Electronic Supplementary Information (ESI)

Chiral *N,N'*-Dioxide/Co(II)-Promoted Asymmetric 1,3-Dipolar Cycloaddition of Nitrones with Methyleneindolinones

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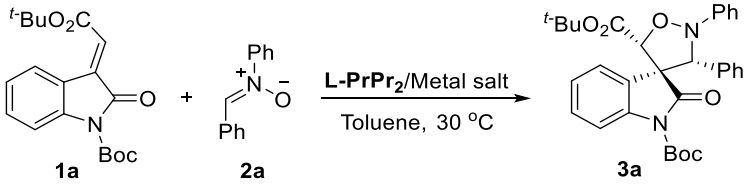
I. General information.

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO, δ = 2.49). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO, δ = 39.6). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 ºC. Optical rotations were reported as follows: $[a]^{T}{}_{D}$ (c g/100 mL, in CH_2Cl_2). HRMS was recorded on a commercial apparatus (ESI Source). All reagents were obtained from commercial suppliers and used without further purification except as indicated below. All catalytic reactions were run in dried glassware. All the solvents were purified by usual methods before use. Chiral *N*,*N*′-dioxide ligands were prepared using literature method.[1]

II. Optimization of reaction conditions.

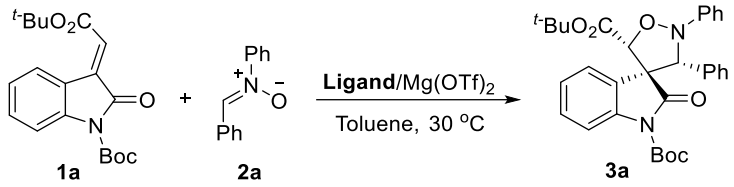
Table S1: **Optimization of different kinds of metals.**



Entry[a]	Metal salt	Yield[b] (%)	dr[c]	ee[c] (%)
1	$Mg(OTf)_2$	78	50:50	79
2	$Ni(OTf)_2$	87	85:15	46
3	$Sc(OTf)_3$	70	70:30	70
4	$Y(OTf)_3$	87	77:23	60
5	$Zn(BF_4)_2$ $6H_2O$	82	71:29	80
6	$Co(ClO_4)_2$ $6H_2O$	90	63:32	83
7	$Cu(OTf)_2$	71	72:28	74
8	$Mg(ClO_4)_2$	82	68:32	80
9	$Co(BF_4)_2$ $6H_2O$	88	66:34	91
10	CoF_2	74	82:18	76
11	$Co(OAc)_2$	88	84:16	63
12	$Co_3(PO_4)_2$ $8H_2O$	84	83:17	76

[a] Unless otherwise noted, all reactions were carried out with Methyleneindolinone **1a** (0.1mmol), nitrone **2a** (0.11mmol), **L-PrPr$_2$**/Metal salt (1:1, 10 mol%) in toluene (1.0 mL) under N_2 at 30 ℃ for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

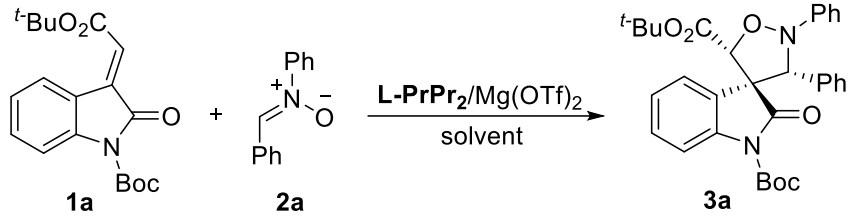
Table S2: Optimization of the ligands.



Entry[a]	Ligand	Yield[b] (%)	dr[c]	ee[c] (%)
1	**L-PiPr$_2$**	90	67:33	87
2	**L-PiPr$_3$**	94	56:44	67
3	**L-RaPr$_2$**	80	50:50	77
4	**L-RaEt$_2$**	95	72:28	83
5	**L-RaPr$_3$**	88	57:43	83
6	**L-PrPr$_3$**	91	64:36	79
7	**L-PrPh**	86	80:20	63
8	**L-PrPr$_2$**	88	66:34	91
9	**L-PrAd**	94	70:30	61

[a] Unless otherwise noted, all reactions were carried out with Methyleneindolinone **1a** (0.1 mmol), nitrone **2a** (0.11mmol), ligand/Mg(OTf)$_2$ (1:1, 10 mol%) in toluene (1.0 mL) under N_2 at 30 ℃ for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table S3: **Optimization of solvents and temperature.**

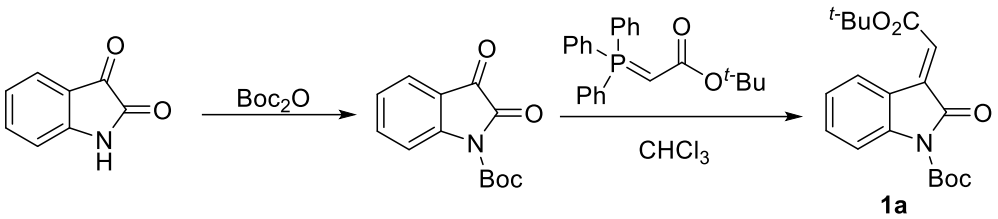


Entry[a]	Solvent	T (°C)	Yield[b] (%)	dr[c]	ee[c] (%)
1	THF	30	56	70:30	67
2	CH_2Cl_2	30	70	60:40	79
4[d]	EtOAc	0	97	96:4	98

[a] Unless otherwise noted, all reactions were carried out with Methyleneindolinone **1a** (0.1mmol), nitrone **2a** (0.11mmol), **L-PrPr**$_2$/Mg(OTf)$_2$ (1:1, 10 mol%) in indicated solvent (1.0 mL) under N_2 at 30 ℃ for 24 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was performed at 0 ℃ for 72 h.

III. Synthesis of substrates.

1. General procedure for preparation of Boc-protected methyleneindolinones.[2]

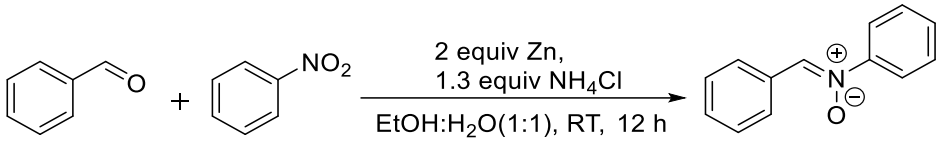


1a

Wittig reagent (1 mmol, 1 equiv) was added to a solution of the Boc-protected isatin (2 mmol, 2equiv) in $CHCl_3$ (5 mL) in a 25 mL round bottom flask. The solution was stirred at room temperature for 30 min. Then, the mixture was purified by flash chromatography to afford the desired product (**1a**) in about 60% yield.

2. General procedure for preparation of nitrones.

All the nitrones were prepared according to the known procedure.[3]



2a

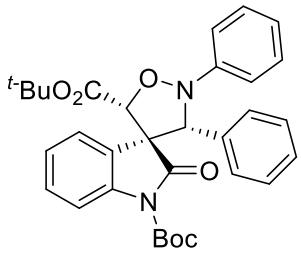
In brief, the nitrobenzene (11.6 g, 94.2 mmol), the benzaldehyde (10 g, 94.2 mmol), NH_4Cl (6.6g, 122.5 mmol), EtOH (100 mL) and water (100 mL) were added to a 500 mL round-bottom flask. The reaction mixture was cooled to 0 ℃, and zinc (12.3g, 188.5mmol) was added slowly over 3 ~ 4 h. The suspension was then warmed to room temperature and stirred for 12 h. The reaction mixture was filtered through celite using DCM and dried by $MgSO_4$. The resulting crude mixture was then concentrated and purified by either recrystallization or column chromatography affords the desired nitrone (**2a**) (15.2 g, 77.2 mmol, 82%) as a yellow solid.

IV. General procedure of the catalytic reactions.

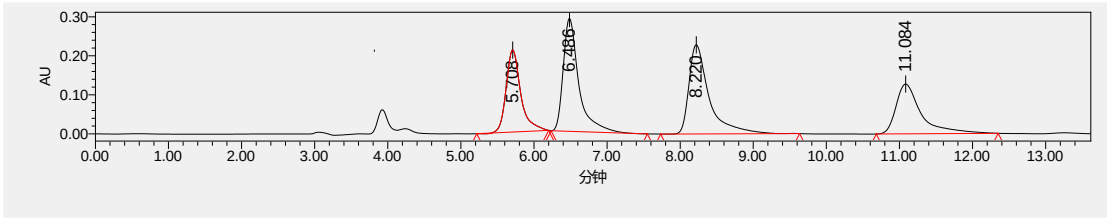
A dry reaction tube was charged with substrate **1** (0.10 mmol), $Co(BF_4)_2$ $6H_2O$ (3.40 mg, 10 mol%) and the ligand **L-PrPr$_2$** (6.3 mg, 10 mol%) under N_2. Then, EtOAc (1.0 mL) was added successively. The mixture was stirred at 30 ^oC for 0.5 h. Finally, the substrate **2** (0.11 mmol) was added one-pot and performed at 0 ^oC for 72 h. The residue was purified by flash chromatography on silica gel (1/10, ethyl acetate/petroleum ether) to afford the desired product.

V. Product characterization data.

Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2-oxo-2',3'-diphenylspiro-[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3a)



Result: 97% yield, 98% ee; $[\alpha]^{25}_{D}$ = −75.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 6.41 min, $t_{R(minor)}$ = 8.25 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.21 (m, 4H), 7.20 – 6.97 (m, 8H), 5.44 (s, 1H), 5.17 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.09, 151.29, 139.62, 135.50, 129.13, 128.94, 128.45, 128.10, 126.60, 126.40, 124.33, 123.92, 122.72, 115.24, 114.26, 84.82, 83.20, 83.09, 79.01, 66.47, 28.06, 27.15; ESI-HRMS calcd for [$C_{32}H_{34}N_2O_6$+Na^+]: 565.2309, found 565.2311.



	Retention Time	% Area
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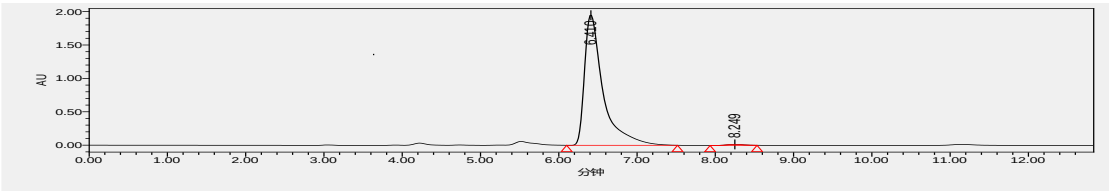
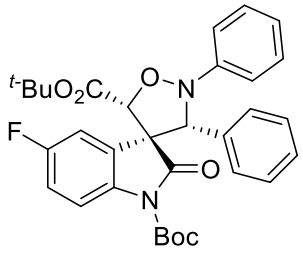
2	6.486	29.31
3	8.220	29.83
4	11.084	20.87



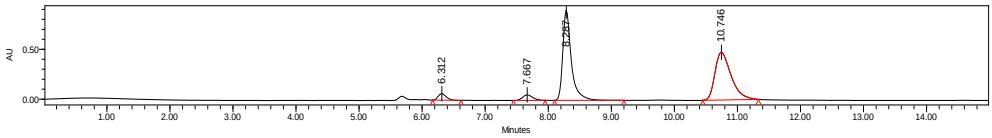
	Retention Time	% Area

1	6.410	99.34
2	8.249	0.66

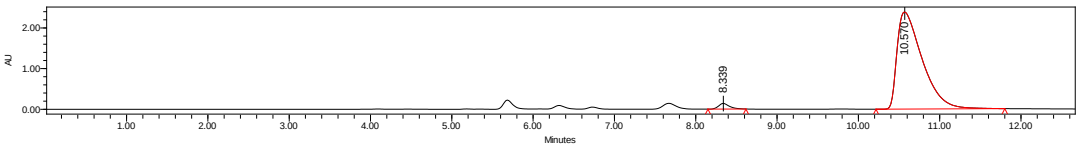
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5-fluoro-2-oxo-2',3'-diphenyl-spiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3b)



Result: 99% yield, 95% ee; $[\alpha]^{25}_{D}$ = −65.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 10.57 min, $t_{R(minor)}$ = 8.34 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 9.2, 4.4 Hz, 1H), 7.34 (dd, *J* = 7.6, 2.8 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.19 – 7.10 (m, 3H), 7.07 – 6.99 (m, 3H), 6.87 (td, *J* = 9.2, 2.8 Hz, 1H), 5.43 (s, 1H), 5.17 (s, 1H), 1.63 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.32, 163.85, 159.47 (d, *J* = 243.2 Hz), 151.02, 148.75, 135.68, 135.65, 135.06, 128.98, 128.64, 128.33, 126.28, 125.778 (d, *J* = 8.9 Hz), 122.95, 115.82, 115.60, 115.53, 115.38, 114.118 (d, *J* = 25.0 Hz), 85.06, 83.40, 82.85, 78.83, 77.25, 66.56, 66.54, 28.05, 27.21; ESI-HRMS calcd for [$C_{32}H_{33}FN_2O_6$+Na^+]: 583.2215, found 583.2229.

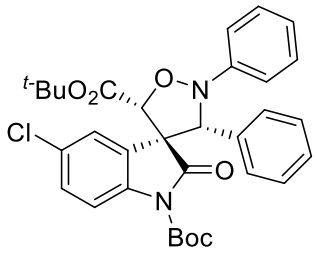


	Retention Time	% Area
1	6.312	3.19
2	7.667	3.38
3	8.287	46.59
4	10.746	46.85

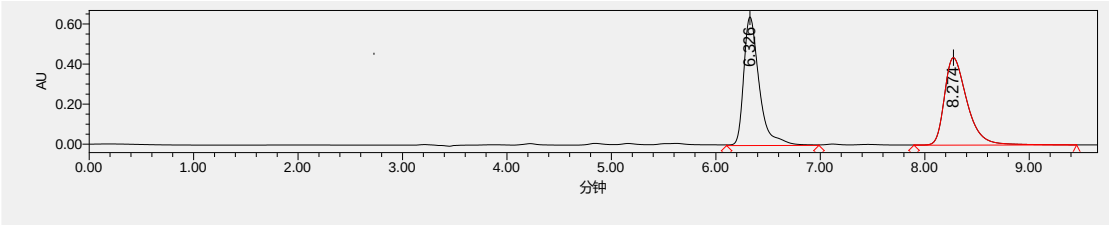


	Retention Time	% Area
1	8.339	2.46
2	10.570	97.54

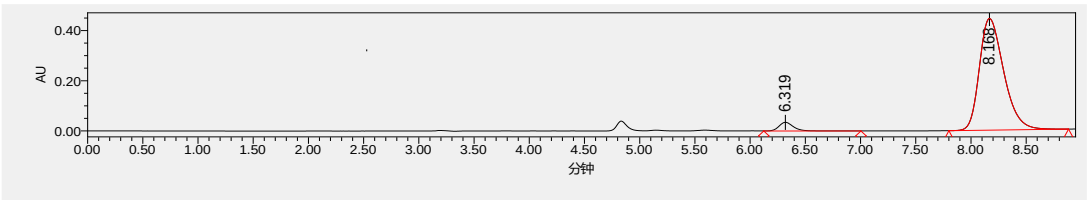
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5-chloro-2-oxo-2',3'-di-phenyl-spiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3c)



Result: 95% yield, 91% ee; $[\alpha]^{25}_{D}$ = −91.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 8.17 min, $t_{R(minor)}$ = 6.32 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.24 (ddd, *J* = 7.6, 3.6, 1.6 Hz, 4H), 7.19 – 7.11 (m, 4H), 7.07 – 6.99 (m, 3H), 5.42 (s, 1H), 5.17 (s, 1H), 1.63 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.07, 163.88, 150.96, 138.15, 134.99, 129.93, 129.13, 128.98, 128.63, 128.39, 126.60, 126.29, 125.72, 122.99, 115.50, 115.43, 85.22, 83.46, 82.86, 78.85, 66.41, 28.08, 28.04, 27.22; ESI-HRMS calcd for $[C_{32}H_{33}{}^{34.9694}Cl\text{-}N_2O_6{+}Na^+]$: 599.1919, found 599.1926, ESI-HRMS calcd for $[C_{32}H_{33}{}^{36.9665}ClN_2O_6\text{-}{+}Na^+]$: 601.1890, found 601.1884.

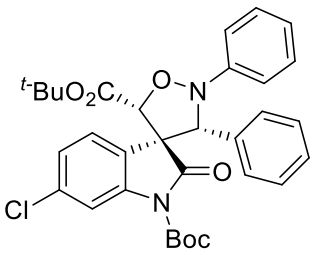


	Retention Time	% Area
1	6.326	50.39
2	8.274	49.61

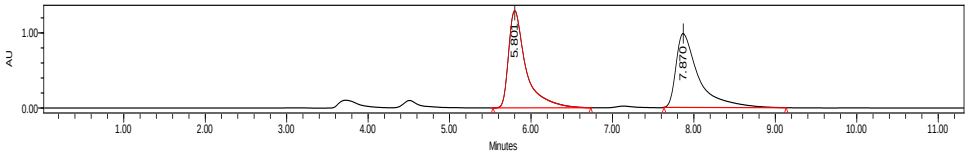


	Retention Time	% Area
1	6.319	4.48
2	8.168	95.52

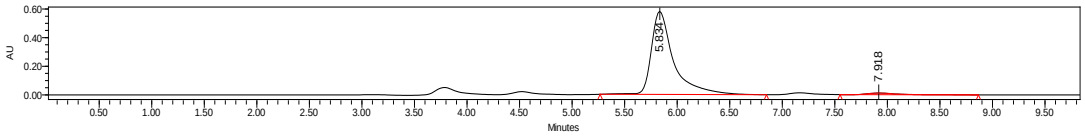
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-6-chloro-2-oxo-2',3'-diphenyl-spiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3d)



Result: 86% yield, 95% ee; $[\alpha]^{25}_{D}$ = −67.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 5.83 min, $t_{R(minor)}$ = 7.92 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.28 (q, *J* = 2.4, 2.0 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.18 – 7.11 (m, 3H), 7.06 – 6.98 (m, 4H), 5.42 (s, 1H), 5.15 (s, 1H), 1.64 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.89, 151.08, 140.53, 135.18, 135.05, 128.98, 128.67, 128.37, 127.43, 126.28, 124.38, 122.89, 122.37, 115.27, 115.08, 85.40, 83.45, 82.98, 78.83, 77.25, 66.23, 28.01, 27.22; ESI-HRMS calcd for [$C_{32}H_{33}{}^{34.9694}$ Cl-N_2O_6 +Na^+]: 599.1919, found 599.1926; ESI-HRMS calcd for [$C_{32}H_{33}{}^{36.9665}$ Cl-N_2O_6 +Na^+]: 601.1890, found 601.1884.



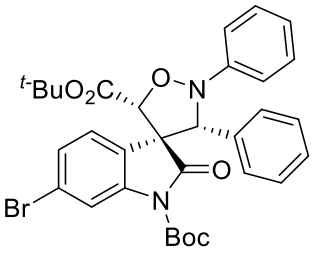
	Retention Time	% Area
1	5.801	50.21
2	7.870	49.79



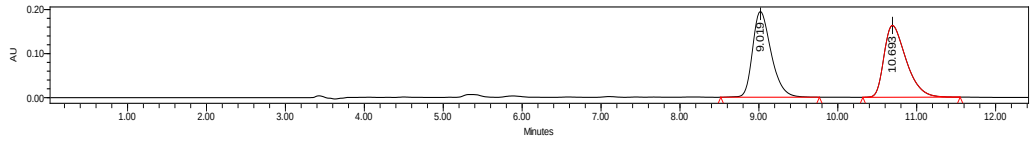
	Retention Time	% Area

1	5.834	97.46
2	7.918	2.54

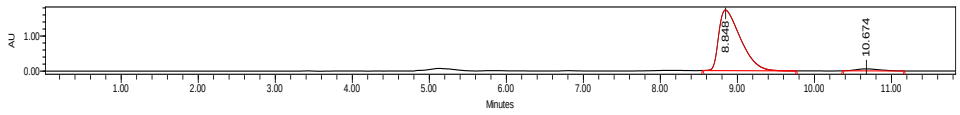
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-6-bromo-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3e)



Result: 88% yield, 93% ee; $[\alpha]^{25}_{D}$ = −65.2 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 8.85 min, $t_{R(minor)}$ = 10.67 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.11 (m, 8H), 7.07 – 6.98 (m, 3H), 5.42 (s, 1H), 5.15 (s, 1H), 1.63 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.19, 163.87, 151.06, 135.14, 128.98, 128.68, 128.39, 127.73, 127.31, 126.29, 122.98, 122.91, 117.83, 115.30, 85.40, 83.47, 82.94, 78.78, 66.29, 28.01, 27.22; ESI-HRMS calcd for $[C_{32}H_{33}{}^{78.9189}BrN_2O_6+Na^+]$: 643.1414, found 643.1420; ESI-HRMS calcd for $[C_{32}H_{33}{}^{80.9168}BrN_2O_6+Na^+]$: 645.1394, found 645.1396.



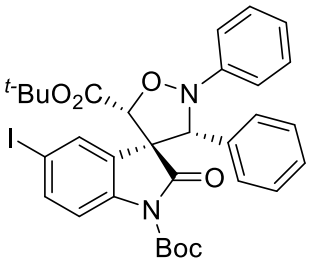
	Retention Time	% Area
1	9.019	50.11
2	10.693	49.89



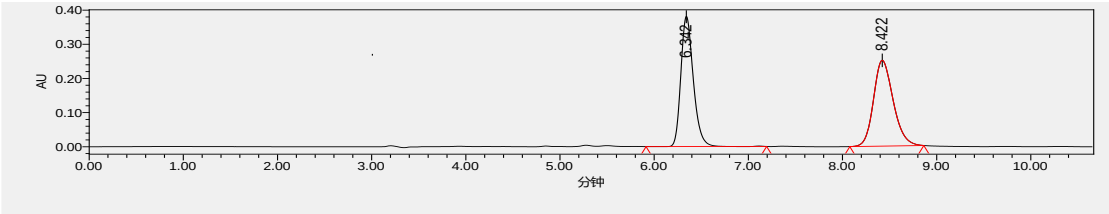
	Retention Time	% Area
1	8.848	96.57

2	10.674	3.43

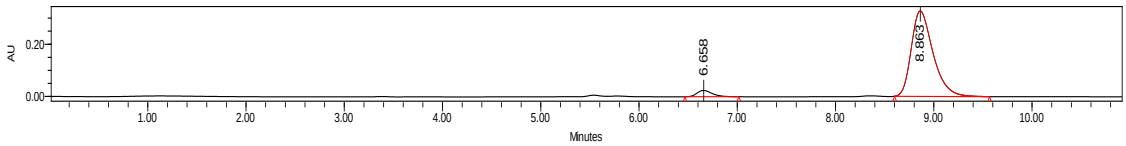
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5-iodo-2-oxo-2',3'-diphenyl-spiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3f)



Result: 91% yield, 90% ee; $[\alpha]^{25}_{D}$ = -51.7 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 8.86 min, $t_{R(minor)}$ = 6.66 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 12.0, 6.8 Hz, 1H), 7.46 (dd, *J* = 9.2, 8.0 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.11 (m, 7H), 7.02 (dd, *J* = 8.4, 7.2 Hz, 3H), 5.41 (s, 1H), 5.15 (s, 1H), 1.63 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.90, 163.77, 150.87, 148.46, 134.90, 129.01, 128.78, 128.51, 126.18, 123.07, 119.78, 115.83, 115.62, 115.41, 105.24, 104.99, 85.56, 83.54, 82.73, 78.68, 66.26, 28.04, 28.00, 27.31; ESI-HRMS calcd for [$C_{32}H_{33}IN_2O_6$+Na^+]: 691.1276, found 691.1280.

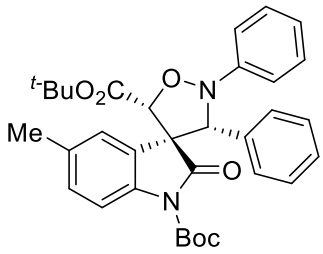


	Retention Time	% Area
1	6.342	50.66
2	8.422	49.34

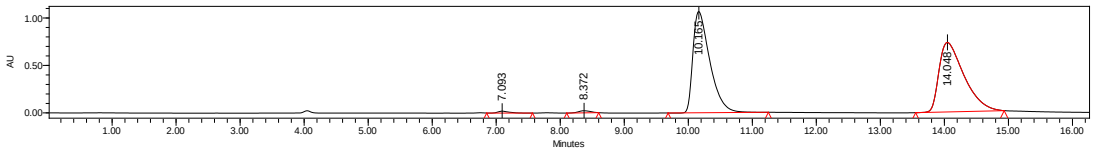


	Retention Time	% Area
1	6.658	4.97
2	8.863	95.03

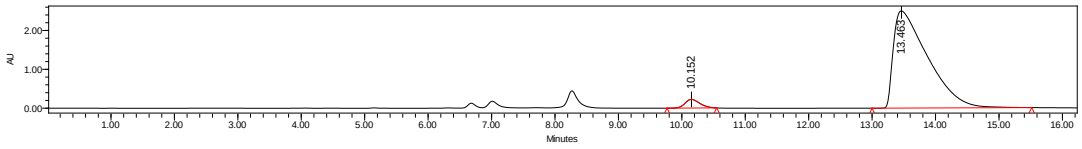
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5-methyl-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3g)



Result: 99% yield, 93% ee; $[\alpha]^{25}_{D}$ = −81.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 13.46 min, $t_{R(minor)}$ = 10.15 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.24 (dt, *J* = 7.2, 2.0 Hz, 3H), 7.15 – 7.07 (m, 3H), 7.07 – 6.92 (m, 4H), 5.43 (s, 1H), 5.16 (s, 1H), 2.22 (s, 3H), 1.63 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.02, 164.15, 151.34, 148.88, 137.26, 135.61, 134.05, 129.75, 129.46, 129.01, 128.93, 128.36, 128.06, 127.00, 126.42, 123.84, 122.66, 115.17, 114.03, 84.62, 83.14, 79.03, 77.26, 66.50, 28.07, 27.12, 25.38, 20.86; ESI-HRMS calcd for $[C_{33}H_{36}N_2O_6+Na^+]$: 579.2466, found 579.2471.

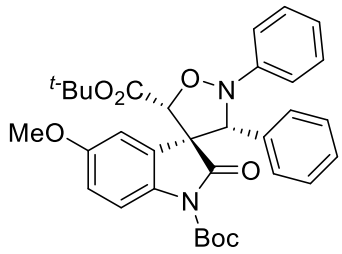


	Retention Time	% Area
1	10.165	49.68
2	14.048	50.32

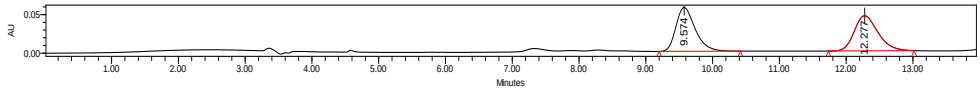


	Retention Time	% Area
1	10.152	3.34
2	13.463	96.66

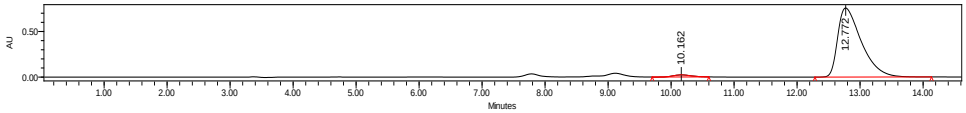
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5-methoxy-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3h)



Result: 97% yield, 95% ee; $[\alpha]^{25}_{D}$ = −83.7 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(minor)}$ = 10.16 min， $t_{R(major)}$ = 12.77 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.20 (m, 4H), 7.18 – 6.96 (m, 7H), 6.69 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.45 (s, 1H), 5.16 (s, 1H), 3.71 (s, 3H), 1.63 (s, 9H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.97, 164.01, 156.60, 151.28, 135.64, 133.09, 128.97, 128.47, 128.13, 126.36, 125.08, 122.71, 115.43, 115.29, 115.10, 111.67, 84.62, 83.22, 83.18, 79.08, 66.85, 55.95, 28.07, 27.18; ESI-HRMS calcd for [$C_{33}H_{36}N_2O_7$+Na^+]: 595.2415, found 595.2425.

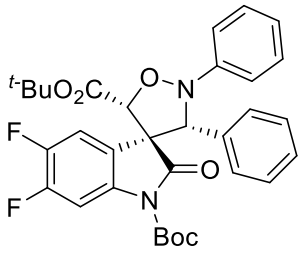


	Retention Time	% Area
1	9.574	50.38
2	12.277	49.62

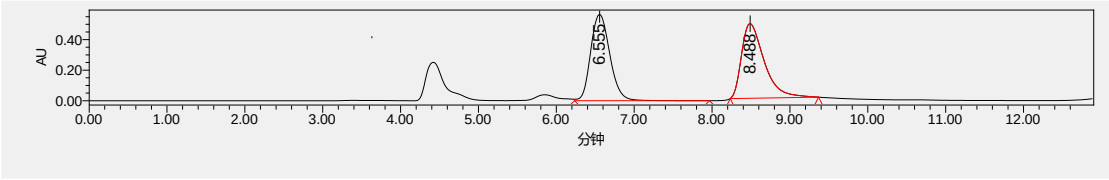


	Retention Time	% Area
1	10.162	2.25
2	12.772	97.75

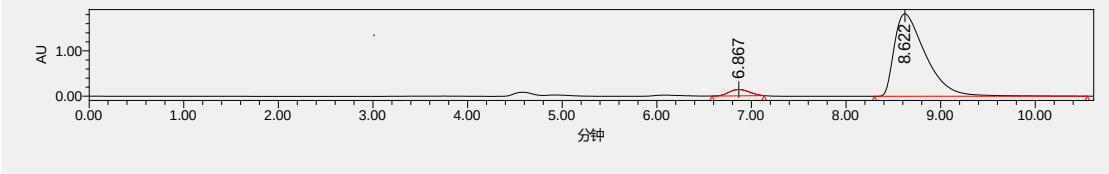
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-5,6-difluoro-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3i)



Result: 85% yield, 90% ee; $[\alpha]^{25}_{D}$ = -46.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(minor)}$ = 6.87 min, $t_{R(major)}$ = 8.62 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 12.0, 6.8 Hz, 1H), 7.46 (dd, *J* = 9.2, 8.0 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.11 (m, 6H), 7.02, 5.41 (s, 1H), 5.15 (s, 1H), 1.63 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.90, 163.77, 150.87, 148.46, 134.90, 129.01, 128.78, 126.18, 123.07, 119.78, 115.83 (d, *J* = 20.6 Hz), 115.62, 115.41, 105.24 (d, *J* = 25.1 Hz), 104.99, 85.56, 83.54, 82.73, 78.68, 66.26, 28.04, 28.00, 27.31; ESI-HRMS calcd for [$C_{32}H_{32}F_2N_2O_6$+Na^+]: 601.2121, found 601.2123.

