Supporting Information

Catalytic asymmetric synthesis of 3,2'-pyrrolinyl spirooxindoles via conjugate addition/Schmidt-type rearrangement of vinyl azides and (*E*)-alkenyloxindoles

Ziwei Zhong, [a] Zhijie Xiao, [a] Xiaohua Liu, [a] Weidi Cao*[a] and Xiaoming Feng*[a]

Abstract: A catalytic asymmetric conjugate addition/Schmidt-type rearrangement of vinyl azides and (*E*)-alkenyloxindoles was realized in the presence of a chiral *N,N'*-dioxide-Nickel(II) complex. A variety of optically active 3,2'-pyrrolinyl spirooxindoles were obtained in high yields (up to 98%) with excellent diastereo- and enantioselectivities (up to 98% ee, >19:1 dr). The gram-scale experiment and further derivation showed the practicality of this catalytic system. In addition, a possible catalytic cycle and transition state model were proposed based on the control experiments and previous works.

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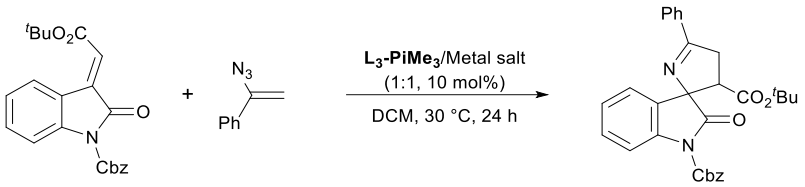
1. General remarks

NMR characterization data were collected on bruker ASCEND™ operating at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR (with complete proton decoupling), and 376 MHz for ^{19}F NMR (with complete proton decoupling). ^{1}H NMR and ^{13}C 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 were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, IC, ID, IF at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. HRMS was recorded on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. and the peaks are reported as absorption maxima (v, cm^{-1}). Circular dichroism spectrum (CD) were recorded on Applied Photophysics Chirascan. Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]_D^{22}$ (*c*: g/100 mL, in CH_2Cl_2). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. The experiments requiring chiral *N*,*N*'-dioxide ligands[1], substrates (*E*)-alkenyloxindoles[2,3], vinyl azides[4] and alkylidene malonate[5] were synthesized according to known procedures. All the solvents including toluene, tetrahydrofuran, diethyl ether, dichloromethane, chloroform, 1,2-dichloroethane, ethyl acetate, acetonitrile and so on were pre-dried over appropriate desiccants, and distilled prior to use. Among them, CH_2Cl_2 was dried over powdered CaH_2 and distilled under nitrogen just before use. Reactions were monitored using thin-layer chromatography (TLC) on GF254 silica gel. Visualization of the developed plates was performed under UV light (254 nm) or using iodine, cobalt thiocyanate or $KMnO_4$. The products were purified by flash column chromatography with silicycle 300-400 mesh silica gel.

2. Optimization of the reaction conditions

Table S1. Screening of metal salts.

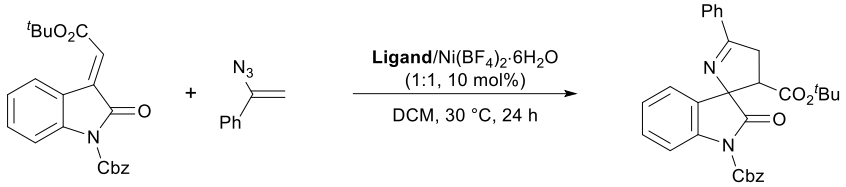


1a **2a** **3aa**

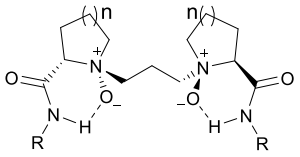
Entry[a]	Metal salts	Yield (%)[b]	ee (%)[c]	dr[d]
1	$Sc(OTf)_3$	48	25	>19:1
2	$Mg(OTf)_2$	80	77	>19:1
3	$Cu(OTf)_2$	37	65	>19:1
4	$Fe(OTf)_3$	43	52	>19:1
5	$Fe(OTf)_2$	47	46	>19:1
6	$Zn(OTf)_2$	74	82	>19:1
7	$Ni(OTf)_2$	85	80	>19:1
8	$Mg(NTf_2)_2$	82	77	>19:1
9	$Mg(ClO_4)_2$	80	74	>19:1
10	$MgBr_2{\cdot}Et_2O$	48	65	>19:1
11	$Ni(NTf_2)_2$	87	80	>19:1
12	$Ni(BF_4)_2{\cdot}6H_2O$	86	83	>19:1

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol) and metal salt/**L_3-PiMe$_3$** (1:1, 10 mol %) in DCM (1.0 mL) at 30 °C for 24 h. [b]Yield of the isolated product. [c]Determined by chiral HPLC analysis. [d]Determined by ^{1}H NMR analysis.

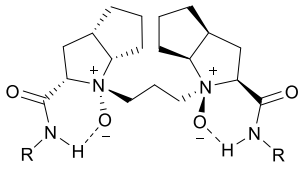
Table S2. Screening of the ligands.



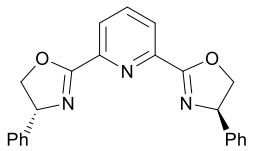
1a **2a** **3aa**



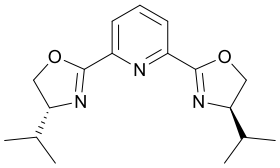
L_3-PiMe$_3$: n = 2, R = 2,4,6-$Me_3C_6H_2$
L_3-PrMe$_3$: n = 1, R = 2,4,6-$Me_3C_6H_2$
L_3-PiMe$_2$: n = 2, R = 2,6-$Me_2C_6H_3$
L_3-PiEt$_2$: n = 2, R = 2,6-$Et_2C_6H_3$
L_3-PiPr$_2$: n = 2, R = 2,6-^{i}Pr$_2$C$_6$H$_3$
L_3-PiPr$_3$: n = 2, R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$
L_3-PiPh: n = 2, R = C_6H_5
L_3-PiCHPh$_2$: n = 2, R = $CHPh_2$
L_3-PiCy: n = 2, R = Cyclopentyl



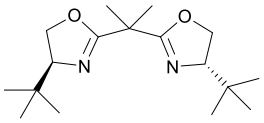
L_3-RaMe$_3$: R = 2,4,6-$Me_3C_6H_2$



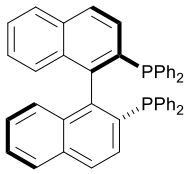
Ph-PyBOX



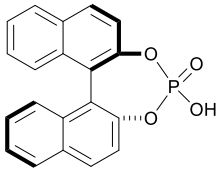
^{i}Pr-PyBOX



^{t}Bu-BOX



BINAP

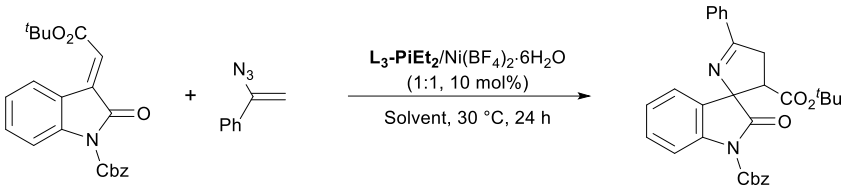


CPA-1

Entry[a]	Ligands	Yield (%)[b]	ee (%)[c]	dr[d]
1	**L_3-PiMe$_3$**	86	83	>19:1
2	**L_3-PrMe$_3$**	80	82	>19:1
3	**L_3-RaMe$_3$**	76	70	>19:1
4	**L_3-PiMe$_2$**	84	86	>19:1
5	**L_3-PiEt$_2$**	88	91	>19:1
6	**L_3-PiPr$_2$**	95	71	>19:1
7	**L_3-PiPr$_3$**	85	68	>19:1
8	**L_3-PiPh**	87	87	>19:1
9	**L_3-PiCHPh$_2$**	56	69	>19:1
10	**L_3-PiCy**	60	43	>19:1
11	**Ph-PyBOX**	52	race	>19:1
12	**^{i}Pr-PyBOX**	63	race	>19:1
13	**^{t}Bu-BOX**	64	race	>19:1
14	**BINAP**	43	race	>19:1
15	**CPA-1**	28	9	>19:1

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Ni(BF_4)_2{\cdot}6H_2O$/**Ligand** (1:1, 10 mol %) in DCM (1.0 mL) at 30 °C for 24 h. [b]Yield of the isolated product. [c]Determined by chiral HPLC analysis. [d]Determined by ^1H NMR analysis.

Table S3. Screening of the solvents.

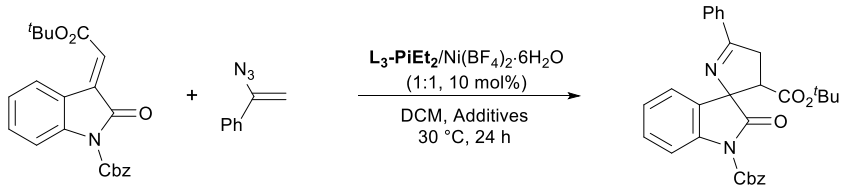


1a **2a** **3aa**

Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]	dr[d]
1	DCE	87	89	>19:1
2	DCM	88	91	>19:1
3	EtOAc	78	60	>19:1
4	Toluene	87	43	>19:1
5	THF	80	76	>19:1
6	MeCN	67	79	>19:1
7	$CHCl_3$	80	87	>19:1
8	Cl_2CHCH_2Cl	87	82	>19:1
9	$Cl_2CHCHCl_2$	84	83	>19:1

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol) and $Ni(BF_4)_2{\cdot}6H_2O$/**L_3-PiEt₂** (1:1, 10 mol %) in solvent (1.0 mL) at 30 °C for 24 h. [b]Yield of the isolated product. [c]Determined by chiral HPLC analysis. [d]Determined by ^1H NMR analysis.

Table S4. Screening of the additives.

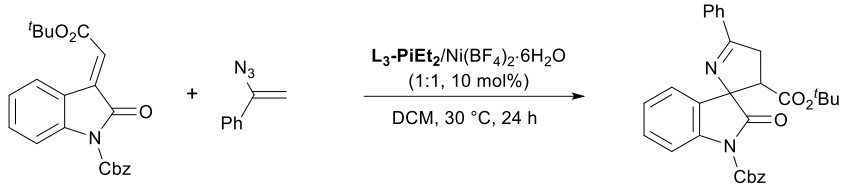


1a **2a** **3aa**

Entry[a]	Additives	Yield (%)[b]	ee (%)[c]	dr[d]
1	4 Å MS (20 mg)	82	87	>19:1
2	3 Å MS (20 mg)	88	80	>19:1
3	5 Å MS (20 mg)	78	78	>19:1
4	$LiNTf_2$ (10 mol%)	70	78	>19:1
5	$NaBAr^F{}_4$ (10 mol%)	85	86	>19:1

[a]The reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), additives and $Ni(BF_4)_2{\cdot}6H_2O$/**L_3-PiEt₂** (1:1, 10 mol %) in DCM (1.0 mL) at 30 °C for 24 h. [b]Yield of the isolated product. [c]Determined by chiral HPLC analysis. [d]Determined by ^1H NMR analysis.

Table S6. Screening of the ratio of the substrates.



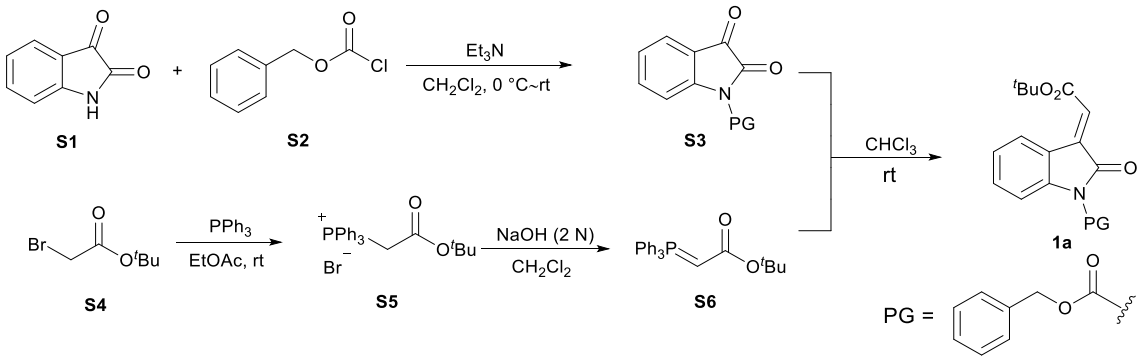
1a **2a** **3aa**

Entry[a]	**1a**(mmol)/**2a**(mmol)	Yield (%)[b]	ee (%)[c]	dr[d]
1	0.10/0.10 (**1:1**)	88	91	>19:1
2	0.10/0.12 (**1:1.2**)	88	91	>19:1
3	0.10/0.14 (**1:1.4**)	90	92	>19:1
4	0.10/0.16 (**1:1.6**)	91	92	>19:1
5	0.10/0.18 (**1:1.8**)	92	92	>19:1
6	0.10/0.20 (**1:2**)	95	92	>19:1

[a]The reactions were performed with **1a**, **2a** and $Ni(BF_4)_2{\cdot}6H_2O$/**L_3-PiEt$_2$** (1:1, 10 mol %) in DCM (1.0 mL) at 30 °C for 24 h. [b]Yield of the isolated product. [c]Determined by chiral HPLC analysis. [d]Determined by ^{1}H NMR analysis.

3. Substrates synthesis

3.1 Typical procedure for the synthesis of (*E*)-alkenyloxindoles



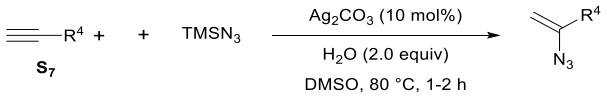
The synthesis of (*E*)-alkenyloxindole **1a**: To a solution of isatin **S1** (2.94 g, 20 mmol) in CH_2Cl_2 (50 mL) was added Et_3N (4.05 g, 40 mmol) at 0 °C, after stirring for 30 min at room temperature, then benzyl carbonochloridate **S2** (4.09 g, 24 mmol) was added at the same temperature, then stirred for 2.5 h. The CH_2Cl_2 was removed under reduced pressure, and the crude product of **S3** was directly used into the next step without further purification.

To a solution of triphenylphosphine (26.23 g, 100 mmol) in ethyl acetate (100 mL) was added *tert*-butyl bromoacetate **S4** (19.51 g, 100 mmol) at room temperature, and the mixture was stirred overnight. The resulting mixture was filtered (solvent: ethyl acetate), and the crude product **S5** (white solid) was directly subjected to the next reaction without further purification. To a solution of **S5** in CH_2Cl_2 (50 mL) was added NaOH (2 N) solution at room temperature until the *p*H value is 12. And the reaction mixture was stirred for another 30 minutes, washed with saturated $NaHCO_3$ solution, and the aqueous layer was extracted with CH_2Cl_2. The combined organic mixtures were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The obtained product **S6** (white solid, 33.48 g, 93 mmol, two steps 93% yield) was used directly for the next step.

To a solution of crude product **S3** in $CHCl_3$ (50 mL) was added **S6** (7.52 g, 20 mmol) at room temperature. After stirring for 30 minutes, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v), the following recrystallization (CH_2Cl_2/PE = 2/1, v/v) was carried out to afford the product (88% yield) as a yellow solid.

Other (*E*)-alkenyloxindoles **1b–1n** were prepared according to the procedure described for **1a**, and **1o–1p** were prepared according to the literature procedure.[3]

3.2 Typical procedure for the synthesis of vinyl azides

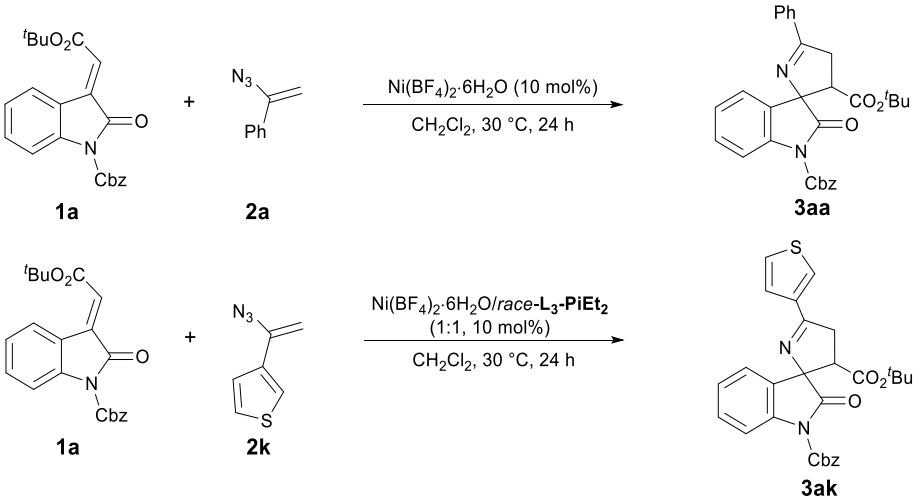


The synthesis of vinyl azide **2a**: To a solution of phenylacetylene **S7** (0.051 mL, 0.5 mmol), $TMSN_3$ (0.132 mL, 1.0 mmol) and H_2O (0.018 mL, 1.0 mmol) in DMSO (2 mL) at 80 °C, Ag_2CO_3 (138 mg, 0.05 mmol) was added. The mixture was then stirred for 1–2 h until the substrate consumed as indicated by TLC. The resulting mixture was concentrated and extracted by CH_2Cl_2 (3 X 15 mL). The organic layer was washed with brine (3 X 40 mL), dried over $MgSO_4$ and concentrated. The crude product was purified with flash column chromatography (silica gel; petroleum ether) and concentrated *in vacuo* to afford vinyl azide **2a** in 75% yield as a pale yellow oil.

Other vinyl azides **2b**–**2m** were prepared according to the procedure described for **2a**.

Safety notice: as with many organic azides, vinyl azides are potentially very dangerous. All users should exercise approriate caution. The explosion danger of organic azides decreases with dimishing fraction of N_3 in the molecular mass. For organic azides to be safely handled or non-explosive, smith rules must be followed. In general, any azides synthesised should be stored below room temperature and in the dark.

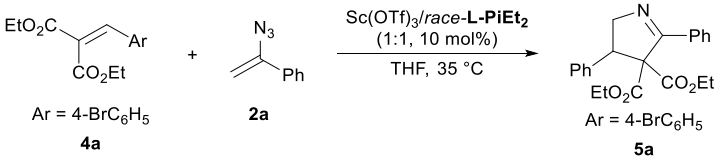
4. General procedure for the preparation of the racemic products 3aa, 5a



An oven-dried test tube was charged with metal salt $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol%, 3.4 mg), **1a** (0.10 mmol, 37.9 mg), **2a** (0.20 mmol, 29.0 mg), and CH_2Cl_2 (1.0 mL) under N_2 atmosphere. The resulted solution was stirred at 30 °C for 24 h. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5/1, v/v) to afford the corresponding racemic product **3aa**.

The reaction was conducted with $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol%, 3.4 mg), ***race*-L$_3$-PiEt$_2$** (10 mol%, 5.9 mg) and **1a** (0.10 mmol, 37.9 mg) in CH_2Cl_2 (1.0 mL) under N_2 atmosphere. The mixture was stirred at 35 °C for 30 min and then cooled to 30 °C. Vinyl azide **2k** (0.20 mmol, 30.0 mg) was added and the resulting mixture was stirred at 30 °C for 24 h. The reaction mixture was subjected to column chromatography on flash silica gel and eluted with petroleum ether/ethyl acetate (5:1, v/v) to afford the corresponding racemic product **3ak**.

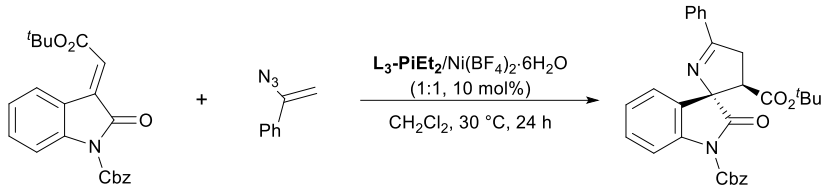
Other racemic products **3** were prepared according to the procedure described for **3aa**.



The reaction was conducted with $Sc(OTf)_3$ (10 mol%, 4.9 mg), ***race*-L$_3$-PiEt$_2$** (10 mol%, 5.9 mg) and **4a** (0.10 mmol, 32.6 mg) in THF (1.0 mL) under N_2 atmosphere. The mixture was stirred at 35 °C for 30 min. Vinyl azide **2a** (0.20 mmol, 29.0 mg) was added and the resulting mixture was stirred at 35 °C for 24 h. The reaction mixture was subjected to column chromatography on flash silica gel and eluted with petroleum ether/ethyl acetate (4:1, v/v) to afford the corresponding racemic product **5a**.

Other racemic products **5** were prepared according to the procedure described for **5a**.

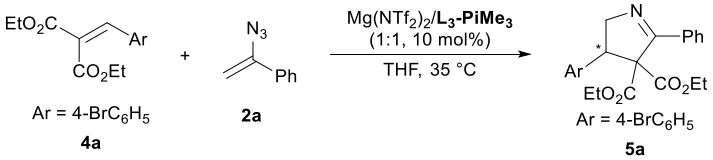
5. General procedure for the preparation of the enantiomerically enriched product 3aa, 5a



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

The reaction was conducted with $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol%, 3.4 mg), **L_3-PiEt$_2$** (10 mol%, 5.9 mg) and **1a** (0.10 mmol, 37.9 mg) in CH_2Cl_2 (1.0 mL) under N_2 atmosphere. The mixture was stirred at 35 °C for 30 min and then cooled to 30 °C. Vinyl azide **2a** (0.20 mmol, 29.0 mg) was added and the resulting mixture was stirred at 30 °C for 24 h. The reaction mixture was subjected to column chromatography on flash silica gel and eluted with petroleum ether/ethyl acetate (5:1, v/v) to afford the corresponding product **3aa**.

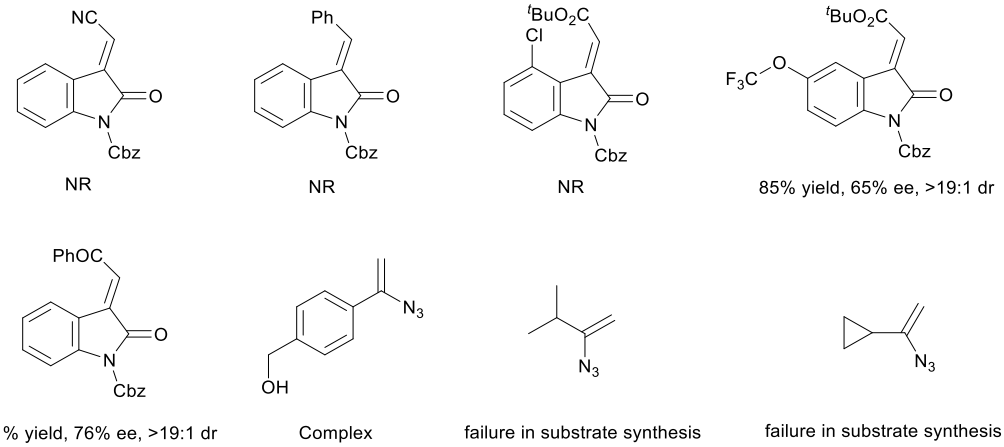
Other catalytic products **3** were prepared according to the procedure described for **3aa**.



The reaction was conducted with $Mg(NTf_2)_2$ (10 mol%, 5.8 mg), **L_3-PiMe$_3$** (10 mol%, 5.6 mg) and **4a** (0.10 mmol, 32.6 mg) in THF (1.0 mL) under N_2 atmosphere. The mixture was stirred at 35 °C for 30 min. Vinyl azide **2a** (0.20 mmol, 29.0 mg) was added and the resulting mixture was stirred at 35 °C for 24 h. The reaction mixture was subjected to column chromatography on flash silica gel and eluted with petroleum ether/ethyl acetate (4:1, v/v) to afford the corresponding racemic product **5a**.

Other catalytic products **5** were prepared according to the procedure described for **5a**.

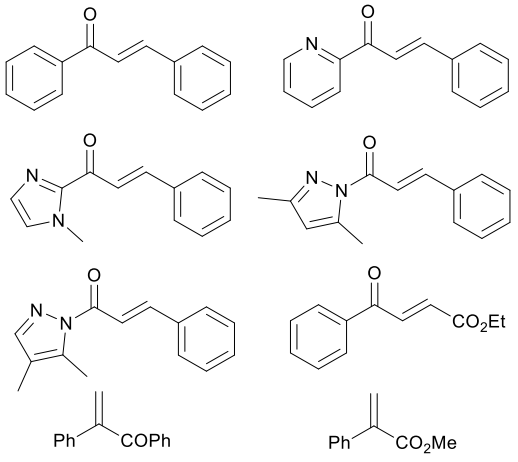
6. Scope limitation



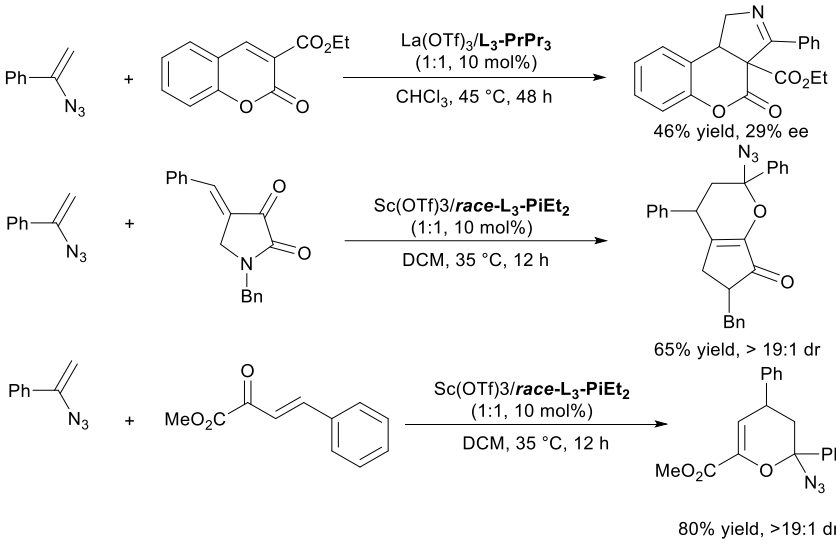
When we change the easter group of (*E*)-alkenyloxindole to cyano group or phenyl group, the reaction didn't occur and the substrate was recovered. The reactions with (*E*)-alkenyloxindoles bearing electron withdrawing halogen group (Cl) at C4-position of phenyl ring was also failed to give the desired product.

We also have tried some other types of substrates to broaden the synthetic scope. There are some substrates that cannot obtain the desired product in our catalytic system. 2-oxo-2H-chromene-3-carboxylate could give the desired product in moderate yield and poor enantioselectivity (46% yield, 29% ee) after conditional screening. In addition, inverse-electron-demand hetero-Diels–Alder reaction could occur when we used (*E*)-1-benzyl-4-benzylidenepyrrolidine-2,3-dion or β,γ-unsaturated α-ketoester as standard substrate.

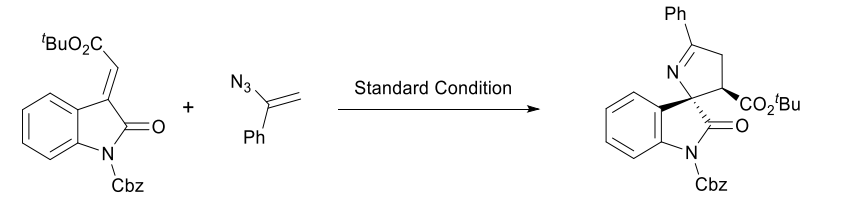
other types of electron-deficient slkenes



NR



7. Experimental procedure for the scale-up reaction



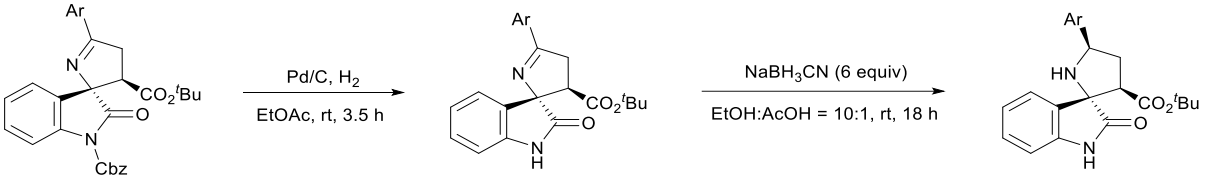
1a
3.0 mmol, 1.137 g

2a
6.0 mmol, 0.870 g

3aa
1.324 g, 89% yield, 92% ee, >19:1 dr

A dry round-bottom flask (50 mL) was charged with $Ni(BF_4)_2{\cdot}6H_2O$ (10 mol%, 0.102 g), **L_3-PiEt$_2$** (10 mol%, 0.177 g) and the substrate **1a** (3.0 mmol, 1.137 g) under N_2 atmosphere. CH_2Cl_2 (30.0 mL) was added and the mixture was stirred at 35 °C for 1 h. Then the mixture was cooled to 30 °C. Subsequently, **2a** (6.0 mmol., 0.870 g) was added. The reaction mixture was stirred at 30 °C for 24 h. The solvent was removed in vacuo and the residue was subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (5:1, v/v) to afford the corresponding product **3aa** (1.324 g, 89% yield, 92% ee, >19:1 dr).

8. General procedure for the synthesis of the compounds 6 and 7



3ai, Ar = 4-ClC$_6$H$_4$
96% ee, >19:1 dr

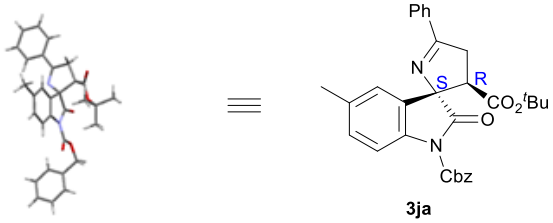
6, Ar = 4-ClC$_6$H$_4$
92% yield, 96% ee, >19:1 dr

7, Ar = 4-ClC$_6$H$_4$
95% yield, 96% ee, >19:1 dr

The compound **3ai** (53.0 mg, 0.10 mmol, 96% ee, >19:1 dr) was dissolved in EtOAc (1.0 mL) and added 10% Pd/C (5.3 mg), and the reaction was stirred at room temperature for 3.5 h under H_2 atmosphere. After completion of the reaction, the reaction mixture was filtered through a pad of celite. Then, the solvent was removed under reduced pressure and the obtained crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give the *N*-H product **6** in 92% yield (36.4 mg) with 96% ee, >19:1 dr.

To a solution of **6** (36.4 mg, 0.09 mmol) in the mixed solvent of EtOH/AcOH (10/1, 1.1 mL) was added $NaBH_3CN$ (0.54 mmol, 34.0 mg) at room temperature. The reaction mixture was stirred for 18 h and then quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with DCM for 2 times. The combined organic layer were washed with brine and dried over Na_2SO_4 The solvent was removed in vacuo and the resulting crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give product **7** in 95% yield (34.8 mg) with 96% ee, >19:1 dr.

