

Supporting Information

Organocatalytic Atroposelective *N*-Alkylation: Divergent Synthesis of Axially Chiral Sulfonamides and Biaryl Amino Phenols

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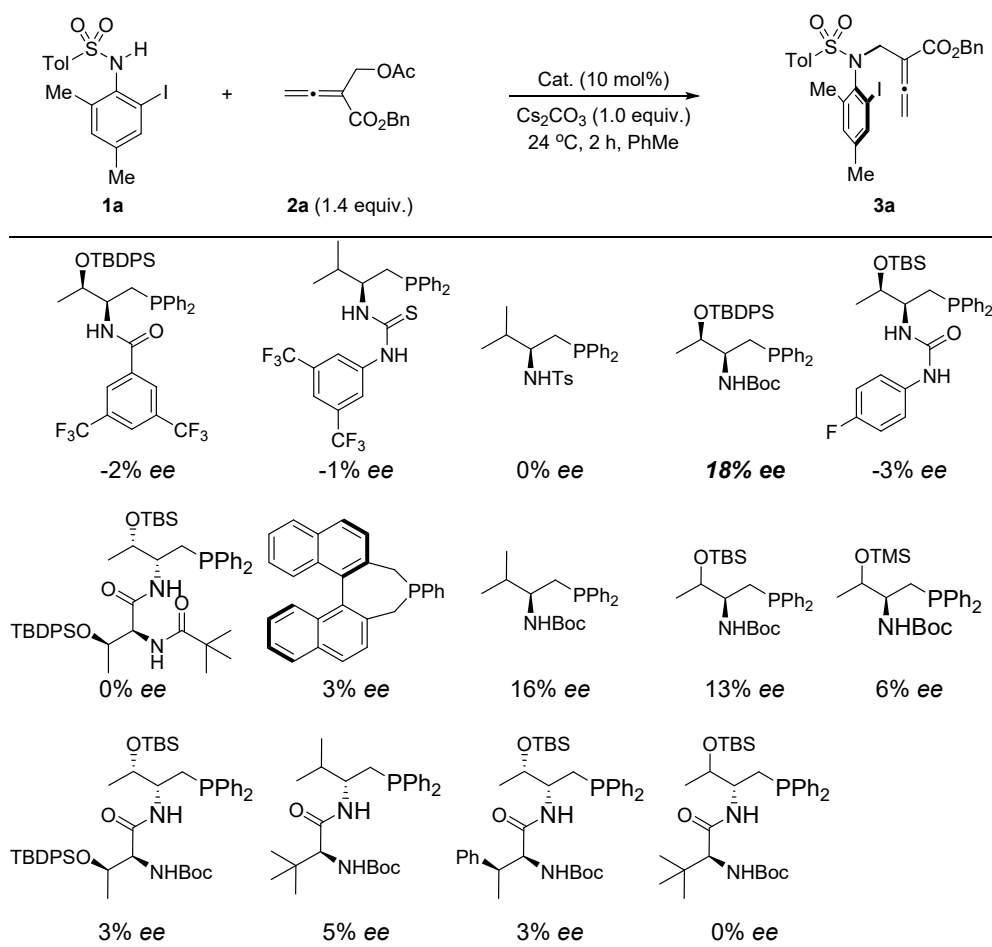
I. Supplementary Methods

General information. All experiments were conducted under air atmosphere unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Bruker AscendTM 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^1H (chloroform δ 7.26; DMSO δ 2.50), ^{13}C (chloroform δ 77.0; DMSO δ 39.5). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254nm. High resolution mass spectra (HRMS) were obtained on an Agilent 1290II-6545 spectrometer. Optical rotations were recorded on a Rudolph Research Analytical Autopol I automatic polarimeter. Enantiomeric excesses (*ee*) were determined by HPLC analysis on Agilent HPLC units, and Waters e2695; column of Chiralcel OD-H, Chiralpak AD-H, AS-H, ID or IE was used. Column chromatography was performed with silica gel (200-300 mesh ASTM). Unless otherwise noted, commercially available reagents purchased from Adamas-beta, TCI, or Energy Chemical and were used as received.

The 2,3-dienoate adducts 2^[1], MBH acetates 4^[2] and *rac*-**8**^[3] were synthesized in one step from commercially available materials by literature methods.

II. Optimization of axially chiral sulfonamides synthesis

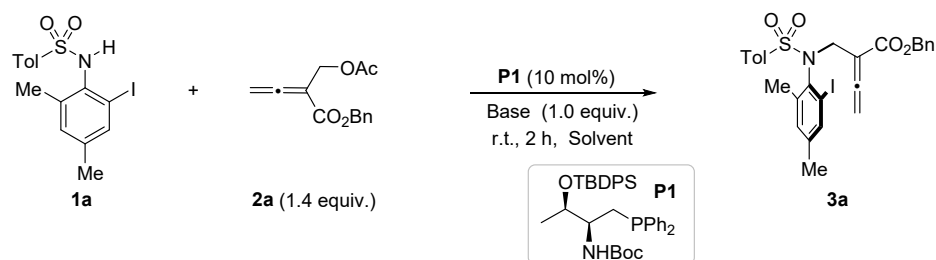
Supplementary Table 1. Attempt of Synthesis of Axially Chiral Sulfonamides from Allenates *via* Phosphine Catalysis^{a,b}



^aUnless noted otherwise, the reactions were performed with **1** (0.05 mmol), **2** (0.07 mmol, 1.4 equiv.), cat. (10 mol%), and Cs₂CO₃ (0.05 mmol, 1.0 equiv.) in toluene (0.5 mL) at 24 °C for 2 h. ^bThe *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **1** (0.1 mmol), phosphine (10 mol%) and Cs₂CO₃ (0.1 mmol, 1.0 equiv.) were added toluene (0.5 mL) and dienolate **2a** (0.14 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 °C for 2 h. Then, the *ee* value of **3a** was determined by chiral HPLC.

Supplementary Table 2. Base and Solvent Screening^a

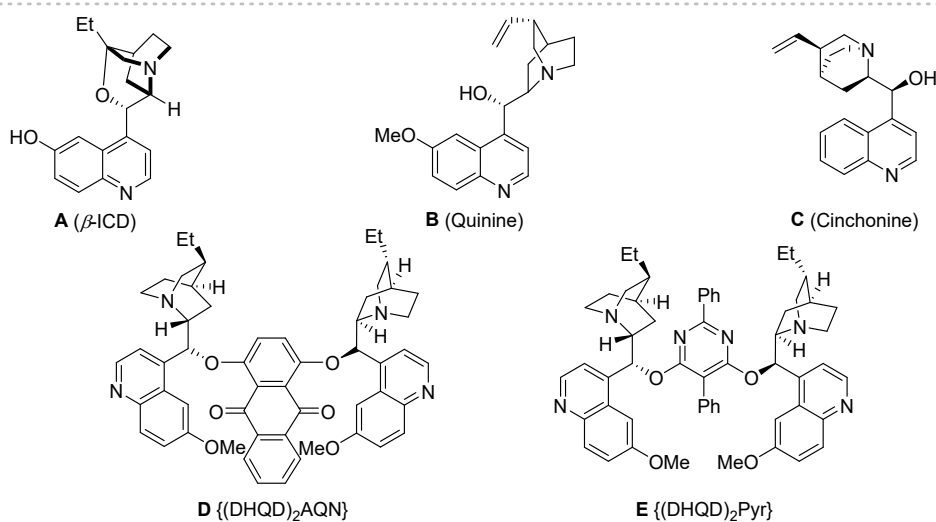
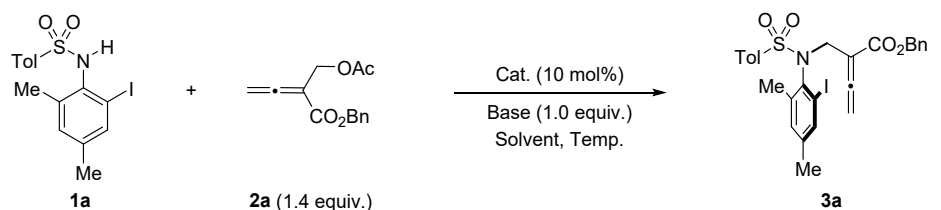


Entry	Base	Solvent	ee (%) ^b
1	Cs₂CO₃	PhMe	18
2	K ₂ CO ₃	PhMe	12
3	Na ₂ CO ₃	PhMe	13
4	Li ₂ CO ₃	PhMe	-
5	KHCO ₃	PhMe	10
6	NaHCO ₃	PhMe	-
7	K ₃ PO ₄	PhMe	7
8	Na ₂ HPO ₄	PhMe	-
9	Cs ₂ CO ₃	THF	0
10	Cs ₂ CO ₃	HCCl ₃	0
11	Cs ₂ CO ₃	Et ₂ O	9
12	Cs ₂ CO ₃	EtOAc	3
13	Cs ₂ CO ₃	CH ₃ CN	3
14	Cs ₂ CO ₃	PhCl	0
15	Cs ₂ CO ₃	Hexanes	3
16	Cs ₂ CO ₃	Acetone	0
17	Cs ₂ CO ₃	PhCF ₃	0

^aUnless noted otherwise, the reactions were performed with **1** (0.05 mmol), **2** (0.07 mmol, 1.4 equiv.), **P1** (10 mol%), and Cs₂CO₃ (0.05 mmol, 1.0 equiv.) in toluene (0.5 mL) at 24 °C for 2 h. ^bThe *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **1** (0.1 mmol), **P1** (10 mol%) and base (0.1 mmol, 1.0 equiv.) were added toluene (0.5 mL) and dienophile **2a** (0.14 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 °C for 2 h. Then, the *ee* value of **3a** was determined by chiral HPLC.

Axially Chiral Sulfonamides from Allenates *via* Amine Catalysis^a



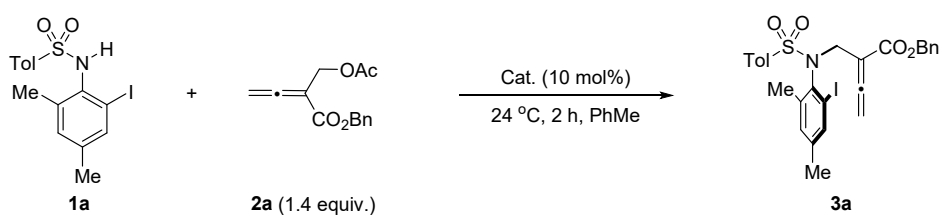
Entry	Cat.	Base	Solvent	Temp. (°C)	Yield (%) ^b	ee (%) ^c
1	A	-	PhMe	24	71	51
2	B	-	PhMe	24	75	21
3	C	-	PhMe	24	63	15
4	D	-	PhMe	24	67	-27
5	E	-	PhMe	24	85	-17
6	A	-	Mesitylene	24	84	72
7 ^d	A	-	Mesitylene	24	83	79
8 ^d	A	-	Mesitylene	-20	9	88
9 ^d	A	Cs ₂ CO ₃	Mesitylene	-20	91	84
10 ^d	A	Cs ₂ CO ₃	Mesitylene	-40	92	89
11 ^d	A	K ₂ CO ₃	Mesitylene	-40	73	88
12 ^d	A	Na ₂ CO ₃	Mesitylene	-40	61	89
13 ^d	A	KHCO ₃	Mesitylene	-40	35	83
14 ^d	A	K ₃ PO ₄	Mesitylene	-40	31	89
15 ^d	A	Cs ₂ CO ₃	Mesitylene	-50	92	90

^aUnless noted otherwise, the reactions were performed with **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.07 mmol, 1.4 equiv.), catalyst (10 mol%), and base (1.0 equiv.) in solvent (0.5 mL) at 24 to -50 °C for 12 h. ^bYield was detected by ¹H-NMR. ^cThe *ee* value was determined by chiral HPLC. ^dMesitylene (4 mL) was added.

To a Schlenk tube containing **1** (0.05 mmol), amine (10 mol%) and base (1.0 equiv.)

were added solvent (4 mL) and dienoate **2a** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 to -50 °C for 12 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **3a**.

Supplementary Table 4. Optimization of the Reaction Conditions via Amine Catalysis^{a,b}



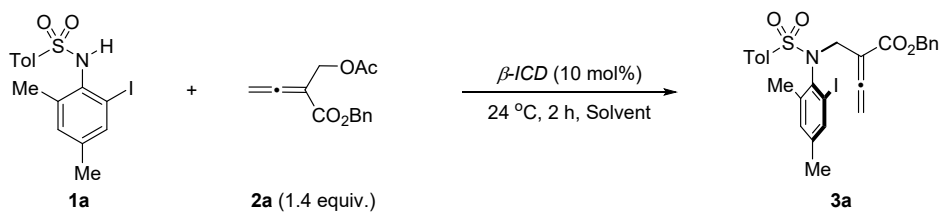
Entry	Cat.	ee (%)
1	Hydroquinine	19
2	<i>β</i>-ICD	51
3	Quinidine	21
4	Cinchonine	15
5	Cinchonidine	14
6	(DHQD) ₂ AQN	-27
7	(DHQD) ₂ Pyr	-17
8	(DHQD) ₂ PHAL	-17
9	(DHQ) ₂ AQN	-27
10	(DHQ) ₂ Pyr	3
11	(DHQD) ₂ PHAL	14

^aUnless noted otherwise, the reactions were performed with **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.07 mmol, 1.4 equiv.), catalyst (10 mol%), in toluene (0.5 mL) at 24 °C for 2 h. ^bThe *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **1** (0.05 mmol), amine (10 mol%) were added PhMe (0.5 mL) and dienoate **2a** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 °C for 2 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **3a**. The *ee* value of **3a** was determined by chiral HPLC.

Supplementary Table 5. Solvent Screening of the Reaction Conditions via Amine

Catalysis^{a,b}

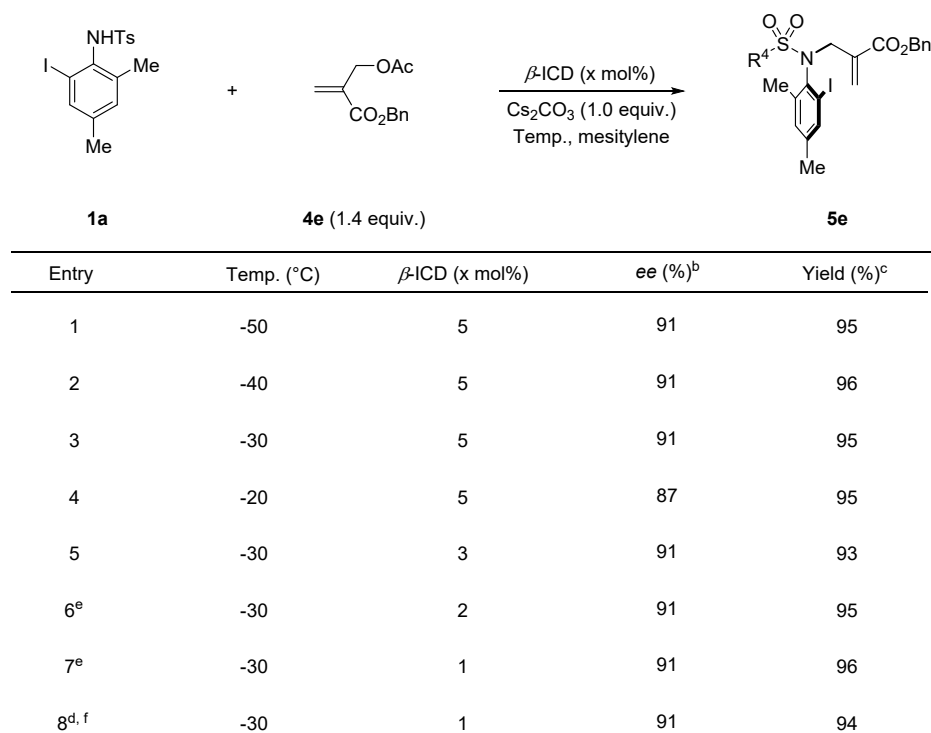


Entry	Solvent	ee (%)
1	DCM	47
2	THF	5
3	EtOAc	21
4	CH ₃ CN	33
5	DMSO	2
6	DMF	0
7	HCCl ₃	49
8	PhCl	57
9	PhF	55
10	<i>o</i> -DCB	53
11	PhCF ₃	41
12	PhH	57
13	Hexanes	32
14	<i>o</i> -Xylene	41
15	<i>m</i> -Xylene	69
16	<i>p</i> -Xylene	67
17	PhEt	70
18	PhOMe	57
19	Mesitylene	72
20^c	Mesitylene	79

^aUnless noted otherwise, the reactions were performed with **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.07 mmol, 1.4 equiv.), catalyst (10 mol%), in toluene (0.5 mL) at 24 °C for 2 h. ^bThe *ee* value was determined by chiral HPLC. ^cMesitylene (4 mL) was added. To a Schlenk tube containing **1** (0.05 mmol), amine (10 mol%) were added PhMe (0.5 mL) and dienoate **2a** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 °C for 2 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **3a**. The *ee* value of **3a** was determined by chiral HPLC.

Supplementary Table 6. Optimization of the Reaction Conditions to Access

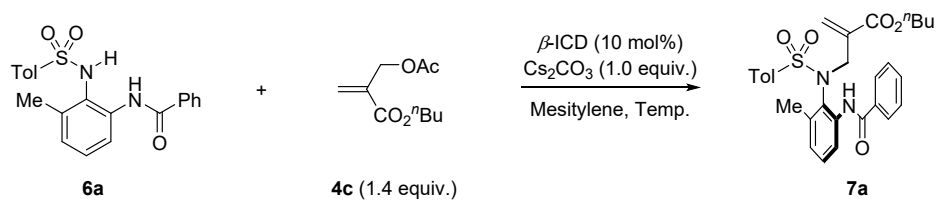
Axially Chiral Sulfonamides from MBH Acetate^a



^aReaction: **1** (0.1 mmol), **4** (0.14 mmol, 1.4 equiv.), β -ICD (x mol%), Cs_2CO_3 (0.1 mmol, 1.0 equiv.) in mesitylene (2 mL) at -30 to -50 °C for 24 h. ^bIsolated yield. ^cThe ee value was determined by chiral HPLC. ^dMesitylene (1 mL) was added. ^e48 h. ^f72 h.

To a Schlenk tube containing **1** (0.1 mmol), β -ICD (x mol%) and Cs_2CO_3 (0.1 mmol, 1.0 equiv.) were added mesitylene and MBH acetate **4e** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at 24 to -50 °C for 12 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **5e**.

Supplementary Table 7. Optimization of the Selective N-H Activation^a

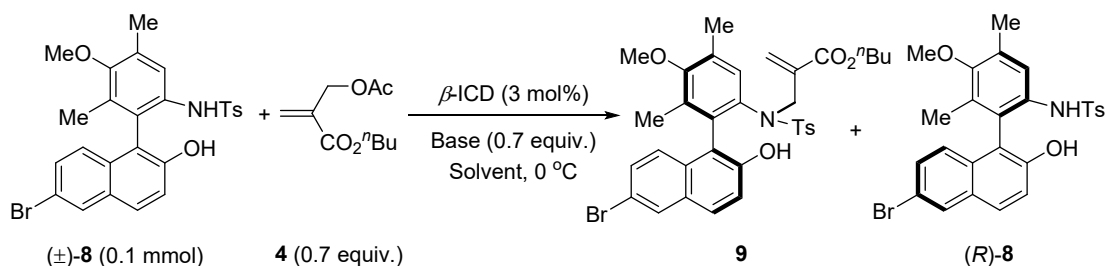


Entry	Temp. (°C)	Yield (%) ^b	ee (%) ^c
1	-30	71	77
2	-50	76	84

^aUnless noted otherwise, the reactions were performed with **6a** (0.05 mmol), **4a** (0.07 mmol, 1.4 equiv.), β -ICD (10 mol%), Cs_2CO_3 (0.05 mmol, 1.0 equiv.) in mesitylene (3 mL) at -30 to -50 °C for 24 h. ^bIsolated yield. ^cThe *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **6a** (0.05 mmol), β -ICD (10 mol%) and Cs_2CO_3 (0.05 mmol, 1.0 equiv.) were added mesitylene (3 mL) and MBH acetate **4c** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at -30 to -50 °C for 24 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **7a**.

Supplementary Table 8. Optimization of Kinetic Resolution of NOBINs^a



Entry	Base	Solvent	Temp. (°C)	C ^b (%)	8a, ee ^c	9a, ee ^c	s ^d
1	Cs_2CO_3	THF	0	54	71	60	8
2	Cs_2CO_3	CH_3CN	0	58	33	24	2
3	Cs_2CO_3	DCM	0	30	30	70	8
4	Cs_2CO_3	toluene	0	32	36	76	11
5	Cs_2CO_3	mesitylene	0	43	37	50	4
6	Cs_2CO_3	Chlorobenzene	0	51	73	70	12
7	K_2CO_3	Chlorobenzene	0	43	60	81	16
8	Na_2CO_3	Chlorobenzene	0	22	23	81	12
9	K_2CO_3	Chlorobenzene	-10	40	52	80	14
10 ^e	K_2CO_3	Chlorobenzene	0	55	77	94	27

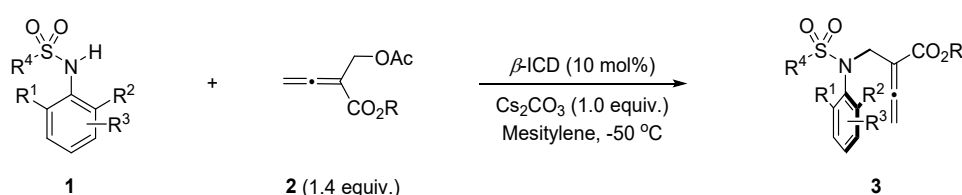
^aUnless noted otherwise, the reactions were performed with **8a** (0.1 mmol), **4a** (0.07 mmol, 0.7 equiv.), β -ICD (3 mol%), Base (0.07 mmol, 0.7 equiv.) in Solvent (2 mL)

at 0 °C for 12 h. ^bConversion (C) = $ee_{8a}/(ee_{8a}+ee_{9a})$. ^cThe *ee* value was determined by chiral HPLC. ^d $S = \ln[(1-\text{Conv.})(1-ee_{8a})]/\ln(1-\text{Conv.})(1+ee_{8a})]$. ^ethe reactions were performed with **8a** (0.1 mmol), **4a** (0.035 mmol, 0.35 equiv.), β -ICD (3 mol%), Base (0.035 mmol, 0.35 equiv.) in Solvent (8 mL) at 0 °C for 36 h

To a Schlenk tube containing **6a** (0.05 mmol), β -ICD (10 mol%) and Cs₂CO₃ (0.05 mmol, 1.0 equiv.) were added mesitylene (3 mL) and MBH acetate **4c** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at -30 to -50 °C for 24 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **7a**.

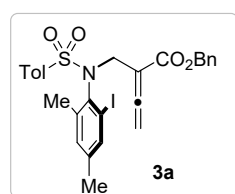
III. General procedure and spectra data of axially chiral sulfonamides and biaryl amino phenols

Representative procedure for synthesis of **3**:



To a Schlenk tube containing **1** (0.05 mmol), β -ICD (1.5 mg, 10 mol%) and Cs₂CO₃ (0.05 mmol, 1.0 equiv.) were added mesitylene (4 mL) and dienophile **2** (0.07 mmol, 1.4 equiv.). The reaction mixture was stirred at -50 °C for 24 hours to 7 days. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography with hexanes/ethyl acetate as the eluent to afford the product **3**.

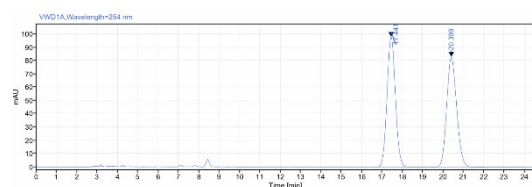
Characterization of compounds **3**:



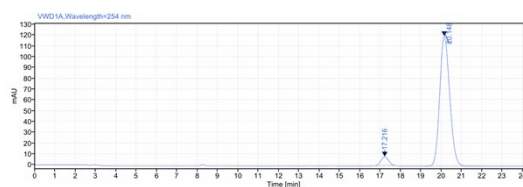
3a (91% yield, Hexane-EtOAc = 10:1, R_f = 0.3). Syrup. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.28 – 7.14 (m, 7H), 6.86 (m, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 4.98 (d, *J* = 14.6 Hz, 1H), 4.95 (d, *J* = 12.5 Hz, 1H), 4.87 (d, *J* = 14.6 Hz, 1H), 4.49 (s, 2H), 2.35 (s, 3H), 2.15 (s, 3H), 2.06 (s, 3H). ¹³C NMR (100

MHz, CDCl₃) δ 216.45, 165.7, 143.4, 141.9, 139.8, 138.9, 138.3, 137.4, 135.7, 132.1, 129.4, 128.4, 128.4, 128.1, 128.1, 101.4, 96.2, 79.3, 66.8, 48.7, 21.6, 20.4, 20.3.
HRMS (ESI) m/z Calcd for [C₂₇H₂₆INO₄S, M + H]⁺: 588.0700; Found: 588.0703.

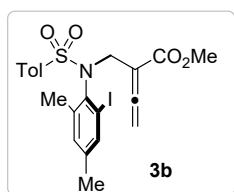
Optical Rotation: [α]²⁵_D -30.0 (*c* = 1.0, CHCl₃). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, *t*_R = 17.216 min for minor isomer, *t*_R = 20.148 min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.441	BB	2.24	2806.96	97.95	49.93	
20.399	BB	2.59	2814.58	82.99	50.07	
	Sum		5621.55			

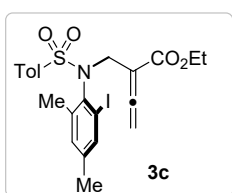
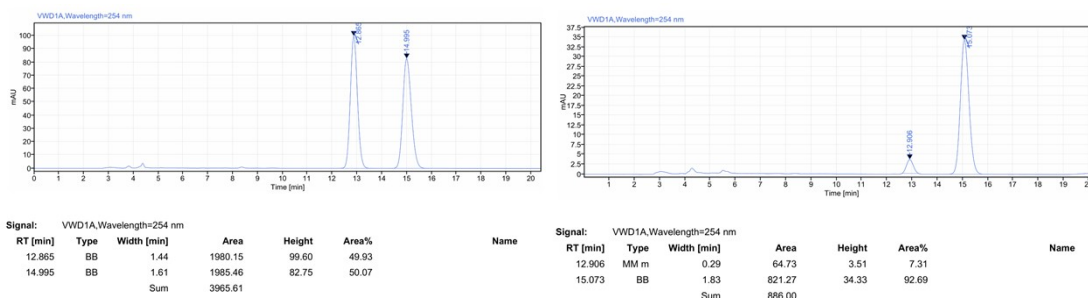


RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.216	MM m	0.42	216.58	8.22	5.02	
20.148	BB	2.66	4100.12	120.05	94.98	
	Sum		4316.70			



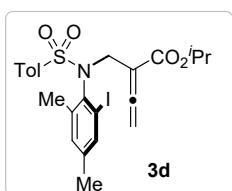
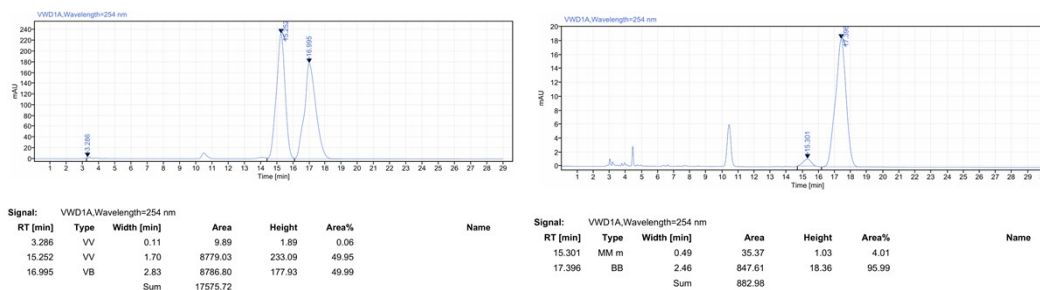
3b (92% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 5.03 (d, *J* = 14.6 Hz, 1H), 4.93 (d, *J* = 14.6 Hz, 1H), 4.54 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 216.2, 166.2, 143.4, 141.9, 139.8, 138.9, 138.2, 137.3, 132.1, 129.3, 128.3, 101.4, 96.0, 79.2, 52.4, 48.7, 21.5, 20.3, 20.2.
HRMS (ESI) m/z Calcd for [C₂₀H₂₂INO₄S, M + Na]⁺: 532.0050; Found: 532.0053.

Optical Rotation: [α]²⁵_D -35.0 (*c* = 1.0, CHCl₃). 85% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, *t*_R = 12.906 min for minor isomer, *t*_R = 15.073 min for major isomer).



3c (85% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 5.04 (d, *J* = 14.5 Hz, 1H), 4.93 (d, *J* = 14.5 Hz, 1H), 4.64 – 4.46 (m, 2H), 4.13 – 3.96 (m, 2H), 2.41 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 216.2, 165.7, 143.4, 141.9, 139.8, 138.9, 138.2, 137.3, 132.0, 129.3, 128.3, 101.4, 96.23, 79.1, 61.3, 48.6, 21.5, 20.3, 20.2, 14.0. HRMS (ESI) *m/z* Calcd for [C₂₂H₂₄INO₄S, M + Na]⁺: 548.0363; Found: 548.0365.

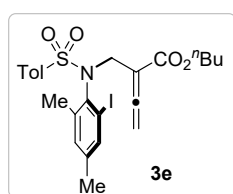
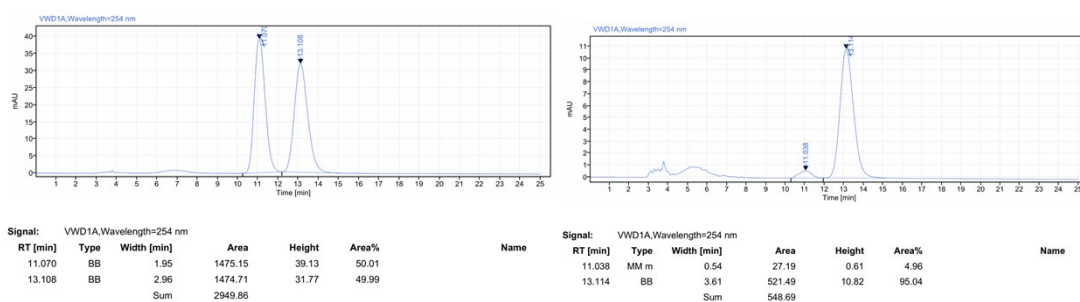
Optical Rotation: [α]_D²⁵ -30.0 (*c* = 1.0, CHCl₃). 92% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, *t*_R = 15.301 min for minor isomer, *t*_R = 17.396 min for major isomer).



3d (95% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 5.03 (d, *J* = 14.4 Hz, 1H), 4.92

(d, $J = 14.4$ Hz, 1H), 4.90 – 4.84 (m, 1H), 4.64 – 4.46 (m, 2H), 2.42 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.14 (d, $J = 6.3$ Hz, 3H), 1.11 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.2, 165.3, 143.4, 142.1, 139.8, 138.9, 138.4, 137.2, 132.1, 129.4, 128.29, 101.3, 96.5, 78.9, 68.8, 48.5, 21.6, 21.5, 20.3, 20.3. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{24}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 548.0363; Found: 548.0368.

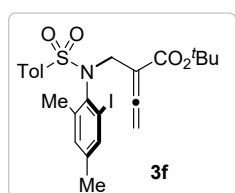
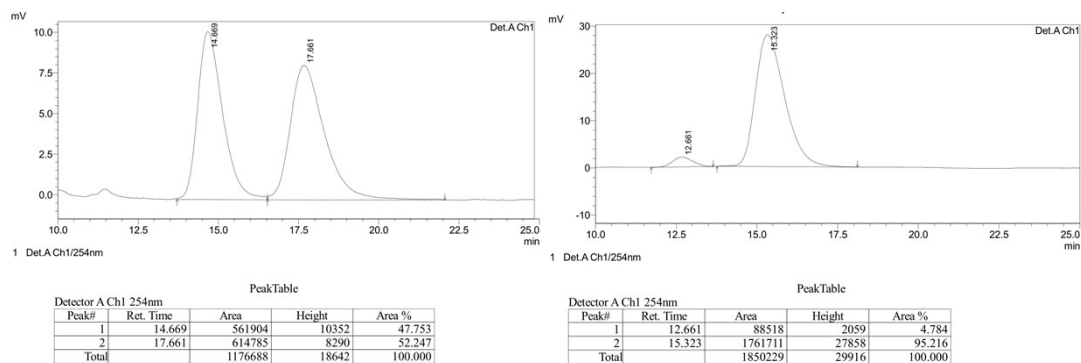
Optical Rotation: $[\alpha]^{25}_{\text{D}} -30.0$ ($c = 1.0$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 11.038$ min for minor isomer, $t_{\text{R}} = 13.114$ min for major isomer).



3e. (94% yield, Hexane-EtOAc = 5:1, $R_f = 0.4$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 0.9$ Hz, 1H), 7.28 (d, $J = 8.3$ Hz, 2H), 6.99 (d, $J = 0.9$ Hz, 1H), 5.05 (d, $J = 14.5$ Hz, 1H), 4.94 (d, $J = 14.5$ Hz, 1H), 4.63 – 4.47 (m, 2H), 3.99 (qt, $J = 10.8, 6.7$ Hz, 2H), 2.42 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.52-1.45 (m, 6.8 Hz, 2H), 1.31-1.26 (m, $J = 15.2, 7.5$ Hz, 2H), 0.88 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.2, 165.8, 143.4, 141.9, 139.8, 138.9, 138.3, 137.4, 132.0, 129.4, 128.3, 101.4, 96.3, 79.1, 65.2, 48.6, 30.4, 21.6, 20.3, 20.2, 19.0, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{24}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 576.0676; Found: 576.0680.

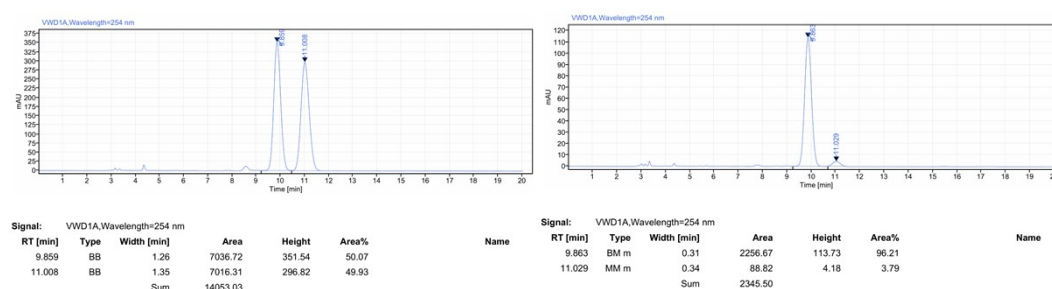
Optical Rotation: $[\alpha]^{25}_{\text{D}} -32.0$ ($c = 1.0$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min,

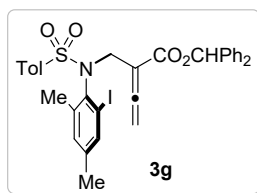
wavelength = 254 nm, $t_R = 12.661$ min for minor isomer, $t_R = 15.323$ min for major isomer).



3f (94% yield, Hexane-EtOAc = 5:1, $R_f = 0.4$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.50 (dd, $J = 1.4$, 0.5 Hz, 1H), 7.27 (d, $J = 8.3$ Hz, 2H), 6.99 (dd, $J = 1.4$, 0.5 Hz, 1H), 5.01 (d, $J = 14.3$ Hz, 1H), 4.87 (d, $J = 14.3$ Hz, 1H), 4.56 (d, $J = 14.1$ Hz, 1H), 4.48 (d, $J = 14.1$ Hz, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 2.23 (s, 3H), 1.32 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.3, 164.8, 143.3, 142.2, 139.8, 138.9, 138.5, 137.4, 132.1, 129.3, 128.3, 101.1, 97.5, 81.2, 78.6, 48.5, 27.7, 21.5, 20.3, 20.3. **HRMS (ESI)** m/z Calcd for $[\text{C}_{24}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 576.0676; Found: 576.0681.

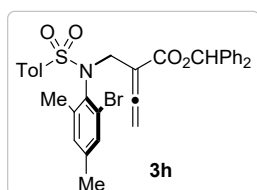
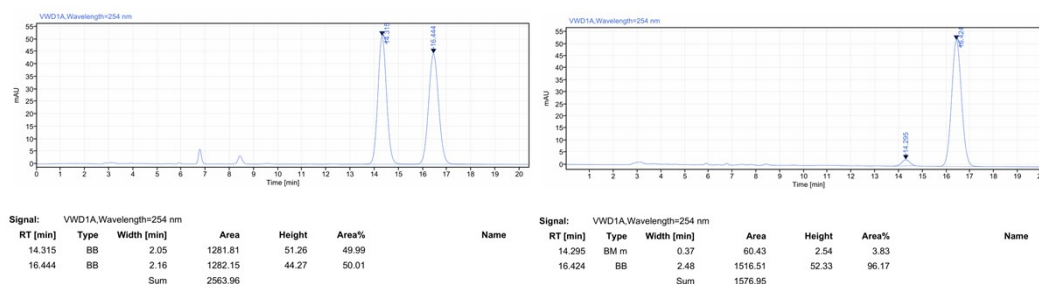
Optical Rotation: $[\alpha]_D^{25} -30.0$ ($c = 1.0$, CHCl_3). 92% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 11.029$ min for minor isomer, $t_R = 9.863$ min for major isomer).





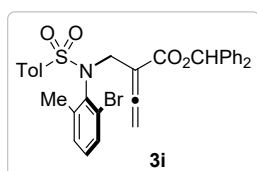
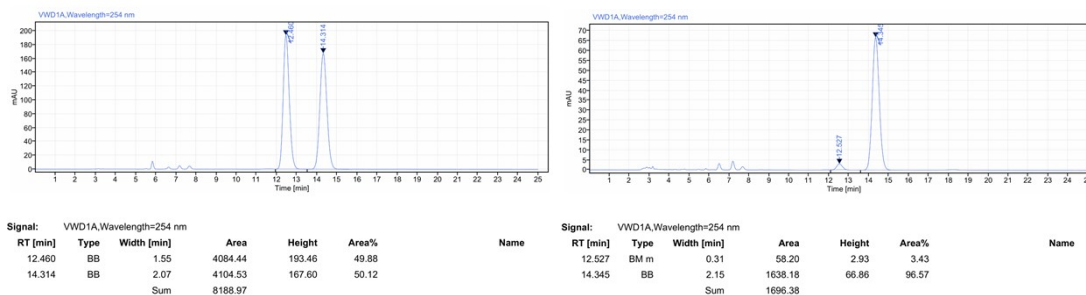
3g (85% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.5). syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, J = 8.0 Hz, 2H), 7.35 (s, 1H), 7.19-7.14 (m, 12H), 6.74 (s, 1H), 6.70 (s, 1H), 5.03 (d, J = 14.6 Hz, 1H), 4.92 (d, J = 14.6 Hz, 1H), 4.49 (s, 2H), 2.32 (s, 3H), 2.09 (s, 3H), 1.94 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.7, 164.8, 143.3, 141.9, 140.0, 139.7, 138.9, 138.3, 137.2, 132.0, 129.3, 128.3, 127.8, 127.7, 127.2, 126.9, 101.3, 96.1, 79.1, 77.3, 48.5, 21.5, 20.3, 20.0. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{30}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 686.0832; Found: 686.0834.

Optical Rotation: $[\alpha]_D^{25}$ -30.0 (c = 1.0, CHCl_3). 92% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 14.295 min for minor isomer, t_R = 16.424 min for major isomer).



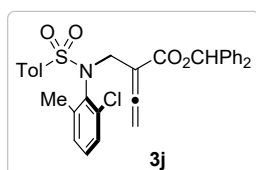
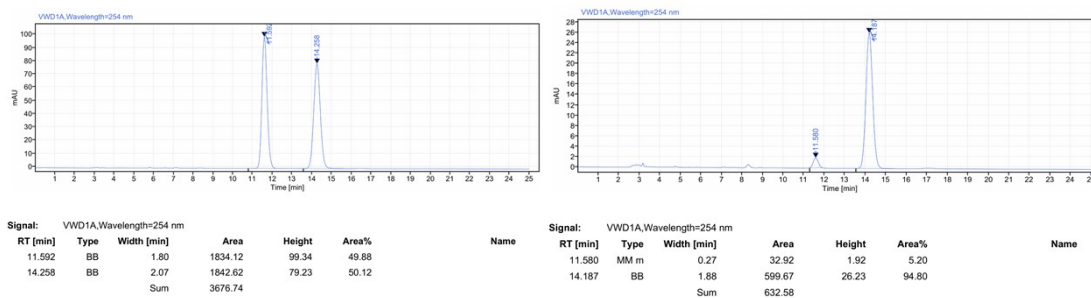
3h (92% yield, Hexane-EtOAc = 5:1, R_f = 0.3). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (d, J = 7.8 Hz, 2H), 7.29 – 7.10 (m, 12H), 7.03 (s, 1H), 6.74 (s, 1H), 6.70 (s, 1H), 5.06 (d, J = 14.6 Hz, 1H), 4.92 (d, J = 14.6 Hz, 1H), 4.53 (d, J = 14.1 Hz, 1H), 4.40 (d, J = 14.1 Hz, 1H), 2.33 (s, 3H), 2.13 (s, 3H), 1.99 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.6, 164.9, 143.3, 142.8, 140.15, 139.7, 138.0, 133.8, 132.0, 131.2, 129.3, 128.4, 128.2, 127.9, 127.8, 127.2, 127.0, 125.0, 96.3, 79.3, 77.4, 48.3, 21.6, 20.7, 19.8. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{30}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 638.0971, 640.0956; Found: 638.0976, 640.0958.

Optical Rotation: $[\alpha]^{25}_D$ -8.5 ($c = 0.5$, CHCl_3). 93% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 12.527$ min for minor isomer, $t_R = 14.345$ min for major isomer).



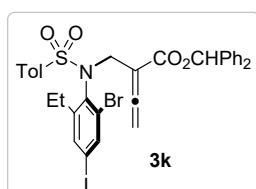
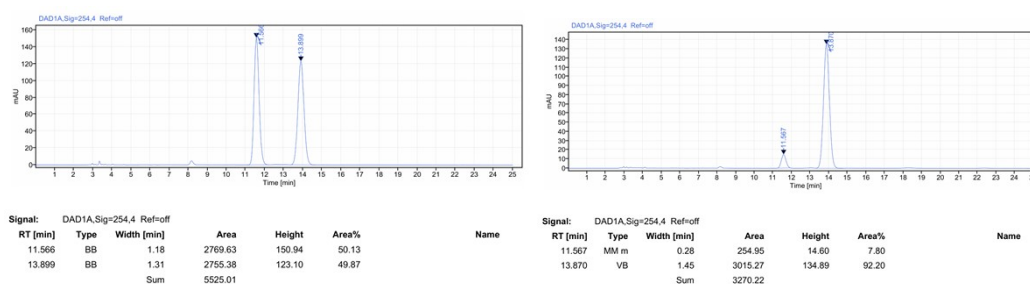
3i (84% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.8$ Hz, 2H), 7.41 – 7.23 (m, 13H), 7.05-6.98 (m, 2H), 6.80 (s, 1H), 5.14 (d, $J = 14.7$ Hz, 1H), 4.98 (d, $J = 14.7$ Hz, 1H), 4.64 (d, $J = 14.1$ Hz, 1H), 4.51 (d, $J = 14.1$ Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.5, 164.7, 143.5, 143.3, 140.0, 137.8, 136.4, 131.4, 130.2, 129.4, 129.3, 128.3, 128.1, 127.8, 127.7, 127.1, 126.9, 125.3, 96.1, 79.2, 77.4, 48.1, 21.5, 19.8. **HRMS (ESI)** m/z Calcd for $[\text{C}_{32}\text{H}_{28}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 624.0815, 626.0799; Found: 625.0811, 626.0804.

Optical Rotation: $[\alpha]^{25}_D$ -10.6 ($c = 0.5$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 11.580$ min for minor isomer, $t_R = 14.187$ min for major isomer).



3j (91% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, J = 8.2 Hz, 2H), 7.33 – 7.21 (m, 12H), 7.12–7.03 (m, 2H), 7.01–6.99 (m, 1H), 6.79 (s, 1H), 5.13 (d, J = 14.6 Hz, 1H), 4.97 (d, J = 14.6 Hz, 1H), 4.66 (d, J = 14.0 Hz, 1H), 4.41 (d, J = 14.0 Hz, 1H), 2.41 (s, 3H), 2.13 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.4, 164.7, 143.4, 143.3, 140.0, 137.6, 135.0, 134.9, 129.6, 129.3, 129.1, 128.4, 128.0, 127.9, 127.8, 127.8, 127.1, 126.9, 96.1, 79.2, 77.4, 48.1, 21.5, 19.4. **HRMS (ESI)** m/z Calcd for $[\text{C}_{32}\text{H}_{28}\text{ClNO}_4\text{S}, \text{M} + \text{Na}]^+$: 580.1320, 582.1304; Found: 580.1325, 582.1308.

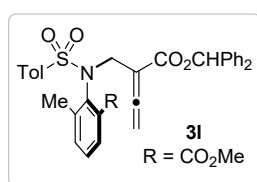
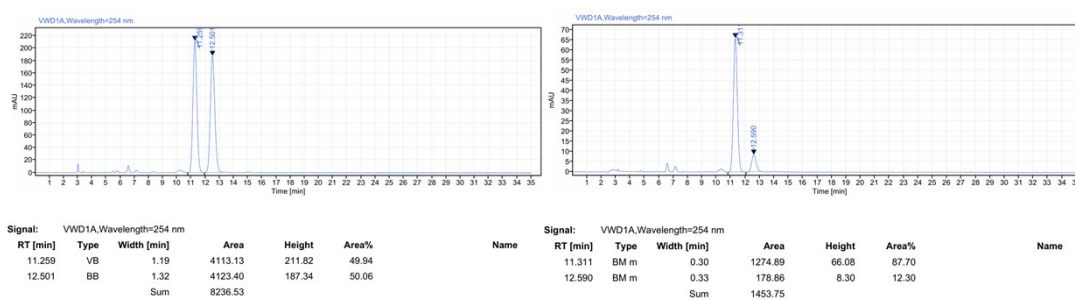
Optical Rotation: $[\alpha]_D^{25}$ -5.4 (c = 0.25, CHCl_3). 84% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 11.567 min for minor isomer, t_R = 13.870 min for major isomer).



3k (98% yield, Hexane-EtOAc = 5:1, R_f = 0.3). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.67 (m, 3H), 7.37 – 7.22 (m, 13H), 6.80 (s, 1H), 5.15 (d, J = 14.8 Hz, 1H), 5.04 (d, J = 14.8 Hz, 1H).

14.8 Hz, 1H), 4.58 (d, $J = 14.2$ Hz, 1H), 4.52 (d, $J = 14.2$ Hz, 1H), 2.56 (dq, $J = 15.1$, 7.5 Hz, 1H), 2.43 (s, 3H), 2.31 (dq, $J = 15.0$, 7.5 Hz, 1H), 0.97 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.8, 164.7, 149.8, 143.7, 140.1, 139.9, 138.7, 138.0, 132.1, 129.4, 128.4, 127.9, 127.8, 127.3, 127.0, 123.0, 102.0, 95.9, 79.4, 77.5, 48.8, 25.3, 21.6, 14.0. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{29}\text{BrINO}_4\text{S}, \text{M} + \text{Na}]^+$: 763.9938, 765.9922; Found: 763.9939, 769.9924.

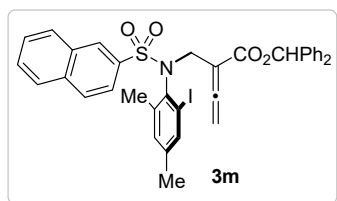
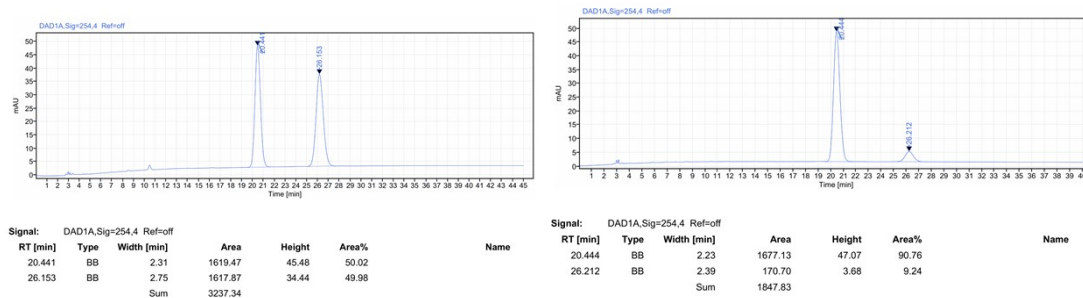
Optical Rotation: $[\alpha]_D^{25}$ -15.3 ($c = 0.5$, CHCl_3). 75% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 12.590$ min for minor isomer, $t_R = 11.311$ min for major isomer).



3I (72% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 6.6$, 2.8 Hz, 1H), 7.55 (d, $J = 8.2$ Hz, 2H), 7.29-7.18 (m, 14H), 6.78 (s, 1H), 5.15 (d, $J = 14.6$ Hz, 1H), 5.03 (d, $J = 14.6$ Hz, 1H), 4.75 (d, $J = 14.4$ Hz, 1H), 4.66 (d, $J = 14.4$ Hz, 1H), 3.45 (s, 3H), 2.39 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.7, 166.6, 165.2, 142.9, 141.3, 140.2, 138.3, 136.5, 134.8, 132.4, 129.5, 129.3, 128.4, 128.3, 128.1, 127.8, 127.8, 127.5, 127.0, 96.9, 78.9, 51.8, 50.3, 21.5, 18.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{34}\text{H}_{31}\text{NO}_6\text{S}, \text{M} + \text{Na}]^+$: 604.1764; Found: 604.1767.

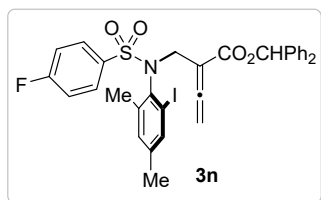
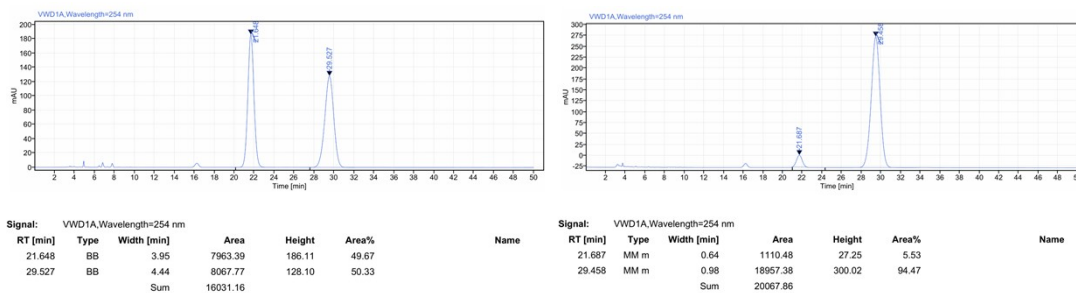
Optical Rotation: $[\alpha]_D^{25}$ -45.0 ($c = 1.0$, CHCl_3). 82% *ee* (HPLC conditions:

Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 26.212 min for minor isomer, t_R = 20.444 min for major isomer).



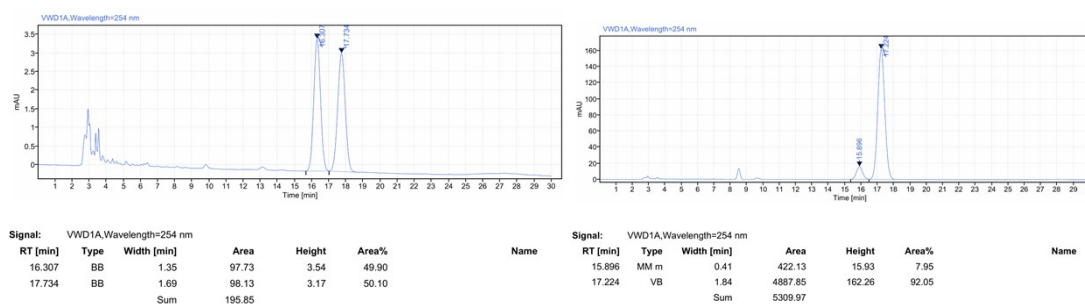
3m (98% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.5). White solid. MP: 69-70 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.40 (s, 1H), 7.94 – 7.82 (m, 4H), 7.26-7.53 (m, 2H), 7.40 (d, J = 1.4 Hz, 1H), 7.25 – 7.19 (m, 10H), 6.85 – 6.79 (m, 1H), 6.75 (s, 1H), 5.08 (d, J = 14.7 Hz, 1H), 4.97 (d, J = 14.7 Hz, 1H), 4.63 (s, 2H), 2.16 (s, 3H), 1.99 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.8, 164.9, 142.0, 140.1, 140.1, 139.9, 139.0, 138.3, 137.1, 135.0, 132.3, 132.2, 129.8, 129.5, 129.4, 128.9, 128.6, 128.4, 127.9, 127.9, 127.8, 127.3, 127.0, 124.1, 101.4, 96.1, 79.3, 77.4, 48.8, 20.5, 20.2. **HRMS (ESI)** m/z Calcd for $[\text{C}_{36}\text{H}_{30}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 722.0832; Found: 722.0833.

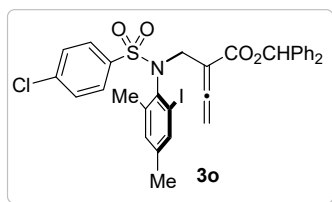
Optical Rotation: $[\alpha]_D^{25}$ -44.0 (c = 1.0, CHCl_3). 89% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 21.687 min for minor isomer, t_R = 29.458 min for major isomer).



3n (90% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.5). White solid. MP: 69-70 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88-7.84 (m, 2H), 7.43 (s, 1H), 7.30 – 7.19 (m, 10H), 7.10 (t, J = 8.6 Hz, 2H), 6.85 (s, 1H), 6.78 (s, 1H), 5.08 (d, J = 14.7 Hz, 1H), 4.97 (d, J = 14.7 Hz, 1H), 4.59 (d, J = 14.2 Hz, 1H), 4.54 (d, J = 14.2 Hz, 1H), 2.19 (s, 3H), 2.04 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.7, 165.2 (d, $^1J_{\text{C-F}}$ = 252.7 Hz), 164.8, 141.9, 140.0, 140.0, 138.9, 137.3 (d, $^4J_{\text{C-F}}$ = 3.0 Hz), 136.9, 132.2, 131.0 (d, $^3J_{\text{C-F}}$ = 9.3 Hz), 128.3, 127.9, 127.8, 127.2, 126.9, 115.8 (d, $^2J_{\text{C-F}}$ = 22.4 Hz), 101.0, 95.9, 79.2, 77.4, 48.8, 20.6, 20.0. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -105.53. **HRMS (ESI)** m/z Calcd for $[\text{C}_{32}\text{H}_{27}\text{FINO}_4\text{S}, \text{M} + \text{Na}]^+$: 690.0582; Found: 690.0587.

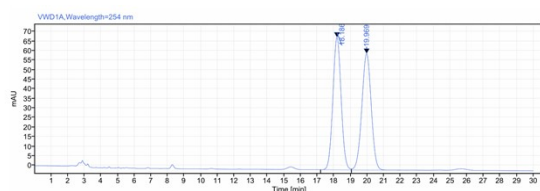
Optical Rotation: $[\alpha]_{\text{D}}^{25}$ -30.0 (c = 1.0, CHCl_3). 84% ee (HPLC conditions: Chiralpak AD-H column, n -Hexane/ i -PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_{R} = 15.896 min for minor isomer, t_{R} = 17.224 min for major isomer).



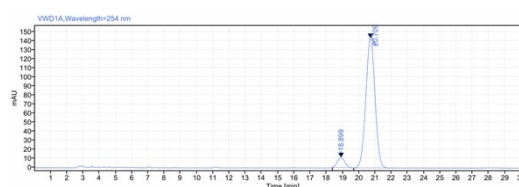


3o (98% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_f = 0.5$). White solid. MP: 139-140 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.45 (s, 1H), 7.43 (d, $J = 8.6$ Hz, 2H), 7.33 – 7.25 (m, 10H), 6.88 (s, 1H), 6.81 (s, 1H), 5.10 (d, $J = 14.7$ Hz, 1H), 4.99 (d, $J = 14.7$ Hz, 1H), 4.63 (d, $J = 14.1$ Hz, 1H), 4.56 (d, $J = 14.1$ Hz, 1H), 2.21 (s, 3H), 2.05 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.7, 164.8, 141.9, 140.0, 139.9, 139.7, 139.0, 138.9, 136.8, 132.2, 129.8, 128.9, 128.3, 127.9, 127.8, 127.3, 126.9, 101.1, 95.9, 77.4, 48.9, 20.4, 20.0. **HRMS (ESI)** m/z Calcd for $[\text{C}_{32}\text{H}_{27}\text{ClINO}_4\text{S}, \text{M} + \text{Na}]^+$: 706.0286; Found: 706.0286.

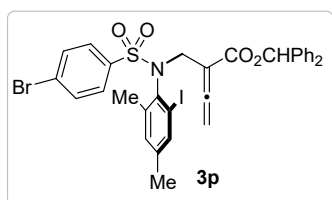
Optical Rotation: $[\alpha]_D^{25}$ -33.0 ($c = 1.0$, CHCl_3). 88% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 18.899$ min for minor isomer, $t_R = 20.709$ min for major isomer).



Signal: VWD1A.Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
18.186	BV	1.85	2382.74	69.18	49.92
19.969	VB	2.96	2390.02	60.76	50.08
Sum			4772.77		



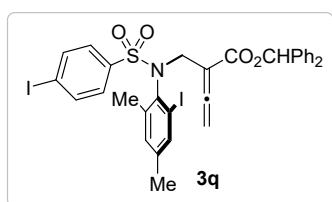
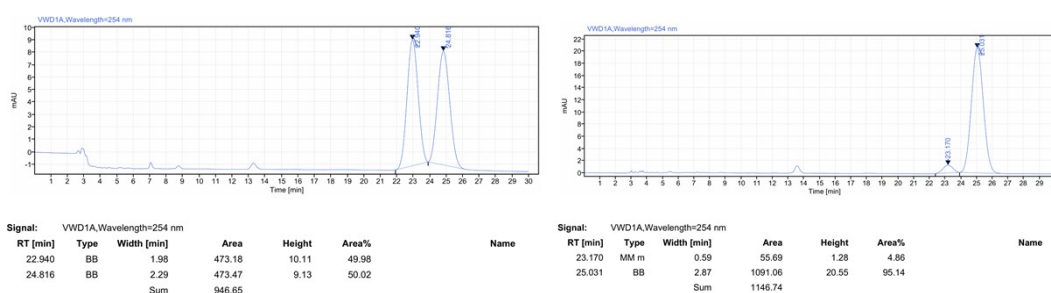
Signal: VWD1A.Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
18.899	MM m	0.52	357.49	10.95	5.95
20.709	BB	2.45	5651.63	143.25	94.05
Sum			6009.12		



3p (92% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_f = 0.4$). White solid. MP: 139-149 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.45 (s, 1H), 7.34 – 7.22 (m, 10H), 6.88 (s, 1H), 6.81 (s, 1H), 5.09 (d, $J = 14.7$ Hz, 1H), 4.99 (d, $J = 14.7$ Hz, 1H), 4.63 (d, $J = 14.1$ Hz, 1H), 4.56 (d, $J = 14.1$ Hz, 1H), 2.21 (s, 3H), 2.05 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.7, 164.8, 141.9, 140.2, 140.0, 139.9, 138.9, 136.7, 132.2, 131.9, 129.9, 128.3, 127.9, 127.8, 127.5, 127.3, 126.9, 101.1, 95.8, 79.2, 77.4, 48.9, 20.4, 20.0.

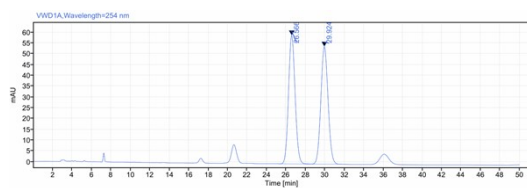
HRMS (ESI) m/z Calcd for $[C_{32}H_{27}BrINO_4S, M + Na]^+$: 749.9781, 751.9765; Found: 749.9785, 751.9761.

Optical Rotation: $[\alpha]^{25}_D$ -32.0 ($c = 1.0$, $CHCl_3$). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 23.170$ min for minor isomer, $t_R = 25.031$ min for major isomer).

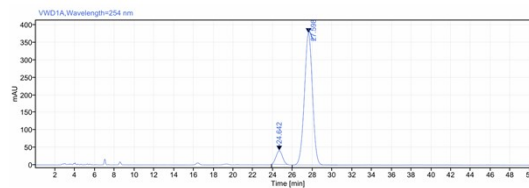


3q (95% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_f = 0.4$). White solid. MP: 139-140 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 7.45 (s, 1H), 7.34 – 7.25 (m, 10H), 6.87 (s, 1H), 6.80 (s, 1H), 5.09 (d, $J = 14.7$ Hz, 1H), 4.98 (d, $J = 14.7$ Hz, 1H), 4.62 (d, $J = 14.1$ Hz, 1H), 4.55 (d, $J = 14.1$ Hz, 1H), 2.21 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.7, 164.8, 141.9, 140.9, 140.0, 139.9, 138.9, 137.9, 136.7, 132.2, 129.8, 128.3, 127.9, 127.8, 127.3, 126.9, 101.2, 100.0, 95.9, 79.2, 77.4, 48.9, 20.4, 20.0. **HRMS (ESI) m/z** Calcd for $[C_{32}H_{27}I_2NO_4S, M + Na]^+$: 797.9642; Found: 797.9647.

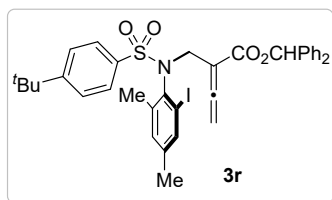
Optical Rotation: $[\alpha]^{25}_D$ -13.0 ($c = 1.0$, $CHCl_3$). 85% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 24.642$ min for minor isomer, $t_R = 27.598$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.566	BB	3.17	2802.16	59.64	49.95	
29.924	BB	3.12	2807.48	54.50	50.05	
Sum			5609.64			

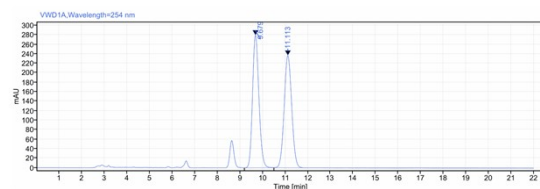


RT [min]	Type	Width [min]	Area	Height	Area%	Name
24.642	MM m	0.71	1760.33	39.05	7.60	
27.598	BB	4.57	2139.192	377.17	92.40	
Sum			23152.25			

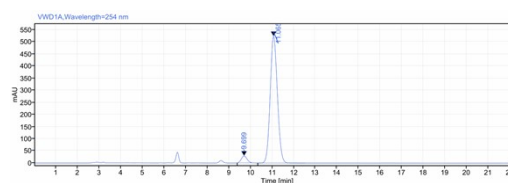


3r (97% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.35 (s, 1H), 7.24 – 7.13 (m, 10H), 6.75 (s, 1H), 6.71 (s, 1H), 5.05 (d, J = 14.6 Hz, 1H), 4.94 (d, J = 14.6 Hz, 1H), 4.50 (s, 2H), 2.11 (s, 3H), 1.95 (s, 3H), 1.25 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.8, 164.8, 156.5, 142.0, 140.1, 140.0, 139.7, 138.9, 138.1, 137.2, 132.1, 128.3, 128.1, 127.8, 127.7, 127.2, 126.9, 125.7, 101.0, 96.3, 79.2, 77.4, 48.5, 35.1, 31.1, 20.3, 20.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{36}\text{H}_{36}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 728.1302; Found: 728.1306.

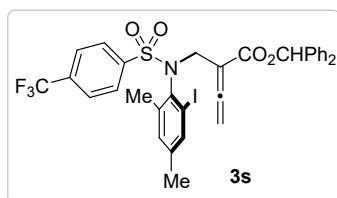
Optical Rotation: $[\alpha]_D^{25}$ -21.6 (c = 0.5, CHCl_3). 92% ee (HPLC conditions: Chiralpak OD-H column, n -Hexane/ i -PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 9.699 min for minor isomer, t_R = 11.065 min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.679	BB	1.30	5475.81	279.22	49.99	
11.113	BB	1.52	5477.56	238.56	50.01	
Sum			10953.37			



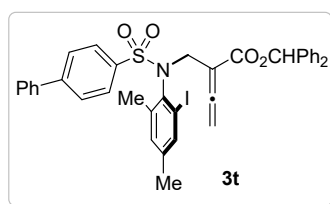
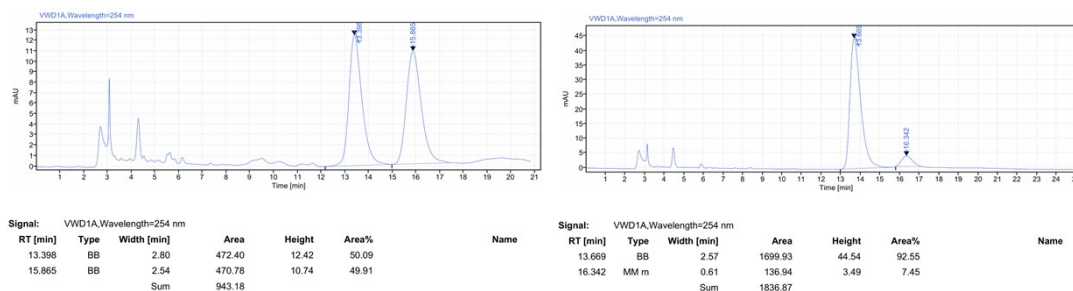
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.659	MM m	0.29	518.69	28.22	4.11	
11.065	BB	2.20	12114.93	522.85	95.89	
Sum			12633.62			



3s (90% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, R_f = 0.5). White solid. MP: 138-139 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.35 (s, 1H), 7.24 – 7.13 (m, 10H), 6.75 (s, 1H), 6.71 (s, 1H), 5.05 (d, J = 14.6 Hz, 1H), 4.94 (d, J = 14.6 Hz, 1H), 4.50 (s, 2H), 2.11 (s, 3H), 1.95 (s, 3H), 1.25 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.8, 164.8, 156.5, 142.0, 140.1, 140.0, 139.7, 138.9, 138.1, 137.2, 132.1, 128.3, 128.1, 127.8, 127.7, 127.2, 126.9, 125.7, 101.0, 96.3, 79.2, 77.4, 48.5, 35.1, 31.1, 20.3, 20.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{36}\text{H}_{36}\text{F}_3\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 761.1302; Found: 761.1306.

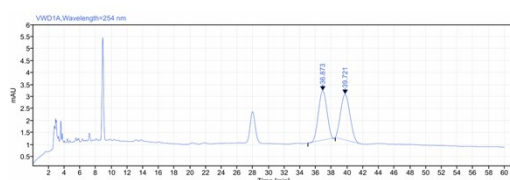
Hz, 2H), 7.45 (s, 1H), 7.35-7.26 (m, 10H), 6.89 (s, 1H), 6.80 (s, 1H), 5.09 (d, $J = 14.8$ Hz, 1H), 4.98 (d, $J = 14.8$ Hz, 1H), 4.66 (d, $J = 14.1$ Hz, 1H), 4.58 (d, $J = 14.1$ Hz, 1H), 2.22 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.8, 164.8, 144.5, 141.9, 140.2, 139.9, 139.9, 139.0, 136.5, 134.2 (q, $^2J_{\text{C-F}} = 32.8$ Hz), 132.3, 128.9, 128.3, 127.9, 127.8, 127.30, 126.9, 125.8 (q, $^3J_{\text{C-F}} = 3.3$ Hz), 123.4 (q, $^1J_{\text{C-F}} = 271.2$ Hz), 101.0, 95.8, 79.2, 77.5, 49.1, 20.4, 20.0. ^{19}F NMR (376 MHz, CDCl_3) δ -62.85. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{27}\text{F}_3\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 740.0550; Found: 740.0552.

Optical Rotation: $[\alpha]_{\text{D}}^{25}$ -28 ($c = 1.0$, CHCl_3). 85% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 16.342$ min for minor isomer, $t_{\text{R}} = 13.669$ min for major isomer).

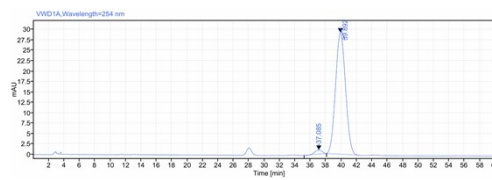


3t (93% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_{\text{f}} = 0.5$). White solid. MP: 77-78 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 7.5$ Hz, 2H), 7.51 – 7.39 (m, 4H), 7.27-7.22 (m, 10H), 6.86 (s, 1H), 6.80 (s, 1H), 5.13 (d, $J = 14.7$ Hz, 1H), 5.01 (d, $J = 14.7$ Hz, 1H), 4.63 (s, 2H), 2.20 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.8, 164.8, 145.4, 142.0, 140.0, 139.8, 139.8, 139.4, 138.9, 137.1, 132.1, 129.0, 128.8, 128.3, 128.3, 127.8, 127.7, 127.3, 127.3, 127.2, 126.9, 101.2, 96.1, 79.2, 77.4, 48.7, 20.4, 20.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{38}\text{H}_{32}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 748.0989; Found: 748.0991.

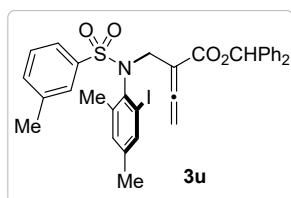
Optical Rotation: $[\alpha]_D^{25}$ -31.0 ($c = 1.0$, CHCl_3). 95% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 37.085$ min for minor isomer, $t_R = 39.892$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
36.873	MM m	0.88	152.85	2.05	49.25	
39.721	MM m	0.97	157.48	1.90	50.75	
Sum			310.33			

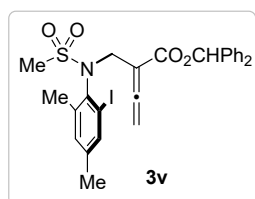
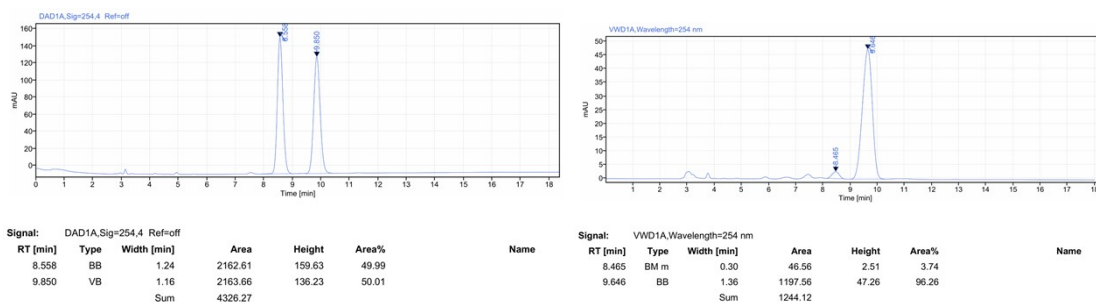


RT [min]	Type	Width [min]	Area	Height	Area%	Name
37.085	MM m	0.73	58.37	0.94	2.18	
39.892	MM m	1.39	2622.29	29.17	97.82	
Sum			2680.66			



3u (83% yield). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (s, 1H), 7.66-7.64 (m, 1H), 7.43 (s, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.22 (m, 10H), 6.83 (s, 1H), 6.77 (s, 1H), 5.12 (d, $J = 14.6$ Hz, 1H), 5.00 (d, $J = 14.6$ Hz, 1H), 4.57 (s, 2H), 2.37 (s, 3H), 2.18 (s, 3H), 2.02 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.8, 164.8, 142.0, 141.0, 140.0, 140.0, 139.8, 138.9, 138.9, 137.1, 133.4, 132.1, 128.7, 128.6, 128.3, 127.8, 127.7, 127.2, 126.9, 125.3, 101.1, 96.1, 79.2, 77.3, 48.6, 21.3, 20.4, 20.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{30}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 686.0832; Found: 686.0837.

Optical Rotation: $[\alpha]_D^{25}$ -45.0 ($c = 1.0$, CHCl_3). 93% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 8.465$ min for minor isomer, $t_R = 9.646$ min for major isomer).

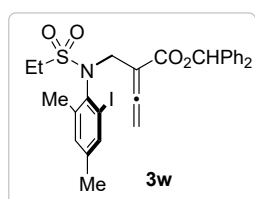
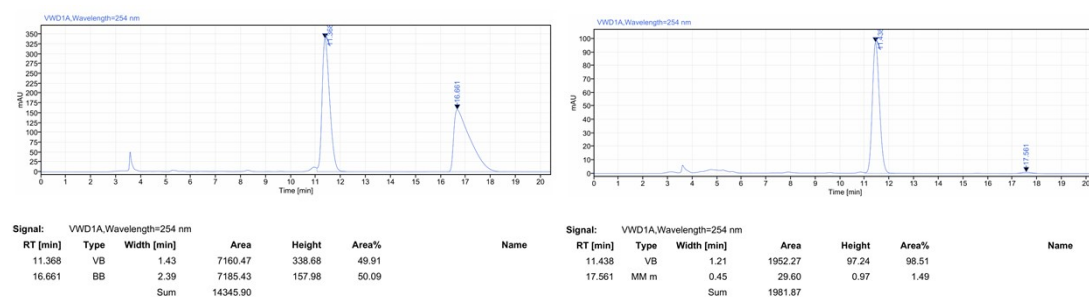


3v (90% yield, Hexane-EtOAc = 5:1, R_f = 0.3). White solid.

MP: 134-135 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (s, 1H), 7.34 – 7.12 (m, 10H), 6.89 (s, 1H), 6.84 (s, 1H), 4.90 (d, J = 14.7 Hz, 1H), 4.78 (d, J = 14.7 Hz, 1H), 4.64 (d, J = 14.2 Hz, 1H), 4.02 (d, J = 14.2 Hz, 1H), 3.26 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.6, 165.4, 140.9, 140.0, 134.0, 139.8, 138.4, 137.2, 132.5, 128.4, 128.4, 128.0, 127.9, 127.6, 126.9, 103.6, 95.5, 78.8, 77.6, 48.9, 42.7, 20.4, 19.9.

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.6, 165.4, 140.9, 140.0, 134.0, 139.8, 138.4, 137.2, 132.5, 128.4, 128.4, 128.0, 127.9, 127.6, 126.9, 103.6, 95.5, 78.8, 77.6, 48.9, 42.7, 20.4, 19.9. **HRMS (ESI)** m/z Calcd for $[\text{C}_{27}\text{H}_{26}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 610.0519; Found: 610.0524.

Optical Rotation: $[\alpha]_D^{25}$ -5.0 (c = 1.0, CHCl_3). 97% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 17.561 min for minor isomer, t_R = 11.438 min for major isomer).

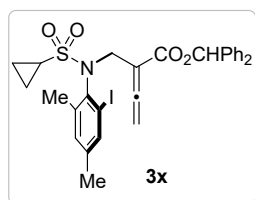
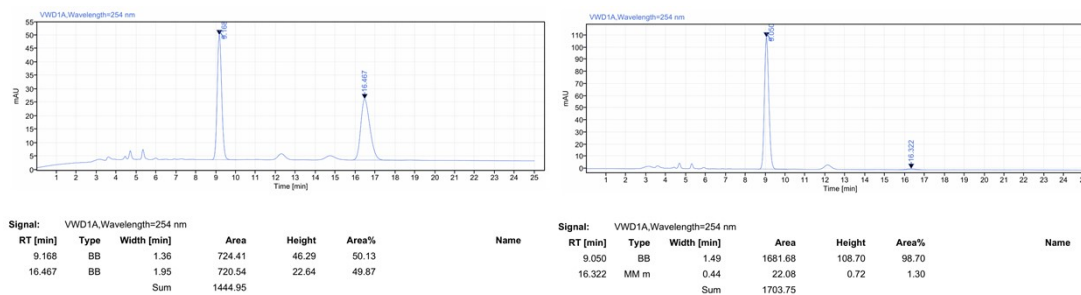


3w (97% yield, Hexane-EtOAc = 5:1, R_f = 0.4). White solid.

MP: 114-115 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (s, 1H), 7.33 – 7.13 (m, 10H), 6.87 (s, 1H), 6.81 (s, 1H), 4.90 (d, J = 14.7 Hz, 1H), 4.79 (d, J = 14.7 Hz, 1H), 4.61 (d, J = 14.0 Hz,

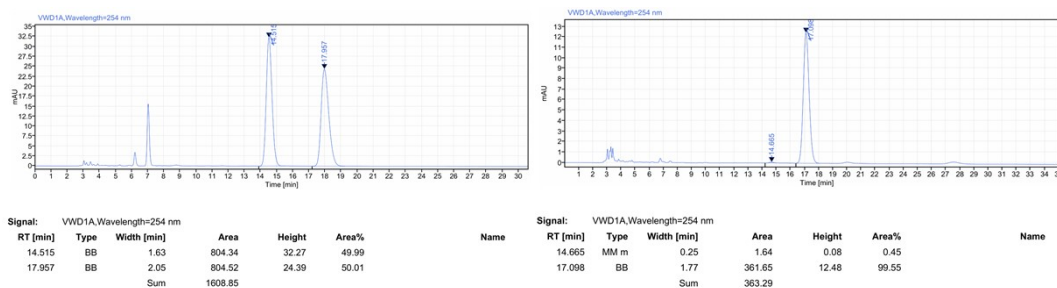
1H), 4.07 (d, $J = 14.0$ Hz, 1H), 3.48 (dq, $J = 14.7, 7.4$ Hz, 1H), 3.39 (dq, $J = 14.7, 7.4$ Hz, 1H), 2.23 (s, 3H), 2.14 (s, 3H), 1.35 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.8, 165.3, 141.2, 140.0, 139.9, 139.9, 138.4, 137.1, 132.5, 128.4, 128.4, 128.0, 127.9, 127.5, 126.9, 103.5, 95.6, 78.8, 77.5, 49.9, 48.9, 20.4, 20.0, 8.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{28}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 624.0676; Found: 624.0672.

