

SUPPORTING INFORMATION

Enantioselective Synthesis of 3-Fluoro-3-allyl-oxindoles via Phos-phine-Catalyzed Asymmetric γ -addition of 3-Fluoro-Oxindoles to 2,3-Butadienoates

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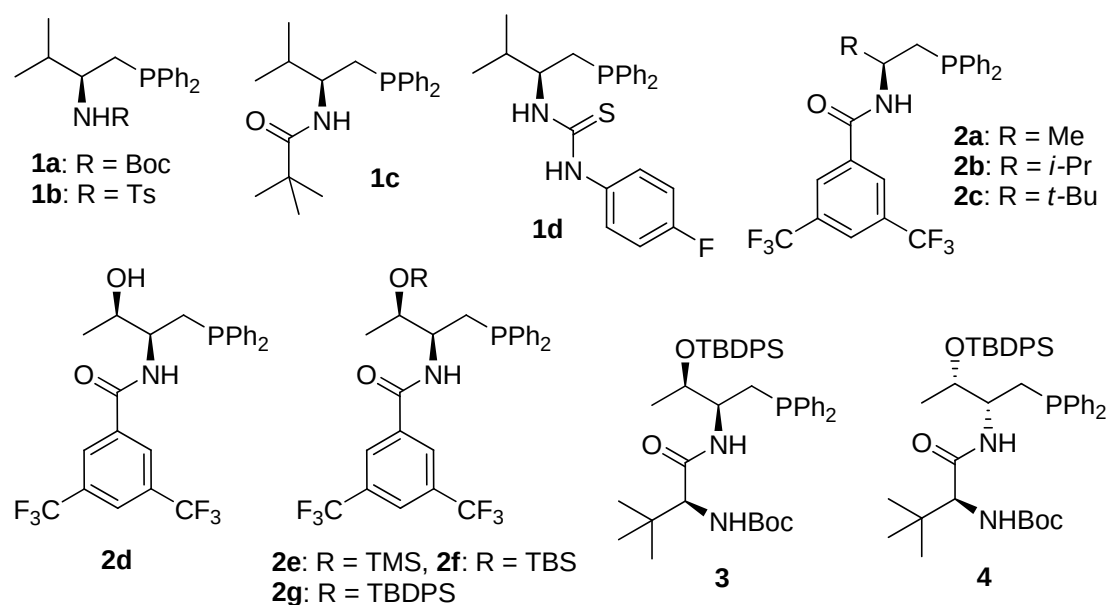
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded at ambient temperature in CDCl_3 or D_2O on a Bruker ACF300 or AMX500 (500 MHz) spectrometer. The chemical shifts are reported in parts permillion (ppm) relative to CDCl_3 ($\delta = 7.26$) for ^1H -NMR and relative to the central resonances of CDCl_3 ($\delta = 77.0$) for ^{13}C -NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants (J) were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on 200-300 mesh silica gel. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail. Optical rotations were measured with polarimeter.

All the chiral phosphine catalysts were prepared by following our previously reported procedures.^[1] All the 3-fluoro-substituted oxindoles were synthesized based on known methods reported in literature.^[2]

The absolute configuration of **7a₁** was assigned by comparing optical rotation of the corresponding derivative **9** (Scheme S3) with the value reported in the literature,^[3] and the configuration of other γ -addition products were assigned by analogy.

2. Optimization of Reaction Conditions

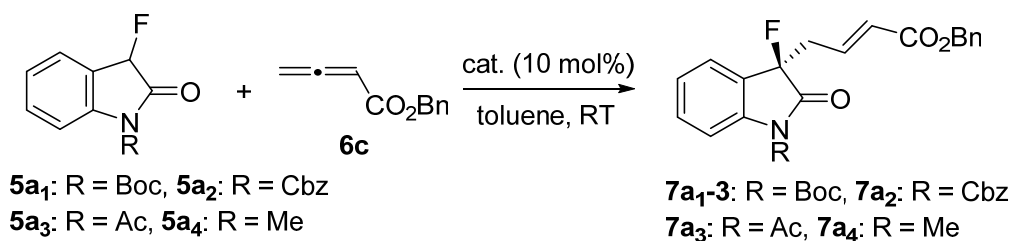


Scheme S1: Chiral phosphine catalysts used in this study.

(TBDPS = *tert*-butyldiphenylsilyl, TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl, Ts = 4-toluenesulfonyl)

A. Optimization of conditions for γ -Addition of 3-fluoro-oxindoles

Table S1: Asymmetric γ -addition of 3-fluoro-oxindole **5a** with allenolate **6c** catalyzed by different chiral phosphines in toluene^[a]

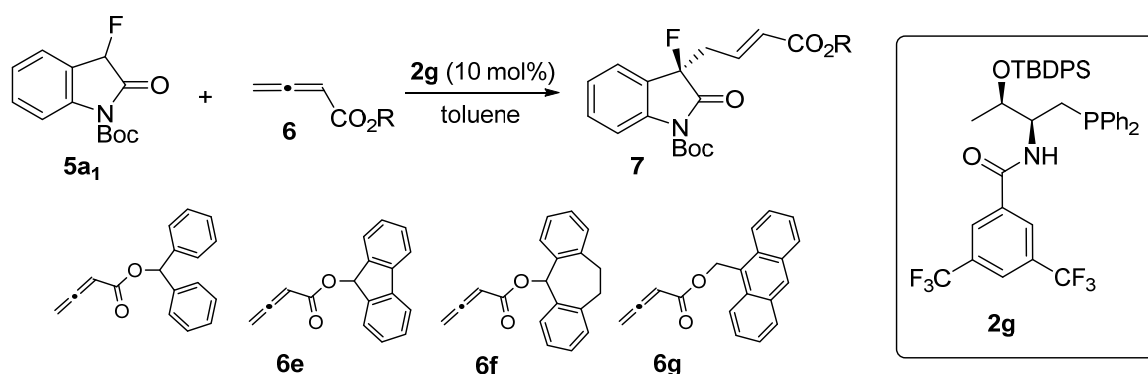


Entry	Cat.	R(5a)	<i>t</i> [h]	Yield [%] ^[b]	ee [%] ^[c]
1	1a	Boc(5a₁)	1	88	32
2	1b	Boc(5a₁)	0.5	95	55
3	1c	Boc(5a₁)	1	88	41
4	1d	Boc(5a₁)	0.5	98	77

5	2a	Boc(5a₁)	1	95	90
6	2b	Boc(5a₁)	1	93	90
7	2c	Boc(5a₁)	2	88	88
8	2d	Boc(5a₁)	2	89	64
9	2e	Boc(5a₁)	2	93	93
10	2f	Boc(5a₁)	2	92	92
11	2g	Boc(5a₁)	2	95	93
12	3	Boc(5a₁)	2	90	6
13	4	Boc(5a₁)	2	90	-9
14	2g	Cbz(5a₂)	2	86	93
15	2g	Ac(5a₃)	4	82	83
16	2g	Me(5a₄)	4	<5	--

[a] Reactions were performed with **5a** (0.05 mmol), **6c** (0.06 mmol) and catalyst (0.005 mmol) in toluene (0.5 mL) at room temperature. [b] Yields of isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S2: Asymmetric γ -addition of 3-fluoro-oxindole (**5a₁**) with different allenates (**6**) catalyzed by phosphine catalyst **2g** in toluene ^[a]

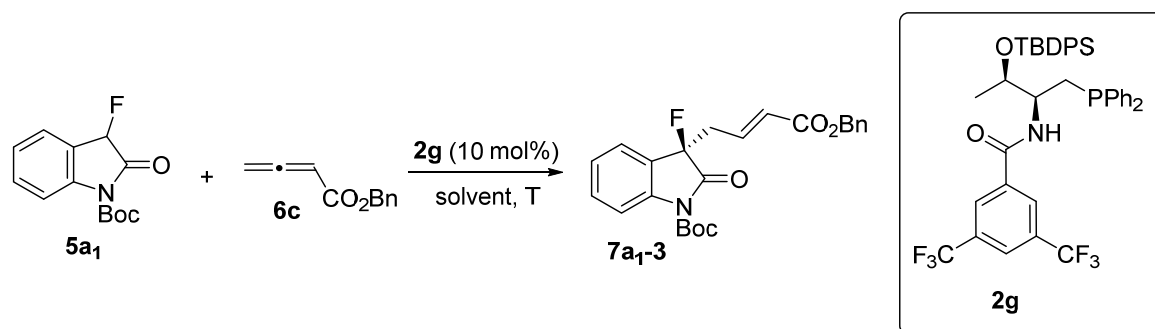


Entry	R (6)	7	Yield [%] ^[b]	ee [%] ^[c]
1	Me(6a)	7a₁-1	92	91
2	<i>t</i> -Bu(6b)	7a₁-2	90	91

3	Bn(6c)	7a₁-3	95	93
4	6d	7a₁-4	91	93
5	6e	7a₁-5	92	93
6	6f	7a₁-6	89	92
7	6g	7a₁-7	85	86
8	Ph(6h)	7a₁-8	88	77

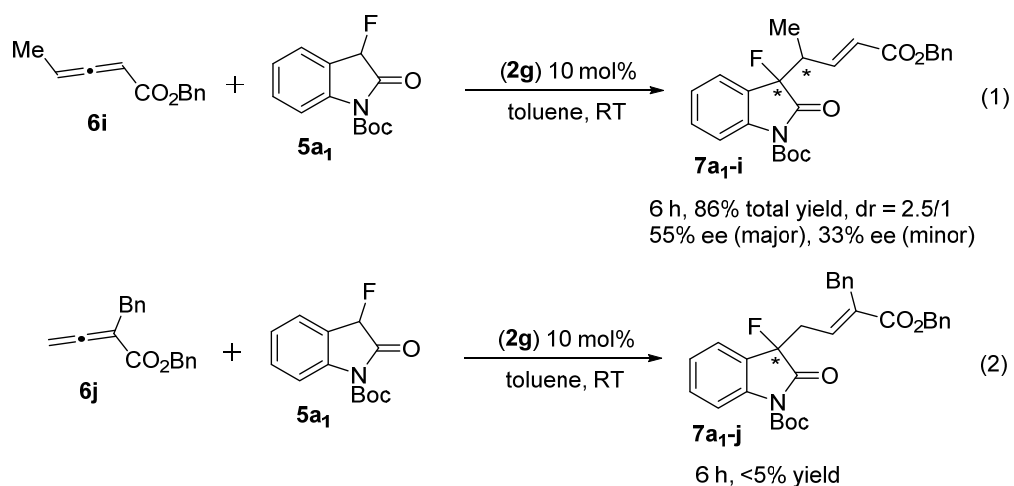
[a] Reaction conditions: **5a₁** (0.05 mmol), **6** (0.06 mmol), and the catalyst **2g** (0.005 mmol) in toluene (0.5 mL). [b] Yields of isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S3: Asymmetric γ -addition oxindole **5a₁** with allenolate **6c** catalyzed by **2g**: optimizing the solvents and other reaction conditions ^[a]



Entry	Solvent	T [°C]	t [h]	Yield [%] ^[b]	ee [%] ^[c]
1	toluene	RT	2	95	93
2	xylene	RT	2	95	90
3	Et ₂ O	RT	2	88	73
4	CHCl ₃	RT	4	90	88
5	CH ₂ Cl ₂	RT	4	92	92
6	EA	RT	6	81	45
7	toluene	0	12	83	69

[a] Reaction conditions: **5a₁** (0.05 mmol), **6c** (0.06 mmol), and the catalyst **2g** (0.005 mmol) in solvent (0.5 mL). [b] Yields of isolated products. [c] Determined by HPLC analysis on a chiral stationary phase.



Scheme S2: Reactions of α -substituted and γ -substituted allenoates (**6i** and **6j**) with *N*-Boc-3-fluoro-oxindole (**5a₁**) by catalyst **2g**.

3. Proposed Reaction Cycle

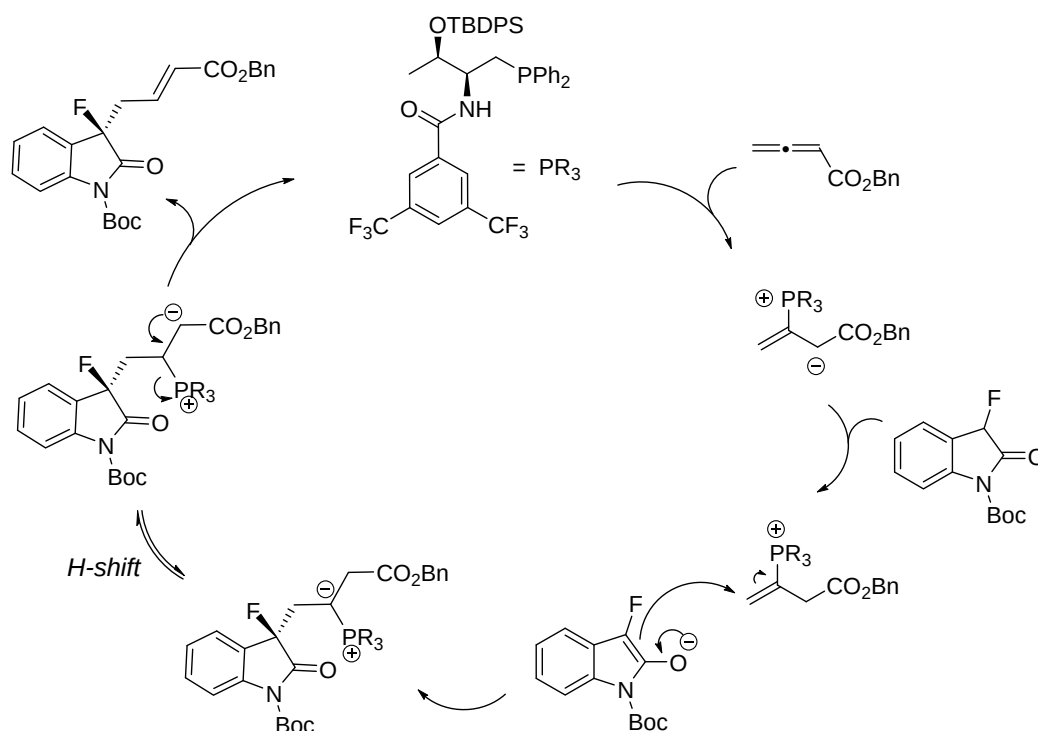


Figure S1: Proposed catalytic cycle.

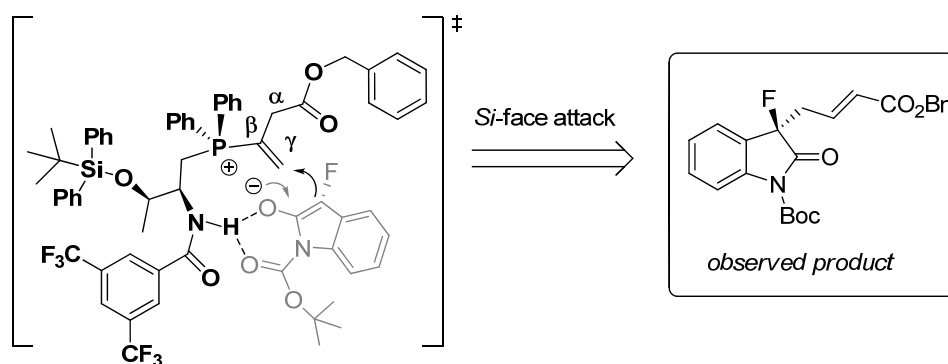
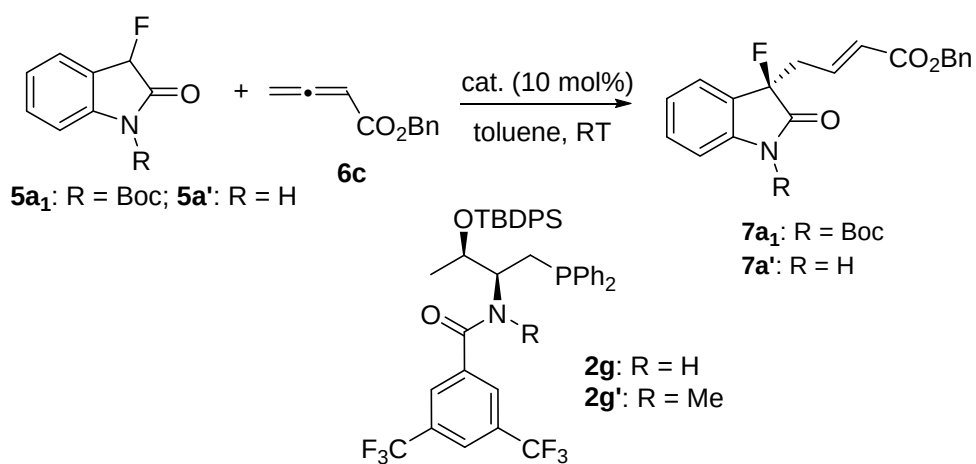


Figure S2. Proposed transition-state model.

Table S4. Asymmetric γ -addition promoted by different phosphine catalysts: investigating the H-bonding effect.^[a]

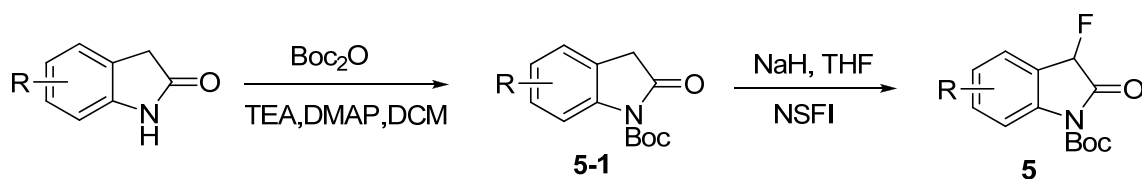


Entry	Sub.	Cat.	<i>t</i> [h]	7/Yield [%] ^[b]	ee [%] ^[c]
1	5a₁	2g	2	7a /95	93
2	5a₁	2g'	4	7a /85	37
3	5a'	2g	2	7a' /81	43

[a] Reaction conditions: substrate (0.05 mmol), **6c** (0.06 mmol), and catalyst (0.005 mmol) in toluene (0.5 mL) at room temperature. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

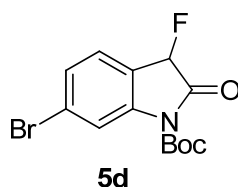
4. Preparation of the 3-fluoro-substituted oxindoles

General procedure for preparing 3-fluoro-substituted oxindoles 5:^[2]



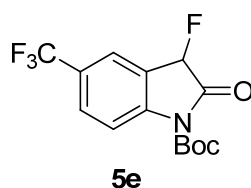
All 3-fluoro-substituted oxindoles **5** were prepared from compounds **5-1** via known fluorination using NFSI as F-source following literature procedure (16-48% yields).^[2] Substrates **5a-c** and **5f-h** are known compounds, and their characterization data were in agreement with those reported in the literature.^[2] Unknown compounds **5d**, **5e** and **5a'** were fully characterized.

tert-Butyl 6-bromo-3-fluoro-2-oxindoline-1-carboxylate (5d)



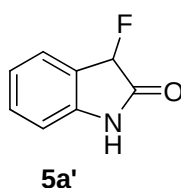
A white solid; ^1H NMR (500 MHz, CDCl_3) δ 8.13 (s, 1H), 7.40-7.35 (m, 2H), 5.70 (d, $J = 51.1$ Hz, 1H), 1.64 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.34 (d, $J = 18.2$ Hz), 148.40, 141.89 (d, $J = 4.6$ Hz), 128.14 (d, $J = 2.7$ Hz), 127.08, 125.81 (d, $J = 3.6$ Hz), 119.23, 85.62, 85.23 (d, $J = 189.5$ Hz), 27.99; ^{19}F NMR (282.38 MHz, CDCl_3) δ -187.10 (d, $J = 51.5$ Hz); HRMS (ESI) m/z calcd $\text{C}_{13}\text{H}_{13}\text{BrFNNaO}_3$ $[\text{M}+\text{Na}]^+ = 351.9955$, found = 351.9950.

tert-Butyl 3-fluoro-2-oxo-5-(trifluoromethyl)indoline-1-carboxylate (5e)



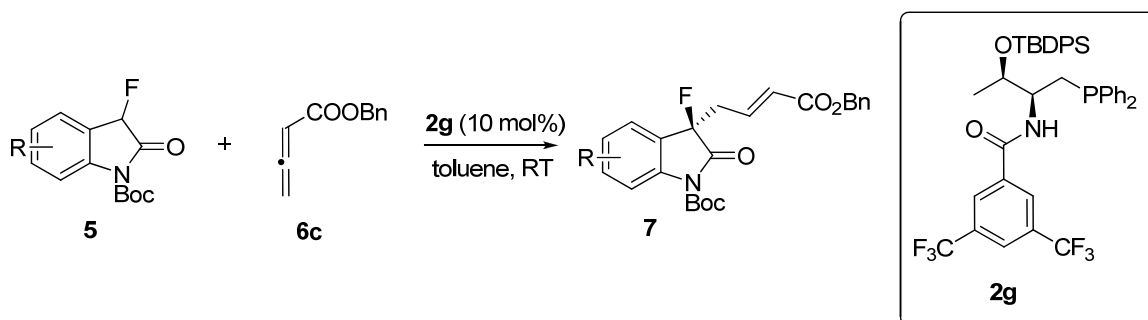
A white solid; ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, J = 8.8 Hz, 1H), 7.39 (s, 1H), 7.31 (d, J = 8.9 Hz, 1H), 5.71 (d, J = 50.4 Hz, 1H), 1.63 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.17 (d, J = 17.3 Hz), 148.45, 146.10, 139.35 (d, J = 4.6 Hz), 124.61, 123.15 (d, J = 17.3 Hz), 121.43, 119.24 (d, J = 32.8 Hz), 116.99, 85.54, 85.19 (d, J = 190.4 Hz), 27.98; ^{19}F NMR (282.38 MHz, CDCl_3) δ -58.28, -188.44 (d, J = 50.5 Hz); HRMS (ESI) m/z calcd $\text{C}_{14}\text{H}_{13}\text{F}_4\text{NNaO}_3$ $[\text{M}+\text{Na}]^+ = 342.0729$, found = 342.0720.

3-Fluoroindolin-2-one (5a')



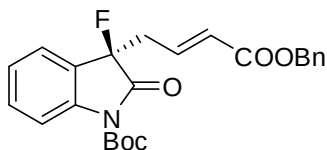
A white solid; ^1H NMR (500 MHz, CDCl_3) δ 9.07 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 5.74 (d, J = 51.1 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.87 (d, J = 18.2 Hz), 141.96 (d, J = 5.5 Hz), 131.51 (d, J = 2.7 Hz), 126.27, 123.32 (d, J = 2.7 Hz), 123.26 (d, J = 16.4 Hz), 110.90, 86.67 (d, J = 188.6 Hz); ^{19}F NMR (282.38 MHz, CDCl_3) δ -193.68 (d, J = 50.5 Hz); HRMS (ESI) m/z calcd $\text{C}_8\text{H}_6\text{FNNaO}$ $[\text{M}+\text{H}]^+ = 174.0331$, found = 174.0229.

5. Representative Procedure for γ -Addition of 3-Fluorinated Oxindoles



To dried schlenk tube equipped with a stirrer bar were added 3-fluoro-oxindole **5a₁** (12.5 mg, 0.05 mmol) and catalyst **2g** (3.8 mg, 0.005 mmol), followed by the addition of dry toluene (0.5 mL). Allenolate **6c** (10.5 mg, 0.06 mmol) was slowly added via syringe, and the reaction mixture was stirred at room temperature for 2 h. Then, the solvent of toluene was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 15:1) to afford **7a₁** (20.3 mg, 95% yield) as a white foam.

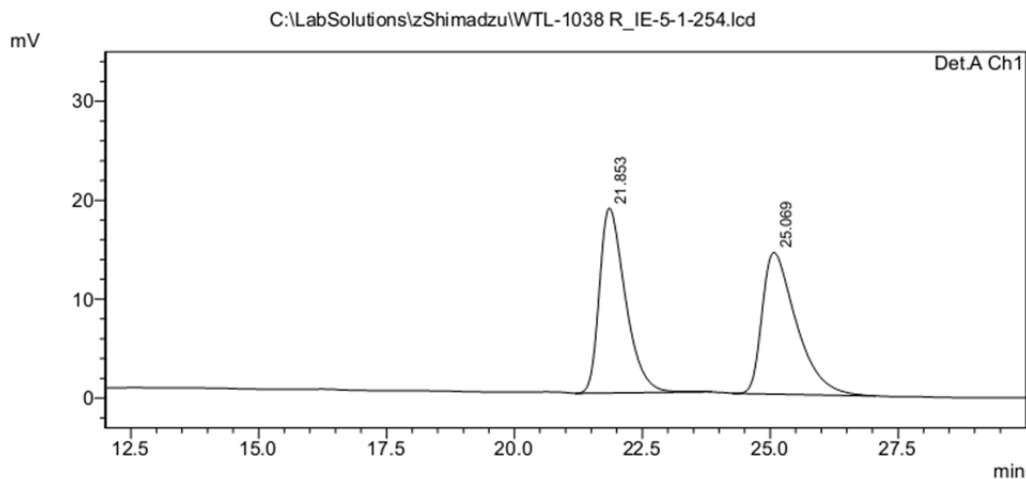
(R,E)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-3-fluoro-2-oxoindoline-1-carboxylate (7a₁)



7a₁

A white foam; $[\alpha]_D^{25} = +25.5$ (c 0.40, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.47-7.41 (m, 2H), 7.38-7.31 (m, 5H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.90-6.83 (m, 1H), 5.97 (d, *J* = 15.8 Hz, 1H), 5.17 (s, 2H), 3.15-3.09 (m, 1H), 2.97-2.88 (m, 1H), 1.63 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 170.01 (d, *J* = 21.0 Hz), 165.25, 148.51, 140.11 (d, *J* = 4.6 Hz), 138.78 (d, *J* = 7.3 Hz), 135.74, 131.83 (d, *J* = 3.6 Hz), 128.53, 128.23, 128.12, 126.71, 125.09 (d, *J* = 2.7 Hz), 124.86, 123.92 (d, *J* = 19.1 Hz), 115.72, 91.69 (d, *J* = 189.5 Hz), 85.19, 66.31, 38.34 (d, *J* = 30.1 Hz), 27.98; ¹⁹F NMR (282.38 MHz, CDCl₃) δ -149.02 (dd, *J*_{1,2} = 12.4 Hz, *J*_{1,3} = 18.6 Hz); HRMS (ESI) *m/z* calcd for C₂₄H₂₄FNNaO₅ [M+Na]⁺ = 448.1531, found = 448.1543; The ee value was 93%, *t*_R (major) = 25.3 min, *t*_R (minor) = 22.4 min (Chiralcel IE, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>



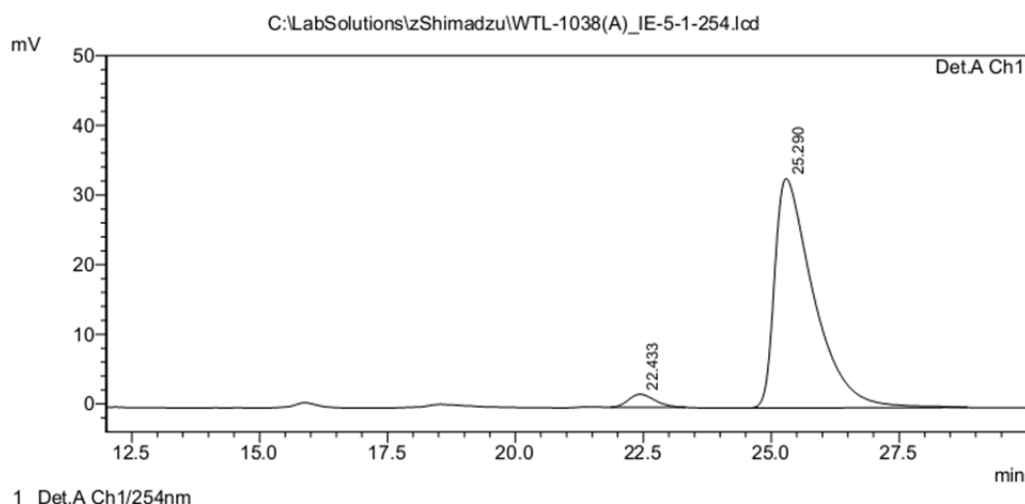
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Detector A Ch1 254nm

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Racemic 7a

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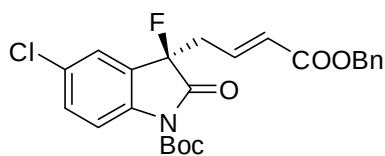


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
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2	25.290	1746754	32907	96.306	94.660
Total		1813745	34763	100.000	100.000

Enantiomerically enriched **7a**

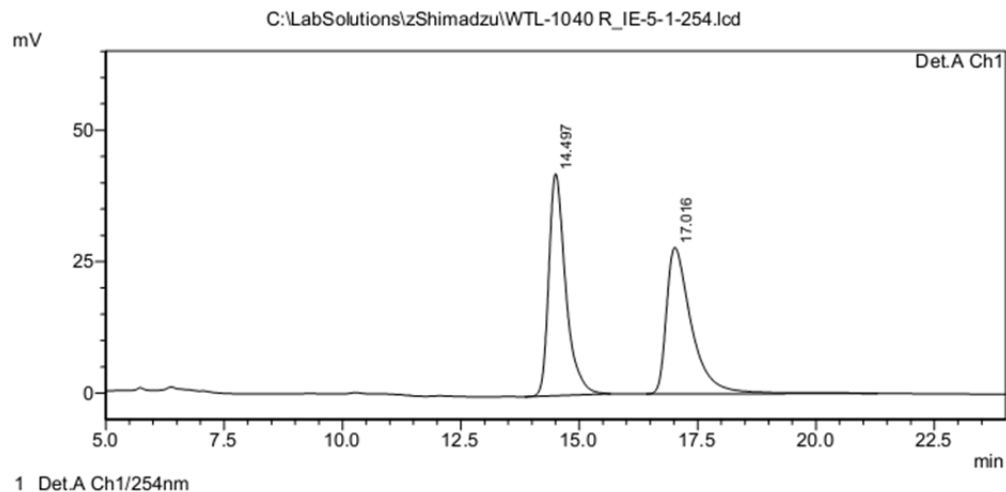
(R,E)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-5-chloro-3-fluoro-2-oxindoline-1-carboxylate (7b)