9. X-ray structure



3ja

The absolute configuration of the product **3ja** (the single crystal was grown applying CH_2Cl_2 as solvent and petroleum ether as anti-solvent) was determined by its X-ray crystal structure. CCDC **1977126** contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Datablock: cu_20191124ZZW_0m_a

```
Bond precision:  C-C = 0.0027 A          Wavelength=1.54178

Cell:            a=10.5509(13)     b=15.2802(19)     c=16.524(2)
                 alpha=90          beta=90           gamma=90
Temperature:     200 K

                 Calculated                Reported
Volume           2664.0(6)                 2664.0(6)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C31 H30 N2 O5             ?
Sum formula      C31 H30 N2 O5             C31 H30 N2 O5
Mr               510.57                    510.57
Dx,g cm-3        1.273                     1.273
Z                4                         4
Mu (mm-1)        0.702                     0.702
F000             1080.0                    1080.0
F000'            1083.32
h,k,lmax         12,18,20                  12,18,20
Nref             5085[ 2873]               5043
Tmin,Tmax        0.745,0.804               0.606,0.753
Tmin'            0.729

Correction method= # Reported T Limits: Tmin=0.606 Tmax=0.753
AbsCorr = MULTI-SCAN

Data completeness= 1.76/0.99      Theta(max)= 70.255

R(reflections)= 0.0332( 4990)     wR2(reflections)= 0.0887( 5043)

S = 1.066                 Npar= 347
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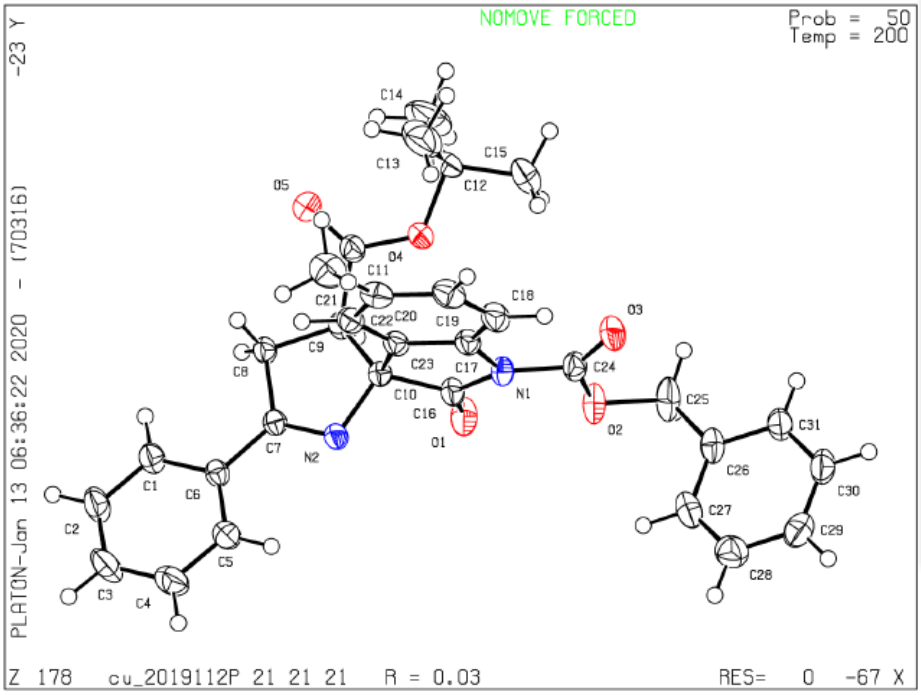


Crystallographic Data for $C_{31}H_{30}N_2O_5$.

Formula	$C_{31}H_{30}N_2O_5$
Formula mass (amu)	510.57
Space group	$P2_12_12_1$
a (Å)	10.5509 (13)
b (Å)	15.2802 (19)
c (Å)	16.524 (2)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2664.0 (6)
Z	4
λ (Å)	1.54178
T (K)	200 K
ρ_{calcd} (g cm^{-3})	1.273
μ (mm^{-1})	0.702
Transmission factors	0.606-0.753
$2\theta_{max}$ (deg)	70.255
No. of unique data, including $F_o^2 < 0$	5043
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4990
No. of variables	347
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0332
$R_w(F_o^2)$ [b]	0.0887
Goodness of fit	1.066

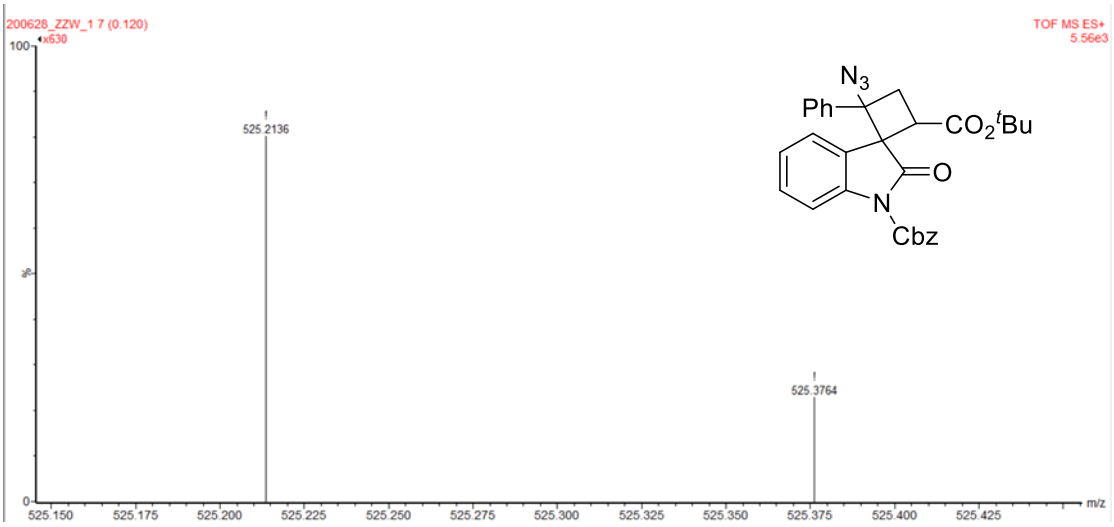
[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

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

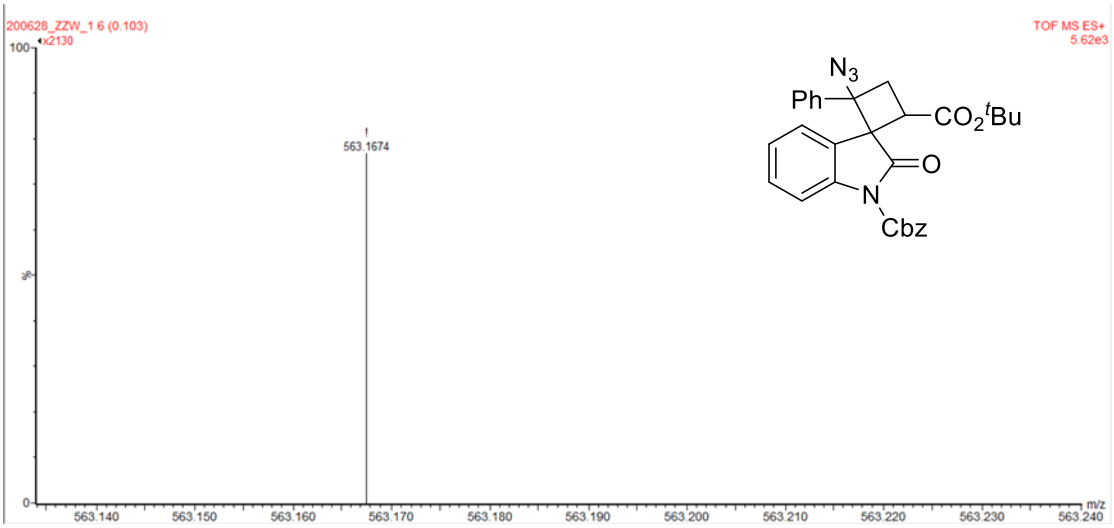
10. HRMS analysis

Copies of HRMS (ESI) of azidocyclobutane intermediate for standard reaction in the mixture of $Ni(BF_4)_2 \cdot 6H_2O$, L_3-$PiEt_2$, **1a** and **2a** (1:1:1:2) in DCM.

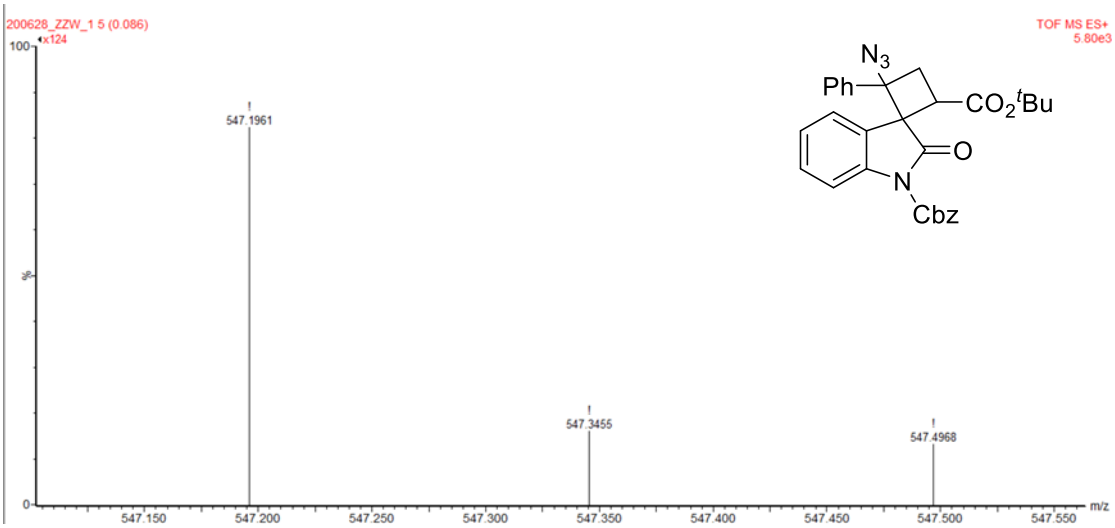
HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{29}N_4O_5^+$ 525.2132; Found 525.2136.



HRMS (FTMS+c ESI) m/z: $[M + K]^+$ calcd for $C_{30}H_{28}KN_4O_5^+$ 563.1691; Found 563.1674.

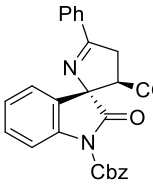


HRMS (FTMS+c ESI) m/z: $[M + Na]^+$ calcd for $C_{30}H_{28}N_4NaO_5^+$ 547.1952; Found 547.1961.



11. The characterization of typical products

1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3aa)



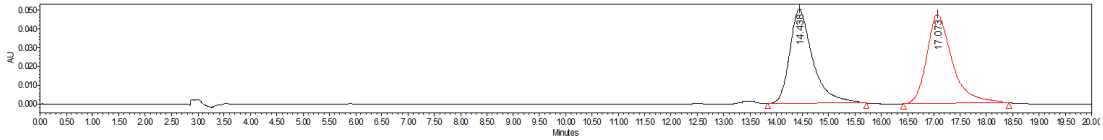
47.1 mg, 95% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 17.42 min, t_r (minor) = 14.89 min, ee = 92%, d.r. > 19:1. $[\alpha]^{22}_D$ = +27.49 (*c* = 0.68 in CH_2Cl_2). Melting point: 104–106 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.58 – 7.32 (m, 9H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 5.50 (q, *J* = 12.0 Hz, 2H), 3.96 (t, *J* = 9.8 Hz, 1H), 3.76 (dd, *J* = 17.4, 10.0 Hz, 1H), 3.46 (dd, *J* = 17.4, 9.7 Hz, 1H), 0.94 (s, 9H) ppm.

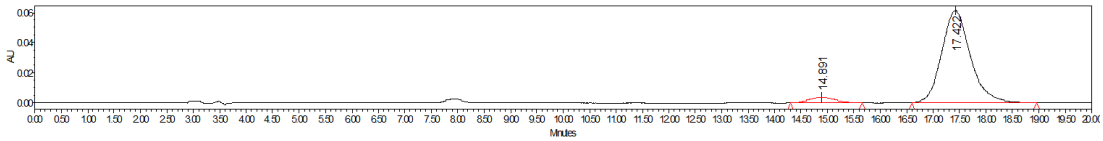
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.4, 175.3, 168.8, 150.9, 139.7, 135.0, 133.1, 131.8, 130.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.2, 125.2, 124.4, 115.4, 82.6, 81.9, 68.8, 52.2, 37.8, 27.2 ppm.

IR (neat): 2976, 2361, 1778, 1731, 1606, 1574, 1475, 1376, 1345, 1287, 1227, 1160, 1084, 1013, 922, 844, 755, 694, 512 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{30}H_{29}N_2O_5^+$ 487.2071; Found 487.2076.

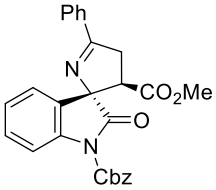


Peak	Retention Time	Area	% Area
1	14.438	1497334	49.38
2	17.073	1535019	50.62



Peak	Retention Time	Area	% Area
1	14.891	89568	3.74
2	17.422	2307558	96.26

1-benzyl 3'-methyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ba)



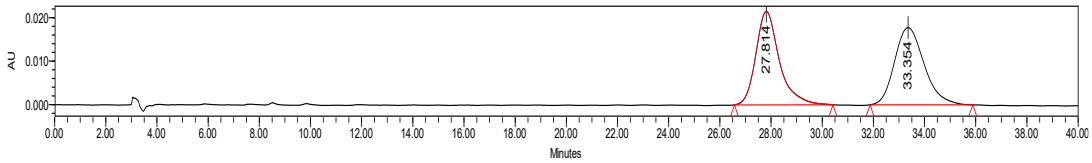
41.3mg, 91% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 33.38 min, t_r (minor) = 27.89 min, ee = 85%. d.r. > 19:1. $[\alpha]^{22}_D$ = +41.07 (*c* = 0.34 in CH_2Cl_2). Melting point: 78–80 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.60 – 7.28 (m, 9H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (ddd, *J* = 7.5, 1.4, 0.6 Hz, 1H), 5.50 (q, *J*=12.0 Hz, 2H), 4.00 (dd, *J* = 9.7, 8.5 Hz, 1H), 3.89 (dd, *J* = 17.3, 8.5 Hz, 1H), 3.54 (dd, *J* = 17.3, 9.7 Hz, 1H), 3.23 (s, 3H) ppm.

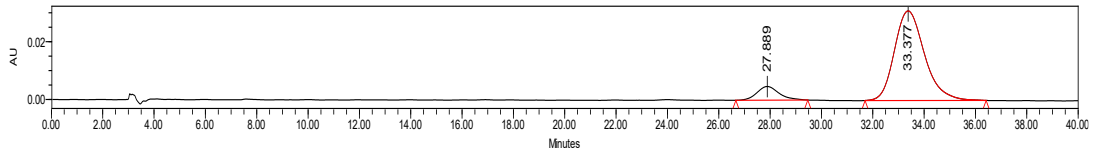
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.3, 174.9, 170.8, 150.8, 139.3, 134.9, 132.9, 131.9, 130.3, 128.8, 128.7, 128.6, 128.4, 128.1, 126.9, 125.1, 124.2, 115.5, 83.3, 68.9, 52.1, 50.9, 38.6 ppm.

IR (neat): 2951, 2361, 1775, 1735, 1608, 1575, 1473, 1381, 1344, 1285, 1224, 1164, 1083, 1013, 949, 902, 757, 695, 551, 496 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{23}N_2O_5^+$ 455.1601; Found 455.1608.

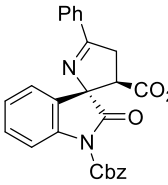


Peak	Retention Time	Area	% Area
1	27.814	1373427	49.11
2	33.354	1423419	50.89



Peak	Retention Time	Area	% Area
1	27.889	206084	7.56
2	33.377	2519281	92.44

1-benzyl 3'-ethyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ca)



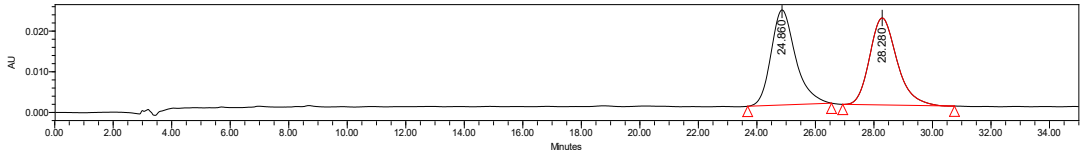
42.1 mg, 90% yield; white solid ; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), t_r (major) = 27.90 min, t_r (minor) = 24.66 min, ee = 89%, d.r. > 19:1, $[\alpha]^{22}_D$ = +54.56 (*c* = 1.25 in CH_2Cl_2). Melting point: 84–86 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.59 – 7.30 (m, 9H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (ddd, *J* = 7.6, 1.4, 0.6 Hz, 1H), 5.50 (q, *J* = 12.0Hz, 2H), 3.99 (t, *J* = 9.4 Hz, 1H), 3.87 (dd, *J* = 17.3, 9.1 Hz, 1H), 3.71 (qd, *J* = 7.1, 2.2 Hz, 2H), 3.52 (dd, *J* = 17.3, 9.7 Hz, 1H), 0.67 (t, *J* = 7.1 Hz, 3H) ppm.

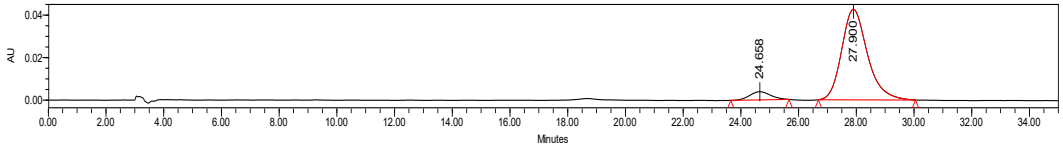
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.3, 175.1, 170.1, 150.8, 139.5, 135.0, 133.0, 131.9, 130.3, 128.8, 128.72, 128.6, 128.4, 128.1, 126.9, 125.1, 124.3, 115.4, 83.1, 68.9, 61.2, 51.0, 38.4, 13.5 ppm.

IR (neat): 2980, 2361, 1776, 1734, 1607, 1574, 1473, 1380, 1345, 1286, 1224, 1164, 1085, 1017, 918, 755, 694, 550, 511 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{25}N_2O_5^+$ 469.1758; Found 469.1762.

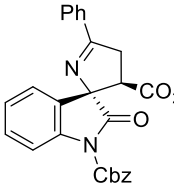


Peak	Retention Time	Area	% Area
1	24.860	1356985	49.45
2	28.280	1386935	50.55



Peak	Retention Time	Area	% Area
1	24.658	2486400	5.55
2	27.900	42331275	94.45

1-benzyl 3'-isopropyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3da)



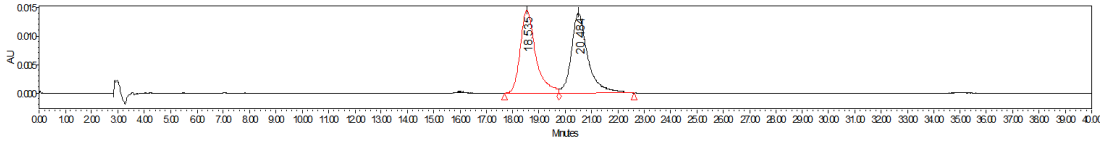
44.3 mg, 92% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 20.57 min, t_r (minor) = 18.53 min, ee = 89%, d.r. > 19:1. $[\alpha]^{22}_D$ = +46.30 (*c* = 0.84 in CH_2Cl_2). Melting point: 80–82 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.97 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.61 – 7.29 (m, 9H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.51 (q, *J* =12.0 Hz, 2H), 4.59 (h, *J* = 6.3 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.86 (dd, *J* = 17.3, 9.4 Hz, 1H), 3.51 (dd, *J* = 17.3, 9.7 Hz, 1H), 1.00 (d, *J* = 6.3 Hz, 3H), 0.44 (d, *J* = 6.2 Hz, 3H) ppm.

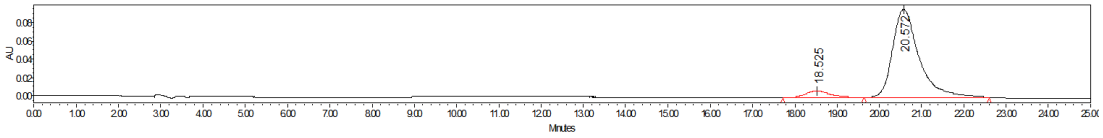
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.3, 175.1, 169.5, 150.8, 139.6, 135.0, 133.0, 131.9, 130.2, 128.8, 128.7, 128.6, 128.4, 128.1, 126.9, 125.1, 124.4, 115.5, 82.9, 69.0, 68.9, 51.1, 38.3, 21.7, 20.5 ppm.

IR (neat): 2980, 2361, 2336, 1778, 1732, 1607, 1574, 1473, 1379, 1346, 1285, 1225, 1165, 1107, 1014, 902, 754, 694, 502 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{27}N_2O_5^+$ 483.1914; Found 483.1921.

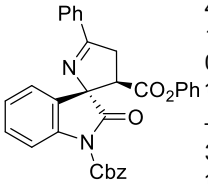


Peak	Retention Time	Area	% Area
1	18.535	591297	49.35
2	20.484	606983	50.65



Peak	Retention Time	Area	% Area
1	18.525	233429	5.34
2	20.572	4135804	94.66

1-benzyl 3'-phenyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ea)



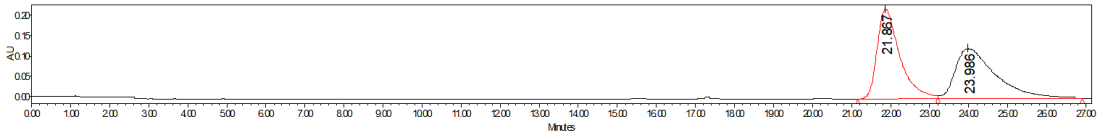
47.4 mg, 92% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IF, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 23.82 min, t_r (minor) = 22.03 min, ee = 86%; d.r. > 19:1. $[\alpha]^{22}_{D}$ = –27.49 (*c* = 0.86 in CH_2Cl_2). Melting point: 75–77°C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.06 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.97 – 7.89 (m, 2H), 7.53 – 7.33 (m, 9H), 7.21 – 7.08 (m, 5H), 6.29 – 6.16 (m, 2H), 5.47 (q, *J* = 12Hz, 2H), 4.34 – 4.22 (m, 1H), 3.96 (dd, *J* = 17.6, 9.1 Hz, 1H), 3.64 (dd, *J* = 17.6, 9.9 Hz, 1H) ppm.

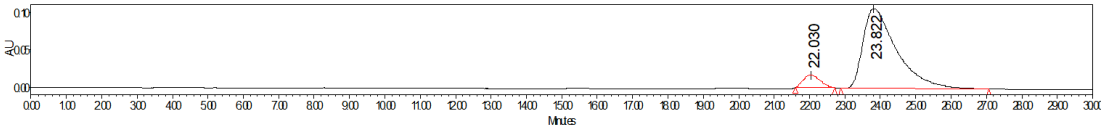
