Supporting Information

Asymmetric synthesis of chiral 1,2-oxazinane and hexahydropyridazin spirocyclic scaffolds by organocatalytic [4+2] cycloaddition

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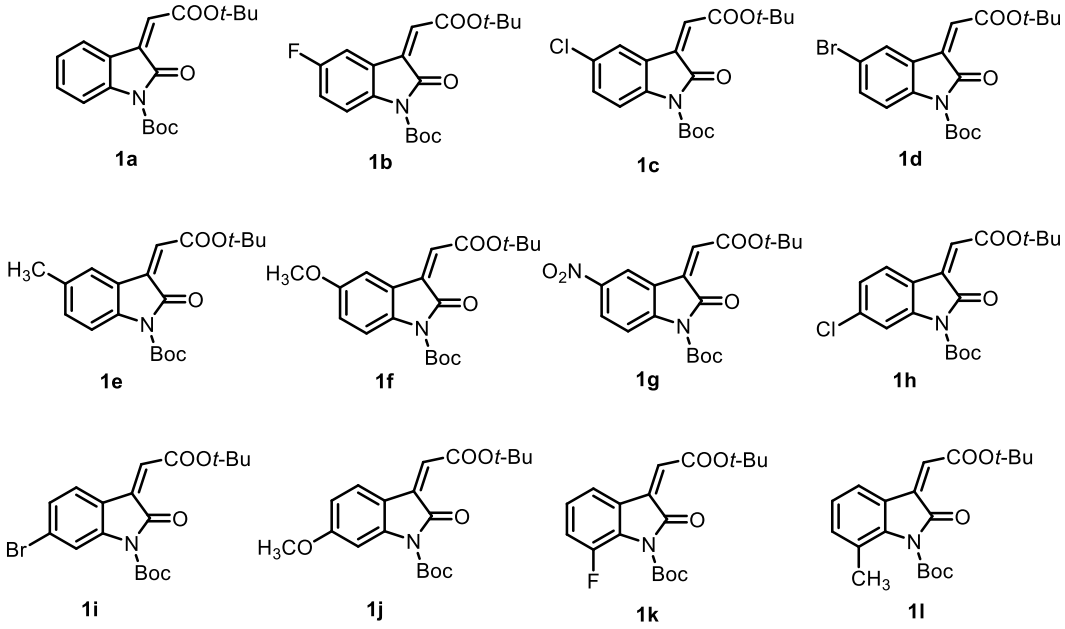
1. General Information

All reagents and all solvents were obtained from commercial suppliers and used without further purification except as indicated below. The silica gel (300-400 mesh) was used for column chromatography and TLC inspections were on silica gel GF 254 plates (0.25 mm layer thickness). NMR spectra were all recorded on a Bruker AM400 (400 MHz) spectrometer. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-d (δ 77.16) for ^{13}C NMR. Enantioselectivities were determined by high-performance liquid chromatography (HPLC) with an Aglilent-1260 intelligent uv/vis detector (λ = 214 nm, 220nm or 254 nm) and a Daicel IA. Optical rotations were measured in CH_2Cl_2 or $CHCl_3$ on a Pekin-Elmer 241MC automatic polarimeter. HRESIMS were recorded on an Agilent 6210 TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive or negative ion mode.

2. General procedure

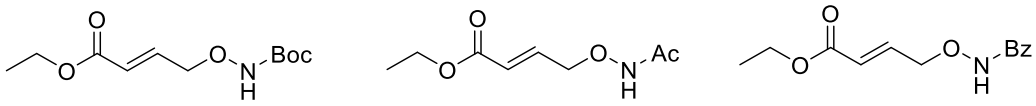
General procedure A: the synthesis of methyleneindolinones 1a-m:

Methyleneindolinones 1 were prepared according to the following representative procedure.[2]



General procedure B: the synthesis of *γ*-aminooxy-*α,β*-unsaturated ester 2a-c:

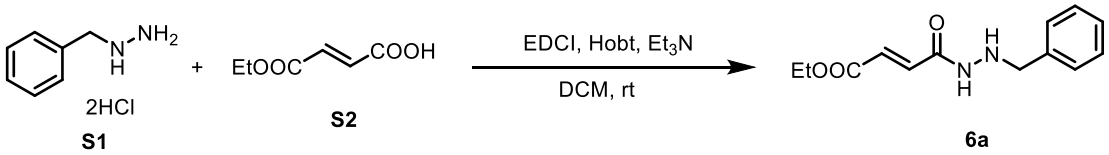
***γ*-aminooxy-*α,β*-unsaturated ester 2** were prepared according to the following representative procedure.[1]



2a **2b** **2c**

General procedure C: the synthesis of fumaric acid monoester monoamide 6a–c:

Fumaric acid monoester monoamide 6 were prepared according to the following representative methods.

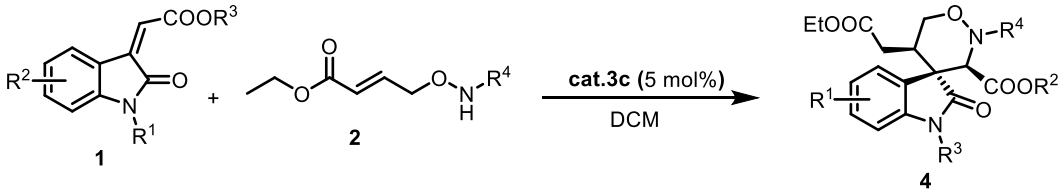


S1 **S2** **6a**

6b **6c**

To a solution of **S2** (10.0 mmol) in DCM (25 mL) was added EDCI (11.0mmol) and Hobt(11mmol) under ice bath. After 30 min, **S1**(10.0 mmol) was added into the solution, followed by the addition of Et_3N(30.0 mmol). Then the reaction was warmed to room temperature and stirred overnight. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with DCM (30 mL x 2). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired product **6a**.

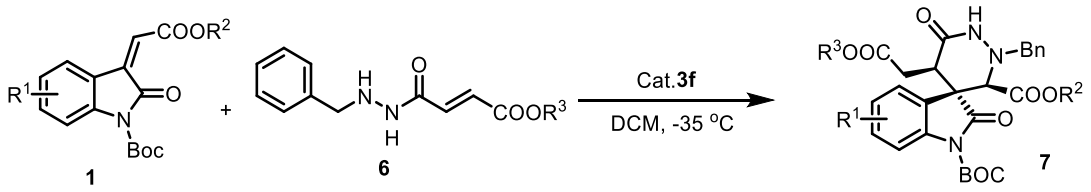
General procedure D: the synthesis of Chiral 1,2-oxazinane Spirocyclic 4:



1 **2** **4**

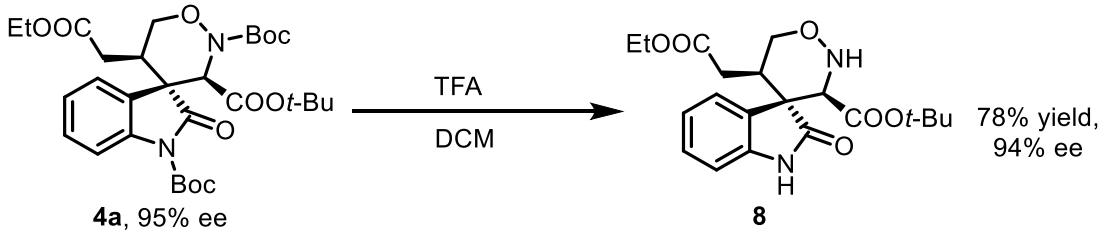
A solution of **2** (0.20 mmol), **1** (0.22 mmol) and Cat **3c** (0.05 mmol) in CH_2Cl_2 (0.4 mL) was stirred at room temperature (25 °C) for 48 h. The mixture was concentrated under reduced pressure and the residue was purified via flash chromatograph on silica gel (EtOAc/Petrol Ether = 1/3, v/v as eluent) to afford the desired product **4**.

General procedure E: the synthesis of Chiral Hexahydropyridazin Spirocycle 7:

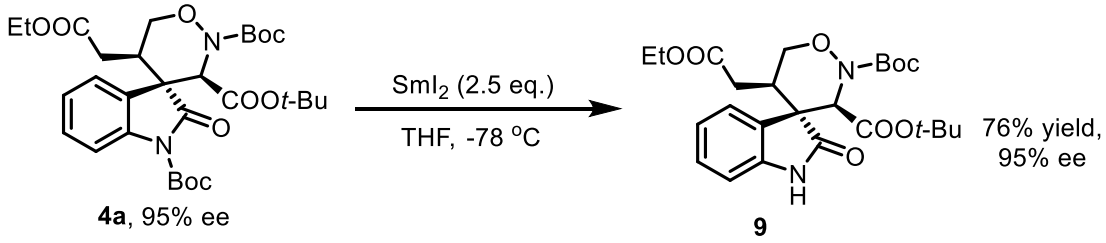


A solution of **6** (0.20 mmol), **1** (0.24 mmol) and Cat.**3f** (0.03 mmol) in CH_2Cl_2 (0.2 mL) was stirred at -35 °C for 10-14d. The mixture was concentrated under reduced pressure and the residue was purified via flash chromatograph on silica gel (EtOAc/Petrol Ether = 1/3, v/v as eluent) to afford the desired product **7**.

Transformations of product 4a:

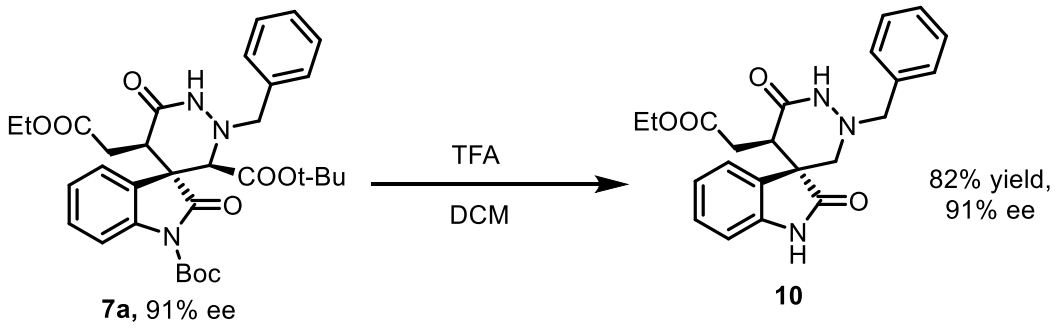


To a solution of **4a** (0.2 mmol) in DCM (2.0 mL) was added TFA (2.0 mmol). The resultant reaction solution was allowed to stir 2h at room temperature before the reaction was quenched by the addition of saturated aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired product **8**.



To a stirring solution of **4a** (0.1 mmol) in degassed dry methanol (1 mL) was added samarium iodide (0.1 M in THF, 2.5 equiv.) slowly at -78 °C. After stirring for 30 min, the solvent was warmed to room temperature, and saturated aqueous $Na_2S_2O_3$ (10 mL) were added. The aqueous layer was extracted with EA (10 ml x 3), and the organic layers were combined and dried over anhydrous sodium sulfate (Na_2SO_4). After filtration and concentration, the obtained crude product was purified by column chromatography (PE/EtOAc = 3/1) to afford **9**.

Transformations of product 7a:



7a, 91% ee

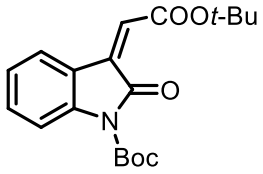
10

To a solution of **7a** (0.2 mmol) in DCM (2.0 mL) was added TFA (1 ml). The resultant reaction solution was allowed to stir overnight at room temperature before the reaction was quenched by the addition of saturated aqueous Na_2CO_3 and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic fractions were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 1/1) to afford the desired product **10**.

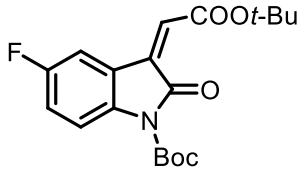
References:

1. Drelich, P.; Moczulski, M.; Albrecht, Ł. *Org. Lett.* **2017***, 19,* 3143−3146.
2. Tang, Q-G.; Cai, S-L.; Wang, C-C.; Lin, G-Q.; Sun, X-W. *Org. Lett.* **2020**, *22*, 3351–3355.

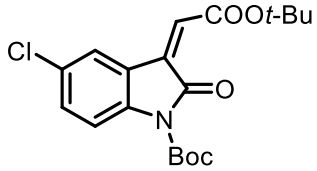
3. Analytical data of the products



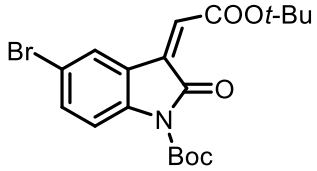
1a, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.25 (m, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 6.0 Hz, 2H), 1.59 (m, 18H).



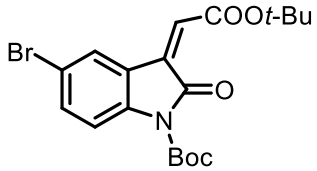
1b, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.0 Hz, 1H), 7.89 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.13 (s, 1H), 6.90 (s, 1H), 1.65 (s, 9H), 1.57 (s, 9H).



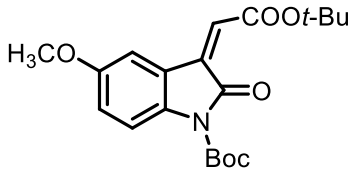
1c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.89 (s, 1H), 1.64 (s, 9H), 1.58 (s, 9H).



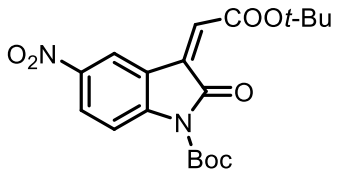
1d, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 6.88 (s, 1H), 1.70 – 1.55 (m, 18H).



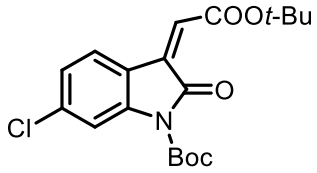
1e, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.17 (m, 1H), 6.84 (s, 1H), 2.38 (s, 3H), 1.65 (s, 9H), 1.58 (s, 9H).



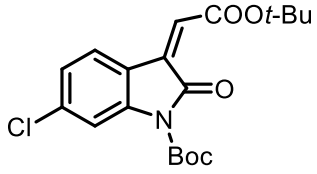
1f, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.86 (s, 1H), 3.85 (s, 3H), 1.68 – 1.54 (m, 18H).



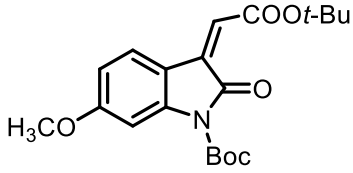
1g, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.34 (d, *J* = 9.0 Hz, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.00 (s, 1H), 1.67 – 1.59 (m, 18H).



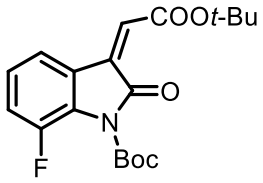
1h, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.86 (s, 1H), 1.65 (s, 9H), 1.57 (s, 9H).



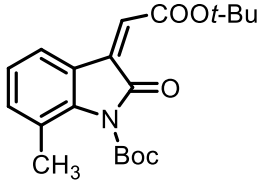
1i, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.14 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 1.65 (s, 9H), 1.58 (s, 9H).



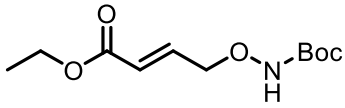
1j, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 6.77 – 6.68 (m, 2H), 3.90 (s, 3H), 1.65 (s, 9H), 1.58 (s, 9H).



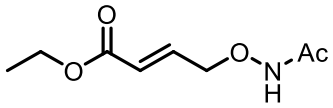
1k, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.0 Hz, 1H), , 7.18 (d, *J* = 7.8 Hz, 2H), 6.92 (s, 1H), 1.65 – 1.54 (m, 18H).



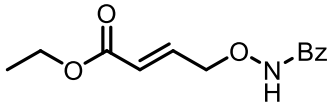
1l, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.17 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 2.23 (s, 3H), 1.67 – 1.56 (m, 18H).



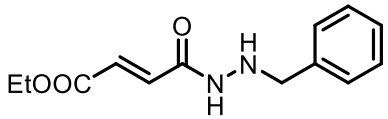
2a, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.99 – 6.95 (m, 1H), 6.06 (d, *J* = 15.8 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.49 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H).



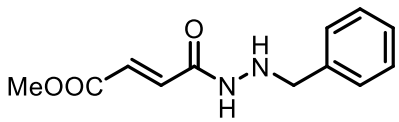
2b, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 6.87 (dt, *J* = 15.8, 5.2 Hz, 1H), 6.00 (d, *J* = 15.8 Hz, 1H), 4.49 (d, *J* = 4.4 Hz, 2H), 4.12 (dd, *J* = 14.2, 7.2 Hz, 2H), 1.86 (s, 3H), 1.37 – 1.04 (m, 3H).



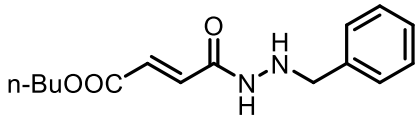
2c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.77 (dd, *J* = 24.2, 7.4 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 6.97 (dt, *J* = 15.8, 5.4 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 4.64 (dd, *J* = 5.4, 1.2 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.36 – 1.18 (m, 3H).



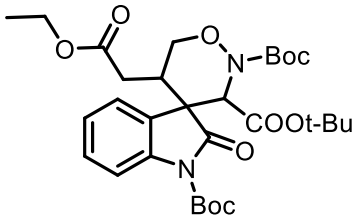
6a, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.11 (m, 5H), 6.93 – 6.71 (m, 2H), 4.36 – 4.14 (m, 2H), 4.04 (d, *J* = 8.8 Hz, 2H), 1.50 – 1.19 (m, 3H).



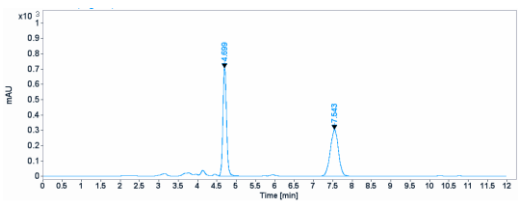
6b, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 7.04 – 6.76 (m, 2H), 4.05 (s, 2H), 3.82 (s, 2H).



6c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 6.84 (dt, *J* = 15.4, 11.6 Hz, 2H), 4.25 – 4.18 (m, 2H), 4.05 (s, 2H), 1.77 – 1.59 (m, 2H), 1.55 – 1.34 (m, 2H), 1.10 – 0.90 (m, 3H).



4a, yellow oil, 106 mg, 90% yield, >20:1 dr, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 8.03 min, t_{minor} = 4.71 min); $[\alpha]_D^{25}$ = -2.4 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 4.98 (s, 1H), 4.70 (t, *J* = 9.2, 1H), 4.07-3.94 (m, 2H), 3.62 (t, *J* = 10.0, 1H), 3.07-2.92 (m, 1H), 2.15 (dd, *J* = 16.0, 2.4 Hz, 1H), 1.68-1.57 (m, 10H), 1.46 (s, 9H), 1.16 (t, *J* = 7.2, 3H), 0.90 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 170.0, 165.6, 154.2, 148.7, 140.9, 129.4, 127.3, 125.2, 124.6, 114.8, 85.0, 82.4, 82.3, 70.6, 65.7, 61.0, 53.1, 36.7, 33.4, 28.1, 28.1, 28.0, 26.9, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{42}N_2O_{10}$ $[M+Na]^+$ 613.2732, found 613.2731.



Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
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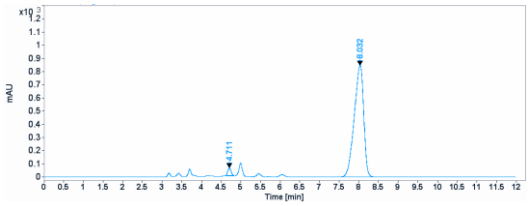
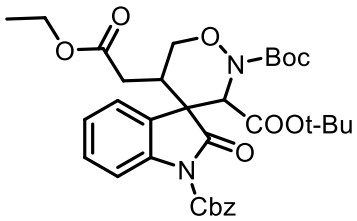
7.543	0.231	4422.288	301.693	48.9662
	Sum	9031.3125		



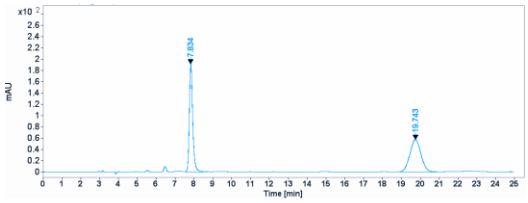
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.711	0.099	339.253	57.160	2.3423
8.032	0.261	14144.621	845.081	97.6577
	Sum	14483.8740		



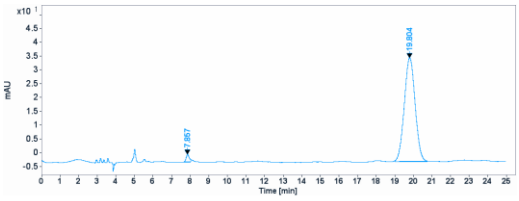
4b, yellow oil, 66 mg, 53% yield, >20:1 dr, 96% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 18.80 min, t_{minor} = 7.86 min); $[\alpha]_D^{25}$ = -0.5 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.55-7.46 (m, 2H), 7.44-7.31 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 5.46 (dd, *J* = 21.6, 12.0 Hz, 2H), 5.00 (s, 1H), 4.71 (t, *J* = 8.8 Hz, 1H), 4.07-3,90 (m, 2H), 3.63 (t, *J* = 9.6 Hz, 1H), 3.09-2.97 (m, 1H), 2.18-2.07 (m, 1H), 1.67-1.57 (m, 1H), 1.48 (s, 10H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 170.0, 165.5, 154.2,

150.4, 140.5, 134.7, 129.6, 128.7, 128.7, 128.3, 127.4, 125.6, 124.7, 115.0, 82.6, 82.5, 70.6, 69.1, 65.7, 61.0, 53.3, 36.9, 33.4, 28.2, 26.9, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{33}H_{40}N_2O_{10}$ $[M+Na]^+$ 647.2575, found 647.2572.



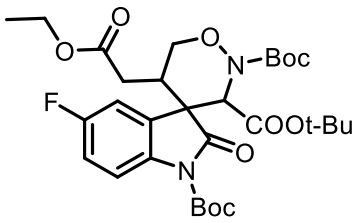
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.834	0.192	2395.876	190.899	50.7317
19.743	0.633	2326.765	56.961	49.2683
	Sum	4722.6409		

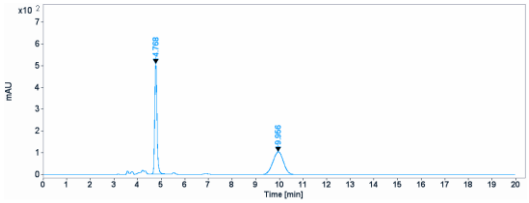


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.857	0.206	33.435	2.709	2.1570
19.804	0.627	1516.635	37.542	97.8430
	Sum	1550.0696		

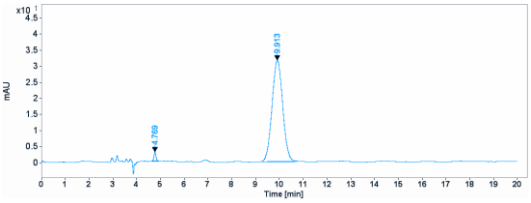


4c, yellow oil, 115 mg, 95% yield, >20:1 dr, 96% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 9.91 min, t_{minor} = 4.77 min); $[\alpha]_D^{25}$ = -0.5 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 8.8 Hz, 1H), 4.94 (s, 1H), 4.68 (t, *J* = 8.8 Hz, 1H), 4.00 (q, *J* = 6.8 Hz, 2H), 3.58 (t, *J* = 10.0 Hz, 1H), 2.97 (q, *J* = 9.6, 9.2 Hz, 1H), 2.19-2.06 (m, 1H), 1.64-1.55 (m, 10H), 1.44 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 169.8, 165.3, 160.2 (d, *J* = 243.6 Hz), 154.0, 148.6, 136.8 (d, *J* = 2.8 Hz), 126.4 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 7.8 Hz), 115.9 (d, *J* = 22.8 Hz), 115.0 (d, *J* = 25.6 Hz), 85.2, 82.6, 82.5, 70.6, 65.5, 61.0, 53.4, 36.7, 33.3, 28.1, 28.0, 26.9, 14.0 ppm; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.4 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}FN_2O_{10}$ $[M+Na]^+$ 631.2637, found 631.2648.



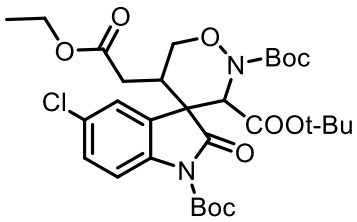
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.768	0.110	3325.345	505.807	50.3736
9.956	0.495	3276.025	104.233	49.6264
	Sum	6601.3708		

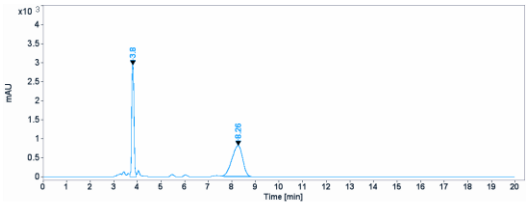


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.769	0.094	17.879	2.893	1.7872
9.913	0.480	982.522	31.512	98.2128
	Sum	1000.4018		

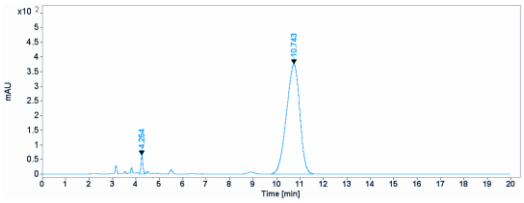


4d, yellow oil, 113 mg, 90% yield, >20:1 dr, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 10.74 min, t_{minor} = 4.25 min); $[\alpha]_D^{25}$ = 2.0 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.60 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 4.94 (s, 1H), 4.68 (t, *J* = 8.8 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.59 (t, *J* = 10.0 Hz, 1H), 2.98 (q, *J* = 9.6 Hz, 1H), 2.17-2.06 (m, 1H), 1.66-1.57 (m, 10H), 1.45 (s, 9H), 1.16 (t, *J* = 6.8 Hz, 3H), 0.94 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 169.8, 165.4, 154.1, 148.5, 139.5, 131.0, 129.5, 127.3, 126.5, 116.1, 85.4, 82.7, 82.5, 70.6, 65.5, 61.1, 53.3, 36.8, 33.3, 28.2, 28.0, 27.0, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}ClN_2O_{10}$ $[M+Na]^+$ 647.2342, found 647.2331.



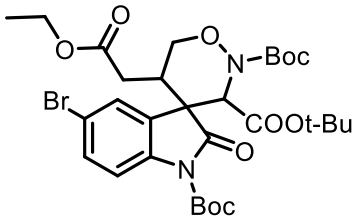
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
3.800	0.105	19381.105	2936.171	43.2374
8.260	0.523	25443.736	811.335	56.7626
	Sum	44824.8418		

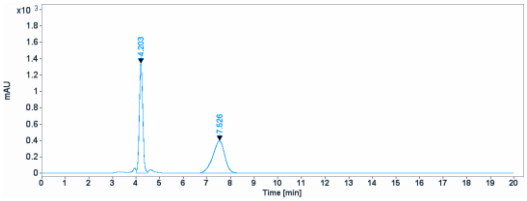


Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.254	0.091	383.163	64.461	2.5262
10.743	0.619	14784.509	374.467	97.4738
	Sum	15167.6718		

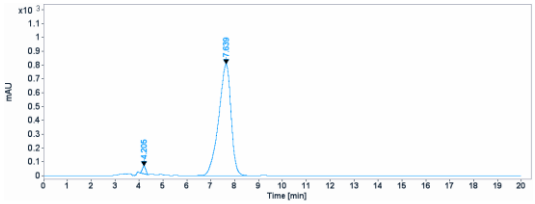


4e, yellow oil, 124 mg, 93% yield, >20:1 dr, 96% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 7.64 min, t_{minor} = 4.21 min); $[\alpha]_D^{25}$ = 2.9 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.8 Hz, 1H), 7.72 (s, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 4.93 (s, 1H), 4.67 (t, *J* = 9.2 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.58 (t, *J* = 10.0 Hz, 1H), 3.04-2.87 (m, 1H), 2.17-2.03 (m, 1H), 1.67-1.55 (m, 10H), 1.44 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 169.8, 165.3, 154.0, 148.4, 139.9, 132.4, 130.0, 126.8, 118.4, 1165, 85.4, 82.7, 82.5, 77.4, 77.1, 76.8, 70.5, 65.5, 61.1, 53.2, 36.7, 33.3, 28.1, 27.9, 26.9, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}BrN_2O_{10}$ $[M+Na]^+$ 691.1837; 693.1818, found 691.1826; 693.1812.



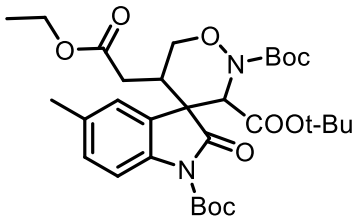
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.203	0.164	13777.761	1343.483	49.7907
7.526	0.532	13893.616	395.197	50.2093
	Sum	27671.3770		

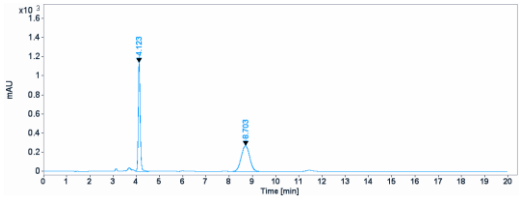


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.205	0.160	532.132	55.358	1.8021
7.639	0.546	28996.404	805.686	98.1979
	Sum	29528.5359		

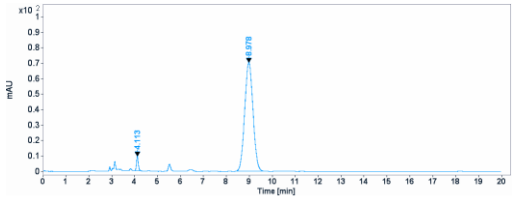


4f, yellow oil, 85 mg, 70% yield, >20:1 dr, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 8.98 min, t_{minor} = 4.11 min); $[\alpha]_D^{25}$ = -1.1 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0, 1H), 7.41 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 4.97 (s, 1H), 4.69 (t, *J* = 8.8, 1H), 4.10-3.94 (m, 2H), 3.63 (t, *J* = 10.0, 1H), 2.99 (q, *J* = 10.2 Hz, 1H), 2.27 (s, 3H), 2.19-2.10 (m, 1H), 1.63 (m, 10H), 1.46 (s, 9H), 1.17 (t, *J* = 7.2, 3H), 0.91 (s, *J* = 1.7 Hz, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 170.1, 165.6, 154.3, 148.7, 138.4, 135.0, 129.7, 127.7, 124.5, 114.6, 84.8, 82.3, 82.3, 70.6, 65.7, 60.9, 53.1, 36.6, 33.4, 28.1, 28.04, 28.00, 27.97, 26.9, 21.0, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{31}H_{44}N_2O_{10}$ $[M+Na]^+$ 627.2888, found 627.2883.



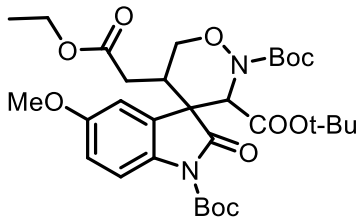
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.123	0.090	6670.075	1138.030	49.5278
6.703	0.402	6797.248	267.945	50.4722
	Sum	13467.3228		

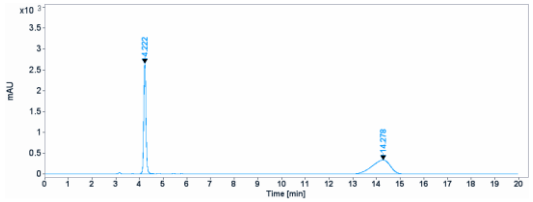


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.113	0.089	49.283	9.268	2.7015
6.978	0.395	1775.007	70.250	97.2985
	Sum	1824.2893		

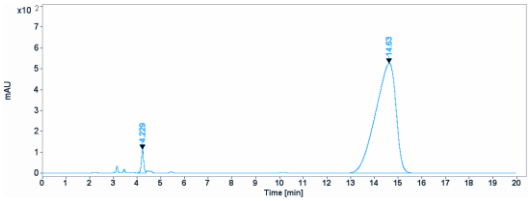


4g, yellow oil, 85 mg, 69% yield, >20:1 dr, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 14.63 min, t_{minor} = 4.23 min); $[\alpha]_D^{25}$ = 1.5 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 9.2 Hz, 1H), 7.18 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.98 (s, 1H), 4.70 (t, *J* = 8.8 Hz, 1H), 4.06-3.93 (m, 2H), 3.72 (s, 3H), 3.62 (t, *J* = 10.0 Hz, 1H), 2.97 (q, *J* = 10.0 Hz, 1H), 2.15 (dt, *J* = 16.0, 2.8 Hz, 1H), 1.67-1.57 (s, 10H), 1.46 (s, 9H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 170.1, 165.5, 157.5, 154.1, 148.7, 134.1, 125.8, 115.8, 115.0, 112.8, 84.8, 82.34, 82.27, 70.6, 65.5, 61.0, 55.9, 53.4, 36.6, 33.4, 28.1, 28.0, 26.9, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{31}H_{44}N_2O_{11}$ $[M+Na]^+$ 643.2837, found 643.2830.



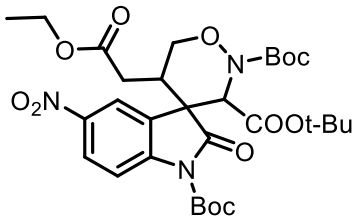
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.222	0.103	17568.924	2647.572	49.0033
14.278	0.856	18283.613	336.470	50.9967
	Sum	35852.5371		

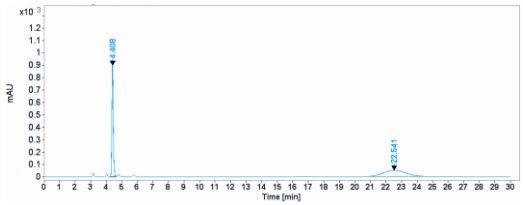


Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.229	0.100	746.724	111.939	2.3209
14.630	0.923	31427.014	525.687	97.6791
	Sum	32173.7379		

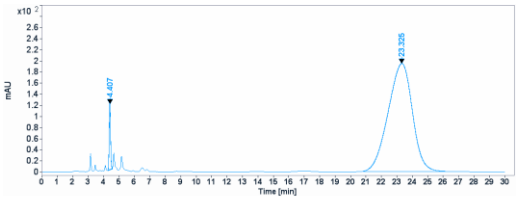


4h, yellow oil, 117 mg, 90% yield, >20:1 dr, 93% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 23.33 min, t_{minor} = 4.41 min); $[\alpha]_D^{25}$ = 5.3 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.28 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 9.2 Hz, 1H), 4.98 (s, 1H), 4.72 (t, *J* = 9.2 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.63 (t, *J* = 10.2 Hz, 1H), 3.12-2.93 (m, 1H), 2.10 (dd, *J* = 16.2, 3.6 Hz, 1H), 1.65-1.56 (m, 10H), 1.46 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 169.5, 165.2, 153.8, 148.2, 146.2, 145.1, 126.1, 125.8, 122.7, 115.1, 86.4, 83.0, 82.8, 77.4, 77.1, 76.8, 70.5, 65.4, 61.2, 53.2, 37.0, 33.2, 28.1, 28.0, 27.1, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}N_3O_{12}$ $[M+Na]^+$ 658.2582, found 658.2587.



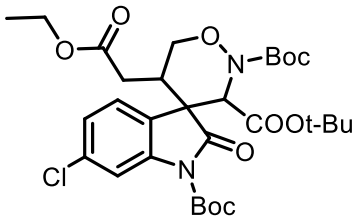
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.408	0.104	5603.733	894.319	50.9211
22.541	1.569	5400.999	50.688	49.0789
	Sum	11004.7319		



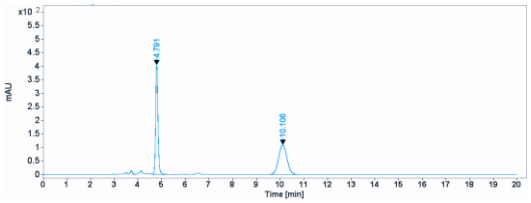
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.407	0.103	734.710	118.772	3.3453
23.325	1.686	21227.809	194.134	96.6547
	Sum	21962.5189		



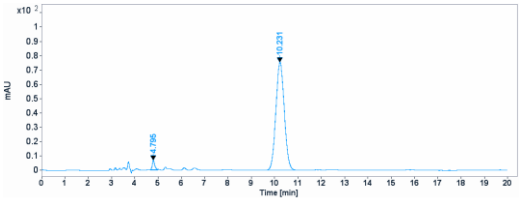
4i, yellow oil, 114 mg, 91% yield, >20:1 dr, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 10.23 min, t_{minor} = 4.80 min); $[\alpha]_D^{25}$ = -3.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.92 (s, 1H), 4.67 (t, *J* = 8.8 Hz, 1H), 3.99 (q, *J* = 6.8 Hz, 2H), 3.55 (t, *J* = 10.0 Hz, 1H), 3.02-2.86 (m, 1H), 2.16-2.03 (m, 1H),

1.64-1.58 (m, 10H), 1.44 (s, 9H), 1.15 (t, J = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 169.8, 165.4, 154.1, 148.4, 141.8, 135.4, 128.3, 125.0, 122.9, 115.6, 85.5, 82.6, 82.5, 70.6, 65.6, 61.0, 52.9, 36.7, 33.3, 28.1, 28.0, 27.9, 27.0, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}ClN_2O_{10}$ $[M+Na]^+$ 647.2342, found 647.2344.



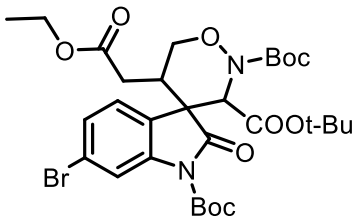
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.791	0.102	2692.766	405.291	50.0179
10.106	0.384	2690.837	109.746	49.9821
	Sum	5383.6028		

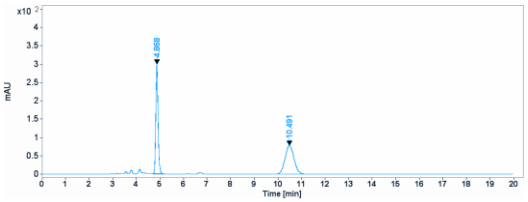


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.795	0.111	50.589	6.748	2.6112
10.231	0.391	1886.788	75.170	97.3888
	Sum	1937.3773		

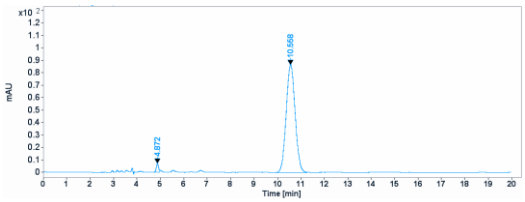


4j, yellow oil, 119 mg, 89% yield, >20:1 dr, 96% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 10.56 min, t_{minor} = 4.87 min); $[\alpha]_D^{25}$ = -2.7 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.92 (s, 1H), 4.66 (t, J = 8.8 Hz, 1H), 3.99 (q, J = 6.8 Hz, 2H), 3.54 (t, J = 10.0 Hz, 1H), 3.00-2.89 (m, 1H), 2.16-2.03 (m, 1H), 1.64-1.57 (m, 10H), 1.43 (s, 9H), 1.15 (t, J = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 169.8, 165.3, 154.1, 148.4, 141.9, 128.6, 128.0, 123.5, 123.3, 118.3, 85.6, 82.6, 82.5, 70.5, 65.5, 61.0, 53.0, 36.6, 33.3, 28.1, 27.9, 27.0, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}BrN_2O_{10}$ $[M+Na]^+$ 691.1837, 693.1818; found 691.1833, 693.1817.