7b

A white foam; $[\alpha]_D^{25} = +29.8$ (c 0.64, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 8.8$ Hz, 1H), 7.43 (dt, $J_{1,2} = 1.9$ Hz, $J_{1,3} = 8.9$ Hz, 1H), 7.40-7.37 (m, 1H), 7.35-7.31 (m, 5H), 6.84-6.78 (m, 1H), 5.98 (d, $J = 15.8$ Hz, 1H), 5.17 (s, 2H), 3.12-3.05 (m, 1H), 2.98-2.90 (m, 1H), 1.62 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.33 (d, $J = 21.0$ Hz), 165.12, 148.34, 138.63 (d, $J = 5.5$ Hz), 138.00 (d, $J = 7.4$ Hz), 135.70, 131.87 (d, $J = 2.7$ Hz), 130.73 (d, $J = 2.7$ Hz), 128.58, 128.28, 128.15, 127.13, 125.54 (d, $J = 19.1$ Hz), 125.01, 117.15, 91.34 (d, $J = 191.3$ Hz), 85.60, 66.42, 38.23 (d, $J = 29.2$ Hz), 27.97; ^{19}F NMR (282.38 MHz, CDCl_3) δ -149.61 (t, $J = 14.4$ Hz); HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{FCINNaO}_5$ $[\text{M}+\text{Na}]^+ = 482.1141$, found = 482.1150; The ee value was 83%, t_R (major) = 16.9 min, t_R (minor) = 14.6 min (Chiralcel IE, $\lambda = 254$ nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>

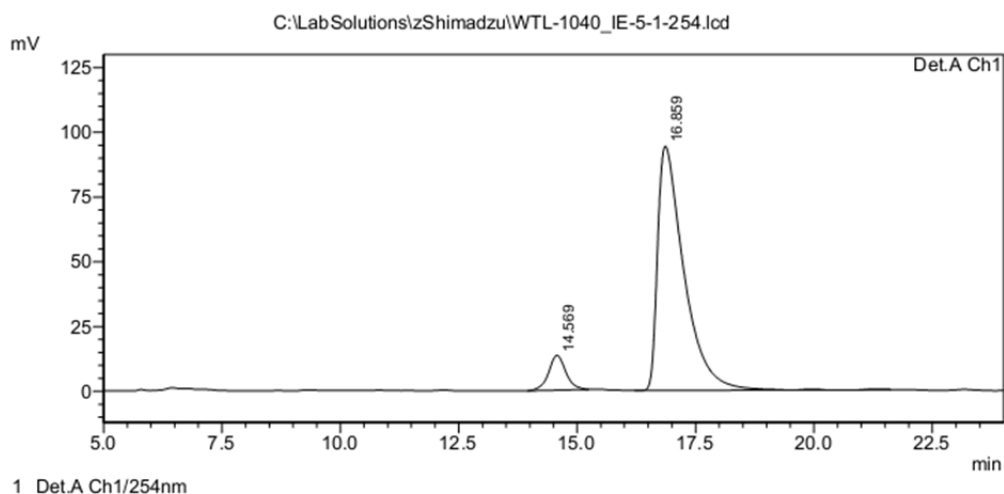


PeakTable

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2	17.016	1033247	27829	49.656	39.768
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Racemic **7b**

<Chromatogram>

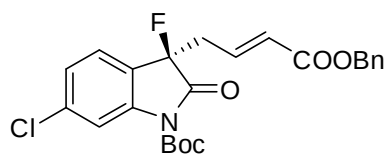


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Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.569	339868	13433	8.520	12.462
2	16.859	3649168	94358	91.480	87.538
Total		3989036	107792	100.000	100.000

Enantiomerically enriched **7b**

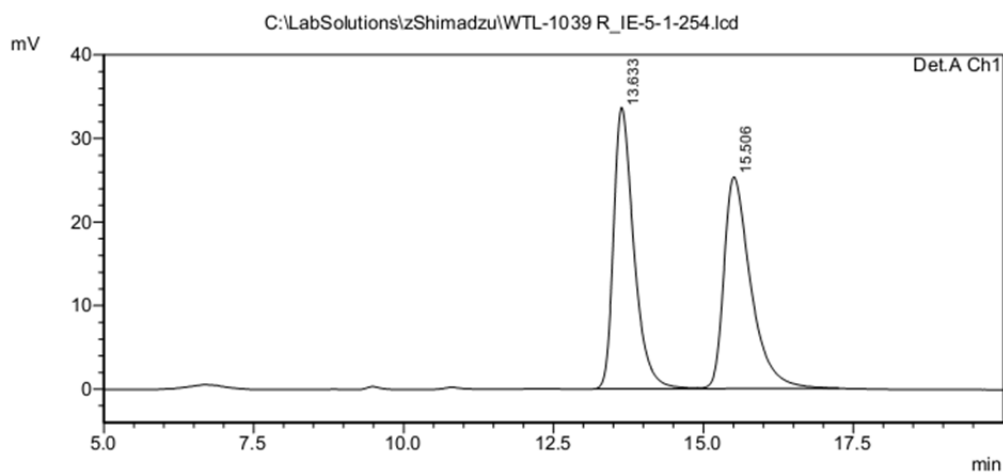
(*R,E*)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-6-chloro-3-fluoro-2-oxoindoline-1-carboxylate (7c)



7c

A white foam; $[\alpha]_D^{25} = +43.4$ (c 0.47, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.99 (s, 1H), 7.38-7.32 (m, 6H), 7.21 (dd, $J_{1,2} = 1.3$ Hz, $J_{1,3} = 8.2$ Hz, 1H), 6.86-6.80 (m, 1H), 5.98 (d, $J = 15.1$ Hz, 1H), 5.17 (s, 2H), 3.14-3.07 (m, 1H), 2.94-2.85 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.57 (d, $J = 21.0$ Hz), 165.17, 148.27, 141.06 (d, $J = 5.5$ Hz), 138.23 (d, $J = 7.3$ Hz), 137.87 (d, $J = 3.7$ Hz), 135.67, 128.58, 128.31, 128.19, 127.02, 125.82, 125.28 (d, $J = 2.8$ Hz), 122.08, 116.60, 91.27 (d, $J = 190.5$ Hz), 85.78, 66.43, 38.21 (d, $J = 29.2$ Hz), 27.95; ^{19}F NMR (282.38 MHz, CDCl_3) δ -148.82 (dd, $J_{1,2} = 12.4$ Hz, $J_{1,3} = 19.6$ Hz); HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{FCINNaO}_5$ $[\text{M}+\text{Na}]^+ = 482.1141$, found = 482.1147; The ee value was 94%, t_R (major) = 15.3 min, t_R (minor) = 13.7 min (Chiralcel IE, $\lambda = 254$ nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>



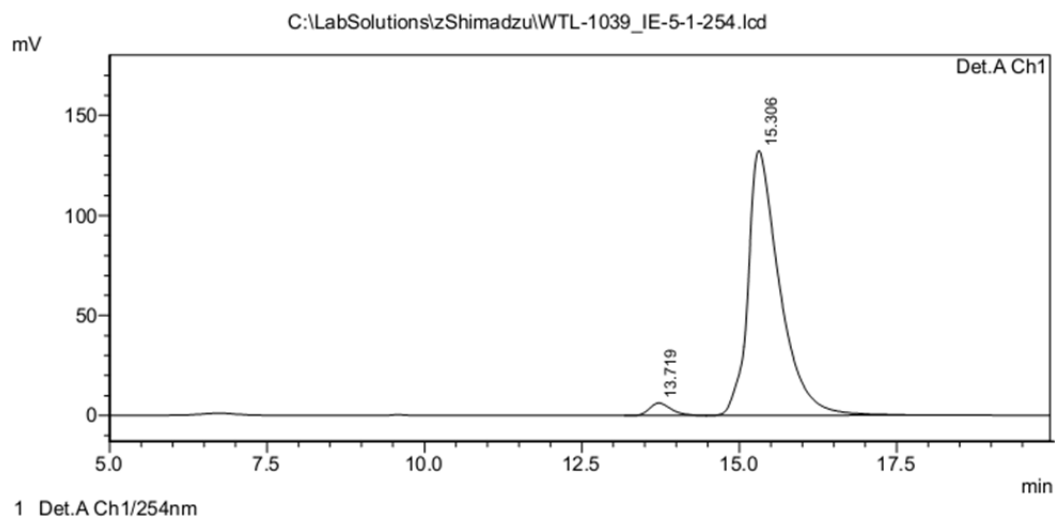
1 Det.A Ch1/254nm

PeakTable

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Total		1582783	59006	100.000	100.000

Racemic 7c

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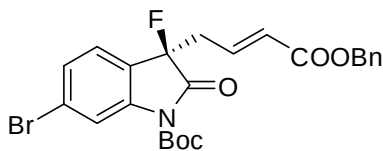


PeakTable

Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
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Total		4779132	138585	100.000	100.000

Enantiomerically enriched **7c**

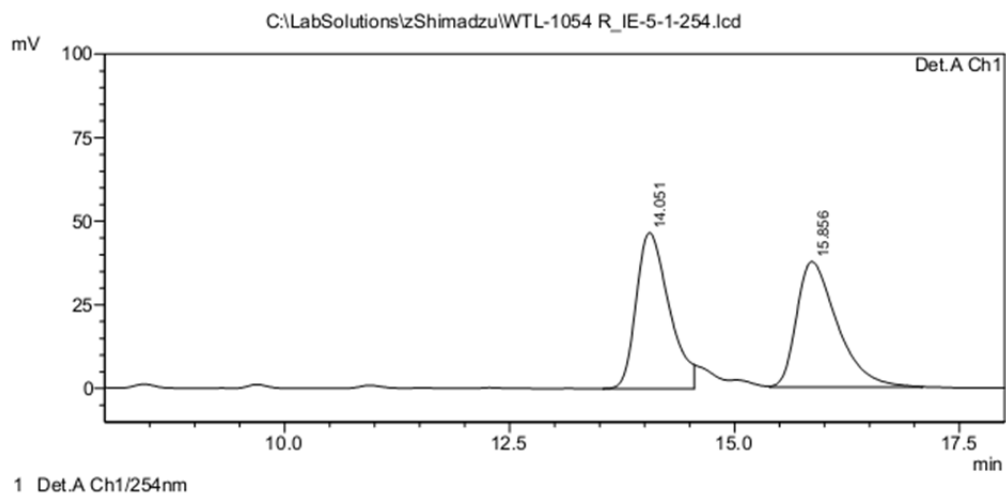
(*R,E*)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-6-bromo-3-fluoro-2-oxindoline-1-carboxylate (7d)



7d

A white foam; $[\alpha]_D^{25} = +34.6$ (c 0.77, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.16 (s, 1H), 7.39-7.33 (m, 7H), 6.85-6.79 (m, 1H), 5.98 (d, $J = 15.8$ Hz, 1H), 5.17 (s, 2H), 3.13-3.06 (m, 1H), 2.93-2.85 (m, 1H), 1.63 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.50 (d, $J = 21.0$ Hz), 165.17, 148.29, 141.09 (d, $J = 4.6$ Hz), 138.27 (d, $J = 7.3$ Hz), 135.69, 128.60 (d, $J = 12.8$ Hz), 128.33, 128.20, 128.02, 127.85, 127.07, 126.06, 122.75 (d, $J = 19.1$ Hz), 119.39, 91.33 (d, $J = 190.4$ Hz), 85.80, 66.44, 38.18 (d, $J = 29.2$ Hz), 27.97; ^{19}F NMR (282.38 MHz, CDCl_3) δ -149.24 (dd, $J_{1,2} = 12.4$ Hz, $J_{1,3} = 19.6$ Hz); HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{BrFNNaO}_5$ $[\text{M}+\text{Na}]^+ = 526.0636$, found = 526.0645; The ee value was 94%, t_R (major) = 15.8 min, t_R (minor) = 14.1 min (Chiralcel IE, $\lambda = 254$ nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>

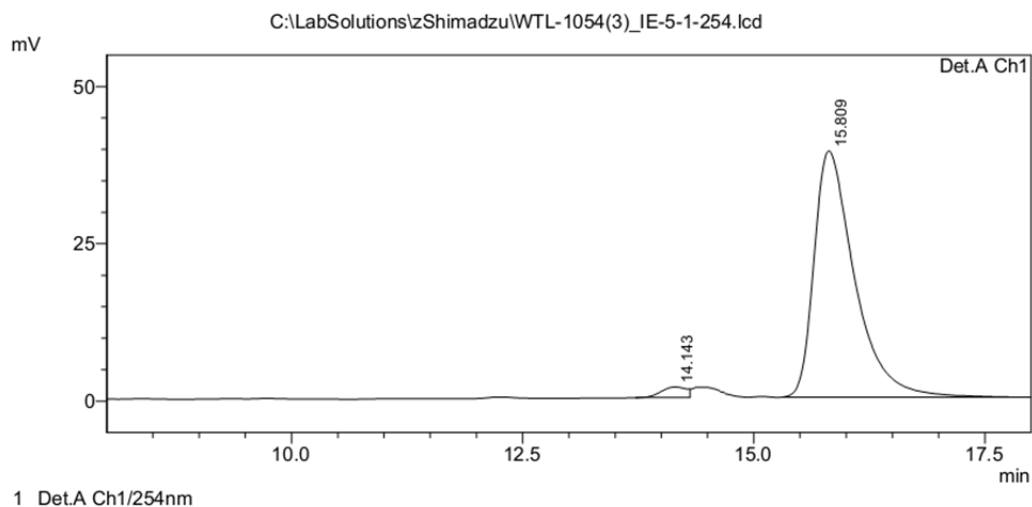


PeakTable

Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.051	1188842	46658	50.085	55.425
2	15.856	1184820	37524	49.915	44.575
Total		2373661	84182	100.000	100.000

Racemic **7d**

<Chromatogram>

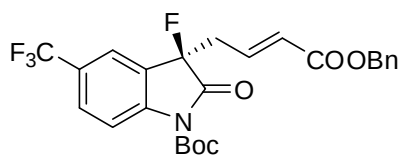


PeakTable

Detector A Ch1 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.143	32090	1685	2.615	4.127
2	15.809	1195056	39130	97.385	95.873
Total		1227146	40814	100.000	100.000

Enantiomerically enriched **7d**

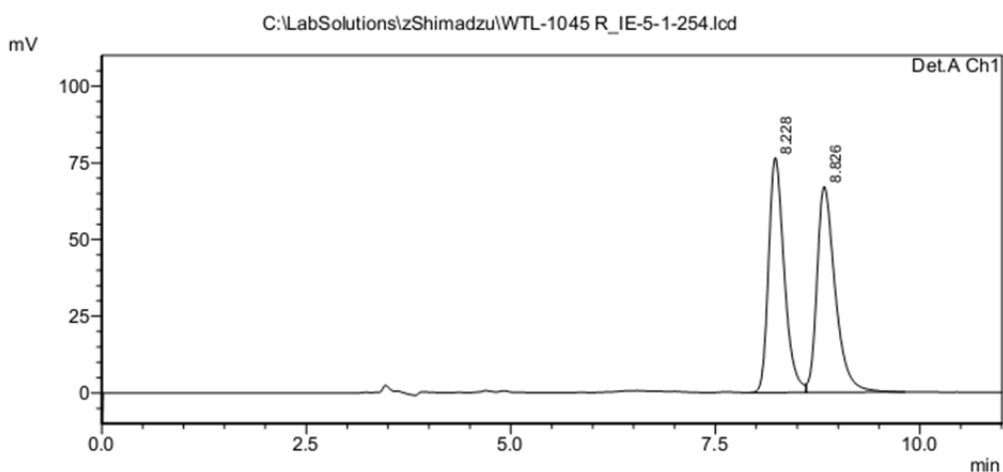
(R,E)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-3-fluoro-2-oxo-5-(trifluoromethyl)indoline-1-carboxylate (7e)



7e

A white foam; $[\alpha]_D^{25} = +26.7$ (*c* 0.27, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.37-7.31 (m, 6H), 7.27 (d, *J* = 8.2 Hz, 1H), 6.87-6.81 (m, 1H), 5.99 (d, *J* = 15.8 Hz, 1H), 5.17 (s, 2H), 3.15-3.08 (m, 1H), 2.95-2.86 (m, 1H), 1.63 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 169.44 (d, *J* = 21.0 Hz), 165.06, 148.34, 146.07, 138.55 (d, *J* = 5.5 Hz), 137.87 (d, *J* = 6.4 Hz), 135.69, 128.57, 128.29 (d, *J* = 16.2 Hz), 127.32, 125.45 (d, *J* = 19.1 Hz), 124.68, 121.40, 119.35, 118.16, 117.18, 91.30 (d, *J* = 192.2 Hz), 85.73, 66.45, 38.32 (d, *J* = 29.2 Hz), 27.97; ¹⁹F NMR (282.38 MHz, CDCl₃) δ -58.28, -150.80 (dd, *J*_{1,2} = 13.4 Hz, *J*_{1,3} = 20.6 Hz); HRMS (ESI) *m/z* calcd for C₂₅H₂₃F₄NKO₅ [M+K]⁺ = 532.1149, found = 532.1143; The ee value was 92%, *t*_R (major) = 8.8 min, *t*_R (minor) = 8.2 min (Chiralcel IE, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>



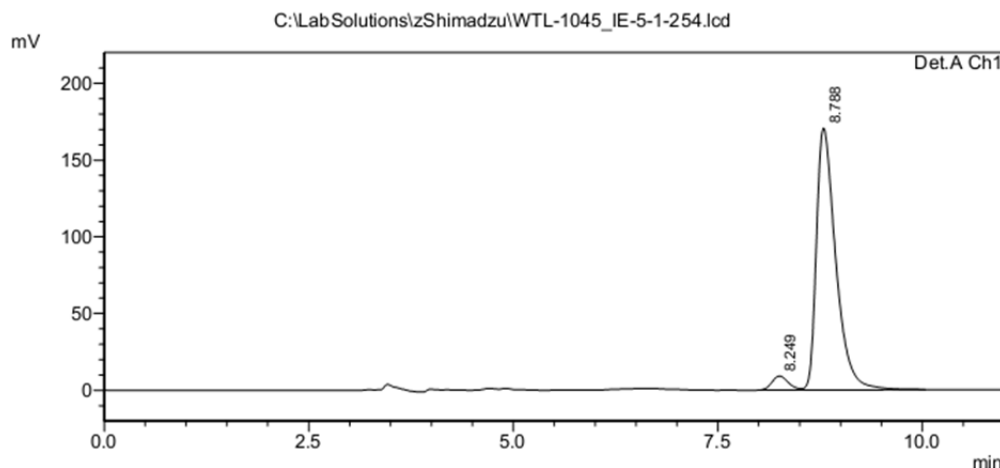
1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.228	1018655	76568	49.417	53.314
2	8.826	1042694	67048	50.583	46.686
Total		2061350	143615	100.000	100.000

Racemic 7e

<Chromatogram>

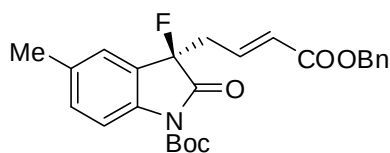


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.249	126296	9143	4.297	5.079
2	8.788	2812956	170864	95.703	94.921
Total		2939251	180008	100.000	100.000

Enantiomerically enriched **7e**

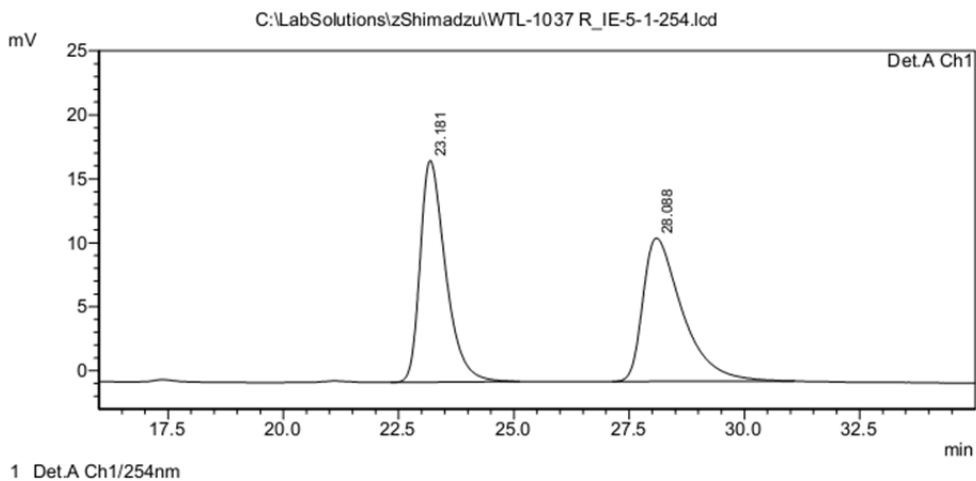
(R,E)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-3-fluoro-5-methyl-2-oxoindoline-1-carboxylate (7f)



7f

A white foam; $[\alpha]_D^{25} = +17.1$ (c 0.88, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 8.2$ Hz, 1H), 7.38-7.31 (m, 5H), 7.25-7.21 (m, 2H), 6.86-6.80 (m, 1H), 5.99 (d, $J = 15.5$ Hz, 1H), 5.17 (s, 2H), 3.12-3.05 (m, 1H), 2.97-2.91 (m, 1H), 2.35 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.26 (d, $J = 21.0$ Hz), 165.31, 148.59, 138.91 (d, $J = 7.3$ Hz), 137.76 (d, $J = 5.5$ Hz), 135.79, 134.97 (d, $J = 2.7$ Hz), 132.35 (d, $J = 2.7$ Hz), 128.56, 128.26, 128.13, 126.63, 125.27, 123.86 (d, $J = 18.2$ Hz), 115.55, 91.86 (d, $J = 189.5$ Hz), 85.02, 66.31, 38.36 (d, $J = 30.1$ Hz), 28.02, 20.98; ^{19}F NMR (282.38 MHz, CDCl_3) δ -148.47 (dd, $J_{1,2} = 13.4$ Hz, $J_{1,3} = 18.6$ Hz); HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{FNNaO}_5$ $[\text{M}+\text{Na}]^+ = 462.1687$, found = 462.1701; The ee value was 90%, t_R (major) = 27.9 min, t_R (minor) = 23.3 min (Chiralcel IE, $\lambda = 254$ nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>



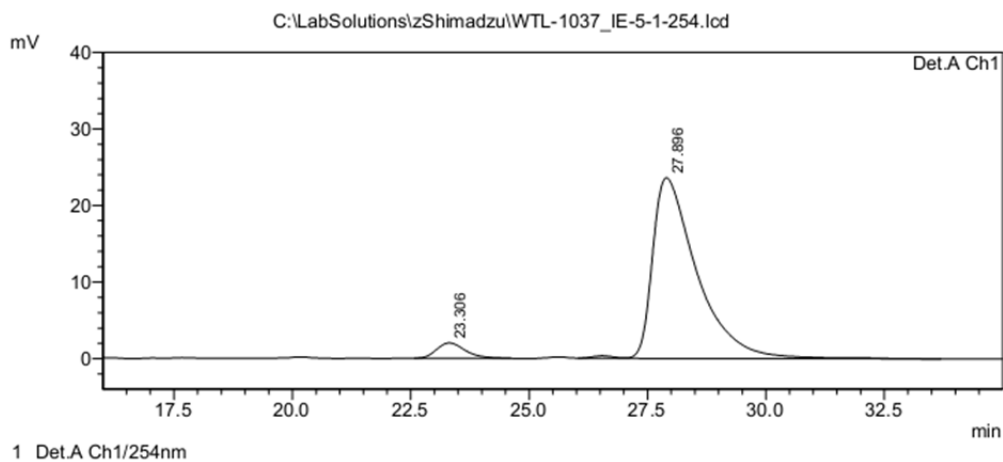
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.181	668231	17336	49.995	60.721
2	28.088	668365	11215	50.005	39.279
Total		1336596	28551	100.000	100.000

Racemic 7f

<Chromatogram>



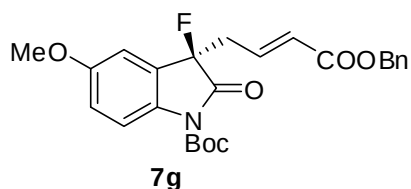
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.306	85735	2019	5.256	7.880
2	27.896	1545369	23599	94.744	92.120
Total		1631104	25618	100.000	100.000

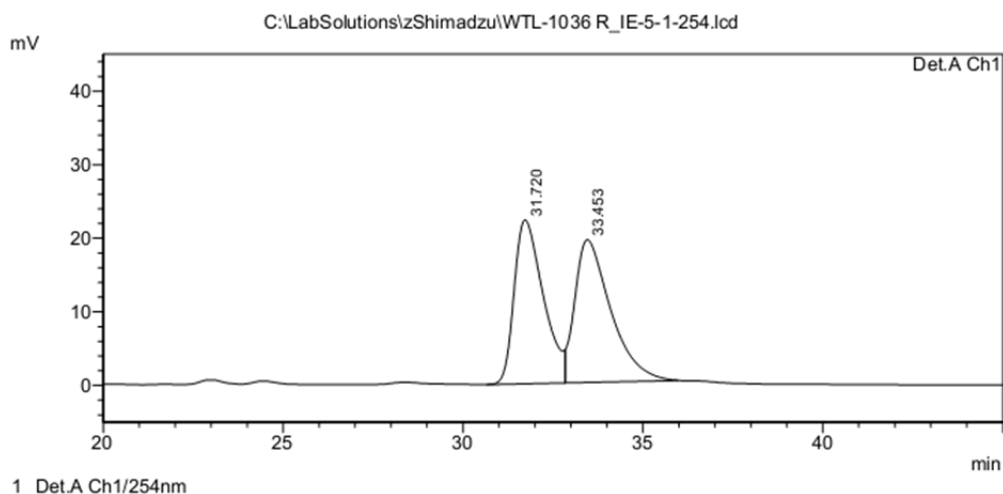
Enantiomerically enriched 7f

(R,E)-tert-Butyl 3-(4-(benzyloxy)-4-oxobut-2-enyl)-3-fluoro-5-methoxy-2-oxindoline-1-carboxylate (7g)



A white foam; $[\alpha]_D^{25} = +15.6$ (*c* 0.40, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.38-7.31 (m, 5H), 6.98-6.94 (m, 2H), 6.88-6.82 (m, 1H), 5.99 (d, *J* = 15.8 Hz, 1H), 5.16 (s, 2H), 3.77 (s, 3H), 3.13-3.06 (m, 1H), 2.95-2.86 (m, 1H), 1.62 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 170.19 (d, *J* = 21.0 Hz), 165.25, 157.15 (d, *J* = 2.7 Hz), 148.61, 138.75 (d, *J* = 7.3 Hz), 135.76, 133.24 (d, *J* = 5.5 Hz), 128.56, 128.27 (d, *J* = 10.9 Hz), 126.79, 124.97 (d, *J* = 18.2 Hz), 117.02, 117.00, 116.88, 110.46, 91.92 (d, *J* = 190.5 Hz), 84.99, 66.34, 55.67, 38.42 (d, *J* = 29.2 Hz), 28.03; ¹⁹F NMR (282.38 MHz, CDCl₃) δ -149.56 (dd, *J*_{1,2} = 14.4 Hz, *J*_{1,3} = 19.6 Hz); HRMS (ESI) *m/z* calcd for C₂₅H₂₆FNNaO₆ [M+Na]⁺ = 478.1636, found = 478.1647; The ee value was 94%, *t*_R (major) = 33.0 min, *t*_R (minor) = 31.7 min (Chiralcel IE, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>



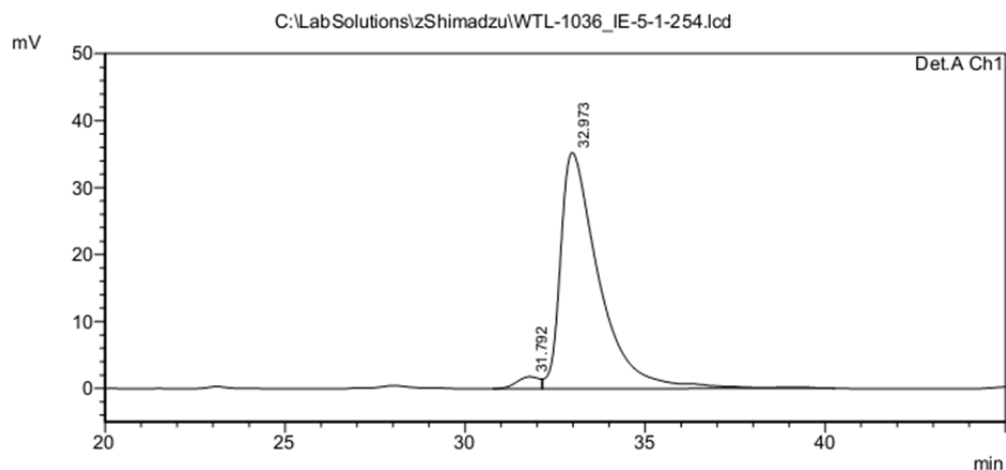
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.720	1258281	22182	49.550	53.678
2	33.453	1281161	19142	50.450	46.322
Total		2539442	41323	100.000	100.000

Racemic 7g

<Chromatogram>



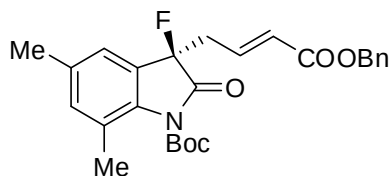
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.792	77738	1766	2.875	4.769
2	32.973	2625807	35270	97.125	95.231
Total		2703545	37037	100.000	100.000

