Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Asymmetric synthesis of polycyclic spiroindolines via Dy-catalyzed cascade reaction of 3-(2-isocyanoethyl)indoles with aziridines

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Content

(A) General information

^{1}H NMR spectra were recorded on a Bruker ASCEND^{TM} 400M (400MHz) or 600M (600MHz) in $CDCl_3$. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. **^{13}C{^{1}H} NMR** spectra were collected were collected on a Bruker ASCENDTM 400M (101MHz) or 600M (151MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). High-resolution mass spectra (**HRMS**) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Enantiomeric excess (ee) was determined by HPLC analysis using the corresponding commercially chiral column as stated in the experimental procedures at 23 °C with UV detector. Infrared spectra (IR) were recorded on Bruker Tensor Ⅱ spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (v, cm^{-1}). Optical rotations were measured with a Perkin-Elmer model 241 polarimeter and reported as follows: $[\alpha]_{\lambda}^{T}$ (c: g/100 mL, in DCM, λ). Commercially available reagents were used without further purification. Molecular sieves were activated at 500 °C for 5 h, then cooled and stored under N_2 atmosphere. All the imines were prepared according to literature.[1] Chloroform was dried with $CaCl_2$, and distilled according to *Purification of Laboratory Chemicals* (Fifth Edition). Chromatography: Silica gel (HG/T2354-2010) made in Qingdao Haiyang Chemical Co., Ltd.

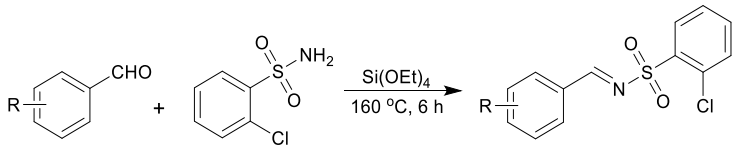
(B) General procedures for the preparation of chiral *N,N'*-dioxide

The chiral *N,N'*-dioxide ligands were prepared by the similar procedure in the literatures.[2]

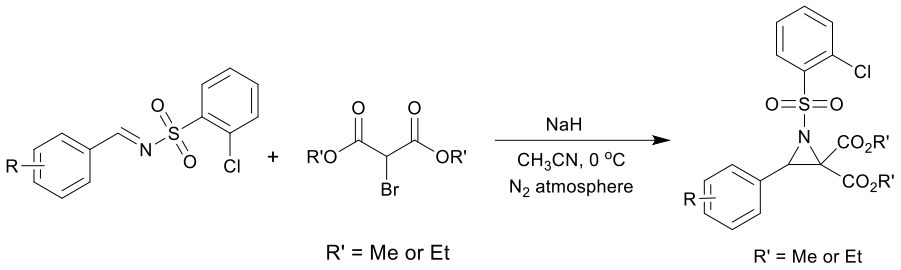
(C) General procedures for the preparation of substrates

1. Preparation of aziridines

All the aziridines were prepared according to the literature.[3]



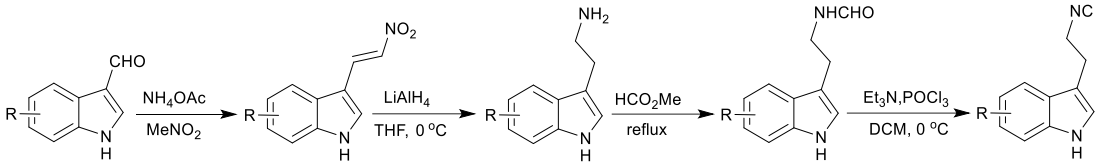
2-Chlorobezenesulfonamide (10 mmol) and tetraethyl orthosilicate (1.1 equiv, 11 mmol) were combined with the respective aldehyde (10 mmol) in a 50 mL round-bottomed flask equipped with a magnetic stirrer under an inert nitrogen atmosphere and a short still head (Approx. 3–4 cm length), connected to a receiving flask. The reaction mixture was heated at 160 °C, and ethanol, upon formation, was collected in the receiving flask. After cooling, the reaction mixture was diluted with ether, suction filtered and the precipitate washed with cold Et_2O (3×15 mL). The resulting powder was recrystallized to afford imines in the desired purity.



A solution of imine (5 mmol, 1.0 equiv), diethyl bromomalonate or dimethyl bromomalonate (5.25 mmol, 1.05 equiv) in 25 mL of dry CH_3CN was cooled to 0 °C, and treated with NaH (60% dispersion in mineral oil, 1.1 equiv). The resultant mixture was warmed up and stirred at room temperature. After 10-20 mins when the reaction completed (determined by TLC analysis), the reaction mixture was then passed over a small plug of silica gel eluted with CH_2Cl_2, after evaporation under reduced pressure, the curde product can be purified by flash chromatography on 12cm-long silica gel (eluent, ethyl acetate in petroleum ether) to afford the desired product.

2. Preparation of 2-isocyanoethylindole

The compounds were synthesized by the procedure in the literature.[4]



To a 100 mL schlenk tube were added aldehyde (1.0 equiv), ammonium acetate (3.0 equiv) and nitromethane (20 mL/g of aldehyde), then the reaction mixture was refluxed for 3 hours. The solvent was removed in vacuo and the residue washed with water, filtered and concentrated in vacuo to furnish the desired nitro olefin. No further purification was required and the crude nitroolefin was used directly for further transformation.

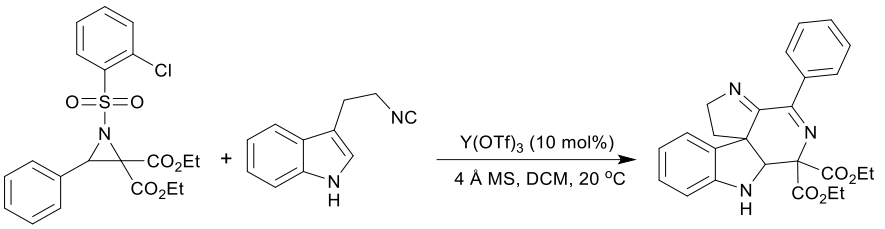
Under an inert nitrogen atmosphere, a tetrahydrofuran solution (10 mL/mmol of nitroolefin) of nitroolefin (1 equivalent) was added to a stirred slurry of lithium aluminium hydride powder (6 equiv) in tetrahydrofuran (equal volume) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 36 hours. The reaction was quenched by dropwise addition of water until effervescence ceased. The mixture was then diluted with diethyl ether before addition of a saturated aqueous solution of Rochelle's salt and the subsequent biphasic mixture was stirred for 24 hours. The layers were separated and the organic layer was extracted with 1 M aqueous hydrochloric acid. The aqueous phase was basified with 3 M aqueous potassium hydroxide, extracted with diethyl ether, dried over sodium sulfate, filtered and concentrated in vacuo to furnish the desired tryptamine that required no further purification.

A mixture of the crude tryptamine in HCO_2Me (6.0 mL per 10.0 mol) was refluxed for 6 hours. The solvent was removed in vacuum. The corresponding N-(2-(1H-indol-3-yl)ethyl)-formamide was obtained with further purification.

A solution of *N*-(2-(1H-indol-3-yl)ethyl)formamide (1.0 equiv) and Et_3N (5.0 equiv) in anhydrous dichloromethane was treated with $POCl_3$ (1.5 equiv) at −78 °C . After being stirred at −78 °C for 3 hours, the mixture was poured into ice-cold water carefully, extracted with CH_2Cl_2 for 3 times, and the combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, concentrated and purified by a column chromatography to give the desired isocyanid.

(D) Experimental procedures

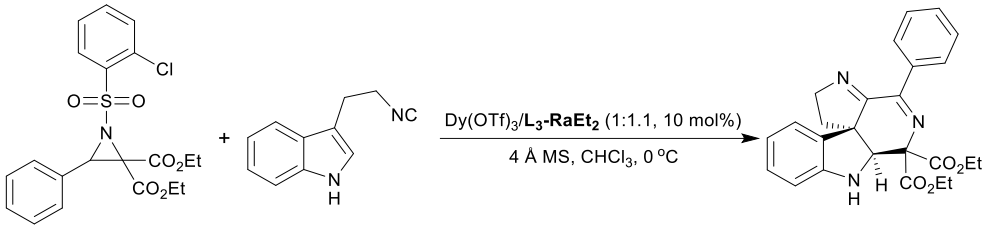
1. Typical procedure for the racemates



A1 **B1** **C1**

$Y(OTf)_3$ (10 mol%, 5.4 mg) and 4 Å MS (80 mg) were flushed with argon and dissolved in DCM (1.0 mL) at 20 °C, then aziridine **A1** (0.13 mmol, 56.9 mg) and 2-isocyanoethylindole **B1** (0.1 mmol, 17.0 mg) were slowly added. When the reaction was complete as monitored by TLC, the reaction mixture was subjected to flash column chromatography on silica gel and eluted with petroleum ether/DCM/ethyl acetate (4:1:1, v/v/v) to afford the desired product **C1**.

2. Typical procedure for the catalytic asymmetric reaction

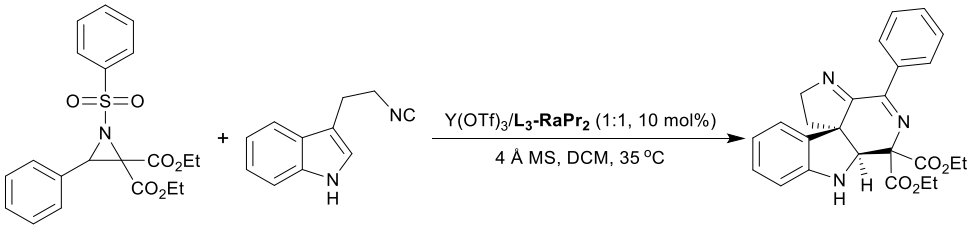


A1 **B1** **C1**

$Dy(OTf)_3$ (0.01 mmol, 6.1 mg), *N,N'*-dioxide ligand $\mathbf{L_3\text{-}RaEt_2}$ (0.011 mmol, 7.2 mg) and 4 Å MS (80 mg) were stirred in 0.5 mL $CHCl_3$ at 35 °C for 0.5 h under nitrogen atmosphere. Then, the resulting solution was stirred at 0 °C for 10 minutes. Subsequently, the solution of aziridine **A1** (0.11 mmol) and 2-isocyanoethylindole **B1** in $CHCl_3$ (0.7 mL) were added. The reaction mixture was stirred at 0 °C for 48 h and monitored by TLC. The resulting mixture was directly purified by flash chromatography on silica gel eluted with petroleum ether/DCM/ethyl acetate (4:1:1, v/v/v) to afford the desired product **C1**.

(E) Optimization of the reaction conditions

Table S1. Screening of solvents.[a]



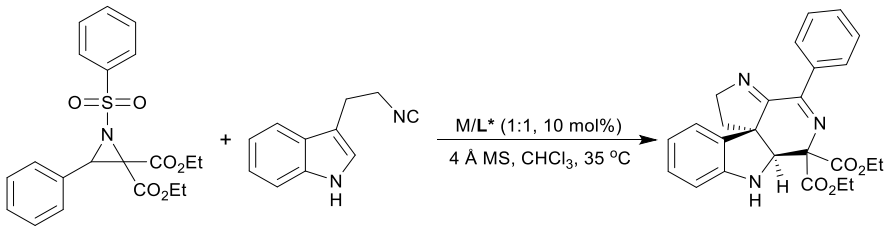
A0 **B1** **C1**

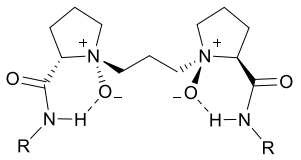
entry	solvent	yield[b] (%)	ee[c] (%)
1	DCM	41	0
2	THF	<5	0

3	Et_2O	trace	0
4	toluene	10	0
5	$CHCl_3$	59	0
6	DCE	71	0
7	CH_3CN	11	0
8	EtOAc	34	0
9[d]	DCM	39	0
10[e]	DCM	37	0
11[d]	EtOAc	29	0
12[e]	EtOAc	21	0

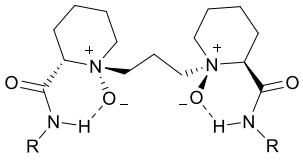
[a] All reactions were performed with **A0** (0.10 mmol), **B1** (0.10 mmol), $Y(OTf)_3$/**L_3-RaPr$_2$** (1:1, 10 mol %), 4 Å MS (80 mg) in solvent (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase. [d] the reaction was performed at 20 °C. [e] the reaction was performed at 0 °C.

Table S2. Screening of metal salts and chiral *N,N'*-dioxide ligands.[a]

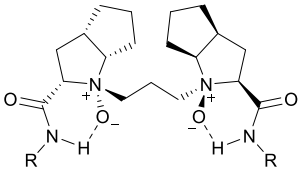




L_3-PrMe$_2$: R = 2,6-$Me_2C_6H_3$
L_3-PrEt$_2$: R = 2,6-$Et_2C_6H_3$
L_3-PrEt$_2$Me: R = 2,6-Et_2-4-MeC_6H_2



L_3-PiMe$_2$: R = 2,6-$Me_2C_6H_3$
L_3-PiEt$_2$: R = 2,6-$Et_2C_6H_3$
L_3-PiEt$_2$Me: R = 2,6-Et_2-4MeC_6H_3



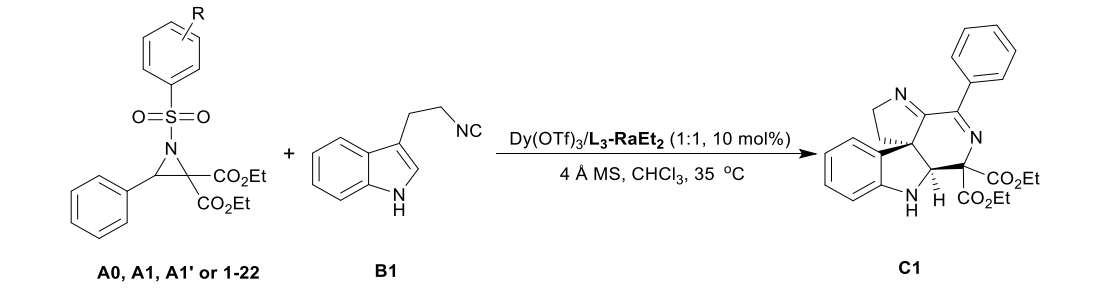
L_3-RaMe$_2$: R = 2,6-$Me_2C_6H_3$
L_3-RaEt$_2$: R = 2,6-$Et_2C_6H_3$
L_3-RaEt$_2$Me: R = 2,6-Et_2-4-MeC_6H_2
L_3-RaEt$_2$Bu: R = 2,6-*i*Pr_2-4-*t*BuC_6H_2
L_3-RaPr$_2$: R = 2,6-*i*PrC_6H_3
L3-RaEt$_2$Ad: R = 2,6-Et_2-4-(1-adamantyl)C_6H_2

entry	metal salt	**L***	yield[b] (%)	ee[c] (%)
1	$Sc(OTf)_3$	**L_3-RaPr$_2$**	trace	0
2	$Y(OTf)_3$	**L_3-RaPr$_2$**	80	0
3	$La(OTf)_3$	**L_3-RaPr$_2$**	24	0
4	$Ce(OTf)_3$	**L_3-RaPr$_2$**	33	0
5	$Pr(OTf)_3$	**L_3-RaPr$_2$**	38	0
6	$Nd(OTf)_3$	**L_3-RaPr$_2$**	47	0
7	$Sm(OTf)_3$	**L_3-RaPr$_2$**	51	0
8	$Eu(OTf)_3$	**L_3-RaPr$_2$**	59	0

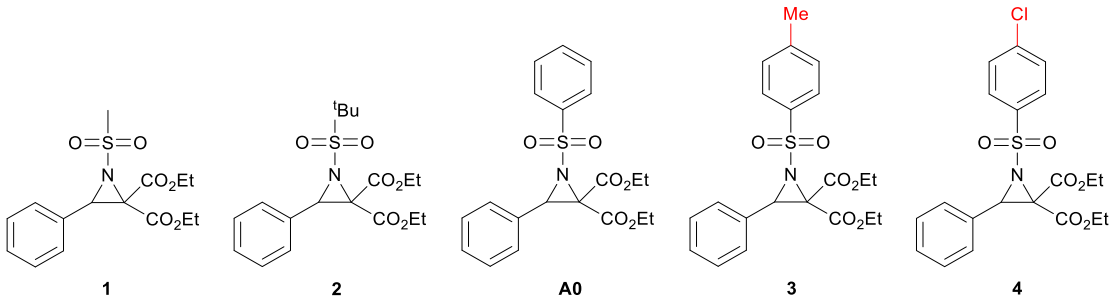
9	$Gd(OTf)_3$	**L_3-RaPr$_2$**	66	1
10	$Tb(OTf)_3$	**L_3-RaPr$_2$**	79	3
11	$Dy(OTf)_3$	**L_3-RaPr$_2$**	81	5
12	$Ho(OTf)_3$	**L_3-RaPr$_2$**	87	4
13	$Er(OTf)_3$	**L_3-RaPr$_2$**	74	2
14	$Tm(OTf)_3$	**L_3-RaPr$_2$**	70	0
15	$Yb(OTf)_3$	**L_3-RaPr$_2$**	61	0
16	$Lu(OTf)_3$	**L_3-RaPr$_2$**	60	0
17	$Dy(OT)_3$	**L_3-RaMe$_2$**	73	3
18	$Dy(OT)_3$	**L_3-RaEt$_2$**	69	6
19	$Dy(OT)_3$	**L_3-RaEt$_2$Me**	71	5
20	$Dy(OT)_3$	**L_3-RaEt$_2$Bu**	76	0
21	$Dy(OT)_3$	**L_3-RaEt$_2$Ad**	65	0
22[d]	$Dy(OT)_3$	**L_3-RaEt$_2$**	49	7
23[e]	$Dy(OT)_3$	**L_3-RaEt$_2$**	37	9

[a] All reactions were performed with **A0** (0.10 mmol), **B1** (0.10 mmol), M/**L*** (1:1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase. [d] the reaction was performed at 20 °C. [e] the reaction was performed at 0 °C.

Table S3. Screening of aziridine.[a]

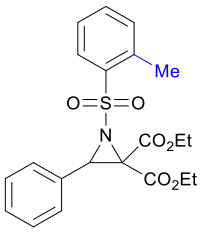


A0, A1, A1' or 1-22 **B1** **C1**



1 **2** **A0** **3** **4**

5 **A1'** **6** **A1** **7**



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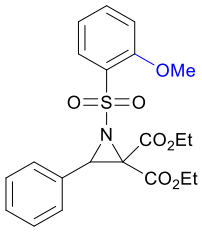

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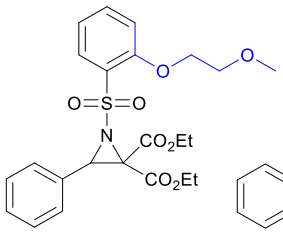

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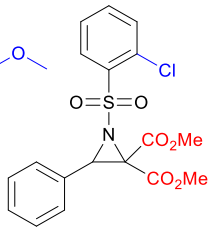

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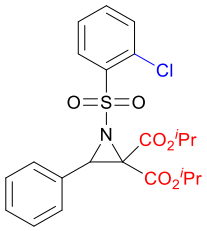

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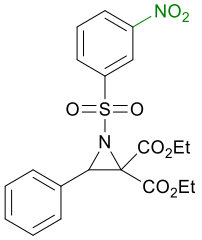

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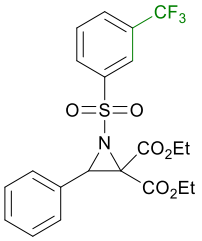

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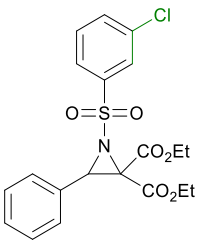

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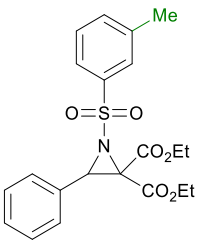

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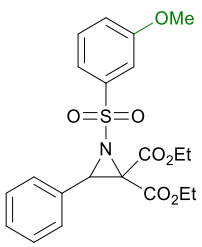

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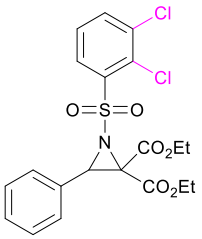

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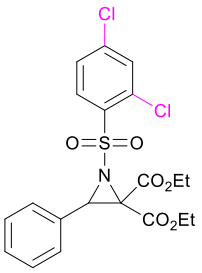

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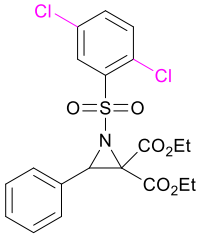

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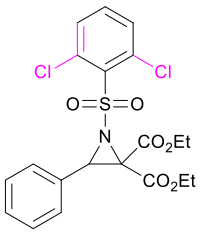

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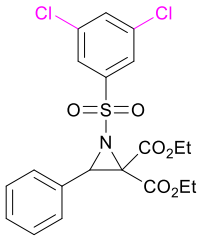

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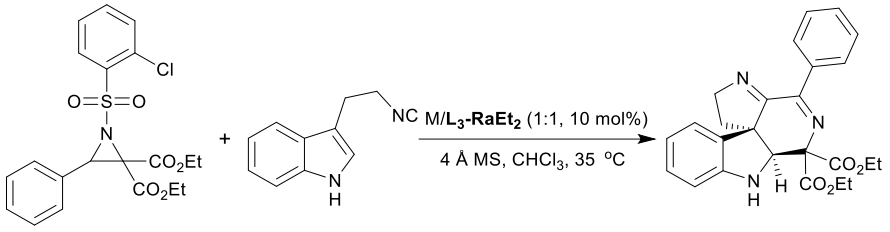
entry	aziridine	yield[b] (%)	ee[c] (%)
1	**1**	27	0
2	**2**	33	0
3	**A0**	69	6
4	**3**	73	3
5	**4**	68	4
6	**5**	70	5
7	**A1'**	41	82
8	**6**	39	43
9	**A1**	62	81
10	**7**	52	19
11	**8**	73	11
12	**9**	56	37
13	**10**	trace	-
14	**11**	43	78
15	**12**	57	45
16	**13**	71	47
17	**14**	49	11
18	**15**	77	41
19	**16**	71	7

20	**17**	41	17
21	**18**	68	51
22	**19**	64	62
23	**20**	39	47
24	**21**	17	10
25	**22**	61	18

[a] All reactions were performed with **aziridine** (0.10 mmol), **B1** (0.10 mmol), $Dy(OTf)_3$/**L_3-RaEt$_2$** (1:1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

Table S4. Screening of the metal salts.[a]

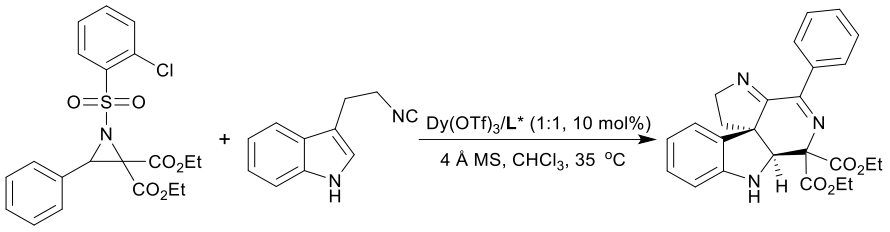


A1 **B1** **C1**

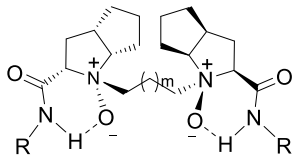
entry	metal salt	Ionic radii (Å)	yield[b] (%)	ee[c] (%)
1	$Sc(OTf)_3$	0.745	-	-
2	$Y(OTf)_3$	1.019	53	37
3	$La(OTf)_3$	1.160	47	21
4	$Ce(OTf)_3$	1.143	51	23
5	$Pr(OTf)_3$	1.126	52	27
6	$Nd(OTf)_3$	1.109	61	44
7	$Sm(OTf)_3$	1.079	69	51
8	$Eu(OTf)_3$	1.066	78	57
9	$Gd(OTf)_3$	1.053	72	60
10	$Tb(OTf)_3$	1.040	67	71
11	$Dy(OTf)_3$	1.027	62	81
12	$Ho(OTf)_3$	1.015	57	68
13	$Er(OTf)_3$	1.004	47	65
14	$Tm(OTf)_3$	0.994	49	60
15	$Yb(OTf)_3$	0.985	41	37
16	$Lu(OTf)_3$	0.977	40	17

[a] All reactions were performed with **A1** (0.10 mmol), **B1** (0.10 mmol), $M(OTf)_3$/**L_3-RaEt$_2$** (1:1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

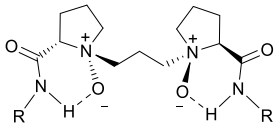
Table S5. Screening of chiral *N*,*N*'-dioxide ligands.[a]



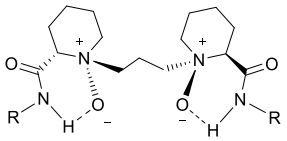
A1 **B1** **C1**



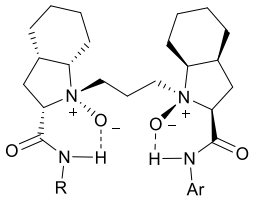
L_2-RaPr$_2$: **m = 3**, R = 2,6-*i*-Pr$_2$C$_6$H$_3$
L_2-RaEt$_2$: **m = 2**, R = 2,6-Et$_2$C$_6$H$_3$
L_3-RaEt$_2$: **m = 3**, R = 2,6-Et$_2$C$_6$H$_3$
L_4-RaEt$_2$: **m = 4**, R = 2,6-Et$_2$C$_6$H$_3$
L_5-RaEt$_2$: **m = 5**, R = 2,6-Et$_2$C$_6$H$_3$
L_3-RaEt$_2$Me: **m = 3**, R = 2,6-Et$_2$-4-MeC$_6$H$_2$
L_3-RaEt$_2$Br: **m = 3**, R = 2,6-Et$_2$-4-BrC$_6$H$_2$



L_3-PrEt$_2$: R = 2,6-*i*-Et$_2$C$_6$H$_3$
L_3-PrPr$_2$: R = 2,6-*i*-Pr$_2$C$_6$H$_3$



L_3-PiPr$_2$: R = 2,6-*i*-Pr$_2$C$_6$H$_3$
L_3-PiEt$_2$: R = 2,6-*i*-Pr$_2$C$_6$H$_3$

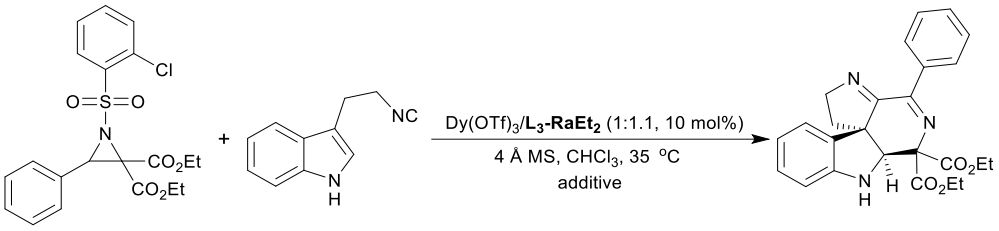


L_3-PeEt$_2$ Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$
L_3-PePr$_2$ Ar = 2,6-*i*-Et$_2$C$_6$H$_3$

entry	L*	yield[b] (%)	ee[c] (%)
1	**L_3-RaMe$_2$**	66	59
2	**L_2-RaEt$_2$**	42	34
3	**L_4-RaEt$_2$**	71	15
4	**L_5-RaEt$_2$**	78	3
5	**L_3-RaEt$_2$**	62	81
6	**L_3-RaEt$_2$Me**	64	77
7	**L_3-RaEt$_2$Bu**	56	28
8	**L_3-RaEt$_2$Ad**	17	3
9	**L_3-RaPr$_2$**	54	67
10	**L_3-PiEt$_2$**	33	11
11	**L_3-PiPr$_2$**	37	17
12	**L_3-PrEt$_2$**	24	0
13	**L_3-PrPr$_2$**	19	3
14	**L_3-PeEt$_2$**	47	0
15	**L_3-PePr$_2$**	33	0

[a] All reactions were performed with **A1** (0.10 mmol), **B1** (0.10 mmol), Dy(OTf)$_3$/**L*** (1:1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

Table S6. Screening of additives.[a]

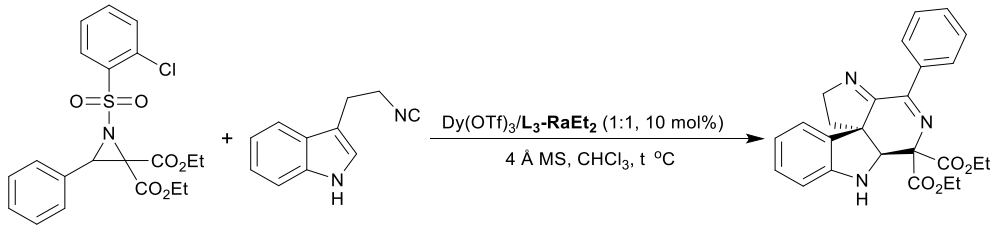


A1 **B1** **C1**

entry	additive	yield[b] (%)	ee[c] (%)
1	H_2O (10 μL)	27	80
2	EtOAc (10 μL)	88	20
3	1,4-dioxane (10 μL)	51	71
4	Toluene (10 μL)	59	79
5	Et_2O (10 μL)	47	61
6	THF (10 μL)	44	73
7	PhCOOH (10 mol%)	37	35
8	$LiNTf_2$ (10 mol%)	68	78
9	$NaBAr_4^F$ (10 mol%)	50	67
10	$NaBAr_4^F$ (2 mol%)	63	80

[a] All reactions were performed with **A1** (0.10 mmol), **B1** (0.10 mmol), Dy(OTf)$_3$/**L$_3$-RaEt$_2$** (1:1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 35 °C under N_2 for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

Table S7. Screening of temperature.[a]

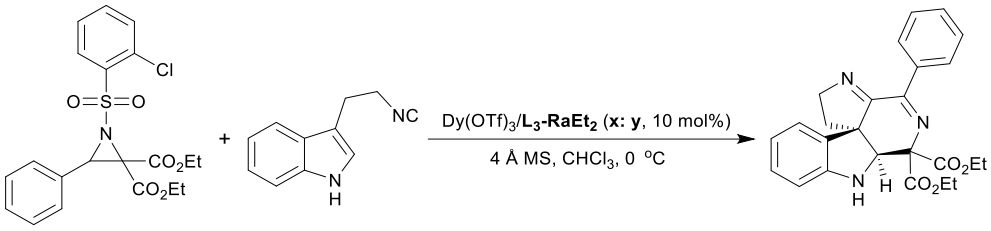


A1 **B1** **C1**

entry	t (°C)	yield[b] (%)	ee[c] (%)
1	–20	37	89
2	–10	59	89
3	0	74	91
4	10	74	89
5	20	67	84

[a] All reactions were performed with **A1** (0.10 mmol), **B1** (0.10 mmol), Dy(OTf)$_3$/**L$_3$-RaEt$_2$** (1:1, 10 mol %), 4 Å MS (80 mg) in solvent (1.2 mL) at t °C under N_2 for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

Table S8. Screening of the ratio of the metal salt and chiral *N*,*N*'-dioxide ligand.[a]

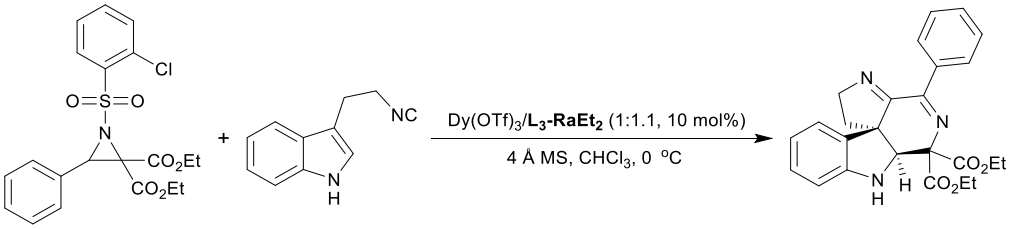


A1 **B1** **C1**

entry	**x: y**	yield[b] (%)	ee[c] (%)
1	1.2:1	67	81
2	1.1:1	68	87
3	1:1	74	91
4	1:1.1	74	93
5	1:1.2	71	91

[a] All reactions were performed with **A1** (0.10 mmol), **B1** (0.10 mmol), Dy(OTf)$_3$/**L$_3$-RaEt$_2$** (**x: y**, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 0 °C under N_2 for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

Table S9. Screening of the ratio of the substrates.[a]

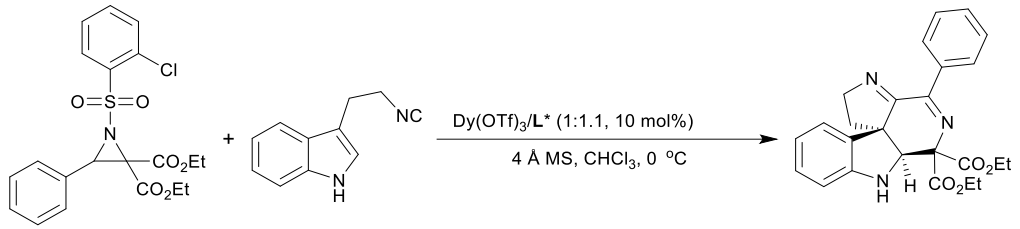


A1 **B1** **C1**

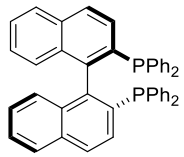
entry	**A1: B1**	yield[b] (%)	ee[c] (%)
1	1.3:1	89	81
2	1.2:1	85	87
3	1.1:1	78	95
4	1:1	74	93
5	1:1.1	71	91
6	1:1.2	67	88
7	1:1.3	61	80
8	1:1.5	60	78

[a] All reactions were performed with **A1**, **B1** at 0.1 mmol scale, Dy(OTf)$_3$/**L$_3$-RaEt$_2$** (1:1.1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 0 °C under N_2 for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

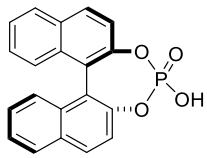
Table S10. Screening of other ligands.[a]



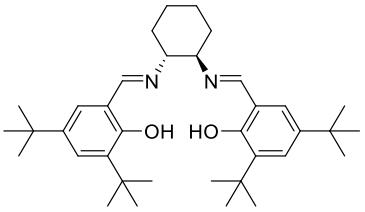
A1 B1 C1



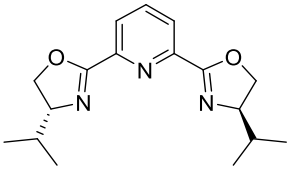
L1: BINAP



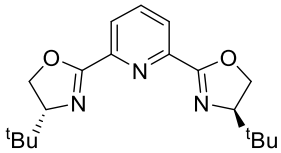
L2: CPA-1



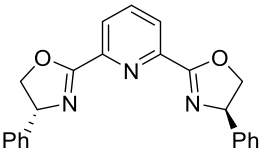
L3: salen



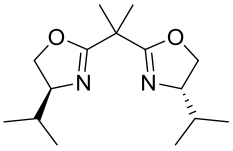
L4: ^{i}Pr-PyBox



L5: ^{t}Bu-Box



L6: Ph-PyBox



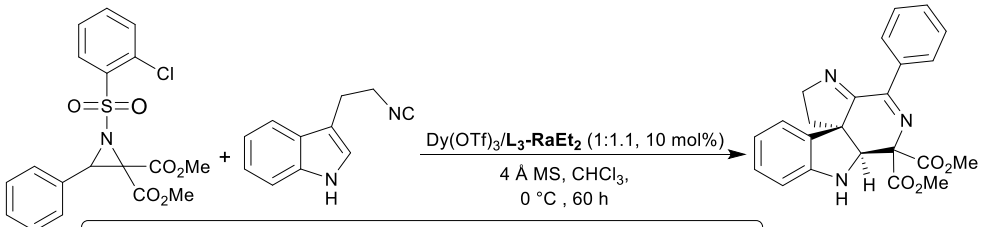
L7: ^{i}Pr-Box

entry	metal salt	L*	yield[b] (%)	ee[c] (%)
1	$Dy(OTf)_3$	**L1**	61	0
2	$Dy(OTf)_3$	**L2**	57	3
3	$Dy(OTf)_3$	**L3**	64	3
4	$Dy(OTf)_3$	**L4**	56	0
5	$Dy(OTf)_3$	**L5**	46	0
6	$Dy(OTf)_3$	**L6**	41	0
7	$Dy(OTf)_3$	**L7**	53	3

[a] All reactions were performed with **A1** (0.11 mmol), **B1** (0.10 mmol), Dy^{III}/**L*** (1:1.1, 10 mol %), 4 Å MS (80 mg) in $CHCl_3$ (1.2 mL) at 0 °C under N_2 for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase.

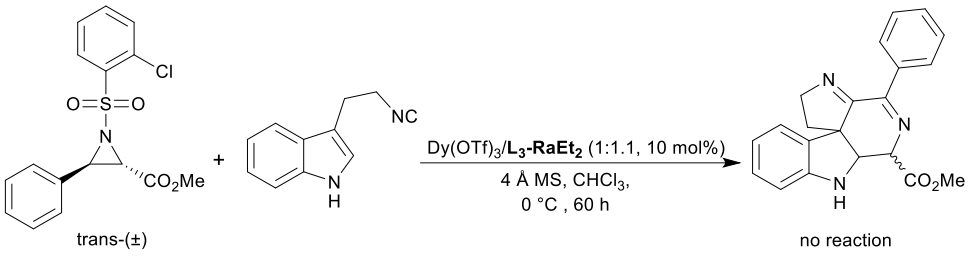
(F) Control experiments

(a) Varition of standard reaction condition



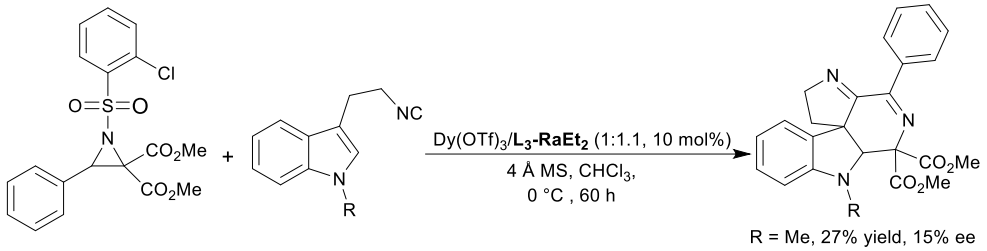
Varition:			
(1) ---	67% yield, 92% ee	(3) w/o L*	**44**% yield, racemate
(2) w/o M/**L***	no reaction	(4) w/o 4 Å MS	50% yield, 77% ee
(3) w/o M	no reaction		

(b) Sunstrate replaced by the aziridine with solo methyl ester group



trans-(±) no reaction

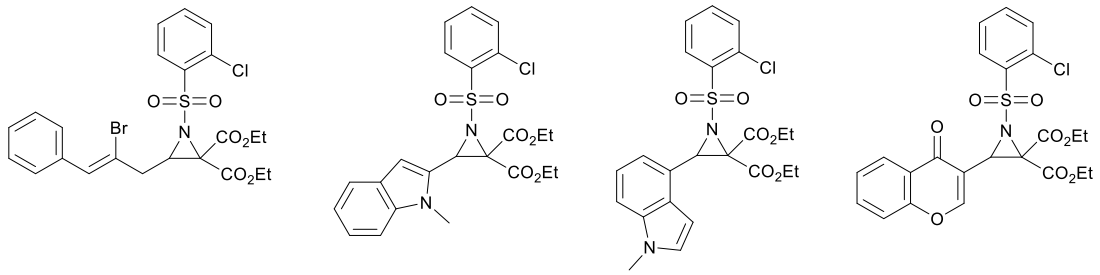
(c) Attempts to investigae the substituented effect of nitrogen on 3-(2-isocyanoethyl) indole

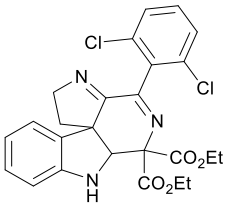


R = Me, 27% yield, 15% ee
R = Bn, 7% yield, 5% ee
R = Boc, trace
R = Ts, trace

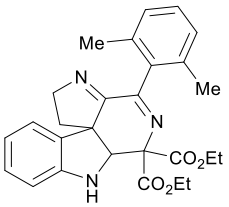
(G) Scope limitation

a) failed to synthesize

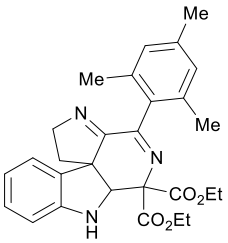




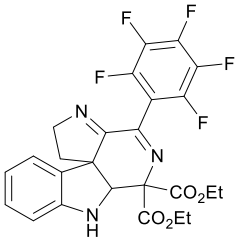
<5% yield, 0% ee



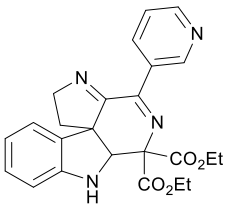
trace, < 5% yield



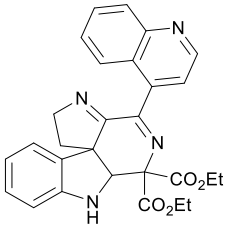
n.r



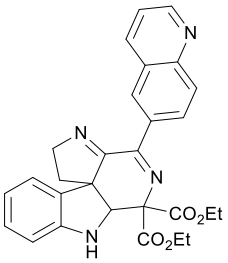
trace, < 8% yield



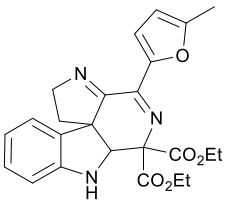
10 °C, 96 h
36%, 31% ee



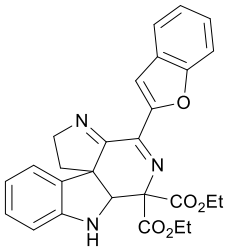
10 °C, 96 h
complex



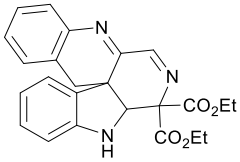
10 °C, 96 h
54% yield，21% ee



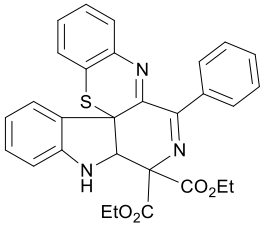
0 °C, 72 h
31% yield, 11% ee



0 °C, 90 h
27% yield, < 5% ee

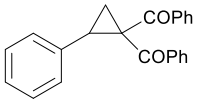


n.r



n.r

c) other dipolarphiles:



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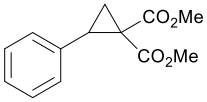

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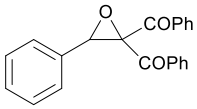
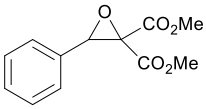
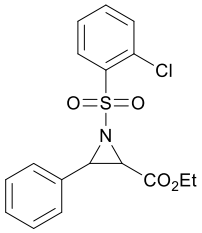


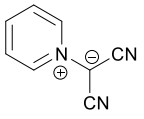
n.r



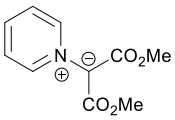
n.r



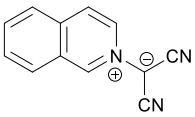
61% yied, 1.2:1 dr, 0% ee



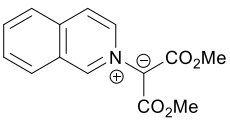
n.r



trace

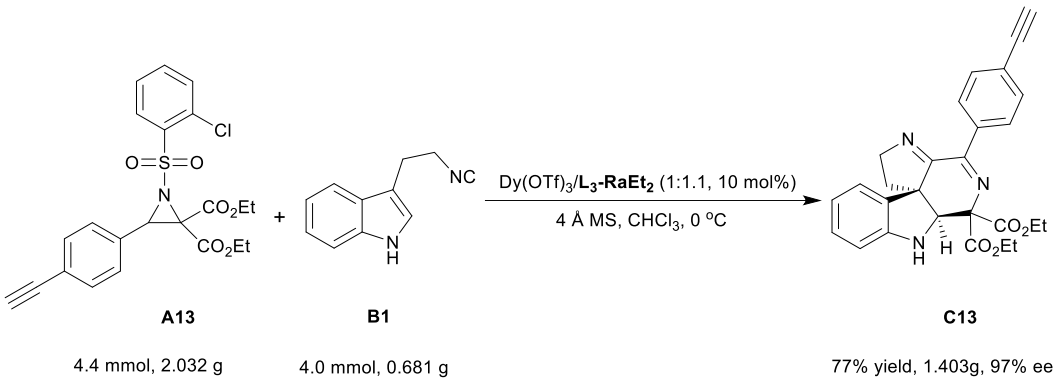


n.r



n.r

(H) Experimental procedure for the scale-up reaction and transformation of the product

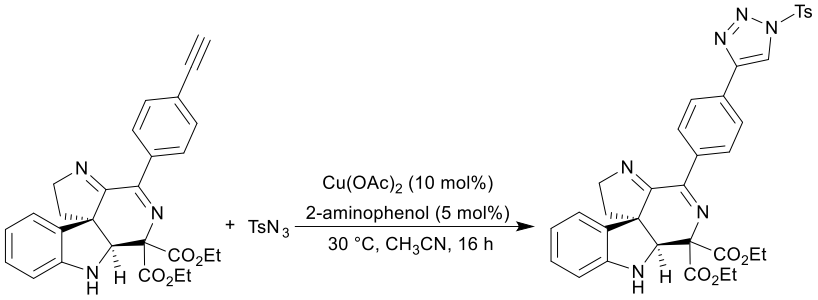


A13 4.4 mmol, 2.032 g

B1 4.0 mmol, 0.681 g

C13 77% yield, 1.403g, 97% ee

An over dried test tube was charged with $Dy(OTf)_3$ (10 mol%, 0.44 mmol, 268.3 mg), **L_3-RaEt$_2$** (11 mol%, 0.484 mmol, 311.7 mg), 4 Å MS (3.52 g) and $CHCl_3$ (22 mL) under N_2 atmosphere and the resulting solution was stirred at 35 °C for 2 h. Then, the resulting solution was stirred at 10 °C for 10 minutes, the solution of **A13** (4.4 mmol, 2.032 g) and **B1** (4.0 mmol, 0.681g) in 22 mL $CHCl_3$ were slowly added into the tube. The reaction mixture was stirred at 10 °C for 60 h. After the reaction was completed, the residue was subjected to column chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 3:1) to afford the enantioenriched product **C13** (77% yield, 1.403 g, 97% ee).



C13, 97% ee

D13, 91% yield, 97% ee

To a stirred solution of **C13** (1 mmol, 455.5 mg), 4-methylbenzenesulfonyl azide (1.1 mmol, 216 mg), and 2-aminophenol (5 mmol%, 5.5 mg) in MeCN (3 mL) was added $Cu(OAc)_2$ (10 mmol%, 18.2 mg) at 30 °C. After **C13** was exhausted monitored by TLC, the solvent was removed off in vacuum. The residue was purified by chromatography (eluent: petroleum ether/ethyl acetate = 2:1) to give the desired product **D13** as a yellow foam in 91% yield with 97% ee.

(I) X-ray crystal structure of product

The following single crystal **C4** was recrystallized from DCM/*n*-hexane. The absolute configuration of **C4** was determined as (6a*S*,11b*R*) by X-ray diffraction. CCDC 2155947 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center.

Datablock dop015 - ellipsoid plot

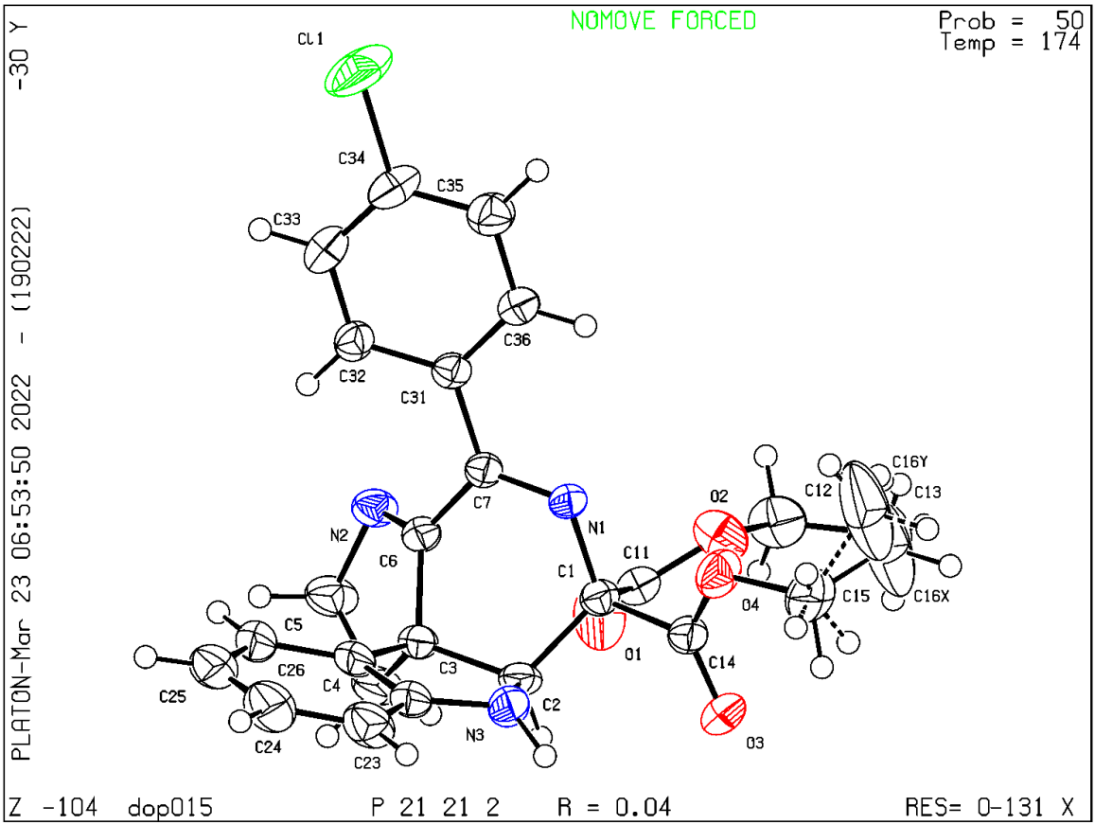


Figure 1. the thermal ellipsoid figure of **C4** with 50% probabilities

Crystallographic Data for **C4**.

Formula	**$C_{25}H_{24}ClN_3O_4S$ (C4)**
Formula mass (amu)	465.92
Space group	P 21 21 2
a (Å)	14.5871(5)
c (Å)	16.9620(6)
c (Å)	c=10.0945(4)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2497.65(16)
Z	4
λ (Å)	1.54178
T (K)	174
ρ_{calcd} (g cm^{-3})	1.239
μ (mm^{-1})	1.640
Transmission factors	0.406,0.885
$2\theta_{max}$ (deg)	68.289
No. of unique data, including $F_o^2 < 0$	4465

No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4264
No. of variables	308
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0448
$R_w(F_o^2)$ [b]	0.1110
Goodness of fit	1.076

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; [b] $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

The crystal of product ***rac*-C1** was obtained recrystallized in the solvents of CH_2Cl_2/*n*-hexane. CCDC (***rac*-C1**: 2071952) contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere.