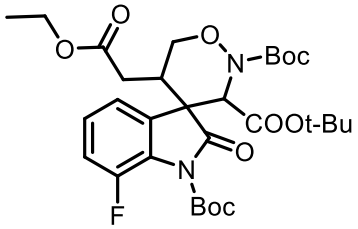
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.868	0.103	2019.980	299.088	49.6880
10.491	0.406	2045.345	78.035	50.3120
	Sum	4065.3251		

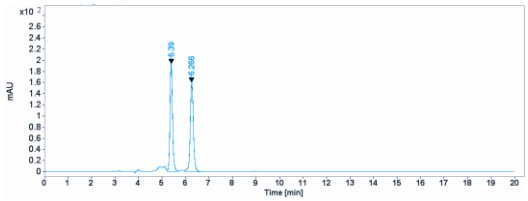


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.872	0.114	47.045	6.901	2.0134
10.558	0.413	2289.564	86.466	97.9866
	Sum	2336.6087		

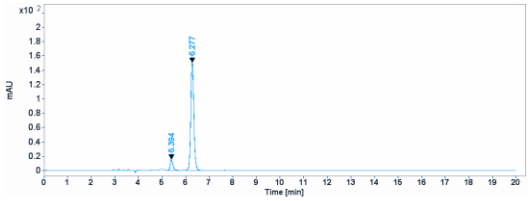


4k, yellow oil, 83 mg, 68% yield, >20:1 dr, 84% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 6.28 min, t_{minor} = 5.39 min); $[\alpha]_D^{25}$ = -3.4 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 1H), 7.15-7.08 (m, 2H), 4.97 (s, 1H), 4.68 (t, *J* = 8.8 Hz, 1H), 4.10-3.92 (m, 2H), 3.62-3.47 (t, *J* = 9.6 Hz, 1H), 3.10-2.90 (m, 1H), 2.25-2.15 (m, 1H), 1.59 (s, 9H), 1.56-1.51 (m, 1H), 1.46 (s, 9H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.98 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 169.9, 165.6, 154.2, 148.4 (d, *J* = 249.6 Hz), 146.9, 127.7 (d, *J* = 9.2 Hz), 127.5, 125.9 (d, *J* = 6.8 Hz), 123.2, 123.2, 117.7 (d, *J* = 20.0 Hz), 85.7, 82.7, 82.5, 70.6, 65.3, 61.0, 53.5, 36.8, 33.1, 28.1, 27.6, 27.1, 14.0 ppm; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -120.4 ppm; **HRMS (ESI)** *m/z* calcd for $C_{30}H_{41}FN_2O_{10}$ $[M+Na]^+$ 631.2637, found 631.2628.



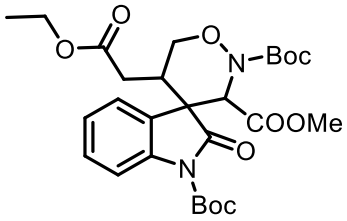
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.390	0.117	1469.103	193.250	49.7147
6.266	0.142	1485.965	159.840	50.2853
	Sum	2955.0686		

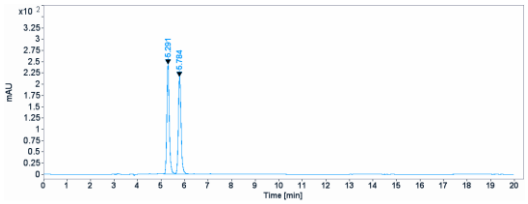


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.394	0.118	122.962	15.520	8.1928
6.277	0.143	1377.886	150.778	91.8072
	Sum	1500.8491		

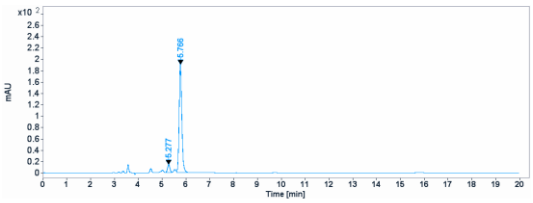


4l, yellow oil, 51 mg, 46% yield, >20:1 dr, 87% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 5.77 min, t_{minor} = 5.28 min); $[\alpha]_D^{25}$ = 1.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.16 (s, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 4.11-3.96 (m, 2H), 3.66 (t, *J* = 10.0 Hz, 1H), 3.18 (s, 3H), 3.06-2.92 (m, 1H), 2.19-2.08 (m, 1H), 1.68-1.62 (m, 10H), 1.49 (s, 9H), 1.19 (d, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9, 170.0, 167.6, 154.1, 148.6, 140.7, 129.5, 126.7, 125.0, 124.2, 115.0, 85.1, 82.8, 70.4, 65.5, 61.0, 53.2, 51.8, 36.6, 33.3, 28.2, 28.1, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{27}H_{36}N_2O_{10}$ $[M+Na]^+$ 571.2262, found 571.2268.



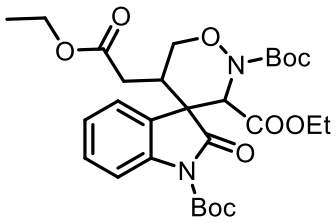
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.291	0.111	1768.169	243.477	50.4843
5.784	0.124	1734.246	215.798	49.5157
	Sum	3502.4146		

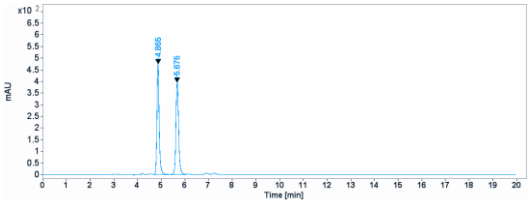


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.277	0.111	101.663	13.985	6.3148
5.766	0.123	1508.236	190.217	93.6852
	Sum	1609.8989		

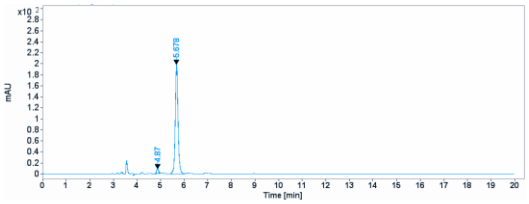


4m, yellow oil, 65 mg, 58% yield, >20:1 dr, 94% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 5.68 min, t_{minor} = 4.87 min); $[\alpha]_D^{25}$ = 2.1 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 5.12 (s, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 4.08-3.94 (m, 2H), 3.73-3.50 (m, 3H), 3.08-2.99 (m, 1H), 2.19-2.08 (m, 1H), 1.67-1.60 (m, 10H), 1.48 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.9, 170.0, 166.9, 154.1, 148.6, 140.8, 129.5, 126.9, 125.0, 124.1, 114.9, 85.1, 82.6, 70.4, 65.2, 61.2, 61.0, 53.1, 36.6, 33.3, 28.2, 28.1, 28.0, 28.0, 14.0, 13.2 ppm; **HRMS (ESI)** *m/z* calcd for $C_{28}H_{38}N_2O_{10}$ $[M+Na]^+$ 585.2419, found 585.2429.



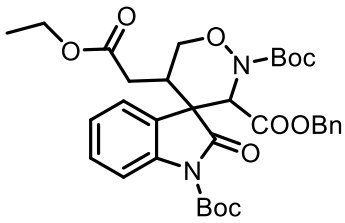
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.865	0.099	3143.327	476.162	49.7765
5.675	0.121	3171.557	395.933	50.2235
	Sum	6314.8840		

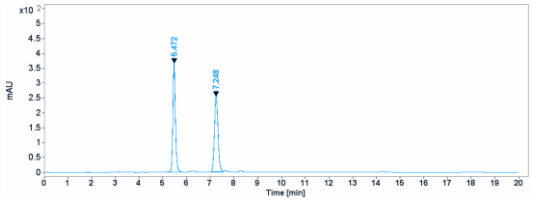


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.870	0.099	49.970	8.276	2.9809
5.678	0.122	1593.804	198.608	97.0191
	Sum	1642.7742		

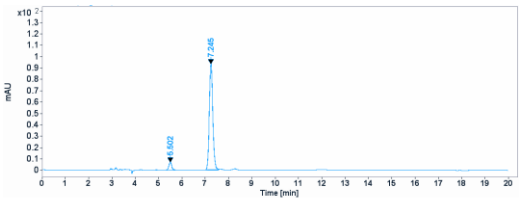


4n, yellow oil, 85 mg, 68% yield, >20:1 dr, 87% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 7.25 min, t_{minor} = 5.50 min); $[\alpha]_D^{25}$ = 3.9 (c = 1.0, $CHCl_3$).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.31-7.17 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.97-6.85 (m, 2H), 5.20 (s, 1H), 4.79-4.64 (m, 2H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.09-3.94 (m, 2H), 3.63 (t, *J* = 10.0 Hz, 1H), 3.07-2.91 (m, 1H), 2.17-2.04 (m, 1H), 1.61-1.55 (m, 10H), 1.48 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 170.0, 167.0, 154.1, 148.4, 140.6, 134.2, 129.5, 128.5, 128.4, 128.3, 126.6, 125.0, 123.9, 115.1, 84.9, 82.7, 70.4, 67.2, 65.1, 61.0, 53.03, 36.7, 33.2, 28.2, 28.0, 14.0 ppm; **HRMS (ESI)** *m/z* calcd for $C_{33}H_{40}N_2O_{10}$ $[M+Na]^+$ 647.2575, found 647.2578.



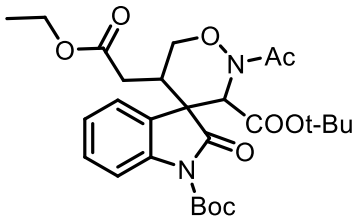
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.472	0.115	2795.228	366.829	51.2058
7.248	0.162	2663.582	254.839	48.7942
	Sum	5458.8098		

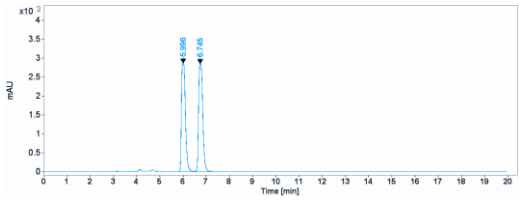


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.502	0.136	60.625	6.945	5.8832
7.245	0.161	969.843	93.174	94.1168
	Sum	1030.4673		

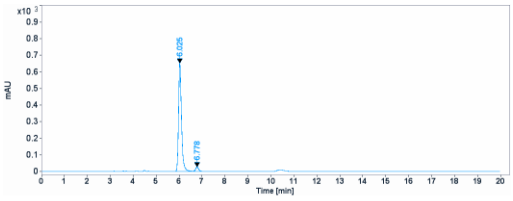


4o, yellow oil, 97 mg, 92% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 6.03 min, t_{minor} = 6.78 min); $[\alpha]_D^{25}$ = 2.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.35 (td, *J* = 8.0, 1.2 Hz, 1H), 7.15 (td, *J* = 7.6, 1.2 Hz, 1H), 5.31 (s, 1H), 4.67 (dd, *J* = 10.4, 8.0 Hz, 1H), 4.10-3.91 (m, 2H), 3.70 (t, *J* = 10.0 Hz, 1H), 3.01-2.84 (m, 1H), 2.24 (s, 3H), 2.17 (dd, *J* = 16.4, 3.6 Hz, 1H), 1.65-1.56 (m, 10H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 170.1, 164.5, 148.6, 141.0, 129.6, 126.8, 125.1, 124.3, 115.0, 85.1, 82.8, 71.6, 63.0, 61.0, 52.6, 36.3, 33.2, 28.0, 27.1, 26.9, 20.3, 14.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_{27}H_{34}N_2O_9$ $[M+Na]^+$ 555.2313, found 555.2311.



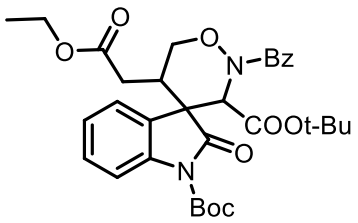
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.996	0.186	33774.172	2858.120	48.6794
6.745	0.198	35606.727	2845.979	51.3206
	Sum	69380.8984		



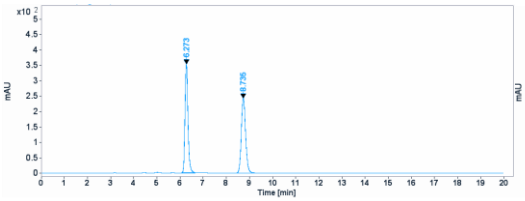
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.025	0.137	5862.545	651.952	95.7484
6.778	0.154	260.317	25.754	4.2516
	Sum	6122.8625		



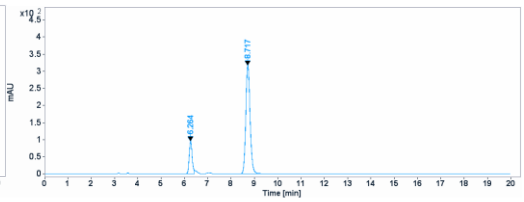
4p, yellow oil, 94 mg, 82% yield, >20:1 dr, 66% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 8.72 min, t_{minor} = 6.26 min); $[\alpha]_D^{25}$ = 3.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.90-7.69 (m, 2H), 7.60 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50-7.33 (m, 4H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 5.59 (br, 1H), 4.55 (br, 1H), 4.09-3.91 (m, 2H), 3.63 (t, *J* = 10.0 Hz,

1H), 3.08-2.93 (m, 1H), 2.20 (dd, *J* = 16.4, 3.6 Hz, 1H), 1.68-1.59 (m, 10H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 170.0, 169.9, 164.6, 148.7, 141.0, 133.1, 131.2, 129.6, 128.4, 128.0, 126.9, 125.1, 124.3, 115.0, 85.1, 82.8, 71.6, 63.6, 61.0, 52.8, 36.3, 33.2, 28.0, 27.0, 14.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_{27}H_{34}N_2O_9$ $[M+Na]^+$ 617.2470, found 617.2476.



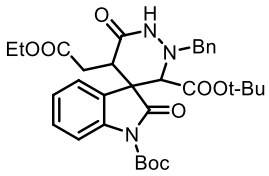
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.273	0.136	3143.399	353.184	50.2866
8.735	0.197	3107.572	242.841	49.7134
	Sum	6250.9709		

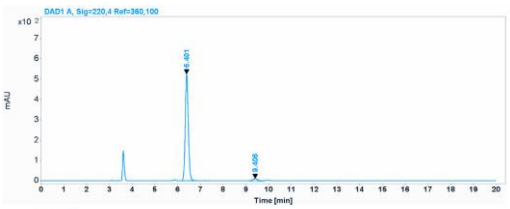


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.264	0.146	830.940	94.960	17.0248
8.717	0.199	4049.811	316.249	82.9752
	Sum	4880.7512		

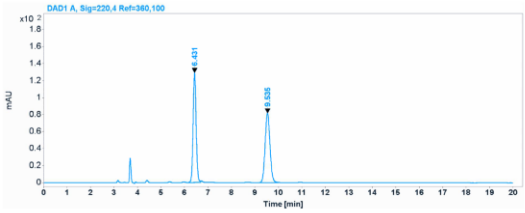


7a, white solid, m.p. =90.1-91.1℃, 88 mg, 74% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 6.40 min, t_{minor} = 9.40 min); $[\alpha]_D^{25}$ = -14.6 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.33 (m, 4H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 4.57 – 4.44 (m, 2H), 4.37 (s, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.77 (d, *J* = 10.4 Hz, 1H), 2.10 (m, 1H), 1.86 (d, *J* = 16.6 Hz, 1H), 1.65 (s, 9H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.87 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.77, 172.33, 170.73, 166.98, 148.58, 140.16, 136.06, 129.66, 128.86, 128.75, 128.00, 125.31, 124.94, 124.53, 114.92, 85.15, 82.16, 69.69, 64.80, 60.88, 58.42, 42.84, 29.11, 27.98, 26.93, 14.01. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{39}N_3O_8$ $[M+H]^+$ 594.2810, found 594.2816.



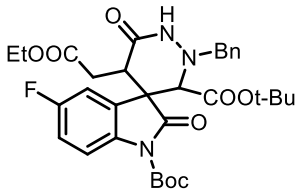
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.401	0.146	4968.451	524.590	95.8985
9.406	0.304	212.494	11.644	4.1015
	Sum	5180.9455		



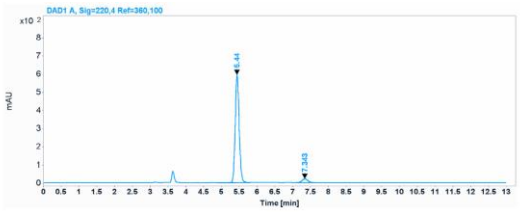
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.431	0.140	1163.652	128.673	50.0447
9.535	0.222	1161.572	81.433	49.9553
	Sum	2325.2242		



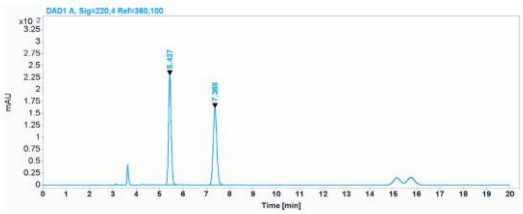
7b, white solid, m.p. =86.7-87.6℃, 73 mg, 60% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 5.40 min, t_{minor} = 7.30 min); $[\alpha]_D^{25}$ = 13.2 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.42 –

7.31 (m, 3H), 7.07 (t, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 4.6 Hz, 2H), 4.38 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.78 (d, *J* = 10.4 Hz, 1H), 2.15 (dd, *J* = 16.2, 10.8 Hz, 1H), 1.88 (d, *J* = 16.2 Hz, 1H), 1.65 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.95 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.31, 172.01, 170.57, 166.75, 160.12(*J* = 244.8), 148.58, 136.24, 135.92, 128.91, 128.84, 128.14, 126.77(*J* = 7.8), 116.28(*J* = 22.3), 116.26(*J* = 7.8), 112.54(*J* = 25.3), 85.42, 82.45, 69.68, 64.84, 61.02, 58.53, 42.89, 29.12, 28.01, 27.04, 14.04. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.7 ppm; **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}F_1N_3O_8$ $[M+H]^+$ 612.2716, found 612.2719.



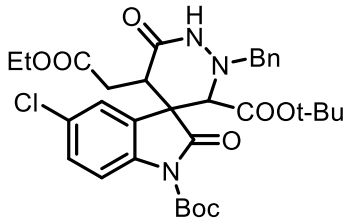
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.440	0.121	4667.597	596.142	95.7300
7.343	0.162	208.196	19.857	4.2700
	Sum	4875.7928		

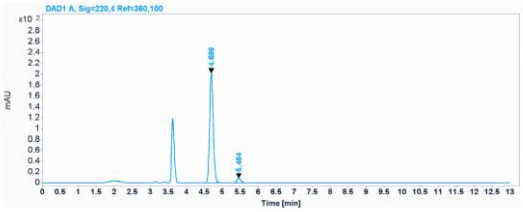


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.437	0.120	1775.621	229.402	50.8992
7.368	0.166	1712.884	160.797	49.1008
	Sum	3488.5055		

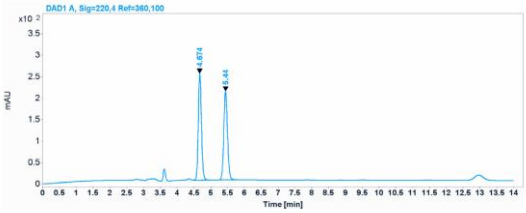


7c, white solid, m.p. =92.3-94.8℃, 80 mg, 64% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.70 min, t_{minor} = 5.48 min); $[\alpha]_D^{25}$ = 11.0 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.31 (m, 5H), 7.19 (s, 1H), 4.49 (s, 2H), 4.37 (s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.78 (d, *J* = 10.6 Hz, 1H), 2.17 (dd, *J* = 16.0, 10.6 Hz, 1H), 1.88 (d, *J* = 16.2 Hz, 1H), 1.65 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.07, 171.89, 170.56, 166.71, 148.46, 138.77, 135.92, 130.99, 129.78, 128.90, 128.83, 128.14, 126.83, 124.77, 116.17, 85.60, 82.53, 69.77, 64.82, 61.04, 58.39, 42.88, 29.12, 28.00, 27.04, 14.05. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}Cl_1N_3O_8$ $[M+H]^+$ 628.2420, found 628.2421.



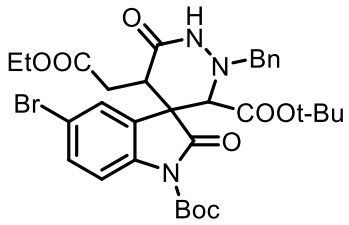
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.699	0.109	1404.854	202.486	95.6495
5.464	0.120	63.898	8.316	4.3505
	Sum	1468.7521		

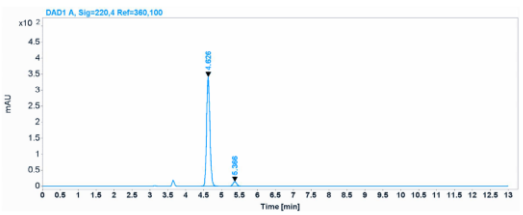


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.674	0.102	1622.633	248.413	50.8394
5.440	0.119	1569.048	205.494	49.1606
	Sum	3191.6808		

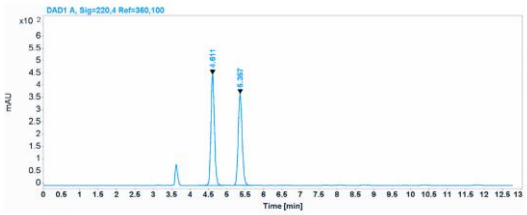


7d, white solid, m.p. =96.5-98.3℃, 81 mg, 61% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.63 min, t_{minor} = 5.37 min); $[\alpha]_D^{25}$ = 8.6 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.46 (m, 4H), 7.38 – 7.28 (m, 4H), 4.53 – 4.45 (m, 2H), 4.36 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.78 (d, *J* = 10.4 Hz, 1H), 2.18 (dd, *J* = 16.2, 10.8 Hz, 1H), 1.87 (d, *J* = 16.2 Hz, 1H), 1.65 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.95 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.94, 171.87, 170.55, 166.72, 148.43, 139.29, 135.93, 132.74, 128.91, 128.83, 128.13, 127.51, 127.20, 118.42, 116.54, 85.61, 82.55, 69.75, 64.79, 61.04, 58.32, 42.89, 29.13, 28.00, 27.04, 14.05. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}Br_1N_3O_8$ $[M+H]^+$ 672.1915, found 672.1917.



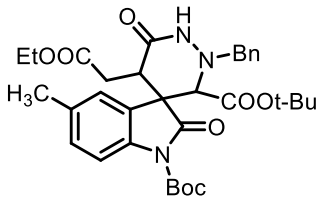
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.626	0.098	2179.064	341.485	95.5142
5.366	0.117	102.340	13.726	4.4858
	Sum	2281.4041		

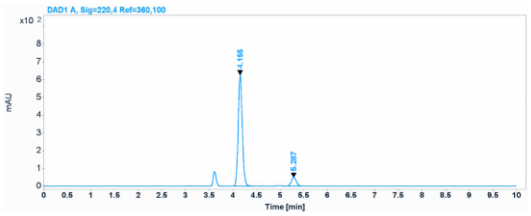


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.611	0.104	3016.213	452.740	51.5448
5.357	0.119	2835.417	372.425	48.4552
	Sum	5851.6294		

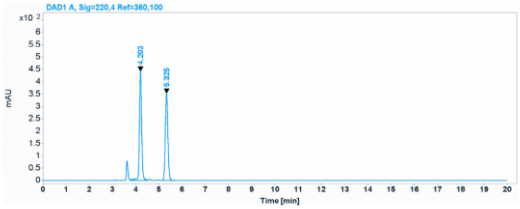


7e, white solid, m.p. =86.1-88.7℃, 109 mg, 90% yield, >20:1 dr, 83% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.16 min, t_{minor} = 5.29 min); $[\alpha]_D^{25}$ = 6.6 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 4.50 (s, 2H), 4.38 (s, 1H), 4.14 (q, *J* = 6.8 Hz, 2H), 3.77 (d, *J* = 10.6 Hz, 1H), 2.26 (s, 3H), 2.15 (dd, *J* = 16.4, 10.8 Hz, 1H), 1.89 (d, *J* = 16.4 Hz, 1H), 1.66 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.90 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.98, 172.33, 170.80, 167.05, 148.68, 137.82, 136.16, 135.12, 130.10, 128.90, 128.78, 128.04, 125.03, 124.95, 114.76, 84.99, 82.16, 69.88, 64.89, 60.91, 58.48, 42.93, 29.19, 28.04, 26.93, 21.02, 14.05. **HRMS (ESI)** *m/z* calcd for $C_{33}H_{41}N_3O_8$ $[M+H]^+$ 608.2966, found 608.2976.



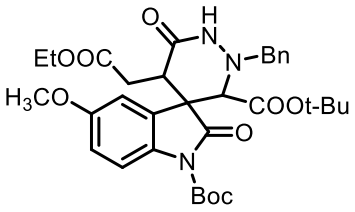
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.155	0.095	3829.010	626.974	91.2862
5.287	0.116	365.502	48.531	8.7138
	Sum	4194.5115		

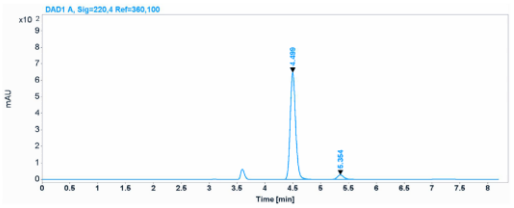


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.203	0.099	2924.772	441.350	52.1304
5.325	0.119	2685.725	352.420	47.8696
	Sum	5610.4976		

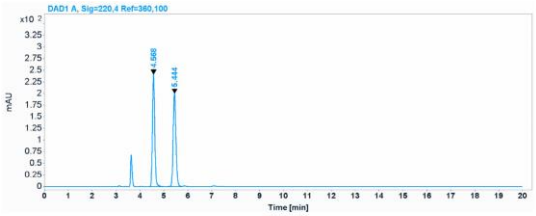


7f, white solid, m.p. =84.0-86.3℃, 92 mg, 74% yield, >20:1 dr, 90% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.50 min, t_{minor} = 5.35 min); $[\alpha]_D^{25}$ = 6.6 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.0 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.31 (m, 4H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.76 (s, 1H), 4.51 (s, 2H), 4.39 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.78 (d, *J* = 10.6 Hz, 1H), 3.72 (s, 3H), 2.16 (dd, *J* = 16.4, 11.0 Hz, 1H), 1.89 (d, *J* = 16.6 Hz, 1H), 1.66 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.88, 172.35, 170.75, 167.00, 157.37, 148.70, 136.11, 133.38, 128.92, 128.80, 128.06, 126.13, 115.92, 115.03, 110.46, 84.96, 82.21, 69.80, 64.84, 60.93, 58.78, 55.68, 42.95, 29.16, 28.05, 27.02, 14.05. **HRMS (ESI)** *m/z* calcd for $C_{33}H_{41}N_3O_9$ $[M+H]^+$ 624.2916, found 624.2922.



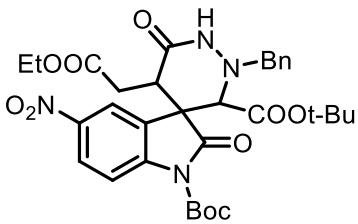
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.499	0.105	4389.369	648.443	95.0417
5.354	0.130	228.992	26.837	4.9583
	Sum	4618.3612		



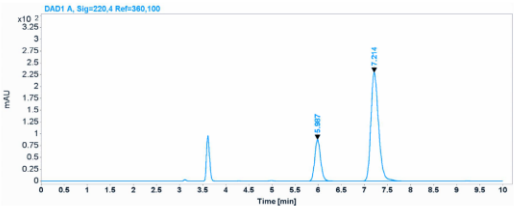
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.568	0.104	1606.316	240.428	50.2041
5.444	0.123	1593.252	199.582	49.7959
	Sum	3199.5675		



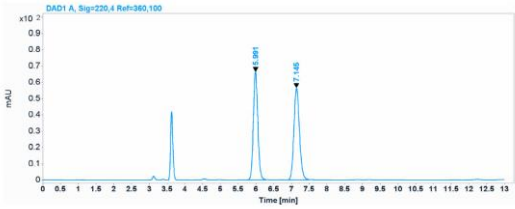
7g, white solid, m.p. =105.1-105.7℃, 62 mg, 49% yield, >20:1 dr, 55% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 7.21 min, t_{minor} = 5.99 min); $[\alpha]_D^{25}$ = 3.4 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.09 (m, 2H), 7.48 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.31 (m, 3H), 4.55 – 4.48 (m, 2H), 4.41 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.83 (dd, *J* = 10.6, 3.2 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.88 (dd, *J* = 16.2, 3.2 Hz, 1H), 1.68 (s, 9H), 1.25 (t, *J* = 7.2

Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.61, 171.44, 170.26, 166.44, 148.16, 145.41, 144.91, 135.67, 128.92, 128.29, 126.45, 125.97, 120.05, 115.14, 86.56, 82.80, 69.78, 64.90, 61.18, 58.17, 42.98, 29.04, 27.96, 27.09, 14.02. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}N_4O_{10}$ $[M+H]^+$ 639.2661, found 639.2670.



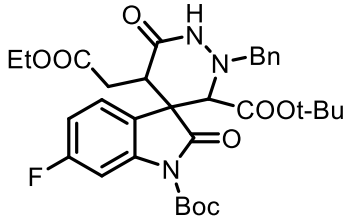
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.987	0.136	768.834	88.033	22.4395
7.214	0.179	2657.423	229.732	77.5605
	Sum	3426.2574		

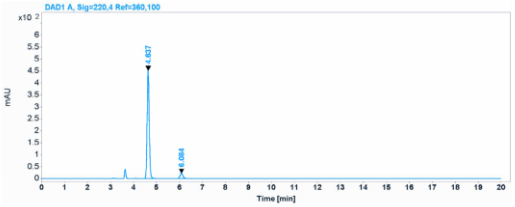


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.991	0.133	574.813	66.367	48.5229
7.145	0.168	609.810	56.283	51.4771
	Sum	1184.6221		

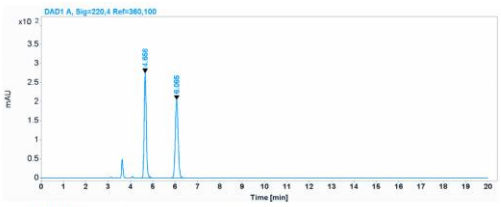


7h, white solid, m.p. =180.5-182.1℃, 73 mg, 60% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.64 min, t_{minor} = 6.08 min); $[\alpha]_D^{25}$ = -15.2 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 10.0 Hz, 1H), 7.59 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.27 (m, 3H), 7.20 – 7.13 (m, 1H), 6.81 (t, *J* = 8.6 Hz, 1H), 4.54 – 4.45 (m, 2H), 4.35 (s, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.77 (d, *J* = 10.4 Hz, 1H), 2.14 (dd, *J* = 16.2, 10.6 Hz, 1H), 1.85 (d, *J* = 16.2 Hz, 1H), 1.65 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.56, 172.21, 170.62, 166.90, 163.39(*J* = 246.1), 148.35, 141.50(*J* = 12.4), 135.96, 128.87, 128.82, 128.10, 125.88(*J* = 9.5), 120.45, 111.81(*J* = 22.2), 103.93(*J* = 29.8), 85.71, 82.34, 69.76, 64.77, 60.98, 58.15, 42.91, 29.11, 27.98, 27.07, 14.04. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.6 ppm; **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}F_1N_3O_8$ $[M+H]^+$ 612.2716, found 612.2727.



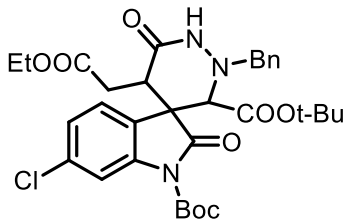
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.637	0.097	2839.760	452.646	93.8267
6.084	0.136	186.840	21.001	6.1733
	Sum	3026.6002		

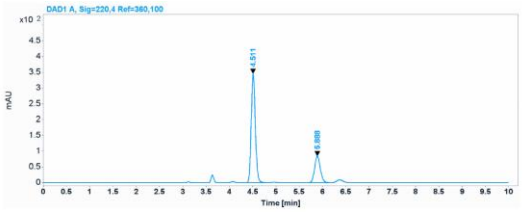


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.658	0.102	1796.304	274.474	50.1319
6.065	0.136	1786.852	204.711	49.8681
	Sum	3583.1564		

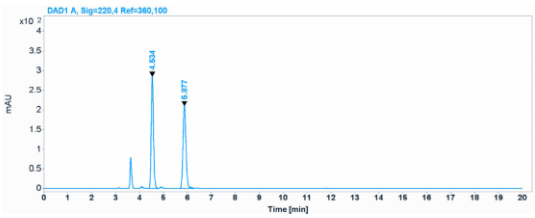


7i, white solid, m.p. =187.2-188.9℃, 65 mg, 52% yield, >20:1 dr, 50% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.51 min, t_{minor} = 5.89 min); $[\alpha]_D^{25}$ = -14.0 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.13 (s, 2H), 4.52 – 4.40 (m, 2H), 4.36 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.78 (dd, *J* = 10.6, 3.2 Hz, 1H), 2.14 (dd, *J* = 16.2, 10.6 Hz, 1H), 1.86 (dd, *J* = 16.2, 3.2 Hz, 1H), 1.66 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.95 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.27, 172.08, 170.58, 166.79, 148.37, 141.20, 135.94, 135.79, 128.87 128.84, 128.14, 125.48, 125.25, 123.36, 115.75, 85.77, 82.50, 69.83, 64.82, 61.01, 58.23, 42.83, 29.11, 27.98, 27.06, 14.04. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}Cl_1N_3O_8$ $[M+H]^+$ 628.2420, found 628.2419.



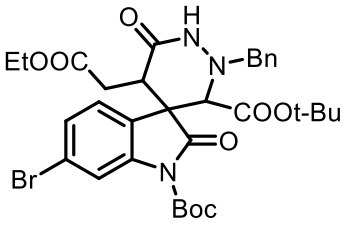
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.511	0.096	2132.297	346.580	74.6625
5.888	0.132	723.618	84.360	25.3375
	Sum	2855.9144		

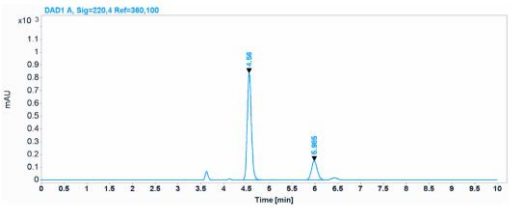


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.534	0.100	1847.348	285.343	50.5427
5.877	0.132	1807.678	210.037	49.4573
	Sum	3655.0254		

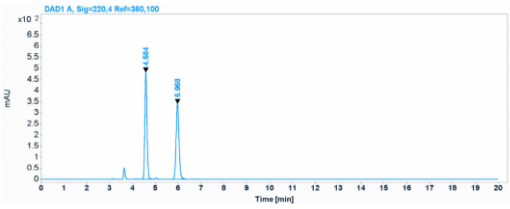


7j, white solid, m.p. =187.3-189.3℃, 56 mg, 52% yield, >20:1 dr, 60% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.56 min, t_{minor} = 5.99 min); $[\alpha]_D^{25}$ = -13.8 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.44 (d, *J* = 8.3 Hz, 3H), 7.40 – 7.29 (m, 3H), 7.25 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.33 (s, 1H), 4.12 (q, *J* = 6.8 Hz, 2H), 3.76 (d, *J* = 10.4 Hz, 1H), 2.12 (dd, *J* = 16.2, 10.8 Hz, 1H), 1.84 (d, *J* = 16.2 Hz, 1H), 1.64 (s, 9H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.93 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.13, 172.07, 170.55, 166.77, 148.32, 141.24, 135.87, 128.84, 128.80, 128.19, 128.10, 125.73, 123.87, 123.58, 118.48, 85.75, 82.50, 69.65, 64.75, 60.99, 58.25, 42.69, 29.07, 27.94, 27.01, 14.01. **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}Br_1N_3O_8$ $[M+H]^+$ 672.1915, found 672.1913.



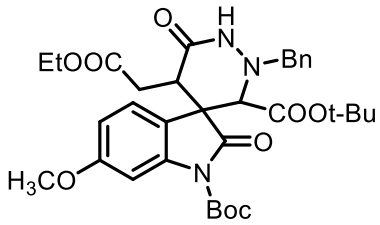
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.560	0.098	5318.936	836.512	80.0790
5.985	0.137	1323.178	149.599	19.9210
	Sum	6642.1141		

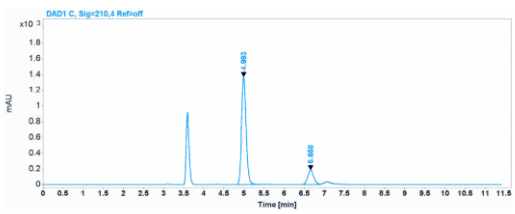


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.584	0.100	3125.278	482.862	51.2137
5.968	0.134	2977.151	340.952	48.7863
	Sum	6102.4285		

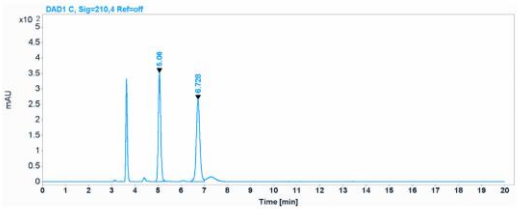


7k, white solid, m.p. =105.3-106.4℃, 99 mg, 80% yield, >20:1 dr, 70% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 4.99 min, t_{minor} = 6.66 min); $[\alpha]_D^{25}$ = 12.0 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.30 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 4.49 (s, 2H), 4.35 (s, 1H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.75 (d, *J* = 10.6 Hz, 1H), 2.15 (dd, *J* = 16.0, 10.6 Hz, 1H), 1.88 (d, *J* = 16.2 Hz, 1H), 1.66 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.20, 172.47, 170.83, 167.15, 160.96, 148.57, 141.31, 136.14, 128.90, 128.78, 128.03, 125.30, 116.60, 110.03, 102.40, 85.17, 82.11, 70.03, 64.87, 60.89, 58.10, 55.65, 43.07, 29.18, 28.03, 27.10, 14.05. **HRMS (ESI)** *m/z* calcd for $C_{33}H_{41}N_3O_9$ $[M+H]^+$ 624.2916, found 624.2932.



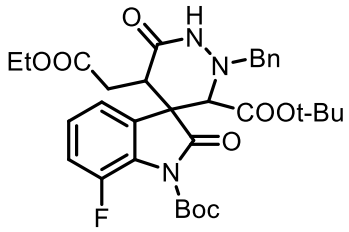
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
4.993	0.122	10832.946	1367.289	84.8757
6.658	0.164	1930.363	181.987	15.1243
	Sum	12763.3093		

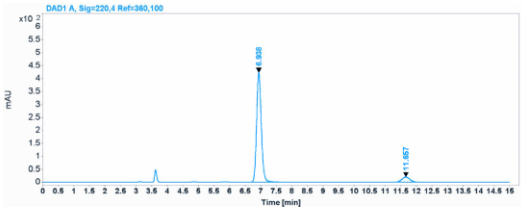


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.060	0.111	2561.870	350.377	47.8354
6.728	0.161	2793.720	264.956	52.1646
	Sum	5355.5901		

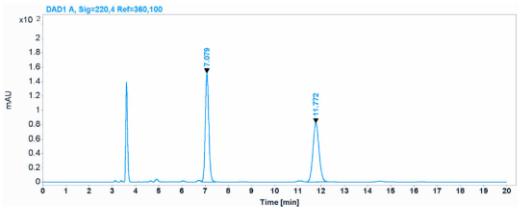


7l, white solid, m.p. =82.1-83..4℃, 76 mg, 63% yield, >20:1 dr, 85% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 6.94 min, t_{minor} = 11.66 min); $[\alpha]_D^{25}$ = 16.0 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.21 – 7.09 (m, 2H), 7.01 (d, *J* = 7.0 Hz, 1H), 4.51 (q, *J* = 13.2 Hz, 2H), 4.38 (s, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.82 (d, *J* = 10.6 Hz, 1H), 2.08 (dd, *J* = 16.2, 10.2 Hz, 1H), 1.90 (d, *J* = 16.2 Hz, 1H), 1.63 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.98 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.10, 172.00, 170.59, 167.00, 146.99(*J* = 29.2), 136.00, 128.87, 128.83, 128.26, 128.11, 126.90(*J* = 8.8), 126.22(*J* = 6.7), 120.63, 118.03(*J* = 20.0), 85.88, 82.54, 69.40, 64.37, 61.00, 58.99, 42.90, 28.91, 27.64, 27.21, 14.03. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -119.8 ppm; **HRMS (ESI)** *m/z* calcd for $C_{32}H_{38}F_1N_3O_8$ $[M+H]^+$ 612.2716, found 612.2721.