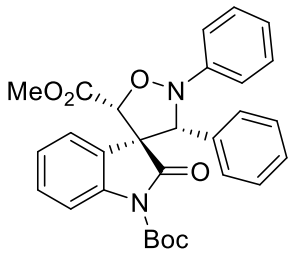


	Retention Time	% Area
1	6.555	49.51
2	8.488	50.49

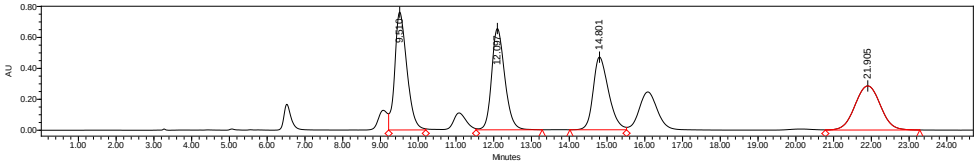


	Retention Time	% Area
1	6.867	4.78
2	8.622	95.22

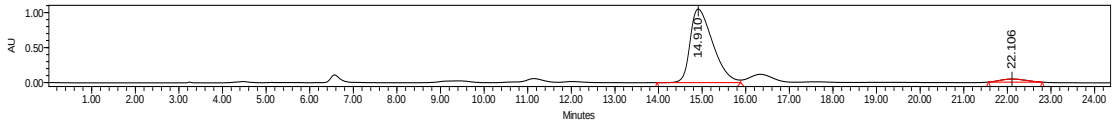
1-(tert-butyl)-5'-methyl-(3*R*,3'*R*,5'*R*)-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3j)



Result: 86% yield, 91% ee; $[\alpha]^{19}_{D}$ = −51.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min), $t_{R(major)}$ = 22.11 min, $t_{R(minor)}$ = 14.91 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.29 – 7.20 (m, 5H), 7.20 – 7.13 (m, 2H), 7.12 – 7.00 (m, 5H), 5.42 (s, 1H), 5.32 (s, 1H), 3.37 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.08, 150.87, 139.36, 134.93, 129.31, 128.98, 128.41, 128.24, 126.46, 126.33, 124.26, 123.37, 123.17, 115.81, 114.45, 84.90, 82.98, 78.68, 66.69, 52.24, 28.07; ESI-HRMS calcd for [$C_{29}H_{28}N_2O_6$+Na+]: 523.1840, found 523.1848.

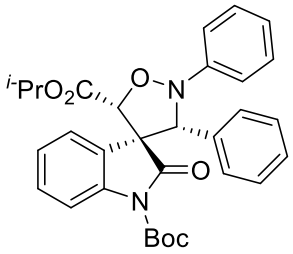


	Retention Time	% Area
1	9.510	28.73
2	12.097	26.71
3	14.801	22.50
4	21.905	22.06

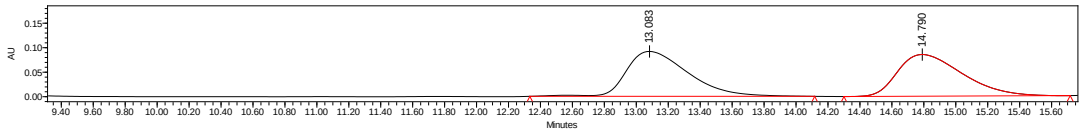


	Retention Time	% Area
1	14.910	95.48
2	22.106	4.52

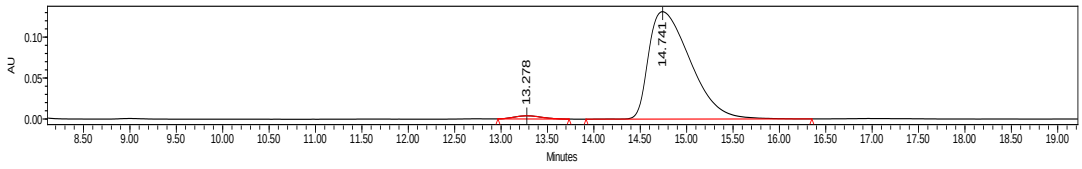
1-(tert-butyl)-5'-isopropyl-(3*R*,3'*R*,5'*R*)-2-oxo-2',3'-di-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3k)



Result: 96% yield, 96% ee; $[\alpha]^{19}_{D} = -63.7$ (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 14.74 min, $t_{R(minor)}$ = 13.28 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.27 – 7.22 (m, 4H), 7.18 – 7.09 (m, 4H), 7.08 – 6.98 (m, 4H), 5.45 (s, 1H), 5.23 (s, 1H), 4.69 (p, *J* = 6.4 Hz, 1H), 1.65 (s, 9H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.61 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.72, 151.20, 139.58, 135.30, 129.22, 128.96, 128.45, 128.15, 126.58, 126.43, 124.29, 123.46, 122.87, 115.38, 114.36, 84.85, 82.95, 78.83, 69.51, 66.53, 53.46, 28.08, 21.40, 20.62; ESI-HRMS calcd for [$C_{31}H_{32}N_2O_6$+Na^+]: 551.2153, found 551.2162.

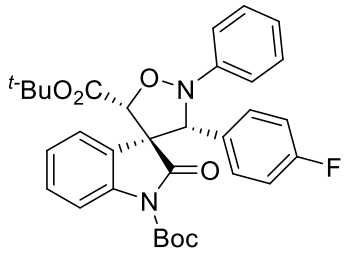


	Retention Time	% Area
1	13.083	50.82
2	14.790	49.18

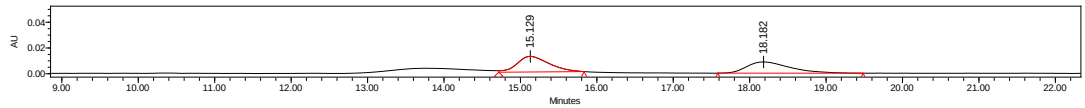


	Retention Time	% Area
1	13.278	1.88
2	14.741	98.12

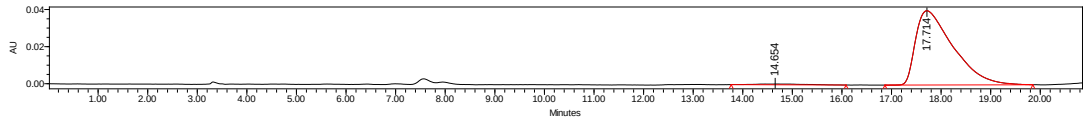
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(4-fluorophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3l)



Result: 95% yield, 97% ee; $[\alpha]^{19}_{D}$ = -48.2 (c 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, n-hexane/i-PrOH 95/5, 1.0 mL/min), t_R(major) = 17.71 min, t_R(minor) = 14.65 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.28 (s, 1H), 7.25 – 7.16 (m, 4H), 7.08 – 6.99 (m, 4H), 6.82 (t, *J* = 8.4 Hz, 2H), 5.40 (s, 1H), 5.17 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.68, 164.00, 162.32, 151.05, 148.72, 139.61, 131.194 (d, *J* = 3.3 Hz), 129.32, 128.99, 128.17 (d, *J* = 8.1 Hz), 126.52, 124.46, 123.73, 122.97, 115.58, 115.37, 114.38, 84.97, 83.28, 83.03, 78.39, 66.40, 28.05, 27.14; ESI-HRMS calcd for [$C_{32}H_{33}FN_2O_6$-+Na+]: 583.2215, found: 583.2221.

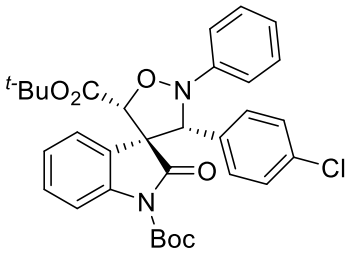


	Retention Time	% Area
1	15.129	50.46
2	18.182	49.54

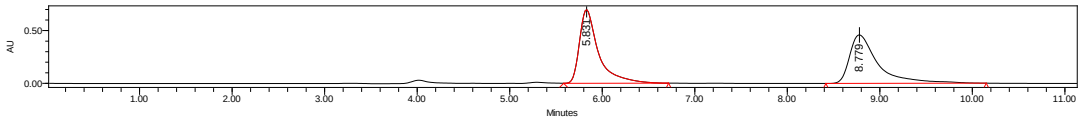


	Retention Time	% Area
1	14.654	1.29
2	17.714	98.71

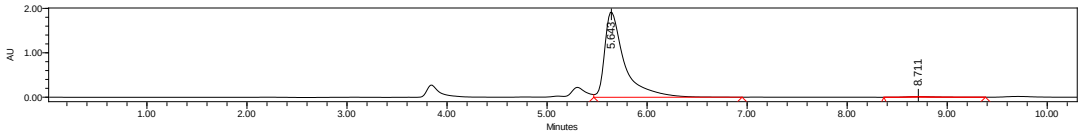
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(4-chlorophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3m)



Result: 83% yield, 98% ee; $[\alpha]^{25}_{D}$ = −50.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 8.71 min, $t_{R(minor)}$ = 5.64 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.32 – 7.22 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 3H), 7.14 – 6.99 (m, 5H), 5.39 (s, 1H), 5.16 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.60, 163.91, 150.99, 148.70, 139.62, 134.07, 133.90, 129.42, 129.01, 128.72, 127.86, 126.48, 124.54, 123.59, 123.00, 115.32, 114.45, 85.01, 83.32, 83.11, 78.35, 66.30, 28.06, 27.14; ESI-HRMS calcd for $[C_{32}H_{33}{}^{34.9694}ClN_2O_6+Na^+]$: 599.1919, found 599.1924; ESI-HRMS calcd for $[C_{32}H_{33}{}^{36.9665}ClN_2O_6+Na^+]$: 601.1890, found 601.1923.

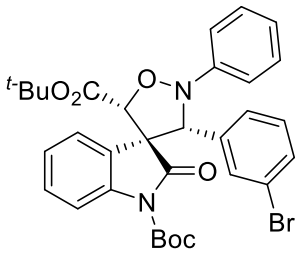


	Retention Time	% Area
1	5.831	50.51
2	8.779	49.49

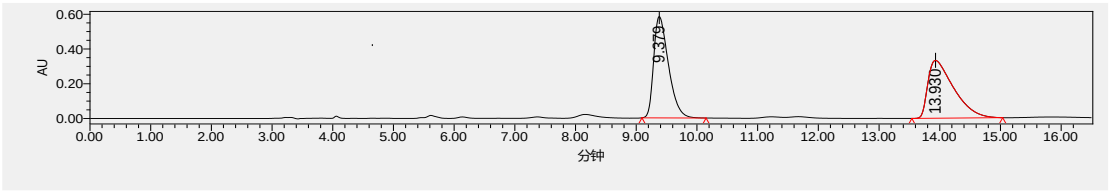


	Retention Time	% Area
1	5.643	99.00
2	8.711	1.00

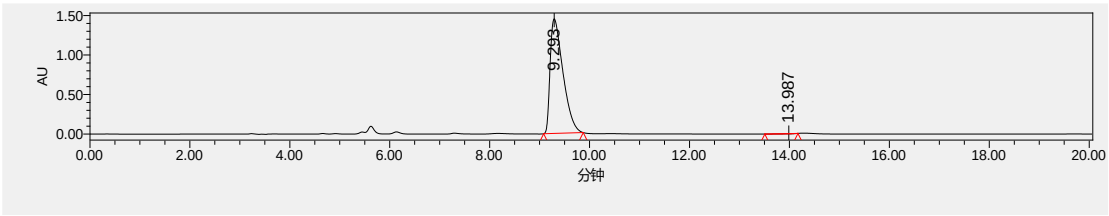
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(3-bromophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3n)



Result: 76% yield, 99% ee; $[\alpha]^{25}_{D} = -44.7$ (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 9.29 min, $t_{R(minor)}$ = 13.99 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 (td, *J* = 8.0, 1.2 Hz, 2H), 7.14 – 6.95 (m, 6H), 5.38 (s, 1H), 5.16 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.85, 150.97, 139.61, 137.96, 131.30, 130.02, 129.51, 129.42, 129.06, 126.44, 124.94, 124.48, 123.53, 122.98, 122.69, 115.16, 114.39, 85.01, 83.36, 83.10, 78.37, 66.43, 28.05, 27.14; ESI-HRMS calcd for [$C_{31}H_{25}NO_6$+Na^+]: 530.1580, found 530.1588.

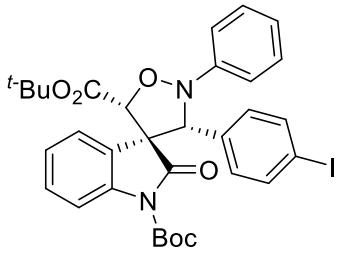


	Retention Time	% Area
1	9.379	50.22
2	13.930	49.78

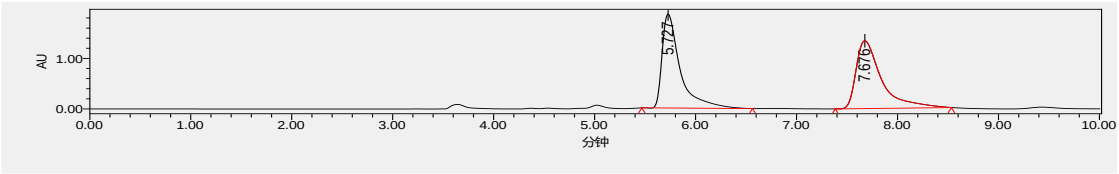


	Retention Time	% Area
1	9.293	99.78
2	13.987	0.22

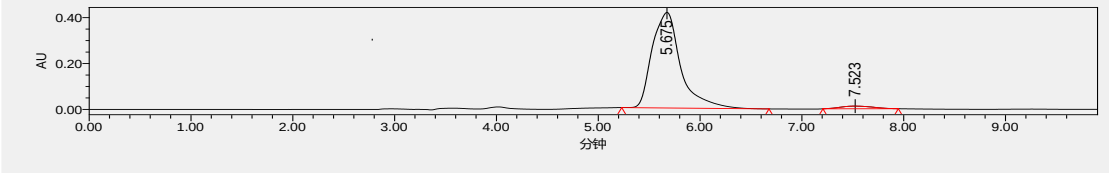
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(4-iodophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3o)



Result: 73% yield, 93% ee; $[\alpha]^{19}_{D}$ = −37.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 5.68 min, $t_{R(minor)}$ = 7.52 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.08 – 6.97 (m, 6H), 5.36 (s, 1H), 5.15 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.58, 163.88, 150.98, 139.62, 137.59, 135.32, 129.45, 129.02, 128.39, 126.46, 124.57, 123.54, 123.00, 115.29, 114.49, 93.93, 85.03, 83.33, 83.15, 78.45, 66.19, 53.46, 28.10, 28.06, 27.14; ESI-HRMS calcd for [$C_{32}H_{33}IN_2O_6$+Na^+]: 691.1276, found 691.1286.

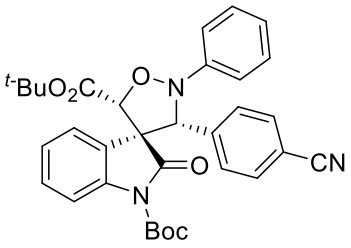


	Retention Time	% Area
1	5.727	49.75
2	7.676	50.25

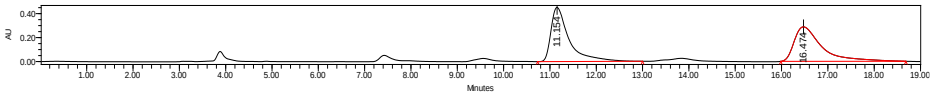


	Retention Time	% Area
1	5.675	96.59
2	7.524	3.41

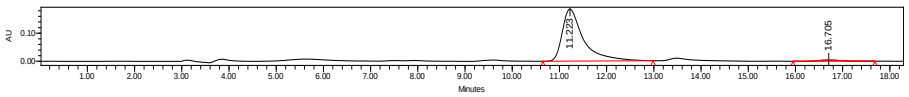
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(4-cyanophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3p)



Result: 75% yield, 95% ee; $[\alpha]^{25}_{D}$ = −36.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min); $t_{R(major)}$ = 11.22 min, $t_{R(minor)}$ = 16.71 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.21 (td, *J* = 8.0, 1.2 Hz, 1H), 7.07 – 6.96 (m, 4H), 5.46 (s, 1H), 5.16 (s, 1H), 1.65 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.59, 150.68, 148.60, 141.28, 139.59, 132.37, 129.67, 129.18, 127.15, 126.28, 124.63, 123.20, 118.31, 114.99, 114.56, 112.10, 85.27, 83.54, 83.37, 78.45, 77.24, 66.39, 28.05, 27.13; ESI-HRMS calcd for [$C_{33}H_{33}N_3O_6$+Na^+]: 590.2262, found 590.2271.

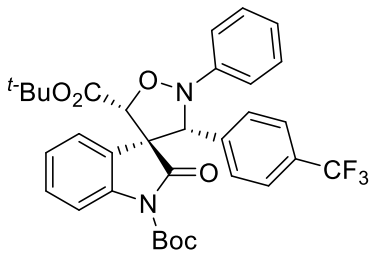


	Retention Time	% Area
1	11.154	50.89
2	16.474	49.11

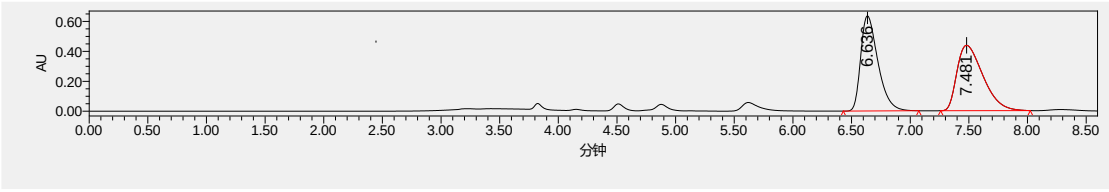


	Retention Time	% Area
1	11.223	97.74
2	16.705	2.26

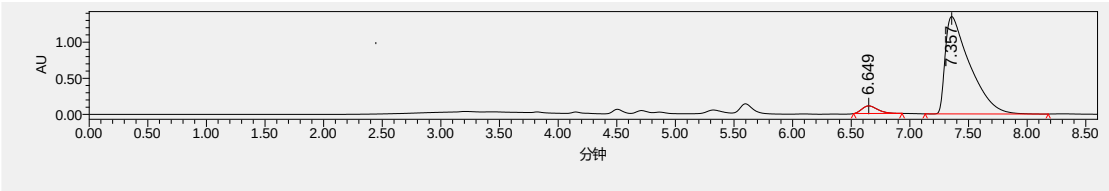
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2-oxo-2'-phenyl-3'-(4-(trifluoromethyl)phenyl)-spiro-[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3q)



Result: 78% yield, 91% ee; $[\alpha]^{25}_{D}$ = −61.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 7.36 min, $t_{R(minor)}$ = 6.65 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.39 (s, 4H), 7.27 (dd, *J* = 6.4, 2.4 Hz, 3H), 7.19 (td, *J* = 8.0, 1.2 Hz, 1H), 7.06 – 6.98 (m, 3H), 5.48 (s, 1H), 5.17 (s, 1H), 1.65 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.74, 150.90, 139.84, 129.51, 129.10, 126.84, 126.36, 125.50 (d, *J* = 3.7 Hz), 124.57, 123.38, 123.05, 115.10, 114.50, 85.12, 83.42, 83.32 (d, *J* = 0.6 Hz), 78.49, 66.38, 28.10, 28.05, 27.14; ESI-HRMS calcd for [$C_{33}H_{33}F_3N_2O_6$+Na^+]: 633.2183, found 633.2184.

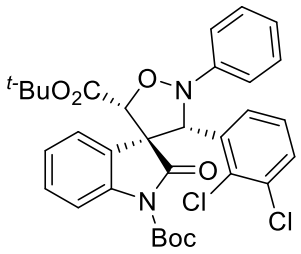


	Retention Time	% Area
1	6.636	49.13
2	7.481	50.87

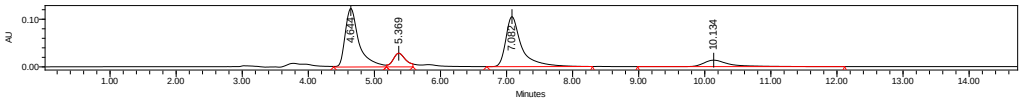


	Retention Time	% Area
1	6.649	4.77
2	7.357	95.23

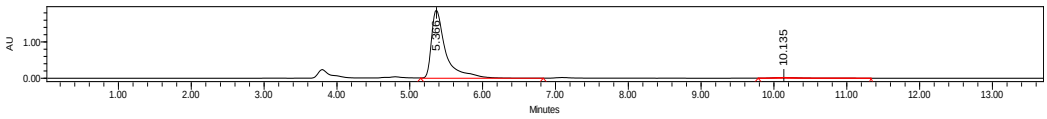
Di-tert-butyl-(3*R*,3'*S*,5'*R*)-3'-(2,3-dichlorophenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3r)



Result: 82% yield, 96% ee; $[\alpha]^{25}_{D} = -21.7$ (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 5.37 min, $t_{R(minor)}$ = 10.14 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 1H), 7.55 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.29 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.25 – 7.17 (m, 2H), 7.12 – 6.99 (m, 5H), 5.35 (s, 1H), 5.15 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.44, 163.71, 150.75, 139.62, 135.96, 132.83, 132.20, 130.53, 129.65, 129.12, 128.52, 126.35, 125.70, 124.65, 123.29, 123.20, 115.24, 114.57, 85.16, 83.45, 83.16, 77.87, 77.24, 66.26, 28.04, 27.14; ESI-HRMS calcd for $[C_{32}H_{32}{}^{34.9694}Cl_2N_2O_6+Na^+]$: 633.1530, found 633.1539; ESI-HRMS calcd for $[C_{32}H_{32}{}^{36.9665}Cl_2N_2O_6+Na^+]$: 635.1500, found 635.1530.

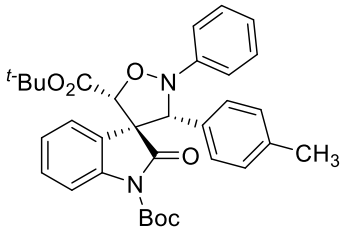


	Retention Time	% Area
1	4.644	41.76
2	5.369	8.78
3	7.082	41.00
4	10.134	8.46

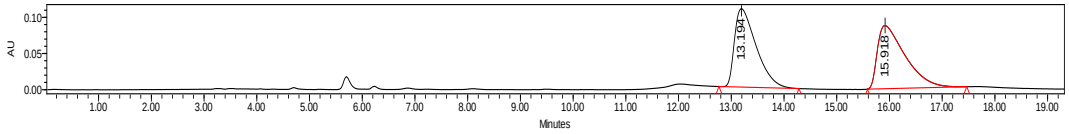


	Retention Time	% Area
1	5.366	98.24
2	10.135	1.76

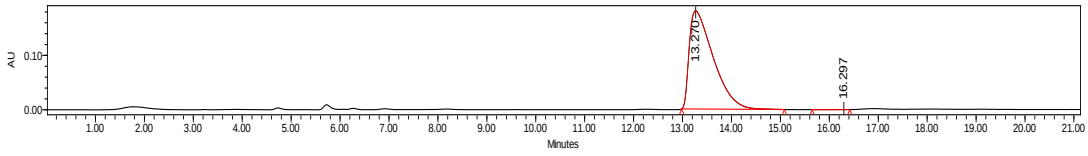
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2-oxo-2'-phenyl-3'-(p-tolyl)spiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3s)



Result: 88% yield, 99% ee; $[\alpha]^{19}_{D}$ = −50.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 13.27 min, $t_{R(minor)}$ = 16.30 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.61 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.10 (m, 5H), 7.08 – 6.96 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 5.16 (s, 1H), 2.18 (s, 3H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.17, 151.35, 139.65, 137.76, 132.29, 129.15, 129.09, 128.88, 126.64, 126.37, 124.36, 124.01, 122.69, 115.37, 114.26, 84.77, 83.15, 83.00, 78.86, 66.37, 28.07, 27.14, 21.07; ESI-HRMS calcd for [$C_{33}H_{36}N_2O_6$+Na^+]: 579.2466, found 579.2467.

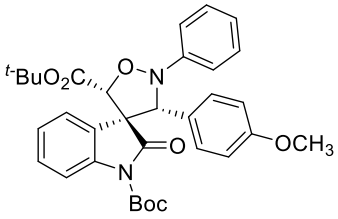


	Retention Time	% Area
1	13.194	49.42
2	15.918	50.58

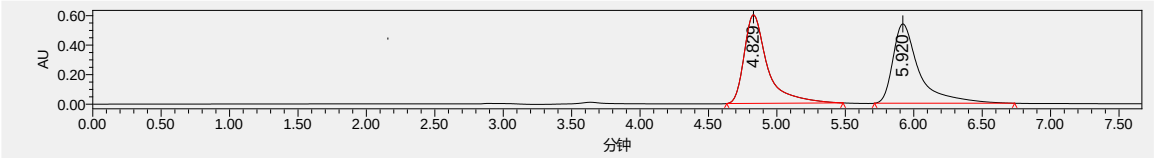


	Retention Time	% Area
1	13.270	99.99
2	16.297	0.01

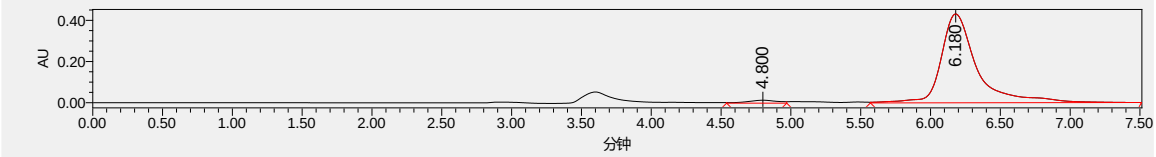
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(4-methoxyphenyl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3t)



Result: 74% yield, 94% ee; $[\alpha]^{19}_D$ = −63.6 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 6.18 min, $t_{R(minor)}$ = 4.80 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.09 – 6.96 (m, 4H), 6.64 (d, *J* = 8.8 Hz, 2H), 5.37 (s, 1H), 5.17 (s, 1H), 3.67 (s, 3H), 1.63 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.78, 164.22, 159.22, 151.30, 148.82, 139.64, 129.14, 128.88, 127.76, 127.15, 126.63, 124.39, 124.01, 122.79, 115.54, 114.31, 113.80, 84.78, 83.13, 82.90, 78.66, 66.37, 55.08, 28.06, 27.14; ESI-HRMS calcd for [$C_{33}H_{36}N_2O_7$+Na^+]: 595.2415, found 595.2418.

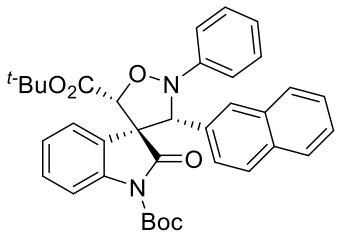


	Retention Time	% Area
1	4.829	49.80
2	5.920	50.20

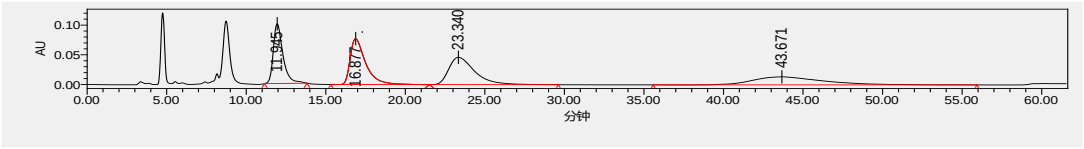


	Retention Time	% Area
1	4.800	2.70
2	6.180	97.30

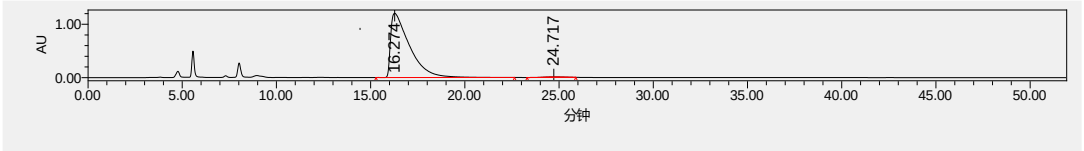
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(naphthalen-2-yl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3u)



Result: 90% yield, 98% ee; $[\alpha]^{25}_{D}$ = −42.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 16.27 min, $t_{R(minor)}$ = 24.72 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (s, 1H), 7.74 – 7.55 (m, 6H), 7.43 – 7.36 (m, 2H), 7.27 – 7.21 (m, 2H), 7.12 – 7.04 (m, 3H), 6.98 (dtd, *J* = 13.2, 7.6, 1.2 Hz, 2H), 5.60 (s, 1H), 5.23 (s, 1H), 1.63 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.05, 151.35, 139.64, 133.08, 133.05, 129.21, 128.99, 128.33, 128.08, 127.59, 126.58, 126.22, 126.15, 125.97, 124.40, 124.01, 123.83, 122.78, 115.26, 114.34, 84.89, 79.25, 66.48, 28.08, 27.17; ESI-HRMS calcd for [$C_{36}H_{36}N_2O_6$+Na^+]: 615.2466, found 615.2473.

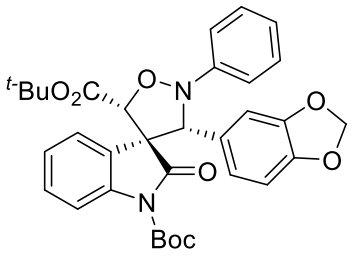


	Retention Time	% Area
1	11.945	22.52
2	16.877	27.78
3	23.340	27.69
4	43.671	22.01

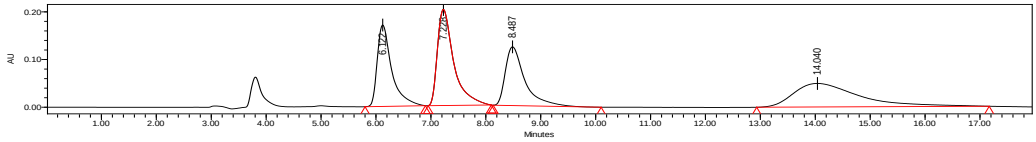


	Retention Time	% Area
1	16.274	99.19
2	24.717	0.81

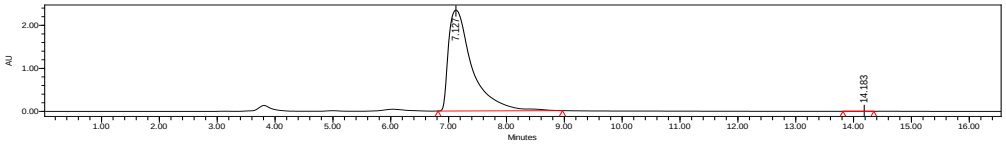
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-3'-(benzo[d][1,3]dioxol-5-yl)-2-oxo-2'-phenylspiro-[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3v)



Result: 87% yield, 99% ee; $[\alpha]^{25}_{D}$ = −50.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 7.13 min, $t_{R(minor)}$ = 14.18 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.18 (m, 3H), 7.12 – 6.99 (m, 4H), 6.79 – 6.71 (m, 2H), 6.56 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.82 (s, 2H), 5.34 (s, 1H), 5.15 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.70, 164.08, 151.19, 147.72, 147.29, 139.69, 129.23, 129.08, 128.91, 126.60, 124.46, 123.85, 122.84, 119.95, 115.43, 114.37, 108.22, 107.11, 101.04, 84.85, 83.20, 82.97, 78.76, 66.36, 28.06, 27.14; ESI-HRMS calcd for [$C_{33}H_{34}N_2O_8$+Na^+]: 609.2207, found 609.2248.

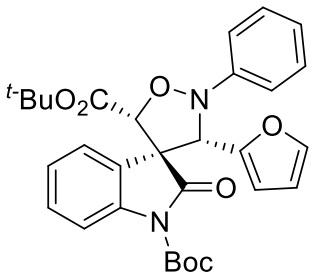


	Retention Time	% Area
1	6.122	21.69
2	7.228	28.88
3	8.487	21.07
4	14.040	28.36

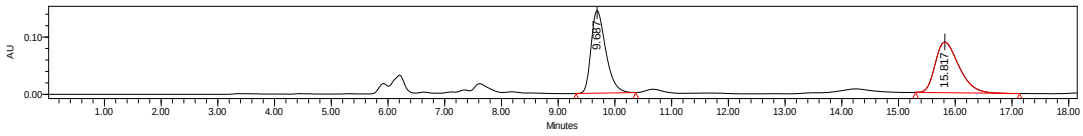


	Retention Time	% Area
1	7.127	99.98
2	14.183	0.02

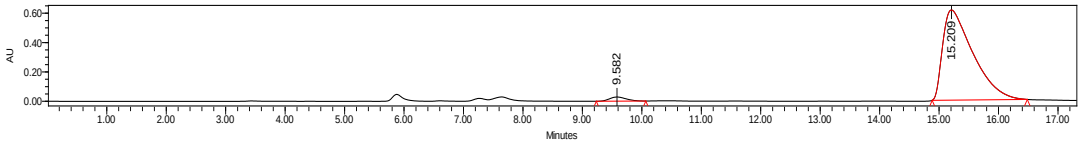
Di-tert-butyl-(3*R*,3'*S*,5'*R*)-3'-(furan-2-yl)-2-oxo-2'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3w)



Result: 72% yield, 95% ee; $[\alpha]^{25}_{D}$ = −101.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 15.21 min, $t_{R(minor)}$ = 9.58 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.23 (m, 4H), 7.19 – 7.10 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 5.98 (s, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 1.64 (s, 9H)，1.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.47, 150.95, 143.58, 141.06, 139.86, 129.38, 128.91, 126.58, 124.60, 124.21, 123.57, 120.42, 116.40, 114.44, 108.73, 84.89, 83.15, 82.63, 72.84, 65.36, 28.05, 27.15. ESI-HRMS calcd for [$C_{30}H_{32}N_2O_7$+Na^+]: 555.2102, found 555.2112.

