

Supporting Information

Bi(OAc)₃/Chiral Phosphoric Acid Catalyzed Enantioselective Allylation of Isatins

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Contents

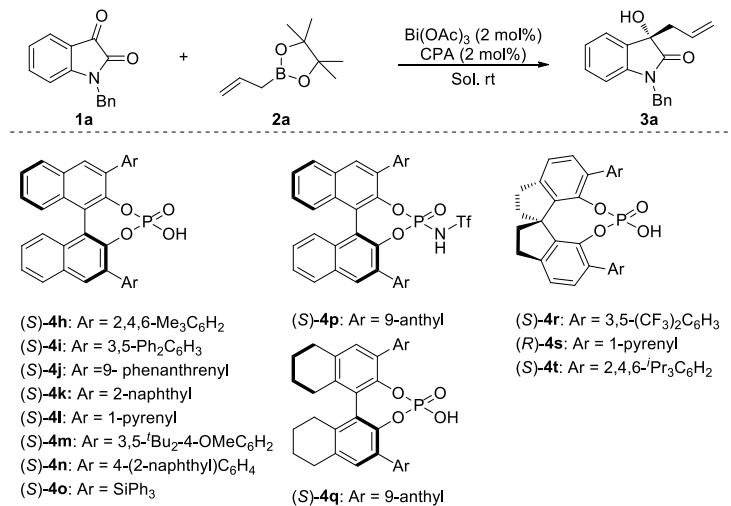
1. General information	2
2. Optimization of the reaction conditions.....	2
3. General procedure for asymmetric allylation of isatins with allylboronates.....	4
4. Characterization data of products 3	4
5. Transformations of products	14
6. References.....	17
7. NMR Spectra.....	19
8. HPLC Spectra	62

1. General information.

Dry cyclohexane was purchased from 3A Chemicals and stored over activated 3 Å molecular sieves. Allylboronic acid pinacol esters were purchased from J&K, or synthesized according to the literature procedure.¹ Isatins were synthesized according to the literature procedure.² ¹H and ¹³C NMR were recorded on a Bruker - DPX 400 spectrometer, chemical shifts were reported in ppm, tetramethylsilane (TMS) served as the internal standard for ¹H NMR, and CDCl₃ served as the internal standard for ¹³C NMR. ¹⁹F NMR were recorded on a Varian NMR 400 spectrometer. The following abbreviations were used to designate the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). HPLC analysis was performed using Chiralcel columns purchased. Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer.

2. Optimization of the reaction conditions.

Table S1. Other CPAs and solvents investigated.^a



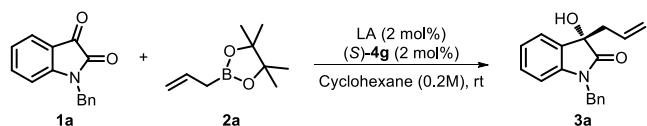
Entry	CPA	Sol.	t/h	Yield [%] ^b	<i>ee</i> [%] ^c
1	4h	Et ₂ O	0.5	96	-24
2	4i	Et ₂ O	0.5	95	-21
3	4j	Et ₂ O	1	98	30
4	4k	Et ₂ O	0.5	92	40
5	4l	Et ₂ O	4	98	31
6	4m	Et ₂ O	0.5	96	17
7	4n	Et ₂ O	2	95	36
8	4o	Et ₂ O	1	98	-6
9	4p	Et ₂ O	0.5	94	35
10	4q	Et ₂ O	0.5	97	37
11	4r	Et ₂ O	0.5	95	27
12	4s	Et ₂ O	1	98	3
13	4t	Et ₂ O	22	96	-5

14	4g	DCE	1.5	98	48
15	4g	CH ₃ CN	20	91	-9
16	4g	1,4-dioxane	20	97	4
17	4g	<i>n</i> -pentane	10	97	84
18	4g	<i>n</i> -hexane	10	98	83
19	4g	PE	13	86	80
20 ^d	4g	cyclohexane	30	97	30
21 ^e	4g	cyclohexane	3	98	83
22 ^f	4g	cyclohexane	32	97	10

^aThe reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), Bi(OAc)₃ (2 mol%), and CPA (2 mol%) in 0.5 mL solvent

at room temperature. ^bYield of isolated products. ^cDetermined by HPLC analysis. ^dH₂O (1.0 equiv.) was added. ^e3 Å molecular sieves (40 mg) were added. ^f4 Å molecular sieves (40 mg) were added.

Table S2. Screening of Lewis acids.^a

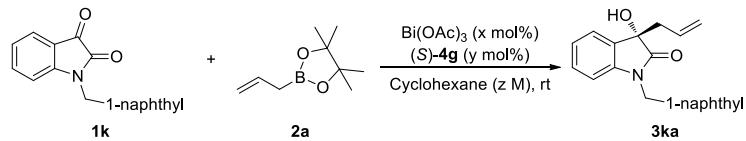


Entry	LA	t/h	Yield [%] ^b	<i>ee</i> [%] ^c
1	Bi(OTf) ₃	10	95	-2
2	BiCl ₃	32	92	42
3	InBr ₃	32	95	<i>rac</i>
4	Cu(OAc) ₂	70	14	<i>rac</i>
5	AgOTf	72	46	<i>rac</i>
6	Sc(OTf) ₃	70	82	19
7	Y(OTf) ₃	70	51	10
8	Yb(OTf) ₃	70	45	13
9	La(OTf) ₃	70	57	9

^aThe reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), Lewis Acid (2 mol%), and (*S*)-**4g** (2 mol%) in 0.5

mL cyclohexane at room temperature. ^bYield of isolated products. ^cDetermined by HPLC analysis.

Table S3. Concentrations and LA/CPA ratios investigated.^a

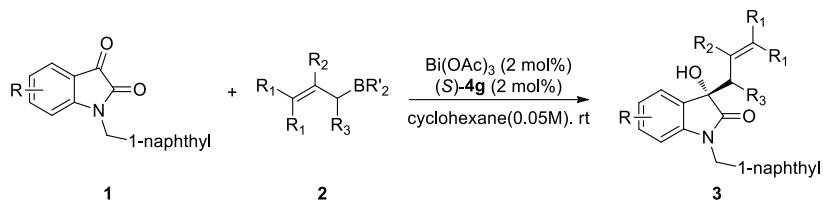


Entry	x	y	z	t/h	Yield [%] ^b	ee [%] ^c
1	2	2	0.2	11	86	90
2	2	2	0.1	25	92	82
3	2	2	0.05	12	93	94
4	2	2	0.025	25	91	82
5	2	3	0.05	20	75	91
6	2	4	0.05	20	89	89

^aThe reactions were carried out with **1k** (0.1 mmol), **2a** (0.12 mmol), Bi(OAc)₃, and (*S*)-**4g** in cyclohexane at room temperature.

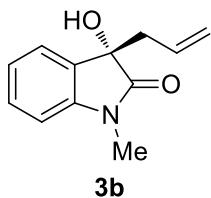
^bYield of isolated products. ^cDetermined by HPLC analysis.

3. General procedure for asymmetric allylation of isatins with allylboronates.

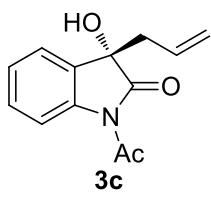


To an oven-dried 10 mL Schrek tube with magnetic stirring bar were added isatins **1** (0.1 mmol), Bi(OAc)_3 (2 mol%) and chiral phosphoric acid catalyst *(S)*-**4g** (2 mol%). Argon gas was pumped three times, dry cyclohexane (2.0 mL) and allylboronates **2** (0.12 mmol) were added in order. After the reaction was stirred at room temperature until completed, the crude mixture was direct purified by silica gel flash chromatography (ethyl acetate/petroleum ether) to afford the product **3**.

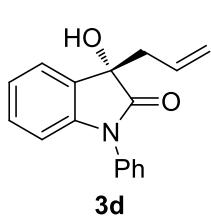
4. Characterization data of products **3**.

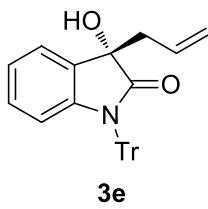


(S)-3-allyl-3-hydroxy-1-methylindolin-2-one (3b): White solid, 19.7 mg, 97% yield, 40% ee; $[\alpha]_D^{27} = -28.4$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 5.73-5.62 (m, 1H), 5.18 - 5.04 (m, 2H), 3.19 (s, 3H), 2.77 (s, 1H), 2.73 (dd, $J = 13.5, 6.5$ Hz, 1H), 2.60 (dd, $J = 13.4, 8.3$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.77, 143.25, 130.50, 129.66, 124.09, 123.05, 120.38, 108.38, 75.86, 42.90, 26.16; HPLC: Daicel Chiraldak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 8.5$ min (minor) and $t_R = 10.8$ min (major).

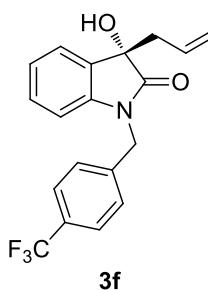


(S)-1-acetyl-3-allyl-3-hydroxyindolin-2-one (3c): White solid, 19.2 mg, 83% yield, 23% ee; $[\alpha]_D^{27} = -9.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.3$ Hz, 1H), 7.43 (d, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 7.25 (t, $J = 7.1$ Hz, 1H), 5.59 - 5.46 (m, 1H), 5.17 - 5.06 (m, 2H), 3.16 (br, 1H), 2.74 (dd, $J = 13.3, 6.2$ Hz, 1H), 2.65 (dd, $J = 13.6, 8.8$ Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.61, 170.63, 139.54, 130.20, 129.68, 128.73, 125.69, 123.74, 121.27, 116.73, 75.93, 43.77, 26.51; HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{NNaO}_3$ [$\text{M}+\text{Na}$] $^+$: 254.0793; found: 254.0780; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 9:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 6.6$ min (minor) and $t_R = 7.1$ min (major).

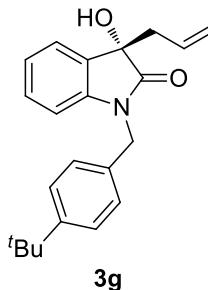




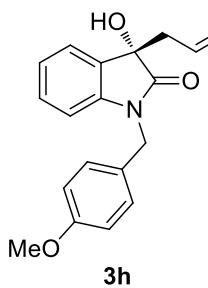
(S)-3-allyl-3-hydroxy-1-tritylindolin-2-one (3e): White solid, 34.0 mg, 79% yield, 29% *ee*; $[\alpha]_D^{27} = -25.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.46 - 7.38 (m, 6H), 7.34 (d, $J = 7.3$ Hz, 1H), 7.30 - 7.16 (m, 9H), 6.96 (t, $J = 7.2$ Hz, 1H), 6.91 (td, $J = 7.8, 1.6$ Hz, 1H), 6.29 (d, $J = 8.0$ Hz, 1H), 5.74-5.64 (m, 1H), 5.24 - 5.13 (m, 2H), 2.79 (dd, $J = 13.2, 6.3$ Hz, 1H), 2.70 (dd, $J = 13.2, 8.5$ Hz, 1H), 2.65 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.84, 142.99, 141.78, 130.92, 129.88, 129.35, 128.09, 127.69, 126.98, 123.34, 122.59, 120.43, 116.16, 109.99, 75.59, 74.56, 44.14; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 6.7$ min (major) and $t_R = 11.9$ min (minor).



(S)-3-allyl-3-hydroxy-1-(4-(trifluoromethyl)benzyl)indolin-2-one (3f): White solid, 34.0 mg, 98% yield, 45% *ee*; $[\alpha]_D^{27} = -3.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.9$ Hz, 2H), 7.41 (dd, $J = 12.7, 7.7$ Hz, 3H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.10 (t, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 7.9$ Hz, 1H), 5.61 (dq, $J = 16.4, 9.0$ Hz, 1H), 5.24 - 5.02 (m, 3H), 4.79 (d, $J = 16.1$ Hz, 1H), 3.15 (d, $J = 22.1$ Hz, 1H), 2.83 (dd, $J = 13.3, 6.2$ Hz, 1H), 2.71 (dd, $J = 13.3, 8.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.06, 142.01, 139.48, 130.42, 130.21, 129.89, 129.73, 129.60, 127.52, 125.79 (q, $J = 3.8$ Hz), 125.31, 124.37, 123.48, 122.61, 120.76, 109.21, 76.04, 43.38, 43.01; ^{19}F NMR (376 MHz, CDCl_3) δ -62.51; HRMS (ESI): *m/z* calcd for $\text{C}_{19}\text{H}_{16}\text{F}_3\text{NNaO}_2$ [M+Na] $^+$: 370.1031; found: 370.1014; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 7.5$ min (minor) and $t_R = 8.7$ min (major).

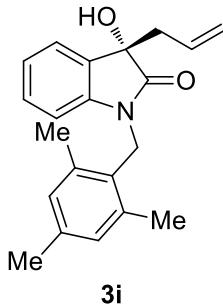


(S)-3-allyl-1-(4-(tert-butyl)benzyl)-3-hydroxyindolin-2-one (3g): White solid, 32.5 mg, 97% yield, 78% *ee*; $[\alpha]_D^{27} = -9.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.3$ Hz, 1H), 7.32 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 8.3$ Hz, 3H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 5.74 - 5.57 (m, 1H), 5.21 - 5.06 (m, 2H), 4.84 (dd, $J = 110.2, 15.6$ Hz, 2H), 2.96 (s, 1H), 2.80 (dd, $J = 13.3, 6.2$ Hz, 1H), 2.68 (dd, $J = 13.3, 8.4$ Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.84, 150.61, 142.59, 132.37, 130.57, 129.67, 129.59, 127.03, 125.66, 124.12, 123.01, 120.56, 109.55, 75.91, 43.50, 43.05, 34.51, 31.32; HRMS (ESI): *m/z* calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_2$ [M+H] $^+$: 336.1964; found: 336.1950; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 6.6$ min (minor) and $t_R = 7.4$ min (major).

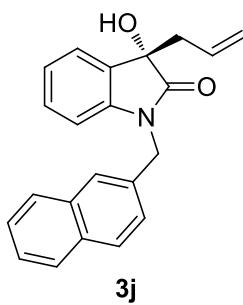


(S)-3-allyl-3-hydroxy-1-(4-methoxybenzyl)indolin-2-one (3h): White solid, 27.8 mg, 90% yield, 80% *ee*; $[\alpha]_D^{27} = -11.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.3$ Hz, 1H), 7.22-7.18 (d, $J = 6.5$ Hz, 3H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 6.6$ Hz, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 5.61 (dq, $J = 16.8, 8.5$ Hz, 1H), 5.21 - 5.02 (m, 2H), 4.94 (d, $J = 15.5$ Hz, 1H), 4.65 (d, $J = 15.4$ Hz, 1H), 3.76 (s, 3H), 3.35 (s, 1H), 2.81 (dd, $J = 13.5, 6.2$ Hz, 1H), 2.69 (dd, $J = 13.4, 8.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.82, 159.07, 142.46, 130.56, 129.66, 129.59, 128.71, 127.46, 124.12, 123.04, 120.56, 114.12, 109.51, 75.93, 55.26, 43.30, 43.04; HRMS (ESI): *m/z* calcd for $\text{C}_{19}\text{H}_{19}\text{NNaO}_3$ [M+Na] $^+$: 332.1263;

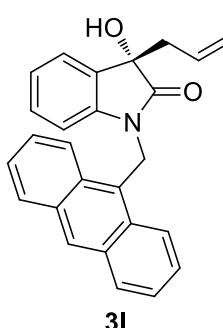
found: 332.1250; HPLC: Daicel Chiraldak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 10.0 min (minor) and t_R = 17.0 min (major).



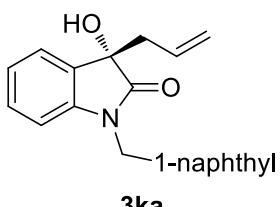
(*S*)-3-allyl-3-hydroxy-1-(2,4,6-trimethylbenzyl)indolin-2-one (3i): White solid, 28.9 mg, 90% yield, 85% ee; $[\alpha]_D^{27} = -7.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.3$ Hz, 1H), 7.08 (t, $J = 7.8$ Hz, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.86 (s, 2H), 6.39 (d, $J = 7.8$ Hz, 1H), 5.88 - 5.63 (m, 1H), 5.21 - 5.09 (m, 2H), 4.97 (d, $J = 15.3$ Hz, 2H), 4.86 (d, $J = 15.3$ Hz, 2H), 3.21 (s, 1H), 2.77 (dd, $J = 13.5, 6.3$ Hz, 1H), 2.63 (dd, $J = 13.5, 8.4$ Hz, 2H), 2.32 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.53, 142.78, 137.49, 137.30, 130.63, 129.80, 129.72, 129.63, 127.89, 124.05, 122.70, 120.57, 109.89, 75.26, 42.98, 39.79, 20.91, 20.42; HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_2$ [$\text{M}+\text{H}$] $^+$: 322.1807; found: 322.1789; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 5.6 min (minor) and t_R = 6.4 min (major).



(*S*)-3-allyl-3-hydroxy-1-(naphthalen-2-ylmethyl)indolin-2-one (3j): White solid, 28.0 mg, 85% yield, 87% ee; $[\alpha]_D^{27} = +8.4$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.79 (q, $J = 8.5, 6.9$ Hz, 3H), 7.73 (s, 1H), 7.50 - 7.44 (m, 2H), 7.40 (t, $J = 9.3$ Hz, 2H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.73 (d, $J = 7.8$ Hz, 1H), 5.70-5.59 (m, 1H), 5.26 - 5.03 (m, 3H), 4.86 (d, $J = 15.8$ Hz, 1H), 3.16 (s, 1H), 2.86 (dd, $J = 13.3, 6.2$ Hz, 1H), 2.75 (dd, $J = 13.3, 8.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.94, 142.45, 133.25, 132.89, 132.84, 130.57, 129.67, 129.60, 128.75, 127.74, 127.72, 126.37, 126.14, 126.08, 125.20, 124.13, 123.17, 120.71, 109.59, 76.05, 44.09, 43.13; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{19}\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 352.1313; found: 352.1297; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 10.2 min (minor) and t_R = 12.9 min (major).

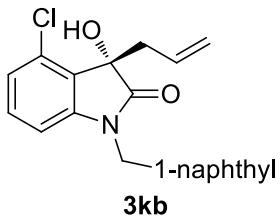


(*S*)-3-allyl-1-(anthracen-9-ylmethyl)-3-hydroxyindolin-2-one (3l): White solid, 20.0 mg, 53% yield, 87% ee; $[\alpha]_D^{27} = +113.0$ ($c = 0.2$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.42 (d, $J = 8.9$ Hz, 2H), 8.05 (d, $J = 8.4$ Hz, 2H), 7.63 - 7.54 (m, 2H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 6.8$ Hz, 1H), 6.85 (t, $J = 7.5$ Hz, 1H), 6.79 (t, $J = 7.8$ Hz, 1H), 6.28 (d, $J = 7.8$ Hz, 1H), 6.06 (d, $J = 15.5$ Hz, 1H), 5.82 - 5.64 (m, 2H), 5.13 (dd, $J = 24.0, 13.6$ Hz, 2H), 2.85 (s, 1H), 2.73 (dd, $J = 13.6, 6.5$ Hz, 1H), 2.61 (dd, $J = 13.6, 8.3$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.72, 142.51, 131.37, 130.84, 130.41, 129.73, 129.62, 129.51, 129.01, 126.89, 125.69, 125.13, 123.80, 123.70, 122.66, 120.69, 110.52, 75.53, 43.12, 37.71; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{21}\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 402.1470; found: 402.1457; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 9.2 min (minor) and t_R = 12.0 min (major).



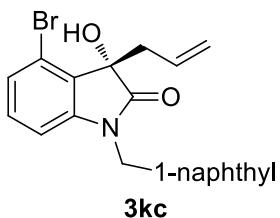
(*S*)-3-allyl-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3ka): White solid, 30.6 mg, 93% yield, 94% ee; $[\alpha]_D^{27} = 1.2$ ($c = 0.5$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.3$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz,

1H), 7.75 (d, J = 8.1 Hz, 1H), 7.52 (dt, J = 18.5, 7.1 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.10 (t, J = 7.7 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 5.74 - 5.59 (m, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.21 - 5.00 (m, 3H), 4.04 (br, 1H), 2.86 (dd, J = 13.3, 6.3 Hz, 1H), 2.75 (dd, J = 13.3, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 142.8, 133.9, 131.0, 130.6, 130.2, 129.9, 129.6, 129.0, 128.4, 126.6, 126.0, 125.3, 124.6, 124.2, 123.2, 122.9, 120.7, 109.9, 76.2, 43.0, 42.1; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{19}\text{NNaO}_2$ [M+Na] $^+$: 352.1313; found: 352.1313; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 9.6 min (major) and t_R = 10.9 min (minor).



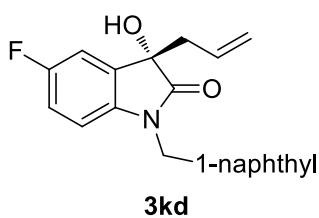
(S)-3-allyl-4-chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

(3kb): White solid, 32.7 mg, 90% yield, 92% ee; $[\alpha]_D^{27} = +32.8$ (c = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.62 - 7.51 (m, 3H), 7.36 (t, J = 7.6 Hz, 1H), 7.26 (dd, J = 7.1, 1.2 Hz, 2H), 7.08 (t, J = 8.0 Hz, 1H), 7.00 (dd, J = 8.2, 0.9 Hz, 1H), 6.55 (dd, J = 7.8, 0.9 Hz, 1H), 5.58 - 5.43 (m, 2H), 5.23 - 5.13 (m, 2H), 5.04 (dd, J = 10.1, 1.8 Hz, 1H), 3.25 (dd, J = 12.9, 6.6 Hz, 1H), 3.03 (br, 1H), 2.98 (dd, J = 12.9, 8.3 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 144.8, 133.9, 131.5, 130.9, 130.9, 130.1, 129.7, 129.0, 128.5, 126.7, 126.1, 125.8, 125.2, 124.5, 124.2, 122.7, 120.8, 108.4, 42.2, 40.4; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{ClNNaO}_2$ [M+Na] $^+$: 386.0924; found: 386.0923; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 12.6 min (major) and t_R = 14.6 min (minor).



(S)-3-allyl-4-bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

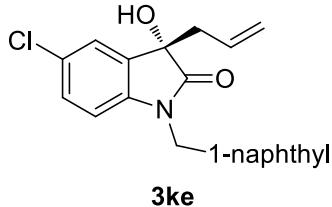
e (3kc): White solid, 40.3 mg, 99% yield, 91% ee; $[\alpha]_D^{27} = +23.2$ (c = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.56 (dt, J = 18.6, 7.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 6.4 Hz, 3H), 7.17 (d, J = 8.2 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H), 5.54 (d, J = 16.3 Hz, 1H), 5.55 - 5.40 (m, 1H), 5.18 (dd, J = 16.7, 8.2 Hz, 2H), 5.04 (d, J = 10.1 Hz, 1H), 3.32 (dd, J = 12.9, 6.6 Hz, 1H), 3.02 (br, 1H), 2.96 (dd, J = 12.9, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.7, 145.0, 133.9, 131.1, 130.9, 130.0, 129.7, 129.0, 128.6, 127.5, 127.2, 126.7, 126.1, 125.2, 124.5, 122.7, 120.8, 119.4, 108.9, 77.8, 77.2, 42.2, 40.2; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{BrNNaO}_2$ [M+Na] $^+$: 430.0419, 432.0398; found: 430.0418, 432.0398; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 13.6 min (major) and t_R = 16.5 min (minor).



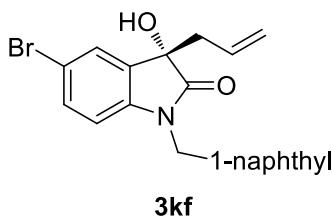
(S)-3-allyl-5-fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one

(3kd): White solid, 33.3 mg, 96% yield, 90% ee; $[\alpha]_D^{27} = -9.2$ (c = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.50 (dt, J = 15.2, 7.0 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.27 - 7.18 (m, 1H), 7.12 (dd, J = 7.7, 2.6 Hz, 1H), 6.78 (td, J = 8.9, 2.6 Hz, 1H), 6.52 (dd, J = 8.6, 4.1 Hz, 1H), 5.63 (td, J = 16.8, 9.2 Hz, 1H), 5.49 (d, J = 16.3 Hz, 1H), 5.17 - 5.01 (m, 3H), 3.84 (s, 1H), 2.80 (dd, J = 13.4, 6.4 Hz, 1H), 2.68 (dd, J = 13.4, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.2, 159.5 (d, J = 242.3 Hz), 138.5, 133.9, 131.5 (d, J = 7.8 Hz), 130.9, 130.1, 129.9, 129.0, 128.6, 126.7,

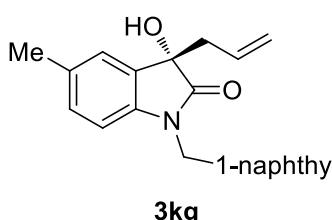
126.1, 125.2, 124.7, 122.8, 121.1, 115.8 (d, J = 23.5 Hz), 112.4 (d, J = 25.0 Hz), 110.6 (d, J = 8.0 Hz), 76.3, 43.0, 42.3; ^{19}F NMR (376 MHz, CDCl_3) δ -119.29; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{FNNaO}_2$ [$\text{M}+\text{Na}]^+$: 370.1219; found: 370.1218; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 9.2 min (major) and t_{R} = 10.0 min (minor).



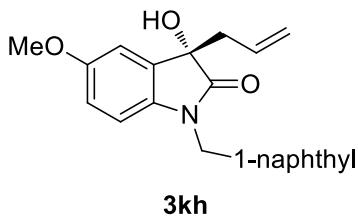
(S)-3-allyl-5-chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3ke): White solid, 34.1 mg, 94% yield, 87.5% *ee*; $[\alpha]_D^{27} = +2.0$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.62 - 7.50 (m, 2H), 7.39 (d, J = 2.0 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.26 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 8.4, 2.2 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 5.76-5.66 (m, 1H), 5.55 (d, J = 16.3 Hz, 1H), 5.26 - 5.09 (m, 3H), 3.13 (s, 1H), 2.82 (dd, J = 13.4, 6.3 Hz, 1H), 2.70 (dd, J = 13.4, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.8, 141.3, 133.9, 131.4, 130.9, 130.0, 129.7, 129.6, 129.0, 128.7, 128.6, 126.7, 126.1, 125.2, 124.7, 124.7, 122.8, 121.3, 110.9, 76.0, 43.0, 42.3; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{ClNNaO}_2$ [$\text{M}+\text{Na}]^+$: 386.0924; found: 386.0922; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 6.4 min (minor) and t_{R} = 8.6 min (major).



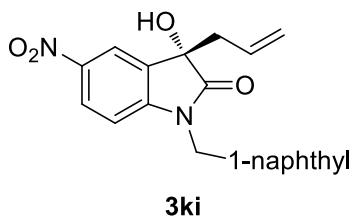
(S)-3-allyl-5-bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kf): White solid, 35.0 mg, 86% yield, 92% *ee*; $[\alpha]_D^{27} = +6.8$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.63 - 7.51 (m, 3H), 7.38 (t, J = 7.7 Hz, 1H), 7.32 - 7.22 (m, 2H), 6.54 (d, J = 8.4 Hz, 1H), 5.76-5.65 (m, 1H), 5.54 (d, J = 16.3 Hz, 1H), 5.30 - 5.09 (m, 3H), 3.40 (s, 1H), 2.83 (dd, J = 13.4, 6.3 Hz, 1H), 2.72 (dd, J = 13.4, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.6, 141.8, 133.9, 132.5, 131.7, 130.9, 130.0, 129.7, 129.0, 128.6, 127.5, 126.7, 126.1, 125.2, 124.6, 122.8, 121.3, 116.0, 111.4, 75.9, 43.0, 42.2; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{BrNNaO}_2$ [$\text{M}+\text{Na}]^+$: 430.0419, 432.0398; found: 430.0418, 432.0397; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 6.4 min (minor) and t_{R} = 9.1 min (major).



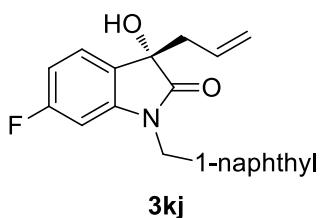
(S)-3-allyl-3-hydroxy-5-methyl-1-(naphthalen-1-ylmethyl)indolin-2-one (3kg): White solid, 28.8 mg, 84% yield, 87% *ee*; $[\alpha]_D^{27} = -1.4$ ($c = 1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.3 Hz, 1H), 7.87 (dd, J = 7.7, 1.5 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.57-7.49 (m, 2H), 7.34 (dd, J = 8.1, 7.1 Hz, 1H), 7.27 (d, J = 5.9 Hz, 1H), 7.23 (d, J = 1.6 Hz, 1H), 6.93 (d, J = 8.9 Hz, 1H), 6.53 (d, J = 7.9 Hz, 1H), 5.74-5.65 (m, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.24 - 5.05 (m, 3H), 3.21 (s, 1H), 2.81 (dd, J = 13.3, 6.3 Hz, 1H), 2.71 (dd, J = 13.3, 8.4 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.9, 140.4, 133.8, 132.8, 131.0, 130.6, 130.3, 129.9, 129.7, 128.9, 128.3, 126.5, 126.0, 125.2, 124.9, 124.7, 122.9, 120.7, 109.7, 76.0, 43.1, 42.1, 21.1; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}_2$ [$\text{M}+\text{Na}]^+$: 366.1470; found: 366.1468; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 9.0 min (major) and t_{R} = 10.1 min (minor).



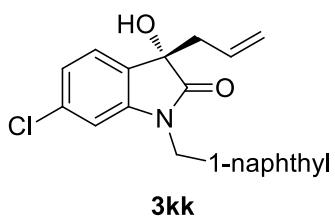
(S)-3-allyl-3-hydroxy-5-methoxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kh): White solid, 33.4 mg, 93% yield, 86% *ee*; $[\alpha]_D^{27} = +10.0$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.55 (dt, $J = 15.0, 7.2$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.1$ Hz, 1H), 7.03 (s, 1H), 6.67 (d, $J = 8.3$ Hz, 1H), 6.57 (d, $J = 8.6$ Hz, 1H), 5.71 (dq, $J = 16.7, 8.9$ Hz, 1H), 5.54 (d, $J = 16.2$ Hz, 1H), 5.24 - 5.07 (m, 3H), 3.75 (s, 3H), 3.25 (s, 1H), 2.83 (dd, $J = 13.5, 6.3$ Hz, 1H), 2.72 (dd, $J = 13.4, 8.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.7, 156.4, 136.1, 133.9, 131.1, 131.0, 130.5, 130.4, 128.9, 128.4, 126.6, 126.0, 125.2, 124.8, 122.9, 120.8, 114.2, 111.3, 110.4, 76.3, 55.8, 43.2, 42.3; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}_3$ [$\text{M}+\text{Na}]^+$: 382.1419; found: 382.1418; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 13.2$ min (major) and $t_R = 14.5$ min (minor).



(S)-3-allyl-3-hydroxy-1-(naphthalen-1-ylmethyl)-5-nitroindolin-2-one (3ki): White solid, 34.2 mg, 91.5% yield, 78% *ee*; $[\alpha]_D^{27} = -3.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 2.3$ Hz, 1H), 8.09 (dd, $J = 8.7, 2.3$ Hz, 1H), 8.02 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 7.2$ Hz, 1H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.56 (dqd, $J = 8.1, 6.9, 1.5$ Hz, 2H), 7.37 (dd, $J = 8.2, 7.1$ Hz, 1H), 7.24 (d, $J = 6.2$ Hz, 2H), 6.73 (d, $J = 8.7$ Hz, 1H), 5.75-5.64 (m, 1H), 5.58 (d, $J = 16.3$ Hz, 1H), 5.25 - 5.14 (m, 3H), 3.21 (s, 1H), 2.85 (dd, $J = 13.4, 6.4$ Hz, 1H), 2.72 (dd, $J = 13.5, 8.4$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 148.4, 143.8, 134.0, 130.8, 130.6, 129.3, 129.2, 129.1, 129.0, 126.9, 126.7, 126.3, 125.2, 124.8, 122.6, 122.1, 120.1, 109.7, 75.4, 42.9, 42.5; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{NaO}_4$ [$\text{M}+\text{Na}]^+$: 397.1164; found: 397.1164; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 13.7$ min (minor) and $t_R = 14.6$ min (major).

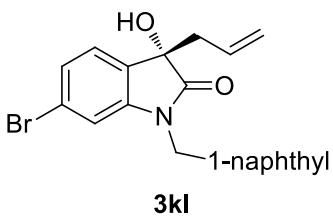


(S)-3-allyl-6-fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kj): White solid, 32.3 mg, 93% yield, 89% *ee*; $[\alpha]_D^{27} = -16.0$ ($c = 0.2$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.90 (dd, $J = 8.3, 1.4$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.63 - 7.50 (m, 2H), 7.43 - 7.33 (m, 2H), 7.30 (dd, $J = 7.2, 1.2$ Hz, 1H), 6.73 (ddd, $J = 9.3, 8.2, 2.3$ Hz, 1H), 6.42 (dd, $J = 9.0, 2.3$ Hz, 1H), 5.74-5.63 (m, 1H), 5.55 (d, $J = 16.3$ Hz, 1H), 5.22 - 5.08 (m, 3H), 3.27 (s, 1H), 2.83 (dd, $J = 13.3, 6.3$ Hz, 1H), 2.71 (dd, $J = 13.3, 8.4$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.3, 164.9, 162.5, 144.4 (d, $J = 11.1$ Hz), 132.4 (d, $J = 300.8$ Hz), 130.2, 129.7, 129.0, 128.7, 126.7, 126.1, 125.4 (d, $J = 9.9$ Hz), 125.2, 125.1 (d, $J = 2.5$ Hz), 124.8, 122.8, 121.0, 109.3 (d, $J = 22.0$ Hz), 98.8 (d, $J = 28.2$ Hz), 75.6, 43.0, 42.4; ^{19}F NMR (376 MHz, CDCl_3) δ 138.79; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{FNNaO}_2$ [$\text{M}+\text{Na}]^+$: 370.1219; found: 370.1218; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 6.3$ min (minor) and $t_R = 8.2$ min (major).

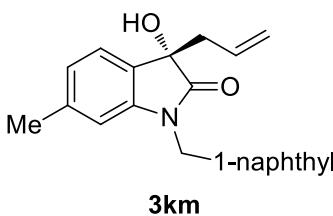


(S)-3-allyl-6-chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kk): White solid, 34.8 mg, 96% yield, 87% *ee*; $[\alpha]_D^{27} = -11.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 1H), 7.54 (p, $J =$

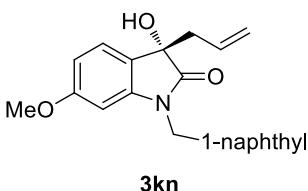
6.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 6.65 (s, 1H), 5.64 (dq, J = 16.9, 8.5 Hz, 1H), 5.52 (d, J = 16.4 Hz, 1H), 5.20 - 4.97 (m, 3H), 3.91 (s, 1H), 2.83 (dd, J = 13.4, 6.3 Hz, 1H), 2.71 (dd, J = 13.4, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.4, 144.0, 135.4, 133.9, 130.9, 130.2, 129.6, 129.0, 128.6, 128.2, 126.7, 126.2, 125.3, 125.2, 124.5, 123.2, 122.8, 121.0, 110.5, 75.9, 42.9, 42.3; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{ClNNaO}_2$ [$\text{M}+\text{Na}]^+$: 386.0924; found: 386.0923; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 6.2 min (minor) and t_{R} = 7.8 min (major).



(S)-3-allyl-6-bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kl): White solid, 37.9 mg, 93% yield, 89.5% *ee*; $[\alpha]_D^{27} = -9.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.56 (p, J = 6.8 Hz, 2H), 7.38 (t, J = 7.7 Hz, 1H), 7.30 - 7.22 (m, 2H), 7.19 (d, J = 7.9 Hz, 1H), 6.81 (s, 1H), 5.65 (td, J = 17.0, 9.0 Hz, 1H), 5.53 (d, J = 16.4 Hz, 1H), 5.19 - 5.03 (m, 3H), 3.87 (s, 1H), 2.83 (dd, J = 13.4, 6.3 Hz, 1H), 2.71 (dd, J = 13.4, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.3, 144.1, 133.9, 130.8, 130.2, 129.6, 129.0, 128.8, 128.6, 126.7, 126.2, 126.1, 125.6, 125.3, 124.4, 123.3, 122.8, 121.1, 113.3, 75.9, 42.9, 42.3; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{BrNNaO}_2$ [$\text{M}+\text{Na}]^+$: 430.0419, 432.0398; found: 430.0418, 432.0401; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 6.3 min (minor) and t_{R} = 7.9 min (major).

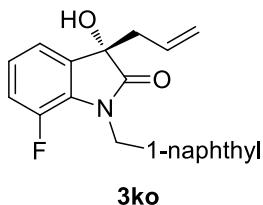


(S)-3-allyl-3-hydroxy-6-methyl-1-(naphthalen-1-ylmethyl)indolin-2-one (3km): White solid, 34.0 mg, 99% yield, 89.5% *ee*; $[\alpha]_D^{27} = -3.6$ ($c = 1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.54 (dq, J = 14.5, 7.0 Hz, 2H), 7.38 - 7.21 (m, 3H), 6.85 (d, J = 7.5 Hz, 1H), 6.47 (s, 1H), 5.68 (td, J = 16.7, 8.4 Hz, 1H), 5.52 (d, J = 16.4 Hz, 1H), 5.20 - 5.05 (m, 3H), 3.66 (s, 1H), 2.84 (dd, J = 13.3, 6.3 Hz, 1H), 2.73 (dd, J = 13.3, 8.4 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.7, 142.9, 140.0, 133.8, 130.9, 130.8, 130.3, 129.0, 128.3, 126.9, 126.6, 126.0, 125.3, 124.2, 124.0, 123.8, 122.9, 120.6, 110.6, 76.1, 43.0, 42.0, 21.9; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}_2$ [$\text{M}+\text{Na}]^+$: 366.1470; found: 366.1469; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_{R} = 8.6 min (minor) and t_{R} = 10.0 min (major).

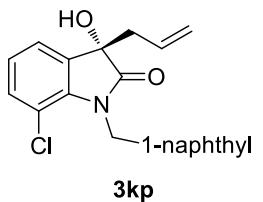


(S)-3-allyl-3-hydroxy-6-methoxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kn): White solid, 28.4 mg, 79% yield, 89.5% *ee*; $[\alpha]_D^{27} = -5.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.62 - 7.48 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 6.54 (dd, J = 8.2, 2.3 Hz, 1H), 6.26 (d, J = 2.2 Hz, 1H), 5.75-5.65 (m, 1H), 5.53 (d, J = 16.2 Hz, 1H), 5.21 - 5.06 (m, 3H), 3.65 (s, 3H), 3.14 (s, 1H), 2.83 (dd, J = 13.3, 6.3 Hz, 1H), 2.71 (dd, J = 13.3, 8.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.5, 161.2, 144.3, 133.9, 131.0, 130.8, 130.3,

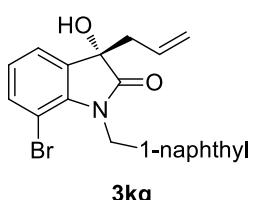
128.9, 128.5, 126.6, 126.0, 125.2, 124.9, 124.8, 122.9, 121.6, 120.6, 106.8, 97.9, 75.7, 55.4, 43.1, 42.2; HRMS (ESI): *m/z* calcd for C₂₃H₂₁NNaO₃ [M+Na]⁺: 382.1419; found: 382.1417; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 12.1 min (major) and t_R = 13.7 min (minor).



(S)-3-allyl-7-fluoro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3ko): White solid, 31.9 mg, 92% yield, 90.5% *ee*; $[\alpha]_D^{27} = -20.8$ (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.62 - 7.50 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.04 (ddd, *J* = 8.4, 7.3, 4.4 Hz, 1H), 6.94 (ddd, *J* = 11.3, 8.4, 1.1 Hz, 1H), 5.74 - 5.61 (m, 1H), 5.62 (d, *J* = 16.8 Hz, 1H), 5.44 (d, *J* = 16.4 Hz, 1H), 5.17 (d, *J* = 5.5 Hz, 1H), 5.14 (s, 1H), 3.90 (s, 1H), 2.87 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.78 (dd, *J* = 13.3, 8.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 178.12, 147.64 (d, *J* = 245.7 Hz), 133.73, 132.67 (d, *J* = 2.7 Hz), 131.45 (d, *J* = 1.1 Hz), 130.63, 130.18, 129.27 (d, *J* = 8.7 Hz), 128.89, 127.93, 126.36, 125.88, 125.31, 124.15 (d, *J* = 6.3 Hz), 122.67, 122.65, 121.11, 120.19 (d, *J* = 3.3 Hz), 117.98, 117.79, 76.26 (d, *J* = 2.4 Hz), 43.17, 43.16, 43.13; ¹⁹F NMR (376 MHz, CDCl₃) δ -134.06 (d, *J* = 7.5 Hz); HRMS (ESI): *m/z* calcd for C₂₂H₁₈FNNaO₂ [M+Na]⁺: 370.1219; found: 370.1219; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 6.4 min (minor) and t_R = 9.4 min (major).

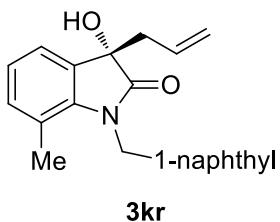


(S)-3-allyl-7-chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kp): White solid, 35.2 mg, 97% yield, 92% *ee*; $[\alpha]_D^{27} = -44.0$ (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 6.8 Hz, 1H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.10 - 7.02 (m, 2H), 5.80 (d, *J* = 17.0 Hz, 1H), 5.76 - 5.63 (m, 2H), 5.25 - 5.14 (m, 2H), 3.37 (s, 1H), 2.86 (dd, *J* = 13.2, 6.3 Hz, 1H), 2.77 (dd, *J* = 13.3, 8.5 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 178.48, 138.78, 133.74, 132.54, 132.25, 132.08, 130.22, 130.14, 128.90, 127.59, 126.33, 125.85, 125.39, 124.18, 122.86, 122.36, 121.69, 121.27, 116.19, 75.47, 43.32, 43.00; HRMS (ESI): *m/z* calcd for C₂₂H₁₈ClNNaO₂ [M+Na]⁺: 386.0924; found: 386.0922; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 9.2 min (major) and t_R = 9.8 min (minor).

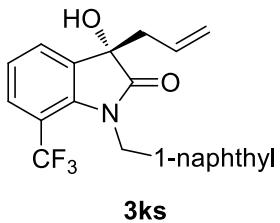


(S)-3-allyl-7-bromo-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kq): White solid, 35.8 mg, 88% yield, 81% *ee*; $[\alpha]_D^{27} = -34.4$ (c = 0.5, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.61-7.52 (m, 2H), 7.42 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.38 - 7.29 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 5.83 (d, *J* = 17.1 Hz, 1H), 5.79 - 5.62 (m, 2H), 5.23 - 5.14 (m, 2H), 3.59 (s, 1H), 2.86 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.78 (dd, *J* = 13.2, 8.5 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 178.78, 140.17, 135.60, 133.74, 132.92, 132.05, 130.16, 128.91, 127.58, 126.35, 125.86, 125.44, 124.57, 123.44, 122.40, 121.81, 121.30, 103.17, 75.43, 43.31, 42.86; HRMS (ESI): *m/z* calcd for C₂₂H₁₈BrNNaO₂ [M+Na]⁺: 430.0419, 432.0398; found: 430.0418, 432.0398; HPLC: Daicel Chiralpak

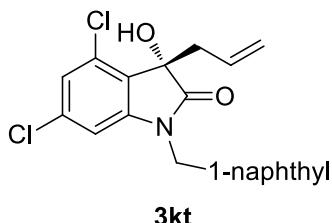
AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 9.3 min (major) and t_R = 10.3 min (minor).



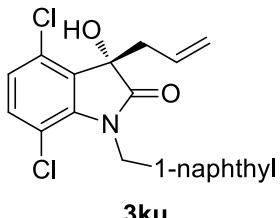
(S)-3-allyl-3-hydroxy-7-methyl-1-(naphthalen-1-ylmethyl)indolin-2-on e (3kr): White solid, 28.1 mg, 82% yield, 96% *ee*; $[\alpha]_D^{27} = -18.0$ ($c = 0.2$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.6$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 8.2$ Hz, 1H), 7.62 - 7.50 (m, 2H), 7.36 - 7.27 (t, $J = 9.2$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 6.6$ Hz, 1H), 5.76 - 5.59 (m, 2H), 5.48 (d, $J = 17.3$ Hz, 1H), 5.18 (d, $J = 5.2$ Hz, 1H), 5.14 (s, 1H), 3.52 (s, 1H), 2.85 (dd, $J = 13.2, 6.3$ Hz, 1H), 2.78 (dd, $J = 13.2, 8.5$ Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.04, 140.59, 133.79, 133.70, 131.97, 130.81, 130.51, 130.05, 128.99, 127.81, 126.52, 125.99, 125.58, 123.34, 122.20, 122.18, 122.05, 120.74, 120.43, 75.38, 43.33, 43.13, 18.03; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 366.1470; found: 366.1469; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 9.8 min (major) and t_R = 11.8 min (minor).



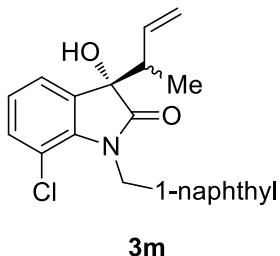
(S)-3-allyl-3-hydroxy-1-(naphthalen-1-ylmethyl)-7-(trifluoromethyl)indolin-2-one (3ks): White solid, 39.3 mg, 99% yield, 78% *ee*; $[\alpha]_D^{27} = -31.2$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.3$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.60 - 7.55 (m, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 7.2$ Hz, 1H), 5.77 - 5.55 (m, 3H), 5.26 - 5.14 (m, 2H), 3.32 (s, 1H), 2.85 (dd, $J = 13.4, 6.3$ Hz, 1H), 2.76 (dd, $J = 13.4, 8.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.62, 140.83, 133.66, 132.68, 130.80, 130.40, 129.92, 128.92, 128.07, 127.82 (q, $J = 6.1$ Hz), 127.46, 126.29, 125.82, 125.18, 124.45, 122.92, 122.19, 121.74, 121.35, 121.01, 74.15, 43.67 (q, $J = 4.9$ Hz), 43.16; ^{19}F NMR (376 MHz, CDCl_3) δ -55.38; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{NO}_2$ [$\text{M}+\text{H}$] $^+$: 398.1368; found: 398.1358; HPLC: Daicel Chiraldak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 6.5 min (major) and t_R = 7.6 min (minor).



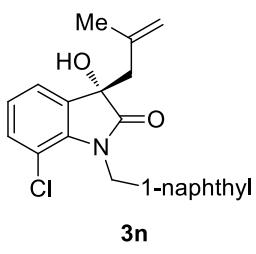
(S)-3-allyl-4,6-dichloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3kt): White solid, 30.2 mg, 76% yield, 94.5% *ee*; $[\alpha]_D^{27} = +21.6$ ($c = 0.5$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.2$ Hz, 1H), 7.91 (d, $J = 8.5$ Hz, 1H), 7.82 (d, $J = 8.3$ Hz, 1H), 7.57 (p, $J = 6.8$ Hz, 2H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.02 (s, 1H), 6.55 (s, 1H), 5.57 - 5.40 (m, 2H), 5.23 - 5.01 (m, 3H), 3.22 (dd, $J = 12.9, 6.8$ Hz, 1H), 3.16 (s, 1H), 2.96 (dd, $J = 12.9, 8.2$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.89, 145.60, 136.22, 133.89, 132.08, 130.74, 129.71, 129.09, 129.06, 128.76, 126.78, 126.23, 125.24, 124.29, 124.26, 123.89, 122.65, 121.21, 109.20, 42.45, 40.30; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 420.0534; found: 420.0533; HPLC: Daicel Chiraldak OD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 8.1 min (minor) and t_R = 26.5 min (major).



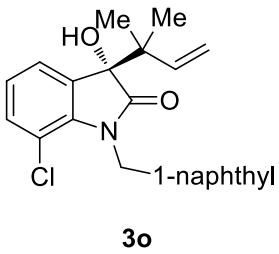
(S)-3-allyl-4,7-dichloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3ku): White solid, 39.3 mg, 99% yield, 92% *ee*; $[\alpha]_D^{27} = -9.6$ (*c* = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.58-7.50 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 5.78 (d, *J* = 17.0 Hz, 1H), 5.69 (d, *J* = 17.0 Hz, 1H), 5.57-5.47 (m, 1H), 5.19 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.30 (dd, *J* = 12.8, 6.8 Hz, 1H), 3.02 (s, 1H), 2.96 (dd, *J* = 12.9, 8.3 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.30, 140.59, 133.73, 133.27, 131.75, 130.40, 130.06, 129.80, 128.95, 128.20, 127.72, 126.43, 125.92, 125.34, 125.20, 122.28, 121.69, 121.33, 114.83, 43.12, 40.25; HRMS (ESI): *m/z* calcd for $\text{C}_{22}\text{H}_{17}\text{Cl}_2\text{NNaO}_2$ [$\text{M}+\text{H}]^+$: 420.0534; found: 420.0533; HPLC: Daicel Chiraldak IC, *n*-hexane/*i*-PrOH = 9:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 13.5 min (minor) and t_R = 14.6 min (major).



(S)-3-(but-3-en-2-yl)-7-chloro-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (3m): White solid, 30.2 mg, 80% yield, 1:1 dr, 90% *ee* and 75%; $[\alpha]_D^{27} = -59.6$ (*c* = 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.65 - 7.50 (m, 2H), 7.42 - 7.30 (m, 2H), 7.19 (ddd, *J* = 8.2, 3.9, 1.2 Hz, 1H), 7.11 (t, *J* = 7.1 Hz, 1H), 7.08 - 6.99 (m, 1H), 6.08 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 0.5H), 5.92 - 5.63 (m, 2.5H), 5.38 - 5.15 (m, 2H), 3.20 (s, 0.5H), 3.10 (s, 0.5H), 2.95 (h, *J* = 6.1, 5.5 Hz, 0.5H), 2.91 - 2.80 (m, 0.5H), 1.13 (d, *J* = 6.9 Hz, 1.5H), 1.01 (d, *J* = 6.8 Hz, 1.5H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.39, 178.23, 139.54, 139.32, 136.77, 136.33, 133.70, 132.29, 132.23, 131.72, 131.43, 130.20, 128.91, 127.58, 127.54, 126.33, 126.31, 125.86, 125.82, 125.42, 125.40, 124.06, 123.91, 123.53, 122.86, 122.37, 121.83, 121.71, 119.75, 118.53, 116.07, 116.01, 77.62, 47.31, 45.08, 43.17, 43.05, 14.40, 13.31; HRMS (ESI): *m/z* calcd for $\text{C}_{23}\text{H}_{21}\text{ClNO}_2$ [$\text{M}+\text{H}]^+$: 378.1261; found: 378.1256; HPLC: Daicel Chiraldak IF, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 8.1 min (minor) and t_R = 11.6 min (major), t_R = 8.8 min (minor) and t_R = 10.2 min (major).



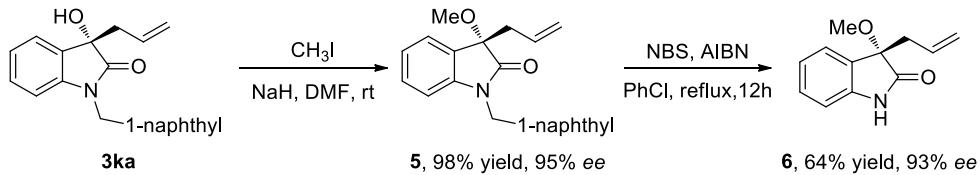
(S)-7-chloro-3-hydroxy-3-(2-methylallyl)-1-(naphthalen-1-ylmethyl)indolin-2-one (3n): White solid, 35.4 mg, 94% yield, 75% *ee*; $[\alpha]_D^{27} = +21.2$ (*c* = 0.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.60-7.52 (m, 2H), 7.40 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.36 - 7.28 (m, 1H), 7.17 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.10 - 7.01 (m, 2H), 5.75 (dd, *J* = 44.0, 17.2 Hz, 2H), 4.89 (s, 1H), 4.70 (s, 1H), 3.42 (s, 1H), 2.82 (dd, *J* = 19.2, 12.8 Hz, 2H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.67, 139.04, 138.53, 133.71, 132.74, 132.28, 132.12, 130.22, 128.90, 127.57, 126.31, 125.83, 125.35, 124.03, 123.19, 122.37, 121.75, 116.99, 116.14, 75.99, 46.41, 43.05, 24.24; HRMS (ESI): *m/z* calcd for $\text{C}_{23}\text{H}_{21}\text{ClNO}_2$ [$\text{M}+\text{H}]^+$: 378.1261; found: 378.1254; HPLC: Daicel Chiraldak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, λ = 210 nm, t_R = 6.2 min (major) and t_R = 9.0 min (minor).



