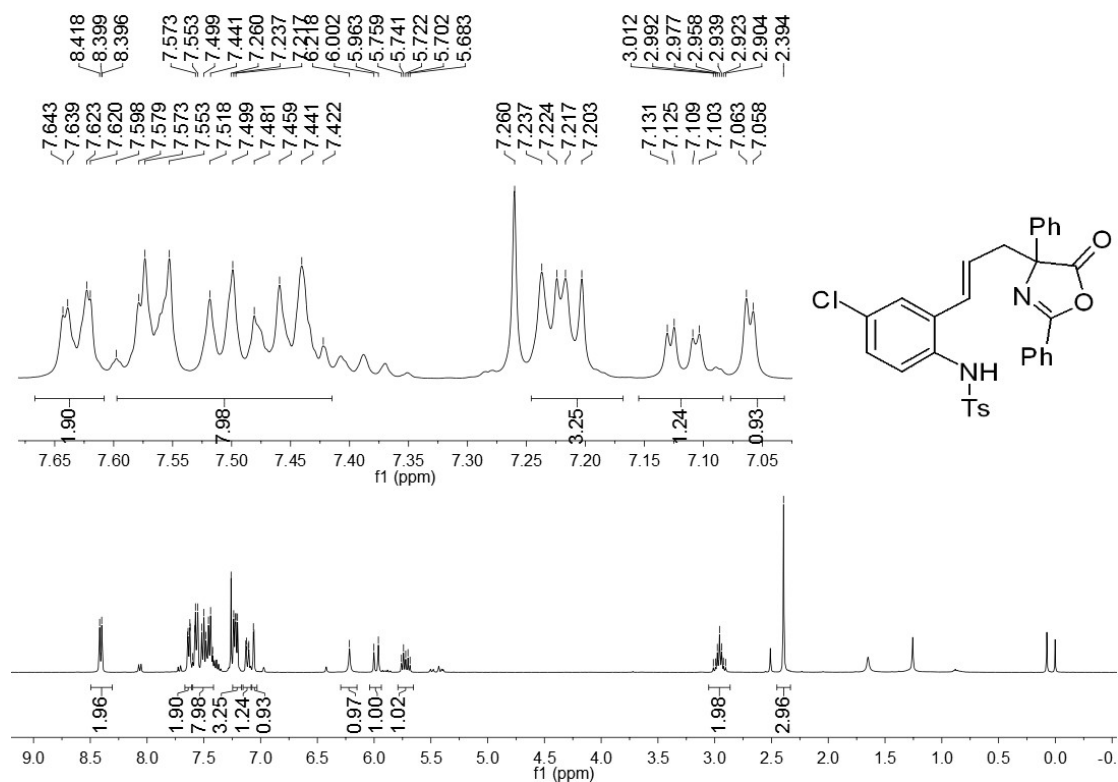
^1H NMR (400 MHz, CDCl_3) of compound **5fa**: inseparable *E/Z*-isomers (*E/Z* = 89:11)



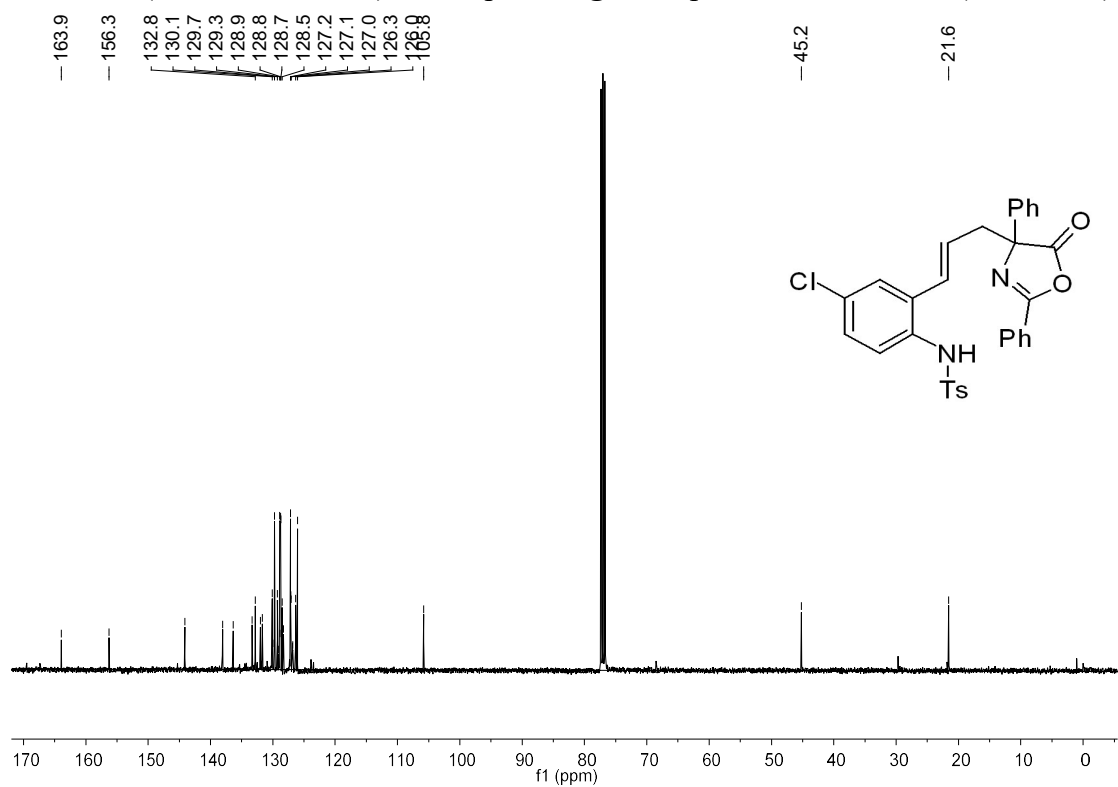
^{13}C NMR (100 MHz, CDCl_3) of compound **5fa**: inseparable *E/Z*-isomers (*E/Z* = 89:11)



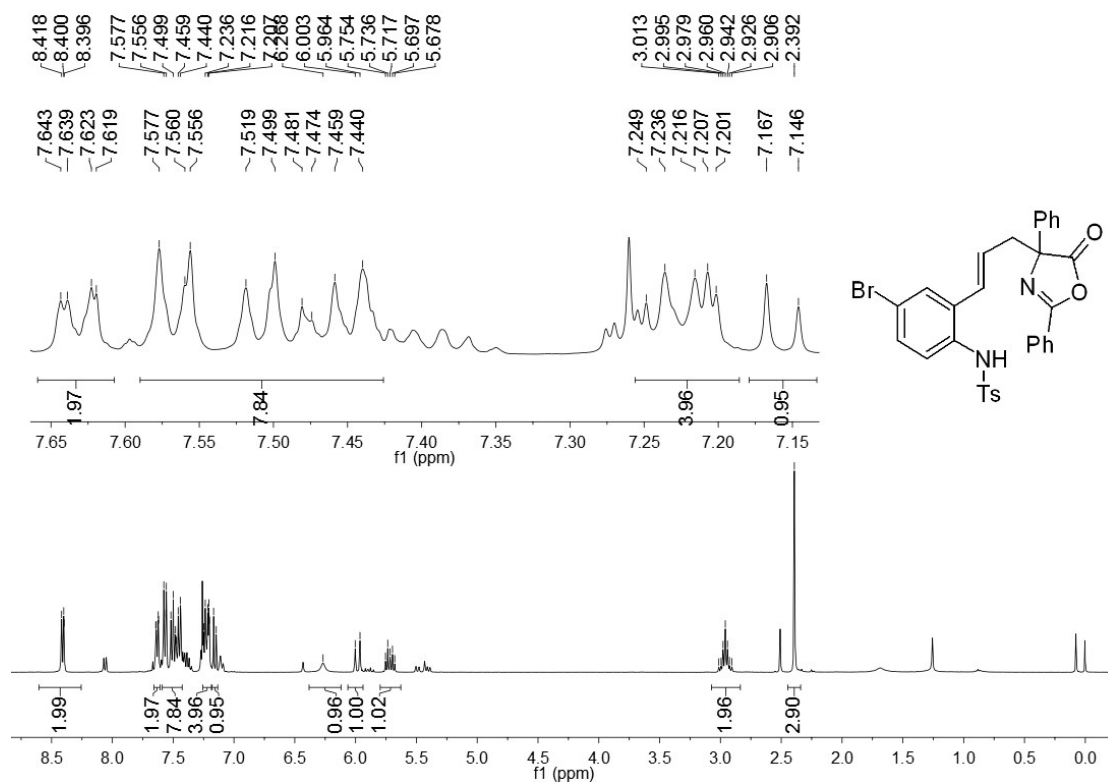
^1H NMR (400 MHz, CDCl_3) of compound **5ga**: inseparable *E/Z*-isomers (*E/Z*=87:13)