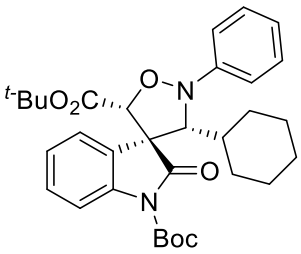


	Retention Time	% Area
1	9.687	50.18
2	15.817	49.82

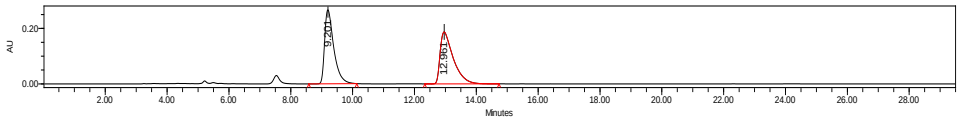


	Retention Time	% Area
1	9.582	2.48
2	15.209	97.52

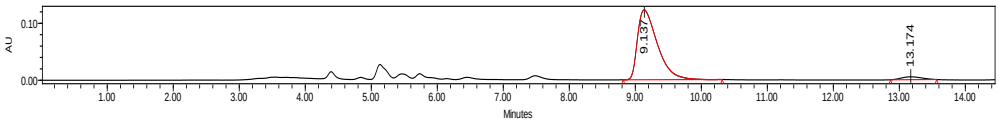
Di-tert-butyl-(3R,3'R,5'R)-3'-cyclohexyl-2-oxo-2'-(p-tolyl)spiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3x)



Result: 98% yield, 92% ee; $[\alpha]^{25}_{D} = -38.7$ (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 9.14 min, $t_{R(minor)}$ = 13.17 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz 1H), 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.35-7.31 (m, 3H), 7.28 – 7.19 (m, 2H), 7.03 (s, 1H), , 4.73 (s, 1H), 4.09 (s, 1H), 1.97 (d, *J* = 12.0 Hz, 1H), 1.65 (d, *J* = 2.0 Hz, 3H), 1.61 (s, 9H), 1.59 (s, 4H), 1.57 (s, 1H), 1.52 (s, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15, 163.76, 140.22, 129.35, 129.05, 125.95, 124.80, 124.43, 122.65, 115.65, 114.72, 85.27, 84.68, 82.97, 79.94, 64.80, 64.44, 60.41, 53.43, 40.54, 32.28, 29.10, 29.06, 28.04, 27.12, 26.21, 26.13, 25.61, 25.36, 22.62, 20.45, 14.33, 14.20, 11.44; ESI-HRMS calcd for [$C_{32}H_{40}N_2O_6$+Na^+]: 571.2779, found 571.2784.

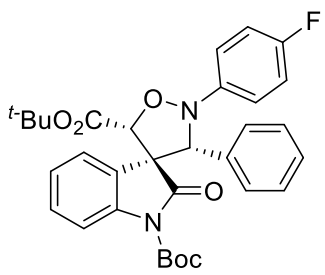


	Retention Time	% Area
1	9.201	49.78
2	12.961	50.22

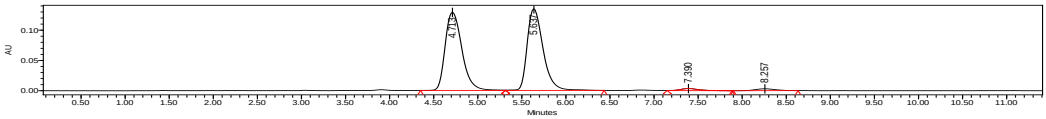


	Retention Time	% Area
1	9.137	96.02
2	13.174	3.98

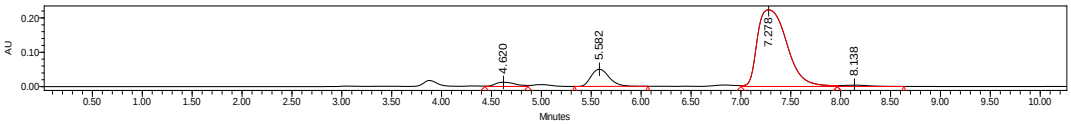
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2'-(4-fluorophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3y)



Result: 75% yield, 97% ee; $[\alpha]^{25}_{D}$ = −81.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 7.28 min, $t_{R(minor)}$ = 8.14 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (s, 1H), 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.12 – 7.08 (m, 3H), 7.07 – 7.02 (m, 3H), 6.98 – 6.91 (m, 2H), 5.35 (s, 1H), 5.20 (s, 1H), 1.63 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.73, 164.19, 160.29, 157.88, 148.75, 147.15, 139.62, 134.75, 129.22, 128.46, 128.28, 126.58 (d, *J* = 3.8 Hz), 125.78, 124.36, 123.76, 119.32, 117.62 (d, *J* = 7.8 Hz), 115.54, 115.25, 114.31, 84.88, 83.24, 82.81, 79.19, 71.74, 66.43, 65.68, 28.10, 28.05, 27.14 ; ESI-HRMS calcd for $[C_{32}H_{33}FN_2O_6 + Na^+]$: 583.2215, found 583.2218.



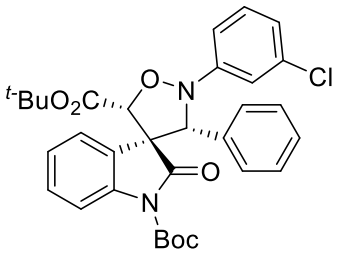
	Retention Time	% Area
1	4.713	48.91
2	5.637	48.29
3	7.390	1.42
4	8.257	1.38



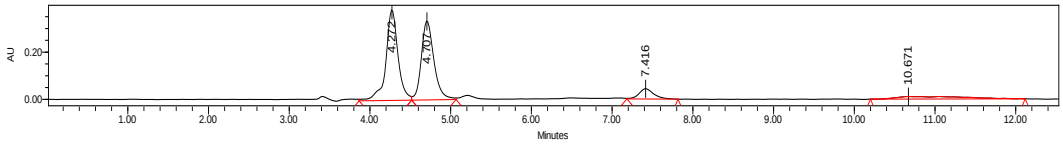
	Retention Time	% Area
1	4.620	3.24
2	5.582	11.60

3	7.278	83.89
4	8.138	1.27

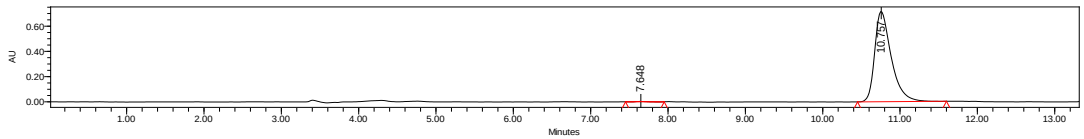
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2'-(3-chlorophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3z)



Result: 96% yield, 99% ee; $[\alpha]^{25}_{D}$ = −67.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 10.76 min, $t_{R(minor)}$ = 7.65 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.13 (m, 6H), 7.03 – 6.95 (m, 2H), 6.80 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 5.41 (s, 1H), 5.14 (s, 1H), 1.64 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72, 152.54, 139.64, 135.16, 134.85, 130.04, 129.26, 128.59, 128.28, 126.50, 126.23, 124.37, 123.66, 122.58, 115.08, 114.33, 112.98, 84.95, 83.43, 83.31, 79.03, 66.43, 28.05, 27.13; ESI-HRMS calcd for $[C_{32}H_{33}{}^{34.9694}ClN_2O_6+Na^+]$: 599.1919, found 599.1929; ESI-HRMS calcd for $[C_{32}H_{33}{}^{36.9665}ClN_2O_6+Na^+]$: 601.1890, found 601.1913.

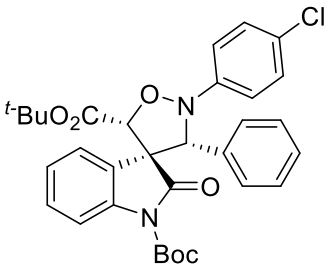


	Retention Time	% Area
1	4.272	43.41
2	4.707	42.34
3	7.416	6.53
4	10.671	7.73

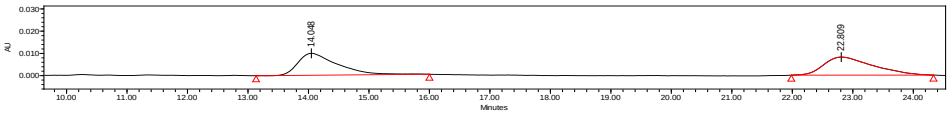


	Retention Time	% Area
1	7.648	0.25
2	10.757	99.75

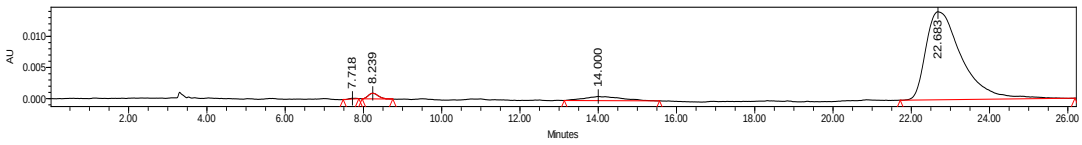
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2'-(4-chlorophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3aa)



Result: 95% yield, 91% ee; $[\alpha]^{21}_{D} = -66.3$ (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 21.83 min, $t_{R(minor)}$ = 14.46 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.16 – 7.09 (m, 5H), 7.03 (t, *J* = 7.2 Hz, 3H), 6.98 – 6.87 (m, 3H), 5.29 (s, 1H), 5.08 (s, 1H), 1.56 (s, 9H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.67, 163.92, 149.80, 148.75, 139.63, 134.98, 129.25, 128.90, 128.54, 128.29, 127.92, 126.53, 126.36, 124.37, 123.67, 116.65, 114.32, 84.93, 83.37, 83.05, 79.01, 66.40, 28.05, 27.13; ESI-HRMS calcd for $[C_{32}H_{33}{}^{34.9694}ClN_2O_6+Na^+]$: 599.1919, found 599.1921; ESI-HRMS calcd for $[C_{32}H_{33}{}^{36.9665}ClN_2O_6+Na^+]$: 601.1890, found 601.1910.

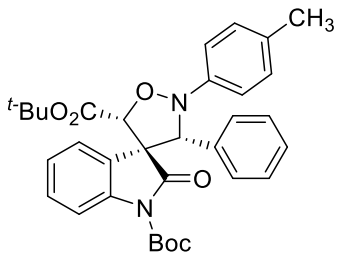


	Retention Time	% Area
1	14.048	49.32
2	22.809	50.68

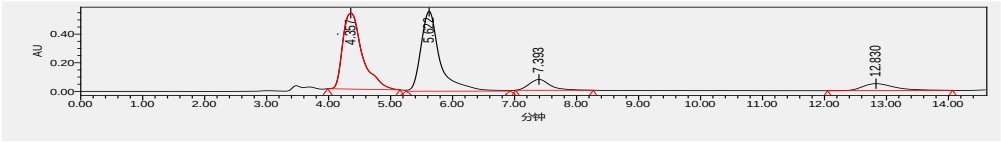


	Retention Time	% Area
1	14.000	4.72
2	22.683	95.28

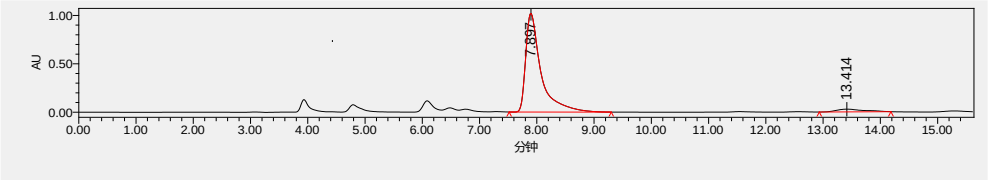
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2-oxo-3'-phenyl-2'-(p-tolyl)spiro[indoline-3,4'-isoxazolidine]-1,5'-di-carboxylate (3ab)



Result: 85% yield, 91% ee; $[\alpha]^{19}_{D}$ = −46.3 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min), $t_{R(major)}$ = 7.90 min, $t_{R(minor)}$ = 13.41 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.25 – 7.21 (m, 2H), 7.16 (td, *J* = 8.0, 1.2 Hz, 1H), 7.12 – 7.00 (m, 6H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 5.19 (s, 1H), 2.27 (s, 3H), 1.63 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.33, 148.70, 139.60, 135.28, 132.51, 129.43, 129.09, 128.36, 128.06, 126.65, 126.54, 124.31, 123.97, 115.92, 114.23, 84.78, 83.10, 82.86, 78.91, 66.43, 28.10, 28.06, 27.14, 20.64; ESI-HRMS calcd for [$C_{33}H_{36}N_2O_6$+Na^+]: 579.2466, found 579.2473.

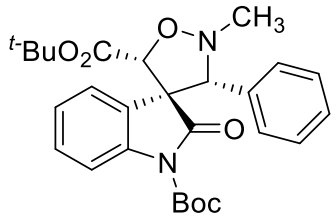


	Retention Time	% Area
1	4.357	43.22
2	5.622	43.77
3	7.393	6.56
4	12.830	6.45

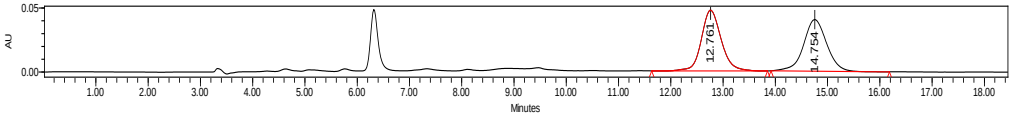


	Retention Time	% Area
1	7.897	95.23
2	13.414	4.77

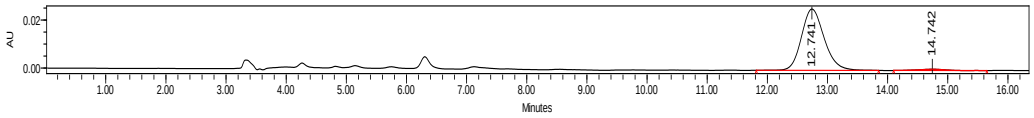
Di-tert-butyl-(3*R*,3'*R*,5'*R*)-2'-methyl-2-oxo-3'-phenyl-spiro[indoline-3,4'-isoxazolidine]-1,5'-dicarboxylate (3ac)



Result: 45% yield, 95% ee; $[\alpha]^{25}_{D}$ = −22.0 (*c* 0.10, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min), $t_{R(major)}$ = 12.74 min, $t_{R(minor)}$ = 14.74 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.17 (tt, *J* = 7.9, 1.5 Hz, 1H), 7.14 – 6.99 (m, 6H), 5.20 (d, *J* = 1.5 Hz, 1H), 4.52 (s, 1H), 2.89 (d, *J* = 1.5 Hz, 3H), 1.61(s, 9H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.10, 139.56, 128.97, 128.36, 128.10, 127.49, 126.95 , 124.15 , 114.20 , 84.65 , 82.39 , 81.52 , 80.48 , 65.75 , 44.43 , 28.10 , 28.04 , 27.13. ESI-HRMS calcd for [$C_{27}H_{32}N_2O_6$+Na^+]: 503.2153, found 503.2147.

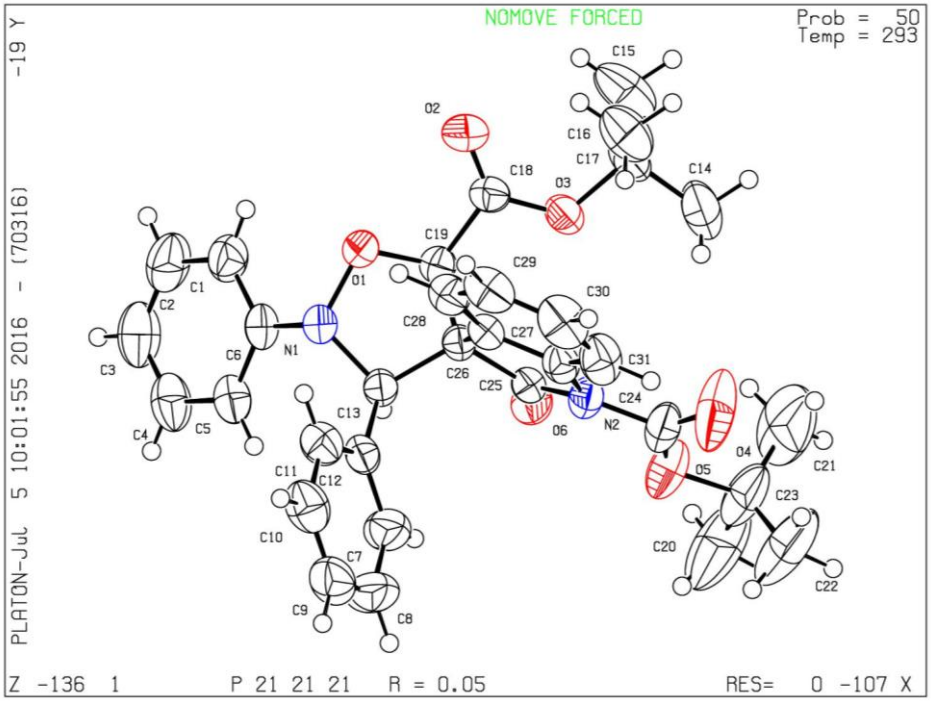


	Retention Time	% Area
1	12.761	50.14
2	14.754	49.86



	Retention Time	% Area
1	12.741	97.69
2	14.742	2.31

VI. Crystal data of compound 3a.



Datablock:

Empirical formula	$C_{32}H_{34}N_2O_6$
Formula weight	542.61
Temperature	293K
Crystal system	monoclinic
Unit cell dimensions	a = 10.21904(12) Å, b = 11.88874(13) Å, c = 24.5399(3) Å, α = 90 °β= 90° γ= 90°
Cell Volume	2981.39(6)
Z	4
F(000)	1152
CCDC deposition number	1509652

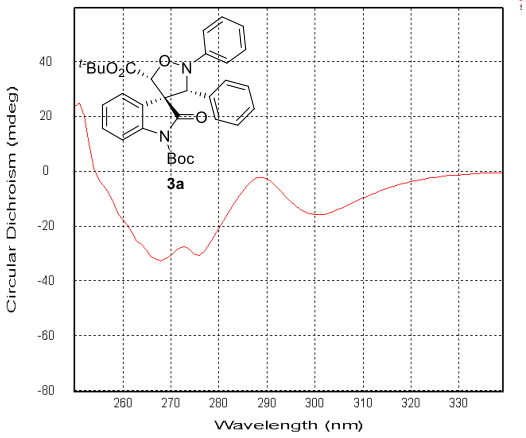
VII. References

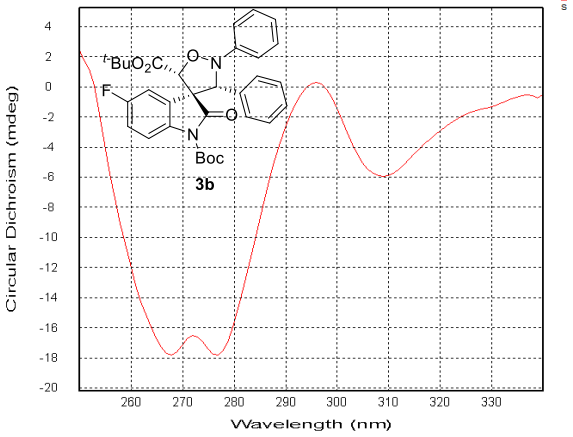
1. (a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett*, 2005, **2445**; (b) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem., Int. Ed*., 2008, **47**, 1308; (c) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.*, 2009, **11**, 1401.

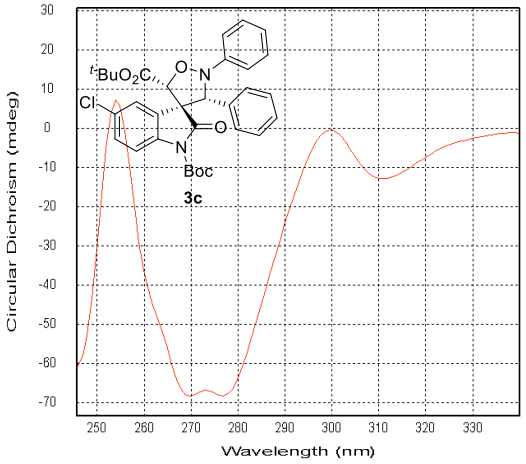
2. B. Tan, N. R. Candeias, C. F. Barbas III, *J. Am. Chem. Soc.*, 2011, **133**, 4672.

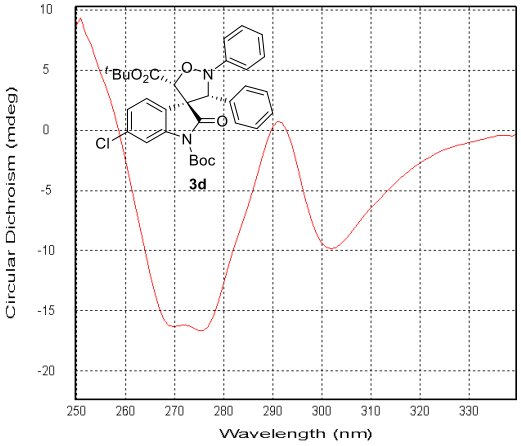
3. (a) M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 4572; (b) D. A. Evans, H. -J. Song, K. R. Fandrick, *Org. Lett.*, 2006, **8,** 3351; (c) P. R. West, G. C. Davis, *J. Org. Chem.*, 1989, **54**, 5176; (d) D. V, R.-S. Liu, *Chem. Eur. J.*, 2012, **18**, 13638.

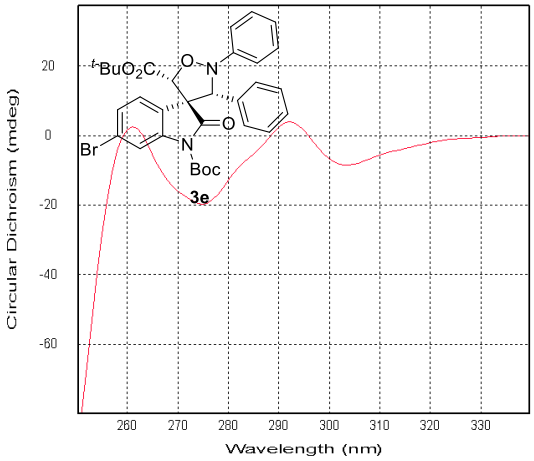
VIII. Copies of CD Spectra and their Absolute Configurations