3o

(S)-7-chloro-3-hydroxy-3-(2-methylbut-3-en-2-yl)-1-(naphthalen-1-ylmethyl)indolin-2-one (3o): White solid, 30.1 mg, 77% yield, 73% *ee*; $[\alpha]_D^{27} = -96.6$ ($c = 1.0, \text{CHCl}_3$); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.60–7.52 (m, 2H), 7.40 (d, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 8.2$ Hz, 1H), 7.12 (d, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 7.8$ Hz, 1H), 6.19 (dd, $J = 17.5, 10.8$ Hz, 1H), 5.85 (d, $J = 17.0$ Hz, 1H), 5.65 (d, $J = 17.0$ Hz, 1H), 5.28 (d, $J = 10.8$ Hz, 1H), 5.17 (d, $J = 17.5$ Hz, 1H), 3.03 (s, 1H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.65, 141.62, 139.73, 133.71, 132.35, 132.12, 131.51, 130.26, 128.91, 127.52, 126.29, 125.81, 125.39, 124.69, 123.21, 122.40, 121.95, 116.03, 115.71, 79.44, 43.93, 43.18, 22.37, 20.13; HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{23}\text{ClNO}_2$ [$\text{M}+\text{H}]^+$: 392.1417; found: 392.1413; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 8.4$ min (minor) and $t_R = 13.4$ min (major).

5. Transformations of products.



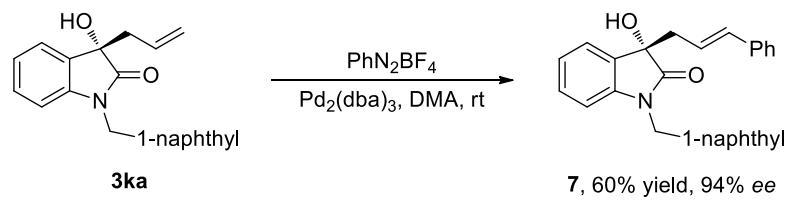
(S)-3-allyl-3-methoxy-1-(naphthalen-1-ylmethyl)indolin-2-one (**5**)^{3a}

To a stirred solution of compound **3ka** (164.50 mg, 0.50 mmol) in dry DMF (10.0 mL) was added NaH (60% in oil, 30.00 mg, 0.75 mmol) at room temperature. After stirring for 30 min, iodomethane (47.00 μ L, 0.75 mmol) was added. The resulting mixture continued to stir for 30min until disappearance of **3ka** monitored by TLC, and water (20 mL) was added. The mixture was extracted with EtOAc (30 mL \times 3), and the combined organic layers were concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford white solid **5** (168.05mg, 98% yield, 95% ee); $[\alpha]_D^{27} = +7.6$ ($c = 0.5$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.62 – 7.49 (m, 2H), 7.42 – 7.29 (m, 3H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 7.7$ Hz, 1H), 5.63 (td, $J = 16.8, 8.2$ Hz, 1H), 5.50 – 5.31 (m, 2H), 5.15 – 5.02 (m, 2H), 3.13 (s, 3H), 2.85 (dd, $J = 13.3, 6.4$ Hz, 1H), 2.73 (dd, $J = 13.3, 8.3$ Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 175.8, 143.48, 133.86, 130.99, 130.71, 130.39, 129.76, 128.95, 128.51, 126.74, 126.61, 126.08, 125.16, 124.95, 124.56, 123.04, 122.95, 120.05, 109.91, 82.52, 53.26, 42.21; HRMS (ESI): m/z calcd for C₂₃H₂₂NO₂ [M+H]⁺: 344.1651; found: 344.1650; HPLC: Daicel Chiralpak OD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, t_R = 7.6 min (minor) and t_R = 8.4 min (major).

(S)-3-allyl-3-methoxyindolin-2-one (6) ^{3b}

To a 25 mL double neck round bottom flask with a magnetic stirring bar were added compound **5** (102.90 mg, 0.30 mmol), NBS (64.08 mg, 0.36 mmol) and AIBN (9.85 mg, 0.06 mmol). Dissolved in chlorobenzene (5 mL), and then refluxed under a nitrogen atmosphere. After 5h further AIBN (0.1 equiv.) and NBS (0.2 equiv.) were added. The solution was cooled to room temperature after refluxing overnight. Diethyl ether (10 ml) and water (10 ml) were added to the residue which was stirred for 5 h.

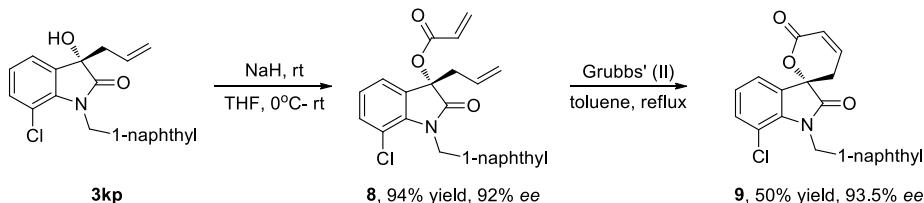
The organic layer was separated, evaporated and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/3, v/v) to afford white solid **6** (38.98 mg, 64% yield, 93% ee); $[\alpha]_D^{27} = -2.8$ ($c = 1.0, \text{CHCl}_3$); ^1H NMR (400 MHz, CDCl_3) δ 8.58 (br, 1H), 7.29 (dd, $J = 10.1, 7.5$ Hz, 2H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.7$ Hz, 1H), 5.69 – 5.51 (m, 1H), 5.13 – 4.96 (m, 2H), 3.10 (s, 3H), 2.76 (dd, $J = 13.5, 6.6$ Hz, 1H), 2.63 (dd, $J = 13.4, 8.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.83, 141.01, 130.54, 129.78, 126.96, 124.94, 122.86, 119.68, 110.25, 82.79, 53.55, 53.12, 41.95; HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{13}\text{NNaO}_2$ [$\text{M}+\text{Na}$] $^+$: 226.0844; found: 226.0837; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 9:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 7.1$ min (major) and $t_R = 7.8$ min (minor).



(*S*)-3-cinnamyl-3-hydroxy-1-(naphthalen-1-ylmethyl)indolin-2-one (7)^{4b}

Benzenediazonium salt was synthesized according to a previously reported procedure.^{4a}

To an oven dried 25 mL Schrek tube with magnetic stirring bar was charged with benzenediazonium salt (52.80 mg, 0.275 mmol). To an oven dried 10 mL round bottomed flask was added Pd₂dba₃ (6.90 mg, 0.0075 mmol) and 3 mL DMA. To an oven dried 10 mL round bottomed flask was added **3ka** (82.25 mg, 0.25 mmol) and 2 mL DMA. To the Schrek tube containing benzenediazonium salt was added the solution of **3ka**, followed quickly by the solution of Pd₂dba₃. The mixture was stirred for 30 min and diluted with 20 mL Et₂O. The aqueous layer was extracted twice with 20 mL Et₂O, and the combined organic layers were dried over MgSO₄. Filtered and concentrated in vacuo, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/1) to give white solid **7** (60.75 mg, 60% yield, 94% ee); $[\alpha]_D^{27} = -5.0$ ($c = 1.0$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, $J = 8.3$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.48 (dd, $J = 12.8$, 7.3 Hz, 2H), 7.30 – 7.17 (m, 5H), 7.14 (t, $J = 7.7$ Hz, 1H), 7.08 (q, $J = 7.5$, 7.0 Hz, 2H), 6.84 (t, $J = 7.7$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 1H), 6.46 (d, $J = 15.8$ Hz, 1H), 6.10 – 5.93 (m, 1H), 5.61 (d, $J = 16.4$ Hz, 1H), 5.04 (d, $J = 16.4$ Hz, 1H), 3.20 (br, 1H), 3.03 (dd, $J = 13.2$, 6.4 Hz, 1H), 2.93 (dd, $J = 13.2$, 8.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 178.09, 142.85, 136.85, 135.46, 133.77, 130.80, 129.91, 129.79, 129.68, 128.91, 128.56, 128.12, 127.56, 126.52, 126.38, 125.94, 125.30, 124.15, 124.11, 123.25, 122.66, 121.69, 109.91, 76.52, 42.38, 42.03; HRMS (ESI): *m/z* calcd for C₂₈H₂₄NO₂ [M+H]⁺: 406.1807; found: 406.1803; HPLC: Daicel Chiralpak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, t_R = 10.2 min (minor) and t_R = 14.9 min (major).



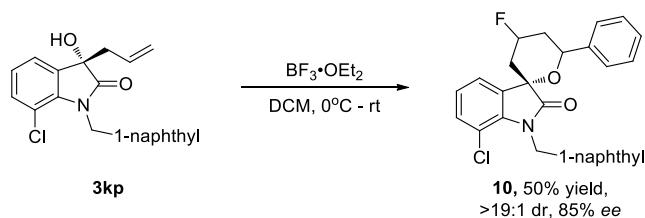
(S)-3-allyl-7-chloro-1-(naphthalen-1-ylmethyl)-2-oxoindolin-3-yl acrylate (8)⁵

To a stirred suspension of NaH (60% in oil, 40.00 mg, 1.0 mmol) in 10 mL dry THF was added compound **3kp** (181.50 mg, 0.5 mmol), and the resulting mixture was stirred for 30 min at room

temperature. Then, acryloyl chloride (52.60 μ L, 0.65 mmol) was added at 0 °C and continue stirred 1 hour at room temperature. After adding saturated aqueous sodium hydrogen carbonate at 0 °C, the mixture was extracted twice with ethyl acetate (20 x 3 mL). The combined organic layer was washed with brine, dried with MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5) to give white solid **8** (195.55 mg, 94% yield, 92% ee); $[\alpha]_D^{27} = +333.0$ ($c = 0.2$, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 7.2$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.58 (t, $J = 6.8$ Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 (d, $J = 7.2$ Hz, 1H), 7.44 – 7.38 (m, 1H), 7.20 (dd, $J = 10.3, 7.8$ Hz, 2H), 7.03 – 6.97 (m, 1H), 6.47 (d, $J = 17.3$ Hz, 1H), 6.19 (dd, $J = 17.3, 10.5$ Hz, 1H), 5.92 (d, $J = 10.5$ Hz, 1H), 5.80 (s, 2H), 5.75–5.65 (m, 1H), 5.28 – 5.10 (m, 2H), 2.98 (dd, $J = 13.4, 6.3$ Hz, 1H), 2.79 (dd, $J = 13.4, 8.3$ Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 174.69, 163.97, 139.23, 133.64, 132.79, 132.75, 132.32, 130.19, 130.09, 129.06, 128.87, 127.39, 127.10, 126.20, 125.70, 125.66, 123.62, 122.38, 121.56, 121.51, 116.07, 78.91, 43.46, 41.58; HRMS (ESI): *m/z* calcd for C₂₅H₂₀ClNNaO₃ [M+Na]⁺: 440.1029; found: 440.1014; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, t_R = 7.3 min (major) and t_R = 7.9 min (minor).

(S)-7-chloro-1-(naphthalen-1-ylmethyl)spiro[indoline-3,2'-pyran]-2,6'(3'H)-dione (9)⁵

A mixture of compound **8** (125.10 mg, 0.30 mmol) and Grubbs 2nd (25.47 mg, 0.03 mmol) in toluene (3.0 mL) was refluxed for 1 h. After cooling to room temperature, the crude mixture was directly purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/2) to give white solid **9** (58.35 mg, 50% yield, 93.5% ee); $[\alpha]_D^{27} = -45.0$ ($c = 0.2$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.57 (dt, $J = 19.5, 7.1$ Hz, 2H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.23 (d, $J = 8.2$ Hz, 1H), 7.09 – 7.00 (m, 2H), 6.96 (dt, $J = 9.3, 4.2$ Hz, 1H), 6.30 (d, $J = 10.0$ Hz, 1H), 5.86 – 5.68 (m, 2H), 3.01 (dd, $J = 18.2, 3.2$ Hz, 1H), 2.91 (d, $J = 17.4$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.48, 161.59, 141.51, 138.54, 133.78, 133.57, 131.49, 130.51, 130.12, 128.96, 127.79, 126.44, 125.95, 125.51, 124.54, 122.94, 122.23, 121.56, 121.35, 116.62, 79.42, 43.03, 30.90; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2\text{O}_3$ [$\text{M}+\text{NH}_4^+$]: 407.1162; found: 407.1151; HPLC: Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 3:2, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 16.8$ min (major) and $t_R = 25.7$ min (minor).



(2'S)-7-chloro-4'-fluoro-1-(naphthalen-1-ylmethyl)-6'-phenyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (10)⁶

To a mixture of compound **3kp** (108.90 mg, 0.30 mmol) and benzaldehyde (36.5 μ L, 0.36 mmol) in anhydrous DCM (5 mL) was added $\text{BF}_3\text{-OEt}_2$ (55.5 μ L, 0.45 mmol) at 0 °C. The resulting mixture was warmed to room temperature and allowed to stir 4 h. After completion of the reaction monitored by TLC, sat. NaHCO_3 solution was added. Extracted twice with ethyl acetate, and the combined organic extracts were concentrated on a rotary evaporator. The resulting crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20) to afford the pure product **10** as

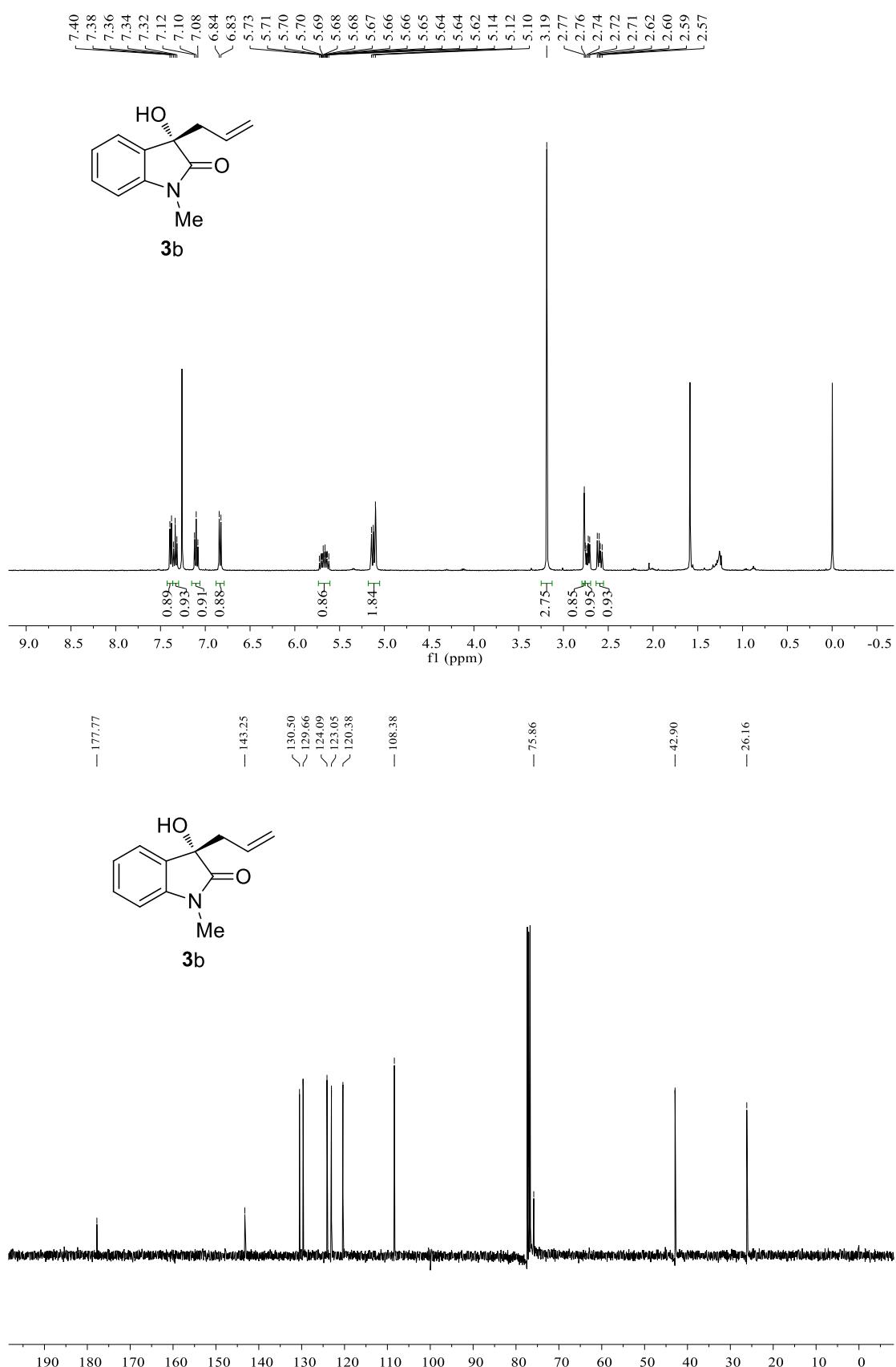
colorless oil (70.65 mg, 50% yield, 85% *ee*); $[\alpha]_D^{27} = +5.0$ ($c = 1.0$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.8$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.61 – 7.56 (m, 1H), 7.56 – 7.50 (m, 1H), 7.41 (dt, $J = 8.1, 1.8$ Hz, 3H), 7.38 – 7.27 (m, 4H), 7.16 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.09 – 7.04 (m, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 5.91 – 5.56 (m, 4H), 2.60 – 2.50 (m, 1H), 2.45 (m, 1H), 2.20 (m, 1H), 2.04 – 1.89 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.09, 140.92, 138.54, 133.78, 132.64, 132.24, 132.03, 130.23, 128.94, 128.58, 128.13, 127.66, 126.39, 126.31, 125.91, 125.55, 124.43, 122.72, 122.31, 121.37, 116.03, 85.45 (d, $J = 174.5$ Hz), 73.06 (d, $J = 11.7$ Hz), 42.41, 40.25 (d, $J = 17.3$ Hz), 37.83 (d, $J = 18.9$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -177.85 (d, $J = 50.4$ Hz); HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{24}\text{ClFNO}_2$ [$\text{M}+\text{H}]^+$: 472.1480; found: 472.1472; HPLC: Daicel Chiraldak IC, *n*-hexane/*i*-PrOH = 4:1, Flow rate = 1.0 mL/min, $\lambda = 210$ nm, $t_R = 5.2$ min (major) and $t_R = 8.9$ min (minor).

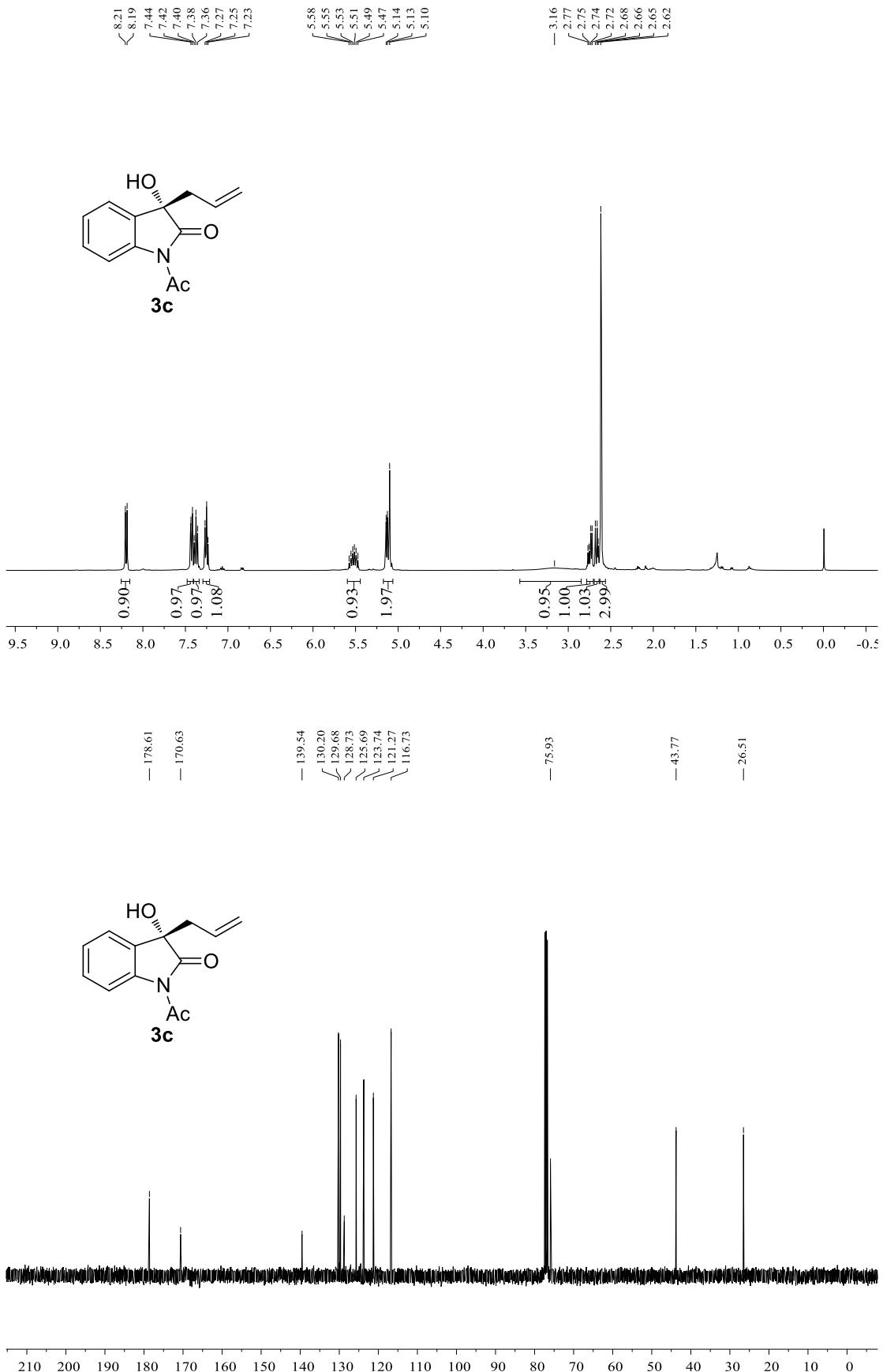
6. References.

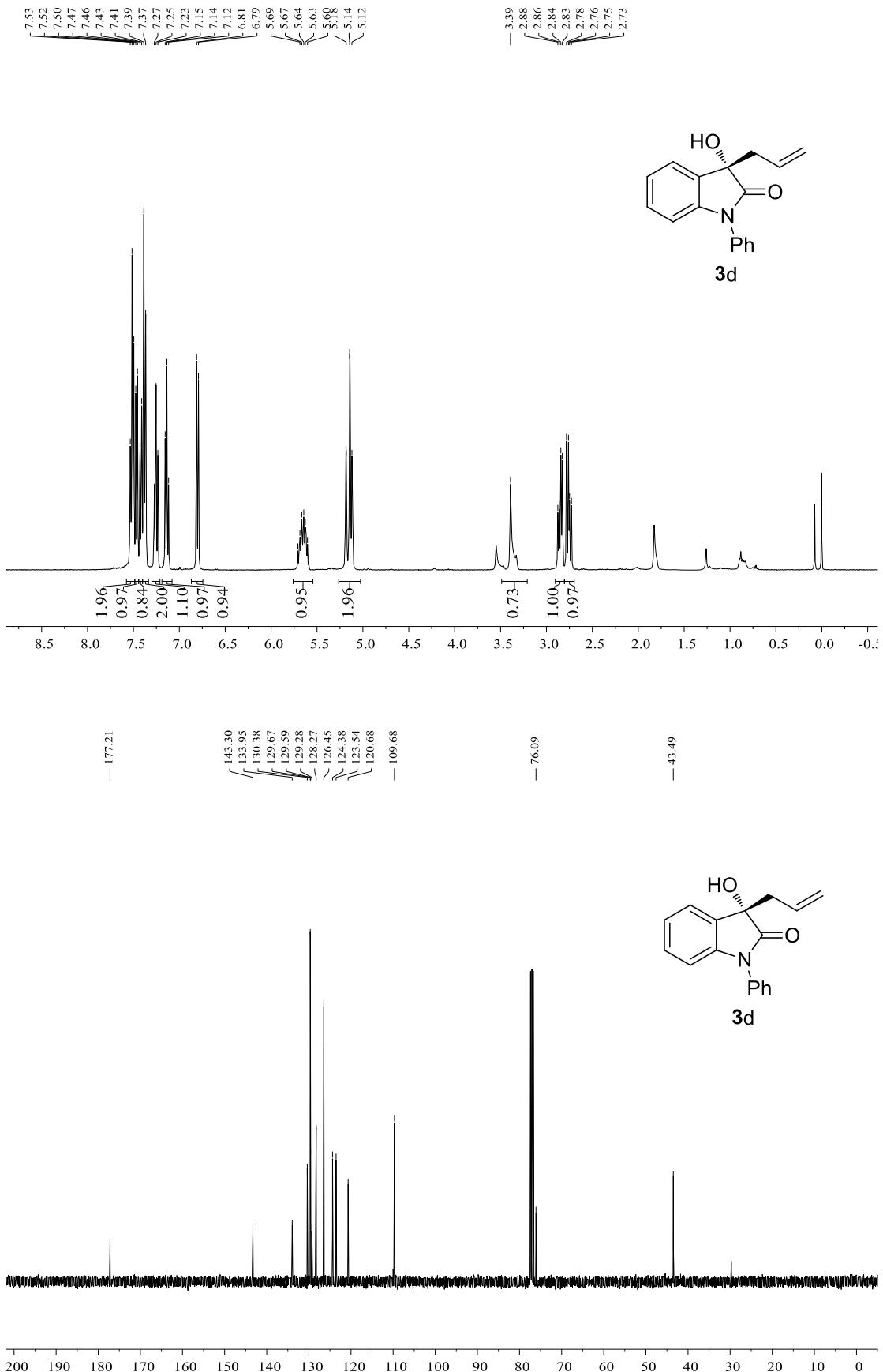
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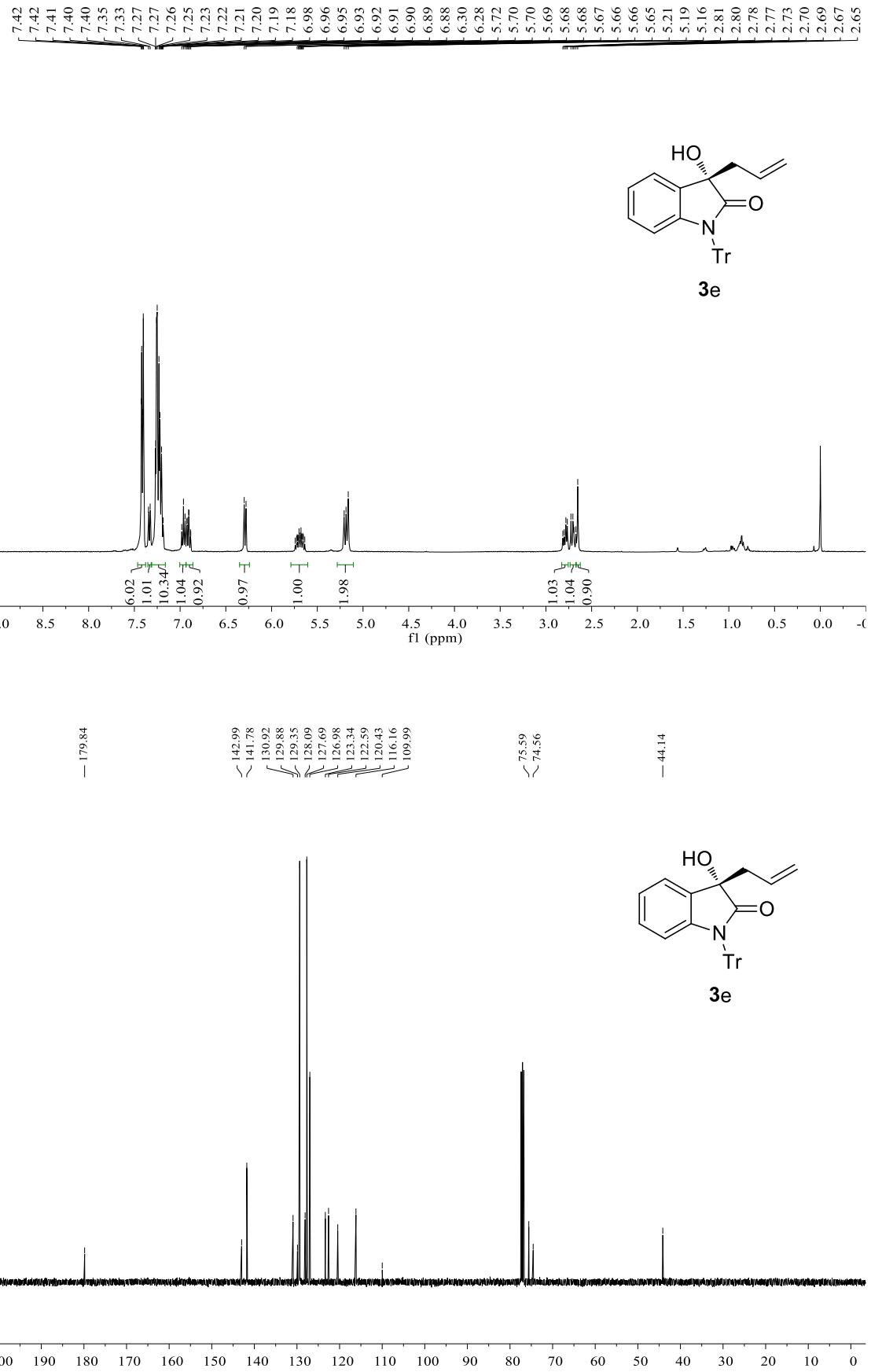
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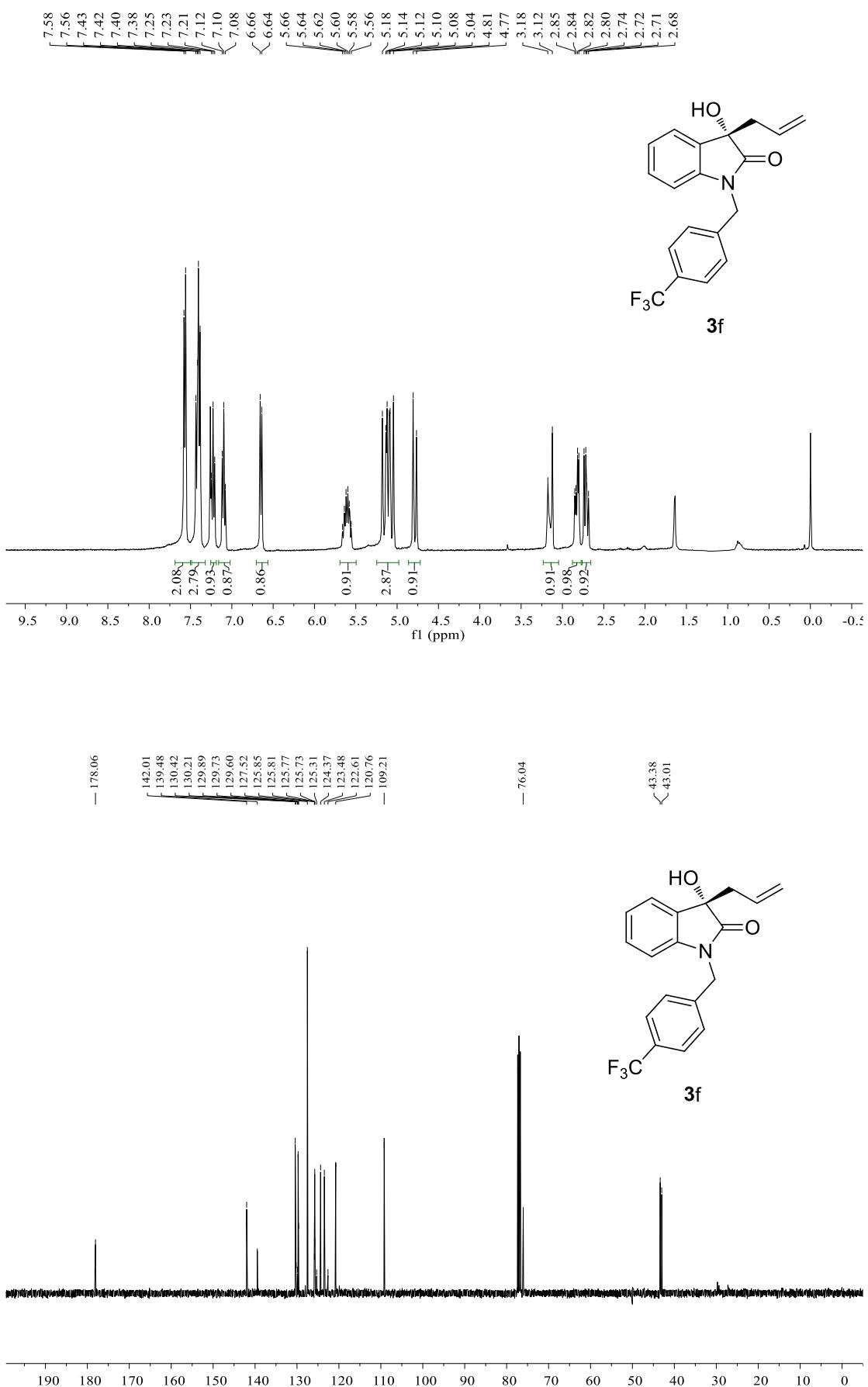
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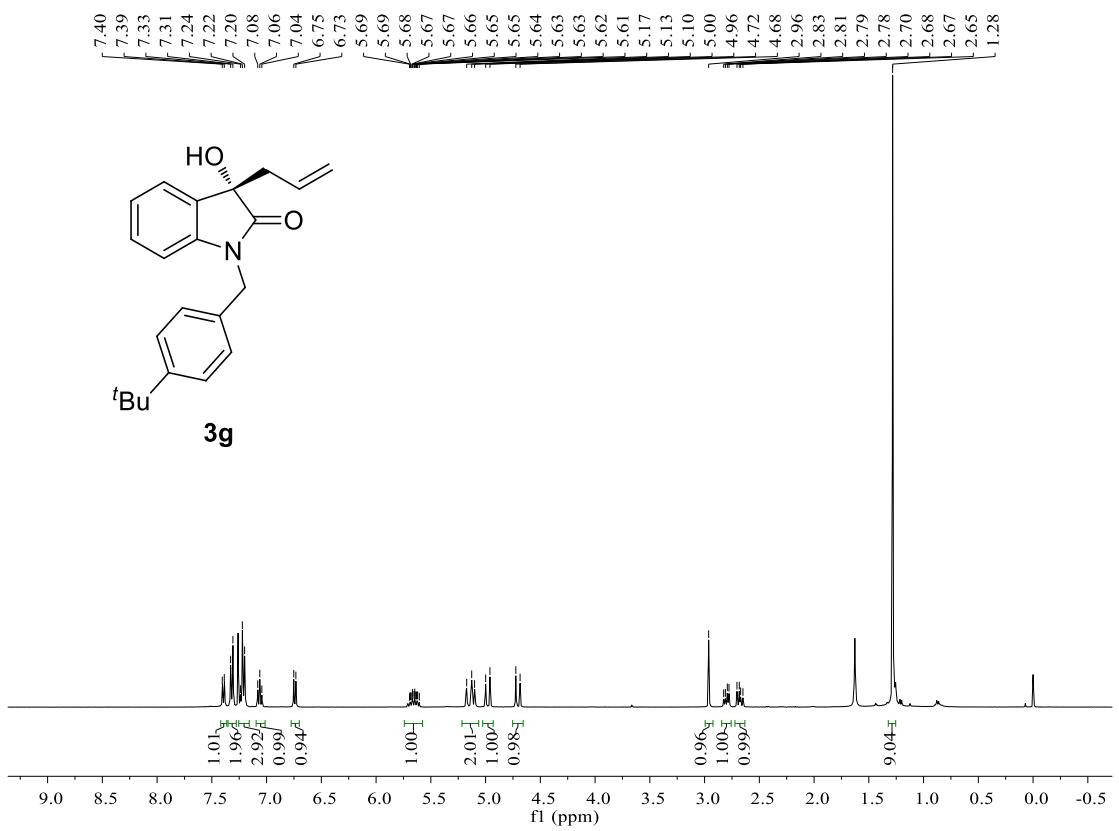
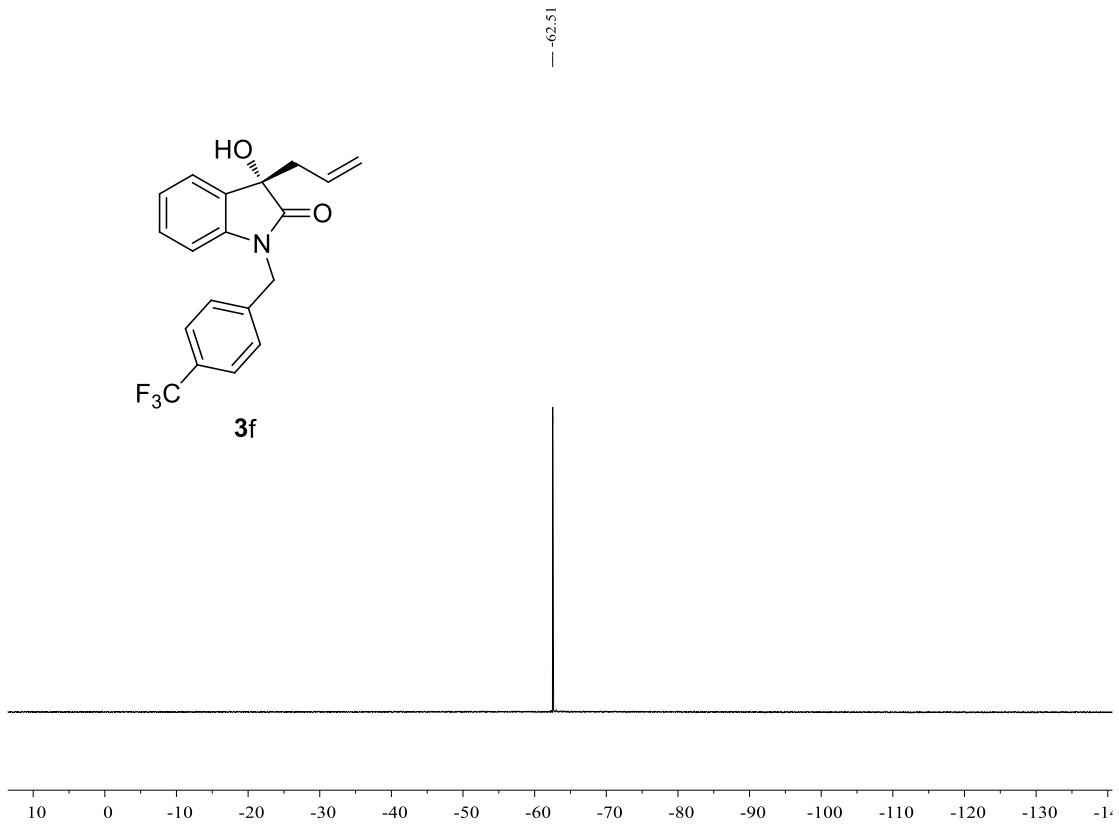


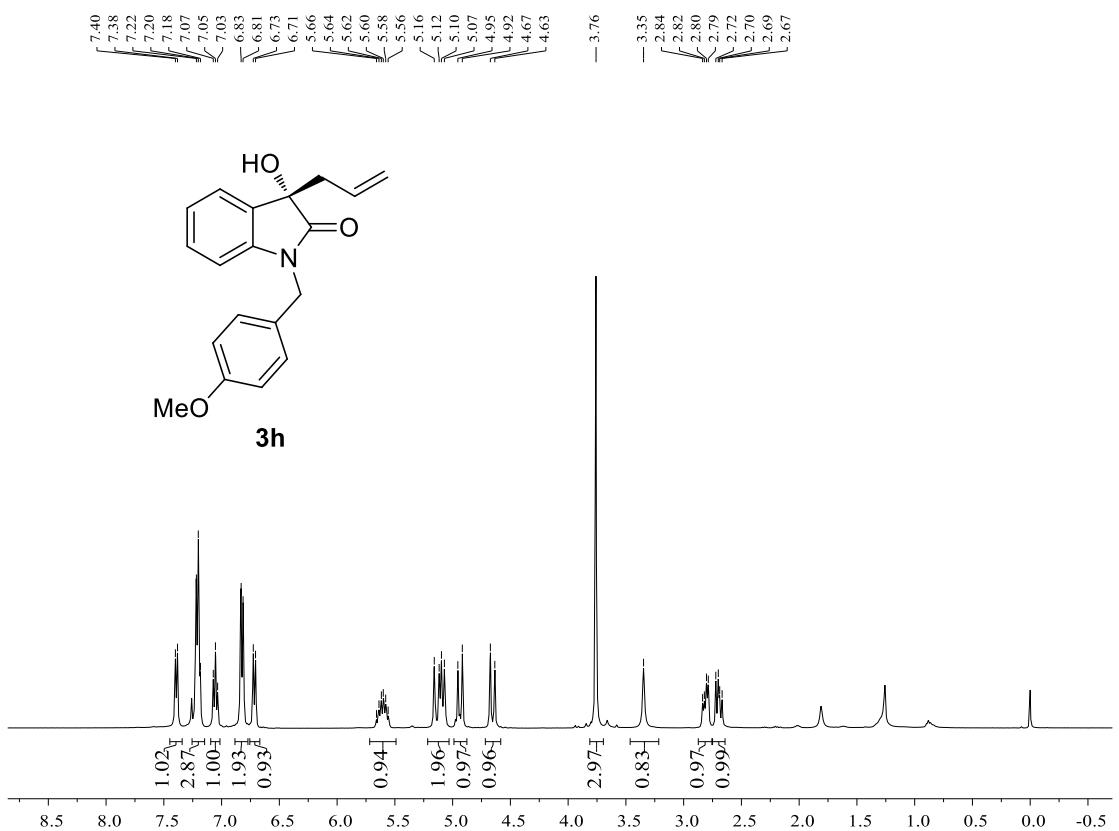
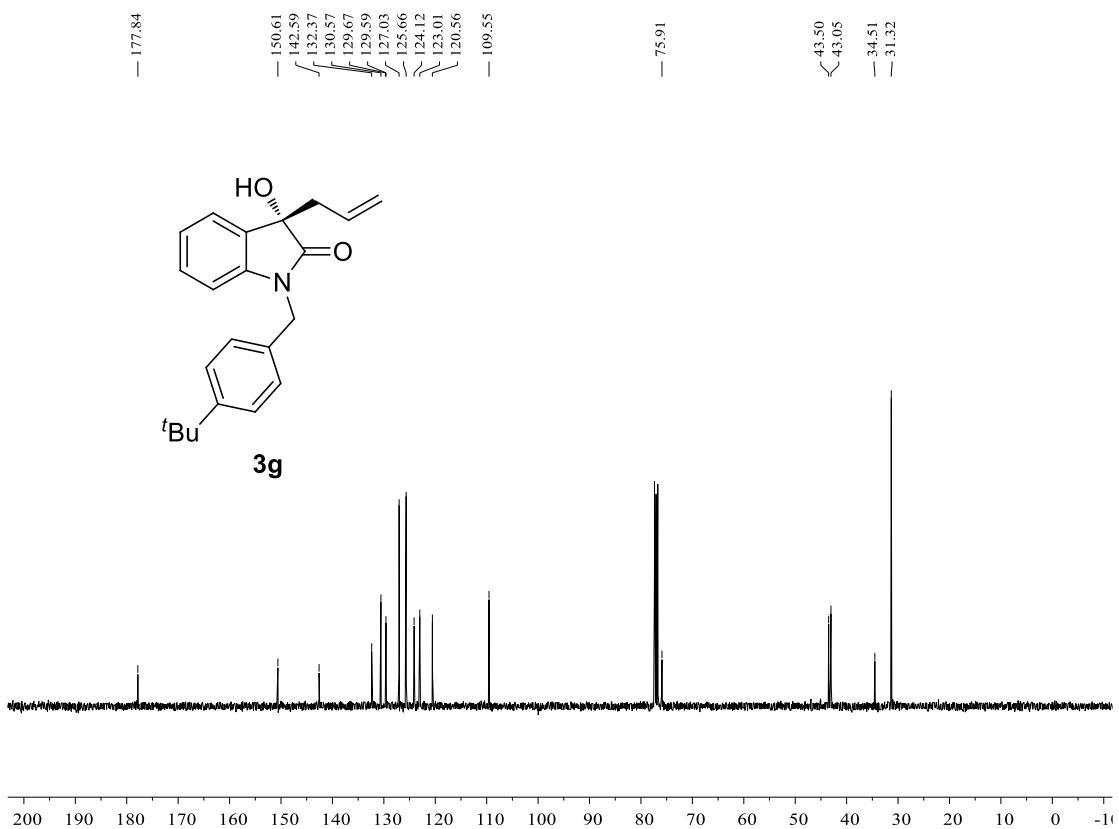


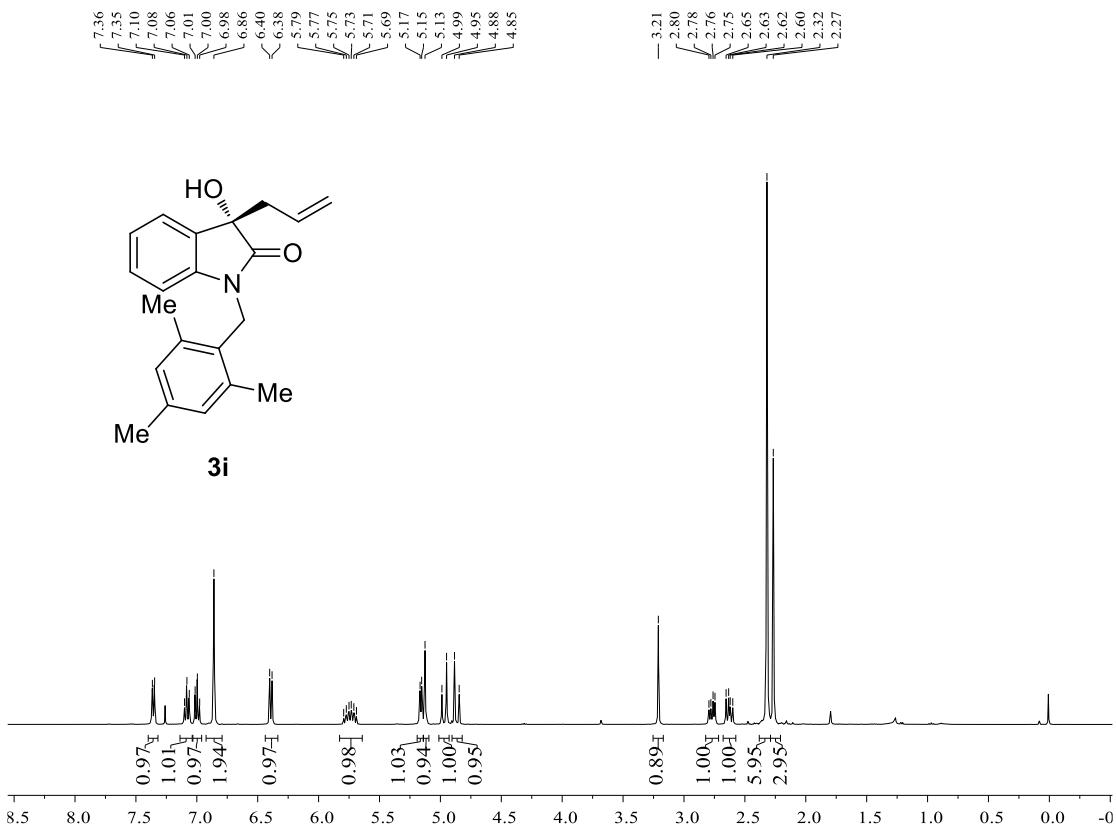
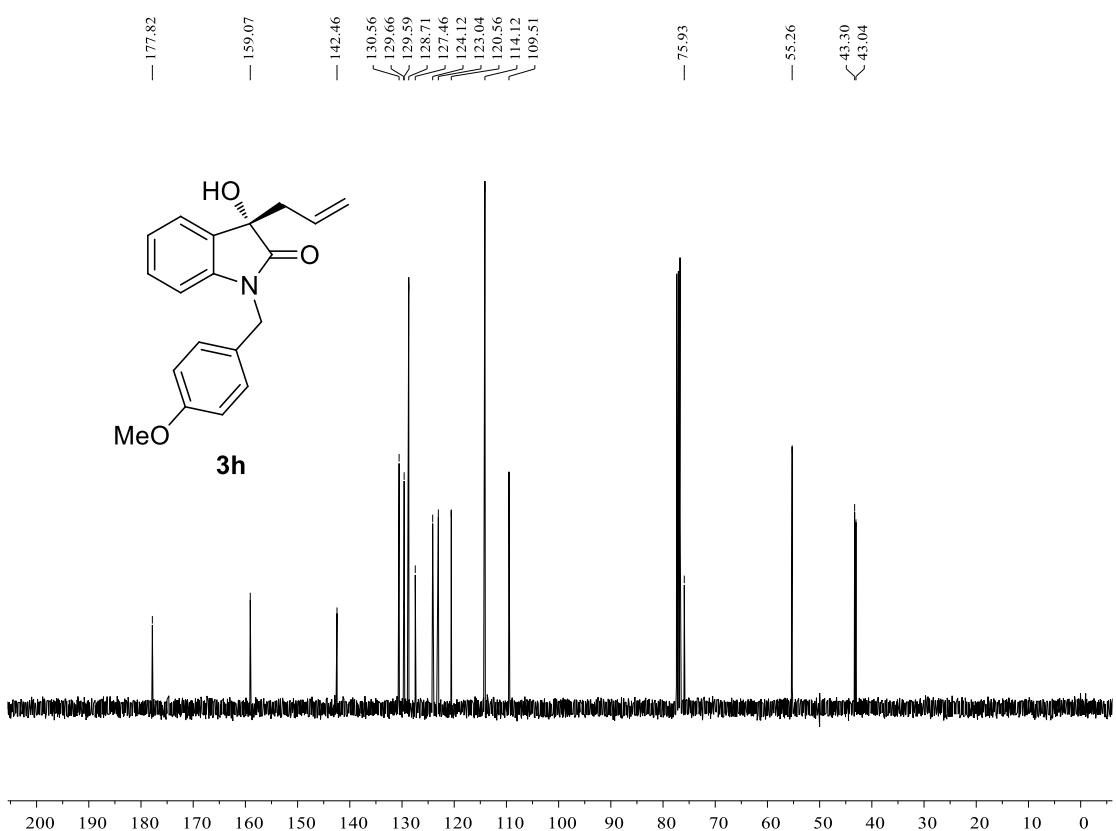


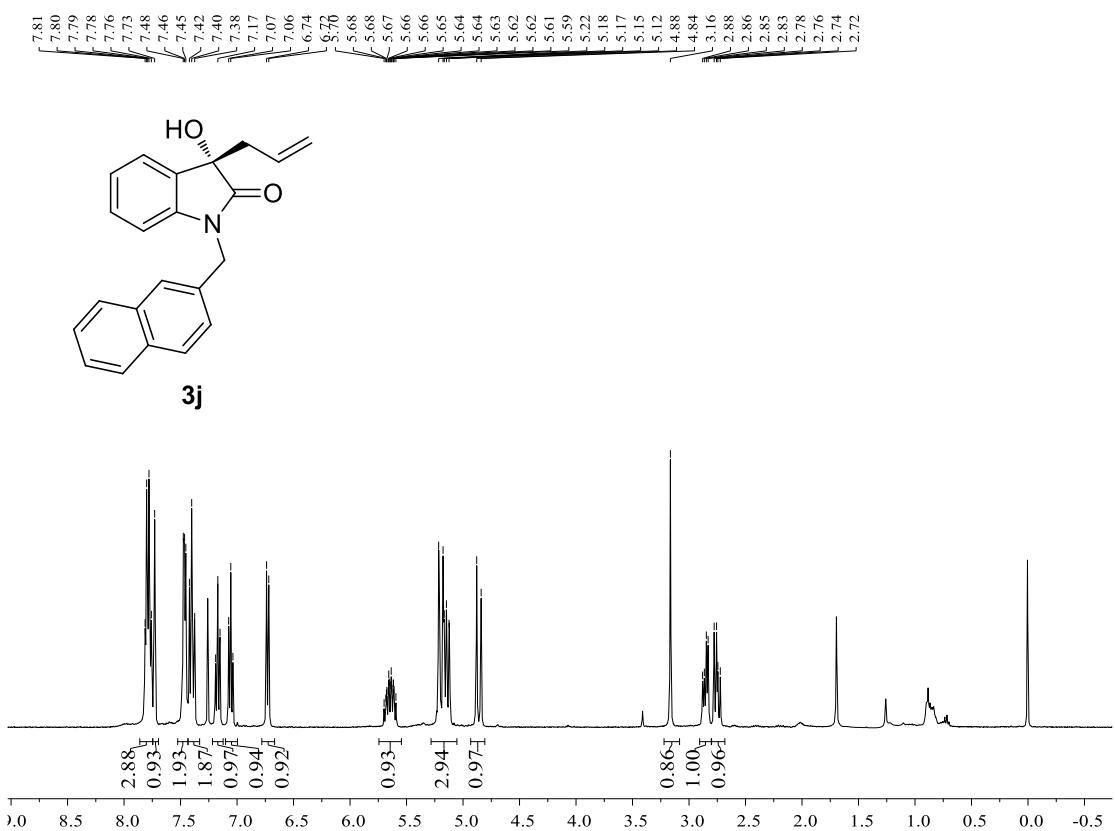
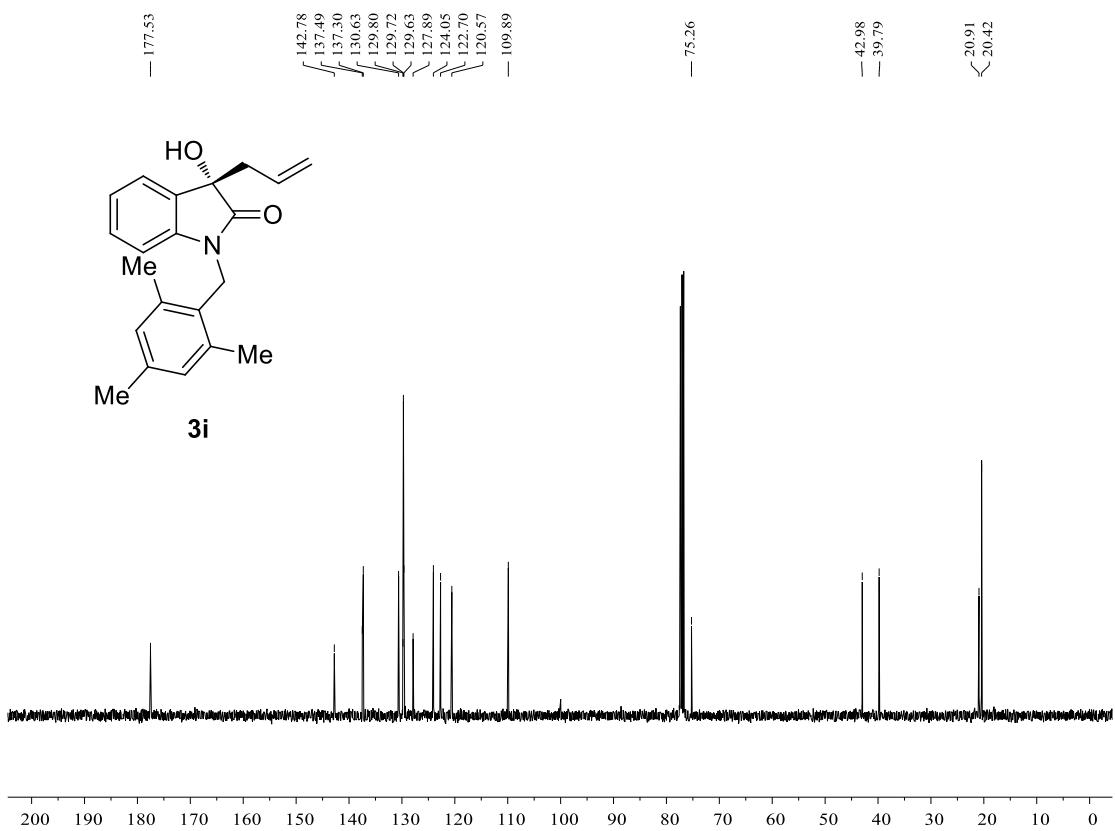