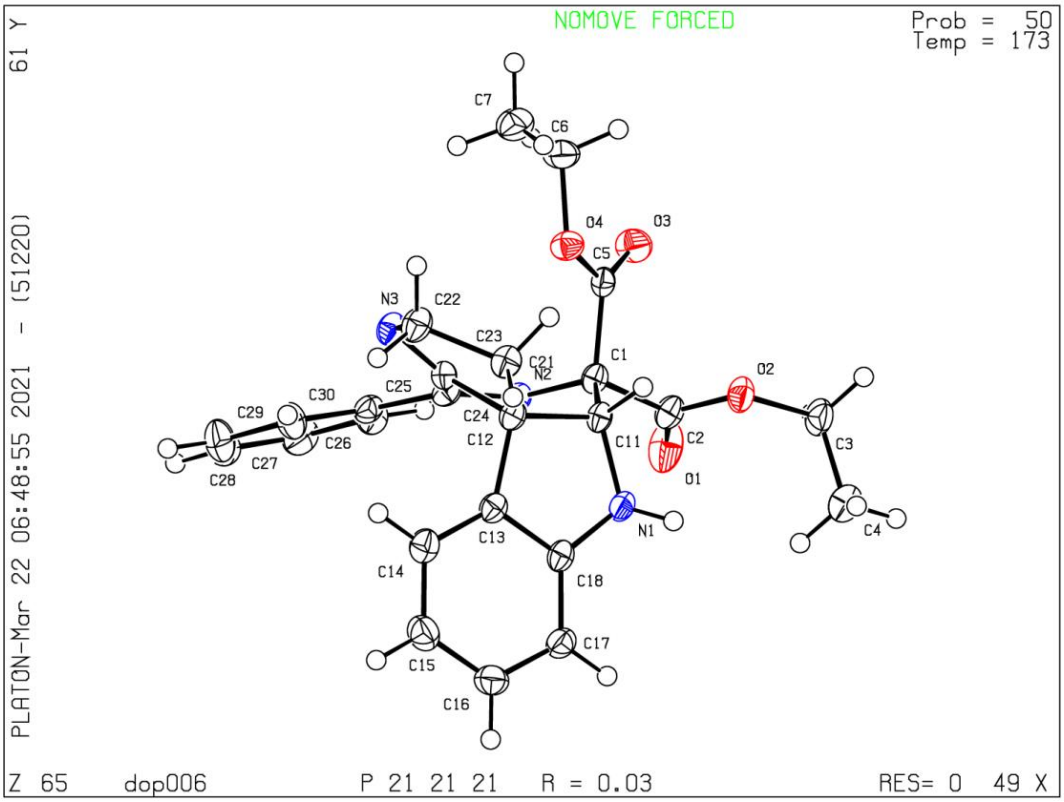


Figure 2. the thermal ellipsoid figure of ***rac*-C1** with 50% probabilities

Crystallographic Data for ***rac*-C1:**

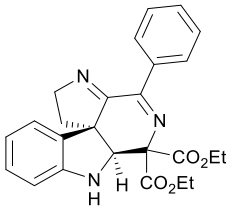
Formula	**$C_{26}H_{26}N_2O_4$ (C1)**
Formula mass (amu)	431.48
Space group	P 21 21 21
a (Å)	11.2538(5)
c (Å)	11.8895(5)
c (Å)	15.8258(7)
α (deg)	90
β (deg)	90
γ (deg)	90

V (Å^3)	2117.52(16)
Z	4
λ (Å)	1.54178
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.353
μ (mm^{-1})	0.755
Transmission factors	0.801,0.926
$2\theta_{max}$ (deg)	68.189
No. of unique data, including $F_o^2 < 0$	3791
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3694
No. of variables	295
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0299
$R_w(F_o^2)$ [b]	0.0873
Goodness of fit	1.115

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; [b] $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

(J) Spectral characterization data for the products

Diethyl (6a*S*,11b*R*)-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C1)



0.1 mmol scale reaction, 48 h, 33.6 mg, 78% yield; yellow solid. Melting point: 122 – 123 ºC. 95% ee. $[\alpha]_D^{15}$ = +67.3 (c = 0.26 in CH_2Cl_2).

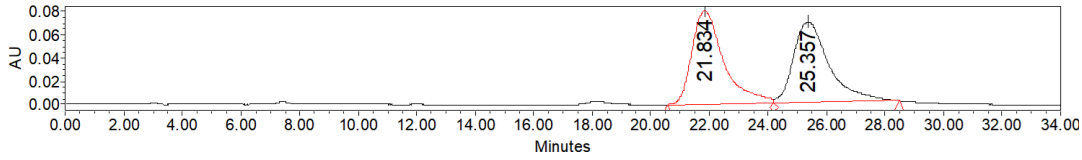
HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 22.06 min, t_r (major) = 25.68 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.94 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.04 – 6.91 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.24 (d, *J* = 5.4 Hz, 1H), 4.53 – 4.42 (m, 2H), 4.38 (dt, *J* = 16.6, 8.2 Hz, 1H), 4.26 (m, 2H), 4.21 – 4.08 (m, 2H), 2.73 – 2.56 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H)

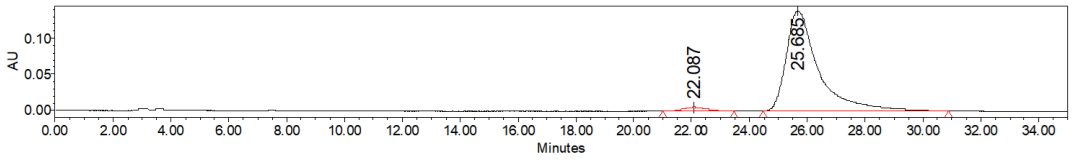
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.05, 168.61, 167.944, 166.55, 149.15, 134.80, 131.59, 131.07, 129.20, 128.69, 128.33, 122.71, 119.77, 110.22, 76.10, 70.88, 62.76, 62.74, 62.59, 60.53, 41.44, 14.36, 14.00.

HR-MS (ESI) calcd for $C_{25}H_{25}N_3O_4$ ([M]+Na^+) = 454.1737, found 454.1733.

IR (neat) ***ν*** (cm^{-1}): 3366, 2980, 2360, 1765, 1732, 1636, 1600, 1567, 1486, 1447, 1365, 1250, 1215, 1080, 1027, 983, 912, 858, 802, 726, 691, 488, 461.

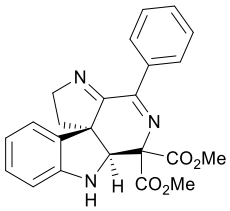


	Retention Time	% Area
1	21.834	50.76
2	25.357	49.24



	Retention Time	% Area
1	22.060	2.46
2	25.684	97.54

Dimethyl (6a*S*,11b*R*)-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C2)



0.1 mmol scale reaction, 60 h, 27.0 mg, 67% yield; yellow solid. Melting point: 155 – 156 ºC. 92% ee. $[\alpha]_D^{15}$ = +31.8 (c = 0.18 in CH_2Cl_2).

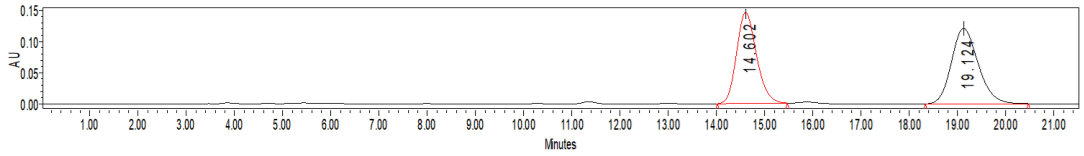
HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH =80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 14.58 min, t_r (major) = 18.99 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.90 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.96 – 6.86 (m, 2H), 6.61 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 4.4 Hz, 1H), 4.35 (m, 1H), 4.27 – 4.13 (m, 2H), 3.94 (s, 3H), 3.63 (s, 3H), 2.77 – 2.35 (m, 2H).

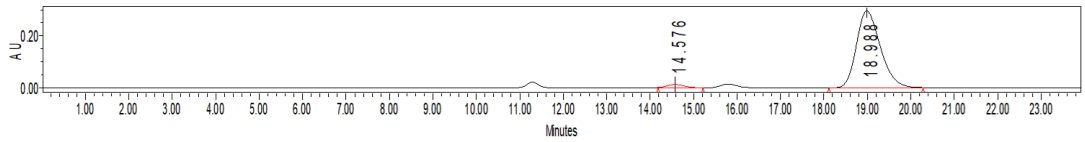
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.79, 168.83, 167.83, 166.95, 149.02, 134.50, 131.66, 130.98, 129.16, 128.59, 128.28, 122.65, 119.85, 110.27, 71.22, 62.74, 60.53, 53.67, 53.53, 41.36.

HR-MS (ESI) calcd for $C_{23}H_{21}N_3O_4$ ([M]+Na^+) = 426.1424, found 426.1421.

IR (neat) ***ν*** (cm^{-1}): 3366, 2980, 2357, 1757, 1733, 1635, 1602, 1557, 1478, 1441, 1341, 1217, 1088, 1017, 977, 861, 802, 723, 697, 481, 457.

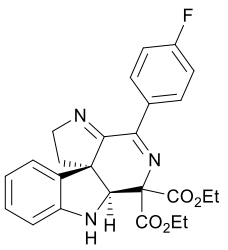


	Retention Time	% Area
1	14.602	47.31
2	19.124	52.69



	Retention Time	% Area
1	14.576	3.88
2	18.988	96.12

Diethyl (6a*S*,11b*R*)-4-(4-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C3)



0.1 mmol scale reaction, 60 h, 34.0 mg, 76% yield; yellow foam. Melting point: 150 – 152 ºC. 95% ee. $[\alpha]_D^{15}$ = +112.7 (c = 0.86 in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 15.95 min,

t_r (major) =29.98 min.

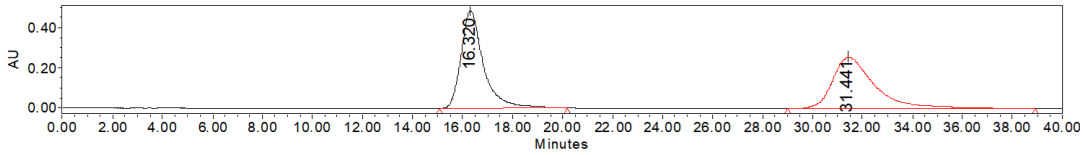
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (dd, J = 8.4, 5.4 Hz, 2H), 6.99 (m, 4H), 6.65 (t, J = 7.6 Hz, 1H), 6.49 (d, J = 8.4 Hz, 1H), 5.22 (d, J = 5.4 Hz, 1H), 4.46 (d, J = 7.2 Hz, 2H), 4.38 (m, 1H), 4.30 – 4.21 (m, 2H), 4.20 – 4.09 (m, 2H), 2.72 – 2.54 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 169.00, 167.88, 167.32, 166.49, 166.00, 164.33 (d, J = 254.0 Hz)), 131.01(d, J = 8.8 Hz), 130.95, 129.29, 122.63, 119.86, 115.54, 115.39 (d, J = 20.4 Hz), 110.32, 70.81, 62.81, 62.77, 62.66, 60.57, 41.40, 14.38, 14.02.

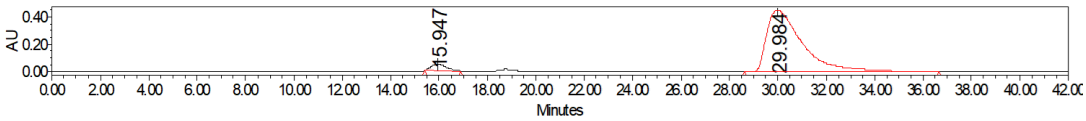
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ = –108.29.

HR-MS (ESI) calcd for $C_{25}H_{24}FN_3O_4$ ([M]+Na^+) = 472.1643, found 472.1644.

IR (neat) ***v*** (cm^{-1}): 3365, 2980, 2361, 1734, 1602, 1573, 1508, 1486, 1411, 1365, 1252, 1157, 1080, 1029, 847, 744.

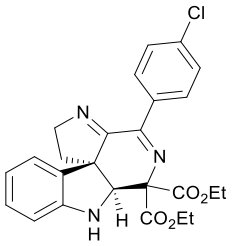


	Retention Time	% Area
1	16.320	50.20
2	31.441	49.80



	Retention Time	% Area
1	15.947	2.30
2	29.984	97.70

Diethyl (6a*S*,11b*R*)-4-(4-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C4)



0.1 mmol scale reaction, 60 h, 36.3 mg, 71% yield; yellow foam. Melting point: 109 – 110 ºC. 93% ee. $[\alpha]_D^{15}$ = +97.4 (c = 0.46 in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 19.11 min, t_r (major) = 33.54 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.96 (t, J = 8.0 Hz, 2H), 6.64 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 5.23 (d, J = 4.8 Hz, 1H), 4.56 – 4.41 (m, 2H), 4.38 (m, 1H), 4.31 – 4.20 (m, 2H), 4.20 – 4.07 (m, 2H), 2.76 – 2.50 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H).

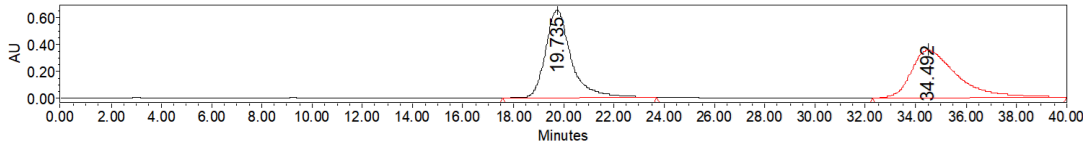
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 167.74, 166.58, 166.26, 165.22, 147.94, 136.80, 131.99, 129.79, 128.84, 128.15, 127.48, 121.46, 118.72, 109.17, 75.04, 69.67, 61.67, 61.63, 61.51, 59.43, 40.20, 13.21, 12.85.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{34.9689}ClN_3O_4$ ([M]+Na^+) = 488.1348, found 488.1347.

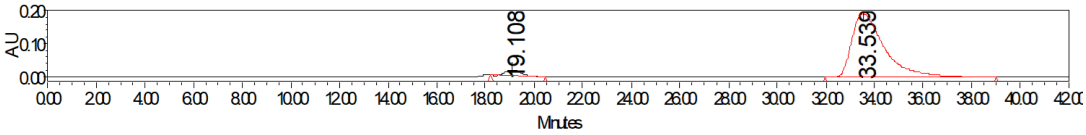
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{36.9659}ClN_3O_4$ ([M]+Na^+) = 490.1318, found 490.1315.

IR (neat) ***v*** (cm^{-1}): 3364, 2980, 1734, 1589, 1560, 1487, 1402, 1366, 1252, 1216, 1080, 1030, 912, 841, 803, 739,

498, 464.

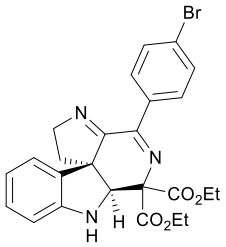


	Retention Time	% Area
1	19.735	50.93
2	34.492	49.07



	Retention Time	% Area
1	19.108	3.02
2	33.539	96.98

Diethyl (6a*S*,11b*R*)-4-(4-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C5)



0.1 mmol scale reaction, 60 h, 37.8 mg, 74% yield; yellow foam. Melting point: 137 – 139 ºC. 95% ee. $[\alpha]_D^{15}$ = +127.8 (c = 0.88 in CH_2Cl_2).

HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.55 min, t_r (minor) = 18.99 min.

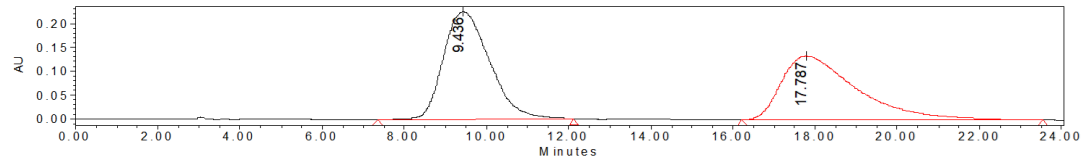
^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.85 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.96 (m, 2H), 6.65 (d, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 4.8 Hz, 1H), 4.50 – 4.42 (m, 2H), 4.37 (m, 1H), 4.26 (m, 2H), 4.20 – 4.08 (m, 2H), 2.72 – 2.54 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.87, 167.68, 167.54, 166.32, 149.09, 133.56, 131.59, 130.92, 130.17, 129.31, 126.61, 122.60, 119.88, 110.32, 70.81, 62.83, 62.78, 62.67, 60.58, 41.34, 14.36, 13.99.

HR-MS (ESI) calcd for $C_{25}H_{24}^{78.9183}BrN_3O_4$ ([M]+Na^+) = 532.0842, found 532.0841.

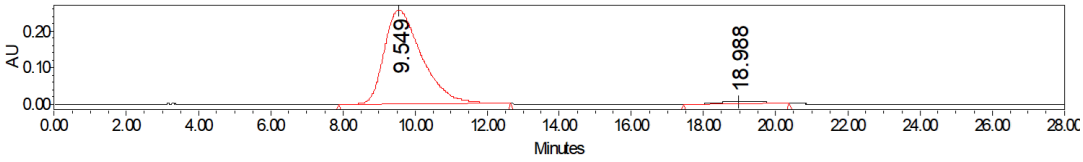
HR-MS (ESI) calcd for $C_{25}H_{24}^{80.9163}BrN_3O_4$ ([M]+Na^+) = 534.0822, found 534.0825.

IR (neat) ***ν*** (cm^{-1}): 3366, 2980, 1734, 1585, 1557, 1486, 1396, 1366, 1252, 1216, 1069, 1030, 837, 742, 645, 494, 465.



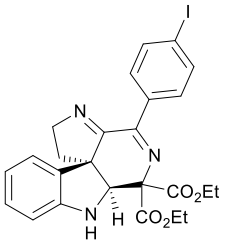
	Retention Time	% Area

1	9.436	50.77
2	17.787	49.23



	Retention Time	% Area
1	9.549	97.27
2	18.988	2.73

Diethyl (6a*S*,11b*R*)-4-(4-iodophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C6)



0.1 mmol scale reaction, 60 h, 32.9 mg, 59% yield; yellow foam. Melting point: 167 – 171 ºC. 90% ee. $[\alpha]_D^{17}$ = +36.4 (c = 0.19 in CH_2Cl_2).

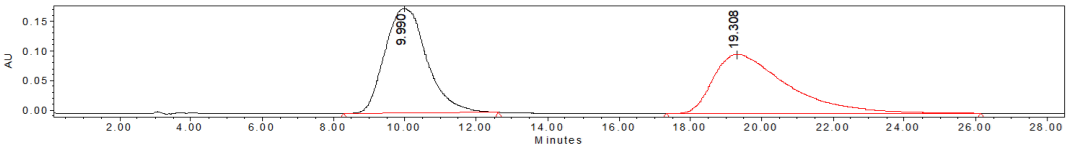
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.03 min, t_r (minor) = 20.43 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.69 (dd, *J* = 10.8, 5.6 Hz, 4H), 6.99 – 6.87 (m, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 5.4 Hz, 1H), 4.50 – 4.40 (m, 2H), 4.40 – 4.33 (m, 1H), 4.25 (m, 2H), 4.20 – 4.07 (m, 2H), 2.72 – 2.51 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

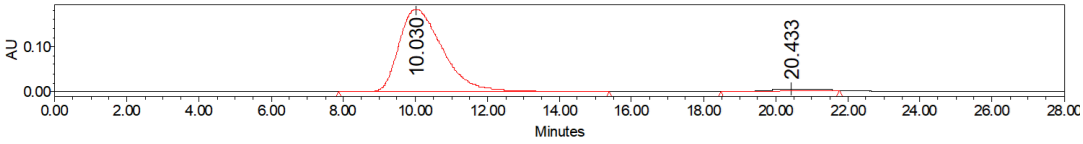
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.87, 167.76, 167.64, 166.31, 149.09, 137.58, 134.13, 130.93, 130.17, 129.31, 122.61, 119.89, 110.31, 99.16, 76.22, 70.82, 62.84, 62.78, 62.67, 60.59, 41.34.

HR-MS (ESI) calcd for $C_{25}H_{24}IN_3O_4$ ([M]+Na^+) = 580.0704, found 580.0701.

IR (neat) ***ν*** (cm^{-1}): 3367, 2979, 2361, 2156, 1967, 1735, 1602, 1581, 1553, 1485, 1251, 1081, 1029, 831, 745, 491, 461.

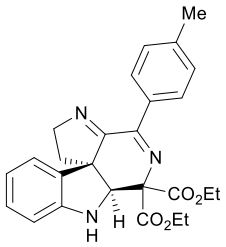


	Retention Time	% Area
1	9.990	50.18
2	19.308	49.82



	Retention Time	% Area
1	10.030	95.37
2	20.433	4.63

Diethyl (6a*S*,11b*R*)-4-(p-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C7)



0.1 mmol scale reaction, 60 h, 34.7 mg, 78% yield; yellow foam. Melting point: 122 – 123 ºC. 93% ee. $[\alpha]_D^{15}$ = +117.9 (c = 0.26 in CH_2Cl_2).

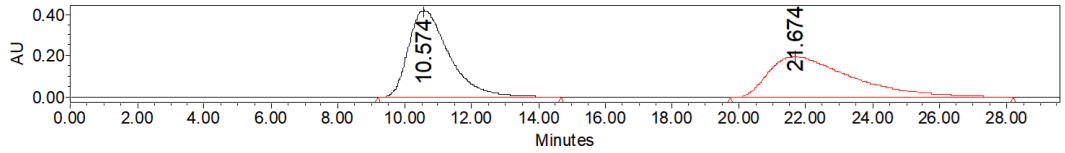
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.43 min, t_r (minor) = 22.23 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 4.8 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.37 (m, 1H), 4.30 – 4.20 (m, 2H), 4.19 – 4.07 (m, 2H), 2.63 (m, 2H), 2.31 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

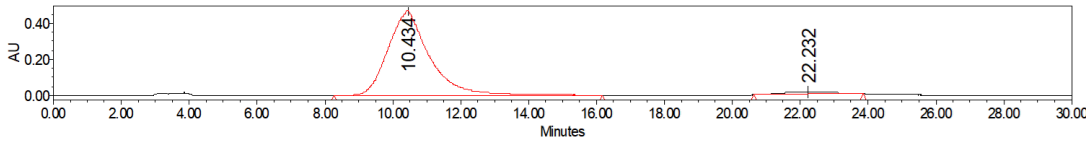
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 169.05, 168.29, 167.93, 166.59, 149.08, 141.95, 132.04, 131.06, 129.05, 128.97, 128.57, 122.63, 119.63, 110.11, 62.69, 62.60, 62.49, 60.42, 41.36, 21.56, 14.27, 13.91.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^+) =468.1894, found 468.1892.

IR (neat) ***v*** (cm^{-1}): 3368, 2980, 1734, 1604, 1561, 1486, 1366, 1251, 1216, 1081, 130, 859, 827, 746, 497, 465.

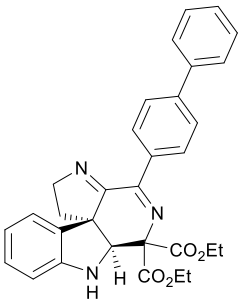


	Retention Time	% Area
1	10.574	50.52
2	21.674	49.48



	Retention Time	% Area
1	10.434	96.28
2	22.232	3.72

Diethyl (6a*S*,11b*R*)-4-([1,1'-biphenyl]-4-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C8)



0.1 mmol scale reaction, 72 h, 41.1 mg, 71% yield; yellow foam. Melting point: 148 – 150 ºC. 91% ee. $[\alpha]_D^{15}$ = +175.4 (c = 0.33 in CH_2Cl_2).

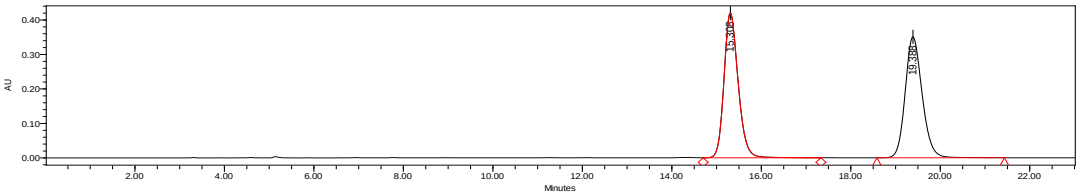
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH =85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 15.46 min, t_r (minor) = 19.67 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.05 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 4H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.67 (t, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.26 (d, *J* = 4.2 Hz, 1H), 4.53 – 4.44 (m, 2H), 4.43 – 4.37 (m, 1H), 4.29 (m, 2H), 4.23 – 4.09 (m, 2H), 2.79 – 2.57 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

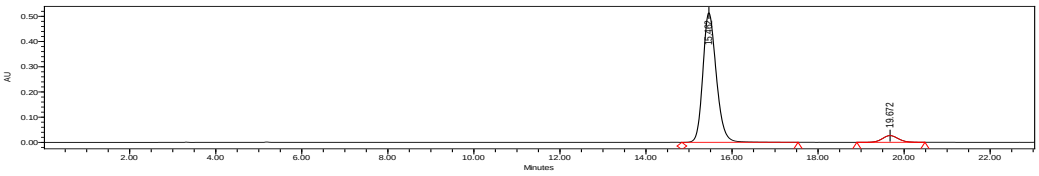
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.02, 168.10, 167.95, 166.55, 149.15, 140.47, 131.07, 129.18, 129.12, 128.86, 127.83, 127.25, 127.04, 122.67, 119.74, 110.20, 76.13, 70.88, 62.73, 62.72, 62.56, 60.51, 41.42, 14.33, 13.98.

HR-MS (ESI) calcd for $C_{31}H_{29}N_3O_4$ ([M]+Na^+) = 530.2050, found 530.2047.

IR (neat) ***ν*** (cm^{-1}): 3371, 2980, 1734, 1603, 1551, 1468, 1405, 1366, 1250, 1216, 1081, 1030, 852, 741, 698.

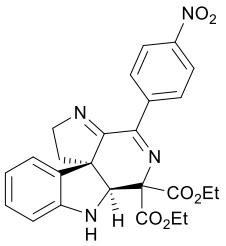


	Retention Time	% Area
1	15.308	50.05
2	19.388	49.95



	Retention Time	% Area
1	15.462	94.25
2	19.672	5.75

Diethyl (6a*S*,11b*R*)-4-(4-nitrophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C9)



0.1 mmol scale reaction, 96 h, 24.3 mg, 51% yield; yellow foam. Melting point: 171– 173 ºC. 92% ee. $[\alpha]_D^{16}$ = +77.4 (c = 0.31 in CH_2Cl_2).

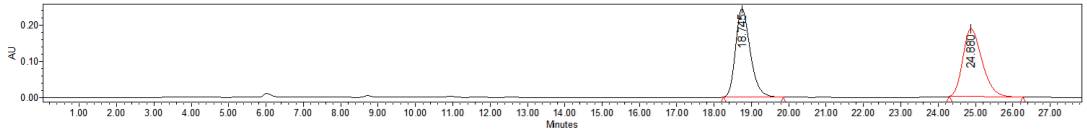
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 28.43 min, t_r (minor) = 24.54 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.17 (s, 4H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 1H), 4.55 – 4.36 (m, 3H), 4.34 – 4.22 (m, 2H), 4.16 (m, 2H), 2.74 – 2.56 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

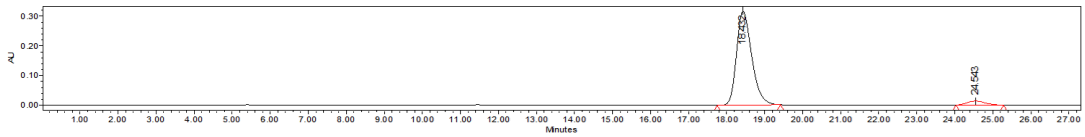
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 168.47, 167.41, 167.16, 165.86, 149.51, 148.93, 139.89, 129.53, 129.40, 123.41, 122.46, 119.95, 110.28, 70.69, 62.92, 62.74, 60.59, 41.15, 14.25, 13.88.

HR-MS (ESI) calcd for $C_{25}H_{24}N_4O_6$ ([M]+Na^+) = 499.1588, found 499.1585.

IR (neat) ***v*** (cm^{-1}): 3373, 2980, 2361, 1736, 1602, 1579, 1522, 1468, 1347, 1251, 1216, 1081, 1030, 854, 747, 721.

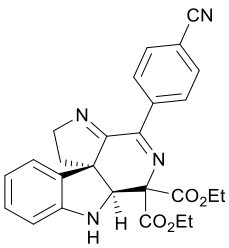


	Retention Time	Area
1	18.745	6652159
2	24.880	6694782



	Retention Time	% Area
1	18.432	96.09
2	24.543	3.91

Diethyl (6a*S*,11b*R*)-4-(4-cyanophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate （C10）



0.1 mmol scale reaction, 96 h, 31.0 mg, 68% yield; yellow foam. Melting point: 135 – 137 ºC. 93% ee. $[\alpha]_D^{16}$ = +147.8 (c = 0.11 in CH_2Cl_2).

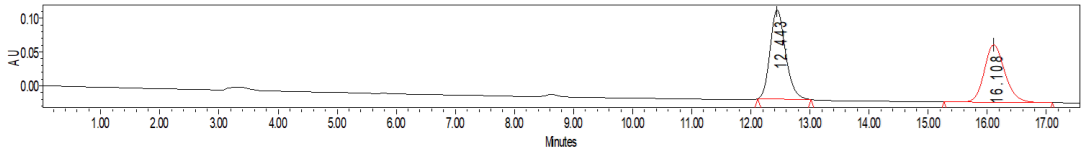
HPLC (Daicel chiralcel OXH hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 12.30 min, t_r (minor) = 15.93 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.02 – 6.90 (m, 2H), 6.67 (d, J = 7.4 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 4.54 – 4.34 (m, 3H), 4.33 – 4.22 (m, 2H), 4.21 – 4.08 (m, 2H), 2.74 – 2.55 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

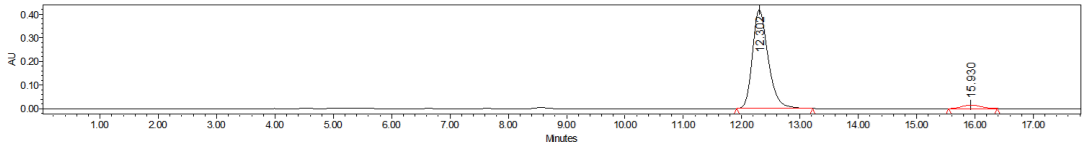
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 168.51, 167.36, 166.93, 165.92, 148.94, 138.32, 132.05, 129.37, 129.04, 122.45, 119.90, 118.47, 110.25, 70.67, 62.87, 62.70, 62.64, 60.55, 14.24, 13.88.

HR-MS (ESI) calcd for $C_{26}H_{24}N_4O_4$ ([M]+Na^+) = 479.1690, found 558.1687.

IR (neat) ***ν*** (cm^{-1}): 3366, 2981, 2229, 1735, 1601, 1554, 1487, 1406, 1366, 1251, 1216, 1080, 1029, 853, 747, 546, 455.

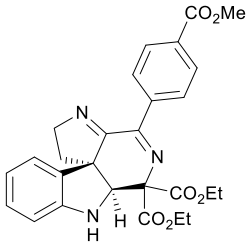


	Retention Time	% Area
1	12.443	53.86
2	16.108	46.14



	Retention Time	% Area
1	12.302	96.60
2	15.930	3.40

Diethyl (6a*S*,11b*R*)-4-(4-(methoxycarbonyl)phenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C11)



0.1 mmol scale reaction, 96 h, 31.3 mg, 64% yield; yellow foam. Melting point: 159– 161 ºC. 91% ee. $[\alpha]_D^{17}$ = +44.7 (c = 0.08 in CH_2Cl_2).

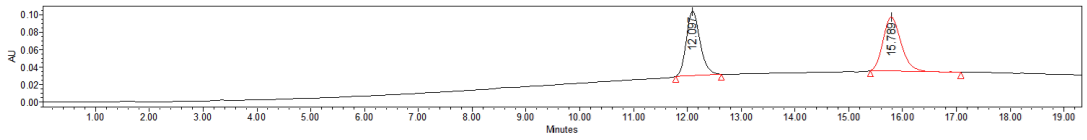
HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 12.20 min, t_r (minor) = 16.01 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dd, J = 16.8, 8.4 Hz, 4H), 7.00 – 6.92 (m, 2H), 6.65 (t, J = 7.4 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 5.24 (s, 1H), 4.54 – 4.34 (m, 3H), 4.33 – 4.21 (m, 2H), 4.15 (m, 2H), 3.89 (s, 3H), 2.75 – 2.55 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

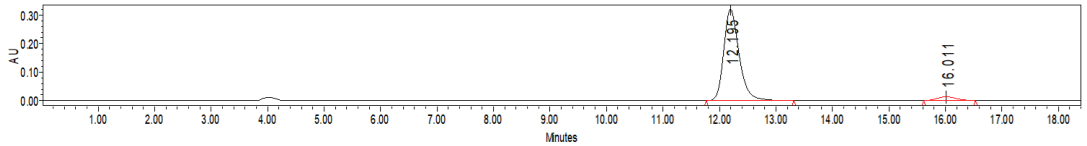
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 168.72, 167.81, 167.67, 166.16, 148.99, 138.42, 132.41, 130.78, 129.45, 129.24, 128.52, 122.56, 119.80, 110.19, 70.81, 62.76, 62.58, 60.51, 52.25, 41.22, 14.24, 13.88.

HR-MS (ESI) calcd for $C_{27}H_{27}N_3O_7$ ([M]+Na^+) = 528.1741, found 528.1744.

IR (neat) ***ν*** (cm^{-1}): 3367, 2952, 1726, 1602, 1561, 1486, 1438, 1407, 1367, 1108, 1079, 1024, 861, 780, 747, 464.

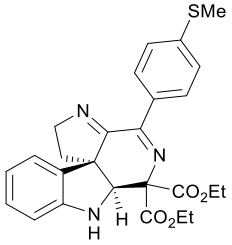


	Retention Time	% Area
1	12.097	47.69
2	15.789	52.31



	Retention Time	% Area
1	12.195	95.24
2	16.011	4.76

Diethyl (6a*S*,11b*R*)-4-(4-(methylthio)phenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C12)



0.1 mmol scale reaction, 48 h, 40.1 mg, 84% yield; yellow foam. Melting point: 105 – 107 ºC. 88% ee. $[\alpha]_D^{15}$ = +167.5 (c = 0.23 in CH_2Cl_2).

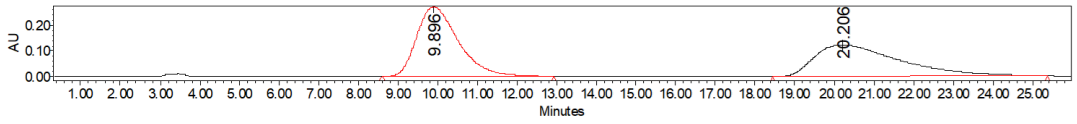
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.98 min, t_r (minor) = 20.87 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.90 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.22 (d, *J* = 4.8 Hz, 1H), 4.50 – 4.41 (m, 2H), 4.37 (m, 1H), 4.30 – 4.21 (m, 2H), 4.19 – 4.08 (m, 2H), 2.74 – 2.54 (m, 2H), 2.44 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2Hz, 3H).

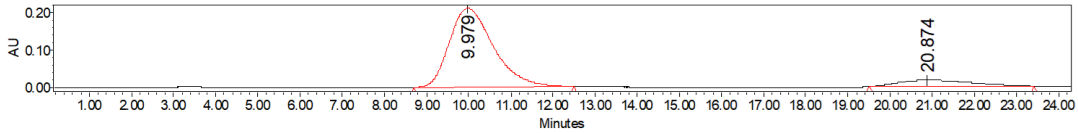
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.06, 167.89, 167.74, 166.59, 149.13, 143.54, 131.21, 131.07, 129.16, 128.92, 125.25, 122.62, 119.73, 110.22, 76.01, 70.90, 62.77, 62.70, 62.57, 60.51, 41.39, 15.12, 14.34, 13.98.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4S$ ([M]+Na^+) = 500.1615, found 500.1614.

IR (neat) ***ν*** (cm^{-1}): 3366, 2980, 1765, 1733, 1599, 1578, 1546, 1486, 1402, 1365, 1250, 1216, 104, 1030, 982, 830, 745, 500, 467.

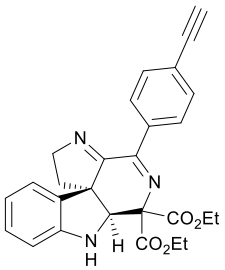


	Retention Time	% Area
1	9.896	50.86
2	20.206	49.14



	Retention Time	% Area
1	9.979	93.71
2	20.874	6.29

Diethyl (6a*S*,11b*R*)-4-(4-ethynylphenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C13)



0.1 mmol scale reaction, 60 h, 35.0 mg, 77% yield; yellow foam. Melting point: 144 – 146ºC. 97% ee. $[\alpha]_D^{15}$ = +57.4 (c = 0.08 in CH_2Cl_2).

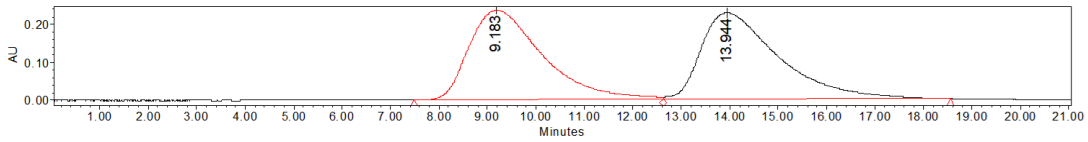
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.78 min, t_r (minor) = 15.59 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.95 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.23 (d, *J* = 4.8 Hz, 1H), 4.51 – 4.42 (m, 2H), 4.38 (m, 1H), 4.31 – 4.22 (m, 2H), 4.21 – 4.08 (m, 2H), 3.16 (s, 1H), 2.75 – 2.54 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

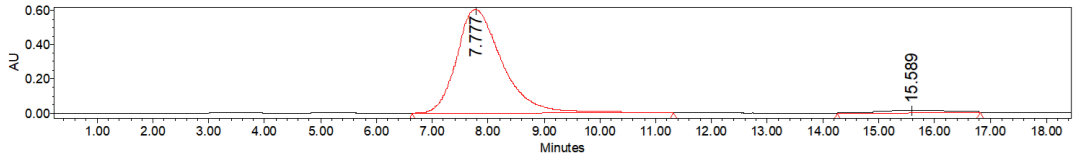
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.89, 167.73, 166.36, 149.08, 134.77, 132.07, 130.93, 129.26, 128.50, 125.23, 122.62, 119.85, 110.28, 79.48, 76.25, 70.88, 62.81, 62.79, 62.64, 60.56, 41.35, 14.34, 13.98.

HR-MS (ESI) calcd for $C_{27}H_{25}N_3O_4$ ([M]+Na^+) = 478.1737, found 478.1741.

IR (neat) ***ν*** (cm^{-1}): 3277, 2981, 134, 1602, 1650, 1486, 1406, 1366, 1251, 1217, 1080, 1029, 851, 746, 652, 531, 470.

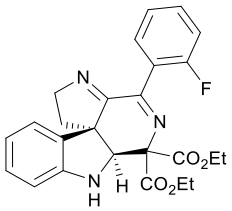


	Retention Time	% Area
1	9.183	49.64
2	13.944	50.36



	Retention Time	% Area
1	7.777	98.38
2	15.589	1.62

Diethyl (6a*S*,11b*R*)-4-(2-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C14)



0.1 mmol scale reaction, 60 h, 27.4 mg, 61% yield; yellow foam. Melting point: 154 – 157 ºC. 91% ee. $[\alpha]_D^{15}$ = +176.3 (c = 0.37 in CH_2Cl_2).

HPLC (Daicel chiralcel OXH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 12.02 min, t_r (major) = 21.03 min,

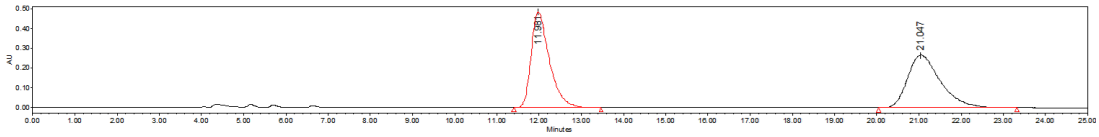
^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.71 (td, *J* = 7.6, 1.6 Hz, 1H), 7.37 (q, *J* = 5.4 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 – 6.91 (m, 3H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 4.52 – 4.38 (m, 2H), 4.32 (m, 1H), 4.26 – 4.10 (m, 4H), 2.73 – 2.56 (m, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.55, 166.89, 166.05, 165.16 (d, *J* = 242.4 Hz), 148.02, 131.88 (d, *J* = 8.6 Hz), 131.79, 130.00, 129.92, 128.00, 123.13, 123.08, 122.75, 122.72, 118.56, 115.11 (d, *J* = 21.2 Hz), 114.90, 108.86, 69.53, 61.64, 61.47, 60.85, 40.81, 13.18, 12.91.

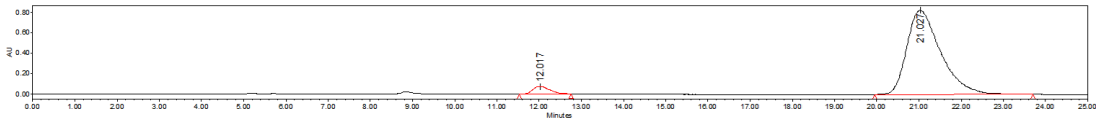
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) *δ* = –110.14.

HR-MS (ESI) calcd for $C_{25}H_{24}FN_3O_4$ ([M]+Na^+) = 472.1643, found 472.1647.

IR (neat) ***v*** (cm^{-1}): 3364, 2981, 1735, 1602, 1487, 1457, 1367, 1251, 1216, 1108, 1031, 859, 748, 462.

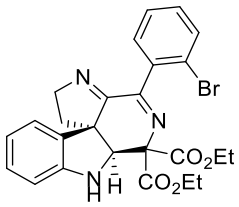


	Retention Time	% Area
1	11.981	50.18
2	21.047	49.82



	Retention Time	% Area
1	12.017	4.64
2	21.027	95.36

Diethyl (6a*S*,11b*R*)-4-(2-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C15)



0.1 mmol scale reaction, 60 h, 40.5 mg, 87% yield; yellow foam. Melting point: 139 – 141 ºC. 88% ee. $[\alpha]_D^{15}$ = +257.3 (c = 0.62 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.66 min, t_r (minor) = 12.01 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.90 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.93 (t, *J* = 7.8 Hz, 2H), 6.62 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.20 (d, *J* = 4.8 Hz, 1H), 4.43 (m, 2H), 4.35 – 4.27 (m, 1H), 4.23

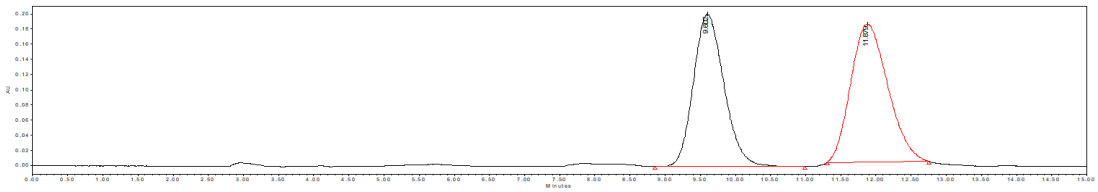
(m, 2H), 4.18 – 4.04 (m, 2H), 2.61 (m, *J* = 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, Chloroform-*d*) δ 167.94, 166.78, 165.46, 165.42, 148.14, 137.00, 132.19, 129.99, 129.04, 128.35, 127.68, 121.66, 118.92, 109.37, 75.24, 69.87, 61.87, 61.83, 61.71, 59.63, 40.40, 13.41, 13.05.

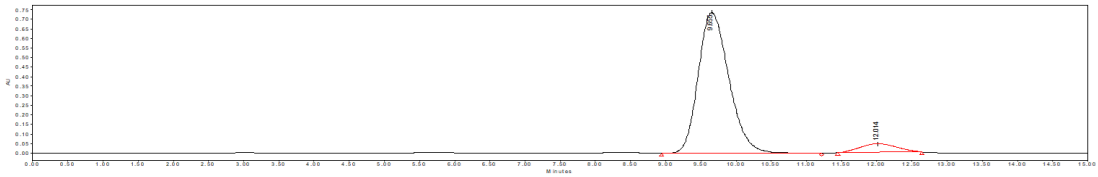
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{34.9689}ClN_3O_4$ ([M]+Na^+) = 488.1348, found 488.1341.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{36.9659}ClN_3O_4$ ([M]+Na^+) = 490.1318, found 490.1313.

IR (neat) ***ν*** (cm^{-1}): 3377, 2978, 1736, 1603, 1563, 1461, 1366, 1251, 1216, 1079, 1030, 859, 797, 746, 683.

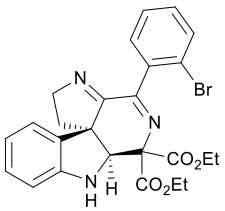


	Retention Time	% Area
1	9.602	48.04
2	11.879	51.96



	Retention Time	% Area
1	9.655	94.10
2	12.014	5.90

Diethyl (6a*S*,11b*R*)-4-(2-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C16)



0.1 mmol scale reaction, 60 h, 35.2 mg, 69% yield; yellow foam. Melting point: 126 – 128 ºC. 71% ee. $[\alpha]_D^{15}$ = +166.3 (c = 0.71 in CH_2Cl_2).

HPLC (Daicel chiralcel ODH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.91 min, t_r (minor) = 9.02 min.

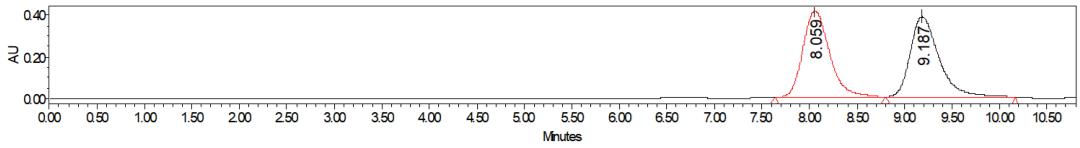
^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.89 (m, 2H), 6.59 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 5.16 (d, *J* = 4.8 Hz, 1H), 4.44 – 4.35 (m, 2H), 4.35 – 4.27 (m, 1H), 4.19 (m, 2H), 4.14 – 4.02 (m, 2H), 2.67 – 2.42 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

$^{13}C\{^1H\}$ NMR (151 MHz, Chloroform-*d*) δ 167.56, 166.37, 166.24, 165.01, 147.78, 132.25, 129.62, 128.00, 125.30, 121.30, 118.58, 109.01, 69.50, 61.52, 61.47, 61.36, 40.04, 13.05.

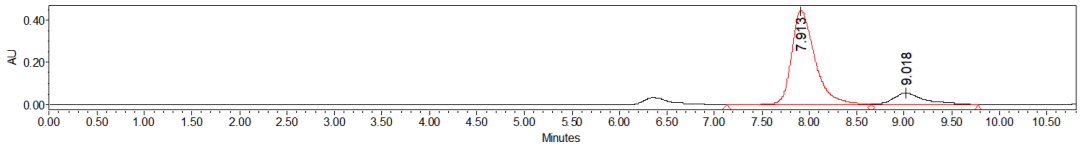
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{78.9183}BrN_3O_4$ ([M]+Na^+) = 532.0842, found 532.0847.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{80.9163}BrN_3O_4$ ([M]+Na^+) = 534.0822, found 534.0828

IR (neat) ***ν*** (cm^{-1}): 3375, 2981, 1733, 1638, 1600, 1557, 1485, 1365, 1250, 1214, 1080, 1028, 858, 796, 736, 682, 465.

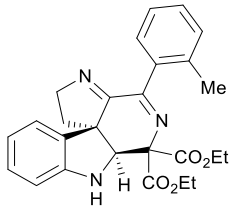


	Retention Time	% Area
1	8.059	50.17
2	9.187	49.83



	Retention Time	% Area
1	7.913	85.71
2	9.018	14.29

Diethyl (6a*S*,11b*R*)-4-(o-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C17)



0.1 mmol scale reaction, 48 h, 29.0 mg, 81% yield; yellow foam. Melting point: 144– 147 ºC. 90% ee. $[\alpha]_D^{15}$ = +126.3 (c = 0.96 in CH_2Cl_2).

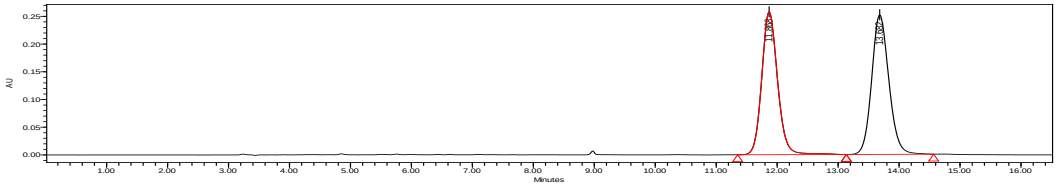
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 11.87 min, t_r (minor) = 13.72 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.20 (t, *J* = 7.8 Hz, 1H), 7.12 (m, 3H), 7.06 – 6.96 (m, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 4.6 Hz, 1H), 4.48 – 4.33 (m, 3H), 4.33 – 4.23 (m, 1H), 4.19 (m, 3H), 2.64 – 2.54 (m, 2H), 2.26 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

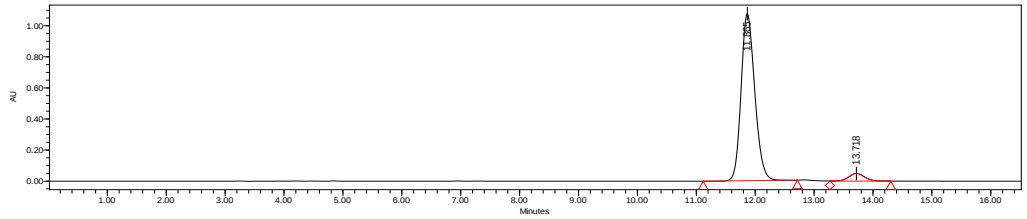
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 170.38, 167.92, 167.82, 165.40, 148.17, 136.58, 134.18,130.02, 129.82, 128.98, 128.81, 128.26, 124.37, 122.06, 118.39, 108.79, 74.98, 68.93, 61.60, 61.37, 60.96, 59.08, 19.35, 13.12, 12.88.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^+) = 468.1894, found 468.1897.

IR (neat) ***v*** (cm^{-1}): 3223, 2980, 1733, 1601, 1486, 1365, 1249, 1013, 1116, 1077, 1028, 859, 734, 645, 455.

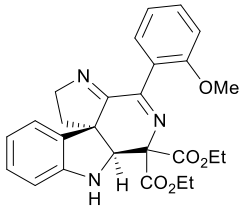


	Retention Time	% Area
1	11.868	48.57
2	13.682	51.43



	Retention Time	% Area
1	11.865	94.98
2	13.718	5.02

Diethyl (6a*S*,11b*R*)-4-(2-methoxyphenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C18)



0.1 mmol scale reaction, 60 h, 25.8 mg, 58% yield; yellow foam. Melting point: 159 – 161 ºC. 75% ee. $[\alpha]_D^{17}$ = +86.5 (c = 0.63 in CH_2Cl_2).

