Supporting Information for

Highly Enantioselective Synthesis of Aza-Spirocyclic Indanones via Rhodium Catalysis

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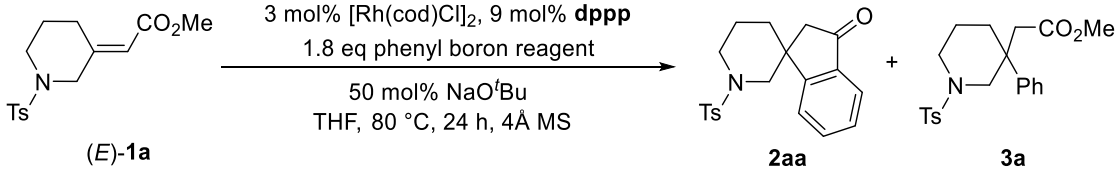
General Information

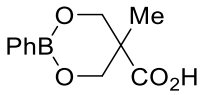
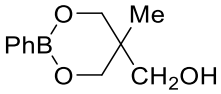
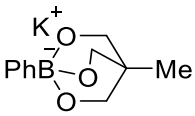
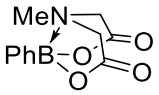
All air or moisture sensitive reactions were conducted in oven-dried glassware under argon atmosphere using dry solvents. Anhydrous solvents were treated as follow: tetrahydrofuran, toluene and diethylene glycol dimethyl ether were distilled from sodium under argon atmosphere, dichloromethane was distilled from calcium hydride under argon atmosphere. All aryl boronic acids were sublimated. Unless otherwise noted, other anhydrous solvents and reagents were obtained from commercial sources (Adamas-beta®, Energy Chemical®) and used without further purification. For product purification by flash column chromatography, silicagel (200~300 mesh). NMR data including ^{1}H NMR, ^{13}C NMR spectra were recorded on Bruker Ascend^{TM} 400MHz. ^{1}H NMR Chemical shifts were reported in ppm relative to residual signals of the solvents ($CDCl_3$: 7.26 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$: 77.16 ppm). Chiral HPLC analyses were performed on Agilent 1100 Series using Chiralpak AD-H (4.6 mm x 250 mm) column or OD-H (4.6 mm x 250 mm) column with hexane/^{i}PrOH as the eluent. High resolution mass spectra were obtained from Thermo Scientific Q Exactive. X-ray diffraction data collection of the compounds were recorded by Bruker D8 VENTURE system with PHOTON II CPAD detector and a Ga-target Liquid METALJET D2 PLUS X-ray Source (λ = 1.34139 Å). The structure was solved by SHELXT (version 2018/2) and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3) through the OLEX2 graphical interface.

Optimization Experiments

Investigation of Phenyl Boronic Reagent [a,b]

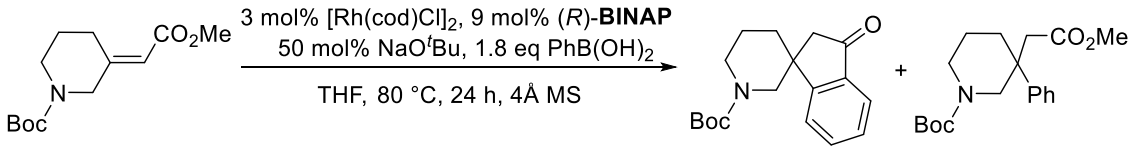


(*E*)-**1a** **2aa** **3a**

Entry	Boron Reagent	Conv. (%)	2aa (%)	3a (%)
1	$Ph(OH)_2$	73	42	31
2	PhBpin	84	41	43
3		NR		
4		45	31	14
5		71	25	46
6		18	<5	14
7	$PhBF_3K$	NR		
8	$NaBPh_4$	NR		

[a]Conditions: (*E*)-**1a** (0.22 mmol), phenyl boron reagent (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), **dppp** (9 mol%), NaO^{t}Bu (50 mol%), THF (2 mL), 4Å MS, 80 °C, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard.

Investigation of Privileged Substrate [a,b,c]

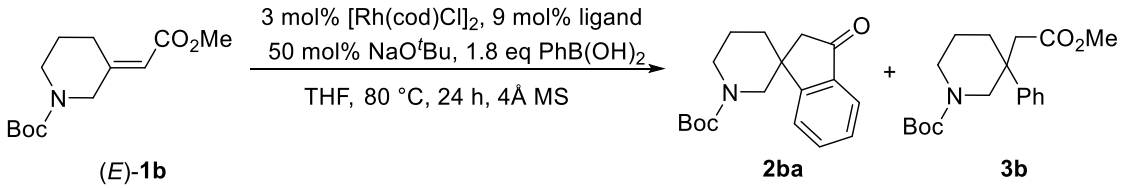


1b **2ba** **3b**

Entry	Substrate	Conv. (%)	2ba (%)	3b (%)	Ee (%)
1	(*E*)-**1b**	>99	31	69	89
2	(*Z*)-**1b**	>99	57	42	-51

[a]Conditions: **1b** (0.22 mmol), phenyl boronic acid (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), (*R*)-**BINAP** (9 mol%), NaO^{t}Bu (50 mol%), THF (2 mL), 4Å MS, 80 °C, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard. [c]The enantiomeric excess (ee) was determined by chiral HPLC.

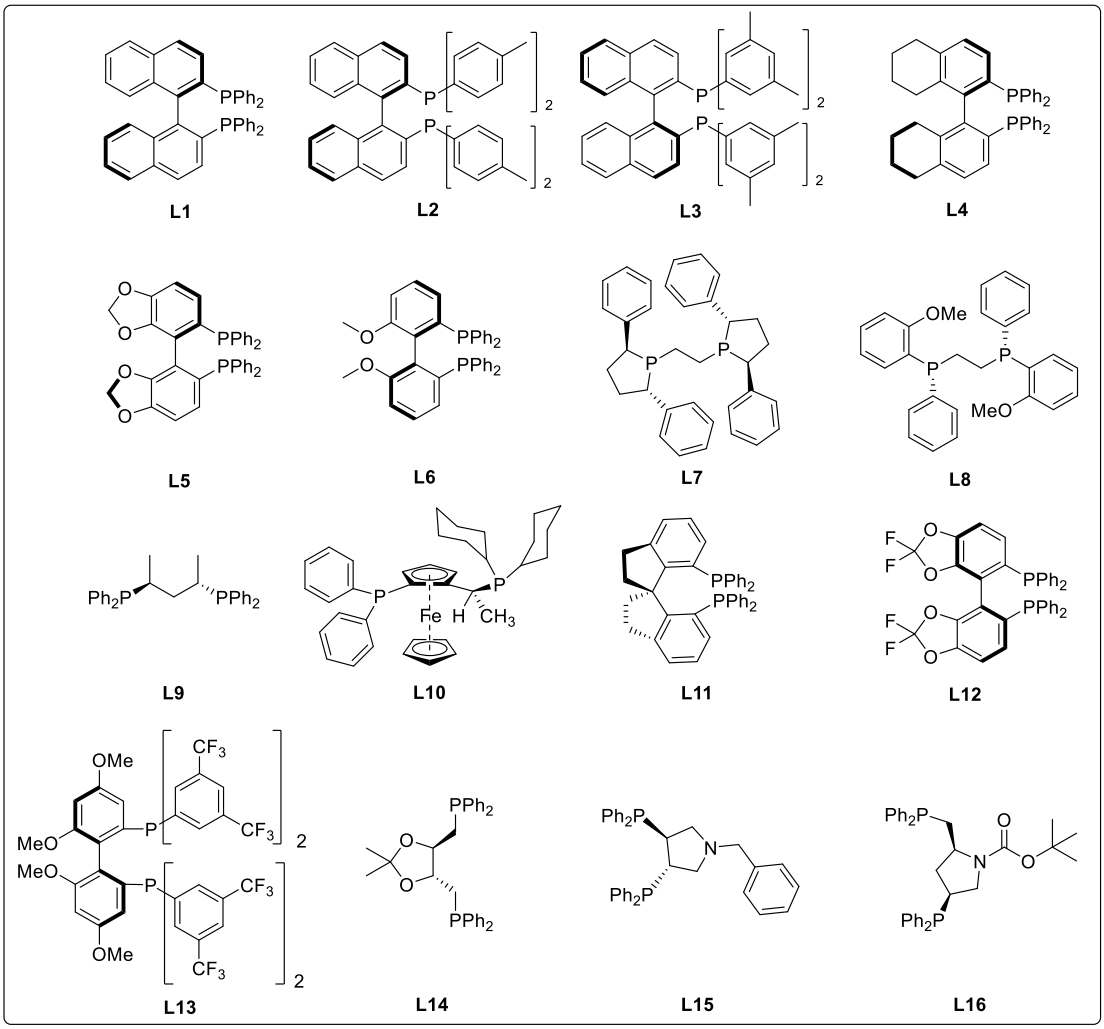
Investigation of Ligand [a,b,c]



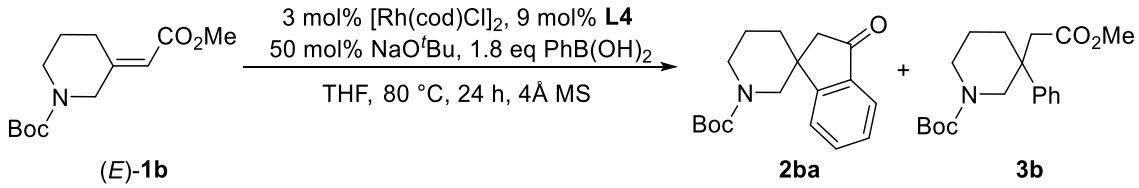
(*E*)-**1b** **2ba** **3b**

Entry	Ligand	Conv. (%)	2ba (%)	3b (%)	Ee (%)
1	**L1**	>99	31	69	89
2	**L2**	>99	33	67	89
3	**L3**	>99	37	63	-86
4	**L4**	>99	38	62	91
5	**L5**	>99	41	59	87
6	**L6**	>99	28	72	87
7	**L7**	>99	46	54	46
8	**L8**	87	46	41	2
9	**L9**	31	<5	26	-
10	**L10**	48	8	40	-
11	**L11**	10	<5	6	-
12	**L12**	>99	41	59	-85
13	**L13**	>99	35	65	-70
14	**L14**	40	27	13	-14
15	**L15**	82	39	42	-19
16	**L16**	16	8	8	-

[a]Conditions: (*E*)-**1b** (0.22 mmol), phenyl boronic acid (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), ligand (9 mol%), NaO^{t}Bu (50 mol%), THF (2 mL), 4Å MS, 80 °C, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard. [c]The enantiomeric excess (ee) was determined by chiral HPLC.


L1
L2
L3
L4
L5
L6
L7
L8
L9
L10
L11
L12
L13
L14
L15
L16

Effect of dewatering conditions on background reactions [a,b,c]

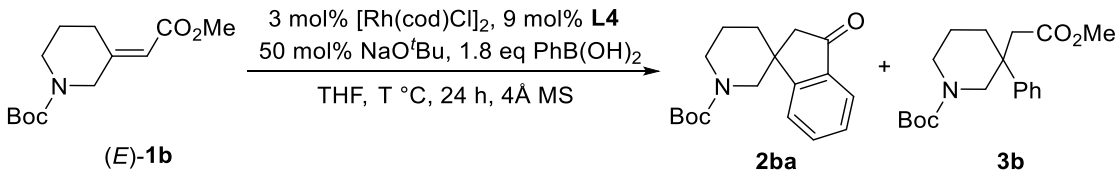


(*E*)-**1b** **2ba** **3b**

Entry	Dewatering conditions	Conv. (%)	2ba (%)	3b (%)	Ee (%)
1	Schlenk line	>99	38	62	91
2	Glove box	>99	65	35	91

[a]Conditions: (*E*)-**1b** (0.22 mmol), phenyl boronic acid (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), **L4** (9 mol%), NaO^{t}Bu (50 mol%), THF (2 mL), 4Å MS, 80 °C, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard. [c]The enantiomeric excess (ee) was determined by chiral HPLC.

Investigation of Temperature [a,b,c,d]

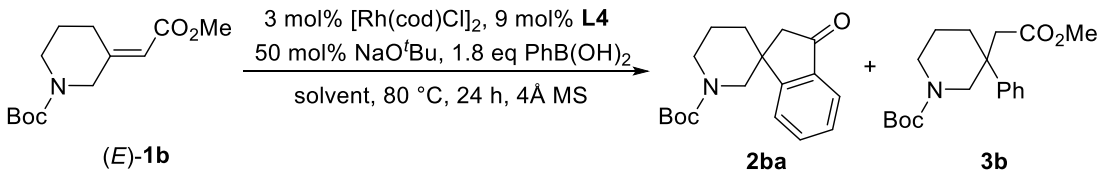


(*E*)-**1b** **2ba** **3b**

Entry	Temperature	Conv. (%)	2ba (%)	3b (%)	Ee (%)
1	60	>99	61	39	89
2	80	>99	65	35	91
3	90	>99	69	22	83
4	110	>99	75	21	40

[a]Conditions: (*E*)-**1b** (0.22 mmol), phenyl boronic acid (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), **L4** (9 mol%), NaO^{t}Bu (50 mol%), THF (2 mL), 4Å MS, heat, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard. [c]The enantiomeric excess (ee) was determined by chiral HPLC. [d]All reactions were set up in glovebox.

Investigation of Solvent [a,b,c,d]

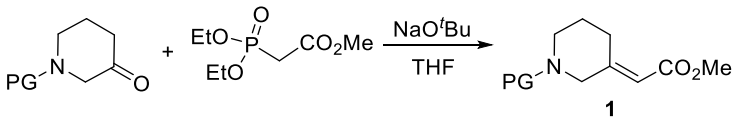


(*E*)-**1b** **2ba** **3b**

Entry	Solvent	Conv. (%)	2ba (%)	3b (%)	Ee (%)
1	THF	>99	65	35	91
2	DME	>99	68	32	93
3	Toluene	>99	71	29	91
4	Dioxane	NR			

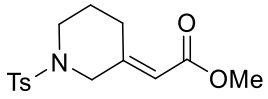
[a]Conditions: (*E*)-**1b** (0.22 mmol), phenyl boronic acid (1.8 eq), $[Rh(cod)Cl]_2$ (3 mol%), **L4** (9 mol%), NaO^{t}Bu (50 mol%), solvent (2 mL), 4Å MS, 80 °C, 24 h. [b]Conversion and yield were determined by ^{1}H NMR analysis using trimethoxybenzene as an internal standard. [c]The enantiomeric excess (ee) was determined by chiral HPLC. [d]All reactions were set up in glovebox.

General Procedure for the Synthesis of 1 and Characterization Data



1

General Procedure: solution of NaO^{t}Bu (499 mg, 5.20 mmol) in THF (10 mL) was cooled in a 100 mL flask in an ice bath. A solution of phosphonate ester (6.76 mmol, 1.30 equiv) in THF (10 mL) was added drop-wise. The reaction was warmed to room temperature for 1 h then cooled back to 0 °C. Then a solution of 3-Piperidinone (5.20 mmol, 1.00 equiv) in THF (10 mL) was added drop-wise over 30 min. The resulting reaction mixture was stirred overnight at room temperature, then quenched with water and concentrated to remove THF. The resulting aqueous solution was extracted with ethyl acetate. The combined organic layers were washed with brine and dried with Na_2SO_4, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give product[1].



1a

Methyl (*E*)-2-(1-tosylpiperidin-3-ylidene)acetate (1a)

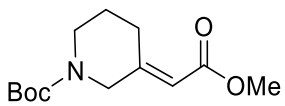
Following the general procedure, the desired product **1a** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as a white solid (1.19 g, 74%).

mp: 113-115℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.79 (s, 1H), 3.69 (s, 3H), 3.55 (s, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 5.7 Hz, 2H), 2.43 (s, 3H), 1.78 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 152.23, 143.94, 133.08, 129.87, 127.89, 116.79, 53.52, 51.37, 46.60, 26.90, 24.85, 21.67.

HRMS (ESI) *m/z* calcd for $C_{15}H_{20}NO_4S^+$ $(M+H)^+$ 310.1108, found 310.1105.



1b

***Tert*-butyl (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1b)**

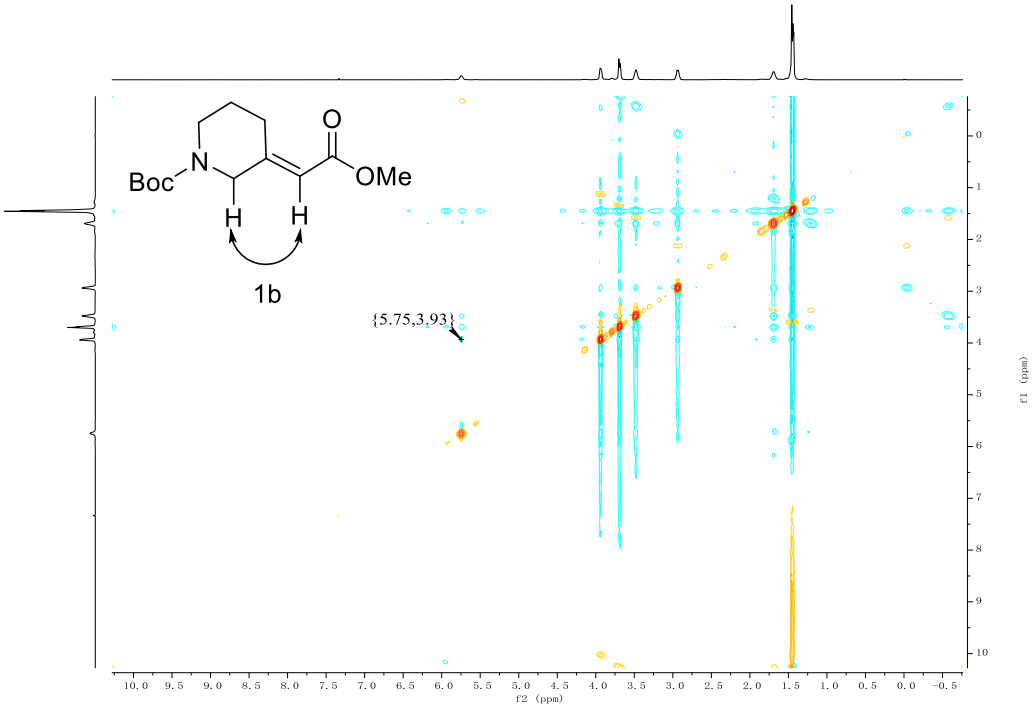
Following the general procedure, the desired product **1b** was obtained by silica gel column

chromatography (PE : EA = 30 : 1) as a white solid (1.03 g, 78%).