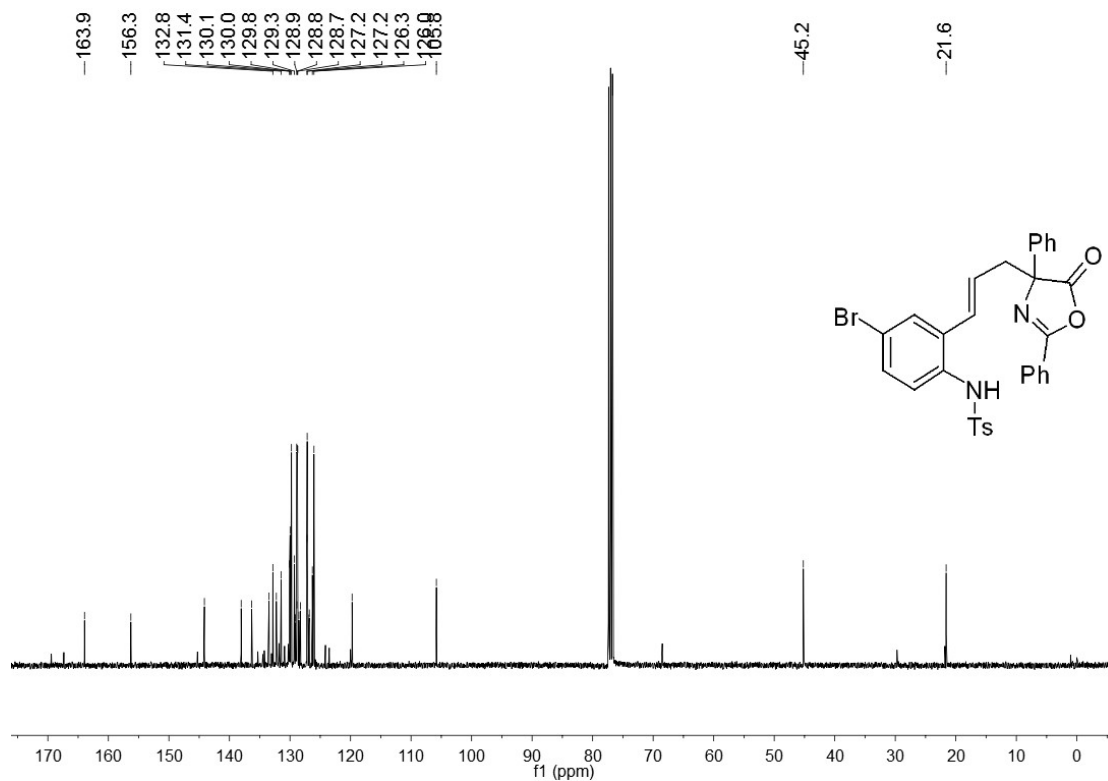
^{13}C NMR (100 MHz, CDCl_3) of compound **5ga**: inseparable *E/Z*-isomers (*E/Z*=87:13)



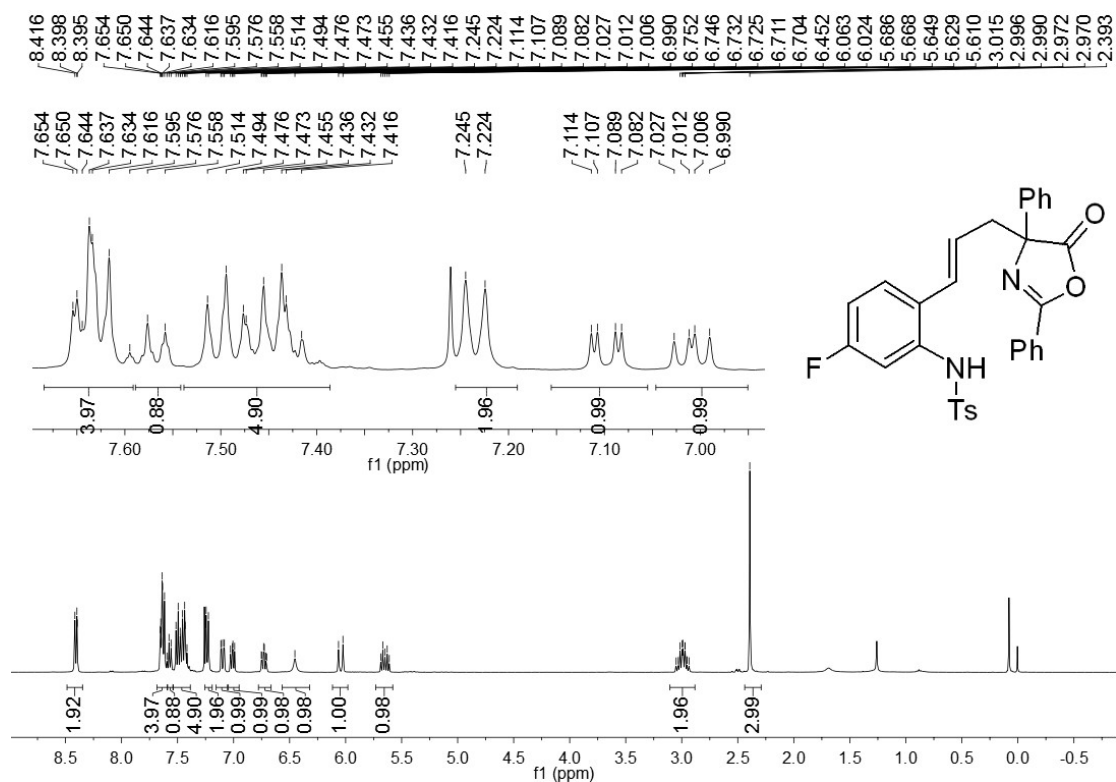
^1H NMR (400 MHz, CDCl_3) of compound **5ha**: inseparable *E/Z*-isomers (*E/Z*=83:17)



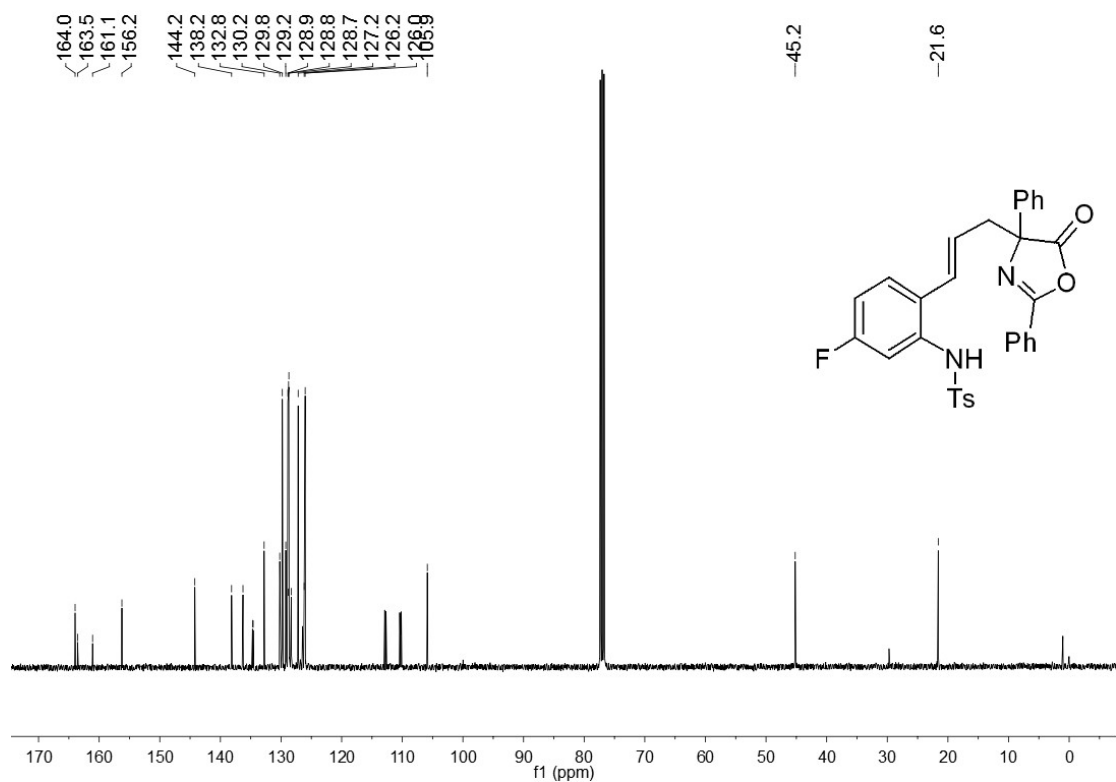
^{13}C NMR (100 MHz, CDCl_3) of compound **5ha**: inseparable *E/Z*-isomers (*E/Z*=83:17)