Enantiomerically enriched **7g**

(R,E)-tert-Butyl

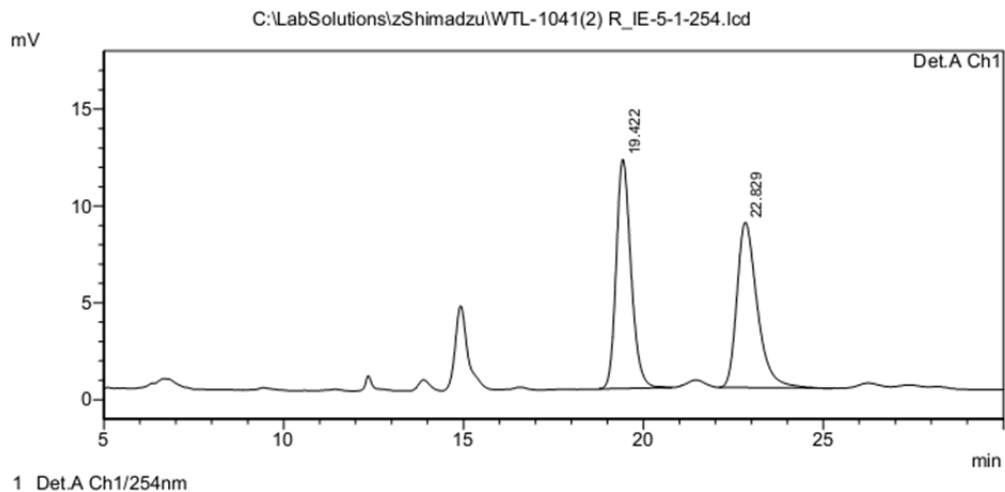
3-(4-(benzyloxy)-4-oxobut-2-enyl)-3-fluoro-5,7-dimethyl-2-oxoindoline-1-carboxylate (7h)



7h

A white foam; $[\alpha]_D^{25} = +12.4$ (c 0.36, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.32 (m, 5H), 7.05 (s, 2H), 6.85-6.79 (m, 1H), 5.97 (d, $J = 15.8$ Hz, 1H), 5.16 (s, 2H), 3.08-3.01 (m, 1H), 2.97-2.88 (m, 1H), 2.31 (s, 1H), 2.19 (s, 1H), 1.60 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.25 (d, $J = 21.0$ Hz), 165.29, 148.41, 139.05 (d, $J = 7.3$ Hz), 136.14 (d, $J = 5.5$ Hz), 135.86, 135.28 (d, $J = 3.7$ Hz), 134.96 (d, $J = 2.7$ Hz), 128.54, 128.21, 128.11, 126.50, 125.26 (d, $J = 18.2$ Hz), 124.55, 122.79, 92.61 (d, $J = 190.4$ Hz), 85.28, 66.26, 38.57 (d, $J = 30.1$ Hz), 27.76, 20.85, 19.48; ^{19}F NMR (282.38 MHz, CDCl_3) δ -149.29 (t, $J = 12.4$ Hz); HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{28}\text{FNNaO}_5$ $[\text{M}+\text{Na}]^+ = 476.1844$, found = 476.1858; The ee value was 90%, t_R (major) = 22.2 min, t_R (minor) = 19.1 min (Chiralcel IE, $\lambda = 254$ nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>

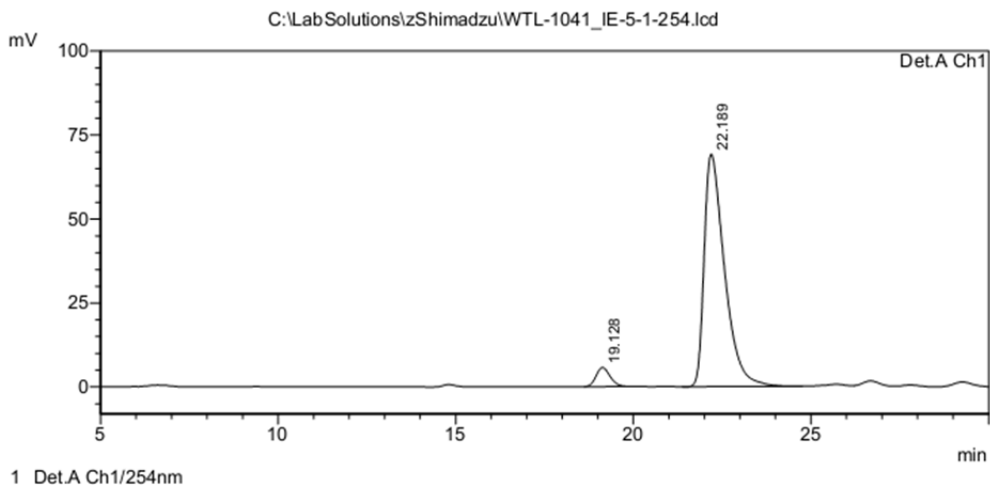


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.422	339283	11837	50.253	58.095
2	22.829	335873	8538	49.747	41.905
Total		675156	20375	100.000	100.000

Racemic **7h**

<Chromatogram>

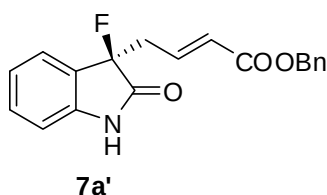


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.128	155331	5679	5.327	7.578
2	22.189	2760546	69264	94.673	92.422
Total		2915876	74943	100.000	100.000

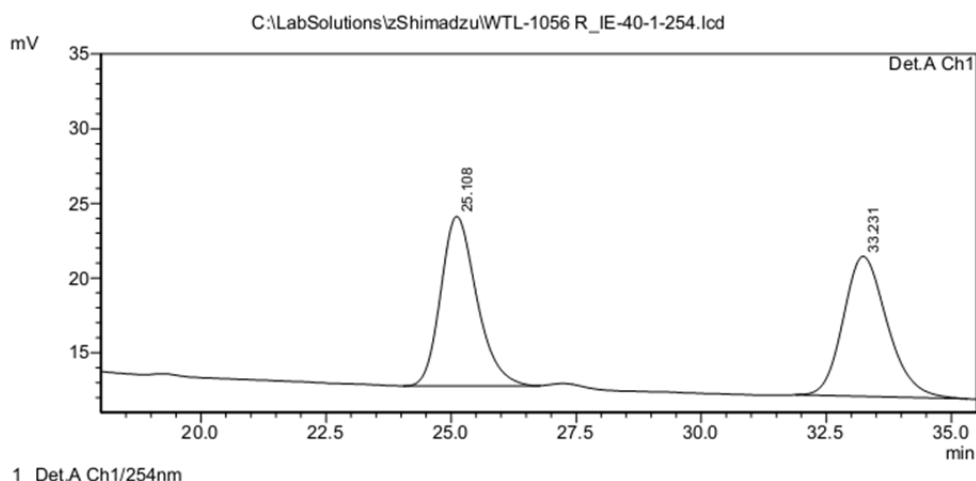
Enantiomerically enriched **7h**

(R,E)- Benzyl 4-(3-fluoro-2-oxoindolin-3-yl)but-2-enoate (7a')



A white foam; $[\alpha]_D^{25} = +5.6$ (c 0.22, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 7.0 Hz, 1H), 7.38-7.32 (m, 5H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.97 (dt, *J*_{1,2} = 4.4 Hz, *J*_{1,3} = 15.8 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.97 (dt, *J*_{1,2} = 1.9 Hz, *J*_{1,3} = 15.8 Hz, 1H), 5.78 (d, *J* = 51.1 Hz, 1H), 5.16 (s, 2H), 4.55-4.50 (m, 1H), 4.42-4.37 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.85 (d, *J* = 18.2 Hz), 165.17, 143.26 (d, *J* = 4.6 Hz), 140.53, 135.53, 131.58 (d, *J* = 2.7 Hz), 128.60, 128.40 (d, *J* = 2.7 Hz), 126.40, 123.67 (d, *J* = 2.7 Hz), 123.10, 122.75 (d, *J* = 16.4 Hz), 109.28, 85.97 (d, *J* = 188.6 Hz), 66.63, 40.62; ¹⁹F NMR (282.38 MHz, CDCl₃) δ -192.47 (d, *J* = 50.5 Hz); HRMS (ESI) *m/z* calcd for C₁₉H₁₆FNNaO₃ [M+Na]⁺ = 348.1012, found = 348.1017; The ee value was 43%, *t*_R (major) = 32.5 min, *t*_R (minor) = 24.5 min (Chiralcel IE, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

<Chromatogram>

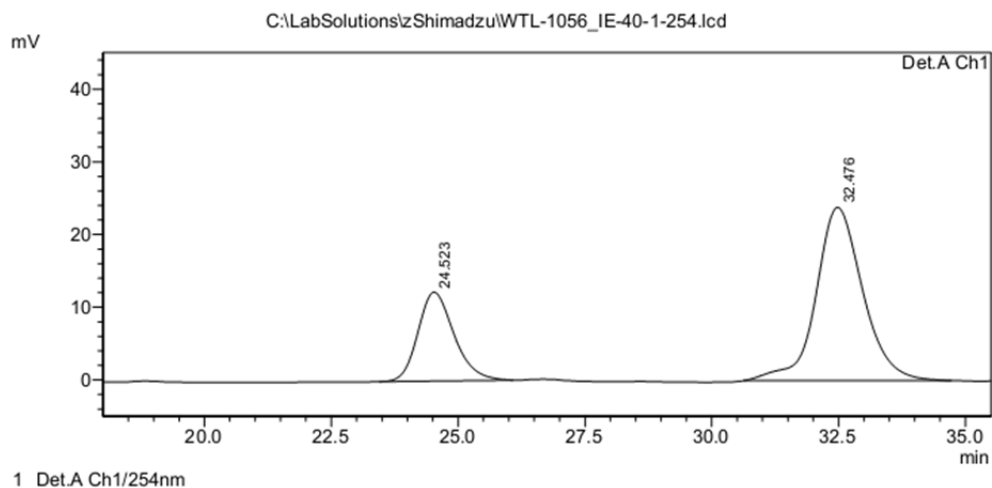


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.108	569067	11349	49.738	54.767
2	33.231	575058	9374	50.262	45.233
Total		1144126	20723	100.000	100.000

Racemic 7a'

<Chromatogram>

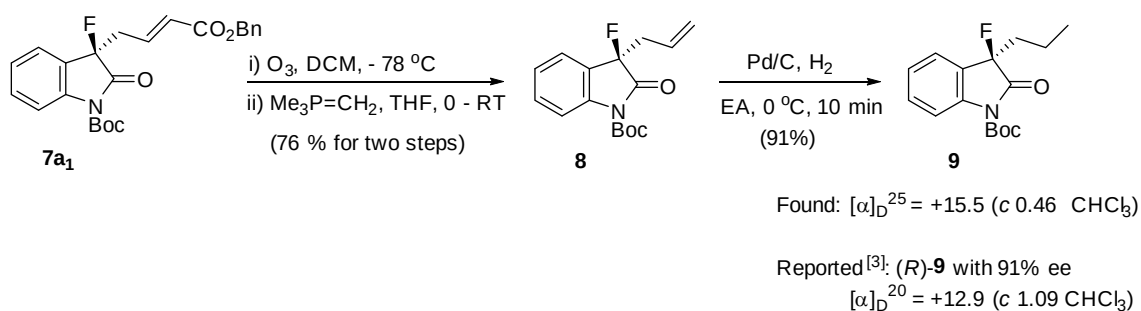


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.523	604596	12222	28.379	33.915
2	32.476	1525804	23816	71.621	66.085
Total		2130400	36038	100.000	100.000

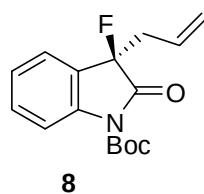
Enantiomerically enriched **7a'**

6. Asymmetric Synthesis of Chiral 3-Fluoro-3-allyl Oxindole Derivatives



Scheme S3: Synthesis of chiral 3-fluoro-3-allyl oxindole and its derivatives.

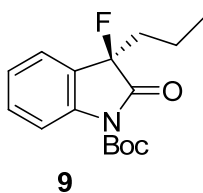
(R)-tert-Butyl 3-allyl-3-fluoro-2-oxindoline-1-carboxylate (**8**)



To a solution of **7a₁** (85 mg, 0.20 mmol) in CH₂Cl₂ (3.0 mL) at -78 °C, O₃ was bubbled until the reaction was complete (monitored by TLC). Ph₃P was added to quench the reaction at -78 °C, and then kept stirring for another 10 min. The reaction mixture was warmed to room temperature and passed through a short pad of silica gel, and eluted with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography on silical gel (hexane/ethyl acetate = 5:1) to afford the corresponding aldehyde as a white foam, which was used directly in the next step.

To a solution of methyltrimethylphosphonium iodide (54 mg, 0.30 mmol) in dry THF (3.0 mL) at -78 °C, *n*-BuLi (133 μL, 2.0 M in hexane, 0.30 mmol) was slowly added and the mixture was kept stirring at -78 °C for 1 h. Then, the mixture was warmed to 0 °C and stirred for another 1 h. The above crude aldehyde in dry THF (2.0 mL) was introduced dropwise, and the resulting mixture was stirred at 0 °C until the reaction was completed (monitored by TLC). The reaction mixture was filtrated by a short pad of silica gel, and eluted with CH₂Cl₂. The filtrate was concentrated and the residue was purified by flash column chromatography (hexane/ethyl acetate = 20:1) to afford pure compound **8** as a white foam-oil (44.1 mg, 76% total yield). $[\alpha]_D^{25} = +13.5$ (c 0.22, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.47-7.41 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 5.60-5.53 (m, 1H), 5.16 (d, *J* = 6.3 Hz, 1H), 5.13 (s, 1H), 3.01-2.94 (m, 1H), 2.88-2.80 (m, 1H), 1.64 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 170.78 (d, *J* = 21.0 Hz), 148.71, 140.21 (d, *J* = 4.6 Hz), 131.40 (d, *J* = 2.7 Hz), 128.44 (d, *J* = 8.2 Hz), 124.84, 124.68, 124.52, 121.50, 115.47, 92.50 (d, *J* = 188.6 Hz), 84.93, 40.06 (d, *J* = 28.2 Hz), 28.04; ¹⁹F NMR (282.38 MHz, CDCl₃) δ -149.45 (dd, *J*_{1,2} = 11.4 Hz, *J*_{1,3} = 16.5 Hz); HRMS (ESI) *m/z* calcd for C₁₆H₁₈FNNaO₃ [M+Na]⁺ = 314.1170, found = 314.1168.

(R)-tert-Butyl 3-fluoro-2-oxo-3-propylindoline-1-carboxylate (9)



To a mixture of compound **8** (29 mg, 0.10 mmol) and 10% Pd/C (3 mg) in EtOAc (1.0 mL) at 0 °C, H₂ was bubbled about 5 min, and the TLC shows that the reaction is completed. The catalyst Pd/C was removed by filtration. The filtrate was concentrated and further purified by flash column chromatography (hexane/ethyl acetate = 20:1) to give the known compound **9** as a white foam-solid (26.5 mg, 91% yield). $[\alpha]_D^{25} = +15.5$ (c 0.46, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 2.23-2.07 (m, 2H), 1.64 (s, 9H), 1.33-1.25 (m, 1H), 1.21-1.13 (m, 1H), 0.90 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.41 (d, *J* = 21.9

Hz), 148.81, 140.29 (d, $J = 5.5$ Hz), 131.27 (d, $J = 2.7$ Hz), 125.28 (d, $J = 19.1$ Hz), 124.95 (d, $J = 2.7$ Hz), 124.42, 115.50, 93.57 (d, $J = 184.9$ Hz), 84.90, 37.80 (d, $J = 27.3$ Hz), 28.05, 16.15 (d, $J = 6.4$ Hz), 13.95; ^{19}F NMR (282.38 MHz, CDCl_3) δ -148.30 (t, $J = 13.4$ Hz).

(*R*)-**9** was reported in literature^[3]: 91% ee, $[\alpha]_{\text{D}}^{20} = +12.9$ (c 1.09, CHCl_3). The above obtained compound **9** was found to have an $[\alpha]_{\text{D}}^{25} = +15.5$ (c 0.46, CHCl_3). Therefore, the absolute configuration of oxindole **7a₁** was deduced to be *R*.

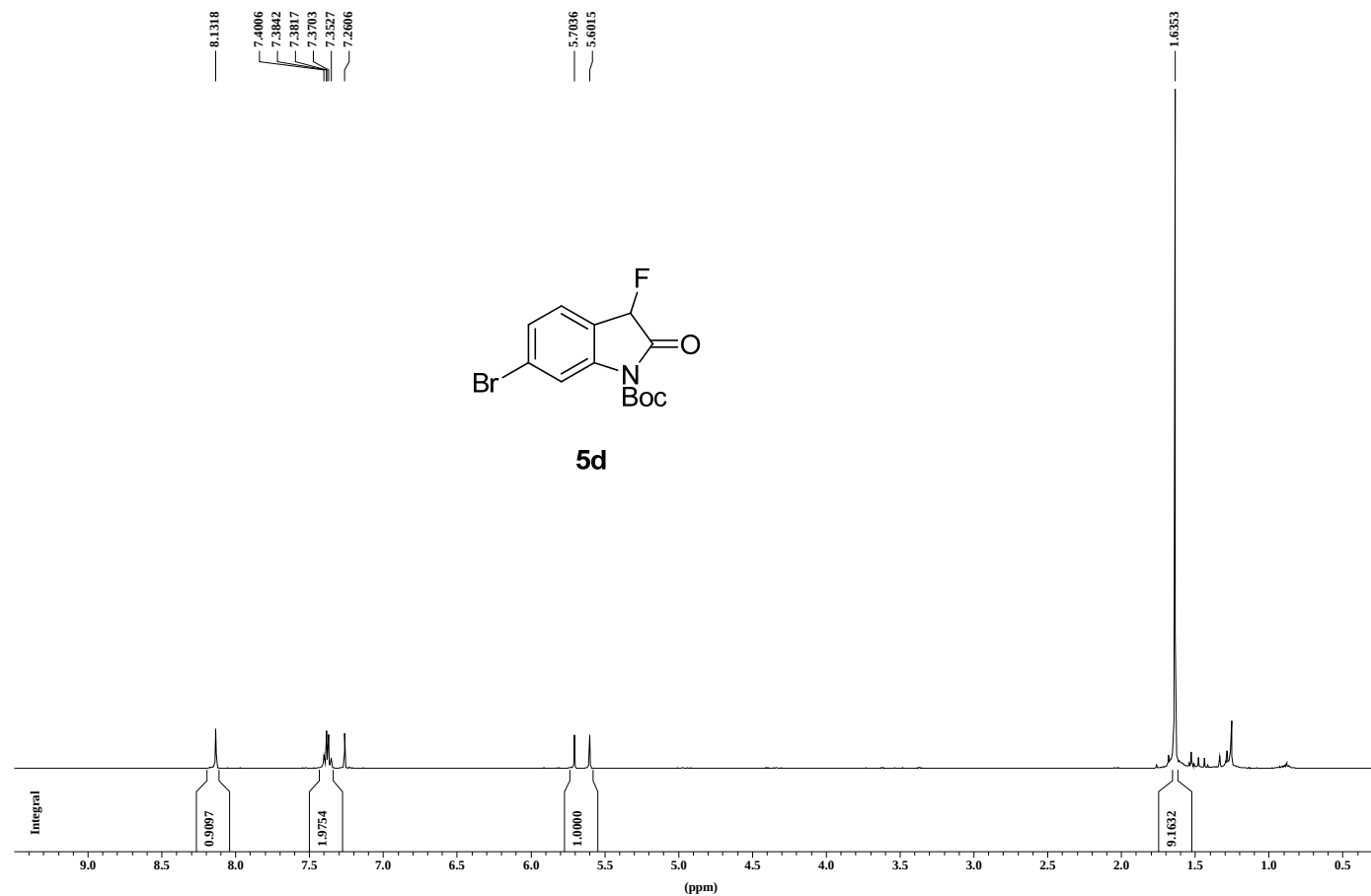
7. References

- [1] (a) X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* 2011, **133**, 1726; (b) X. Han, F. Zhong, Y. Wang, Y. Lu, *Angew. Chem. Int. Ed.* 2012, **51**, 767; (c) F. Zhong, X. Han, Y. Wang, Y. Lu, *Chem. Sci.* 2012, **3**, 1231; (d) F. Zhong, X. Han, Y. Wang, Y. Lu, *Angew. Chem. Int. Ed.* 2011, **50**, 7837; (e) F. Zhong, J. Luo, G.-Y. Chen, X. Dou, Y. Lu, *J. Am. Chem. Soc.* 2012, **134**, 10222; (f) F. Zhong, X. Dou, X. Han, W. Yao, Q. Zhu, Y. Meng, Y. Lu, *Angew. Chem. Int. Ed.* 2013, **52**, 943; (g) T. Wang, W. Yao, F. Zhong, G. H. Pang, Y. Lu, *Angew. Chem. Int. Ed.* 2014, **53**, 2964.
- [2] X. Dou, Y. Lu, *Org. Biomol. Chem.*, 2013, **11**, 5217.
- [3] X. Gu, Y. Zhang, Z.-J. Xu, C.-M. Che, *Chem. Commun.*, 2014, **50**, 7870.

8. NMR Spectra of the Products

¹H AMX500

HDL-75

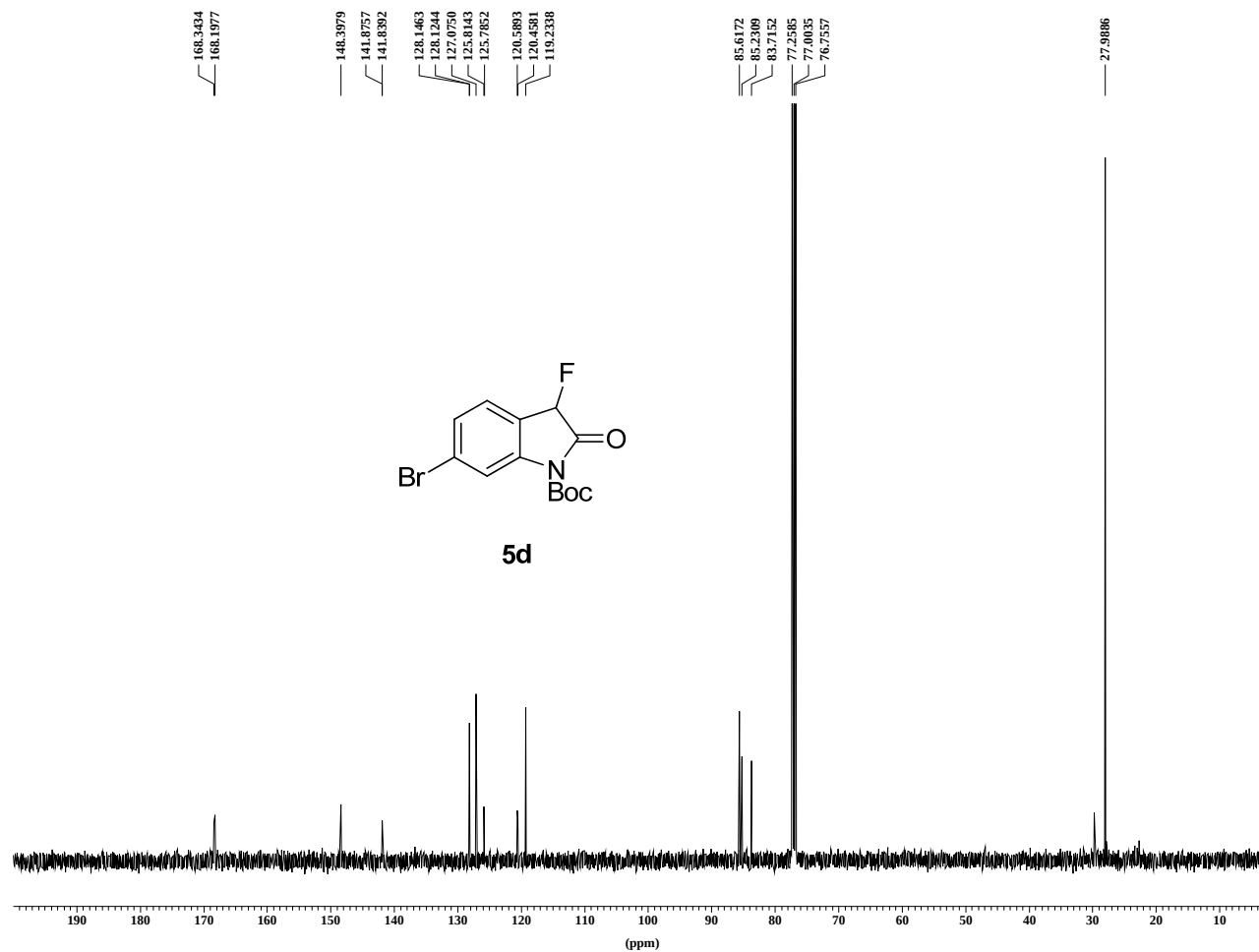


*** Current Data Parameters ***

NAME : wtl-1114
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 37
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 297.9 K
*** Processing Parameters ***
LB : 0.30 Hz
SF : 500.1300134 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

¹³C AMX500

HDL-75



*** Current Data Parameters ***

NAME : wtl-1114
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 415
NUCLEUS : off
OI : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536
TE : 298.5 K

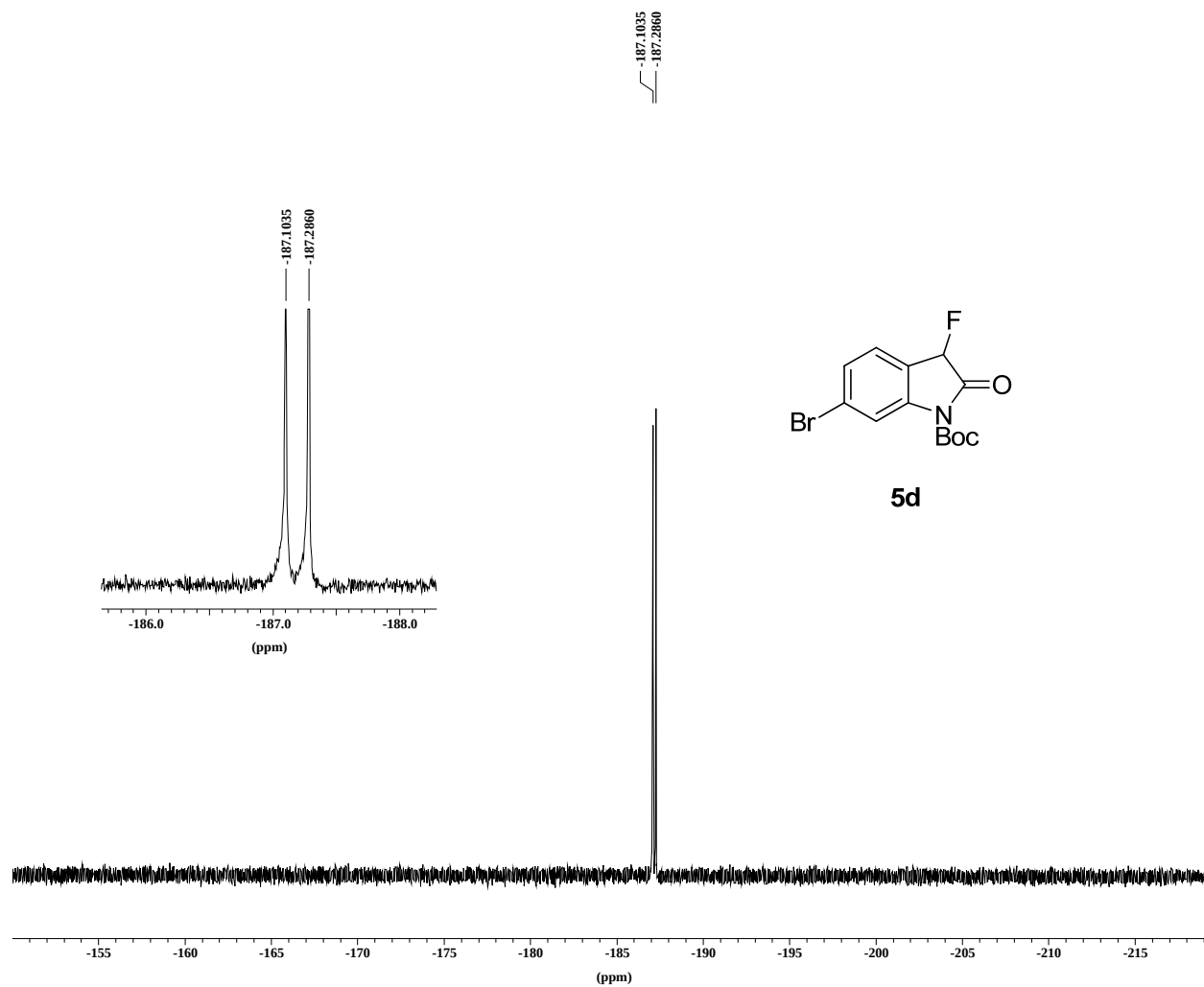
*** Processing Parameters ***

LB : 1.00 Hz
SF : 125.7577906 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)
HDL-75



*** Current Data Parameters ***

NAME : nov14~1
EXPNO : 4
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 43
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SF01 : 282.3761148 MHz
SOLVENT : DMSO
SW : 239.2822 ppm
TD : 131072
TE : 296.3 K