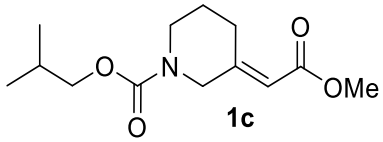
mp: 39-41℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (s, 1H), 3.94 (s, 2H), 3.70 (s, 3H), 3.48 (t, *J* = 4.0 Hz, 2H), 2.94 (t, *J* = 5.6 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.45 (s, 9H).

NOESY spectrum of **(*E*)-1b**:



The *E* configuration of 1b is confirmed by the correlation signals of H (5.75) and H (3.93).

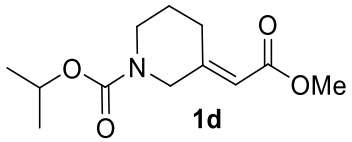


Isobutyl (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1c)

Following the general procedure, the desired product **1c** was obtained by silica gel column chromatography (PE : EA = 6 : 1) as colorless oil (1.02 g, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 1H), 3.94 (s, 2H), 3.80 (d, *J* = 6.7 Hz, 2H), 3.64 (s, 3H), 3.49 (t, *J* = 5.0 Hz, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.80 (m, 1H), 1.71 – 1.60 (m, 2H), 0.88 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.62, 155.37, 154.48, 115.35, 71.62, 51.47, 51.10, 44.26, 27.97, 27.50, 25.28, 19.09.
HRMS (ESI) *m/z* calcd for $C_{13}H_{21}NO_4Na^+$ $(M+Na)^+$ 278.1363, found 278.1366.



1d

Isopropyl (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1d)

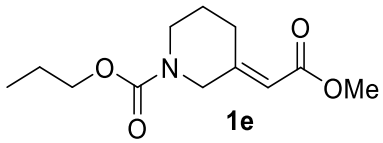
Following the general procedure, the desired product **1d** was obtained by silica gel column chromatography (PE : EA = 15 : 1) as a white solid (953 mg, 76%).

mp: 47-49℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 4.95 – 4.85 (m, 1H), 3.97 (s, 2H), 3.69 (s, 3H), 3.52 (t, *J* = 5.8 Hz, 2H), 2.94(t, *J* = 5.9 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.23 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.83, 155.12, 154.76, 115.38, 68.92, 51.25, 44.28, 27.65, 25.37, 22.34.

HRMS (ESI) *m/z* calcd for $C_{12}H_{19}NO_4Na^+$ $(M+Na)^+$ 264.1207, found 264.1212.



1e

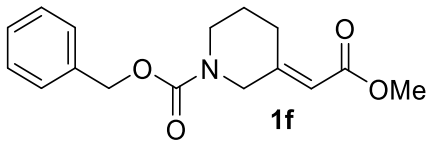
Propyl (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1e)

Following the general procedure, the desired product **1e** was obtained by silica gel column chromatography (PE : EA = 6 : 1) as colorless viscous liquid (890 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (s, 1H), 3.99 (t, *J* = 8.0 Hz, 2H), 3.95 (s, 2H), 3.66 (s, 3H), 3.50 (t, *J* = 4.0 Hz, 2H), 2.92 (t, *J* = 6.4 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.64 – 1.55 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 155.47, 154.55, 115.42, 67.16, 51.17, 44.29, 27.55, 25.30, 22.38, 18.45, 10.47.

HRMS (ESI) *m/z* calcd for $C_{12}H_{19}NO_4Na^+$ $(M+Na)^+$ 264.1207, found 264.1203.



1f

Benzyl (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (1f)

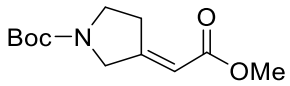
Following the general procedure, the desired product **1f** was obtained by silica gel column

chromatography (PE : EA = 6 : 1) as colorless viscous liquid (1.03 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 5H), 5.78 (s, 1H), 5.12 (s, 2H), 4.01 (s, 2H), 3.69 (s, 3H), 3.56 (t, *J* = 5.8 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 1.77 – 1.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.75, 154.35, 136.68, 128.69, 128.61, 128.15, 128.00, 115.67, 67.37, 51.26, 44.47, 27.55, 25.28, 14.36.

HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NO_4Na^+$ $(M+Na)^+$ 312.1207, found 312.1210.



1g

***tert*-Butyl (*E*)-3-(2-methoxy-2-oxoethylidene)pyrrolidine-1-carboxylate (1g)**

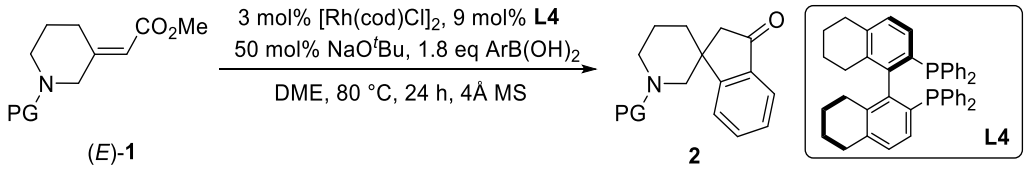
Following the general procedure, the desired product **1g** was obtained by silica gel column chromatography (PE : EA = 15 : 1) as colorless viscous liquid (953 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 4.12 (s, 2H), 3.71 (s, 3H), 3.56 (s, 2H), 3.13 (t, *J* = 8.0 Hz, 2H), 1.47 (s, 9H).

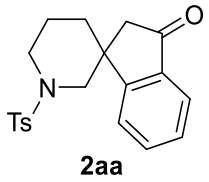
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 166.52, 121.83, 112.28, 79.94, 51.62, 51.33, 28.58, 28.41, 28.12.

HRMS (ESI) *m/z* calcd for $C_{12}H_{19}NO_4Na^+$ $(M+Na)^+$ 264.1207, found 264.1211.

General Procedure for the Synthesis of 2 and Characterization Data



General Procedure: An oven-dried Schlenk tube (10 mL) containing a stirring bar was cooled to room temperature. The Schlenk tube was then introduced in a glovebox, where it was charged with $[Rh(cod)Cl]_2$ (3.3 mg, 0.0066 mmol, 3 mol%), ligand **L4** (12.5 mg, 0.0198 mmol, 9 mol%), NaO^{t}Bu (10.6 mg, 0.11 mmol, 50 mol%), aryl boronic acid (0.40 mmol, 1.8 equiv), (*E*)-3-(2-methoxy-2-oxoethylidene)piperidine-1-carboxylate (*E*)-**1** (0.22 mmol, 1.0 equiv) and 4Å MS. The tube was taken out of the glovebox. Subsequently, the degassed anhydrous DME (2 mL) was added into the tube and the tube was sealed. The reaction mixture was stirred at 80 °C in an oil bath for 24 h. After being allowed to cool to room temperature, the resulting reaction mixture was quenched with aqueous NH_4Cl, then diluted with ethyl acetate, filtered through a Celite plug, and concentrated to remove DME. If necessary, the crude product was analyzed by ^{1}H NMR for the conversion and yield. The crude mixture was purified by column chromatography on silica gel to afford the desired product[2].



2aa

1'-tosylspiro[indene-1,3'-piperidin]-3(2*H*)-one (2aa)

Following the general procedure, the desired product **2aa** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as a white solid (47.7 mg, 61% yield). ee = 91%. $[\alpha]_D^{25}$ = – 43.2 (*c* 1.0, CH_2Cl_2).

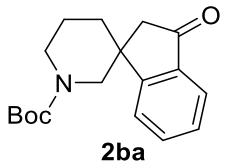
mp: 128-130℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.37 (d, *J* = 11.4 Hz, 1H), 2.94 (d, *J* = 19.2 Hz, 1H), 2.56 (d, *J* = 9.7 Hz, 2H), 2.51 (s, 1H), 2.44 (s, 3H), 1.93 – 1.79 (m, 2H), 1.73 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.28, 158.61, 143.85, 136.65, 134.96, 133.25, 129.89, 128.79, 127.75, 124.33, 124.16, 56.02, 47.84, 46.30, 42.73, 35.79, 22.88, 21.70.

HRMS (ESI) *m/z* calcd for $C_{20}H_{21}NO_3SNa^+$ $(M+Na)^+$ 378.1135, found 378.1135.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 22.23 min, t2 (major) = 34.04 min.



2ba

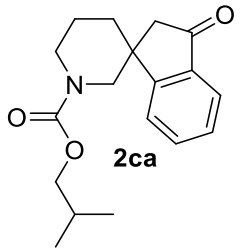
***tert*-Butyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2ba)**

Following the general procedure, the desired product **2ba** was obtained by silica gel column chromatography (PE : EA = 7 : 1) as light yellow viscous liquid (38.4 mg, 58% yield). ee = 92%. $[\alpha]_D^{25}$ = +2.4 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 1H), 7.67 – 7.58 (m, 1H), 7.54 – 7.47 (m, 1H), 7.47 – 7.37 (m, 1H), 4.26 – 3.66 (m, 2H), 3.12 – 2.66 (m, 3H), 2.46 (d, *J* = 18.7 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.82 – 1.68 (m, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.95, 159.59, 136.59, 134.99, 129.85, 128.49, 124.21, 124.06, 80.16, 47.27, 43.31, 36.74, 29.83, 28.54, 23.00, 22.82.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 21.86 min, t2 (major) = 33.66 min.



2ca

Isobutyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2ca)

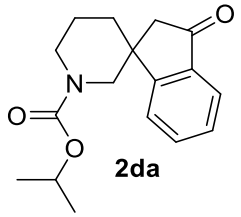
Following the general procedure, the desired product **2ca** was obtained by silica gel column chromatography (PE : EA = 4 : 1) as yellow viscous liquid (27.2 mg, 41% yield). ee = 93%. $[\alpha]_D^{25}$ = +7.6 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 4.31 – 4.12 (m, 1H), 4.02 – 3.73 (m, 3H), 3.19 – 2.66 (m, 3H), 2.47 (d, *J* = 19.0 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.85 – 1.67 (m, 3H), 1.35 – 1.22 (m, 1H), 0.99 – 0.78 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.70, 159.37, 155.60, 136.62, 135.03, 128.56, 124.21, 124.10, 71.88, 54.07, 47.29, 43.95, 43.19, 36.63, 28.06, 22.94, 19.23.

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}NO_3Na^+$ $(M+Na)^+$ 324.1571, found 324.1576.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 365 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t1 (minor) = 16.79 min, t2 (major) = 18.25 min.



Isopropyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2da)

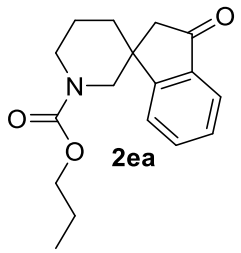
Following the general procedure, the desired product **2da** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as light yellow viscous liquid (39.2 mg, 62% yield). ee = 91%. $[\alpha]_D^{25}$ = +2.9 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.97 – 4.84 (m, 1H), 4.35 – 3.73 (m, 2H), 3.19 – 2.61 (m, 3H), 2.46 (d, *J* = 19.1 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.82 – 1.59 (m, 3H), 1.22 (d, *J* = 8.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.81, 159.45, 155.22, 136.64, 135.00, 128.53, 124.21, 124.07, 69.01, 47.24, 43.84, 43.25, 36.70, 22.97, 22.36, 22.30.

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}NO_3Na^+$ $(M+Na)^+$ 310.1414, found 310.1418.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 365 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t1 (minor) = 14.13 min, t2 (major) = 16.15 min.



Propyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2ea)

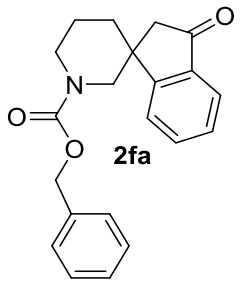
Following the general procedure, the desired product **2ea** was obtained by silica gel column chromatography (PE : EA = 6 : 1) as colorless viscous liquid (29.7 mg, 47% yield). ee = 91%. $[\alpha]_D^{25}$ = +19.8 (*c* 0.6, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 4.25 (s, 1H), 4.09 – 3.97 (m, 2H), 3.82 (d, *J* = 11.8 Hz, 1H), 3.15 – 2.68 (m, 3H), 2.48 (d, *J* = 19.1 Hz, 1H), 2.00 (q, *J* = 6.0 Hz, 1H), 1.67 – 1.60 (m, 3H), 1.25 (s, 2H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.80, 159.41, 136.65, 135.04, 130.16, 129.87, 128.58, 124.11, 67.35, 47.29, 43.21, 36.64, 29.85, 25.66, 22.84, 22.46, 10.55.

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}NO_3Na^+$ $(M+Na)^+$ 310.1414, found 310.1419.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (major) = 29.76 min, t2 (minor) = 32.94 min.



2fa

Benzyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2fa)

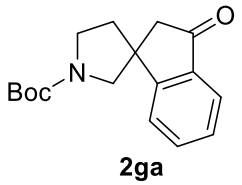
Following the general procedure, the desired product **2fa** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as colorless viscous liquid (42.7 mg, 58% yield). ee = 93%. $[\alpha]_D^{25}$ = –144.5 (*c* 0.4, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.25 (m, 5H), 5.22 – 4.98 (m, 2H), 4.31 – 3.81 (m, 2H), 3.20 – 2.64 (m, 3H), 2.46 (d, *J* = 19.0 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.83 – 1.63 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.53, 159.17, 155.28, 136.52, 134.95, 128.58, 128.49, 128.27,128.16, 128.05, 124.13, 123.98, 67.37, 54.04, 47.20, 44.04, 43.07, 36.51, 22.79.

HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_3Na^+$ $(M+Na)^+$ 358.1414, found 358.1418.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 365 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t1 (minor) = 35.85 min, t2 (major) = 39.22 min.



2ga

***tert*-Butyl 3-oxo-2,3-dihydrospiro[indene-1,3'-pyrrolidine]-1'-carboxylate (2ga)**

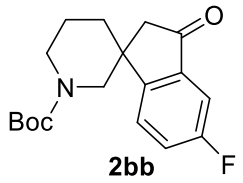
Following the general procedure, the desired product **2ga** was obtained by silica gel column chromatography (PE : EA = 8 : 1) as colorless viscous liquid (34.1 mg, 54% yield). ee = 81%. $[\alpha]_D^{25}$ = +1.7 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 3.81 – 3.68 (m, 1H), 3.66 – 3.46 (m, 3H), 2.79 – 2.61 (m, 2H), 2.37 – 2.24 (m, 2H), 1.48 (d, *J* = 18.4 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.28, 157.25, 154.57, 136.85, 135.52, 128.62, 124.11, 123.84, 79.93, 58.94, 50.10, 45.62, 40.22, 38.99, 28.62.

HRMS (ESI) *m/z* calcd for $C_{17}H_{21}NO_3Na^+$ $(M+Na)^+$ 310.1414, found 310.1418.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 20.74 min, t2 (major) = 29.22 min.



2bb

***tert*-Butyl 5-fluoro-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bb)**

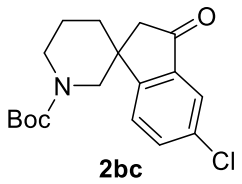
Following the general procedure, the desired product **2bb** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as colorless oil (38.6 mg, 55% yield). ee = 98%. $[\alpha]_D^{25}$ = – 10.4 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.6, 4.5 Hz, 1H), 7.41 – 7.28 (m, 2H), 4.25 – 3.64 (m, 2H), 3.10 – 2.68 (m, 3H), 2.48 (d, *J* = 19.1 Hz, 1H), 1.89 (t, *J* = 12.6 Hz, 1H), 1.82 – 1.65 (m, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.66, 203.64, 164.14, 161.67, 155.05, 155.03, 138.50, 138.43, 125.78, 125.70, 122.66, 122.43, 110.02, 109.81, 80.22, 54.53, 47.63, 42.93, 36.79, 29.80, 28.50, 23.02.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}FNO_3Na^+$ $(M+Na)^+$ 342.1476, found 342.1479.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 22.77 min, t2 (major) = 27.73 min.



2bc

***tert*-Butyl 5-chloro-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bc)**

Following the general procedure, the desired product **2bc** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as a white solid (29.5 mg, 40% yield). ee = 92%. $[\alpha]_D^{25}$ = +15.8 (*c* 0.8, CH_2Cl_2).

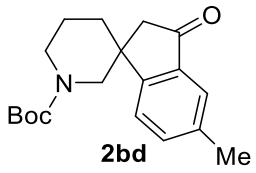
mp: 107-109℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.58 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 4.22 – 3.69 (m, 2H), 3.09 – 2.70 (m, 3H), 2.49 (d, *J* = 19.1 Hz, 1H), 1.95 – 1.84 (m, 1H), 1.82 – 1.68 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.39, 157.59, 138.12, 134.97, 129.30, 128.53, 125.52, 123.92, 80.32, 47.42, 43.11, 36.67, 29.83, 28.52, 22.96, 14.27.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}ClNO_3Na^+$ $(M+Na)^+$ 358.1181, found 358.1199.

HPLC conditions: hexane/2-propanol = 85/15, 1 mL/min, λ = 365 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t1 (major) = 17.36 min, t2 (minor) = 20.96 min.



