Asymmetric synthesis of dihydrocarbazoles through Friedel-Crafts alkylation/annulation sequential reaction of indoles

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Electronic Supporting Information

Content

1. General Information

NMR characterization data were collected on Bruker ASCEND™ 400M. ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{1}H} NMR: chemical shifts δ were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for ^{1}H NMR: $CDCl_3$ = 7.26 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration.

Enantiomeric excesses (ee) were determined by HPLC (High performance liquid chromatography) analysis using the corresponding commercial chiralpak column (ADH, ODH, etc.) as stated in the experimental procedures at 25 ℃.

Optical rotations measured on Rudolph Research Analytic Automatic Polarimeter were reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in CH_2Cl_2).

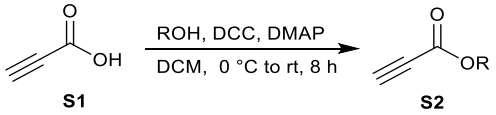
HRMS (High resolution mass spectra) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z).

Infrared spectra (IR) were recorded on Shimadzu IRTracer-100 or Bruker Tensor II spectrometer with Plantium ATR accessory. The peaks are reported as absorption maxima ($\tilde{\nu}$, cm^{-1}).

X-Ray crystallographic data were collected by a Bruker D8 Venture Photon II.

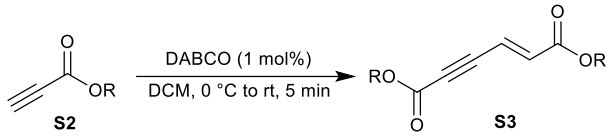
The ***N,N′*-dioxides** were prepared according to the methods reported in the literature.[1]

2. General procedure for the synthesis of diazoacetoacetate enones



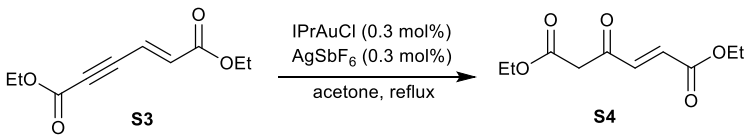
S1 **S2**

A solution of DMAP (0.1 mmol, 0.01 equiv) and DCC (24 mmol, 1.2 equiv) in CH_2Cl_2 (25 mL) was added slowly over 1 h to a solution of propiolic acid **S1** (20 mmol, 1 equiv) and alcohol (22 mmol, 1.1 equiv) in CH_2Cl_2 (20 mL) in a 50 mL round bottom flask at 0 ℃. The suspension was then stirred for 5 h at room temperature. Afterwards, the product was purified by flash chromatography (Eluent: petroleum ether/ethyl acetate 20:1 to 10:1) to afford the desired product **S2** in about 50-85% yield. All the alkynyl esters were prepared in a similar manner using the above-mentioned procedure.



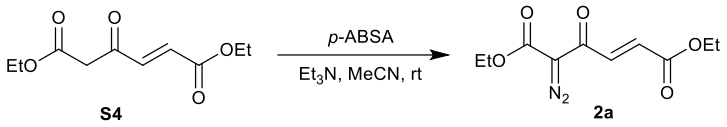
S2 **S3**

The corresponding propiolates **S2** (10 mmol, 1 equiv) was dissolved in CH_2Cl_2 (10 mL), then DABCO (0.1 mmol, 1 mol%) was added into the solution at 0 ℃. The mixture was stirred at room temperature for 5 min. The product **S3** was afforded through flash chromatography (Eluent: petroleum ether/ethyl acetate 20:1) in about 95-99% yield. All the products were prepared in a similar manner using the above-mentioned procedure.[2]



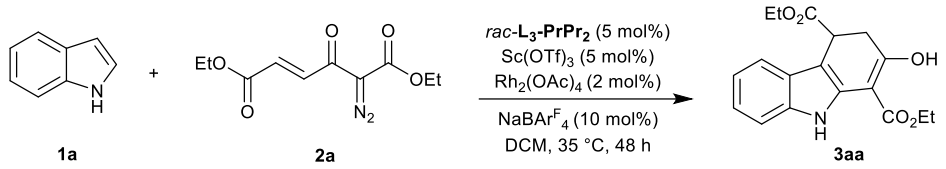
S3 **S4**

The diethyl (*E*)-hex-2-en-4-ynedioate **S3** (2.1 g, 10 mmol) was attempted using $Ph_3PAuCl/AgSbF_6$ (0.2 mmol, 0.02 equiv) in refluxing acetone at 60 ℃ for 5 h. The crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1), affording the product **S4** as a yellow oil in about 83% yield. All the other products were prepared by the similar procedure.[3]



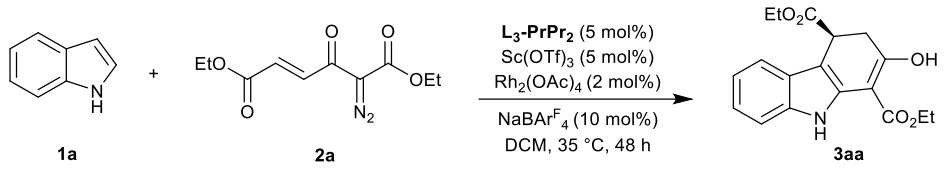
To a solution of diethyl (*E*)-4-oxohex-2-enedioate **S4** (2.1 g, 10 mmol) and p-ABSA (3.12 g, 13 mmol) in dry CH_3CN (20 mL) was added Et_3N (1.8 mL, 13 mmol) dropwise at 0 ℃. Then the mixture was stirred overnight at room temperature. The reaction was then quenched with 10 w% NH_4Cl, followed by extraction with Et_2O (2 x 20 mL). The combined organic extracts were treated with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The yellow crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 10:1) to give the product diethyl (*E*)-5-diazo-4-oxohex-2-enedioate **2a** as a yellow oil (1.21 g,50% yield). The other diazoacetoacetate enones were prepared by the similar procedure.[4]

3. Typical procedure for the preparation of the racemic products



$Sc(OTf)_3$ (2.4 mg, 5 mol%), *N*,*N*′-dioxide ligand of ***rac*-L_3-$PrPr_2$** (3.2 mg, 5 mol%), $NaBAr_4^F$ (8.8 mg, 10 mol%) and diazoacetoacetate enone **2a** (0.15 mmol) were weighted into a test tube under an inert atmosphere. Anhydrous CH_2Cl_2 (1.0 mL) was added and the solution was stirred at 35 ℃ for 0.5 h. Subsequently indole **1a** (11.7 mg, 0.1 mmol) was added into reaction system at 35 ℃ and the reaction mixture was stirred for 45 h. Then $Rh_2(OAc)_4$ was added into the reaction system and the mixture stirred for additional 3 h. The racemic product **3aa** was directly purified by flash column chromatography (Petroleum ether: ethyl acetate = 6:1).

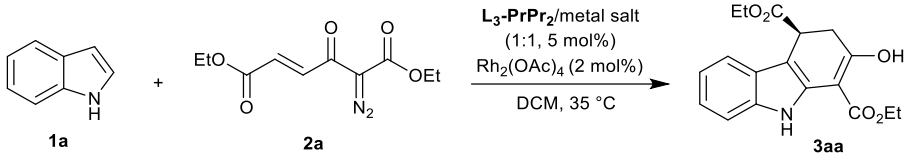
4. Typical procedure for the catalytic asymmetric reaction



$Sc(OTf)_3$ (2.4 mg, 5 mol%), *N*,*N*′-dioxide ligand of **L_3-$PrPr_2$** (3.2 mg, 5 mol%), $NaBAr_4^F$ (8.8 mg, 10 mol%) and diazoacetoacetate enone **2a** (0.15 mmol) were weighted into a test tube under an inert atmosphere. Anhydrous CH_2Cl_2 (1.0 mL) was added and the solution was stirred at 35 ℃ for 0.5 h. Subsequently indole **1a** (11.7 mg, 0.1 mmol) was added into reaction system at 35 ℃ and the reaction mixture was stirred for 45 h. Then $Rh_2(OAc)_4$ was added into the reaction system and the mixture stirred for additional 3 h. The product **3aa** was directly purified by flash column chromatography (Petroleum ether: ethyl acetate = 6:1).

5. Optimization of reaction conditions

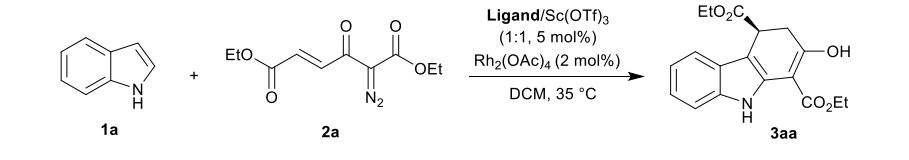
Table S1: Optimization of metal salts

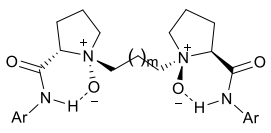


entry[a]	metal salt	yield[b] (%)	ee[c] (%)
1	$Sc(OTf)_3$	51	92
2	$Mg(OTf)_2$	trace	-
3	$Al(OTf)_3$	trace	-
4	$In(OTf)_3$	trace	-
5	$Fe(OTf)_3$	trace	-
6	$Co(OTf)_3$	trace	-
7	$Ni(OTf)_2$	trace	-
8	$Cu(OTf)_2$	trace	-
9	$Zn(OTf)_2$	trace	-
10	$Gd(OTf)_3$	trace	-
11	$Y(OTf)_3$,	trace	-
12	$Yb(OTf)_3$	trace	-

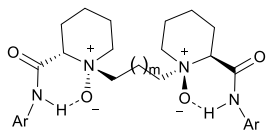
[a]Unless otherwise noted, all reactions were carried out with indole **1a** (0.1 mmol), diazoacetoacetate enone **2a** (0.15 mmol), $Rh_2(OAc)_4$ (2 mol%), **L_3-PrPr$_2$**/metal salt (1:1, 5 mol%) in CH_2Cl_2 (1.0 mL) under N_2 at 35 ℃ for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table S2: Optimization of the ligands

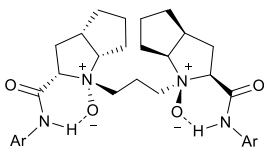




L_3-PrPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, m=1
L_3-PrPr$_3$: Ar = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, m=1
L_3-PrMe$_2$: Ar = 2,6-Me$_2$C$_6$H$_3$, m=1
L_3-PrEt$_2$: Ar = 2,6-Et$_2$C$_6$H$_3$, m=1
L_2-PrPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, m=0



L_3-PiPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 1
L_2-PiPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, m = 0

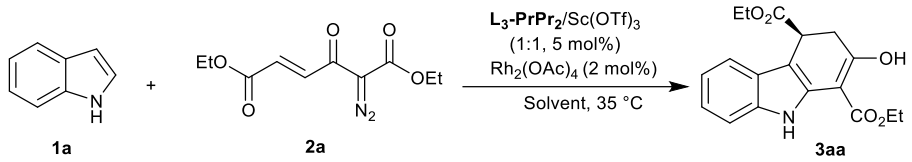


L_3-RaPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

entry[a]	ligand	yield[b] (%)	ee[c] (%)
1	**L_3-PiPr$_2$**	39	43
2	**L_3-RaPr$_2$**	-	-
3	**L_3-PrPr$_3$**	40	92
4	**L_3-PrMe$_2$**	30	76
5	**L_3-PrEt$_2$**	43	89
6	**L_2-PrPr$_2$**	32	0
7	**L_3-PrPr$_2$**	51	92

[a]All reactions were carried out with indole **1a** (0.1 mmol), diazoacetoacetate enone **2a** (0.15 mmol), $Rh_2(OAc)_4$ (2 mol%), **Ligand**/$Sc(OTf)_3$ (1:1, 5 mol%) in DCM (1.0 mL) under N_2 at 35 ℃ for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

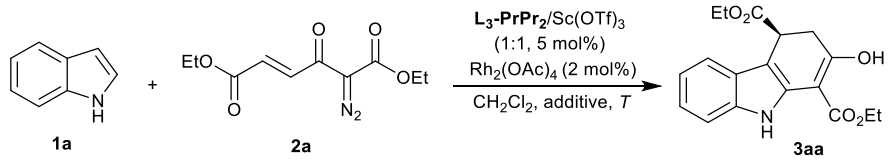
Table S3: Optimization of solvents



entry[a]	solvent	yield[b] (%)	ee[c] (%)
1	CH_2ClCH_2Cl	35	90
2	$CHCl_2CHCl_2$	21	95
3	$CHCl_3$	-	-
4	$CH_2ClCHCl_2$	11	60
5	PhBr	18	20
6	PhCl	-	-
7	THF	-	-
8	Et_2O	23	95
9	PhMe	-	-
10	CH_2Cl_2	51	92

[a]All reactions were carried out with indole **1a** (0.1 mmol), diazoacetoacetate enone **2a** (0.15 mmol), $Rh_2(OAc)_4$ (2 mol%), **L_3-PrPr$_2$**/$Sc(OTf)_3$ (1:1, 5 mol%) in solvent (1.0 mL) under N_2 at 35 ℃ for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table S4: Optimization of additives and temperature

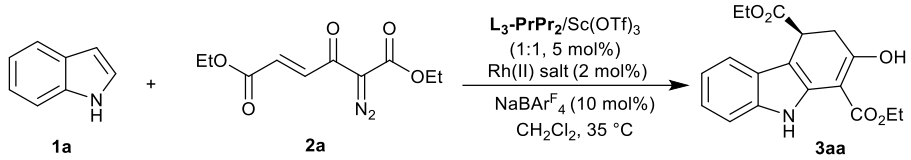


entry[a]	additive	Temp (℃)	yield[b] (%)	ee[c] (%)
1	3 Å MS (20 mg)	35	32	85
2	4 Å MS (20 mg)	35	32	91
3	5 Å MS (20 mg)	35	45	93
4	$NaBAr^F_4$ (10 mol%)	35	70	93
5	$PhCO_2H$ (10 mol%)	35	59	0
6	MeOH (10 μL)	35	-	-
7	H_2O (10 μL)	35	30	87
8	$LiNTf_2$ (10 mol%)	35	64	63
9	LiBr (10 mol%)	35	-	-
10	K_2CO_3 (10 mol%)	35	-	-
11	Et_3N (10 mol%)	35	-	-

12	$NaBF_4$ (10 mol%)	35	42	15
13	$NaBPh_4$ (10 mol%)	35	68	81
14	$MgCl_2$ (10 mol%)	35	38	0
15	LiCl (10 mol%)	35	13	0
16	$NaBAr^F_4$ (10 mol%)	10	18	93
17	$NaBAr^F_4$ (10 mol%)	20	25	92
18	$NaBAr^F_4$ (10 mol%)	45	43	89

[a]All reactions were carried out with indole **1a** (0.1 mmol), diazoacetoacetate enone **2a** (0.15 mmol), $Rh_2(OAc)_4$ (2 mol%), **L3-PrPr2**/$Sc(OTf)_3$ (1:1, 5 mol%), and additives in CH_2Cl_2 (1.0 mL) under N_2 at *T* ℃ for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table S5: Optimization of different Rh(II) salts

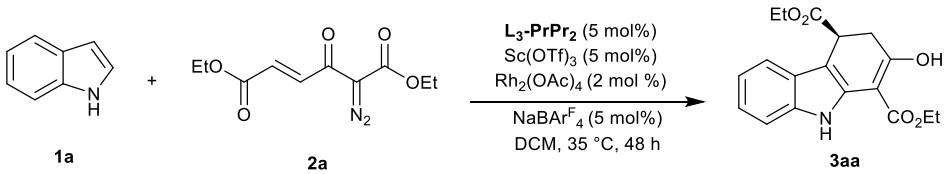


1a **2a** **3aa**

entry[a]	metal salt	yield[b] (%)	ee[c] (%)
1	$Rh_2(OPiv)_4$	50	93
2	$Rh_2(esp)_2$	50	93
3	$Rh_2(oct)_4$	46	92
4	$Rh_2(OAc)_4$	70	93

[a]All reactions were carried out with indole **1a** (0.1 mmol), diazoacetoacetate enone **2a** (0.15 mmol), Rh(II) salt (2 mol%), **L3-PrPr2**/$Sc(OTf)_3$ (1:1, 5 mol%), and $NaBAr^F_4$ (10 mol%) in CH_2Cl_2 (1.0 mL) under N_2 at 35 ℃ for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

6. Scaled-up version of the asymmetric reaction and further transformations

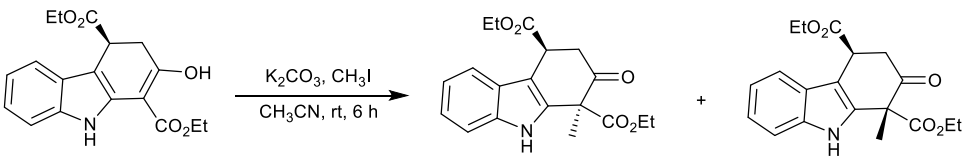


1a 4 mmol, 0.468 g

2a 4.8 mmol, 1.15 g

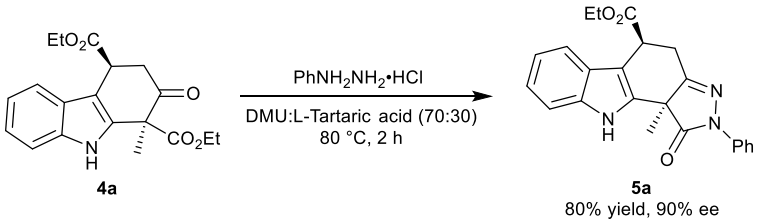
3aa 57% yield, 93% ee, 0.74 g

A dry round flask under nitrogen atmosphere was charged with $Sc(OTf)_3$ (5 mol%, 98.4 mg), **L3-PrPr2** (5 mol%, 124.0 mg), $NaBAr^F_4$ (10 mol%, 176 mg), diazoacetoacetate enone **2a** (4.8 mmol, 1.15 g), and CH_2Cl_2 (20 mL). The reaction mixture was stirred at 35 ℃ for 30 min. Then, indole **1a** (4 mmol, 0.468 g) was added and the reaction mixture continued stirring at 35 ℃ for 45 h. Subsequently, $Rh_2(OAc)_4$ (2 mol%, 40 mg) was added into the reaction system under nitrogen atmosphere and the reaction mixture was stirred at 35 ℃ for another 3 h. The residue was purified by flash chromatography on silica gel (Eluent: petroleum ether/ethyl acetate = 6:1) to afford the desired product **3aa**.

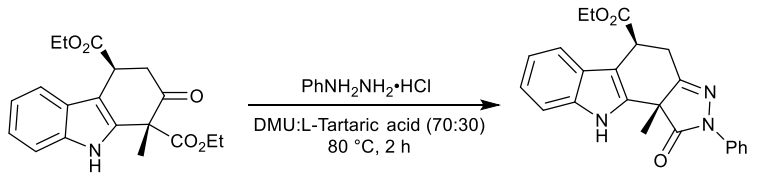


3aa **4a** 45% yield, 90% ee **4a'** 37% yield, 88% ee

To a round flask were added **3aa** (32.9 mg, 0.1 mmol), CH_3I (80 μL) and CH_3CN (1 mL). The reaction mixture was stirred at rt for 5 h. Finally, the mixture was purified by flash chromatography on silica gel (Eluent: petroleum ether/ethyl acetate = 3/1) to afford the desired product **4a** and **4a′** respectively.



4a **5a**
80% yield, 90% ee

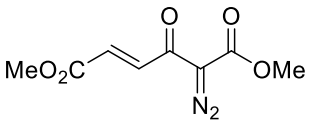


4a' **5a'**
78% yield, 90% ee

A dry reaction tube was charged with the mixture of DMU and L-tartaric acid (70:30, 0.7 g), then the mixture was heated to 80 ℃ until the solids melt to liquid. Subsequently, $PhNHNH_2 \cdot HCl$ (17.6 mg, 0.12 mmol) and **4a** (34.3 mg, 0.1 mmol) were added into the reaction system simultaneously under stirring at 80 ℃ for 2 h. After completion of the reaction as monitored by TLC, H_2O (1 mL) were added into the reaction system to quench the reaction. The crude product was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 8:1), affording the product **5a**.

The corresponding products **5a′** were also obtained through above procedure.

7. The analytical and spectral characterization data of products

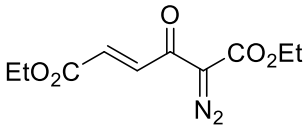


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.6 Hz, 1H), 6.86 (d, *J* = 15.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 165.6, 161.0, 135.8, 130.7, 52.5, 52.3.

IR: 2957, 2140, 1716, 1649, 1618, 1436, 1294, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_8H_9N_2O_5^+$ [M+H$^+$] 213.0506; Found 213.0509.

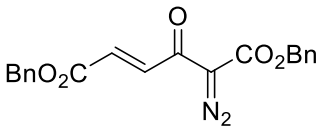


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 6.4 Hz, 3H), 1.32 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 165.2, 160.6, 135.7, 131.1, 61.9, 61.2, 14.3, 14.1.

IR: 2985, 2140, 1720, 1649, 1619, 1469, 1371 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{10}H_{13}N_2O_5^+$ [M+H$^+$] 241.0819; Found 241.0818.

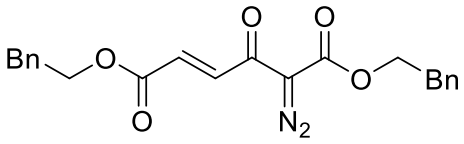


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 15.2 Hz, 1H), 7.42 – 7.30 (m, 10H), 6.89 (d, *J* = 15.6 Hz, 1H), 5.30 (s, 2H), 5.25 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 164.9, 160.4, 136.2, 135.4, 134.8, 130.9, 128.8, 128.8, 128.6, 128.5, 128.4, 128.3, 67.4, 66.9.

IR: 3034, 2139, 1716, 1649, 1618, 1455, 1328 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{20}H_{17}N_2O_5^+$ [M+H$^+$] 365.1132; Found 365.1130.

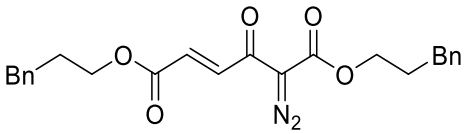


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.6 Hz, 1H), 7.38 – 7.12 (m, 10H), 6.82 (d, *J* = 15.6 Hz, 1H), 4.47 (t, *J* = 7.2 Hz, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 3.00 (q, *J* = 6.4 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.5, 164.9, 160.3, 137.4, 136.9, 135.8, 130.8, 128.9, 128.8, 128.6, 128.5, 126.8, 126.6, 66.1, 65.7, 35.0, 34.9.

IR: 2958, 2139, 1717, 1648, 1618, 1386, 1329 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{22}H_{21}N_2O_5^+$ [M+H$^+$] 393.1445; Found 393.1442.



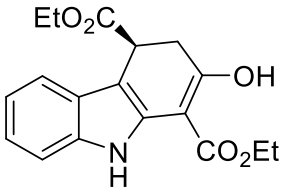
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 15.2 Hz, 1H), 7.37 – 7.12 (m, 10H), 6.86 (d, *J* = 15.6 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 2.76 – 2.63 (m, 4H), 2.11 – 1.94 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.4, 165.0, 160.4, 140.8, 140.5, 135.8, 130.8, 128.4, 128.3, 128.3, 128.2, 126.1, 125.9, 65.1, 64.4, 32.0, 31.9, 29.9, 29.9.

IR: 2954, 2138, 1717, 1648, 1618, 1328, 1293 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{25}N_2O_5^+$ [M+H$^+$] 421.1758; Found 421.1765.

Diethyl (*S*)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3aa)



Yellow oil. 70% yield, 93% ee, $[\alpha]_{436}^{24.1}$= -105.7 (c = 0.348, CH_2Cl_2).

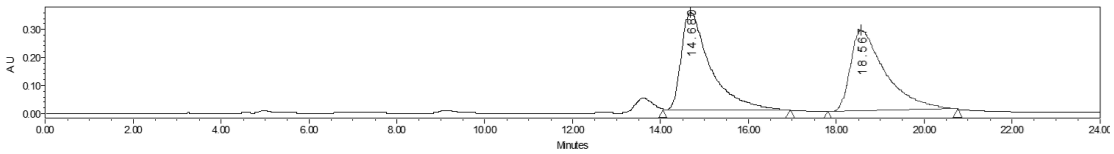
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 18.36 min, t (minor) = 14.54 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.98 (s, 1H), 8.80 (s, 1H), 7.58 – 7.50 (m, 1H), 7.35 – 7.28 (m, 1H), 7.14 – 7.05 (m, 2H), 4.47 (q, J = 7.2 Hz, 2H), 4.23 – 3.96 (m, 3H), 3.17 – 2.97 (m, 2H), 1.48 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H).

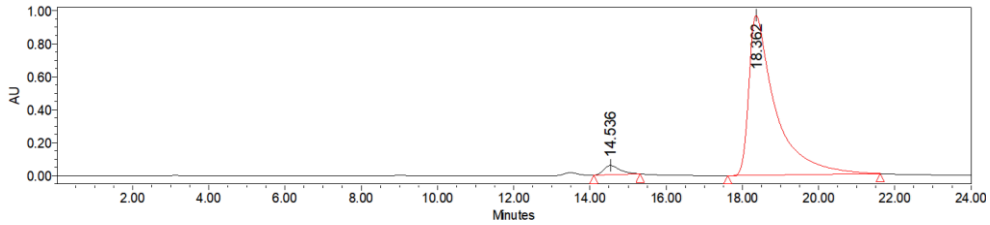
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 135.6, 130.3, 126.3, 120.7, 120.1, 118.0, 110.8, 99.8, 94.4, 61.5, 61.0, 36.0, 32.4, 14.5, 14.1.

IR: 3474, 2922, 2856, 1720, 1640, 1561, 1453, 1228, 1078, 1033 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{20}NO_5^+$ [M+H$^+$] 330.1336; Found 330.1333.

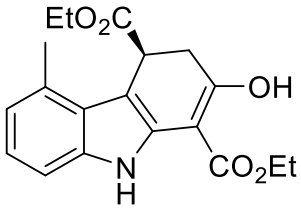


	Retention Time	Area	% Area
1	14.680	16912051	50.59
2	18.567	16518399	49.41



	Retention Time	Area	% Area
1	14.536	1662841	3.42
2	18.362	46949219	96.58

Diethyl (S)-2-hydroxy-5-methyl-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ab)



Yellow liquid. 48% yield, 93% ee, $[\alpha]_{436}^{24.8}$ = -283.9 (*c* = 0.406, CH_2Cl_2).

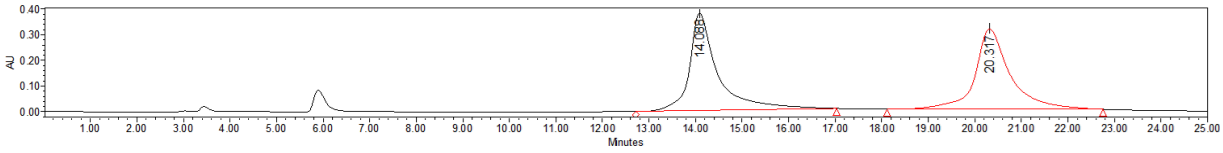
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 20.16 min, t (minor) = 14.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.98 (s, 1H), 8.82 (s, 1H), 7.15 (d, J = 8.4Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.32-4.26 (m, 1H), 4.07 (m, 2H), 3.16 – 2.97 (m, 2H), 2.71 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

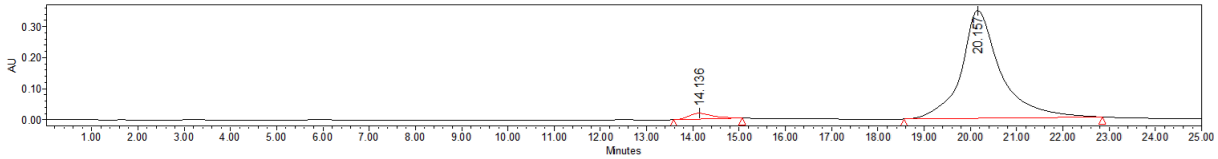
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 135.6, 130.3, 129.2, 125.2, 121.6, 120.8, 108.7, 100.7, 94.5, 61.5, 61.0, 36.8, 33.4, 19.7, 14.5, 14.0.

IR: 3475, 2920, 2854, 1711, 1638, 1460, 1316, 1256, 1075, 1032 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1492.

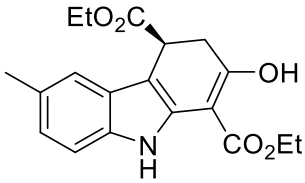


	Retention Time	Area	% Area
1	14.088	16021594	49.26
2	20.317	16500650	50.74



	Retention Time	Area	% Area
1	14.136	678905	3.22
2	20.157	20417808	96.78

Diethyl (S)-2-hydroxy-6-methyl-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ac)



Yellow solid. 63% yield, 89% ee, M.p. 90 – 94 ℃, $[\alpha]_{436}^{24.7}$ = -324.2 (*c* = 0.194, CH_2Cl_2).

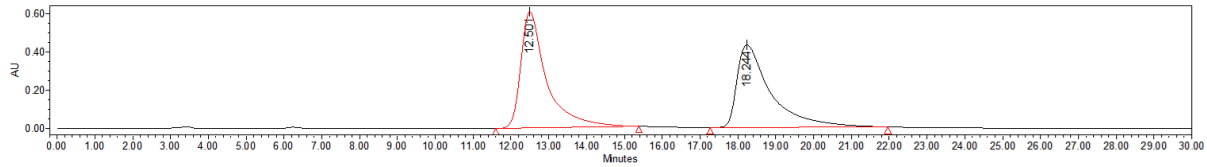
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 18.89 min, t (minor) = 13.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.97 (s, 1H), 8.71 (s, 1H), 7.32 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.94-6.87 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.19 – 4.01 (m, 3H), 3.15 – 2.96 (m, 2H), 2.44 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

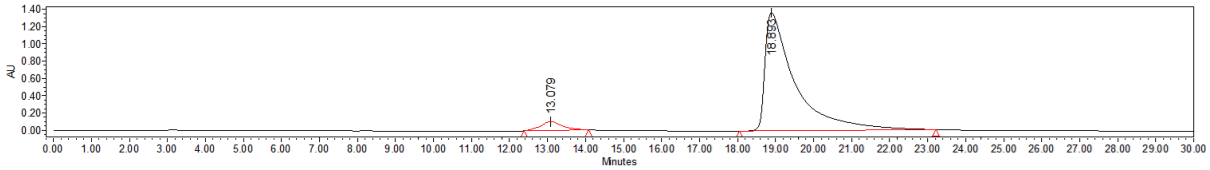
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 134.0, 130.4, 129.3, 126.5, 122.2, 117.7, 110.4, 99.3, 94.5, 61.4, 60.9, 36.1, 32.4, 21.6, 14.5, 14.1.

IR: 3474, 3428, 2980, 2913, 1724, 1645, 1599, 1308, 1227, 1077 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [$M+H^+$] 344.1492; Found 344.1491.

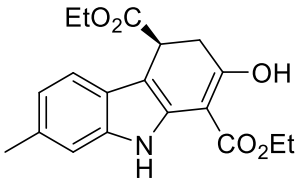


	Retention Time	Area	% Area
1	12.501	28490994	51.64
2	18.244	26683121	48.36



	Retention Time	Area	% Area
1	13.079	4128146	5.21
2	18.893	75103214	94.79

Diethyl (S)-2-hydroxy-7-methyl-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ad)



Yellow solid. 63% yield, 94% ee, M.p. 95 – 100 ℃, $[\alpha]_{589}^{23.3}$ = -63.4 (*c* = 0.410, CH_2Cl_2).

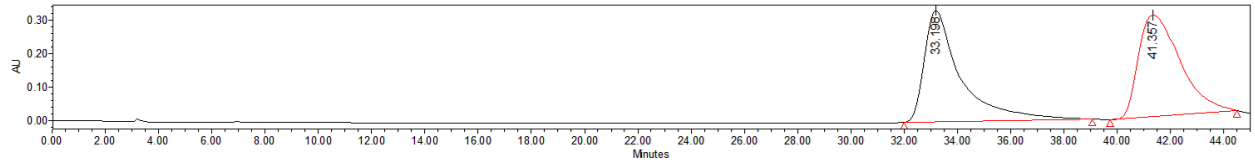
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 41.44 min, t (minor) = 33.40 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.95 (s, 1H), 8.67 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 6.93 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.19 – 3.98 (m, 3H), 3.14 – 2.99 (m, 2H), 2.44 (s, 3H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

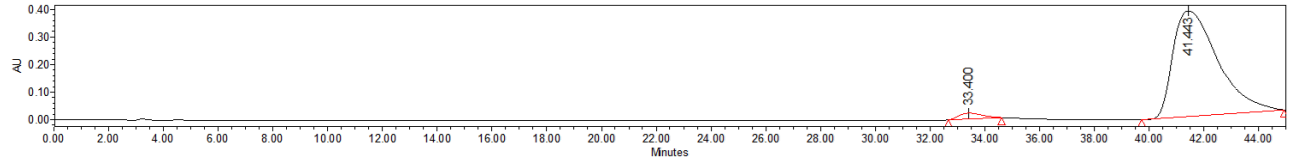
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 136.1, 130.4, 129.6, 124.1, 121.7, 117.7, 110.8, 99.6, 94.5, 61.4, 60.9, 36.1, 32.4, 21.7, 14.5, 14.1.

IR: 3473, 2922, 2855, 1719, 1639, 1456, 1312, 1260, 1079, 1028, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1491.

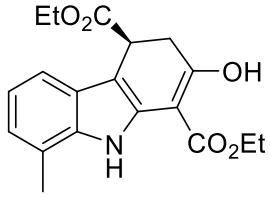


	Retention Time	Area	% Area
1	33.198	31431134	48.93
2	41.357	32811606	51.07



	Retention Time	Area	% Area
1	33.400	1237644	2.76
2	41.443	43610178	97.24

Diethyl (S)-2-hydroxy-8-methyl-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ae)



Yellow solid. 65% yield, 95% ee, M.p. 147 – 151 ℃, $[\alpha]_{436}^{24.3}$ = -59.0 (*c* = 0.266, CH_2Cl_2).

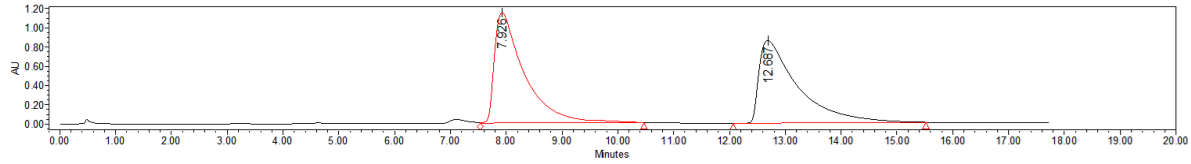
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 13.15 min, t (minor) = 8.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.89 (s, 1H), 8.77 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.2, Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.19 – 3.98 (m, 3H), 3.18 – 2.98 (m, 2H), 2.46 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

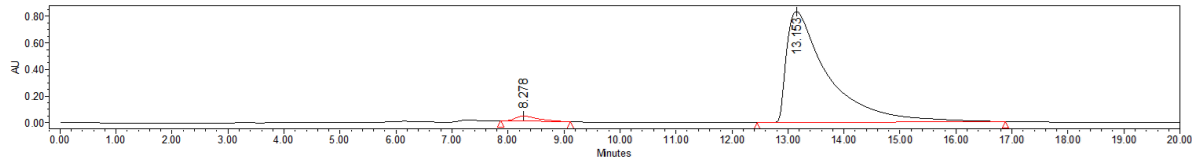
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 135.1, 130.0, 125.8, 121.4, 120.2, 119.7, 115.8, 100.3, 94.4, 61.4, 60.9, 36.2, 32.4, 16.3, 14.3, 14.1.

IR: 3481, 2980, 2932, 1728, 1651, 1450, 1310, 1226, 1099, 1026, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1491.

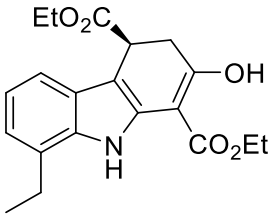


	Retention Time	Area	% Area
1	7.926	42560262	50.70
2	12.687	41379814	49.30



	Retention Time	Area	% Area
1	8.278	1025314	2.32
2	13.153	43204677	97.68

Diethyl (*S*)-8-ethyl-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3af)



Yellow oil. 62% yield, 92% ee, $[\alpha]_{589}^{26.2}$= -53.8 (c = 0.418, CH_2Cl_2).

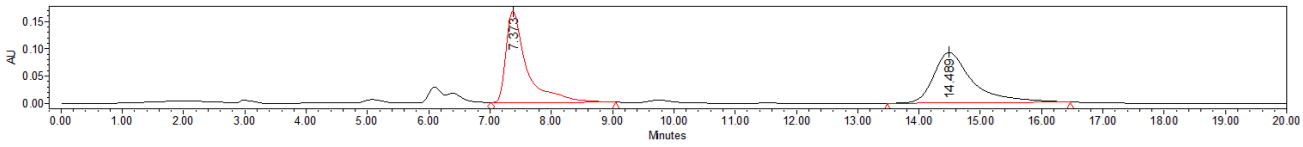
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 14.15 min, t (minor) = 7.36 min,

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.88 (s, 1H), 8.83 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.2 Hz, 1H), 4.46 (q, J = 7.2 Hz, 2H), 4.19 – 3.99 (m, 3H), 3.16 – 2.98 (m, 2H), 2.84 (q, J = 7.6 Hz, 2H), 1.50 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.6 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H).

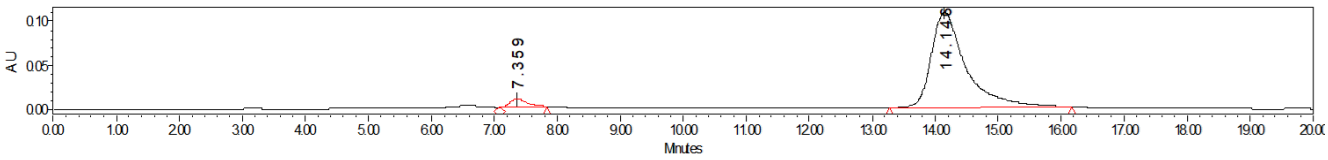
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 134.4, 129.9, 126.0, 125.9, 120.3, 119.5, 115.9, 100.2, 94.3, 61.4, 60.9, 36.1, 32.4, 24.1, 14.3, 14.1, 13.6.

IR: 3484, 2923, 2855, 1729, 1641, 1457, 1255, 1221, 1086, 1033, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{20}H_{24}NO_5^+$ [M+H$^+$] 358.1649; Found 358.1648.

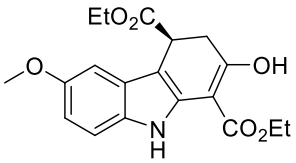


	Retention Time	Area	% Area
1	7.373	3897816	50.35
2	14.489	3843129	49.65



	Retention Time	Area	% Area
1	7.359	172134	3.98
2	14.146	4155321	96.02

Diethyl (*S*)-2-hydroxy-6-methoxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ag)



Yellow solid. 56% yield, 99% ee, M.p.126 – 129 ℃, $[\alpha]_{589}^{24.4}$ = -37.8 (c = 0.410, CH_2Cl_2).

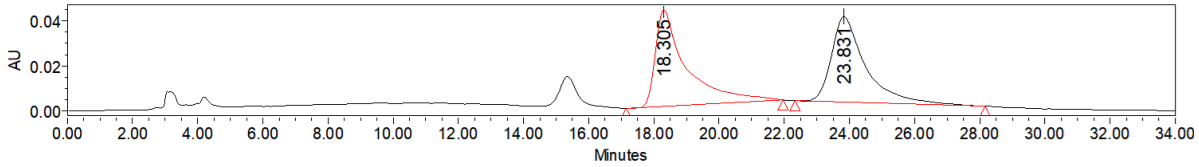
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 23.96 min, t (minor) = 18.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.99 (s, 1H), 8.69 (s, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.75 (dd, J = 8.8, 2.4 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.20 – 4.00 (m, 3H), 3.86 (s, 3H), 3.14 – 3.00 (m, 2H), 1.48 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

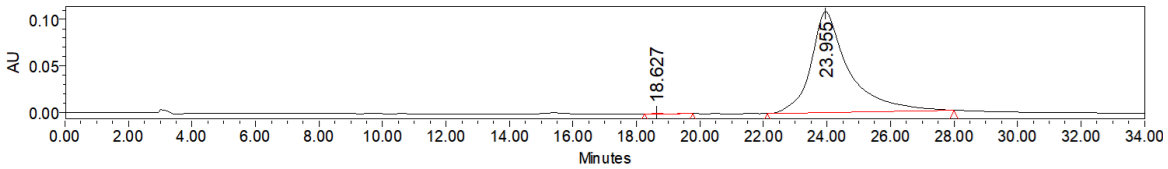
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 154.5, 131.0, 130.7, 126.8, 111.4, 110.5, 100.1, 99.6, 94.4, 61.5, 60.9, 55.8, 36.0, 32.3, 14.5, 14.2.

IR: 3476, 2922, 2853, 1715, 1639, 1455, 1302, 1212, 1151, 1033, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_6^+$ [M+H$^+$] 360.1441; Found 360.1441.

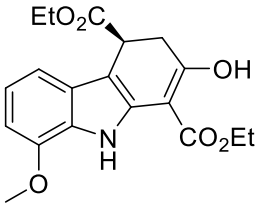


	Retention Time	Area	% Area
1	18.305	2858834	50.94
2	23.831	2753105	49.06



	Retention Time	Area	% Area
1	18.627	7738	0.09
2	23.955	9001395	99.91

Diethyl (*S*)-2-hydroxy-8-methoxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ah)



Yellow oil. 62% yield, 93% ee, $[\alpha]_{436}^{25.6}$ = -25.2 (*c* = 0.178, CH_2Cl_2)

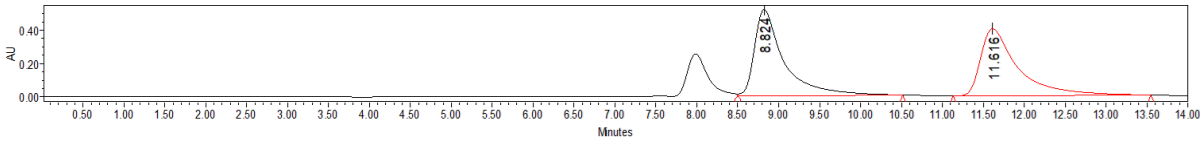
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 11.29 min, t (minor) = 8.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.94 (s, 1H), 8.93 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.18 – 4.00 (m, 3H), 3.95 (s, 3H), 3.15 – 2.98 (m, 2H), 1.49 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

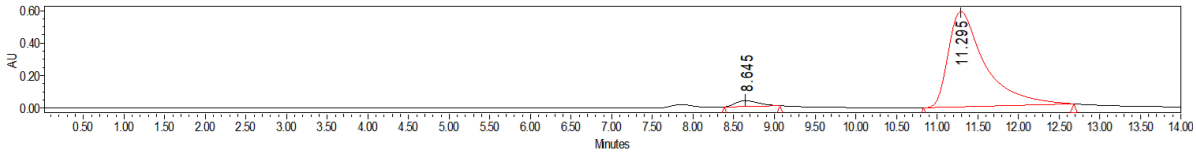
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 145.8, 129.8, 127.5, 125.8, 120.4, 110.9, 101.1, 100.3, 94.5, 61.4, 60.9, 55.3, 36.2, 32.4, 14.4, 14.1.