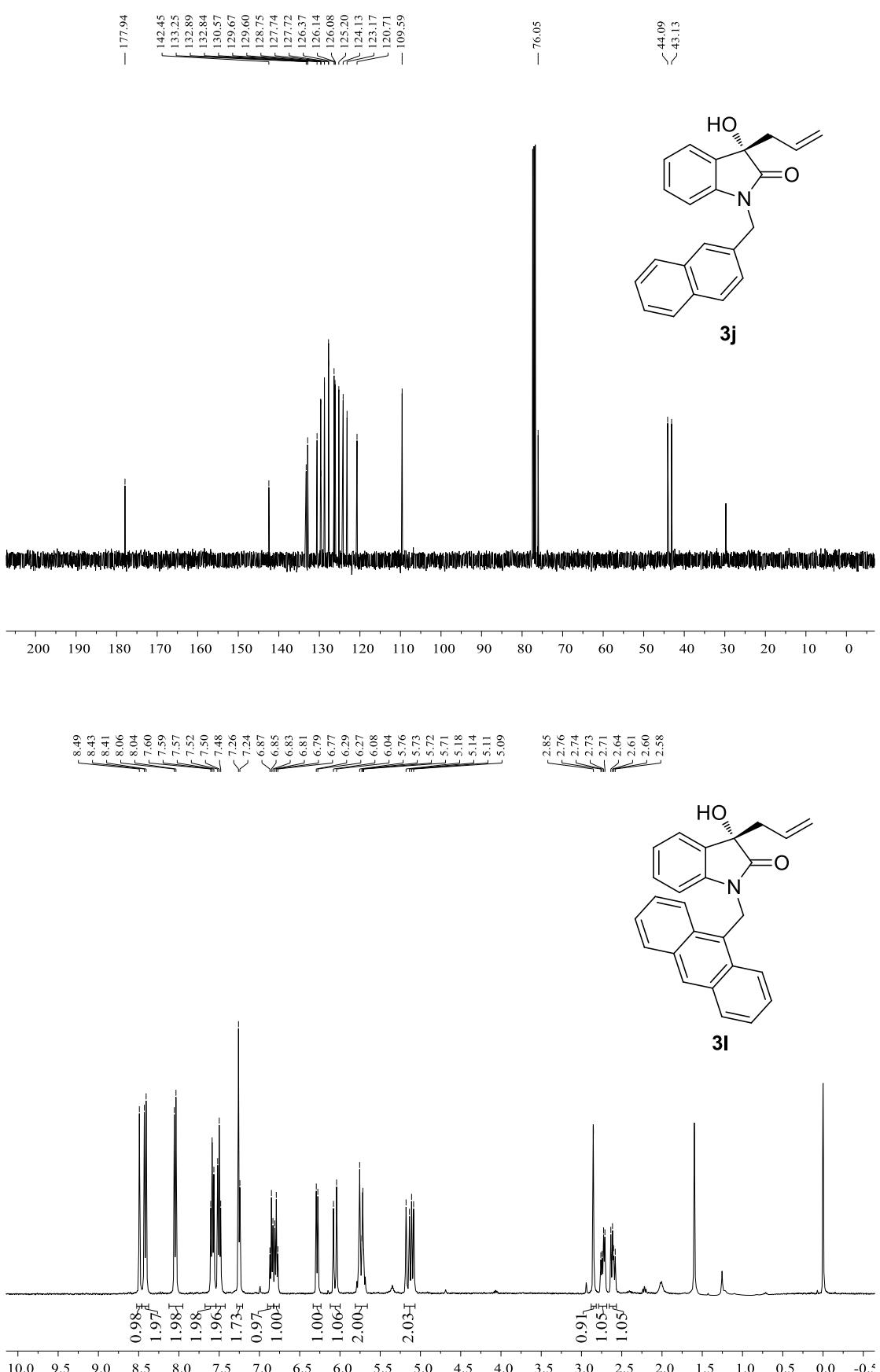


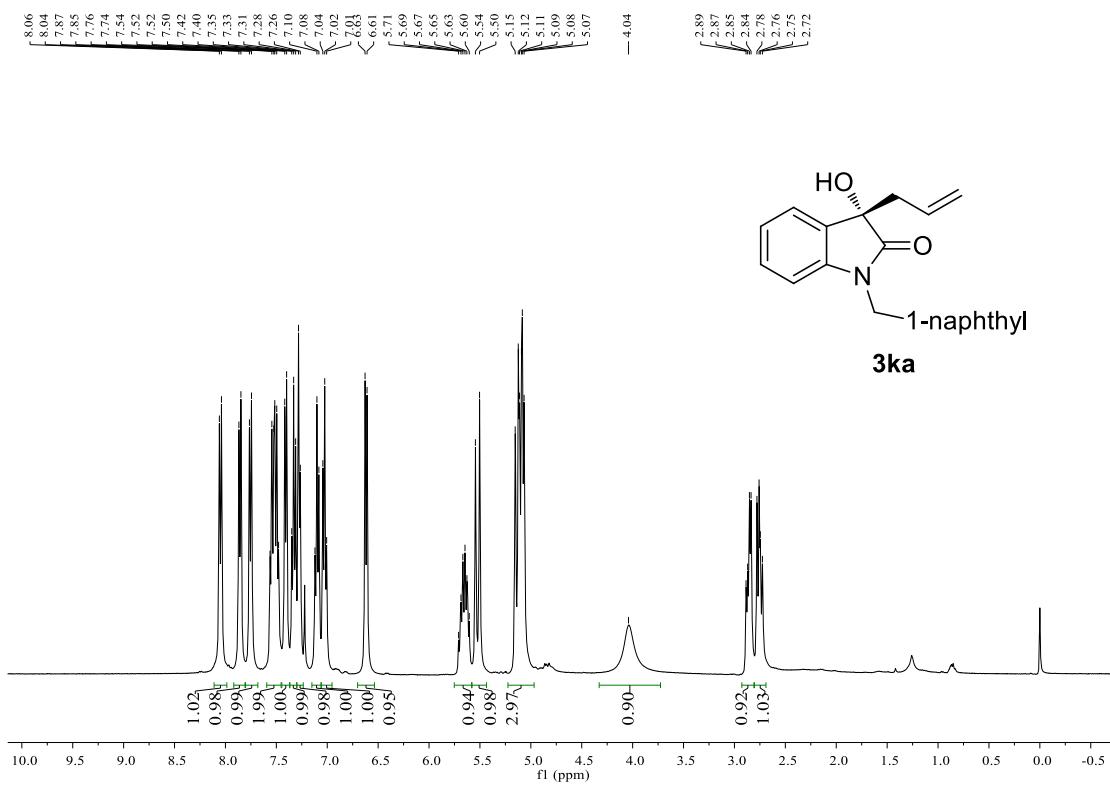
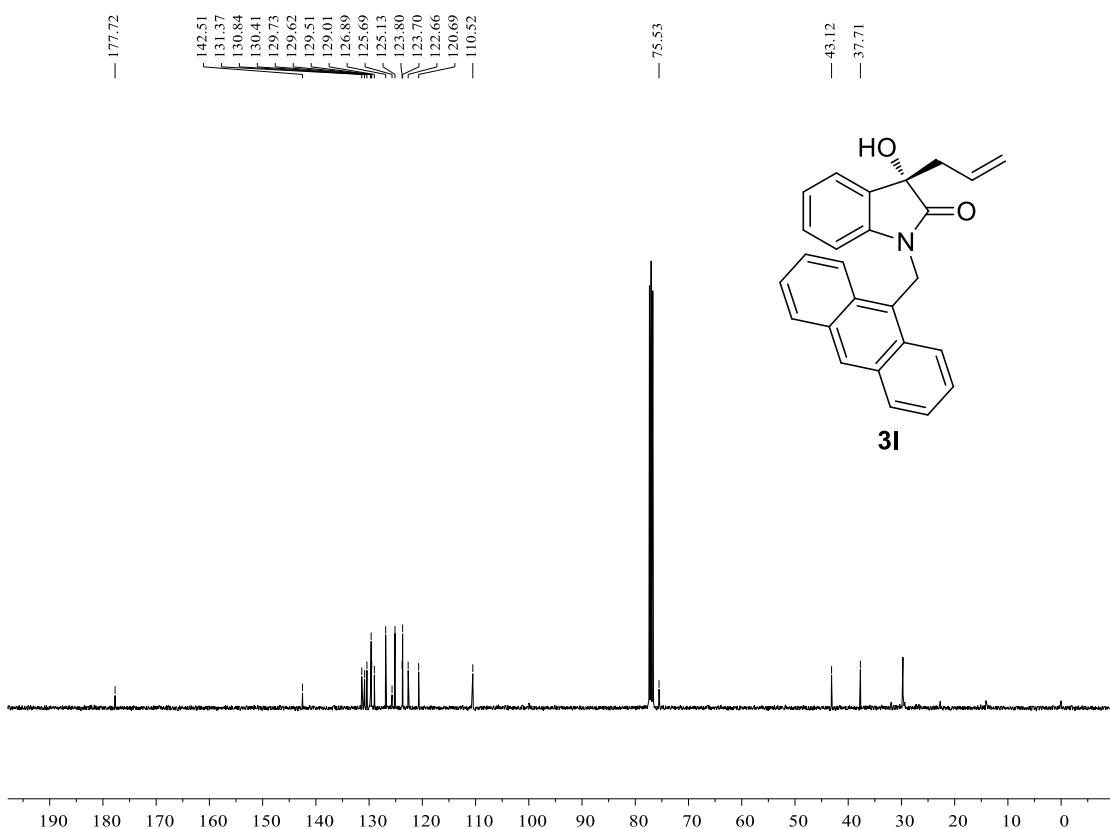


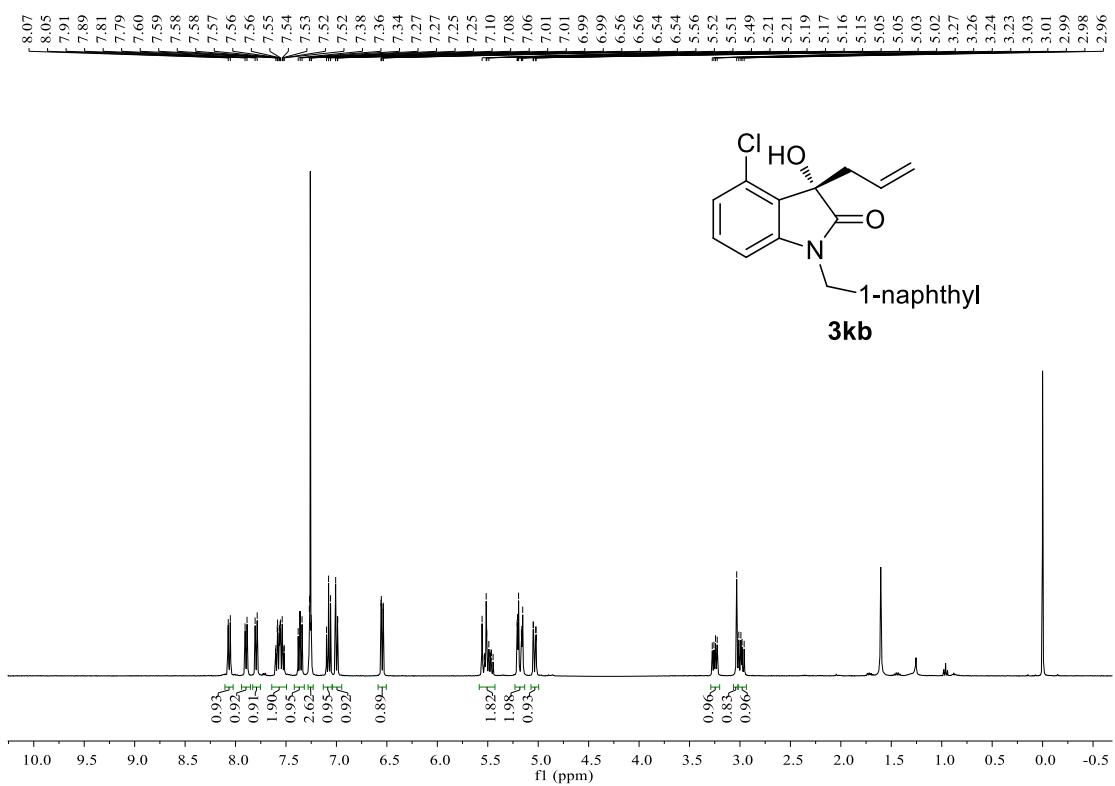
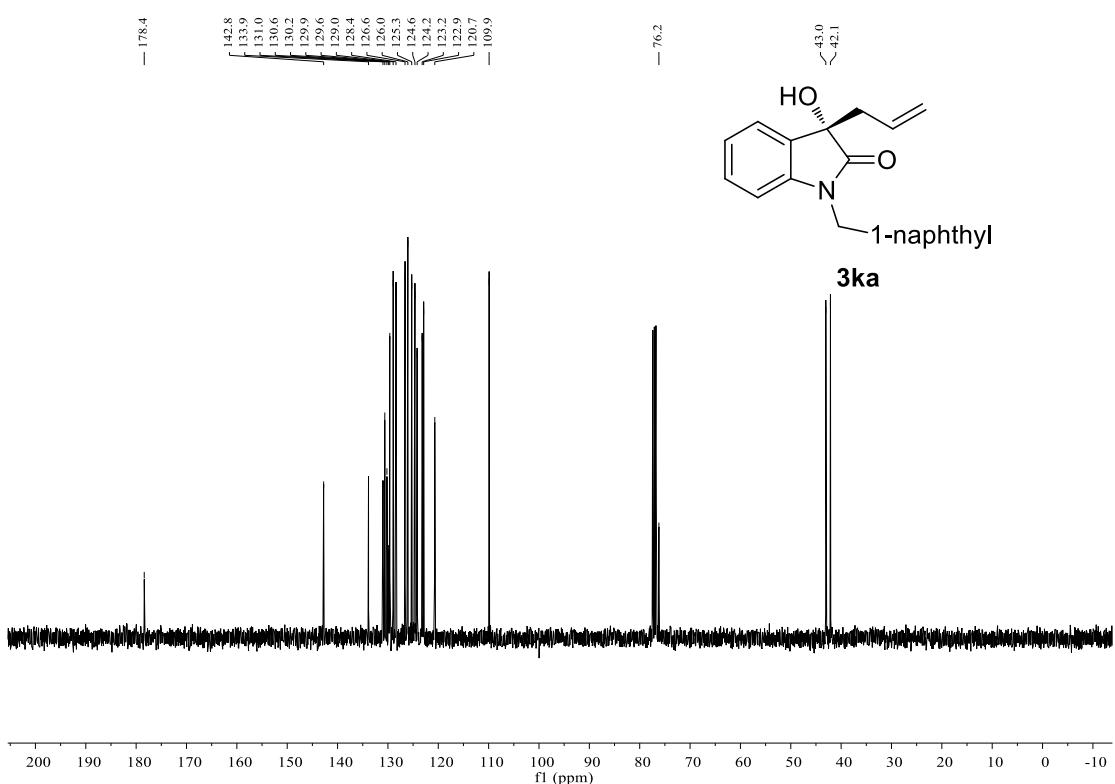


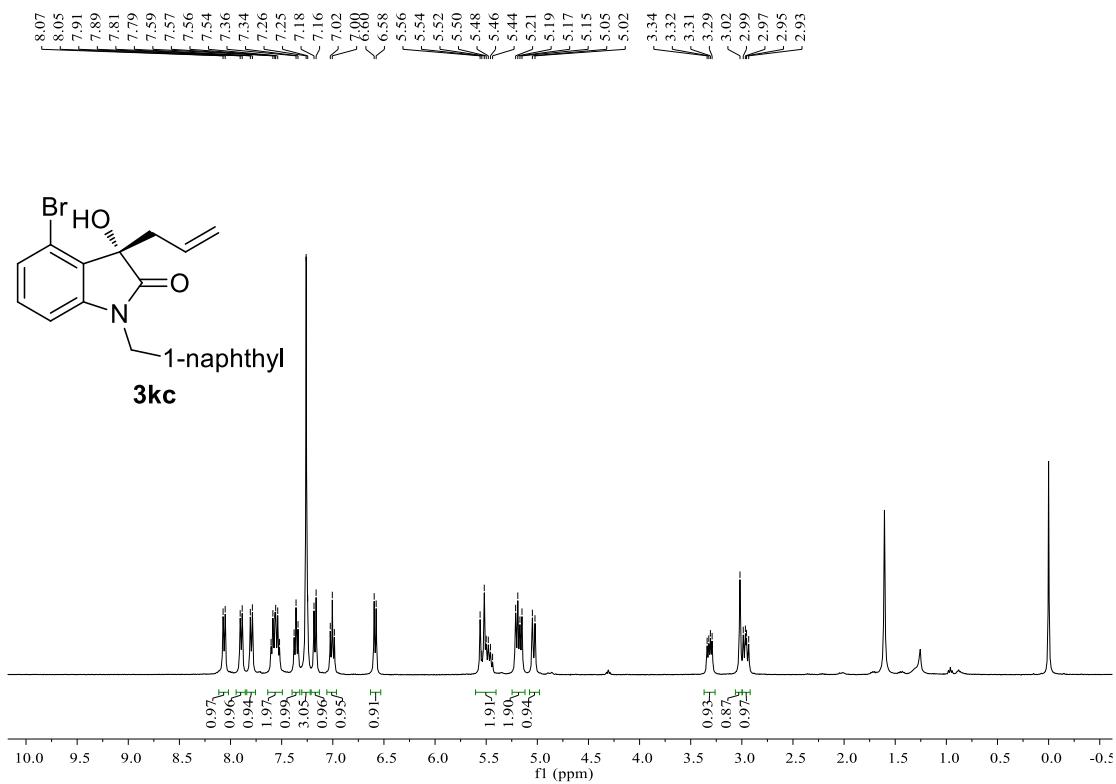
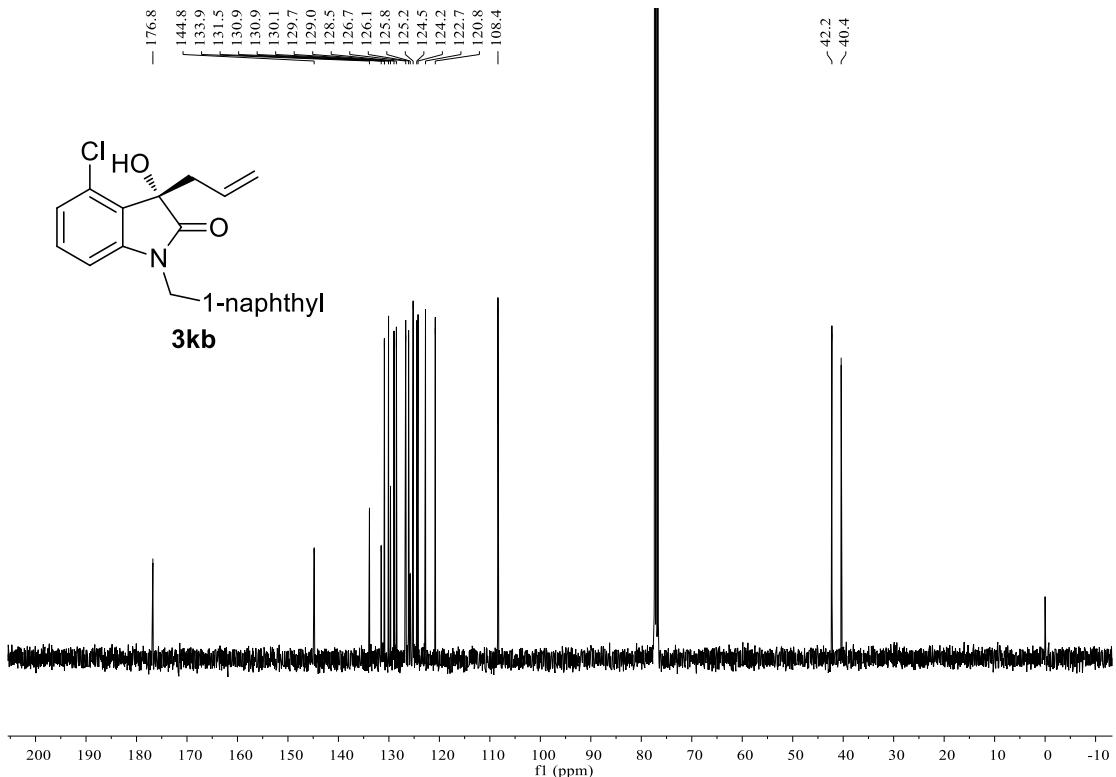


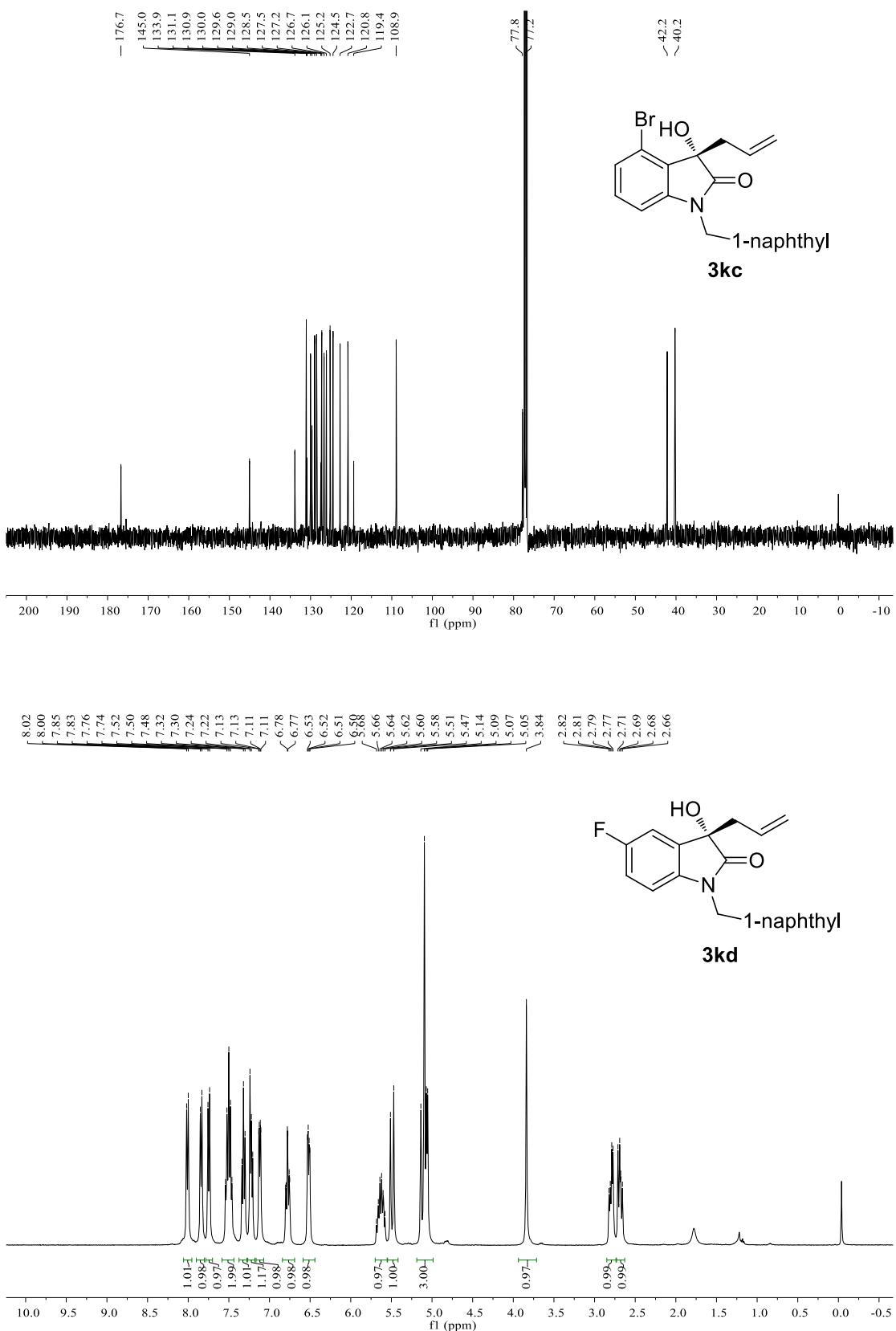


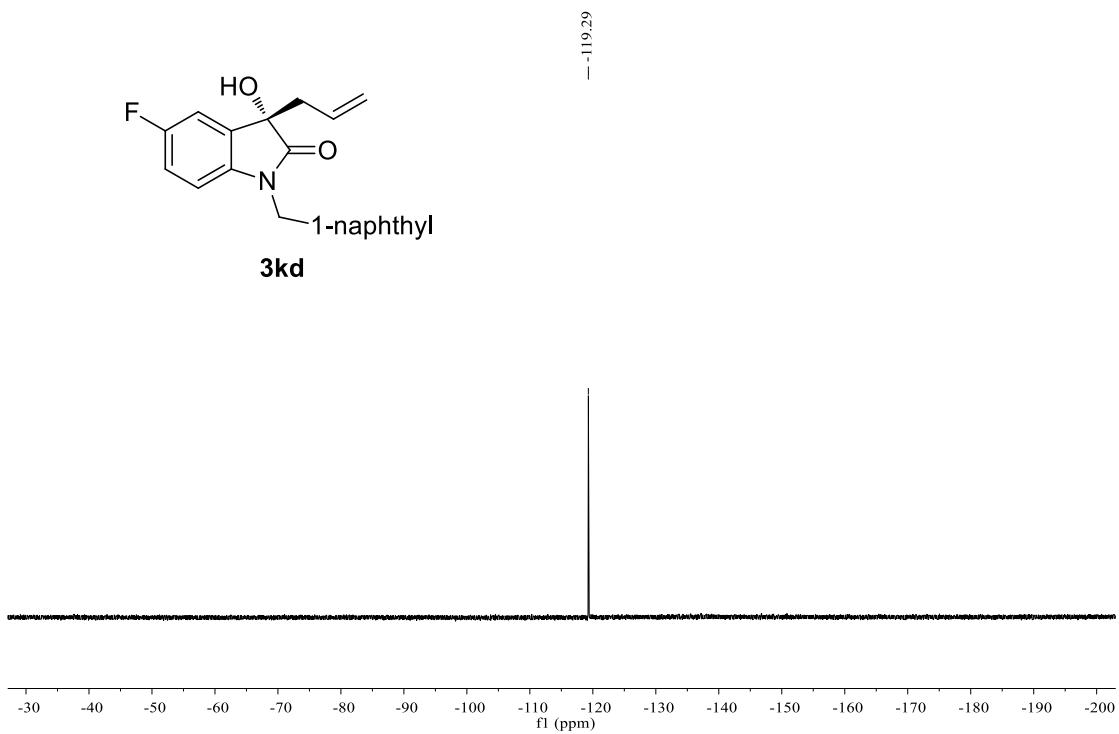
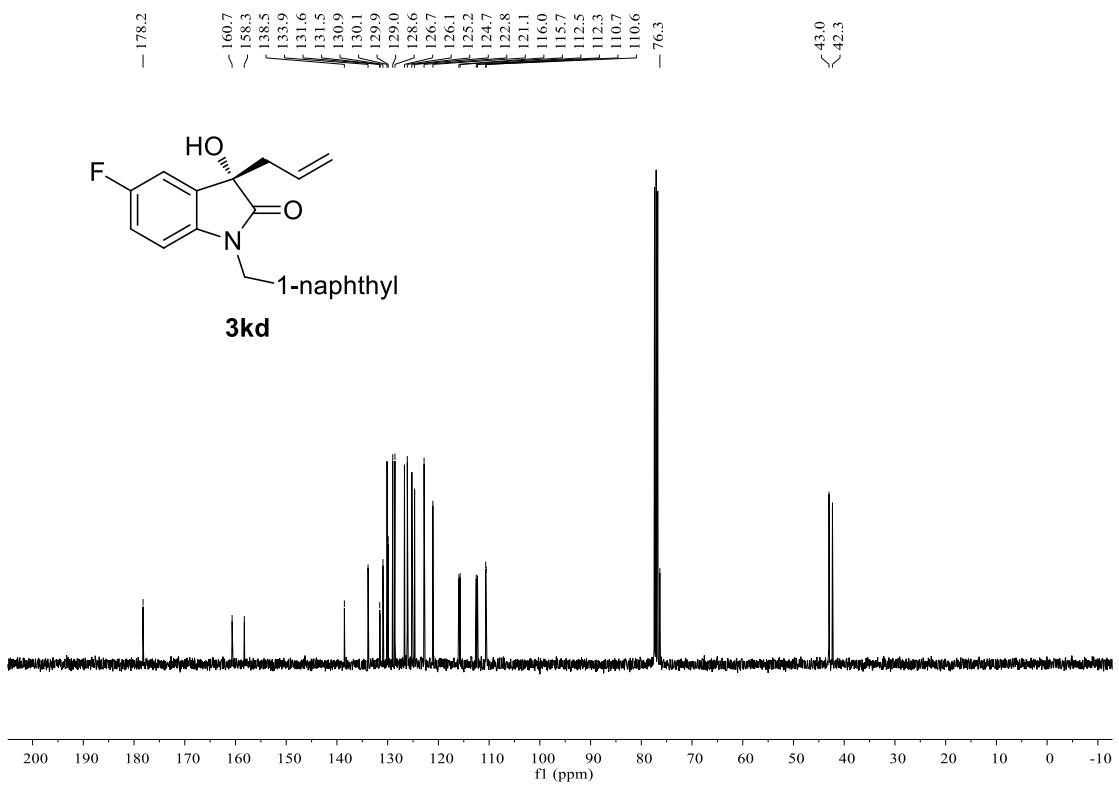


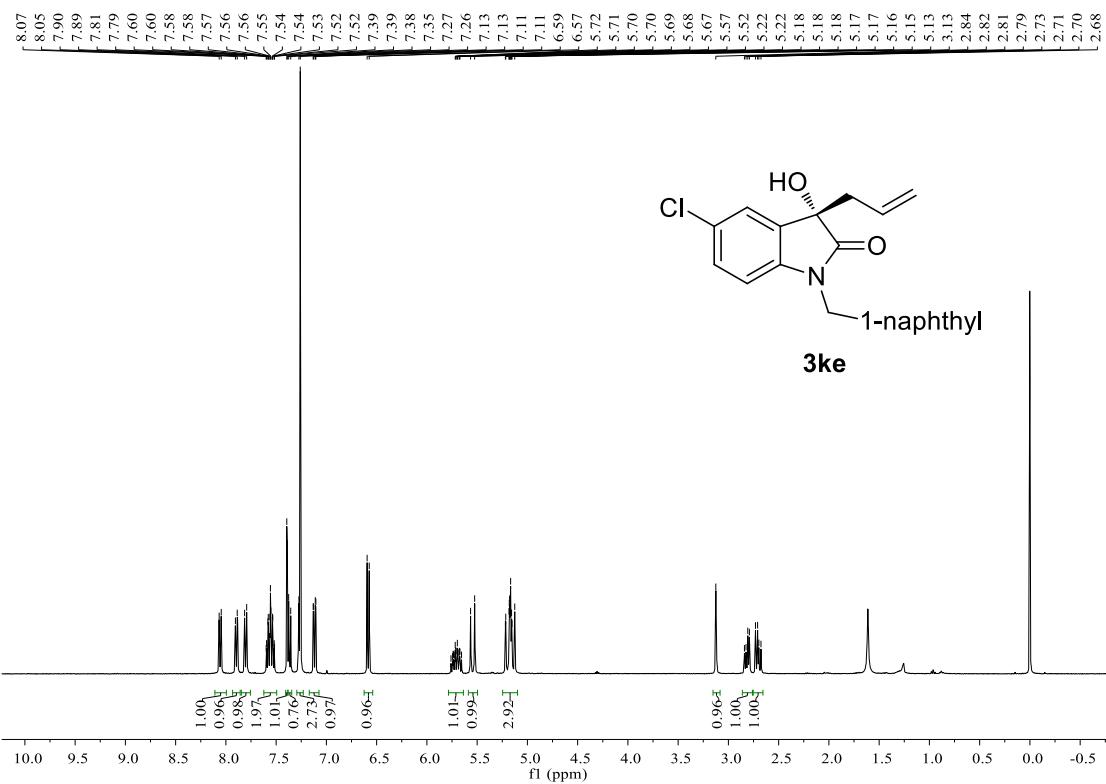


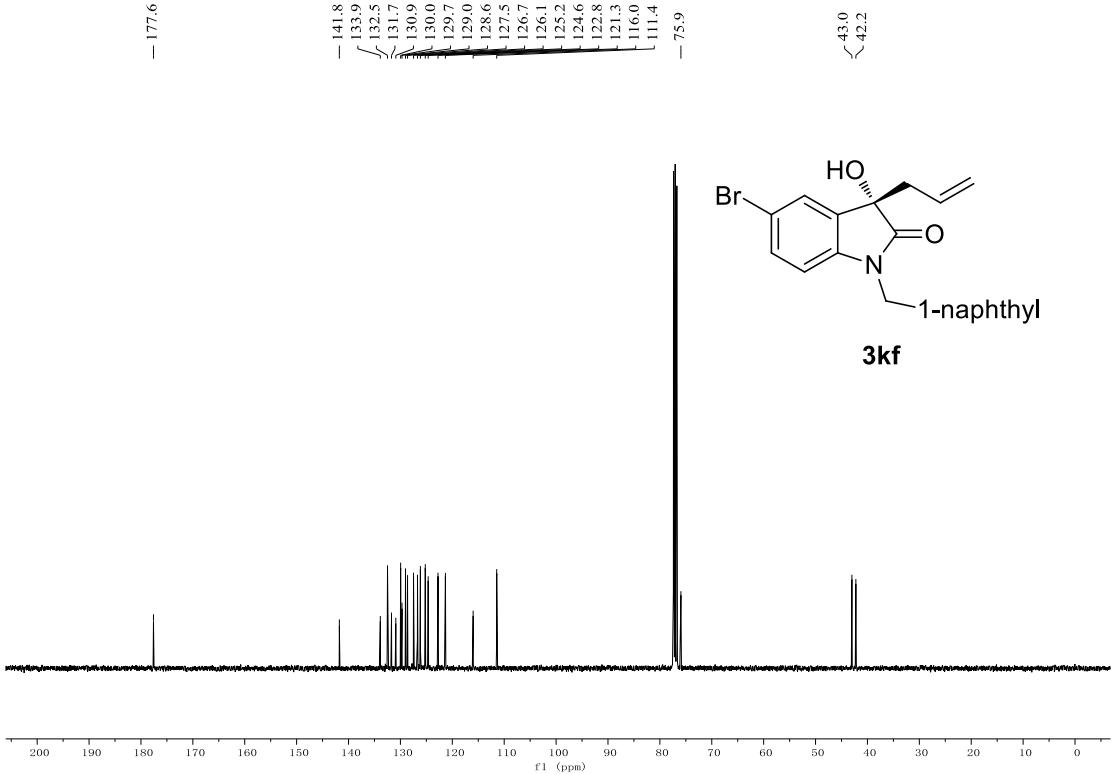
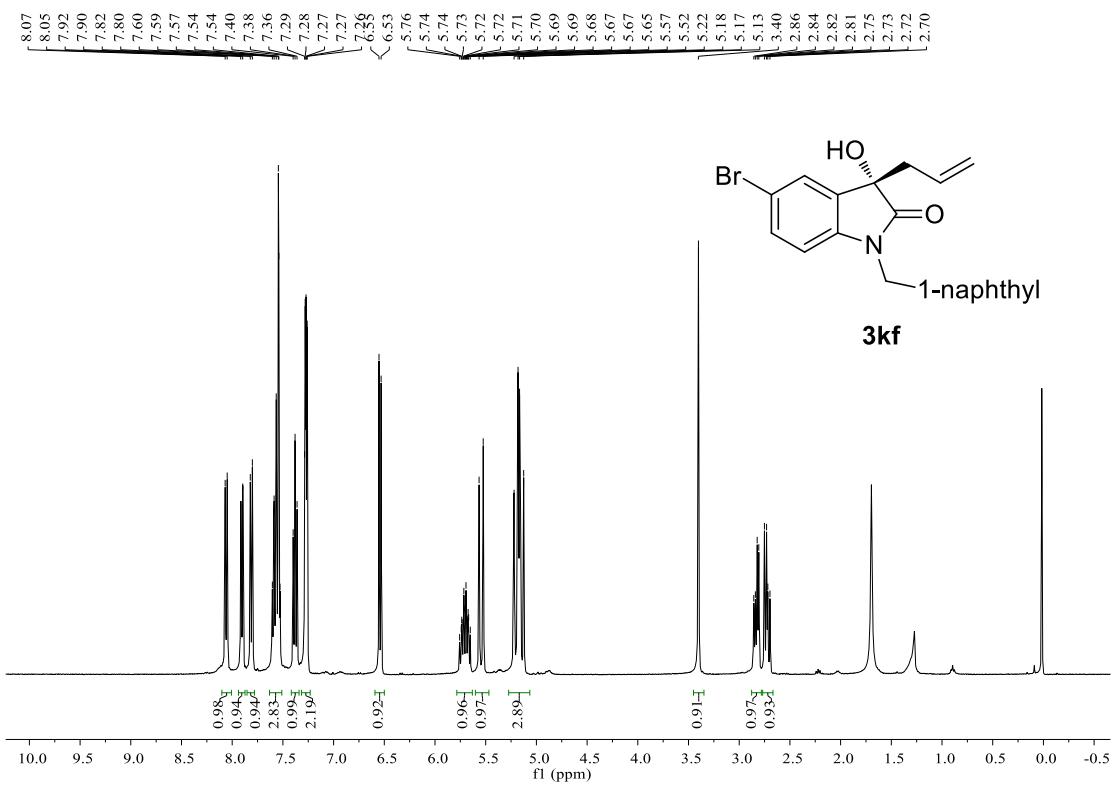


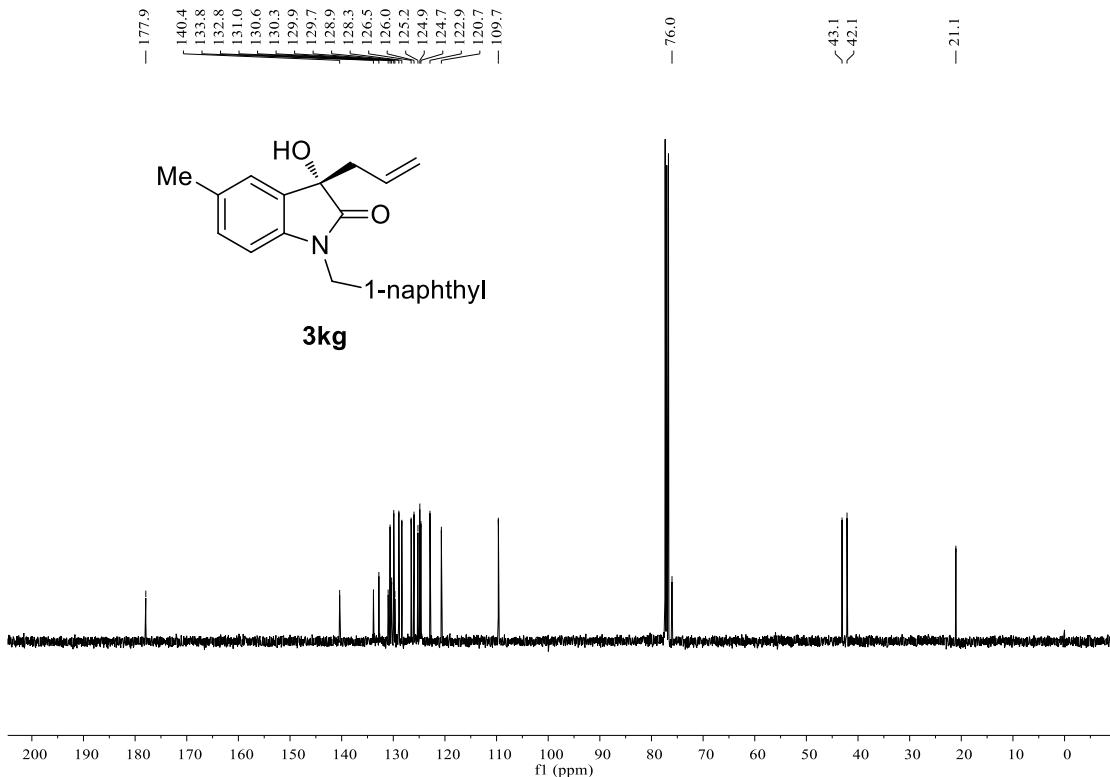
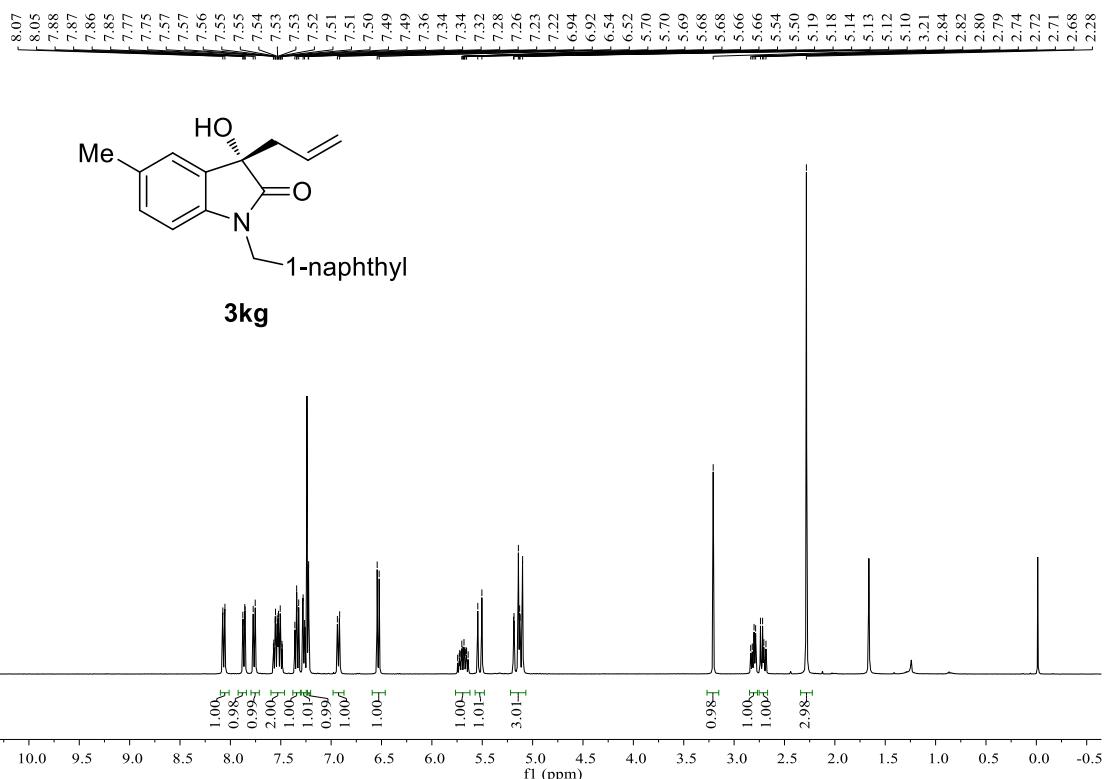


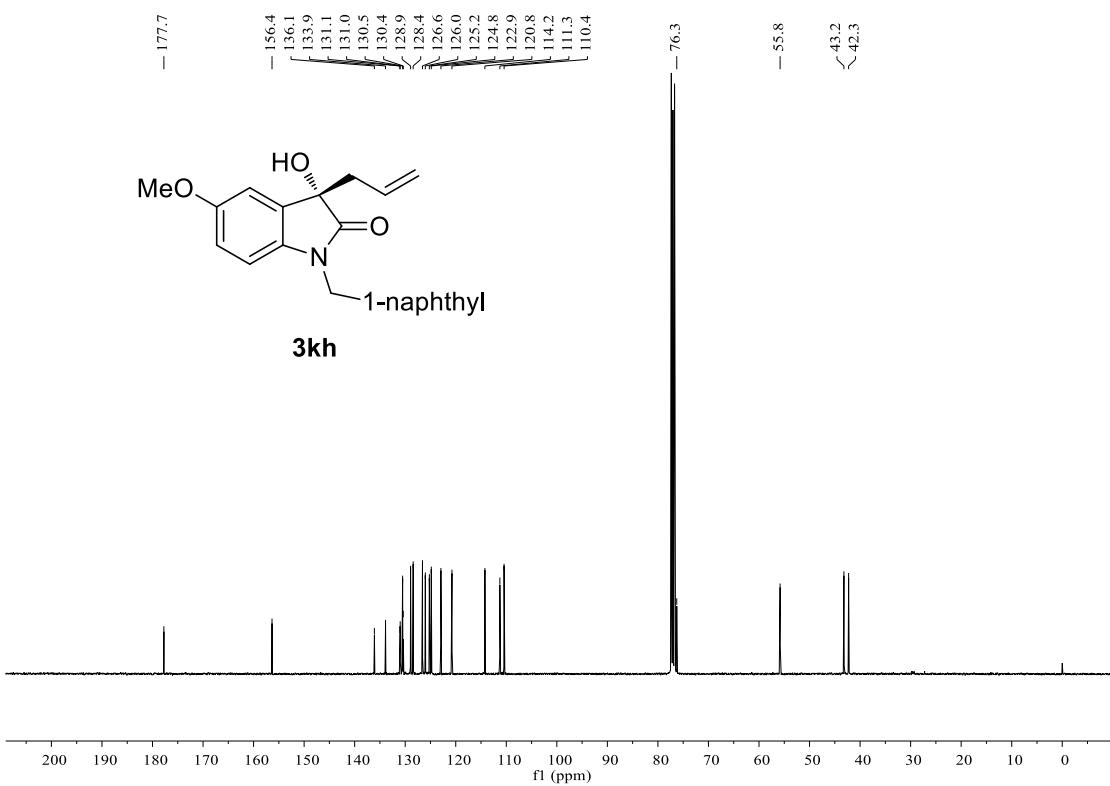
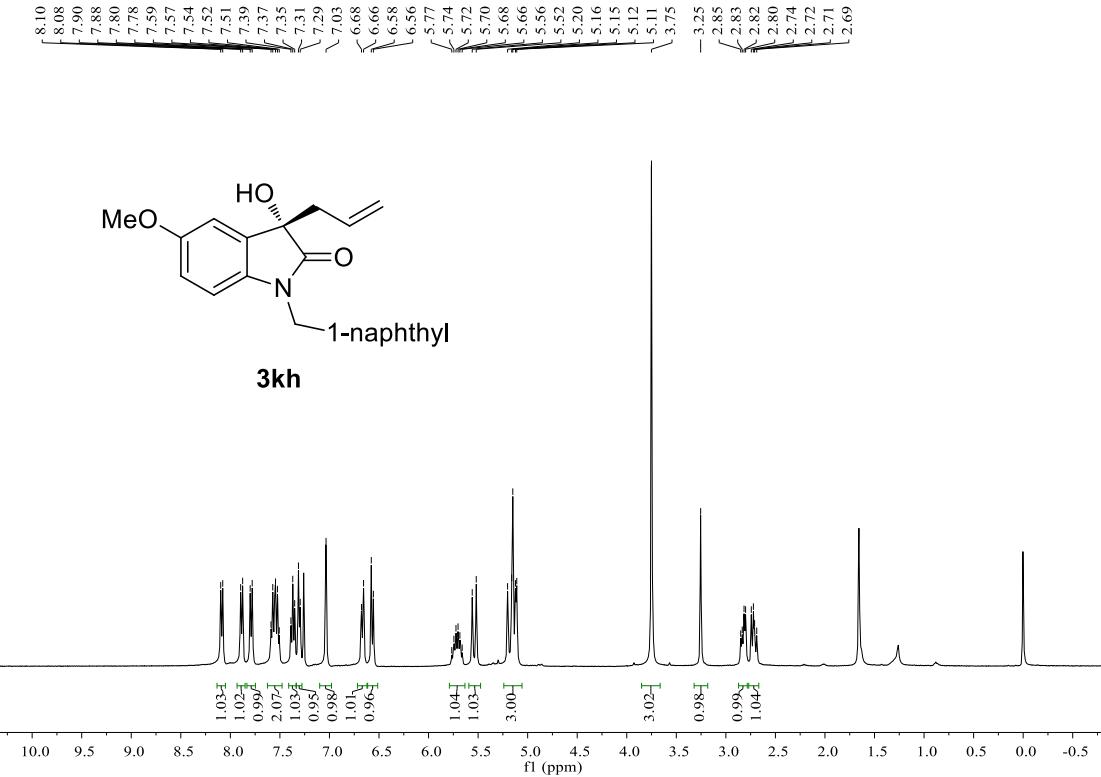