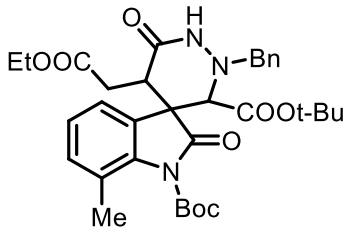
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
6.938	0.161	4390.824	422.838	92.6147
11.657	0.283	350.116	19.327	7.3853
	Sum	4740.7399		

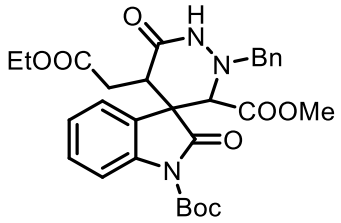


Signal: DAD1 A, Sig=220,4 Ref=360,100

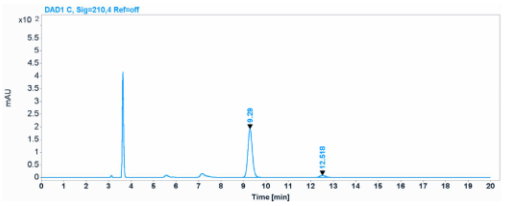
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.079	0.163	1595.902	151.293	51.7006
11.772	0.282	1490.913	81.944	48.2994
	Sum	3086.8156		



7m, white solid, m.p. =77.3-75.8℃, 40 mg, 33% yield, >20:1 dr, 20% ee. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.18 – 7.11 (m, 1H), 7.05 – 6.99 (m, 2H), 4.59 – 4.43 (m, 2H), 4.37 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.79 (dd, *J* = 10.6, 3.2 Hz, 1H), 2.26 (s, 3H), 2.08 (dd, *J* = 16.6, 10.6 Hz, 1H), 1.88 (dd, *J* = 16.6, 3.2 Hz, 1H), 1.65 (s, 9H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.94 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.44, 172.25, 170.91, 167.26, 148.83, 138.45, 136.28, 132.60, 128.79, 128.00, 125.92, 124.99, 122.81, 122.42, 85.54, 82.30, 69.53, 64.44, 60.86, 58.54, 43.01, 28.91, 27.74, 27.16, 19.43, 14.04. **HRMS (ESI)** *m/z* calcd for $C_{33}H_{41}N_3O_8$ $[M+H]^+$ 608.2966, found 608.2965.

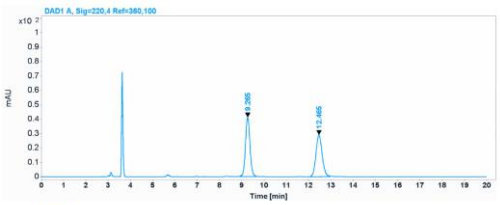


7n, white solid, m.p. =170.6-172.3℃, 36 mg, 33% yield, >20:1 dr, 85% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 9.29 min, t_{minor} = 12.52 min); $[\alpha]_D^{25}$ = -19.4 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.31 (m, 5H), 7.12 (s, 2H), 4.63 – 4.43 (m, 3H), 4.14 (q, *J* = 6.8 Hz, 2H), 3.90 (d, *J* = 10.4 Hz, 1H), 3.05 (s, 3H), 2.20 (dd, *J* = 16.6, 11.0 Hz, 1H), 1.84 (d, *J* = 16.6 Hz, 1H), 1.69 (s, 9H), 1.24 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.94, 172.37, 170.69, 168.76, 148.57, 139.83, 135.97, 129.73, 128.97, 128.84, 128.13, 125.05, 124.83, 124.03, 114.96, 85.37, 69.94, 63.91, 60.95, 58.87, 51.53, 42.61, 29.34, 28.08, 14.03. **HRMS (ESI)** *m/z* calcd for $C_{29}H_{33}N_3O_8$ $[M+H]^+$ 552.2340, found 552.2330.



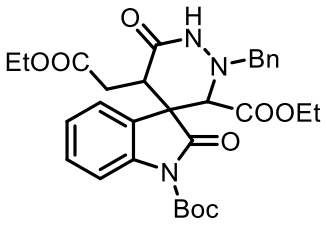
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
9.290	0.215	2630.997	190.758	94.5301
12.518	0.285	152.240	7.832	5.4699
	Sum	2783.2365		

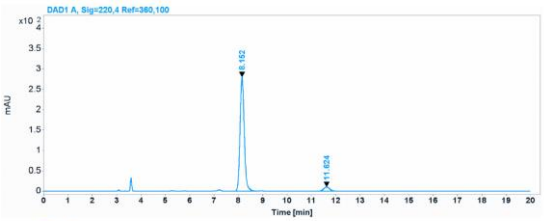


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
9.265	0.216	568.761	41.077	50.6686
12.465	0.298	553.752	28.798	49.3314
	Sum	1122.5129		

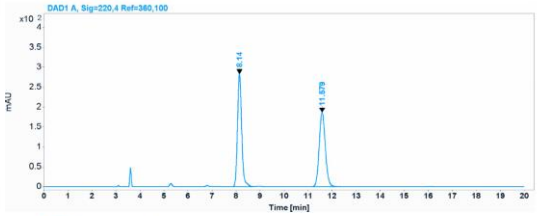


7o, white solid, m.p. =158.5-160.5℃, 67 mg, 60% yield, >20:1 dr, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 8.15 min, t_{minor} = 11.62 min); $[\alpha]_D^{25}$ = -14.2 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.29 (m, 5H), 7.18 – 7.06 (m, 2H), 4.60 – 4.43 (m, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.86 (d, *J* = 8.6 Hz, 1H), 3.69 – 3.56 (m, 1H), 3.41 – 3.29 (m, 1H), 2.16 (dd, *J* = 16.6, 10.6 Hz, 1H), 1.84 (d, *J* = 16.2 Hz, 1H), 1.67 (s, 9H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.68 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.93, 172.33, 170.71, 168.26, 148.55, 140.01, 136.00, 129.74, 128.96, 128.84, 128.12, 125.15, 124.80, 124.24, 114.94, 85.32, 69.81, 64.28, 61.01, 60.95, 58.74, 42.73, 29.27, 28.06, 14.04, 13.19. **HRMS (ESI)** *m/z* calcd for $C_{30}H_{35}N_3O_8$ $[M+H]^+$ 566.2497, found 566.2494.



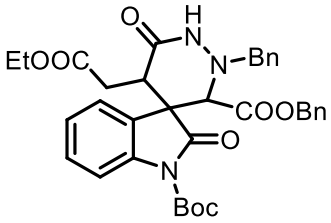
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
8.152	0.183	3346.564	280.236	94.9512
11.624	0.282	177.947	9.994	5.0488
	Sum	3524.5109		



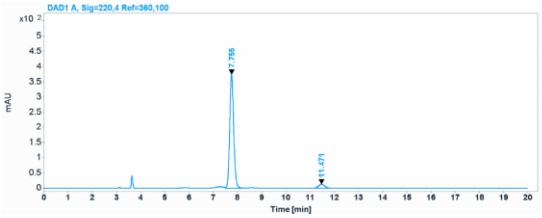
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
8.140	0.184	3396.986	282.527	50.7627
11.579	0.274	3294.907	186.158	49.2373
	Sum	6691.8931		



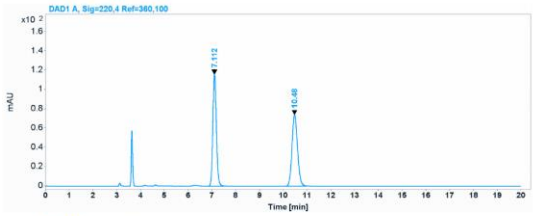
7p, white solid, m.p. =64.7-65.8℃, 68 mg, 55% yield, >20:1 dr, 92% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 7.76 min, t_{minor} = 11.47 min); $[\alpha]_D^{25}$ = 2.8 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.45 (m, 3H), 7.41 – 7.22 (m, 7H), 7.14 (m, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.64 – 4.43 (m, 3H), 4.16 – 4.08 (m,

3H), 3.88 (d, *J* = 10.6 Hz, 1H), 2.15 (dd, *J* = 16.0, 11.0 Hz, 1H), 1.83 (d, *J* = 16.4 Hz, 1H), 1.62 (s, 9H), 1.23 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.77, 172.33, 170.68, 168.25, 154.47, 148.37, 139.84, 135.99, 134.14, 129.78, 128.94, 128.85, 128.46, 128.38, 128.13, 125.10, 124.62, 124.06, 115.16, 85.18, 69.87, 67.07, 64.16, 60.95, 58.80, 42.86, 29.21, 28.03, 14.03. **HRMS (ESI)** *m/z* calcd for $C_{35}H_{37}N_3O_8$ $[M+H]^+$ 628.2653, found 628.2648.



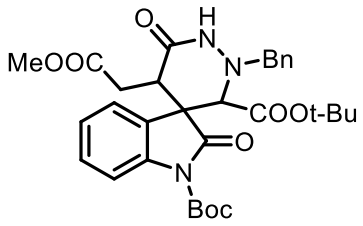
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.755	0.178	4283.765	373.046	94.7976
11.471	0.285	235.089	12.870	5.2024
	Sum	4518.8537		

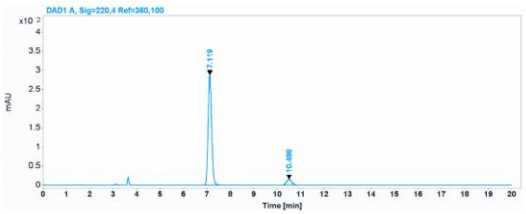


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.112	0.161	1199.097	115.805	50.2174
10.480	0.250	1188.717	73.722	49.7826
	Sum	2387.8141		

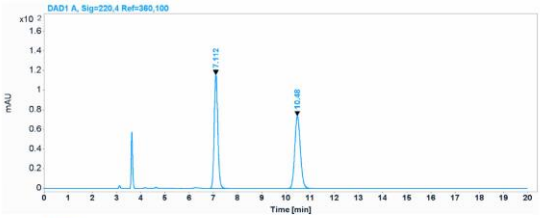


7q, white solid, m.p. =90.2-91.5℃, 86 mg, 75% yield, >20:1 dr, 90% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 7.16 min, t_{minor} = 10.50 min); $[\alpha]_D^{25}$ = 6.6 (c = 1.0, CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 3H), 7.42 – 7.30 (m, 4H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.54 – 4.46 (m, 2H), 4.38 (s, 1H), 3.77 (d, *J* = 10.4 Hz, 1H), 3.67 (s, 3H), 2.15 (dd, *J* = 16.2, 10.6 Hz, 1H), 1.88 (d, *J* = 16.2 Hz, 1H), 1.66 (s, 9H), 0.89 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.73, 172.31, 171.28, 166.99, 148.62, 140.23, 136.06, 129.75, 128.92, 128.81, 128.07, 125.35, 124.91, 124.57, 114.96, 85.20, 82.25, 69.76, 64.84, 58.45, 52.02, 42.98, 28.96, 28.03, 26.98. **HRMS (ESI)** *m/z* calcd for $C_{31}H_{37}N_3O_8$ $[M+H]^+$ 580.2653, found 580.2659.



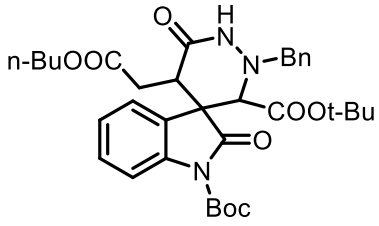
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.119	0.161	2978.687	287.898	92.7567
10.498	0.251	232.605	14.391	7.2433
	Sum	3211.2920		



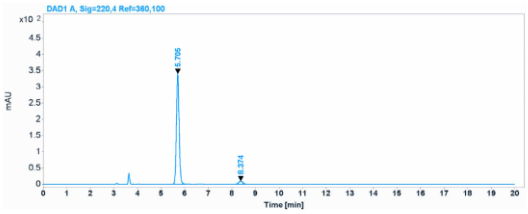
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
7.112	0.161	1199.097	115.805	50.2174
10.480	0.250	1188.717	73.722	49.7826
	Sum	2387.8141		



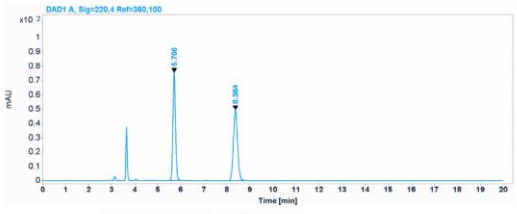
7r, white solid, m.p. =98.5-100.4℃, 86 mg, 70% yield, >20:1 dr, 90% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 220 nm, t_{major} = 5.71 min, t_{minor} = 6.37 min); $[\alpha]_D^{25}$ = 5.6 (c = 1.0,

CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.29 (m, 7H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 4.56 – 4.46 (s, 2H), 4.38 (s, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 3.79 (d, *J* = 10.6 Hz, 1H), 2.12 (dd, *J* = 16.2, 11.0 Hz, 1H), 1.88 (d, *J* = 16.4 Hz, 1H), 1.66 (s, 9H), 1.62 – 1.54 (m, 2H), 1.42 – 1.30 (m, 2H), 0.98 – 0.81 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.82, 172.35, 170.81, 167.00, 148.63, 140.22, 136.14, 129.71, 128.87, 128.79, 128.05, 125.35, 124.97, 124.59, 114.97, 85.19, 82.22, 69.91, 64.90, 64.83, 58.49, 42.92, 30.52, 29.14, 28.03, 26.99, 19.06, 13.66. **HRMS (ESI)** *m/z* calcd for $C_{34}H_{43}N_3O_8$ $[M+H]^+$ 622.3123, found 622.3117.



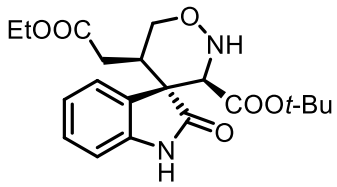
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.705	0.125	2769.675	340.126	95.8138
8.374	0.195	121.010	9.588	4.1862
	Sum	2890.6843		

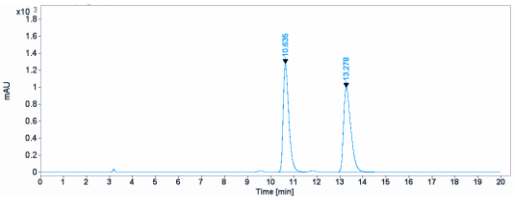


Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
5.706	0.126	607.991	75.297	49.2948
8.364	0.198	625.387	49.175	50.7052
	Sum	1233.3785		

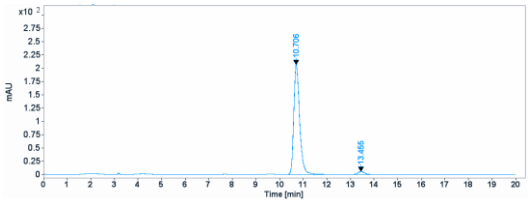


8, yellow oil, 59 mg, 78% yield, 94% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 13.46 min, t_{minor} = 10.71 min). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.38-7.17 (m, 1H), 7.11-6.91 (m, 2H), 5.97 (s, 1H), 4.29 (s, 1H), 4.18 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.89 (t, *J* = 11.6 Hz, 1H), 2.91-2.80 (m, 1H), 2.00 (dd, *J* = 16.4, 3.2 Hz, 1H), 1.55 (dd, *J* = 16.4, 11.2 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.06 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.3, 171.1, 166.4, 142.0, 128.9, 127.8, 126.4, 122.5, 110.1, 83.3, 69.7, 64.3, 60.8, 52.6, 39.3, 31.4, 27.4, 27.2, 14.1 ppm. **HRMS (ESI)** *m/z* calcd for $C_{27}H_{34}N_2O_9$ $[M+H]^+$ 391.1864, found 391.1867.



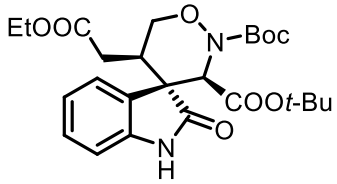
Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
10.635	0.261	21776.484	1274.530	49.9735
13.278	0.335	21799.578	996.548	50.0265
	Sum	43576.0625		

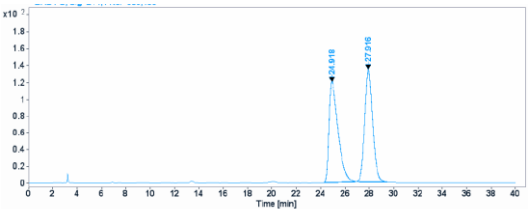


Signal: DAD1 C, Sig=210,4 Ref=off

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
10.706	0.288	3571.150	206.733	97.0907
13.455	0.275	107.008	5.511	2.9093
	Sum	3678.1585		

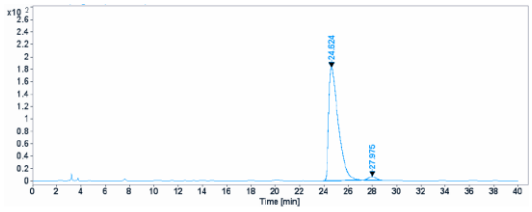


9, yellow oil, 37 mg, 76% yield, 95% ee (Chiralcel IA column, i-PrOH/n-hexane = 10/90, 1.0 mL/min, λ = 210 nm, t_{major} = 24.62 min, t_{minor} = 27.98 min). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.69-7.48 (m, 1H), 7.38-7.16 (m, 1H), 7.13-6.93 (m, 2H), 4.94 (s, 1H), 4.72 (dd, J = 10.0, 7.6 Hz, 1H), 4.02 (qd, J = 7.2, 2.8 Hz, 2H), 3.67 (t, J = 10.0 Hz, 1H), 3.09-2.87 (m, 1H), 2.27 (dd, J = 16.0, 3.6 Hz, 1H), 1.65 (dd, J = 16.0, 11.2 Hz, 1H), 1.49 (s, 9H), 1.17 (t, J = 7.2 Hz, 3H), 0.96 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.2, 170.7, 166.2, 154.6, 142.4, 129.4, 128.1, 126.0, 123.4, 110.3, 82.5, 82.4, 71.2, 65.1, 61.0, 53.2, 35.9, 33.3, 28.3, 27.2, 14.2 ppm. **HRMS (ESI)** *m/z* calcd for $C_{25}H_{34}N_2O_8$ $[M+Na]^+$ 513.2207, found 513.2204.



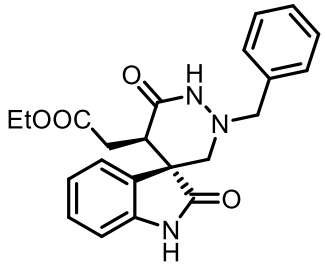
Signal: DAD1 C, Sig=214,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
24.918	0.748	6163.124	120.313	50.0016
27.916	0.711	6162.722	133.926	49.9984
	Sum	12325.8452		



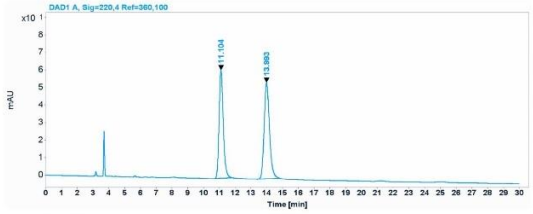
Signal: DAD1 C, Sig=214,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
24.624	0.782	9860.643	182.682	97.3700
27.975	0.524	266.337	6.088	2.6300
	Sum	10126.9800		



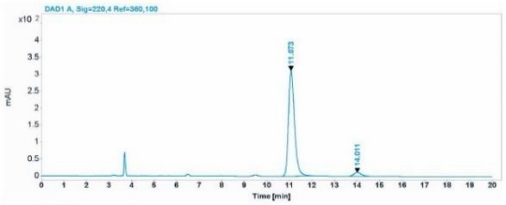
10, white solid, 64 mg, 82% yield, 91% ee (Chiralcel IA column, i-PrOH/n-hexane = 20/80, 1.0 mL/min, λ = 210 nm, t_{major} = 11.07 min, t_{minor} = 14.01 min); $[\alpha]_D^{25}$ = 13.2 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.43 – 7.29 (m, 5H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.11 – 7.02 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.29 (d, *J* = 13.0 Hz, 1H), 4.18 (d, *J* = 13.0 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.88 (dd, *J* =

10.0, 3.8 Hz, 1H), 3.43 (d, *J* = 13.0 Hz, 1H), 3.25 (d, *J* = 13.0 Hz, 1H), 2.38 (dd, *J* = 16.4, 10.0 Hz, 1H), 1.79 (dd, *J* = 16.4, 3.8 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.98, 171.49, 171.29, 140.23, 135.65, 129.18, 129.11, 129.03, 128.73, 128.09, 124.94, 123.39, 110.15, 62.31, 60.72, 59.48, 53.83, 41.09, 30.48, 14.00. **HRMS (ESI)** *m/z* calcd for $C_{22}H_{23}N_3O_4$ $[M+H]^+$ 394.1761, found 394.1767.



Signal: DAD1 A, Sig=220,4 Ref=360,100

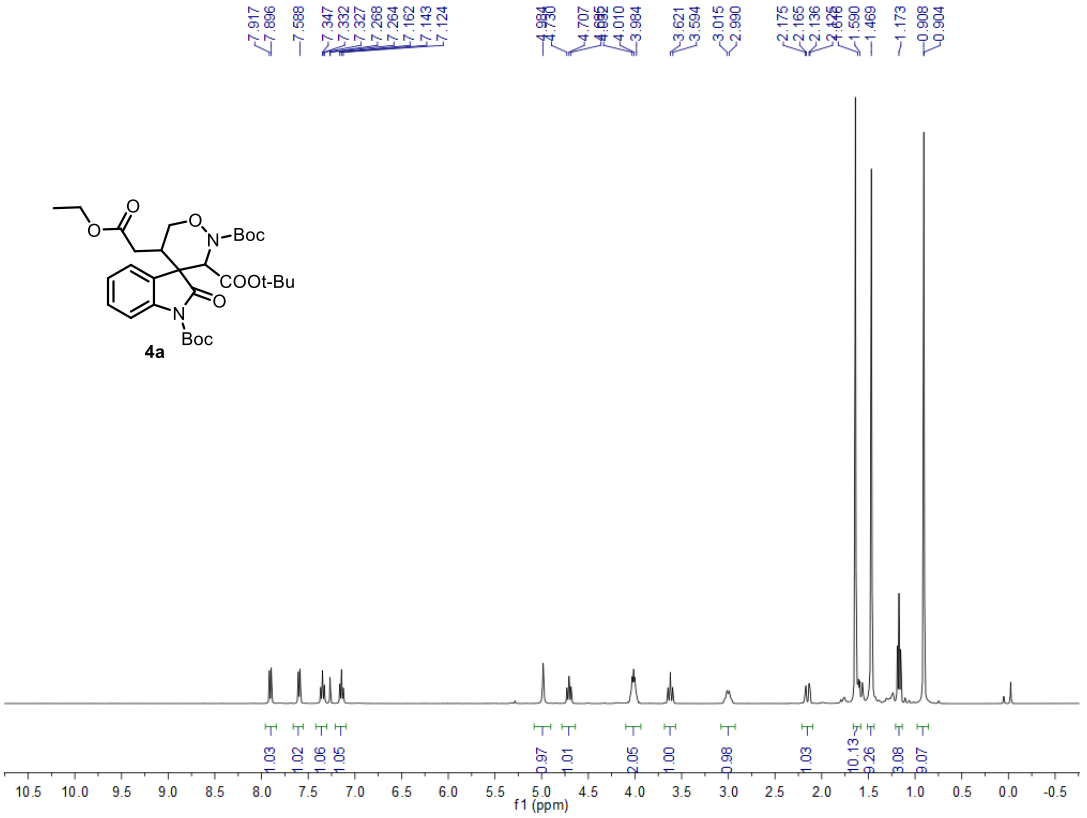
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
11.104	0.281	1135.527	61.735	46.9095
13.993	0.358	1285.147	54.807	53.0905
	Sum	2420.6744		

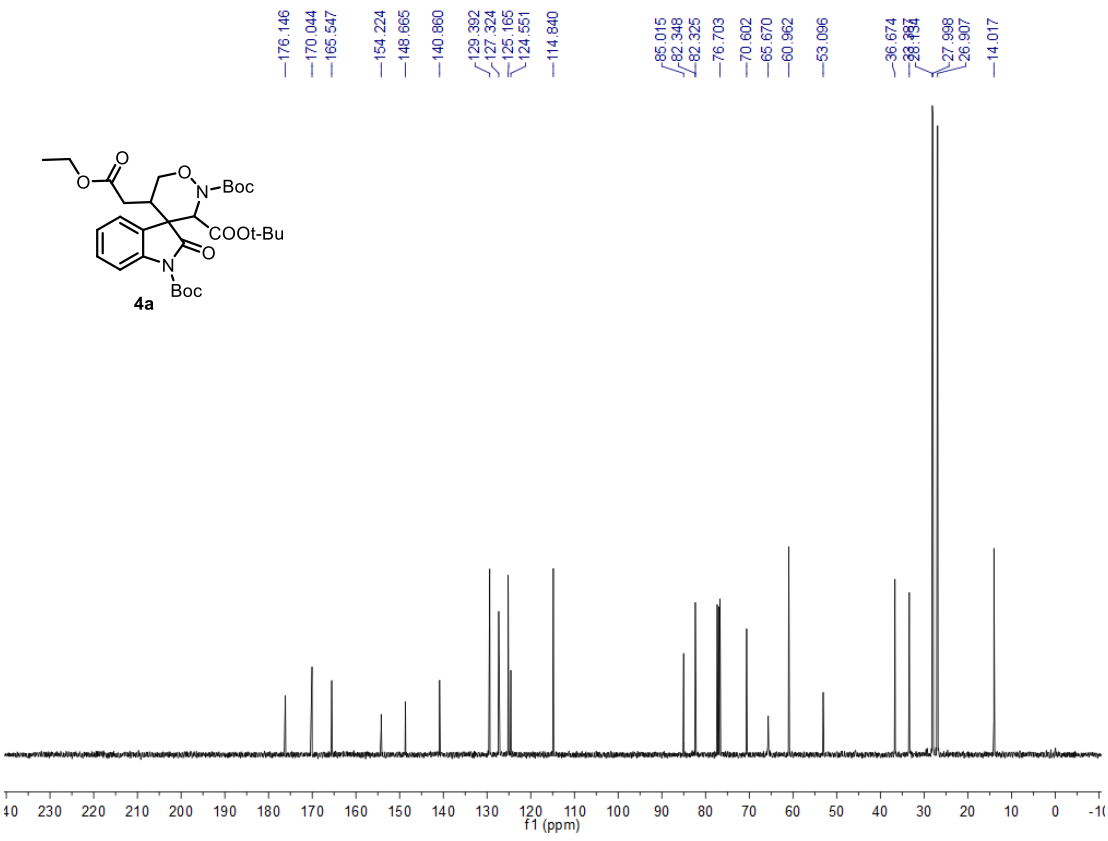


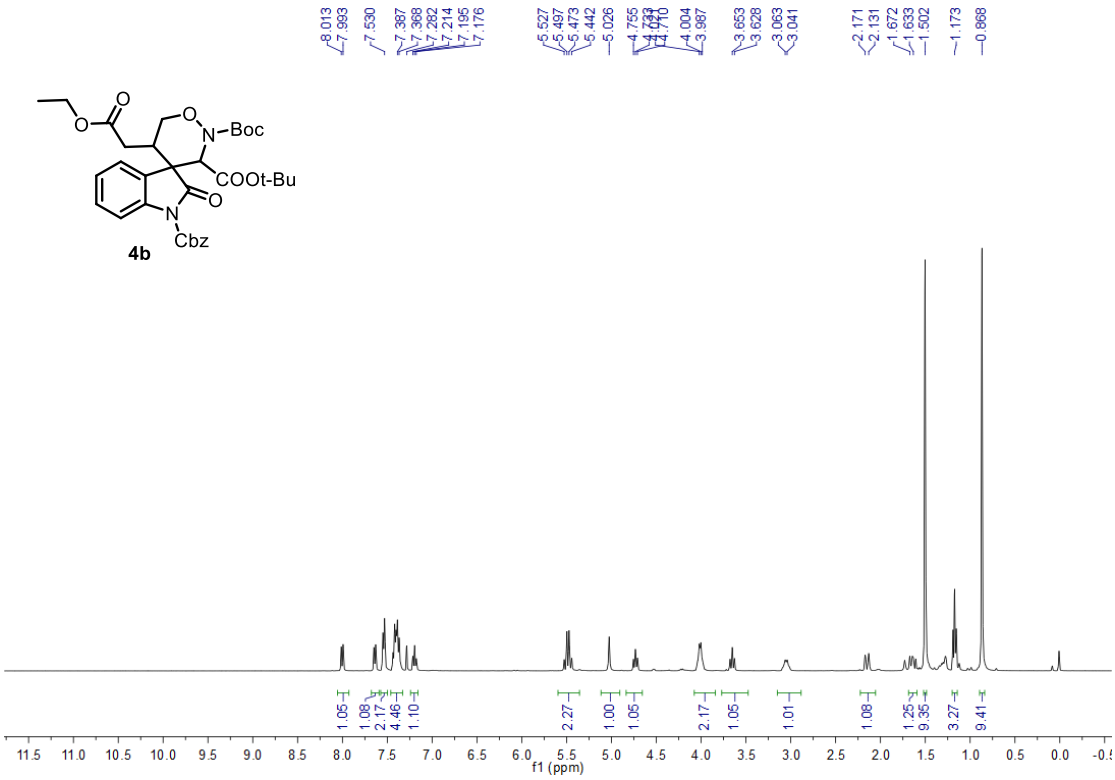
Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
11.073	0.283	5744.892	311.182	95.6481
14.011	0.365	261.389	11.101	4.3519
	Sum	6006.2807		

4. ^{1}H and ^{13}C NMR spectra



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7.176
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5.473
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5.026
4.755
4.733
4.710
4.004
3.987
3.653
3.628
3.063
3.041
2.171
2.131
1.672
1.633
1.502
1.173
0.868
O
O
N
Boc
COOt-Bu
O
N
Cbz
4b
1.05
1.08
2.17
4.46
1.10
2.27
1.00
1.05
2.17
1.05
1.01
1.08
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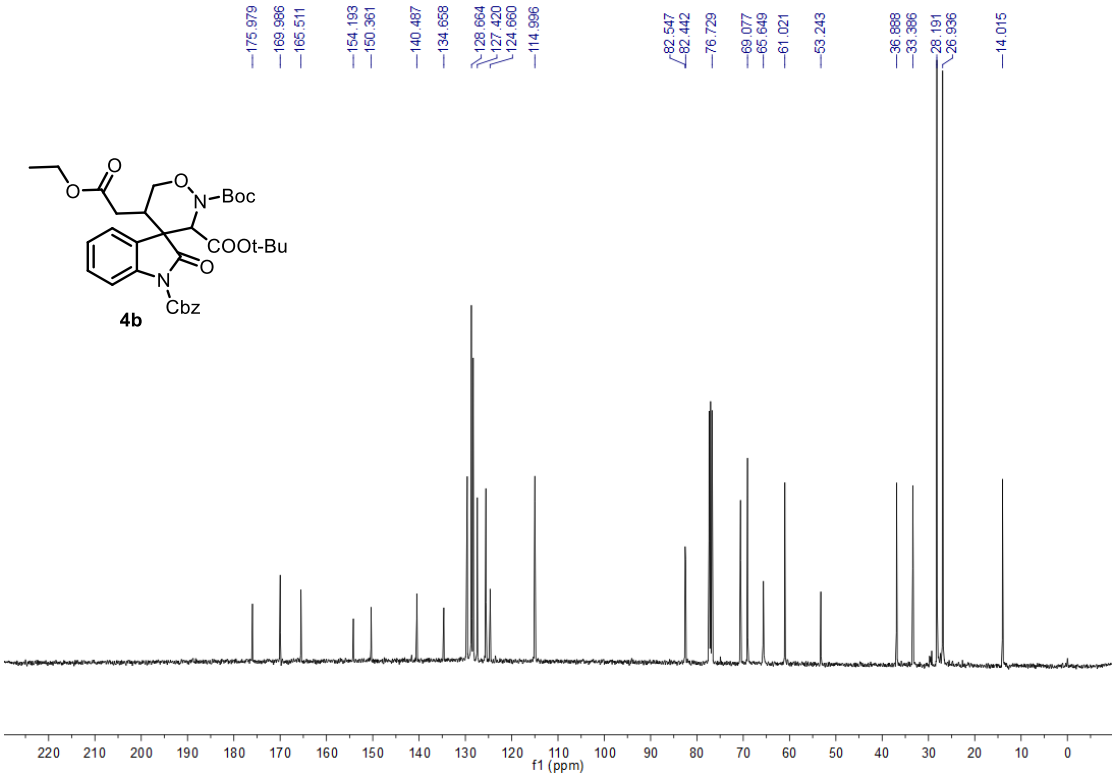
3.27
9.41
f1 (ppm)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82.442
76.729
69.077
65.649
61.021
53.243
36.888
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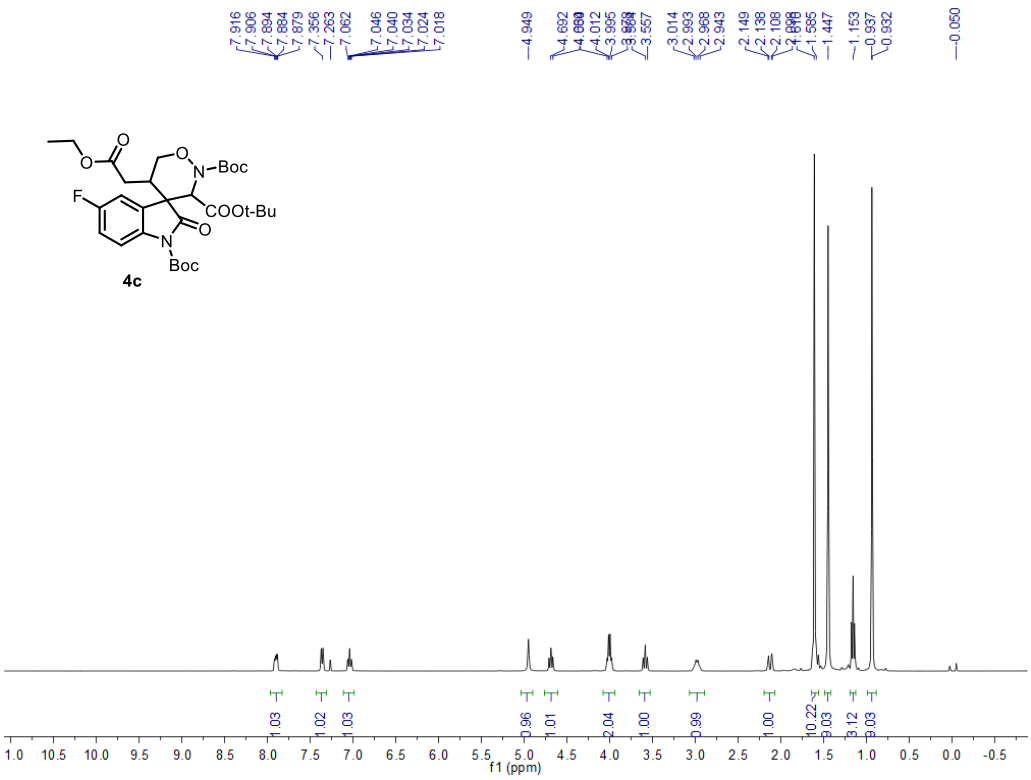
14.015
O
O
N
Boc
COOt-Bu
O
N
Cbz
4b
f1 (ppm)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7.034
7.024
7.018
4.949
4.692
4.012
3.995
3.557
3.014
2.993
2.968
2.943
2.149
2.138
2.108
1.585
1.447
1.153
0.937
0.932
0.050
O
O
N
Boc
F
COOt-Bu
O
N
Boc
4c
1.03
1.02
1.03
0.96
1.01
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1.00
0.99
1.00
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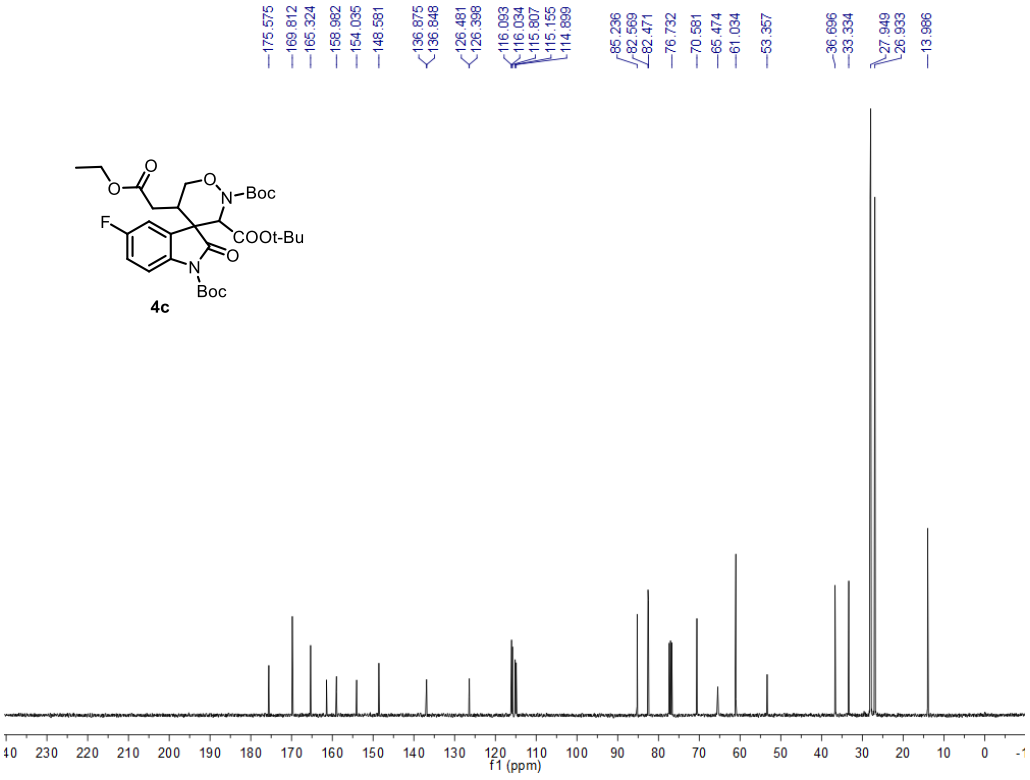
9.03
3.12
9.03
f1 (ppm)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114.899
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82.569
82.471
76.732
70.581
65.474
61.034
53.357
36.696
33.334
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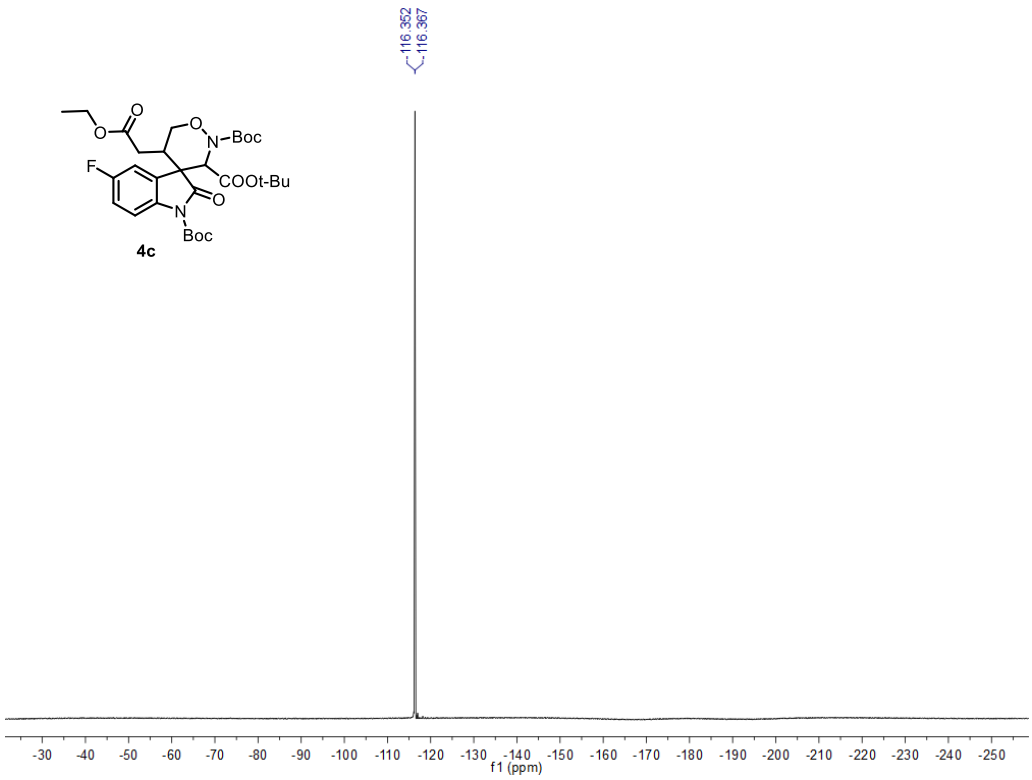
26.933
13.986
O
O
N
Boc
F
COOt-Bu
O
N
Boc
4c
f1 (ppm)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116.367
O
O
O
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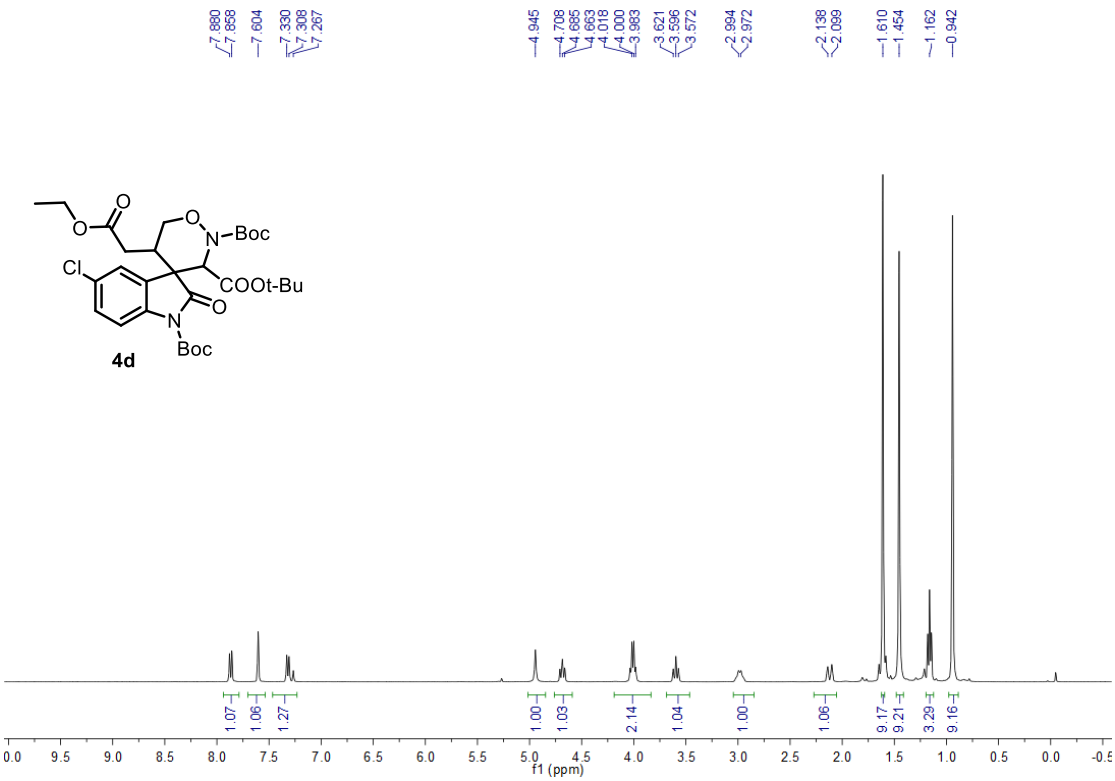
F
COOt-Bu
O
N
Boc
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