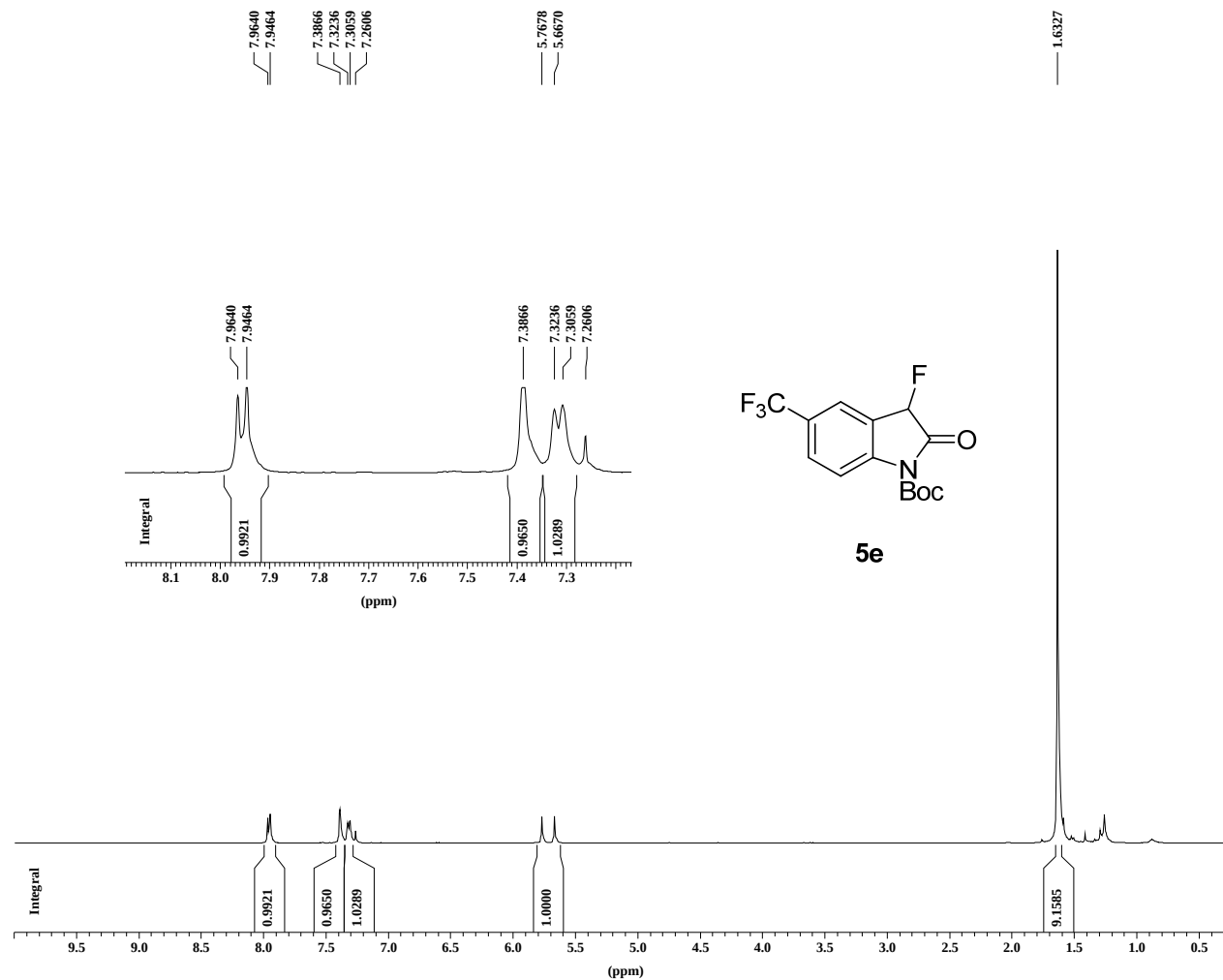
*** Processing Parameters ***

LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500
hdl-70(5-CF₃ sub)



*** Current Data Parameters ***

NAME : wtl-1108
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 34
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
TE : 300.0 K

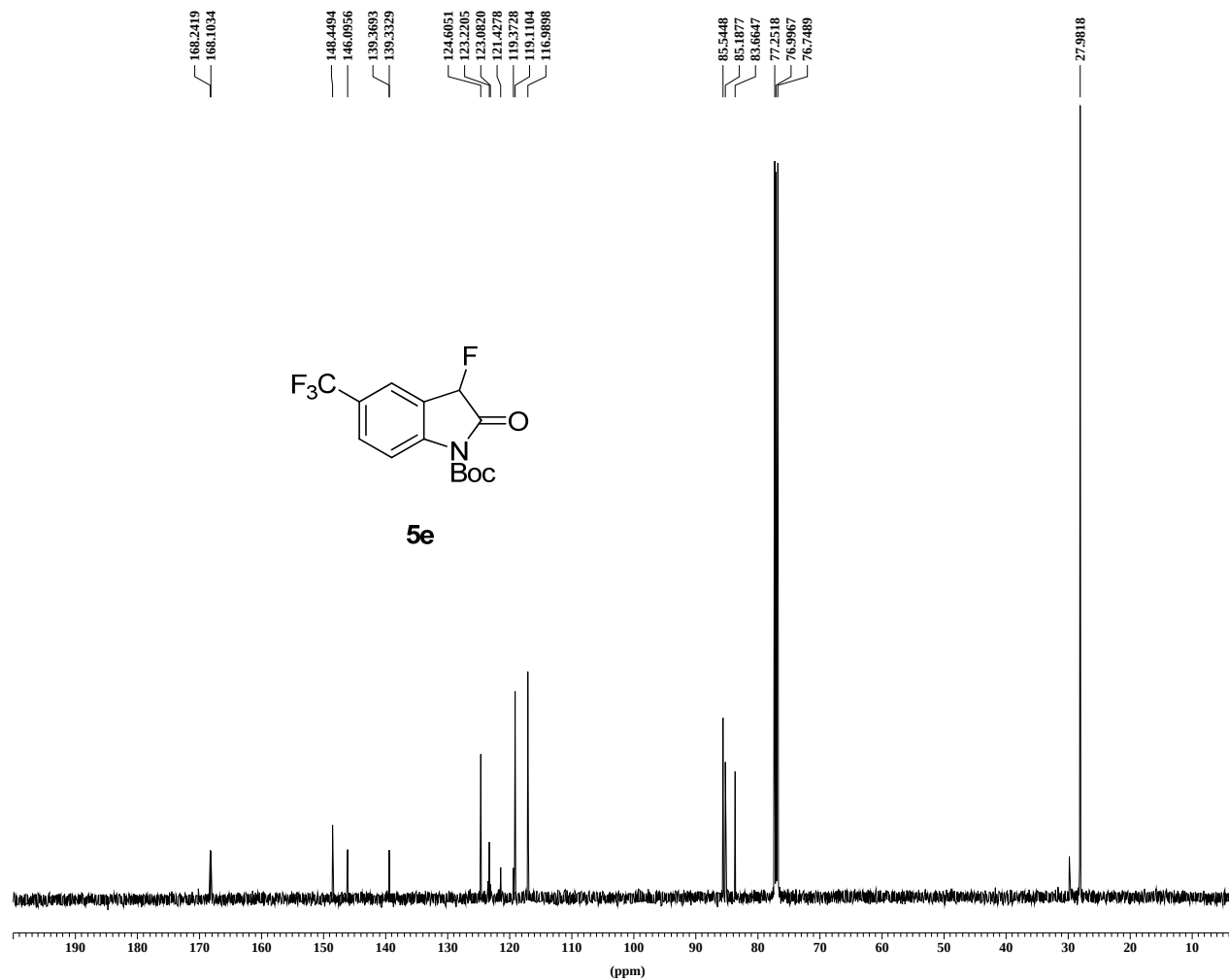
*** Processing Parameters ***

LB : 0.30 Hz
SF : 500.1300134 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C AMX500
hdl-70(5-CF3 sub)



*** Current Data Parameters ***

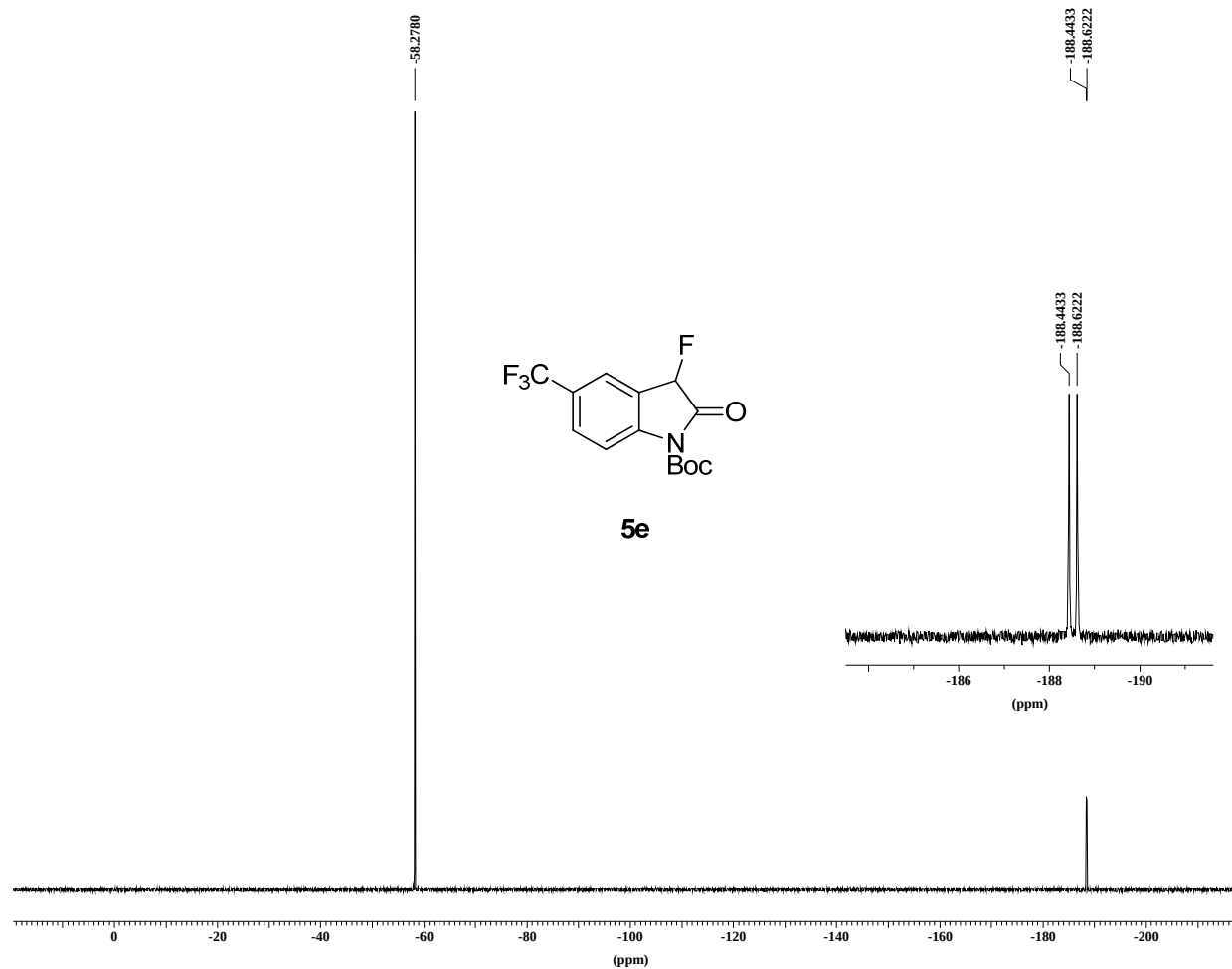
NAME : wtl-1108
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 743
NUCLEUS : off
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536
TE : 300.2 K

*** Processing Parameters ***

LB : 1.00 Hz
SF : 125.7577906 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

F19(no decoupled)

hdl-70(5-CF3 sub)



*** Current Data Parameters ***

NAME : nov08~1
EXPNO : 8
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 14
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl3
SW : 239.2822 ppm
TD : 131072
TE : 298.5 K

*** Processing Parameters ***

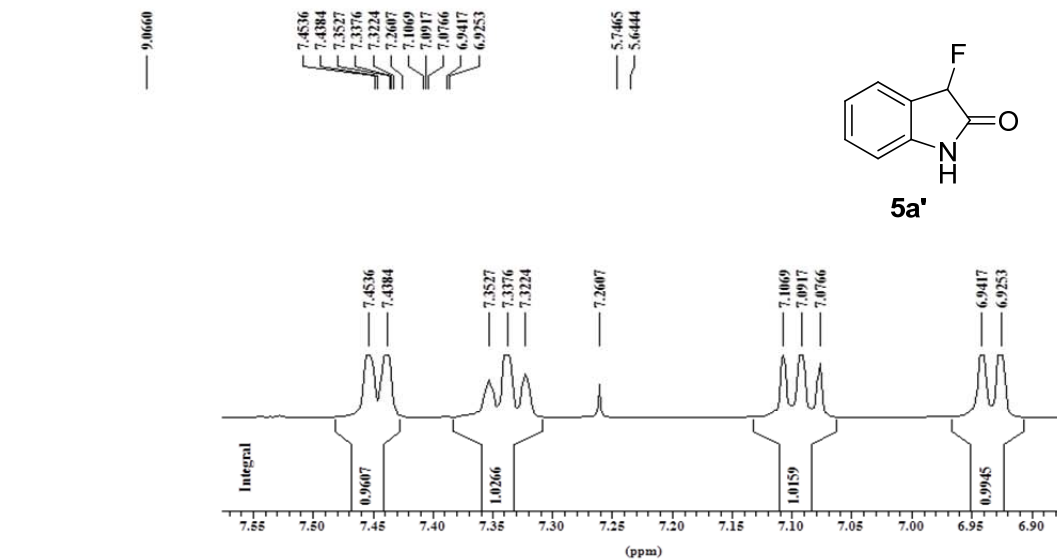
LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500

wtl-1051



*** Current Data Parameters ***

NAME : wtl-1120

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 21

NUCLEUS : off

O1 : 3088.51 Hz

PULPROG : zg30

SFO1 : 500.1330885 MHz

SOLVENT : CDCl3

SW : 20.6557 ppm

TD : 32768

TE : 298.5 K

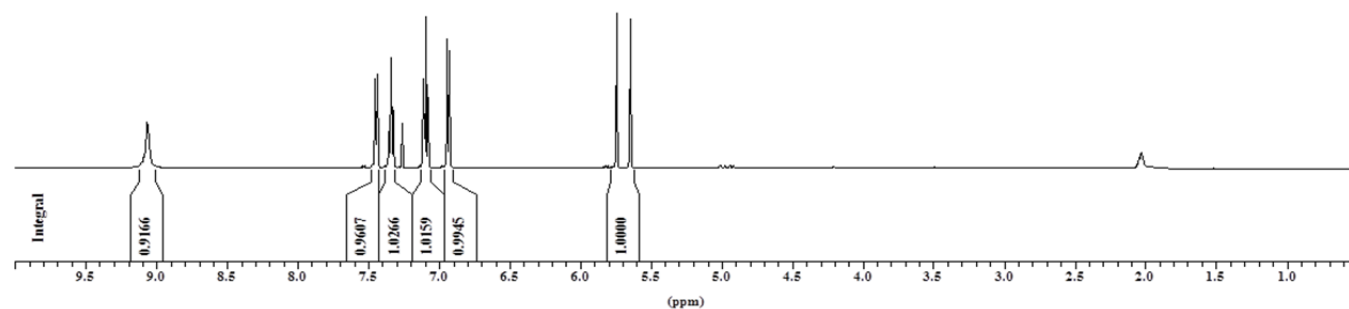
*** Processing Parameters ***

LB : 0.30 Hz

SF : 500.1300134 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off



¹³C AMX500

wtl-1051

173.8679
173.7221

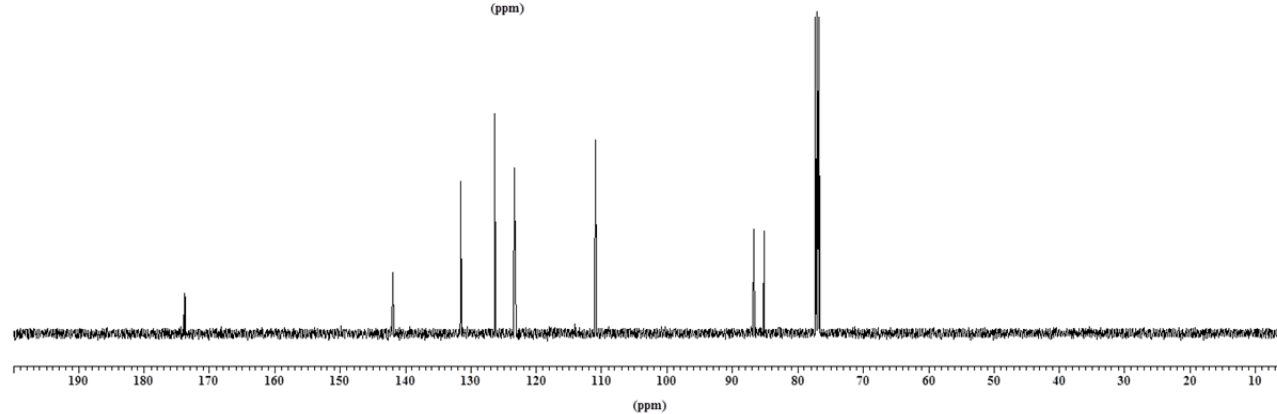
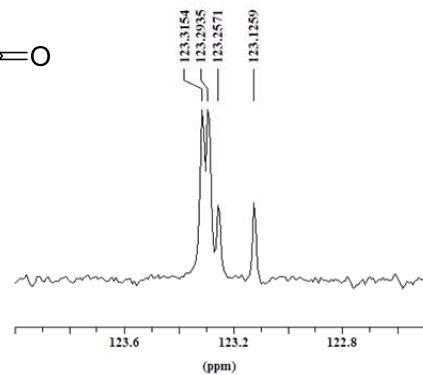
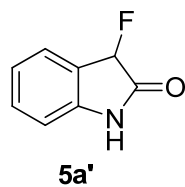
141.9637
141.9200

131.5137
131.4918
126.2740
123.3154
123.2935
123.2571
123.1259

110.8977

86.6745
85.1660

77.2519
76.5968
76.7418



*** Current Data Parameters ***

NAME : wtl-1120

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 96

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 298.6 K

*** Processing Parameters ***

LB : 1.00 Hz

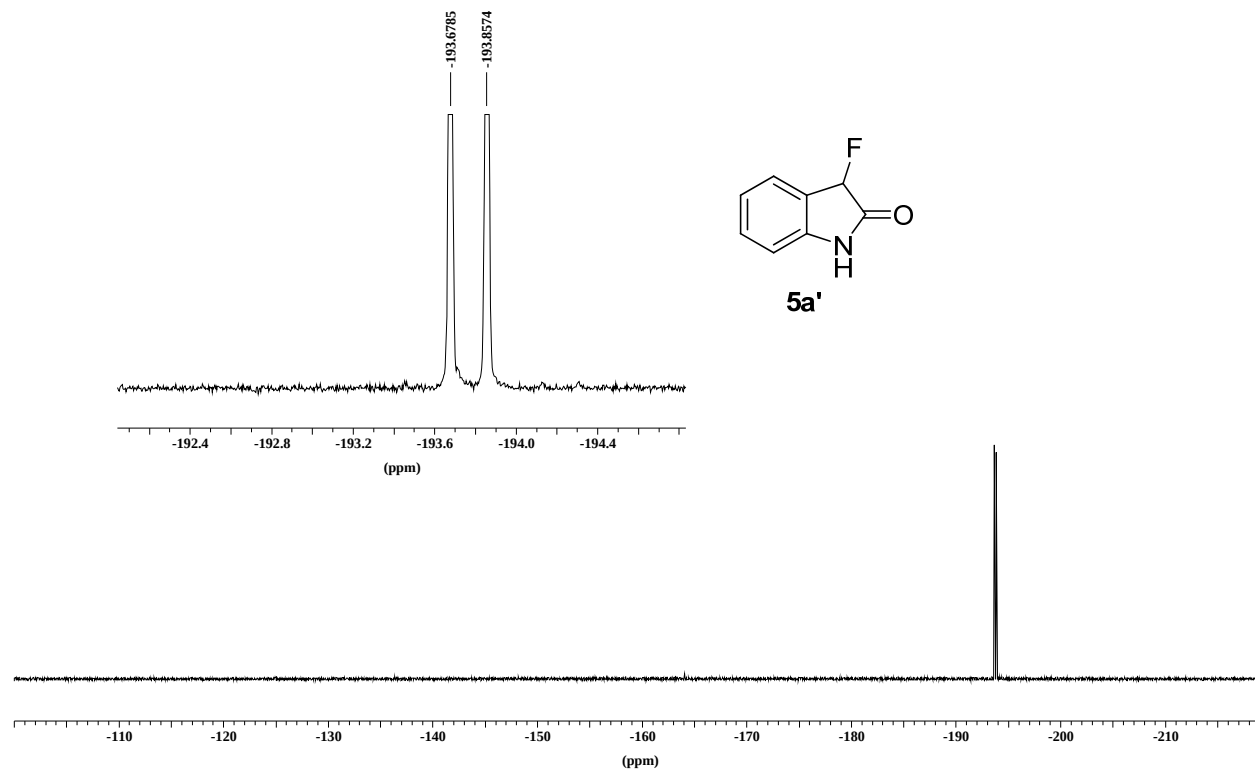
SF : 125.7577961 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)

wtl-1051



*** Current Data Parameters ***

NAME : nov20~1

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 17

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 299.1 K

*** Processing Parameters ***

LB : 0.30 Hz

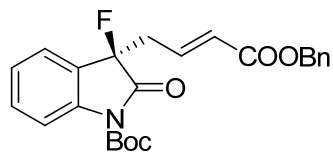
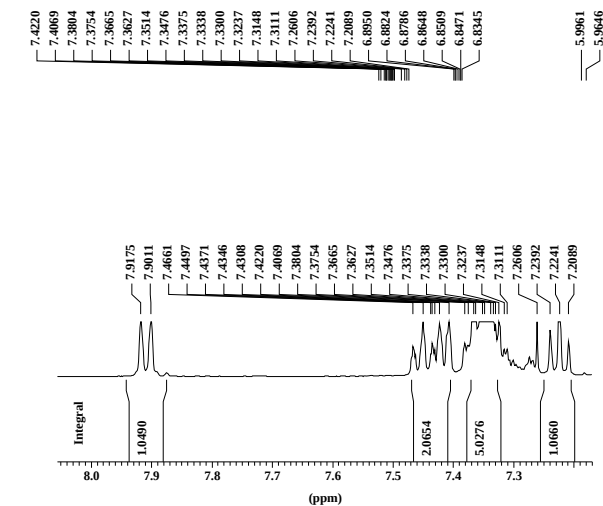
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

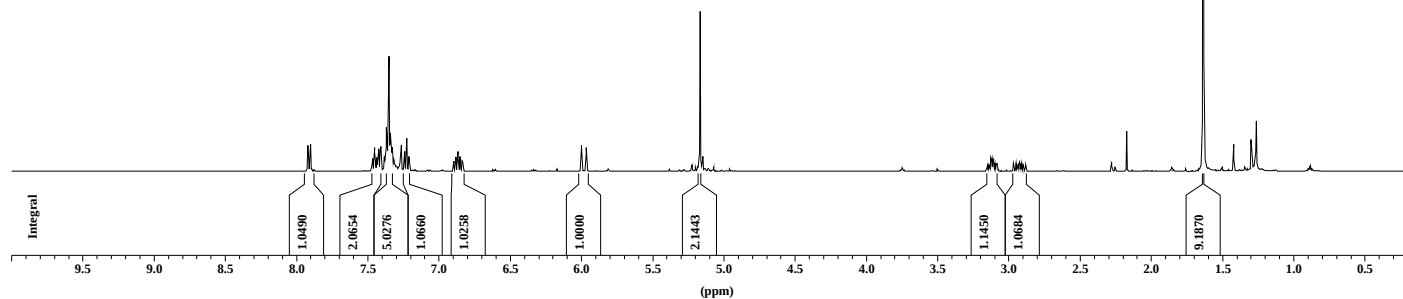
NUCLEUS : off

¹H AMX500

wtl-1038



7a



***** Current Data Parameters *****

NAME : wtl-1101
EXPNO : 3
PROCNO : 1

***** Acquisition Parameters *****

LOCNUC : 2H
NS : 30
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 297.8 K

***** Processing Parameters *****

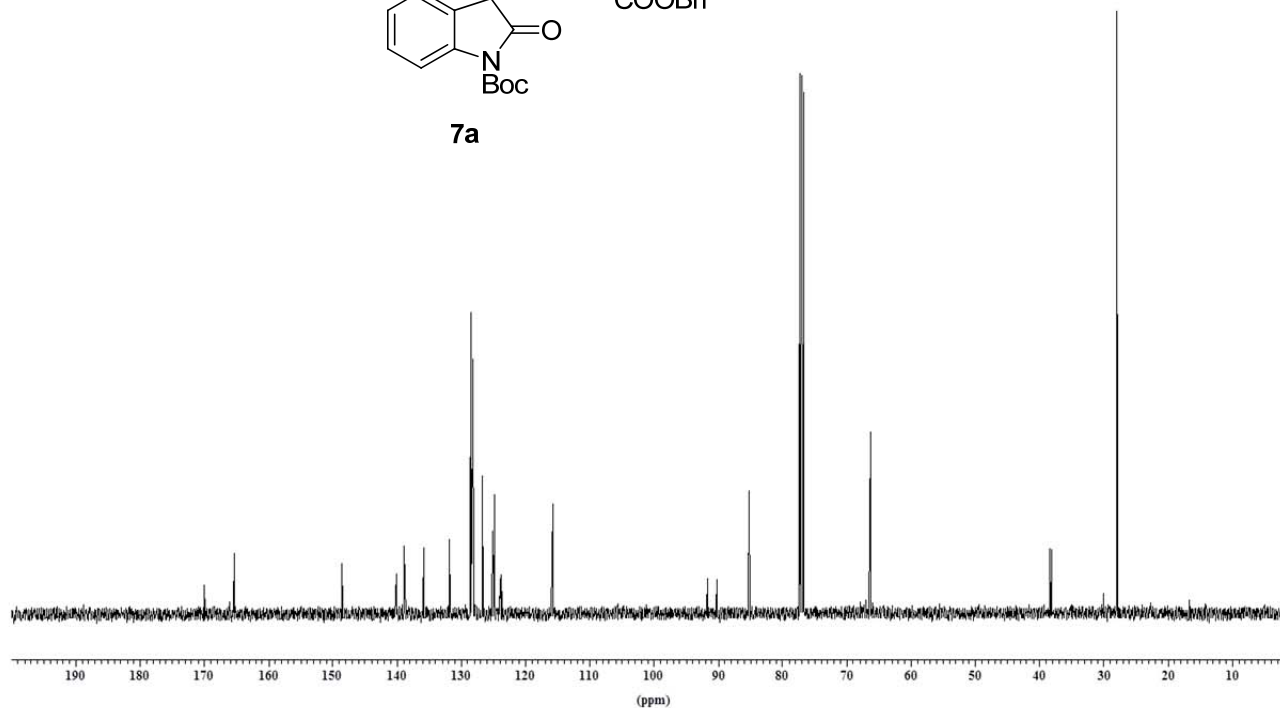
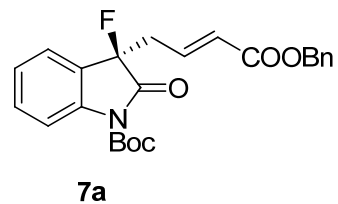
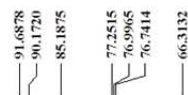
LB : 0.30 Hz
SF : 500.1300134 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS : off

¹³C AMX500

wtl-1038



*** Current Data Parameters ***

NAME : wtl-1101

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 172

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 297.9 K

*** Processing Parameters ***

LB : 1.00 Hz

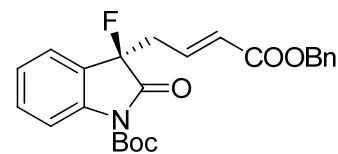
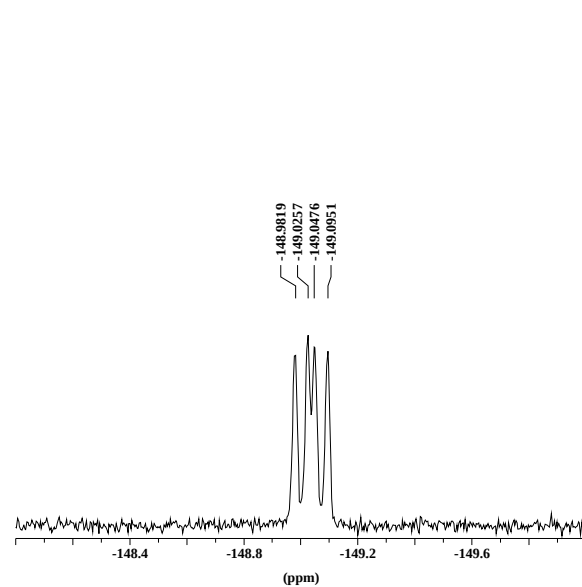
SF : 125.7577952 MHz