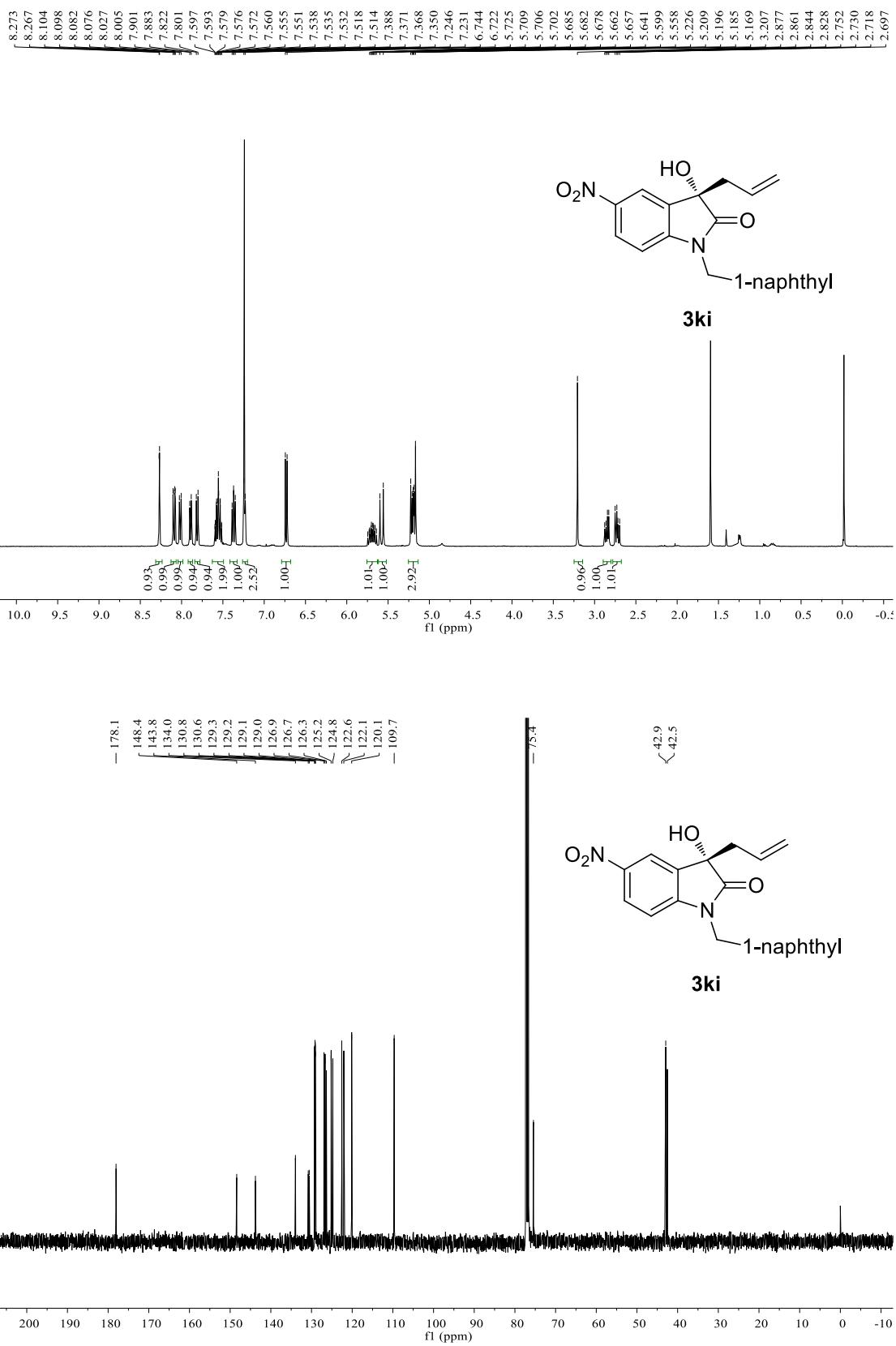


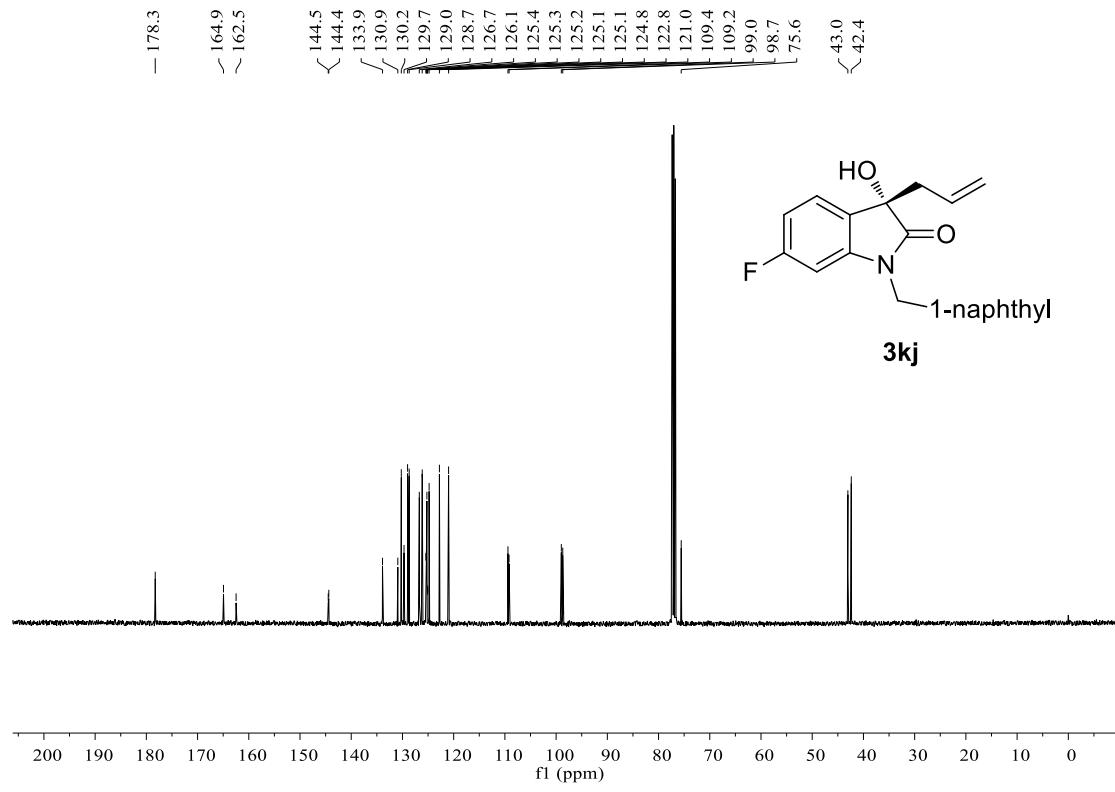
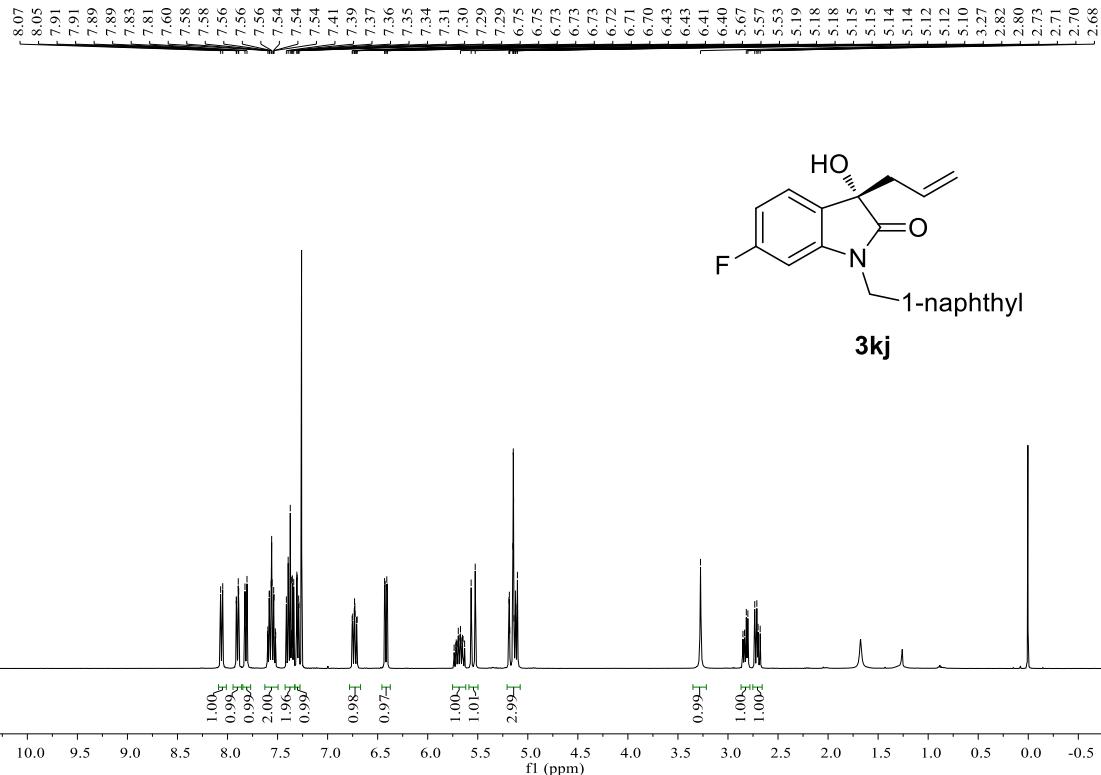


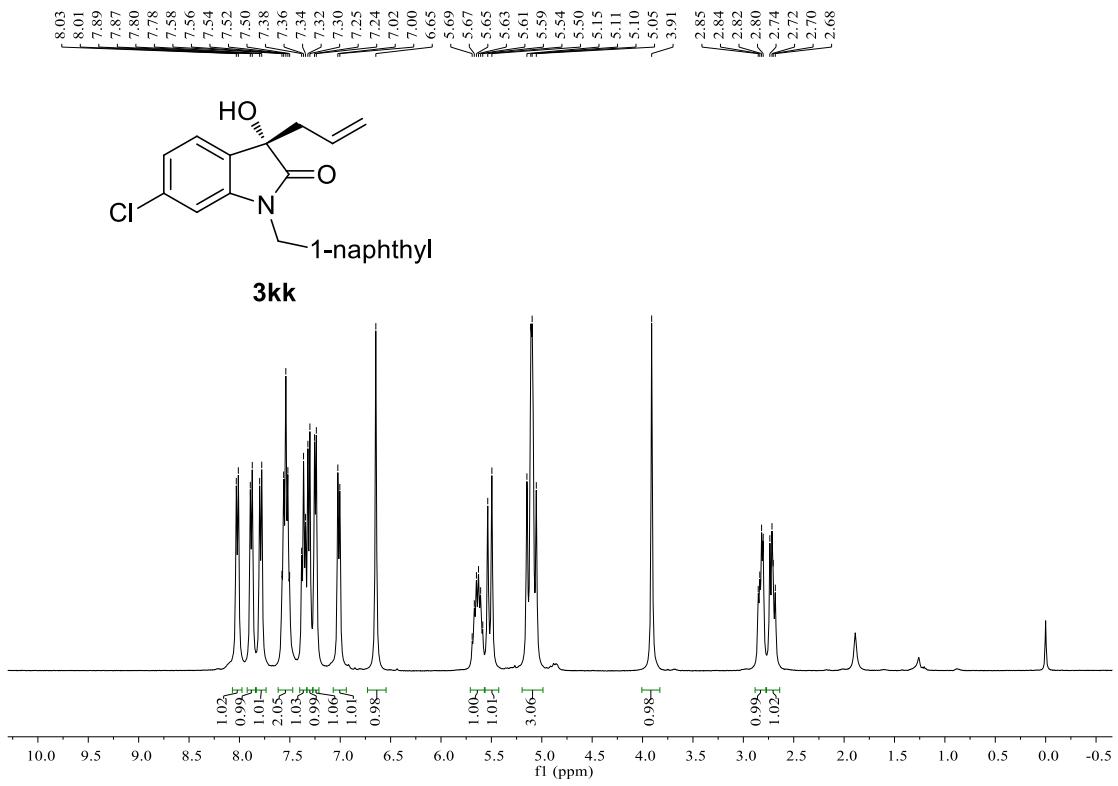
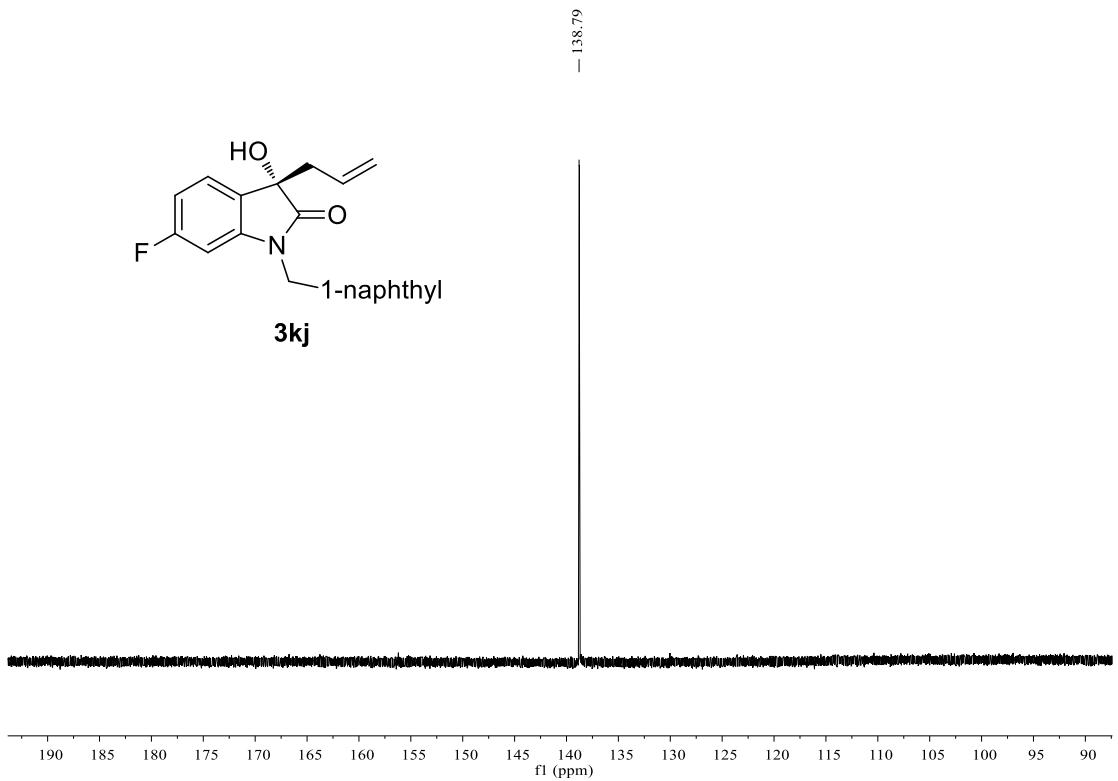


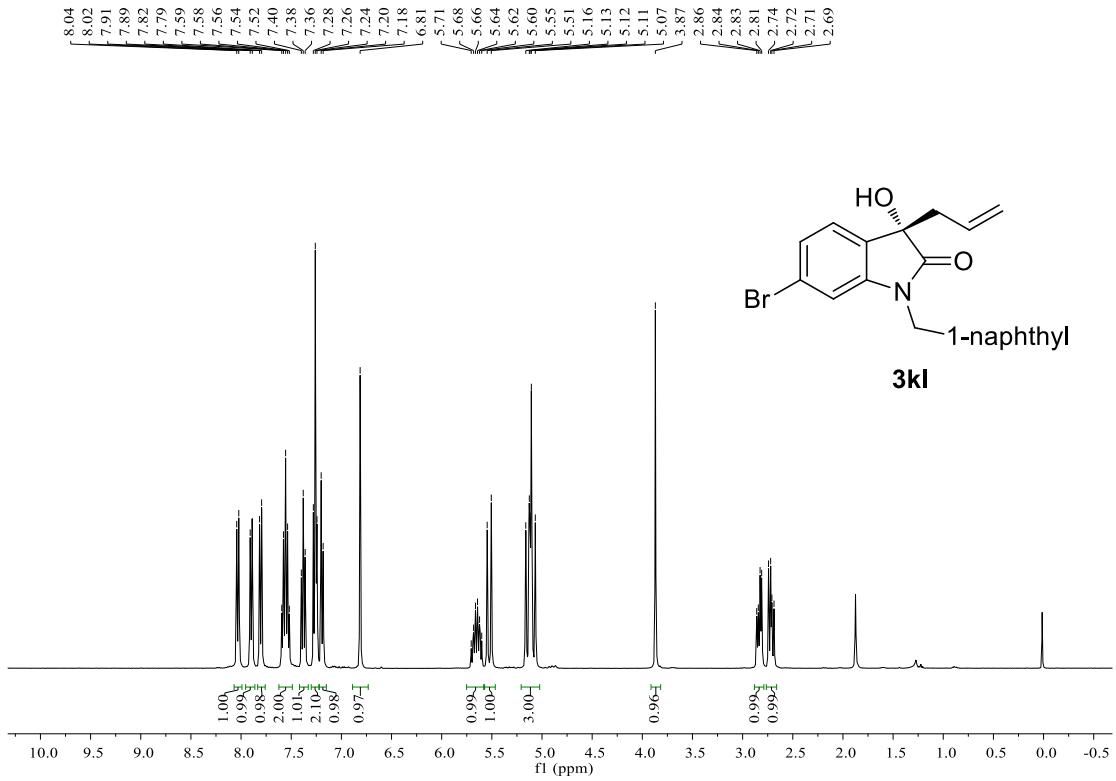
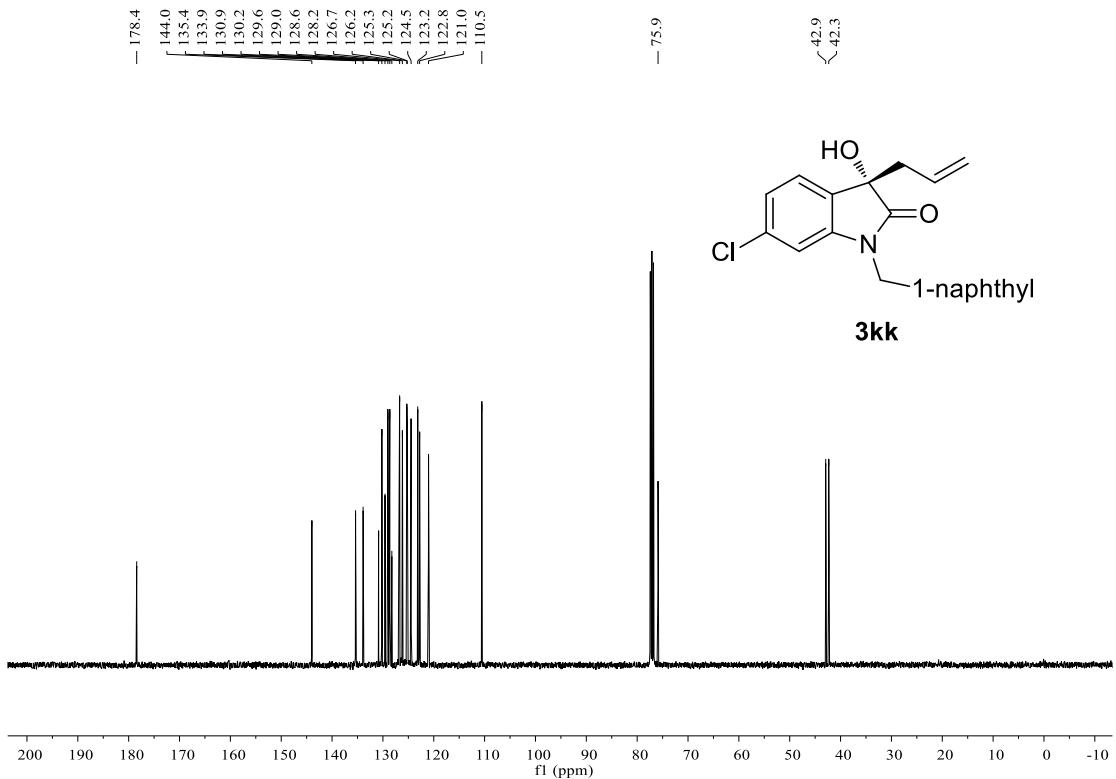


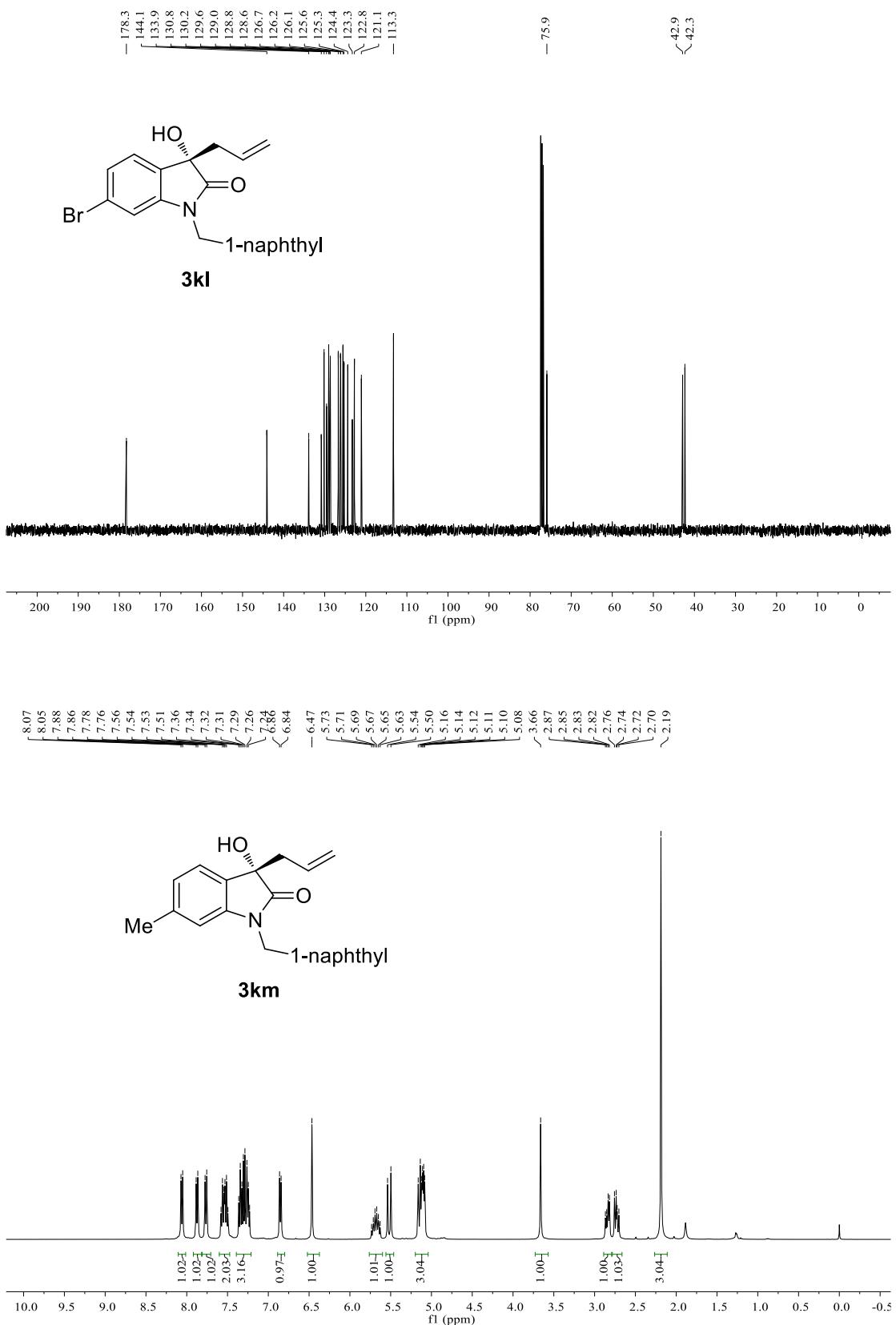


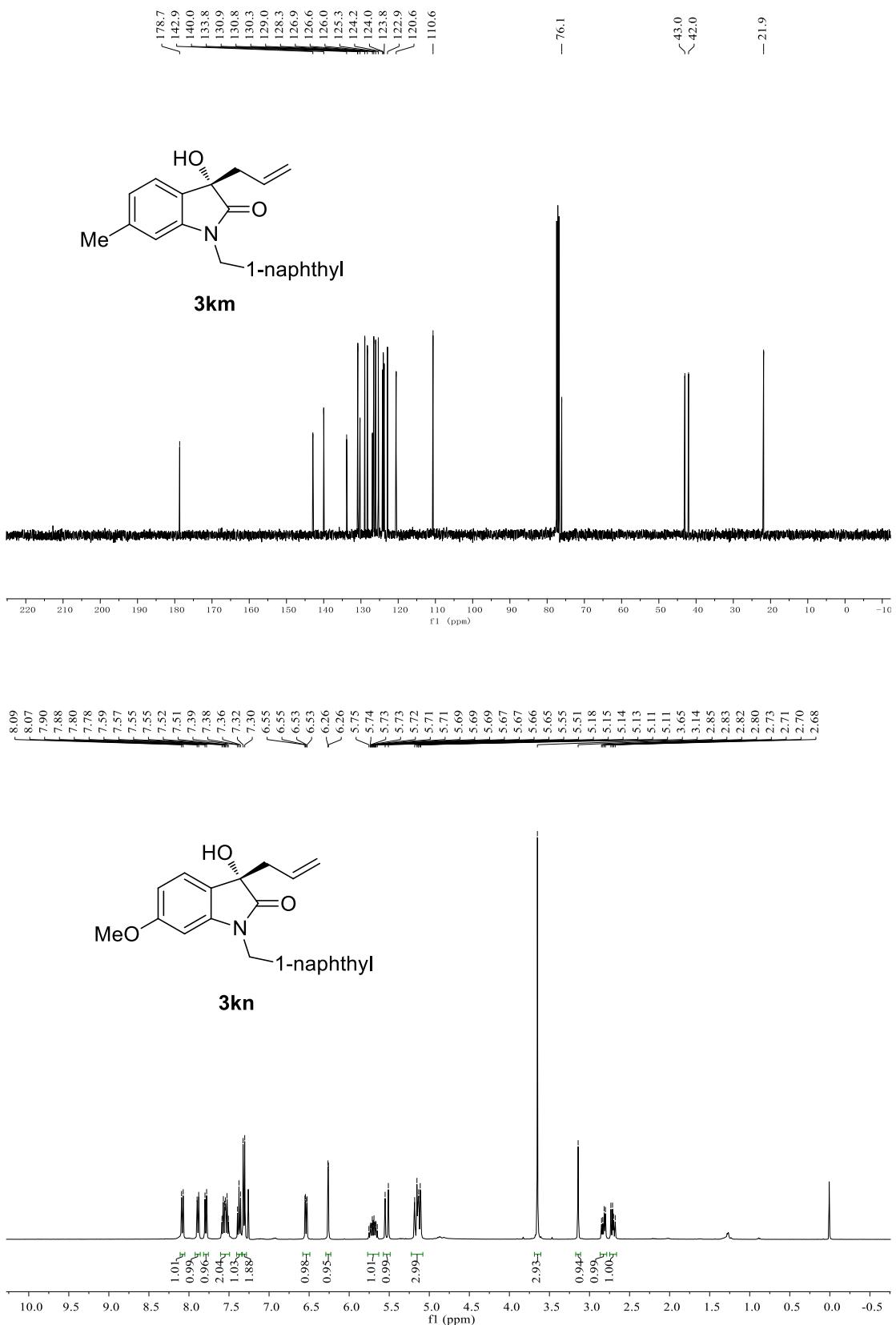


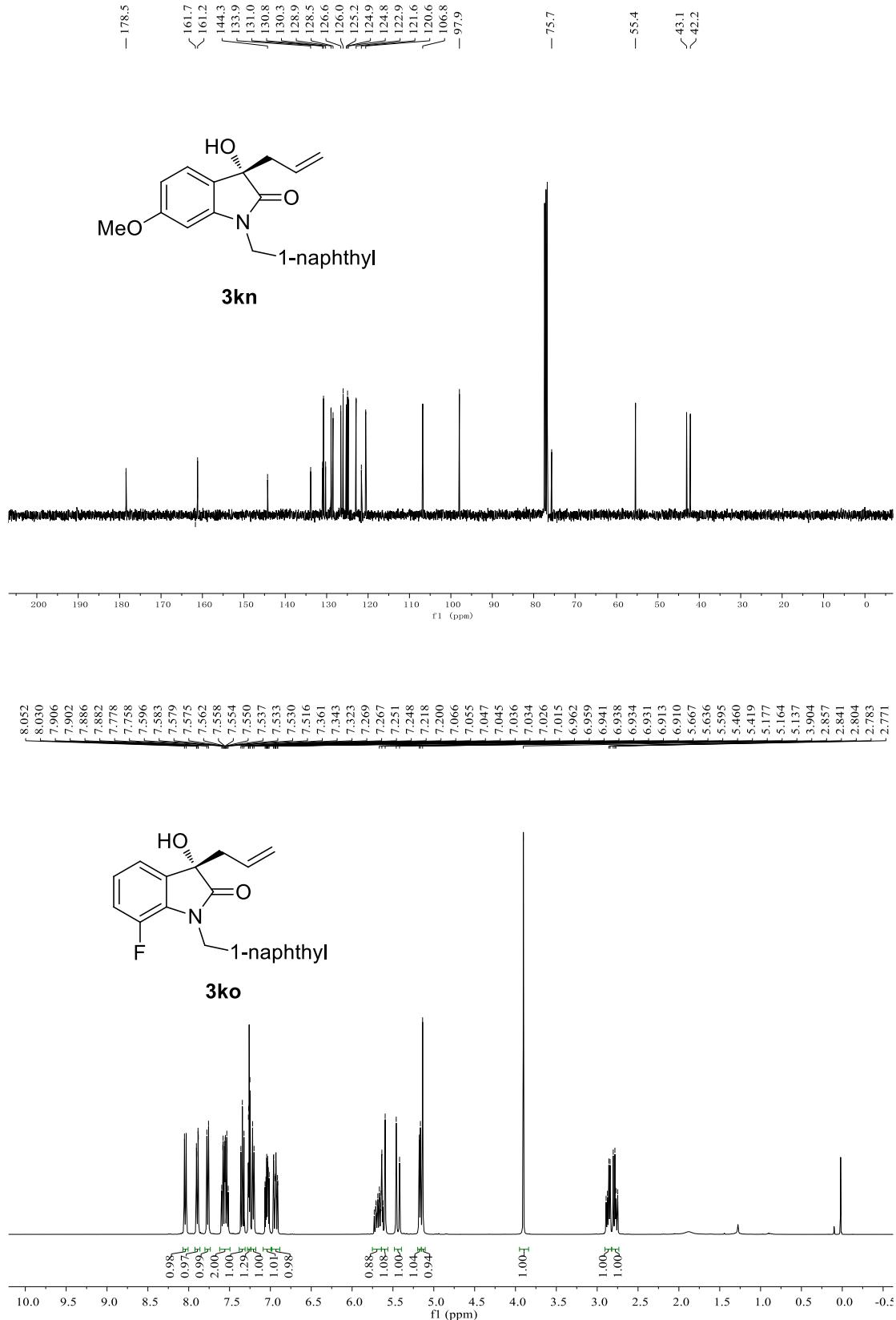


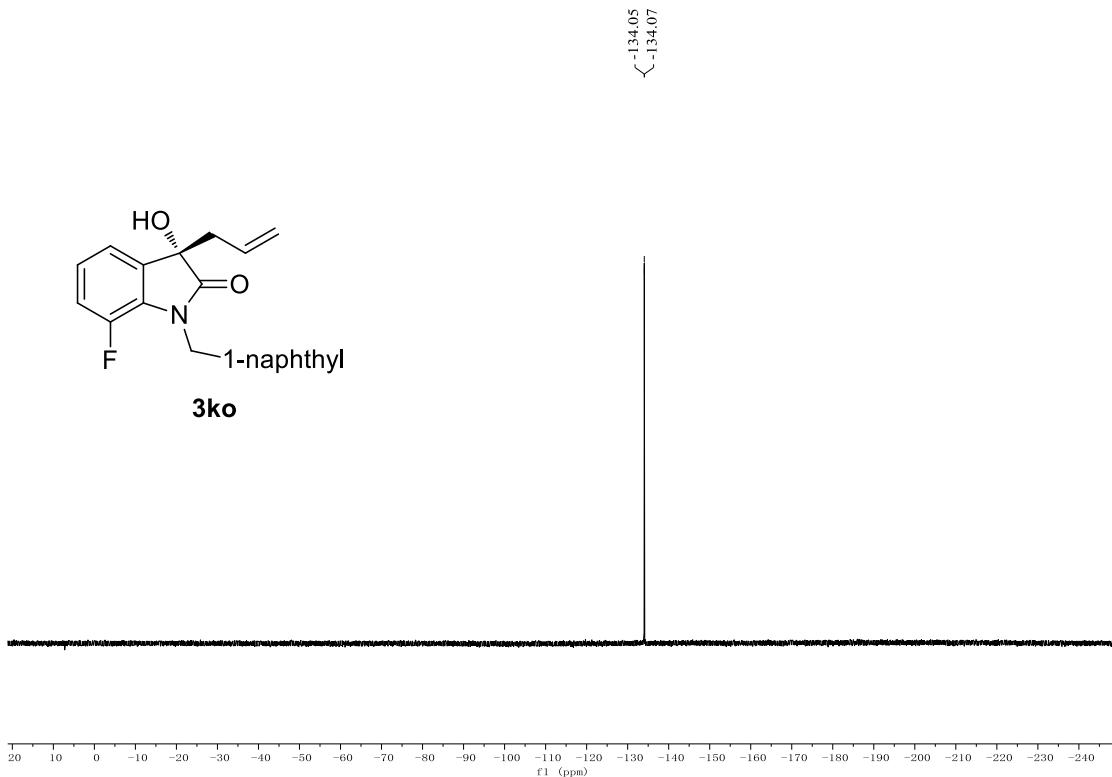
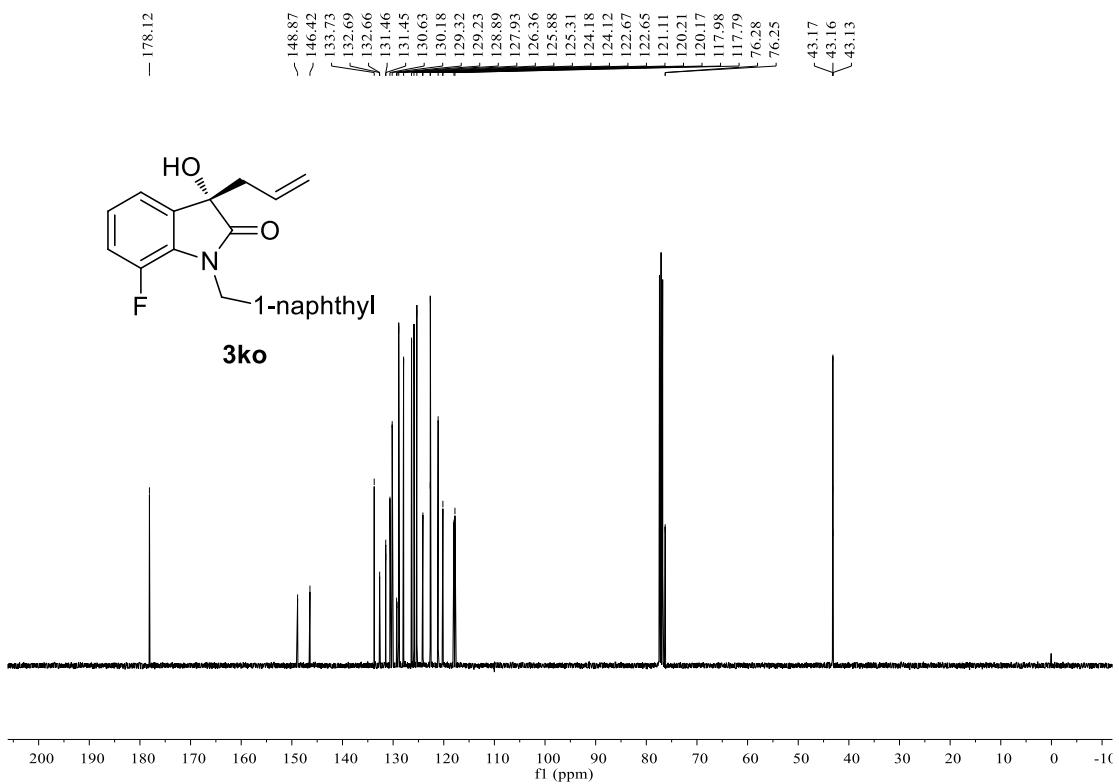


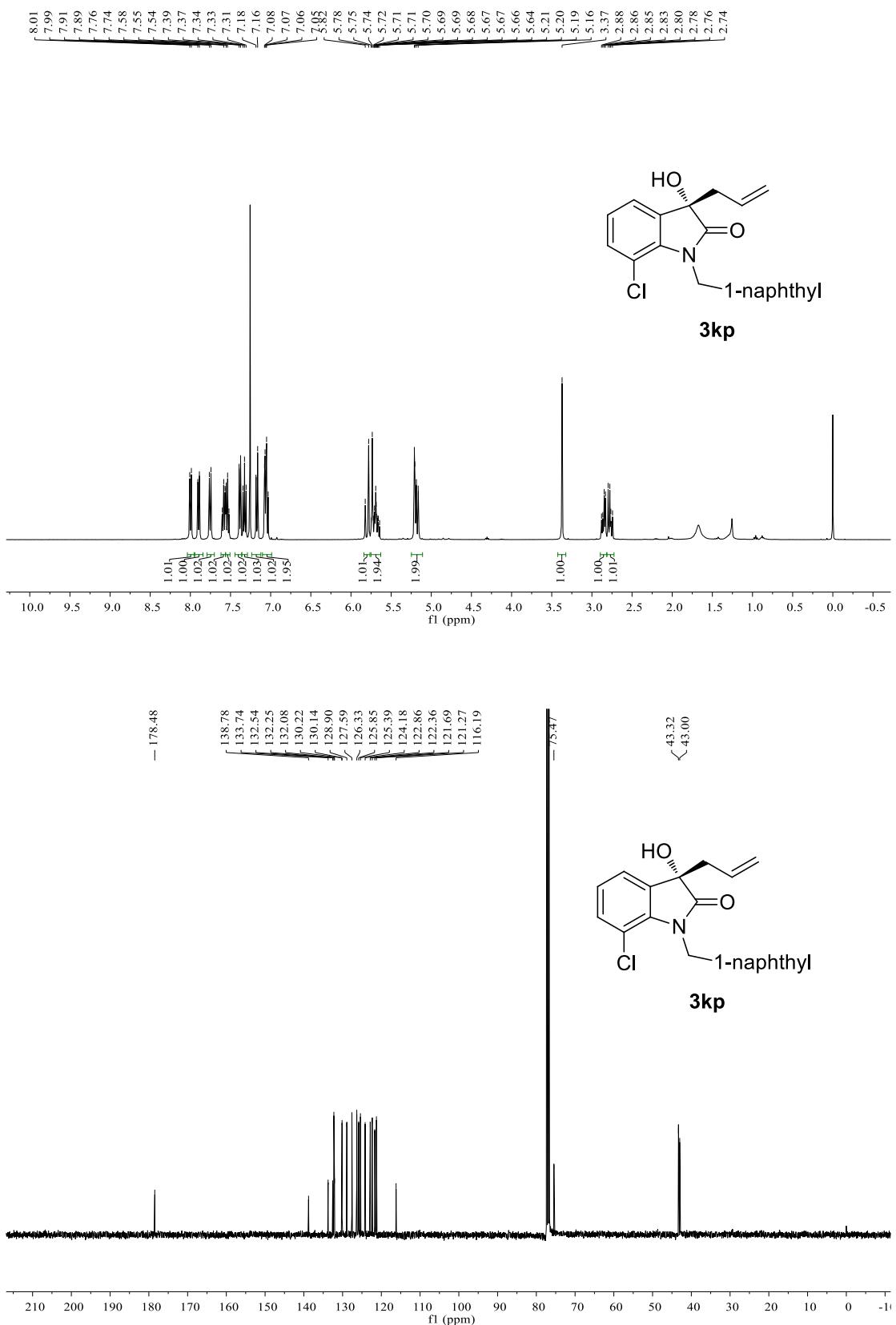


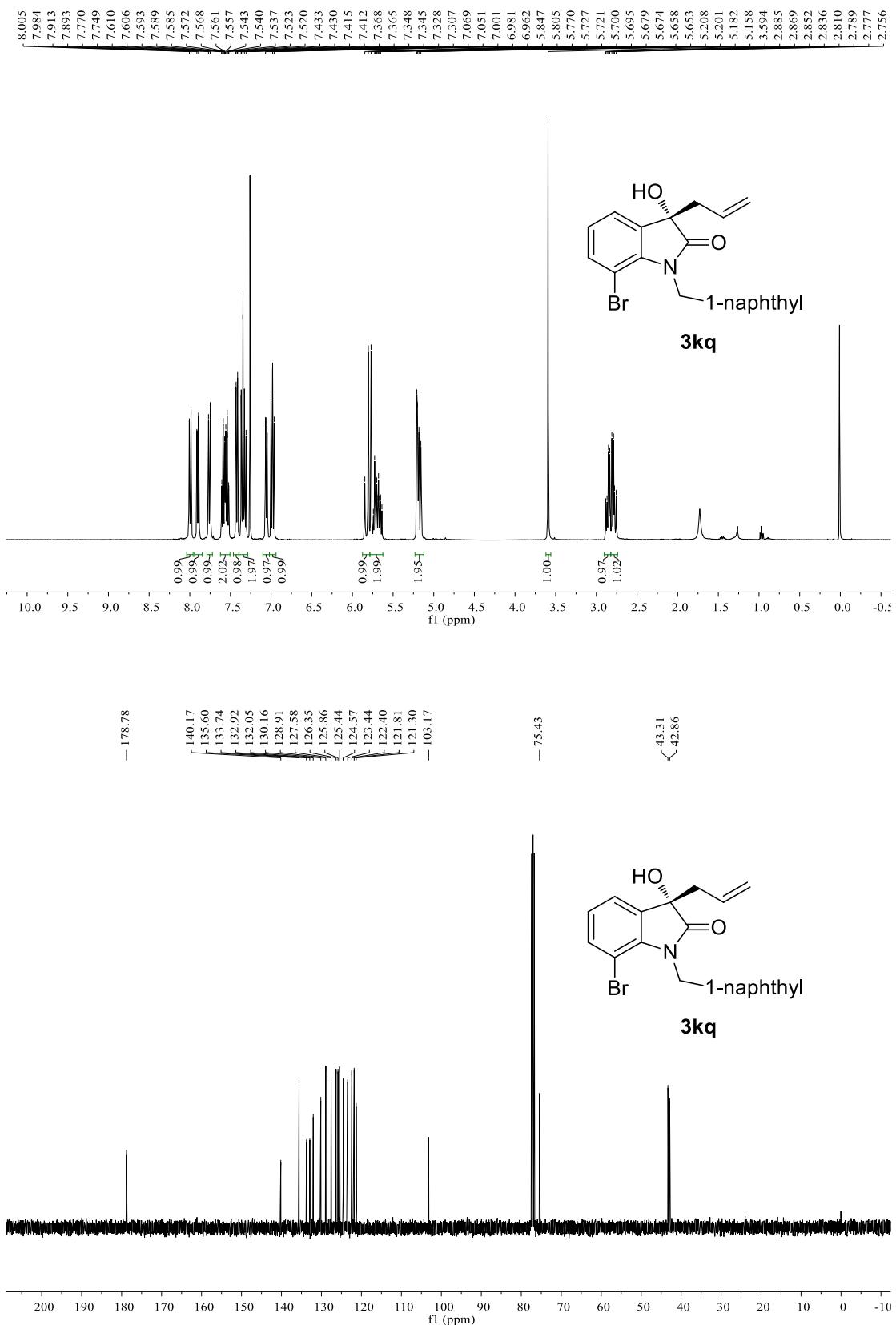


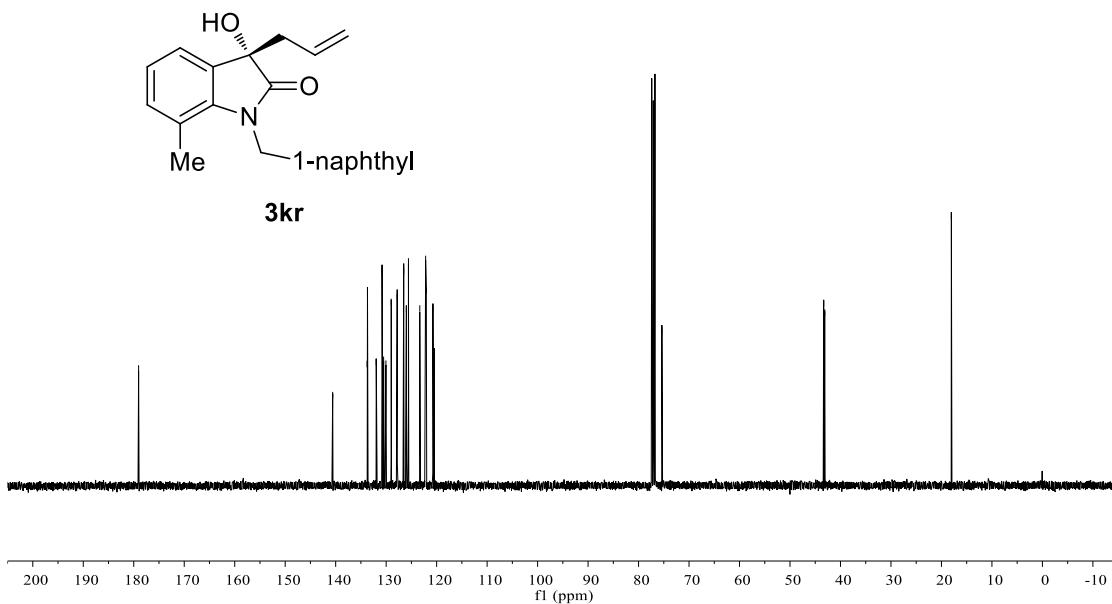
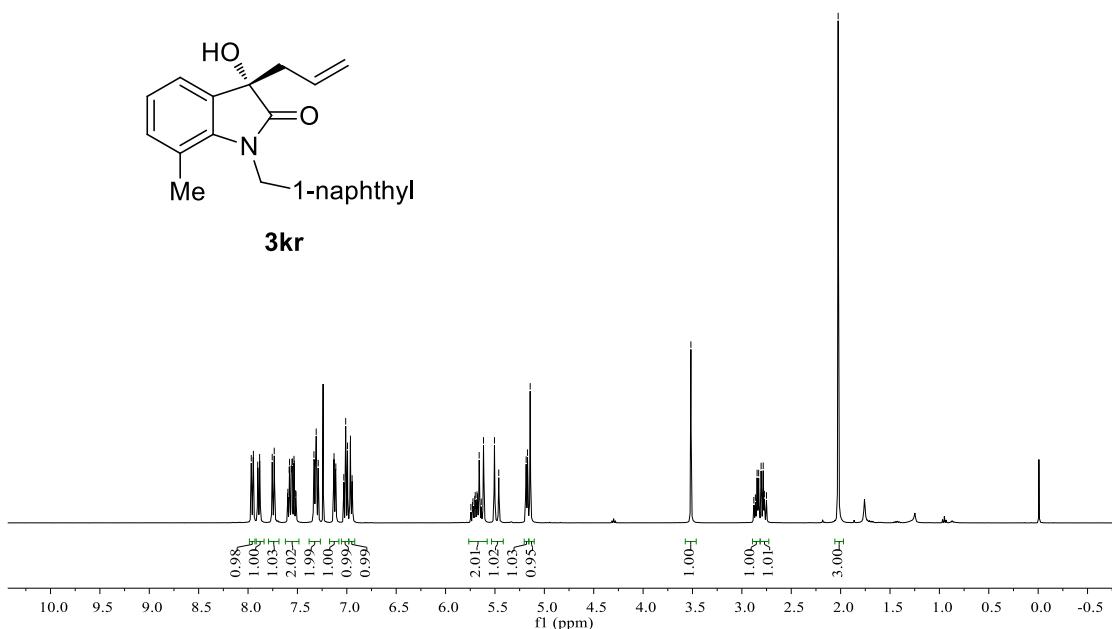


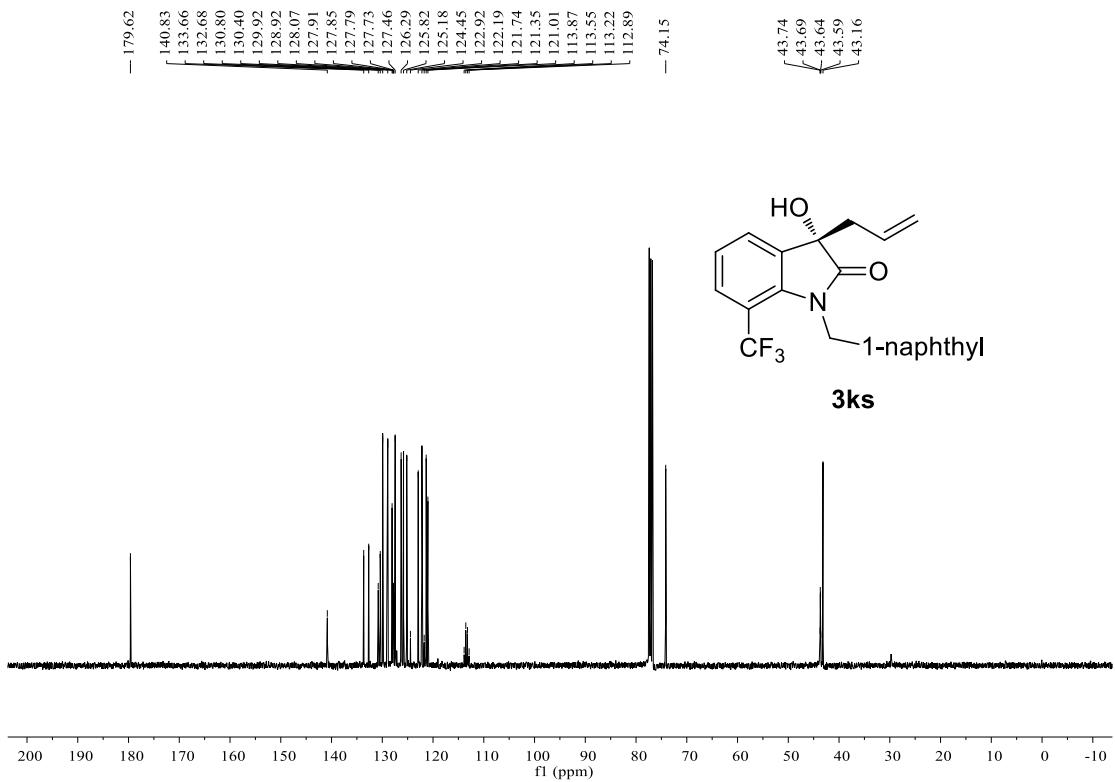
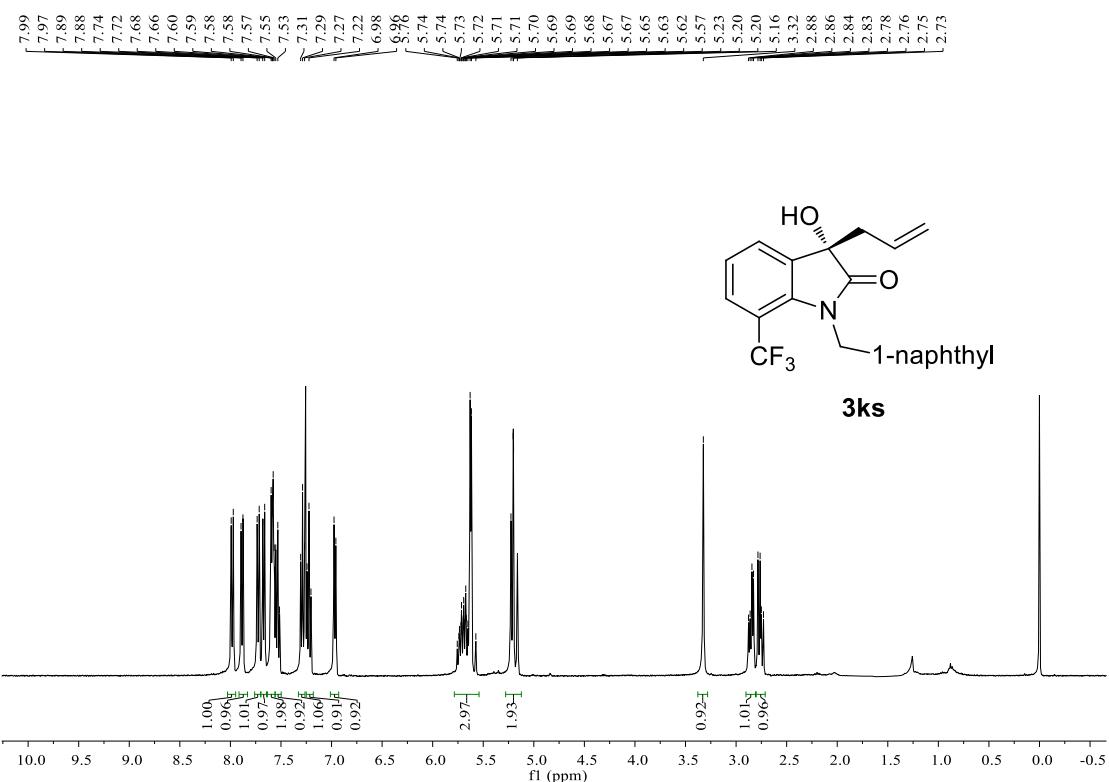