IR: 3486, 2924, 2854, 1727, 1641, 1561, 1441, 1317, 1259, 1074, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_6^+$ [M+H$^+$] 360.1441; Found 360.1441.

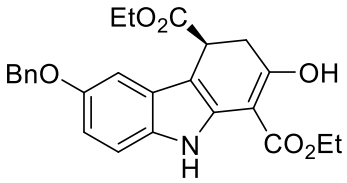


	Retention Time	Area	% Area
1	8.824	13021754	50.62
2	11.616	12702511	49.38



	Retention Time	Area	% Area
1	8.645	716746	3.50
2	11.295	19771383	96.50

Diethyl (S)-6-(benzyloxy)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ai)



Yellow solid. 45% yield, 94% ee, M.p.136 -141 ℃, $[\alpha]_{436}^{24.2}$ = -196.1 (*c* = 0.282, CH_2Cl_2).

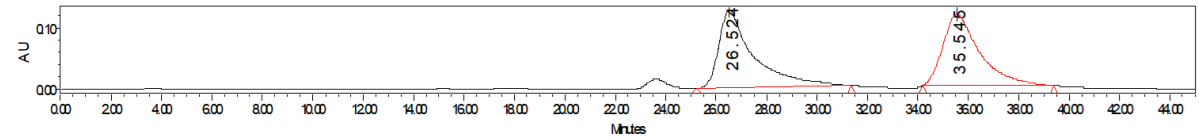
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 35.51 min, t (minor) = 26.67 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.97 (s, 1H), 8.70 (s, 1H), 7.51 – 7.44 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.11 (s, 2H), 4.51-4.35 (m, 2H), 4.15 – 3.96 (m, 3H), 3.14 – 2.98 (m, 2H). 1.46 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H).

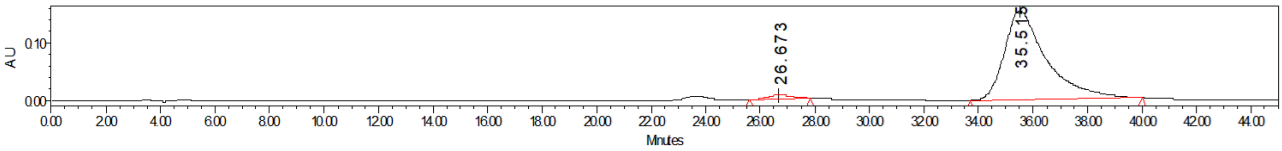
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 153.7, 137.8, 131.1, 131.0, 128.5, 127.7, 127.5, 126.8, 111.4, 111.3, 101.7, 99.7, 94.4, 70.8, 61.5, 60.9, 36.0, 32.3, 14.5, 14.2.

IR: 3473, 3428, 2979, 2926, 1725, 1645, 1452, 1315, 1227, 1151, 1026, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{25}H_{26}NO_6^+$ [M+H$^+$] 436.1754; Found 436.1754.

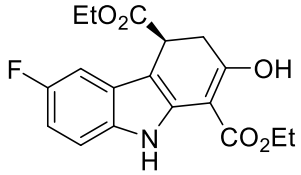


	Retention Time	Area	% Area
1	26.524	12140146	50.70
2	35.545	11804338	49.30



	Retention Time	Area	% Area
1	26.673	459559	2.72
2	35.515	16420657	97.28

Diethyl (S)-6-fluoro-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3aj)



Yellow solid. 43% yield, 93% ee, M.p. 134 -138 ℃, $[\alpha]_{436}^{25.6}$ = -398.0 (*c* = 0.204, CH_2Cl_2).

HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 23.53 min, t (minor) = 17.15 min.

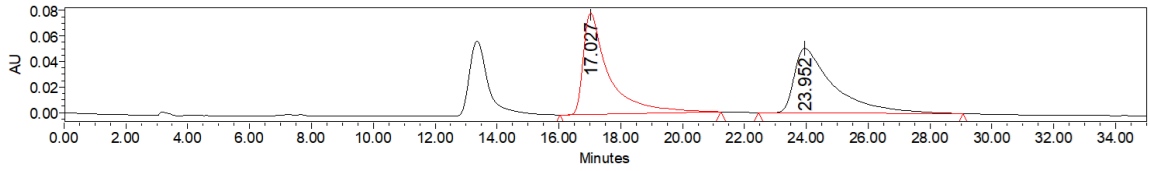
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.03 (s, 1H), 8.80 (s, 1H), 7.23 – 7.15 (m, 2H), 6.81 (td, J = 18.4, 9.6, 2.8 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.20 – 3.97 (m, 3H), 3.15 – 2.97 (m, 2H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 158.3 (d, J = 235.3 Hz), 132.2, 132.1, 126.8 (d, J = 10.6 Hz), 111.3 (d, J = 9.9 Hz), 108.7 (d, J = 26.4 Hz), 103.1 (d, J = 24.4 Hz), 99.9 (d, J = 4.6 Hz), 94.2, 61.6, 61.1, 35.9, 32.2, 14.5, 14.1.

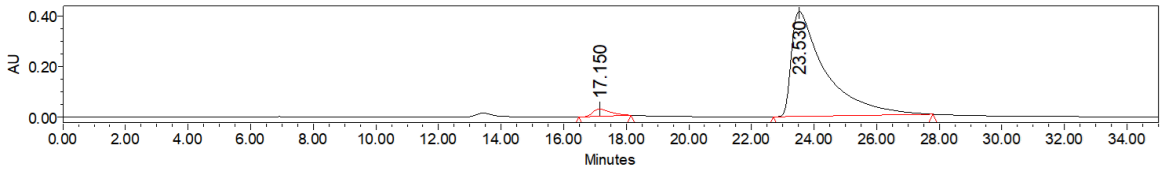
^{19}F NMR (376 MHz, $CDCl_3$) δ -124.0.

IR: 3470, 3423, 2920, 2854, 1723, 1641, 1449, 1308, 1225, 1144, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}FNO_5^+$ [M+H$^+$] 348.1242; Found 348.1241.

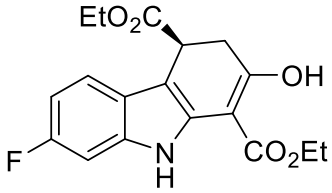


	Retention Time	Area	% Area
1	17.027	4560767	50.52
2	23.952	4467171	49.48



	Retention Time	Area	% Area
1	17.150	1129172	3.48
2	23.530	31352533	96.52

Diethyl (S)-7-fluoro-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ak)



Yellow solid. 48% yield, 96% ee, M.p. 131-136 ℃, $[\alpha]_{589}^{23.1}$ = -68.7 (c = 0.448, CH_2Cl_2).

HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 21.61 min, t (minor) = 15.04 min.

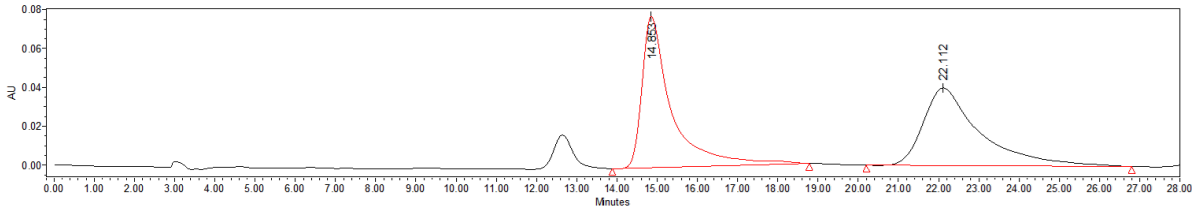
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.97 (s, 1H), 8.79 (s, 1H), 7.43 (dd, J = 8.8, 5.2 Hz, 1H), 7.01 (dd, J = 9.6, 2.0 Hz, 1H), 6.87 (m, 1H), 4.47 (q, J =7.2 Hz, 2H), 4.18 – 4.01 (m, 3H), 3.16 – 2.98 (m, 2H), 1.48 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 159.1 (d, J = 237.4 Hz), 135.5 (d, J = 12.12 Hz), 130.6, 122.9, 118.6 (d, J = 10.1 Hz), 108.5 (d, J = 17.17 Hz), 99.7, 97.4 (d, J = 27.3Hz), 94.3, 61.6, 61.1, 36.0, 32.3, 14.6, 14.1.

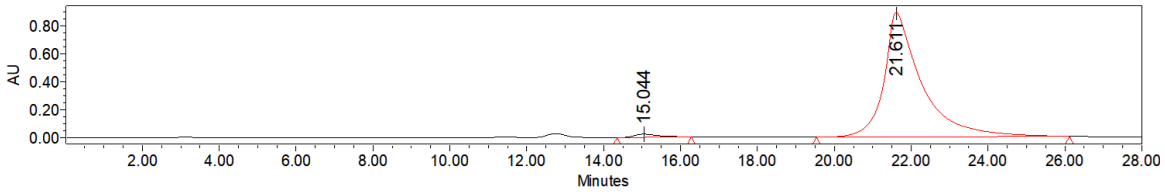
^{19}F NMR (376 MHz, $CDCl_3$) δ -122.5.

IR: 3472, 2923, 2857, 1726, 1632, 1451, 1376, 1234, 1032, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}FNO_5^+$ [M+H$^+$] 348.1242; Found 348.1241.

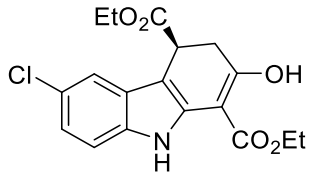


	Retention Time	Area	% Area
1	14.853	3753574	50.07
2	22.112	3742937	49.93



	Retention Time	Area	% Area
1	15.044	999280	1.62
2	21.611	60559754	98.38

Diethyl (S)-6-chloro-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3al)



Yellow solid. 47% yield, 93% ee, M.p.117 -121 ℃, $[\alpha]_{436}^{25.4}$ = -224.3 (*c* = 0.236, CH_2Cl_2).

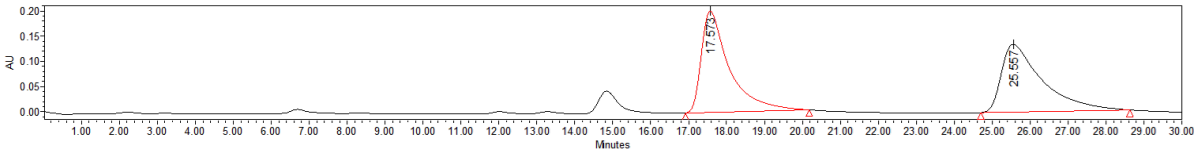
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 25.14 min, t (minor) = 17.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.04 (s, 1H), 8.83 (s, 1H), 7.51 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.07 –6.98 (m, 1H), 4.48 (q, *J* = 7.2 Hz, 2H), 4.24 – 3.89 (m, 3H), 3.24 – 2.95 (m, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

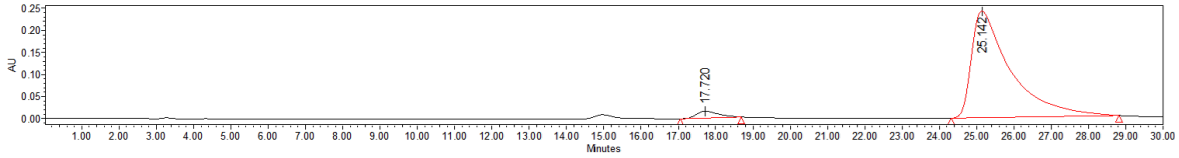
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 134.0, 131.9, 127.4, 125.8, 120.8, 117.5, 111.6, 99.5, 94.1, 61.6, 61.1, 35.8, 32.2, 14.5, 14.1.

IR: 3468, 3417, 2925, 2854, 1724, 1648, 1596, 1444, 1309, 1227, 1084, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}^{34.9689}ClNO_5^+$ [M+H$^+$] 364.0946; Found 364.0945, $C_{18}H_{19}^{36.9659}ClNO_5H^+$ 366.0916; Found 366.0915.

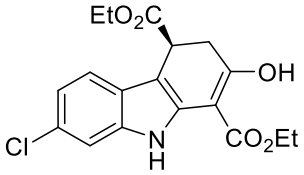


	Retention Time	Area	% Area
1	17.573	10363078	50.64
2	25.557	10100480	49.36



	Retention Time	Area	% Area
1	17.720	637020	3.50
2	25.142	17559097	96.50

Diethyl (S)-7-chloro-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3am)



Yellow solid. 55% yield, 95% ee, M.p.113 – 116 ℃, $[\alpha]_{436}^{24.9}$ = -343.3 (c = 0.242, CH_2Cl_2).

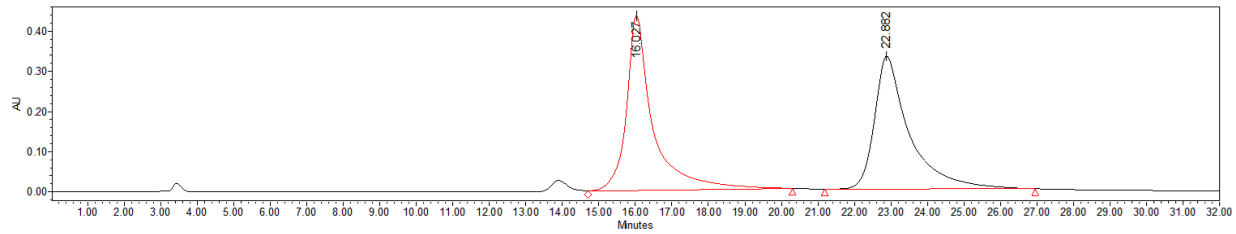
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 22.61 min, t (minor) = 16.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.01 (s, 1H), 8.79 (s, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.4, 2.0 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.19 – 3.99 (m, 3H), 3.18 – 2.98 (m, 2H), 1.48 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H).

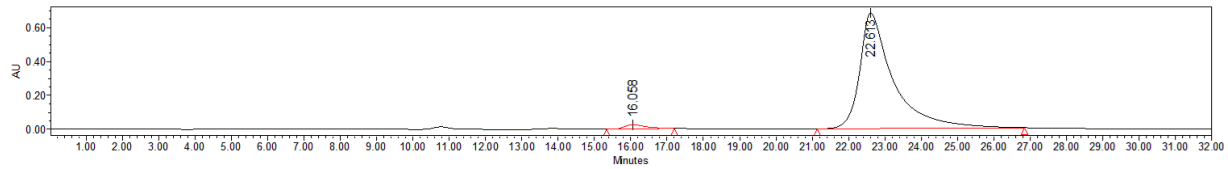
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 136.0, 131.1, 126.3, 124.9, 120.7, 118.8, 110.8, 99.8, 94.2, 61.6, 61.1, 35.9, 32.2, 14.5, 14.1.

IR: 3468, 3411, 2922, 2954, 1723, 1647, 1596, 1306, 1223, 1079, 1028, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}^{34.9689}ClNO_5^+$ [M+H$^+$] 364.0946; Found 364.0946, $C_{18}H_{19}^{36.9659}ClNO_5H^+$ 366.0916; Found 366.0916.

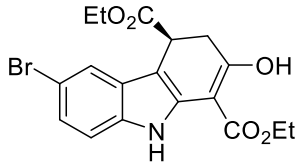


	Retention Time	Area	% Area
1	16.027	21995840	50.15
2	22.882	21867421	49.85



	Retention Time	Area	% Area
1	16.058	1027700	2.29
2	22.613	43841249	97.71

Diethyl (S)-6-bromo-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3an)



Yellow solid. 55% yield, 93% ee, M.p. 133 – 137 ℃, $[\alpha]_{436}^{25.3}$ = -423.0 (*c* = 0.226, CH_2Cl_2).

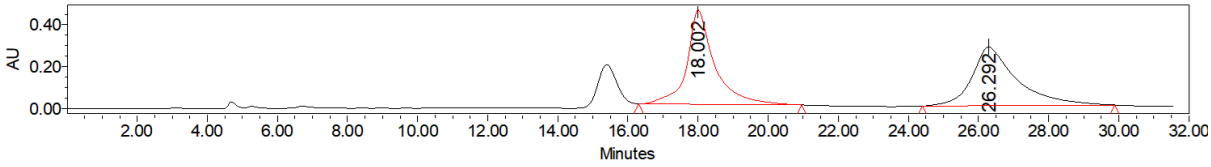
.HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 26.40 min, t (minor) = 18.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.04 (s, 1H), 8.83 (s, 1H), 7.66 (s, 1H), 7.19-7.12 (m, 2H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.19 – 3.98 (m, 3H), 3.17 – 2.99 (m, 2H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

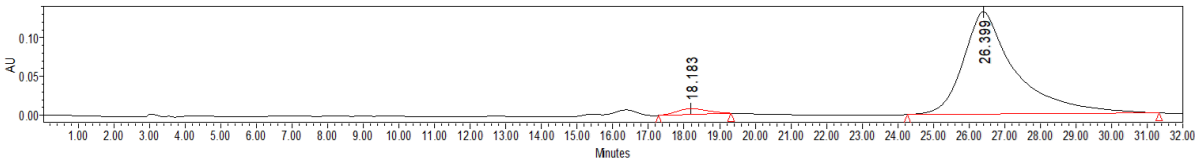
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 134.3, 131.7, 128.1, 123.3, 120.6, 113.3, 112.1, 99.3, 94.1, 61.6, 61.1, 35.8, 32.2, 14.5, 14.1.

IR: 3468, 3412, 2922, 2854, 1721, 1640, 1562, 1448, 1227, 1080, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}^{78.9183}BrNO_5^+$ [M+H$^+$] 408.0441; Found 408.0441, $C_{18}H_{19}^{80.9163}BrNO_5H^+$ 410.0421; Found 410.0420.

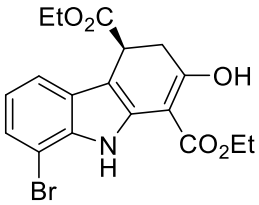


	Retention Time	Area	% Area
1	18.002	25445575	49.17
2	26.292	26301377	50.83



	Retention Time	Area	% Area
1	18.183	445561	3.22
2	26.399	13411627	96.78

Diethyl (S)-8-bromo-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ao)



Yellow solid. 54% yield, 91% ee, M.p.151 -156 ℃, $[\alpha]_{436}^{23.9}$ = -64.5 (*c* = 0.254, CH_2Cl_2).

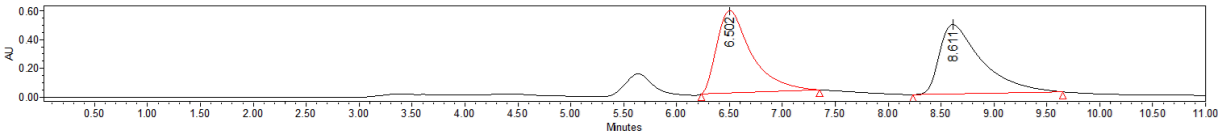
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.67 min, t (minor) = 6.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.95 (s, 1H), 9.02 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 4.52 – 4.40 (q, J = 7.2 Hz, 2H), 4.18 – 3.98 (m, 3H), 3.21 – 3.00 (m, 2H), 1.53 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

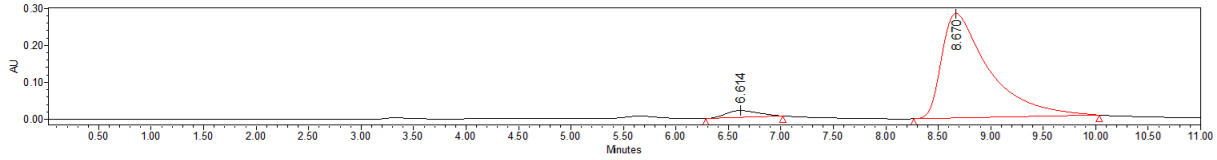
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 134.3, 131.1, 127.5, 122.8, 121.2, 117.2, 104.3, 100.7, 94.1, 61.6, 61.1, 36.2, 32.2, 14.2, 14.1.

IR: 3468, 2923, 2856, 1722, 1648, 1569, 1425, 1309, 1206, 1090, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}^{78.9183}BrNO_5^+$ [M+H$^+$] 408.0441; Found 408.0442, $C_{18}H_{19}^{80.9163}BrNO_5H^+$ 410.0421; Found 410.0421.

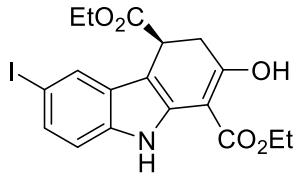


	Retention Time	Area	% Area
1	6.502	13060535	49.37
2	8.611	13395251	50.63



	Retention Time	Area	% Area
1	6.614	394468	4.27
2	8.670	8845375	95.73

Diethyl (S)-2-hydroxy-6-iodo-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ap)



Yellow solid. 43% yield, 91% ee, M.p. 122 – 123 ℃, $[\alpha]_{436}^{24.7}$ = -153.6 (*c* = 0.138, CH_2Cl_2).

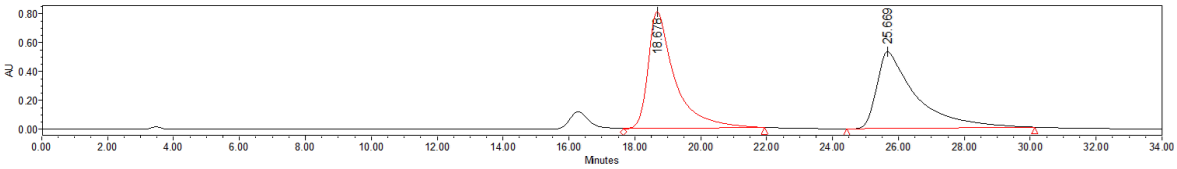
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 25.23 min, t (minor) = 18.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.05 (s, 1H), 8.83 (s, 1H), 7.93 – 7.83 (m, 1H), 7.37 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.18 – 3.98 (m, 3H), 3.19 – 2.96 (m, 2H), 1.47 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

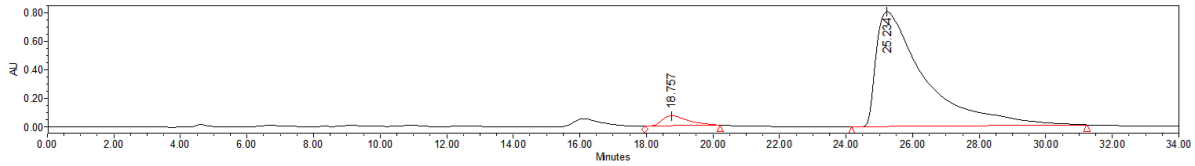
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 134.8, 131.3, 128.9, 128.8, 126.9, 112.7, 98.9, 94.1, 83.6, 61.7, 61.2, 35.8, 32.2, 14.6, 14.2.

IR: 3467, 2923, 2856, 1723, 1640, 1561, 1449, 1227, 1079, 1026 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{18}H_{19}INO_5^+$ [M+H$^+$] 456.0302; Found 456.0302.

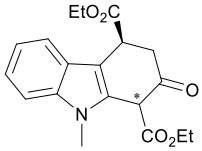


	Retention Time	Area	% Area
1	18.678	45654783	50.71
2	25.669	44368017	49.29



	Retention Time	Area	% Area
1	18.757	3759594	4.41
2	25.234	81415422	95.59

Diethyl (4S)-9-methyl-2-oxo-2,3,4,9-tetrahydro-1H-carbazole-1,4-dicarboxylate (3aq)



Yellow liquid. 62% yield, 63:37 d.r. (determined by ^{1}H NMR), 79% ee for the major isomer and 78% ee for the minor isomer, $[\alpha]_{589}^{24.2}$ = -35.1 (*c* = 0.262, CH_2Cl_2).

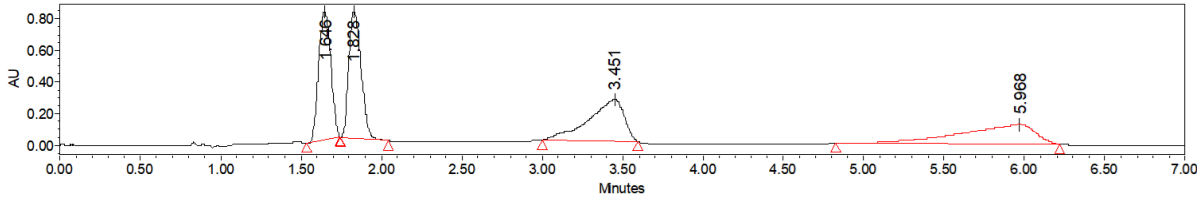
Dissolved in MeOH for SFC; SFC (Daicel chiralcel OD-3, CO_2/MeOH=80/20, flow rate = 1.5 mL/min, λ = 254 nm) $t_{major\ isomer}$ = 1.83 min (major), 1.64 min (minor); $t_{minor\ isomer}$ = 5.93 min (major), 3.43 min (minor);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.0, 2.8 Hz, 1H), 7.36 – 7.24 (m, 2H), 7.22 – 7.12 (m, 1H), 4.65 (d, J = 2.6 Hz, 1H), 4.43 (dd, J = 6.8, 2.4 Hz, 1H), 4.35 – 4.16 (m, 2H), 4.17 – 4.02 (m, 2H), 3.68 – 3.59 (m, 3H), 3.15 (dd, J = 14.2, 6.7 Hz, 1H), 2.95 (dd, J = 14.2, 2.2 Hz, 1H), 1.32 – 1.23 (m, 3H), 1.19 (t, J = 7.2 Hz, 3H).

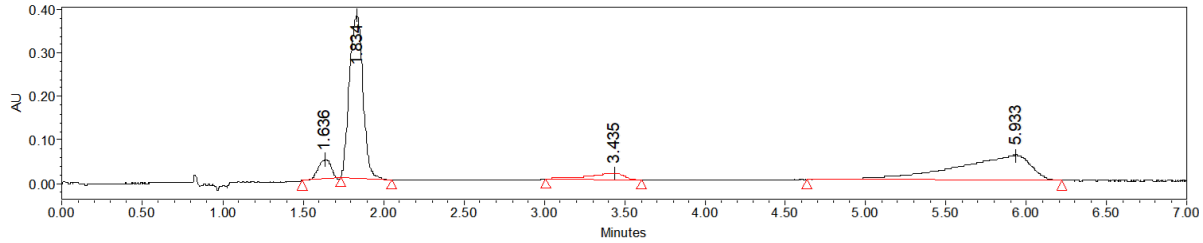
^{13}C NMR (101 MHz, CDCl3) δ 199.6, 173.0, 166.8, 137.9, 130.9, 125.1, 122.5, 119.9, 119.2, 109.3, 107.7, 62.6, 61.4, 54.7, 40.0, 38.9, 29.9, 14.0.

IR: 2981, 1729, 1469, 1413, 1370, 1335, 1241, 1176, 1031, 856 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1486.

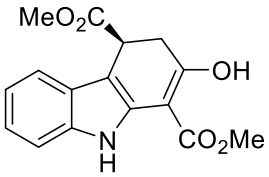


	Retention Time	Area	% Area
1	1.646	4291296	25.81
2	1.828	4281541	25.75
3	3.451	4044040	24.32
4	5.968	4011389	24.12



	Retention Time	Area	% Area
1	1.636	244460	5.37
2	1.834	2204435	48.47
3	3.435	225082	4.95
4	5.933	1874381	41.21

Dimethyl (S)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3ar)



Yellow solid. 65% yield, 95% ee, M.p.164 -168 ℃, $[\alpha]_{589}^{24.1}$ = -82.7 (*c* = 0.318, CH_2Cl_2).

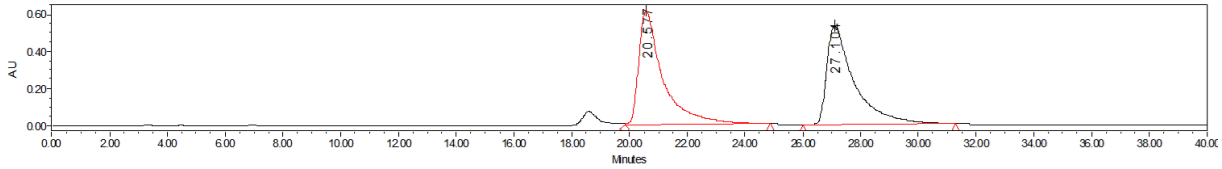
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 27.06 min, t (minor) = 20.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.87 (s, 1H), 8.81 (s, 1H), 7.55 – 7.47 (m, 1H), 7.36 – 7.28 (m, 1H), 7.16 – 7.06 (m, 2H), 4.12 – 4.04 (m, 1H), 3.98 (s, 3H), 3.64 (s, 3H), 3.16 – 3.00 (m, 2H).

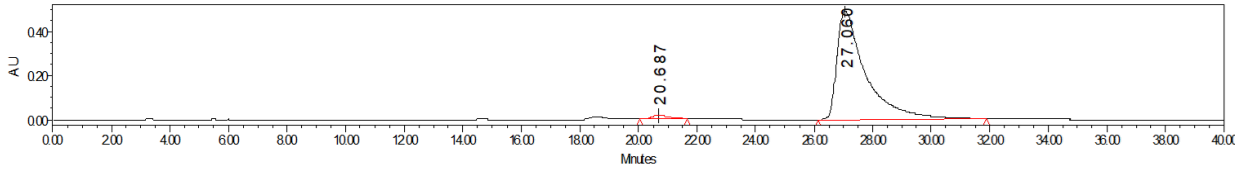
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 135.7, 130.1, 126.2, 120.7, 120.1, 117.8, 110.8, 99.7, 94.3, 52.2, 52.1, 35.81, 32.5.

IR: 3473, 2922, 2855, 1719, 1639, 1456, 1312, 1260, 1079, 1028, cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{16}H_{16}NO_5^+$ [M+H$^+$] 302.1023; Found 302.1021.

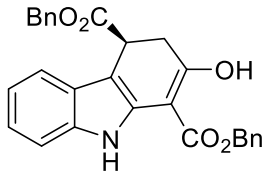


	Retention Time	Area	% Area
1	20.577	36088638	50.67
2	27.104	35133325	49.33



	Retention Time	Area	% Area
1	20.687	790329	2.30
2	27.060	33631551	97.70

Dibenzyl (S)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3as)



Yellow solid. 48% yield, 93% ee, M.p. 116-119 ℃, $[\alpha]_{589}^{20.4}$ = -47.1 (*c* = 0.316, CH_2Cl_2).

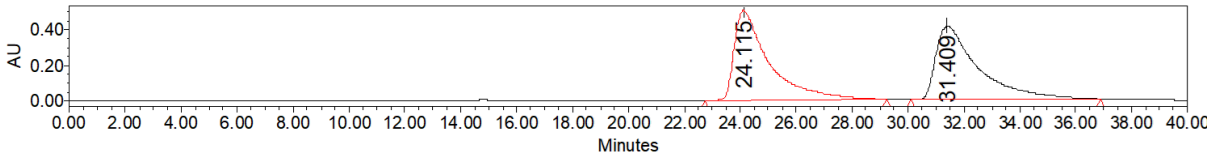
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 31.28 min, t (minor) = 24.47 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.89 (s, 1H), 8.74 (s, 1H), 7.53 – 7.36 (m, 6H), 7.29 – 7.23 (m, 3H), 7.23 – 7.16 (m, 3H), 7.10 – 6.99 (m, 2H), 5.53 – 5.32 (m, 2H), 5.12 (d, *J* = 12.4 Hz, 1H), 5.00 (d, *J* = 12.4 Hz, 1H), 4.14 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.18 – 3.03 (m, 2H).

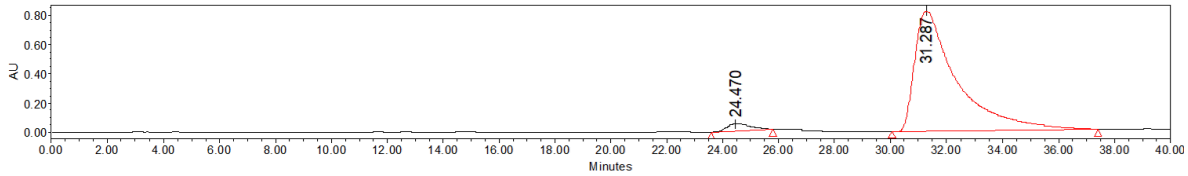
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 135.7, 135.6, 135.0, 130.2, 129.0, 128.9, 128.4, 128.3, 128.0, 127.9, 127.0, 126.1, 120.8, 120.1, 118.1, 110.7, 99.7, 94.4, 67.2, 66.7, 36.1, 32.5.

IR: 3470, 2923, 2855, 1716, 1639, 1453, 1405, 1311, 1256, 1074 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{28}H_{24}NO_5^+$ [M+H$^+$] 454.1649; Found 454.1647.

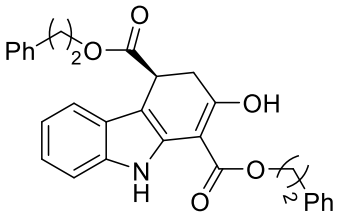


	Retention Time	Area	% Area
1	24.115	44145070	50.47
2	31.409	43321565	49.53



	Retention Time	Area	% Area
1	24.470	2854957	3.19
2	31.287	86606874	96.81

Diphenethyl (S)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3at)



Yellow liquid. 55% yield, 90% ee, $[\alpha]_{436}^{16.9}$ = -173.9 (*c* = 0.184, CH_2Cl_2).

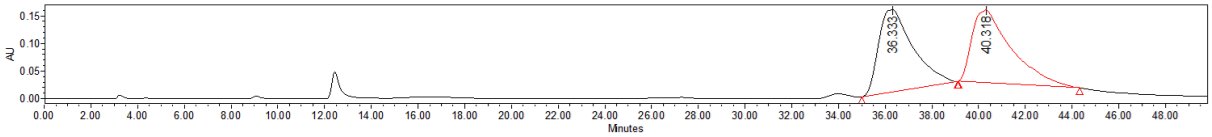
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 40.29 min, t (minor) = 36.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.91 (s, 1H), 8.19 (s, 1H), 7.49 – 7.29 (m, 6H), 7.25 – 7.14 (m, 3H), 7.12 – 6.96 (m, 5H), 4.83 – 4.54 (m, 2H), 4.83 – 4.54 (m, 2H), 4.08 – 3.84 (m, 1H), 3.23 – 2.91 (m, 4H), 2.81 (t, *J* = 6.8 Hz, 2H).

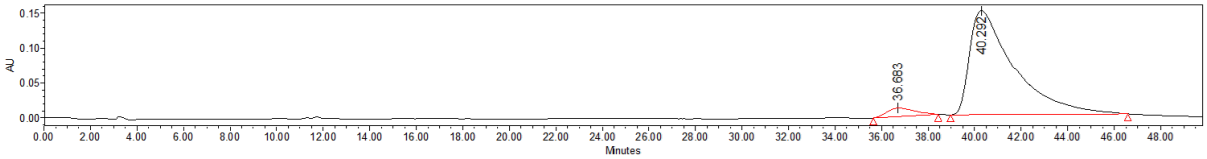
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 137.7, 135.5, 130.1, 129.2, 128.8, 128.6, 128.3, 127.2, 126.3, 126.1, 120.5, 119.9, 117.8, 110.8, 99.5, 94.3, 65.4, 65.0, 35.8, 34.9, 32.3.

IR: 3445, 2922, 2853, 1727, 1644, 1598, 1453, 1310, 1225, 1080 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{30}H_{28}NO_5^+$ [M+H$^+$] 482.1960; Found 482.1959.

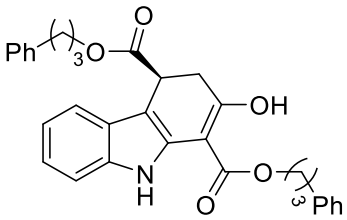


	Retention Time	Area	% Area
1	36.333	15279594	49.82
2	40.318	15386984	50.18



	Retention Time	Area	% Area
1	36.683	1010535	4.86
2	40.292	19769017	95.14

Bis(3-phenylpropyl) (S)-2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate (3au)



Yellow liquid. 53% yield, 92% ee, $[\alpha]_{589}^{17.5}$ = -60.8 (*c* = 0.462, CH_2Cl_2).

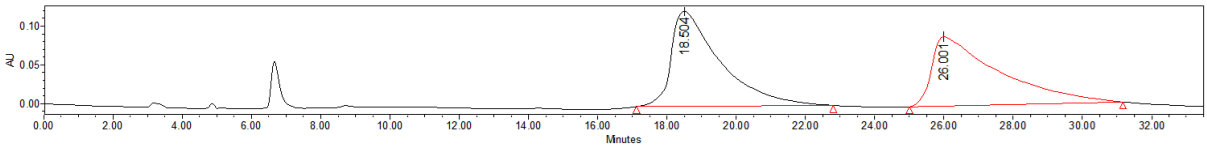
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 25.50 min, t (minor) = 19.00 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.03 (s, 1H), 8.71 (s, 1H), 7.64 – 7.56 (m, 1H), 7.35 – 7.27 (m, 3H), 7.25 – 7.16 (m, 5H), 7.17 – 7.09 (m, 3H), 6.95 (d, *J* = 6.8 Hz, 2H), 4.41 (t, *J* = 6.7 Hz, 2H), 4.14 – 3.91 (m, 3H), 3.23 – 2.98 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 8.0 Hz, 2H), 2.24 – 2.10 (m, 2H), 1.87 – 1.77 (m, 2H).

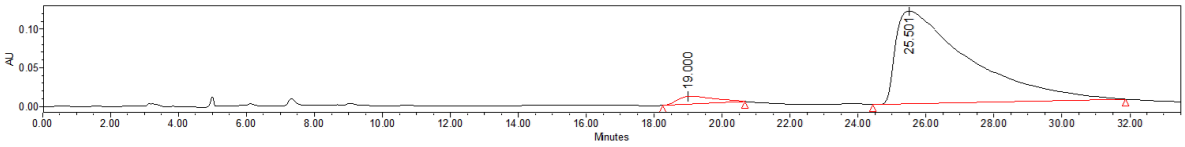
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 141.1, 140.5, 135.6, 130.1, 128.6, 128.4, 128.3, 128.3, 126.3, 126.3, 125.8, 120.8, 120.2, 118.0, 110.8, 99.9, 94.3, 64.8, 64.1, 35.9, 32.4, 32.2, 31.9, 30.3, 30.2.

IR: 3472, 3025, 2953, 1723, 1645, 1595, 1449, 1309, 1221, 1077 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{32}H_{32}NO_5^+$ [M+H$^+$] 510.2275; Found 510.2275.

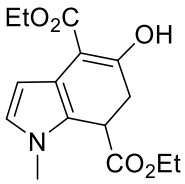


	Retention Time	Area	% Area
1	18.504	12046230	50.08
2	26.001	12009179	49.92



	Retention Time	Area	% Area
1	19.000	743832	3.97
2	25.501	17985652	96.03

Diethyl 5-hydroxy-1-methyl-6,7-dihydro-1H-indole-4,7-dicarboxylate (3av)



Yellow liquid. 42% yield, 52% ee, $[\alpha]_{589}^{22.8}$ = +100.3 (*c* = 0.382, CH_2Cl_2).

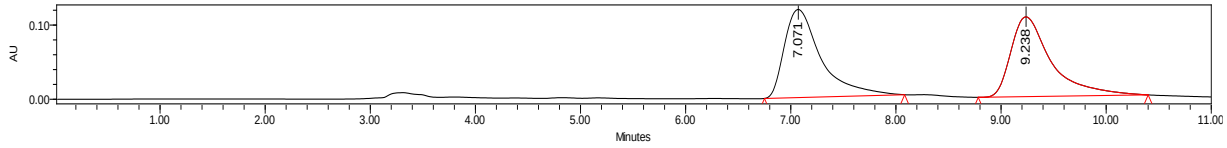
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.11 min, t (minor) = 9.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (s, 1H), 6.52 (s, 1H), 6.35 (s, 1H), 4.41 – 4.24 (m, 2H), 4.17 – 4.04 (m, 2H), 3.75 (dd, *J* = 6.8, 3.6 Hz, 1H), 3.63 (s, 3H), 3.06 – 2.91 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

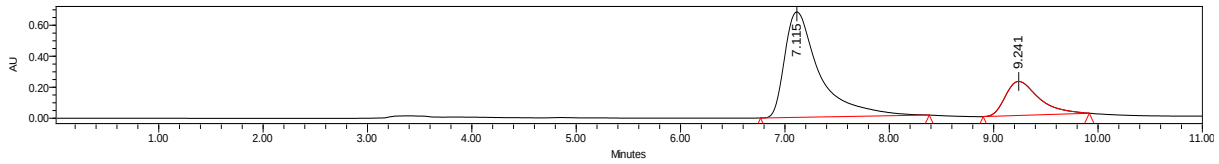
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 171.0, 169.5, 121.9, 119.2, 114.9, 105.4, 97.1, 61.3, 60.6, 36.2, 33.7, 32.3, 14.3, 14.1.

IR: 2982, 1730, 1645, 1600, 1407, 1327, 1217 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{15}H_{20}NO_5^+$ [M+H$^+$] 294.1336; Found 294.1336.

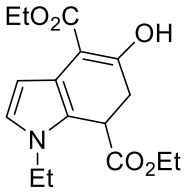


	Retention Time	Area	% Area
1	7.071	2885667	50.10
2	9.238	2874183	49.90



	Retention Time	Area	% Area
1	7.115	15773189	76.20
2	9.241	4926180	23.80

Diethyl 1-ethyl-5-hydroxy-6,7-dihydro-1H-indole-4,7-dicarboxylate (3aw)



Yellow liquid. 40% yield, 72% ee, $[\alpha]_{589}^{22.1}$ = +157.8 (*c* = 0.282, CH_2Cl_2).

