Supporting Information

Asymmetric Synthesis of Acyclic N–N Axially Chiral Indole Compounds via Catalytic *N*-acylation Reaction

Zilu Huang,[‡,a] Yunyi Xu,[‡,b] Wei Lin,[a] Rui Qian,[b] Wei Zhang,*[b] and Xin Li*[a]

[a] State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China; Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

[b] West China School of Public Health and West China Fourth Hospital, Sichuan University, Chengdu 610041, China

[‡] These authors contributed equally to this work

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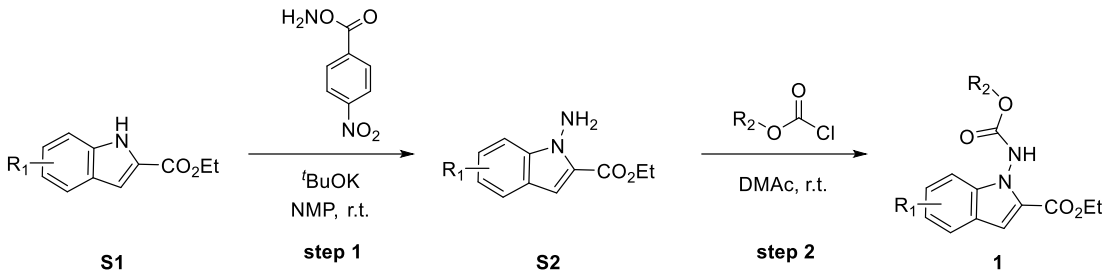
1. General Information

Commercially available chemicals were obtained from Bidepharm, Adamas, Energy Chemical, Heowns and DAMAO used as received unless otherwise stated. Chiral isothiourea organocatalysts were purchased from Bidepharm. Anhydrides were purchased from Bidepharm, Alfa Aesar and Heowns. Na_2CO_3 was purchased from DAMAO. DCE was purchased from DAMAO and used directly. ^{1}H, and ^{13}C NMR were recorded on a Bruker-DPX 400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). ^{19}F NMR were recorded on a Varian NMR 400 spectrometer. Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer.

2. General Procedure for the Synthesis of Substrates[1]



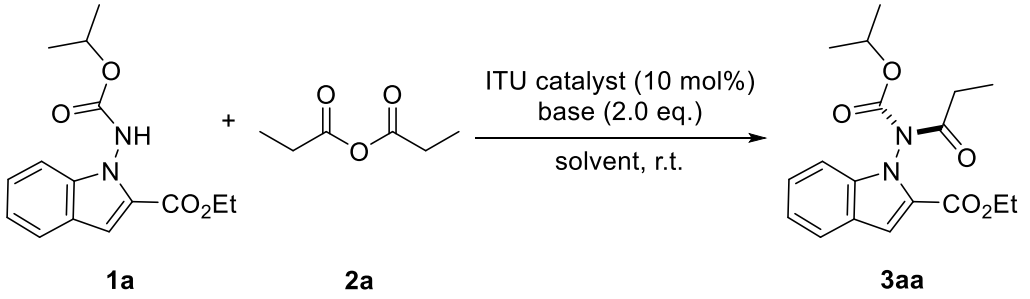
S1 S2 1

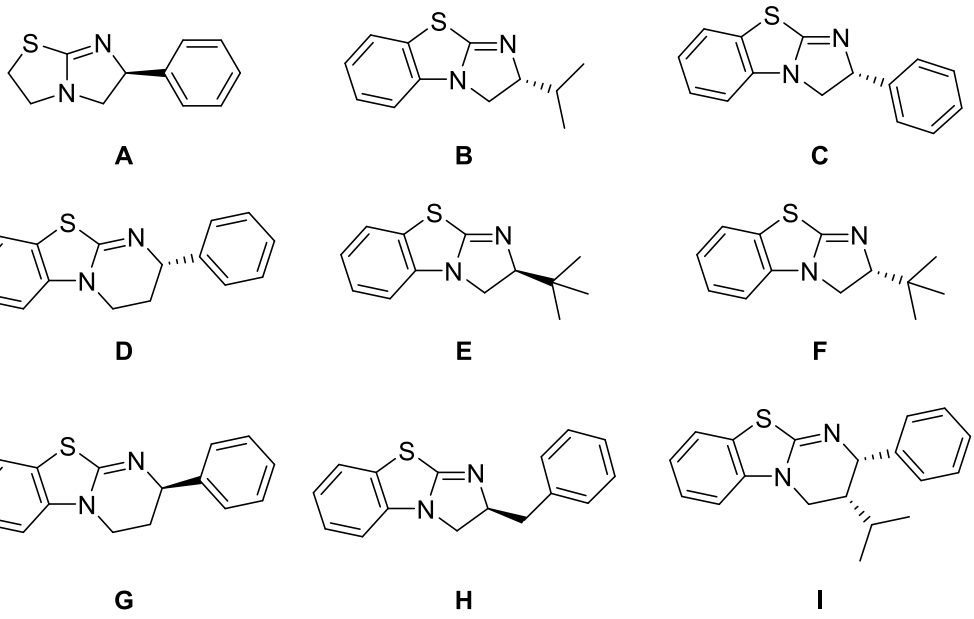
Step 1: To a solution of **S1** (5 mmol) in 30 mL *N*-methylpyrrolidone (NMP) was added 6 mL ^{t}BuOK (1M in THF) and the reaction mixture was stirred at r.t. for 0.5 h. Then, a solution of O-(4-Nitrobenzoyl)hydroxylamine (6 mmol) was added to the mixture, which was stirred at r.t. for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with H_2O, and extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified through flash column chromatography on silica gel to afford pure product **S2** as a yellow oil.

Step 2: The solution of **S2** in 15 mL *N*,*N*-dimethylacetamide (DMAc) was cooled to 0 ºC in an ice bath. Chloroformate (1.2 equiv) was added dropwise to the mixture and then stirred at room temperature for 12 h. After the completion of the reaction (monitored by TLC), the reaction was quenched with H_2O, and extracted with EtOAc (3×10 mL). The organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified through flash column chromatography on silica gel to afford pure product **1** as white solids.

3. Reaction Optimization

Table S1. Reaction optimization[a]



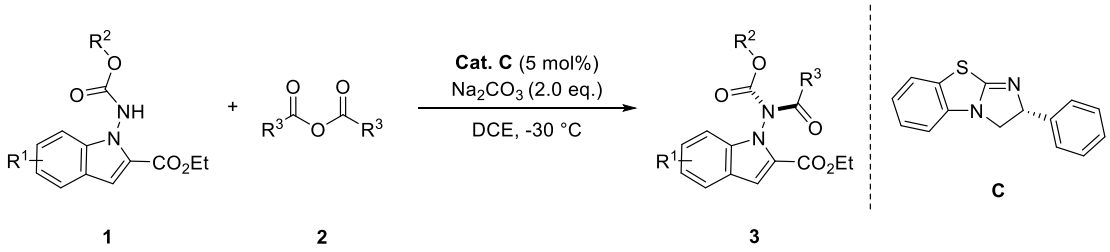


Entry	Cat.	Solvent	Base	Yield(%)[b]	er[c]
1	A	DCM	Na_2CO_3	44	39:61
2	B	DCM	Na_2CO_3	64	87.5:12.5
3	C	DCM	Na_2CO_3	53	89:11
4	D	DCM	Na_2CO_3	51	69.5:30.5
5	E	DCM	Na_2CO_3	35	34:66
6	F	DCM	Na_2CO_3	41	66:34
7	G	DCM	Na_2CO_3	69	33.5:66.5
8	H	DCM	Na_2CO_3	72	25:75
9	I	DCM	Na_2CO_3	60	59:41
10	C	DCE	Na_2CO_3	46	90:10
11	C	THF	Na_2CO_3	49	60.5:39.5
12	C	$CHCl_3$	Na_2CO_3	50	83.5:16.5
13	C	CCl_4	Na_2CO_3	64	82:18
14	C	$Cl_2(CH)_2Cl_2$	Na_2CO_3	53	85.5:14.5

15	C	Toluene	Na_2CO_3	71	89.5:10.5
16	C	*n*-Hexane	Na_2CO_3	39	88:12
17	C	*n*-Heptane	Na_2CO_3	33	84.5:15.5
18	C	CH_3CN	Na_2CO_3	79	80:20
19	C	C_6H_5Cl	Na_2CO_3	44	86.5:13.5
20	C	Anisole	Na_2CO_3	65	86:14
21	C	MTBE	Na_2CO_3	37	86.5:13.5
22	C	DCE	K_2CO_3	49	88.5:11.5
23	C	DCE	Cs_2CO_3	74	85:15
24	C	DCE	KO^{t}Bu	64	55.5:44.5
25	C	DCE	DBU	75	67:33
26	C	DCE	$NaHCO_3$	29	87.5:12.5
27	C	DCE	K_3PO_4	75	87.5:12.5
28	C	DCE	K_2HPO_4	59	89:11
29	C	DCE	NaOAc	40	86:14
30	C	DCE	KOH	79	79.5:20.5
31	C	DCE	NaOH	47	70.5:29.5
32	C	DCE	DIPEA	71	88.5:11.5
33[d]	C	DCE	Na_2CO_3	79	91:9
34[e]	C	DCE	Na_2CO_3	80	93:7
35[g]	C	Toluene	Na_2CO_3	79	89:11
36[f]	C	DCE:Toluene (1:1)	Na_2CO_3	66	93:7
37[g]	C	DCE:Toluene (1:1)	Na_2CO_3	40	91.5:8.5
39[e,h]	C	DCE	Na_2CO_3	81	95:5
39[e,i]	C	DCE	Na_2CO_3	73	92.5:7.5
40[e,j]	C	DCE	Na_2CO_3	38	92:8

[a] Reaction conditions: a mixture of **1a** (0.1 mmol), **2a** (0.12 mmol), base (2.0 eq) and ITU Catalyst (10 mol%) in solvent (1 mL) was stirred at room temperature for 12 h. [b] Isolated yield. [c] er values were determined by HPLC analysis. [d] 0 ºC for 72 h. [e] -30 ºC for 72 h. [f] -35 ºC for 72 h. [g] -40 ºC for 72 h. [h] Catalyst loading (5 mol%). [i] Catalyst loading (2 mol%). [j] Molecular sieve (4 Å) was added as an additive.

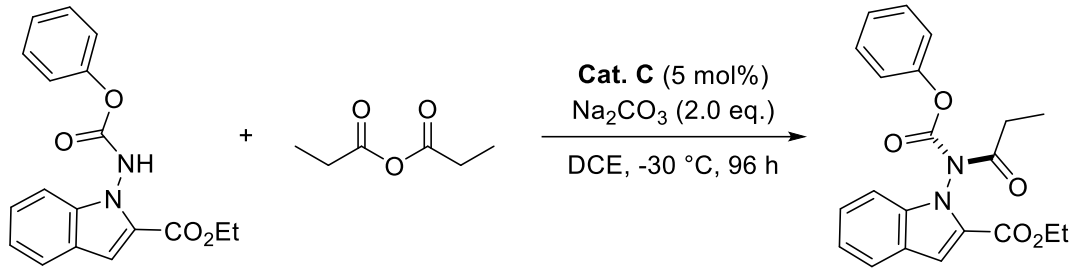
4. General Procedure for the Synthesis of 3



A mixture of ethyl carbamido-indole-2-carboxylates **1** (0.1 mmol), anhydrides **2** (0.12 mmol), Na_2CO_3 (2.0 equiv), and **Cat. C** (5 mol%) in DCE (1.0 mL) was stirred at -30 ^oC for 72 h, and then the solvent was removed under reduced pressure. The residue was purified through flash column chromatography on silica gel to afford product **3** as a colorless oil.

5. The Large-scale Reaction and Synthetic Transformations

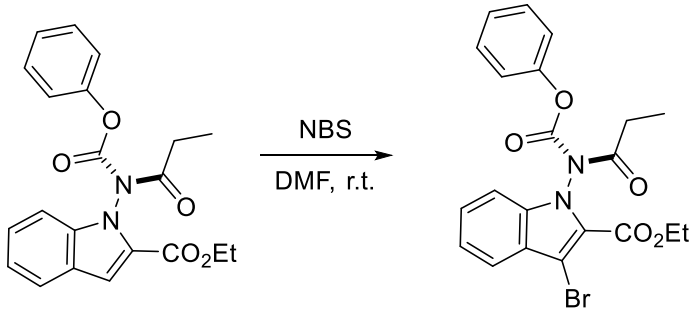
The large-scale reaction of 3sa



1s 1 mmol | **2a** 1.2 mmol | **3sa** 86%, 97.5:2.5 e.r.

Ethyl 1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate **1s** (324 mg, 1 mmol), Na_2CO_3 (212 mg, 2.0 eq.) and **Cat. C** (13.0 mg, 0.05 mmol) were added to a dried flask. Then, a solution of propionic anhydride **2a** (156 mg, 1.2 mmol) in DCE (10 mL) was added to the reaction mixture, which was stirred at -30 °C for 96 h. After the completion of the reaction (monitored by TLC), the reaction mixture was concentrated under the reduced pressure to give the residue, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to afford product **3sa** in 86% yield (327 mg) and 97.5:2.5 er.

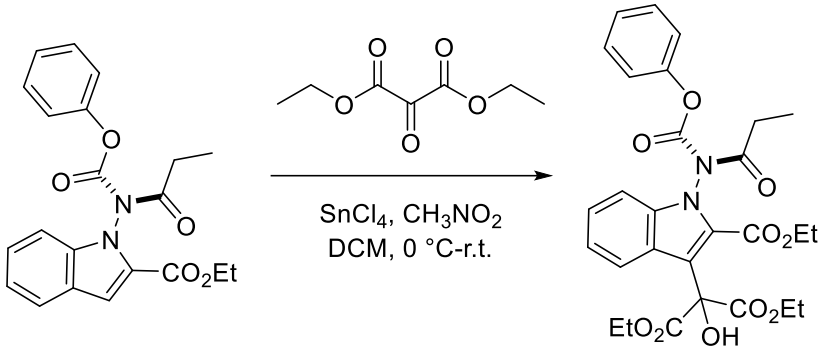
Synthetic transformations of 3sa[2]



3sa 97.5:2.5 e.r. | **4** 70%, 97.5:2.5 e.r.

To a stirring solution of **3sa** (0.1 mmol, 97.5:2.5 er) in DMF (1 mL) was added N-bromosuccinimide (NBS) (0.12 mmol). The resulting mixture was allowed to stir at r.t. for 24 h. After the completion of the reaction (monitored by TLC), the reaction was quenched with water, and extracted with EtOAc. The organic layers were dried over

anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified through flash column chromatography on silica gel (petroleum ether/EtOAc = 24:1) to afford compound **4** (70%, 97.5:2.5 er) as a yellow oil.



3sa
97.5:2.5 e.r.

5
54%, 97.5:2.5 e.r.

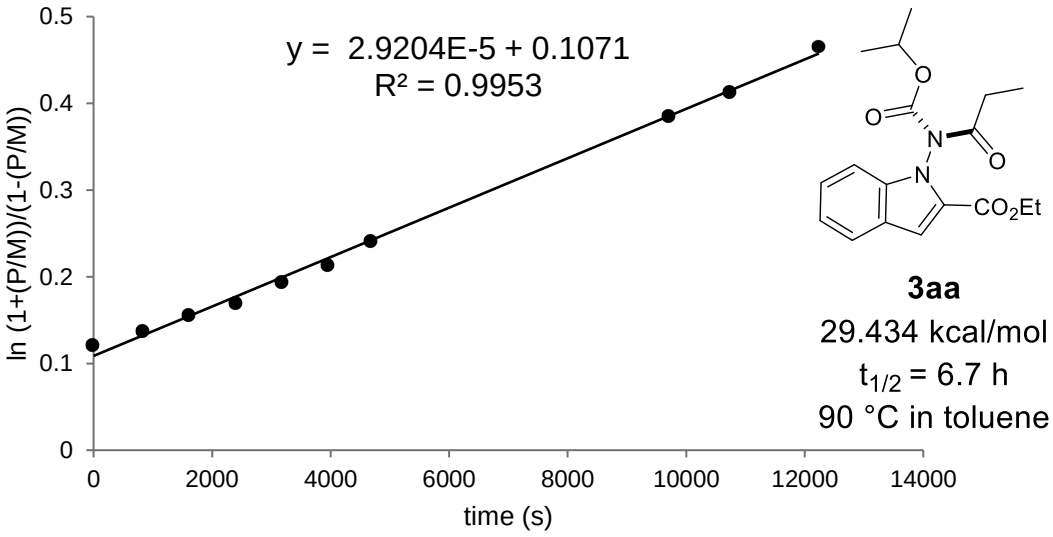
3sa (0.1 mmol, 97.5:2.5 er) was dissolved in 0.5 mL DCM under a nitrogen atmosphere, and the solution was cooled to 0 °C. To the stirring solution was added $SnCl_4$ (0.12 mmol) in a single portion via syringe. After the ice bath was removed, the mixture was stirred at room temperature for 30 min, and then the diethyl ketomalonate (0.12 mmol) was added in small portions, followed by the addition of nitromethane (0.5 mL). The reaction mixture was stirred at room temperature overnight. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched by the cold water and the mixture was extracted with EtOAc. The organic layers were dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified through flash column chromatography on silica gel (petroleum ether/EtOAc = 24:5) to afford compound **5** (54%, 97.5:2.5 er) as a colorless oil.

6. Racemization Experiment

Table S2. Measured data of rotation barrier and half-life of **3aa**

t	P/M	（1+(P/M)）/(1-(P/M))	ln
0	0.0604	1.1286	0.1210
840	0.0683	1.1467	0.1369
1620	0.0775	1.1682	0.1554
2400	0.0845	1.1848	0.1696
3180	0.0964	1.2135	0.1935
3960	0.1061	1.2376	0.2131
4680	0.1198	1.2722	0.2407
9720	0.1904	1.4705	0.3856
10740	0.2033	1.5105	0.4124
12240	0.2285	1.5923	0.4652

Scheme S1. Rotational energy barrier and half-life of **3aa**



7. Biological Evaluation of N–N Axially Chiral Aminoindole Products

We performed a preliminary investigation on the cytotoxicity of N–N axially chiral aminoindole products against U266 human myeloma cells and LNCaP prostate cancer cells. As shown in Figure S1, N–N axially chiral aminoindoles exhibited better cytotoxicity with an IC_{50} value of 0.87–67.00 μM against U266 and LNCaP cells, compared to their racemic products.

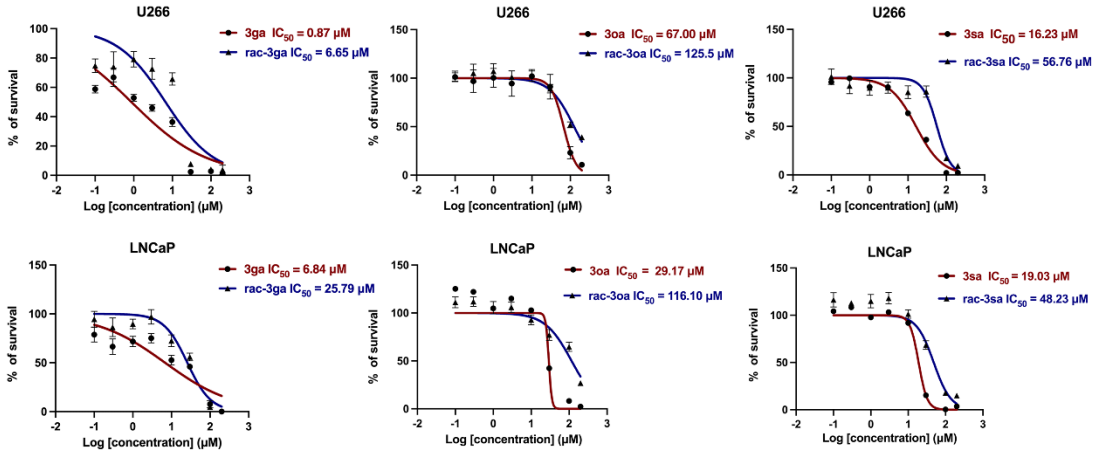


Figure S1. Cytotoxicity of different products on human myeloma cells U266 and prostate cancer cells LNCaP. The IC_{50} value corresponded to the compound concentration causing 50% mortality in cancer cells.

Procedure for determination of U266 and LNCaP viability by CCK-8 asssay

Human myeloma cells (U266) and prostate cancer cells (LNCaP) were seeded in 96-well plates at the density of 8,000 cells and 10,000 cells per well with 100 μL of complete culture medium. After 24 hours, selected different products were added to the medium with eight concentrations ranging from 0.1 μM to 200 μM. The cells were then cultured for another 72 h. Cells without product exposure were used as control, and the wells to which only culture medium was added served as blank. At the end of stimulation, 10 μL Cell-Counting-Kit-8 (CCK-8, HY-K0301, MCE, USA) was added to the medium, and the cells were cultured for 1 - 3 h at 37 °C. Then, the culture plates were shaken for 10 seconds, and the optical density (OD) values were read at wave-length of 450 nm in microplate reader (Thermo Scientific™ Multiskan™ FC, USA).

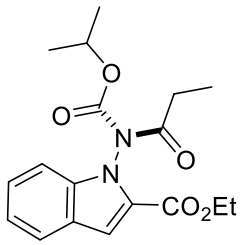
Note: N = 6 for each experimental group, and measurements were taken from 3 distinct samples.

Data analysis

Data are represented as means ± SD, and IC_{50} was performed using Prism 9.0 software (Graphpad Prism).

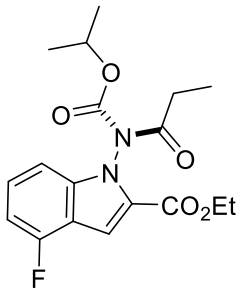
8. Characterization Data

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3aa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 28.0 mg, 81% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.42-7.30 (m, 2H), 7.25-7.13 (m, 2H), 5.01 (h, *J* = 6.2 Hz, 1H), 4.40-4.23 (m, 2H), 3.05 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.4, 152.4, 138.4, 126.6, 126.5, 124.1, 122.9, 121.9, 110.7, 108.8, 72.2, 60.8, 30.5, 21.5, 21.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{22}N_2O_5$) requires m/z 369.1421, found m/z 369.1421. The enantiomeric ratio was determined to be 95:5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.6 min (minor), 10.6 min (major). $[\alpha]^{25}_D$ = -24.8 (c = 1.00, $CHCl_3$).

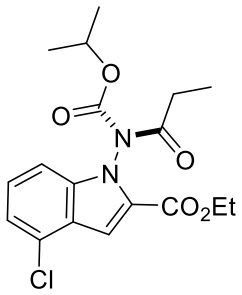
(R_a)-ethyl-4-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ba)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 35.6 mg, 98% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.32-7.23 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.86 (dd, *J* = 9.9, 7.9 Hz, 1H), 5.01 (h, *J* = 6.2 Hz, 1H), 4.37-4.26 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.0, 157.2 (d, *J* = 251.9 Hz), 152.2, 140.4 (d, *J* = 9.6 Hz), 127.2 (d, *J* = 7.8 Hz), 126.7, 113.8 (d, *J* = 23.8 Hz), 106.6 (d, *J* = 18.8 Hz), 106.4, 104.9 (d, *J* = 4.0 Hz), 72.4, 61.0, 30.6, 21.5, 21.4, 14.2, 8.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.5. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}FN_2O_5$) requires m/z 387.1327, found m/z 387.1325. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 9:1,

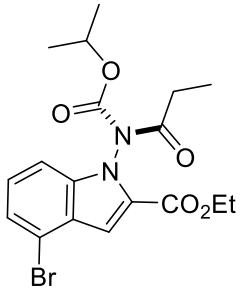
1.0 mL/min]: 4.2 min (minor), 5.5 min (major). $[\alpha]^{25}_D$ = -13.2 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-4-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 38.4 mg, 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (s, 1H), 7.31-7.19 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 5.02 (h, *J* = 6.3 Hz, 1H), 4.41-4.24 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.0, 152.2, 138.9, 128.4, 127.0, 126.9, 123.1, 121.7, 108.7, 107.5, 72.4, 61.0, 30.6, 21.5, 21.4, 14.2, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}ClN_2O_5$) requires m/z 403.1031, found m/z 403.1033. The enantiomeric ratio was determined to be 95:5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.8 min (minor), 4.5 min (major). $[\alpha]^{25}_D$ = -13.9 (c = 1.00, $CHCl_3$).

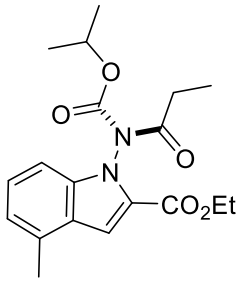
(R_a)-ethyl-4-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3da)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 37.4 mg, 88% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.34 (m, 2H), 7.24-7.18 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.02 (h, *J* = 6.3 Hz, 1H), 4.41-4.24 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.1, 152.2, 141.2, 138.6, 127.2, 127.0, 124.9, 117.1, 110.3, 108.1, 72.5, 61.1, 30.7, 21.5, 21.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}BrN_2O_5$) requires m/z 447.0526, found m/z 447.0525. The enantiomeric ratio was determined to be 95.5:4.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.9 min (minor), 4.4 min (major). $[\alpha]^{25}_D$ = -12.1 (c =

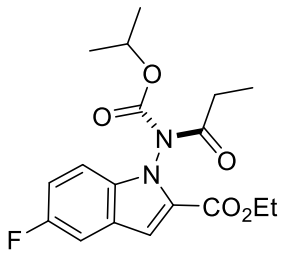
1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-4-methyl-1H-indole-2-carboxylate (3ea)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 26.6 mg, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 1.0 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.02-6.95 (m, 2H), 5.01 (h, *J* = 6.3 Hz, 1H), 4.40-4.23 (m, 2H), 3.03 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.4, 152.4, 138.3, 132.7, 126.7, 125.9, 124.1, 122.1, 109.3, 106.4, 72.2, 60.7, 30.5, 21.5, 21.4, 18.2, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_5$) requires m/z 383.1577, found m/z 383.1578. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.0 min (minor), 4.5 min (major). $[\alpha]^{25}_D$ = -8.6 (c = 1.00, $CHCl_3$).

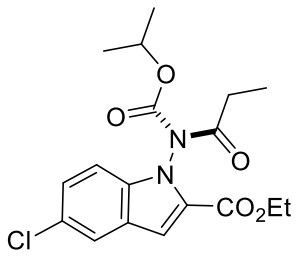
(R_a)-ethyl-5-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3fa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 29.2 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37-7.29 (m, 2H), 7.17-7.05 (m, 2H), 5.01 (h, *J* = 6.3 Hz, 1H), 4.40-4.23 (m, 2H), 3.07 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 160.1, 158.8 (d, *J* = 237.8 Hz), 152.3, 134.9, 128.0, 124.3 (d, *J* = 10.5 Hz), 115.3 (d, *J* = 26.9 Hz), 110.2 (d, *J* = 5.1 Hz), 109.9 (d, *J* = 9.6 Hz), 107.5 (d, *J* = 23.9 Hz), 72.3, 60.9, 30.6, 21.5, 21.4, 14.2, 8.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}FN_2O_5$) requires m/z 387.1327, found m/z 387.1325. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H

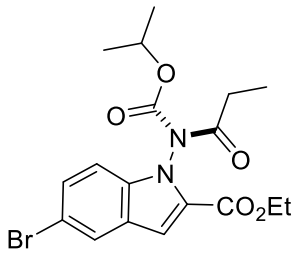
column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.9 min (minor), 4.6 min (major). $[\alpha]^{25}_{D}$ = -11.8 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-5-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ga)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 25.4 mg, 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 1.9 Hz, 1H), 7.37-7.26 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 1H), 5.01 (h, *J* = 6.3 Hz, 1H), 4.40-4.23 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 160.0, 152.2, 136.7, 127.7, 127.5, 126.9, 124.9, 122.1, 110.1, 109.7, 72.4, 61.0, 30.6, 21.5, 21.4, 14.2, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}ClN_2O_5$) requires m/z 403.1031, found m/z 403.1032. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.8 min (minor), 4.4 min (major). $[\alpha]^{25}_{D}$ = -8.4 (c = 1.00, $CHCl_3$).

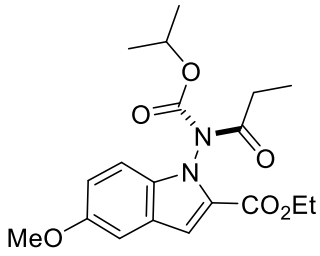
(R_a)-ethyl-5-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ha)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 32.8 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.44 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.28 (s, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 5.01 (h, *J* = 6.3 Hz, 1H), 4.4-4.23 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.0, 152.2, 136.9, 129.4, 127.5, 125.5, 125.3, 115.0, 110.4, 109.6, 72.4, 61.0, 30.6, 21.5, 21.4, 14.2, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}BrN_2O_5$) requires m/z 447.0526, found m/z 447.0523. The enantiomeric ratio was determined to

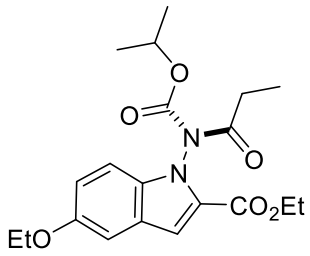
be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.9 min (minor), 4.4 min (major). $[\alpha]^{25}_D$ = -10.0 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-methoxy-1H-indole-2-carboxylate (3ia)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 30.2 mg, 80% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 1H), 7.10-7.06 (m, 2H), 7.02-6.99 (m, 1H), 5.00 (h, *J* = 6.2 Hz, 1H), 4.39-4.22 (m, 2H), 3.84 (s, 3H), 3.03 (q, *J* = 7.3 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.3, 155.6, 152.4, 133.7, 126.9, 124.5, 117.6, 110.1, 109.8, 103.4, 72.2, 60.7, 55.8, 30.5, 21.5, 21.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_6$) requires m/z 399.1527, found m/z 399.1527. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.7 min (minor), 6.1 min (major). $[\alpha]^{25}_D$ = -5.4 (c = 1.00, $CHCl_3$).

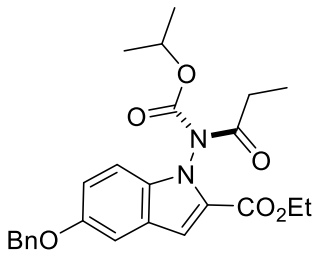
(R_a)-ethyl-5-ethoxy-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ja)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 35.2 mg, 90% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 0.8 Hz, 1H), 7.11-7.05 (m, 1H), 7.06-6.97 (m, 2H), 5.00 (h, *J* = 6.3 Hz, 1H), 4.38-4.21 (m, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.02 (q, *J* = 7.3 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.3, 154.8, 152.4, 133.7, 126.9, 124.5, 118.1, 110.2, 109.7, 104.3, 72.1, 64.1, 60.7, 30.5, 21.5, 21.4, 14.9, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{26}N_2O_6$) requires m/z 413.1683, found m/z 413.1681. The

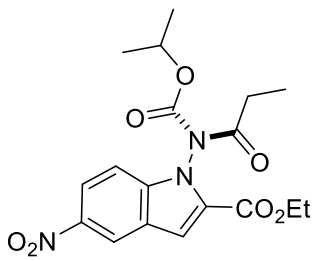
enantiomeric ratio was determined to be 93:7 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.3 min (minor), 5.9 min (major). $[\alpha]^{25}_{D}$ = -6.4 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-5-(benzyloxy)-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ka)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 41.0 mg, 91% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50-7.43 (m, 2H), 7.43-7.36 (m, 2H), 7.36-7.28 (m, 1H), 7.27 (d, *J* = 0.8 Hz, 1H), 7.18-7.14 (m, 1H), 7.13-7.09 (m, 1H), 7.09-7.02 (m, 1H), 5.09 (s, 2H), 5.00 (h, *J* = 6.3 Hz, 1H), 4.38-4.21 (m, 2H), 3.03 (q, *J* = 7.3 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.3, 154.7, 152.4, 137.2, 133.8, 128.6, 128.0, 127.6, 126.9, 124.4, 118.2, 110.2, 109.8, 104.9, 72.2, 70.7, 60.7, 30.6, 21.5, 21.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{25}H_{28}N_2O_6$) requires m/z 475.1840, found m/z 475.1843. The enantiomeric ratio was determined to be 92.5:7.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 6.7 min (minor), 9.6 min (major). $[\alpha]^{25}_{D}$ = -4.8 (c = 1.00, $CHCl_3$).

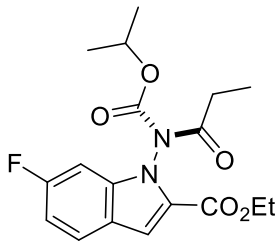
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-nitro-1H-indole-2-carboxylate (3la)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 37.8 mg, 97% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 2.1 Hz, 1H), 8.26 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.51 (s, 1H), 7.27 (s, 1H), 5.04 (h, *J* = 6.3 Hz, 1H), 4.43-4.26 (m, 2H), 3.16 (q, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.3 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 159.6, 151.8, 143.5, 140.7, 129.5, 123.2, 121.5, 120.1, 111.7, 109.4, 72.9, 61.4, 30.8, 21.5, 21.4, 14.2, 8.7.

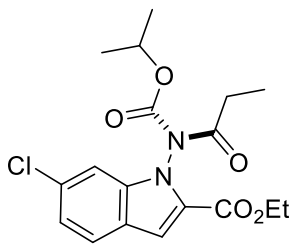
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}N_3O_7$) requires m/z 414.1272, found m/z 414.1275. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 5.0 min (minor), 5.9 min (major). $[\alpha]^{25}_D$ = -4.9 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-6-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ma)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 25.8 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.7, 5.1 Hz, 1H), 7.34 (s, 1H), 6.96 (td, *J* = 9.1, 2.3 Hz, 1H), 6.83 (dd, *J* = 9.0, 2.3 Hz, 1H), 5.02 (h, *J* = 6.3 Hz, 1H), 4.39-4.22 (m, 2H), 3.08 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 162.5 (d, *J* = 244.9 Hz), 160.1, 152.2, 138.8 (d, *J* = 12.4 Hz), 127.2 (d, *J* = 4.0 Hz), 124.3 (d, *J* = 10.2 Hz), 120.5, 111.4 (d, *J* = 25.1 Hz), 110.7, 95.4 (d, *J* = 27.1 Hz), 72.4, 60.8, 30.7, 21.5, 21.4, 14.3, 8.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.6. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}FN_2O_5$) requires m/z 387.1327, found m/z 387.1325. The enantiomeric ratio was determined to be 93:7 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.0 min (minor), 5.9 min (major). $[\alpha]^{25}_D$ = -14.3 (c = 1.00, $CHCl_3$).

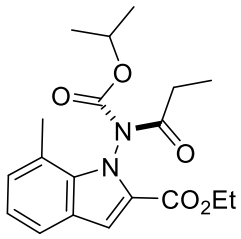
(R_a)-ethyl-6-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3na)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 26.0 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 9.2 Hz, 1H), 7.33 (s, 1H), 7.24-7.04 (m, 2H), 5.02 (h, *J* = 6.3 Hz, 1H), 4.39-4.22 (m, 2H), 3.09 (q, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR

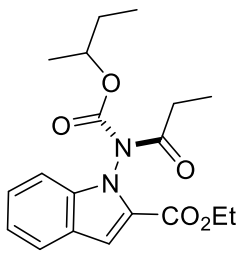
(101 MHz, Chloroform-*d*) δ 174.0, 160.1, 152.2, 138.7, 132.7, 127.2, 123.9, 123.0, 122.5, 110.5, 109.0, 72.5, 60.9, 30.7, 21.5, 21.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{18}H_{21}ClN_2O_5$) requires m/z 403.1031, found m/z 403.1032. The enantiomeric ratio was determined to be 88:12 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 3.9 min (minor), 4.8 min (major). $[\alpha]^{25}_D$ = -12.9 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-7-methyl-1H-indole-2-carboxylate (3oa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 30.8 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (p, *J* = 3.5 Hz, 1H), 7.35 (s, 1H), 7.07 (d, *J* = 4.8 Hz, 2H), 5.06 (h, *J* = 6.2 Hz, 1H), 4.38-4.21 (m, 2H), 3.17-2.95 (m, 2H), 2.40 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.14 (t, *J* = 5.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 160.4, 152.8, 136.8, 128.7, 126.6, 124.7, 121.8, 120.9, 120.7, 111.3, 72.2, 60.7, 30.6, 21.5, 21.4, 17.4, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_5$) requires m/z 383.1577, found m/z 383.1577. The enantiomeric ratio was determined to be 96:4 by HPLC. [OD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.3 min (minor), 8.2 min (major). $[\alpha]^{25}_D$ = -7.1 (c = 1.00, $CHCl_3$).

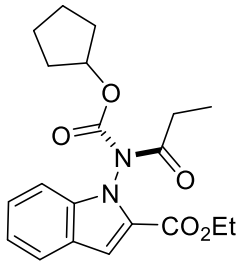
(R_a)-ethyl-1-(N-(sec-butoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3pa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 36.0 mg, 99% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.37 (s, 2H), 7.19 (q, *J* = 8.3 Hz, 2H), 4.82 (h, *J* = 6.2 Hz, 1H), 4.39-4.22 (m, 2H), 3.07 (q, *J* = 7.3 Hz, 2H), 1.44-1.38 (m, 2H), 1.37-1.31 (m, 3H), 1.22 (t, *J* = 7.3 Hz, 3H), 1.09 (dd, *J* = 27.9, 6.2 Hz, 3H), 0.64 (dt, *J* = 62.5, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.4, 152.6, 138.4, 126.5, 124.1, 122.9,

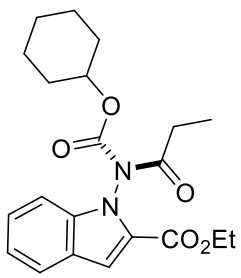
121.9, 121.8, 110.7, 108.8, 76.6, 60.8, 30.5, 28.4, 19.1, 14.3, 9.1, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_5$) requires m/z 383.1577, found m/z 383.1575. The enantiomeric ratio was determined to be 94:6 by HPLC. [IA column, 254 nm, *n*-hexane:IPA = 9:1, 1.0 mL/min]: 5.3 min (minor), 6.0 min (major). $[\alpha]^{25}_D$ = -12.4 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-((cyclopentyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3qa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 34.6 mg, 93% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 2H), 7.24-7.12 (m, 2H), 5.17-5.15 (m, 1H), 4.34-4.25 (m, 2H), 3.06 (qd, *J* = 7.3, 3.6 Hz, 2H), 1.77-1.63 (m, 2H), 1.50-1.41 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 5H), 1.22 (t, *J* = 7.3 Hz, 5H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 160.4, 152.4, 138.4, 126.6, 126.5, 124.0, 122.9, 121.9, 110.7, 108.8, 81.3, 60.8, 32.4, 32.3, 30.5, 23.1, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{24}N_2O_5$) requires m/z 395.1577, found m/z 395.1575. The enantiomeric ratio was determined to be 94.5:5.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 25:1, 1.0 mL/min]: 13.4 min (minor), 14.3 min (major). $[\alpha]^{25}_D$ = -14.1 (c = 1.00, $CHCl_3$).

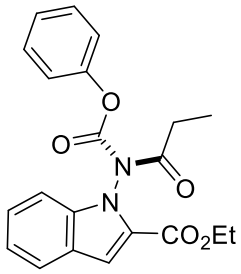
(R_a)-ethyl-1-(N-((cyclohexyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3ra)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 26.3 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.2-7.13 (m, 2H), 4.8-4.80 (m, 1H), 4.3-4.24 (m, 2H), 3.07 (qd, *J* = 7.3, 2.8 Hz, 2H), 1.6-1.57 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 5H), 1.3-1.27 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 5H), 1.17 (d, *J* = 21.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 160.4, 152.2, 138.4, 126.6, 126.5, 124.1, 122.9, 121.9, 110.7, 108.8, 76.1, 60.8, 30.8, 30.5, 25.0, 22.7, 22.6, 14.3, 8.8. HRMS (ESI): exact mass

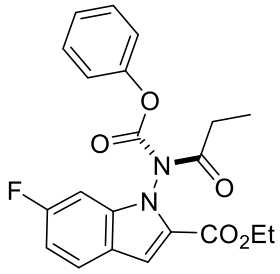
calculated for $[M+Na]^+$ ($C_{21}H_{26}N_2O_5$) requires m/z 409.1734, found m/z 409.1738. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 9:1, 1.0 mL/min]: 7.2 min (minor), 7.8 min (major). $[\alpha]^{25}_D$ = -15.9 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3sa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 32.8 mg, 86% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.36-7.28 (m, 3H), 7.26-7.19 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.37 (qd, *J* = 7.1, 3.8 Hz, 2H), 3.13 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.6, 152.1, 150.2, 138.4, 129.5, 129.4, 126.8, 126.5, 124.2, 123.2, 122.2, 121.3, 111.1, 108.8, 61.0, 30.8, 14.3, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{21}H_{20}N_2O_5$) requires m/z 403.1264, found m/z 403.1262. The enantiomeric ratio was determined to be 97.5:2.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 8.2 min (minor), 9.0 min (major). $[\alpha]^{25}_D$ = -32.4 (c = 1.00, $CHCl_3$).

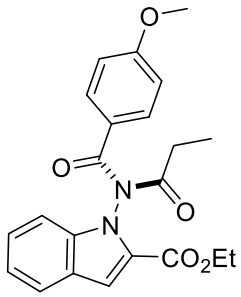
(R_a)-ethyl-6-fluoro-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ta)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 30.6 mg, 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 2.4 Hz, 1H), 7.38-7.33 (m, 2H), 7.32 (s, 1H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 1H), 7.04-6.97 (m, 2H), 4.37 (qd, *J* = 7.1, 3.9 Hz, 2H), 3.14 (qd, *J* = 7.3, 3.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 160.4, 159.0 (d, *J* = 238.3 Hz), 151.9, 150.1, 134.9, 129.6, 127.8, 126.6, 124.5 (d, *J* = 10.3 Hz), 121.2, 115.7 (d, *J* = 27.1 Hz), 110.6 (d, *J* = 5.1 Hz), 109.9 (d, *J* = 9.6 Hz), 107.8 (d, *J* = 23.6 Hz), 61.2, 30.8, 14.3, 8.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -121.2. HRMS (ESI): exact mass calculated for $[M+Na]^+$

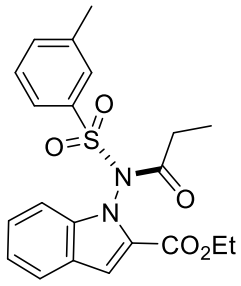
($C_{21}H_{19}FN_2O_5$) requires m/z 421.1170, found m/z 421.1173. The enantiomeric ratio was determined to be 96:4 by HPLC. [IC column, 254 nm, *n*-hexane:IPA = 9:1, 1.0 mL/min]: 5.9 min (minor), 7.4 min (major). $[\alpha]^{25}_D$ = -46.7 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(4-methoxy-N-propionylbenzamido)-1H-indole-2-carboxylate (3ua)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 24.1 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.43-7.32 (m, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 2.54 (t, *J* = 6.9 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.2, 167.7, 160.4, 131.9, 128.5, 128.0, 126.6, 124.4, 123.1, 123.0, 122.3, 120.6, 111.5, 110.7, 110.0, 61.0, 55.5, 29.7, 14.2, 8.3. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{22}N_2O_5$) requires m/z 417.1421, found m/z 417.1424. The enantiomeric ratio was determined to be 96:4 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 9.4 min (minor), 9.9 min (major). $[\alpha]^{25}_D$ = -19.1 (c = 1.00, $CHCl_3$).