Optical Rotation: $[\alpha]^{25}_{\text{D}} -4$ ($c = 1.0, \text{CHCl}_3$). 97% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 16.322$ min for minor isomer, $t_{\text{R}} = 9.050$ min for major isomer).

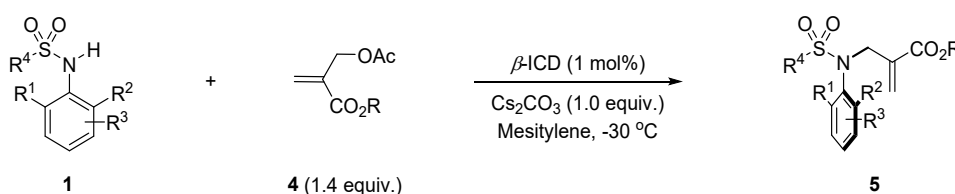


3x (95% yield, Hexane-EtOAc = 5:1, $R_f = 0.3$). White solid. MP: 96-97 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 0.8$ Hz, 1H), 7.38 – 7.23 (m, 10H), 6.91 (d, $J = 0.8$ Hz, 1H), 6.86 (s, 1H), 4.98 (s, 2H), 4.65 (d, $J = 14.0$ Hz, 1H), 4.37 (d, $J = 14.0$ Hz, 1H), 2.93-2.86 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H), 1.31 – 1.23 (m, 1H), 1.21 – 1.14 (m, 1H), 1.10 – 1.01 (m, 1H), 1.0 – 0.94 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 216.7, 165.0, 141.2, 140.0, 139.9, 139.8, 138.5, 137.2, 132.3, 128.4, 128.3, 127.9, 127.8, 127.3, 126.9, 103.1, 95.8, 78.9, 77.4, 48.8, 32.2, 20.4, 20.0, 7.2, 6.5. **HRMS (ESI)** m/z Calcd for $[\text{C}_{29}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 636.0676; Found: 636.0677.

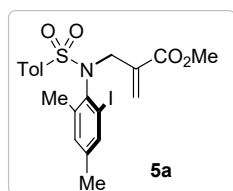
Optical Rotation: $[\alpha]^{25}_{\text{D}} -3.0$ ($c = 1.0, \text{CHCl}_3$). 99% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 14.665$ min for minor isomer, $t_{\text{R}} = 17.098$ min for major isomer).



Representative procedure for synthesis of 5:

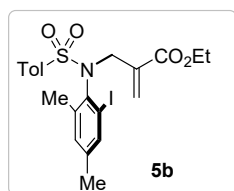
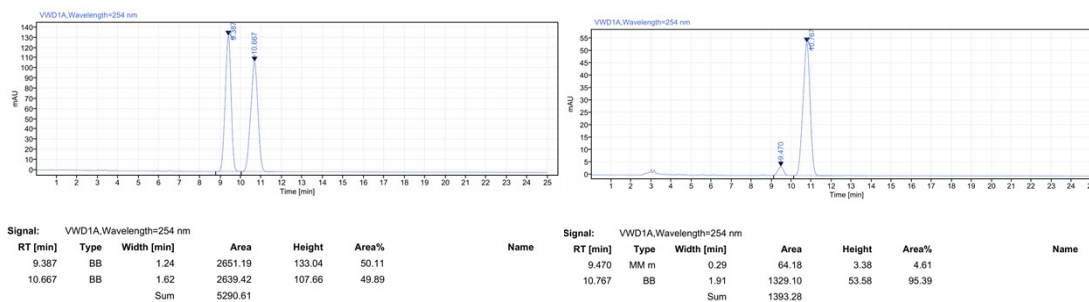


To a Schlenk tube containing **6** (0.05 mmol), β -ICD (1.5 mg, 10 mol%) and Cs_2CO_3 (0.05 mmol, 1.0 equiv.) were added mesitylene (3 mL) and MBH acetate **4** (0.14 mmol, 1.4 equiv.). The reaction mixture was stirred at $-50\text{ }^\circ\text{C}$ for 24 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **5**.



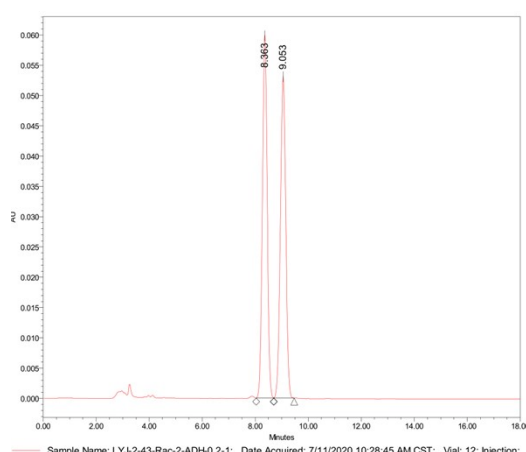
Characterization of compounds 5 5a. (94% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.2$ Hz, 2H), 7.50 (s, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 6.98 (s, 1H), 6.27 (d, $J = 0.8$ Hz, 1H), 5.76 (s, 1H), 4.57 (d, $J = 14.2$ Hz, 1H), 4.51 (d, $J = 14.2$ Hz, 1H), 3.55 (s, 3H), 2.42 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.5, 143.5, 141.8, 139.8, 139.0, 138.2, 137.1, 135.4, 132.2, 131.9, 129.4, 128.3, 100.8, 51.9, 50.0, 21.5, 20.3, 20.2. **HRMS (ESI)** m/z Calcd for $[\text{C}_{20}\text{H}_{22}\text{INO}_4\text{S}, \text{M} + \text{H}]^+$: 500.0387; Found: 500.0391.

Optical Rotation: $[\alpha]_D^{25} - 32.0$ ($c = 1.0$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 10.767$ min for minor isomer, $t_R = 9.470$ min for major isomer).

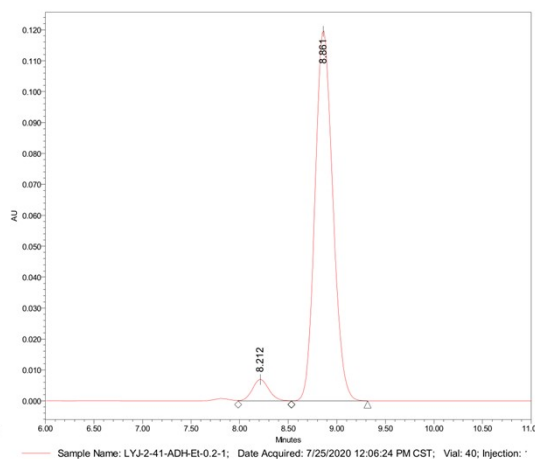


5b. (95% yield, Hexane-EtOAc = 5:1, R_f = 0.5). White solid. **MP:** 122-124 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, J = 8.2 Hz, 2H), 7.50 (s, 1H), 7.28 (d, J = 8.2 Hz, 2H), 6.98 (s, 1H), 6.29 (s, 1H), 5.80 (s, 1H), 4.58 (d, J = 14.2 Hz, 1H), 4.52 (d, J = 14.2 Hz, 1H), 4.13–3.92 (m, 2H), 2.42 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 143.4, 142.1, 139.8, 139.0, 138.4, 137.3, 135.9, 132.2, 131.6, 129.4, 128.3, 100.6, 60.9, 49.9, 21.5, 20.3, 20.3, 13.8. **HRMS (ESI)** m/z Calcd for $[\text{C}_{21}\text{H}_{24}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 536.0363; Found: 536.0366.

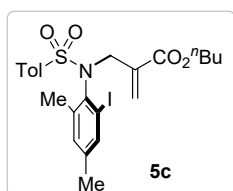
Optical Rotation: $[\alpha]_D^{25}$ - 24.0 (c = 1.0, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 8.212 min for minor isomer, t_R = 8.861 min for major isomer).



Peak Table				
Retention Time (min)	Area	Height	% Area	
1	9.053	752997	53200	49.83
2	8.363	758140	60017	50.17
Sum	1511137.2	113217.1		

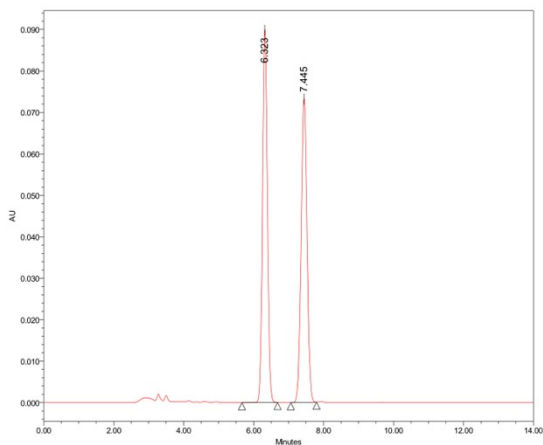


Peak Table				
Retention Time (min)	Area	Height	% Area	
1	8.861	1528150	119833	94.99
2	8.212	80604	6902	5.01
Sum	1608753.7	126735.2		



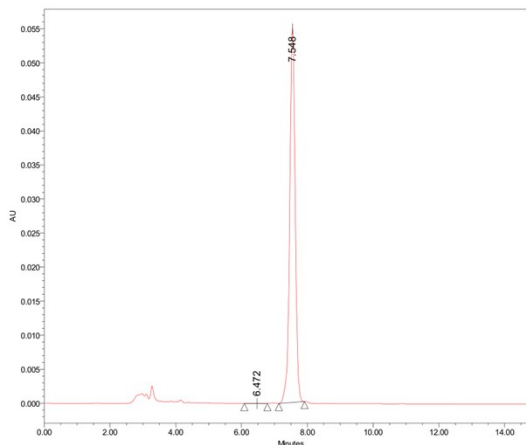
5c. (97% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, J = 8.3 Hz, 2H), 7.49 (s, 1H), 7.28 (d, J = 8.3 Hz, 2H), 6.98 (s, 1H), 6.29 (d, J = 0.9 Hz, 1H), 5.83 (s, 1H), 4.58 (d, J = 14.3 Hz, 1H), 4.51 (d, J = 14.3 Hz, 1H), 4.04 – 3.85 (m, 2H), 2.41 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H), 1.50 – 1.41 (m, 2H), 1.28 (dq, J = 14.4, 7.3 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 143.4, 142.0, 139.7, 139.0, 138.3, 137.3, 135.9, 132.2, 131.6, 129.4, 128.2, 100.6, 64.8, 49.9, 30.3, 21.5, 20.3, 20.3, 19.0, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 564.0676; Found: 564.0677.

Optical Rotation: $[\alpha]_D^{25}$ - 24.0 (c = 1.0, CHCl_3). >99% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 6.472 min for minor isomer, t_R = 7.548 min for major isomer).



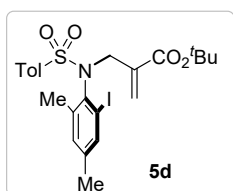
Sample Name: LYJ-2-43-Rac-4-ADH-0.2-1; Date Acquired: 7/11/2020 11:20:06 AM CST; Vial: 14; Injection:

Peak Table			
	Retention Time (min)	Area	Height
1	7.445	865405	73458
2	6.323	866786	90358
Sum		1732191.3	163816.7



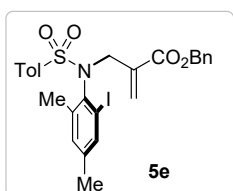
Sample Name: LYJ-2-41-ADH-4-0.2-1; Date Acquired: 7/12/2020 12:11:40 PM CST; Vial: 16; Injection:

Peak Table			
	Retention Time (min)	Area	Height
1	7.548	629951	54969
2	6.472	831	-26
Sum		630781.9	54942.8



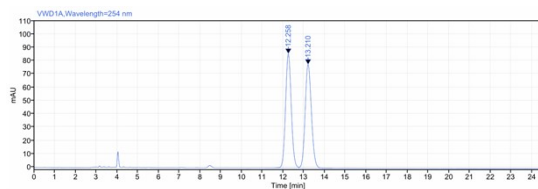
5d. (94% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2H), 7.42 (s, 1H), 7.20 (d, $J = 8.2$ Hz, 2H), 6.92 (s, 1H), 6.18 (d, $J = 0.9$ Hz, 1H), 5.73 (s, 1H), 4.50 (d, $J = 14.3$ Hz, 1H), 4.39 (d, $J = 14.3$ Hz, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H), 1.24 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.1, 143.4, 142.4, 139.8, 139.0, 138.5, 137.2, 132.2, 131.2, 129.4, 128.3, 100.3, 81.0, 49.7, 27.7, 21.5, 20.5, 20.3. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{28}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 564.0676; Found: 564.0681.

Optical Rotation: $[\alpha]_D^{25} - 14.0$ ($c = 1.0$, CHCl_3). 91% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.470$ min for minor isomer, $t_R = 10.767$ min for major isomer).

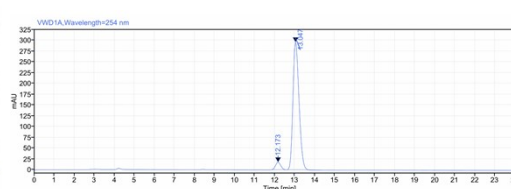


5e. (94% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 0.6 Hz, 1H), 7.27 – 7.20 (m, 3H), 7.19 – 7.13 (m, 4H), 6.83 (d, J = 0.6 Hz, 1H), 6.25 (d, J = 0.8 Hz, 1H), 5.76 (s, 1H), 4.98 (d, J = 12.4 Hz, 1H), 4.88 (d, J = 12.4 Hz, 1H), 4.50 (d, J = 14.3 Hz, 1H), 4.45 (d, J = 14.3 Hz, 1H), 2.32 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.8, 143.4, 141.8, 139.7, 139.0, 138.1, 137.2, 135.6, 135.4, 132.1, 132.1, 129.4, 128.3, 128.2, 128.1, 128.1, 100.7, 66.6, 50.0, 21.5, 20.3, 20.2. **HRMS (ESI)** m/z Calcd for $[\text{C}_{26}\text{H}_{26}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 598.0519; Found: 598.0523.

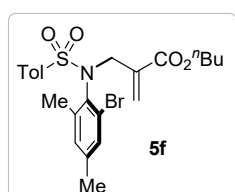
Optical Rotation: $[\alpha]_D^{25}$ - 24.0 (c = 1.0, CHCl_3). 91% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 12.137 min for minor isomer, t_R = 13.047 min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%
12.258	BV	1.65	1645.74	85.93	50.30
13.210	VB	1.60	1626.31	77.90	49.70
Sum			3272.05		



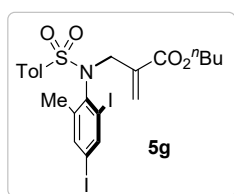
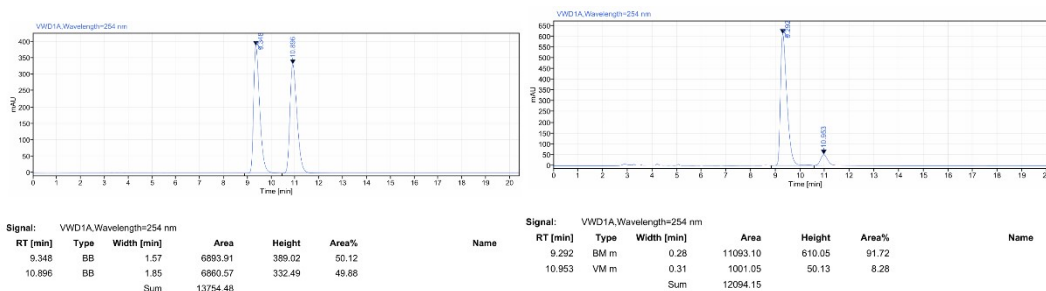
RT [min]	Type	Width [min]	Area	Height	Area%
12.173	MM m	0.28	307.04	17.16	4.69
13.047	MB m	0.33	6246.10	295.44	95.31
Sum			6553.14		



5f. (92% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.17 (s, 1H), 6.97 (s, 1H), 6.27 (s, 1H), 5.80 (s, 1H), 4.61 (d,

$J = 14.2$ Hz, 1H), 4.44 (d, $J = 14.2$ Hz, 1H), 4.13 – 3.82 (m, 2H), 2.42 (s, 3H), 2.25 (s, 6H), 1.52–1.45 (m, 2H), 1.35 – 1.24 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 143.4, 142.8, 139.6, 137.9, 136.0, 133.9, 132.1, 131.3, 131.2, 129.4, 128.1, 124.6, 64.8, 49.7, 30.4, 21.6, 20.6, 20.0, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{28}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 516.0815; Found: 516.0819.

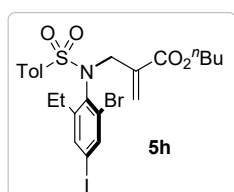
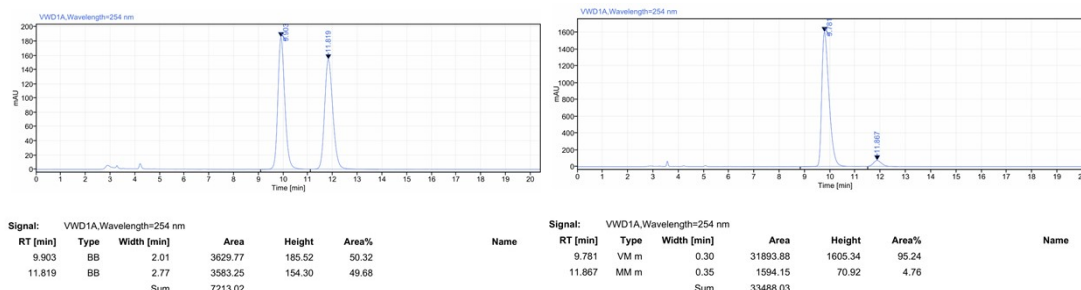
Optical Rotation: $[\alpha]^{25}_{\text{D}} - 4.2$ ($c = 1.0$, CHCl_3). 83% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 10.953$ min for minor isomer, $t_{\text{R}} = 9.292$ min for major isomer).



5g. (82% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 1.6$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 1.6$ Hz, 1H), 7.30 (d, $J = 8.2$ Hz, 2H), 6.33 (s, 1H), 5.88 (s, 1H), 4.56 (d, $J = 14.3$ Hz, 1H), 4.49 (d, $J = 14.3$ Hz, 1H), 4.00 (dt, $J = 10.9, 6.8$ Hz, 1H), 3.91 (dt, $J = 10.9, 6.8$ Hz, 1H), 2.43 (s, 3H), 2.18 (s, 3H), 1.50 – 1.41 (m, 2H), 1.33 – 1.26 (m, 2H), 0.90 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 146.1, 144.6, 143.8, 140.3, 140.2, 138.0, 135.7, 132.0, 129.6, 128.3, 101.9, 94.8, 65.0, 50.0, 30.3, 21.6, 20.2, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{I}_2\text{NO}_4\text{S}, \text{M} + \text{Na}]^+$: 675.9486; Found: 675.9491.

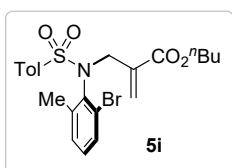
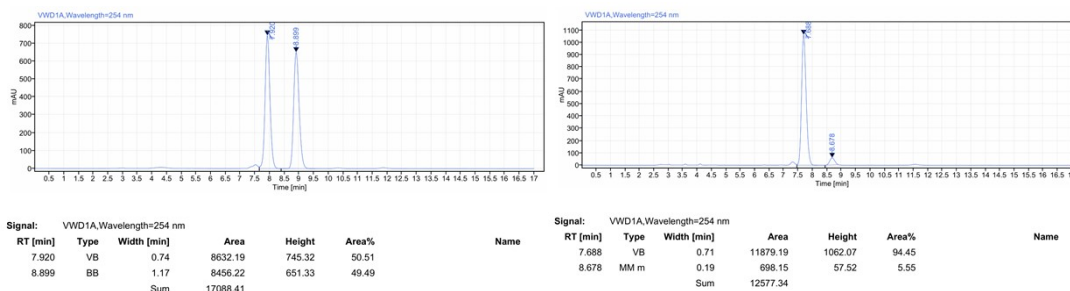
Optical Rotation: $[\alpha]^{25}_{\text{D}} - 2.4$ ($c = 0.5$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min,

wavelength = 254 nm, $t_R = 11.867$ min for minor isomer, $t_R = 9.781$ min for major isomer).



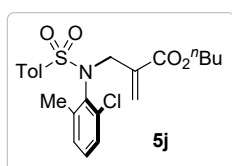
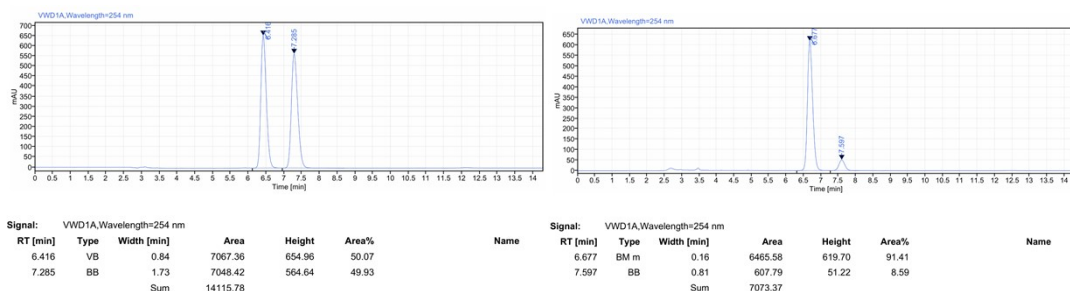
5h. (80% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 1.8$ Hz, 1H), 7.73 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 1.8$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 2H), 6.34 (s, 1H), 5.86 (s, 1H), 4.54 (d, $J = 14.3$ Hz, 1H), 4.49 (d, $J = 14.3$ Hz, 1H), 4.03 – 3.96 (m, 1H), 3.96 – 3.88 (m, 1H), 2.66 (dq, $J = 15.1, 7.5$ Hz, 1H), 2.50 (dq, $J = 15.1, 7.5$ Hz, 1H), 2.44 (s, 3H), 1.50 – 1.43 (m, 2H), 1.33 – 1.25 (m, 2H), 1.14 (t, $J = 7.5$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H).. $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.0, 162.5, 149.9, 143.8, 140.3, 138.7, 138.0, 135.5, 132.2, 129.6, 128.3, 123.0, 101.3, 65.0, 50.0, 30.4, 25.4, 21.6, 19.1, 14.2, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{27}\text{BrINO}_4\text{S}, \text{M} + \text{Na}]^+$: 641.9781; Found: 641.9785.

Optical Rotation: $[\alpha]_D^{25} = -5.6$ ($c = 1.0$, CHCl_3). 89% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 8.678$ min for minor isomer, $t_R = 7.688$ min for major isomer)



5i. (95% yield, Hexane-EtOAc = 5:1, R_f = 0.5). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.5 Hz, 1H), 7.04 (dd, J = 7.9, 7.5 Hz, 1H), 6.28 (s, 1H), 5.82 (s, 1H), 4.62 (d, J = 14.3 Hz, 1H), 4.47 (d, J = 14.3 Hz, 1H), 4.00 (dt, J = 11.0, 6.6 Hz, 1H), 3.91 (dt, J = 11.0, 6.6 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.52 – 1.43 (m, 2H), 1.34 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 143.6, 143.5, 137.9, 136.7, 135.9, 131.6, 131.3, 130.4, 129.4, 129.4, 128.1, 125.0, 64.9, 49.7, 30.4, 21.6, 20.1, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{26}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 502.0658; Found: 502.0662.

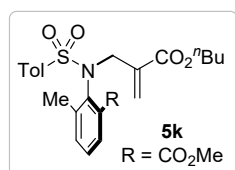
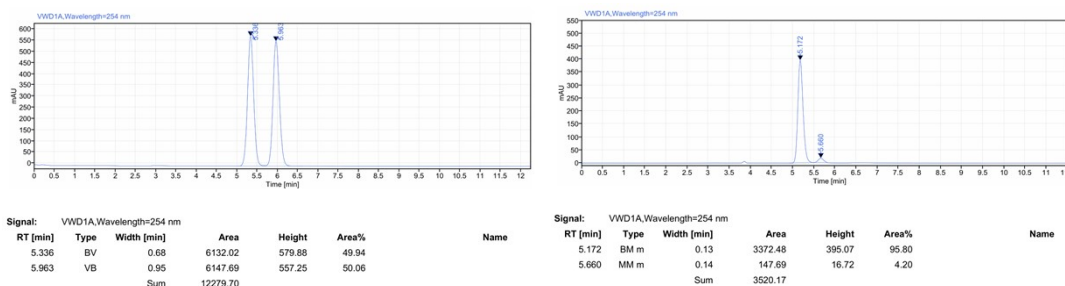
Optical Rotation: $[\alpha]_D^{25}$ - 10.4 (c = 1.0, CHCl_3). 83% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 7.597 min for minor isomer, t_R = 6.677 min for major isomer)



5j. (92% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.68 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 7.04 (dd, J = 7.9, 7.5 Hz, 1H), 6.28 (s, 1H), 5.82 (s, 1H), 4.62 (d, J = 14.3 Hz, 1H), 4.47 (d, J = 14.3 Hz, 1H), 4.00 (dt, J = 11.0, 6.6 Hz, 1H), 3.91 (dt, J = 11.0, 6.6 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.52 – 1.43 (m, 2H), 1.34 – 1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.1, 143.6, 143.5, 137.9, 136.7, 135.9, 131.6, 131.3, 130.4, 129.4, 129.4, 128.1, 125.0, 64.9, 49.7, 30.4, 21.6, 20.1, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{ClNO}_4\text{S}, \text{M} + \text{Na}]^+$: 487.0662; Found: 487.0662.

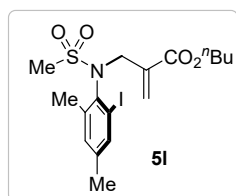
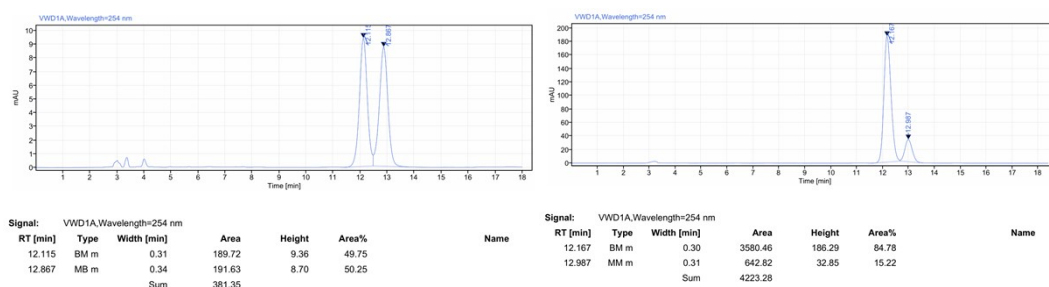
2H), 7.18 – 7.02 (m, 3H), 6.23 (d, $J = 1.1$ Hz, 1H), 5.77 (s, 1H), 4.61 (d, $J = 14.2$ Hz, 1H), 4.37 (d, $J = 14.2$ Hz, 1H), 3.99 (dt, $J = 10.9, 6.7$ Hz, 1H), 3.91 (dt, $J = 10.9, 6.7$ Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H), 1.51 – 1.42 (m, 2H), 1.33 – 1.23 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.32, 143.77, 143.64, 137.95, 136.23, 135.47, 135.12, 131.31, 130.09, 129.69, 129.40, 128.40, 128.31, 65.15, 50.00, 30.68, 21.86, 20.06, 19.36, 13.95. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{26}\text{ClNO}_4\text{S}, \text{M} + \text{Na}]^+$: 458.1163; Found: 458.1168.

Optical Rotation: $[\alpha]^{25}_{\text{D}} - 2.6$ ($c = 1.0$, CHCl_3). 92% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 5.660$ min for minor isomer, $t_{\text{R}} = 5.172$ min for major isomer).



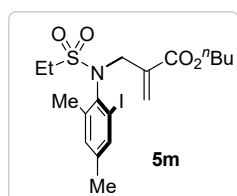
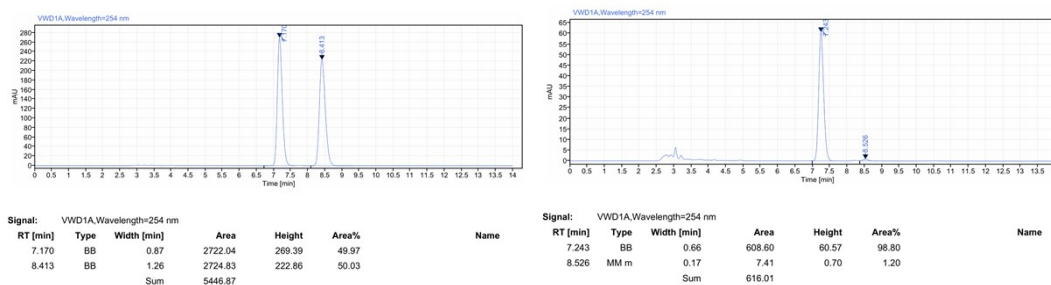
5k. (87% yield, Hexane-EtOAc-Chlorobenzene = 7:1:1, $R_{\text{f}} = 0.6$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.31 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.25 – 7.22 (m, 1H), 7.20 (d, $J = 8.3$ Hz, 2H), 6.31 (d, $J = 1.3$ Hz, 1H), 5.90 (s, 1H), 4.64 (d, $J = 14.6$ Hz, 1H), 4.58 (d, $J = 14.6$ Hz, 1H), 3.90 (t, $J = 6.7$ Hz, 2H), 3.54 (s, 3H), 2.38 (s, 3H), 1.94 (s, 3H), 1.41 – 1.32 (m, 2H), 1.26 – 1.16 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 166.4, 143.0, 140.9, 138.1, 136.9, 135.0, 132.6, 131.1, 129.4, 128.1, 127.5, 64.7, 51.9, 51.8, 30.3, 21.5, 19.0, 18.9, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{24}\text{H}_{29}\text{NO}_6\text{S}, \text{M} + \text{H}]^+$: 460.1788; Found: 460.1783.

Optical Rotation: $[\alpha]^{25}_D - 0.4$ ($c = 1.0$, CHCl_3). 70% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 90:0, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 12.987$ min for minor isomer, $t_R = 12.167$ min for major isomer).



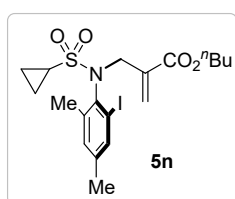
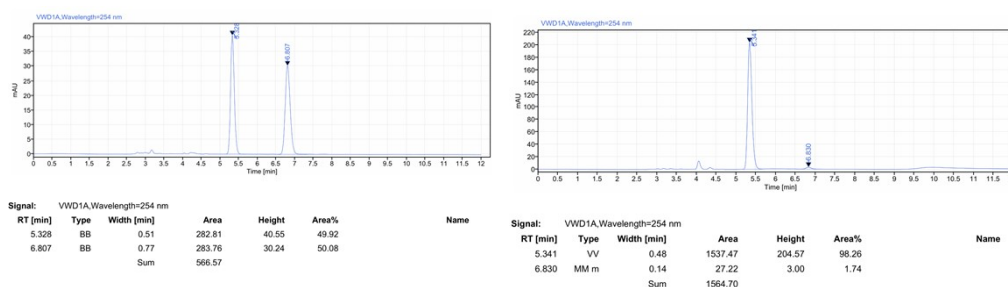
51. (97% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.03 (s, 1H), 6.22 (s, 1H), 5.45 (s, 1H), 4.71 (d, $J = 14.1$ Hz, 1H), 4.21 – 4.03 (m, 3H), 3.40 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H), 1.63 – 1.57 (m, 2H), 1.46 – 1.32 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.3, 140.9, 140.1, 138.6, 137.2, 135.2, 132.6, 131.7, 103.1, 65.1, 50.5, 42.8, 30.5, 20.4, 20.1, 19.2, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{17}\text{H}_{24}\text{INO}_4\text{S}, \text{M} + \text{H}]^+$: 466.0543; Found: 466.0547

Optical Rotation: $[\alpha]^{25}_D - 7.8$ ($c = 1.0$, CHCl_3). 98% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 7.17$ min for minor isomer, $t_R = 8.413$ min for major isomer).



5m. (92% yield, Hexane-EtOAc = 5:1, R_f = 0.5). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.03 (s, 1H), 6.22 (s, 1H), 5.49 (s, 1H), 4.69 (d, J = 14.0 Hz, 1H), 4.19 (d, J = 14.0 Hz, 1H), 4.16 – 3.96 (m, 2H), 3.75 – 3.46 (m, 2H), 2.38 (s, 3H), 2.24 (s, 3H), 1.61 – 1.54 (m, 2H), 1.47 (t, J = 7.4 Hz, 3H), 1.41 – 1.31 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 141.2, 140.0, 138.6, 137.2, 135.4, 132.6, 131.8, 103.0, 65.1, 50.4, 50.0, 30.5, 20.3, 20.2, 19.2, 13.7, 8.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{18}\text{H}_{26}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 502.0519; Found: 502.0523.

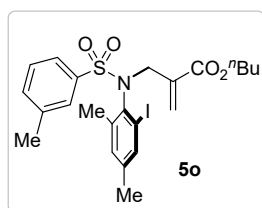
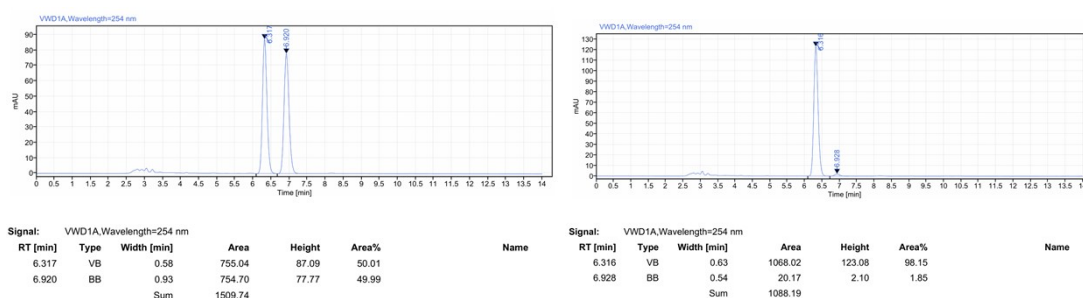
Optical Rotation: $[\alpha]_D^{25} - 4.6$ (c = 1.0, CHCl_3). 98% ee (HPLC conditions: Chiralpak OD-H column, n -Hexane/ i -PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 6.830 min for minor isomer, t_R = 5.341 min for major isomer).



5n. (87% yield, Hexane-EtOAc = 5:1, R_f = 0.5). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 1H), 7.01 (s, 1H), 6.24 (s, 1H), 5.63 (s, 1H), 4.64 (d, J = 14.1 Hz, 1H), 4.42 (d, J = 14.1 Hz, 1H), 4.20 – 3.88 (m, 2H), 3.12 – 2.78 (m, 1H), 2.35 (s, 3H), 2.24 (s, 3H),

1.58 – 1.51 (m, 2H), 1.38 – 1.31 (m, 2H), 1.28 – 1.15 (m, 2H), 1.15 – 1.01 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 141.4, 139.9, 138.7, 137.4, 135.7, 132.4, 131.6, 102.4, 65.0, 50.4, 32.4, 30.4, 20.3, 20.3, 19.1, 13.7, 7.2, 6.5. **HRMS (ESI)** m/z Calcd for $[\text{C}_{19}\text{H}_{26}\text{INO}_4\text{S}, \text{M} + \text{Na}]^+$: 514.0519; Found: 514.0521.

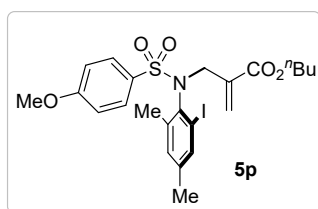
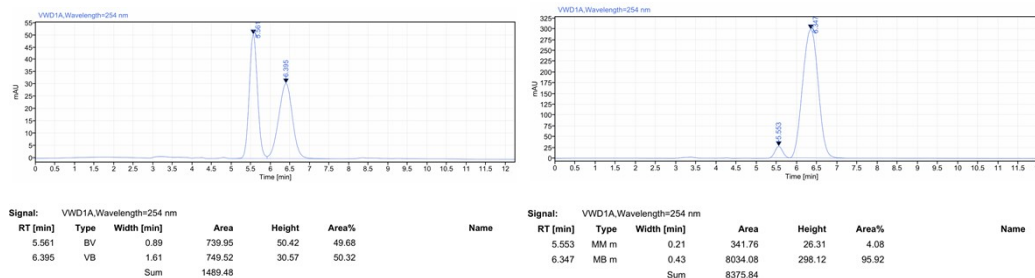
Optical Rotation: $[\alpha]_D^{25} - 2.3$ ($c = 1.0$, CHCl_3). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.928$ min for minor isomer, $t_R = 6.316$ min for major isomer).



5o. (78% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.67–7.65 (m, 2H), 7.50 (s, 1H), 7.40–7.37 (m, 2H), 6.99 (s, 1H), 6.30 (s, 1H), 5.85 (s, 1H), 4.59 (d, $J = 14.2$ Hz, 1H), 4.52 (d, $J = 14.2$ Hz, 1H), 4.05 – 3.95 (m, 1H), 3.95 – 3.85 (m, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 1.51 – 1.42 (m, 2H), 1.31 – 1.24 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 142.2, 141.1, 139.8, 139.1, 139.0, 137.3, 136.0, 133.5, 132.2, 131.7, 128.7, 128.7, 125.4, 100.4, 64.9, 50.0, 30.4, 21.3, 20.4, 20.3, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{28}\text{NO}_4\text{S}, \text{M} + \text{Na}]^+$: 564.0676; Found: 564.0681.

Optical Rotation: $[\alpha]_D^{25} - 0.4$ ($c = 1.0$, CHCl_3). 92% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min,

wavelength = 254 nm, t_R = 5.553 min for minor isomer, t_R = 6.347 min for major isomer).

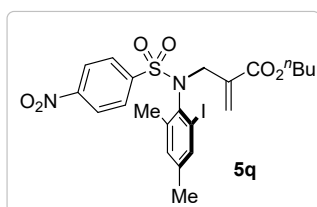
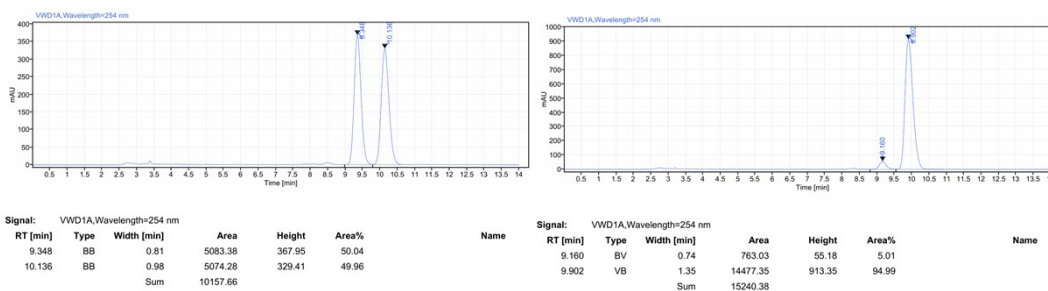


5p. (64% yield, Hexane-EtOAc = 5:1, R_f = 0.5). Syrup.

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.7 Hz, 2H), 7.50 (s, 1H), 6.99 (s, 1H), 6.96 (d, J = 8.7 Hz, 2H), 6.29 (s, 1H), 5.83 (s, 1H), 4.57 (d, J = 14.3 Hz, 1H), 4.51 (d, J =

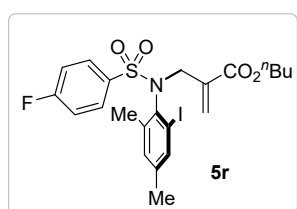
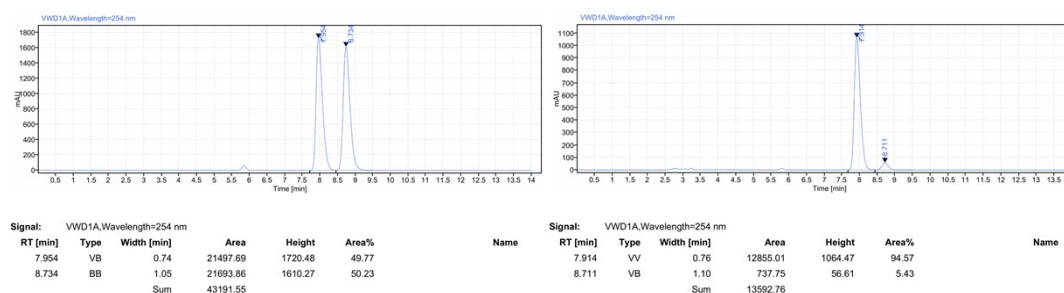
14.3 Hz, 1H), 4.00 (dt, J = 11.2, 6.8 Hz, 1H), 3.91 (dt, J = 11.2, 6.8 Hz, 1H), 3.87 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.53 – 1.41 (m, 2H), 1.34 – 1.24 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ 166.2, 163.1, 142.1, 139.8, 139.1, 137.5, 136.0, 133.2, 132.3, 131.5, 130.4, 113.9, 100.5, 64.9, 55.6, 50.0, 30.4, 20.4, 20.3, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{23}\text{H}_{28}\text{INO}_5\text{S}, \text{M} + \text{H}]^+$: 558.0806; Found: 558.0811.

Optical Rotation: $[\alpha]^{25}_{\text{D}}$ – 19.0 (c = 1.0, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 9.160 min for minor isomer, t_R = 9.902 min for major isomer).



5q. (86% yield, Hexane-EtOAc = 5:1, $R_f = 0.4$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.5$ Hz, 2H), 8.05 (d, $J = 8.5$ Hz, 2H), 7.49 (s, 1H), 7.03 (s, 1H), 6.31 (s, 1H), 5.78 (s, 1H), 4.65 (d, $J = 14.1$ Hz, 1H), 4.57 (d, $J = 14.1$ Hz, 1H), 4.09 – 3.98 (m, 1H), 3.98 – 3.89 (m, 1H), 2.25 (s, 3H), 2.23 (s, 3H), 1.55 – 1.44 (m, 2H), 1.35 – 1.25 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.9, 150.1, 146.7, 142.3, 140.5, 139.2, 136.2, 135.3, 132.5, 132.2, 129.6, 124.1, 99.9, 65.0, 50.5, 30.4, 20.4, 20.4, 19.1, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{IN}_2\text{O}_6\text{S}, \text{M} + \text{Na}]^+$: 595.0370; Found: 595.0373.

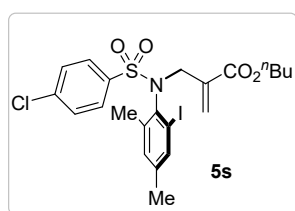
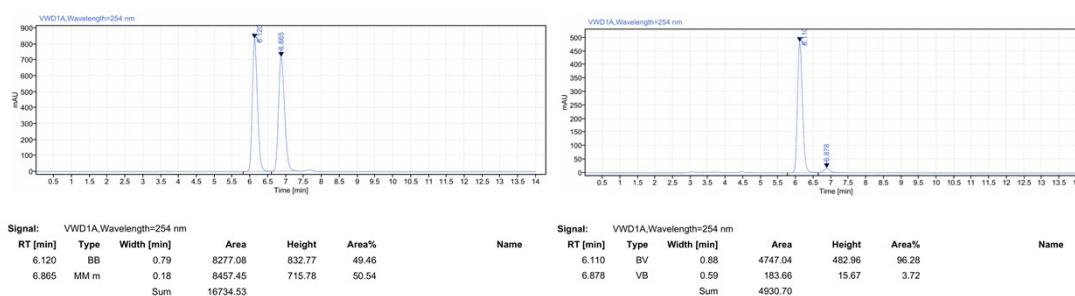
Optical Rotation: $[\alpha]_D^{25} - 15.6$ ($c = 1.0$, CHCl_3). 89% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 7.914$ min for minor isomer, $t_R = 8.711$ min for major isomer).



5r. (97% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (dd, $J = 8.6, 5.2$ Hz, 2H), 7.49 (s, 1H), 7.17 (t, $J = 8.6$ Hz, 2H), 7.00 (s, 1H), 6.30 (s, 1H), 5.80 (s, 1H), 4.60 (d, $J = 14.2$ Hz, 1H), 4.52 (d, $J =$

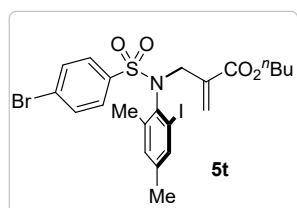
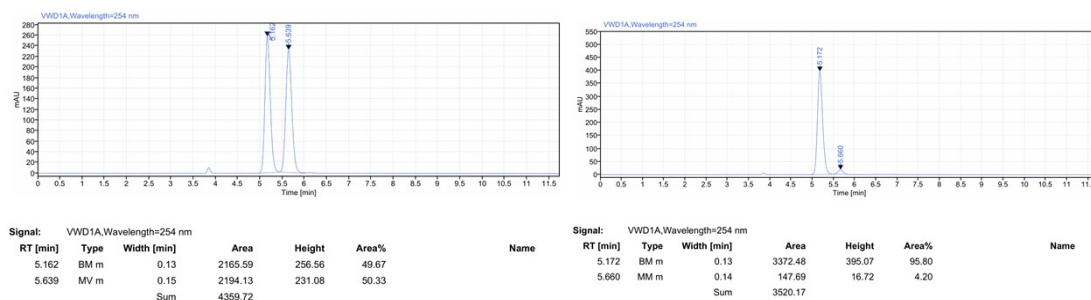
14.2 Hz, 1H), 4.09 – 3.97 (m, 1H), 3.97 – 3.88 (m, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 1.52 – 1.43 (m, 2H), 1.34 – 1.25 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 165.3 ($^1J_{\text{C-F}} = 253.0$ Hz), 142.2, 140.1, 139.2, 137.4 (d, $^4J_{\text{C-F}} = 3.3$ Hz), 137.0, 135.8, 132.4, 131.8, 131.0 (d, $^3J_{\text{C-F}} = 9.3$ Hz), 116.0 (d, $^2J_{\text{C-F}} = 22.5$ Hz), 100.2, 64.9, 50.2, 30.4, 20.4, 20.3, 19.1, 13.7. ^{19}F NMR (376 MHz, CDCl_3) δ -105.46. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{FINO}_4\text{S}, \text{M} + \text{Na}]^+$: 568.0425; Found: 568.0429.

Optical Rotation: $[\alpha]_{\text{D}}^{25} - 30.0$ ($c = 1.0$, CHCl_3). 93% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 6.878$ min for minor isomer, $t_{\text{R}} = 6.110$ min for major isomer).



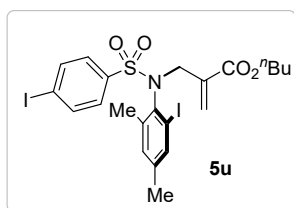
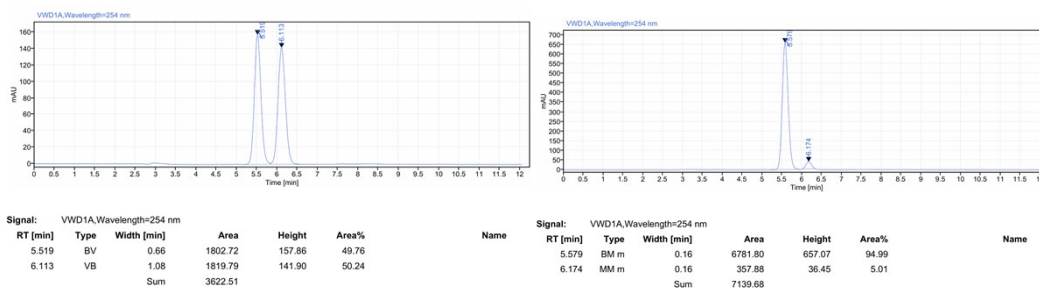
5s. (92% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.2$ Hz, 2H), 7.50 (s, 1H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.00 (s, 1H), 6.30 (s, 1H), 5.80 (s, 1H), 4.60 (d, $J = 14.2$ Hz, 1H), 4.52 (d, $J = 14.2$ Hz, 1H), 4.10 – 3.97 (m, 1H), 3.97 – 3.88 (m, 1H), 2.24 (s, 3H), 2.21 (s, 3H), 1.52 – 1.43 (m, 2H), 1.34 – 1.25 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 142.2, 140.1, 139.7, 139.2, 139.2, 136.9, 135.7, 132.4, 131.9, 129.8, 129.1, 100.2, 65.0, 50.2, 30.4, 20.4, 20.3, 19.1, 13.7. **HRMS (ESI)** m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{ClINO}_4\text{S}, \text{M} + \text{H}]^+$: 584.0130; Found: 584.0132.

Optical Rotation: $[\alpha]_D^{25} - 15.0$ ($c = 1.0$, CHCl_3). 92% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 5.660$ min for minor isomer, $t_R = 5.172$ min for major isomer).



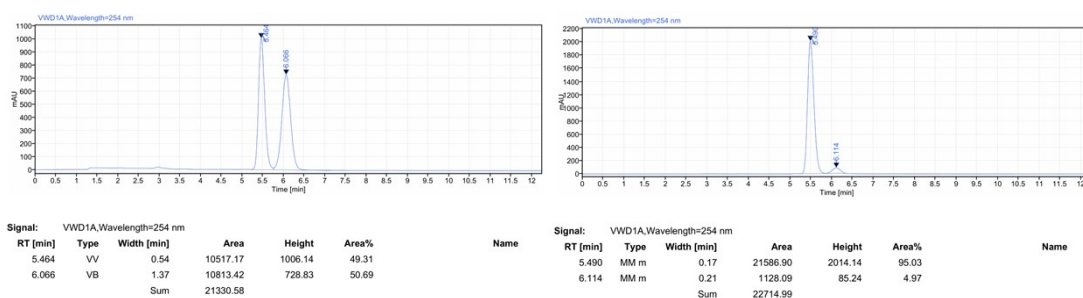
5t. (97% yield, Hexane-EtOAc = 5:1, $R_f = 0.4$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.7$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 2H), 7.49 (s, 1H), 7.00 (s, 1H), 6.29 (d, $J = 0.8$ Hz, 1H), 5.79 (s, 1H), 4.59 (d, $J = 14.2$ Hz, 1H), 4.52 (d, $J = 14.2$ Hz, 1H), 4.01 (dt, $J = 10.9, 6.6$ Hz, 1H), 3.92 (dt, $J = 10.9, 6.6$ Hz, 1H), 2.23 (s, 3H), 2.20 (s, 3H), 1.51 – 1.43 (m, 2H), 1.33 – 1.25 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 142.1, 140.2, 140.0, 139.1, 136.8, 135.6, 132.3, 132.1, 131.8, 129.8, 127.7, 100.2, 64.9, 50.2, 30.3, 20.4, 20.3, 19.0, 13.6. HRMS (ESI) m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{BrINO}_4\text{S}, \text{M} + \text{Na}]^+$: 627.9625; Found: 627.9630.

Optical Rotation: $[\alpha]_D^{25} - 25.5$ ($c = 1.0$, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 6.173$ min for minor isomer, $t_R = 5.579$ min for major isomer).

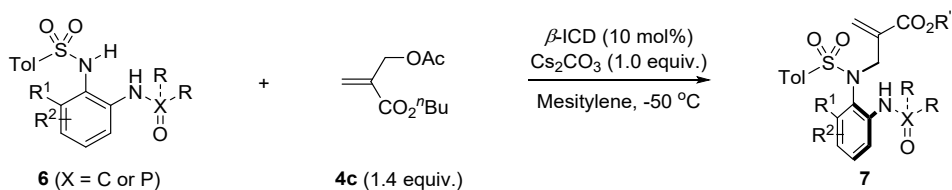


5u. (98% yield, Hexane-EtOAc = 5:1, R_f = 0.5). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.49 (s, 1H), 6.99 (s, 1H), 6.29 (d, J = 0.8 Hz, 1H), 5.79 (s, 1H), 4.59 (d, J = 14.2 Hz, 1H), 4.51 (d, J = 14.2 Hz, 1H), 4.00 (dt, J = 10.8, 6.8 Hz, 1H), 3.92 (dt, J = 10.8, 6.6 Hz, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.50 – 1.43 (m, 2H), 1.33 – 1.24 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 142.1, 140.8, 140.0, 139.1, 138.0, 136.8, 135.6, 132.3, 131.8, 129.7, 100.2, 100.1, 64.9, 50.2, 30.3, 20.4, 20.3, 19.0, 13.6. HRMS (ESI) m/z Calcd for $[\text{C}_{22}\text{H}_{25}\text{BrI}_2\text{NO}_4\text{S}, \text{M} + \text{Na}]^+$: 675.9486; Found: 675.9491.

Optical Rotation: $[\alpha]_D^{25} - 25.7$ (c = 1.0, CHCl_3). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:25, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 6.114 min for minor isomer, t_R = 5.490 min for major isomer).

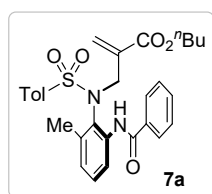


Representative procedure for synthesis of 7:



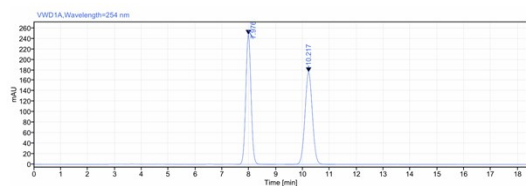
To a Schlenk tube containing **6**^[4] (0.05 mmol), β -ICD (1.5 mg, 10 mol%) and Cs_2CO_3 (0.05 mmol, 1.0 equiv.) were added mesitylene (3 mL) and MBH acetate **4c** (0.14 mmol, 1.4 equiv.). The reaction mixture was stirred at $-50\text{ }^\circ\text{C}$ for 24 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography with hexanes/ethyl acetate as the eluent to afford the product **7**.

Characterization of compounds of **7**:

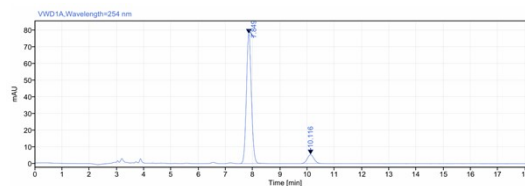


7a. (76% yield, Hexane-EtOAc = 3:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.15 (s, 1H), 8.07 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 7.4$ Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H), 7.48-7.44 (m, 1H), 7.41-7.38 (m, 2H), 7.19-7.14 (m, 3H), 6.82 (d, $J = 7.5$ Hz, 1H), 6.03 (s, 1H), 5.53 (s, 1H), 4.72 (d, $J = 14.0$ Hz, 1H), 4.02 (d, $J = 14.0$ Hz, 1H), 3.72 – 3.54 (m, 2H), 2.31 (s, 3H), 1.60 (s, 3H), 1.33-1.26 (m, 2H), 1.15-1.06 (m, 2H), 0.75 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.6, 165.0, 144.2, 138.5, 138.3, 136.1, 135.2, 134.4, 131.7, 130.9, 129.7, 129.2, 128.5, 127.8, 127.8, 127.4, 127.1, 121.7, 64.8, 51.1, 30.2, 21.5, 18.9, 17.9, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_5\text{S}, \text{M} + \text{Na}]^+$: 543.1924; Found: 543.1929.

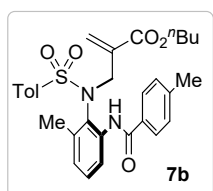
Optical Rotation: $[\alpha]^{25}_{\text{D}}$ 60.0 ($c = 1.0$, CHCl_3). 84% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 10.116$ min for minor isomer, $t_R = 7.849$ min for major isomer).



Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
7.976	BB	1.42	3363.98	247.26	49.99
10.217	BB	1.87	3364.89	175.73	50.01
	Sum		6728.87		

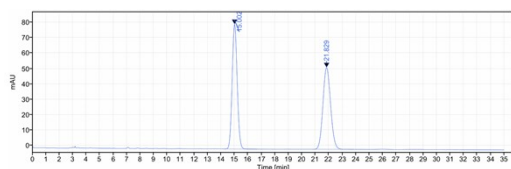


Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
7.849	BB	0.80	986.53	78.00	91.79
10.116	MM m	0.26	88.20	5.25	8.21
	Sum		1074.73		

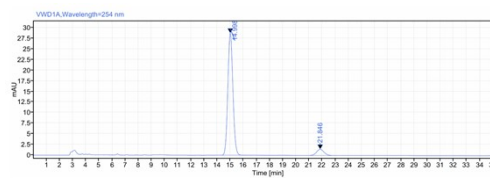


7b. (81% yield, Hexane-EtOAc = 3:1, $R_f = 0.4$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.11 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 3H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 7.5$ Hz, 1H), 6.03 (s, 1H), 5.53 (s, 1H), 4.71 (d, $J = 14.0$ Hz, 1H), 4.02 (d, $J = 14.0$ Hz, 1H), 3.71-3.58 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.59 (s, 3H), 1.34 – 1.26 (m, 2H), 1.16-1.06 (m, 2H), 0.75 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.6, 165.0, 144.2, 142.2, 138.5, 138.4, 136.1, 135.2, 131.6, 131.0, 129.7, 129.2, 129.2, 127.8, 127.7, 127.4, 127.0, 121.7, 64.9, 51.1, 30.2, 21.6, 21.5, 18.9, 17.9, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_4\text{S}, \text{M} + \text{Na}]^+$: 557.2081; Found: 557.2085.

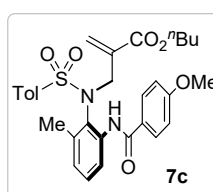
Optical Rotation: $[\alpha]_D^{25}$ 51.0 ($c = 1.0$, CHCl_3). 86% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 21.846$ min for minor isomer, $t_R = 14.998$ min for major isomer).



Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
15.002	BB	2.44	2104.92	81.80	50.01
21.829	BB	3.04	2104.09	53.10	49.99
	Sum		4209.01		



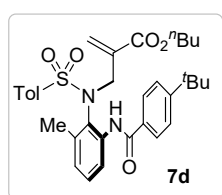
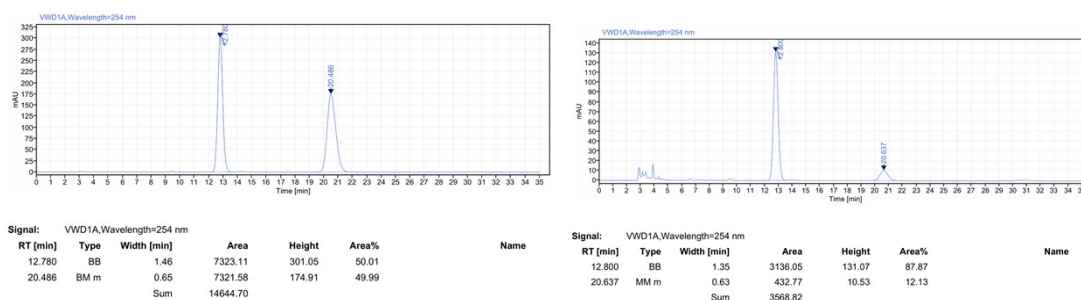
Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
14.998	BB	1.99	769.83	28.74	92.86
21.846	MM m	0.58	59.22	1.47	7.14
	Sum		829.05		



7c. (45% yield, Hexane-EtOAc = 3:1, $R_f = 0.4$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.15 (s, 1H), 8.12 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.63 (d, $J = 8.2$ Hz, 2H), 7.26 – 7.15 (m, 3H),

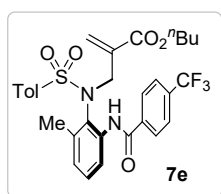
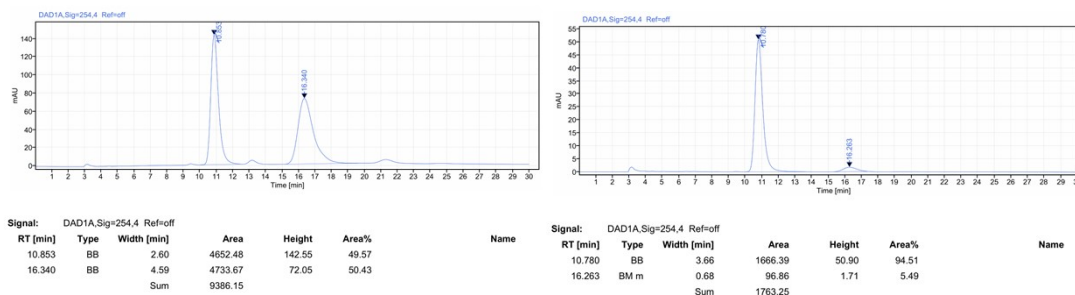
6.96 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 7.4$ Hz, 1H), 6.10 (s, 1H), 5.58 (s, 1H), 4.79 (d, $J = 14.0$ Hz, 1H), 4.07 (d, $J = 14.0$ Hz, 1H), 3.86 (s, 3H), 3.76 (dt, $J = 10.9, 6.8$ Hz, 1H), 3.68 (dt, $J = 10.9, 6.8$ Hz, 1H), 2.39 (s, 3H), 1.65 (s, 3H), 1.42 – 1.31 (m, 2H), 1.18 (dq, $J = 14.5, 7.3$ Hz, 2H), 0.82 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 164.6, 162.4, 144.2, 138.4, 136.1, 135.1, 130.9, 129.7, 129.3, 129.1, 127.8, 127.6, 126.8, 126.7, 121.6, 113.7, 64.8, 55.4, 51.0, 30.2, 21.5, 18.9, 17.9, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_6\text{S}, \text{M} + \text{Na}]^+$: 573.2030; Found: 573.2034.

Optical Rotation: $[\alpha]^{25}_{\text{D}}$ 34.0 ($c = 1.0$, CHCl_3). 76% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 20.637$ min for minor isomer, $t_{\text{R}} = 12.800$ min for major isomer).



7d. (74% yield, Hexane-EtOAc = 3:1, $R_f = 0.4$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 1H), 8.13 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.5$ Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.27 – 7.21 (m, 3H), 6.88 (d, $J = 7.5$ Hz, 1H), 6.10 (s, 1H), 5.58 (s, 1H), 4.78 (d, $J = 14.0$ Hz, 1H), 4.09 (d, $J = 14.0$ Hz, 1H), 3.74 (dt, $J = 10.8, 6.8$ Hz, 1H), 3.65 (dt, $J = 10.8, 6.8$ Hz, 1H), 2.39 (s, 3H), 1.66 (s, 3H), 1.42 – 1.28 (m, 11H), 1.17 (dq, $J = 14.4, 7.4$ Hz, 2H), 0.81 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 164.9, 155.2, 144.1, 138.5, 138.4, 136.1, 135.1, 131.4, 131.0, 129.7, 129.1, 127.8, 127.7, 127.2, 127.0, 125.5, 121.7, 64.8, 51.0, 34.9, 31.1, 30.2, 21.5, 18.9, 17.9, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_5\text{S}, \text{M} + \text{Na}]^+$: 599.2550; Found: 599.2554.

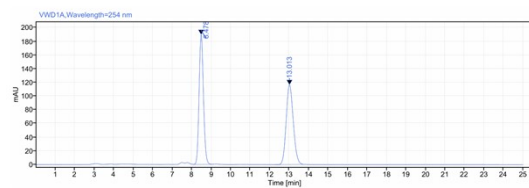
Optical Rotation: $[\alpha]^{25}_D$ 45.0 ($c = 1.0$, CHCl_3). 89% *ee* (HPLC conditions: Chiralpak OZ-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 16.263$ min for minor isomer, $t_R = 10.780$ min for major isomer).



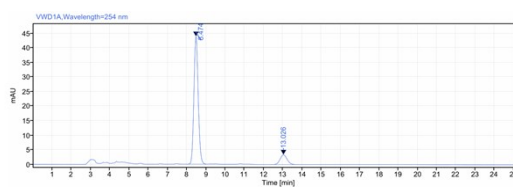
7e. (55% yield, Hexane-EtOAc = 3:1, $R_f = 0.4$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.33 (s, 1H), 8.10 (d, $J = 8.1$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 8.1$ Hz, 2H), 6.87 (d, $J = 7.5$ Hz, 1H), 6.07 (s, 1H), 5.58 (s, 1H), 4.79 (d, $J = 13.9$ Hz, 1H), 3.99 (d, $J = 13.9$ Hz, 1H), 3.74 – 3.55 (m, 2H), 2.35 (s, 3H), 1.62 (s, 3H), 1.35 – 1.27 (m, 2H), 1.12 (dq, $J = 14.4, 7.3$ Hz, 2H), 0.77 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.6, 163.7, 144.3, 138.5, 138.0, 137.7, 135.9, 135.2, 133.3 ($^2J_{C-F} = 32.5$ Hz), 131.1, 129.7, 129.3, 127.9, 127.9, 127.7, 127.5, 125.6 ($^3J_{C-F} = 3.8$ Hz), 123.7 ($^1J_{C-F} = 270.8$ Hz), 121.5, 64.9, 51.3, 30.2, 21.5, 18.9, 17.9, 13.5. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) 62.94. **HRMS (ESI)** m/z Calcd for $[\text{C}_{30}\text{H}_{31}\text{F}_3\text{N}_2\text{O}_5\text{S}, \text{M} + \text{Na}]^+$: 599.2550; Found: 599.2554.

Optical Rotation: $[\alpha]^{25}_D$ 32.0 ($c = 1.0$, CHCl_3). 78% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 13.026$ min for minor isomer, $t_R = 8.474$ min for major isomer).

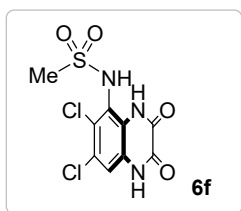
Figure 50. HPLC Trace of **7e**.



Signal: VWD1A,Wavelength=254 nm						
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.478	VB	0.95	2937.87	189.33	49.95	
13.013	BM m	0.39	2943.35	116.35	50.05	
	Sum		5881.21			

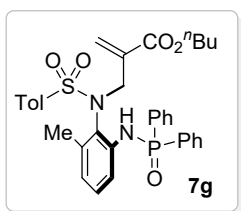


Signal: VWD1A,Wavelength=254 nm						
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.474	BB	1.12	662.31	43.92	88.92	
13.026	BB	1.57	85.03	3.35	11.08	
	Sum		747.34			



6f^[5]. (85% yield). Yellow solid. **MP**: 91-92 °C. ¹H NMR (400 MHz, DMSO) δ 12.12 (s, 1H), 11.04 (s, 1H), 9.49 (s, 1H), 7.29 (s, 1H), 3.16 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 154.7, 154.5, 126.6, 126.2, 125.3, 121.5, 115.1, 41.7. **HRMS (ESI)**

m/z Calcd for [C₉H₇Cl₂N₃O₄S, M + Na]⁺: 345.9427, 347.9396; Found: 345.9428, 347.9400.

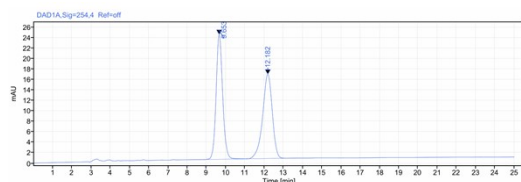


7g. (38% yield, Hexane-EtOAc = 2:1, R_f = 0.4). Syrup. ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.90 (m, 2H), 7.89 – 7.81 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.35 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.54 (d, *J* =

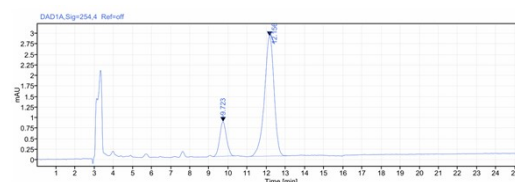
7.4 Hz, 1H), 6.42 (d, *J* = 10.6 Hz, 1H), 6.06 (s, 1H), 5.56 (s, 1H), 4.58 (d, *J* = 14.1 Hz, 1H), 4.04 (d, *J* = 14.1 Hz, 1H), 3.85 – 3.69 (m, 2H), 2.33 (s, 3H), 1.65 (s, 3H), 1.44 – 1.32 (m, 2H), 1.22 – 1.16 (m, 2H), 0.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 144.0, 141.2, 138.8, 136.3, 135.5, 132.4 (¹*J*_{C-P} = 128.3 Hz), 132.2 (²*J*_{C-P} = 10.2 Hz), 132.0 (¹*J*_{C-P} = 128.9 Hz), 132.0 (³*J*_{C-P} = 2.5 Hz), 131.9 (³*J*_{C-P} = 2.7 Hz), 131.5 (²*J*_{C-P} = 10 Hz), 130.9, 129.7, 129.1, 128.5 (²*J*_{C-P} = 24.7 Hz), 128.6, 128.5, 127.9, 125.9 (³*J*_{C-P} = 8.5 Hz), 123.7, 116.5 (³*J*_{C-P} = 4.7 Hz), 65.0, 50.6, 30.3, 21.6, 19.0, 18.4, 13.7. ³¹P NMR (162 MHz, CDCl₃) 18.02 (d, *J* = 11.1 Hz). **HRMS (ESI)** m/z Calcd for [C₃₄H₃₇N₂O₅PS, M + Na]⁺: 639.2053; Found: 639.2058.

Optical Rotation: [α]_D²⁵ 48.0 (*c* = 1.0, CHCl₃). 66% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254

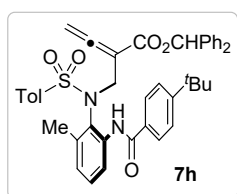
nm, $t_R = 9.723$ min for minor isomer, $t_R = 12.157$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.653	BB	2.13	561.71	23.76	50.16	
12.162	BB	1.99	558.02	16.03	49.84	
	Sum		1119.74			



RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.723	MM m	0.32	20.06	0.82	16.83	
12.156	BB	1.91	99.10	2.84	83.17	
	Sum		119.15			



7h. (53% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$

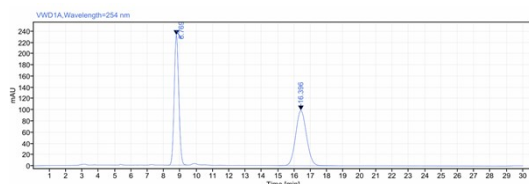
(400 MHz, CDCl_3) δ 9.11 (s, 1H), 8.21 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.27– 7.22 (m, 4H), 7.21 – 7.13 (m, 7H), 7.12 – 7.04 (m,

2H), 6.83 (d, $J = 7.3$ Hz, 1H), 6.48 (s, 1H), 4.92 (d, $J = 14.9$ Hz, 1H), 4.86 (d, $J = 14.9$ Hz, 1H), 4.73 (d, $J = 13.8$ Hz, 1H), 4.19 (d, $J = 13.8$ Hz, 1H), 2.34 (s, 3H), 1.64 (s, 3H), 1.35 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 215.9, 164.8, 164.8, 155.0, 144.0, 140.0, 139.8, 138.9, 138.5, 136.2, 131.4, 129.7, 129.2, 128.3, 128.2, 127.7, 127.6, 127.3, 127.2, 127.0, 126.7, 126.5, 125.3, 121.0, 95.6, 79.9, 77.6, 49.1, 34.9, 31.1, 21.5, 18.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{43}\text{H}_{42}\text{IN}_2\text{O}_5\text{S}, \text{M}+\text{Na}]^+$: 721.2707; Found: 721.2711.

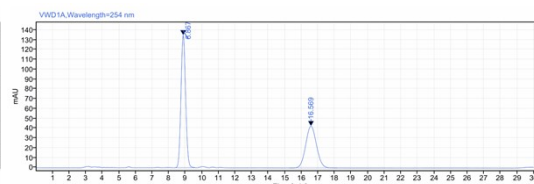
Optical Rotation: $[\alpha]_D^{25} -7.2$ ($c = 0.5$, CHCl_3). 16% *ee* (HPLC conditions: Chiralpak

AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254

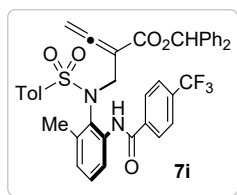
nm, $t_R = 16.569$ min for minor isomer, $t_R = 8.867$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.769	BB	1.27	4522.29	231.69	49.95	
16.396	BB	4.02	4531.20	98.22	50.05	
	Sum		9053.49			

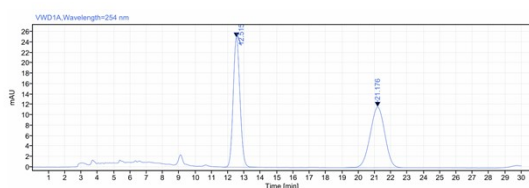


RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.867	BB	1.31	2625.78	134.70	57.76	
16.569	BM m	0.70	1919.99	42.53	42.24	
	Sum		4545.77			

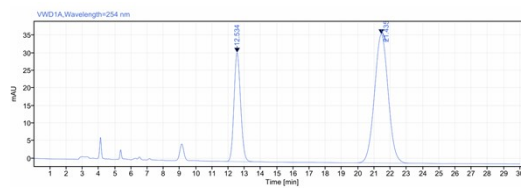


7i. (46% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.12 (s, 1H), 8.19 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.26 – 7.21 (m, 3H), 7.20 – 7.11 (m, 7H), 7.08 – 7.03 (m, 2H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.47 (s, 1H), 4.97 (d, $J = 14.9$ Hz, 1H), 4.91 (d, $J = 14.9$ Hz, 1H), 4.84 (d, $J = 13.6$ Hz, 1H), 4.10 (d, $J = 13.6$ Hz, 1H), 2.32 (s, 3H), 1.71 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 216.1, 165.0, 163.5, 144.2, 139.9, 139.7, 138.9, 138.2, 137.4, 136.2, 132.9 ($^2J_{\text{C-F}} = 32.3$ Hz), 129.7, 129.3, 128.4, 128.3, 127.9, 127.8, 127.7, 127.3, 127.2, 126.9, 126.2, 125.3 ($^3J_{\text{C-F}} = 3.7$ Hz), 123.7 ($^1J_{\text{C-F}} = 270.9$ Hz), 120.9, 95.4, 79.7, 77.7, 49.2, 21.5, 18.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) 62.83. **HRMS (ESI)** m/z Calcd for $[\text{C}_{40}\text{H}_{33}\text{F}_3\text{N}_2\text{O}_5\text{S}, \text{M} + \text{Na}]^+$: 733.1954; Found: 733.1959.

Optical Rotation: $[\alpha]_D^{25} -6.6$ ($c = 0.5$, CHCl_3). 42% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 12.534$ min for minor isomer, $t_R = 21.435$ min for major isomer).

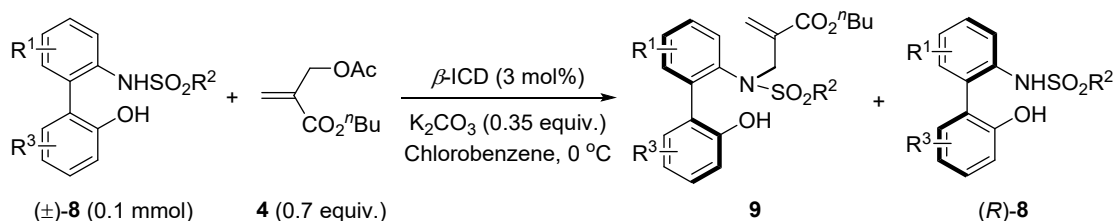


Signal: VWD1A,Wavelength=254 nm						Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%	RT [min]	Type	Width [min]	Area	Height	Area%
12.515	BB	2.26	719.69	24.89	49.85	12.534	BB	2.21	878.16	31.00	29.01
21.176	BB	3.65	723.92	11.65	50.15	21.435	BB	3.58	2148.75	36.68	70.99
Sum			1443.62			Sum			3026.90		

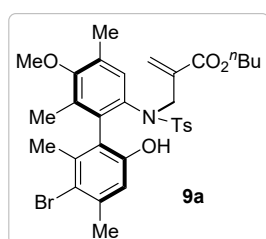


Signal: VWD1A,Wavelength=254 nm						Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%	RT [min]	Type	Width [min]	Area	Height	Area%
12.515	BB	2.26	719.69	24.89	49.85	12.534	BB	2.21	878.16	31.00	29.01
21.176	BB	3.65	723.92	11.65	50.15	21.435	BB	3.58	2148.75	36.68	70.99
Sum			1443.62			Sum			3026.90		

Representative procedure for synthesis of 8:

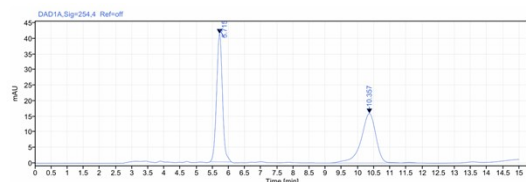


To a Schlenk tube containing *rac*-**8** (0.1 mmol), β -ICD (1.0 mg, 3 mol%) and K_2CO_3 (0.035 mmol, 0.35 equiv.) were added chlorobenzene (8 mL) and MBH acetate **4** (0.07 mmol, 0.7 equiv.). The reaction mixture was allowed to stir at 0 °C for 72 h. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography to afford the product **9** and unreacted starting material **8**.

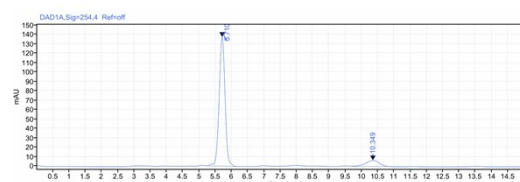


9a. (56% yield, Hexane-EtOAc = 5:1, R_f = 0.4). Syrup. 1H NMR (400 MHz, DMSO- d_6) δ 9.32 (s, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.74 (s, 1H), 6.70 (s, 1H), 5.96 (s, 1H), 5.35 (s, 1H), 4.18 (d, J = 16.7 Hz, 1H), 3.96 (t, J = 6.6 Hz, 2H), 3.89 (d, J = 16.7 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.19 (s, 3H), 1.96 (s, 3H), 1.78 (s, 3H), 1.55 – 1.42 (m, 2H), 1.32 – 1.23 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 165.5, 156.1, 153.3, 143.5, 137.5, 137.3, 137.0, 136.2, 135.0, 134.3, 131.1, 130.4, 129.4, 129.4, 128.2, 127.8, 124.0, 116.8, 115.2, 64.1, 59.6, 50.3, 30.0, 23.7, 21.3, 21.0, 18.6, 15.7, 13.6, 13.1. HRMS (ESI) m/z Calcd for $[C_{32}H_{38}BrNO_6S, M + Na]^+$: 666.1495, 668.1480; Found: 666.1497, 668.1481.