2bd

***tert*-Butyl 5-methyl-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bd)**

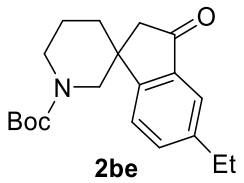
Following the general procedure, the desired product **2bd** was obtained by silica gel column chromatography (PE : EA = 6 : 1) as colorless oil (24.9 mg, 36% yield). ee = 92%. $[\alpha]_D^{25}$ = +65.0 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 4.27 – 3.67 (m, 2H), 3.10 – 2.66 (m, 3H), 2.46 (d, *J* = 19.0 Hz, 1H), 2.42 (s, 3H), 1.96 – 1.84 (m, 1H), 1.79 – 1.61 (m, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.06, 157.07, 154.71, 138.57, 136.75, 136.16, 124.00, 123.90, 80.09, 54.52, 47.56, 42.97, 36.81, 29.84, 28.54, 23.05, 21.25.

HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NO_3Na^+$ $(M+Na)^+$ 338.1727, found 338.1731.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 19.51 min, t2 (major) = 26.81 min.



2be

***tert*-Butyl 5-ethyl-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2be)**

Following the general procedure, the desired product **2be** was obtained by silica gel column chromatography (PE : EA = 7 : 1) as a white solid (41.3 mg, 57% yield). ee = 93%. $[\alpha]_D^{25}$ = +6.5 (*c* 0.8, CH_2Cl_2).

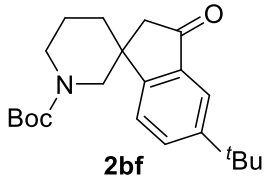
mp: 49-51℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 6.1 Hz, 1H), 4.25 – 3.70 (m, 2H), 3.08 – 2.68 (m, 5H), 2.46 (d, *J* = 18.8 Hz, 1H), 1.91 (t, *J* = 12.3 Hz, 1H), 1.81 – 1.65 (m, 3H), 1.42 (s, 9H), 1.27 – 1.24 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.16, 157.32, 154.75, 144.91, 136.79, 135.23, 123.99, 122.72, 80.08, 54.53, 47.57, 42.97, 36.79, 29.83, 28.62, 23.06, 15.53.

HRMS (ESI) *m/z* calcd for $C_{20}H_{27}NO_3Na^+$ $(M+Na)^+$ 352.1884, found 352.1888.

HPLC conditions: hexane/2-propanol = 85/15, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 25.91 min, t2 (major) = 38.88 min.



2bf

***tert*-Butyl 5-(*tert*-butyl)-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bf)**

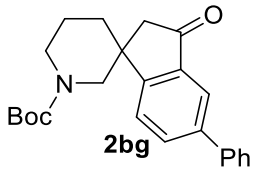
Following the general procedure, the desired product **2bf** was obtained by silica gel column chromatography (PE : EA = 10 : 1) as colorless viscous liquid (53.4 mg, 68% yield). ee = 93 %. $[\alpha]_D^{25}$ = +12.8 (*c* 0.8, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 4.25 – 3.72 (m, 2H), 3.10 – 2.68 (m, 3H), 2.47 (d, *J* = 18.9 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.80 – 1.68 (m, 3H), 1.42 (s, 9H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.36, 157.09, 154.79, 152.02, 136.51, 132.78, 123.80, 120.37, 80.08, 47.69, 42.90, 36.80, 35.05, 31.45, 29.84, 28.57, 23.11, 14.27.

HRMS (ESI) *m/z* calcd for $C_{22}H_{31}NO_3Na^+$ $(M+Na)^+$ 380.2197, found 380.2207.

HPLC conditions: hexane/2-propanol = 85/15, 1 mL/min, λ = 365 nm, Chiralpak OD-H column (4.6 mm x 250 mm), t1 (major) = 10.91 min, t2 (minor) = 12.59 min.



***tert*-Butyl 3-oxo-5-phenyl-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate(2bg)**

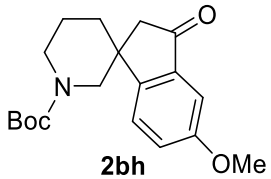
Following the general procedure, the desired product **2bg** was obtained by silica gel column chromatography (PE : EA = 9 : 1) as light yellow oil (50.6 mg, 61% yield). ee = 91%. $[\alpha]_D^{25}$ = +24.6 (*c* 0.3, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.8 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.36 (m, 1H), 4.30 – 3.74 (m, 2H), 3.17 – 2.70 (m, 3H), 2.53 (d, *J* = 19.1 Hz, 1H), 1.98 (td, *J* = 13.4, 4.6 Hz, 1H), 1.85 – 1.65 (m, 3H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.88, 158.48, 141.89, 139.87, 137.25, 133.04, 129.13, 128.05, 127.31, 124.60, 122.22, 80.20, 47.66, 47.64, 43.16, 36.82, 29.85, 28.57, 23.05.

HRMS (ESI) *m/z* calcd for $C_{24}H_{27}NO_3Na^+$ $(M+Na)^+$ 400.1884, found 400.1889.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 36.14 min, t2 (major) = 46.68 min.



***tert*-Butyl 5-methoxy-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bh)**

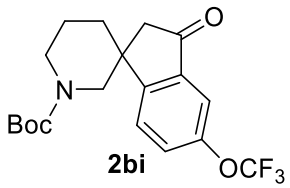
Following the general procedure, the desired product **2bh** was obtained by silica gel column chromatography (PE : EA = 7 : 1) as colorless viscous liquid (32.1 mg, 44% yield). ee = 95%. $[\alpha]_D^{25}$ = –2.4 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.19 (s, 1H), 4.18 (s, 1H), 3.84 (s, 3H), 3.71 (s, 1H), 3.12 – 2.63 (m, 3H), 2.47 (d, *J* = 19.0 Hz, 1H), 1.89 (td, *J* = 12.7, 3.8 Hz, 1H), 1.80 – 1.64 (m, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.85, 160.65, 160.18, 152.49, 137.86, 124.98, 124.13, 105.26, 80.11, 55.79, 47.75, 42.68, 36.86, 29.84, 28.54, 23.24, 23.17.

HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NO_4Na^+$ $(M+Na)^+$ 354.1676, found 354.1655.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 24.26 min, t2 (major) = 31.86 min.



2bi

***tert*-Butyl 3-oxo-5-(trifluoromethoxy)-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bi)**

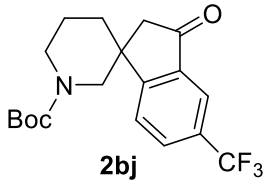
Following the general procedure, the desired product **2bi** was obtained by silica gel column chromatography (PE : EA = 8 : 1) as colorless oil (42.4 mg, 50% yield). ee = 98%. $[\alpha]_D^{25}$ = – 2.0 (*c* 0.3, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 4.24 – 3.71 (m, 2H), 3.13 – 2.73 (m, 3H), 2.52 (d, *J* = 19.2 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.84 – 1.65 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.38, 157.54, 149.53, 138.26, 127.76, 125.78, 121.80, 119.23, 115.82, 80.33, 47.58, 43.16, 36.71, 29.86, 28.54, 22.94, 22.84.

HRMS (ESI) *m/z* calcd for $C_{19}H_{22}F_3NO_4Na^+$ $(M+Na)^+$ 408.1394, found 408.1392.

HPLC conditions: hexane/2-propanol = 85/15, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (major) = 16.29 min, t2 (minor) = 24.93 min.



2bj

***tert*-Butyl 3-oxo-5-(trifluoromethyl)-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bj)**

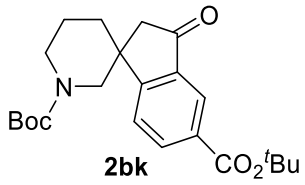
Following the general procedure, the desired product **2bj** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as colorless viscous liquid (45.5 mg, 56% yield). ee = 92%. $[\alpha]_D^{25}$ = +3.8 (*c* 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 4.21 (s, 1H), 3.75 (s, 1H), 3.18 – 2.71 (m, 3H), 2.53 (d, *J* = 19.3 Hz, 1H), 2.01 – 1.90 (m, 1H), 1.83 – 1.63 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.39, 162.53, 154.65, 137.05, 131.55, 131.52, 131.48, 131.45, 129.00, 125.09, 122.38, 121.44, 121.40, 121.37, 121.33, 80.38, 54.19, 52.80, 47.35, 43.65, 36.56, 28.50, 22.81.

HRMS (ESI) *m/z* calcd for $C_{19}H_{22}F_3NO_3Na^+$ $(M+Na)^+$ 392.1444, found 392.1458.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 13.66 min, t2 (major) = 20.81 min.



2bk

Di-*tert*-butyl 3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1',5-dicarboxylate (2bk)

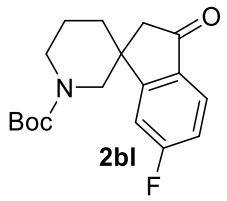
Following the general procedure, the desired product **2bk** was obtained by silica gel column chromatography (PE : EA = 9 : 1) as colorless oil (46.8 mg, 53% yield). ee = 91 %. $[\alpha]_D^{25}$ = +17.2 (*c* 0.7, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.27 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 4.21 (s, 1H), 3.72 (s, 1H), 3.11 – 2.75 (m, 3H), 2.52 (d, *J* = 19.1 Hz, 1H), 1.95 (t, *J* = 12.9 Hz, 1H), 1.84 – 1.69 (m, 3H), 1.60 (s, 9H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.17, 171.32, 164.82, 163.27, 136.71, 135.82, 132.81, 125.33, 124.20, 82.00, 80.30, 60.56, 47.48, 43.57, 29.85, 28.53, 28.32, 21.22, 14.35.

HRMS (ESI) *m/z* calcd for $C_{23}H_{31}NO_5Na^+$ $(M+Na)^+$ 424.2095, found 424.2097.

HPLC conditions: hexane/2-propanol = 95/5, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 30.92 min, t2 (major) = 46.68 min.



***tert*-Butyl 6-fluoro-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bl)**

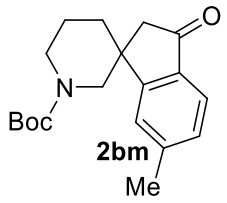
Following the general procedure, the desired product **2bl** was obtained by silica gel column chromatography (PE : EA = 8 : 1) as light yellow viscous liquid (32.3 mg, 46% yield). ee = 90%. $[\alpha]_D^{25}$ = –2.0 (*c* 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (td, *J* = 7.9, 4.9 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 8.7 Hz, 1H), 4.28 – 3.69 (m, 2H), 3.11 – 2.68 (m, 3H), 2.49 (d, *J* = 18.9 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.68 – 1.56 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.99, 161.70, 160.13, 157.50, 136.95, 136.87, 124.38, 124.26, 120.05, 120.01, 115.52, 115.33, 80.31, 47.72, 43.48, 36.71, 32.05, 29.82, 28.52, 22.82.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}FNO_3Na^+$ $(M+Na)^+$ 342.1476, found 342.1490.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 24.39 min, t2 (major) = 38.25 min.



***tert*-Butyl 6-methyl-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bm)**

Following the general procedure, the desired product **2bm** was obtained by silica gel column chromatography (PE : EA = 5 : 1) as colorless oil (38.1 mg, 55% yield). ee = 94%. $[\alpha]_D^{25}$ = +15.8 (*c* 0.8, CH_2Cl_2).

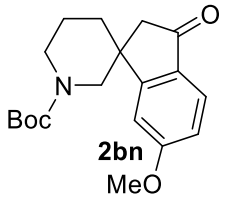
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.28 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 4.26 – 3.70 (m, 2H), 3.10 – 2.64 (m, 3H), 2.52 – 2.38 (m, 4H), 1.91 (td, *J* = 13.3, 3.6 Hz, 1H), 1.82 – 1.64 (m, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.45, 160.09, 154.75, 146.19, 134.31, 129.70, 124.59, 123.87, 80.07, 54.48, 53.56, 47.47, 43.10, 36.70, 28.52, 23.00, 22.39.

HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NO_3Na^+$ $(M+Na)^+$ 338.1727, found 338.1731.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H

column (4.6 mm x 250 mm), t1 (minor) = 18.19 min, t2 (major) = 30.90 min.



***tert*-Butyl 6-methoxy-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bn)**

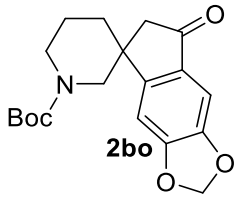
Following the general procedure, the desired product **2bn** was obtained by silica gel column chromatography (PE : EA = 3 : 1) as colorless viscous liquid (21.9 mg, 30% yield). ee = 92%. $[\alpha]_D^{25}$ = +16.5 (*c* 0.4, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 4.31 – 4.07 (m, 1H), 3.90 – 2.72 (m, 4H), 3.08 – 2.66 (m, 3H), 2.45 (d, *J* = 18.9 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.81 – 1.64 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.12, 165.45, 162.44, 154.76, 129.85, 125.86, 115.65, 108.17, 80.14, 55.88, 47.53, 43.12, 36.68, 29.81, 28.55, 22.94, 22.85.

HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NO_4Na^+$ $(M+Na)^+$ 354.1676, found 354.1690.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 29.14 min, t2 (major) = 39.81 min.



***tert*-Butyl 7-oxo-6,7-dihydrospiro[indeno[5,6-d][1,3]dioxole-5,3'-piperidine]-1'-carboxylate (2bo)**

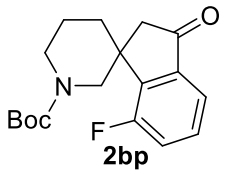
Following the general procedure, the desired product **2bo** was obtained by silica gel column chromatography (PE : EA = 4 : 1) as light yellow viscous liquid (38.0 mg, 50% yield). ee = 91 %. $[\alpha]_D^{25}$ = –6.1 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.14 (s, 2H), 4.24 – 3.70 (m, 2H), 3.01 – 2.67 (m, 3H), 2.46 (d, *J* = 19.0 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.73 (d, *J* = 12.0 Hz, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.99, 153.82, 151.99, 148.38, 143.60, 119.76, 116.36, 114.31, 103.29, 80.09, 54.76, 47.92, 43.56, 37.04, 29.83, 28.54, 27.35.

HRMS (ESI) *m/z* calcd for $C_{19}H_{23}NO_5Na^+$ $(M+Na)^+$ 368.1469, found 368.1477.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 45.29 min, t2 (major) = 60.91 min.



2bp

***tert*-Butyl 7-fluoro-3-oxo-2,3-dihydrospiro[indene-1,3'-piperidine]-1'-carboxylate (2bp)**

Following the general procedure, the desired product **2bp** was obtained by silica gel column chromatography (PE : EA = 8 : 1) as a white solid (28.1 mg, 40% yield). ee = 90%. $[\alpha]_D^{25}$ = – 6.4 (*c* 0.3, CH_2Cl_2).

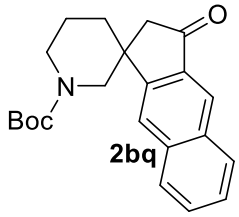
mp: 118-120℃

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.42 (td, *J* = 7.8, 4.3 Hz, 1H), 7.29 (t, *J* = 9.1 Hz, 1H), 4.36 – 3.77 (m, 2H), 3.44 – 3.23 (m, 1H), 2.92 – 2.68 (m, 2H), 2.52 (d, *J* = 19.4 Hz, 1H), 2.30 (td, *J* = 13.0, 3.9 Hz, 1H), 1.81 – 1.61 (m, 3H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.77, 161.78, 159.28, 144.34, 139.74, 130.48, 130.41, 122.33, 122.11, 120.00, 80.13, 52.10, 47.22, 43.75, 43.71, 34.59, 34.57, 29.85, 28.56, 23.10.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}FNO_3Na^+$ $(M+Na)^+$ 342.1476, found 342.1471.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 21.66 min, t2 (major) = 25.37 min.



2bq

***tert*-Butyl 3-oxo-2,3-dihydrospiro[cyclopenta[*b*]naphthalene-1,3'-piperidine]-1'-carboxylate (2bq)**

Following the general procedure, the desired product **2bq** was obtained by silica gel column chromatography (PE : EA = 7 : 1) as yellow viscous liquid (44.8 mg, 58% yield). ee = 90%. $[\alpha]_D^{25}$ = +88.9 (*c* 0.6, CH_2Cl_2).

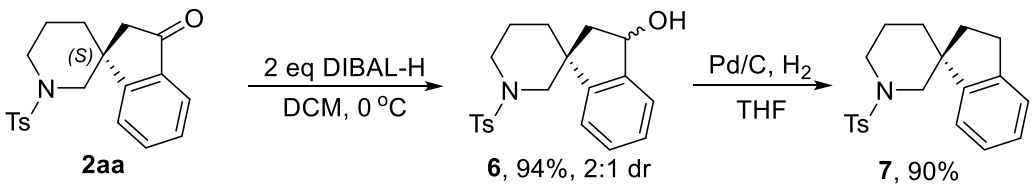
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 4.27 – 3.76 (m, 2H), 3.25 – 2.77 (m, 3H), 2.58 (d, *J* = 19.0 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.84 (d, *J* = 13.9 Hz, 2H), 1.77 – 1.65 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.88, 158.48, 154.71, 141.89, 139.87, 137.25, 134.04, 129.13, 128.05, 127.31, 124.60, 122.22, 80.20, 54.45, 47.66, 43.16, 36.82, 29.85, 28.57, 23.05.

HRMS (ESI) *m/z* calcd for $C_{22}H_{25}NO_3Na^+$ $(M+Na)^+$ 374.1727, found 374.1724.

HPLC conditions: hexane/2-propanol = 80/20, 1 mL/min, λ = 365 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t1 (minor) = 31.77 min, t2 (major) = 55.70 min.