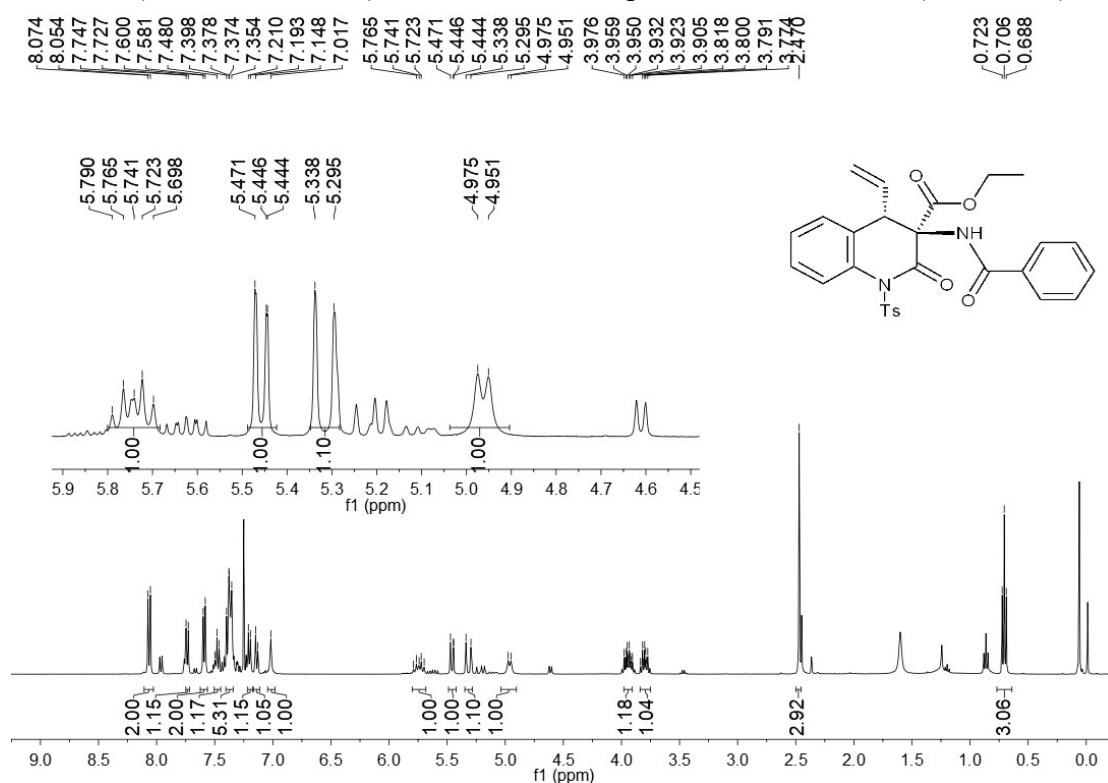
^1H NMR (400 MHz, CDCl_3) of compound **5ia**:



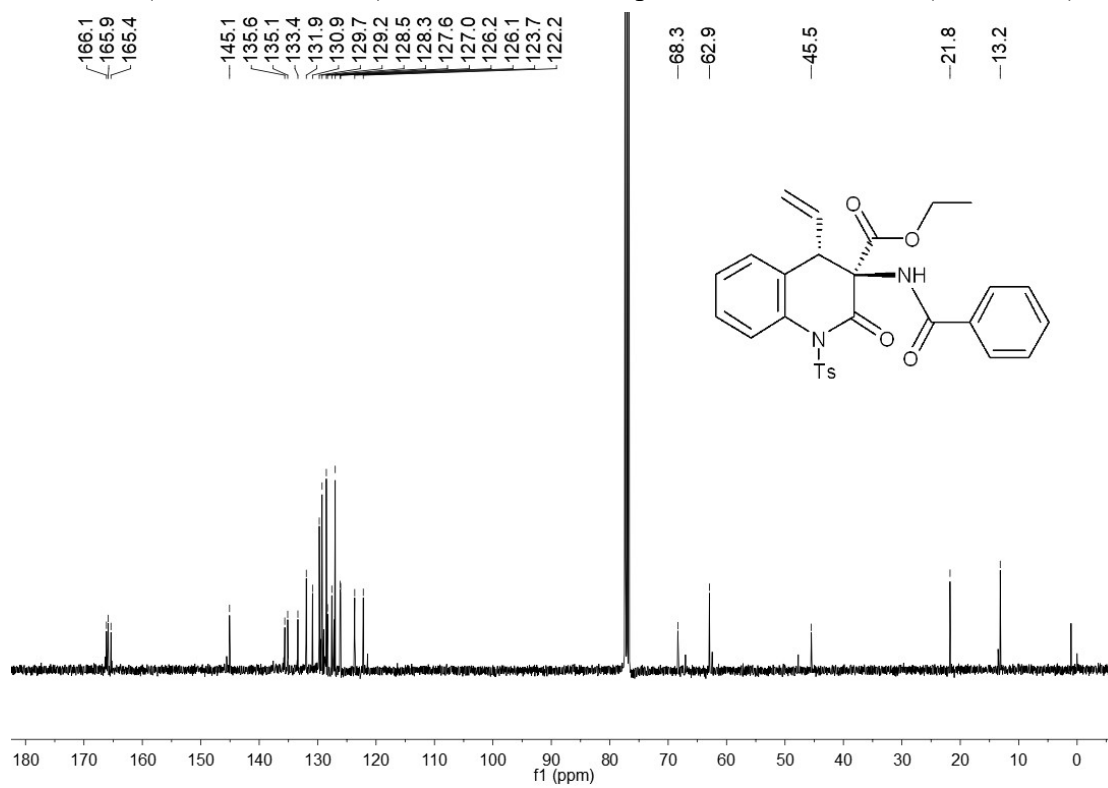
^{13}C NMR (100 MHz, CDCl_3) of compound **5ia**:



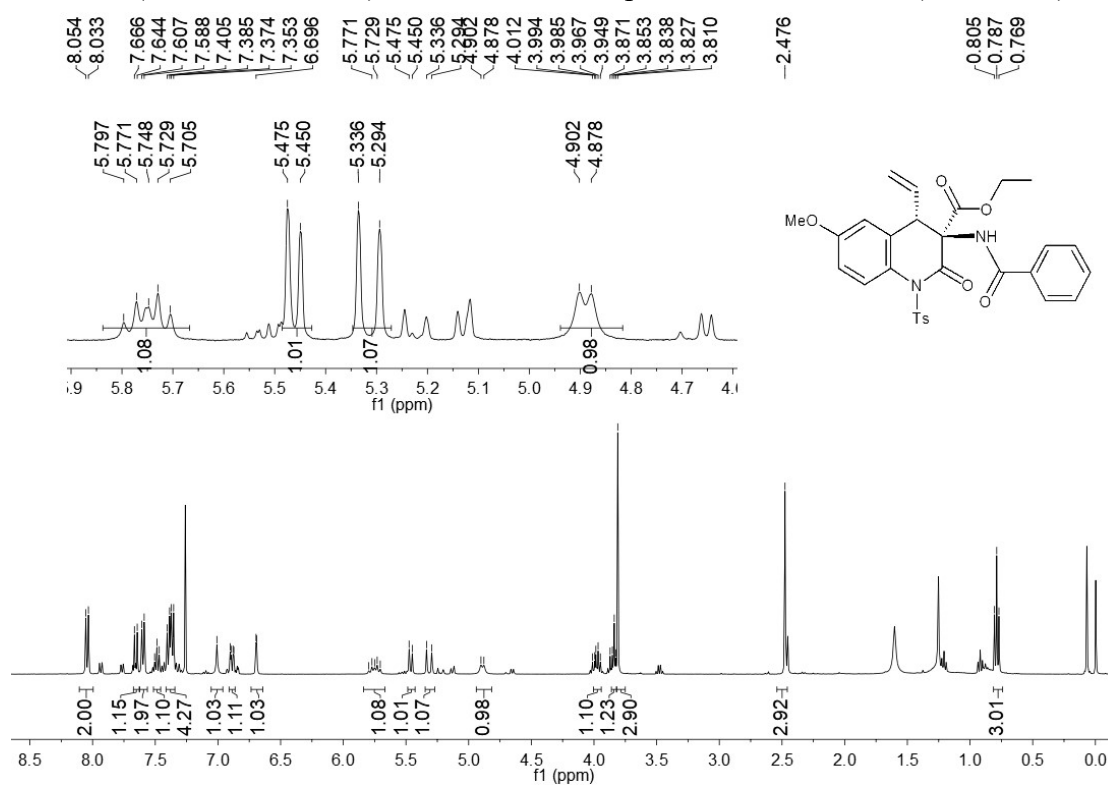
^1H NMR (400 MHz, CDCl_3) of **chiral 3aa**: inseparable diastereomers (dr = 84:16)