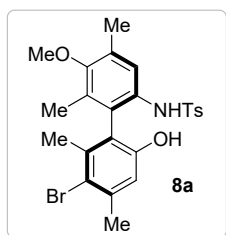
Optical Rotation: $[\alpha]^{25}_D$ 90.0 (c = 1.0, $CHCl_3$). 80% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 10.349 min for minor isomer, t_R = 5.710 min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%
5.715	MM m	0.20	518.24	41.06	50.44
10.357	MM m	0.48	509.24	15.89	49.56
Sum			1027.49		

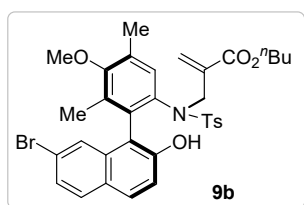
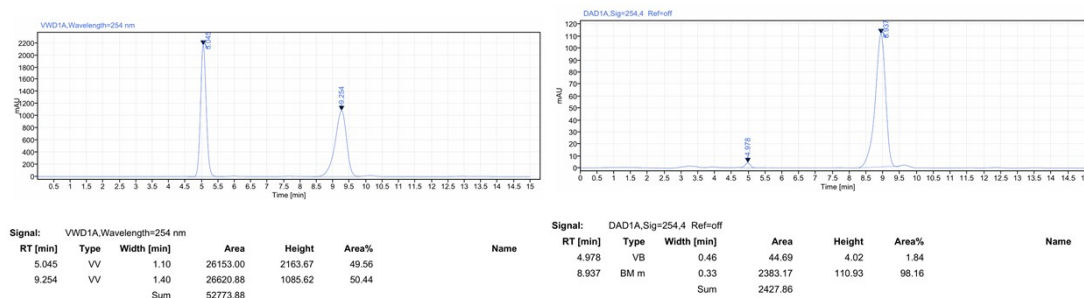


RT [min]	Type	Width [min]	Area	Height	Area%
5.710	MM m	0.20	1738.97	137.10	90.08
10.349	VM m	0.45	191.52	6.45	9.92
Sum			1930.49		



8a. (38% yield, Hexane-EtOAc = 2:1, R_f = 0.4). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.76 (s, 1H), 6.08 (s, 1H), 4.41 (s, 1H), 3.67 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 2.31 (s, 3H), 1.80 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.3, 151.6, 144.0, 140.3, 137.7, 136.3, 132.7, 131.8, 131.1, 129.7, 127.1, 124.1, 120.4, 120.0, 119.4, 115.7, 60.0, 24.2, 21.5, 20.4, 16.5, 13.1. **HRMS (ESI)** m/z Calcd for $[\text{C}_{24}\text{H}_{26}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 526.0658, 528.0640; Found: 526.0661, 528.0644.

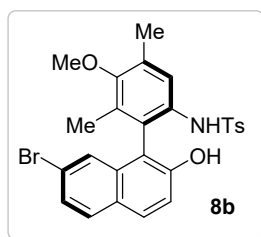
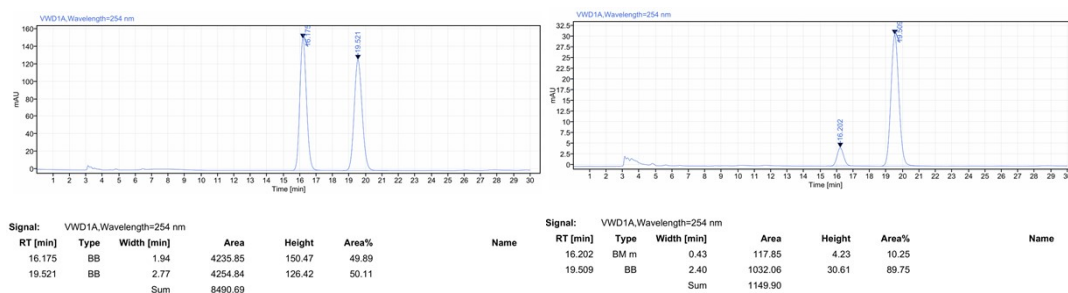
Optical Rotation: $[\alpha]_D^{25}$ -34.0 (c = 1.0, CHCl_3). 96% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, t_R = 4.978 min for minor isomer, t_R = 8.937 min for major isomer).



9b. (58% yield, Hexane-EtOAc = 5:1, R_f = 0.5) Syrup. ^1H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.79 (t, J = 9.4 Hz, 1H), 7.38 (d, J = 8.9 Hz, 1H), 7.25 (d, J = 8.9 Hz, 2H), 7.20 – 6.97 (m, 4H), 6.88 (s, 1H), 5.84 (s, 1H), 5.13 (s, 1H), 4.14– 4.02 (m, 1H), 3.95 (t, J = 6.5 Hz, 2H), 3.83 (d, J = 16.7 Hz, 1H), 3.71 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 1.71 (s, 3H), 1.52 – 1.43 (m, 2H), 1.29– 1.22 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.6, 156.1, 151.9, 135.7, 135.2, 135.2, 135.0, 133.3, 131.8, 131.7, 129.6, 129.4, 128.9, 127.9, 127.7, 127.7, 127.6, 126.1, 126.1, 124.1, 122.7, 118.3, 117.1, 64.1, 59.5,

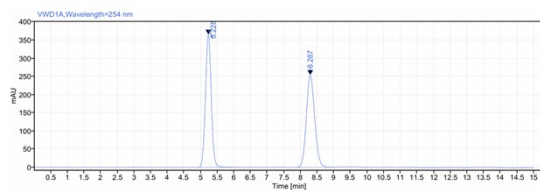
54.9, 49.6, 30.0, 18.6, 15.9, 13.6, 13.0. **HRMS (ESI)** m/z Calcd for $[C_{34}H_{36}BrNO_6S, M + Na]^+$: 688.1339, 690.1324; Found: 688.1337, 690.1324.

Optical Rotation: $[\alpha]_D^{25}$ 48 ($c = 1.0$, $CHCl_3$). 80% *ee* (HPLC conditions: Chiralpak IE column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 16.202$ min for minor isomer, $t_R = 19.509$ min for major isomer).

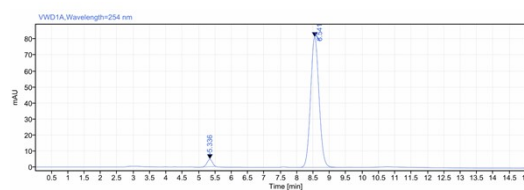


8b. (32% yield, Hexane-EtOAc = 3:1, $R_f = 0.3$). Syrup. **1H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.9$ Hz, 1H), 7.68 (d, $J = 8.7$ Hz, 1H), 7.49 (s, 1H), 7.41 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 8.9$ Hz, 1H), 7.09 (d, $J = 8.1$ Hz, 2H), 6.87 (d, $J = 1.6$ Hz, 1H), 6.07 (s, 1H), 4.98 (s, 1H), 3.72 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 1.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 151.8, 143.9, 135.8, 133.8, 133.3, 132.6, 131.7, 130.9, 130.0, 129.6, 127.6, 127.3, 127.0, 125.4, 125.4, 122.0, 122.0, 121.3, 118.1, 113.3, 60.1, 21.7, 16.6, 13.3. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{24}BrNO_4S, M + Na]^+$: 548.0502, 550.0484; Found: 548.0504, 550.0479.

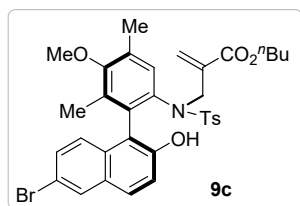
Optical Rotation: $[\alpha]_D^{25}$ -53 ($c = 1.0$, $CHCl_3$). 93% *ee* (HPLC conditions: Chiralpak IE column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 5.336$ min for minor isomer, $t_R = 8.541$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.228	BB	2.02	4445.66	365.70	50.26	
8.287	BB	1.15	4399.59	253.75	49.74	
	Sum		8845.26			

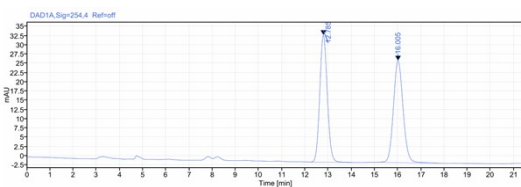


RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.336	MM m	0.18	52.63	4.65	3.44	
8.541	BB	1.33	1475.86	81.55	96.56	
	Sum		1528.49			

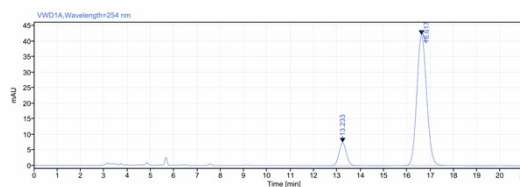


9c. (56% yield, Hexane-EtOAc = 4:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, DMSO- d_6) δ 9.67 (br, 1H), 8.08 (d, $J = 1.8$ Hz, 1H), 7.81 (d, $J = 8.9$ Hz, 1H), 7.33 (d, $J = 8.7$ Hz, 1H), 7.26 (d, $J = 8.9$ Hz, 1H), 7.24 – 6.89 (m, 5H), 6.87 (s, 1H), 5.88 (s, 1H), 5.21 (s, 1H), 4.12 (s, 1H), 3.95 (t, $J = 6.4$ Hz, 2H), 3.84 (d, $J = 16.6$ Hz, 1H), 3.70 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 1.69 (s, 3H), 1.54 – 1.42 (m, 2H), 1.31 – 1.22 (m, 2H), 0.86 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 165.5, 156.2, 152.4, 143.3, 136.0, 135.3, 134.9, 134.9, 132.0, 131.9, 130.6, 129.8, 129.3, 129.1, 128.7, 128.4, 128.0, 128.0, 127.7, 127.1, 119.3, 117.4, 115.5, 64.1, 59.6, 50.3, 30.0, 21.0, 18.6, 15.8, 13.6, 13.0. HRMS (ESI) m/z Calcd for $[\text{C}_{34}\text{H}_{36}\text{BrNO}_6\text{S}, \text{M} + \text{Na}]^+$: 688.1339, 690.1324; Found: 688.1338, 690.1321.

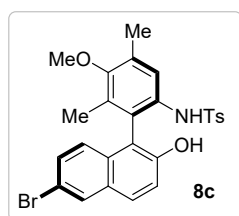
Optical Rotation: $[\alpha]^{25}_D$ 68 ($c = 1.0$, CHCl_3). 77% *ee* (HPLC conditions: Chiralpak IE column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 13.233$ min for minor isomer, $t_R = 16.617$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.785	BB	1.91	775.64	34.41	49.41	
16.005	BB	2.95	794.31	27.59	50.59	
	Sum		1569.95			



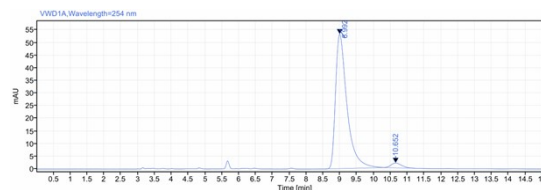
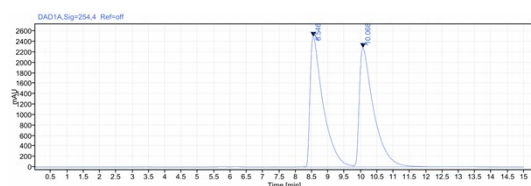
RT [min]	Type	Width [min]	Area	Height	Area%	Name
13.233	BB	1.32	161.33	7.35	11.59	
16.617	BB	2.13	1230.36	41.97	88.41	
	Sum		1391.69			



8c. (32% yield, Hexane-EtOAc = 3:1, $R_f = 0.3$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 1.8$ Hz, 1H), 7.75 (d, $J = 8.9$ Hz, 1H), 55/150

Hz, 1H), 7.54 (s, 1H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.9$ Hz, 1H), 7.13 (dd, $J = 8.9, 1.8$ Hz, 1H), 7.05 (d, $J = 8.2$ Hz, 2H), 6.52 (d, $J = 8.9$ Hz, 1H), 6.02 (s, 1H), 4.96 (s, 1H), 3.72 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 151.2, 144.0, 136.0, 133.2, 132.6, 131.7, 131.0, 130.5, 130.2, 129.9, 129.5, 127.0, 125.0, 122.4, 121.5, 118.8, 117.5, 114.2, 60.1, 21.6, 16.6, 13.2. **HRMS (ESI)** m/z Calcd for $[\text{C}_{26}\text{H}_{24}\text{BrNO}_4\text{S}, \text{M} + \text{Na}]^+$: 548.0502, 550.0484; Found: 548.0505, 550.0489.

Optical Rotation: $[\alpha]_{\text{D}}^{25} -82$ ($c = 1.0$, CHCl_3). 94% *ee* (HPLC conditions: Chiralpak IE column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_{\text{R}} = 10.652$ min for minor isomer, $t_{\text{R}} = 8.992$ min for major isomer).

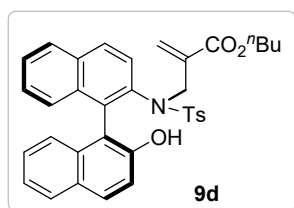


Signal: DAD1A, Sig=254.4, Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.546	VV	1.53	69515.78	2493.05	49.87	
10.068	VB	2.67	69867.29	2277.23	50.13	
Sum			139383.06			

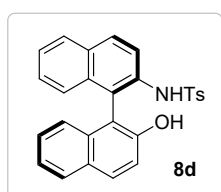
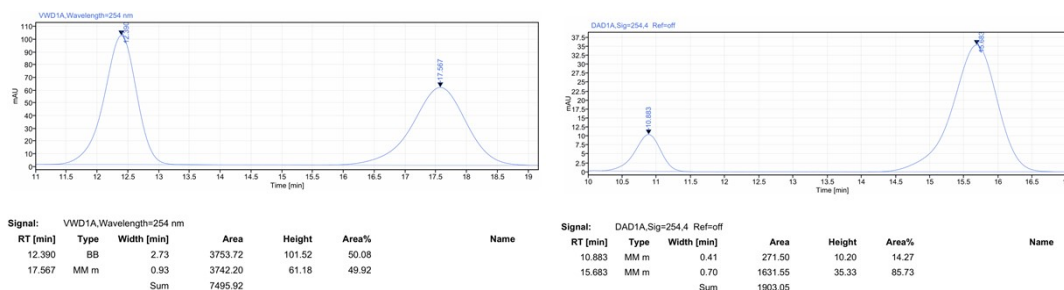
Signal: VWD1A, Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.992	BB	1.72	1251.84	53.19	96.88	
10.652	BM m	0.33	40.28	1.88	3.12	
Sum			1292.12			



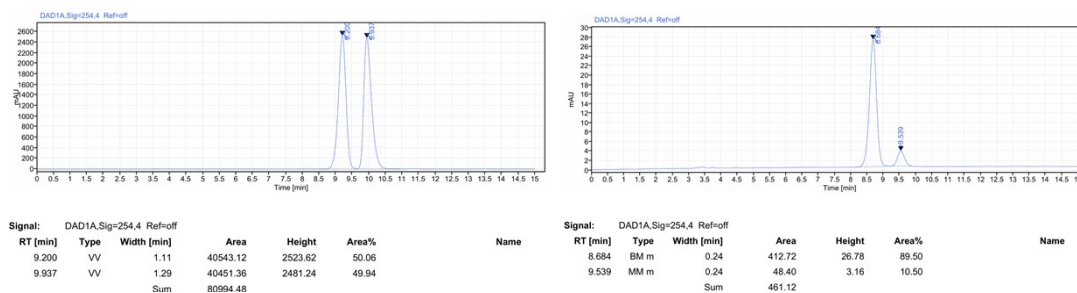
9d. (43% yield, Hexane-EtOAc = 5:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 8.02 (d, $J = 8.6$ Hz, 2H), 7.96 – 7.85 (m, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 1H), 7.34 – 7.24 (m, 3H), 7.23 – 7.05 (m, 5H), 7.04 (d, $J = 8.5$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 5.87 (s, 1H), 5.21 (s, 1H), 4.21 (d, $J = 16.6$ Hz, 1H), 3.96 (t, $J = 5.3$ Hz, 2H), 3.88 (d, $J = 16.6$ Hz, 1H), 2.30 (s, 3H), 1.51 – 1.40 (m, 2H), 1.28 – 1.19 (m, 2H), 0.83 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.4, 152.7, 143.5, 137.3, 135.9, 135.0, 134.0, 133.9, 133.5, 132.4, 129.7, 129.2, 128.6, 128.1, 127.9, 127.8, 127.7, 126.5, 126.5, 126.2, 126.0, 125.0, 122.7, 118.1, 115.5, 64.1, 49.7, 40.1, 38.9, 30.0, 20.9, 18.6, 13.6. **HRMS (ESI)** m/z Calcd for $[\text{C}_{35}\text{H}_{33}\text{NO}_5\text{S}, \text{M} + \text{Na}]^+$: 602.1972; Found: 602.1969.

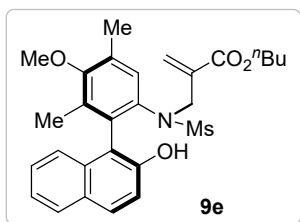
Optical Rotation: $[\alpha]^{25}_D$ 70 ($c = 1.0$, CHCl_3). 71% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 10.883$ min for minor isomer, $t_R = 15.683$ min for major isomer).



8d. (51% yield, Hexane-EtOAc = 4:1, $R_f = 0.5$). Syrup. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 9.0$ Hz, 1H), 8.04 – 7.93 (m, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 8.9$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 1H), 7.12 – 7.07 (m, 3H), 7.04 (d, $J = 8.5$ Hz, 1H), 6.64 (d, $J = 8.5$ Hz, 1H), 6.51 (s, 1H), 4.69 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.8, 144.0, 135.8, 134.5, 132.9, 132.9, 131.5, 131.1, 130.5, 129.6, 129.2, 128.4, 128.2, 127.5, 127.4, 127.1, 125.6, 125.2, 123.9, 123.7, 119.1, 118.4, 117.8, 111.9, 21.48. **HRMS (ESI)** m/z Calcd for $[\text{C}_{27}\text{H}_{21}\text{NO}_3\text{S}, \text{M}+\text{Na}]^+$: 462.1134; Found: 462.1135.

Optical Rotation: $[\alpha]^{25}_D$ -47 ($c = 1.0$, CHCl_3). 79% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.539$ min for minor isomer, $t_R = 8.684$ min for major isomer).



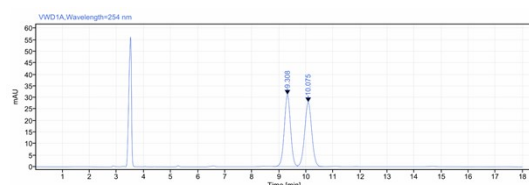


9e. (60% yield, Hexane-EtOAc = 3:1, $R_f = 0.6$). Syrup.

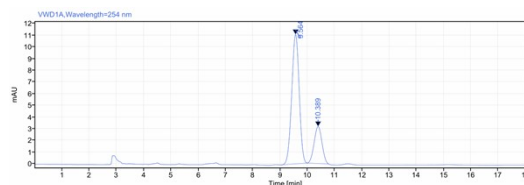
$^1\text{H NMR}$ (400 MHz, DMSO) δ 9.55 (s, 1H), 7.81 – 7.71 (m, 2H), 7.25 – 7.13 (m, 3H), 7.06 (s, 1H), 6.97 (d, $J = 13.3$ Hz, 1H), 6.03 (s, 1H), 5.56 (s, 1H), 4.18 – 3.75 (m, 4H), 3.61 (s, 3H), 2.54 – 2.29 (m, 3H), 2.25 (s, 3H), 1.61

(s, 3H), 1.49 – 1.36 (m, 2H), 1.26 – 1.17 (m, 2H), 0.80 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO- d_6) δ 165.6, 156.1, 151.9, 135.7, 135.2, 135.1, 133.3, 131.8, 131.7, 129.7, 129.4, 127.9, 127.7, 126.1, 124.2, 124.2, 122.7, 118.3, 117.1, 64.1, 59.5, 49.6, 39.9, 30.0, 18.6, 15.9, 13.6, 13.0. **HRMS (ESI)** m/z Calcd for $[\text{C}_{28}\text{H}_{33}\text{NO}_6\text{S}, \text{M} + \text{Na}]^+$: 534.1921; Found: 534.1921.

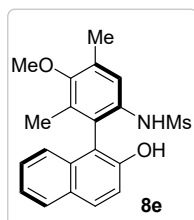
Optical Rotation: $[\alpha]^{25}_{\text{D}}$ 26.0 ($c = 1.0$, CHCl_3). 54% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 10.389$ min for minor isomer, $t_R = 9.564$ min for major isomer).



RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.308	BV	0.88	500.94	31.03	49.84	
10.075	VB	1.00	508.24	27.79	50.36	
Sum			1009.19			



RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.564	BB	0.96	211.26	11.07	76.99	
10.389	BM m	0.31	63.16	3.16	23.01	
Sum			274.42			



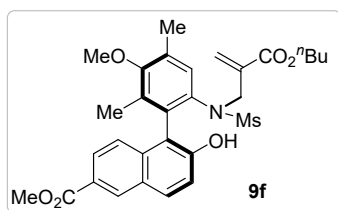
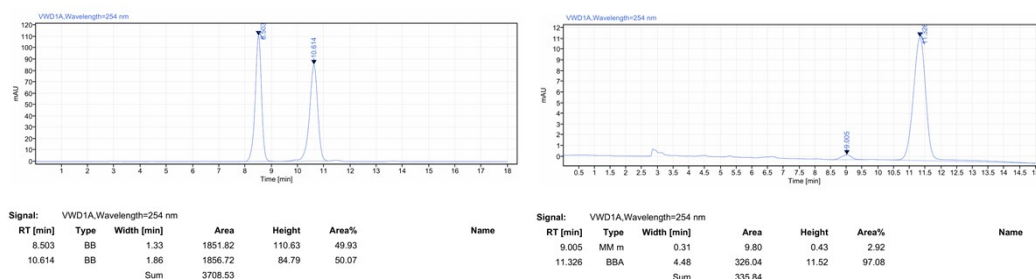
8e. (26% yield, Hexane-EtOAc = 5:1, $R_f = 0.2$). Syrup. $^1\text{H NMR}$

(400 MHz, CDCl_3) δ 7.87 – 7.83 (m, 2H), 7.48 (s, 1H), 7.40 – 7.31 (m, 2H), 7.24 (s, 1H), 7.13 – 7.04 (m, 1H), 5.77 (s, 1H), 5.22 (s, 1H), 3.75 (s, 3H), 2.69 (s, 3H), 2.40 (s, 3H), 1.86 (s, 3H). $^{13}\text{C NMR}$ (100

MHz, CDCl_3) δ 155.0, 151.0, 133.23, 133.0, 132.4, 132.0, 131.1, 129.4, 128.7, 127.6, 124.2, 123.6, 123.1, 121.5, 117.7, 114.1, 60.1, 39.6, 16.5, 13.3.

HRMS (ESI) m/z Calcd for $[\text{C}_{20}\text{H}_{21}\text{NO}_4\text{S}, \text{M} + \text{Na}]^+$: 394.1083; Found: 394.1086.

Optical Rotation: $[\alpha]_D^{25}$ -30.0 ($c = 1.0$, CHCl_3). 94% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.005$ min for minor isomer, $t_R = 11.326$ min for major isomer).

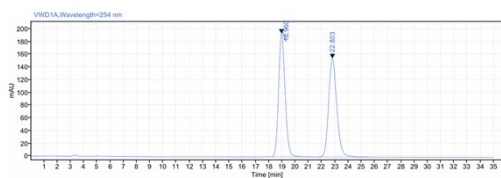


9f. (60% yield, Hexane-EtOAc = 5:1, $R_f = 0.4$) Syrup.

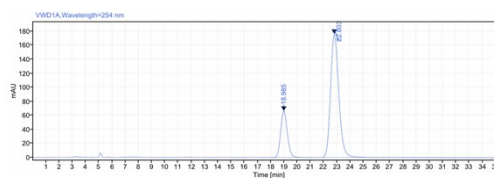
^1H NMR (400 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.55 (d, $J = 1.4$ Hz, 1H), 8.07 (d, $J = 8.9$ Hz, 1H), 7.70 (dd, $J = 8.9, 1.6$ Hz, 1H), 7.37 (d, $J = 8.9$ Hz, 1H), 7.15 (s, 1H),

7.09 (d, $J = 7.0$ Hz, 1H), 6.02 (s, 1H), 5.57 (s, 1H), 4.14 – 3.98 (m, 4H), 3.87 (s, 3H), 3.70 (s, 3H), 2.50 (s, 3H), 2.32 (s, 3H), 1.68 (s, 3H), 1.51 – 1.40 (m, 2H), 1.29 – 1.23 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.5, 165.5, 156.1, 154.4, 135.8, 135.5, 135.3, 134.5, 131.7, 131.5, 131.2, 130.8, 130.1, 127.9, 127.8, 126.8, 125.0, 123.7, 119.3, 117.4, 64.1, 59.6, 52.0, 49.8, 39.7, 30.0, 18.6, 15.9, 13.5, 13.0. **HRMS (ESI)** m/z Calcd for $[\text{C}_{30}\text{H}_{35}\text{NO}_8\text{S}, \text{M} + \text{Na}]^+$: 592.1976; Found: 592.1978.

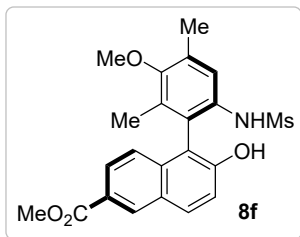
Optical Rotation: $[\alpha]_D^{25}$ 10.3 ($c = 1.0$, CHCl_3). 53% *ee* (HPLC conditions: Chiralpak IE column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 18.985$ min for minor isomer, $t_R = 22.803$ min for major isomer).



Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
18.960	BB	3.11	6601.10	193.16	49.89
22.803	BB	5.23	6630.70	154.34	50.11
Sum			13231.81		

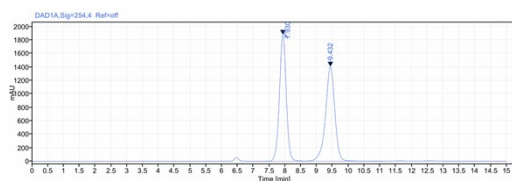


Signal: VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%
18.985	BB	2.95	2312.45	66.28	23.27
22.803	BB	5.15	7625.97	176.17	76.73
Sum			9938.42		

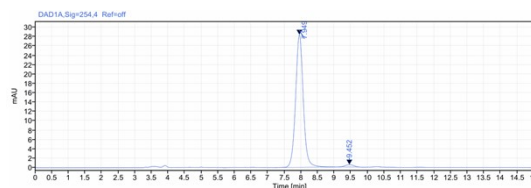


8f. (33% yield, Hexane-EtOAc = 2:1, $R_f = 0.4$) Syrup. ^1H NMR (400 MHz, CDCl_3) δ 8.61 (d, $J = 1.5$ Hz, 1H), 8.00 (d, $J = 8.8$ Hz, 1H), 7.94 (dd, $J = 8.8, 1.5$ Hz, 1H), 7.49 (s, 1H), 7.35 (d, $J = 8.8$ Hz, 1H), 7.14 (d, $J = 8.8$ Hz, 1H), 5.75 (s, 1H), 5.53 (brs, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 2.74 (s, 3H), 2.42 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 155.1, 153.2, 135.0, 133.7, 133.0, 132.6, 132.0, 131.8, 128.4, 127.1, 125.8, 123.4, 122.8, 121.5, 118.8, 114.4, 60.2, 52.3, 39.8, 16.6, 13.3. HRMS (ESI) m/z Calcd for $[\text{C}_{22}\text{H}_{23}\text{NO}_6\text{S}, \text{M} + \text{Na}]^+$: 452.1138; Found: 452.1139.

Optical Rotation: $[\alpha]_D^{25}$ -36.0 ($c = 1.0$, CHCl_3). 97% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 9.452$ min for minor isomer, $t_R = 7.949$ min for major isomer).



Signal: DAD1A,Sig=254.4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%
7.930	BV	1.32	28396.09	1879.94	49.67
9.432	VB	2.45	28772.42	1405.30	50.33
Sum			57168.51		



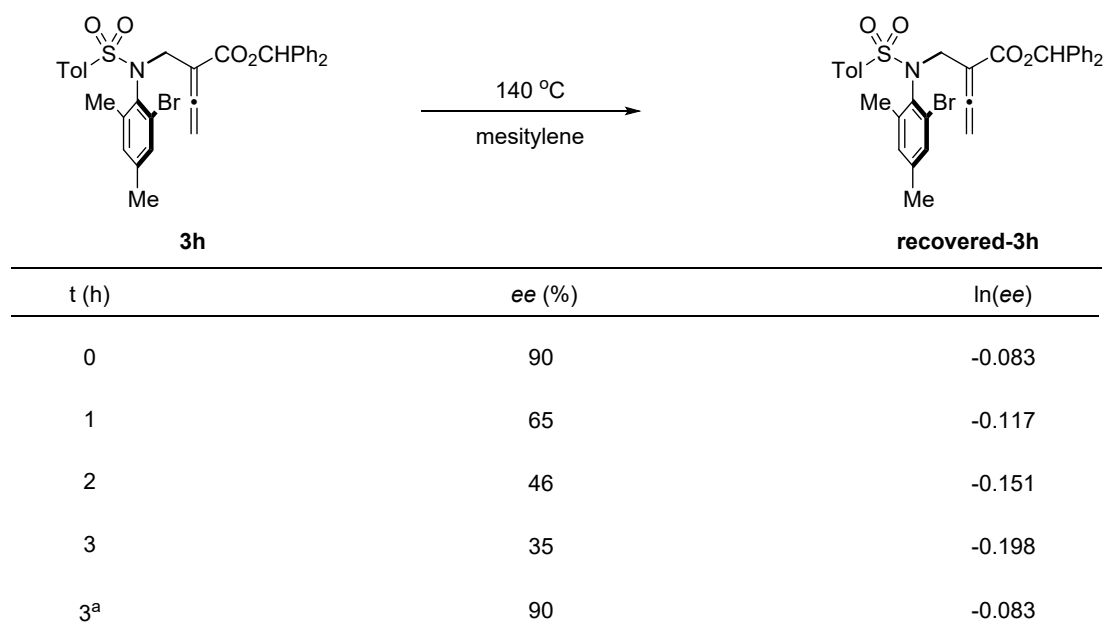
Signal: DAD1A,Sig=254.4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%
7.949	BB	1.80	457.04	28.34	98.25
9.452	MM m	0.24	8.12	0.47	1.75
Sum			465.16		

IV. Racemization experiment

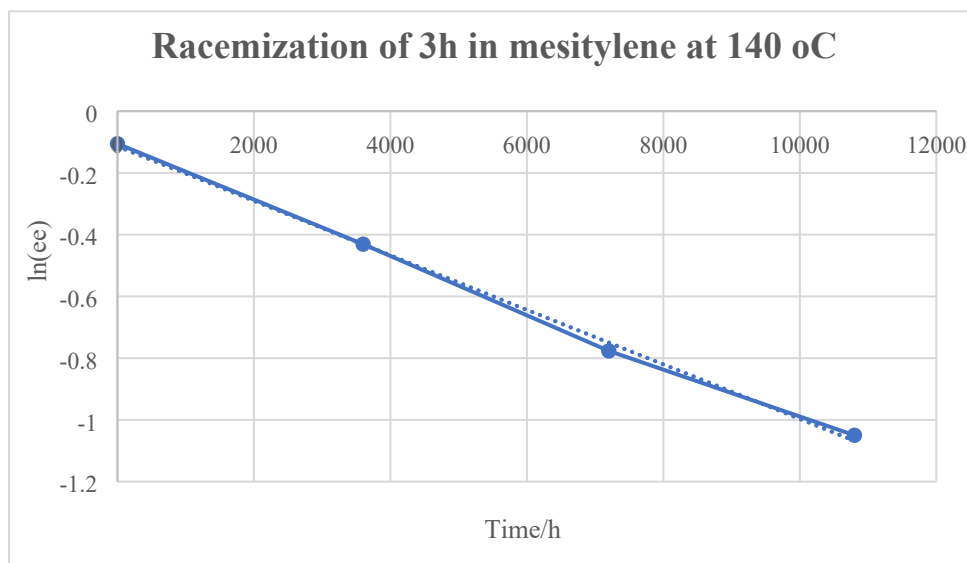
$$\Delta G^\ddagger = RT \ln \left(\frac{K_B \cdot T}{h K_{\text{enantiomerization}}} \right) K_{\text{enantiomerization}} = \frac{1}{2} K_{\text{rac}}$$

K_B is the Boltzmann, $K_B = 1.38066E - 23$ J·K⁻¹. T is temperature. h is the Planck constant. $h = 6.62608E-34$ Js. R is the specific gas constant, $R = 8.31451$ J·K⁻¹·mol⁻¹

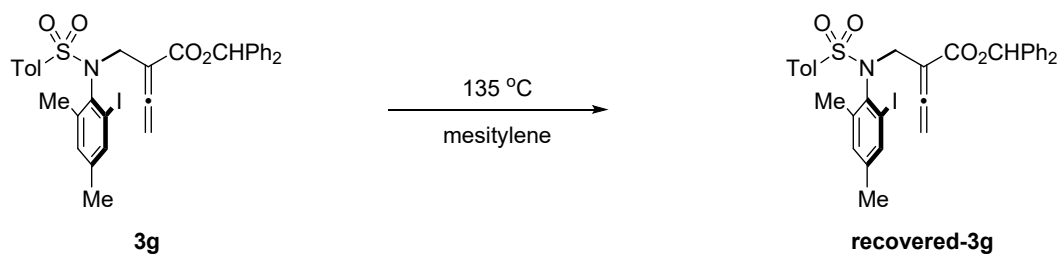
Compound (0.1 mmol) was dissolved in mesitylene (1 mL) in a Schlenk tube. The tube was immersed in a pre-heated oil bath at 100-140 °C. At given interval of time, small samples (50 μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess.



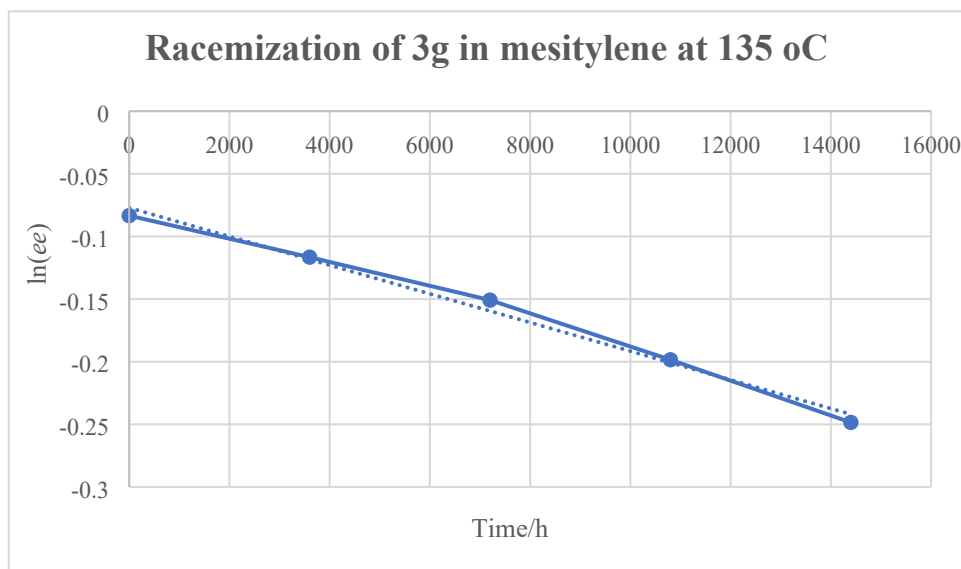
^aT = 110 °C



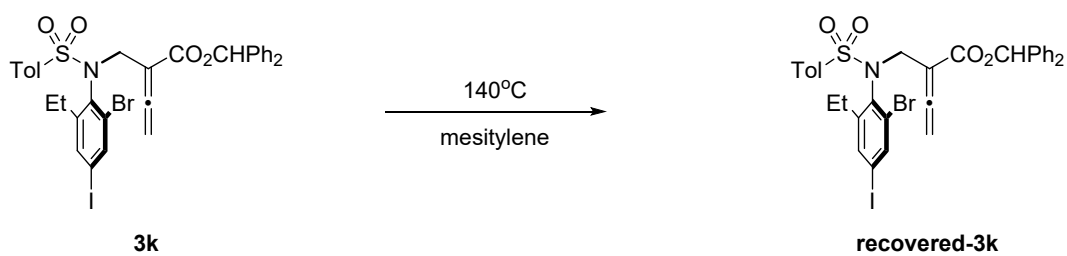
$$K_{\text{rac}} = 9\text{E-}5, K_{\text{enantiomerization}} = 4.5\text{E-}5, \Delta G^\ddagger = 32.65 \text{ Kcal/mol}$$



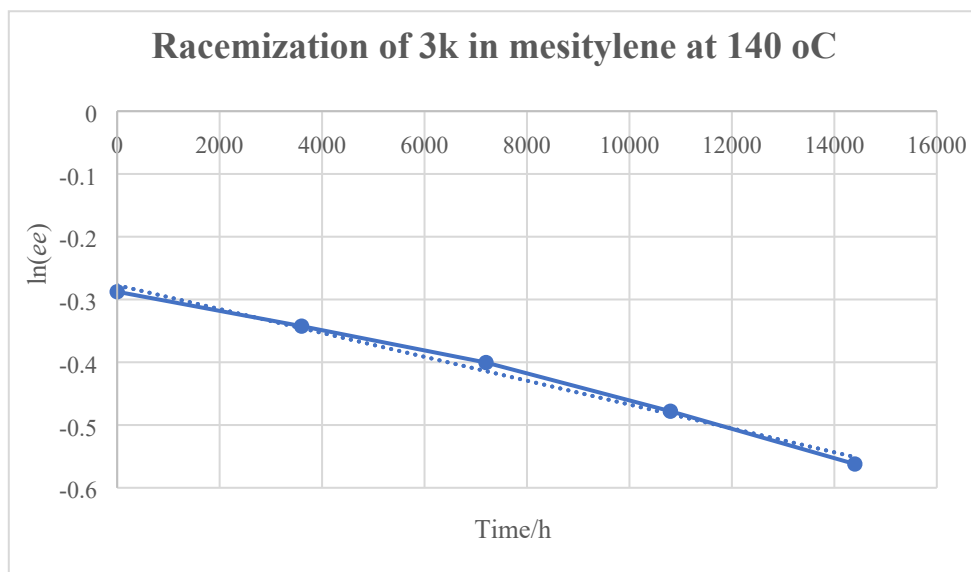
t (h)	ee (%)	ln(ee)
0	92	-0.083
1	89	-0.117
2	86	-0.151
3	82	-0.198



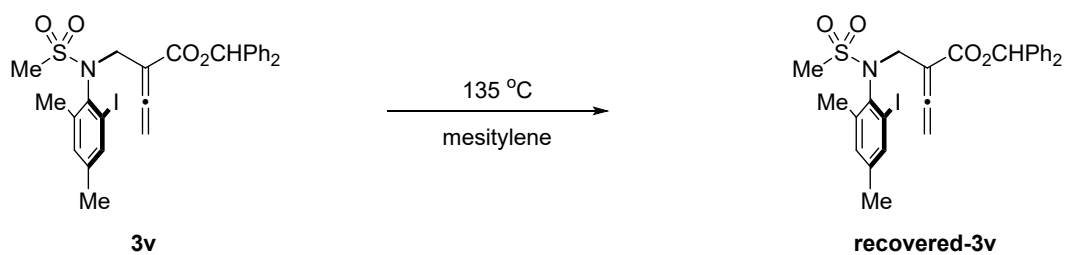
$$K_{\text{rac}} = 1\text{E-}5, K_{\text{enantiomerization}} = 5\text{E-}6, \Delta G^\ddagger = 34.02 \text{ Kcal/mol}$$



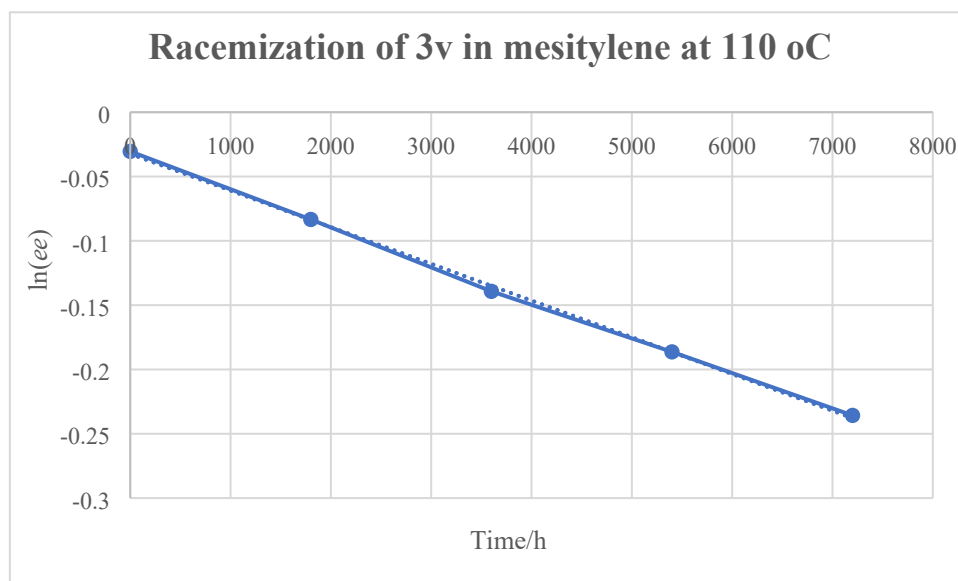
t (h)	ee (%)	ln(ee)
0	75	-0.288
1	71	-0.342
2	67	-0.400
3	62	-0.478
4	66	-0.562



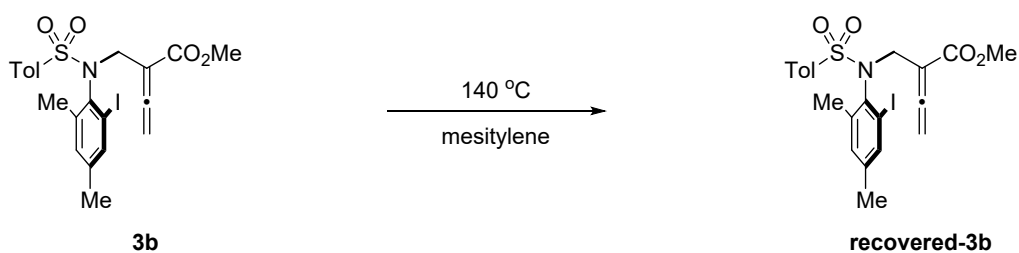
$$K_{\text{rac}} = 2\text{E-}5, K_{\text{enantiomerization}} = 1\text{E-}5, \Delta G^\ddagger = 33.88 \text{ Kcal/mol}$$



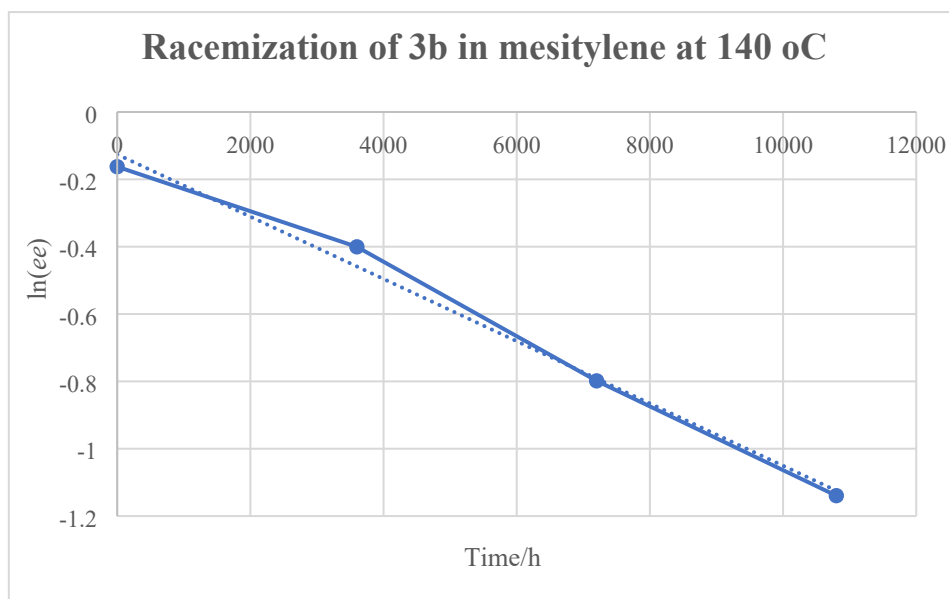
t (h)	ee (%)	ln(ee)
0	97	-0.030
0.5	92	-0.083
1	87	-0.139
1.5	83	-0.186
2	79	-0.236



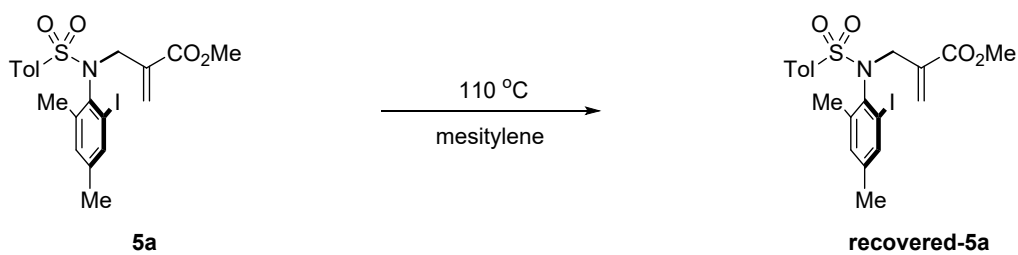
$$K_{\text{rac}} = 3\text{E-}5, K_{\text{enantiomerization}} = 1.5\text{E-}5, \Delta G^\ddagger = 33.13 \text{ Kcal/mol}$$



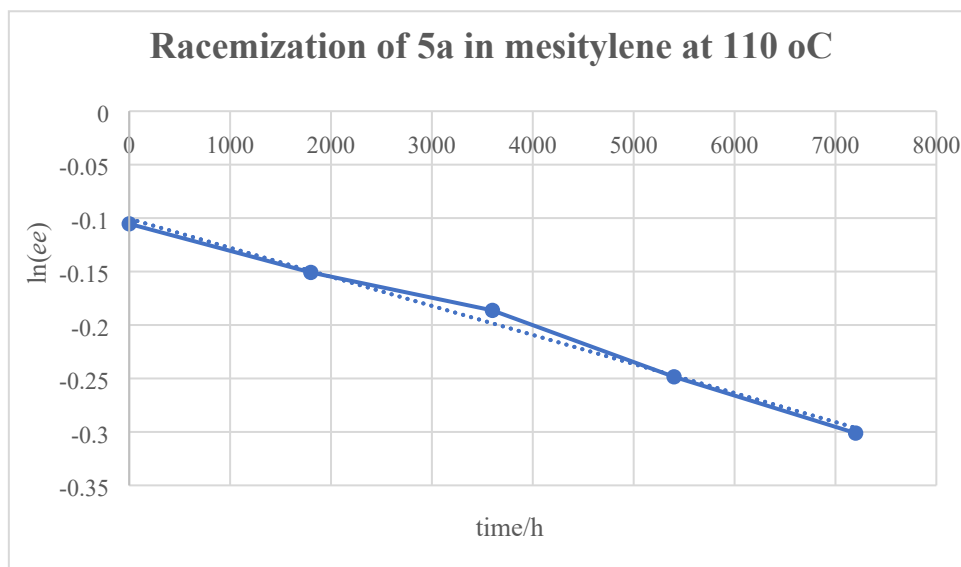
t (h)	ee (%)	ln(ee)
0	85	-0.163
1	68	-0.400
2	45	-0.799
3	32	-1.139



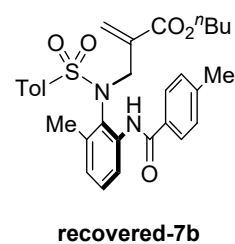
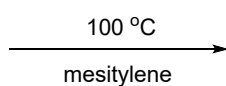
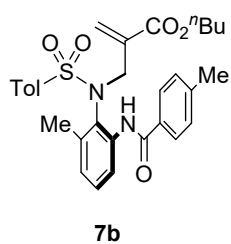
$$K_{\text{rac}} = 9\text{E-}5, K_{\text{enantiomerization}} = 4.5\text{E-}5, \Delta G^\ddagger = 32.65 \text{ Kcal/mol}$$



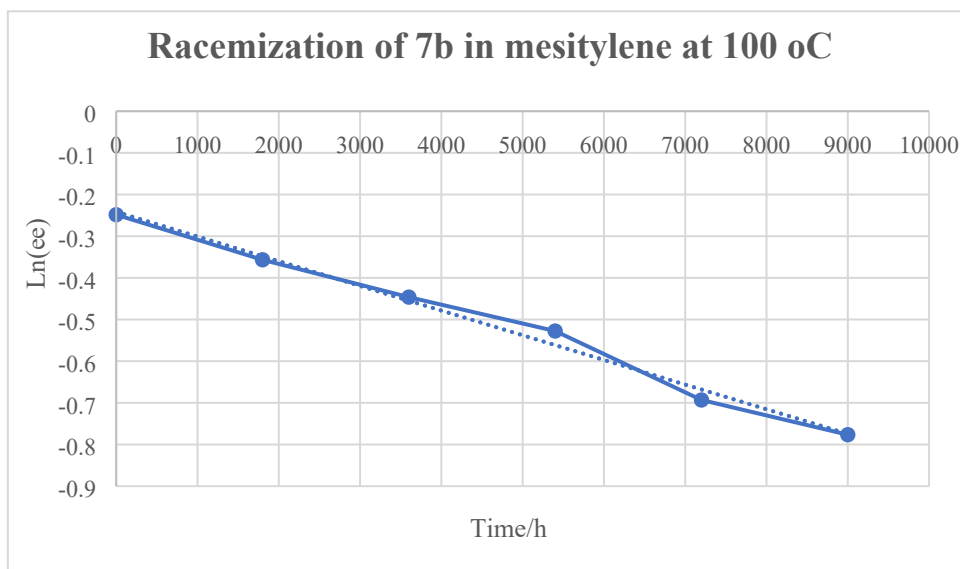
t (h)	ee (%)	ln(ee)
0	90	-0.105
0.5	86	-0.151
1	83	-0.186
1.5	78	-0.248
2	74	-0.301



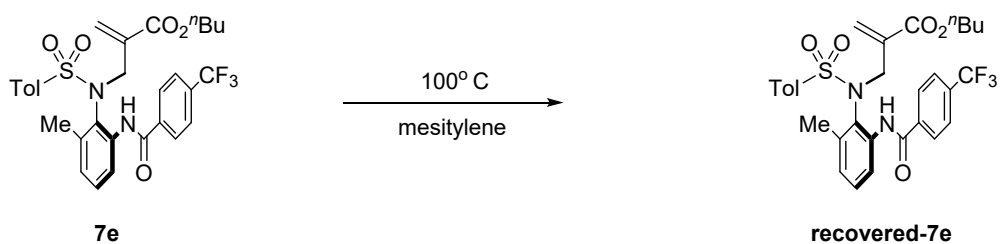
$$K_{\text{rac}} = 3\text{E-}5, K_{\text{enantiomerization}} = 1.5\text{E-}5, \Delta G^\ddagger = 31.05 \text{ Kcal/mol}$$



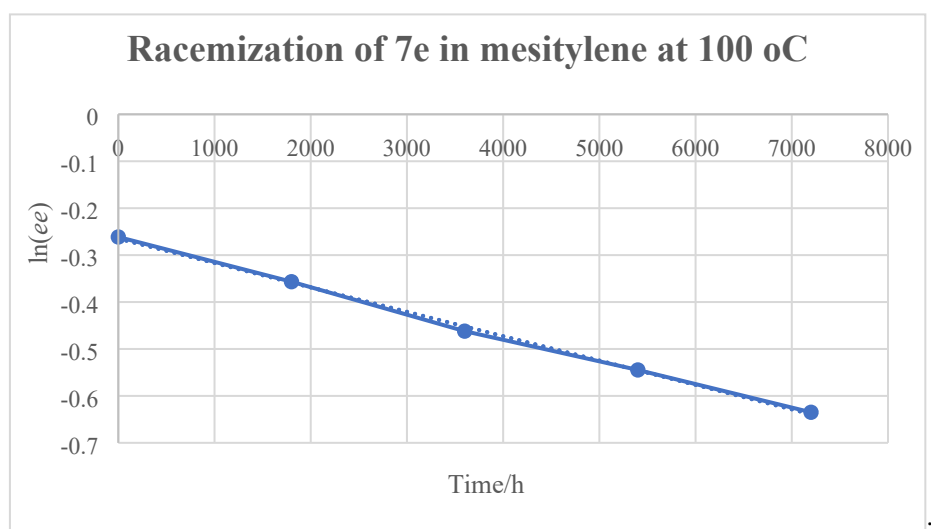
t (h)	ee (%)	ln(ee)
0	78	-0.248
0.5	70	-0.357
1	64	-0.446
1.5	59	-0.528
2	50	-0.693
2.5	46	-0.777



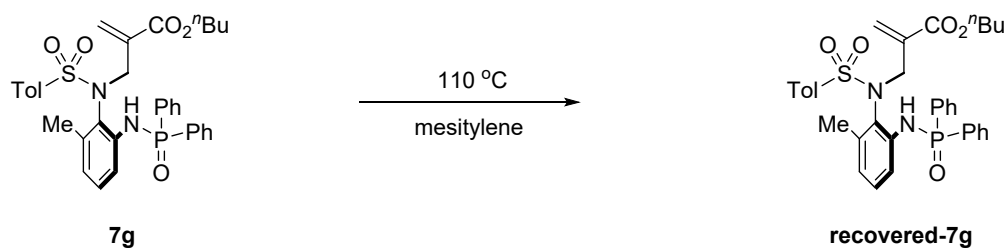
$$K_{\text{rac}} = 6\text{E-}5, K_{\text{enantiomerization}} = 3\text{E-}5, \Delta G^\ddagger = 29.83 \text{ Kcal/mol}$$



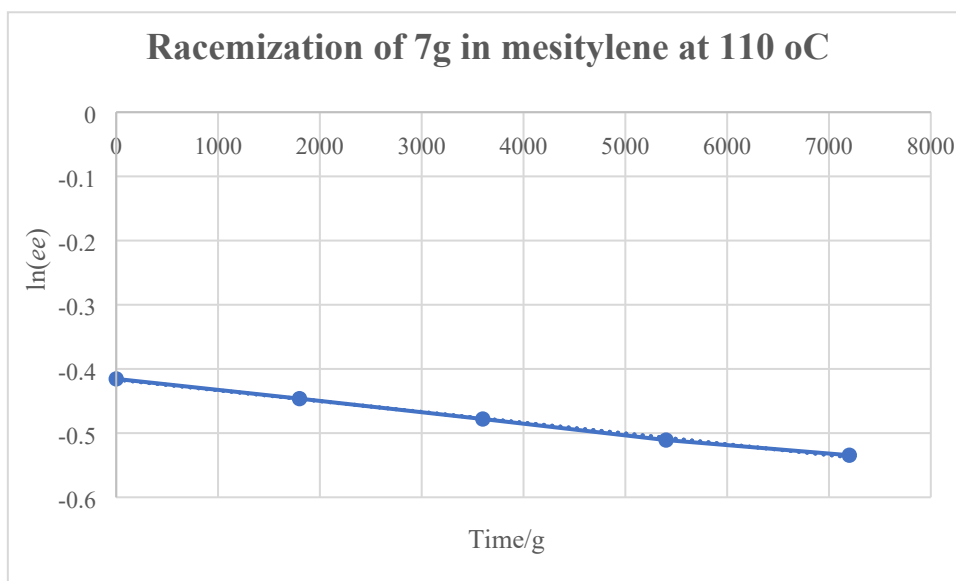
t (h)	ee (%)	ln(ee)
0	77	-0.261
0.5	70	-0.357
1	63	-0.462
1.5	58	-0.545
2	53	-0.635



$$K_{\text{rac}} = 5\text{E-}5, K_{\text{enantiomerization}} = 2.5\text{E-}5, \Delta G^\ddagger = 29.85 \text{ Kcal/mol}$$

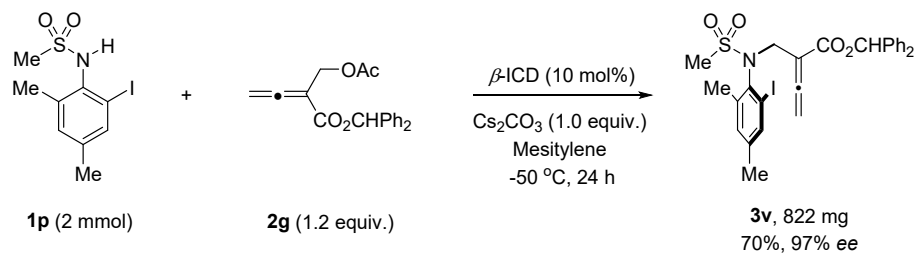


t (h)	ee (%)	ln(ee)
0	66	-0.416
0.5	64	-0.446
1	62	-0.478
1.5	60	-0.511
2	57	-0.534

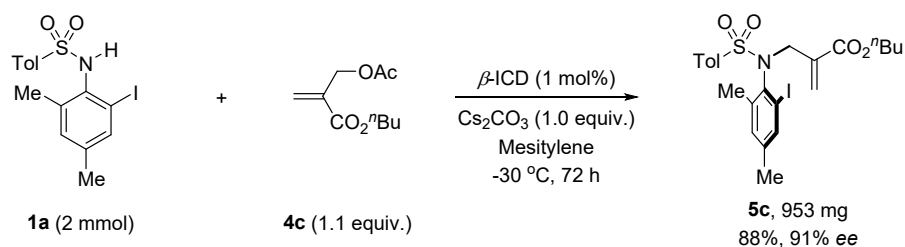


$$K_{\text{rac}} = 2\text{E-}5, K_{\text{enantiomerization}} = 1\text{E-}5, \Delta G^\ddagger = 31.36 \text{ Kcal/mol}$$

V. Gram scale reaction

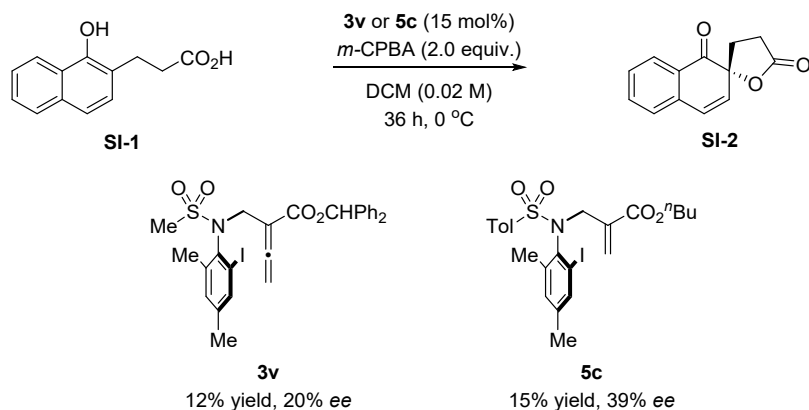


To a three-necked flask containing **1p** (650.3 mg, 2 mmol), β -ICD (60 mg, 0.2 mmol, 10 mol%) and Cs_2CO_3 (651.6 mg, 2 mmol, 1.0 equiv.) were added mesitylene (120 mL) and dienoate **2g** (773.7 mg, 2.4 mmol, 1.2 equiv.). The reaction mixture was stirred at -50 °C for 24 hours. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography (Hexane-EtOAc = 5:1) to afford the product **3v** (822 mg) in 70% yield with 97% *ee*.

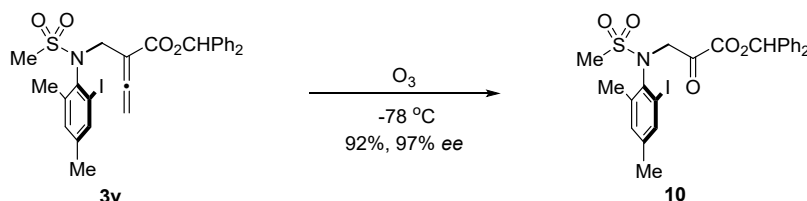
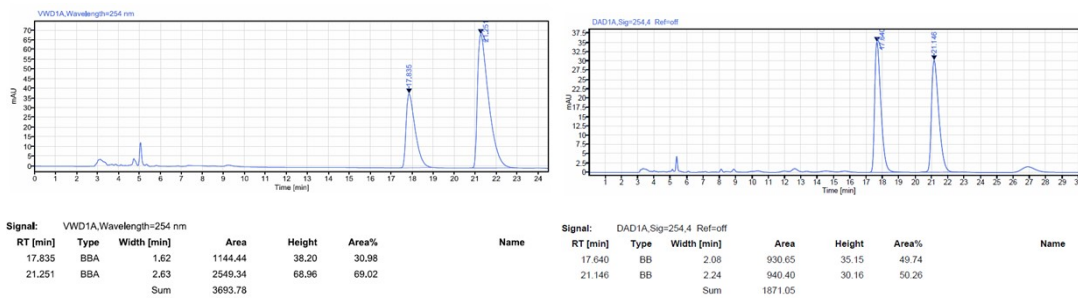


To a three-necked flask containing **1a** (802.5 mg, 2 mmol), β -ICD (6 mg, 0.02 mmol, 1 mol%) and Cs_2CO_3 (651.6 mg, 2 mmol, 1.0 equiv.) were added mesitylene (20 mL) and MBH acetate **4c** (440.5 mg, 2.2 mmol, 1.1 equiv.). The reaction mixture was stirred at -30 °C for 72 hours. The solvent was removed by silica gel column chromatography and the residue was then purified by silica gel column chromatography (Hexane-EtOAc = 15:1) to afford the product **5c** (953 mg) in 88% yield with 91% *ee*.

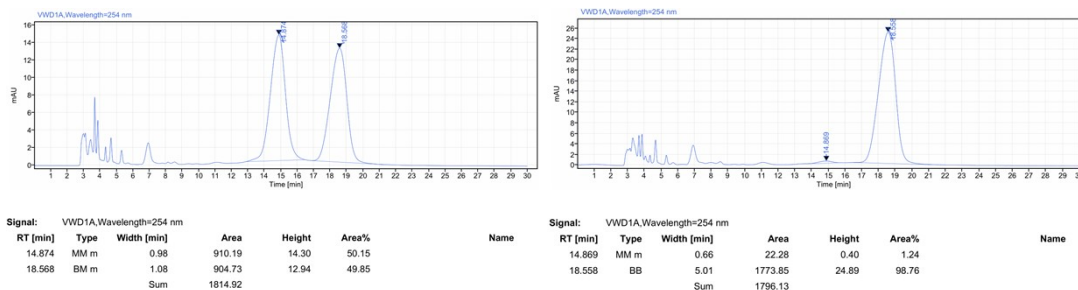
VI. Further transformation

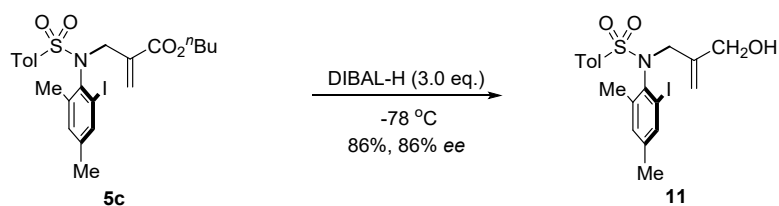


A solution of **3w** or **5c** (26.6 mg, 0.123 mmol, 15 mol%) and *m*-CPBA (85%, 37.3 mg, 0.218 mmol, 1.5 equiv.) in CH₂Cl₂ was stirred at 0 °C for 5 min, then 3-(1-hydroxy-2-naphthyl)propionic acid **SI-1** was added. After 36 h, the resulting mixture poured into aqueous Na₂S₂O₃ (5 mL) and aqueous NaHCO₃, and extracted with CH₂Cl₂. The organic layers were dried over anhydrous Na₂SO₄ and solvents were removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: Hexane-EtOAc-CH₂Cl₂ = 8:1:1) to give **SI-2**. ¹H NMR (CDCl₃, 400 MHz) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.5, 1.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 9.9 Hz, 1H), 6.20 (d, *J* = 9.9 Hz, 1H), 2.90 (ddd, *J* = 9.7, 11.2, 17.6 Hz, 1H), 2.59 (ddd, *J* = 2.0, 9.6, 17.6 Hz, 1H), 2.41 (ddd, *J* = 2.0, 9.6, 13.2 Hz, 1H), 2.18 (ddd, *J* = 9.8, 11.2, 13.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 196.5, 176.5, 136.8, 135.7, 132.3, 128.9, 127.9, 127.9, 127.7, 127.3, 83.4, 31.2, 26.5; **MS** (EI) *m/z* 214.06 (M⁺); HPLC condition: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wavelength = 254 nm, *t*_R = 17.6 min for minor isomer, *t*_R = 21.1 min for major isomer).



Through a solution containing **3v** (108 mg, 0.2 mmol) in 2 mL of CH_2Cl_2 was bubbled an ozone-oxygen stream at $-78\text{ }^\circ\text{C}$ until the starting material was consumed. The resulting mixture poured into aqueous $\text{Na}_2\text{O}_3\text{S}_2$ (5 mL) and extracted with CH_2Cl_2 . The organic layer is dried on anhydrous Na_2SO_4 and the solvent is removed in vacuum to obtain the product **10**. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.43 – 7.31 (m, 10H), 7.06 (s, 1H), 6.96 (s, 1H), 5.05 (d, $J = 19.5$ Hz, 1H), 4.91 (d, $J = 19.5$ Hz, 1H), 3.36 (s, 3H), 2.53 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 188.0, 159.1, 141.6, 141.0, 139.4, 139.3, 138.8, 133.1, 129.0, 128.8, 128.8, 127.6, 127.4, 101.2, 79.9, 58.9, 44.0, 20.6. HRMS (ESI) m/z Calcd for $[\text{C}_{25}\text{H}_{24}\text{INO}_5\text{S}, \text{M} + \text{Na}]^+$: 600.0310; Found: 600.0311. $[\alpha]_D^{25}$ -13.3 ($c = 1.0$, CHCl_3). 97% *ee*. HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 14.869$ min for minor isomer, $t_R = 18.558$ min for major isomer).



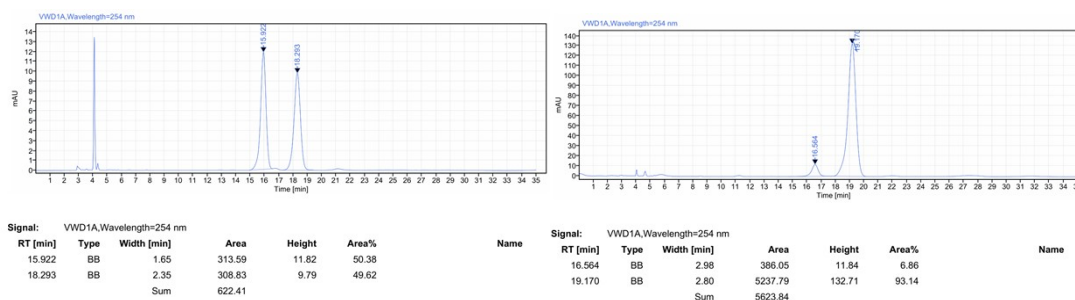


A solution of **5c** (108 mg, 0.2 mmol) and DIBAL-H (0.4 mL, 0.6 mmol, 3 equiv.) in CH_2Cl_2 (0.6 mL) was stirred at $-78\text{ }^\circ\text{C}$ for 8 h. the resulting mixture poured into aqueous NH_4Cl (5 mL) and extracted with CH_2Cl_2 . The organic layers were dried over anhydrous Na_2SO_4 and solvents were removed in vacuo. The residue was purified by column chromatography on silica gel (Hexane-EtOAc = 4:1) to give **11**.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.2$ Hz, 2H), 7.51 (s, 1H), 7.28 (d, $J = 8.1$ Hz, 2H), 7.01 (s, 1H), 5.06 (s, 1H), 4.67 (s, 1H), 4.43 (d, $J = 14.0$ Hz, 1H), 4.29 (dd, $J = 14.6, 2.7$ Hz, 2H), 4.16 (d, $J = 14.6$ Hz, 1H), 2.50 (s, 1H), 2.42 (s, 3H), 2.23 (s, 6H).

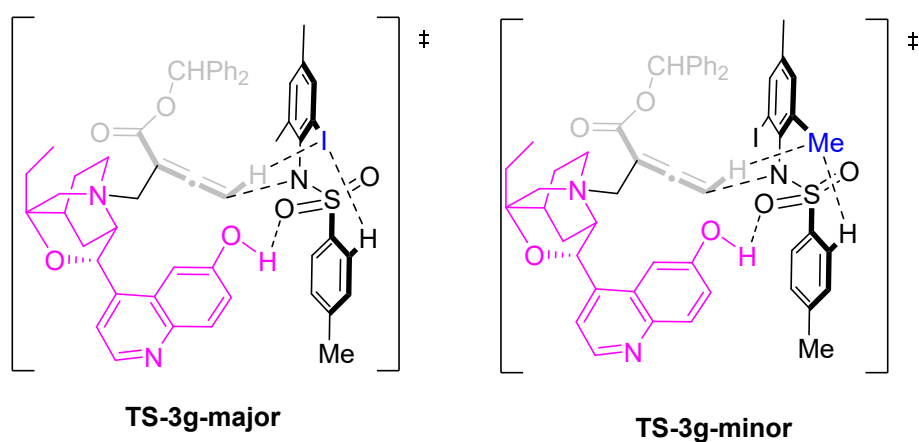
^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 143.4, 142.2, 140.0, 139.3, 138.1, 136.9, 132.5, 129.6, 128.2, 117.6, 100.1, 64.3, 52.4, 21.5, 20.4, 20.3. HRMS (ESI) m/z Calcd for $[\text{C}_{19}\text{H}_{22}\text{INO}_3\text{S}, \text{M} + \text{Na}]^+$: 494.0257; Found: 494.0258. $[\alpha]_D^{25}$ -22.5 ($c = 1.0, \text{CHCl}_3$).

86% ee. HPLC conditions: Chiralpak AD-H column, n -Hexane/ i -PrOH = 90:10, flow rate = 1.0 mL/min, wavelength = 254 nm, $t_R = 16.564$ min for minor isomer, $t_R = 19.170$ min for major isomer).



VII. Geometries of the enantiomeric transition states

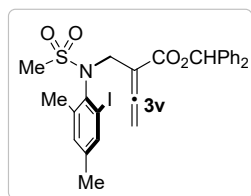
The atroposelective model are depicted as follows: the deprotonated **1g** binds to catalyst β -ICD by hydrogen-bonding interaction between the S=O oxygen of **1g** and the OH of β -ICD; subsequently, the product **3g** was readily afforded by nucleophilic attack under the chiral environment; the orientation of the electronic abundant iodine atom in the favored TS-3g-major shows more favorable noncovalent interactions with hydrogens; hence placing the *ortho*-iodine inside gives rise to the favored transition state TS-3g-major, while placing the *ortho*-methyl inside results in the less favored TS-3g-minor.



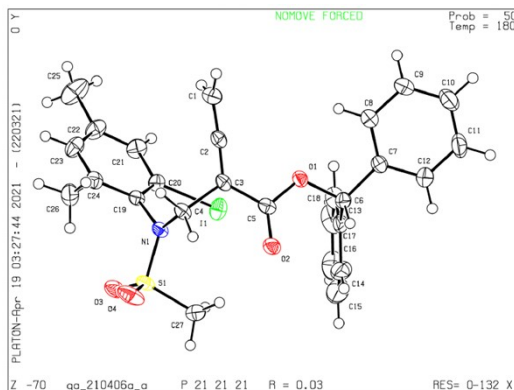
VIII. References

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IX. X-Ray crystallography analysis of compound 3v (CCDC-2078431)



≡



Datablock: ga_210406a_a

Bond precision:	C-C = 0.0065 Å		Wavelength=1.34138
Cell:	a=9.5319(7)	b=15.1834(11)	c=18.2181(14)
	alpha=90	beta=90	gamma=90
Temperature:	180 K		
Volume	Calculated	Reported	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C27 H26 I N O4 S	?	
Sum formula	C27 H26 I N O4 S	C27 H26 I N O4 S	
Mr	587.45	587.45	
Dx, g cm ⁻³	1.480	1.480	
Z	4	4	
Mu (mm ⁻¹)	7.205	7.205	
F000	1184.0	1184.0	
F000'	1187.51		
h, k, lmax	11, 19, 22	11, 19, 22	
Nref	5475 [3091]	5459	
Tmin, Tmax	0.374, 0.487	0.430, 0.752	
Tmin'	0.178		
Correction method-	# Reported T Limits: Tmin=0.430 Tmax=0.752		
AbsCorr	= MULTI-SCAN		
Data completeness-	1.77/1.00	Theta(max)= 57.467	
R(reflections)-	0.0295 (5355)	wR2(reflections)- 0.0723 (5459)	
S	1.055	Npar= 318	

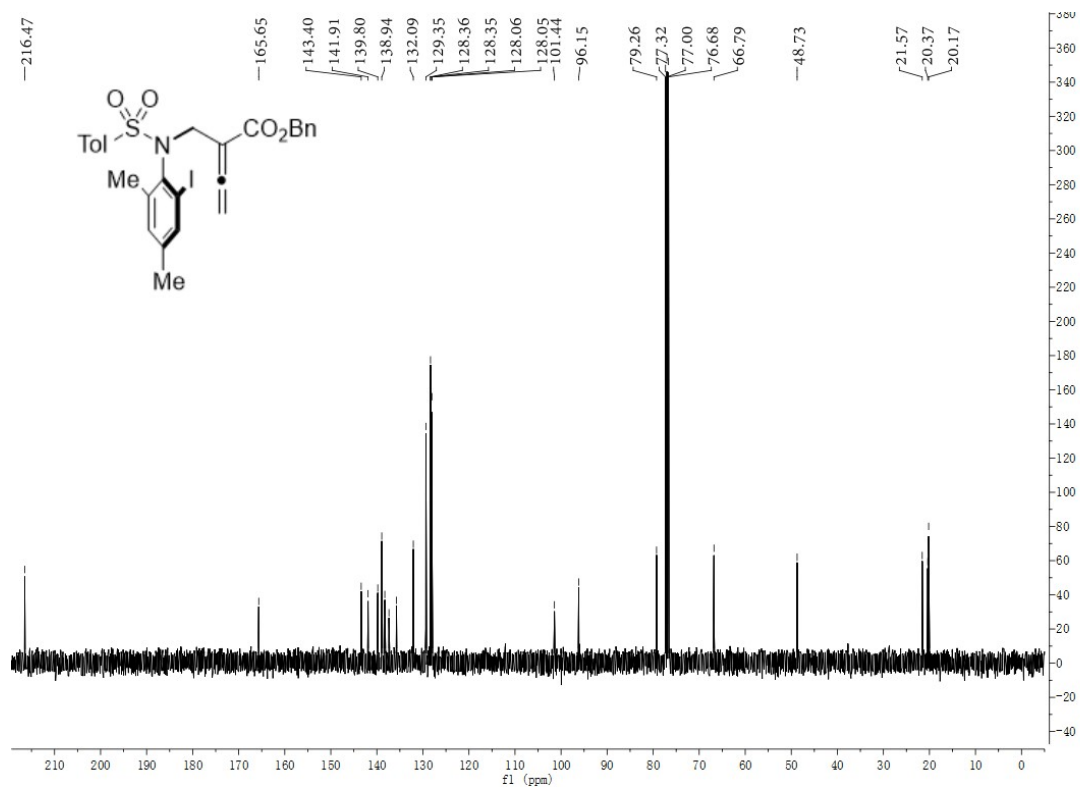
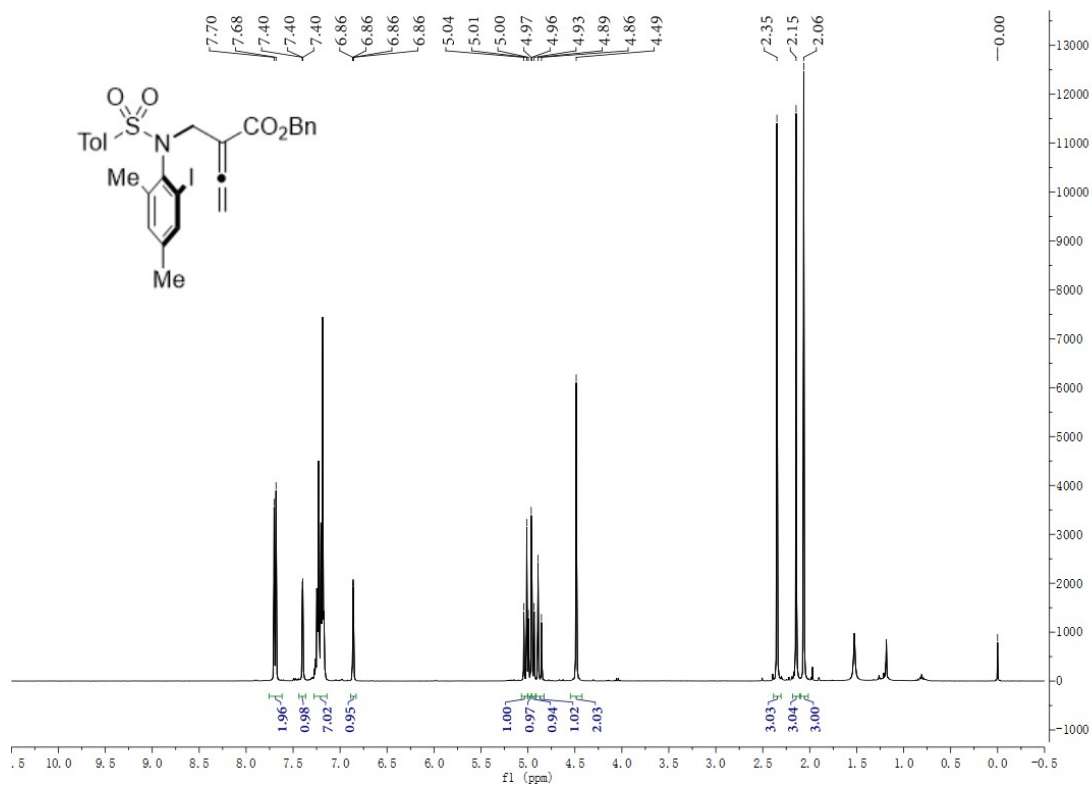
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test-name ALERT alert-type alert-level.
 Click on the hyperlinks for more details of the test.