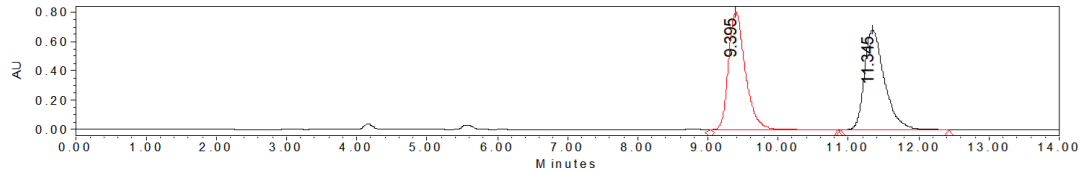
HPLC (Daicel chiralcel OXH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 8.52 min, t_r (major) = 10.72 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.49 (d, *J* = 8.8 Hz, 1H), 7.21 (m, 1H), 7.03 – 6.92 (m, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.71 – 6.62 (m, 2H), 6.45 (d, *J* = 7.6 Hz, 1H), 5.15 (s, 1H), 4.35 – 4.29 (m, 2H), 4.24 – 4.19 (m, 1H), 4.21 – 4.08 (m, 3H), 4.08 – 3.97 (m, 1H), 3.31 (s, 3H), 2.51 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 4H).

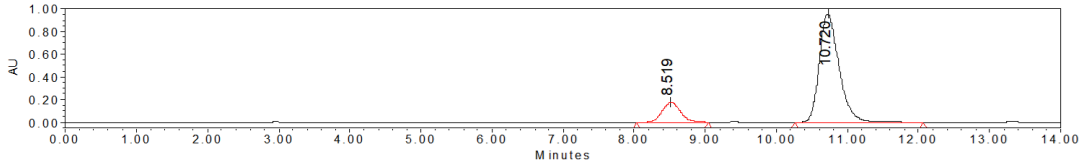
^{13}C NMR (101 MHz, Chloroform-*d*) *δ* 169.26, 167.98, 167.56, 165.31, 157.07, 148.08, 131.14, 131.06, 129.81, 127.69, 125.20, 122.85, 119.65, 117.84, 110.23, 108.54, 74.95, 69.23, 61.53, 61.44, 60.18, 58.73, 54.04, 40.88, 13.16.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_5$([M]+Na^+) = 484.1843, found 484.1843.

IR (neat) ***v*** (cm^{-1}): 3320, 2937, 1734, 1601, 1490, 1465, 1366, 1251, 1214, 1117, 1026, 860, 750, 463.



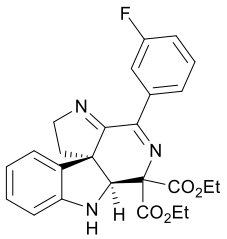
	Retention Time	% Area
1	9.395	49.95
2	11.345	50.05



	Retention Time	% Area
1	8.519	12.46
2	10.720	87.54

Diethyl (6a*S*,11b*R*)-4-(3-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-

b]indole-6,6-dicarboxylate (C19)



0.1 mmol scale reaction, 60 h, 34.6 mg, 77% yield; yellow foam. Melting point: 117 – 119 ºC. 94% ee. $[\alpha]_D^{15}$ = +203.9 (c = 0.47 in CH_2Cl_2).

HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.02 min, t_r (minor) = 20.15 min.

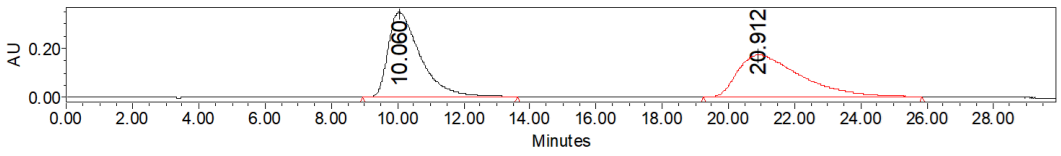
^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.74 (t, *J* = 10.2 Hz, 2H), 7.37 – 7.27 (m, 1H), 7.12 (t, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.55 – 6.47 (m, 1H), 5.26 (d, *J* = 3.6 Hz, 1H), 4.51– 4.47 (m, 2H), 4.43 – 4.36 (m, 1H), 4.34 – 4.25 (m, 2H), 4.23 – 4.12 (m, 2H), 2.74 – 2.58 (m, 2H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.87, 167.67, 167.42, 163.54 (d, *J* = 246.2 Hz), 149.08, 136.81(d, *J* = 7.6 Hz), 130.90, 129.93(d, *J* = 8.0 Hz), 129.88, 129.30, 124.61, 122.65, 119.89, 118.66, 118.52(d, *J* = 21.2 Hz), 115.22, 110.27, 76.25, 70.83, 62.85, 62.74, 62.67, 41.37, 14.34, 13.99.

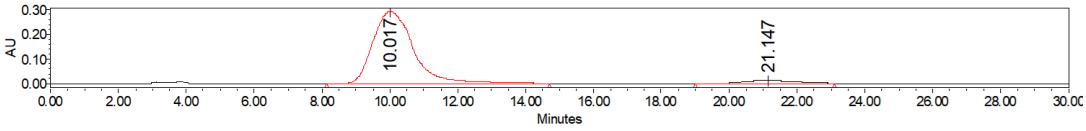
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) *δ* = – 112.94.

HR-MS (ESI) calcd for $C_{25}H_{24}FN_3O_4$ ([M]+Na^+) = 472.1643, found 472.1647.

IR (neat) ***ν*** (cm^{-1}): 3372, 2982, 1735, 1602, 1574, 1486, 1447, 1366, 1251, 1216, 1151, 1083, 1030, 859, 747, 682,

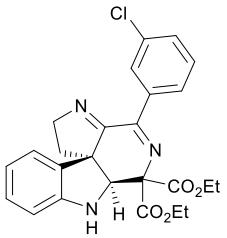


	Retention Time	% Area
1	10.060	50.44
2	20.912	49.56



	Retention Time	% Area
1	10.017	96.87
2	21.147	3.13

Diethyl (6a*S*,11b*R*)-4-(3-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C20)



0.1 mmol scale reaction, 60 h, 40.5 mg, 87% yield; yellow foam. Melting point: 139 – 141 ºC. 95% ee. $[\alpha]_D^{15}$ =

+189.8 (c = 0.17 in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 13.41 min, t_r (major) = 15.73 min.

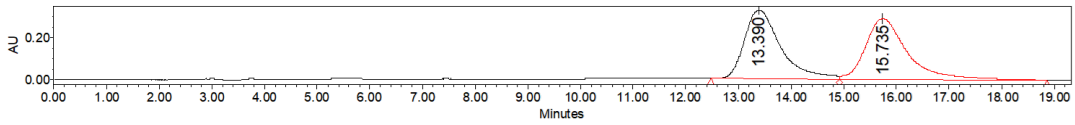
^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.01 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 6.96 (t, *J* = 6.6 Hz, 2H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 4.8 Hz, 1H), 4.51 – 4.43 (m, 2H), 4.39 – 4.25 (m, 1H), 4.31 – 4.23 (m, 2H), 4.22 – 4.09 (m, 2H), 2.72 – 2.55 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.83, 167.61, 167.32, 166.28, 136.36, 134.56, 131.61, 130.87, 129.60, 129.30, 128.24, 127.09, 122.64, 119.90, 110.28, 76.26, 70.84, 62.87, 62.76, 62.69, 60.57, 41.35, 14.34, 13.99.

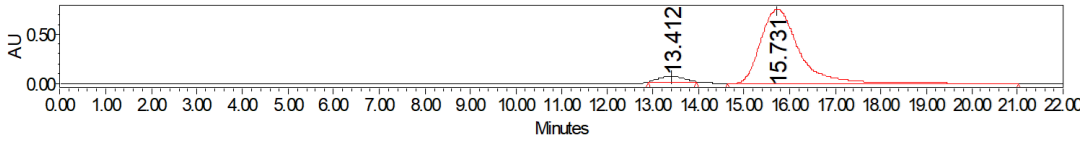
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{34.9689}ClN_3O_4$ ([M]+Na^+) = 488.1348, found 488.1344.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{36.9659}ClN_3O_4$ ([M]+Na^+) = 490.1318, found 490.1317.

IR (neat) ***ν*** (cm^{-1}): 3373, 2981, 1735, 1601, 1563, 1485, 1366, 1251, 1216, 1079, 1030, 859, 797, 746, 683.

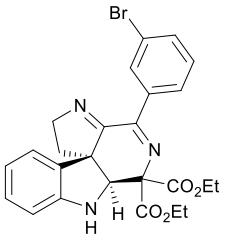


	Retention Time	% Area
1	13.390	49.62
2	15.735	50.38



	Retention Time	% Area
1	13.412	2.68
2	15.731	97.32

Diethyl (6a*S*,11b*R*)-4-(3-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C21)



0.1 mmol scale reaction, 60 h, 37.3 mg, 73% yield; yellow foam. Melting point: 155 – 157ºC. 92% ee. $[\alpha]_D^{15}$ = +243.3 (c = 0.58 in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 11.81 min, t_r (major) = 15.07 min.

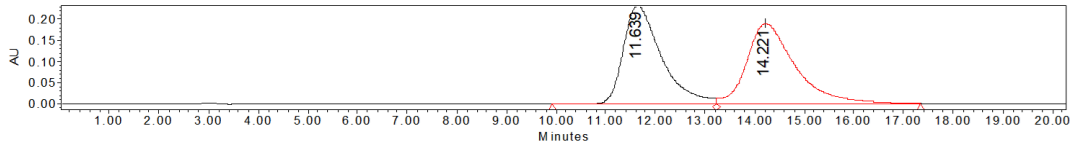
^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.17 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.67 (s, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 4.8 Hz, 1H), 4.50 – 4.41 (m, 2H), 4.38 – 4.33 (m, 1H), 4.27 – 4.21 (m, 2H), 4.21 – 4.09 (m, 2H), 2.74 – 2.55 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.82, 167.59, 167.23, 166.28, 149.07, 136.58, 134.53, 131.02, 130.86, 129.84, 129.31, 127.60, 122.72, 122.63, 119.90, 110.29, 76.25, 70.85, 62.88, 62.77, 62.70, 60.58, 41.33, 14.34, 13.99.

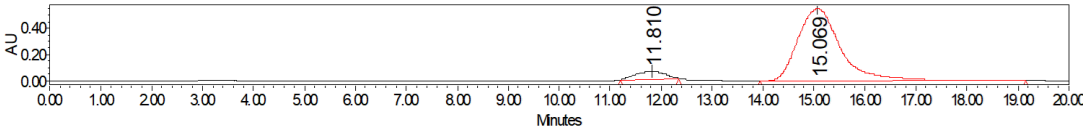
HR-MS (ESI) calcd for $C_{25}H_{24}^{78.9183}BrN_3O_4$ ([M]+Na^+) = 532.0842, found 532.0838.

HR-MS (ESI) calcd for $C_{25}H_{24}^{80.9163}BrN_3O_4$ ([M]+Na^+) = 534.0822, found 534.0828

IR (neat) ν (cm^{-1}): 3375, 2981, 1733, 1638, 1600, 1557, 1485, 1365, 1250, 1214, 1080, 1028, 858, 796, 736, 682, 465.

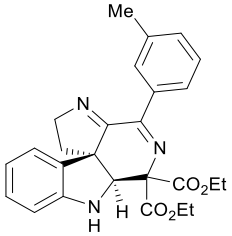


	Retention Time	% Area
1	11.639	49.11
2	14.221	50.89



	Retention Time	% Area
1	11.810	3.71
2	15.069	96.29

Diethyl (6a*S*,11b*R*)-4-(m-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C22)



0.1 mmol scale reaction, 45 h, 39.2 mg, 88% yield; yellow foam. Melting point: 129 – 131ºC. 96% ee. $[\alpha]_D^{15}$ = +114.5 (c = 0.36 in CH_2Cl_2).

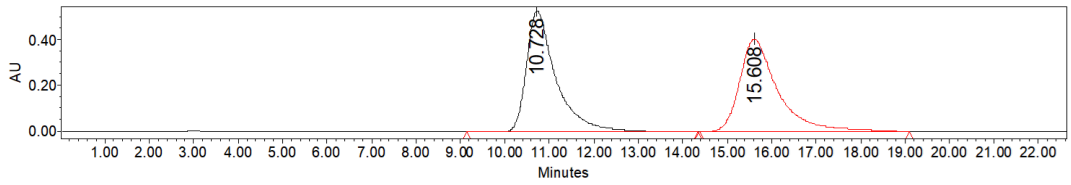
HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.76 min, t_r (major) = 15.49 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.68 (s, 1H), 7.20 (d, *J* = 4.8 Hz, 2H), 7.02 – 6.91 (m, 2H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.24 (d, *J* = 3.2 Hz, 1H), 4.51 – 4.42 (m, 2H), 4.40 – 4.33 (m, 1H), 4.29 – 4.24 (m, 2H), 4.21 – 4.09 (m, 2H), 2.72 – 2.54 (m, 2H), 2.32 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

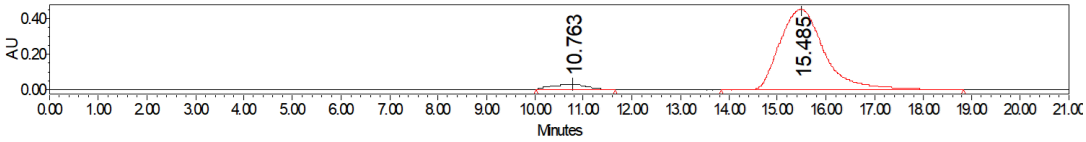
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 169.01, 168.76, 168.00, 166.54, 149.14, 138.00, 134.63, 132.47, 131.06, 129.12, 128.53, 128.13, 126.29, 122.70, 119.71, 110.19, 76.00, 62.79, 62.71, 62.58, 60.49, 41.39, 21.41, 14.33, 13.97.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^+) = 468.1894, found 468.1887.

IR (neat) ν (cm^{-1}): 3372, 2980, 1765, 1733, 1602, 1572, 1486, 1366, 1250, 1213, 1163, 1083, 1031, 859, 746, 692, 466.

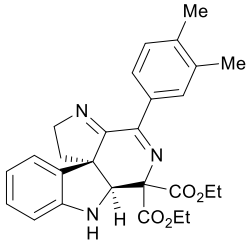


	Retention Time	% Area
1	10.728	50.46
2	15.608	49.54



	Retention Time	% Area
1	10.763	2.25
2	15.485	97.75

Diethyl (6aS,11bR)-4-(3,4-dimethylphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C23)



0.1 mmol scale reaction, 60 h, 37.7 mg, 82% yield; yellow foam. Melting point: 144 – 147ºC. 92% ee. $[\alpha]_D^{15}$ = +167.1 (c = 0.72 in CH_2Cl_2).

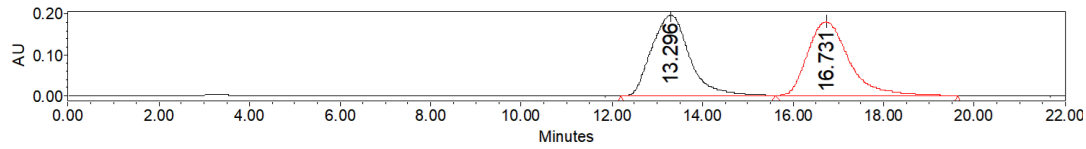
HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 13.26 min, t_r (major) = 16.63 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.80 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.63 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.23 (d, *J* = 4.2 Hz, 1H), 4.54 – 4.41 (m, 2H), 4.37 (m, 1H), 4.29 – 4.23 (m, 2H), 4.20 – 4.09 (m, 2H), 2.73 – 2.53 (m, 2H), 2.27 – 2.20 (m, 6H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.06, 168.50, 167.99, 166.64, 149.11, 136.54, 132.32, 131.09, 129.45, 129.01, 128.92, 126.64, 119.60, 110.10, 75.83, 71.00, 62.77, 62.61, 62.51, 60.43, 41.35, 19.91, 19.71, 14.28, 13.92.

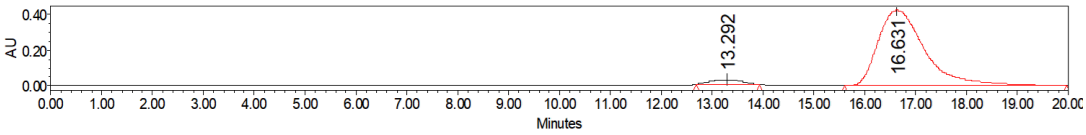
HR-MS (ESI) calcd for $C_{27}H_{29}N_3O_4$ ([M]+Na^+) = 482.2050, found 482.2057.

IR (neat) ***ν*** (cm^{-1}): 3373, 2979, 1766, 1733, 1603, 1560, 1486, 1367, 1248, 1215, 1163, 1082, 1030, 983, 858, 742, 446.



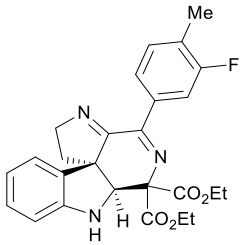
	Retention Time	% Area

1	13.296	50.18
2	16.731	49.82



	Retention Time	% Area
1	13.257	3.68
2	16.631	96.32

Diethyl (6aS,11bR)-4-(3-fluoro-4-methylphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C24)



0.1 mmol scale reaction, 60 h, 35.2 mg, 76% yield; yellow foam. Melting point: 166 – 168 ºC. 94% ee. $[\alpha]_D^{15}$ = +156.8 (c = 0.39 in CH_2Cl_2).

HPLC (Daicel chiralcel OJH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 8.63 min, t_r (major) = 9.81 min.

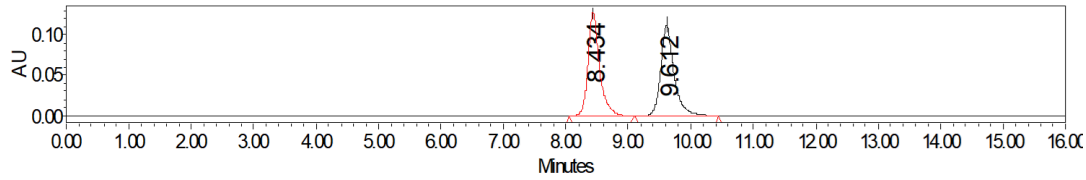
^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.66 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.67 – 6.61 (m, 1H), 6.51 – 6.47 (m, 1H), 5.22 (s, 1H), 4.47 – 4.41 (m, 2H), 4.38 – 4.32 (m, 1H), 4.26 – 4.22 (m, 2H), 4.20 – 4.08 (m, 2H), 2.75 – 2.52 (m, 2H), 2.24 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.88, 167.65, 167.26, 166.36, 161.87 (d, *J* = 244.8 Hz), 149.02, 131.22, 131.19 (d, *J* = 7.8 Hz), 130.89, 129.14, 124.23, 124.21, 122.58, 119.74, 114.86 (d, *J* = 24.2 Hz), 114.70, 110.16, 76.03, 70.80, 62.71, 62.68, 62.56, 60.45, 14.76, 14.73, 14.26, 13.90.

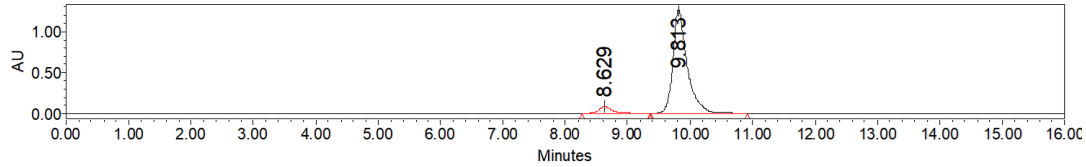
^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) *δ* = –117.34.

HR-MS (ESI) calcd for $C_{26}H_{26}FN_3O_4$ ([M]+Na^+) = 482.1800, found 482.1807.

IR (neat) ***ν*** (cm^{-1}): 3371, 2981, 1765, 1734, 1602, 1565, 1486, 1422, 1367, 1249, 1214, 1158, 1071, 1030, 858, 747, 457.

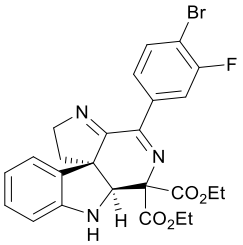


	Retention Time	% Area
1	8.434	50.17
2	9.612	49.83



	Retention Time	% Area
1	8.629	3.59
2	9.813	97.41

Diethyl (6a*S*,11b*R*)-4-(4-bromo-3-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C25)



0.1 mmol scale reaction, 72 h, 33.8 mg, 64% yield; yellow foam. Melting point: 171 – 173 ºC. 92% ee. $[\alpha]_D^{15}$ = +173.2 (c = 0.55 in CH_2Cl_2).

HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 12.02 min, t_r (major) = 21.03 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.87 (s, 1H), 7.62(d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 4.8 Hz, 1H), 4.51 – 4.47 (m, 2H), 4.44 – 4.41 (m, 1H), 4.34 – 4.29 (m, 2H), 4.18 – 4.14 (m, 2H), 2.64 – 2.57 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

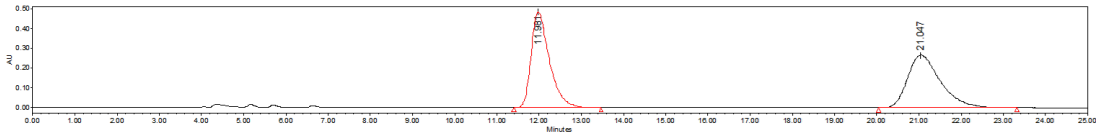
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.60, 166.29, 165.34, 165.01, 159.101 (d, *J* = 248.0 Hz), 147.90, 132.32 (d, *J* = 7.2 Hz), 129.67, 128.25, 124.28, 124.24, 121.44, 118.82, 115.24 (d, *J* = 25.2 Hz), 115.00, 109.16, 75.23, 69.64, 61.77, 61.66, 61.57 (d, *J* = 7.6 Hz), 59.48, 40.15, 13.21, 12.84.

^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) *δ* = –113.52

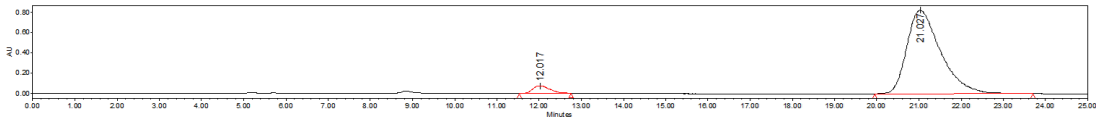
HR-MS (ESI) calcd for $C_{25}H_{23}{}^{78.9183}BrFN_3O_4$ ([M]+Na^+) = 550.0748, found 550.0751.

HR-MS (ESI) calcd for $C_{25}H_{23}{}^{80.9163}BrFN_3O_4$ ([M]+Na^+) = 552.0728, found 550.0734.

IR (neat) ***ν*** (cm^{-1}): 3369, 2981, 1734, 1639, 1601, 1564, 1484, 1422, 1367, 1247, 1213, 1163, 1081, 1038, 858, 742, 545, 466.

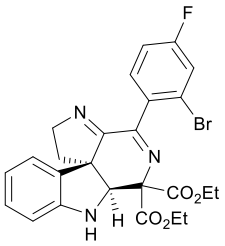


	Retention Time	% Area
1	11.981	50.18
2	21.047	49.82



	Retention Time	% Area	Height
1	12.017	3.64	77173
2	21.027	96.36	820974

Diethyl (6a*S*,11b*R*)-4-(2-bromo-4-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C26)



0.1 mmol scale reaction, 72 h, 36.5mg, 69% yield; white foam. Melting point: 171 – 173 ºC. 71% ee. $[\alpha]_D^{15}$ = +41.6 (c = 0.63 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 13.51 min, t_r (major) = 15.74 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 7.81 (d, *J* = 9.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.03 – 6.91 (m, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.22 (d, *J* = 4.8 Hz, 1H), 4.48 – 4.41 (m, 2H), 4.39 – 4.32 (m, 1H), 4.31 – 4.22 (m, 2H), 4.20 – 4.09 (m, 2H), 2.71 – 2.55 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

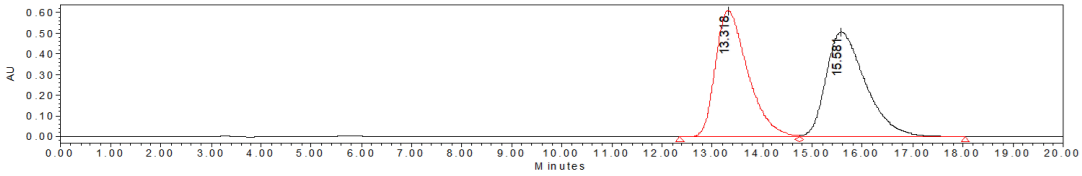
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.64, 167.33, 166.42, 166.05, 159.73 (d, *J* = 247.6 Hz), 148.94, 135.76 (d, *J* = 6.8 Hz), 133.38, 130.71, 129.30, 125.32, 122.49, 119.89, 116.24 (d, *J* = 24.2 Hz), 116.08, 110.25, 76.26, 70.68, 62.84, 62.69 (d, *J* = 7.6 Hz), 62.64, 60.53, 41.21, 14.26, 13.90.

^{19}F{^{1}H} NMR (565 MHz, Chloroform-*d*) *δ* = –106.85.

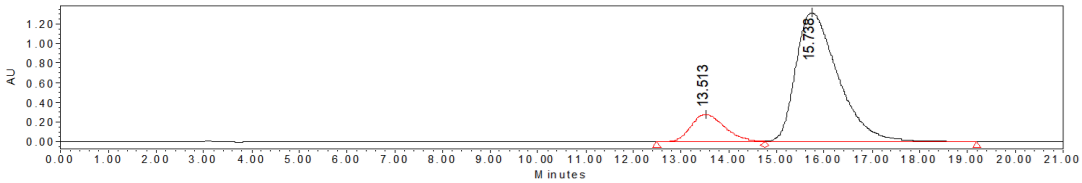
HR-MS (ESI) calcd for $C_{25}H_{23}{}^{78.9183}BrFN_3O_4$ ([M]+Na^+) = 550.0748, found 550.0747.

HR-MS (ESI) calcd for $C_{25}H_{23}{}^{80.9163}BrFN_3O_4$ ([M]+Na^+) = 552.0728, found 550.0729.

IR (neat) ***ν*** (cm^{-1}): 3369, 2981, 1734, 1639, 1601, 1564, 1484, 1422, 1367, 1247, 1213, 1163, 1081, 1038, 858, 742, 545, 466.

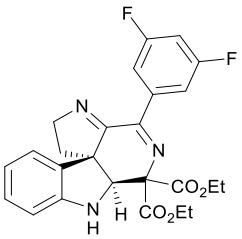


	Retention Time	% Area
1	13.318	49.73
2	15.581	50.27



	Retention Time	% Area
1	13.513	14.49
2	15.738	85.51

Diethyl (6a*S*,11b*R*)-4-(3,5-difluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C27)



0.1 mmol scale reaction, 60 h, 35.0 mg, 75% yield; white foam. Melting point: 146 – 148 ºC. 95% ee. $[\alpha]_D^{17}$ = +279.3 (c = 0.78 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 21.69 min, t_r (minor) = 23.27 min.

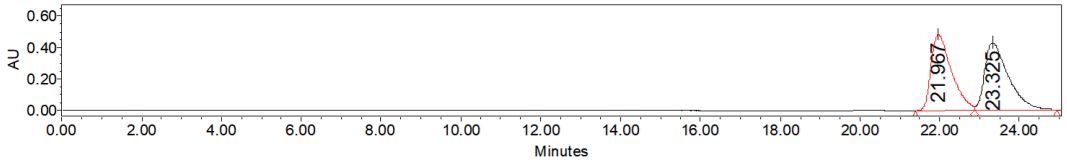
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.02 – 6.94 (m, 2H), 6.85 (t, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.23 (d, *J* = 5.4 Hz, 1H), 4.49 – 4.43 (m, 2H), 4.40 – 4.36 (m, 1H), 4.32 – 4.22 (m, 2H), 4.21 – 4.10 (m, 2H), 2.69 – 2.56 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) δ 168.61, 167.26, 166.23, 166.00, 163.612 (d, *J* = 248.9 Hz) 148.92, 130.67, 129.32, 122.53, 122.35, 119.95, 119.70, 111.62 (d, *J* = 27.3 Hz), 111.44, 110.24, 76.31, 70.69, 62.88 (d, *J* = 7.6 Hz), 62.66, 60.52, 41.24, 14.26, 13.90.

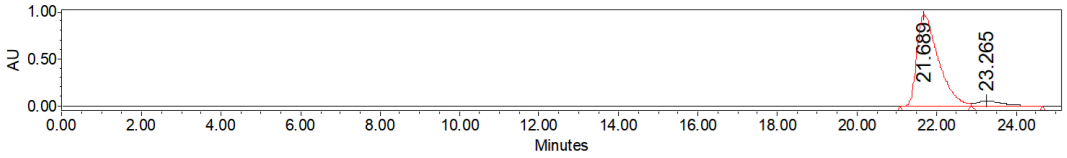
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ = –109.28.

HR-MS (ESI) calcd for $C_{25}H_{23}NF_2N_3O_4$ ([M]+Na^+) = 490.1549, found 490.1541.

IR (neat) ***v*** (cm^{-1}): 3374, 2983, 1735, 1601, 1581, 1485, 1440, 1369, 1299, 1250, 1214, 1156, 1119, 1079, 986, 858, 744, 676, 464.

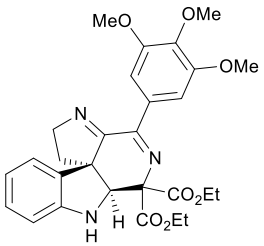


	Retention Time	% Area
1	21.967	49.32
2	23.325	50.68



	Retention Time	% Area
1	21.689	97.61
2	23.265	2.29

Diethyl (6a*S*,11b*R*)-4-(3,4,5-trimethoxyphenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C28)



0.1 mmol scale reaction, 96 h, 34.4 mg, 66% yield; yellow foam. Melting point: 121 – 123 ºC. 94% ee. $[\alpha]_D^{17}$ =

+261.9 (c = 0.83 in CH_2Cl_2).

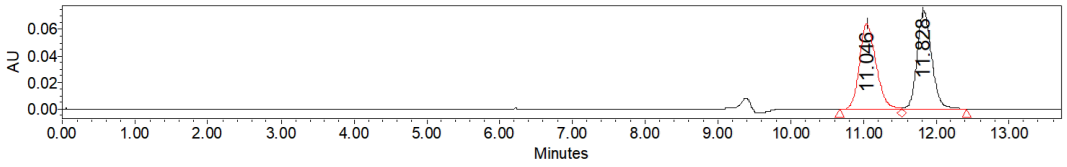
HPLC (Daicel chiralcel OJH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.94 min, t_r (minor) = 12.11 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.19 (s, 1H), 7.08 (s, 2H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.57 (t, *J* = 7.4 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 4.33 – 4.24 (m, 1H), 4.24 – 4.15 (m, 2H), 4.14 – 4.02 (m, 2H), 3.75 (m, 9H), 2.65 – 2.49 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H).

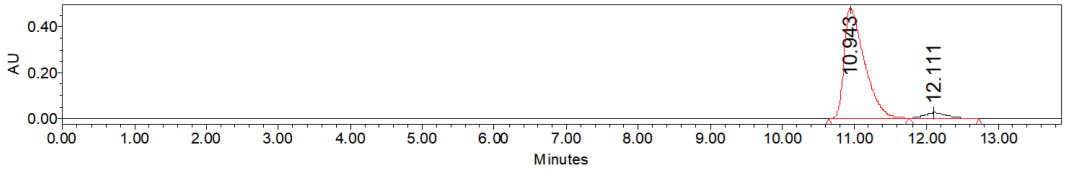
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.890, 167.20, 151.85, 148.10, 140.25, 129.85, 129.30, 128.19, 121.34, 118.41, 109.18, 105.06, 69.91, 61.87, 61.60, 61.43, 59.79, 59.53, 55.16, 28.68, 13.21, 12.88.

HR-MS (ESI) calcd for $C_{28}H_{31}N_3O_7$ ([M]+Na^+) = 544.2054, found 544.2049.

IR (neat) ***ν*** (cm^{-1}): 3353, 2931, 1734, 1598, 1568, 1369, 1244, 1125, 1090, 1031, 860, 802, 745, 465.

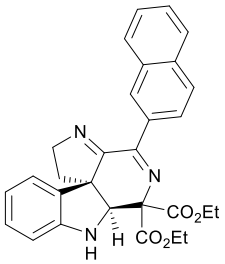


	Retention Time	% Area
1	11.046	49.90
2	11.828	50.10



	Retention Time	% Area
1	10.943	96.98
2	12.111	3.02

Diethyl (6a*S*,11b*R*)-4-(naphthalen-2-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C29)



0.1 mmol scale reaction, 60 h, 29.3 mg, 67% yield; yellow foam. Melting point: 155 – 157 ºC. 92% ee. $[\alpha]_D^{15}$ = +168.7 (c = 0.14 in CH_2Cl_2).

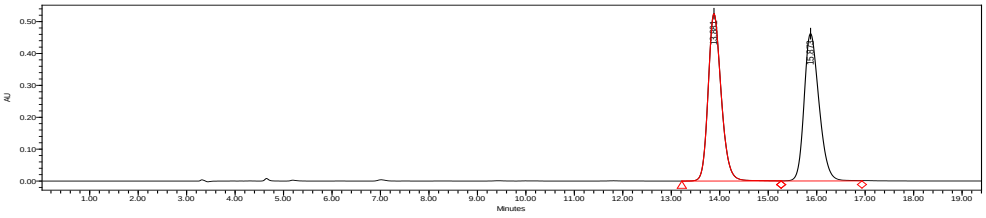
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.90 min, t_r (minor) =16.03 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.48 (s, 1H), 8.16 (d, *J* = 10.2 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.47 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.28 (d, *J* = 4.8 Hz, 1H), 4.57 – 4.40 (m, 3H), 4.32 (m, 1H), 4.25 (m, 1H), 4.22 – 4.10 (m, 2H), 2.81 – 2.57 (m, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

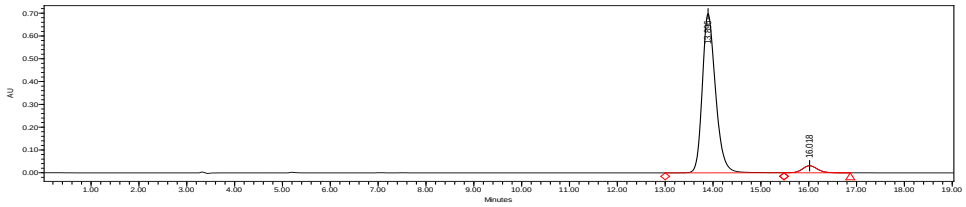
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 169.10, 168.36, 168.07, 166.62, 135.06, 132.82, 132.13, 130.21, 129.20, 128.09, 127.71, 127.62, 126.23, 124.55, 122.73, 119.84, 110.27, 76.20, 71.13, 63.02, 62.82, 62.69, 60.67, 41.47, 14.40, 14.02.

HR-MS (ESI) calcd for $C_{29}H_{27}N_3O_4$ ([M]+Na^+) = 504.1894, found 504.1891.

IR (neat) ***ν*** (cm^{-1}): 3369, 2980, 1734, 1602,1486, 1367, 1253, 1217, 1075, 1029, 862, 821, 747,472.

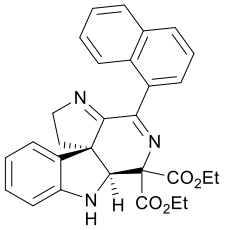


	Retention Time	% Area
1	13.881	50.06
2	15.873	49.94



	Retention Time	% Area
1	13.896	95.68
2	16.018	4.12

Diethyl (6a*S*,11b*R*)-4-(naphthalen-1-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C30)



0.1 mmol scale reaction, 60 h, 32.0 mg, 68% yield; yellow foam. Melting point: 161 – 163 ºC. 67% ee. $[\alpha]_D^{15}$ = +31.3 (c = 0.13 in CH_2Cl_2).

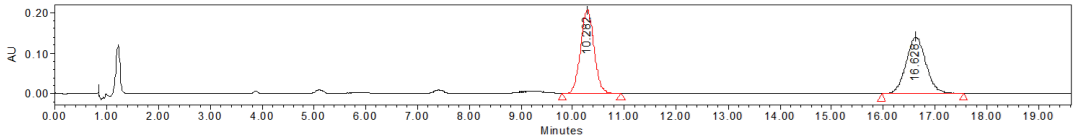
HPLC (Daicel chiralcel OJH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.27 min, t_r (major) = 16.56 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.30 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.31 (m, 4H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.32 (d, *J* = 4.8 Hz, 1H), 4.50 – 4.37 (m, 3H), 4.31 – 4.25 (m, 3H), 4.19 (m, 1H), 2.65 (s, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

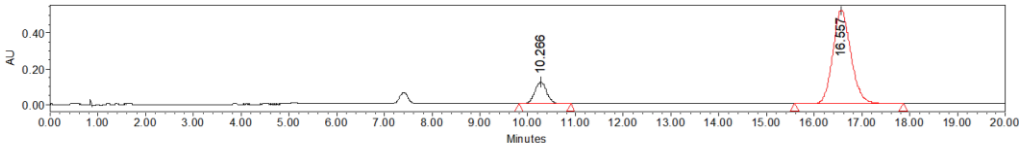
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 171.20, 169.49, 168.99, 166.53, 149.37, 133.94, 133.04, 131.16, 131.11, 130.84, 129.55, 129.21, 128.21, 126.95, 126.03, 125.99, 124.78, 123.24, 119.54, 110.01, 76.29, 70.21, 62.91, 62.65, 62.27, 60.29, 14.27, 14.07.

HR-MS (ESI) calcd for $C_{29}H_{27}N_3O_4$ ([M]+Na^+) = 504.1894, found 504.1890.

IR (neat) ***ν*** (cm^{-1}): 3367, 2979, 2361, 2156, 1967,1735, 1601, 1581, 1552, 1485, 1394, 1366, 1252, 1216, 1081, 1029, 831, 745, 491, 461.

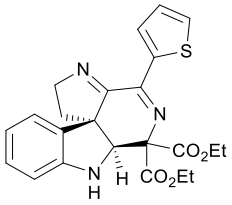


	Retention Time	% Area
1	10.282	50.24
2	16.628	49.76



	Retention Time	% Area
1	10.266	16.39
2	16.557	83.61

Diethyl (6a*S*,11b*R*)-4-(thiophen-2-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C31)



0.1 mmol scale reaction, 60 h, 36.7 mg, 84% yield; yellow foam. Melting point: 136 – 138 ºC. 92% ee. $[\alpha]_D^{17}$ = +37.9 (c = 0.11 in CH_2Cl_2).

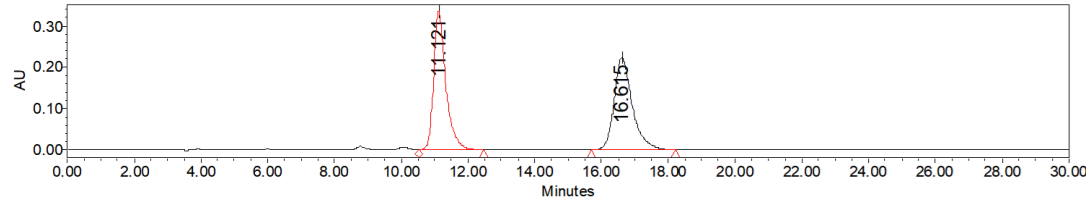
HPLC (Daicel chiralcel OJH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 11.15 min, t_r (major) = 16.54 min.

^{1}H NMR (600 MHz, Chloroform-*d*) *δ* 8.05 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 5.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.98 – 6.89 (m, 2H), 6.62 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 4.50 – 4.40 (m, 2H), 4.37 – 4.31 (m, 1H), 4.27 – 4.23 (m, 2H), 4.21 – 4.14 (m, 1H), 4.14 – 4.06 (m, 1H), 2.72 – 2.53 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

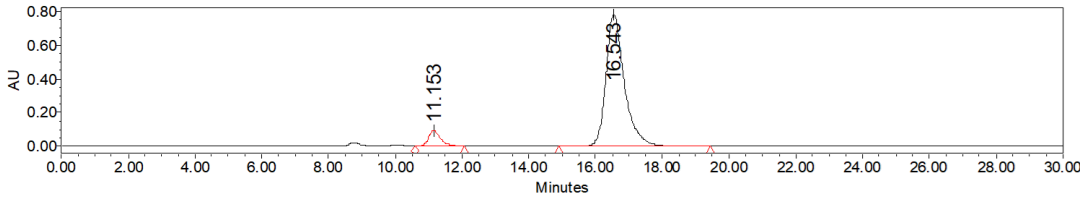
^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*) *δ* 168.95, 168.22, 166.62, 163.53, 148.96, 138.14, 131.19, 129.07, 125.74, 122.55, 119.72, 110.16, 75.86, 70.34, 62.67, 62.47, 62.25, 60.30, 41.56, 14.27, 13.91.

HR-MS (ESI) calcd for $C_{23}H_{23}N_3O_4$([M]+Na^+) = 460.1302, found 460.1307.

IR (neat) ***ν*** (cm^{-1}): 3365,2980, 1764, 1731, 1601, 1573, 1519, 1486, 1367, 1251, 1215, 1089, 1069, 1029, 858, 814, 742, 466.

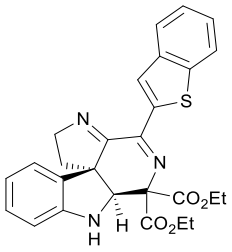


	Retention Time	% Area
1	11.121	50.05
2	16.615	49.95



	Retention Time	% Area
1	11.153	4.49
2	16.543	95.51

Diethyl (6a*S*,11b*R*)-4-(benzo[b]thiophen-2-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C32)



0.1 mmol scale reaction, 60 h, 35.6 mg, 73% yield; yellow foam. Melting point: 149 – 151 ºC. 95% ee. $[\alpha]_D^{17}$ = +154.9 (c = 0.67 in CH_2Cl_2).

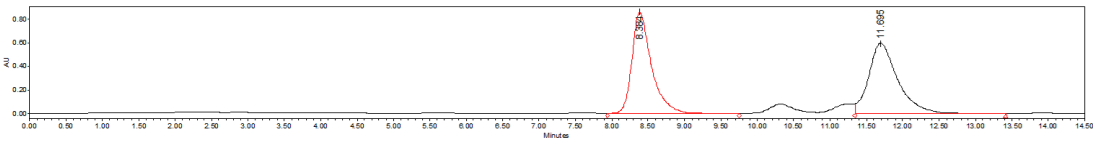
HPLC (Daicel chiralcel OJH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 8.35 min, t_r (major) = 11.47 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.02 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.27 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 5.21 (d, *J* = 2.8 Hz, 1H), 4.50 – 4.46 (m, 2H), 4.43 – 4.31 (m, 2H), 4.30 – 4.21 (m, 1H), 4.19 – 4.12 (m, 2H), 2.75 – 2.54 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

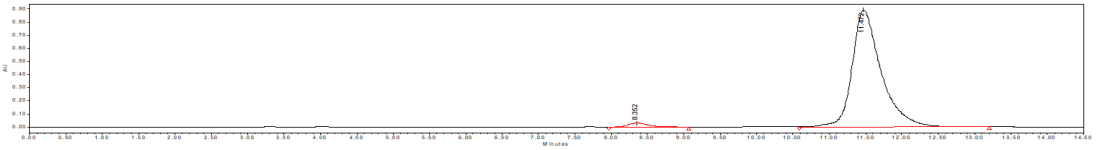
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.75, 166.44, 165.18, 163.17, 148.53, 147.94, 135.89, 129.96, 129.71, 128.27, 128.24, 128.11, 126.30, 126.04, 125.92, 121.50, 118.87, 109.19, 69.68, 61.81, 61.65, 61.61, 59.55, 40.24, 13.23.

HR-MS (ESI) calcd for $C_{27}H_{25}N_3O_4S$ ([M]+Na^+) = 510.1458, found 510.1455.

IR (neat) ***ν*** (cm^{-1}): 3365,2980, 1764, 1731, 1601, 1573, 1519, 1486, 1367, 1251, 1215, 1089, 1069, 1029, 858, 811, 742, 463.

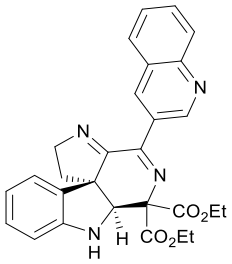


	Retention Time	% Area
1	8.384	49.31
2	11.695	50.69



	Retention Time	% Area
1	8.352	2.19
2	11.472	97.81

Diethyl (6a*S*,11b*R*)-4-(quinolin-3-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C33)



0.1 mmol scale reaction, 96 h, 33.3 mg, 69% yield; yellow foam. Melting point: 147 – 149 ºC. 87% ee. $[\alpha]_D^{17}$ = +117.4 (c = 0.16 in CH_2Cl_2).

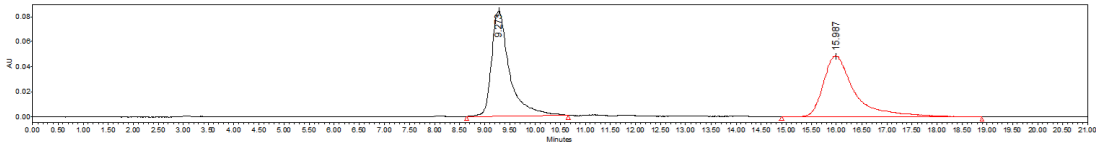
HPLC (Daicel chiralcel OXH, hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 9.23 min, t_r (major) = 15.82 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 9.48 (d, *J* = 1.8 Hz, 1H), 8.79 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.28 (d, *J* = 4.8 Hz, 1H), 4.51 – 4.43 (m, 3H), 4.34 – 4.28 (m, 2H), 4.21 – 4.16 (m, 2H), 2.77 – 2.58 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

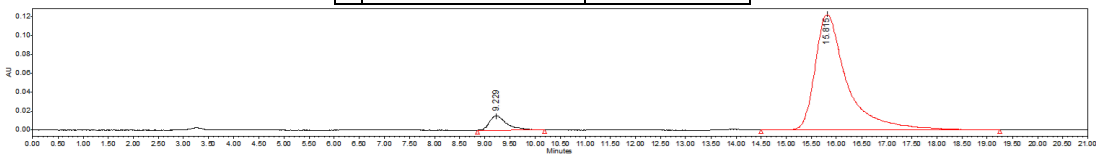
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.75, 166.44, 165.18, 163.17, 148.53, 147.94, 135.89, 129.96, 129.71, 128.27, 128.24, 128.11, 126.30, 126.04, 125.92, 121.50, 118.87, 109.19, 69.68, 61.81, 61.65, 61.61, 59.55, 40.24, 13.23.

HR-MS (ESI) calcd for $C_{28}H_{26}N4O_4$ ([M]+Na^+) = 505.1846, found 505.1852.

IR (neat) ***ν*** (cm^{-1}): 3372, 2979, 2361, 1972, 1735, 1602, 1488, 1370, 1250, 1215, 1078, 1030, 861, 790, 749, 477.

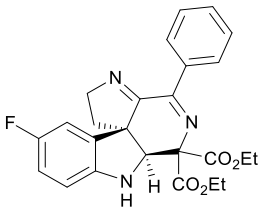


	Retention Time	% Area
1	9.273	49.99
2	15.987	50.01



	Retention Time	% Area
1	9.229	6.43
2	15.815	93.57

Diethyl (6a*S*,11b*R*)-10-fluoro-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C34)



0.1 mmol scale reaction, 72 h, 31.9 mg, 71% yield; yellow foam. Melting point: 153 – 155 ºC. 91% ee. $[\alpha]_D^{17}$ = +89.7 (c = 0.09 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 19.30 min, t_r (major) = 26.94 min.

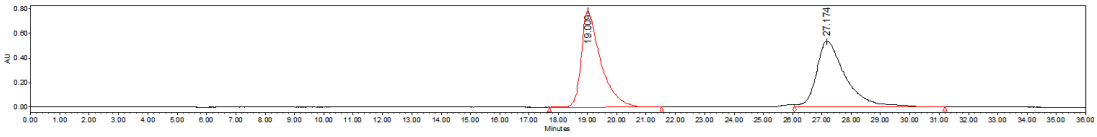
^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.72 (t, *J* = 8.8 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.13 – 7.06 (m, 1H), 7.00 – 6.93 (m, 2H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 5.2 Hz, 1H), 4.46 (m, 2H), 4.41 – 4.33 (m, 1H), 4.29 – 4.24 (m, 2H), 4.21 – 4.17 (m, 2H), 2.74 – 2.53 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.76, 166.55, 166.30, 166.26 (d, *J* = 246.7 Hz), 160.39, 165.20,162.84, 147.96, 129.78, 128.79 (d, *J* = 8.0 Hz), 128.71, 128.17, 123.48, 123.45, 121.53, 118.73, 117.53, 114.30 (d, *J* = 23.2 Hz), 114.07, 109.09, 61.69, 61.64 (d, *J* = 7.2 Hz), 61.51, 59.43, 40.22, 13.20, 12.85.

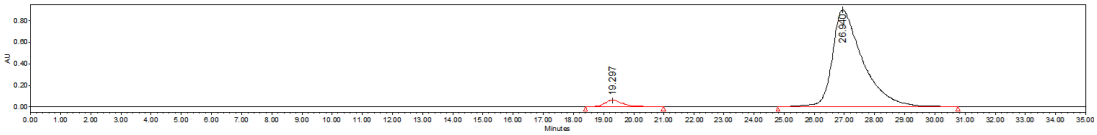
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) *δ* = –112.98.

HR-MS (ESI) calcd for $C_{25}H_{24}FN_3O_4$ ([M]+Na^+) = 472.1643, found 472.1649.

IR (neat) ***ν*** (cm^{-1}): 3367, 2977, 1738, 1610, 1571, 1467, 1451, 1368, 1244, 1212, 1159, 1071, 1023, 856, 737, 681.

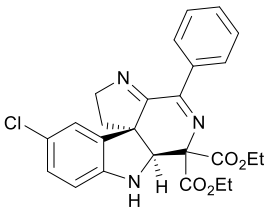


	Retention Time	% Area
1	19.009	49.24
2	27.174	50.76



	Retention Time	% Area
1	19.297	4.48
2	26.940	95.52

Diethyl (6a*S*,11b*R*)-10-chloro-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C35)



0.1 mmol scale reaction, 72 h, 31.2 mg, 67% yield; yellow foam. Melting point: 161 – 163 ºC. 93% ee. $[\alpha]_D^{17}$ = +269.4 (c = 0.71 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 17.49 min, t_r (major) = 22.75 min.

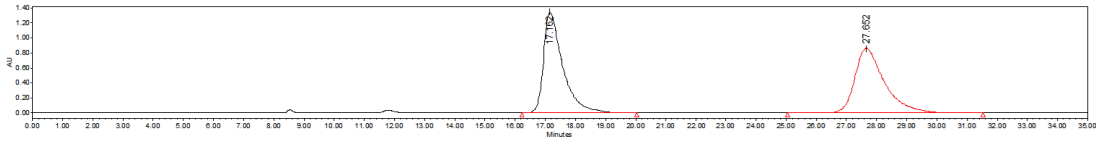
^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.89 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 4.8 Hz, 1H), 4.46 – 4.39 (m, 2H), 4.36 – 4.28 (m, 1H), 4.27 – 4.17 (m, 2H), 4.13 – 4.07 (m, *J* = 2H), 2.68 – 2.50 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.77, 166.61, 166.26, 165.25, 147.98, 136.81, 132.05, 129.80, 128.86, 128.17, 127.48, 121.47, 118.72, 109.13, 75.07, 69.69, 61.67, 61.50, 59.43, 40.20, 13.21, 12.85.