Transformation Applications of Products



1'-tosyl-2,3-dihydrospiro[indene-1,3'-piperidin]-3-ol (6)

Following the reported procedure[3], to a solution of **2aa** (29.0 mg, 0.0815 mmol) in 2 mL of DCM at 0 °C under Ar was added dropwise a solution of DIBAL-H (1.2 M solution in hexane, 0.2 mL, 0.1632 mmol). Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and then carefully added dropwise to a stirred mixture of 2 M HCl (4 mL) and ice. After stirring for 30 min, the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford a colorless oil that was subjected to flash chromatography purification (PE : EA = 2 : 1) to afford **6** as colorless viscous liquid (27.3 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 11.0, 8.0 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.35 – 7.27 (m, 4H), 7.21 – 7.18 (m, 1H), 5.36 (t, *J* = 6.7 Hz, 1H), 5.25 (t, *J* = 5.3 Hz, 1H), 3.82 – 3.73 (m, 1H), 3.65 (d, *J* = 10.9 Hz, 1H), 3.50 (d, *J* = 11.4 Hz, 1H), 3.28 (d, *J* = 11.4 Hz, 1H), 2.93 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.56 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 2.40 – 2.31 (m, 1H), 2.28 (dd, *J* = 9.2, 3.1 Hz, 1H), 2.25 – 2.17 (m, 1H), 1.84 – 1.77 (m, 2H), 1.75 – 1.69 (m, 2H), 1.62 (dd, *J* = 13.8, 5.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.53, 146.88, 145.15, 144.81, 143.58, 143.54, 133.65, 133.48, 129,78, 129.77, 128.83, 128.66, 128.40, 128.33, 127.74, 127.71, 125.24, 124.91, 123.41, 123.10, 74.11, 74.01, 56.61, 55.51, 46.51, 46.49, 46.46, 46.14, 45.92, 36.17, 35.50, 29.85, 29.80, 22.62, 22.48, 21.68, 14.27.

HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_3SNa^+$ $(M+Na)^+$ 380.1291, found 380.1299.

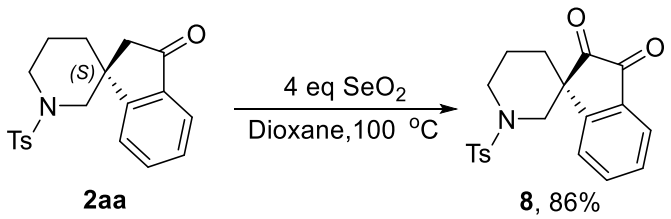
1'-tosyl-2,3-dihydrospiro[indene-1,3'-piperidine] (7)

A mixture of Pd/C(2.5 mg, 5% Pd on activated carbon) and **6** (27.3 mg, 0.0763 mmol) in MeOH (2 mL) is stirred under H_2 atmosphere (balloon) for 24 h. The resulting mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (PE : EA = 8 : 1) to afford **7** as white oil (23.4 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.12 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 3.75 (d, *J* = 11.1 Hz, 1H), 3.38 (d, *J* = 11.4 Hz, 1H), 3.01 (dt, *J* = 16.4, 8.2 Hz, 1H), 2.95 – 2.84 (m, 1H), 2.48 (ddd, *J* = 12.6, 8.4, 4.0 Hz, 1H), 2.43 (s, 3H), 2.38 (dd, *J* = 11.4, 3.4 Hz, 1H), 2.25 (d, *J* = 11.4 Hz, 1H), 1.89 – 1.73 (m, 3H), 1.71 – 1.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.67, 144.28, 143.46, 133.49, 129.73, 127.75, 127.63, 126.39, 125.16, 122.95, 54.38, 47.93, 46.59, 35.14, 34.90, 29.85, 22.46, 21.86.

HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_2SNa^+$ $(M+Na)^+$ 364.1342, found 364.1336.



2aa **8**, 86%

1'-tosylspiro[indene-1,3'-piperidine]-2,3-dione (8)

Following the reported procedure[4], compound **2aa** (31.0 mg, 0.0872 mmol) and SeO_2 (38.6 mg, 0.3488 mmol, 4 equiv) were added to an oven-dried Schlenk tube. The tube was purged with vacuum and argon for three cycles, and finally filled with argon. 1,4-Dioxane (2 mL) was added and the tube was sealed. The mixture was heated at 100 °C for 48 h; after cooling to room temperature, water (4 mL) was added and the product extracted with EtOAc (3 x 7 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated. Purification of the crude by flash column chromatography (PE : EA = 2 : 1) to afford **8** (27.7 mg, 86%) as a pink solid.

mp: 177-179℃

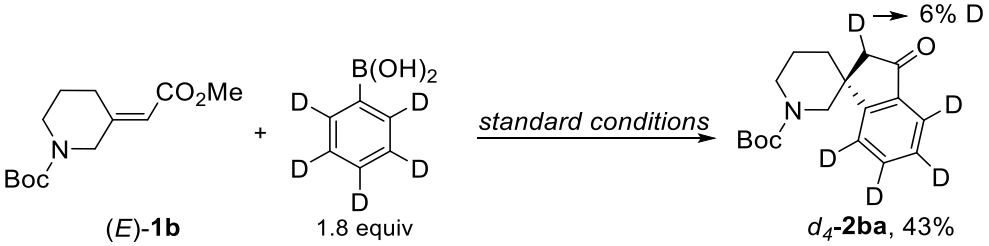
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.85 (td, *J* = 7.7, 1.3 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.96 – 3.85 (m, 1H), 3.64 (d, *J* = 11.5 Hz, 1H), 2.85 (d, *J* = 11.7 Hz, 1H), 2.55 (td, *J* = 11.5, 3.3 Hz, 1H), 2.46 (s, 3H), 2.16 – 2.02 (m, 1H), 1.95 – 1.85 (m, 1H), 1.80 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.56, 186.61, 153.07, 144.30, 138.54, 135.21, 132.53, 130.08, 129.21, 127.94, 127.77, 125.41, 50.85, 46.32, 46.21, 32.76, 21.73, 20.42.

HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_4SNa^+$ $(M+Na)^+$ 392.0927, found 392.0935.

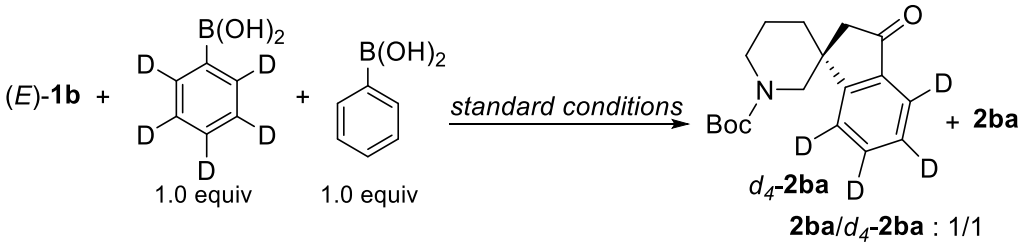
Deuterium-labled Experiments

Deuteration Experiment A



Following the general procedure, the reaction was performed with (*E*)-**1b** (56.1 mg, 0.22 mmol, 1.0 equiv), $[Rh(cod)Cl]_2$ (3.3 mg, 0.0066 mmol, 3 mol%), ligand **L4** (12.5 mg, 0.0198 mmol, 9 mol%), NaO^{t}Bu (10.6 mg, 0.11 mmol, 0.5 equiv), d_5-phenyl boronic acid (48.3 mg, 0.40 mmol, 1.8 equiv) and 4Å MS in 2.0 mL of DME at 80 °C in an oil bath for 24 h. Purification by flash chromatography (PE : EA = 6 : 1) afforded the product ***d*$_4$-2ba** (28.5 mg, 43%) .

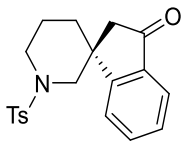
Deuteration Experiment B



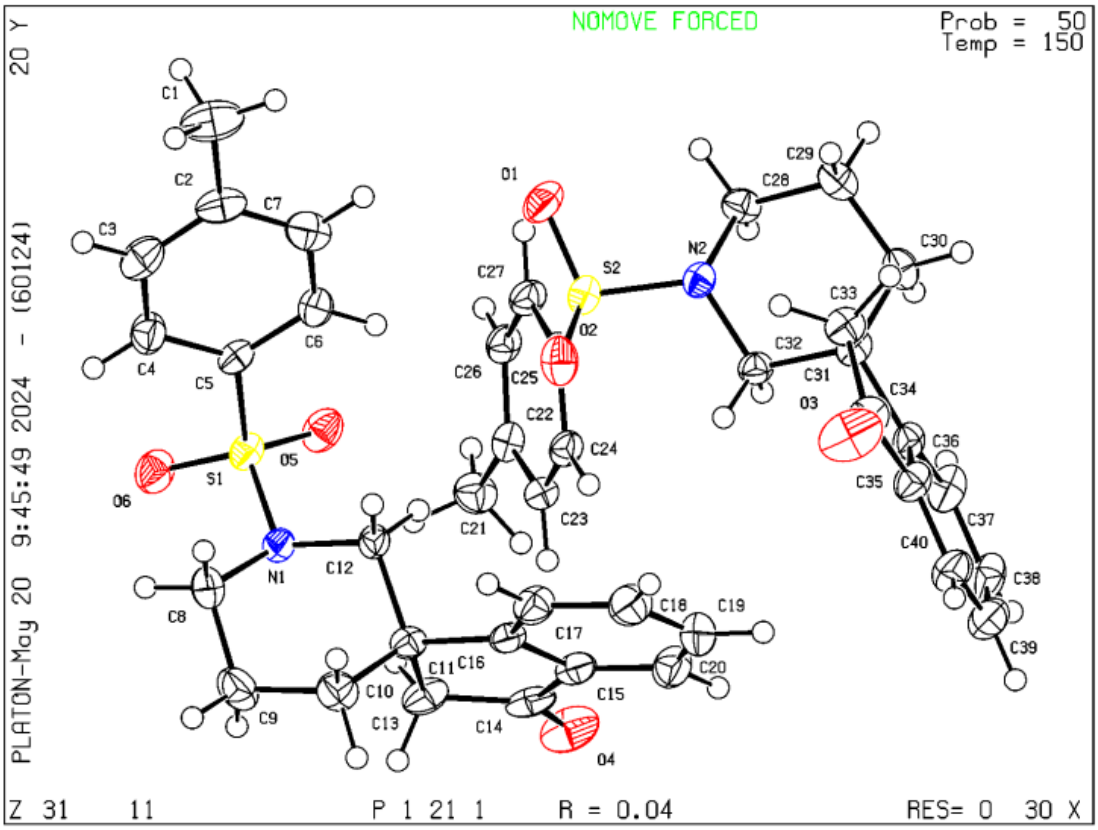
Following the general procedure, the reaction was performed with (*E*)-**1b** (56.1 mg, 0.22 mmol, 1.0 equiv), $[Rh(cod)Cl]_2$ (3.3 mg, 0.0066 mmol, 3 mol%), ligand **L4** (12.5 mg, 0.0198 mmol, 9 mol%), NaO^{t}Bu (10.6 mg, 0.11 mmol, 0.5 equiv), phenyl boronic acid (26.8 mg, 0.22 mmol, 1.0 equiv), d_5-phenyl boronic acid (26.8 mg, 0.22 mmol, 1.0 equiv) and 4Å MS in 2.0 mL of DME at 80 °C in an oil bath for 24 h. Purification by flash chromatography (PE : EA = 6 : 1) afforded the product **2ba** and *d*$_4$-**2ba** (37.1 mg, 56%) .

Crystal Data for 2aa

The crystals for X-ray diffraction were prepared by recrystallization from hexane and 2-propanol at room temperature.



(*S*)-**2aa**



The above figure was drawn as ellipsoids at 50% probability level.

Bond precision:	C-C = 0.0050 A	Wavelength=1.34139	
Cell:	a=12.3191(6)	b=11.9918(7)	c=12.3216(6)
	alpha=90	beta=90.368(2)	gamma=90
Temperature:	150 K		

	Calculated	Reported
Volume	1820.21 (16)	1820.21 (16)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb

Moiety formula	C20 H21 N O3 S	C20 H21 N O3 S
Sum formula	C20 H21 N O3 S	C20 H21 N O3 S
Mr	355.44	355.44
Dx,g cm-3	1.297	1.297
Z	4	4
Mu (mm-1)	1.129	1.129
F000	752.0	752.0
F000’	754.74	
h,k,lmax	15,14,15	15,14,15
Nref	7464[3919]	5822
Tmin,Tmax	0.850,0.893	0.612,0.751
Tmin’	0.798	

Correction method= # Reported T Limits: Tmin=0.612 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 1.49/0.78	Theta(max)= 56.953
R(reflections)= 0.0411(5397)	wR2(reflections)= 0.1081(5822)
S = 1.031	Npar= 453

Supplementary References

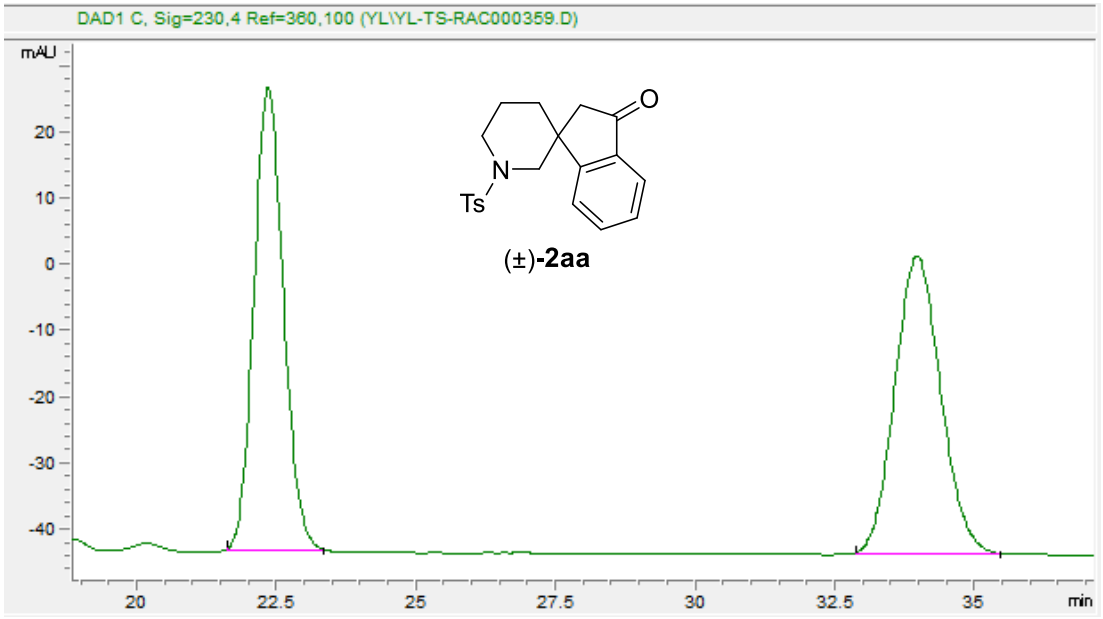
1. Yang, X; Kong, W.-Y.; Gao, J.-N.; Cheng, L.; Li, N.-N.; Li, M.; Li, H.-T.; Fan, J.; Gao, J.-M.; Ouyang, Q.; Xie, J.-B. Rhodium catalyzed C–C bond cleavage/coupling of 2-(azetidin-3-ylidene) acetates and analogs. *Chem. Commun*. **2019**, *55*, 12707–12710.

2. Sun, L.-Z.; Yang, X.; Li, N.-N.; Li, M.; Ouyang, Q.; Xie, J.-B. Rhodium-Catalyzed Ring Expansion of Azetidines via Domino Conjugate Addition/N-Directed α -C(sp^3) – H Activation. *Org. Lett.* **2022**, *24*, *10*, 1883–1888

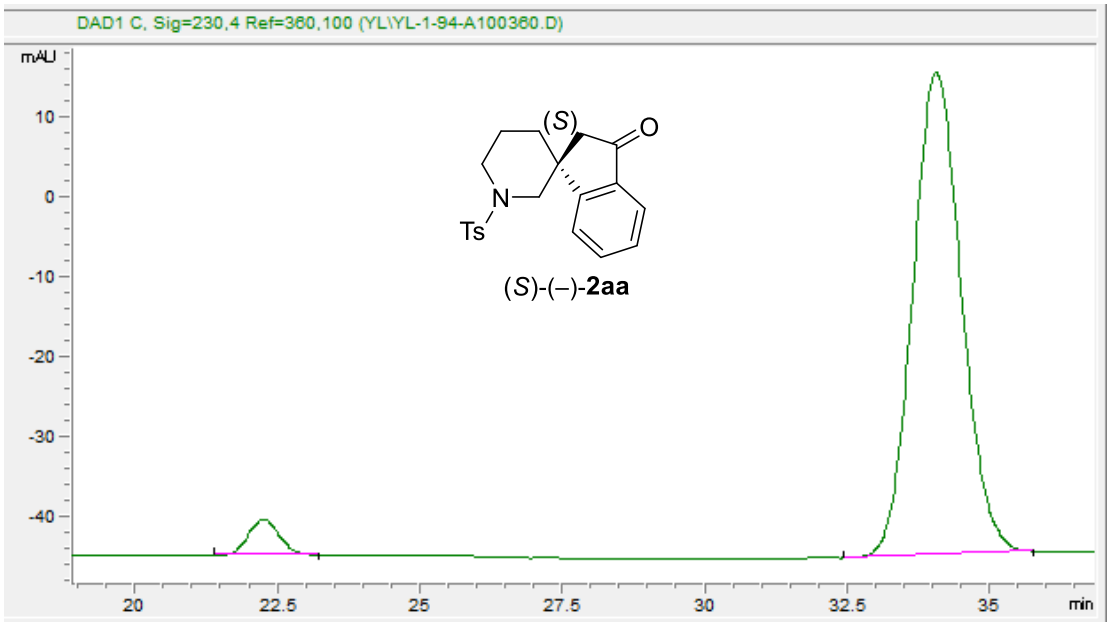
3. Amberchan, G.; Snelling, R. A.; Moya, E.; Landi, M.; Lutz, K.; Gatihi, R.; Singaram, B. Reaction of Diisobutylaluminum Borohydride, a Binary Hydride, with Selected Organic Compounds Containing Representative Functional Groups. *J. Org. Chem.* **2021**, *86*, *9*, 6207–6227.