*** 1D NMR Plot Parameters ***

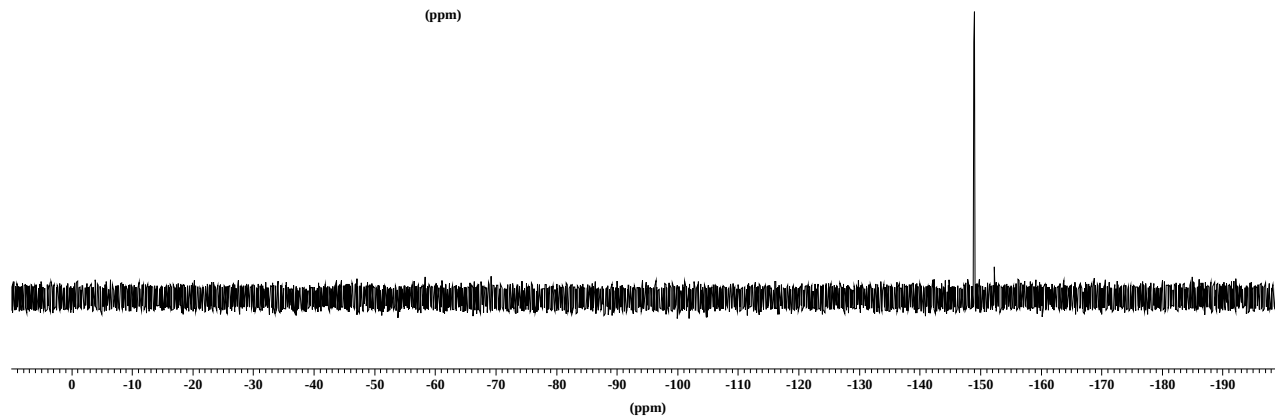
NUCLEUS : off

F19(no decoupled)

wtl-1038



7a



*** Current Data Parameters ***

NAME : nov08~1

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 6

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 298.5 K

*** Processing Parameters ***

LB : 0.30 Hz

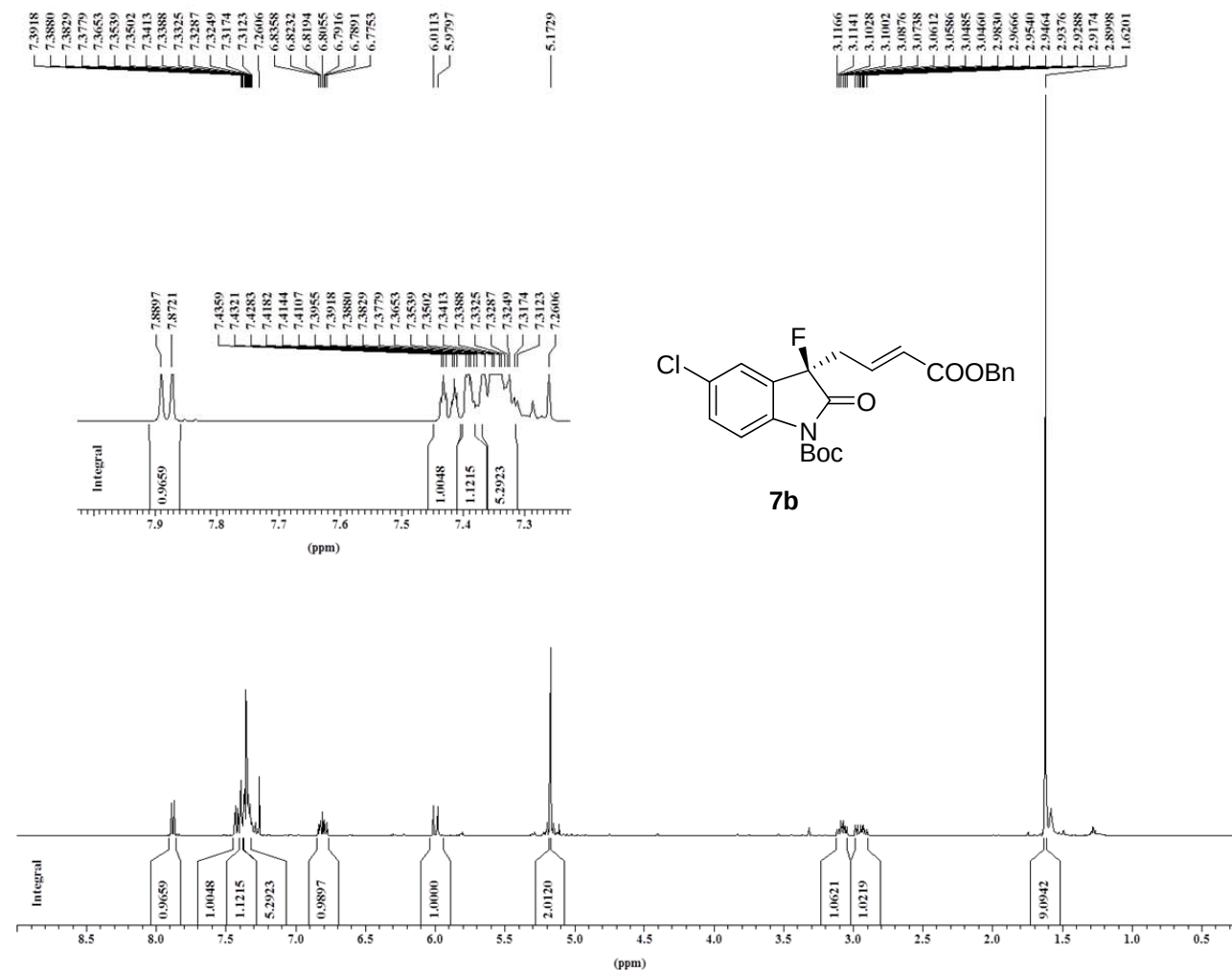
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500

wtl-1040

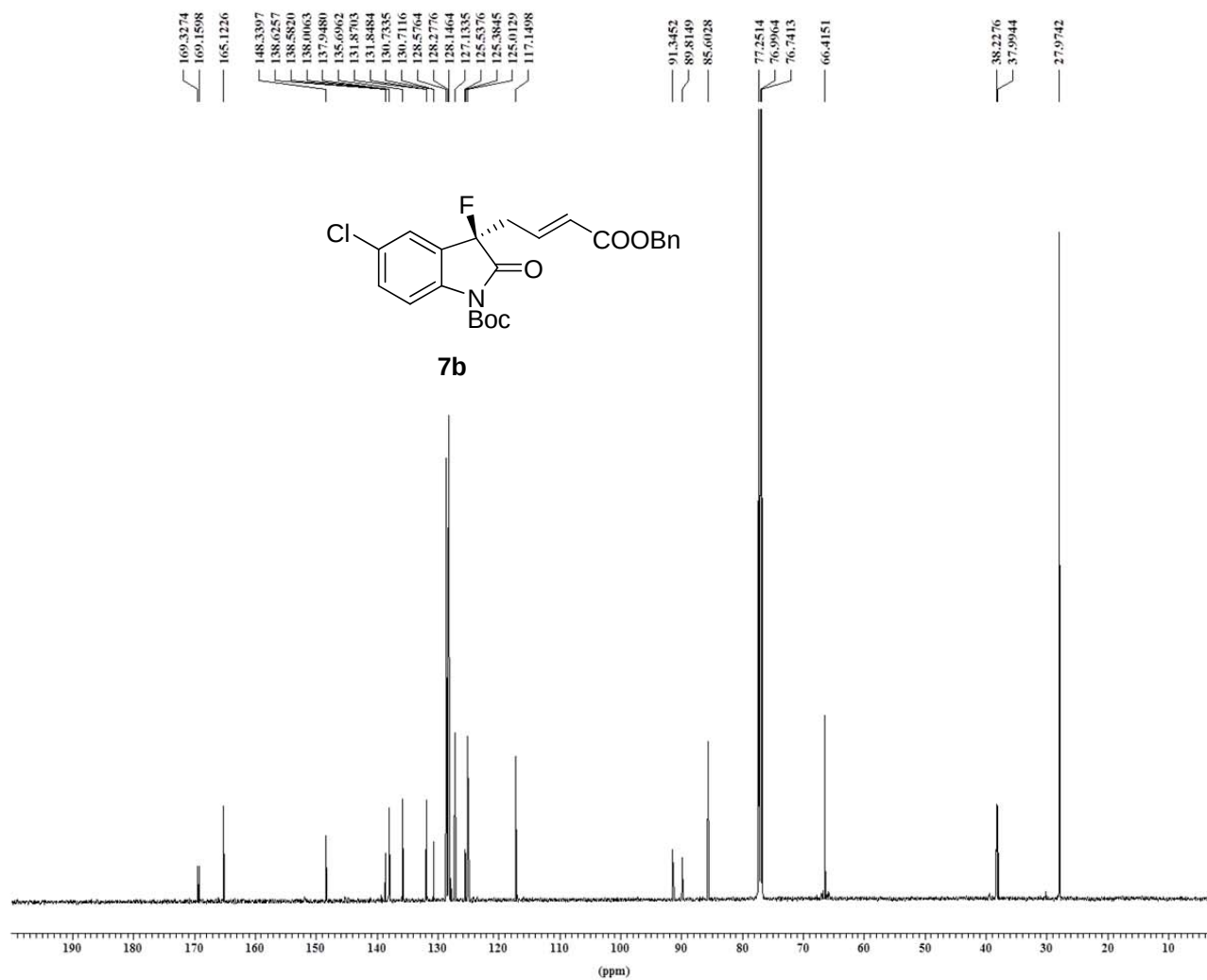


*** Current Data Parameters ***

NAME : wtl-1101
 EXPNO : 5
 PROCNO : 1
 *** Acquisition Parameters ***
 LOCNUC : 2H
 NS : 21
 NUCLEUS : off
 O1 : 3088.51 Hz
 PULPROG : zg30
 SFO1 : 500.1330885 MHz
 SOLVENT : CDCl3
 SW : 20.6557 ppm
 TD : 32768
 TE : 297.7 K
 *** Processing Parameters ***
 LB : 0.30 Hz
 SF : 500.1300134 MHz
 *** 1D NMR Plot Parameters ***
 NUCLEUS : off

¹³C AMX500

wtl-1040



*** Current Data Parameters ***

NAME : wtl-1101

EXPNO : 6

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 17345

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 297.8 K

*** Processing Parameters ***

LB : 1.00 Hz

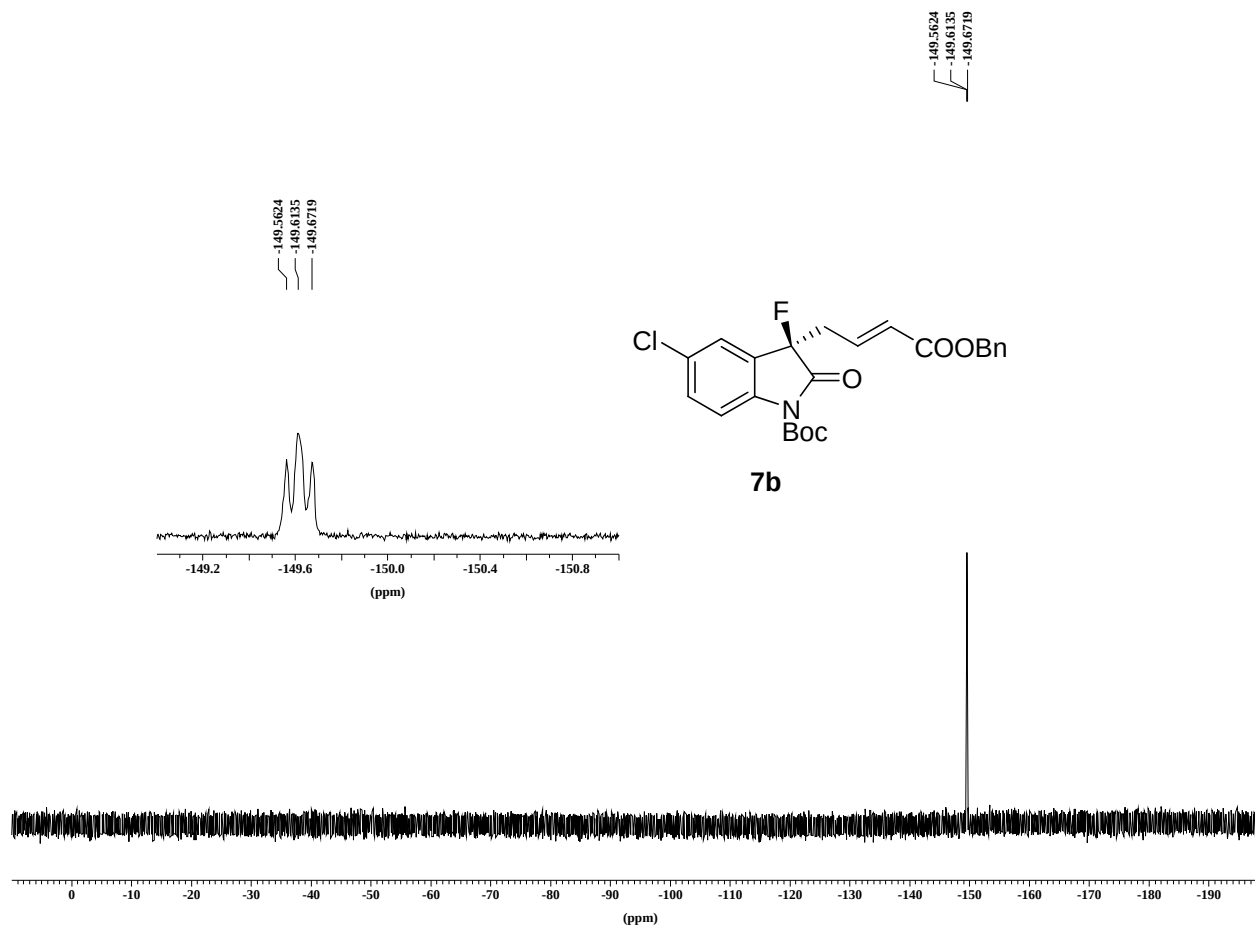
SF : 125.7577924 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)

wtl-1040



*** Current Data Parameters ***

NAME : nov08~1

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 35

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 298.6 K

*** Processing Parameters ***

LB : 0.30 Hz

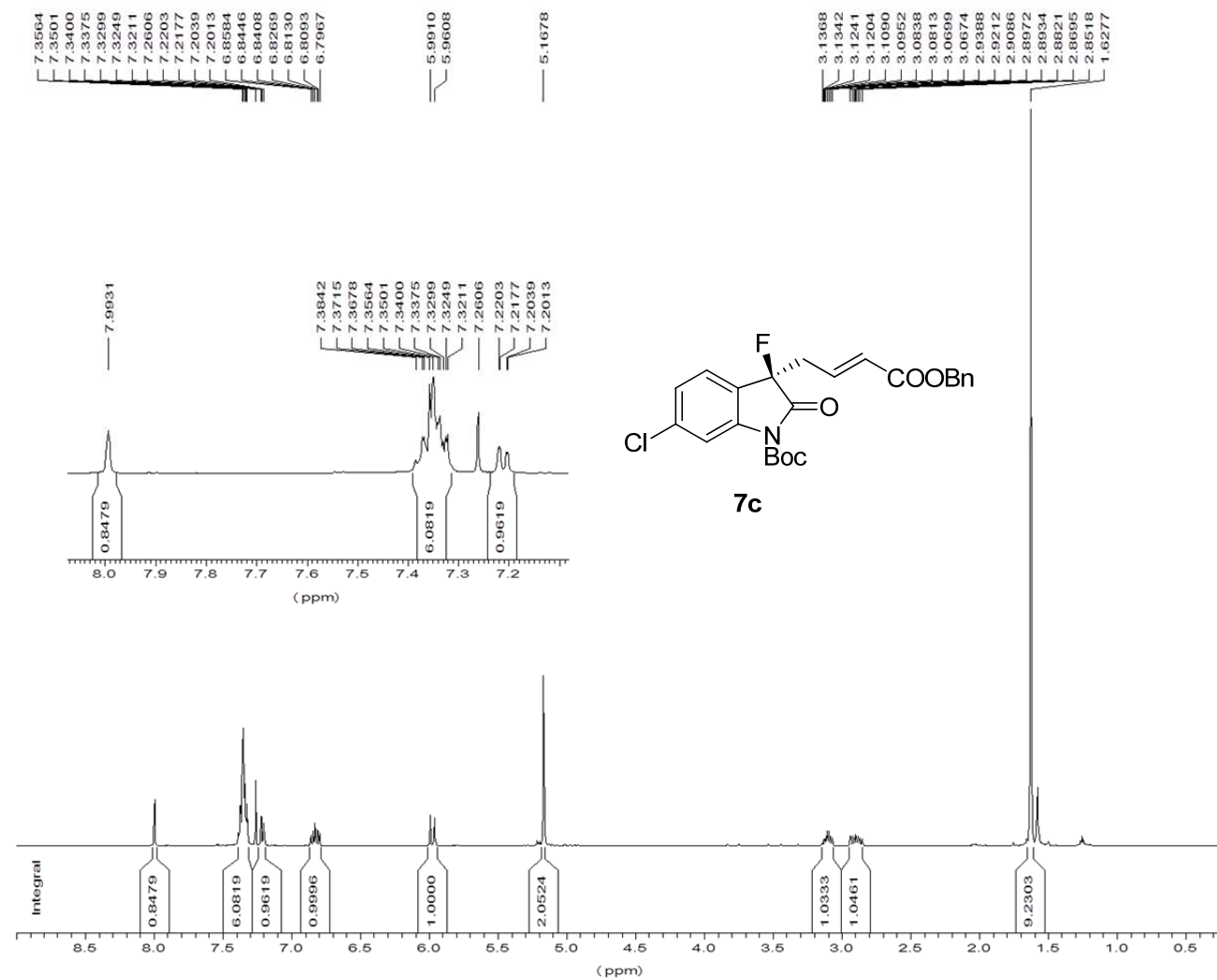
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500

wtl-1039



*** Current Data Parameters ***

NAME : wtl-1029
 EXPNO : 2
 PROCNO : 1
 *** Acquisition Parameters ***
 DS : 0
 INSTRUM : spect
 LOCNUC : 2H
 NS : 23
 NUCLEUS : off
 O1 : 3088.51 Hz
 PULPROG : zg30
 SFO1 : 500.1330885 MHz
 SOLVENT : CDCl3
 SW : 20.6557 ppm
 TD : 32768
 TE : 296.6 K
 *** Processing Parameters ***
 LB : 0.30 Hz
 OFFSET : 16.477 ppm
 SI : 16384
 *** 1D NMR Plot Parameters ***
 NUCLEUS : off

¹³C AMX500

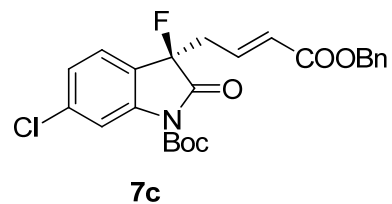
wtl-1039

169.5679
169.4003
165.1736
148.2742
141.0597
141.0159
138.2977
138.2394
137.8897
137.8605
135.6743
128.5764
128.3140
128.1902
127.0242
125.8218
125.2825
125.2606
122.0761
116.6032

91.2723
85.7777

77.2514
76.9964
76.7413
66.4297

38.2130
37.9798
27.9524



*** Current Data Parameters ***

NAME : wtl-1029
EXPNO : 3
PROCNO : 1

*** Acquisition Parameters ***

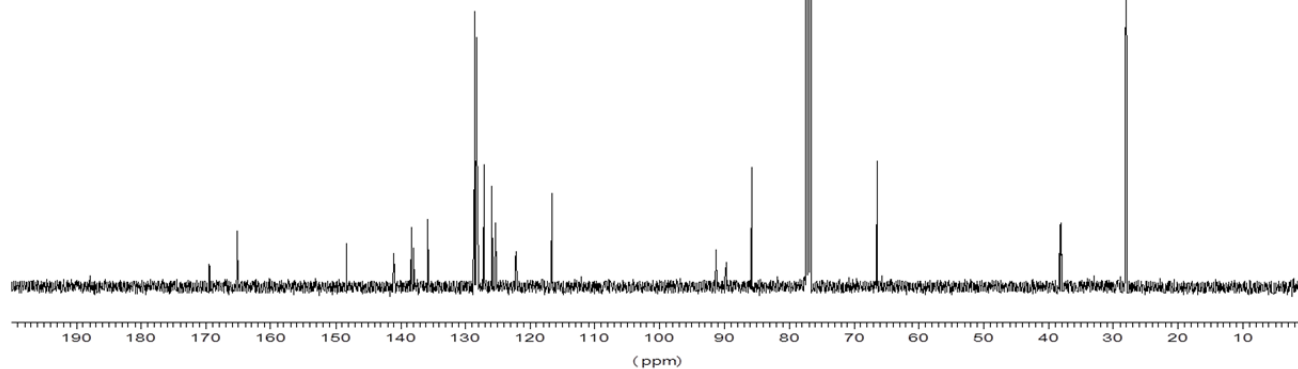
DS : 0
INSTRUM : spect
LOCNUC : 2H
NS : 884
NUCLEUS : off
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536
TE : 296.7 K

*** Processing Parameters ***

LB : 1.00 Hz
OFFSET : 224.369 ppm
SI : 32768

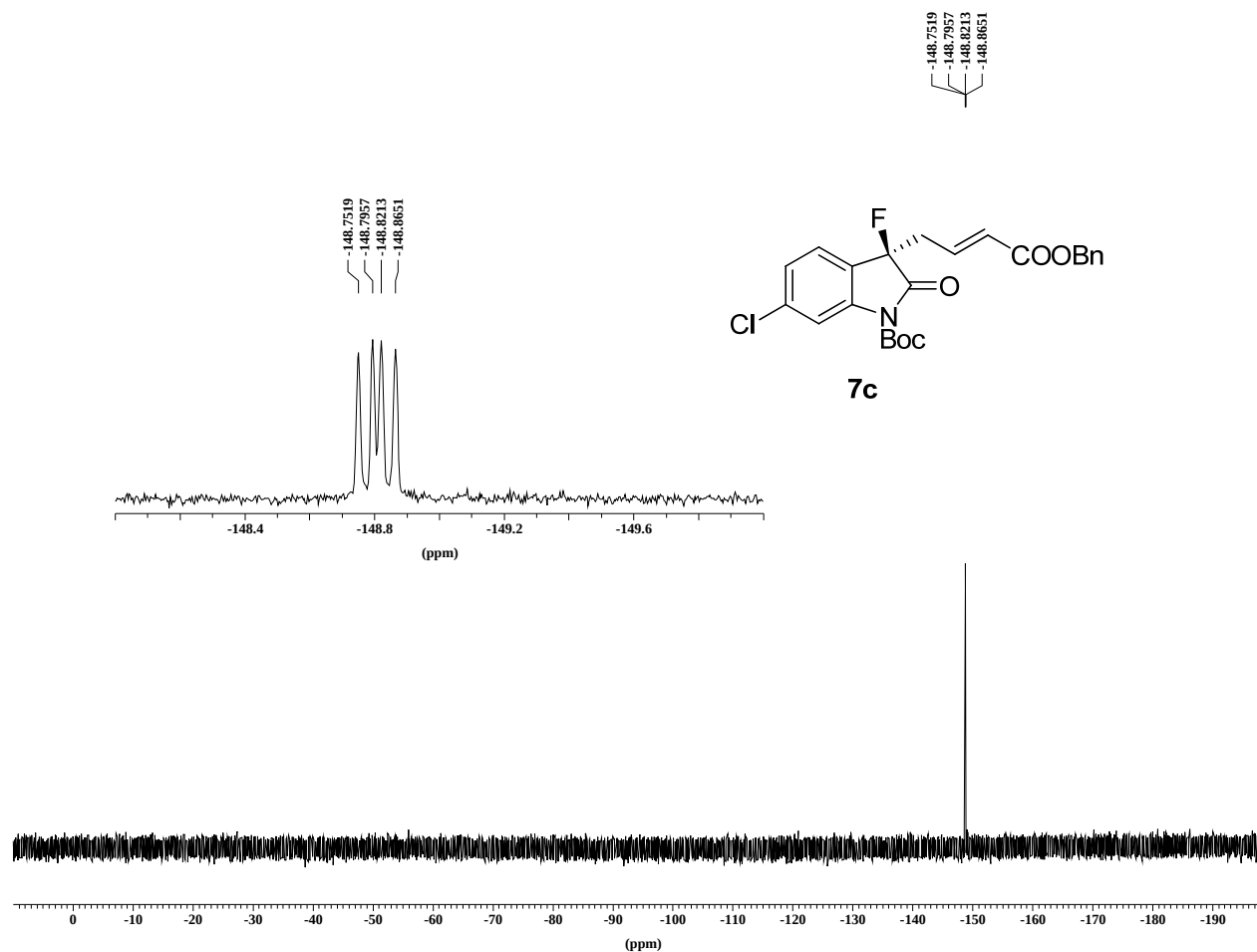
*** 1D NMR Plot Parameters ***

NUCLEUS : off



F19(no decoupled)

wtl-1039



*** Current Data Parameters ***

NAME : nov08~1

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 37

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 298.5 K

*** Processing Parameters ***

LB : 0.30 Hz

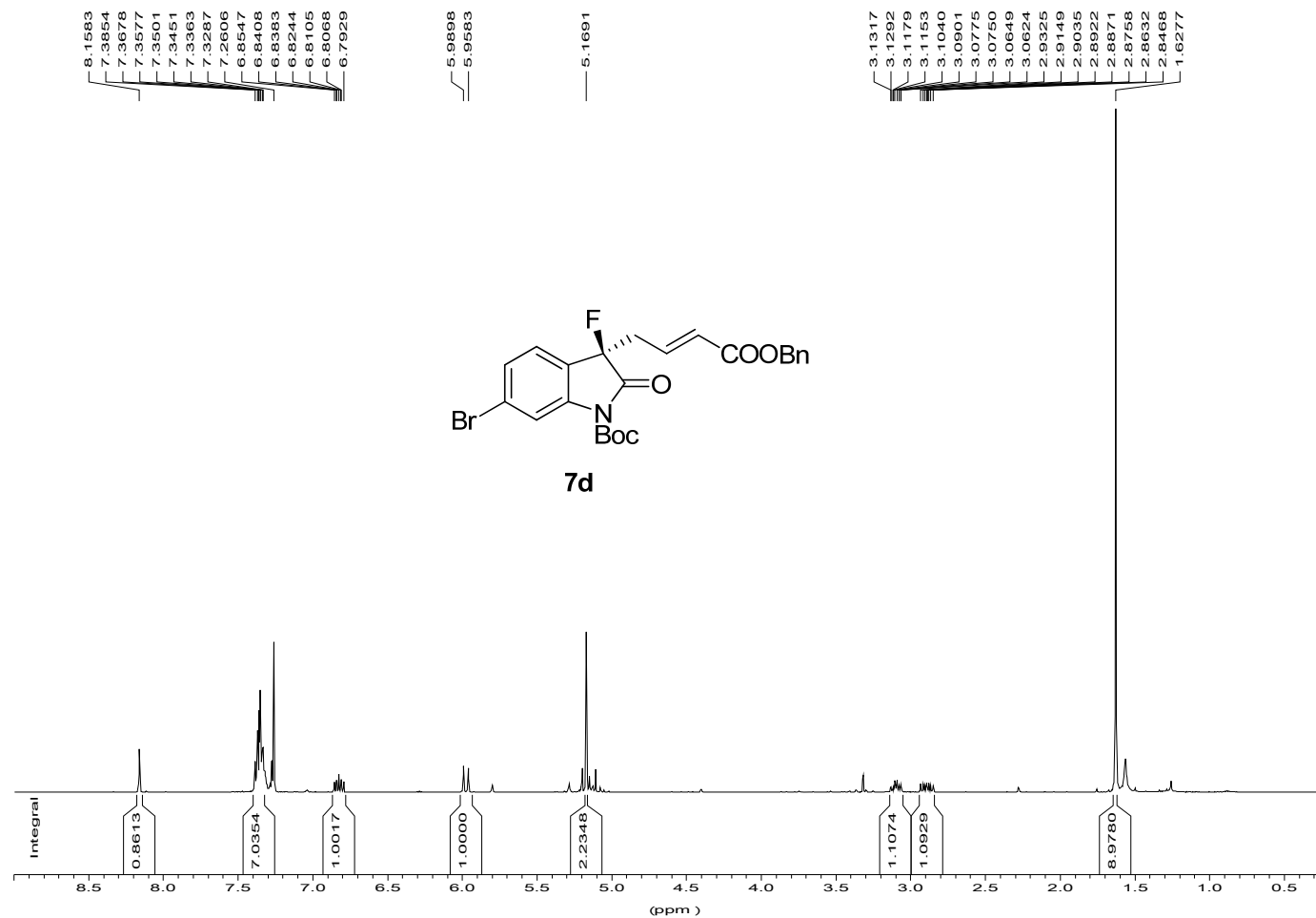
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

1H AMX500

wtl-1054

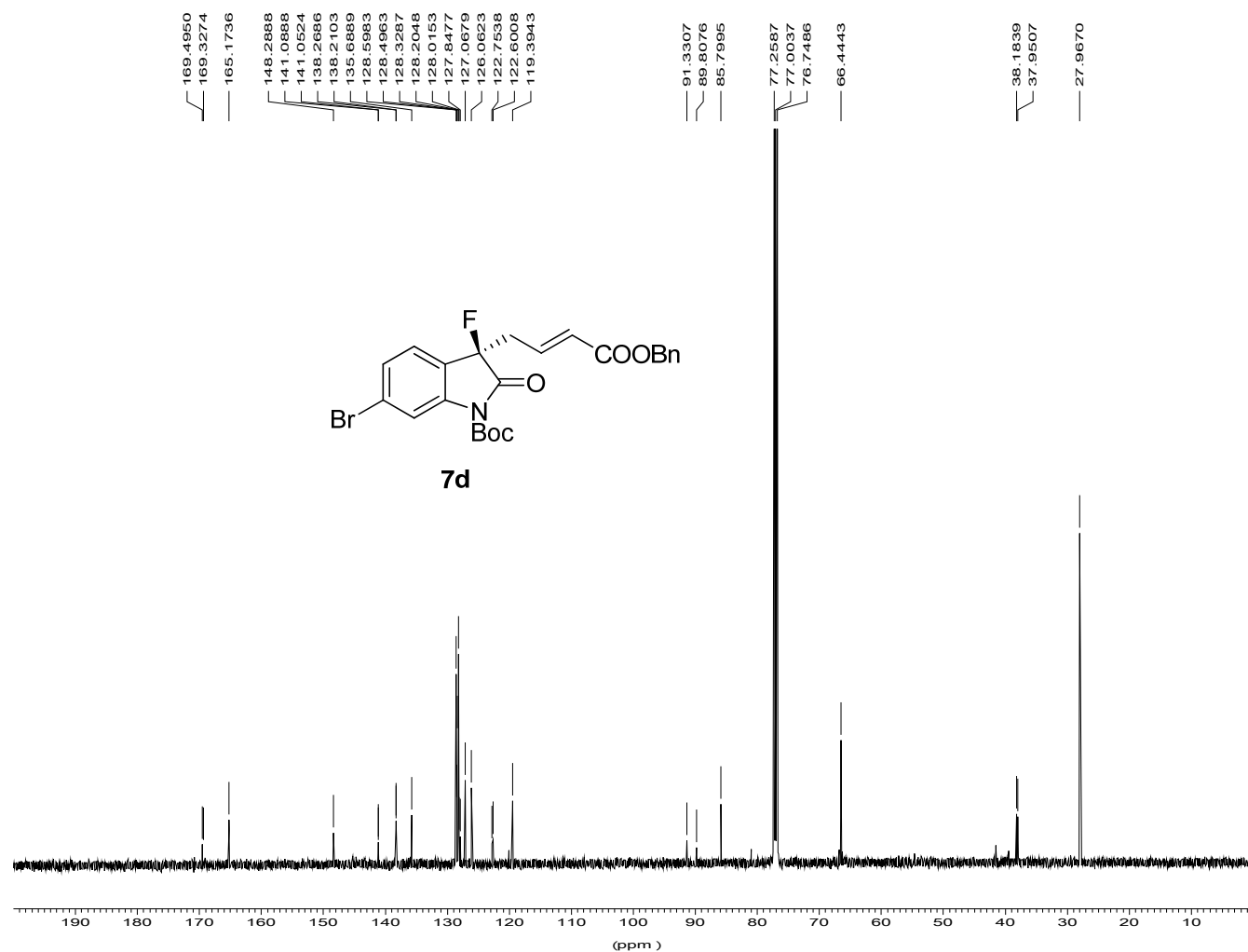


*** Current Data Parameters ***

NAME : wtl-1115
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DS : 0
INSTRUM : spect
LOCNUC : 2H
NS : 30
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl₃
SW : 20.6557 ppm
TD : 32768
TE : 297.8 K
*** Processing Parameters ***
LB : 0.30 Hz
OFFSET : 16.477 ppm
SI : 16384
*** 1D NMR Plot Parameters ***
NUCLEUS : off