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.1, 174.8, 169.1, 150.7, 150.0, 139.8, 134.9, 132.9, 132.0, 130.6, 129.4, 128.8, 128.6, 128.5, 128.1, 126.9, 126.2, 125.4, 124.7, 121.1, 115.8, 83.2, 69.0, 50.8, 38.6 ppm.

IR (neat): 3061, 2361, 1770, 1736, 1606, 1483, 1381, 1344, 1284, 1223, 1163, 1079, 1015, 1083, 1041, 1013, 844, 755, 699 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{25}N_2O_5^+$ 517,1758; Found 517.1763.

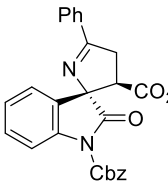


Peak	Retention Time	Area	% Area
1	21.867	8838870	50.55
2	23.986	8648160	49.45



Peak	Retention Time	Area	% Area
1	22.030	544348	7.14
2	23.822	7083489	92.86

dibenzyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3fa)



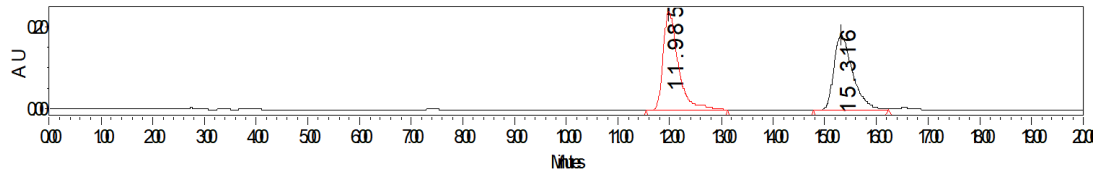
48.2 mg, 91% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 12.01 min, t_r (minor) = 15.76 min, ee = 91%, d.r. >19:1. $[\alpha]^{23}_D$ = +48.38 (*c* = 0.68 in CH_2Cl_2). Melting point: 84–86°C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.85 – 7.73 (m, 3H), 7.44 – 7.07 (m, 12H), 6.97 (td, *J* = 7.6, 1.1 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.85 – 6.66 (m, 2H), 5.33 (q, *J* = 12 Hz, 2H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 3.95 (t, *J* = 9.4 Hz, 1H), 3.80 (dd, *J* = 17.4, 9.0 Hz, 1H), 3.46 (dd, *J* = 17.3, 9.7 Hz, 1H) ppm.

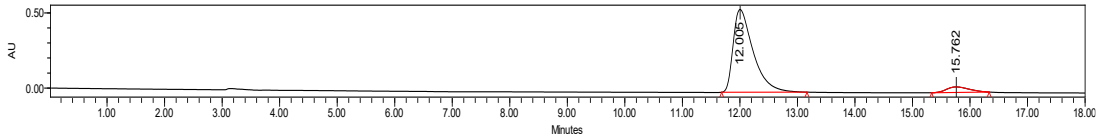
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.2, 174.9, 170.1, 150.6, 139.3, 135.0, 134.6, 133.0, 131.9, 130.3, 128.8, 128.7, 128.6, 128.4, 128.4, 128.1, 126.6, 125.1, 124.2, 115.6, 83.1, 68.8, 67.3, 50.9, 38.5 ppm.

IR (neat): 3033, 2361, 1776, 1736, 1606, 1575, 1459, 1382, 1345, 1285, 1224, 1164, 1084, 1015, 752, 695(cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{27}N_2O_5^+$ 531.1914; Found 531.1922.

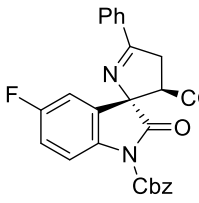


Peak	Retention Time	Area	% Area
1	11.985	4867309	50.72
2	15.316	4729915	49.28



Peak	Retention Time	Area	% Area
1	12.005	13581952	95.49
2	15.762	641286	4.51

1-benzyl 3'-(tert-butyl) (3S,3'R)-5-fluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ga)



47.8 mg, 93% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 20.97 min, t_r (minor) = 14.21 min, ee = 91%, d.r.> 19:1. $[\alpha]^{27}_D$ = +47.38 (*c* = 0.308 in CH_2Cl_2). Melting point: 79–81 °C.

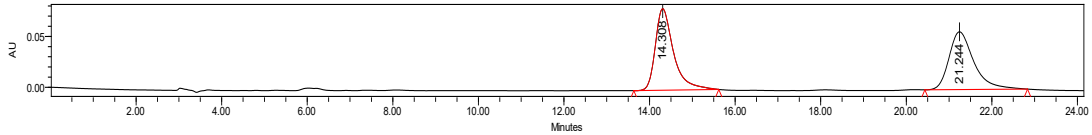
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.93 – 7.83 (m, 2H), 7.59 – 7.31 (m, 8H), 7.06 (td, *J* = 8.9, 2.8 Hz, 1H), 6.73 (dd, *J* = 7.4, 2.7 Hz, 1H), 5.49 (q, *J* = 12.0 Hz, 2H), 3.95 (t, *J* = 9.8 Hz, 1H), 3.75 (dd, *J* = 17.5, 9.8 Hz, 1H), 3.47 (dd, *J* = 17.5, 9.8 Hz, 1H), 0.99 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.0, 174.9, 168.6, 160.2 (d, *J* = 246.4 Hz), 150.8, 135.7 (d, *J* = 2.0 Hz) , 135.0, 132.9, 132.0, 128.9 (d, *J* = 8.1 Hz), 128.8, 128.6, 128.4, 128.2, 116.8, 116.8, 116.7 (d, *J* = 19.2 Hz), 112.1 (d, *J* =24.2 Hz), 82.6 (d, *J* = 2.0 Hz), 82.1, 69.0, 52.1, 38.0, 27.3 ppm.

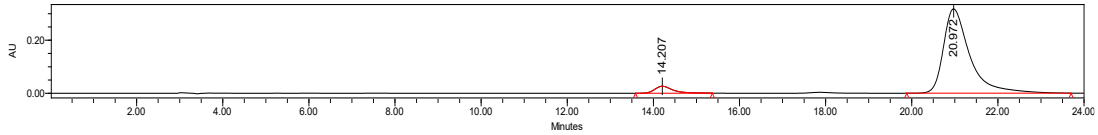
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -116.7 ppm.

IR (neat): 2977, 2361, 1780, 1731, 1608, 1574, 1484, 1453, 1376, 1344, 1275, 1228, 1156, 1080, 1027, 826, 762, 693, 596, 517 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}FN_2O_5^+$ 515.1977; Found 515.1982.

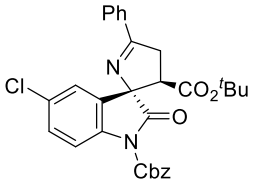


Peak	Retention Time	Area	% Area
1	14.308	2370916	50.89
2	21.244	2287593	49.11



Peak	Retention Time	Area	% Area
1	14.207	645479	4.57
2	20.972	13487787	95.43

1-benzyl 3'-(tert-butyl) (3S,3'R)-5-chloro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ha)



46.1 mg, 87% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 21.18 min, t_r (minor) = 12.96 min, ee = 91%; d.r. > 19:1. $[\alpha]^{23}_D$ = +22.19 (*c* = 0.77 in CH_2Cl_2). Melting point: 81–83 °C.

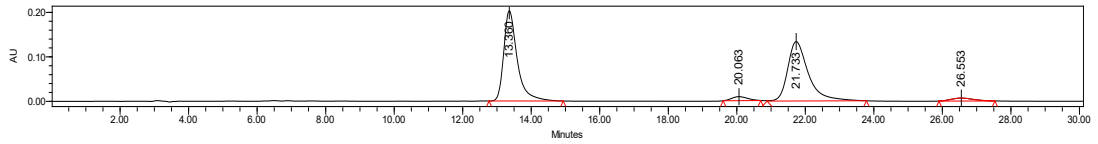
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.7 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.56 – 7.32 (m, 9H), 6.97 (d, *J* = 2.3 Hz, 1H), 5.49 (q, J = 12.0 Hz, 2H), 3.94 (t, *J* = 9.8 Hz, 1H), 3.76 (dd, *J* = 17.5, 9.8 Hz, 1H), 3.48 (dd, *J* = 17.6, 9.8 Hz, 1H), 0.99 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 177.0, 174.6, 168.6, 150.7, 138.2, 134.9, 132.9, 132.1, 130.7, 130.1, 129.0, 128.8, 128.7, 128.4, 128.4, 128.2, 124.7, 116.7, 82.5, 82.2, 69.1, 52.1, 38.0, 27.3 ppm.

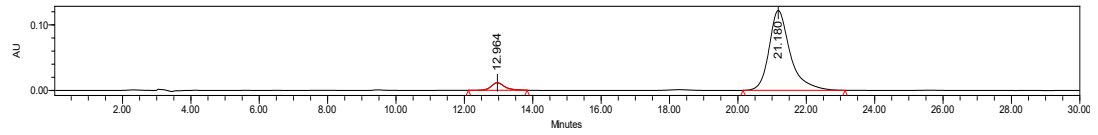
IR (neat): 2975, 2361, 1781, 1731, 1605, 1574, 1474, 1375, 1337, 1296, 1269, 1227, 1158, 1073, 1025, 874, 826, 796, 760, 693, 550, 500 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{35}ClN_2O_5^+$ 531.1681; Found 531.1689.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{37}ClN_2O_5^+$ 533.1651; Found 533.1657.

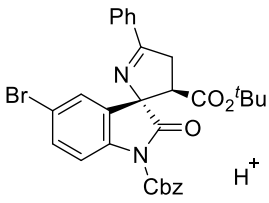


Peak	Retention Time	Area	% Area
1	13.360	5545305	47.42
2	20.063	289210	2.47
3	21.733	5568910	47.62
4	26.533	290347	2.48



Peak	Retention Time	Area	% Area
1	12.964	241494	4.43
2	21.180	5212689	95.57

1-benzyl 3'-(tert-butyl) (3S,3'R)-5-bromo-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ia)



48.8 mg, 85% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 22.41 min, t_r (minor) = 13.76 min, ee = 91%, d.r. > 19:1. $[\alpha]^{24}_D$ = +18.50 (*c* = 0.69 in CH_2Cl_2). Melting point: 79–81 °C.

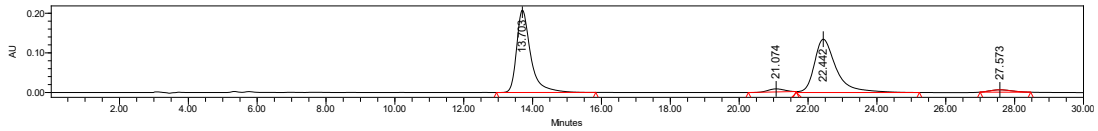
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.92 – 7.85 (m, 3H), 7.54 – 7.34 (m, 9H), 7.10 (d, *J* = 2.1 Hz, 1H), 5.53 – 5.43 (m, 2H), 3.94 (t, *J* = 9.7 Hz, 1H), 3.76 (dd, *J* = 17.5, 9.7 Hz, 1H), 3.48 (dd, *J* = 17.5, 9.8 Hz, 1H), 1.00 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.0, 174.5, 168.6, 150.7, 138.7, 134.9, 133.1, 132.9, 132.1, 129.4, 128.8, 128.7, 128.5, 128.4, 128.2, 127.5, 118.1, 117.1, 82.4, 82.2, 69.1, 52.1, 38.0, 27.3 ppm.

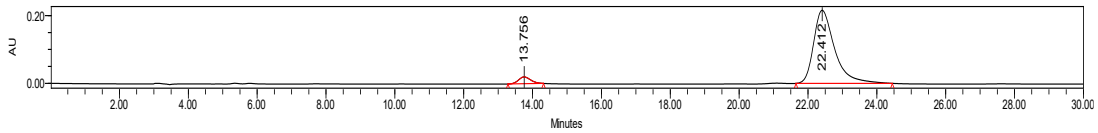
IR (neat): 2974, 2361, 1780, 1730, 1605, 1574, 1472, 1374, 1336, 1296, 1267, 1226, 1157, 1092, 1063, 1023, 874, 823, 737, 694, 552, 498 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{79}BrN_2O_5^+$ 575.1176; Found 577.1182.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{81}BrN_2O_5^+$ 577.1156; Found 577.1163.

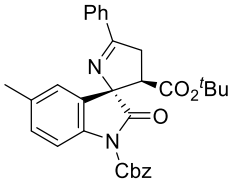


Peak	Retention Time	Area	% Area
1	13.703	5897877	47.84
2	21.074	252722	2.05
3	22.442	5920843	48.02
4	27.573	257691	2.09



Peak	Retention Time	Area	% Area
1	13.756	434811	4.45
2	22.412	9333049	95.55

1-benzyl 3'-(tert-butyl) (3S,3'R)-5-methyl-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ja)



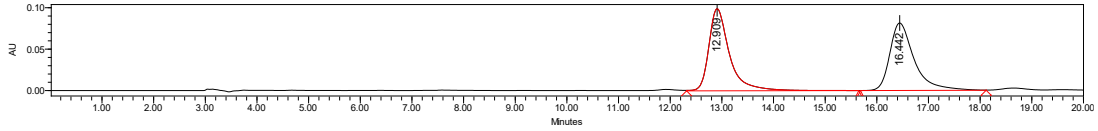
48.5 mg, 95% yield; white solide; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 16.81 min, t_r (minor) = 13.52 min, ee = 88%; d.r. > 19:1. $[\alpha]^{22}_D$ = +27.37 (*c* = 0.72 in CH_2Cl_2). Melting point: 88–90°C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 – 7.76 (m, 3H), 7.62 – 7.31 (m, 8H), 7.17 – 7.10 (m, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 5.49 (q, *J* = 12.0 Hz, 2H), 3.95 (t, *J* = 9.8 Hz, 1H), 3.77 (dd, *J* = 17.4, 9.9 Hz, 1H), 3.45 (dd, *J* = 17.4, 9.8 Hz, 1H), 2.24 (s, 3H), 0.95 (s, 9H) ppm.

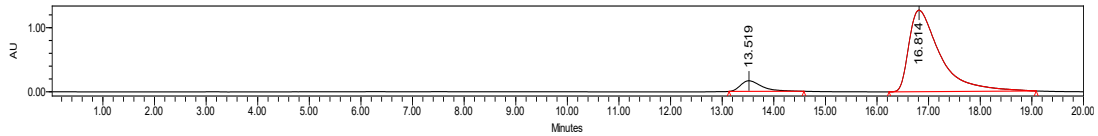
^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ = 176.2, 175.5, 168.9, 150.9, 137.3, 135.1, 135.0, 133.2, 131.8, 130.6, 128.8, 128.7, 128.5, 128.4, 128.1, 127.1, 124.9, 115.2, 82.8, 81.8, 68.7, 52.1, 37.9, 27.2, 21.0 ppm.

IR (neat): 3730, 2971, 2361, 2336, 1777, 1730, 1605, 1574, 1489, 1451, 1375, 1338, 1306, 1278, 1226, 1154, 1087, 1023, 819, 736, 693, 591, 550, 512 (cm^{-1}).

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{31}N_2O_5^+$ 511.2227; Found 511.2232.



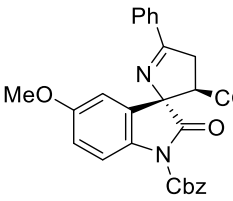
Peak	Retention Time	Area	% Area
1	12.909	2742360	50.75
2	16.422	2660812	49.25



Peak	Retention Time	Area	% Area
1	13.519	3310821	5.91

2	16.814	52708337	94.09

1-benzyl 3'-(tert-butyl) (3S,3'R)-5-methoxy-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ka)



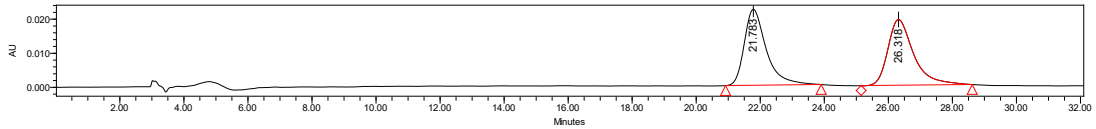
47.9 mg, 91% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 26.15 min, t_r (minor) = 21.99 min, ee = 87%; d.r.> 19:1. $[\alpha]^{27}_D$ = +22.92 (*c* = 0.29 in CH_2Cl_2). Melting point: 98–100 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.94 – 7.85 (m, 3H), 7.55 – 7.32 (m, 8H), 6.87 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 5.58 (q, *J* = 12.0 Hz, 2H), 3.95 (t, *J* = 9.8 Hz, 1H), 3.76 (dd, *J* = 17.5, 9.9 Hz, 1H), 3.70 (s, 3H), 3.46 (dd, *J* = 17.5, 9.8 Hz, 1H), 0.97 (s, 9H) ppm.

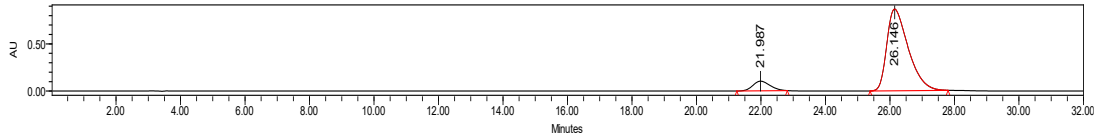
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.4, 175.3, 168.9, 157.4, 150.9, 135.1, 133.1, 133.0, 131.9, 128.8, 128.7, 128.5, 128.4, 128.4, 128.1, 116.4, 115.2, 110.6, 83.0, 81.8, 68.7, 55.9, 52.1, 37.9, 27.3 ppm.

IR (neat): 3726, 2974, 2361, 2336, 1777, 1730, 1606, 1489, 1454, 1376, 1343, 1280, 1227, 1160, 1085, 1020, 819, 756, 692 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{31}N_2O_6^+$ 521.2177; Found 521.2182.

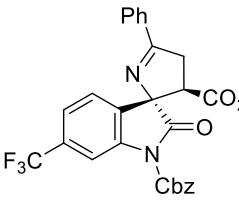


Peak	Retention Time	Area	% Area
1	21.783	1062724	49.71
2	26.318	1074996	50.29



Peak	Retention Time	Area	% Area
1	21.987	2720518	6.38
2	26.146	39901707	93.62