4. Scarpi, D.; Petrovic, M.; Fiser, B.; Gómez-Bengoa, E.; Occhiato, E. G. Construction of cyclopenta[*b*]indol-1-ones by a tandem gold (I)-catalyzed rearrangement/Nazarov reaction and application to the synthesis of Bruceolline H. *Org. Lett*. **2016**, *18*, *15*, 3922–3925.

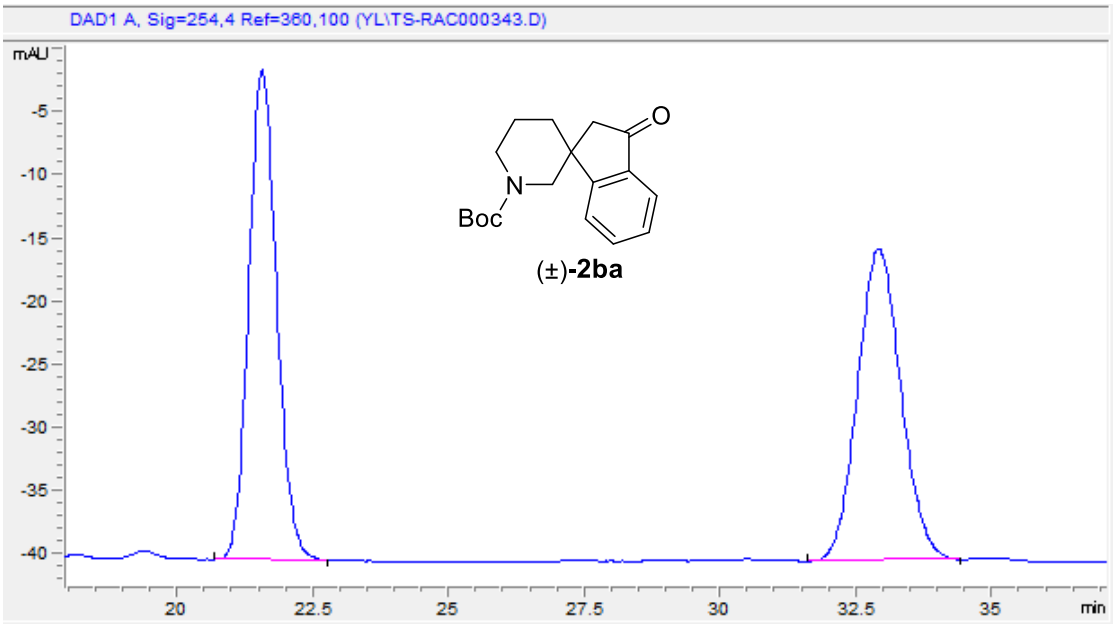
HPLC Spectra



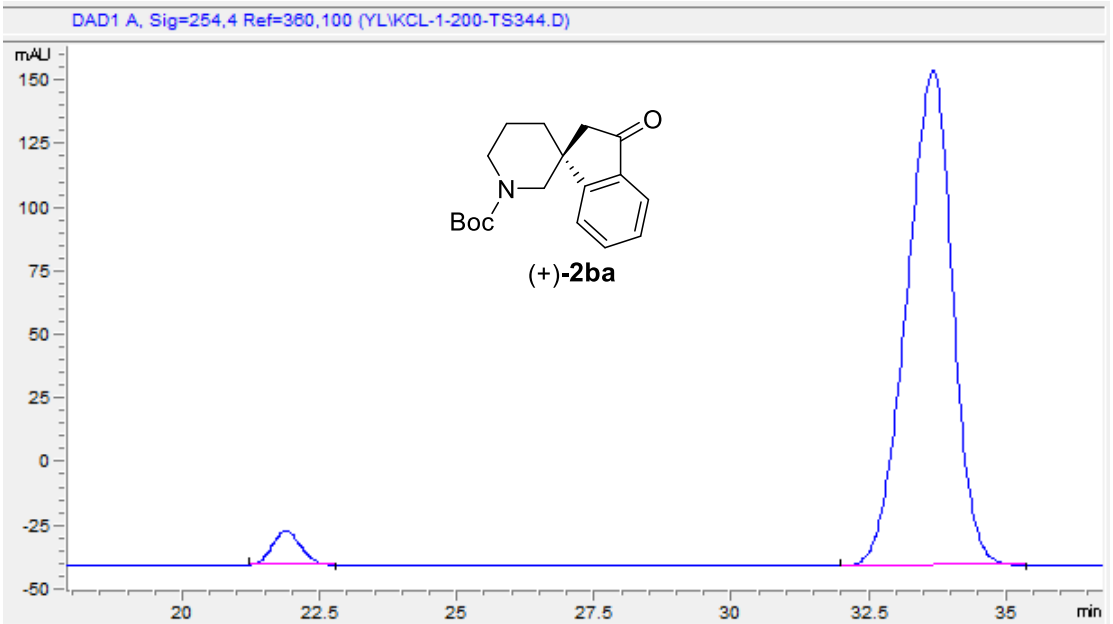
1	22.336	2600.4	70.1	0.577	0.874	50.189
2	33.954	2580.8	45	0.8928	0.881	49.811



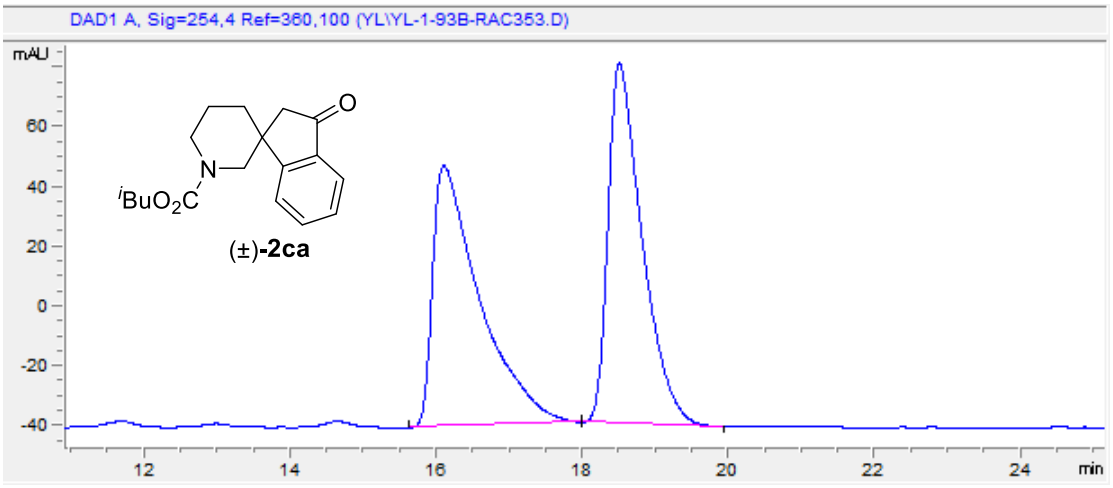
1	22.239	162.6	4.4	0.498	0.916	4.364
2	34.048	3563.1	60.4	0.906	0.901	95.636



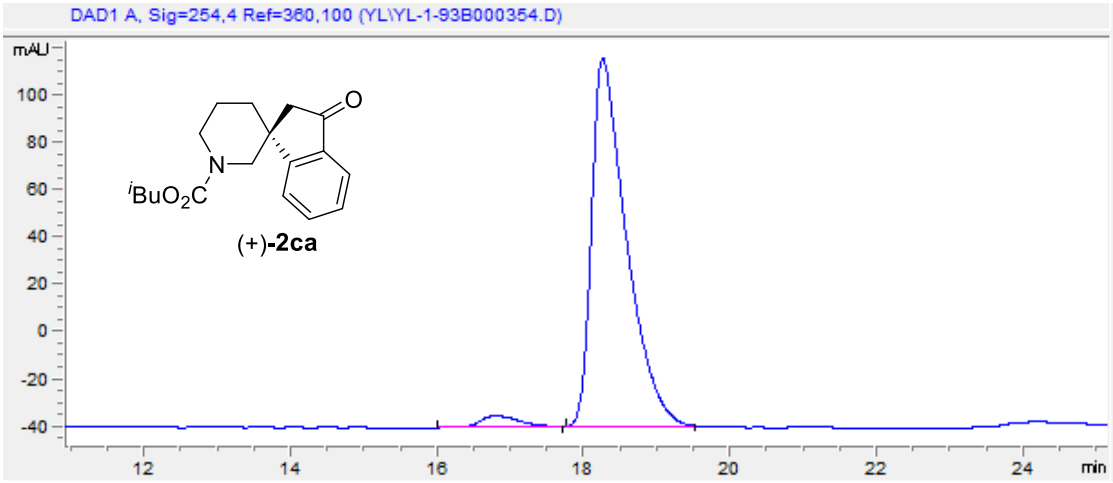
1	21.55	1383.9	38.8	0.5585	0.873	50.530
2	32.901	1354.8	24.6	0.8497	0.891	49.470



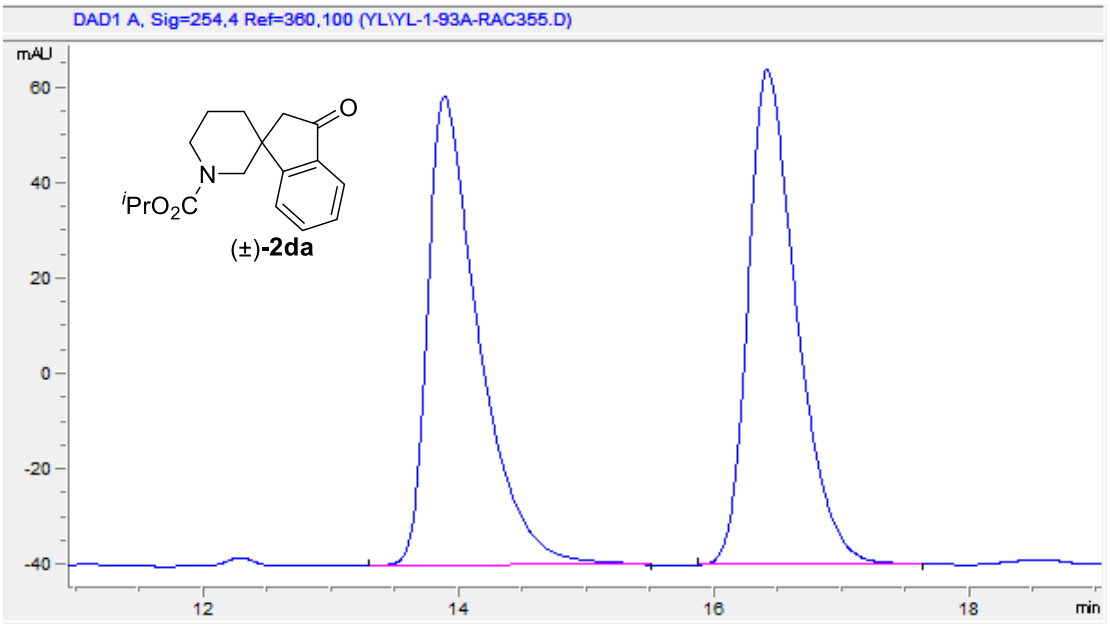
1	21.862	488.6	13.5	0.5571	0.862	4.132
2	33.661	11337.2	194.7	0.8953	1.298	95.868



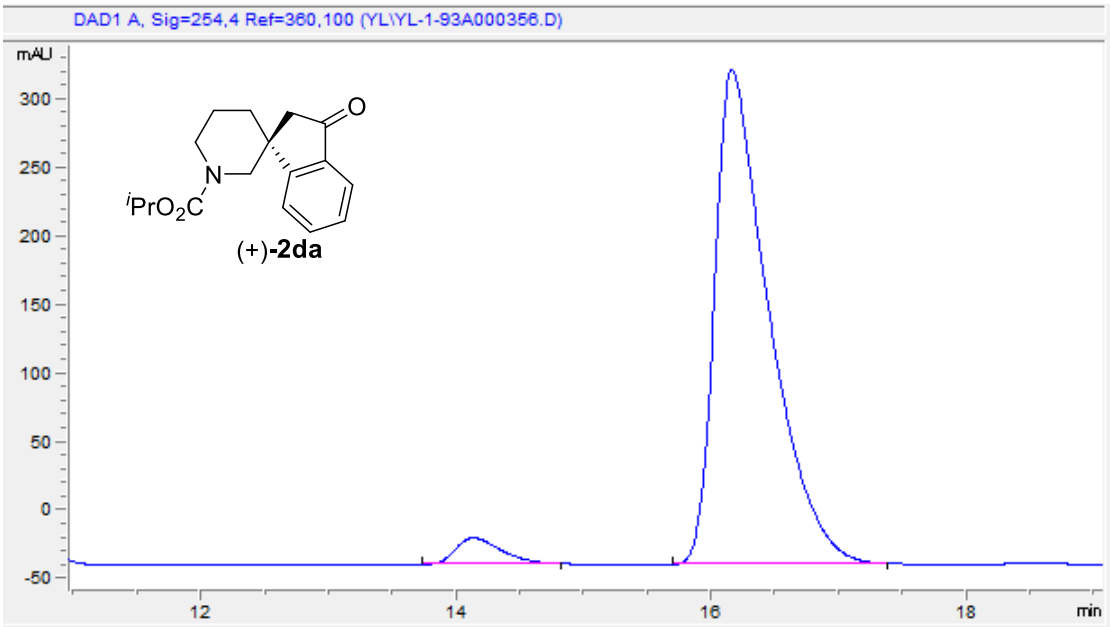
1	16.095	4002.5	87.5	0.6455	0.277	50.070
2	18.5	3991.2	121.6	0.4808	0.478	49.930



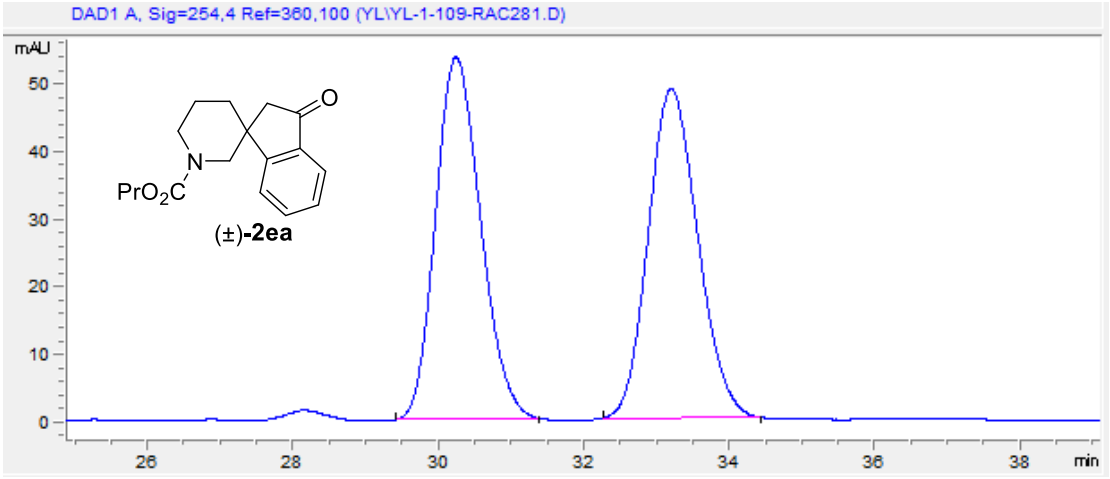
1	16.798	478.5	12.1	0.6579	0.694	3.549
2	18.252	13002.5	393.1	0.5513	0.46	96.451



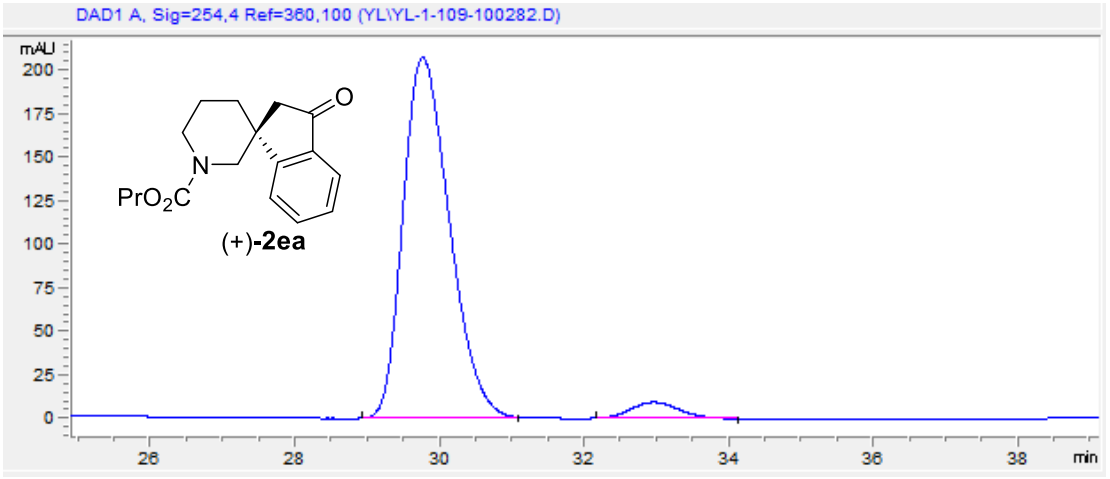
1	13.886	2762.6	98.5	0.4673	0.476	49.889
2	16.415	2775	104.1	0.4441	0.633	50.111