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PLAT025 ALERT 2 C	U(isc) H1B Smaller than U(sq) C1 by	0.016	Ang**2
PLAT011 ALERT 1 C	Missing PCP Refl Between Thmin & Sth/Lc	0.600	2 Report
PLAT007 ALERT 1 C	The Flack x is >> 0 - Do a BASF/TWIN Refinement		Please Check
Alert level C			
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PLAT104 ALERT 4 C	Nr. of Refined C-H H-Atoms in Heavy-Atom Struct.		2 Note
PLAT172 ALERT 4 C	The CIF-Embedded .res File Contains DFIX Records		1 Report
PLAT012 ALERT 2 C	Short Inter X...Y Contact O4 ..C5 -1/2+x,3/2-y,1-z =	2.94	Ang- 4.466 Check
PLAT060 ALERT 3 C	Number of Least-Squares Restraints		2 Note
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<p>0 ALERT level A - Most likely a serious problem - resolve or explain 0 ALERT level B - A potentially serious problem, consider carefully 4 ALERT level C - Check. Ensure it is not caused by an omission or oversight 11 ALERT level G - General information/check it is not something unexpected</p> <p>3 ALKHT type 1 CIF construction/syntax error, inconsistent or missing data 6 ALKHT type 2 Indicator that the structure model may be wrong or deficient 3 ALKHT type 3 Indicator that the structure quality may be low 3 ALKHT type 4 Improvement, methodology, query or suggestion 0 ALKHT type 5 Informative message, check</p>			

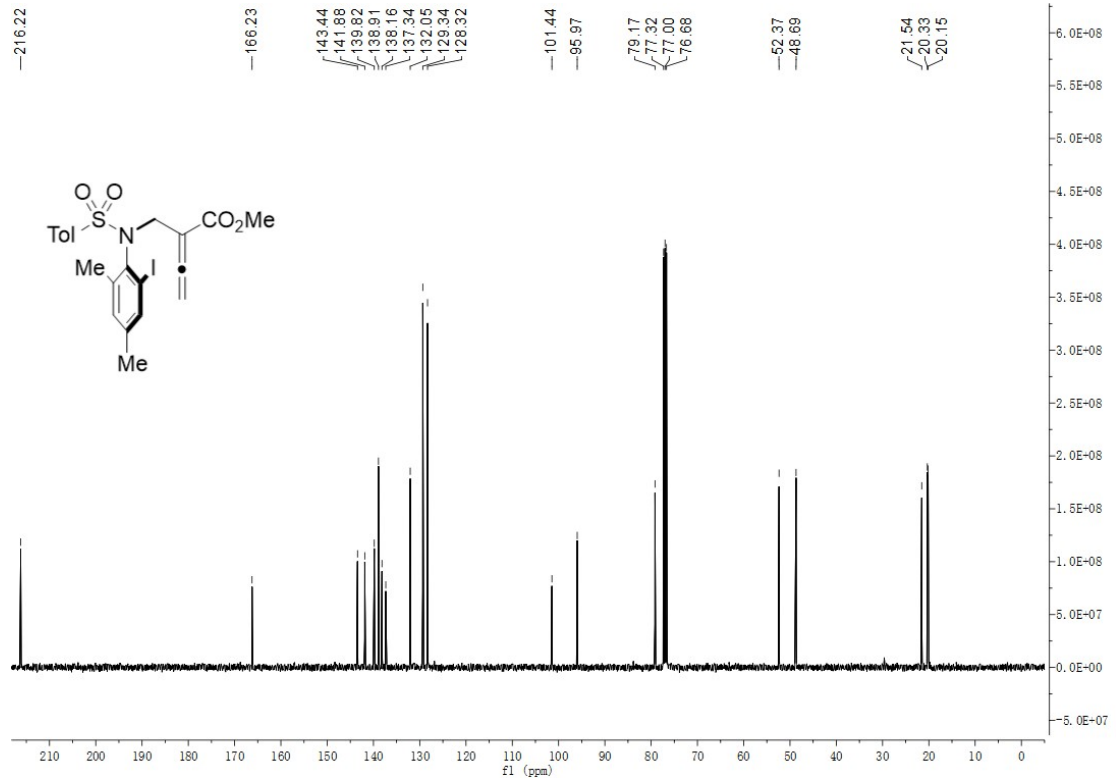
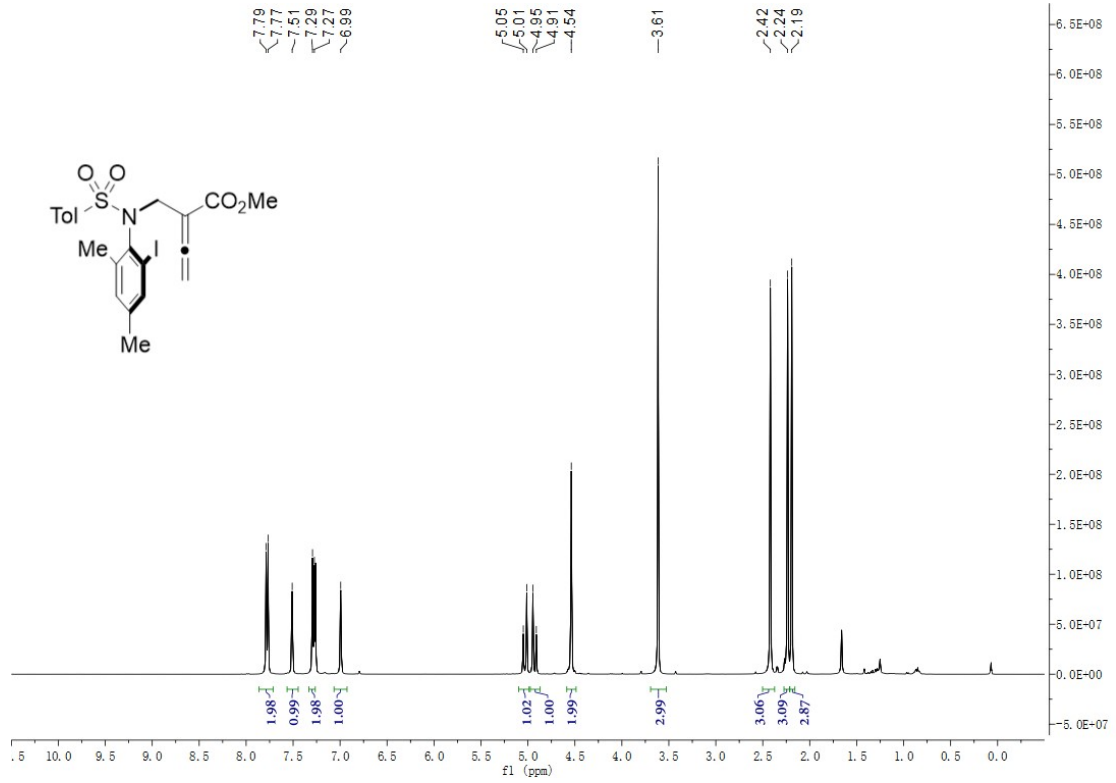
All these data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci.

X. NMR Spectra

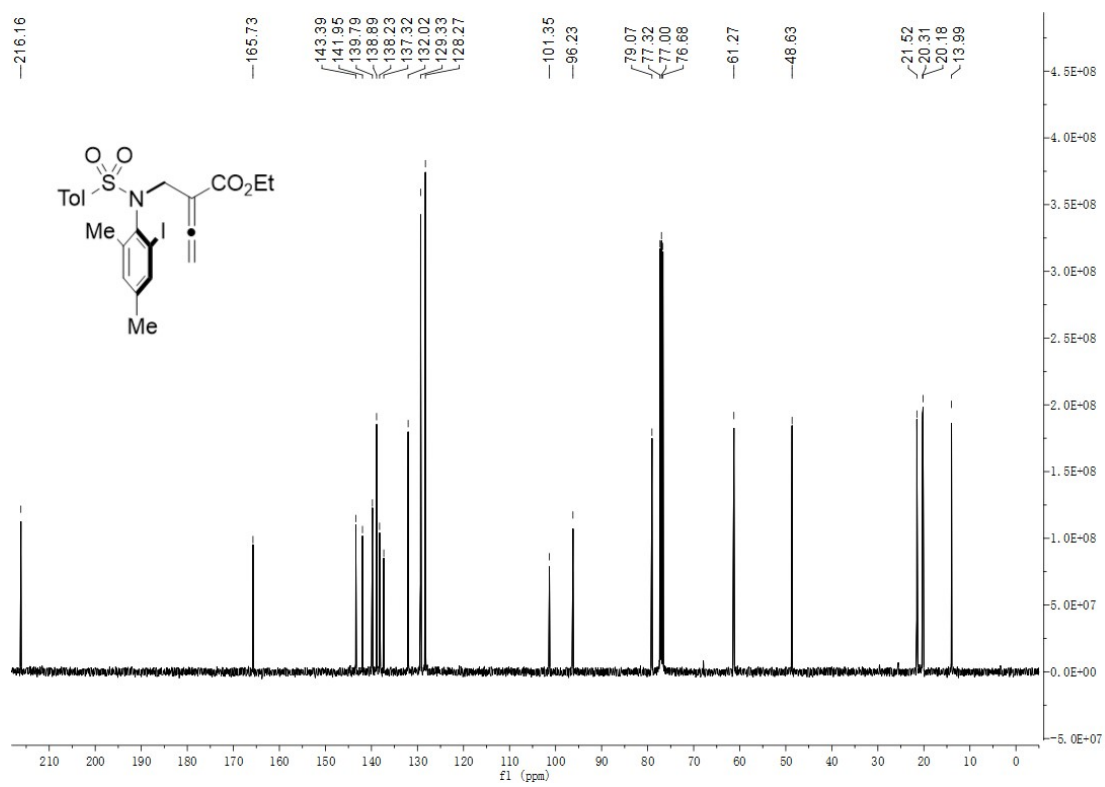
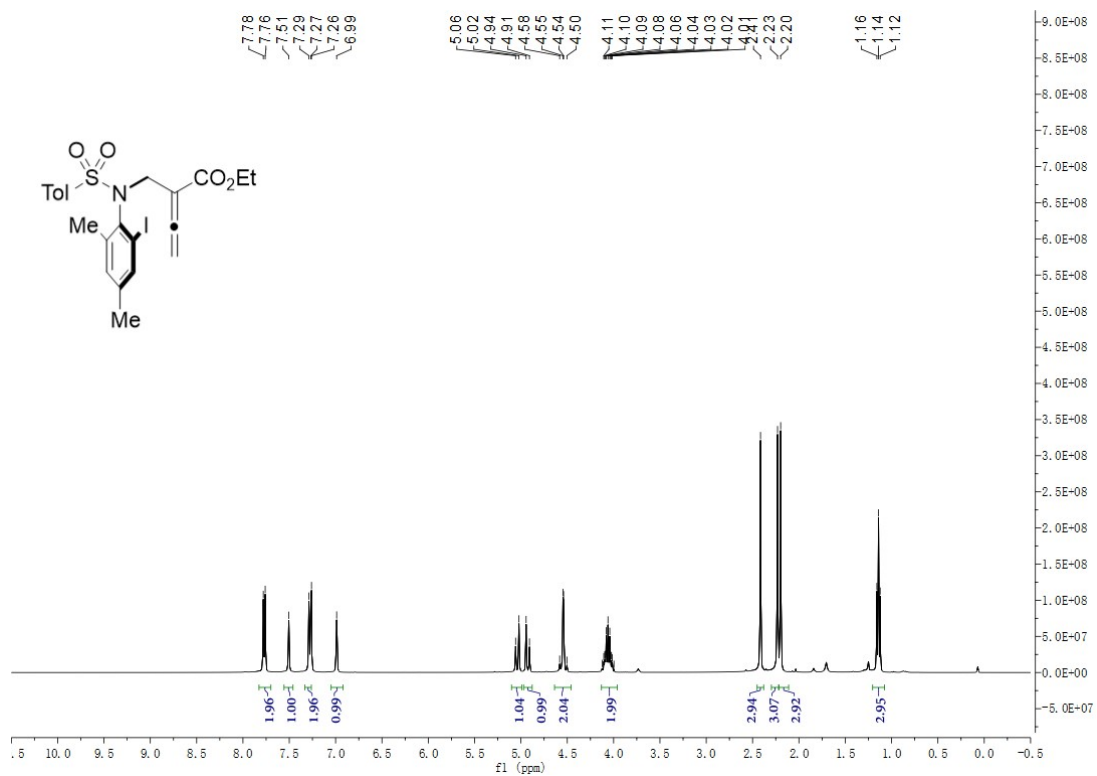
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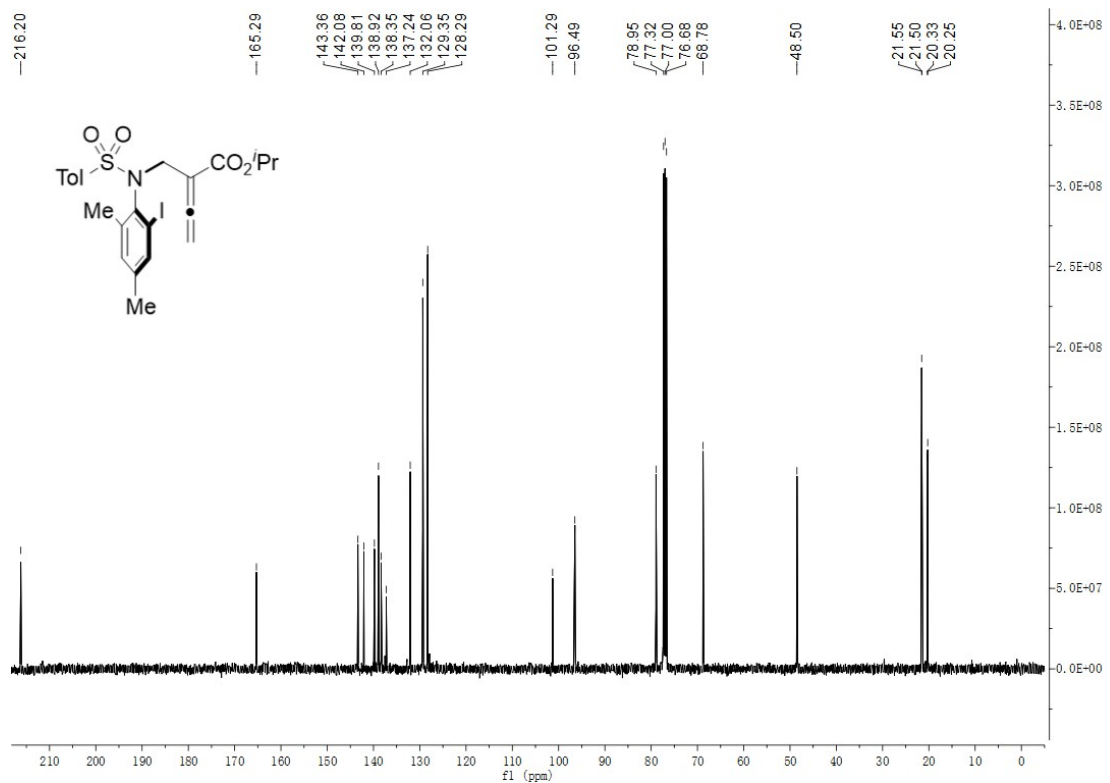
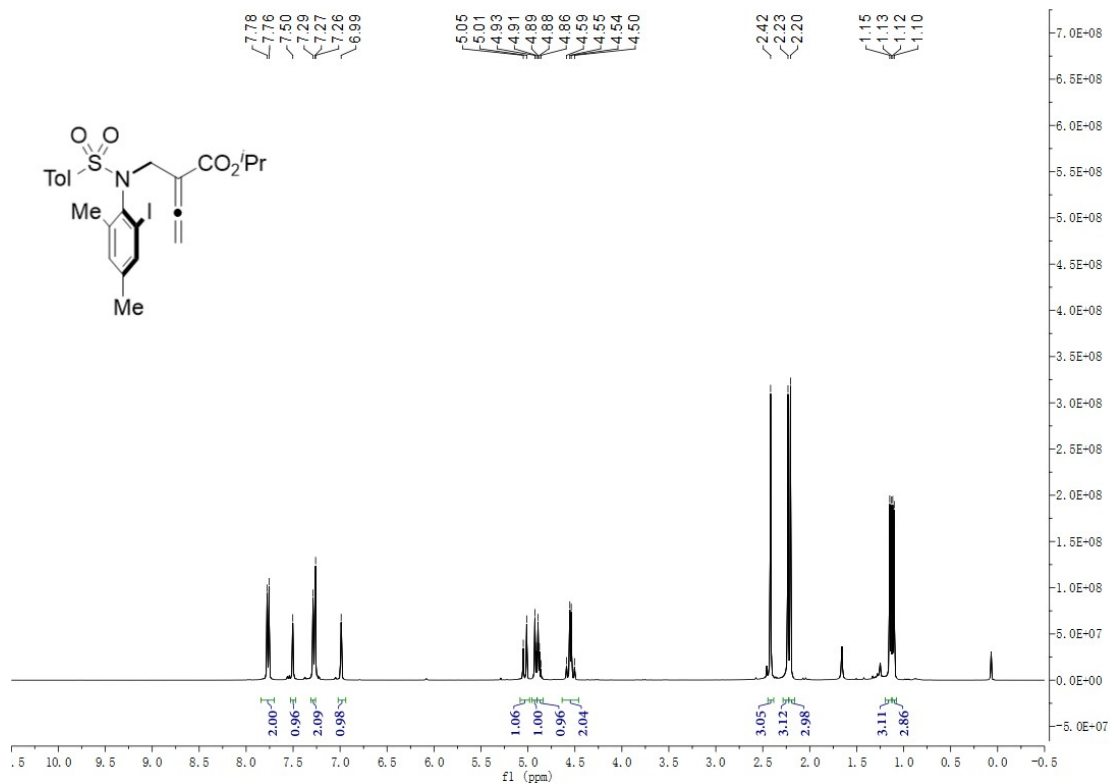
Compound **3b**



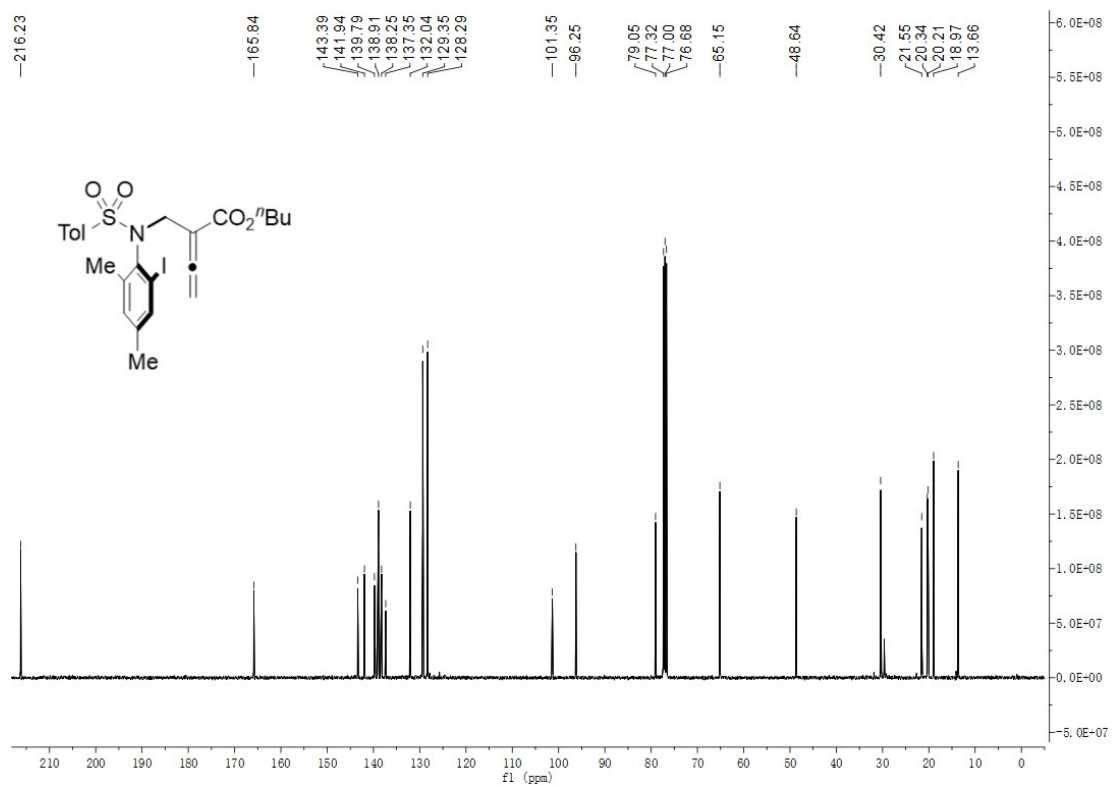
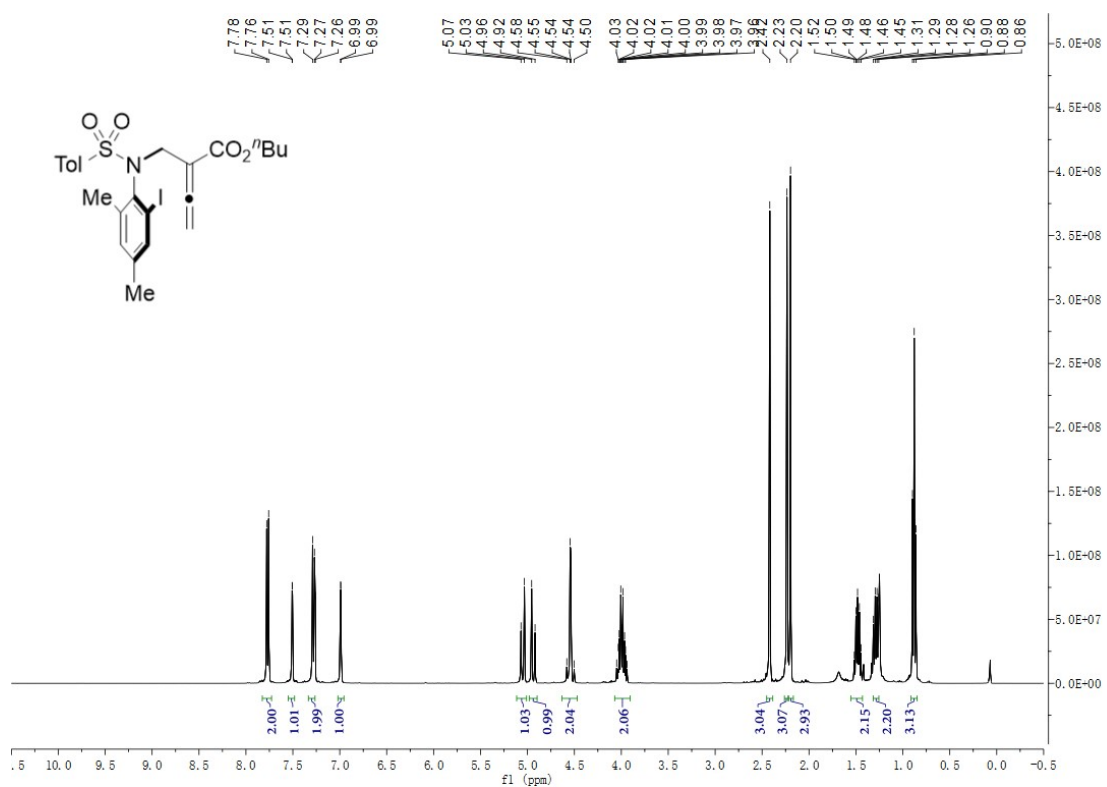
Compound 3c



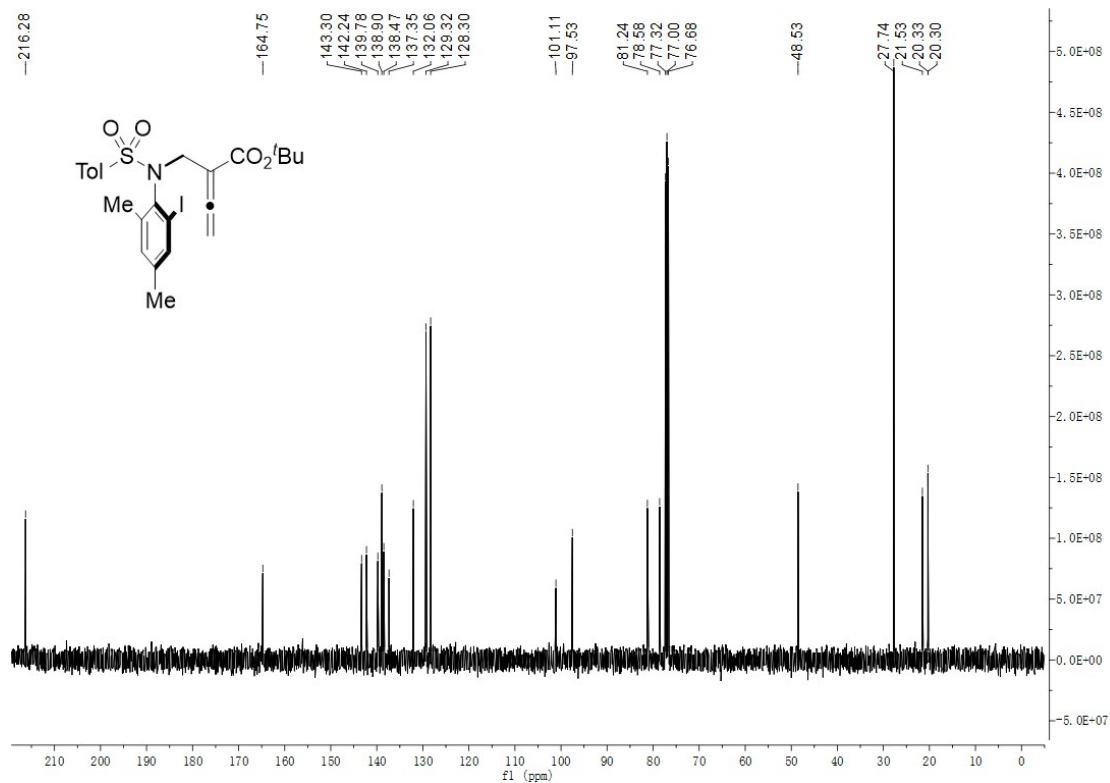
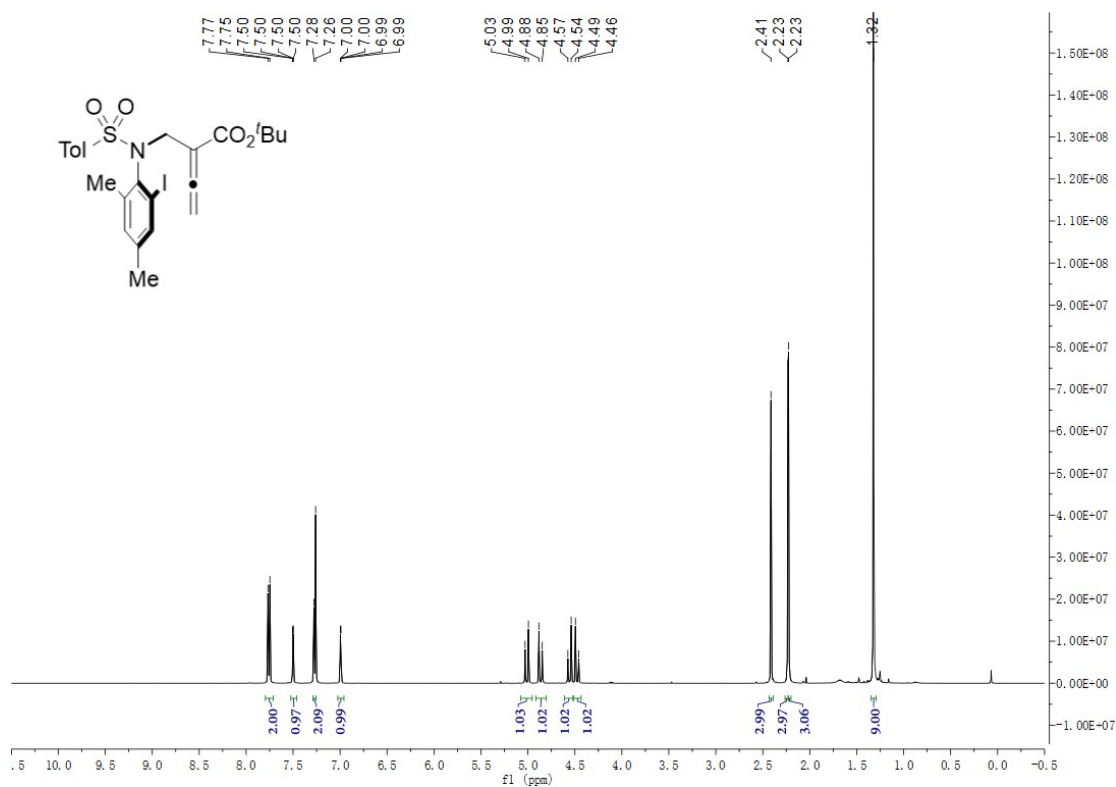
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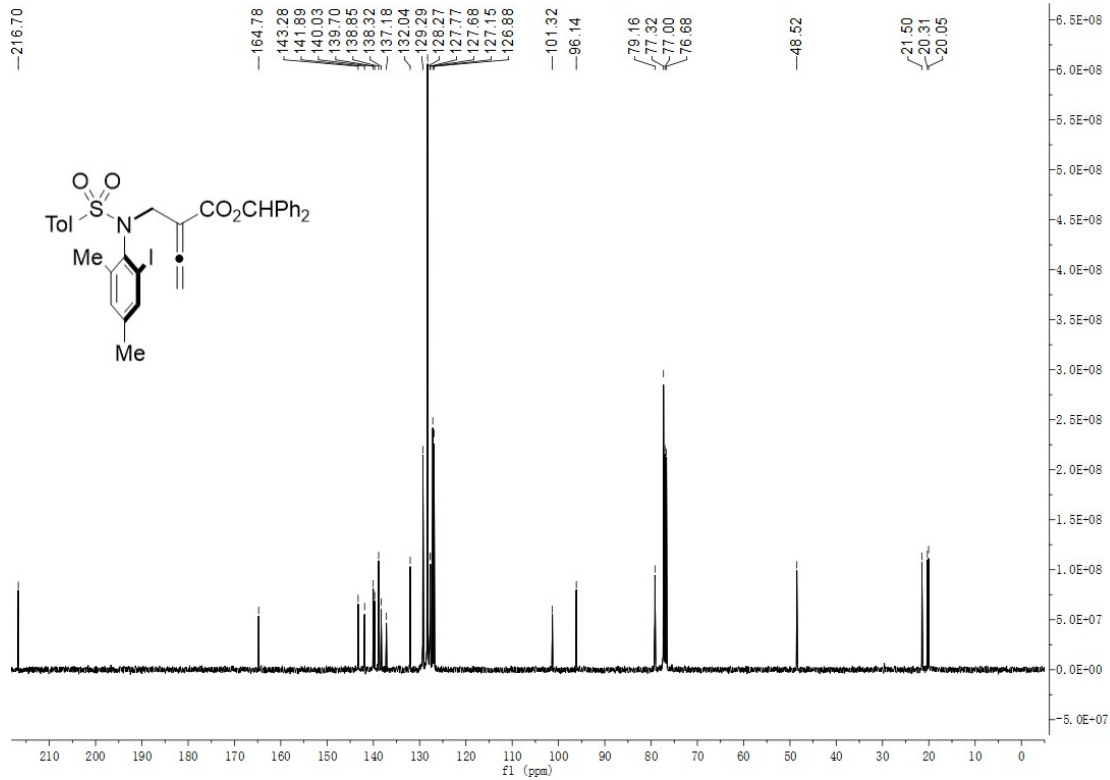
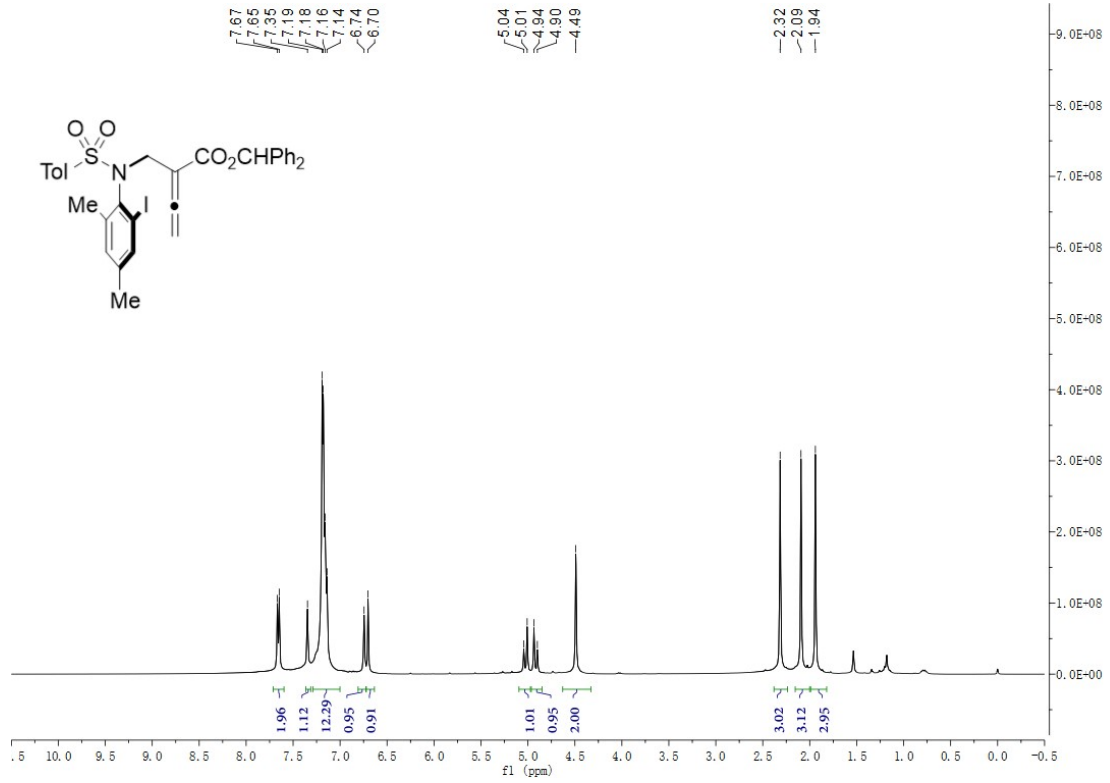
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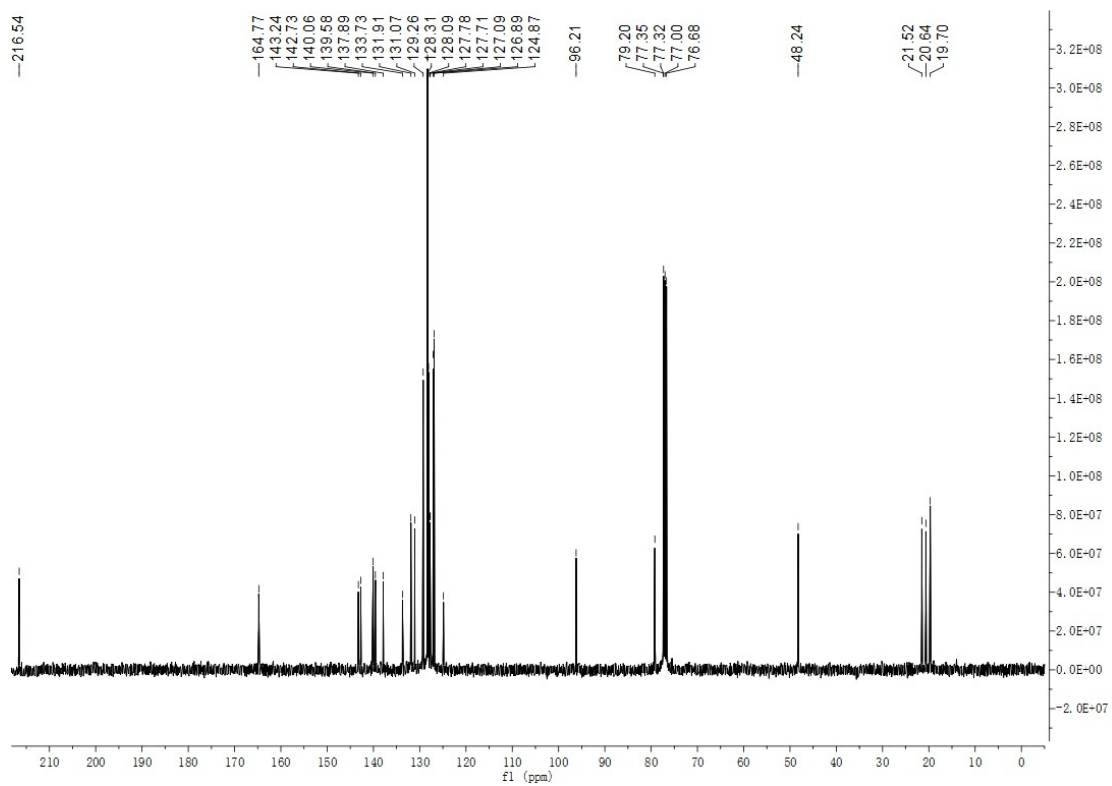
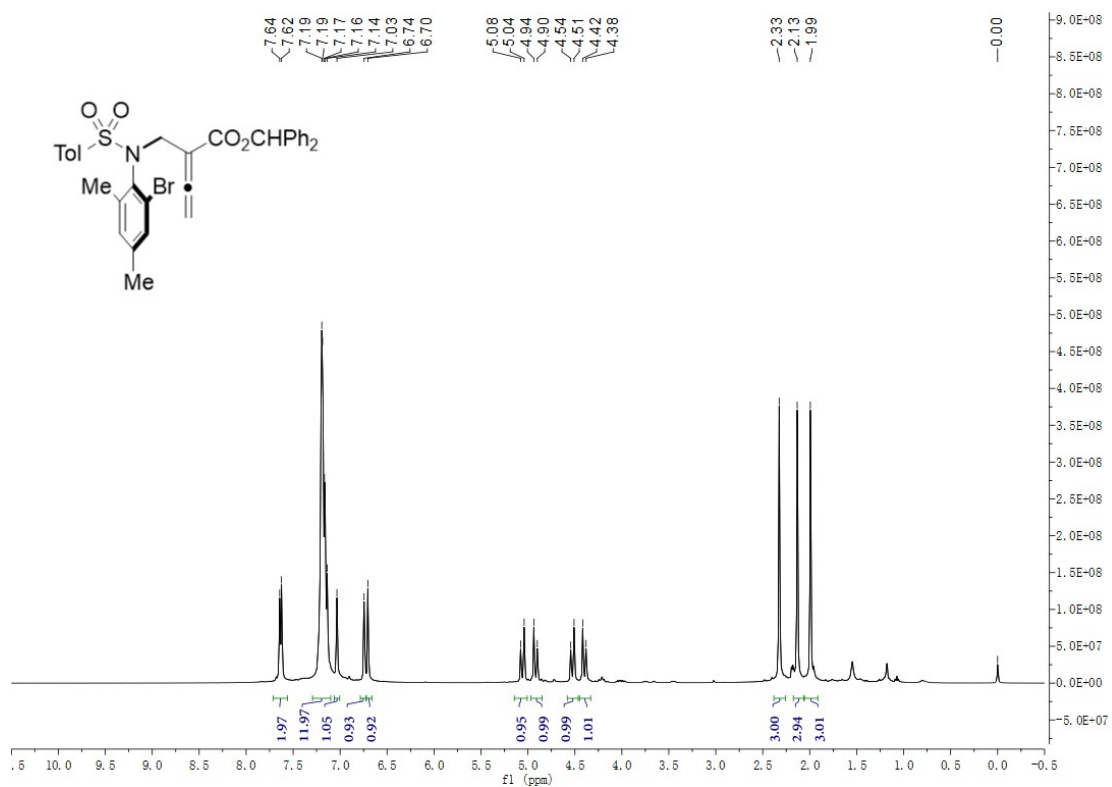
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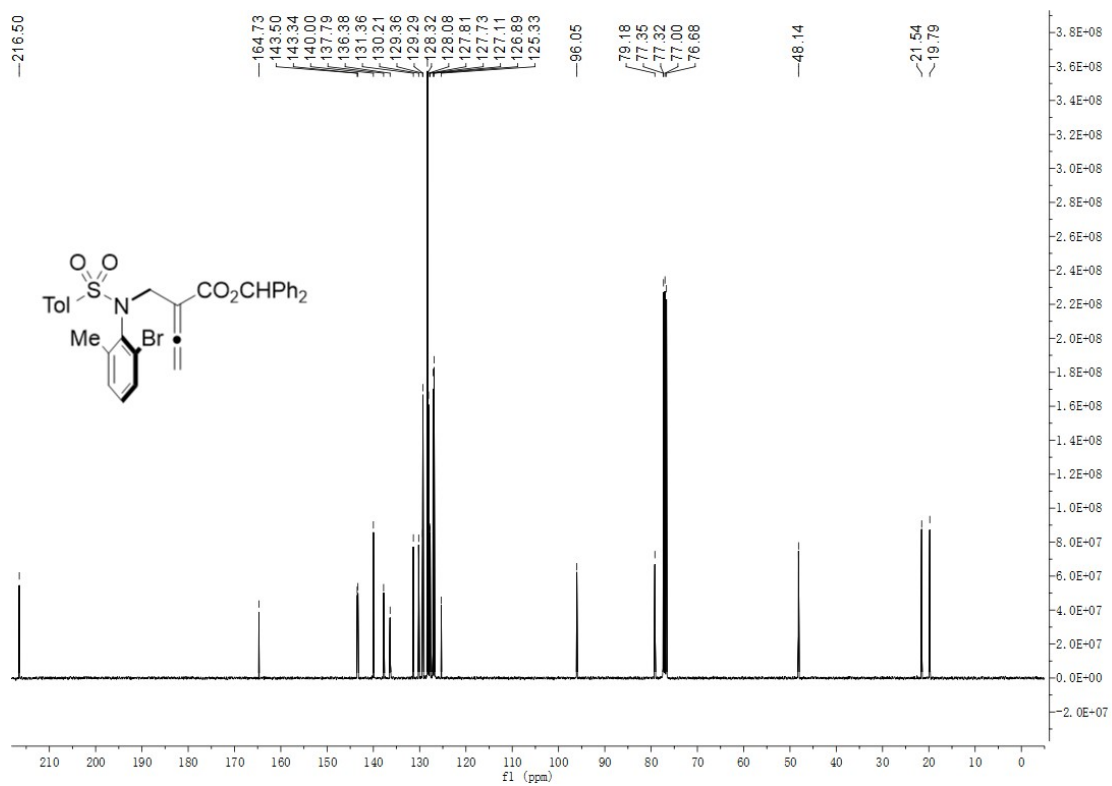
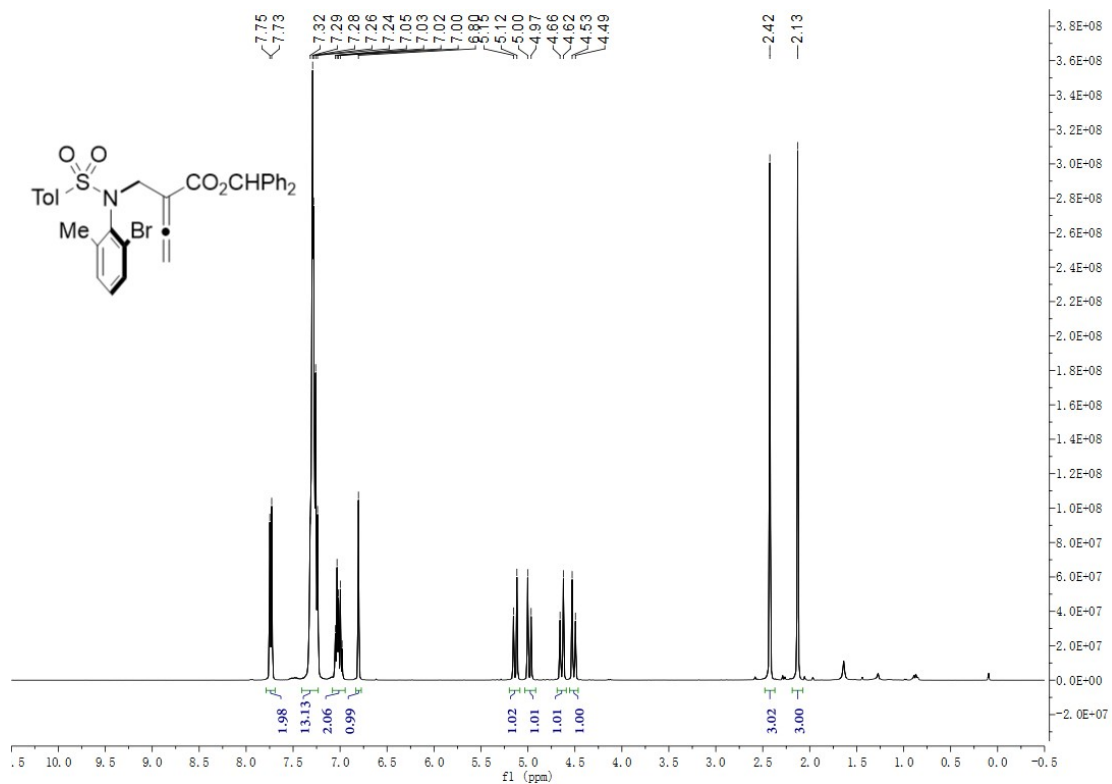
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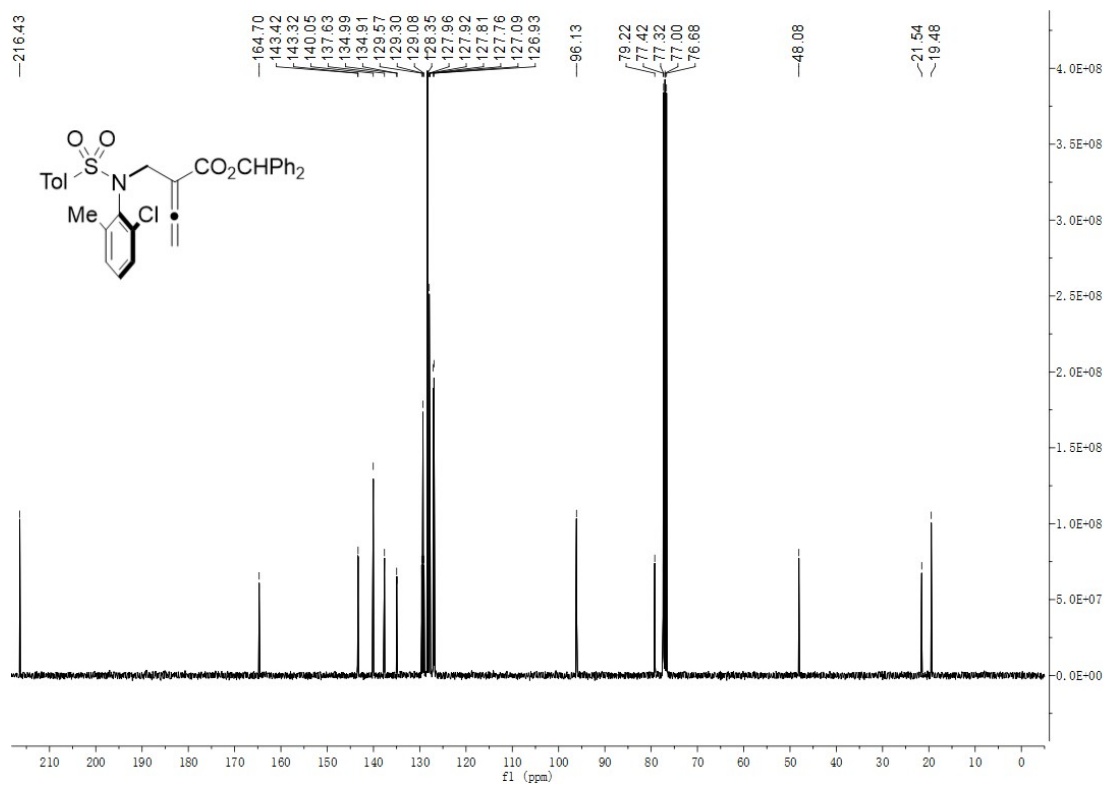
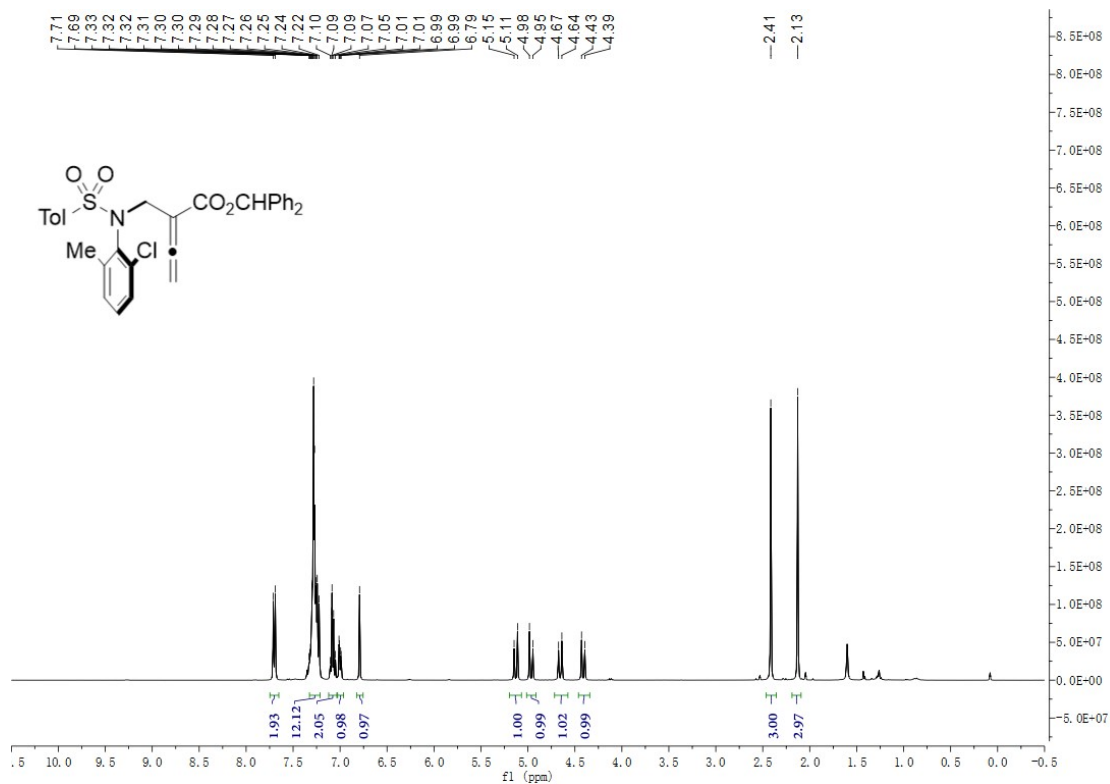
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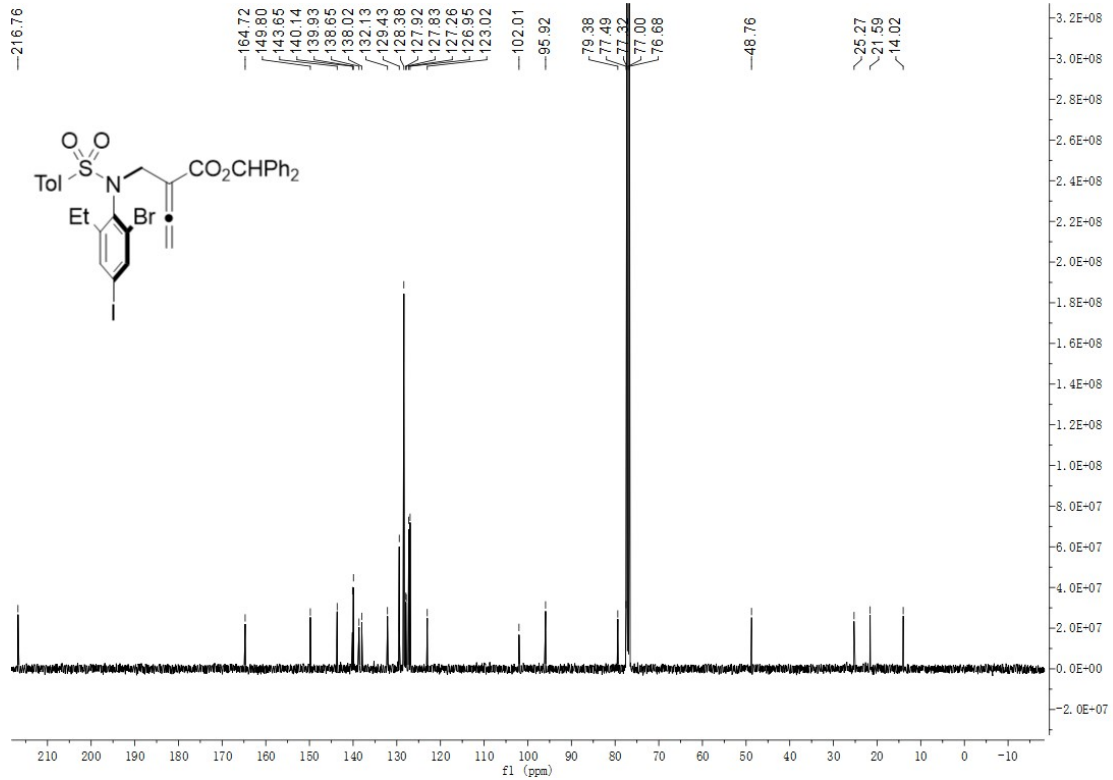
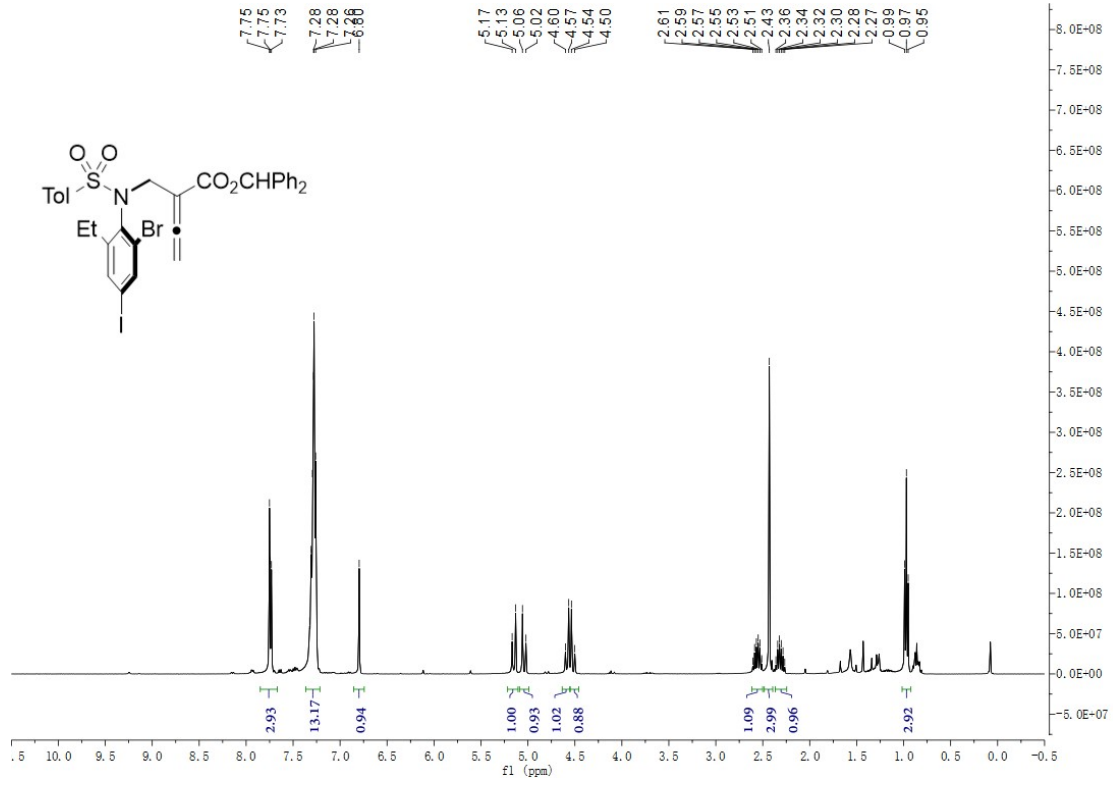
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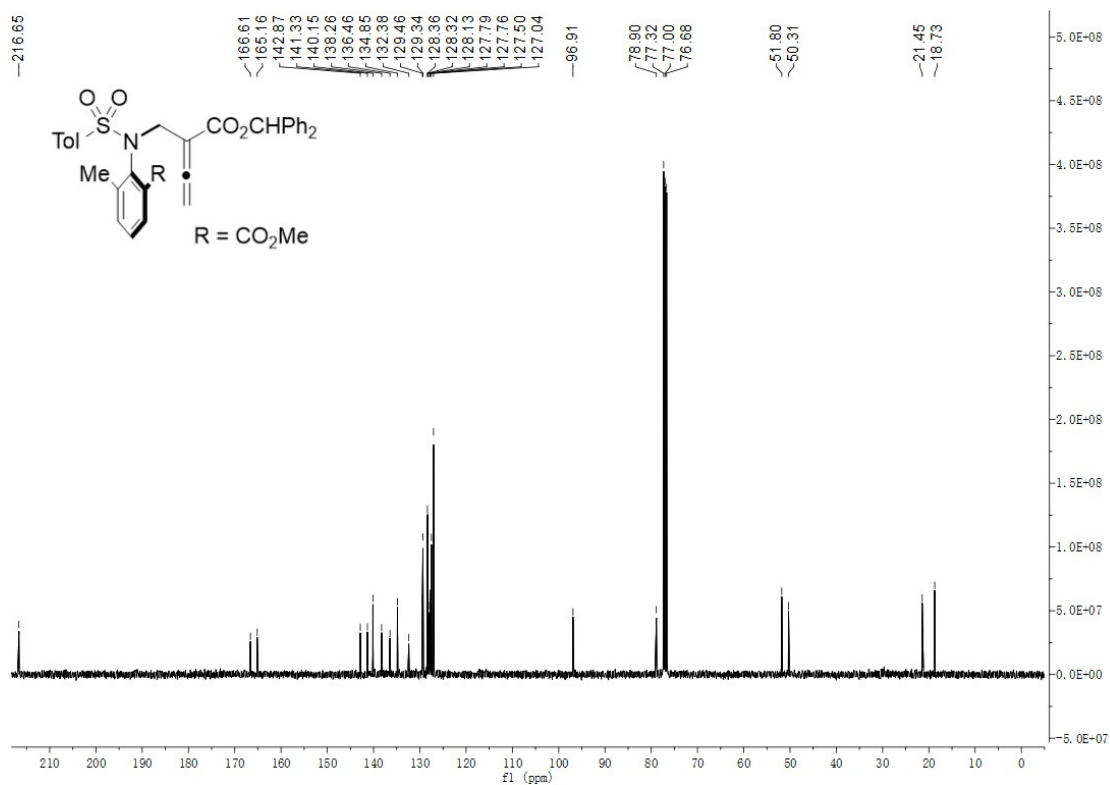
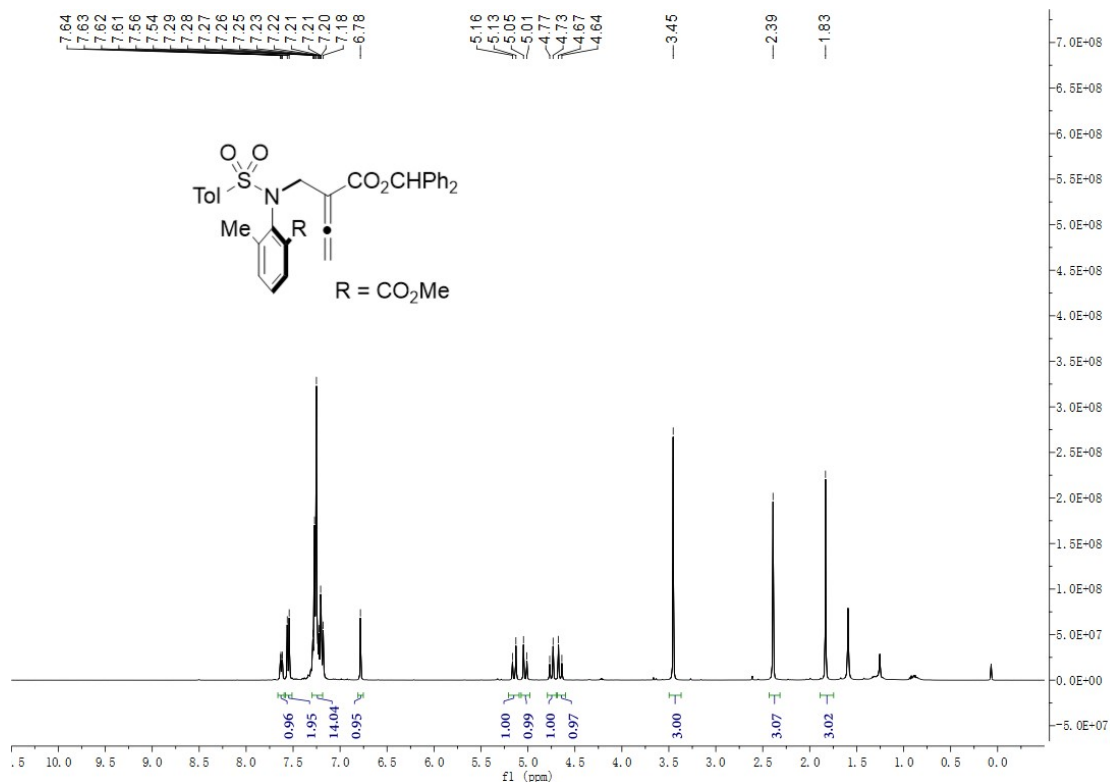
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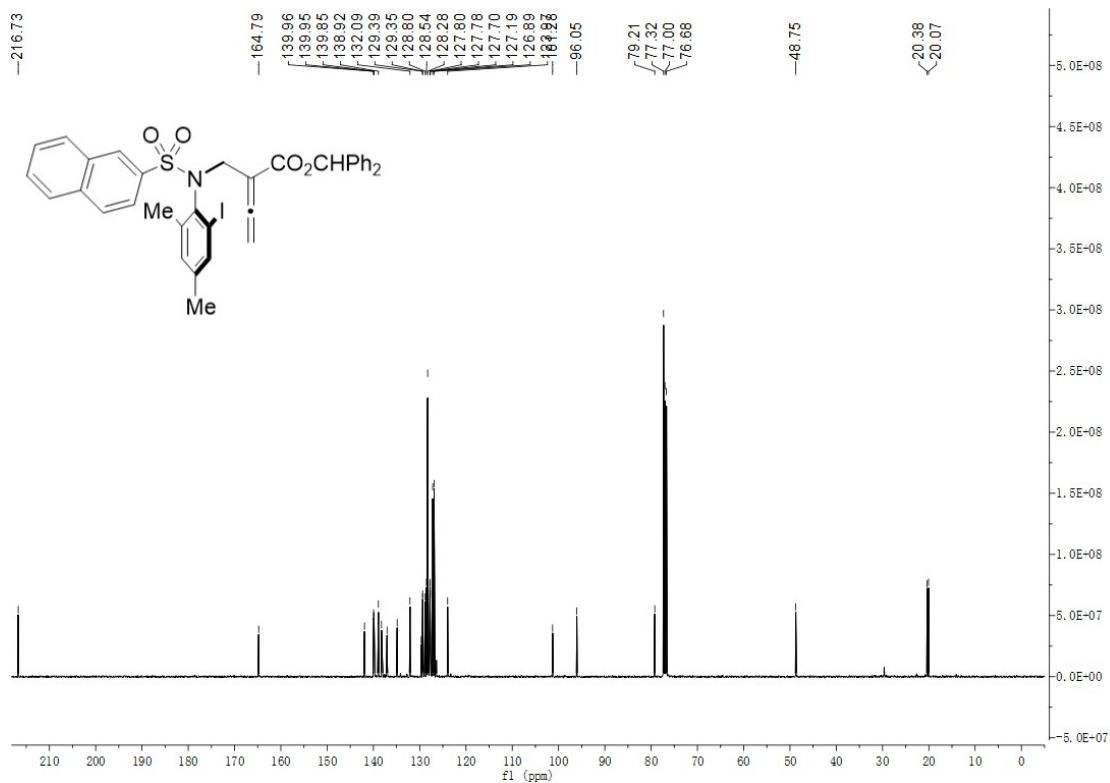
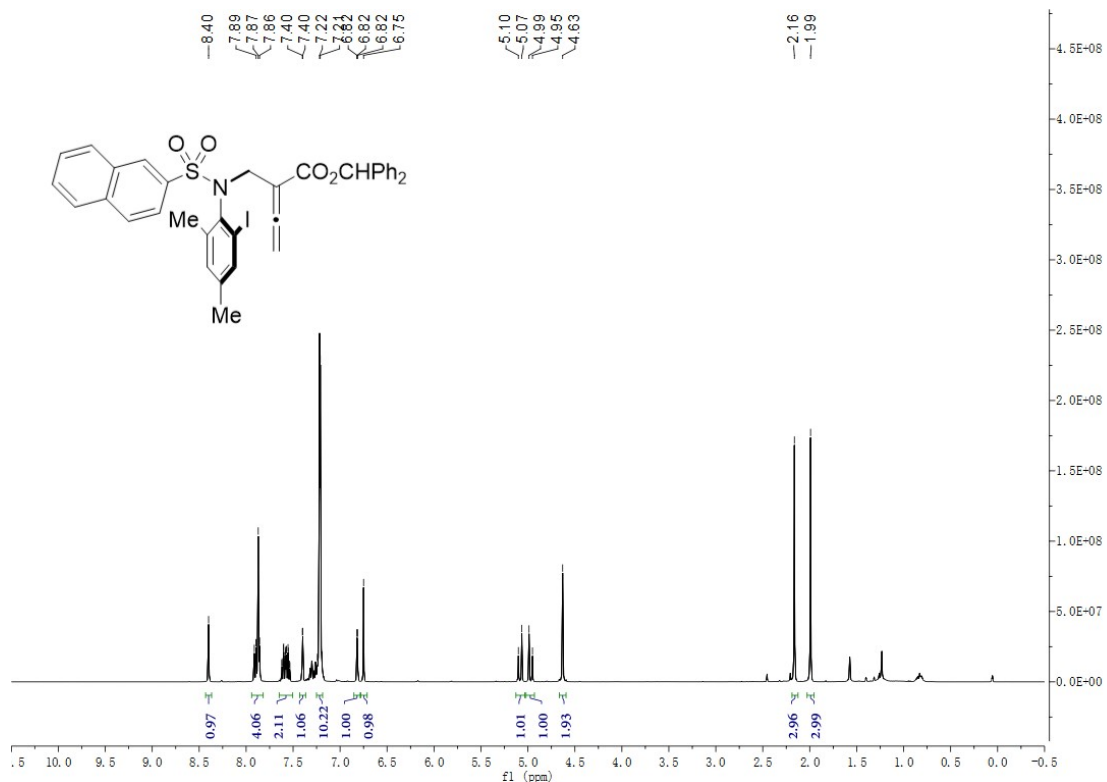
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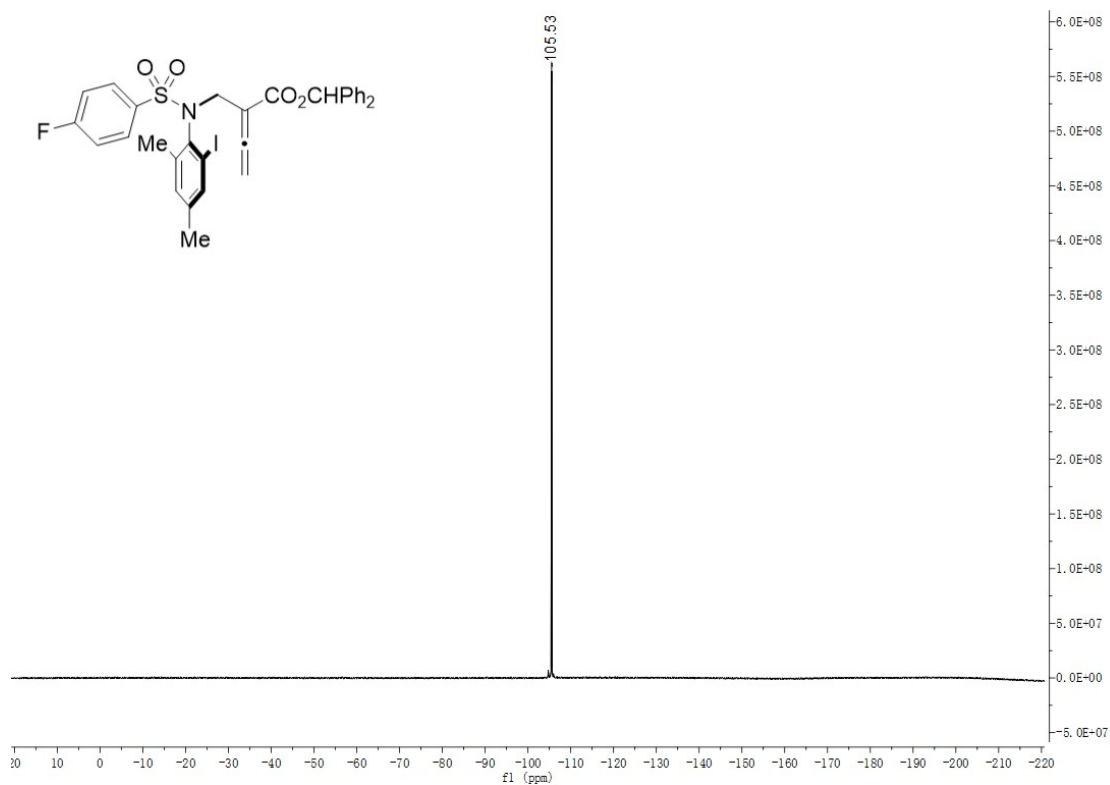
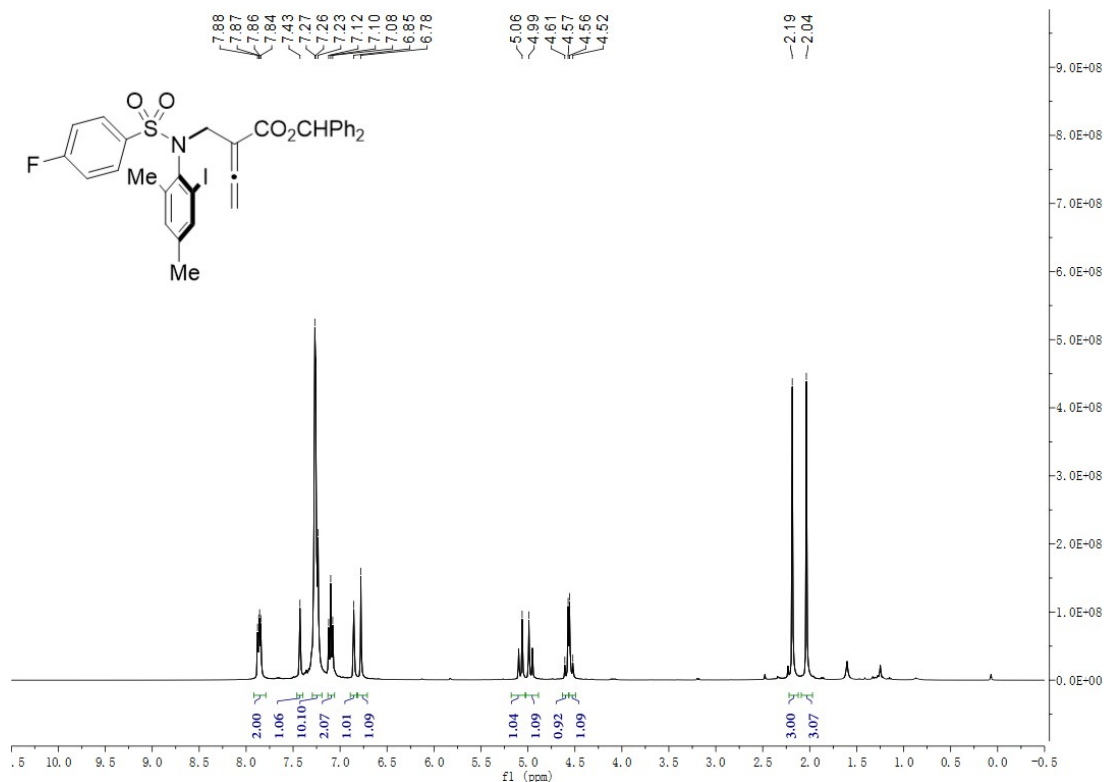
Compound 31