4c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4.018
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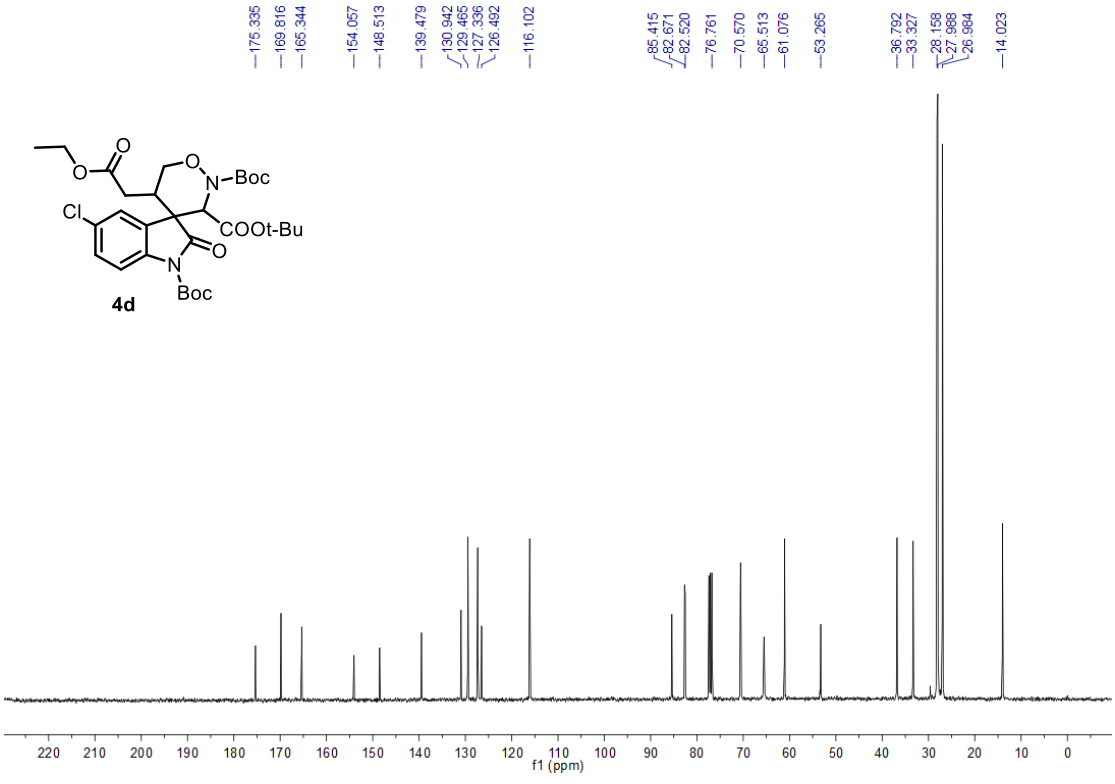
3.983
3.621
3.596
3.572
2.994
2.972
2.138
2.099
1.610
1.454
1.162
0.942
O
O
O
N
Boc
Cl
COOt-Bu
O
N
Boc
4d
1.07
1.06
1.27
1.00
1.03
2.14
1.04
1.00
1.06
9.17
9.21
3.29
9.16
f1 (ppm)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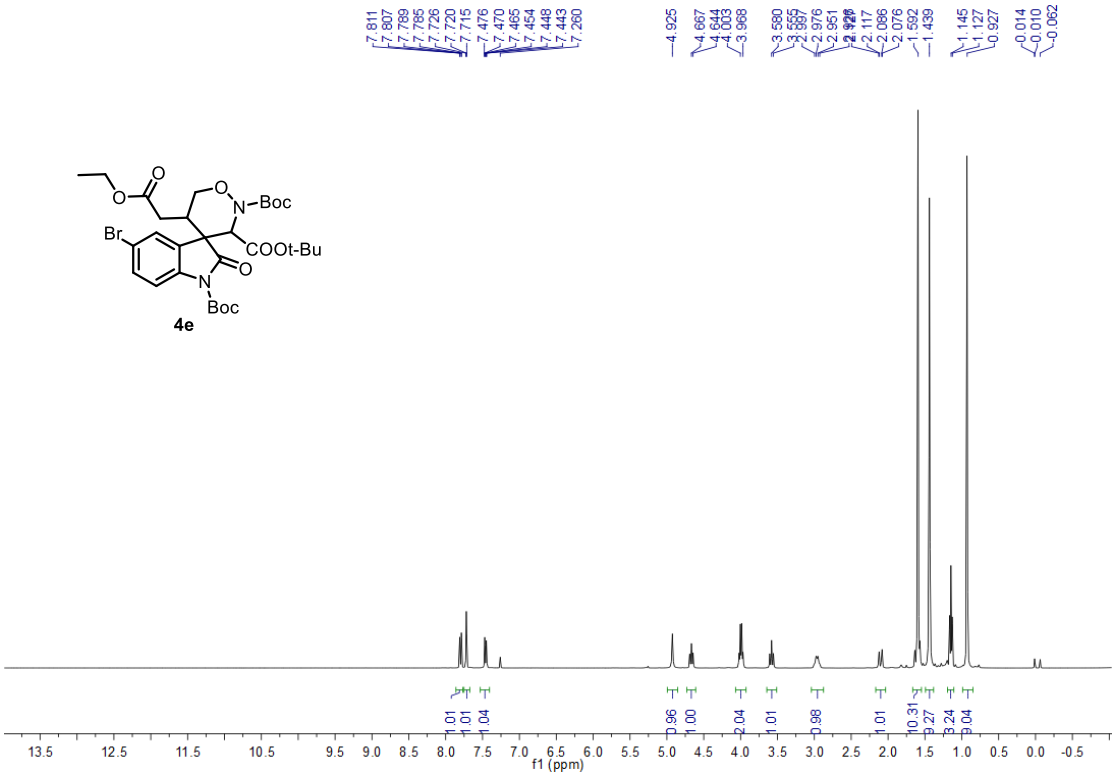
129.465
127.336
126.492
116.102
85.415
82.671
82.520
76.761
70.570
65.513
61.076
53.265
36.792
33.327
28.158
27.988
26.984
14.023
O
O
O
N
Boc
Cl
COOt-Bu
O
N
Boc
4d
f1 (ppm)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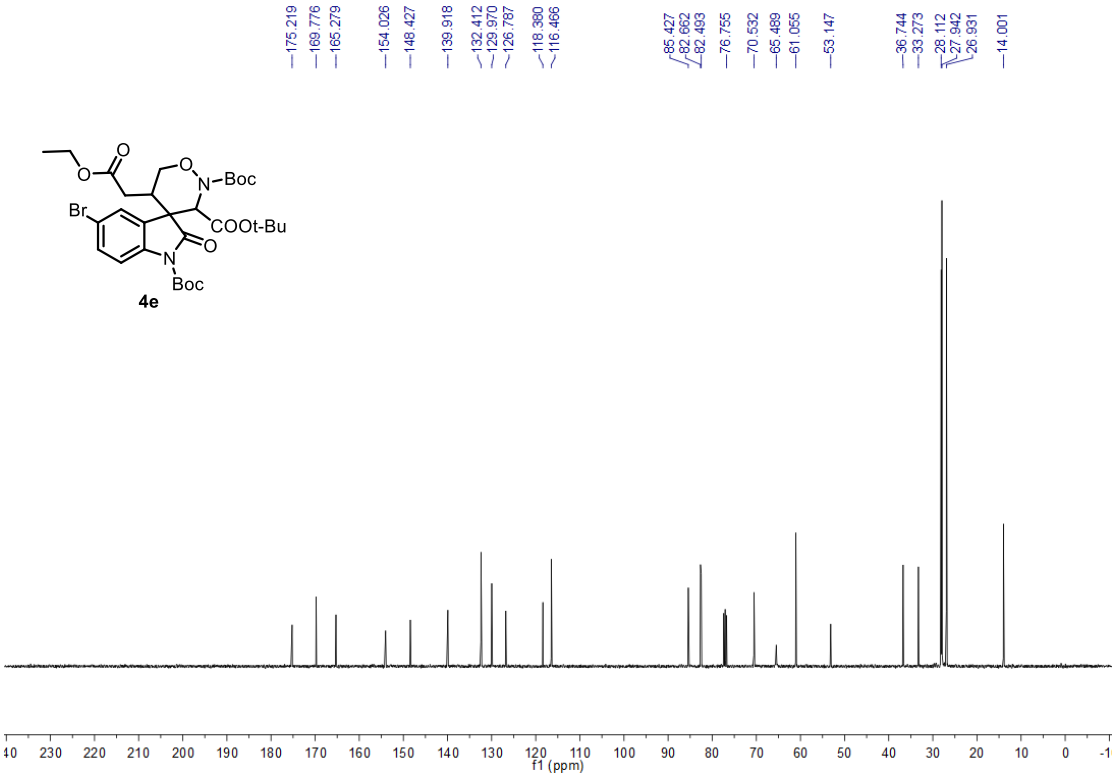
7.789
7.785
7.726
7.720
7.715
7.476
7.470
7.465
7.454
7.448
7.443
7.260
4.925
4.667
4.644
4.003
3.988
3.580
3.555
2.997
2.976
2.951
2.117
2.086
2.076
1.592
1.439
1.145
1.127
0.927
0.014
0.010
0.062
Br
O
N-Boc
COOt-Bu
N
Boc
4e
1.01
1.01
1.04
0.96
1.00
2.04
1.01
0.98
1.01
10.31
9.27
3.24
9.04
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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129.970
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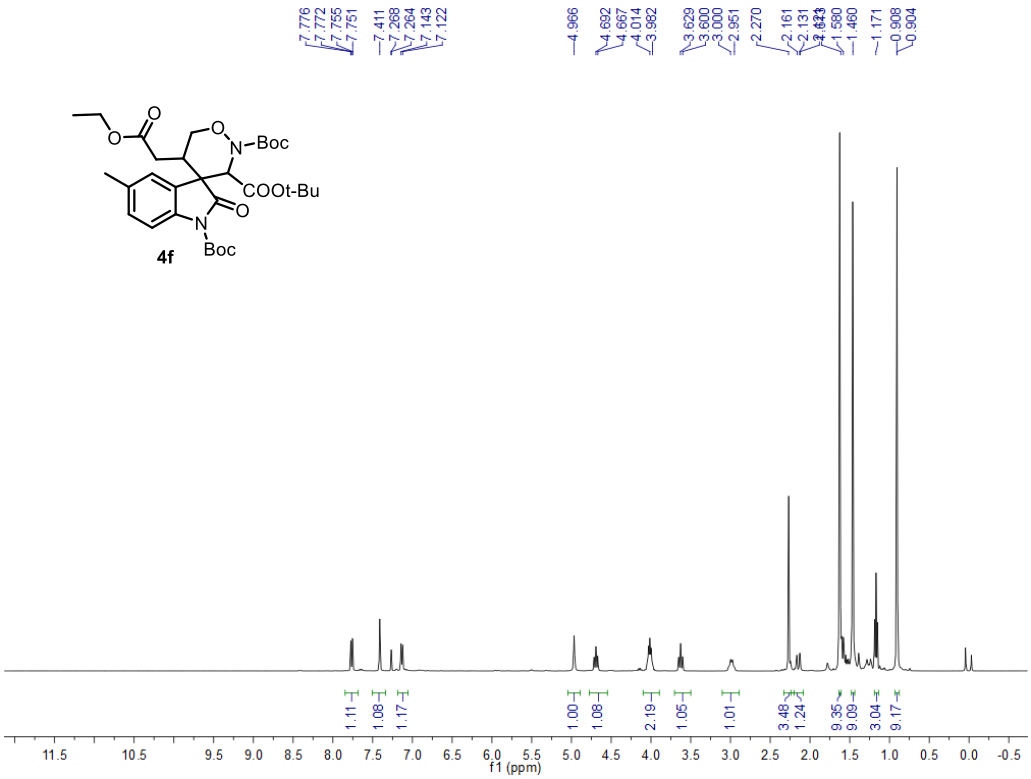
82.662
82.493
76.755
70.532
65.489
61.055
53.147
36.744
33.273
28.112
27.942
26.931
14.001
Br
O
N-Boc
COOt-Bu
N
Boc
4e
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.143
7.122
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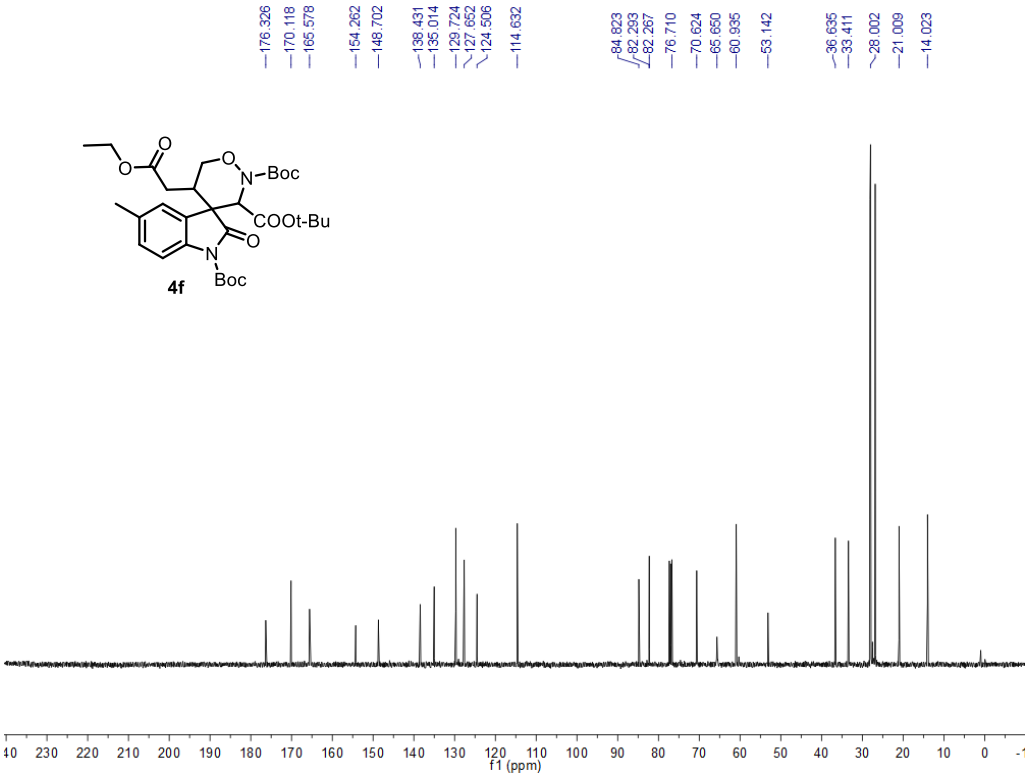
4.692
4.667
4.014
3.982
3.629
3.600
3.000
2.951
2.270
2.161
2.131
1.580
1.460
1.171
0.908
0.904
Boc
COOt-Bu
Boc
4f
1.11
1.08
1.17
1.00
1.08
2.19
1.05
1.01
3.48
1.24
9.35
9.09
3.04
9.17
f1 (ppm)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84.823
82.293
82.267
76.710
70.624
65.650
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33.411
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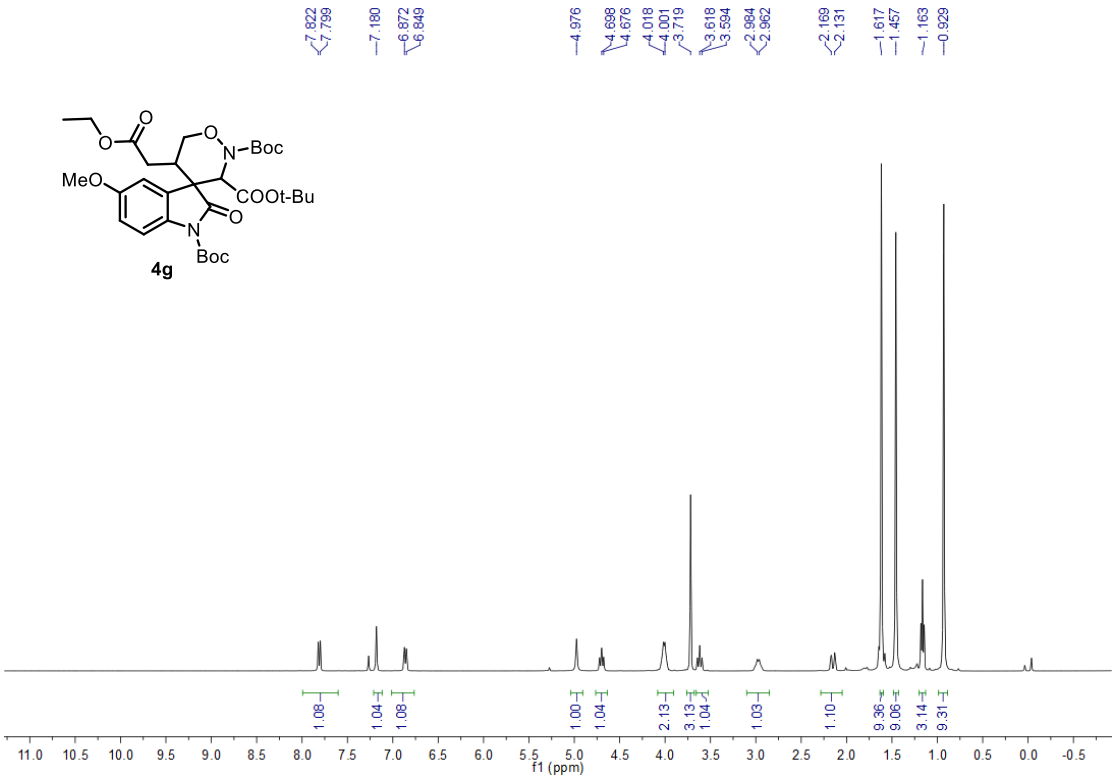
21.009
14.023
Boc
COOt-Bu
Boc
4f
f1 (ppm)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4.001
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3.618
3.594
2.984
2.962
2.169
2.131
1.617
1.457
1.163
0.929
MeO
Boc
COOt-Bu
Boc
4g
1.08
1.04
1.08
1.00
1.04
2.13
3.13
1.04
1.03
1.10
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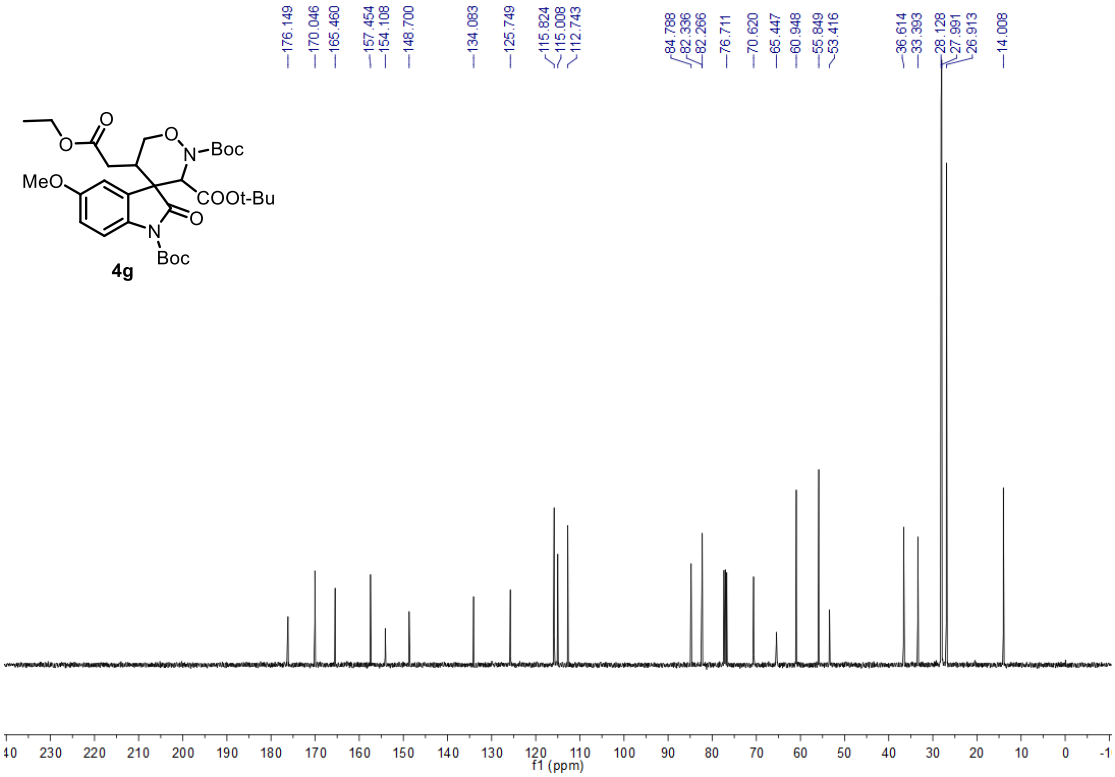
9.06
3.14
9.31
f1 (ppm)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125.749
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115.008
112.743
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82.336
82.266
76.711
70.620
65.447
60.948
55.849
53.416
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27.991
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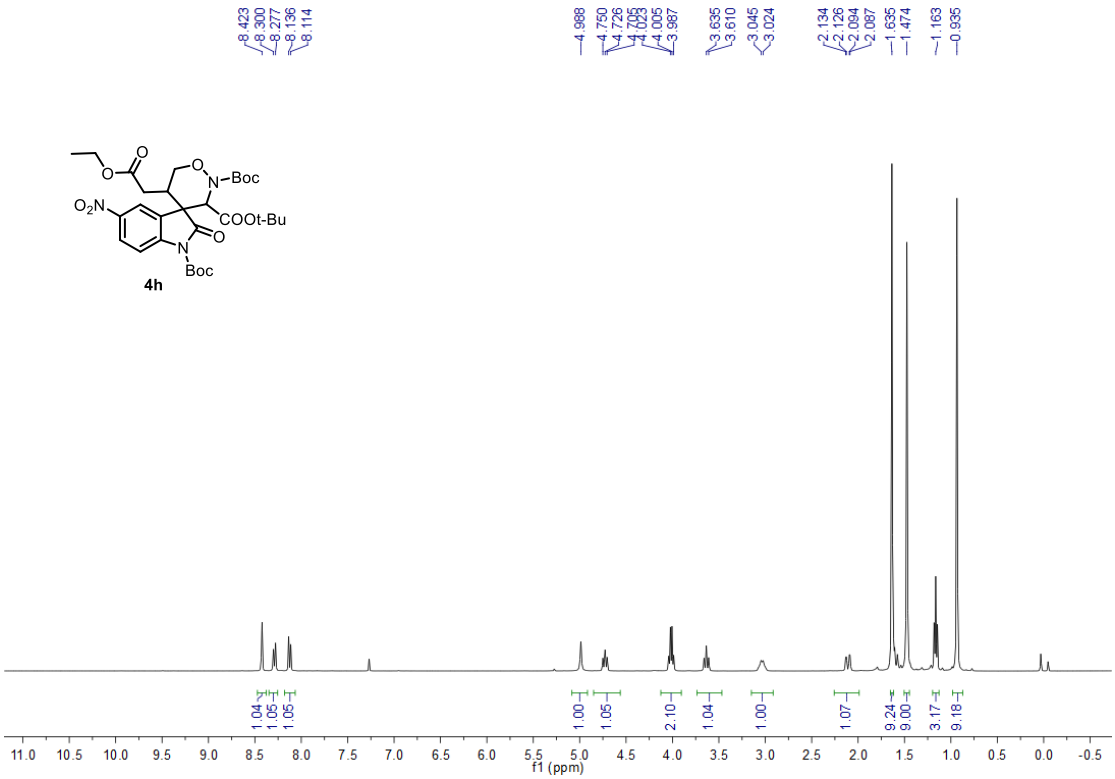
MeO
Boc
COOt-Bu
Boc
4g
f1 (ppm)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3.987
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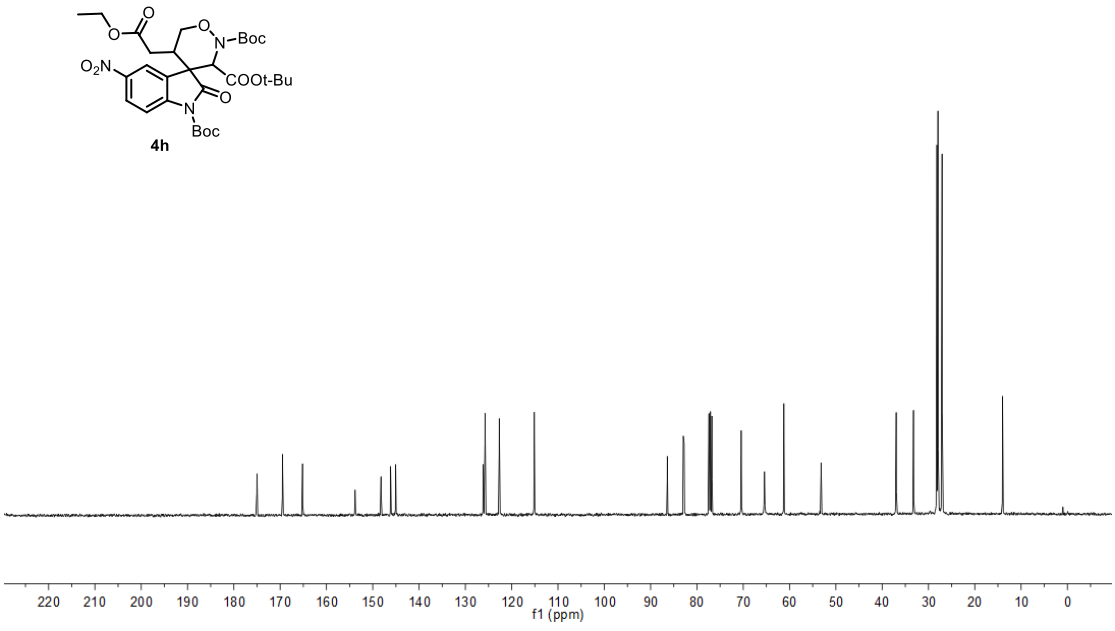
3.610
3.045
3.024
2.134
2.126
2.094
2.087
1.635
1.474
1.163
0.935
Boc
COOt-Bu
Boc
4h
1.04
1.05
1.05
1.00
1.05
2.10
1.04
1.00
1.07
9.24
9.00
3.17
9.18
f1 (ppm)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76.758
70.440
65.408
61.232
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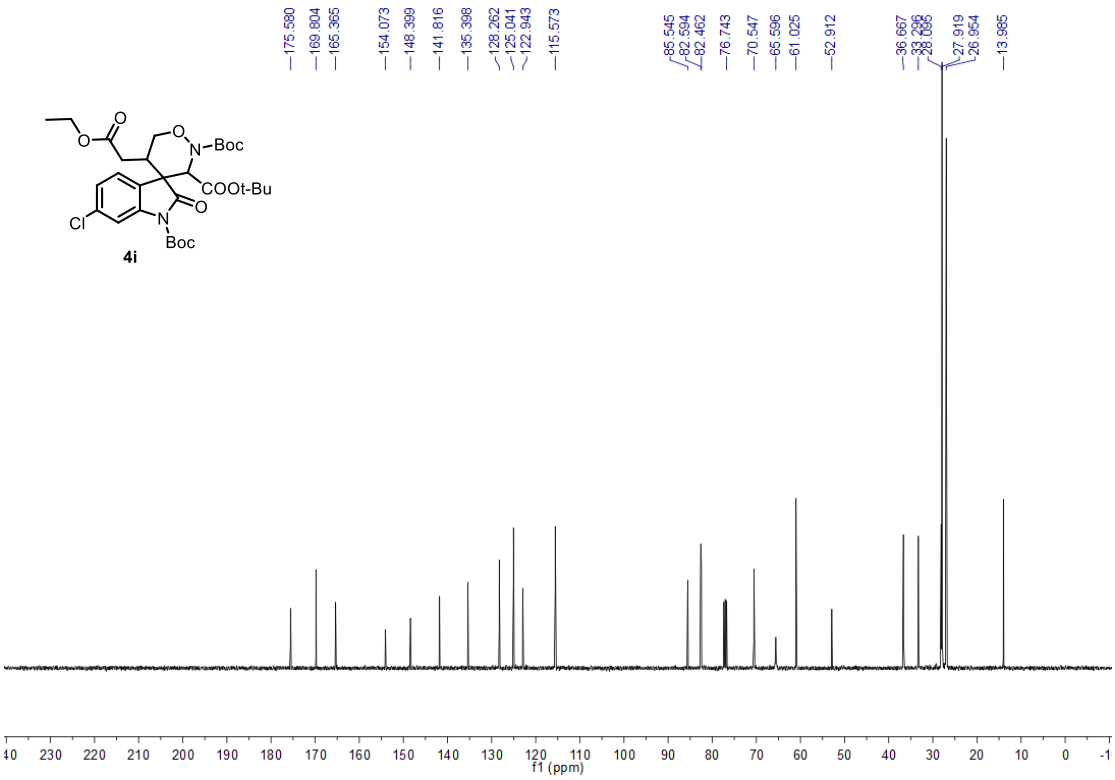
28.183
27.947
27.059
13.998
Boc
COOt-Bu
Boc
4h
f1 (ppm)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128.262
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85.545
82.594
82.462
76.743
70.547
65.596
61.025
52.912
36.667
33.296
28.095
27.919
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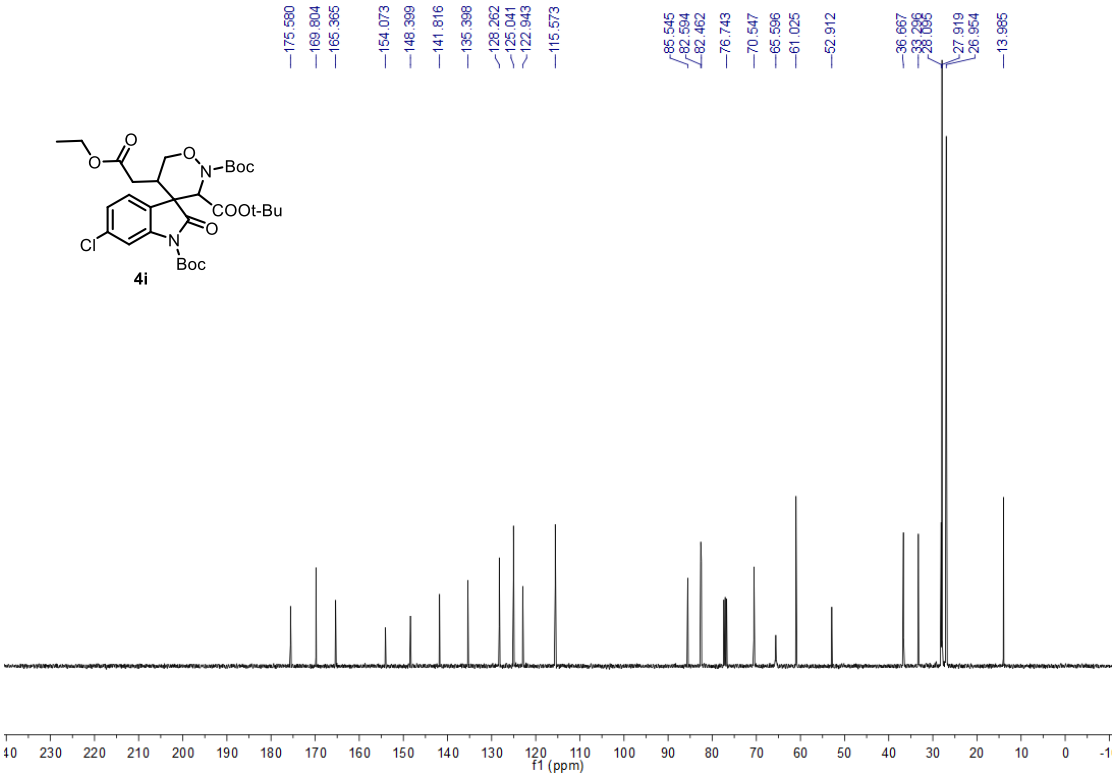
O
O
O
N
Boc
COOt-Bu
O
Cl
N
Boc
4i
f1 (ppm)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154.073
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141.816
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122.943
115.573
85.545
82.594
82.462
76.743
70.547
65.596
61.025
52.912
36.667
33.296
28.095
27.919
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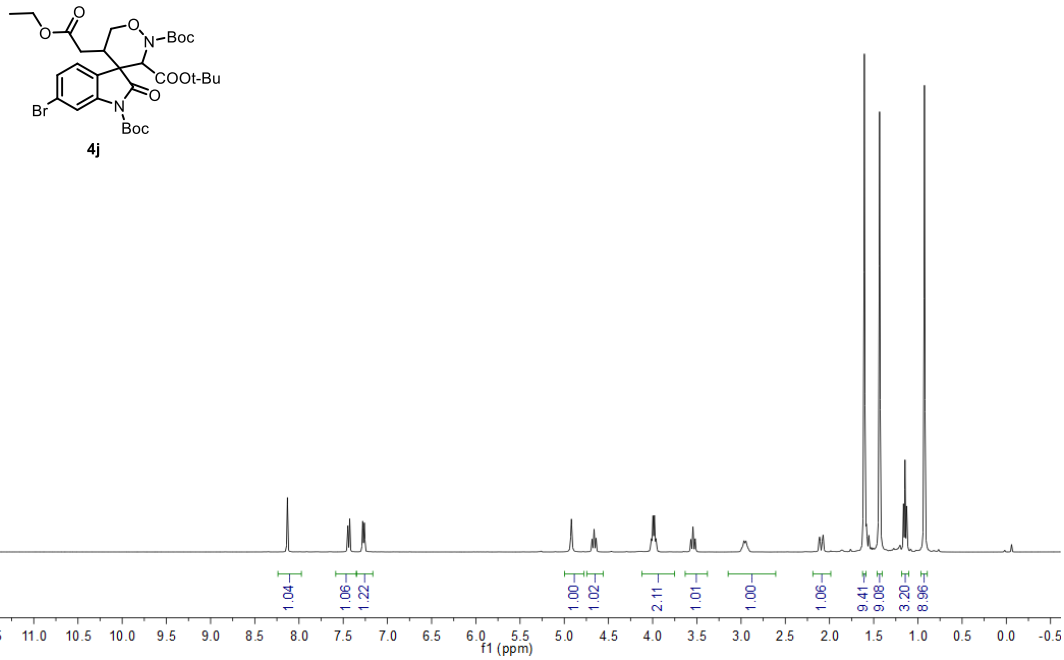
O
O
N
Boc
COOt-Bu
O
Cl
N
Boc
4i
f1 (ppm)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2.944
2.080
2.073
1.579
1.433
1.128
0.926
0.059
Boc
COOt-Bu
Br
Boc
4j
1.04
1.06
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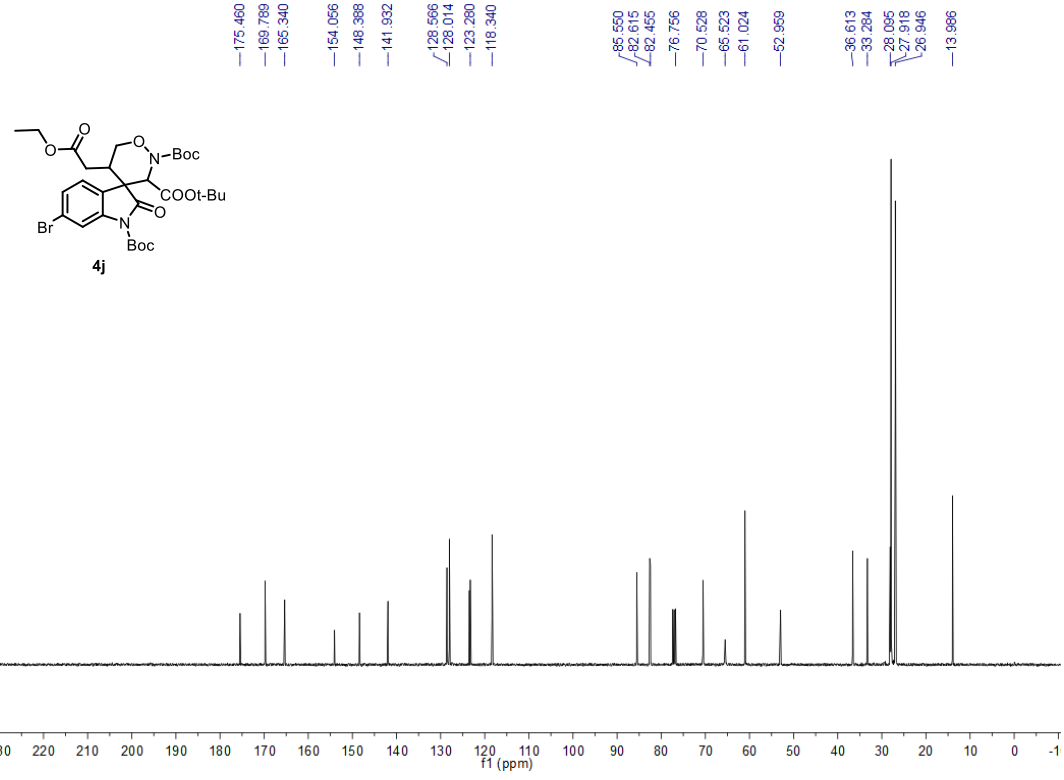
1.02
2.11
1.01
1.00
1.06
9.41
9.08
3.20
8.96
f1 (ppm)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27.918
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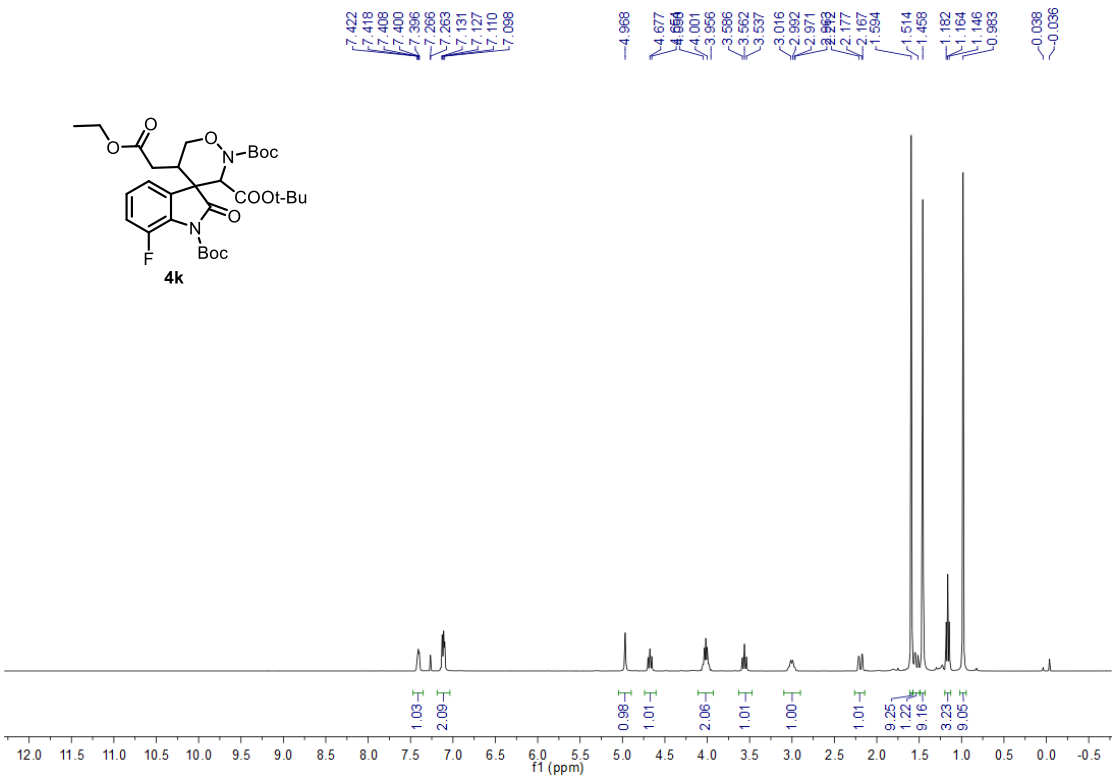
13.986
Boc
COOt-Bu
Br
Boc
4j
f1 (ppm)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7.131
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7.110
7.098
4.968
4.677
4.001
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3.596
3.562
3.537
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2.971
2.177
2.167
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1.514
1.458
1.182
1.164
1.146
0.983
0.038
0.036
O
O
N
Boc
COOt-Bu
O
N
Boc
F
4k
1.03
2.09
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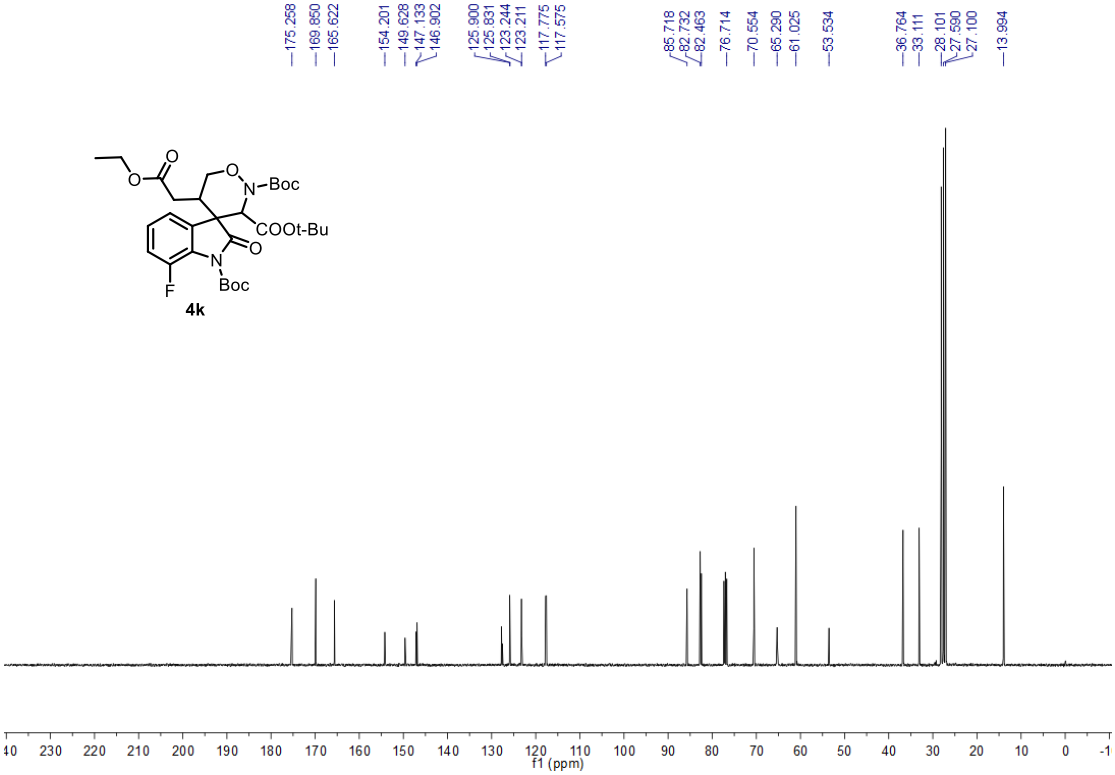
1.01
2.06
1.01
1.00
1.01
9.25
1.22
9.16
3.23
9.05
f1 (ppm)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123.211
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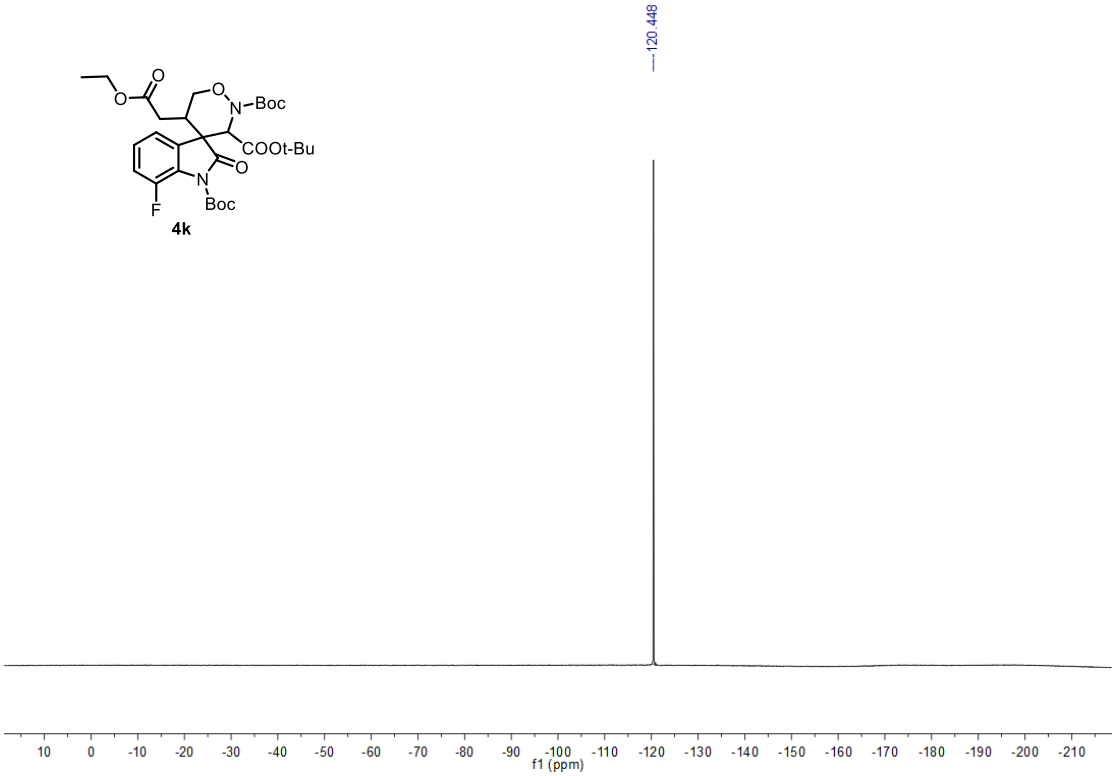
117.575
85.718
82.732
82.463
76.714
70.554
65.290
61.025
53.534
36.764
33.111
28.101
27.590
27.100
13.994
O
O
N
Boc
COOt-Bu
O
N
Boc
F
4k
f1 (ppm)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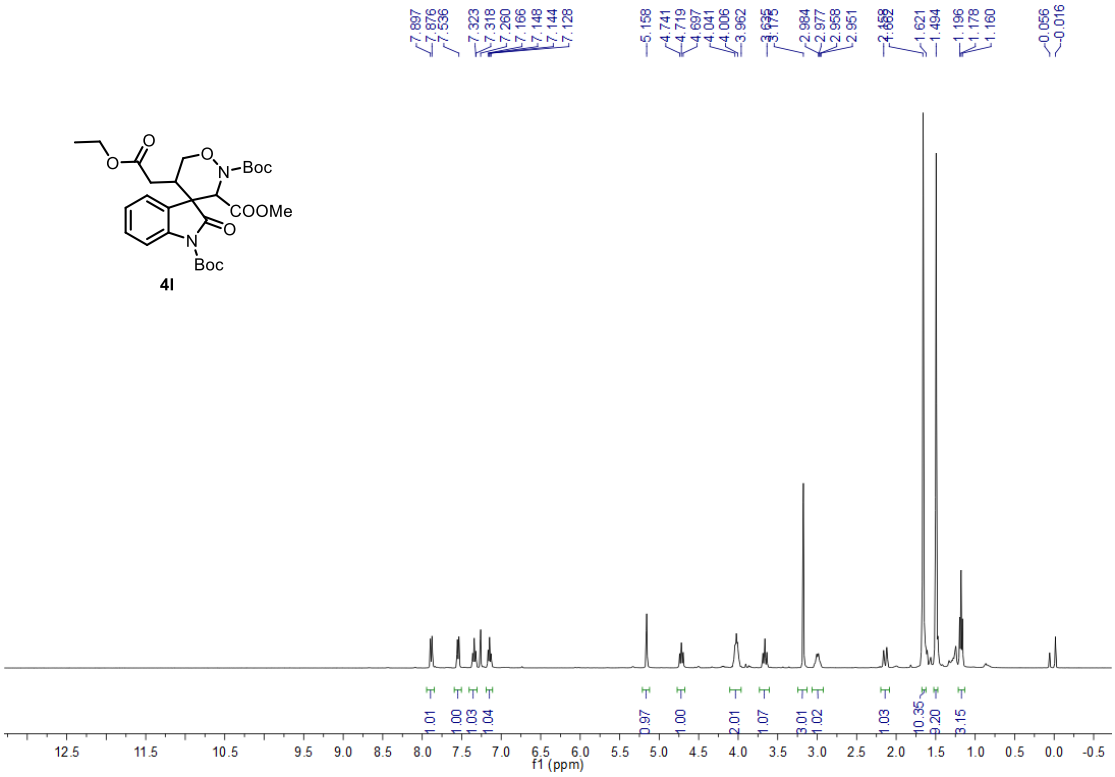
O
O
N
Boc
COOt-Bu
O
N
Boc
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