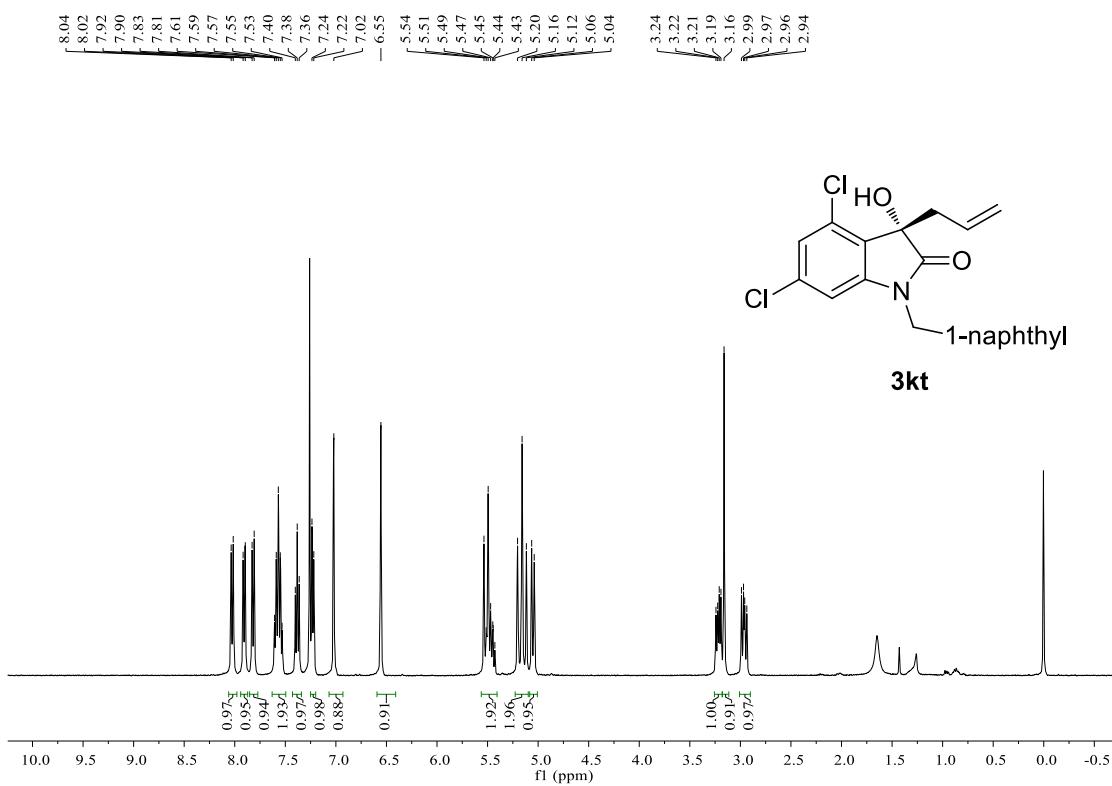
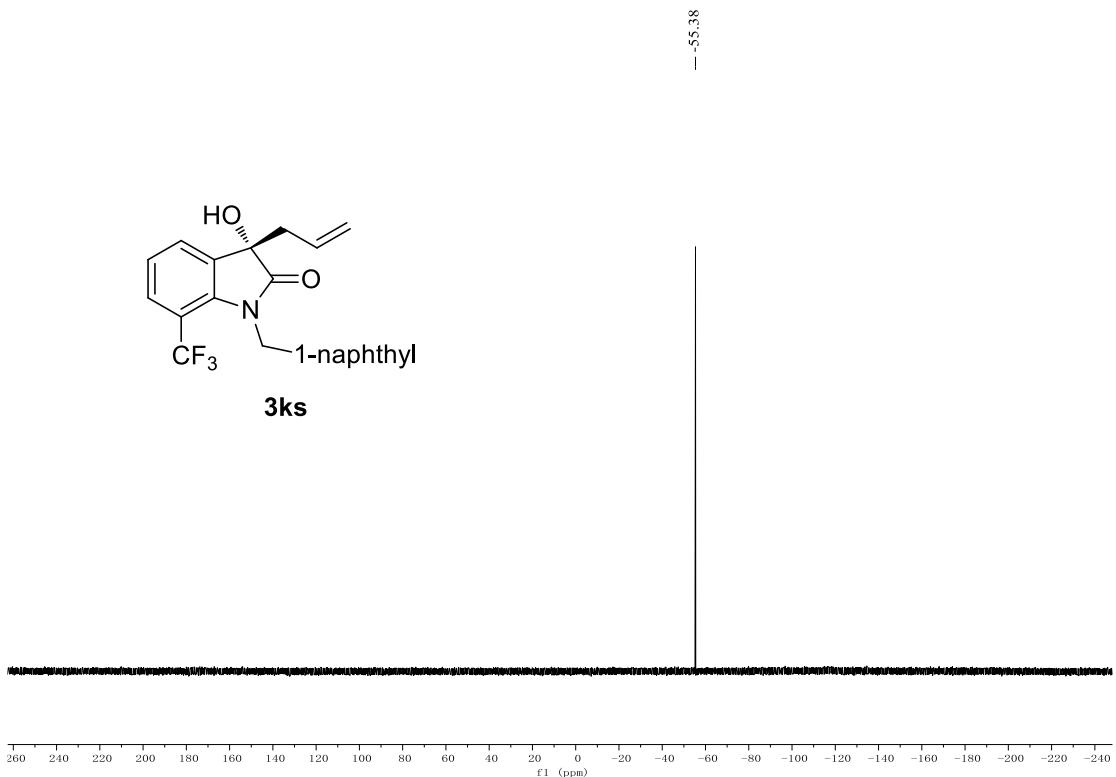


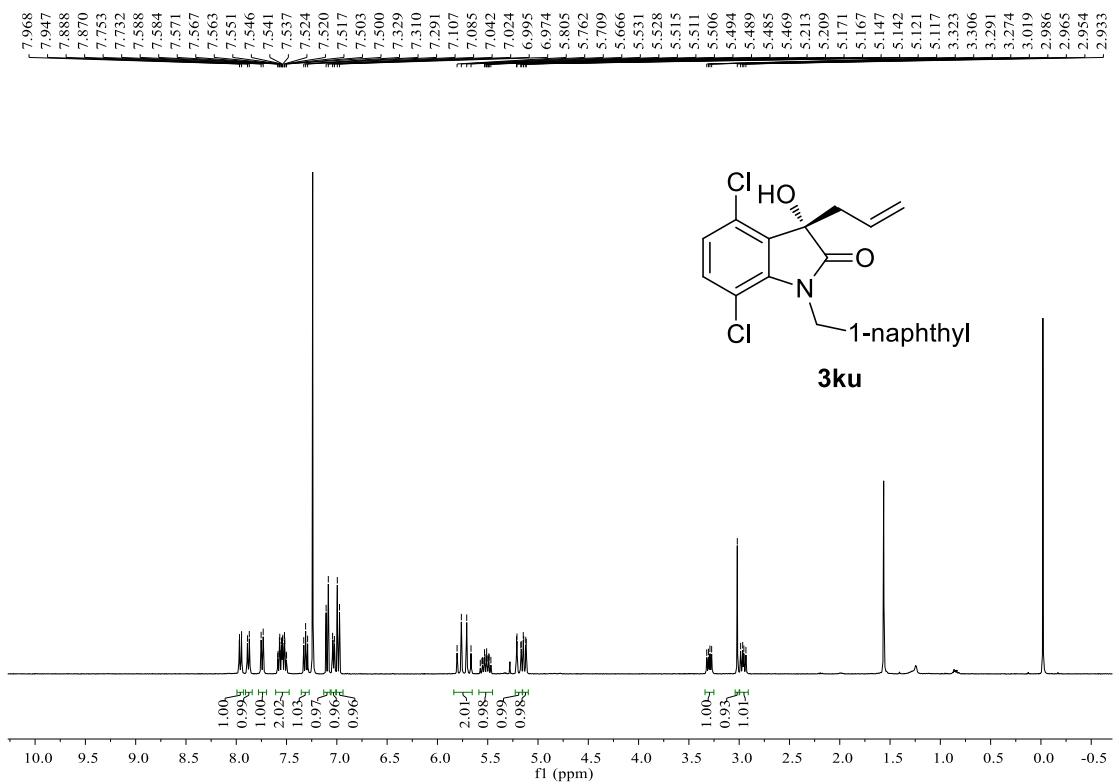
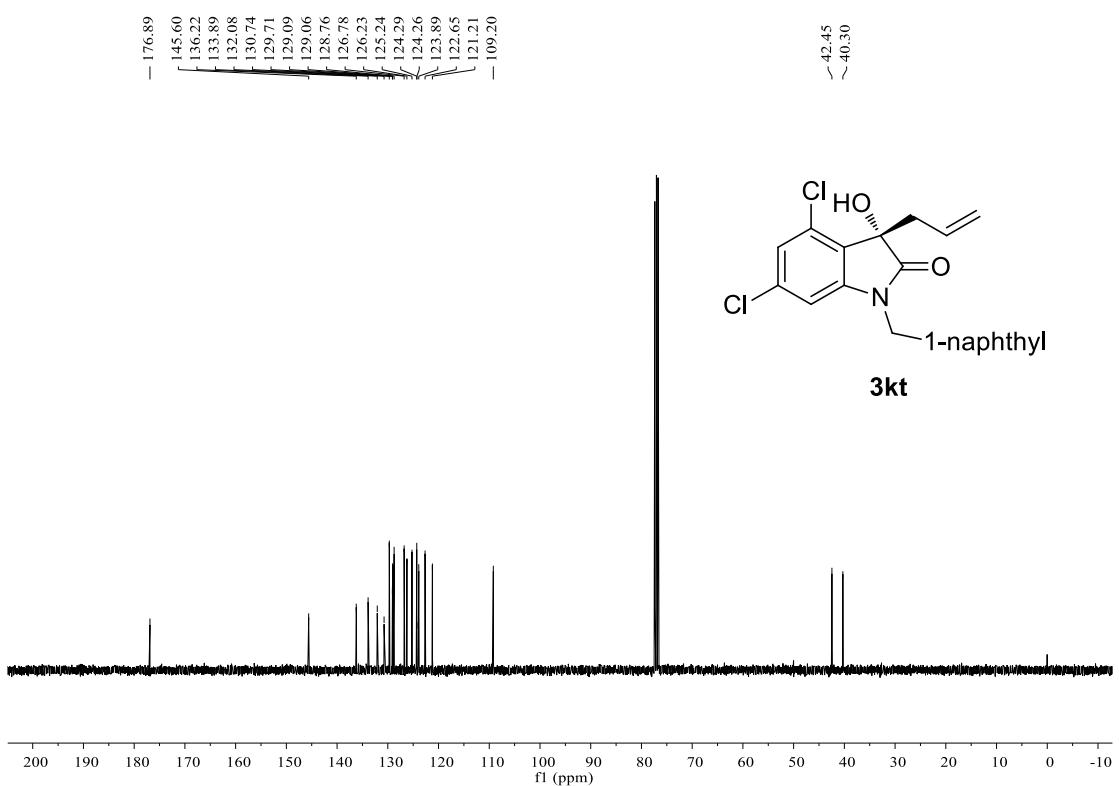


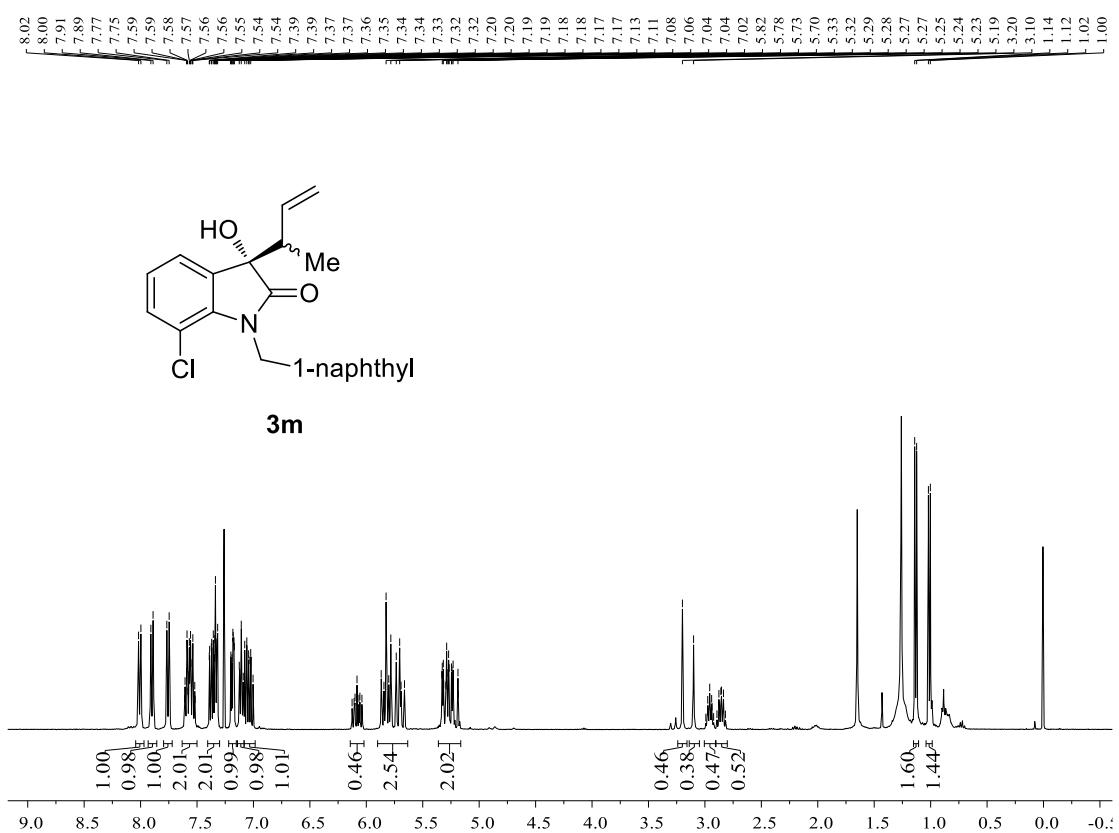
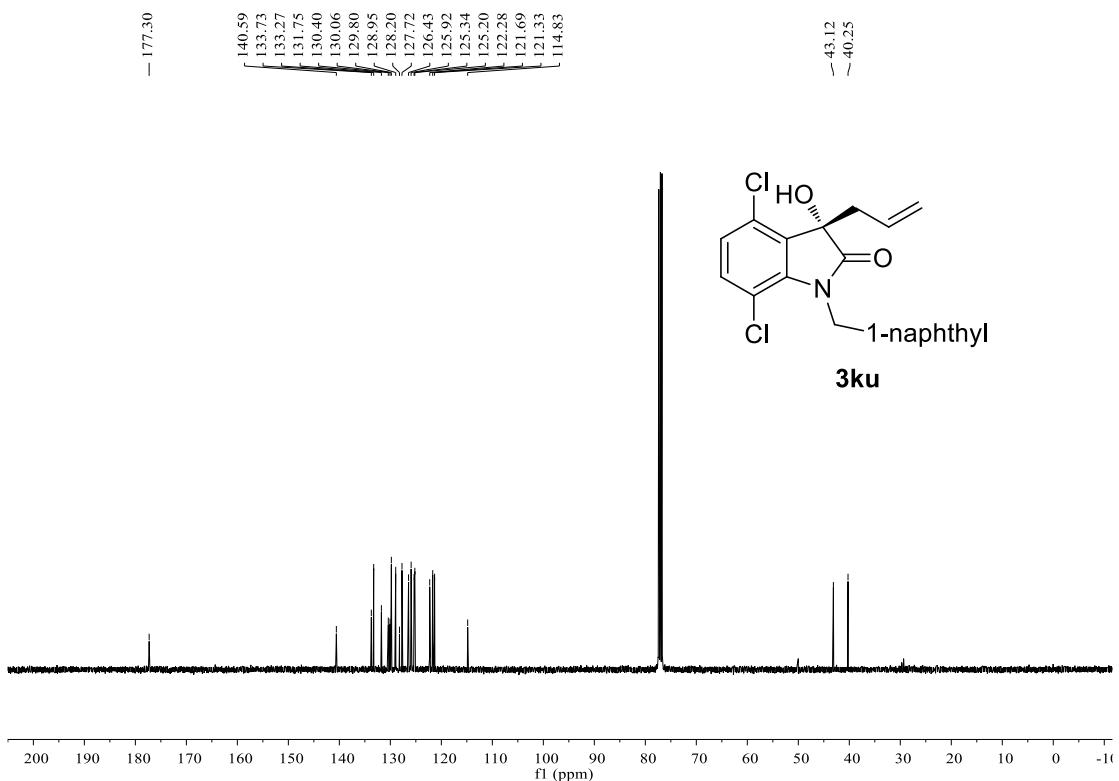


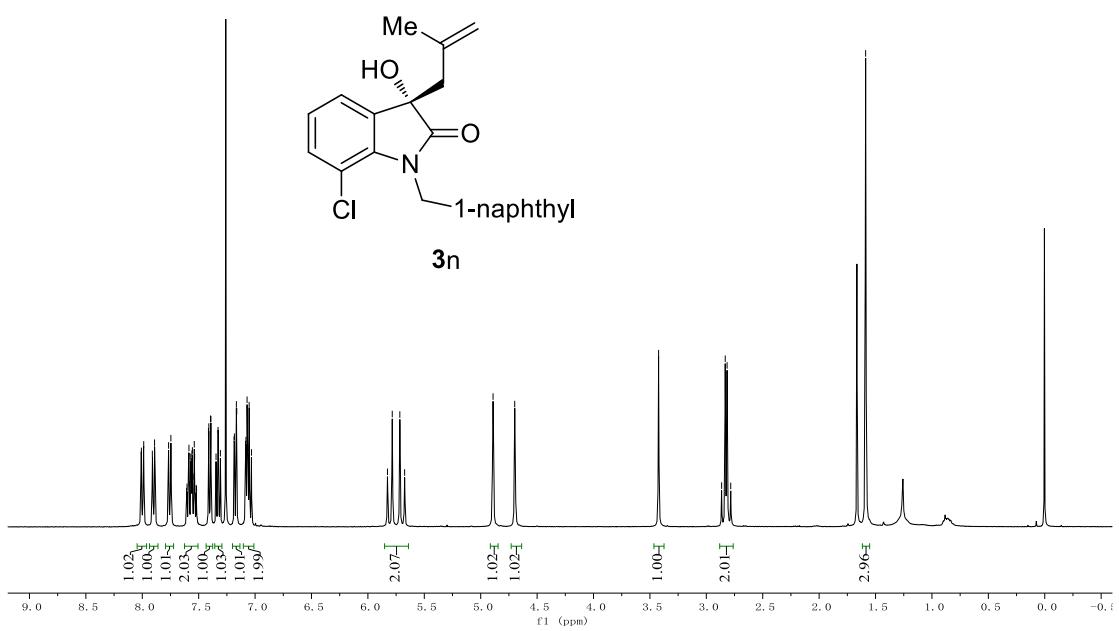
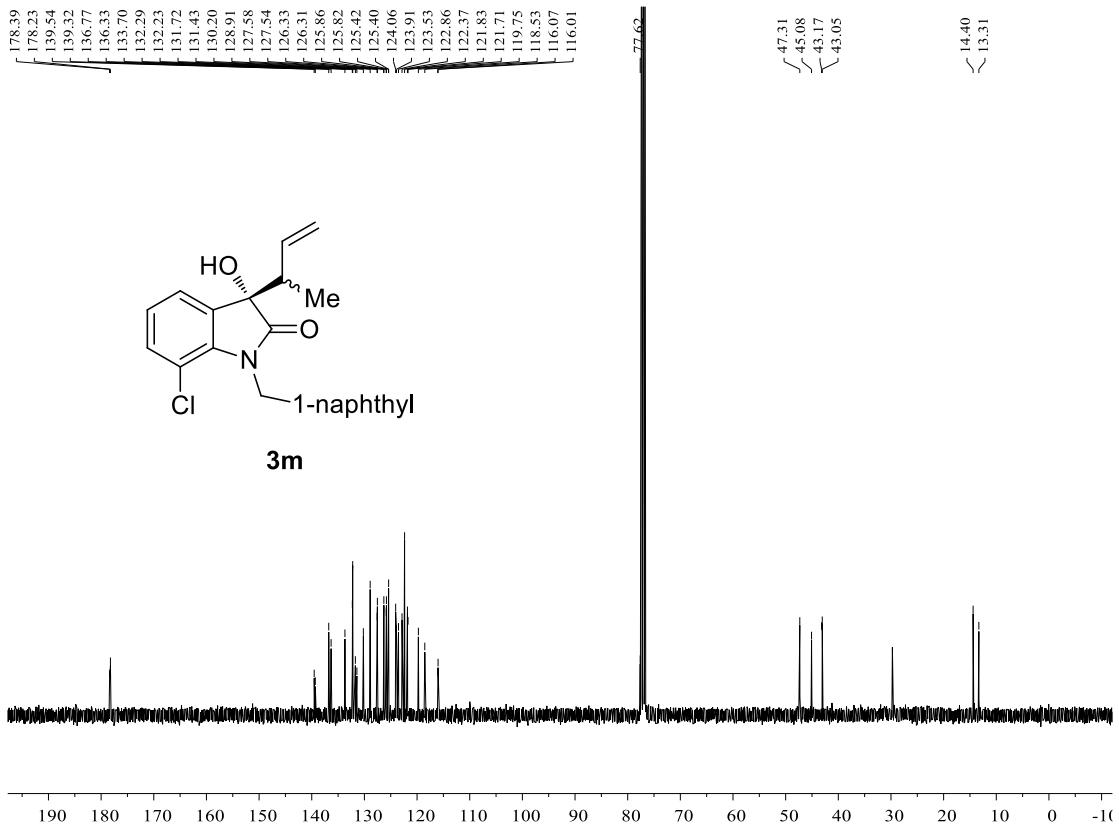


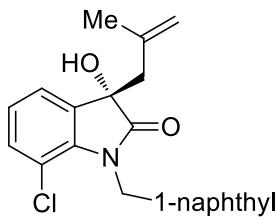
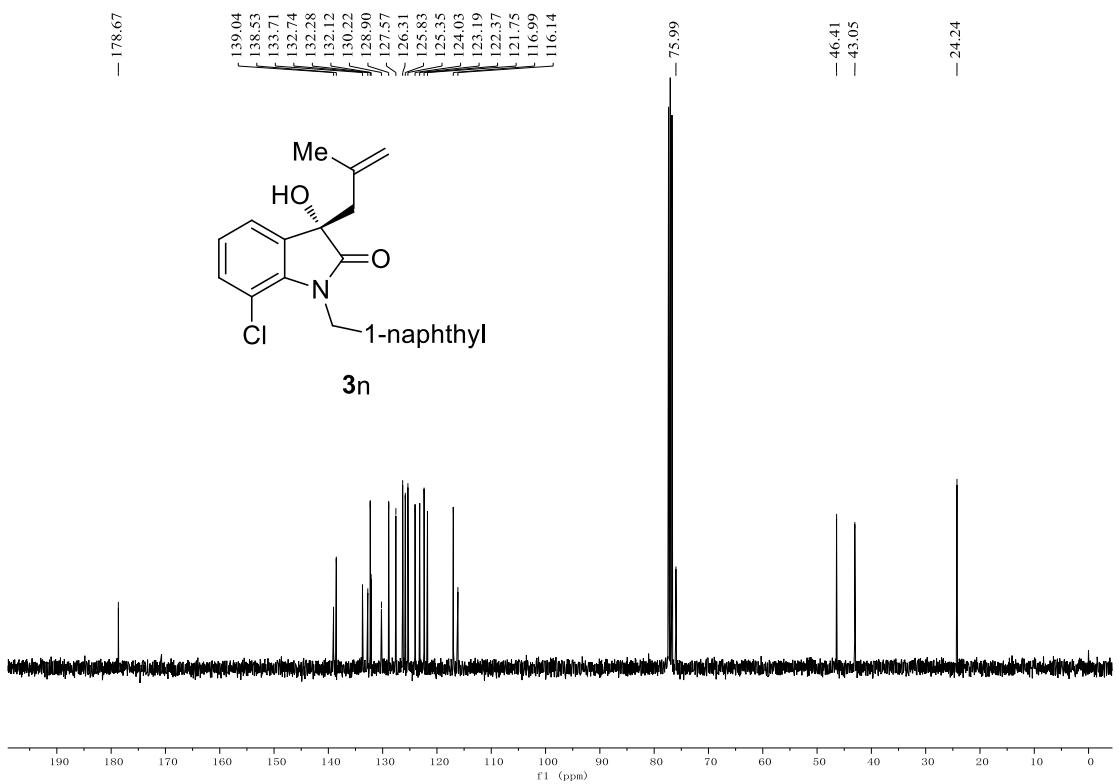




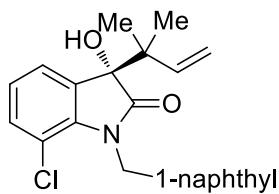
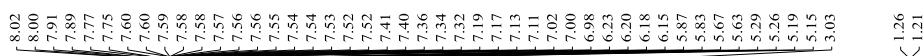




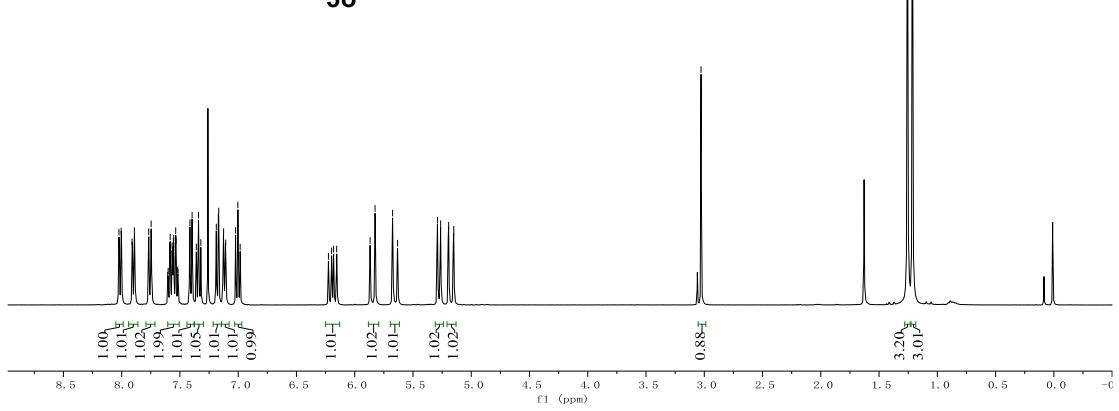


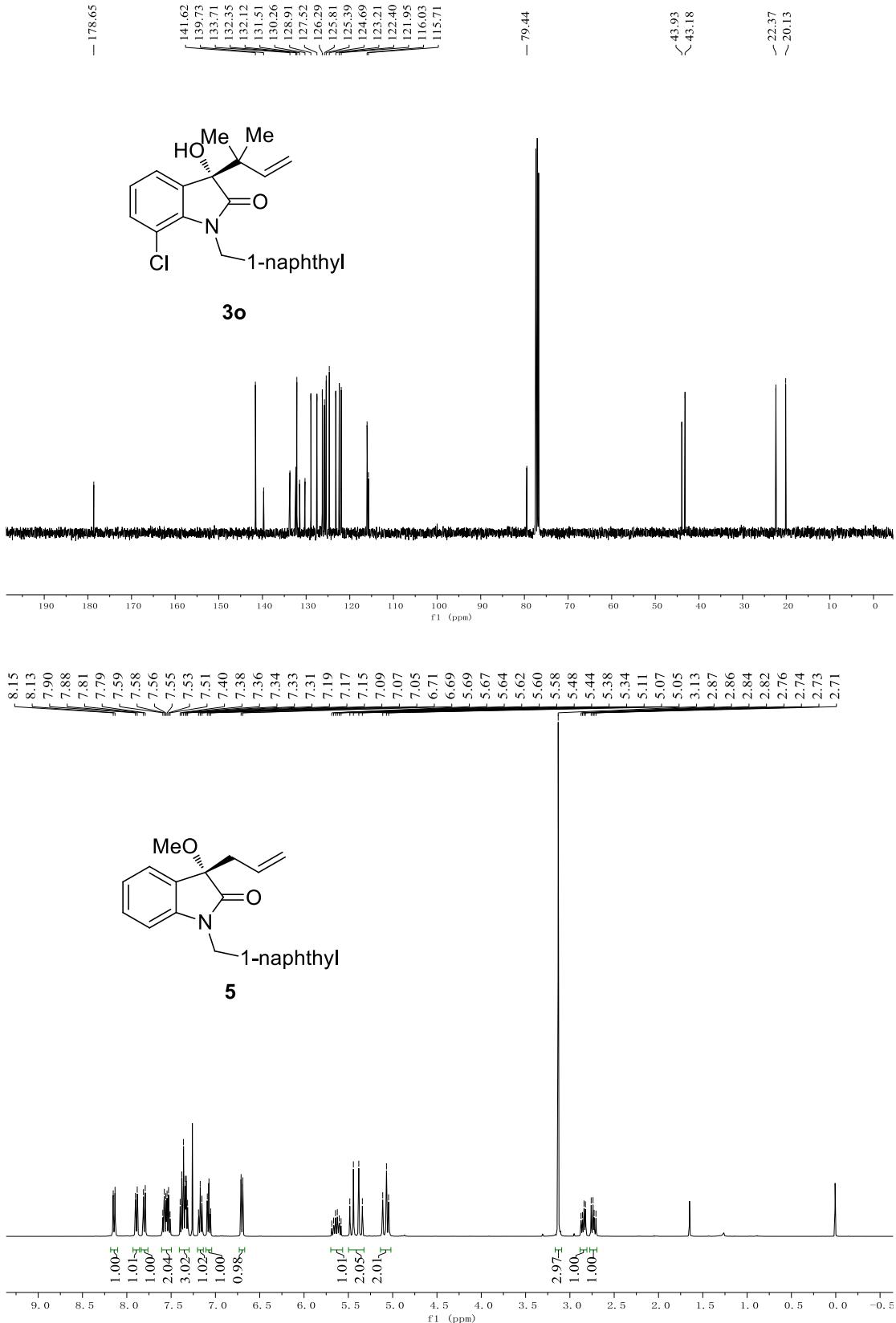


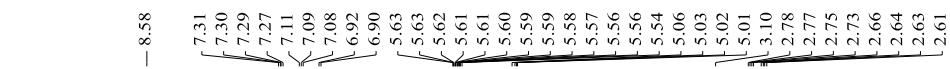
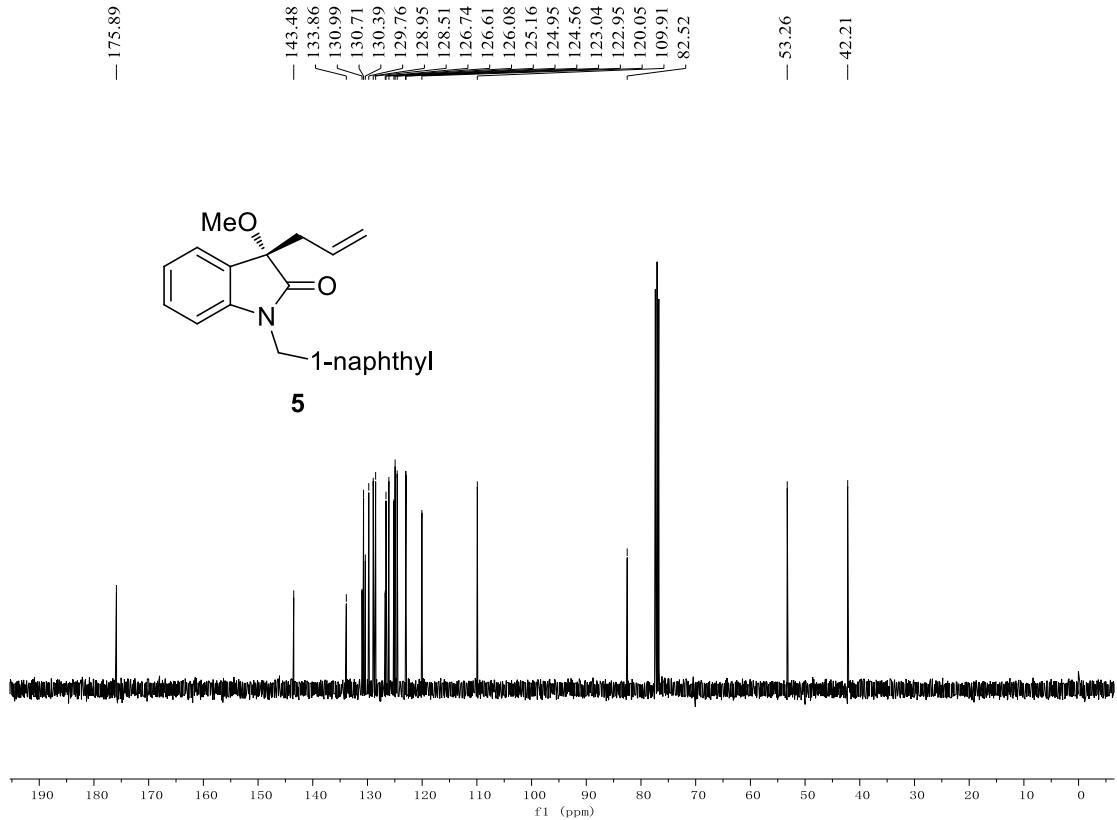
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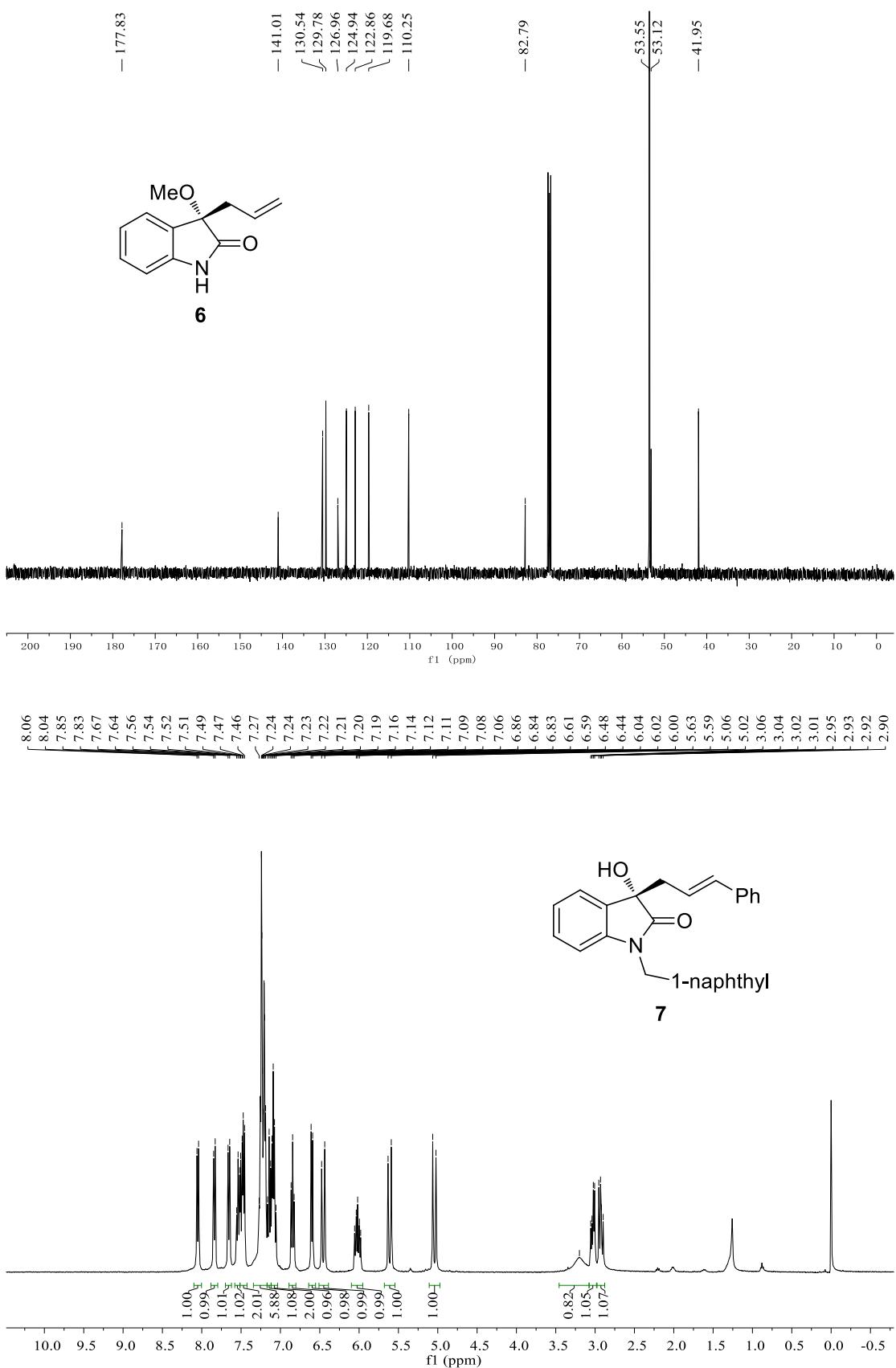


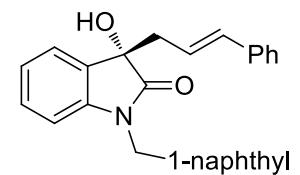
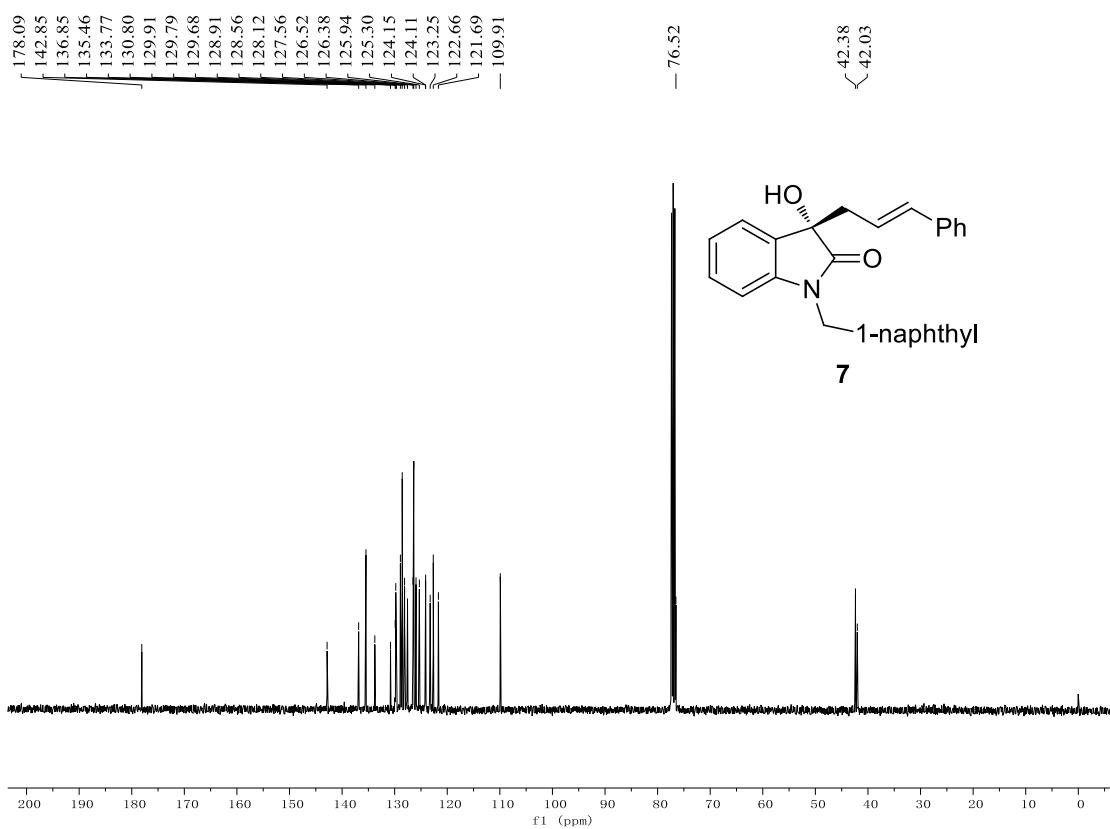
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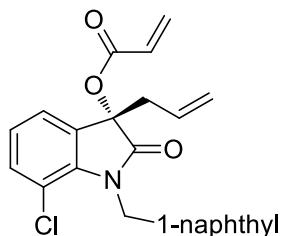
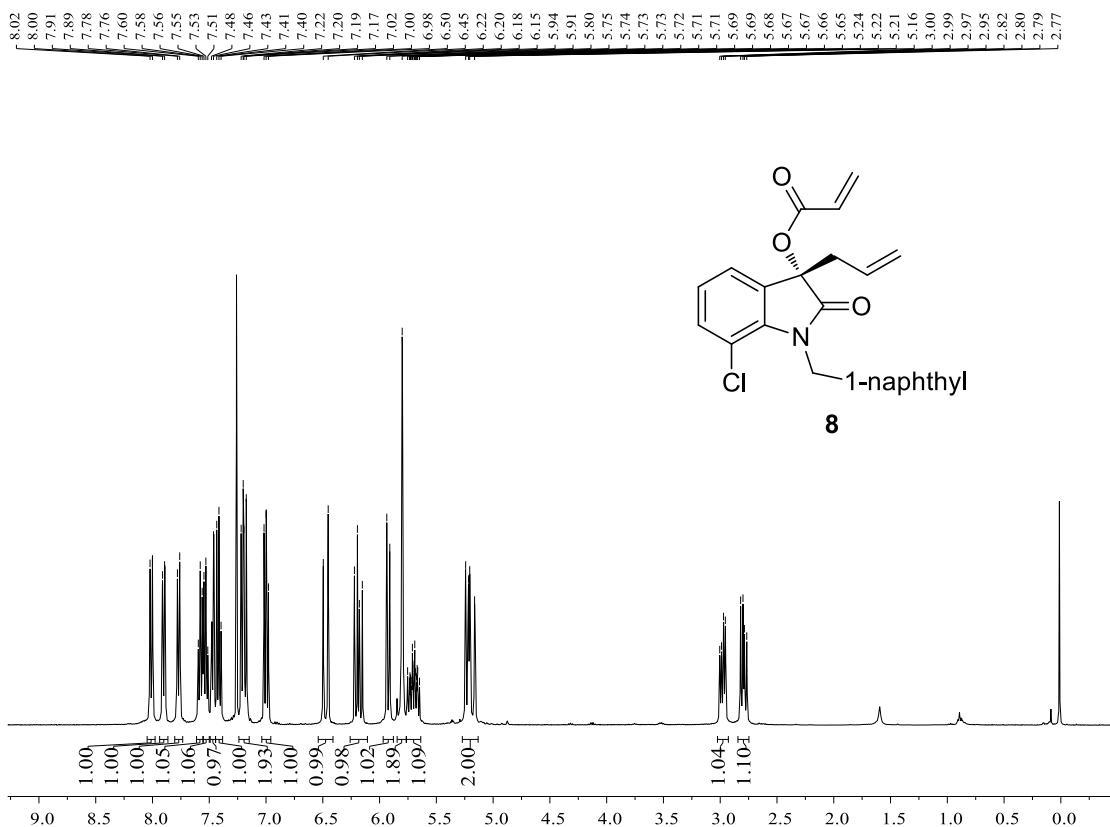




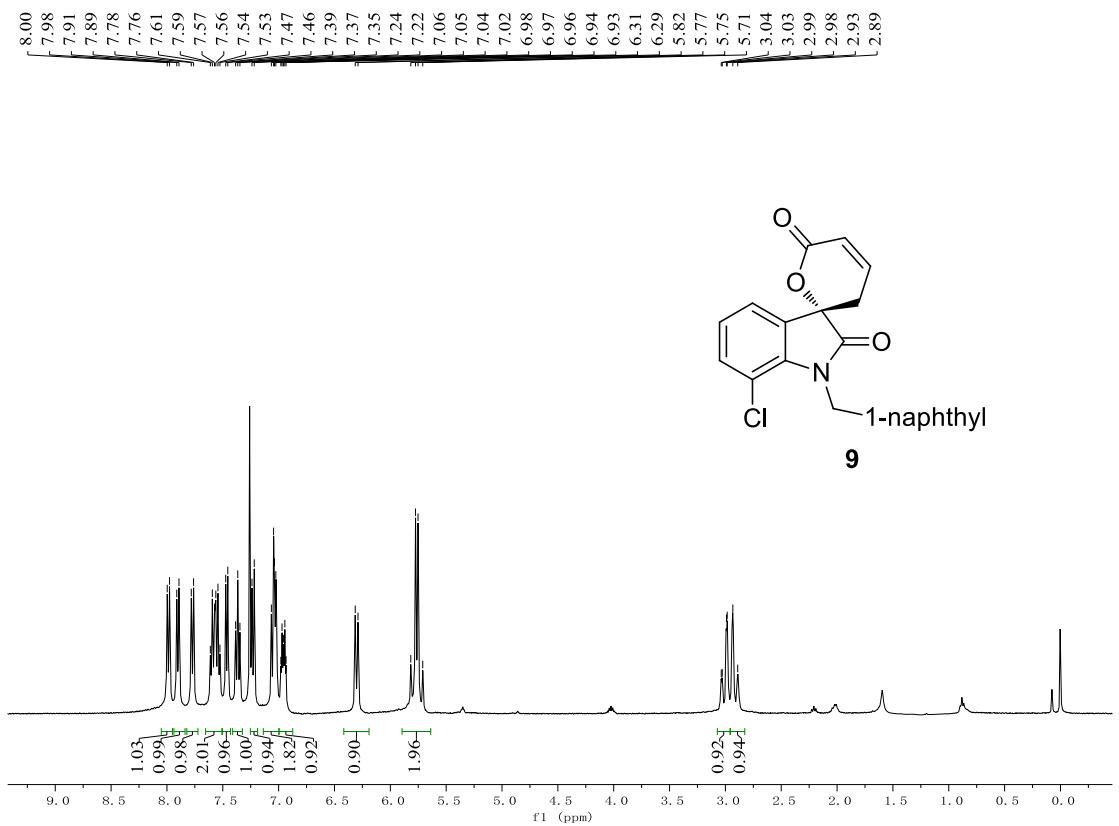
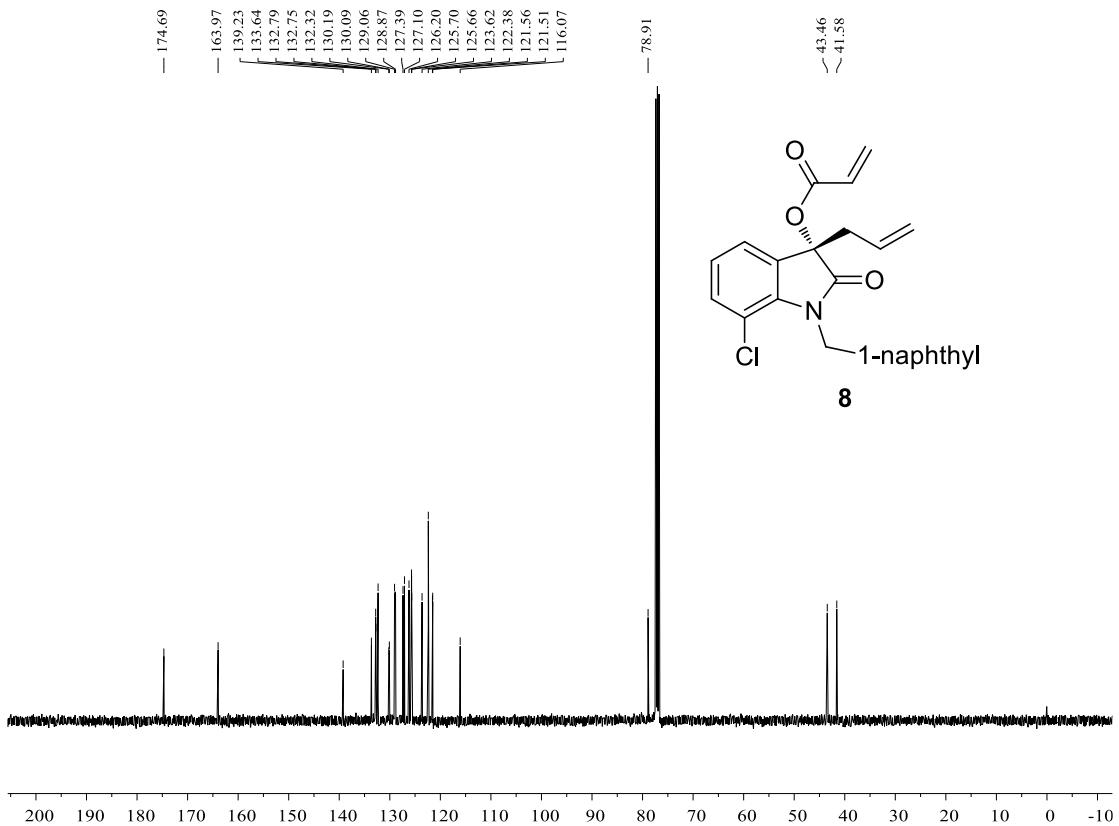


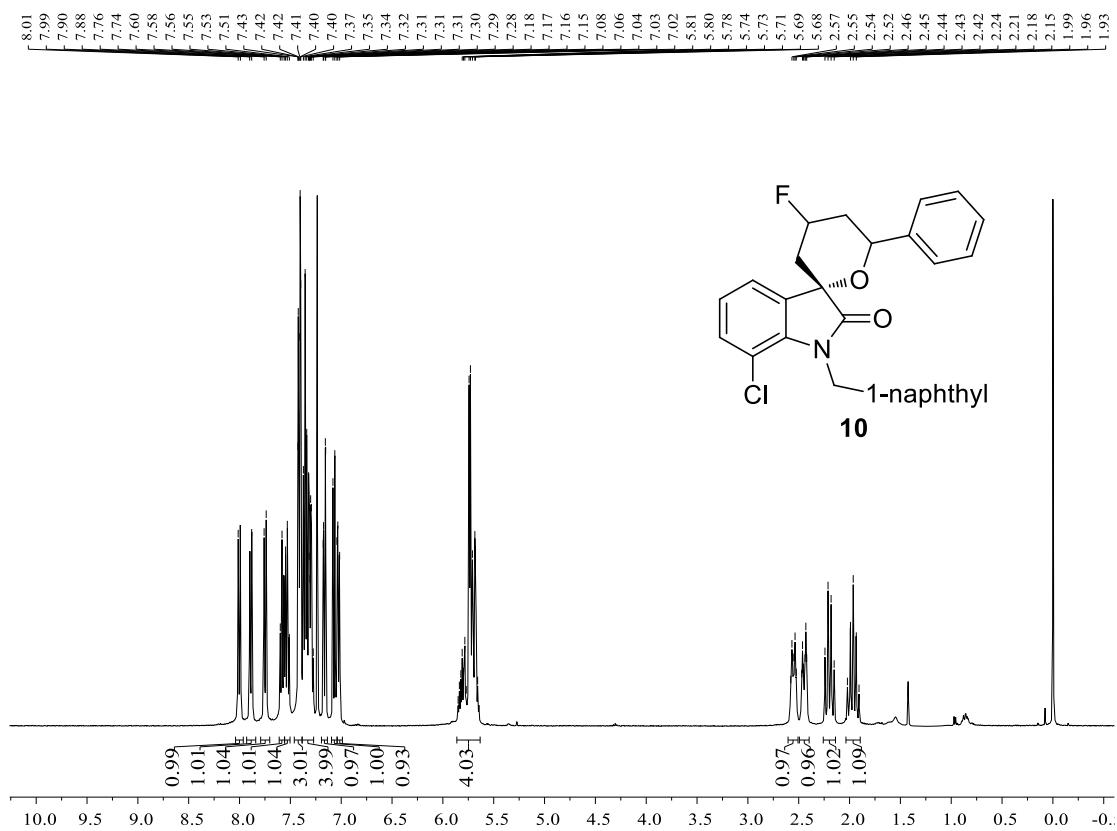
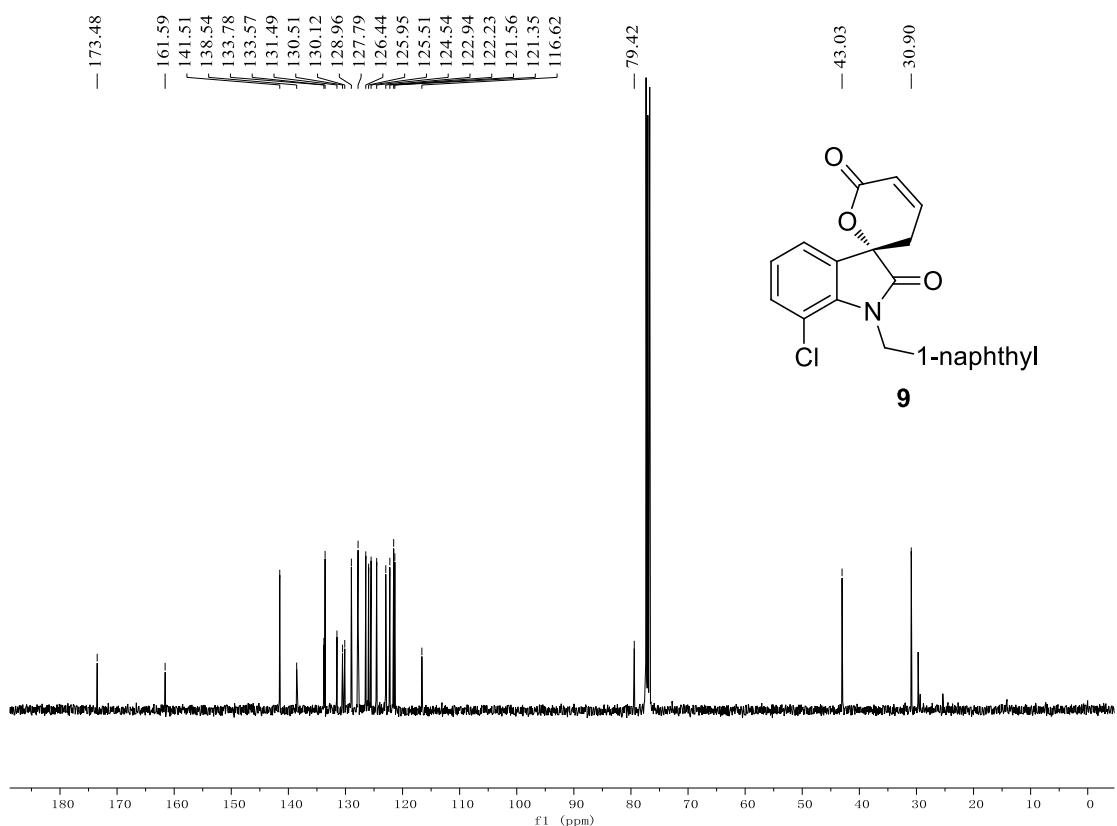