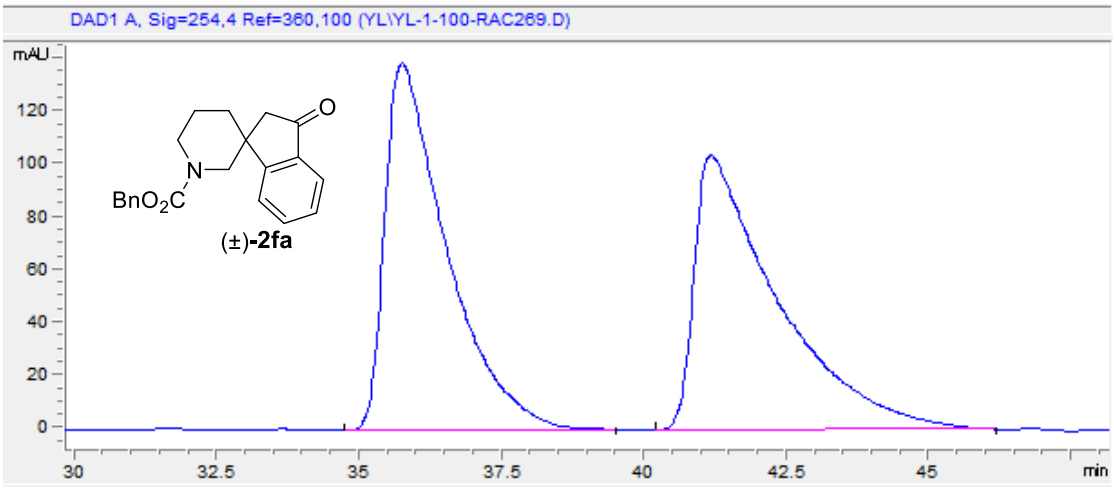
1	14.13	489.7	19.5	0.3749	0.6	4.379
2	16.159	10693.5	361.2	0.4294	0.44	95.621



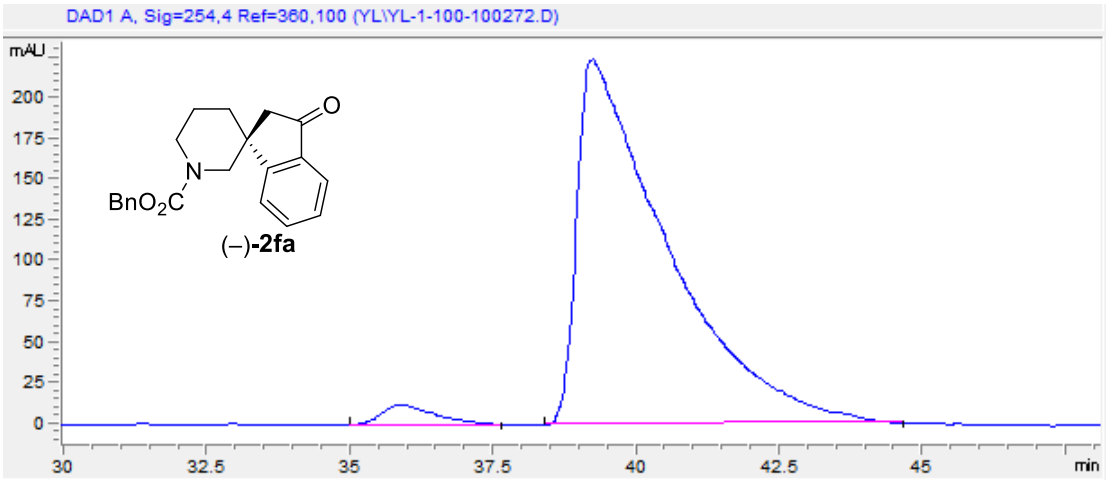
1	30.233	2325.3	53.7	0.7223	0.807	49.878
2	33.193	2336.7	48.9	0.7961	0.848	50.122



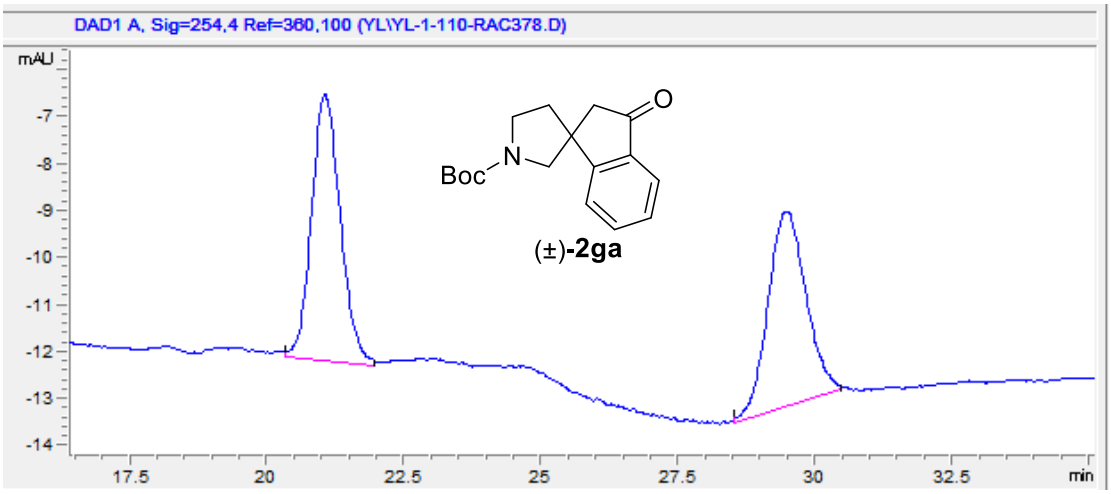
1	29.76	9264.5	207.3	0.6994	0.713	95.507
2	32.949	435.9	9.3	0.687	0.838	4.493



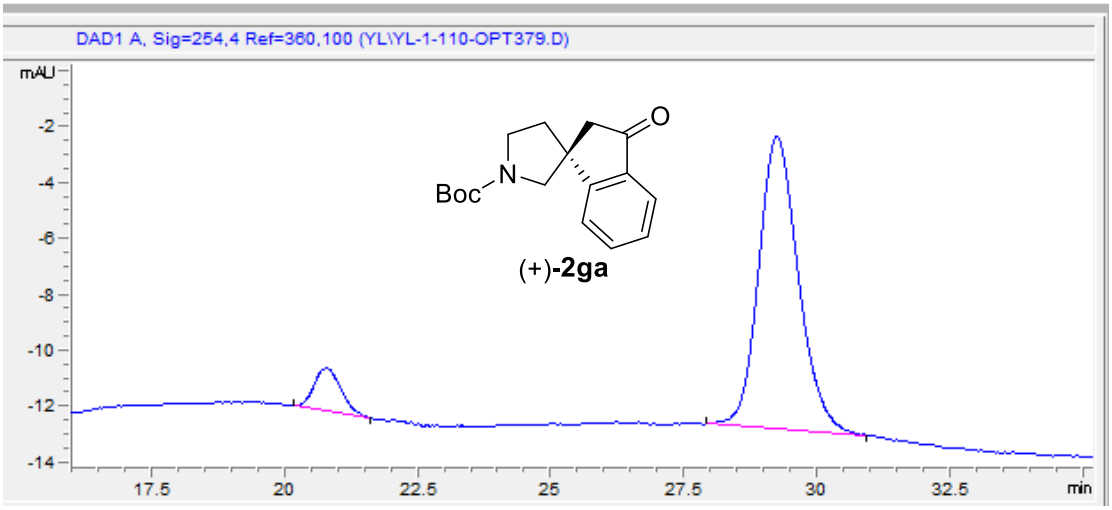
1	35.738	10540.4	139.1	1.2632	0.366	49.953
2	41.163	10560.4	104	1.6917	0.243	50.047



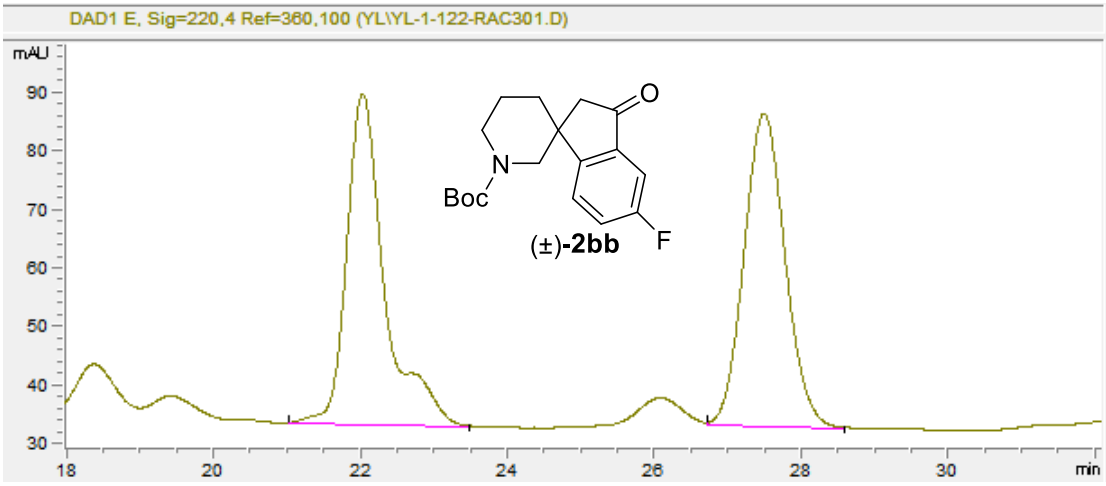
1	35.859	848.6	12.7	1.1175	0.529	3.331
2	39.221	24624.5	224.1	1.8314	0.201	96.669



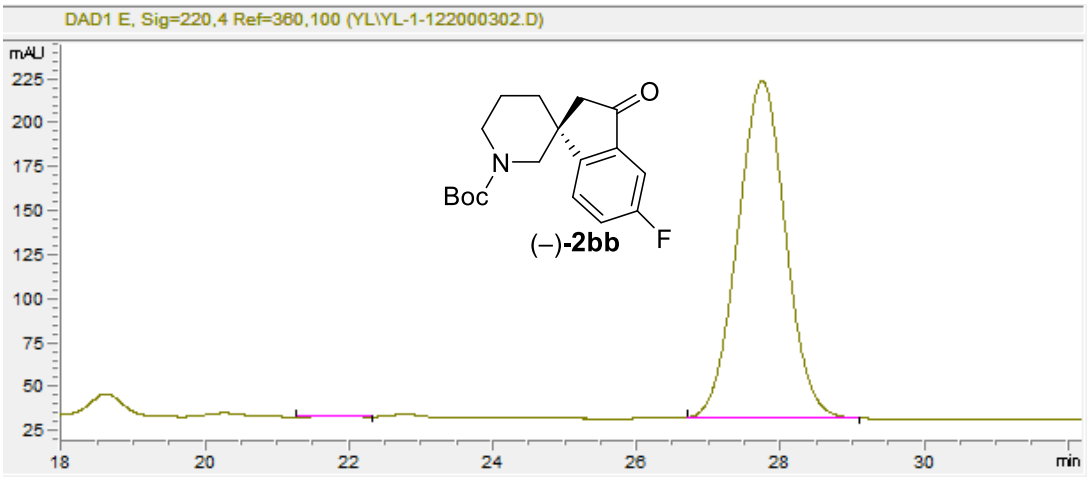
1	21.045	207.7	5.7	0.6098	0.828	50.556
2	29.451	203.1	4.2	0.8106	0.861	49.444



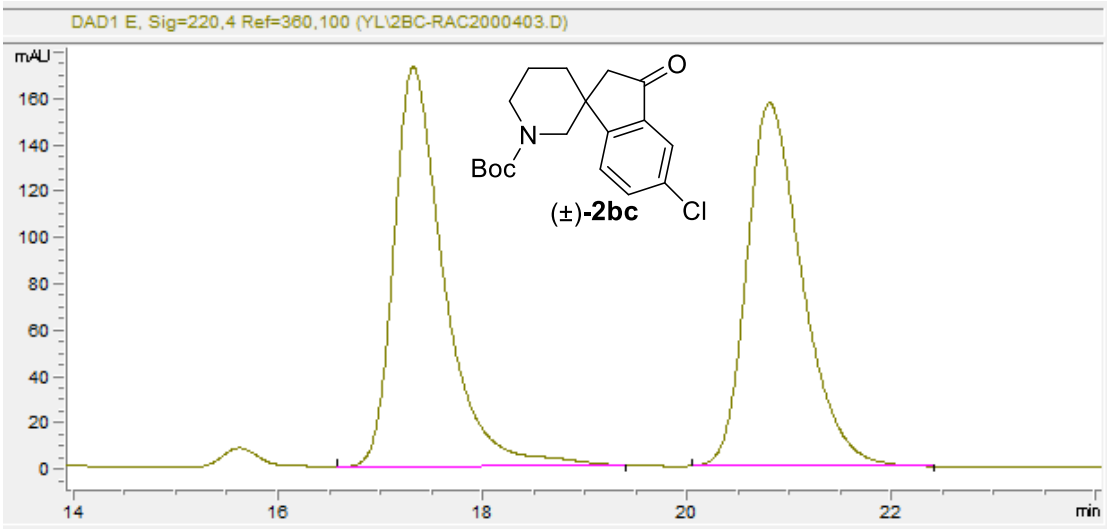
1	20.749	57.1	1.6	0.6064	0.76	9.465
2	29.229	546	10.5	0.8686	0.8	90.535



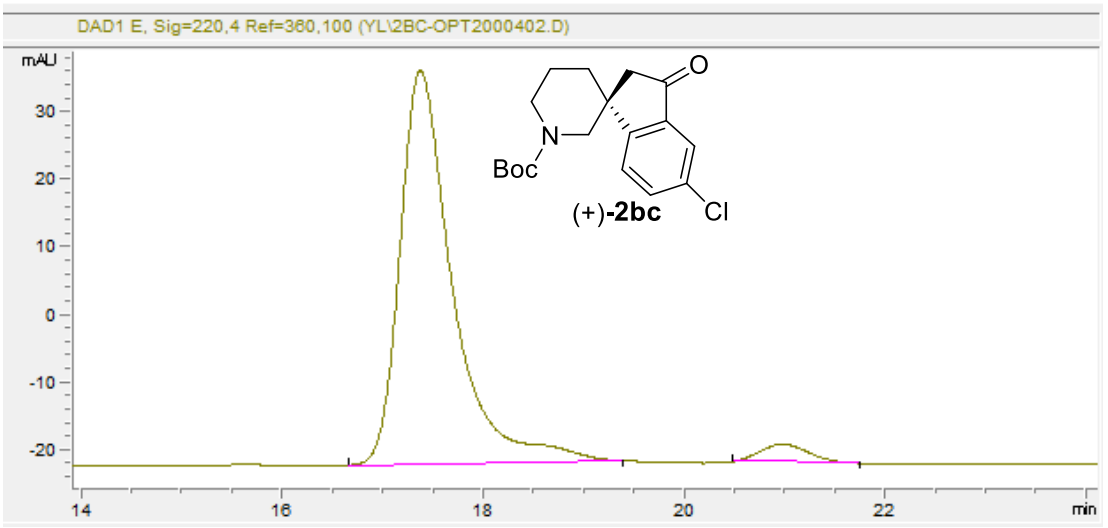
1	22.018	2064.4	57	0.5423	0.639	49.644
2	27.481	2094	53.6	0.6077	0.901	50.356



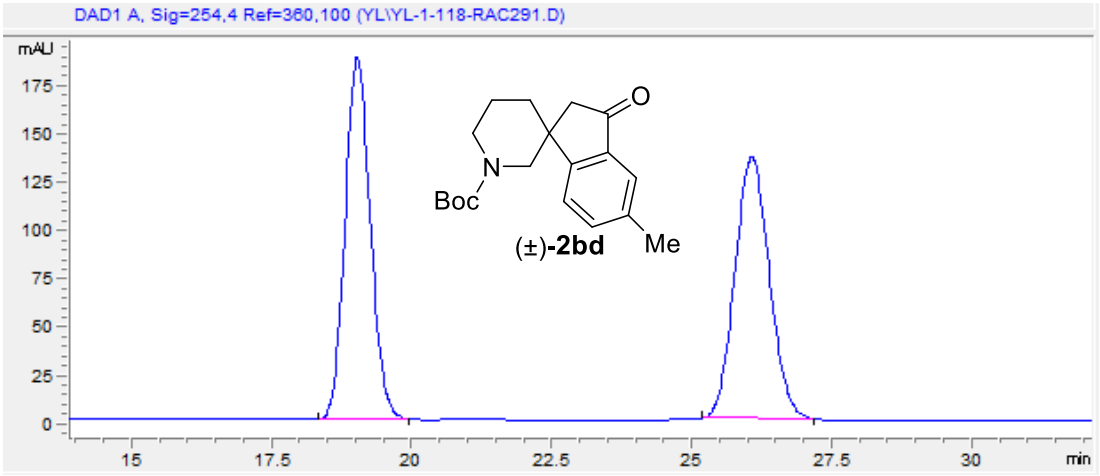
1	22.772	90.7	2.3	0.6634	0.82	1.007
2	27.738	8920.3	192.1	0.7218	1.012	98.993



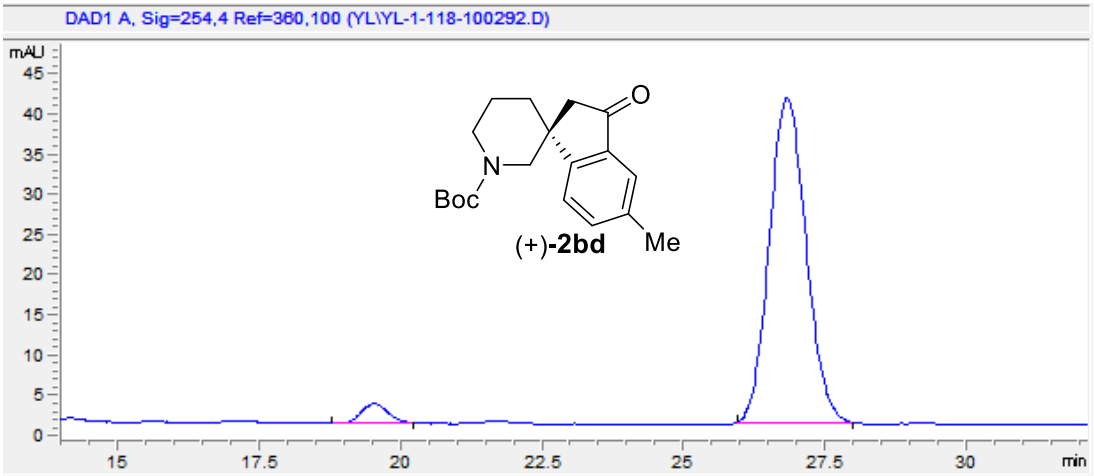
1	17.314	5939.2	172.8	0.5727	0.611	50.112
2	20.799	5912.7	156.9	0.6283	0.683	49.888