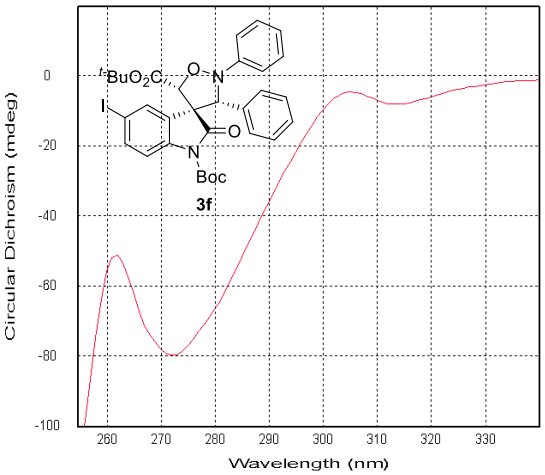


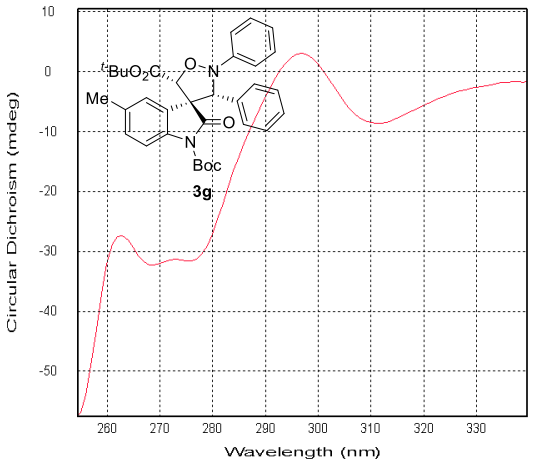


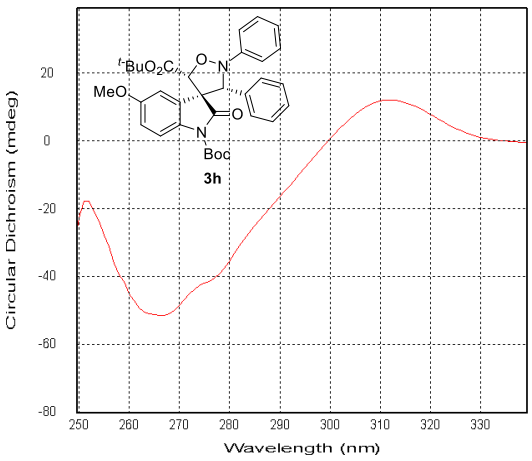


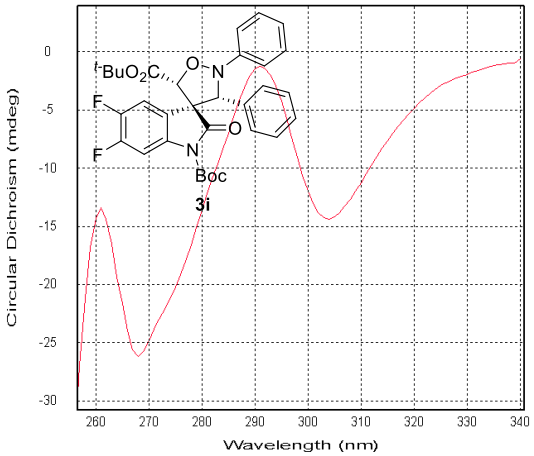


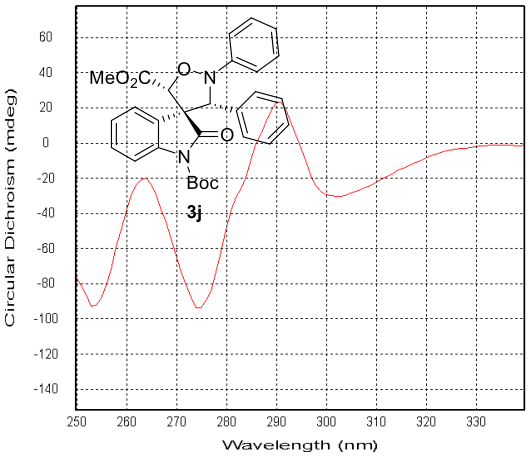


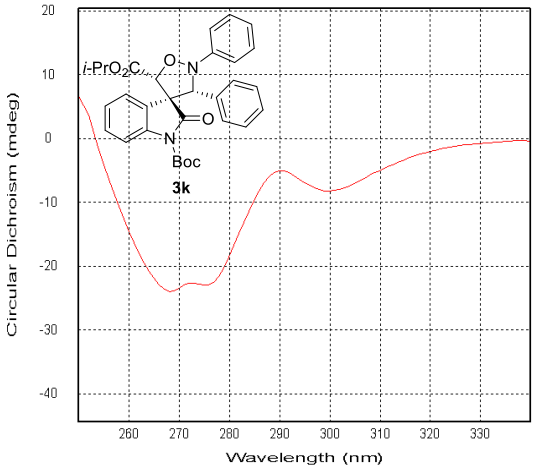


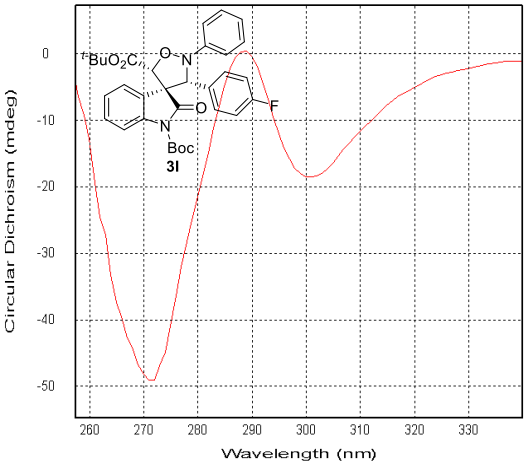

Circular Dichroism (mdeg)
Wavelength (nm)
Me
Boc
3g

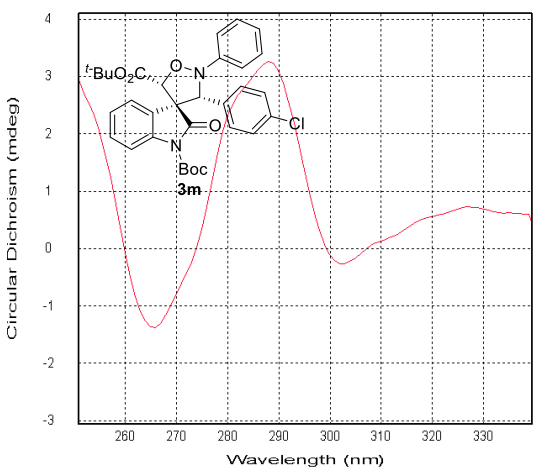

Circular Dichroism (mdeg)
Wavelength (nm)
MeO
Boc
3h

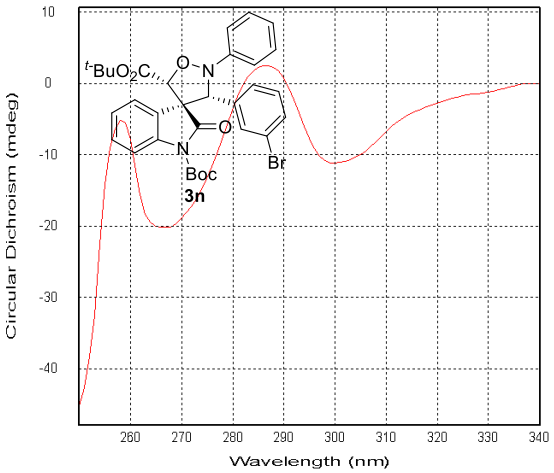

Circular Dichroism (mdeg)
Wavelength (nm)
F
F
Boc
3i

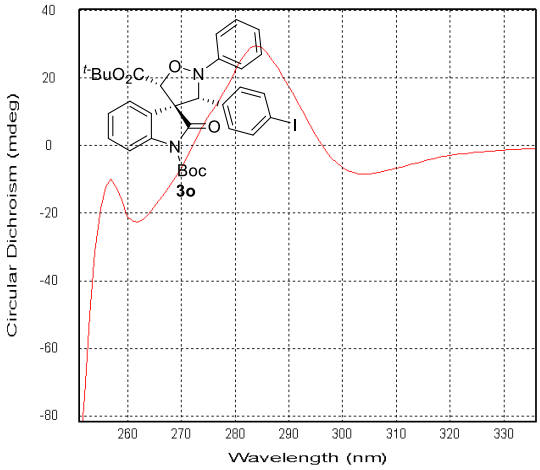

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3j

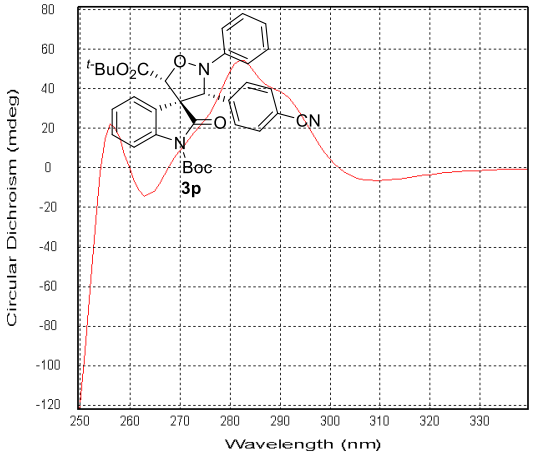

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3k

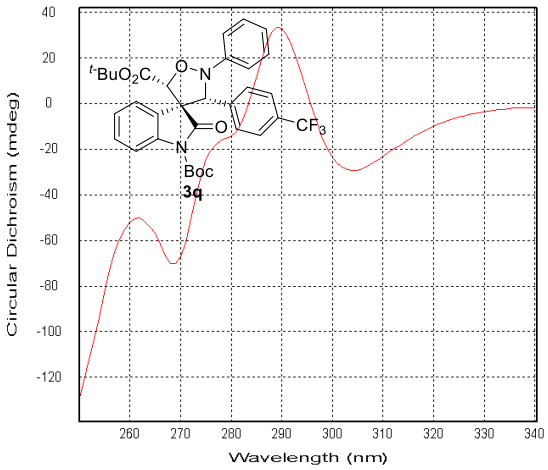

Circular Dichroism (mdeg)
Wavelength (nm)
F
Boc
3l

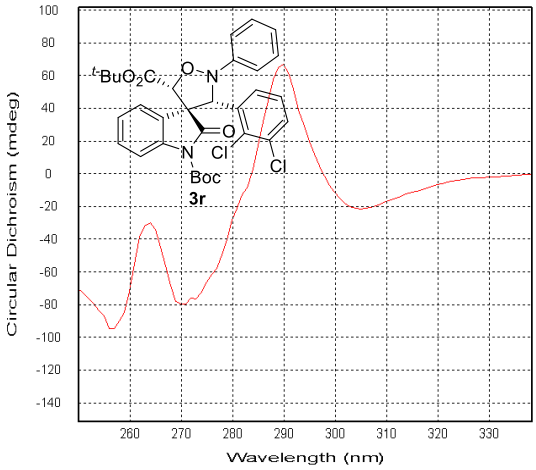

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
Cl
Boc
3m

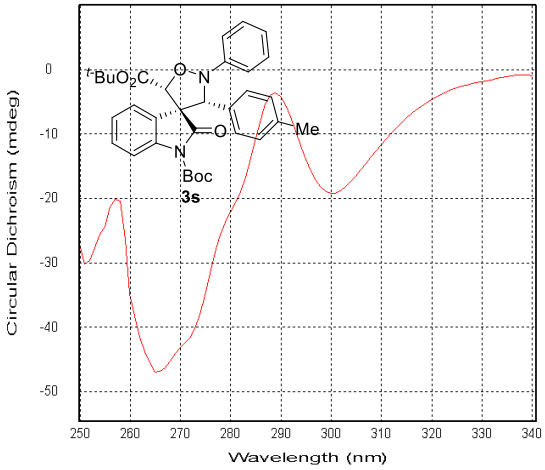

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
Br
Boc
3n

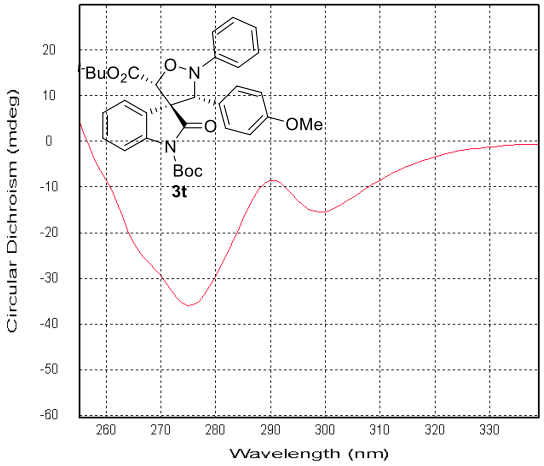

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
I
Boc
3o

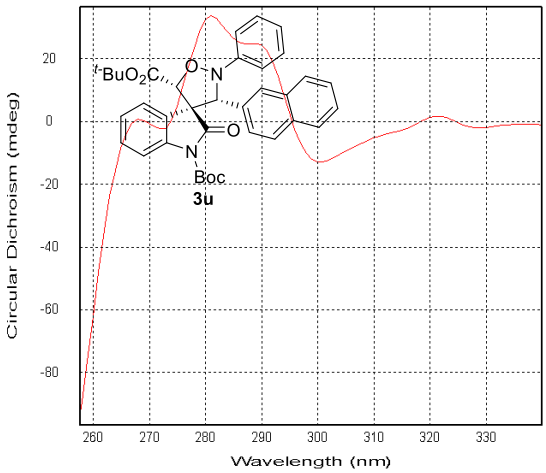

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
CN
Boc
3p

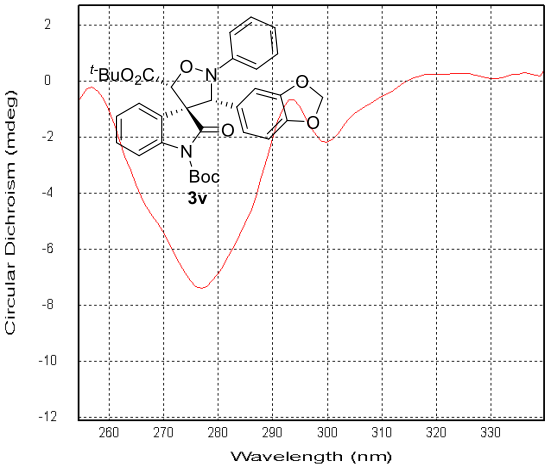

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
CF$_3$
Boc
3q

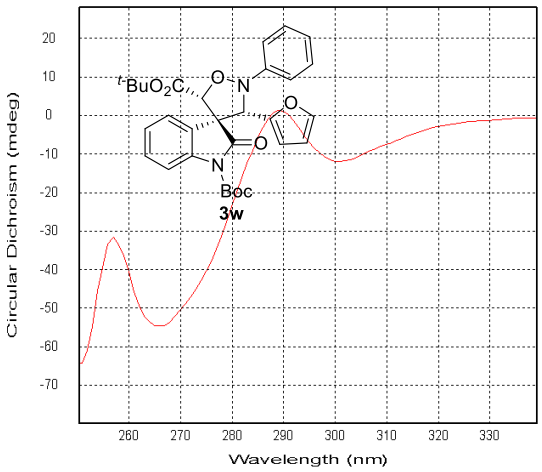

Circular Dichroism (mdeg)
Wavelength (nm)
^{t}BuO$_2$C
Cl
Cl
Boc
3r

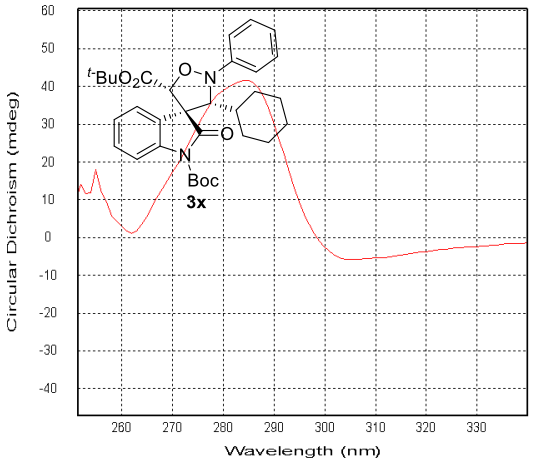

Circular Dichroism (mdeg)
Wavelength (nm)
Me
Boc
3s

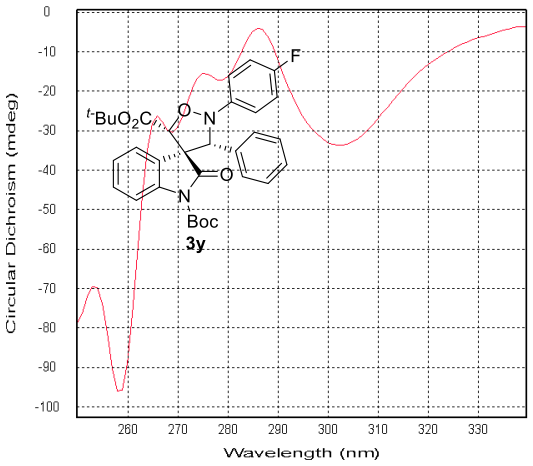

Circular Dichroism (mdeg)
Wavelength (nm)
OMe
Boc
3t

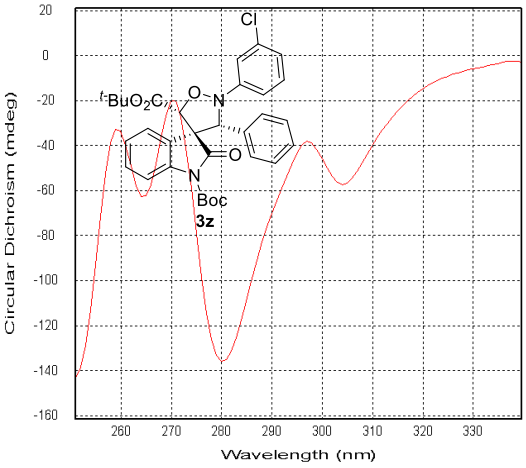

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3u

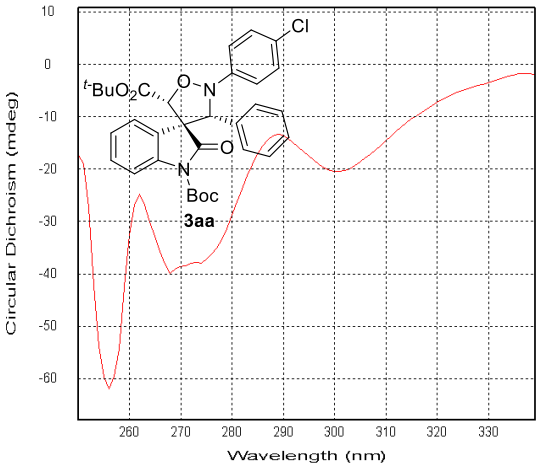

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3v

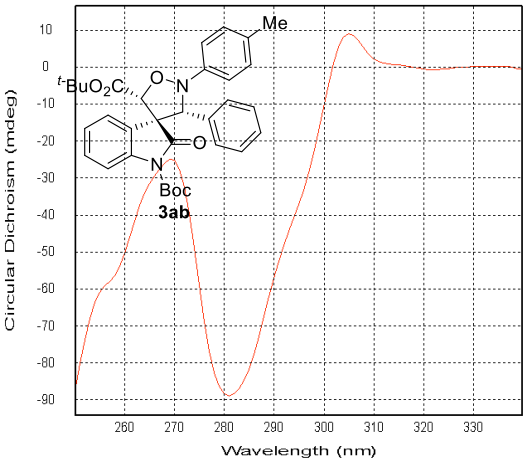

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3w

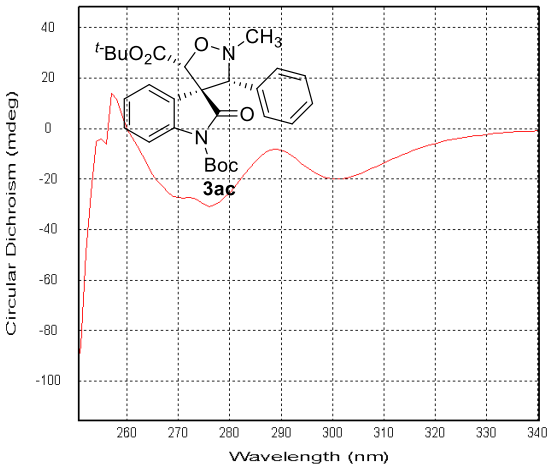

Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3x


Circular Dichroism (mdeg)
Wavelength (nm)
F
Boc
3y

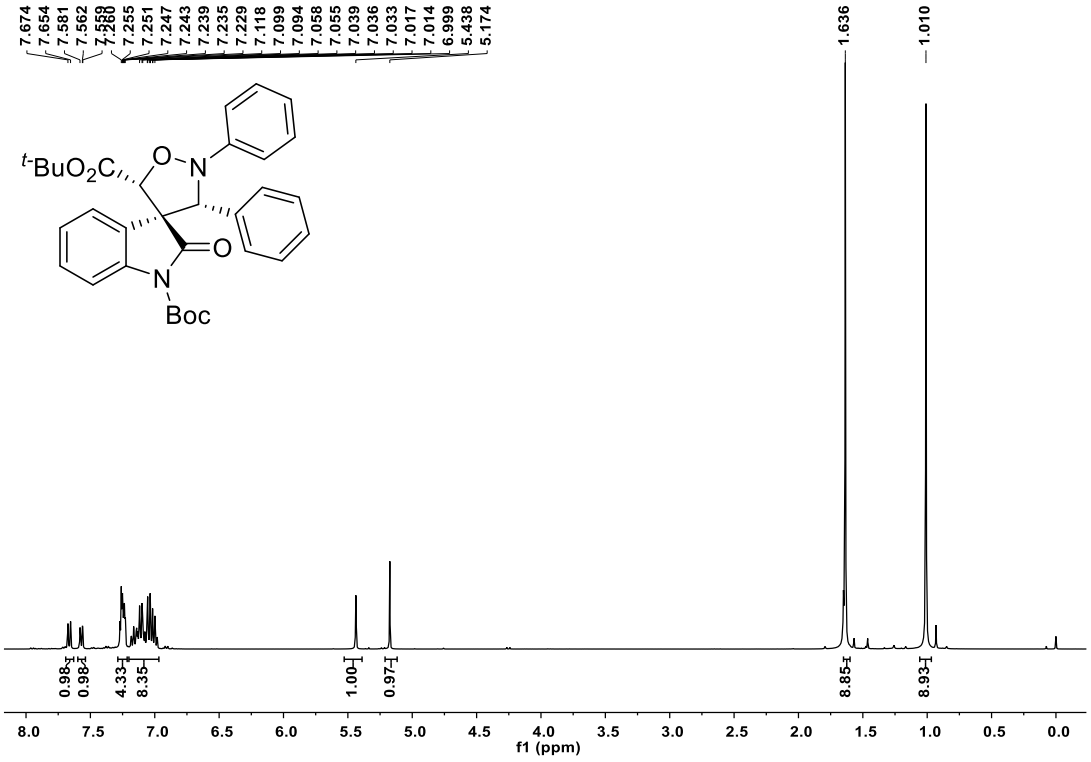

Circular Dichroism (mdeg)
Wavelength (nm)
Cl
Boc
3z

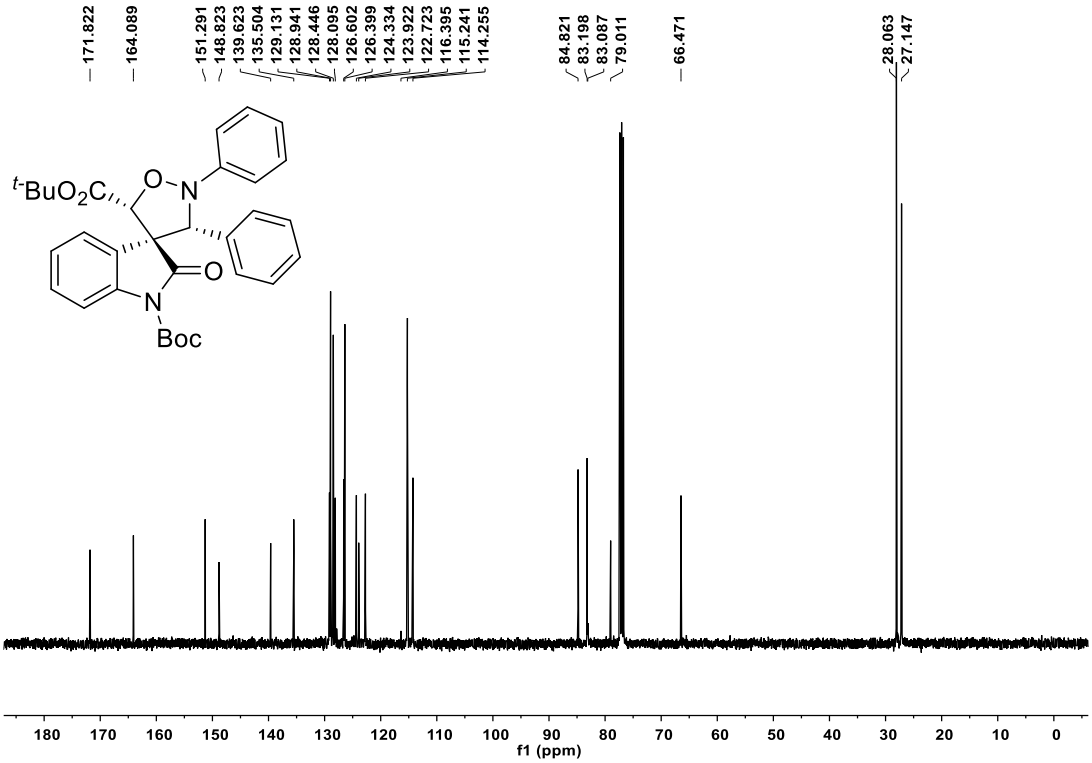

Circular Dichroism (mdeg)
Wavelength (nm)
Cl
Boc
3aa

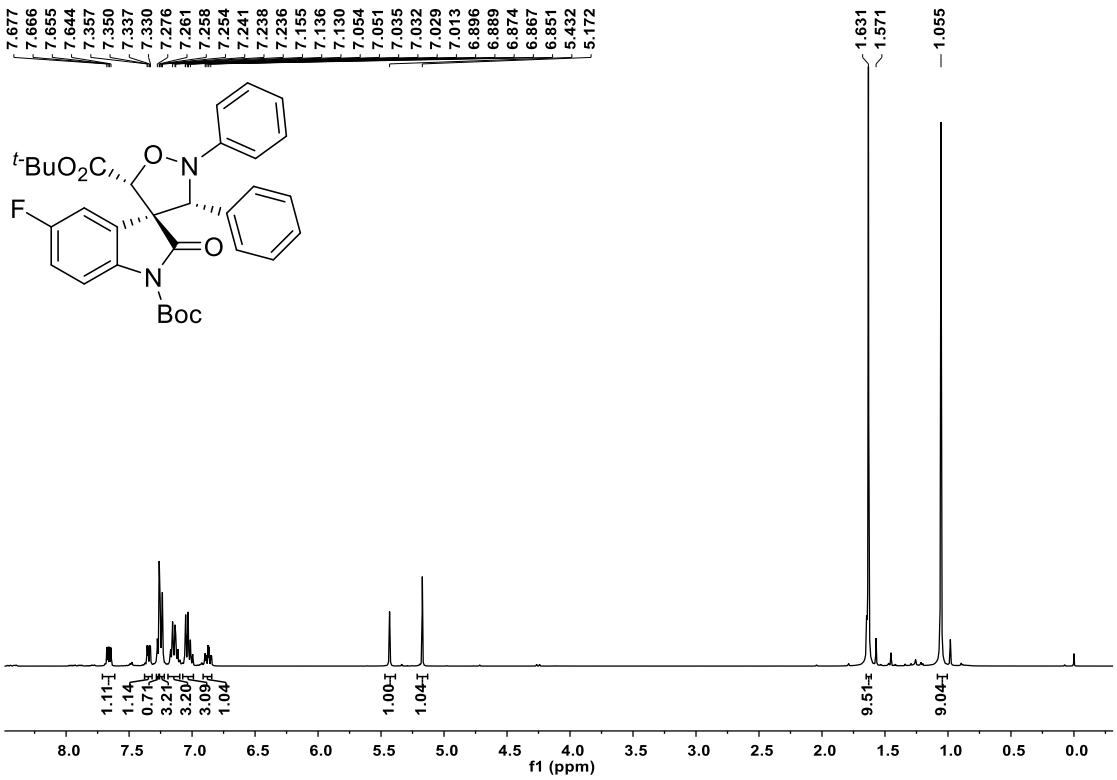

Circular Dichroism (mdeg)
Wavelength (nm)
Me
Boc
3ab


Circular Dichroism (mdeg)
Wavelength (nm)
Boc
3ac

IX. Copies of NMR spectra for the reaction products.



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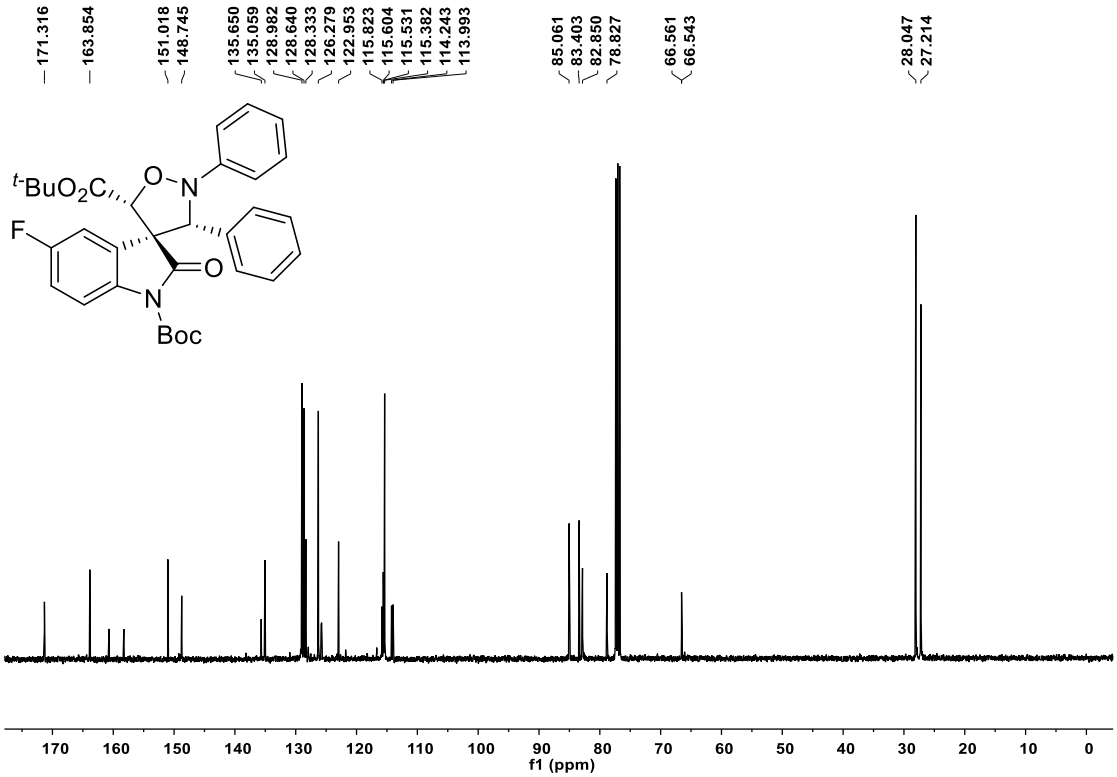
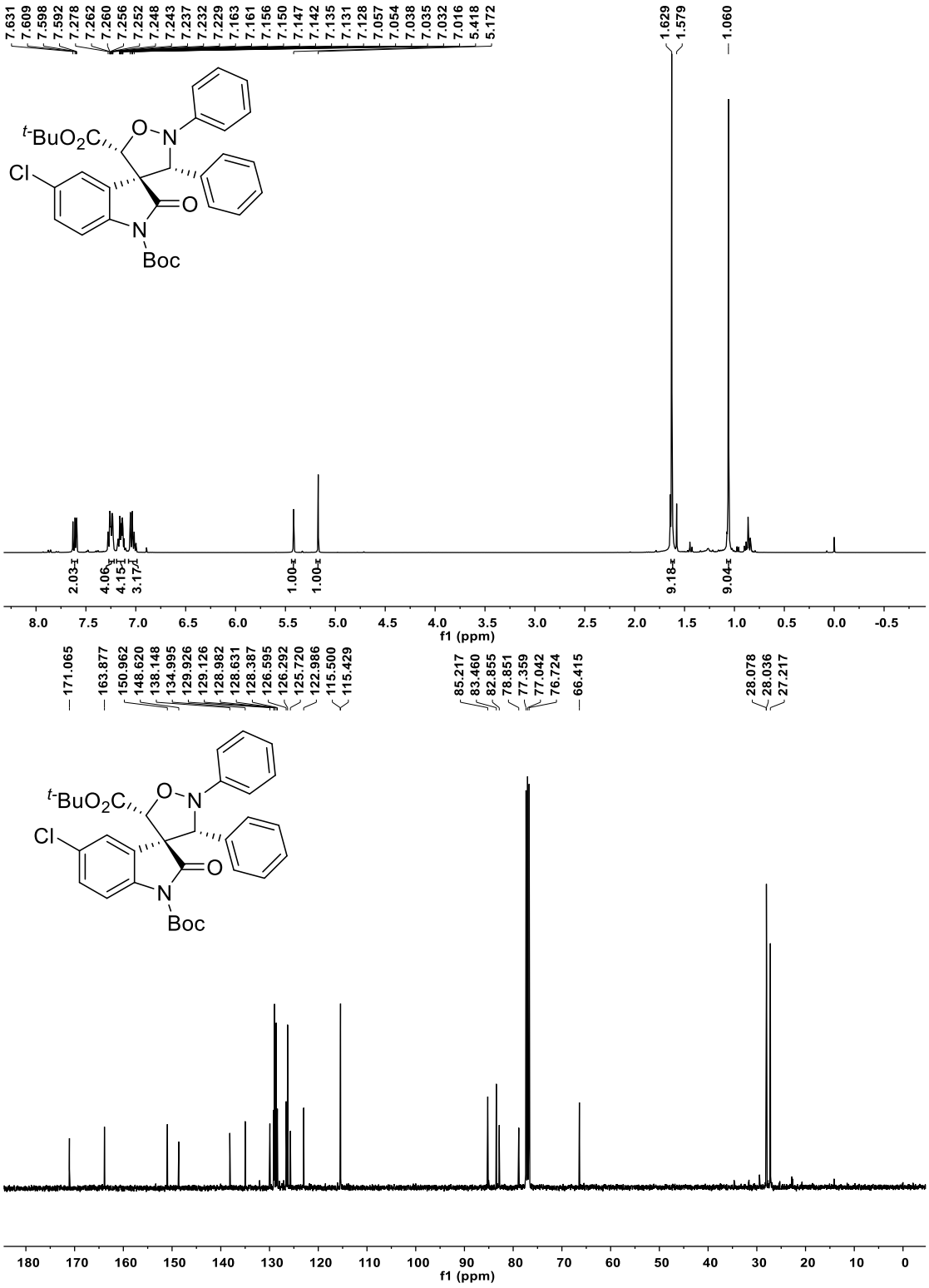
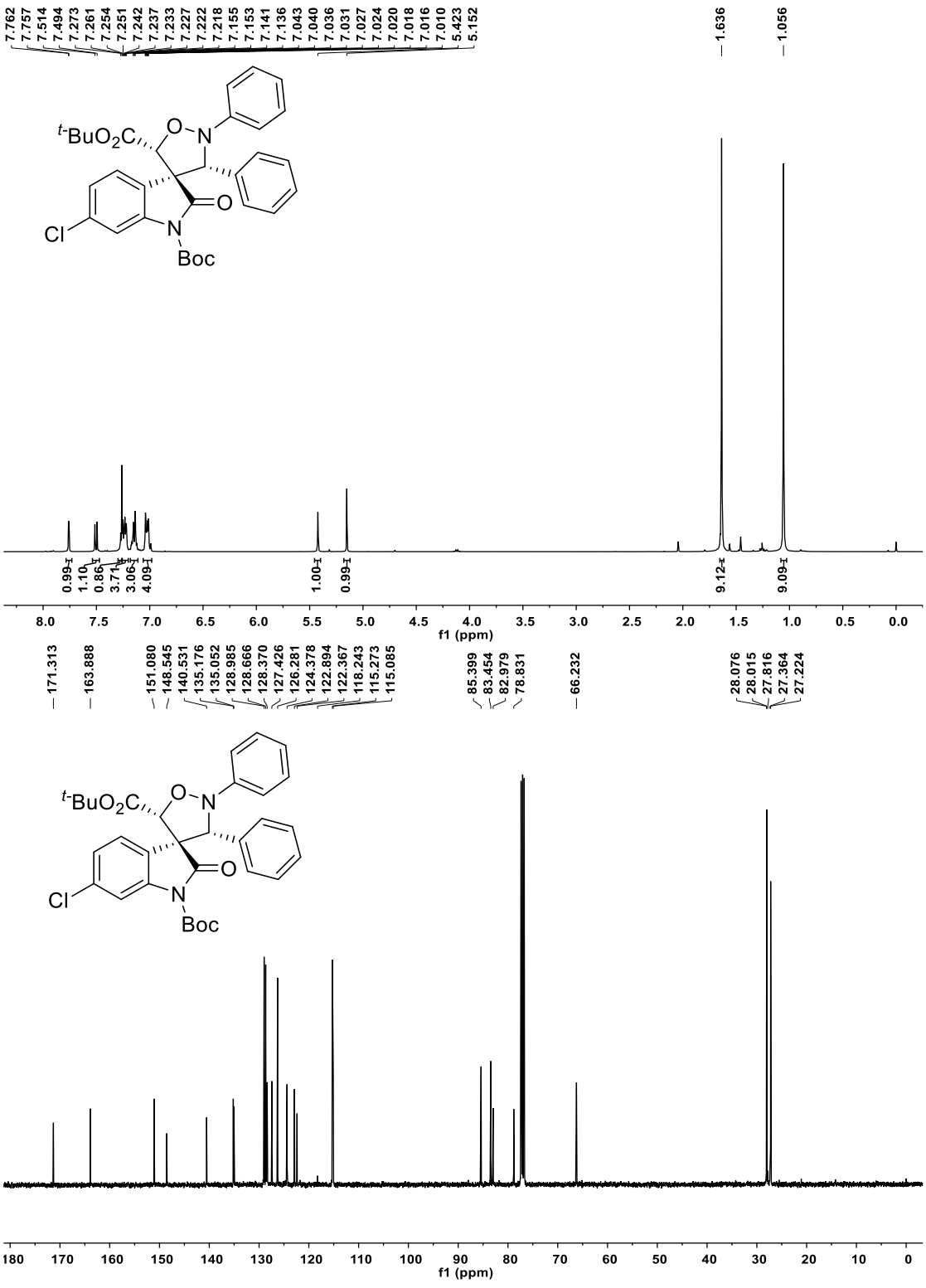
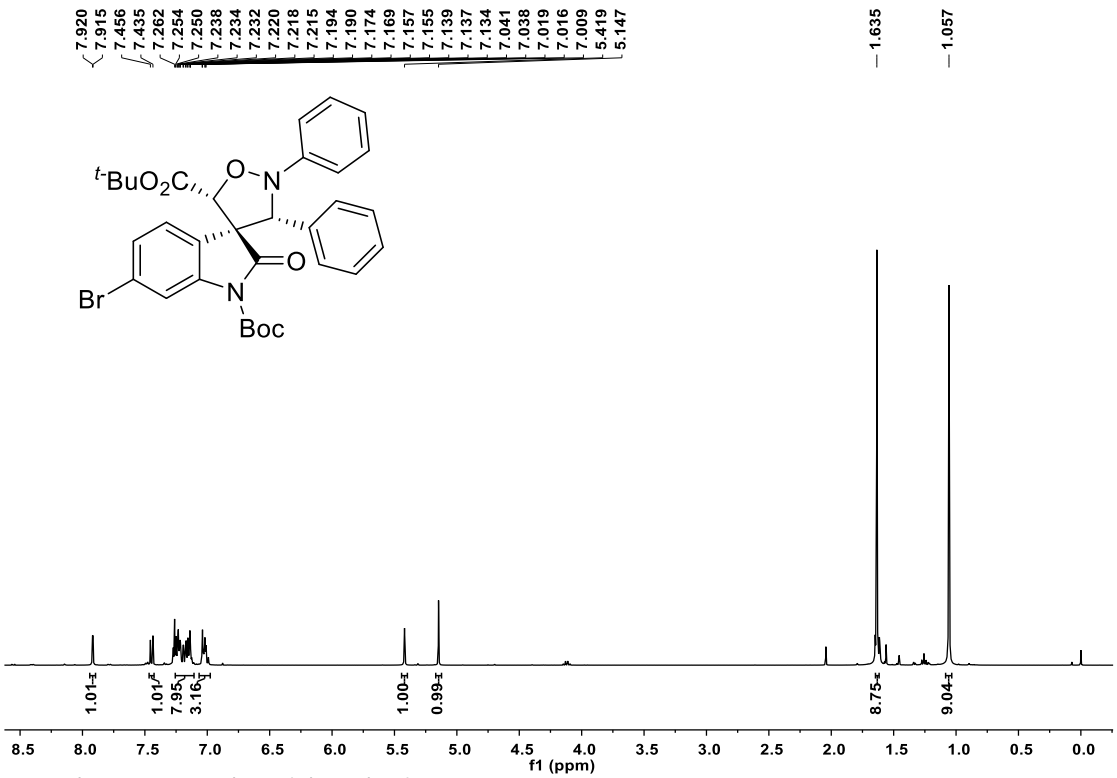
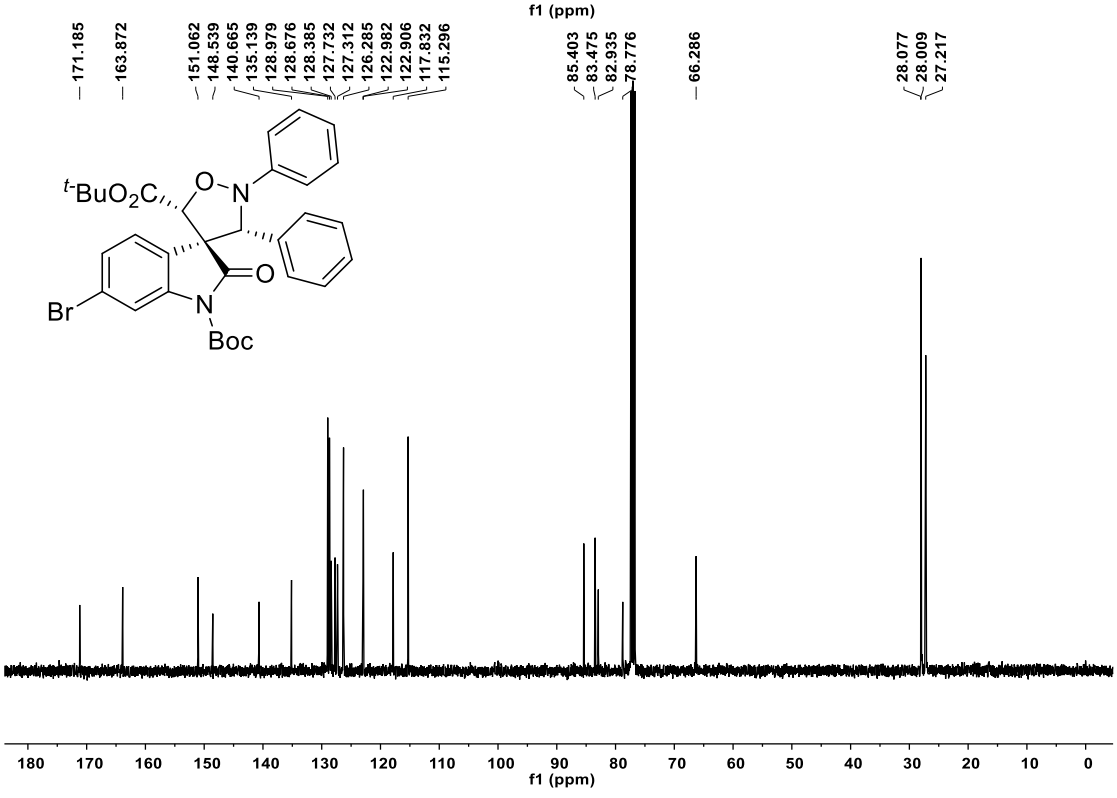
7.666
7.655
7.644
7.357
7.350
7.337
7.330
7.276
7.261
7.258
7.254
7.241
7.238
7.236
7.155
7.136
7.130
7.054
7.051
7.035
7.032
7.029
7.013
6.896
6.889
6.874
6.867
6.851
5.432
5.172
1.631
1.571
1.055
tBuO2C
O
N
F
O
N
Boc
1.11
1.14
0.71
3.21
3.20
3.09
1.04
1.00
1.04
9.51
9.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.316
163.854
151.018
148.745
135.650
135.059
128.982
128.640
128.333
126.279
122.953
115.823
115.604
115.531
115.382
114.243
113.993
85.061
83.403
82.850
78.827
66.561
66.543
28.047
27.214
tBuO2C
O
N
F
O
N
Boc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.631
7.609
7.598
7.592
7.278
7.262
7.260
7.256
7.252
7.248
7.243
7.237
7.232
7.229
7.163
7.161
7.156
7.150
7.147
7.142
7.135
7.131
7.128
7.057
7.054
7.038
7.035
7.032
7.016
5.418
5.172
1.629
1.579
1.060
tBuO2C
Cl
O
N
O
N
Boc
2.03
4.06
4.15
3.17
1.00
1.00
9.18
9.04
f1 (ppm)
171.065
163.877
150.962
148.620
138.148
134.995
129.926
129.126
128.982
128.631
128.387
126.595
126.292
125.720
122.986
115.500
115.429
85.217
83.460
82.855
78.851
77.359
77.042
76.724
66.415
28.078
28.036
27.217
f1 (ppm)