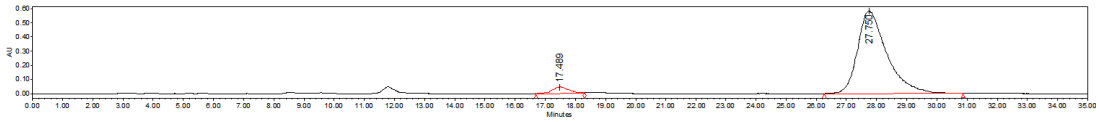
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{34.9689}ClN_3O_4$ ([M]+Na^+) = 488.1348, found 488.1355.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{36.9659}ClN_3O_4$ ([M]+Na^+) = 490.1318, found 490.1326.

IR (neat) ***ν*** (cm^{-1}): 3376, 2978, 1731, 1607, 1557, 1487, 1367, 1246, 1213, 1078, 1049, 879, 778, 741, 677.

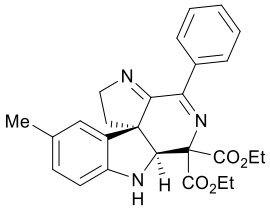


	Retention Time	% Area
1	17.162	50.24
2	27.652	49.76



	Retention Time	% Area
1	17.489	3.74
2	27.750	96.26

Diethyl (6a*S*,11b*R*)-10-methyl-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C36)



0.1 mmol scale reaction, 70 h, 25.0 mg, 56% yield; yellow foam. Melting point: 135 – 137 ºC. 90% ee. $[\alpha]_D^{17}$ = +149.6 (c = 0.85 in CH_2Cl_2).

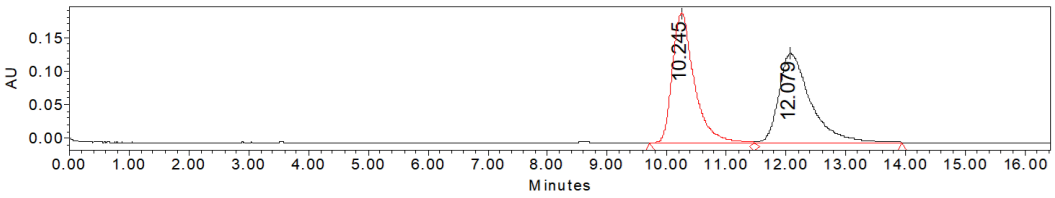
HPLC (Daicel chiralcel OXH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.78 min, t_r (major) = 12.58 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.84 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.89 (m, 2H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 5.21 (d, *J* = 4.8 Hz, 1H), 4.48 – 4.43 (m, 2H), 4.40 – 4.30 (m, 1H), 4.29 – 4.19 (m, 2H), 4.19 – 4.06 (m, 2H), 2.72 – 2.52 (m, 2H), 2.30 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

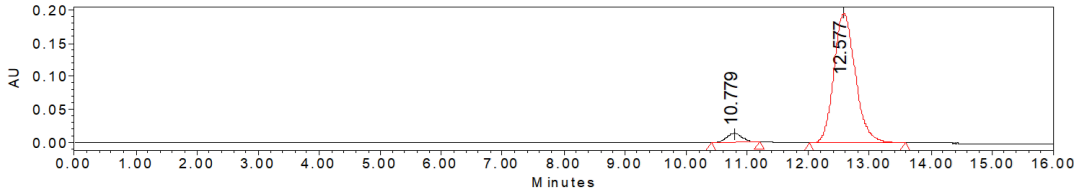
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 169.05, 167.94, 166.59, 165.25, 149.09, 141.92, 132.07, 131.05, 129.05, 128.95, 128.57, 122.62, 119.60, 110.05, 77.36, 70.85, 62.70, 62.57, 62.45, 60.40, 21.52, 14.24, 13.89, 1.03.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^+) = 468.1894, found 468.1889.

IR (neat) ***v*** (cm^{-1}): 3381, 2977, 1731, 1611, 154, 1478, 1365, 1257, 1206, 1087, 863, 817, 746, 497, 461.

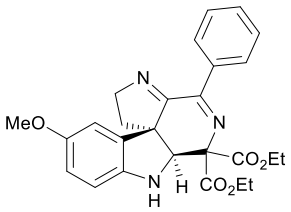


	Retention Time	% Area
1	10.245	50.15
2	12.079	49.85



	Retention Time	% Area
1	10.779	5.02
2	12.577	94.98

Diethyl (6a*S*,11b*R*)-10-methoxy-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C37)



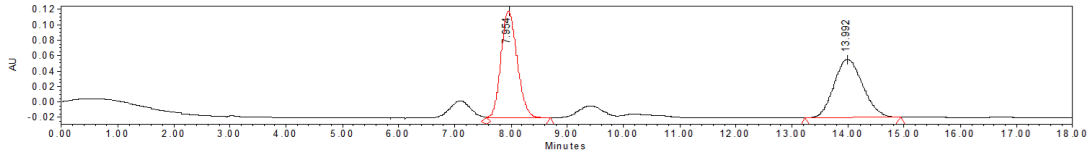
0.1 mmol scale reaction, 72 h, 29.4 mg, 66% yield; yellow foam. Melting point: 123– 125 ºC. 93% ee. $[\alpha]_D^{17}$ = +203.7 (c = 0.39 in CH_2Cl_2).

HPLC (Daicel chiralcel ADH, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.86 min, t_r (minor) = 13.98 min.

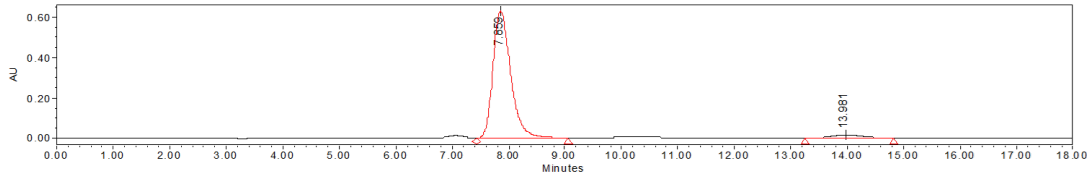
^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.56 (d, *J* = 7.6 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.06 – 7.02 (m, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.79 – 6.68 (m, 2H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.22 (s, 1H), 4.45 – 4.40 (m, 2H), 4.33 – 4.30 (m, 1H), 4.28 – 4.15 (m, 3H), 4.10 (d, 1H), 3.38 (s, 3H), 2.58 (d, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) *δ* 169.54, 167.97, 167.55, 165.30, 157.06, 148.07, 131.13, 131.05, 129.80, 127.68, 125.19, 122.84, 119.64, 117.83, 110.22, 108.53, 74.94, 69.22, 61.52, 61.43, 60.17, 58.72, 54.03, 40.87, 13.15.

IR (neat) ***ν*** (cm^{-1}): 3377, 2987, 1733, 1607, 1571, 1488, 1361, 1254, 1127, 1071, 859, 821, 747, 496, 468.

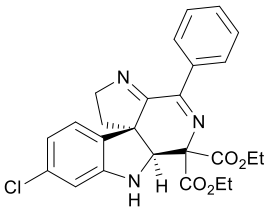


	Retention Time	% Area
1	7.954	50.66
2	13.992	49.34



	Retention Time	% Area
1	7.859	96.72
2	13.981	3.28

Diethyl (6a*S*,11b*R*)-9-chloro-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C38)



0.1 mmol scale reaction, 72 h, 32.6 mg, 70% yield; yellow foam. Melting point: 180– 182 ºC. 95% ee. $[\alpha]_D^{17}$ = +265.9 (c = 0.63 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 11.02 min, t_r (minor) = 26.18 min.

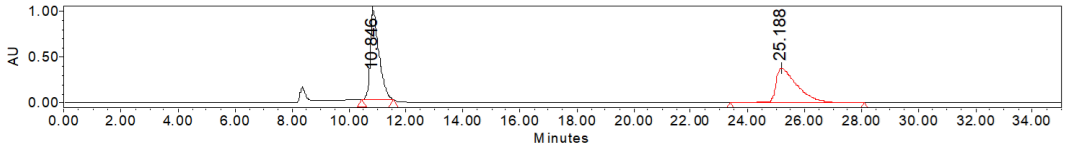
^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.01 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.26 (s, 1H), 7.01 – 6.93 (m, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.23 (d, *J* = 4.8 Hz, 1H), 4.49 – 4.44 (m, 2H), 4.42 – 4.33 (m, 1H), 4.31 – 4.21 (m, 2H), 4.17 – 4.14 (m, 2H), 2.71 – 2.55 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 167.73, 166.50, 166.20, 165.18, 135.28, 133.45, 130.47, 129.76, 128.46, 128.19, 127.16, 125.96, 121.53, 118.76, 109.11, 69.73, 61.72, 61.66, 61.54, 59.46, 40.21, 13.21, 12.85.

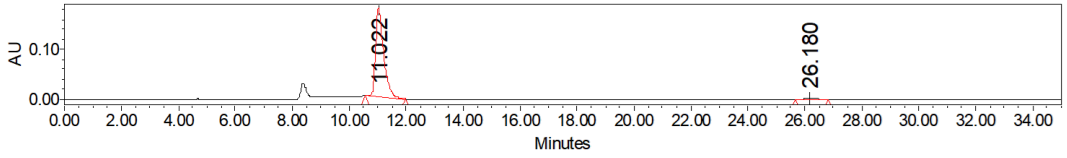
HR-MS (ESI) calcd for $C_{25}H_{24}^{34.9689}ClN_3O_4$ ([M]+Na^+) = 488.1348, found 488.1341

HR-MS (ESI) calcd for $C_{25}H_{24}^{36.9659}ClN_3O_4$ ([M]+Na^+) = 490.1318, found 490.1311.

IR (neat) ***ν*** (cm^{-1}): 3377, 2981, 1733, 1607, 1561, 1487, 1361, 1257, 1210, 1078, 1023, 869, 787, 745, 687.

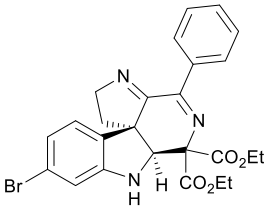


	Retention Time	% Area
1	10.846	51.72
2	25.188	48.28



	Retention Time	% Area
1	11.022	97.36
2	26.180	2.64

Diethyl (6a*S*,11b*R*)-9-bromo-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C39)



0.1 mmol scale reaction, 72 h, 39.8 mg, 78% yield; yellow foam. Melting point: 164 – 167 ºC. 90% ee. $[\alpha]_D^{17}$ = +208.1 (c = 0.59 in CH_2Cl_2).

HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.41 min, t_r

(minor) = 20.77 min.

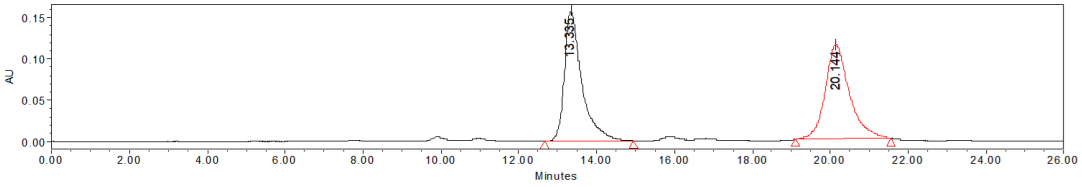
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.90 (t, J = 7.2 Hz, 2H), 6.58 (t, J = 7.4 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 5.14 (d, J = 4.8 Hz, 1H), 4.41 – 4.37 (m, 2H), 4.35 – 4.25 (m, 1H), 4.25 – 4.15 (m, 2H), 4.08 (m, 2H), 2.65 – 2.46 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 168.76, 167.52, 167.13, 166.21, 149.00, 136.54, 134.42, 130.97, 130.78, 129.74, 129.23, 127.51, 122.63, 122.55, 119.79, 110.15, 70.77, 62.77, 62.71, 62.59, 60.50, 41.23, 14.24, 13.89.

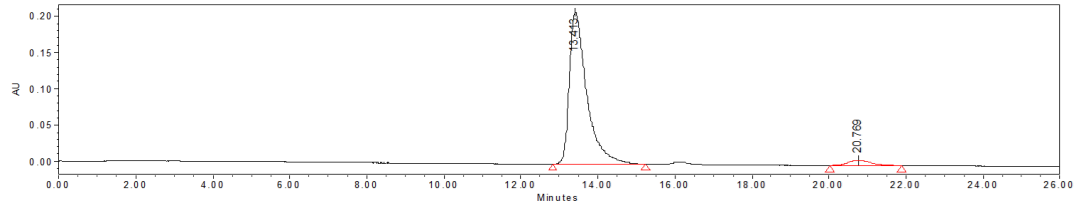
HR-MS (ESI) calcd for $C_{25}H_{24}{}^{78.9183}BrN_3O_4$ ([M]+Na^{+}) = 532.0842, found 532.0846.

HR-MS (ESI) calcd for $C_{25}H_{24}{}^{80.9163}BrN_3O_4$ ([M]+Na^{+}) = 534.0822, found 534.0827.

IR (neat) ν (cm^{-1}): 3379, 2987, 1731, 1631, 1607, 1568, 1481, 1366, 1243, 1211, 1087, 1021, 851, 786, 739, 683, 467.

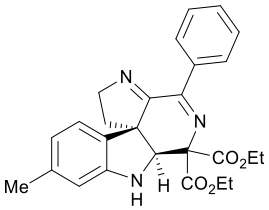


	Retention Time	% Area
1	13.335	49.78
2	20.144	50.22



	Retention Time	% Area
1	13.413	95.17
2	20.769	4.83

Diethyl (6a*S*,11b*R*)-9-methyl-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C40)



0.1 mmol scale reaction, 72 h, 29.8 mg, 67% yield; yellow foam. Melting point: 165– 167 ºC. 91% ee. $[\alpha]_D^{17}$ = +174.3 (c = 0.79 in CH_2Cl_2).

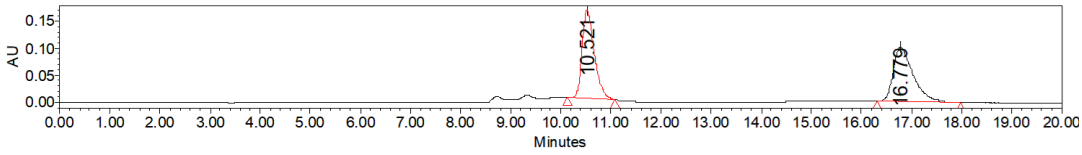
HPLC (Daicel chiralcel ASH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.33 min, t_r (minor) = 16.43 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.65 – 7.58 (m, 1H), 7.13 (d, J = 4.8 Hz, 2H), 6.93 – 6.85 (m, 2H), 6.57 (t, J = 7.2 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 5.16 (s, 1H), 4.39 (m, 2H), 4.30 (m, 1H), 4.21 – 4.16 (m, 2H), 4.13 – 3.99 (m, 2H), 2.72 – 2.47 (m, 2H), 2.25 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H).

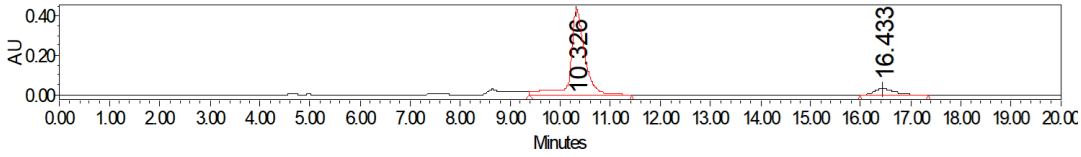
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 167.94, 167.67, 166.92, 165.46, 148.05, 136.89, 133.58, 131.34, 129.97, 127.47, 127.03, 125.18, 121.61, 118.59, 109.04, 74.92, 69.88, 61.71, 61.59, 61.46, 59.39, 40.27, 20.30, 13.22, 12.86.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^{+}) = 468.1894, found 468.1895.

IR (neat) ***ν*** (cm^{-1}): 3377, 2978, 1733, 1617, 1541, 1477, 1361, 1256, 1207, 1088, 859, 816, 741, 499, 467.

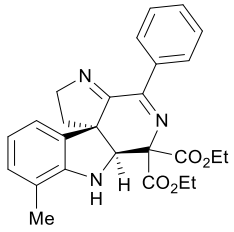


	Retention Time	% Area
1	10.521	50.20
2	16.779	49.80



	Retention Time	% Area
1	10.326	95.44
2	16.433	4.56

Diethyl (6aS,11bR)-8-methyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C41)



0.1 mmol scale reaction,72 h, 27.2mg, 71% yield; yellow foam. Melting point: 144 – 146 ºC. 92% ee. $[\alpha]_D^{17}$ = +73.3 (c = 0.17 in CH_2Cl_2).

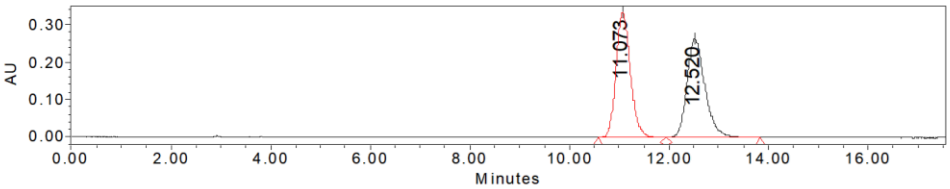
HPLC (Daicel chiralcel AYH, hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 10.63 min, t_r (major) = 12.07 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.81 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.86 (m, 2H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 4.44 – 4.39 (m, 2H), 4.36 – 4.27 (m, 1H), 4.26 – 4.15 (m, 2H), 4.15 – 4.02 (m, 2H), 2.69 – 2.49 (m, 2H), 2.27 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H).

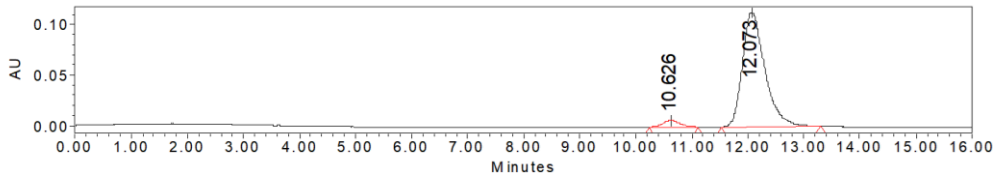
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 168.00, 167.21, 166.90, 165.55, 148.06, 140.86, 131.04, 130.01, 128.00, 127.90, 127.53, 121.57, 118.55, 109.01, 74.85, 69.81, 61.67, 61.52, 61.39, 59.36, 40.29, 20.48, 13.21, 12.85.

HR-MS (ESI) calcd for $C_{26}H_{27}N_3O_4$ ([M]+Na^+) = 468.1894, found 468.1888.

IR (neat) ***ν*** (cm^{-1}): 3388, 2977, 1731, 1609, 1537, 1471, 1369, 1251, 1211, 1077, 867, 823, 747, 491, 459.

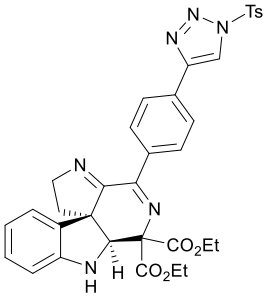


	Retention Time	% Area
1	11.073	50.12
2	12.520	49.88



	Retention Time	% Area
1	10.626	4.00
2	12.073	96.00

Diethyl (3a*S*,6a*S*,11b*R*)-3,7-diacetyl-4-(4-(1-tosyl-1H-1,2,3-triazol-4-yl)phenyl)-1,2,3,3a,6a,7-hexahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (D13)



91% yield; yellow foam. Melting point: 157-159 ºC. 97% ee. $[\alpha]_D^{17}$ = +245.8 (c = 0.27 in CH_2Cl_2).

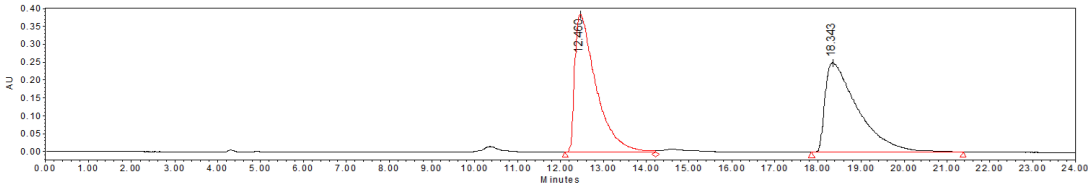
HPLC (Daicel chiralcel ODH, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm) t_r (minor) = 12.91 min, t_r (major) = 18.03 min.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.33 (d, *J* = 7.8 Hz, 1H), 8.02 (m, 4H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.02 – 6.90 (m, 2H), 6.64 (t, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.24 (d, *J* = 4.8 Hz, 1H), 4.52 – 4.37 (m, 3H), 4.31 – 4.27 (m, 2H), 4.21 – 4.17 (m, 1H), 4.14 – 4.05 (m, 1H), 2.74 – 2.55 (m, 2H), 2.42 (m, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) *δ* 168.83, 167.75, 166.32, 149.04, 147.50, 146.61, 135.08, 132.87, 130.90, 130.54, 129.27, 129.17, 128.76, 125.80, 122.59, 119.79, 119.58, 76.18, 70.85, 62.77, 62.74, 62.59, 41.31, 21.89, 14.28, 13.92.

HR-MS (ESI) calcd for $C_{34}H_{32}N_6O_6$ ([M]+Na^+) = 675.1996, found 675.1998.

IR (neat) ***ν*** (cm^{-1}): 3387, 2981, 1734, 1595, 1485, 1394,1330, 1251, 1196, 1177, 1085, 1031, 988, 949, 855, 813, 743, 703, 671, 588, 543, 466.



	Retention Time	% Area
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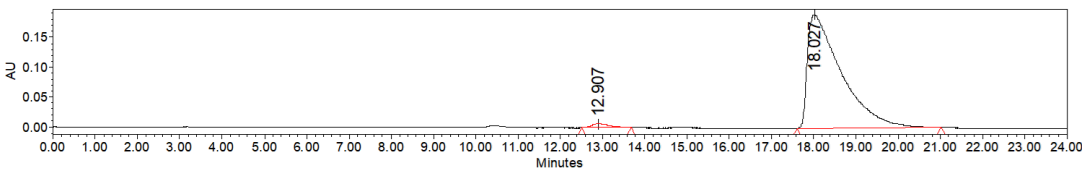
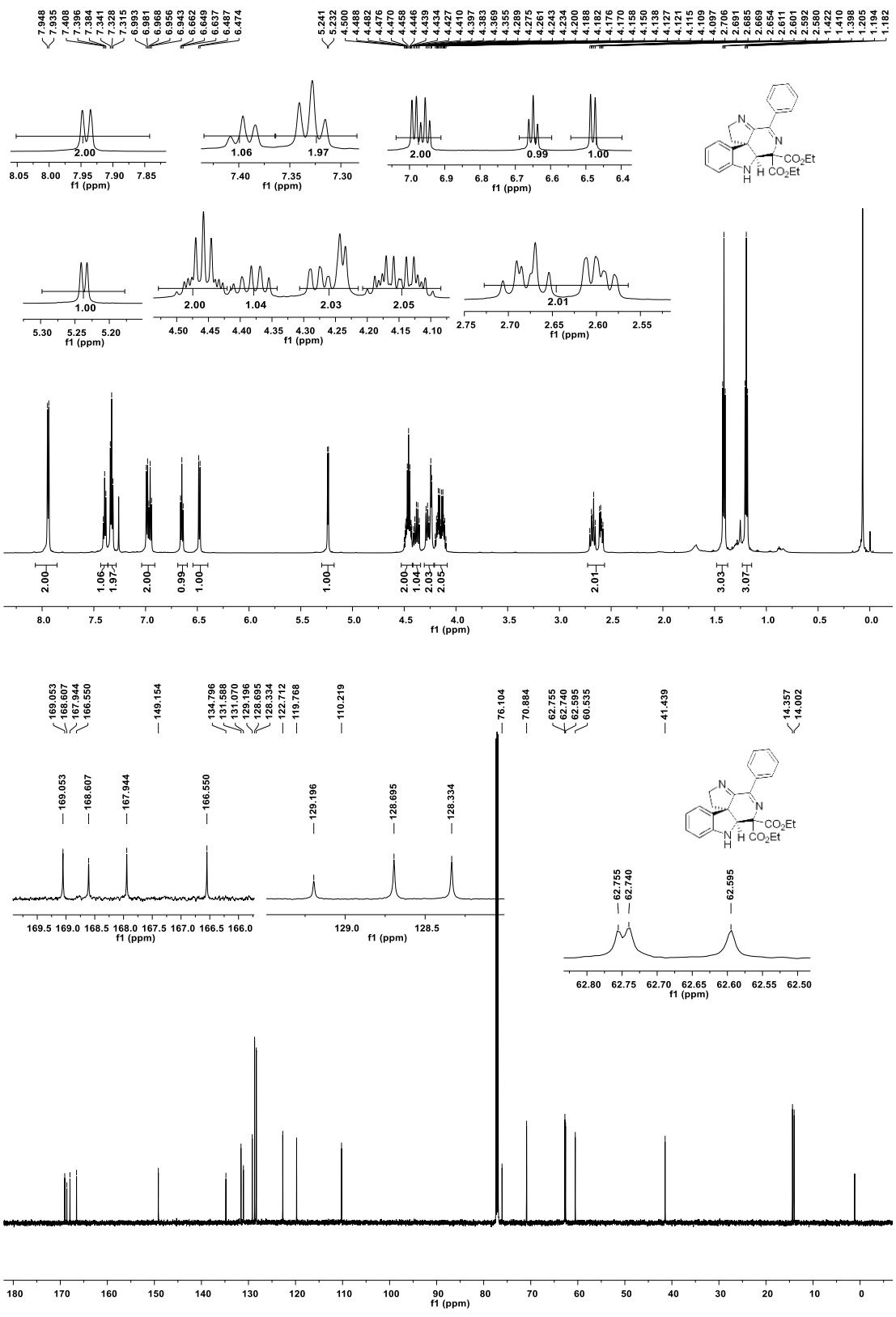
2	18.343	50.01



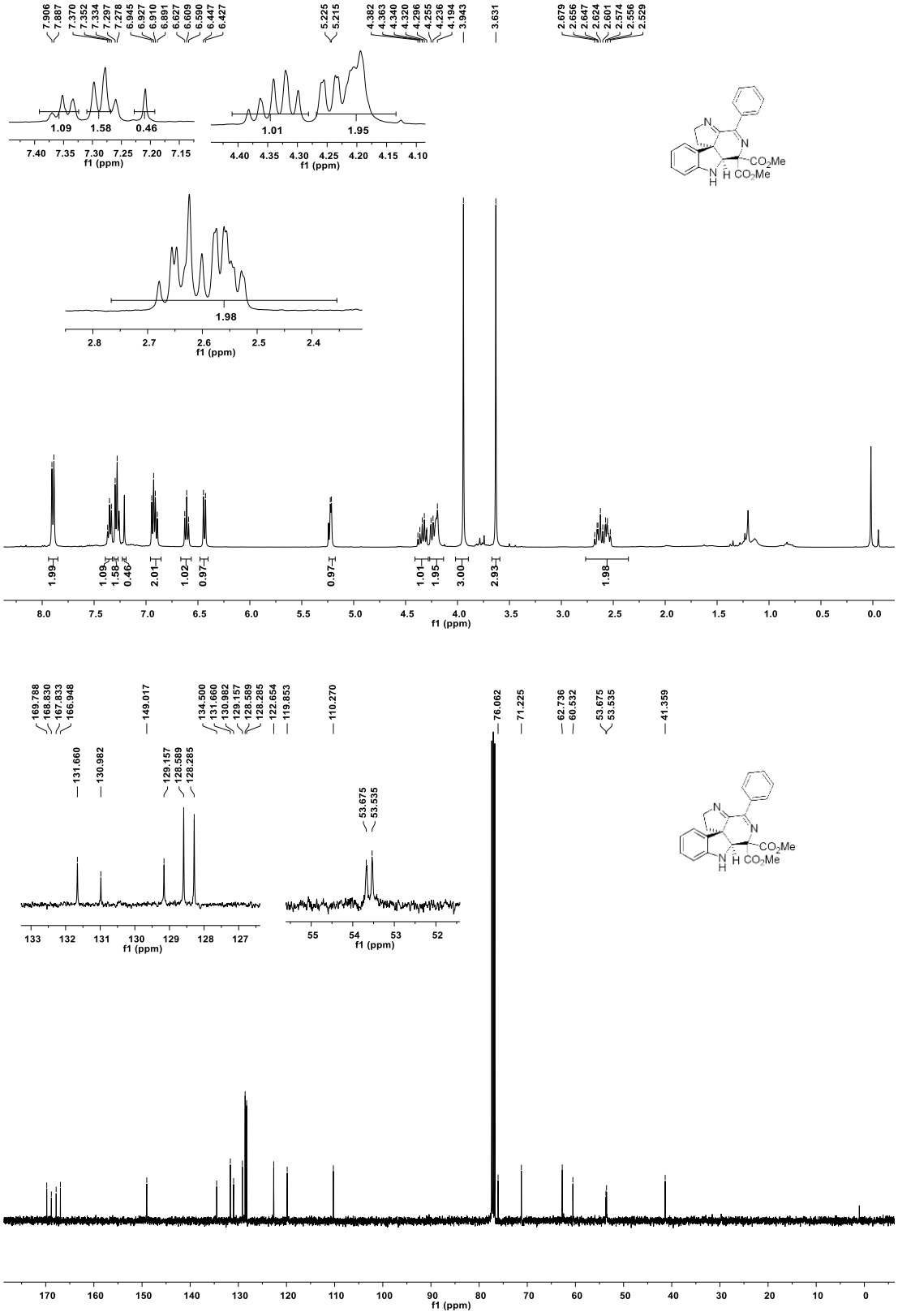
	Retention Time	% Area
1	12.907	1.93
2	18.027	98.07

(K) Copies of NMR spectra for the products

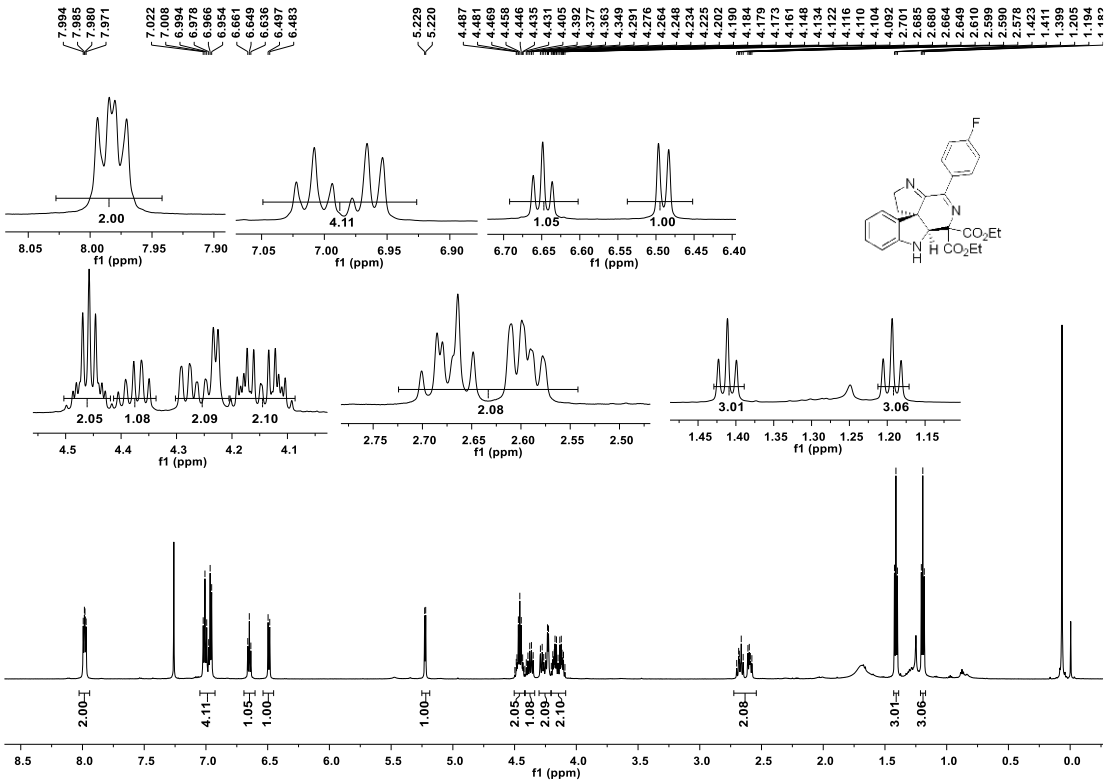
Diethyl (6a*S*,11b*R*)-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C1)



Dimethyl (6a*S*,11b*R*)-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C2)



Diethyl (6a*S*,11b*R*)-4-(4-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C3)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7.008
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6.978
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6.954
6.661
6.649
6.636
6.497
6.483
5.229
5.220
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4.481
4.469
4.458
4.446
4.435
4.431
4.405
4.392
4.377
4.363
4.349
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4.276
4.264
4.248
4.234
4.225
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4.179
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4.134
4.122
4.116
4.110
4.104
4.092
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2.599
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1.05
1.00
2.05
1.08
2.09
2.10
2.08
3.01
3.06
f1 (ppm)
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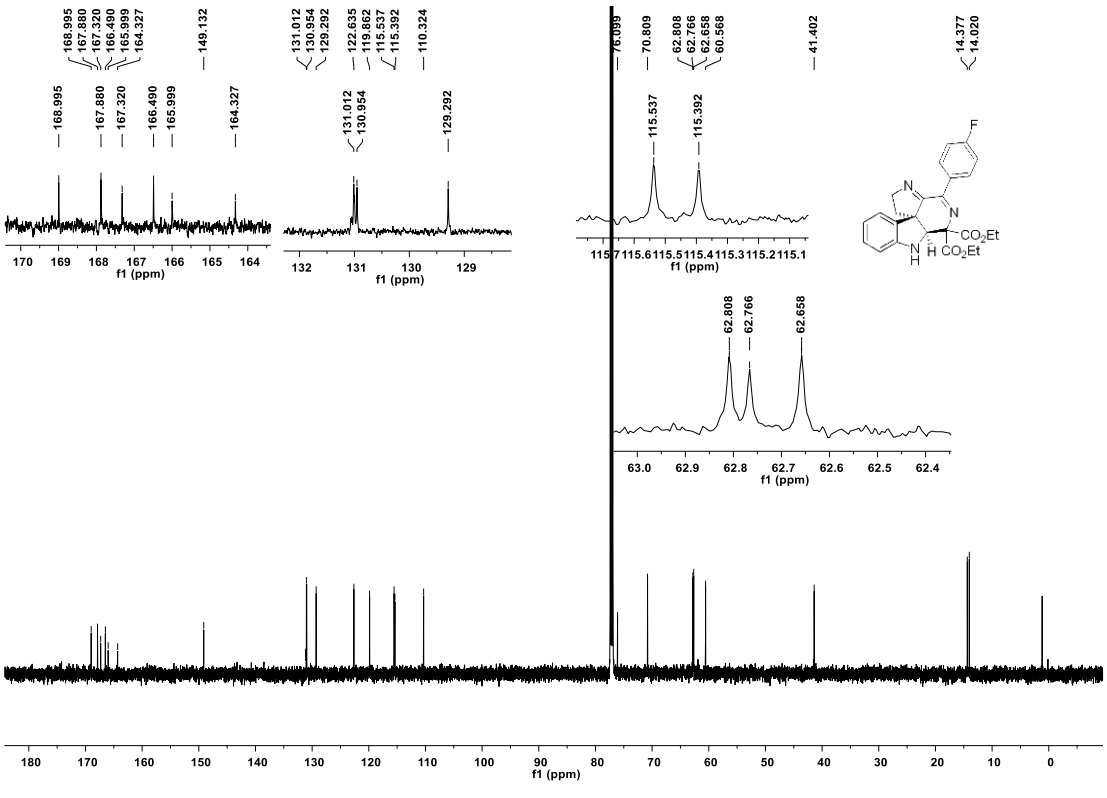
N
N
CO2Et
H CO2Et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164.327
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131.012
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14.377
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f1 (ppm)
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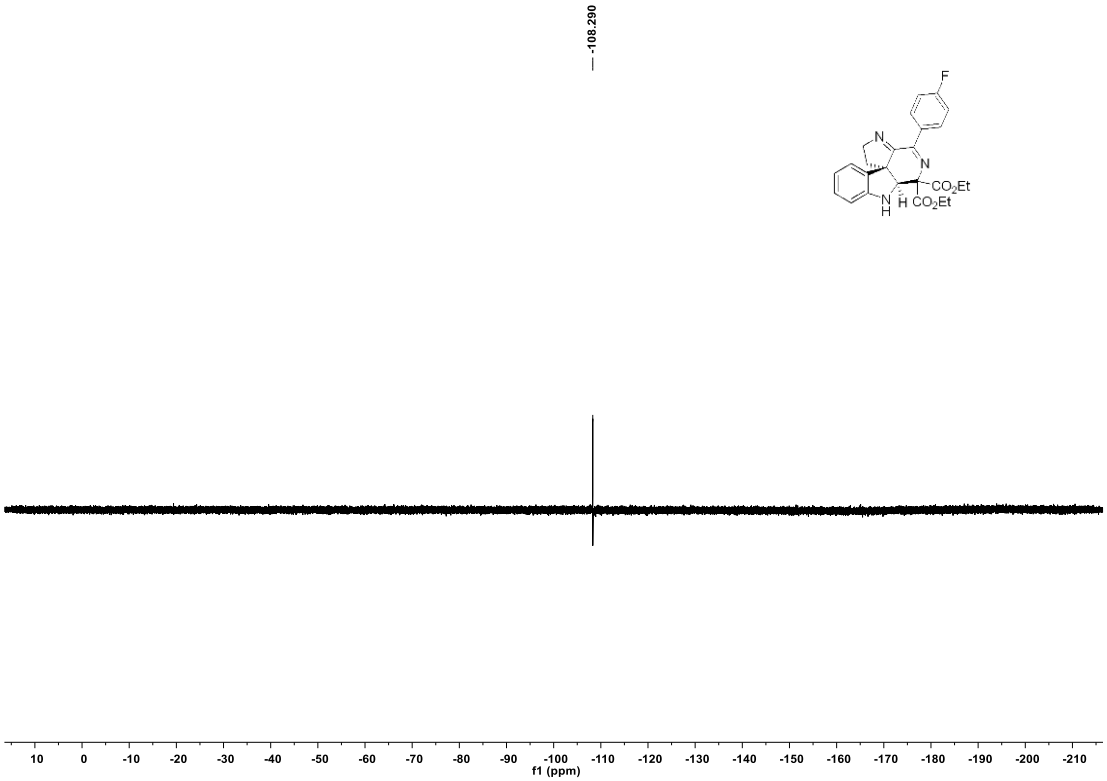
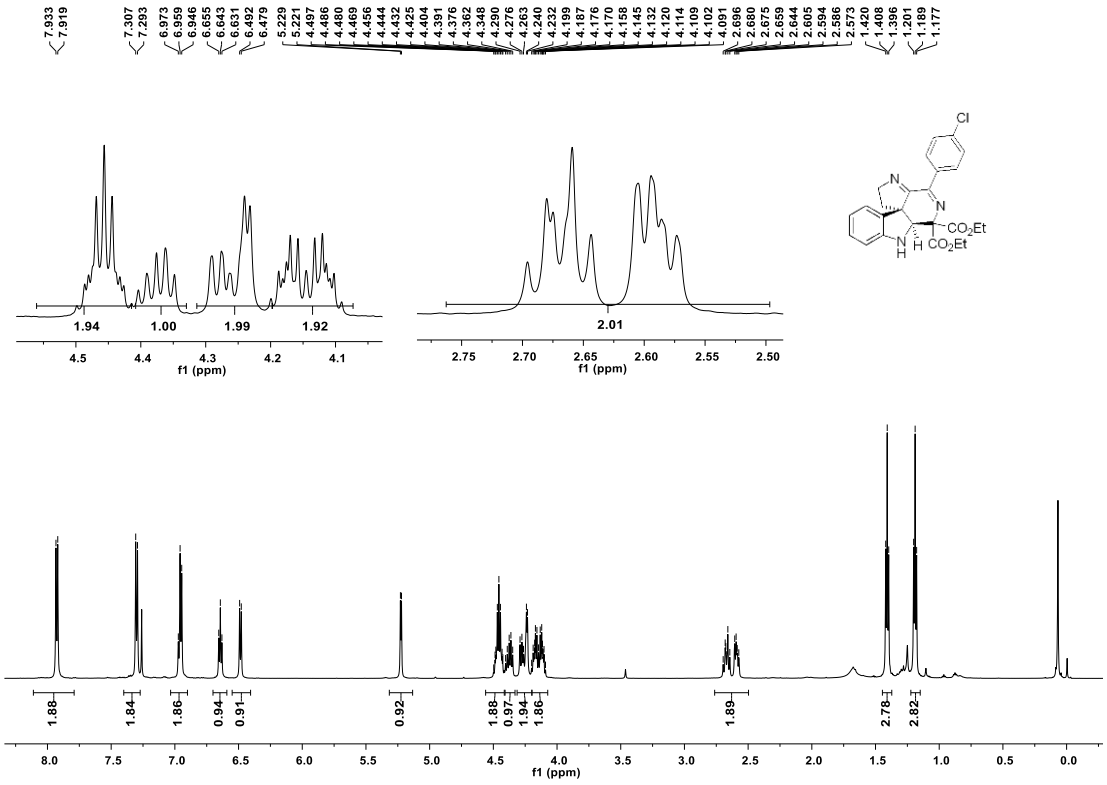
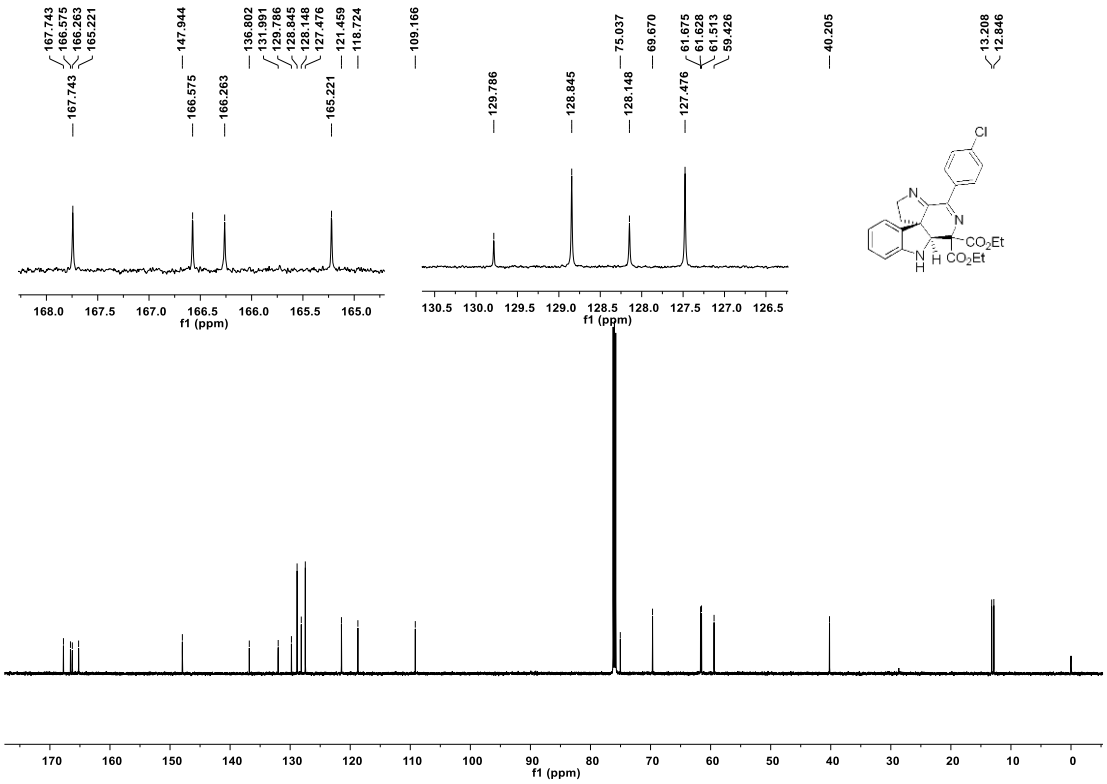
N
CO2Et
H CO2Et

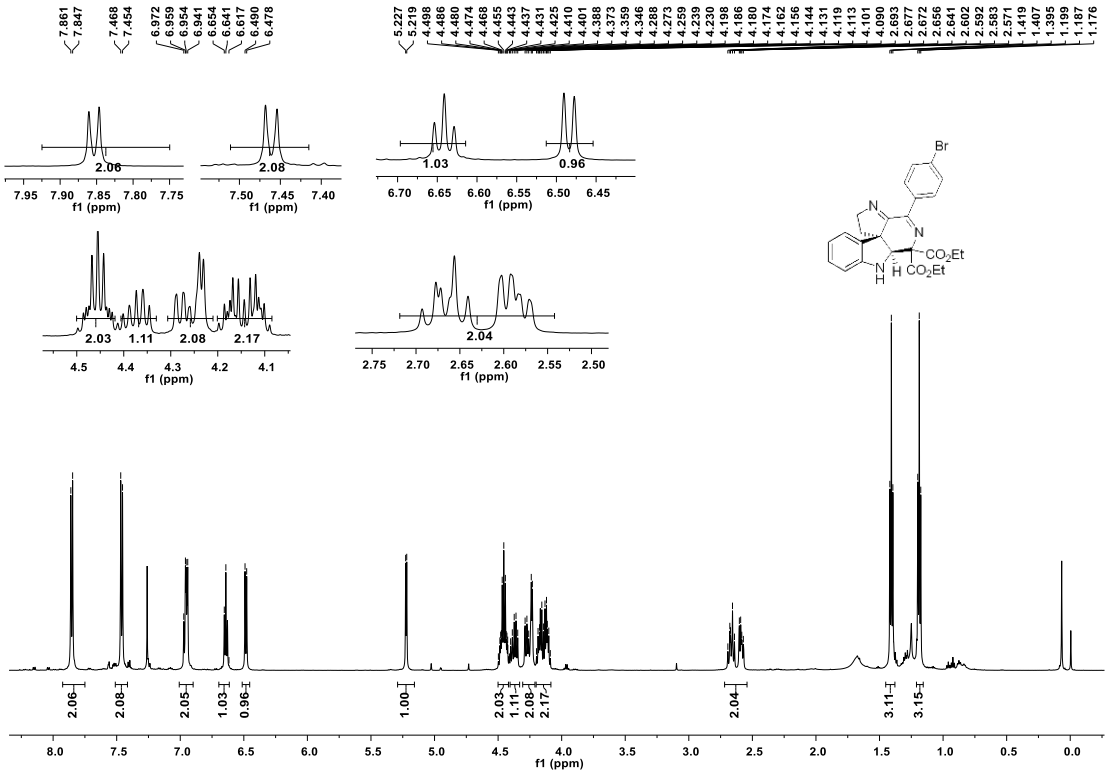


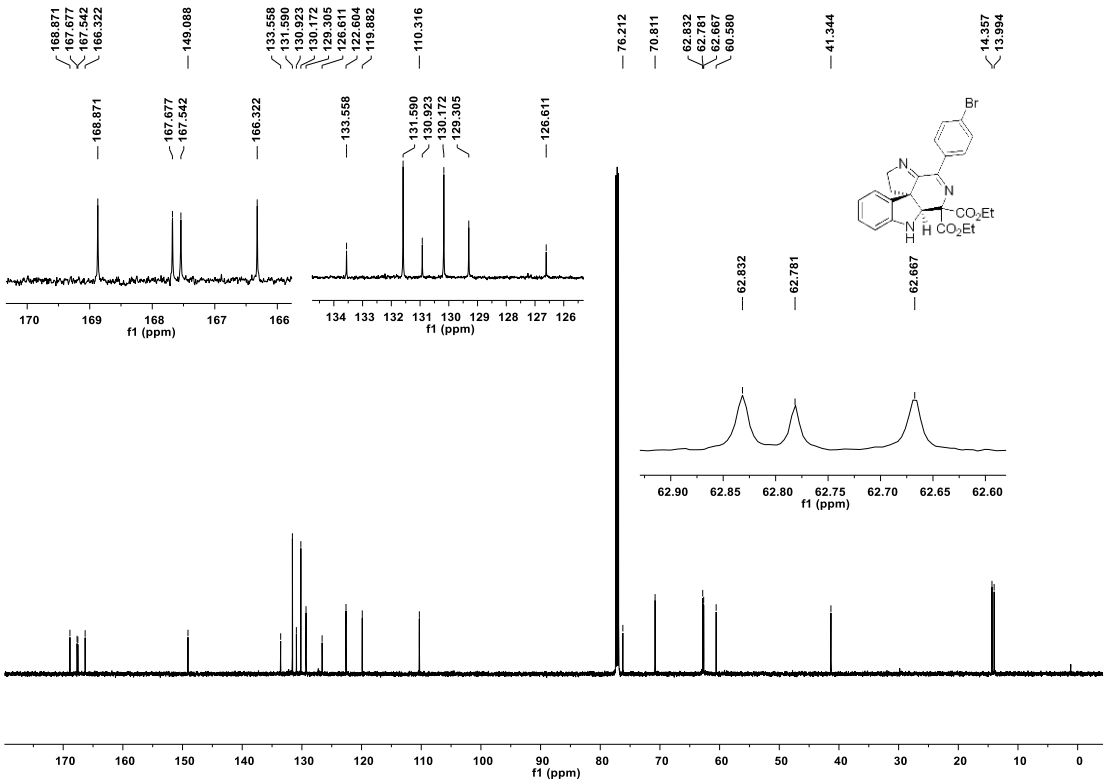
Diethyl (6a*S*,11b*R*)-4-(4-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C4)