1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-phenyl-6-(trifluoromethyl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3la)



49.6 mg, 88% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.02 min, t_r (minor) = 10.79 min, ee = 95%, d.r. > 19:1. $[\alpha]^{22}_D$ = +37.10 (*c* = 0.12 in CH_2Cl_2). Melting point: 82–84 °C.

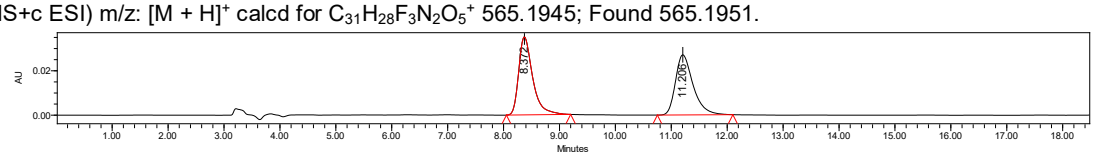
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.36 – 8.27 (m, 1H), 7.91 – 7.83 (m, 2H), 7.57 – 7.36 (m, 9H), 7.11 (d, *J* = 7.8 Hz, 1H), 5.51 (d, *J* = 3.3 Hz, 2H), 3.97 (t, *J* = 9.8 Hz, 1H), 3.78 (dd, *J* = 17.5, 9.9 Hz, 1H), 3.50 (dd, *J* = 17.6, 9.8 Hz, 1H), 0.94 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.3, 174.5, 168.5, 150.6, 140.2, 134.7, 132.8, 132.6 (J_{C-F} = 32.3 Hz), 132.1, 131.1, 128.9, 128.8, 128.7, 128.5, 128.3, 124.9, 123.7 (J_{C-F} = 273.7 Hz),122.1 (J_{C-F} = 5.1 Hz), 112.7 (J_{C-F} = 4.0 Hz), 82.3, 82.2, 69.3, 52.2, 38.0, 27.2 ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ = -62.7 ppm.

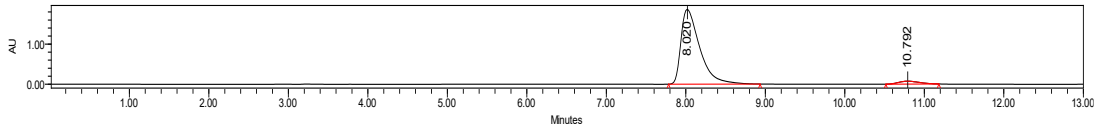
IR (neat): 3730, 2927, 2361, 2336, 1784, 1735, 1607, 1574, 1500, 1441, 1366, 1344, 1280, 1223, 1165, 1128, 1064, 1033, 900, 838, 798, 753, 692 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{28}F_3N_2O_5^+$ 565.1945; Found 565.1951.



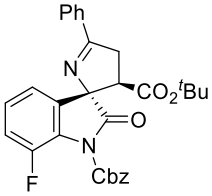
Peak	Retention Time	Area	% Area
1	8.372	608994	50.70

2	11.206	592255	49.30



Peak	Retention Time	Area	% Area
1	8.020	30509835	97.49
2	10.792	786428	2.51

1-benzyl 3'-(tert-butyl) (3S,3'R)-7-fluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ma)



41,6 mg, 81% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel ID, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 17.24 min, t_r (minor) = 22.11 min, ee = 94%, d.r. > 19:1. $[\alpha]^{23}_D$ = +46.86 (*c* = 0.38 in CH_2Cl_2). Melting point: 150–152 °C.

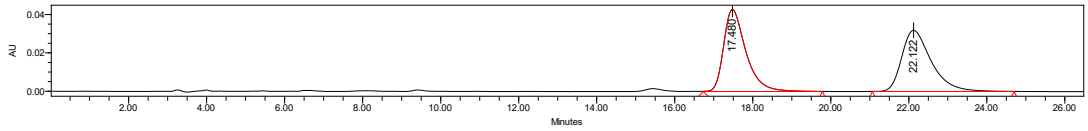
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 – 7.84 (m, 2H), 7.56 – 7.34 (m, 8H), 7.16 – 7.05 (m, 2H), 6.80 (dt, *J* = 7.1, 1.1 Hz, 1H), 5.51 – 5.43 (m, 2H), 3.98 – 3.91 (m, 1H), 3.78 (dd, *J* = 17.4, 9.9 Hz, 1H), 3.46 (dd, *J* = 17.5, 9.7 Hz, 1H), 0.99 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.8, 174.6, 168.8, 149.3, 148.9 (d, *J* = 253.5 Hz), 134.6, 133.0, 132.0, 130.5, 130.5, 128.8, 128.8, 128.7, 128.6 (d, *J* = 25.3 Hz), 126.4, 126.3 (d, *J* = 7.1 Hz), 120.4 (d, *J* = 3.0 Hz), 118.5 (d, *J* = 20.2 Hz), 83.1 (d, *J* = 2.0 Hz), 82.2, 70.0, 52.0, 38.1, 27.4 ppm.

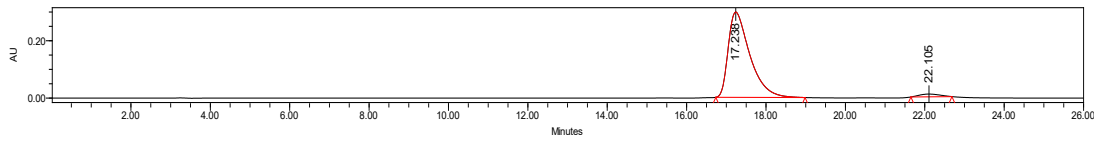
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ = −118.33 ppm.

IR (neat): 2976, 2361, 1755, 1732, 1605, 1574, 1490, 1463, 1348, 1268, 1230, 1191, 1154, 1018, 949, 843, 795, 744, 694, 585 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}FN_2O_5^+$ 515.1977; Found 515.1982.

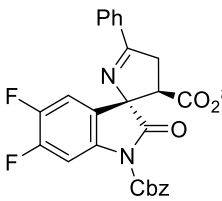


Peak	Retention Time	Area	% Area
1	17.480	1688240	50.26
2	22.122	1670764	49.74



Peak	Retention Time	Area	% Area
1	17,238	11244285	97.08
2	22.105	338043	2.92

1-benzyl 3'-(tert-butyl) (3S,3'R)-5,6-difluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3na)



52.1 mg, 98% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.44 min, t_r (minor) = 11.23 min, ee = 90%, d.r. > 19:1. $[\alpha]^{22}_D$ = +38.44 (*c* = 0.77 in CH_2Cl_2). Melting point: 84–86 °C.

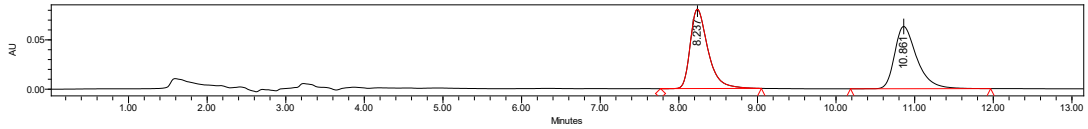
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (dd, *J* = 11.2, 6.9 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.54 – 7.49 (m, 3H), 7.46 – 7.34 (m, 5H), 6.84 (dd, *J* = 8.9, 7.6 Hz, 1H), 5.53 – 5.44 (m, 2H), 3.92 (t, *J* = 9.7 Hz, 1H), 3.73 (dd, *J* = 17.5, 9.7 Hz, 1H), 3.47 (dd, *J* = 17.6, 9.8 Hz, 1H), 1.03 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.1, 174.4, 168.6, 151.2 (J_{C-F} = 250.5 Hz, J_{C-F} = 13.1 Hz), 150.6, 148.0 (J_{C-F} = 249.0 Hz, J_{C-F} = 13.6 Hz), 135.8 (J_{C-F} = 11.0 Hz, J_{C-F} = 2.5 Hz), 134.8, 132.8, 132.2, 128.8, 128.7, 128.4, 128.3, 122.9 (J_{C-F} = 5.6 Hz, J_{C-F} = 4.5 Hz), 113.8 (J_{C-F} = 19.2 Hz), 106.2 (J_{C-F} = 24.2 Hz), 82.3, 82.2, 69.2, 52.0, 37.9, 27.4 ppm.

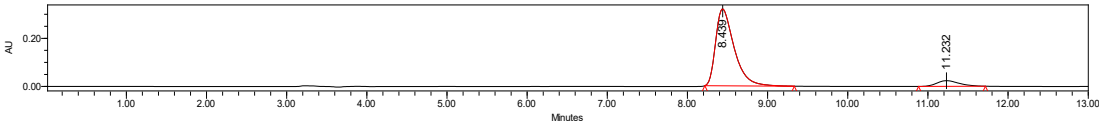
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ = -133.0, -141.2 ppm.

IR (neat): 3730, 2976, 2361, 1784, 1733, 1608, 1574, 1498, 1450, 1391, 1344, 1285, 1262, 1150, 1087, 1027, 878, 793, 763, 692 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{27}F_2N_2O_5^+$ 533.1883; Found 533.1889.

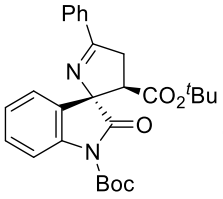


Peak	Retention Time	Area	% Area
1	8.237	1258732	50.43
2	10.861	1237315	49.57



Peak	Retention Time	Area	% Area
1	8.439	5245325	95.03
2	11.232	274452	4.97

di-tert-butyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3oa)



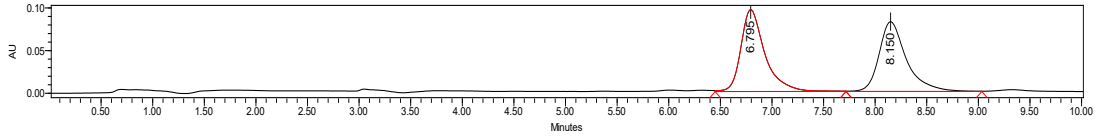
37.0 mg, 80% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.67 min, t_r (minor) = 8.04 min, ee = 98%, d.r. > 19:1. $[\alpha]^{24}_D$ = +40.91 (*c* = 0.13 in CH_2Cl_2). Melting point: 86–88 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.93 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.51 – 7.40 (m, 3H), 7.34 (td, *J* = 7.9, 1.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (dd, *J* = 7.5, 1.4 Hz, 1H), 3.95 (t, *J* = 9.9 Hz, 1H), 3.75 (dd, *J* = 17.4, 10.1 Hz, 1H), 3.44 (dd, *J* = 17.4, 9.7 Hz, 1H), 1.66 (s, 9H), 0.99 (s, 9H) ppm.

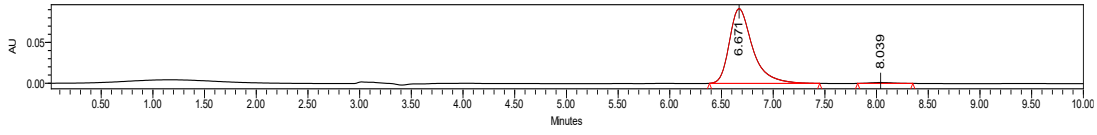
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.2, 175.5, 169.0, 149.3, 140.2, 133.2, 131.8, 130.1, 128.7, 128.4, 127.1, 124.8, 124.3, 115.4, 84.6, 82.6, 81.8, 52.2, 37.8, 28.2, 27.3 ppm.

IR (neat): 3730, 3625, 2978, 2361, 2336, 1777, 1731, 1607, 1476, 1348, 1290, 1250, 1154, 1086, 1006, 843, 757, 688 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{31}N_2O_5^+$ 463.2227; Found 463.2231.

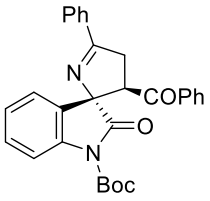


Peak	Retention Time	Area	% Area
1	6.795	1550019	50.71
2	8.150	1506549	49.29



Peak	Retention Time	Area	% Area
1	6.671	1399715	99.17
2	8.039	11671	0.83

tert-butyl (3S,3'R)-3'-benzoyl-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1-carboxylate (3pa)



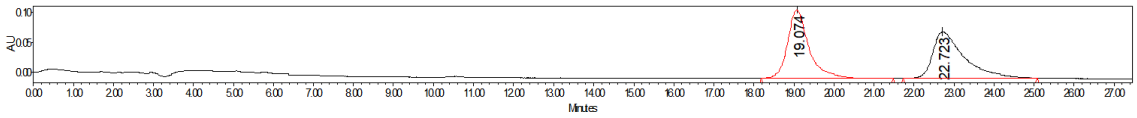
38.2 mg, 82% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 22.50 min, t_r (minor) = 19.07 min, ee = 88%. $[\alpha]^{23}_D$ = +48.63 (*c* = 0.58, in CH_2Cl_2). Melting point: 85–87 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 – 7.90 (m, 2H), 7.52 – 7.35 (m, 7H), 7.22 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.10 (td, *J* = 7.9, 1.4 Hz, 1H), 6.98 (td, *J* = 7.6, 1.1 Hz, 1H), 6.84 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.88 (dd, *J* = 9.5, 8.4 Hz, 1H), 4.25 (dd, *J* = 17.7, 8.4 Hz, 1H), 3.52 (dd, *J* = 17.7, 9.6 Hz, 1H), 1.62 (s, 9H) ppm.

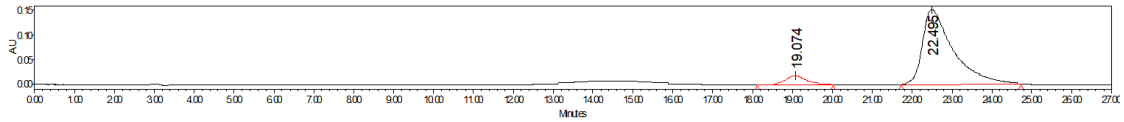
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 197.2, 176.7, 175.9, 148.6, 139.1, 137.0, 133.2, 133.0, 131.8, 129.8, 128.7, 128.5, 128.4, 127.7, 126.0, 125.4, 124.7, 114.7, 84.5, 83.4, 54.2, 37.9, 28.2 ppm.

IR (neat): 2979, 1796, 1767, 1732, 1686, 1607, 1575, 1478, 1465, 1447, 1344, 1288, 1247, 1146, 1088, 1025, 946, 892, 799, 734, 691, 659, 555, 495 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{29}H_{27}N_2O_5^{+}$ 467.1965; Found 467.1972.

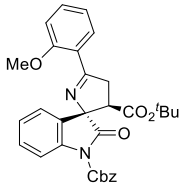


Peak	Retention Time	Area	% Area
1	19.074	4192988	50.05
2	22.723	4184161	49.95



Peak	Retention Time	Area	% Area
1	19.074	520858	6.10
2	22.495	8013276	93.90

benzyl (3R,3'R)-5'-(2-methoxyphenyl)-2-oxo-3'-(pivaloyloxy)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1-carboxylate (3ab)



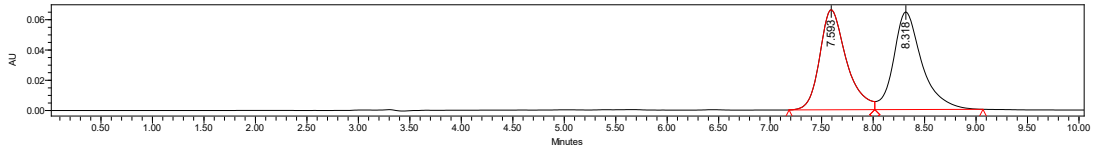
50.0 mg, 95% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.36 min, t_r (minor) = 7.66 min, ee = 92%, d.r. > 19:1. $[\alpha]^{23}_D$ = +86.57 (*c* = 0.65 in CH_2Cl_2). Melting point: 88–90 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.44 – 7.31 (m, 5H), 7.13 – 7.05 (m, 2H), 6.98 – 6.93 (m, 2H), 5.49 (d, *J* = 4.0 Hz, 2H), 3.94 – 3.85 (m, 5H), 3.56 – 3.44 (m, 1H), 0.93 (s, 9H) ppm.

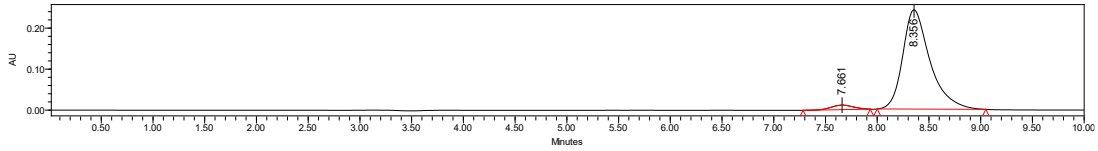
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.8, 175.7, 169.2, 158.8, 150.9, 139.6, 135.1, 132.8, 130.7, 130.0, 128.7, 128.5, 128.1, 127.3, 125.1, 124.4, 122.8, 120.8, 115.3, 111.4, 81.6, 81.0, 68.8, 55.5, 52.7, 41.2, 27.2 ppm.

IR (neat): 3730, 2974, 2361, 1778, 1731, 1598, 1463, 1376, 1344, 1287, 1227, 1160, 1083, 1017, 845, 755, 697, 511 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{31}H_{31}N_2O_6^{+}$ 527.2177; Found 527.2180.

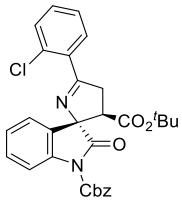


Peak	Retention Time	Area	% Area
1	7.593	1192188	49.20
2	8.318	1231179	50.80



Peak	Retention Time	Area	% Area
1	7.661	165638	3.60
2	8.356	4438423	96.40

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(2-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ac)



48.2 mg, 91% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.11 min, t_r (minor) = 11.11 min, ee = 94%, d.r. > 19:1. $[\alpha]^{25}_D$ = +57.25 (*c* = 0.82 in CH_2Cl_2). Melting point: 83–85 °C.

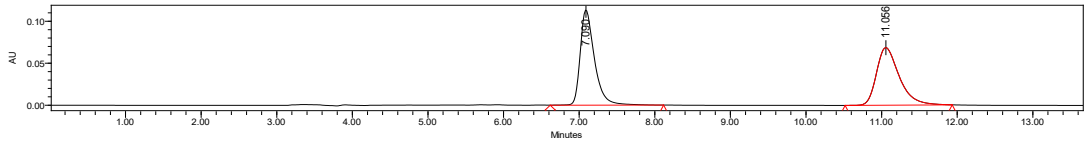