7.762
7.757
7.514
7.494
7.273
7.261
7.254
7.251
7.242
7.237
7.233
7.227
7.222
7.218
7.155
7.153
7.141
7.136
7.043
7.040
7.036
7.031
7.027
7.024
7.020
7.018
7.016
7.010
5.423
5.152
1.636
1.056
tBuO2C
O
N
O
Cl
N
Boc
0.99
1.10
0.86
3.71
3.06
4.09
1.00
0.99
9.12
9.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
171.313
163.888
151.080
148.545
140.531
135.176
135.052
128.985
128.666
128.370
127.426
126.281
124.378
122.894
122.367
118.243
115.273
115.085
85.399
83.454
82.979
78.831
66.232
28.076
28.015
27.816
27.364
27.224
tBuO2C
O
N
O
Cl
N
Boc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.920
7.915
7.456
7.435
7.262
7.254
7.250
7.238
7.234
7.232
7.220
7.218
7.215
7.194
7.190
7.174
7.169
7.157
7.155
7.139
7.137
7.134
7.041
7.038
7.019
7.016
7.009
5.419
5.147
1.635
1.057
tBuO2C
O
N
O
N
Br
Boc
1.01
1.01
7.95
3.16
1.00
0.99
8.75
9.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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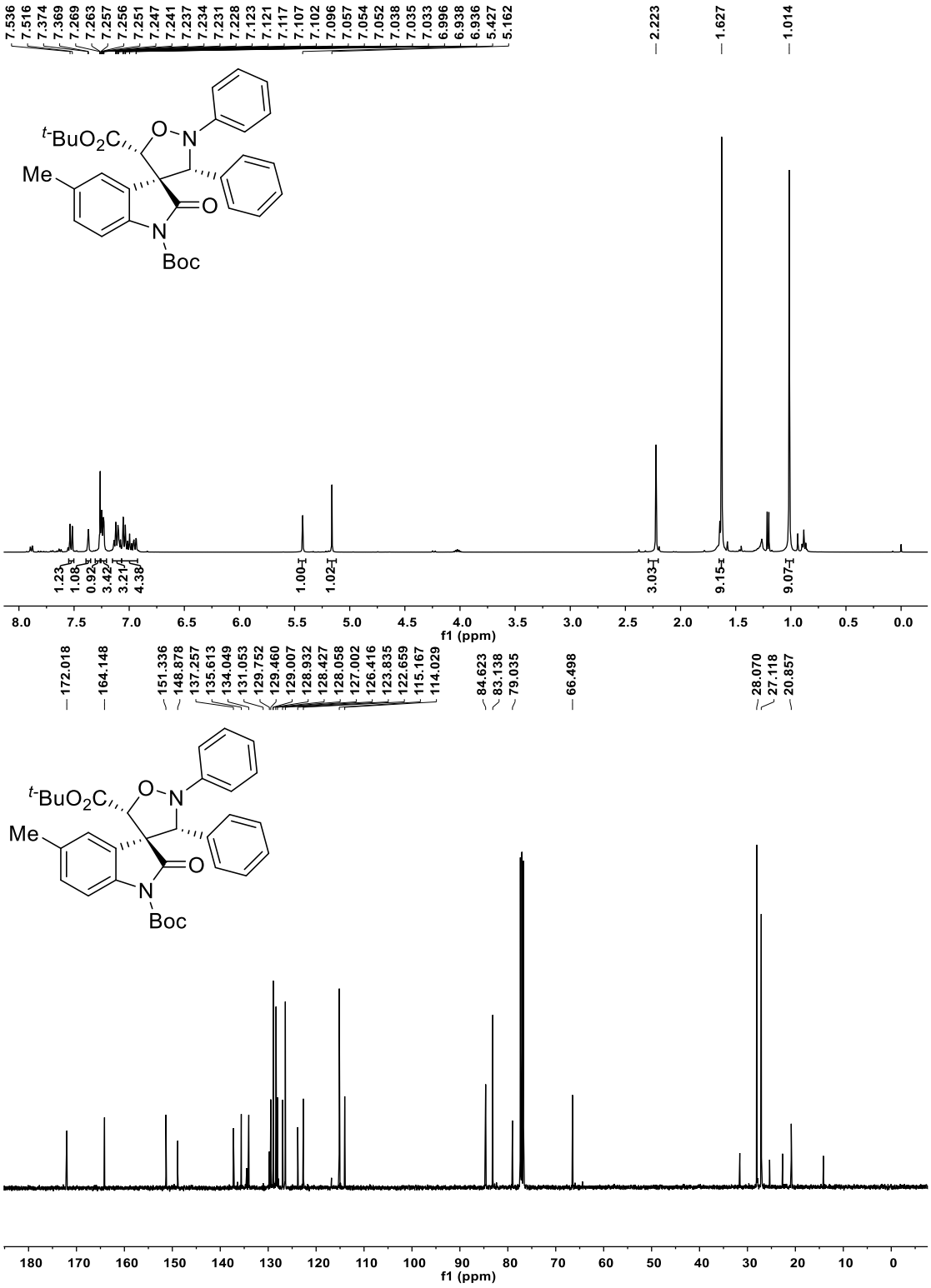
163.872
151.062
148.539
140.665
135.139
128.979
128.676
128.385
127.732
127.312
126.285
122.982
122.906
117.832
115.296
85.403
83.475
82.935
78.776
66.286
28.077
28.009
27.217
tBuO2C
O
N
O
N
Br
Boc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.883
7.878
7.482
7.477
7.444
7.262
7.258
7.239
7.223
7.220
7.168
7.054
7.034
7.032
5.402
5.161
1.637
1.623
1.060
t-BuO2C
O
N
I
O
N
Boc
0.98
1.16
0.99
0.74
2.80
3.04
3.02
1.00
1.00
9.04
8.93
f1 (ppm)
170.859
163.895
150.963
148.573
139.363
138.031
135.054
128.985
128.582
128.394
126.313
126.259
122.957
116.250
115.369
87.462
85.238
83.482
82.935
78.951
77.233
66.244
28.110
28.031
27.218
f1 (ppm)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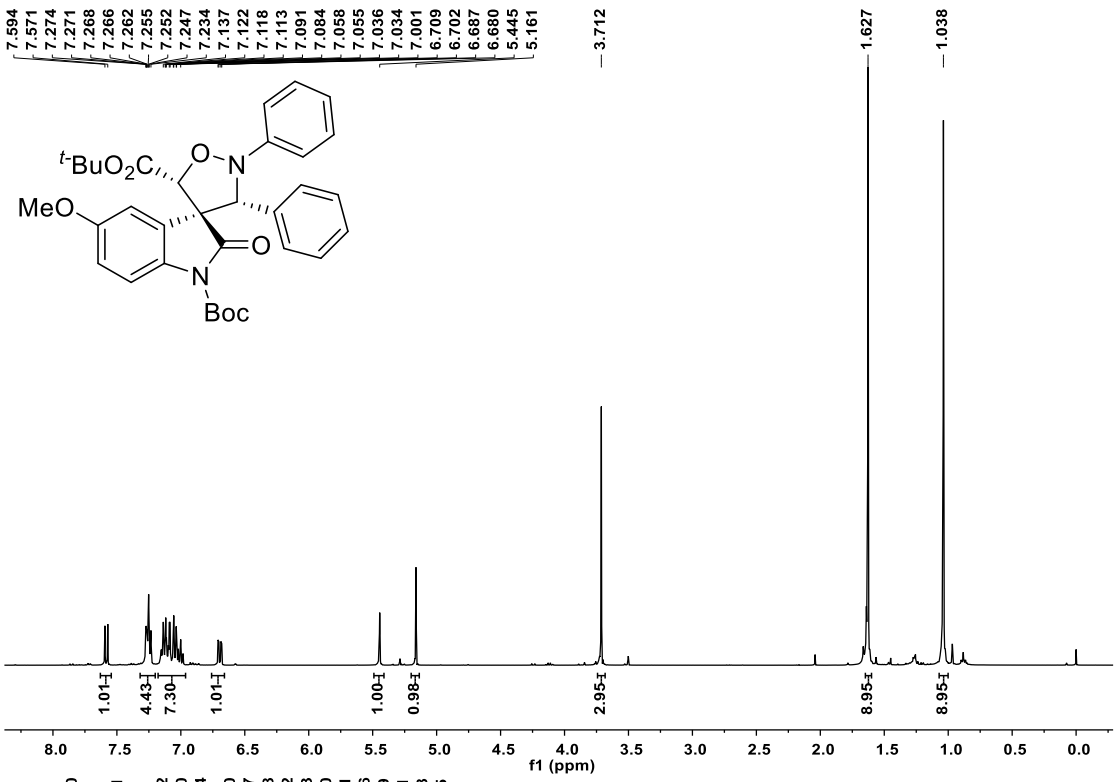
7.516
7.374
7.369
7.269
7.263
7.257
7.256
7.251
7.247
7.241
7.237
7.234
7.231
7.228
7.123
7.121
7.117
7.107
7.102
7.096
7.057
7.054
7.052
7.038
7.035
7.033
6.996
6.938
6.936
5.427
5.162
2.223
1.627
1.014
tBuO2C
O
N
Me
O
N
Boc
1.23
1.08
0.92
3.42
3.21
4.38
1.00
1.02
3.03
9.15
9.07
f1 (ppm)
172.018
164.148
151.336
148.878
137.257
135.613
134.049
131.053
129.752
129.460
129.007
128.932
128.427
128.058
127.002
126.416
123.835
122.659
115.167
114.029
84.623
83.138
79.035
66.498
28.070
27.118
20.857
f1 (ppm)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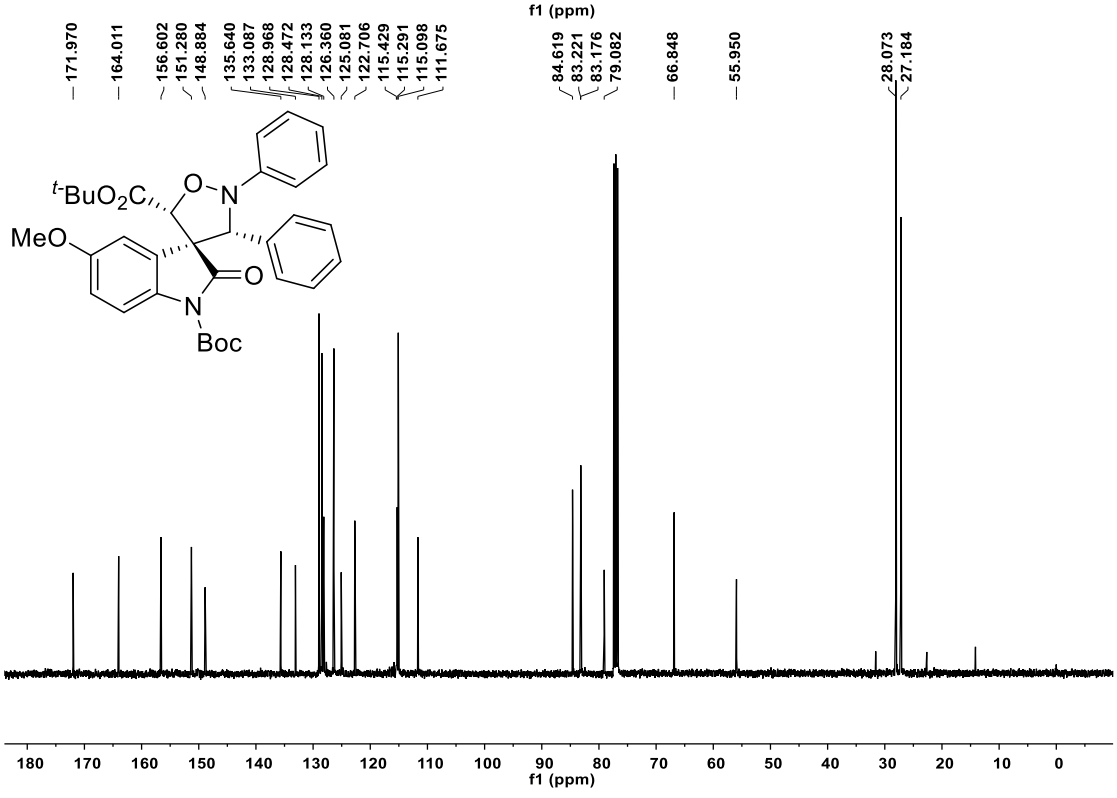
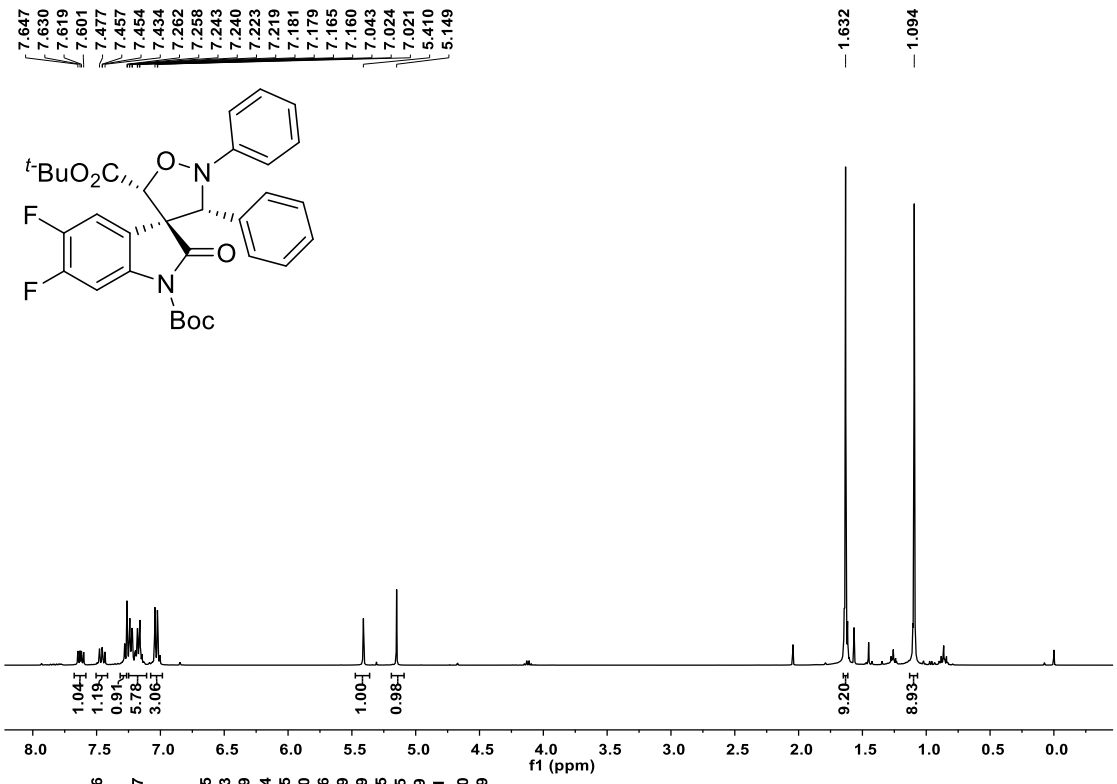
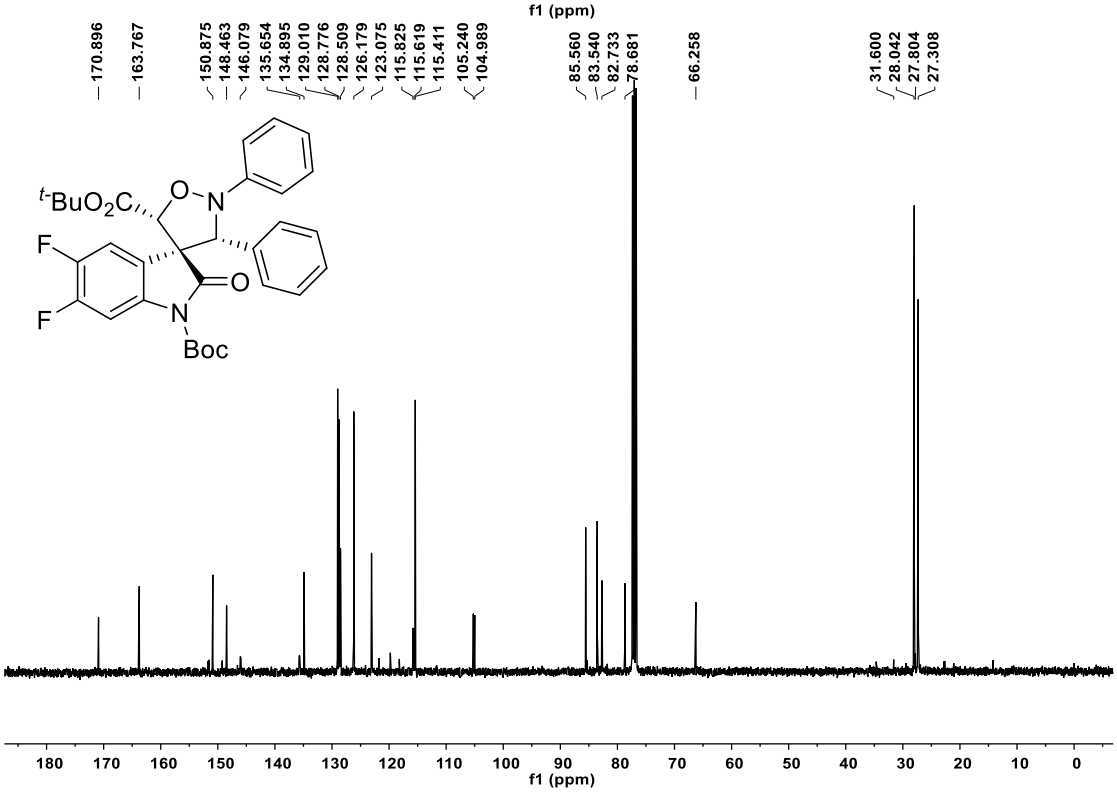
7.274
7.271
7.268
7.266
7.262
7.255
7.252
7.247
7.234
7.137
7.122
7.118
7.113
7.091
7.084
7.058
7.055
7.036
7.034
7.001
6.709
6.702
6.687
6.680
5.445
5.161
3.712
1.627
1.038
tBuO2C
O
N
MeO
O
N
Boc
1.01
4.43
7.30
1.01
1.00
0.98
2.95
8.95
8.95
f1 (ppm)


171.970
164.011
156.602
151.280
148.884
135.640
133.087
128.968
128.472
128.133
126.360
125.081
122.706
115.429
115.291
115.098
111.675
84.619
83.221
83.176
79.082
66.848
55.950
28.073
27.184
tBuO2C
O
N
MeO
O
N
Boc
f1 (ppm)


7.647
7.630
7.619
7.601
7.477
7.457
7.454
7.434
7.262
7.258
7.243
7.240
7.223
7.219
7.181
7.179
7.165
7.160
7.043
7.024
7.021
5.410
5.149
1.632
1.094
t-BuO2C
O
N
F
F
O
N
Boc
1.04
1.19
0.91
5.78
3.06
1.00
0.98
9.20
8.93
f1 (ppm)


170.896
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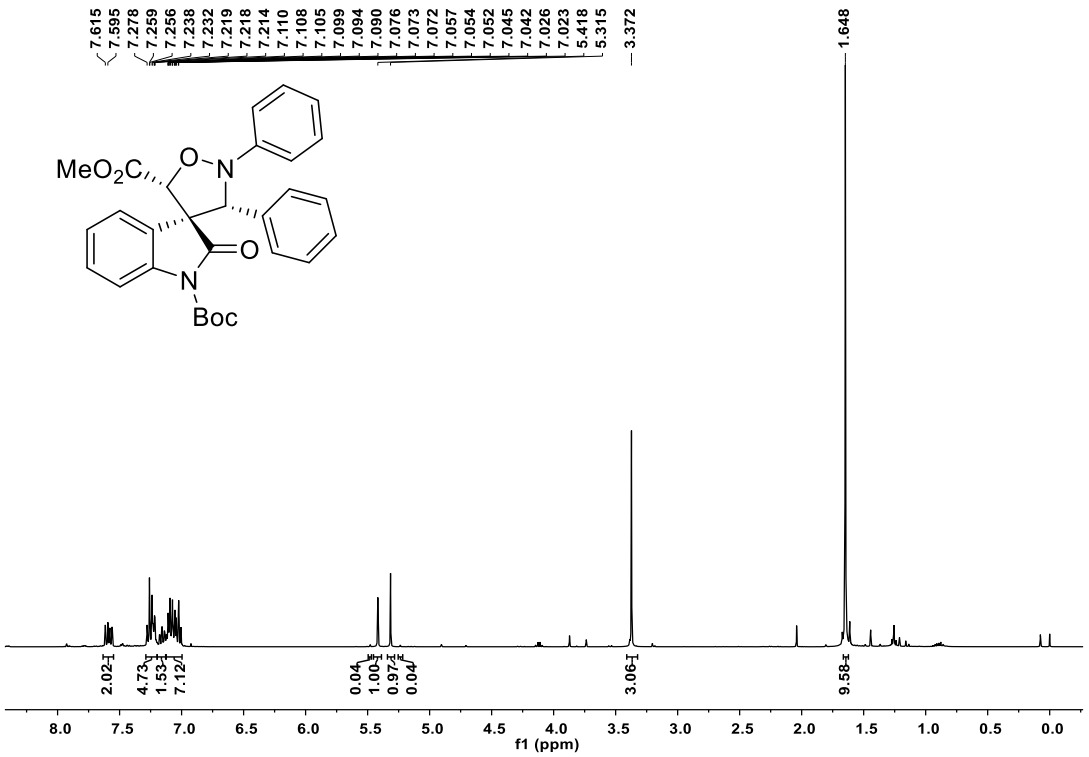
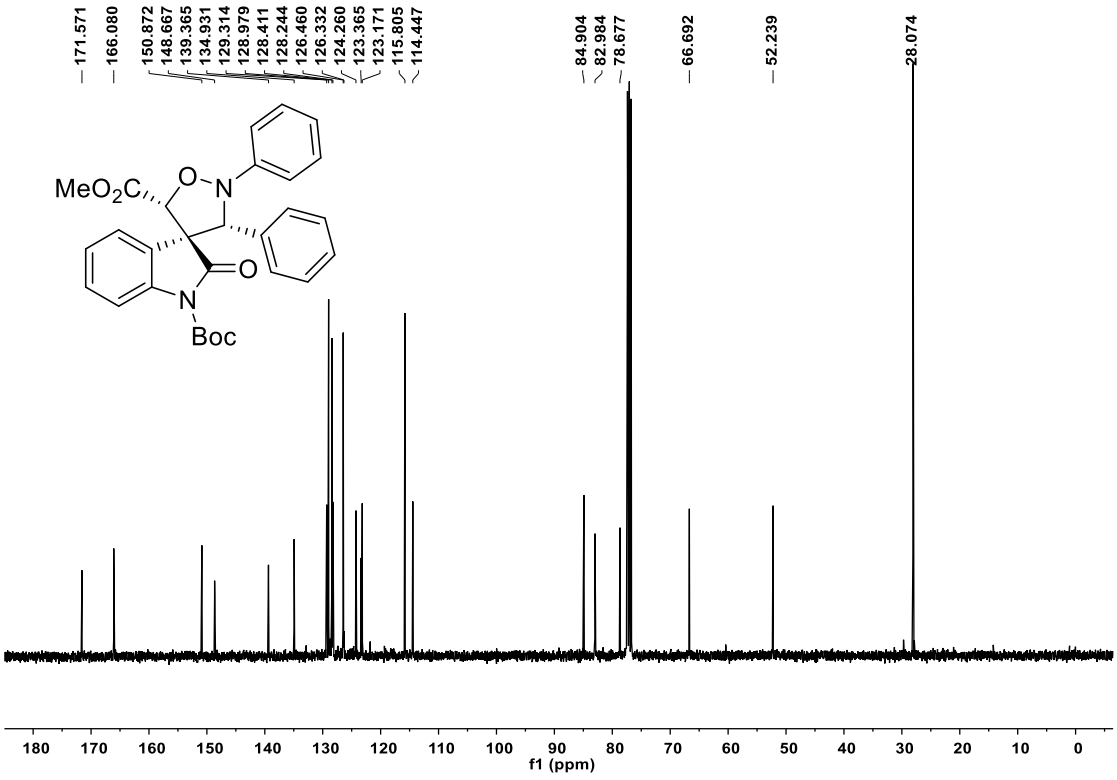
150.875
148.463
146.079
135.654
134.895
129.010
128.776
128.509
126.179
123.075
115.825
115.619
115.411
105.240
104.989
85.560
83.540
82.733
78.681
66.258
31.600
28.042
27.804
27.308
t-BuO2C
O
N
F
F
O
N
Boc
f1 (ppm)