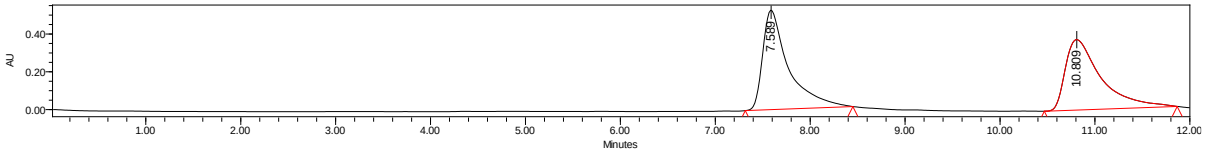
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.85 min, t (minor) = 11.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.66 (s, 1H), 6.61 (s, 1H), 6.40 (s, 1H), 4.42 – 4.23 (m, 2H), 4.21 – 3.84 (m, 4H), 3.75 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.00 – 2.97 (m, 2H), 1.45 – 1.36 (m, 6H), 1.21 (t, *J* = 7.2 Hz, 3H).

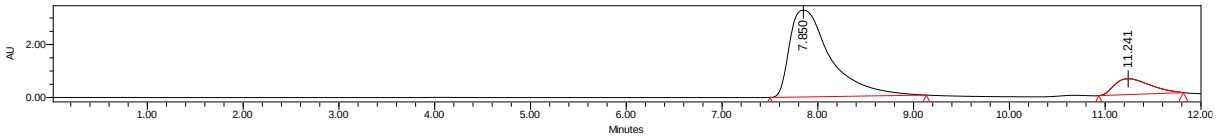
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 171.0, 169.5, 119.5, 118.5, 114.6, 105.7, 97.1, 61.23, 60.5, 41.0, 36.3, 32.5, 16.1, 14.2, 14.0.

IR: 2981, 1730, 1643, 1602, 1408, 1234, 1029 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{16}H_{22}NO_5^+$ [M+H$^+$] 308.1492; Found 308.1492.

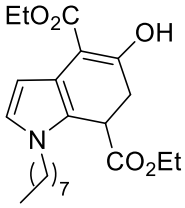


	Retention Time	Area	% Area
1	7.589	9954591	50.60
2	10.809	9718862	49.40



	Retention Time	Area	% Area
1	7.850	97453088	86.31
2	11.241	15454895	13.69

Diethyl 5-hydroxy-1-octyl-6,7-dihydro-1H-indole-4,7-dicarboxylate (3ax)



Yellow liquid. 36% yield, 71% ee, $[\alpha]_{589}^{24.2}$ = +81.0 (*c* = 0.516, CH_2Cl_2,).

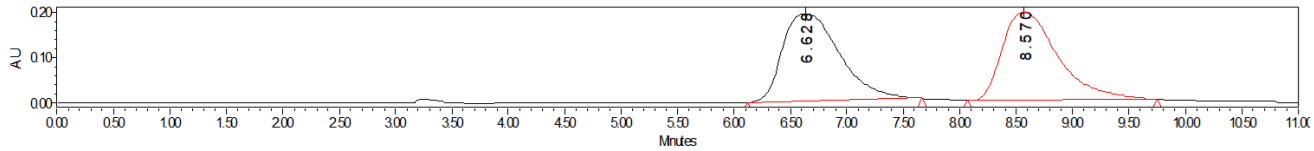
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 6.98 min, t (minor) = 8.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 4.43 – 4.01 (m, 5H), 4.02 – 3.89 (m, 1H), 3.87 – 3.70 (m, 2H), 3.05 – 2.89 (m, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.35 – 1.24 (m, 11H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H).

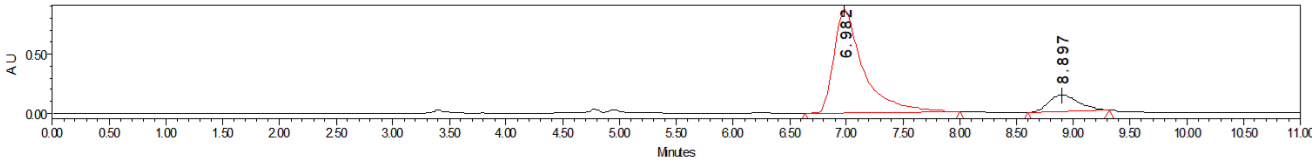
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 171.0, 169.4, 120.4, 118.6, 114.6, 105.5, 97.1, 61.2, 60.5, 46.6, 36.5, 32.6, 31.8, 31.1, 29.3, 29.2, 26.9, 22.6, 14.2, 14.0.

IR: 2927, 2855, 1732, 1642, 1601, 1495, 1327, 1235 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{22}H_{34}NO_5^+$ [M+H$^+$] 392.2431; Found 392.2431.

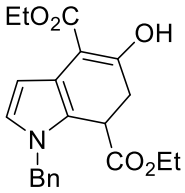


	Retention Time	Area	% Area
1	6.628	6729229	50.30
2	8.570	6649936	49.70



	Retention Time	Area	% Area
1	6.982	15379085	85.70
2	8.897	2566445	14.30

Diethyl 1-benzyl-5-hydroxy-6,7-dihydro-1H-indole-4,7-dicarboxylate (3ay)



Yellow liquid. 40% yield, 64% ee, $[\alpha]_{589}^{22.5}$ = +58.5 (*c* = 0.294, CH_2Cl_2).

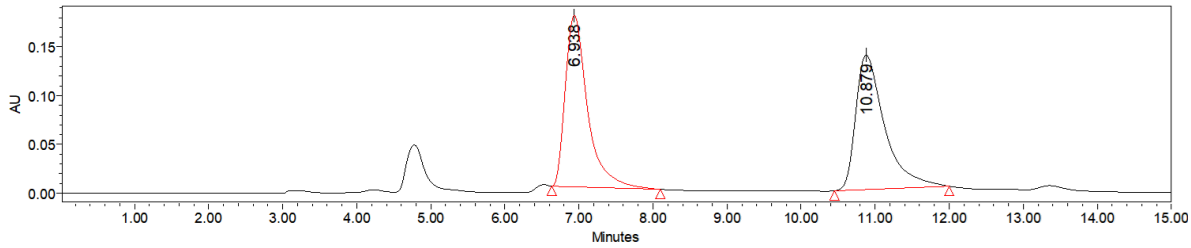
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.03 min, t (minor) = 11.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.67 (s, 1H), 7.37 – 7.24 (m, 3H), 7.06 – 7.02 (m, 2H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.44 (d, *J* = 2.8 Hz, 1H), 5.27 (d, *J* = 16.0 Hz, 1H), 5.07 (d, *J* = 16.0 Hz, 1H), 4.44 – 4.23 (m, 2H), 4.13 – 4.04 (m, 1H), 4.03 – 3.94 (m, 1H), 3.58 (dd, *J* = 6.4, 4.0 Hz, 1H), 2.89 – 2.86 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H).

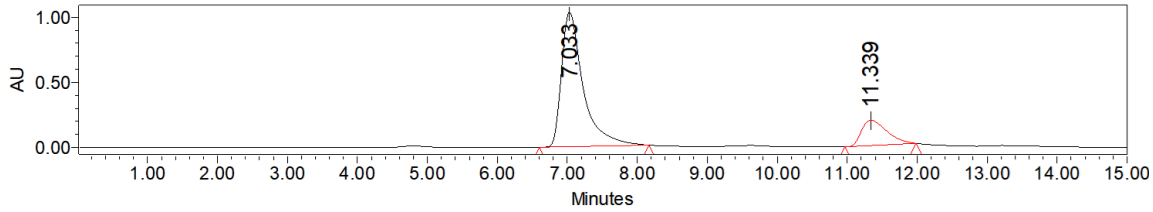
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 170.9, 169.7, 137.8, 128.8, 127.6, 126.5, 121.9, 118.9, 115.6, 105.8, 97.1, 61.3, 60.6, 50.5, 36.4, 32.4, 14.3, 14.0.

IR: 2980, 1729, 1641, 1601, 1408, 1326, 1223 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{24}NO_5^+$ [M+H$^+$] 370.1649; Found 370.1652.

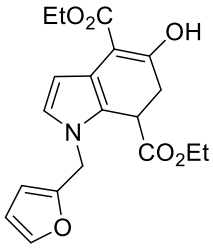


	Retention Time	Area	% Area
1	6.938	3681665	49.63
2	10.879	3736116	50.37



	Retention Time	Area	% Area
1	7.033	22241104	82.00
2	11.339	4881399	18.00

Diethyl 1-(furan-2-ylmethyl)-5-hydroxy-6,7-dihydro-1H-indole-4,7-dicarboxylate (3az)



Yellow liquid, 31% yield, 80% ee, $[\alpha]_{589}^{25.1}$ = +65.2 (*c* = 0.166, CH_2Cl_2).

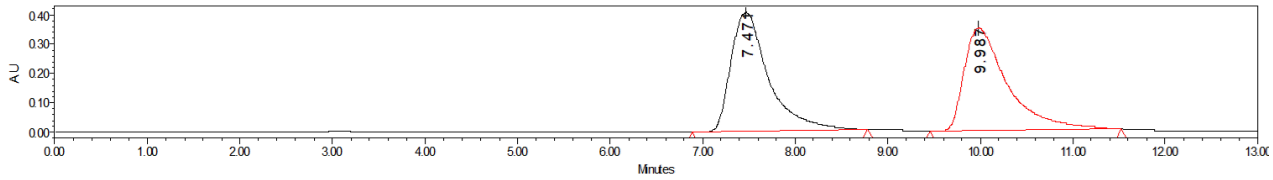
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 7.56 min, t (minor) = 10.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.67 (s, 1H), 7.39 – 7.33 (m, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.39 (d, *J* = 3.2 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 – 6.19 (m, 1H), 5.24 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 16.0 Hz, 1H), 4.41 – 4.25 (m, 2H), 4.16 – 4.03 (m, 2H), 3.85 (t, *J* = 5.2 Hz, 1H), 2.96 (d, *J* = 4.8 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

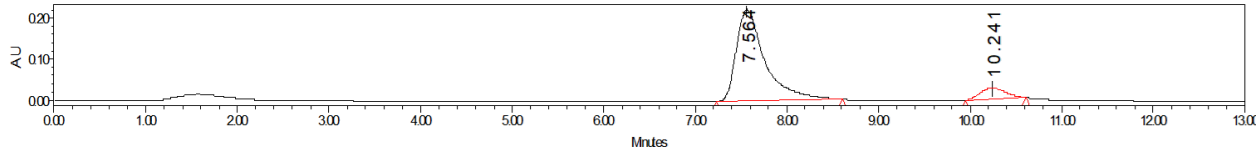
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 170.9, 169.7, 150.5, 142.7, 121.2, 118.7, 115.4, 110.4, 108.0, 105.9, 96.9, 61.3, 60.5, 43.6, 36.2, 32.2, 14.2, 14.0.

IR: 3119, 2981, 2932, 1730, 1641, 1601, 1327, 1236 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_6^+$ [M+H$^+$] 360.1442; Found 360.1442.

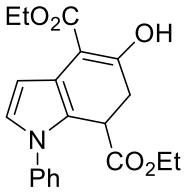


	Retention Time	Area	% Area
1	7.471	11532974	50.31
2	9.987	11390714	49.69



	Retention Time	Area	% Area
1	7.564	4769099	90.09
2	10.241	524395	9.91

Diethyl 5-hydroxy-1-phenyl-6,7-dihydro-1H-indole-4,7-dicarboxylate (3ba)



Yellow liquid 39% yield, 60% ee, $[\alpha]_{589}^{22.2}$ = -23.5 (*c* = 0.202, CH_2Cl_2).

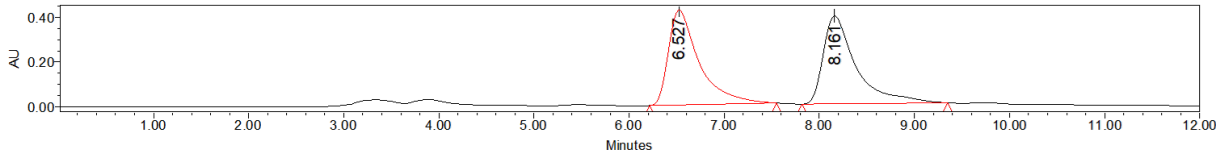
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.26 min, t (minor) = 6.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 3H), 6.78 (s, 1H), 6.57 (s, 1H), 4.49 – 4.26 (m, 2H), 4.07 – 3.87 (m, 2H), 3.79 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.08 – 2.94 (m, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H).

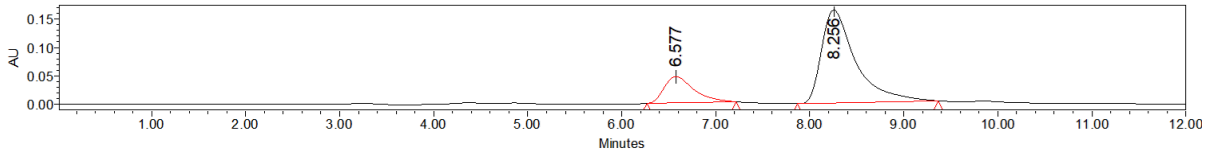
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 171.2, 169.9, 139.7, 129.2, 127.1, 125.3, 122.2, 119.6, 116.6, 107.1, 97.2, 61.1, 60.7, 36.9, 33.2, 14.3, 13.9.

IR: 2982, 1730, 1642, 1600, 1502, 1329, 1225 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{20}H_{22}NO_5^+$ [M+H$^+$] 356.1492; Found 356.1494.

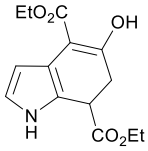


	Retention Time	Area	% Area
1	6.527	9558459	50.21
2	8.161	9477377	49.79



	Retention Time	Area	% Area
1	6.577	1008843	19.71
2	8.256	4108873	80.29

Diethyl 5-hydroxy-6,7-dihydro-1H-indole-4,7-dicarboxylate (3bb)



Yellow liquid. 13% yield, 0% ee.

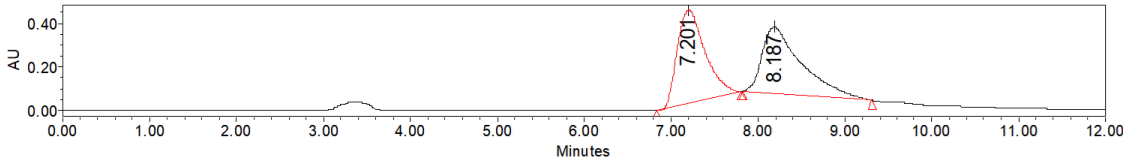
HPLC (Daicel chiralcel IF, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.23 min, t (minor) = 7.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.67 (s, 1H), 8.72 (s, 1H), 6.69 (t, J = 2.7 Hz, 1H), 6.45 (t, J = 2.7 Hz, 1H), 4.35 (qd, J = 7.1, 1.2 Hz, 2H), 4.25 (qd, J = 7.2, 1.6 Hz, 2H), 3.98 (dd, J = 11.6, 7.6 Hz, 1H), 3.05 (dd, J = 17.2, 11.6 Hz, 1H), 2.89 (dd, J = 17.2, 8.0 Hz, 1H), 1.42 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H).

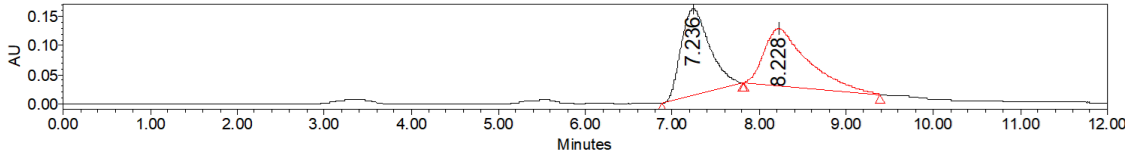
^{13}C NMR (101 MHz, CDCl3) δ 171.4, 171.3, 169.5, 117.5, 117.1, 114.3, 106.7, 97.4, 61.6, 60.7, 37.7, 32.1, 14.2, 14.1.

IR: 3394, 2982, 1727, 1643, 1603, 1409, 1375, 1327, 1226, 1091, 1029 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{14}H_{18}NO_5^+$ [M+H$^+$] 280.1179; Found 280.1174.

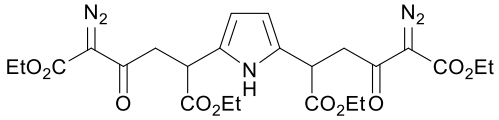


	Retention Time	Area	% Area
1	7.201	9539574	49.71
2	8.187	9649532	50.29



	Retention Time	Area	% Area
1	7.236	3370724	50.00
2	8.228	3371272	50.00

Tetraethyl 5,5'-(1H-pyrrole-2,5-diyl)bis(2-diazo-3-oxohexanedioate) (3bc)



Yellow liquid, 11% yield.

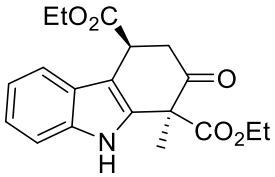
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 5.92 (d, J = 2.8 Hz, 2H), 4.31 (q, J = 7.1 Hz, 4H), 4.21 – 4.13 (m, 6H), 3.73 – 3.60 (m, 2H), 3.38 – 3.26 (m, 2H), 1.34 (t, J = 7.2 Hz, 6H), 1.26 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, CDCl3) δ 190.4, 190.4, 172.1, 161.2, 161.1, 127.2, 106.4, 61.6, 61.3, 42.2, 39.7, 39.6, 14.3, 14.0.

IR: 3367, 2983, 2138, 1717, 1652, 1373, 1306, 1211, 1168, 1025 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{30}N_5O_{10}^+$ $[M+H^+]$ 548.1987; Found 548.1987.

Diethyl (1S,4S)-1-methyl-2-oxo-2,3,4,9-tetrahydro-1H-carbazole-1,4-dicarboxylate (4a)



White solid, 45 yield, 90% ee, M.p.141-143 ℃, $[\alpha]_{436}^{23.6}$ = +67.1 (*c* = 0.134, CH_2Cl_2).

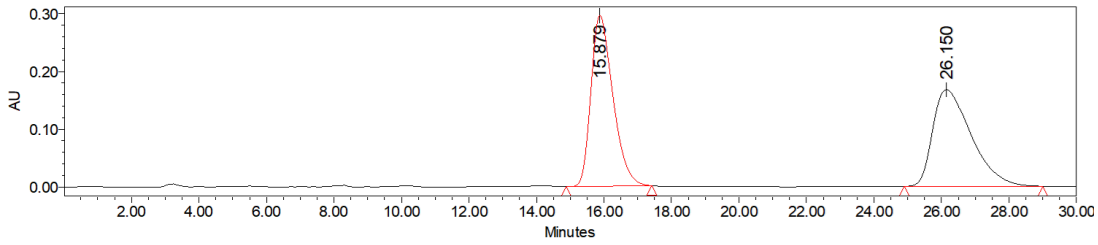
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 15.84 min, t (minor) = 26.68 min

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.29 – 4.04 (m, 5H), 3.29 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.93 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.75 (s, 3H) 1.26 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

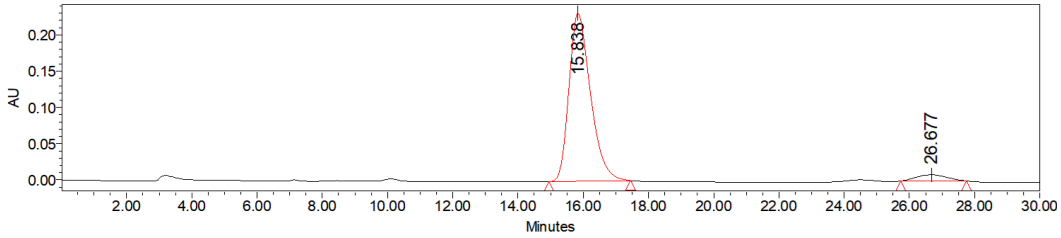
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 172.2, 170.6, 136.8, 133.8, 125.6, 122.9, 120.3, 119.3, 111.3, 107.6, 62.4, 61.3, 55.6, 39.9, 38.7, 21.9, 14.1, 13.8.

IR: 3360, 2959, 2924, 2854, 1731, 1458, 1371, 1257, 1177, 1014 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1489.

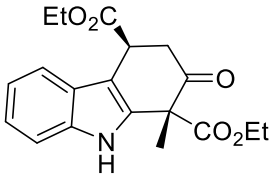


	Retention Time	Area	% Area
1	15.879	13363385	50.16
2	26.150	13278510	49.84



	Retention Time	Area	% Area
1	15.838	10634105	95.04
2	26.677	554828	4.96

Diethyl (1R,4S)-1-methyl-2-oxo-2,3,4,9-tetrahydro-1H-carbazole-1,4-dicarboxylate (4a′)



Yellow liquid, 37% yield, 88% ee, $[\alpha]_{436}^{23.6}$ = -58.8 (*c* = 0.214, CH_2Cl_2).

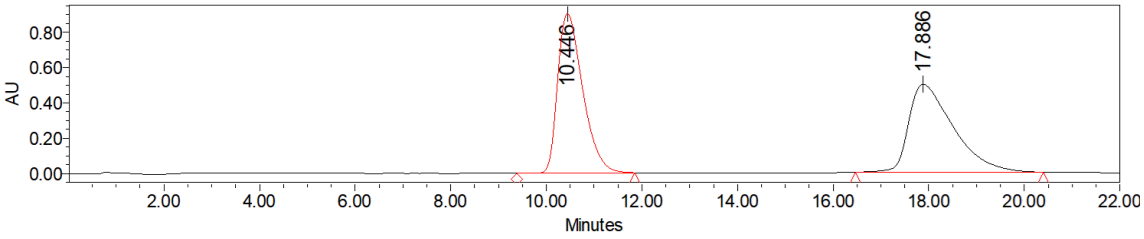
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 17.50 min, t (minor) = 10.31 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.18 (t, J = 7.2 Hz, 1H), 4.33 (dd, *J* = 6.4, 2.0 Hz, 1H), 4.23 – 4.02 (m, 4H), 3.12 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.00 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.79 (s, 3H), 1.23 – 1.19 (m, 3H). 1.19 – 1.14 (m, 3H).

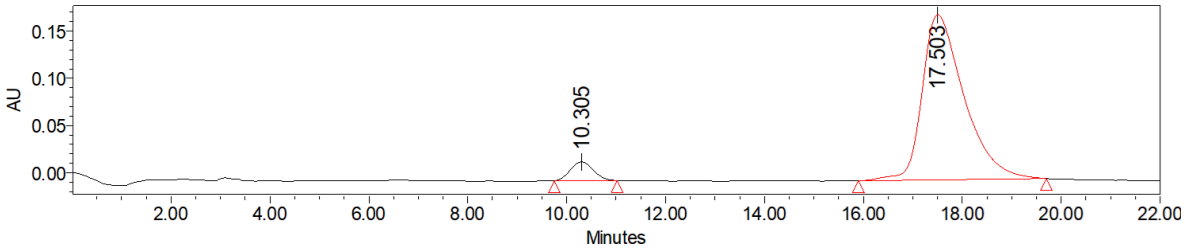
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 172.8, 170.7, 136.5, 134.7, 125.6, 122.9, 120.4, 118.9, 111.3, 107.8, 62.5, 61.4, 54.8, 41.1, 38.5, 21.8, 14.0, 13.9.

IR: 3371, 2983, 2936, 1723, 1456, 1370, 1334, 1238, 1181, 1100 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{22}NO_5^+$ [M+H$^+$] 344.1492; Found 344.1493.

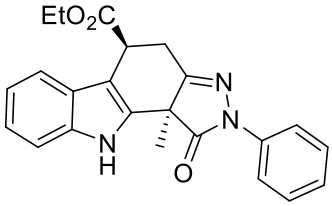


	Retention Time	Area	% Area
1	10.446	33015149	50.18
2	17.886	32783559	49.82



	Retention Time	Area	% Area
1	10.305	642763	5.87
2	17.503	10307095	94.13

Ethyl (5S,10bS)-10b-methyl-1-oxo-2-phenyl-1,2,4,5,10,10b-hexahydropyrazolo[4,3-a]carbazole-5-carboxylate (5a)



White solid 80% yield, 90% ee, M.p.192-194 ℃, $[\alpha]_{589}^{24.3}$ = +22.7 (*c* = 0.176, CH_2Cl_2).

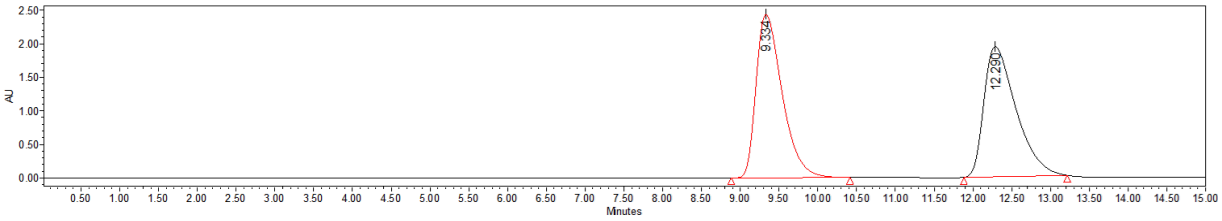
HPLC (Daicel chiralcel ADH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 12.27 min, t (minor) = 9.44 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.96 – 7.89 (m, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.39 (q, *J* = 8.0 Hz, 3H), 7.24 – 7.17 (m, 2H), 7.15 – 7.09 (m, 1H), 4.38 (d, *J* = 7.2 Hz, 1H), 4.13 – 4.01 (m, 2H), 3.33 (d, *J* = 13.6 Hz, 1H), 3.09 (dd, *J* = 13.6, 7.6 Hz, 1H), 1.76 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H).

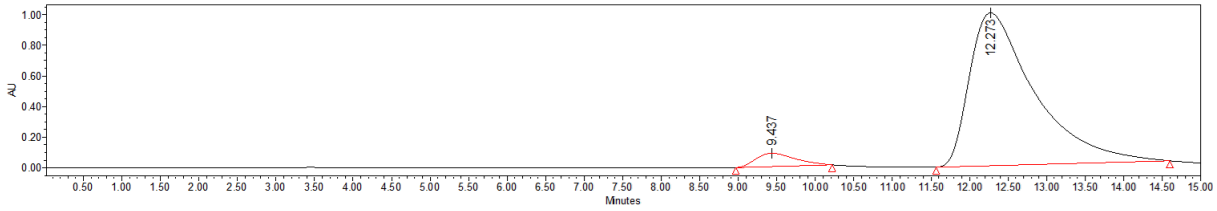
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.1, 163.6, 137.9, 137.0, 131.7, 128.8, 125.9, 125.3, 122.9, 120.2, 119.5, 119.1, 111.6, 107.2, 61.2, 50.5, 40.3, 29.7,26.6, 24.3, 14.1.

IR: 3350, 2977, 2924, 2854, 1697, 1596, 1496, 1457, 1368, 1178 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{22}N_3O_3^+$ [M+H$^+$] 388.1655; Found 388.1654.

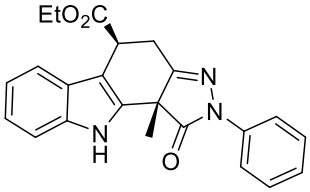


	Retention Time	Area	% Area
1	9.334	57083934	50.57
2	12.290	55804892	49.43



	Retention Time	Area	% Area
1	9.437	3082707	5.00
2	12.273	58553741	95.00

Ethyl (5S,10bR)-10b-methyl-1-oxo-2-phenyl-1,2,4,5,10,10b-hexahydropyrazolo[4,3-a]carbazole-5-carboxylate (5a′)



Yellow solid,78% yield, 90% ee, M.p.175-178 ℃, $[\alpha]_{436}^{22.6}$ = -82.3 (*c* = 0.102, CH_2Cl_2).

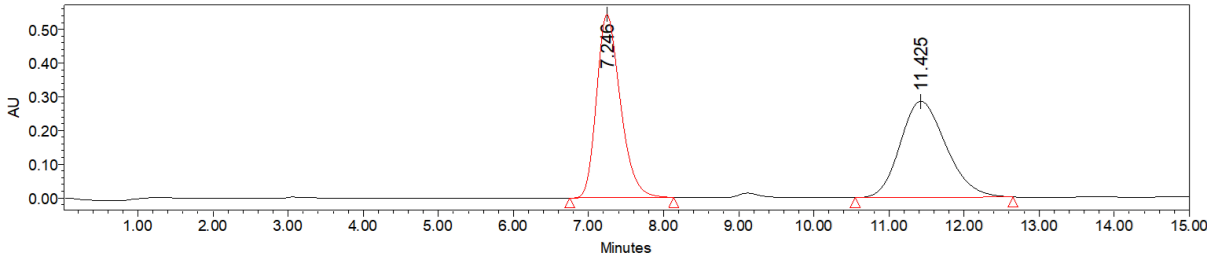
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 11.36 min, t (minor) = 7.28 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.91 – 7.86 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.33 (m, 3H), 7.23 – 7.16 (m, 2H), 7.14 – 7.07 (m, 1H), 4.34 – 4.20 (m, 3H), 3.39 – 3.23 (m, 2H), 1.85 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

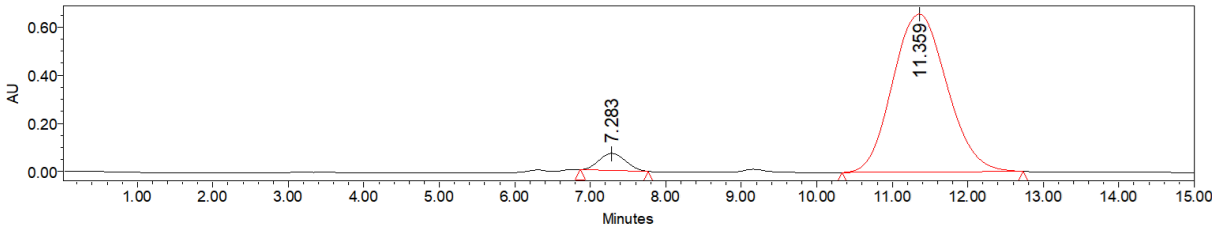
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 173.1, 164.2, 137.8, 136.9, 131.4, 128.9, 125.6, 125.5, 122.9, 120.3, 119.3, 118.9, 111.6, 107.6, 61.6, 50.5, 41.7, 26.7, 23.5, 14.2.

IR: 3349, 2979, 2927, 1701, 1595, 1495, 1455, 1373, 1297, 1178 cm^{-1}.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{22}N_3O_3^+$ [M+H$^+$] 388.1655; Found 388.1653.

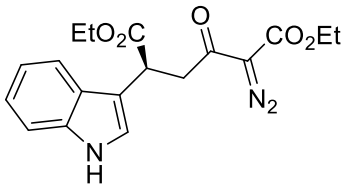


	Retention Time	Area	% Area
1	7.246	11971251	49.78
2	11.425	12079089	50.22



	Retention Time	Area	% Area
1	7.283	1724518	5.00
2	11.359	32748924	95.00

Diethyl (S)-2-diazo-5-(1H-indol-3-yl)-3-oxohexanedioate (6a)



Colourless solid, 94% yield, 91% ee, M.p.85-88 ℃, $[\alpha]_{589}^{23.9}$ = +107.5 (*c* = 0.574, CH_2Cl_2).

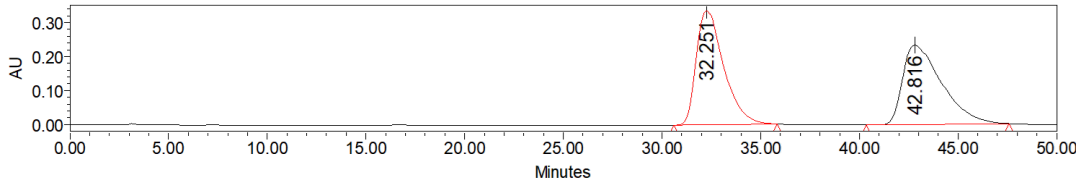
HPLC (Daicel chiralcel ODH, n-hexane/i-PrOH 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 31.71 min, t (minor) = 43.17 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.15 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 4.48 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.12 (m, 2H), 3.94 (dd, *J* = 18.4, 10.4 Hz, 1H), 3.26 (dd, *J* = 18.4, 4.0 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H).

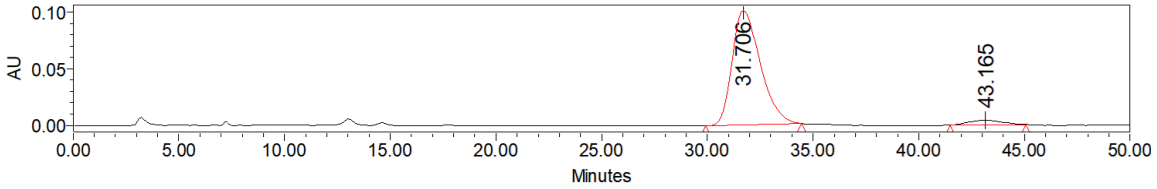
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 173.8, 161.3, 136.2, 126.3, 122.3, 122.2, 119.7, 119.3, 112.7, 111.3, 76.2, 61.5, 61.0, 43.2, 37.9, 14.3, 14.1.

IR: 3394, 2960, 2930, 2866, 2137, 1720, 1653, 1375, 1270, 1120 cm^{-1}.

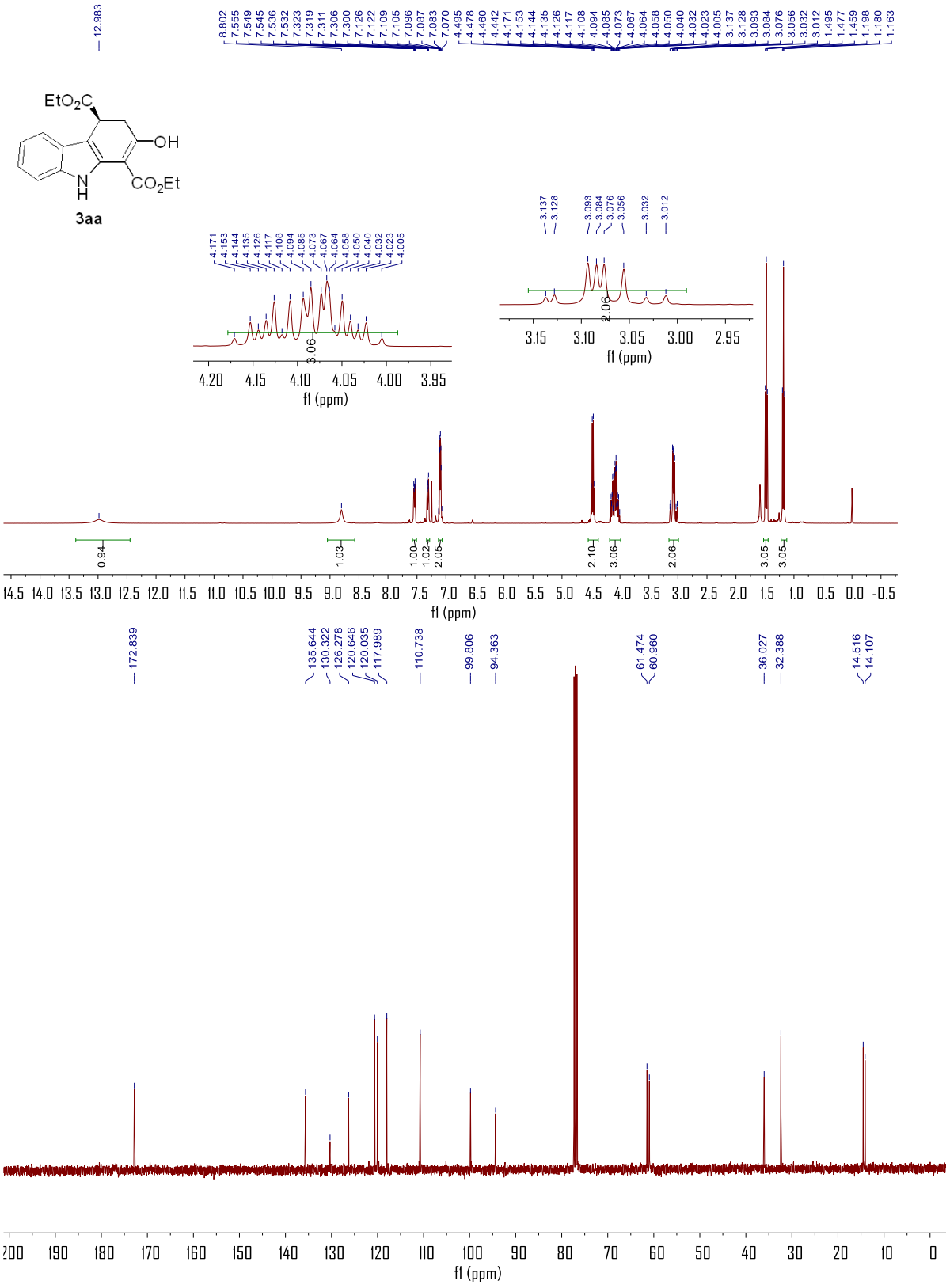
HRMS (FTMS+c ESI): Calcd for $C_{18}H_{20}N_3O_5^+$ [M+H$^+$] 358.1397; Found 358.1398.