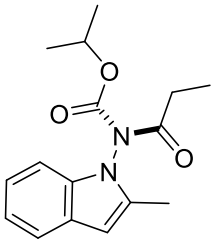
(R_a)-ethyl-1-(N-(m-tolylsulfonyl)propionamido)-1H-indole-2-carboxylate (3va)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 28.2 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89-7.80 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.51-7.43 (m, 3H), 7.47-7.36 (m, 1H), 7.39-7.29 (m, 1H), 7.32-7.24 (m, 1H), 4.17-3.93 (m, 2H), 2.43 (s, 3H), 2.39-2.07 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 159.9, 140.0, 139.0, 137.7, 135.2, 130.1, 128.6, 127.8, 127.5, 127.1, 124.3, 123.2, 123.1, 113.5, 110.4, 61.2, 27.5, 21.3, 14.0, 7.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{21}H_{22}N_2O_5S$) requires m/z 437.1142, found m/z 437.1144. The enantiomeric ratio was determined to be 71.5:28.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 14.3 min (minor), 15.0 min (major). $[\alpha]^{25}_D$ = -

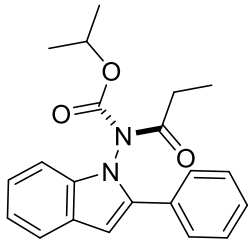
8.6 (c = 1.00, $CHCl_3$).

(R_a)-isopropyl(2-methyl-1H-indol-1-yl)(propionyl)carbamate (3wa)



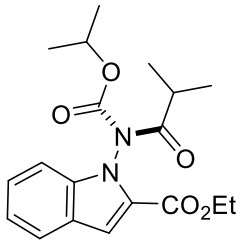
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 10.1 mg, 35% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.0 Hz, 1H), 7.19-7.06 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 5.01 (h, *J* = 6.2 Hz, 1H), 2.79 (qd, *J* = 7.3, 2.6 Hz, 2H), 2.21 (s, 3H), 1.22-1.14 (m, 6H), 1.07 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 152.3, 136.1, 135.9, 126.5, 122.1, 120.8, 120.3, 107.5, 100.2, 72.4, 29.9, 21.5, 21.4, 11.2, 8.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{16}H_{20}N_2O_3$) requires m/z 311.1366, found m/z 311.1369. The enantiomeric ratio was determined to be 83:17 by HPLC. [IC column, 254 nm, *n*-hexane:IPA = 5:1, 1.0 mL/min]: 8.4 min (major), 9.1 min (minor). $[\alpha]^{25}_D$ = -7.4 (c = 1.00, $CHCl_3$).

(R_a)-isopropyl(2-phenyl-1H-indol-1-yl)(propionyl)carbamate (3xa)



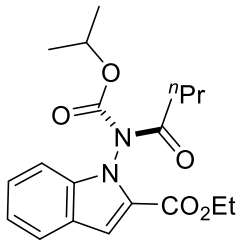
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 17.2 mg, 49% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.45-7.32 (m, 5H), 7.28-7.14 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.67 (s, 1H), 4.93 (h, *J* = 6.2 Hz, 1H), 2.93-2.66 (m, 2H), 1.09 (dt, *J* = 7.3, 4.2 Hz, 6H), 1.02 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 152.4, 140.8, 137.4, 130.8, 128.6, 128.4, 128.3, 126.6, 123.2, 121.5, 121.1, 108.4, 102.1, 72.4, 30.3, 21.4, 8.9. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{21}H_{22}N_2O_3$) requires m/z 373.1523, found m/z 373.1525. The enantiomeric ratio was determined to be 88:12 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.8 min (major), 5.7 min (minor). $[\alpha]^{25}_D$ = 5.2 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)isobutyramido)-1H-indole-2-carboxylate (3ab)



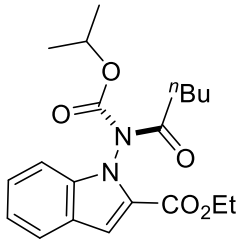
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 25.2 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.40-7.31 (m, 2H), 7.24-7.15 (m, 1H), 7.16-7.09 (m, 1H), 5.02 (h, *J* = 6.2 Hz, 1H), 4.31 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.80 (h, *J* = 6.7 Hz, 1H), 1.38-1.31 (m, 6H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 160.3, 152.3, 138.3, 126.9, 126.4, 124.1, 122.9, 121.9, 110.5, 108.7, 72.2, 60.7, 34.6, 21.5, 21.4, 19.9, 18.9, 14.3. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_5$) requires m/z 383.1577, found m/z 383.1577. The enantiomeric ratio was determined to be 96:4 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.5 min (minor), 5.6 min (major). $[\alpha]^{25}_D$ = -15.2 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)butyramido)-1H-indole-2-carboxylate (3bb)



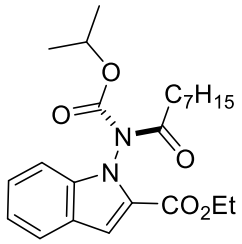
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 24.0 mg, 94% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 9.2 Hz, 2H), 7.24-7.12 (m, 2H), 5.00 (h, *J* = 6.3 Hz, 1H), 4.41-4.19 (m, 2H), 3.01 (q, *J* = 6.9 Hz, 2H), 1.76 (h, *J* = 7.3 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 160.4, 152.4, 138.4, 126.6, 126.4, 124.1, 122.9, 121.9, 110.6, 108.8, 72.2, 60.8, 38.9, 21.5, 21.4, 18.0, 14.3, 13.6. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}N_2O_5$) requires m/z 383.1577, found m/z 383.1574. The enantiomeric ratio was determined to be 92.5:7.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 5.0 min (minor), 5.7 min (major). $[\alpha]^{25}_D$ = -9.8 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)pentanamido)-1H-indole-2-carboxylate (3cb)



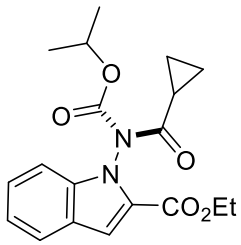
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 26.6 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.39-7.32 (m, 2H), 7.22-7.12 (m, 2H), 5.00 (h, *J* = 6.3 Hz, 1H), 4.39-4.23 (m, 2H), 3.13-2.94 (m, 2H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.47-1.37 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.07 (d, *J* = 6.2 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 160.4, 152.4, 138.4, 126.7, 126.4, 124.1, 122.9, 121.9, 110.6, 108.8, 72.2, 60.8, 36.7, 26.6, 22.2, 21.5, 21.4, 14.3, 13.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{26}N_2O_5$) requires m/z 397.1734, found m/z 397.1732. The enantiomeric ratio was determined to be 93:7 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 5.2 min (minor), 5.9 min (major). $[\alpha]^{25}_D$ = -15.4 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)octanamido)-1H-indole-2-carboxylate (3db)



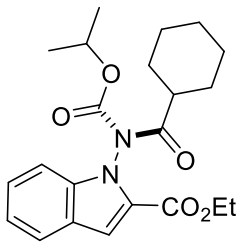
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 28.2 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.39-7.34 (m, 2H), 7.24-7.11 (m, 2H), 5.00 (h, *J* = 6.3 Hz, 1H), 4.32-4.27 (m, 2H), 3.12-2.92 (m, 2H), 1.72 (p, *J* = 7.4 Hz, 2H), 1.37 (s, 2H), 1.34 (d, *J* = 7.2 Hz, 3H), 1.30-1.24 (m, 6H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 160.4, 152.4, 138.4, 126.6, 126.4, 124.1, 122.9, 121.9, 110.6, 108.8, 72.2, 60.8, 37.0, 31.7, 29.1, 29.0, 24.5, 22.6, 21.5, 21.4, 14.3, 14.1. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{32}N_2O_5$) requires m/z 439.2203, found m/z 439.2203. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 4.8 min (minor), 5.1 min (major). $[\alpha]^{25}_D$ = -16.3 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclopropanecarboxamido)-1H-indole-2-carboxylate (3eb)



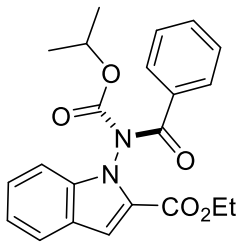
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 22.8 mg, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.42-7.33 (m, 2H), 7.28-7.16 (m, 2H), 5.04 (h, *J* = 6.3 Hz, 1H), 4.33 (p, *J* = 7.0 Hz, 2H), 2.73 (tt, *J* = 8.2, 4.6 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 2H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.2 Hz, 3H), 1.07-0.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 160.3, 152.5, 138.4, 127.1, 126.5, 124.0, 122.9, 122.0, 110.7, 109.0, 72.2, 60.8, 21.5, 21.4, 14.3, 10.9, 10.8. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{22}N_2O_5$) requires m/z 381.1421, found m/z 381.1419. The enantiomeric ratio was determined to be 93.5:6.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 15:1, 1.0 mL/min]: 12.0 min (major), 12.9 min (minor). $[\alpha]^{25}_D$ = -22.7 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclohexanecarboxamido)-1H-indole-2-carboxylate (3fb)



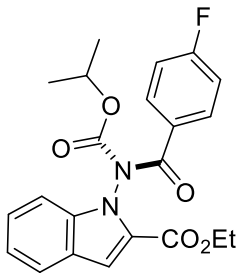
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 27.4 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.38-7.30 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.02 (h, *J* = 6.3 Hz, 1H), 4.38-4.22 (m, 2H), 3.58 (tt, *J* = 11.3, 3.3 Hz, 1H), 2.14-2.03 (m, 2H), 1.88-1.77 (m, 2H), 1.75-1.67 (m, 1H), 1.57-1.48 (m, 2H), 1.46-1.38 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28-1.22 (m, 1H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 160.3, 152.4, 138.3, 126.9, 126.3, 124.1, 122.9, 121.8, 110.4, 108.7, 72.1, 60.7, 44.3, 30.2, 28.8, 25.8, 25.4, 21.5, 21.4, 14.3. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{28}N_2O_5$) requires m/z 423.1890, found m/z 423.1892. The enantiomeric ratio was determined to be 96.5:3.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 5.2 min (minor), 6.7 min (major). $[\alpha]^{25}_D$ = -12.2 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3gb)



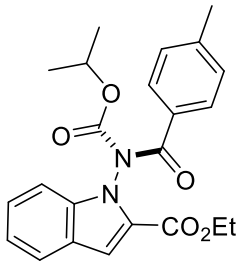
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 24.6 mg, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81-7.75 (m, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.52-7.43 (m, 1H), 7.43-7.35 (m, 2H), 7.34-7.27 (m, 3H), 7.19-7.11 (m, 1H), 4.84 (h, *J* = 6.2 Hz, 1H), 4.37-4.19 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 160.4, 152.5, 138.6, 134.8, 132.0, 128.4, 128.2, 127.4, 126.5, 124.2, 123.0, 122.1, 110.8, 109.0, 72.7, 60.8, 21.3, 21.2, 14.3. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{22}N_2O_5$) requires m/z 417.1421, found m/z 417.1423. The enantiomeric ratio was determined to be 89:11 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 13.0 min (major), 17.3 min (minor). $[\alpha]^{25}_D$ = -6.4 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(4-fluoro-N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3hb)



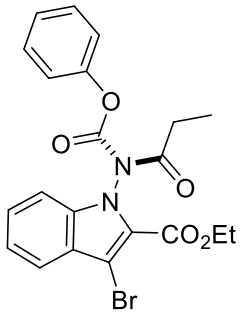
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 24.7 mg, 60% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.47-7.36 (m, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.27-7.19 (m, 1H), 7.19-7.10 (m, 2H), 4.93 (h, *J* = 6.3 Hz, 1H), 4.44-4.26 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.3 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 166.3, 161.0, 160.5, 155.2, 152.5, 138.6, 131.1 (d, *J* = 9.1 Hz), 127.2, 126.6, 124.2, 123.0, 122.2, 115.4 (d, *J* = 22.3 Hz), 109.9 (d, *J* = 199.7 Hz), 72.9, 60.9, 21.4, 21.3, 14.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.2. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{21}FN_2O_5$) requires m/z 435.1327, found m/z 435.1324. The enantiomeric ratio was determined to be 88:12 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 13.4 min (major), 23.3 min (minor). $[\alpha]^{25}_D$ = -22.7 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)-4-methylbenzamido)-1H-indole-2-carboxylate (3ib)



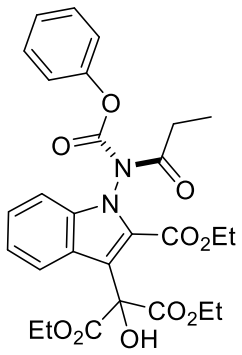
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 12/1. Colorless oil, 25.3 mg, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.43-7.33 (m, 3H), 7.28-7.24 (m, 2H), 7.25-7.16 (m, 1H), 4.92 (h, *J* = 6.3 Hz, 1H), 4.44-4.25 (m, 2H), 2.41 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 160.4, 152.7, 143.0, 138.6, 131.8, 128.9, 128.7, 127.6, 126.5, 124.2, 123.0, 122.1, 110.8, 109.0, 72.6, 60.8, 21.7, 21.4, 21.3, 14.3. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{24}N_2O_5$) requires m/z 431.1577, found m/z 431.1574. The enantiomeric ratio was determined to be 90.5:9.5 by HPLC. [IF column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 11.1 min (major), 15.0 min (minor). $[\alpha]^{25}_D$ = -6.2 (c = 1.00, $CHCl_3$).

(R_a)-ethyl-3-bromo-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (4)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/1. Colorless oil, 32.0 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.38-7.26 (m, 4H), 7.26-7.18 (m, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 4.43 (p, *J* = 7.2 Hz, 2H), 3.12 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 159.9, 151.9, 150.1, 137.3, 129.6, 128.0, 126.6, 125.3, 123.8, 122.9, 122.1, 121.2, 108.8, 101.8, 61.5, 30.8, 14.2, 8.7. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{21}H_{19}BrN_2O_5$) requires m/z 481.0370, found m/z 481.0367. The enantiomeric ratio was determined to be 97.5:2.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 3:1, 1.0 mL/min]: 5.2 min (minor), 5.9 min (major). $[\alpha]^{25}_D$ = -14.0 (c = 1.00, $CHCl_3$).

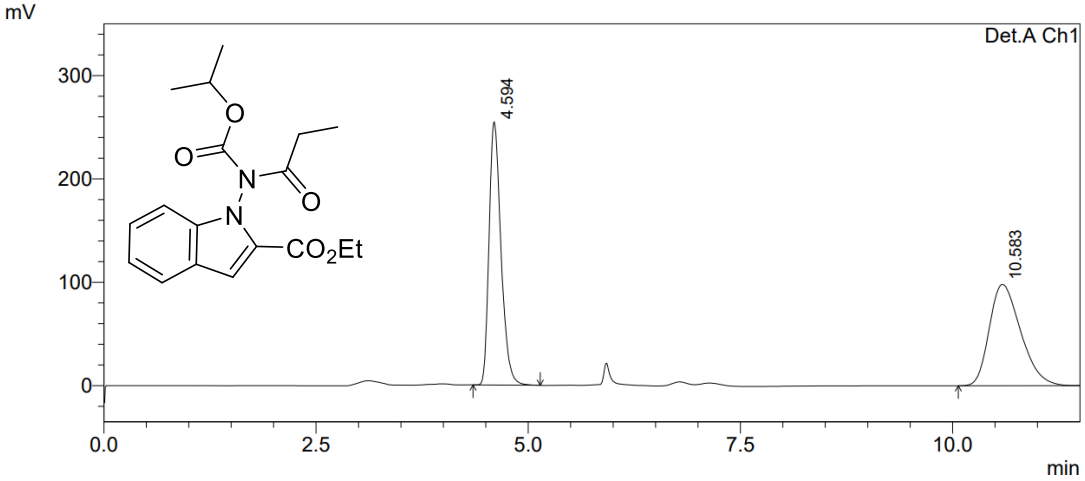
(R_a)-diethyl-2-(2-(ethoxycarbonyl)-1-(N-(phenoxycarbonyl)propionamido)-1H-indol-3-yl)-2-hydroxymalonate (5)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 24/5. Colorless oil, 29.9 mg, 54% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.29 (s, 1H), 7.24-7.20 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 4.79 (s, 1H), 4.34 (q, *J* = 7.0 Hz, 8H), 1.32 (t, *J* = 7.3 Hz, 6H), 1.21 (p, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 169.5, 169.4, 168.4, 160.9, 151.6, 150.0, 136.8, 129.5, 126.8, 126.6, 123.3, 122.7, 122.5, 121.1, 108.8, 90.0, 78.3, 63.5, 62.8, 62.0, 30.4, 14.1, 13.9, 13.8, 8.7. HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{28}H_{30}N_2O_{10}$) requires m/z 577.1793, found m/z 577.1795. The enantiomeric ratio was determined to be 97.5:2.5 by HPLC. [AD-H column, 254 nm, *n*-hexane:IPA = 1:1, 1.0 mL/min]: 9.9 min (major), 14.0 min (minor). $[\alpha]^{25}_D$ = -23.0 (c = 1.00, $CHCl_3$).

9. HPLC Spectra

(*R*$_a$)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3aa)

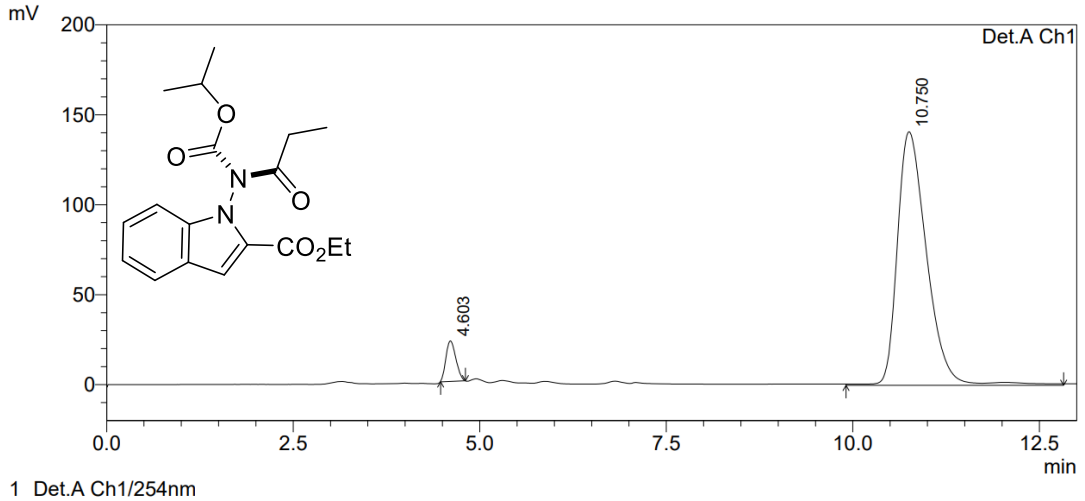


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.594	2485808	254606	49.629	72.198
2	10.583	2522949	98042	50.371	27.802
Total		5008757	352648	100.000	100.000



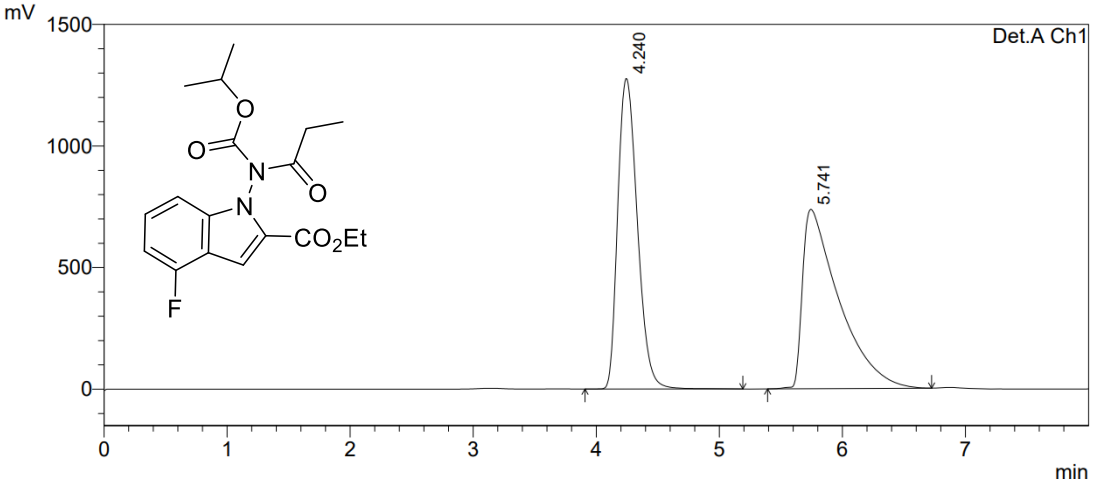
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.603	209004	22508	5.126	13.772
2	10.750	3868128	140928	94.874	86.228
Total		4077133	163435	100.000	100.000

(R_a)-ethyl-4-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ba)

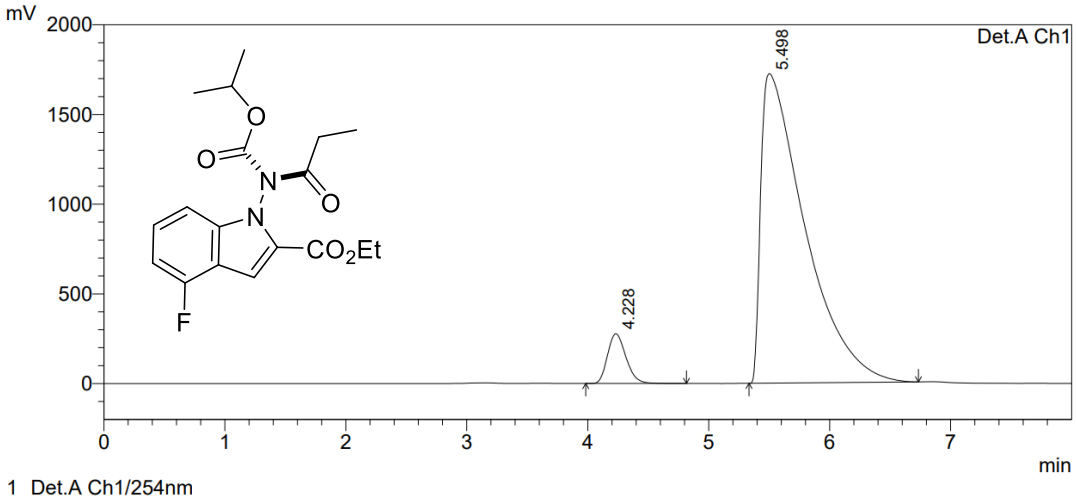


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.240	14148065	1271156	48.180	63.351
2	5.741	15217150	735387	51.820	36.649
Total		29365215	2006543	100.000	100.000



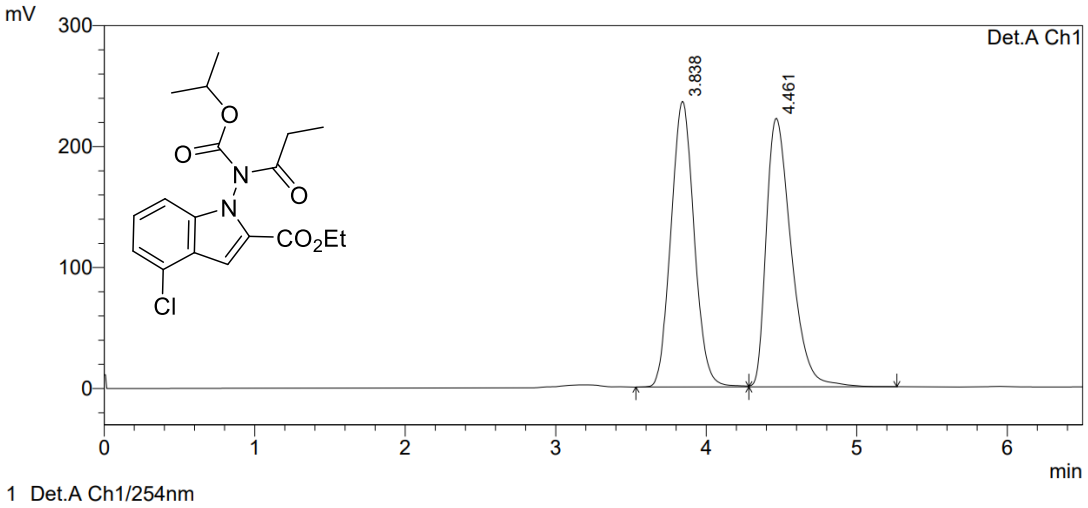
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.228	2929137	276673	6.263	13.831
2	5.498	43842247	1723703	93.737	86.169
Total		46771385	2000376	100.000	100.000

(R_a)-ethyl-4-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ca)

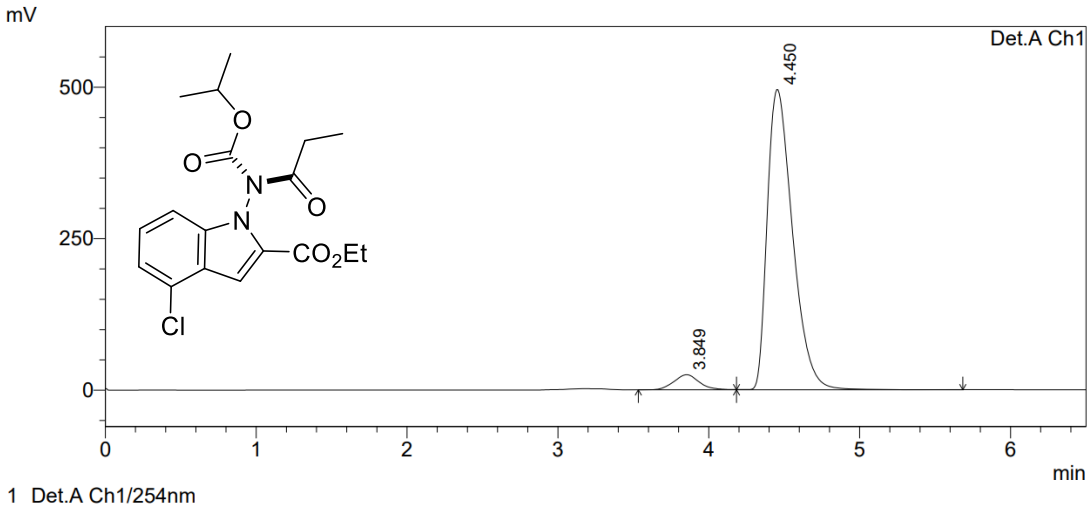


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.838	2522028	235457	49.660	51.496
2	4.461	2556549	221775	50.340	48.504
Total		5078577	457232	100.000	100.000



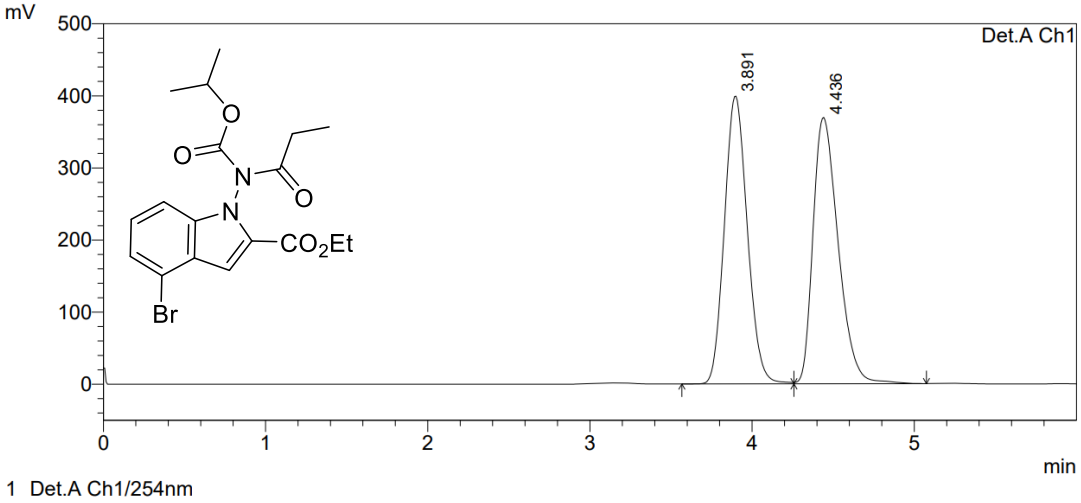
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.849	289017	24811	4.763	4.794
2	4.450	5779166	492745	95.237	95.206
Total		6068183	517556	100.000	100.000

(R_a)-ethyl-4-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3da)

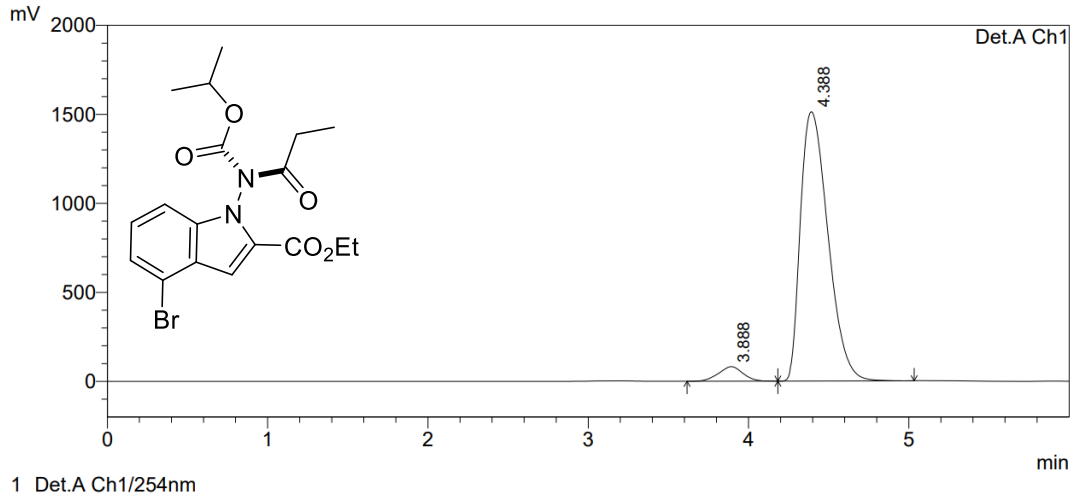


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.891	3930677	398588	49.682	51.932
2	4.436	3981006	368935	50.318	48.068
Total		7911683	767523	100.000	100.000



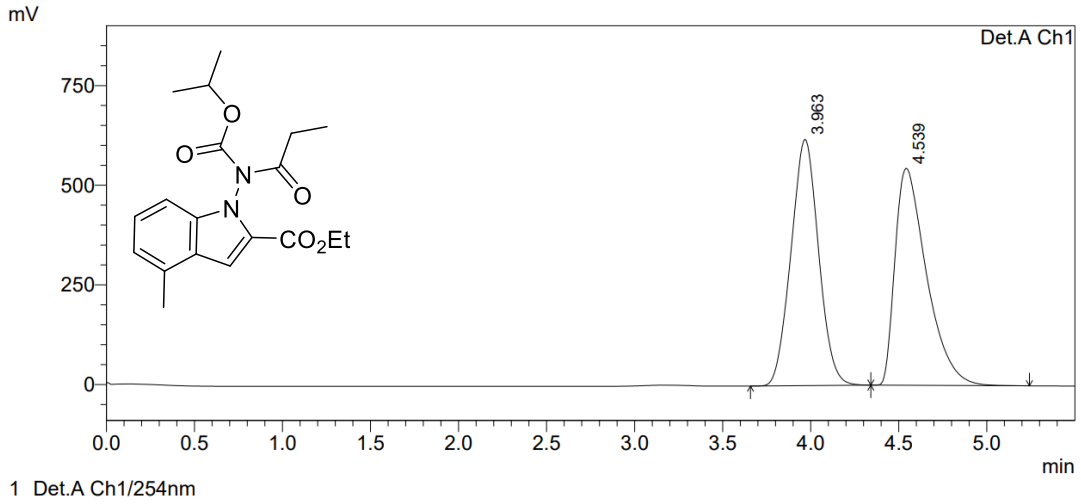
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.888	861416	81539	4.538	5.122
2	4.388	18119317	1510406	95.462	94.878
Total		18980733	1591945	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-4-methyl-1H-indole-2-carboxylate (3ea)

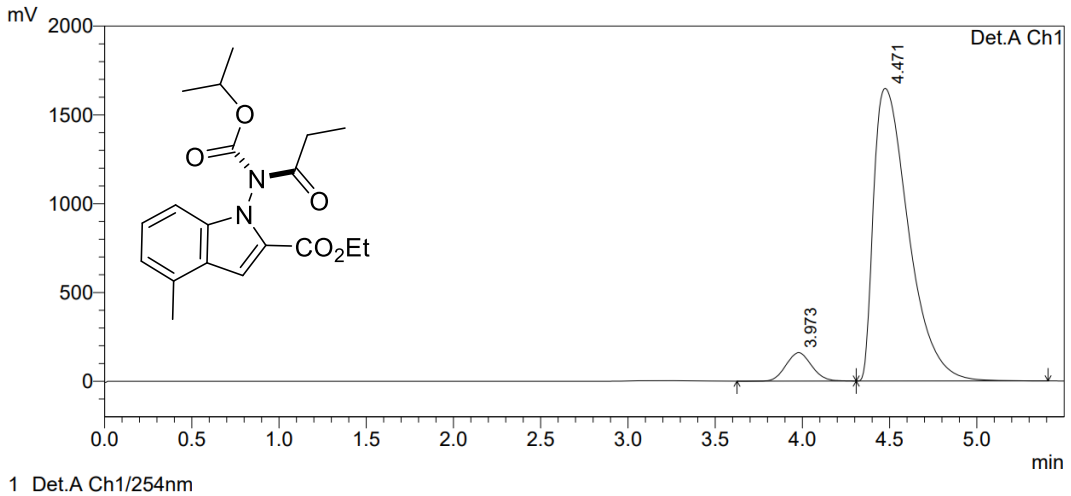


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.963	6739433	616390	49.885	53.188
2	4.539	6770499	542491	50.115	46.812
Total		13509932	1158881	100.000	100.000



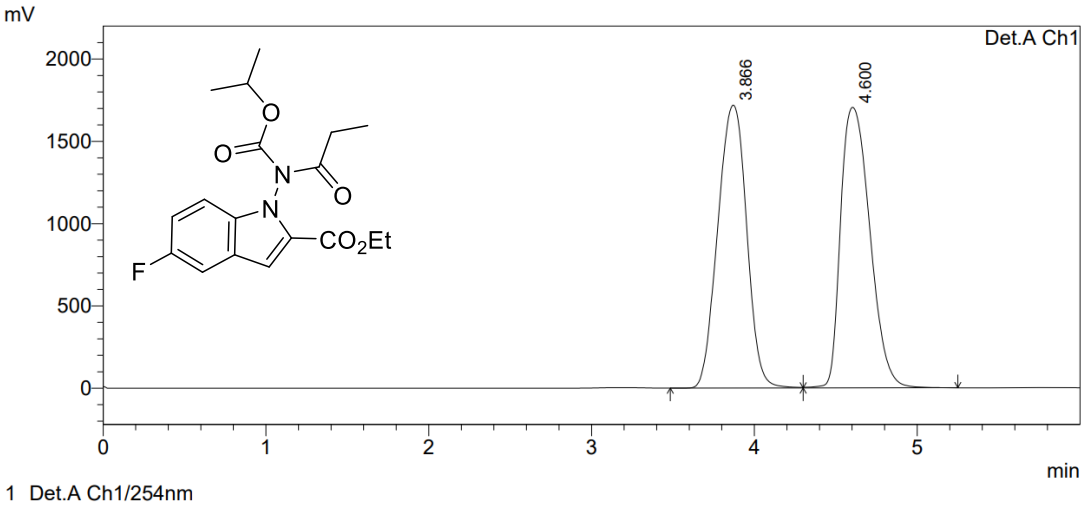
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.973	1629253	159358	6.627	8.829
2	4.471	22955669	1645621	93.373	91.171
Total		24584921	1804980	100.000	100.000

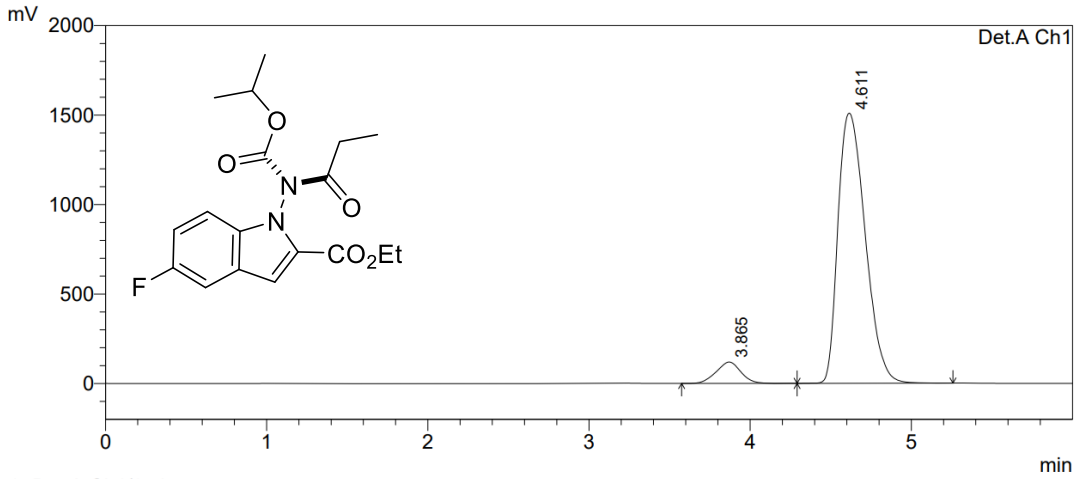
(R_a)-ethyl-5-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3fa)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.866	21226016	1712269	49.898	50.189
2	4.600	21312390	1699365	50.102	49.811
Total		42538406	3411634	100.000	100.000

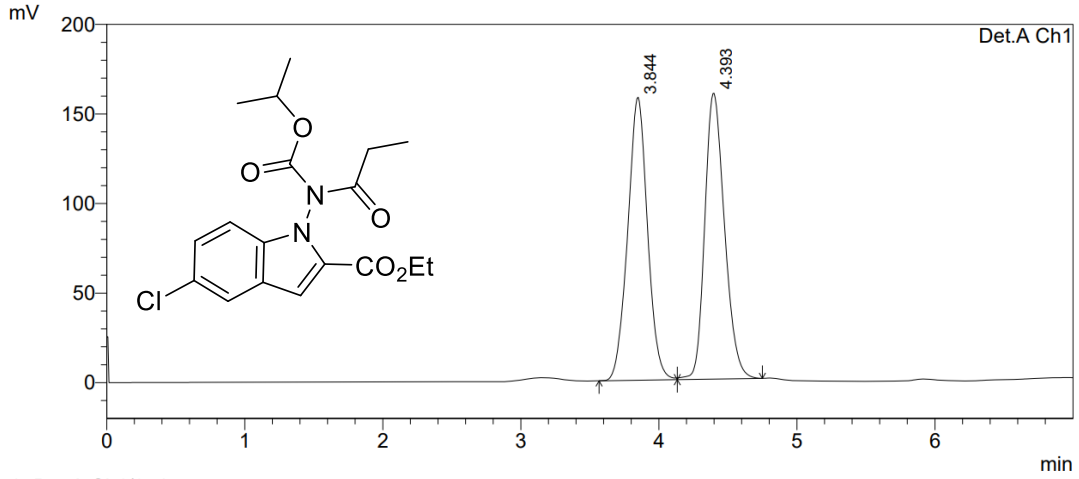


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.865	1272608	119337	6.690	7.346
2	4.611	17749875	1505126	93.310	92.654
Total		19022483	1624463	100.000	100.000

(R_a)-ethyl-5-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ga)

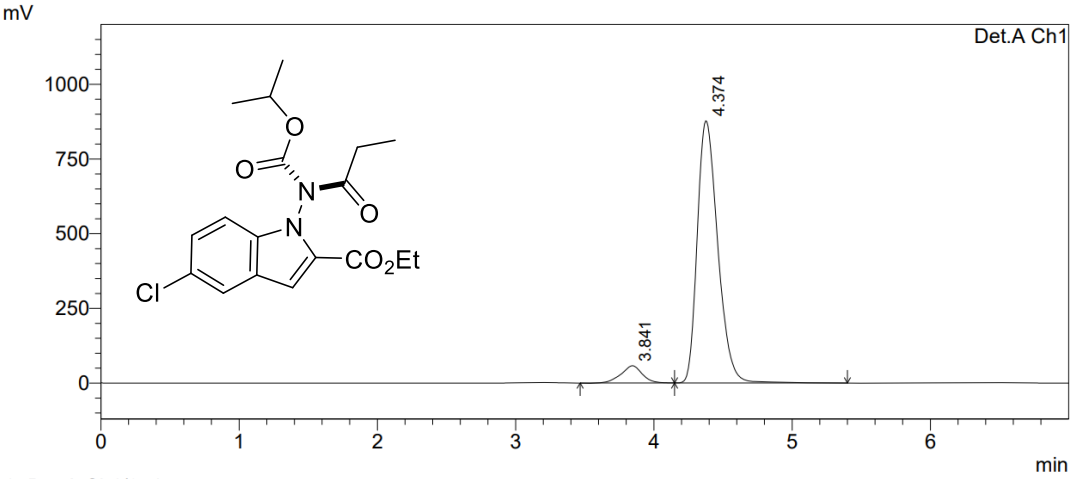


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.844	1577019	157665	49.815	49.712
2	4.393	1588704	159494	50.185	50.288
Total		3165723	317159	100.000	100.000