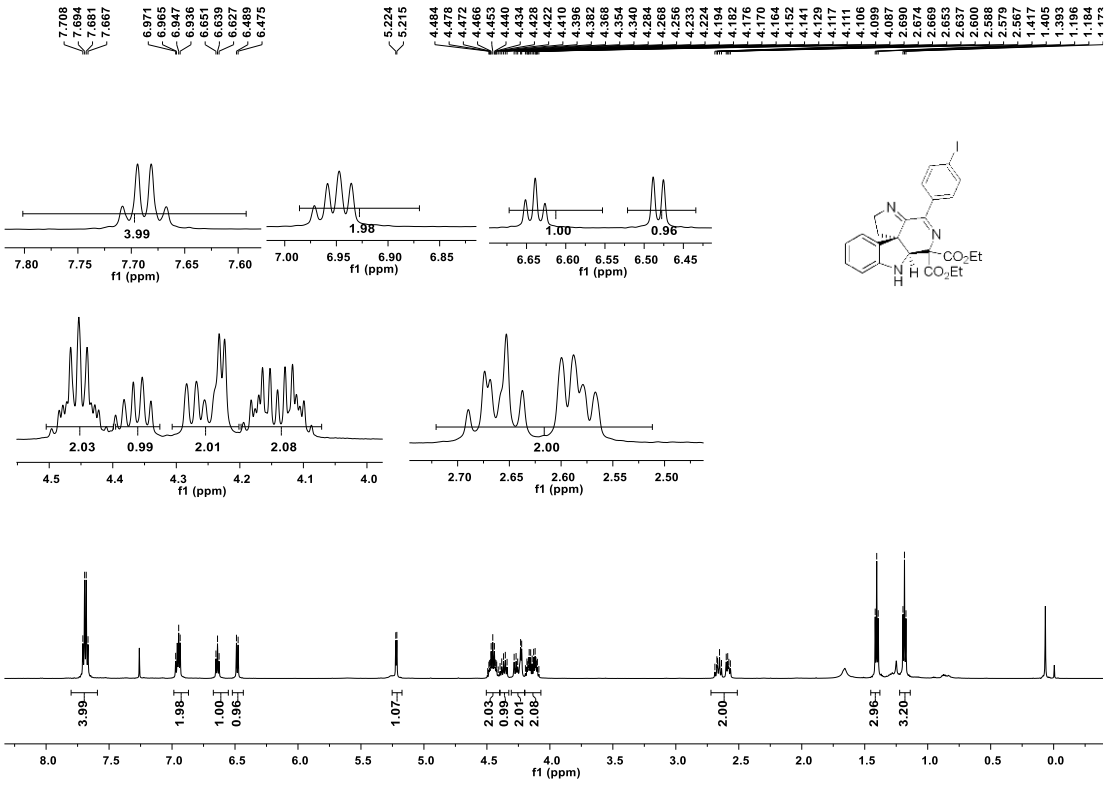


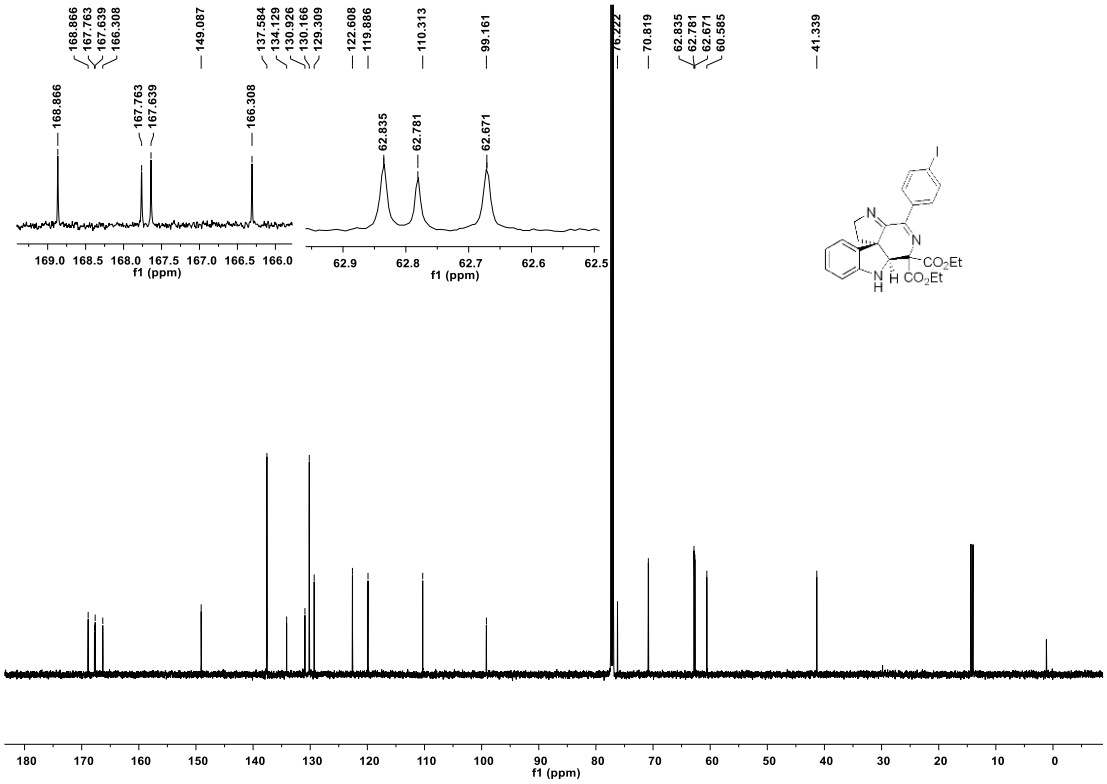
Diethyl (6a*S*,11b*R*)-4-(4-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C5)



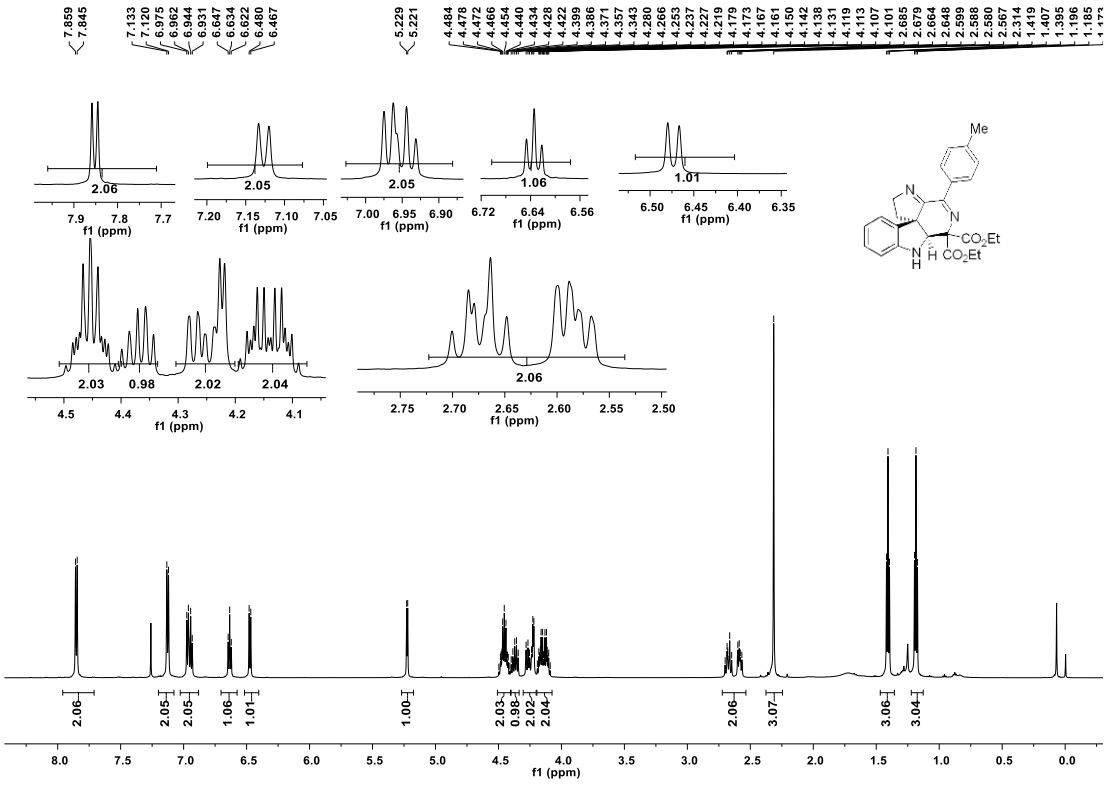


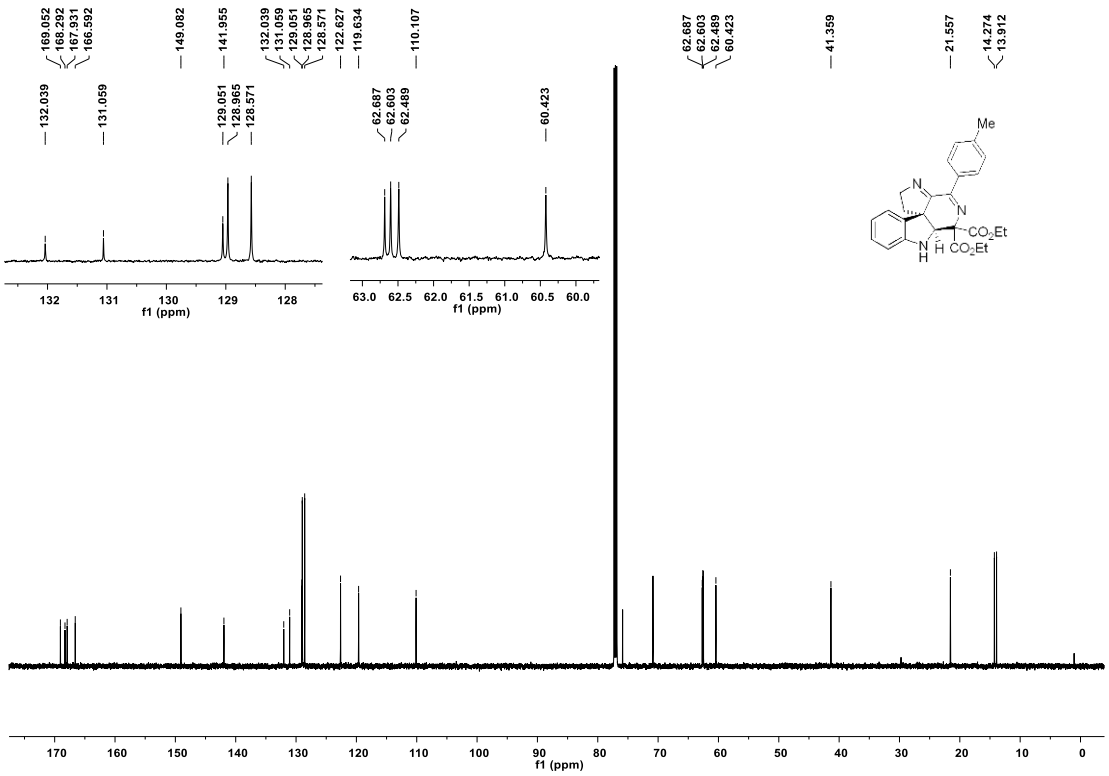
Diethyl (6a*S*,11b*R*)-4-(4-iodophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C6)



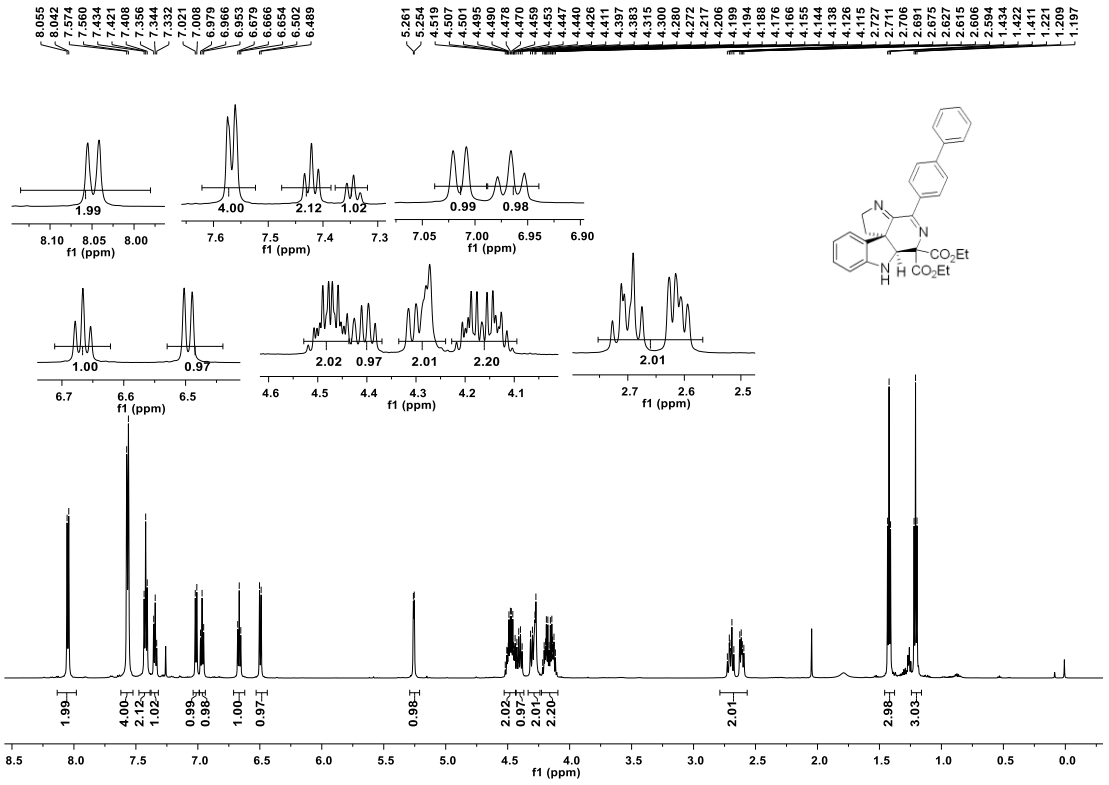


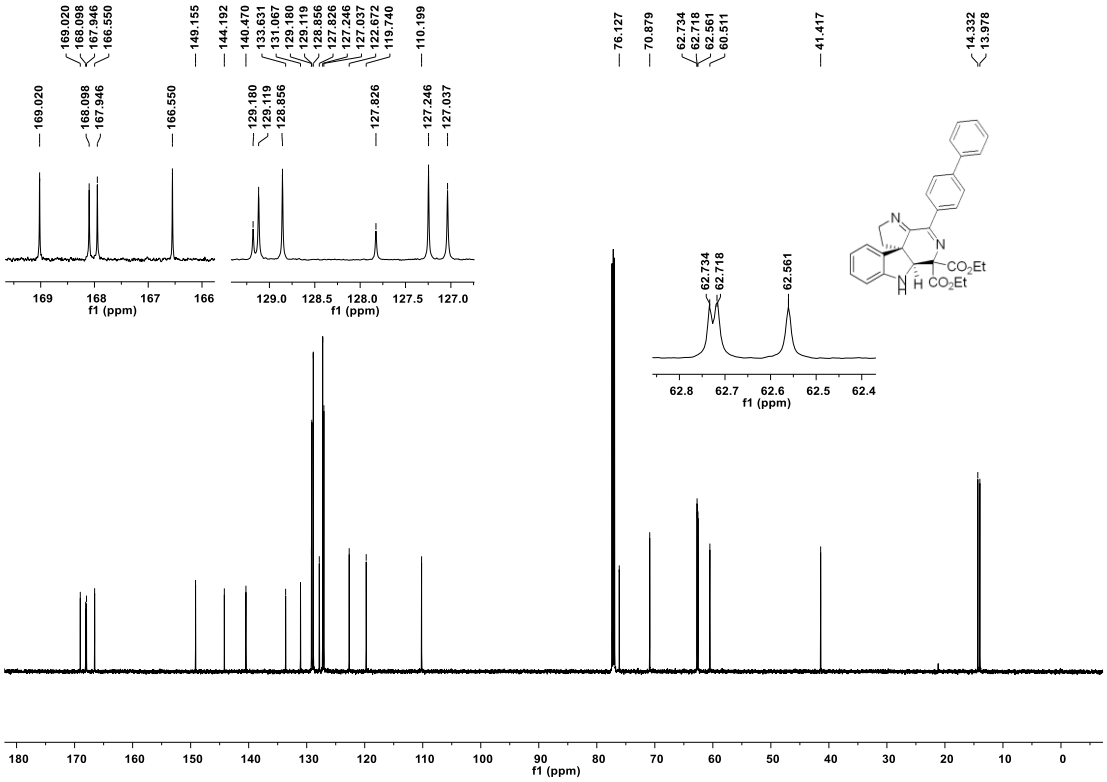
Diethyl (6a*S*,11b*R*)-4-(p-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C7)



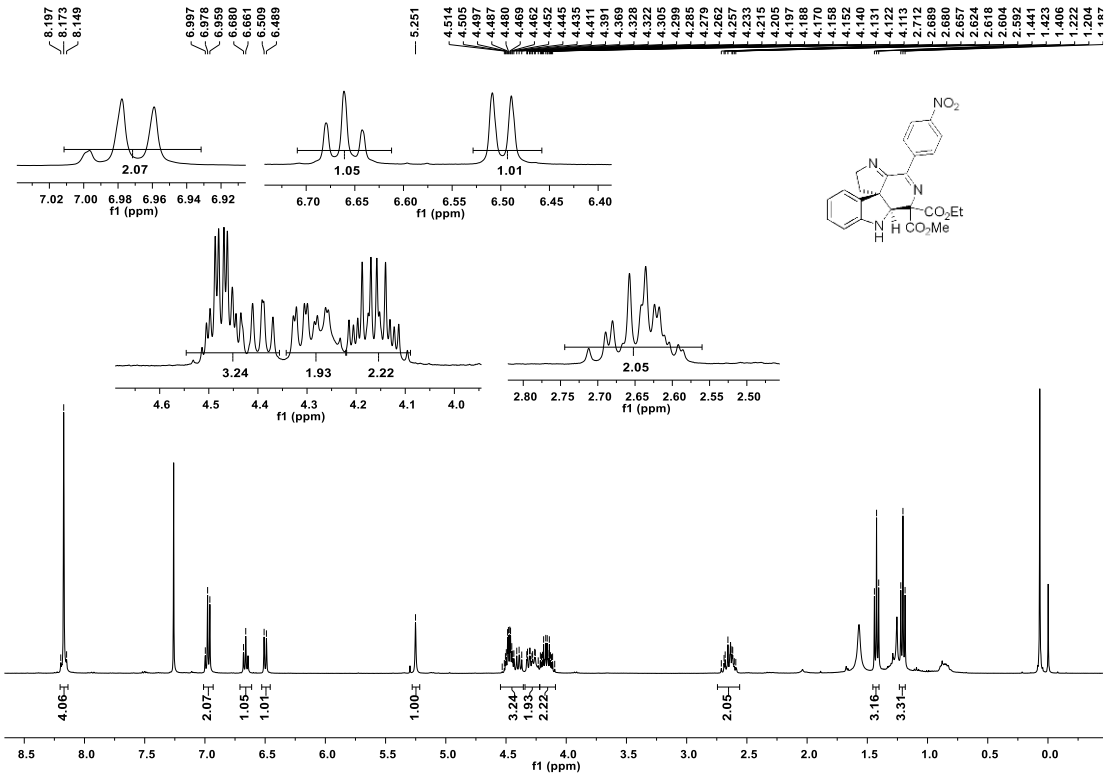


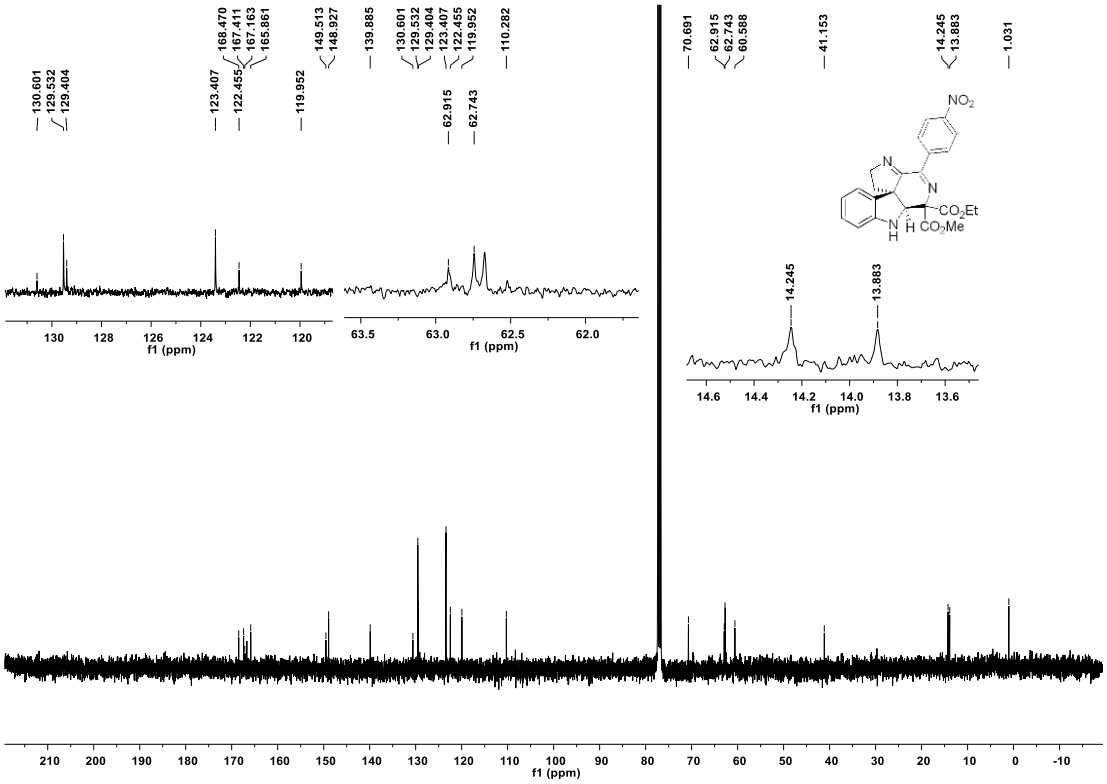
Diethyl (6a*S*,11b*R*)-4-([1,1'-biphenyl]-4-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C8)



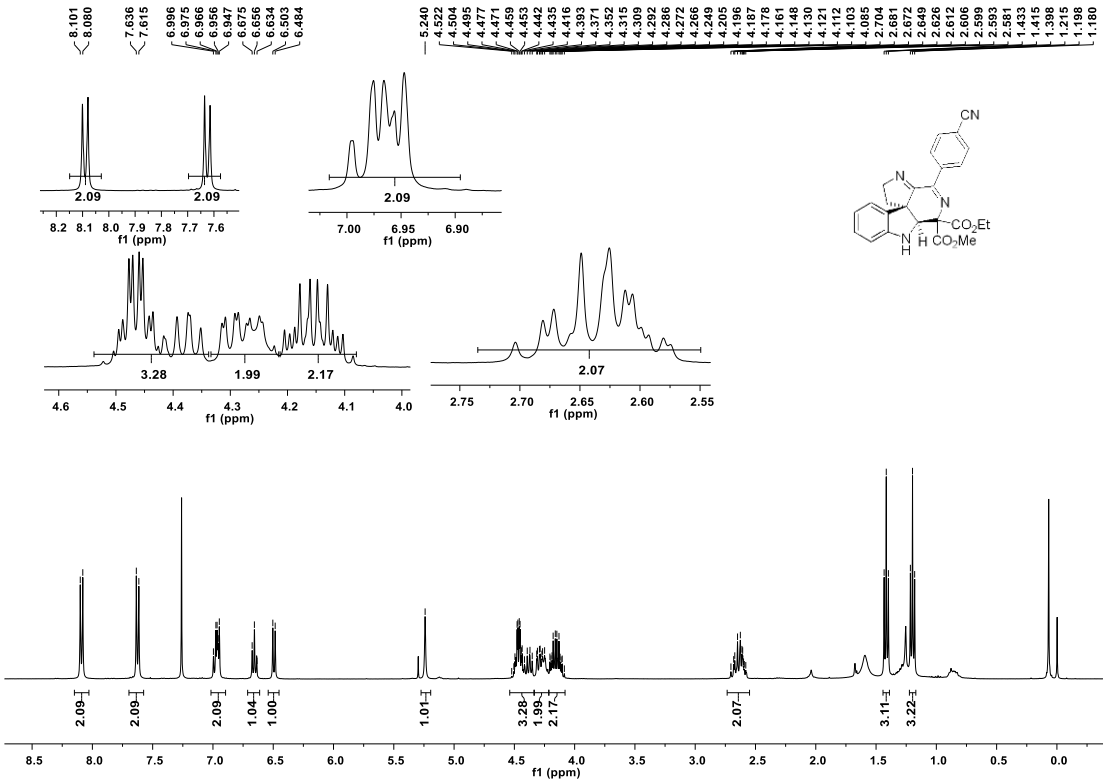


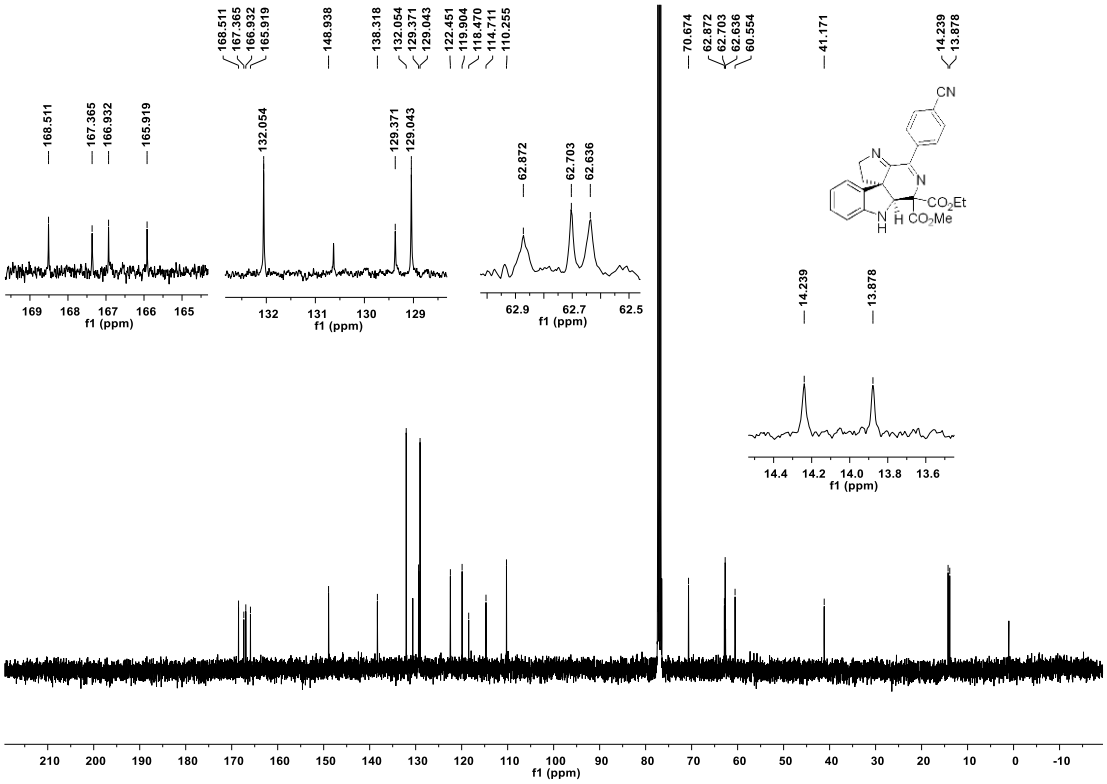
Diethyl (6a*S*,11b*R*)-4-(4-nitrophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C9)



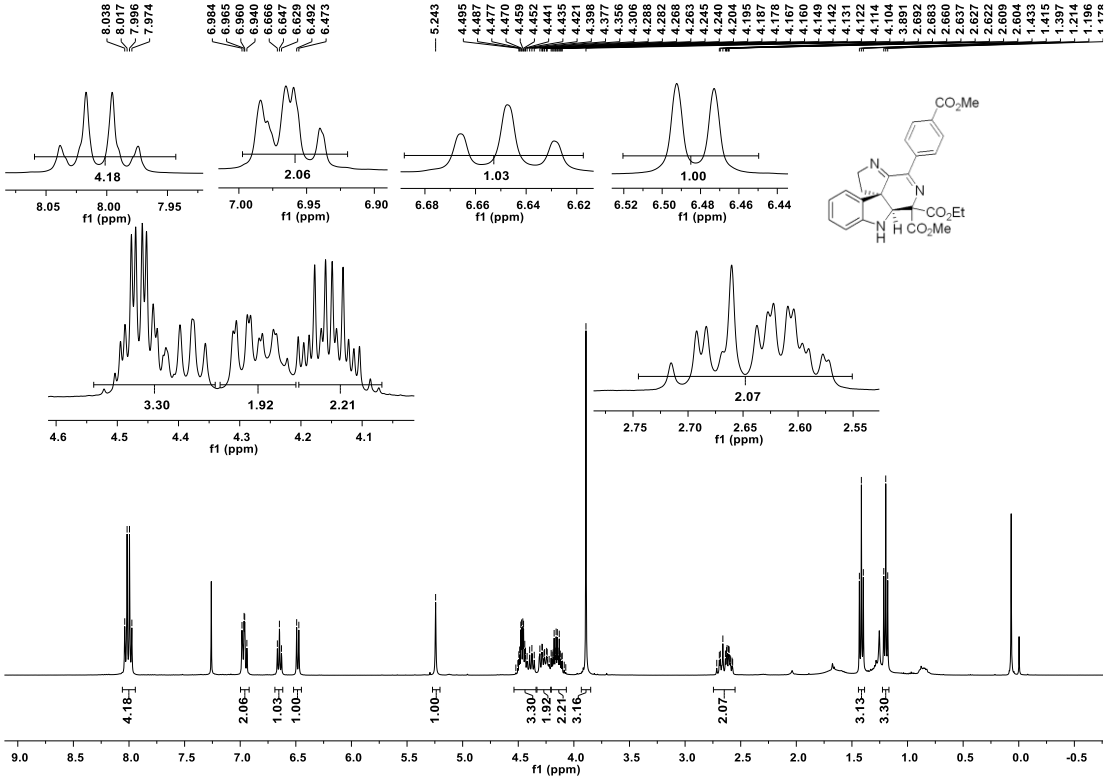


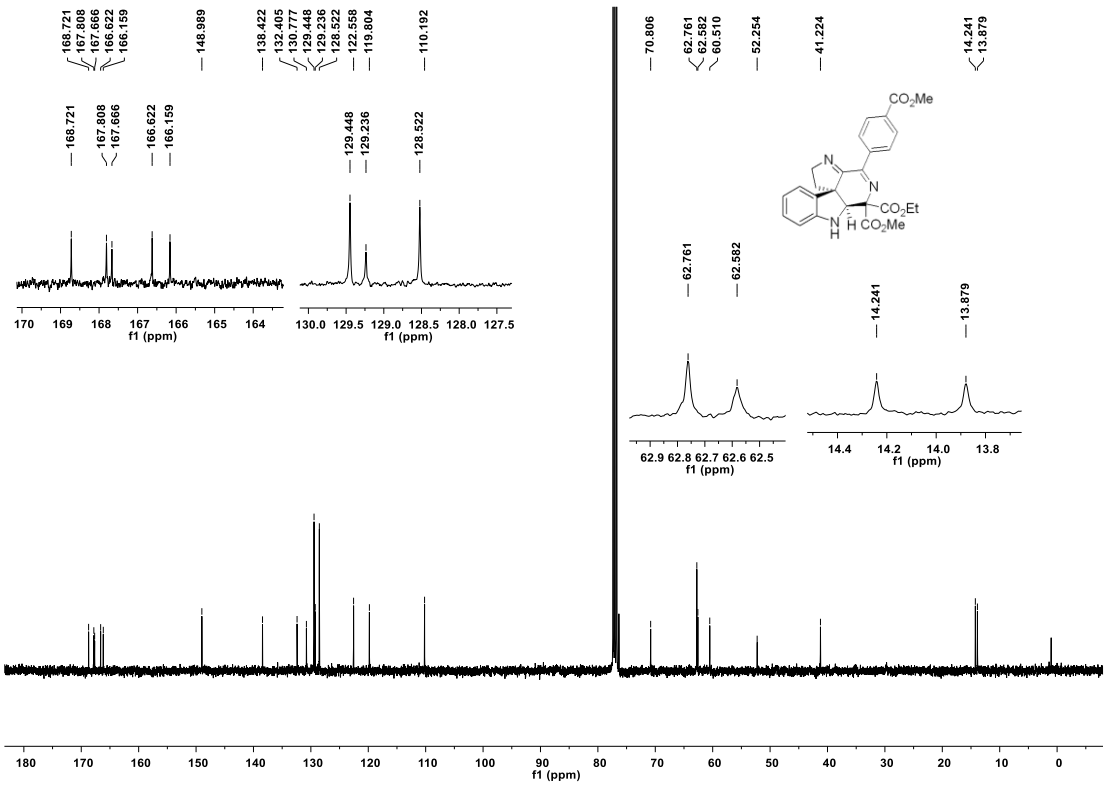
Diethyl (6a*S*,11b*R*)-4-(4-cyanophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate （C10）



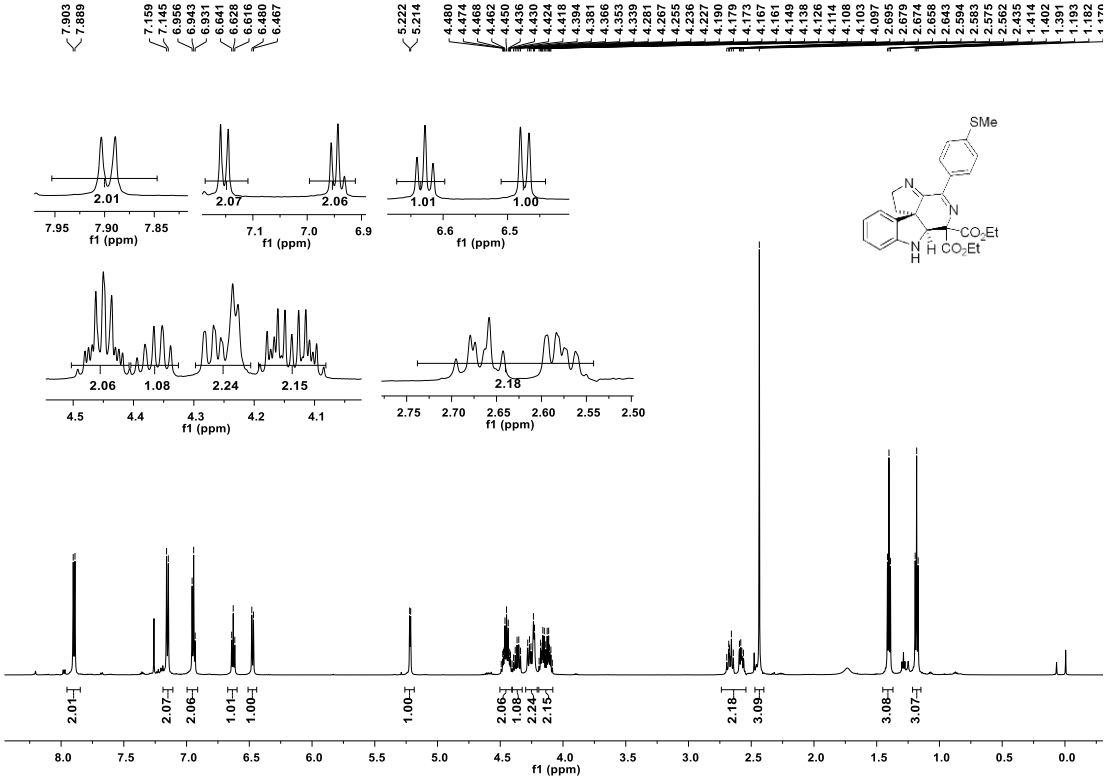


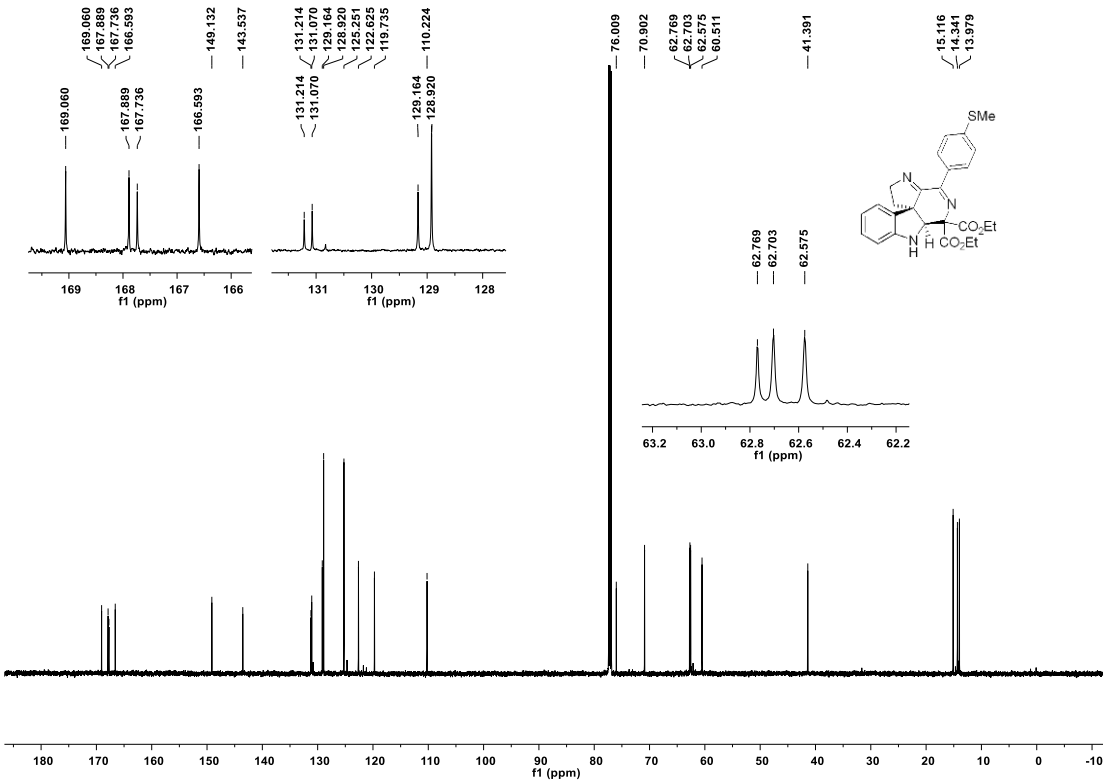
Diethyl (6a*S*,11b*R*)-4-(4-(methoxycarbonyl)phenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C11)



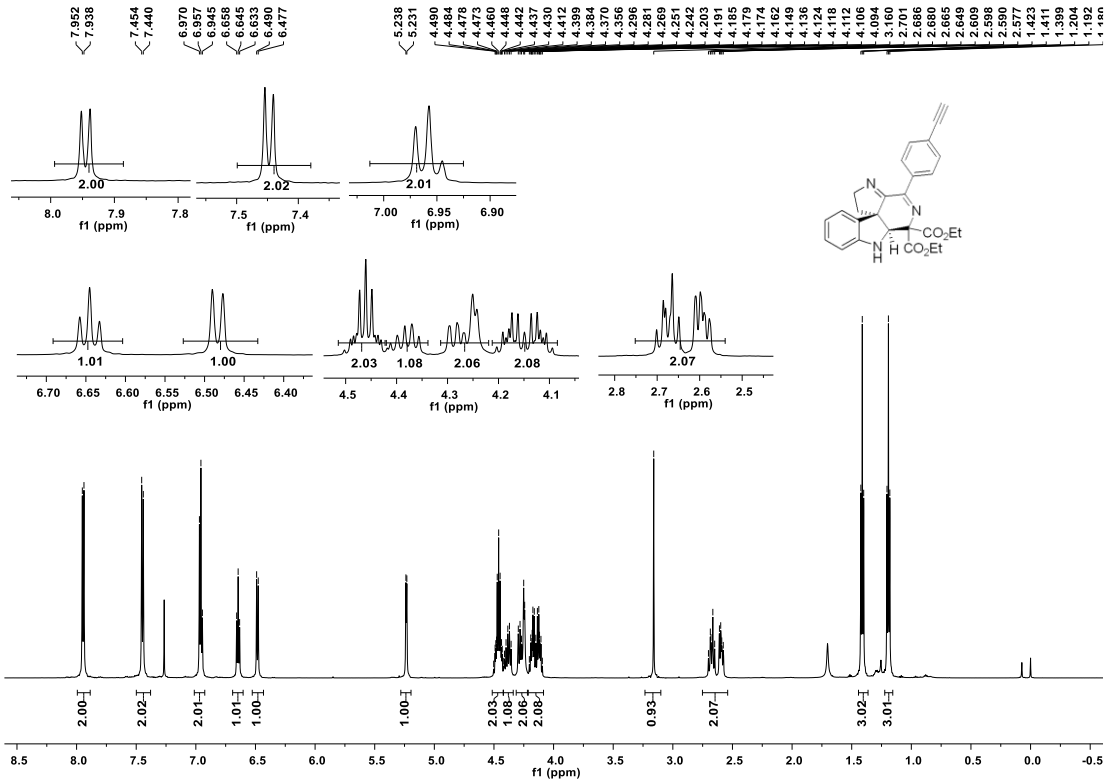


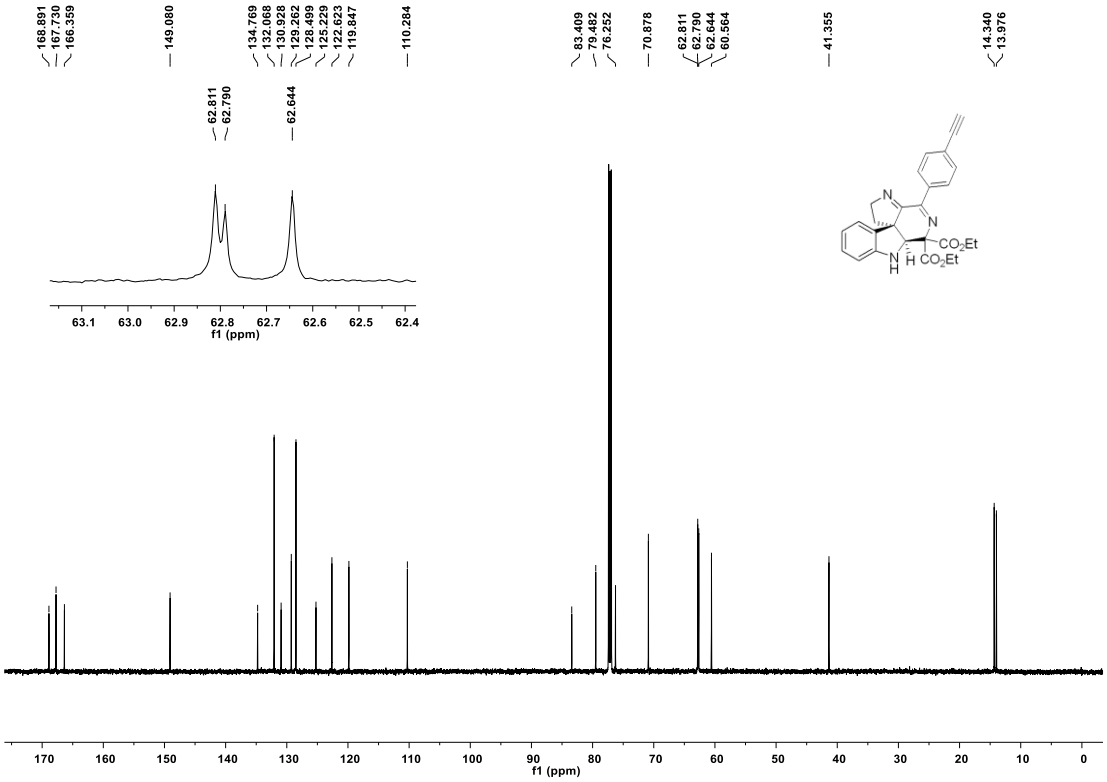
Diethyl (6a*S*,11b*R*)-4-(4-(methylthio)phenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C12)



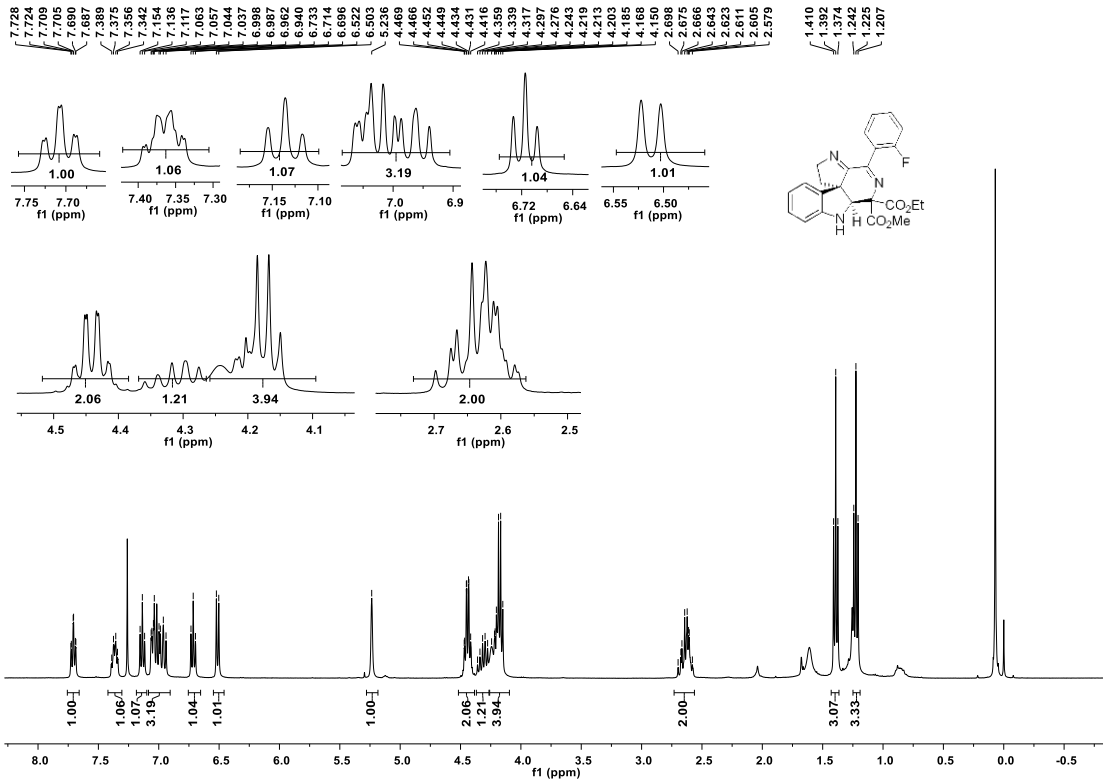


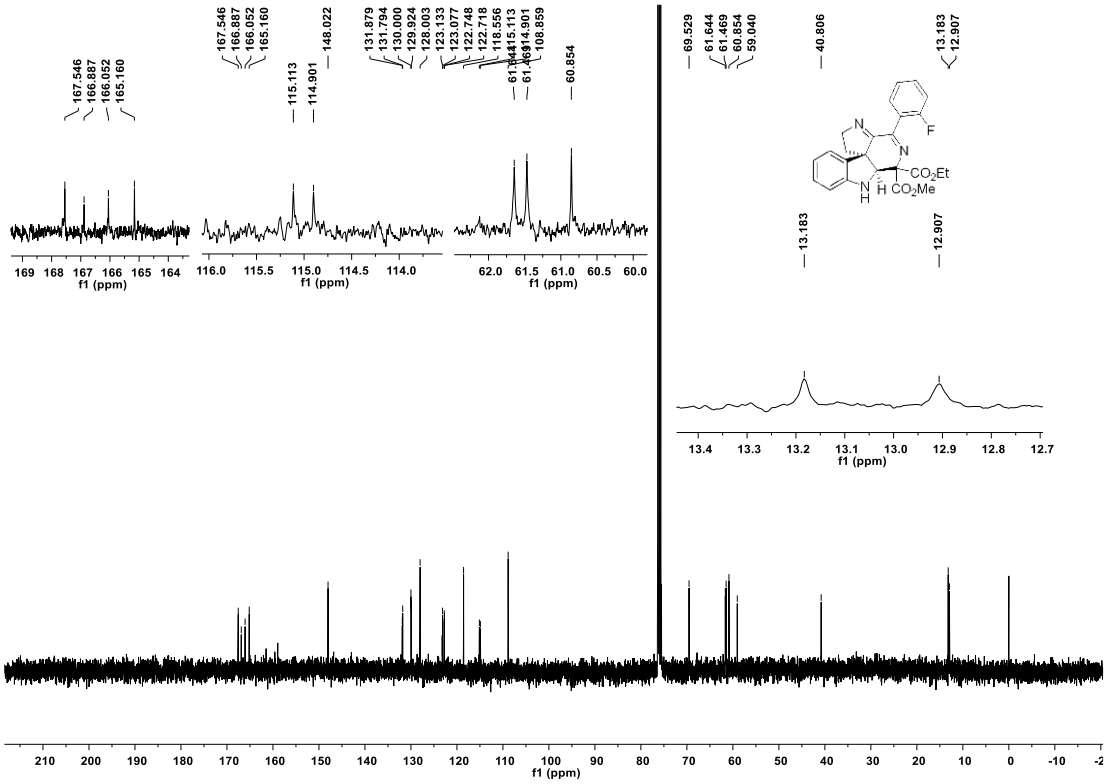
Diethyl (6a*S*,11b*R*)-4-(4-ethynylphenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C13)





Diethyl (6a*S*,11b*R*)-4-(2-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C14)