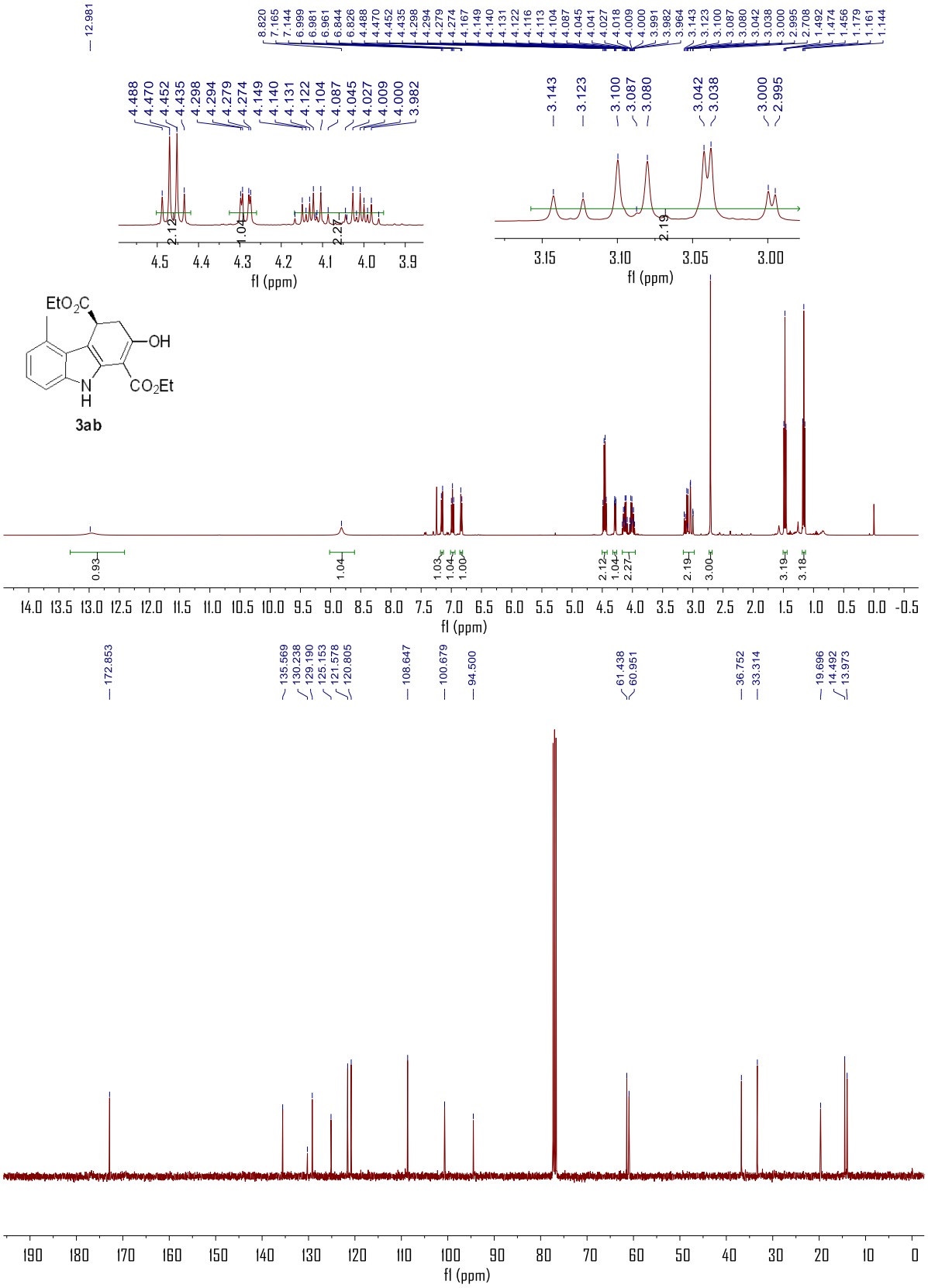


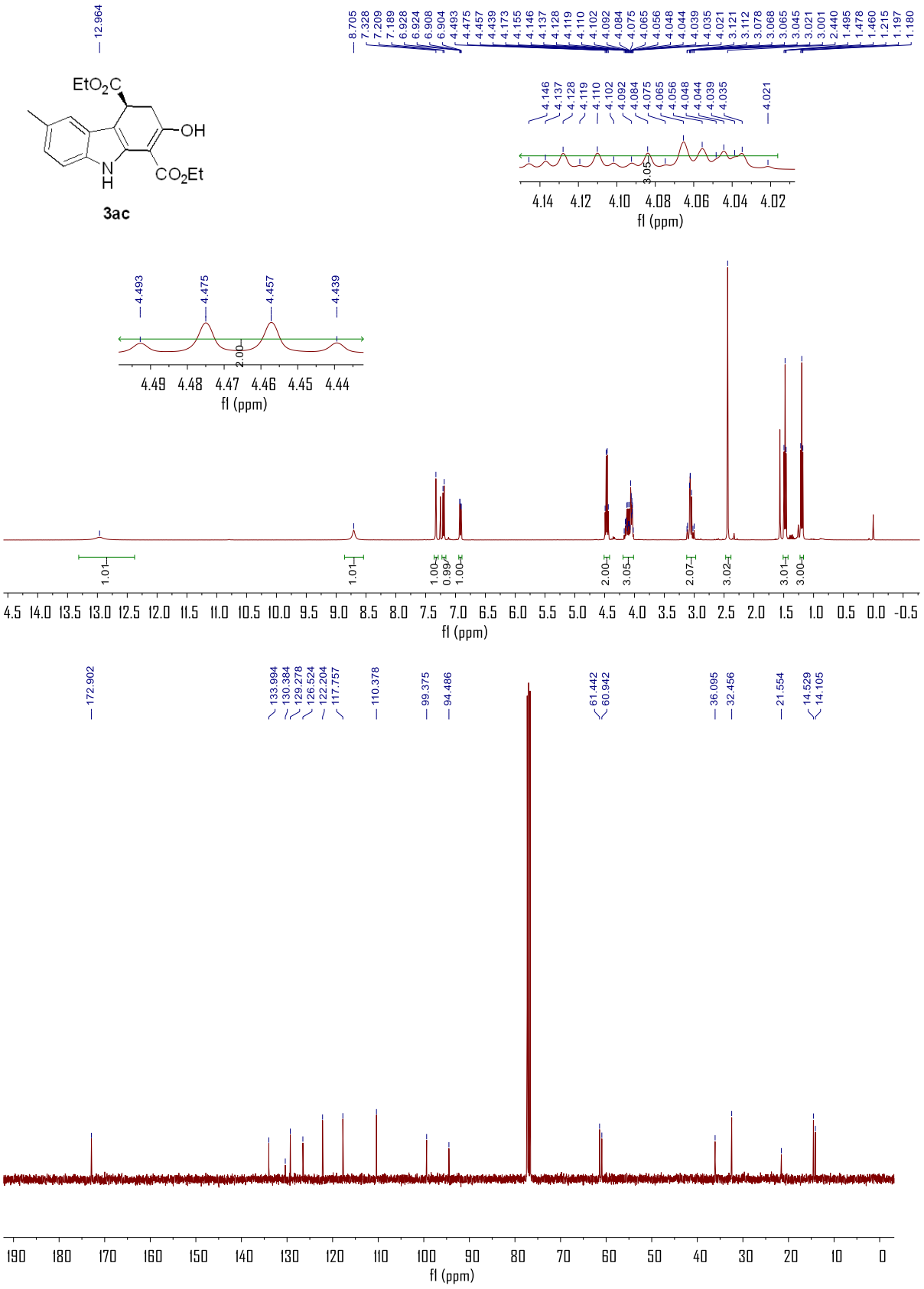
	Retention Time	Area	% Area
1	32.251	32514040	50.35
2	42.816	32062276	49.65

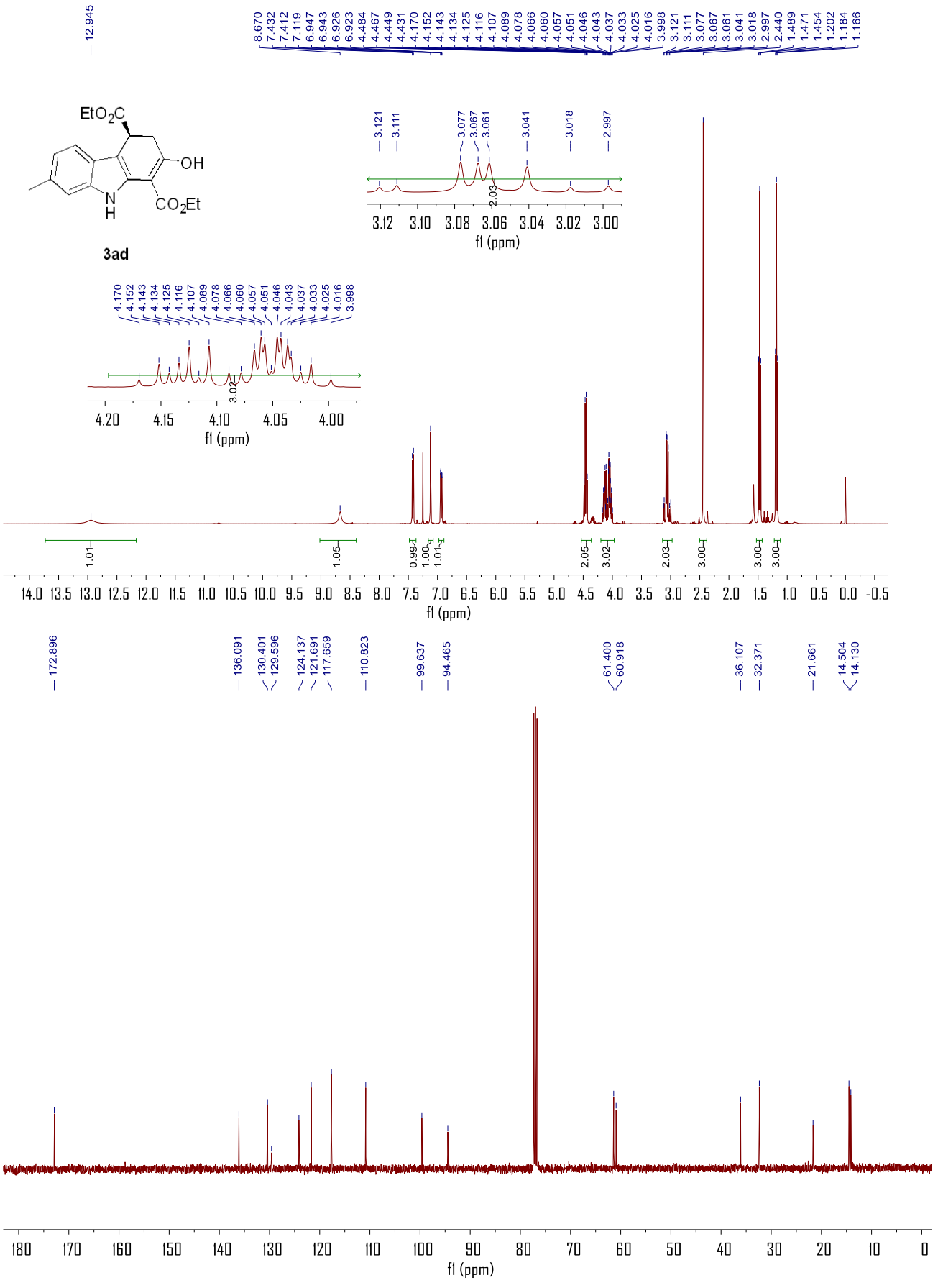


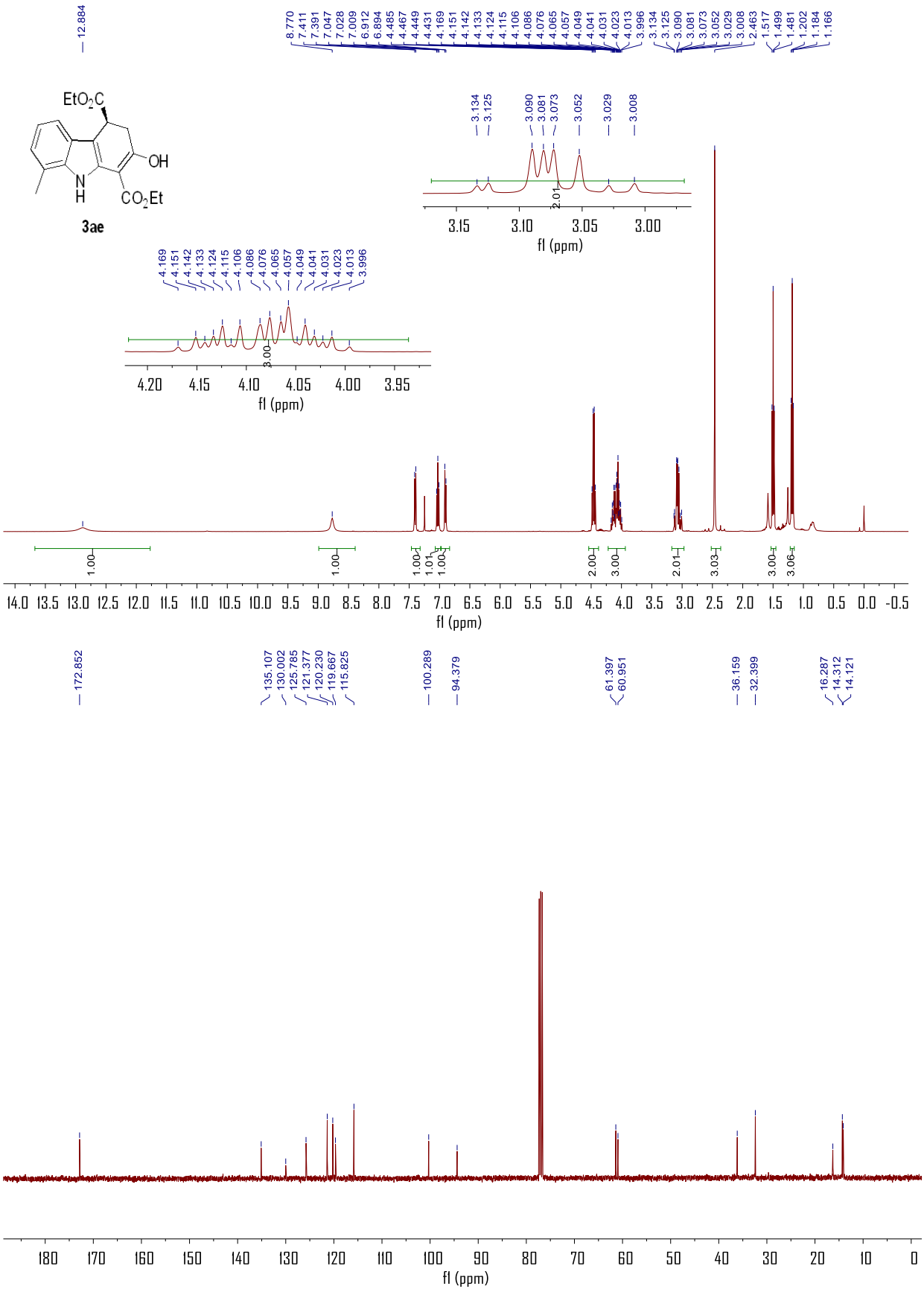
	Retention Time	Area	% Area
1	31.706	9384021	95.57
2	43.165	434830	4.43

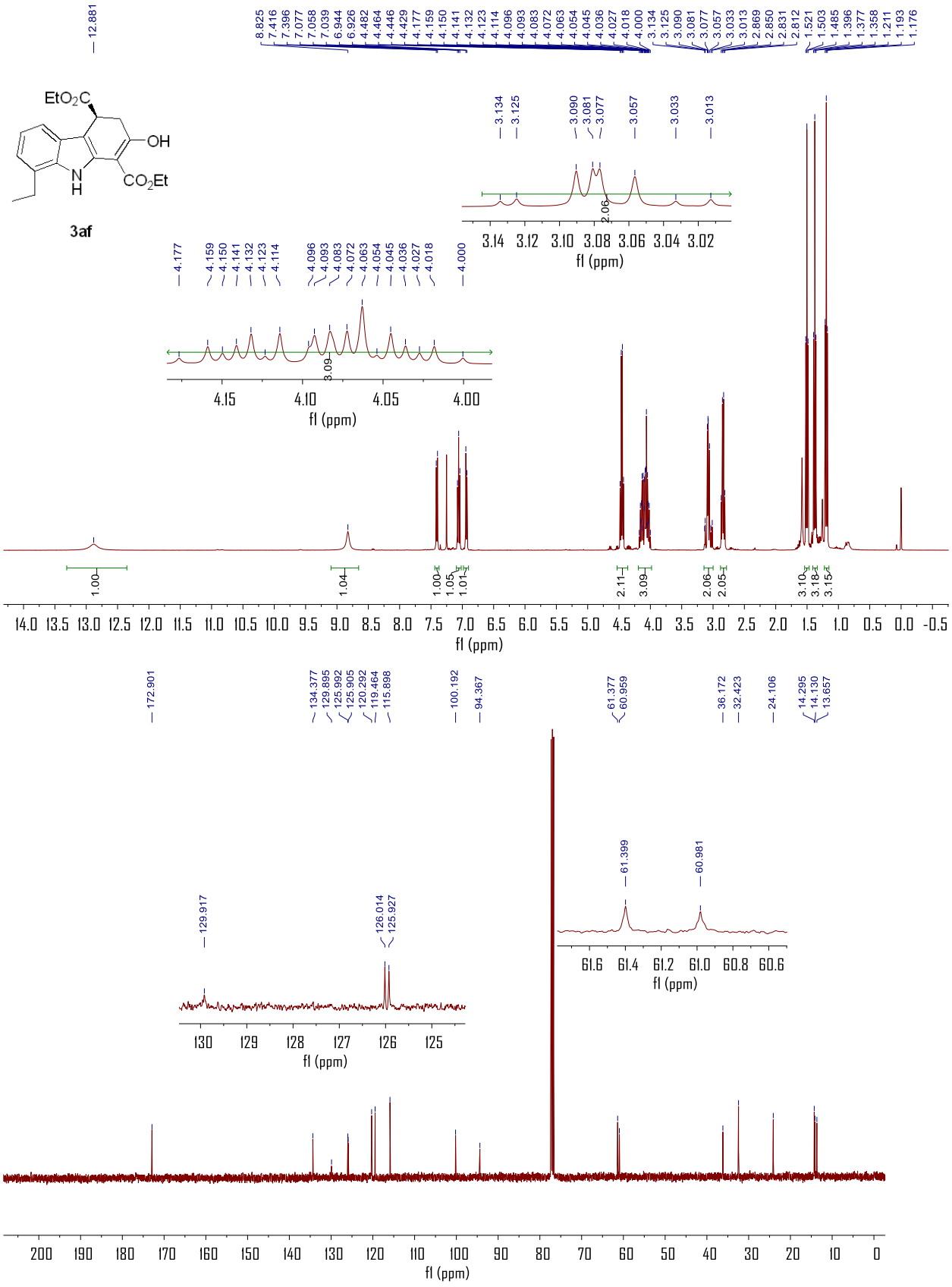

12.983
8.802
7.555
7.549
7.545
7.536
7.532
7.323
7.319
7.311
7.306
7.300
7.126
7.122
7.109
7.105
7.096
7.087
7.083
7.070
4.495
4.478
4.460
4.442
4.171
4.153
4.144
4.135
4.126
4.117
4.108
4.094
4.085
4.073
4.067
4.064
4.058
4.050
4.040
4.032
4.023
4.005
3.137
3.128
3.093
3.084
3.076
3.056
3.032
3.012
1.495
1.477
1.459
1.198
1.180
1.163
EtO2C
OH
CO2Et
N
H
3aa
3.06
fl (ppm)
2.06
fl (ppm)
0.94
1.03
1.00
1.02
2.05
2.10
3.06
2.06
3.05
3.05
fl (ppm)
172.839
135.644
130.322
126.278
120.646
120.035
117.989
110.738
99.806
94.363
61.474
60.960
36.027
32.388
14.516
14.107
fl (ppm)

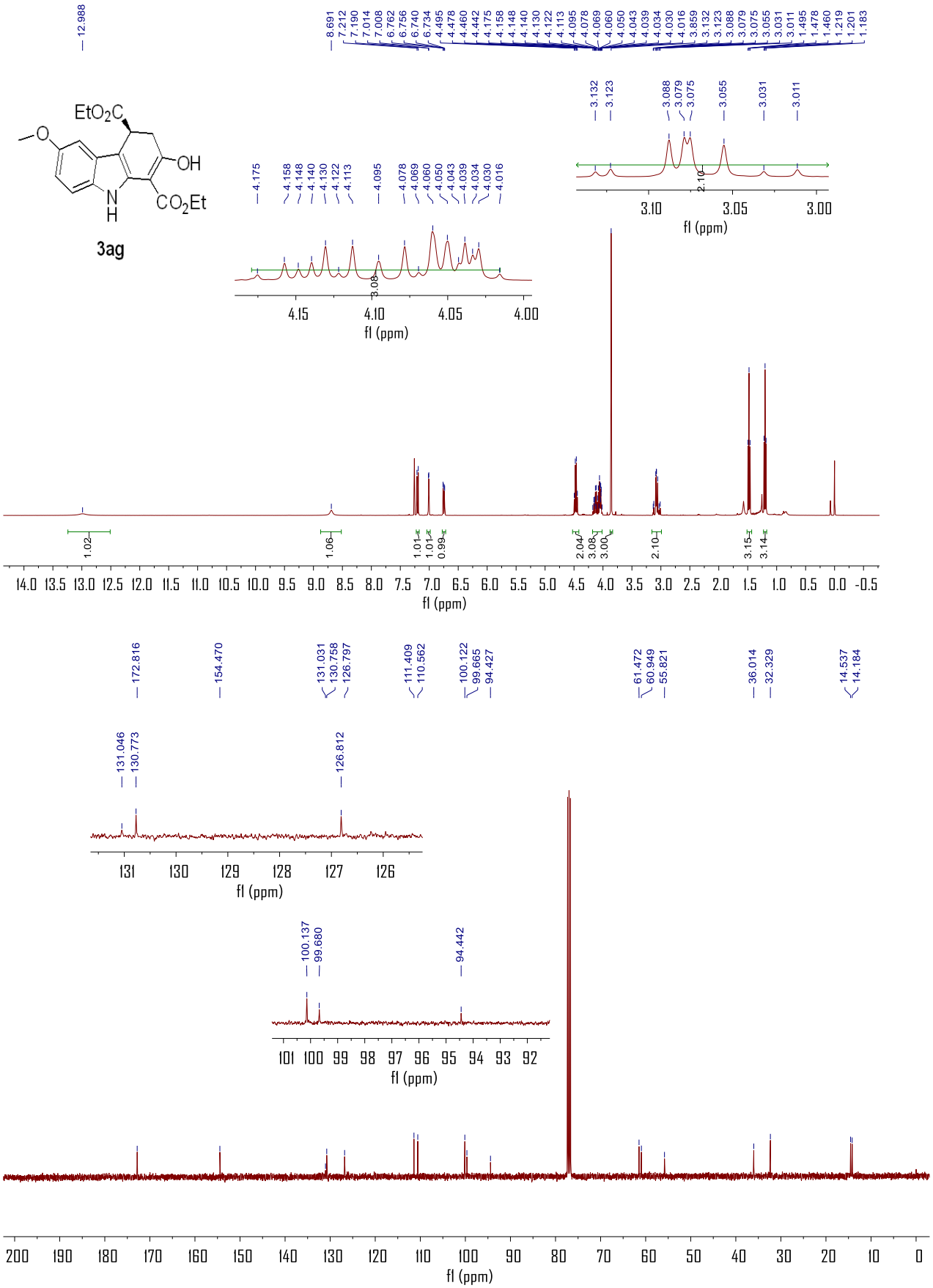

12.981
8.820
7.165
7.144
6.999
6.981
6.961
6.844
6.826
4.488
4.470
4.452
4.435
4.298
4.294
4.279
4.274
4.167
4.149
4.140
4.131
4.122
4.116
4.113
4.104
4.087
4.045
4.041
4.027
4.018
4.009
4.000
3.991
3.982
3.964
3.143
3.123
3.100
3.087
3.080
3.042
3.038
3.000
2.995
2.708
1.492
1.474
1.456
1.179
1.161
1.144
2.12
1.04
2.27
2.19
f1 (ppm)
EtO2C
OH
N
H
CO2Et
3ab
0.93
1.04
1.03
1.04
1.00
2.12
1.04
2.27
2.19
3.00
3.19
3.18
f1 (ppm)
172.853
135.569
130.238
129.190
125.153
121.578
120.805
108.647
100.679
94.500
61.438
60.951
36.752
33.314
19.696
14.492
13.973
f1 (ppm)

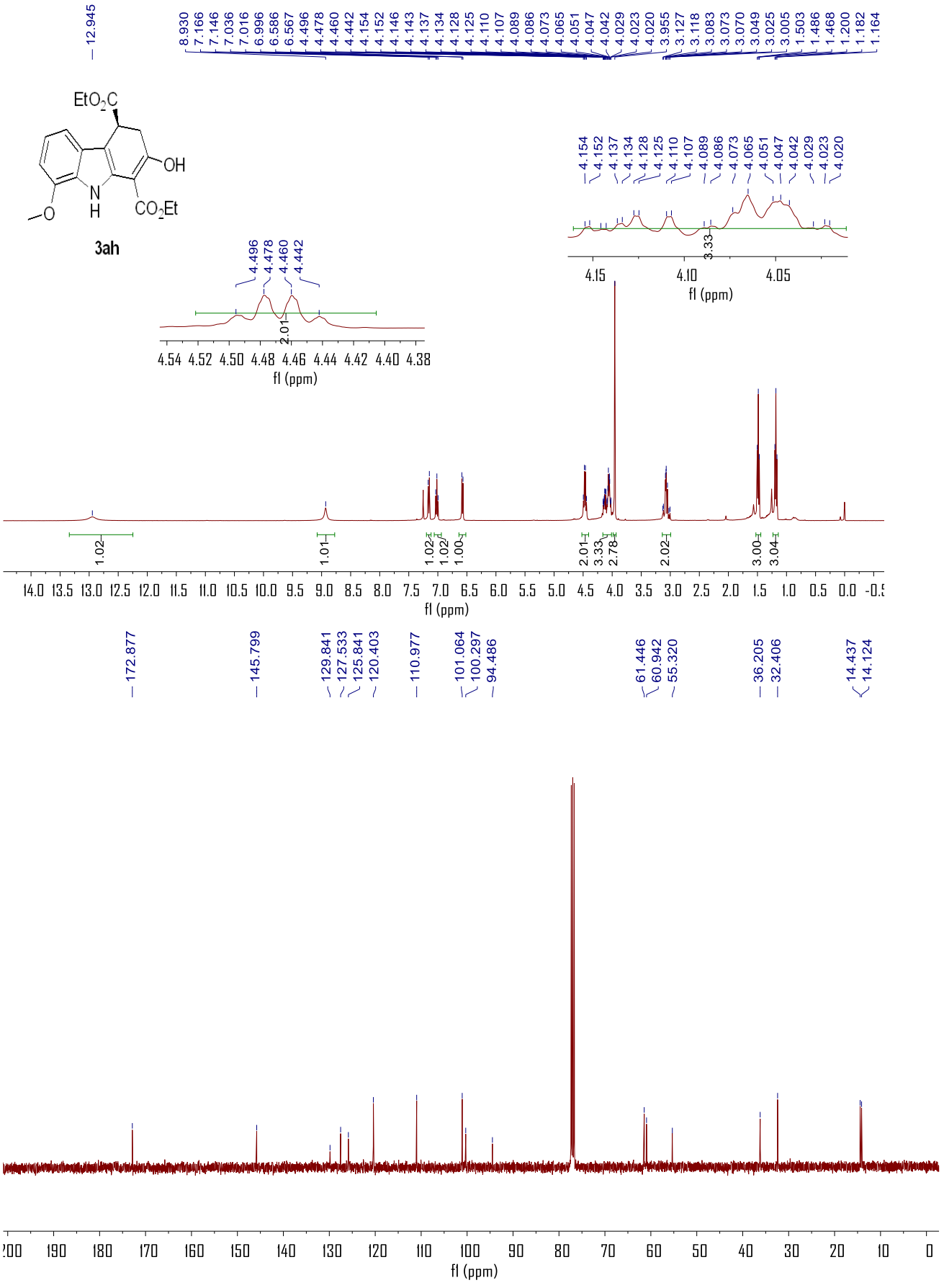

12.964
8.705
7.328
7.209
7.189
6.928
6.924
6.908
6.904
4.493
4.475
4.457
4.439
4.173
4.155
4.146
4.137
4.128
4.119
4.110
4.102
4.092
4.084
4.075
4.065
4.056
4.048
4.044
4.039
4.035
4.021
3.121
3.112
3.078
3.068
3.065
3.045
3.021
3.001
2.440
1.495
1.478
1.460
1.215
1.197
1.180
EtO2C
OH
N
H
CO2Et
3ac
fl (ppm)
fl (ppm)
fl (ppm)
fl (ppm)

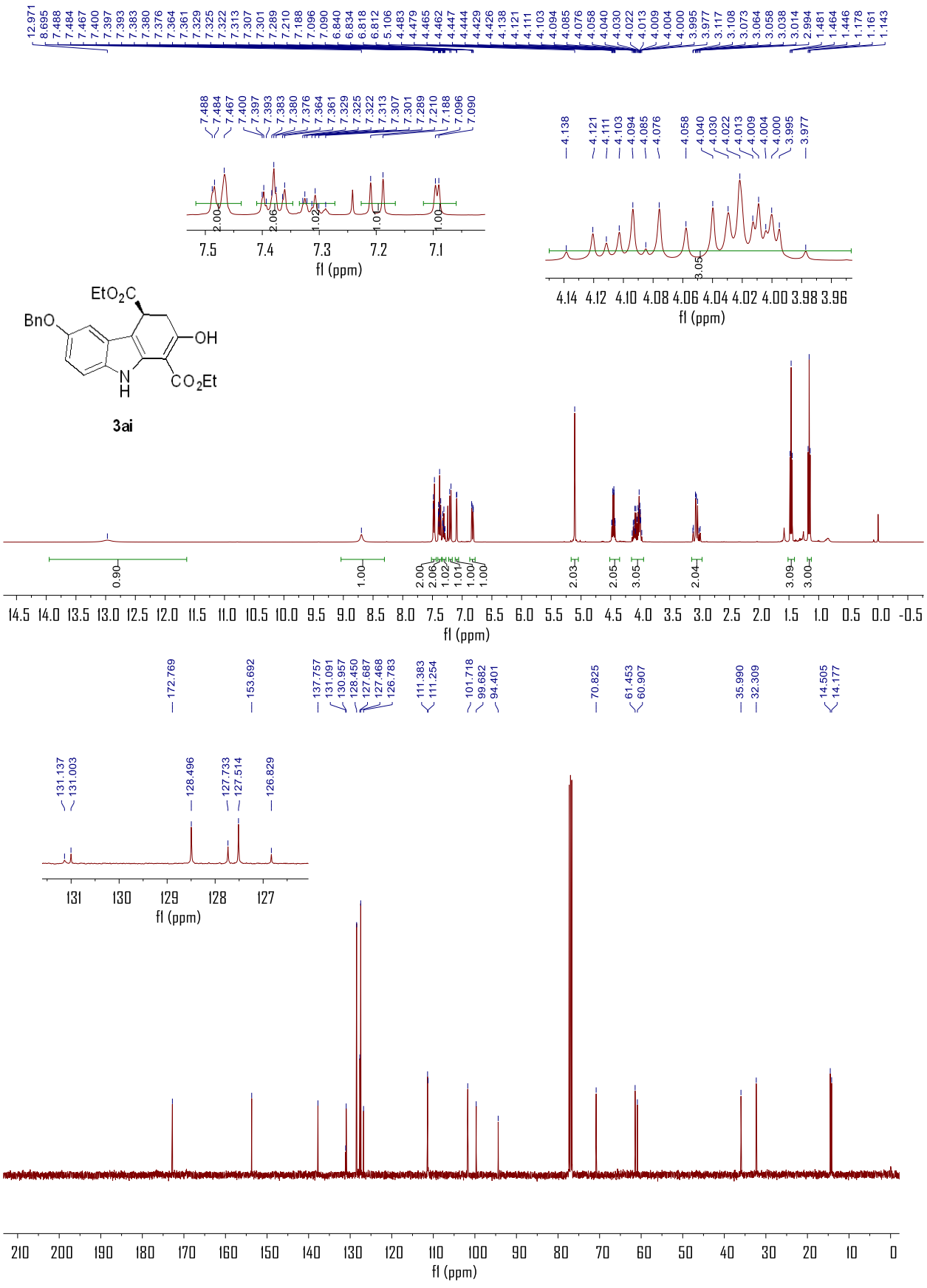

12.945
8.670
7.432
7.412
7.119
6.947
6.943
6.926
6.923
4.484
4.467
4.449
4.431
4.170
4.152
4.143
4.134
4.125
4.116
4.107
4.089
4.078
4.066
4.060
4.057
4.051
4.046
4.043
4.037
4.033
4.025
4.016
3.998
3.121
3.111
3.077
3.067
3.061
3.041
3.018
2.997
2.440
1.489
1.471
1.454
1.202
1.184
1.166
EtO2C
OH
N
H
CO2Et
3ad
f1 (ppm)
f1 (ppm)
f1 (ppm)
172.896
136.091
130.401
129.596
124.137
121.691
117.659
110.823
99.637
94.465
61.400
60.918
36.107
32.371
21.661
14.504
14.130
f1 (ppm)

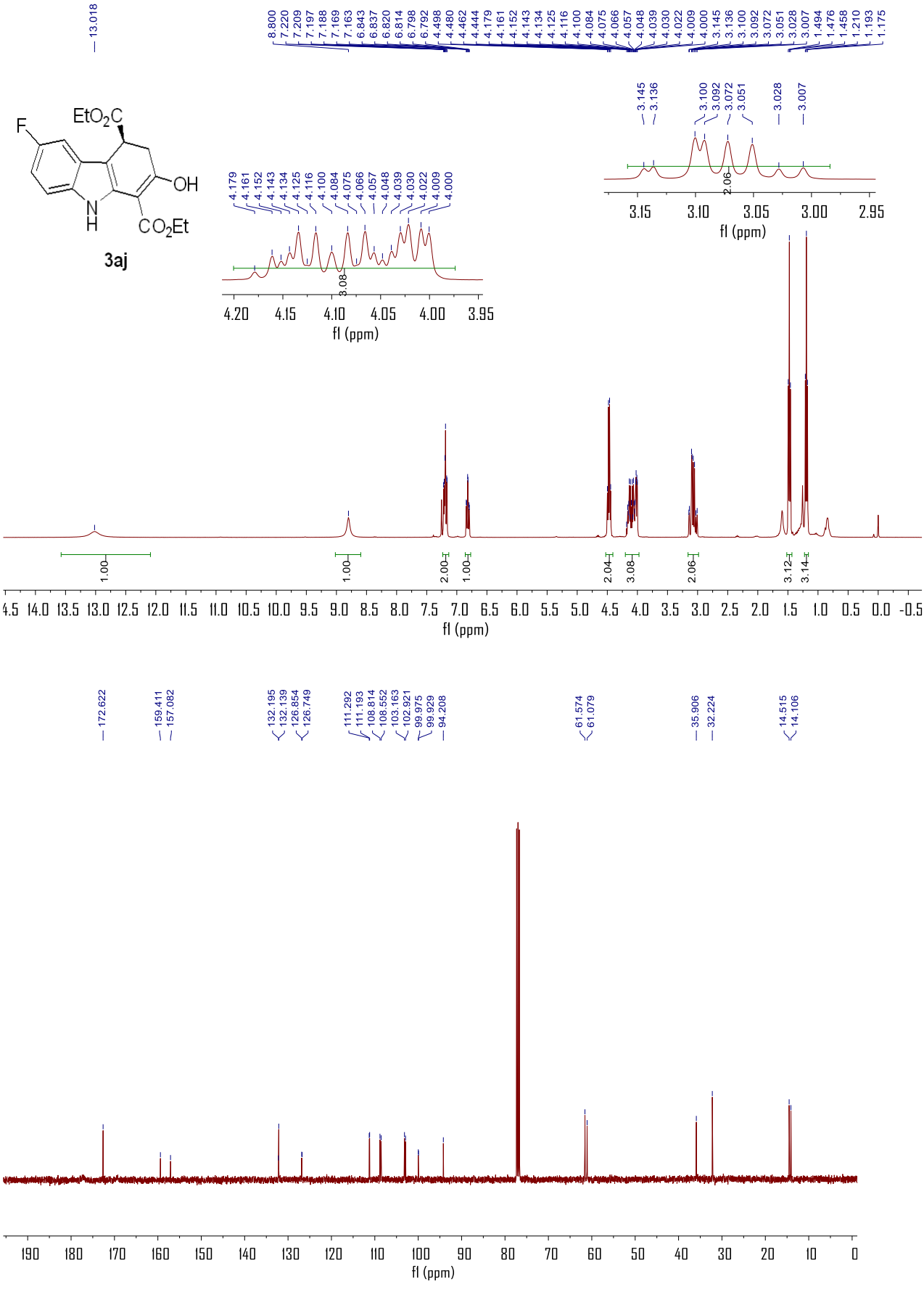

12.884
8.770
7.411
7.391
7.047
7.028
7.009
6.912
6.894
4.485
4.467
4.449
4.431
4.169
4.151
4.142
4.133
4.124
4.115
4.106
4.086
4.076
4.065
4.057
4.049
4.041
4.031
4.023
4.013
3.996
3.134
3.125
3.090
3.081
3.073
3.052
3.029
3.008
2.463
1.517
1.499
1.481
1.202
1.184
1.166
EtO2C
OH
N
H
CO2Et
3ae
fl (ppm)
fl (ppm)
fl (ppm)
172.852
135.107
130.002
125.785
121.377
120.230
119.667
115.825
100.289
94.379
61.397
60.951
36.159
32.399
16.287
14.312
14.121
fl (ppm)

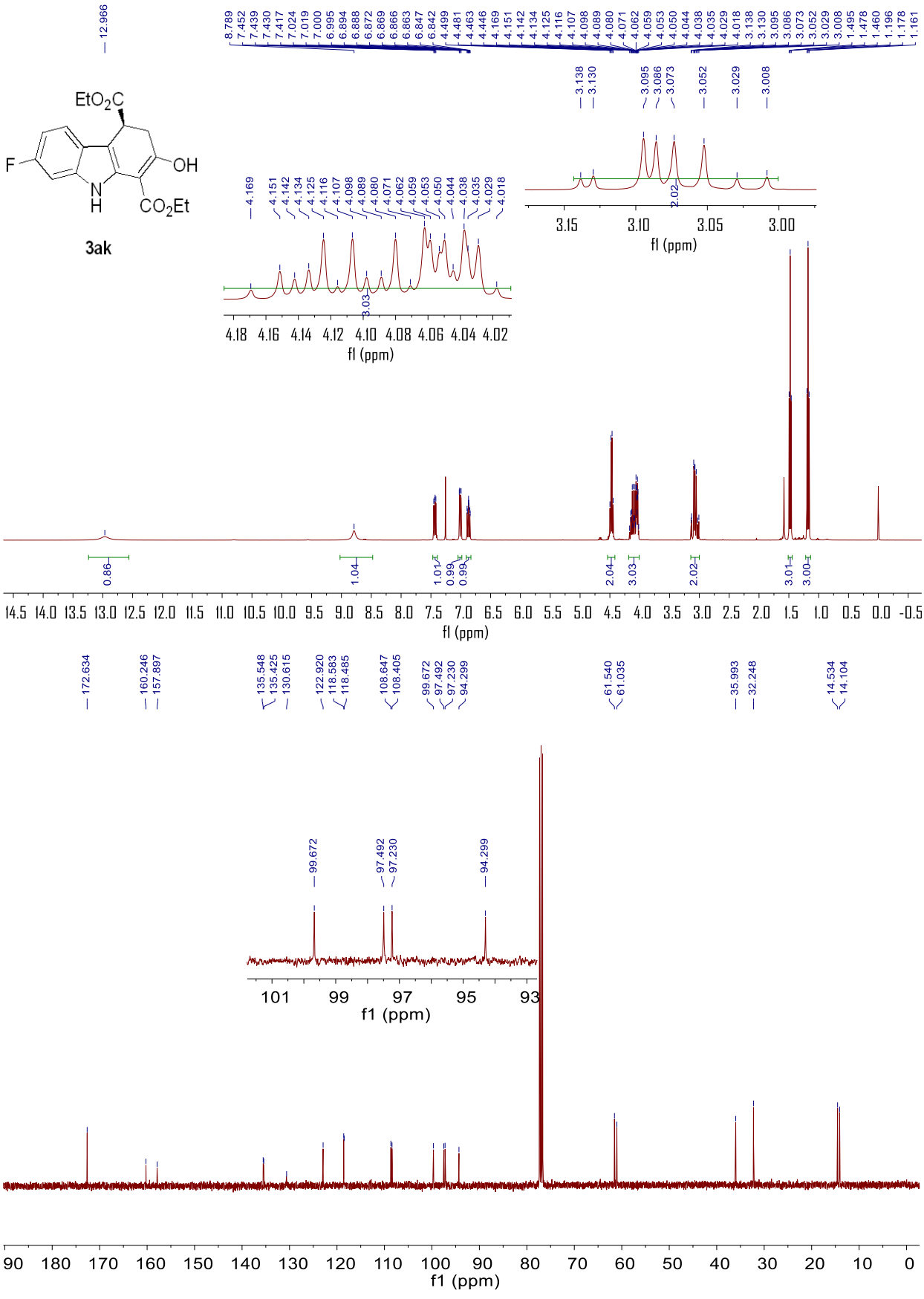

12.881
8.825 7.416 7.396 7.077 7.058 7.039 6.944 6.926 4.482 4.464 4.446 4.429 4.177 4.159 4.150 4.141 4.132 4.123 4.114 4.096 4.093 4.083 4.072 4.063 4.054 4.045 4.036 4.027 4.018 4.000 3.134 3.125 3.090 3.081 3.077 3.057 3.033 3.013 2.869 2.850 2.831 2.812 1.521 1.503 1.485 1.396 1.377 1.358 1.211 1.193 1.176
EtO2C
OH
N
H
CO2Et
3af
4.177 4.159 4.150 4.141 4.132 4.123 4.114 4.096 4.093 4.083 4.072 4.063 4.054 4.045 4.036 4.027 4.018 4.000
3.134 3.125 3.090 3.081 3.077 3.057 3.033 3.013
1.00 1.04 1.00 1.05 1.01 2.11 3.09 2.06 2.05 3.10 3.18 3.15
fl (ppm)
172.901 134.377 129.895 125.992 125.905 120.292 119.464 115.898 100.192 94.367 61.377 60.959 36.172 32.423 24.106 14.295 14.130 13.657
129.917 126.014 125.927
61.399 60.981
fl (ppm)

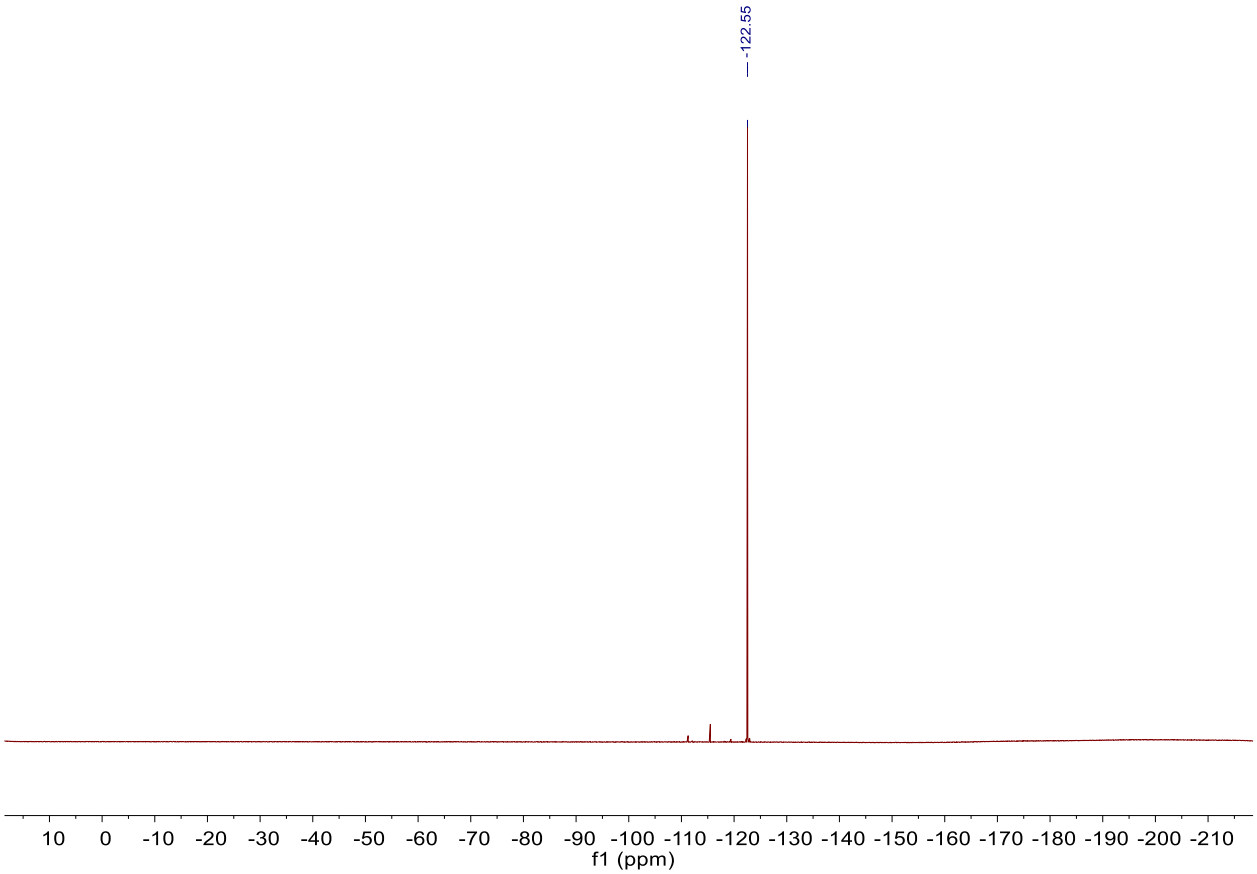

12.988
8.691
7.212
7.190
7.014
7.008
6.762
6.756
6.740
6.734
4.495
4.478
4.460
4.442
4.175
4.158
4.148
4.140
4.130
4.122
4.113
4.095
4.078
4.069
4.060
4.050
4.043
4.039
4.034
4.030
4.016
3.859
3.132
3.123
3.088
3.079
3.075
3.055
3.031
3.011
3.075
3.055
3.031
1.495
1.478
1.460
1.219
1.201
1.183
EtO2C
OH
CO2Et
N
H
3ag
fl (ppm)
1.02
1.06
1.01
1.01
0.99
2.04
3.08
3.00
2.10
3.15
3.14
172.816
154.470
131.031
130.758
126.797
111.409
110.562
100.122
99.665
94.427
61.472
60.949
55.821
36.014
32.329
14.537
14.184
131.046
130.773
126.812
100.137
99.680
94.442