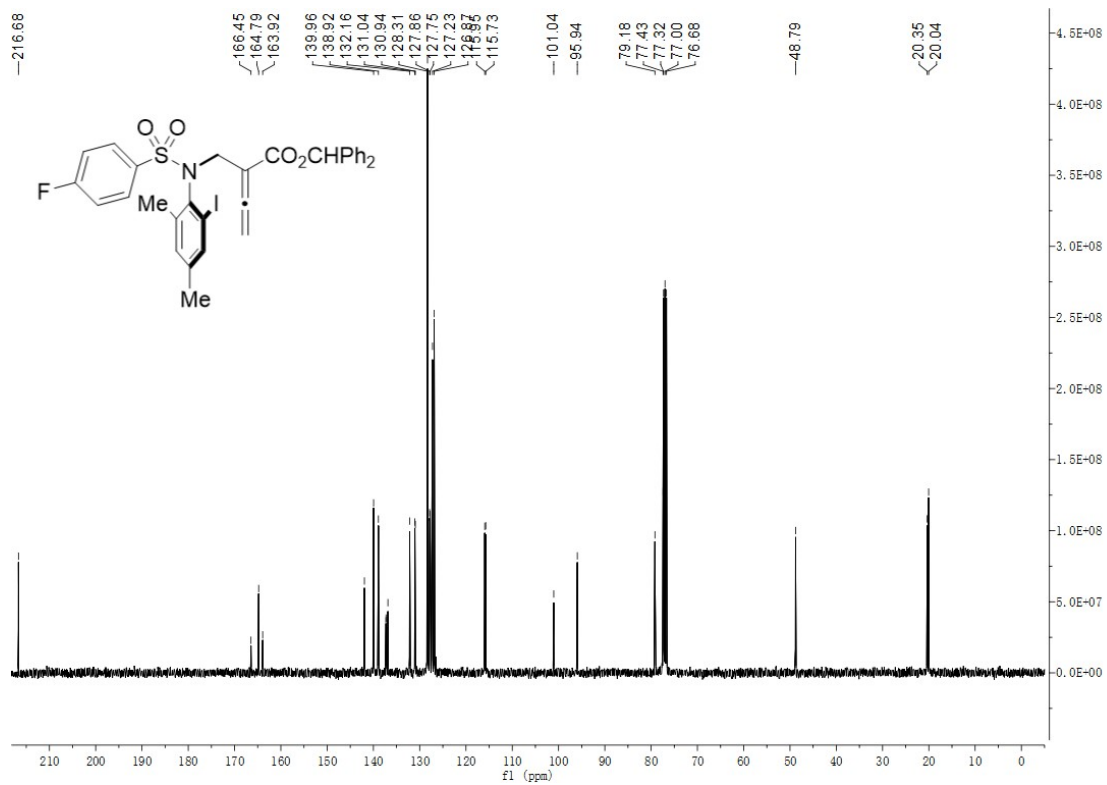


Compound 3m

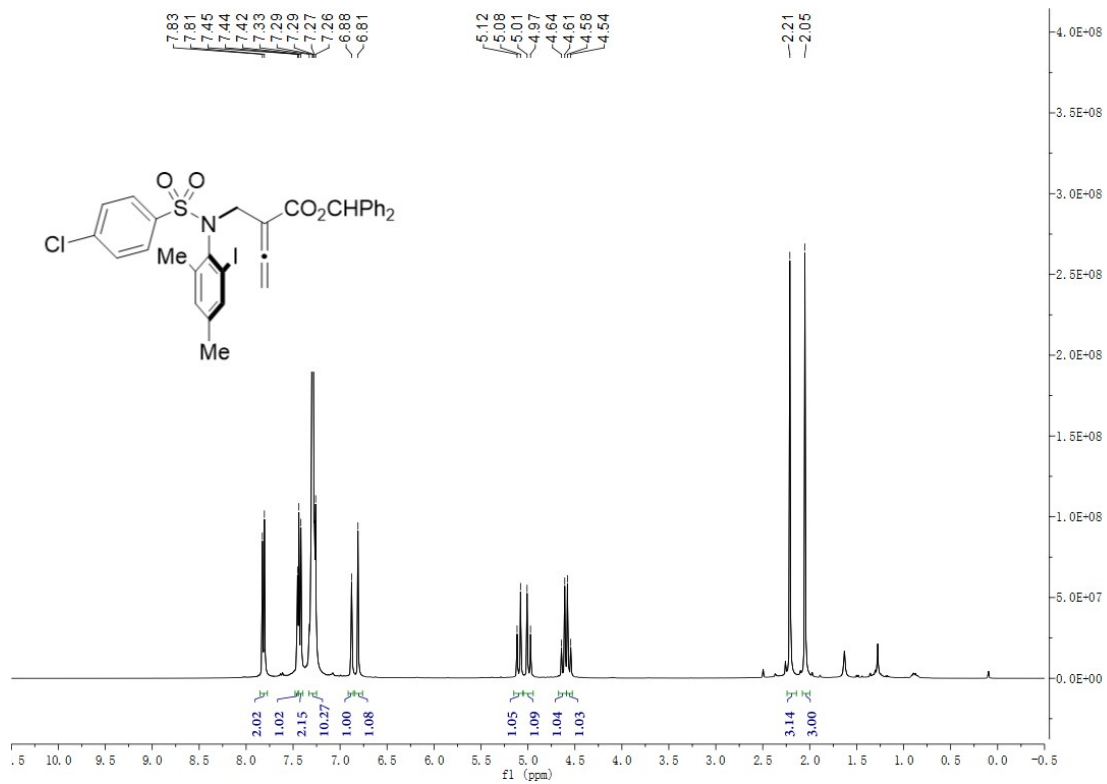


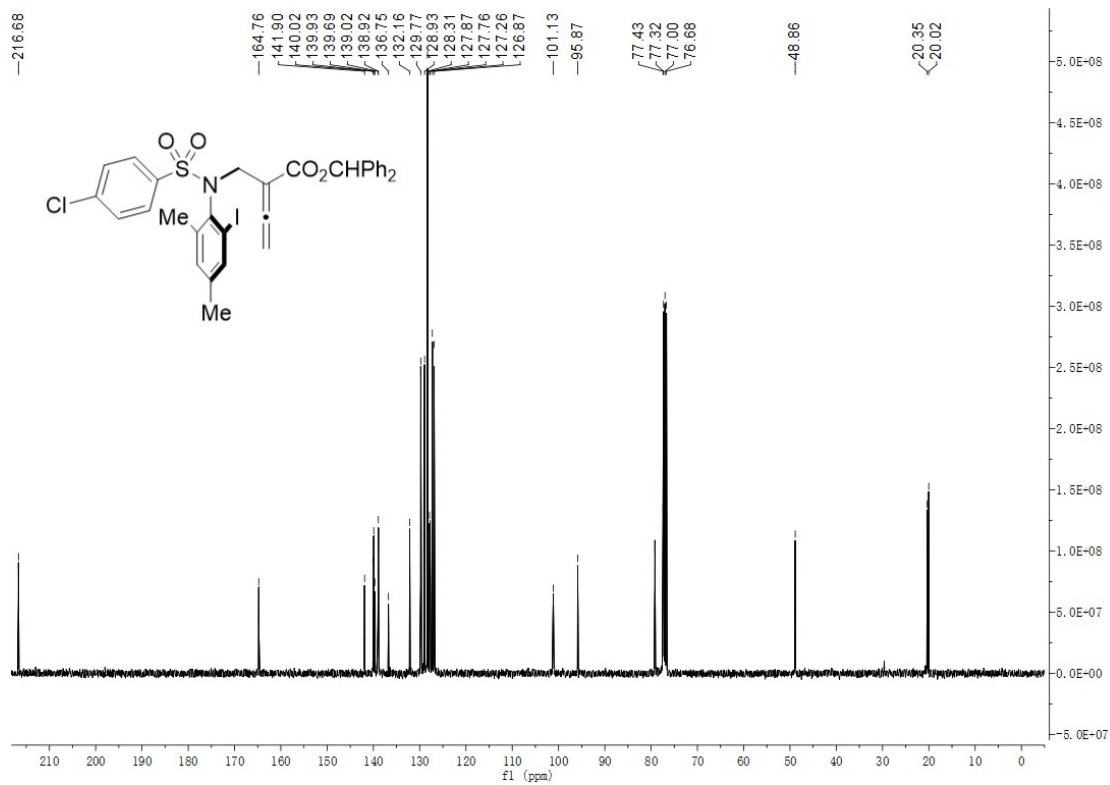
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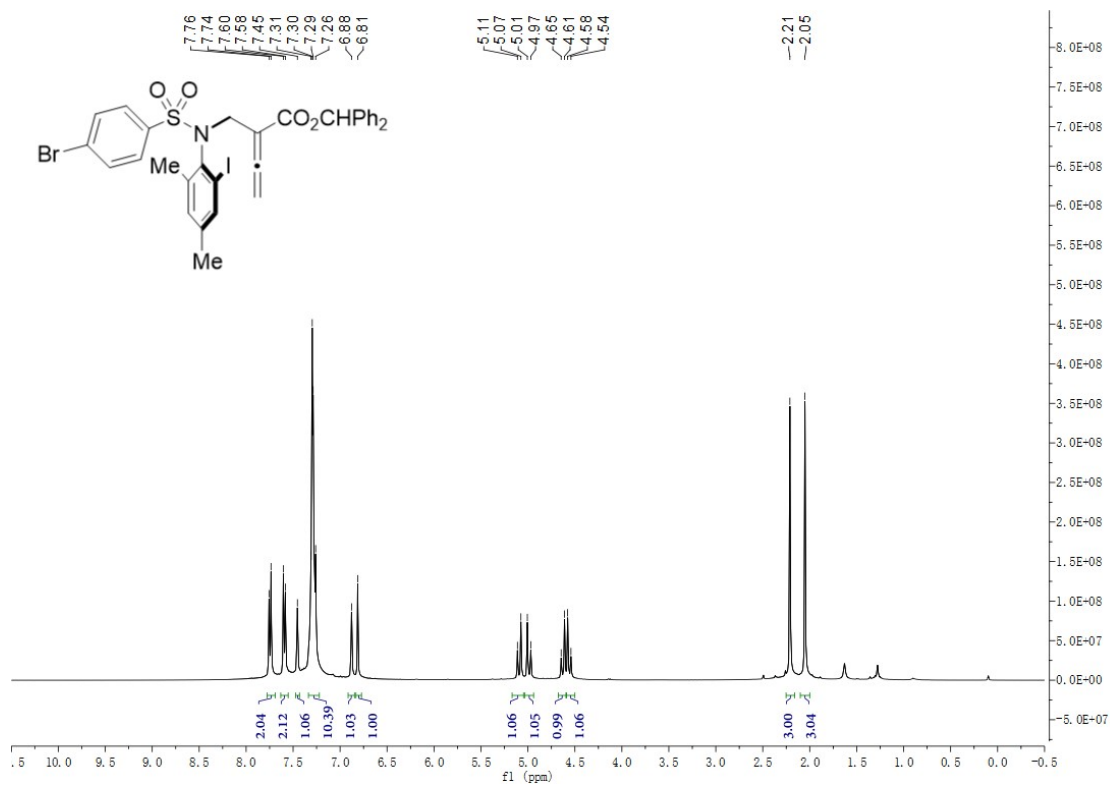


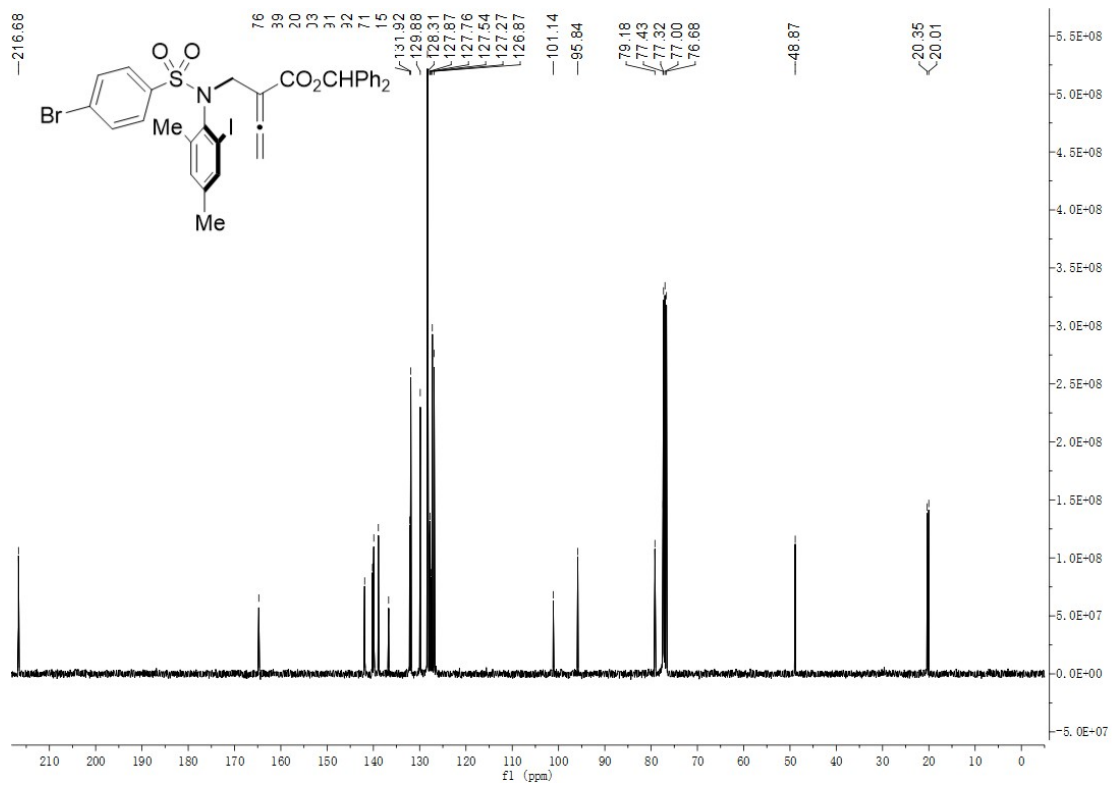
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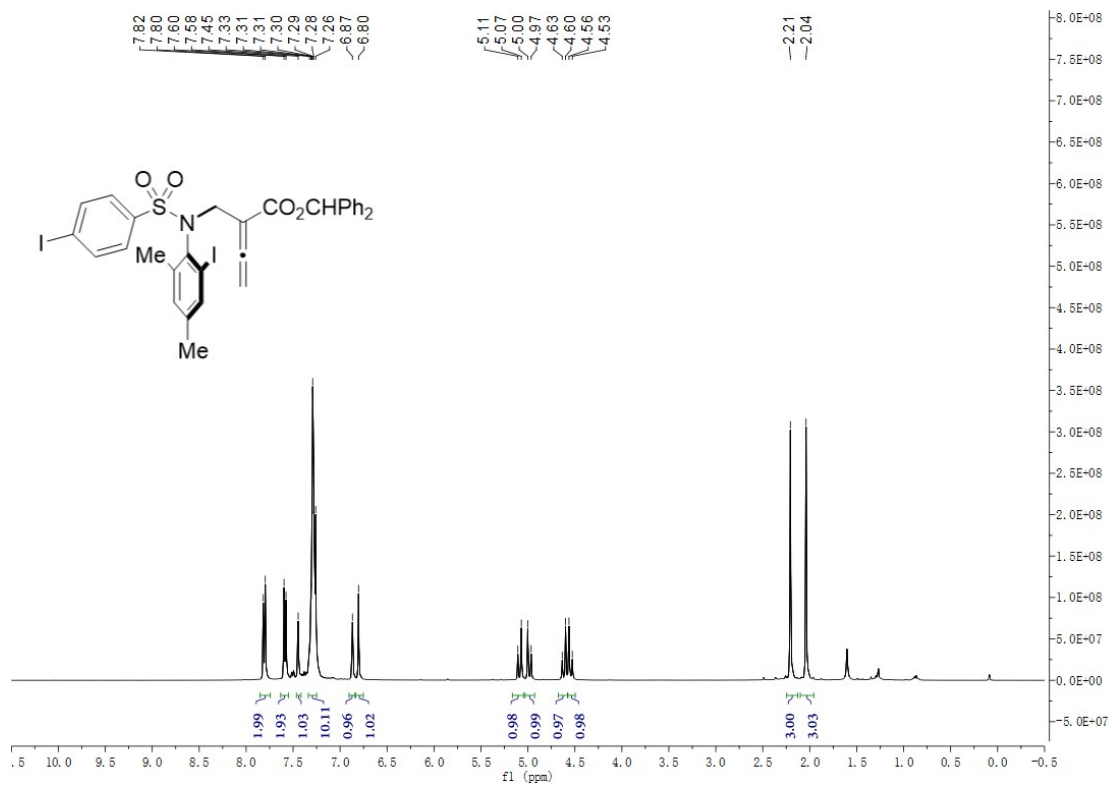


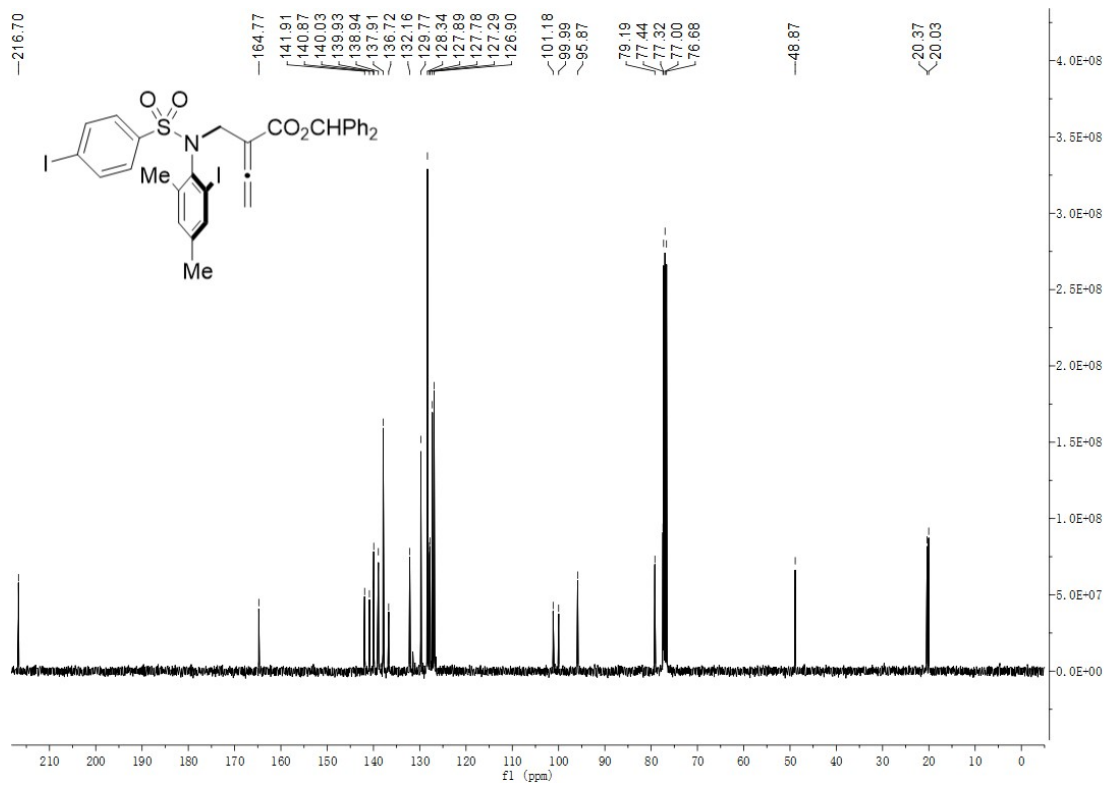
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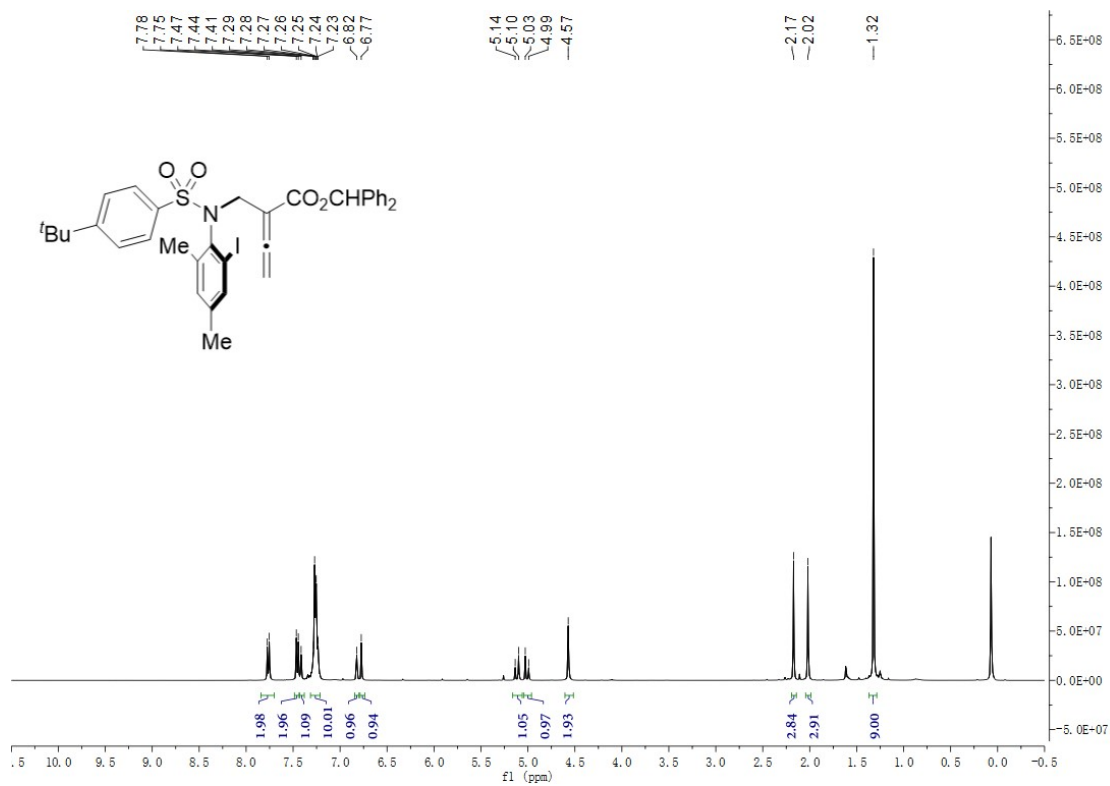


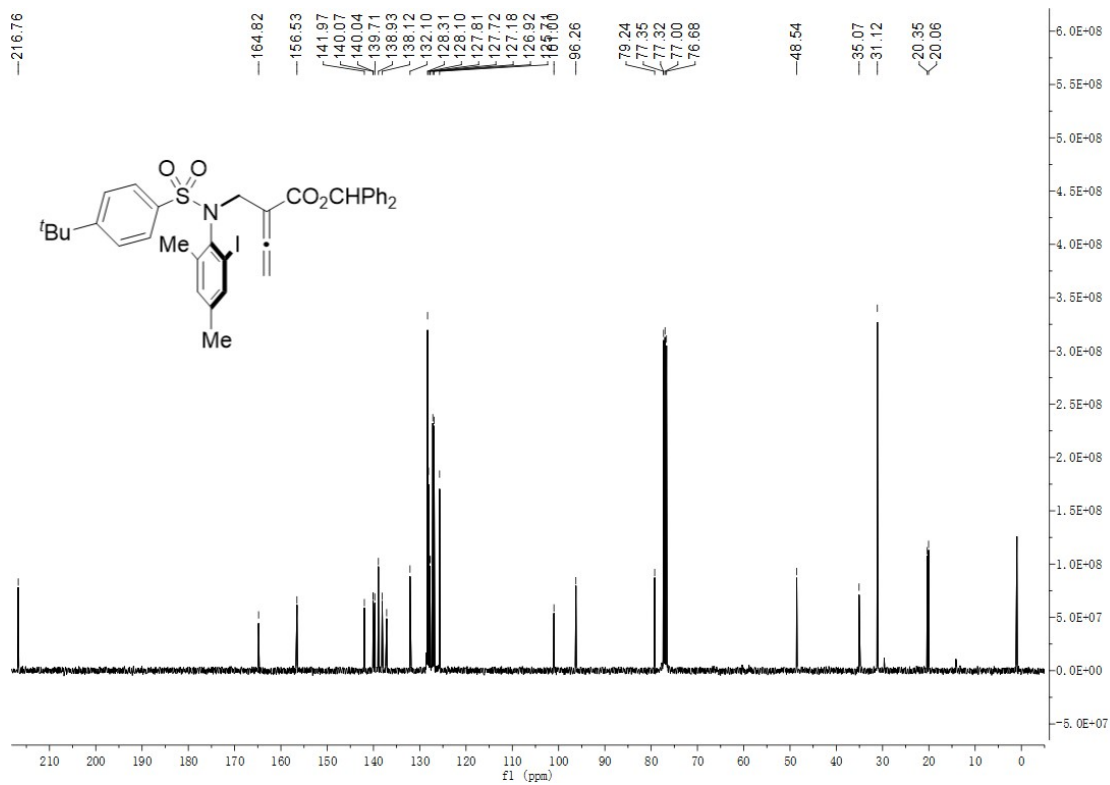
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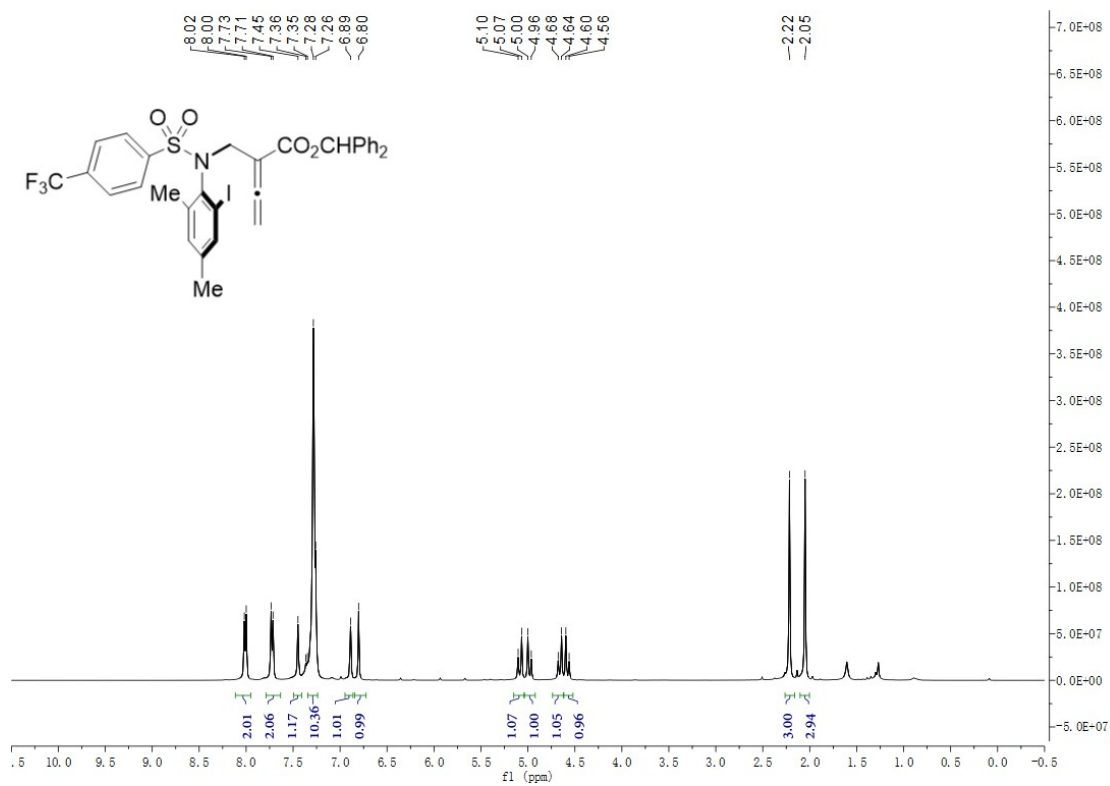


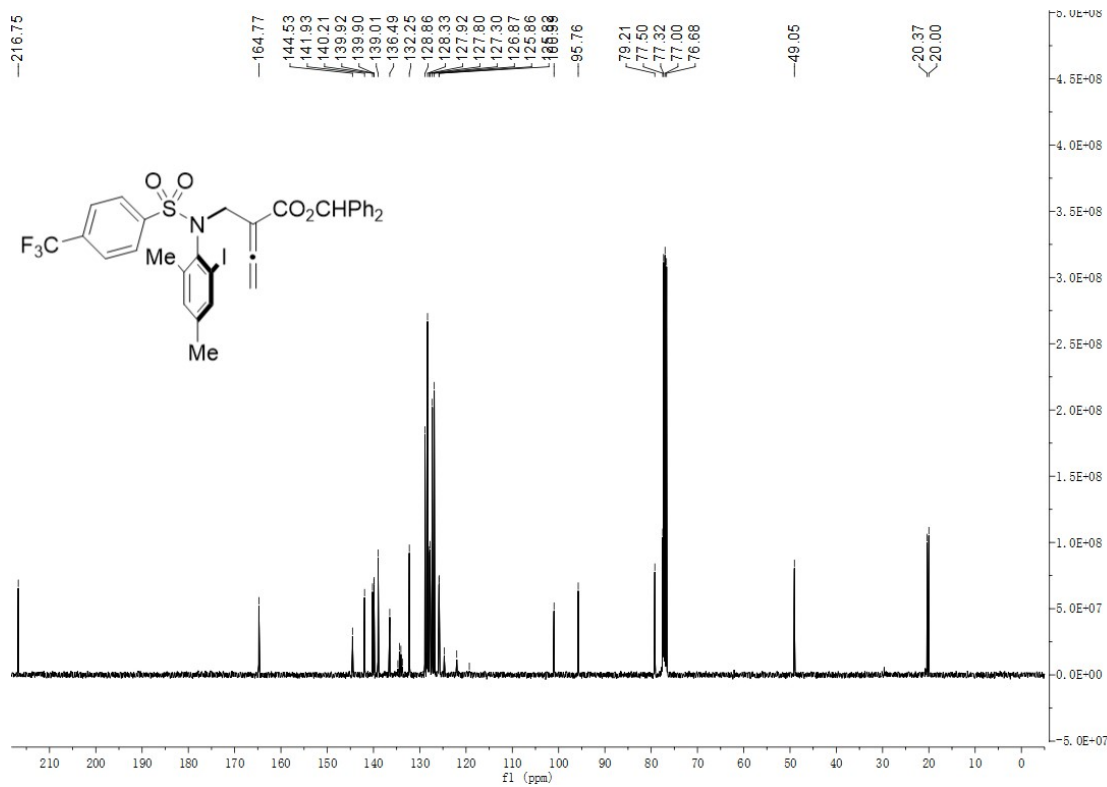
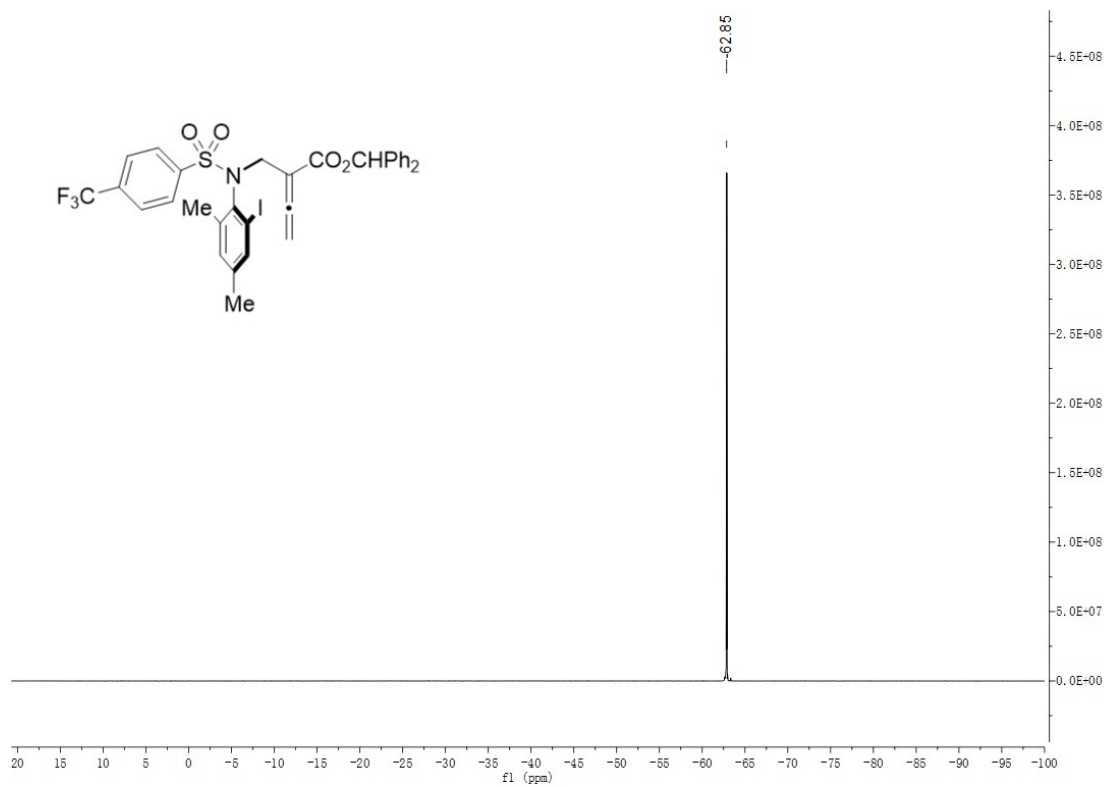
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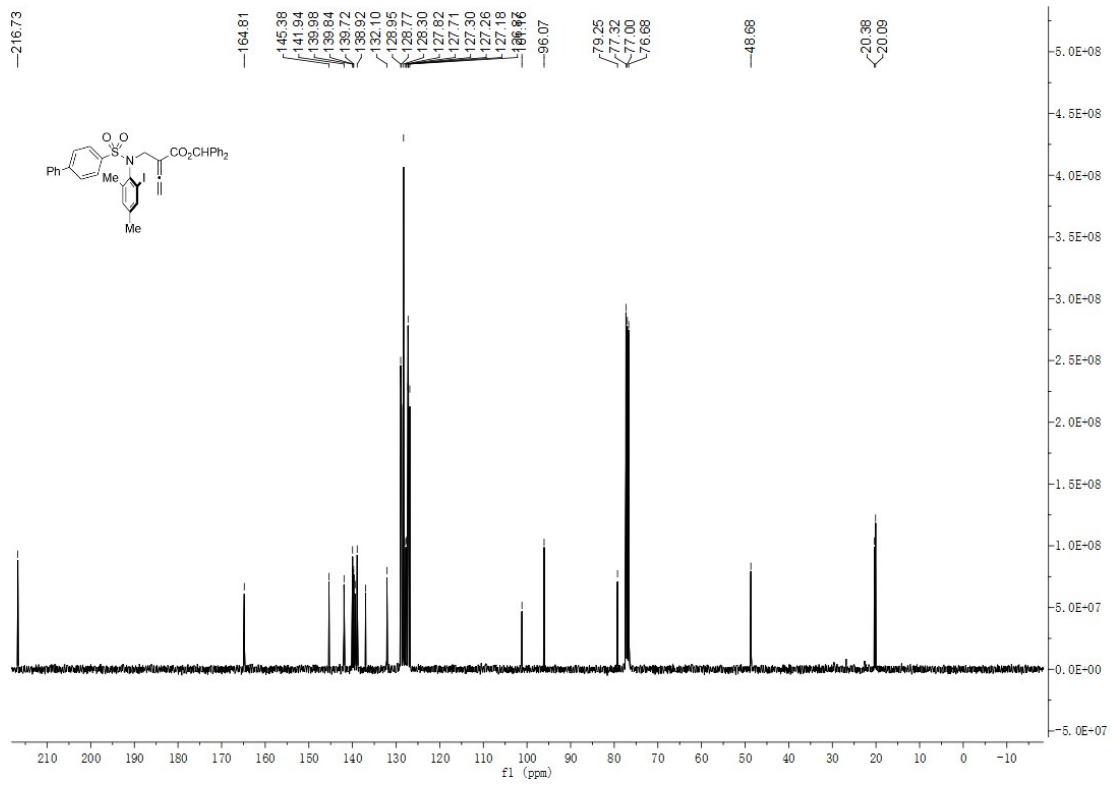
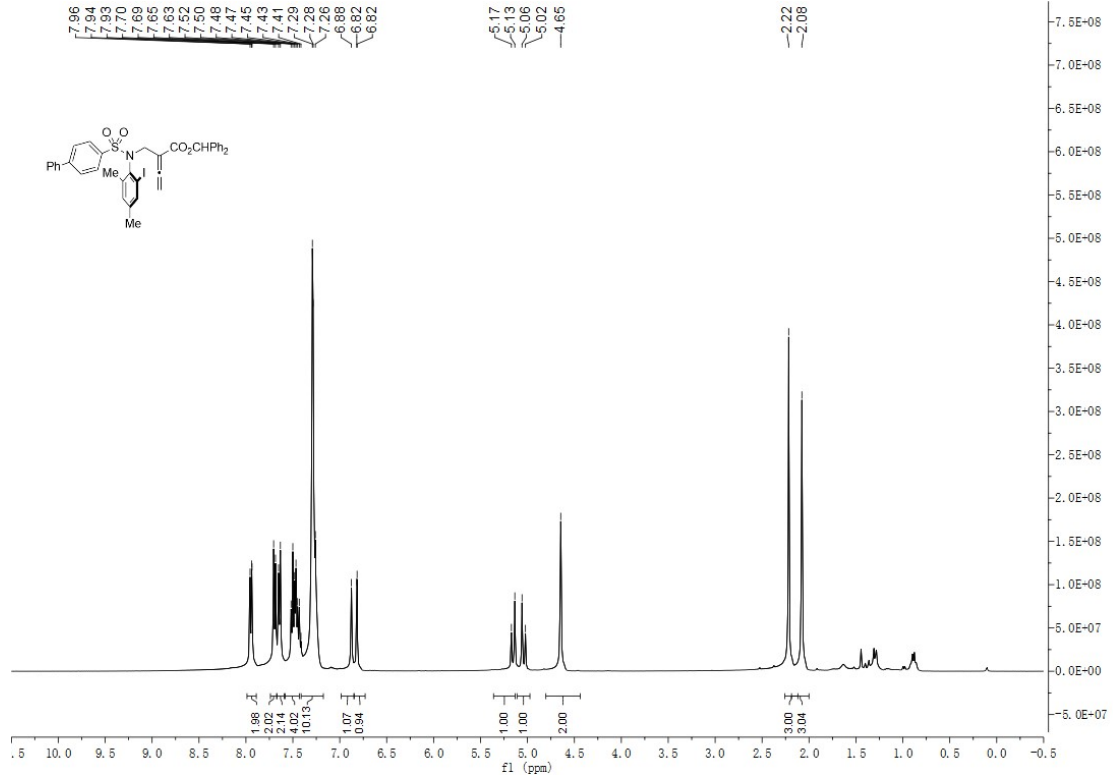


Compound 3s

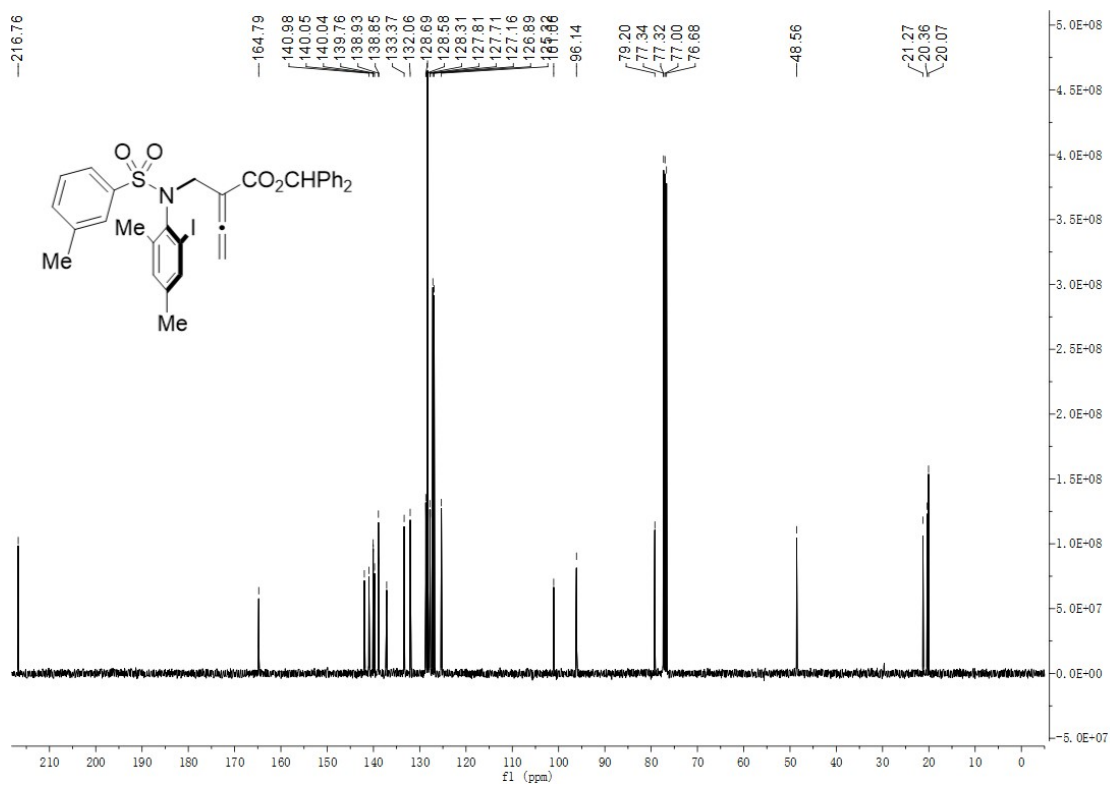
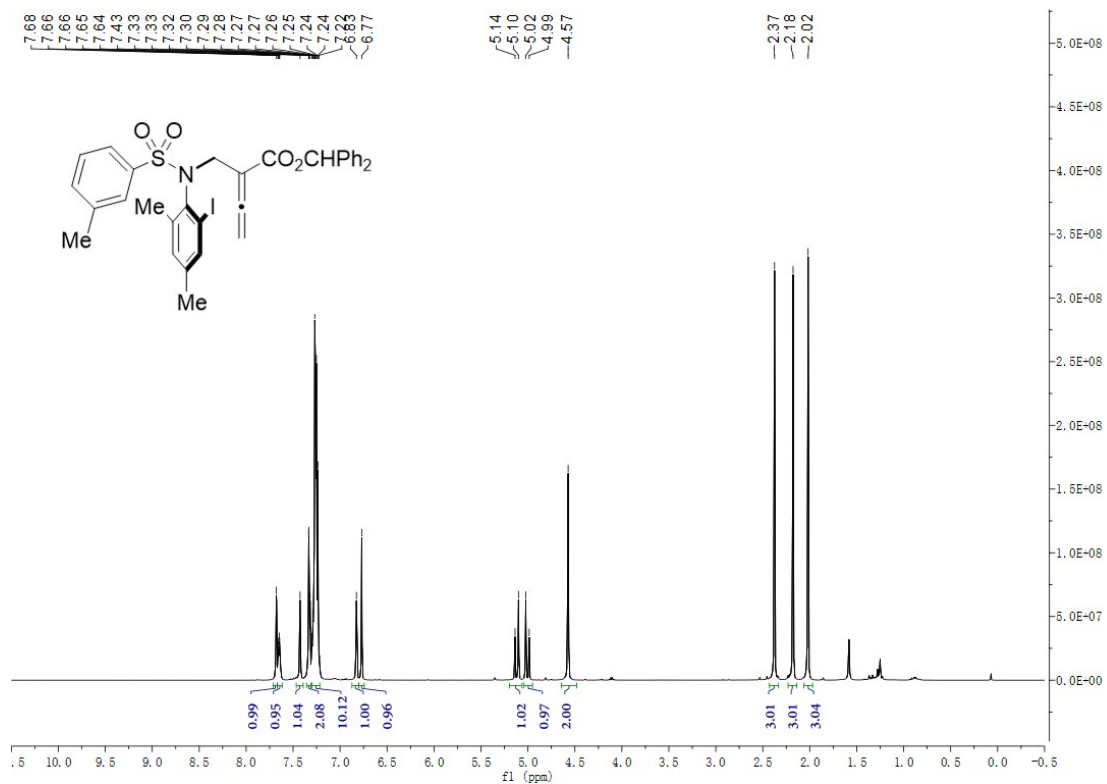




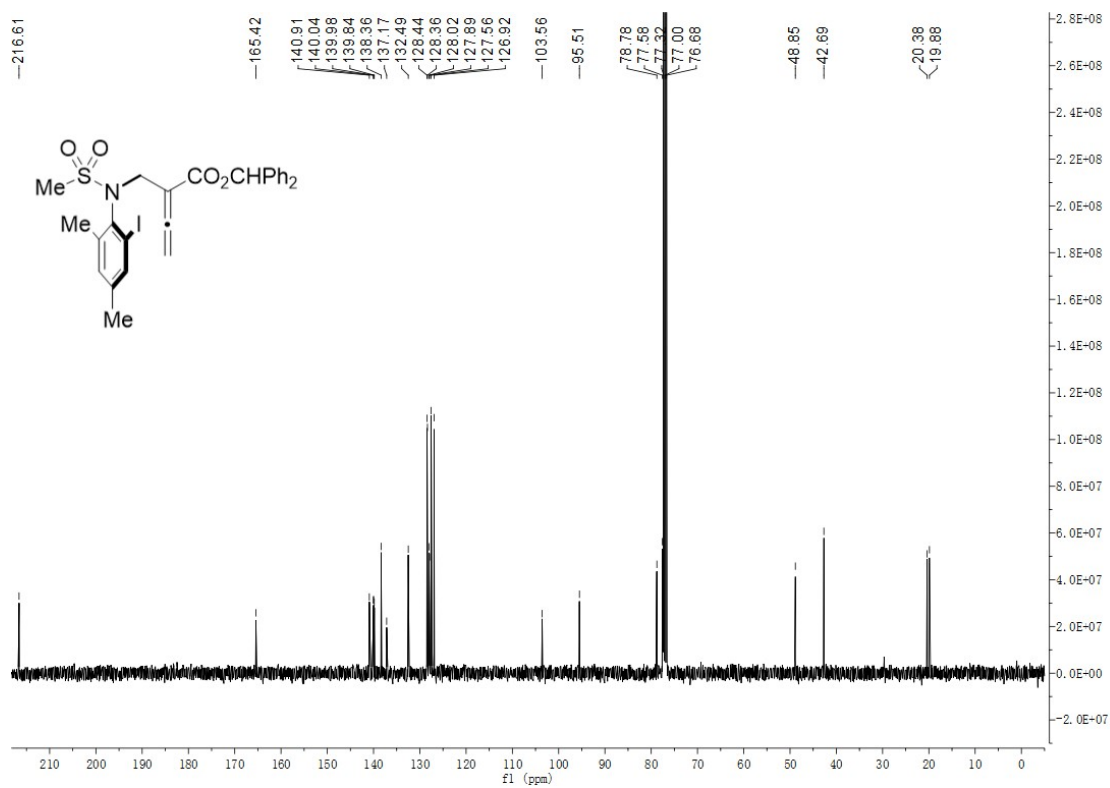
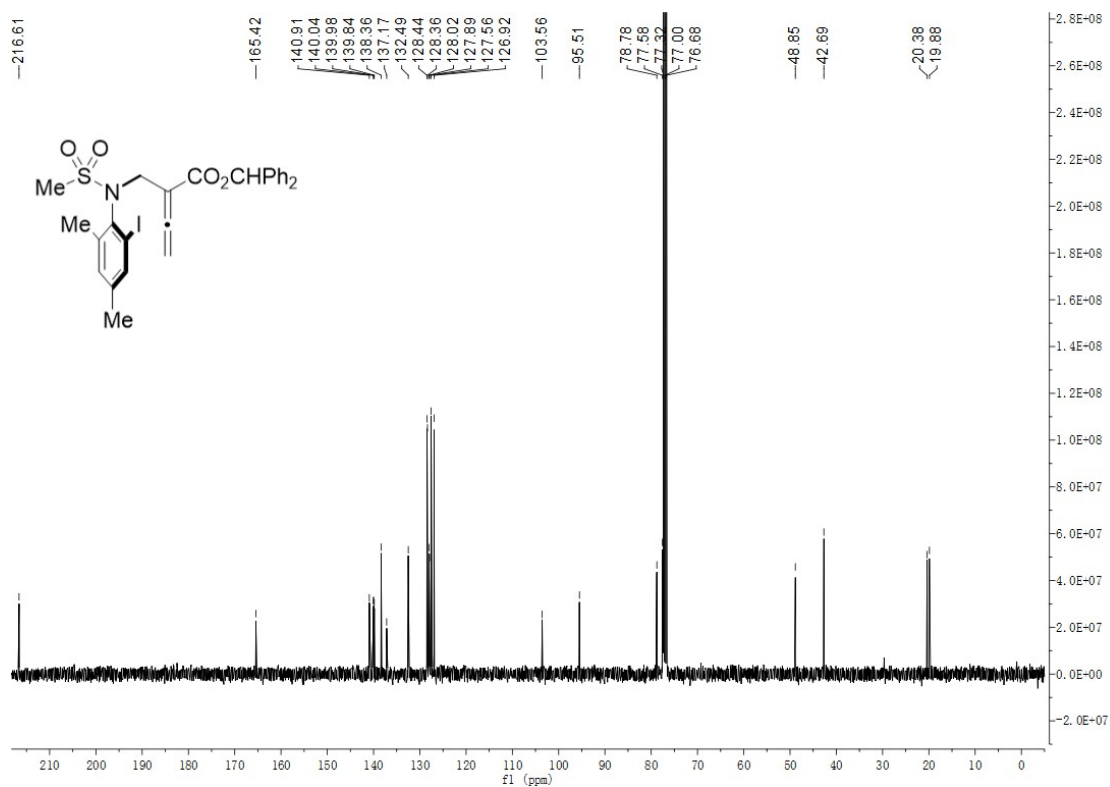
Compound 3t



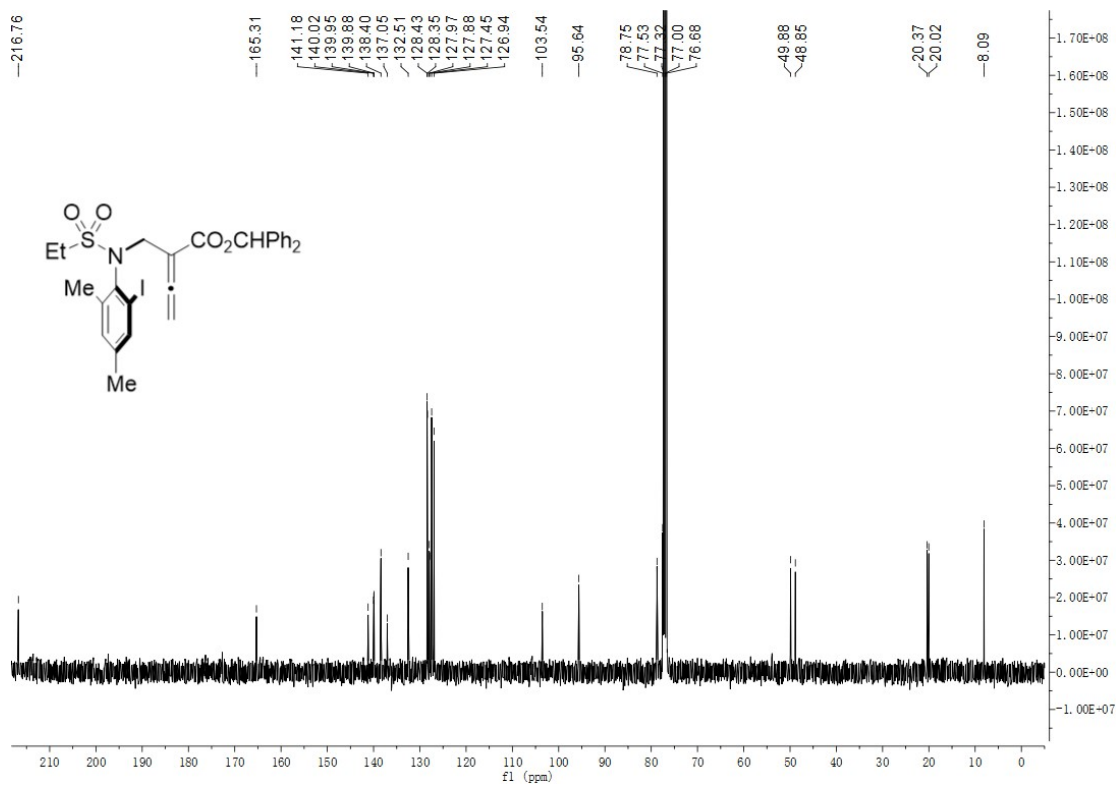
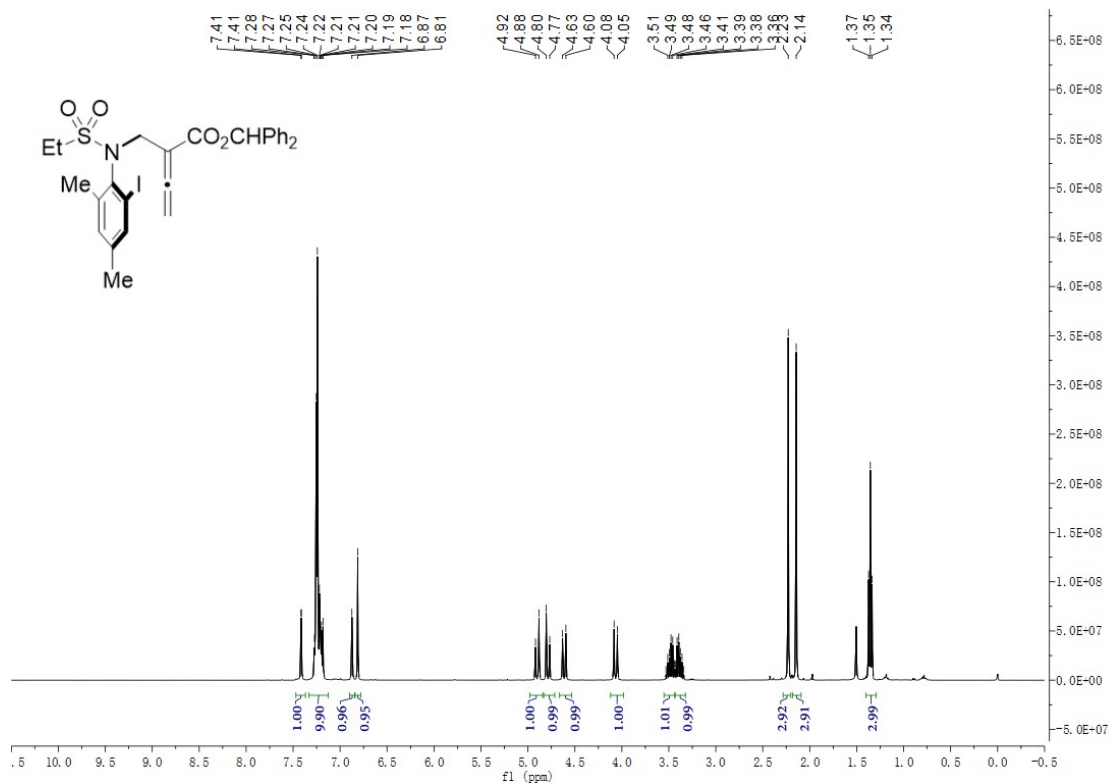
Compound 3u



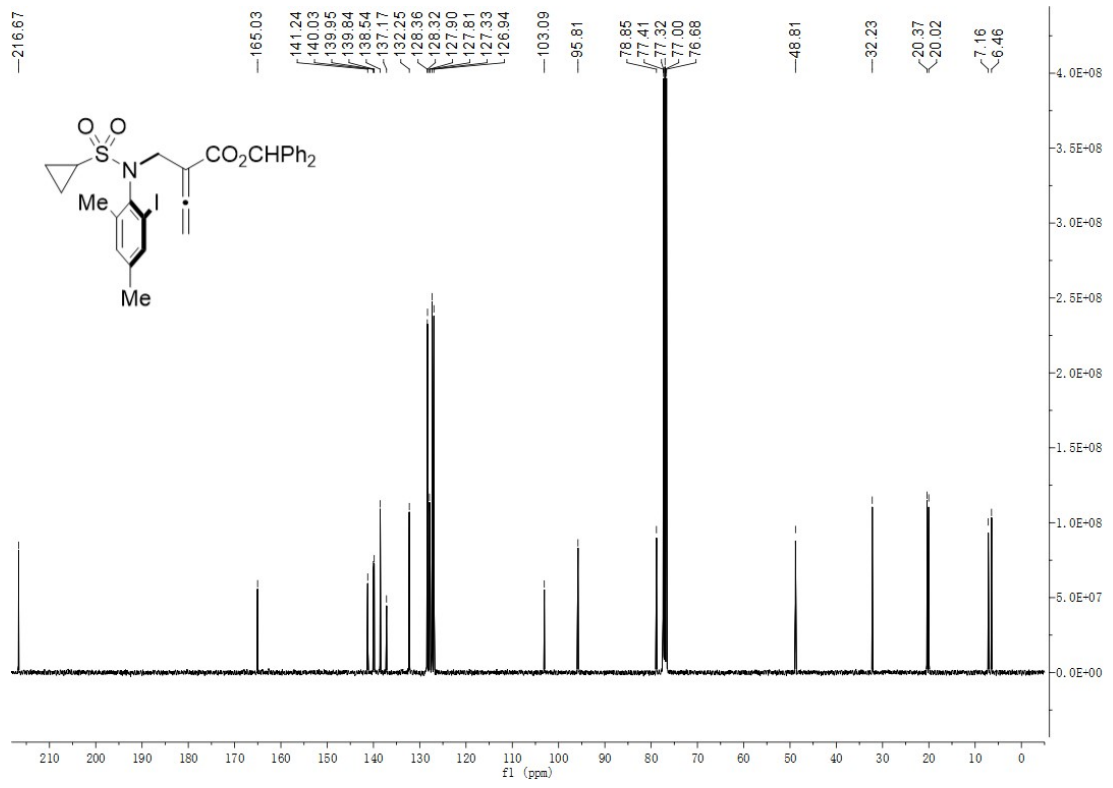
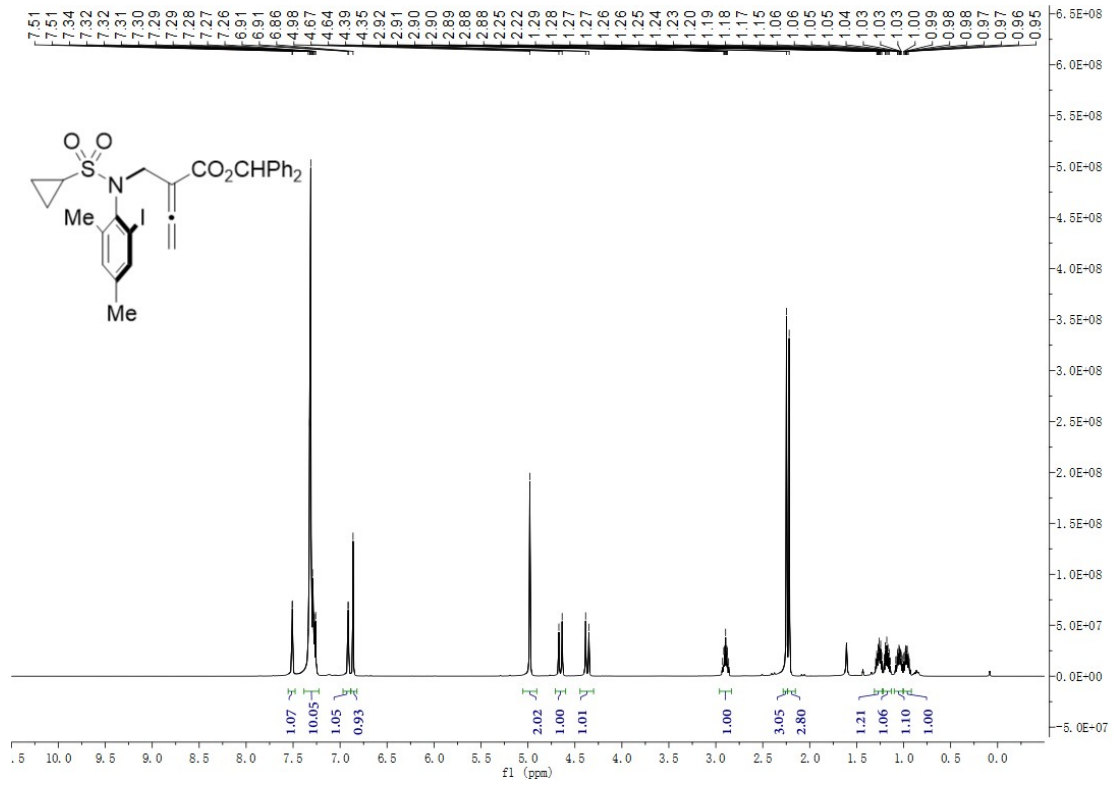
Compound 3v



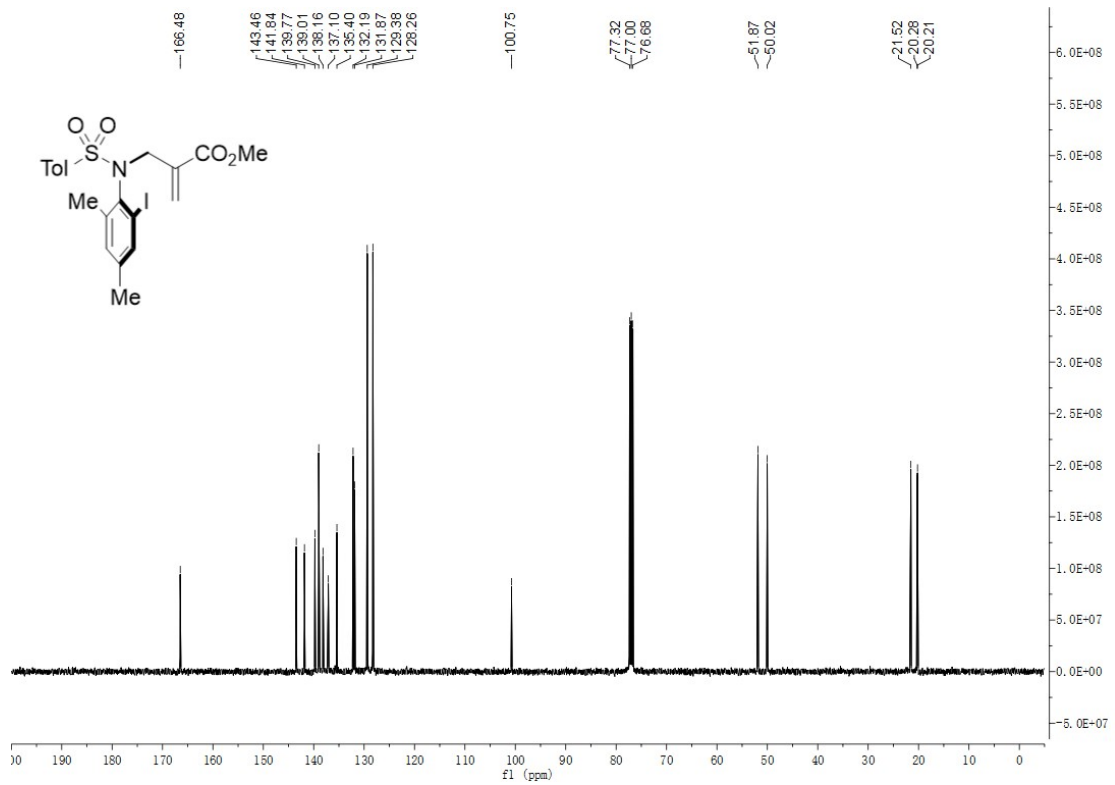
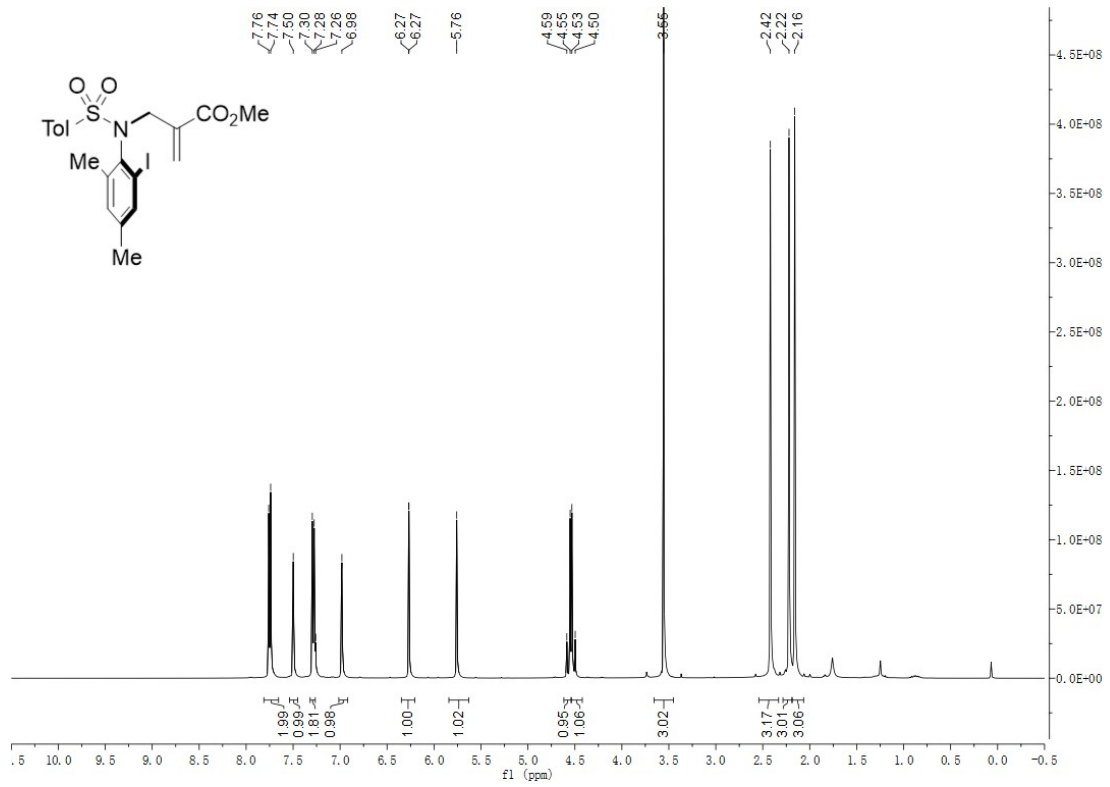
Compound 3w



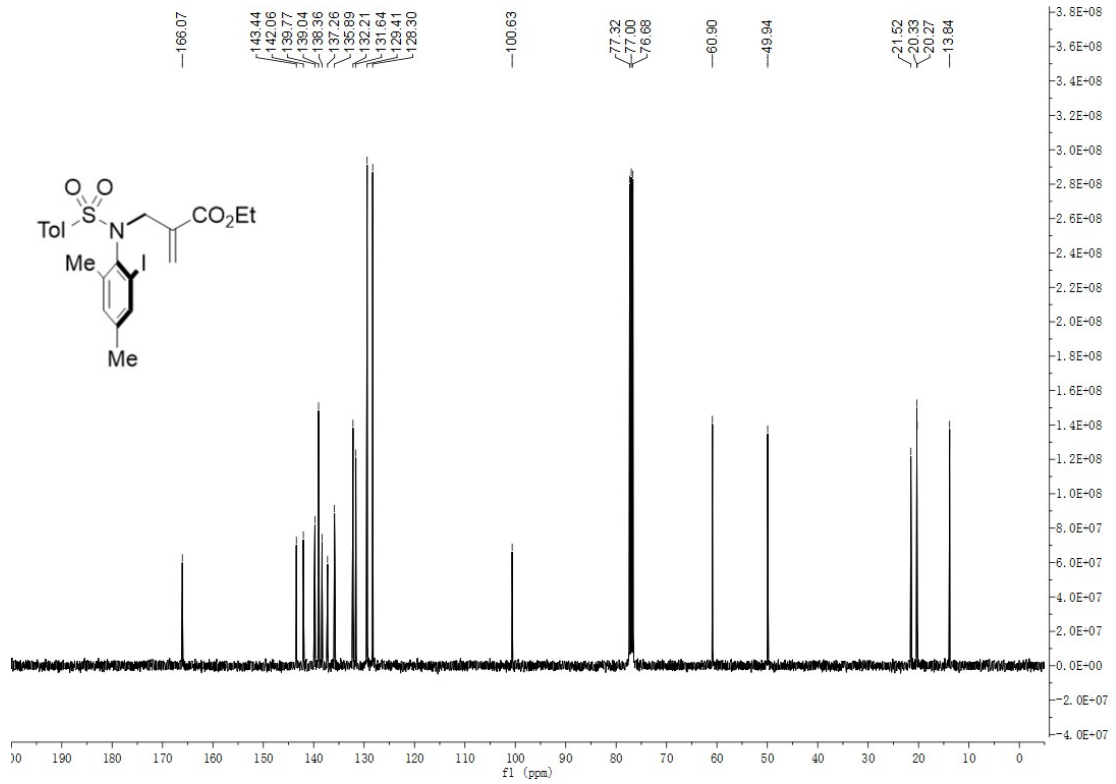
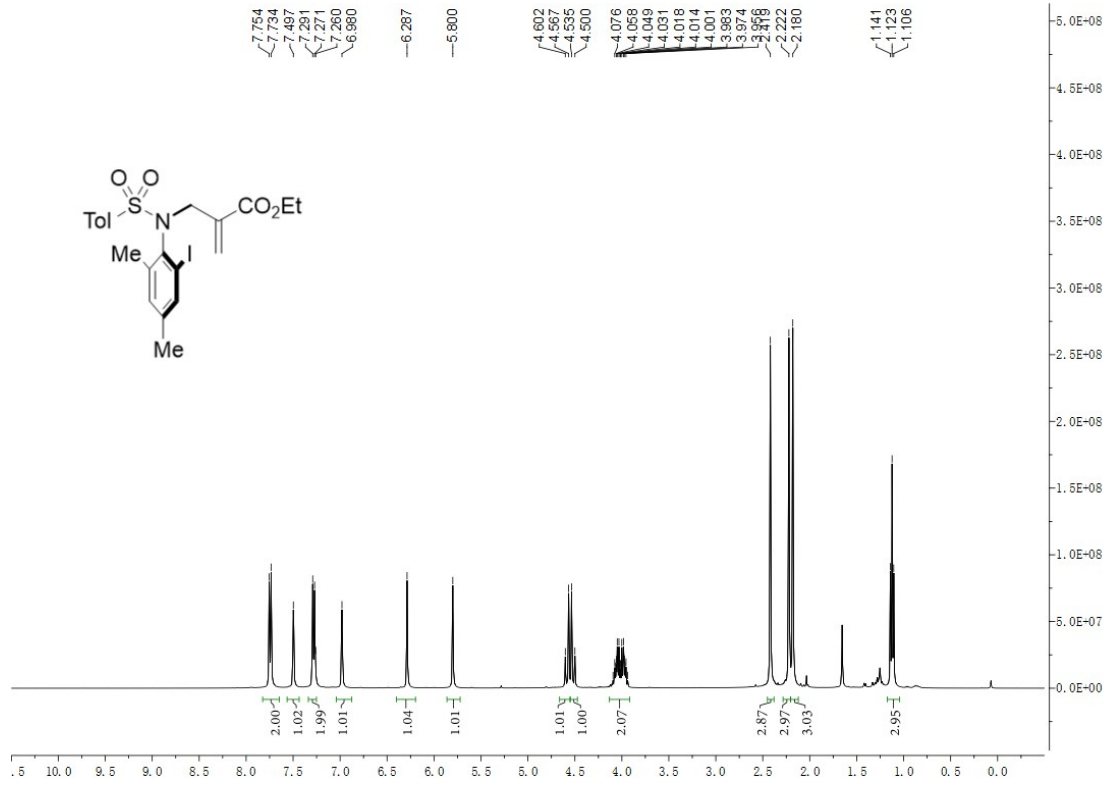
Compound 3x



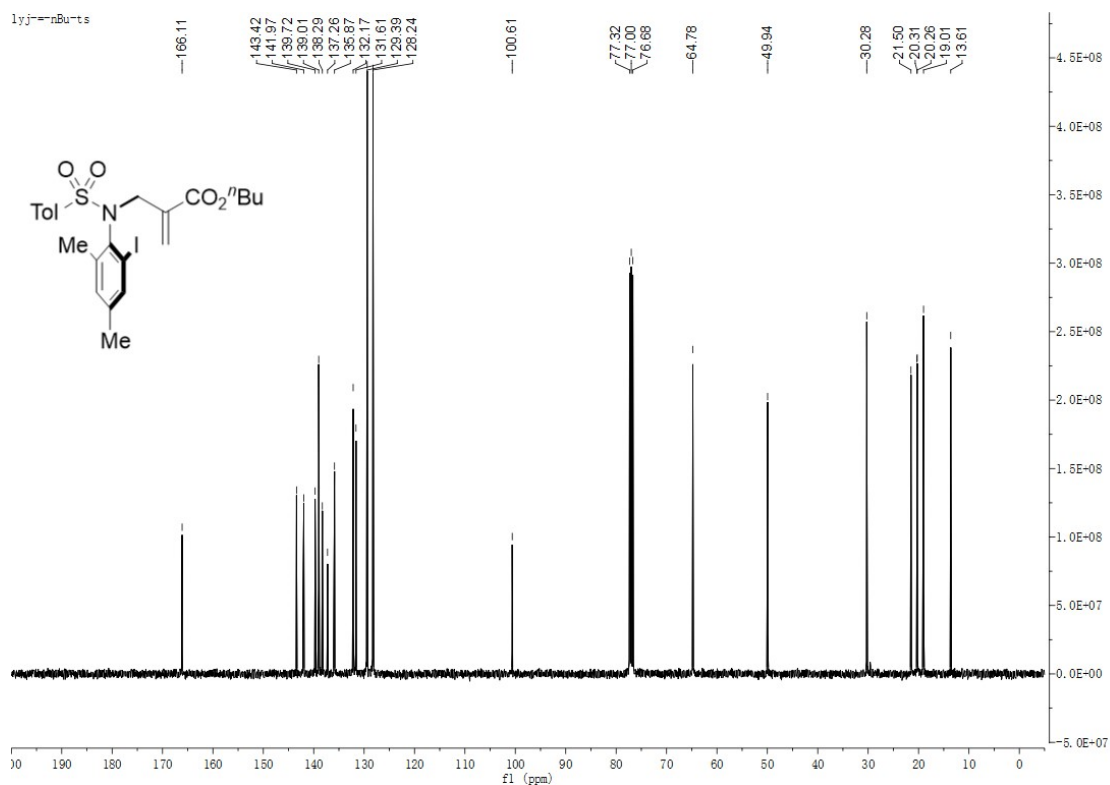
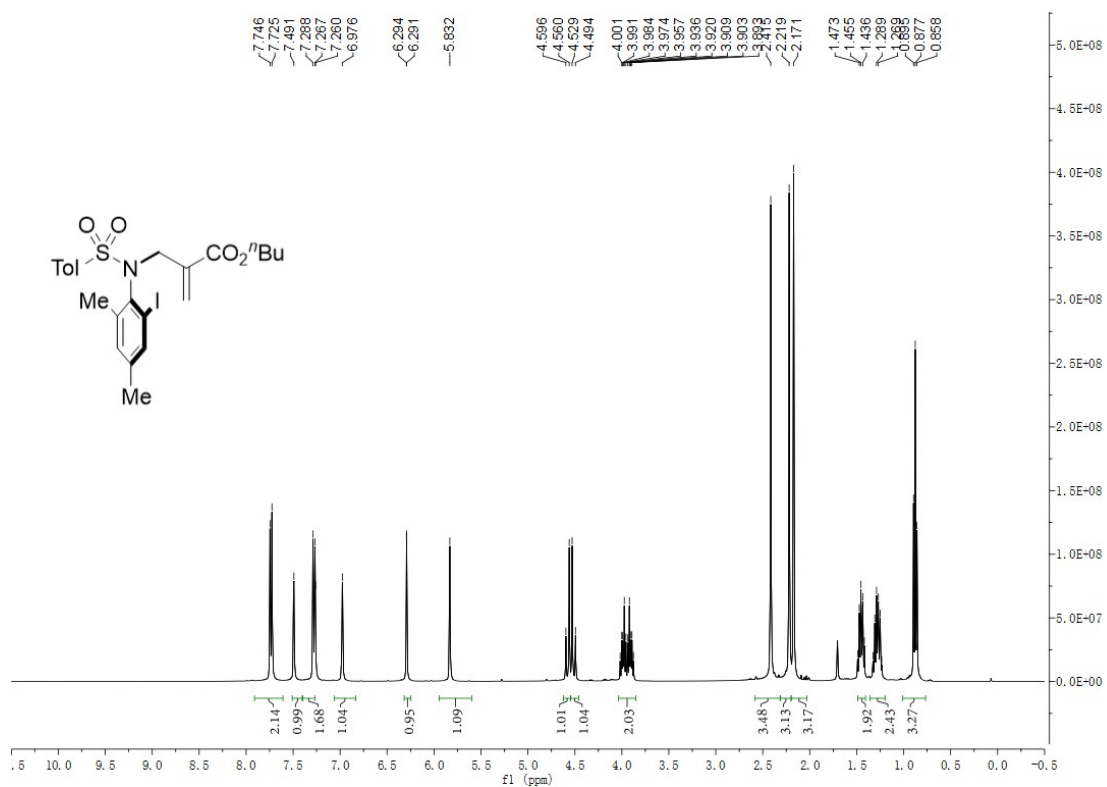
Compound 5a



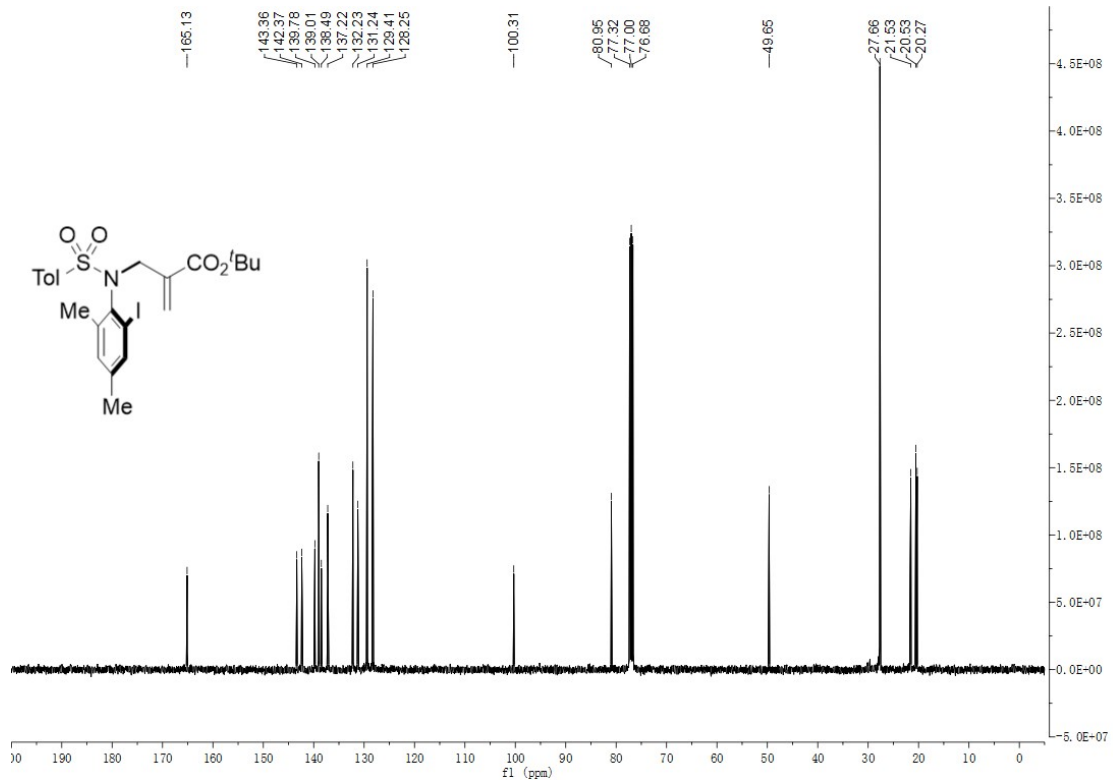
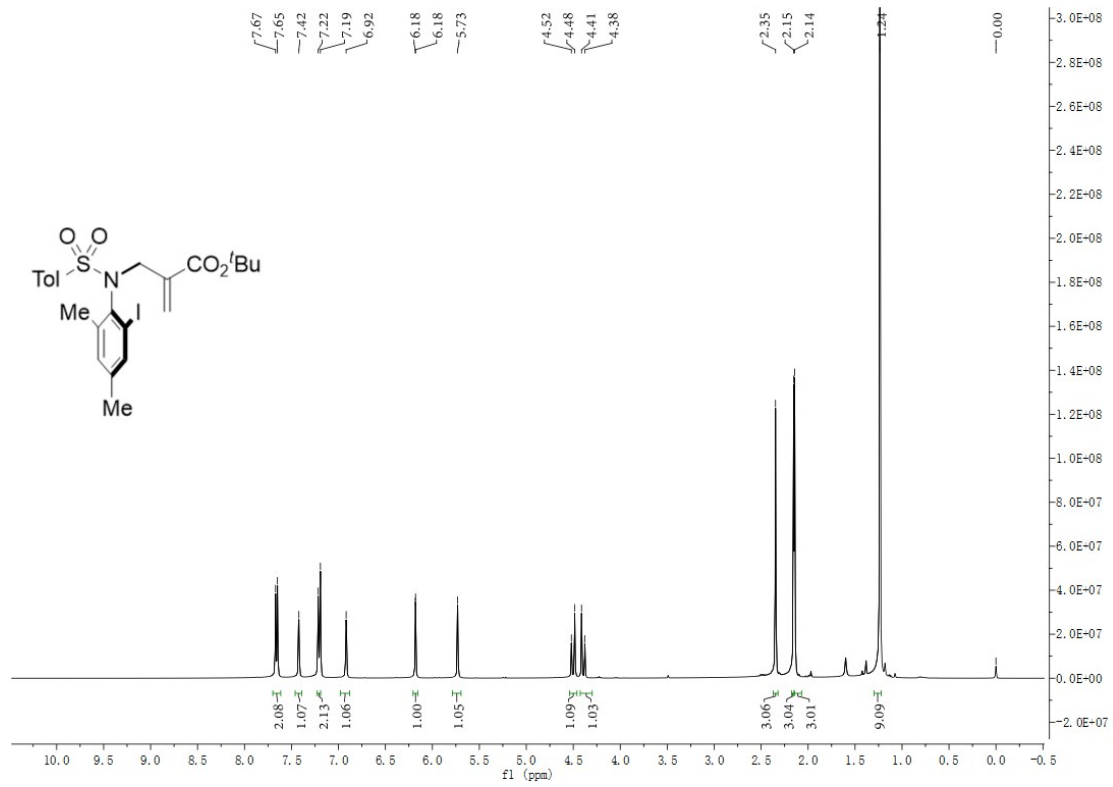
Compound **5b**