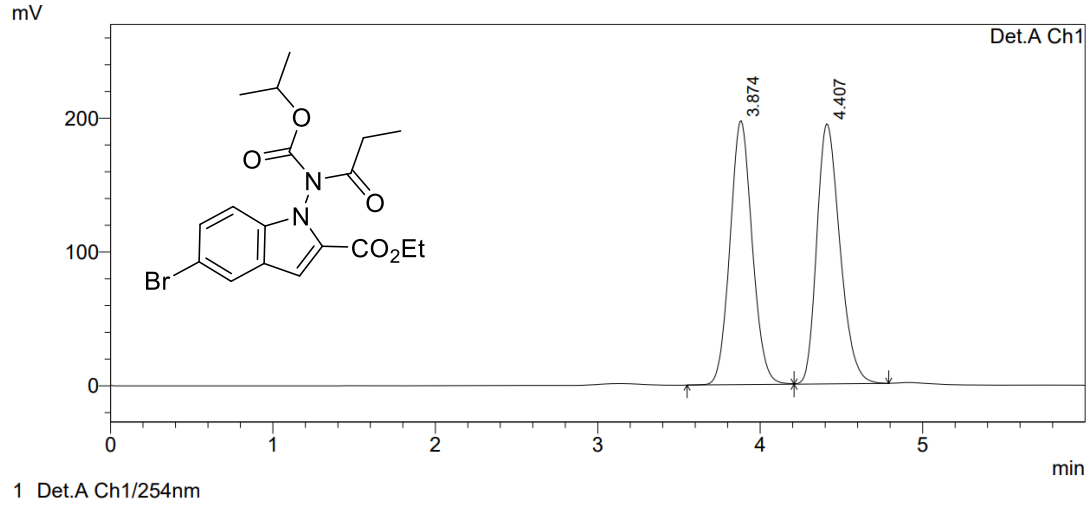
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.841	616147	57616	6.377	6.171
2	4.374	9045430	875973	93.623	93.829
Total		9661577	933589	100.000	100.000

(R_a)-ethyl-5-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ha)

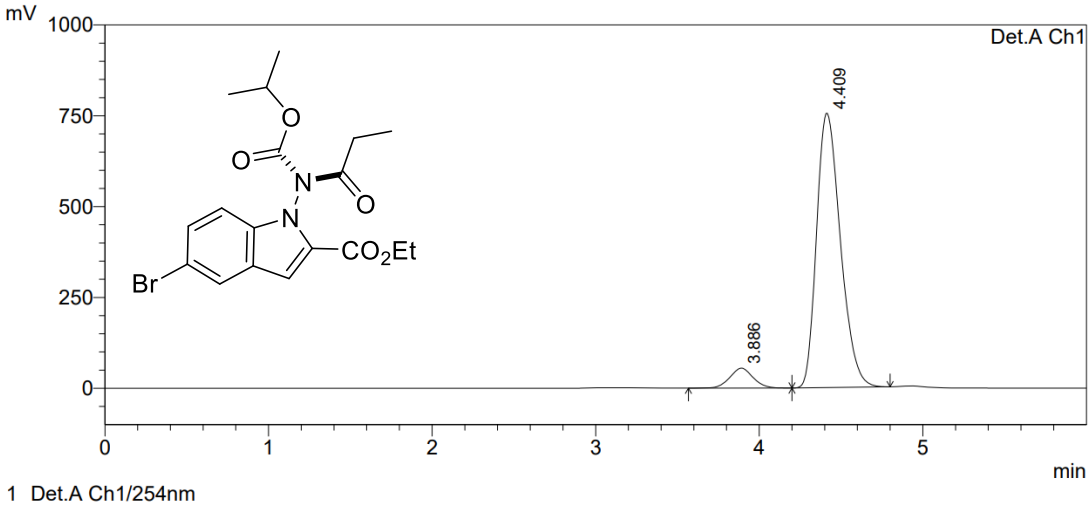


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.874	1877198	196523	49.373	50.451
2	4.407	1924909	193012	50.627	49.549
Total		3802107	389535	100.000	100.000



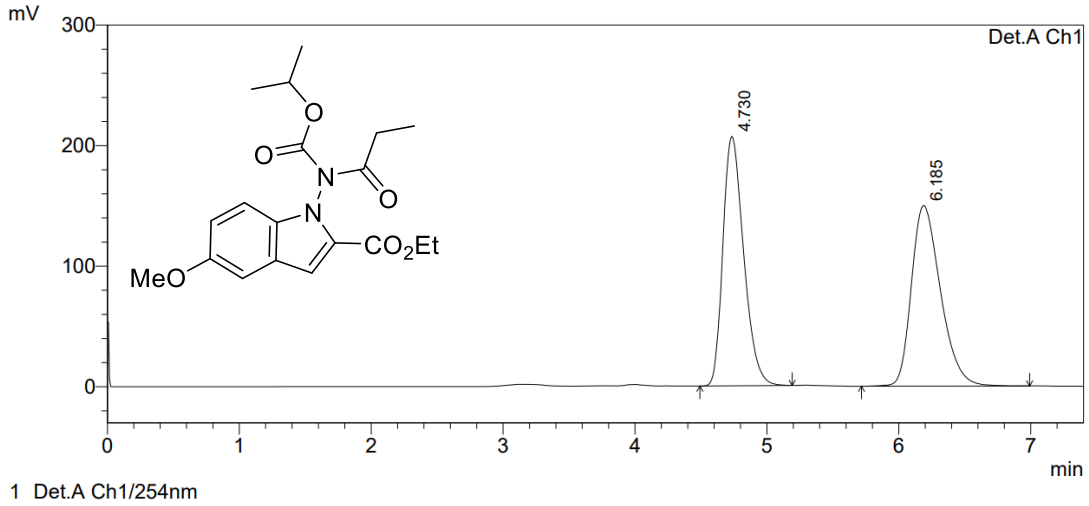
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.886	539032	54509	6.580	6.736
2	4.409	7652723	754735	93.420	93.264
Total		8191755	809244	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-methoxy-1H-indole-2-carboxylate (3ia)

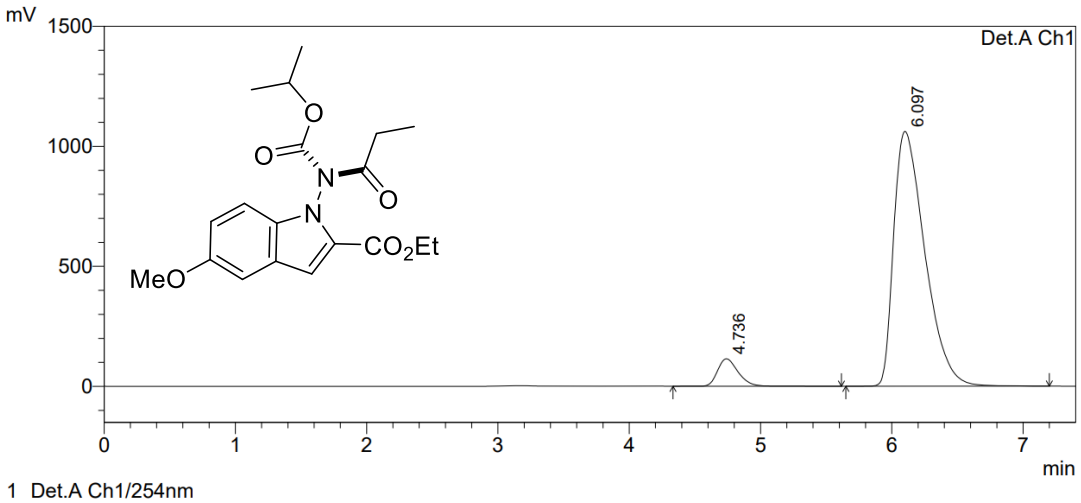


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.730	2263747	206955	49.642	58.011
2	6.185	2296359	149798	50.358	41.989
Total		4560106	356753	100.000	100.000



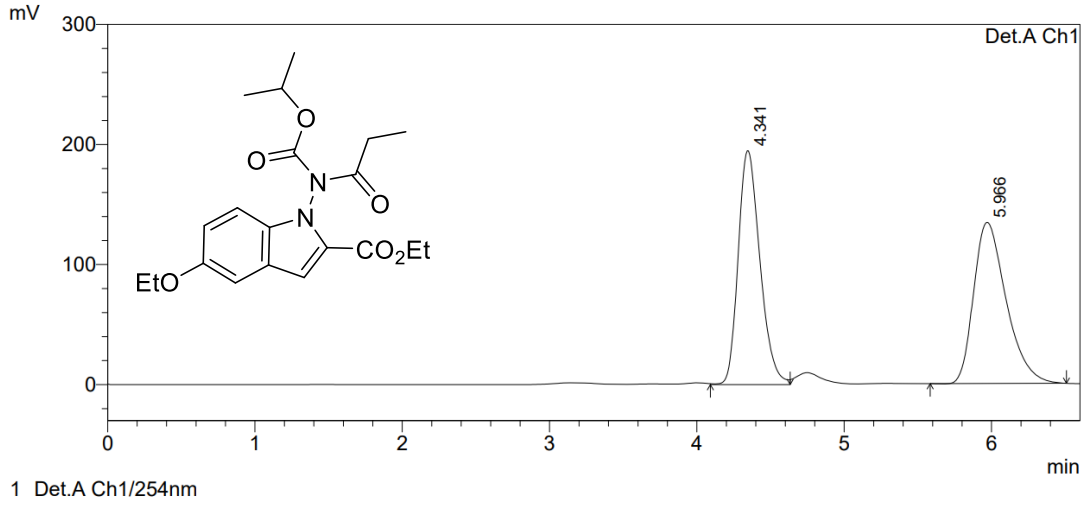
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.736	1247120	113665	6.643	9.684
2	6.097	17525706	1060083	93.357	90.316
Total		18772825	1173749	100.000	100.000

(R_a)-ethyl-5-ethoxy-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ja)

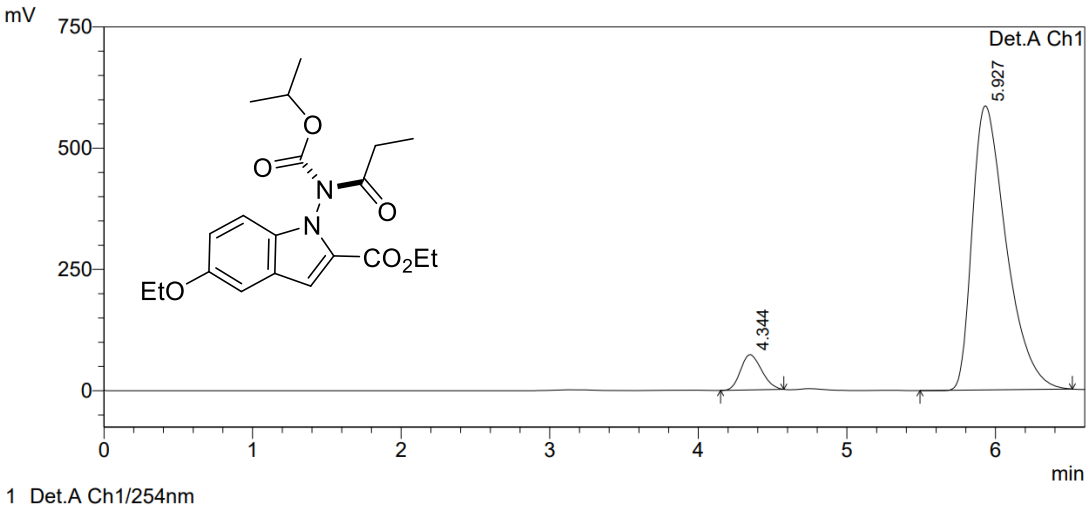


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.341	2004731	194884	49.391	59.222
2	5.966	2054149	134187	50.609	40.778
Total		4058880	329071	100.000	100.000



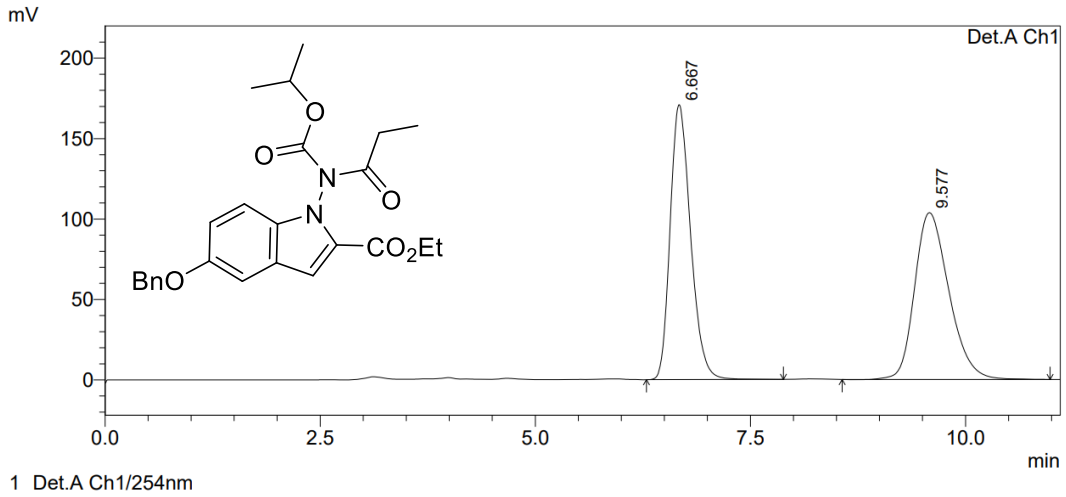
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.344	716478	72878	7.150	11.061
2	5.927	9304046	585966	92.850	88.939
Total		10020524	658844	100.000	100.000

(R_a)-ethyl-5-(benzyloxy)-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ka)

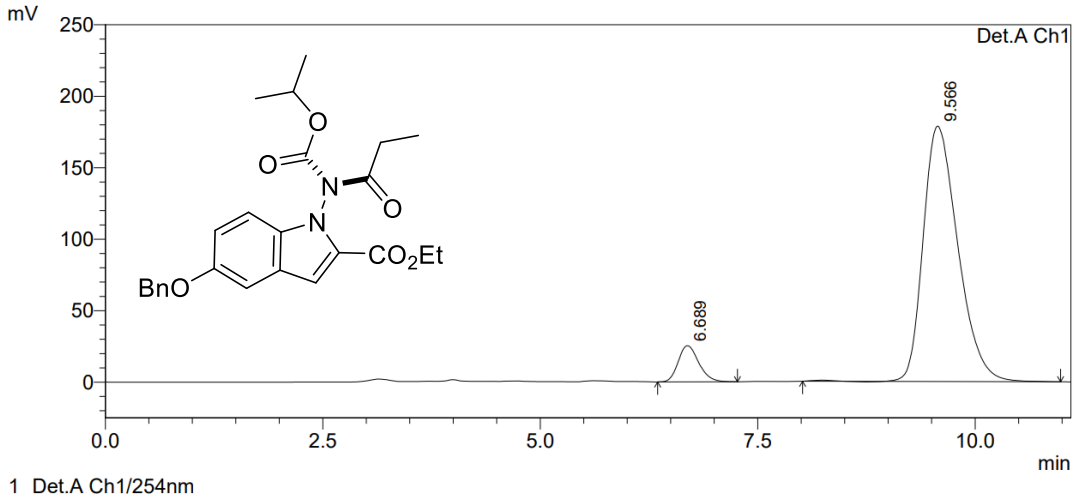


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.667	2825490	170365	49.562	62.218
2	9.577	2875461	103453	50.438	37.782
Total		5700951	273817	100.000	100.000



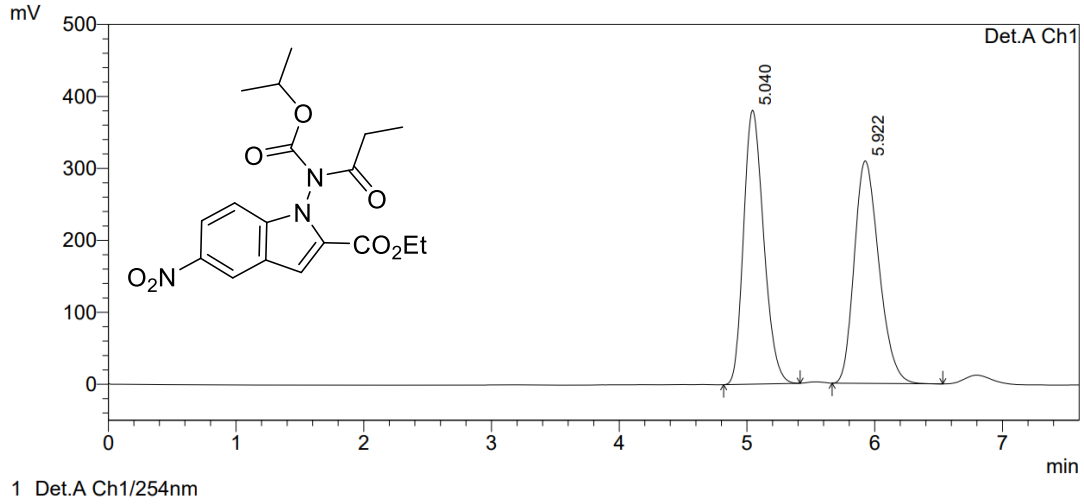
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.689	414568	25318	7.700	12.427
2	9.566	4969684	178421	92.300	87.573
Total		5384252	203738	100.000	100.000

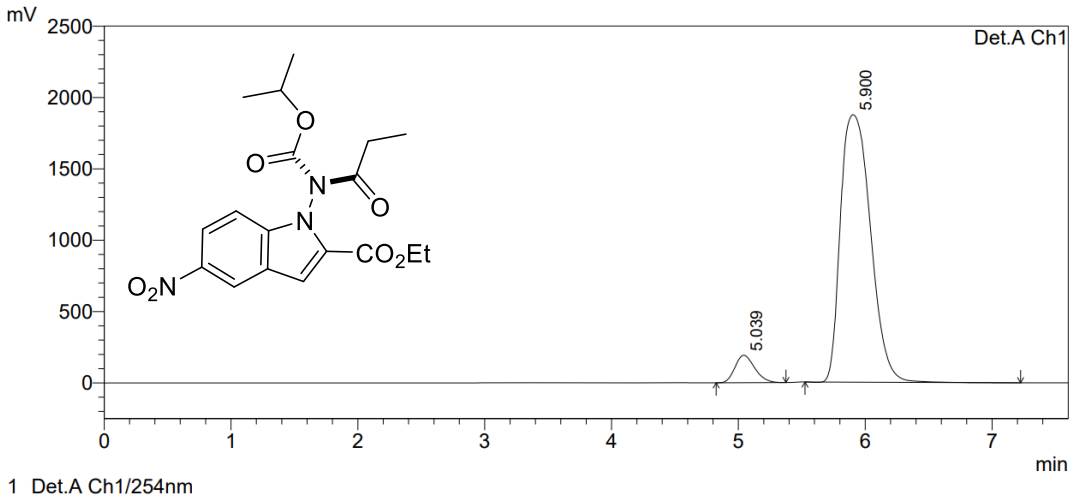
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-nitro-1H-indole-2-carboxylate (3la)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.040	4176279	380267	50.078	55.175
2	5.922	4163297	308940	49.922	44.825
Total		8339576	689207	100.000	100.000

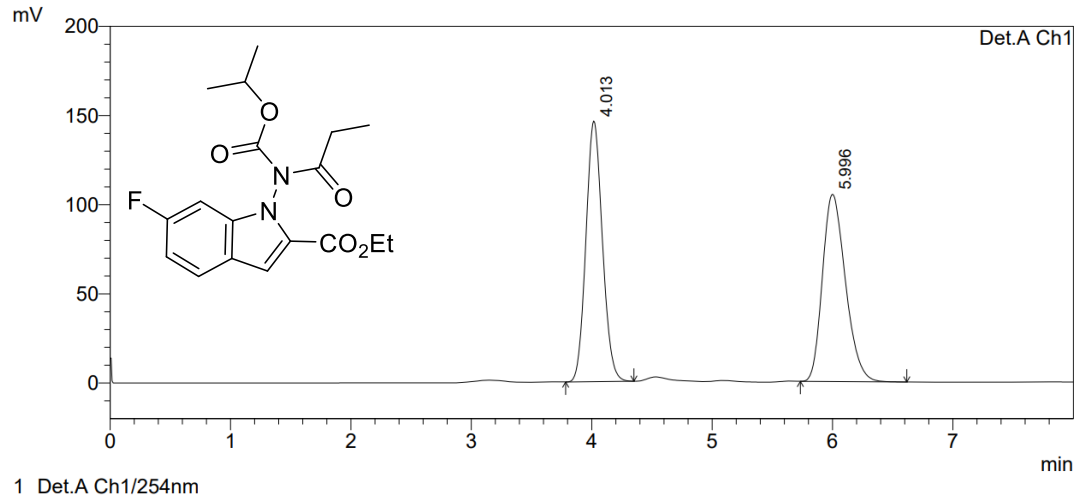


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.039	2085551	192062	6.322	9.297
2	5.900	30902201	1873681	93.678	90.703
Total		32987753	2065743	100.000	100.000

(R_a)-ethyl-6-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ma)

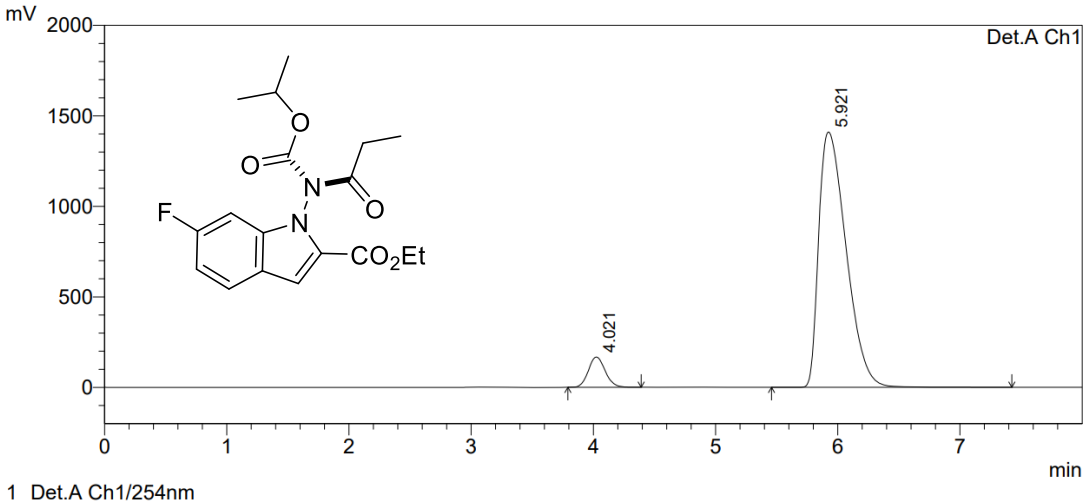


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.013	1390292	145451	49.877	58.121
2	5.996	1397139	104804	50.123	41.879
Total		2787431	250255	100.000	100.000



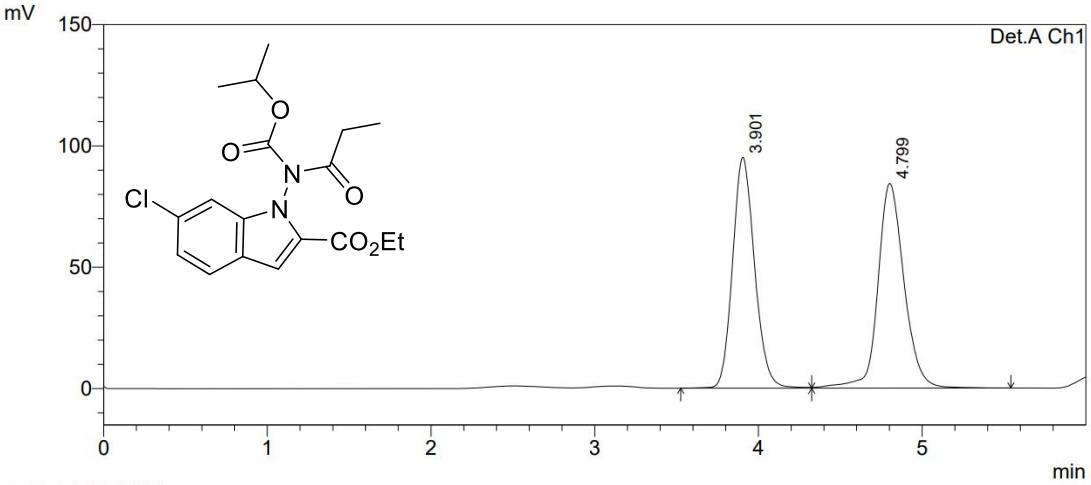
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.021	1597680	167272	6.771	10.610
2	5.921	21998063	1409330	93.229	89.390
Total		23595744	1576602	100.000	100.000

(R_a)-ethyl-6-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3na)

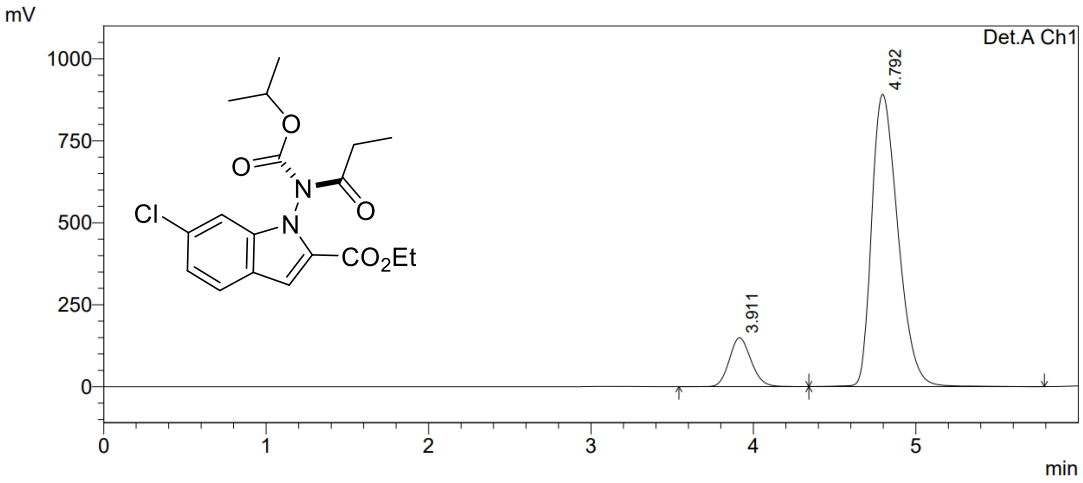


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.901	890792	95034	48.670	53.008
2	4.799	939478	84249	51.330	46.992
Total		1830270	179284	100.000	100.000



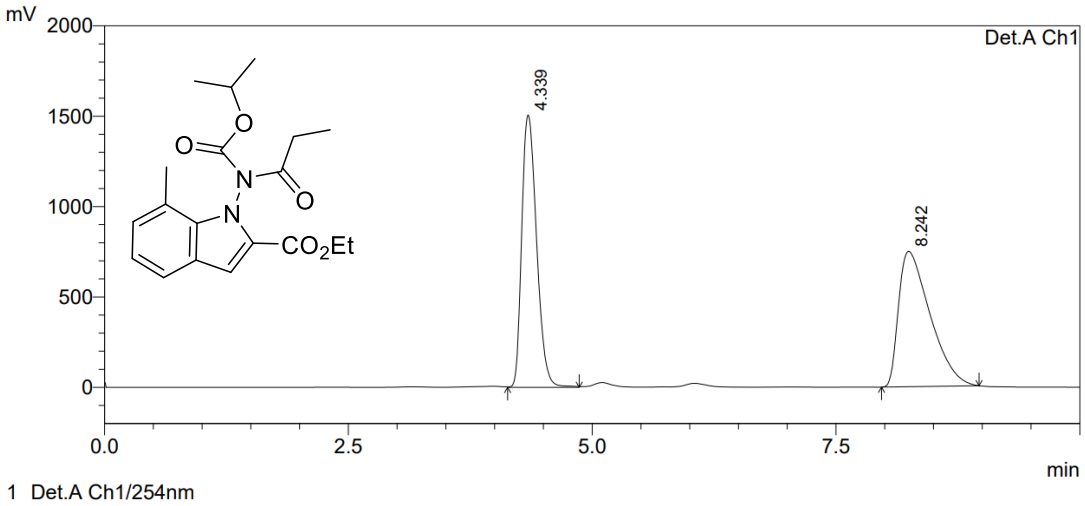
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.911	1393635	148307	12.197	14.349
2	4.792	10032157	885265	87.803	85.651
Total		11425792	1033572	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-7-methyl-1H-indole-2-carboxylate (3oa)

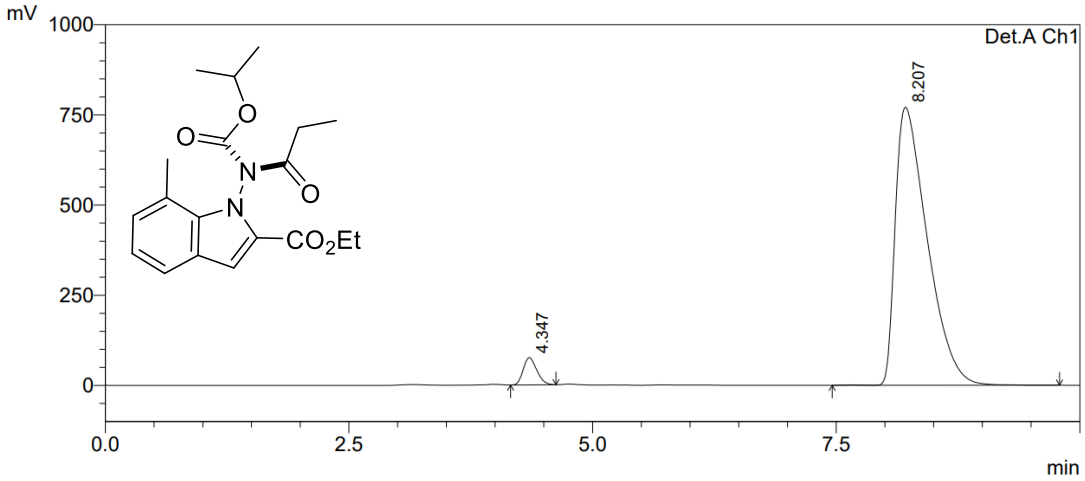


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.339	15949691	1504306	48.723	66.757
2	8.242	16786072	749086	51.277	33.243
Total		32735763	2253392	100.000	100.000



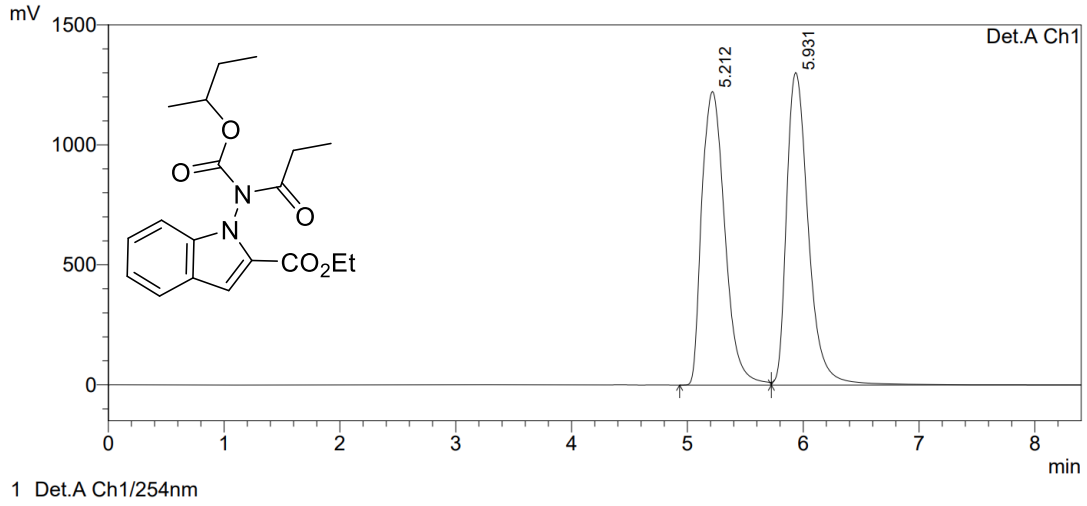
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.347	728109	75359	3.975	8.915
2	8.207	17590616	769939	96.025	91.085
Total		18318725	845297	100.000	100.000

(R_a)-ethyl-1-(N-(sec-butoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3pa)

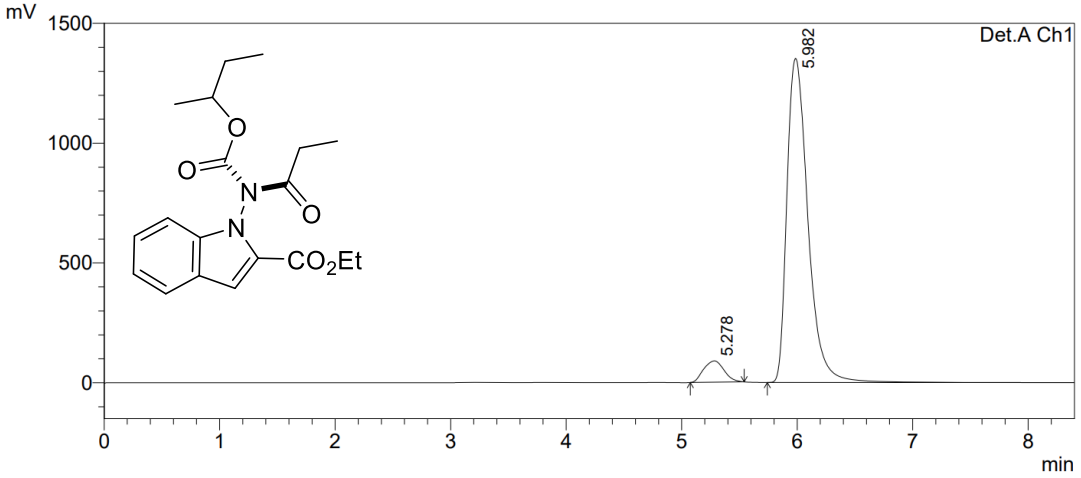


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.212	16929131	1223965	49.720	48.480
2	5.931	17120058	1300734	50.280	51.520
Total		34049189	2524700	100.000	100.000



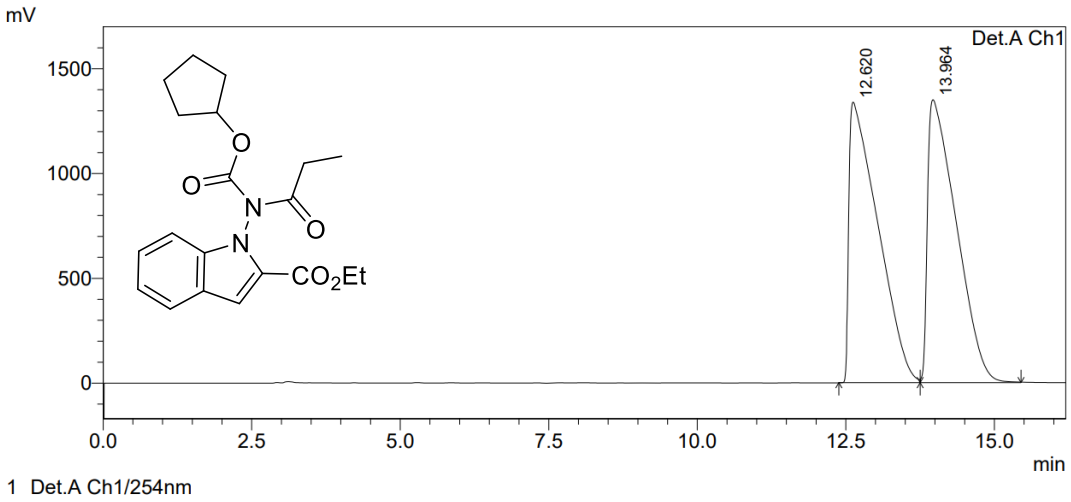
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.278	1093899	89033	5.971	6.179
2	5.982	17225571	1351829	94.029	93.821
Total		18319470	1440862	100.000	100.000

(R_a)-ethyl-1-(N-((cyclopentyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3qa)

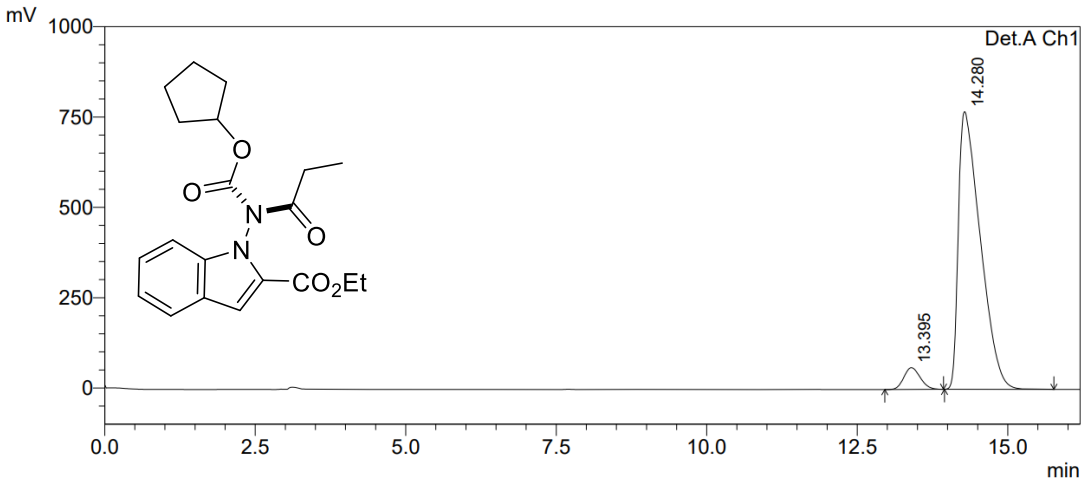


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.620	45405712	1336962	49.932	49.778
2	13.964	45528897	1348870	50.068	50.222
Total		90934608	2685832	100.000	100.000



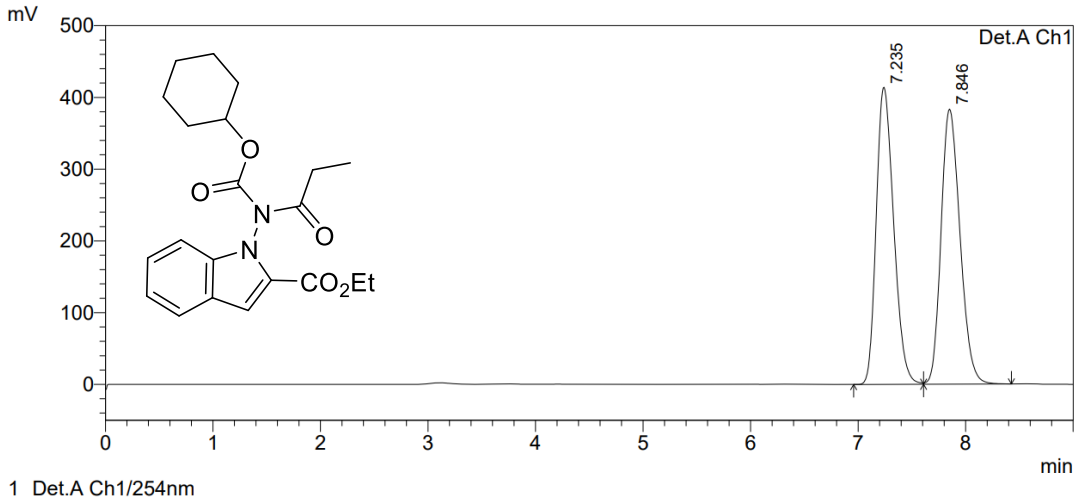
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.395	1137433	60200	5.513	7.269
2	14.280	19492850	768025	94.487	92.731
Total		20630283	828226	100.000	100.000

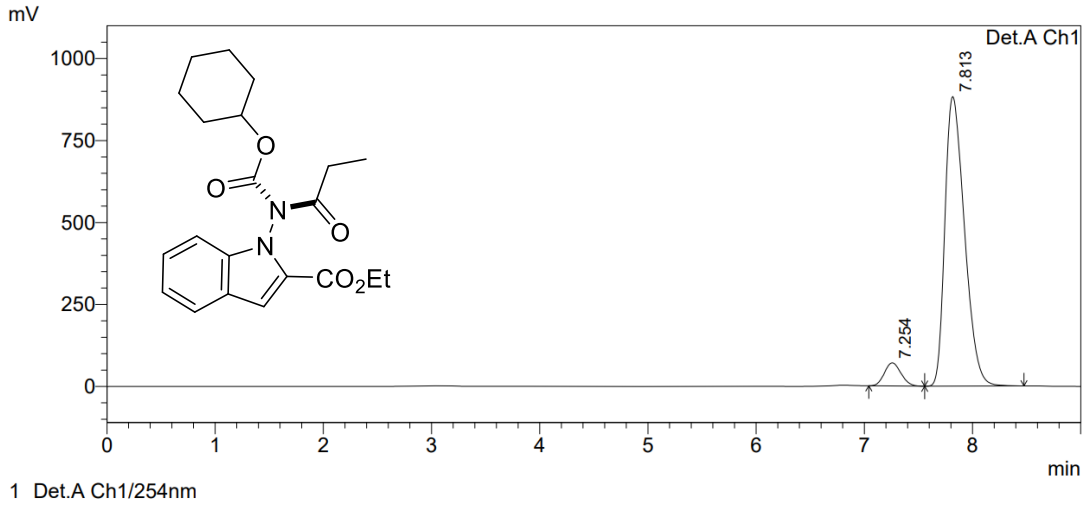
(R_a)-ethyl-1-(N-((cyclohexyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3ra)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.235	4673546	414134	49.830	51.989
2	7.846	4705380	382452	50.170	48.011
Total		9378927	796586	100.000	100.000

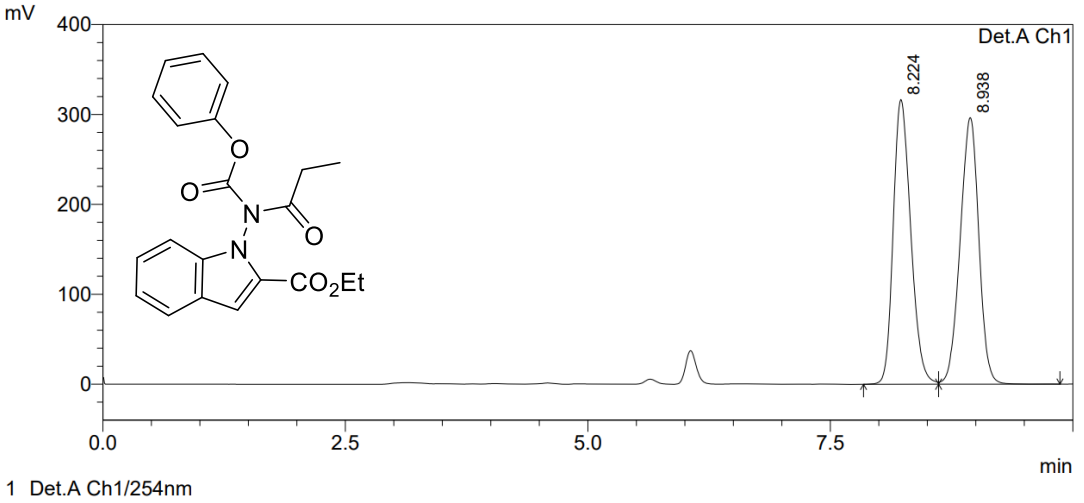


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.254	752620	70452	6.337	7.400
2	7.813	11123369	881651	93.663	92.600
Total		11875989	952103	100.000	100.000