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 – 7.26 (m, 7H), 7.18 – 7.11 (m, 2H), 5.49 (s, 2H), 4.18 – 3.89 (m, 2H), 3.44 (dd, *J* = 17.4, 8.9 Hz, 1H), 0.94 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.3, 174.9, 168.6, 150.8, 139.7, 135.1, 133.5, 132.9, 131.7, 131.2, 130.5, 130.3, 128.8, 128.6, 128.2, 127.1, 126.6, 125.2, 124.4, 115.4, 81.9, 81.8, 68.9, 52.6, 41.1, 27.2 ppm.

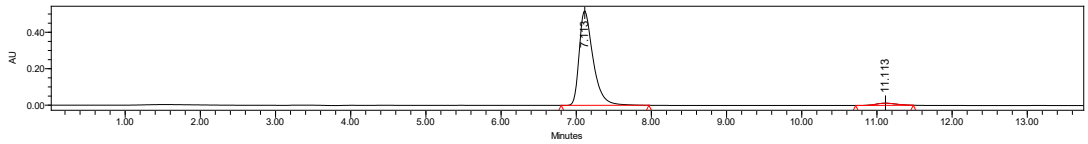
IR (neat): 2976, 2361, 2336, 1779, 1733, 1604, 1476, 1376, 1344, 1287, 1228, 1160, 1083, 1041, 1013, 844, 755, 699 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{30}H_{28}{}^{35}ClN_2O_5^+$ 531.1681; Found 531.1692.

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{30}H_{28}{}^{37}ClN_2O_5^+$ 533.1651; Found 533.1655.

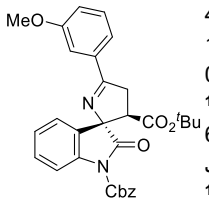


Peak	Retention Time	Area	% Area
1	7.090	1481015	50.85
2	11.056	1431259	49.15



Peak	Retention Time	Area	% Area
1	7.113	6648386	97.07
2	11.113	200453	2.93

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(3-methoxyphenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ad)



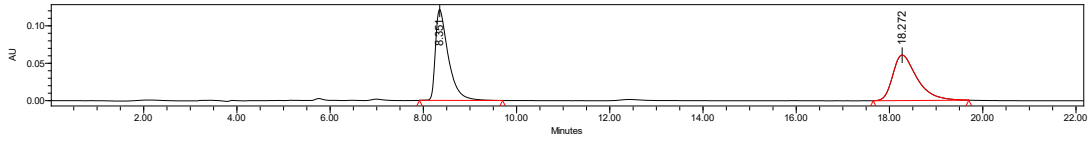
47.3 mg, 90% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 8.19 min, t_r (minor) = 18.35 min, ee = 81%, d.r. > 19:1. $[\alpha]^{23}_D$ = +40.24 (*c* = 0.34 in CH_2Cl_2). Melting point: 76–78 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.39 – 7.22 (m, 7H), 7.05 – 6.89 (m, 3H), 5.51 – 5.35 (m, 2H), 3.87 (t, *J* = 9.8 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 17.4, 10.0 Hz, 1H), 3.35 (dd, *J* = 17.4, 9.8 Hz, 1H), 0.86 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.3, 175.3, 168.8, 159.8, 150.9, 139.7, 135.1, 134.5, 130.2, 129.7, 128.8, 128.6, 128.2, 127.2, 125.2, 124.4, 121.1, 118.5, 115.4, 112.5, 82.6, 81.9, 68.8, 55.5, 52.3, 38.0, 27.2 ppm.

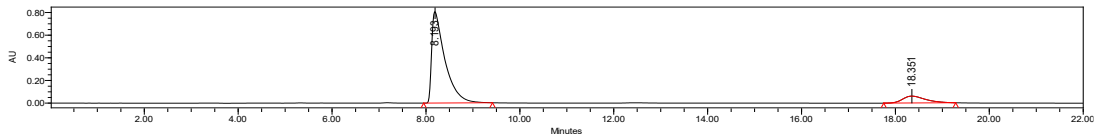
IR (neat): 3730, 2974, 2361, 1778, 1732, 1606, 1579, 1461, 1376, 1345, 1287, 1226, 1160, 1085, 1043, 1014, 845, 752, 692, 510 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{31}N_2O_6^+$ 527.2177; Found 527.2172.



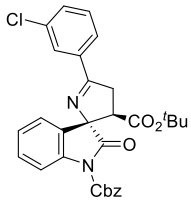
Peak	Retention Time	Area	% Area

1	8.351	2275252	50.78
2	18.272	2205706	49.22



Peak	Retention Time	Area	% Area
1	8.193	15768876	90.58
2	18.351	1639055	9.42

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(3-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ae)



48.8 mg, 92% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.06 min, t_r (minor) = 16.48 min, ee = 82%, d.r. > 19:1. $[\alpha]^{22}_D$ = +36.63 (*c* = 0.80 in CH_2Cl_2). Melting point: 77–79 °C.

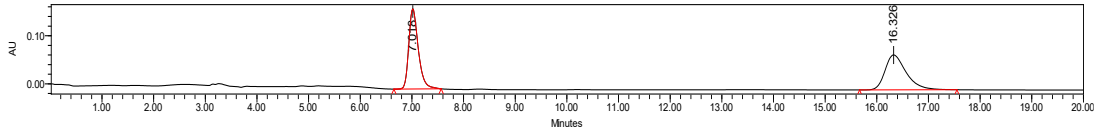
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.57 – 7.52 (m, 2H), 7.44 – 7.34 (m, 5H), 7.19 (tdd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.54 – 5.45 (m, 2H), 3.96 (t, *J* = 9.9 Hz, 1H), 3.74 (dd, *J* = 17.5, 10.0 Hz, 1H), 3.42 (dd, *J* = 17.5, 9.8 Hz, 1H), 0.93 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 175.3, 168.7, 164.1, 161.7, 150.8, 139.7, 135.3, 135.0, 130.4, 130.3, 128.8, 128.6, 128.2, 126.9, 125.2, 124.4, 124.2, 118.9, 115.5, 115.2, 82.7, 82.0, 68.9, 52.2, 37.9, 27.2 ppm.

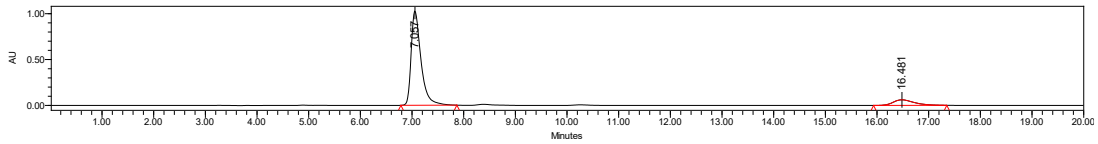
IR (neat): 3730, 2976, 2361, 2336, 1778, 1733, 1609, 1581, 1477, 1376, 1346, 1287, 1227, 1160, 1085, 1014, 891, 752, 688, 520 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{35}ClN_2O_5^+$ 531.1681; Found 531.1689.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{37}ClN_2O_5^+$ 533.1651; Found 533.1656.

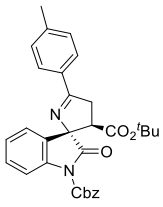


Peak	Retention Time	Area	% Area
1	7.018	2129678	50.80
2	16.326	2062190	49.20



Peak	Retention Time	Area	% Area
1	7.057	13553372	90.96
2	16.481	1347317	9.04

1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-(p-tolyl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3af)

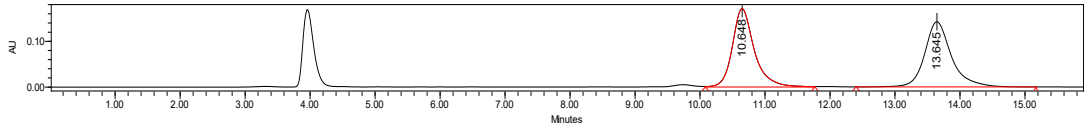


46.9 mg, 92% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.62 min, t_r (minor) = 10.65 min, ee = 84%, d.r. > 19:1. $[\alpha]^{23}_D$ = +41.34 (*c* =0.72 in CH_2Cl_2). Melting point: 80–82 °C.

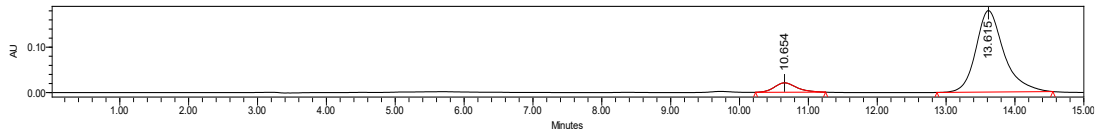
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.58 – 7.51 (m, 2H), 7.42 – 7.31 (m, 4H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.55 – 5.44 (m, 2H), 3.94 (t, *J* = 9.9 Hz, 1H), 3.74 (dd, *J* = 17.4, 10.0 Hz, 1H), 3.44 (dd, *J* = 17.4, 9.8 Hz, 1H), 2.39 (s, 3H), 0.93 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.2, 175.4, 168.9, 150.9, 142.3, 139.6, 135.1, 130.4, 130.1, 129.4, 128.7, 128.5, 128.4, 128.1, 127.3, 125.2, 124.4, 115.4, 82.5, 81.8, 68.8, 52.2, 37.8, 27.2, 21.7 ppm.

IR (neat): 3730, 2976, 2361, 1779, 1732, 1605, 1565, 1475, 1377, 1346, 1287, 1227, 1160, 1085, 1014, 820, 752, 696 (cm^{-1})
HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{31}N_2O_5^+$ 511.2227; Found 511.2280.

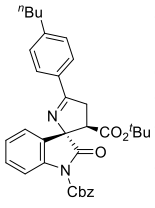


Peak	Retention Time	Area	% Area
1	10.648	4013406	49.62
2	13.645	4075012	50.38

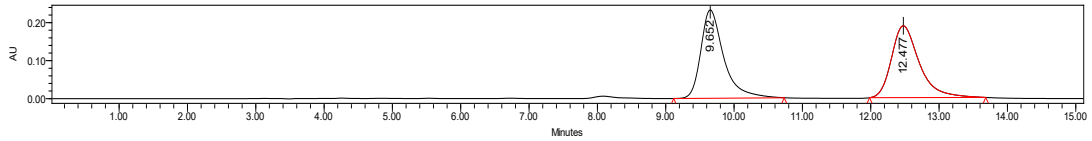


Peak	Retention Time	Area	% Area
1	10.654	435159	7.90
2	13.615	5074129	92.10

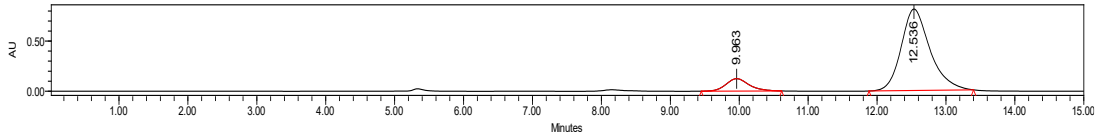
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-butylphenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ag)



50.2 mg, 91% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 12.54 min, t_r (minor) = 9.96 min, ee = 80%, d.r. > 19:1. $[\alpha]^{24}_D$ = +40.11 (*c* = 0.75 in CH_2Cl_2). Melting point: 86–88 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.43 – 7.32 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.56 – 5.44 (m, 2H), 3.95 (t, *J* = 9.9 Hz, 1H), 3.75 (dd, *J* = 17.3, 10.0 Hz, 1H), 3.45 (dd, *J* = 17.4, 9.7 Hz, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.36 (q, *J* = 7.4 Hz, 2H), 0.93 (m, 12H) ppm.
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.2, 175.4, 168.9, 150.9, 147.3, 139.7, 135.1, 130.7, 130.1, 128.8, 128.7, 128.5, 128.4, 128.1, 127.3, 125.1, 124.4, 115.4, 82.5, 81.8, 68.8, 52.3, 37.8, 35.7, 33.4, 27.2, 22.4, 14.0 ppm.
IR (neat): 3730, 2930, 2361, 1779, 1732, 1605, 1563, 1474, 1377, 1346, 1288, 1227, 1160, 1084, 1014, 841, 751, 696 (cm^{-1})
HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{34}H_{37}N_2O_5^+$ 553.2697; Found 553.2701.

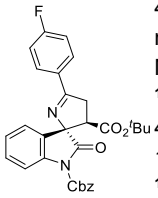


Peak	Retention Time	Area	% Area
1	9.652	5407783	50.25
2	12.447	5353821	49.75



Peak	Retention Time	Area	% Area
1	9.963	2607390	9.95
2	12.536	23599436	90.05

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-fluorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ah)



47.8 mg, 93% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.33 min, t_r (minor) = 11.27 min, ee = 95%, d.r. > 19:1. $[\alpha]^{25}_D$ = +40.11 (*c* =, in CH_2Cl_2). Melting point: 83–85 °C.

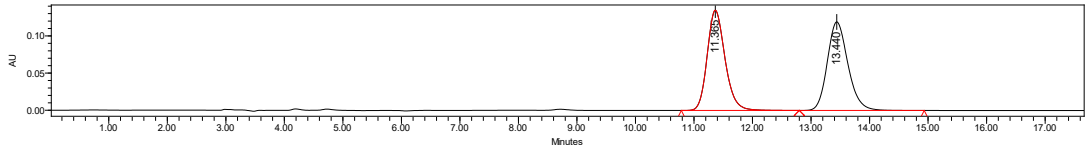
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.56 – 7.49 (m, 2H), 7.42 – 7.30 (m, 4H), 7.15 – 7.07 (m, 3H), 6.98 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.55 – 5.44 (m, 2H), 3.95 (t, *J* = 9.8 Hz, 1H), 3.74 (dd, *J* = 17.4, 10.0 Hz, 1H), 3.42 (dd, *J* = 17.4, 9.8 Hz, 1H), 0.93 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 175.2, 175.1, 168.7, 165.0 (d, *J* = 254.5 Hz), 150.8, 139.7, 135.0, 130.6 (d, *J* = 8.1 Hz) , 130.2, 129.5 (d, *J* = 3.0 Hz), 128.8, 128.6, 128.2, 127.1, 125.2, 124.4, 115.9 (d, *J* = 22.2 Hz), 115.5, 82.6, 81.9, 68.9, 52.3, 37.8, 27.2 ppm.

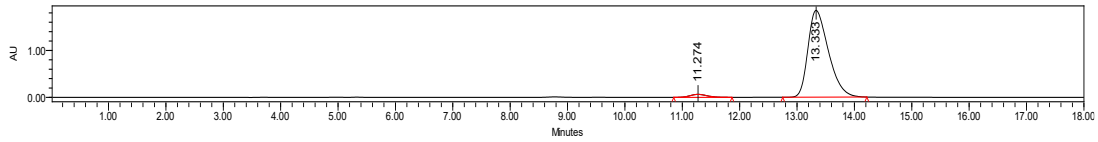
^{19}F{^{1}H} NMR (376 MHz, Chloroform-*d*) δ = -107.5 ppm.

IR (neat): 2976, 2361, 1779, 1732, 1610, 1564, 1470, 1376, 1340, 1286, 1226, 1162, 1080, 1012, 840, 797, 760, 682, 542 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}FN_2O_5^+$ 515.1977; Found 515.1980.

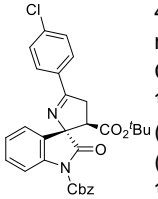


Peak	Retention Time	Area	% Area
1	11.365	2851040	49.45
2	13.440	2914679	50.55



Peak	Retention Time	Area	% Area
1	11.274	1167128	2.48
2	13.333	45826304	97.52

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ai)



46.1 mg, 87% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 18.04 min, t_r (minor) = 16.02 min, ee = 96%, d.r. > 19:1. $[\alpha]^{26}_D$ = +46.67 (*c* = 0.93 in CH_2Cl_2). Melting point: 79–81 °C.

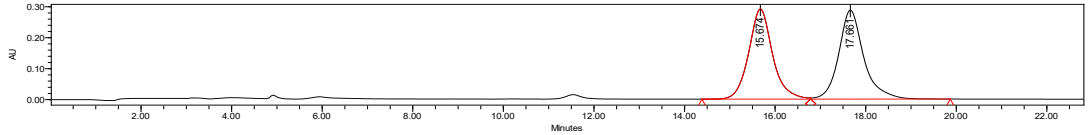
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.57 – 7.50 (m, 2H), 7.44 – 7.32 (m, 6H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.55 – 5.44 (m, 2H), 3.95 (t, *J* = 9.8 Hz, 1H), 3.73 (dd, *J* = 17.4, 9.9 Hz, 1H), 3.41 (dd, *J* = 17.4, 9.8 Hz, 1H), 0.94 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 175.2, 175.1, 168.7, 150.8, 139.7, 138.0, 135.0, 131.6, 130.3, 129.7, 129.0, 128.8, 128.6, 128.2, 127.0, 125.2, 124.4, 115.5, 82.7, 81.9, 68.9, 52.2, 37.8, 27.2 ppm.

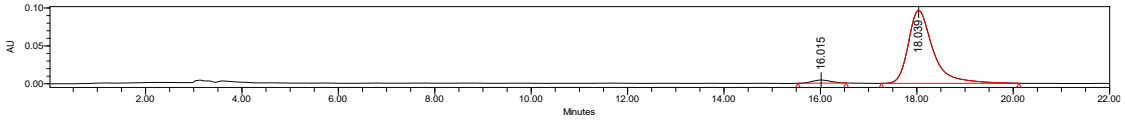
IR (neat): 2976, 2361, 1778, 1731, 1604, 1564, 1475, 1376, 1345, 1286, 1226, 1159, 1086, 1012, 925, 835, 797, 748, 698, 555, 509 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{35}ClN_2O_5^+$ 531.1681; Found 531.1683.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{28}{}^{37}ClN_2O_5^+$ 533.1651; Found 533.1658.

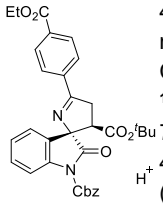


Peak	Retention Time	Area	% Area
1	15.674	10648384	49.14
2	17.661	11019048	50.86



Peak	Retention Time	Area	% Area
1	16.015	69251	1.98
2	18.039	3431849	98.02