4k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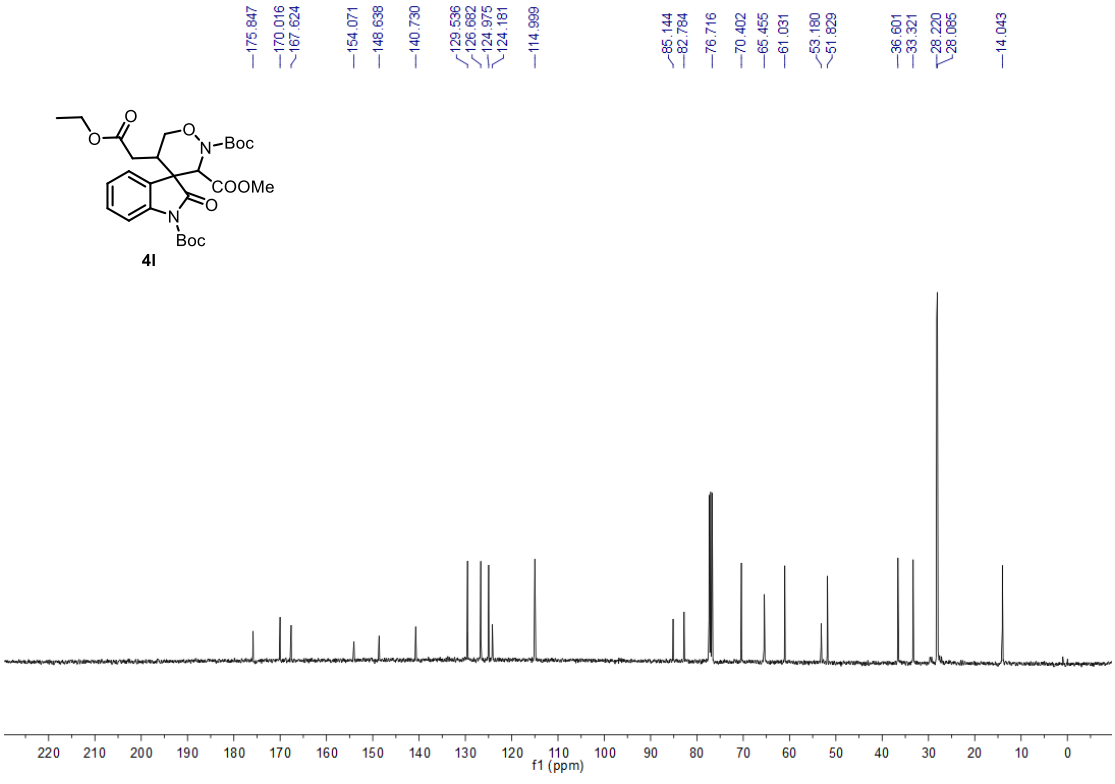
4.719
4.697
4.041
4.006
3.962
3.635
3.175
2.984
2.977
2.958
2.951
2.168
2.082
1.621
1.494
1.196
1.178
1.160
0.056
0.016
Boc
COOMe
Boc
4l
1.01
1.00
1.03
1.04
0.97
1.00
2.01
1.07
3.01
1.02
1.03
10.35
9.20
3.15
f1 (ppm)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124.181
114.999
85.144
82.784
76.716
70.402
65.455
61.031
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28.085
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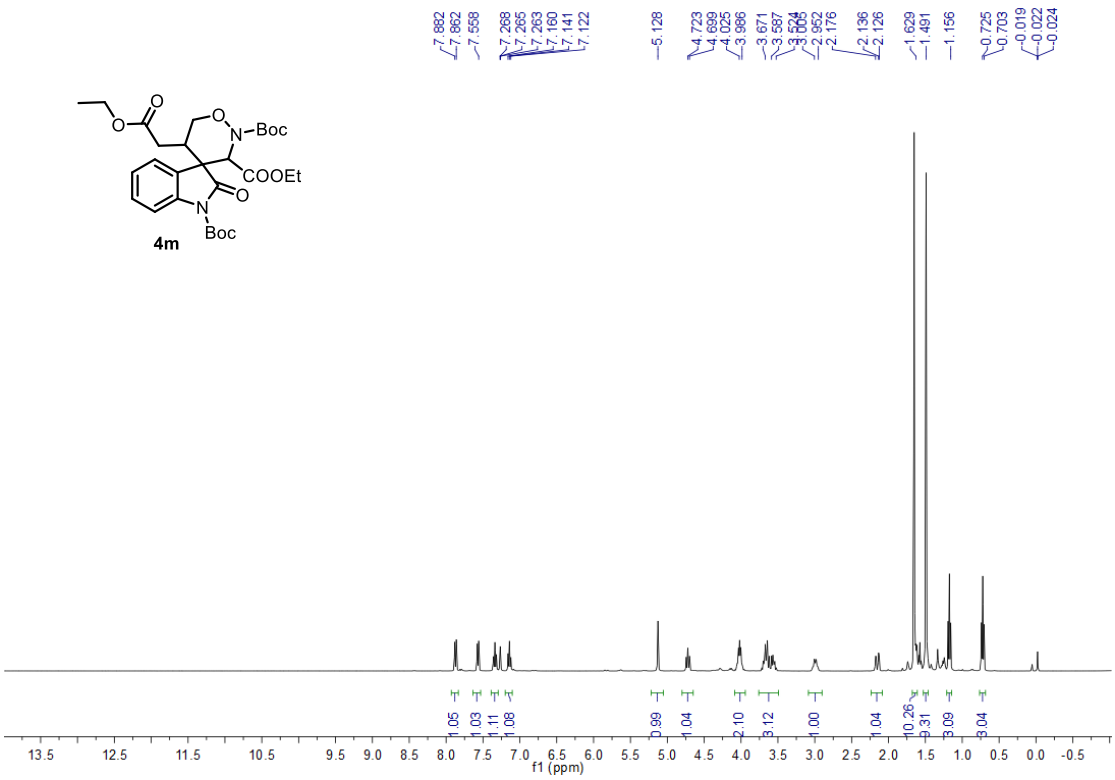
Boc
COOMe
Boc
4l
f1 (ppm)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3.671
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3.605
2.952
2.176
2.136
2.126
1.629
1.491
1.156
0.725
0.703
0.019
0.022
0.024
1.05
1.03
1.11
1.08
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2.10
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1.00
1.04
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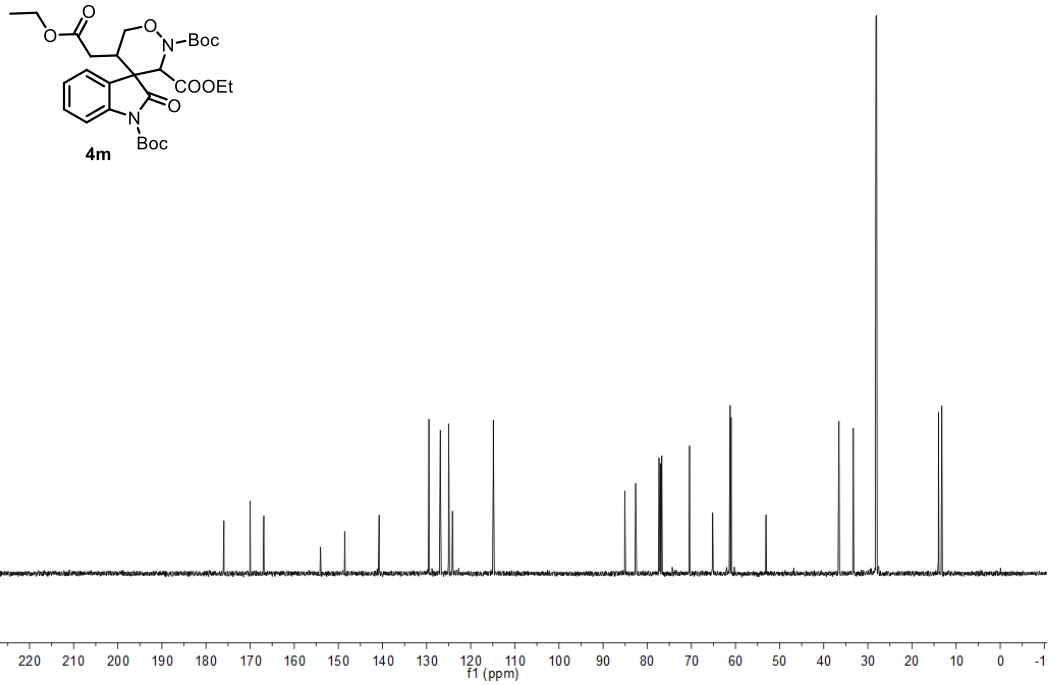
3.09
3.04
f1 (ppm)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28.104
27.956
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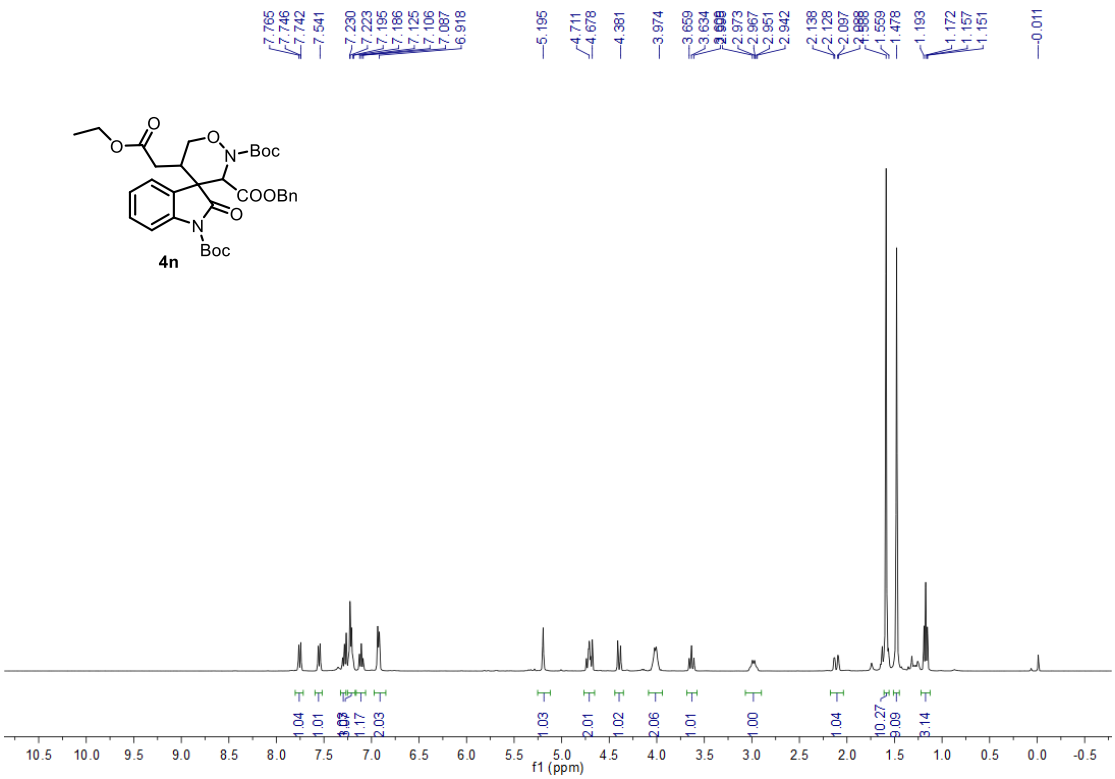
13.237
f1 (ppm)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4.678
4.381
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3.659
3.634
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2.951
2.942
2.138
2.128
2.097
1.559
1.478
1.193
1.172
1.157
1.151
0.011
Boc
COOBn
Boc
4n
1.04
1.01
1.17
2.03
1.03
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1.02
2.06
1.01
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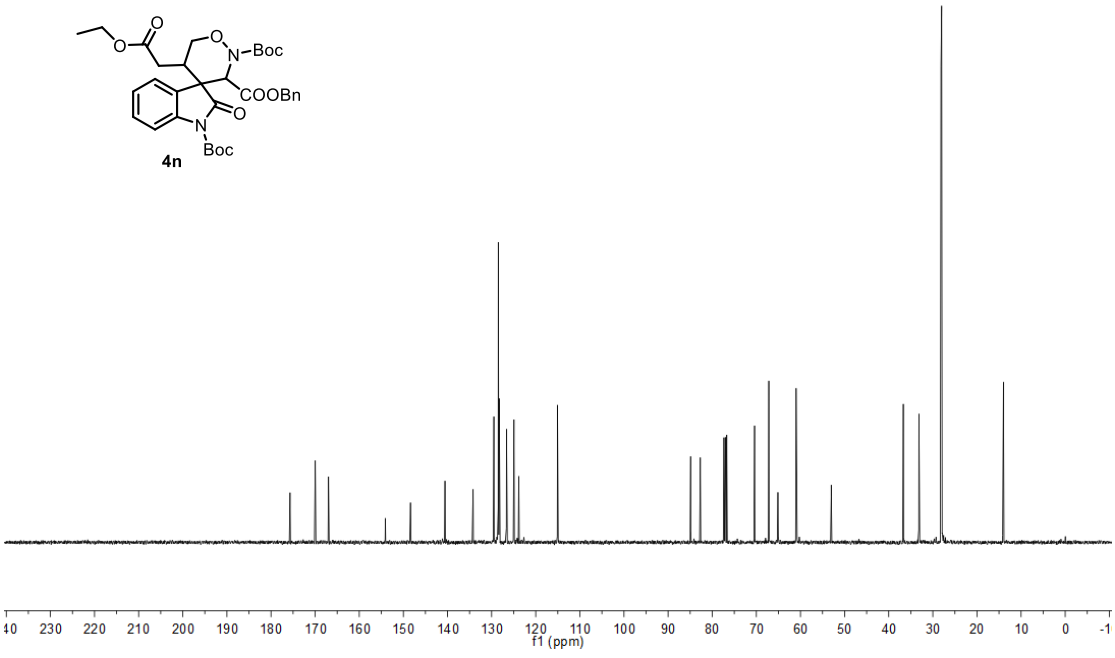
1.04
10.27
9.09
3.14
f1 (ppm)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65.112
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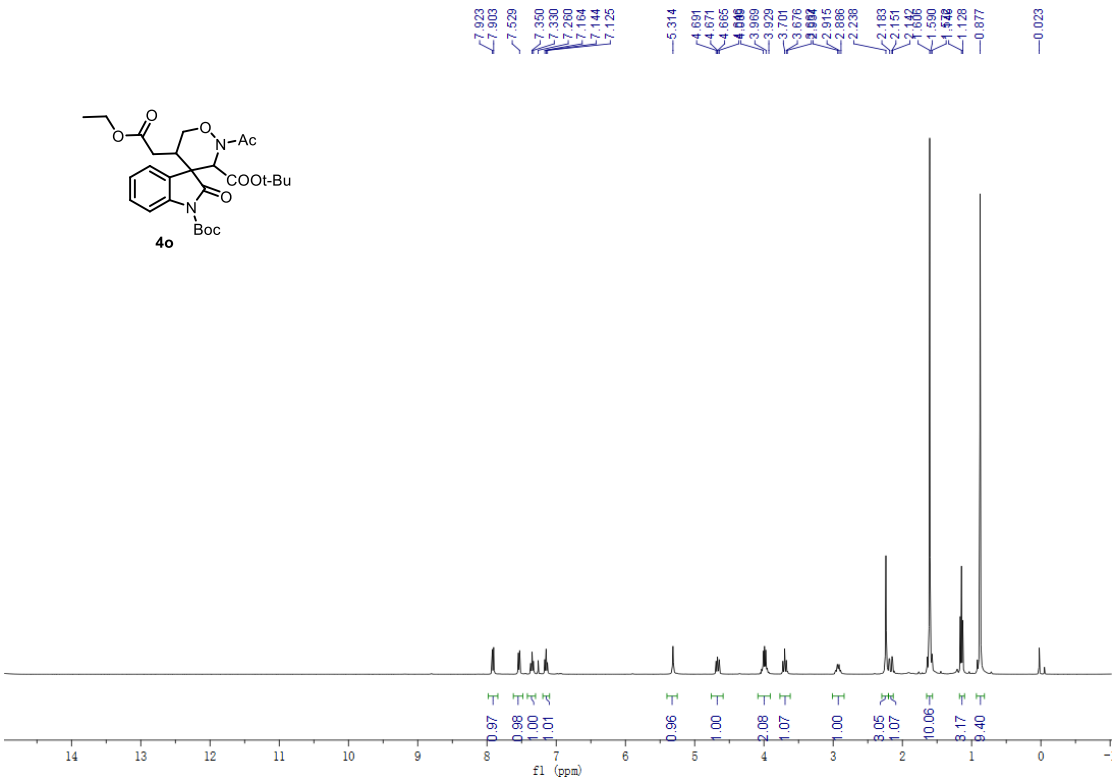
Boc
COOBn
Boc
4n
f1 (ppm)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4.671
4.665
3.969
3.929
3.701
3.676
2.915
2.886
2.238
2.183
2.151
2.142
2.006
1.590
1.128
0.877
0.023
O
O
N
Ac
COOt-Bu
O
N
Boc
4o
0.97
0.98
1.00
1.01
0.96
1.00
2.08
1.07
1.00
3.05
1.07
10.06
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12
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5
4
3
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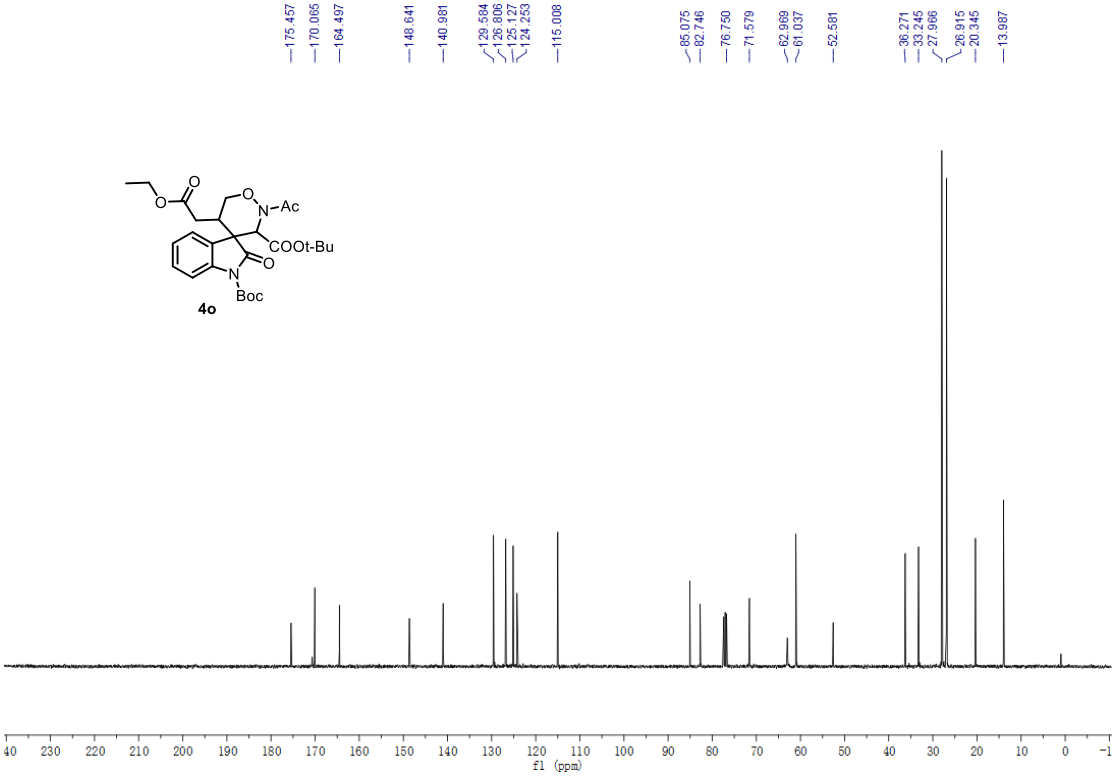
1
0
f1 (ppm)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52.581
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33.245
27.966
26.915
20.345
13.987
O
O
N
Ac
COOt-Bu
O
N
Boc
4o
40
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220
210
200
190
180
170
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120
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40
30
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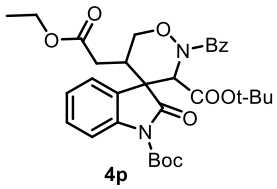
0
-1
f1 (ppm)


O
O
O
N
Bz
COOt-Bu
O
N
Boc

4p

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7.831
7.813
7.587
7.457
7.415
7.391
7.352
7.179
7.141
5.588
4.547
3.981
3.918
3.627
3.005
2.996
2.977
2.229
2.220
1.614
1.123
0.930
1.05
2.02
1.08
4.23
1.10
0.91
0.93
2.09
0.99
1.00
1.04
10.14
3.14
9.07
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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0.0
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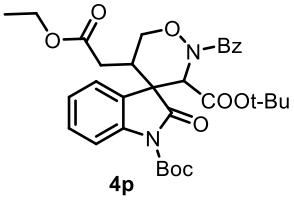
O
O
O
N
Bz
COOt-Bu
O
N
Boc