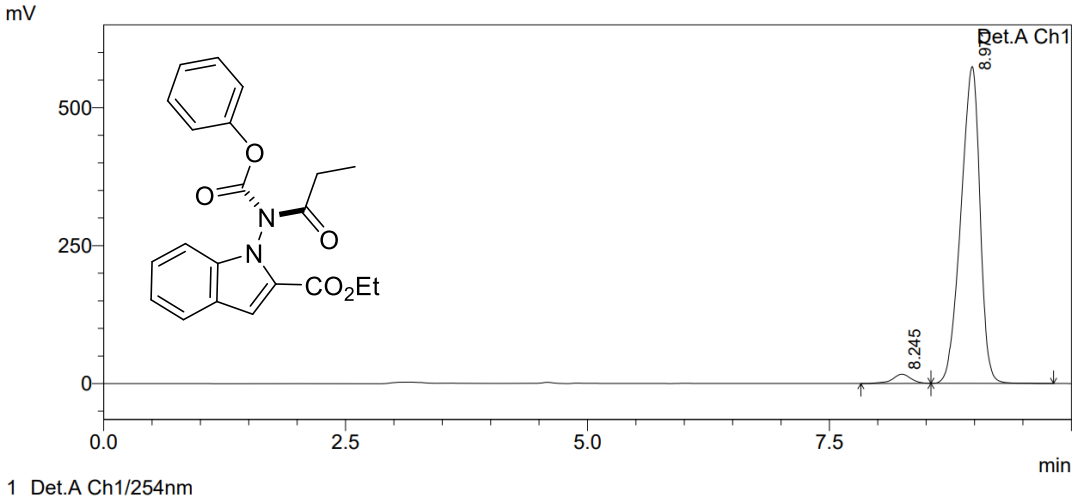
(R_a)-ethyl-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3sa)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.224	3986825	316420	50.037	51.655
2	8.938	3980944	296147	49.963	48.345
Total		7967770	612567	100.000	100.000

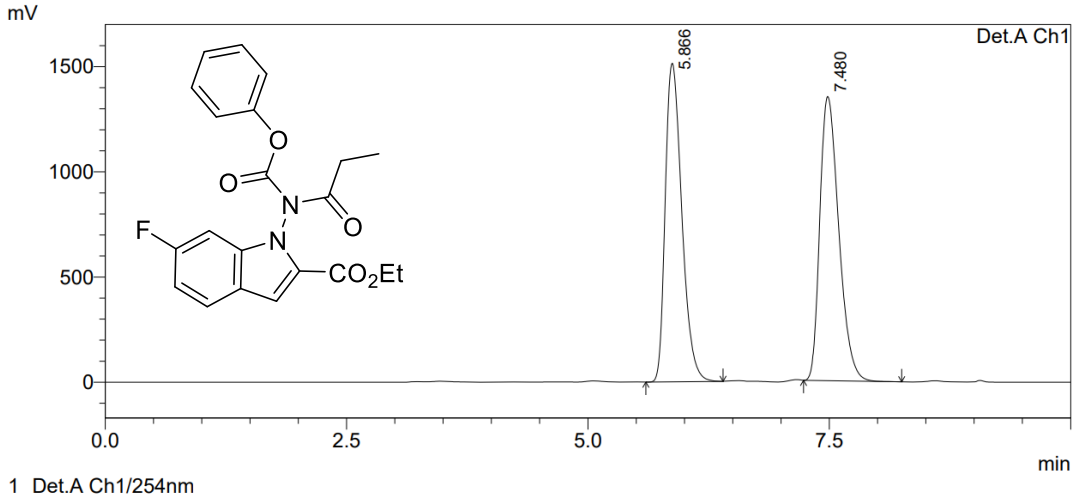


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.245	218347	16599	2.695	2.815
2	8.971	7882102	573110	97.305	97.185
Total		8100449	589709	100.000	100.000

(R_a)-ethyl-6-fluoro-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ta)

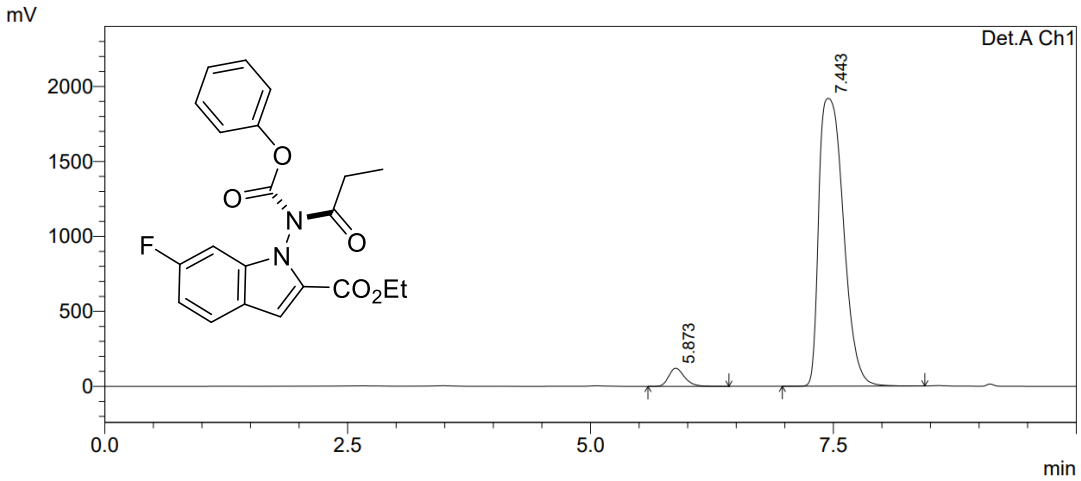


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.866	18093481	1510988	49.528	52.852
2	7.480	18438322	1347909	50.472	47.148
Total		36531802	2858897	100.000	100.000



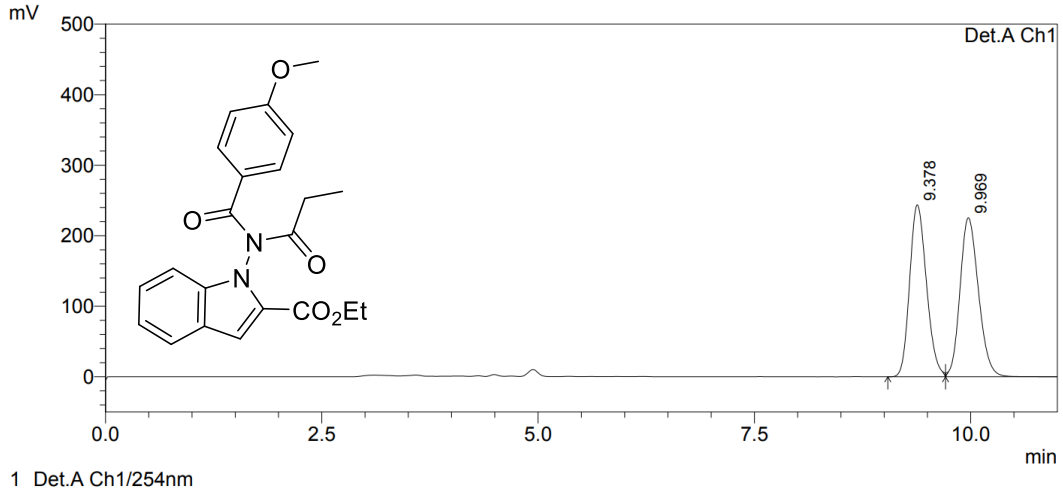
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.873	1366039	120493	3.891	5.910
2	7.443	33738159	1918208	96.109	94.090
Total		35104199	2038701	100.000	100.000

(R_a)-ethyl-1-(4-methoxy-N-propionylbenzamido)-1H-indole-2-carboxylate (3ua)

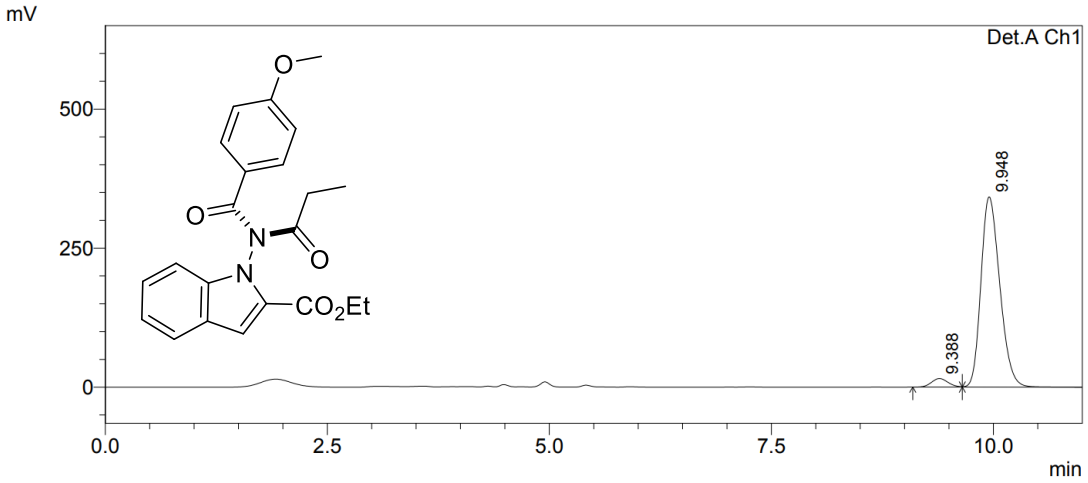


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.378	3306521	243238	49.649	51.902
2	9.969	3353250	225413	50.351	48.098
Total		6659771	468651	100.000	100.000



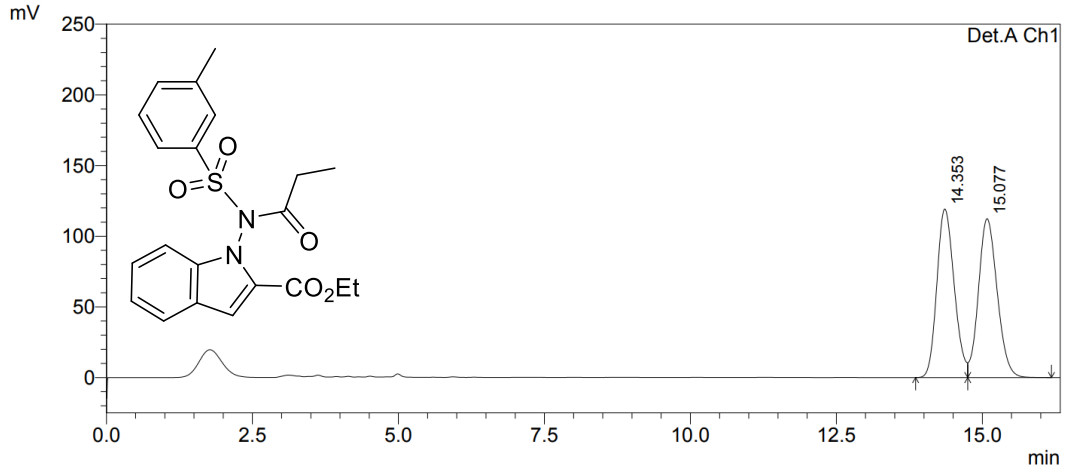
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.388	200333	15349	3.814	4.304
2	9.948	5051969	341302	96.186	95.696
Total		5252302	356651	100.000	100.000

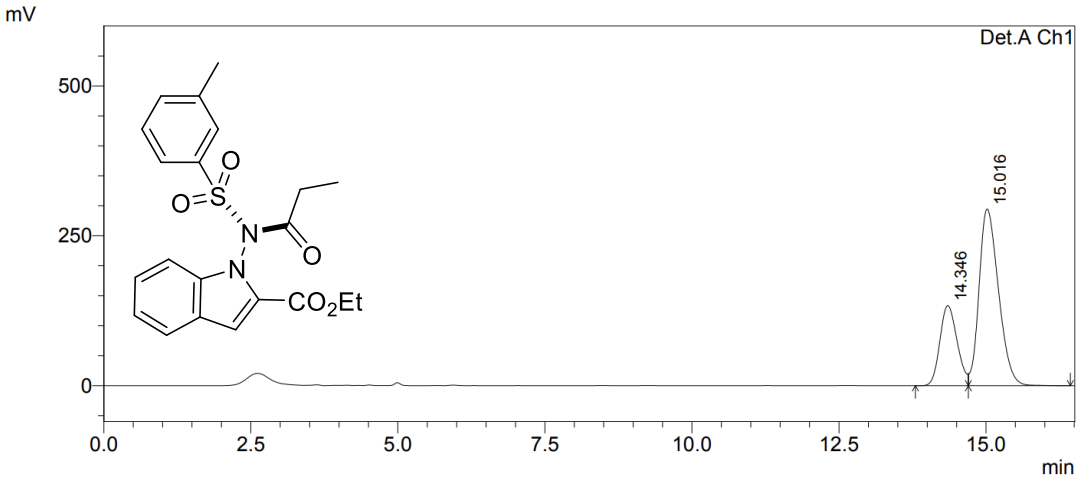
(R_a)-ethyl-1-(N-(m-tolylsulfonyl)propionamido)-1H-indole-2-carboxylate (3va)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.353	2467996	119139	49.609	51.470
2	15.077	2506885	112334	50.391	48.530
Total		4974881	231473	100.000	100.000

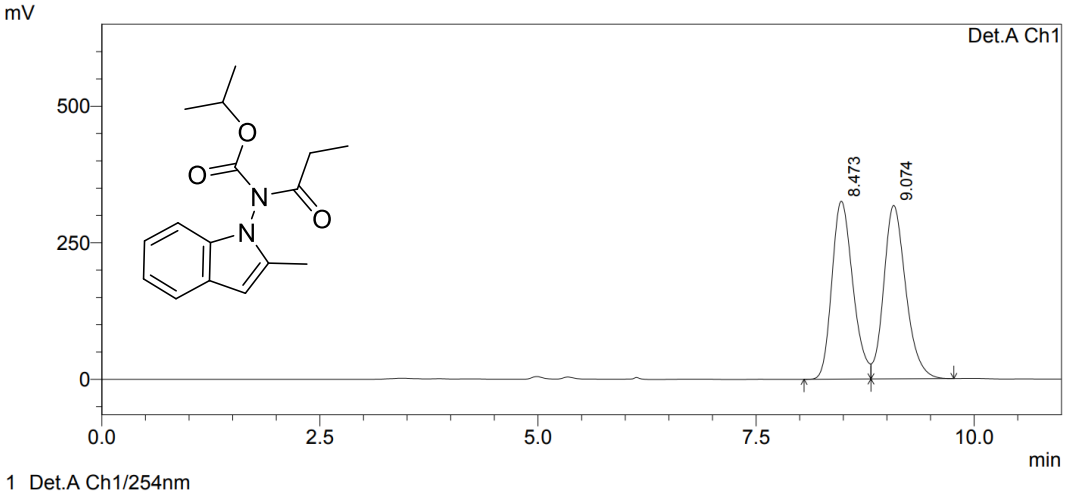


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.346	2734306	133628	28.749	31.229
2	15.016	6776731	294266	71.251	68.771
Total		9511037	427894	100.000	100.000

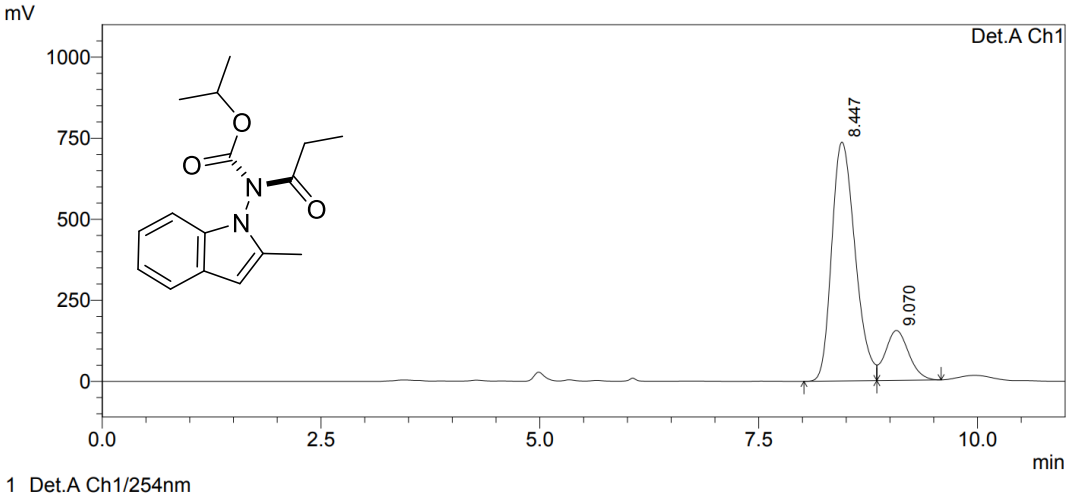
(R_a)-isopropyl(2-methyl-1H-indol-1-yl)(propionyl)carbamate (3wa)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.473	5456722	325707	49.433	50.645
2	9.074	5581834	317417	50.567	49.355
Total		11038556	643124	100.000	100.000

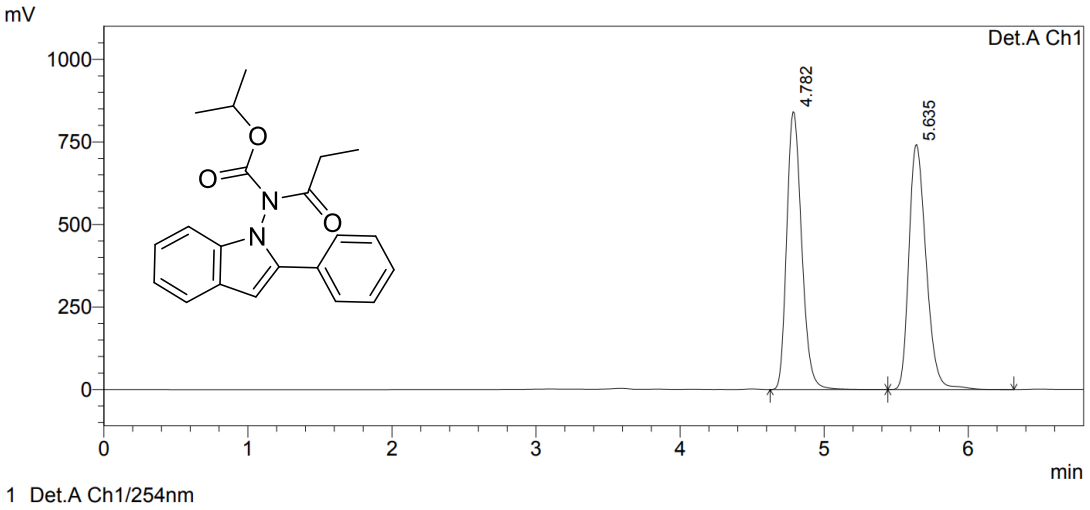


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.447	13732750	736030	82.762	82.712
2	9.070	2860363	153843	17.238	17.288
Total		16593112	889873	100.000	100.000

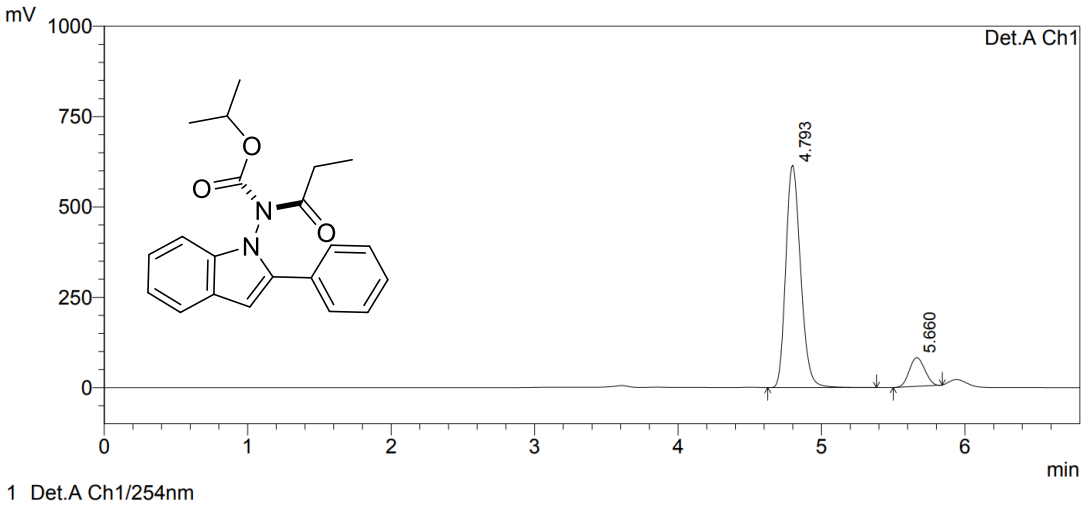
(R_a)-isopropyl(2-phenyl-1H-indol-1-yl)(propionyl)carbamate (3xa)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.782	6063263	841334	49.621	53.133
2	5.635	6155993	742128	50.379	46.867
Total		12219256	1583462	100.000	100.000

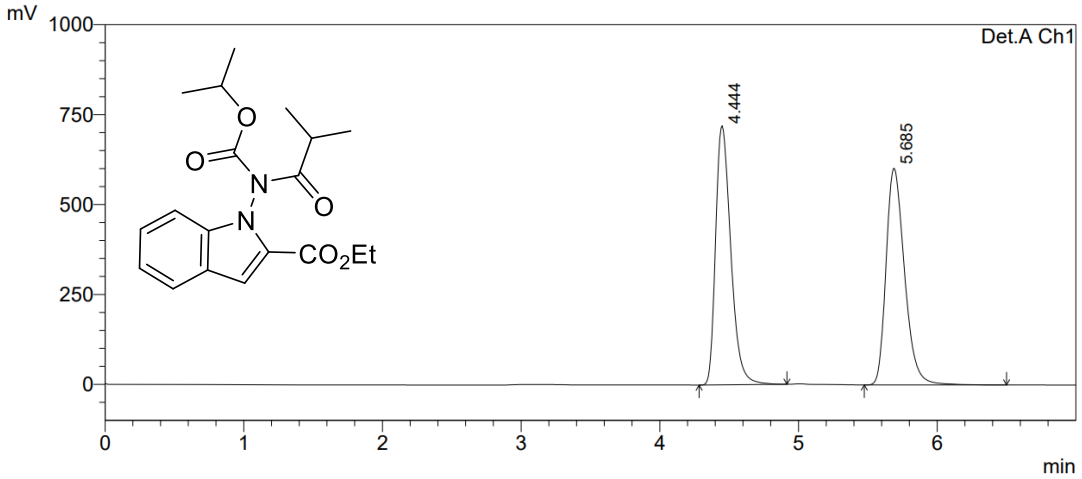


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.793	4408760	615156	88.160	88.552
2	5.660	592079	79527	11.840	11.448
Total		5000839	694684	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)isobutyramido)-1H-indole-2-carboxylate (3ab)

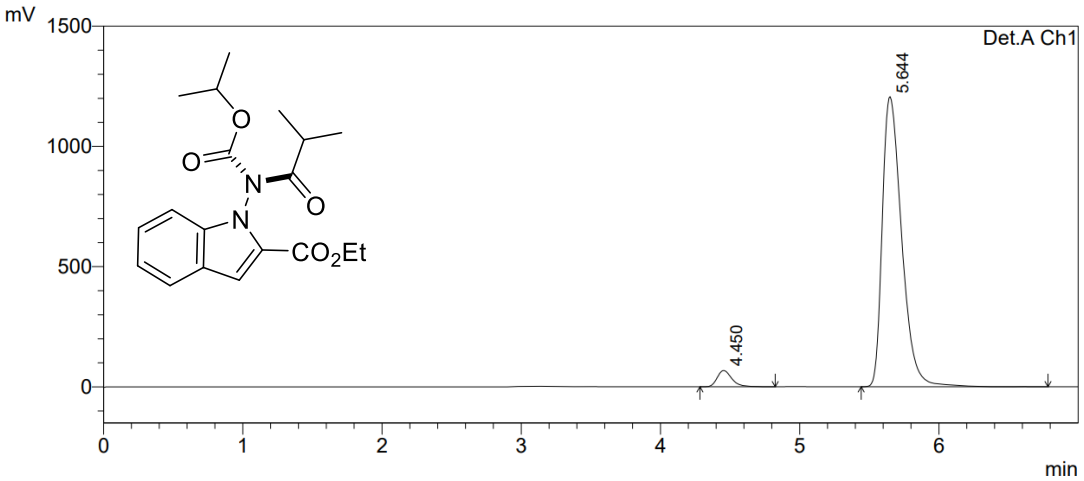


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.444	5480233	720474	49.513	54.468
2	5.685	5587977	602280	50.487	45.532
Total		11068210	1322754	100.000	100.000



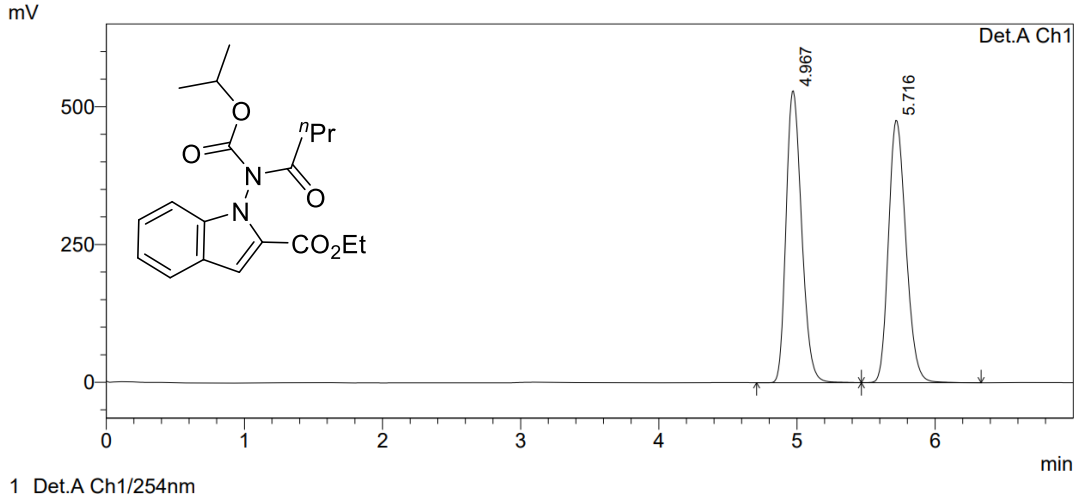
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.450	497778	67705	4.085	5.312
2	5.644	11687439	1206822	95.915	94.688
Total		12185216	1274527	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)butyramido)-1H-indole-2-carboxylate (3bb)

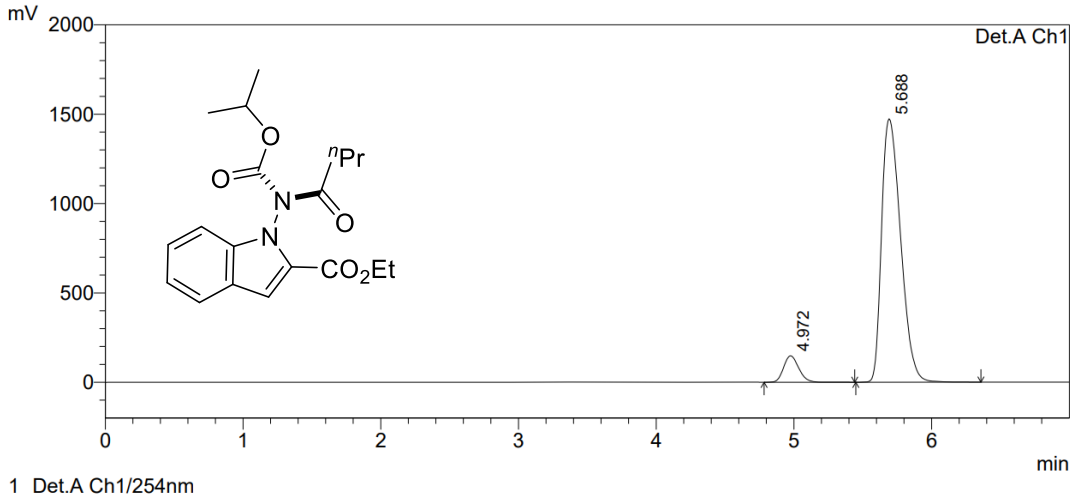


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.967	4142724	529548	49.781	52.654
2	5.716	4179190	476174	50.219	47.346
Total		8321914	1005722	100.000	100.000



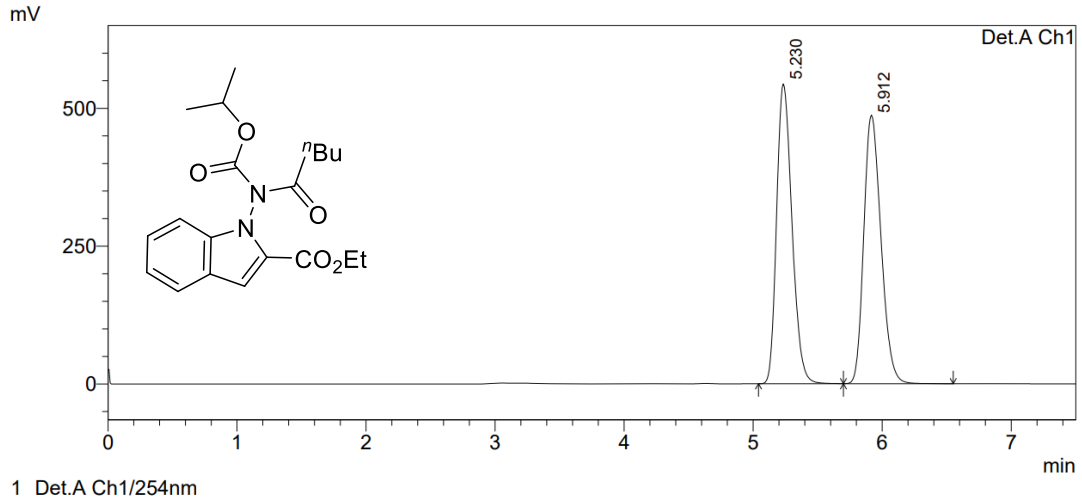
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.972	1127839	148199	7.377	9.134
2	5.688	14160723	1474331	92.623	90.866
Total		15288562	1622530	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)pentanamido)-1H-indole-2-carboxylate (3cb)

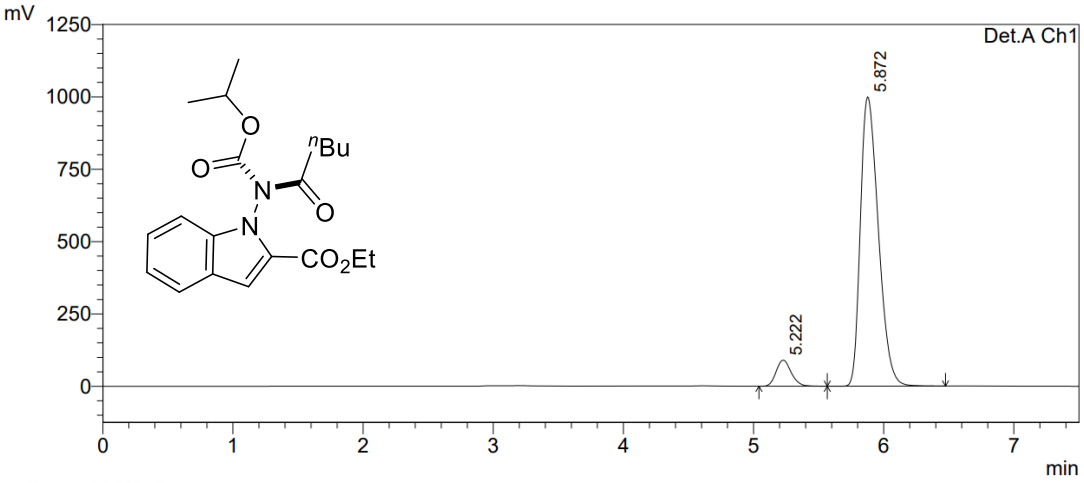


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.230	4498387	543861	49.838	52.739
2	5.912	4527637	487362	50.162	47.261
Total		9026024	1031223	100.000	100.000



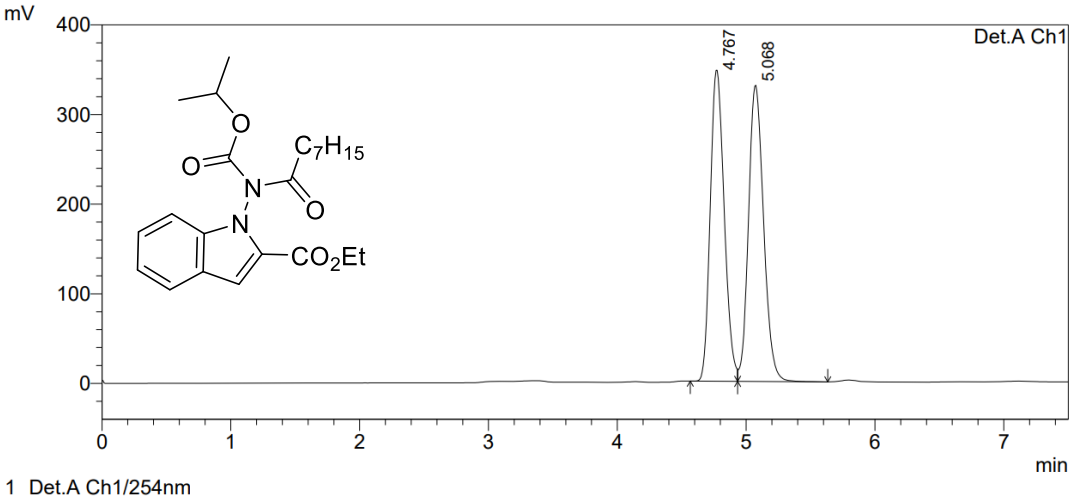
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.222	726038	90325	7.039	8.286
2	5.872	9588457	999804	92.961	91.714
Total		10314495	1090129	100.000	100.000

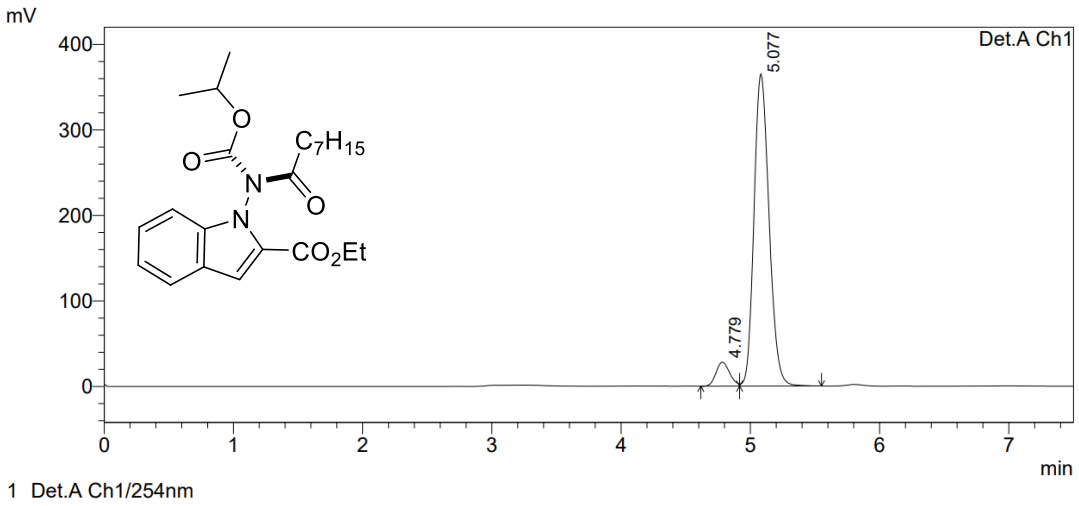
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)octanamido)-1H-indole-2-carboxylate (3db)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.767	2618063	346999	49.288	51.211
2	5.068	2693728	330587	50.712	48.789
Total		5311791	677586	100.000	100.000

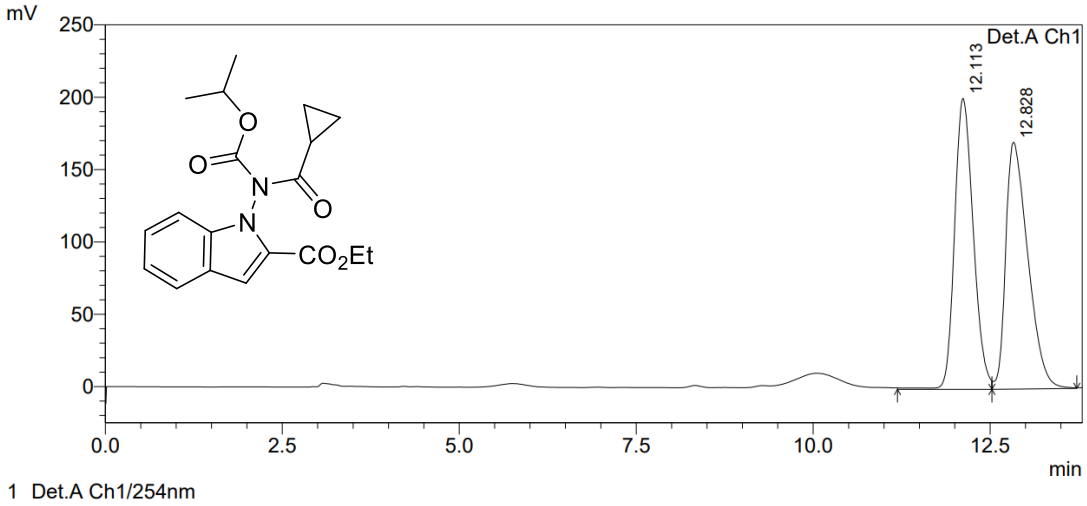


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.779	207244	28031	6.547	7.127
2	5.077	2958375	365282	93.453	92.873
Total		3165619	393313	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclopropanecarboxamido)-1H-indole-2-carboxylate (3eb)

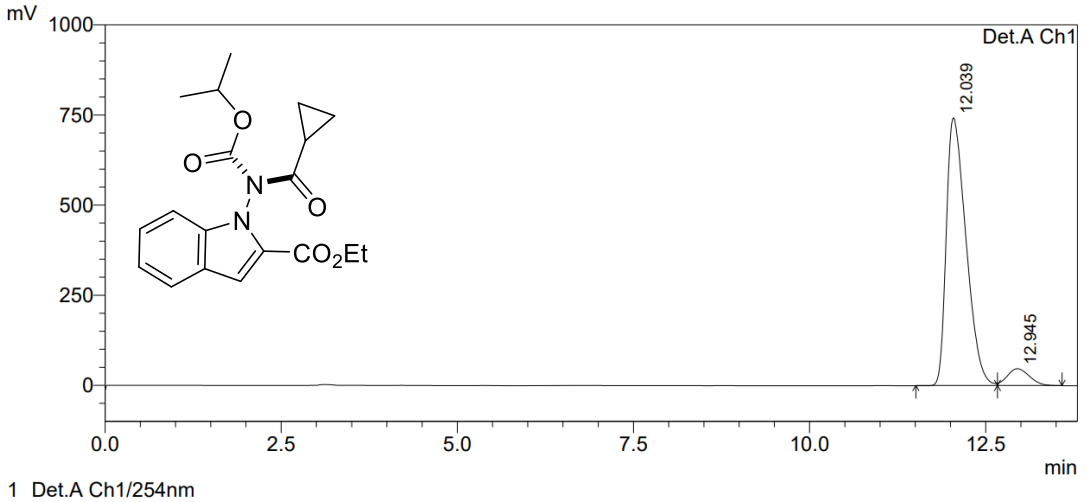


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.113	3698748	200395	49.854	54.203
2	12.828	3720384	169320	50.146	45.797
Total		7419132	369715	100.000	100.000



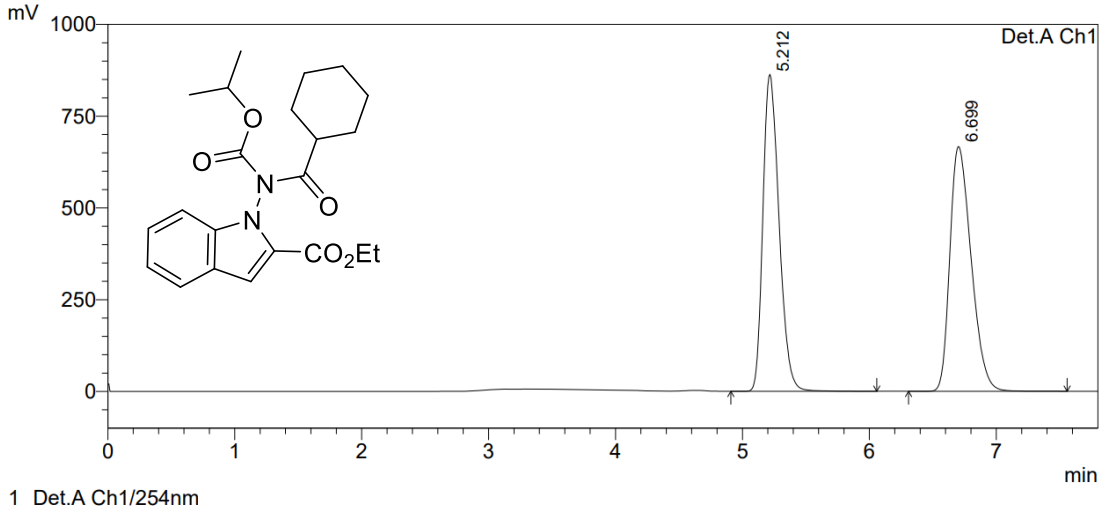
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.039	14420974	742259	93.494	94.101
2	12.945	1003537	46535	6.506	5.899
Total		15424511	788794	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclohexanecarboxamido)-1H-indole-2-carboxylate (3fb)