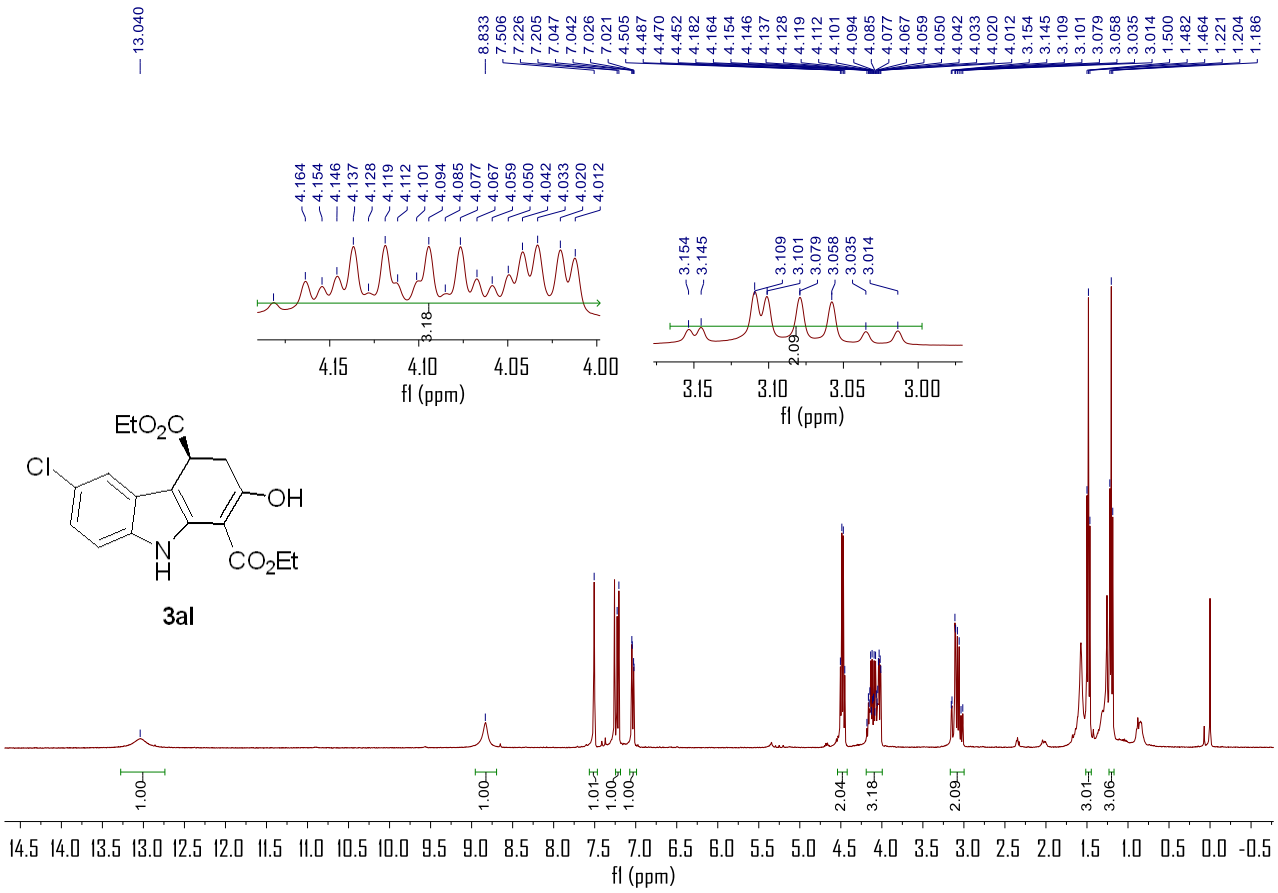

12.945
8.930
7.166
7.146
7.036
7.016
6.996
6.586
6.567
4.496
4.478
4.460
4.442
4.154
4.152
4.146
4.143
4.137
4.134
4.128
4.125
4.110
4.107
4.089
4.086
4.073
4.065
4.051
4.047
4.042
4.029
4.023
4.020
3.955
3.127
3.118
3.083
3.073
3.070
3.049
3.025
3.005
1.503
1.486
1.468
1.200
1.182
1.164
EtO2C
OH
N
H
O
CO2Et
3ah
fl (ppm)
1.02
1.01
1.02
1.02
1.00
2.01
3.33
2.78
2.02
3.00
3.04
172.877
145.799
129.841
127.533
125.841
120.403
110.977
101.064
100.297
94.486
61.446
60.942
55.320
36.205
32.406
14.437
14.124

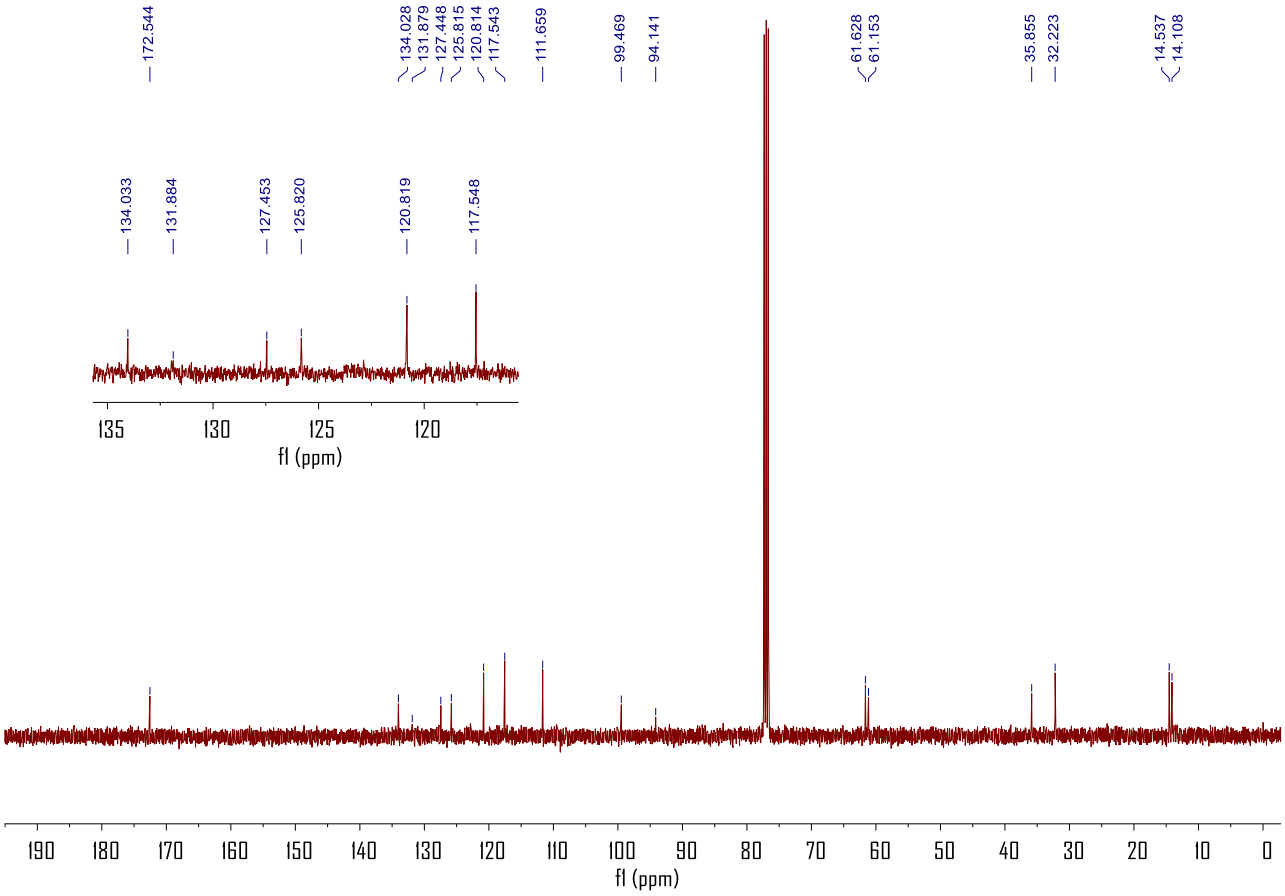

12.971
8.695
7.488
7.484
7.467
7.400
7.397
7.393
7.383
7.380
7.376
7.364
7.361
7.329
7.325
7.322
7.313
7.307
7.301
7.289
7.210
7.188
7.096
7.090
6.840
6.834
6.818
6.812
5.106
4.483
4.479
4.465
4.462
4.447
4.444
4.429
4.426
4.138
4.121
4.111
4.103
4.094
4.085
4.076
4.058
4.040
4.030
4.022
4.013
4.009
4.004
4.000
3.995
3.977
3.117
3.108
3.073
3.064
3.058
3.038
3.014
2.994
1.481
1.464
1.446
1.178
1.161
1.143
2.00
2.06
1.02
1.01
1.00
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
3.05
4.14 4.12 4.10 4.08 4.06 4.04 4.02 4.00 3.98 3.96
f1 (ppm)
EtO2C
BnO
OH
N
H
CO2Et
3ai
0.90
1.00
2.00
2.06
1.02
1.01
1.00
1.00
2.03
2.05
3.05
2.04
3.09
3.00
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
172.769
153.692
137.757
131.091
130.957
128.450
127.687
127.468
126.783
111.383
111.254
101.718
99.682
94.401
70.825
61.453
60.907
35.990
32.309
14.505
14.177
131.137
131.003
128.496
127.733
127.514
126.829
131
130
129
128
127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


13.018
8.800
7.220
7.209
7.197
7.188
7.169
7.163
6.843
6.837
6.820
6.814
6.798
6.792
4.498
4.480
4.462
4.444
4.179
4.161
4.152
4.143
4.134
4.125
4.116
4.100
4.084
4.075
4.066
4.057
4.048
4.039
4.030
4.022
4.009
4.000
3.145
3.136
3.100
3.092
3.072
3.051
3.028
3.007
1.494
1.476
1.458
1.210
1.193
1.175
F
EtO2C
OH
N
H
CO2Et
3aj
3.08
2.06
f1 (ppm)
1.00
2.00
2.04
3.08
2.06
3.12
3.14
172.622
159.411
157.082
132.195
132.139
126.854
126.749
111.292
111.193
108.814
108.552
103.163
102.921
99.975
99.929
94.208
61.574
61.079
35.906
32.224
14.515
14.106


EtO2C
F
OH
N
H
CO2Et
3ak
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)


-122.55
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)


13.040
8.833
7.506
7.226
7.205
7.047
7.042
7.026
7.021
4.505
4.487
4.470
4.452
4.182
4.164
4.154
4.146
4.137
4.128
4.119
4.112
4.101
4.094
4.085
4.077
4.067
4.059
4.050
4.042
4.033
4.020
4.012
3.154
3.145
3.109
3.101
3.079
3.058
3.035
3.014
1.500
1.482
1.464
1.221
1.204
1.186
EtO2C
Cl
OH
N
H
CO2Et
3al
fl (ppm)
1.00
1.00
1.01
1.00
1.00
2.04
3.18
2.09
3.01
3.06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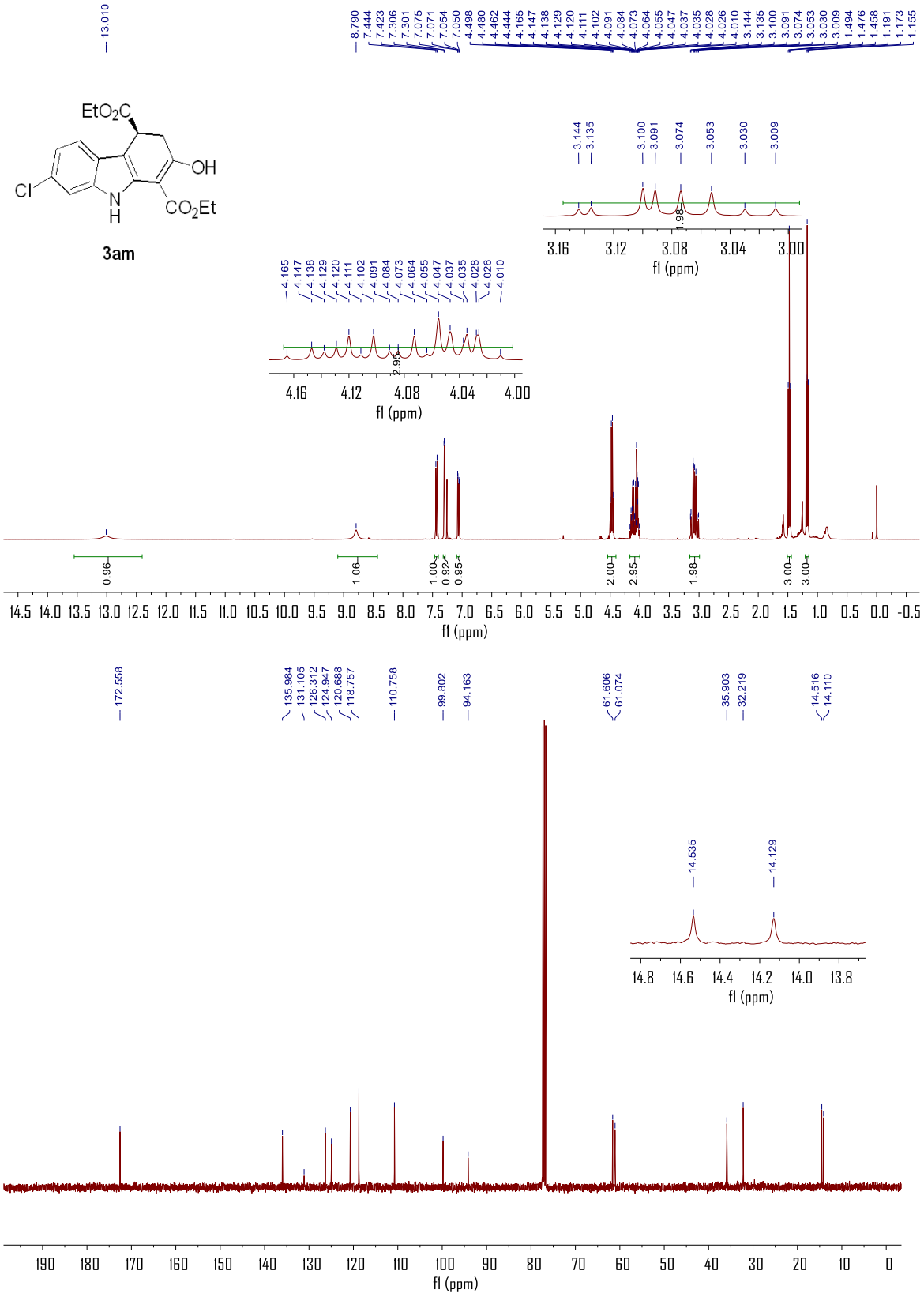
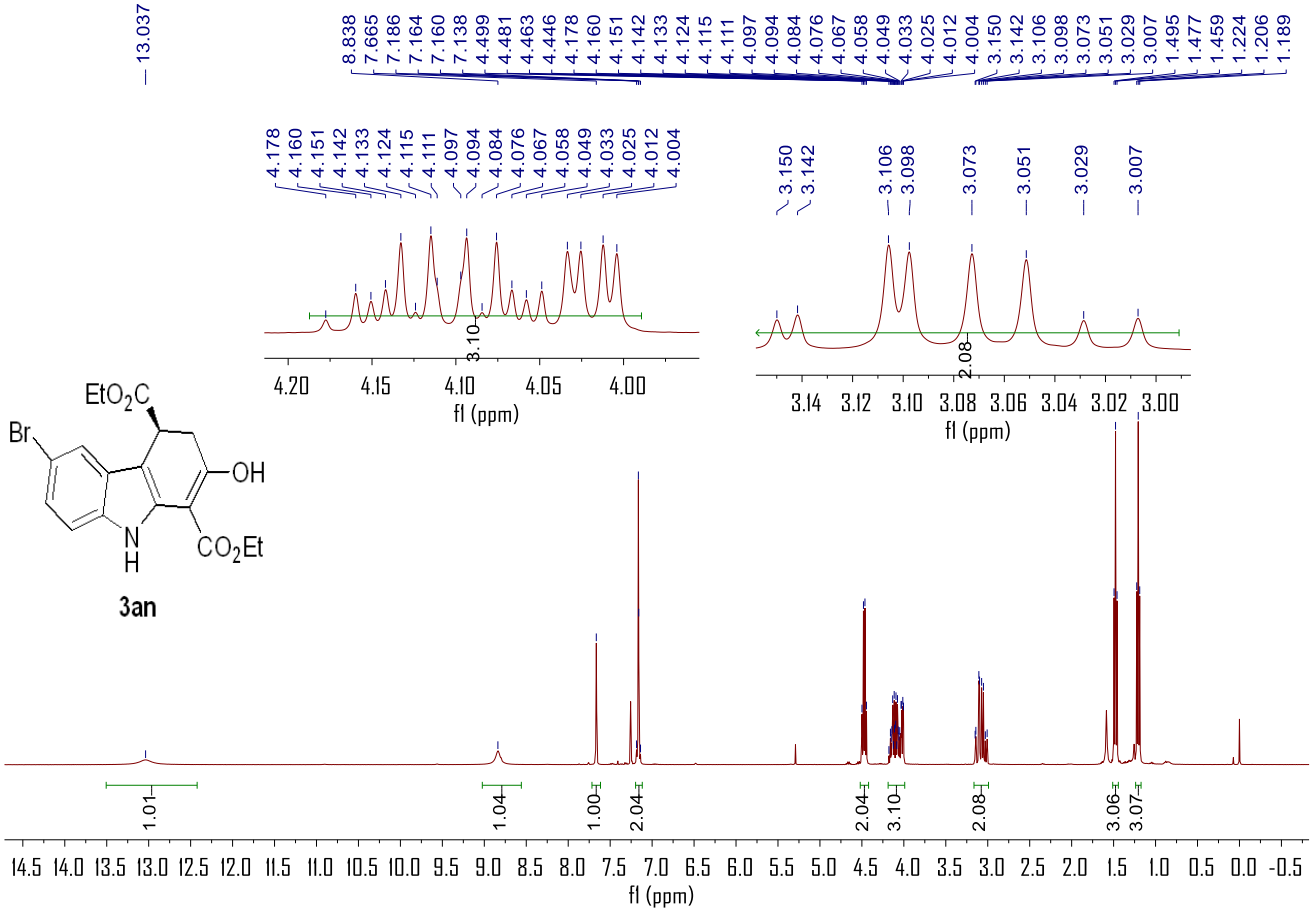
134.028
131.879
127.448
125.815
120.814
117.543
111.659
99.469
94.141
61.628
61.153
35.855
32.223
14.537
14.108
134.033
131.884
127.453
125.820
120.819
117.548
fl (ppm)


13.010
8.790
7.444
7.423
7.306
7.301
7.075
7.071
7.054
7.050
4.498
4.480
4.462
4.444
4.165
4.147
4.138
4.129
4.120
4.111
4.102
4.091
4.084
4.073
4.064
4.055
4.047
4.037
4.035
4.028
4.026
4.010
3.144
3.135
3.100
3.091
3.074
3.053
3.030
3.009
1.494
1.476
1.458
1.191
1.173
1.155
EtO2C
OH
Cl
N
H
CO2Et
3am
f1 (ppm)
0.96
1.06
1.00
0.92
0.95
2.00
2.95
1.98
3.00
3.00
172.558
135.984
131.105
126.312
124.947
120.688
118.757
110.758
99.802
94.163
61.606
61.074
35.903
32.219
14.516
14.110
14.535
14.129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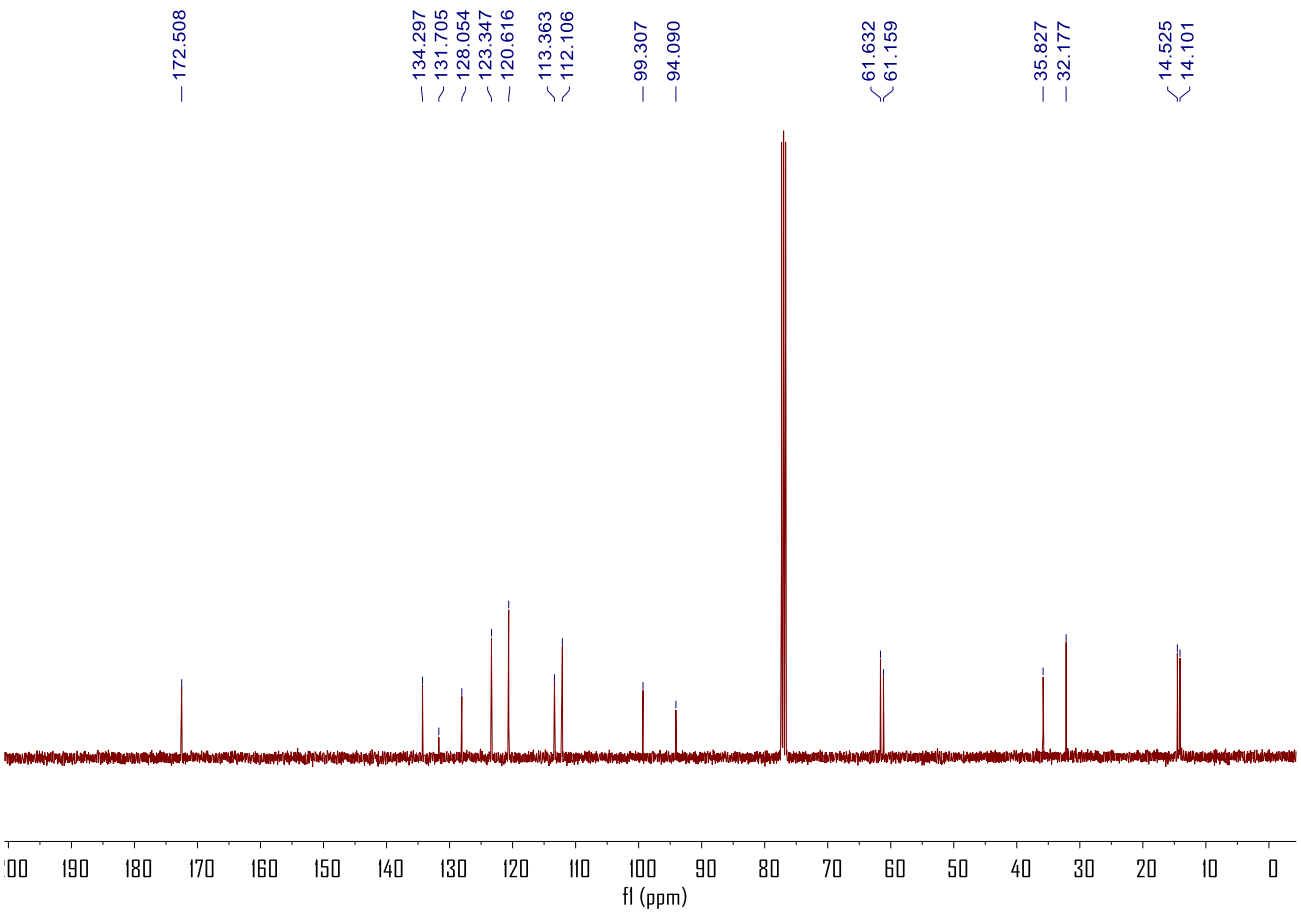
8.838
7.665
7.186
7.164
7.160
7.138
4.499
4.481
4.463
4.446
4.178
4.160
4.151
4.142
4.133
4.124
4.115
4.111
4.097
4.094
4.084
4.076
4.067
4.058
4.049
4.033
4.025
4.012
4.004
3.150
3.142
3.106
3.098
3.073
3.051
3.029
3.007
1.495
1.477
1.459
1.224
1.206
1.189
EtO2C
Br
OH
N
H
CO2Et
3an
1.01
1.04
1.00
2.04
2.04
3.10
2.08
3.06
3.07
f1 (ppm)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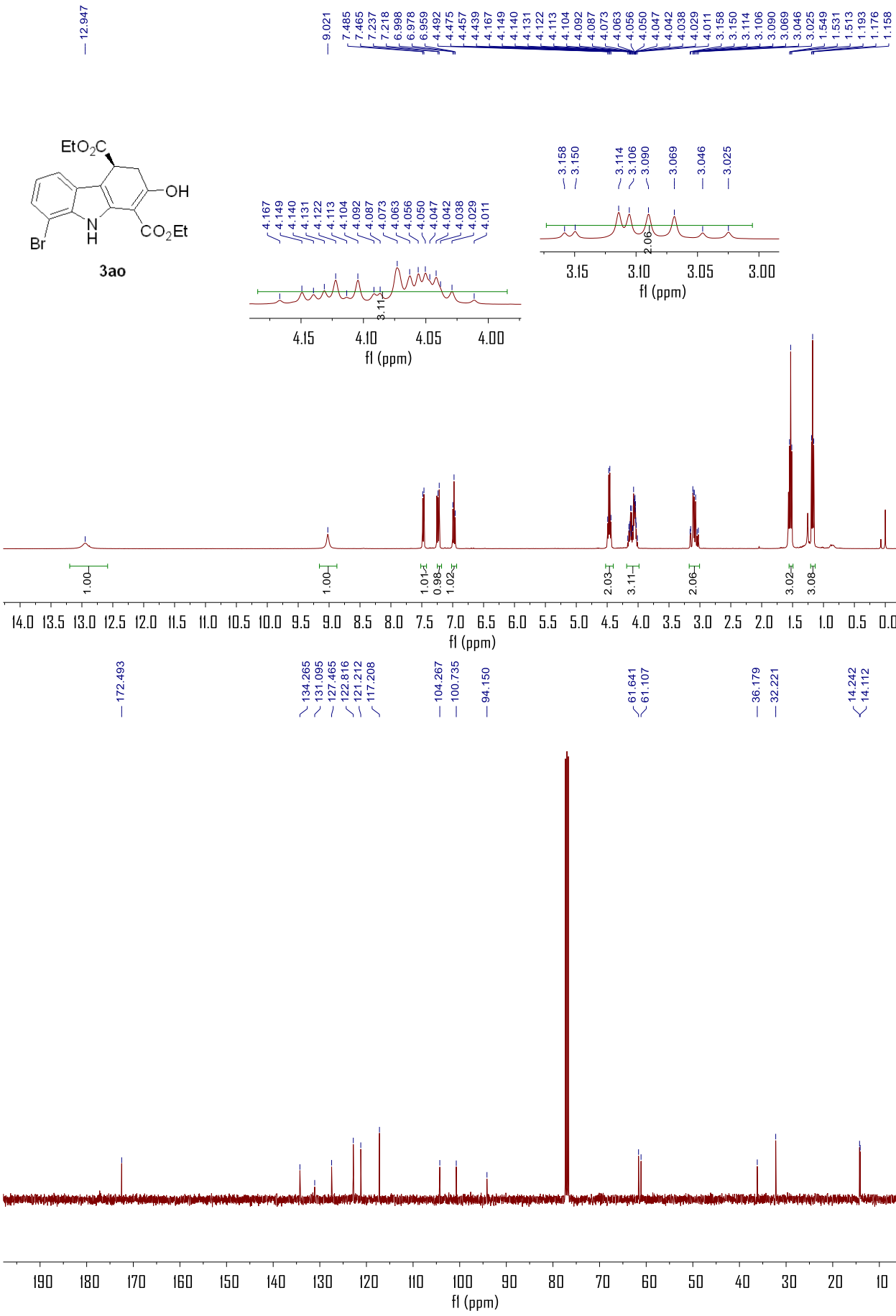
134.297
131.705
128.054
123.347
120.616
113.363
112.106
99.307
94.090
61.632
61.159
35.827
32.177
14.525
14.101
f1 (ppm)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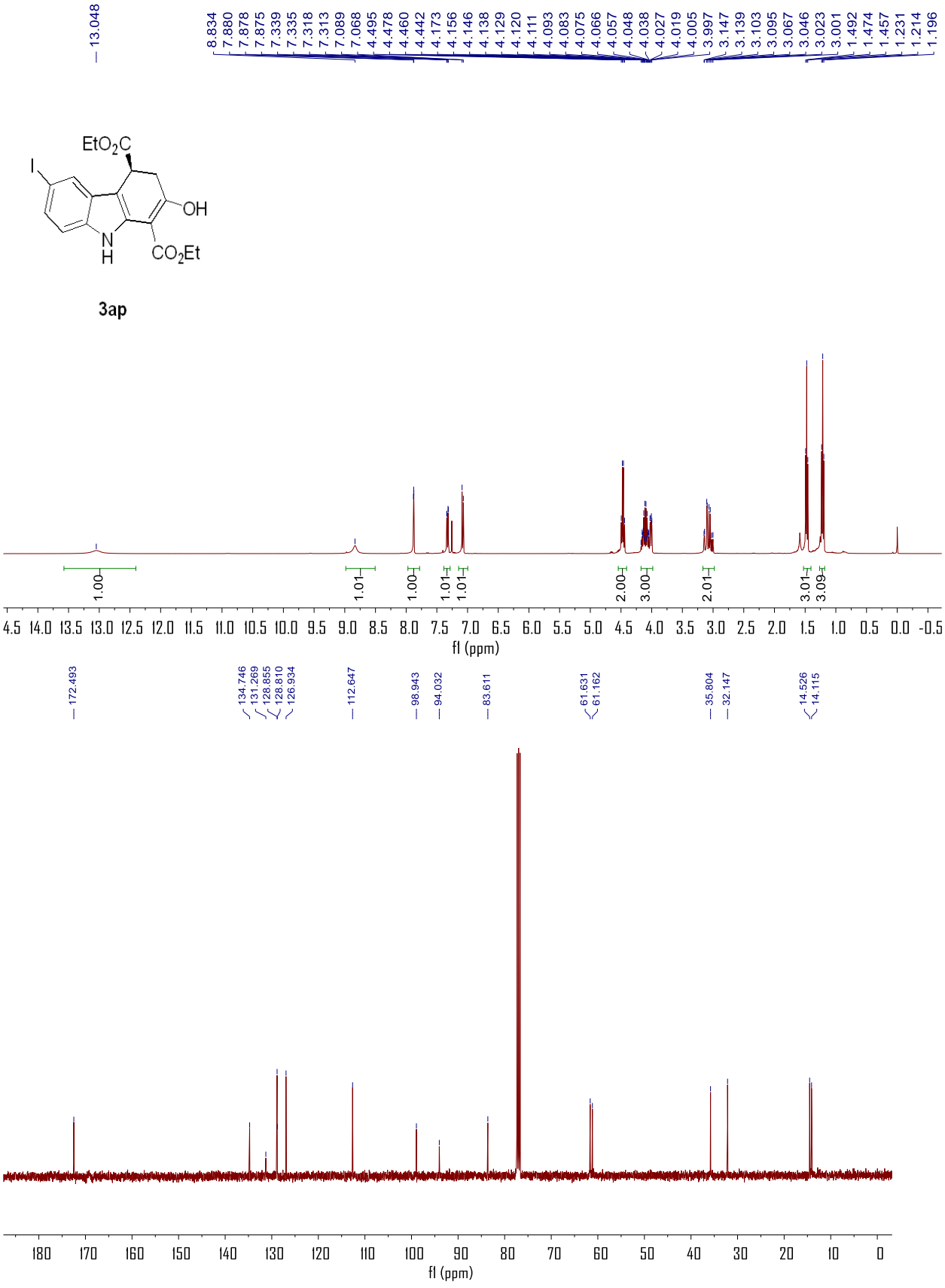
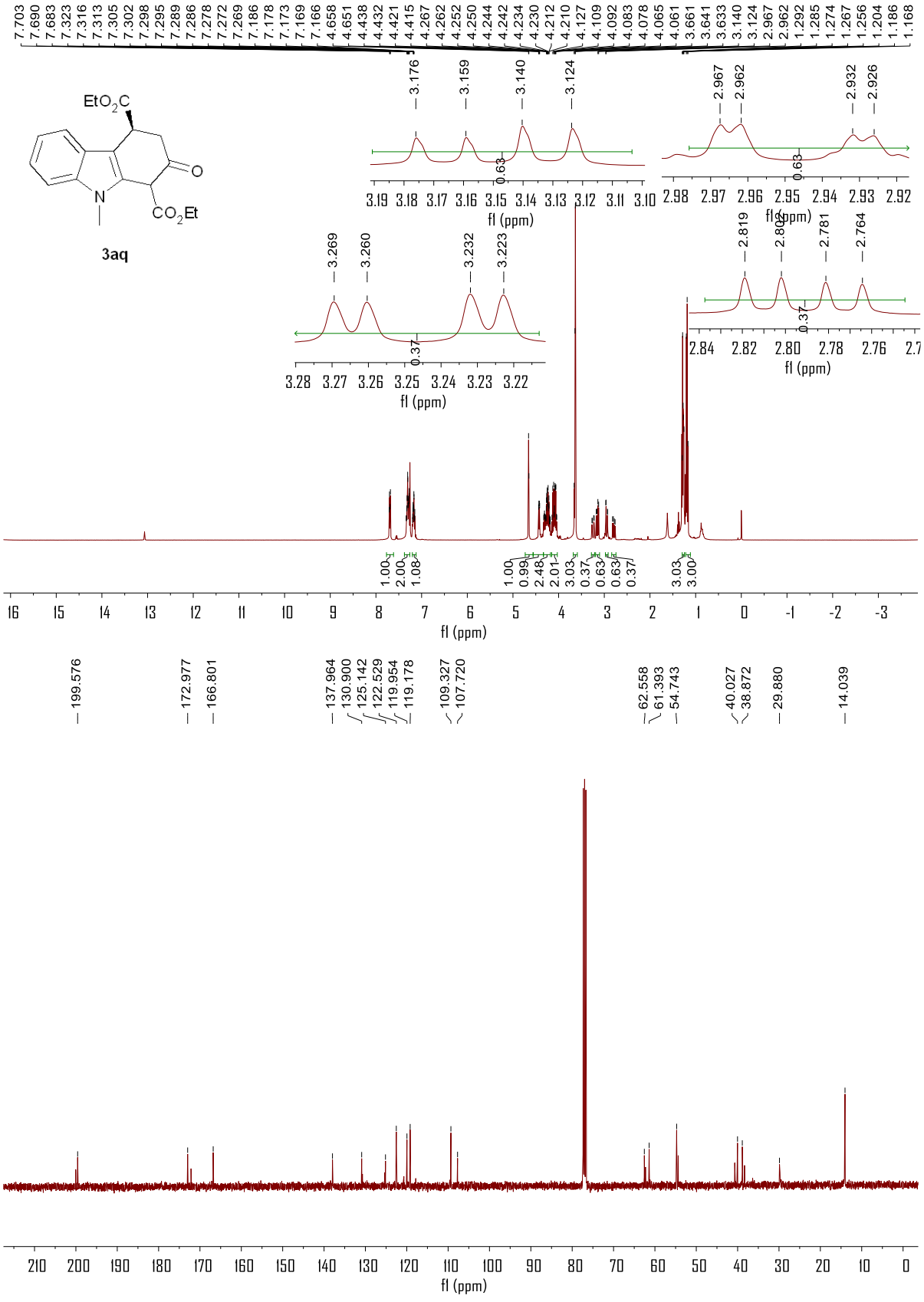
7.485
7.465
7.237
7.218
6.998
6.978
6.959
4.492
4.475
4.457
4.439
4.167
4.149
4.140
4.131
4.122
4.113
4.104
4.092
4.087
4.073
4.063
4.056
4.050
4.047
4.042
4.038
4.029
4.011
3.158
3.150
3.114
3.106
3.090
3.069
3.046
3.025
1.549
1.531
1.513
1.193
1.176
1.158
EtO2C
OH
N
H
Br
CO2Et
3ao
fl (ppm)
1.00
1.00
1.01
0.98
1.02
2.03
3.11
2.06
3.02
3.08
172.493
134.265
131.095
127.465
122.816
121.212
117.208
104.267
100.735
94.150
61.641
61.107
36.179
32.221
14.242
14.112


13.048
8.834
7.880
7.878
7.875
7.339
7.335
7.318
7.313
7.089
7.068
4.495
4.478
4.460
4.442
4.173
4.156
4.146
4.138
4.129
4.120
4.111
4.093
4.083
4.075
4.066
4.057
4.048
4.038
4.027
4.019
4.005
3.997
3.147
3.139
3.103
3.095
3.067
3.046
3.023
3.001
1.492
1.474
1.457
1.231
1.214
1.196
EtO2C
I
OH
N
H
CO2Et
3ap
1.00
1.01
1.00
1.01
1.01
2.00
3.00
2.01
3.01
3.09
f1 (ppm)
172.493
134.746
131.269
128.855
128.810
126.934
112.647
98.943
94.032
83.611
61.631
61.162
35.804
32.147
14.526
14.115
f1 (ppm)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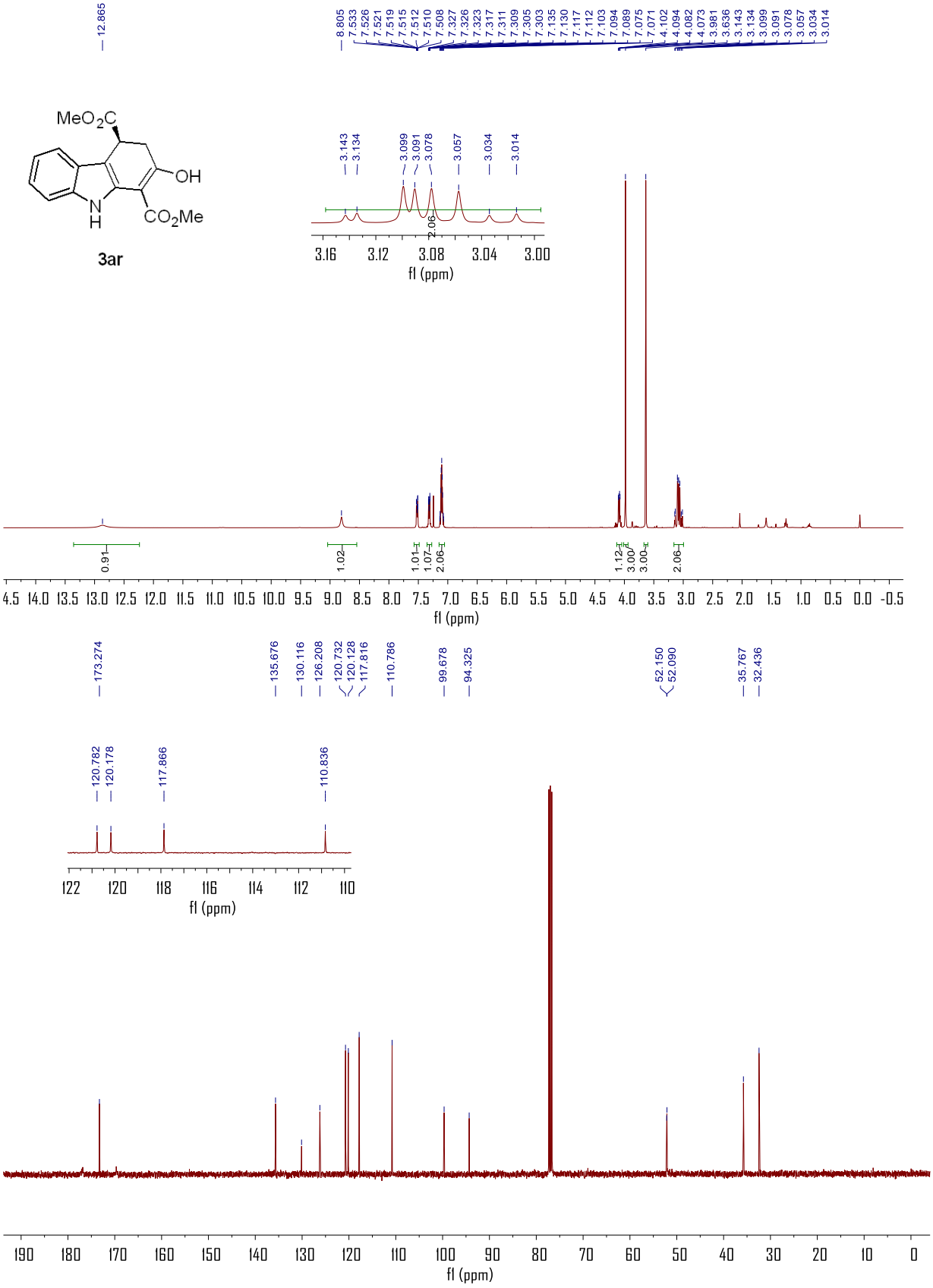
EtO2C
O
N
CO2Et
3aq
3.176 3.159 3.140 3.124
0.63
3.19 3.18 3.17 3.16 3.15 3.14 3.13 3.12 3.11 3.10
fl (ppm)
2.967 2.962 2.932 2.926
0.63
2.98 2.97 2.96 2.95 2.94 2.93 2.92
fl (ppm)
3.269 3.260 3.232 3.223
0.37
3.28 3.27 3.26 3.25 3.24 3.23 3.22
fl (ppm)
2.819 2.800 2.781 2.764
0.37
2.84 2.82 2.80 2.78 2.76
fl (ppm)
1.00 2.00 1.08 1.00 0.99 2.48 2.01 3.03 0.37 0.63 0.37 3.03 3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
fl (ppm)
199.576 172.977 166.801 137.964 130.900 125.142 122.529 119.954 119.178 109.327 107.720 62.558 61.393 54.743 40.027 38.872 29.880 14.039
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
fl (ppm)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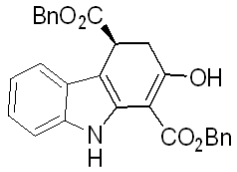
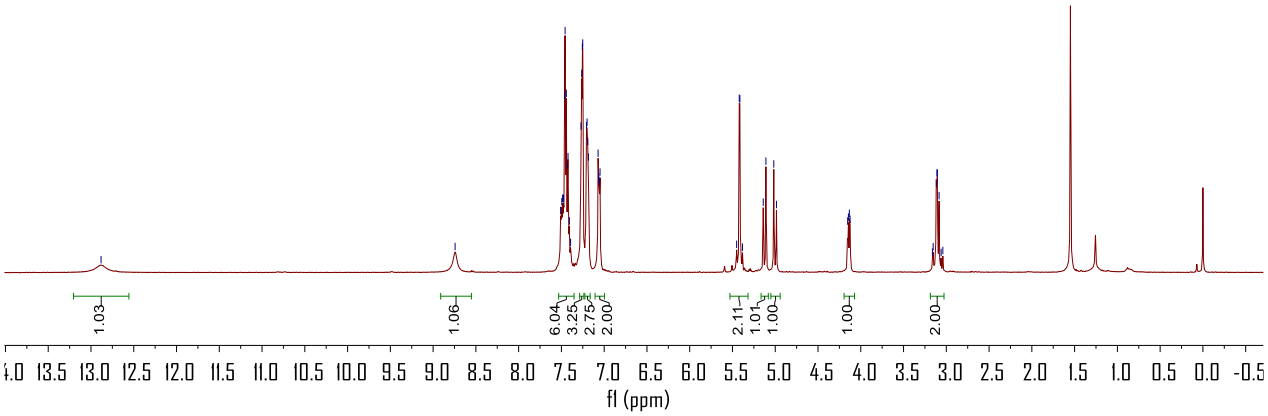
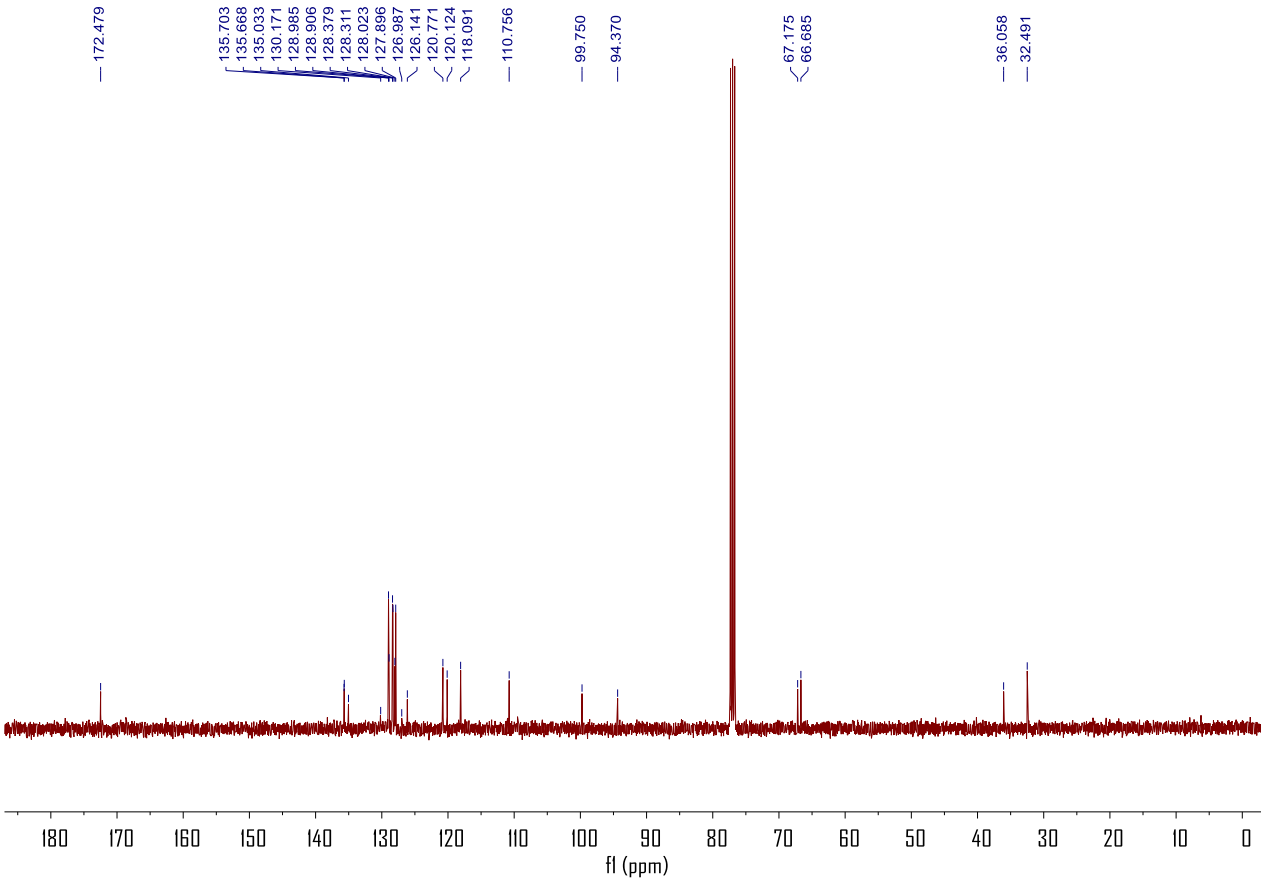
8.805
7.533
7.526
7.521
7.519
7.515
7.512
7.510
7.508
7.327
7.326
7.323
7.317
7.311
7.309
7.305
7.303
7.135
7.130
7.117
7.112
7.103
7.094
7.089
7.075
7.071
4.102
4.094
4.082
4.073
3.981
3.636
3.143
3.134
3.099
3.091
3.078
3.057
3.034
3.014
MeO2C
OH
N
H
CO2Me
3ar
3.143
3.134
3.099
3.091
3.078
3.057
3.034
3.014
2.06
3.16
3.12
3.08
3.04
3.00
f1 (ppm)
0.91
1.02
1.01
1.07
2.06
1.12
3.00
3.00
2.06
4.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
173.274
135.676
130.116
126.208
120.732
120.128
117.816
110.786
99.678
94.325
52.150
52.090
35.767
32.436
120.782
120.178
117.866
110.836
122 120 118 116 114 112 110
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