1-benzyl3'-(tert-butyl) (3S,3'R)-5'-(4-(ethoxycarbonyl)phenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3aj)



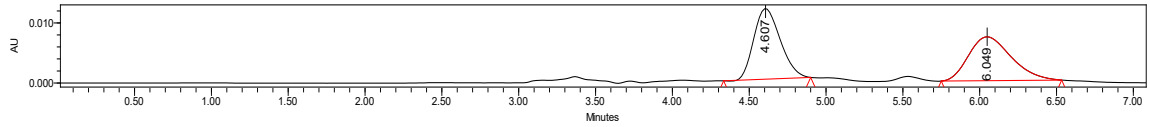
49.9 mg, 88% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.54 min, t_r (minor) = 4.61 min, ee = 94%, d.r. > 19:1. $[\alpha]^{26}_{D}$ = +37.93 (*c* = 0.75, in CH_2Cl_2). Melting point: 86–88°C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.11 – 8.05 (m, 2H), 8.00 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.57 – 7.50 (m, 2H), 7.42 – 7.32 (m, 4H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.98 (dd, *J* = 7.4, 1.3 Hz, 1H), 5.54 – 5.45 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 9.8 Hz, 1H), 3.78 (dd, *J* = 17.5, 9.9 Hz, 1H), 3.46 (dd, *J* = 17.5, 9.8 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 9H) ppm.

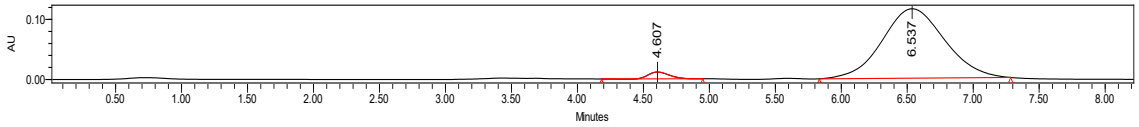
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 175.7, 175.0, 168.6, 166.0, 150.8, 139.7, 136.9, 135.0, 133.2, 130.4, 129.9, 128.8, 128.6, 128.3, 128.2, 126.9, 125.2, 124.4, 115.5, 82.8, 82.0, 68.9, 61.5, 52.2, 38.0, 27.3, 14.4 ppm.

IR (neat): 2978, 2359, 1779, 1731, 1607, 1479, 1465, 1368, 1347, 1247, 1227, 1161, 1107, 1087, 1018, 843, 796, 769, 753, 697 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{33}N_2O_7^+$ 569.2282; Found 569.2286.

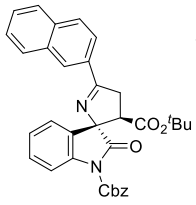


Peak	Retention Time	Area	% Area
1	4.607	141619	50.16
2	6.049	140737	49.84



Peak	Retention Time	Area	% Area
1	4.607	128194	3.25
2	6.537	3813814	96.75

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(naphthalen-2-yl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ak)



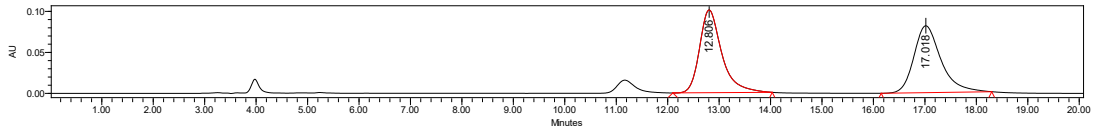
51.8 mg, 95% yield; pale yellow solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 17.35 min, t_r (minor) = 12.95 min, ee = 94%, d.r. > 19:1. $[\alpha]^{23}_{D}$ = +101.04 (*c* = 0.58 in CH_2Cl_2). Melting point: 82–84 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.29 (s, 1H), 8.09 – 7.99 (m, 2H), 7.92 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.86 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.55 (ddd, *J* = 7.1, 5.1, 1.7 Hz, 4H), 7.46 – 7.32 (m, 4H), 7.15 – 6.98 (m, 2H), 5.56 – 5.46 (m, 2H), 4.02 (t, *J* = 9.8 Hz, 1H), 3.89 (dd, *J* = 17.2, 10.0 Hz, 1H), 3.60 (dd, *J* = 17.2, 9.6 Hz, 1H), 0.96 (s, 9H) ppm.

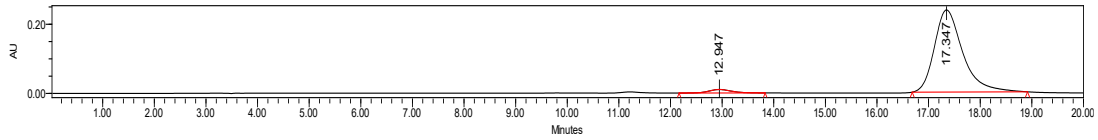
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 176.3, 175.3, 168.9, 150.9, 139.7, 135.1, 135.1, 132.9, 130.7, 130.2, 129.4, 129.1, 128.8, 128.6, 128.5, 128.2, 127.9, 127.9, 127.3, 126.8, 125.2, 124.6, 124.5, 115.5, 82.8, 81.9, 68.9, 52.3, 37.9, 27.3 ppm.

IR (neat): 2976, 2361, 1778, 1732, 1604, 1474, 1349, 1287, 1227, 1160, 1085, 1013, 821, 749, 698, 477 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{34}H_{31}N_2O_5^+$ 547.2227; Found 547.2231.

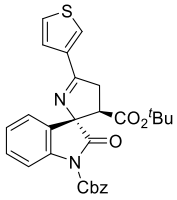


Peak	Retention Time	Area	% Area
1	12.806	3021942	50.35
2	17.018	2980255	49.65



Peak	Retention Time	Area	% Area
1	12.947	271129	2.91
2	17.347	9033747	97.09

1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-(thiophen-3-yl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3al)



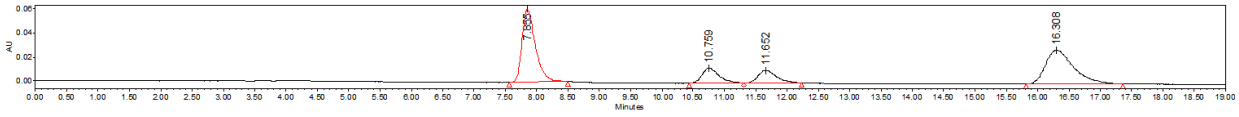
42.7 mg, 85% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) major isomer: t_r (major) = 10.23 min, t_r (minor) = 11.42 min; minor isomer: t_r (major) = 7.66 min, t_r (minor) = 16.02 min, ee = 90%, d.r. = 83:17. $[\alpha]^{24}_{D}$ = +173.69 (*c* = 0.50 in CH_2Cl_2). Melting point: 82–84 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.08 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.45 – 7.29 (m, 5H), 7.25 – 7.06 (m, 3H), 5.56 – 5.46 (m, 2H), 4.01 (dd, *J* = 12.8, 5.5 Hz, 1H), 3.21 (dd, *J* = 18.1, 12.9 Hz, 1H), 3.09 (dd, *J* = 18.1, 5.5 Hz, 1H), 1.02 (s, 9H) ppm.

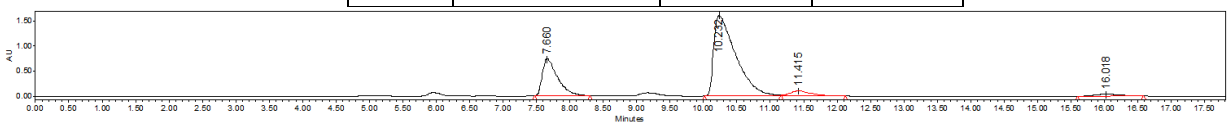
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 189.7, 174.8, 168.1, 153.0, 151.0, 138.8, 138.0, 134.8, 130.0, 129.3, 128.8, 128.7, 128.4, 126.4, 125.5, 124.4, 124.0, 116.0, 83.1, 69.2, 52.9, 48.2, 36.5, 27.3 ppm.

IR (neat): 2975, 2361, 1774, 1731, 1683, 1603, 1525, 1472, 1376, 1344, 1279, 1226, 1158, 1084, 1046, 1013, 896, 841, 800, 737, 697, 591, 512 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{28}H_{27}N_2O_5S^{+}$ 503.1635; Found 503.1641.

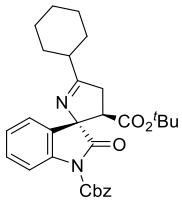


Peak	Retention Time	Area	% Area
1	7.855	899031	40.50
2	10.759	231761	10.44
3	11.652	212731	9.58
4	16.308	876317	39.48



Peak	Retention Time	Area	% Area
1	7.660	11484604	21.97
2	10.232	37862078	72.43
3	11.415	2002095	3.83
4	16.018	920022	1.76

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-cyclohexyl-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3am)



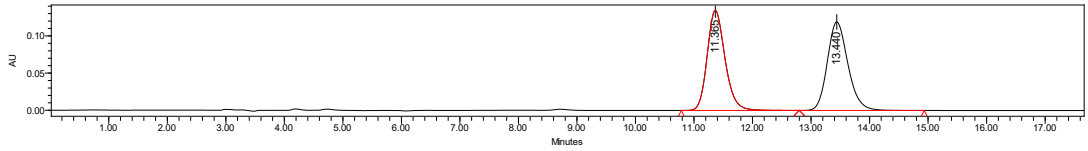
44.2 mg, 88% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IA, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 13.33 min, t_r (minor) = 11.27 min, ee = 95%, d.r. > 19:1. $[\alpha]^{23}_D$ = +17.45 (*c* = 0.87, in CH_2Cl_2). Melting point: 79–81 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.95 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.40 – 7.29 (m, 4H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.90 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.52 – 5.41 (m, 2H), 3.74 (t, *J* = 9.9 Hz, 1H), 3.33 (dd, *J* = 17.8, 10.0 Hz, 1H), 2.92 (dd, *J* = 17.8, 9.7 Hz, 1H), 2.44 (tt, *J* = 11.1, 3.5 Hz, 1H), 2.02 – 1.89 (m, 2H), 1.84 – 1.73 (m, 2H), 1.51 – 1.11 (m, 6H), 0.89 (s, 9H) ppm.

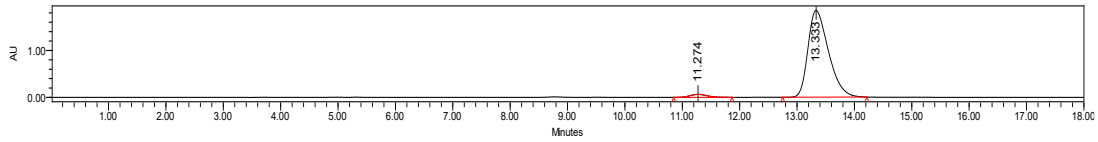
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 186.3, 175.5, 169.0, 150.8, 139.6, 135.1, 130.0, 128.7, 128.5, 128.1, 127.3, 125.1, 124.0, 115.4, 82.0, 81.7, 68.7, 52.0, 42.7, 38.3, 30.7, 30.2, 27.2, 26.0, 25.8 ppm.

IR (neat): 2930, 1780, 1731, 1625, 1479, 1348, 1289, 1227, 1157, 1085, 754, 581 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{30}H_{35}N_2O_5^+$ 503.2540; Found 503.2547.

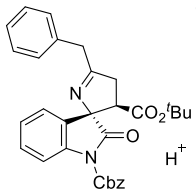


Peak	Retention Time	Area	% Area
1	11.365	2851040	49,45
2	13.440	2914679	50.55



Peak	Retention Time	Area	% Area
1	11.274	1167128	2.48
2	13.333	45826304	97.52

1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-benzyl-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3an)



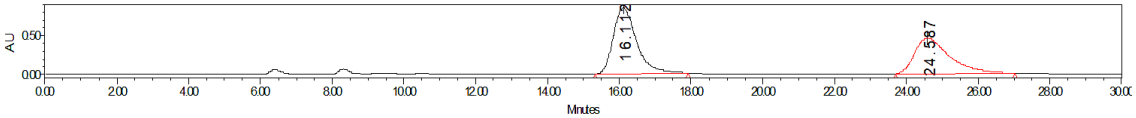
43.9 mg, 86% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel ADH, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 16.28 min, t_r (minor) = 24.84 min, ee = 93%, d.r. > 19:1. $[\alpha]^{23}_D$ = +18.59 (*c* = 0.71, in CH_2Cl_2). Melting point: 88–90 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (m, 1H), 7.54 – 7.50 (m, 2H), 7.40 – 7.29 (m, 9H), 7.10 – 7.06 (m, 1H), 6.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.48 (d, *J* = 3.7 Hz, 2H), 3.85 (d, *J* = 14.4 Hz, 1H), 3.82 – 3.71 (m, 2H), 3.21 (dd, *J* = 18.0, 10.1 Hz, 1H), 2.84 (dd, *J* = 18.0, 9.7 Hz, 1H), 0.87 (s, 9H) ppm.

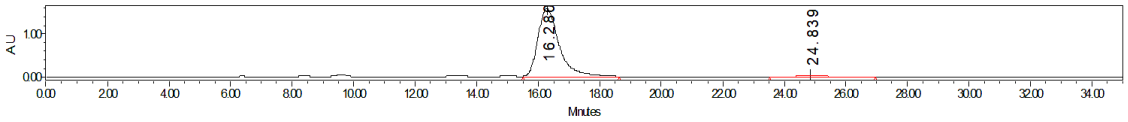
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 181.3, 175.2, 168.7, 150.8, 139.6, 135.8, 135.1, 130.2, 129.1, 129.1, 128.8, 128.6, 128.2, 127.4, 127.1, 125.1, 124.1, 115.4, 82.3, 81.8, 68.8, 52.3, 41.1, 39.4, 27.2 ppm.

IR (neat): 2976, 2359, 1778, 1731, 1631, 1606, 1480, 1465, 1381, 1348, 1289, 1226, 1161, 1085, 1012, 845, 753, 699, 597, 493 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{31}N_2O_5^+$ 511.2227; Found 511.2232.

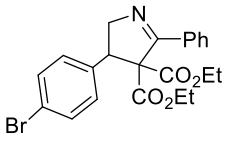


Peak	Retention Time	Area	% Area
1	16.112	31360851	50.25
2	24.587	31052116	49.75



Peak	Retention Time	Area	% Area
1	16.280	73367381	96.43
2	24.839	2719190	3.57

diethyl 4-(4-bromophenyl)-2-phenyl-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5a)



33.7 mg, 76% yield; colourless oil; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 16.30 min, t_r (minor) = 15.22 min, ee = 92%, $[\alpha]^{23}_{D}$ = +28.34 (*c* = 0.62, in CH_2Cl_2).

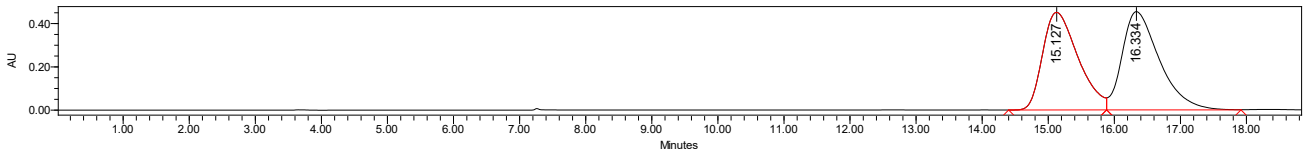
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.02 – 7.93 (m, 2H), 7.54 – 7.43 (m, 3H), 7.41 – 7.34 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.52 – 4.35 (m, 2H), 4.22 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.72 – 3.60 (m, 2H), 3.35 (dd, *J* = 17.3, 5.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.7, 169.1, 167.7, 138.7, 133.3, 131.9, 131.5, 130.2, 128.7, 128.6, 121.4, 91.6, 62.5, 61.6, 48.1, 43.6, 14.2, 13.8 ppm.

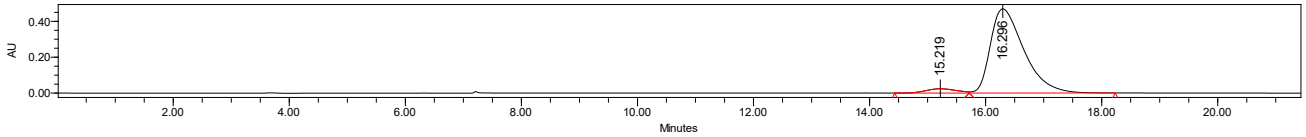
IR (neat): 2982, 2362, 2336, 1997, 1731, 1613, 1489, 1345, 1265, 1215, 1100, 760, 690, 559, 462, 422 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{23}Br^{79}NO_4^+$ 444.0805; Found 444.0807.

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{23}Br^{81}NO_4^+$ 446.0785; Found 446.0791.

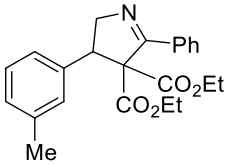


Peak	Retention Time	Area	% Area
1	15.127	16855798	49.56
2	16.334	17155093	50.44



Peak	Retention Time	Area	% Area
1	15.219	866147	3.96
2	16.296	21006251	96.04

diethyl 2-phenyl-4-(m-tolyl)-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5b)



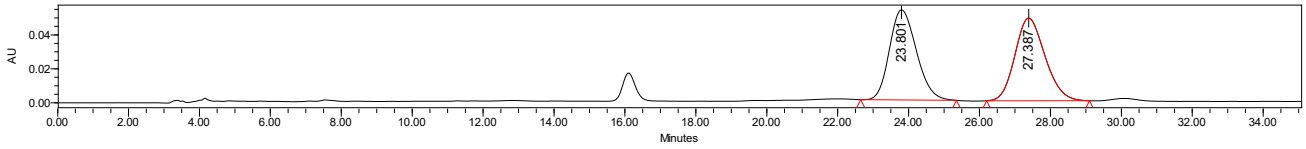