4p

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63.580
61.032
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220
210
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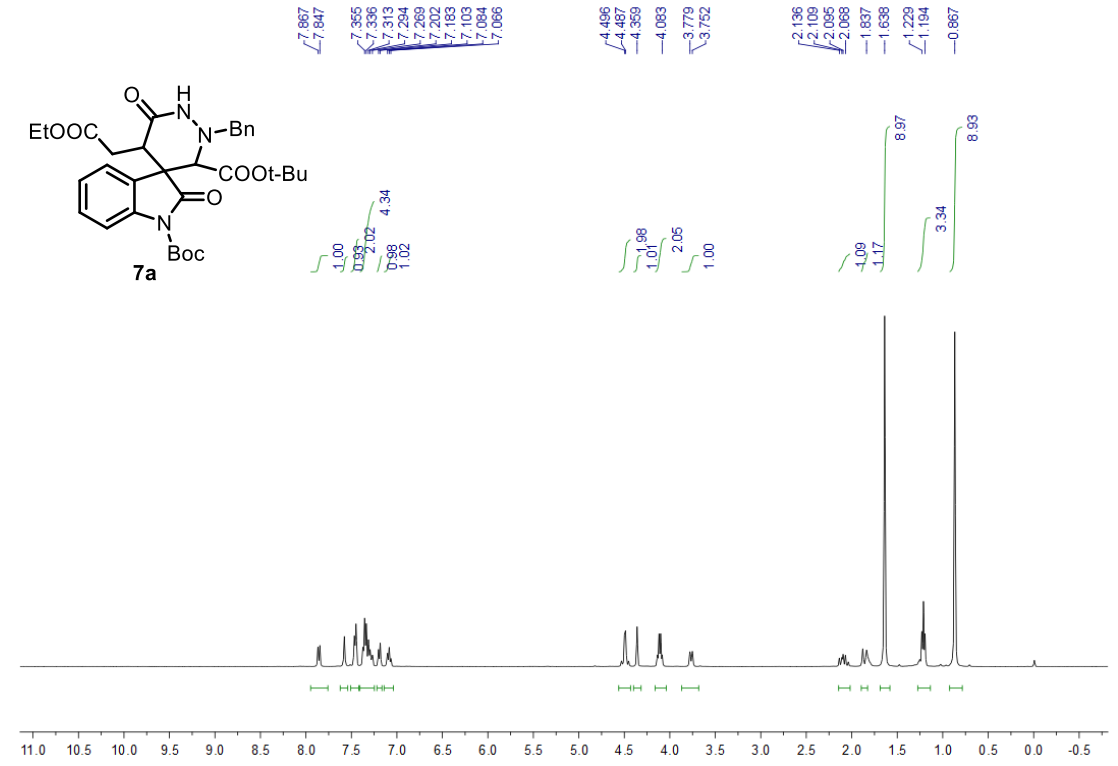
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7.066
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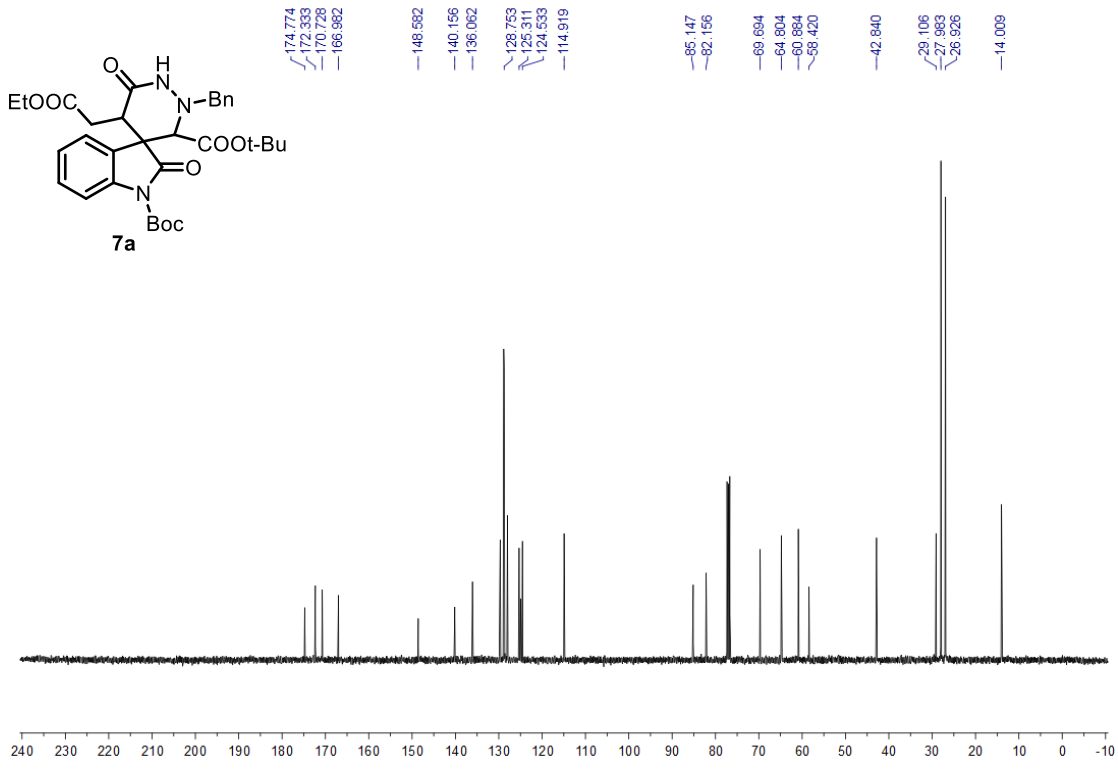
4.487
4.359
4.083
3.779
3.752
2.136
2.109
2.095
2.066
1.837
1.638
1.229
1.194
0.867
EtOOC
Bn
COOt-Bu
Boc
7a
1.00
0.93
2.02
4.34
0.98
1.02
1.98
1.01
2.05
1.00
1.09
1.17
8.97
3.34
8.93
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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69.694
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60.884
58.420
42.840
29.106
27.983
26.926
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Bn
COOt-Bu
Boc
7a
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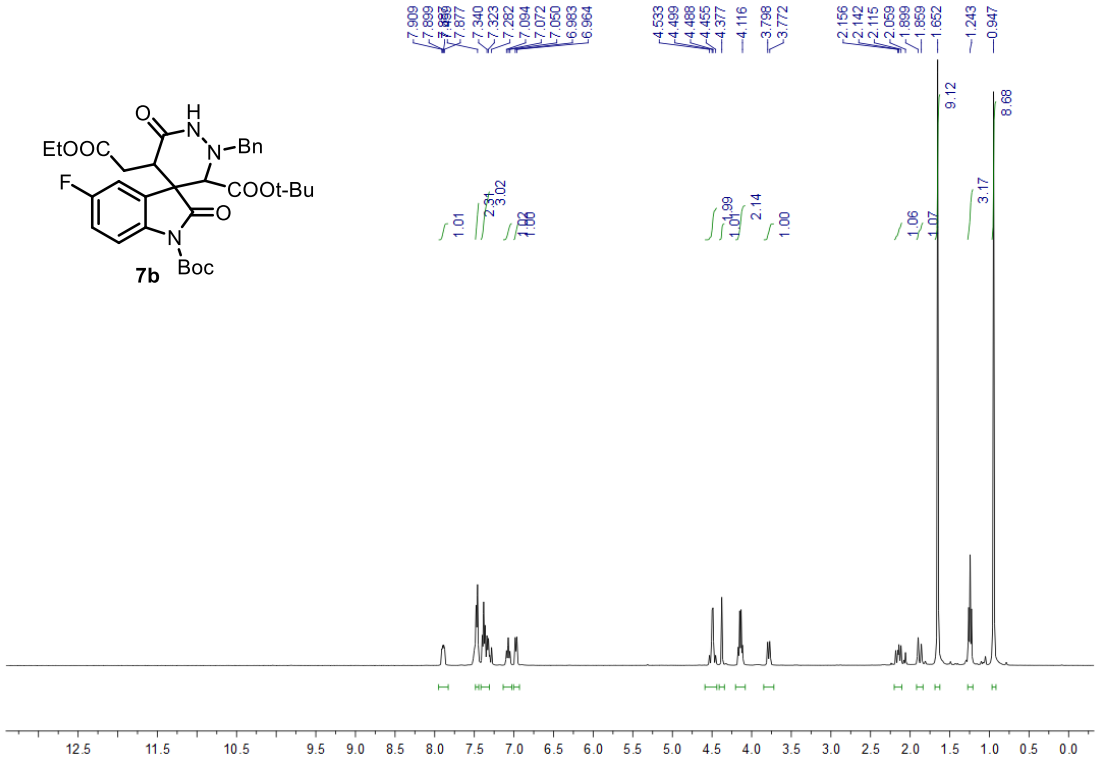
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4.377
4.116
3.798
3.772
2.156
2.142
2.115
2.059
1.899
1.859
1.652
1.243
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8.68
3.17
2.31
3.02
1.99
2.14
1.00
1.06
1.07
1.01
EtOOC
F
O
H
N
N
Bn
COOt-Bu
O
N
Boc
7b
12.5
11.5
10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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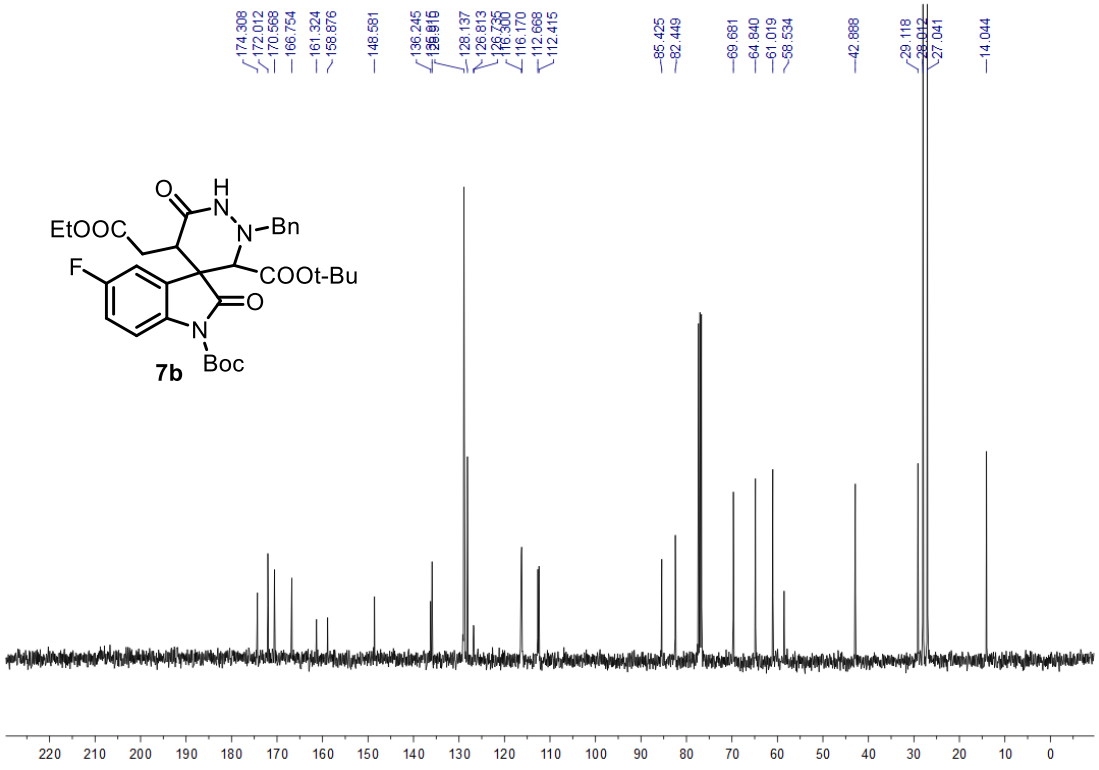
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64.840
61.019
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29.118
28.012
27.041
14.044
EtOOC
F
O
H
N
N
Bn
COOt-Bu
O
N
Boc
7b
220
210
200
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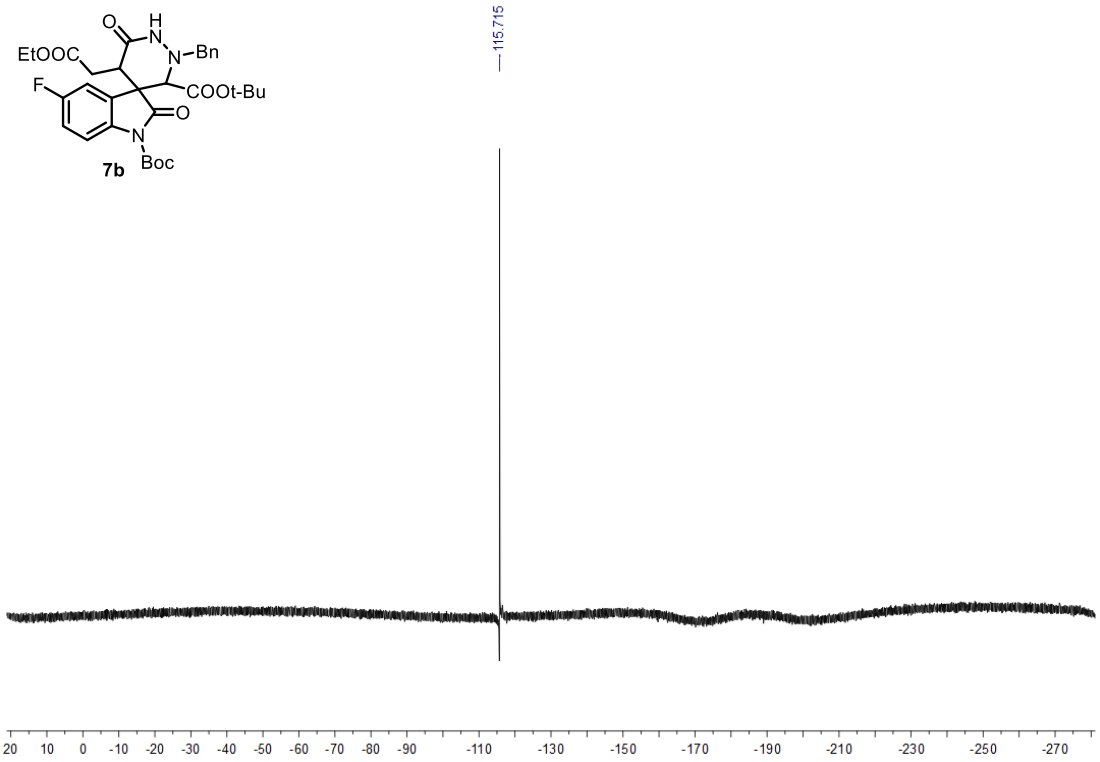
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Bn
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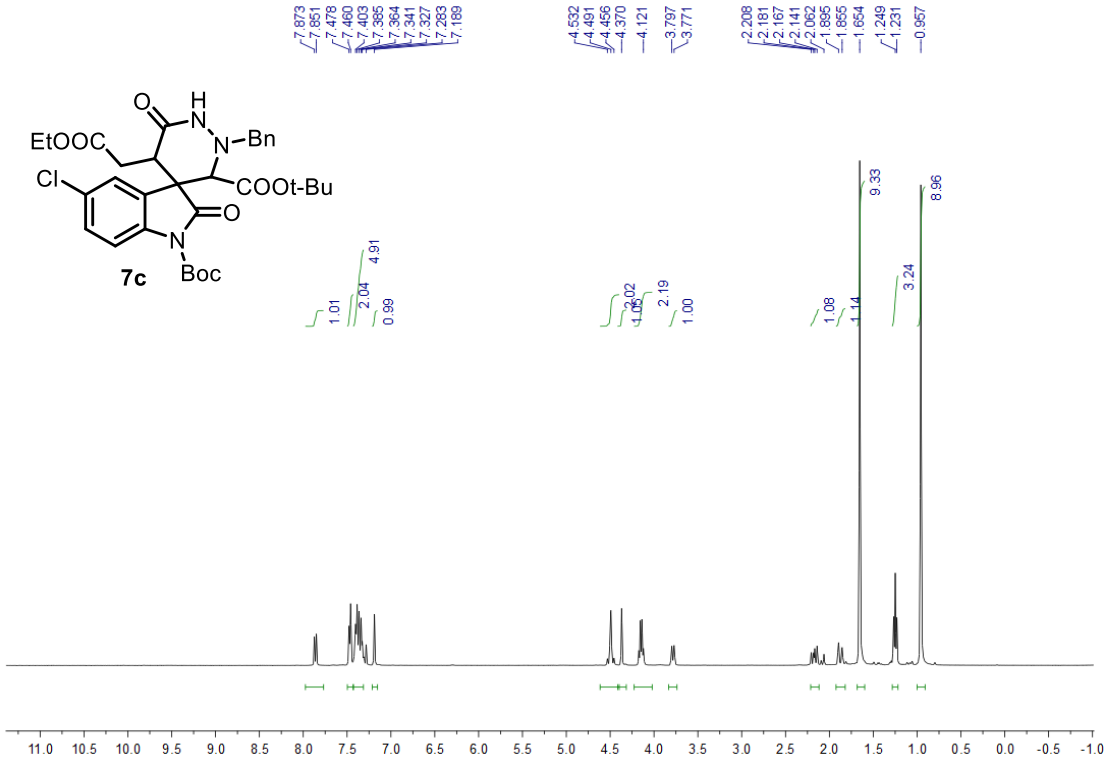
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Cl
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Bn
COOt-Bu
O
N
Boc
7c
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9.33
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7.0
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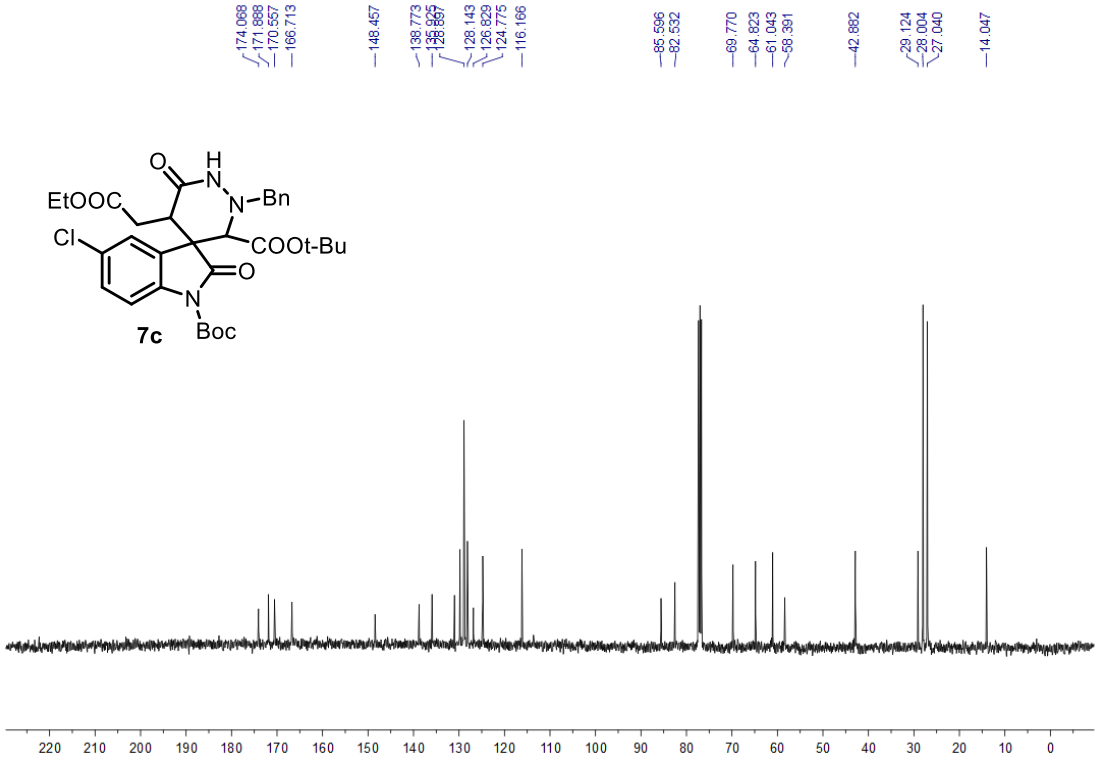
-1.0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H
O
N
Bn
COOt-Bu
O
N
Boc
7c
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210
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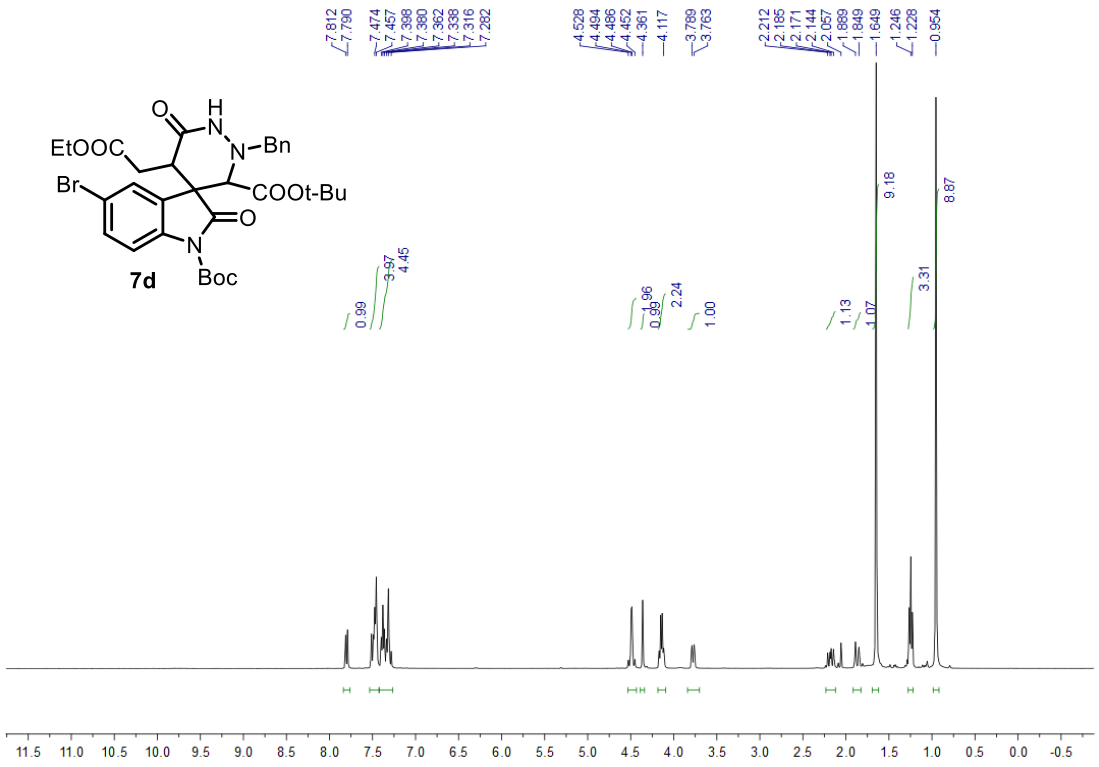
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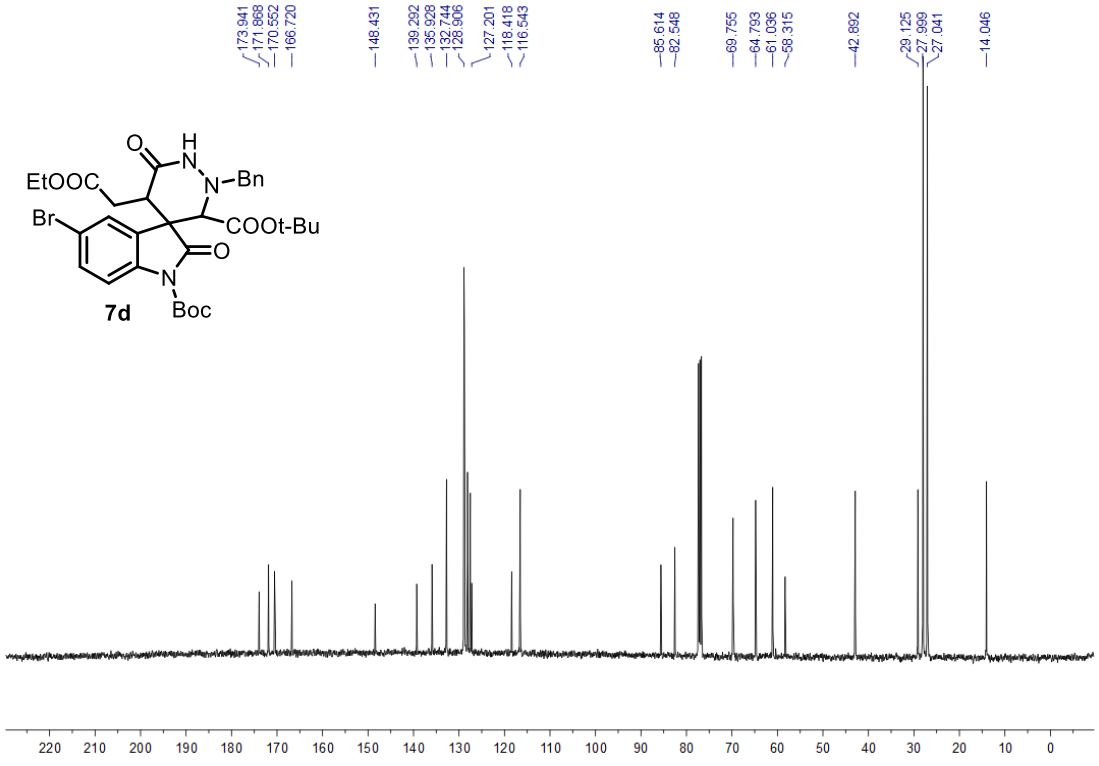
1.13
1.07
3.31
EtOOC
Br
Bn
COOt-Bu
Boc
7d
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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Bn
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Boc
7d
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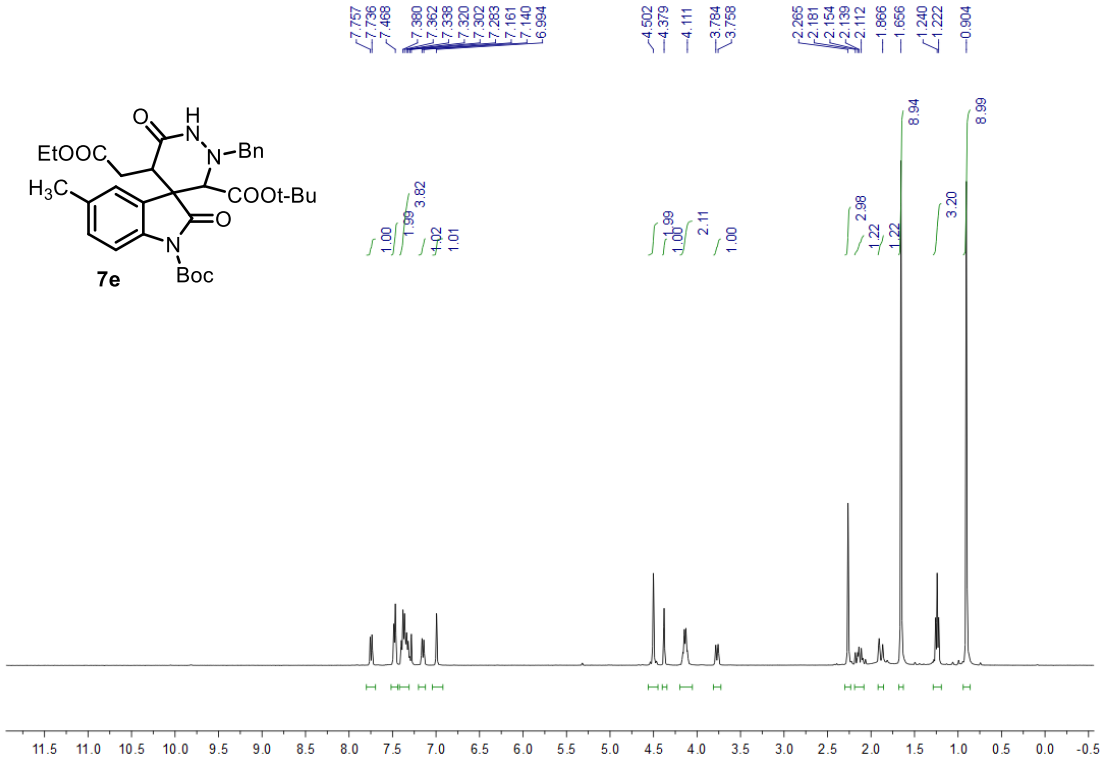
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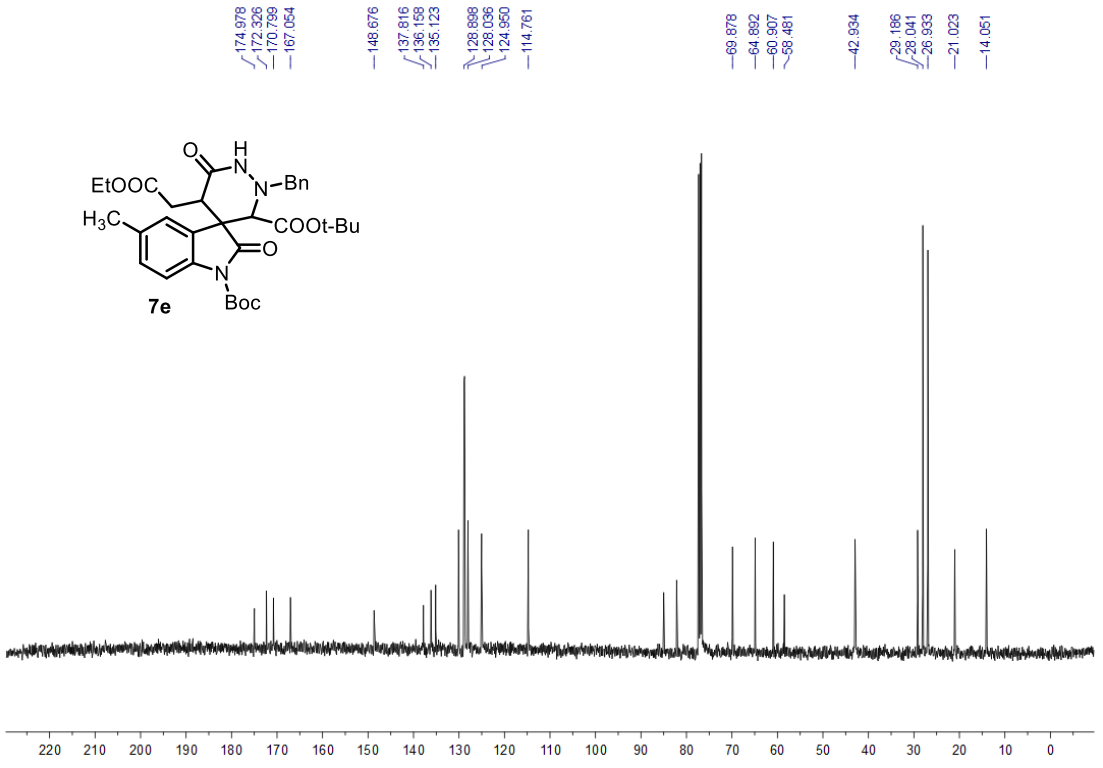
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O
Boc