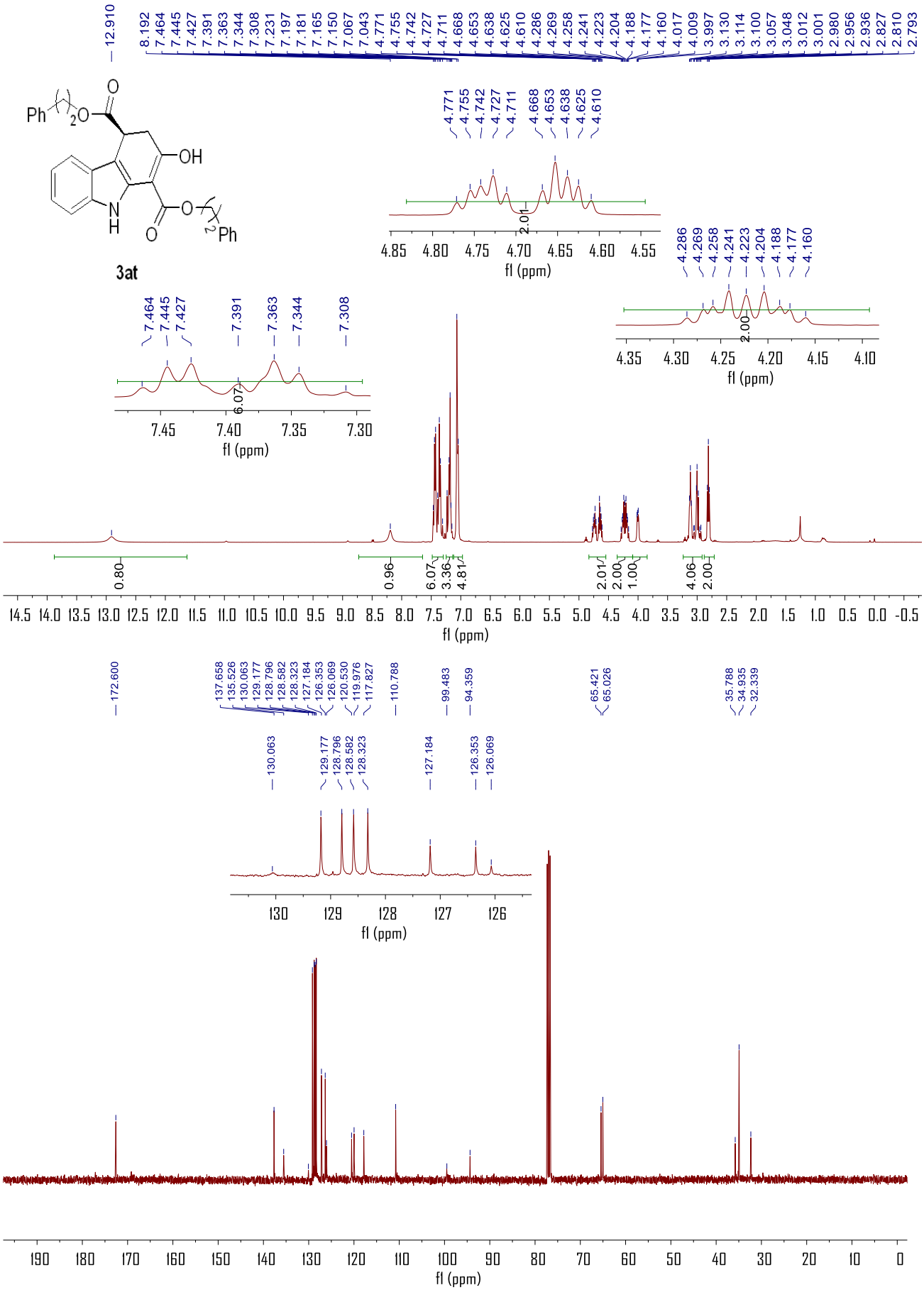

12.882
8.743
7.509
7.495
7.486
7.476
7.463
7.457
7.443
7.428
7.423
7.407
7.393
7.271
7.263
7.255
7.251
7.207
7.200
7.191
7.184
7.071
7.063
7.056
7.048
5.451
5.421
5.413
5.383
5.140
5.109
5.017
4.986
4.153
4.145
4.134
4.125
3.163
3.154
3.119
3.110
3.104
3.084
3.061
3.041


BnO2C
OH
N
H
CO2Bn

3as


1.03
1.06
6.04
3.25
2.75
2.00
2.11
1.01
1.00
1.00
2.00
f1 (ppm)


172.479
135.703
135.668
135.033
130.171
128.985
128.906
128.379
128.311
128.023
127.896
126.987
126.141
120.771
120.124
118.091
110.756
99.750
94.370
67.175
66.685
36.058
32.491
f1 (ppm)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7.464
7.445
7.427
7.391
7.363
7.344
7.308
7.231
7.197
7.181
7.165
7.150
7.067
7.043
4.771
4.755
4.742
4.727
4.711
4.668
4.653
4.638
4.625
4.610
4.286
4.269
4.258
4.241
4.223
4.204
4.188
4.177
4.160
4.017
4.009
3.997
3.130
3.114
3.100
3.057
3.048
3.012
3.001
2.980
2.956
2.936
2.827
2.810
2.793
Ph
O
OH
N
H
3at
2.01
fl (ppm)
6.07
2.00
0.80
0.96
6.07
3.36
4.81
2.01
2.00
1.00
4.06
2.00
172.600
137.658
135.526
130.063
129.177
128.796
128.582
128.323
127.184
126.353
126.069
120.530
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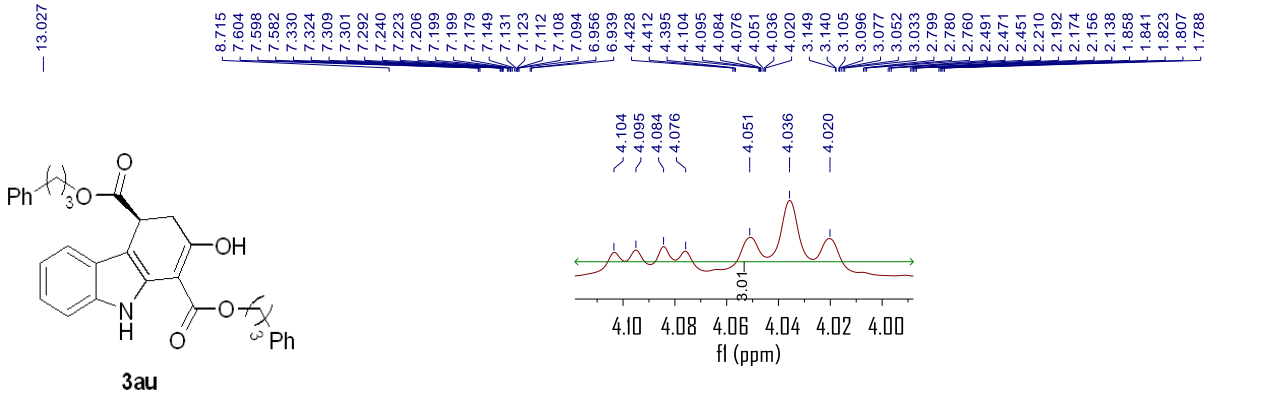
110.788
99.483
94.359
65.421
65.026
35.788
34.935
32.339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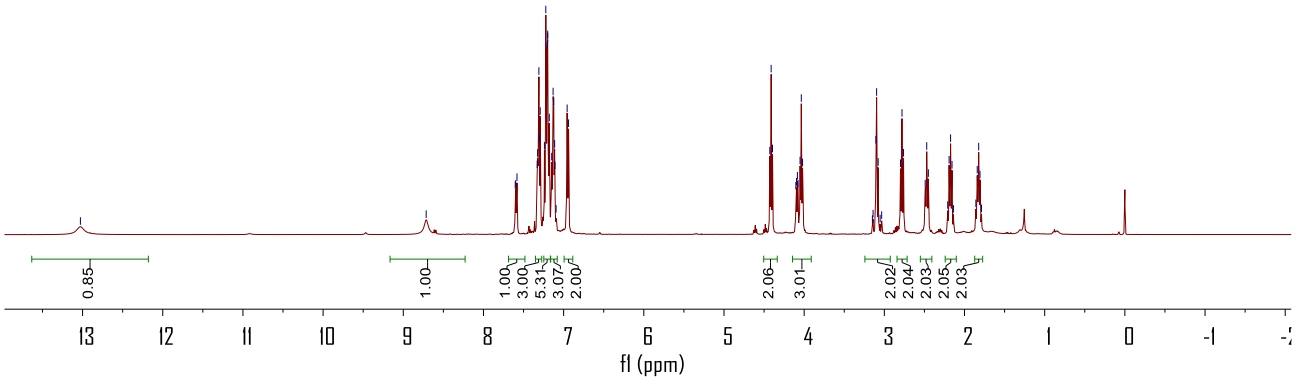
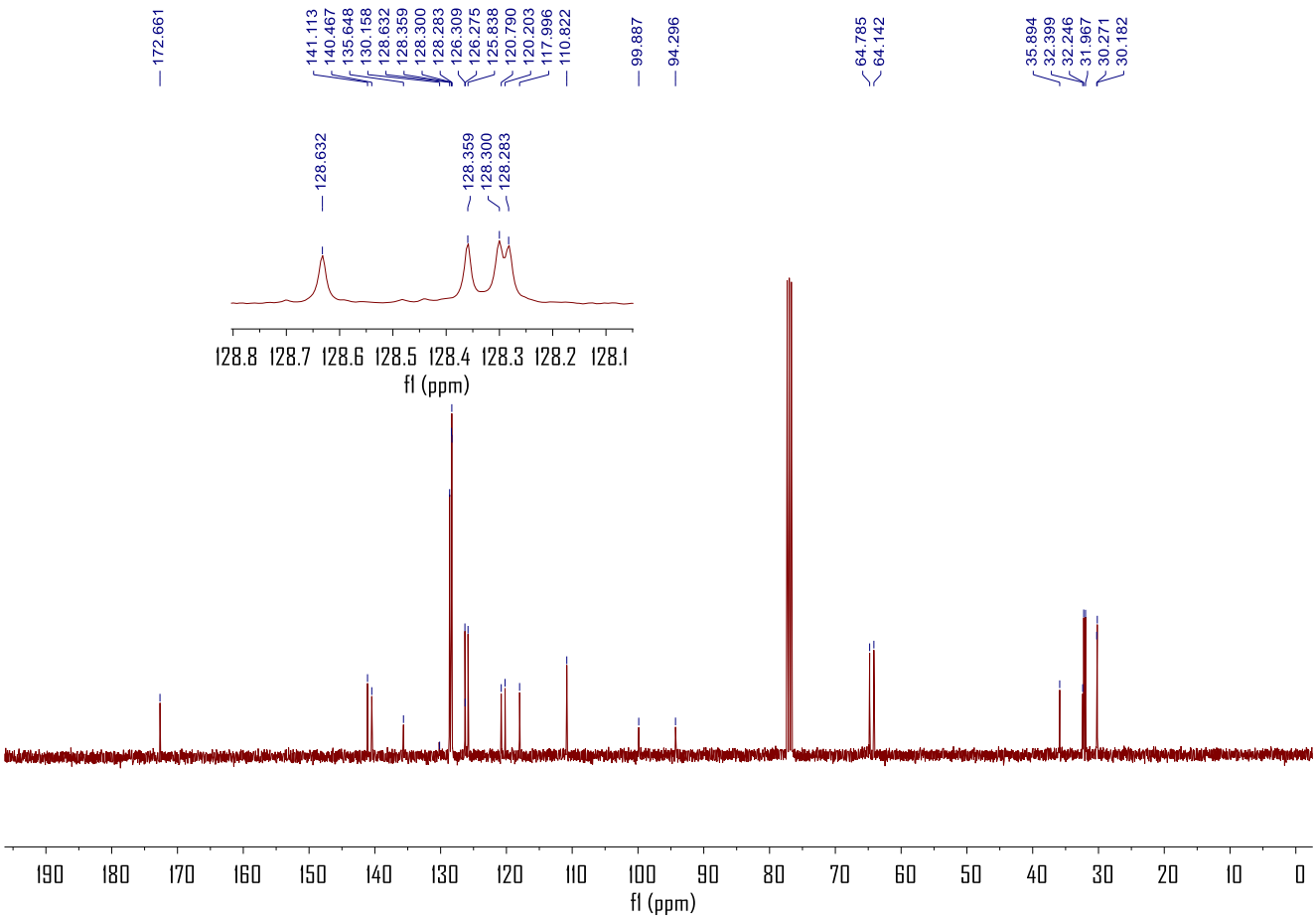
7.598
7.582
7.330
7.324
7.309
7.301
7.292
7.240
7.223
7.206
7.199
7.199
7.179
7.149
7.131
7.123
7.112
7.108
7.094
6.956
6.939
4.428
4.412
4.395
4.104
4.095
4.084
4.076
4.051
4.036
4.020
3.149
3.140
3.105
3.096
3.077
3.052
3.033
2.799
2.780
2.760
2.491
2.471
2.451
2.210
2.192
2.174
2.156
2.138
1.858
1.841
1.823
1.807
1.788
Ph
O
3
O
O
OH
N
H
O
O
3
Ph
3au
4.104
4.095
4.084
4.076
4.051
4.036
4.020
3.01
4.10
4.08
4.06
4.04
4.02
4.00
f1 (ppm)


0.85
1.00
1.00
3.00
5.31
3.07
2.00
2.06
3.01
2.02
2.04
2.03
2.05
2.03
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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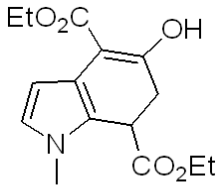
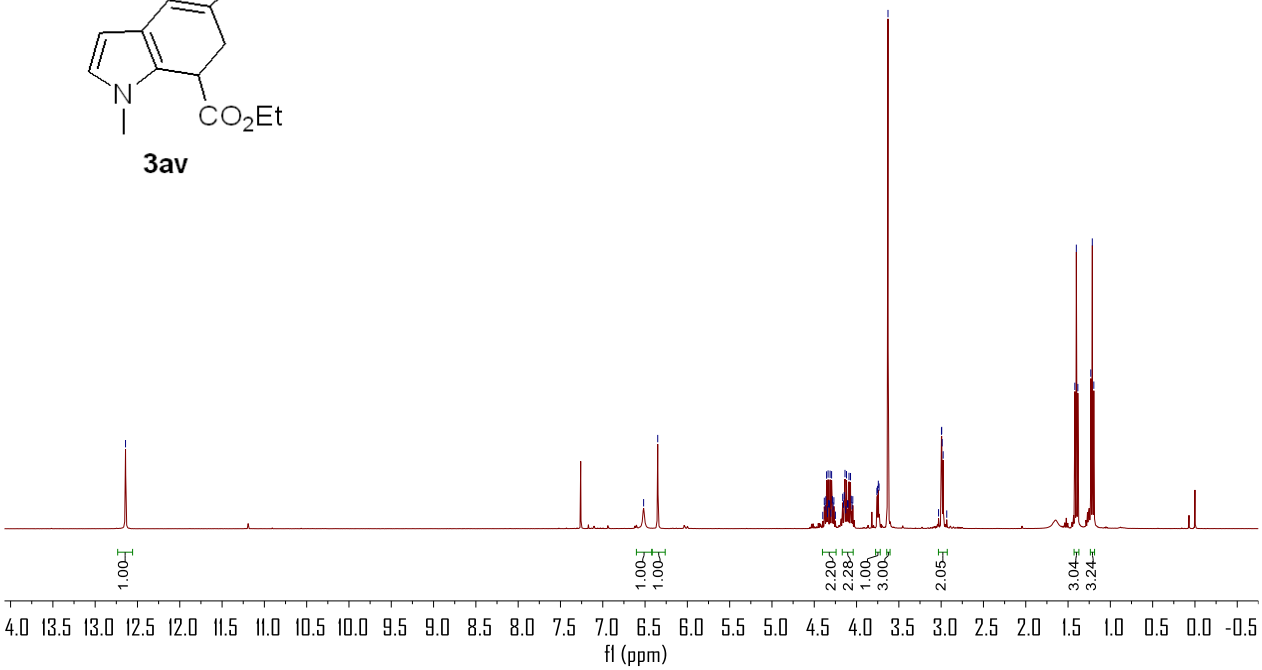
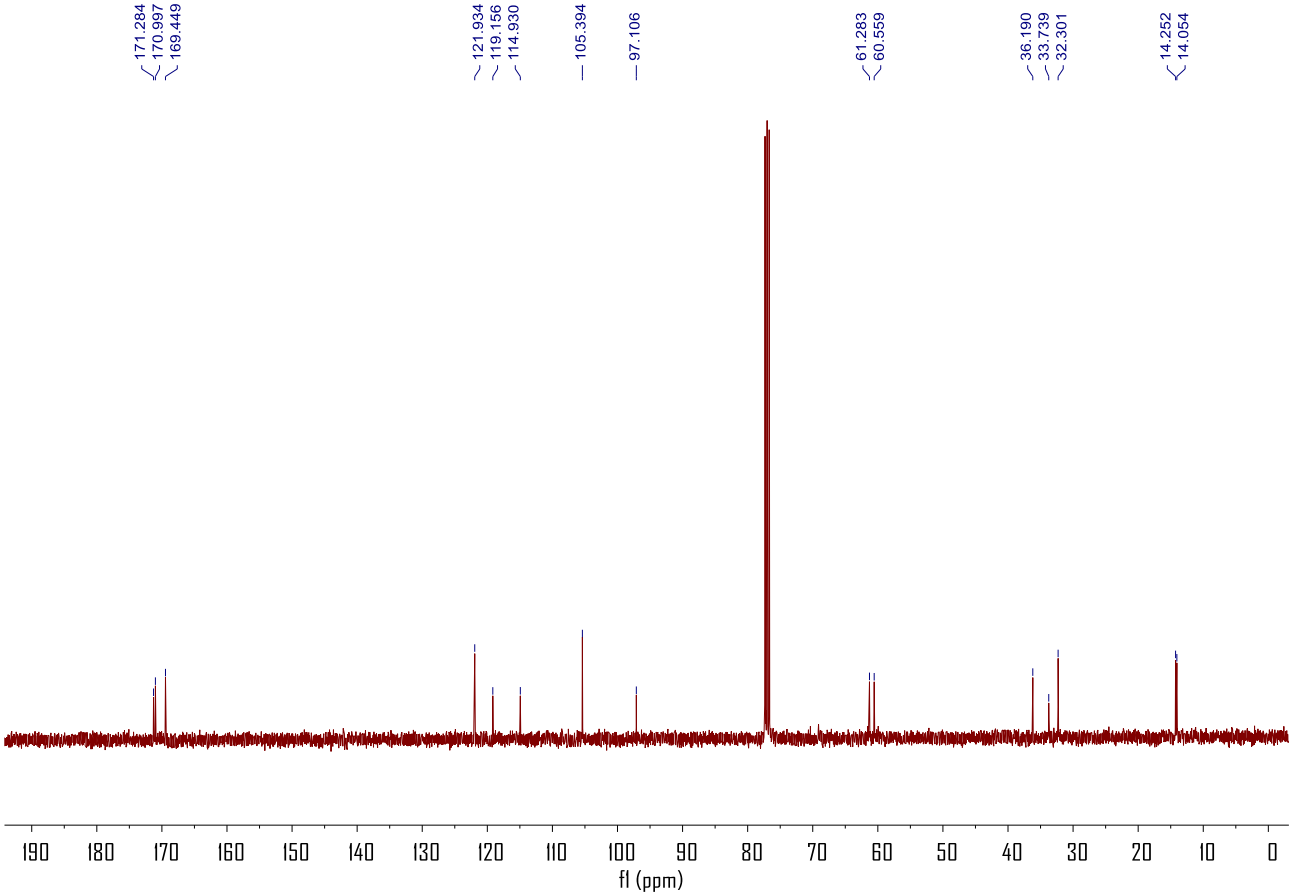
141.113
140.467
135.648
130.158
128.632
128.359
128.300
128.283
126.309
126.275
125.838
120.790
120.203
117.996
110.822
99.887
94.296
64.785
64.142
35.894
32.399
32.246
31.967
30.271
30.182
128.632
128.359
128.300
128.283
128.8
128.7
128.6
128.5
128.4
128.3
128.2
128.1
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

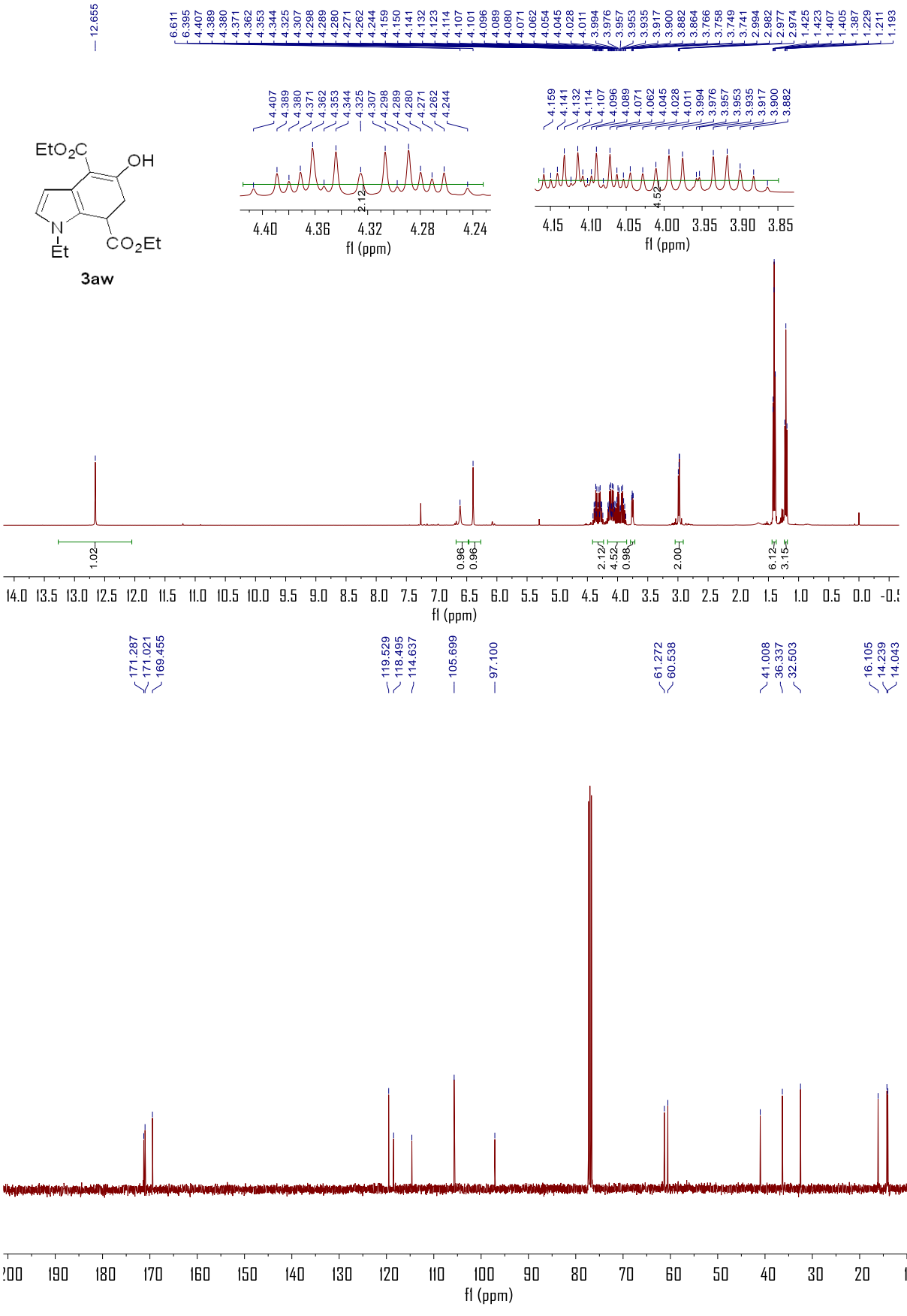

12.641
6.517
6.350
4.399
4.381
4.372
4.363
4.354
4.345
4.343
4.337
4.331
4.319
4.313
4.304
4.295
4.286
4.277
4.268
4.250
4.164
4.155
4.146
4.137
4.128
4.119
4.107
4.101
4.089
4.071
4.062
4.053
4.044
3.760
3.751
3.743
3.734
3.628
3.031
2.996
2.993
2.988
2.976
2.934
1.420
1.402
1.384
1.231
1.213
1.195

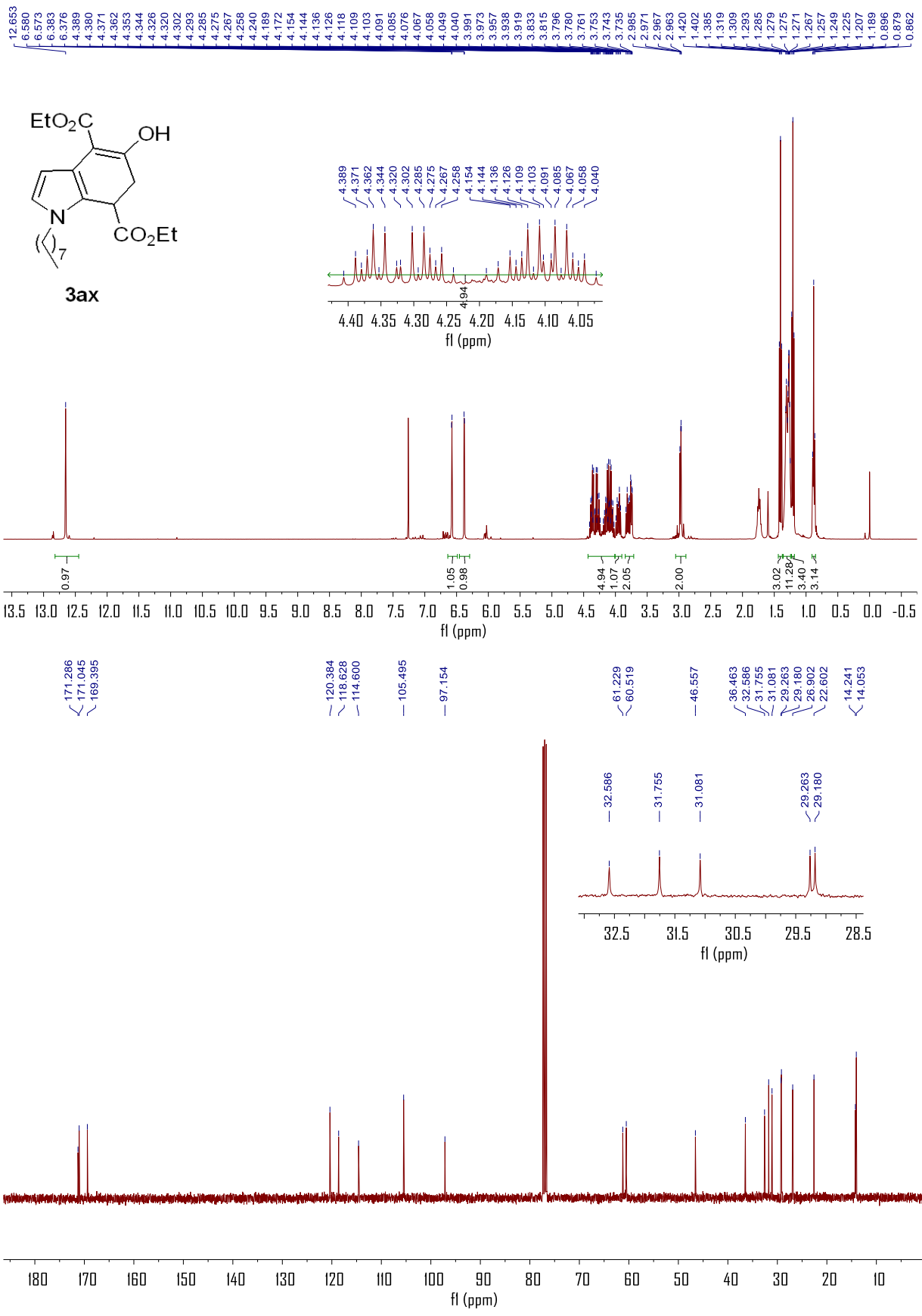

EtO2C
OH
N
CO2Et

3av

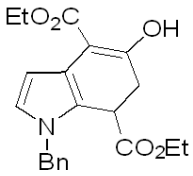

1.00
1.00
1.00
2.20
2.28
1.00
3.00
2.05
3.04
3.24
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.284
170.997
169.449
121.934
119.156
114.930
105.394
97.106
61.283
60.559
36.190
33.739
32.301
14.252
14.054
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

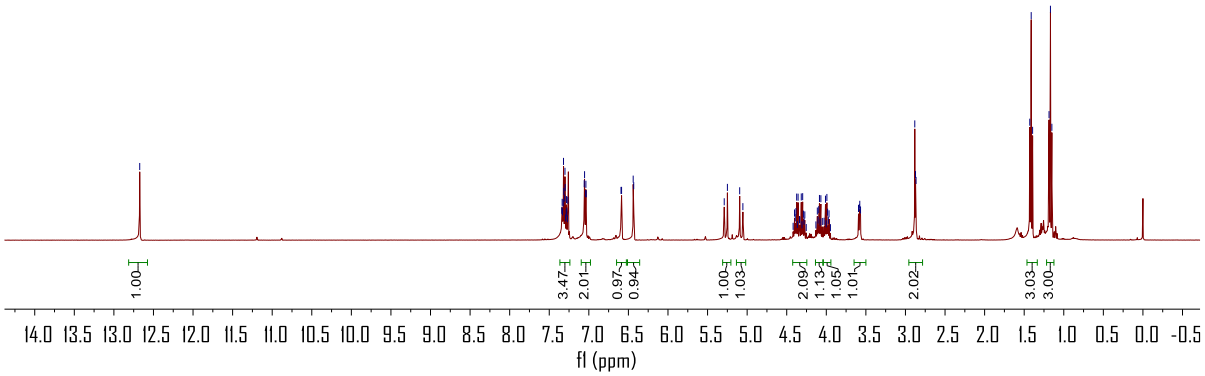

12.655
6.611
6.395
4.407
4.389
4.380
4.371
4.362
4.353
4.344
4.325
4.307
4.298
4.289
4.280
4.271
4.262
4.244
4.159
4.150
4.141
4.132
4.123
4.114
4.107
4.101
4.096
4.089
4.080
4.071
4.062
4.054
4.045
4.028
4.011
3.994
3.976
3.957
3.953
3.935
3.917
3.900
3.882
3.864
3.766
3.758
3.749
3.741
2.994
2.982
2.977
2.974
1.425
1.423
1.407
1.405
1.387
1.229
1.211
1.193
EtO2C
OH
N
Et
CO2Et
3aw
fl (ppm)
fl (ppm)
fl (ppm)
fl (ppm)
171.287
171.021
169.455
119.529
118.495
114.637
105.699
97.100
61.272
60.538
41.008
36.337
32.503
16.105
14.239
14.043


12.653
6.580
6.573
6.383
6.376
4.389
4.380
4.371
4.362
4.353
4.344
4.326
4.320
4.302
4.293
4.285
4.275
4.267
4.258
4.240
4.189
4.172
4.154
4.144
4.136
4.126
4.118
4.109
4.103
4.091
4.085
4.076
4.067
4.058
4.049
4.040
3.991
3.973
3.957
3.938
3.919
3.833
3.815
3.796
3.780
3.761
3.753
3.743
3.735
2.985
2.971
2.967
2.963
1.420
1.402
1.385
1.319
1.309
1.293
1.285
1.279
1.275
1.271
1.267
1.257
1.249
1.225
1.207
1.189
0.896
0.879
0.862
EtO2C
OH
N
CO2Et
7
3ax
4.389
4.371
4.362
4.344
4.320
4.302
4.285
4.275
4.267
4.258
4.154
4.144
4.136
4.126
4.109
4.103
4.091
4.085
4.067
4.058
4.040
4.94
4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05
f1 (ppm)
0.97
1.05
0.98
4.94
1.07
2.05
2.00
3.02
11.28
3.40
3.14
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
171.286
171.045
169.395
120.384
118.628
114.600
105.495
97.154
61.229
60.519
46.557
36.463
32.586
31.755
31.081
29.263
29.180
26.902
22.602
14.241
14.053
32.586
31.755
31.081
29.263
29.180
32.5 31.5 30.5 29.5 28.5
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.674
7.341
7.337
7.333
7.324
7.320
7.315
7.305
7.301
7.299
7.295
7.287
7.283
7.279
7.271
7.265
7.058
7.054
7.039
7.037
7.034
6.593
6.586
6.440
6.433
5.289
5.249
5.094
5.054
4.419
4.401
4.392
4.383
4.374
4.365
4.356
4.338
4.334
4.316
4.307
4.298
4.289
4.281
4.271
4.131
4.113
4.104
4.095
4.086
4.078
4.069
4.051
4.028
4.010
4.001
3.992
3.983
3.975
3.966
3.593
3.583
3.577
3.568
2.882
2.873
2.866
1.429
1.411
1.394
1.186
1.168
1.150