27.3 mg, 72% yield; colourless oil; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IG, hexane/^{i}PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 28.08 min, t_r (minor) = 24.69 min, ee = 90%, $[\alpha]^{23}_{D}$ = +43.16 (*c* = 0.73, in CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.02 – 7.97 (m, 2H), 7.54 – 7.43 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.03 (ddd, *J* = 10.2, 5.1, 2.2 Hz, 3H), 4.50 (dd, *J* = 9.1, 5.7 Hz, 1H), 4.44 – 4.35 (m, 1H), 4.21 (dt, *J* = 10.7, 7.1 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.69 – 3.57 (m, 2H), 3.40 (dd, *J* = 17.4, 5.6 Hz, 1H), 2.29 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm.

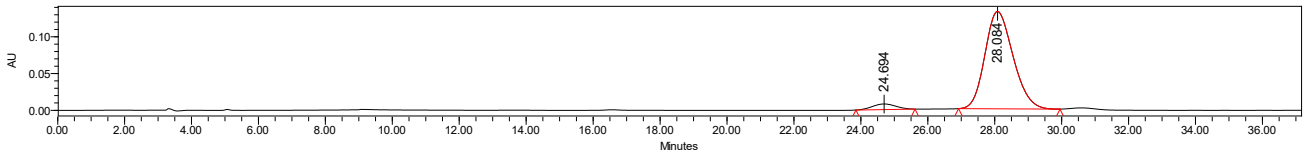
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 177.9, 169.3, 167.9, 139.7, 137.9, 133.5, 131.7, 129.3, 128.7, 128.6, 128.3, 128.2, 125.5, 91.8, 62.4, 61.4, 48.5, 43.9, 21.5, 14.2, 13.7 ppm.

IR (neat): 2925, 2361, 2203, 2052, 1996, 1732, 1612, 1448, 1344, 1264, 1213, 1100, 765, 695, 506, 482, 462, 433 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}NO_4^+$ 380.1856; Found 380.1860.

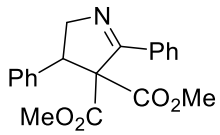


Peak	Retention Time	Area	% Area
1	23.801	16086036	50.63
2	27.387	15683106	49.37



Peak	Retention Time	Area	% Area
1	24.694	370297	4.88
2	28.084	7217756	95.12

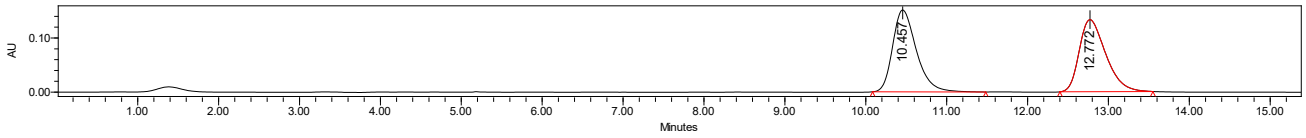
dimethyl 2,4-diphenyl-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5c)



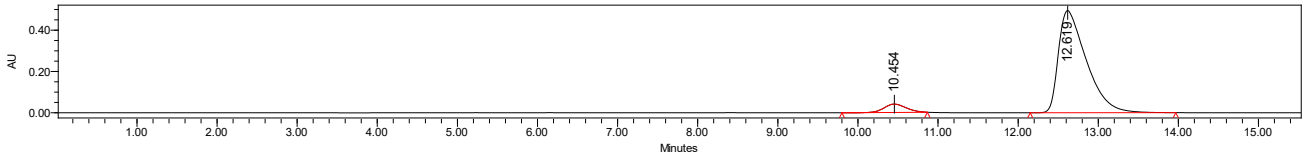
23.6 mg, 70% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel IB, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 12.62 min, t_r (minor) = 10.45 min, ee = 88%, $[\alpha]^{23}_{D}$ = (*c* =, in CH_2Cl_2). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.00 – 7.95 (m, 2H), 7.52 – 7.40 (m, 3H), 7.24 – 7.20 (m, 5H), 4.52 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 17.4, 9.0 Hz, 1H), 3.41 (dd, *J* = 17.4, 5.6 Hz, 1H), 3.24 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ = 178.2, 169.7, 168.2, 139.5, 133.3, 131.9, 128.7, 128.6, 128.5, 128.3, 127.6, 92.0, 53.5, 52.2, 48.7, 43.7 ppm.

IR (neat): 2952, 2362, 1737, 1612, 1438, 1347, 1268, 1221, 1087, 760, 687, 560 (cm^{-1})

HRMS (FTMS+c ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_4^+$ 338.1387; Found 338.1389.

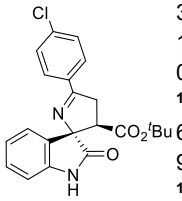


Peak	Retention Time	Area	% Area
1	10.457	3080707	50.53
2	12.772	3016662	49.47



Peak	Retention Time	Area	% Area
1	10.454	774566	6.08
2	12.619	11959686	93.92

tert-butyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-3'-carboxylate (6)



36.4 mg, 92% yield; white solid; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel ID, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 10.18 min, t_r (minor) = 16.70 min, ee = 96%, d.r. > 19:1. $[\alpha]^{23}_{D}$ = +14.35 (*c* = 0.72, in CH_2Cl_2). Melting point: 71–73 °C.

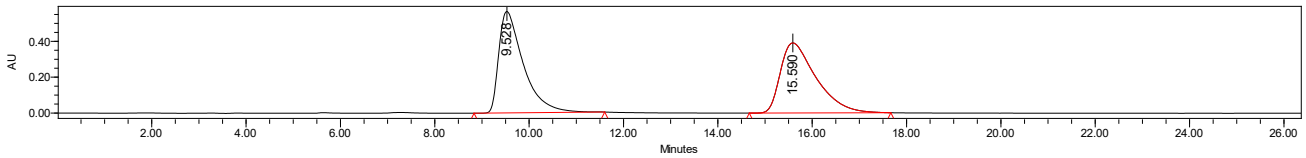
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.21 (s, 1H), 7.85 – 7.80 (m, 2H), 7.42 – 7.38 (m, 2H), 7.25 – 7.21 (m, 1H), 6.97 – 6.91 (m, 3H), 3.92 (t, *J* = 9.7 Hz, 1H), 3.75 (dd, *J* = 17.3, 9.8 Hz, 1H), 3.42 (dd, *J* = 17.3, 9.7 Hz, 1H), 1.02 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 178.8, 175.1, 169.3, 141.2, 137.8, 131.8, 130.0, 129.7, 129.0, 128.4, 126.8, 125.1, 123.1, 110.1, 83.1, 81.7, 50.9, 38.1, 27.4 ppm.

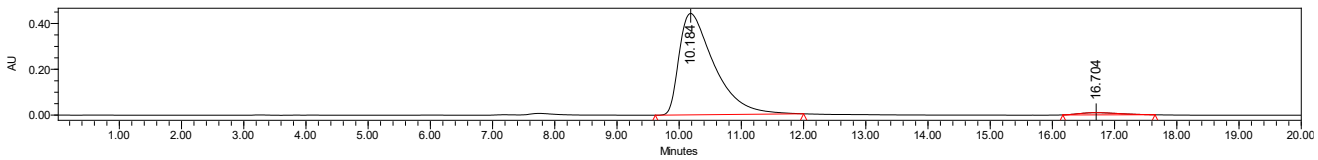
IR (neat): 2977, 2359, 1726, 1619, 1472, 1369, 1344, 1157, 1090, 832, 751, 625 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{22}H_{22}{}^{35}ClN_2O_3^{+}$ 397.1313; Found 397.1320.

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{22}H_{22}{}^{37}ClN_2O_3^{+}$ 399.1283; Found 399.1285.

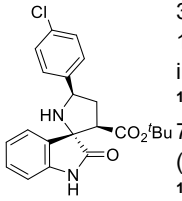


Peak	Retention Time	Area	% Area
1	9.528	20430561	49.97
2	15.590	20454409	50.03



Peak	Retention Time	Area	% Area
1	10.184	17248707	98.13
2	16.704	318053	1.87

tert-butyl (3S,3'R,5'R)-5'-(4-chlorophenyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3'-carboxylate (7)



34.8 mg, 95% yield; colourless oil; Dissolved in ^{i}PrOH for HPLC; HPLC (Chiralcel ID, hexane/^{i}PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.30 min, t_r (minor) = 12.59 min, ee = 96%, d.r. > 19:1. $[\alpha]^{23}_{D}$ = +12.68 (*c* = 0.70, in CH_2Cl_2).

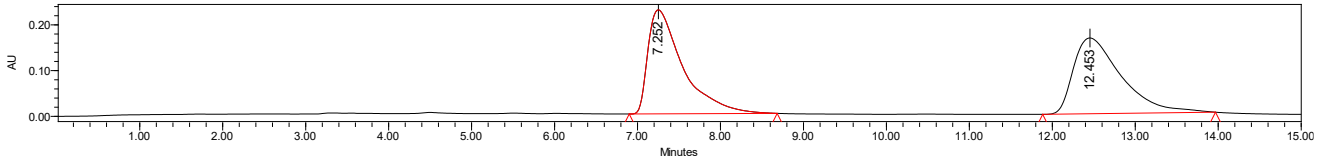
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.18 (s, 1H), 7.52 – 7.28 (m, 5H), 7.23 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.05 (td, *J* = 7.6, 1.0 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 4.75 (dt, *J* = 11.1, 5.6 Hz, 1H), 3.61 (dt, *J* = 12.6, 5.9 Hz, 1H), 2.54 – 2.48 (m, 1H), 2.38 (td, *J* = 12.6, 11.1 Hz, 1H), 1.26 (s, 1H), 1.00 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ = 181.7, 169.2, 141.3, 140.8, 133.2, 132.4, 129.3, 128.8, 128.2, 125.3, 123.3, 109.7, 81.3, 68.8, 61.2, 54.9, 37.7, 27.4 ppm.

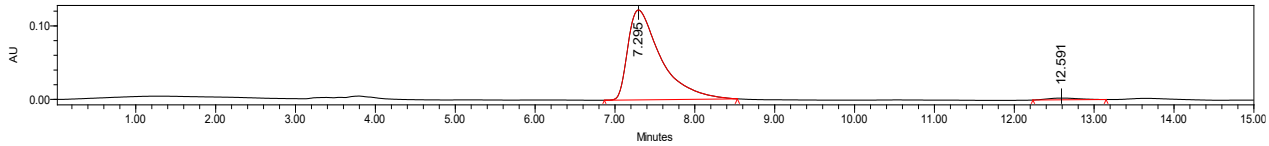
IR (neat): 2928, 2360, 1722, 1620, 1470, 1368, 1264, 1152, 1088, 908, 735 (cm^{-1})

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{22}H_{24}{}^{35}ClN_2O_3^{+}$ 399.1470; Found 399.1473.

HRMS (FTMS+c ESI) m/z: [M + H]$^{+}$ calcd for $C_{22}H_{24}{}^{37}ClN_2O_3^{+}$ 401.1440; Found 401.1442.

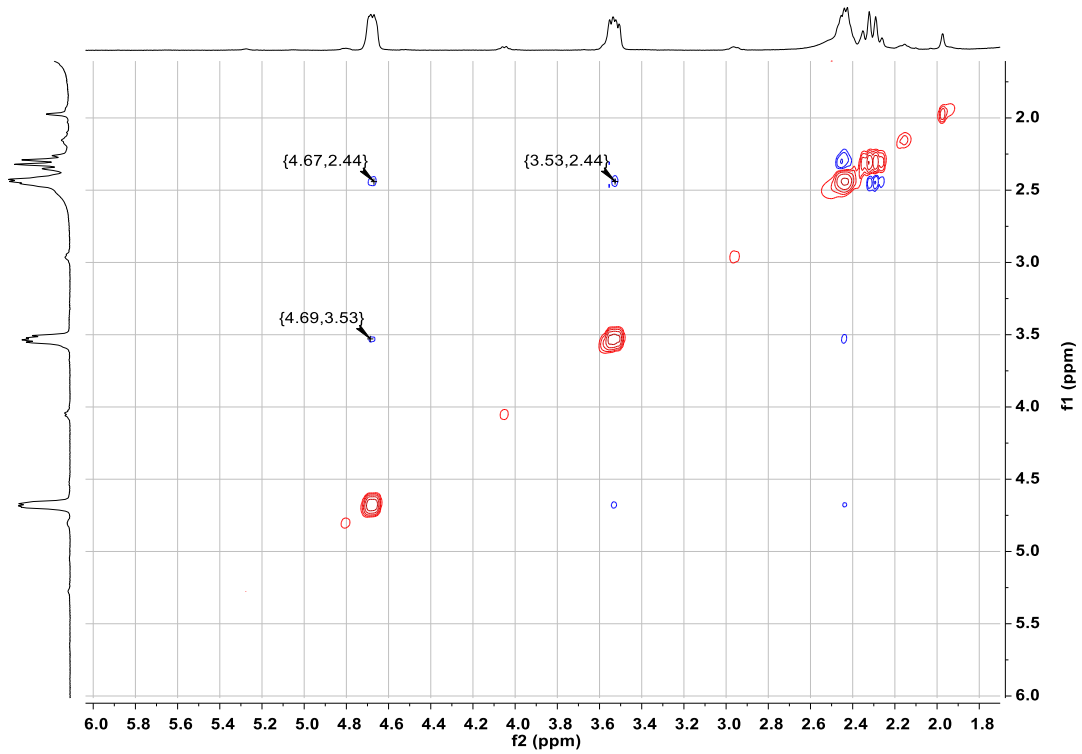


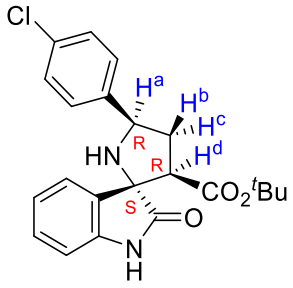
Peak	Retention Time	Area	% Area
1	7.252	6649054	50.03
2	12.453	6641824	49.97



Peak	Retention Time	Area	% Area
1	7.295	3511000	98.18
2	12.591	65019	1.82

12. NOESY spetra analysis for the absolute configuration of the compound 7





7

As can be seen from the results of the NOESY spectra, there is interaction between H^a and H^d. Meanwhile, H^a and H^d have interaction with the same hydrogen atom of methylene group. Herein, we determined the absolute configuration of the compound **7** as (3*S*, 3'*R*, 5'*R*).

13. References

[1] Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* 2005, **2005**, 2445–2448.

[2] (a) B. Tan, N. R. Candeias, C. F. Barbas, III, *J. Am. Chem. Soc.*, 2011, **133**, 4672.; (b) Y. H. Zhou, L. L. Lin, X. H. Liu, X. M. Feng, *Angew. Chem. Int. Ed.*, 2018, **57**, 9113.

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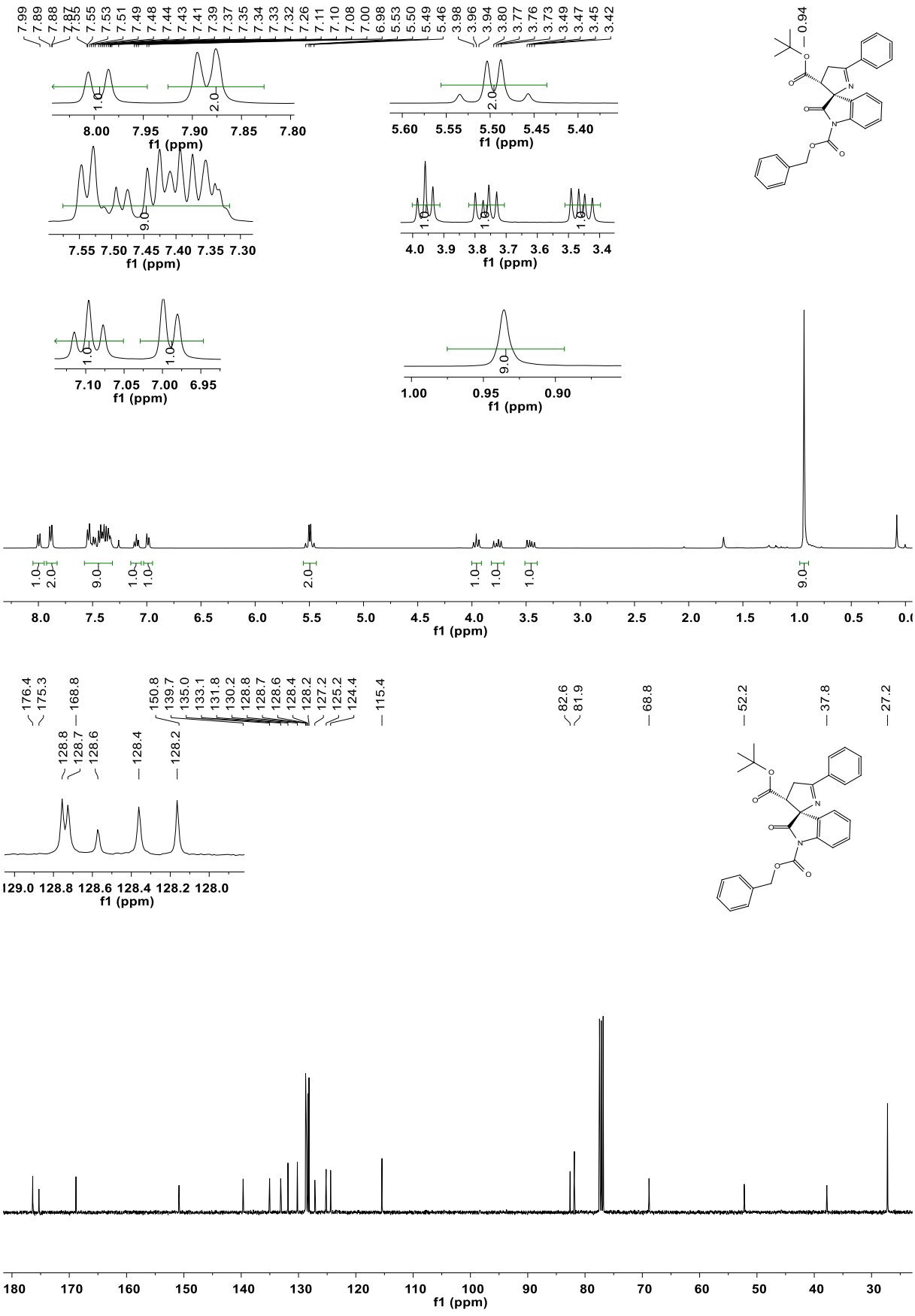
[4] Z. H. Liu, P. Q. Liao and X. H. Bi, *Org. Lett.*, 2014, **16**, 3668.

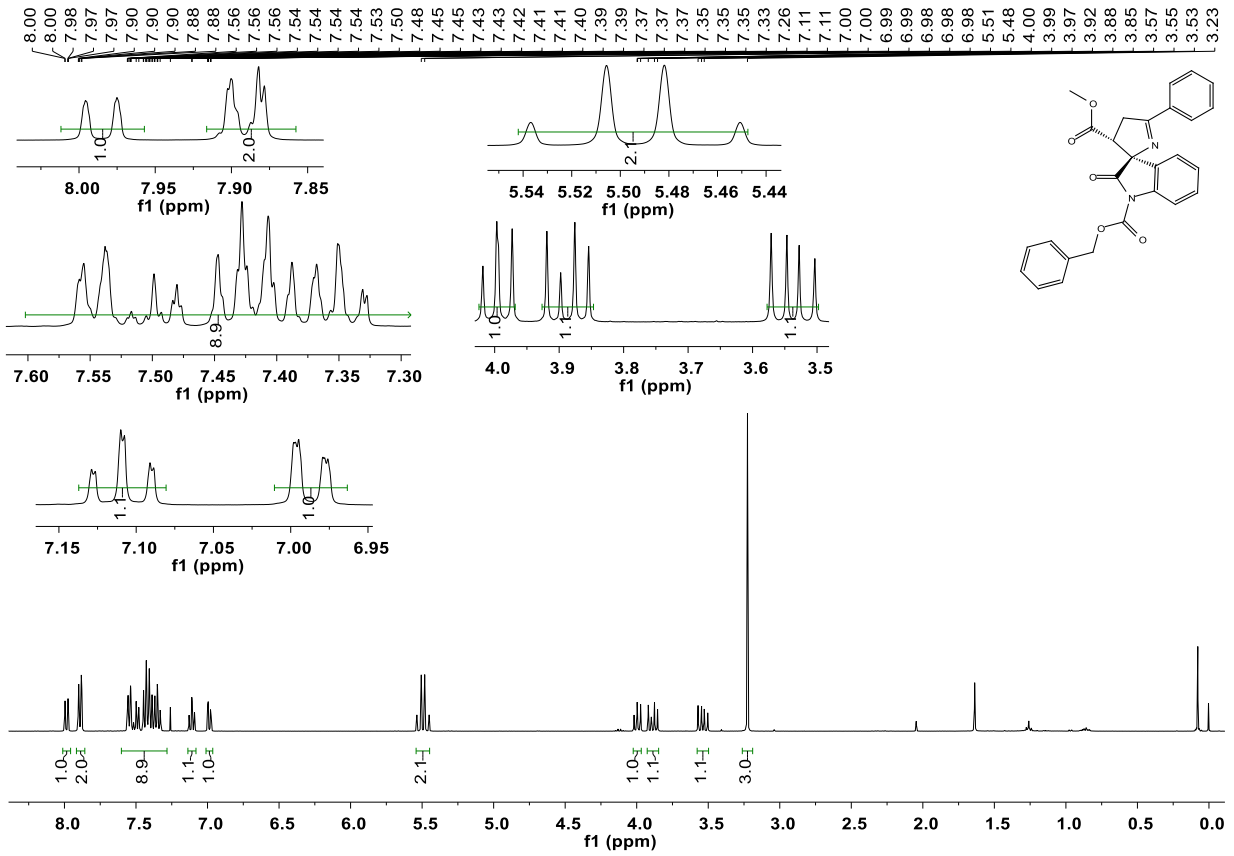
[5] (a) C. K. Sha and R. S. Lee, *Tetrahedron*, 1995, **51**, 193; (b) H. Mukherjee and C. A. Martinez, *ACS Catal.*, 2011, **1**, 1010; (c) O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, A. E. Kaplum, I. V. Trushkov and M. Y. Melnikov, *Adv. Synth. Catal.*, 2011, **353**, 1125; (d) F. Nanteuil and J. Waser, *Angew Chem., Int. Ed.*, 2013, **52**, 9009; (e) W. W. Luo, X. Yuan, L. L. Lin, P. F. Zhou, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2016, **7**, 4736; (f) X. Zhong, Q. Tang, P. F. Zhou, Z. W. Zhong, X. H. Liu and X. M. Feng, *Chem. Commun.*, 2018, **54**, 10511.

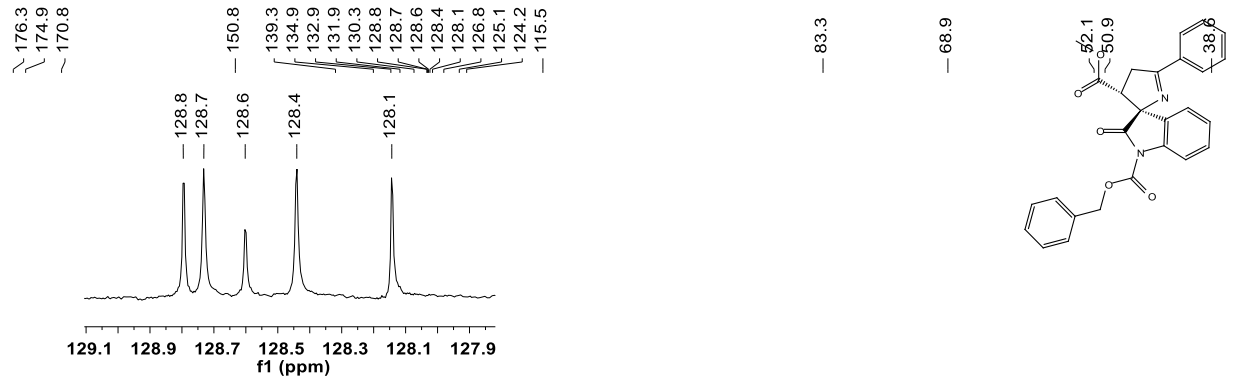
14. Copies of NMR spectra for products

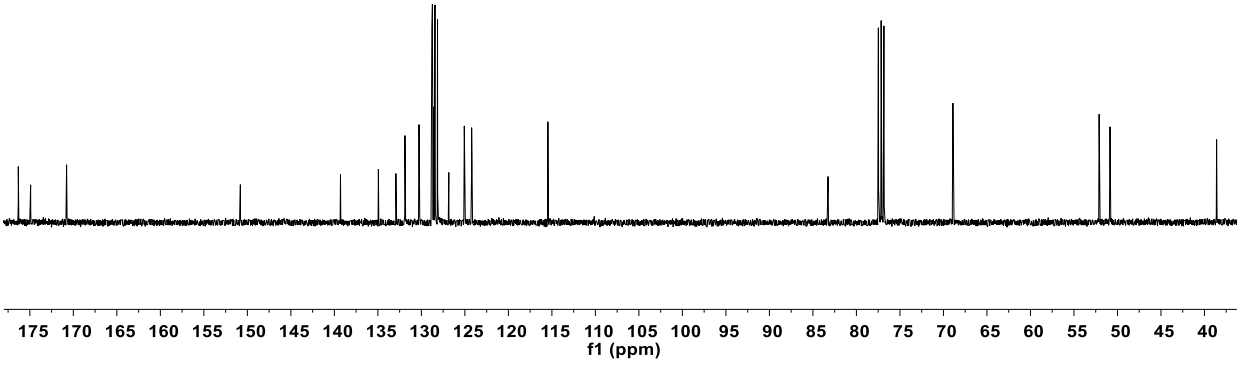
1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3aa)



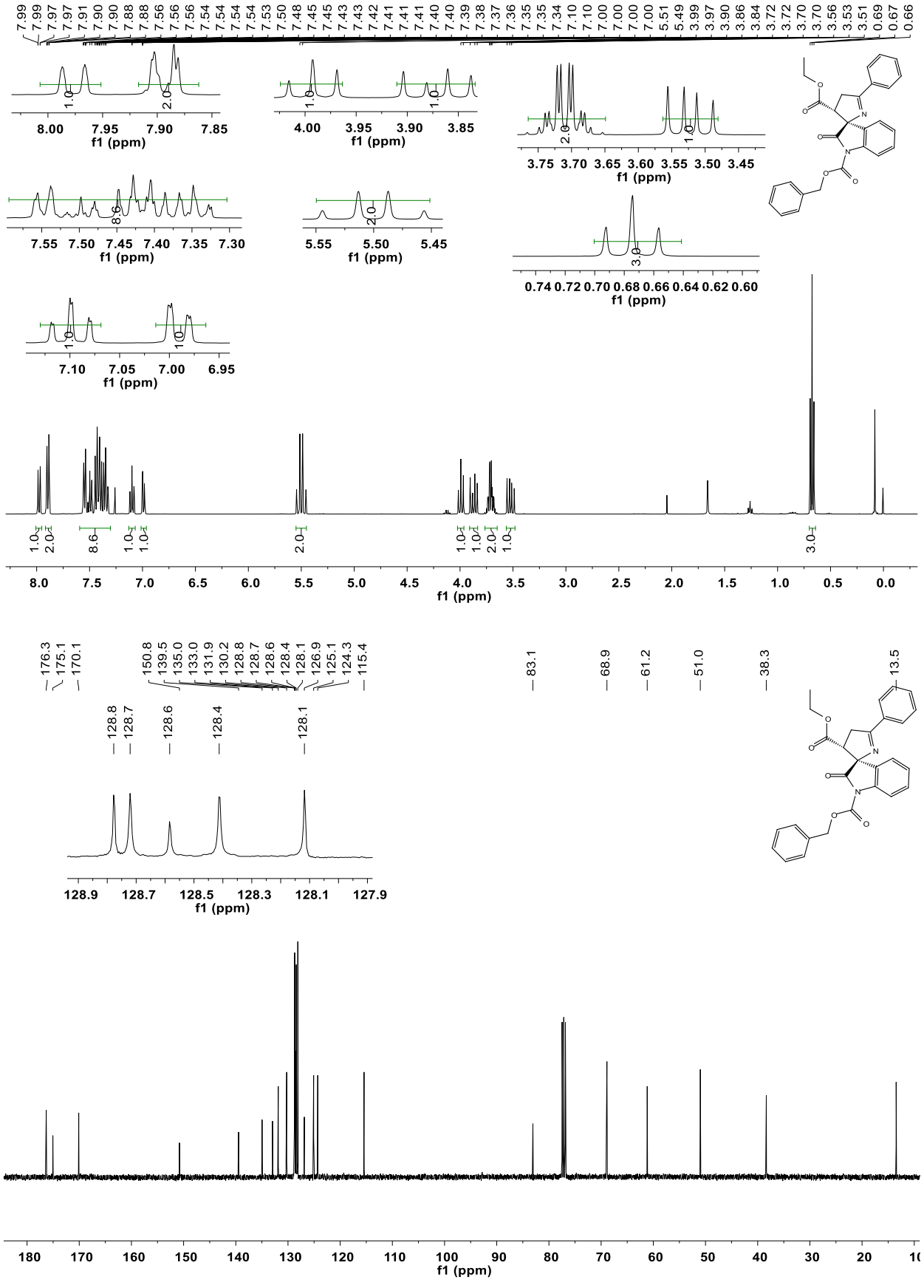
1-benzyl 3'-methyl (3S,3' R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ba)



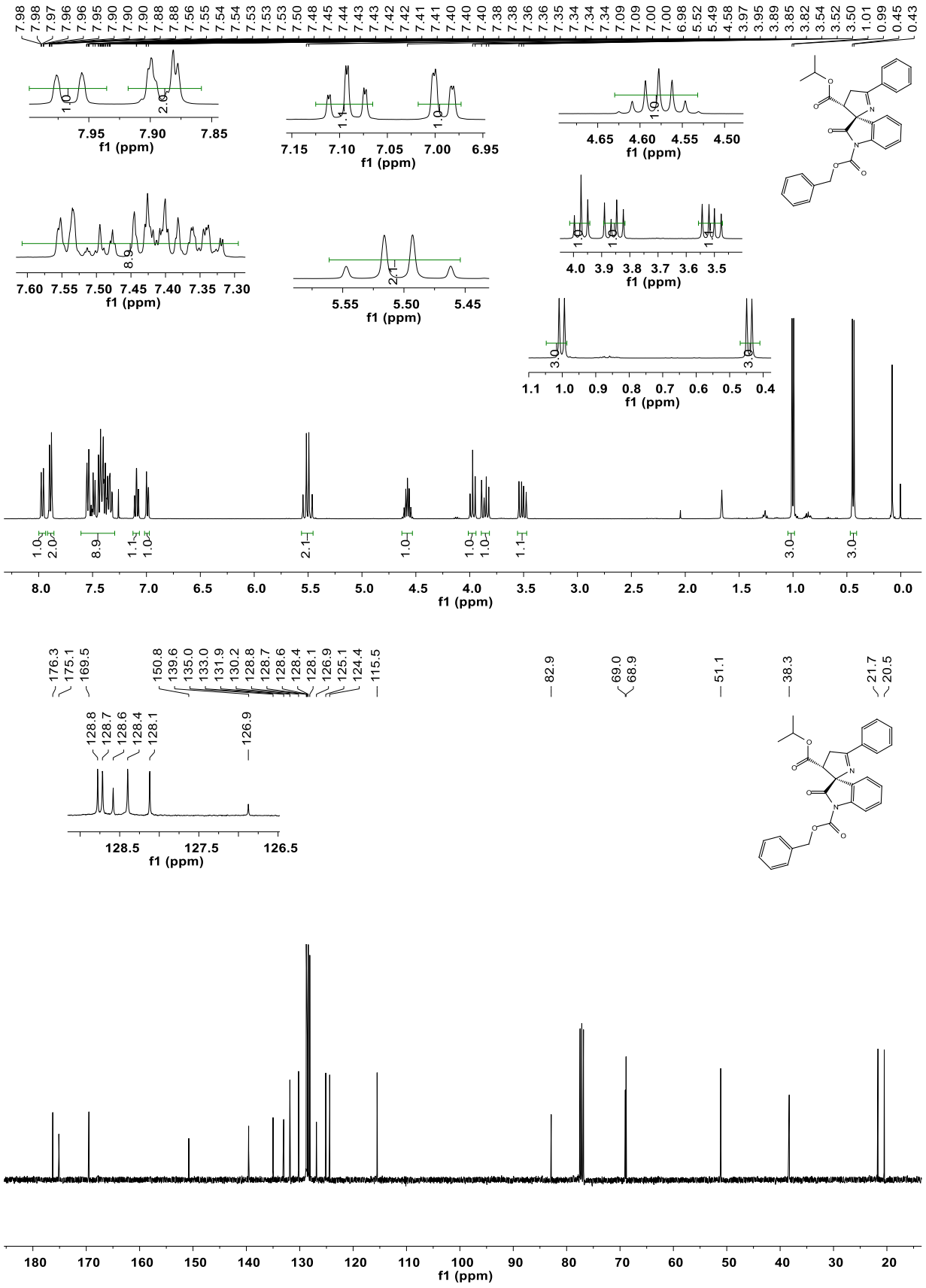




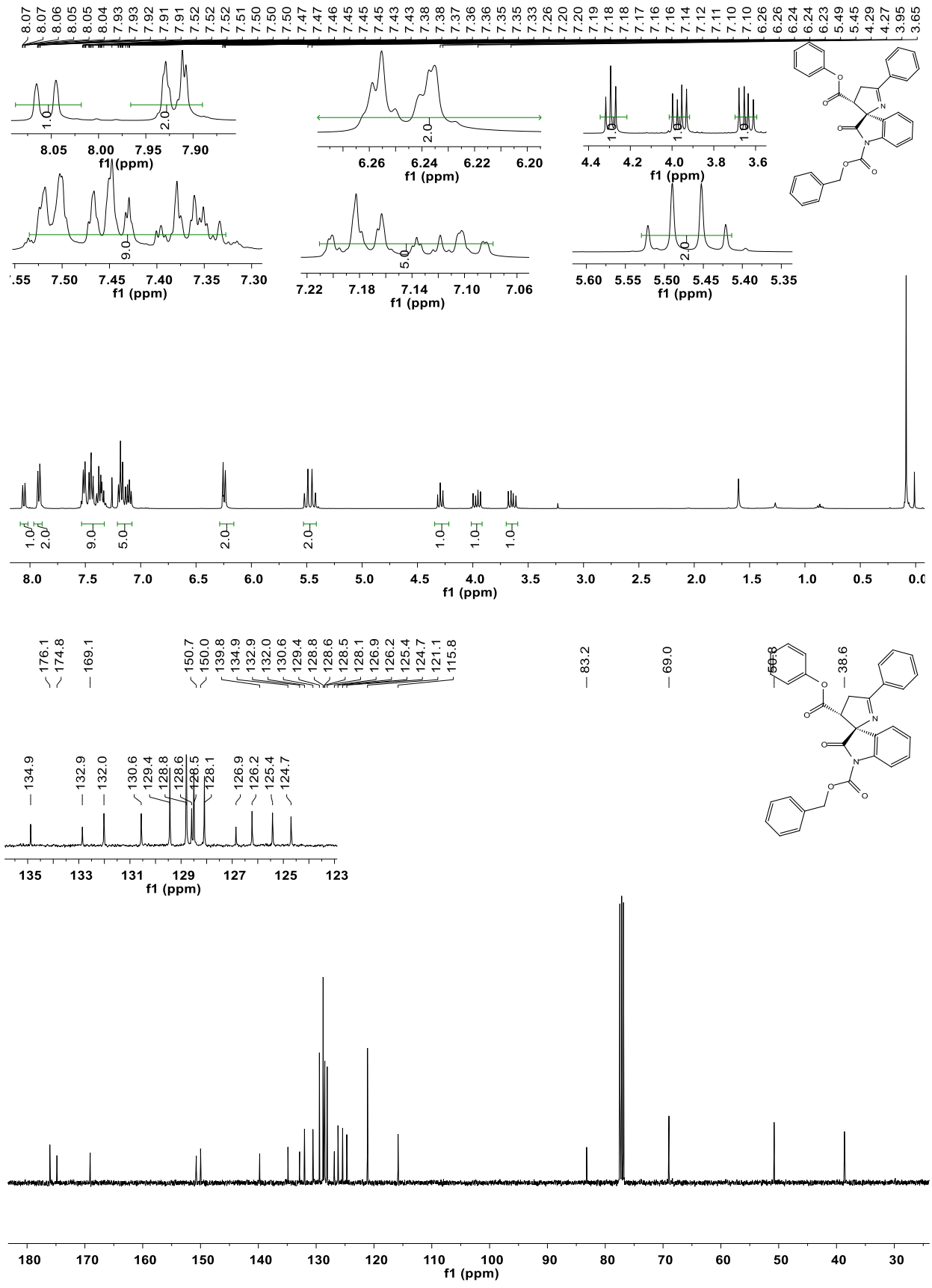
1-benzyl 3'-ethyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ca)



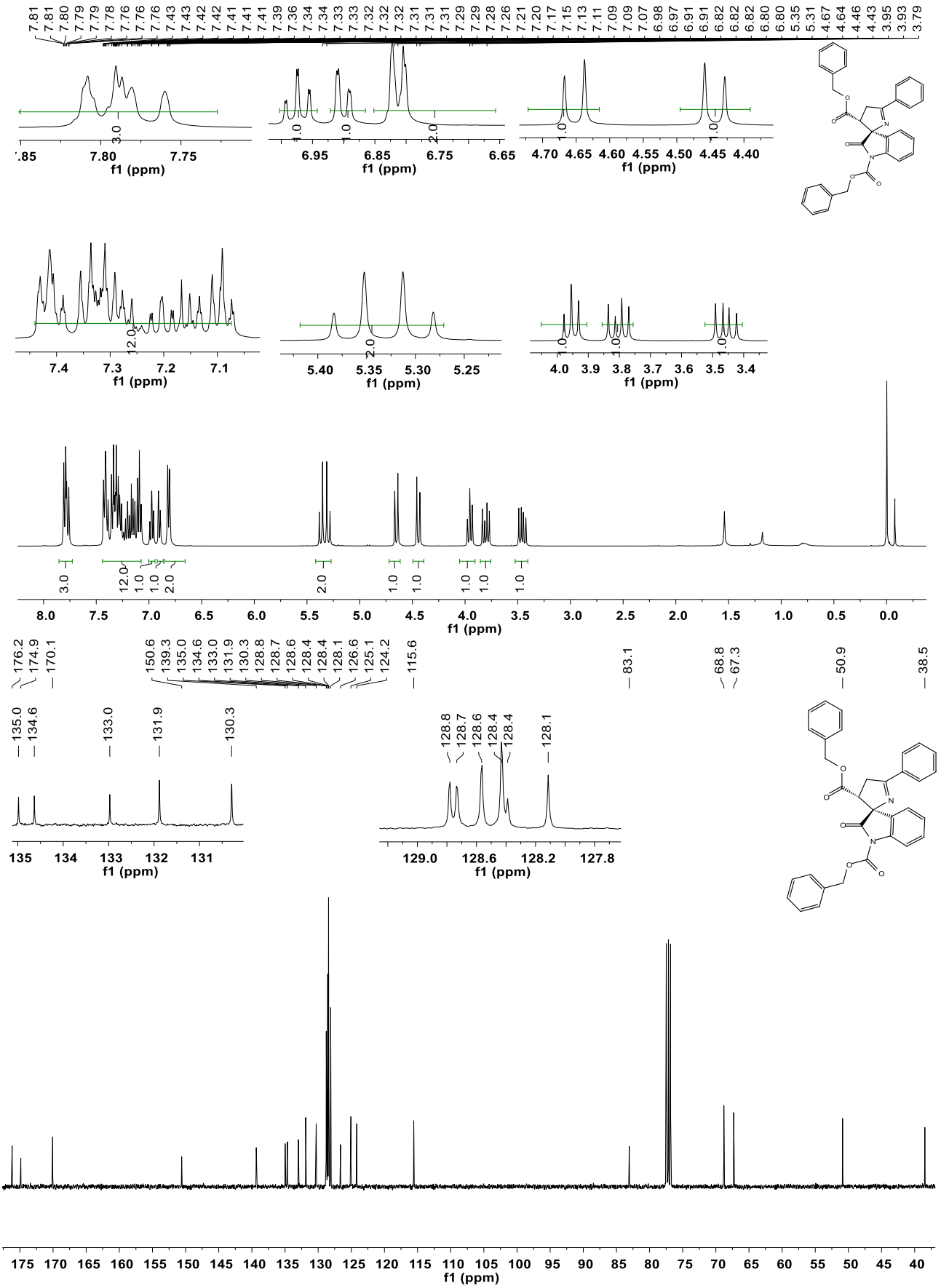
1-benzyl 3'-isopropyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3da)



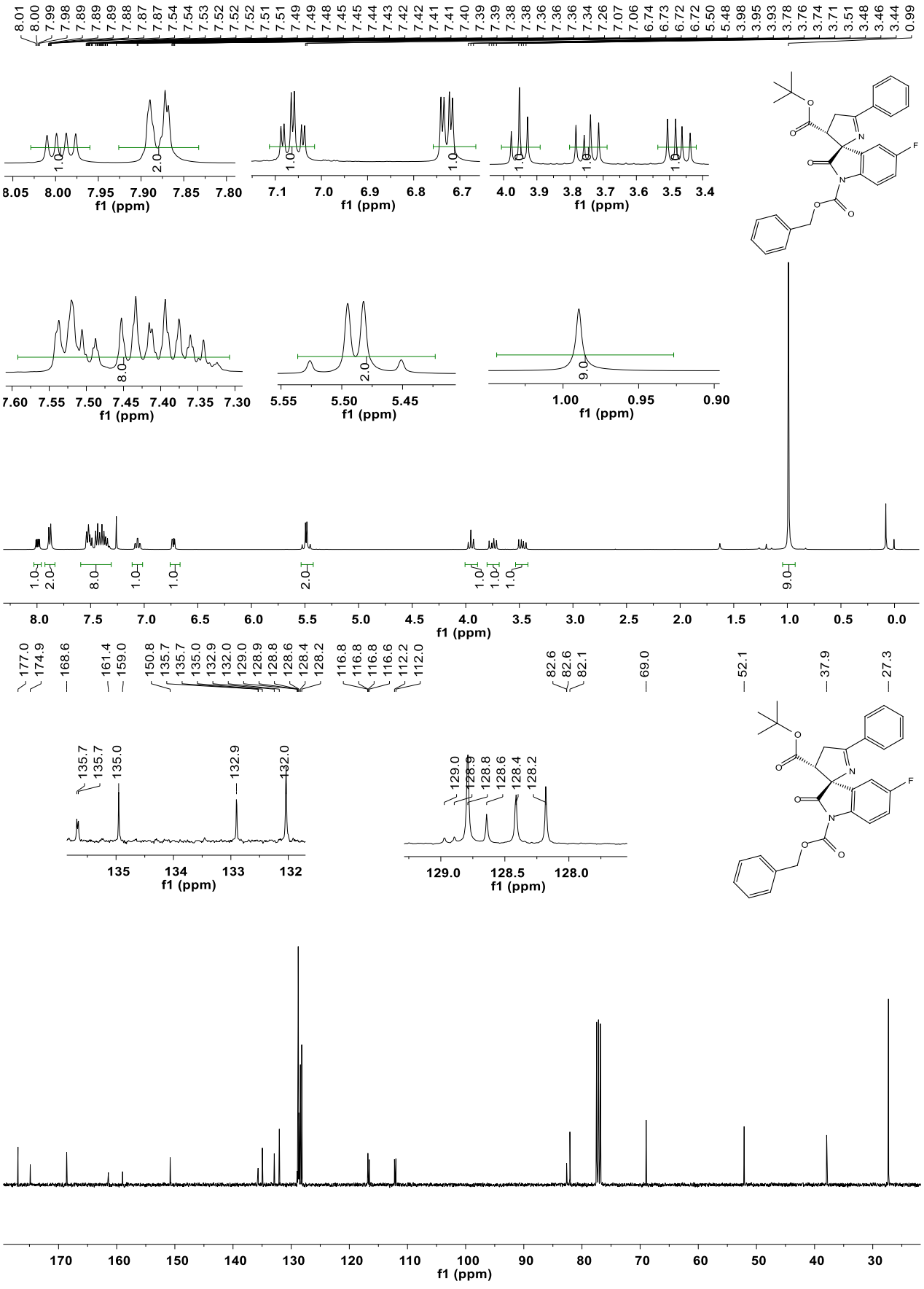
1-benzyl 3'-phenyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ea)

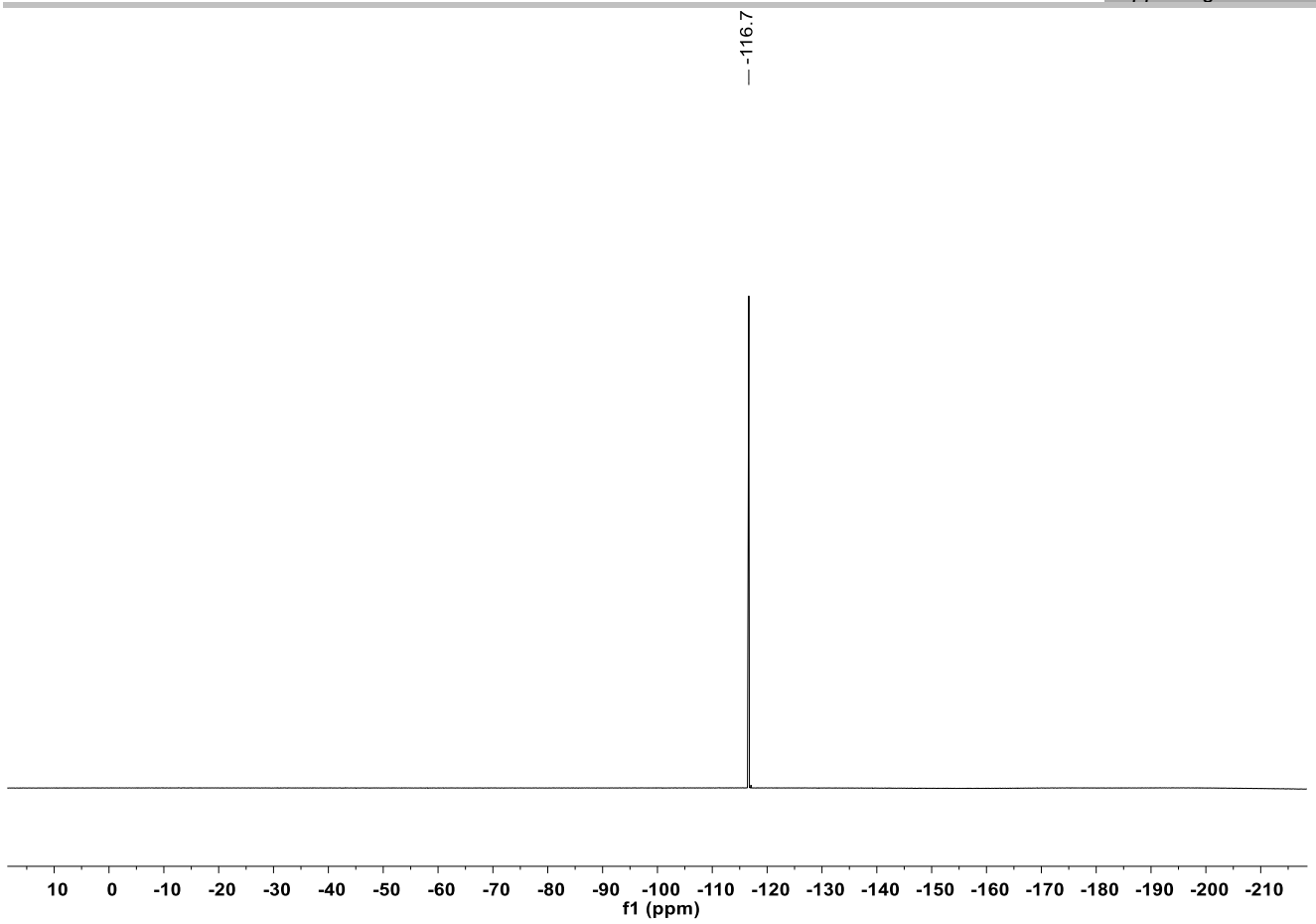


dibenzyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3fa)

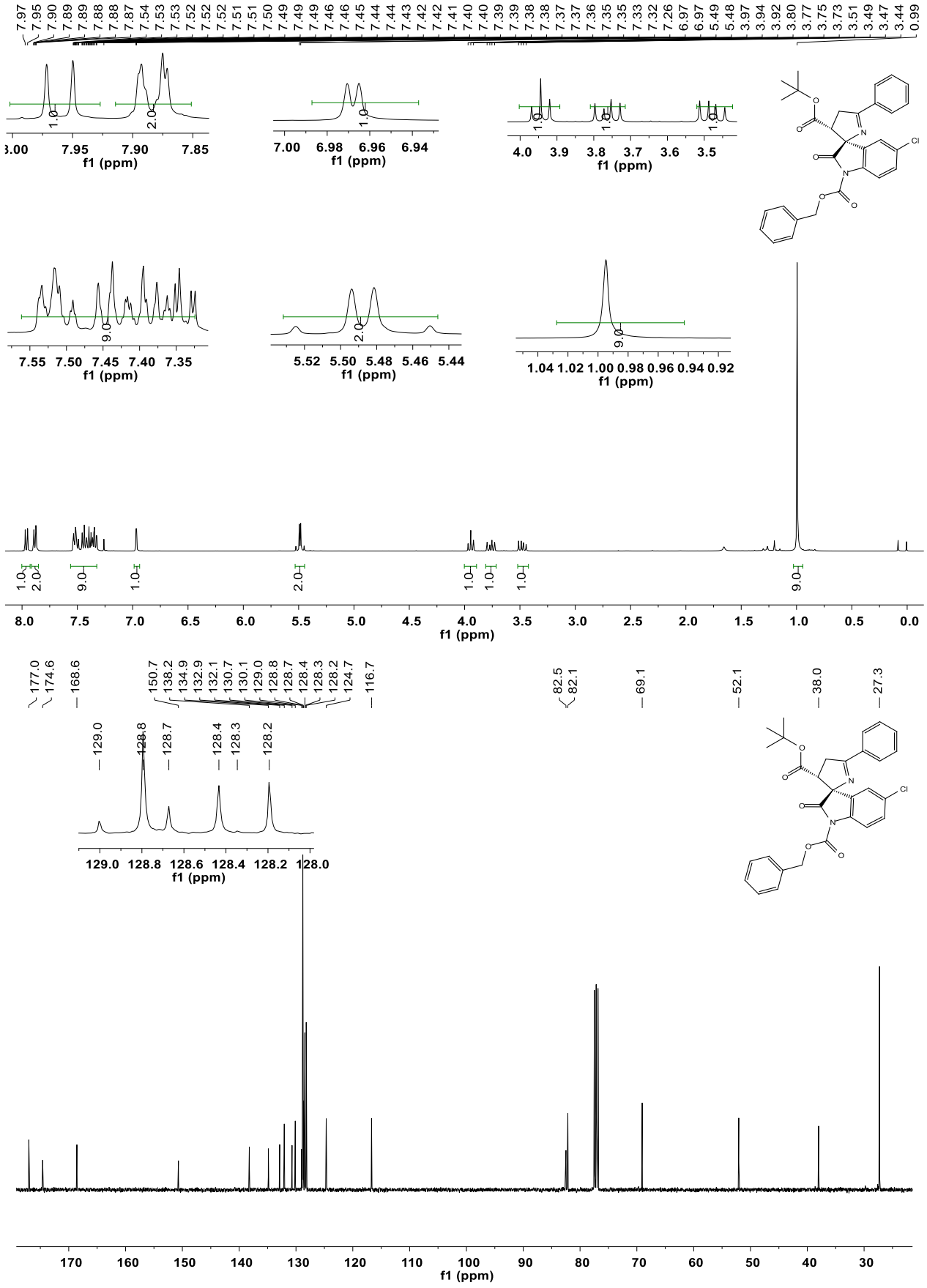


1-benzyl 3'-(tert-butyl) (3S,3'R)-5-fluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ga)

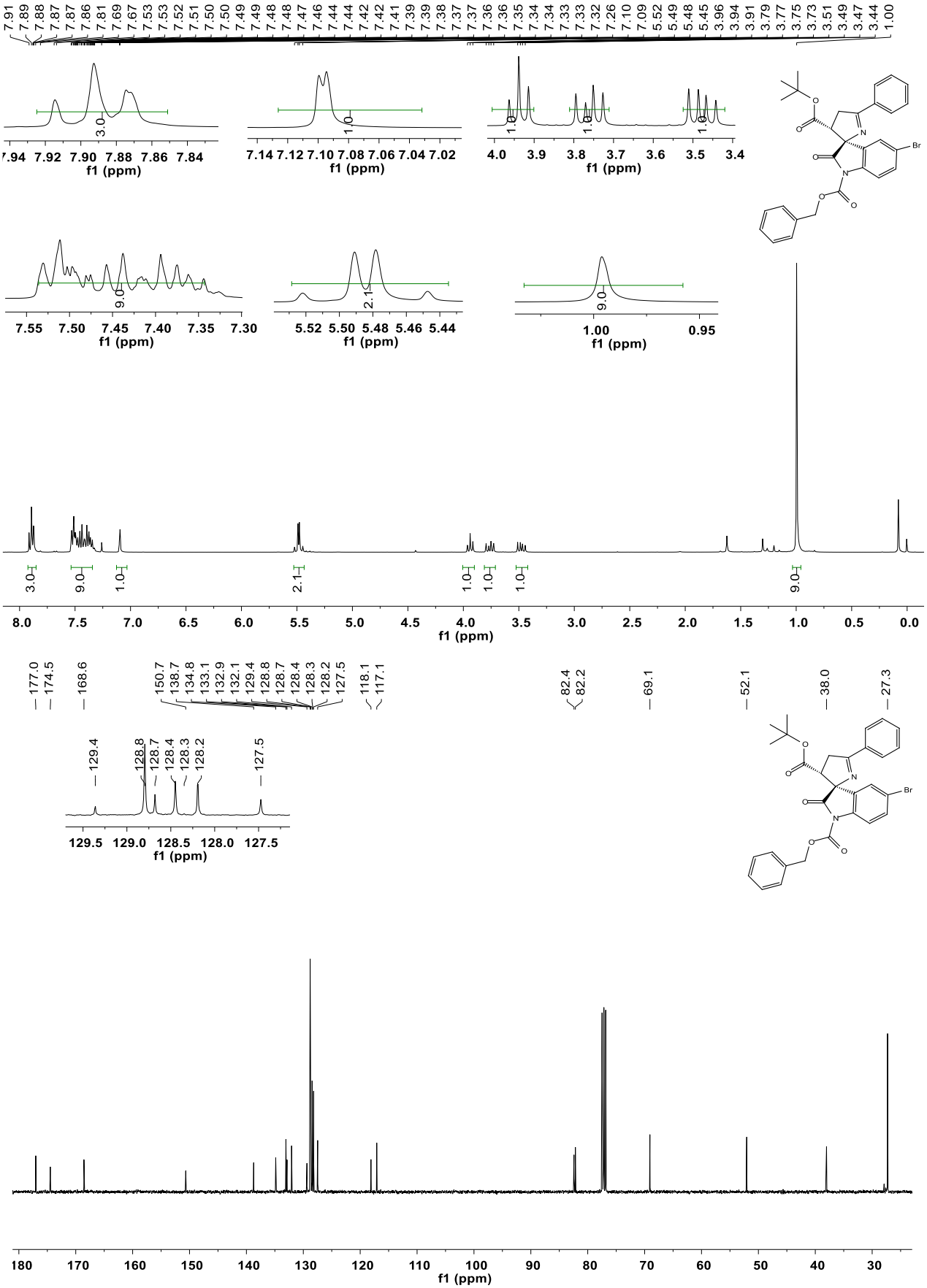



-116.7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

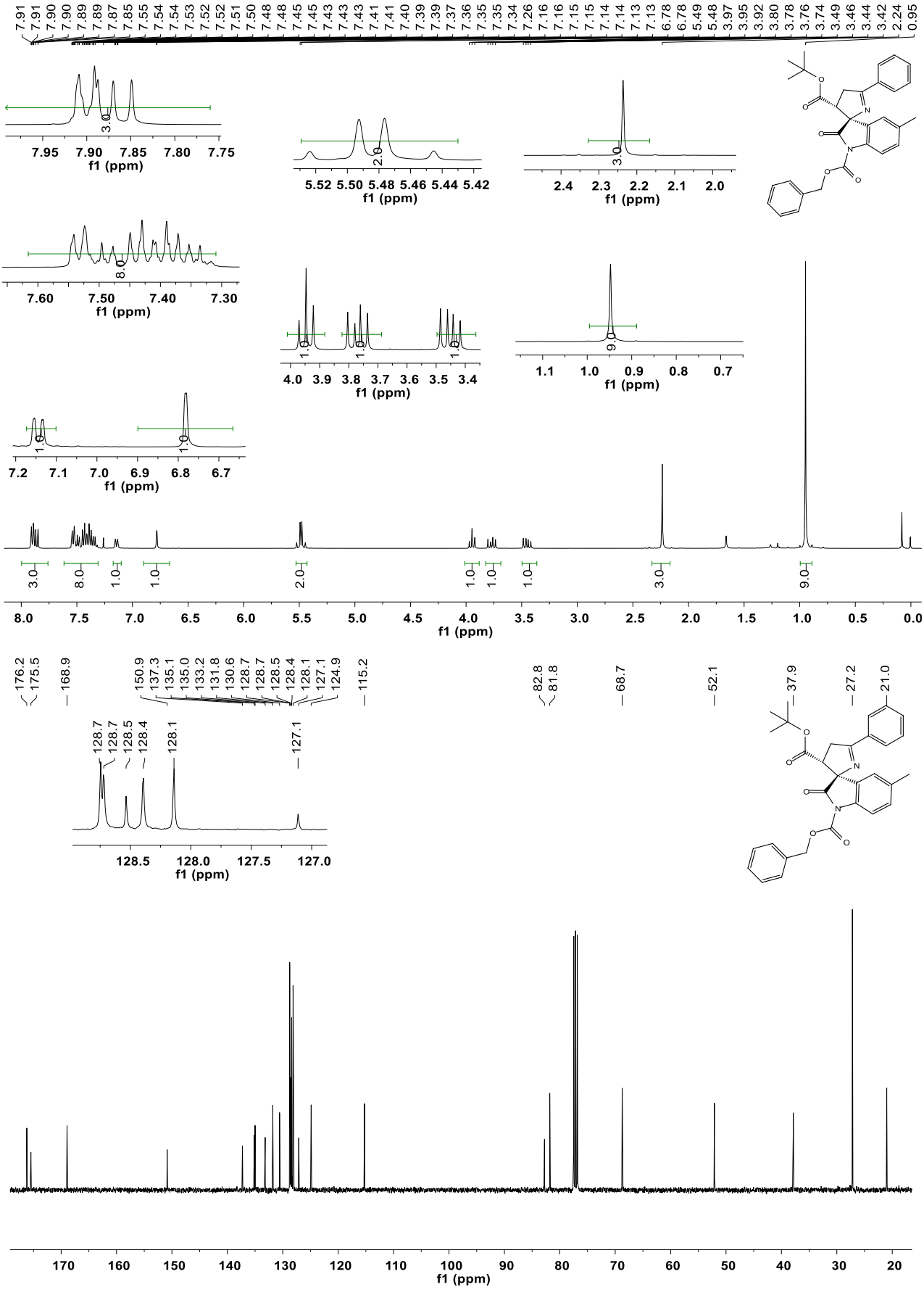
1-benzyl 3'-(tert-butyl) (3S,3'R)-5-chloro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ha)



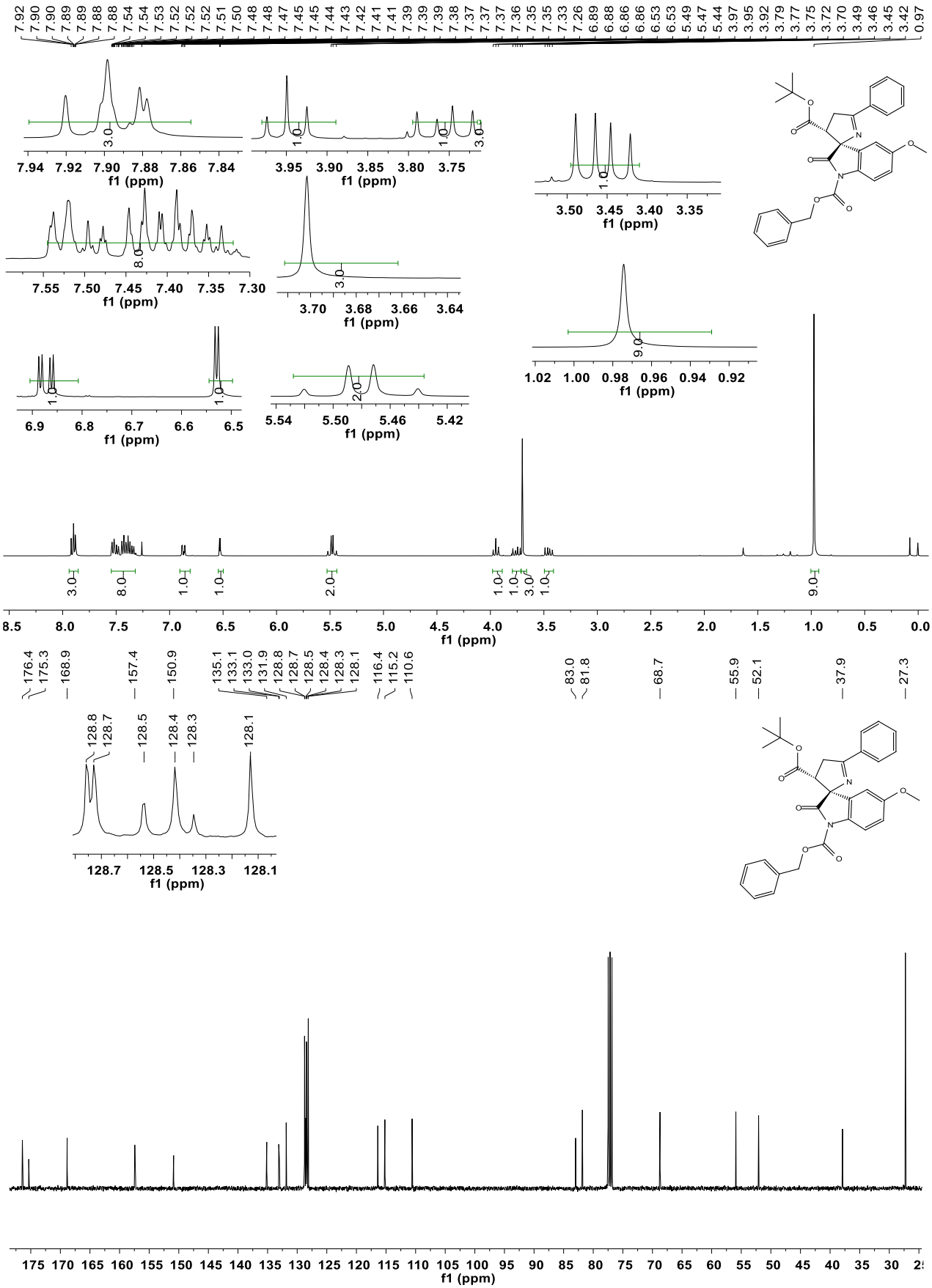
1-benzyl 3'-(tert-butyl) (3S,3'R)-5-bromo-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ia)



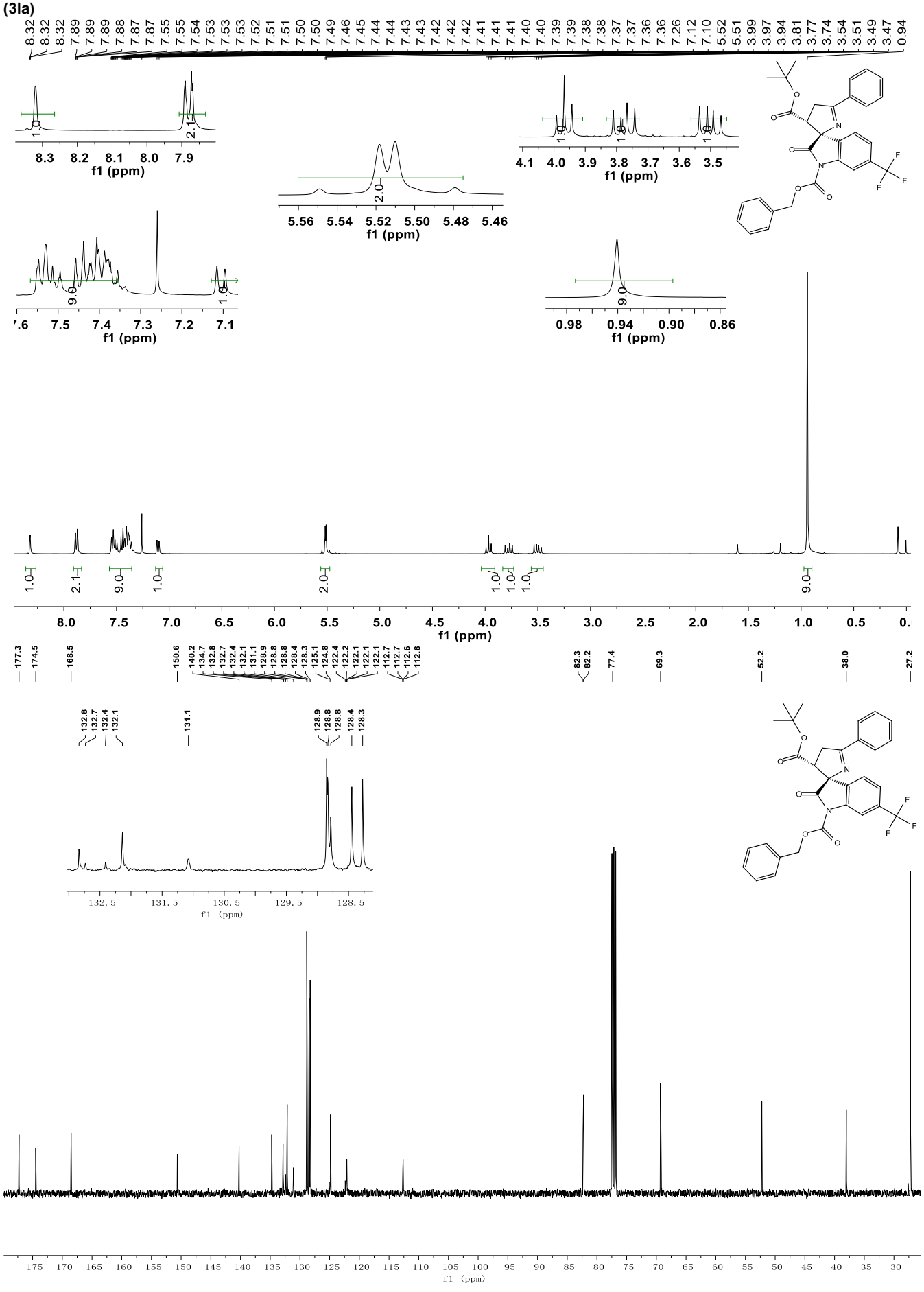
1-benzyl 3'-(tert-butyl) (3S,3'R)-5-methyl-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ja)

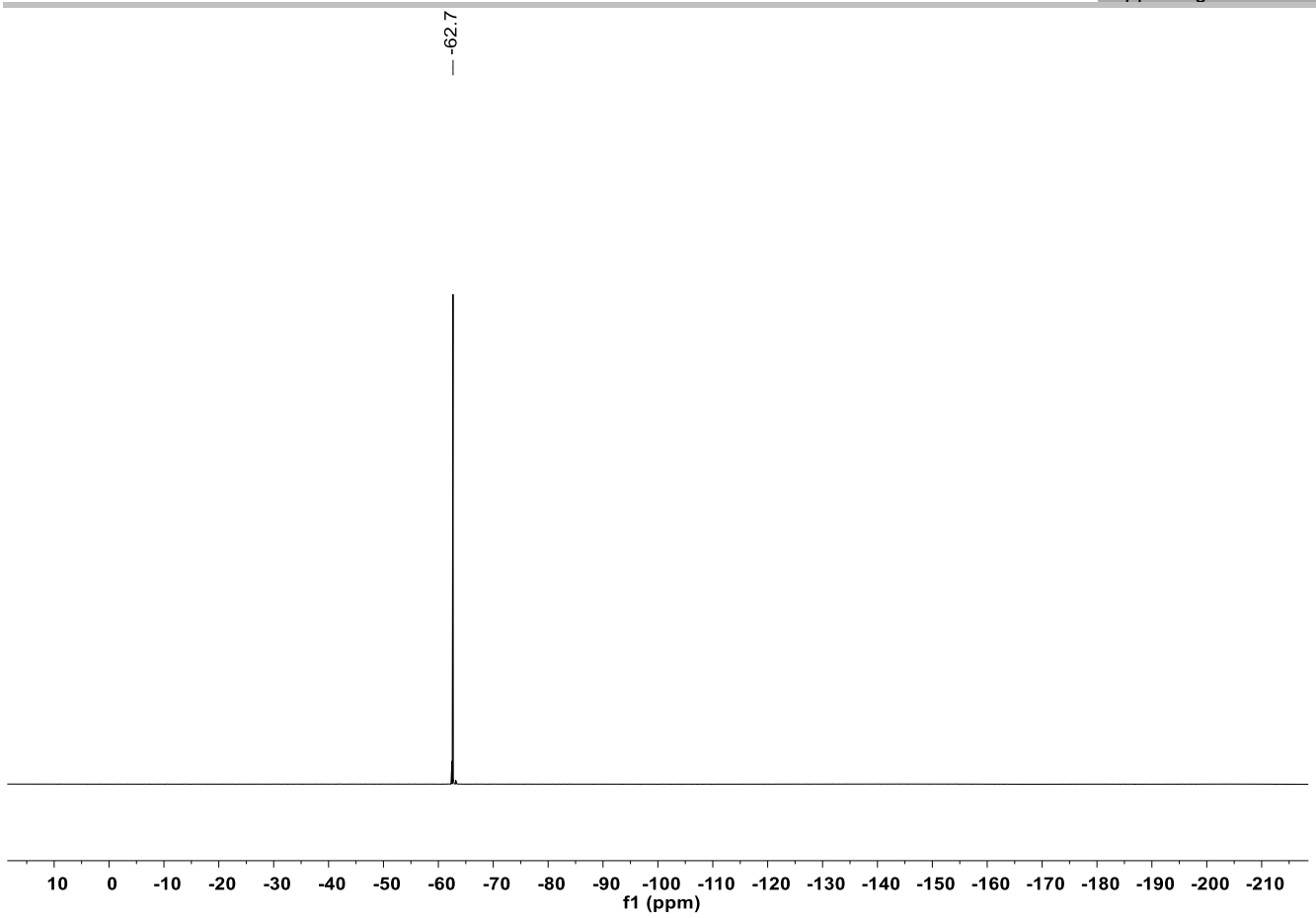


1-benzyl 3'-(tert-butyl) (3S,3'R)-5-methoxy-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ka)



1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-phenyl-6-(trifluoromethyl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3la)




-62.7
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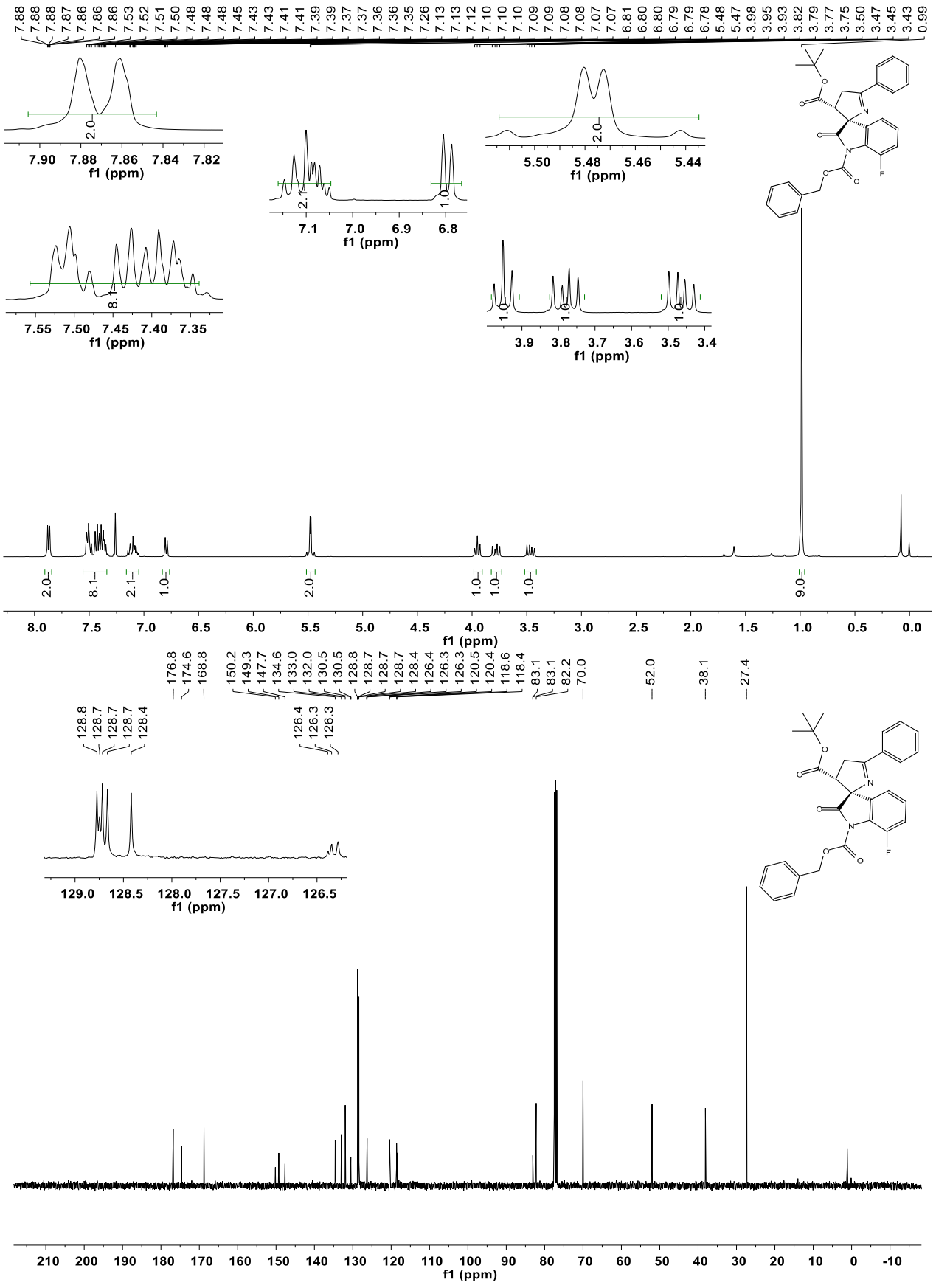
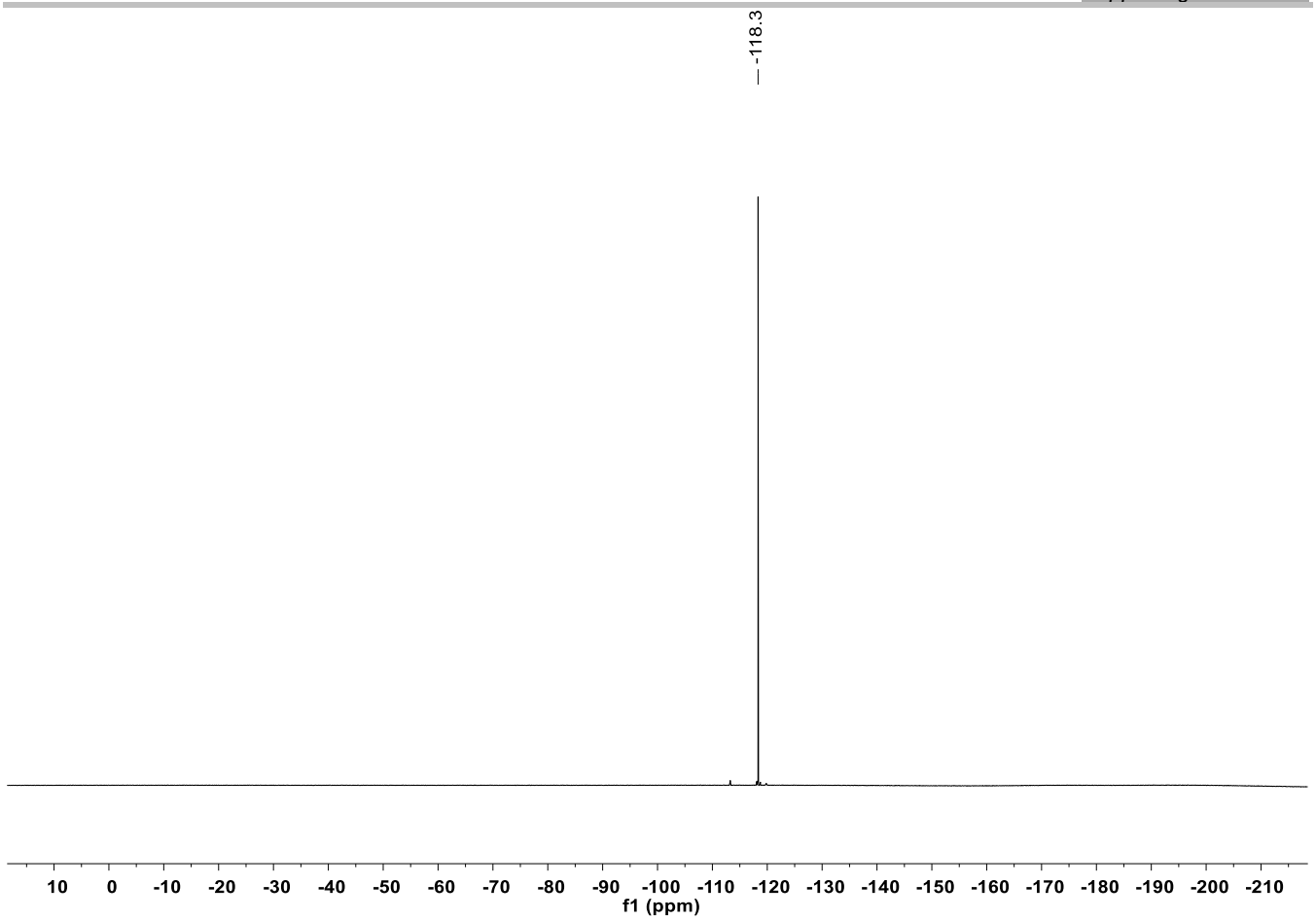
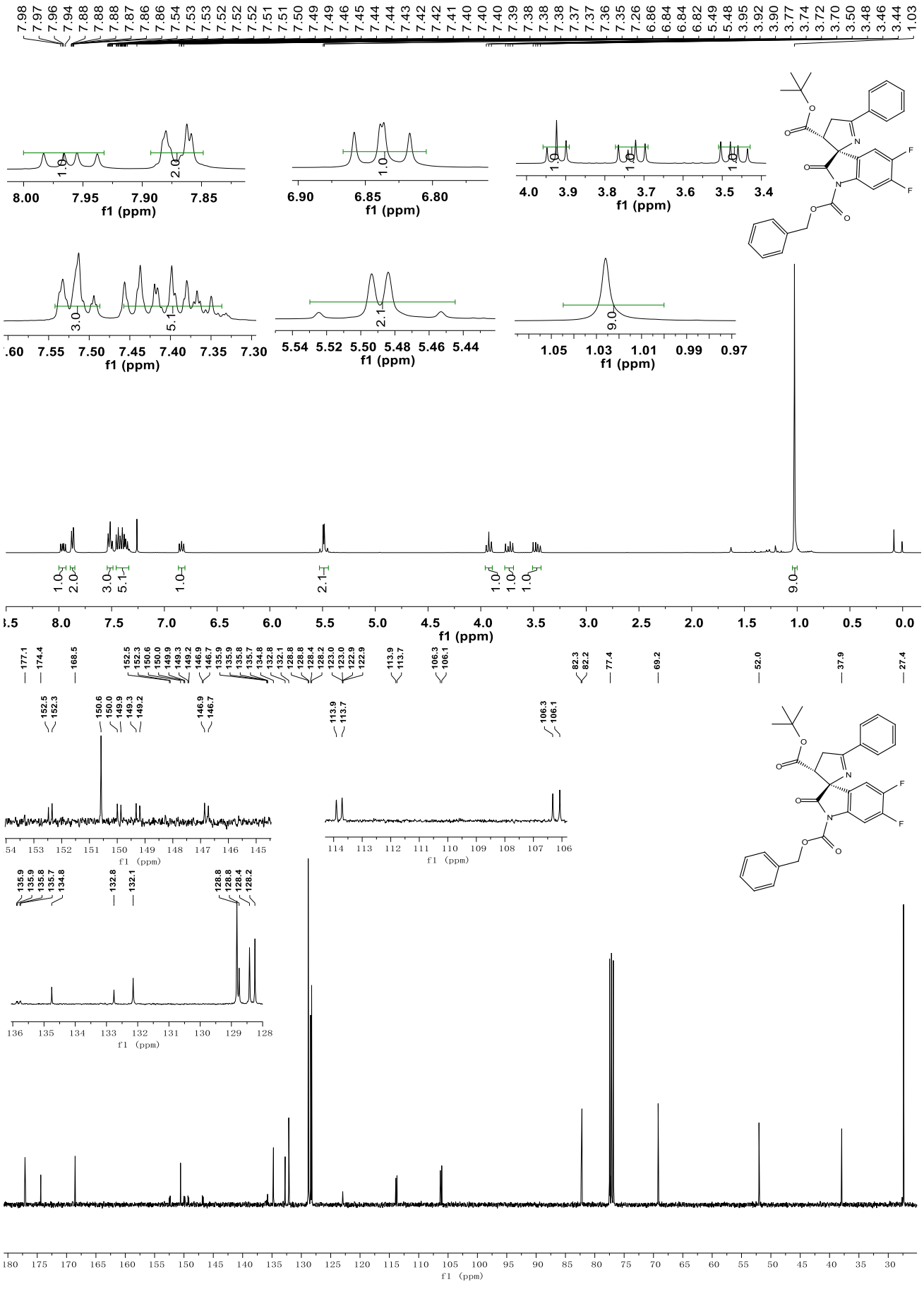
f1 (ppm)

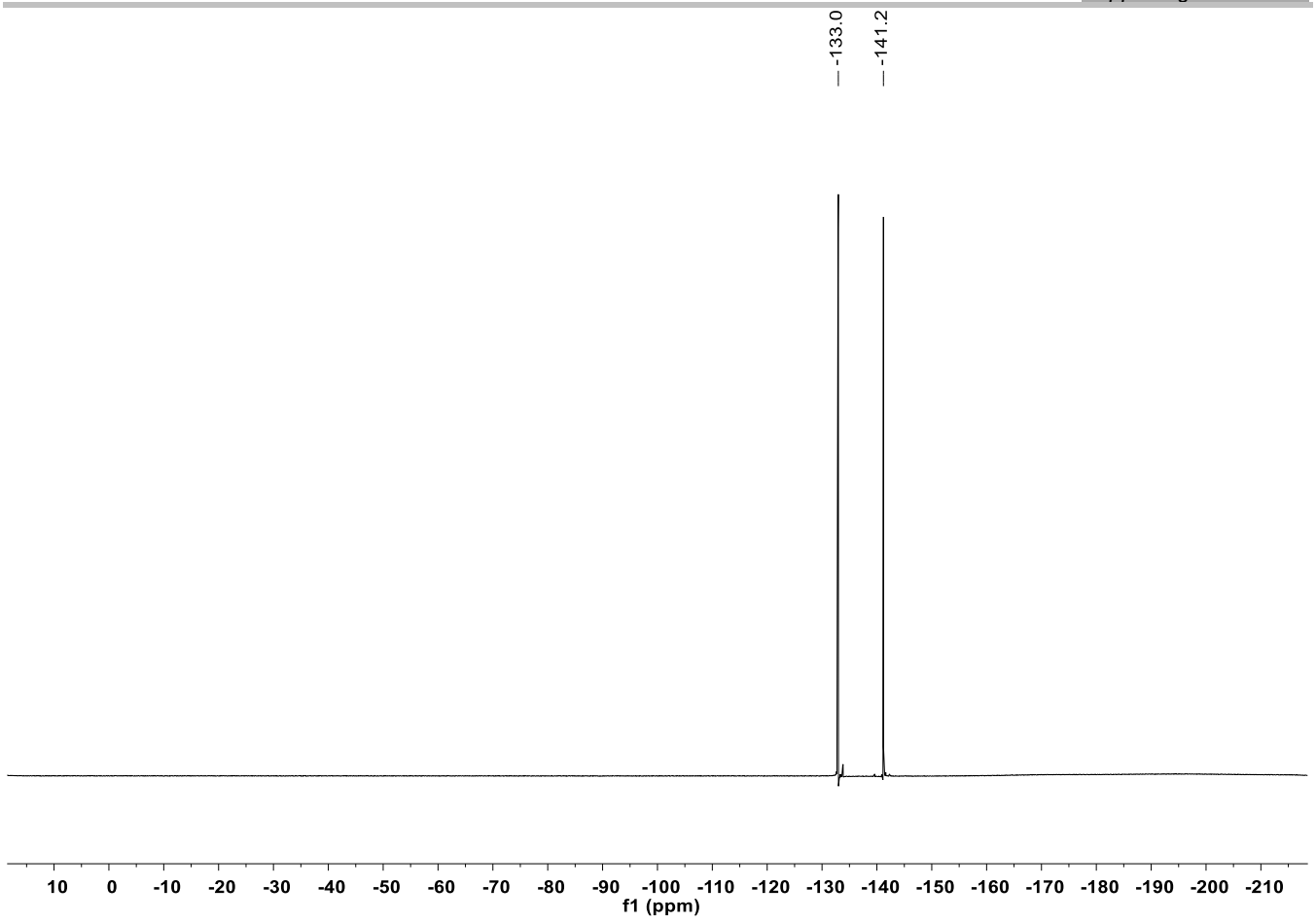
1-benzyl 3'-(tert-butyl) (3S,3'R)-7-fluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ma)



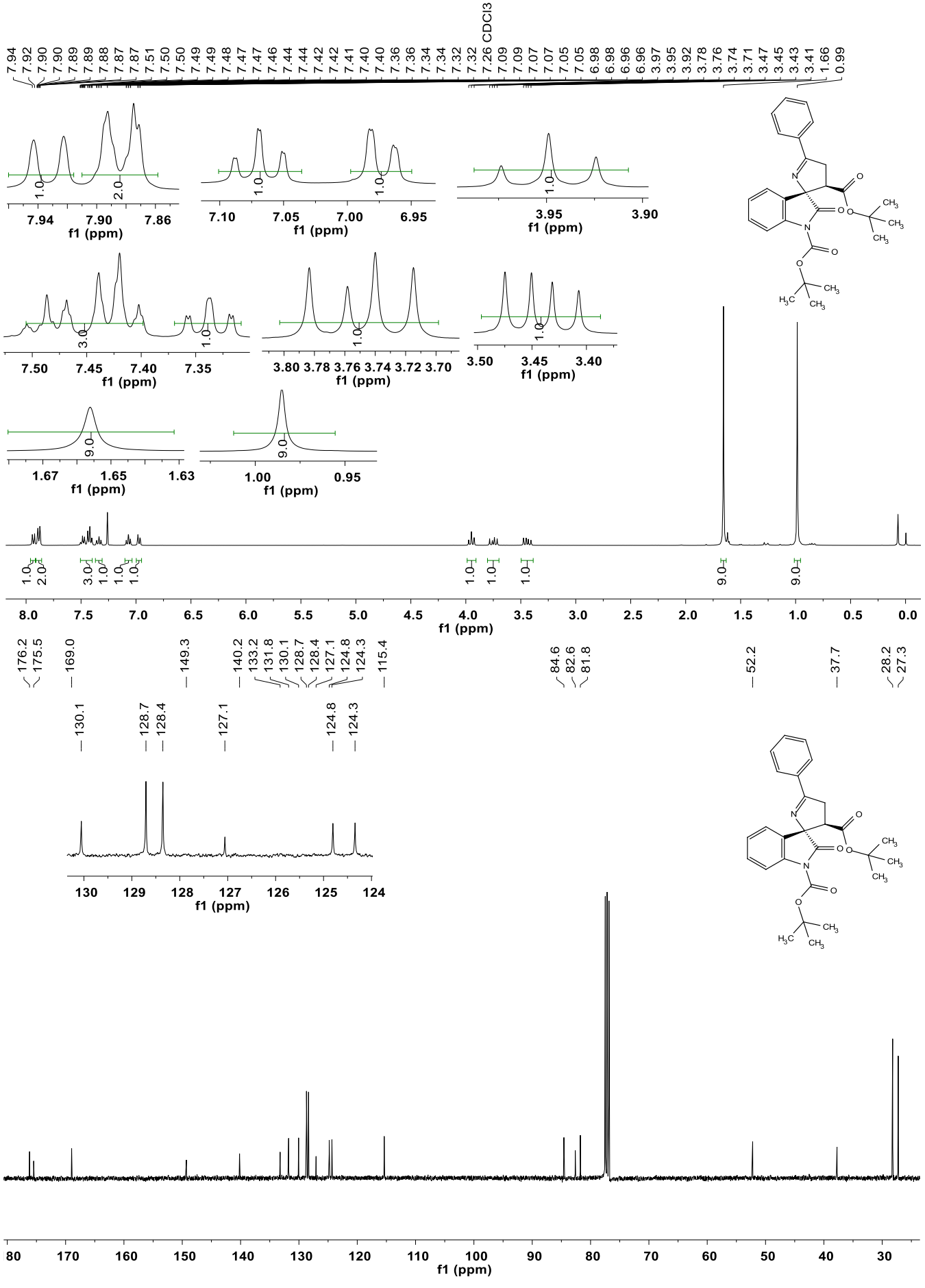

-118.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-benzyl 3'-(tert-butyl) (3S,3'R)-5,6-difluoro-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3na)