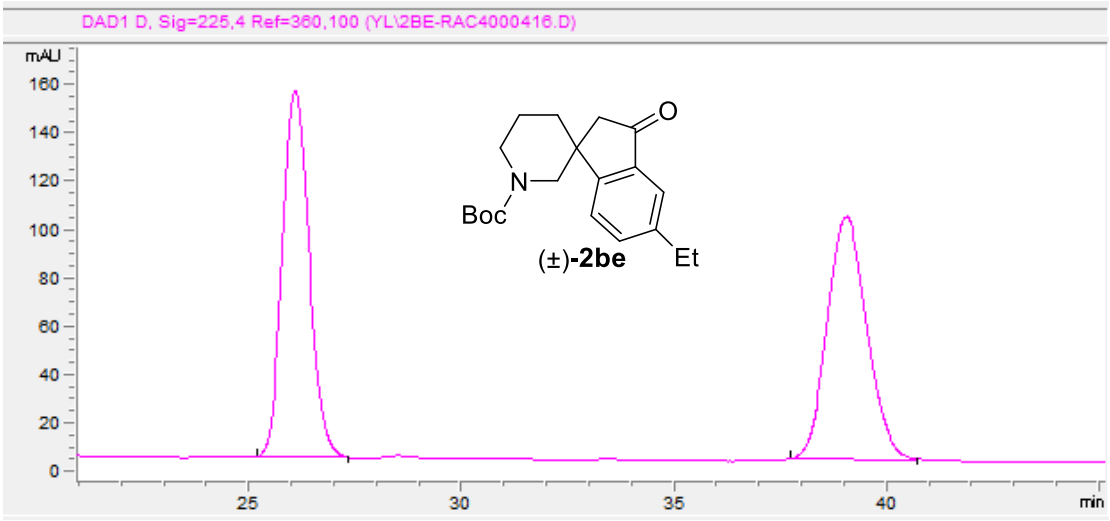
1	17.367	2158.6	58.5	0.6153	0.605	95.769
2	20.968	95.4	2.7	0.4427	0.828	4.231



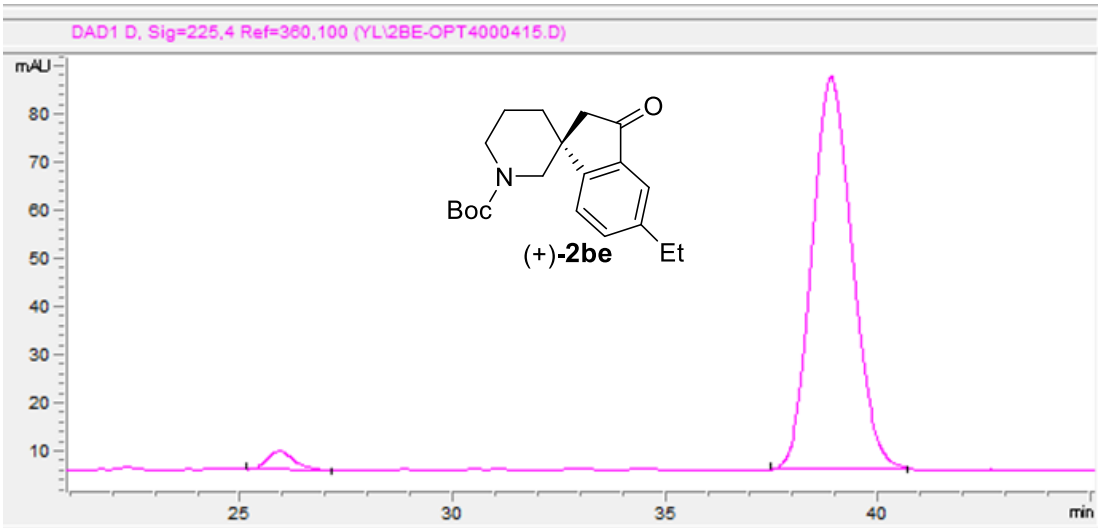
1	19.011	5869.4	187.2	0.4877	0.873	50.225
2	26.054	5816.9	135.7	0.6681	0.907	49.775



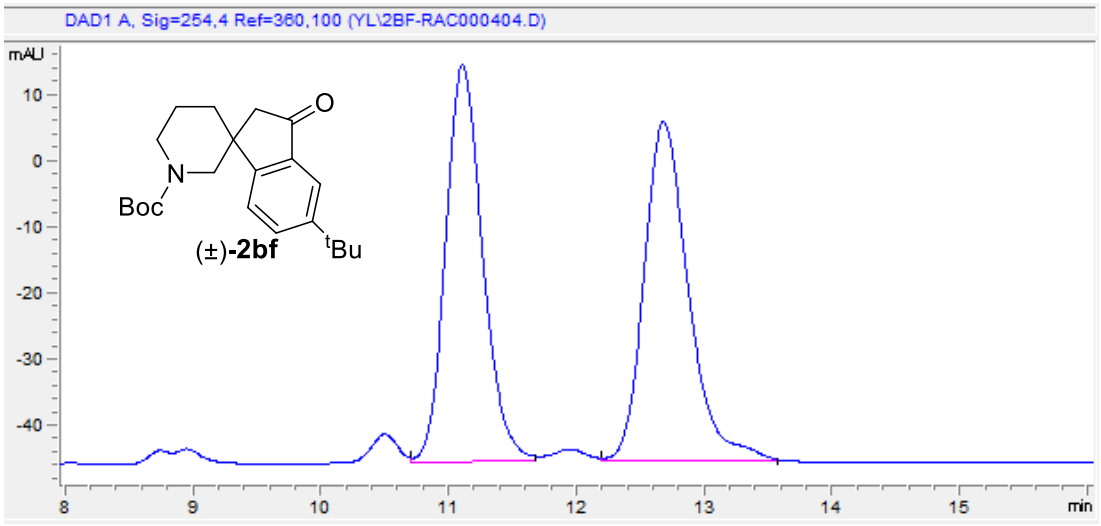
1	19.513	81	2.4	0.5529	0.923	4.207
2	26.813	1843.6	40.6	0.7565	0.904	95.793



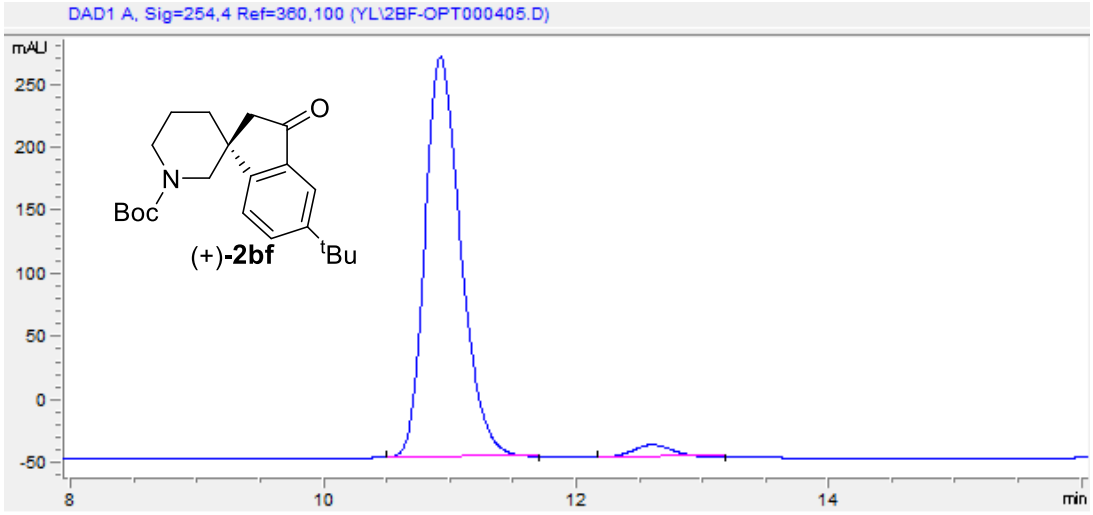
1	26.063	6611.1	151.4	0.6813	0.844	50.135
2	39.026	6575.5	100.8	1.017	0.867	49.865



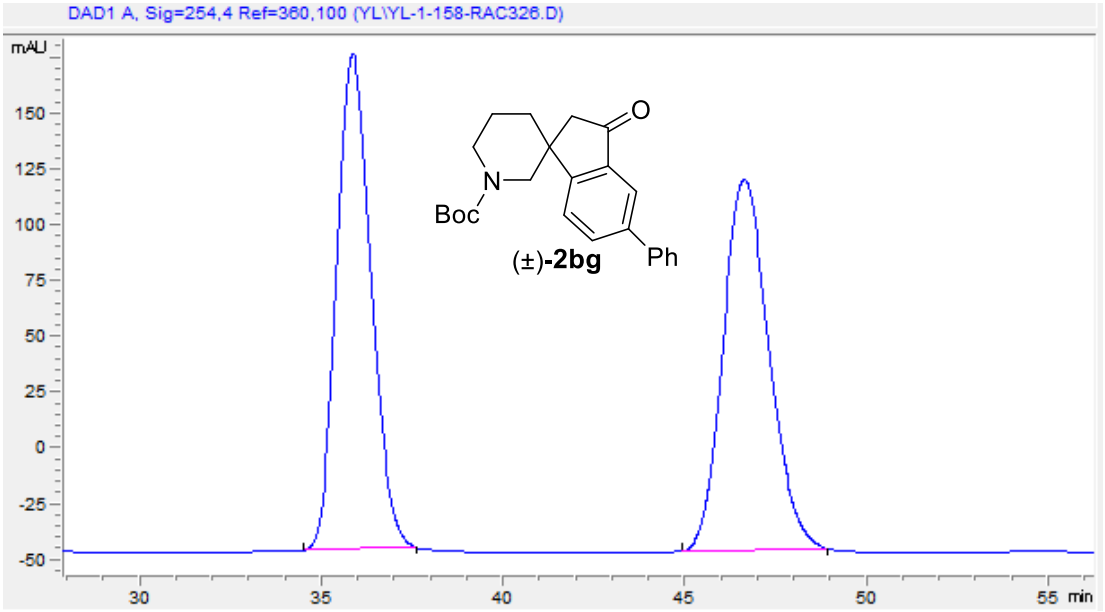
1	25.916	185.4	4.1	0.7489	0.878	3.313
2	38.88	5409.6	81.6	1.1055	0.866	96.687



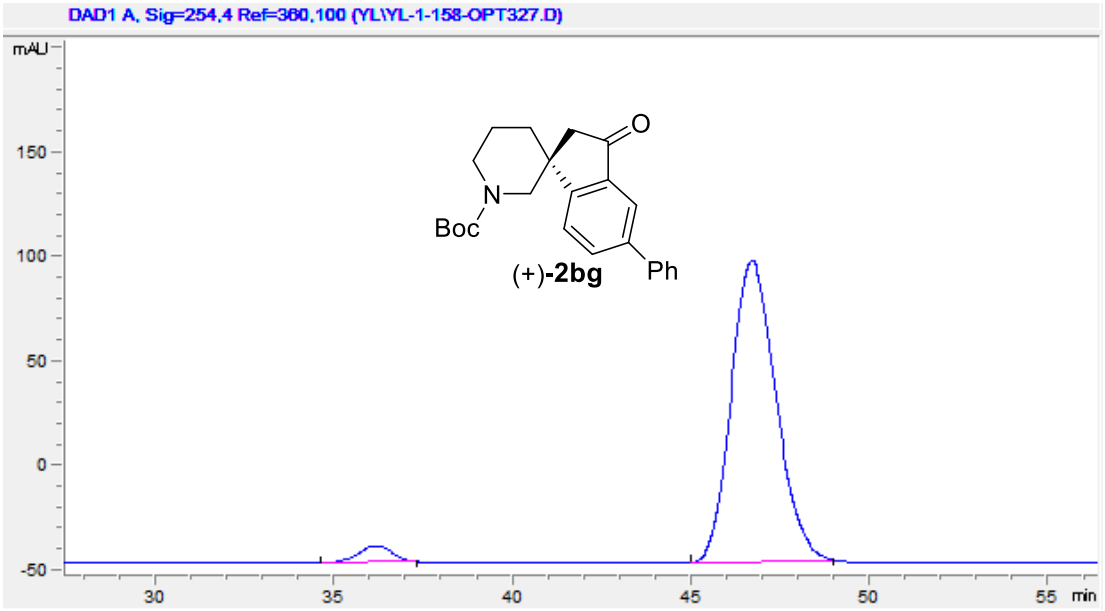
1	11.103	1214.9	60.1	0.312	0.793	49.368
2	12.676	1246	51.3	0.3712	0.732	50.632



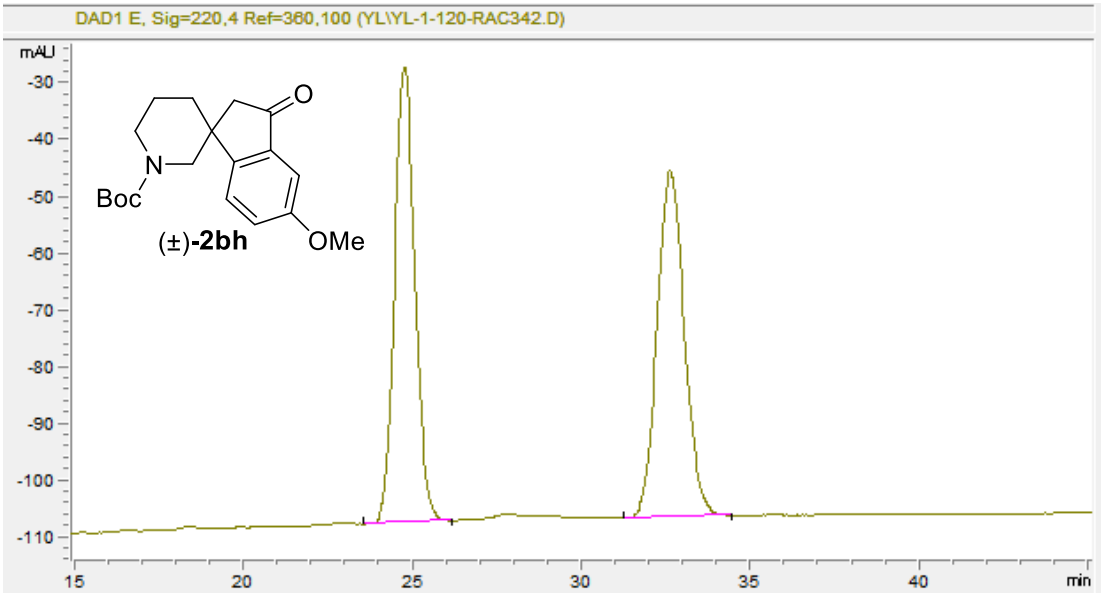
1	10.917	6280.8	317.4	0.3049	0.716	96.726
2	12.594	212.6	9.7	0.3429	0.908	3.274



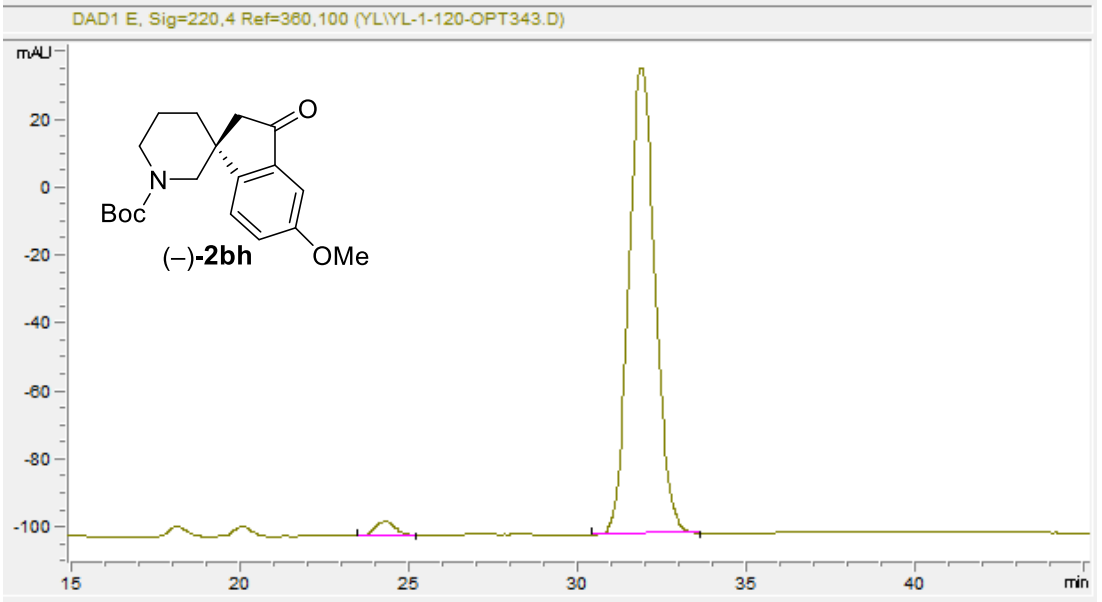
1	35.836	14701.1	222.2	1.0258	0.822	50.112
2	46.609	14635.4	166.2	1.3613	0.81	49.888