EtO2C
OH
N
Bn
CO2Et

3ay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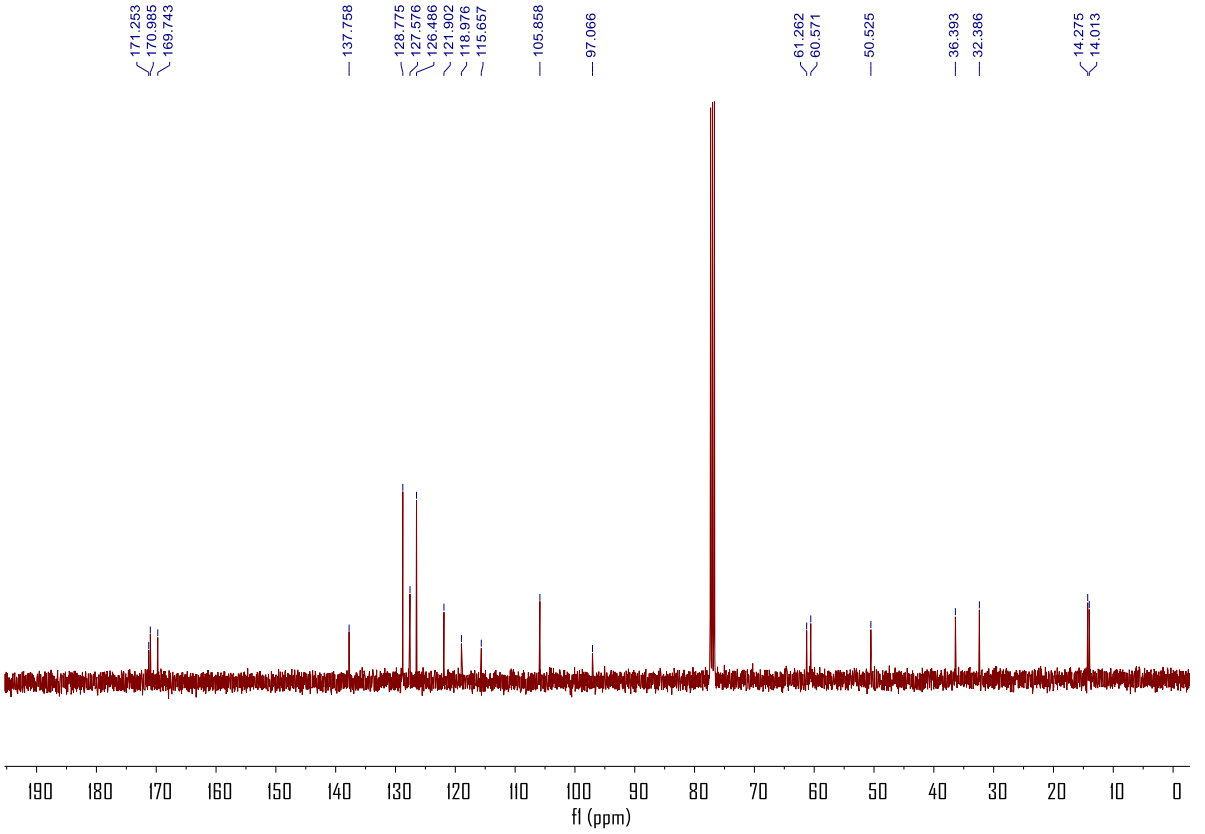
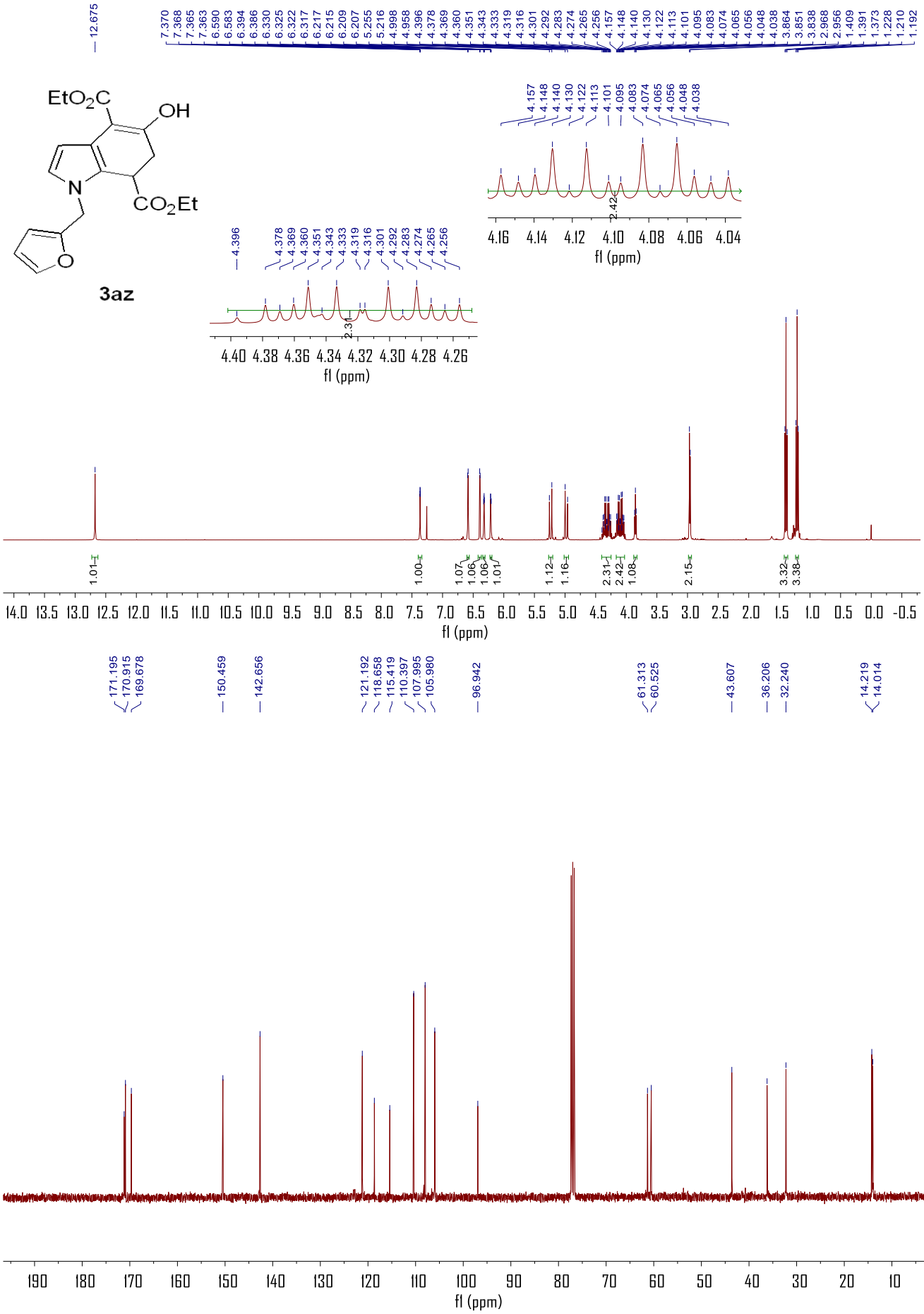
3.47
2.01
0.97
0.94
1.00
1.03
2.09
1.13
1.05
1.01
2.02
3.03
3.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.253
170.985
169.743
137.758
128.775
127.576
126.486
121.902
118.976
115.657
105.858
97.066
61.262
60.571
50.525
36.393
32.386
14.275
14.013
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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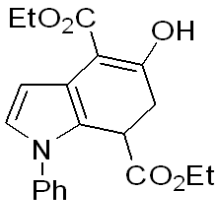
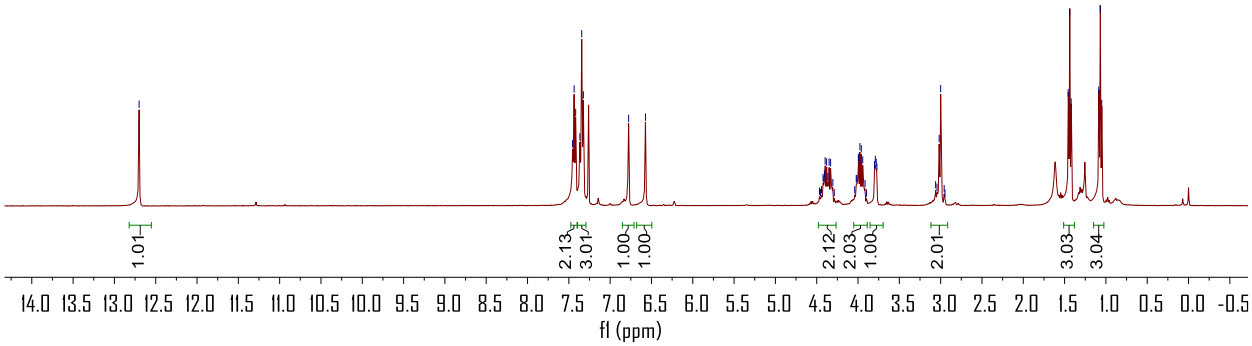
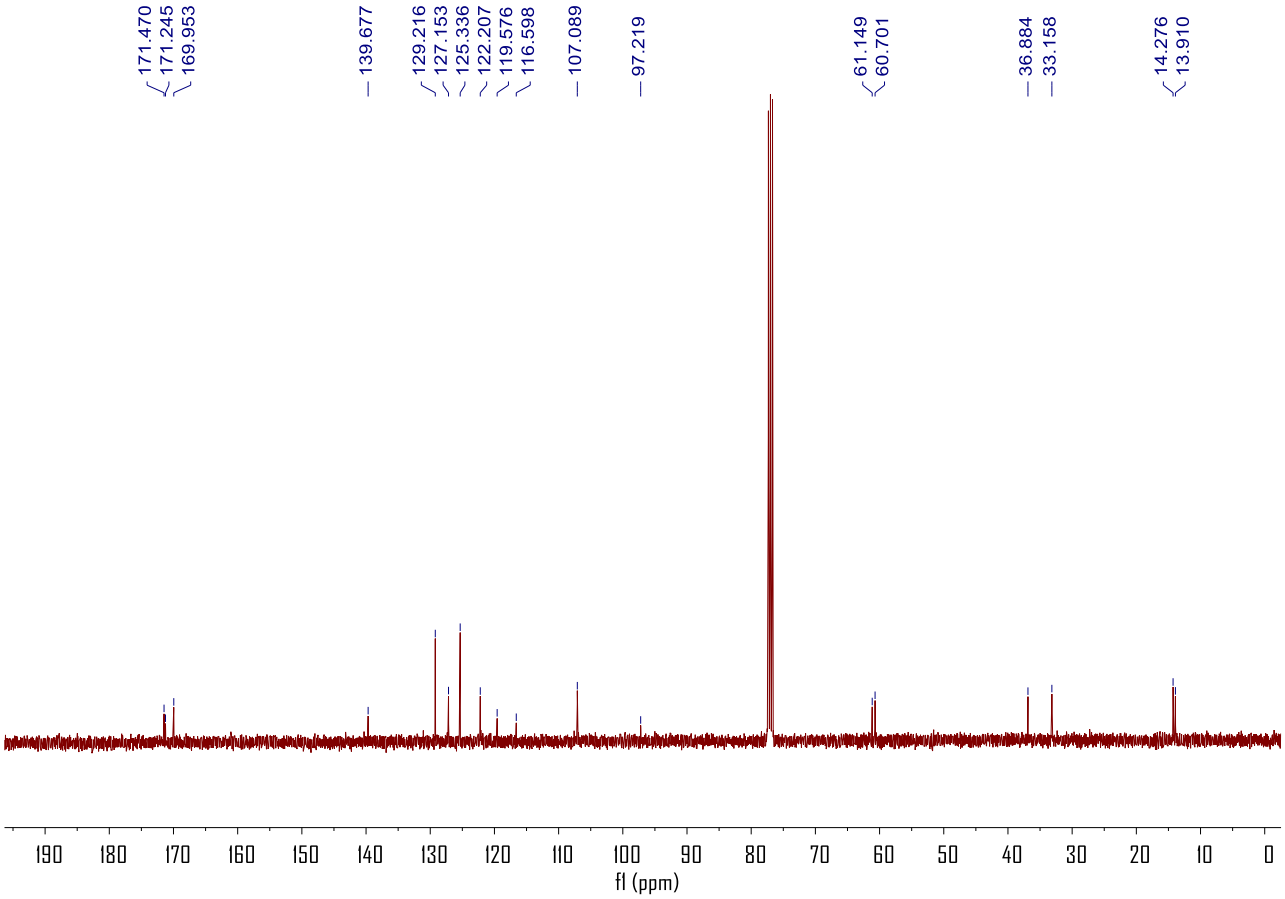
7.370
7.368
7.365
7.363
6.590
6.583
6.394
6.386
6.330
6.325
6.322
6.317
6.217
6.215
6.209
6.207
5.255
5.216
4.998
4.958
4.396
4.378
4.369
4.360
4.351
4.343
4.333
4.319
4.316
4.301
4.292
4.283
4.274
4.265
4.256
4.157
4.148
4.140
4.130
4.122
4.113
4.101
4.095
4.083
4.074
4.065
4.056
4.048
4.038
3.864
3.851
3.838
2.968
2.956
1.409
1.391
1.373
1.228
1.210
1.192
EtO2C
OH
N
CO2Et
O
3az
2.42
4.16 4.14 4.12 4.10 4.08 4.06 4.04
f1 (ppm)
2.31
4.40 4.38 4.36 4.34 4.32 4.30 4.28 4.26
f1 (ppm)
1.01
1.00
1.07
1.06
1.06
1.01
1.12
1.16
2.31
2.42
1.08
2.15
3.32
3.38
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
171.195
170.915
169.678
150.459
142.656
121.192
118.658
115.419
110.397
107.995
105.980
96.942
61.313
60.525
43.607
36.206
32.240
14.219
14.014
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

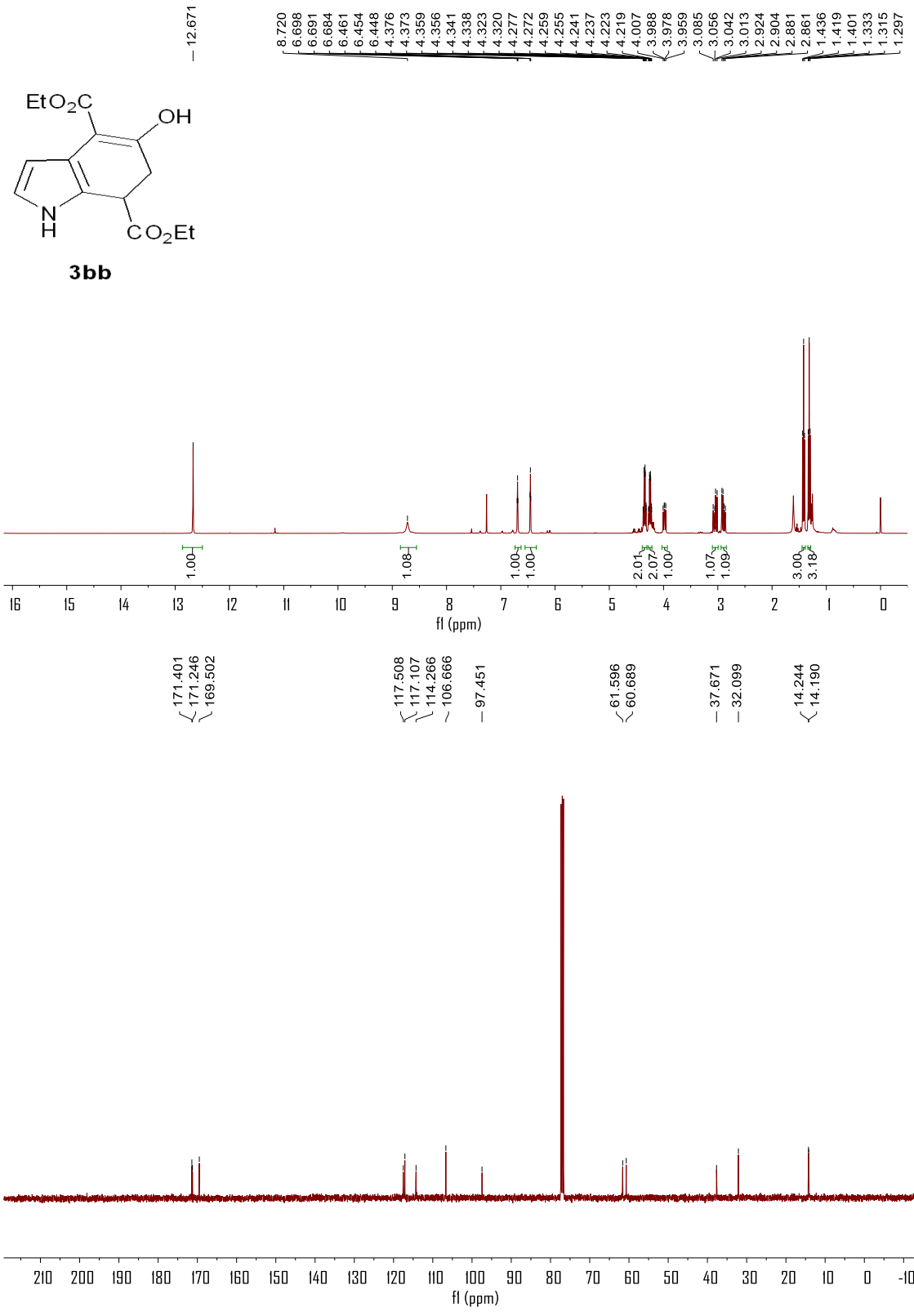

12.701
7.455
7.436
7.417
7.366
7.344
7.324
6.776
6.572
4.466
4.455
4.442
4.424
4.413
4.407
4.398
4.380
4.364
4.350
4.332
4.305
4.287
4.040
4.022
4.014
3.996
3.992
3.977
3.960
3.943
3.915
3.897
3.800
3.791
3.780
3.772
3.061
3.044
3.018
3.000
2.957
2.948
1.456
1.438
1.421
1.086
1.068
1.050


EtO2C
OH
N
Ph
CO2Et

3ba


1.01
2.13
3.01
1.00
1.00
2.12
2.03
1.00
2.01
3.03
3.04
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.470
171.245
169.953
139.677
129.216
127.153
125.336
122.207
119.576
116.598
107.089
97.219
61.149
60.701
36.884
33.158
14.276
13.910
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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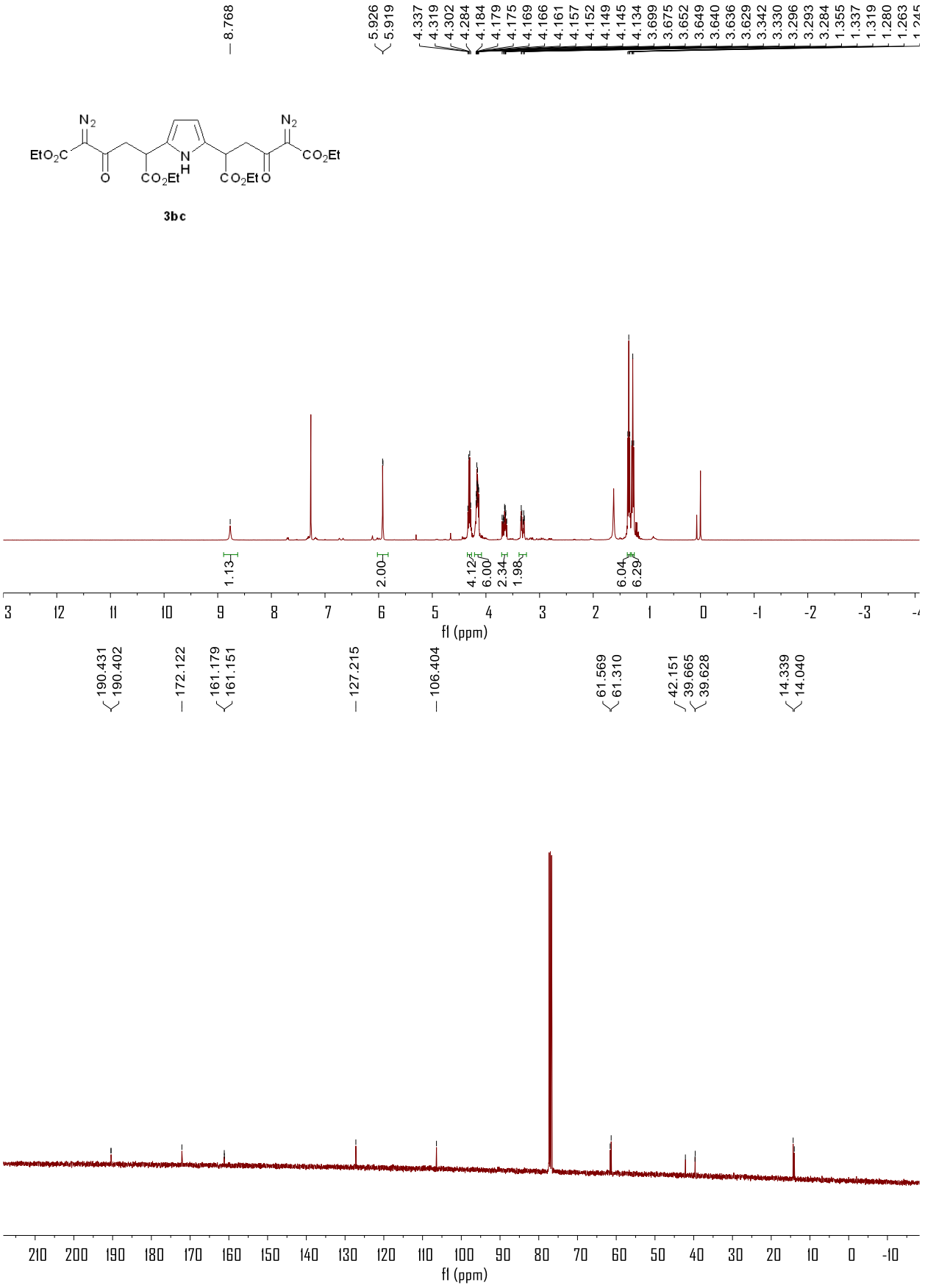
8.720
6.698
6.691
6.684
6.461
6.454
6.448
4.376
4.373
4.359
4.356
4.341
4.338
4.323
4.320
4.277
4.272
4.259
4.255
4.241
4.237
4.223
4.219
4.007
3.988
3.978
3.959
3.085
3.056
3.042
3.013
2.924
2.904
2.881
2.861
1.436
1.419
1.401
1.333
1.315
1.297
EtO2C
OH
N
H
CO2Et
3bb
1.00
1.08
1.00
1.00
2.01
2.07
1.00
1.07
1.09
3.00
3.18
f1 (ppm)
171.401
171.246
169.502
117.508
117.107
114.266
106.666
97.451
61.596
60.689
37.671
32.099
14.244
14.190
f1 (ppm)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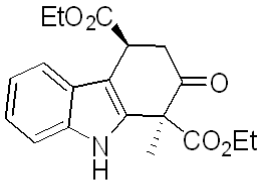
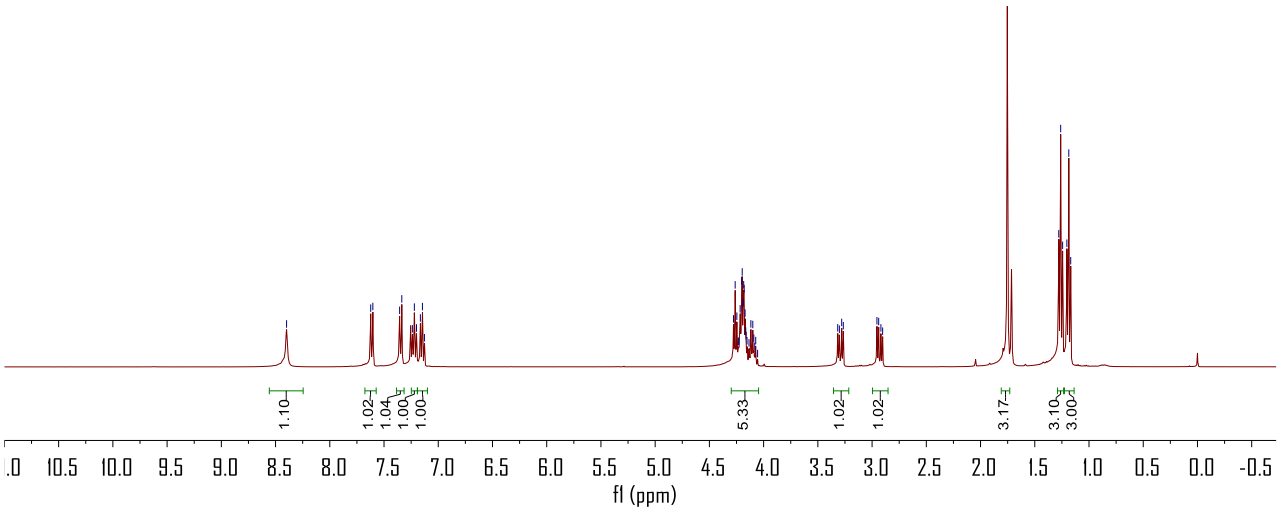
5.926
5.919
4.337
4.319
4.302
4.284
4.184
4.179
4.175
4.169
4.166
4.161
4.157
4.152
4.149
4.145
4.134
3.699
3.675
3.652
3.649
3.640
3.636
3.629
3.342
3.330
3.296
3.293
3.284
1.355
1.337
1.319
1.280
1.263
1.245
N2
EtO2C
N
H
CO2Et
O
CO2Et
CO2Et
O
N2
CO2Et
3bc
1.13
2.00
4.12
6.00
2.34
1.98
6.04
6.29
f1 (ppm)
190.431
190.402
172.122
161.179
161.151
127.215
106.404
61.569
61.310
42.151
39.665
39.628
14.339
14.040
f1 (ppm)


8.398
7.623
7.603
7.356
7.336
7.238
7.220
7.201
7.165
7.146
7.127
4.278
4.262
4.247
4.234
4.228
4.216
4.202
4.197
4.189
4.184
4.179
4.171
4.165
4.161
4.153
4.135
4.117
4.100
4.091
4.082
4.073
4.056
3.317
3.302
3.280
3.265
2.955
2.939
2.919
2.903
1.279
1.261
1.243
1.204
1.186
1.169


EtO2C
O
CO2Et
N
H

4a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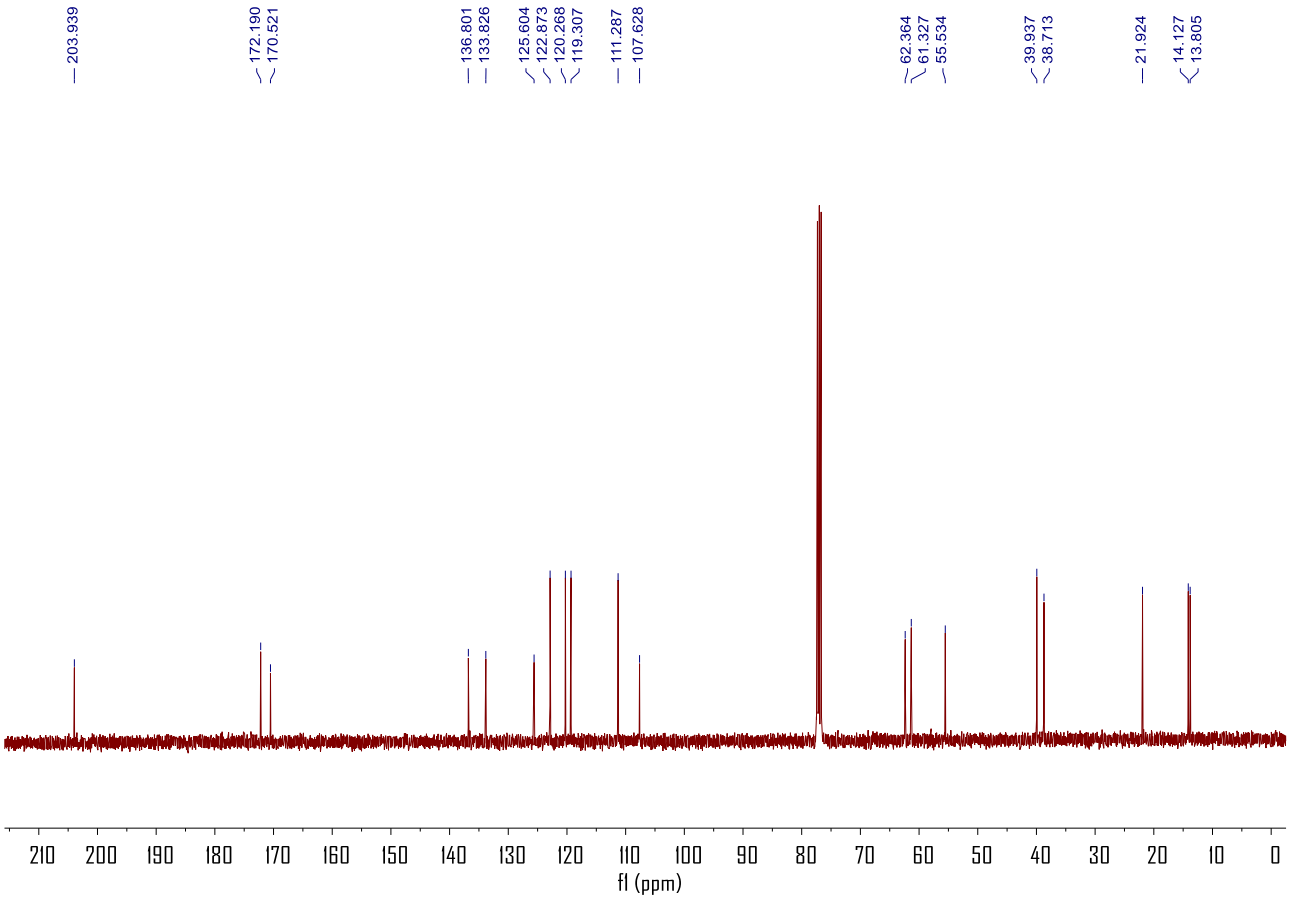
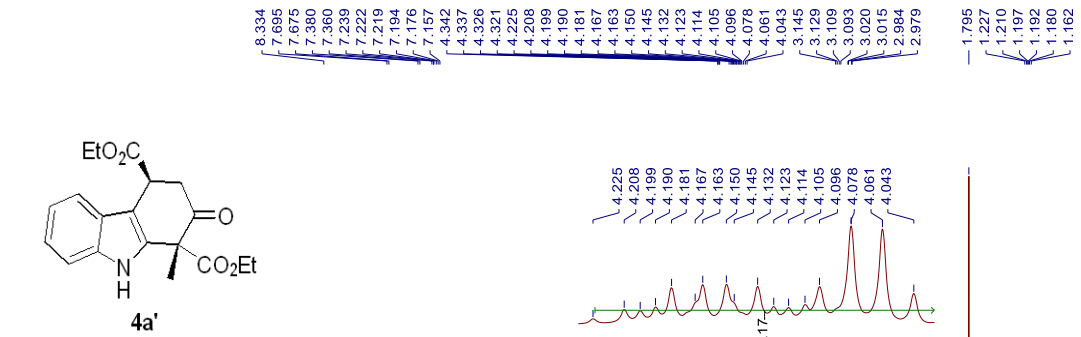
1.02
1.04
1.00
1.00
5.33
1.02
1.02
3.17
3.10
3.00
f1 (ppm)


203.939
172.190
170.521
136.801
133.826
125.604
122.873
120.268
119.307
111.287
107.628
62.364
61.327
55.534
39.937
38.713
21.924
14.127
13.805
f1 (ppm)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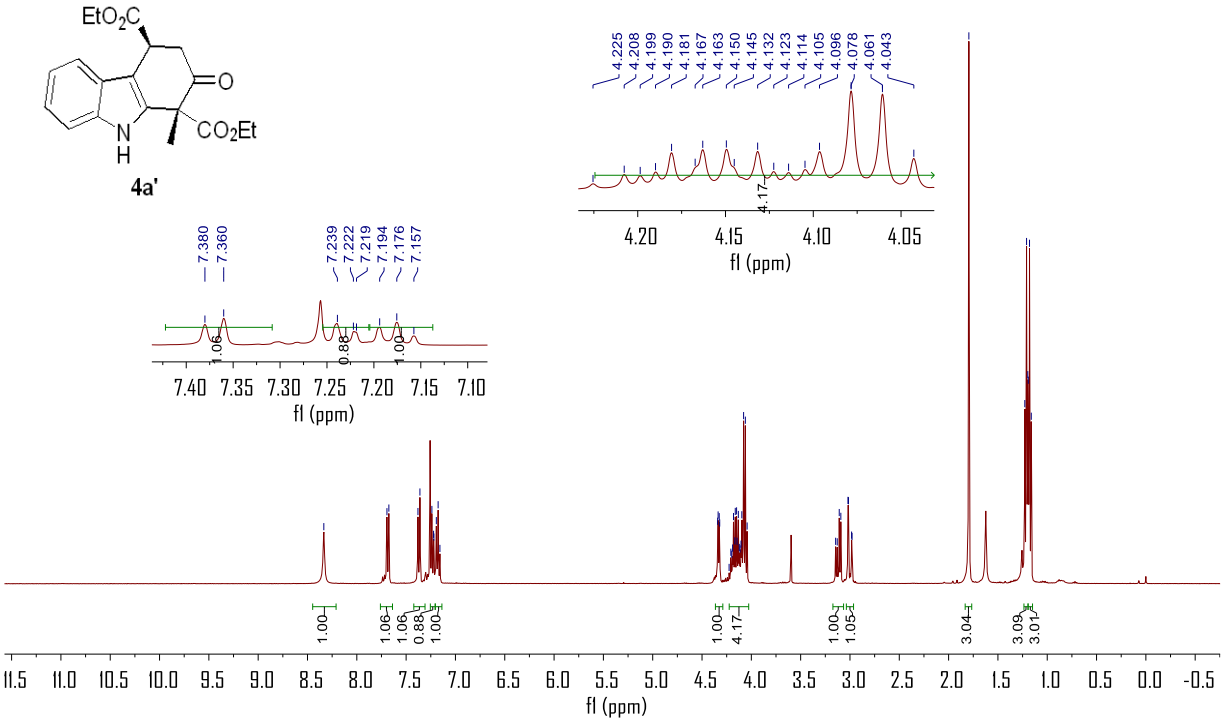
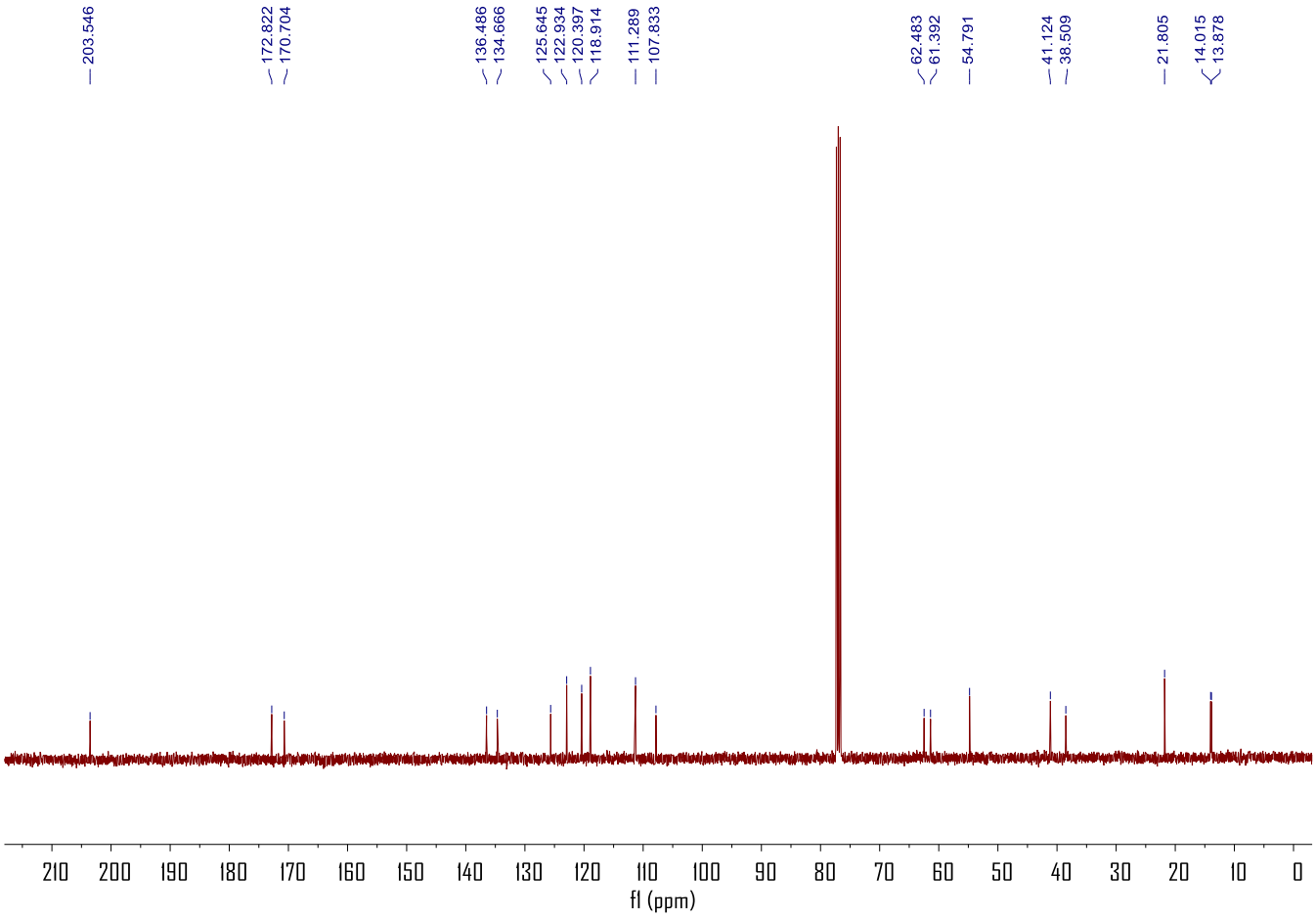
7.695
7.675
7.380
7.360
7.239
7.222
7.219
7.194
7.176
7.157
4.342
4.337
4.326
4.321
4.225
4.208
4.199
4.190
4.181
4.167
4.163
4.150
4.145
4.132
4.123
4.114
4.105
4.096
4.078
4.061
4.043
3.145
3.129
3.109
3.093
3.020
3.015
2.984
2.979
1.795
1.227
1.210
1.197
1.192
1.180
1.162