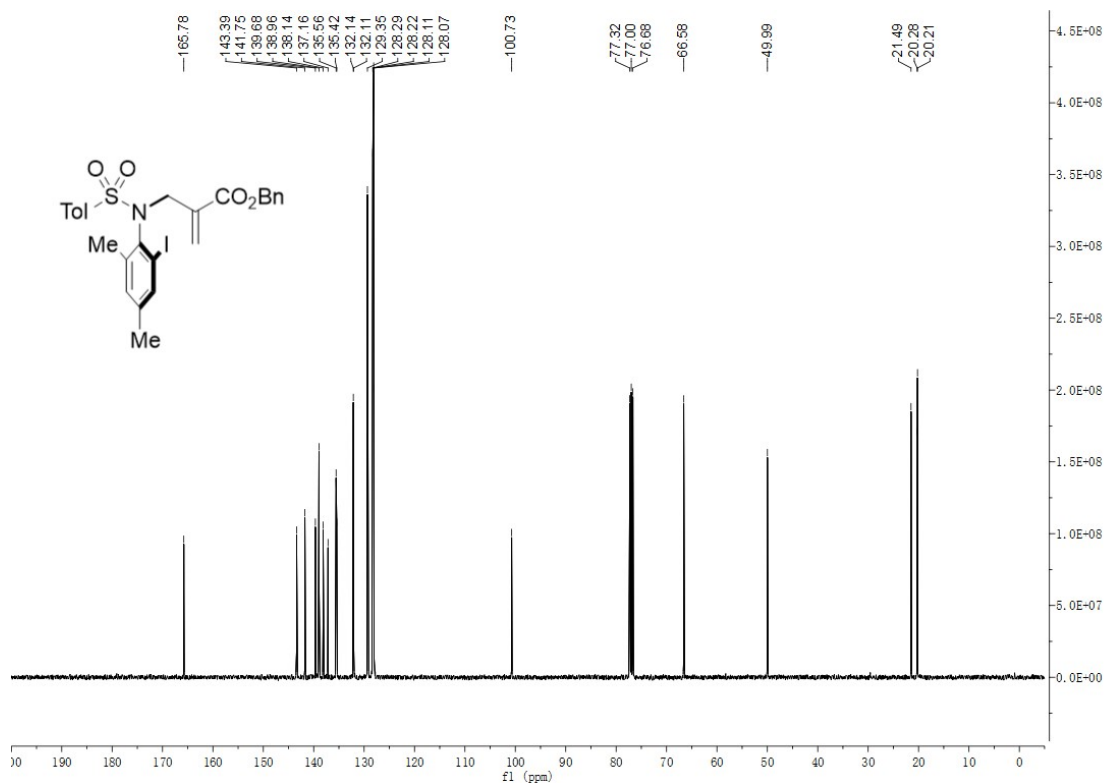
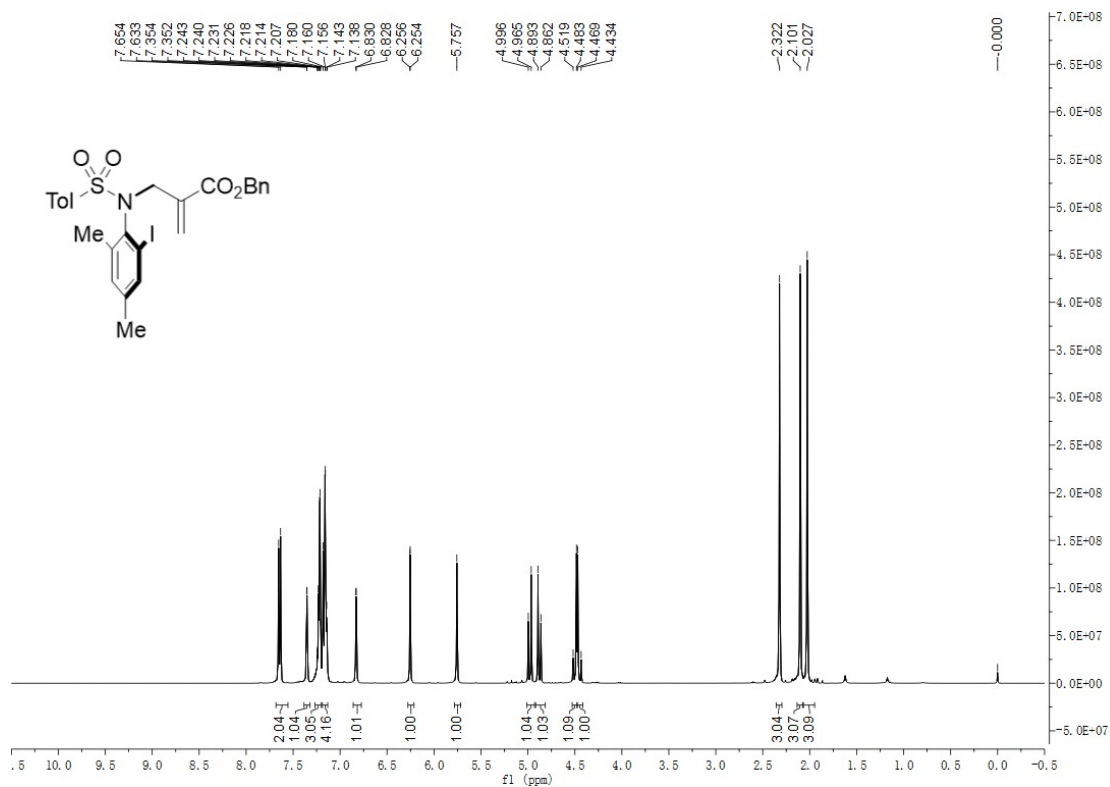
Compound 5c



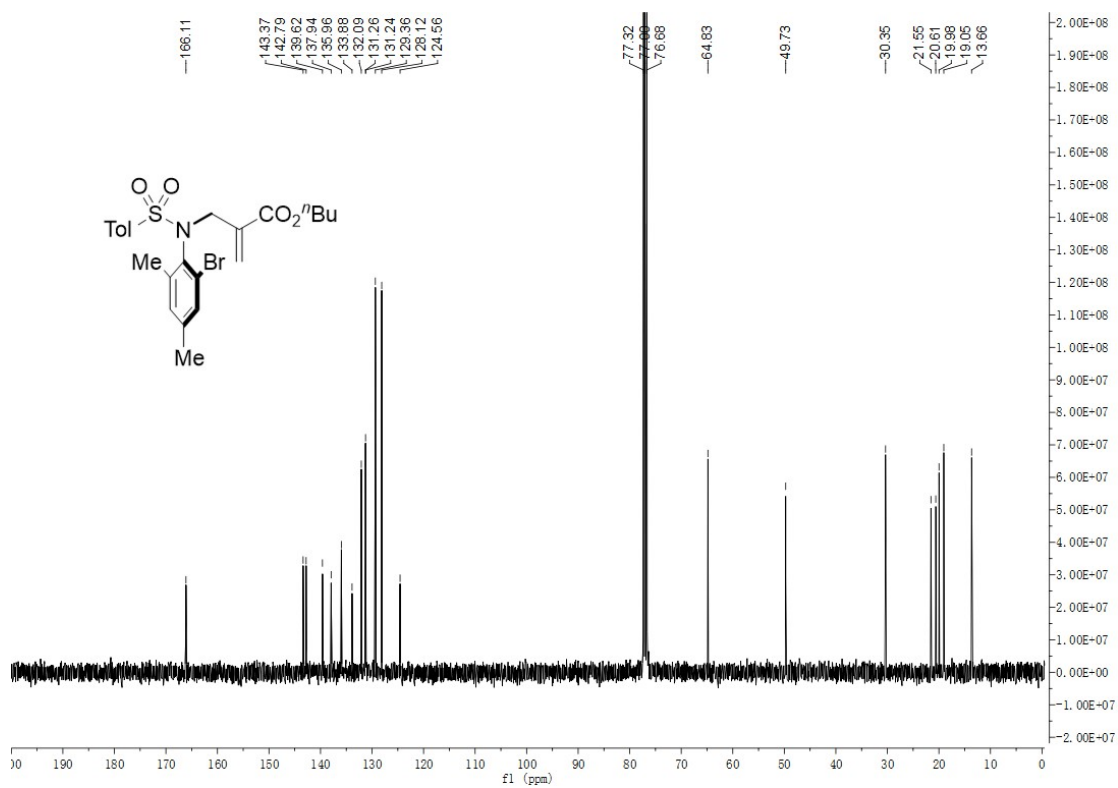
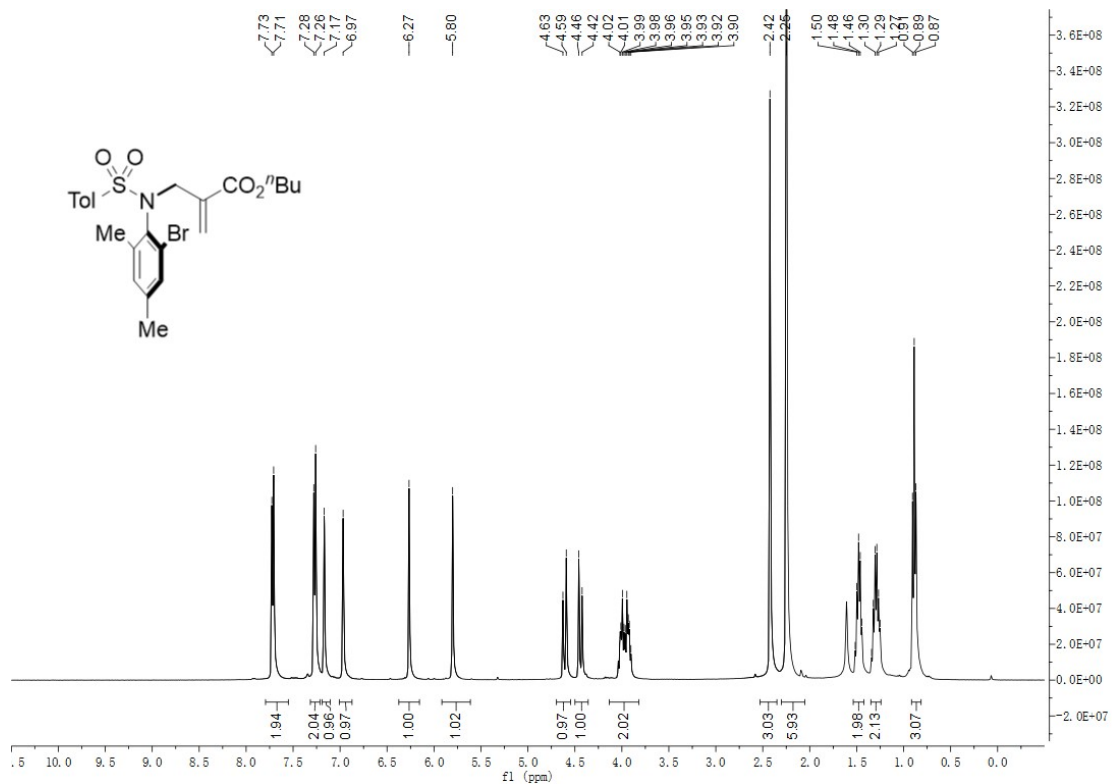
Compound 5d



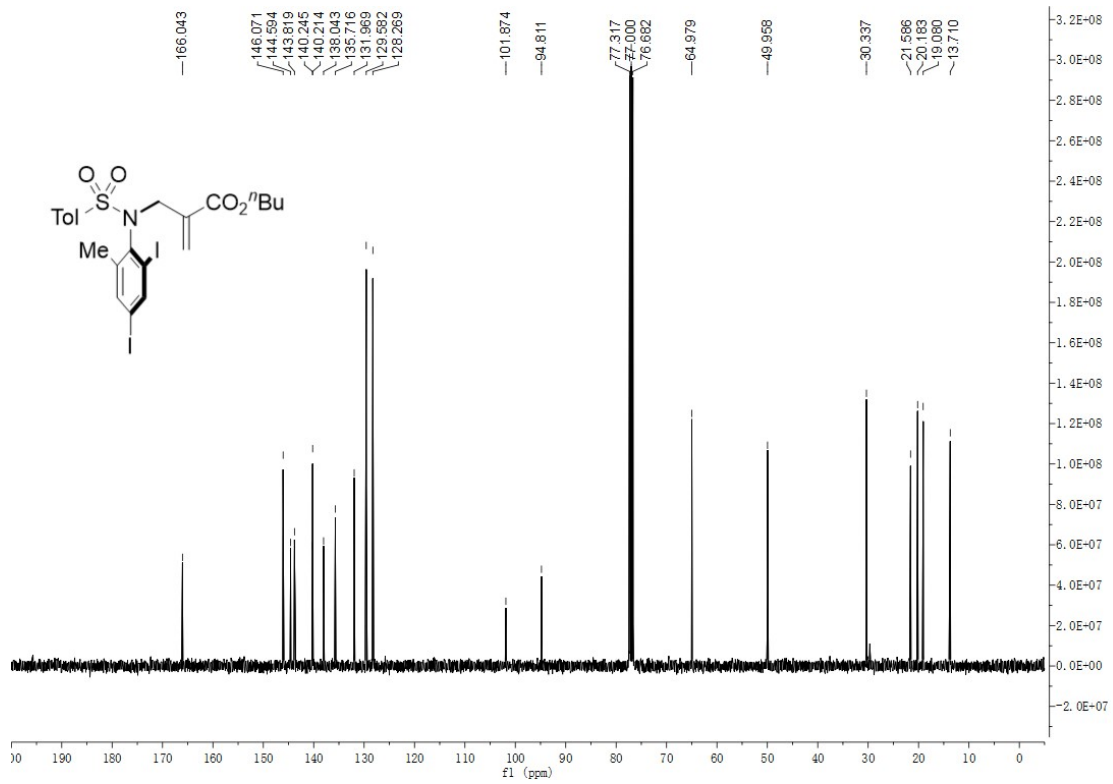
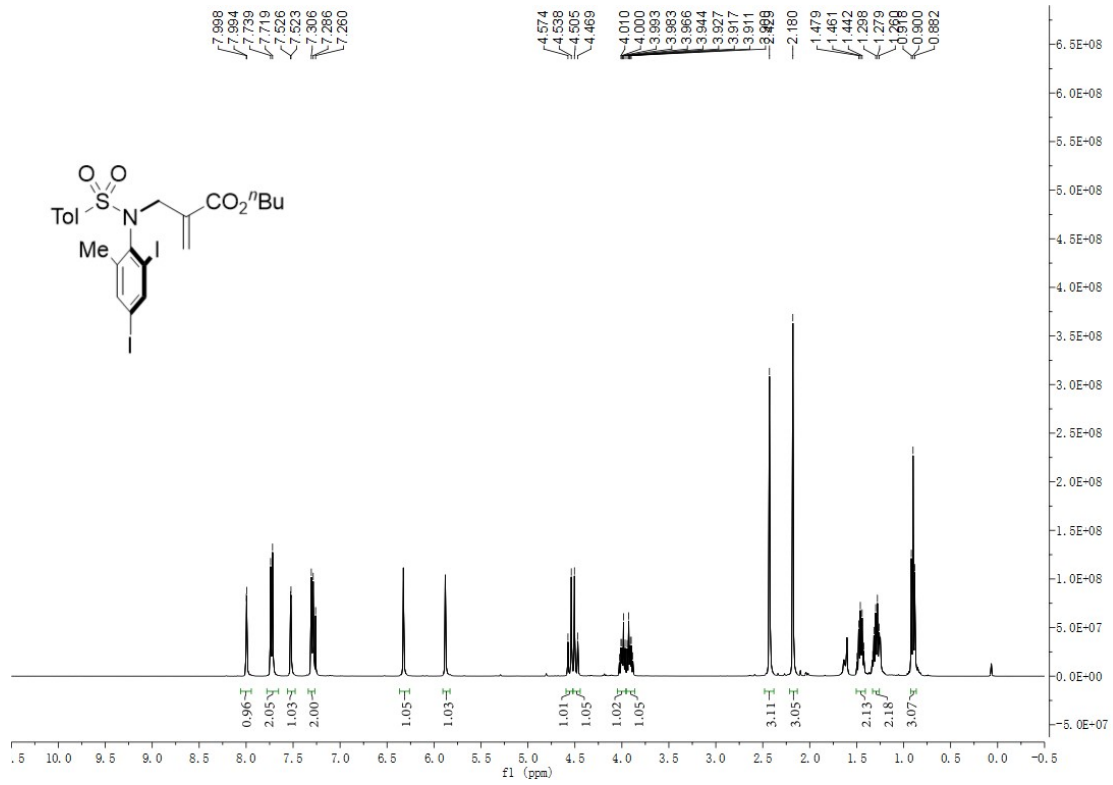
Compound 5e



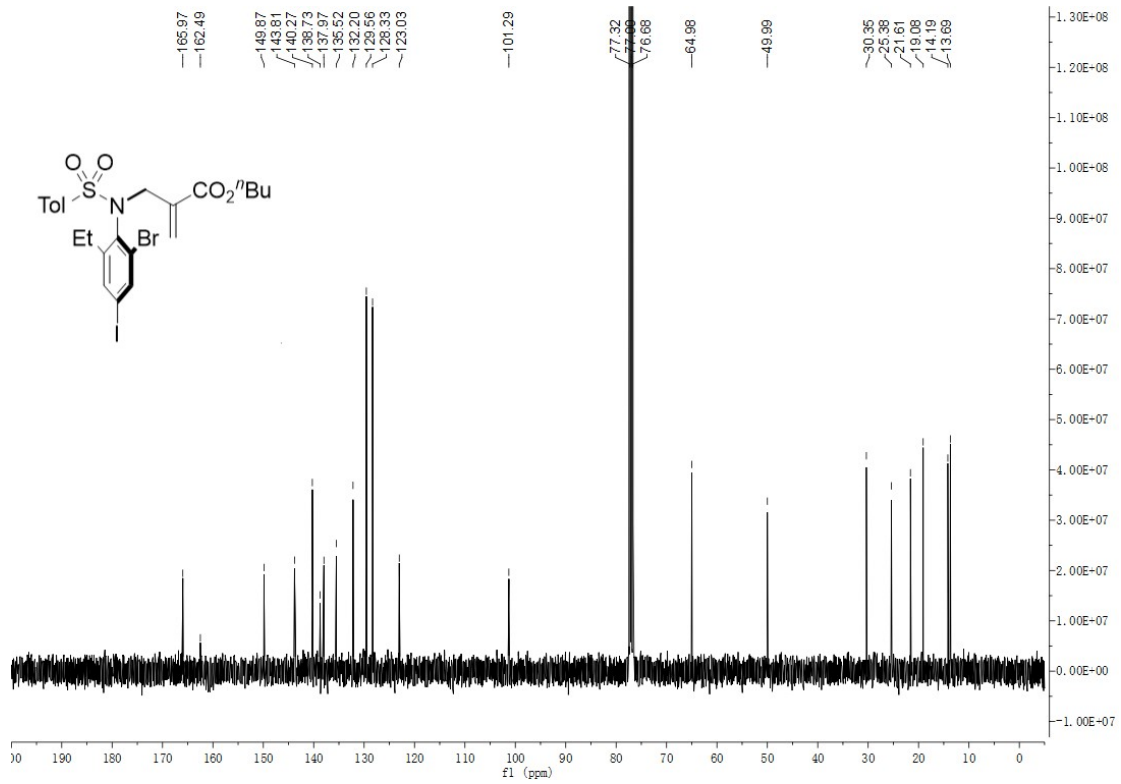
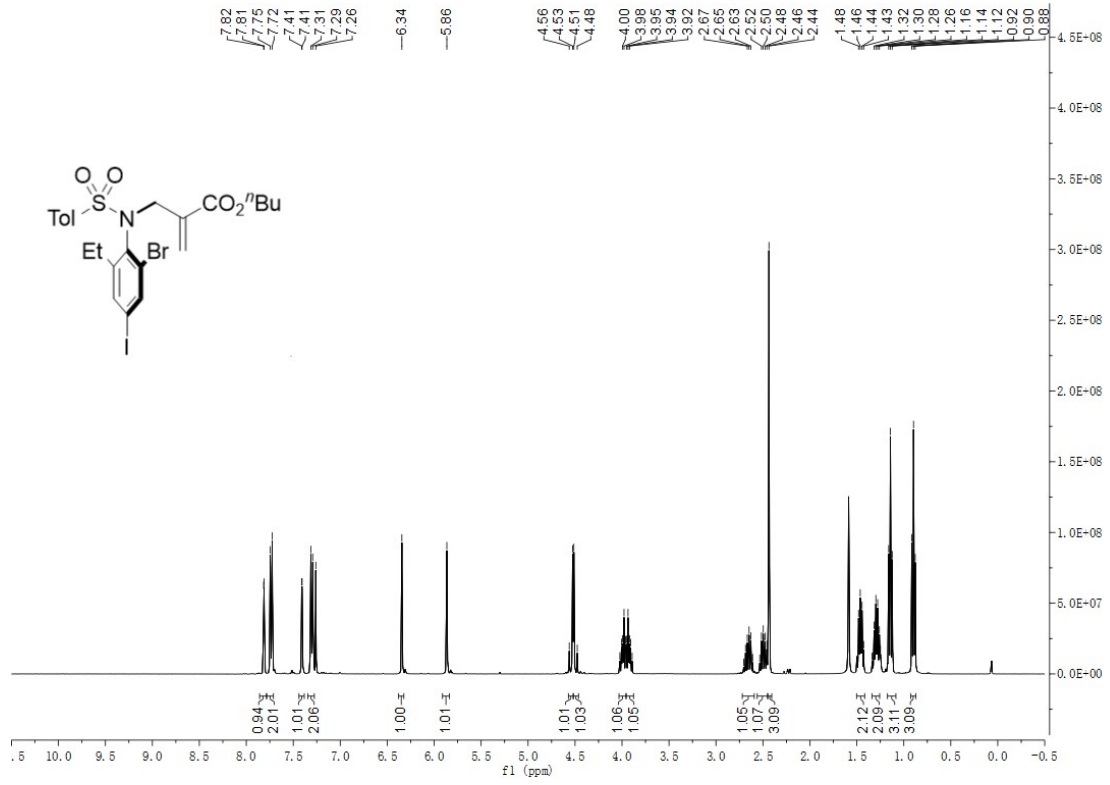
Compound **5f**



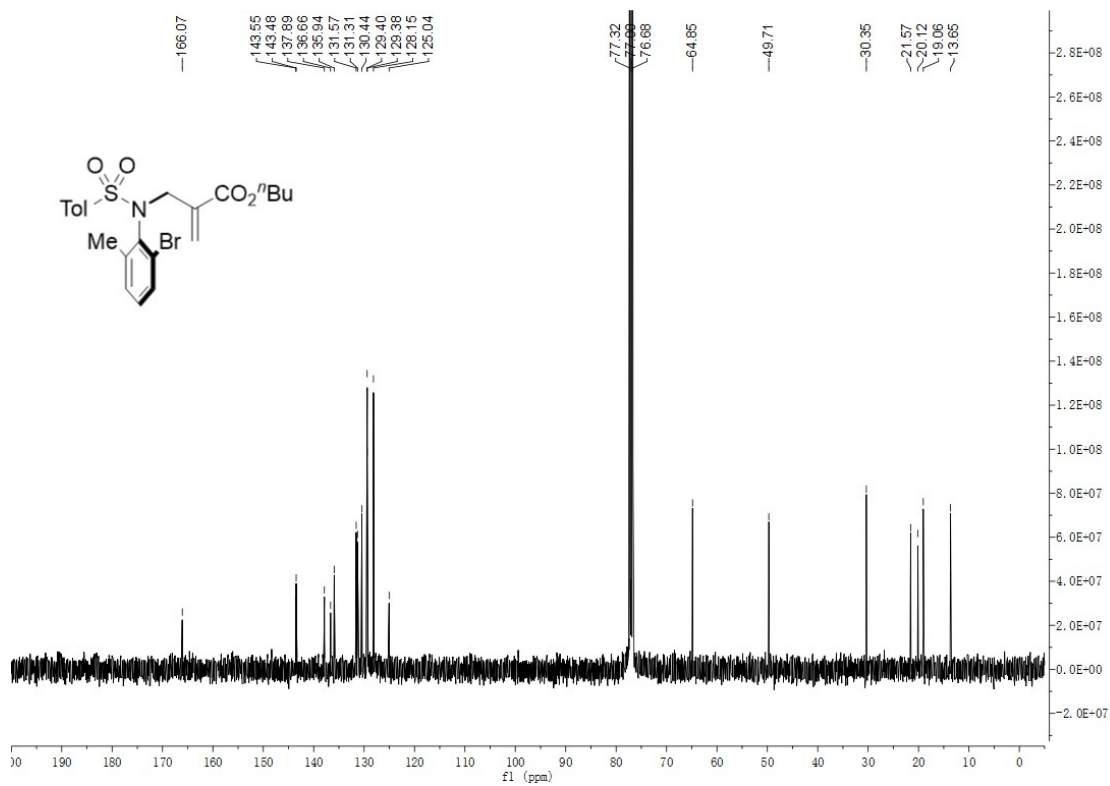
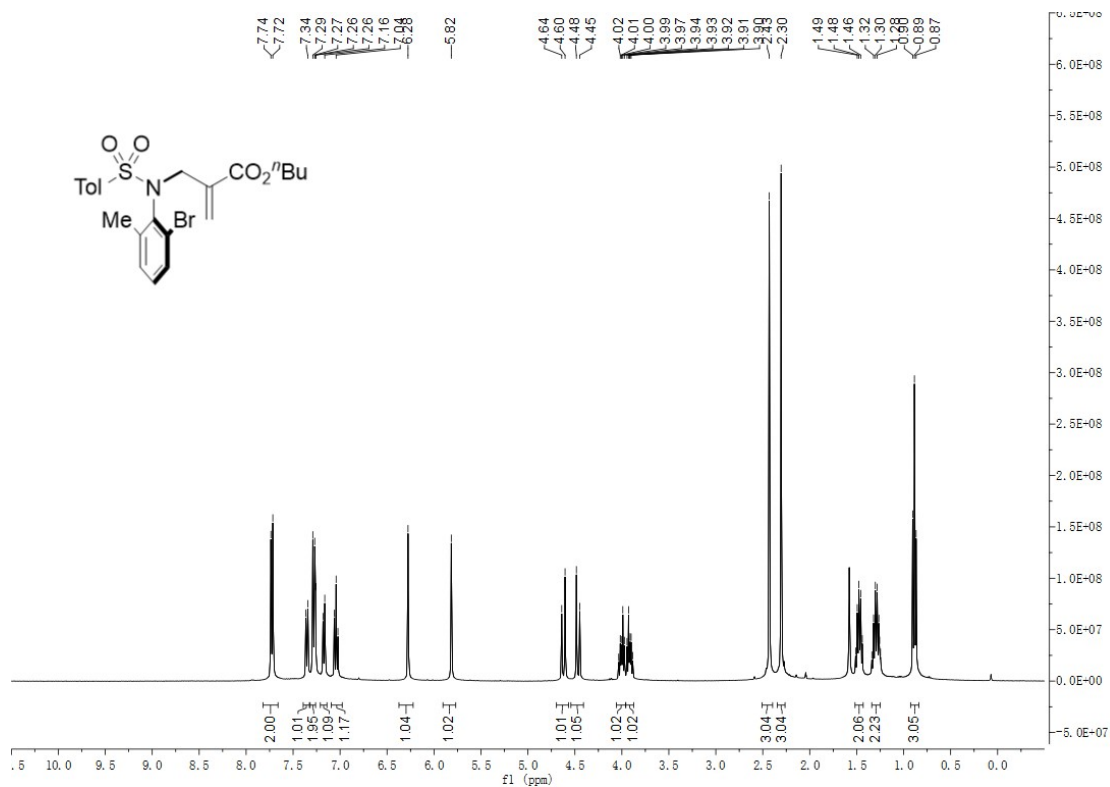
Compound 5g



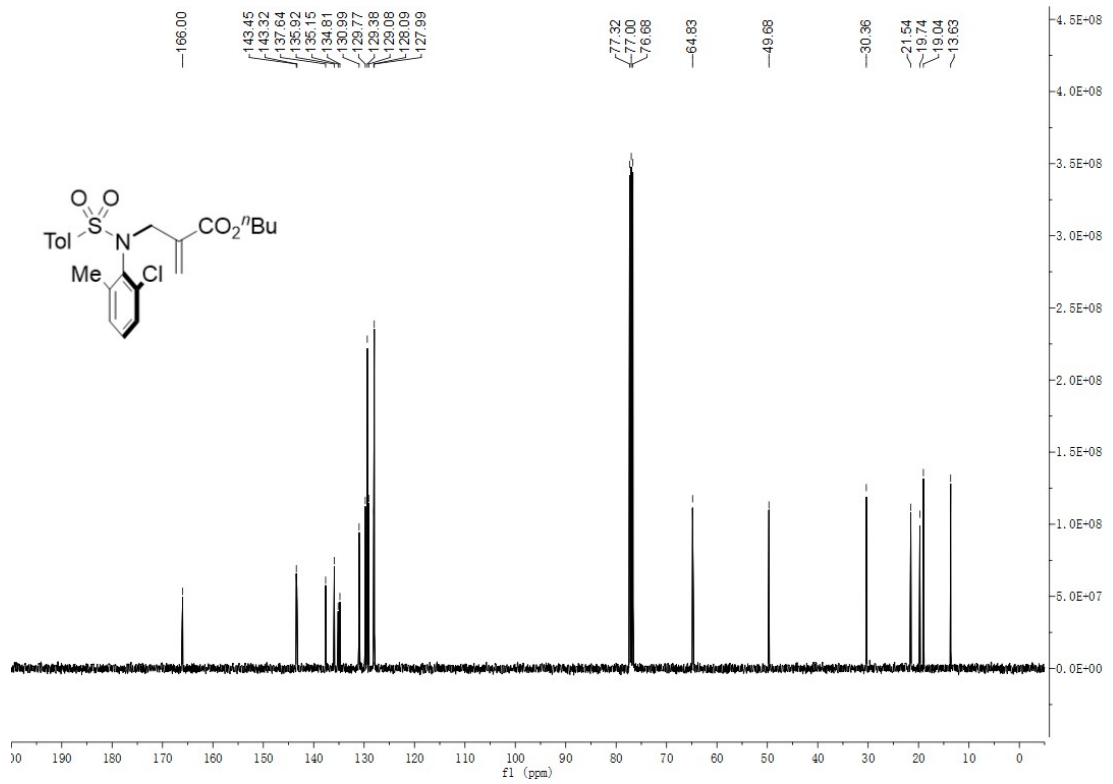
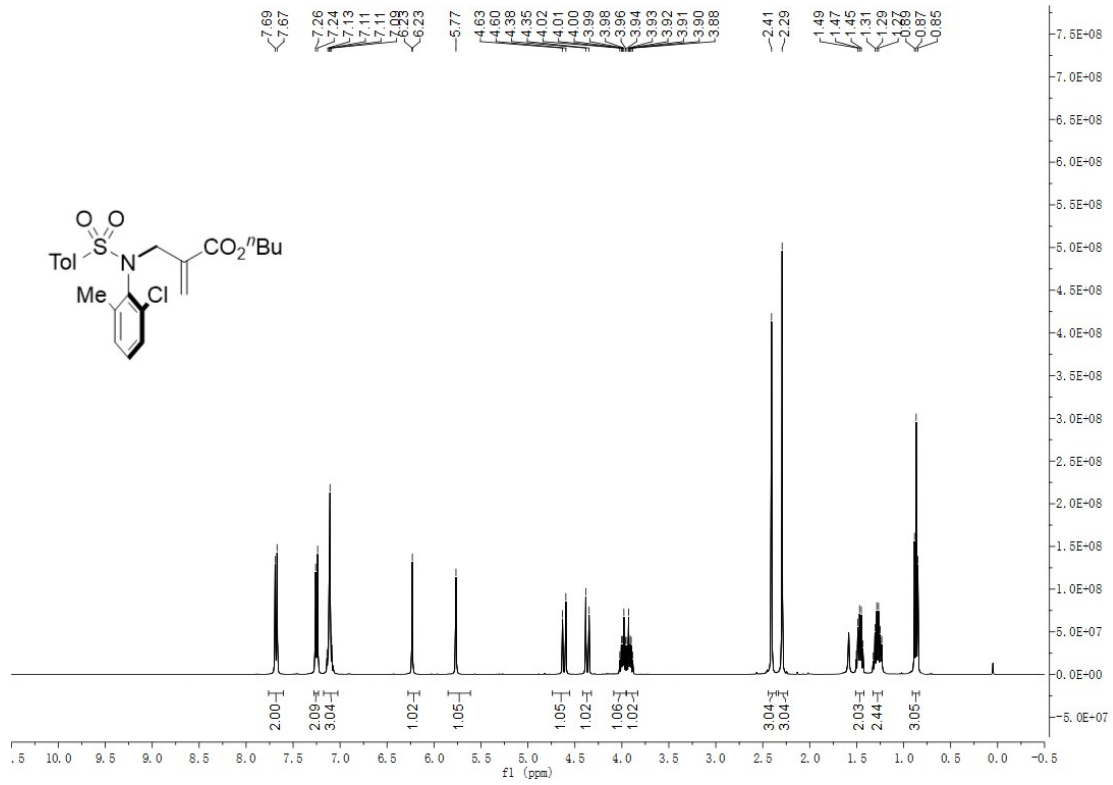
Compound 5h



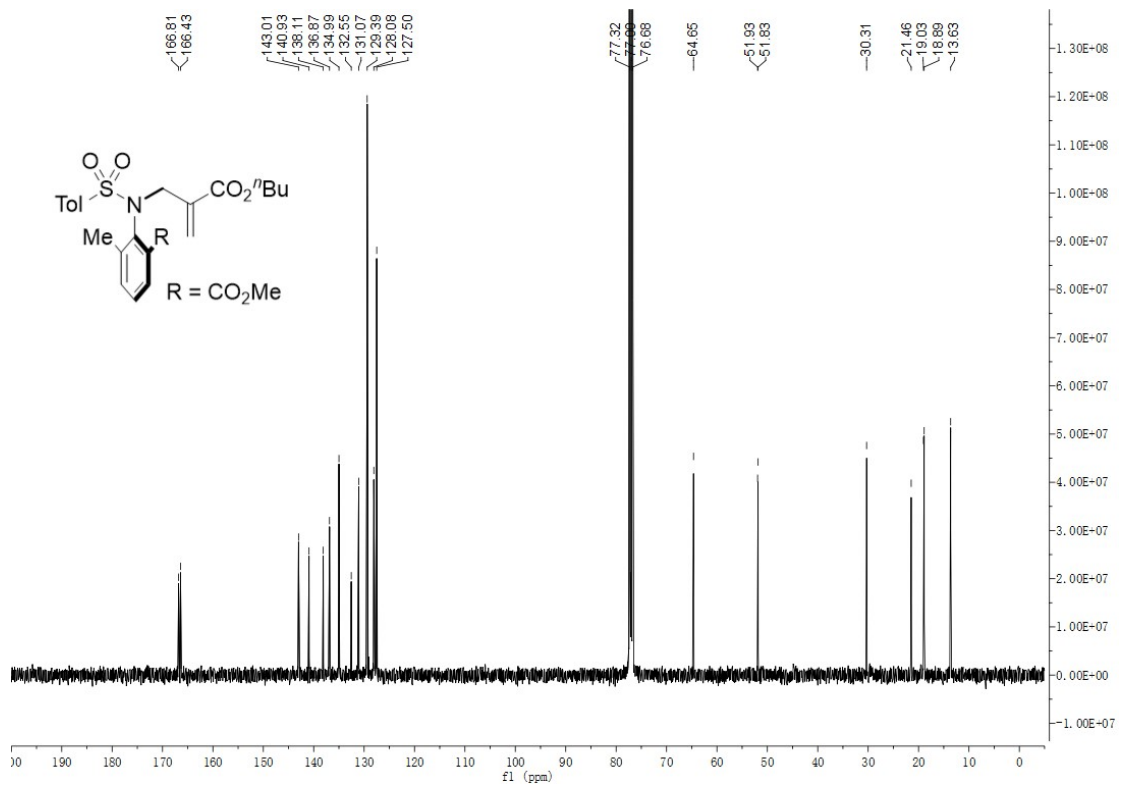
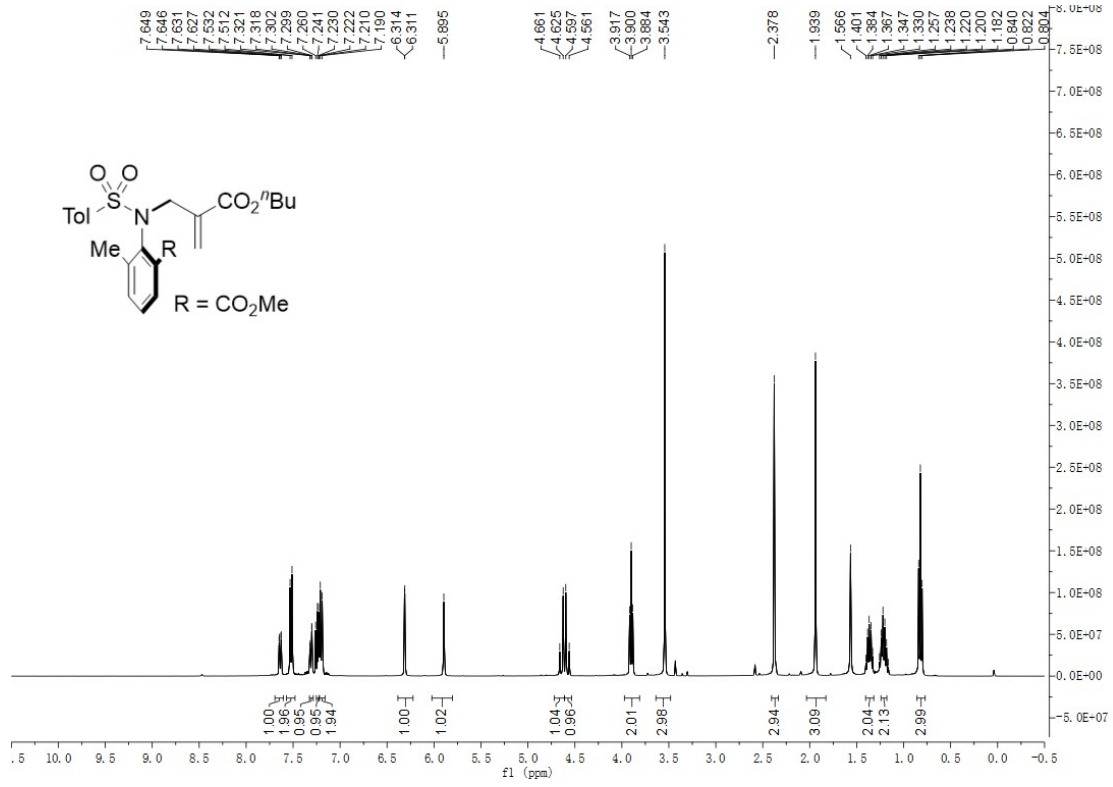
Compound **5i**



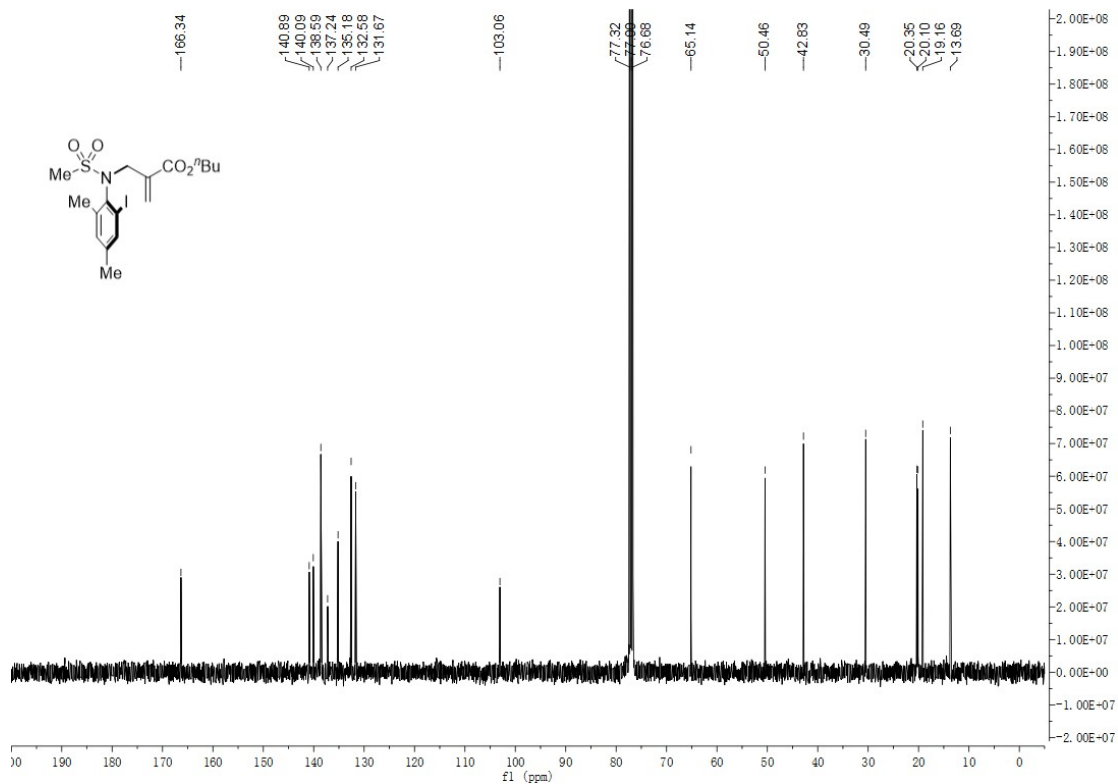
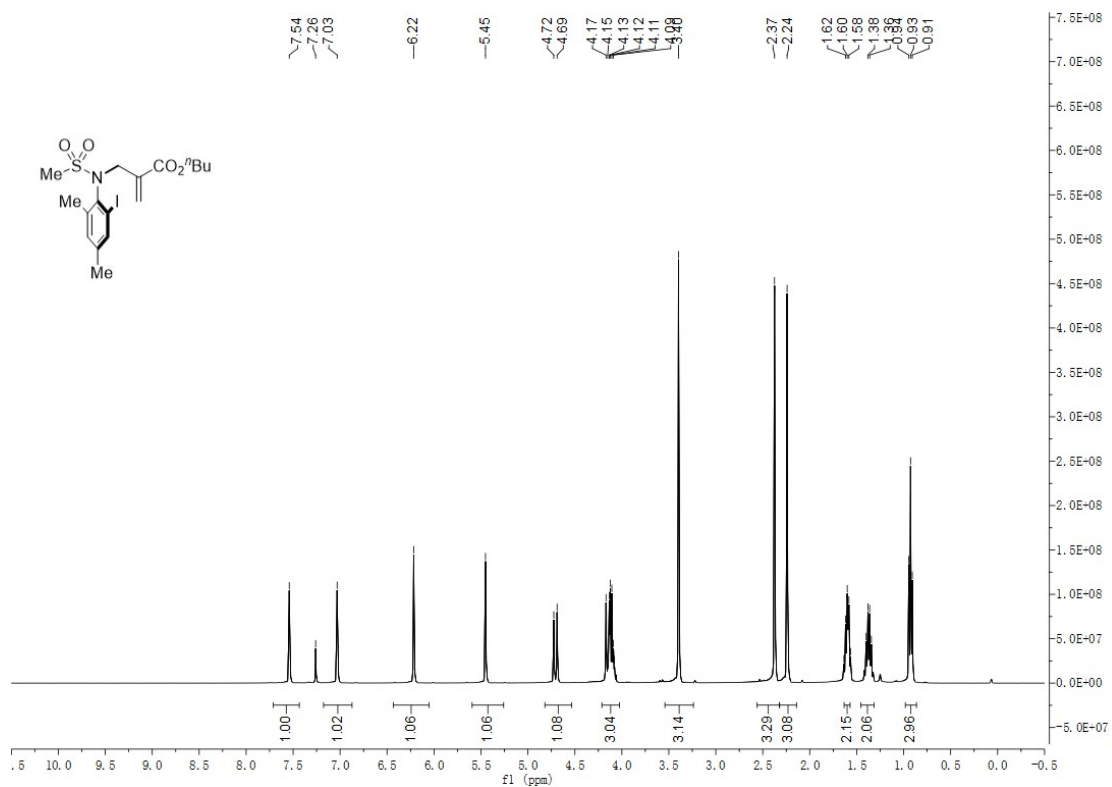
Compound 5j



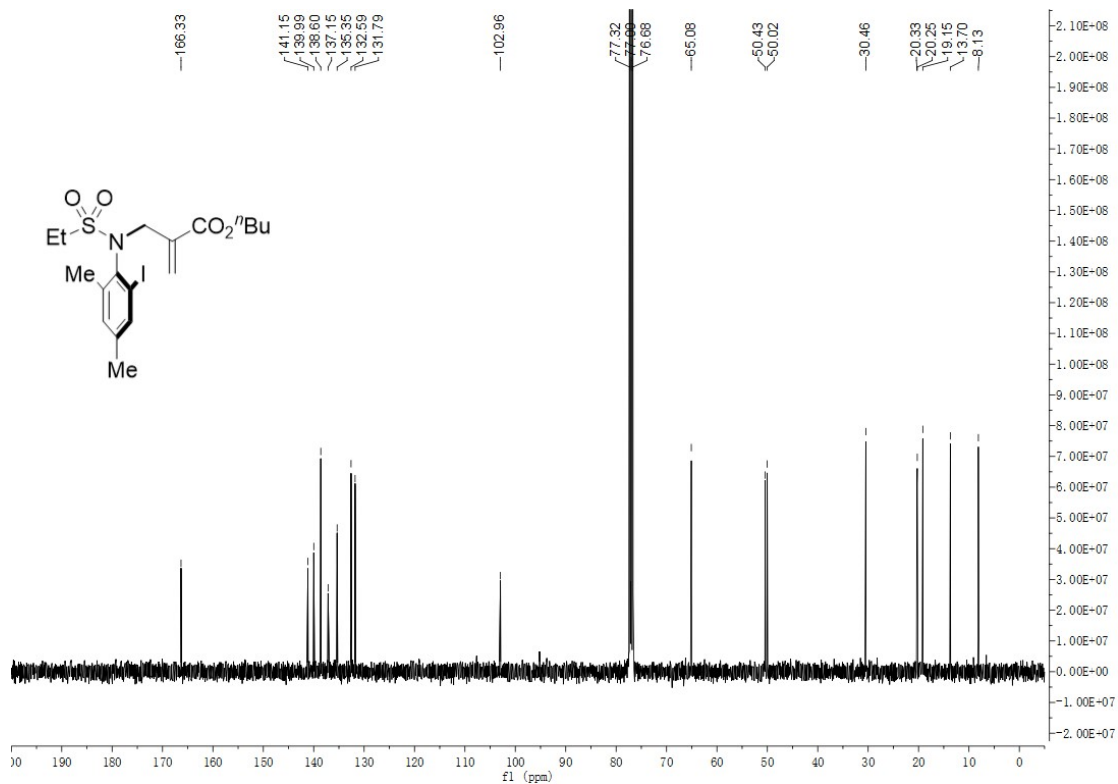
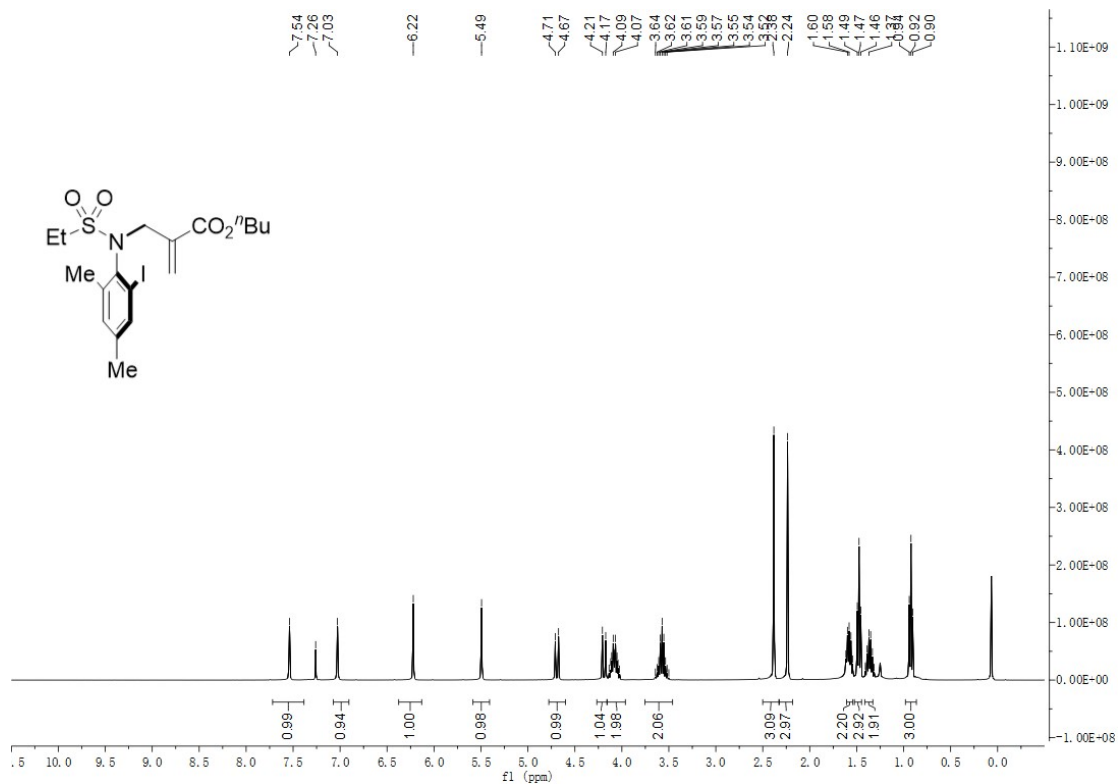
Compound 5k



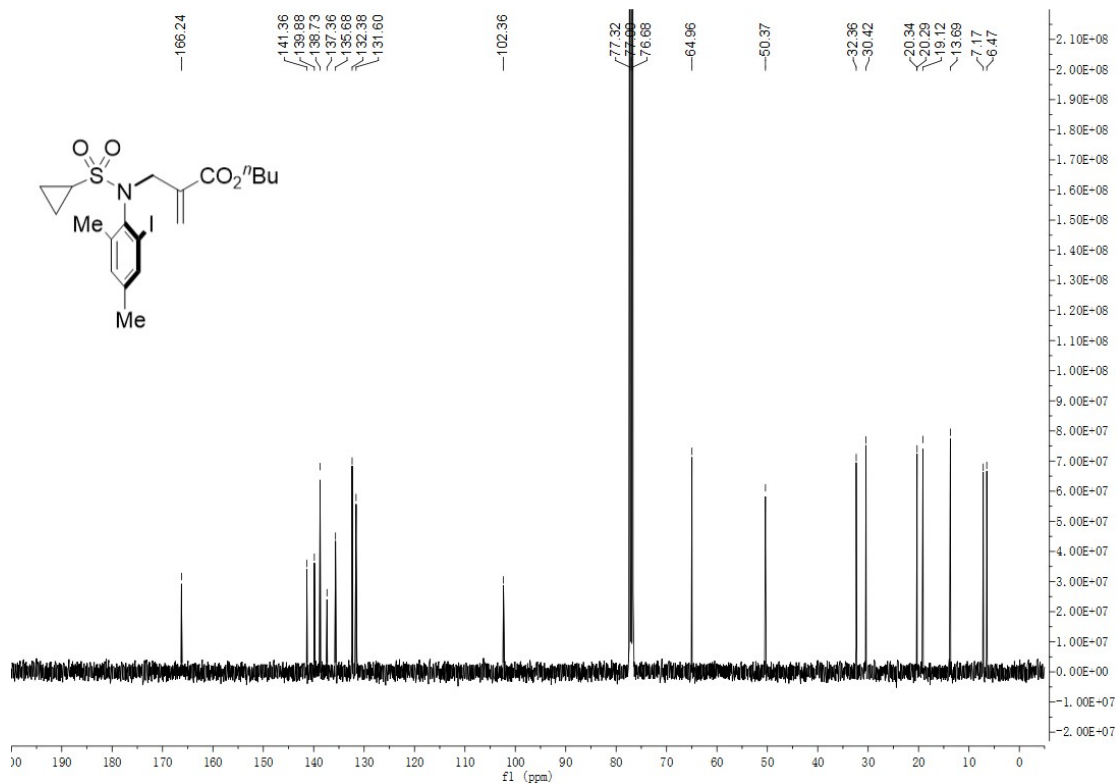
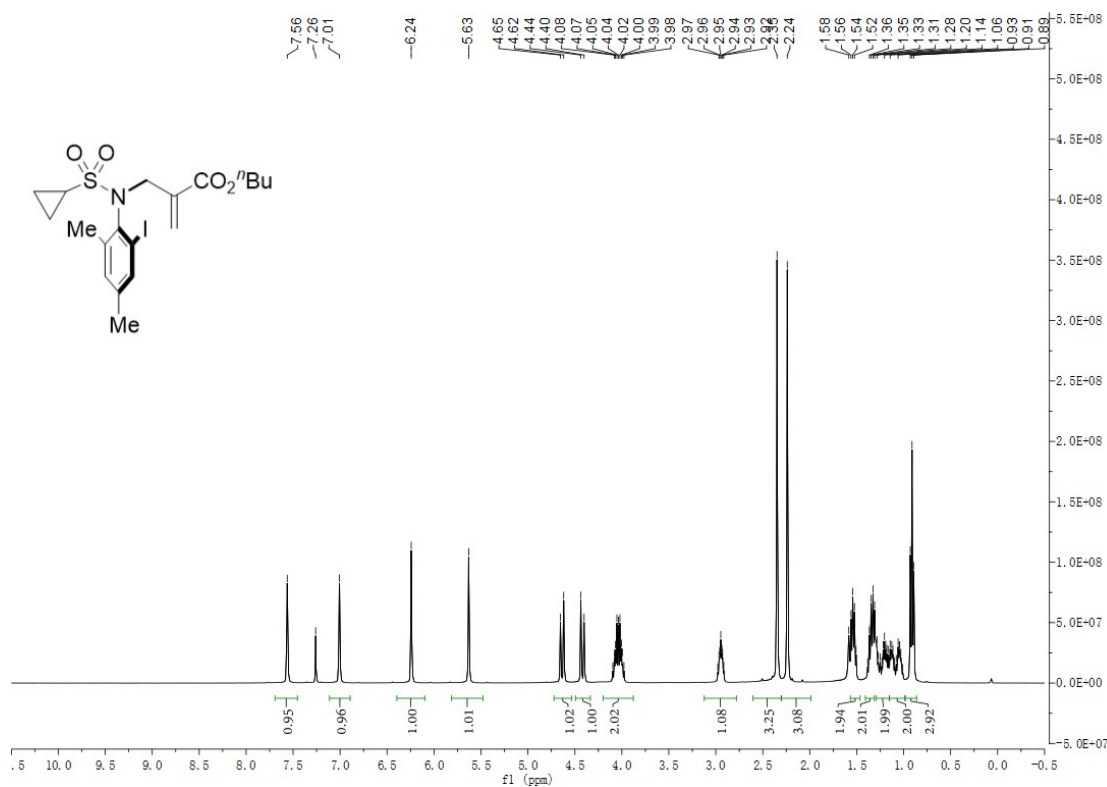
Compound 51



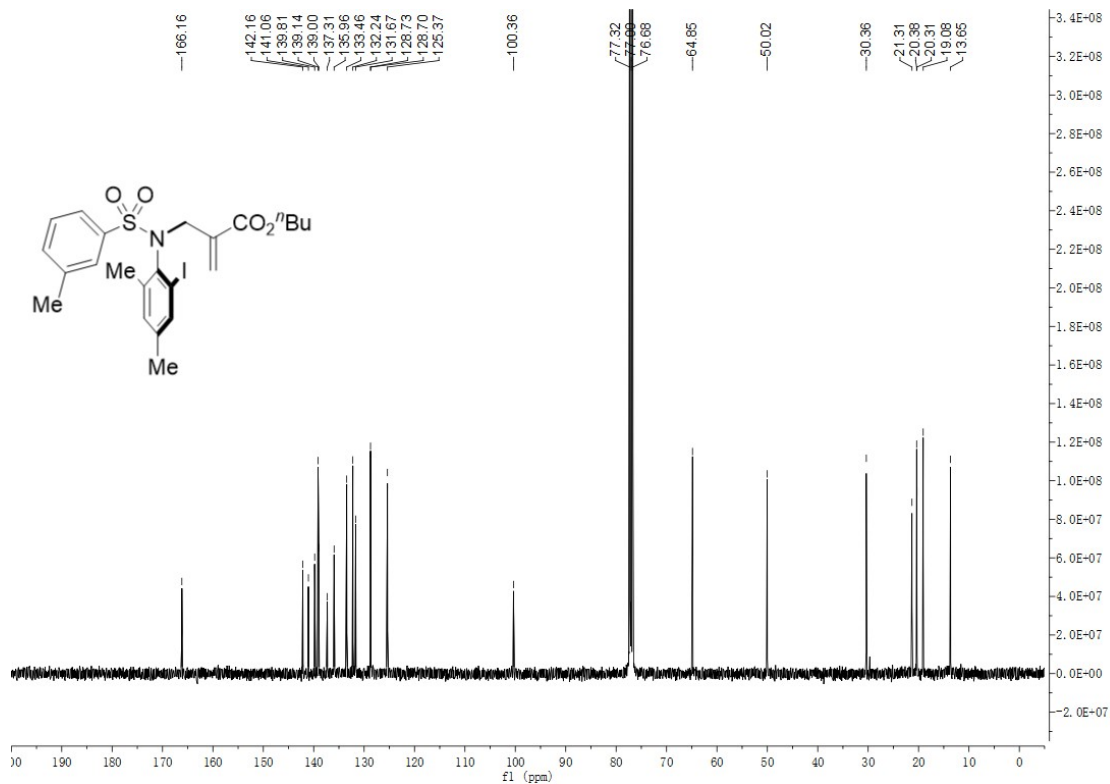
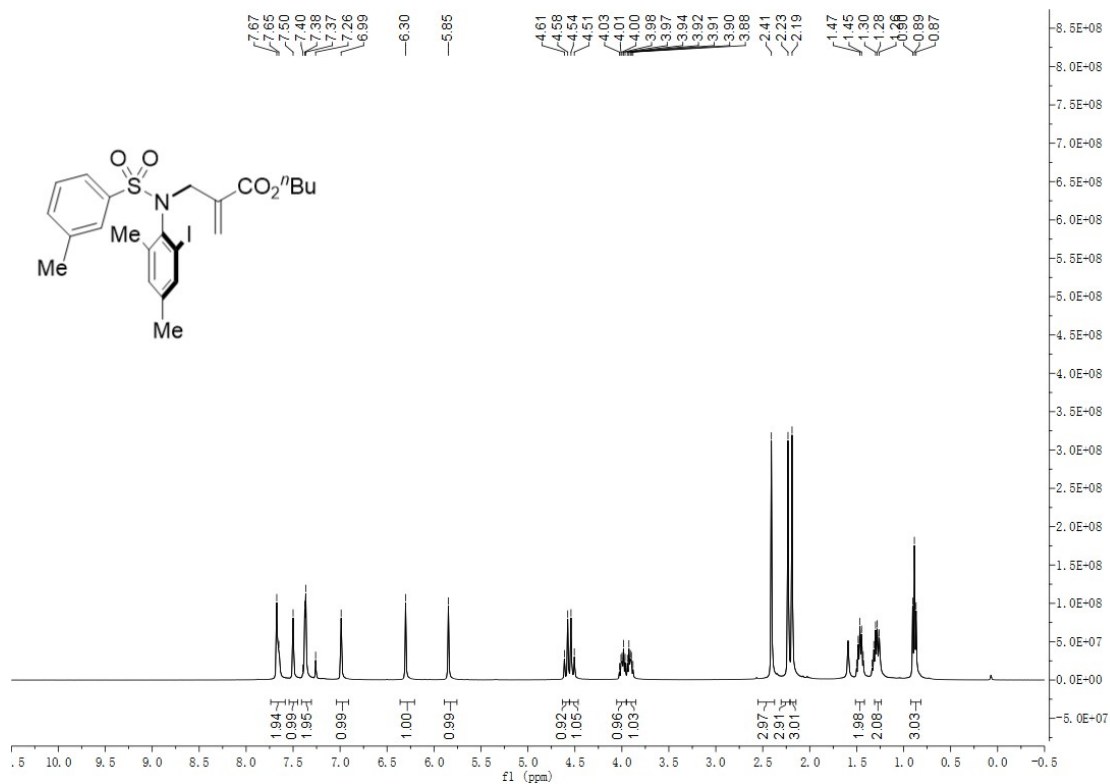
Compound **5m**



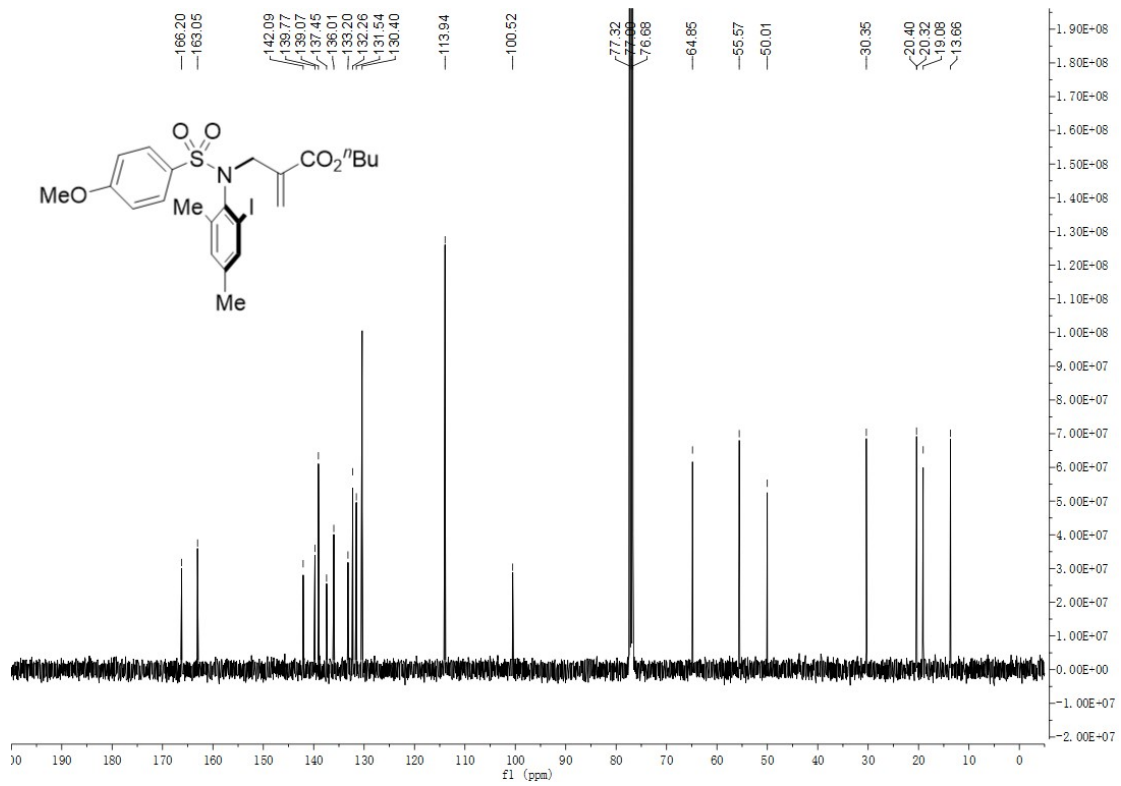
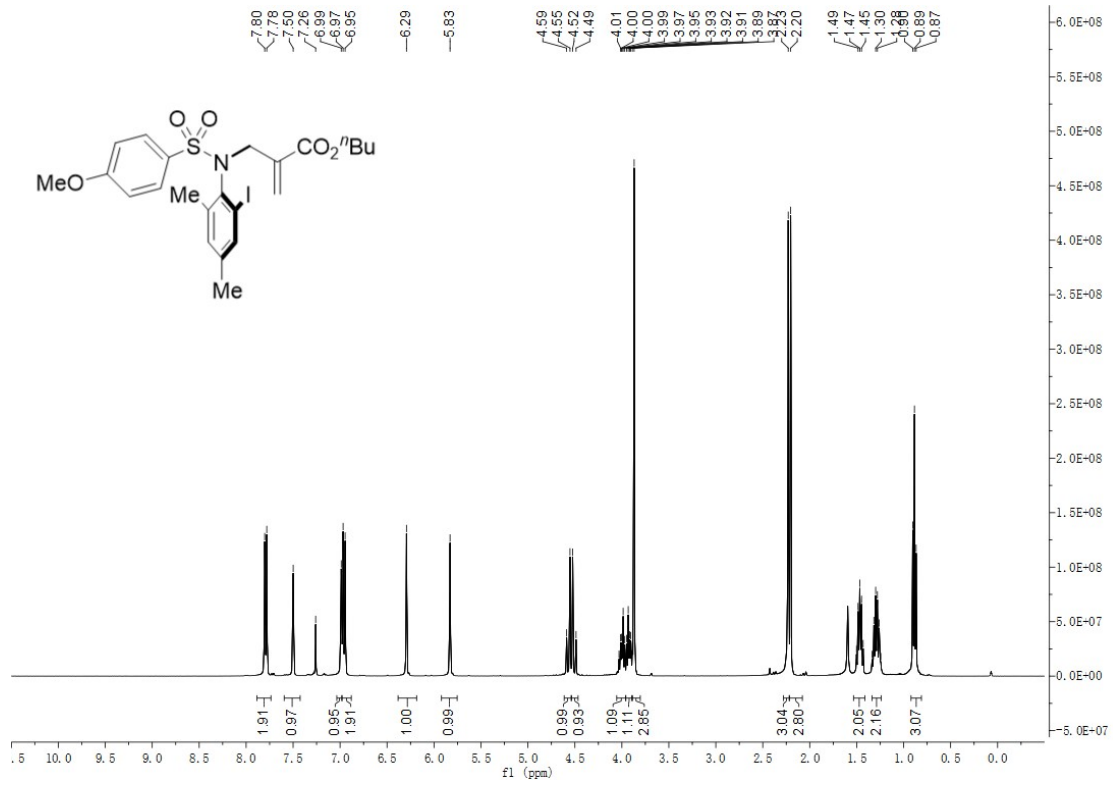
Compound 5n



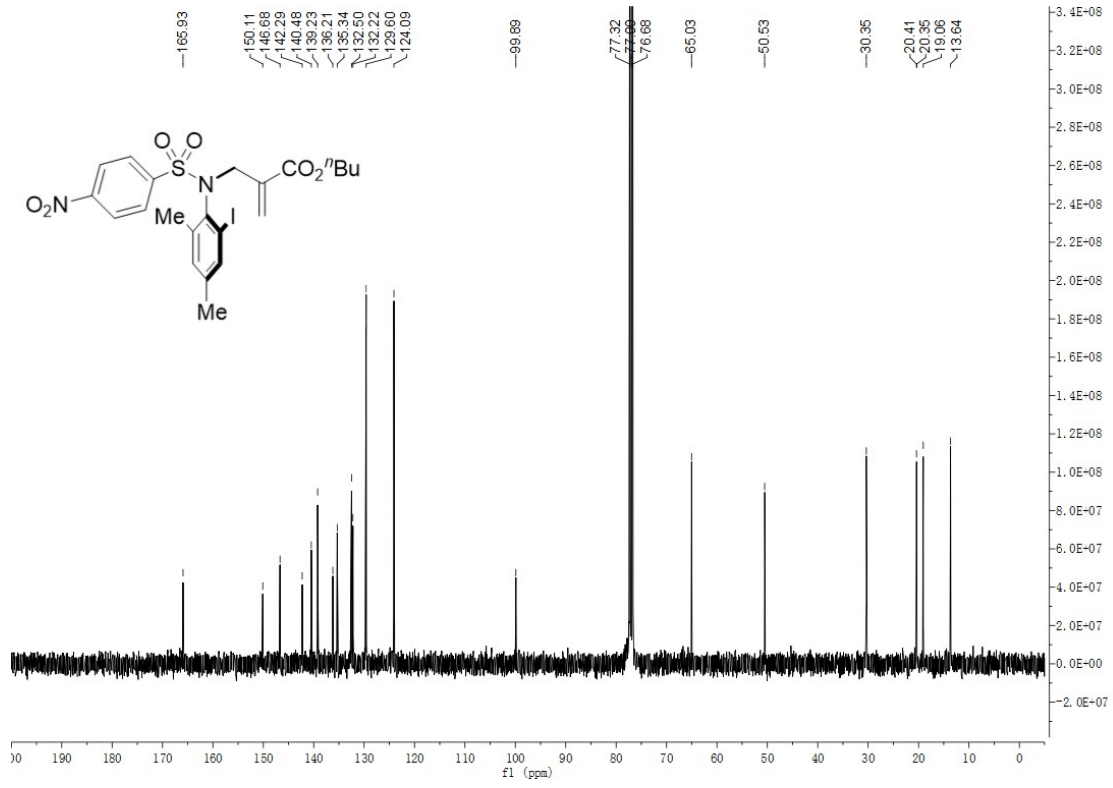
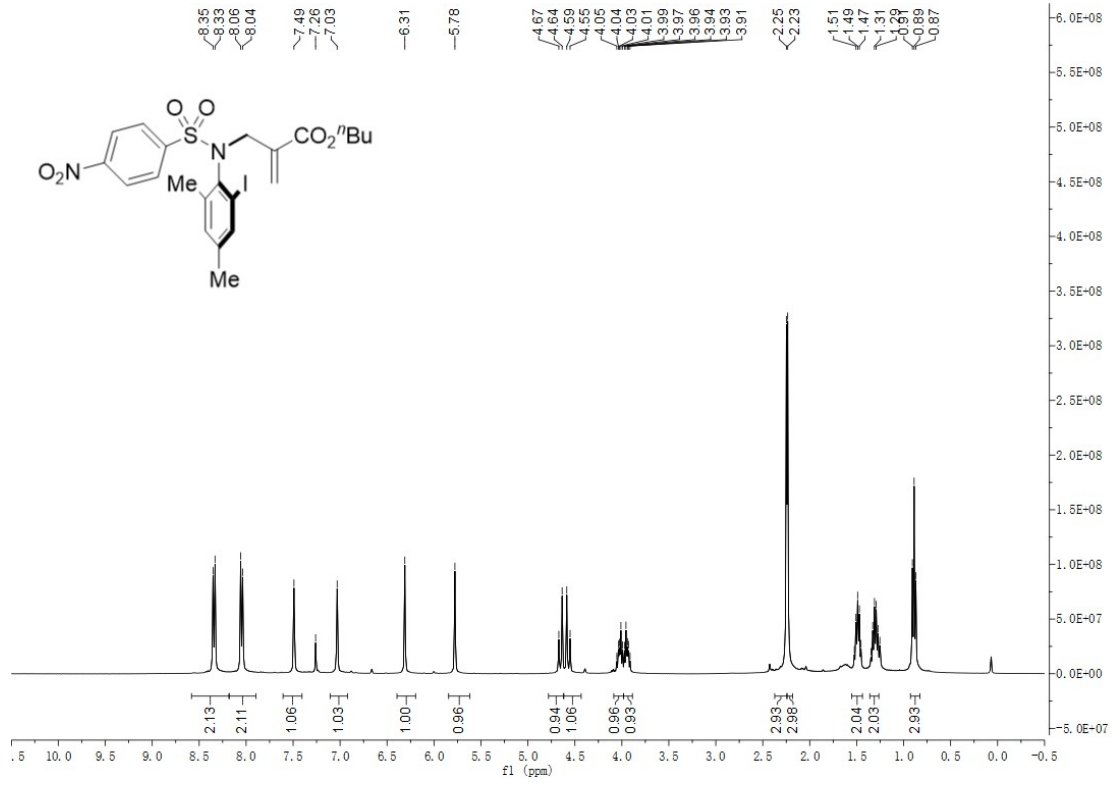
Compound 5o



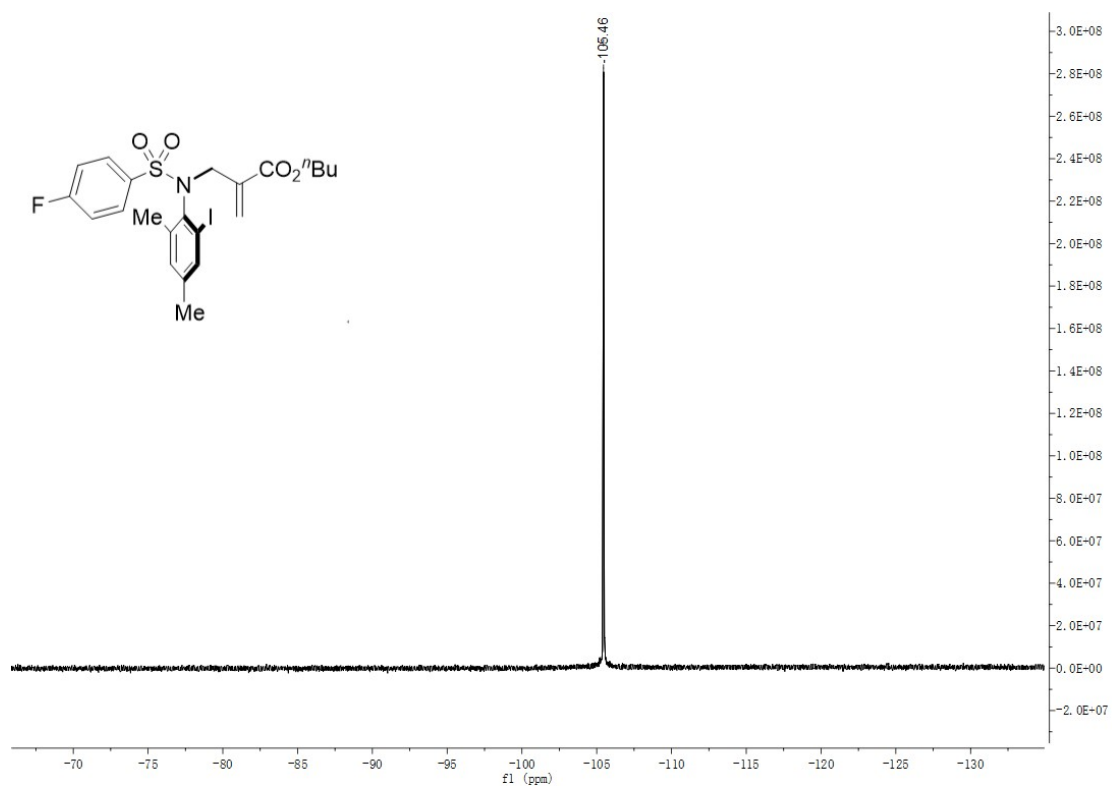
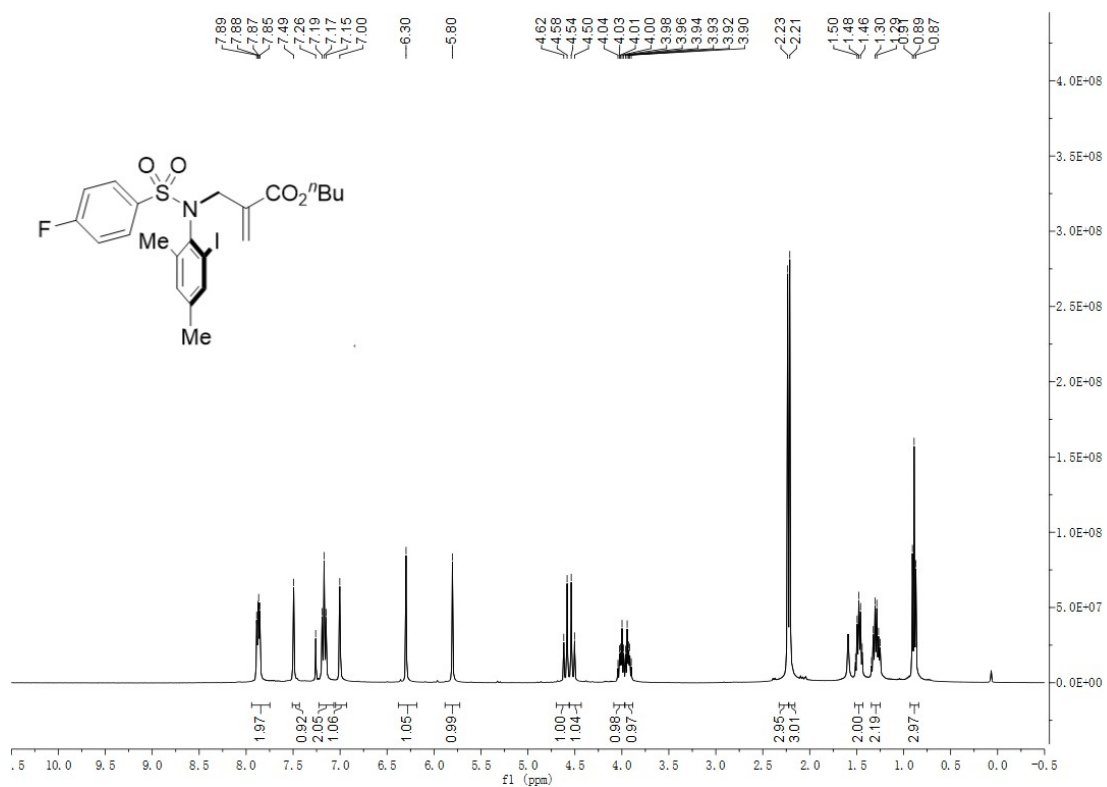
Compound 5p