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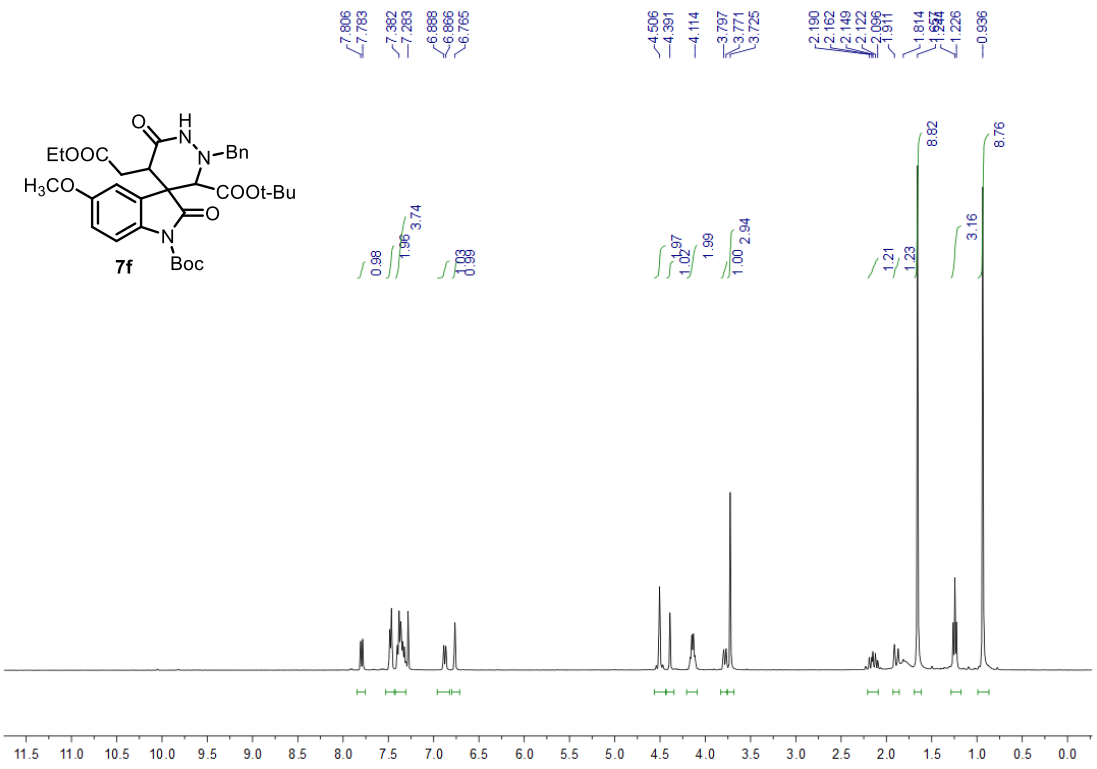
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Bn
COOt-Bu
Boc
7f
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0.99
1.97
1.02
1.99
1.00
2.94
1.21
1.23
3.16
8.82
8.76
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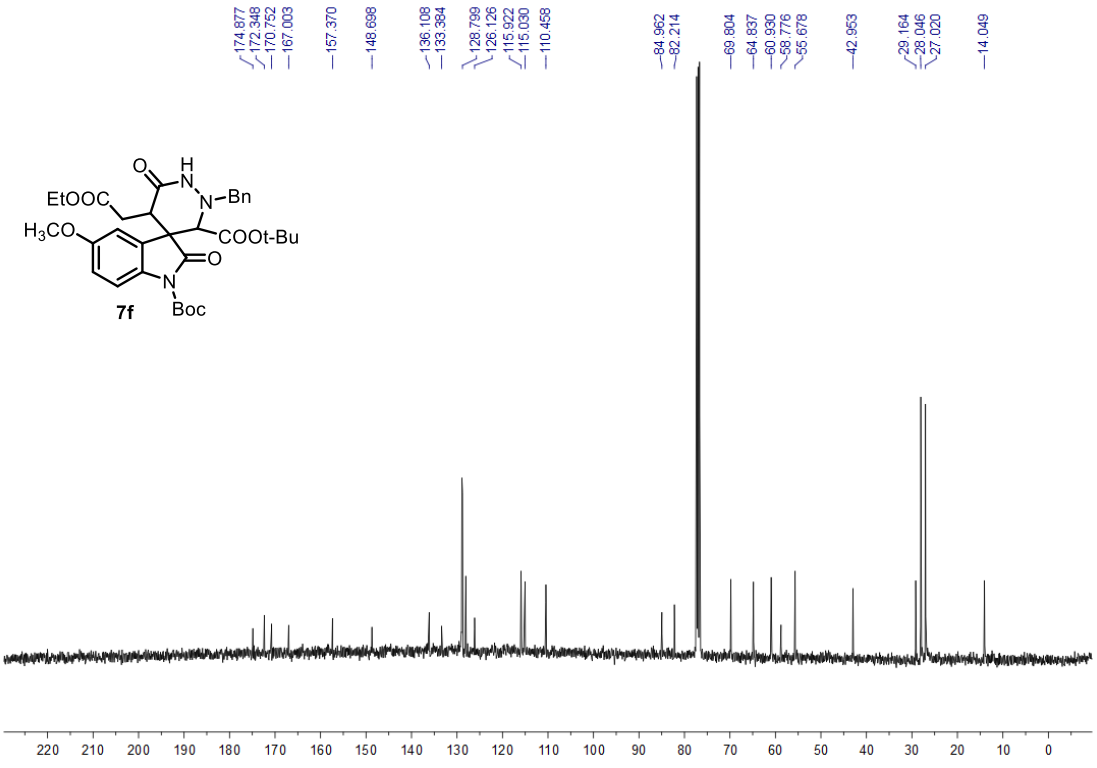
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110.458
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82.214
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Boc
7f
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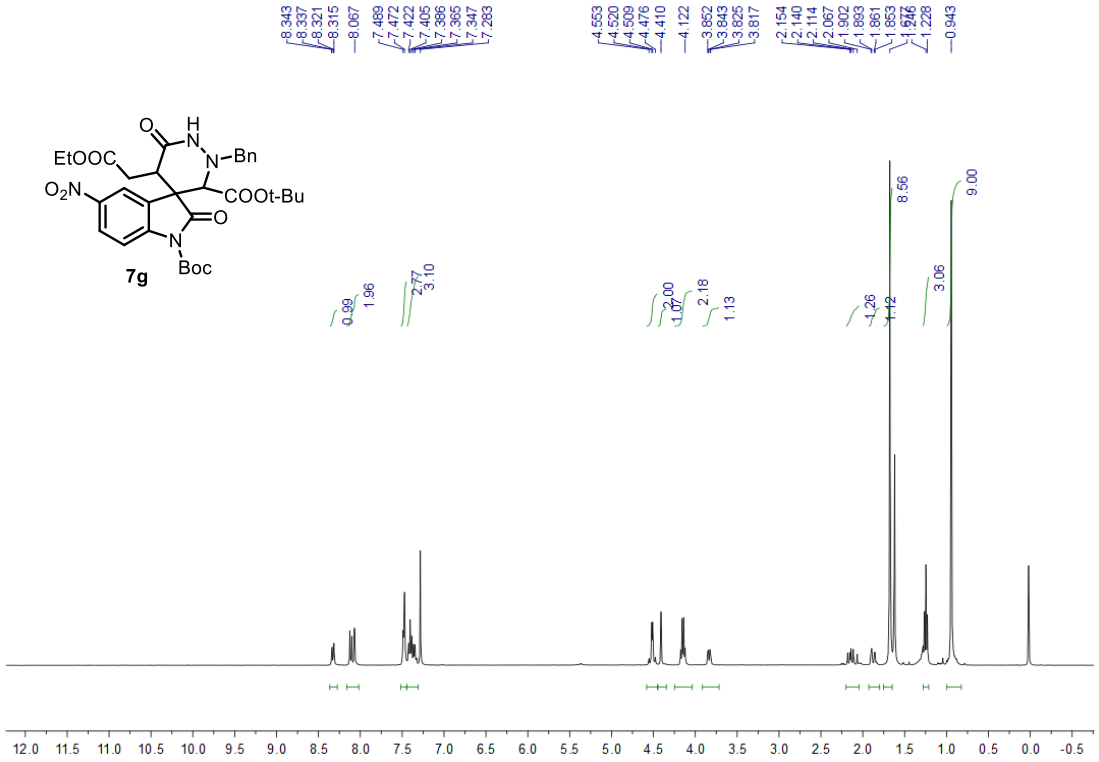
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EtOOC
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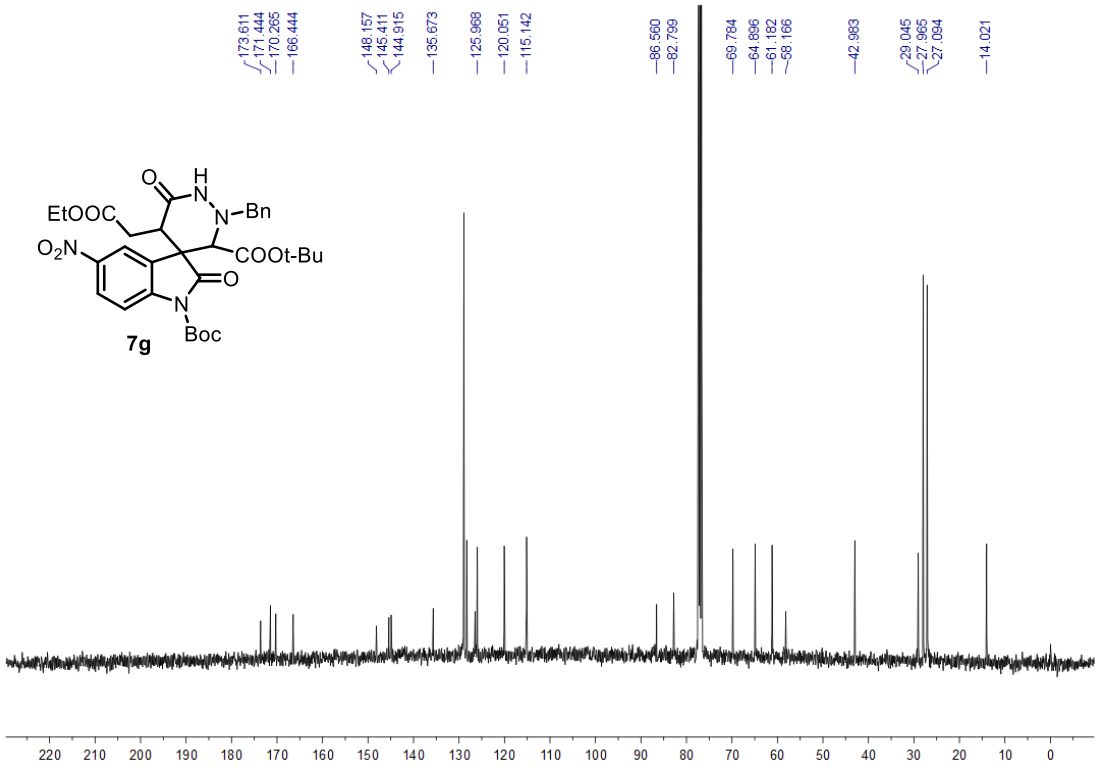
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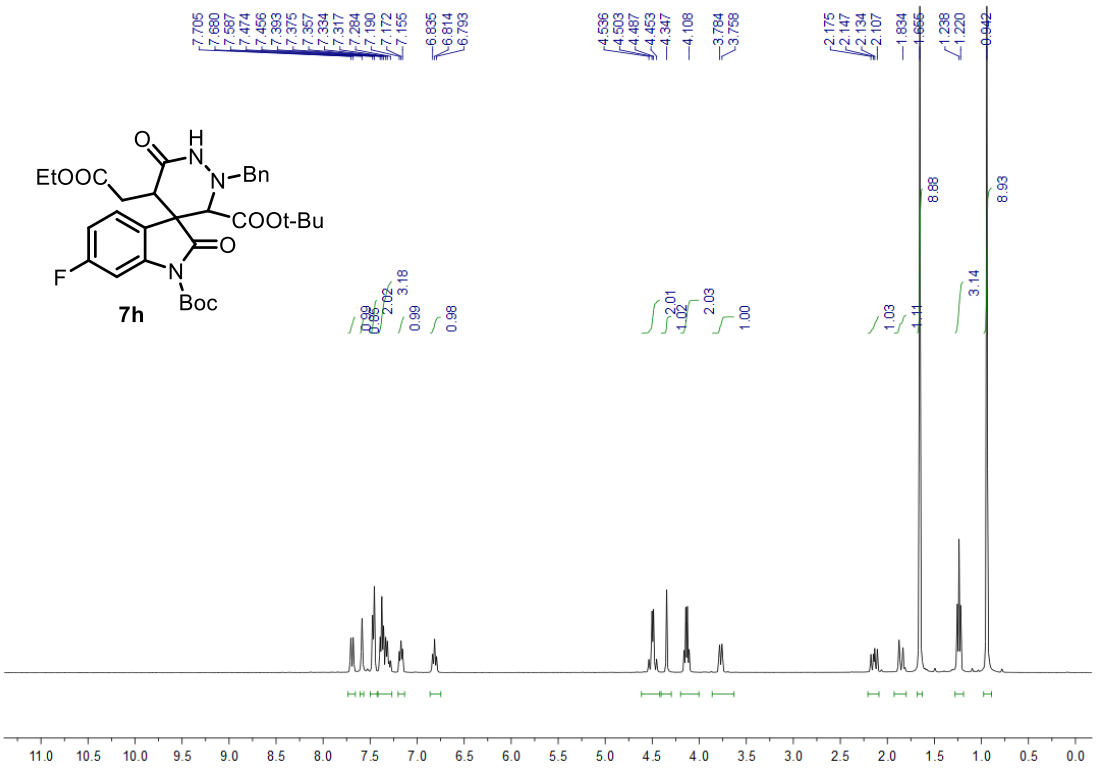
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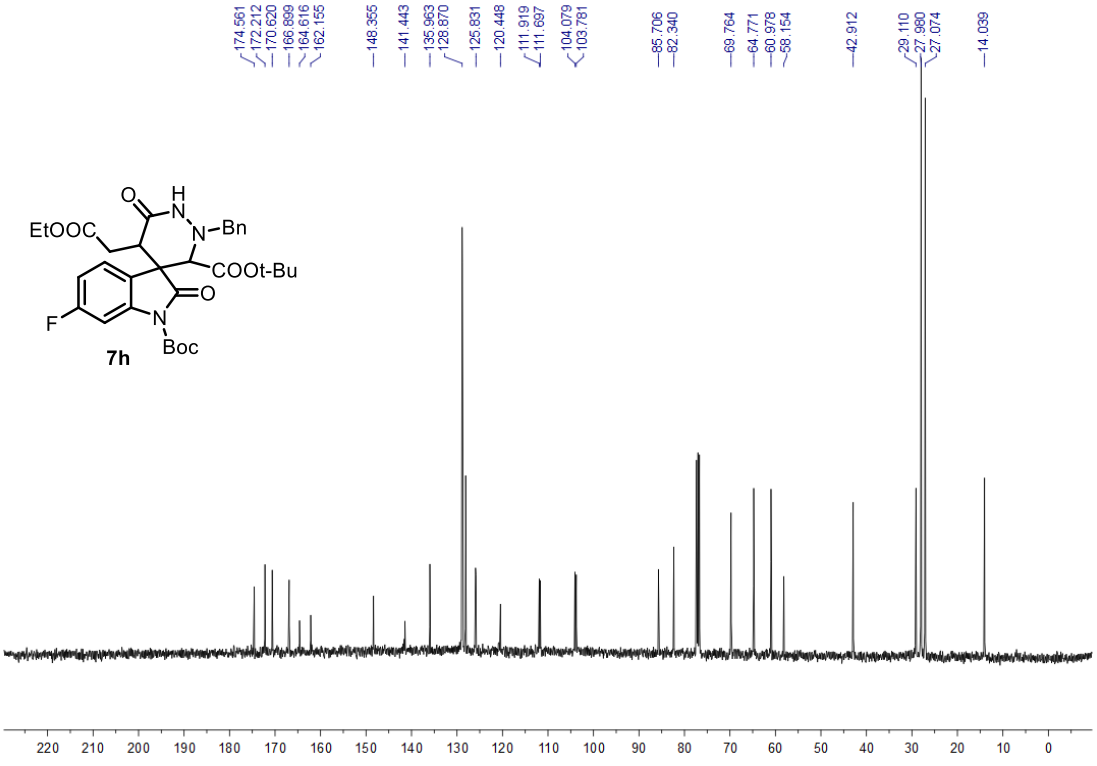
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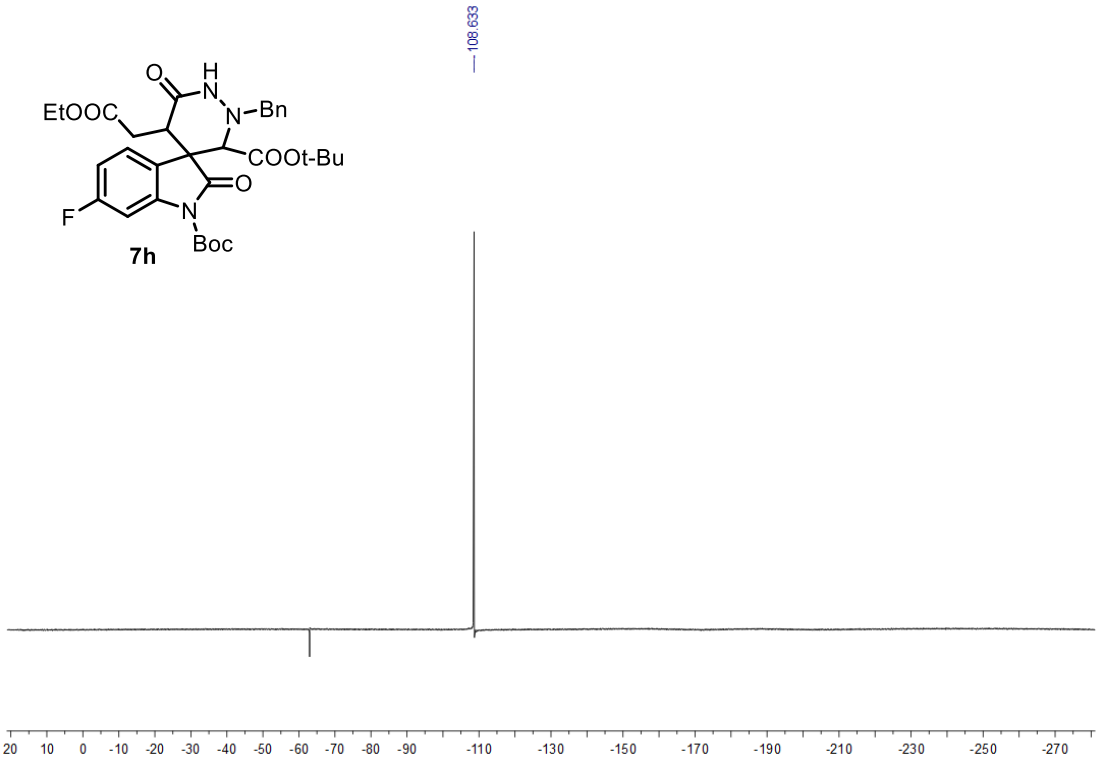
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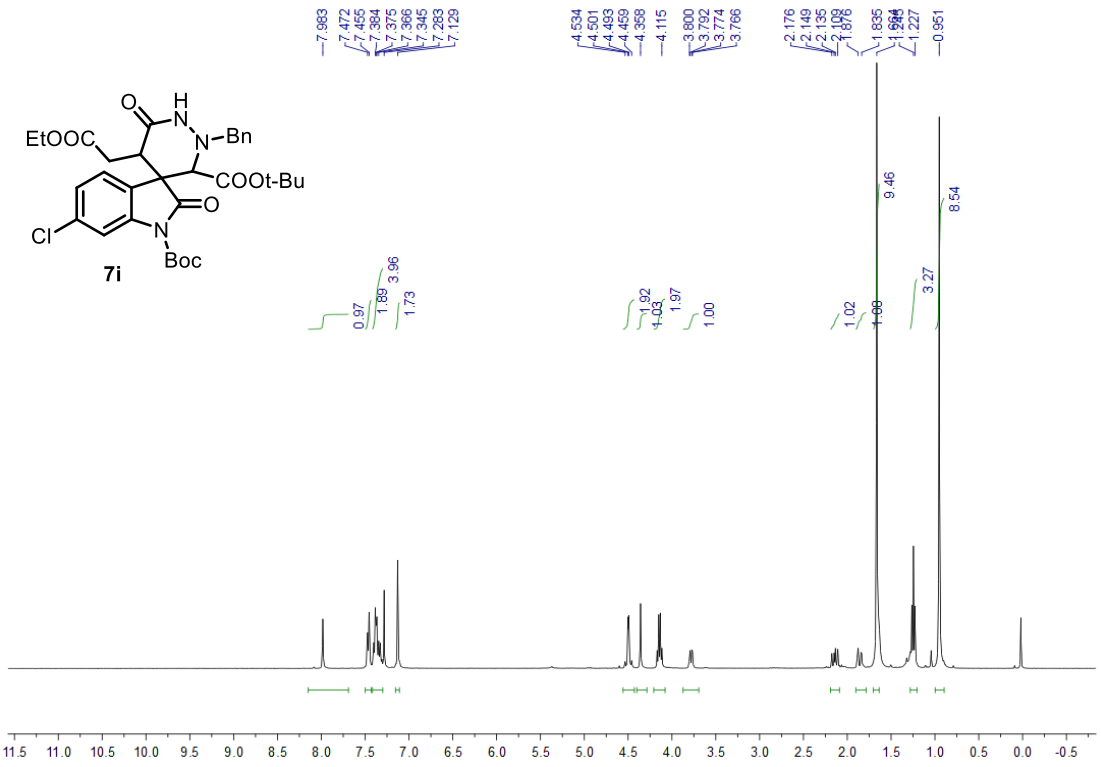
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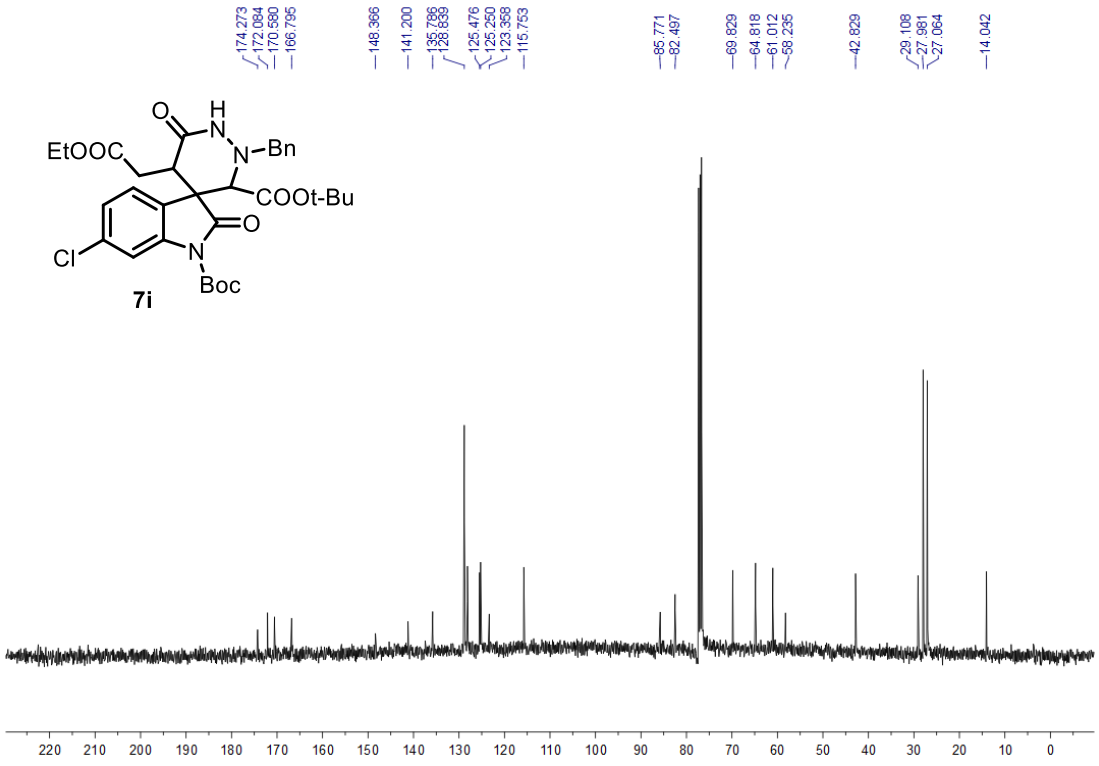
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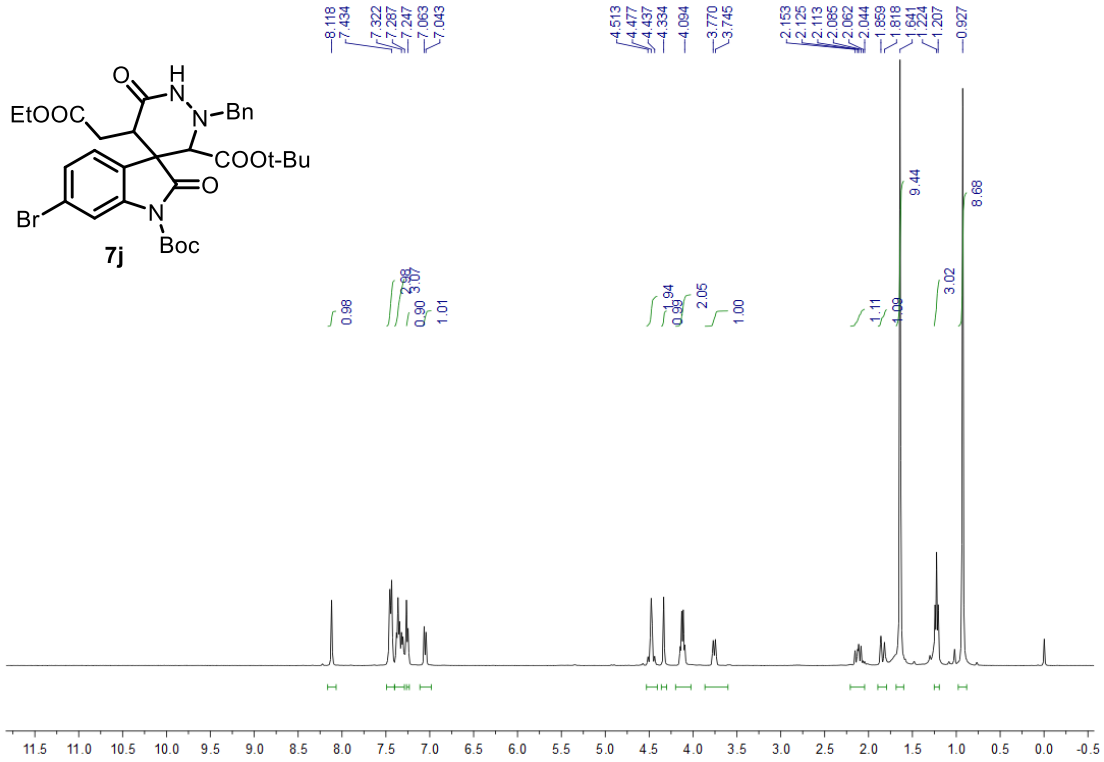
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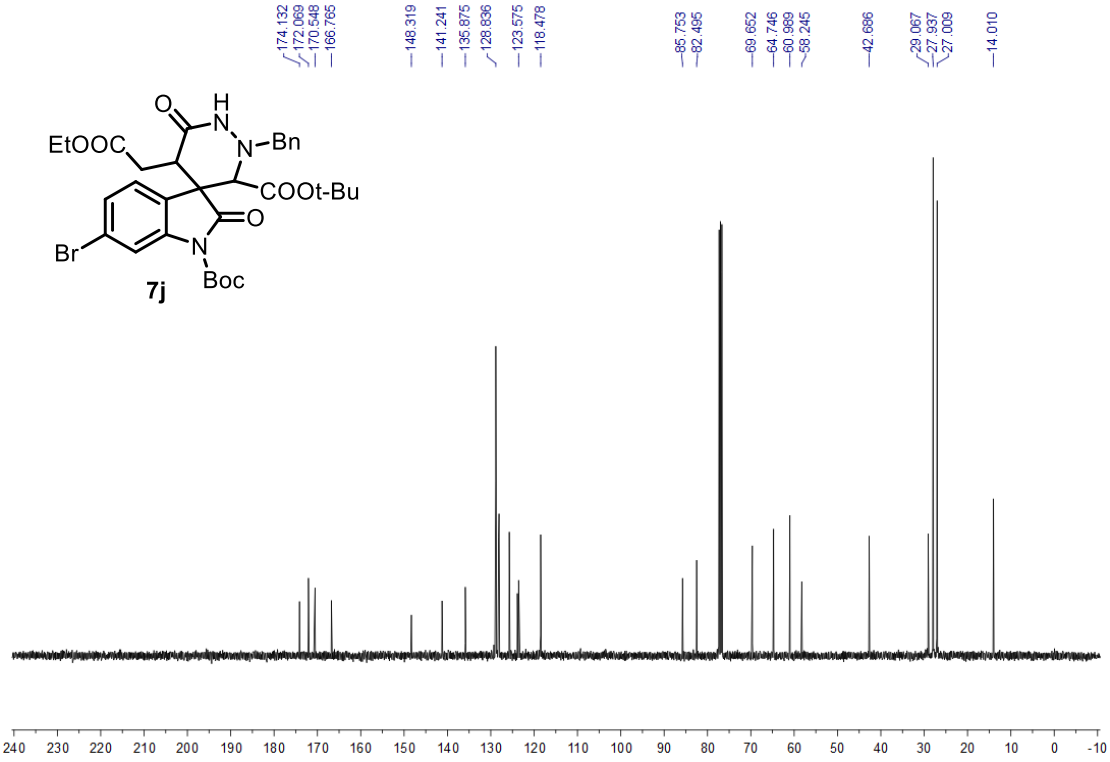
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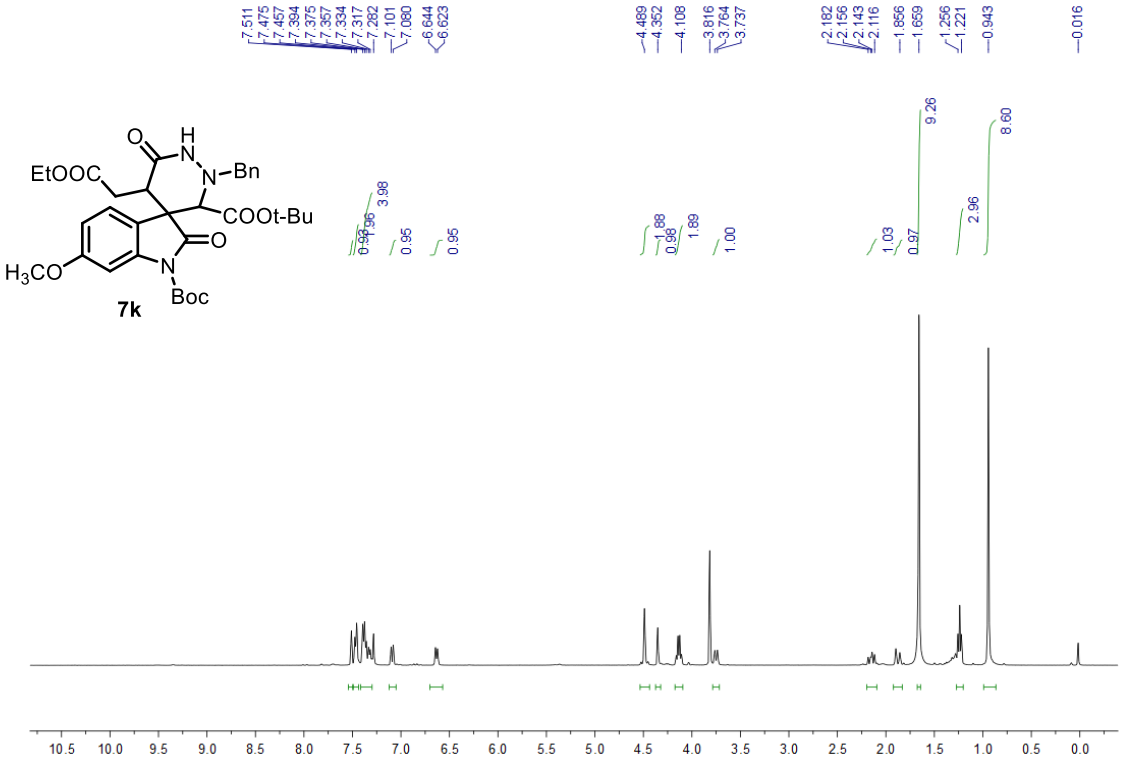
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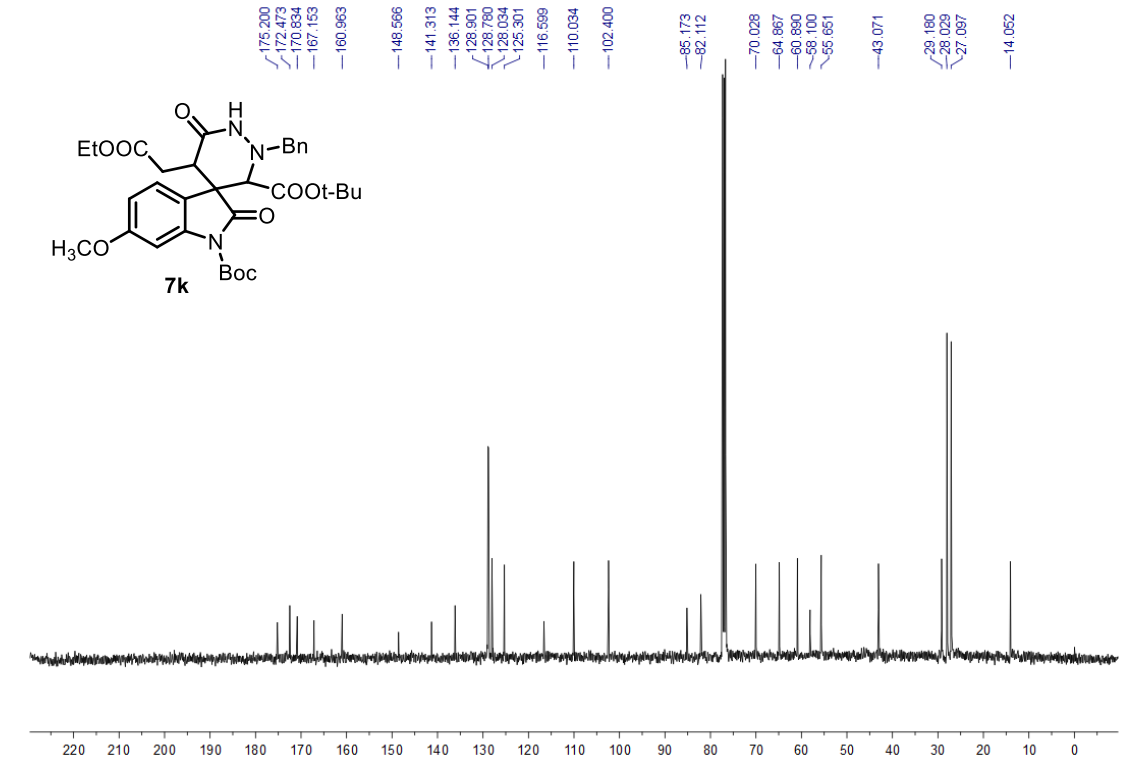
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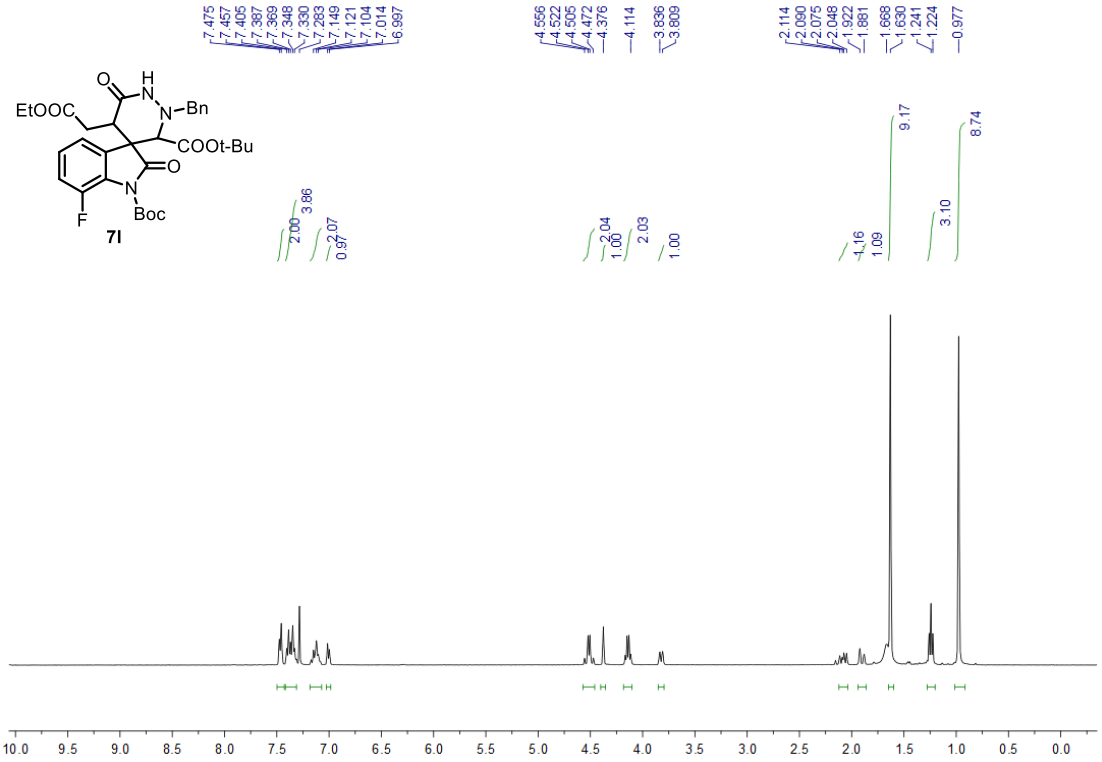
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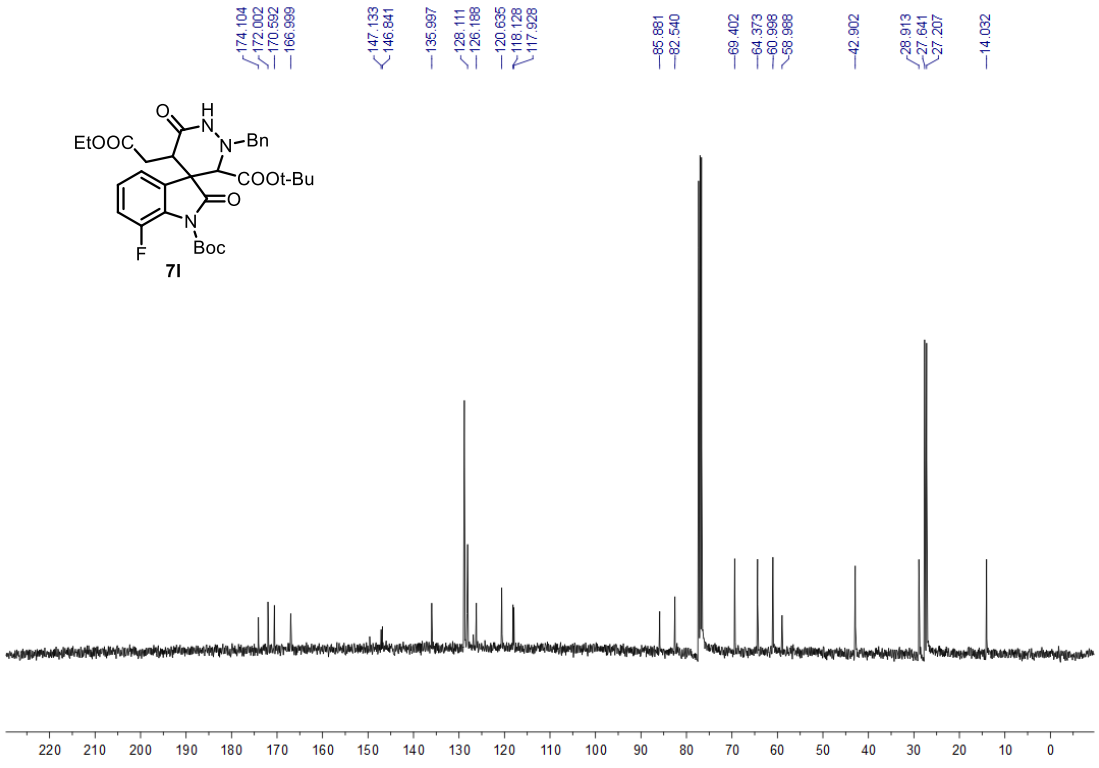
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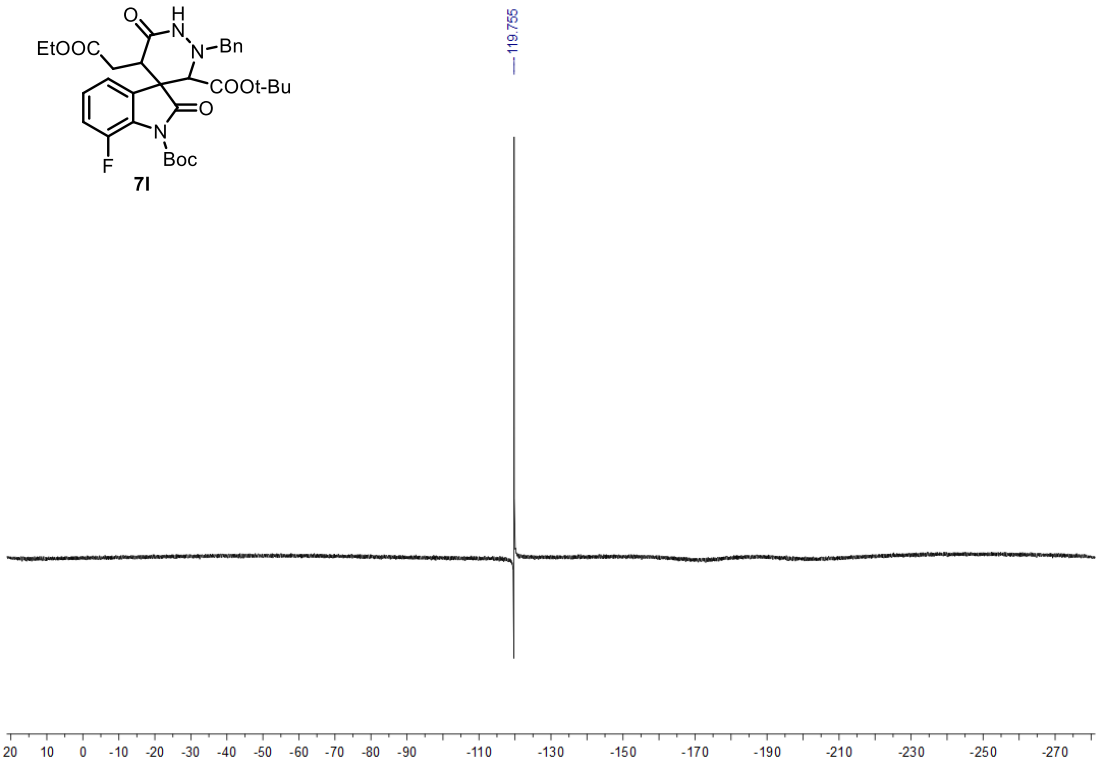
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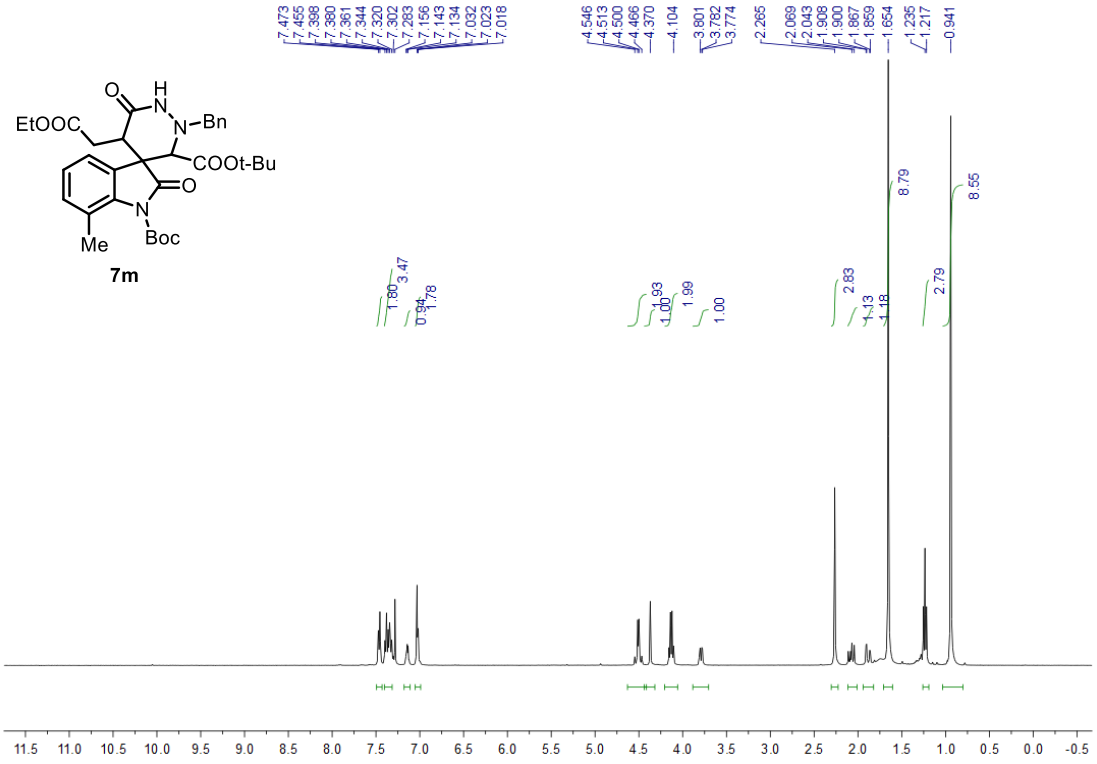
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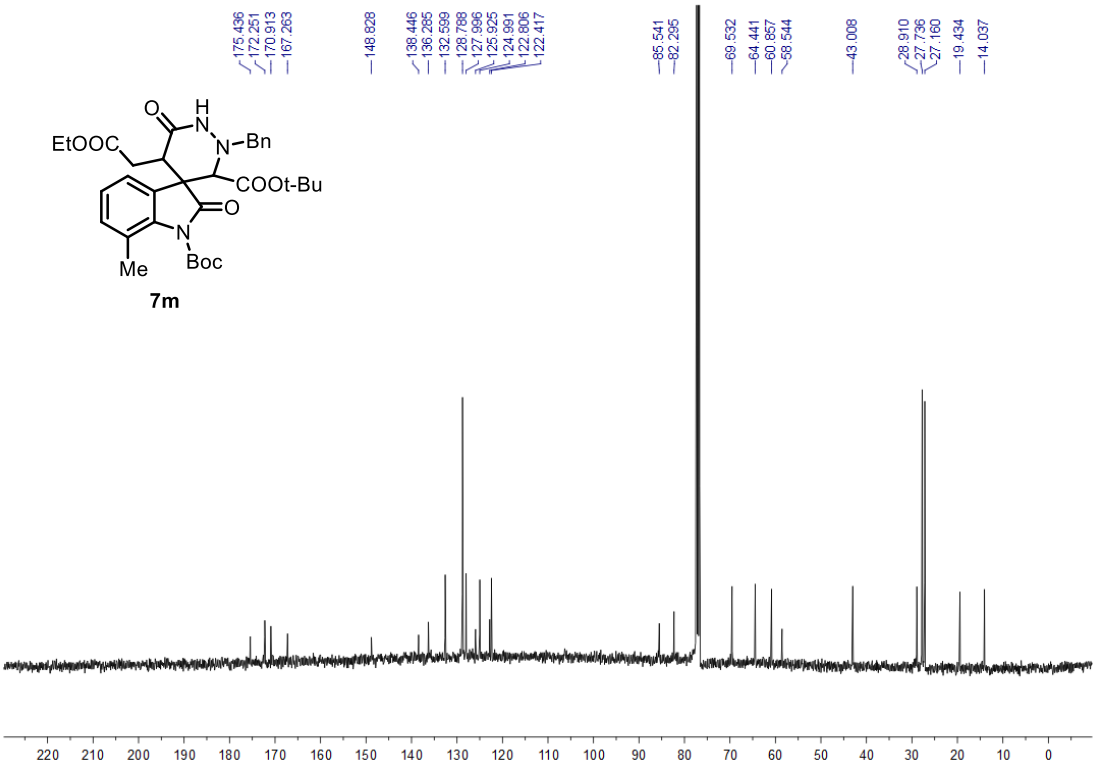
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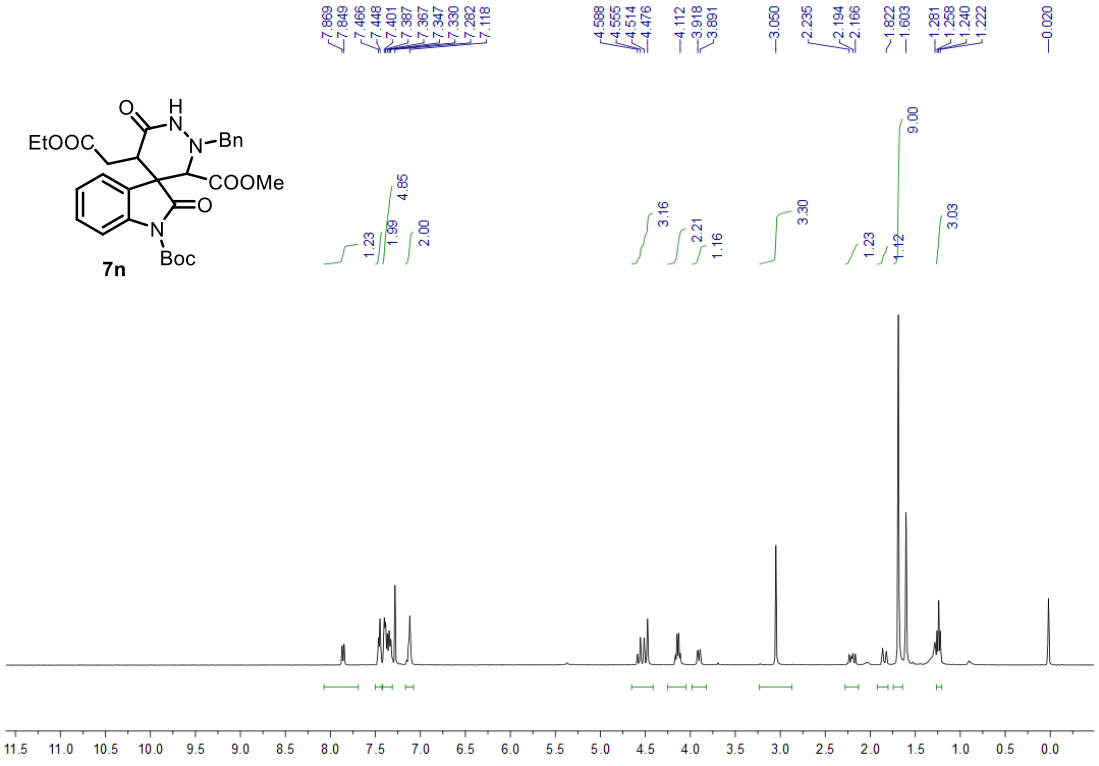
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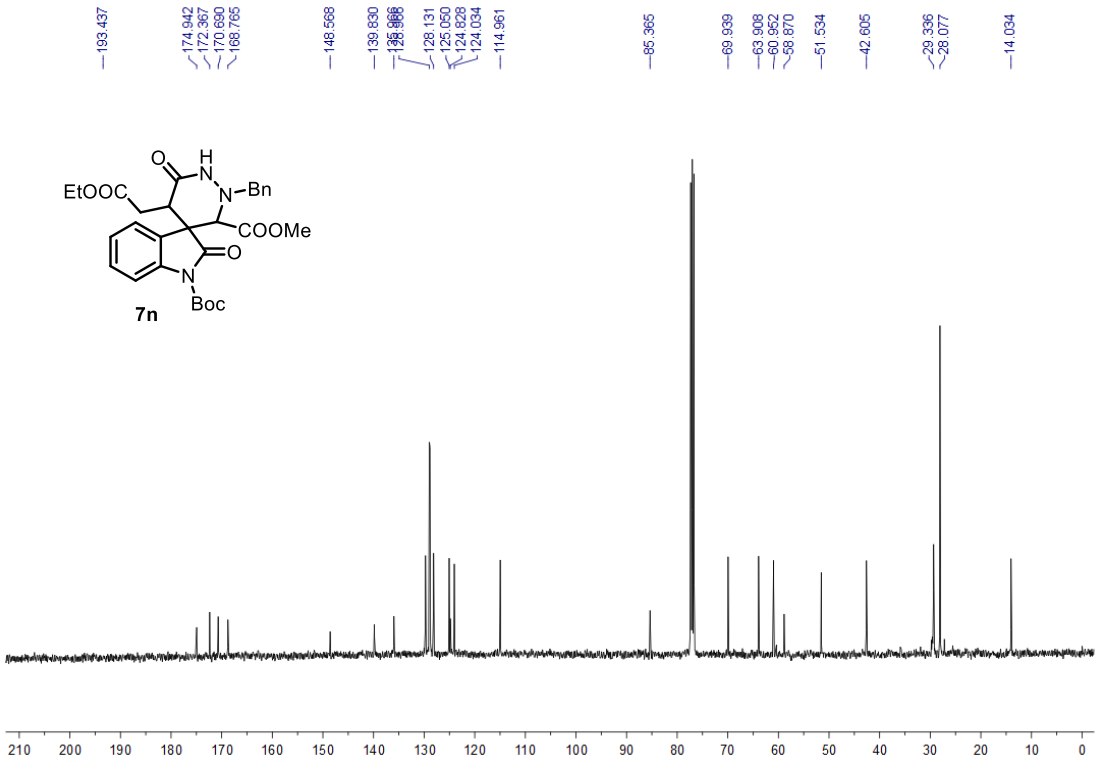
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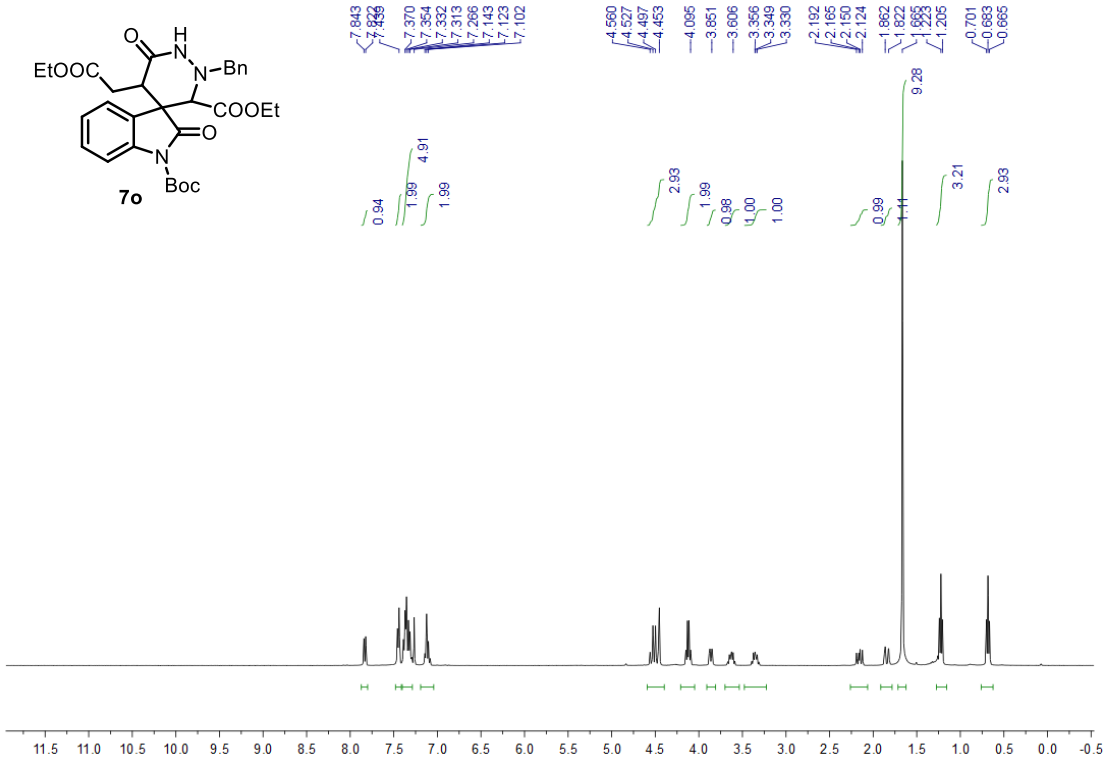
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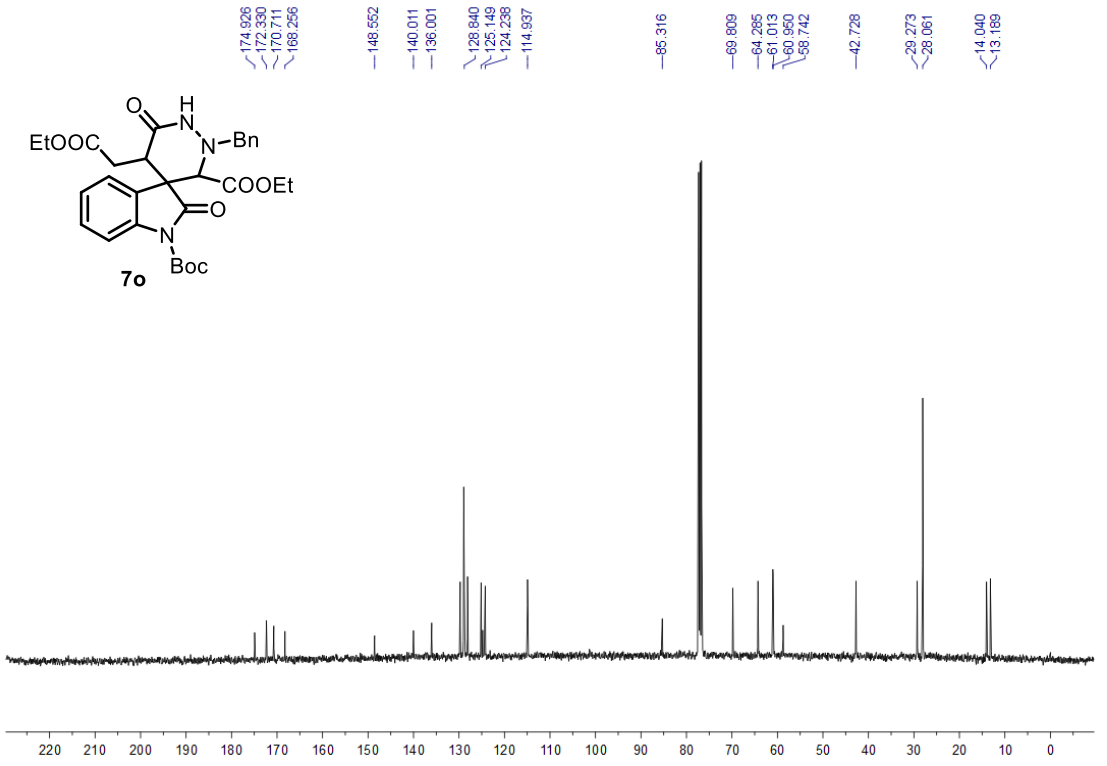
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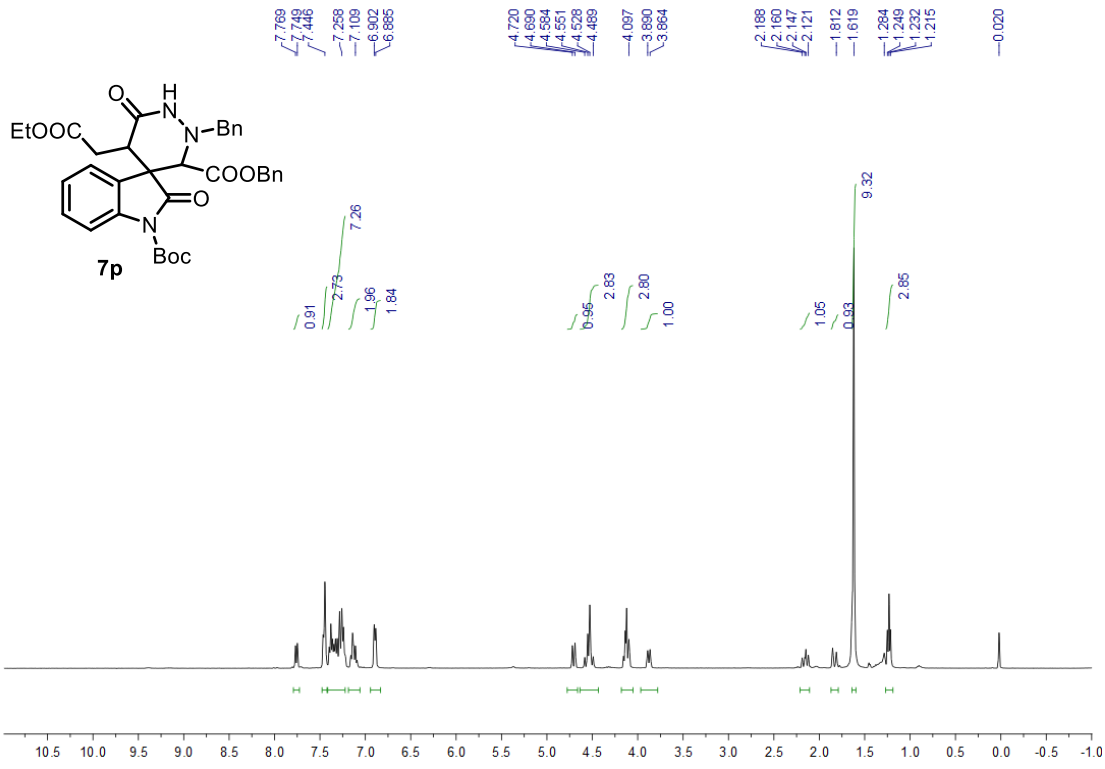
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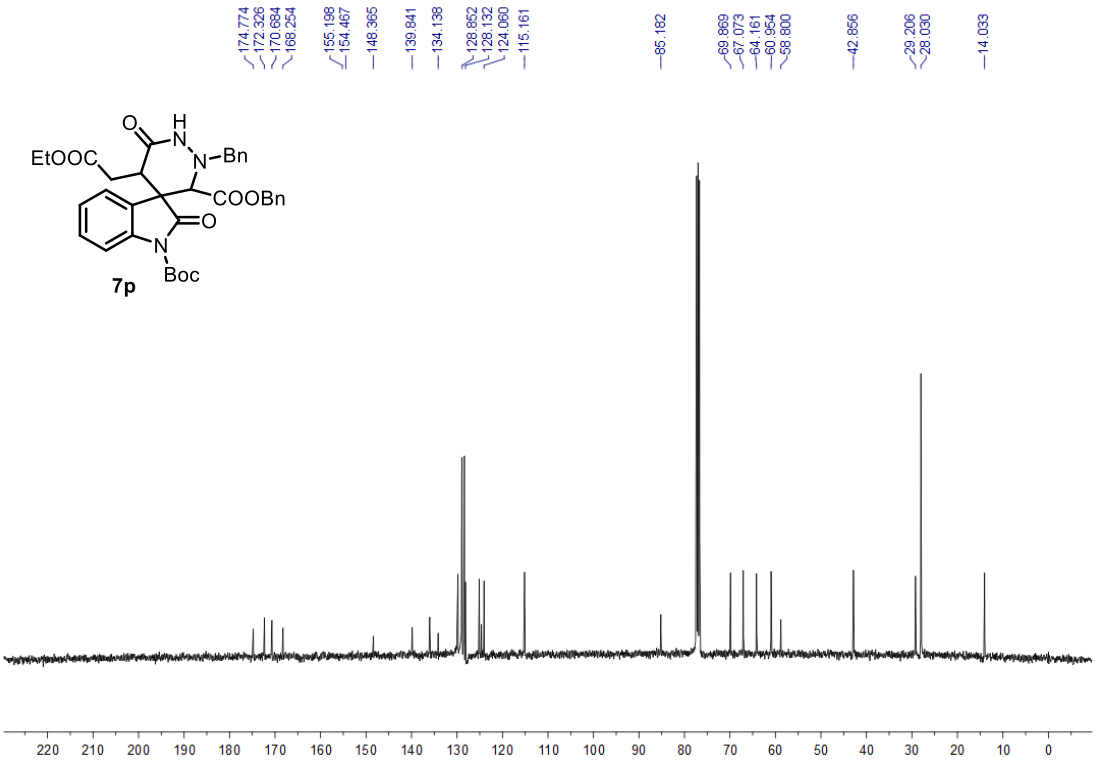
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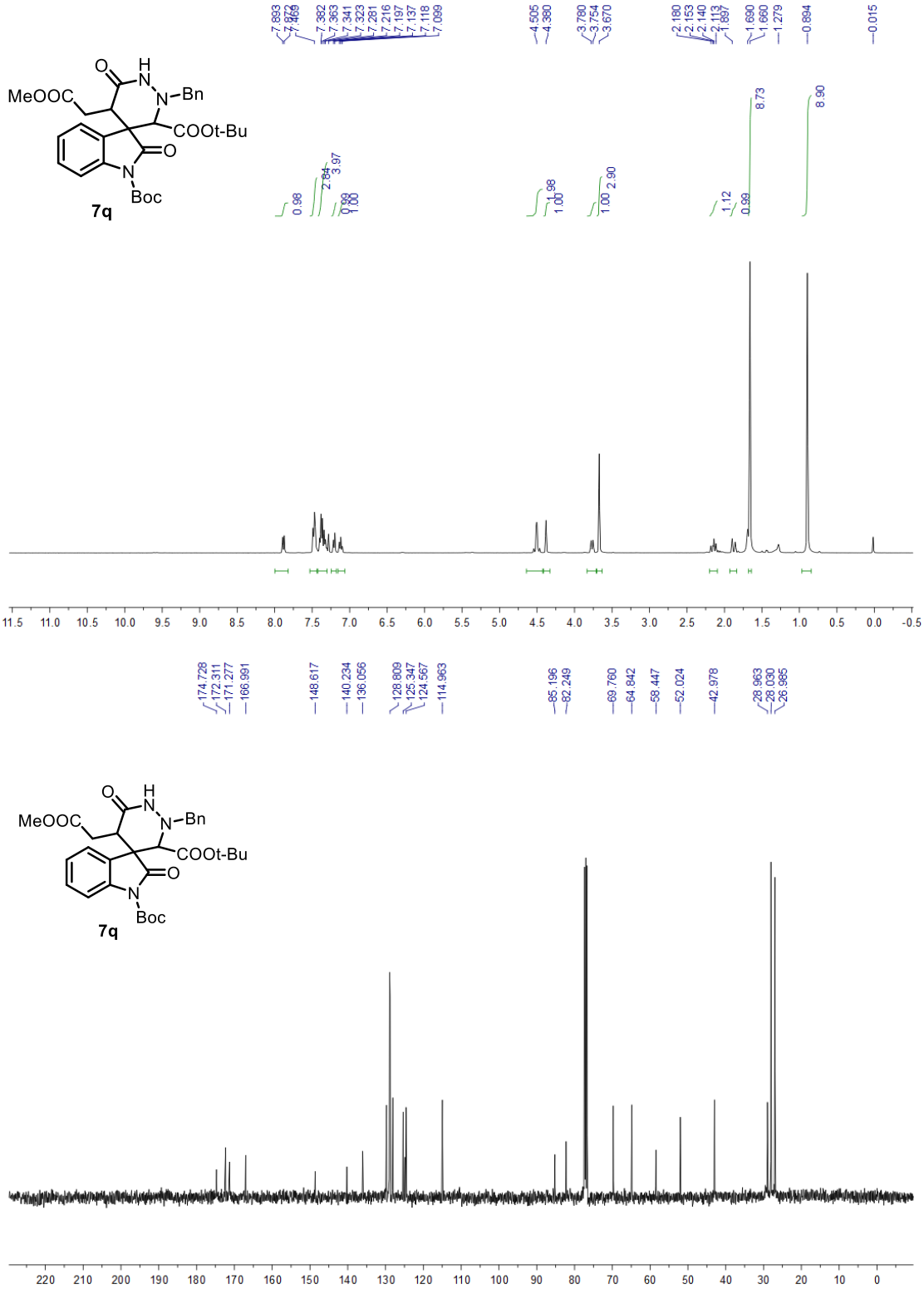
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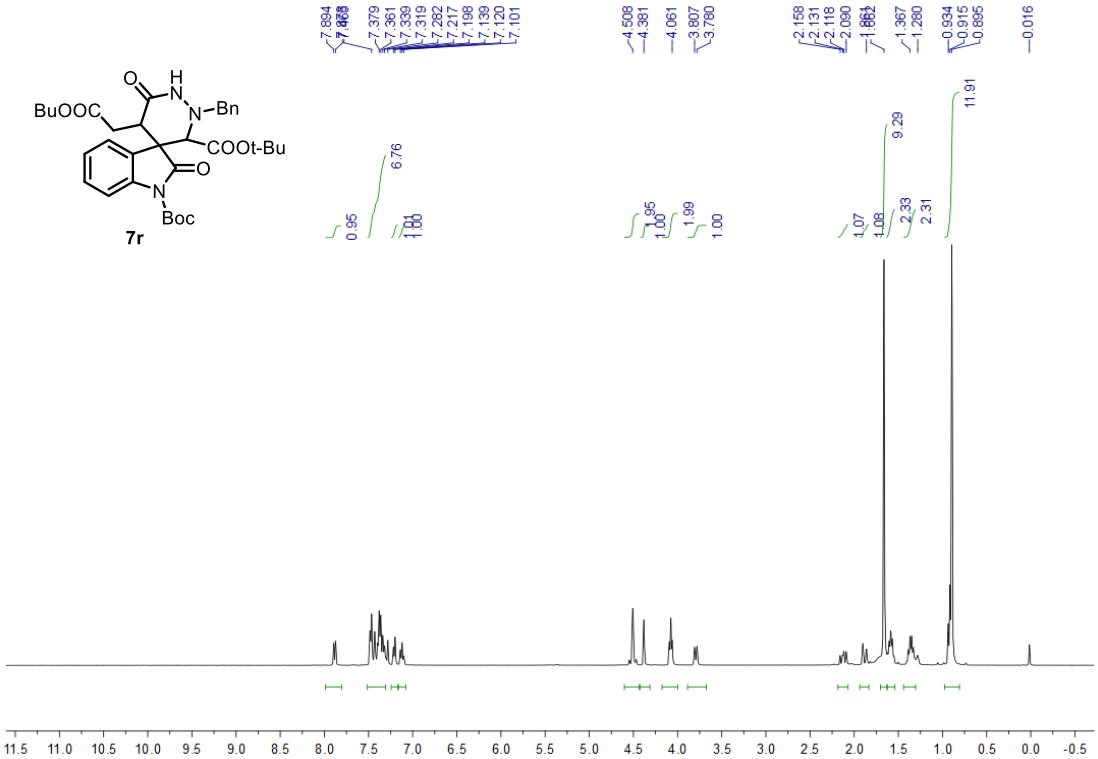
BuOOC
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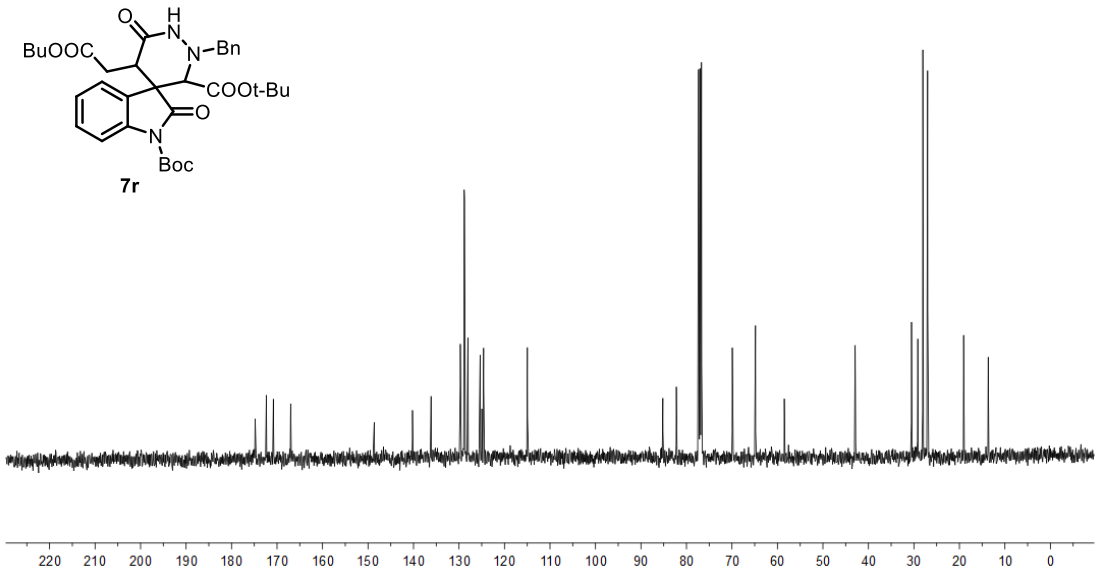
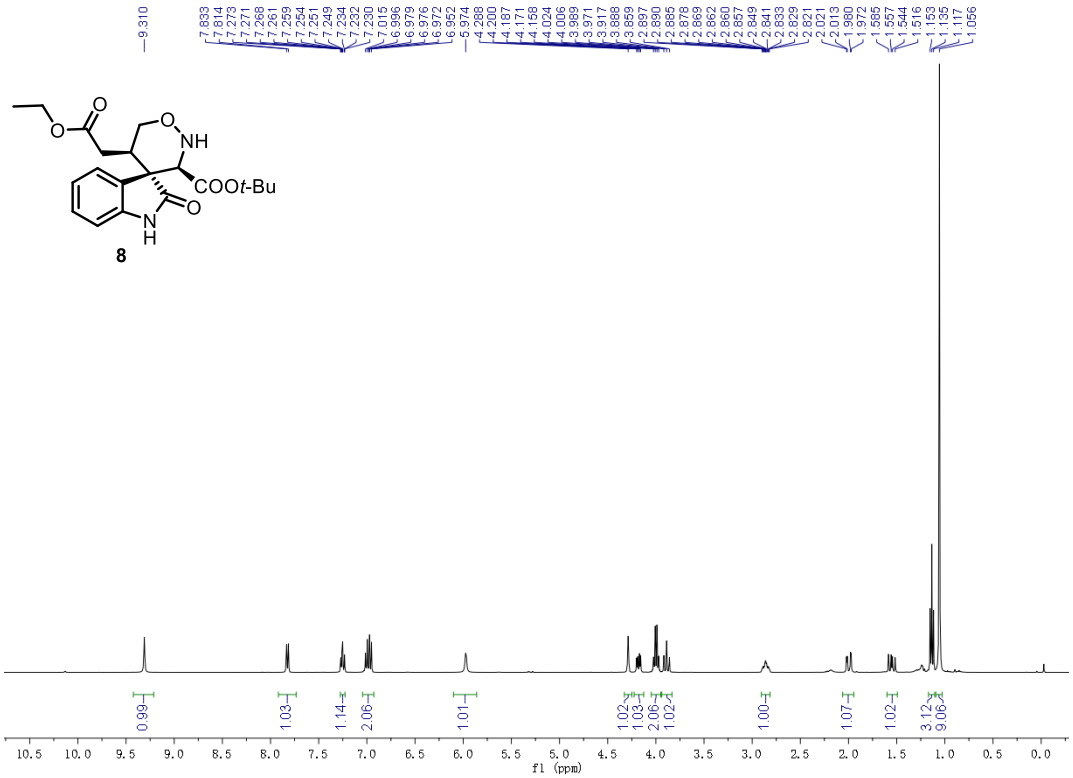
Boc
7r