¹³C AMX500

wtl-1054



*** Current Data Parameters ***

NAME : wtl-1115

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

DS : 0

INSTRUM : spect

LOCNUC : 2H

NS : 3577

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 298.1 K

*** Processing Parameters ***

LB : 1.00 Hz

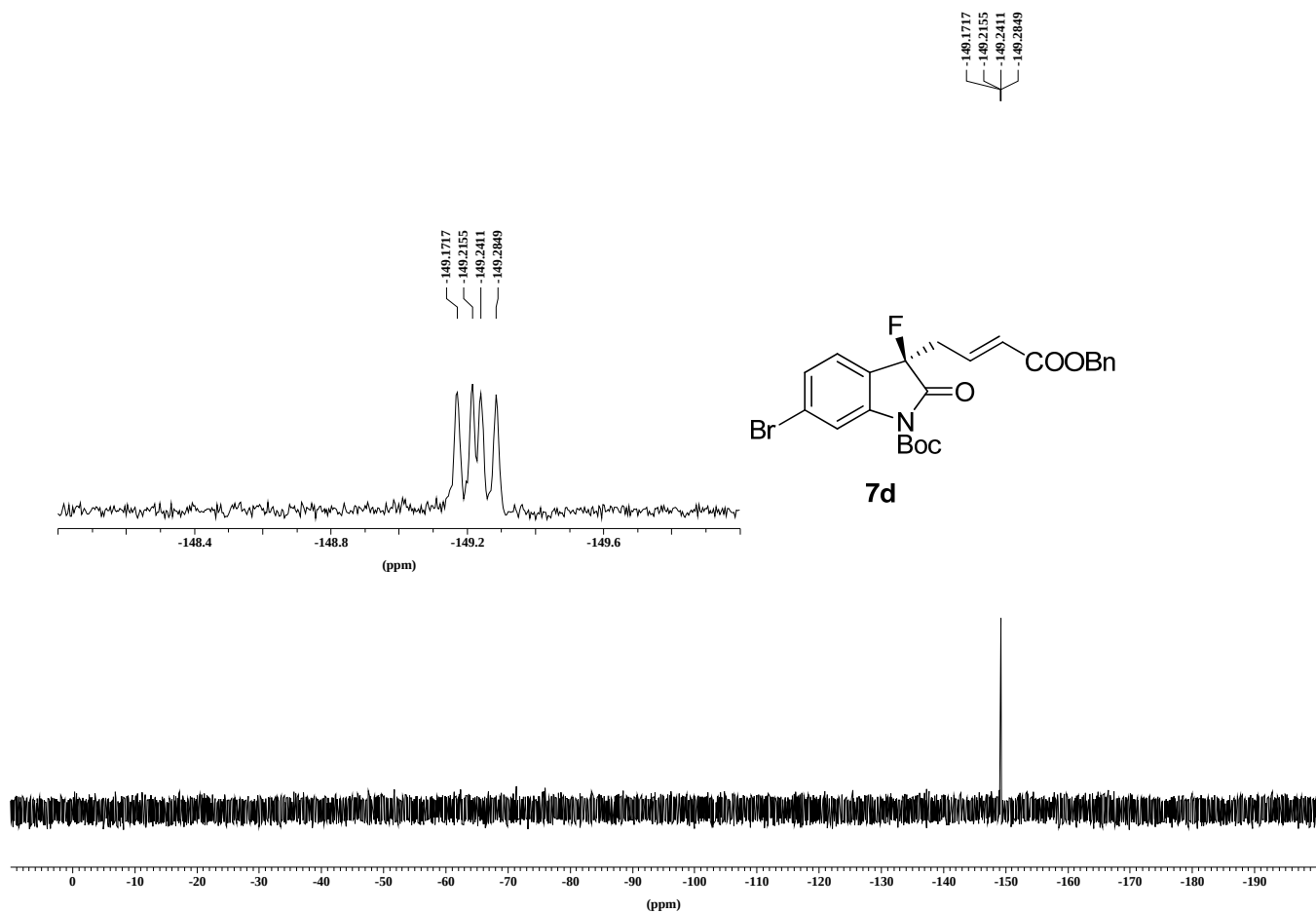
OFFSET : 224.383 ppm

SI : 32768

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)
wtl-1054



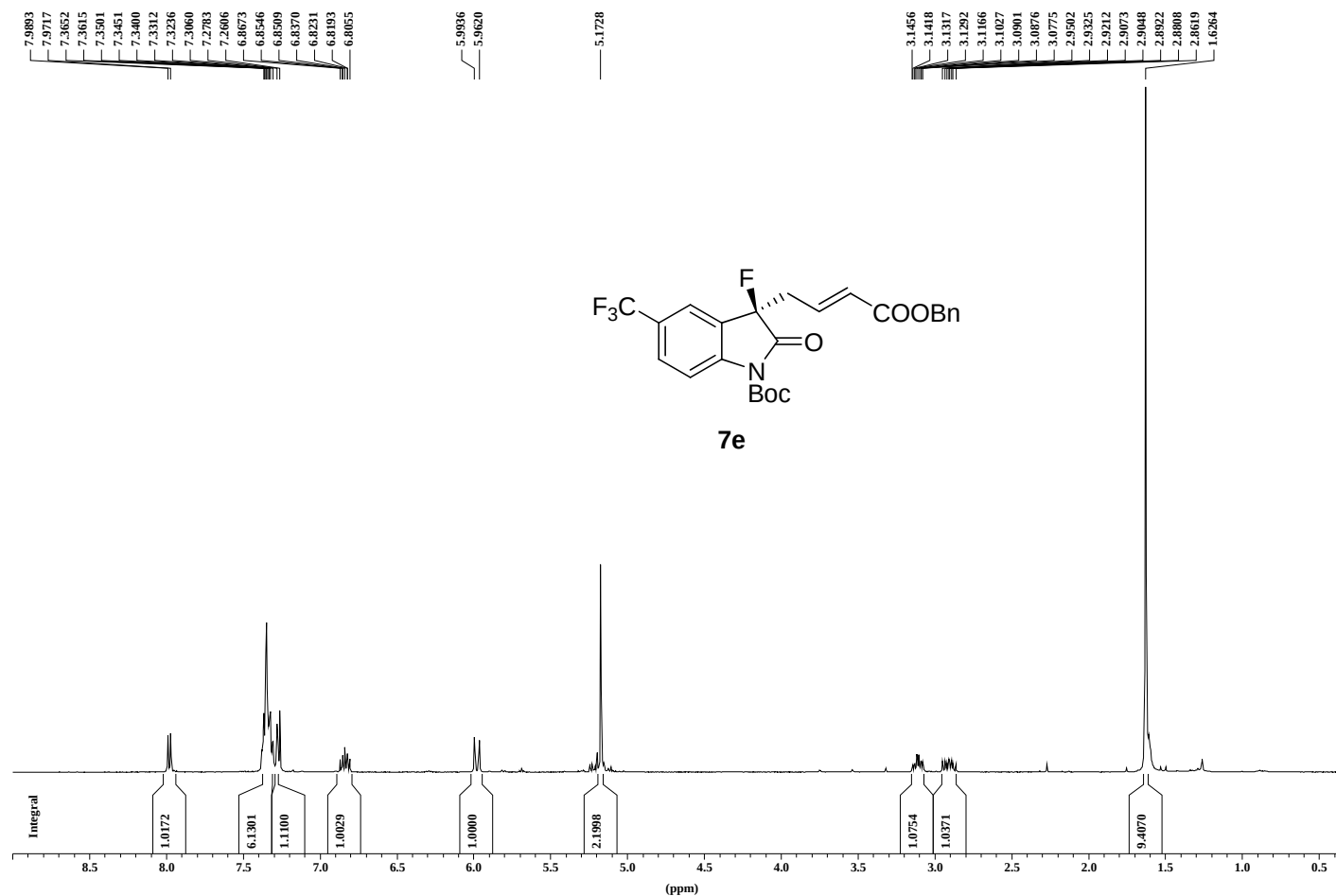
*** Current Data Parameters ***

NAME : nov17-~1
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 93
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl3
SW : 239.2822 ppm
TD : 131072
TE : 299.2 K

*** Processing Parameters ***
LB : 0.30 Hz
SF : 282.4043550 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

1H AMX500

wtl-1045



*** Current Data Parameters ***

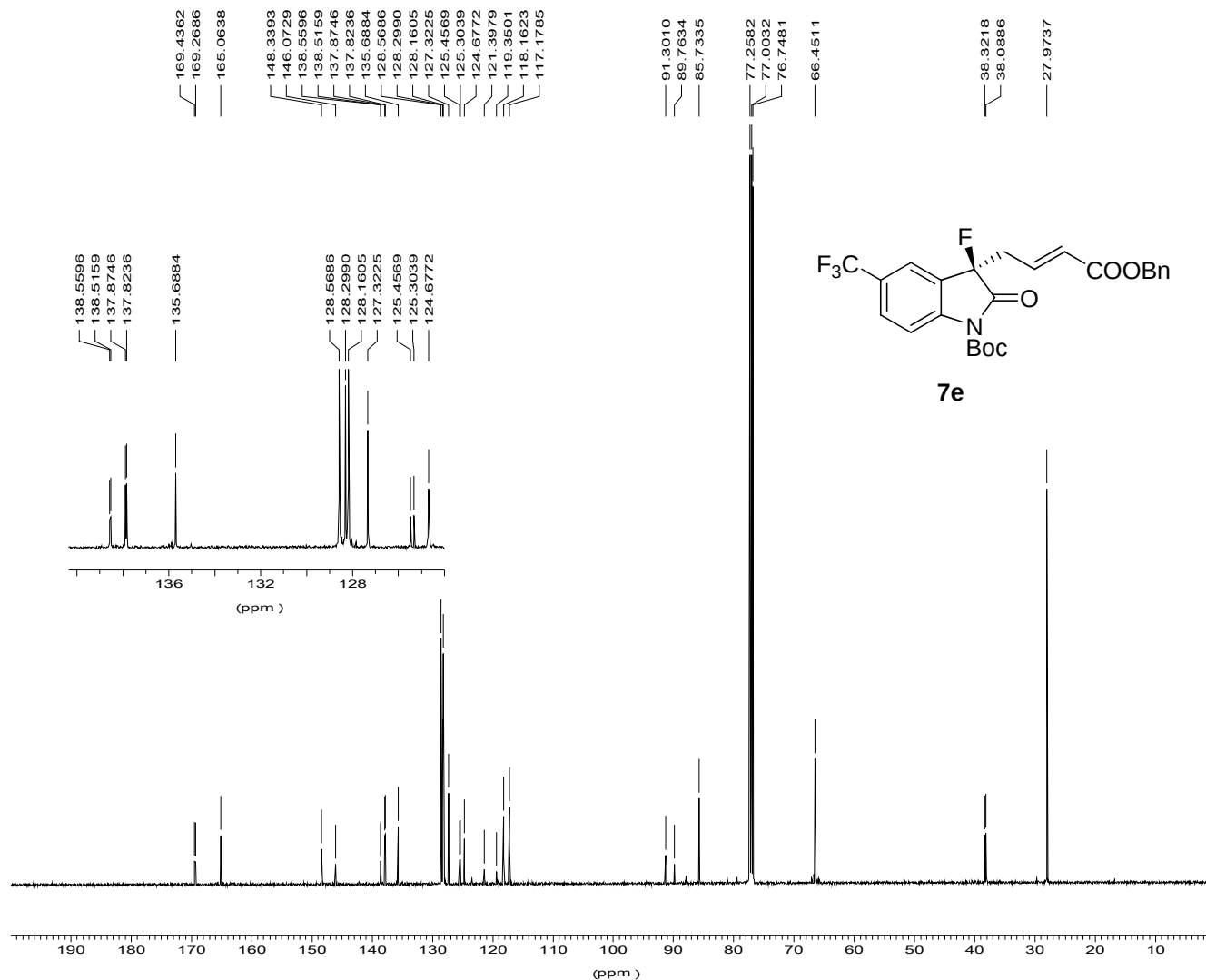
NAME : wtl-1110
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 34
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 299.9 K

*** Processing Parameters ***

LB : 0.30 Hz
SF : 500.1300134 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

¹³C AMX500

wtl-1045



*** Current Data Parameters ***

NAME : wtl-1110
EXPNO : 2
PROCNO : 1

*** Acquisition Parameters ***

DS : 0
INSTRUM : spect
LOCNUC : 2H
NS : 12547
NUCLEUS : off
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536
TE : 300.2 K

*** Processing Parameters ***

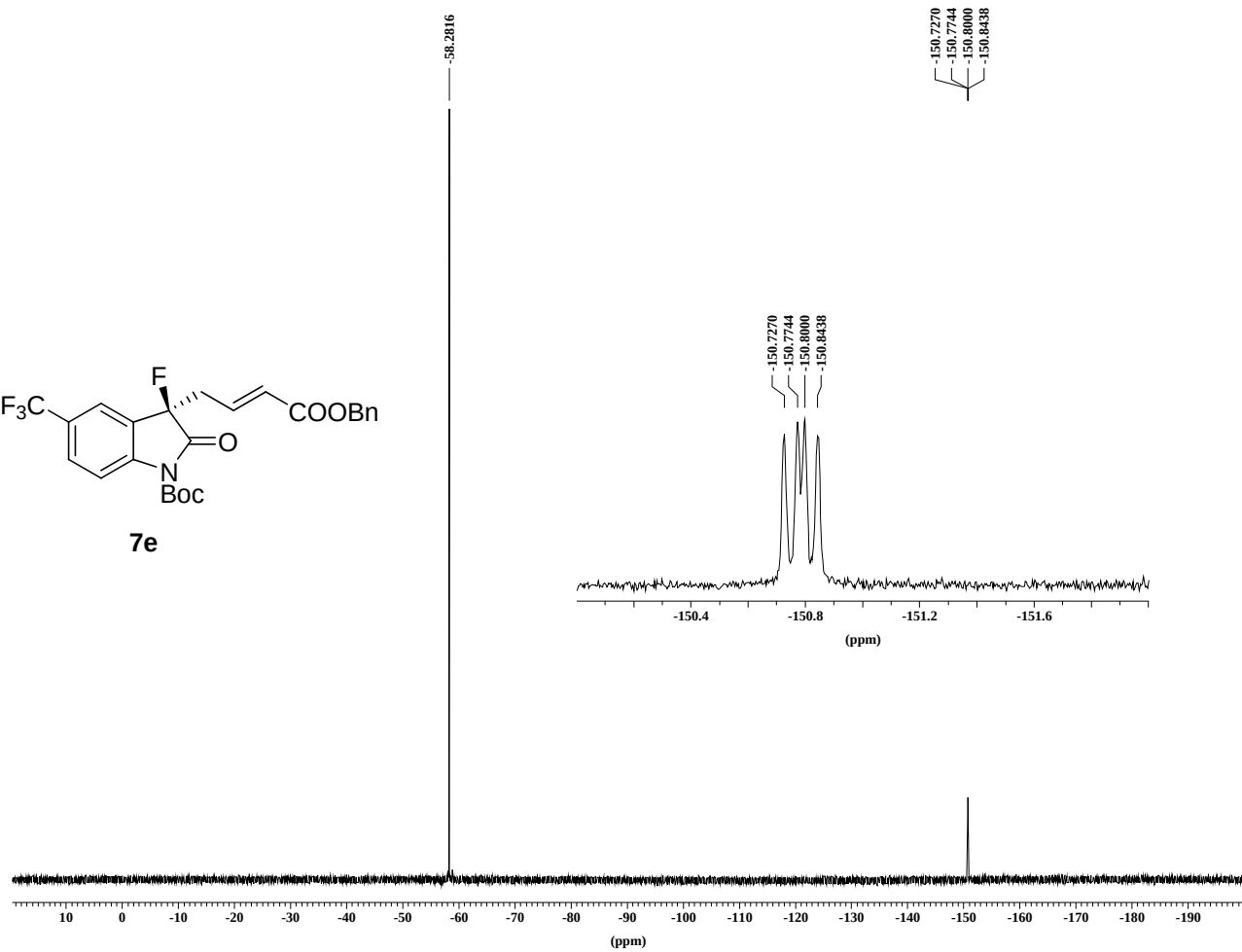
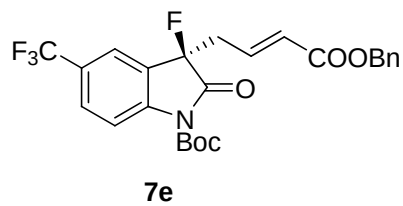
LB : 1.00 Hz
OFFSET : 224.383 ppm
SI : 32768

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)

wtl-1045



*** Current Data Parameters ***

NAME : nov10~1
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 40
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl₃
SW : 239.2822 ppm
TD : 131072
TE : 298.8 K

*** Processing Parameters ***

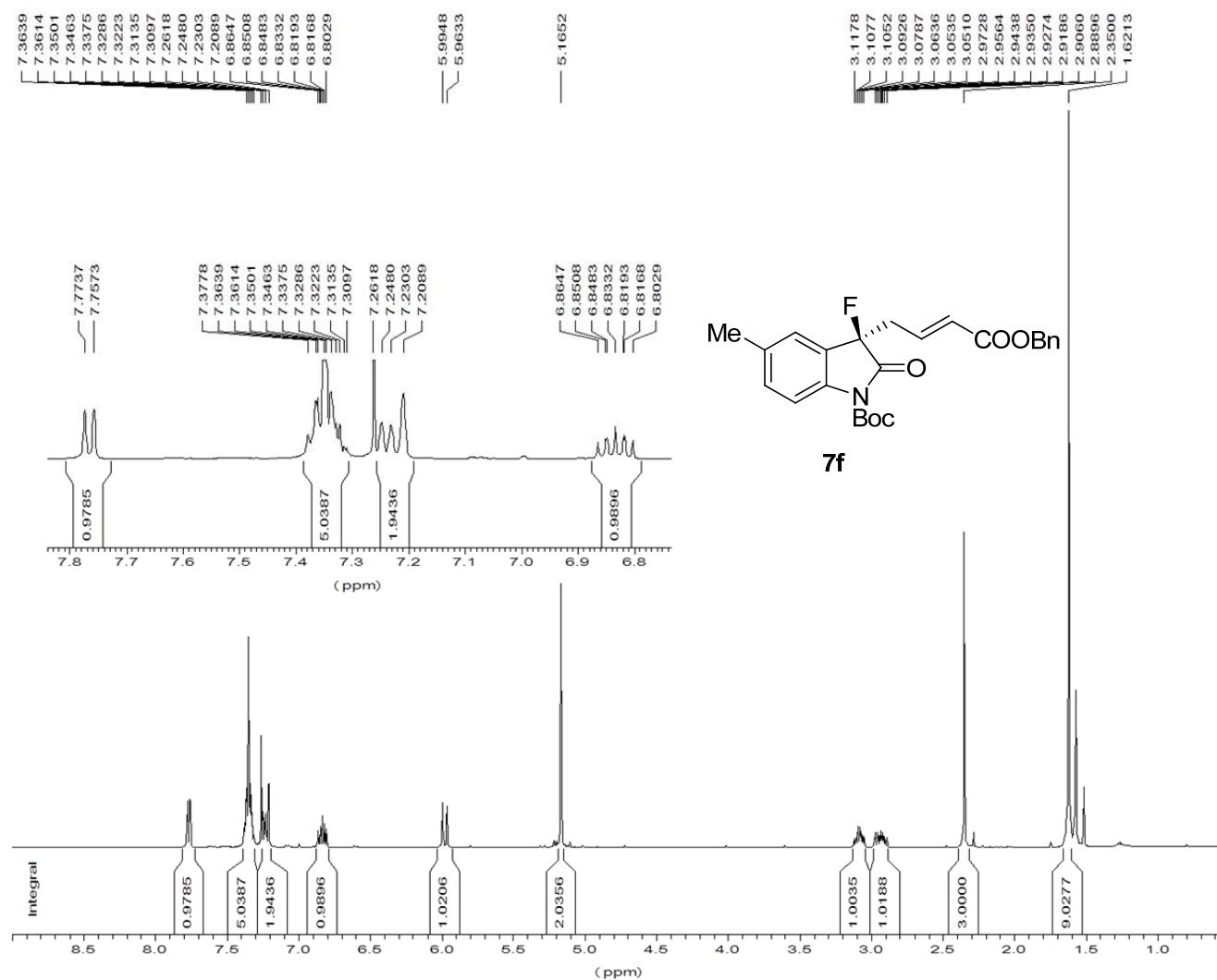
LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

1H AMX500

wtl-1037



*** Current Data Parameters ***

NAME : wtl-1028
 EXPNO : 3
 PROCNO : 1
 DS : 0
 INSTRUM : spect
 LOCNUC : 2H
 NS : 87
 NUCLEUS : off
 O1 : 3088.51 Hz
 PULPROG : zg30
 SFO1 : 500.1330885 MHz
 SOLVENT : CDCl3
 SW : 20.6557 ppm
 TD : 32768
 TE : 297.6 K

*** Processing Parameters ***

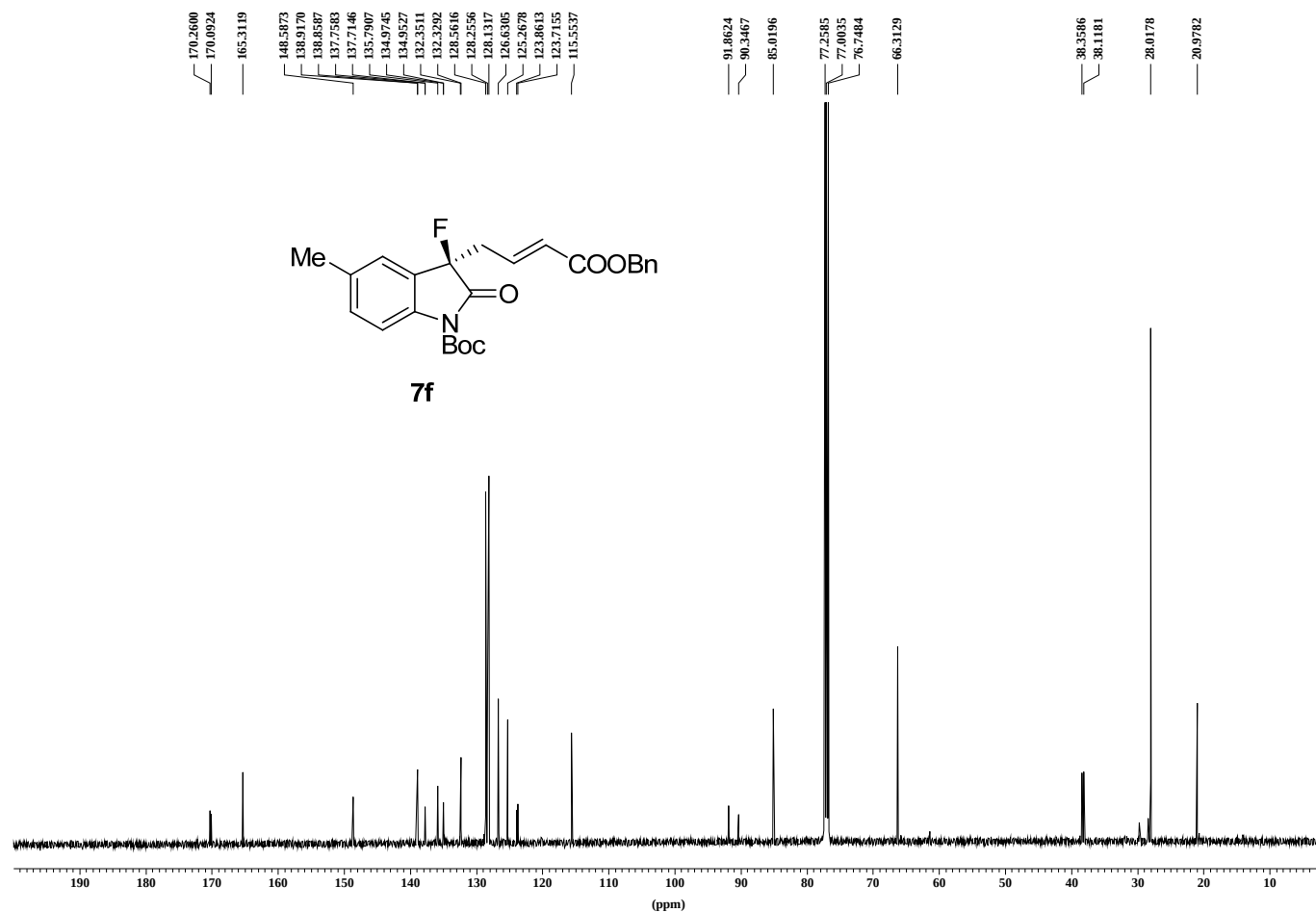
LB : 0.30 Hz
 OFFSET : 16.476 ppm
 SI : 16384