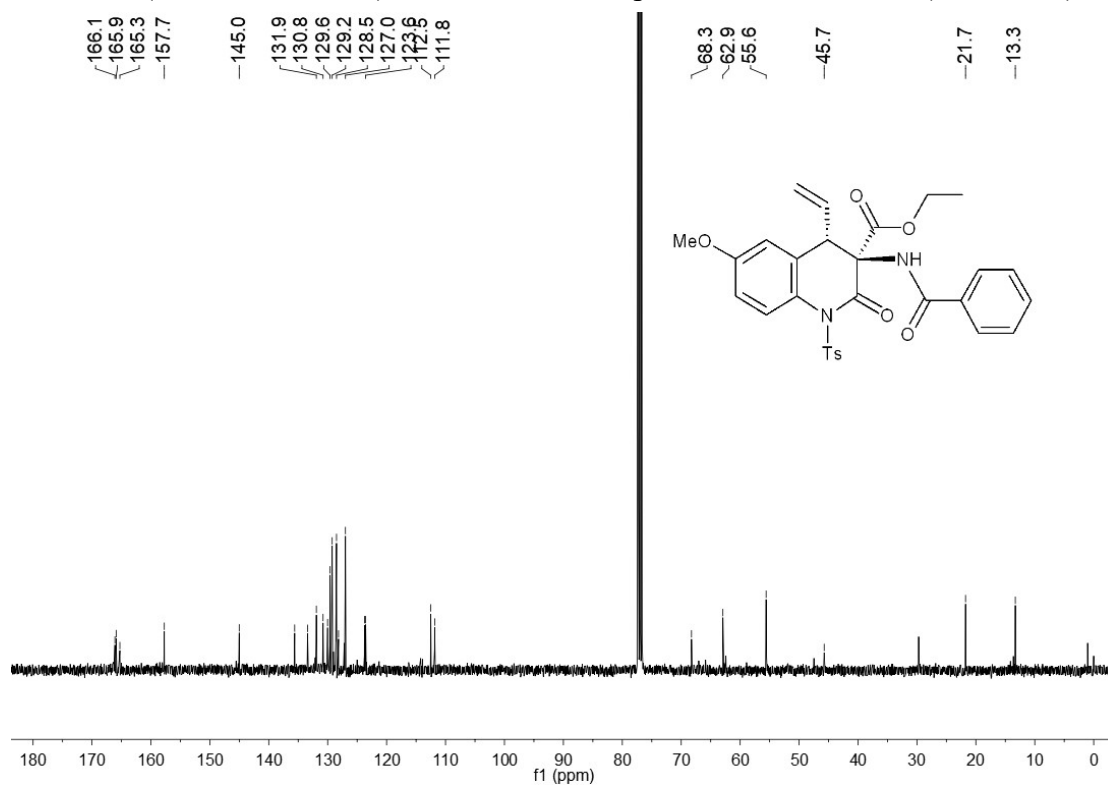
^{13}C NMR (100 MHz, CDCl_3) of **chiral 3aa**: inseparable diastereomers (dr = 84:16)



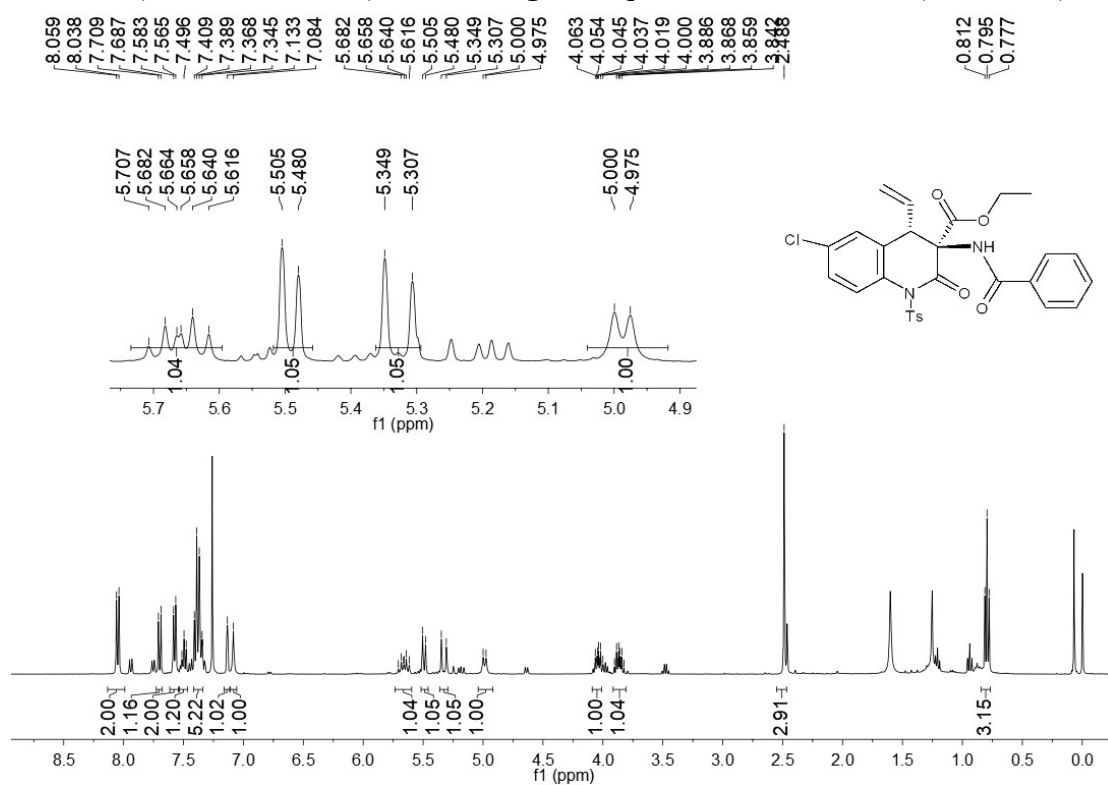
^1H NMR (400 MHz, CDCl_3) of **chiral 3ea**: inseparable diastereomers (dr = 83:17)



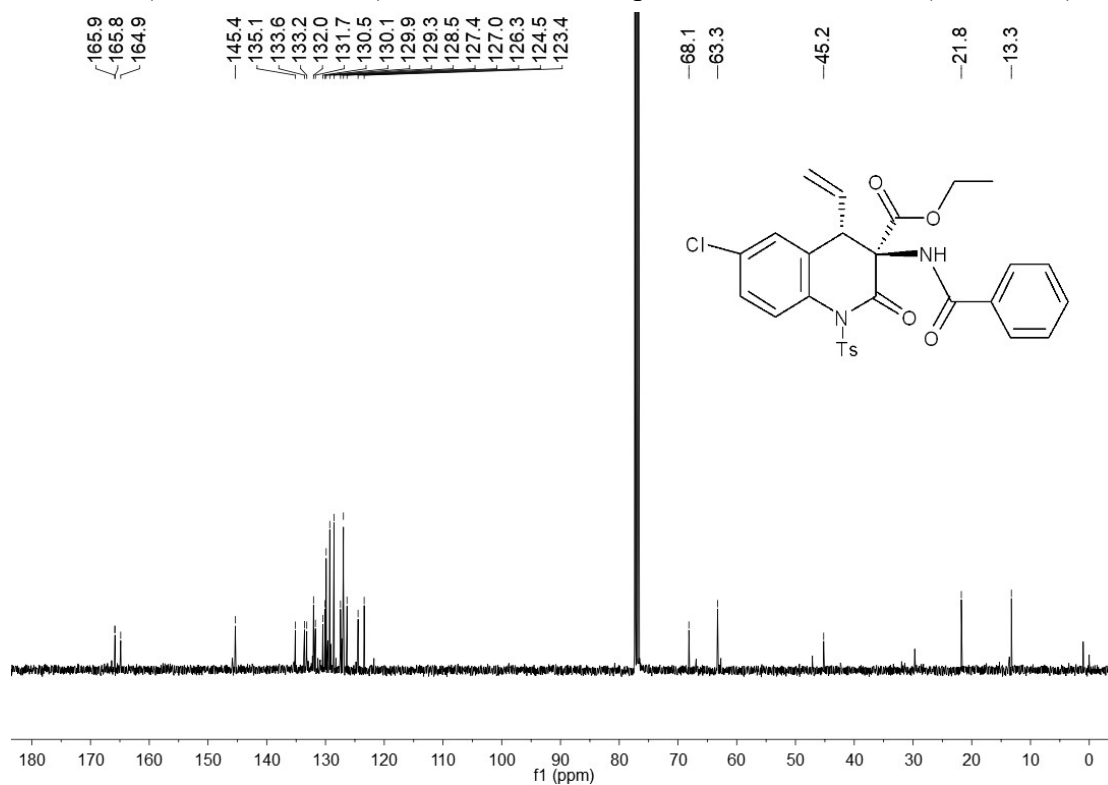
^{13}C NMR (100 MHz, CDCl_3) of **chiral 3ea**: inseparable diastereomers (dr = 83:17)