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118.556
108.859
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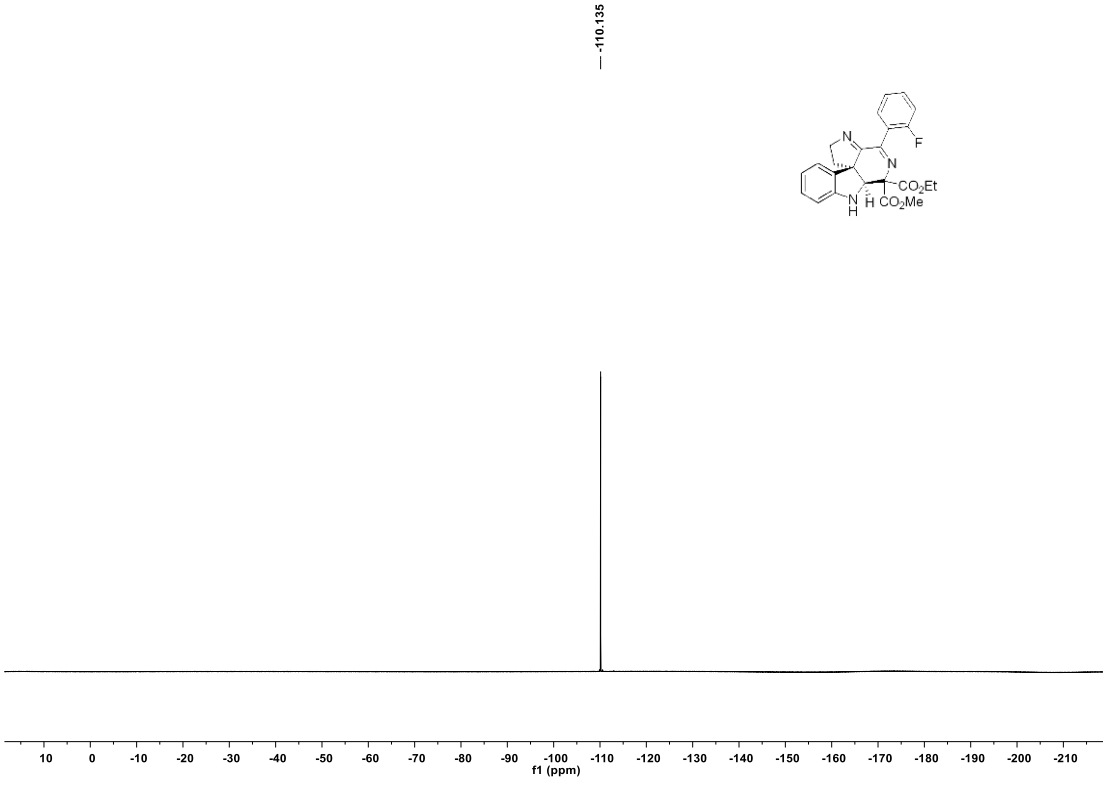
69.529
61.644
61.469
60.854
59.040
40.806
13.183
12.907
F
N
N
CO2Et
H CO2Me
169 168 167 166 165 164
f1 (ppm)
116.0 115.5 115.0 114.5 114.0
f1 (ppm)
62.0 61.5 61.0 60.5 60.0
f1 (ppm)
13.4 13.3 13.2 13.1 13.0 12.9 12.8 12.7
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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F
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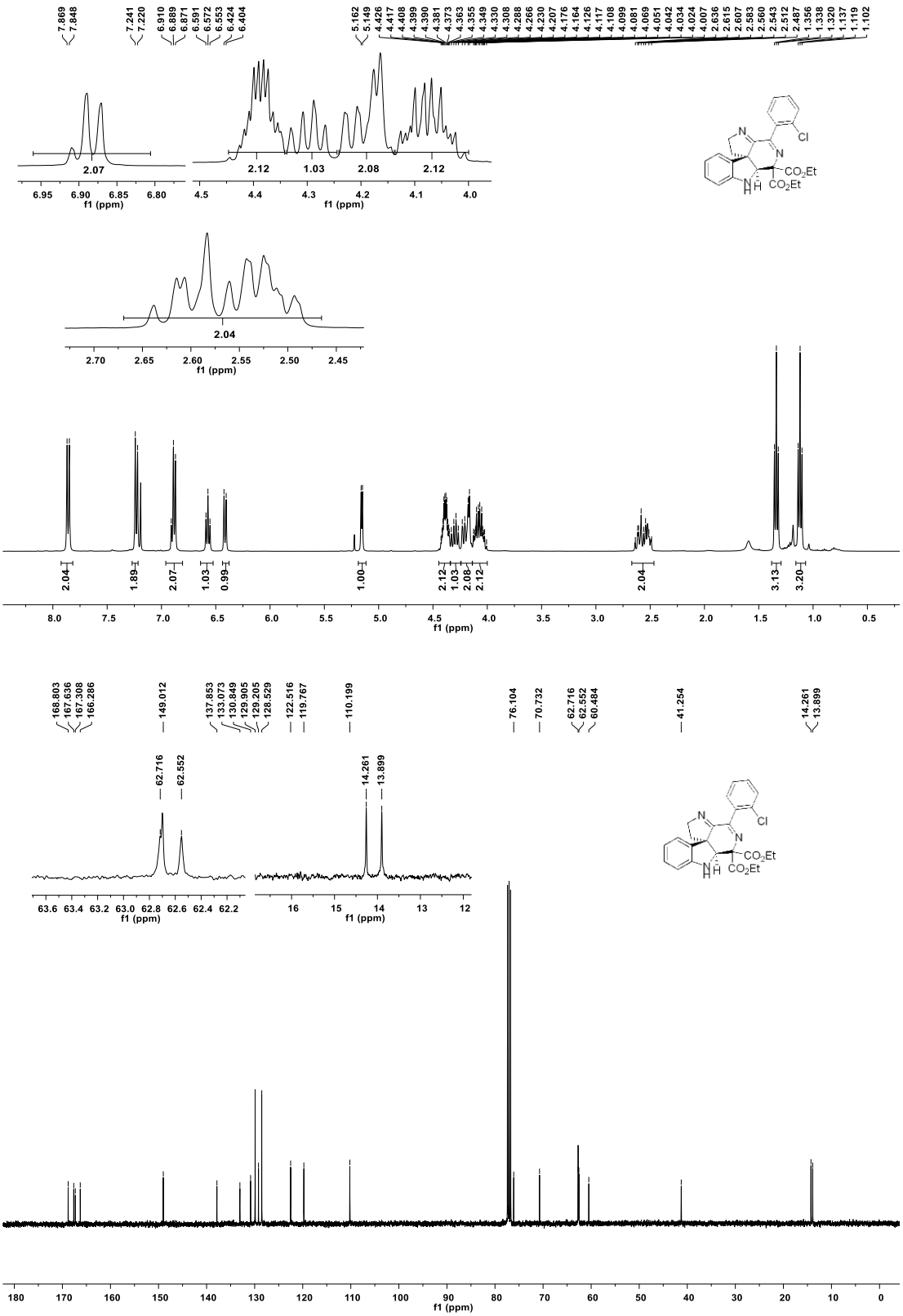
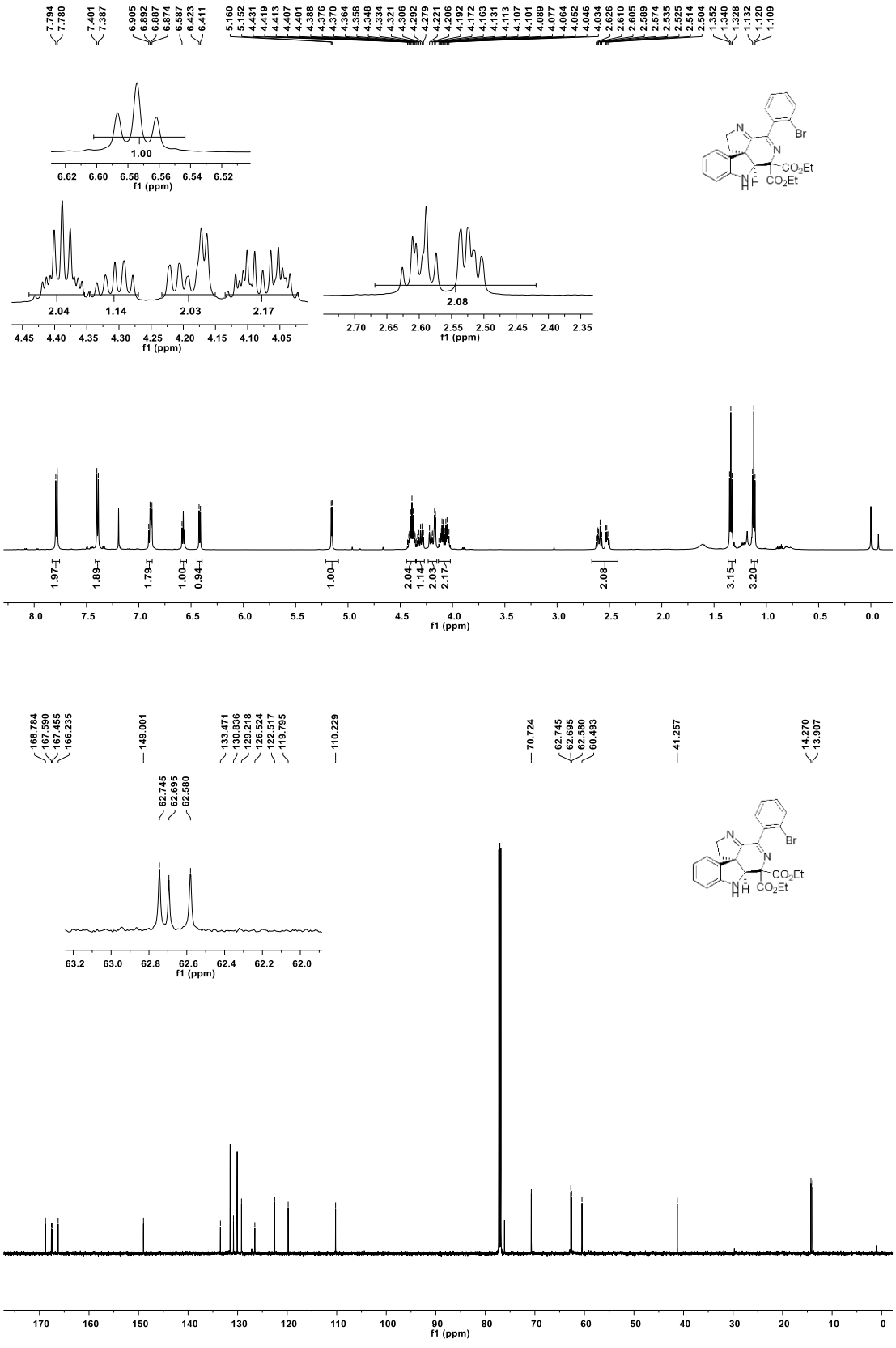
N
CO2Et
H CO2Me
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

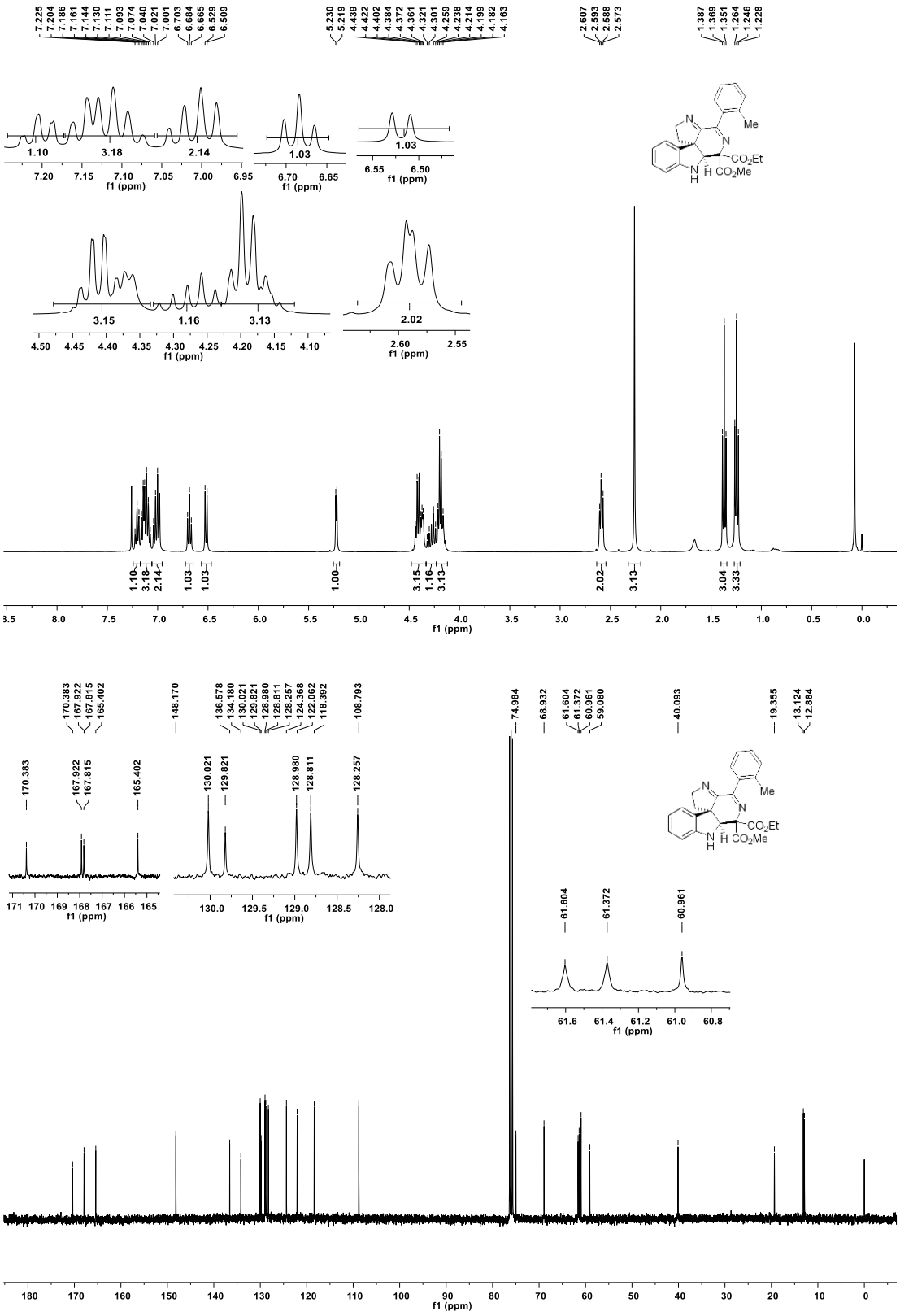
Diethyl (6a*S*,11b*R*)-4-(2-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C15)



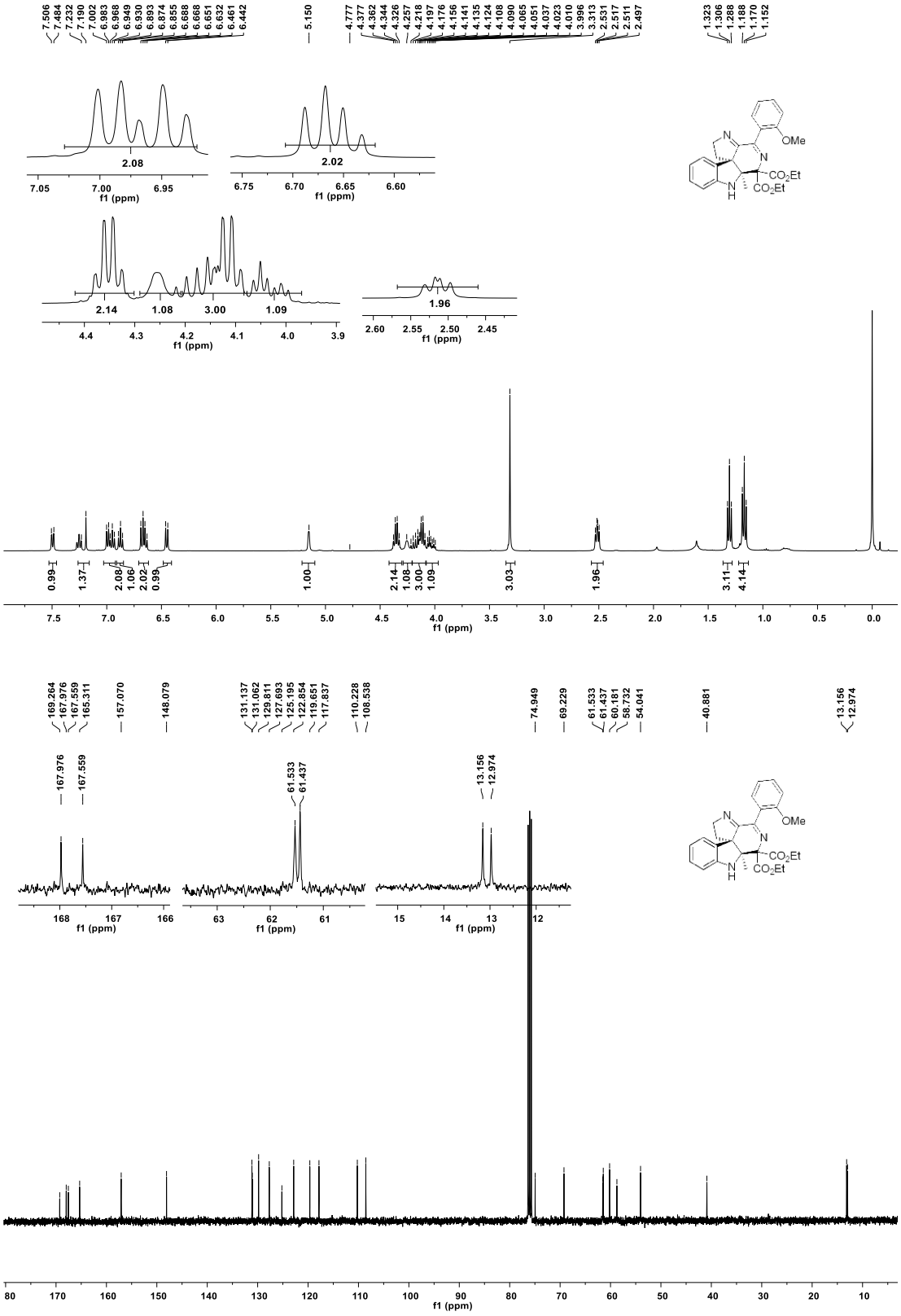
Diethyl (6a*S*,11b*R*)-4-(2-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C16)



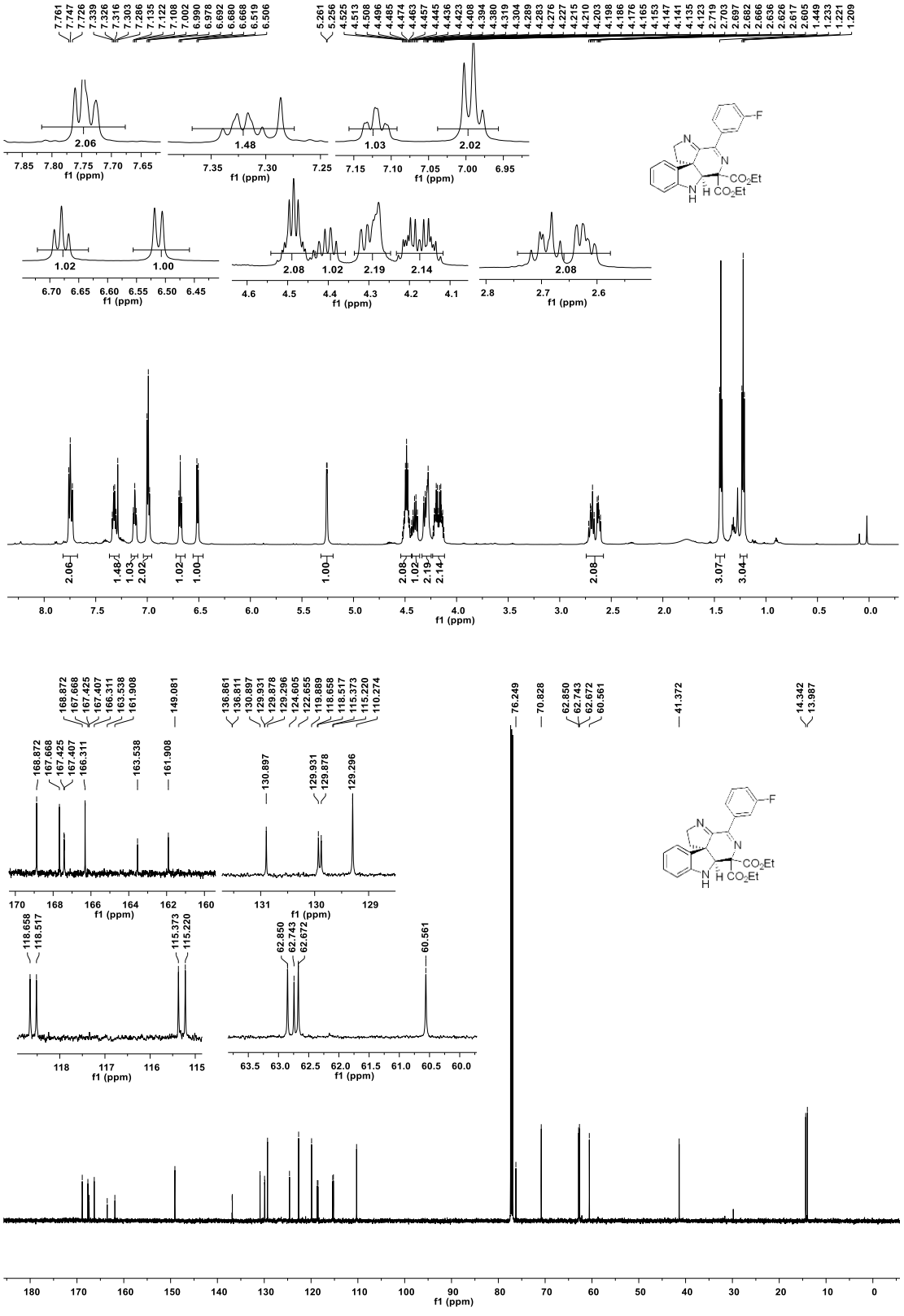
Diethyl (6a*S*,11b*R*)-4-(o-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C17)

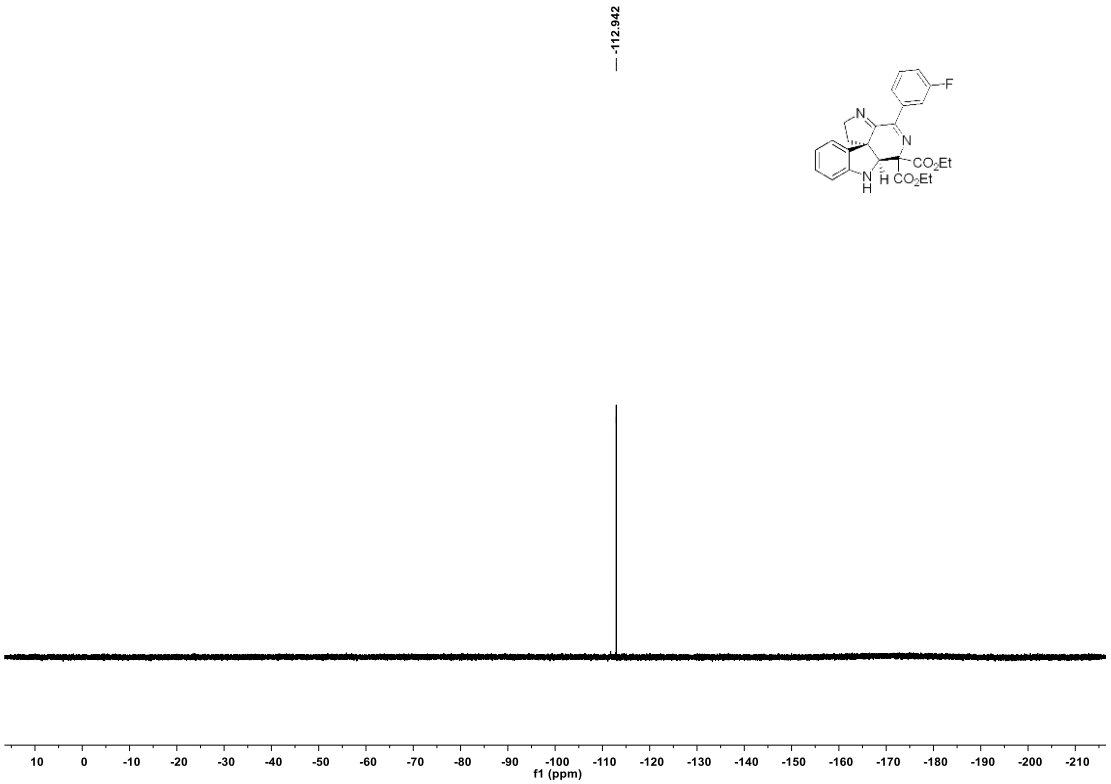


Diethyl (6a*S*,11b*R*)-4-(2-methoxyphenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C18)

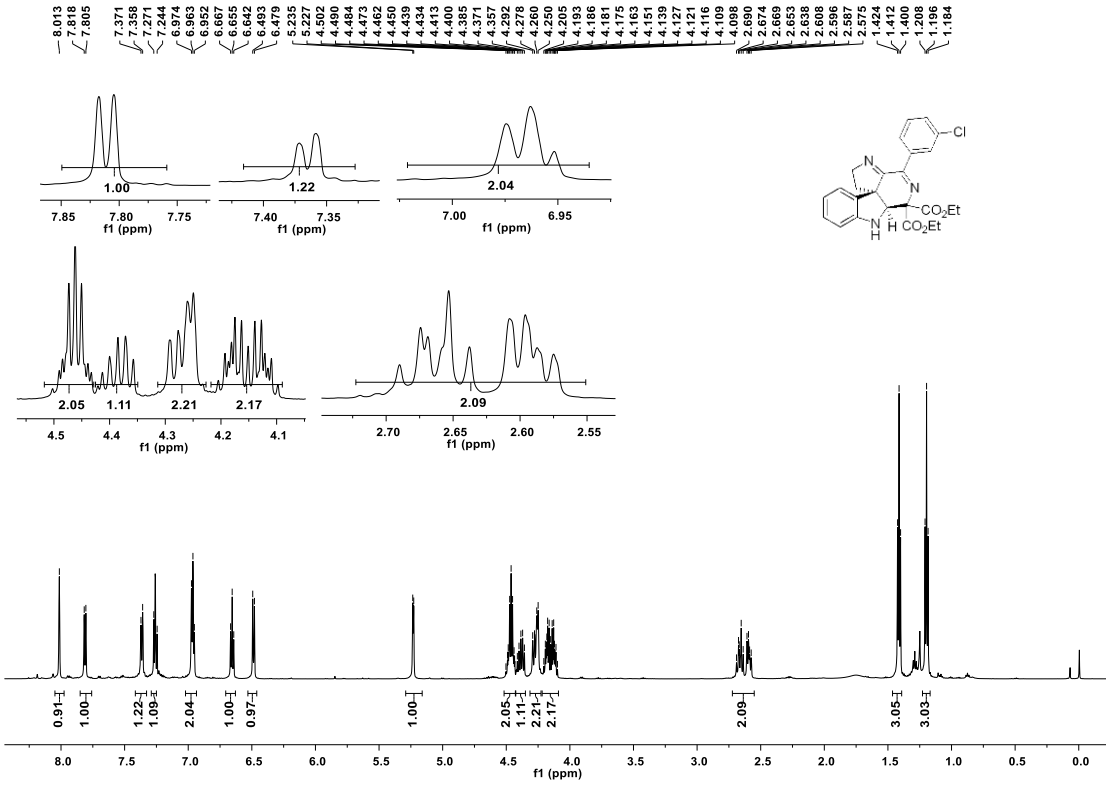


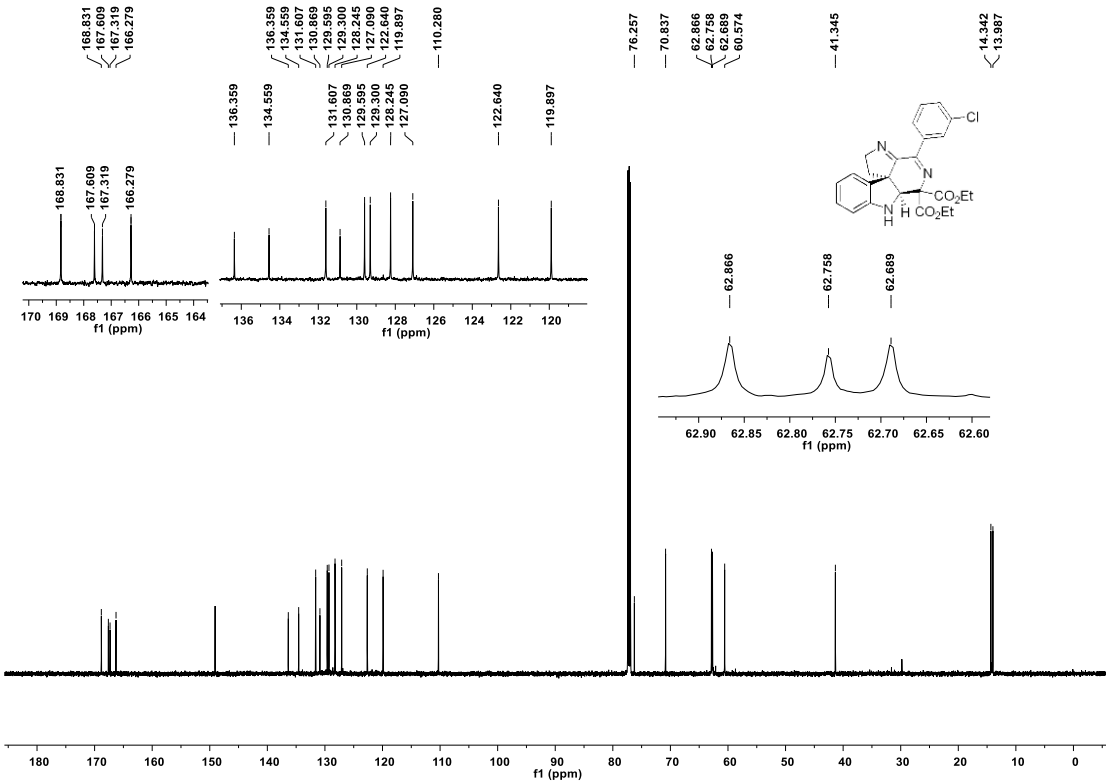
Diethyl (6a*S*,11b*R*)-4-(3-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C19)



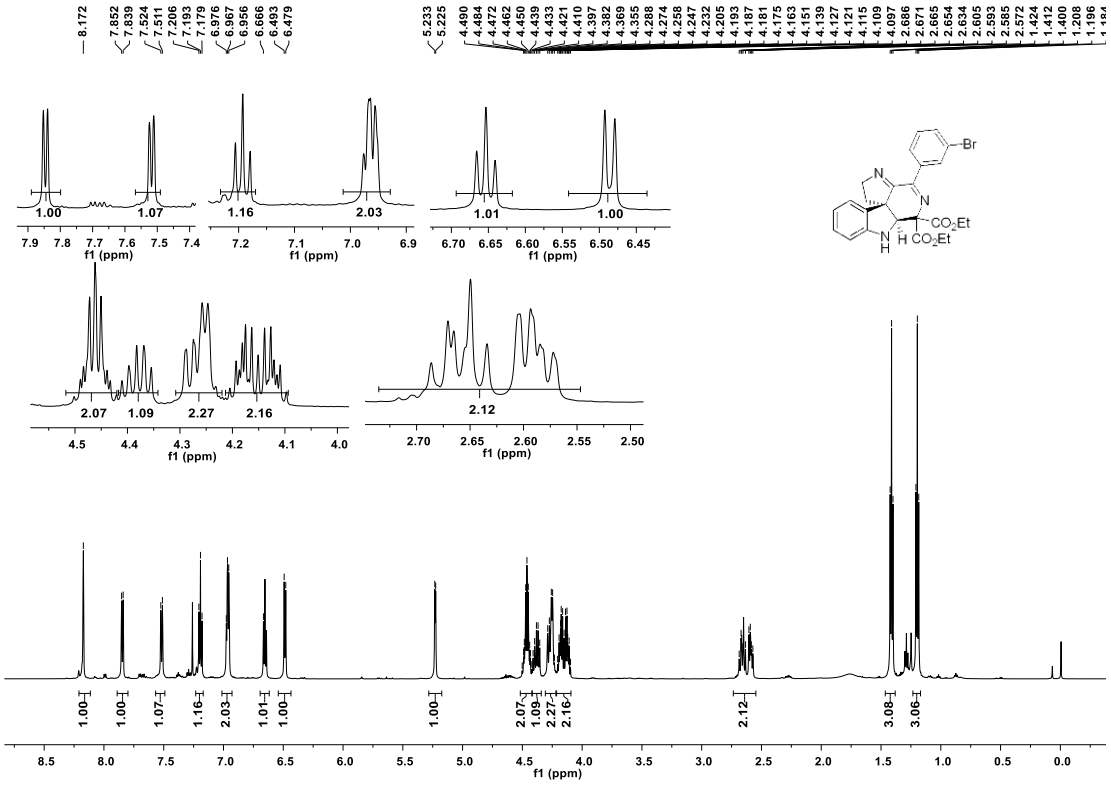


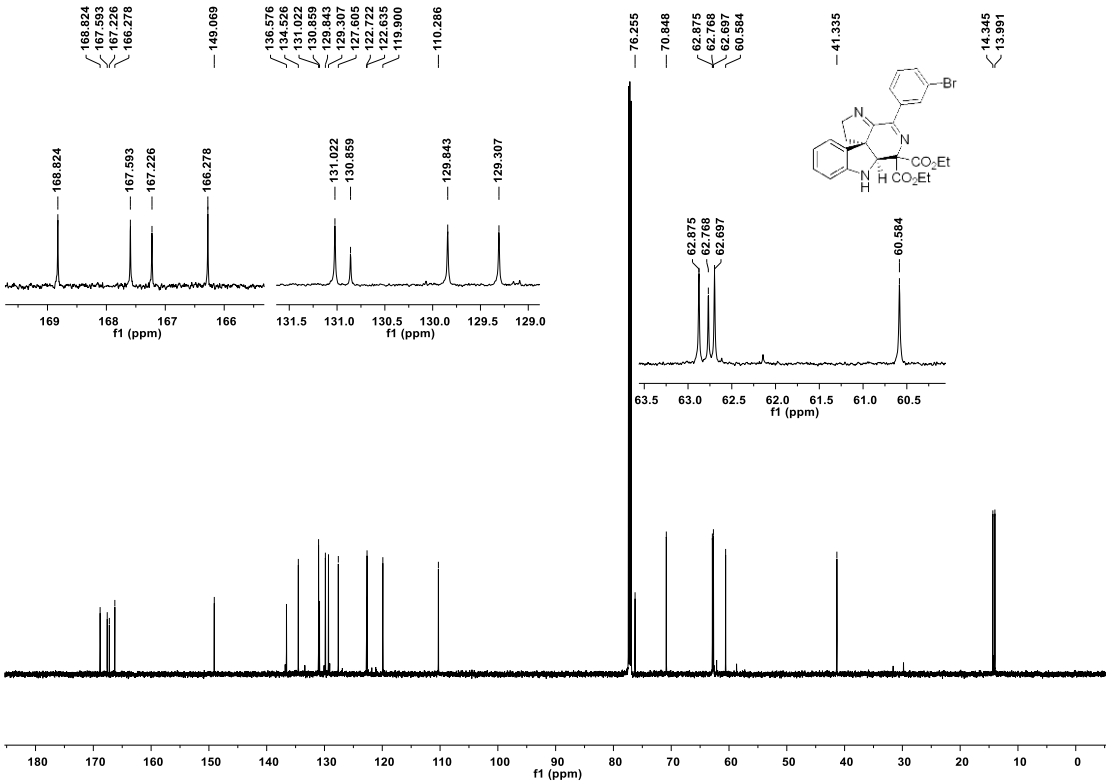
Diethyl (6a*S*,11b*R*)-4-(3-chlorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C20)



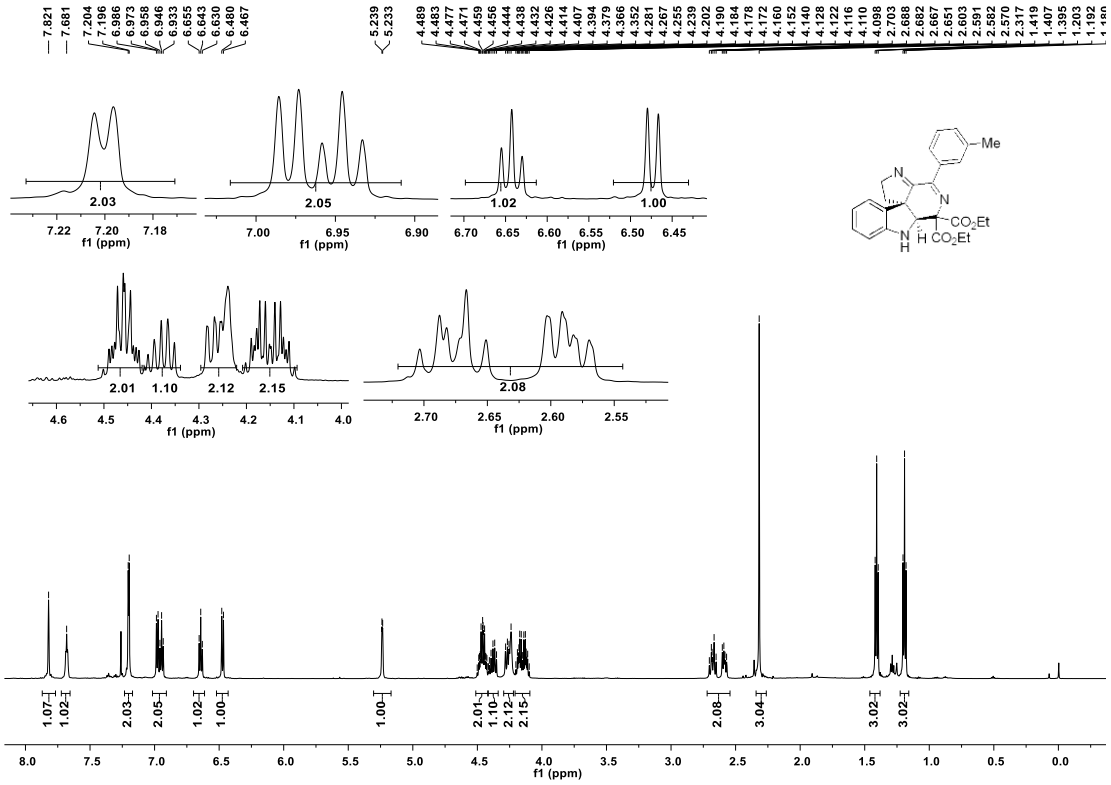


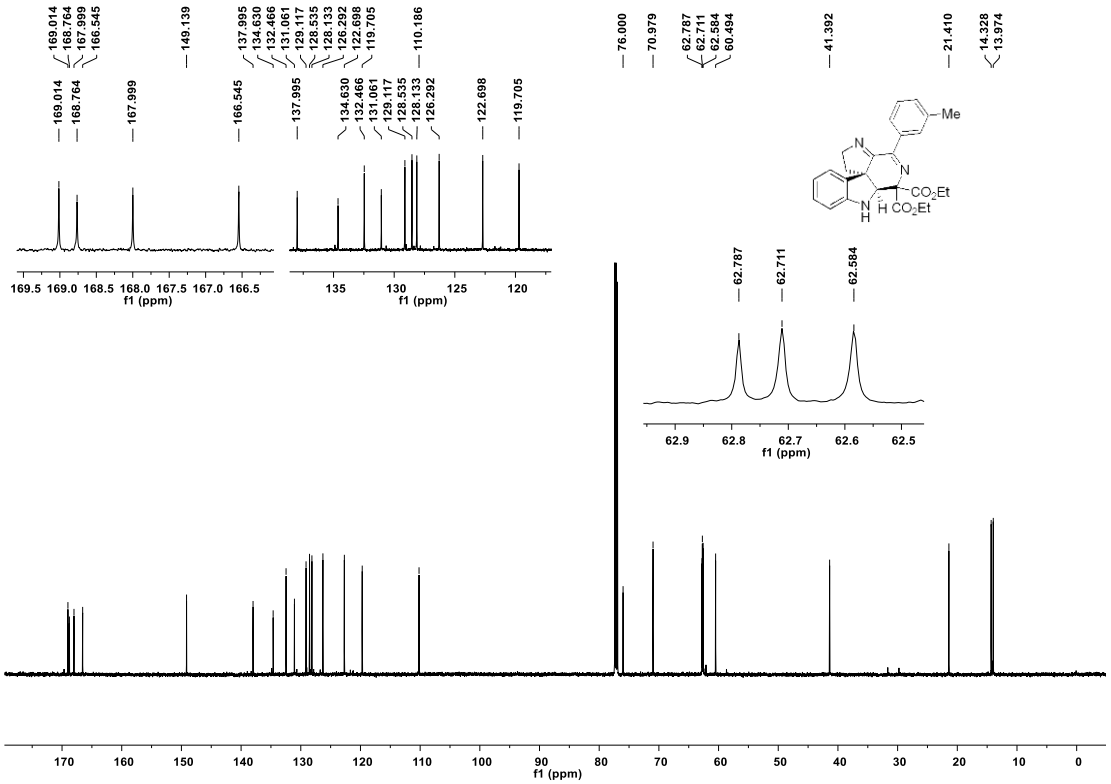
Diethyl (6a*S*,11b*R*)-4-(3-bromophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C21)



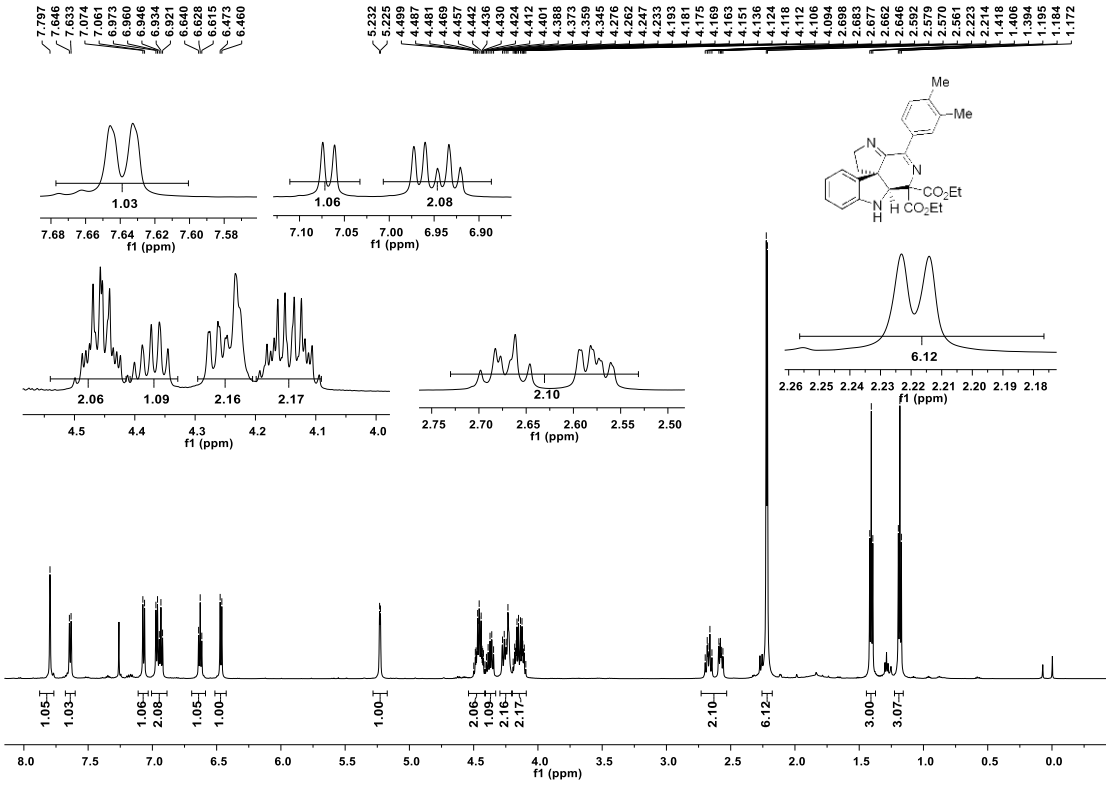


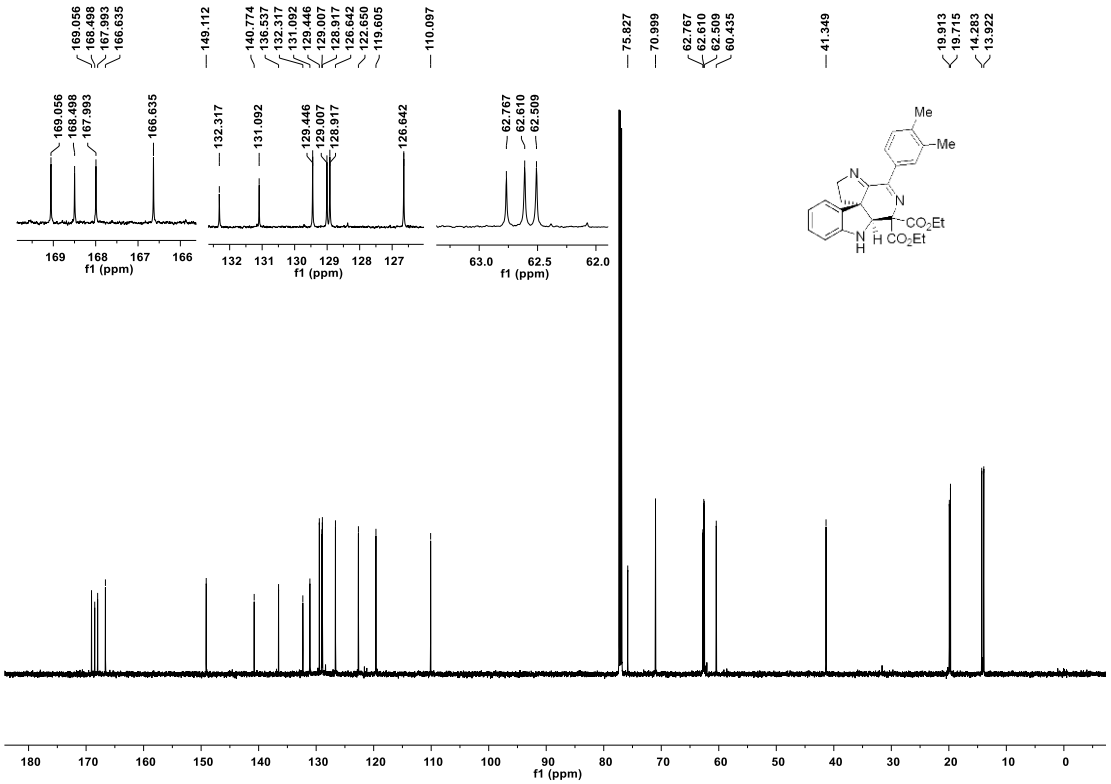
Diethyl (6a*S*,11b*R*)-4-(m-tolyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C22)



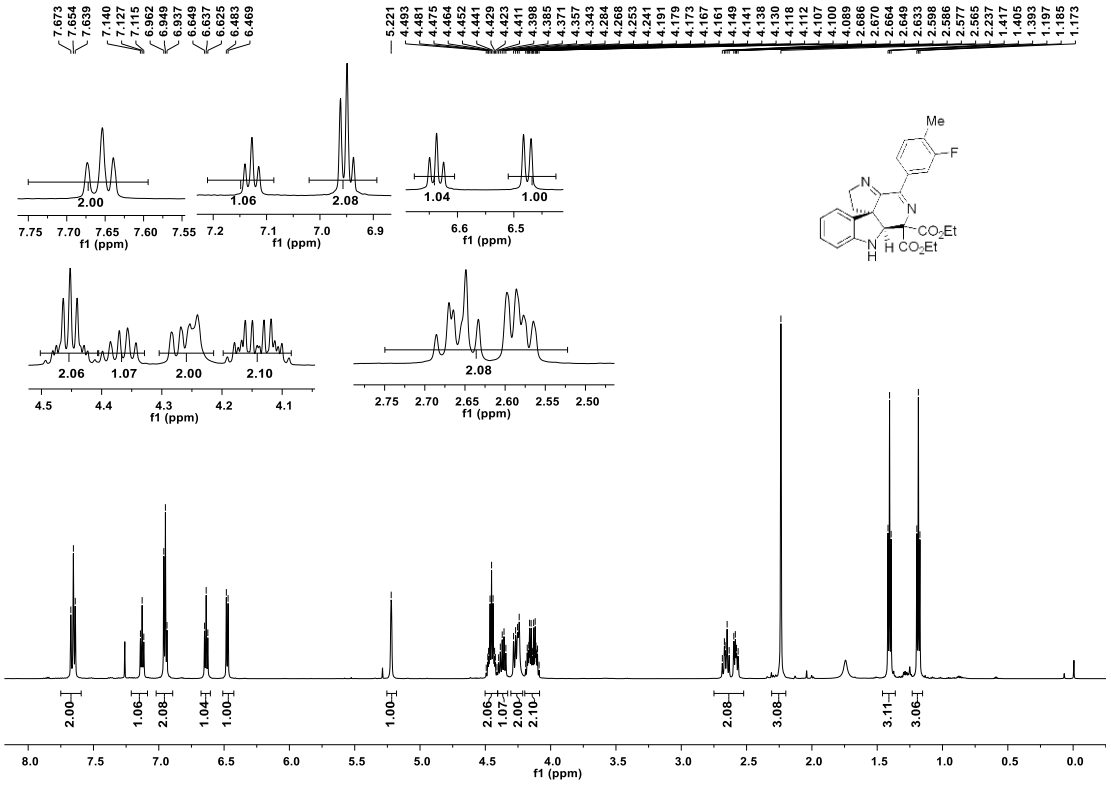


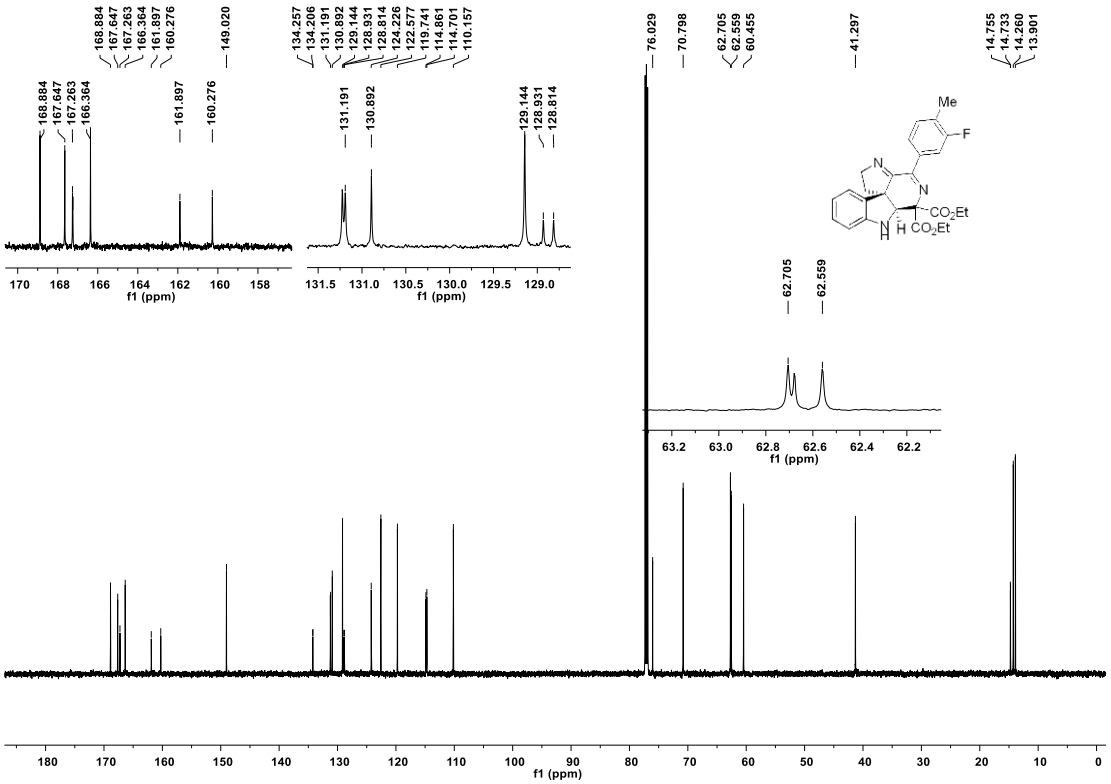
Diethyl (6aS,11bR)-4-(3,4-dimethylphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C23)