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C AMX500

wtl-1037



*** Current Data Parameters ***

NAME : wtl-1101

EXPNO : 2

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 6825

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 298.1 K

*** Processing Parameters ***

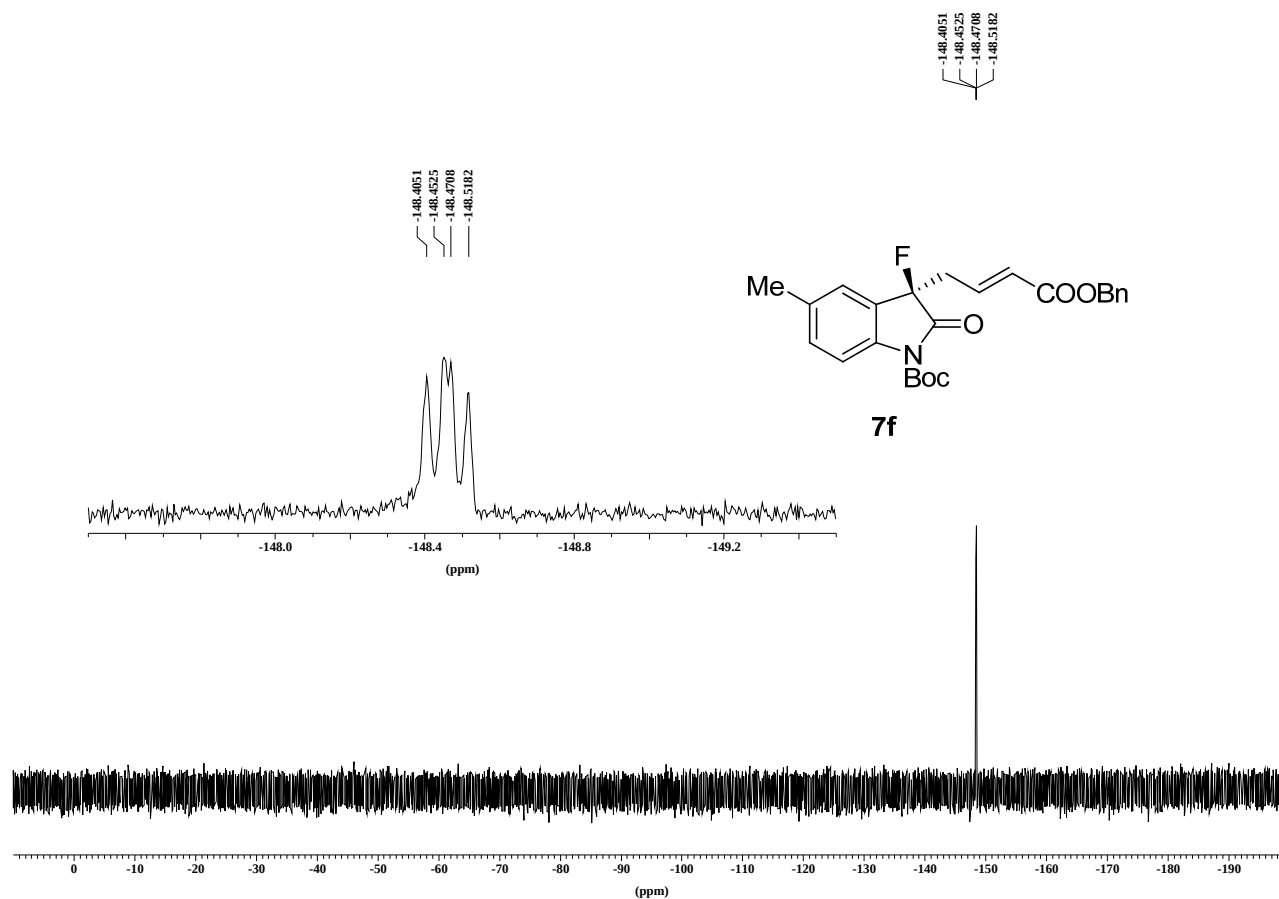
LB : 1.00 Hz

SF : 125.7577916 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)
wtl-1037



*** Current Data Parameters ***

NAME : nov08~1

EXPNO : 6

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 30

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 298.5 K

*** Processing Parameters ***

LB : 0.30 Hz

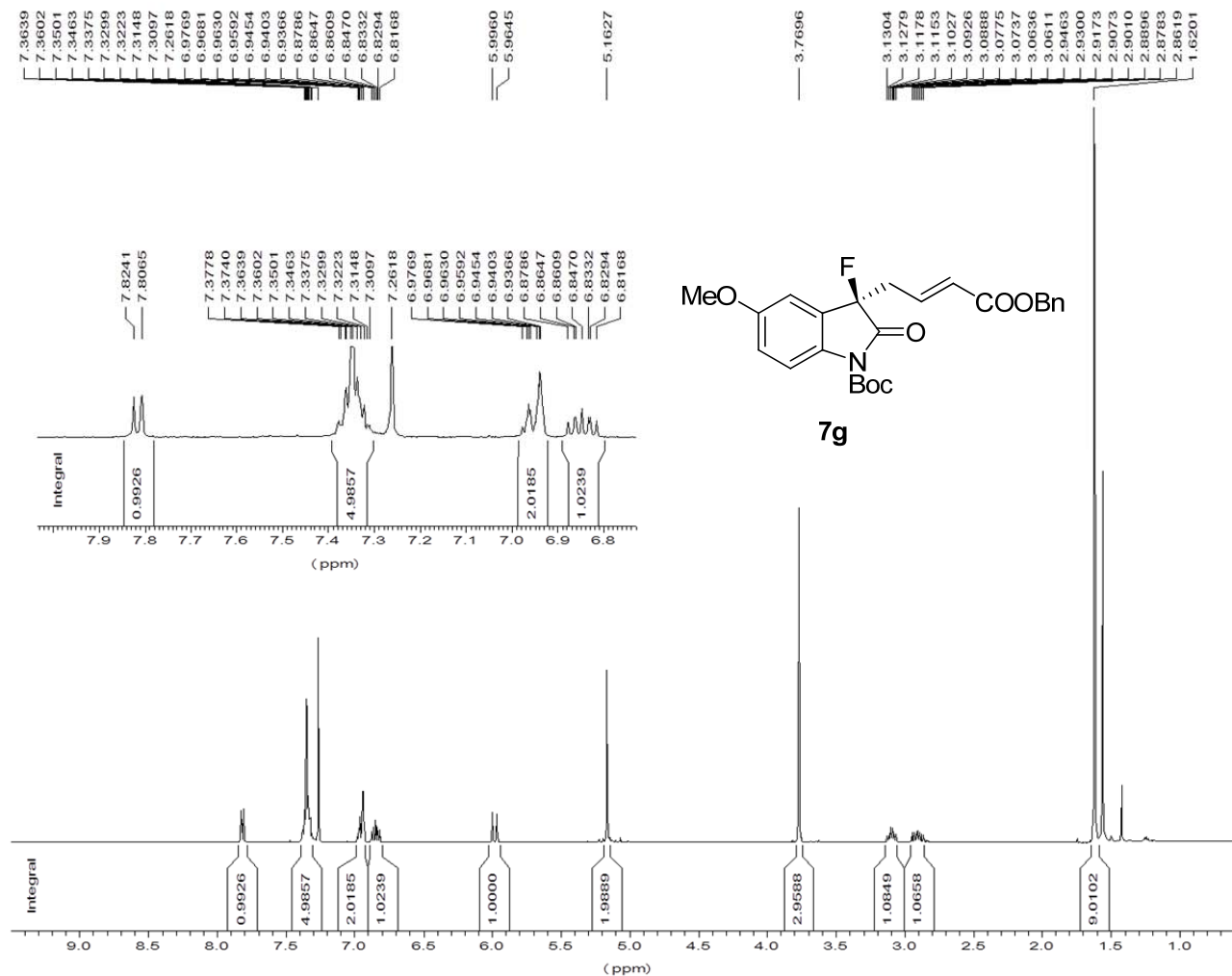
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

1H AMX500

wtl-1036

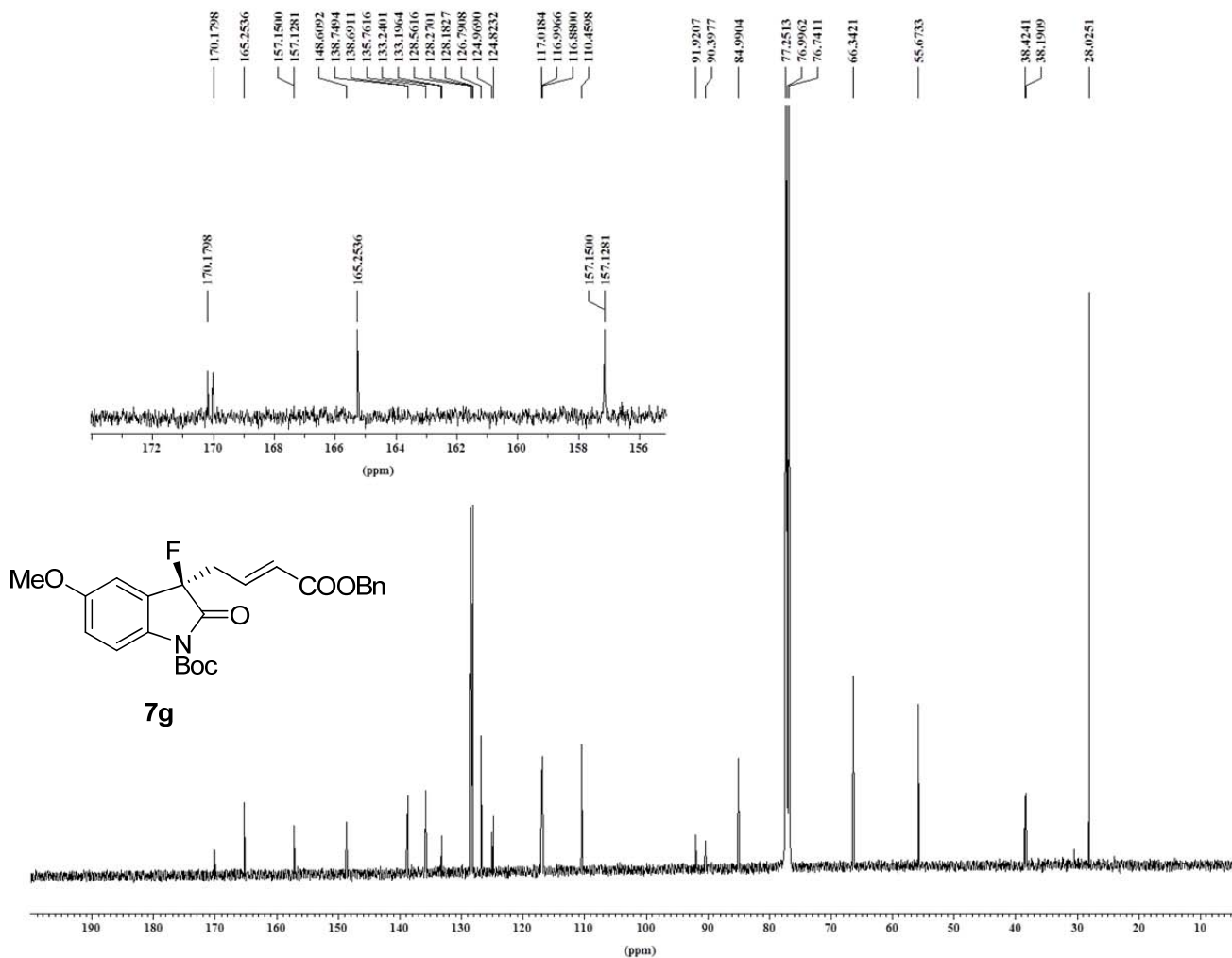


*** Current Data Parameters ***

NAME : wtl-1028
 EXPNO : 1
 PROCNO : 1
 *** Acquisition Parameters ***
 DS : 0
 INSTRUM : spect
 LOCNUC : 2H
 NS : 41
 NUCLEUS : off
 O1 : 3088.51 Hz
 PULPROG : zg30
 SFO1 : 500.1330885 MHz
 SOLVENT : CDCl3
 SW : 20.6557 ppm
 TD : 32768
 TE : 296.9 K
 *** Processing Parameters ***
 LB : 0.30 Hz
 OFFSET : 16.476 ppm
 SI : 16384
 *** 1D NMR Plot Parameters ***
 NUCLEUS : off

¹³C AMX500

wtl-1036



*** Current Data Parameters ***

NAME : wtl-1101

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 18299

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 297.9 K

*** Processing Parameters ***

LB : 1.00 Hz

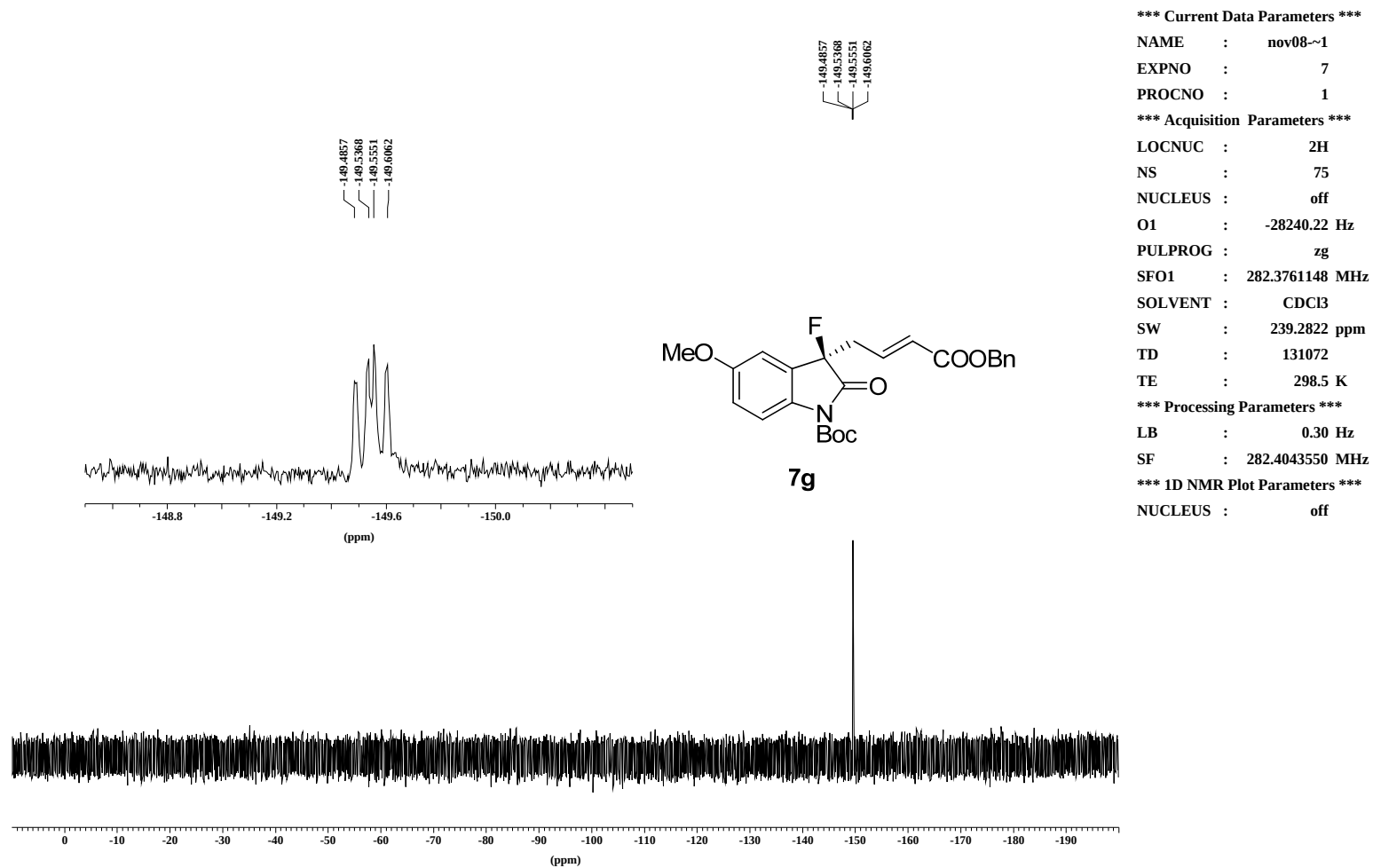
SF : 125.7577916 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

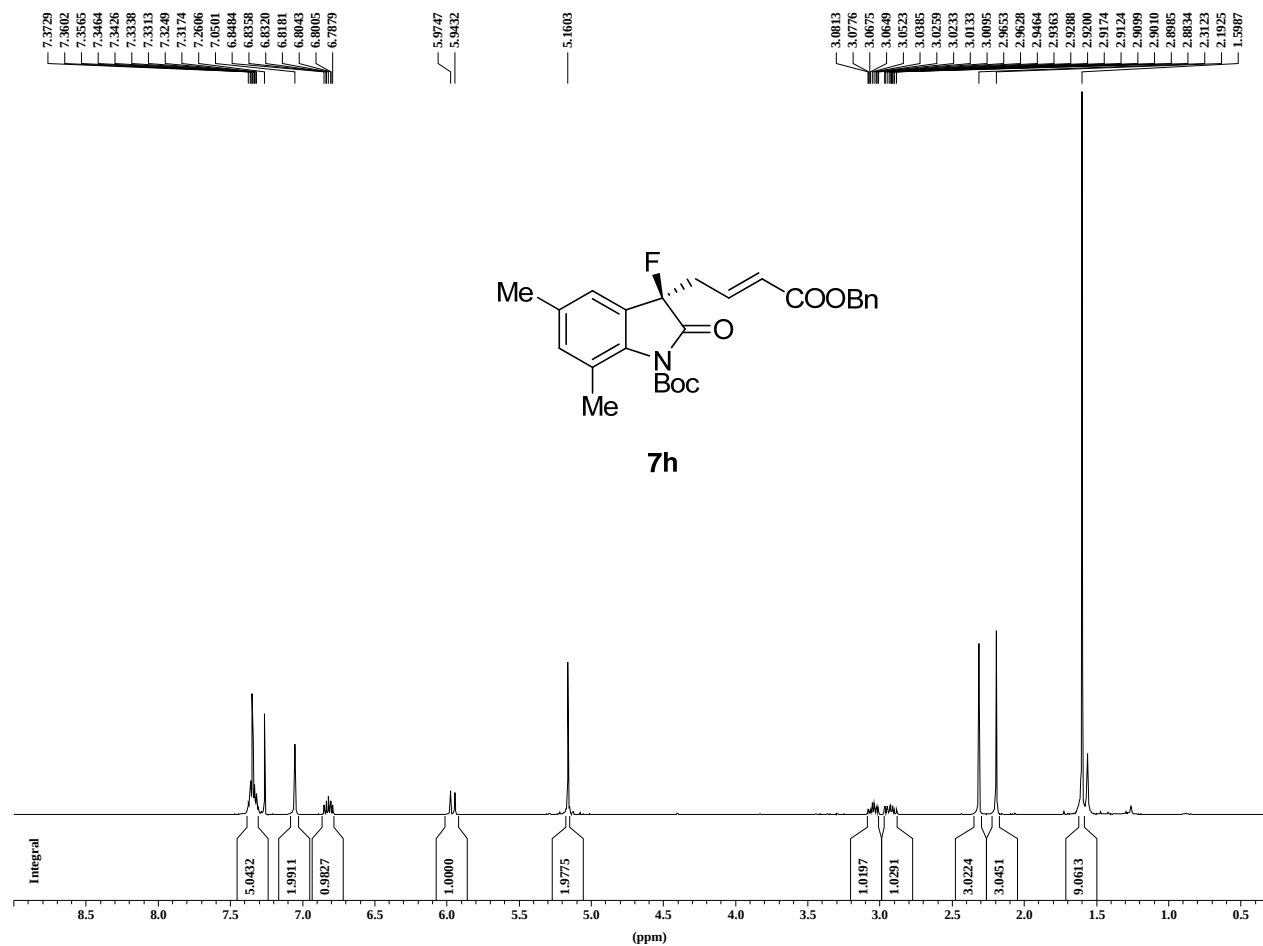
F19(no decoupled)

wtl-1036



1H AMX500

wtl-1041



*** Current Data Parameters ***

NAME : wtl-1105
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 38
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 300.1 K

*** Processing Parameters ***

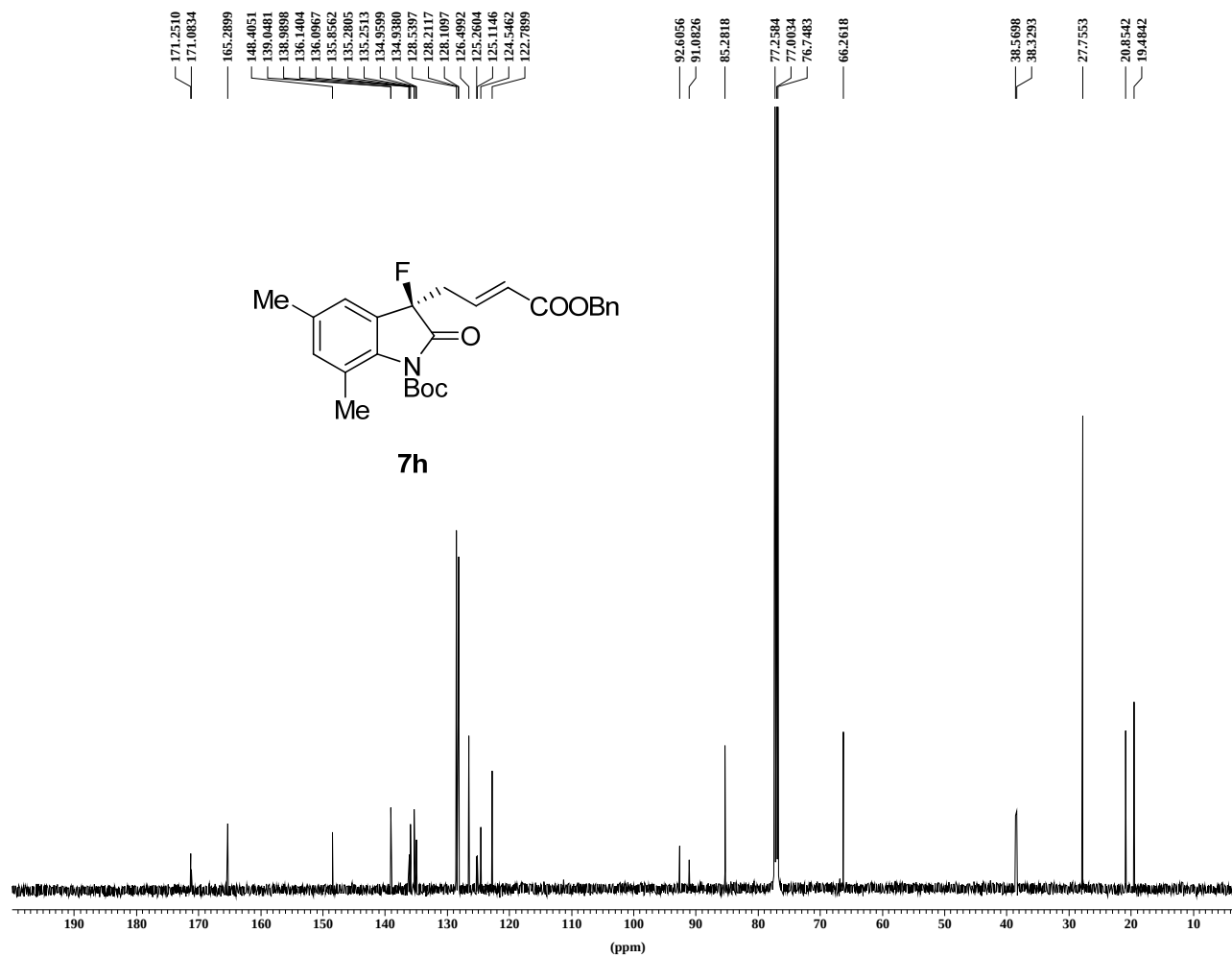
LB : 0.30 Hz
SF : 500.1300134 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C AMX500

wtl-1041



*** Current Data Parameters ***

NAME : wtl-1108

EXPNO : 3

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 3932

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl₃

SW : 238.7675 ppm

TD : 65536

TE : 300.1 K

*** Processing Parameters ***

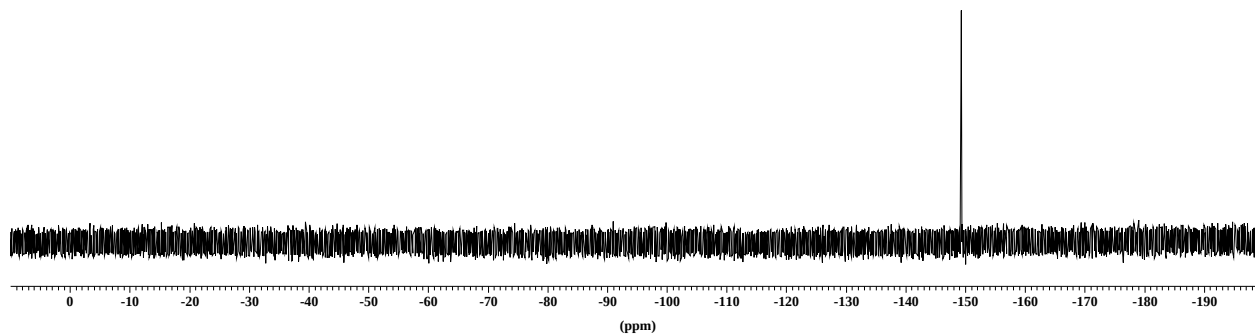
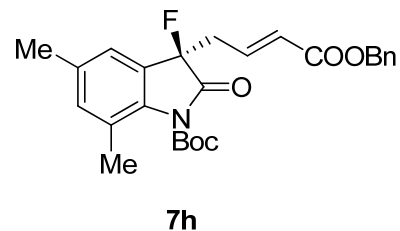
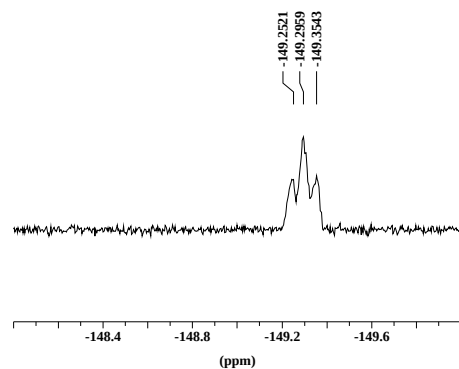
LB : 1.00 Hz

SF : 125.7577906 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)
wtl-1041



*** Current Data Parameters ***

NAME : nov08~1
EXPNO : 1
PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H
NS : 68
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl3
SW : 239.2822 ppm
TD : 131072
TE : 298.6 K

*** Processing Parameters ***

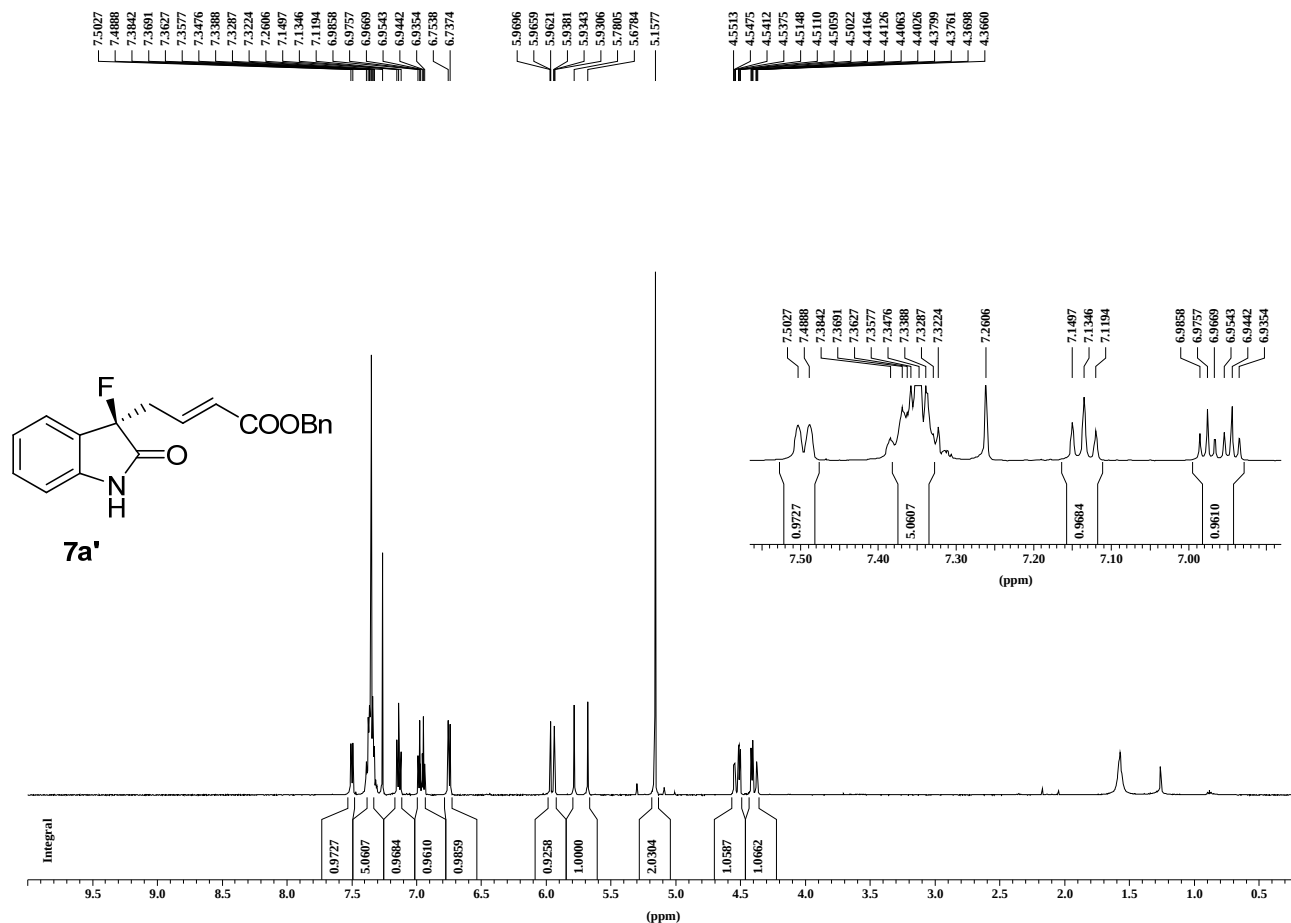
LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

1H AMX500

wtl-1056



*** Current Data Parameters ***

NAME : wtl-1125
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 26
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 299.3 K