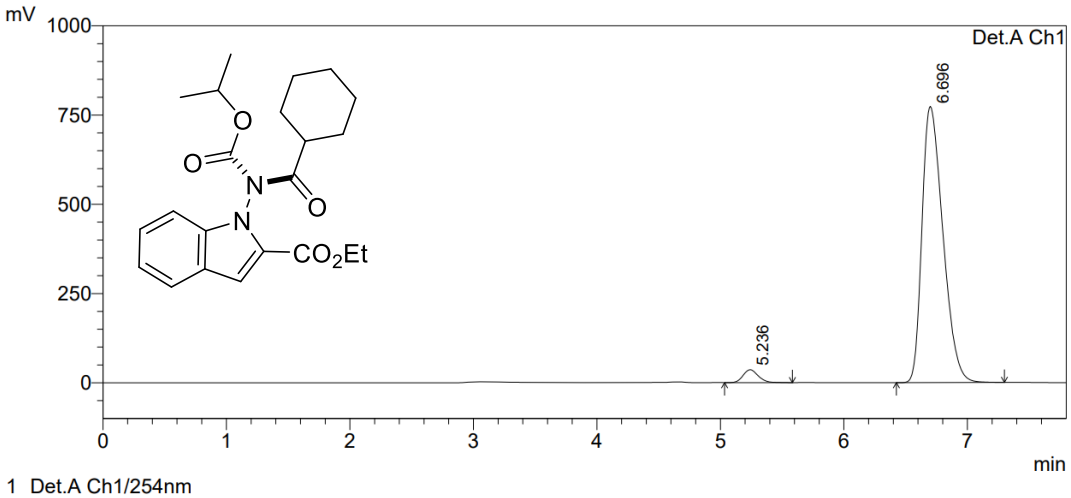


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.212	7672260	858652	49.615	56.302
2	6.699	7791250	666434	50.385	43.698
Total		15463510	1525087	100.000	100.000



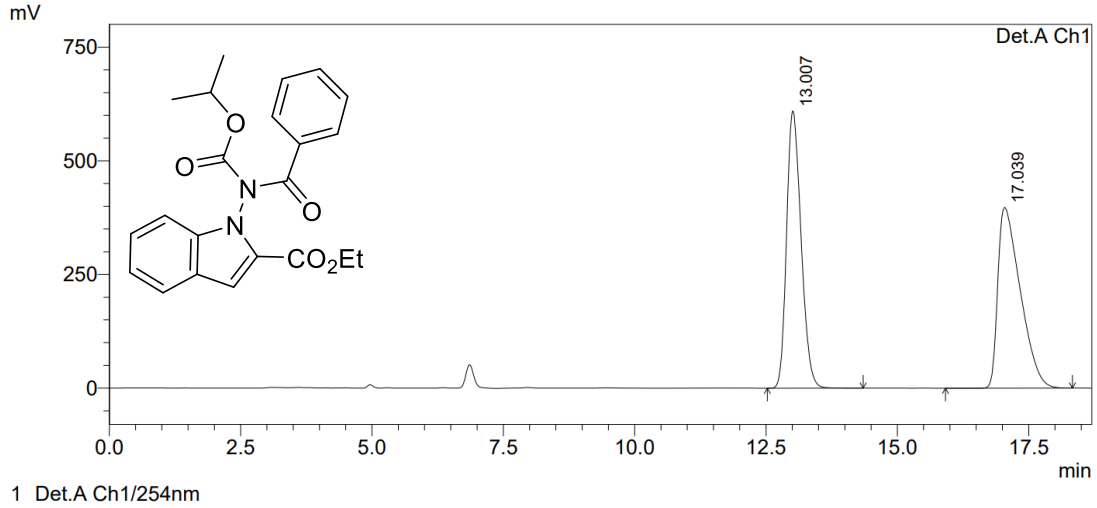
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.236	308451	36074	3.276	4.454
2	6.696	9107693	773919	96.724	95.546
Total		9416144	809994	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3gb)

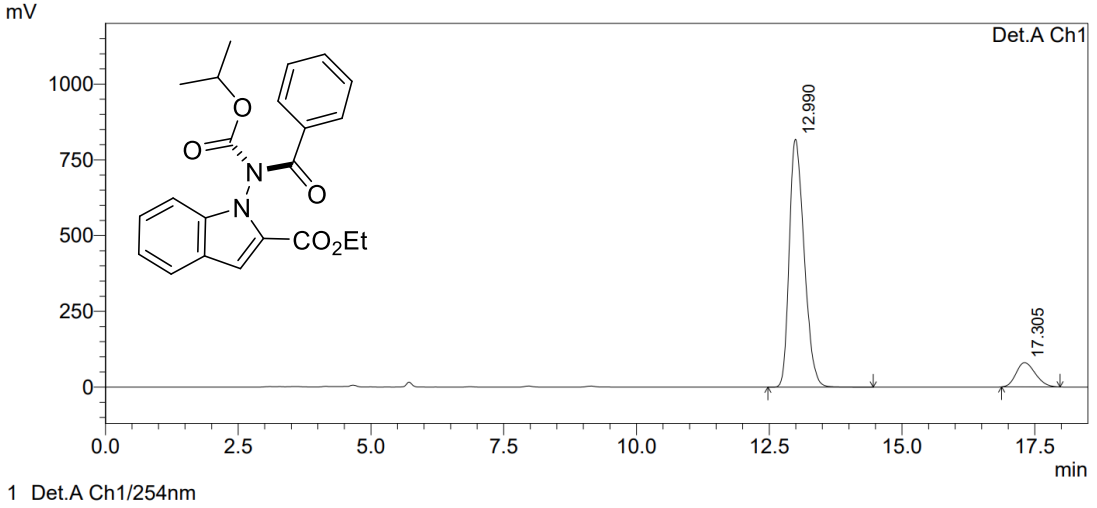


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.007	11718929	609773	49.824	60.533
2	17.039	11801740	397573	50.176	39.467
Total		23520669	1007345	100.000	100.000



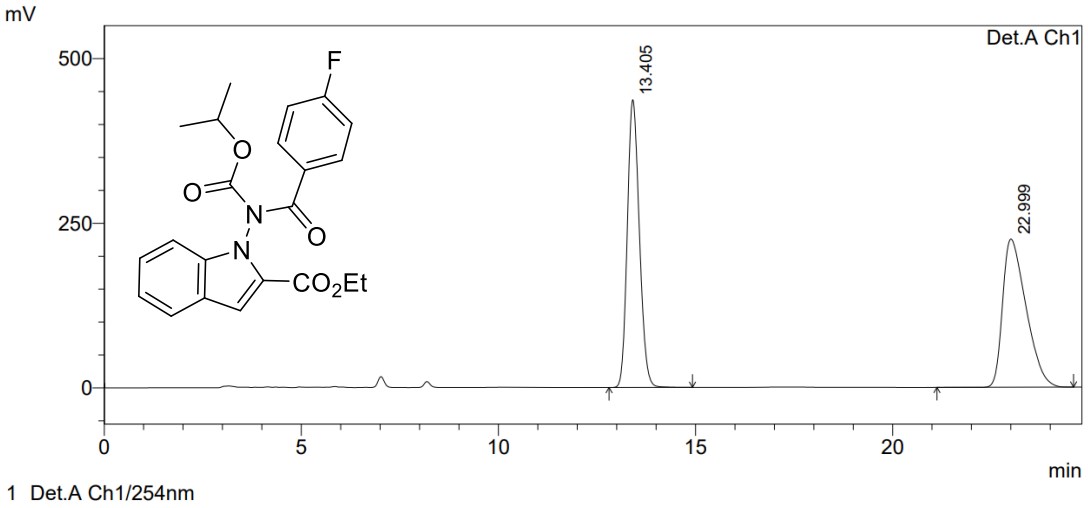
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.990	15961229	817231	88.770	91.069
2	17.305	2019283	80148	11.230	8.931
Total		17980512	897379	100.000	100.000

(R_a)-ethyl-1-(4-fluoro-N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3hb)

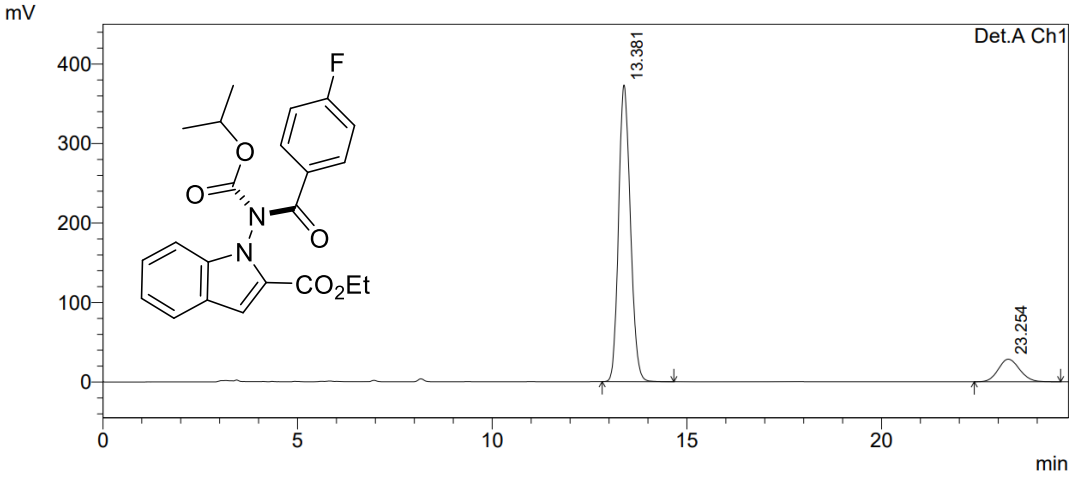


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.405	9273178	436474	49.976	66.000
2	22.999	9282011	224852	50.024	34.000
Total		18555188	661327	100.000	100.000



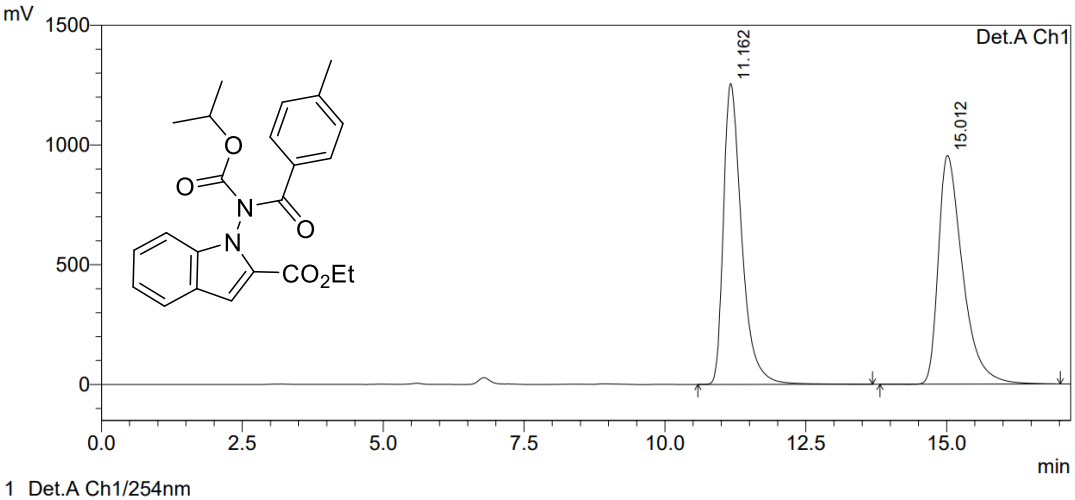
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.381	7867662	372687	87.922	92.919
2	23.254	1080814	28400	12.078	7.081
Total		8948477	401086	100.000	100.000

(R_a)-ethyl-1-(N-(isopropoxycarbonyl)-4-methylbenzamido)-1H-indole-2-carboxylate (3ib)

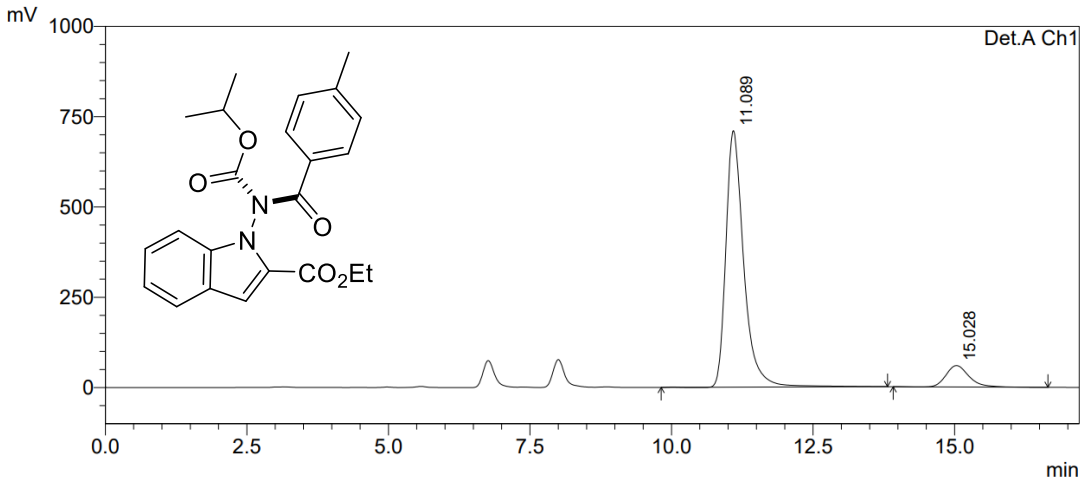


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.162	28411134	1255741	49.828	56.877
2	15.012	28607604	952085	50.172	43.123
Total		57018739	2207826	100.000	100.000



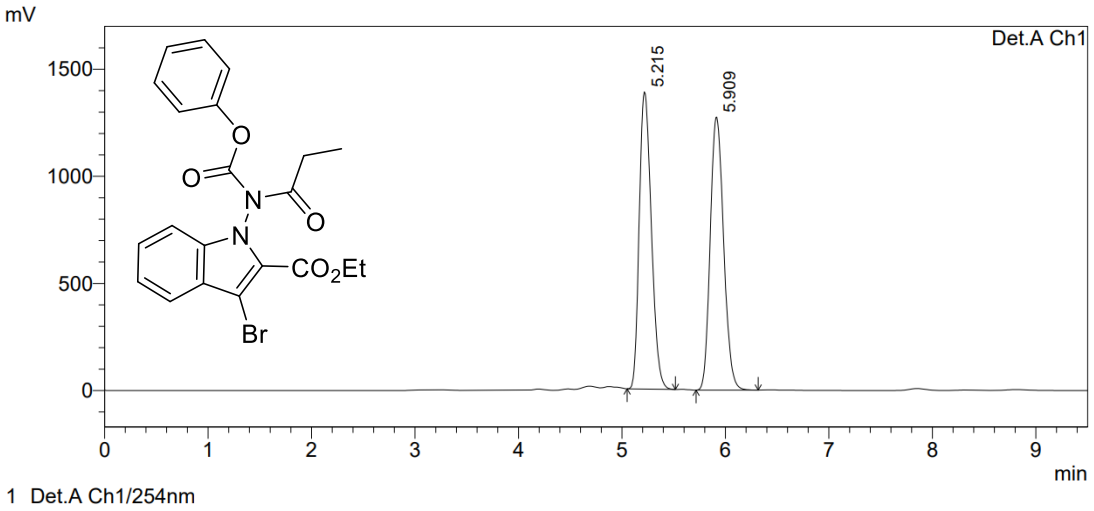
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.089	15625857	709769	90.356	92.296
2	15.028	1667748	59245	9.644	7.704
Total		17293604	769014	100.000	100.000

(R_a)-ethyl-3-bromo-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (4)

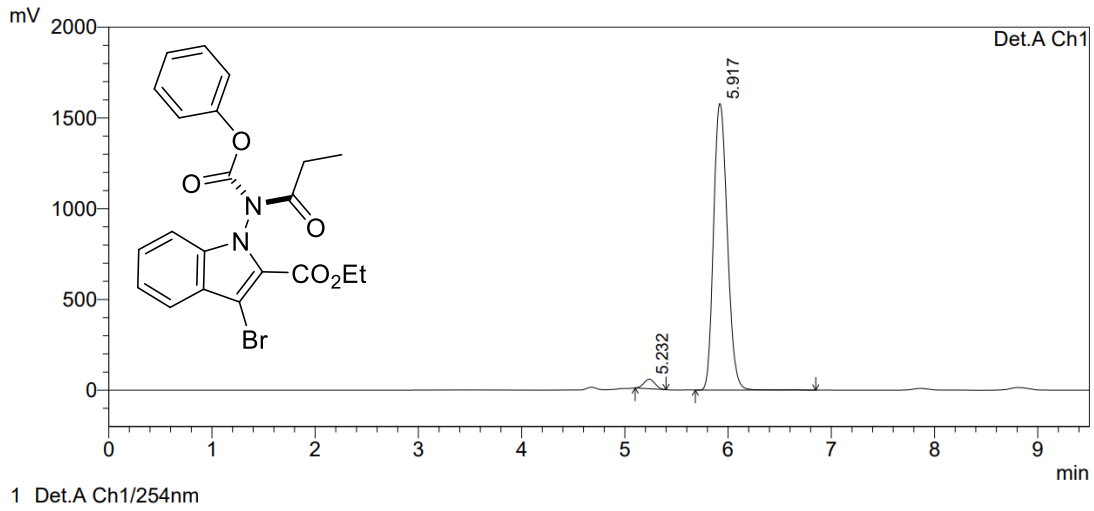


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.215	11268442	1375904	49.550	51.926
2	5.909	11473056	1273818	50.450	48.074
Total		22741499	2649722	100.000	100.000



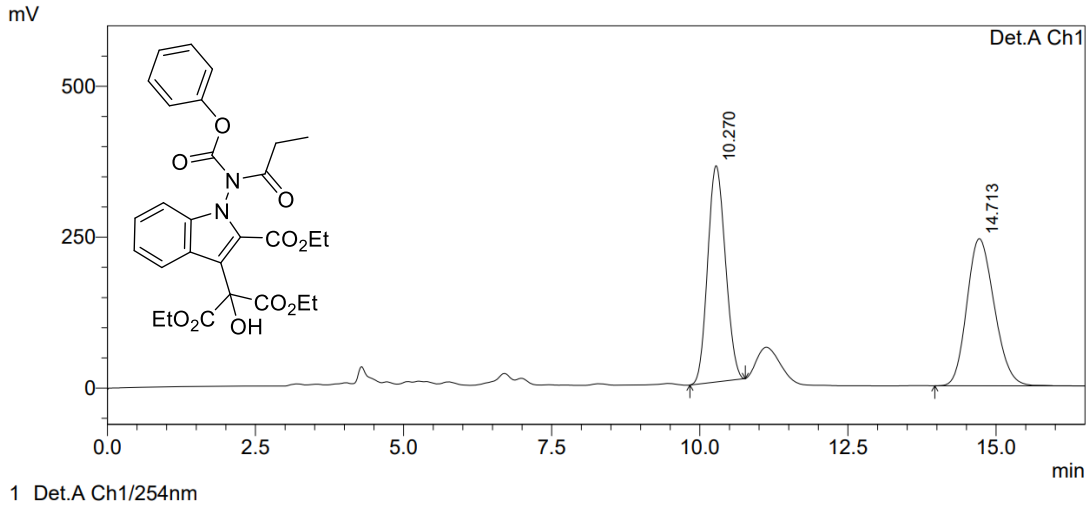
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.232	392455	52020	2.613	3.219
2	5.917	14626687	1564032	97.387	96.781
Total		15019141	1616052	100.000	100.000

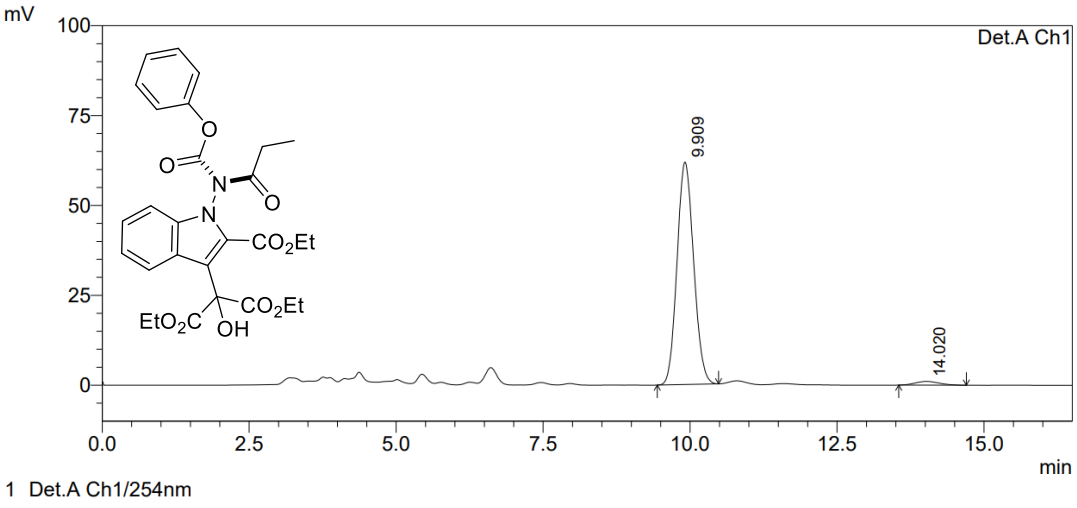
(R_a)-diethyl-2-(2-(ethoxycarbonyl)-1-(N-(phenoxycarbonyl)propionamido)-1H-indol-3-yl)-2-hydroxymalonate (5)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.270	7467384	355940	48.768	59.386
2	14.713	7844647	243425	51.232	40.614
Total		15312032	599365	100.000	100.000



PeakTable

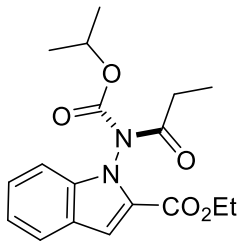
Detector A Ch1 254nm

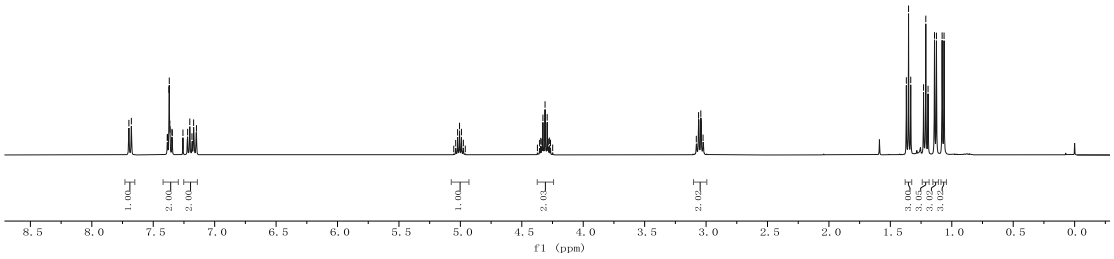
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.909	1218303	61858	97.639	98.344
2	14.020	29465	1042	2.361	1.656
Total		1247767	62900	100.000	100.000

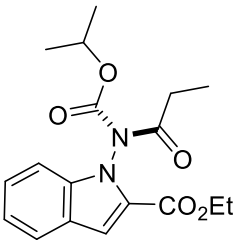
10. NMR Spectra

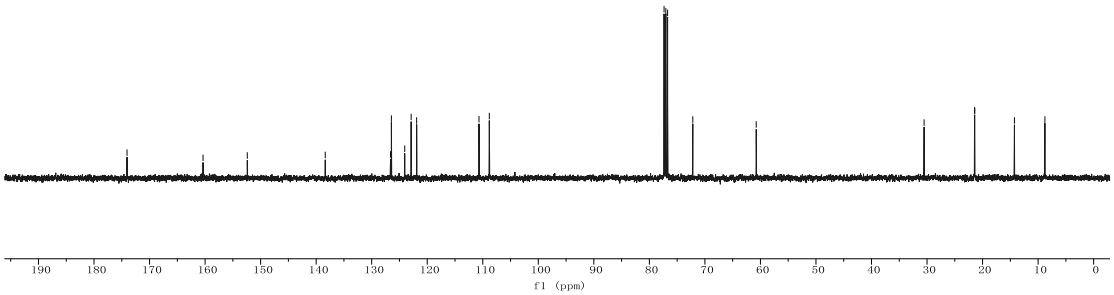
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3aa)



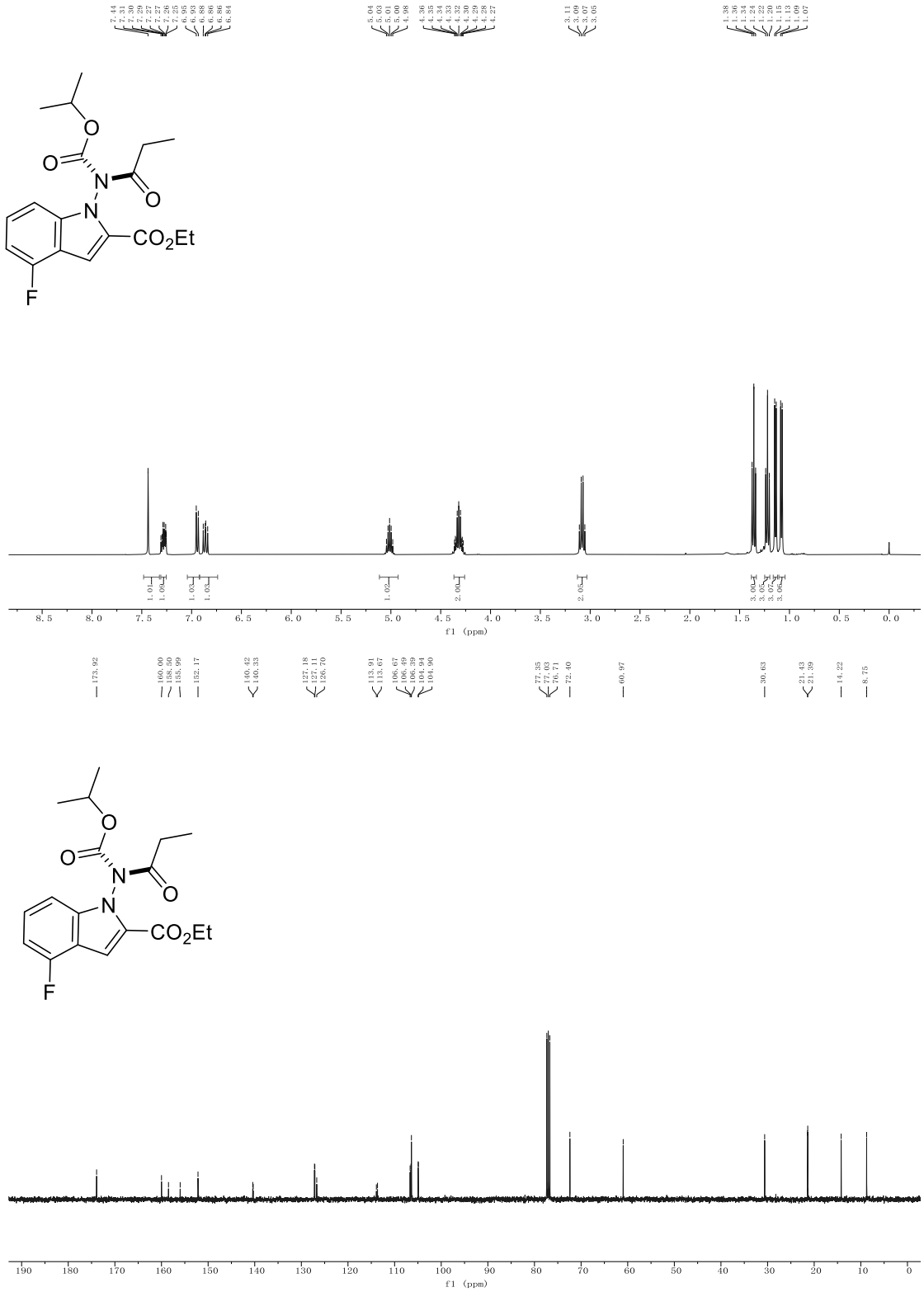



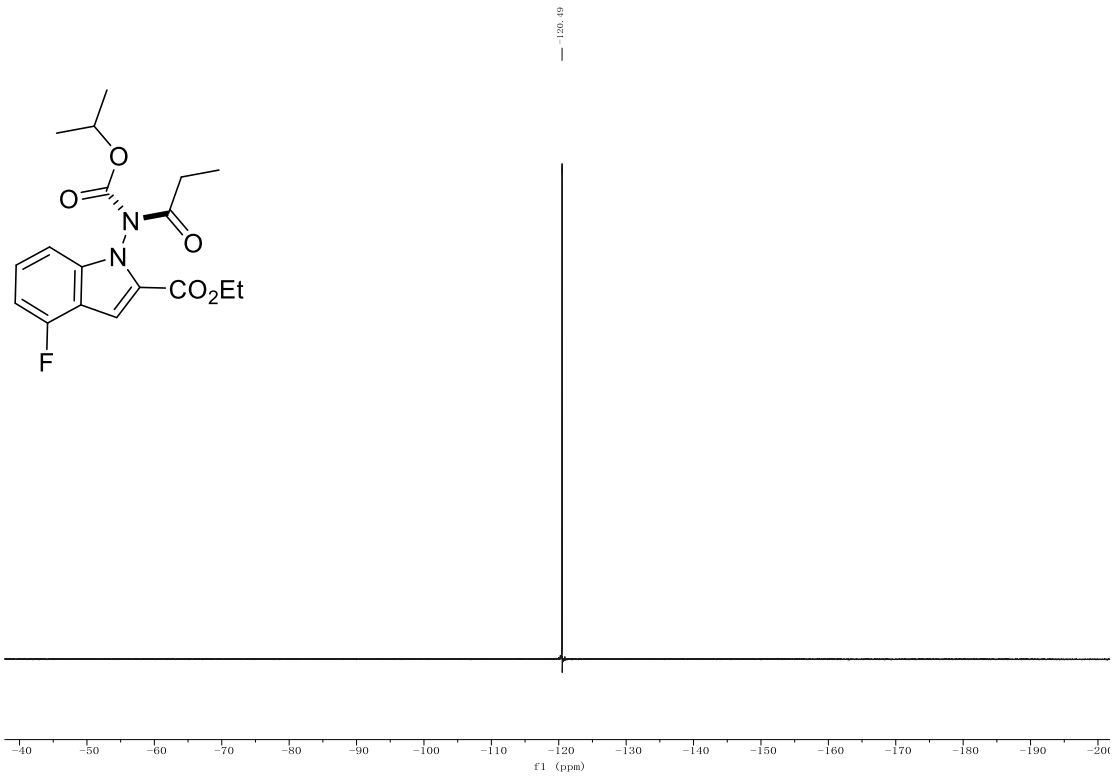




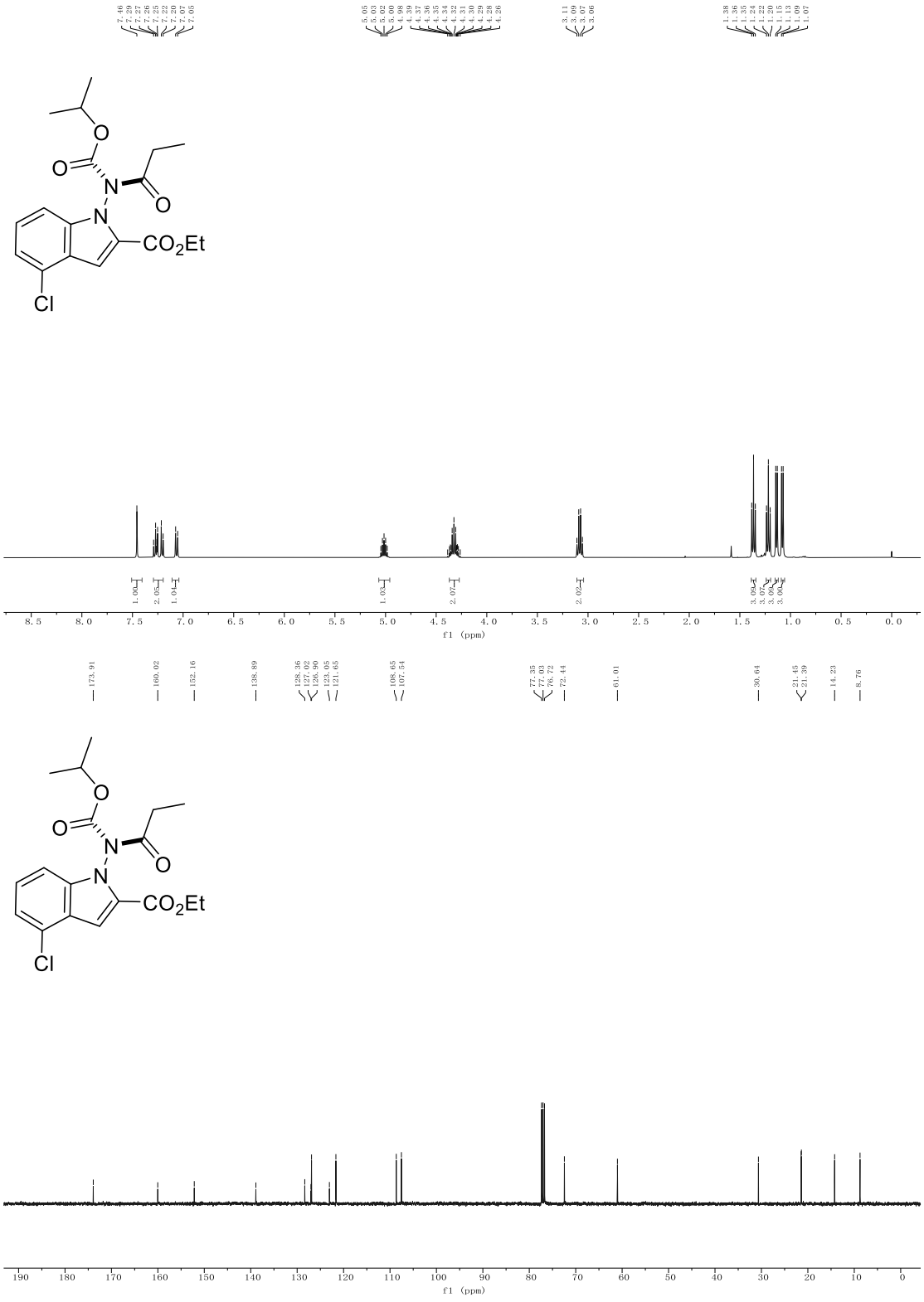


(R_a)-ethyl-4-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ba)

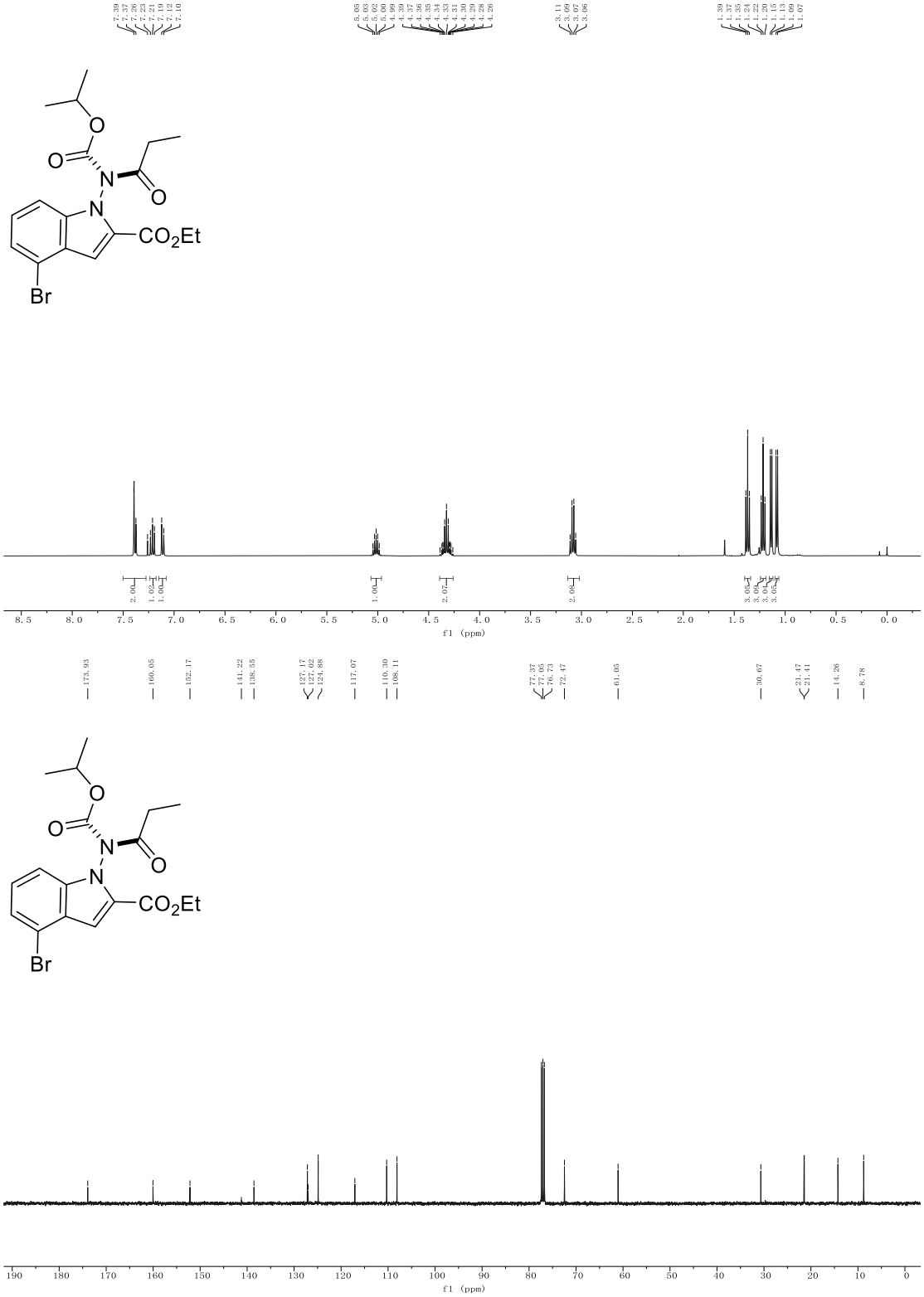



-120.49
O
O
N
O
N
CO2Et
F
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

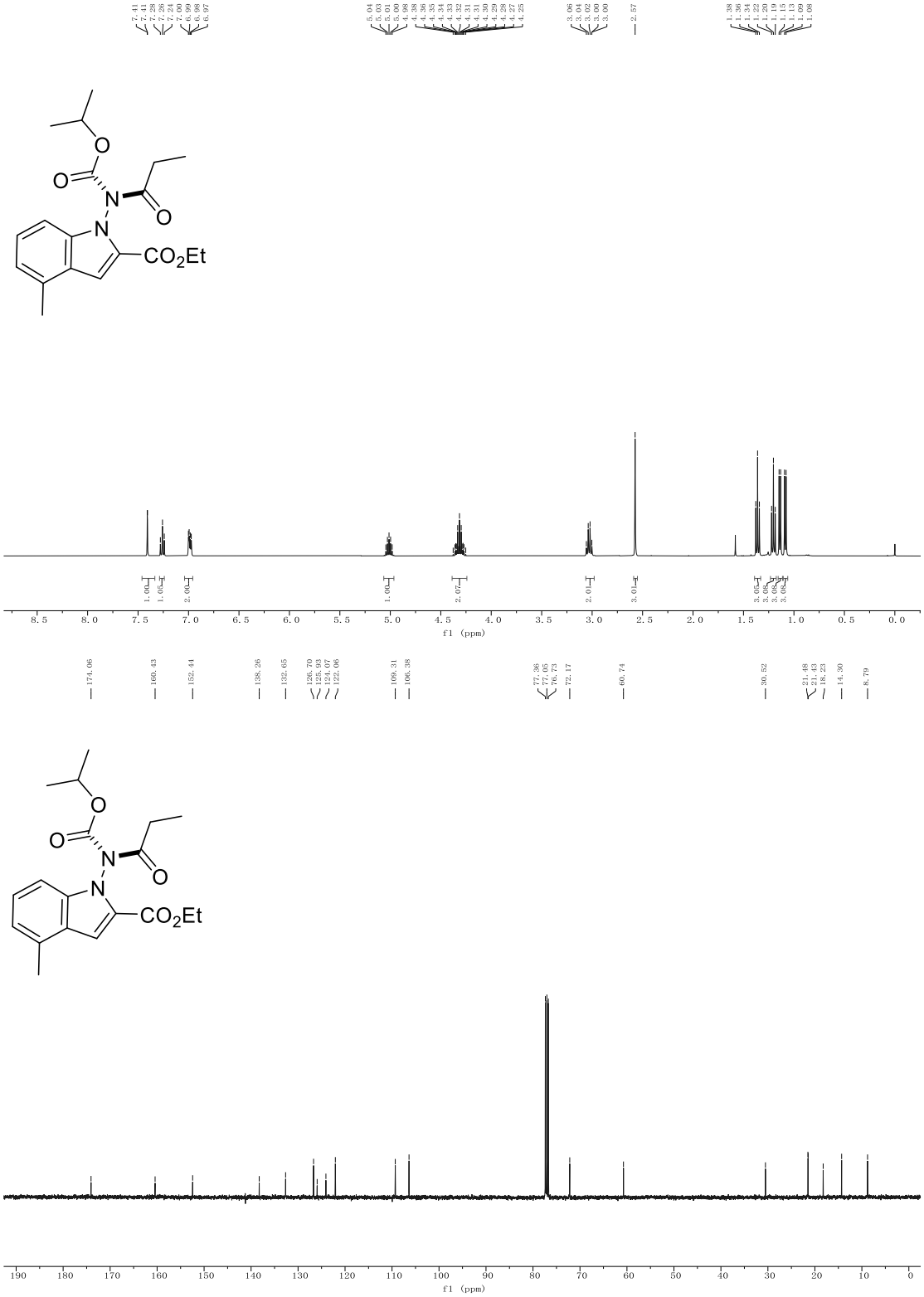
(R_a)-ethyl-4-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ca)