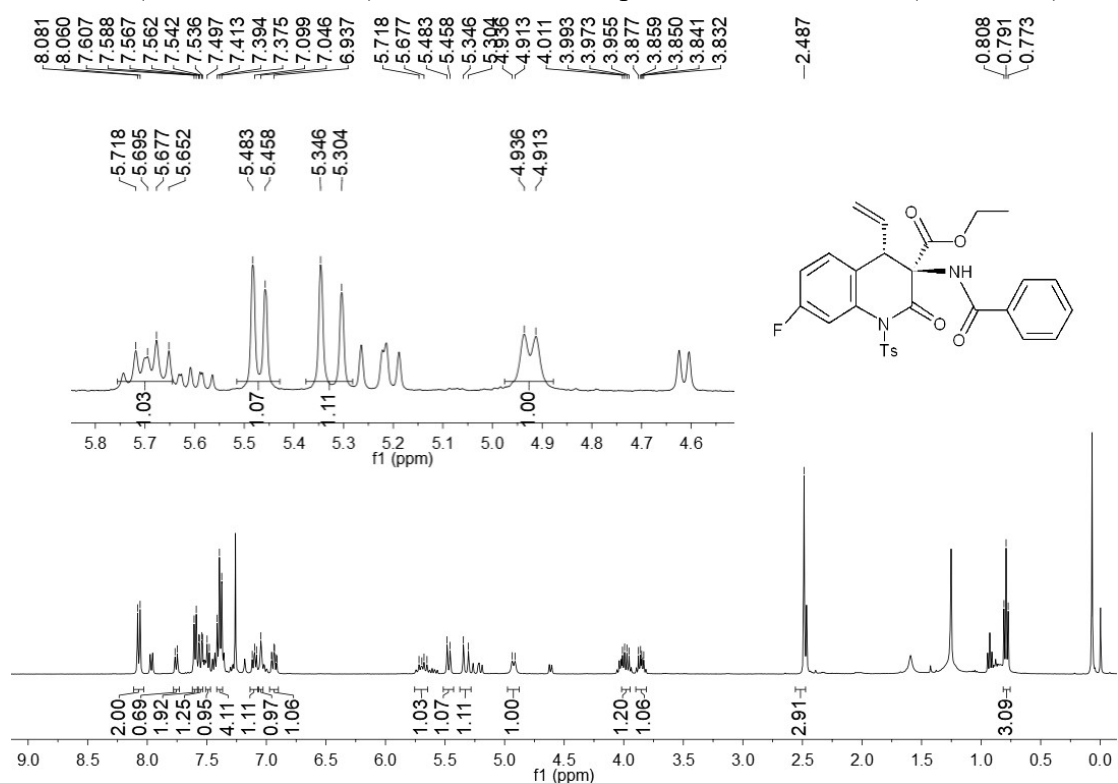
^1H NMR (400 MHz, CDCl_3) of **chiral 3ga**: inseparable diastereomers (dr = 83:17)



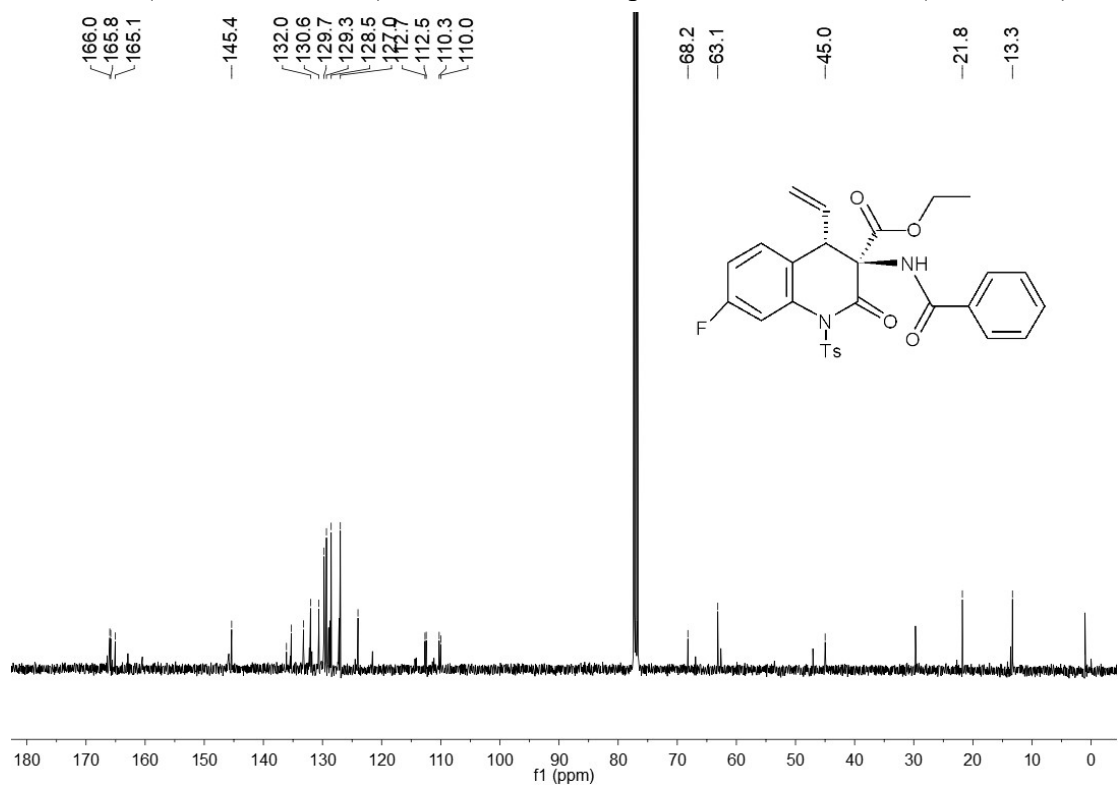
^{13}C NMR (100 MHz, CDCl_3) of **chiral 3ea**: inseparable diastereomers (dr = 83:17)



^1H NMR (400 MHz, CDCl_3) of **chiral 3ia**: inseparable diastereomers (dr = 74:26)



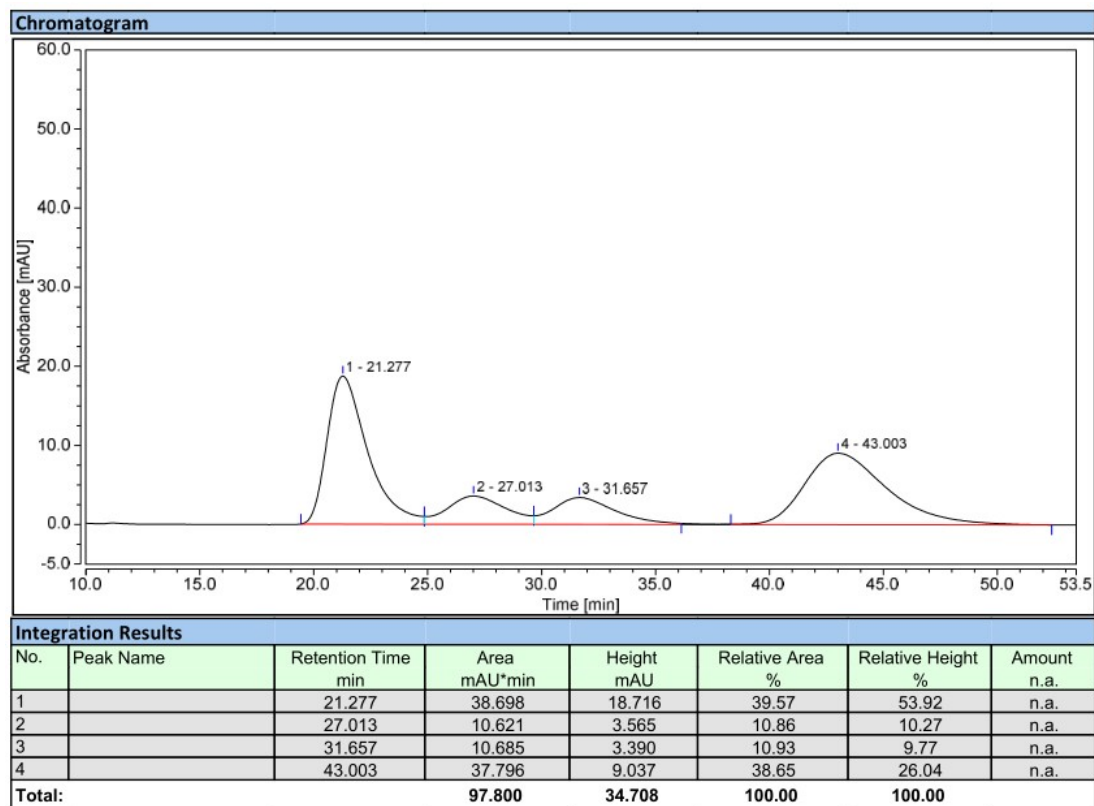
^{13}C NMR (100 MHz, CDCl_3) of **chiral 3ia**: inseparable diastereomers (dr = 74:26)