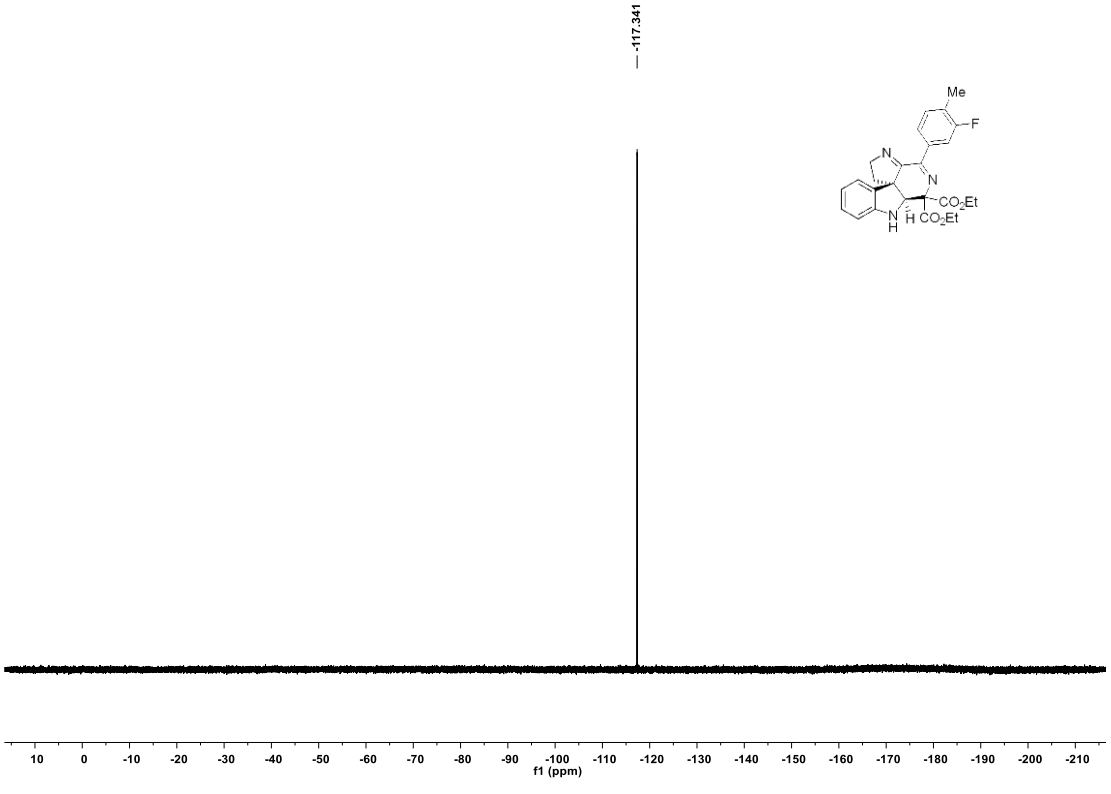




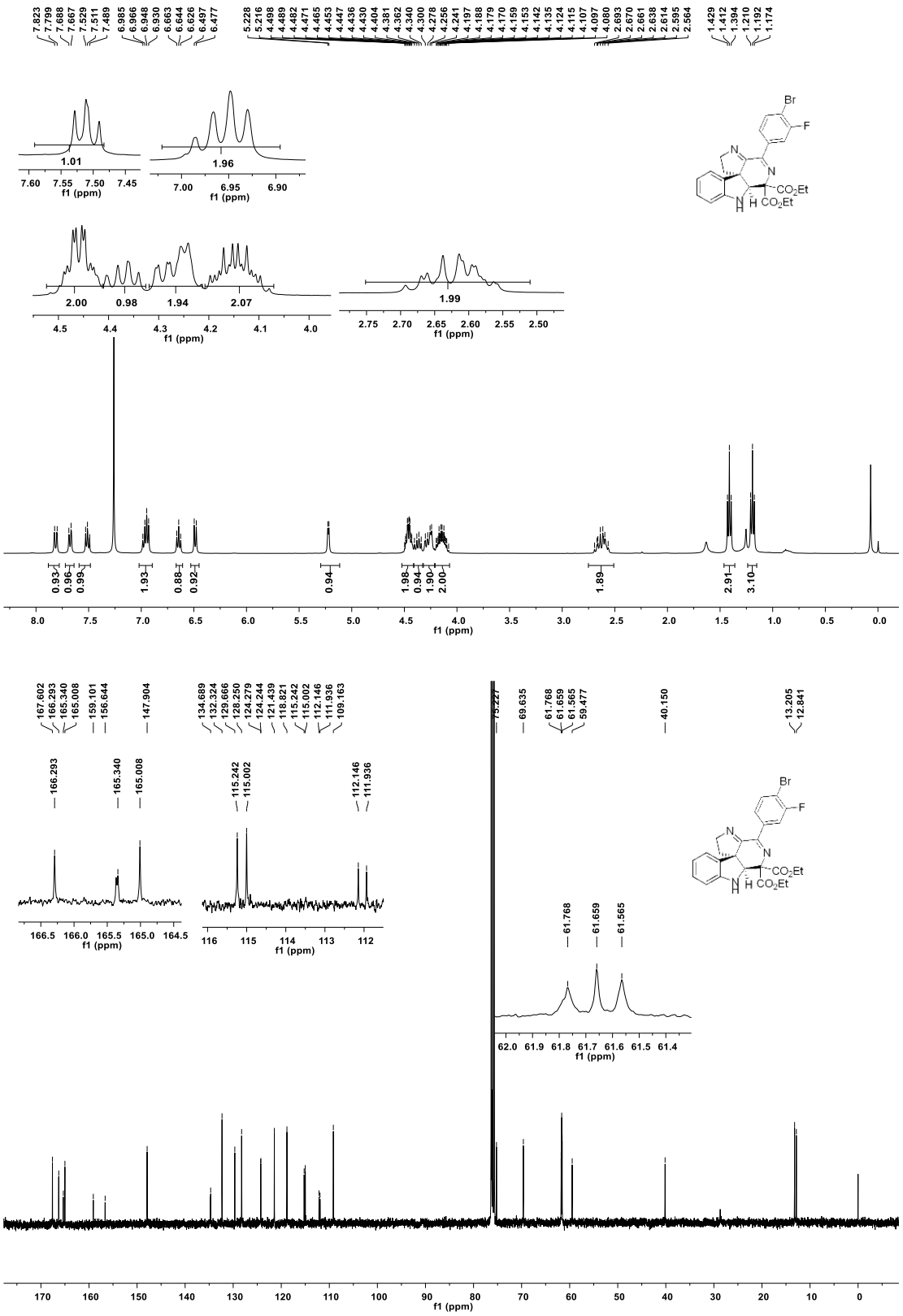
Diethyl (6aS,11bR)-4-(3-fluoro-4-methylphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C24)

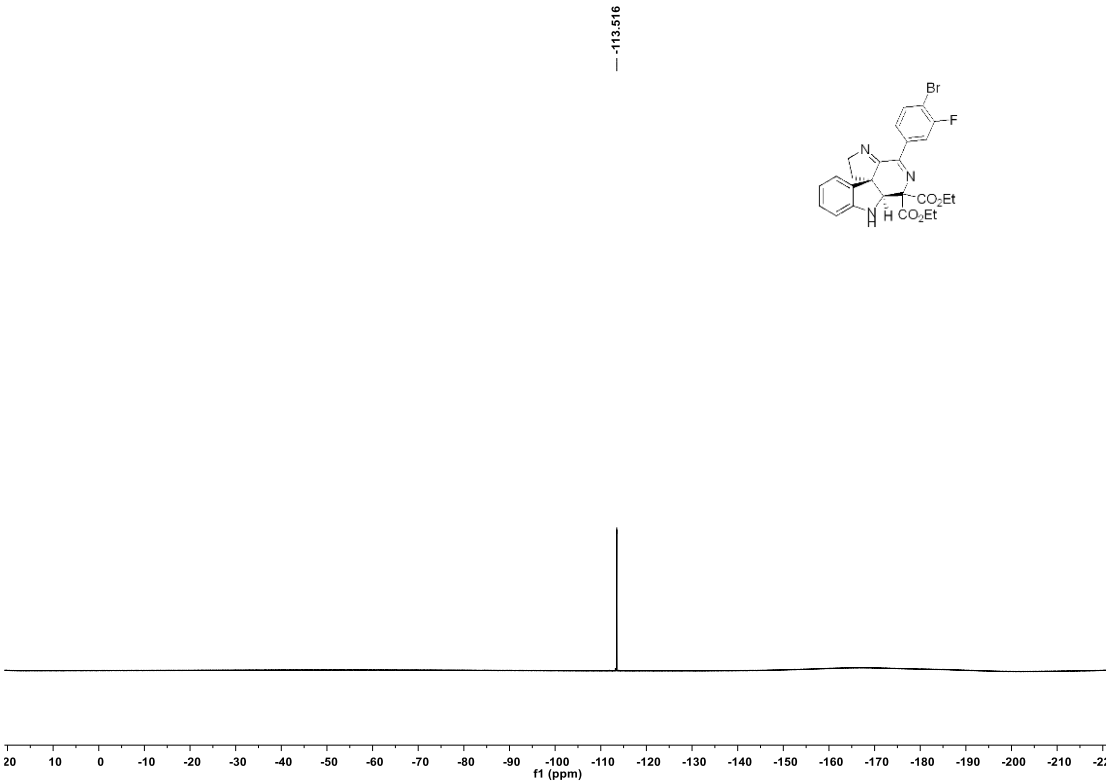



168.884
167.647
167.263
166.364
161.897
160.276
149.020
134.257
134.206
131.191
130.892
129.144
128.931
128.814
124.226
122.577
119.741
114.861
114.701
110.157
76.029
70.798
62.705
62.559
60.455
41.297
14.755
14.733
14.260
13.901
Me
F
N
N
CO2Et
H
N
H CO2Et
f1 (ppm)

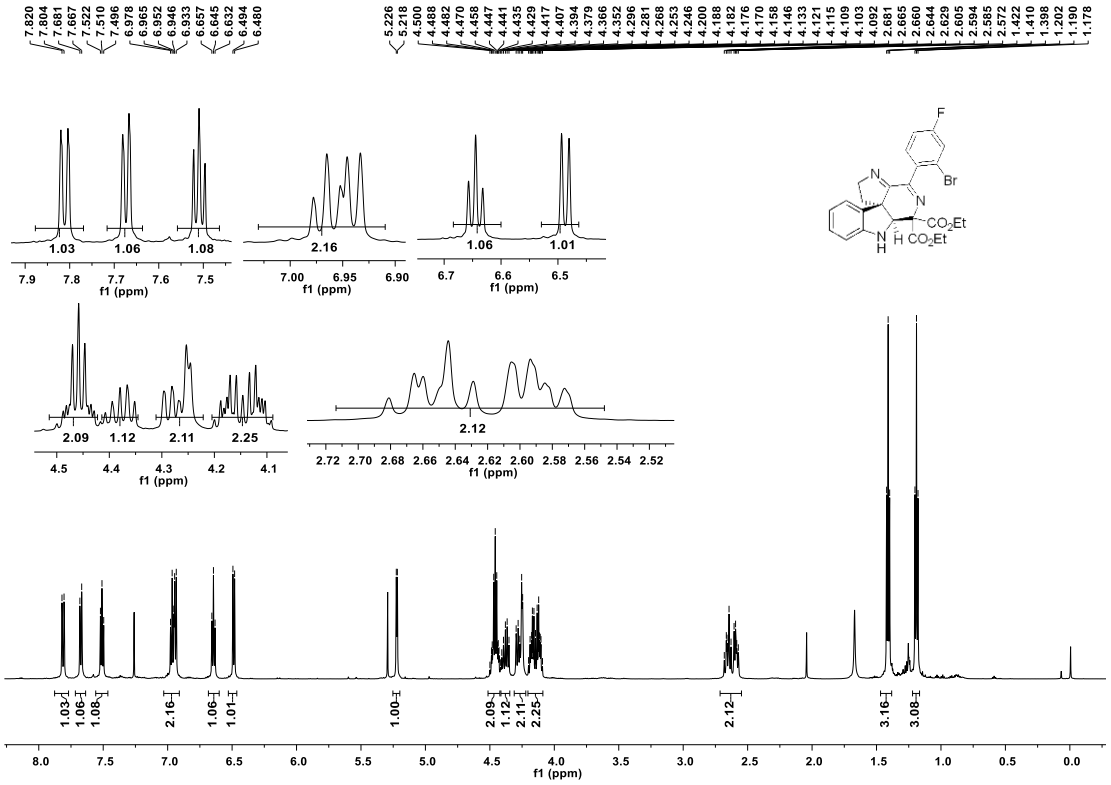

-117.341
Me
F
N
N
CO2Et
H
N
H CO2Et
f1 (ppm)

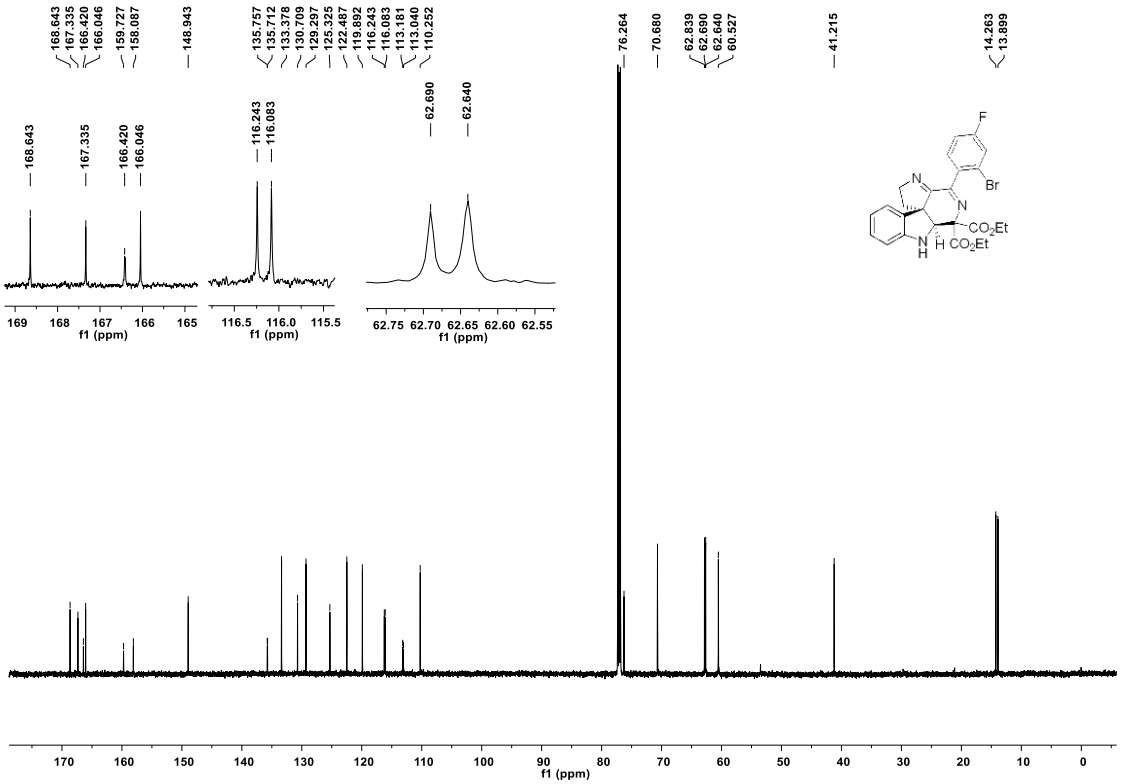
Diethyl (6a*S*,11b*R*)-4-(4-bromo-3-fluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C25)

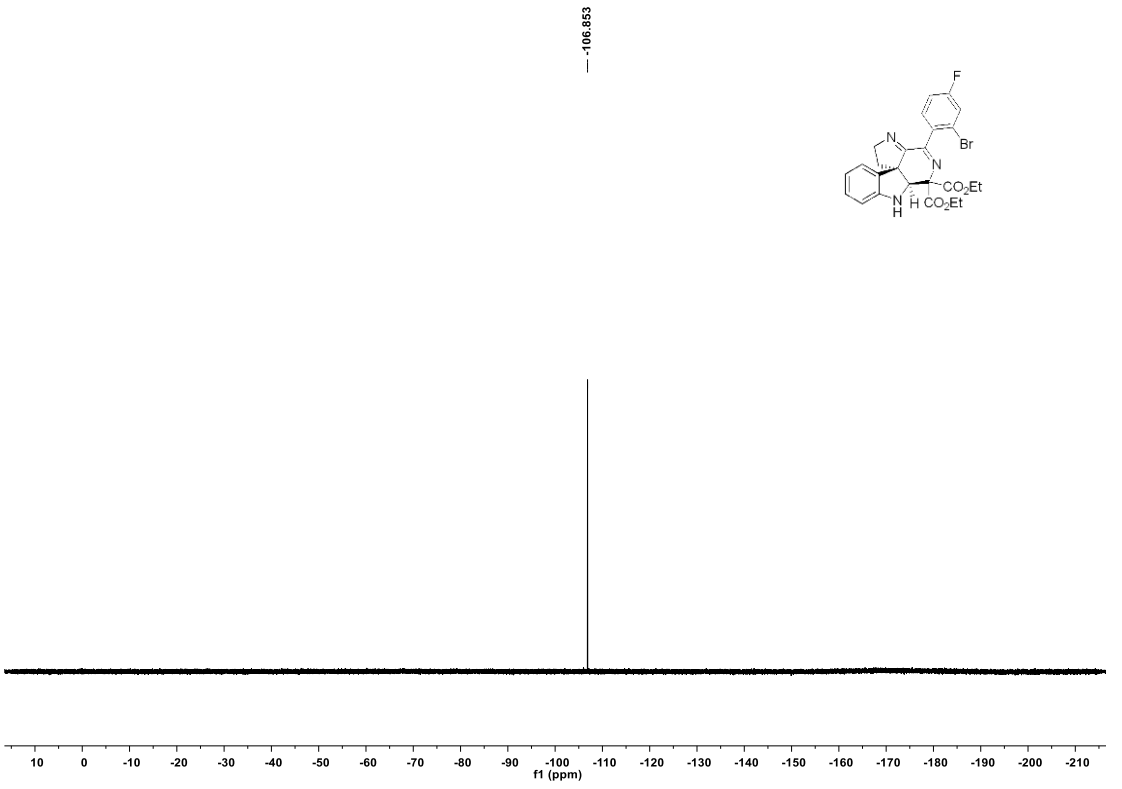




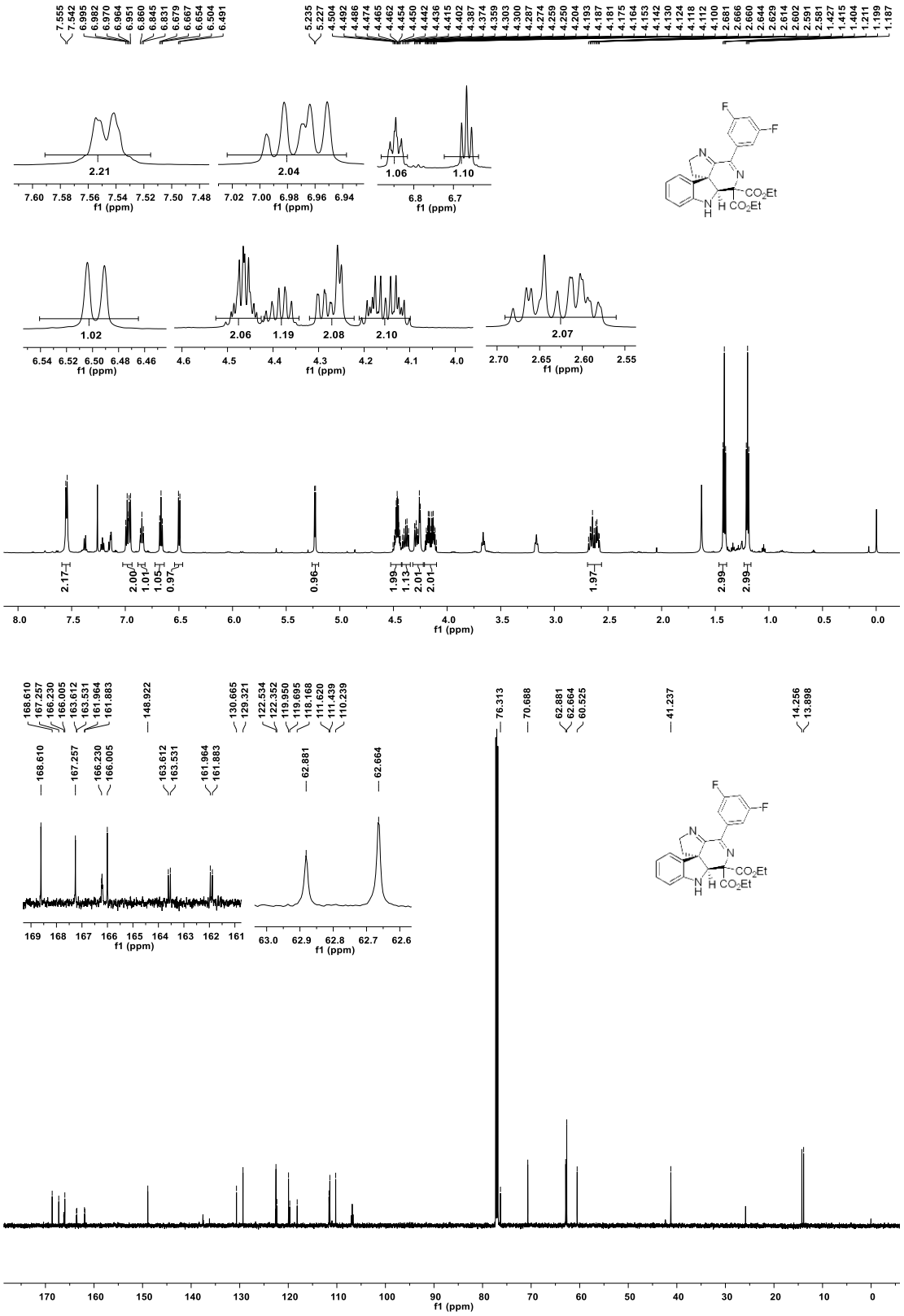
Diethyl (6aS,11bR)-4-(2-bromo-4-fluorophenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C26)

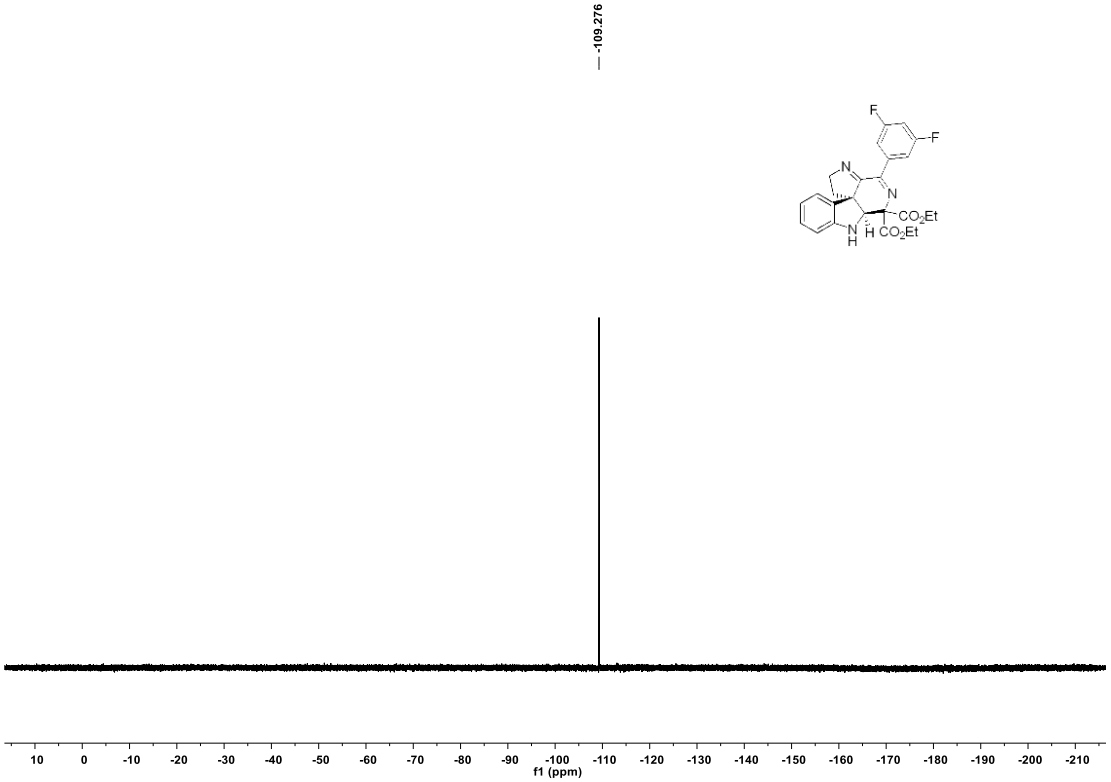



168.643
167.335
166.420
166.046
159.727
158.087
148.943
135.757
135.712
133.378
130.709
129.297
125.325
122.487
119.892
116.243
116.083
113.181
113.040
110.252
76.264
70.680
62.839
62.690
62.640
60.527
41.215
14.263
13.899
f1 (ppm)

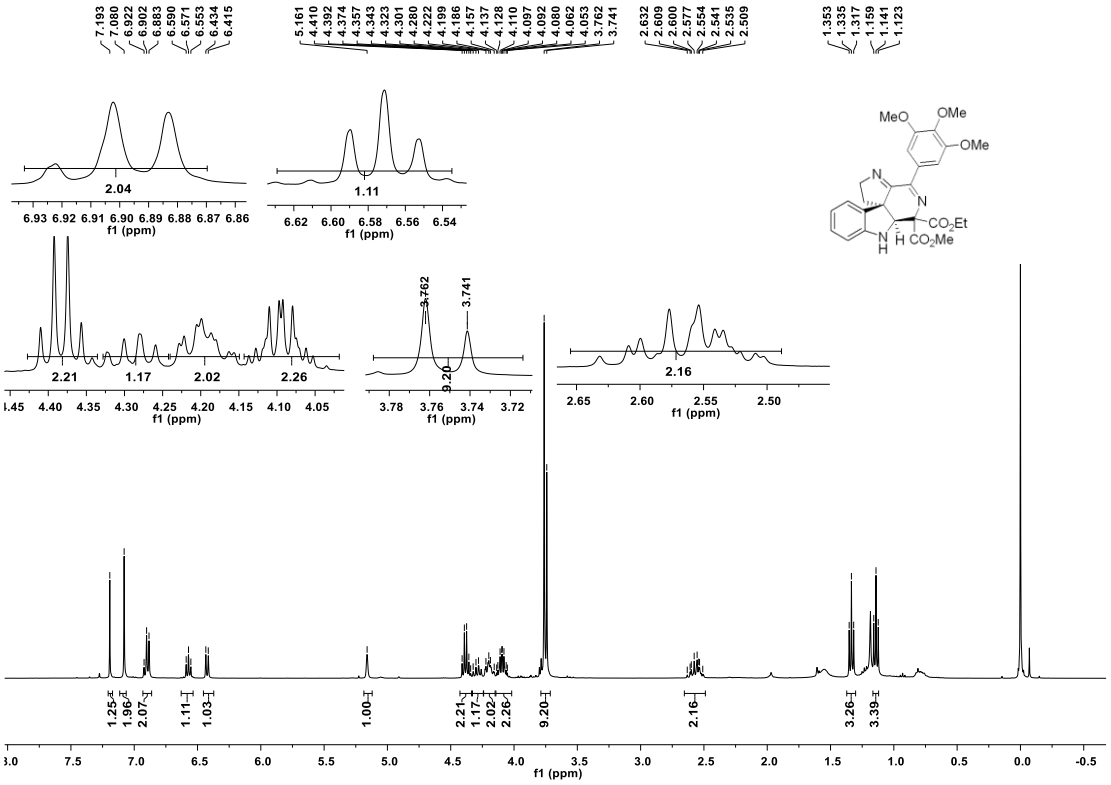

-106.853
f1 (ppm)

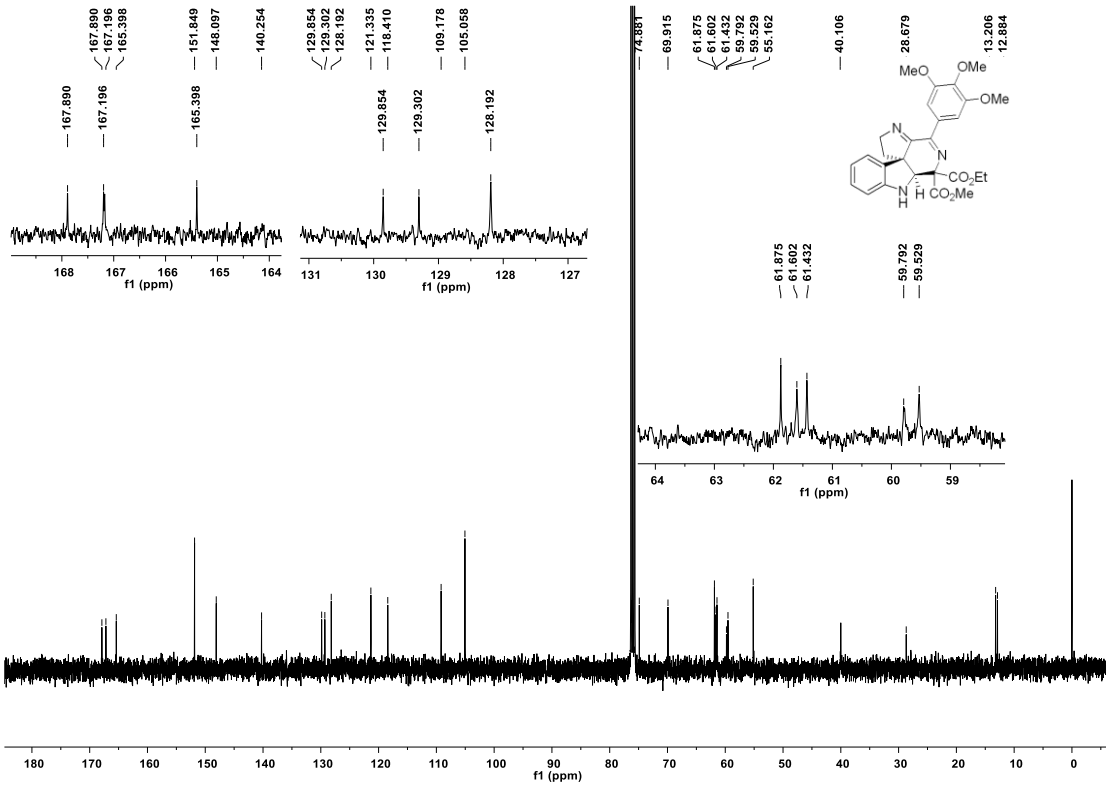
Diethyl (6a*S*,11b*R*)-4-(3,5-difluorophenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C27)



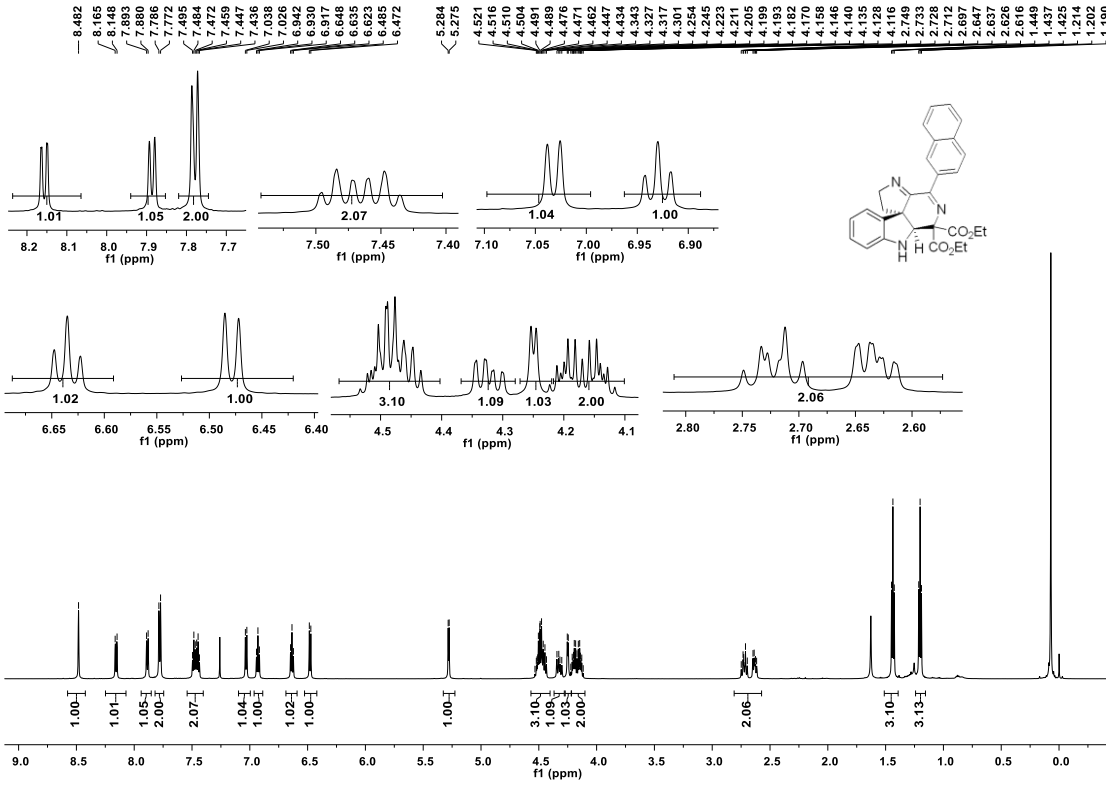


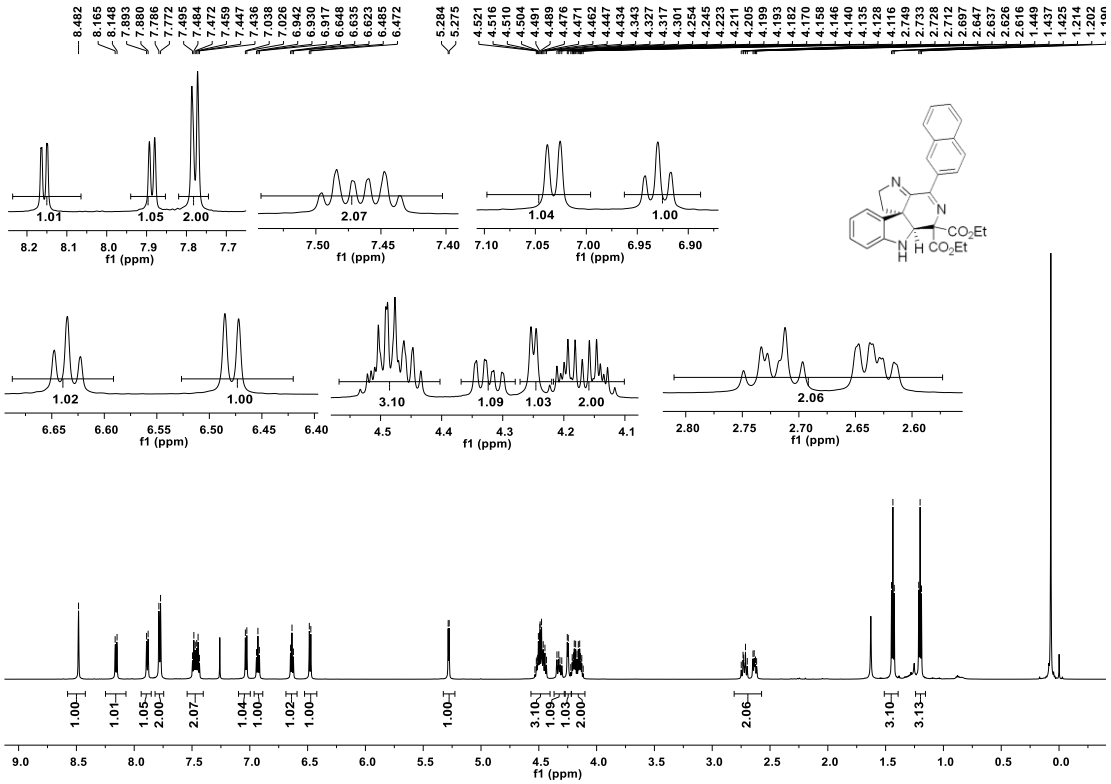
Diethyl (6aS,11bR)-4-(3,4,5-trimethoxyphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C28)



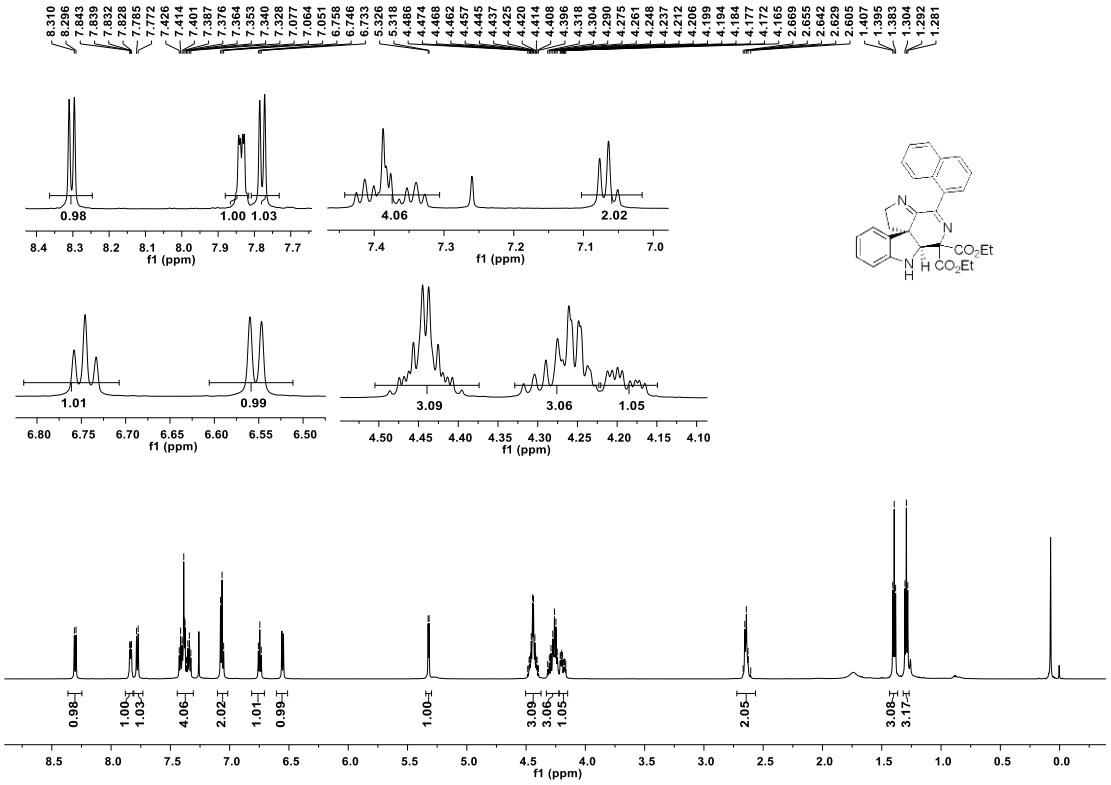


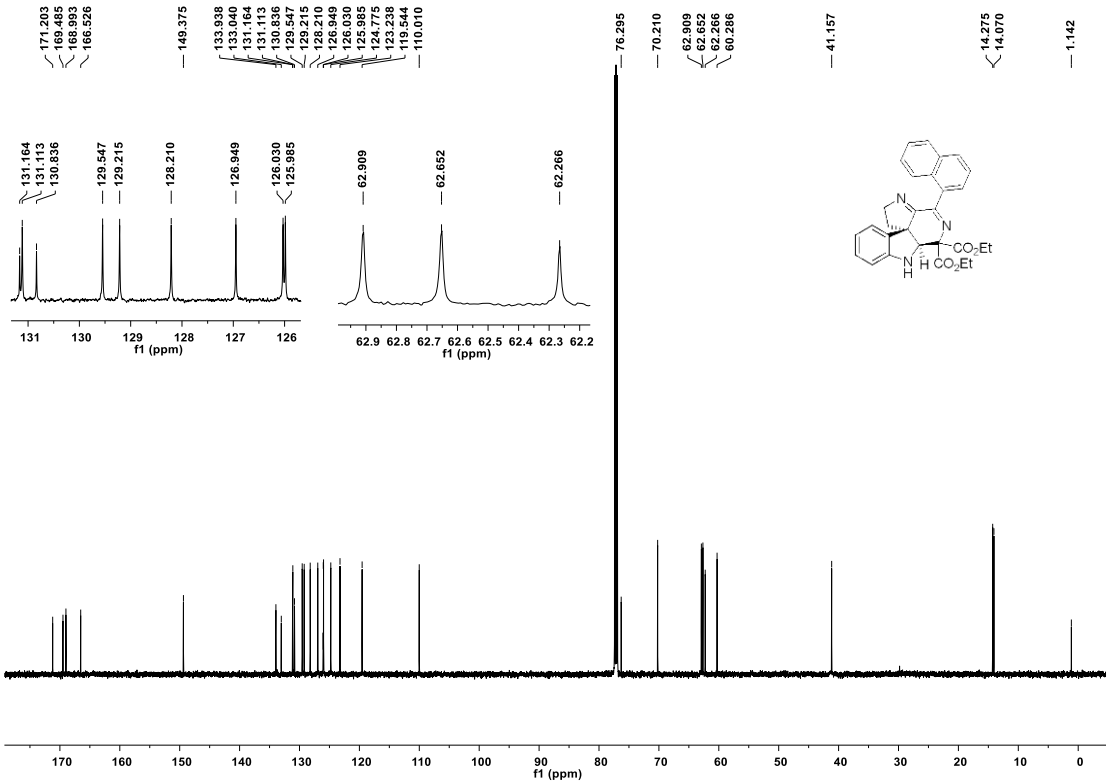
Diethyl (6a*S*,11b*R*)-4-(naphthalen-2-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C29)



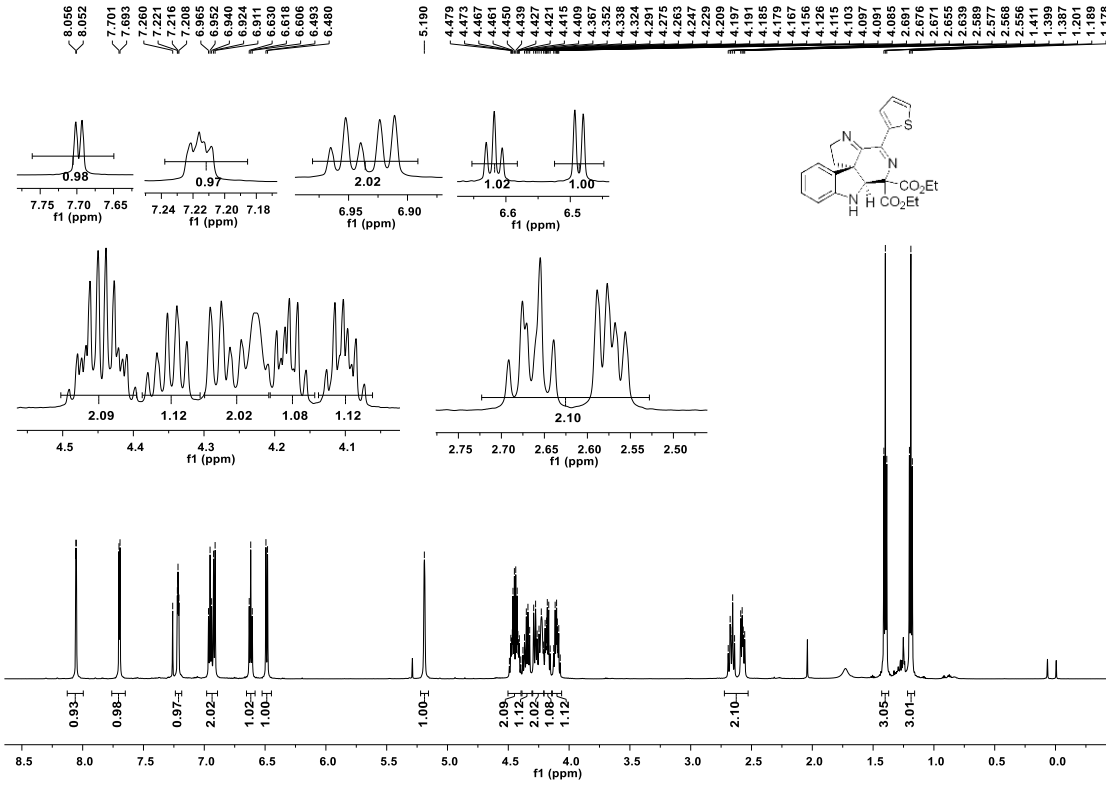


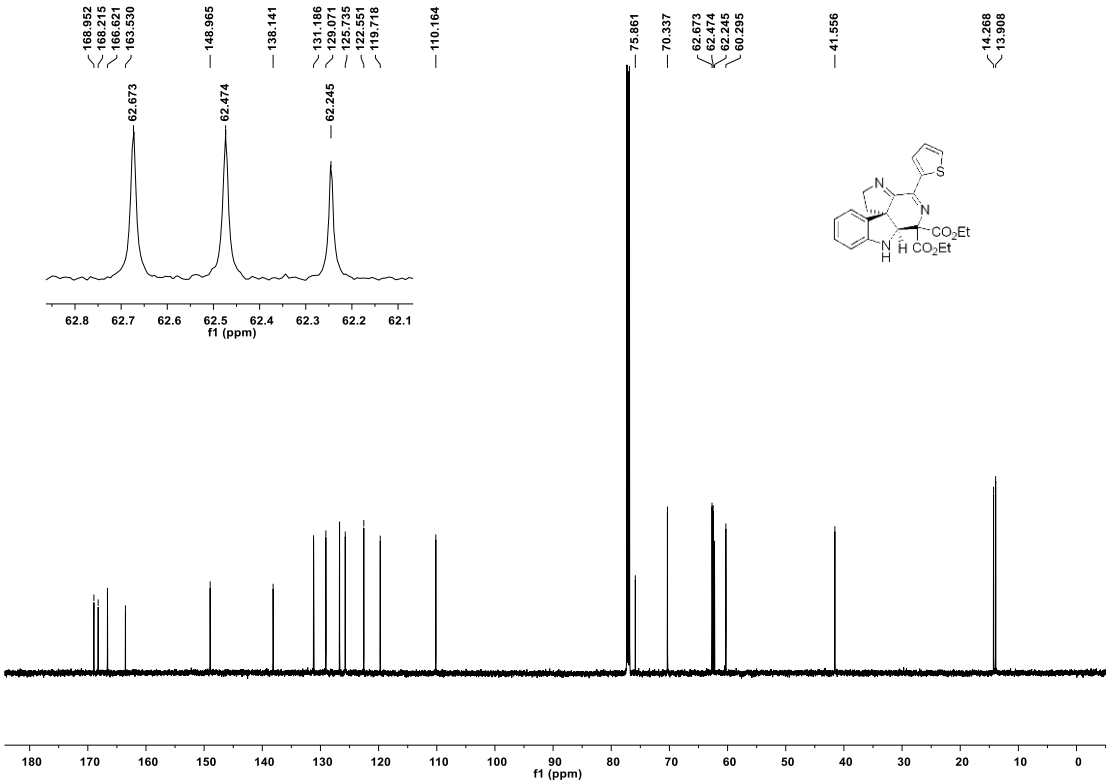
Diethyl (6a*S*,11b*R*)-4-(naphthalen-1-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C30)



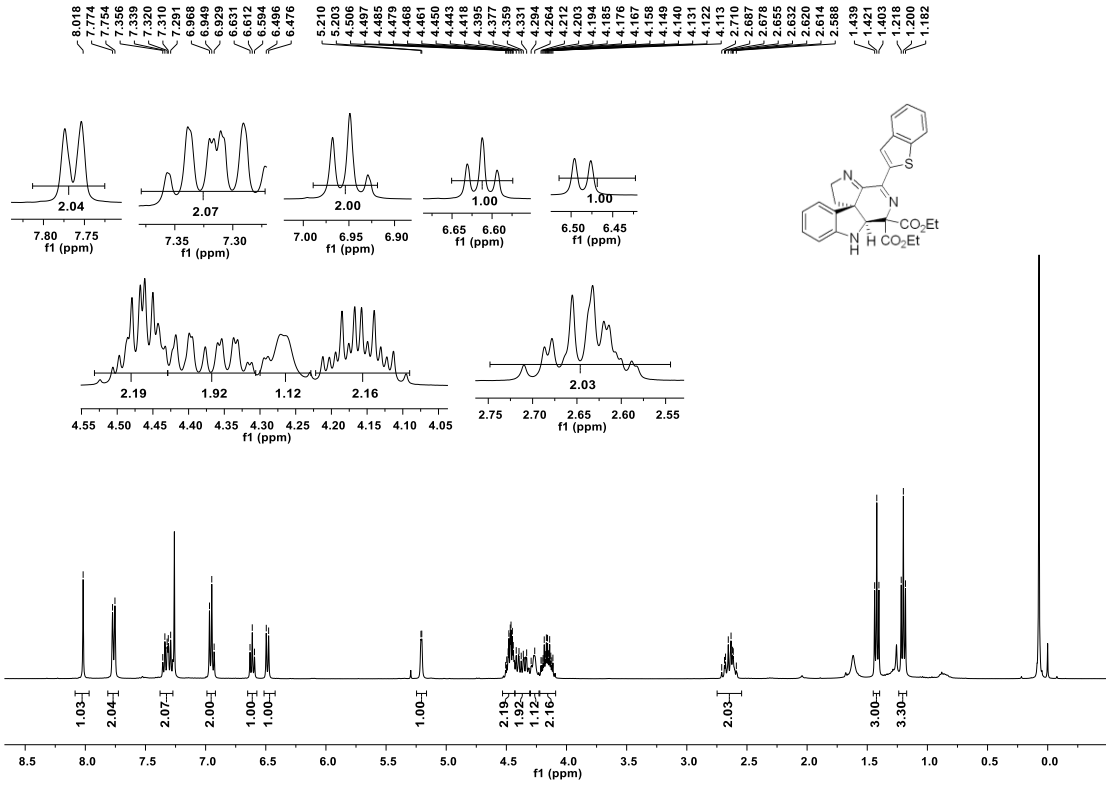


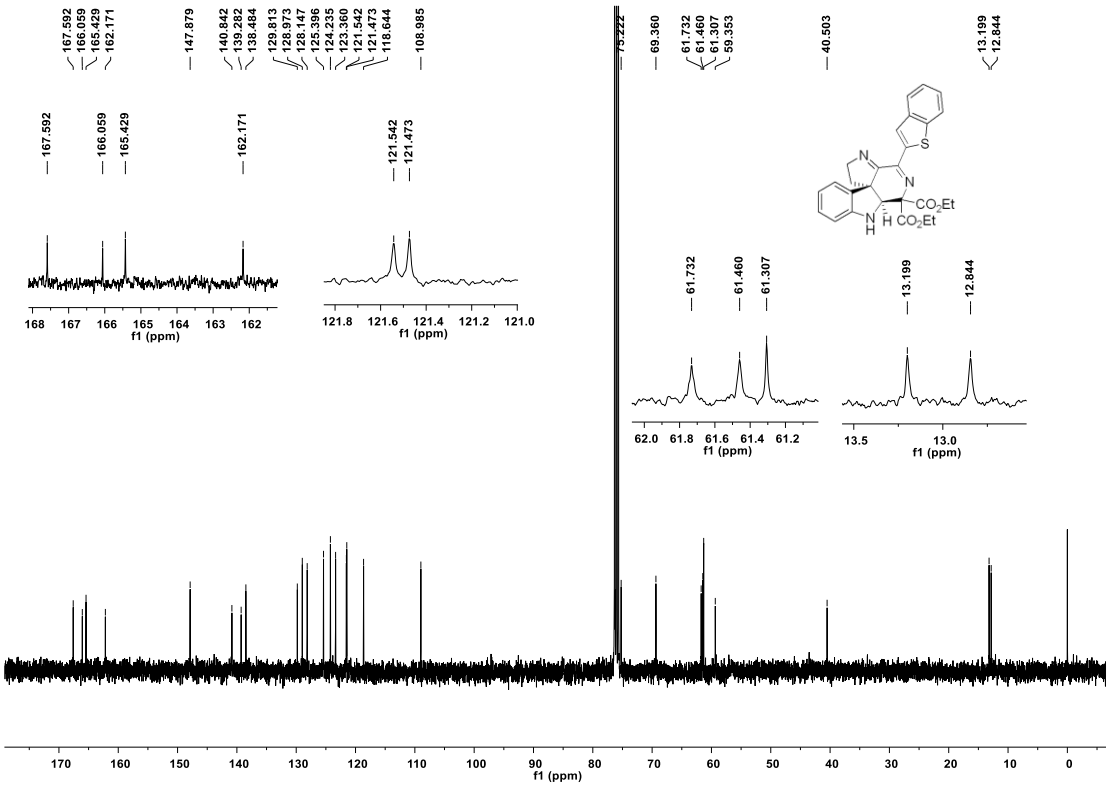
Diethyl (6aS,11bR)-4-(thiophen-2-yl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C31)