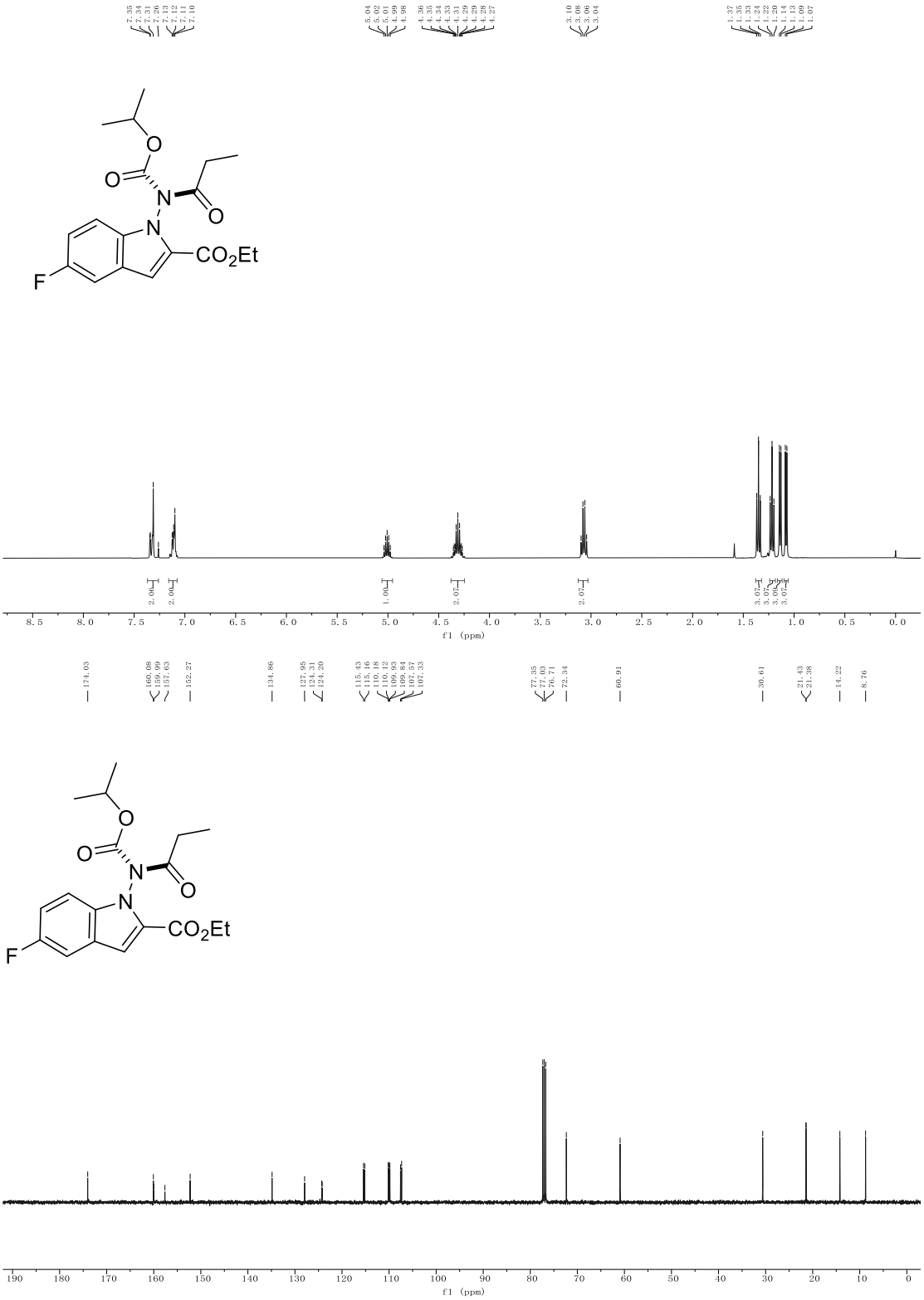
(R_a)-ethyl-4-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3da)

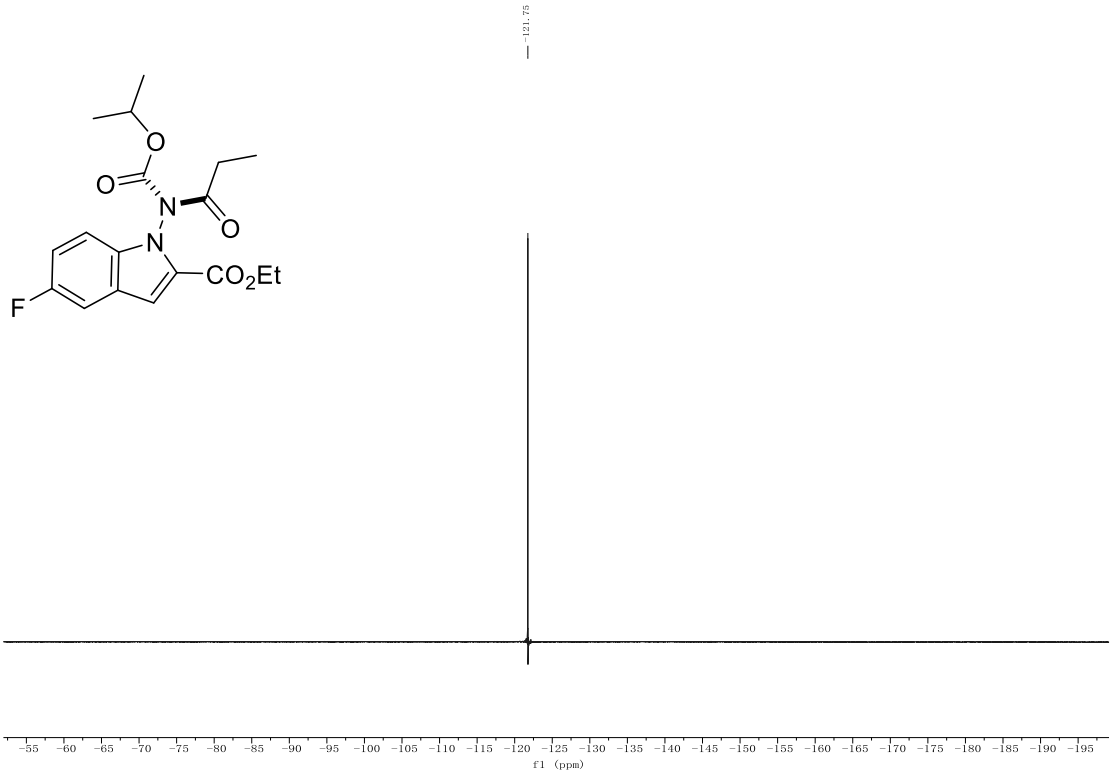


(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-4-methyl-1H-indole-2-carboxylate (3ea)

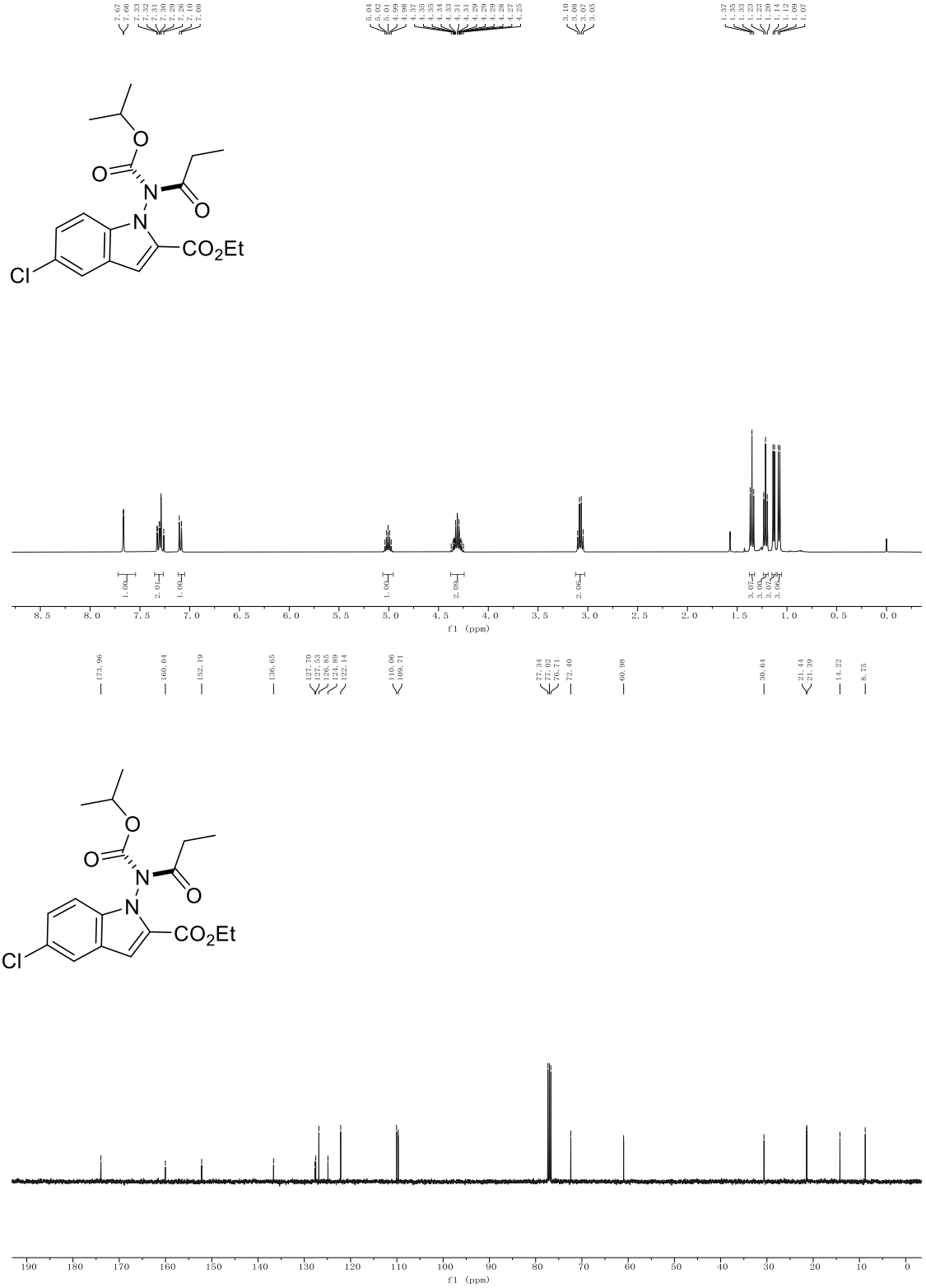


(R_a)-ethyl-5-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3fa)

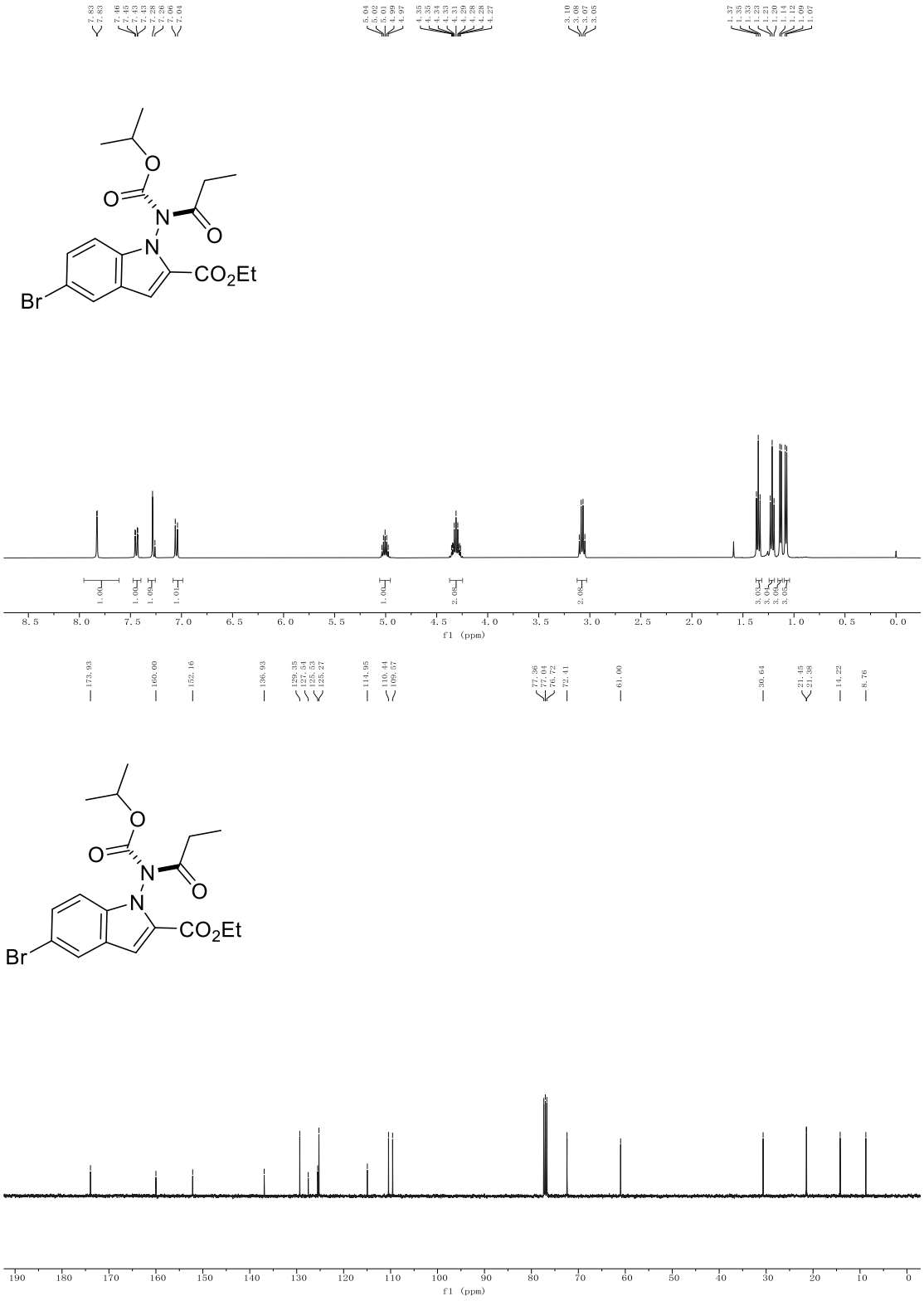



−121.75
O
O
N
O
N
CO2Et
F
−55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175 −180 −185 −190 −195
f1 (ppm)

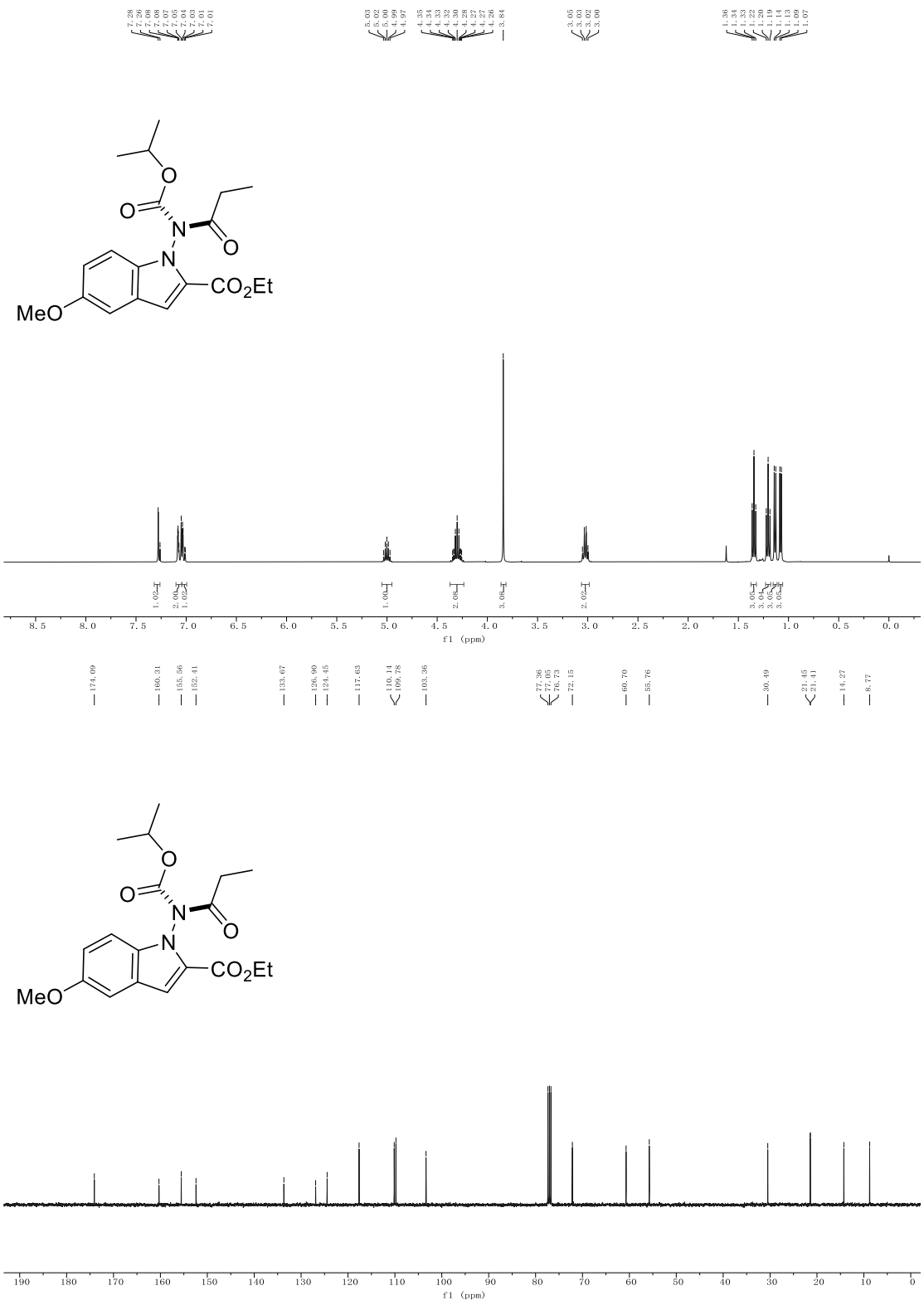
(R_a)-ethyl-5-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ga)



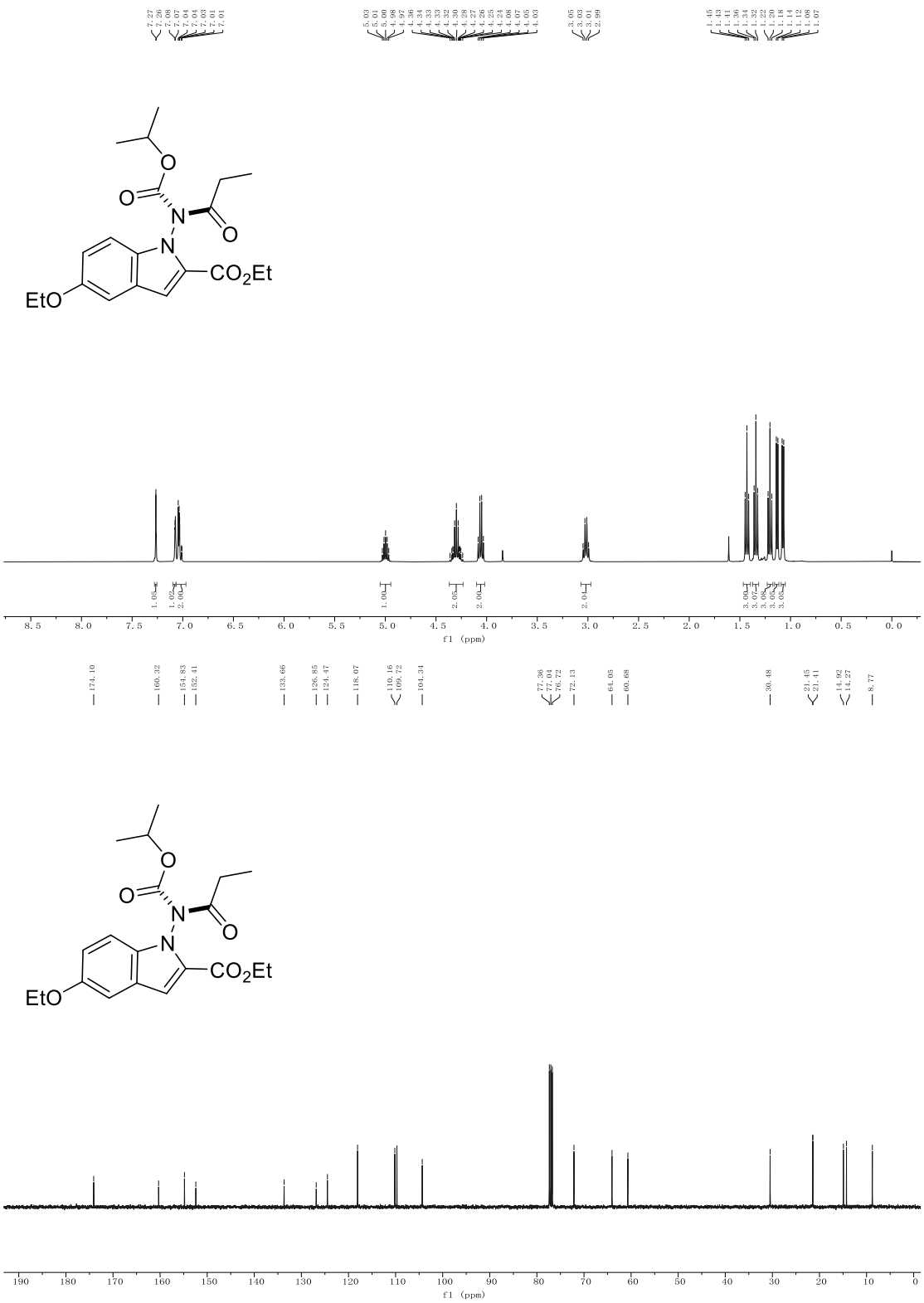
(R_a)-ethyl-5-bromo-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ha)



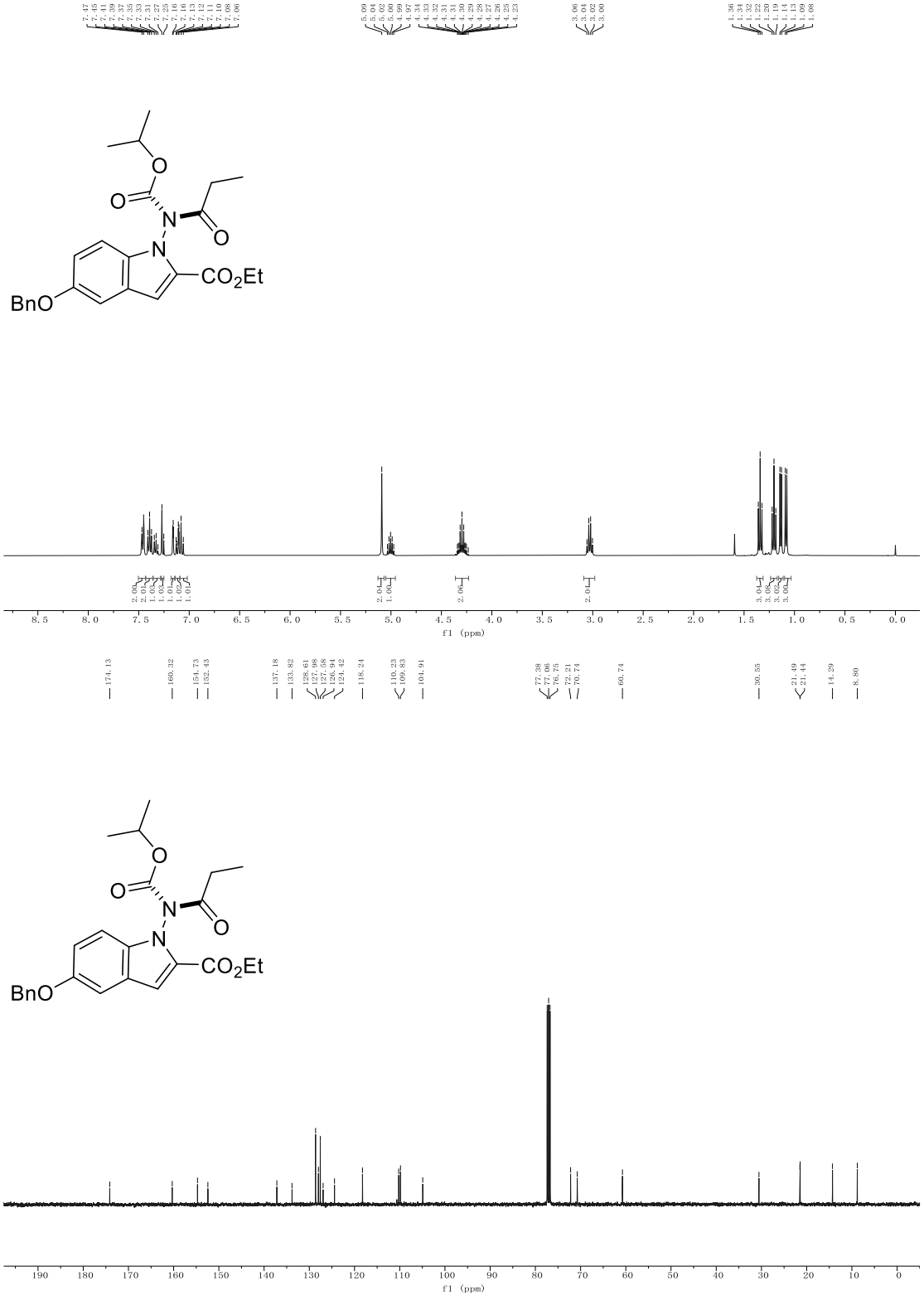
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-methoxy-1H-indole-2-carboxylate (3ia)



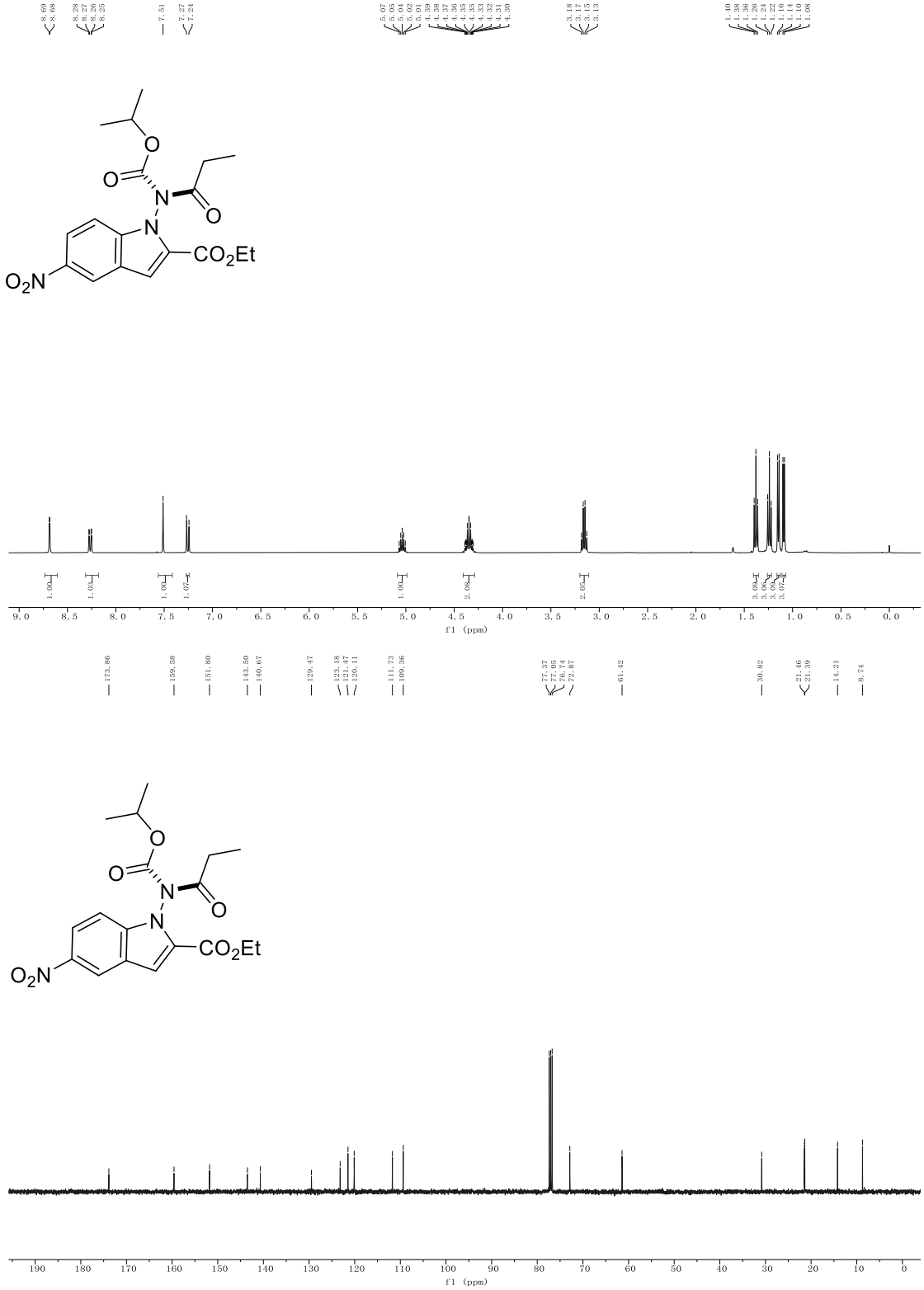
(R_a)-ethyl-5-ethoxy-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ja)



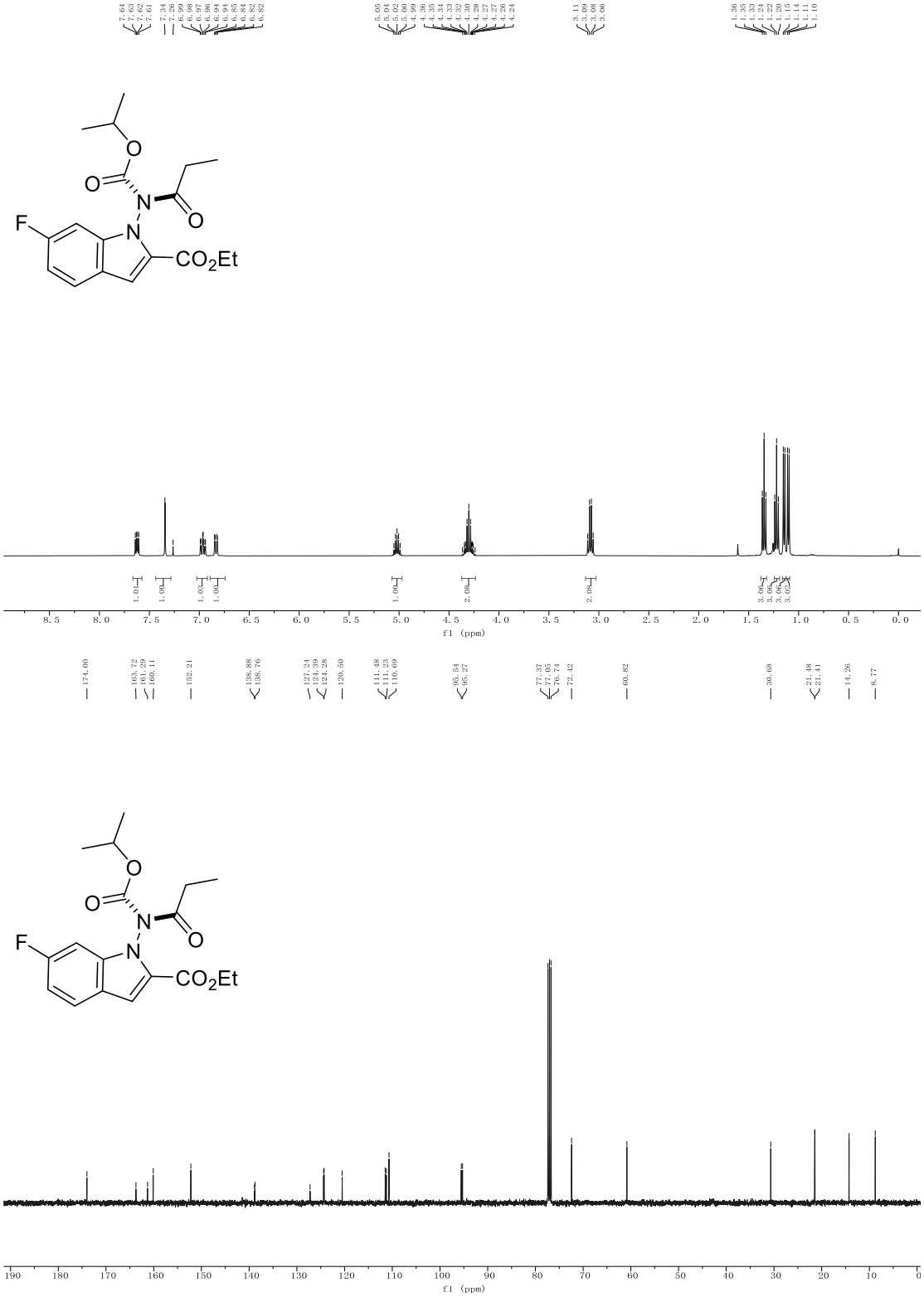
(R_a)-ethyl-5-(benzyloxy)-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ka)

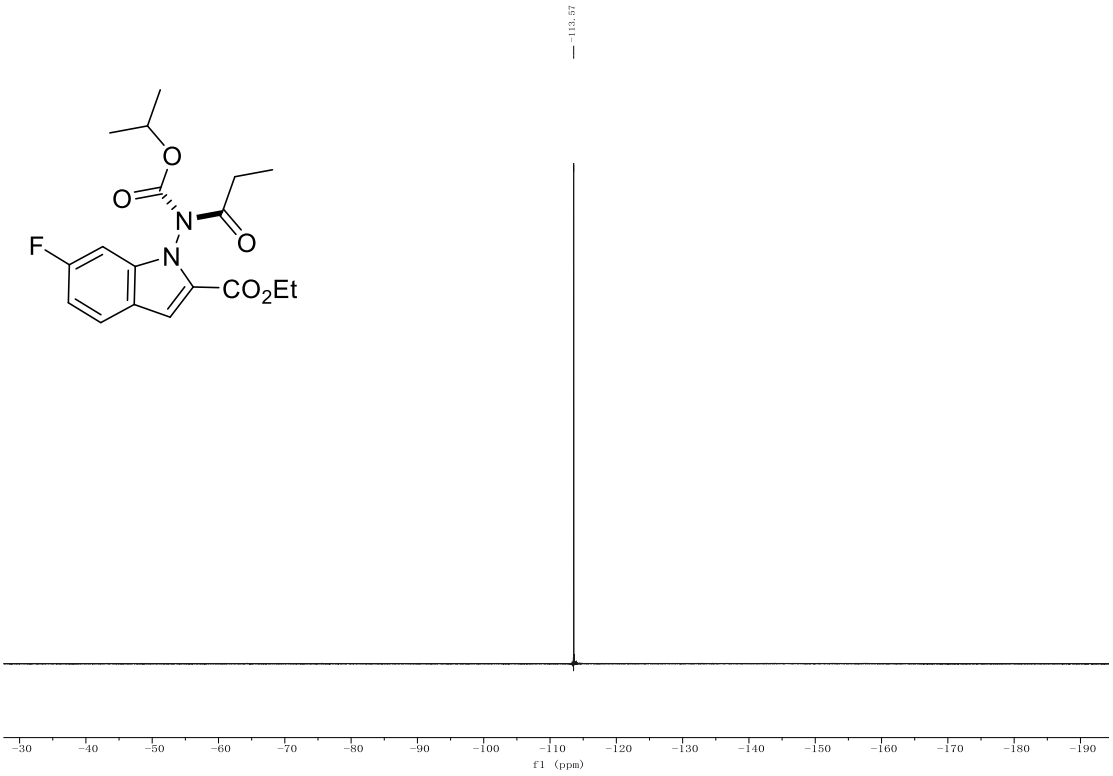


(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-5-nitro-1H-indole-2-carboxylate (3la)

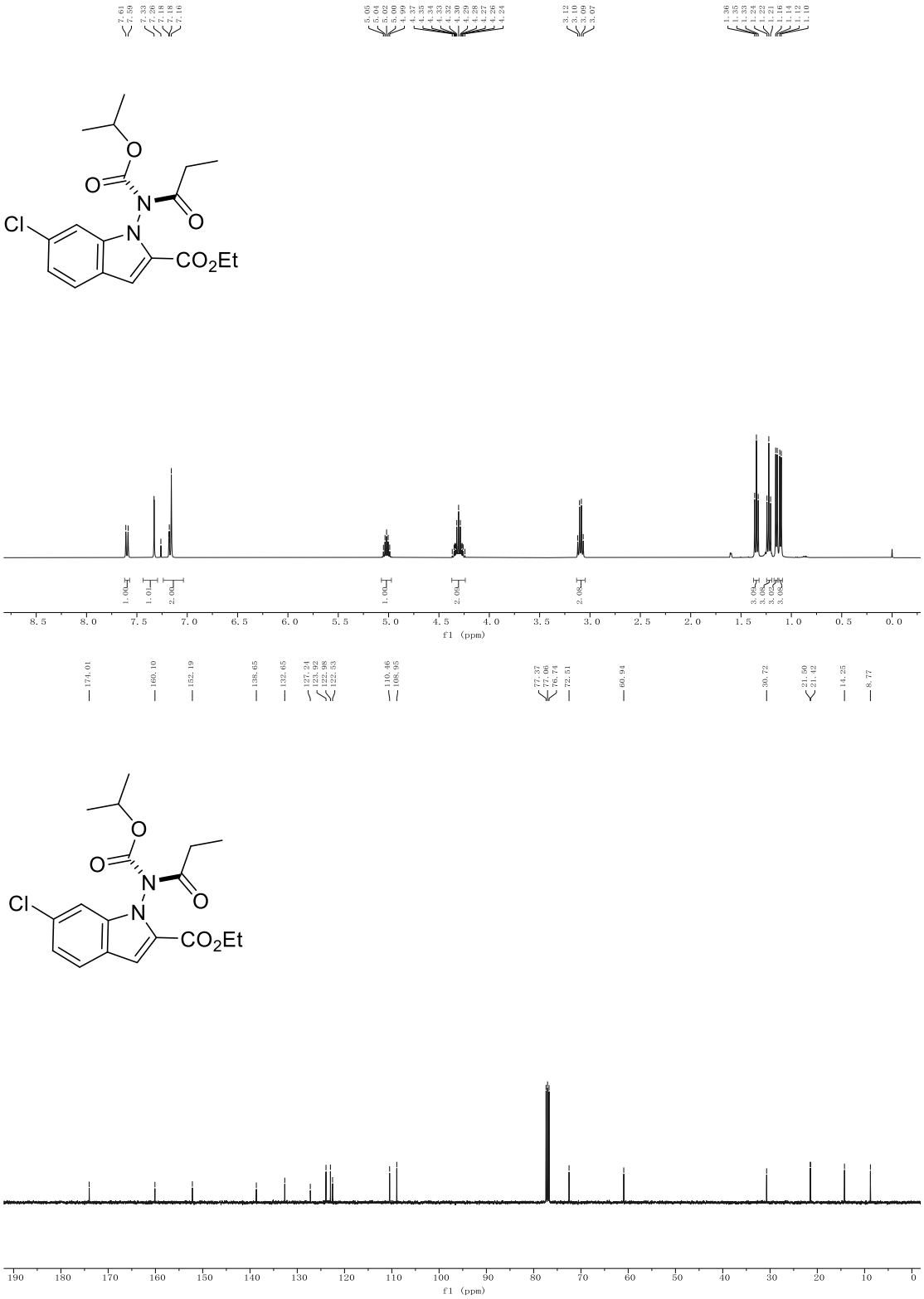


(R_a)-ethyl-6-fluoro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ma)

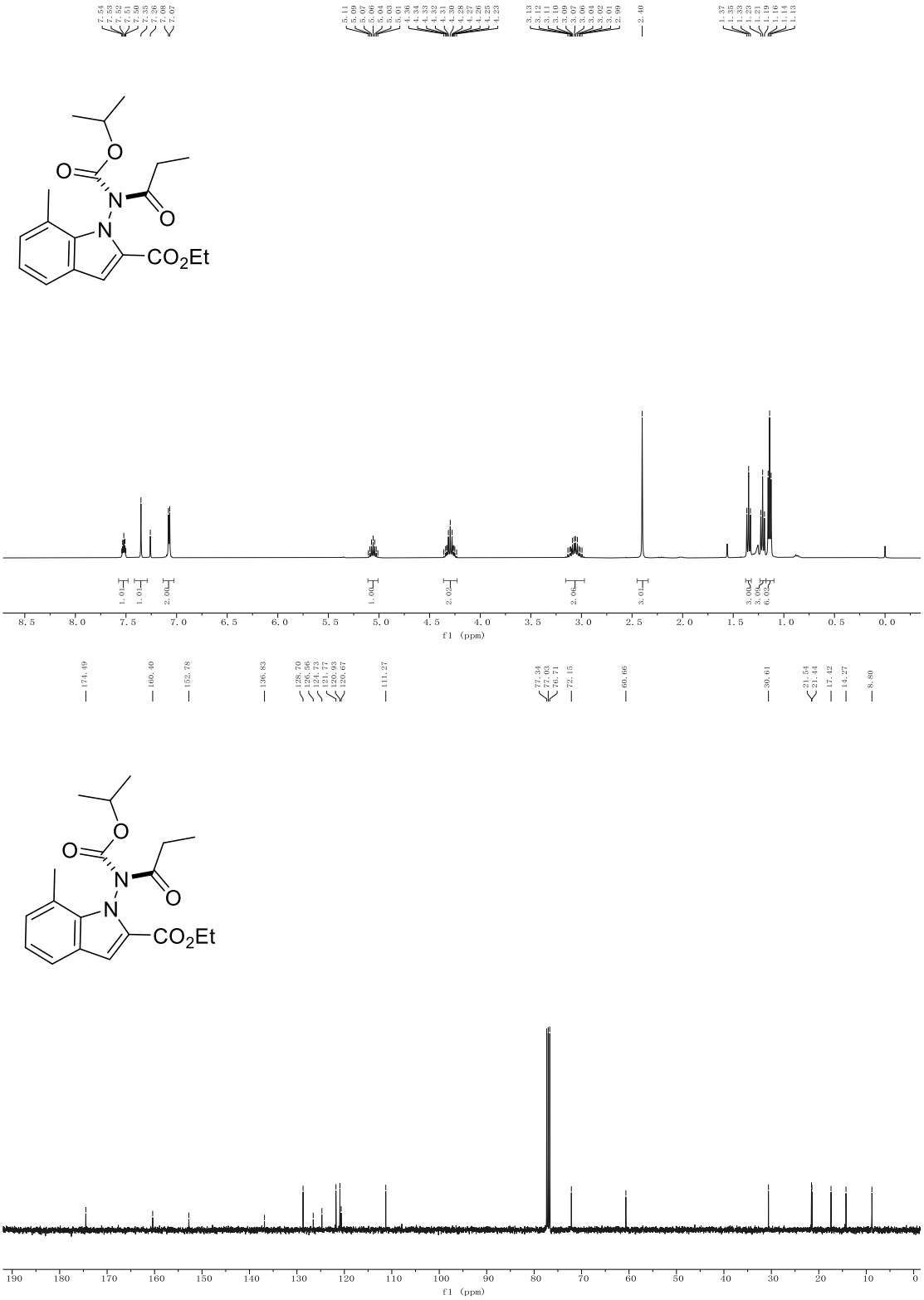



-113.57
O
O
N
O
F
N
CO2Et
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

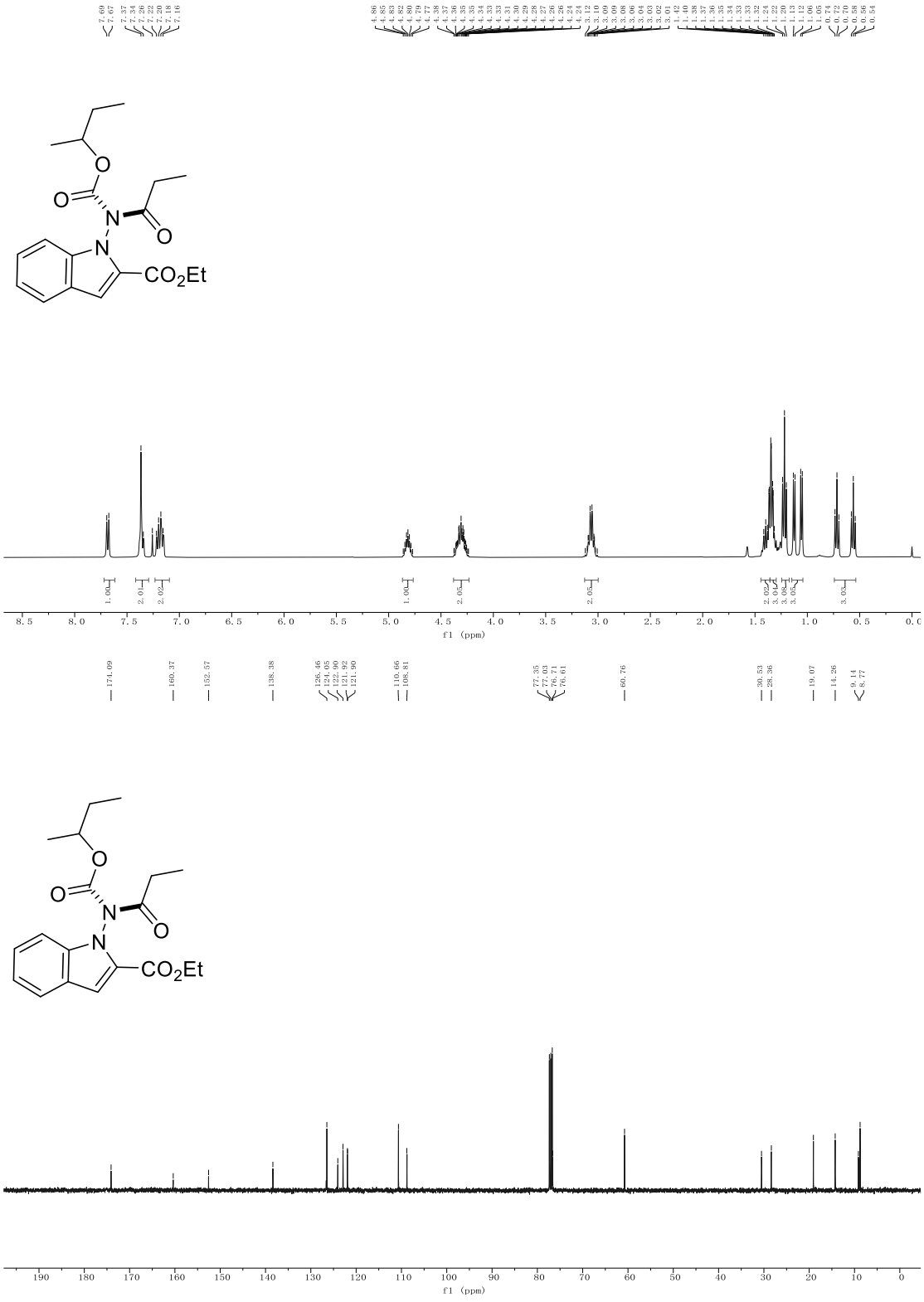
(R_a)-ethyl-6-chloro-1-(N-(isopropoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3na)