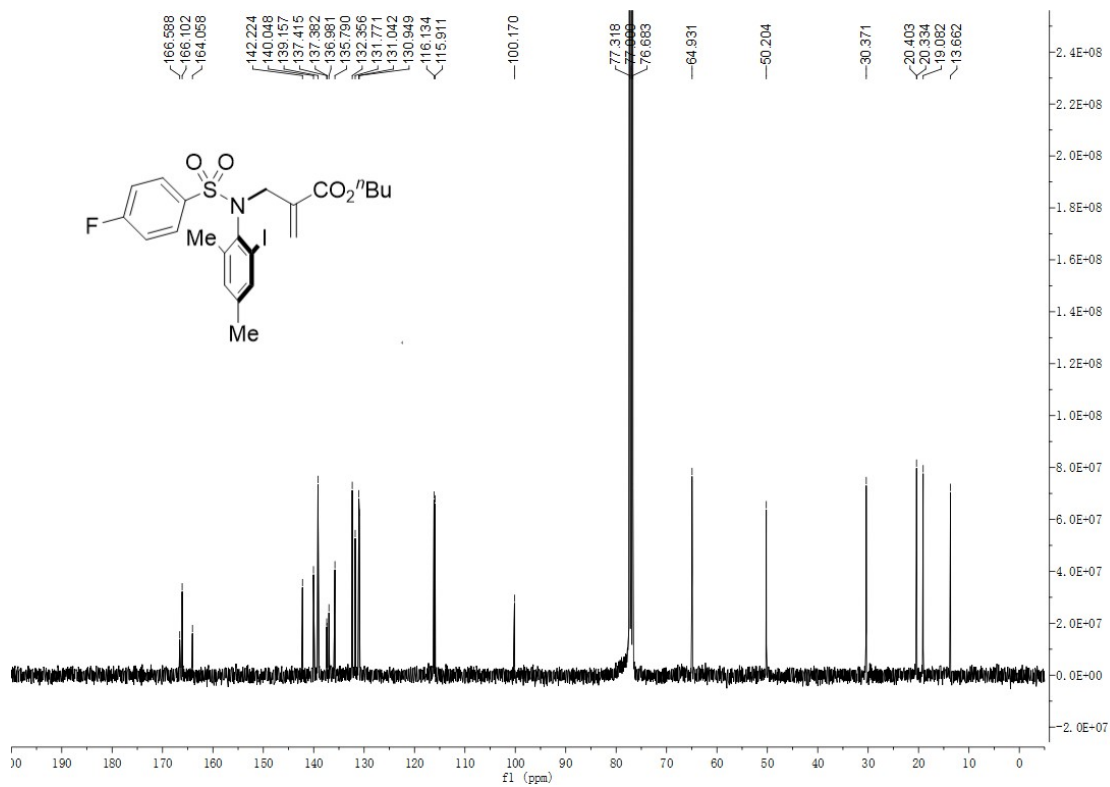


Compound 5q

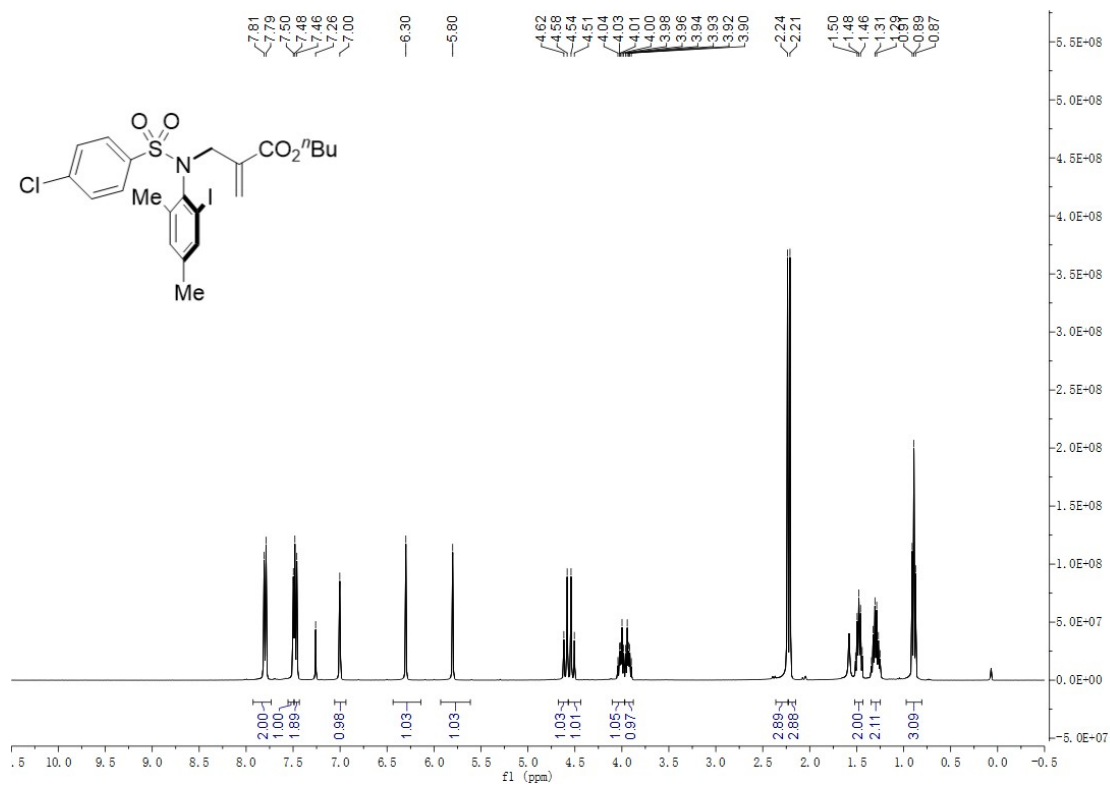


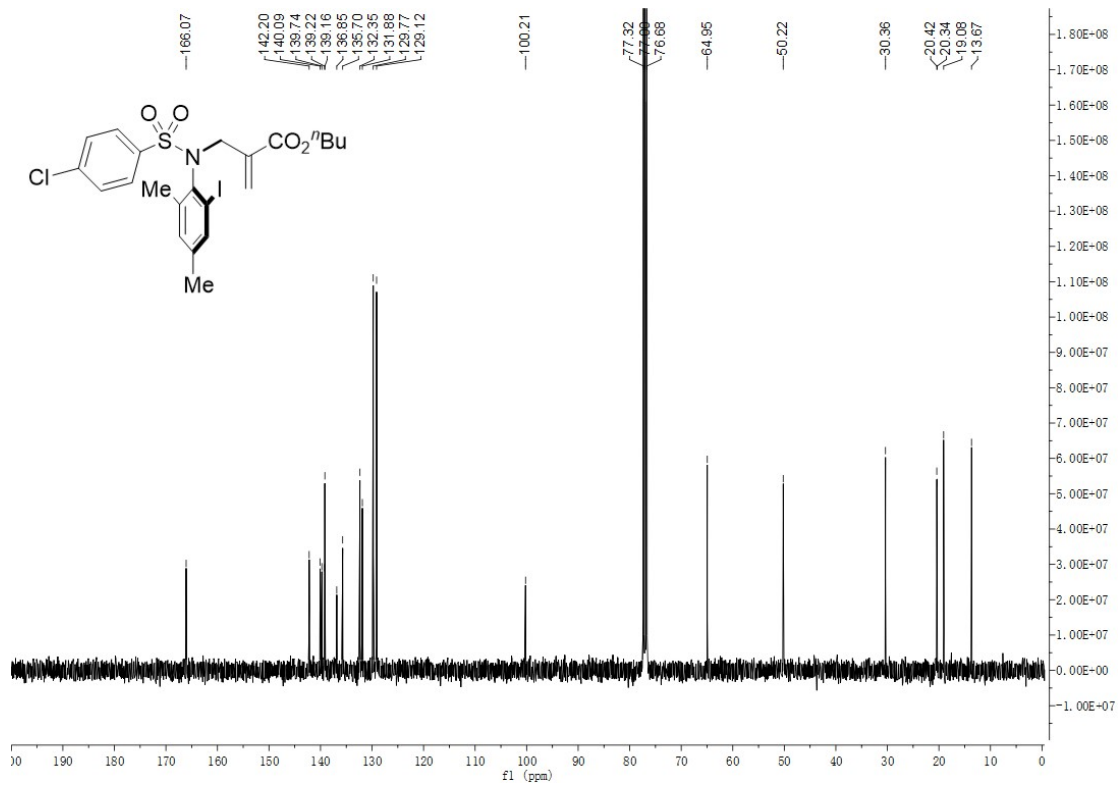
Compound 5r



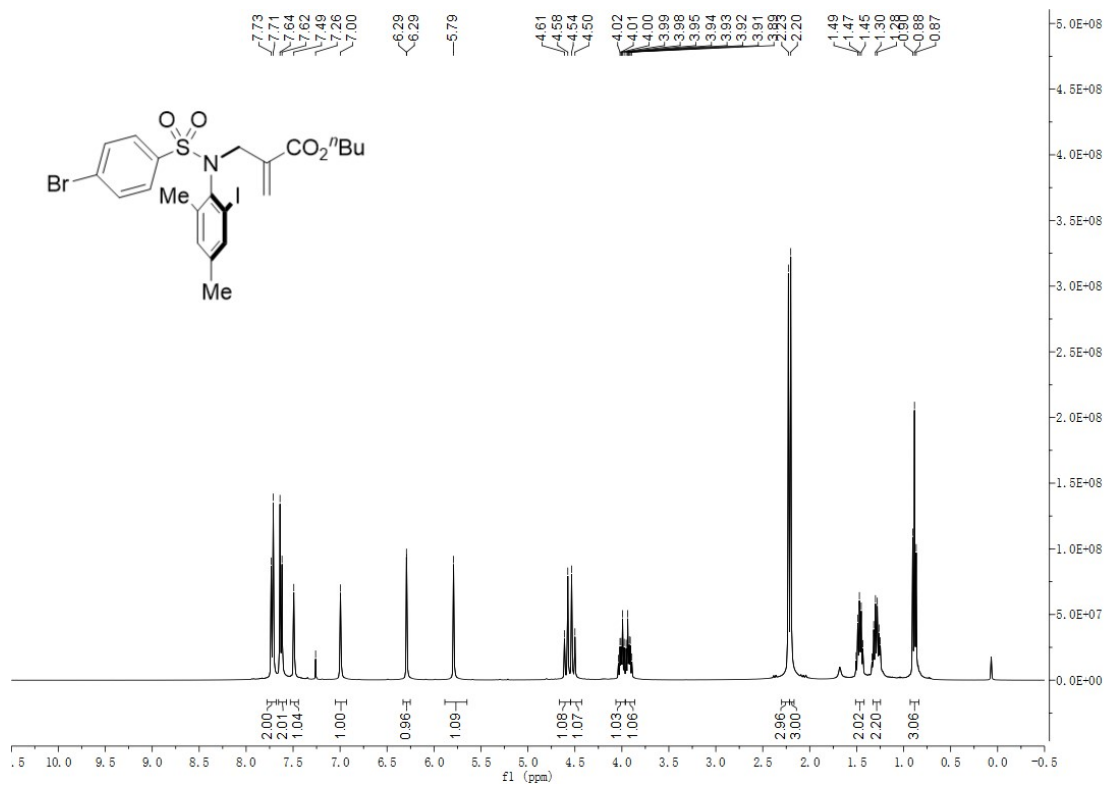


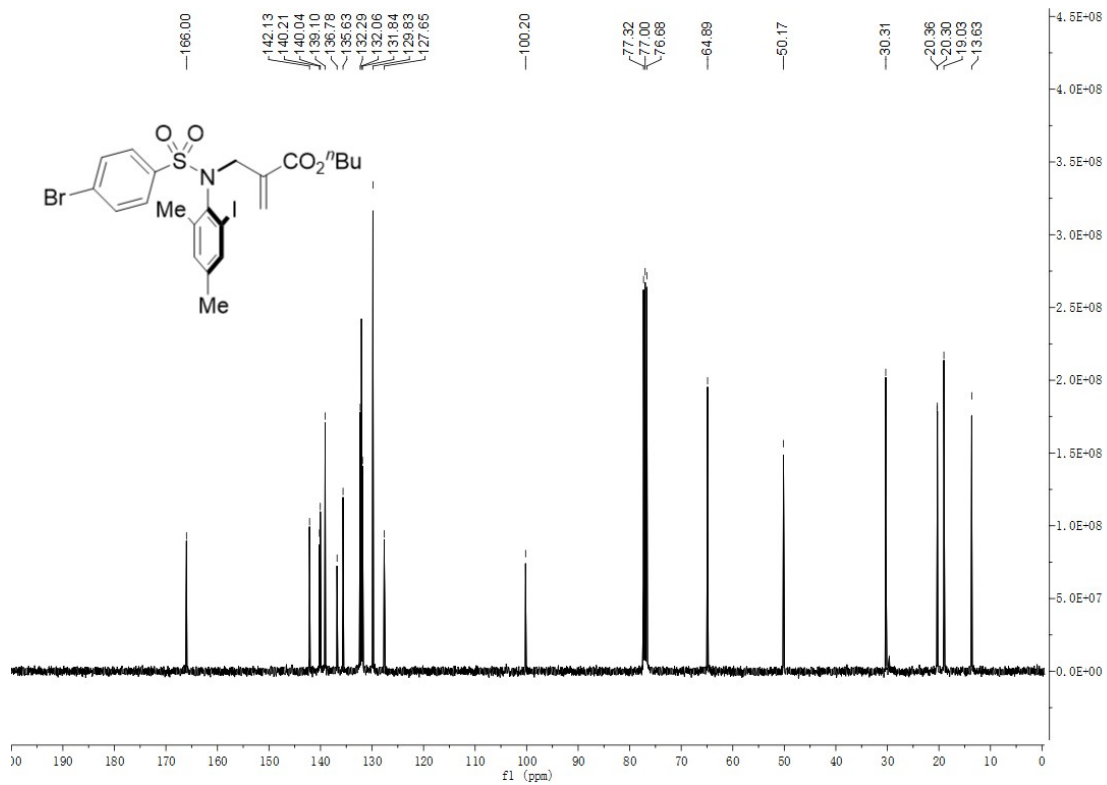
Compound 5s



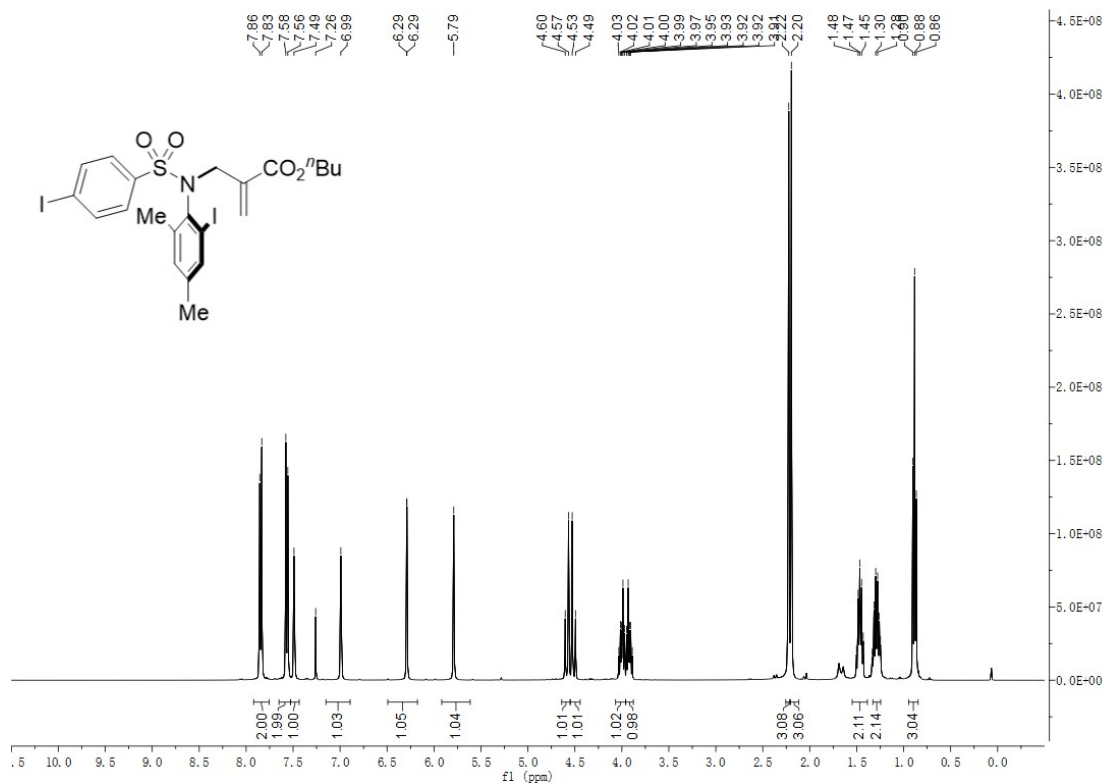


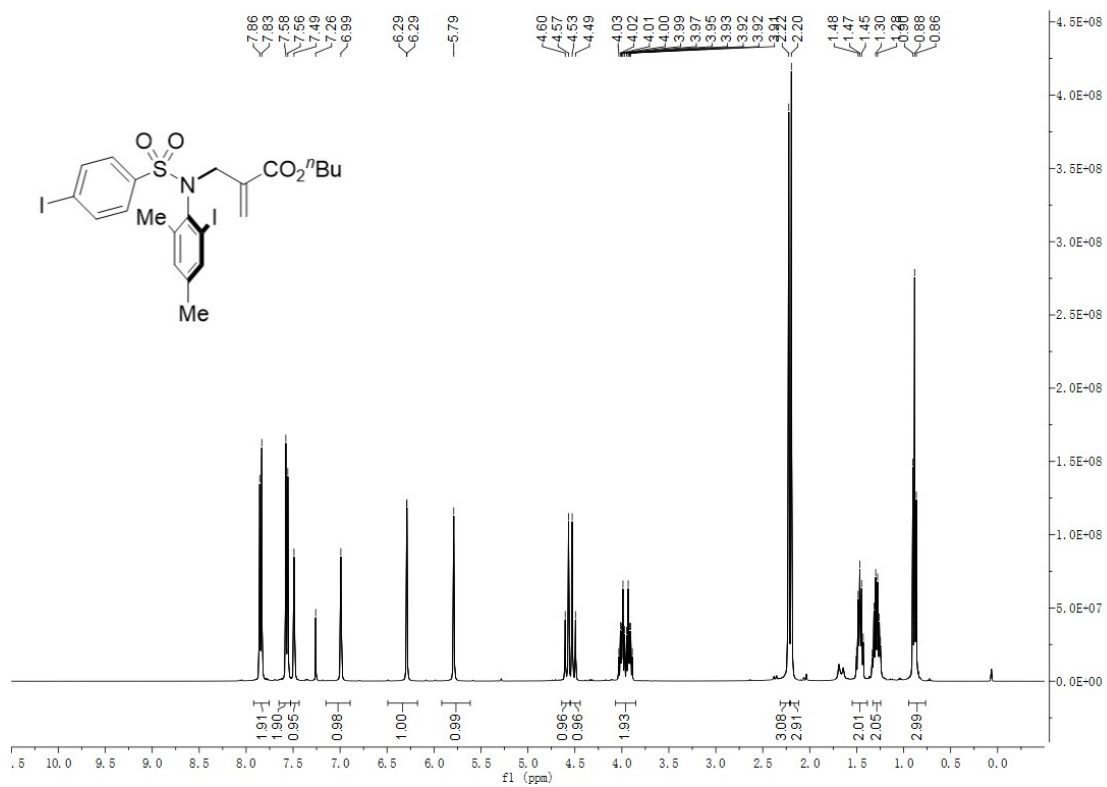
Compound 5t



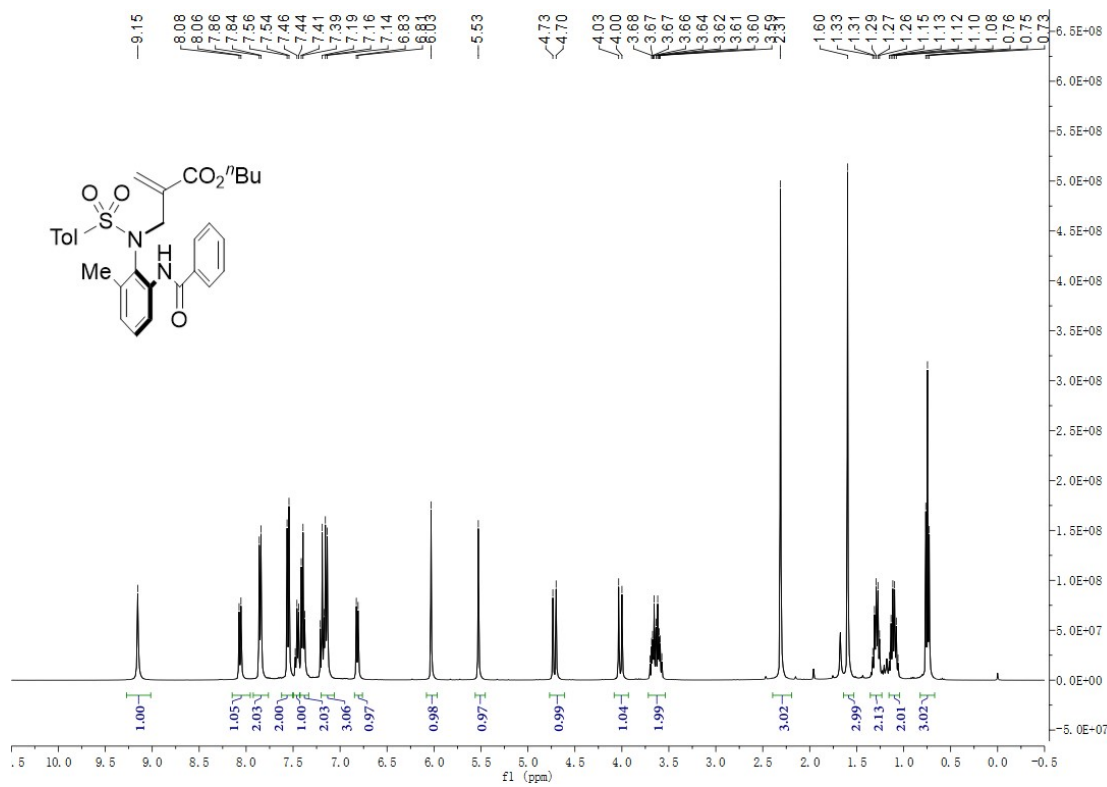


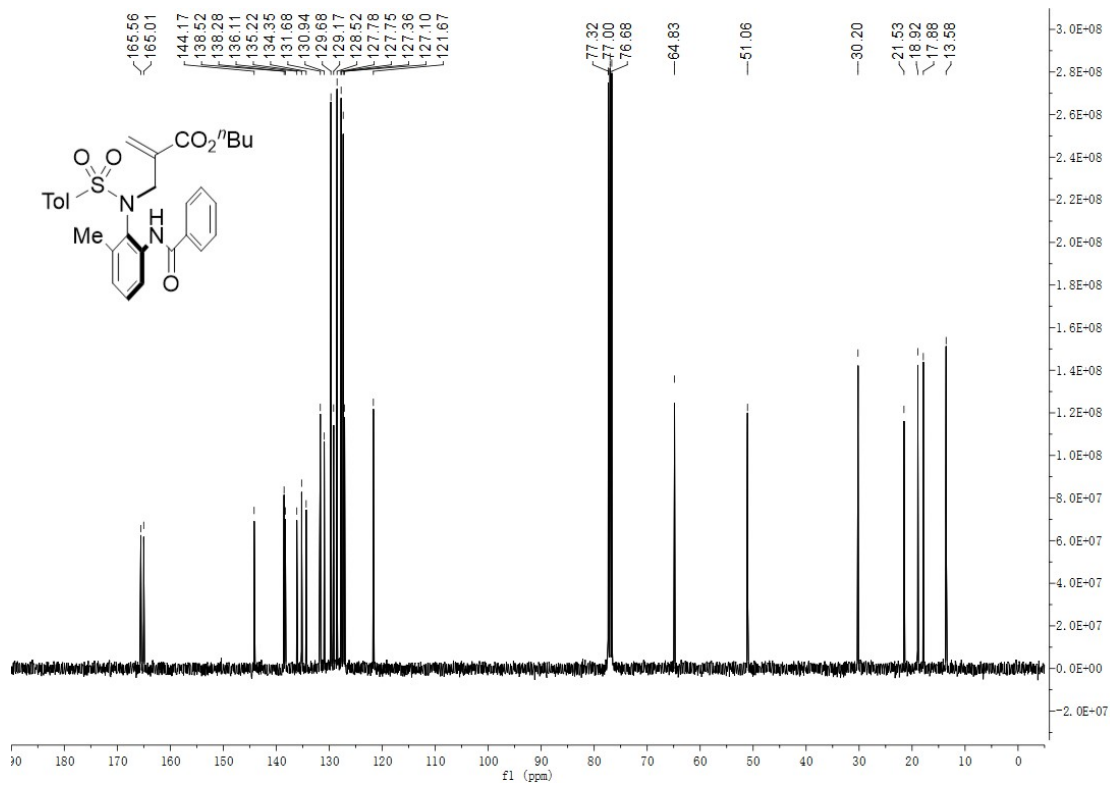
Compound 5u



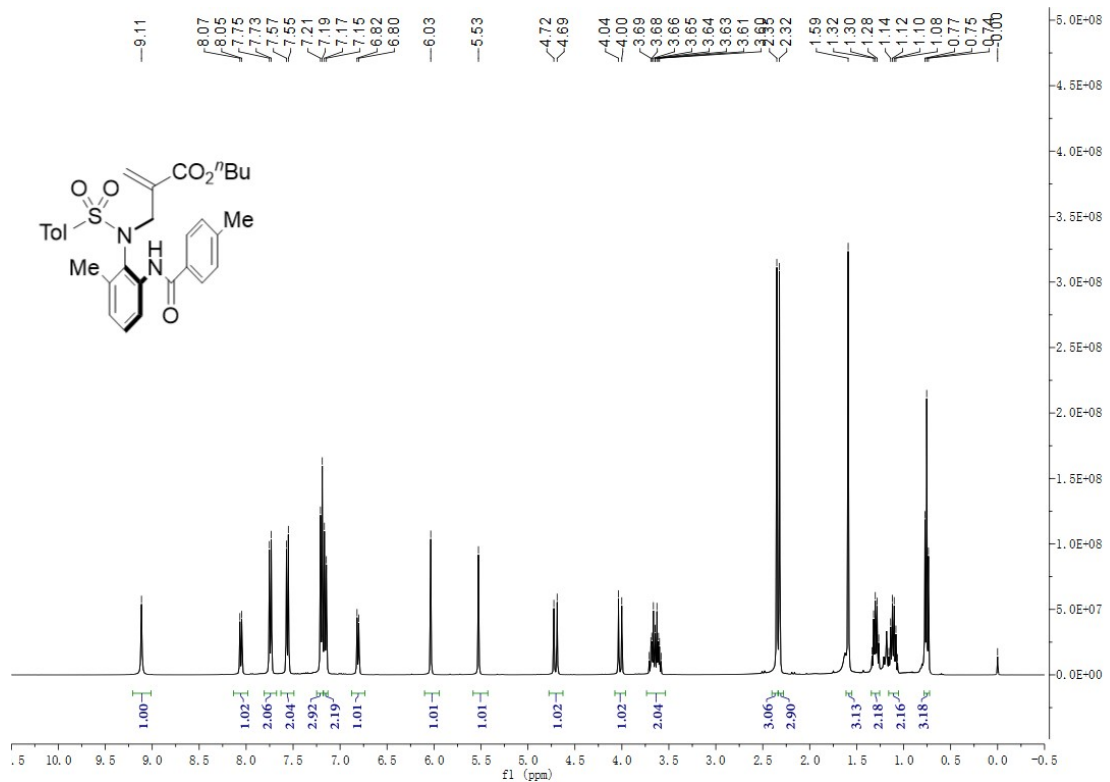


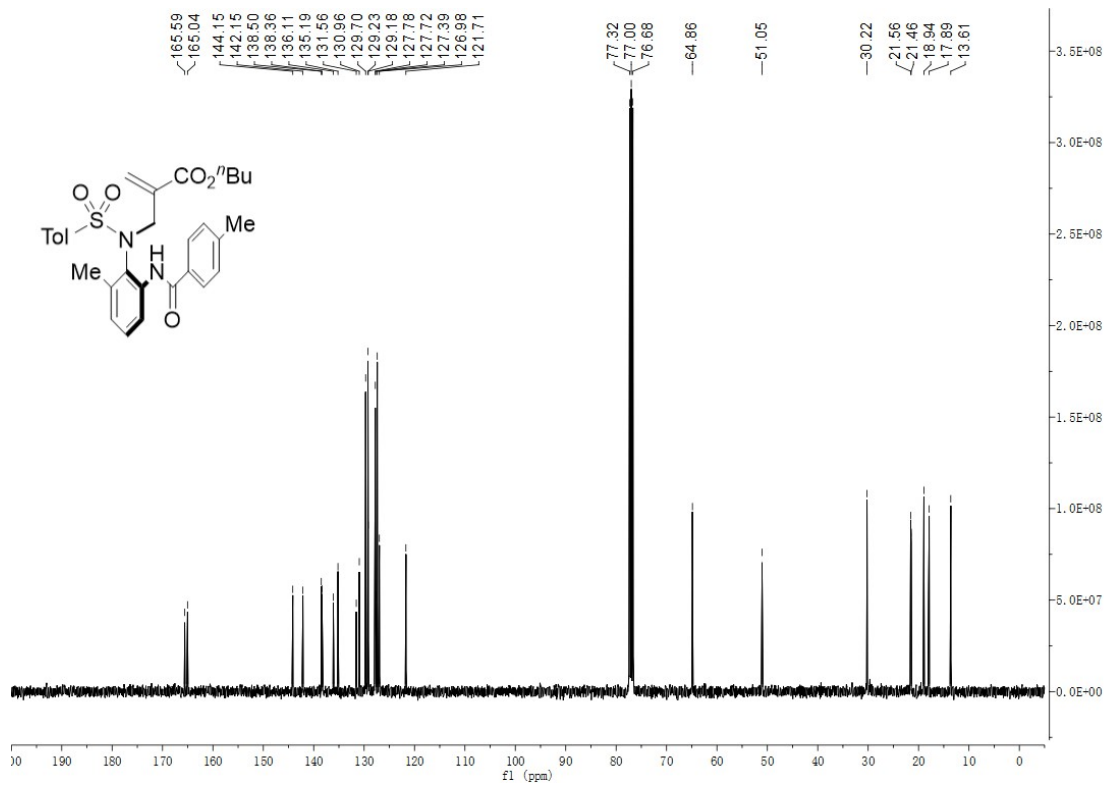
Compound 7a



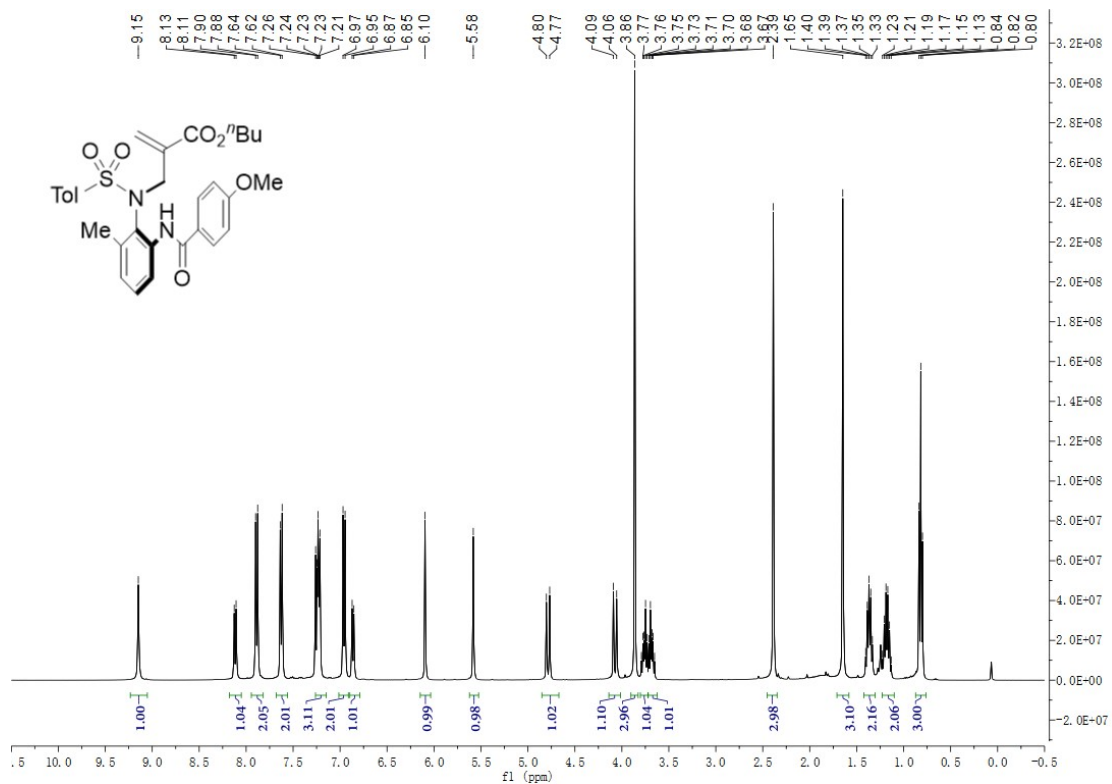


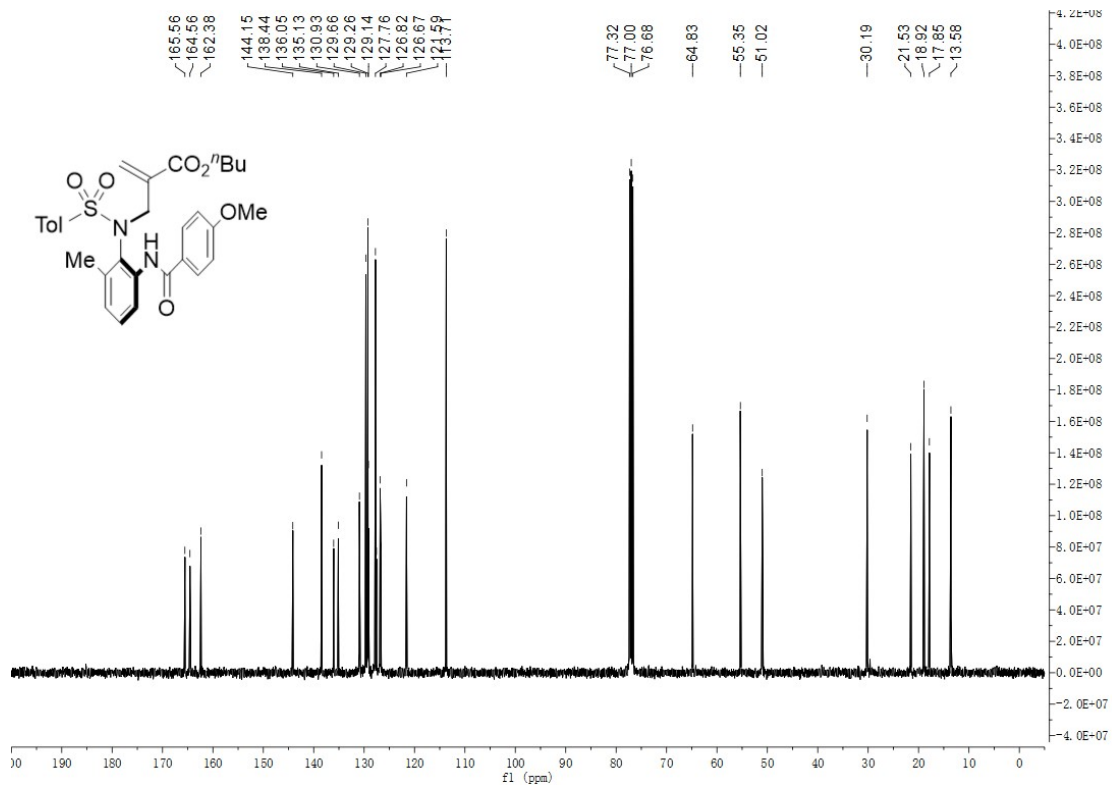
Compound 7b



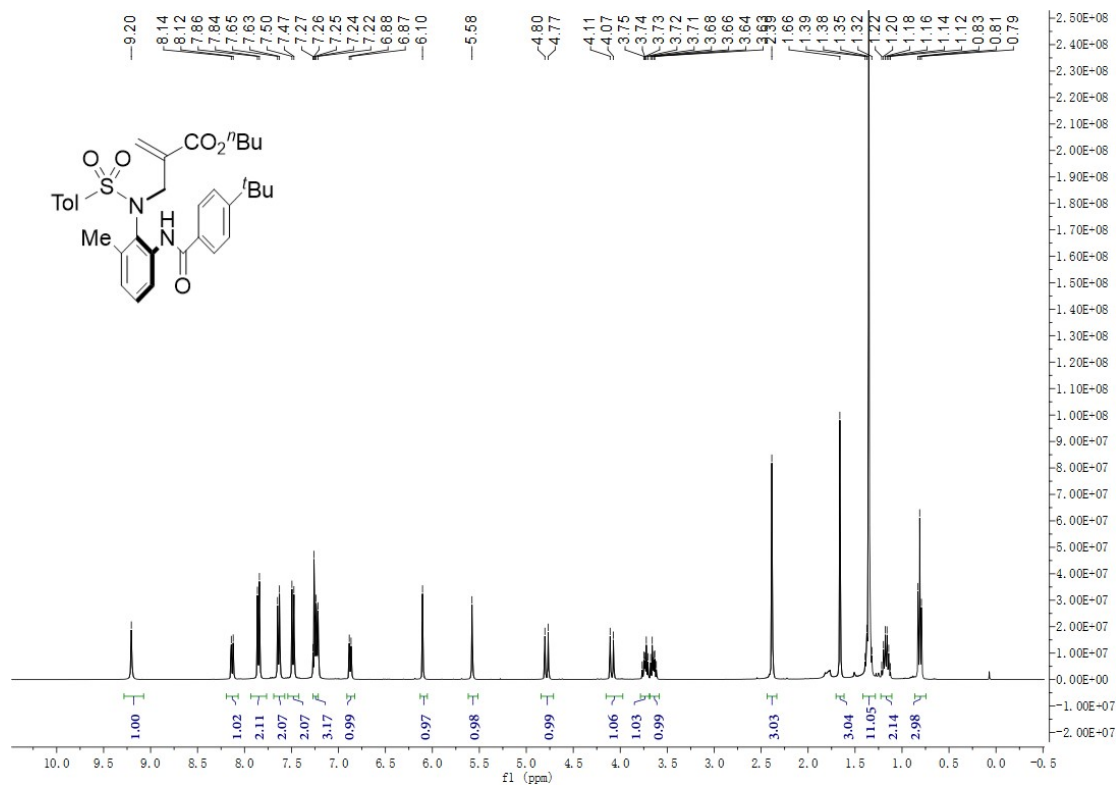


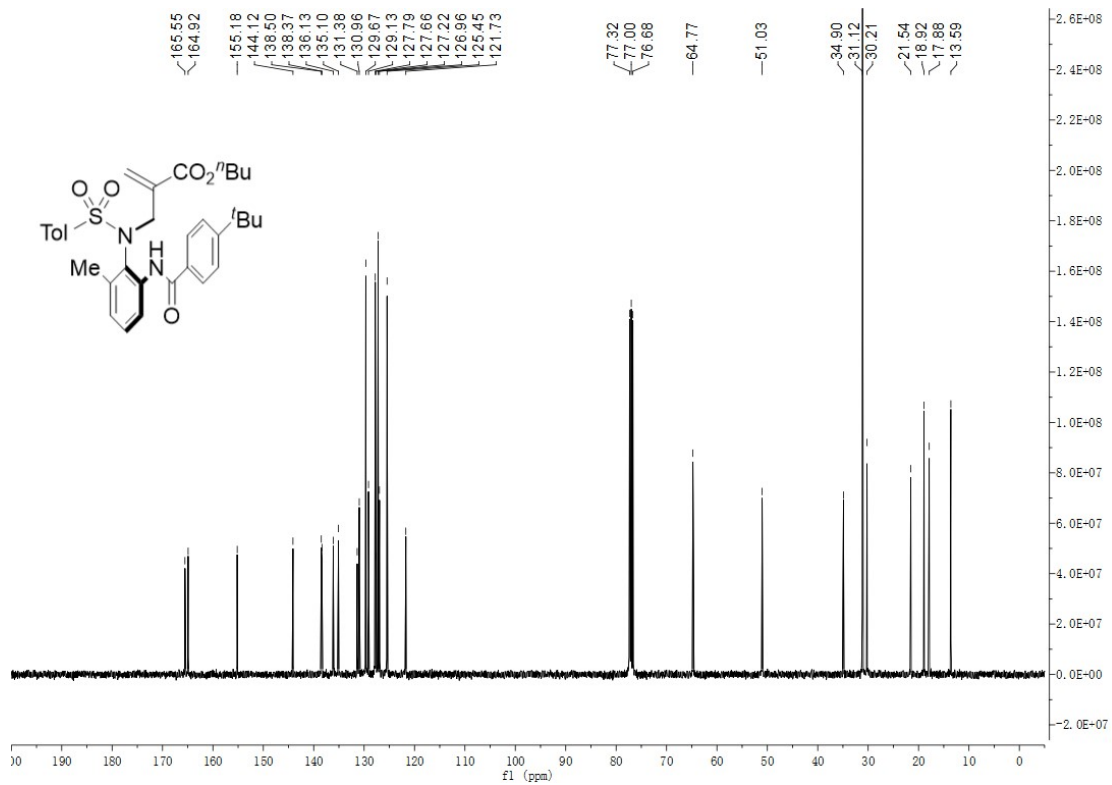
Compound 7c



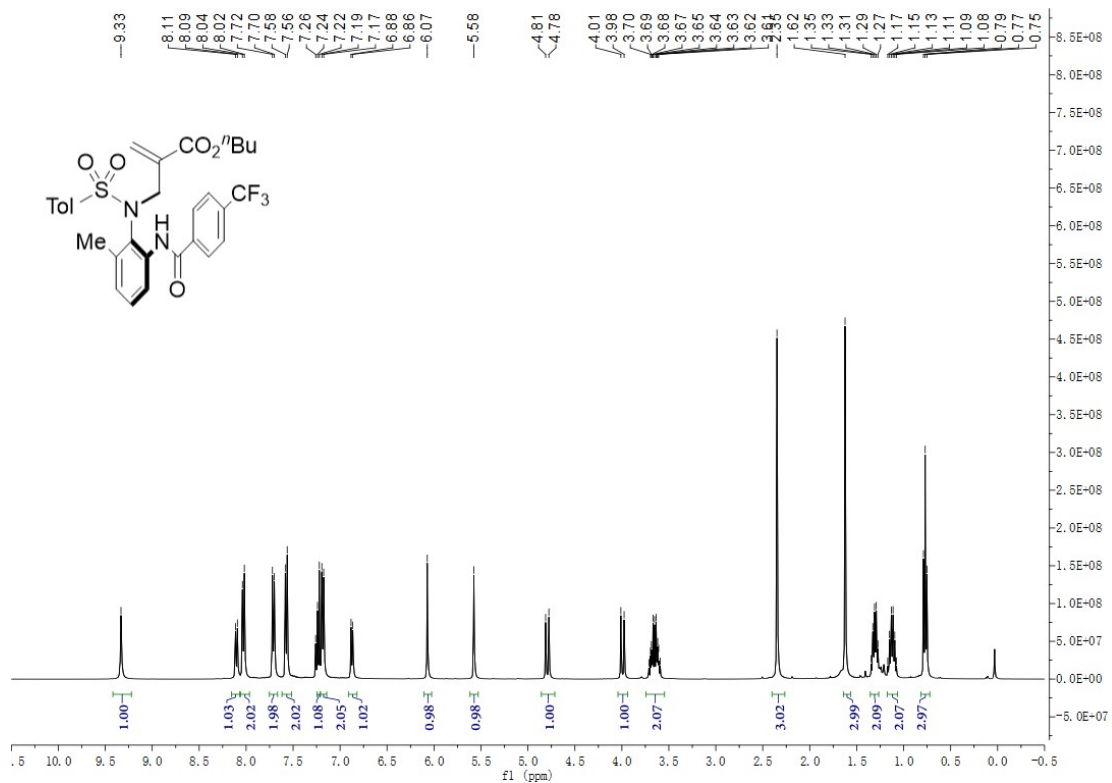


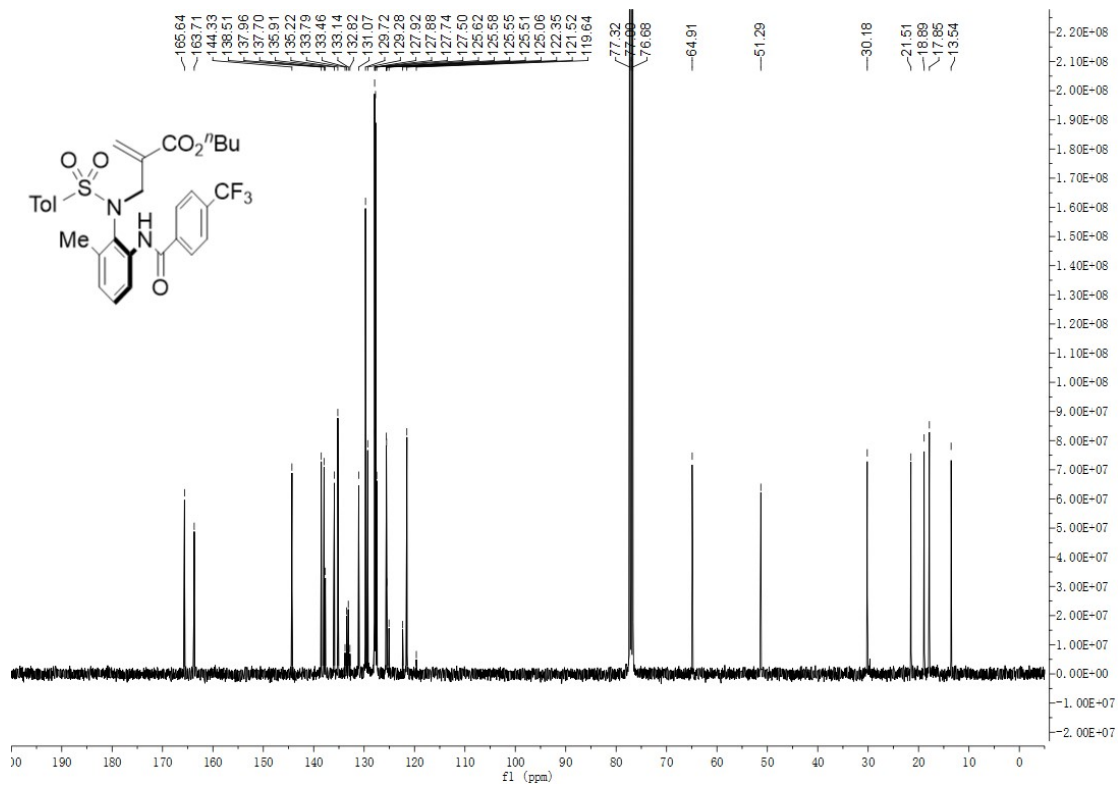
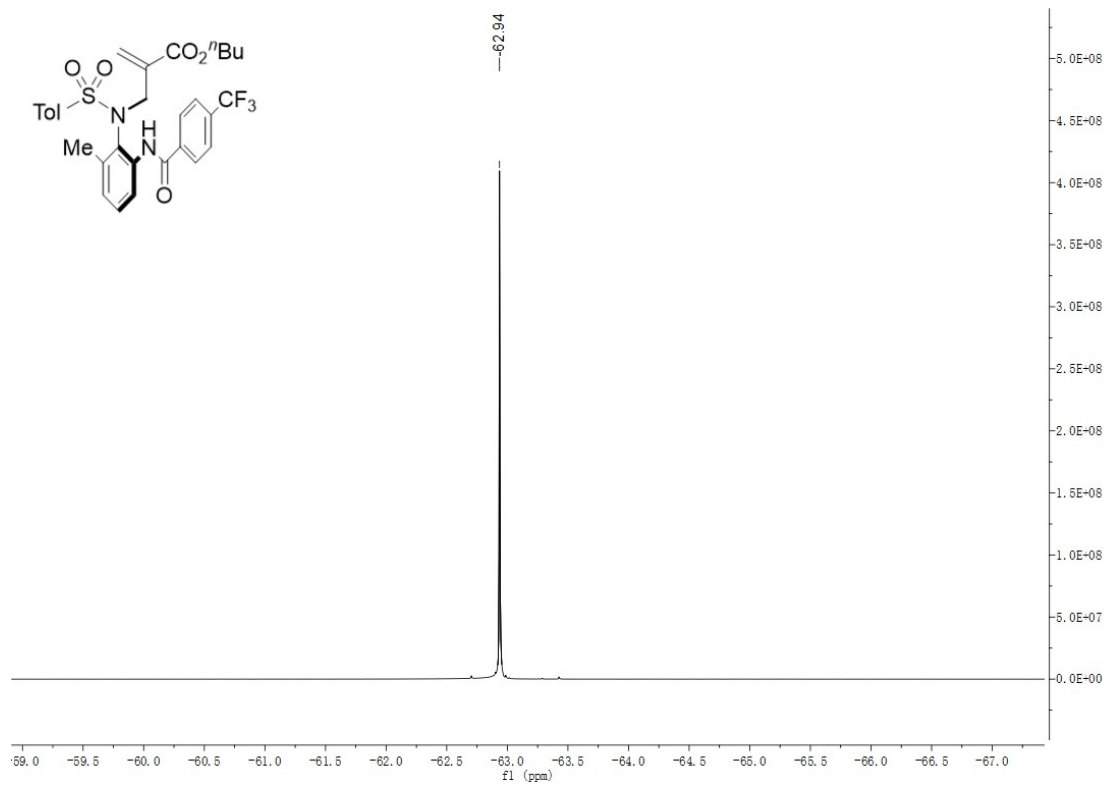
Compound 7d



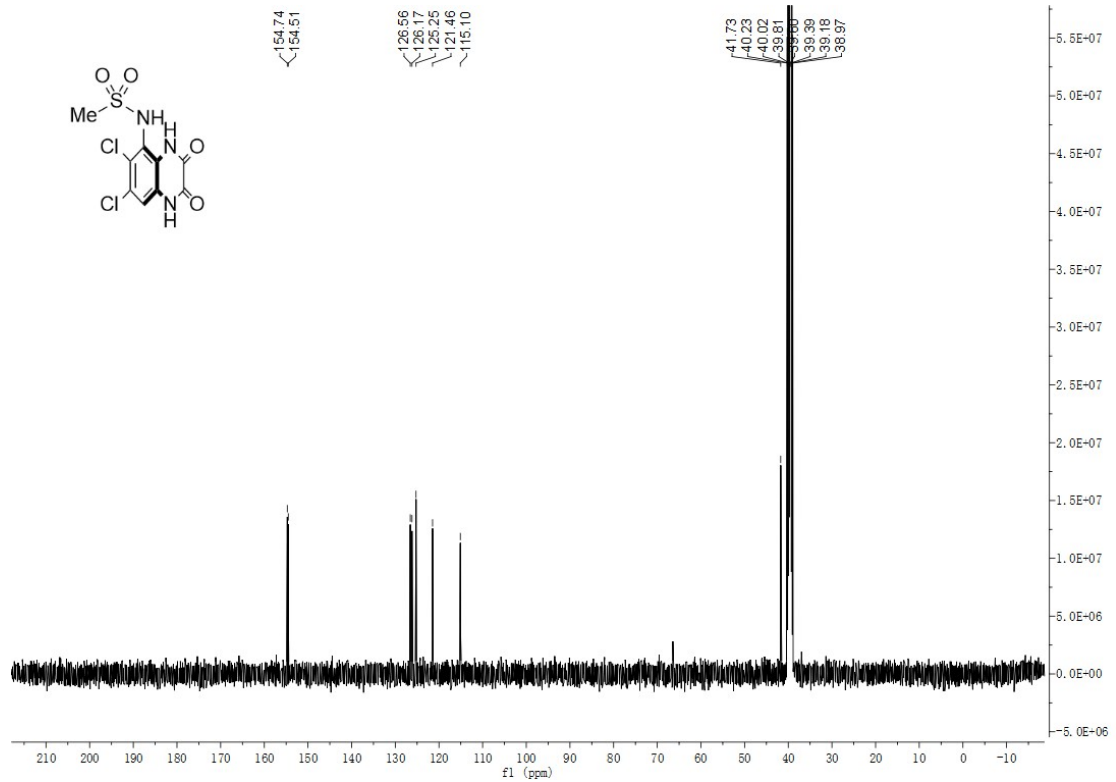
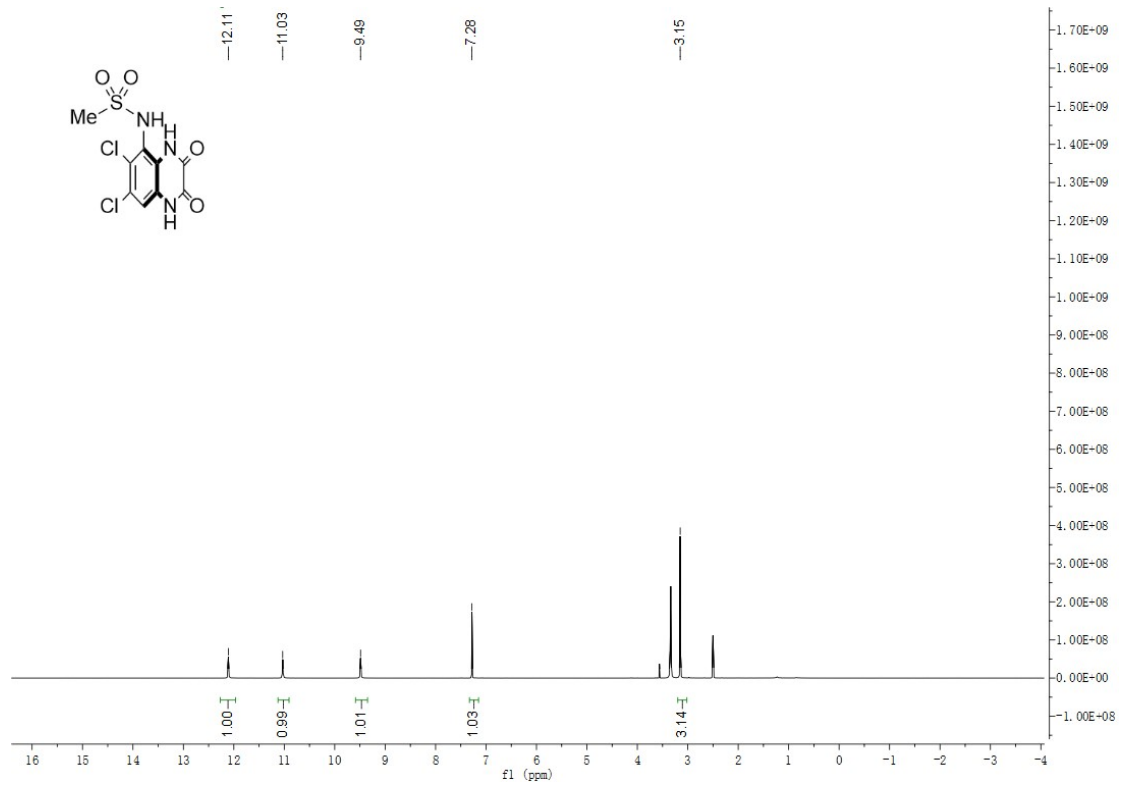


Compound 7e

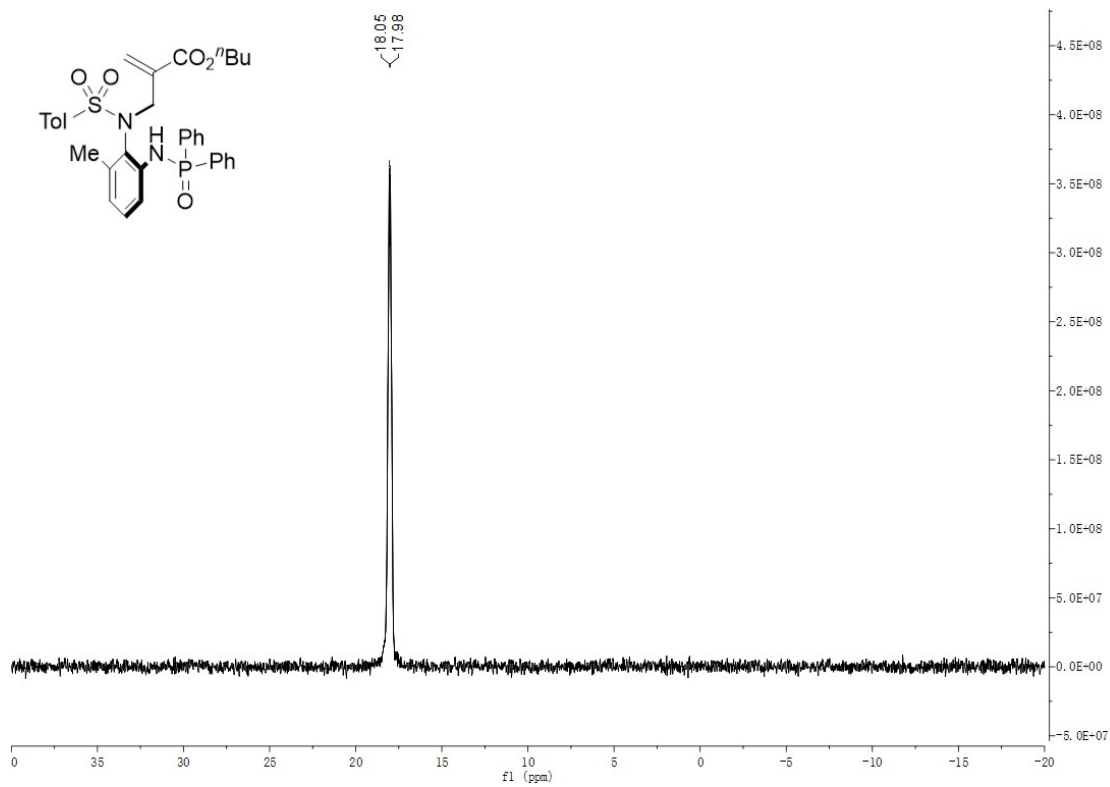
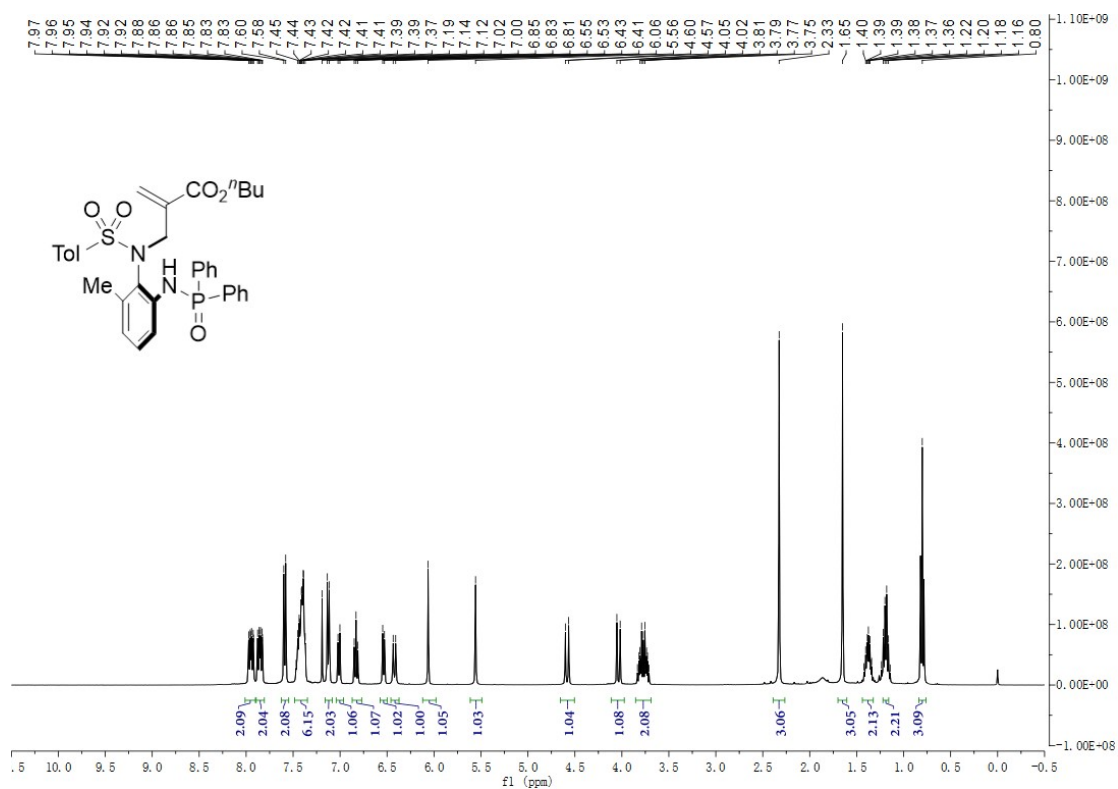


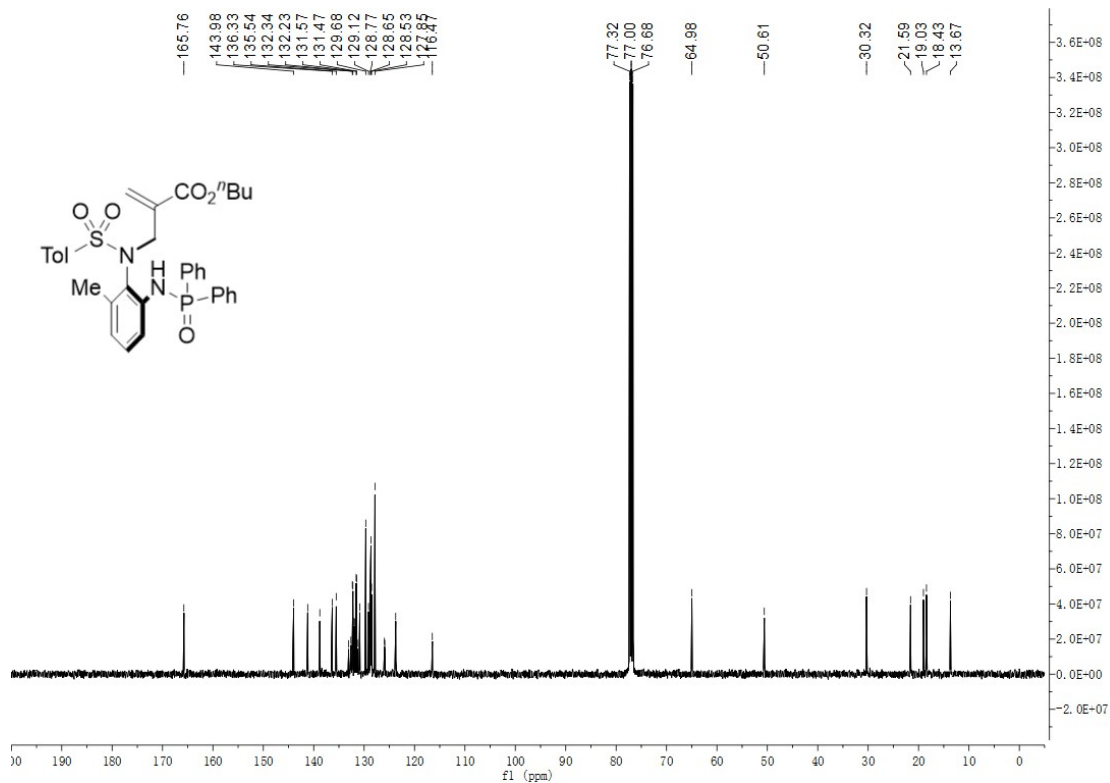


Compound **6f**

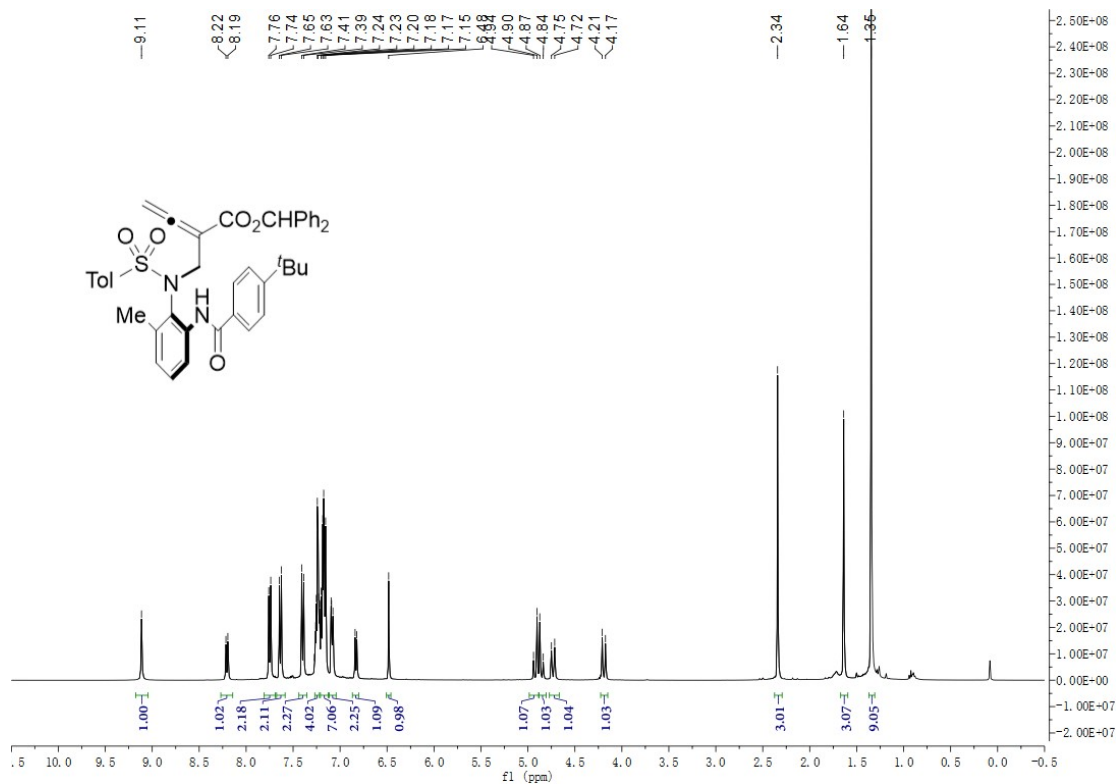


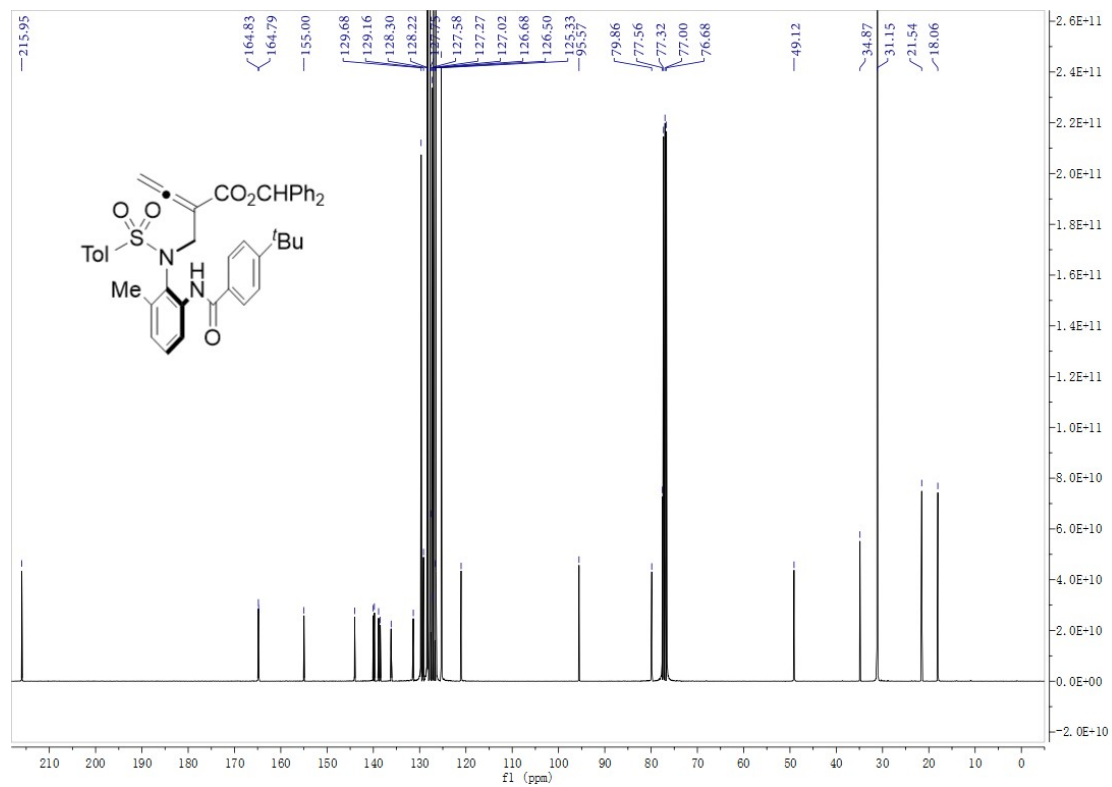
Compound 7g



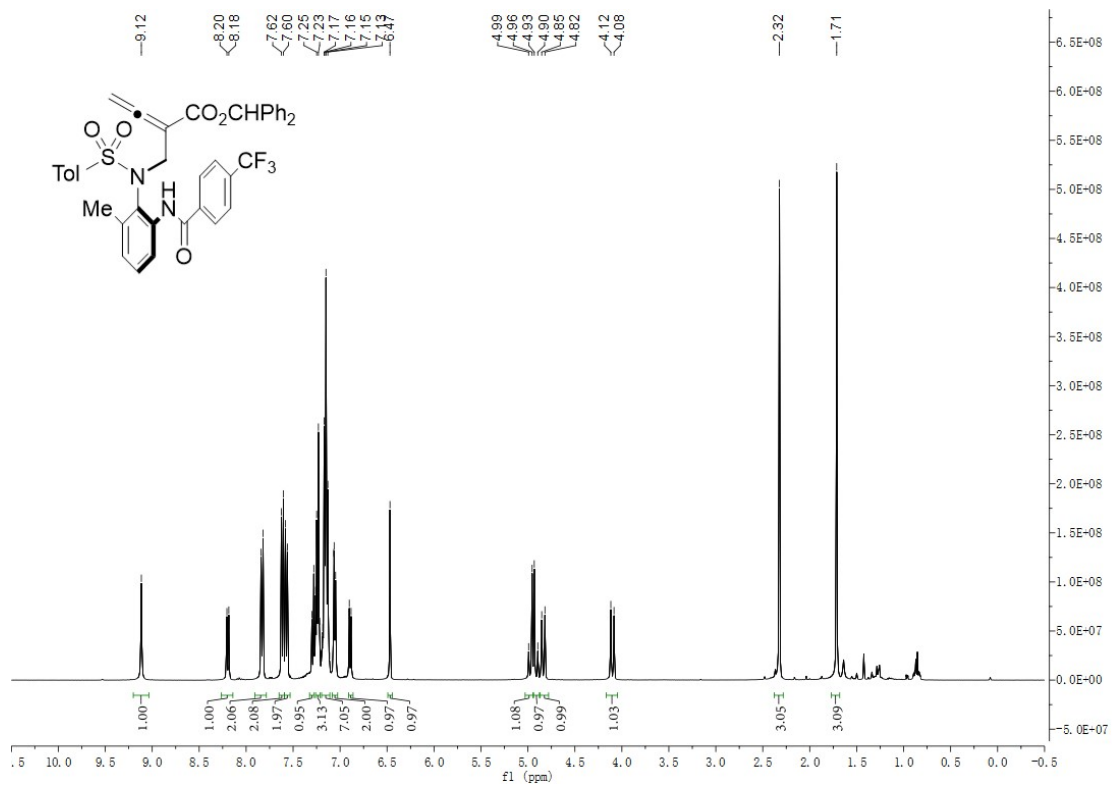


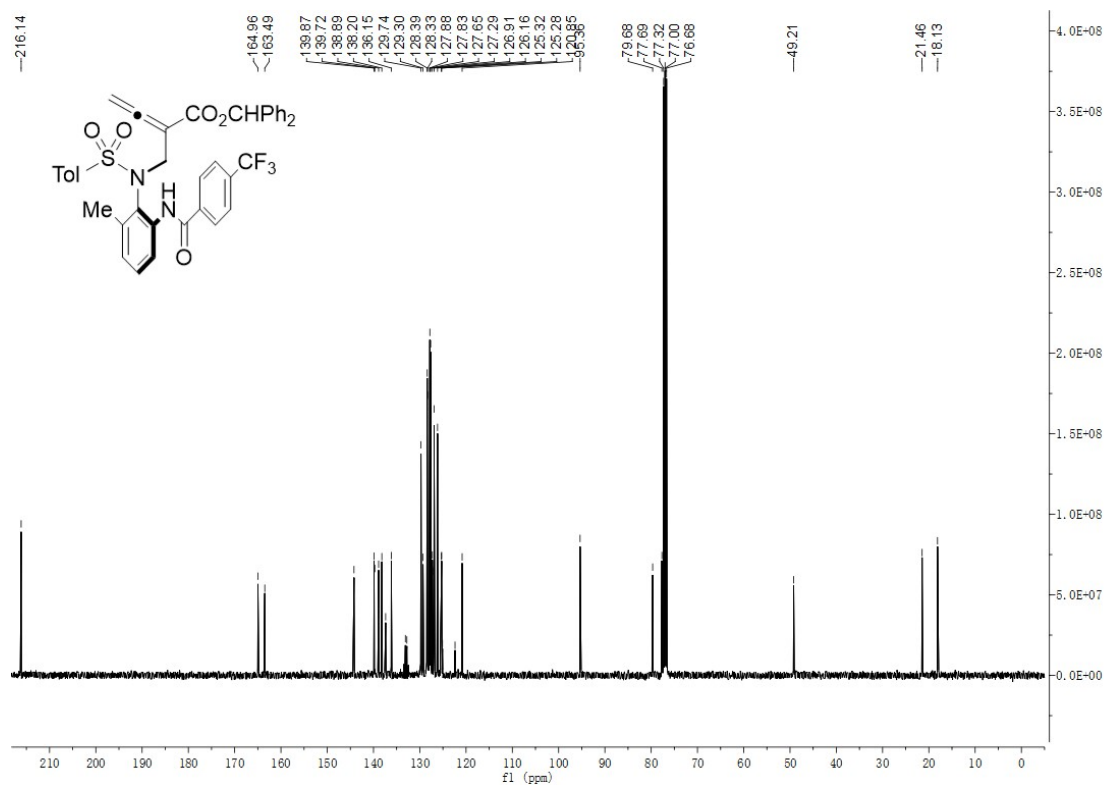
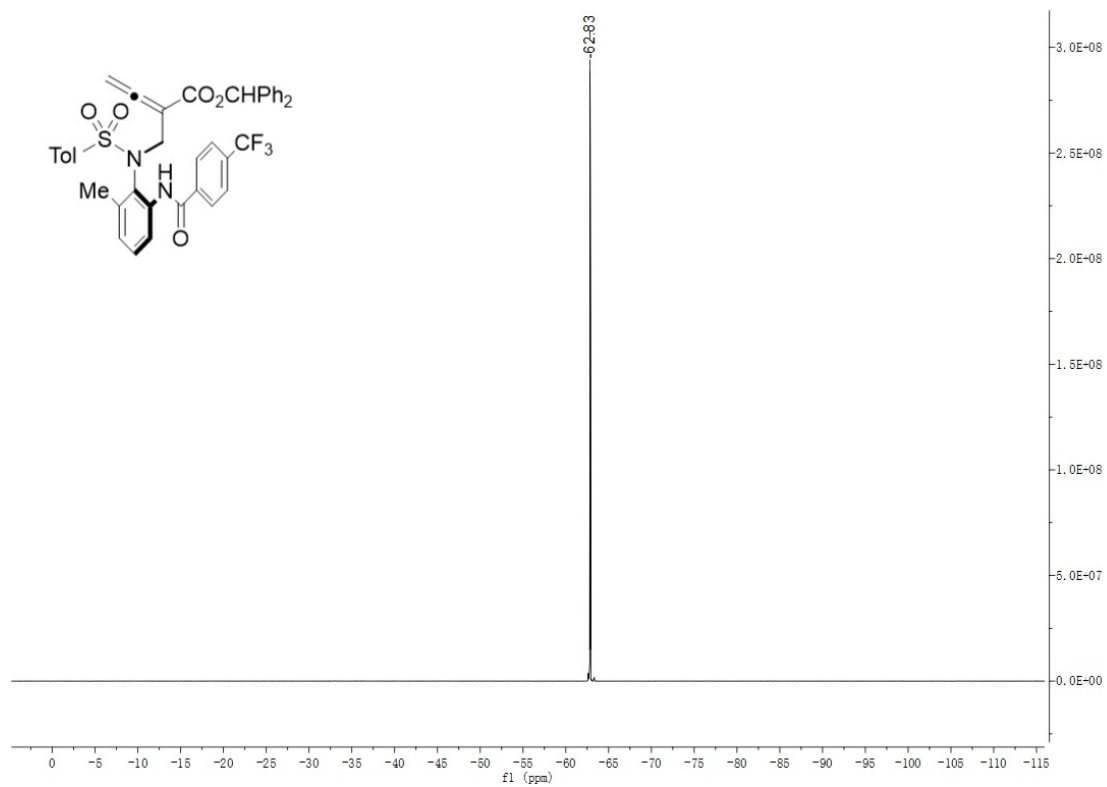
Compound 7h