EtO2C
O
N
H
CO2Et
4a'
7.380
7.360
7.239
7.222
7.219
7.194
7.176
7.157
1.06
0.88
1.00
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
4.225
4.208
4.199
4.190
4.181
4.167
4.163
4.150
4.145
4.132
4.123
4.114
4.105
4.096
4.078
4.061
4.043
4.17
4.20 4.15 4.10 4.05
f1 (ppm)
1.00
1.06
1.06
0.88
1.00
1.00
4.17
1.00
1.06
3.04
3.09
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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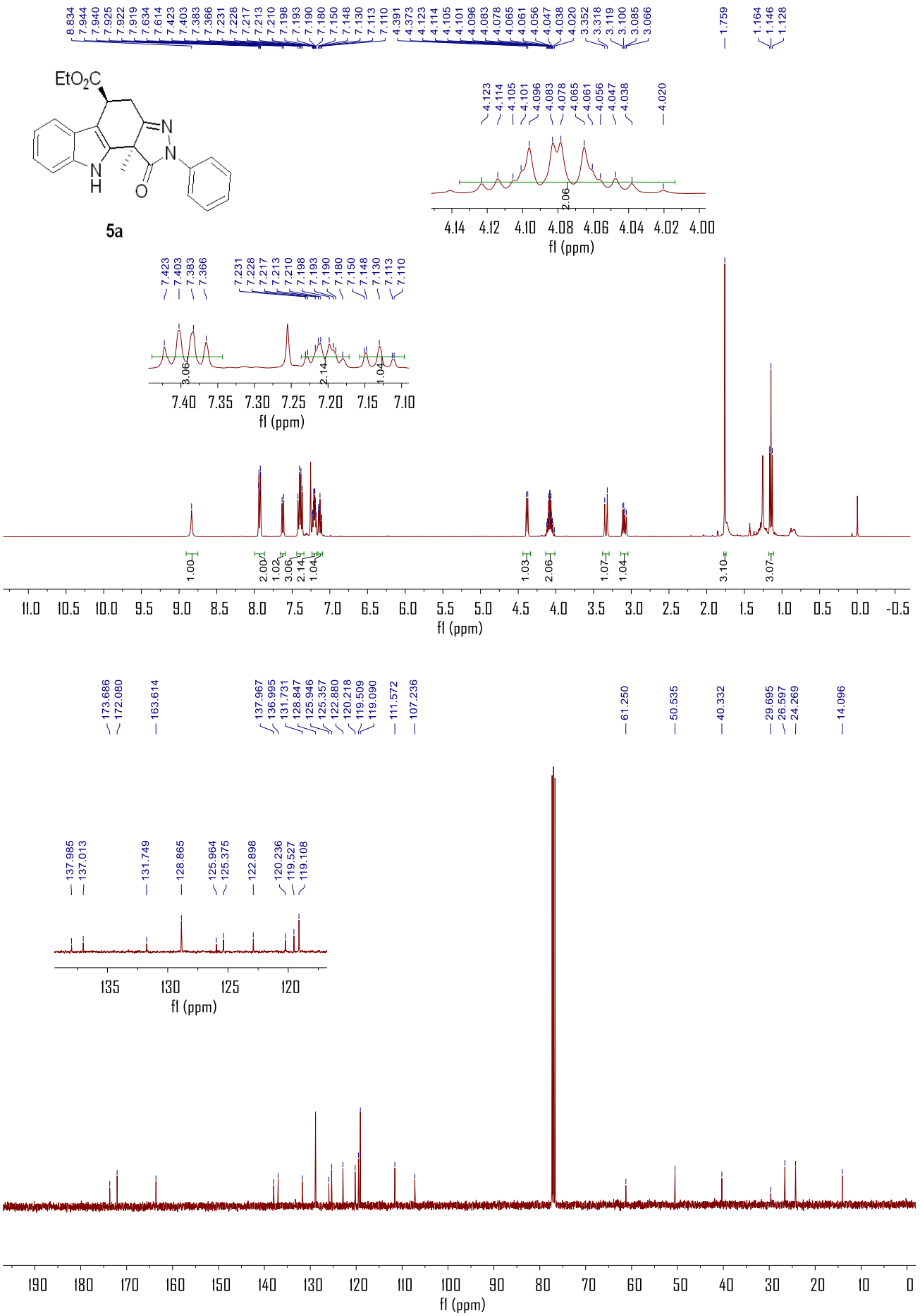
170.704
136.486
134.666
125.645
122.934
120.397
118.914
111.289
107.833
62.483
61.392
54.791
41.124
38.509
21.805
14.015
13.878
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.940
7.925
7.922
7.919
7.634
7.614
7.423
7.403
7.383
7.366
7.231
7.228
7.217
7.213
7.210
7.198
7.193
7.190
7.180
7.150
7.148
7.130
7.113
7.110
4.391
4.373
4.123
4.114
4.105
4.101
4.096
4.083
4.078
4.065
4.061
4.056
4.047
4.038
4.020
3.352
3.318
3.119
3.100
3.085
3.066
1.759
1.164
1.146
1.128
EtO2C
N
N
H
O
5a
fl (ppm)
1.00
2.00
1.02
3.06
2.14
1.04
1.03
2.06
1.07
1.04
3.10
3.07
173.686
172.080
163.614
137.967
136.995
131.731
128.847
125.946
125.357
122.880
120.218
119.509
119.090
111.572
107.236
61.250
50.535
40.332
29.695
26.597
24.269
14.096
137.985
137.013
131.749
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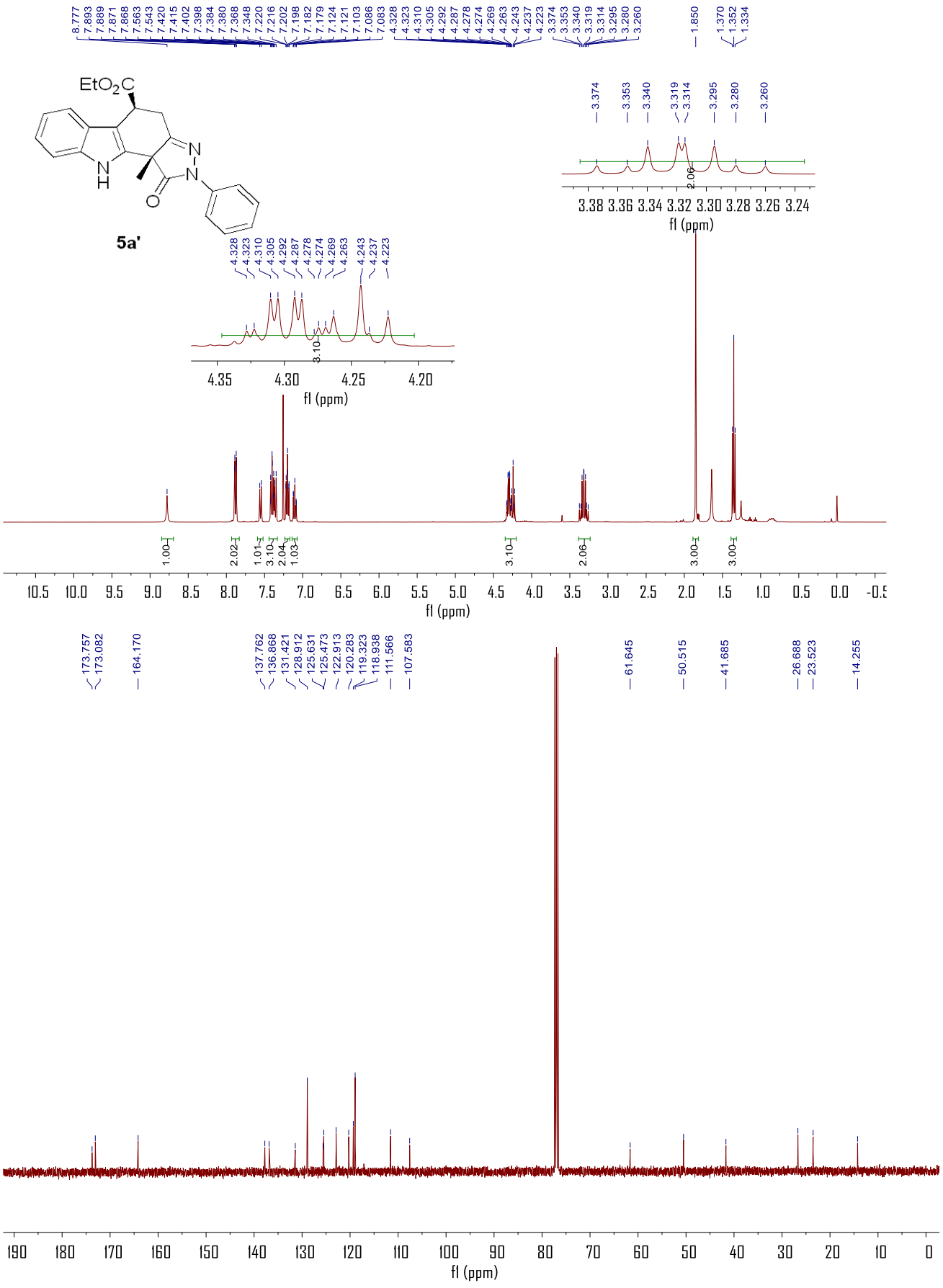
125.375
122.898
120.236
119.527
119.108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7.889
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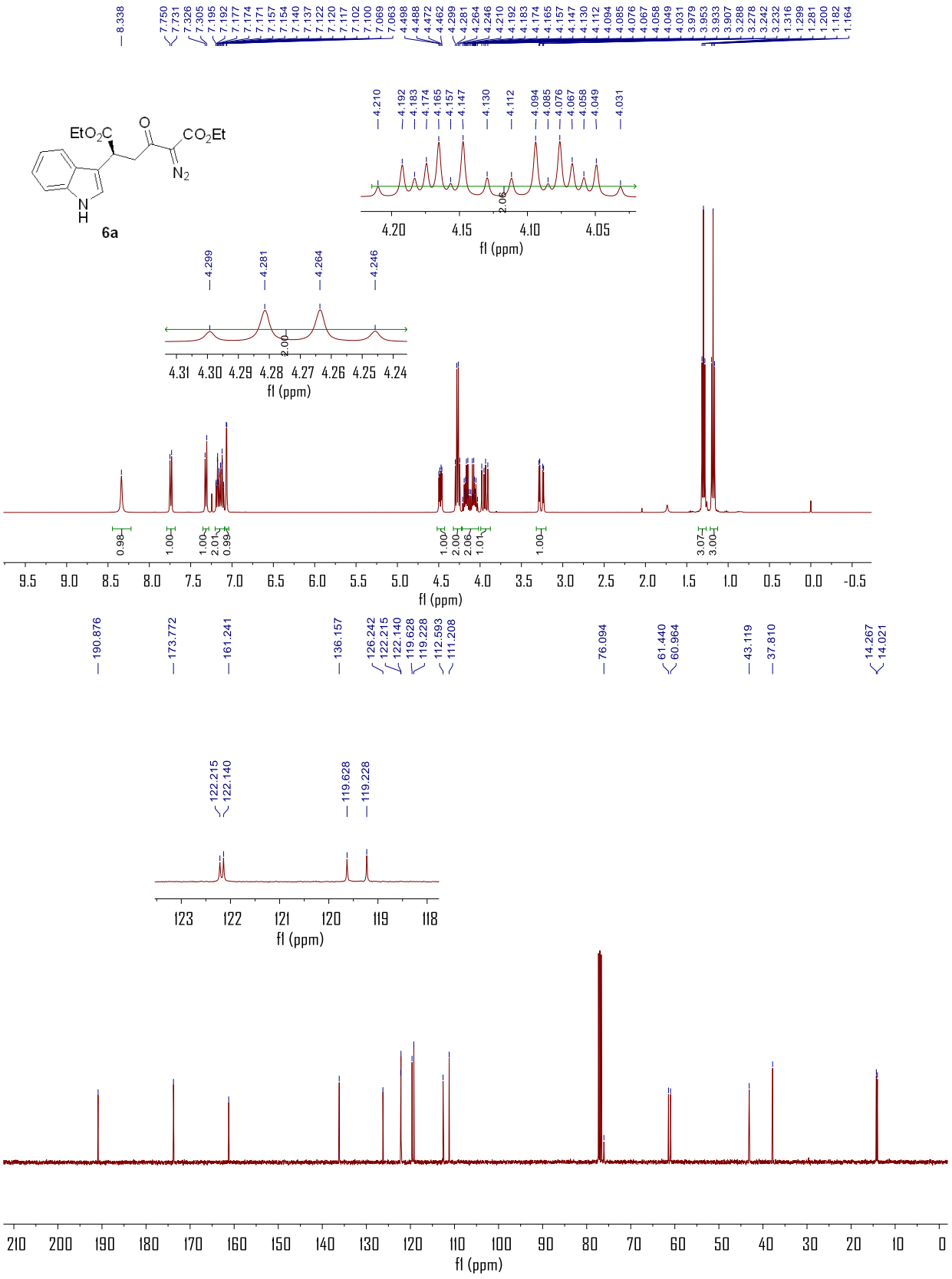
7.563
7.543
7.420
7.415
7.402
7.398
7.384
7.380
7.368
7.348
7.220
7.216
7.202
7.198
7.182
7.179
7.124
7.121
7.103
7.086
7.083
4.328
4.323
4.310
4.305
4.292
4.287
4.278
4.274
4.269
4.263
4.243
4.237
4.223
3.374
3.353
3.340
3.319
3.314
3.295
3.280
3.260
1.850
1.370
1.352
1.334
EtO2C
N
N
H
O
5a'
fl (ppm)
1.00
2.02
1.01
3.10
2.04
1.03
3.10
2.06
3.00
3.00
173.757
173.082
164.170
137.762
136.868
131.421
128.912
125.631
125.473
122.913
120.283
119.323
118.938
111.566
107.583
61.645
50.515
41.685
26.688
23.523
14.255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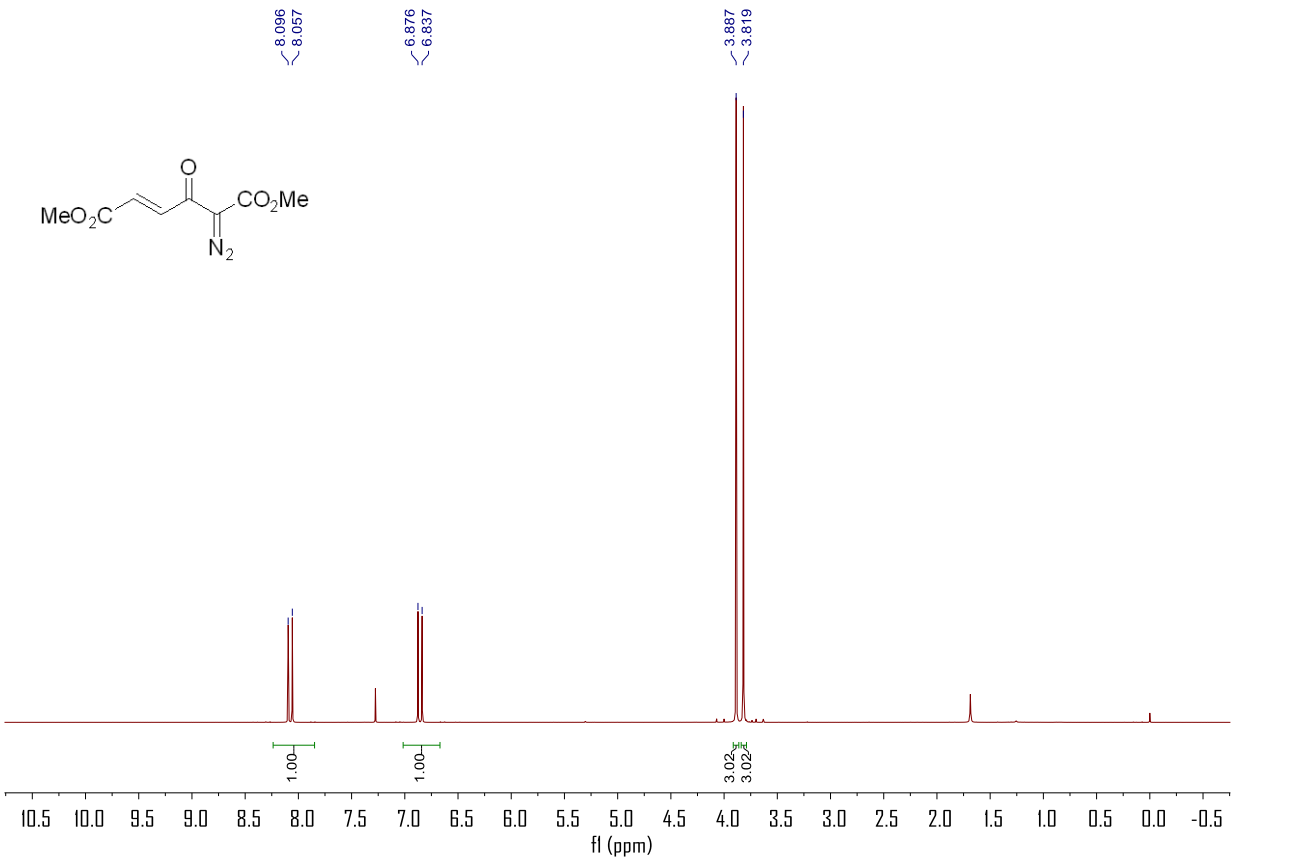
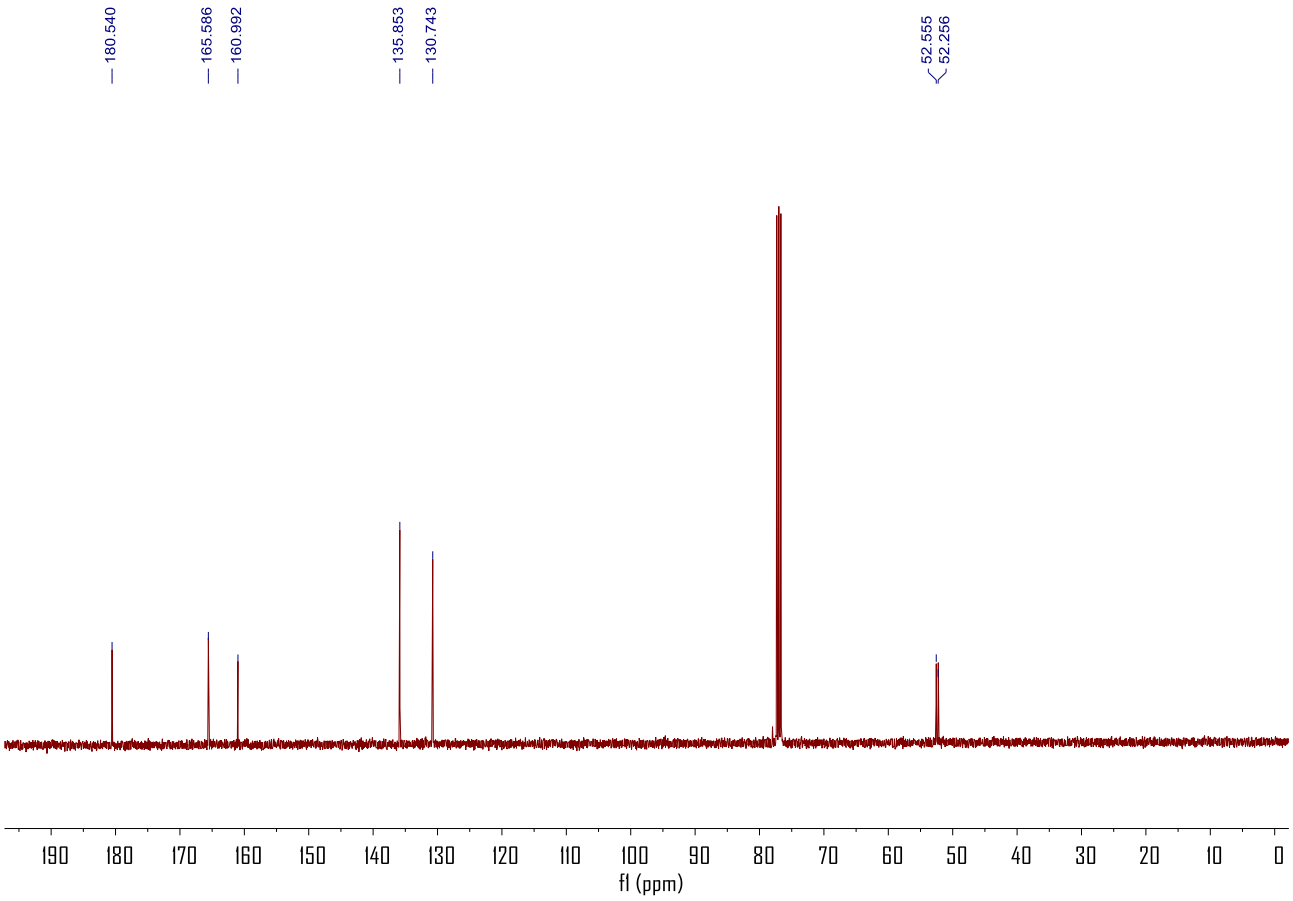
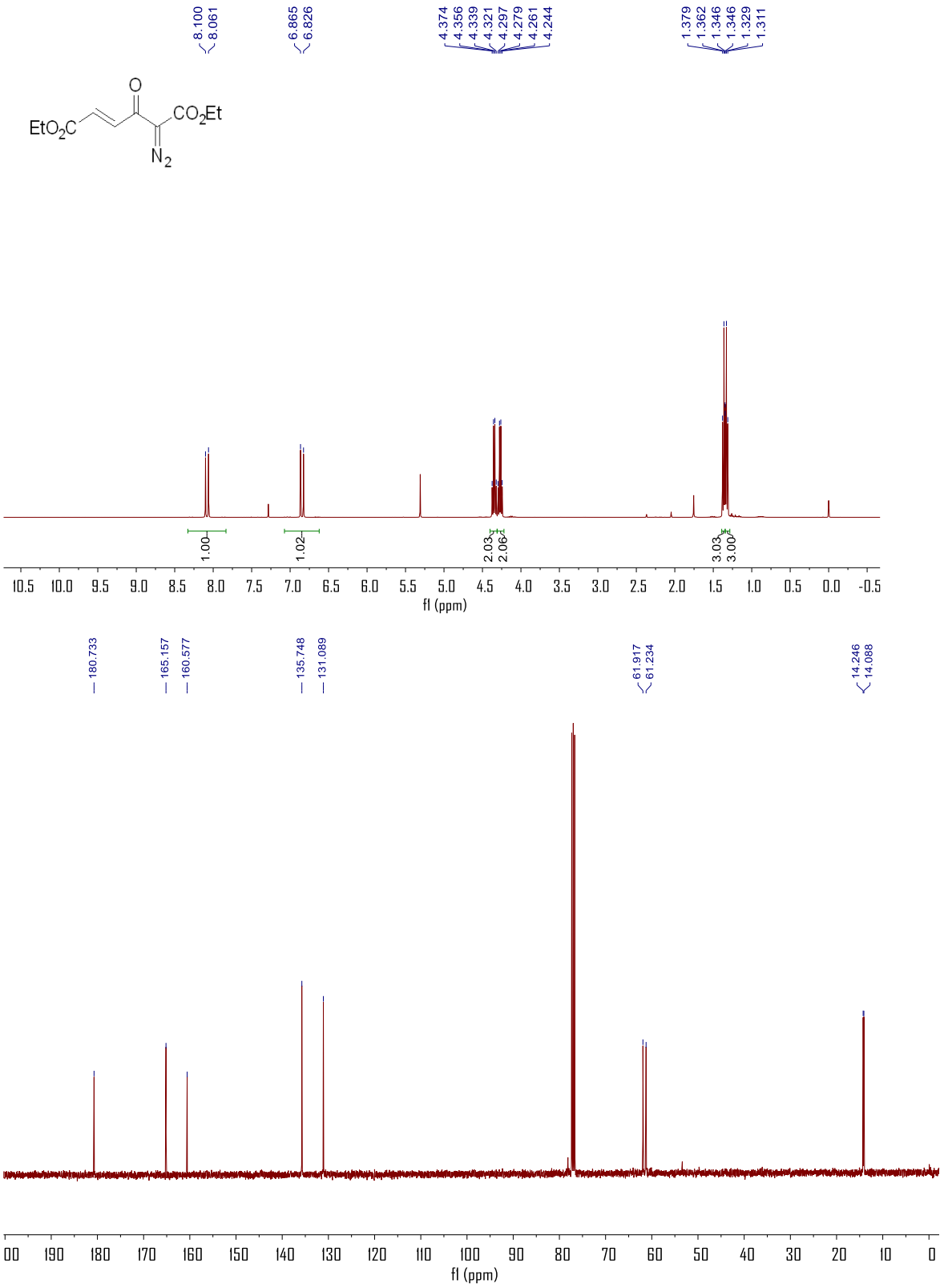
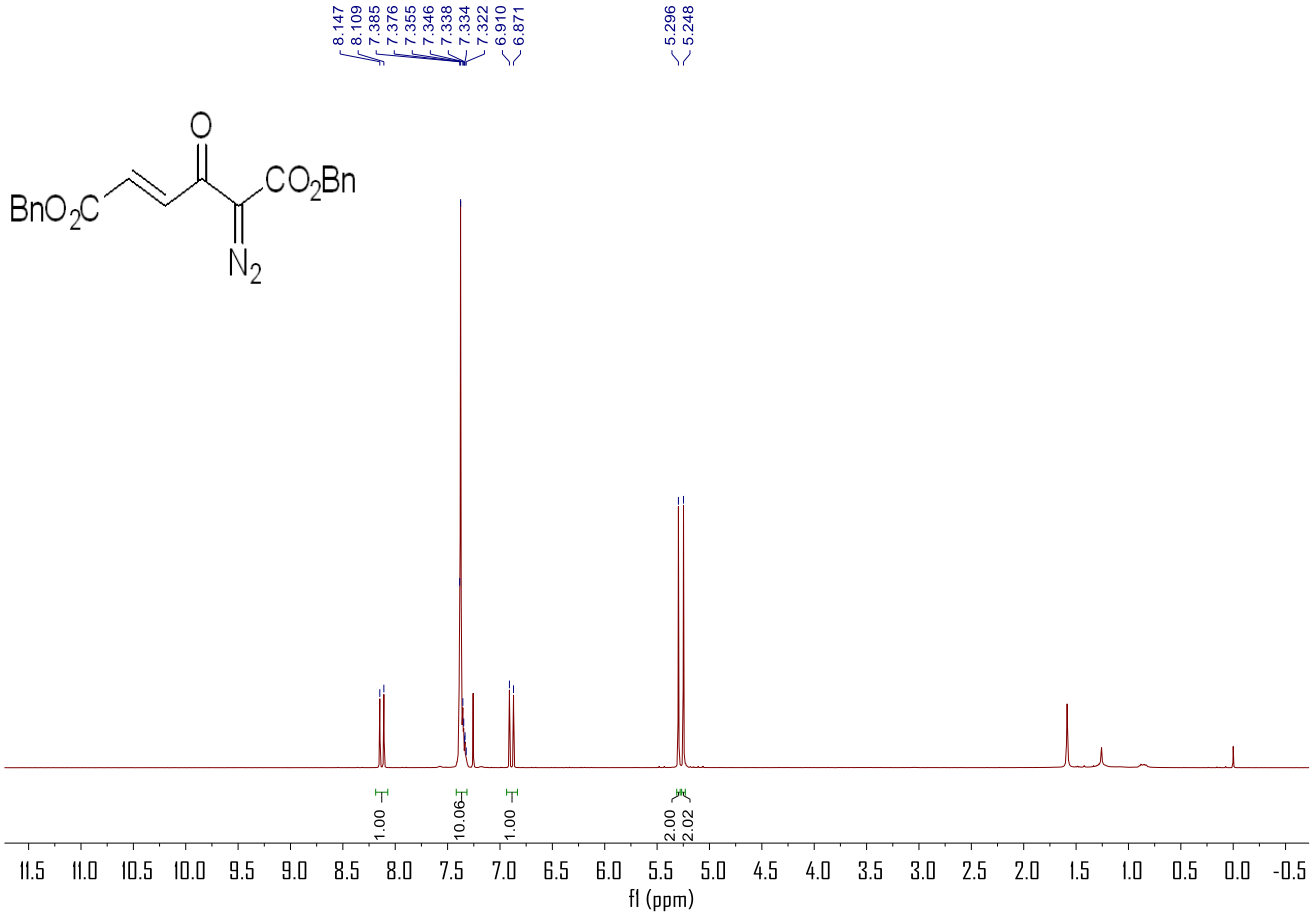
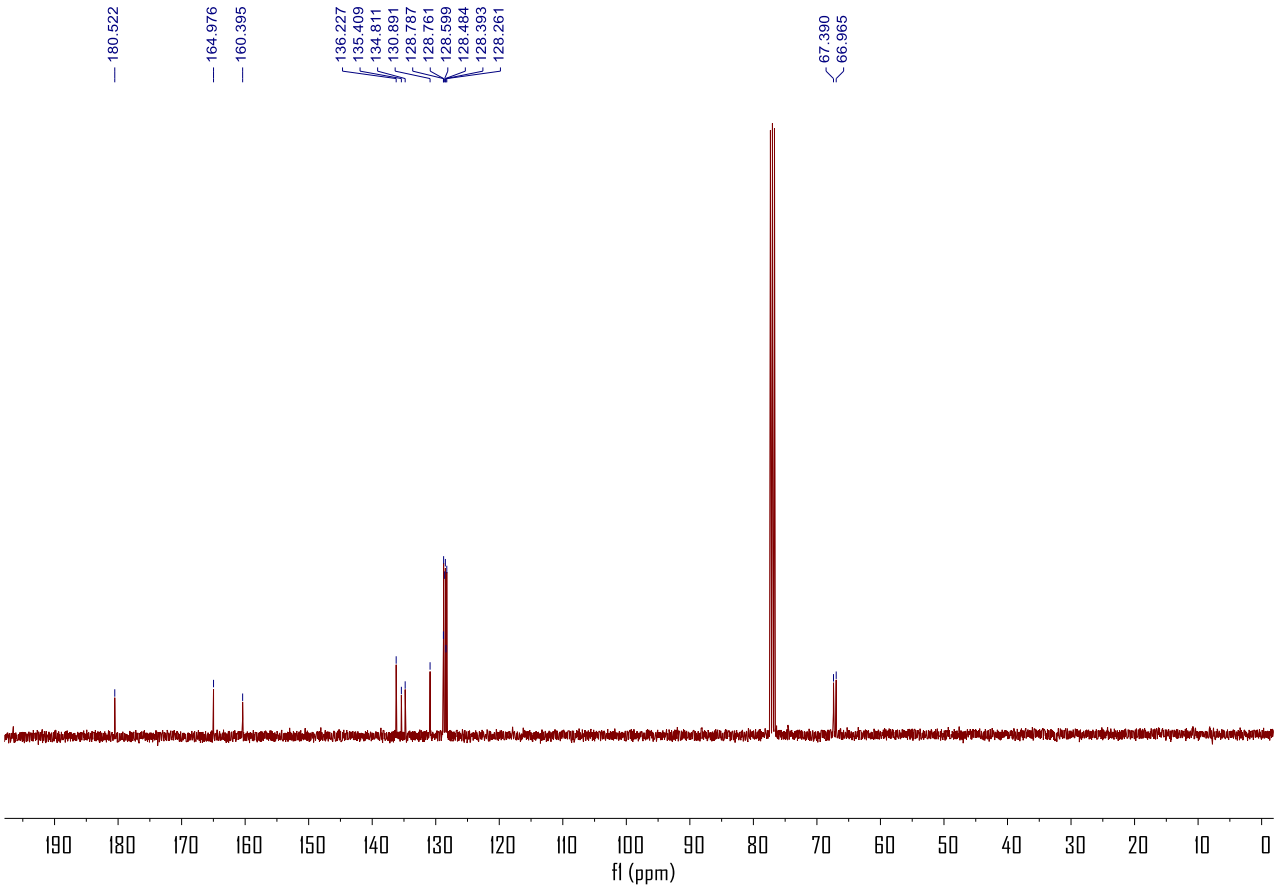
7.177
7.174
7.171
7.157
7.154
7.140
7.137
7.122
7.120
7.117
7.102
7.100
7.069
7.063
4.498
4.488
4.472
4.462
4.299
4.281
4.264
4.246
4.210
4.192
4.183
4.174
4.165
4.157
4.147
4.130
4.112
4.094
4.085
4.076
4.067
4.058
4.049
4.031
3.979
3.953
3.933
3.907
3.288
3.278
3.242
3.232
1.316
1.299
1.281
1.200
1.182
1.164
EtO2C
O
CO2Et
N2
N
H
6a
f1 (ppm)
0.98
1.00
1.00
2.01
0.99
1.00
2.00
2.06
1.01
1.00
3.07
3.00
190.876
173.772
161.241
136.157
126.242
122.215
122.140
119.628
119.228
112.593
111.208
76.094
61.440
60.964
43.119
37.810
14.267
14.021

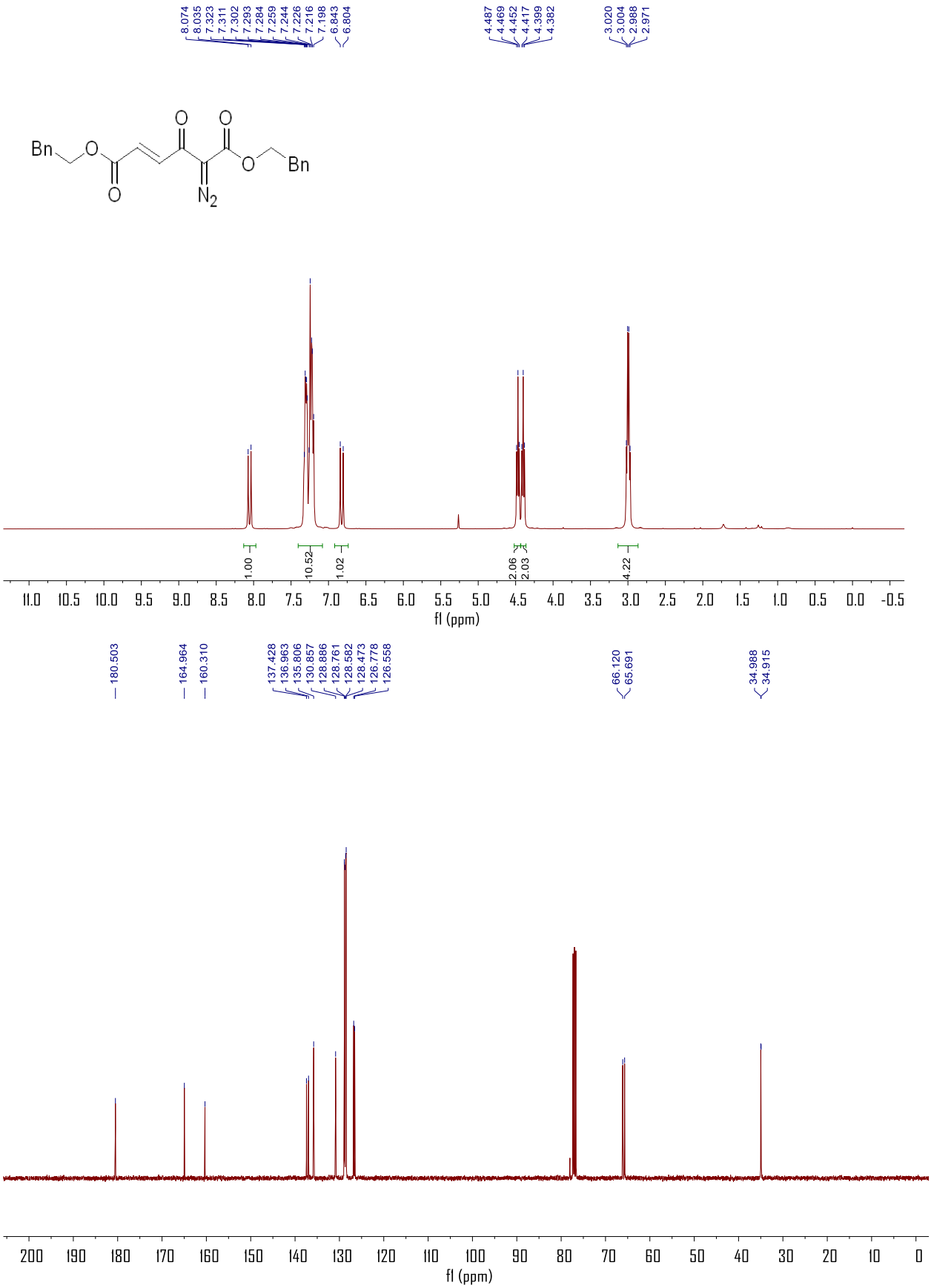

8.096
8.057
6.876
6.837
3.887
3.819
O
MeO2C
CO2Me
N2
1.00
1.00
3.02
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

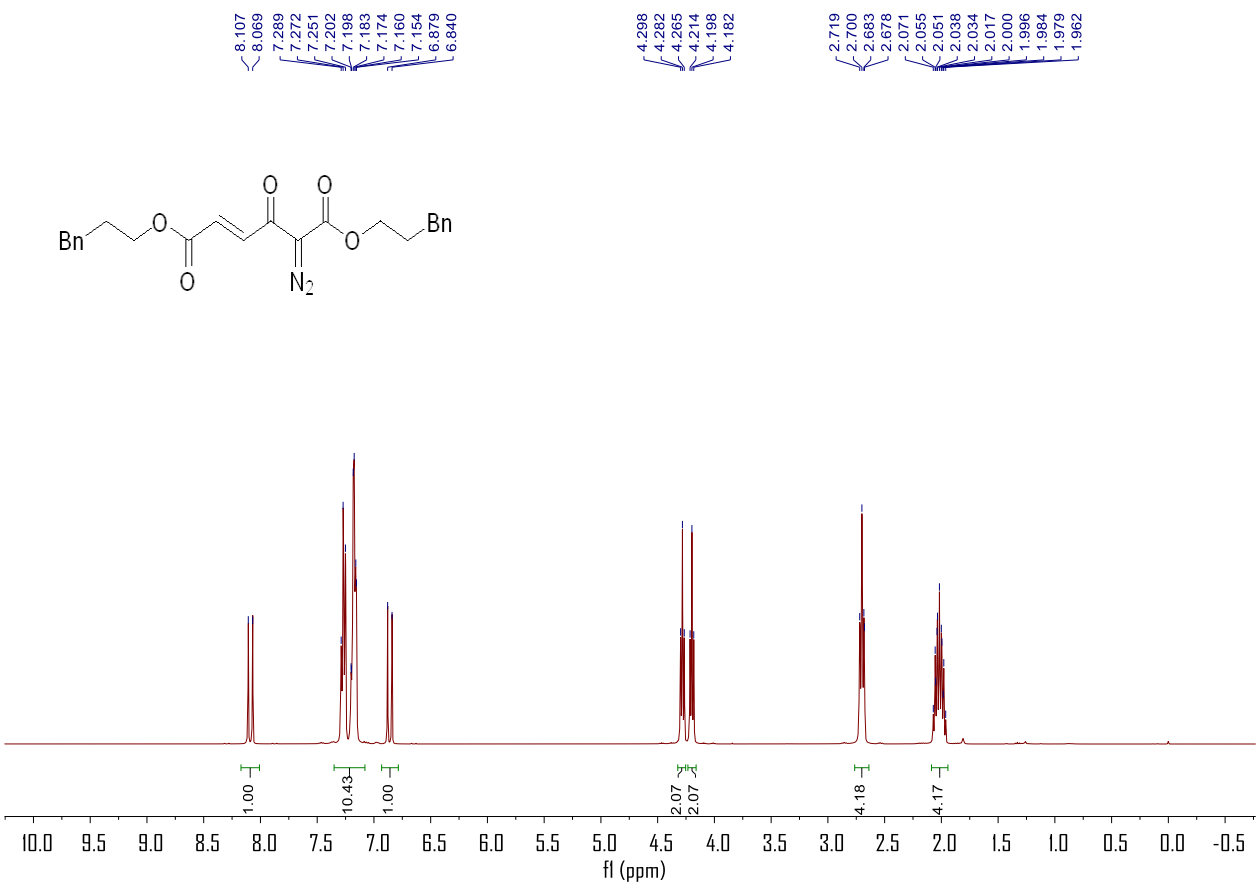

180.540
165.586
160.992
135.853
130.743
52.555
52.256
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

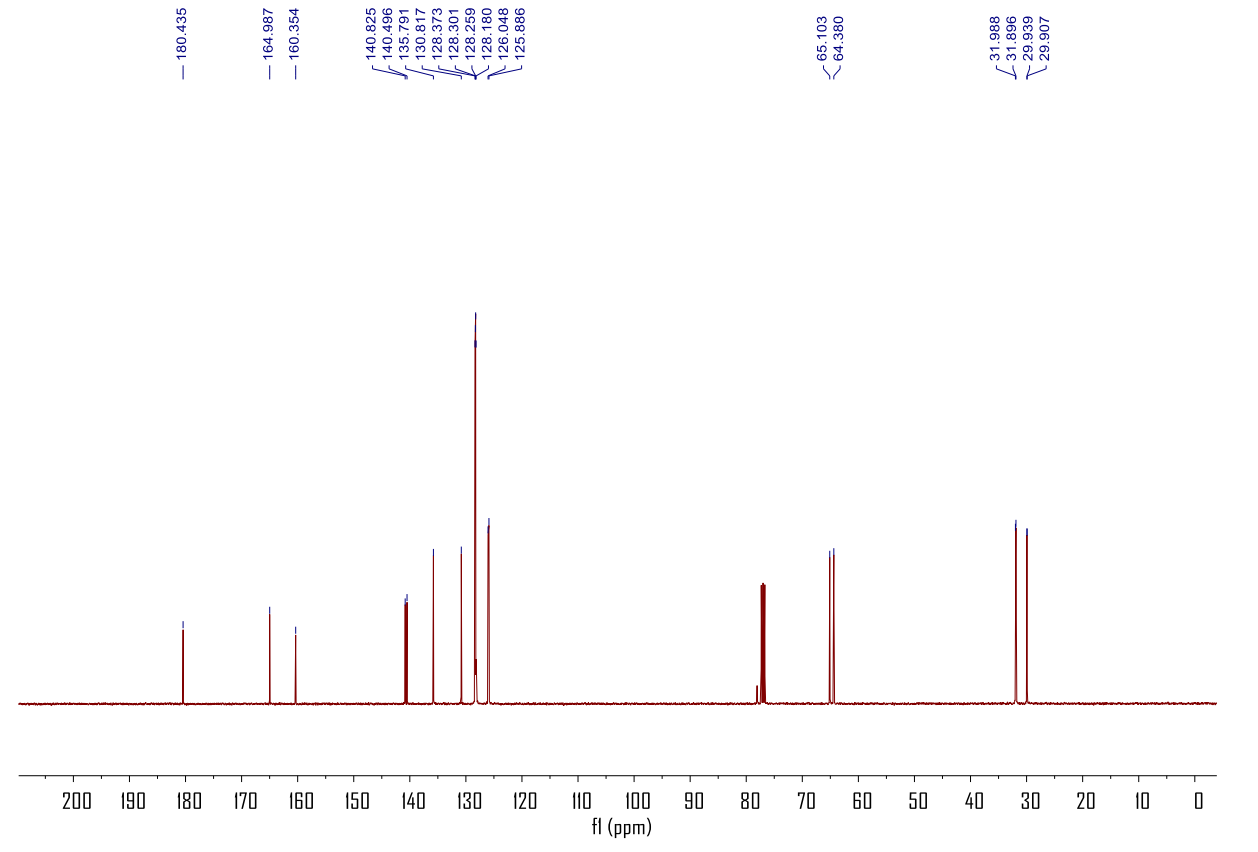

8.100
8.061
6.865
6.826
4.374
4.356
4.339
4.321
4.297
4.279
4.261
4.244
1.379
1.362
1.346
1.329
1.311
O
EtO2C
CO2Et
N2
1.00
1.02
2.03
2.06
3.03
3.00
f1 (ppm)
180.733
165.157
160.577
135.748
131.089
61.917
61.234
14.246
14.088
f1 (ppm)


8.147
8.109
7.385
7.376
7.355
7.346
7.338
7.334
7.322
6.910
6.871
5.296
5.248
O
BnO2C
CO2Bn
N2
1.00
10.06
1.00
2.00
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


180.522
164.976
160.395
136.227
135.409
134.811
130.891
128.787
128.761
128.599
128.484
128.393
128.261
67.390
66.965
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.074
8.035
7.323
7.311
7.302
7.293
7.284
7.259
7.244
7.226
7.216
7.198
6.843
6.804
4.487
4.469
4.452
4.417
4.399
4.382
3.020
3.004
2.988
2.971
Bn
O
O
O
O
Bn
O
N2
1.00
10.52
1.02
2.06
2.03
4.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
180.503
164.964
160.310
137.428
136.963
135.806
130.857
128.886
128.761
128.582
128.473
126.778
126.558
66.120
65.691
34.988
34.915
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

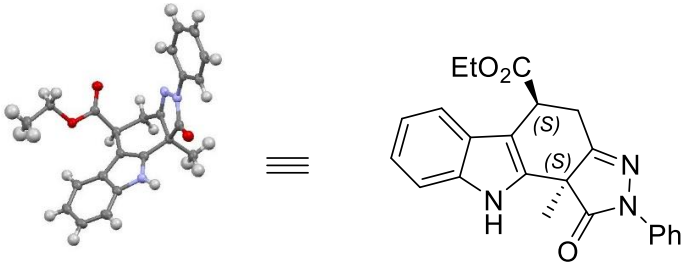

8.107
8.069
7.289
7.272
7.251
7.202
7.198
7.183
7.174
7.160
7.154
6.879
6.840
4.298
4.282
4.265
4.214
4.198
4.182
2.719
2.700
2.683
2.678
2.071
2.055
2.051
2.038
2.034
2.017
2.000
1.996
1.984
1.979
1.962
Bn
O
O
O
O
O
Bn
N2
1.00
10.43
1.00
2.07
2.07
4.18
4.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

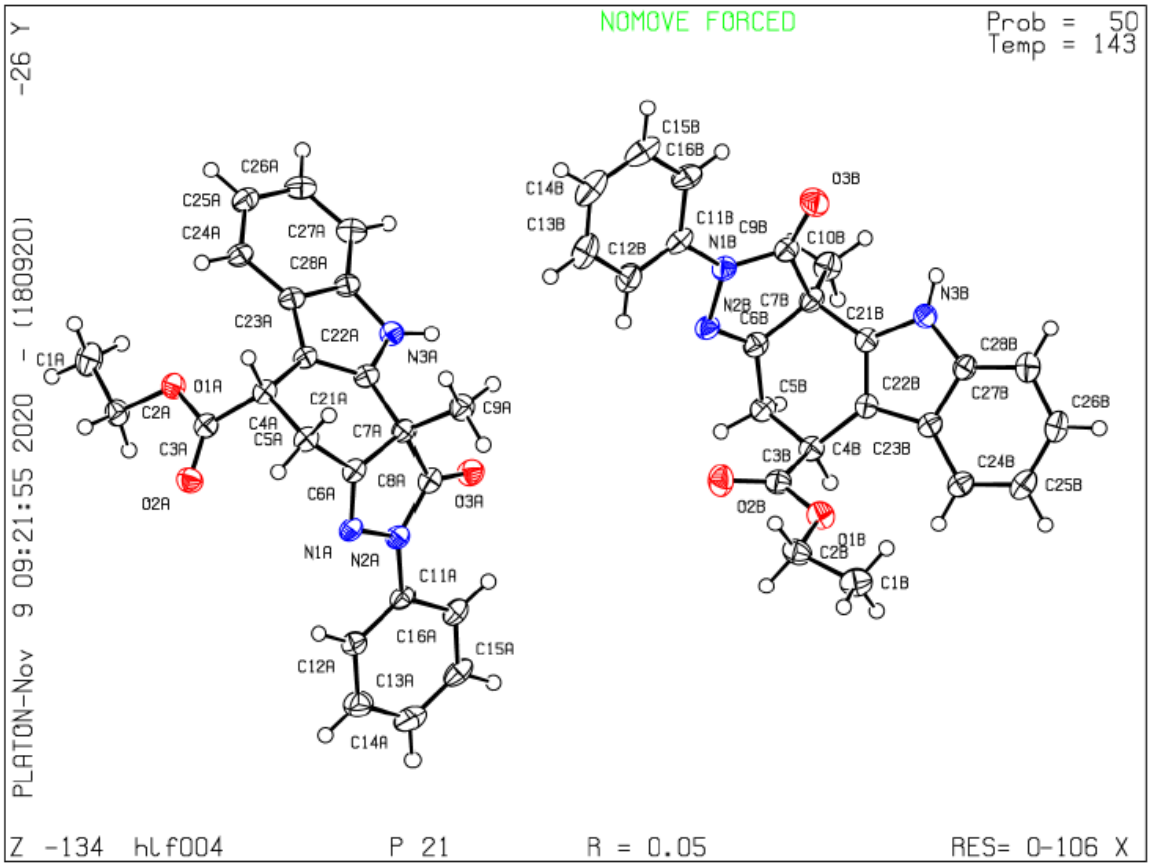

180.435
164.987
160.354
140.825
140.496
135.791
130.817
128.373
128.301
128.259
128.180
126.048
125.886
65.103
64.380
31.988
31.896
29.939
29.907
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8. X-ray crystal structure of product 5a

Single crystal of ($C_{23}H_{21}N_3O_3$) **5a** was recrystallized from mixed solvents of EtOAc and n-hexane. The absolute configuration of the product **5a** was determined to be (*S*,*S*) according to X-ray crystal structural analysis. CCDC 2020511 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Center.

The colourless crystal in flake-shape, with approximate dimensions of 0.222 ×0.085 ×0.069 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 143(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a, b, c, d]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[e].



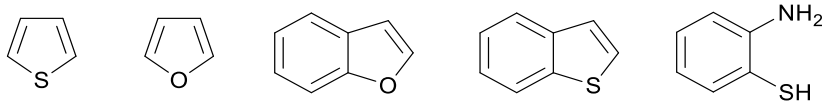


Formula	$C_{23}H_{21}N_3O_3$
Formula mass (amu)	387.43
Space group	$P2_1$
a (Å)	14.9940(4)
b (Å)	7.9399(2)
c (Å)	18.0476(5)
α (deg)	90
β (deg)	110.222(1)
γ (deg)	90
V (Å^3)	2016.14(9)
Z	4
λ (Å)	1.54178
T (K)	143 K
ρ_{calcd} (g cm^{-3})	1.276
μ (mm^{-1})	0.697
Transmission factors	0.797,1.000
θ_{max} (deg)	81.381
No. of unique data, including $F_o^2 < 0$	8393
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	7234
No. of variables	535
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0474
$R_w(F_o^2)$ [b]	0.1117
Goodness of fit	1.047

[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 $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

9. Unsuccessful substrate scopes.



10. Reference

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[c] G. M. Sheldrick, *Acta Cryst*., 2015, **C71**, 3.

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[e] A. L. Spek, *J. Appl. Cryst*., 2003, **36**, 7.