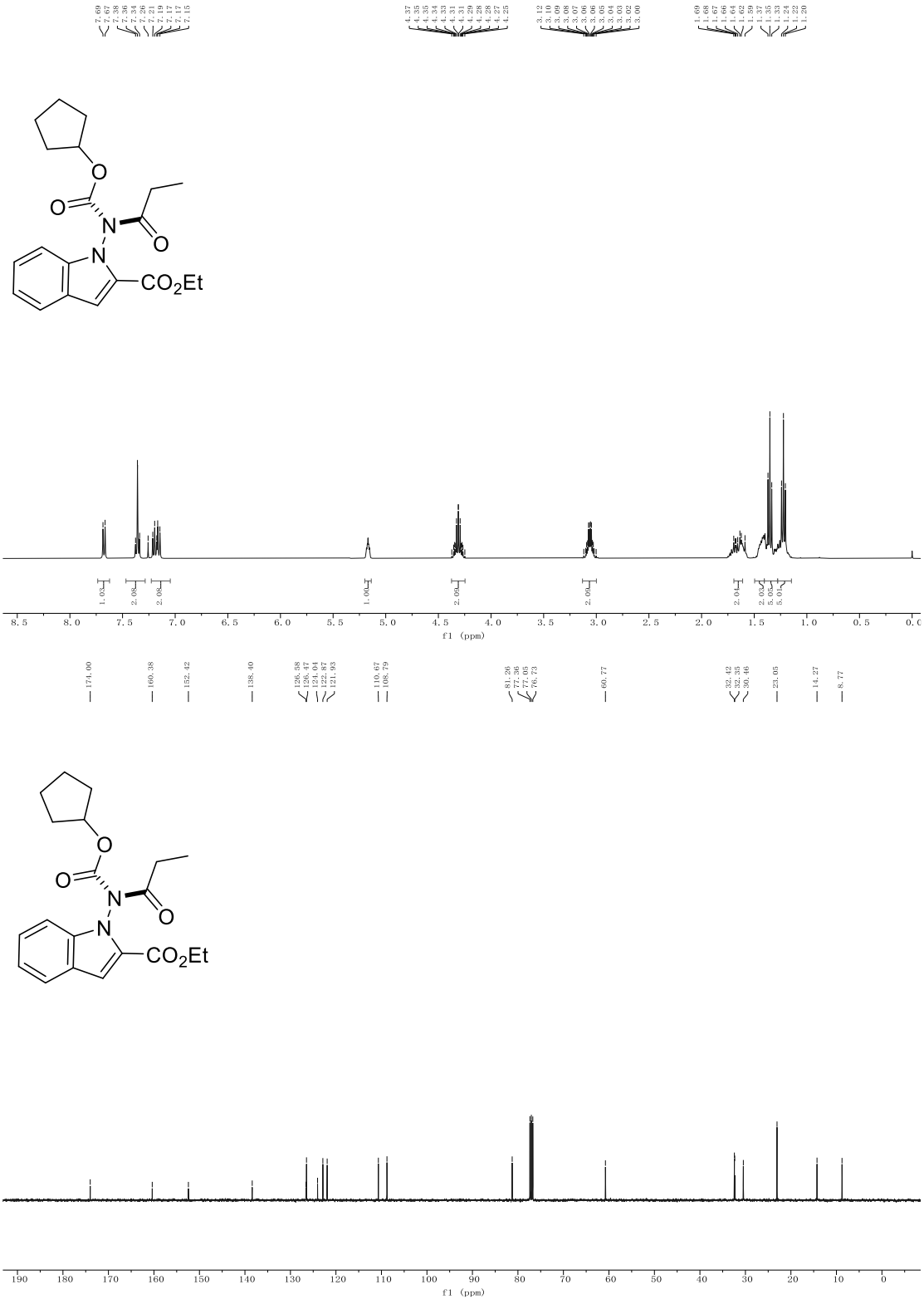
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)propionamido)-7-methyl-1H-indole-2-carboxylate (3oa)



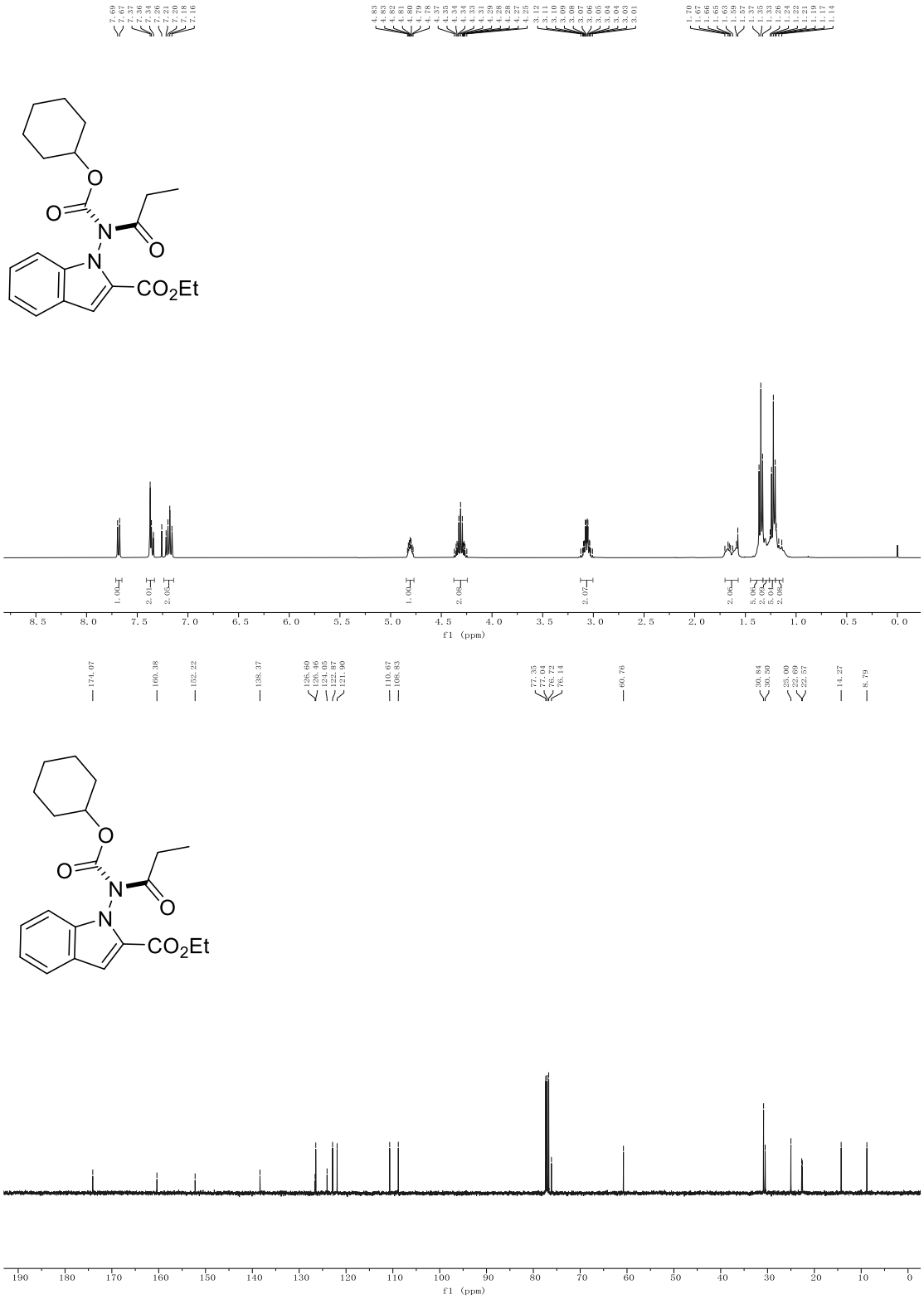
(R_a)-ethyl-1-(N-(sec-butoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3pa)



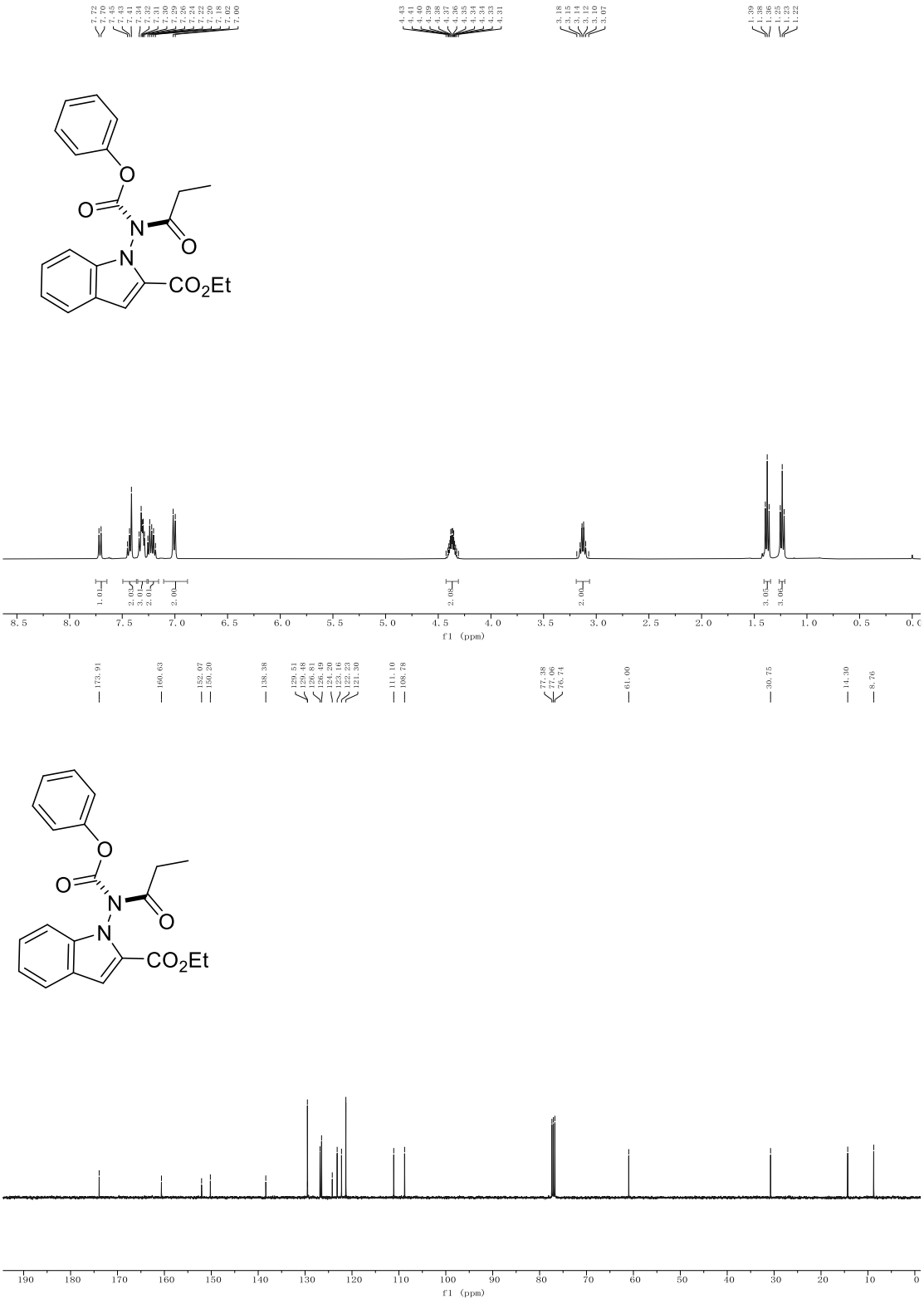
(R_a)-ethyl-1-(N-((cyclopentyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3qa)



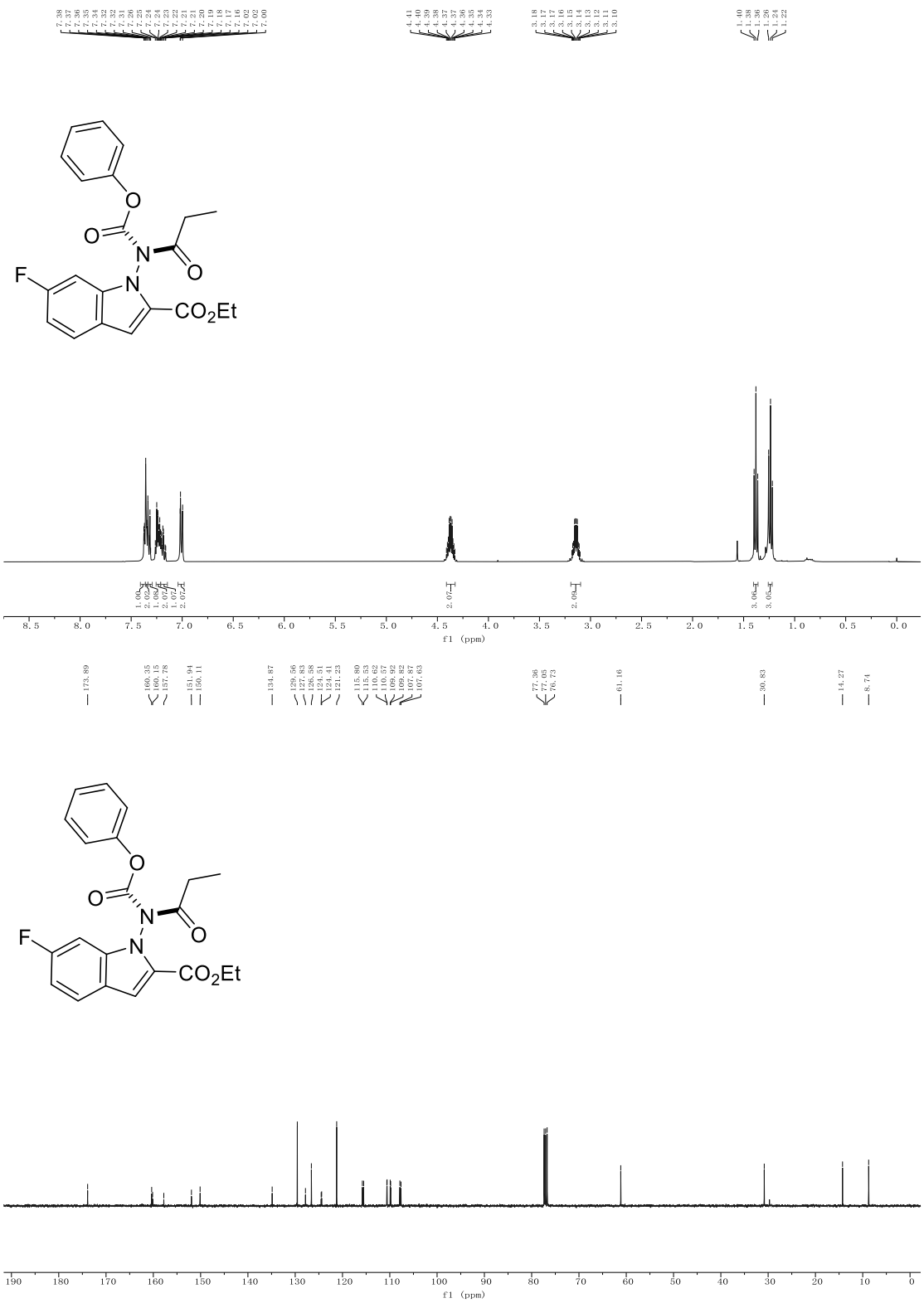
(R_a)-ethyl-1-(N-((cyclohexyloxy)carbonyl)propionamido)-1H-indole-2-carboxylate (3ra)

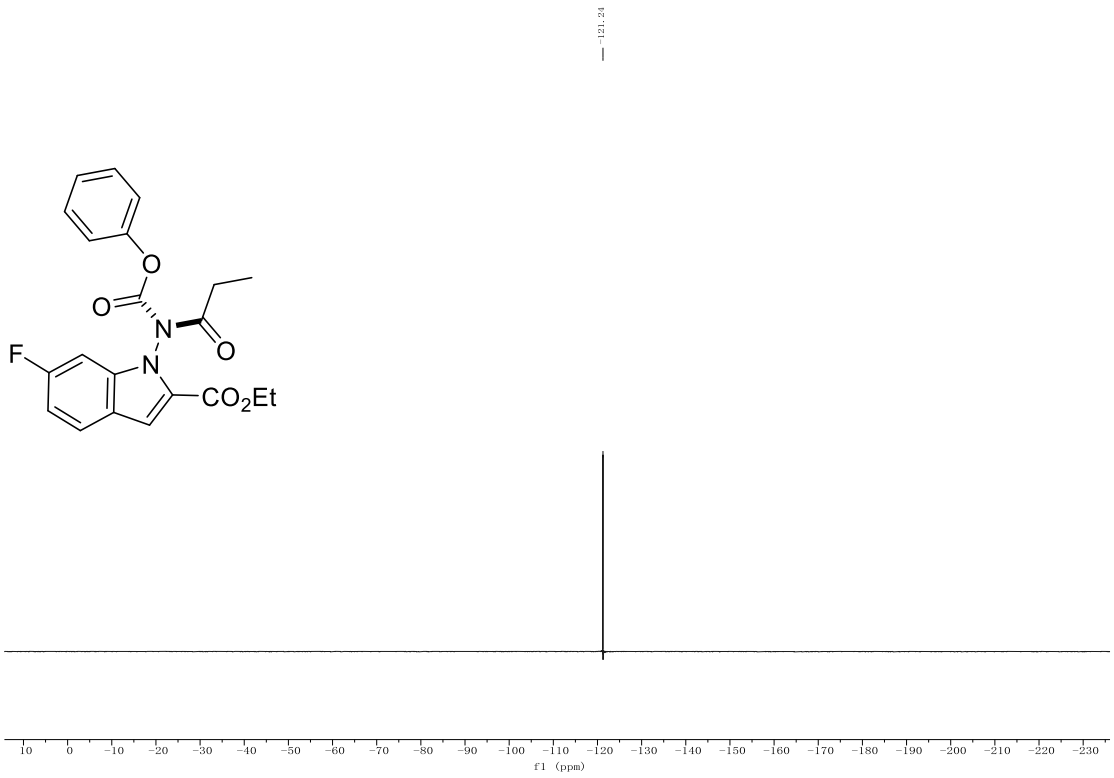


(R_a)-ethyl-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3sa)

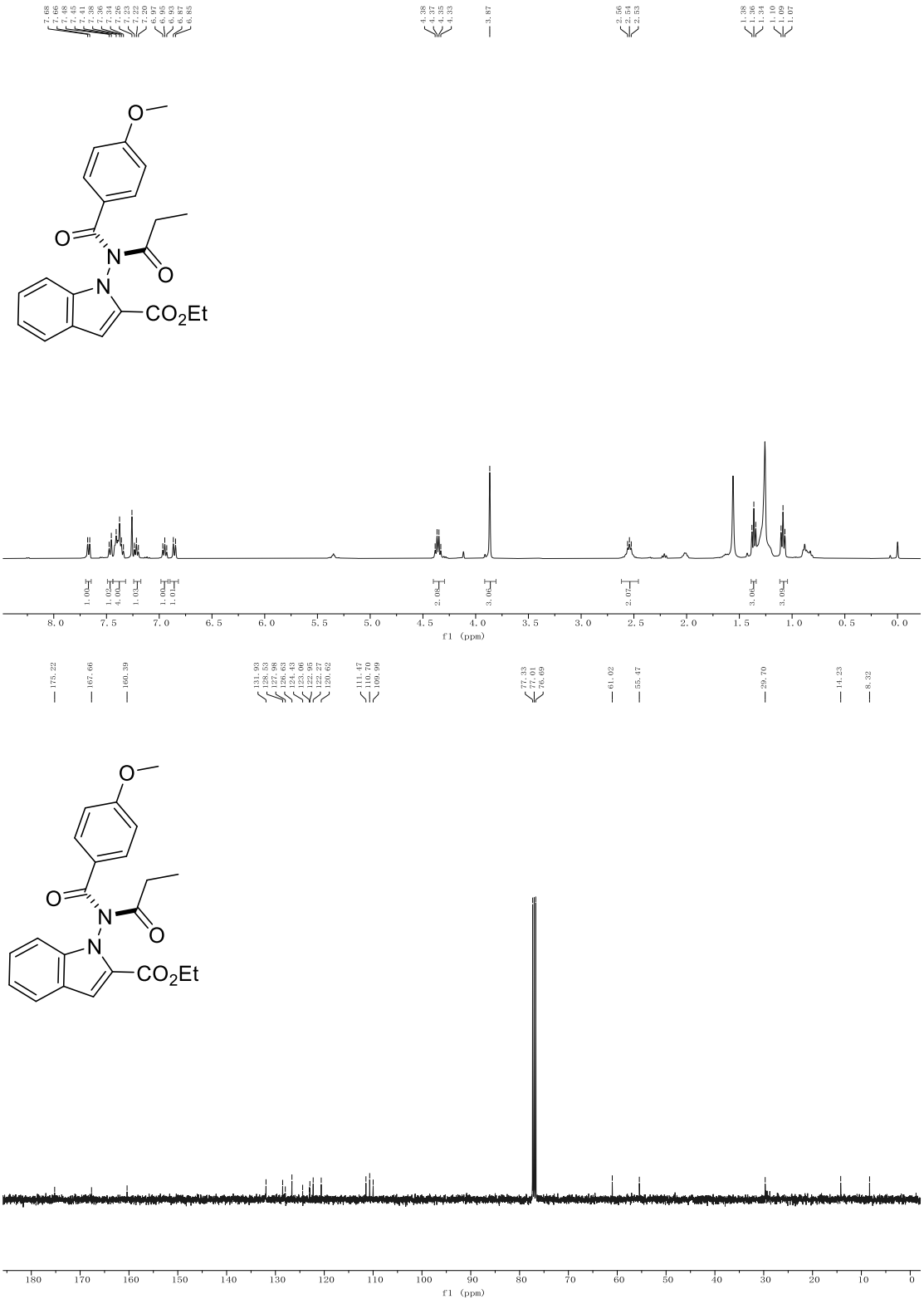


(R_a)-ethyl-6-fluoro-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (3ta)

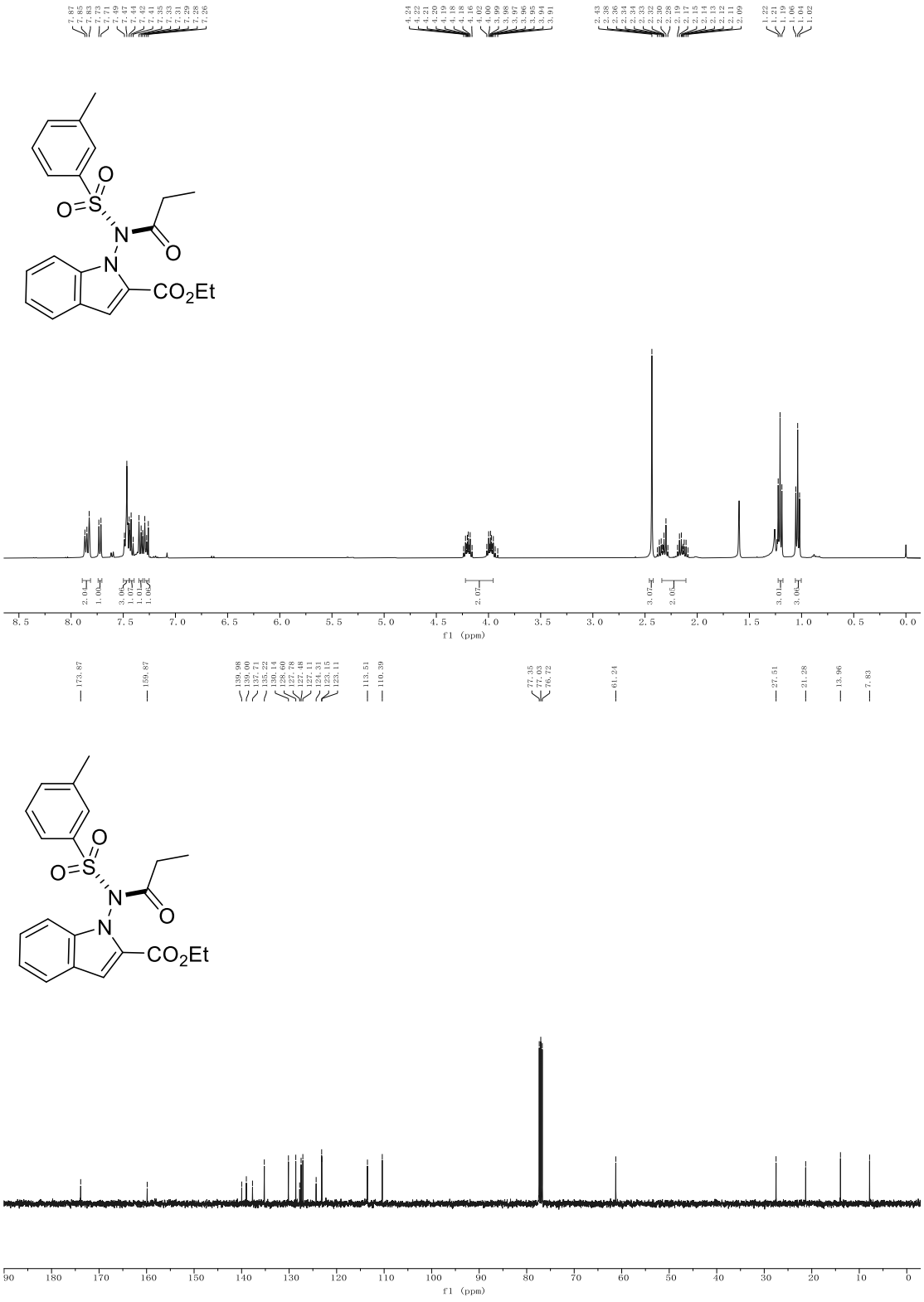



-121.24
O
O
N
O
F
N
CO2Et
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

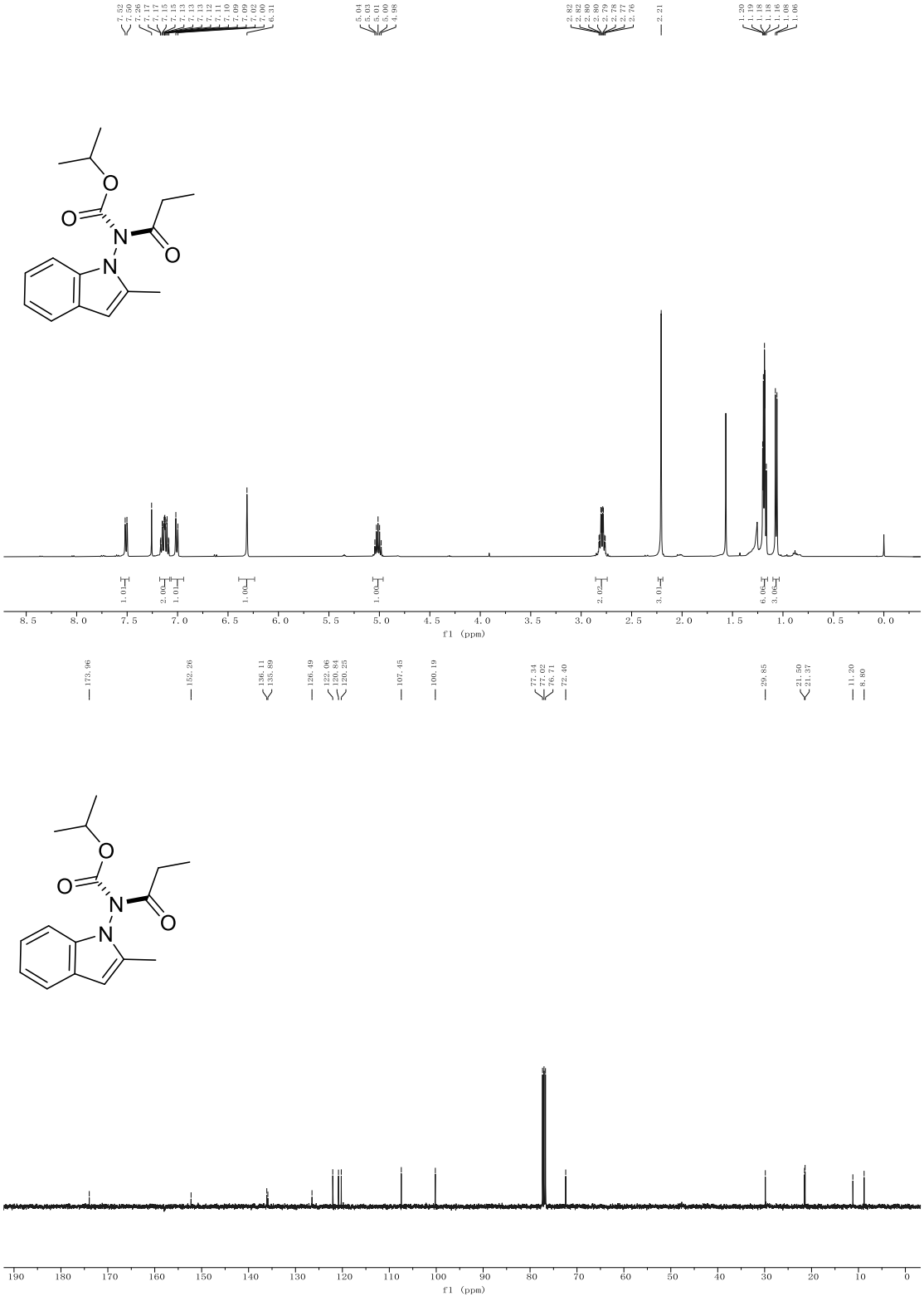
(R_a)-ethyl-1-(4-methoxy-N-propionylbenzamido)-1H-indole-2-carboxylate (3ua)



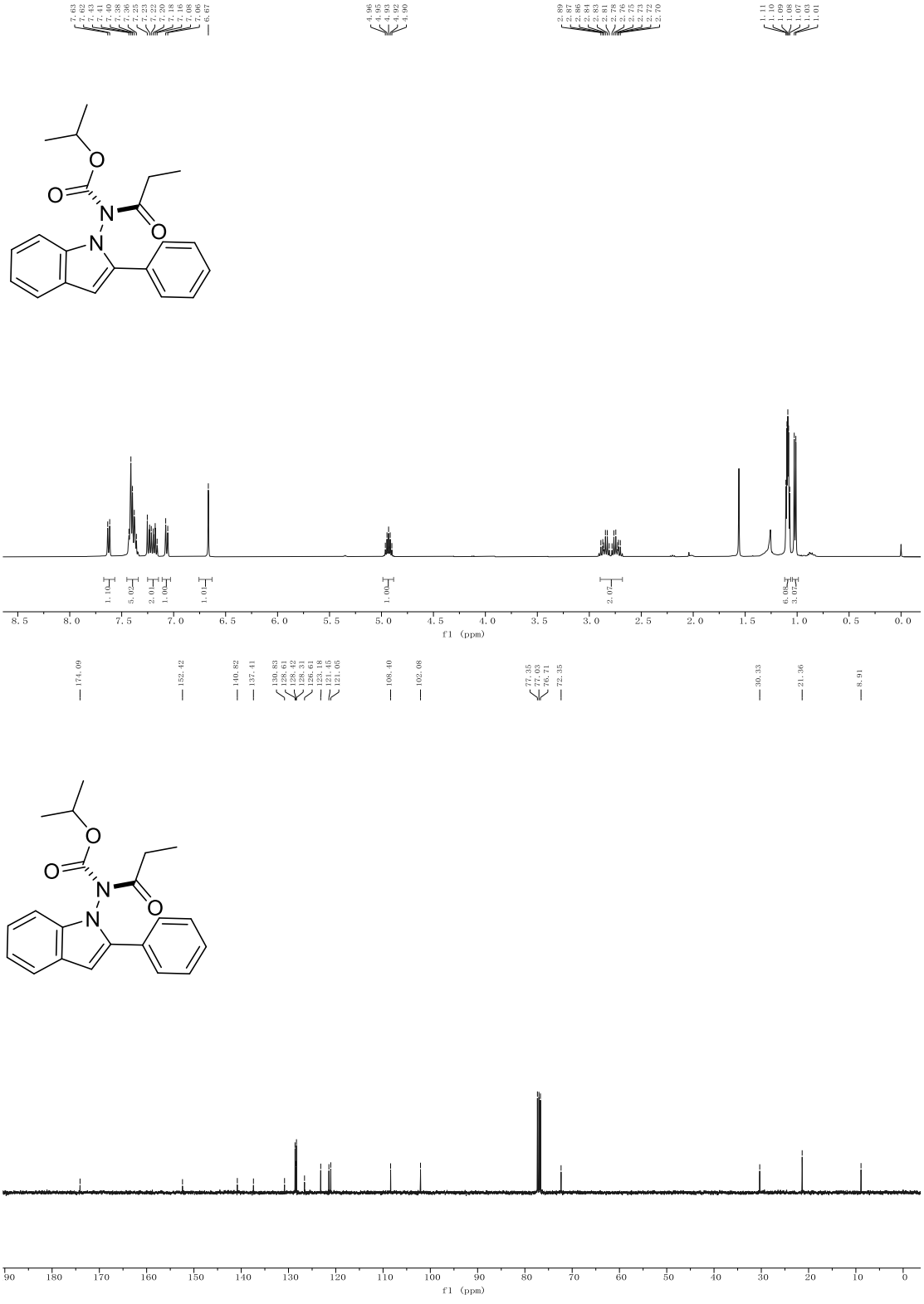
(R_a)-ethyl-1-(N-(m-tolylsulfonyl)propionamido)-1H-indole-2-carboxylate (3va)



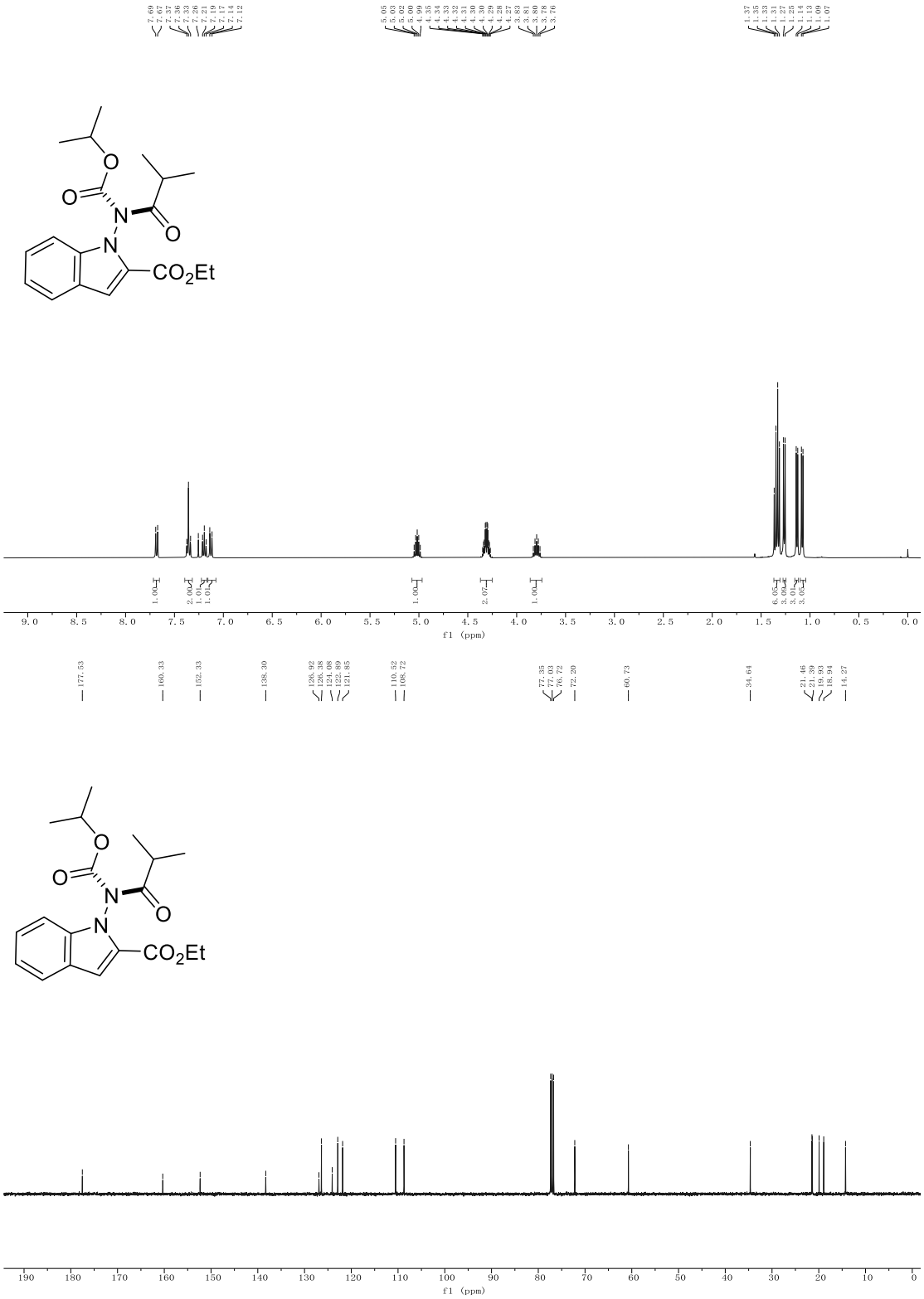
(R_a)-isopropyl(2-methyl-1H-indol-1-yl)(propionyl)carbamate (3wa)



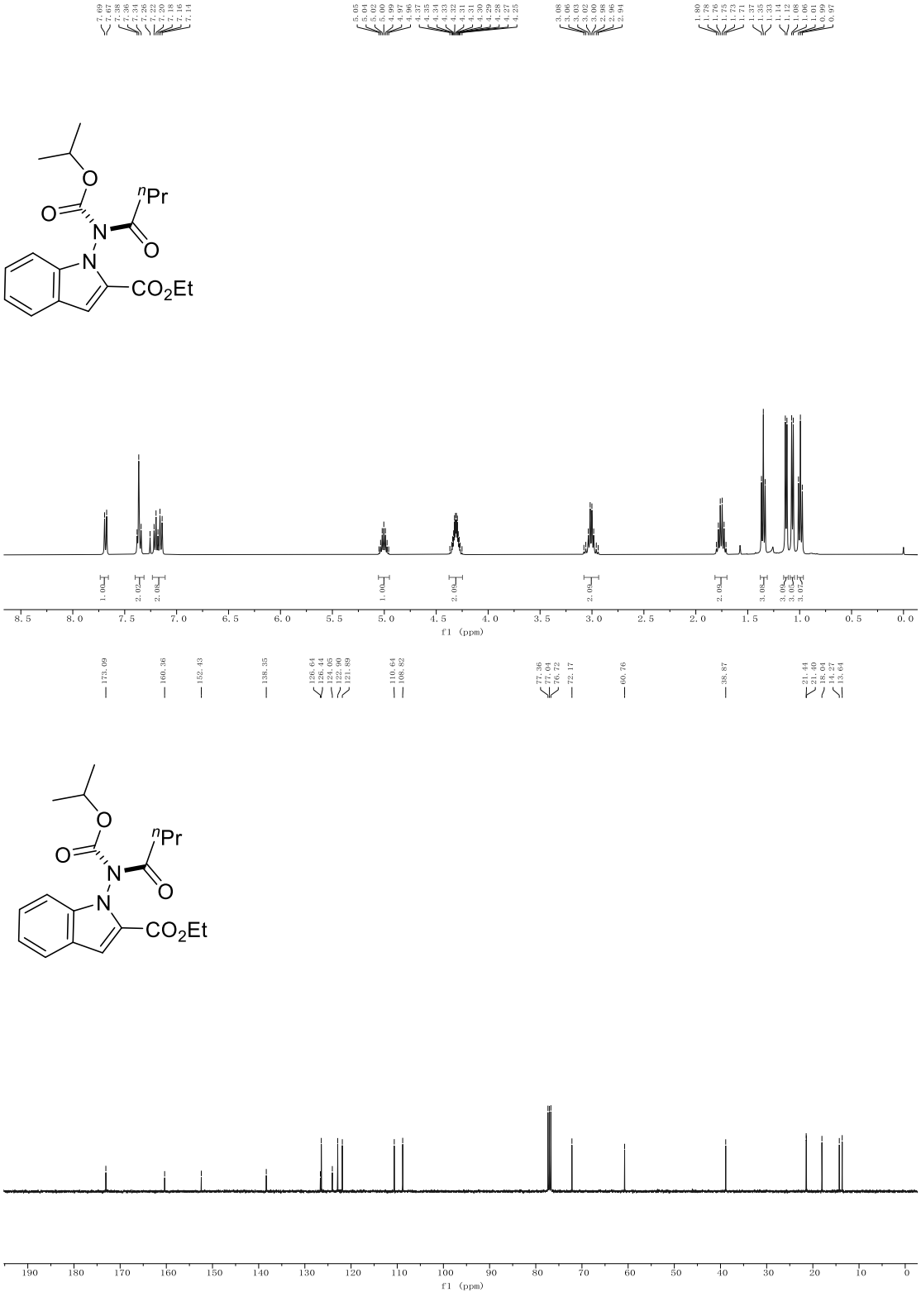
(R_a)-isopropyl(2-phenyl-1H-indol-1-yl)(propionyl)carbamate (3xa)