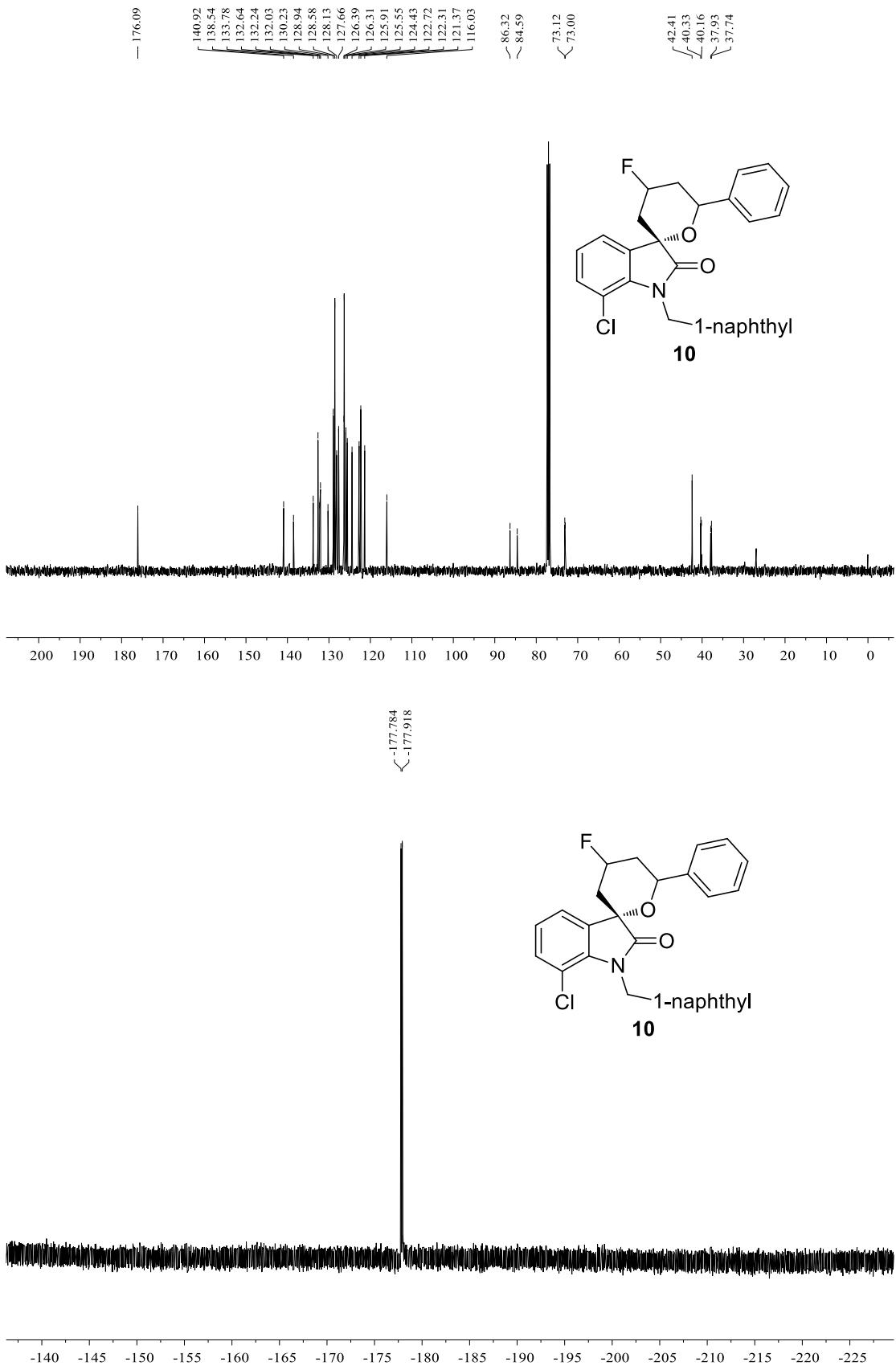
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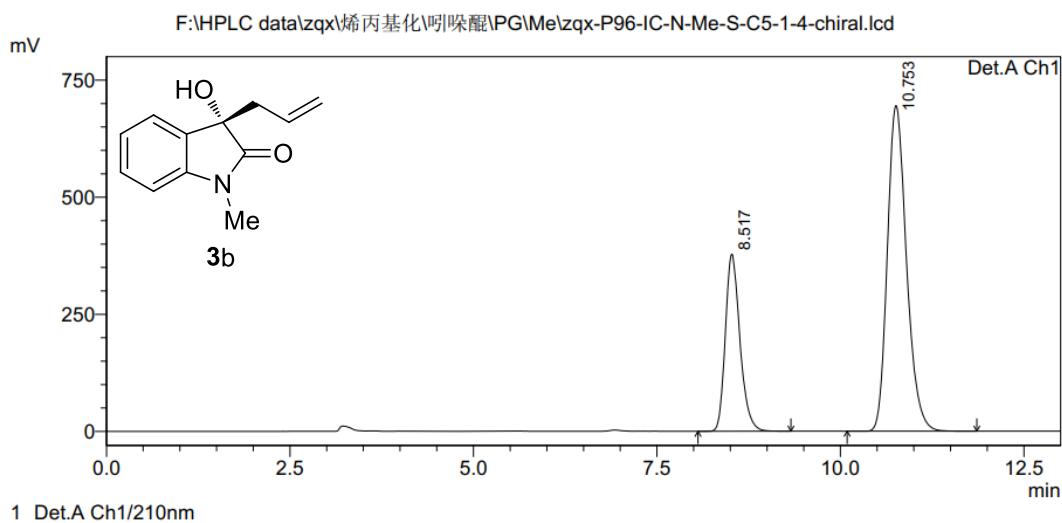
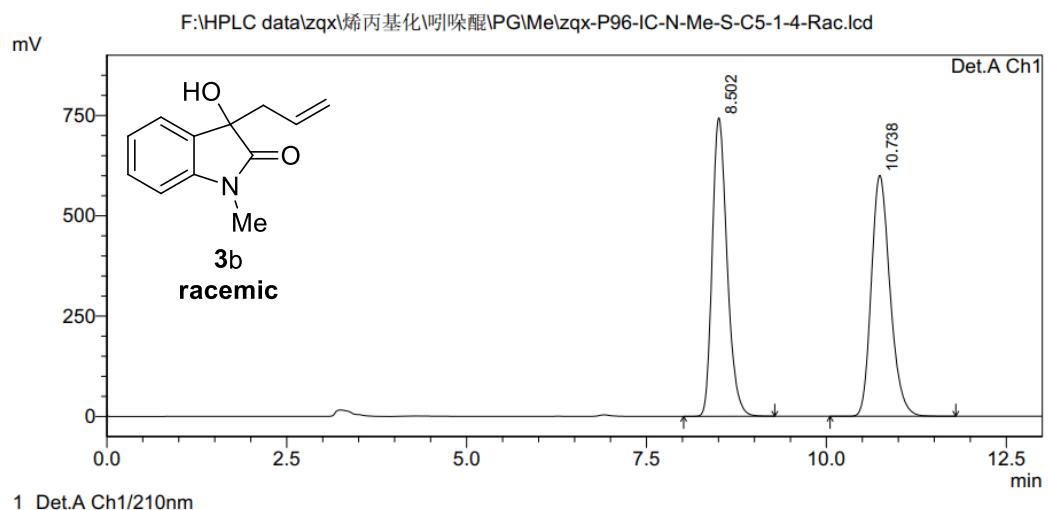
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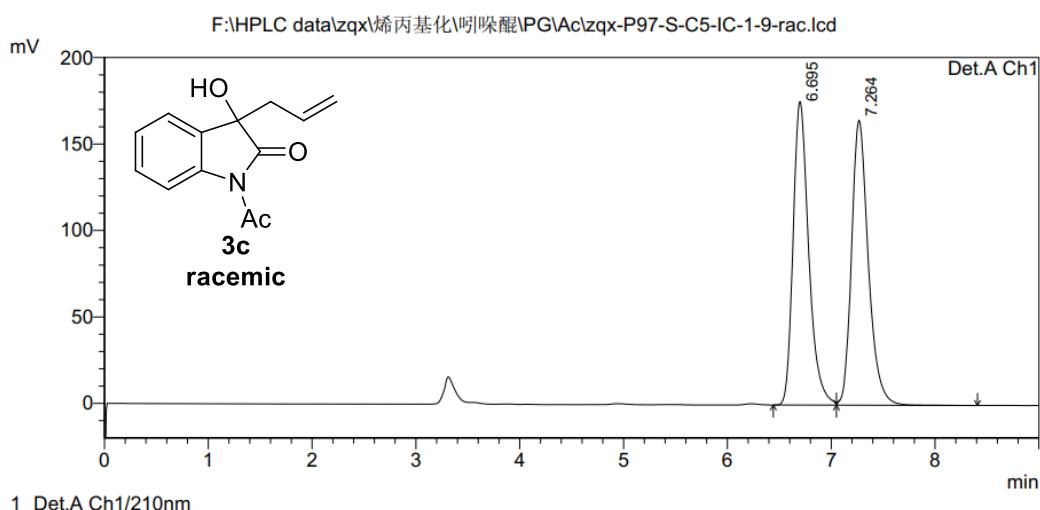






8. HPLC Spectra.

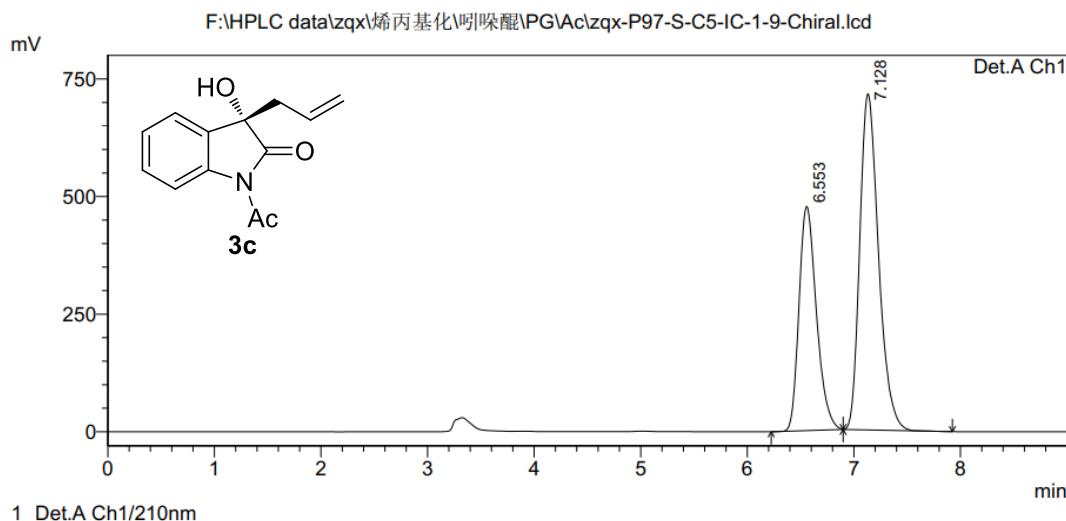




PeakTable

Detector A Ch1 210nm

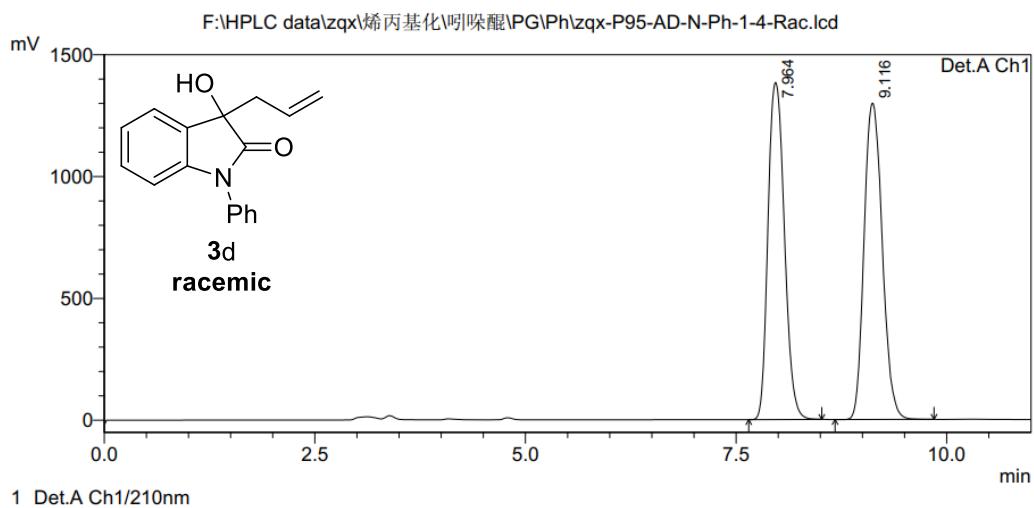
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.695	1839125	175620	49.866	51.591
2	7.264	1849006	164785	50.134	48.409
Total		3688131	340405	100.000	100.000



PeakTable

Detector A Ch1 210nm

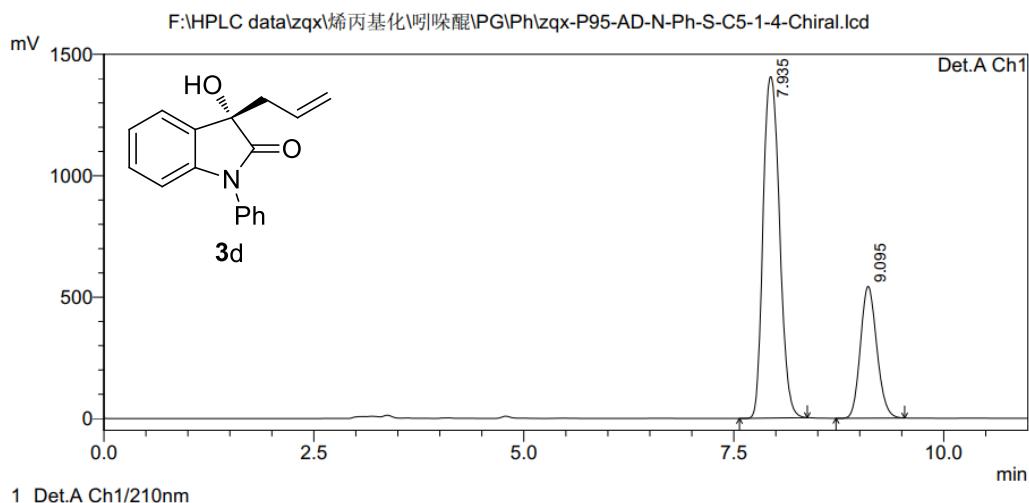
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.553	5405647	476860	38.221	40.015
2	7.128	8737460	714834	61.779	59.985
Total		14143106	1191693	100.000	100.000



PeakTable

Detector A Ch1 210nm

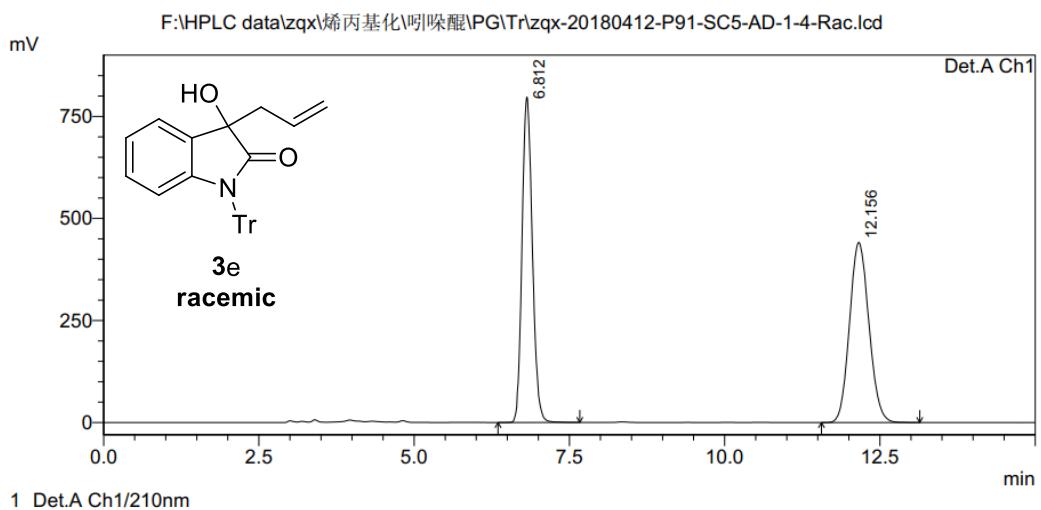
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.964	18729925	1383913	49.025	51.593
2	9.116	19474956	1298469	50.975	48.407
Total		38204881	2682382	100.000	100.000



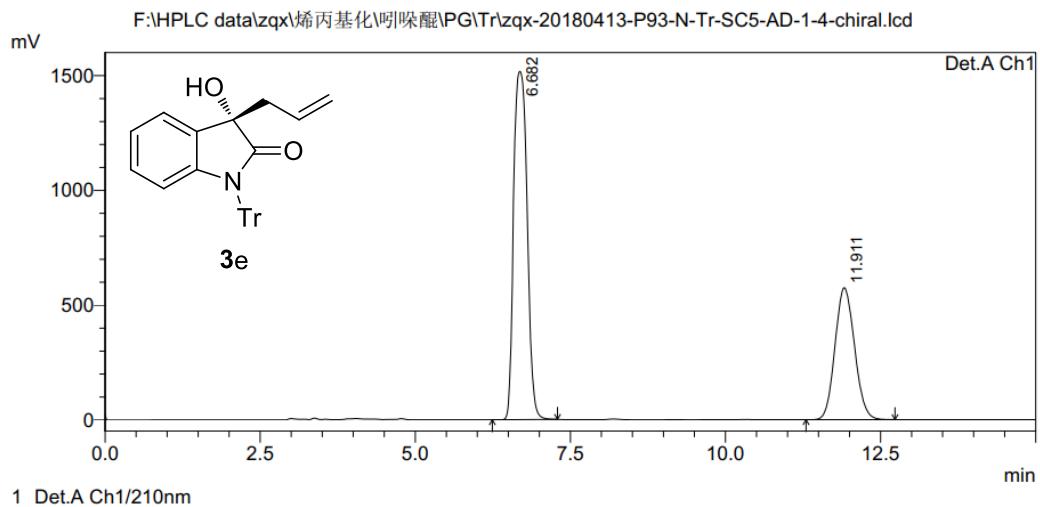
PeakTable

Detector A Ch1 210nm

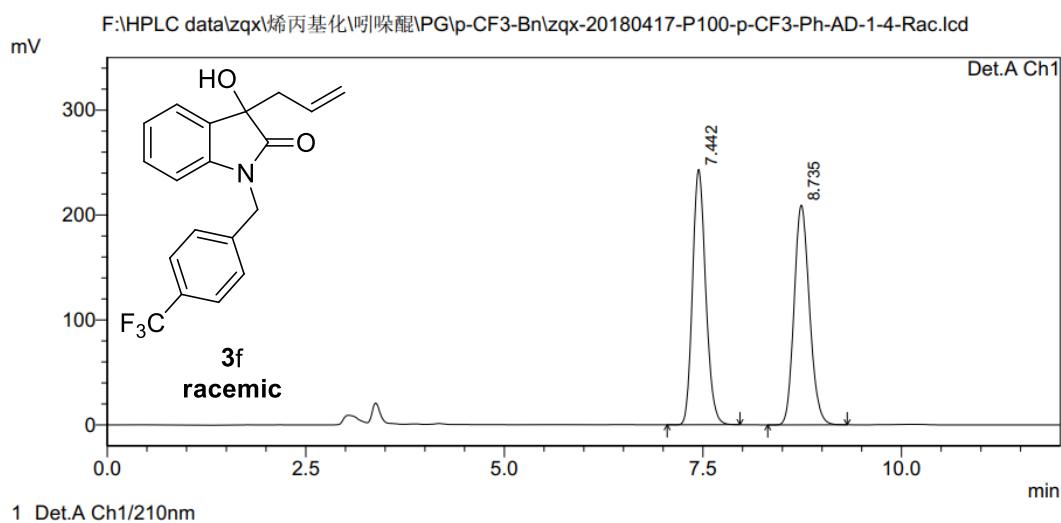
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.935	19174810	1405914	72.254	72.134
2	9.095	7363144	543129	27.746	27.866
Total		26537954	1949043	100.000	100.000



Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.812	9215024	797066	48.965	64.357
2	12.156	9604559	441435	51.035	35.643
Total		18819582	1238501	100.000	100.000



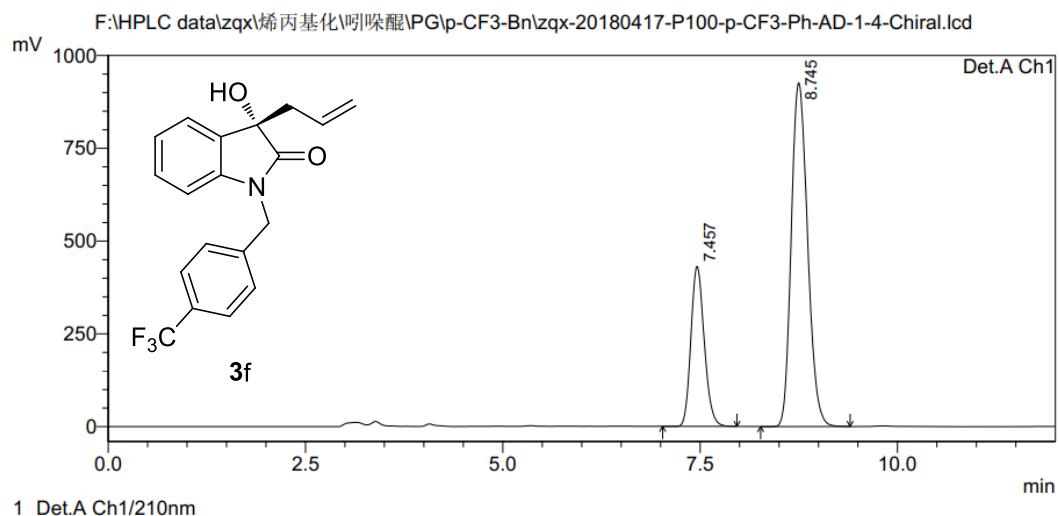
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.682	22953442	1516767	64.623	72.504
2	11.911	12565455	575205	35.377	27.496
Total		35518897	2091972	100.000	100.000



PeakTable

Detector A Ch1 210nm

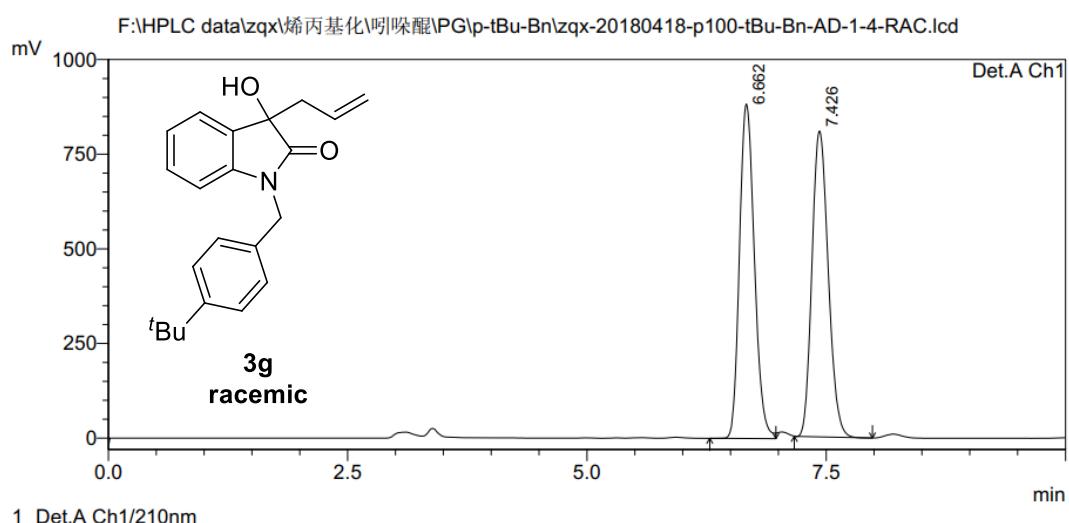
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.442	2812711	243337	49.940	53.735
2	8.735	2819442	209507	50.060	46.265
Total		5632153	452843	100.000	100.000



PeakTable

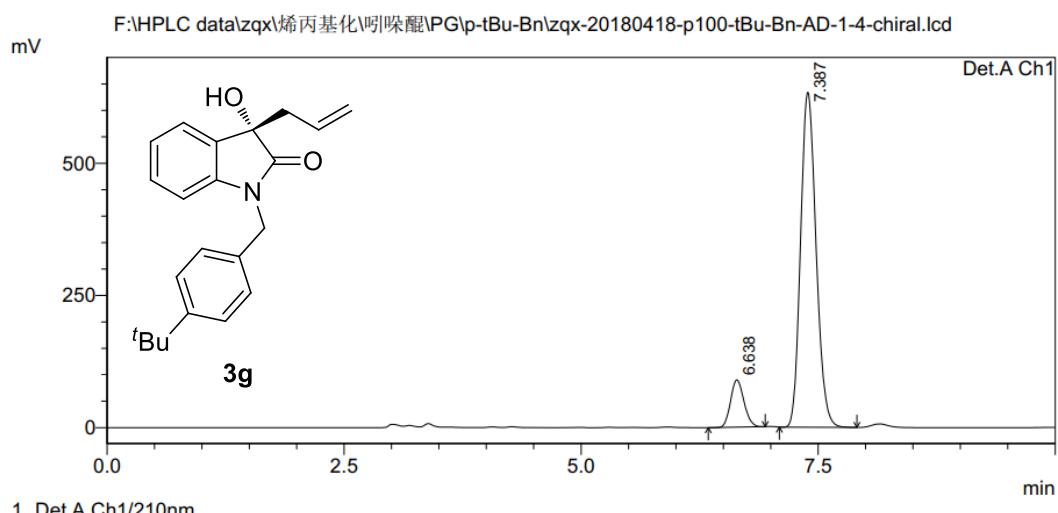
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.457	5068296	431054	27.557	31.756
2	8.745	13323676	926340	72.443	68.244
Total		18391972	1357394	100.000	100.000



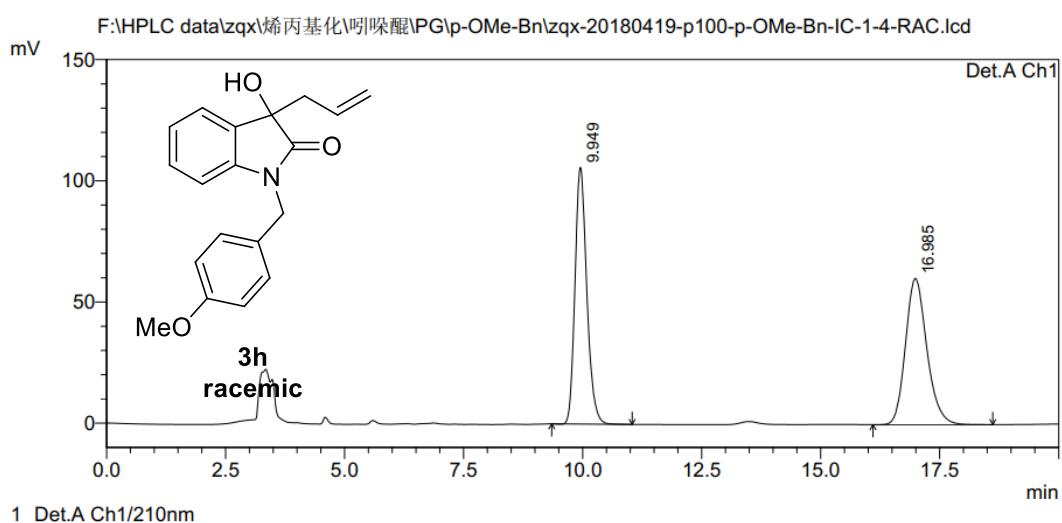
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.662	9558508	883671	50.004	52.247
2	7.426	9557095	807666	49.996	47.753
Total		19115603	1691337	100.000	100.000



PeakTable

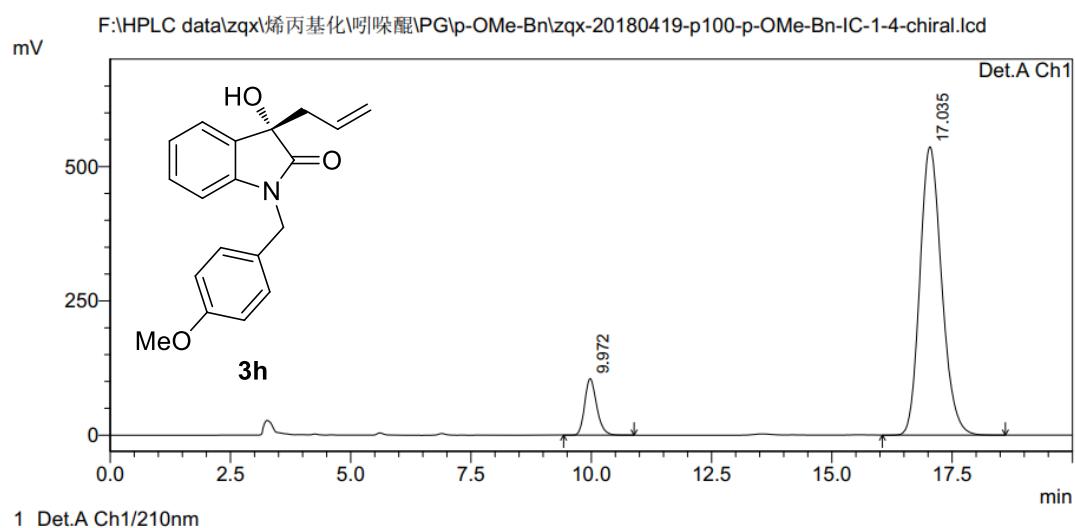
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.638	874329	89473	10.832	12.373
2	7.387	7197477	633671	89.168	87.627
Total		8071806	723144	100.000	100.000



Detector A Ch1 210nm

PeakTable

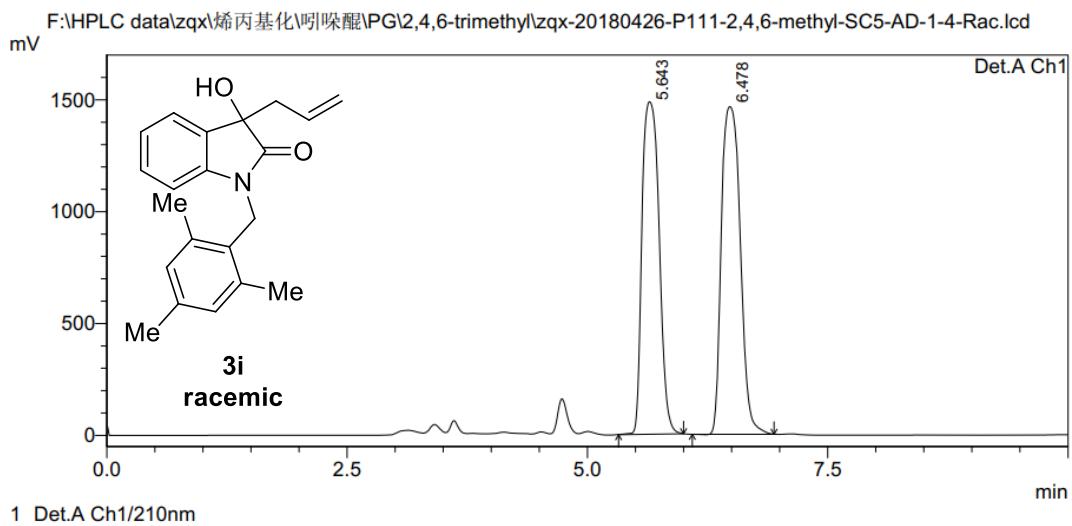
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.949	1829252	105894	49.309	63.717
2	16.985	1880519	60300	50.691	36.283
Total		3709771	166195	100.000	100.000



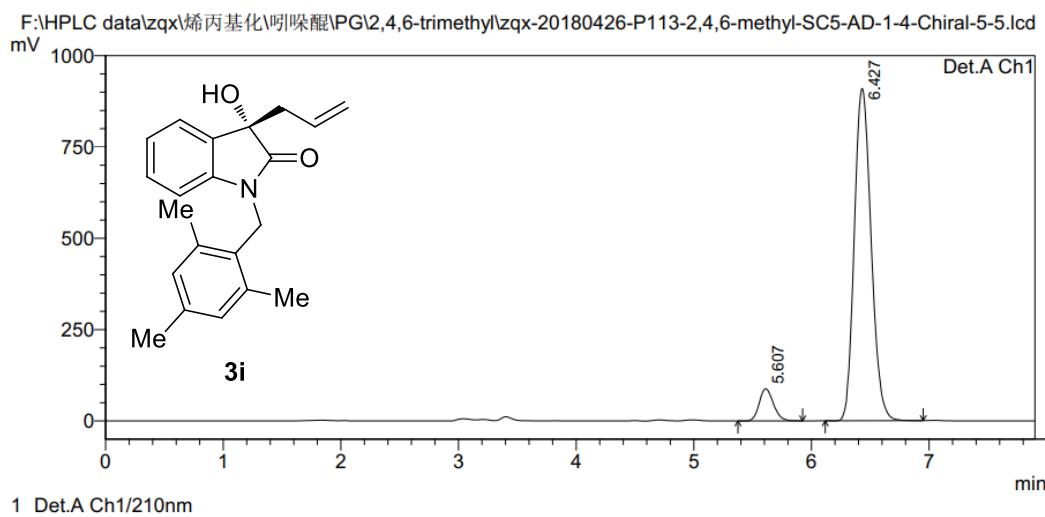
Detector A Ch1 210nm

PeakTable

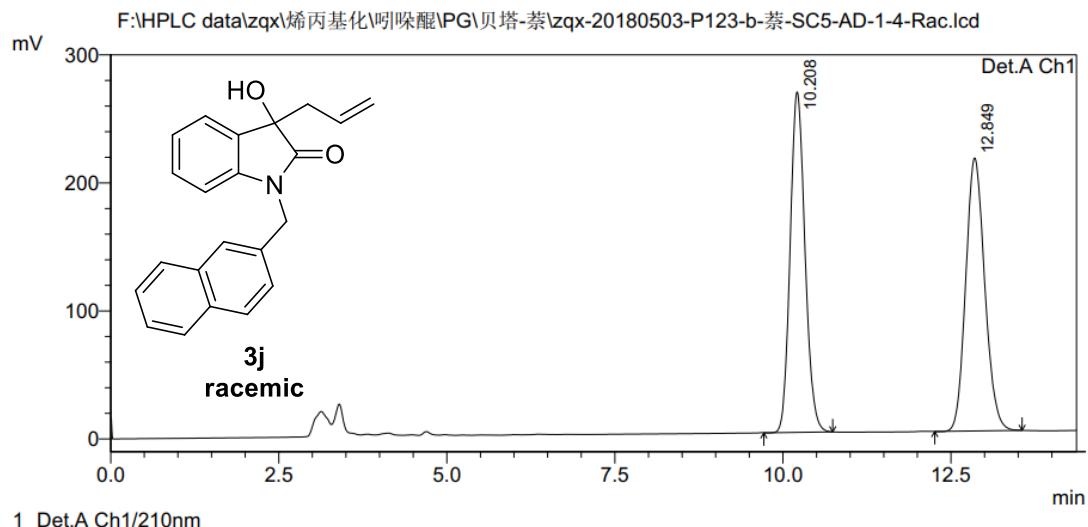
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.972	1815621	105099	9.705	16.374
2	17.035	16892897	536785	90.295	83.626
Total		18708518	641884	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.643	18425621	1486377	47.903	50.353
2	6.478	20038778	1465534	52.097	49.647
Total		38464399	2951911	100.000	100.000

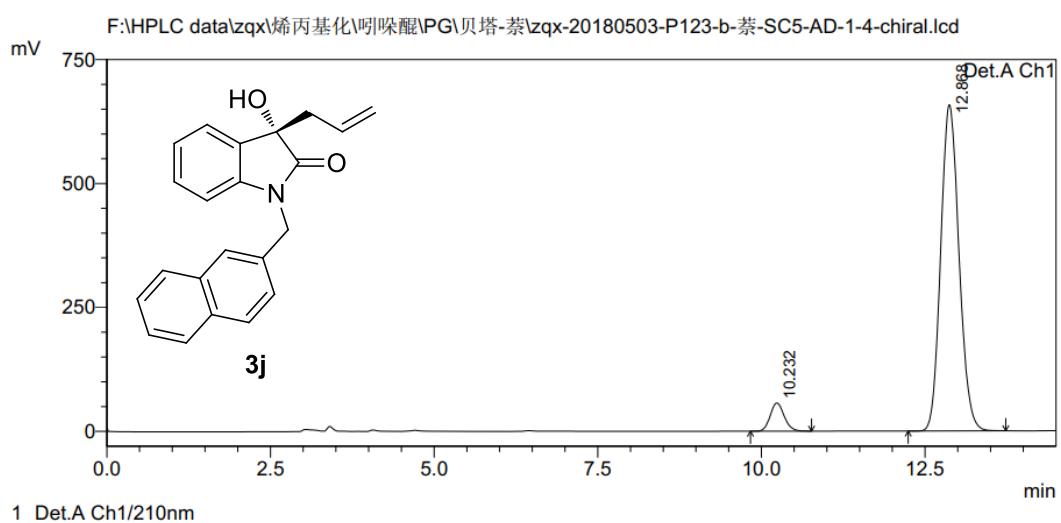


PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.607	734521	88216	7.509	8.838
2	6.427	9047581	909900	92.491	91.162
Total		9782102	998116	100.000	100.000



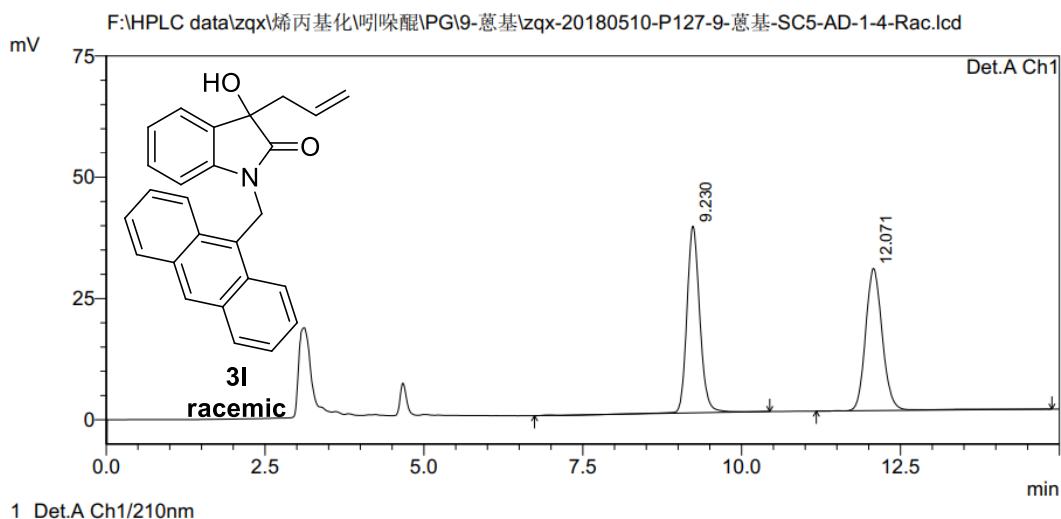
PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.208	4084867	265938	49.301	55.501
2	12.849	4200630	213222	50.699	44.499
Total		8285497	479160	100.000	100.000

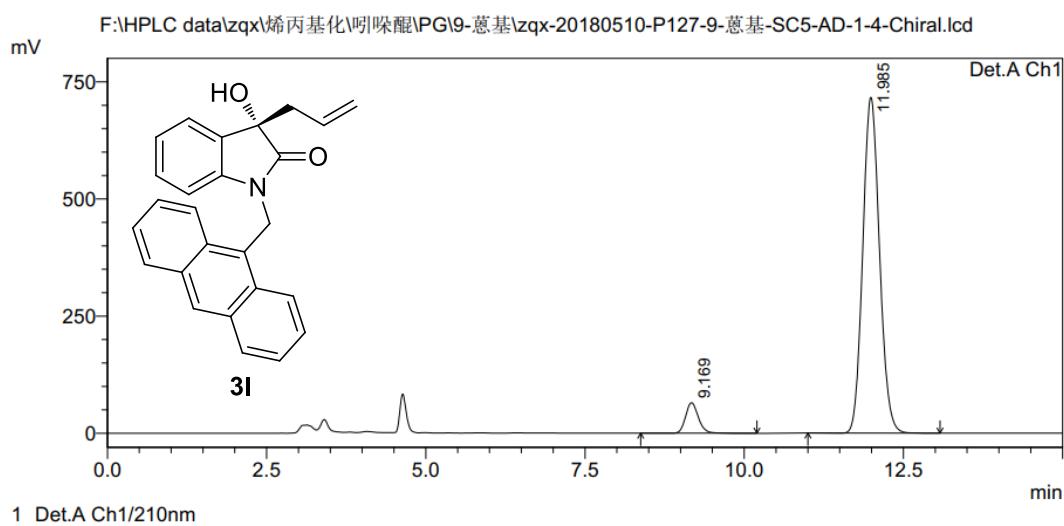


PeakTable

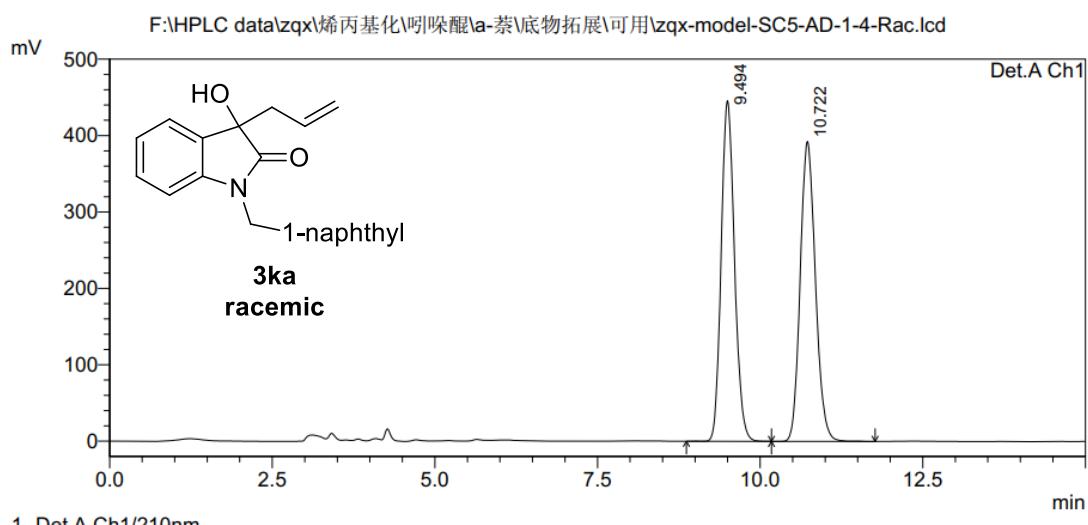
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.232	847162	56837	6.205	7.950
2	12.868	12806179	658050	93.795	92.050
Total		13653342	714887	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.230	541391	38484	49.868	56.757
2	12.071	544253	29321	50.132	43.243
Total		1085644	67805	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.169	900234	65054	6.428	8.322
2	11.985	13103978	716704	93.572	91.678
Total		14004212	781758	100.000	100.000

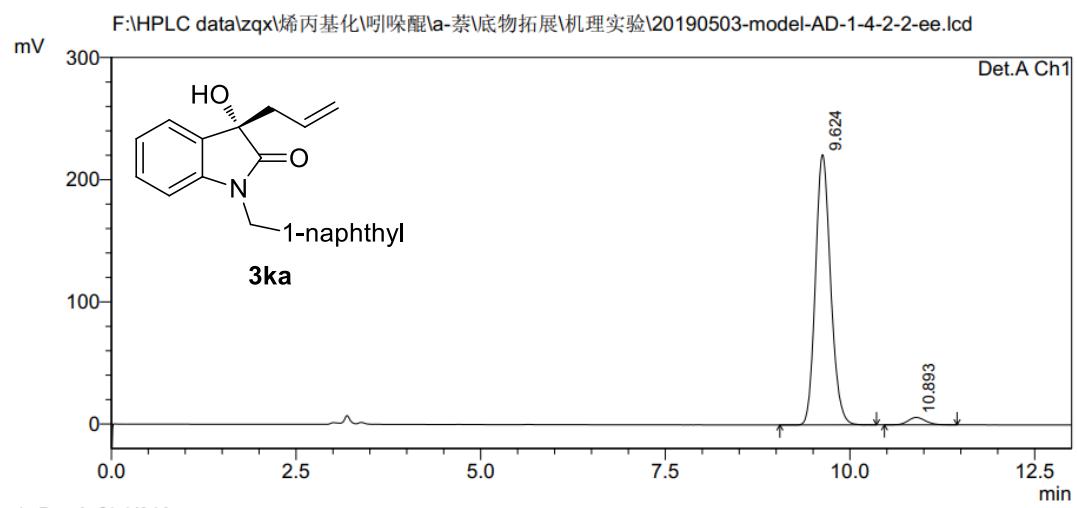


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.494	6346509	445785	49.869	53.169
2	10.722	6379908	392642	50.131	46.831
Total		12726417	838427	100.000	100.000

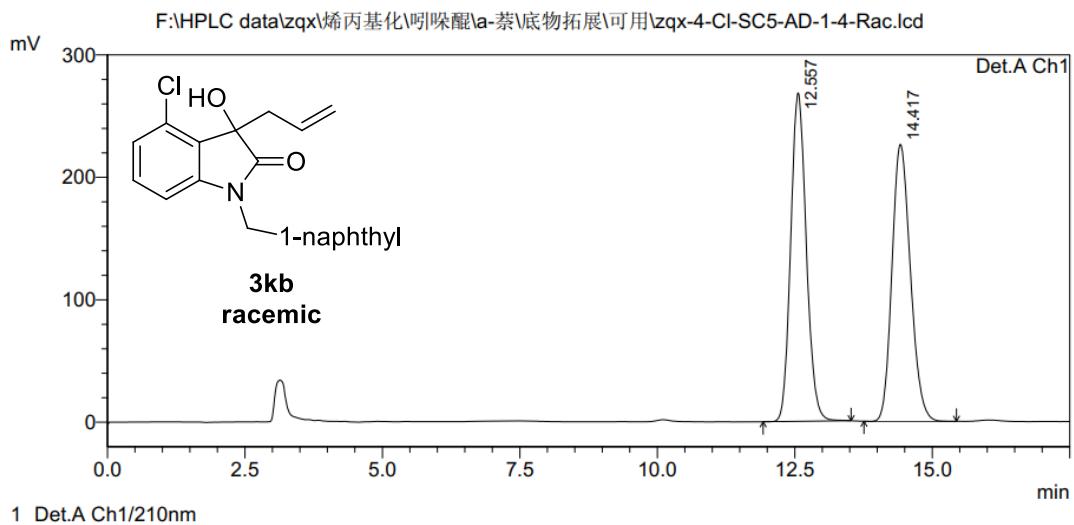


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

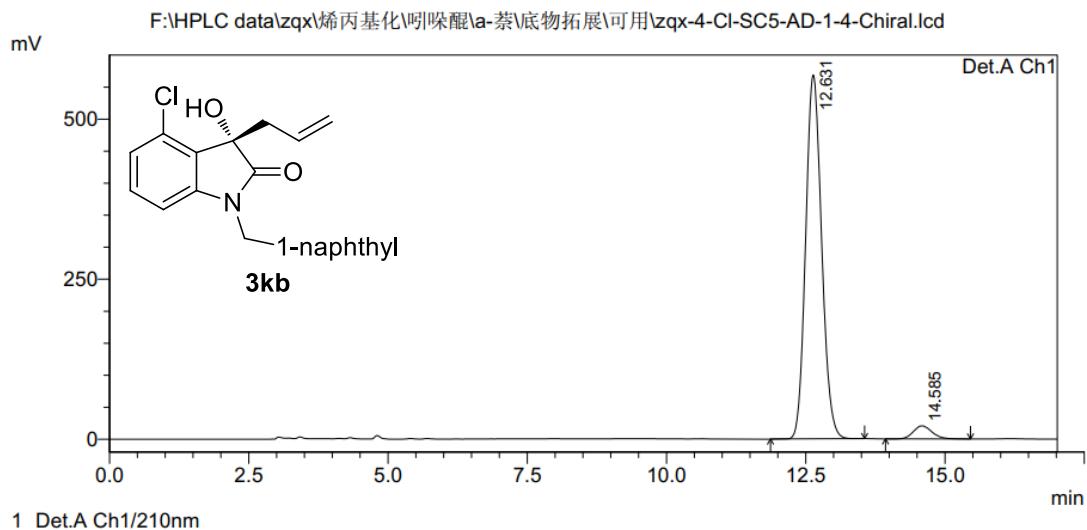
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.624	3161002	221182	96.962	97.329
2	10.893	99051	6071	3.038	2.671
Total		3260053	227253	100.000	100.000



PeakTable

Detector A Ch1 210nm

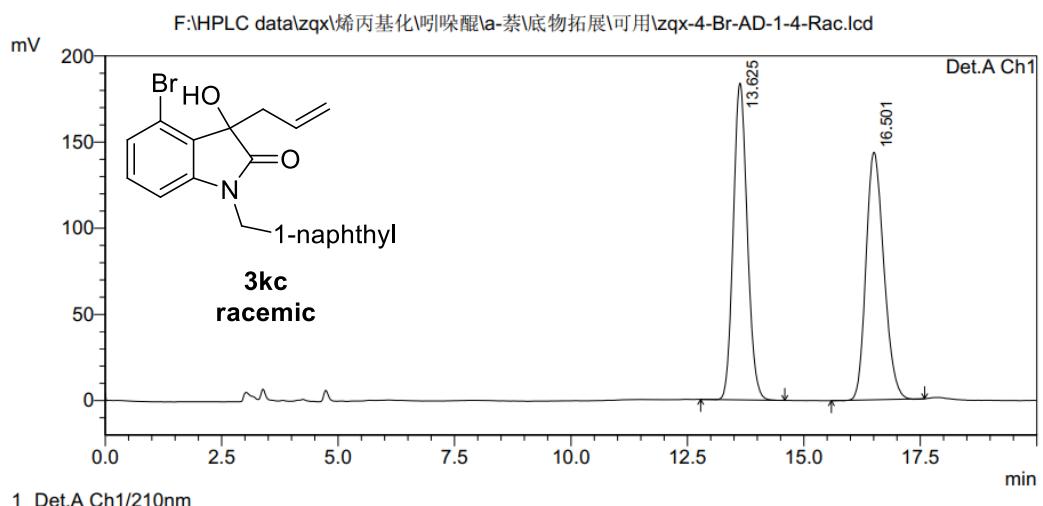
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.557	5292398	268319	50.121	54.267
2	14.417	5266805	226127	49.879	45.733
Total		10559203	494446	100.000	100.000



PeakTable

Detector A Ch1 210nm

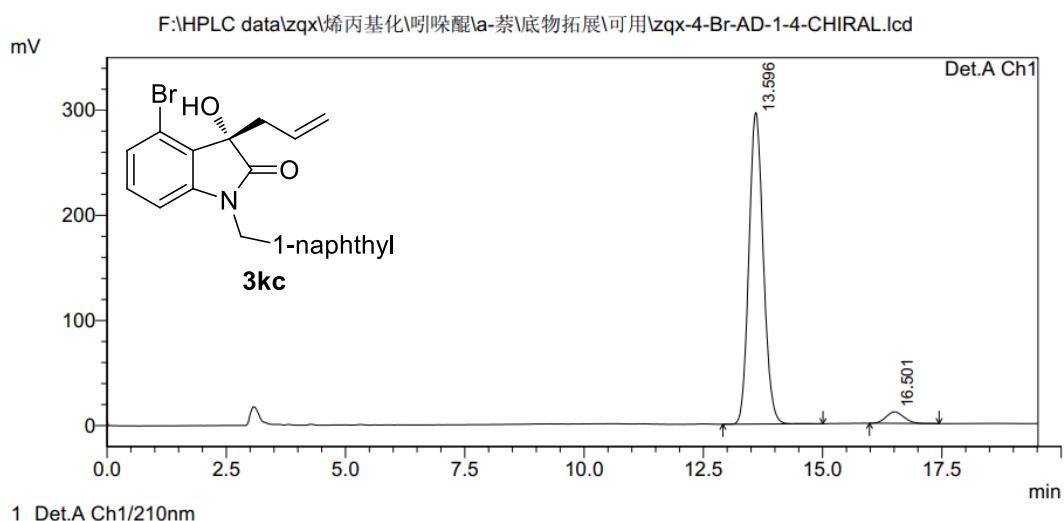
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.631	11312662	568334	95.950	96.524
2	14.585	477546	20468	4.050	3.476
Total		11790208	588802	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

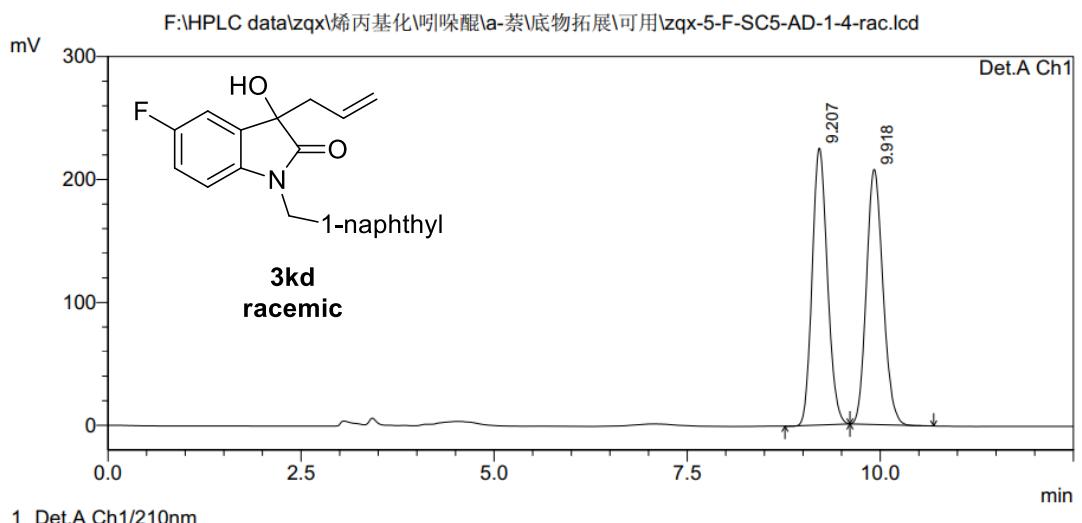
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.625	3838099	183845	50.044	56.123
2	16.501	3831335	143727	49.956	43.877
Total		7669433	327572	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.596	6222818	296564	95.656	96.453
2	16.501	282618	10906	4.344	3.547
Total		6505436	307470	100.000	100.000