BuOOC
Bn
COOt-Bu
Boc
7r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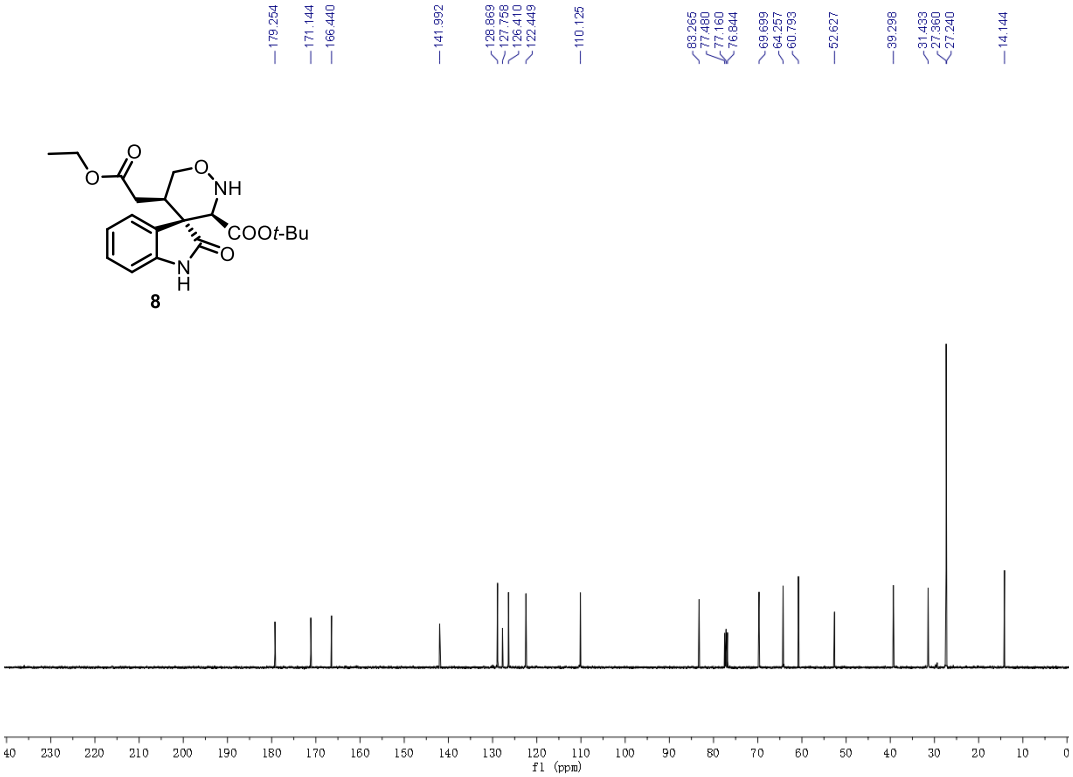
7.814
7.273
7.271
7.268
7.261
7.259
7.254
7.251
7.249
7.234
7.232
7.230
7.015
6.996
6.979
6.976
6.972
6.952
5.974
4.288
4.200
4.187
4.171
4.158
4.024
4.006
3.989
3.971
3.917
3.888
3.859
2.897
2.890
2.885
2.878
2.869
2.862
2.860
2.857
2.849
2.841
2.833
2.829
2.821
2.021
2.013
1.980
1.972
1.585
1.557
1.544
1.516
1.153
1.135
1.117
1.056
O
O
O
NH
COOt-Bu
O
N
H
8
0.99
1.03
1.14
2.06
1.01
1.02
1.03
2.06
1.02
1.00
1.07
1.02
3.12
9.06
f1 (ppm)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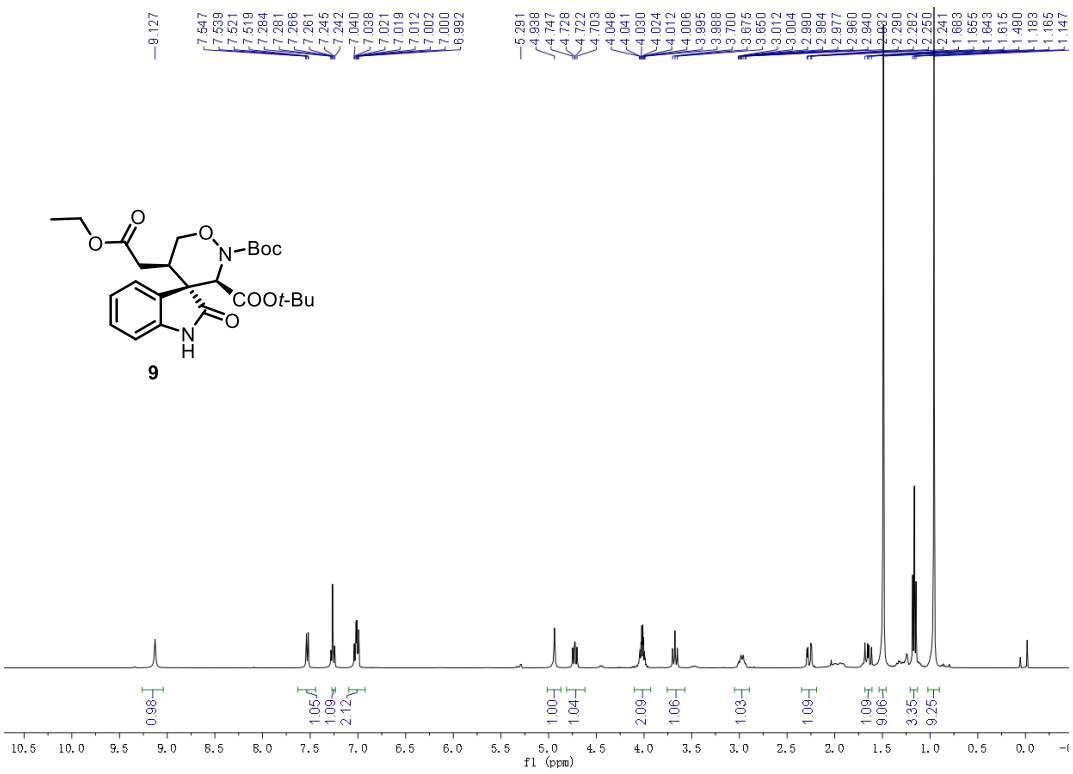
166.440
141.992
128.869
127.758
126.410
122.449
110.125
83.265
77.480
77.160
76.844
69.699
64.257
60.793
52.627
39.298
31.433
27.360
27.240
14.144
O
O
O
NH
COOt-Bu
O
N
H
8
f1 (ppm)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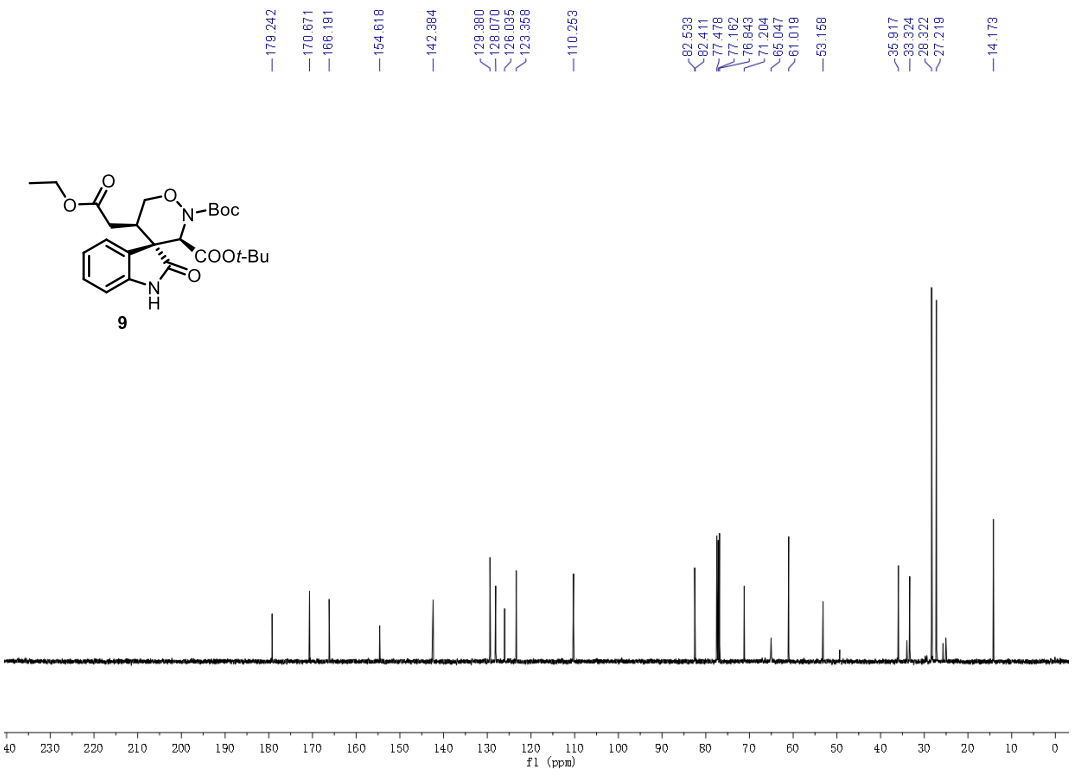
7.539
7.521
7.519
7.284
7.281
7.266
7.261
7.245
7.242
7.040
7.038
7.021
7.019
7.012
7.002
7.000
6.992
5.291
4.838
4.747
4.728
4.722
4.703
4.048
4.041
4.030
4.024
4.012
4.006
3.995
3.988
3.700
3.675
3.650
3.012
3.004
2.980
2.964
2.977
2.960
2.940
2.892
2.290
2.282
2.250
2.241
1.663
1.655
1.643
1.615
1.490
1.183
1.165
1.147
O
O
N-Boc
O
COOt-Bu
O
N
H
9
0.98
1.05
1.09
2.12
1.00
1.04
2.09
1.06
1.03
1.09
1.09
9.06
3.35
9.25
f1 (ppm)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166.191
154.618
142.384
129.380
128.070
126.035
123.358
110.253
82.533
82.411
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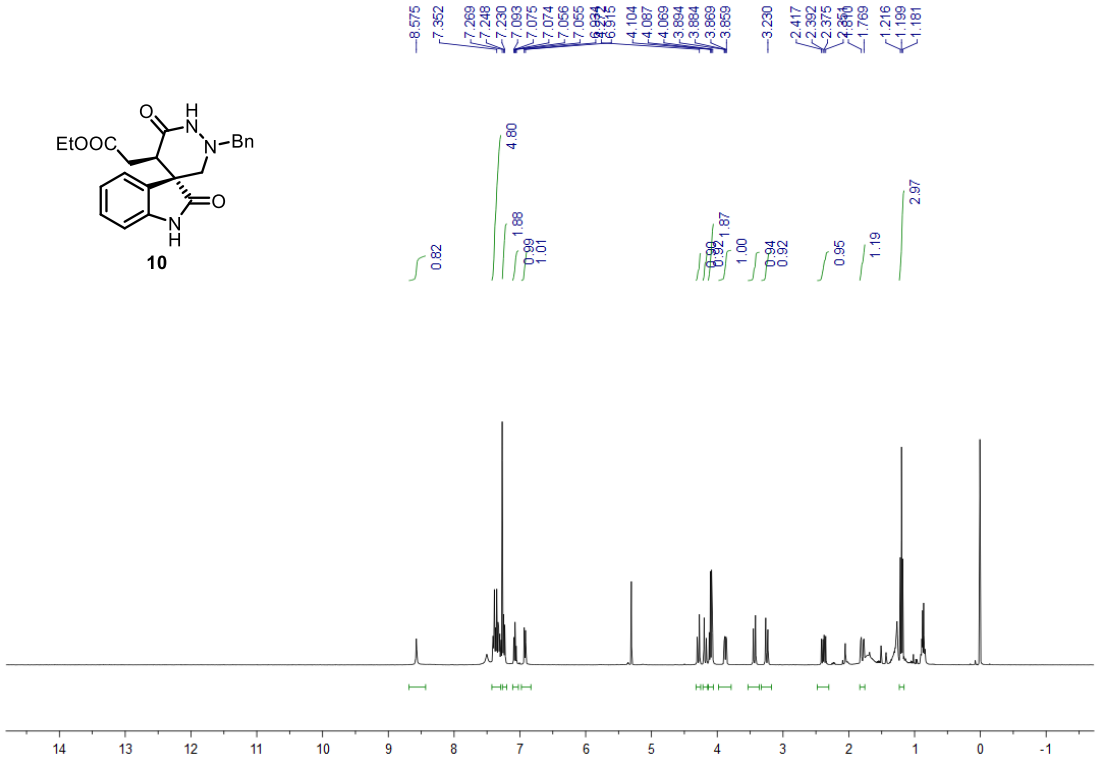
77.162
76.843
71.204
65.047
61.019
53.158
35.917
33.324
28.322
27.219
14.173
O
O
N-Boc
O
COOt-Bu
O
N
H
9
f1 (ppm)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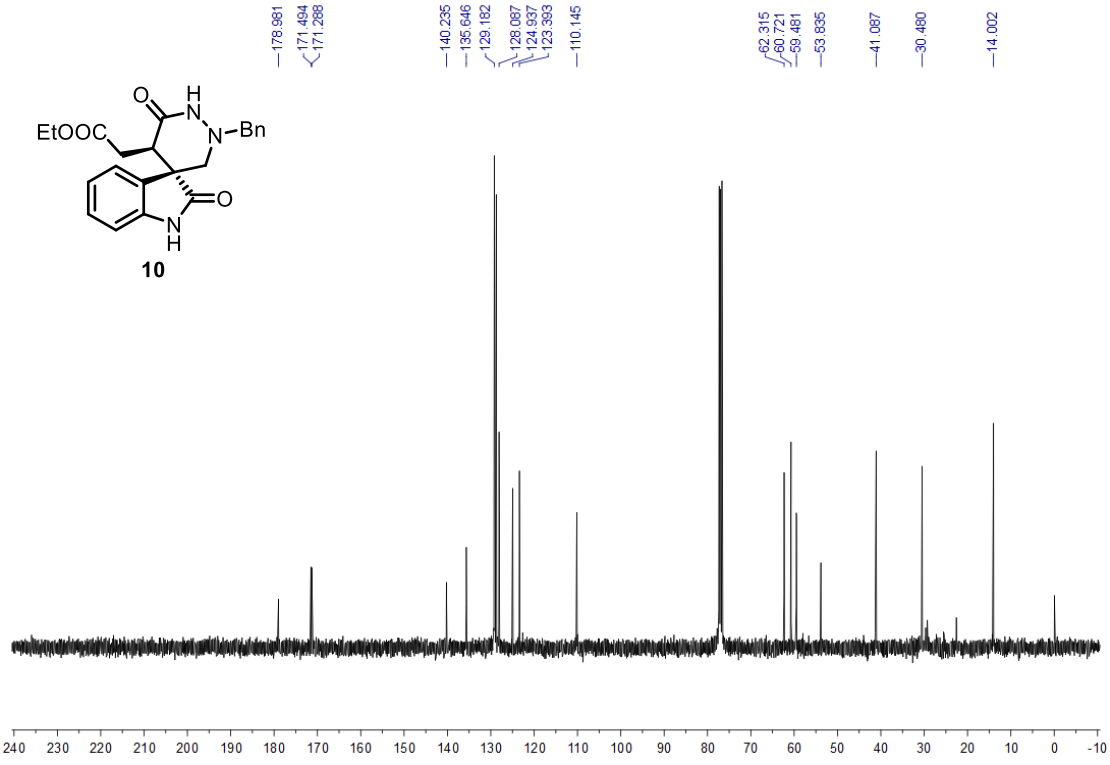
7.362
7.269
7.248
7.230
7.093
7.075
7.074
7.056
7.055
4.104
4.087
4.069
3.894
3.884
3.869
3.859
3.230
2.417
2.392
2.375
1.769
1.216
1.199
1.181
4.80
1.88
0.89
1.01
0.82
1.87
1.00
0.94
0.92
0.95
1.19
2.97
EtOOC
N-Bn
O
H
N
O
N
H
10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171.494
171.288
140.235
135.646
129.182
128.087
124.937
123.393
110.145
62.315
60.721
59.481
53.835
41.087
30.480
14.002
EtOOC
N-Bn
O
H
N
O
N
H
10

5. X-ray data of the product

Figure S1, X-ray crystal structure of 8 (The crystal was obtained by slow evaporation of the solution of diethyl ether and hexane)

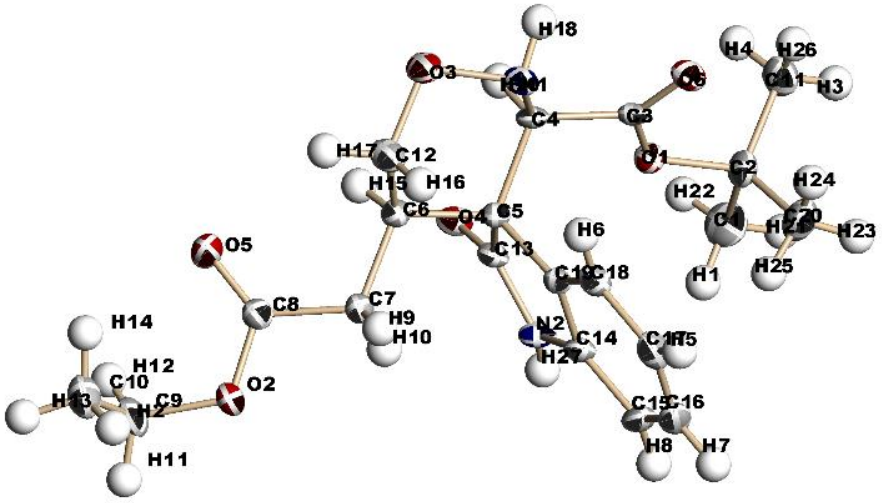

Table S1. Crystal data and structure refinement for CCDC 2153695.

Identification code	20190417tangQG	
Chemical formula	$C_{20}H_{26}N_2O_6$	
Formula weight	390.43 g/mol	
Temperature	274(2) K	
Wavelength	1.54178 Å	
Crystal size	0.070 x 0.100 x 0.300 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.2293(6) Å	α = 90°
	b = 8.1032(5) Å	β = 101°
	c = 11.2293(6) Å	γ = 90°
Volume	1004.55(10) $Å^3$	
Z	2	
Density (calculated)	1.291 g/cm^3	
Absorption coefficient	0.793 mm^{-1}	
F(000)	416	
Theta range for data collection	4.00 to 72.85°	
Index ranges	-13<=h<=13, -10<=k<=7, -13<=l<=13	

Reflections collected	9600
Independent reflections	3056 [R(int) = 0.0591]
Max. and min. transmission	0.9470 and 0.7970
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\ w(Fo^2 - Fc^2)^2$
Data / restraints / parameters	3056 / 1 / 265
Goodness-of-fit on F2	1.091
Final R indices	2984 data; I>2σ(I) R1 = 0.0434, wR2 = 0.1008
	all data R1 = 0.0439, wR2 = 0.1016
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0651P)^2+0.0605P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.02(14)
Largest diff. peak and hole	0.334 and -0.256 eÅ^{-3}
R.M.S. deviation from mean	0.058 eÅ^{-3}

Figure S2, X-ray crystal structure of 7a (The crystal was obtained by slow evaporation of the solution of diethyl ether and hexane)

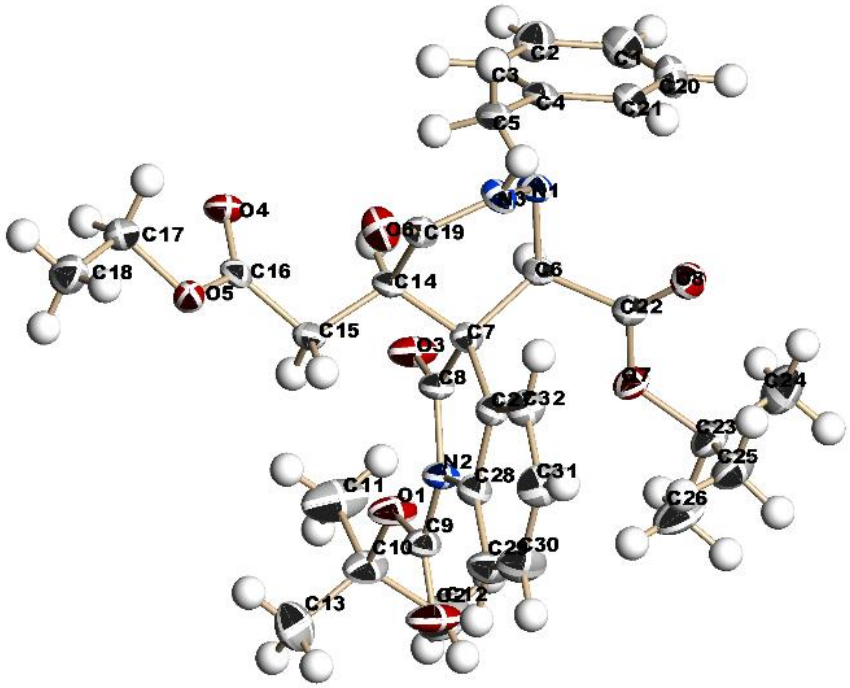

Table S2. Crystal data and structure refinement for CCDC 2153627.

Identification code	20210409THZ_TBUDH	
Chemical formula	$C_{32}H_{39}N_3O_8$	
Formula weight	593.66 g/mol	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal size	0.100 x 0.130 x 0.200 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 12.891(6) Å	α = 90°
	b = 8.629(5) Å	β = 111.57(2)°
	c = 15.510(7) Å	γ = 90°
Volume	1604.5(14) $Å^3$	
Z	2	
Density (calculated)	1.229 g/cm^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	632	
Theta range for data collection	3.69 to 65.01°	
Index ranges	-15<=h<=15, -10<=k<=10, -18<=l<=18	
Reflections collected	19779	
Independent reflections	5367 [R(int) = 0.0869]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7526 and 0.6068	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(Fo^2 - Fc^2)^2$	
Data / restraints / parameters	5367 / 1 / 398	
Goodness-of-fit on F2	1.062	
Final R indices	4848 data; I>2σ(I)	R1 = 0.0332, wR2 = 0.0803
	all data	R1 = 0.0474, wR2 = 0.0836
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0338P)^2+0.1266P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.14(11)	

Largest diff. peak and hole	0.159 and -0.150 eÅ^{-3}
R.M.S. deviation from mean	0.037 eÅ^{-3}