*** Processing Parameters ***

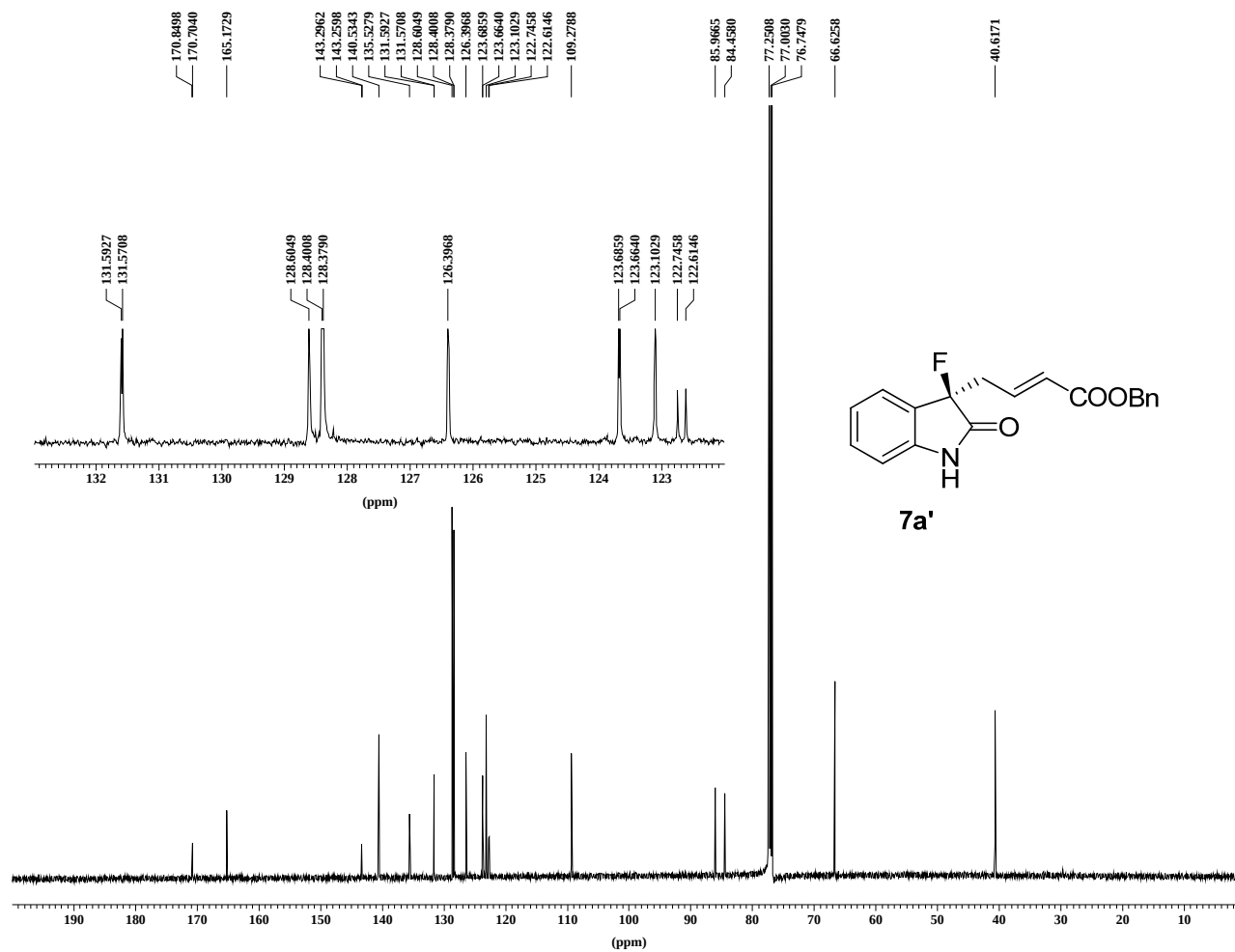
LB : 0.30 Hz
SF : 500.1300134 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C AMX500

wtl-1056



*** Current Data Parameters ***

NAME : wtl-1125

EXPNO : 4

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 12100

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 299.2 K

*** Processing Parameters ***

LB : 1.00 Hz

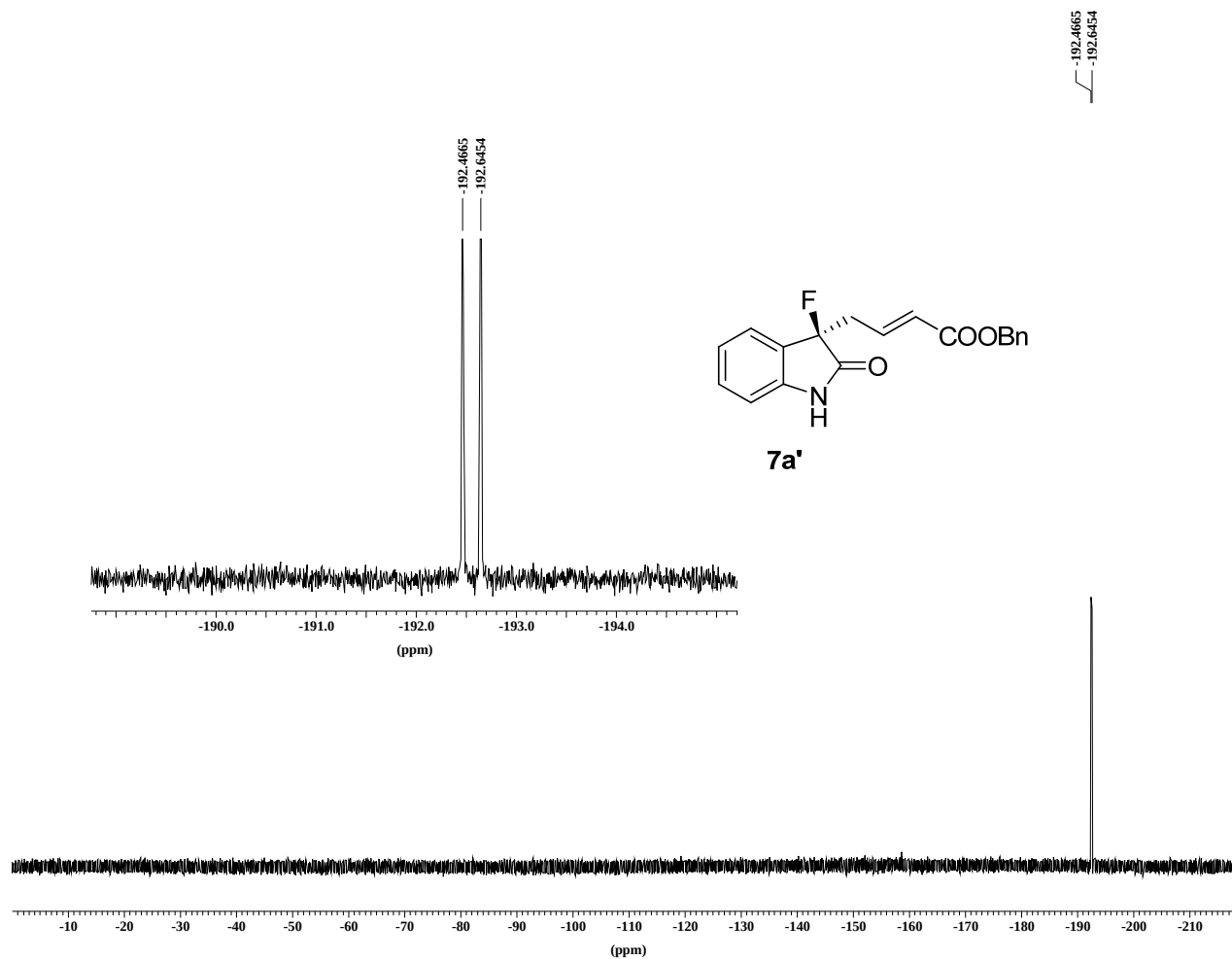
SF : 125.7577907 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)

wtl-1056



*** Current Data Parameters ***

NAME : nov24wtl
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 56
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl3
SW : 239.2822 ppm
TD : 131072
TE : 299.3 K

*** Processing Parameters ***

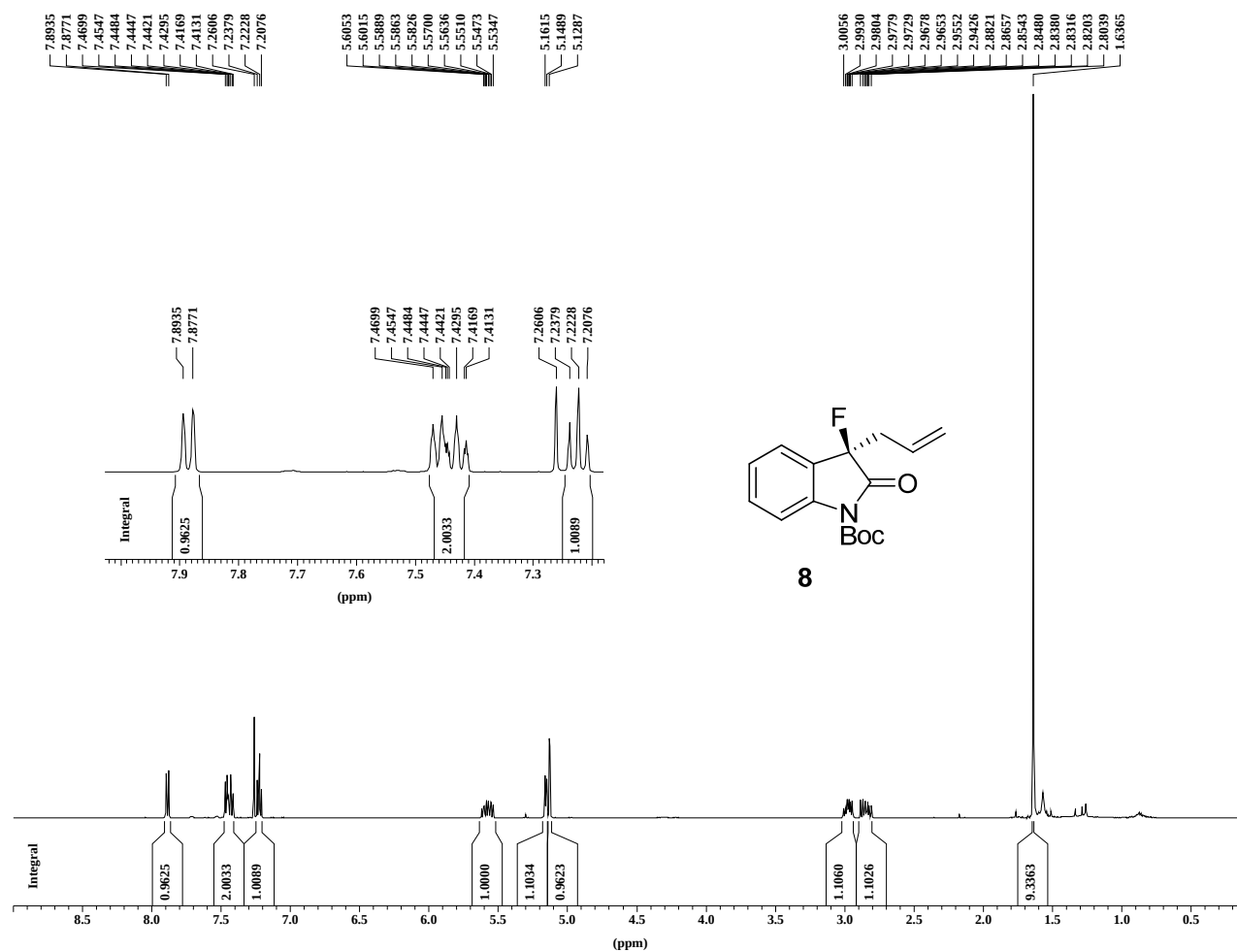
LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹H AMX500

wtl-1057-2



*** Current Data Parameters ***

NAME : wtl-1125
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 30
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 298.8 K

*** Processing Parameters ***

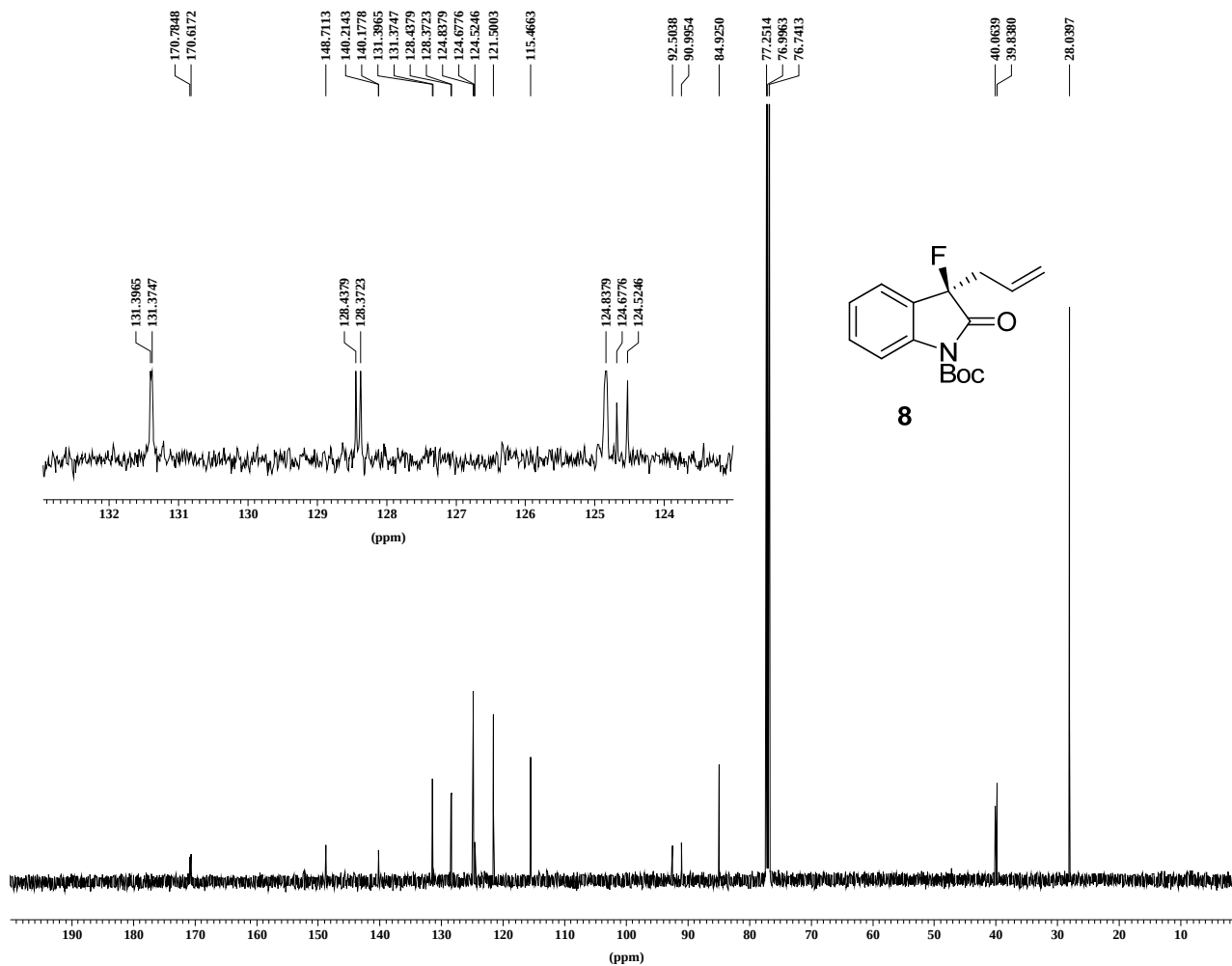
LB : 0.30 Hz
SF : 500.1300134 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

¹³C AMX500

wtl-1057-2



*** Current Data Parameters ***

NAME : wtl-1125
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 766
NUCLEUS : off
O1 : 13204.57 Hz
PULPROG : zgpg30
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
SW : 238.7675 ppm
TD : 65536
TE : 299.5 K

*** Processing Parameters ***

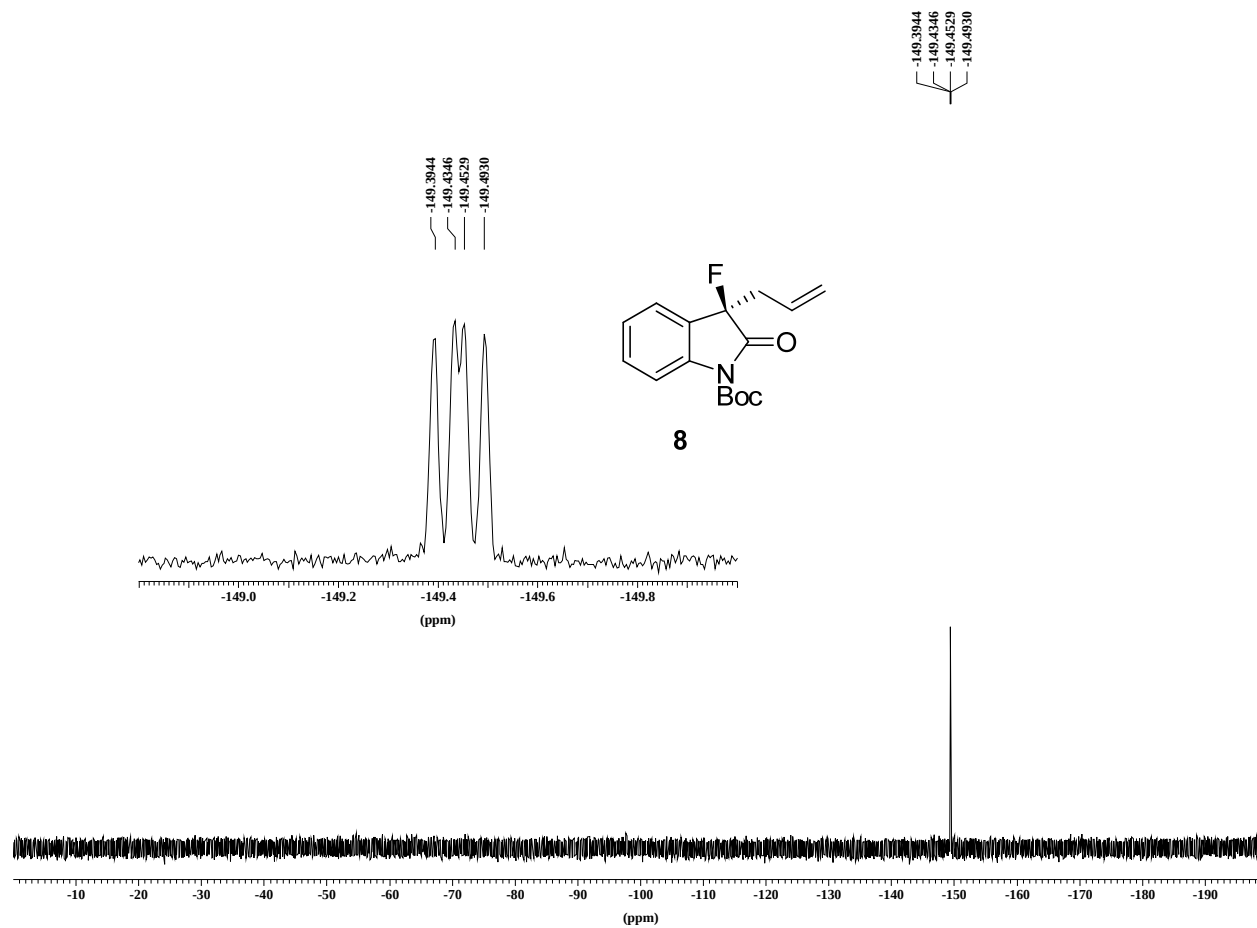
LB : 1.00 Hz
SF : 125.7577906 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

F19(no decoupled)

wtl-1057-2



*** Current Data Parameters ***

NAME : nov24wtl
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 204
NUCLEUS : off
O1 : -28240.22 Hz
PULPROG : zg
SFO1 : 282.3761148 MHz
SOLVENT : CDCl3
SW : 239.2822 ppm
TD : 131072
TE : 299.3 K

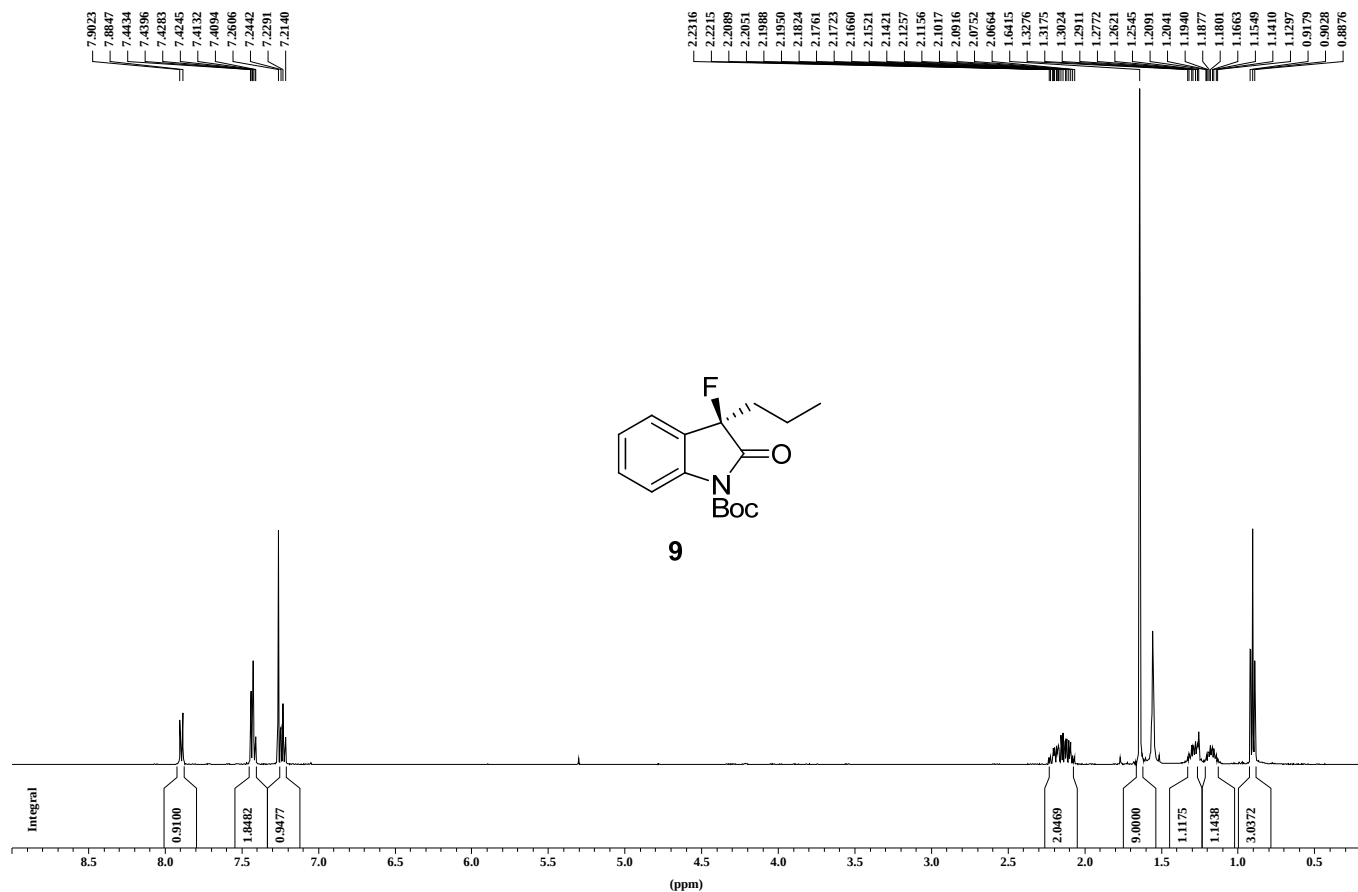
*** Processing Parameters ***

LB : 0.30 Hz
SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off

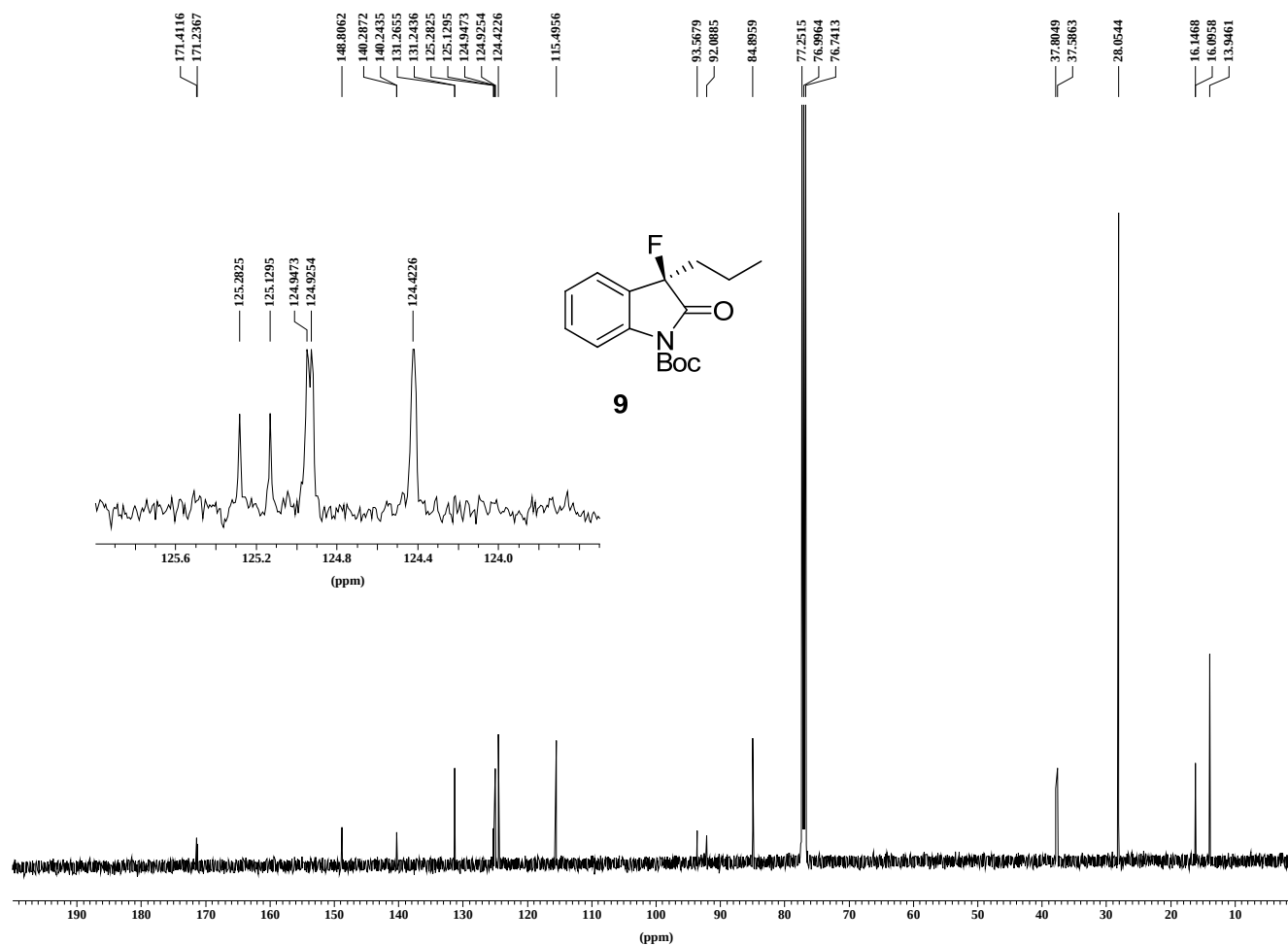
¹H AMX500
wtl-1057-3(a)



*** Current Data Parameters ***
NAME : wtl-1127
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
LOCNUC : 2H
NS : 29
NUCLEUS : off
O1 : 3088.51 Hz
PULPROG : zg30
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
SW : 20.6557 ppm
TD : 32768
TE : 298.8 K
*** Processing Parameters ***
LB : 0.30 Hz
SF : 500.1300134 MHz
*** 1D NMR Plot Parameters ***
NUCLEUS : off

¹³C AMX500

wtl-1057-3(a)



***** Current Data Parameters *****

NAME : wtl-1129

EXPNO : 1

PROCNO : 1

***** Acquisition Parameters *****

LOCNUC : 2H

NS : 3660

NUCLEUS : off

O1 : 13204.57 Hz

PULPROG : zgpg30

SFO1 : 125.7709936 MHz

SOLVENT : CDCl3

SW : 238.7675 ppm

TD : 65536

TE : 299.6 K

***** Processing Parameters *****

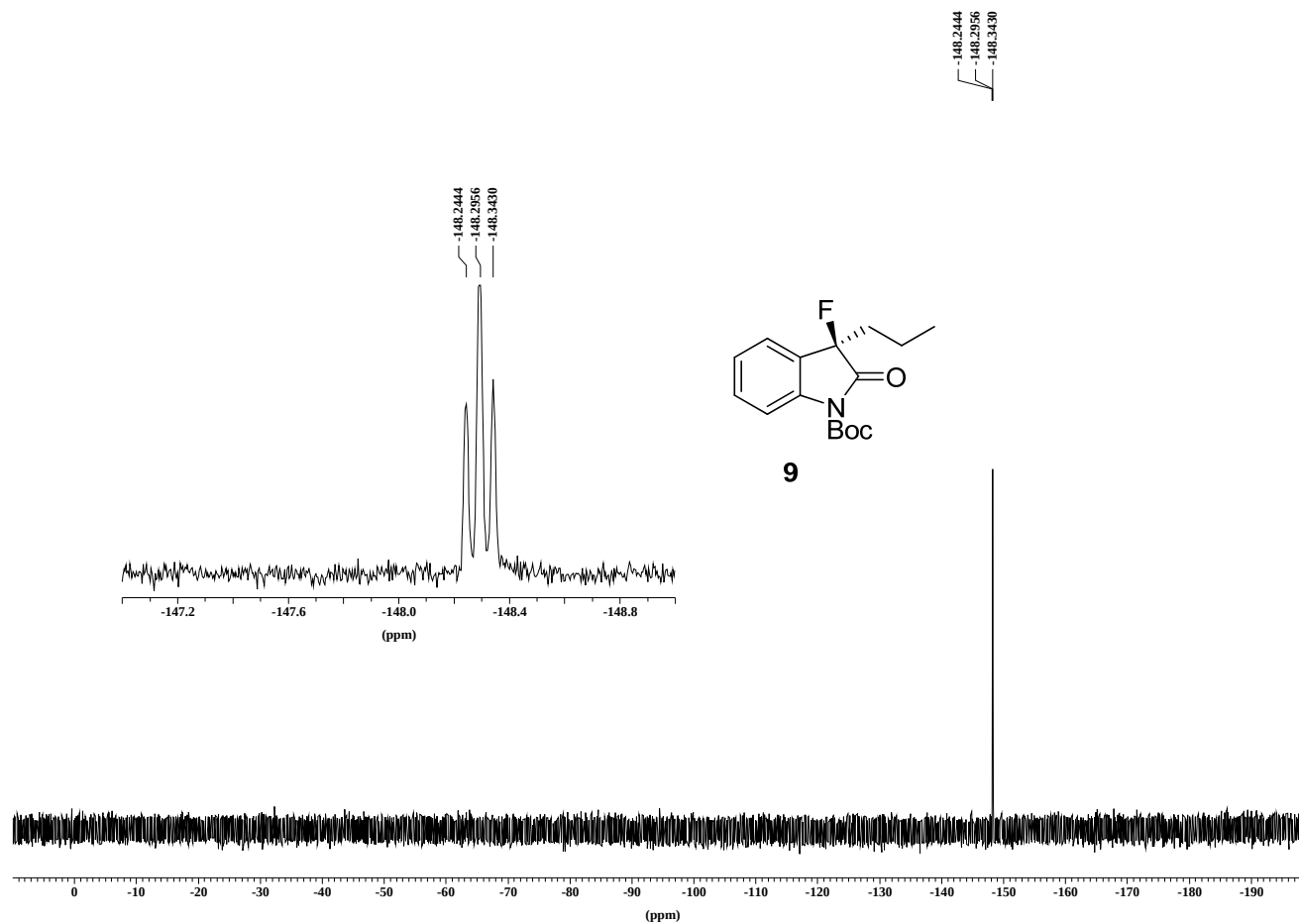
LB : 1.00 Hz

SF : 125.7577906 MHz

***** 1D NMR Plot Parameters *****

NUCLEUS : off

F19(no decoupled)
wtl-1057-3(a)



*** Current Data Parameters ***

NAME : nov27wtl

EXPNO : 1

PROCNO : 1

*** Acquisition Parameters ***

LOCNUC : 2H

NS : 93

NUCLEUS : off

O1 : -28240.22 Hz

PULPROG : zg

SFO1 : 282.3761148 MHz

SOLVENT : CDCl3

SW : 239.2822 ppm

TD : 131072

TE : 298.9 K

*** Processing Parameters ***

LB : 0.30 Hz

SF : 282.4043550 MHz

*** 1D NMR Plot Parameters ***

NUCLEUS : off