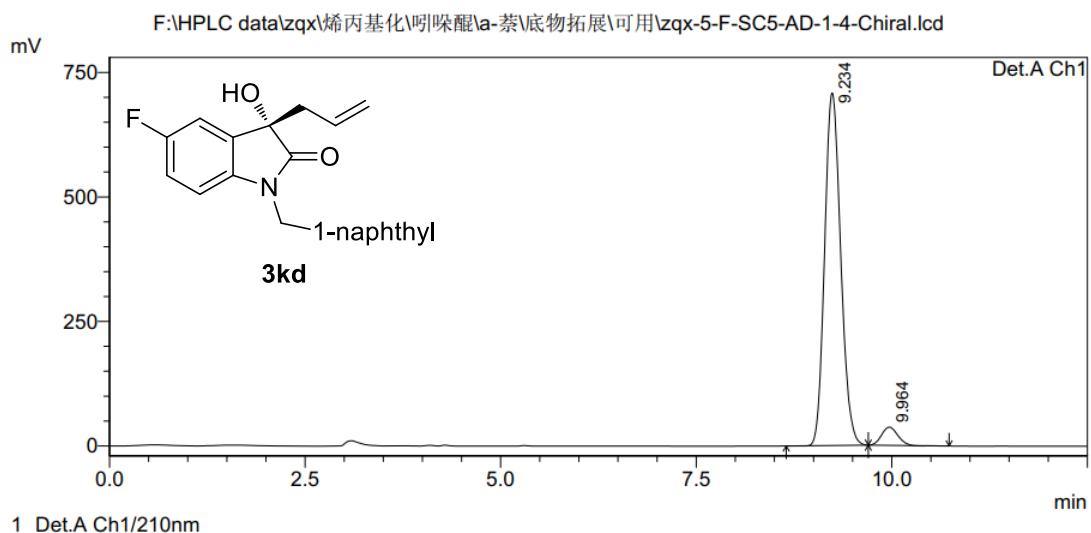


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.207	3084789	225349	49.904	52.055
2	9.918	3096720	207559	50.096	47.945
Total		6181509	432908	100.000	100.000

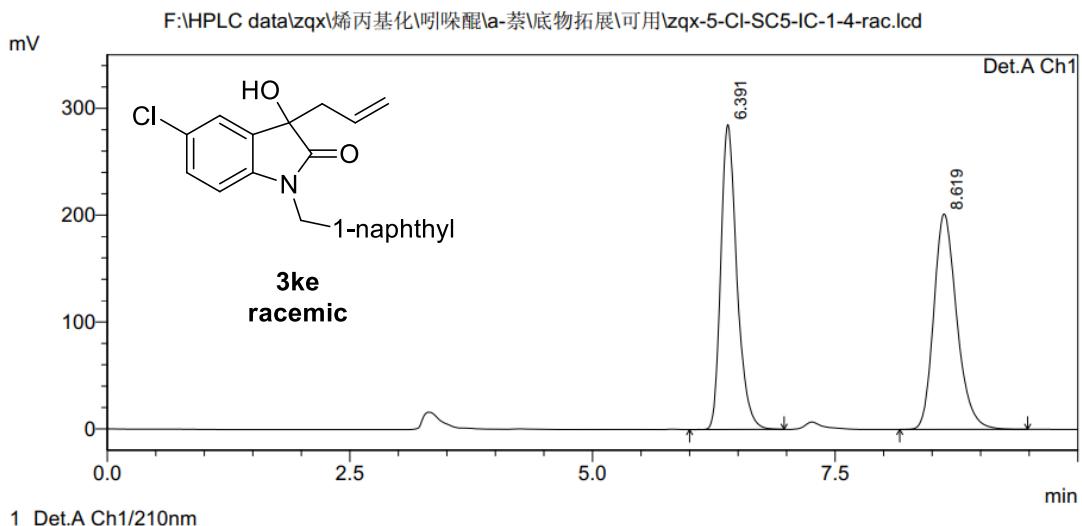


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

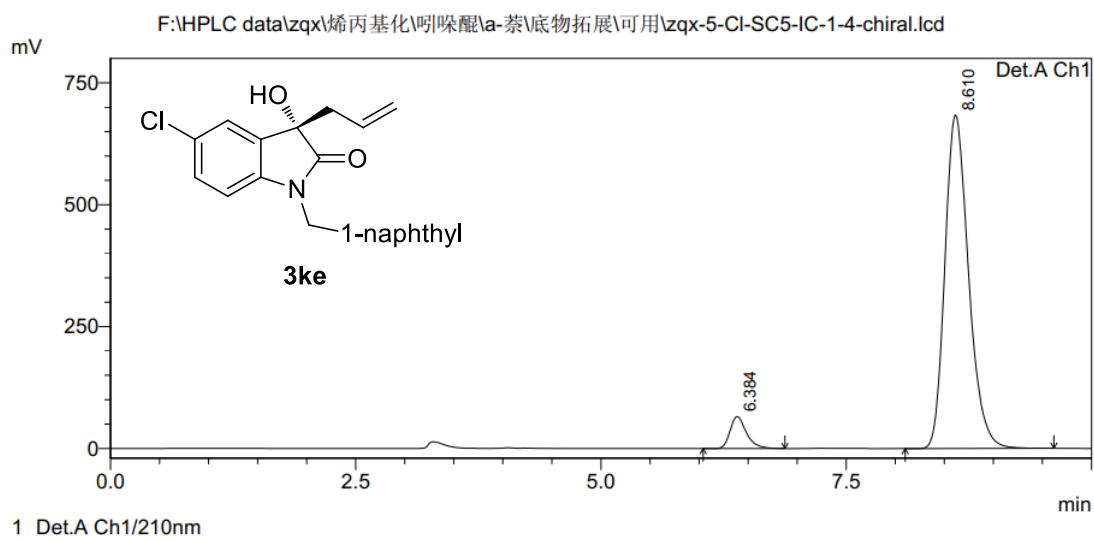
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.234	10107810	707811	95.053	95.060
2	9.964	526051	36779	4.947	4.940
Total		10633861	744590	100.000	100.000



PeakTable

Detector A Ch1 210nm

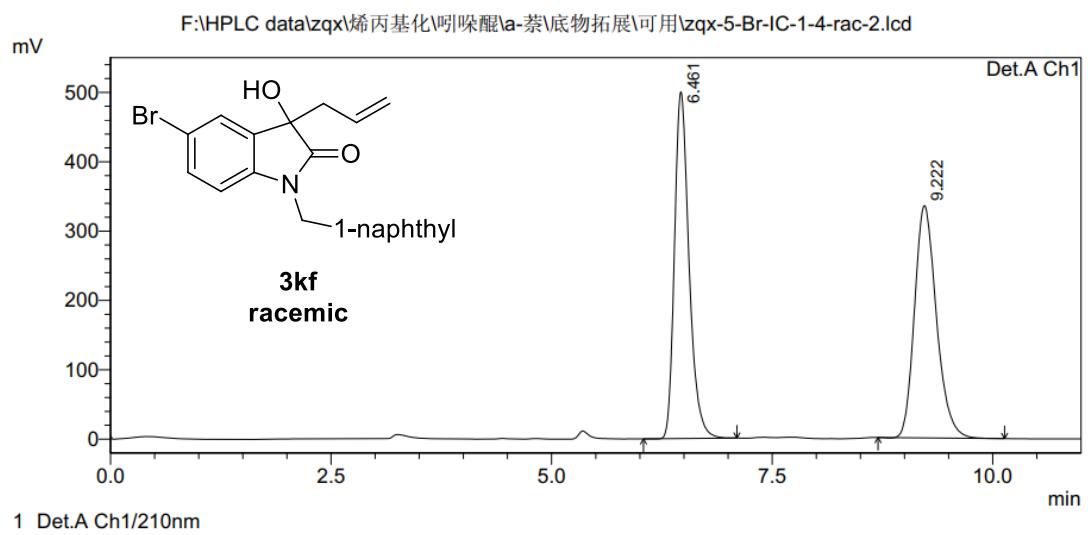
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.391	3283277	285533	49.642	58.593
2	8.619	3330690	201782	50.358	41.407
Total		6613967	487316	100.000	100.000



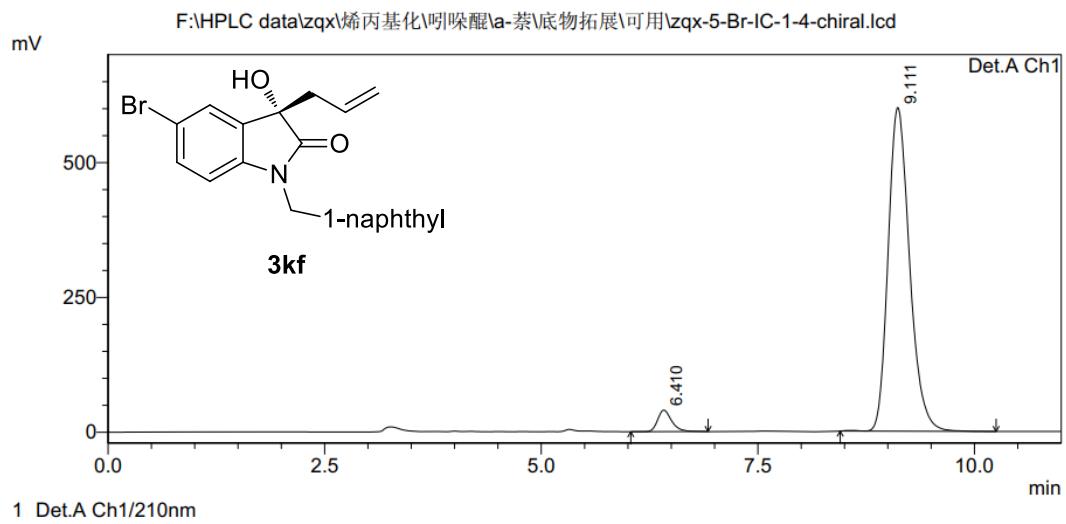
PeakTable

Detector A Ch1 210nm

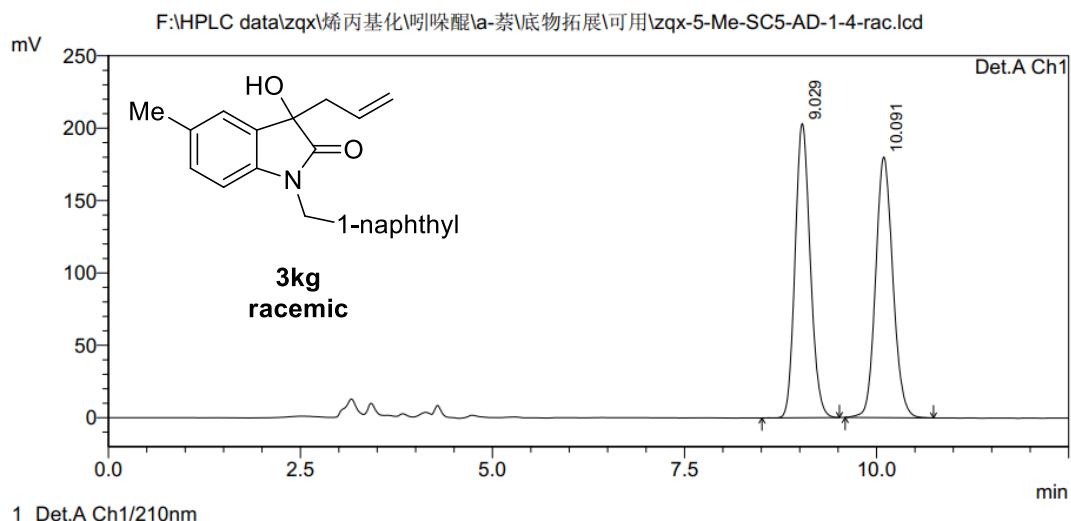
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.384	756553	65593	6.186	8.750
2	8.610	11473374	683997	93.814	91.250
Total		12229927	749590	100.000	100.000



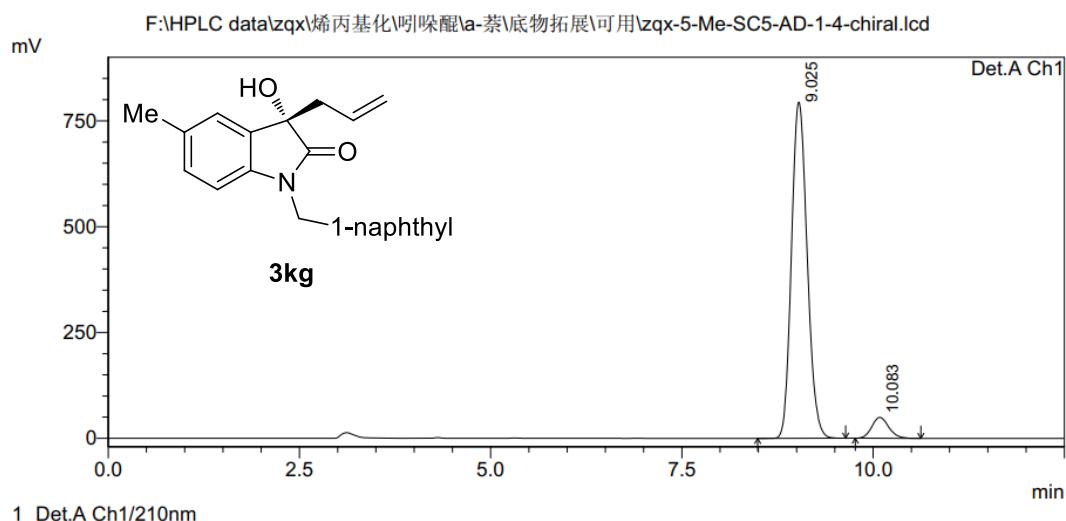
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.461	5731008	500088	49.816	59.880
2	9.222	5773239	335064	50.184	40.120
Total		11504247	835153	100.000	100.000



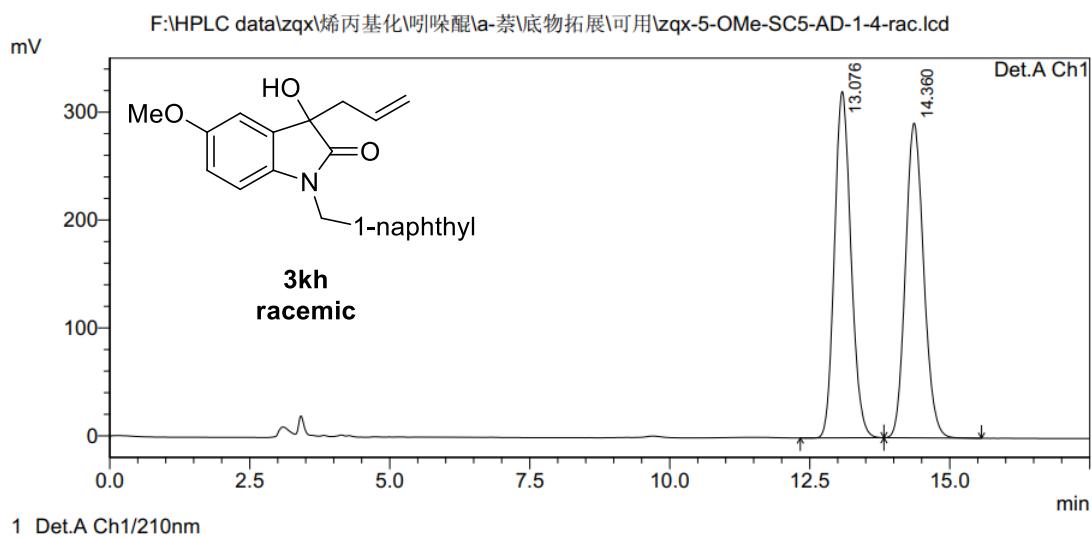
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.410	446030	39800	4.138	6.220
2	9.111	10333182	600115	95.862	93.780
Total		10779213	639915	100.000	100.000



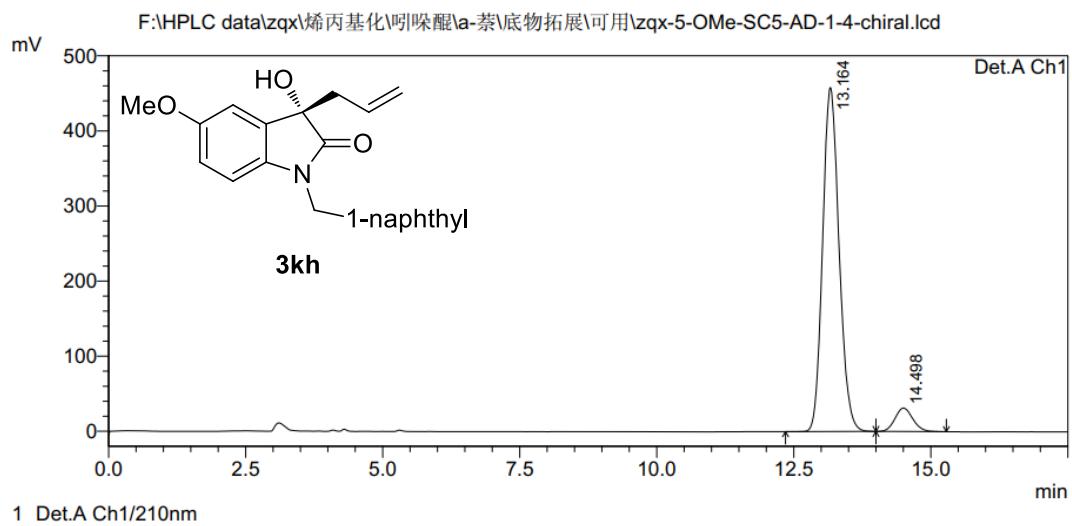
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.029	2785669	203344	49.708	53.042
2	10.091	2818399	180023	50.292	46.958
Total		5604068	383367	100.000	100.000



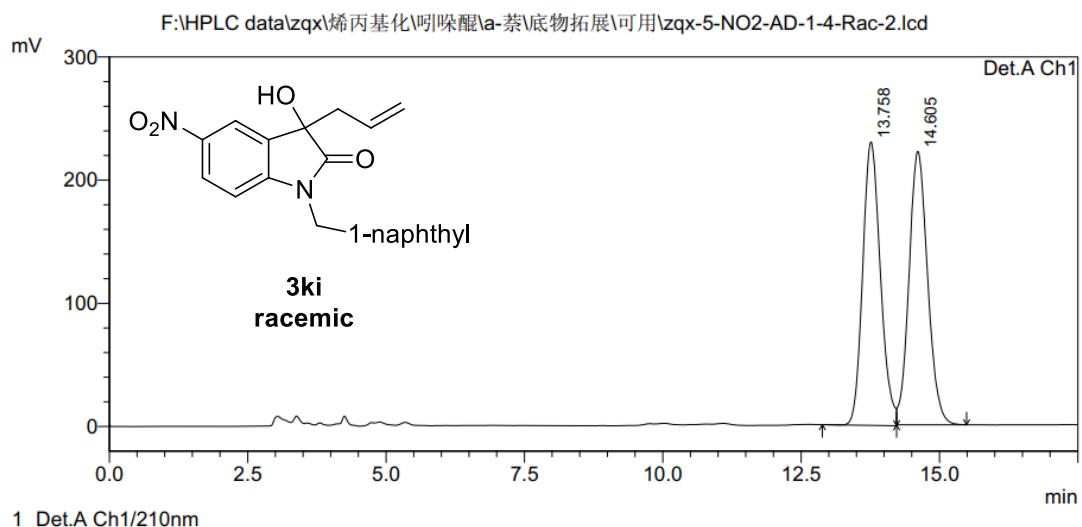
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.025	11338709	794284	93.717	94.149
2	10.083	760208	49360	6.283	5.851
Total		12098918	843644	100.000	100.000



Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.076	6585051	320961	49.883	52.383
2	14.360	6615974	291762	50.117	47.617
Total		13201025	612723	100.000	100.000



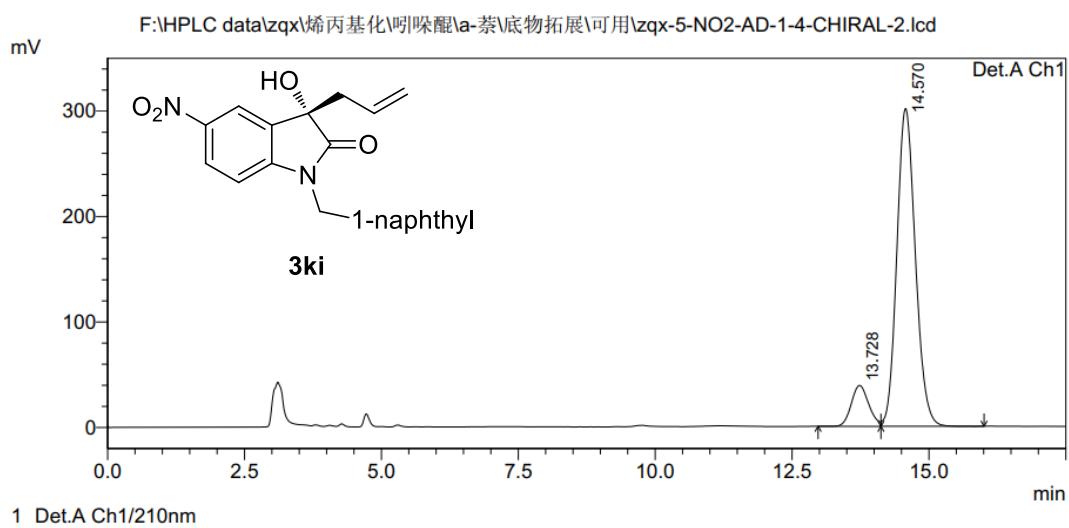
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.164	9550269	458234	93.096	93.603
2	14.498	708236	31317	6.904	6.397
Total		10258504	489551	100.000	100.000



PeakTable

Detector A Ch1 210nm

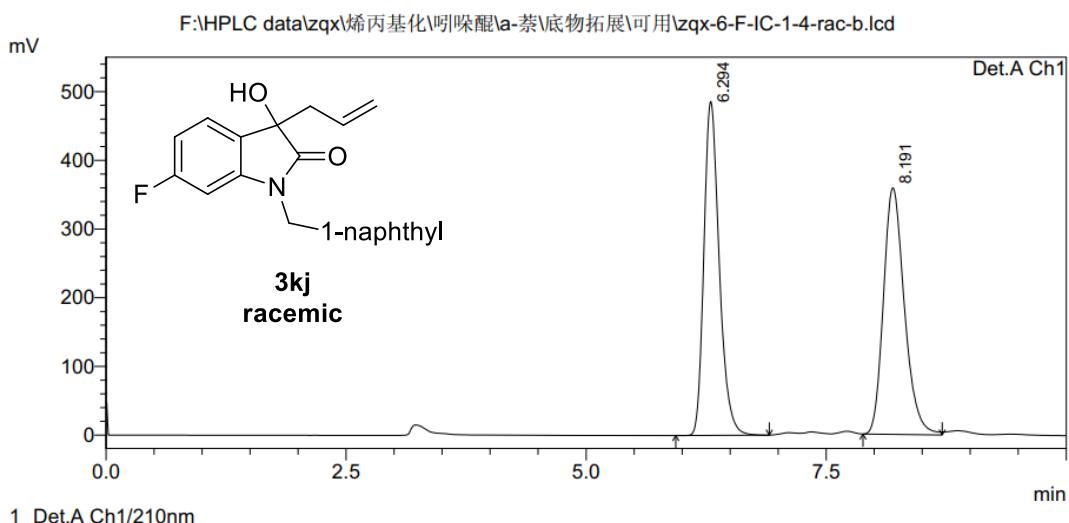
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.758	5113754	230013	49.548	50.892
2	14.605	5206988	221952	50.452	49.108
Total		10320742	451965	100.000	100.000



PeakTable

Detector A Ch1 210nm

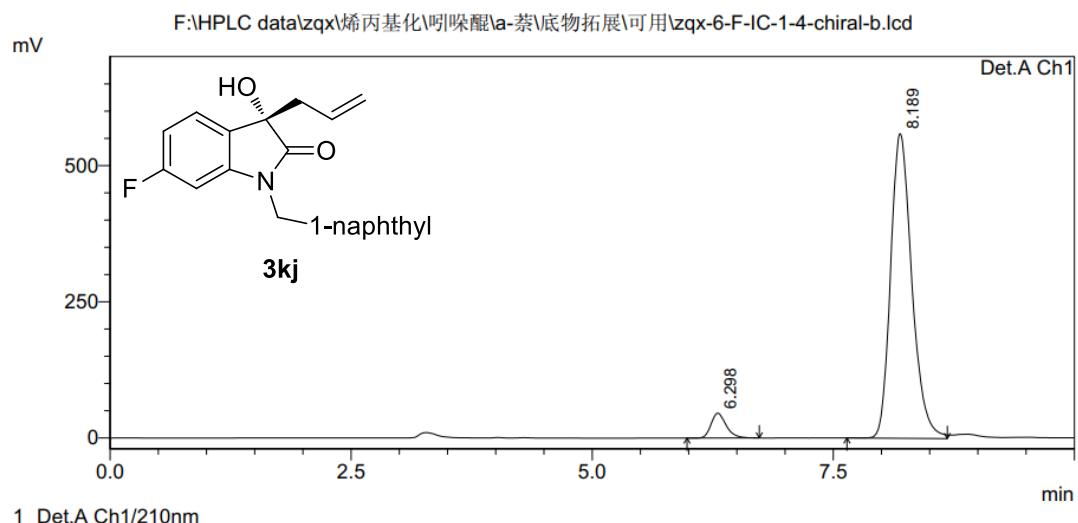
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.728	858339	38861	10.810	11.422
2	14.570	7081721	301385	89.190	88.578
Total		7940060	340246	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

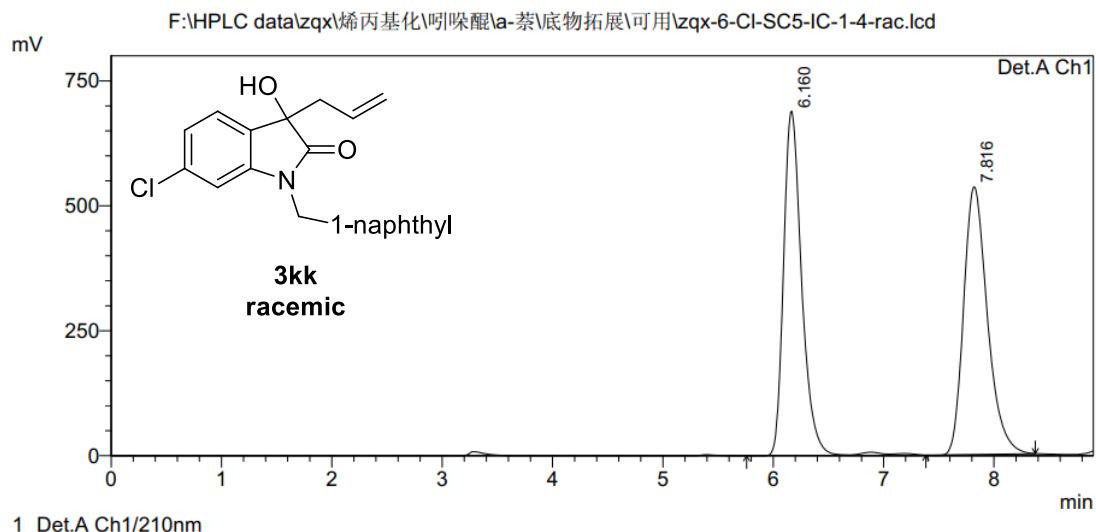
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.294	5398210	486058	49.744	57.526
2	8.191	5453873	358882	50.256	42.474
Total		10852083	844940	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

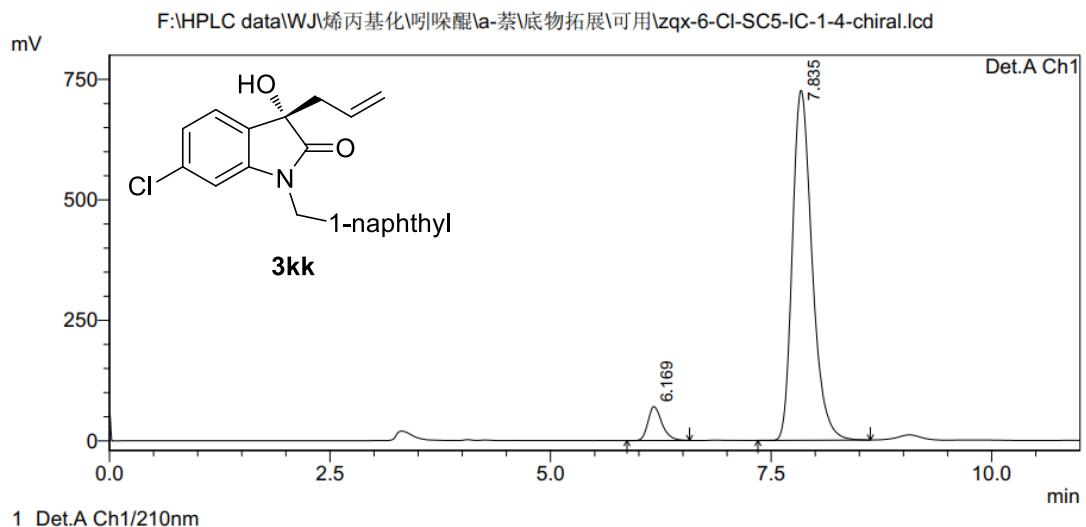
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.298	496500	45699	5.474	7.552
2	8.189	8573146	559427	94.526	92.448
Total		9069646	605126	100.000	100.000



PeakTable

Detector A Ch1 210nm

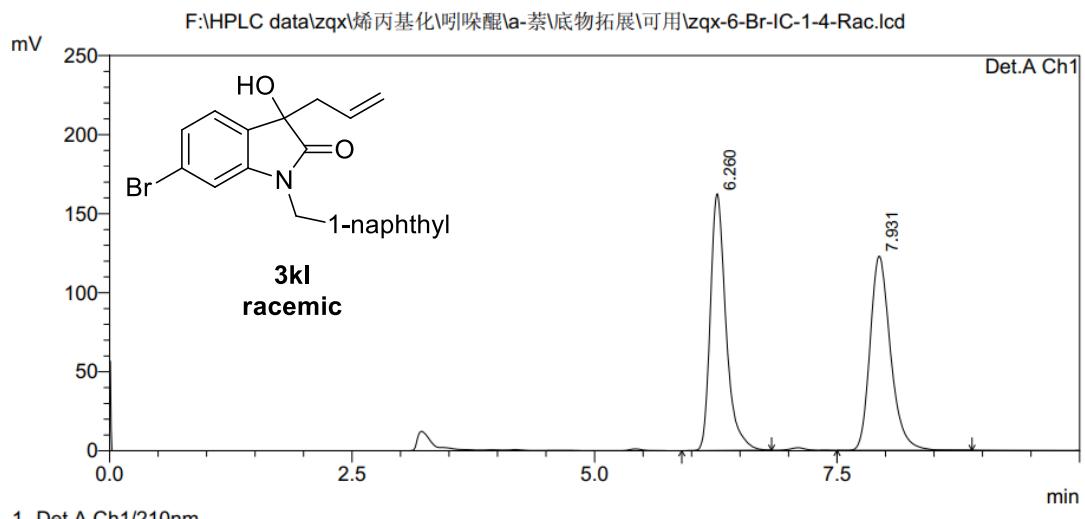
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.160	7836337	689971	49.481	56.316
2	7.816	8000567	535208	50.519	43.684
Total		15836904	1225179	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.169	773278	70342	6.426	8.828
2	7.835	11260962	726442	93.574	91.172
Total		12034239	796784	100.000	100.000

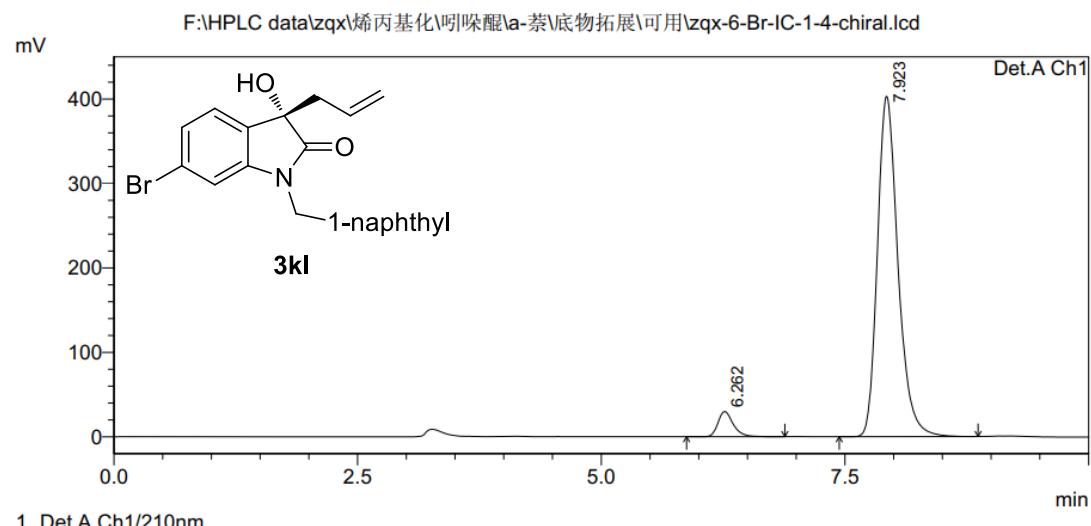


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.260	1817056	162471	50.235	56.938
2	7.931	1800079	122876	49.765	43.062
Total		3617135	285347	100.000	100.000

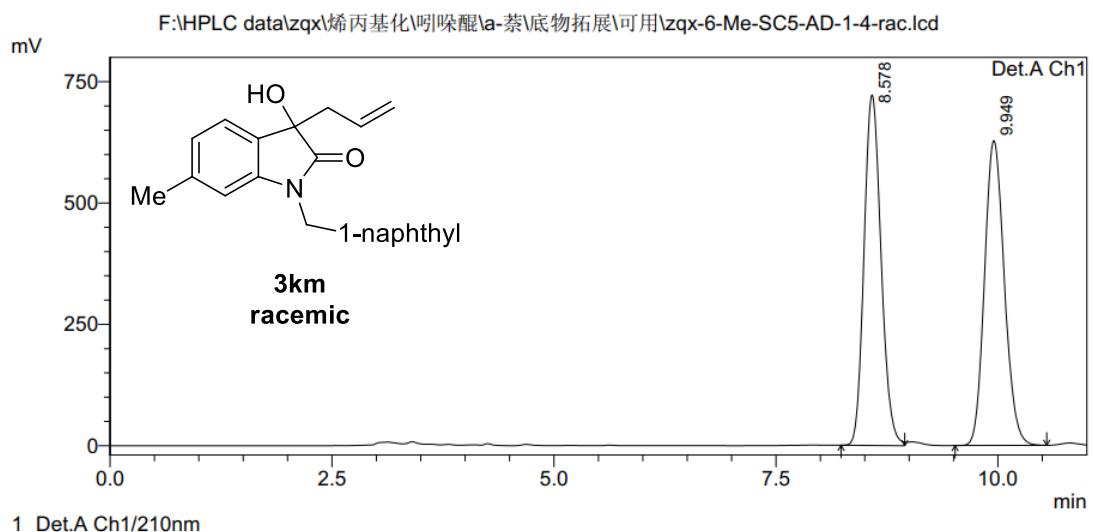


1 Det.A Ch1/210nm

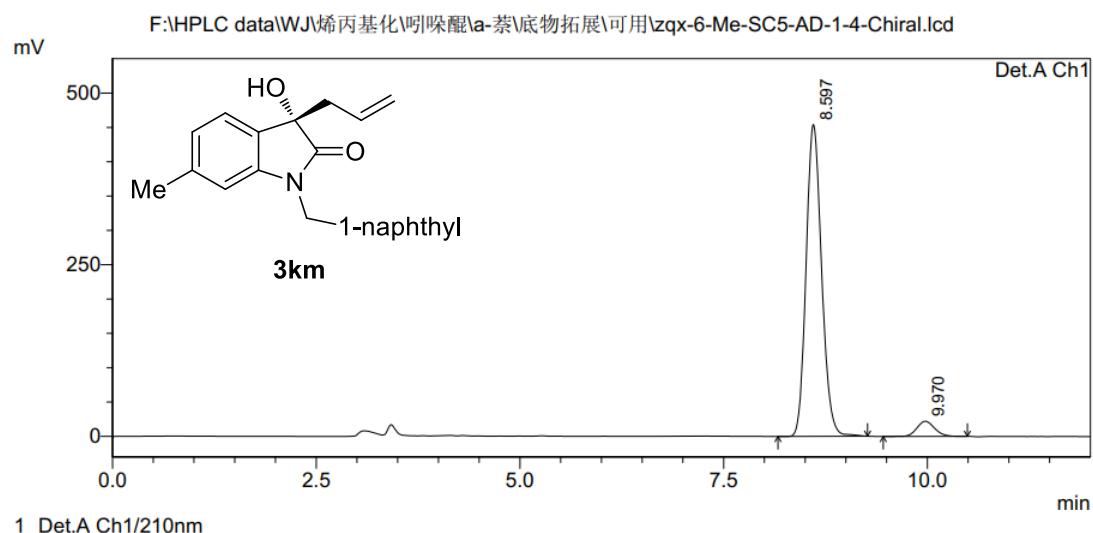
PeakTable

Detector A Ch1 210nm

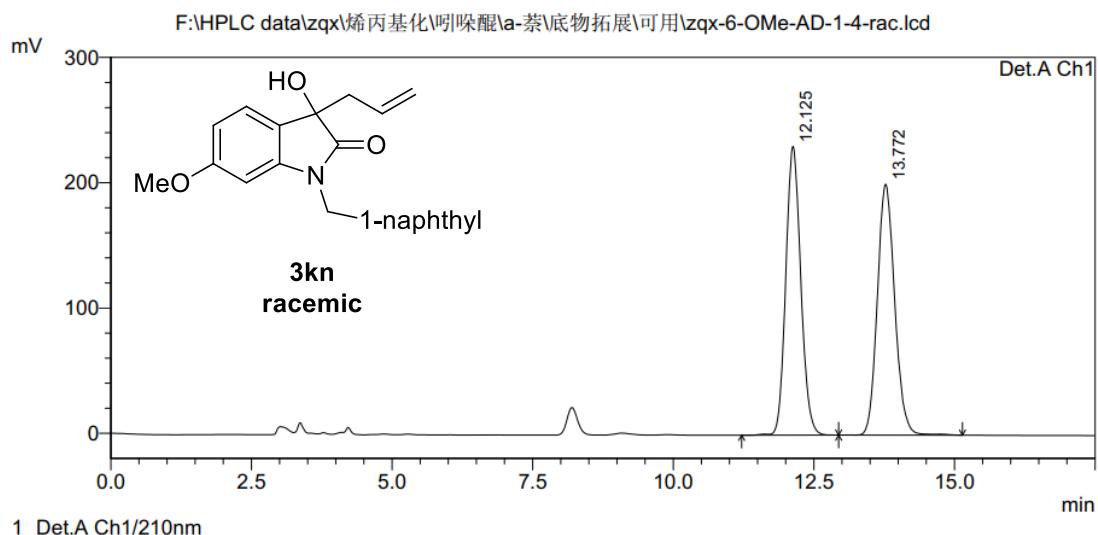
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.262	325122	29958	5.208	6.916
2	7.923	5918208	403229	94.792	93.084
Total		6243330	433187	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.578	9644109	722487	49.699	53.496
2	9.949	9760845	628058	50.301	46.504
Total		19404954	1350545	100.000	100.000



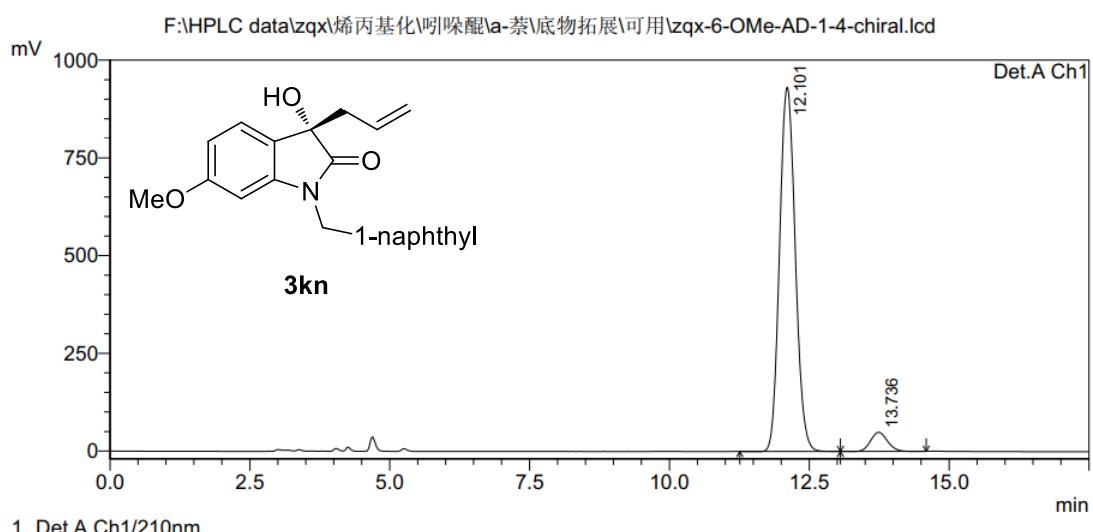
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.597	6009458	454124	94.726	95.353
2	9.970	334614	22132	5.274	4.647
Total		6344072	476256	100.000	100.000



PeakTable

Detector A Ch1 210nm

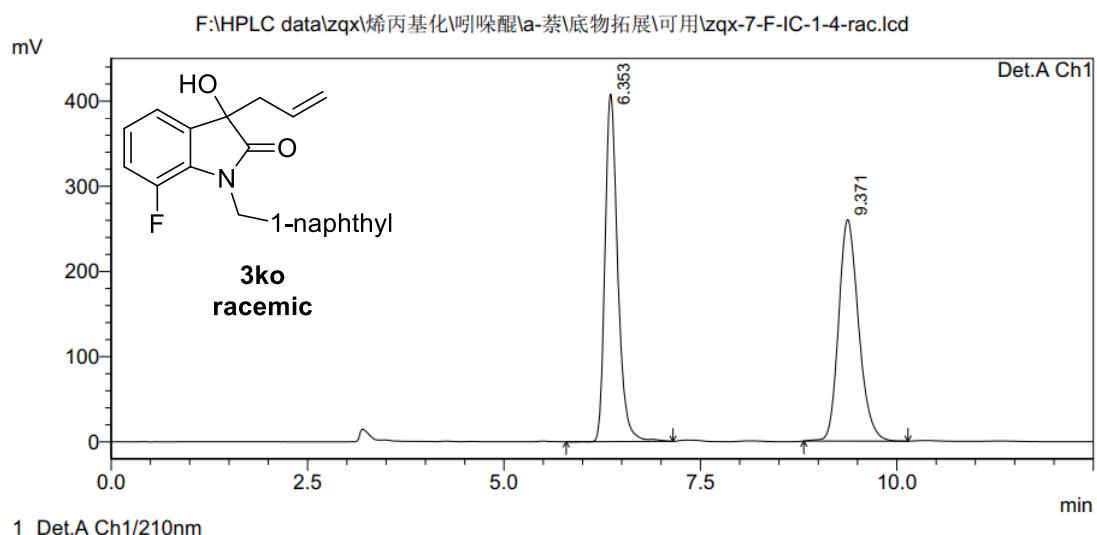
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.125	4273969	230304	49.828	53.489
2	13.772	4303495	200263	50.172	46.511
Total		8577463	430566	100.000	100.000



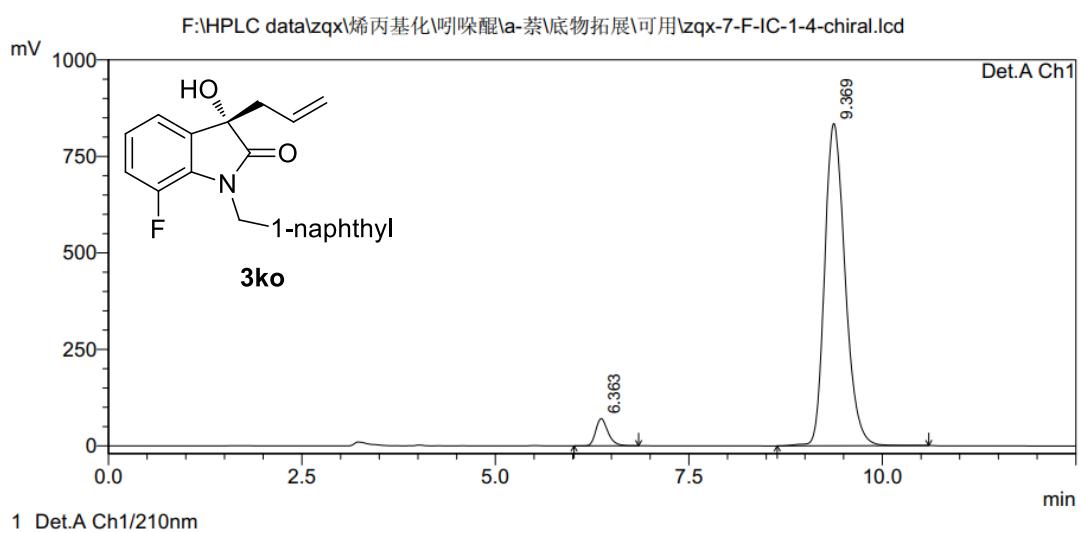
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.101	18250458	931318	94.741	95.029
2	13.736	1013114	48719	5.259	4.971
Total		19263573	980037	100.000	100.000

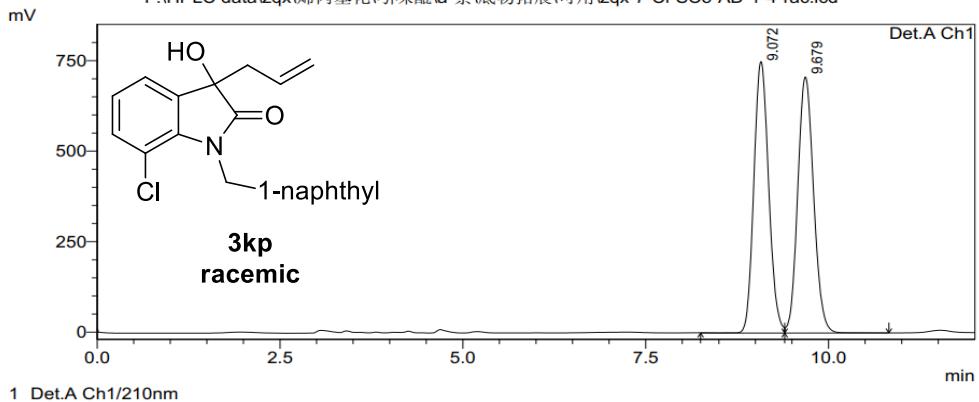


PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.353	4581677	408092	49.914	61.075
2	9.371	4597509	260094	50.086	38.925
Total		9179186	668186	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.363	771645	70800	4.767	7.816
2	9.369	15414123	835022	95.233	92.184
Total		16185768	905822	100.000	100.000

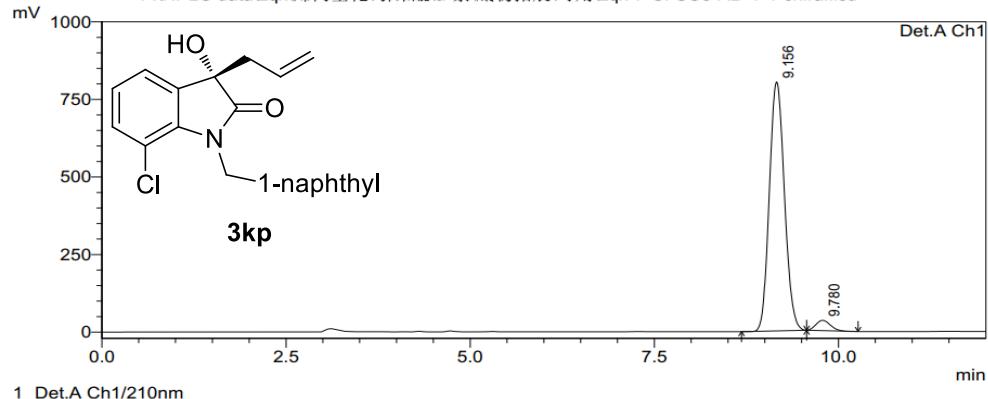
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PeakTable

Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.072	10563596	750071	49.691	51.459
2	9.679	10695095	707536	50.309	48.541
Total		21258691	1457607	100.000	100.000

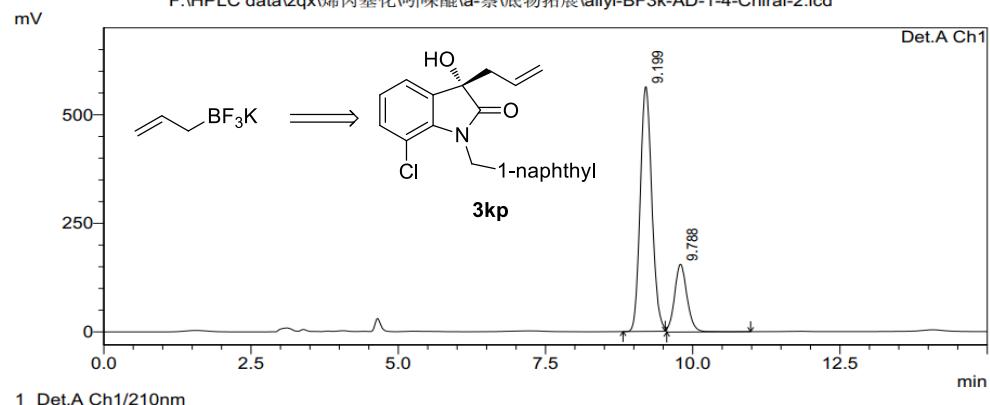
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PeakTable

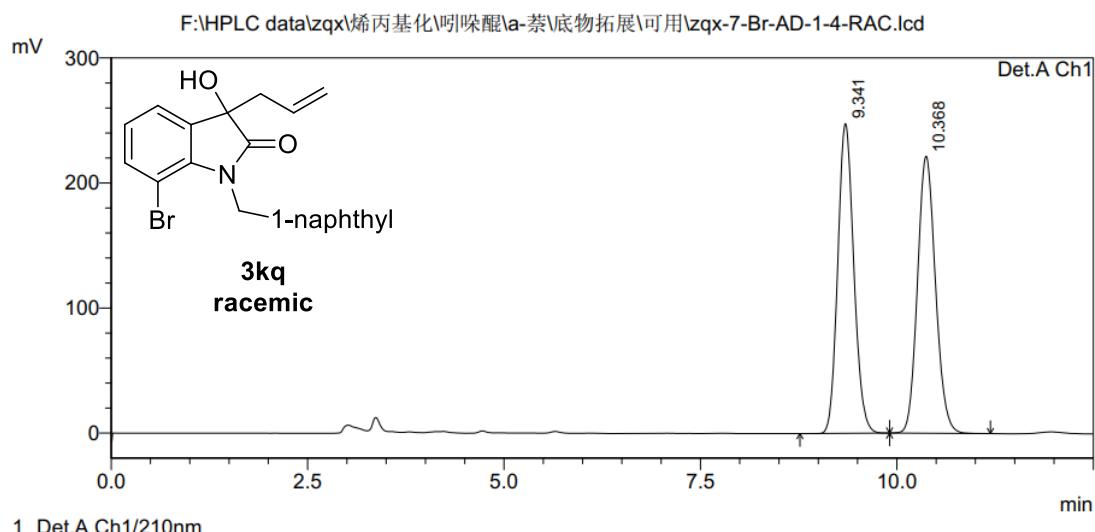
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.156	11406473	802354	96.220	96.020
2	9.780	448145	33255	3.780	3.980
Total		11854618	835609	100.000	100.000

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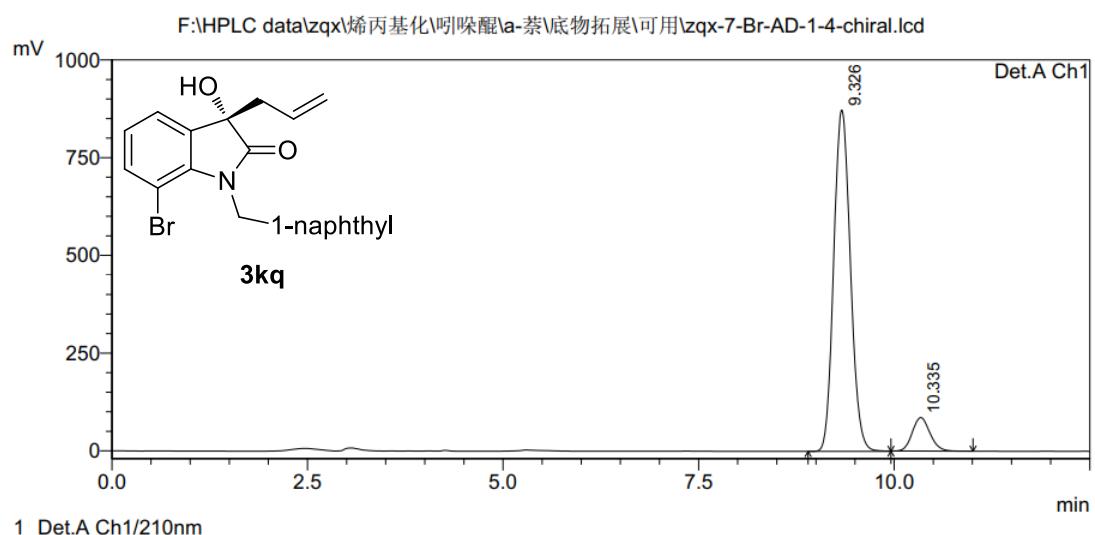