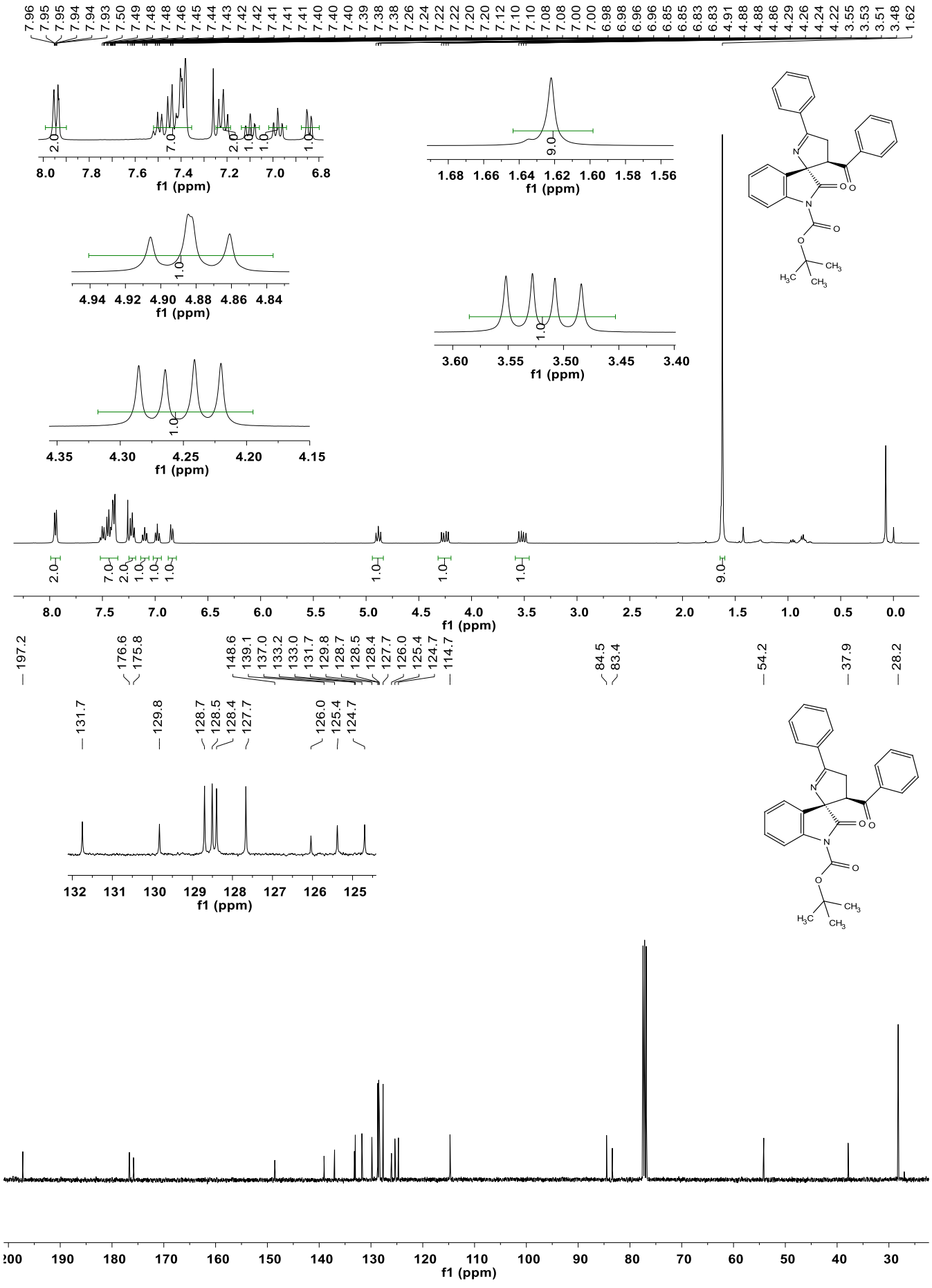



-133.0
-141.2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

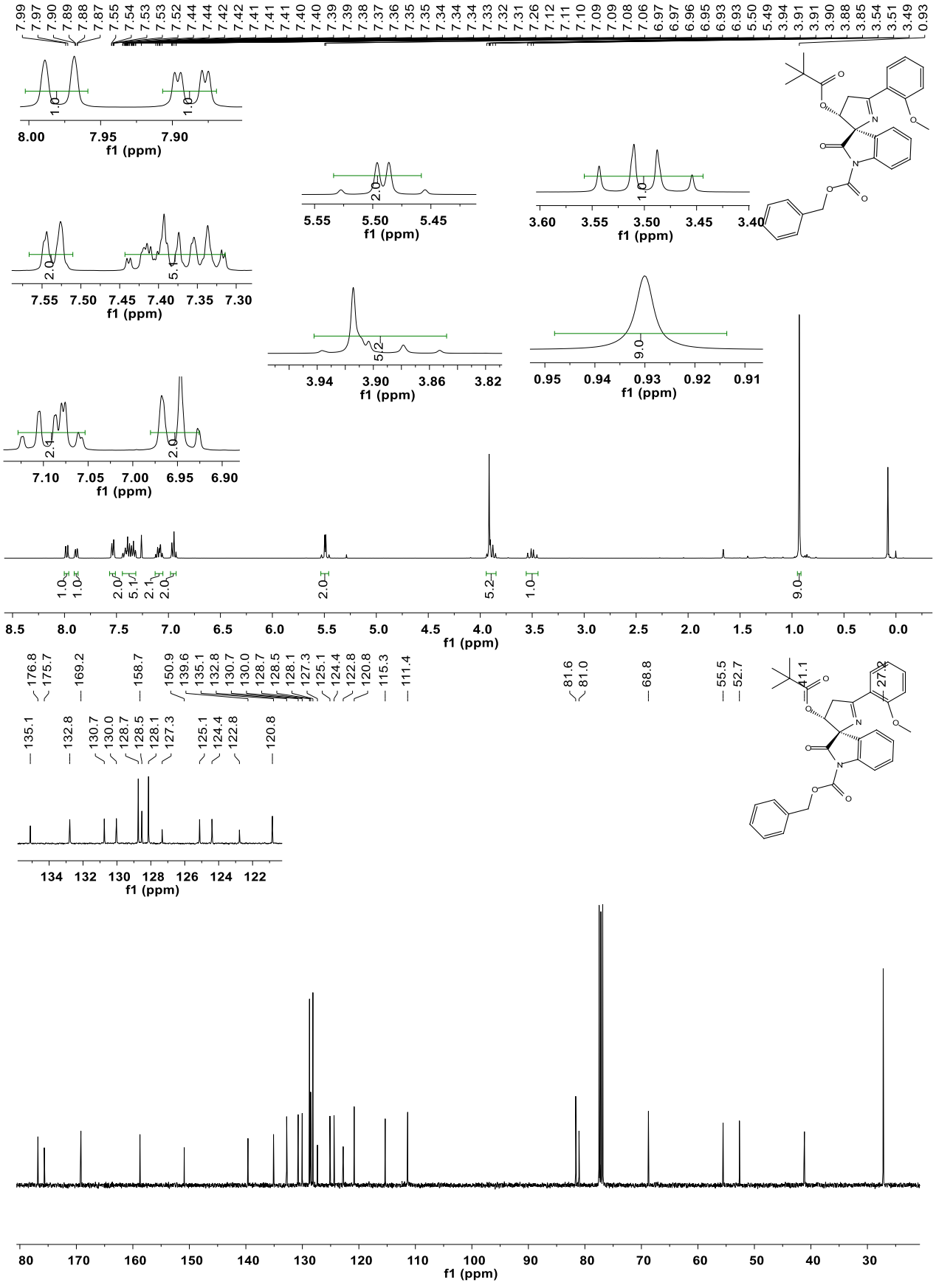
di-tert-butyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3oa)



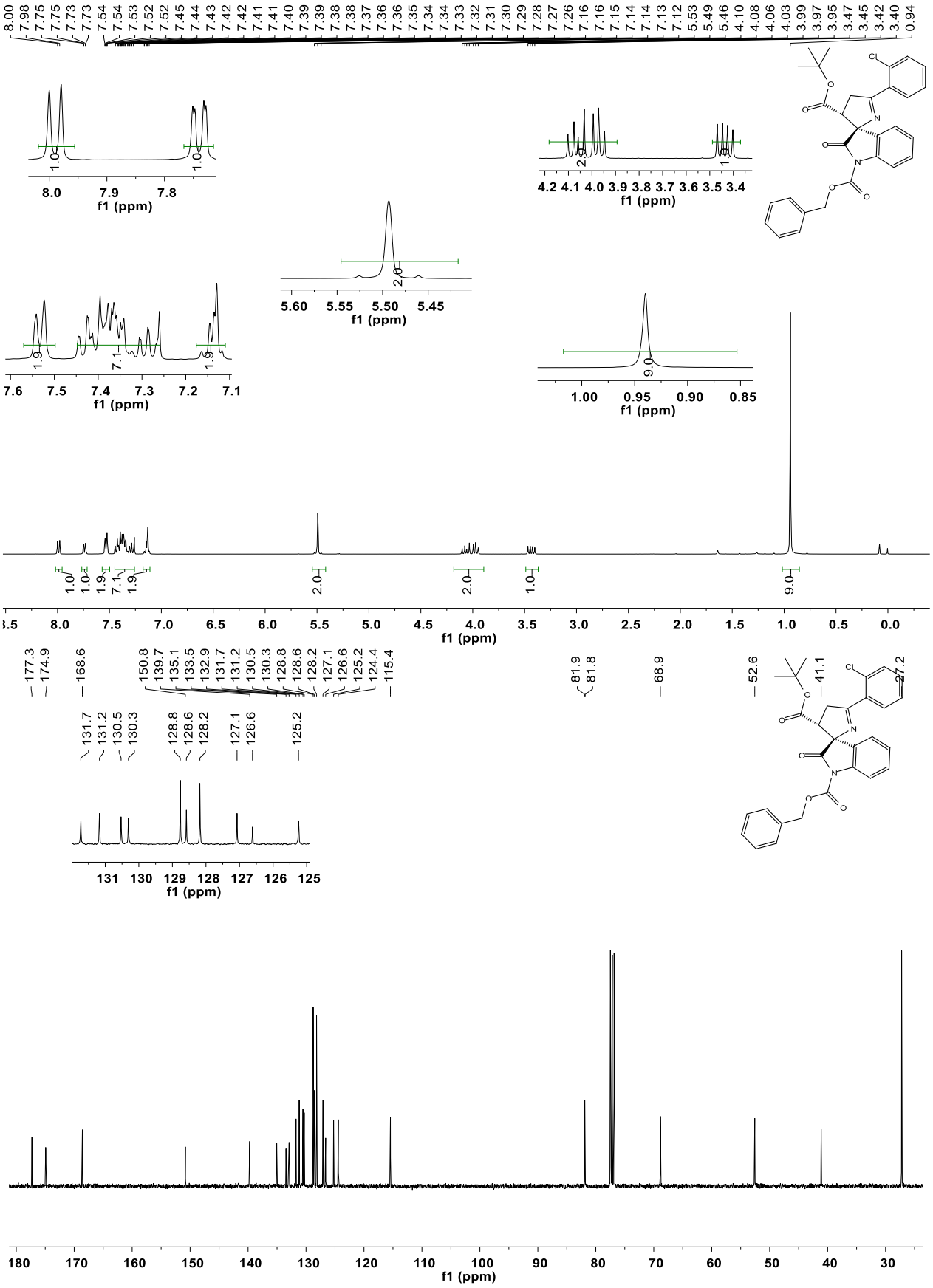
tert-butyl (3S,3'R)-3'-benzoyl-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1-carboxylate (3pa)



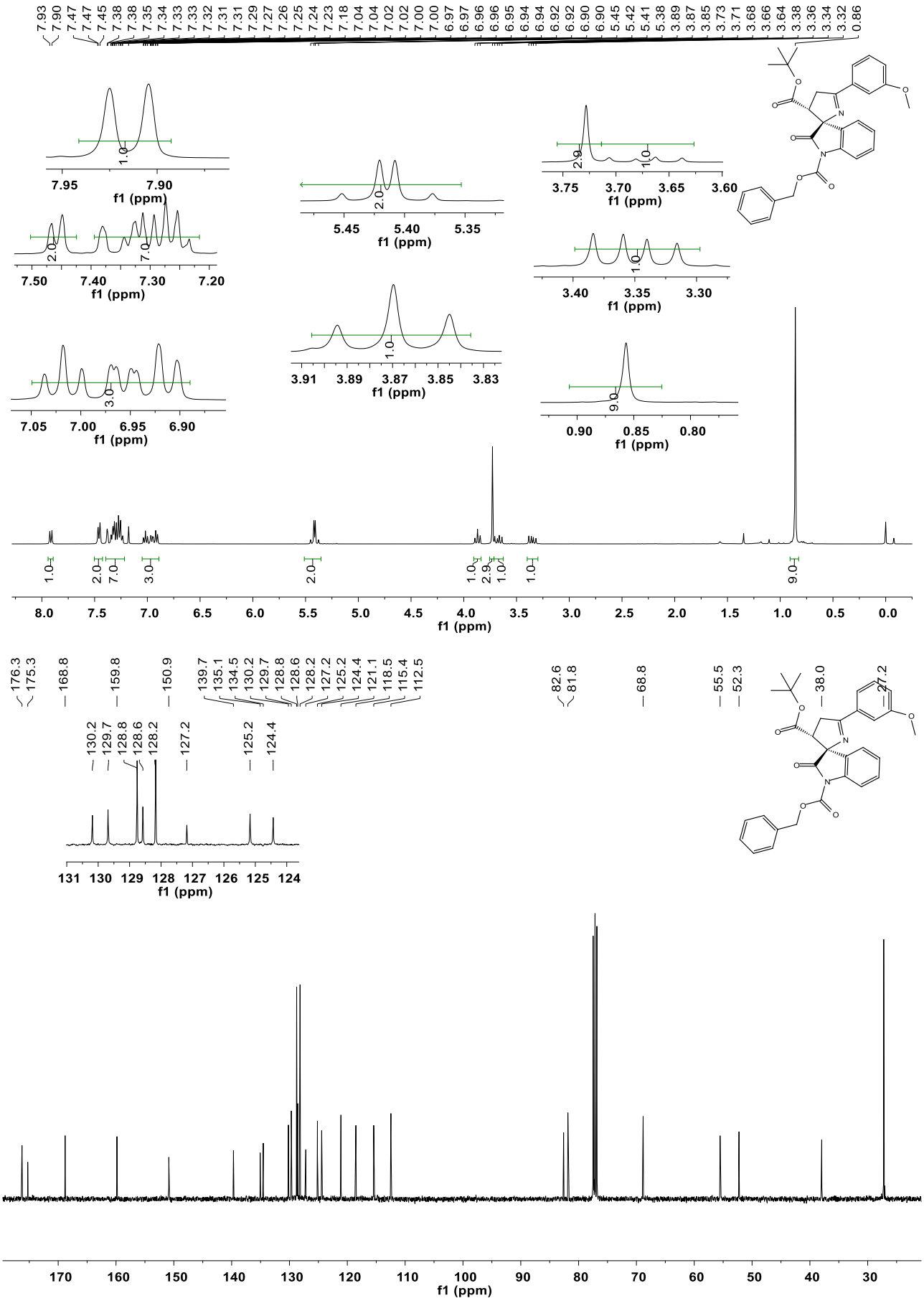
benzyl (3R,3'R)-5'-(2-methoxyphenyl)-2-oxo-3'-(pivaloyloxy)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1-carboxylate (3ab)



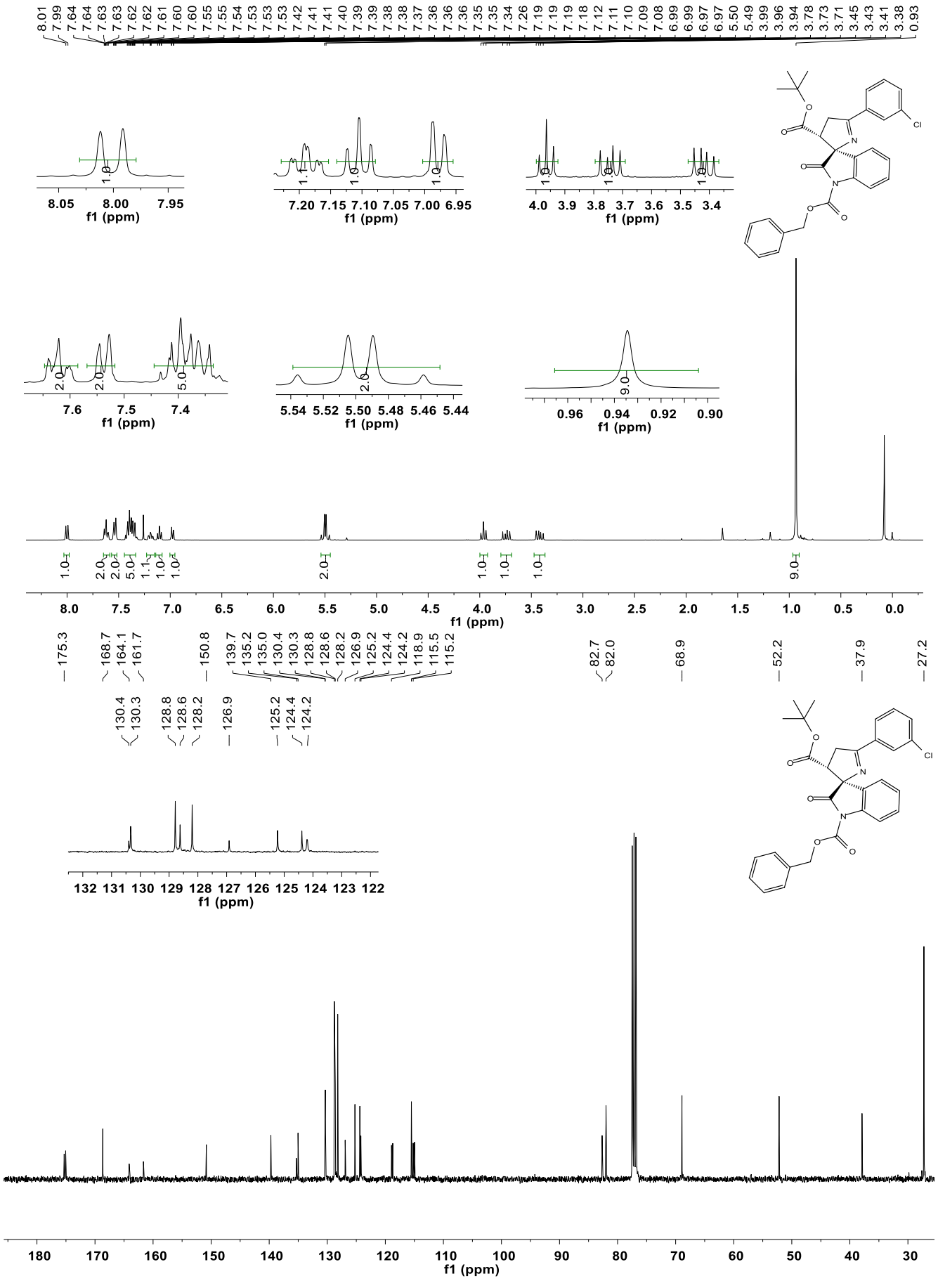
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(2-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ac)



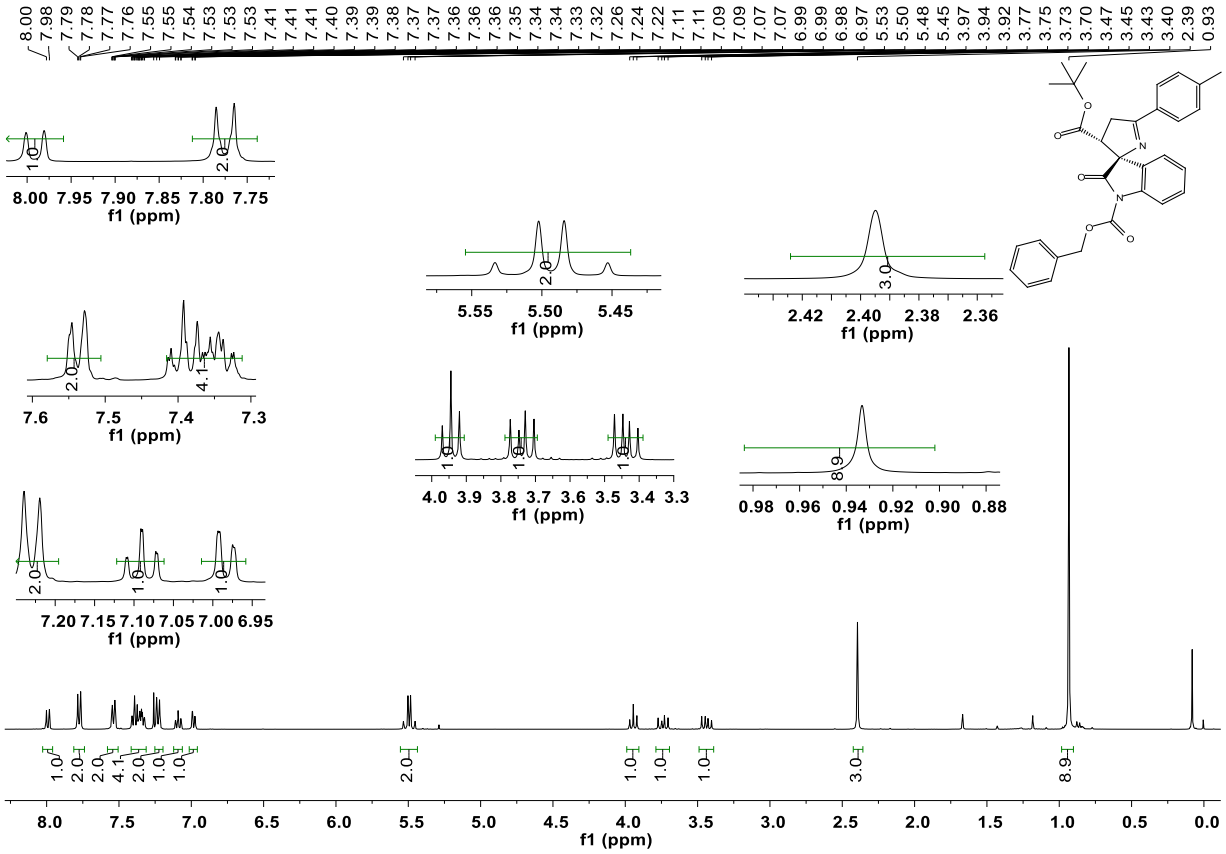
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(3-methoxyphenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ad)

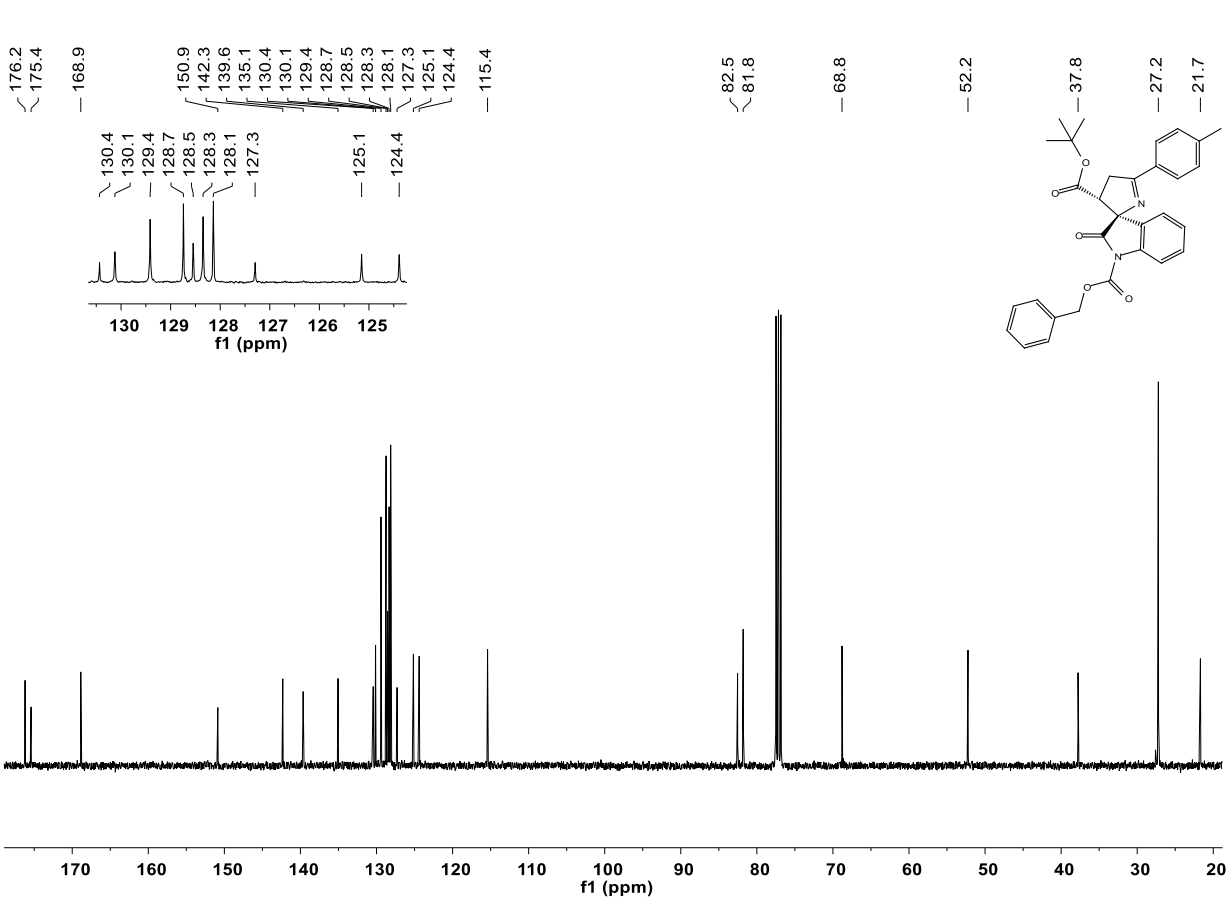


1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(3-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ae)

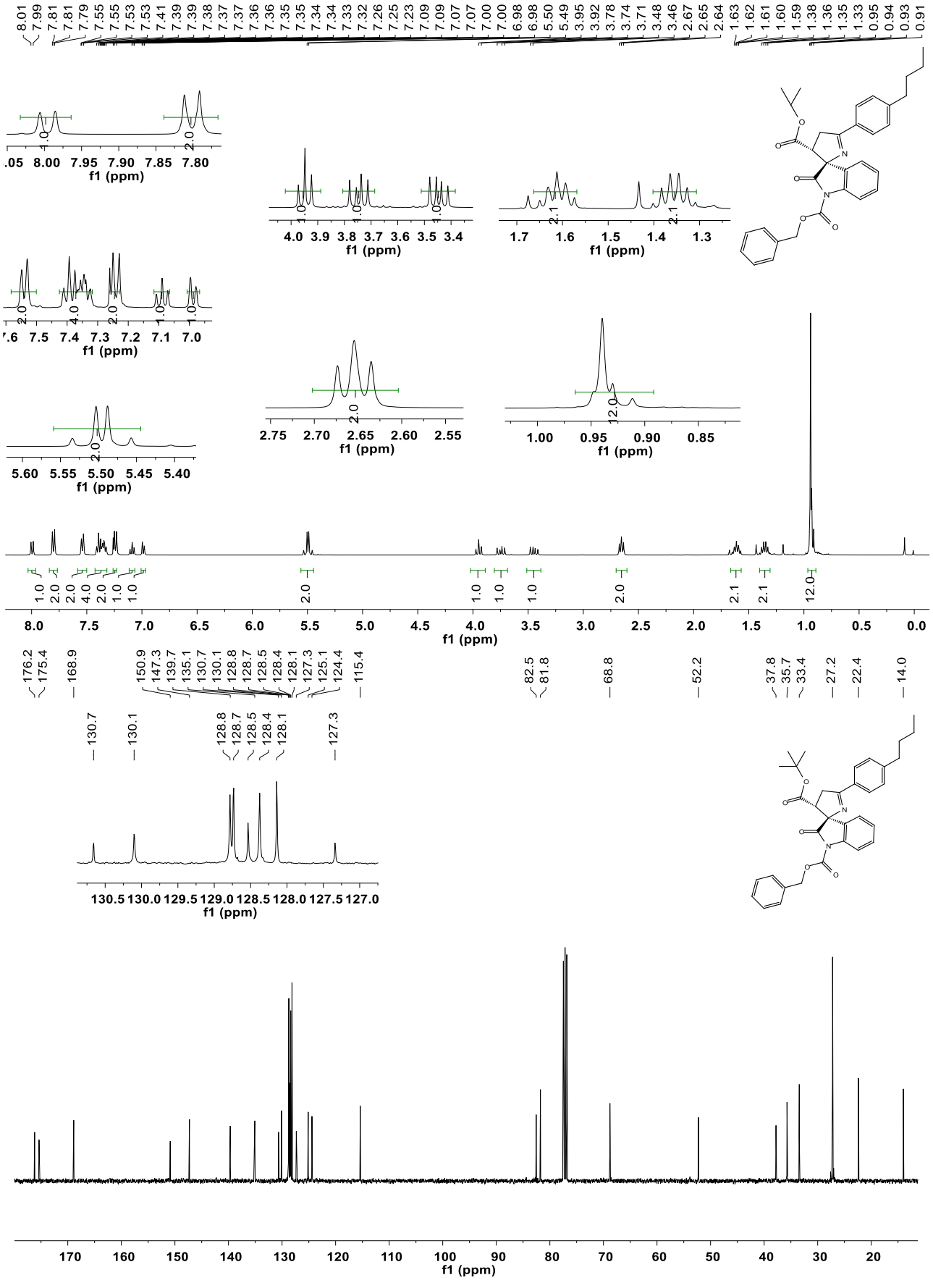


1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-(p-tolyl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3af)

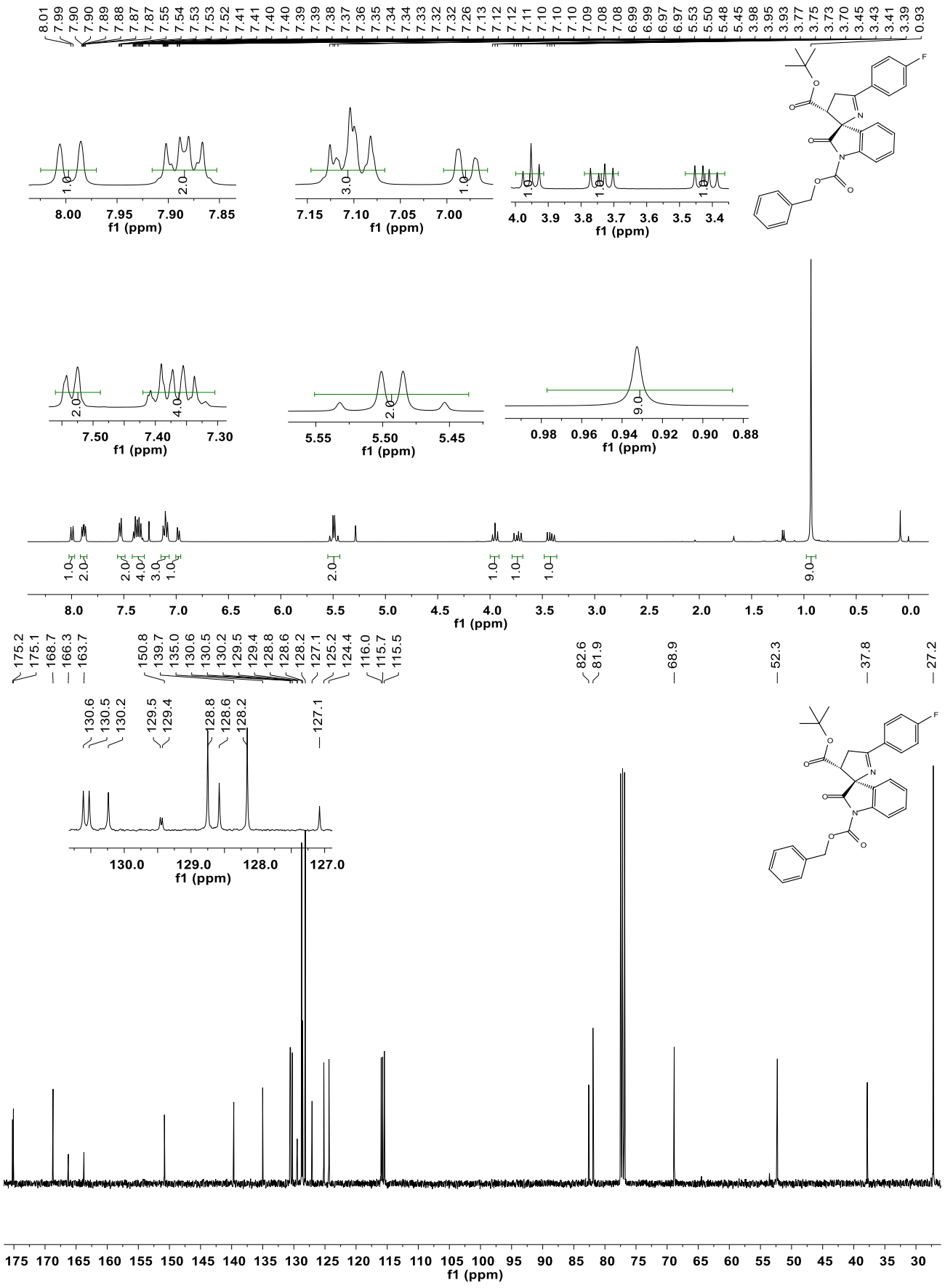


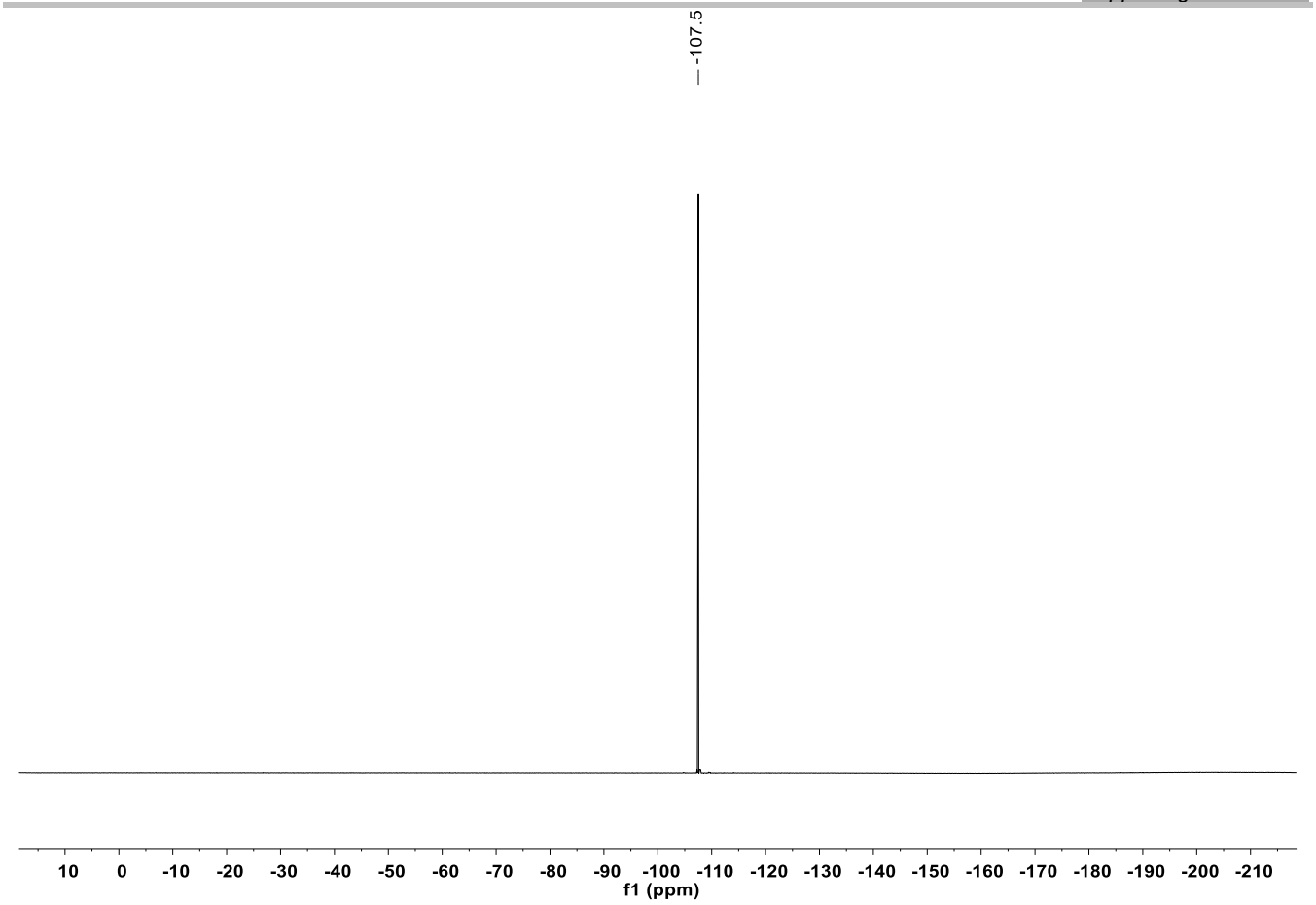


1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-butylphenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ag)

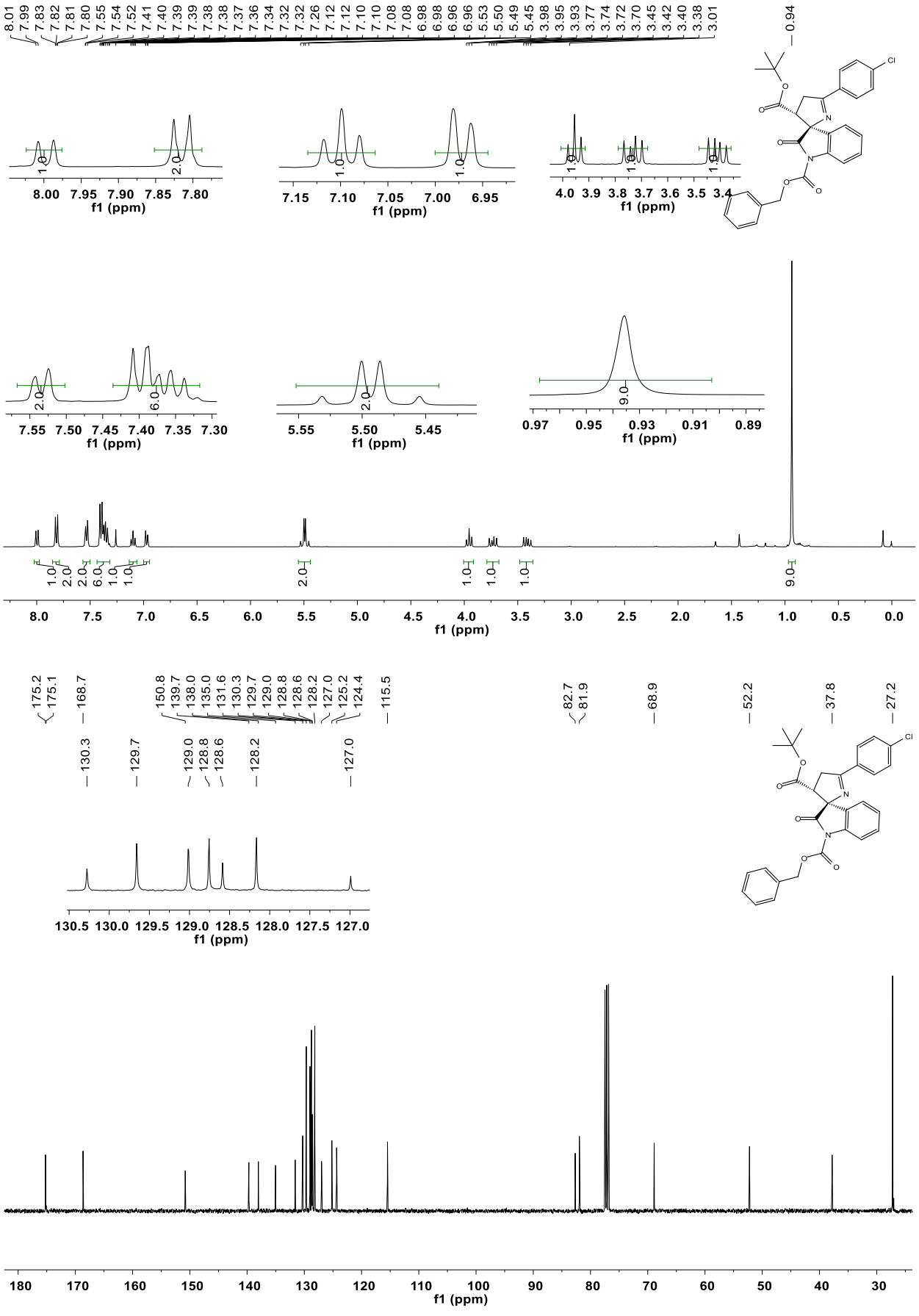


1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-fluorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ah)

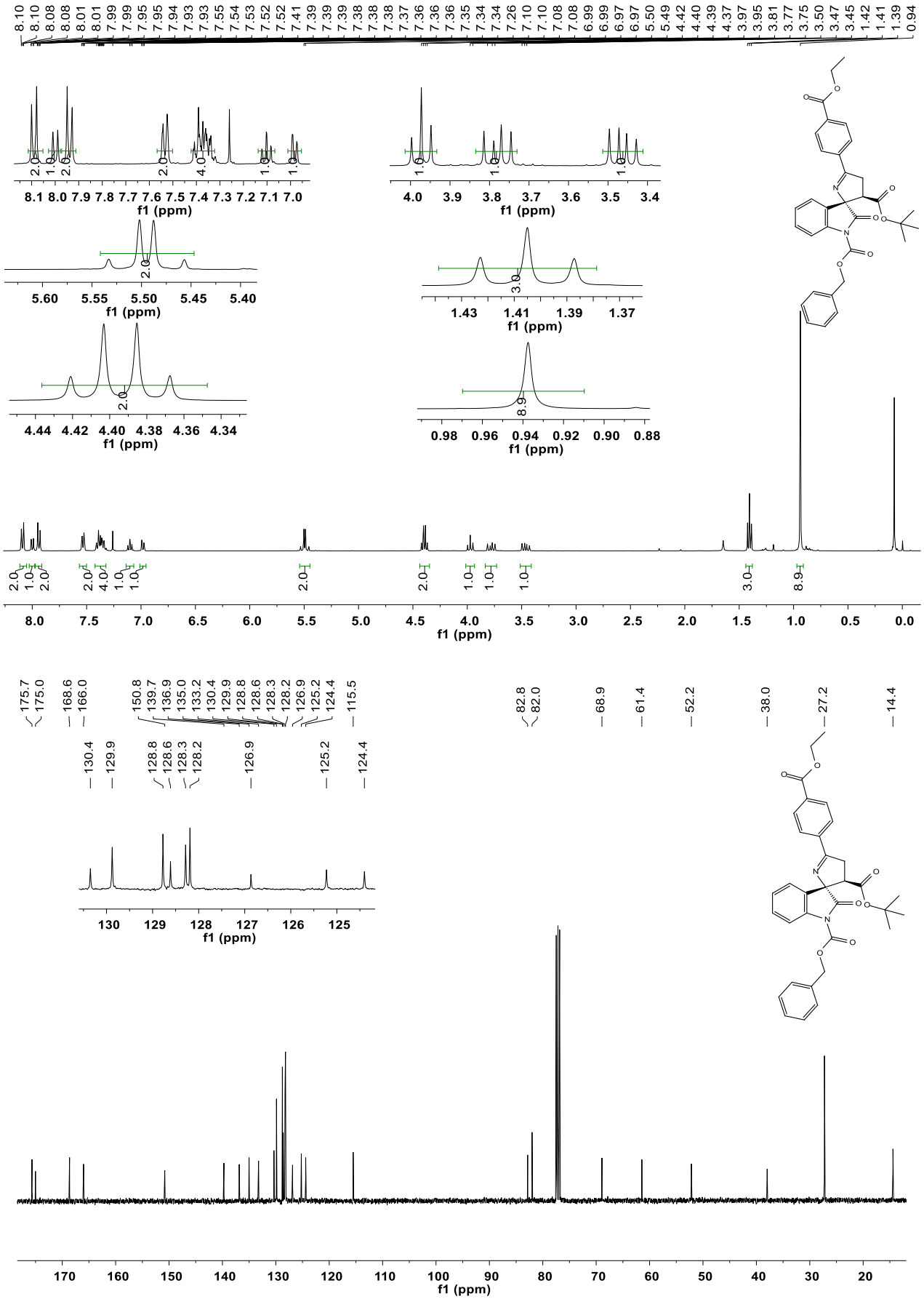



-107.5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

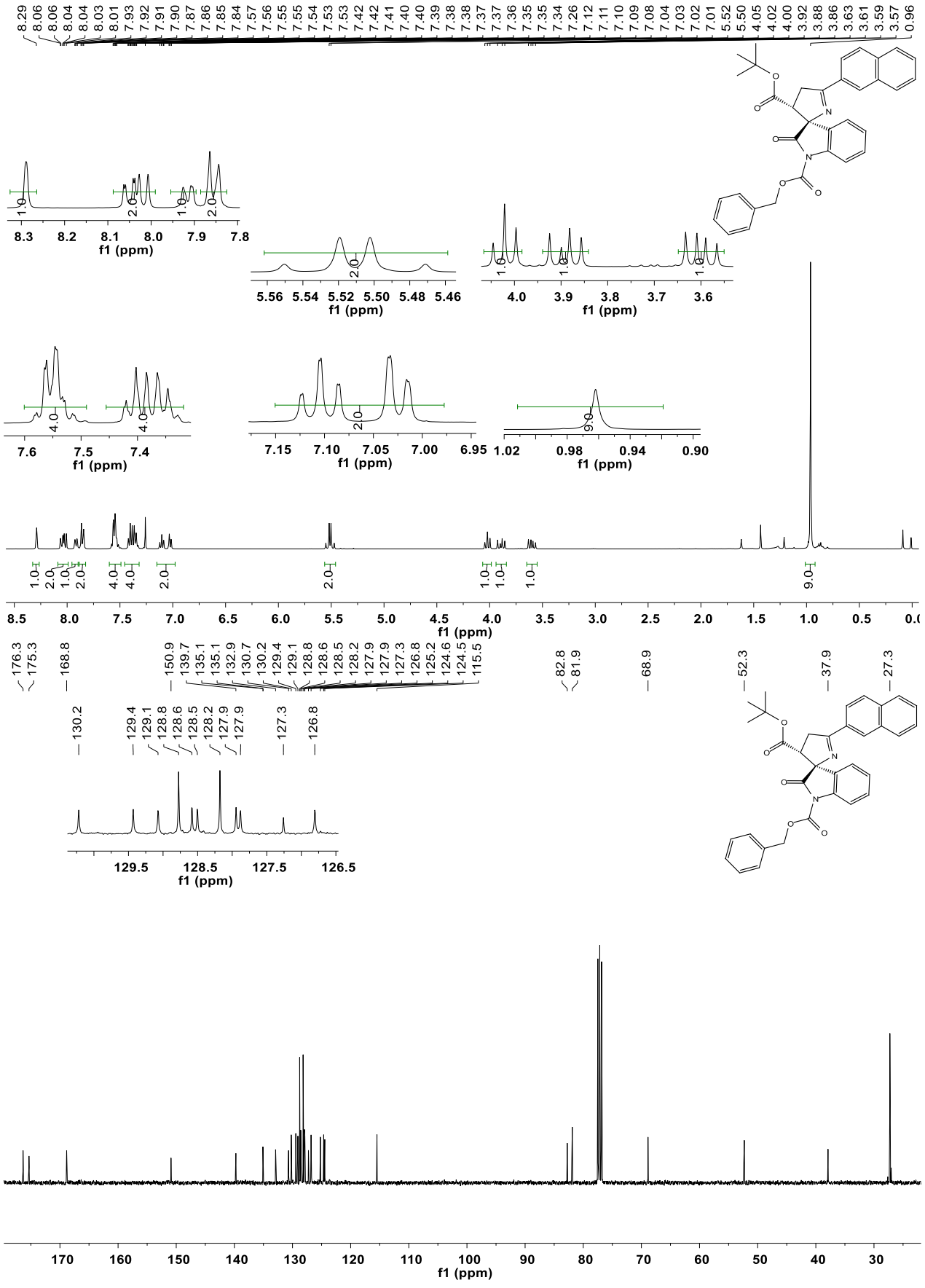
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(4-chlorophenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ai)



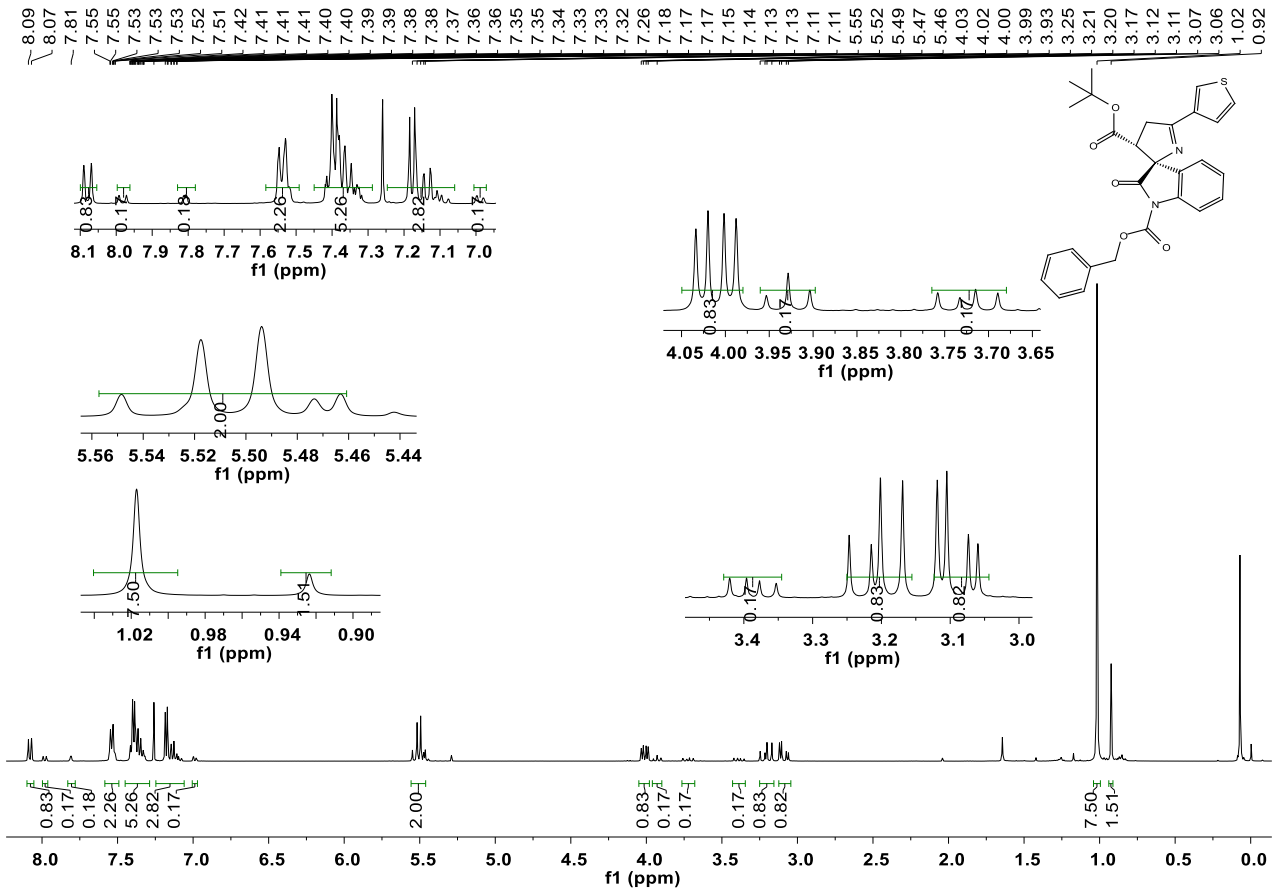
1-benzyl3'-(tert-butyl) (3S,3'R)-5'-(4-(ethoxycarbonyl)phenyl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3aj)

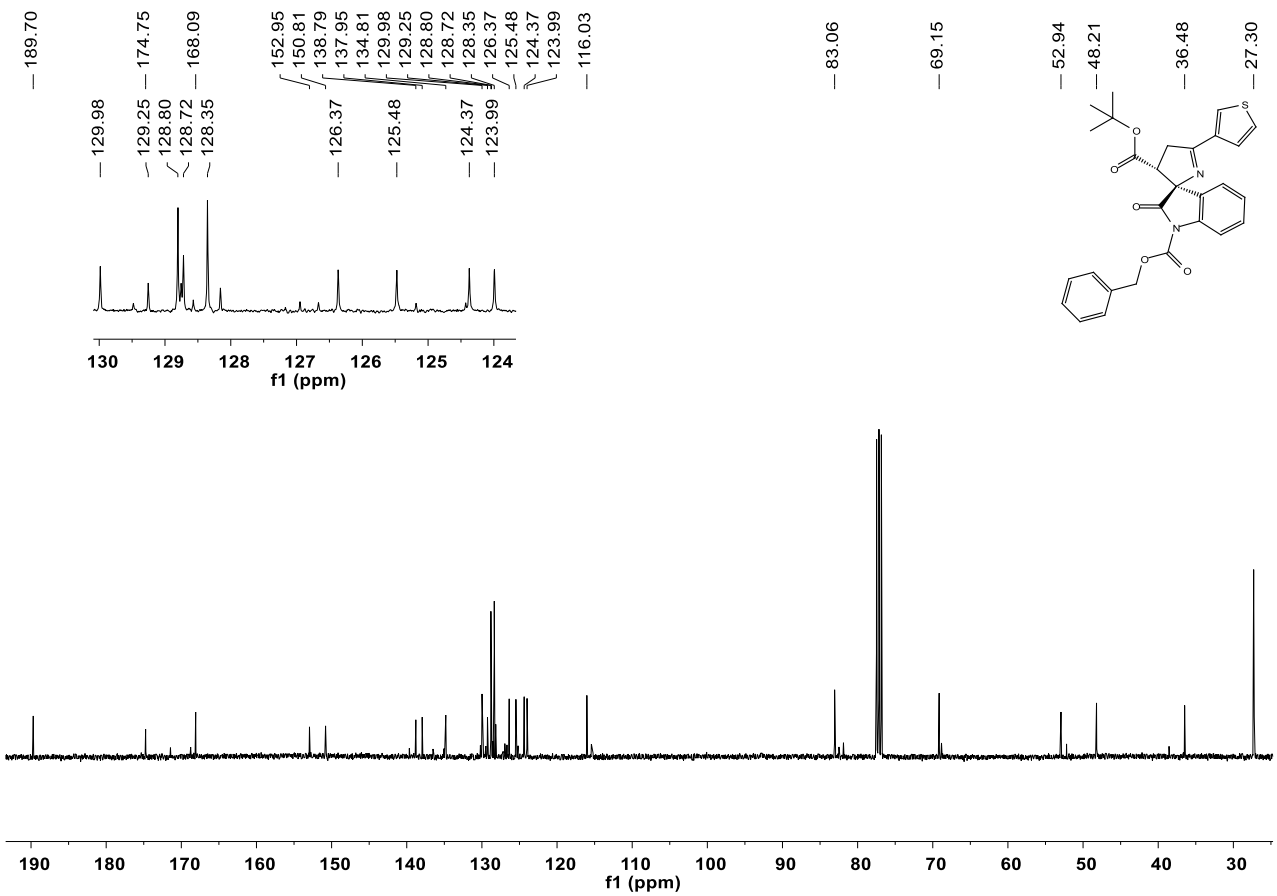


1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-(naphthalen-2-yl)-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3ak)

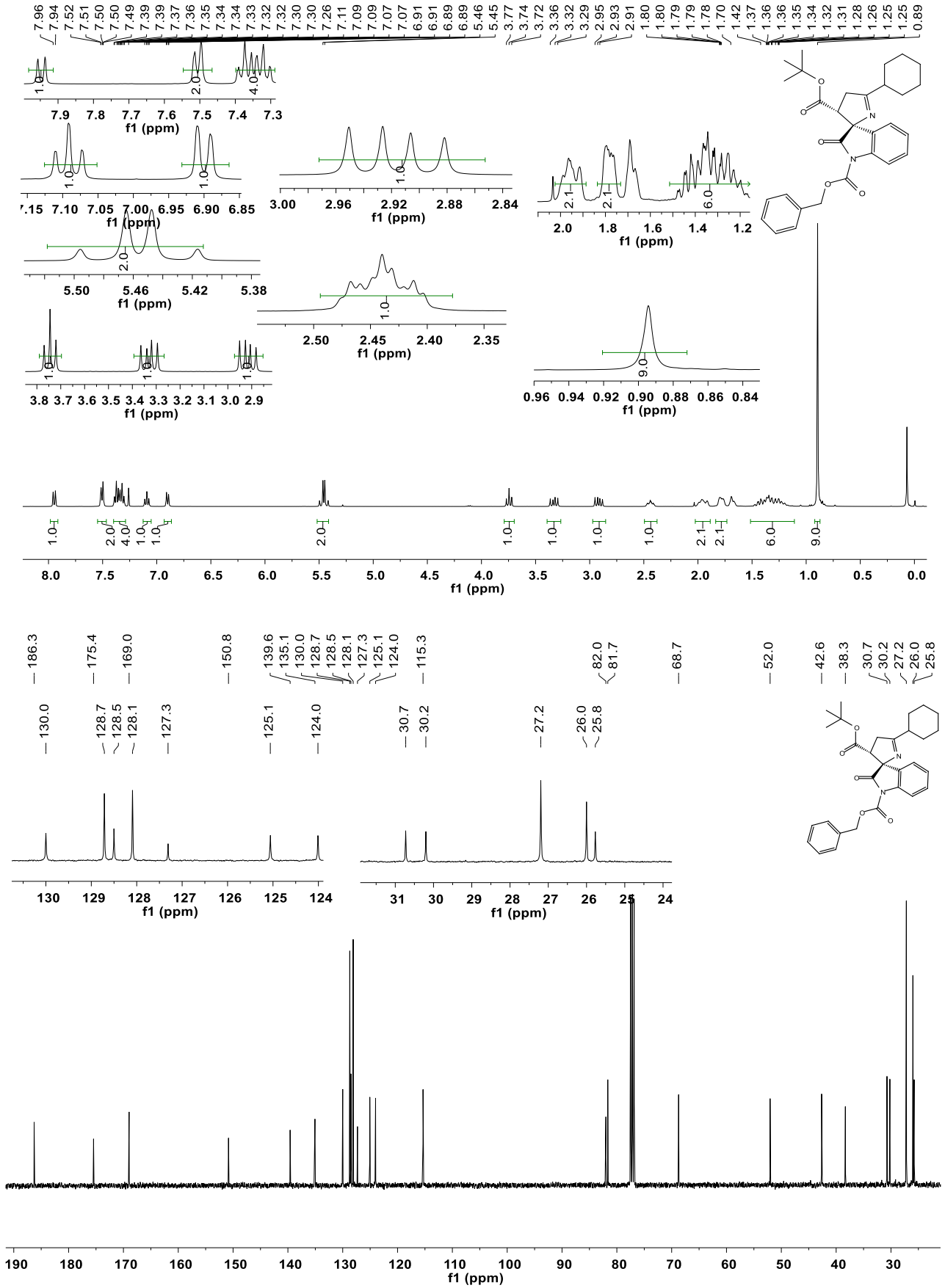


1-benzyl 3'-(tert-butyl) (3S,3'R)-2-oxo-5'-(thiophen-3-yl)-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3al)

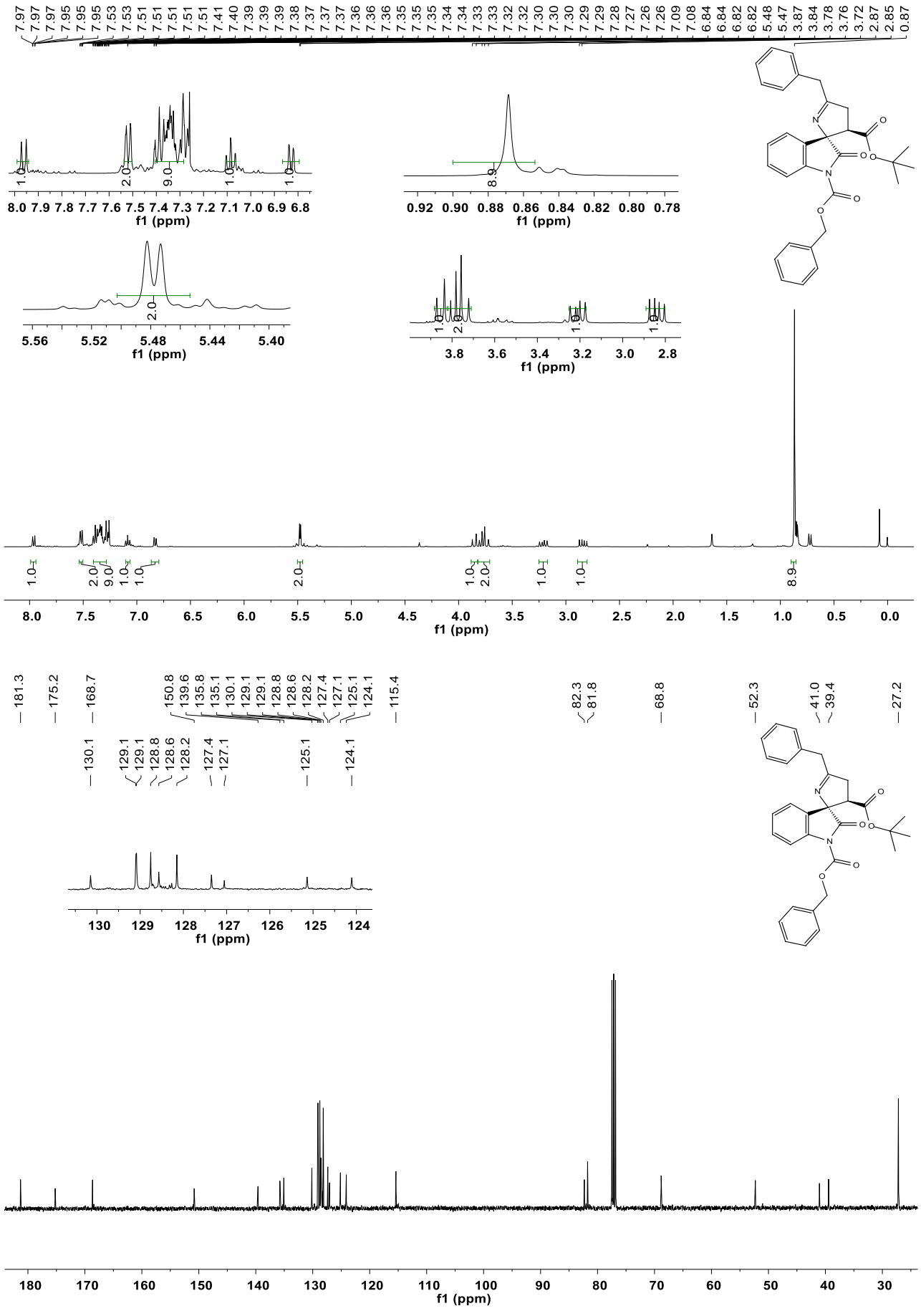




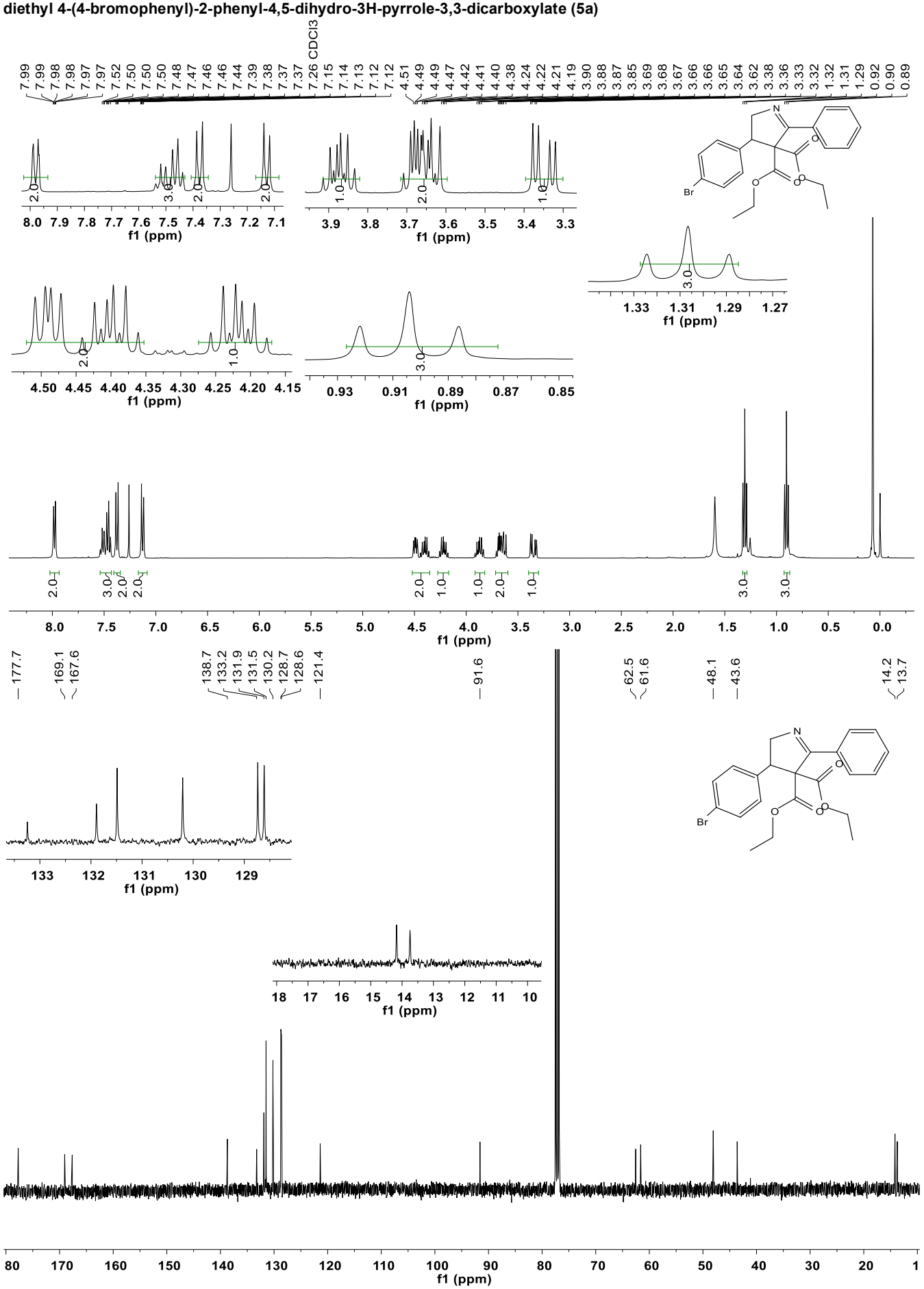
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-cyclohexyl-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3am)



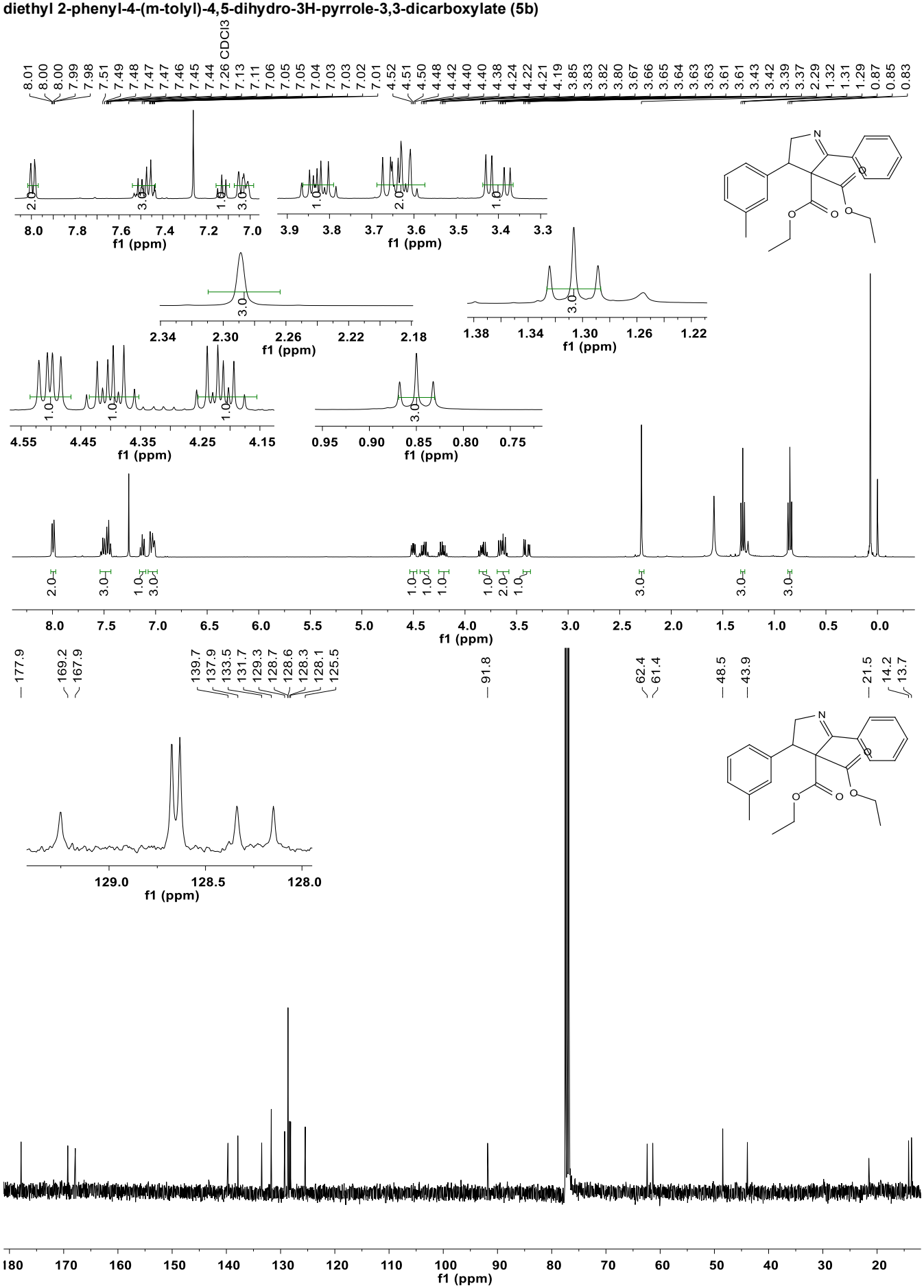
1-benzyl 3'-(tert-butyl) (3S,3'R)-5'-benzyl-2-oxo-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-1,3'-dicarboxylate (3an)



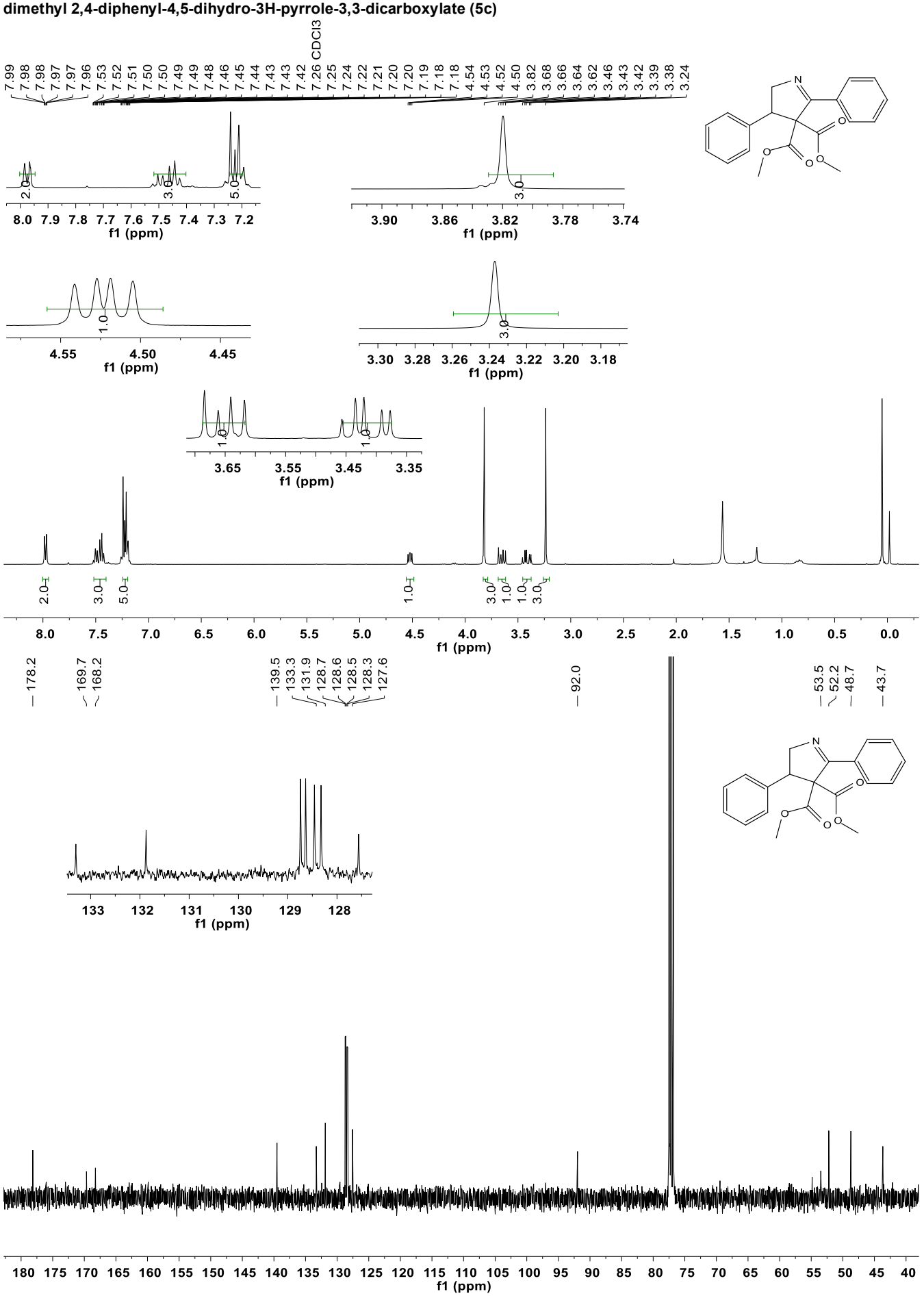
diethyl 4-(4-bromophenyl)-2-phenyl-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5a)



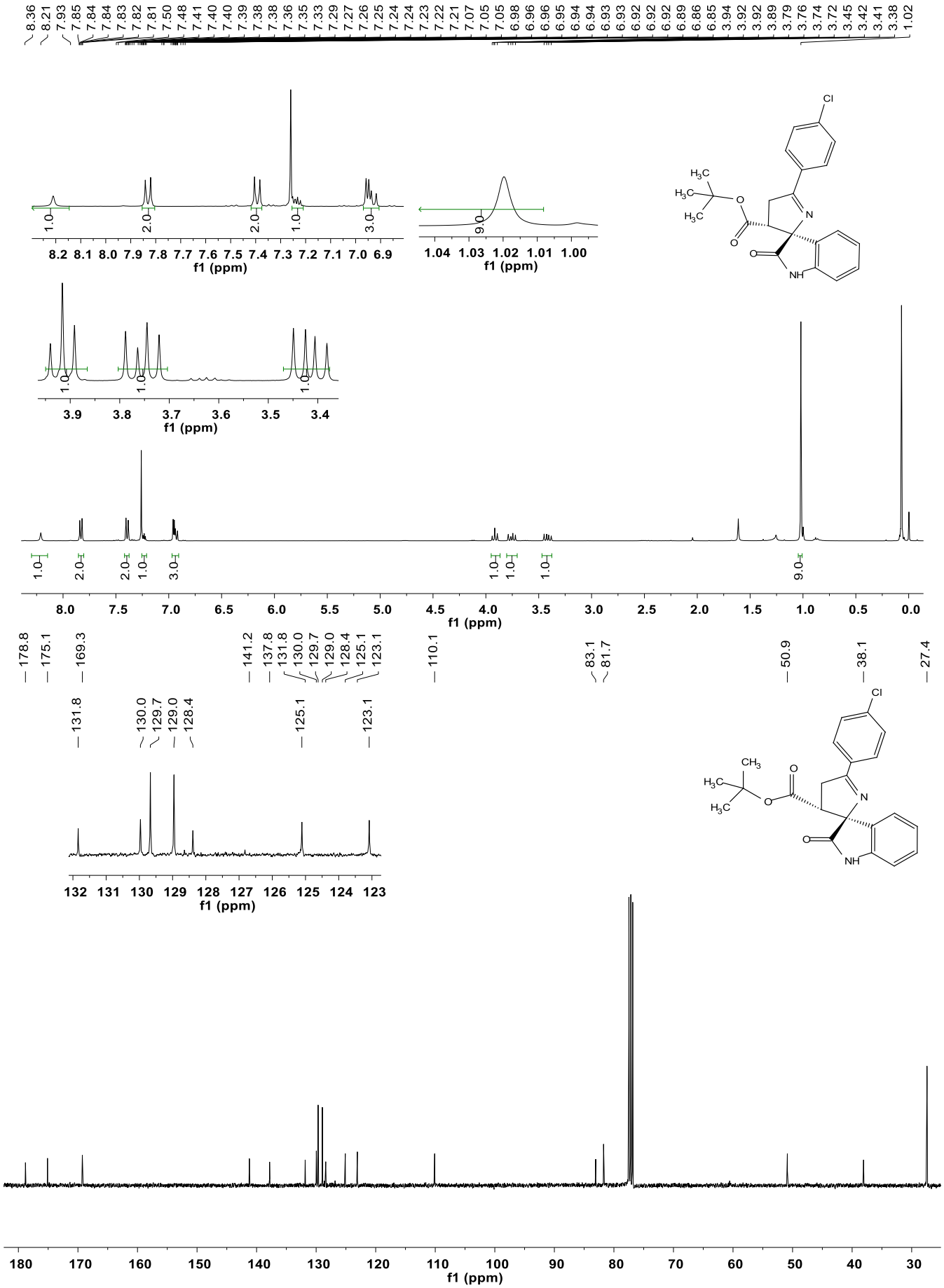
diethyl 2-phenyl-4-(m-tolyl)-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5b)



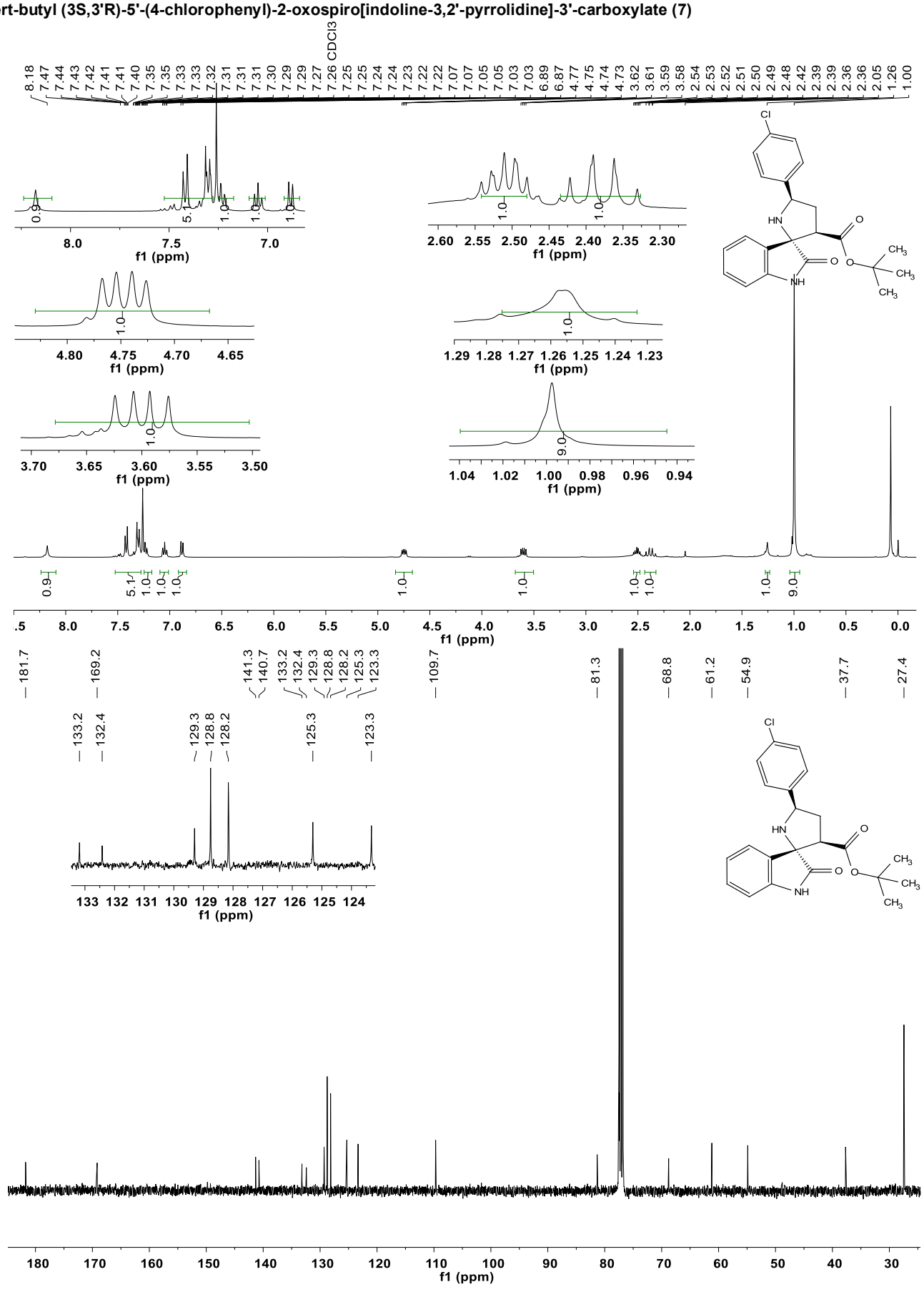
dimethyl 2,4-diphenyl-4,5-dihydro-3H-pyrrole-3,3-dicarboxylate (5c)



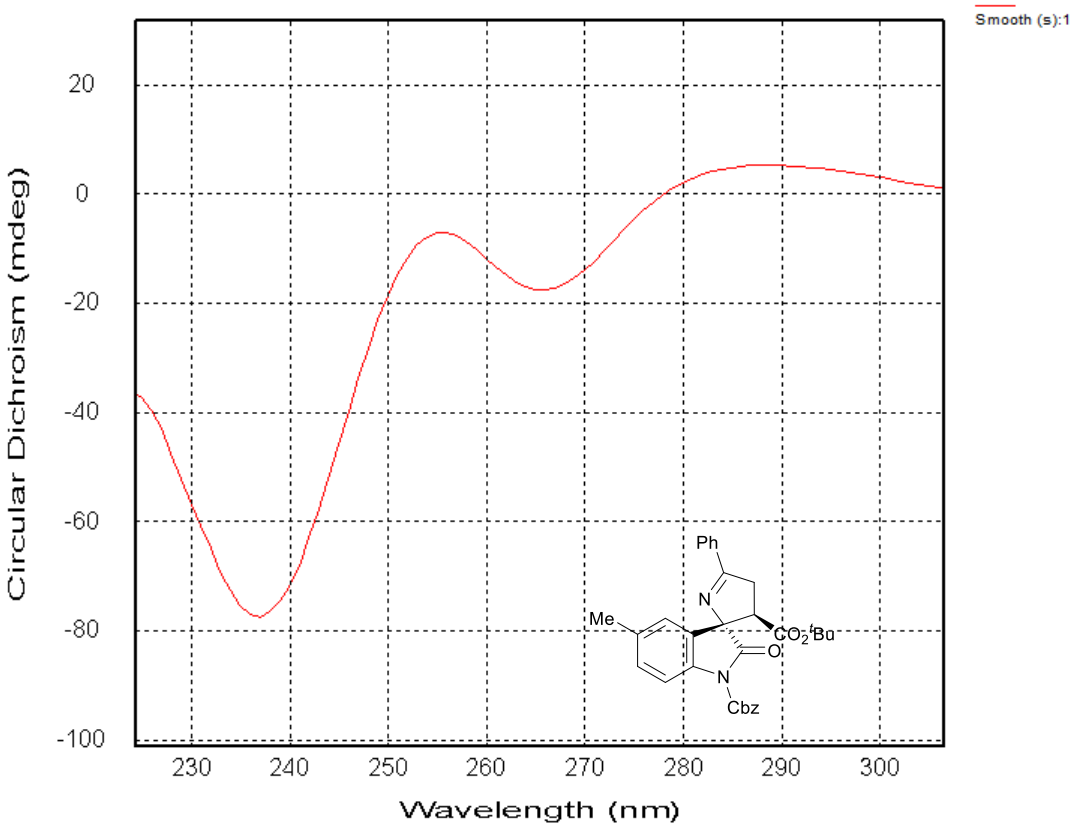
tert-butyl (3S,3'R)-2-oxo-5'-phenyl-3',4'-dihydrospiro[indoline-3,2'-pyrrole]-3'-carboxylate (6)

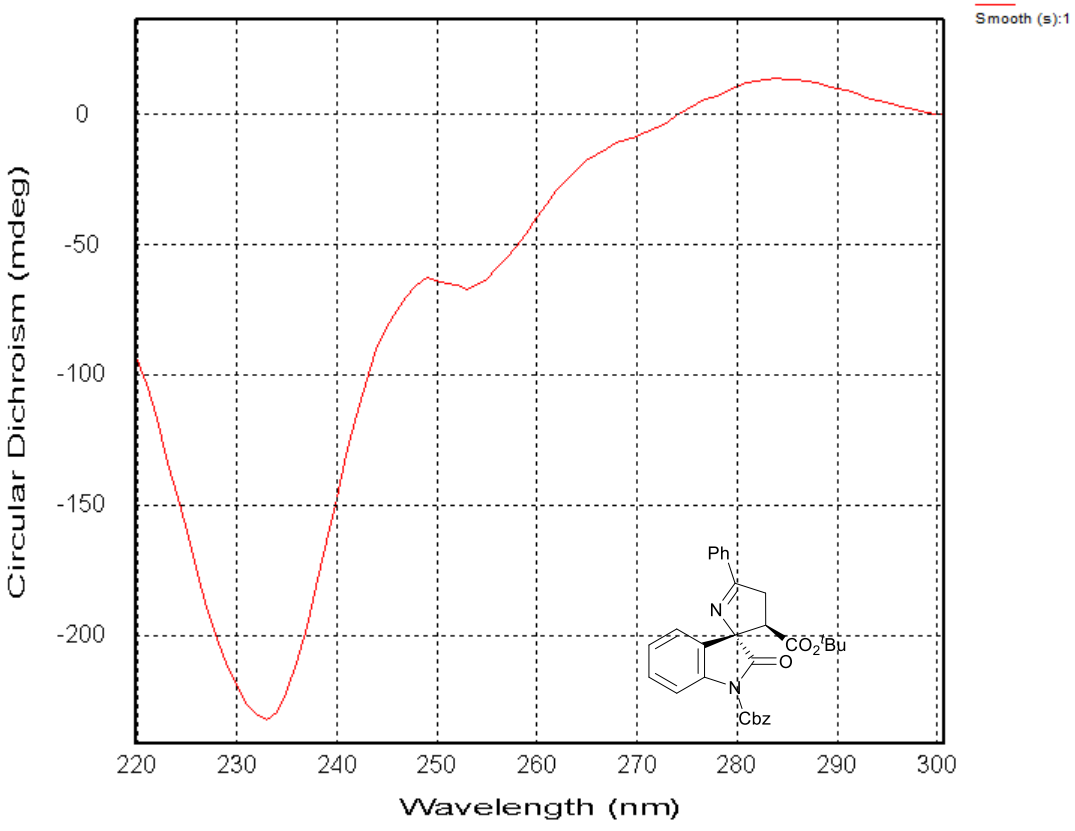


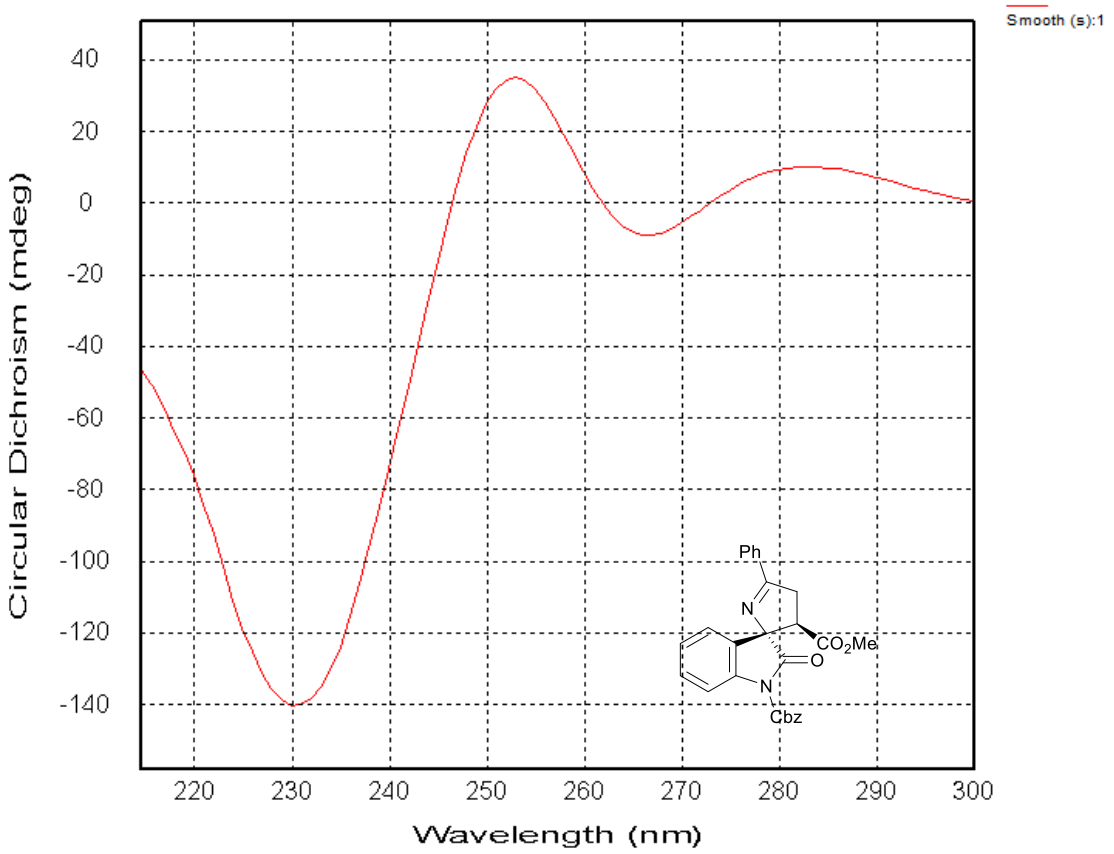
tert-butyl (3S,3'R)-5'-(4-chlorophenyl)-2-oxospiro[indoline-3,2'-pyrrolidine]-3'-carboxylate (7)



15. Copies of CD spectra for products



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-20
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240
250
260
270
280
290
300
Wavelength (nm)
Ph
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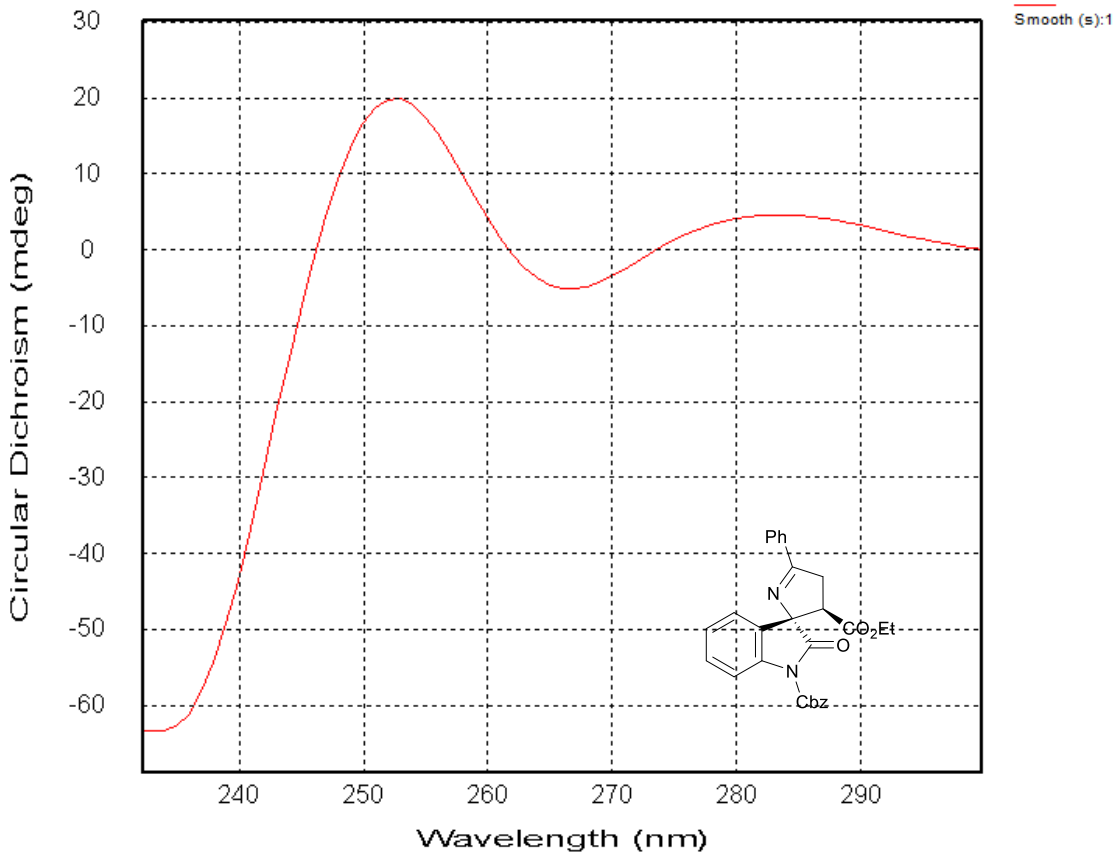
CO2Me
O
N
Cbz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Circular Dichroism (mdeg)
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10
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-10
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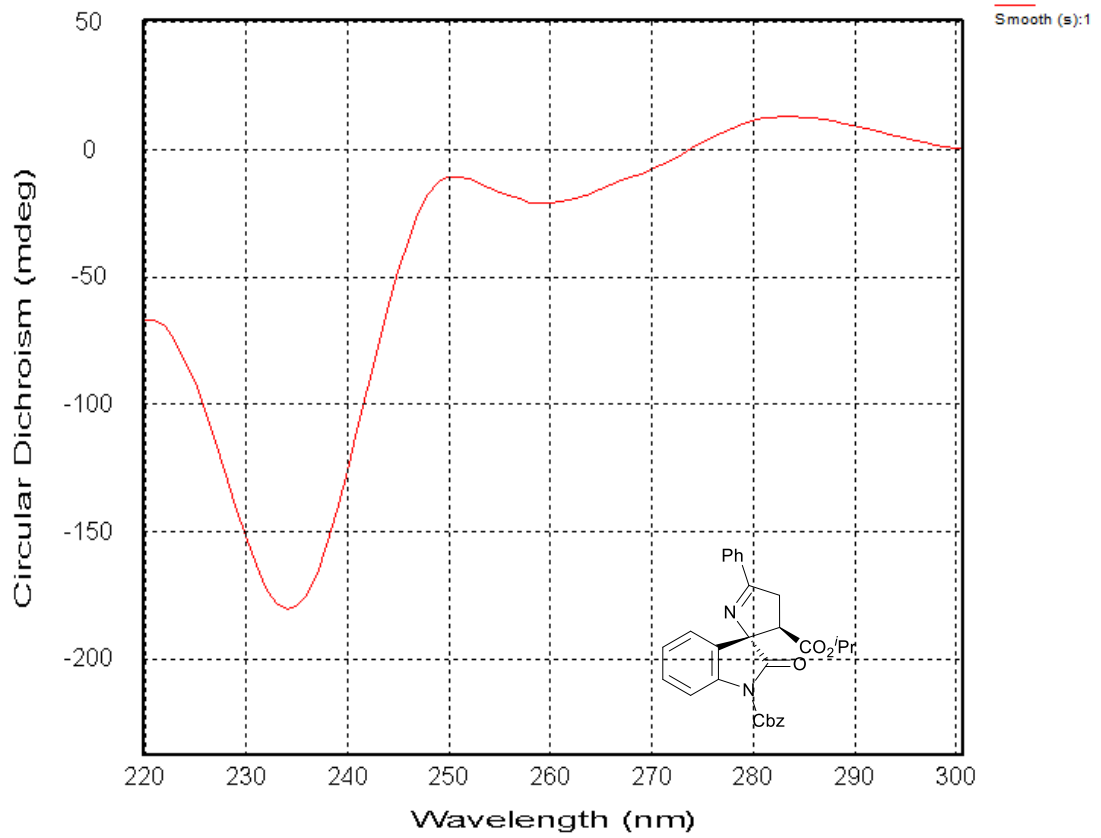
240
250
260
270
280
290
Wavelength (nm)
Ph
N
CO2Et
O
N
Cbz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Circular Dichroism (mdeg)
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Wavelength (nm)
Ph
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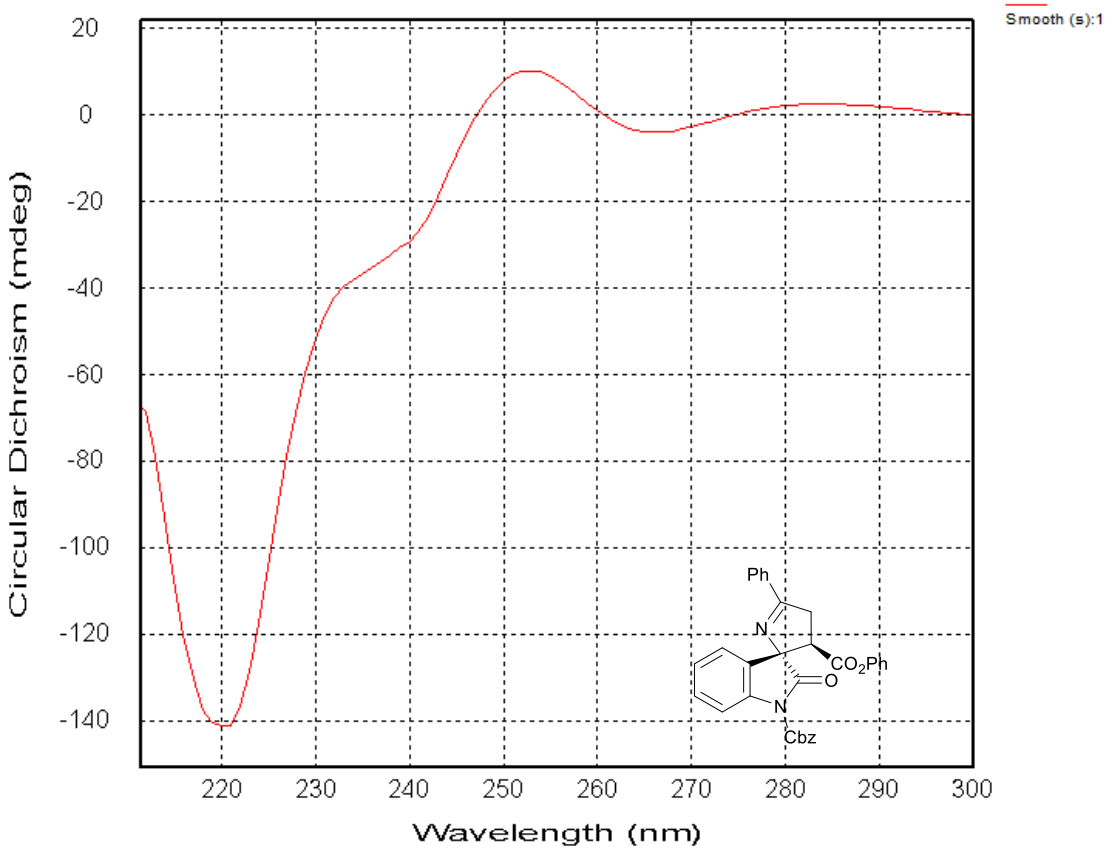
CO2iPr
O
N
Cbz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Wavelength (nm)
Ph
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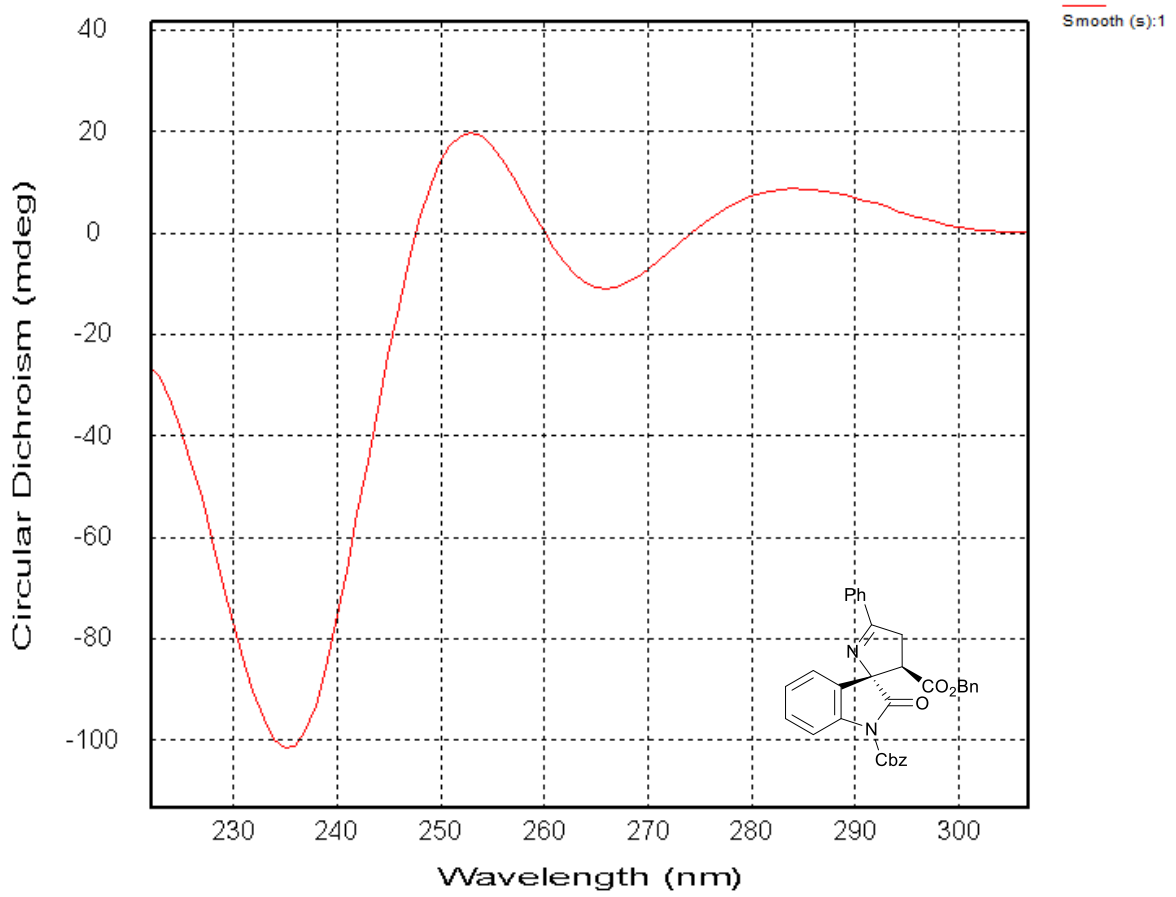
CO2Ph
O
N
Cbz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300
Wavelength (nm)
Ph
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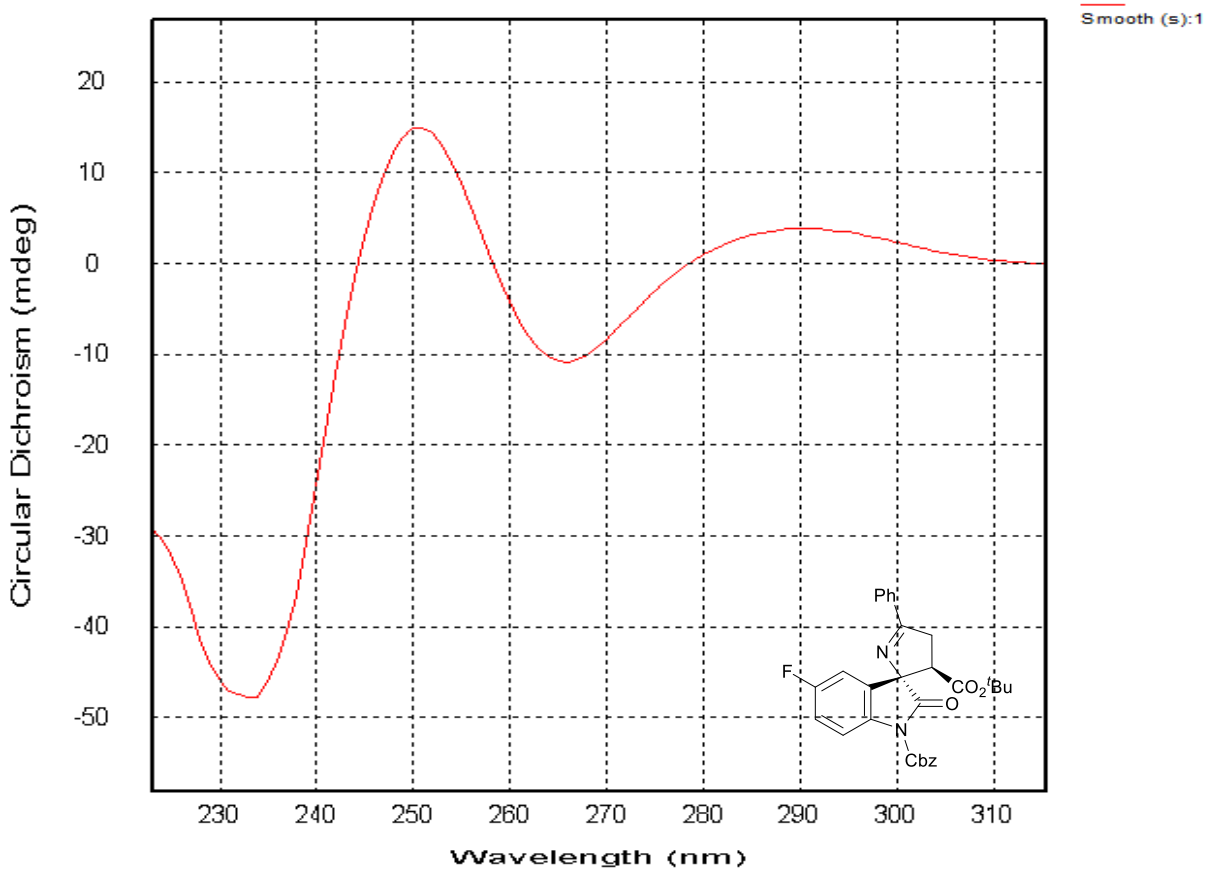
CO2Bn
O
N
Cbz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-30
-40
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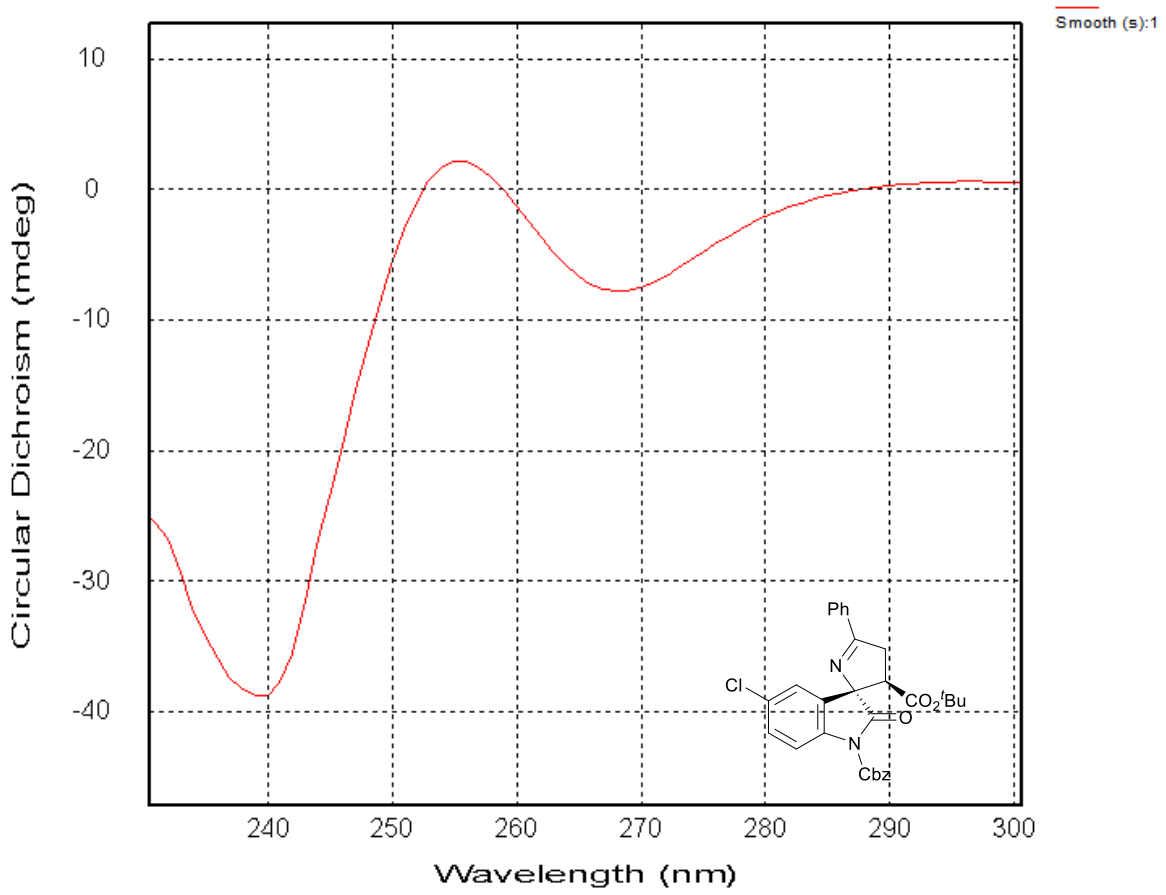
270
280
290
300
310
Wavelength (nm)
Ph
N
F
CO2tBu
O
N
Cbz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270
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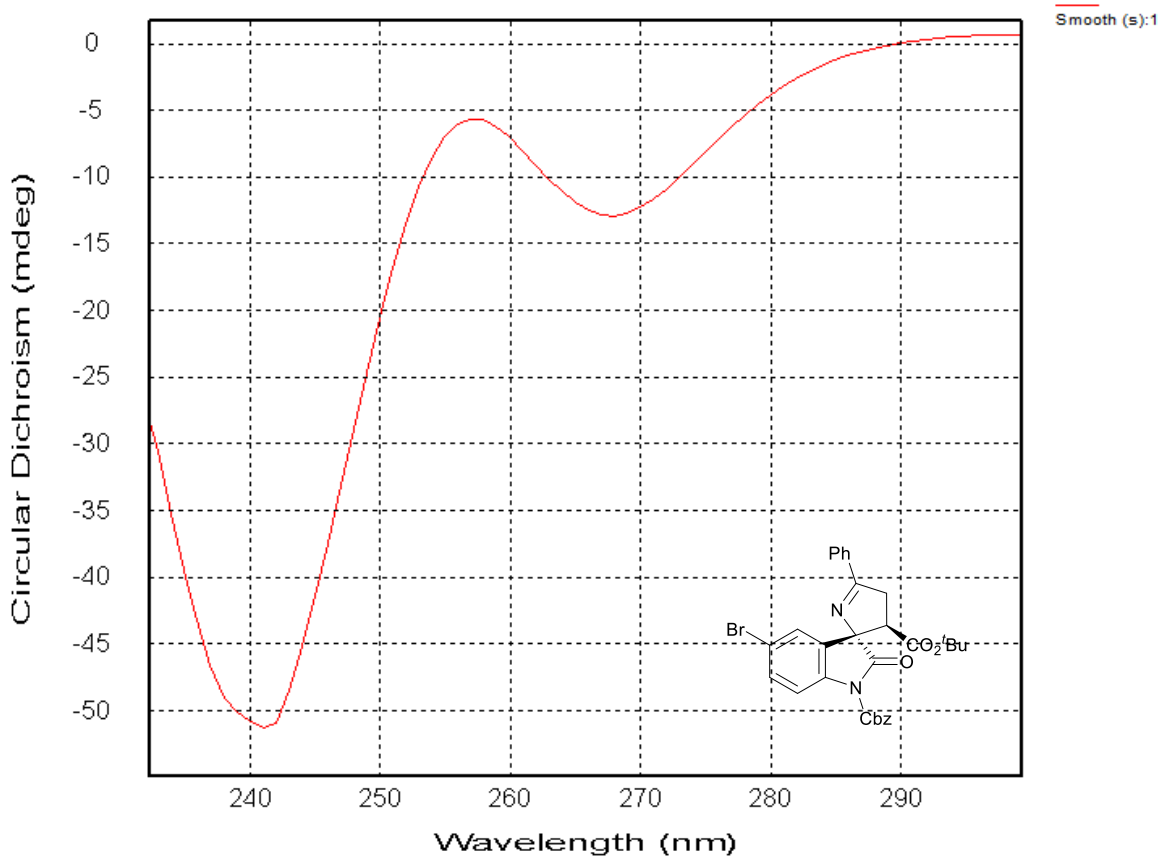
290
300
Wavelength (nm)
Ph
N
Cl
CO2tBu
O
N
Cbz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250
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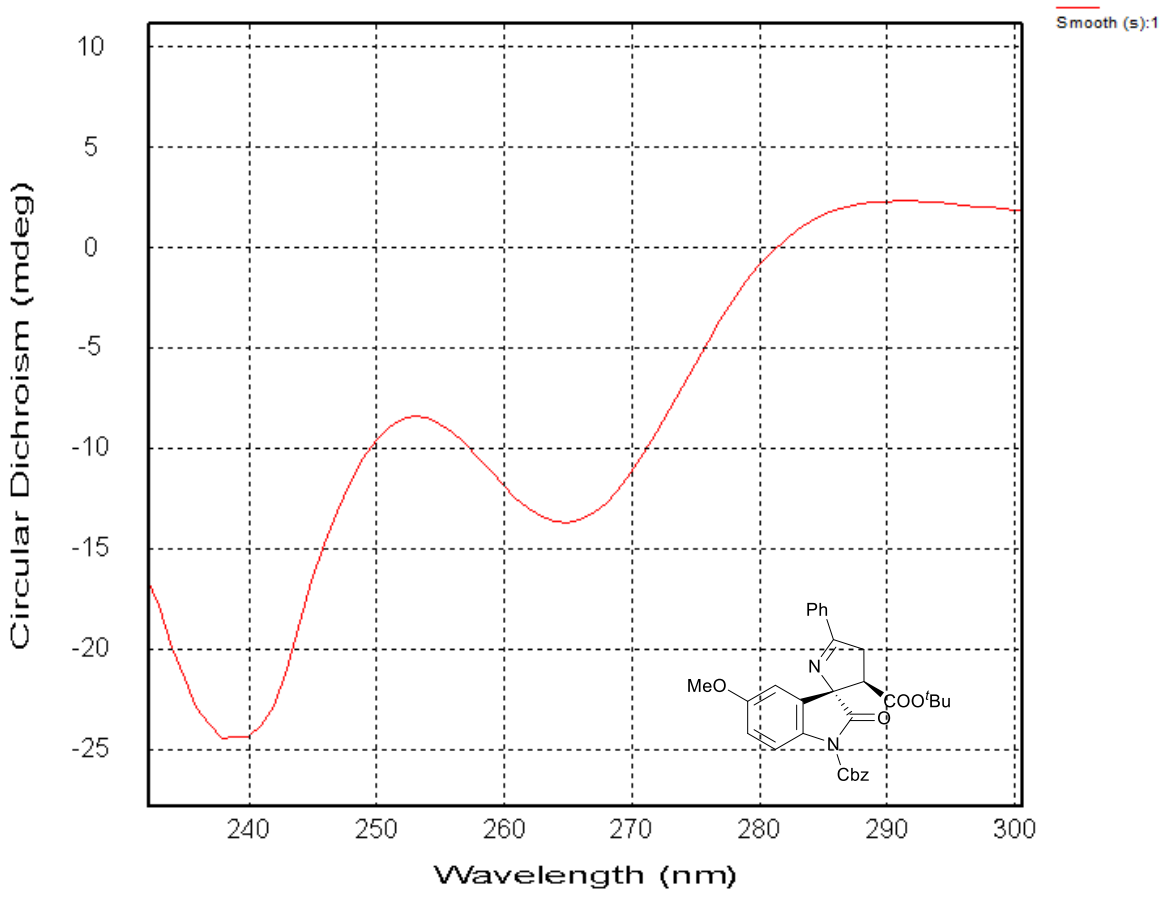
270
280
290
Wavelength (nm)
Ph
N
Br
CO2tBu
O
N
Cbz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Circular Dichroism (mdeg)
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-5
-10
-15
-20
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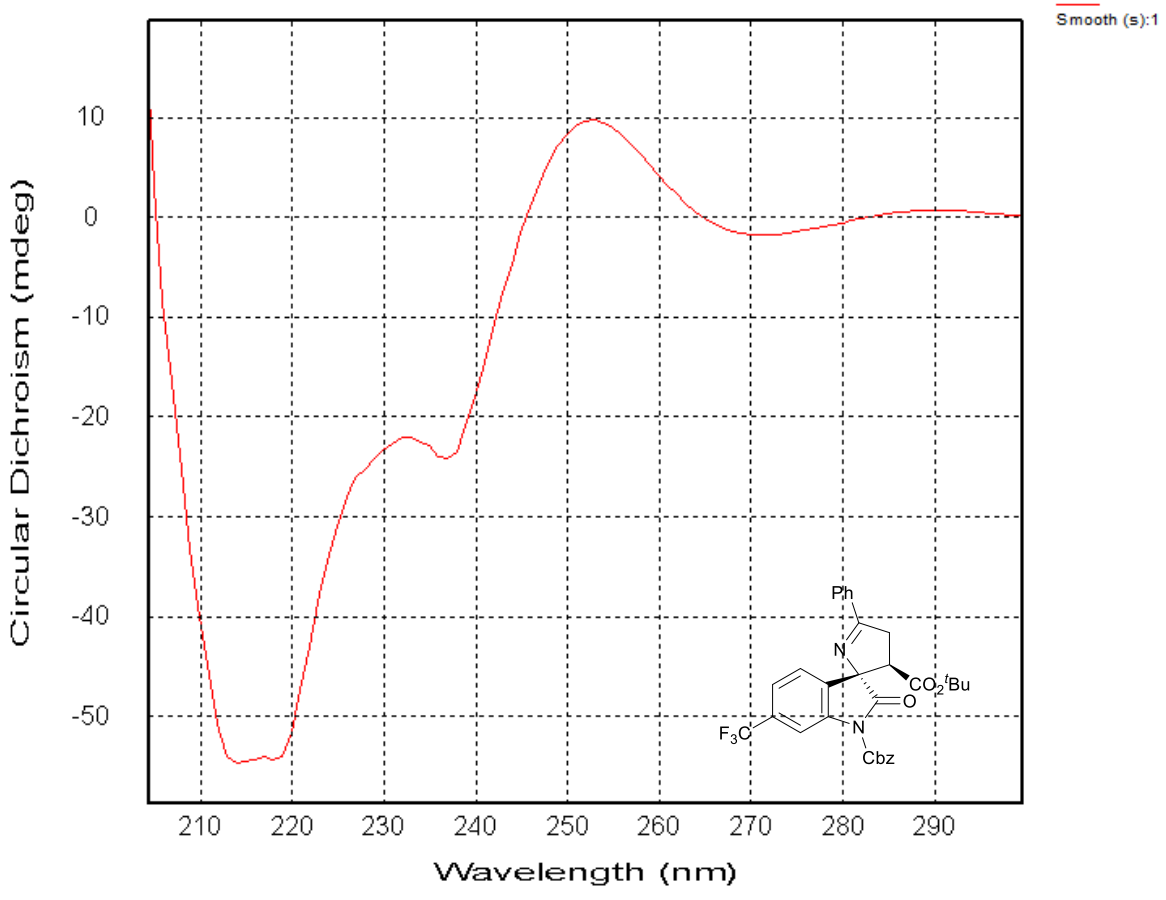
270
280
290
300
Wavelength (nm)
Ph
N
MeO
COO^{t}Bu
O
N
Cbz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Circular Dichroism (mdeg)
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-20
-30
-40
-50
210
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260
270
280
290
Wavelength (nm)
Ph
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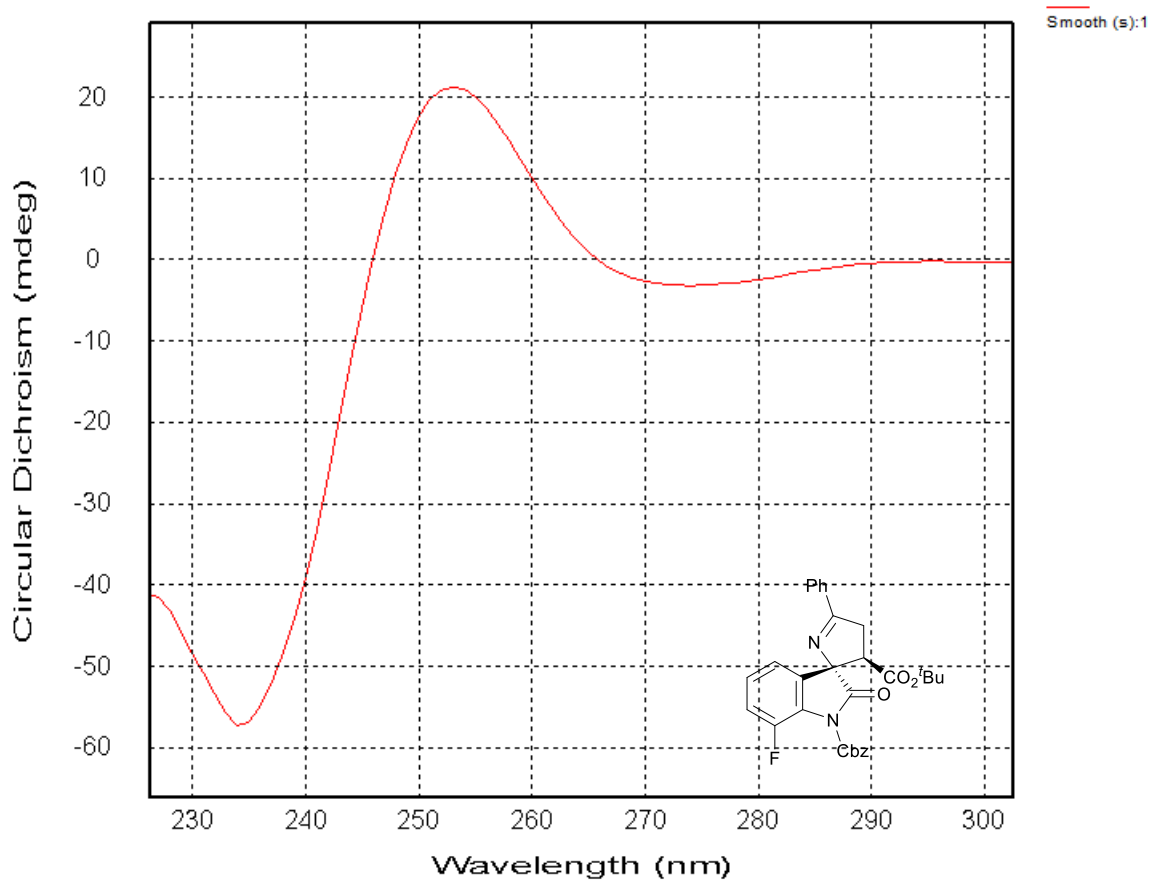
CO$_2$^{t}Bu
O
F$_3$C
N
Cbz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290
300
Wavelength (nm)
Ph
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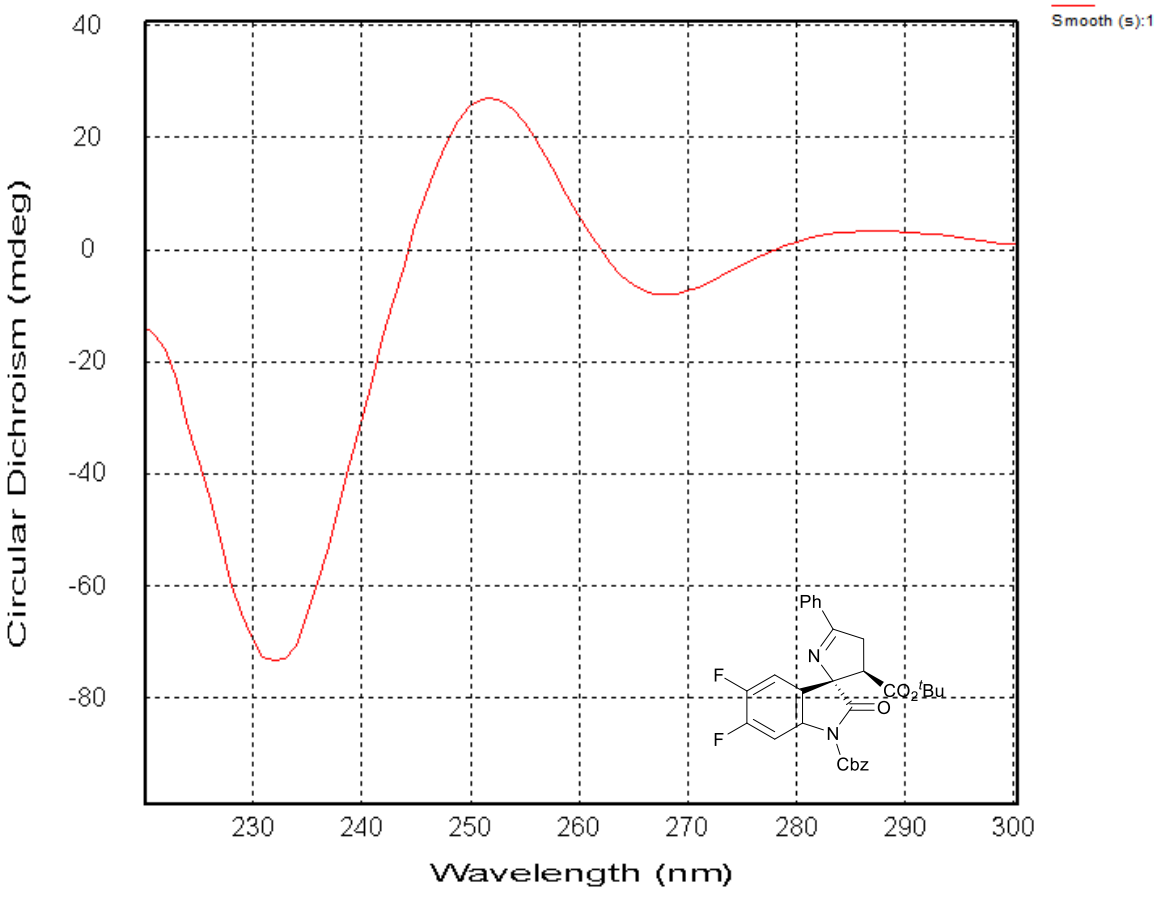
CO2tBu
O
N
Cbz
F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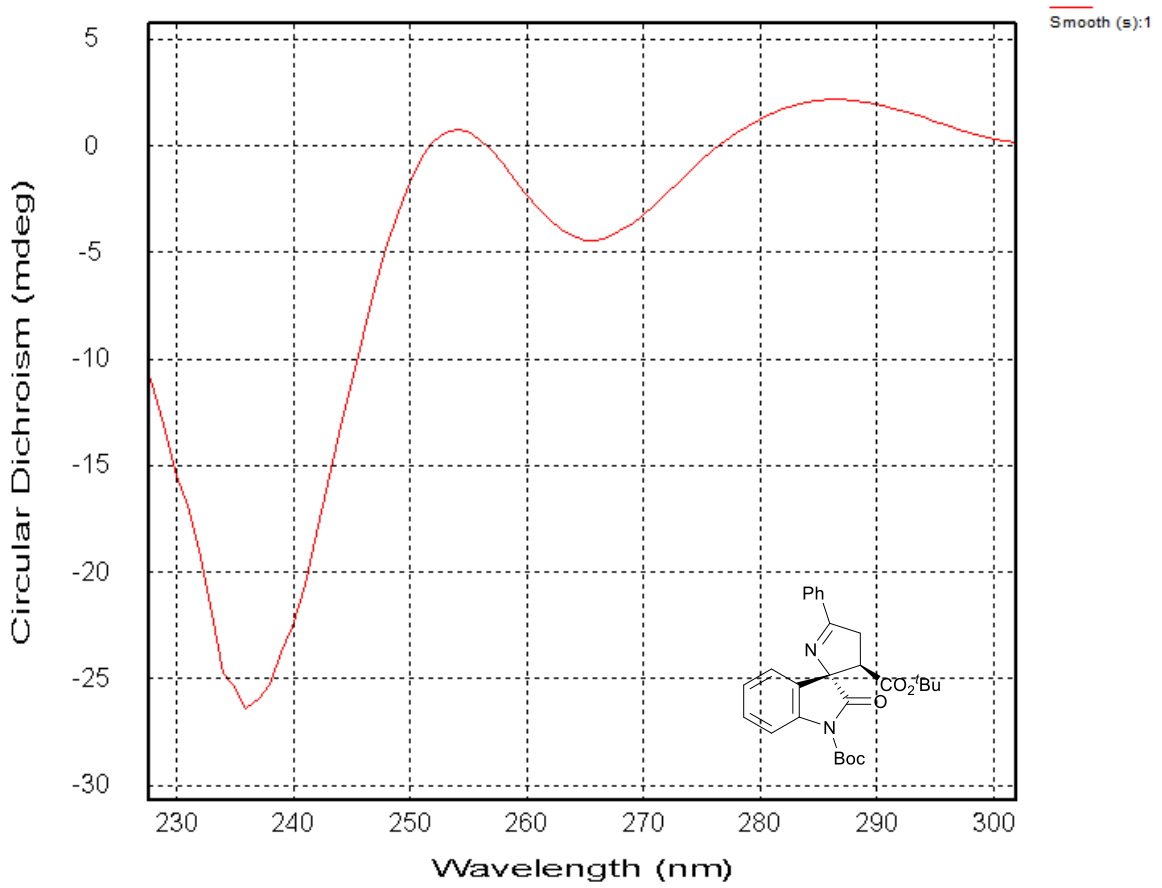
280
290
300
Wavelength (nm)
Ph
N
CO2tBu
O
N
Cbz
F
F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Wavelength (nm)
Ph
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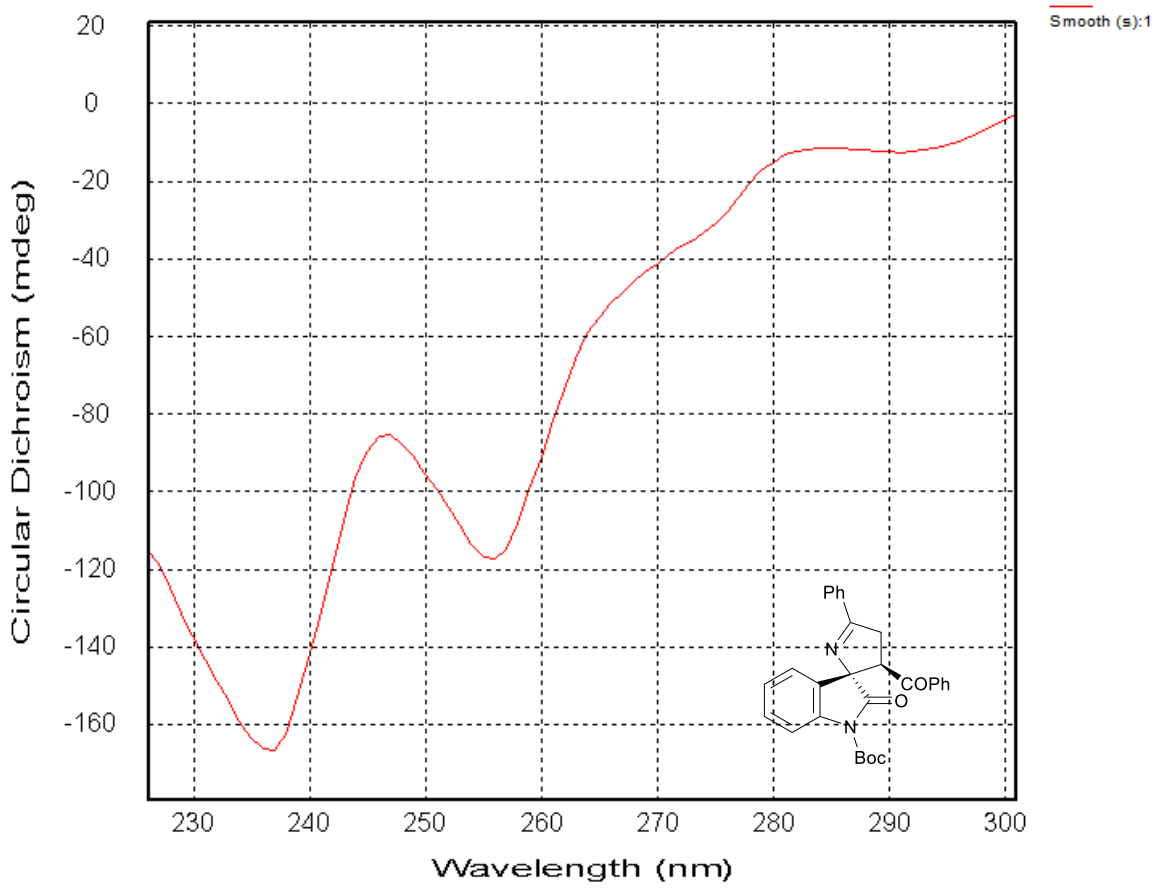
CO2tBu
O
N
Boc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290
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Wavelength (nm)
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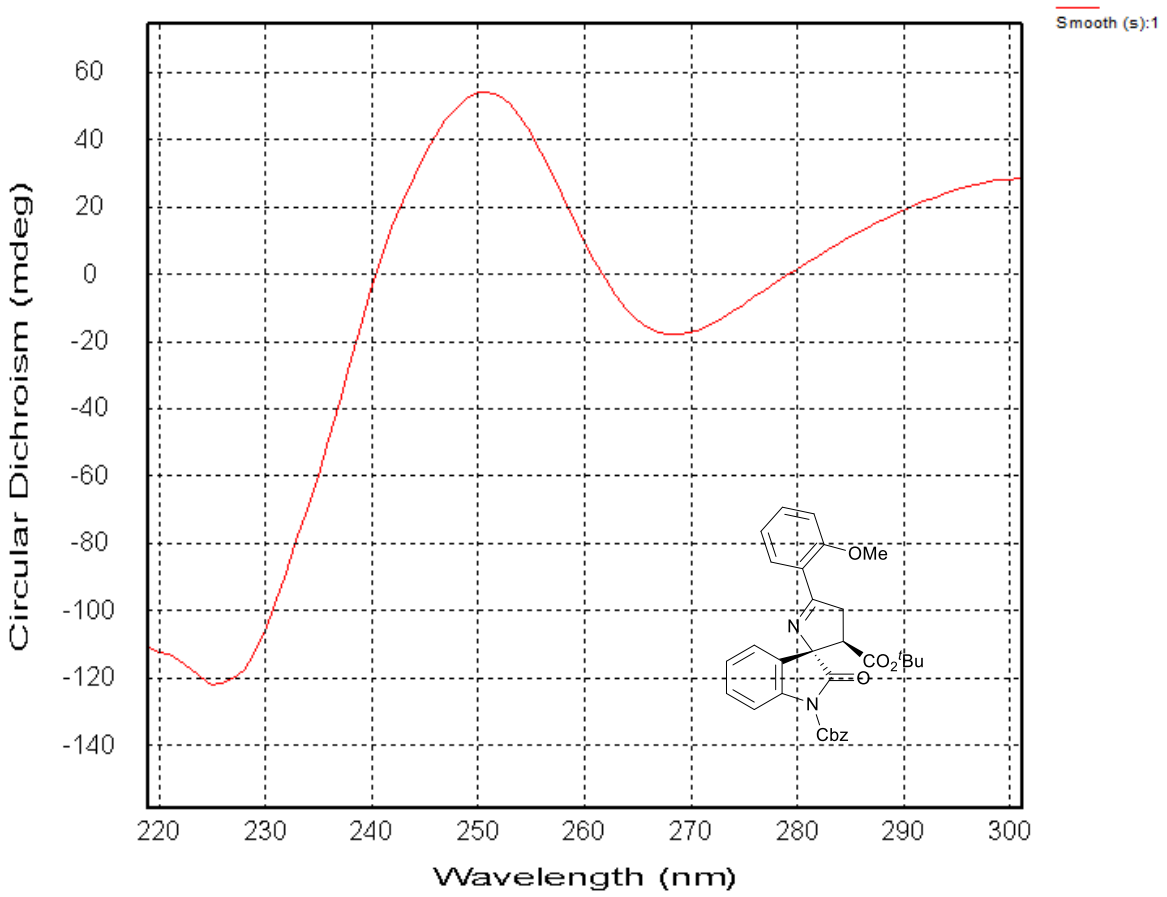
COPh
O
N
Boc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280
290
300
Wavelength (nm)
OMe
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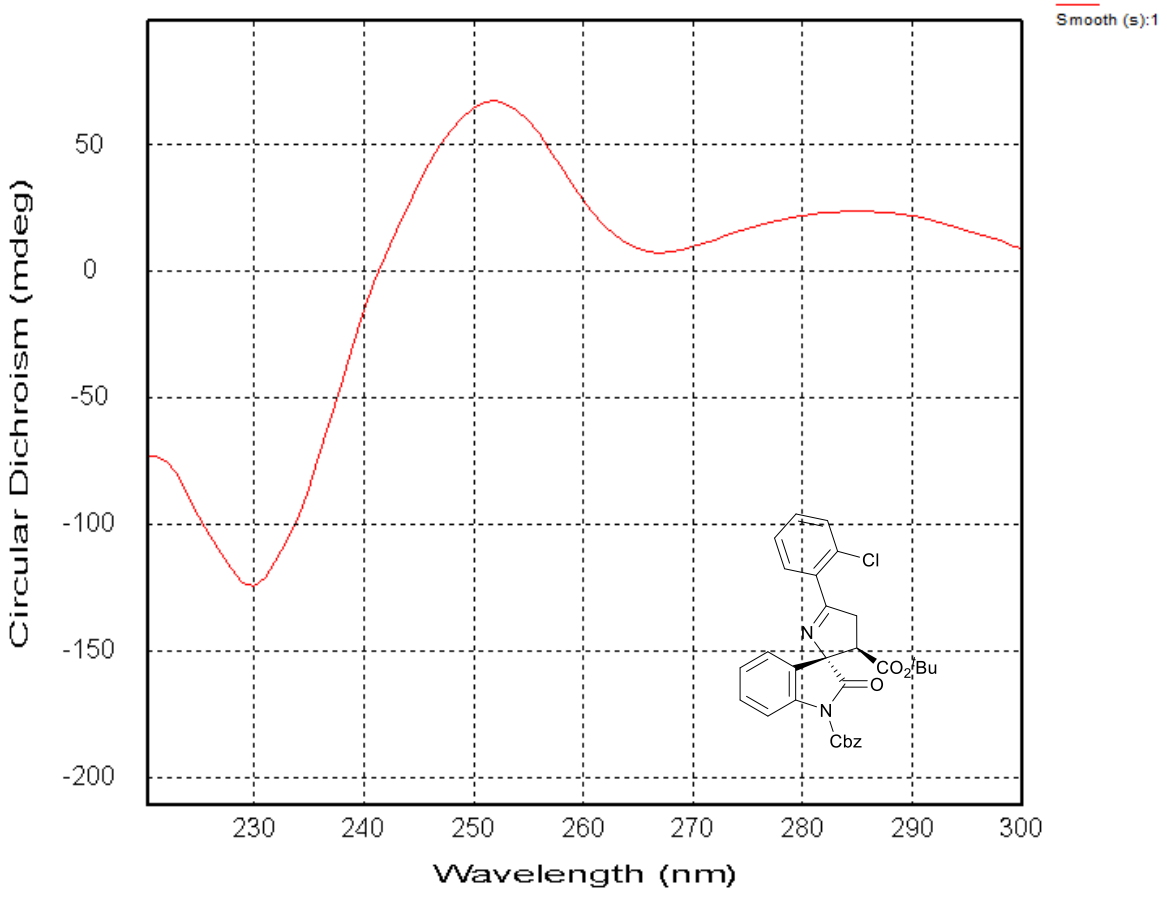
CO2tBu
O
N
Cbz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Circular Dichroism (mdeg)
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-100
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260
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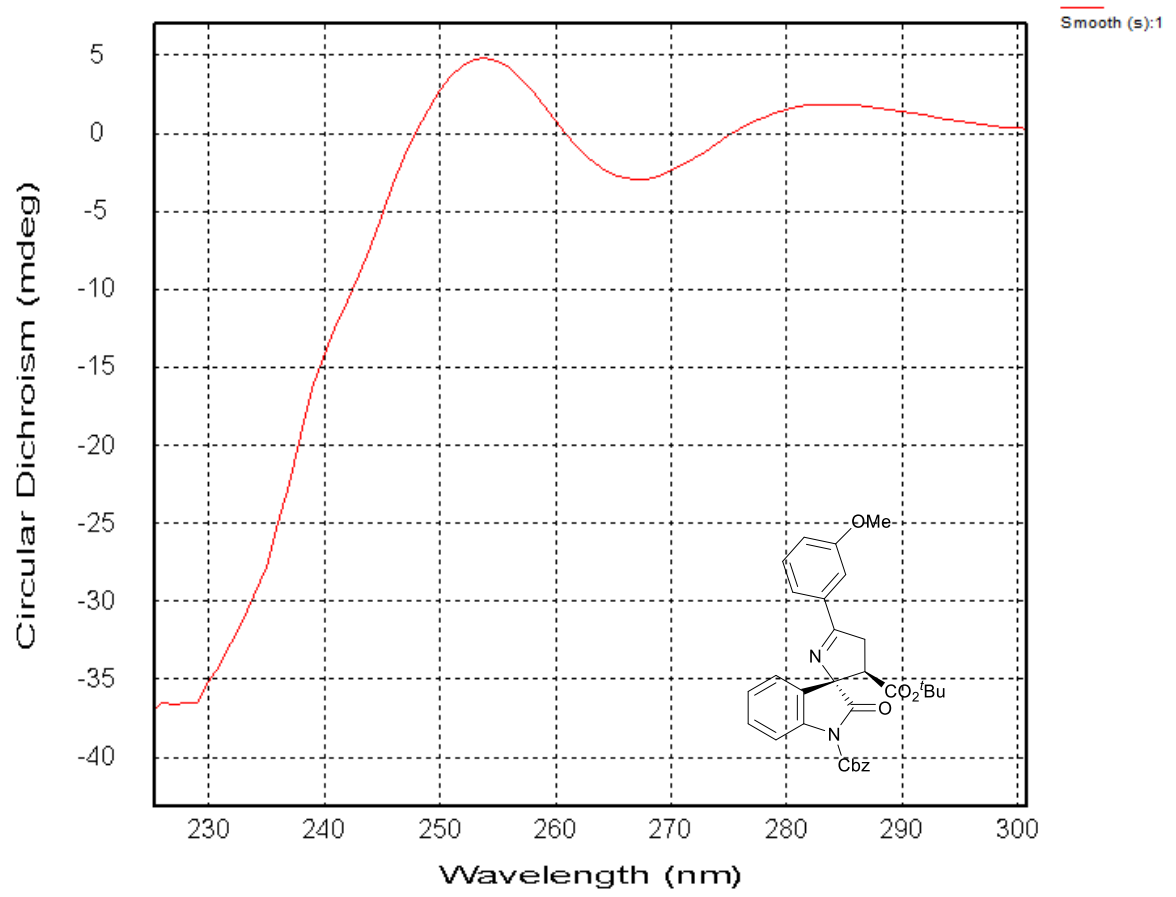
280
290
300
Wavelength (nm)
Cl
N
CO2tBu
O
N
Cbz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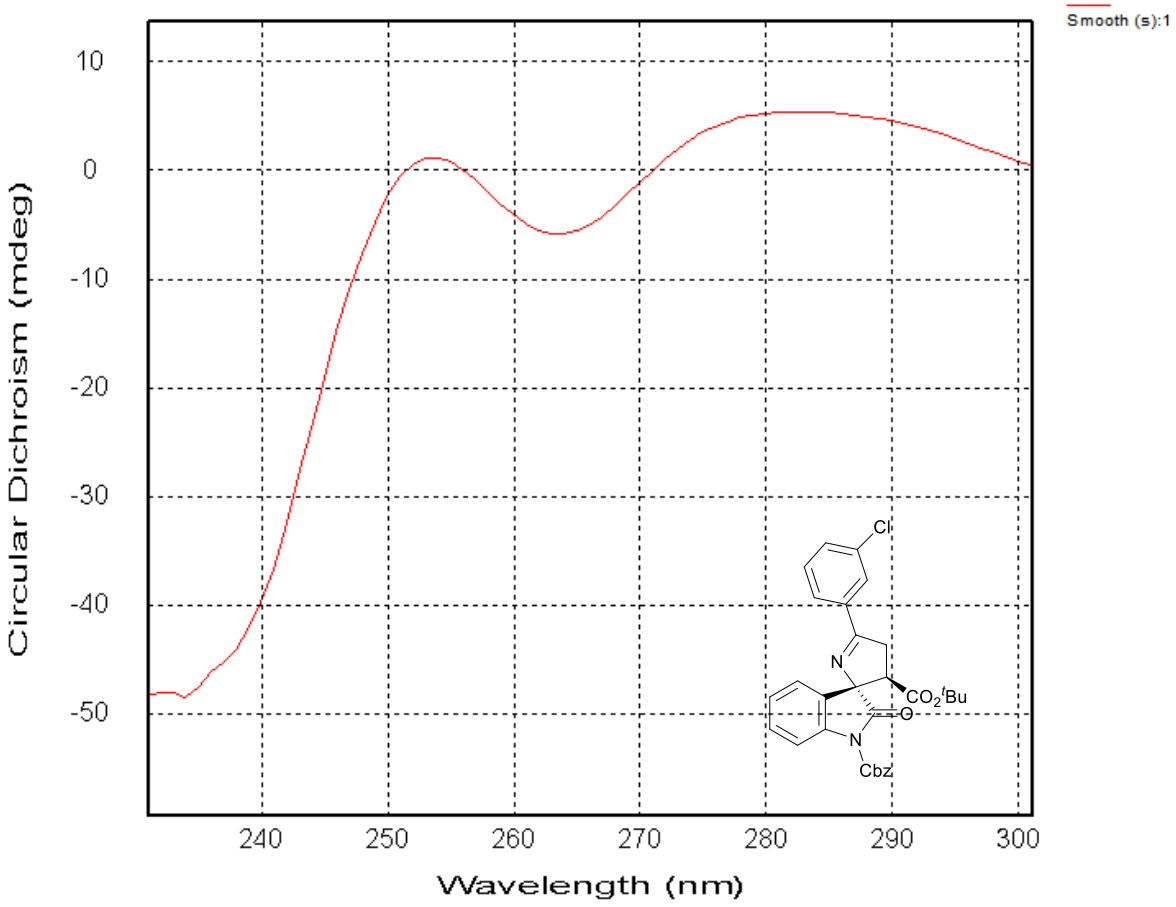
290
300
Wavelength (nm)
OMe
N
CO2tBu
O
N
Cbz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270
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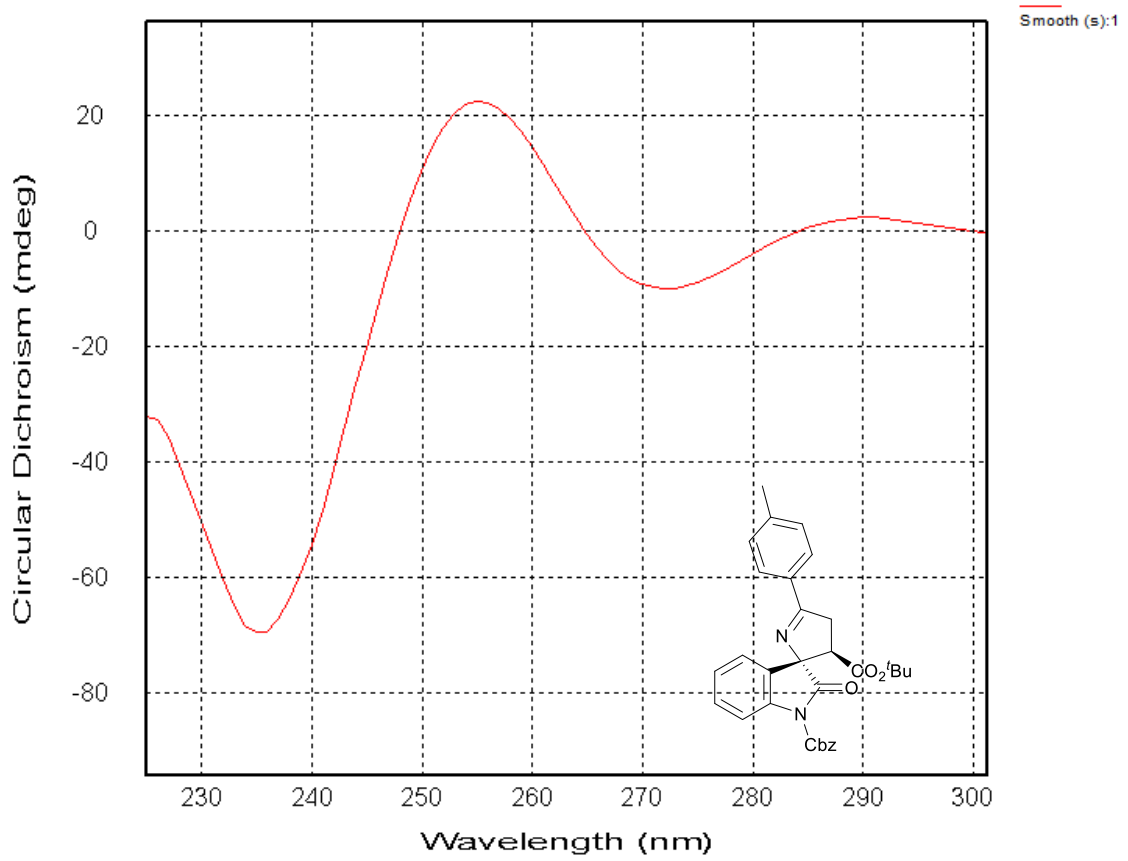
290
300
Wavelength (nm)
Cl
N
CO2tBu
O
N
Cbz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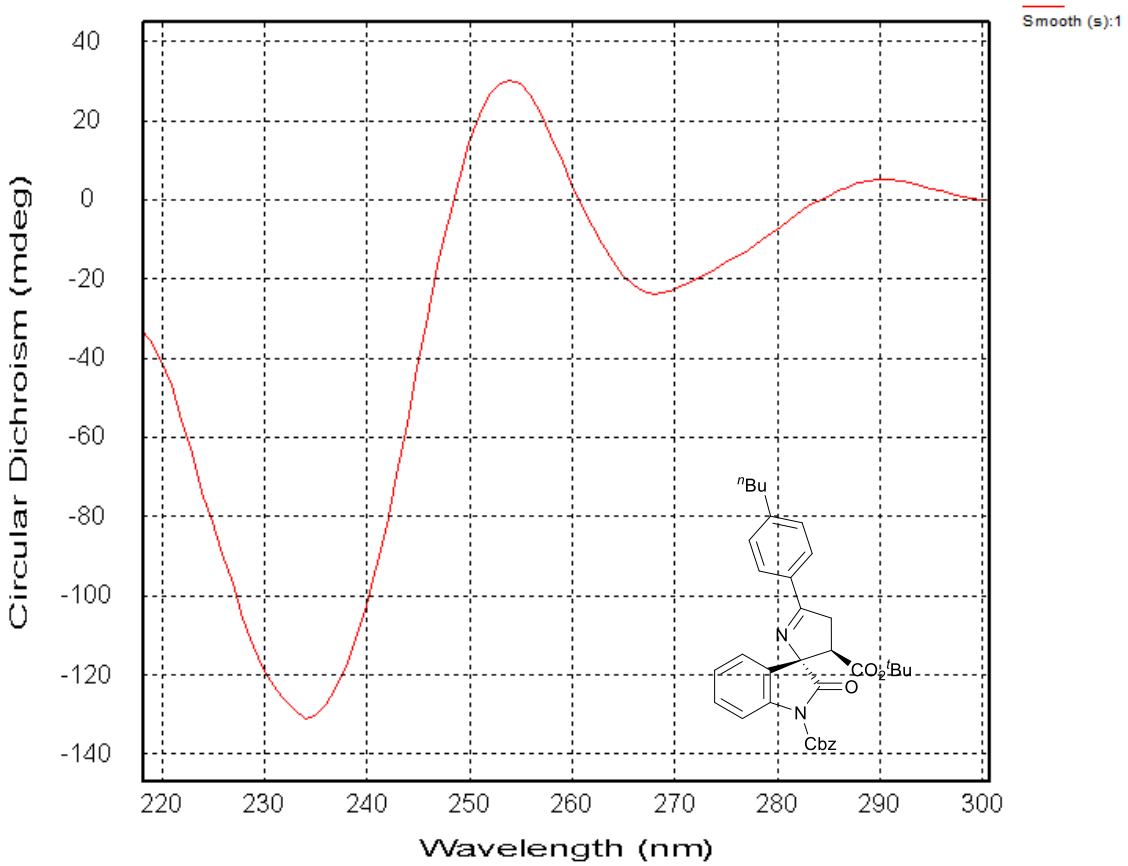
300
Wavelength (nm)
N
CO2tBu
O
N
Cbz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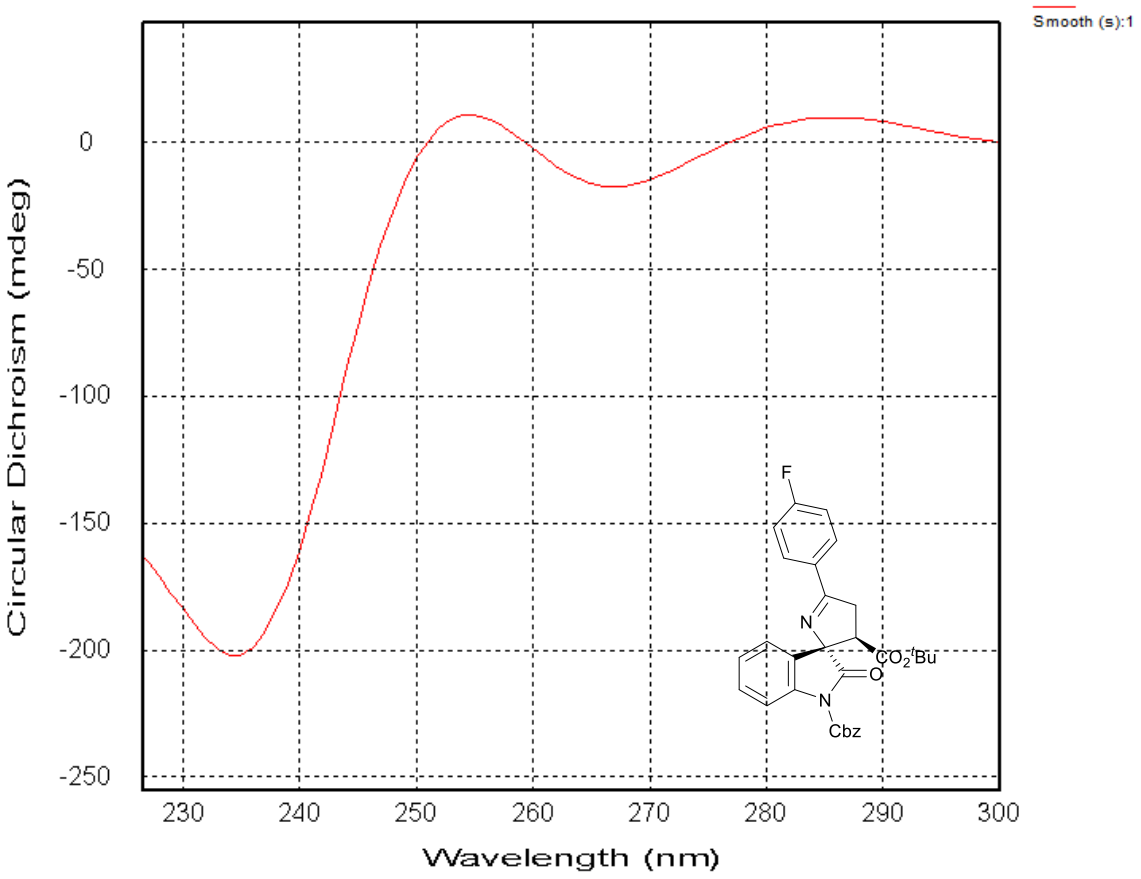
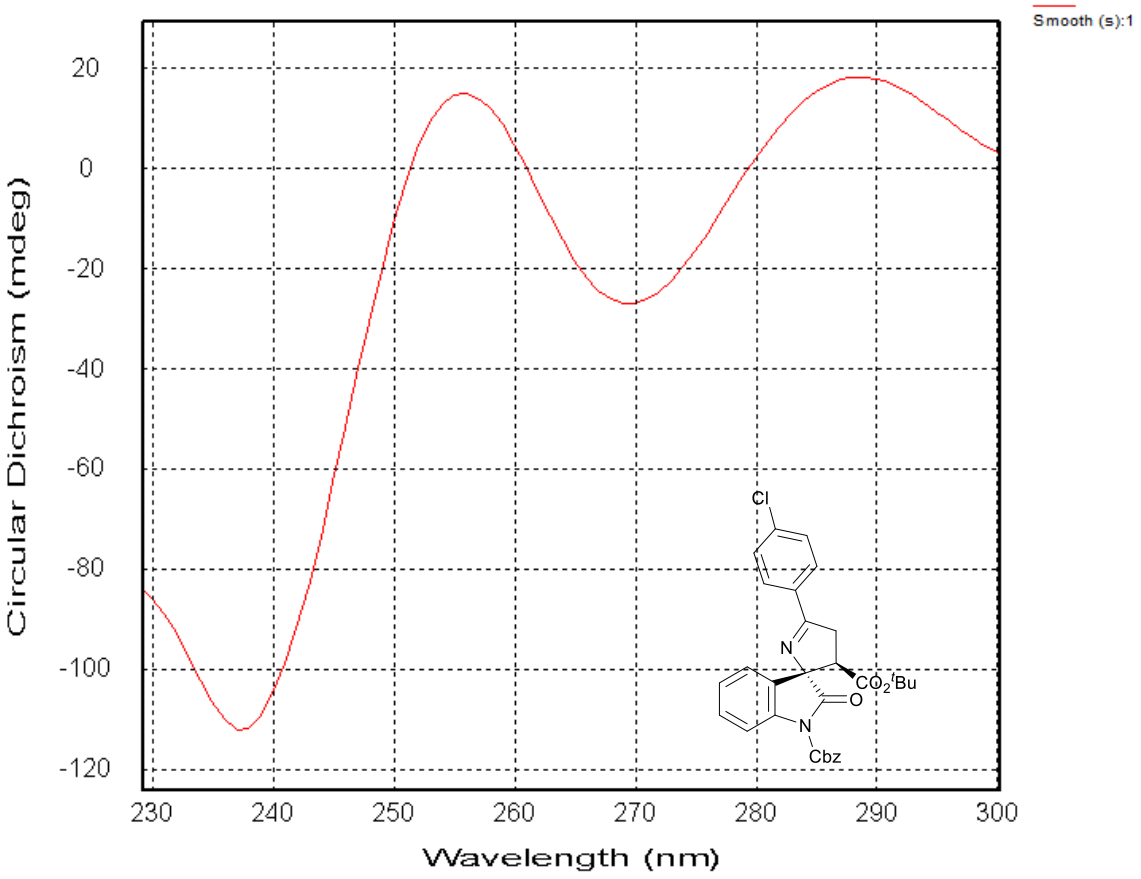
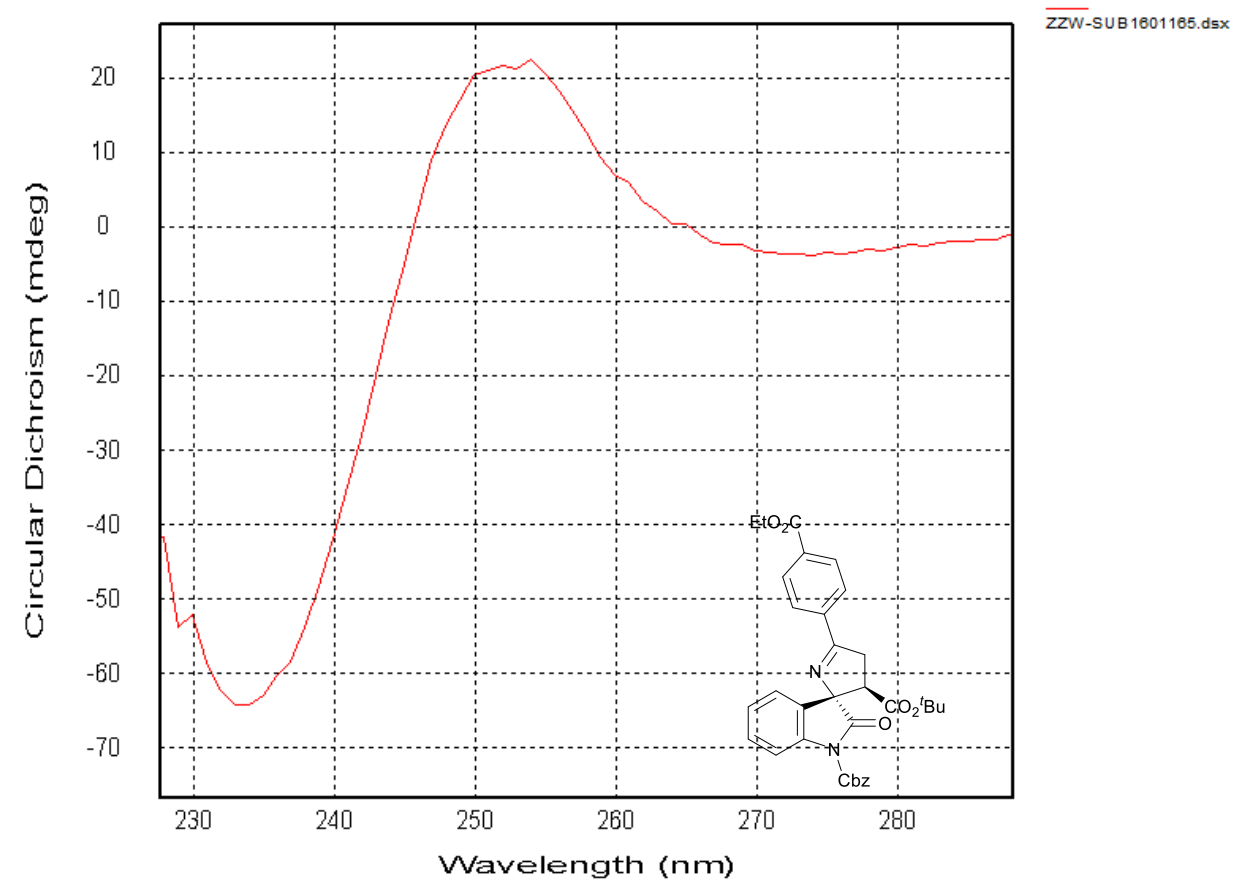
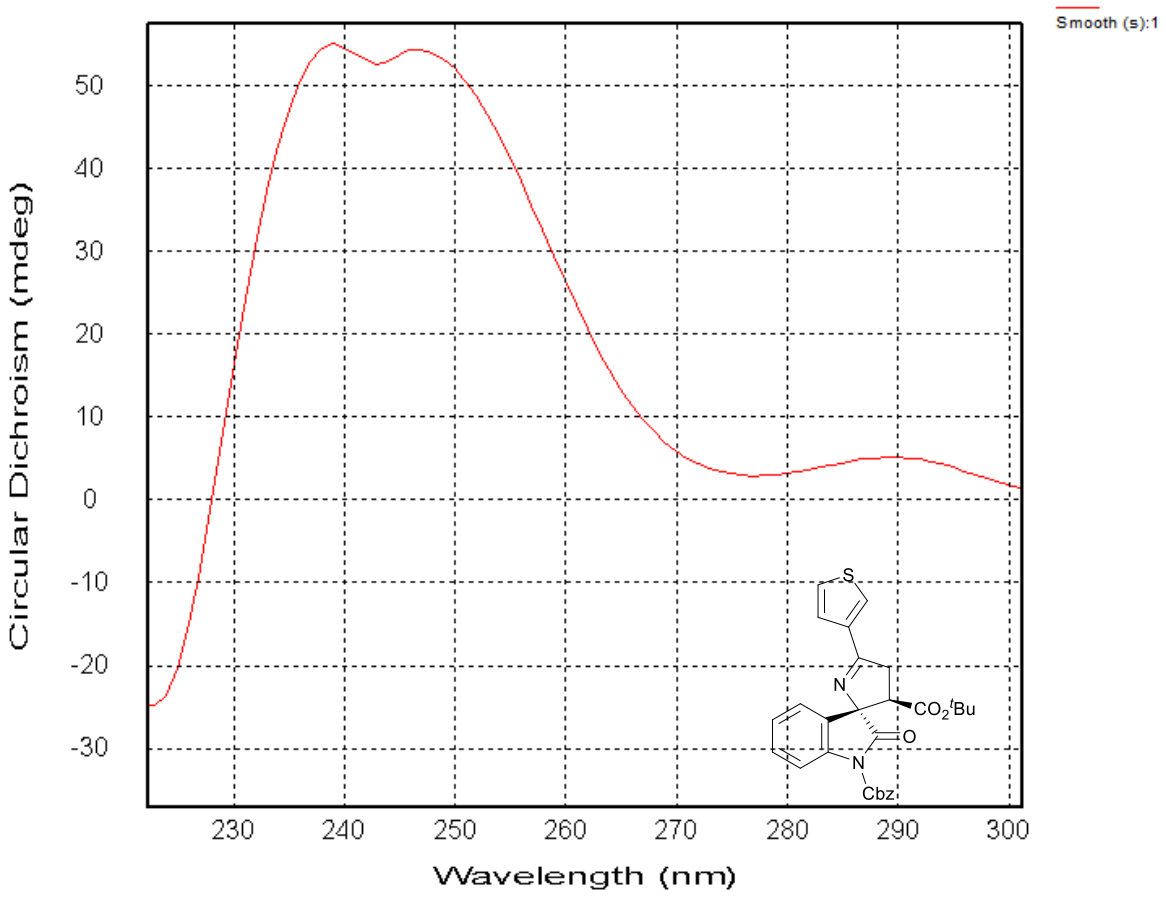
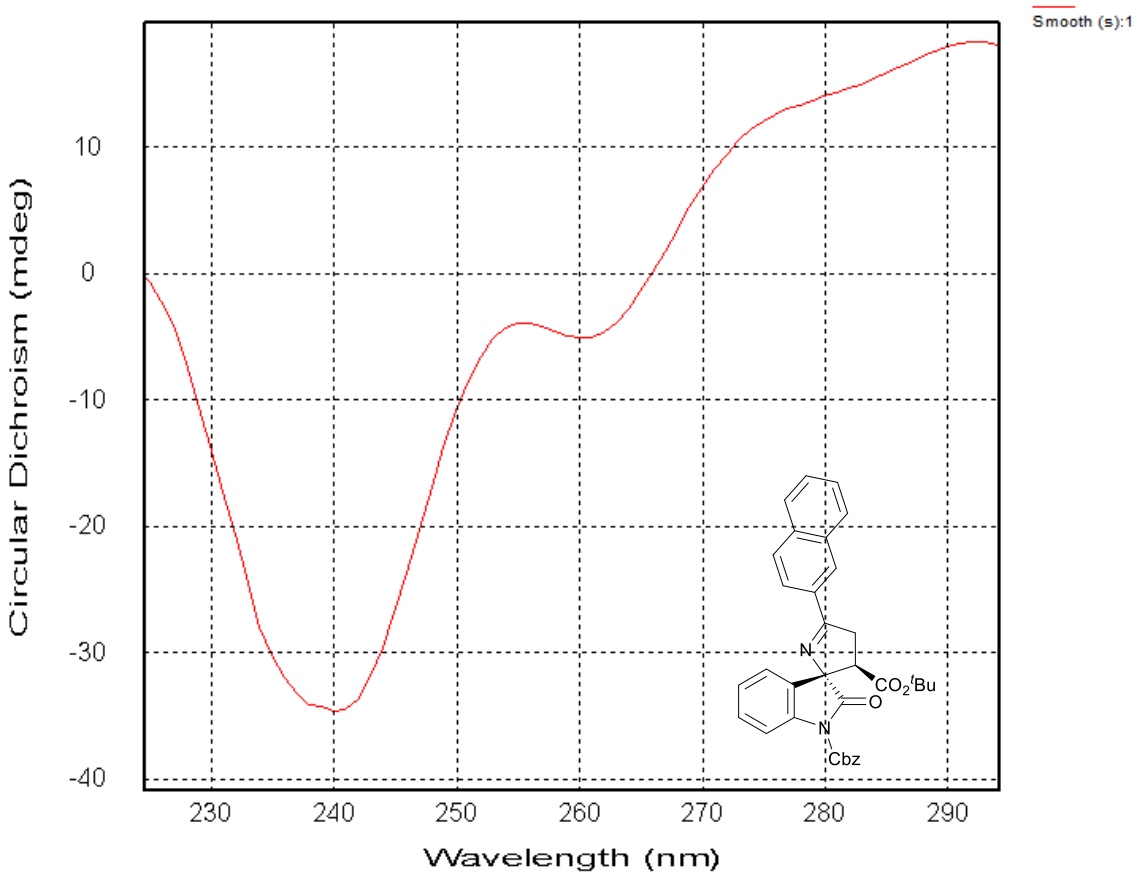
0
-20
-40
-60
-80
-100
-120
-140
220
230
240
250
260
270
280
290
300
Wavelength (nm)
nBu
N
CO2tBu
O
N
Cbz

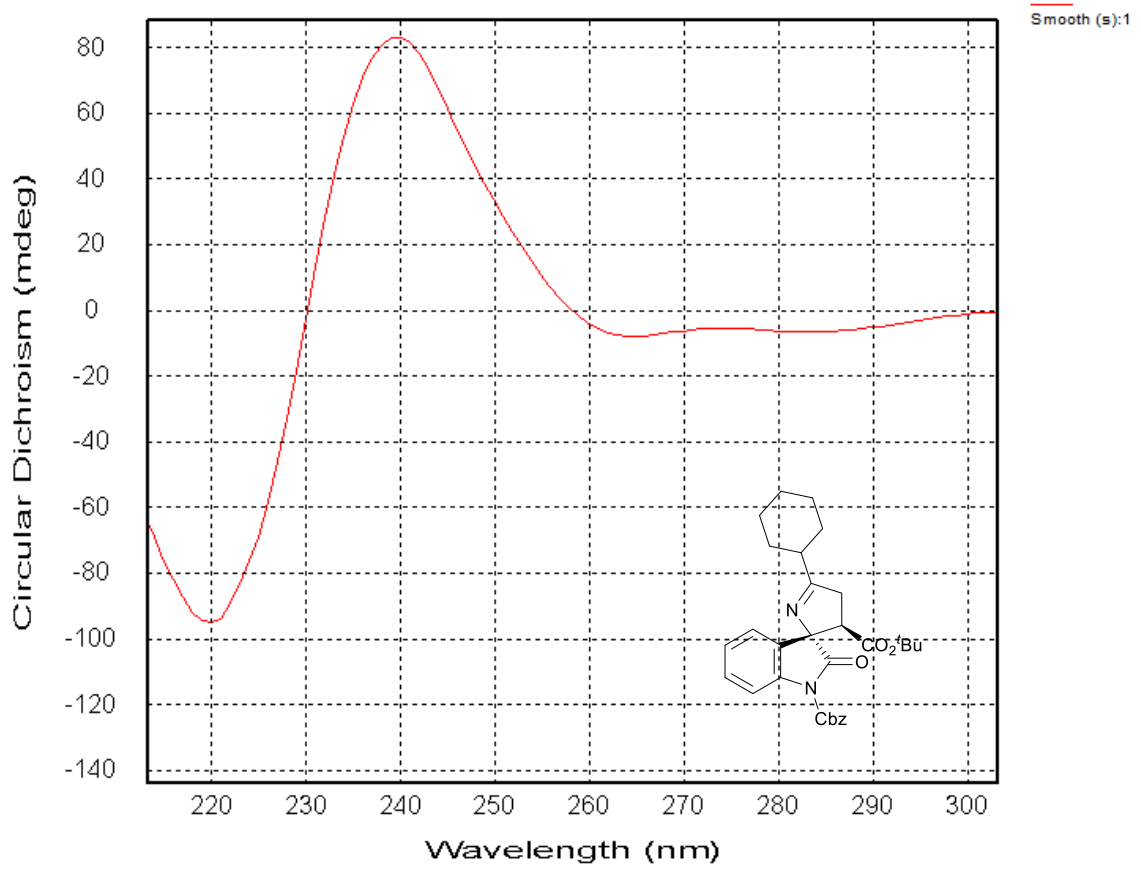

Smooth (s):1
Circular Dichroism (mdeg)
0
-50
-100
-150
-200
-250
230
240
250
260
270
280
290
300
Wavelength (nm)
F
N
CO2tBu
O
N
Cbz

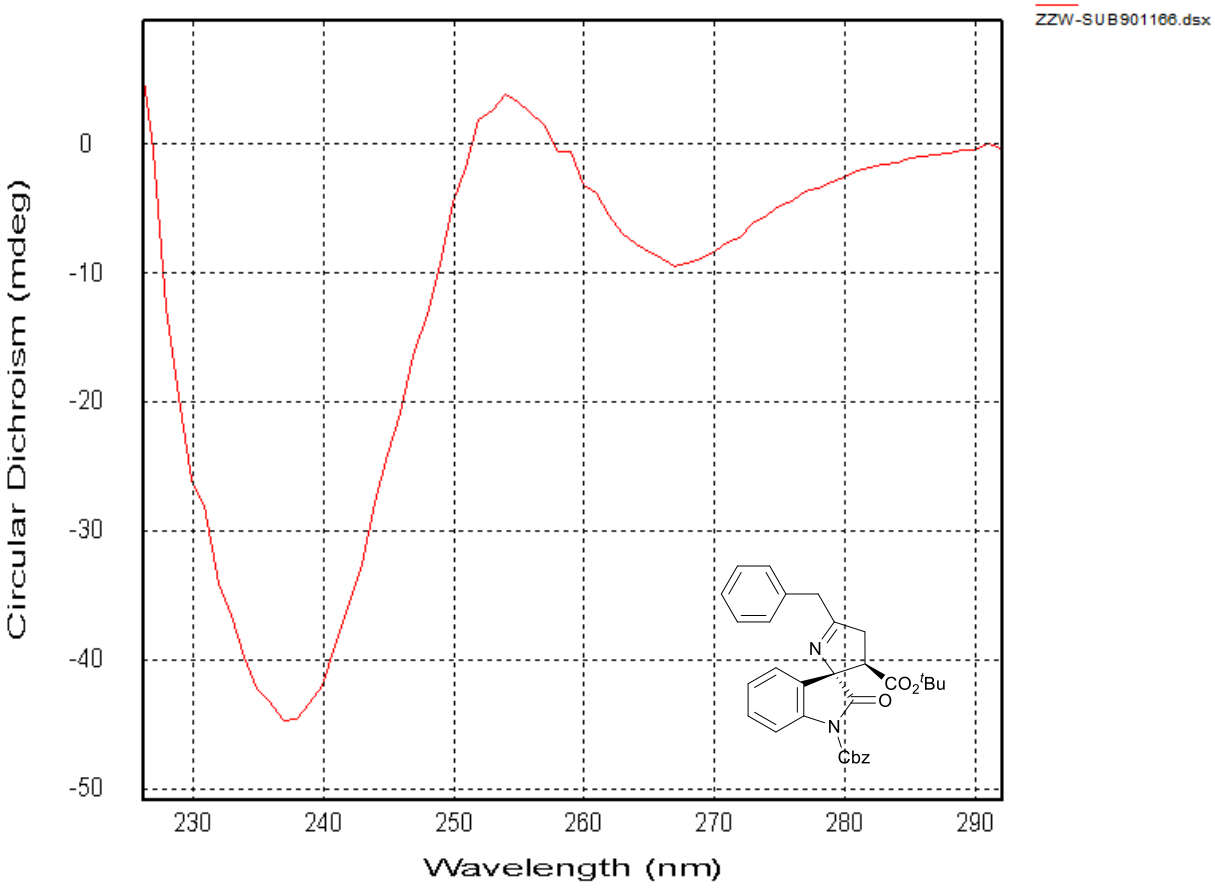

Smooth (s):1
Circular Dichroism (mdeg)
20
0
-20
-40
-60
-80
-100
-120
230
240
250
260
270
280
290
300
Wavelength (nm)
Cl
N
CO2tBu
O
N
Cbz


ZZW-SUB1601165.dsx
Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
-50
-60
-70
230
240
250
260
270
280
Wavelength (nm)
EtO2C
N
CO2tBu
O
N
Cbz


Smooth (s):1
Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
Wavelength (nm)
S
N
CO2tBu
O
N
Cbz


Smooth (s):1
Circular Dichroism (mdeg)
10
0
-10
-20
-30
-40
230
240
250
260
270
280
290
Wavelength (nm)
N
CO2tBu
O
N
Cbz


Smooth (s):1
Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
220
230
240
250
260
270
280
290
300
Wavelength (nm)
N
CO2tBu
O
N
Cbz


ZZW-SUB901166.dsx
Circular Dichroism (mdeg)
0
-10
-20
-30
-40
-50
230
240
250
260
270
280
290
Wavelength (nm)
N
CO2tBu
O
N
Cbz