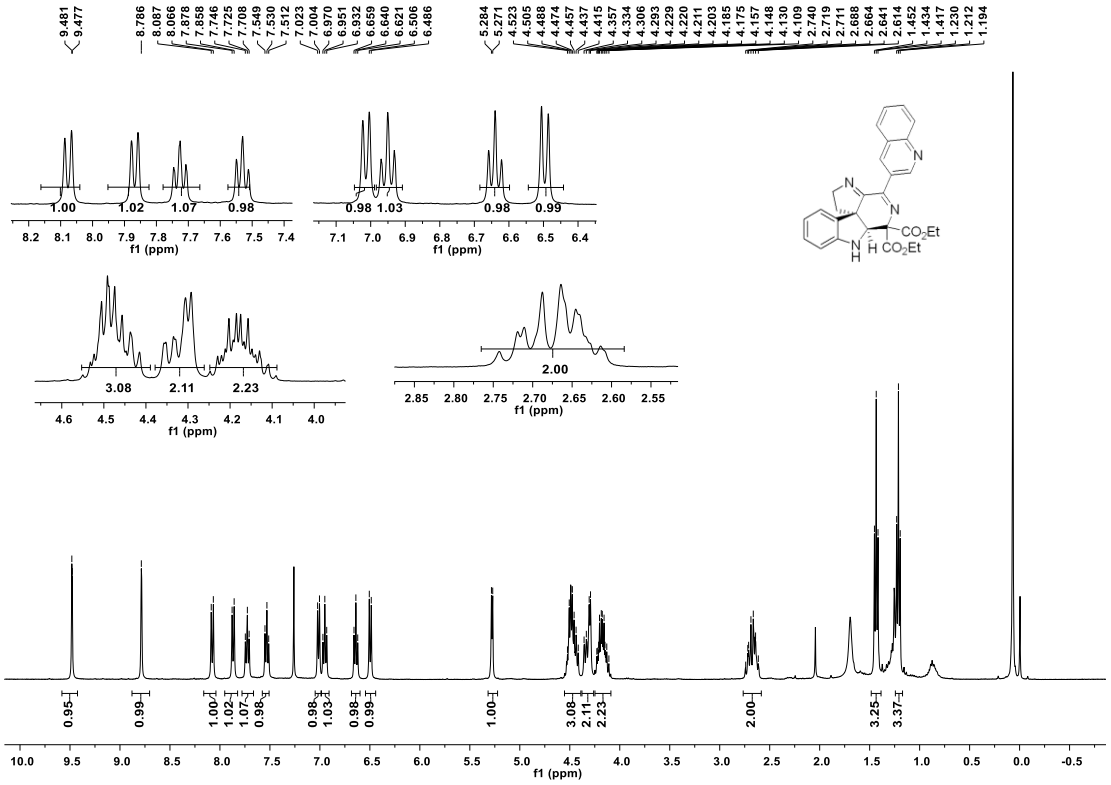


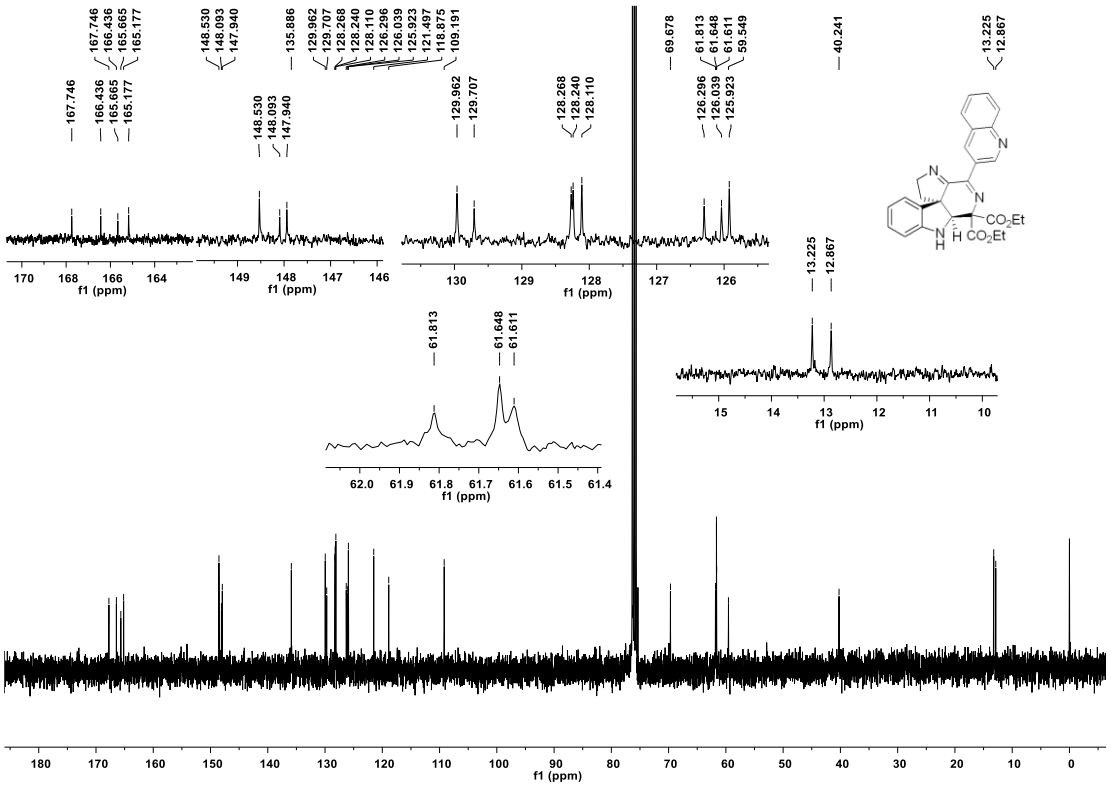
Diethyl (6a*S*,11b*R*)-4-(benzo[b]thiophen-2-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C32)



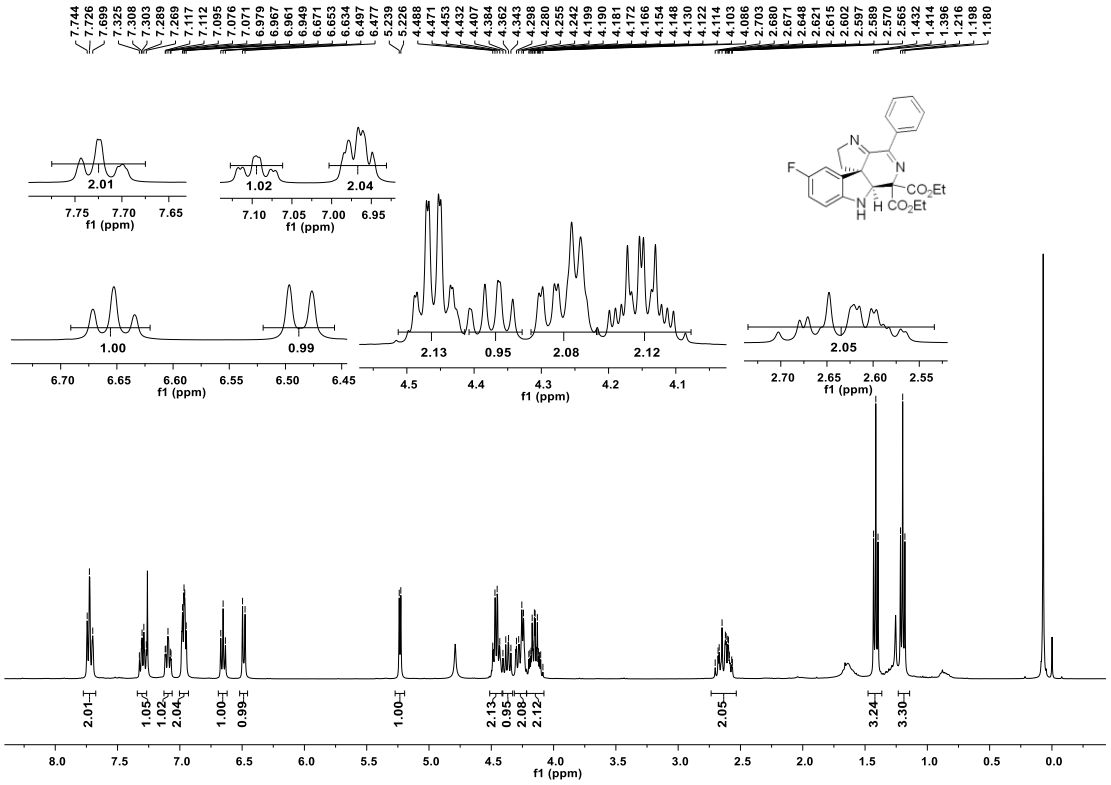


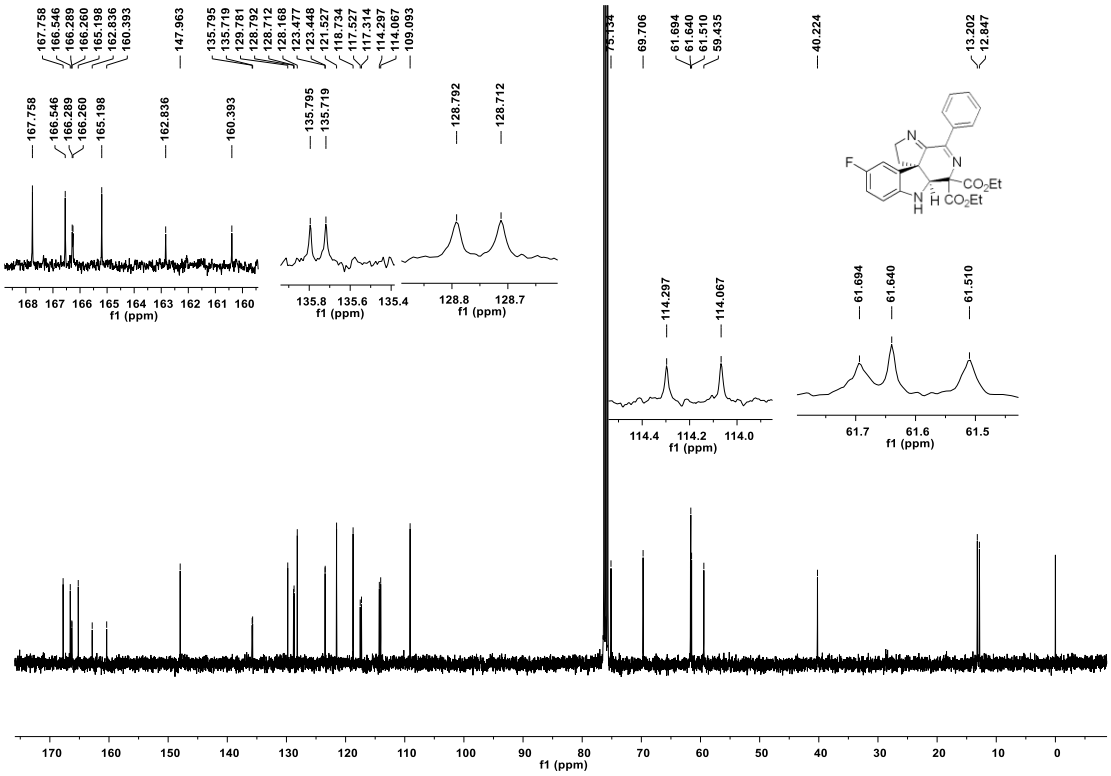
Diethyl (6a*S*,11b*R*)-4-(quinolin-3-yl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C33)

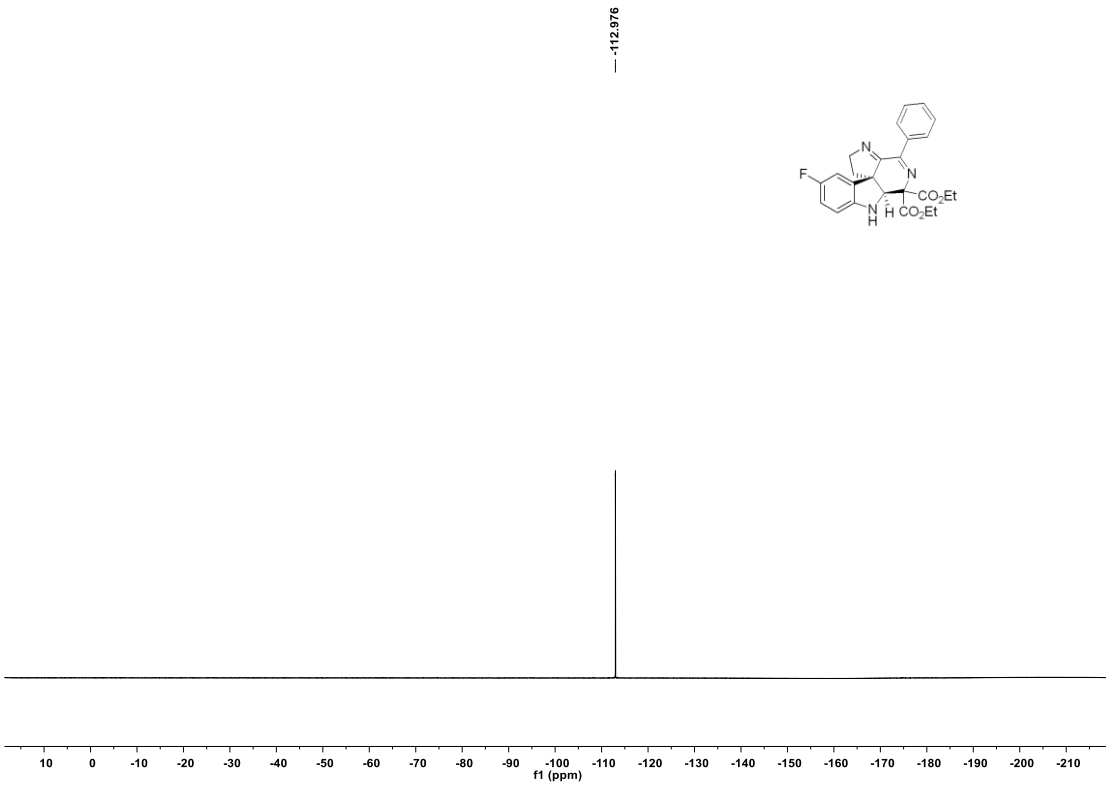




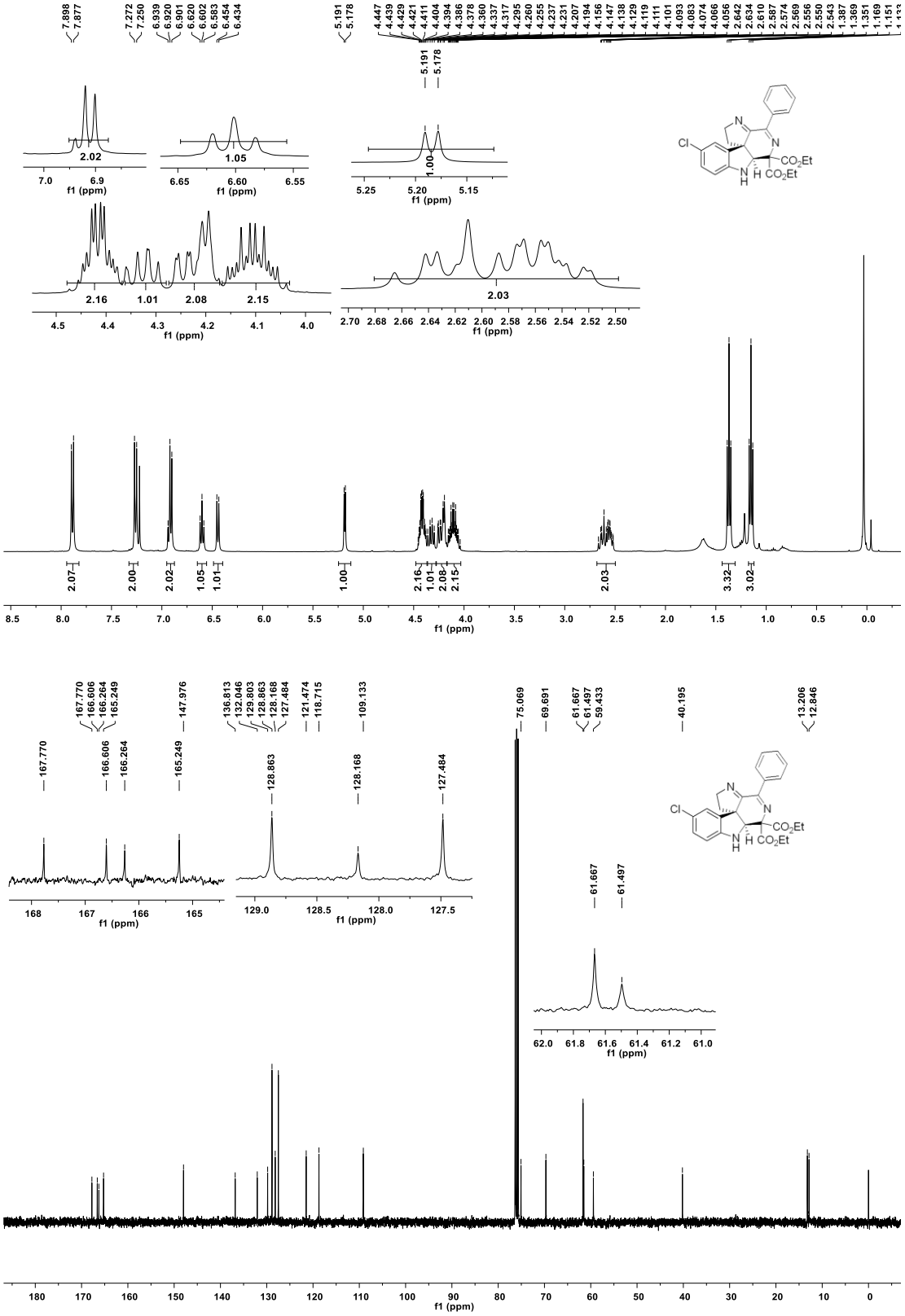
Diethyl (6aS,11bR)-10-fluoro-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C34)



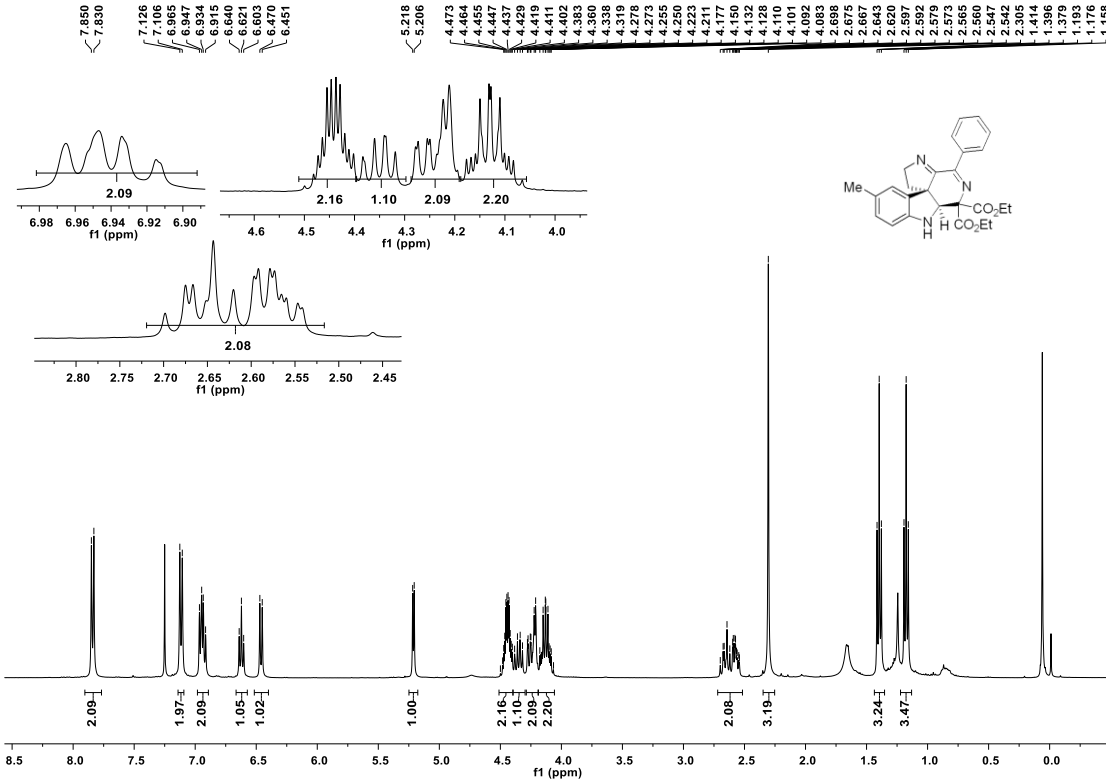

167.758
166.546
166.289
166.260
165.198
162.836
160.393
147.963
135.795
135.719
129.781
128.792
128.712
128.168
123.477
123.448
121.527
118.734
117.527
117.314
114.297
114.067
109.093
75.134
69.706
61.694
61.640
61.510
59.435
40.224
13.202
12.847
f1 (ppm)

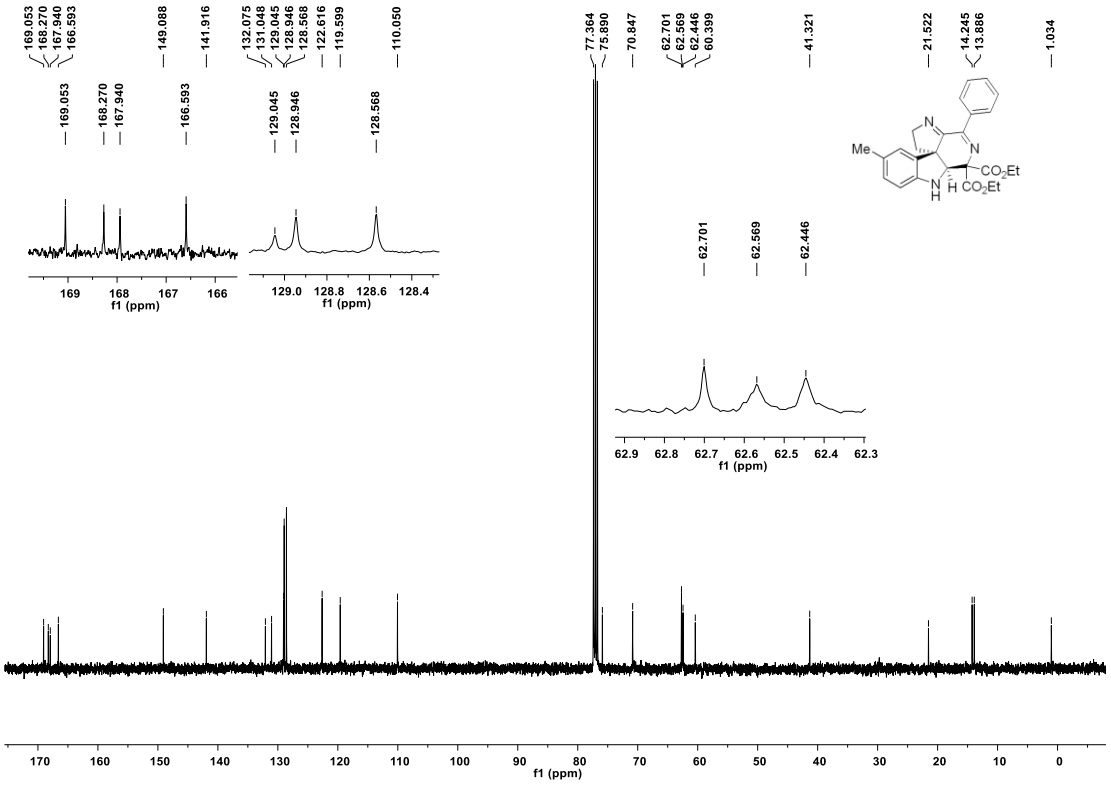

-112.976
f1 (ppm)

Diethyl (6a*S*,11b*R*)-10-chloro-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C35)

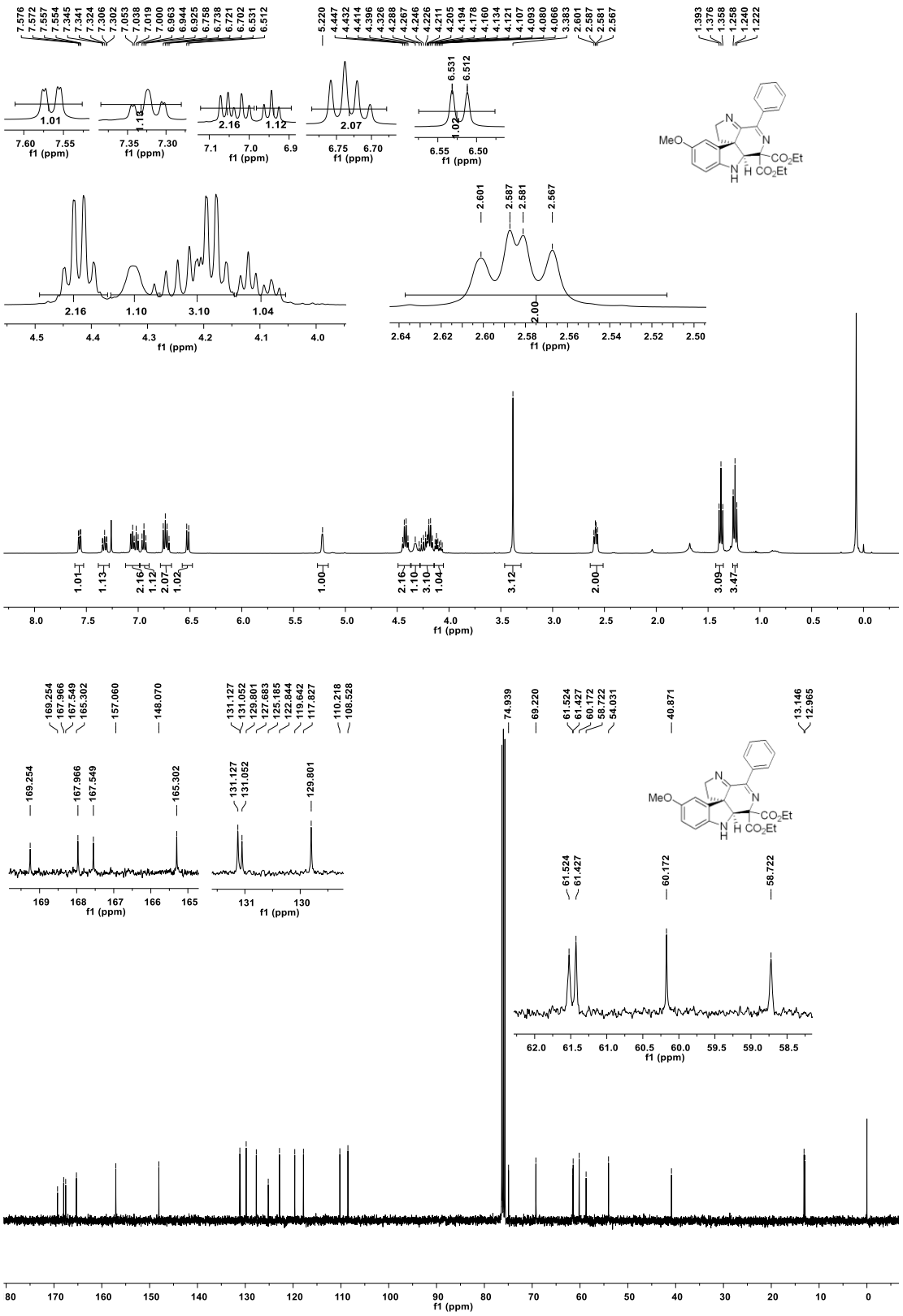


Diethyl (6a*S*,11b*R*)-10-methyl-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C36)

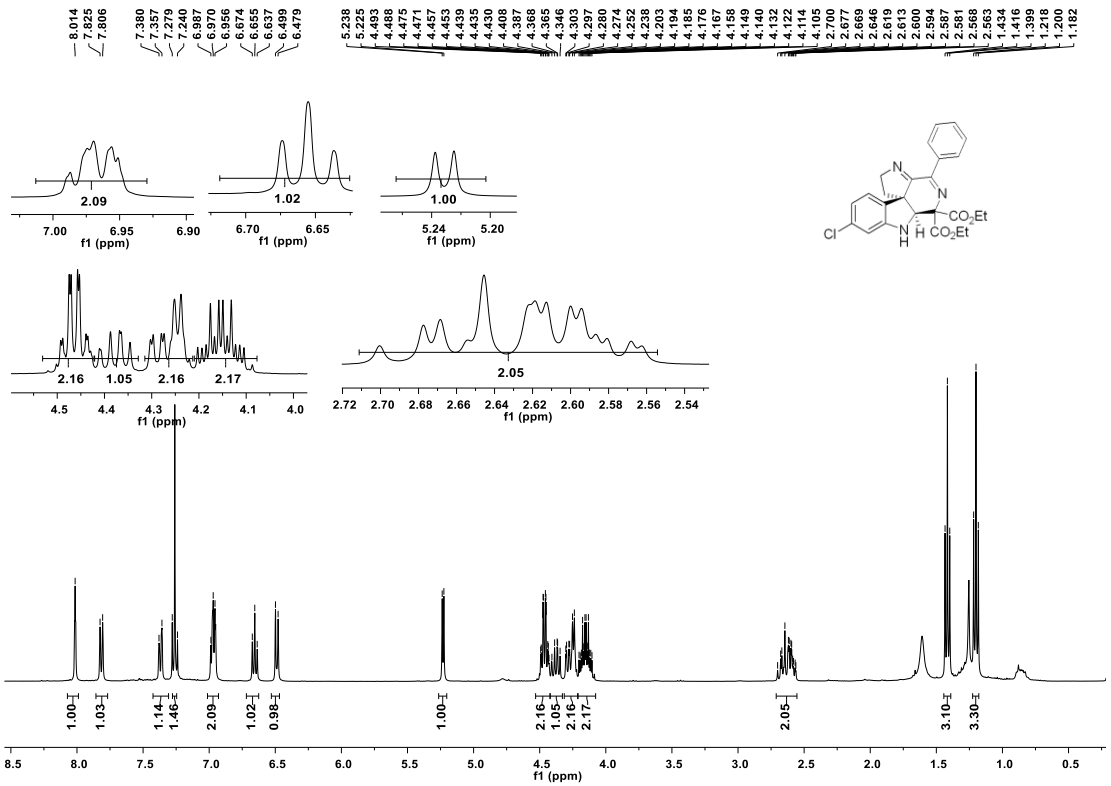


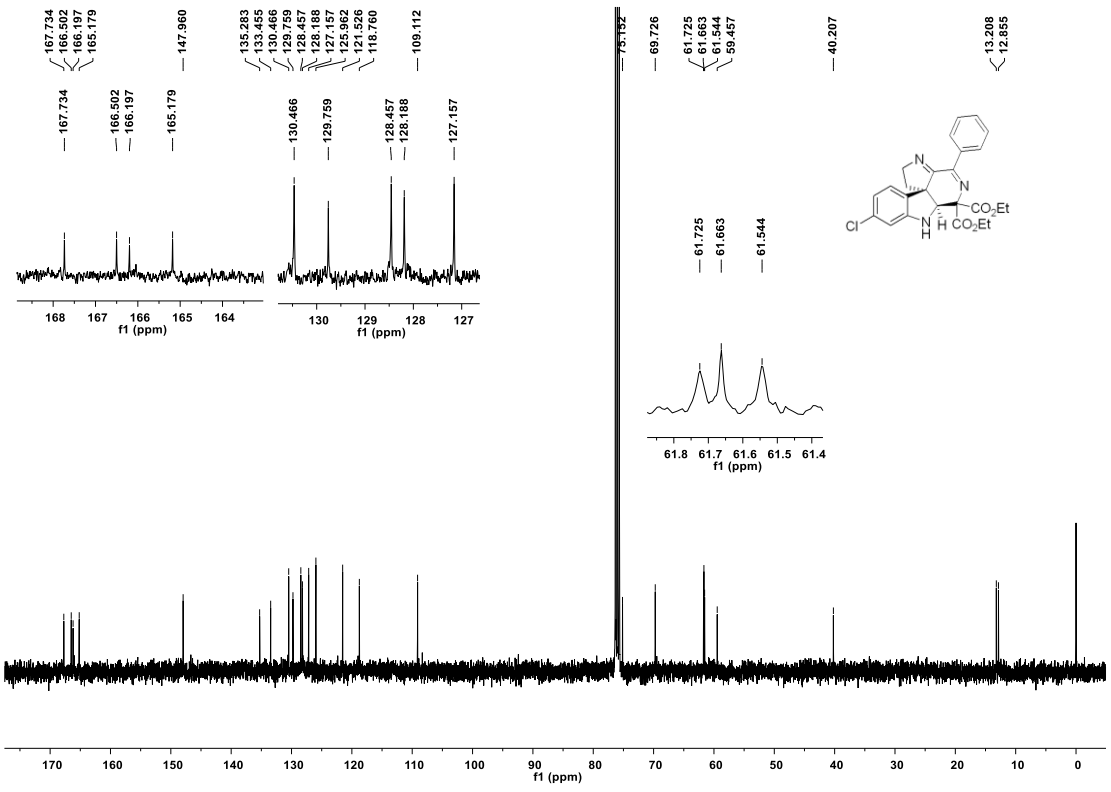


Diethyl (6a*S*,11b*R*)-10-methoxy-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C37)

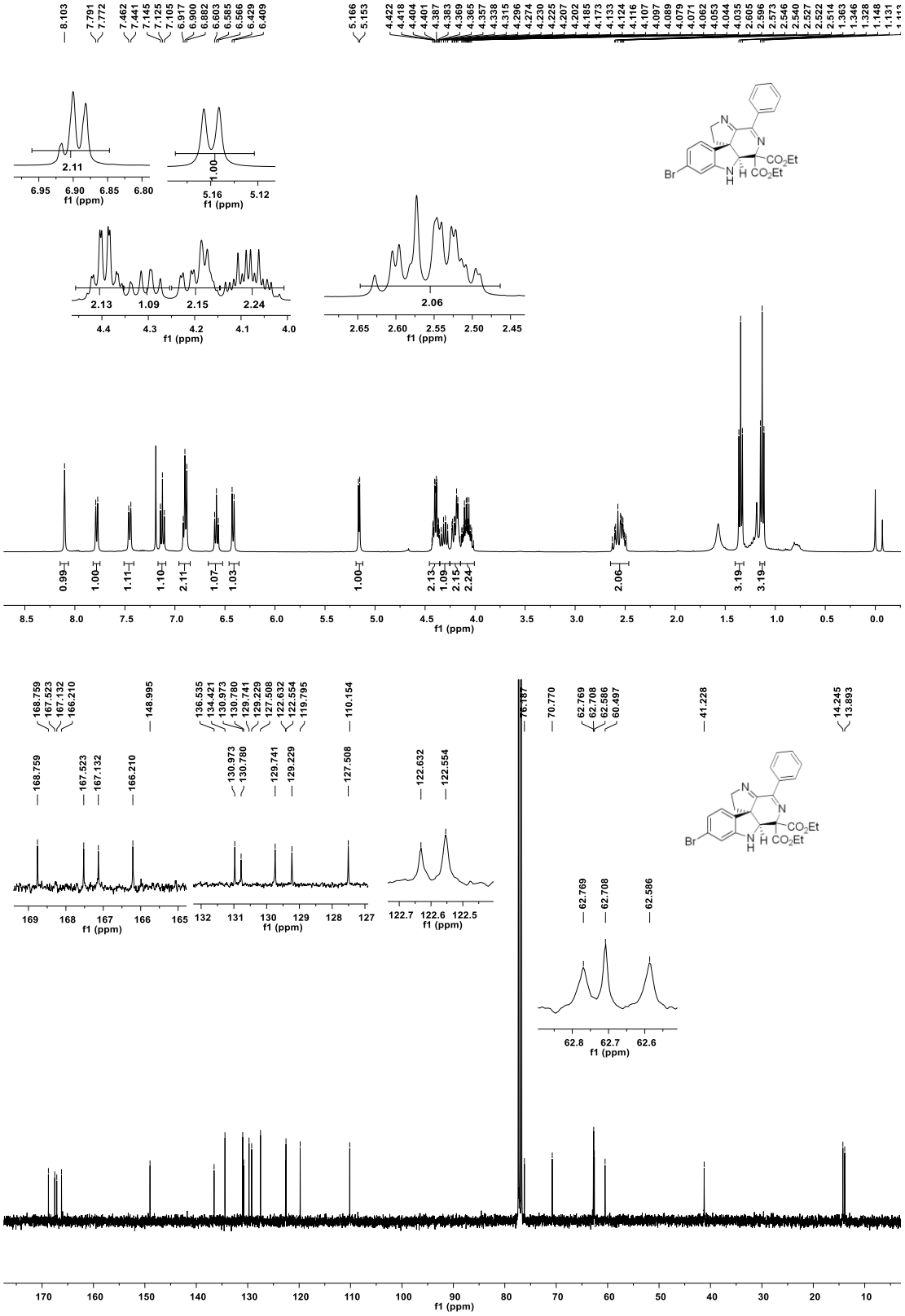


Diethyl (6a*S*,11b*R*)-9-chloro-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C38)

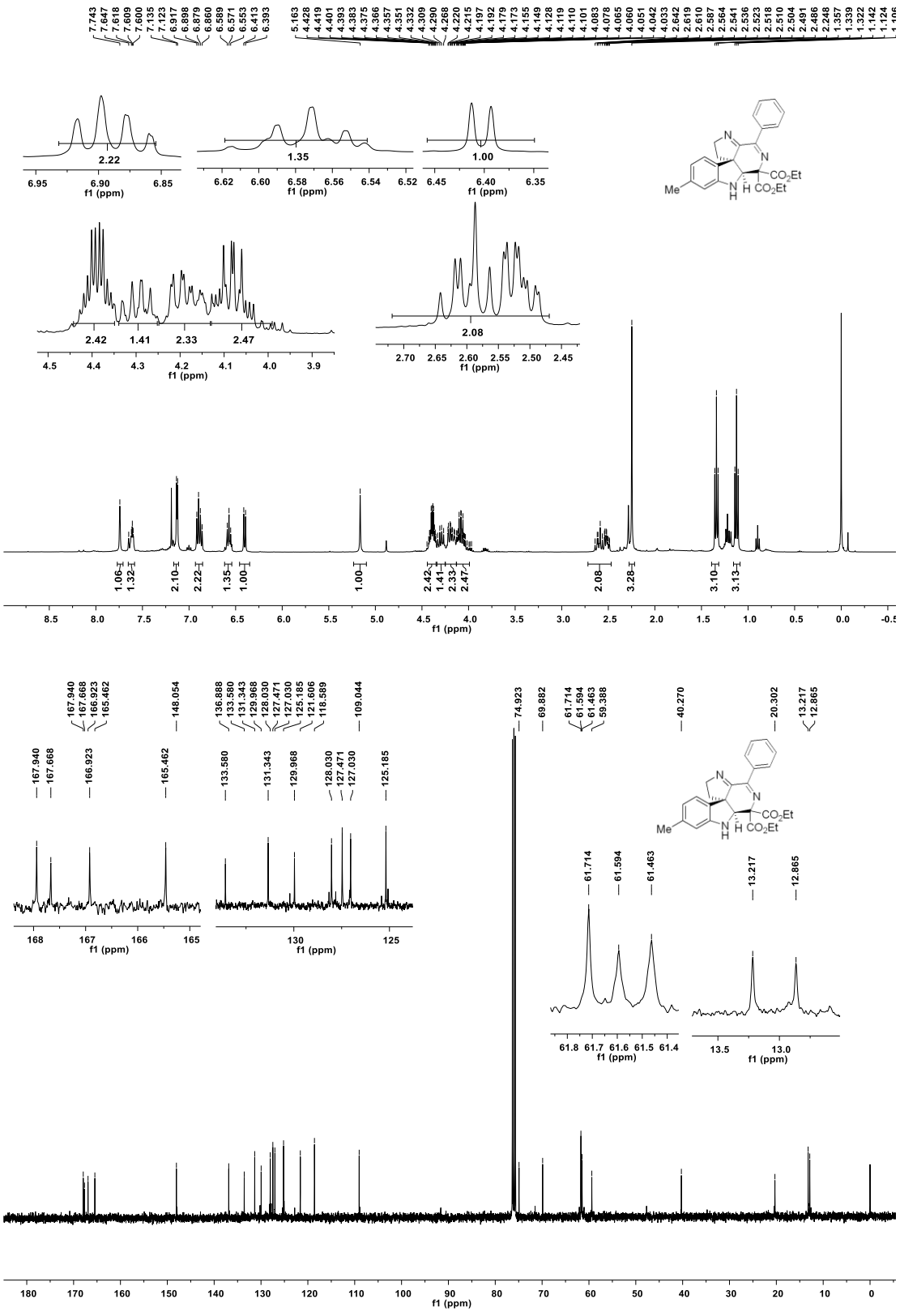




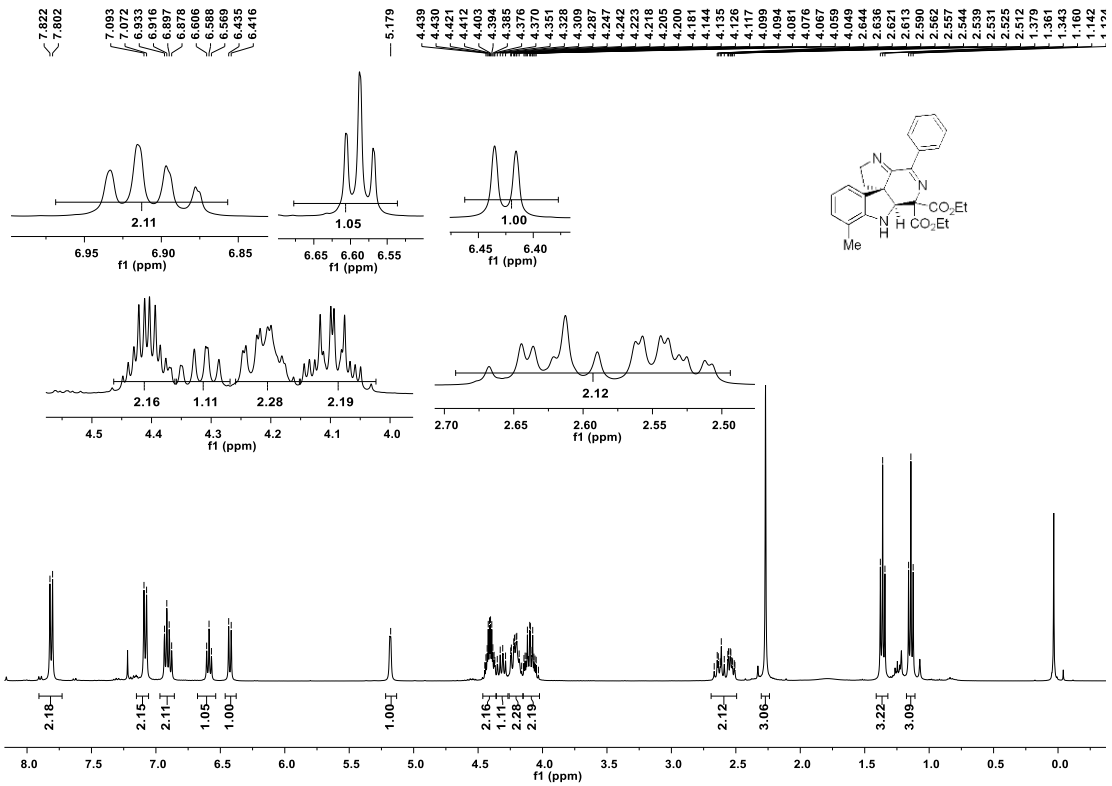
Diethyl (6a*S*,11b*R*)-9-bromo-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C39)

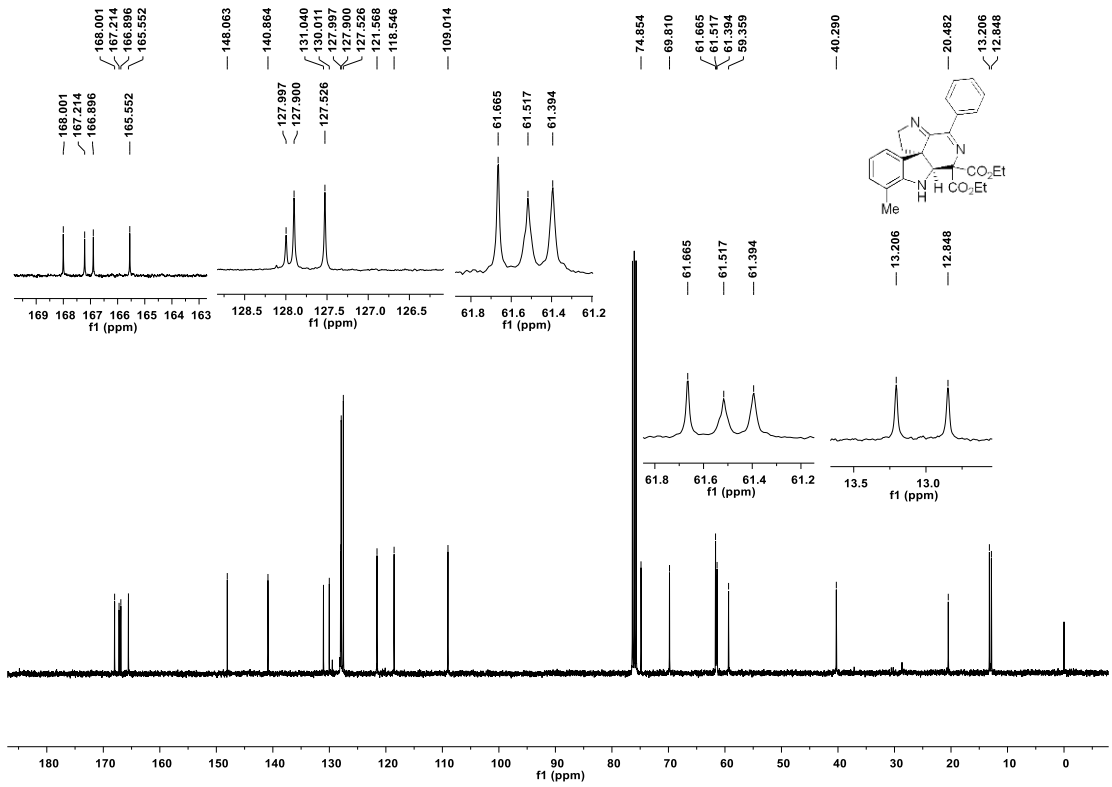


Diethyl (6a*S*,11b*R*)-9-methyl-4-phenyl-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C40)

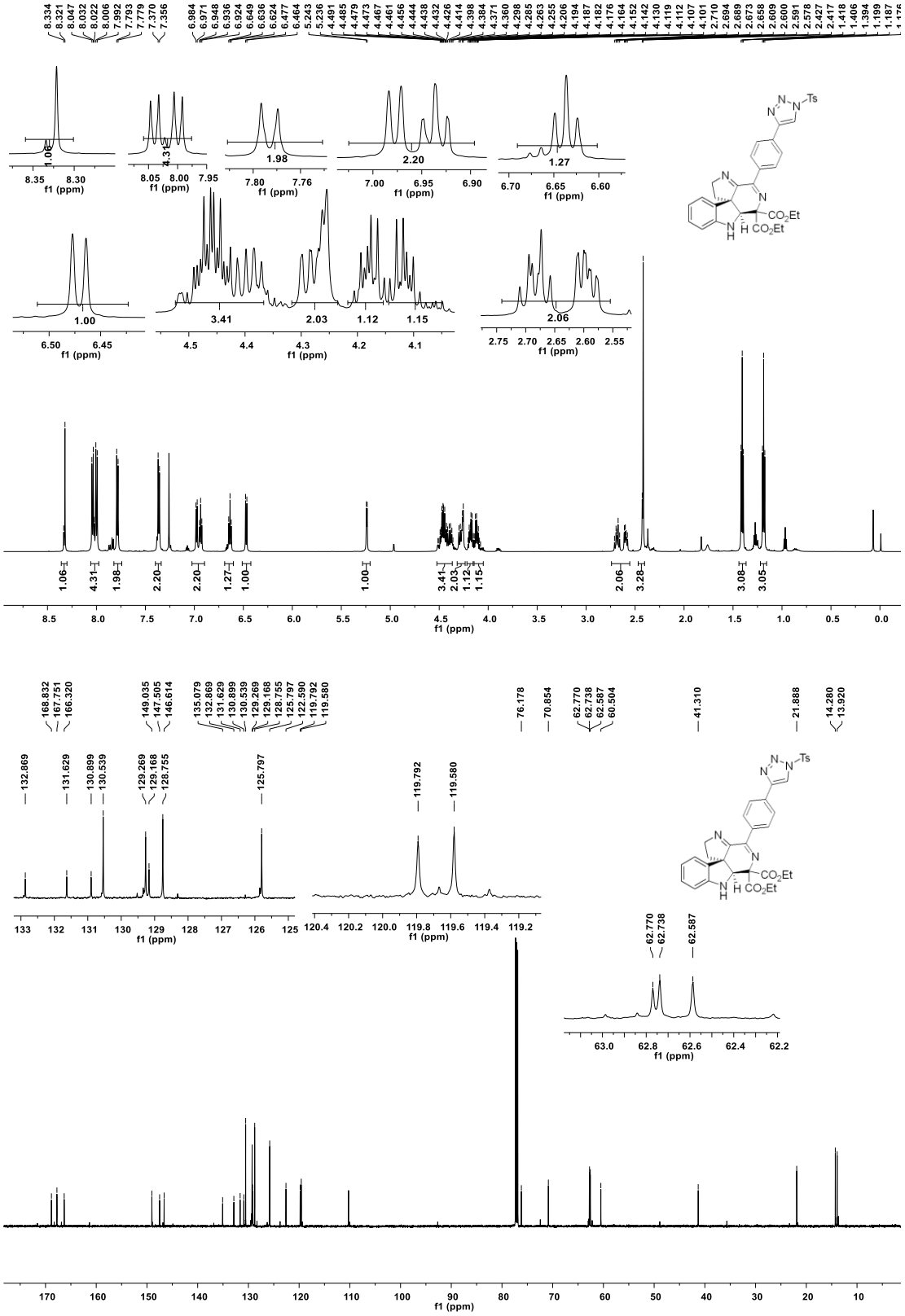


Diethyl (6a*S*,11b*R*)-8-methyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (C41)





Diethyl (6a*S*,11b*R*)-4-(4-(1-tosyl-1H-1,2,3-triazol-4-yl)phenyl)-1,2,6a,7-tetrahydro-6*H*-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate (D13)



(L) Supplementary references

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