PeakTable

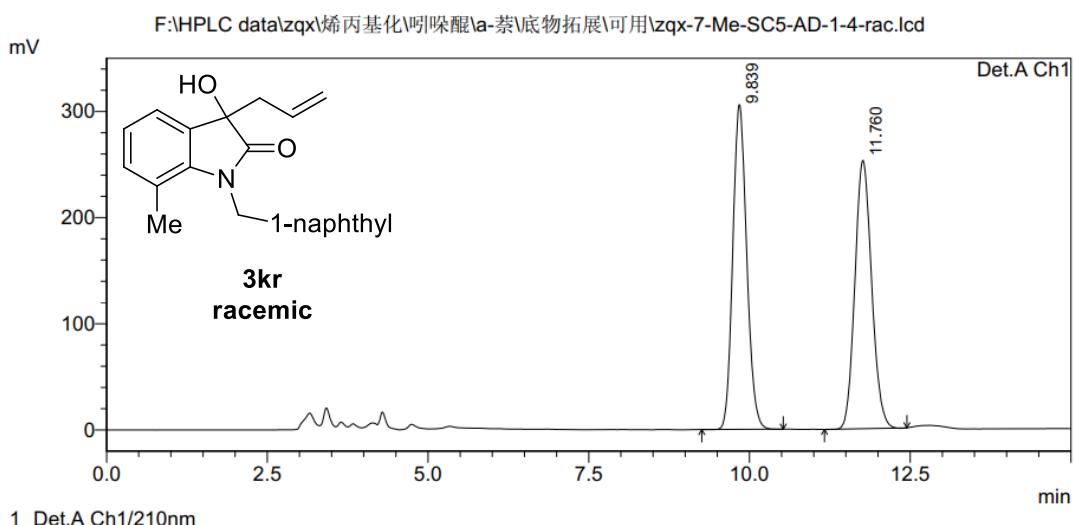
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.199	7727263	563694	77.097	78.313
2	9.788	2295557	156098	22.903	21.687
Total		10022820	719793	100.000	100.000



Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.341	3514720	247685	49.894	52.783
2	10.368	3529601	221568	50.106	47.217
Total		7044322	469253	100.000	100.000



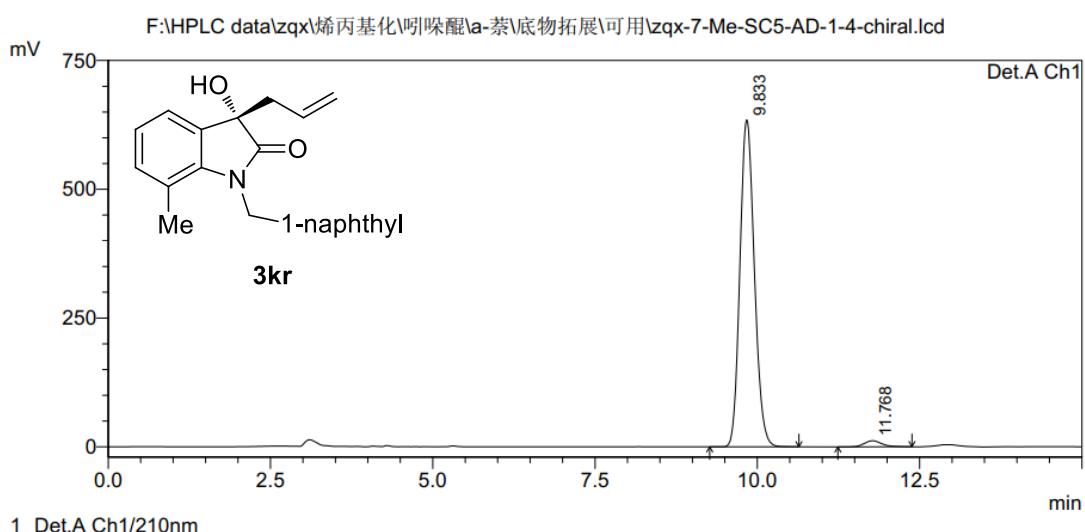
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.326	12978051	873143	90.610	91.058
2	10.335	1344987	85744	9.390	8.942
Total		14323037	958886	100.000	100.000



PeakTable

Detector A Ch1 210nm

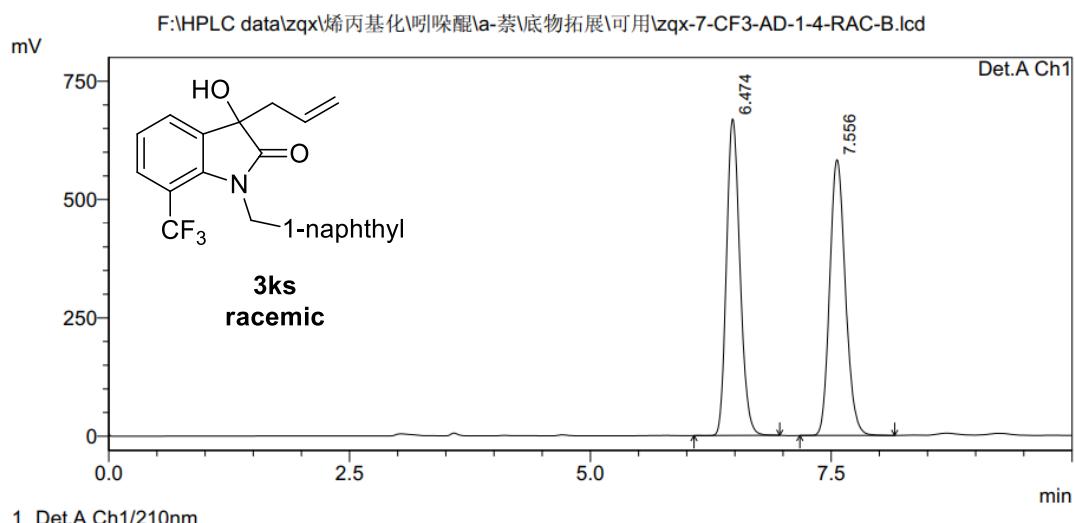
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.839	4617642	306001	50.199	54.748
2	11.760	4581025	252921	49.801	45.252
Total		9198667	558922	100.000	100.000



PeakTable

Detector A Ch1 210nm

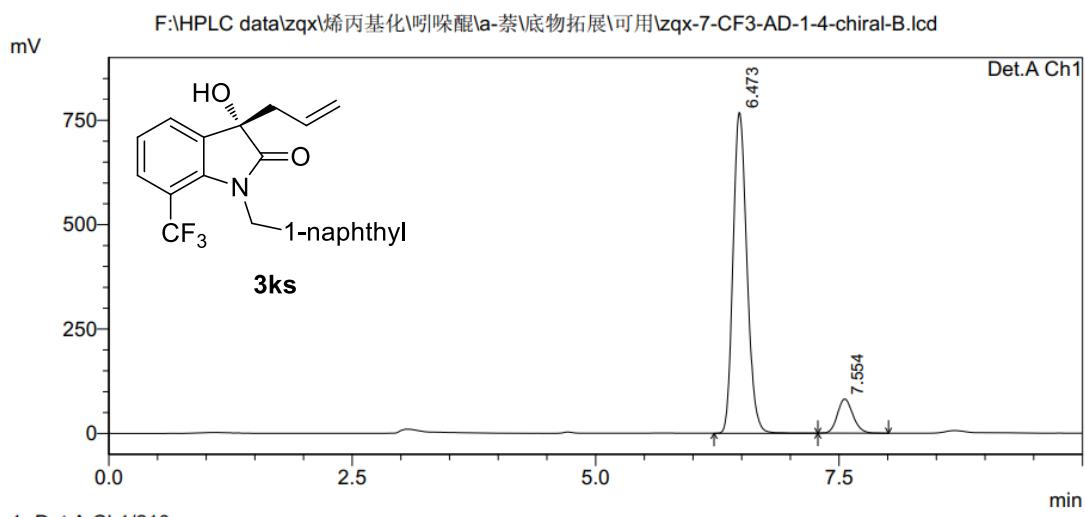
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.833	9821034	634615	97.833	98.189
2	11.768	217508	11703	2.167	1.811
Total		10038542	646318	100.000	100.000



1 Det.A Ch1/210nm

PeakTable

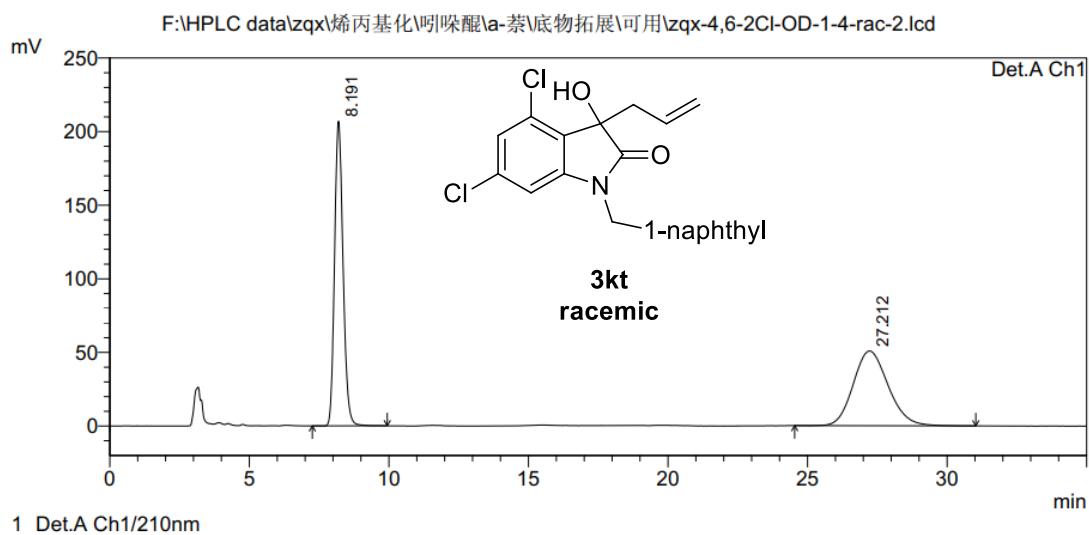
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.474	6506923	668663	49.667	53.429
2	7.556	6594182	582843	50.333	46.571
Total		13101104	1251506	100.000	100.000



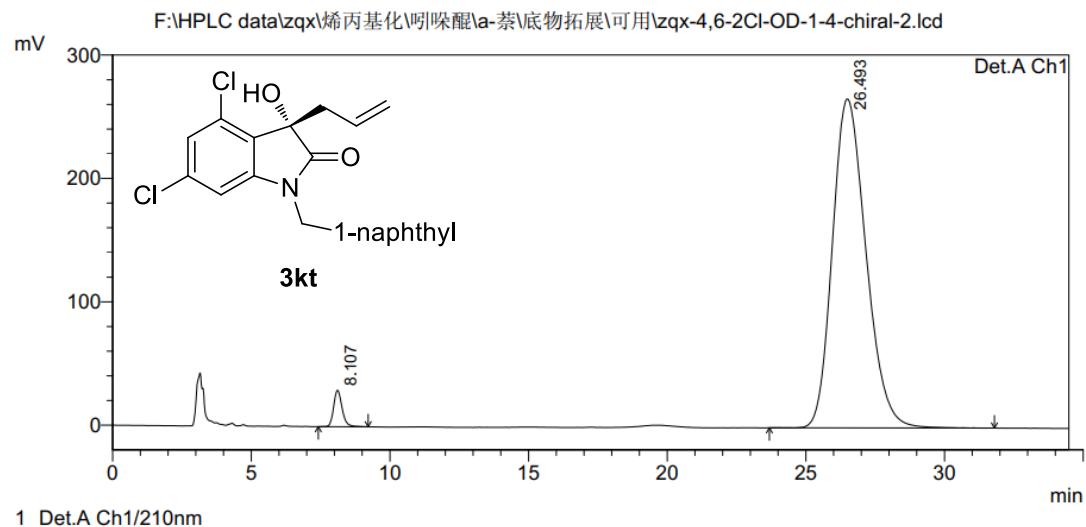
1 Det.A Ch1/210nm

PeakTable

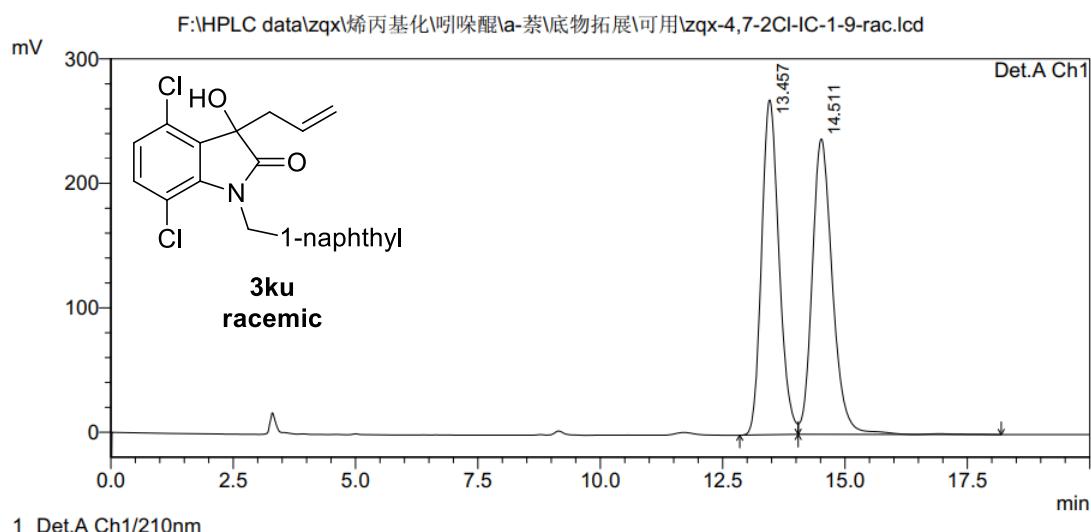
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.473	7608788	768653	89.393	90.392
2	7.554	902852	81704	10.607	9.608
Total		8511641	850357	100.000	100.000



PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.191	4399262	206940	49.943	80.315
2	27.212	4409307	50722	50.057	19.685
Total		8808569	257662	100.000	100.000



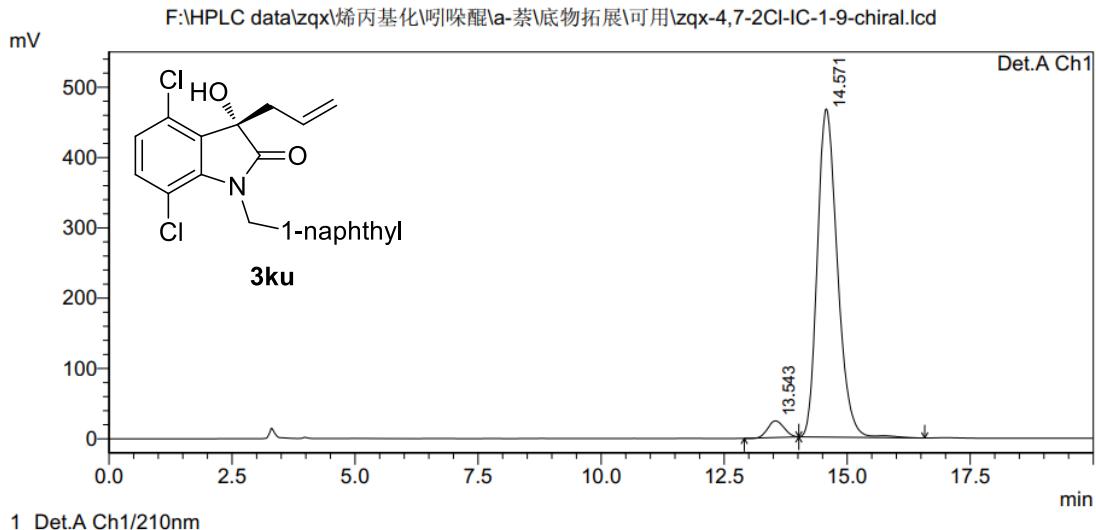
PeakTable					
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.107	626830	29506	2.717	9.963
2	26.493	22443236	266653	97.283	90.037
Total		23070066	296159	100.000	100.000



PeakTable

Detector A Ch1 210nm

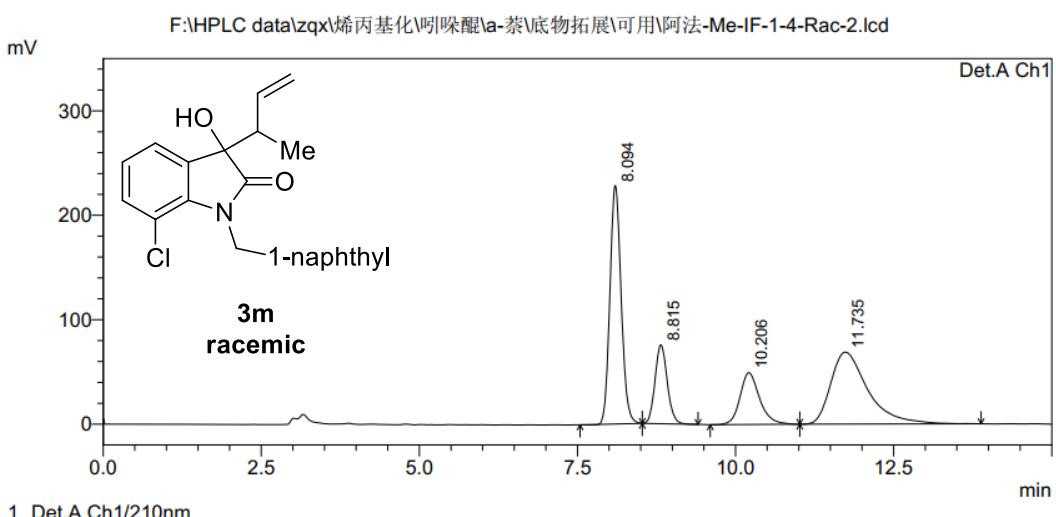
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.457	6649296	269025	49.346	53.120
2	14.511	6825511	237421	50.654	46.880
Total		13474808	506446	100.000	100.000



PeakTable

Detector A Ch1 210nm

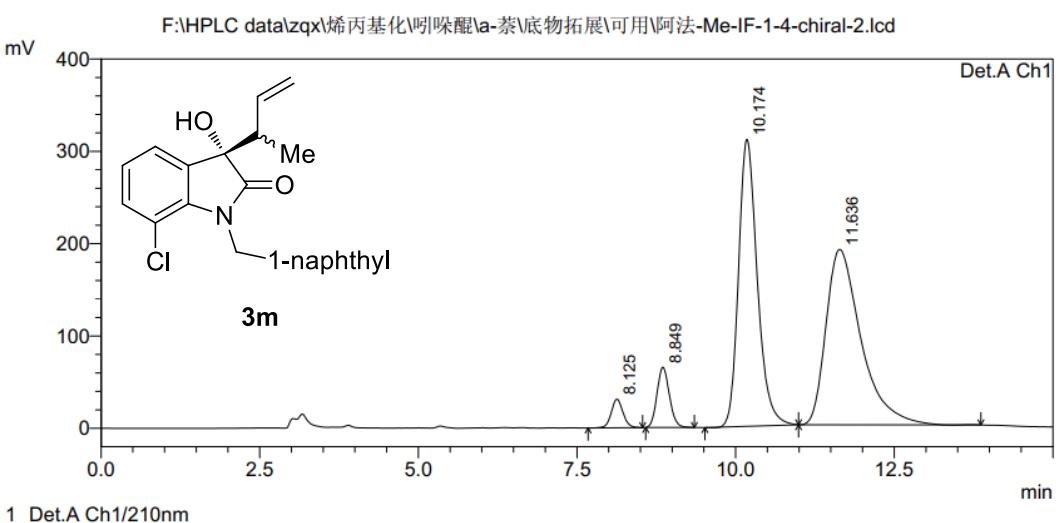
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.543	542265	23857	3.937	4.863
2	14.571	13231039	466766	96.063	95.137
Total		13773304	490623	100.000	100.000



PeakTable

Detector A Ch1 210nm

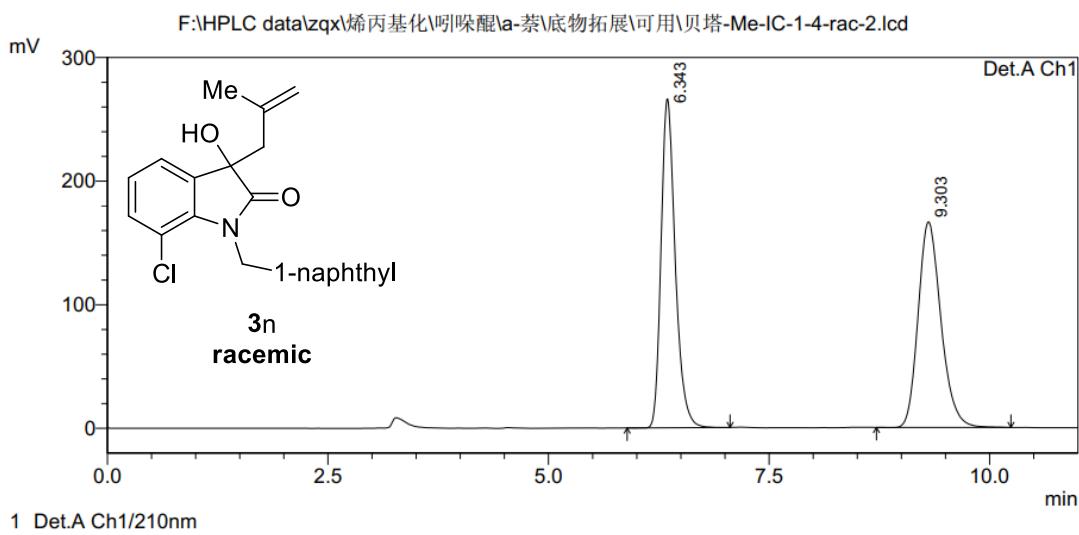
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.094	2810289	228485	36.483	54.069
2	8.815	1014102	75539	13.165	17.876
3	10.206	1065949	49605	13.838	11.739
4	11.735	2812571	68953	36.513	16.317
Total		7702912	422582	100.000	100.000



PeakTable

Detector A Ch1 210nm

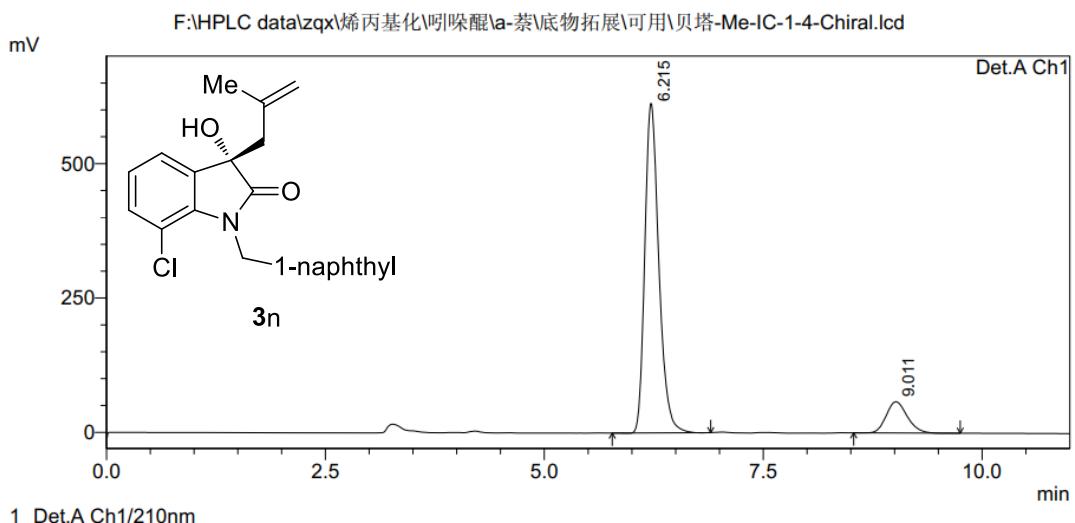
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.125	399716	31032	2.672	5.197
2	8.849	884004	65204	5.909	10.920
3	10.174	6383008	310846	42.663	52.060
4	11.636	7294598	190010	48.756	31.823
Total		14961326	597093	100.000	100.000



PeakTable

Detector A Ch1 210nm

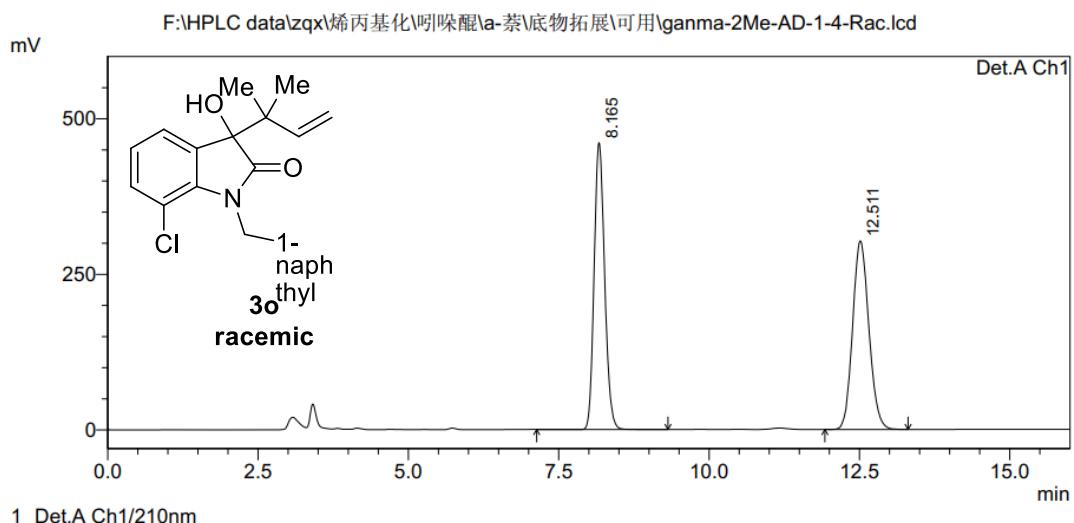
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.343	2980230	266092	49.926	61.526
2	9.303	2989030	166393	50.074	38.474
Total		5969260	432484	100.000	100.000



PeakTable

Detector A Ch1 210nm

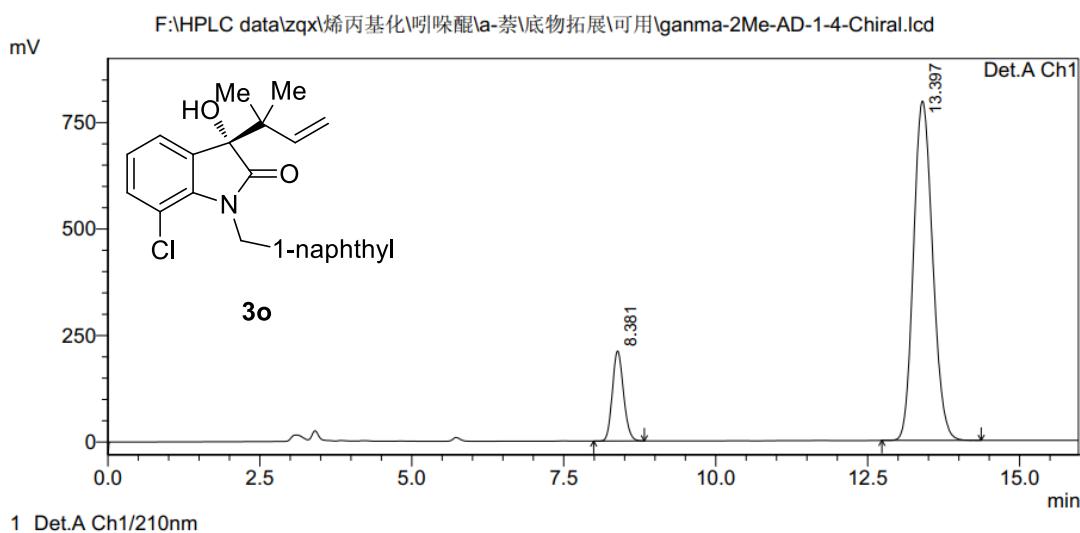
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.215	6839136	613235	87.594	91.328
2	9.011	968631	58227	12.406	8.672
Total		7807767	671462	100.000	100.000



PeakTable

Detector A Ch1 210nm

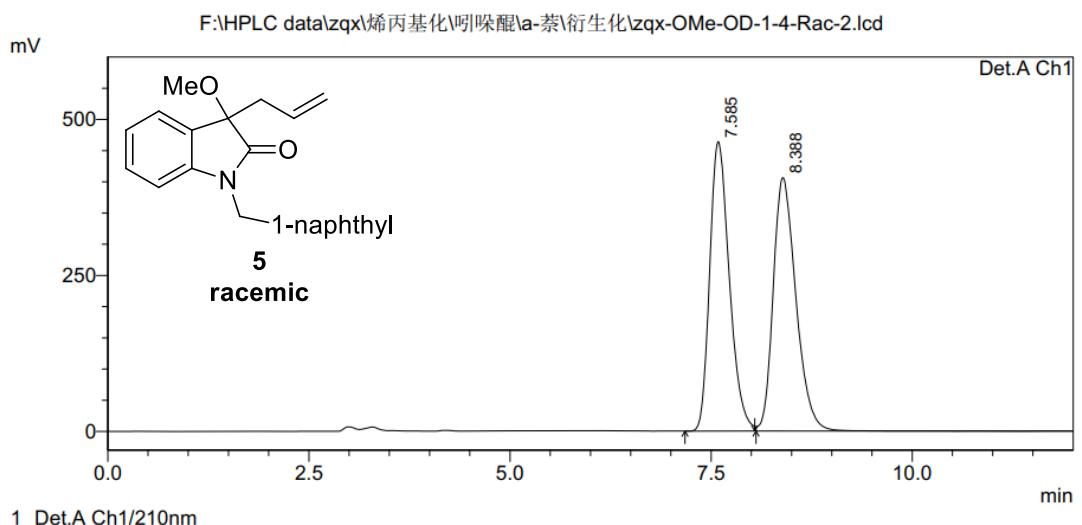
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.165	5586417	460948	49.434	60.321
2	12.511	5714311	303208	50.566	39.679
Total		11300729	764156	100.000	100.000



PeakTable

Detector A Ch1 210nm

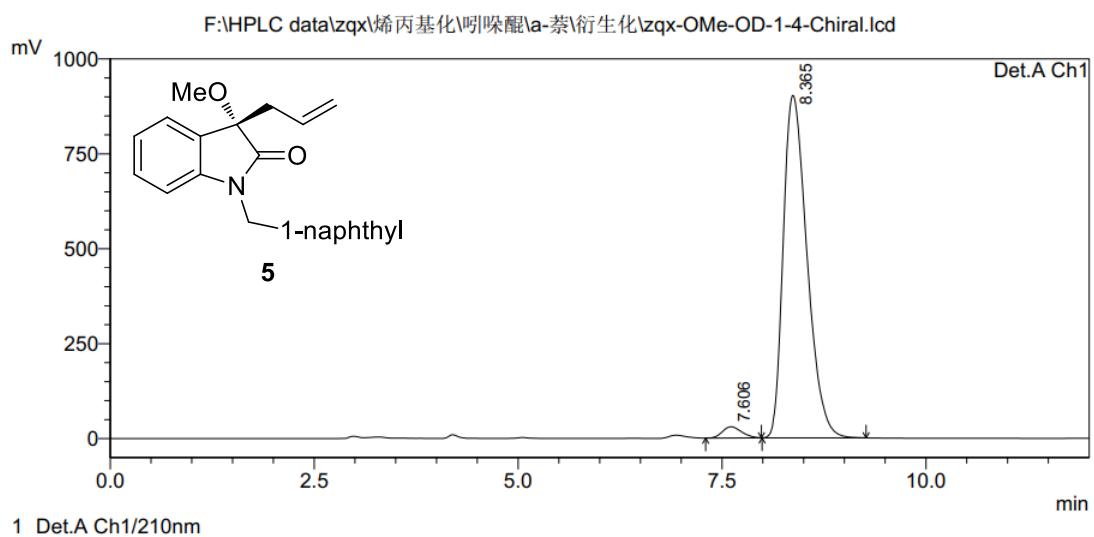
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.381	2696295	211286	13.455	20.965
2	13.397	17343624	796539	86.545	79.035
Total		20039918	1007825	100.000	100.000



PeakTable

Detector A Ch1 210nm

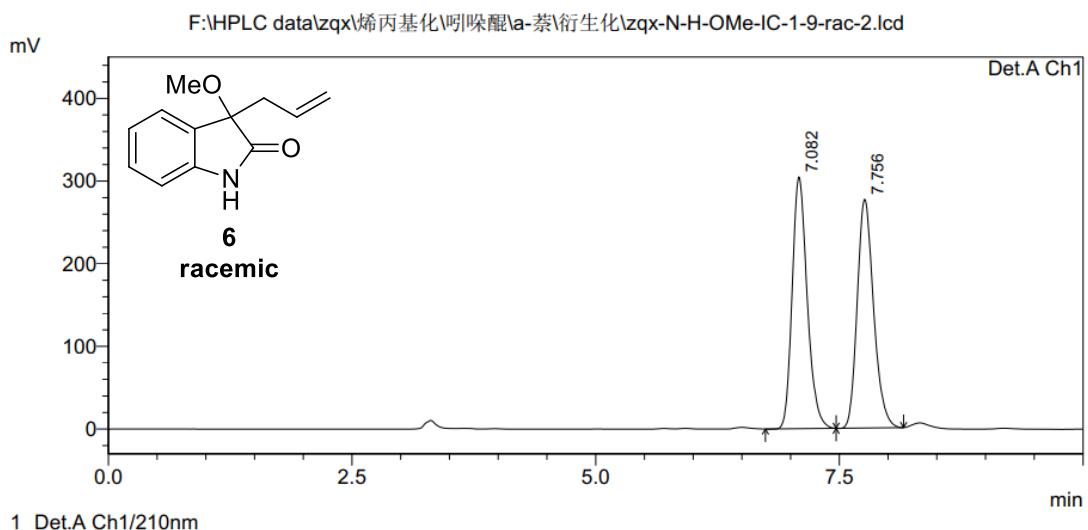
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.585	7854628	463954	49.621	53.322
2	8.388	7974596	406139	50.379	46.678
Total		15829225	870093	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.606	481577	29706	2.571	3.188
2	8.365	18245924	902195	97.429	96.812
Total		18727501	931902	100.000	100.000

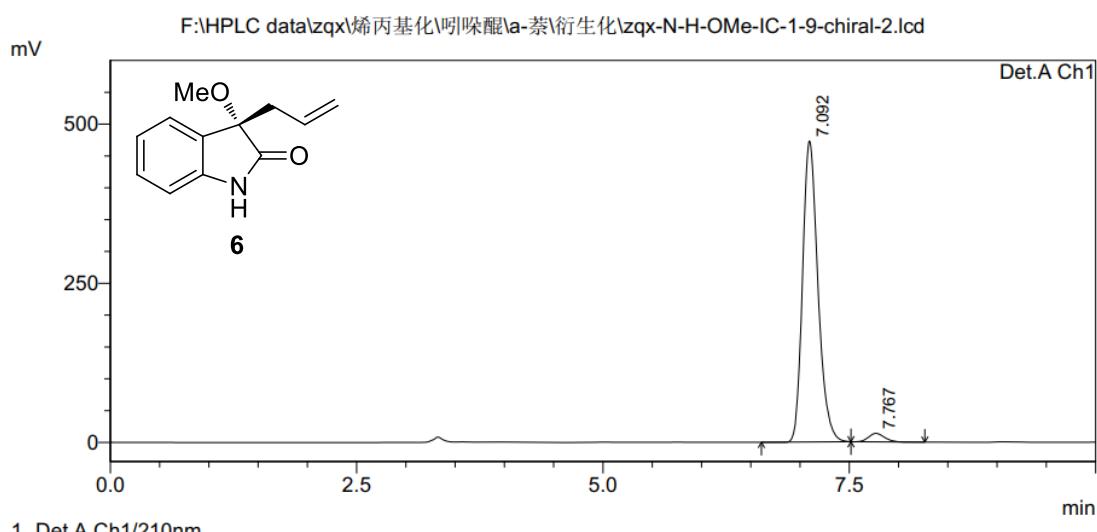


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.082	3265476	304558	50.297	52.388
2	7.756	3226936	276791	49.703	47.612
Total		6492412	581349	100.000	100.000

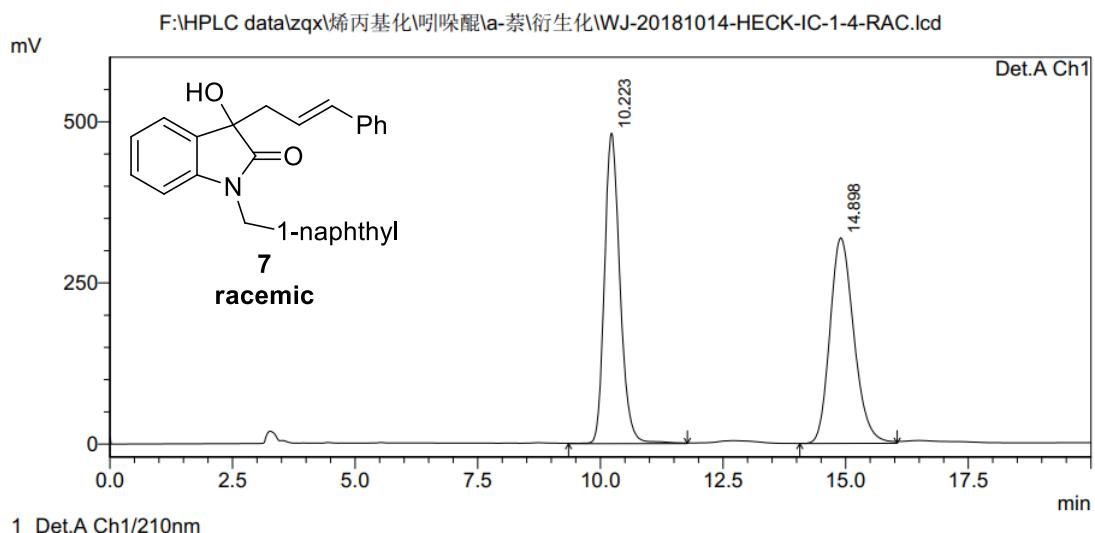


1 Det.A Ch1/210nm

PeakTable

Detector A Ch1 210nm

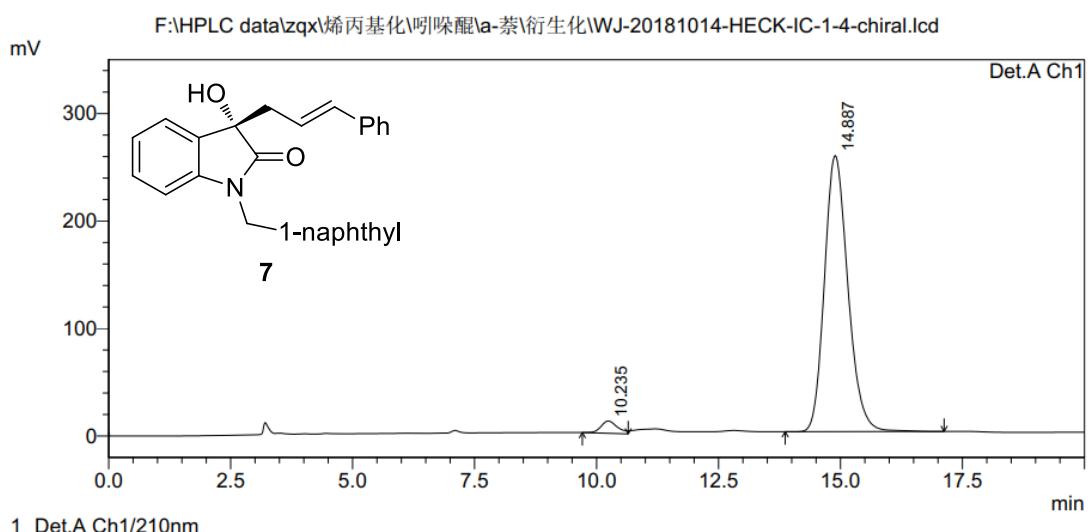
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.092	5121018	472295	97.252	97.266
2	7.767	144716	13276	2.748	2.734
Total		5265733	485572	100.000	100.000



PeakTable

Detector A Ch1 210nm

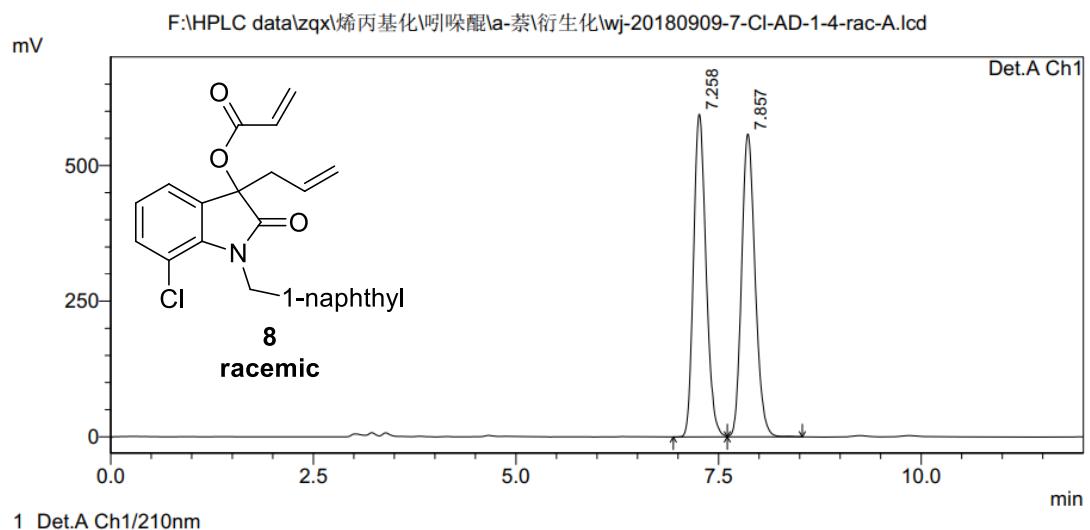
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.223	10630705	481721	49.517	60.187
2	14.898	10837928	318654	50.483	39.813
Total		21468633	800375	100.000	100.000



PeakTable

Detector A Ch1 210nm

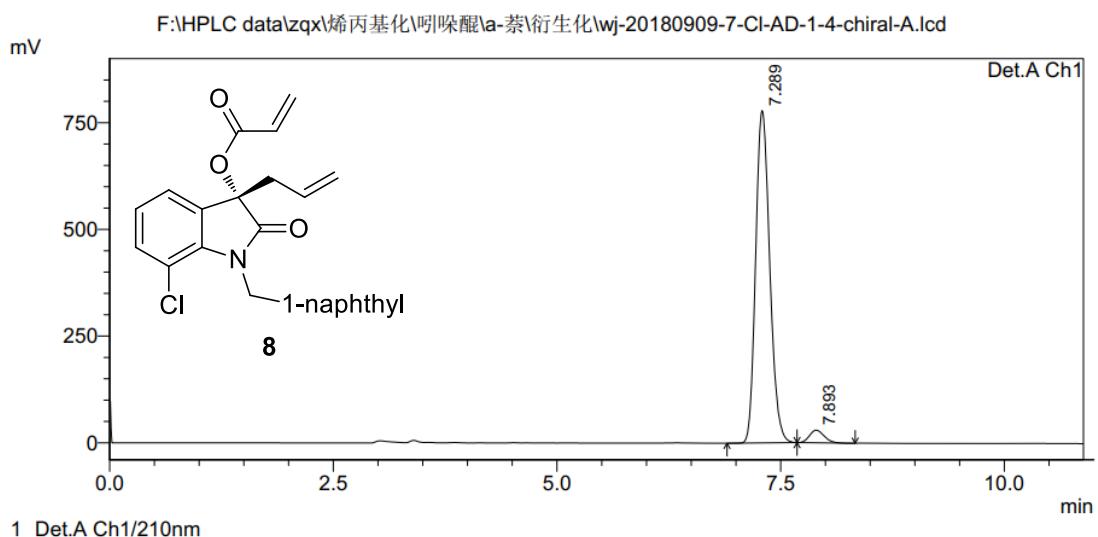
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.235	270815	11412	3.056	4.254
2	14.887	8592019	256843	96.944	95.746
Total		8862834	268255	100.000	100.000



PeakTable

Detector A Ch1 210nm

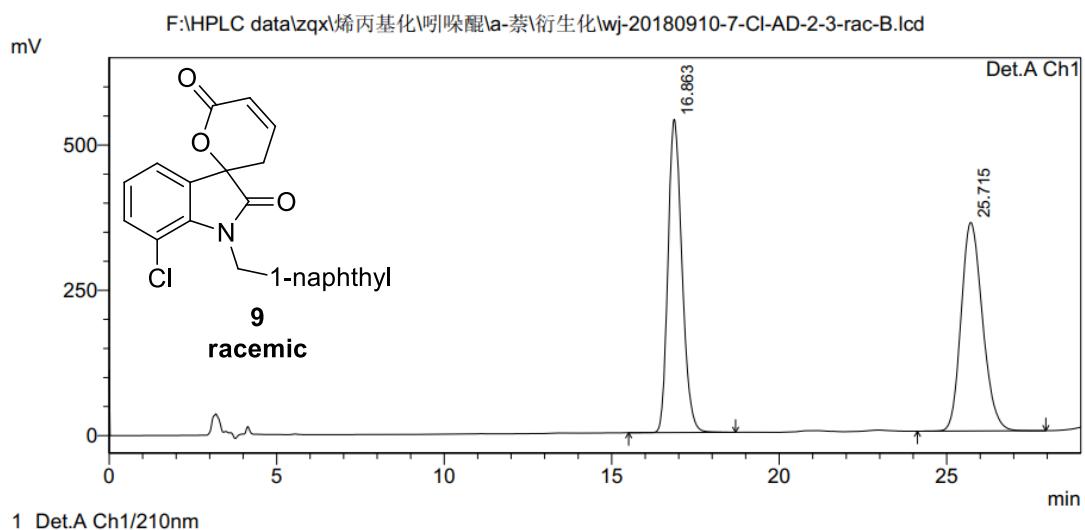
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.258	6360710	594582	49.605	51.582
2	7.857	6462019	558115	50.395	48.418
Total		12822729	1152697	100.000	100.000



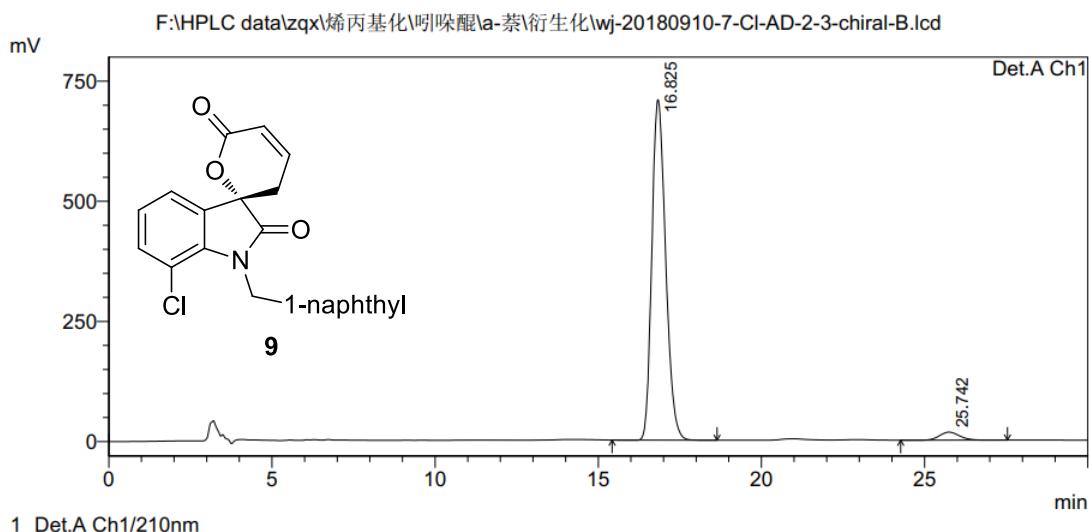
PeakTable

Detector A Ch1 210nm

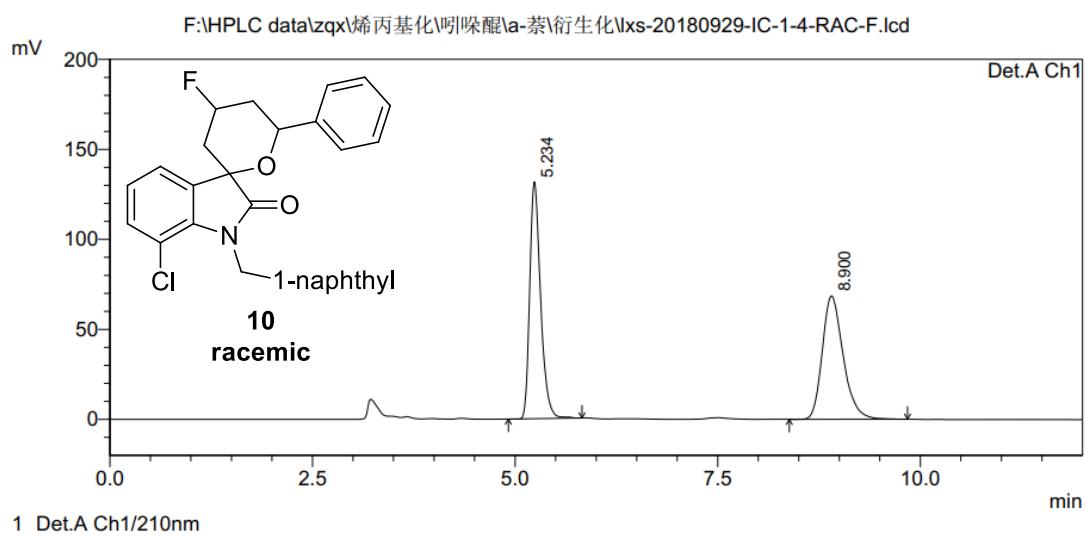
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.289	8491821	778974	96.197	96.329
2	7.893	335752	29684	3.803	3.671
Total		8827573	808657	100.000	100.000



Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.863	15662293	538896	49.576	60.025
2	25.715	15929949	358892	50.424	39.975
Total		31592242	897788	100.000	100.000



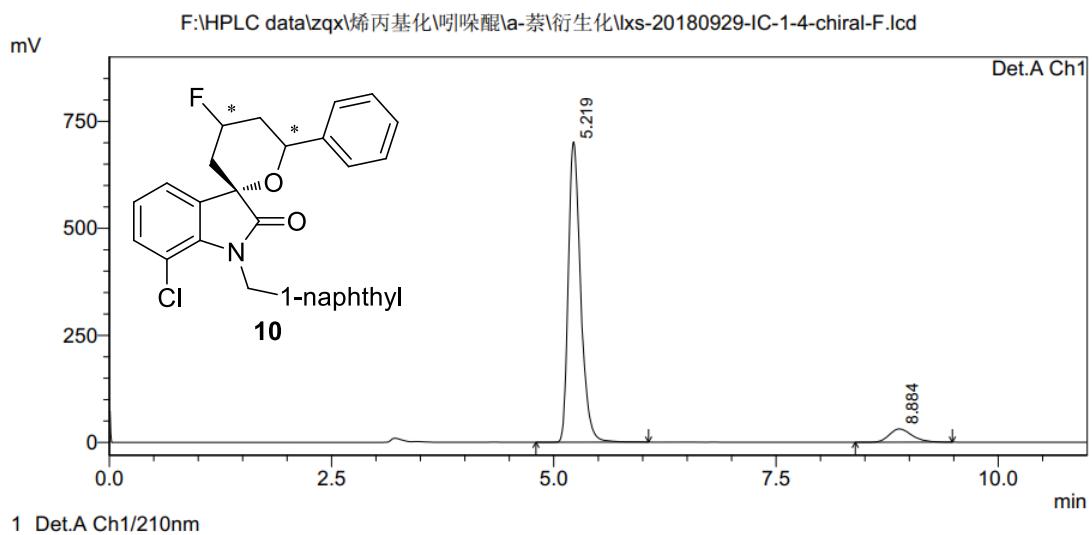
Detector A Ch1 210nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.825	20795154	708535	96.729	97.707
2	25.742	703165	16630	3.271	2.293
Total		21498319	725164	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.234	1223570	131593	49.920	65.769
2	8.900	1227471	68489	50.080	34.231
Total		2451041	200082	100.000	100.000



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.219	6737063	701843	92.418	95.745
2	8.884	552677	31194	7.582	4.255
Total		7289739	733036	100.000	100.000