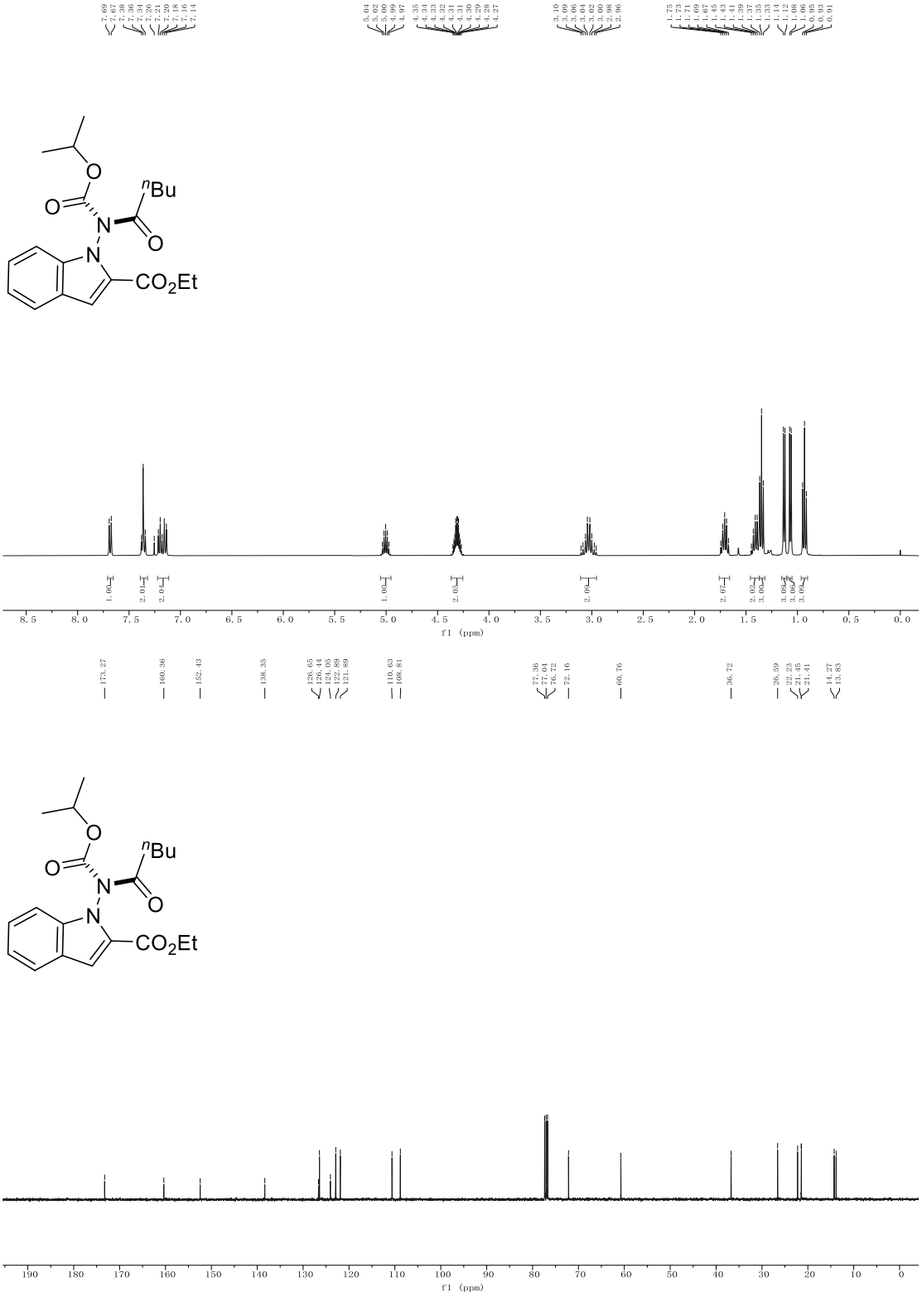
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)isobutyramido)-1H-indole-2-carboxylate (3ab)



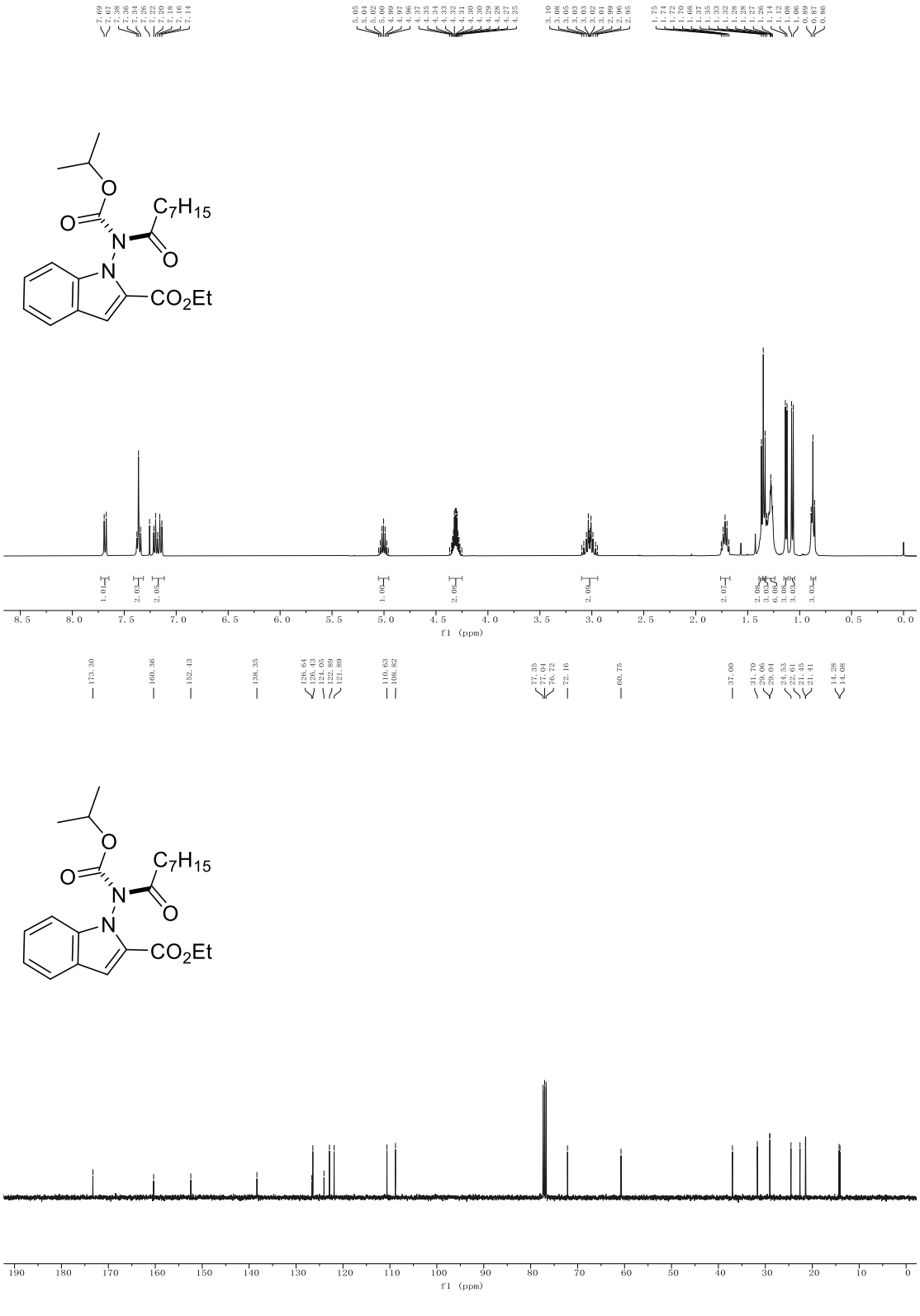
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)butyramido)-1H-indole-2-carboxylate (3bb)



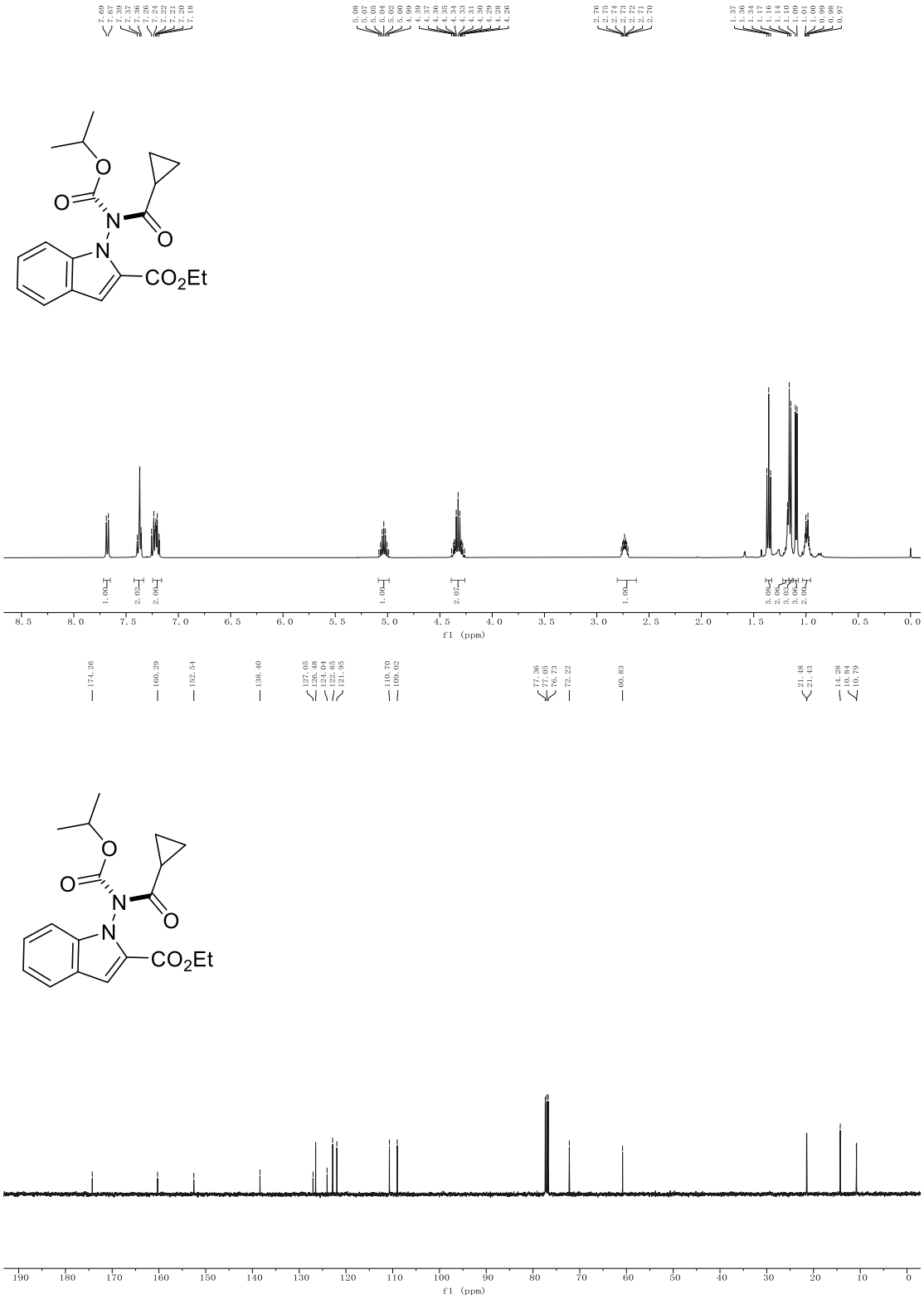
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)pentanamido)-1H-indole-2-carboxylate (3cb)



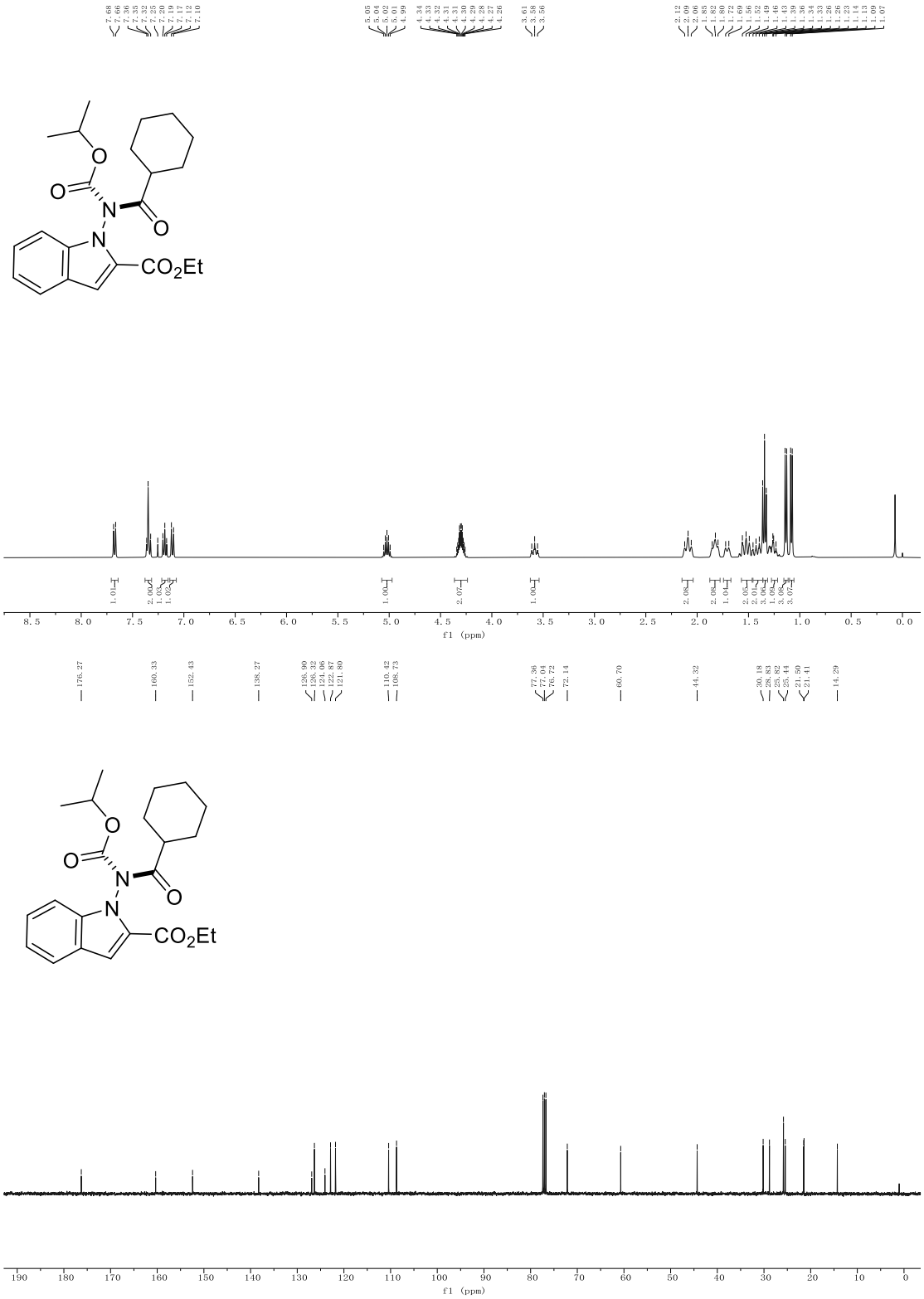
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)octanamido)-1H-indole-2-carboxylate (3db)



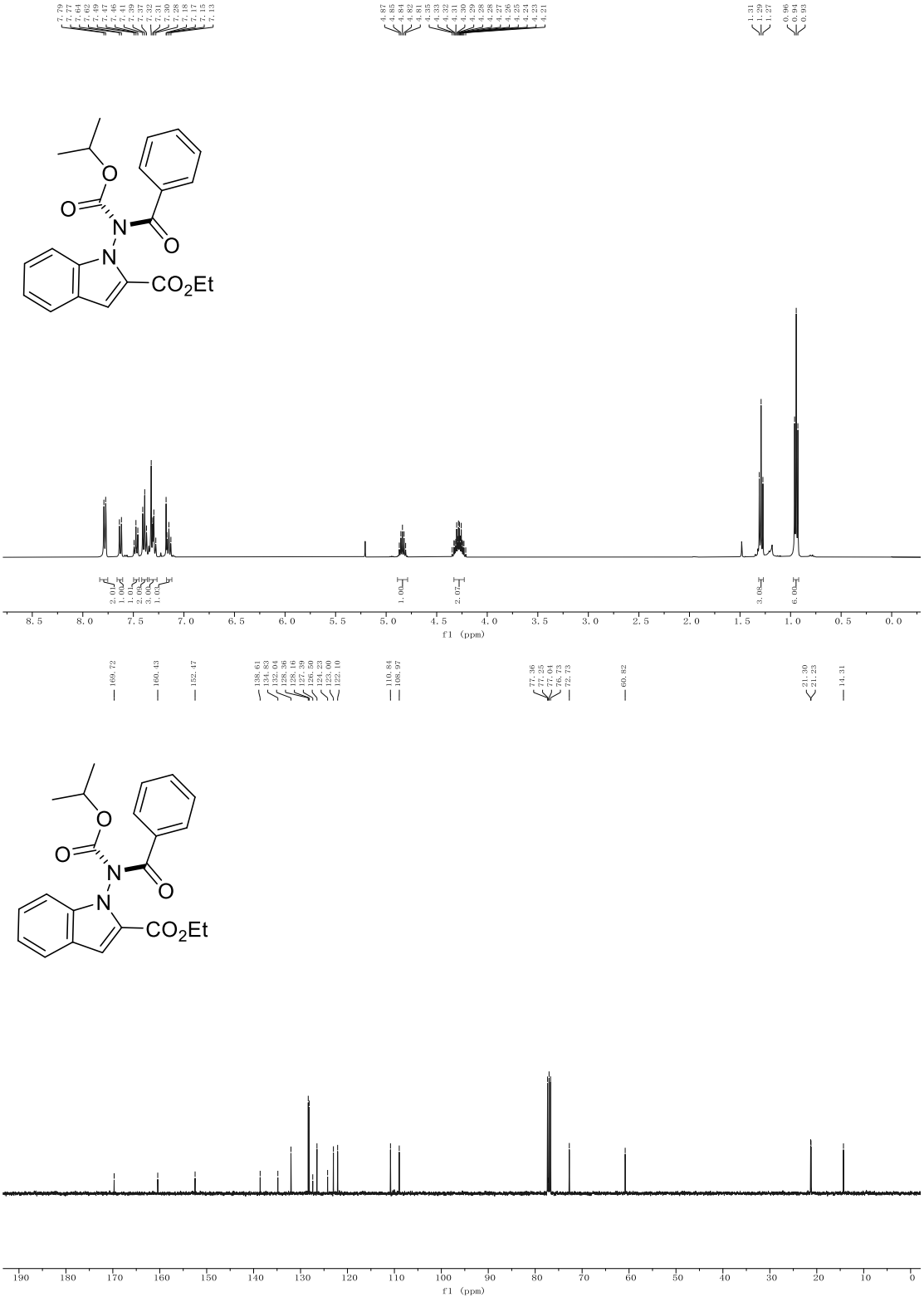
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclopropanecarboxamido)-1H-indole-2-carboxylate (3eb)



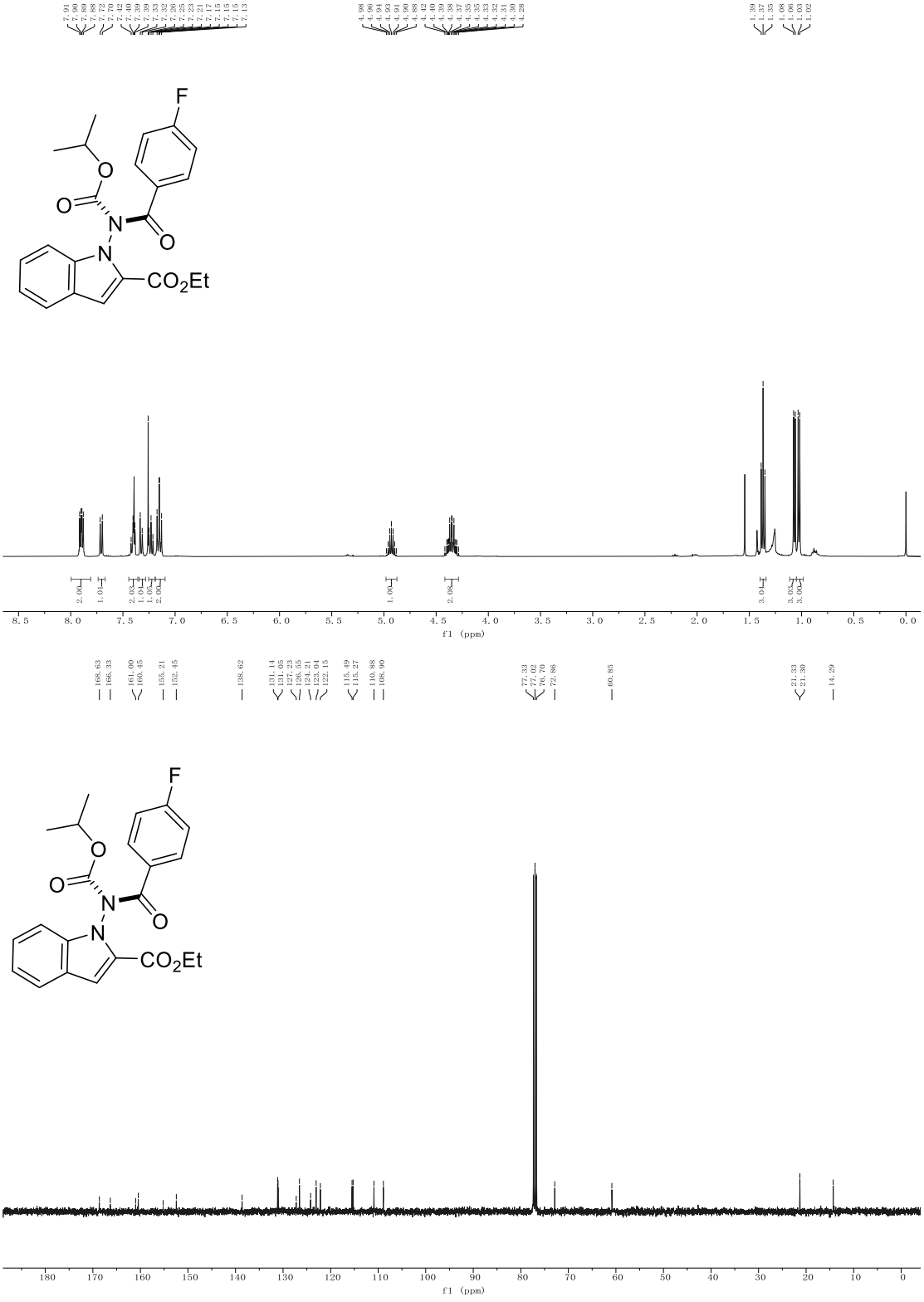
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)cyclohexanecarboxamido)-1H-indole-2-carboxylate (3fb)

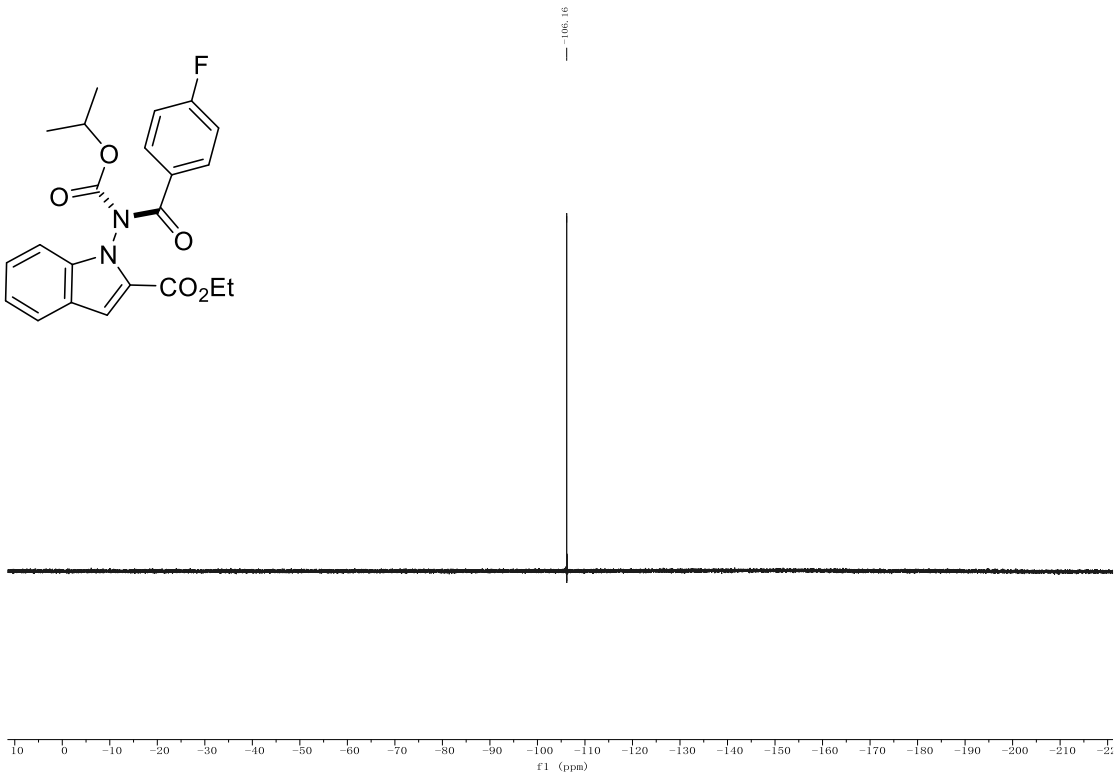


(R_a)-ethyl-1-(N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3gb)

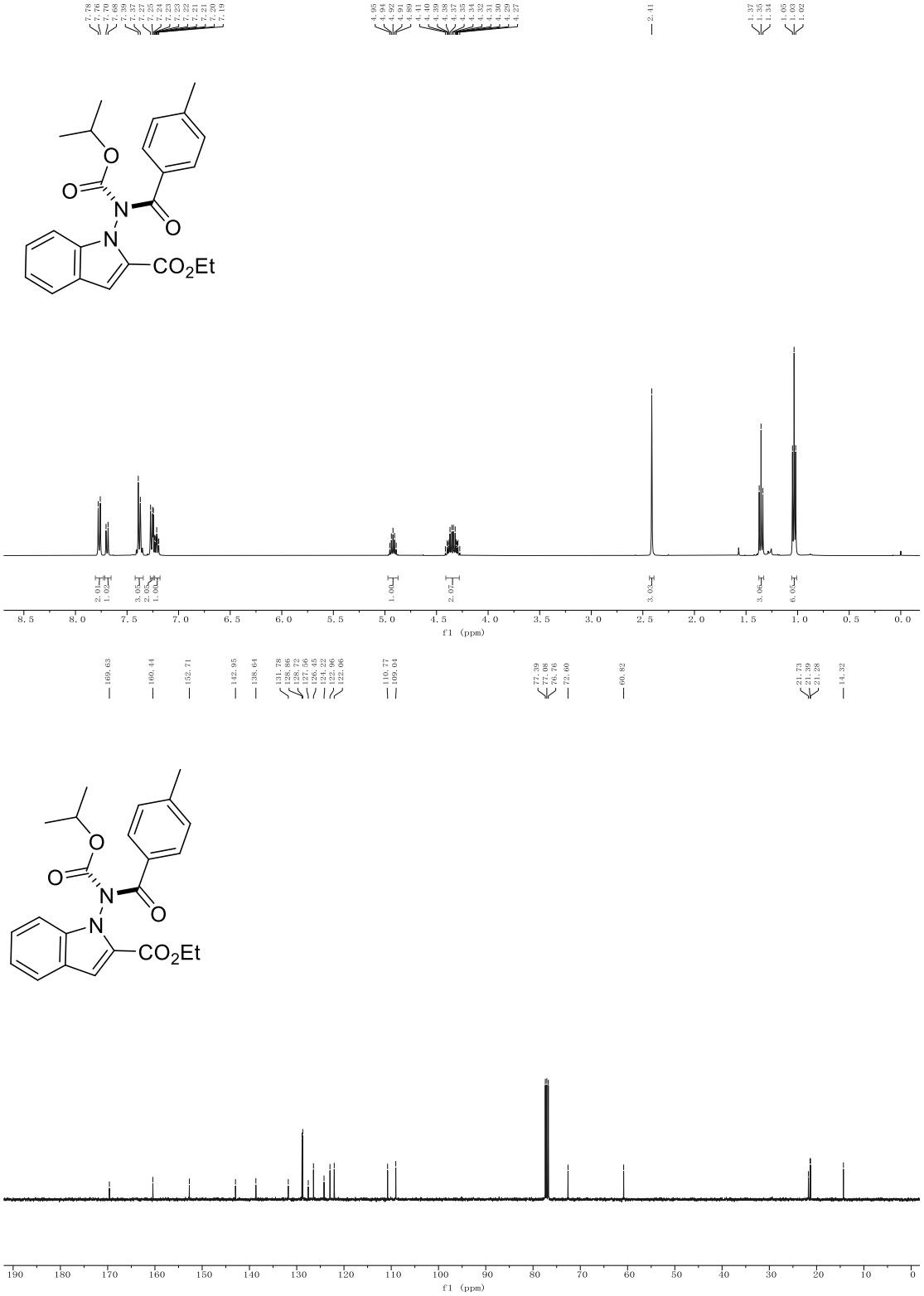


(R_a)-ethyl-1-(4-fluoro-N-(isopropoxycarbonyl)benzamido)-1H-indole-2-carboxylate (3hb)

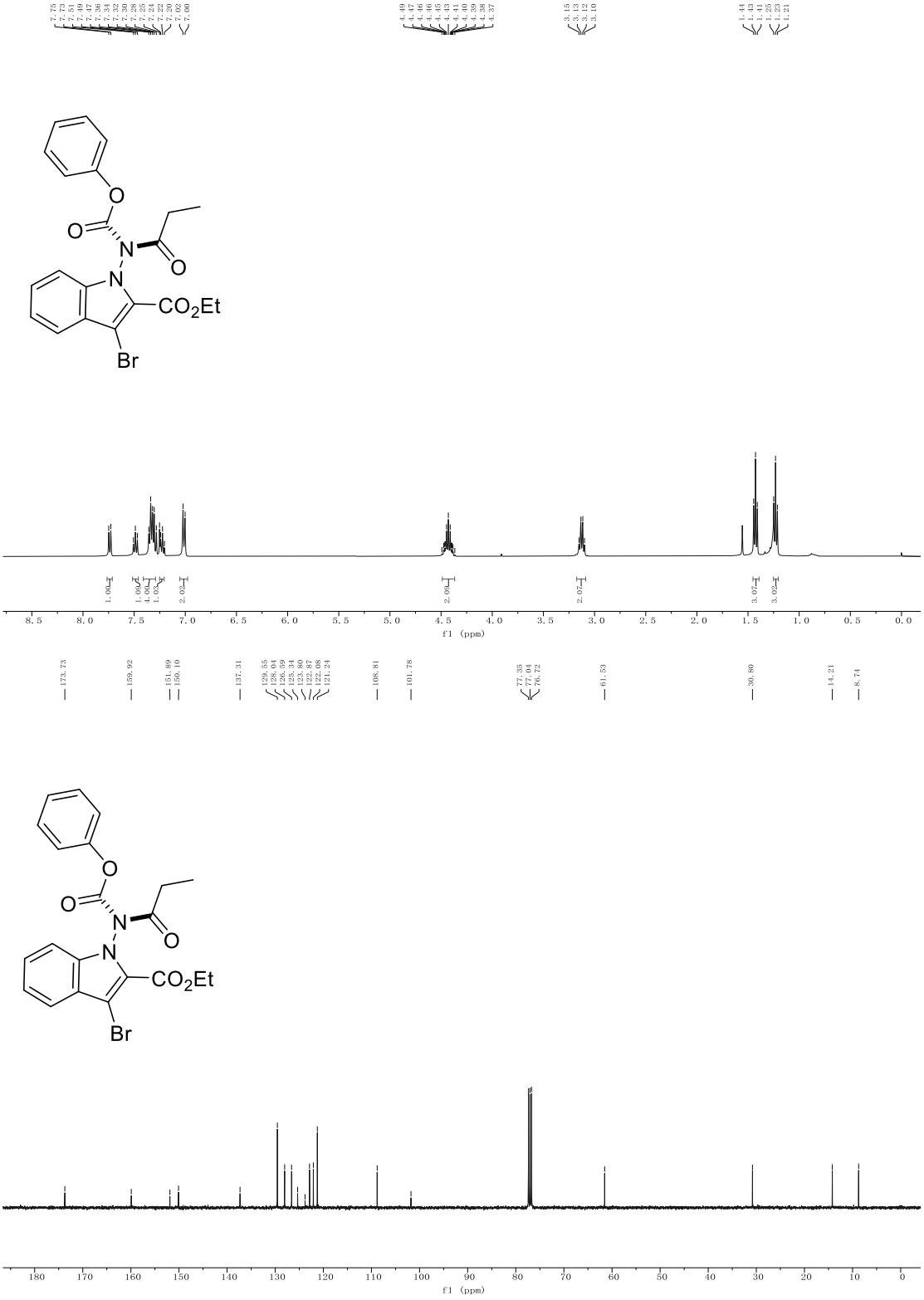



F
O
O
N
O
N
CO2Et
-106.16
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

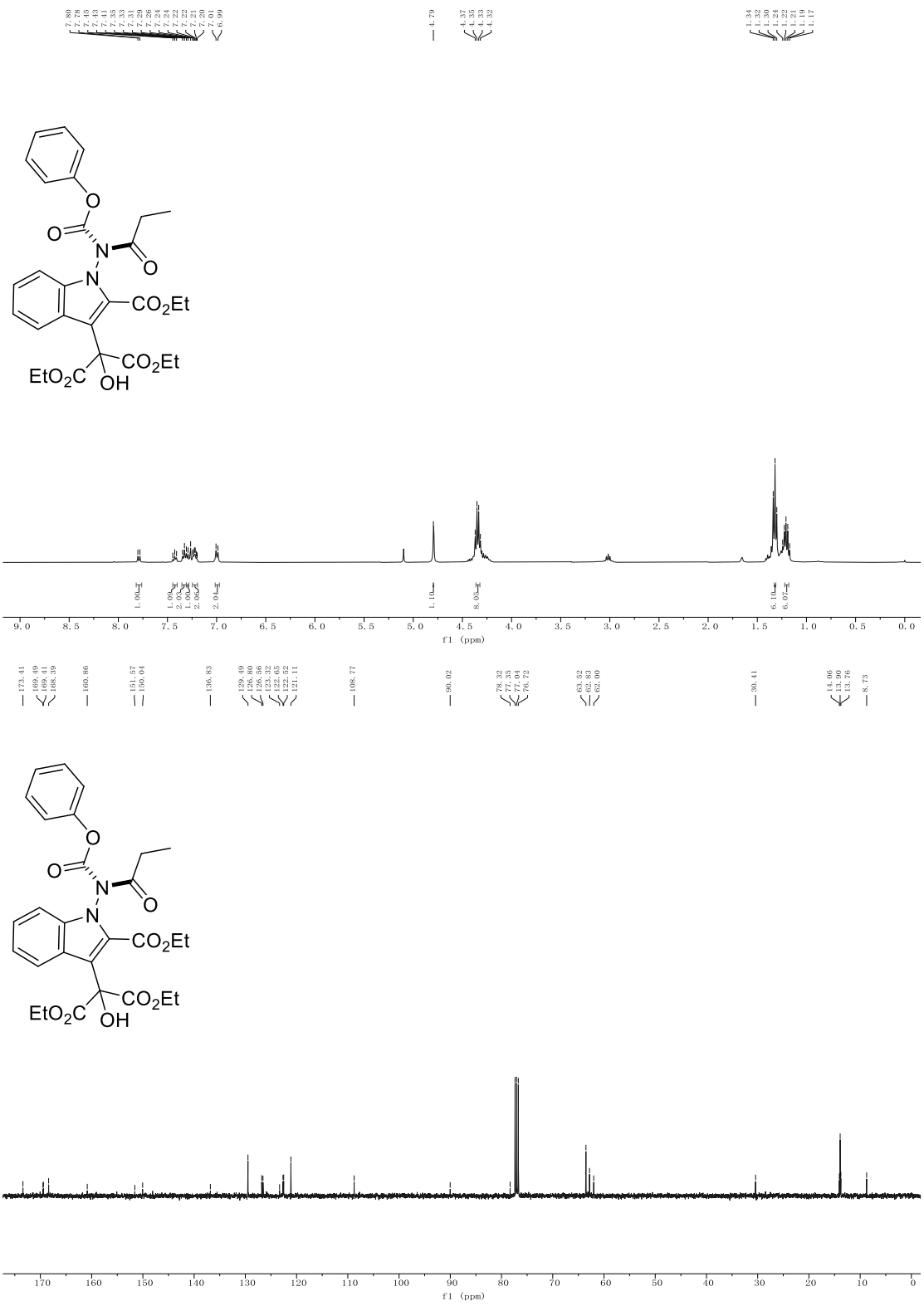
(R_a)-ethyl-1-(N-(isopropoxycarbonyl)-4-methylbenzamido)-1H-indole-2-carboxylate (3ib)



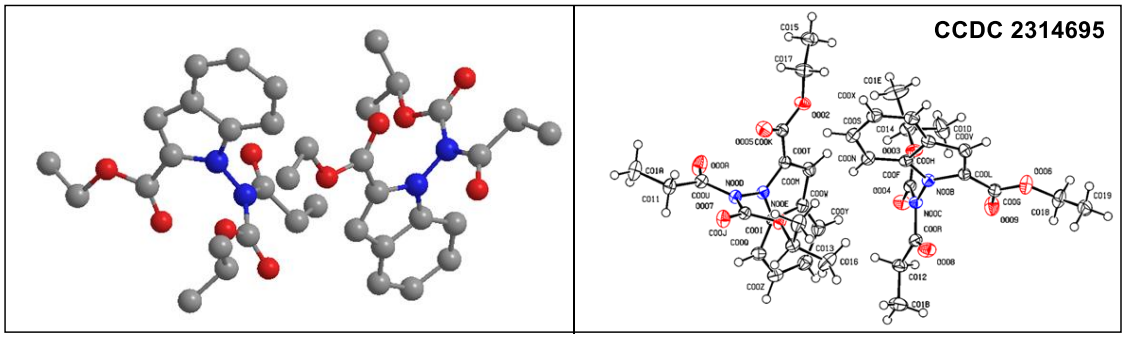
(R_a)-ethyl-3-bromo-1-(N-(phenoxycarbonyl)propionamido)-1H-indole-2-carboxylate (4)



(R_a)-diethyl-2-(2-(ethoxycarbonyl)-1-(N-(phenoxycarbonyl)propionamido)-1H-indol-3-yl)-2-hydroxymalonate (5)



11. *X*-ray Crystallography of 3aa



These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.

Crystal data and structure refinement for CCDC 2314695(**3aa**).

Identification code	P20231105A
Empirical formula	$C_{18}H_{22}N_2O_5$
Formula weight	346.37
Temperature/K	113.15
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	33.1148(2)
b/Å	11.25710(10)
c/Å	9.68660(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3610.94(5)
Z	8
ρ_{calc}g/cm^3	1.274
μ/mm^{-1}	0.775
F(000)	1472.0
Crystal size/mm^3	0.25 × 0.2 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.296 to 158.278
Index ranges	$-42 \le h \le 42$, $-14 \le k \le 13$, $-12 \le l \le 12$
Reflections collected	50987
Independent reflections	7787 [R_{int} = 0.0362, R_{sigma} = 0.0256]
Data/restraints/parameters	7787/0/459
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0304, wR_2 = 0.0778
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0784

Largest diff. peak/hole / e $Å^{-3}$	0.12/-0.19
Flack parameter	-0.05(4)

12. References

(1) (a) K. W. Chen, Z. H. Chen, S. Yang, S. F. Wu, Y. C. Zhang and F. Shi, Organocatalytic Atroposelective Synthesis of N−N Axially Chiral Indoles and Pyrroles by De Novo Ring Formation, *Angew. Chem., Int. Ed.*, 2022, **61**, e202116829. (b) W. Lin, Q. Zhao, Y. Li, M. Pan, C. Yang, G. Yang and X. Li, Asymmetric synthesis of N–N axially chiral compounds via organocatalytic atroposelective N-acylation, *Chem. Sci.*, 2022, **13**, 141-148.

(2) (a) S. Gluszok, R. Frédérick, C. Foulon, F. Klupsch, C. T. Supuran, D. Vullo, A. Scozzafava, J. Goossens, B. Masereel, P. Depreux and L. Goossens, Design, solid-phase synthesis, and biological evaluation of novel 1,5-diarylpyrrole-3-carboxamides as carbonic anhydrase IX inhibitors, *Bioorg. Med. Chem.*, 2010, **18**, 7392-7401. (b) N. Eleftheriadis, C. G. Neochoritis, N. G. J. Leus, P. E. Wouden, A. Dömling and F. J. Dekker, Rational Development of a Potent 15-Lipoxygenase-1 Inhibitor with in Vitro and ex Vivo Anti-inflammatory Properties, *J. Med. Chem.*, 2015, **58**, 7850−7862.