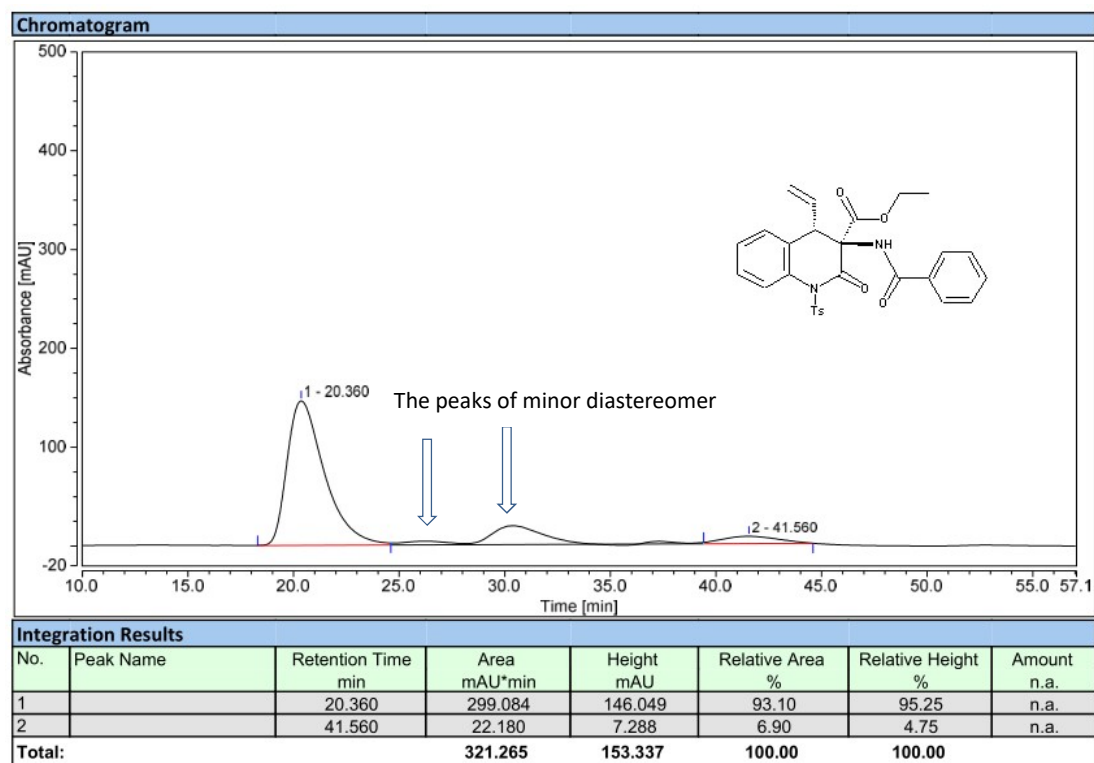
9. HPLC spectra of chiral 3

chiral 3aa:

Racemic:

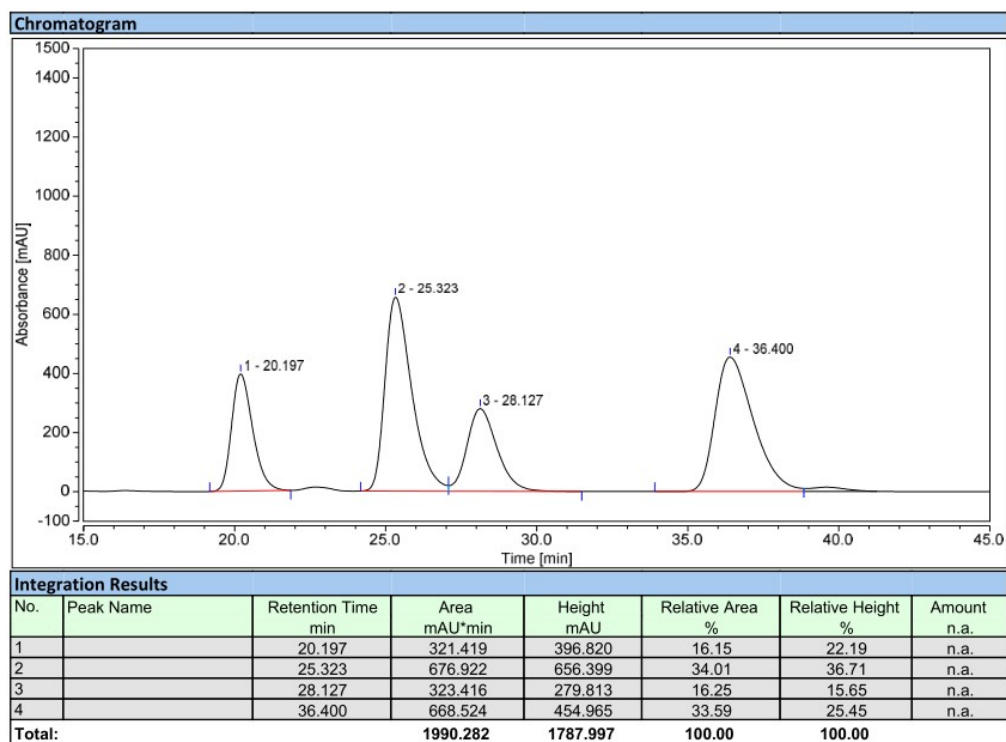


Enantioselective:

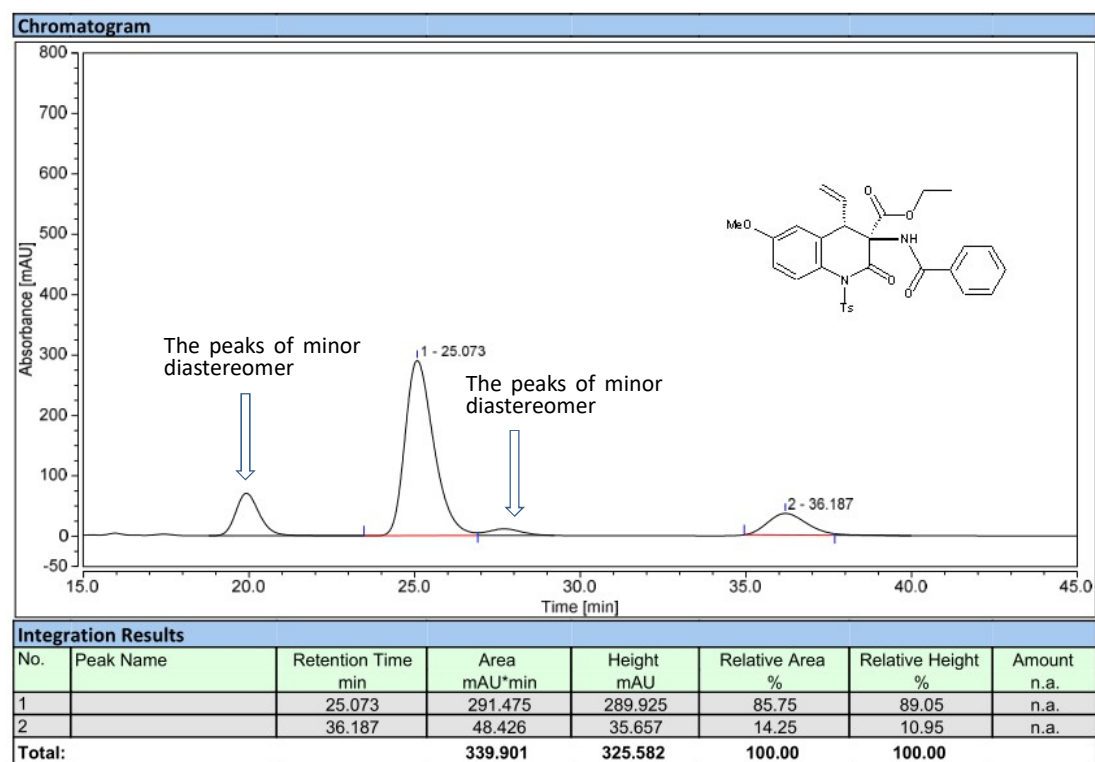


chiral 3ea:

Racemic:

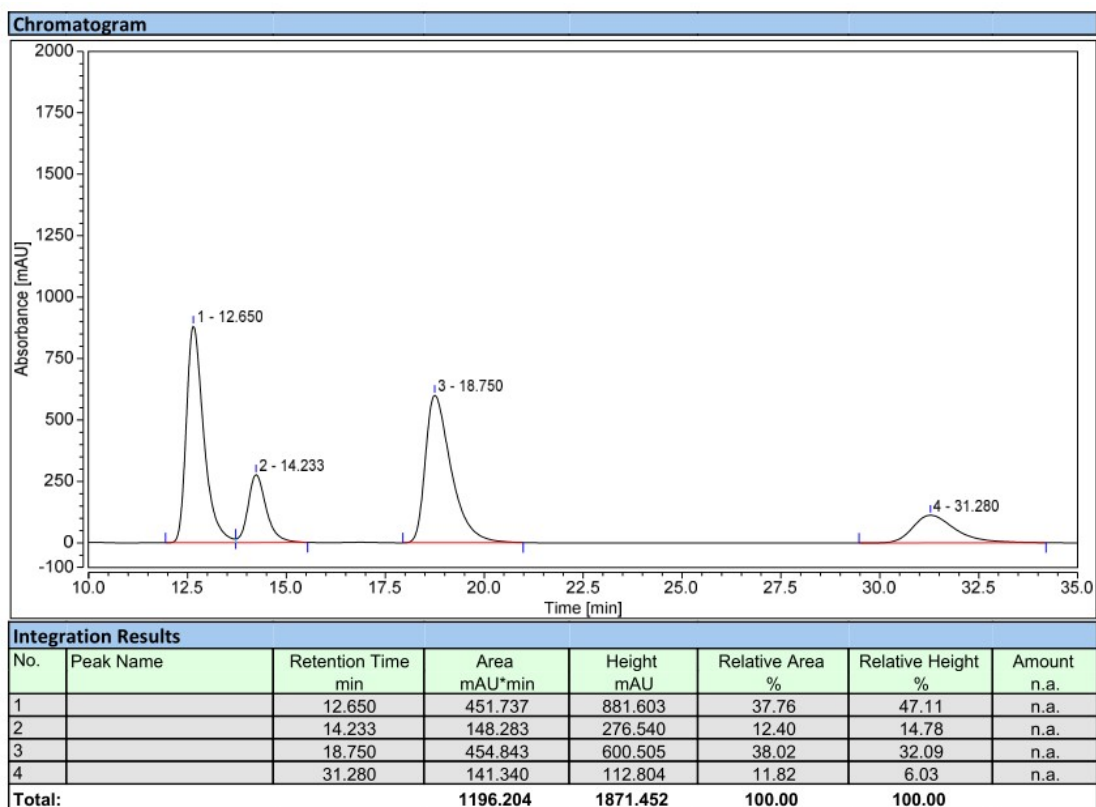


Enantioselective:

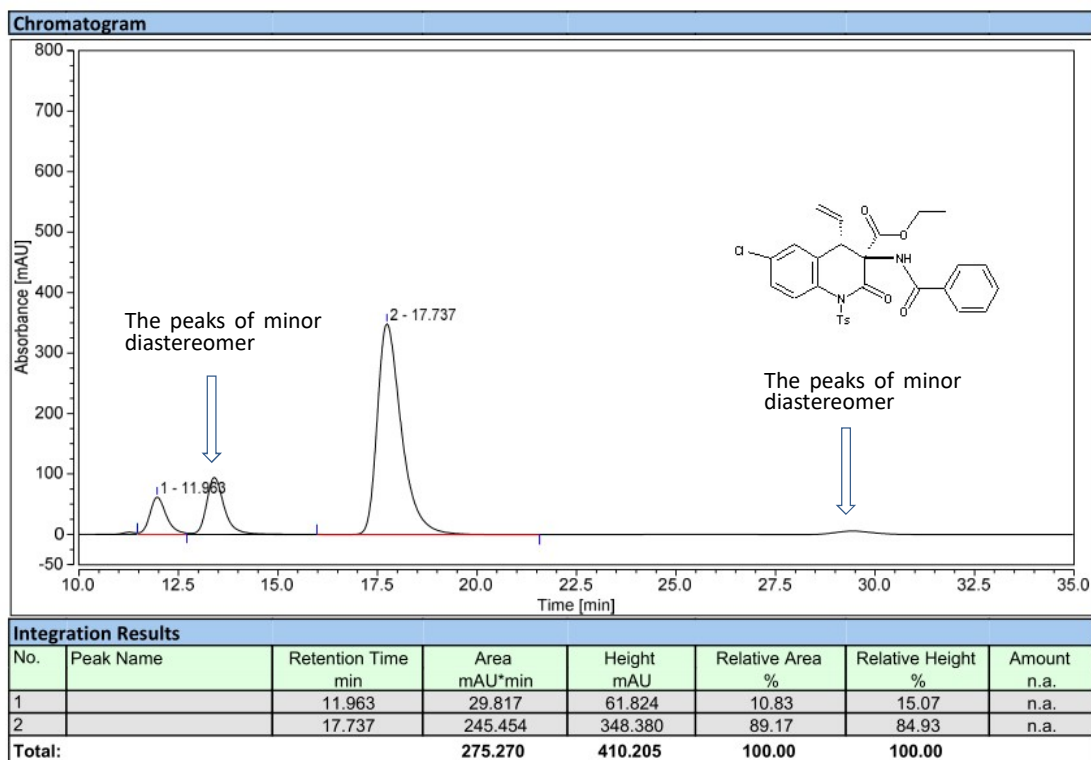


chiral 3ga:

Racemic:

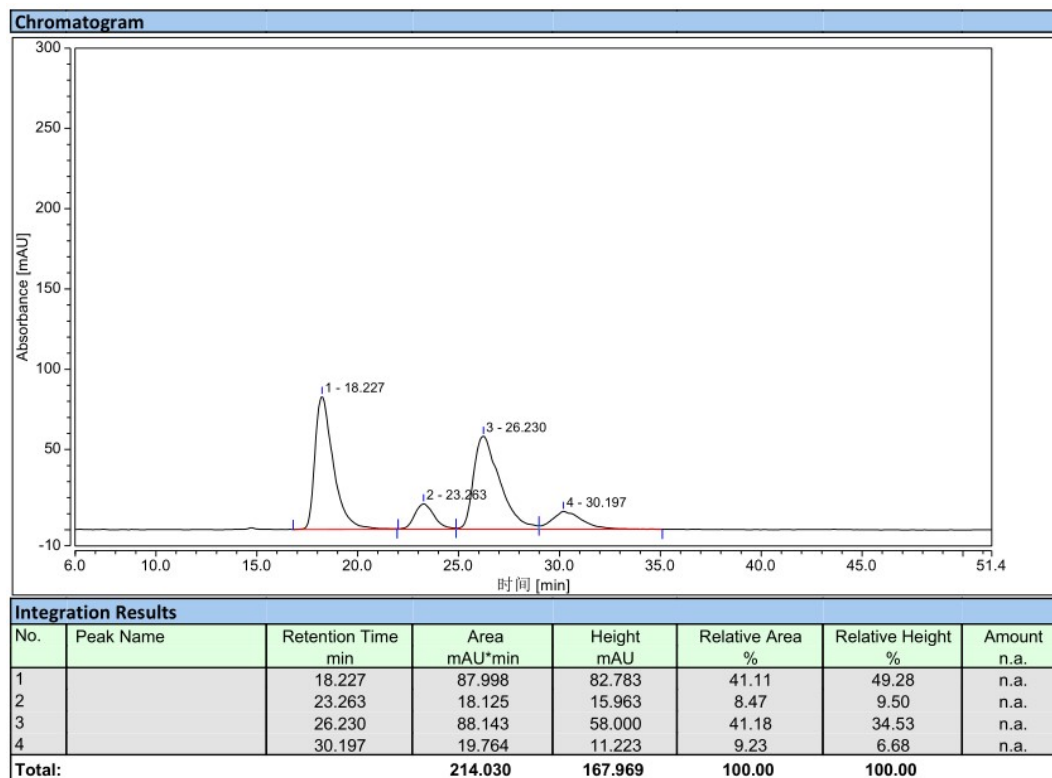


Enantioselective:

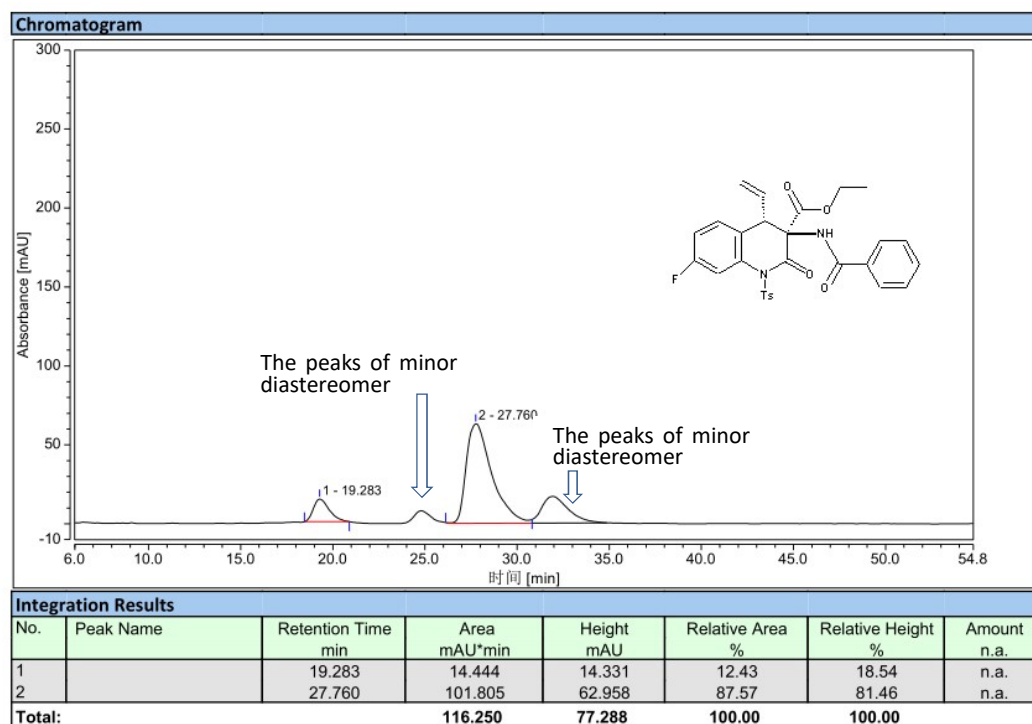


chiral 3ia:

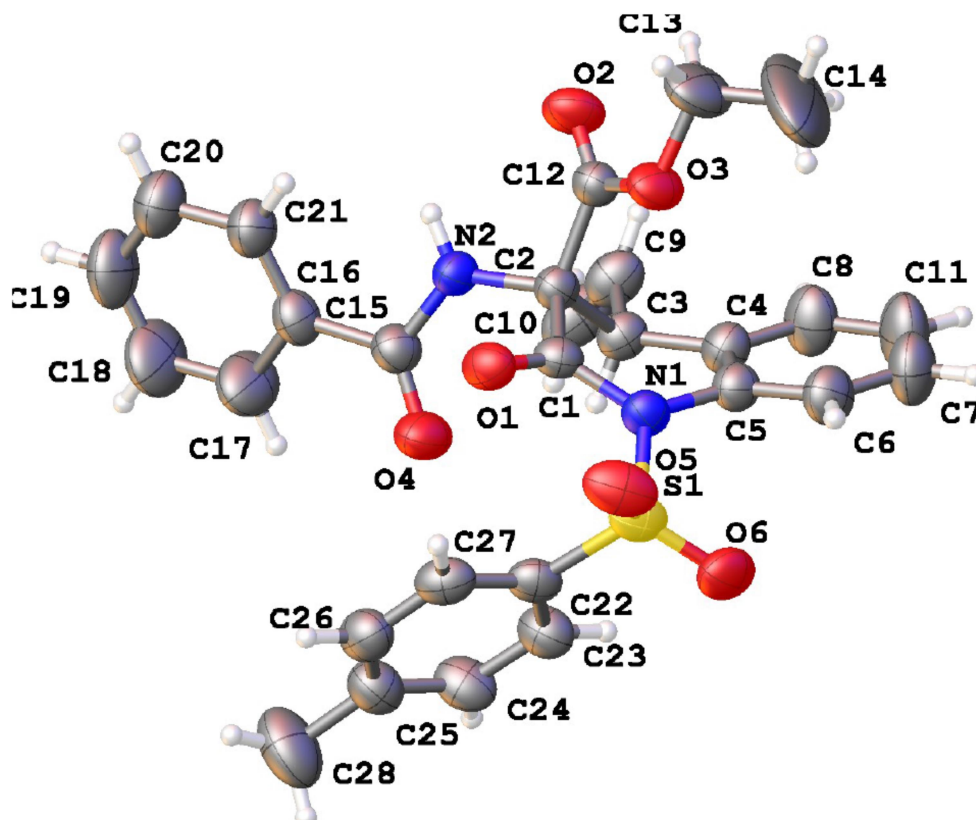
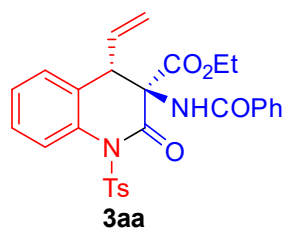
Racemic:



Enantioselective:



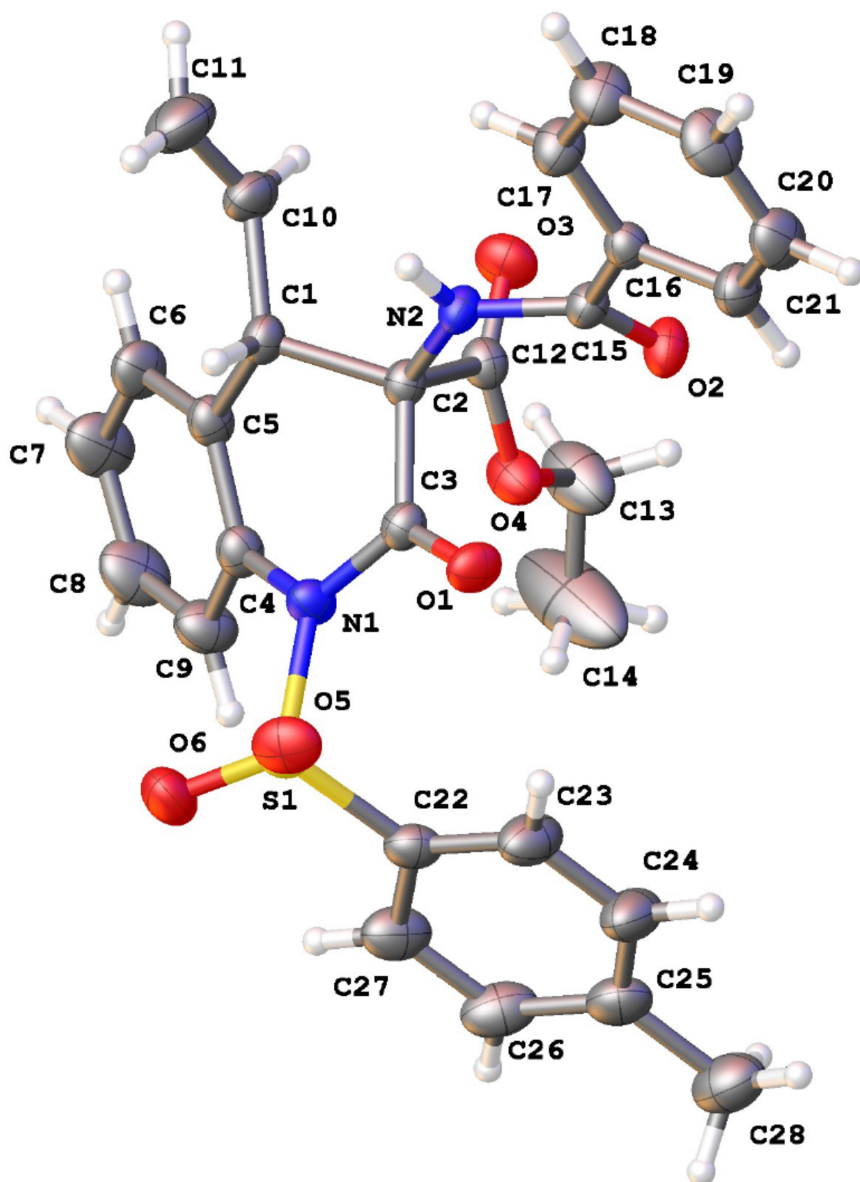
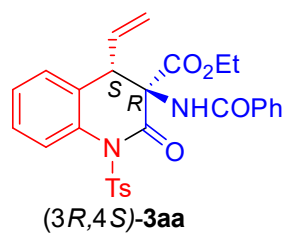
10. X-ray single crystal data for compounds 3aa and chiral 3aa



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

Empirical formula	C ₂₈ H ₂₆ N ₂ O ₆ S	
Formula weight	518.57	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /n 1	
Unit cell dimensions	a = 9.4926(15) Å	α = 90°.
	b = 12.1584(19) Å	β = 94.409(2)°.
	c = 22.925(4) Å	γ = 90°.
Volume	2638.1(7) Å ³	
Z	4	
Density (calculated)	1.306 Mg/m ³	
Absorption coefficient	0.167 mm ⁻¹	

F(000)	1088
Crystal size	0.35 x 0.25 x 0.2 mm ³
Theta range for data collection	2.392 to 27.000°.
Index ranges	-12<=h<=12, -15<=k<=15, -26<=l<=29
Reflections collected	17967
Independent reflections	5729 [R(int) = 0.0790]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.5578
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5729 / 0 / 336
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1512
R indices (all data)	R1 = 0.0717, wR2 = 0.1626
Extinction coefficient	n/a
Largest diff. peak and hole	0.574 and -0.456 e.Å ⁻³



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

Empirical formula	C ₃₁ H ₃₄ N ₂ O ₇ S
Formula weight	578.66
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic

Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 7.8782(19) Å	α = 90°.
	b = 10.747(3) Å	β = 90°.
	c = 35.997(8) Å	γ = 90°.
Volume	3047.8(12) Å ³	
Z	4	
Density (calculated)	1.261 Mg/m ³	
Absorption coefficient	0.154 mm ⁻¹	
F(000)	1224	
Crystal size	0.3 x 0.2 x 0.15 mm ³	
Theta range for data collection	2.544 to 28.484°.	
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -47 ≤ l ≤ 29	
Reflections collected	22026	
Independent reflections	7198 [R(int) = 0.0953]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7198 / 0 / 375	
Goodness-of-fit on F ²	1.081	
Final R indices [I > 2σ(I)]	R1 = 0.0565, wR2 = 0.1332	
R indices (all data)	R1 = 0.0780, wR2 = 0.1412	
Absolute structure parameter	0.09(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.360 and -0.288 e.Å ⁻³	