7.615
7.595
7.278
7.259
7.256
7.238
7.232
7.219
7.218
7.214
7.110
7.108
7.105
7.099
7.094
7.090
7.076
7.073
7.072
7.057
7.054
7.052
7.045
7.042
7.026
7.023
5.418
5.315
3.372
1.648
MeO2C
O
N
O
N
Boc
2.02
4.73
1.53
7.12
0.04
1.00
0.97
0.04
3.06
9.58
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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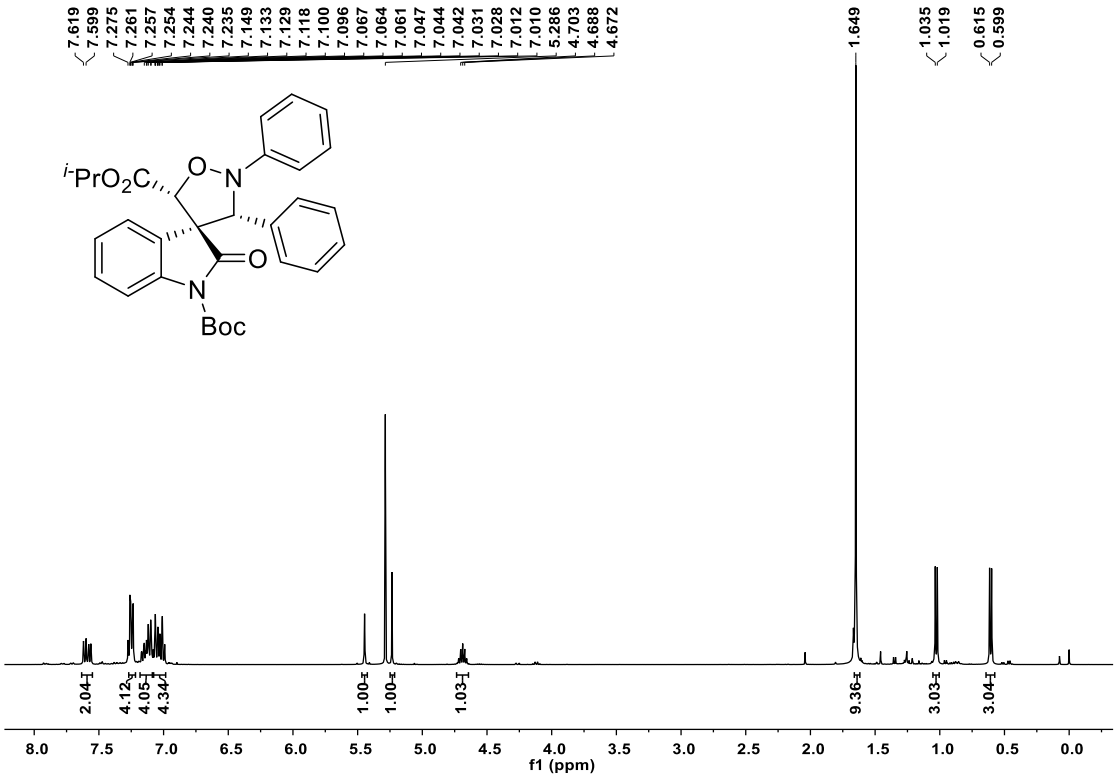
150.872
148.667
139.365
134.931
129.314
128.979
128.411
128.244
126.460
126.332
124.260
123.365
123.171
115.805
114.447
84.904
82.984
78.677
66.692
52.239
28.074
MeO2C
O
N
O
N
Boc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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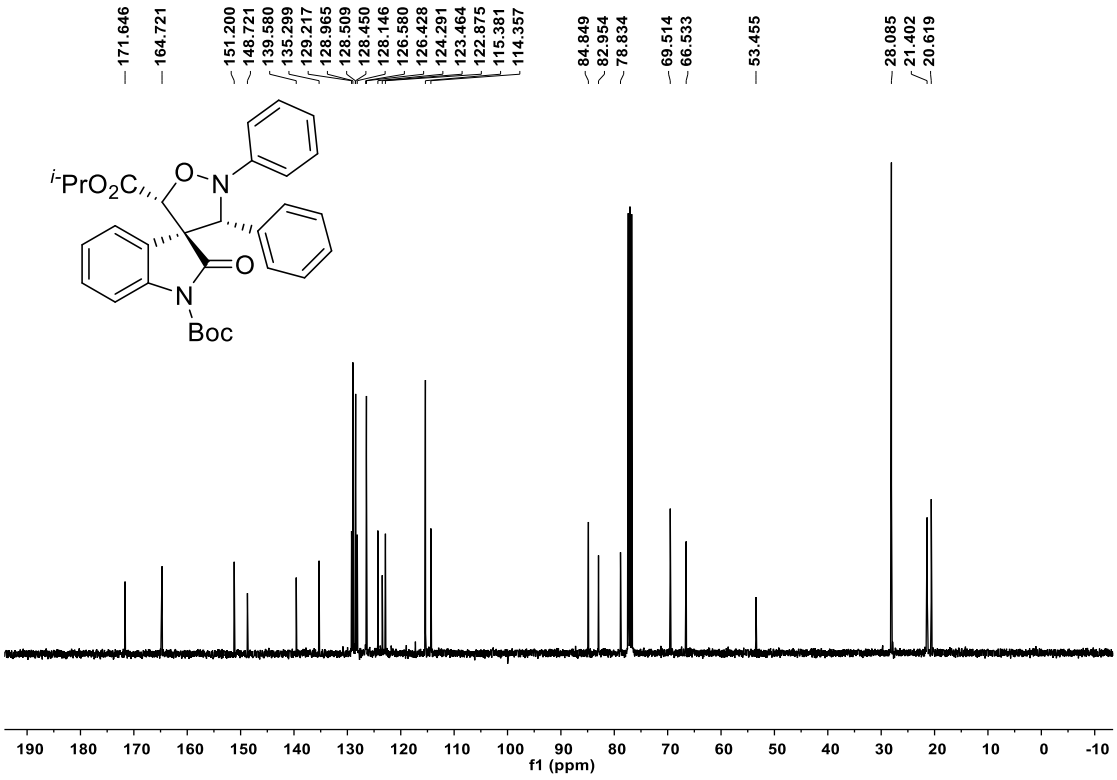
7.275
7.261
7.257
7.254
7.244
7.240
7.235
7.149
7.133
7.129
7.118
7.100
7.096
7.067
7.064
7.061
7.047
7.044
7.042
7.031
7.028
7.012
7.010
5.286
4.703
4.688
4.672
1.649
1.035
1.019
0.615
0.599
i-PrO2C
O
N
O
N
Boc
2.04
4.12
4.05
4.34
1.00
1.00
1.03
9.36
3.03
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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164.721
151.200
148.721
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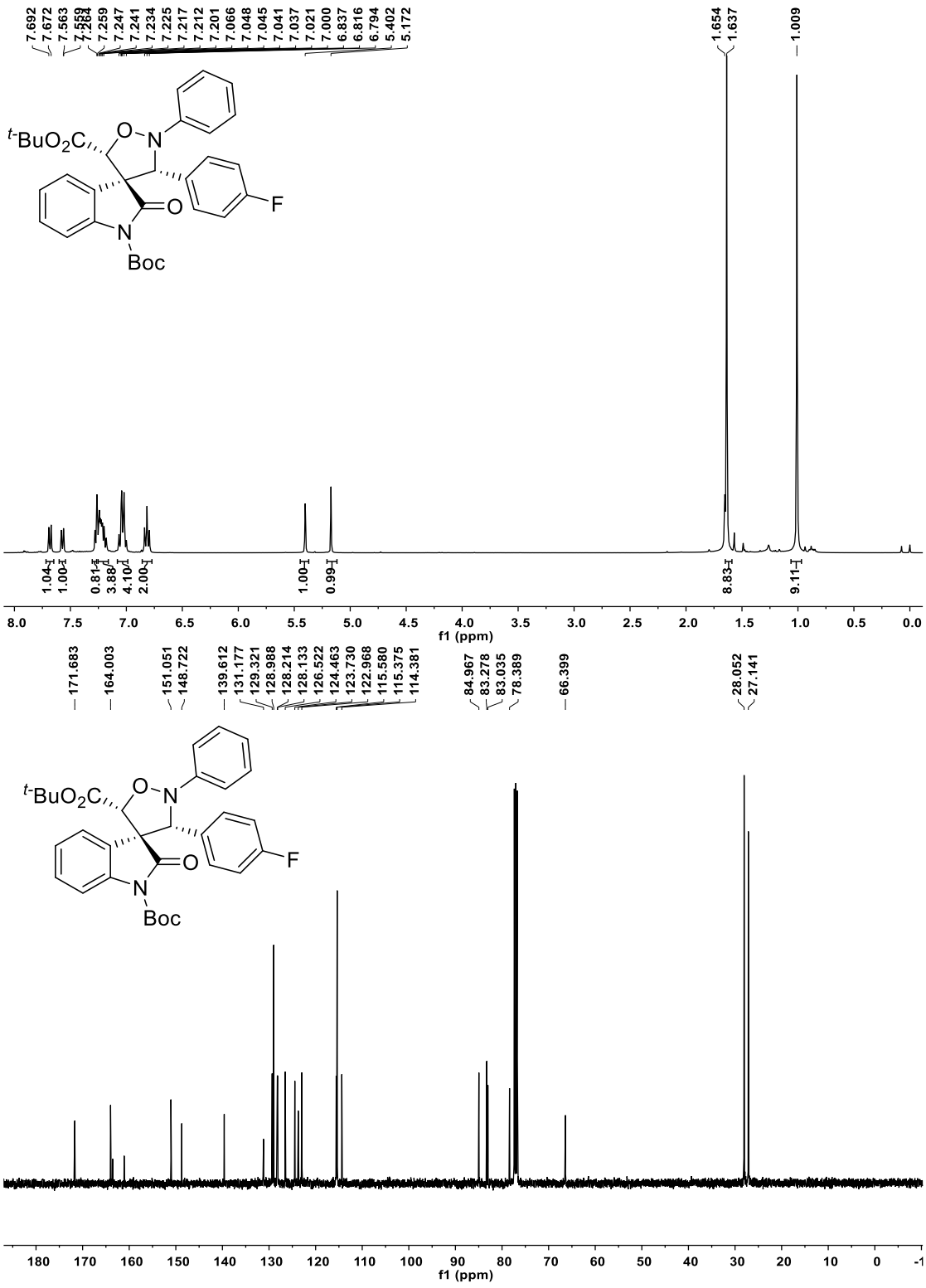
135.299
129.217
128.965
128.509
128.450
128.146
126.580
126.428
124.291
123.464
122.875
115.381
114.357
84.849
82.954
78.834
69.514
66.533
53.455
28.085
21.402
20.619
i-PrO2C
O
N
O
N
Boc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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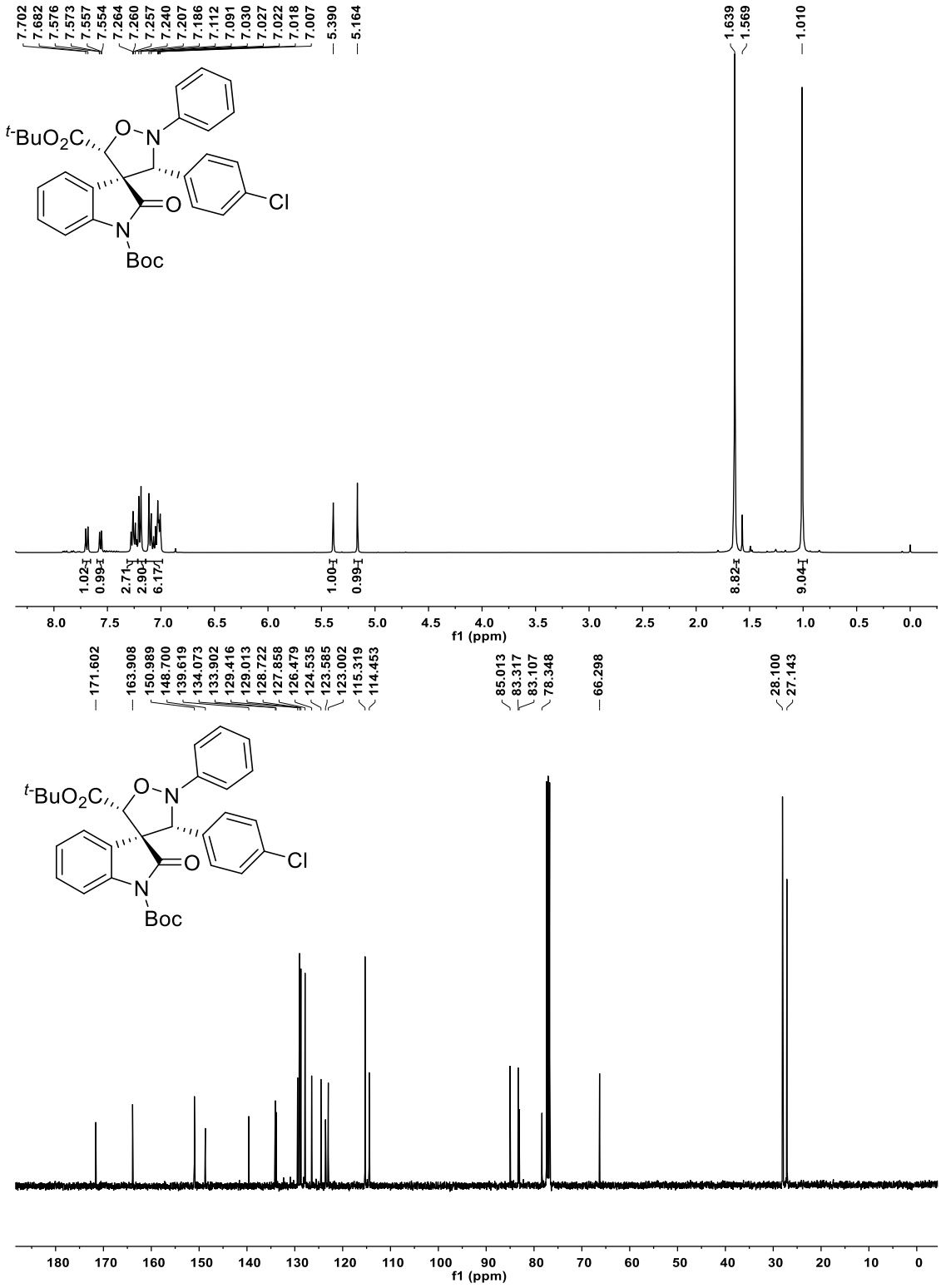
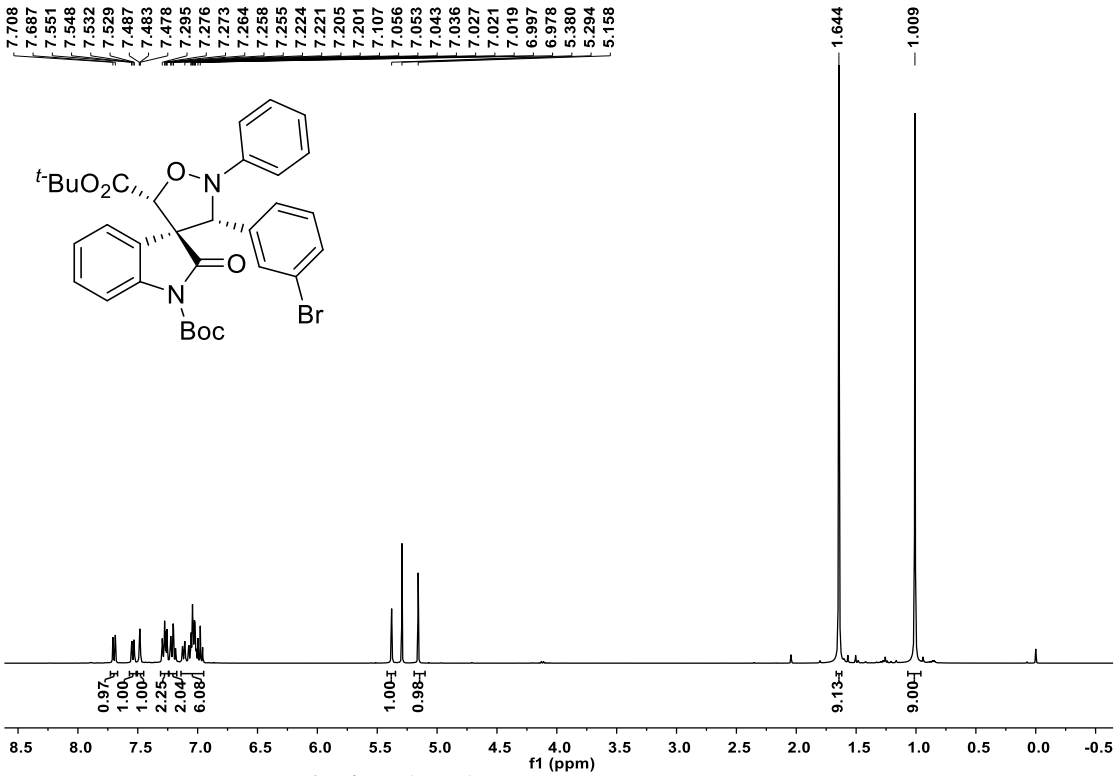
7.672
7.563
7.559
7.554
7.259
7.247
7.241
7.234
7.225
7.217
7.212
7.201
7.066
7.048
7.045
7.041
7.037
7.021
7.000
6.837
6.816
6.794
5.402
5.172
1.654
1.637
1.009
tBuO2C
O
N
O
F
N
Boc
1.04
1.00
0.81
3.88
4.10
2.00
1.00
0.99
8.83
9.11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
171.683
164.003
151.051
148.722
139.612
131.177
129.321
128.988
128.214
128.133
126.522
124.463
123.730
122.968
115.580
115.375
114.381
84.967
83.278
83.035
78.389
66.399
28.052
27.141
tBuO2C
O
N
O
F
N
Boc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.702
7.682
7.576
7.573
7.557
7.554
7.264
7.260
7.257
7.240
7.207
7.186
7.112
7.091
7.030
7.027
7.022
7.018
7.007
5.390
5.164
1.639
1.569
1.010
t-BuO2C
O
N
Cl
O
N
Boc
1.02
0.99
2.71
2.90
6.17
1.00
0.99
8.82
9.04
f1 (ppm)
171.602
163.908
150.989
148.700
139.619
134.073
133.902
129.416
129.013
128.722
127.858
126.479
124.535
123.585
123.002
115.319
114.453
85.013
83.317
83.107
78.348
66.298
28.100
27.143
f1 (ppm)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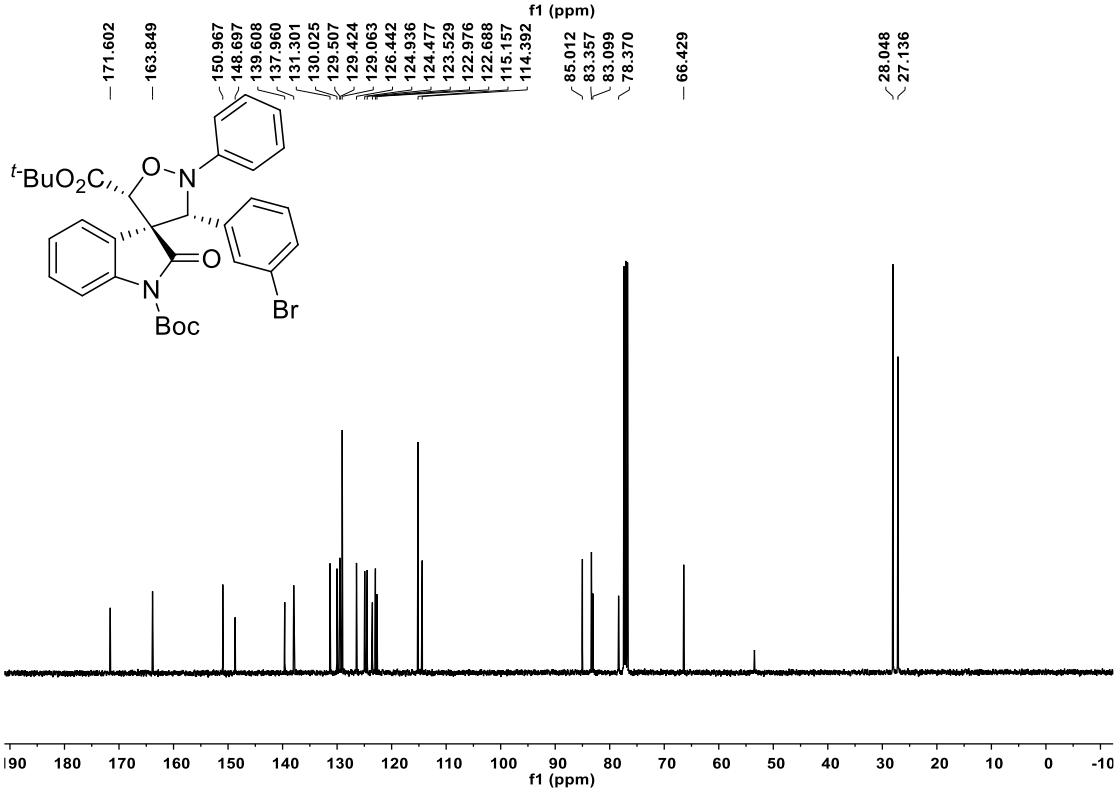
7.687
7.551
7.548
7.532
7.529
7.487
7.483
7.478
7.295
7.276
7.273
7.264
7.258
7.255
7.224
7.221
7.205
7.201
7.107
7.056
7.053
7.043
7.036
7.027
7.021
7.019
6.997
6.978
5.380
5.294
5.158
1.644
1.009
t-BuO2C
O
N
O
N
Boc
Br
0.97
1.00
1.00
2.25
2.04
6.08
1.00
0.98
9.13
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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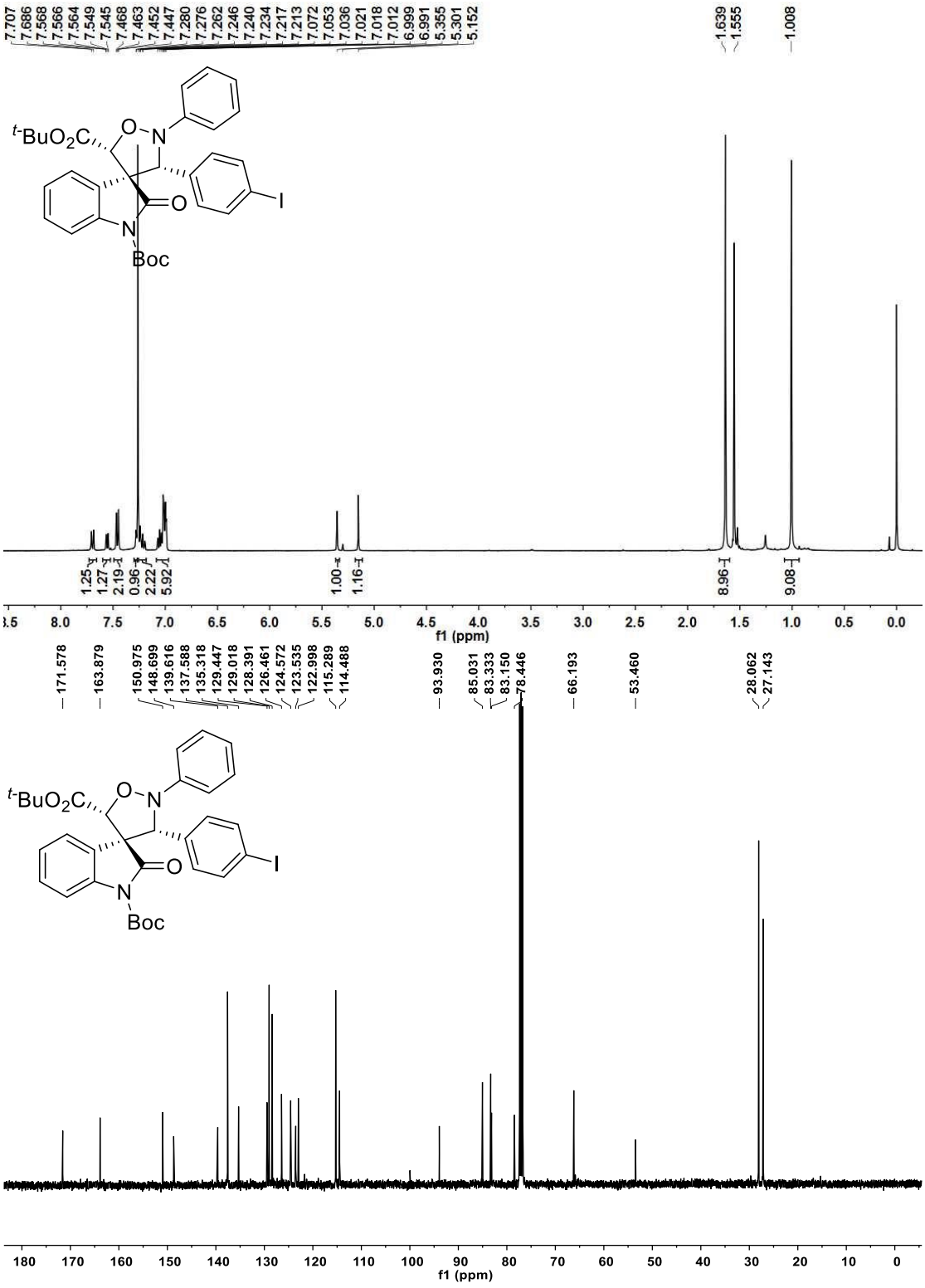
163.849
150.967
148.697
139.608
137.960
131.301
130.025
129.507
129.424
129.063
126.442
124.936
124.477
123.529
122.976
122.688
115.157
114.392
85.012
83.357
83.099
78.370
66.429
28.048
27.136
t-BuO2C
O
N
O
N
Boc
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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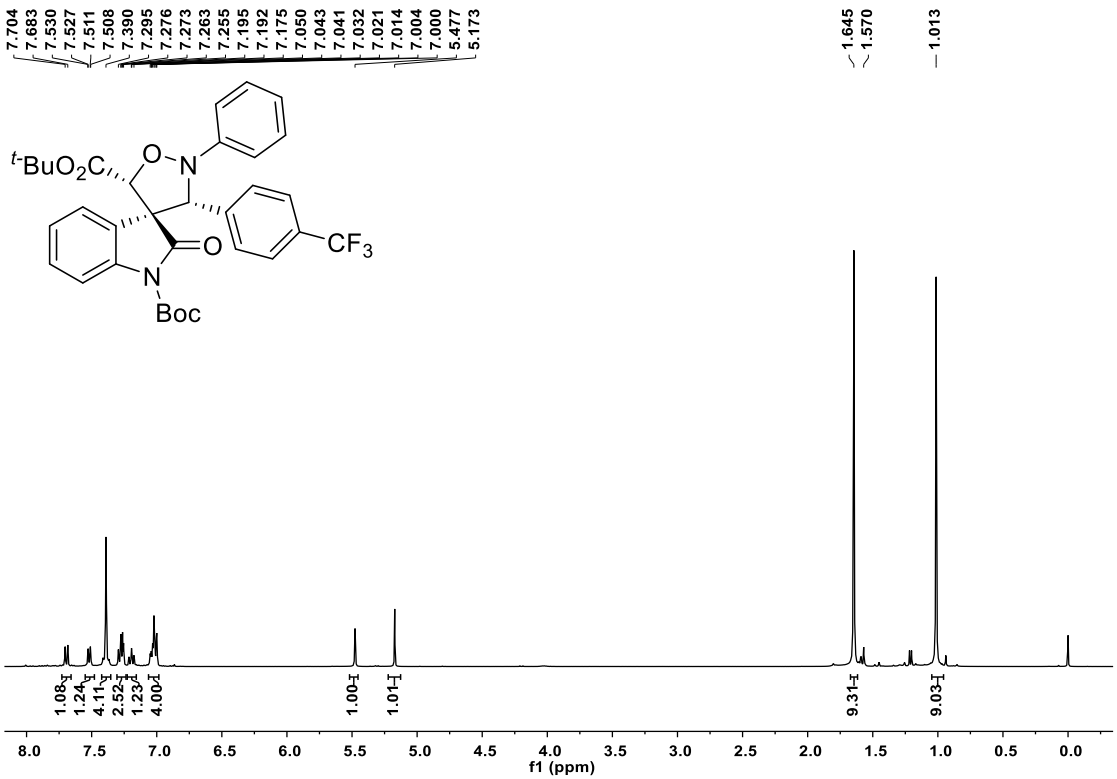
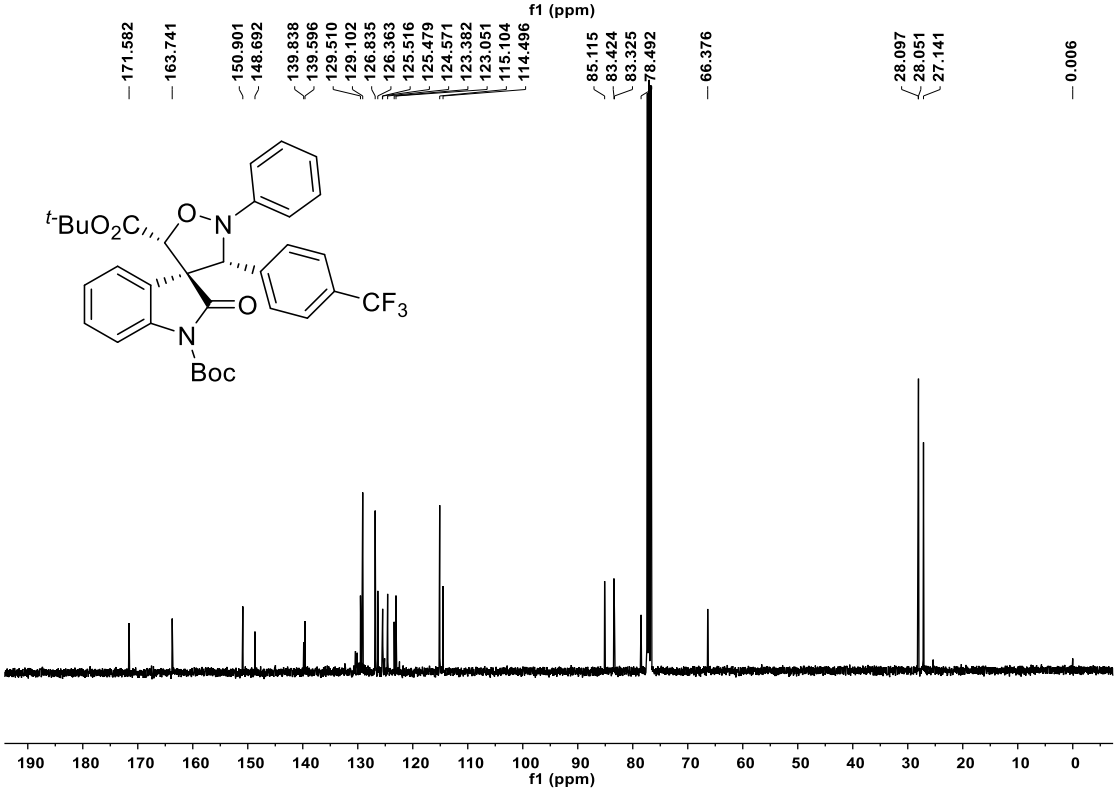
7.686
7.568
7.566
7.564
7.549
7.545
7.468
7.463
7.452
7.447
7.280
7.276
7.262
7.246
7.240
7.234
7.217
7.213
7.072
7.053
7.036
7.021
7.018
7.012
6.999
6.991
5.355
5.301
5.152
1.639
1.555
1.008
t-BuO2C
O
N
O
I
N
Boc
1.25
1.27
2.19
0.96
2.22
5.92
1.00
1.16
8.96
9.08
f1 (ppm)
171.578
163.879
150.975
148.699
139.616
137.588
135.318
129.447
129.018
128.391
126.461
124.572
123.535
122.998
115.289
114.488
93.930
85.031
83.333
83.150
78.446
66.193
53.460
28.062
27.143
f1 (ppm)


7.709
7.689
7.480
7.476
7.461
7.457
7.452
7.447
7.436
7.431
7.390
7.385
7.370
7.303
7.285
7.282
7.266
7.263
7.212
7.209
7.044
7.041
7.038
7.022
7.019
7.006
7.003
7.000
6.997
6.987
6.984
6.981
5.464
5.163
1.645
1.619
1.009
tBuO2C
O
N
O
CN
N
Boc
0.98
3.06
2.04
2.14
1.13
3.98
1.00
0.97
8.85
9.11
f1 (ppm)
171.472
163.588
150.679
148.598
141.277
139.586
132.372
129.670
129.181
127.149
126.281
124.634
123.196
118.309
114.993
114.558
112.098
85.274
83.544
83.375
78.446
66.392
28.049
27.134
tBuO2C
O
N
O
CN
N
Boc
f1 (ppm)