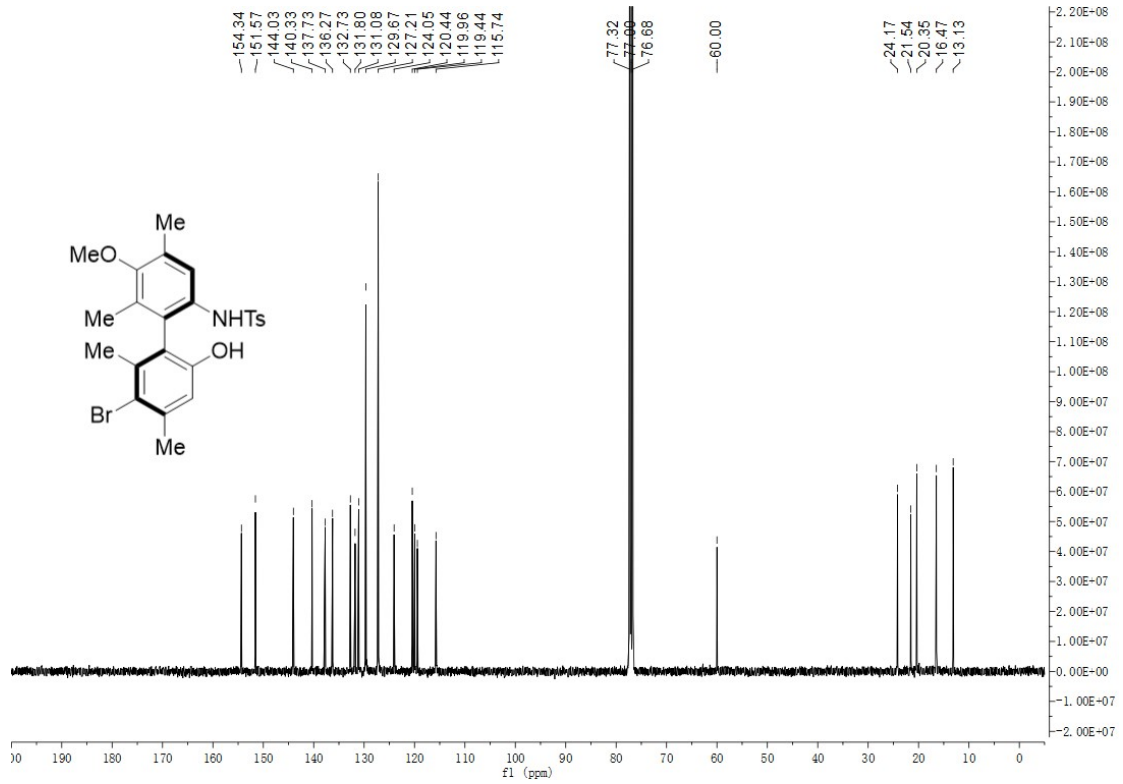
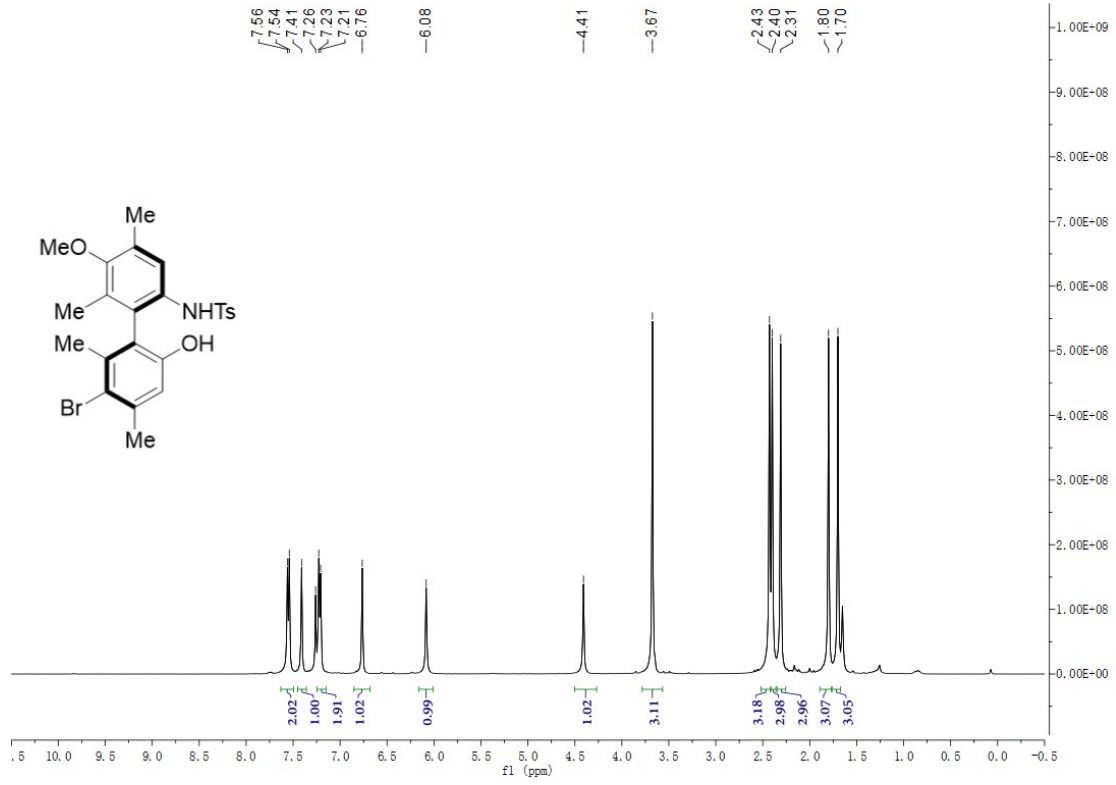


Compound 7i

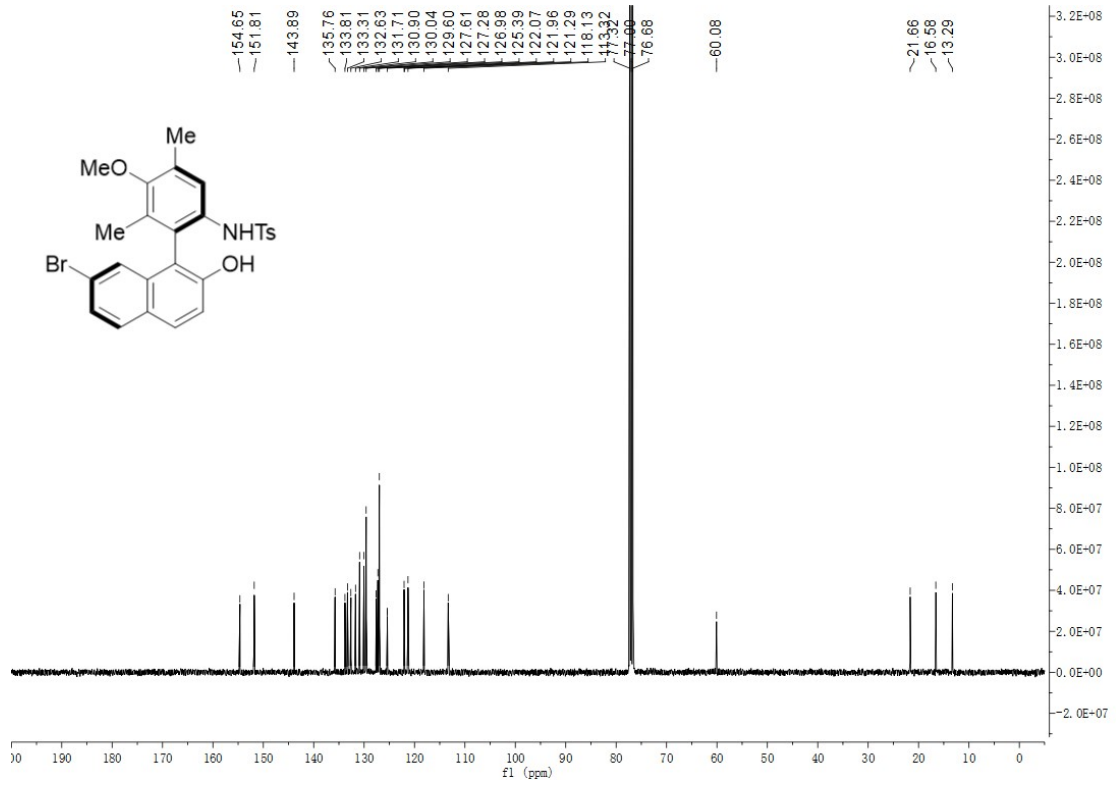
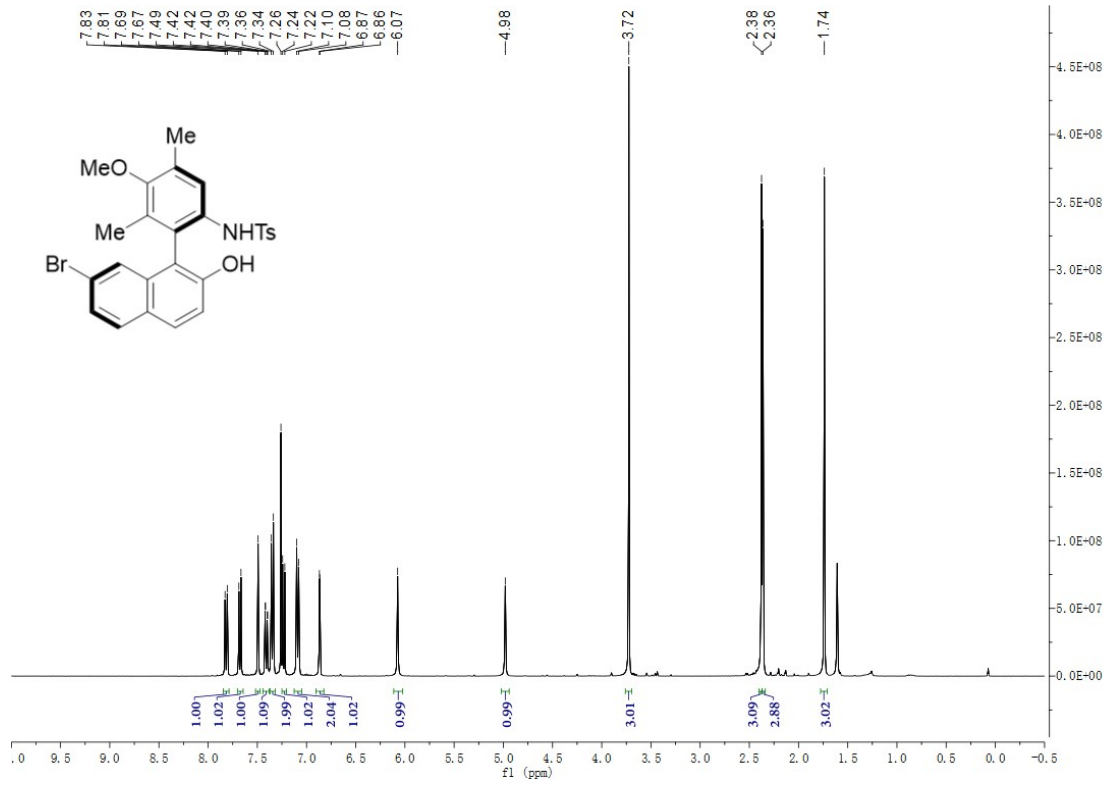




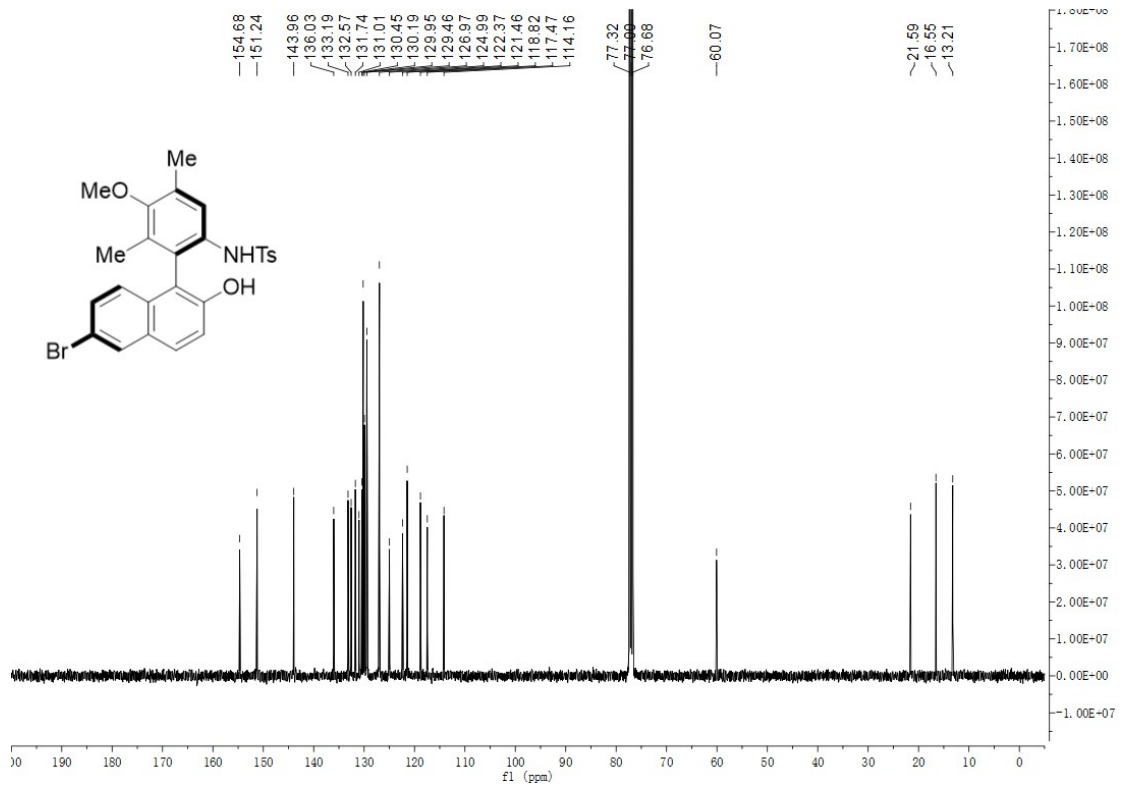
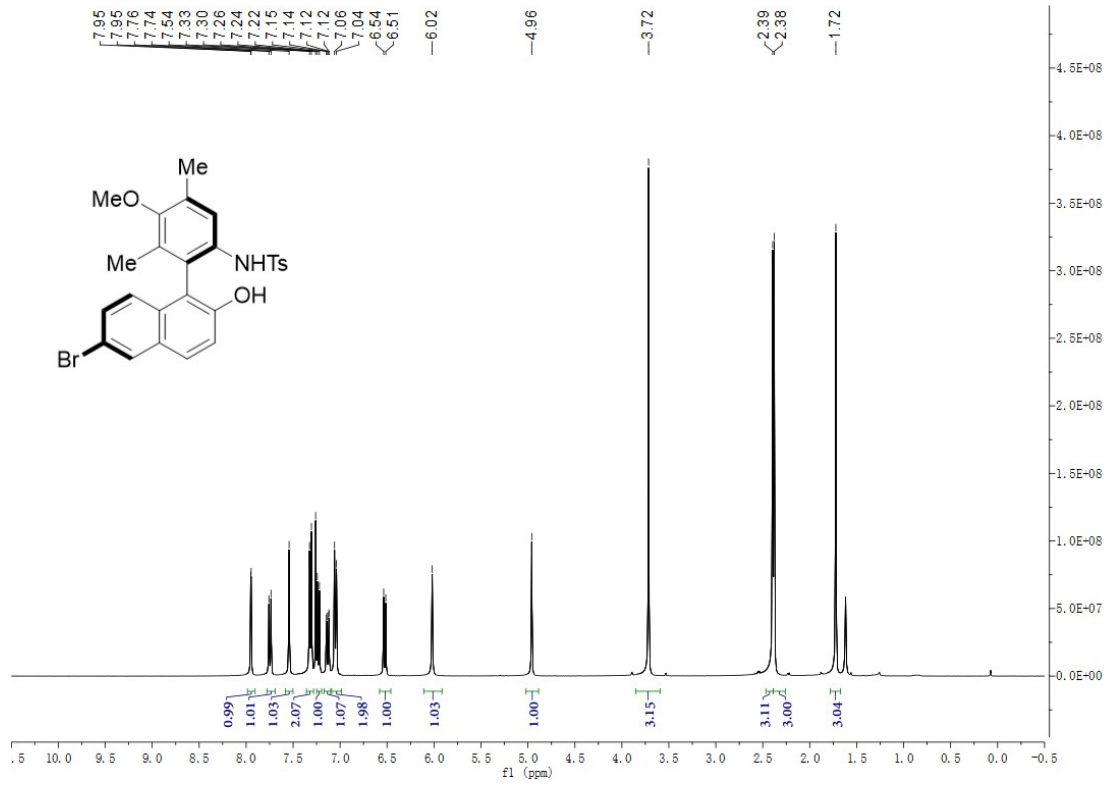
Compound 8a



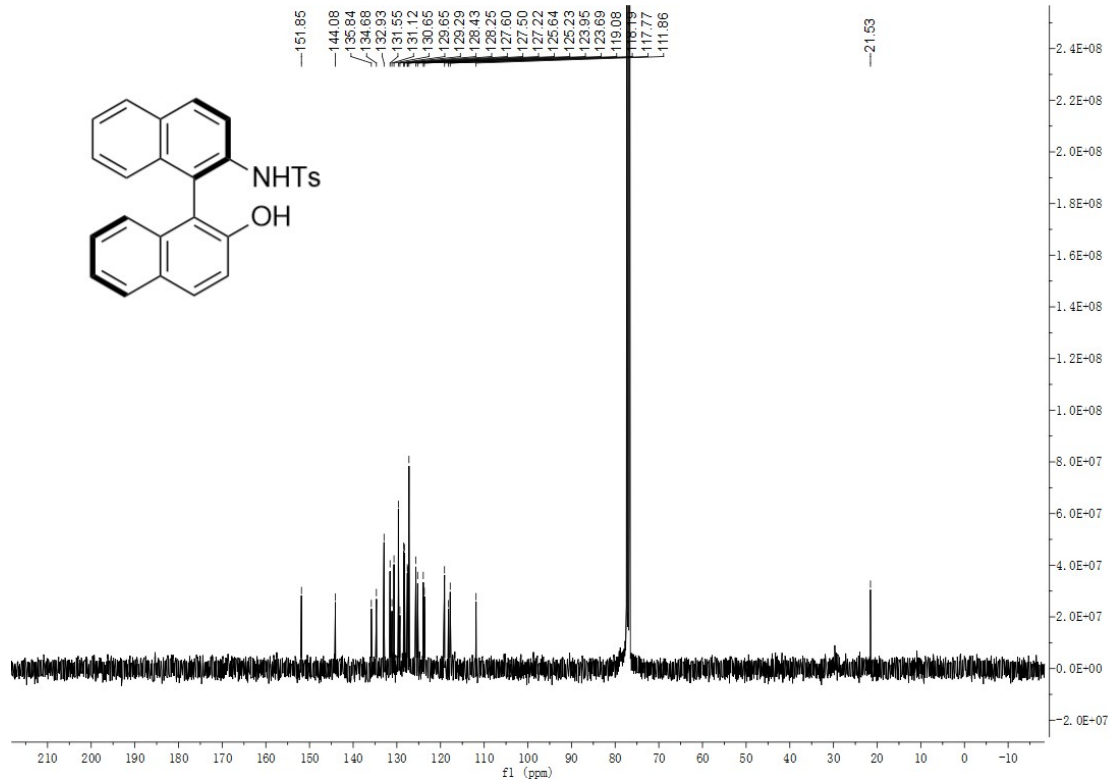
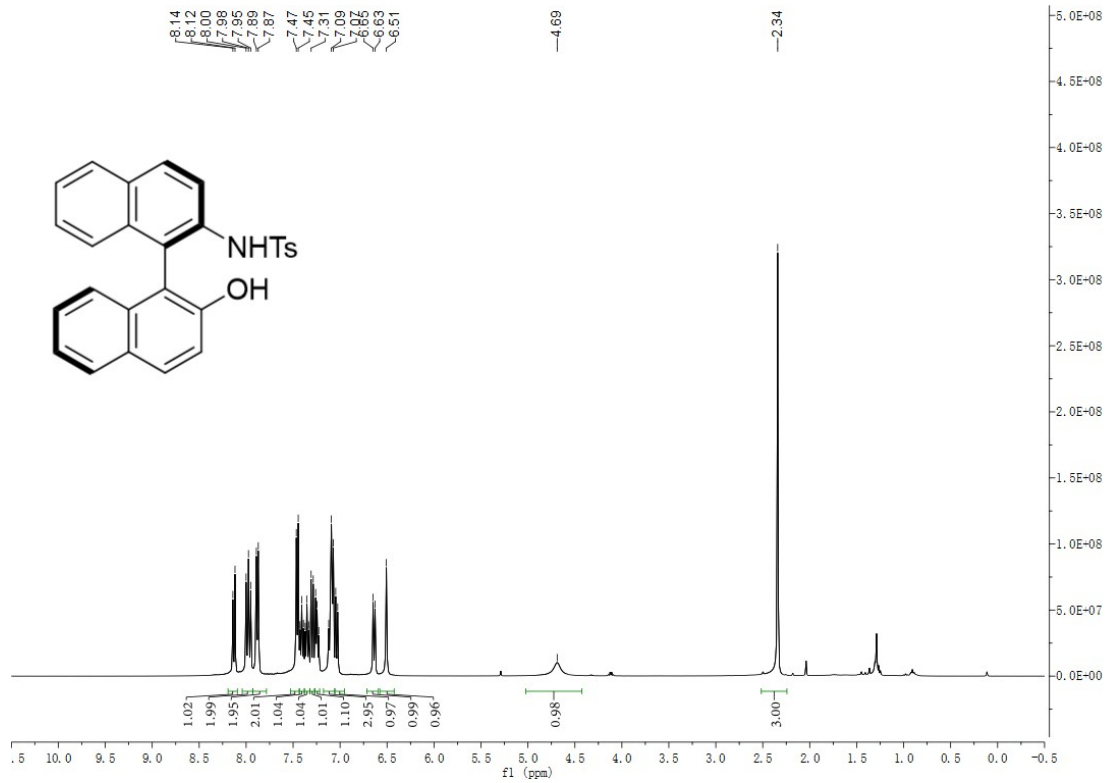
Compound **8b**



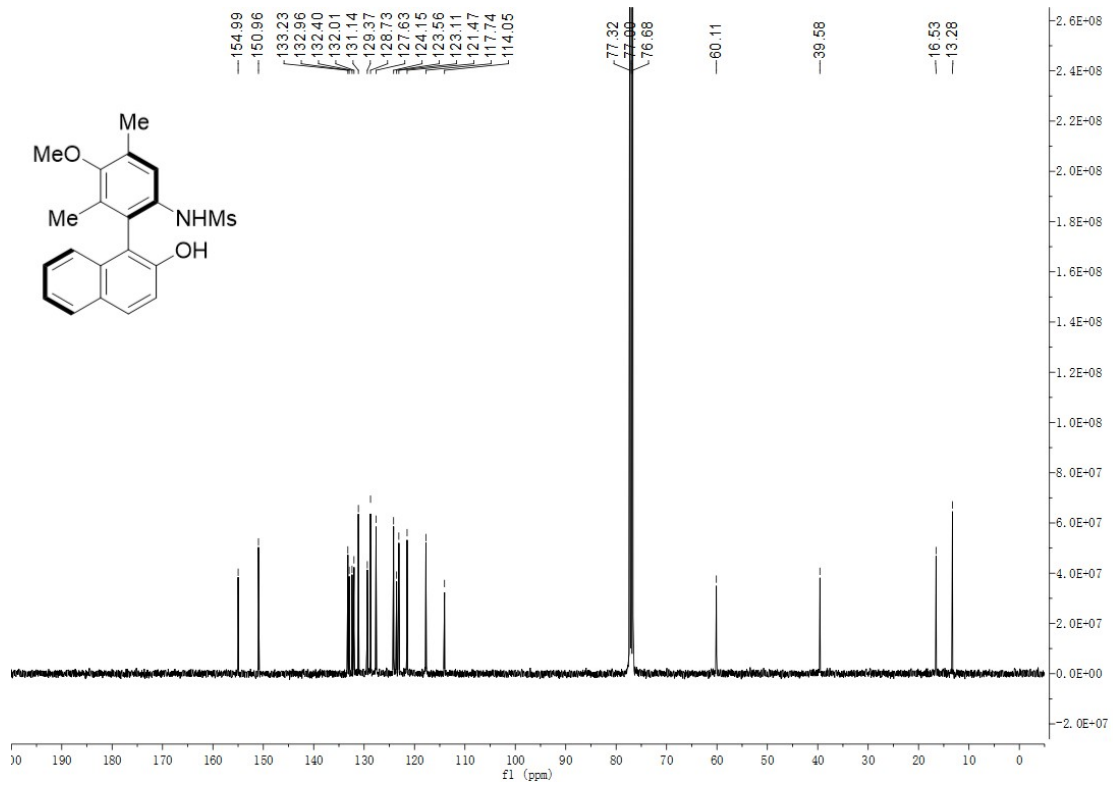
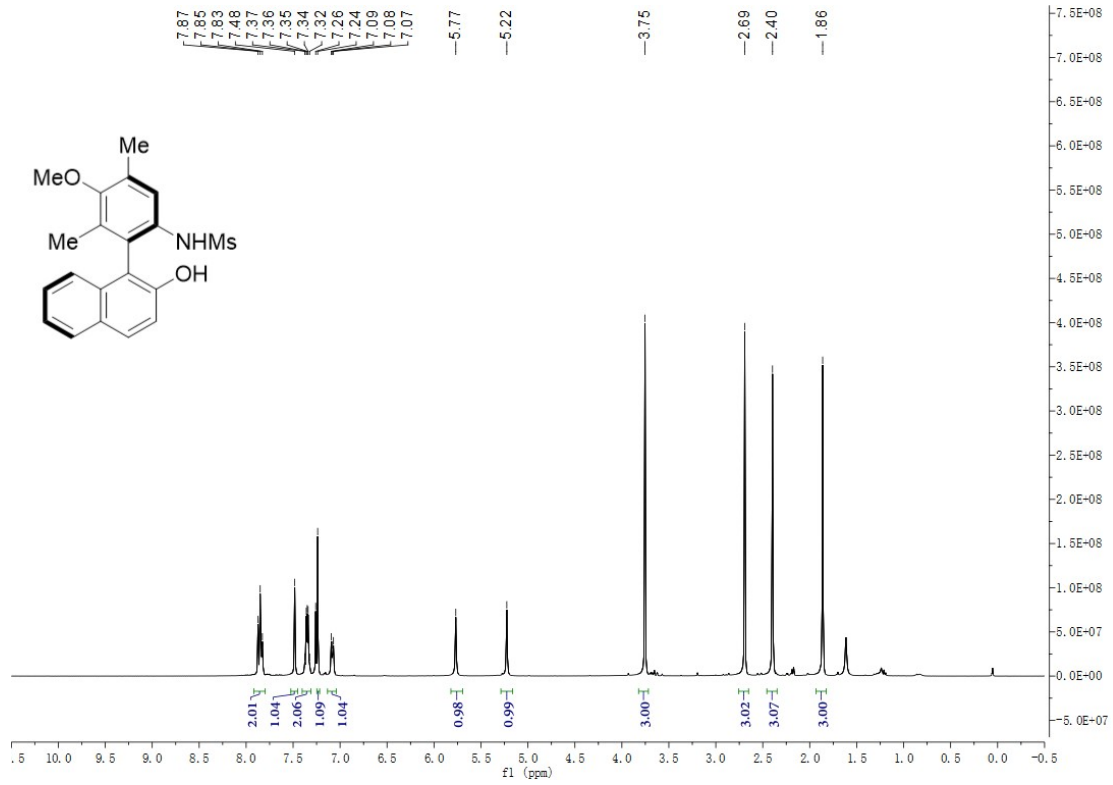
Compound **8c**



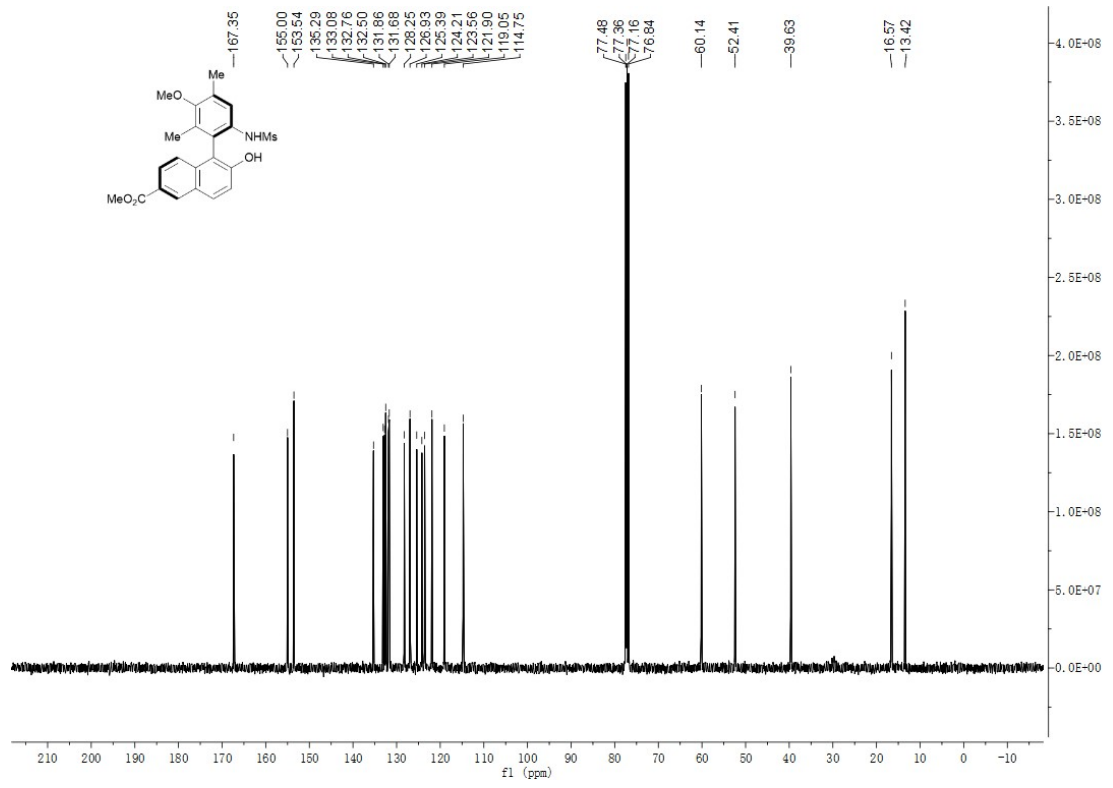
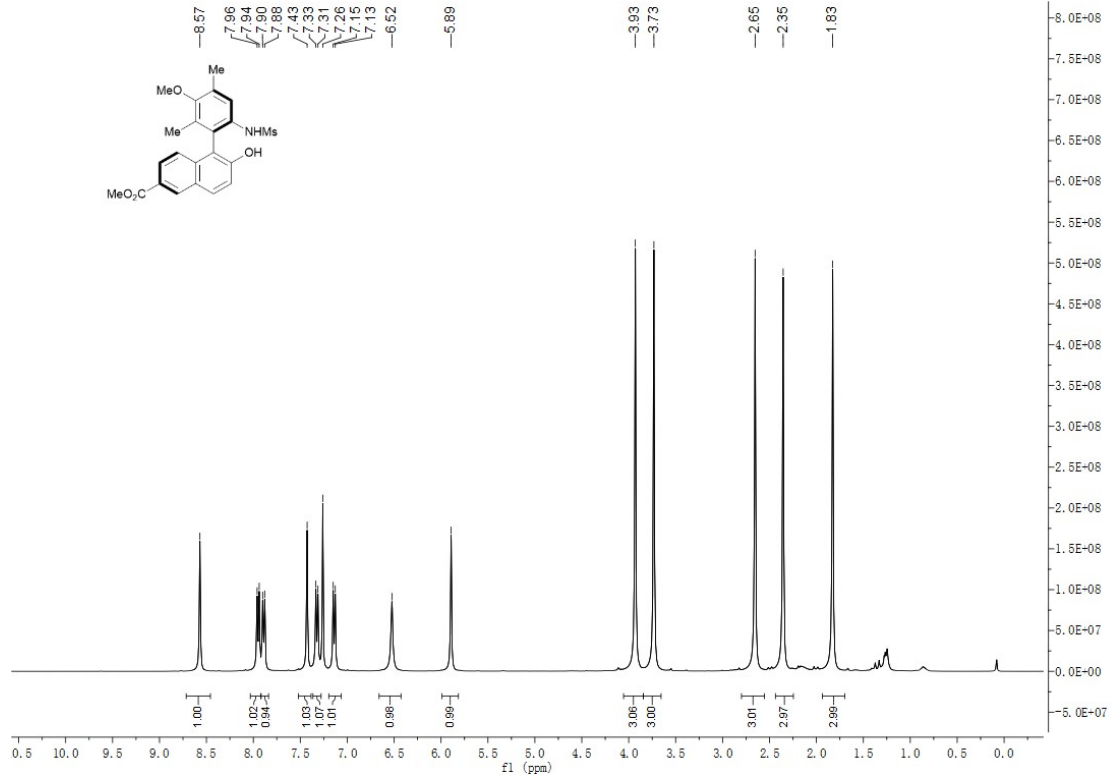
Compound **8d**



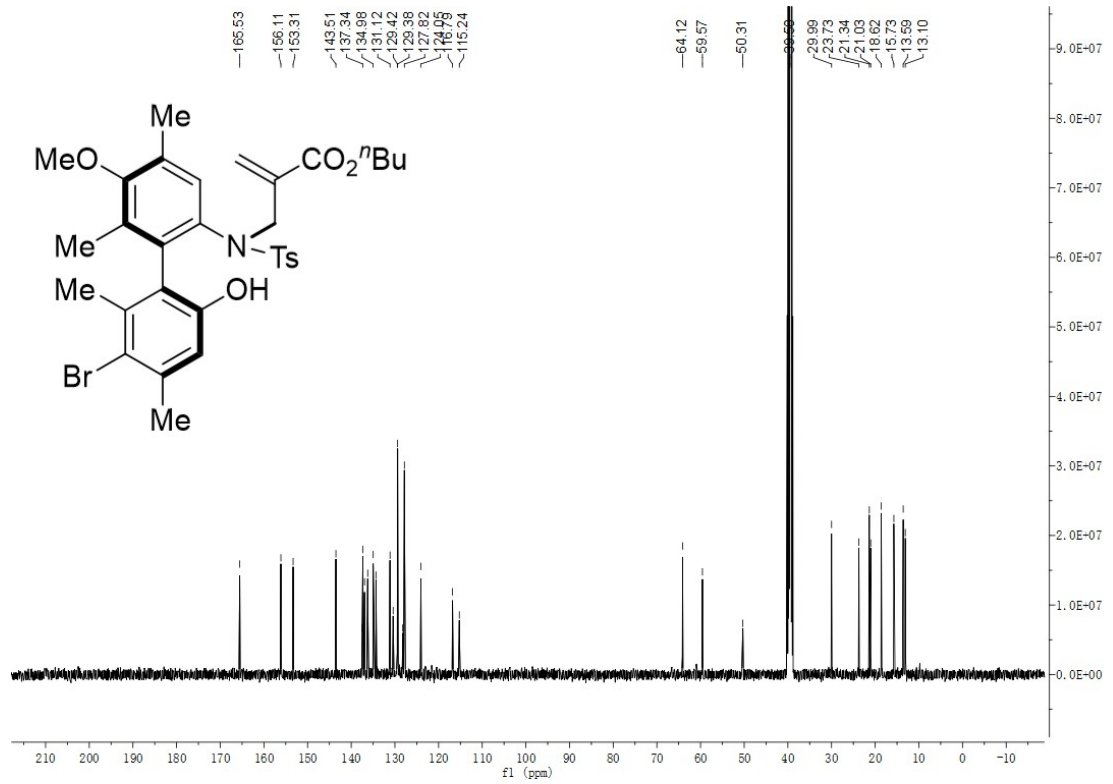
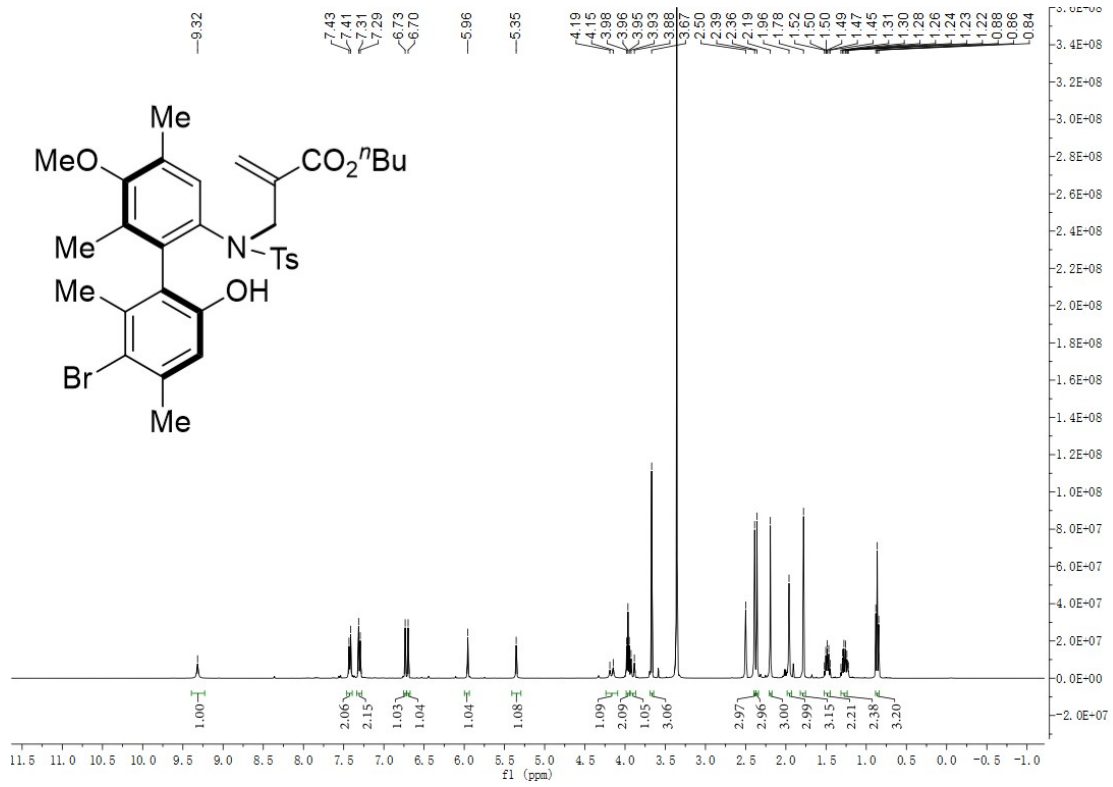
Compound **8e**



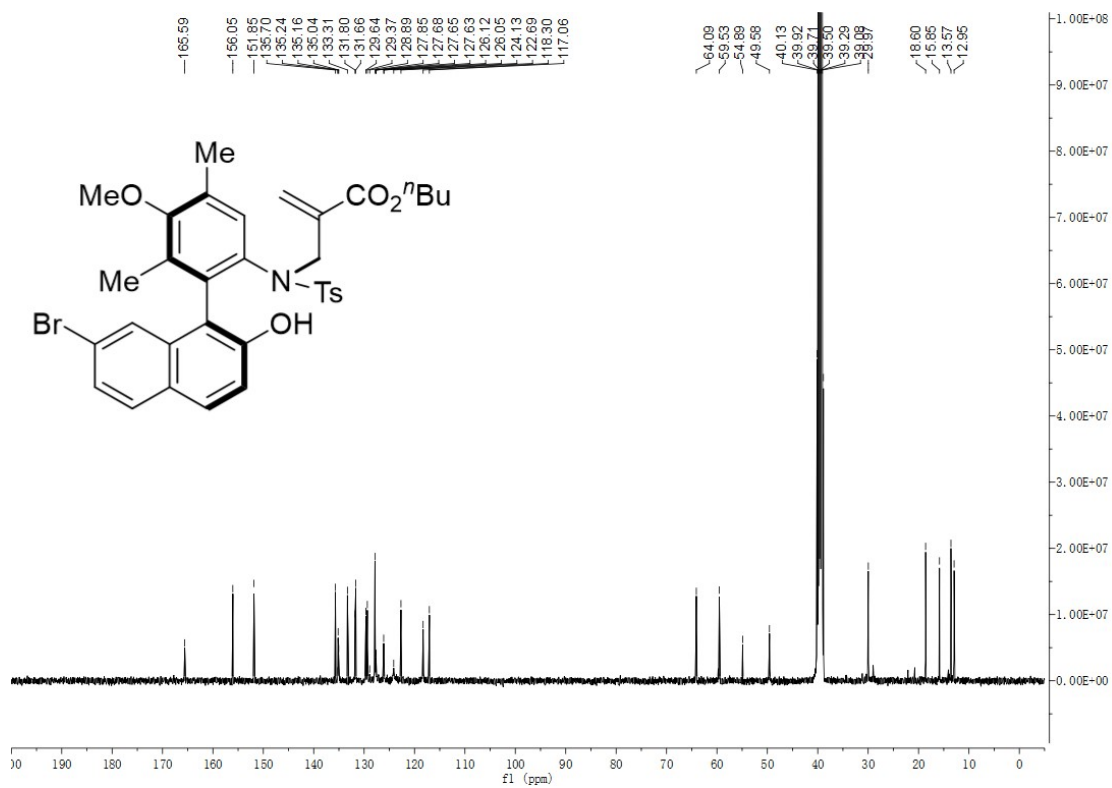
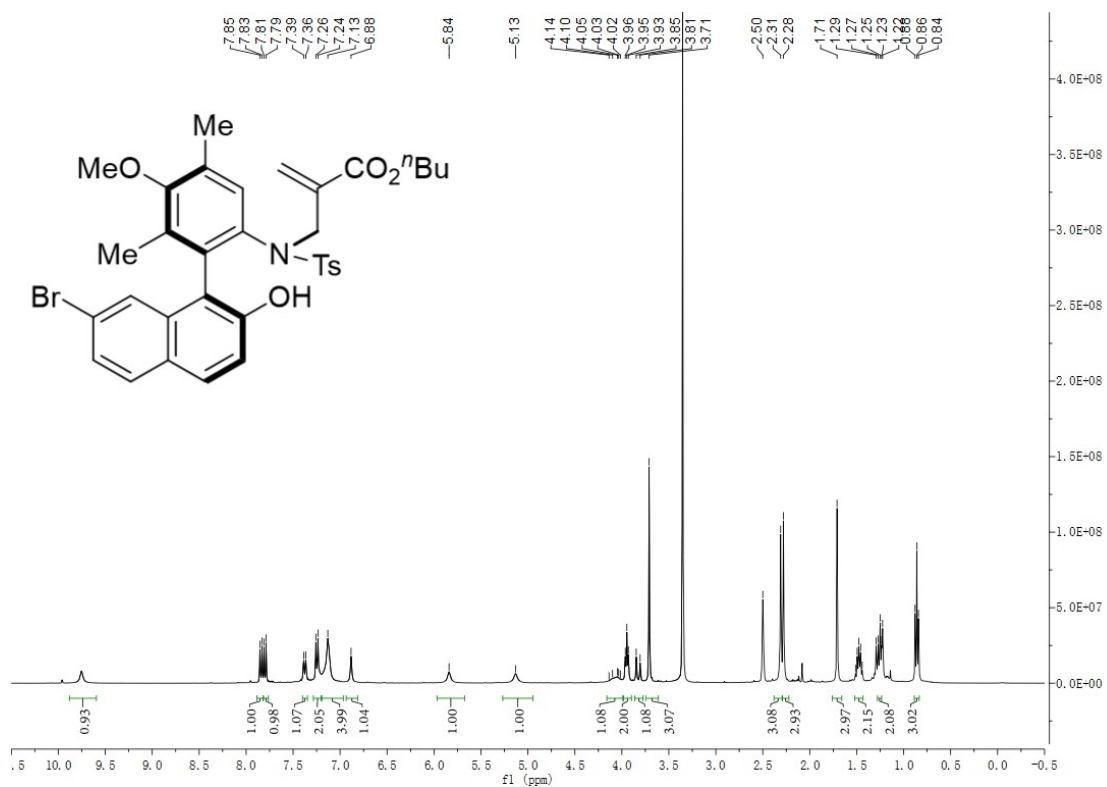
Compound **8f**



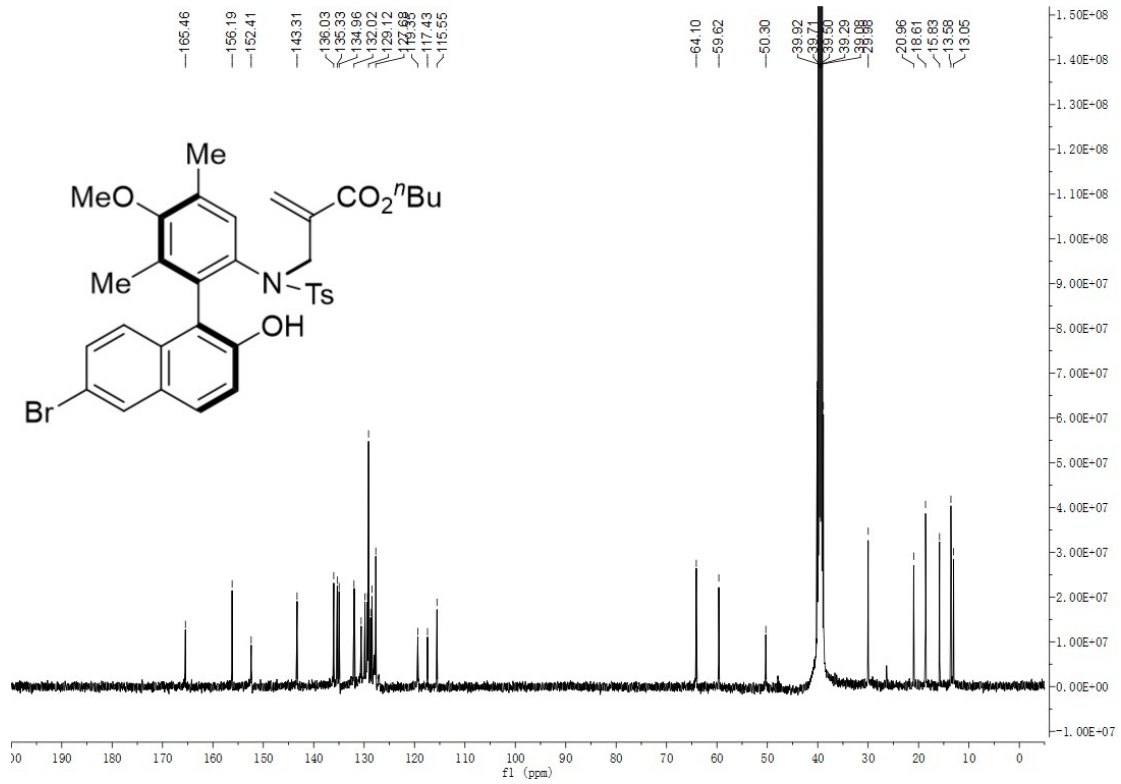
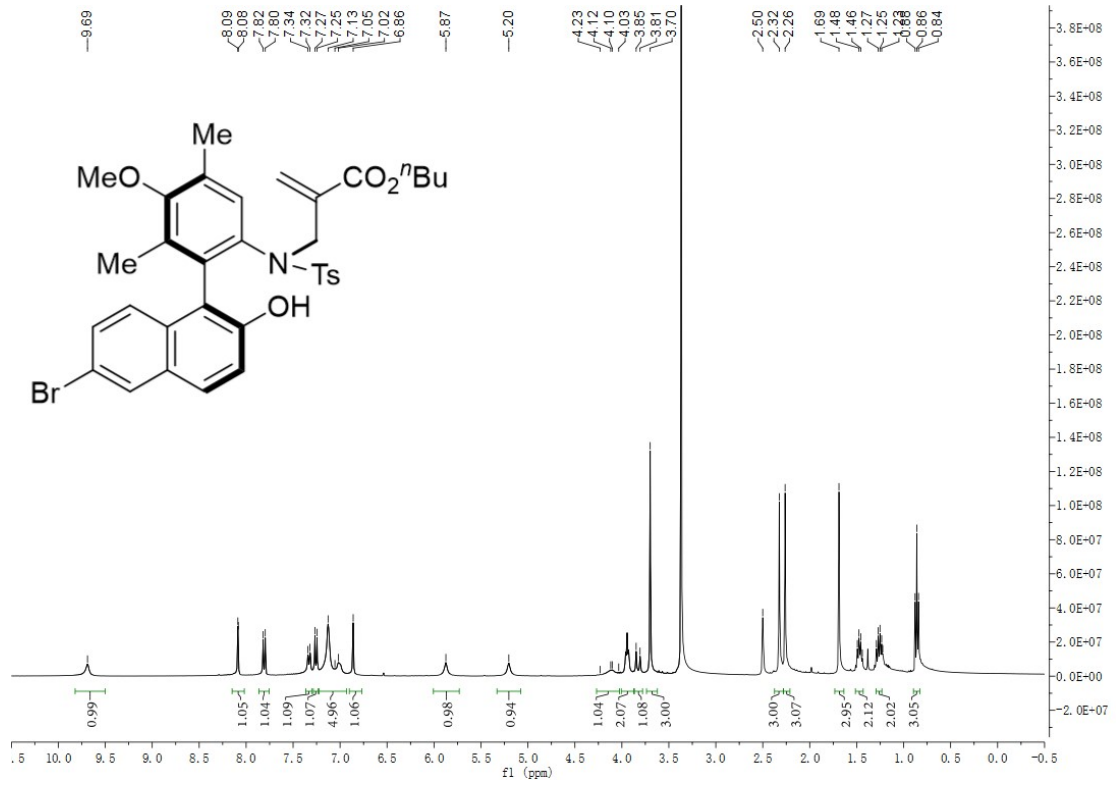
Compound 9a



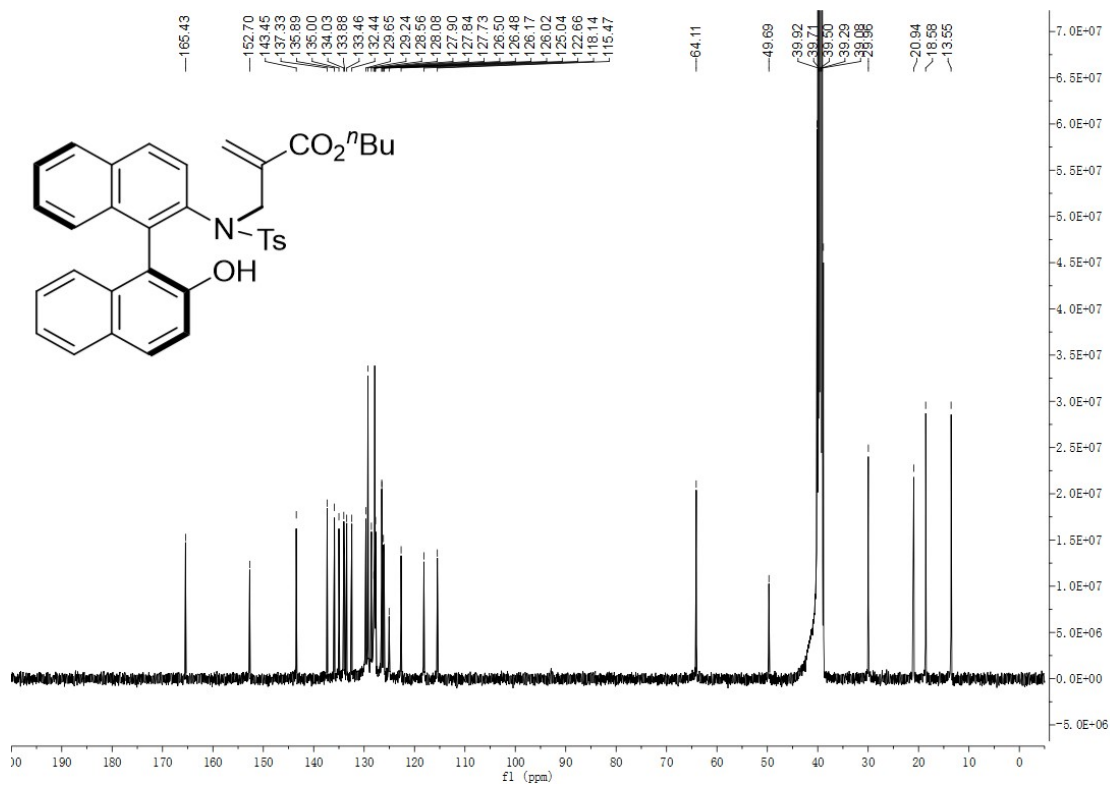
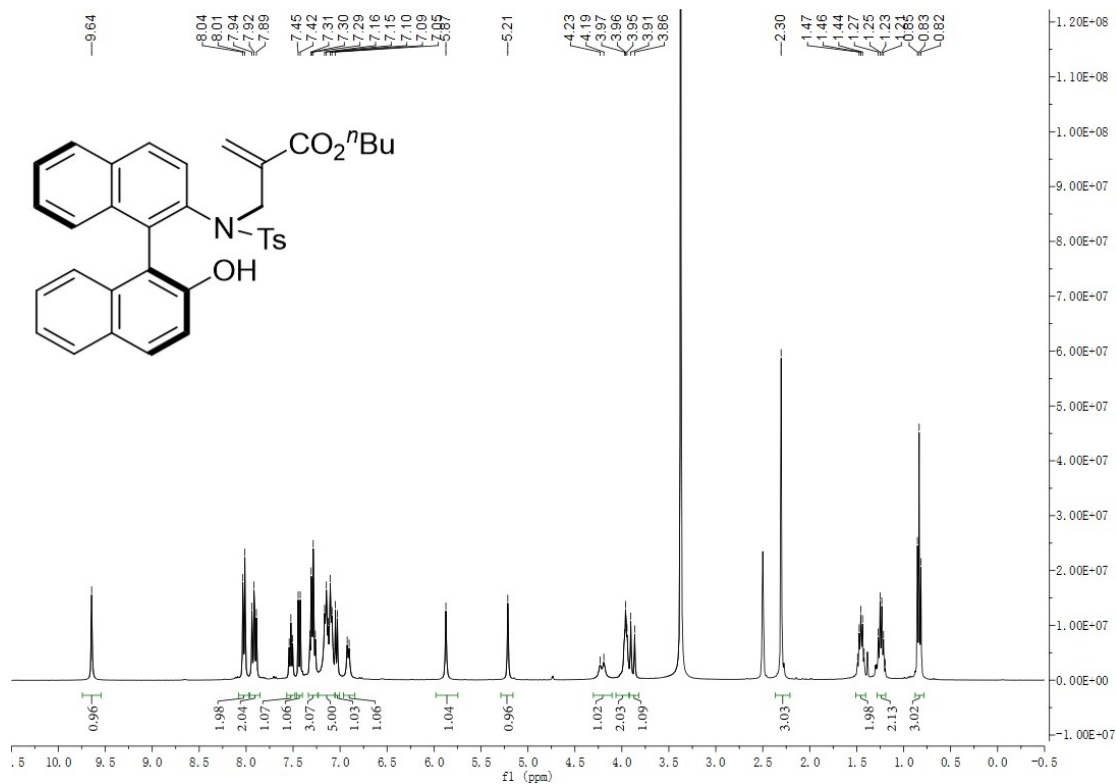
Compound **9b**



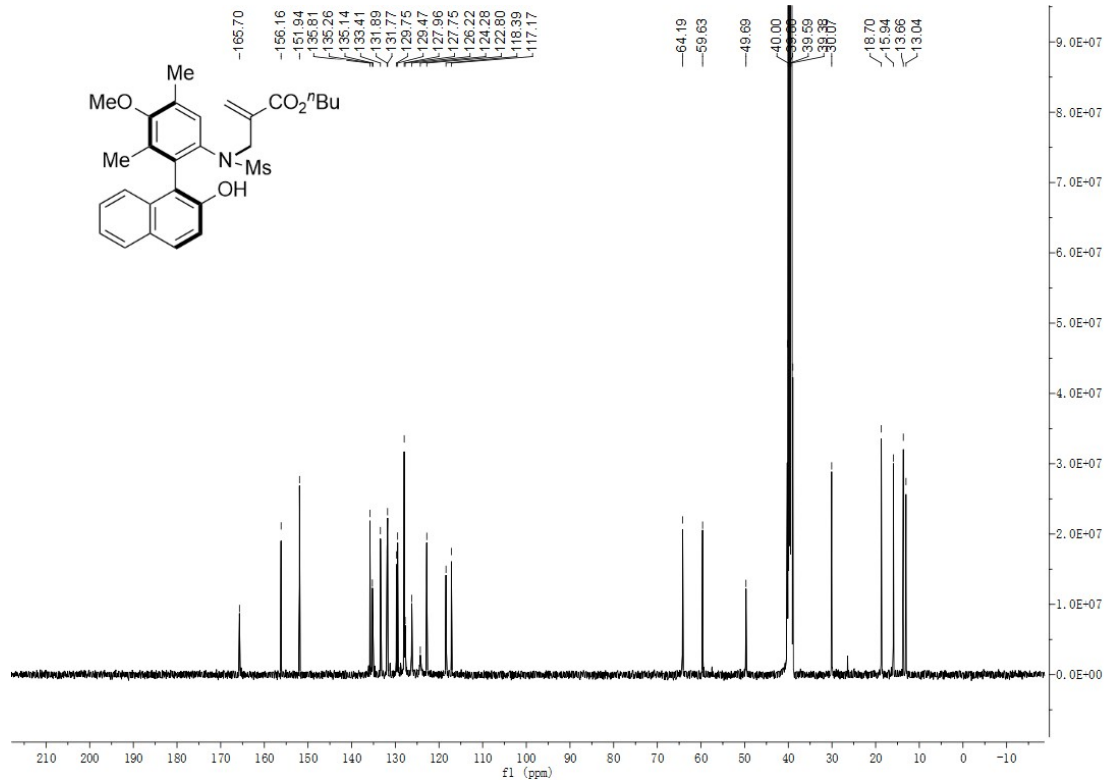
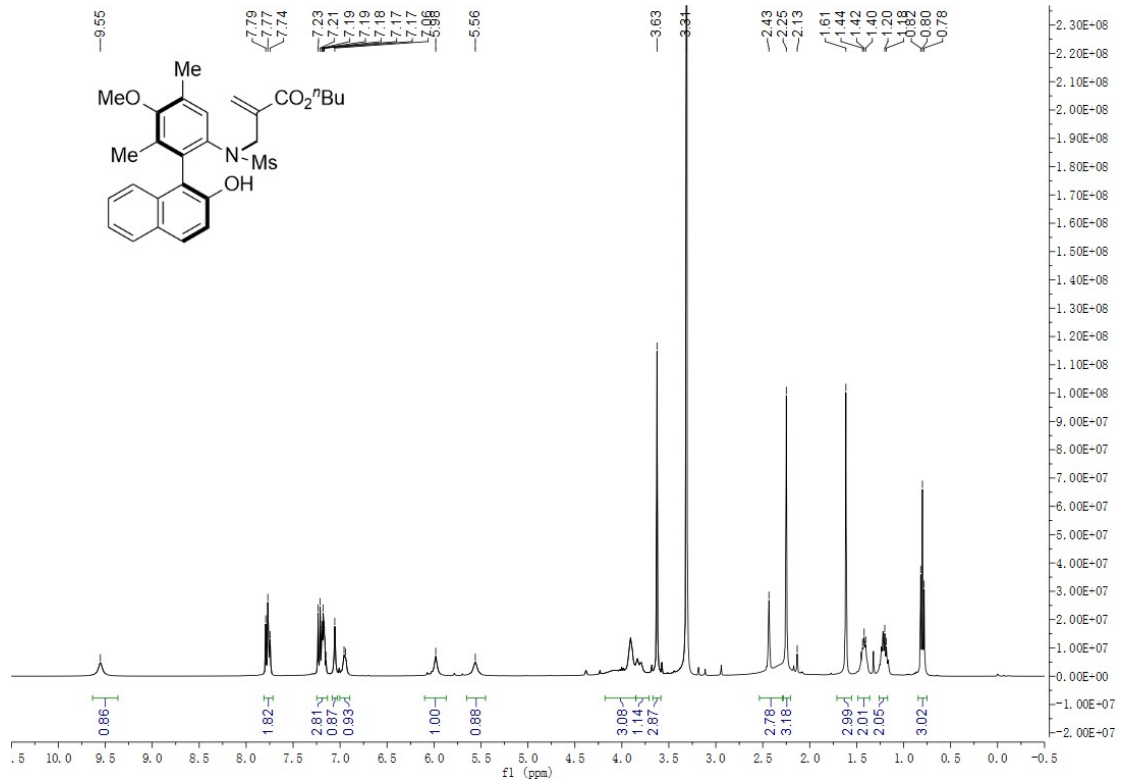
Compound 9c



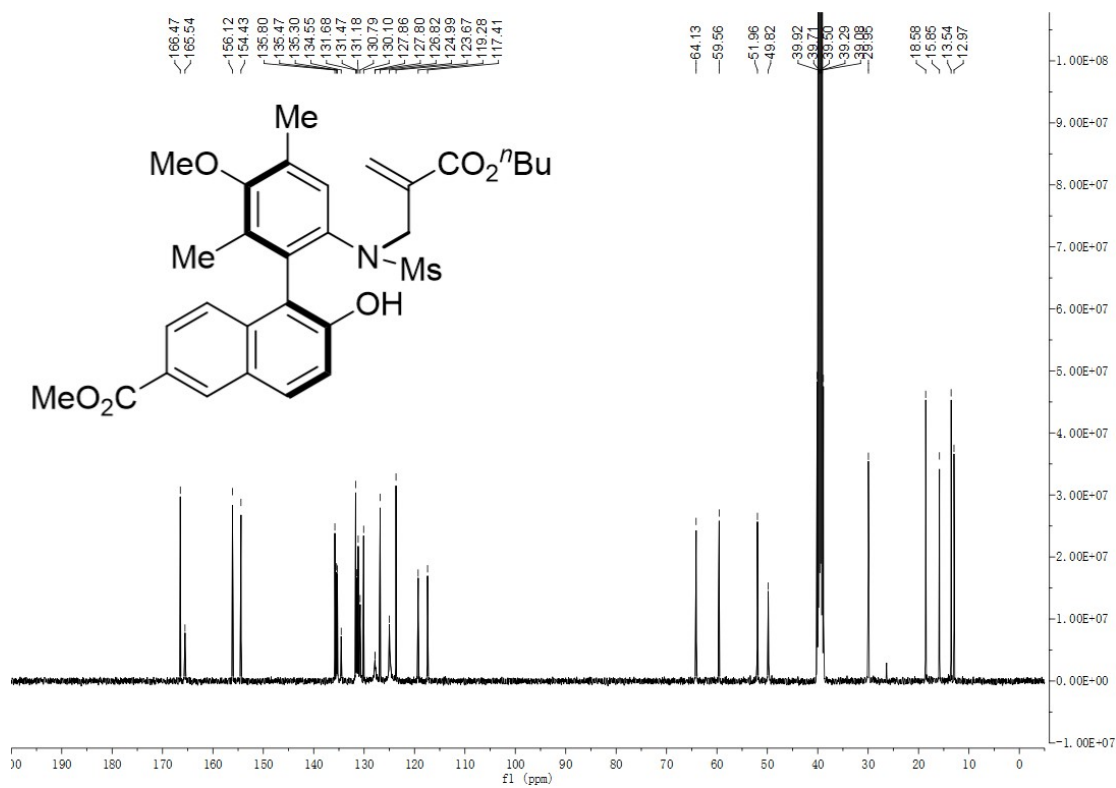
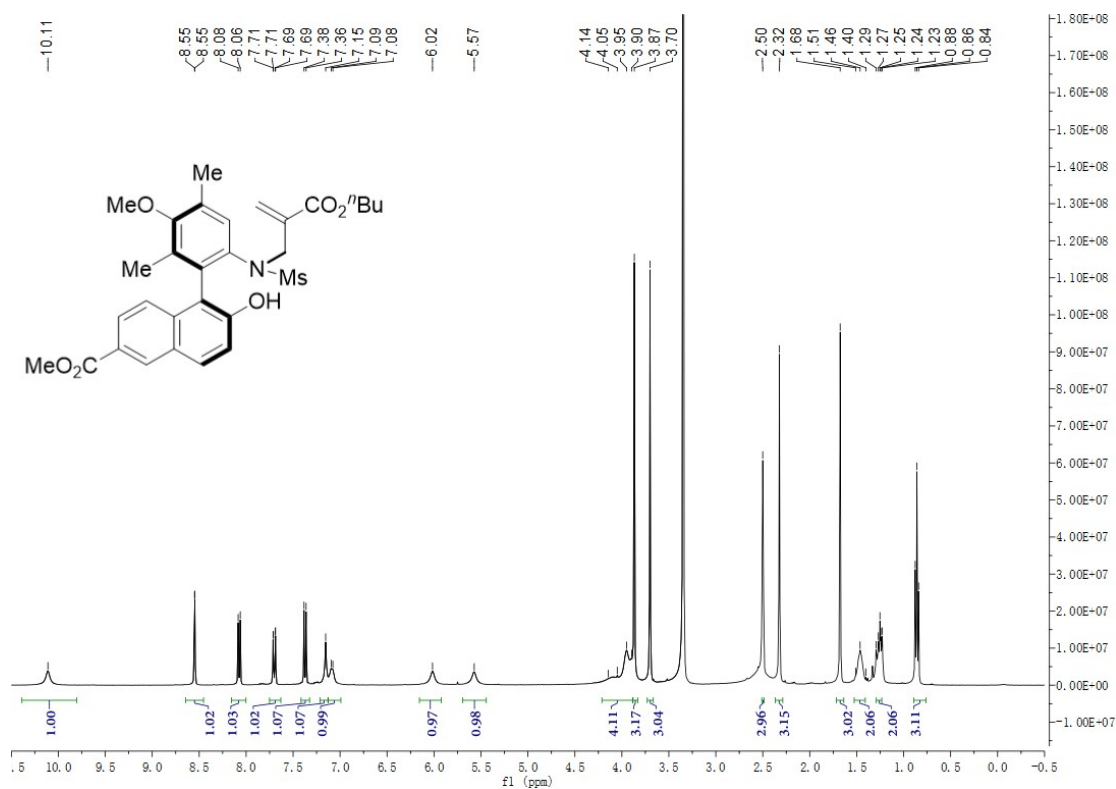
Compound 9d



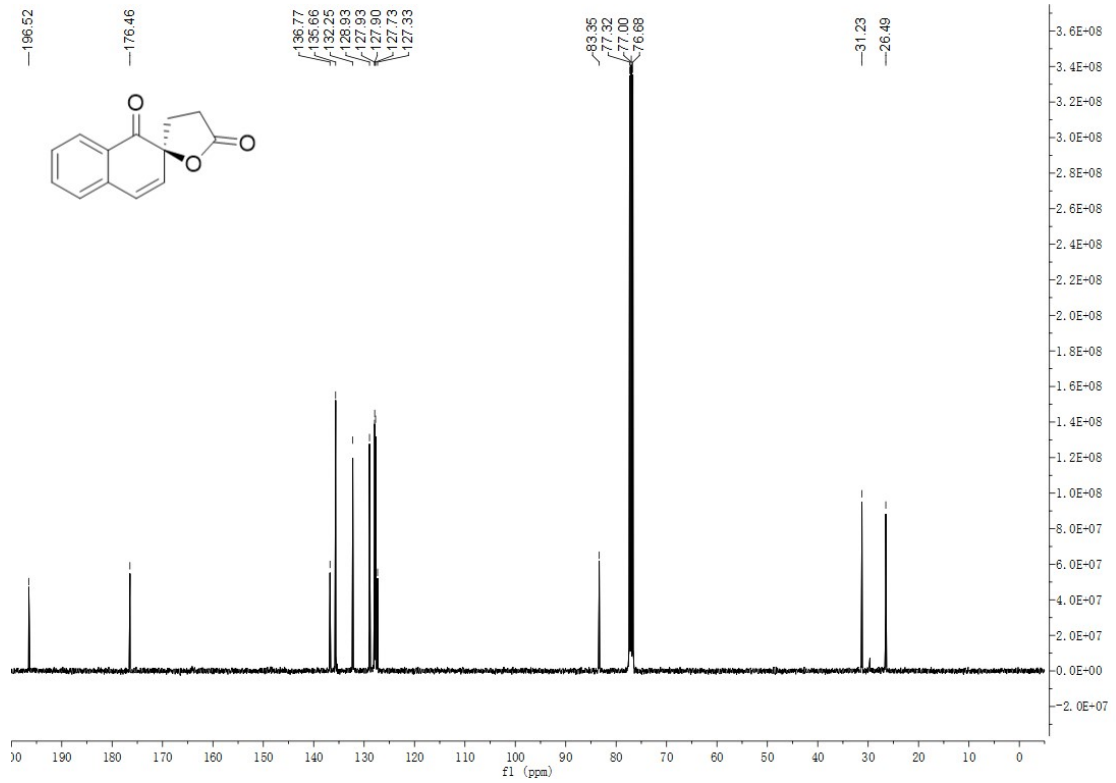
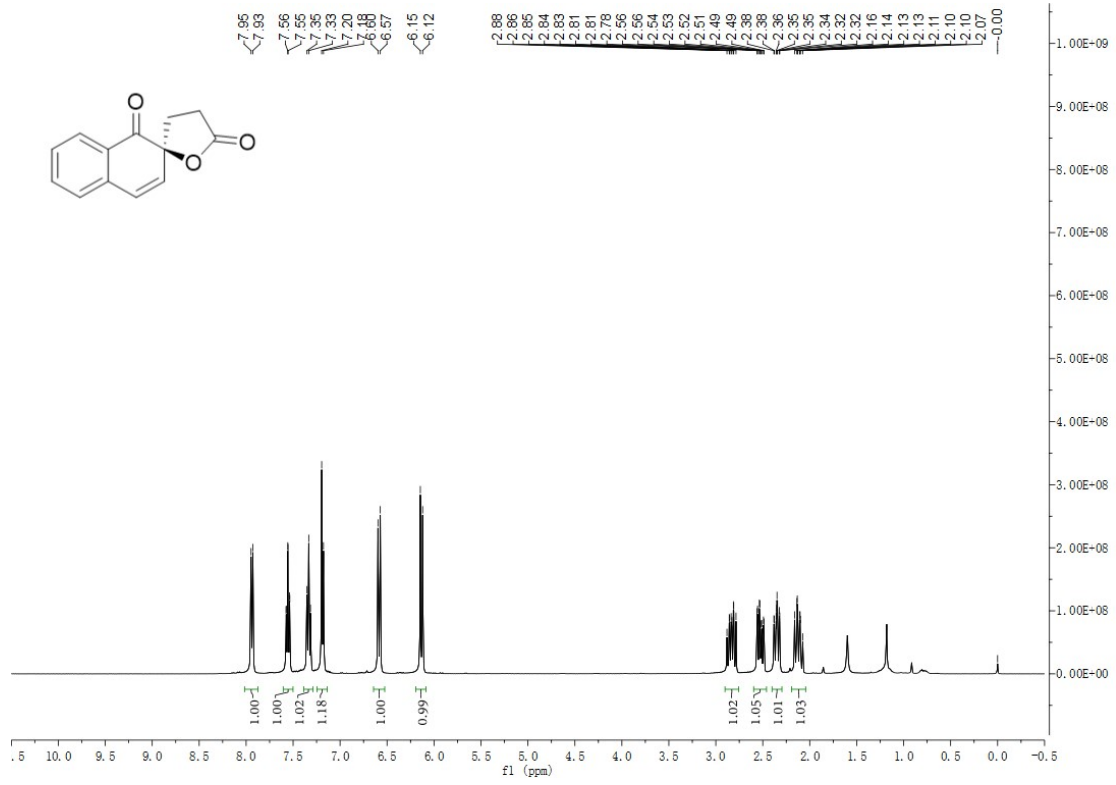
Compound 9e



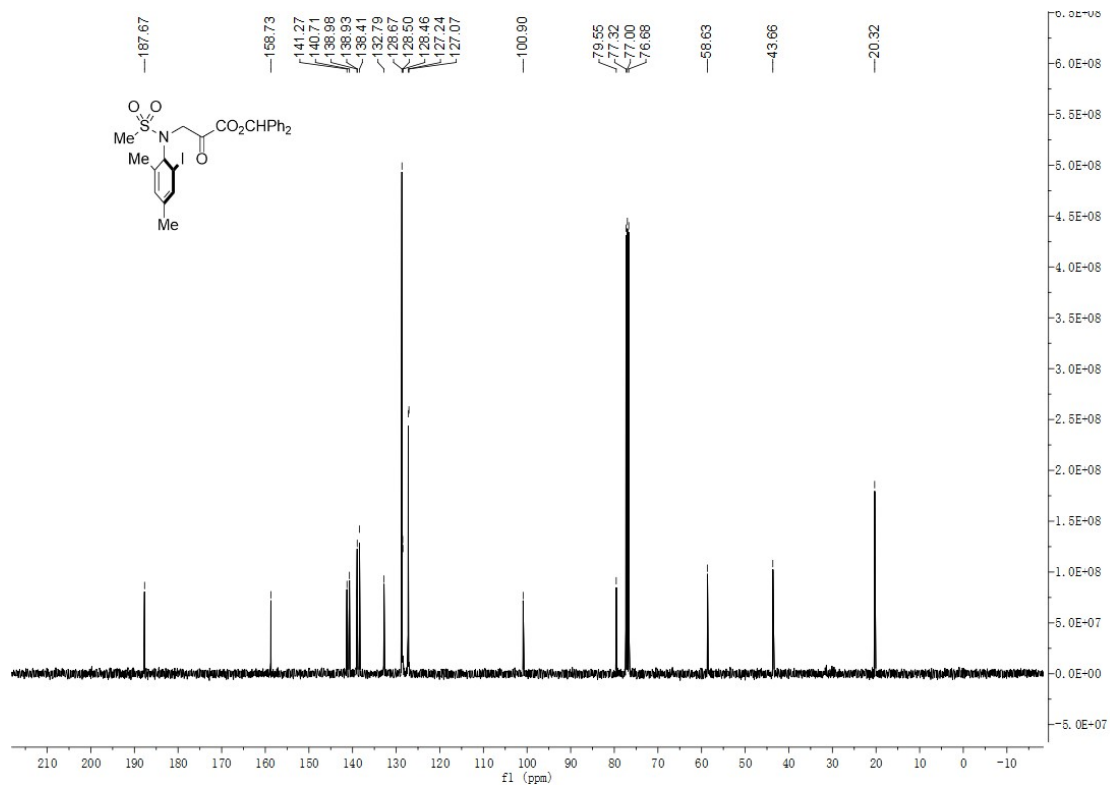
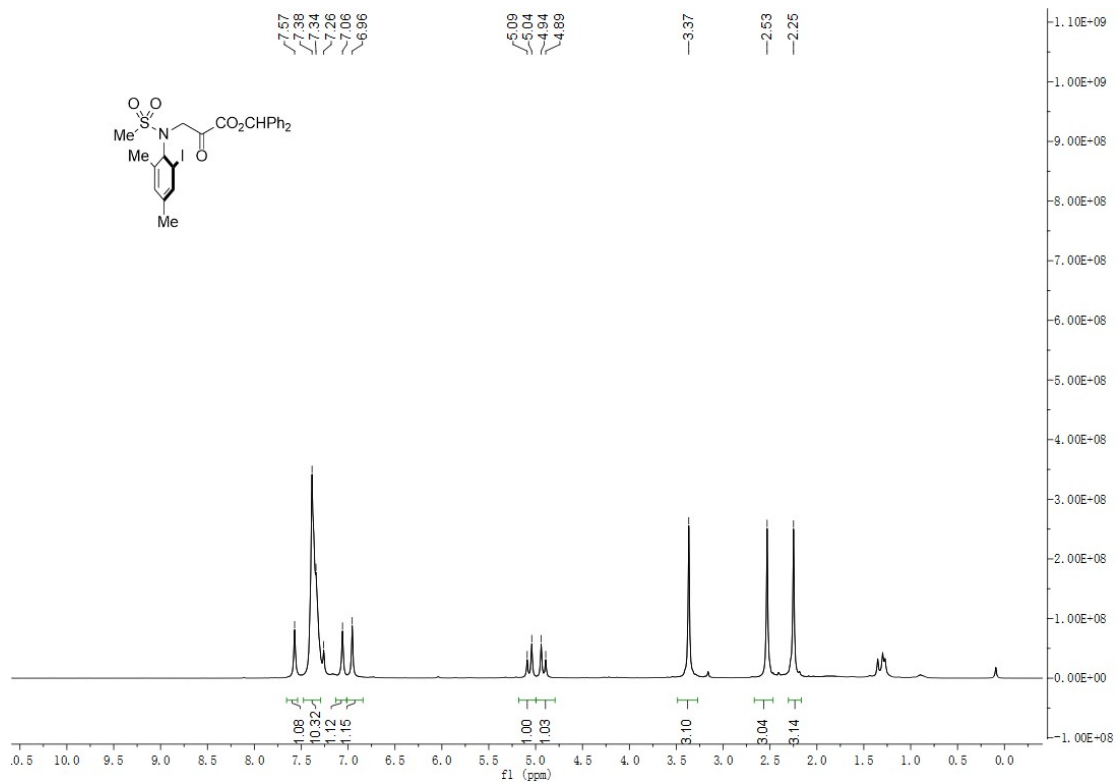
Compound **9f**



Compound SI-2



Compound 10



Compound 11