7.704
7.683
7.530
7.527
7.511
7.508
7.390
7.295
7.276
7.273
7.263
7.255
7.195
7.192
7.175
7.050
7.043
7.041
7.032
7.021
7.014
7.004
7.000
5.477
5.173
1.645
1.570
1.013
^{t}BuO$_2$C
O
N
O
CF$_3$
N
Boc
1.08
1.24
4.11
2.52
1.23
4.00
1.00
1.01
9.31
9.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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139.596
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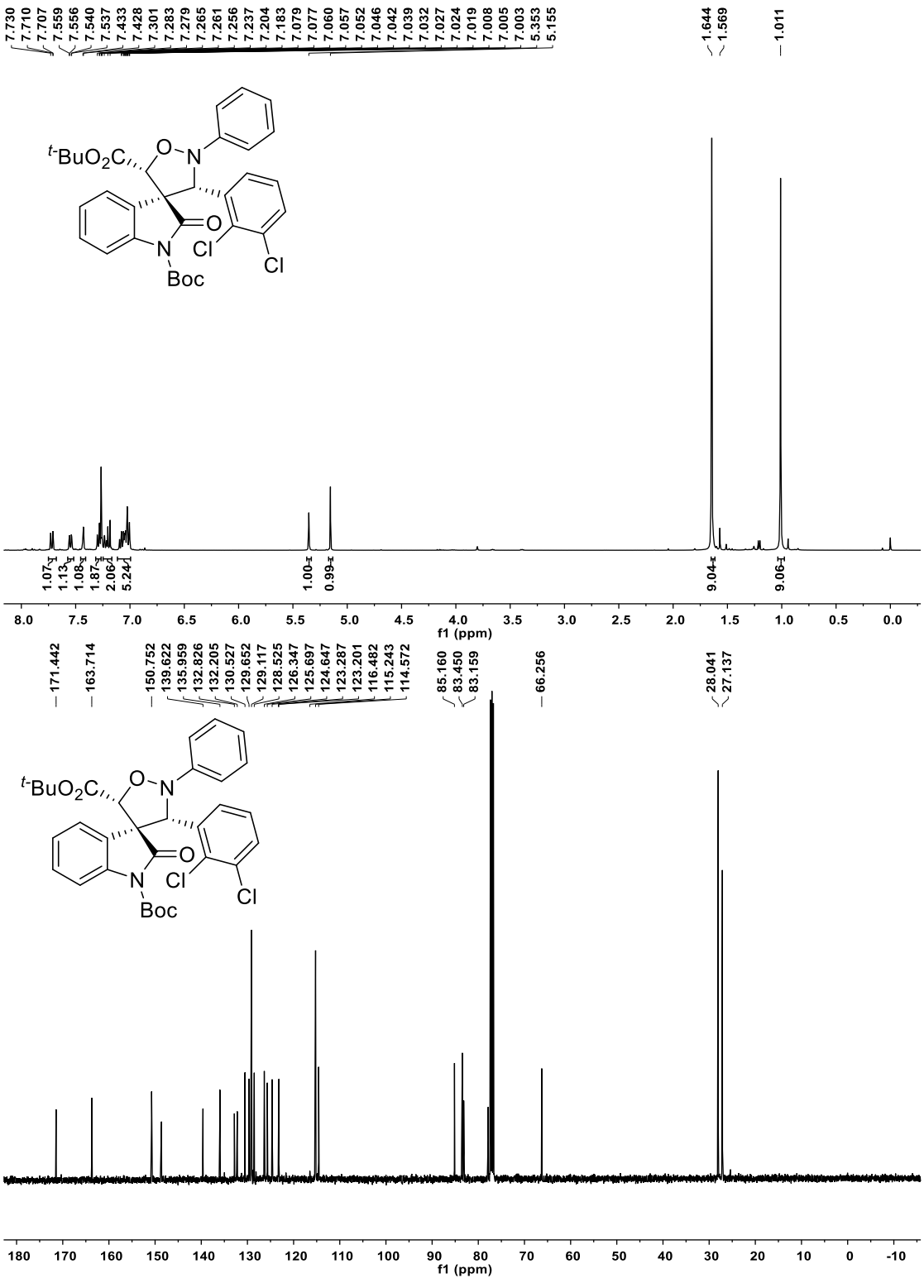
129.102
126.835
126.363
125.516
125.479
124.571
123.382
123.051
115.104
114.496
85.115
83.424
83.325
78.492
66.376
28.097
28.051
27.141
0.006
^{t}BuO$_2$C
O
N
O
CF$_3$
N
Boc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.707
7.559
7.556
7.540
7.537
7.433
7.428
7.301
7.283
7.279
7.265
7.261
7.256
7.237
7.204
7.183
7.079
7.077
7.060
7.057
7.052
7.046
7.042
7.039
7.032
7.027
7.024
7.019
7.008
7.005
7.003
5.353
5.155
1.644
1.569
1.011
t-BuO2C
O
N
O
N
Cl
Cl
Boc
1.07
1.13
1.08
1.87
2.06
5.24
1.00
0.99
9.04
9.06
f1 (ppm)
171.442
163.714
150.752
139.622
135.959
132.826
132.205
130.527
129.652
129.117
128.525
126.347
125.697
124.647
123.287
123.201
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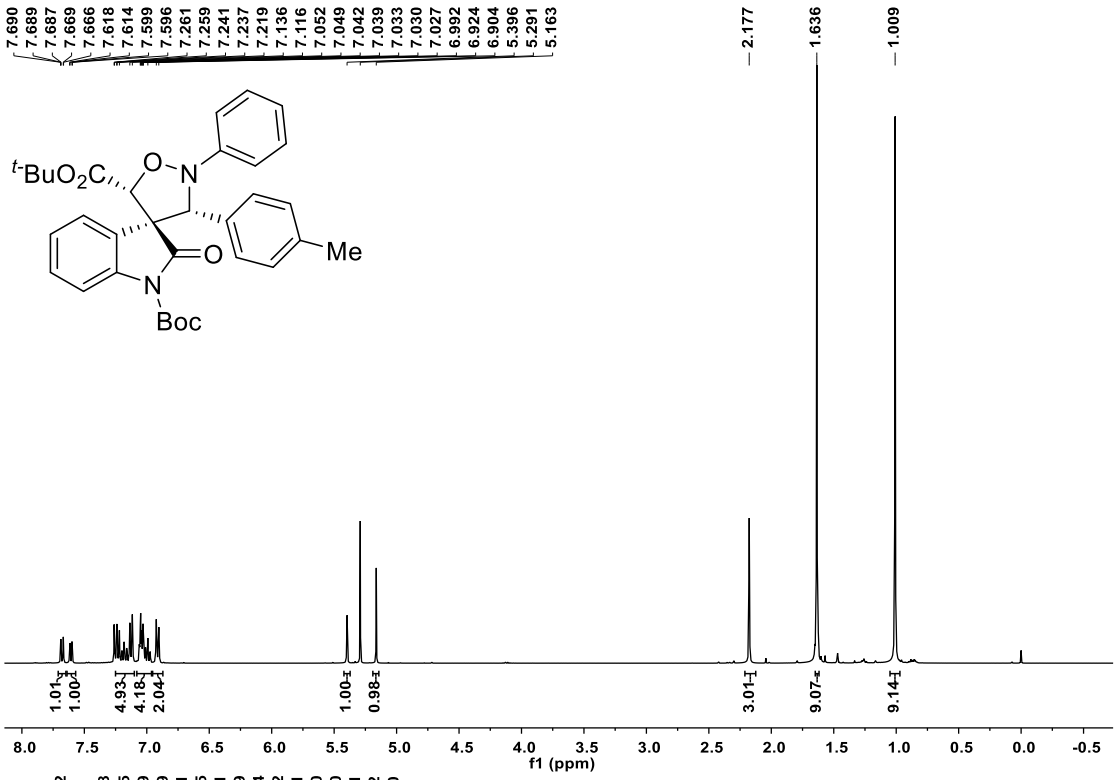
115.243
114.572
85.160
83.450
83.159
66.256
28.041
27.137
f1 (ppm)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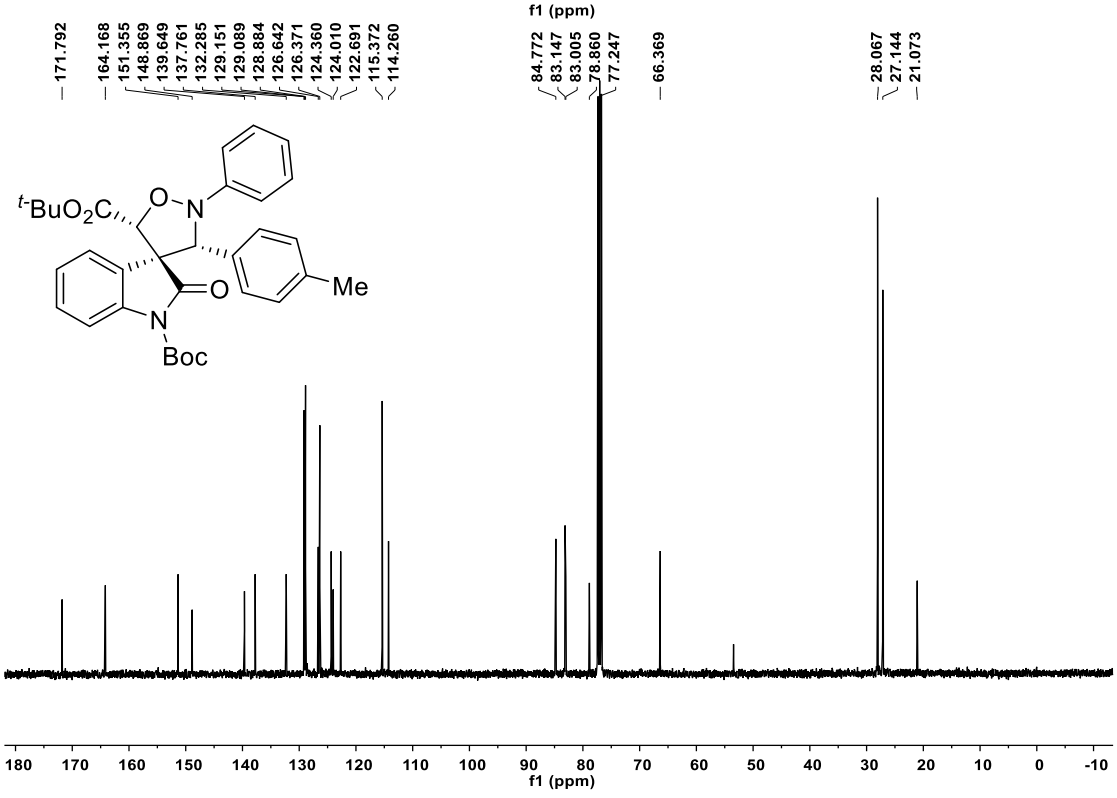
7.689
7.687
7.669
7.666
7.618
7.614
7.599
7.596
7.261
7.259
7.241
7.237
7.219
7.136
7.116
7.052
7.049
7.042
7.039
7.033
7.030
7.027
6.992
6.924
6.904
5.396
5.291
5.163
2.177
1.636
1.009
tBuO2C
O
N
O
N
Boc
Me
1.01
1.00
4.93
4.18
2.04
1.00
0.98
3.01
9.07
9.14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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132.285
129.151
129.089
128.884
126.642
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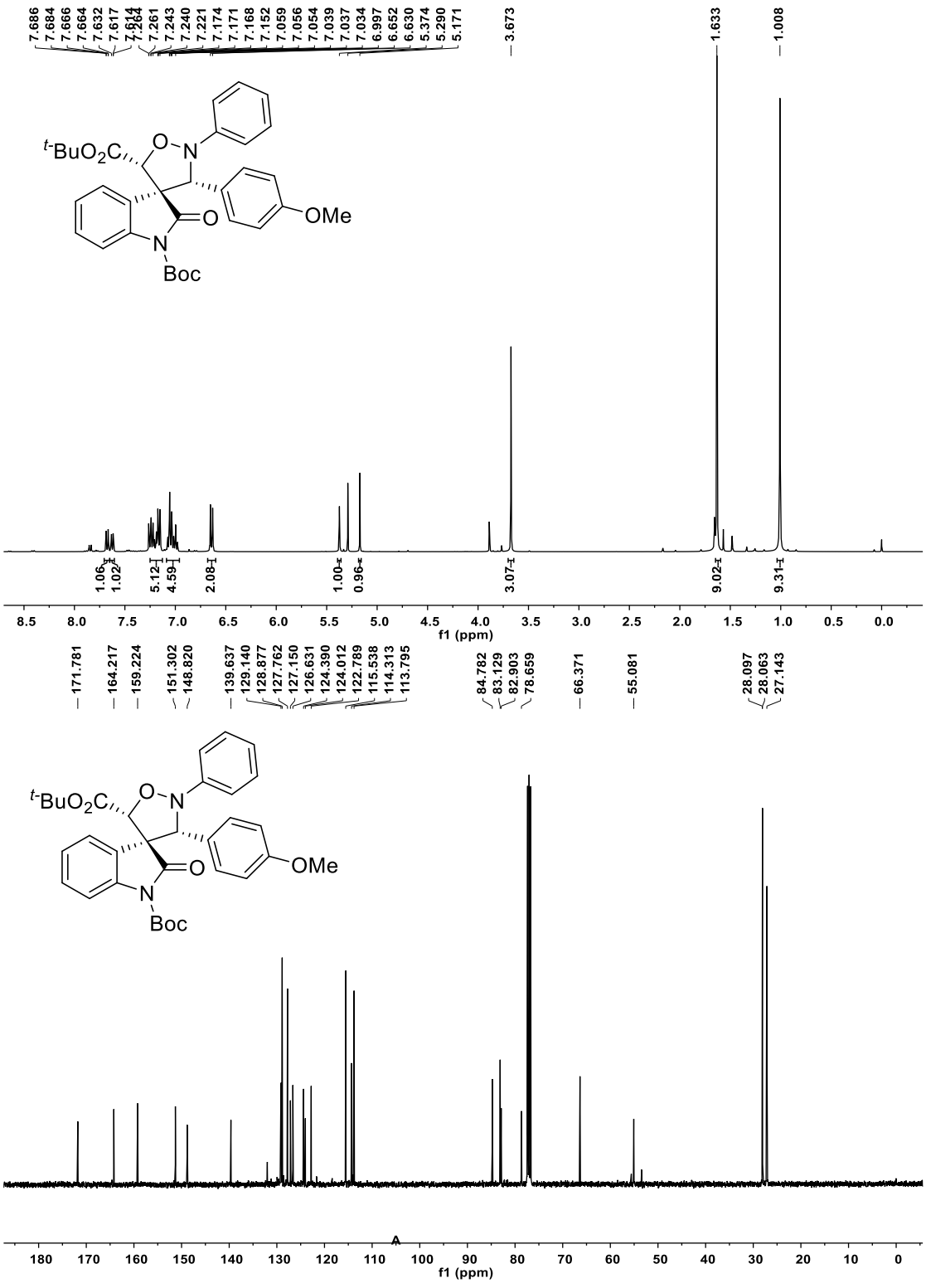
124.360
124.010
122.691
115.372
114.260
84.772
83.147
83.005
78.860
77.247
66.369
28.067
27.144
21.073
tBuO2C
O
N
O
N
Boc
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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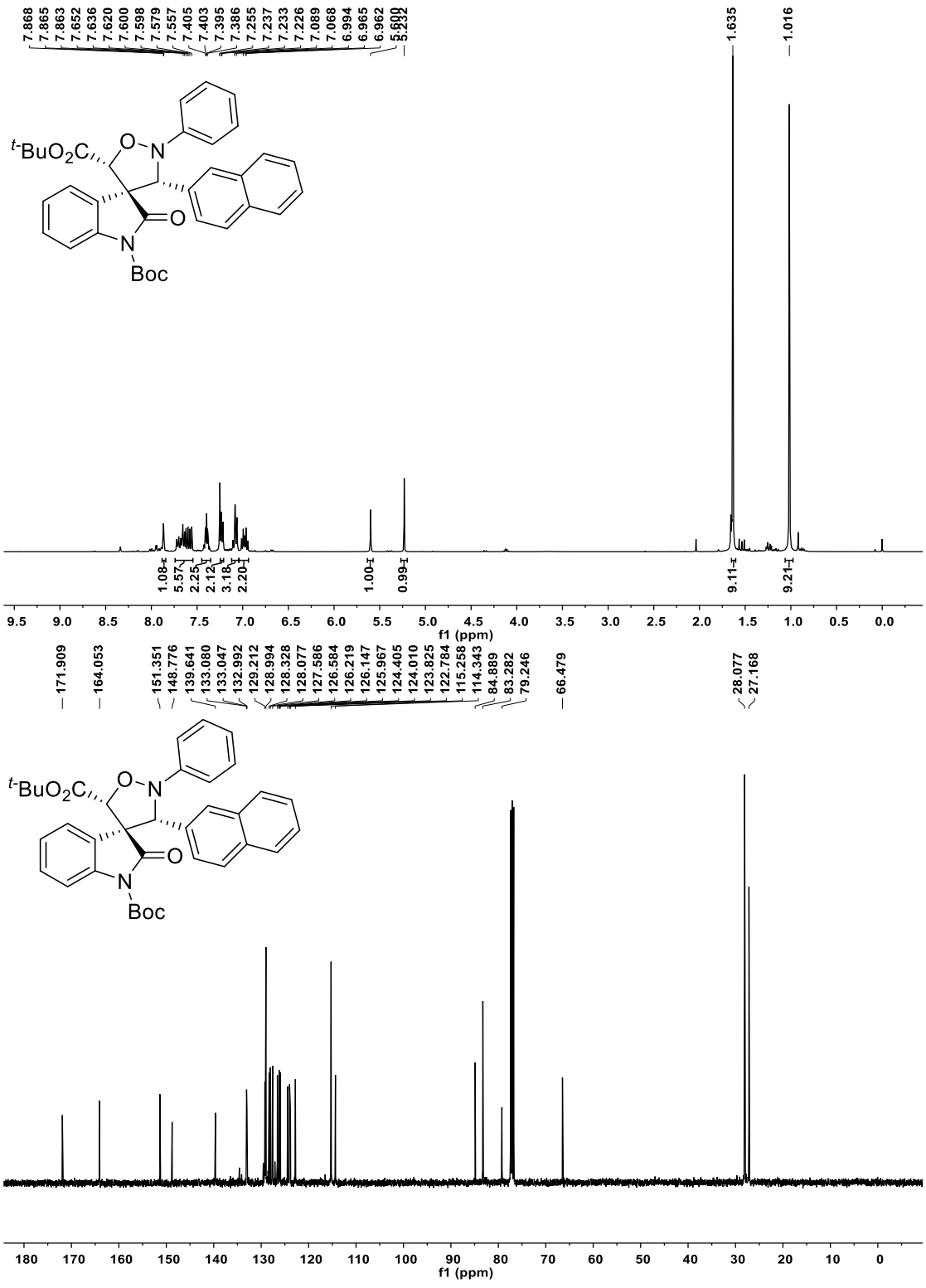
7.666
7.664
7.632
7.617
7.614
7.261
7.243
7.240
7.221
7.174
7.171
7.168
7.152
7.059
7.056
7.054
7.039
7.037
7.034
6.997
6.652
6.630
5.374
5.290
5.171
3.673
1.633
1.008
tBuO2C
O
N
O
OMe
N
Boc
1.06
1.02
5.12
4.59
2.08
1.00
0.96
3.07
9.02
9.31
f1 (ppm)
171.781
164.217
159.224
151.302
148.820
139.637
129.140
128.877
127.762
127.150
126.631
124.390
124.012
122.789
115.538
114.313
113.795
84.782
83.129
82.903
78.659
66.371
55.081
28.097
28.063
27.143
f1 (ppm)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7.652
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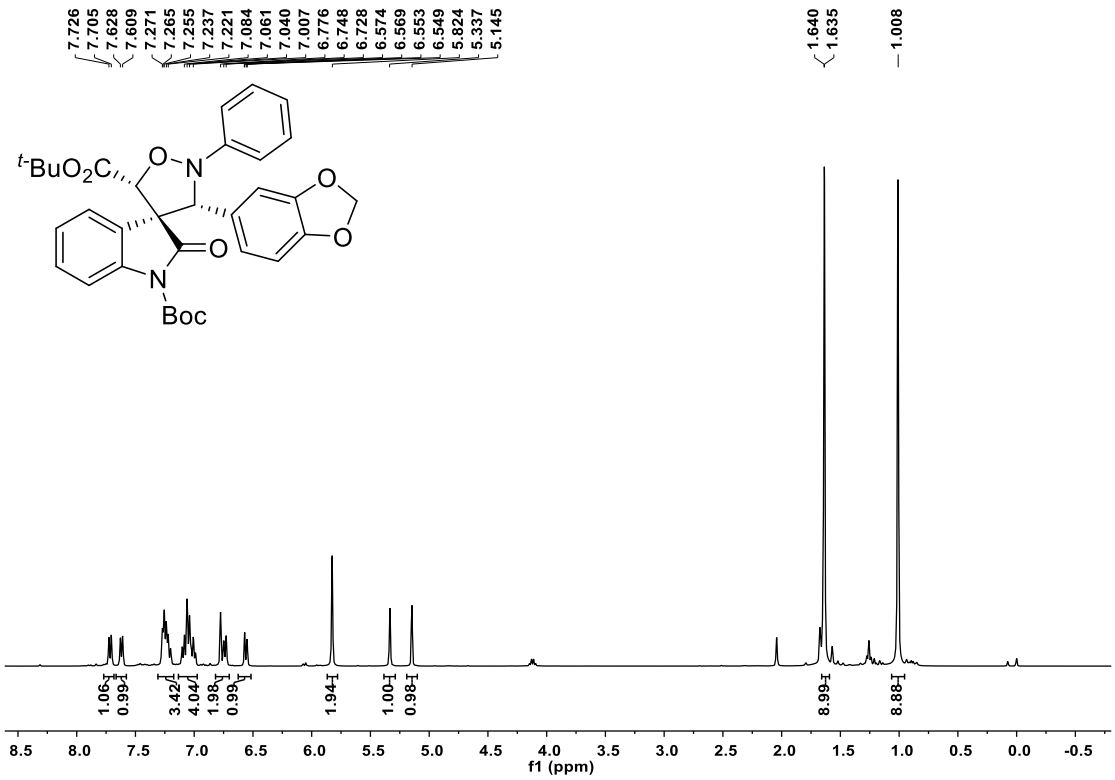
7.600
7.598
7.579
7.557
7.405
7.403
7.395
7.386
7.255
7.237
7.233
7.226
7.089
7.068
6.994
6.965
6.962
5.600
5.592
1.635
1.016
t-BuO2C
O
N
O
N
Boc
1.08
5.57
2.25
2.12
3.18
2.20
1.00
0.99
9.11
9.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
171.909
164.053
151.351
148.776
139.641
133.080
133.047
132.992
129.212
128.994
128.328
128.077
127.586
126.584
126.219
126.147
125.967
124.405
124.010
123.825
122.784
115.258
114.343
84.889
83.282
79.246
66.479
28.077
27.168
t-BuO2C
O
N
O
N
Boc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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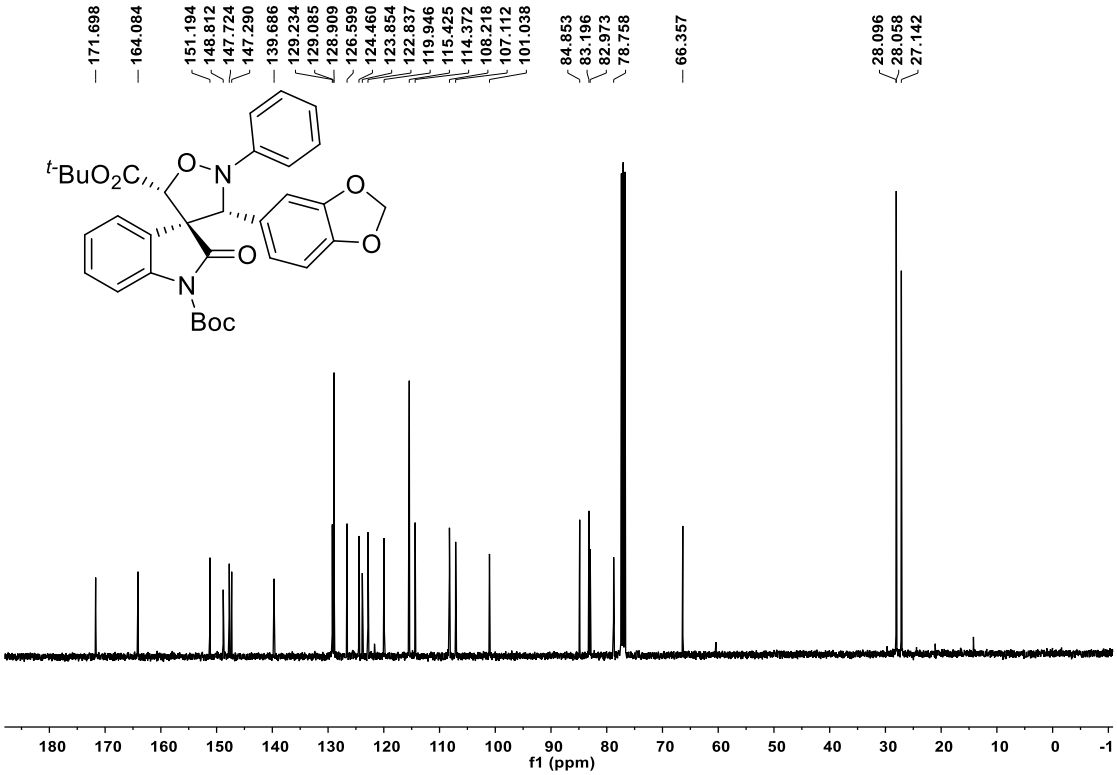
7.705
7.628
7.609
7.271
7.265
7.255
7.237
7.221
7.084
7.061
7.040
7.007
6.776
6.748
6.728
6.574
6.569
6.553
6.549
5.824
5.337
5.145
1.640
1.635
1.008
1.06
0.99
3.42
4.04
1.98
0.99
1.94
1.00
0.98
8.99
8.88
f1 (ppm)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151.194
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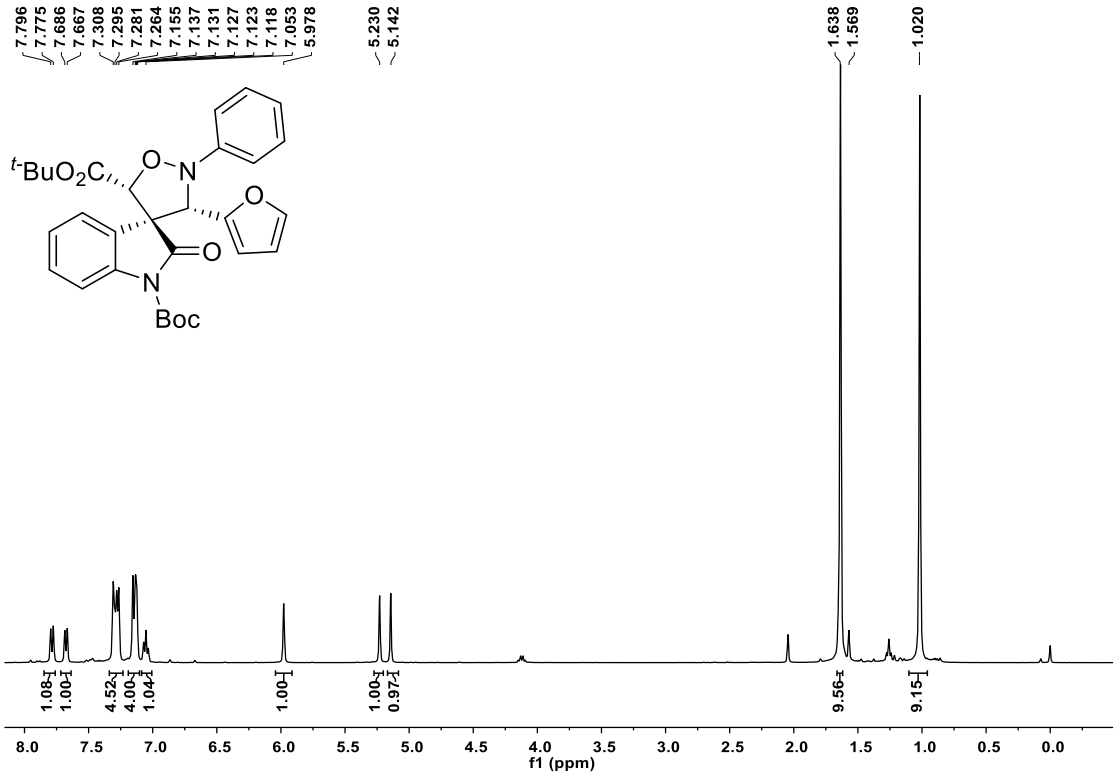
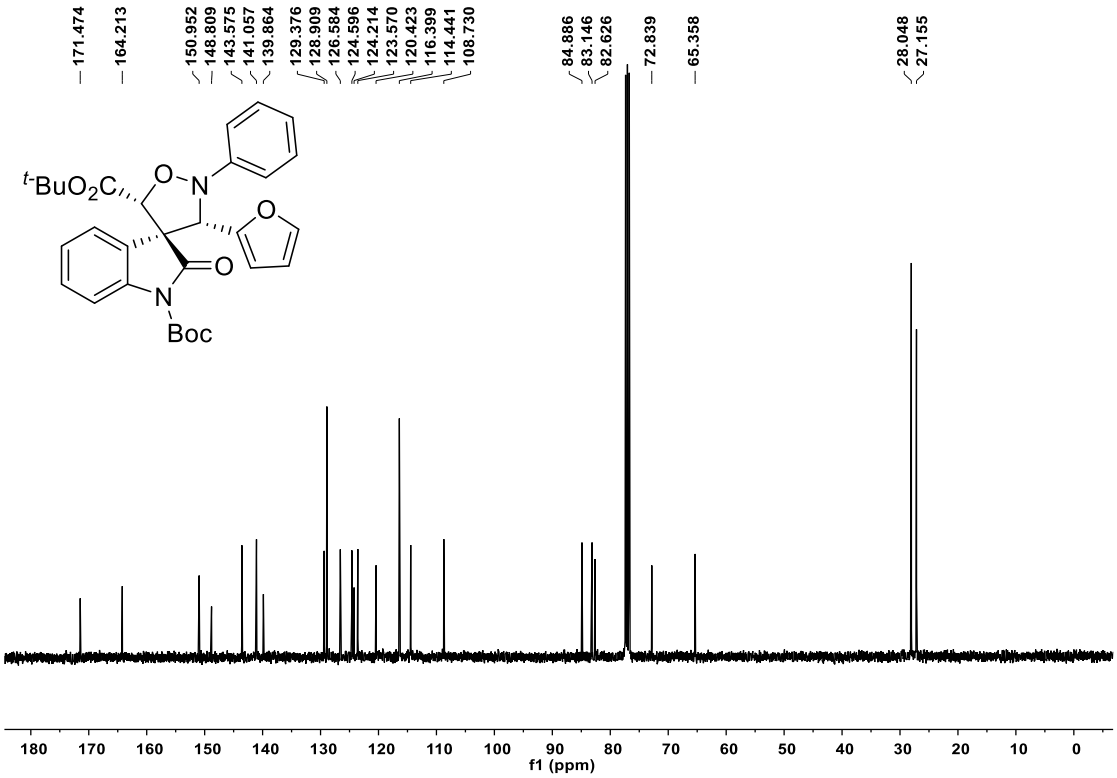
147.290
139.686
129.234
129.085
128.909
126.599
124.460
123.854
122.837
119.946
115.425
114.372
108.218
107.112
101.038
84.853
83.196
82.973
78.758
66.357
28.096
28.058
27.142
f1 (ppm)


7.796
7.775
7.686
7.667
7.308
7.295
7.281
7.264
7.155
7.137
7.131
7.127
7.123
7.118
7.053
5.978
5.230
5.142
1.638
1.569
1.020
^{t}-BuO$_2$C
O
N
O
O
N
Boc
1.08
1.00
4.52
4.00
1.04
1.00
1.00
0.97
9.56
9.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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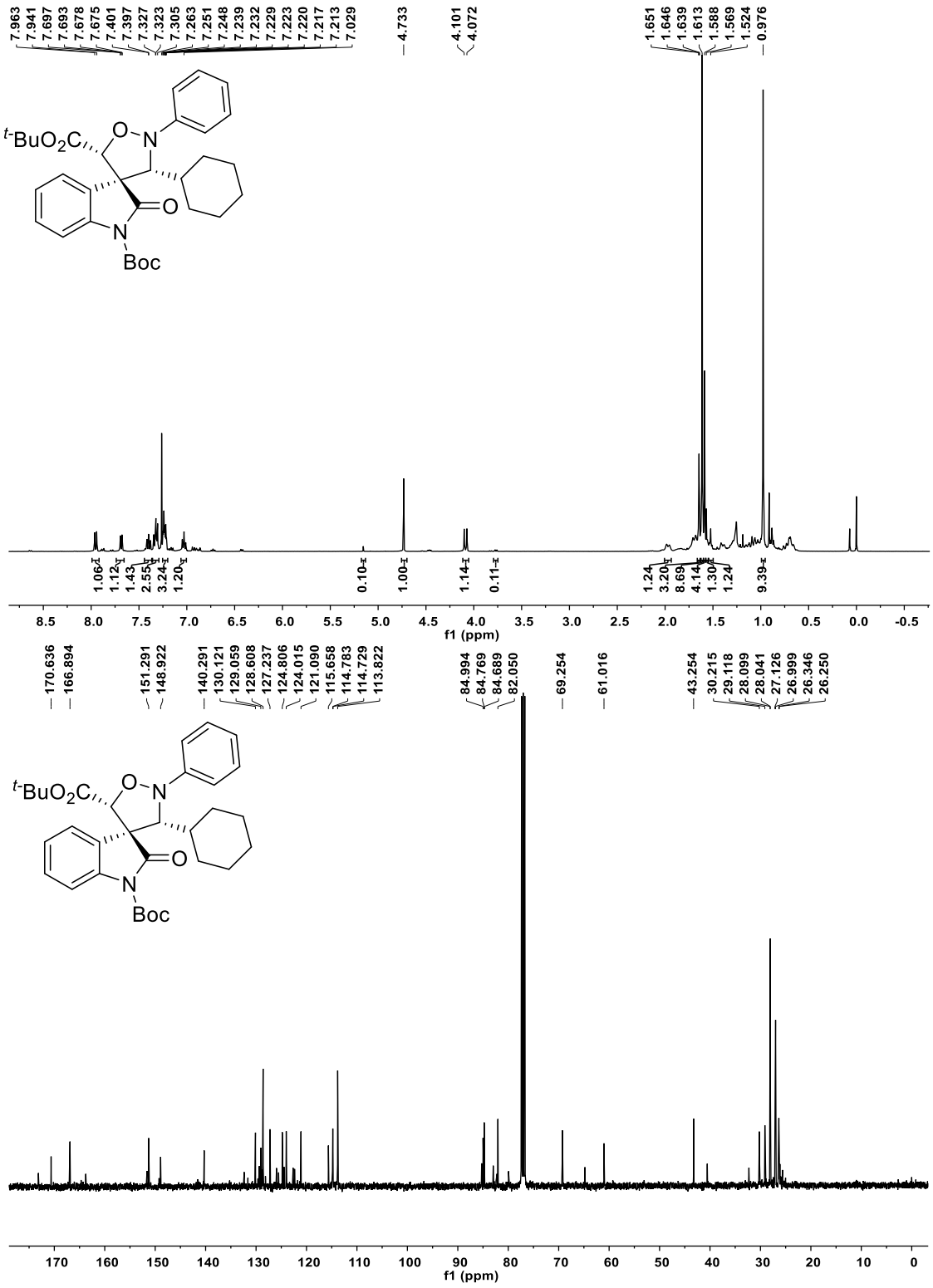
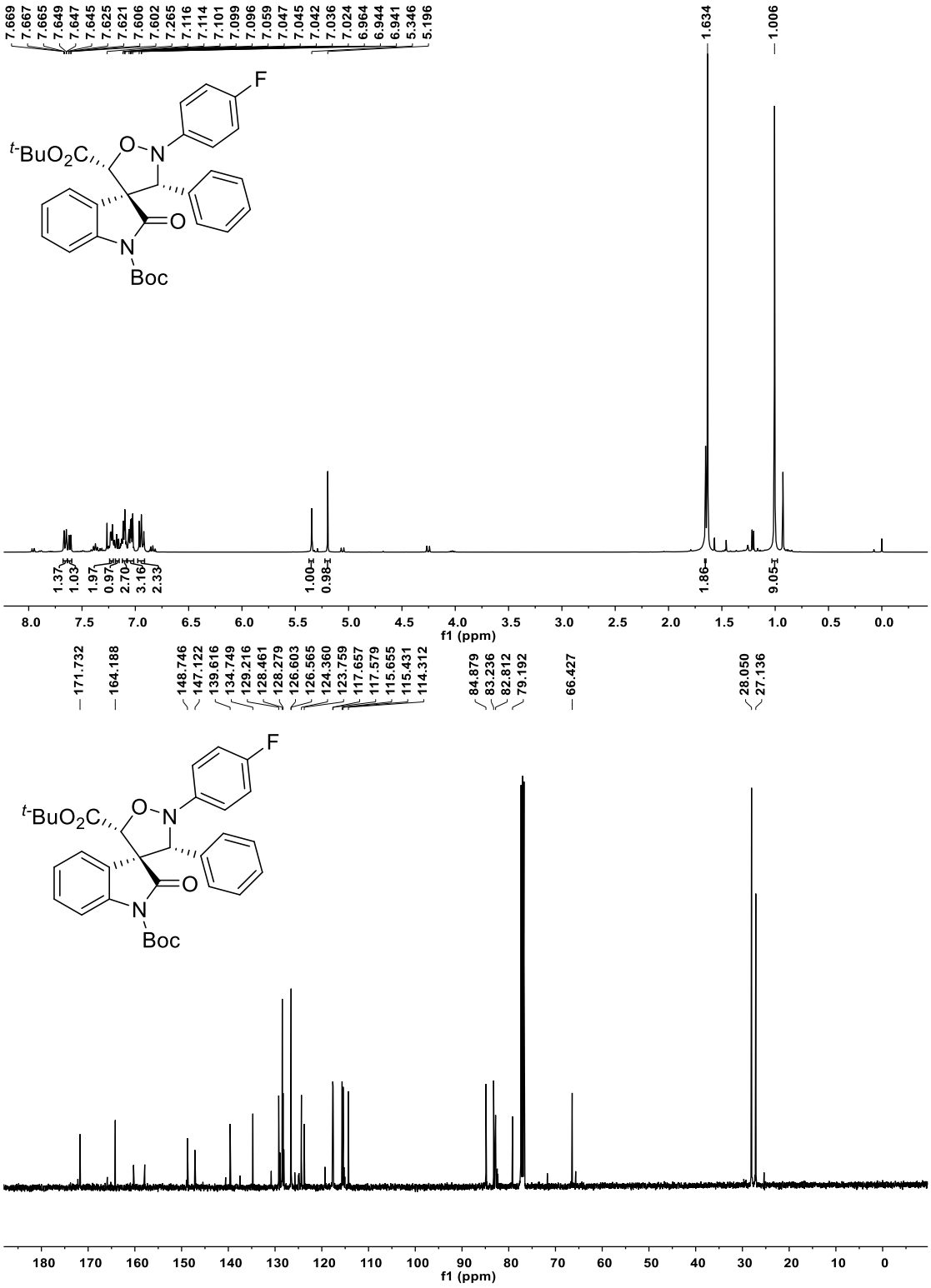
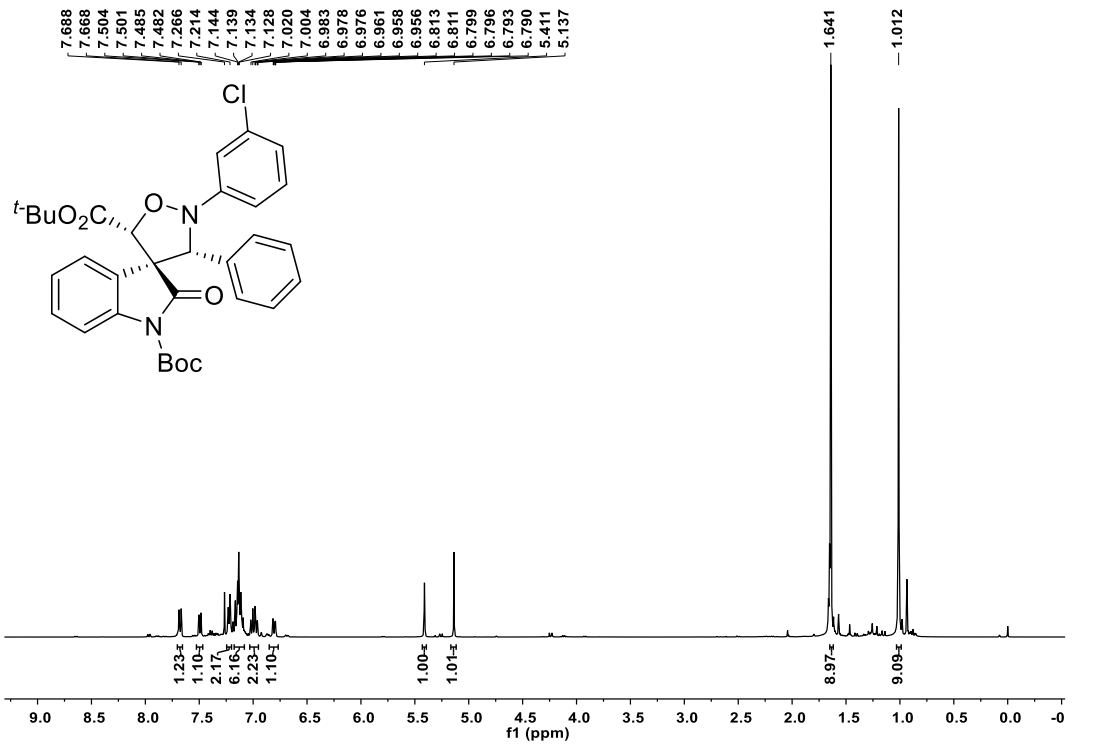
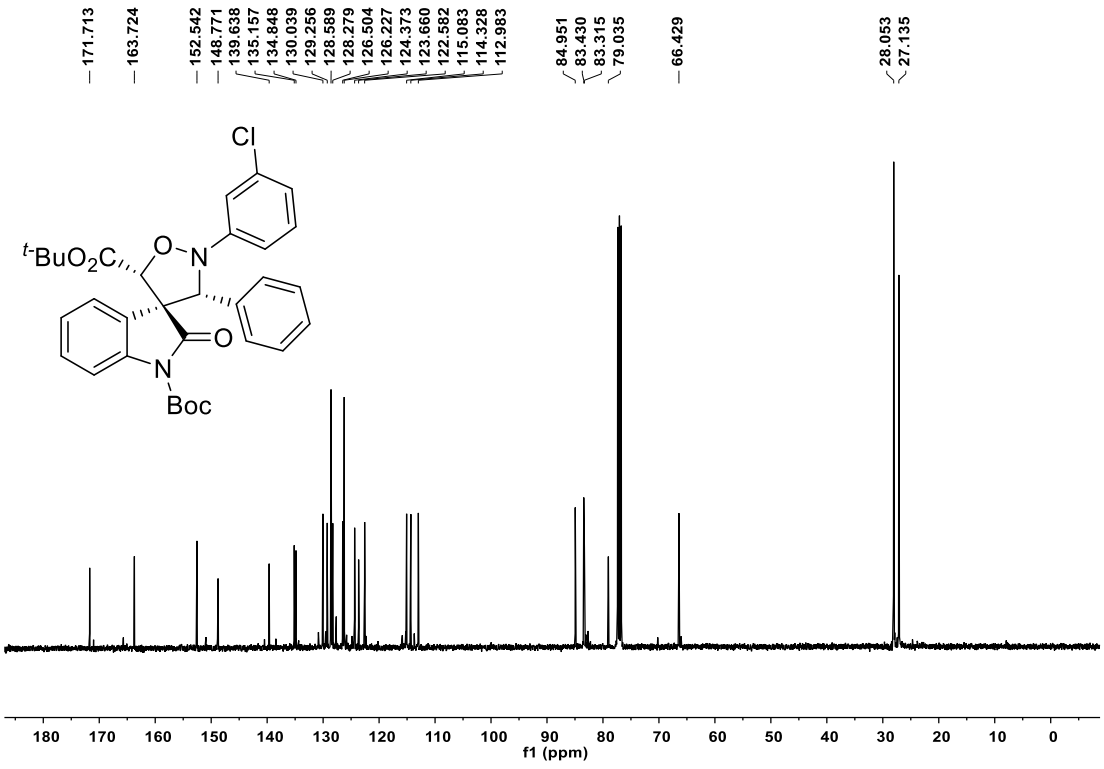
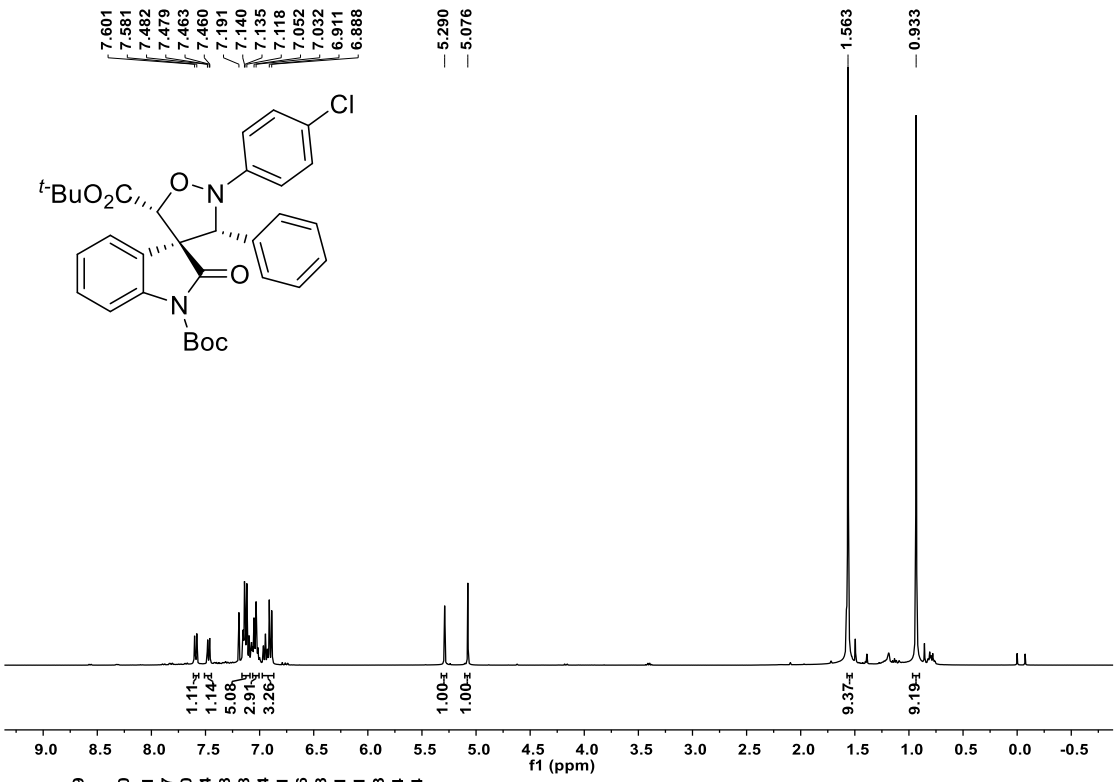
164.213
150.952
148.809
143.575
141.057
139.864
129.376
128.909
126.584
124.596
124.214
123.570
120.423
116.399
114.441
108.730
84.886
83.146
82.626
72.839
65.358
28.048
27.155
^{t}-BuO$_2$C
O
N
O
O
N
Boc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

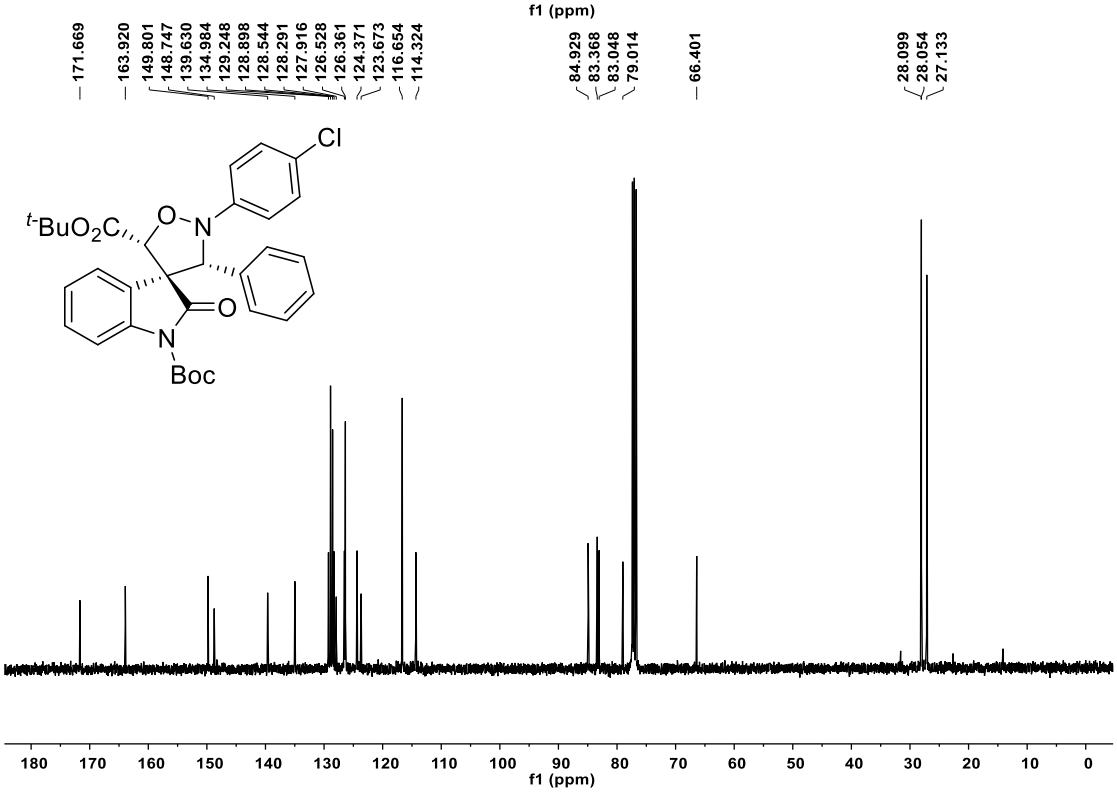

7.963
7.941
7.697
7.693
7.678
7.675
7.401
7.397
7.327
7.323
7.305
7.263
7.251
7.248
7.239
7.232
7.229
7.223
7.220
7.217
7.213
7.029
4.733
4.101
4.072
1.651
1.646
1.639
1.613
1.588
1.569
1.524
0.976
t-BuO2C
O
N
O
N
Boc
1.06
1.12
1.43
2.55
3.24
1.20
0.10
1.00
1.14
0.11
1.24
3.20
8.69
4.14
1.30
1.24
9.39
f1 (ppm)
170.636
166.894
151.291
148.922
140.291
130.121
129.059
128.608
127.237
124.806
124.015
121.090
115.658
114.783
114.729
113.822
84.994
84.769
84.689
82.050
69.254
61.016
43.254
30.215
29.118
28.099
28.041
27.126
26.999
26.346
26.250
t-BuO2C
O
N
O
N
Boc
f1 (ppm)

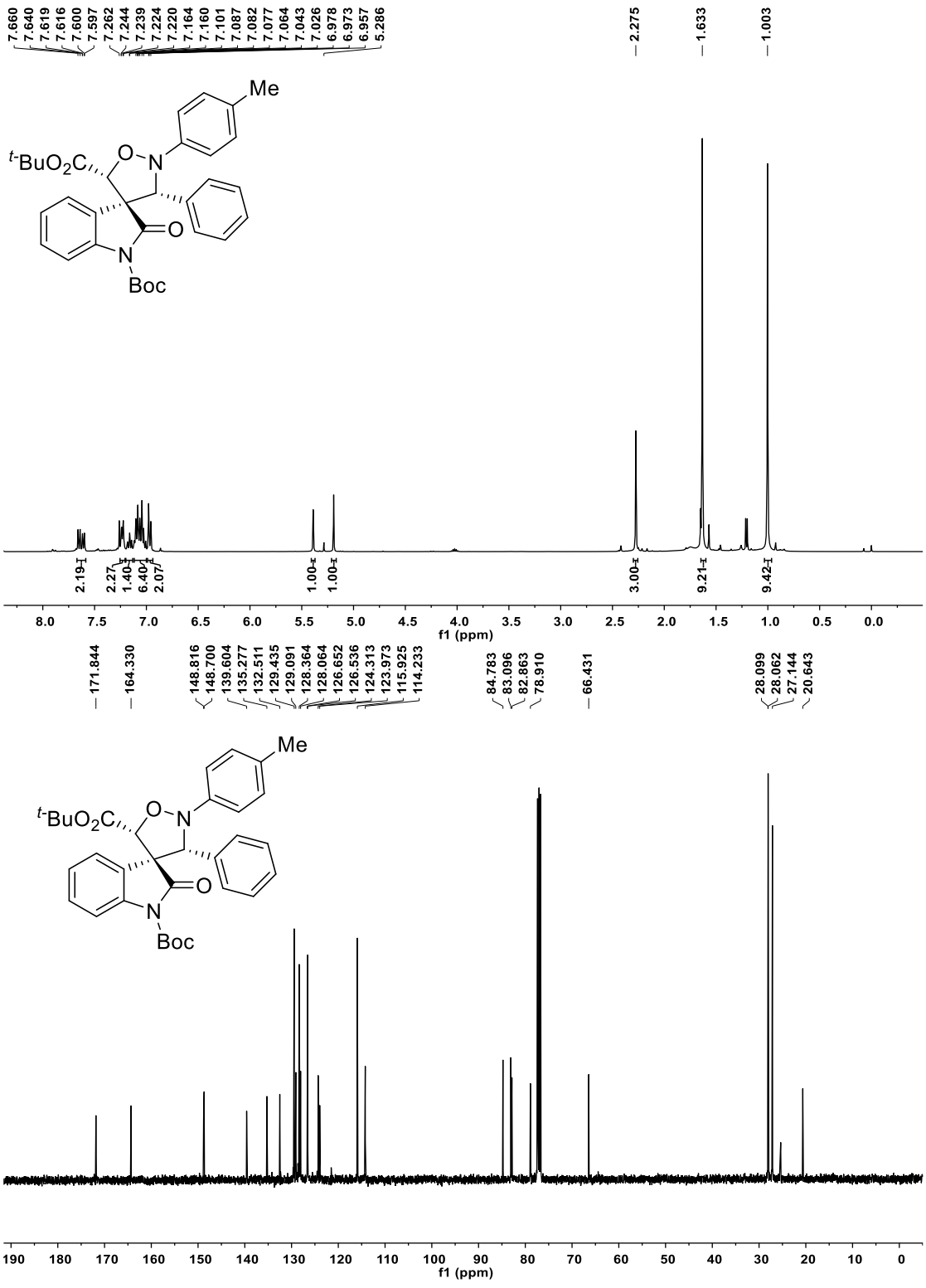

7.669
7.667
7.665
7.649
7.647
7.645
7.625
7.621
7.606
7.602
7.265
7.116
7.114
7.101
7.099
7.096
7.059
7.047
7.045
7.042
7.036
7.024
6.964
6.944
6.941
5.346
5.196
1.634
1.006
F
t-BuO2C
O
N
O
N
Boc
1.37
1.03
1.97
0.97
2.70
3.16
2.33
1.00
0.98
1.86
9.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
171.732
164.188
148.746
147.122
139.616
134.749
129.216
128.461
128.279
126.603
126.565
124.360
123.759
117.657
117.579
115.655
115.431
114.312
84.879
83.236
82.812
79.192
66.427
28.050
27.136
F
t-BuO2C
O
N
O
N
Boc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

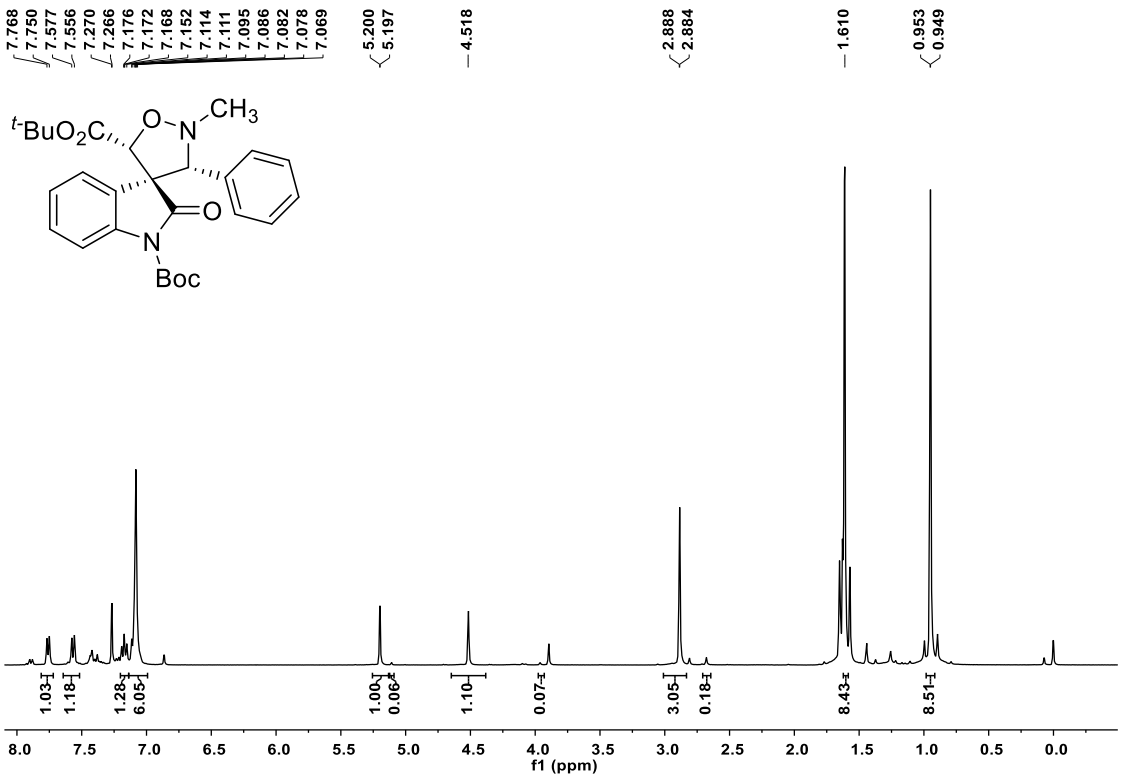

7.688
7.668
7.504
7.501
7.485
7.482
7.266
7.214
7.144
7.139
7.134
7.128
7.020
7.004
6.983
6.978
6.976
6.961
6.958
6.956
6.813
6.811
6.799
6.796
6.793
6.790
5.411
5.137
1.641
1.012
Cl
O
N
O
N
Boc
1.23
1.10
2.17
6.16
2.23
1.10
1.00
1.01
8.97
9.09
f1 (ppm)

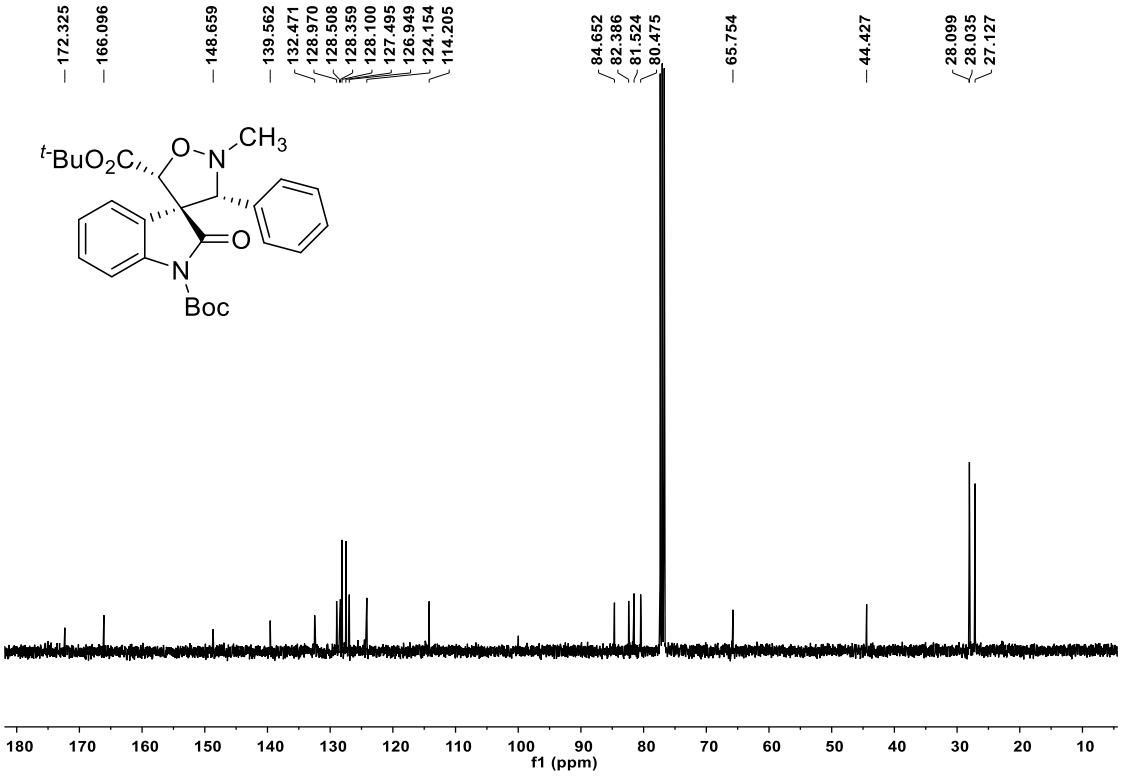

171.713
163.724
152.542
148.771
139.638
135.157
134.848
130.039
129.256
128.589
128.279
126.504
126.227
124.373
123.660
122.582
115.083
114.328
112.983
84.951
83.430
83.315
79.035
66.429
28.053
27.135
Cl
O
N
O
N
Boc
f1 (ppm)


7.601
7.581
7.482
7.479
7.463
7.460
7.191
7.140
7.135
7.118
7.052
7.032
6.911
6.888
5.290
5.076
1.563
0.933
Cl
t-BuO2C
O
N
O
N
Boc
1.11
1.14
5.08
2.91
3.26
1.00
1.00
9.37
9.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.669
163.920
149.801
148.747
139.630
134.984
129.248
128.898
128.544
128.291
127.916
126.528
126.361
124.371
123.673
116.654
114.324
84.929
83.368
83.048
79.014
66.401
28.099
28.054
27.133
Cl
t-BuO2C
O
N
O
N
Boc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.660
7.640
7.619
7.616
7.600
7.597
7.262
7.244
7.239
7.224
7.220
7.164
7.160
7.101
7.087
7.082
7.077
7.064
7.043
7.026
6.978
6.973
6.957
5.286
2.275
1.633
1.003
Me
t-BuO2C
O
N
O
N
Boc
2.19
2.27
1.40
6.40
2.07
1.00
1.00
3.00
9.21
9.42
f1 (ppm)
171.844
164.330
148.816
148.700
139.604
135.277
132.511
129.435
129.091
128.364
128.064
126.652
126.536
124.313
123.973
115.925
114.233
84.783
83.096
82.863
78.910
66.431
28.099
28.062
27.144
20.643
f1 (ppm)


7.768
7.750
7.577
7.556
7.270
7.266
7.176
7.172
7.168
7.152
7.114
7.111
7.095
7.086
7.082
7.078
7.069
5.200
5.197
4.518
2.888
2.884
1.610
0.953
0.949
t-BuO2C
O
N
CH3
O
N
Boc
1.03
1.18
1.28
6.05
1.00
0.06
1.10
0.07
3.05
0.18
8.43
8.51
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.325
166.096
148.659
139.562
132.471
128.970
128.508
128.359
128.100
127.495
126.949
124.154
114.205
84.652
82.386
81.524
80.475
65.754
44.427
28.099
28.035
27.127
t-BuO2C
O
N
CH3
O
N
Boc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)