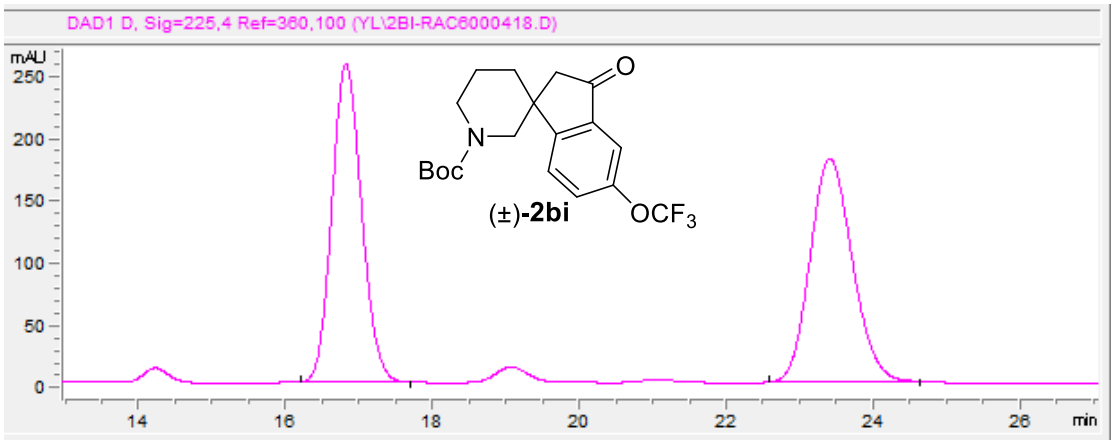
1	36.149	577.5	8.1	1.1823	1.133	4.309
2	46.681	12824.5	145	1.4743	0.824	95.691



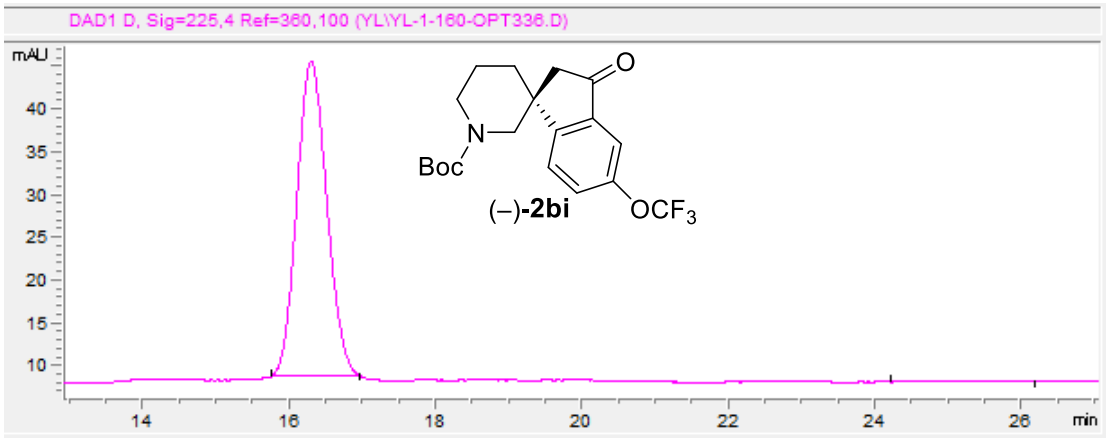
1	24.737	3374.9	80.3	0.7008	0.893	49.618
2	32.603	3426.8	61	0.9361	0.881	50.382



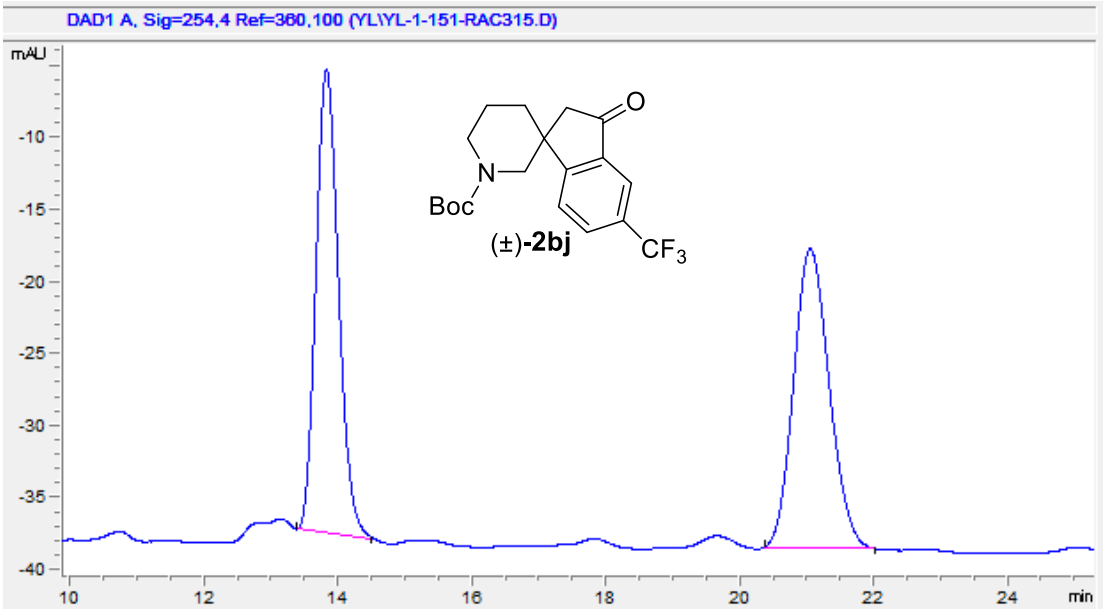
1	24.265	180.2	4.3	0.6918	0.86	2.356
2	31.868	7470.6	137.5	0.9056	0.899	97.644



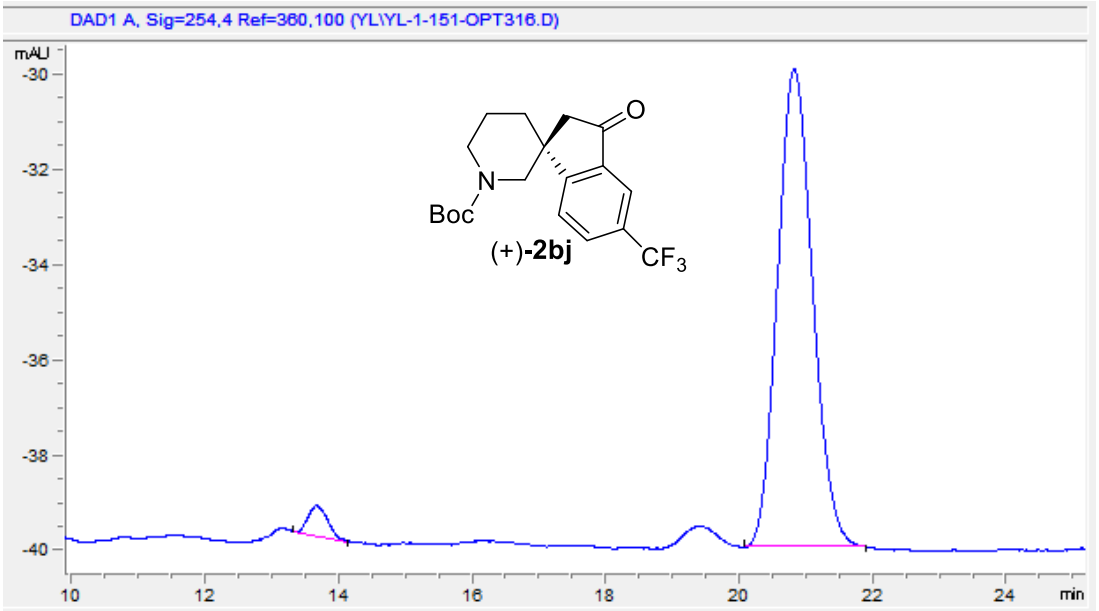
1	16.811	7203.1	255.6	0.4407	0.863	49.909
2	23.399	7229.5	180	0.6226	0.833	50.091



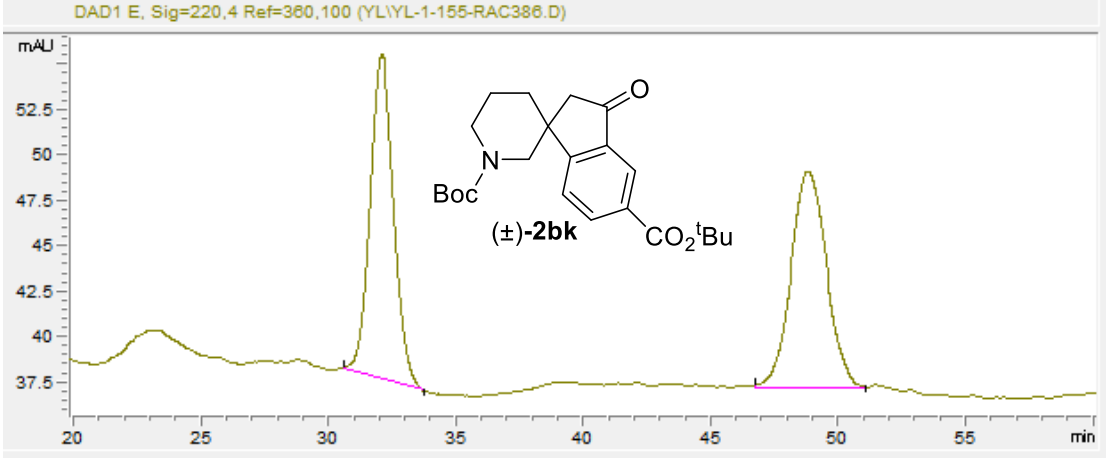
1	16.29	1051	36.9	0.4751	0.876	98.805
2	24.932	11	1.7E-1	1.1001	0.598	1.195



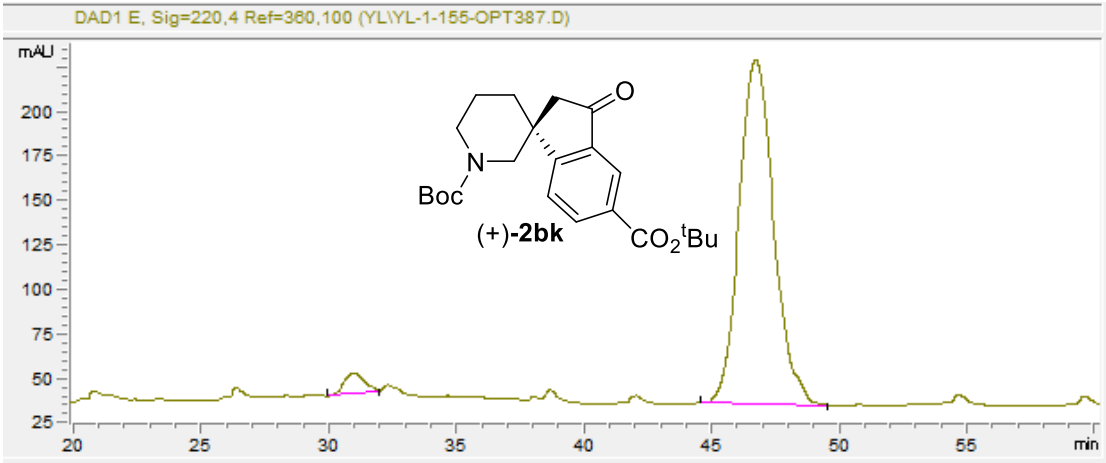
1	13.818	773.7	32.5	0.3971	0.854	49.975
2	21.043	774.4	20.8	0.5742	0.842	50.025



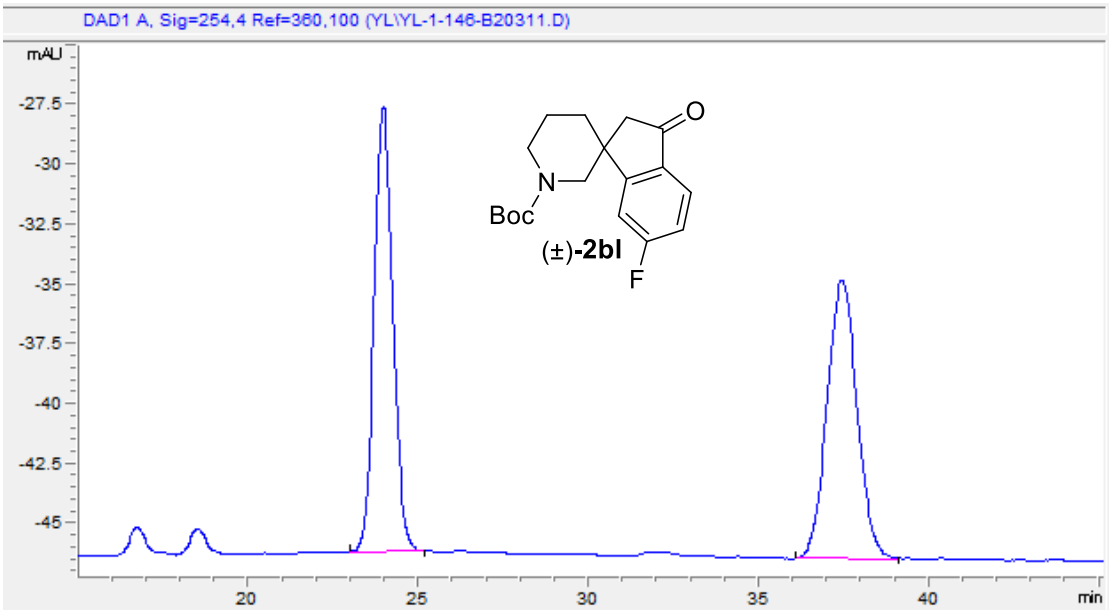
1	13.661	13.6	6.5E-1	0.3494	0.704	4.153
2	20.814	374.9	10.1	0.6195	0.856	95.847



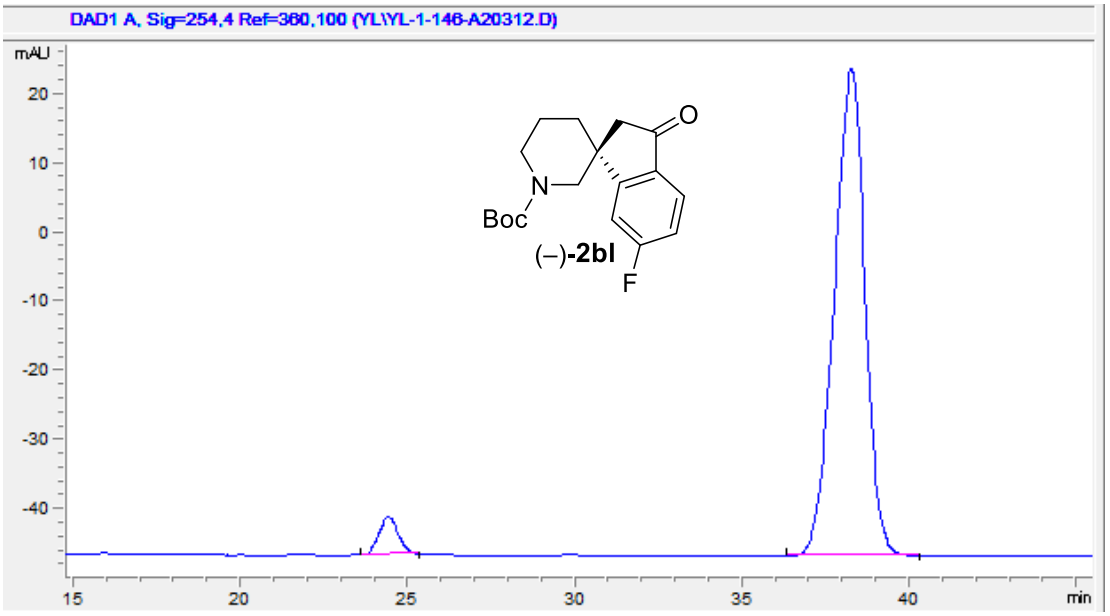
1	32.052	1148.5	17.9	1.0702	0.907	49.907
2	48.796	1152.8	11.9	1.6109	0.924	50.093



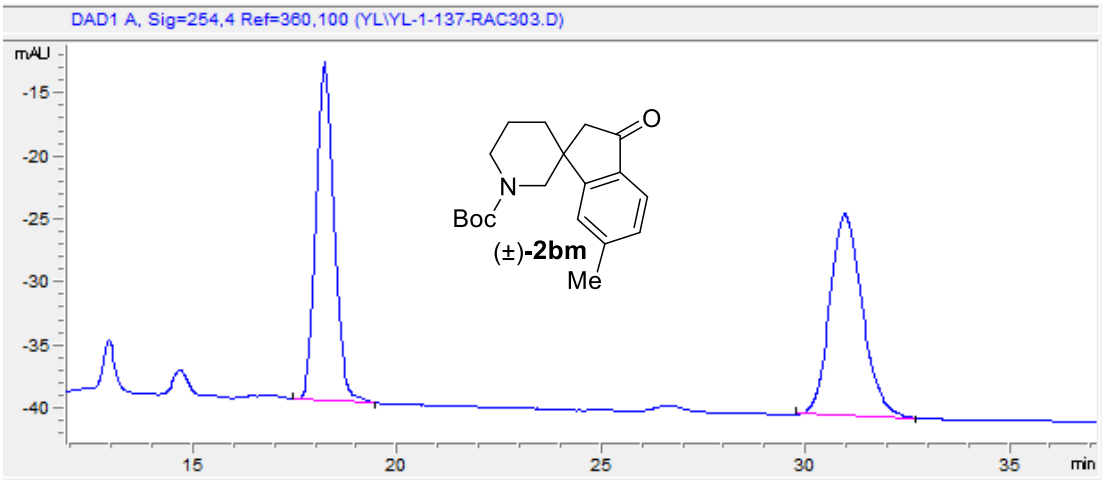
1	30.925	130.8	2.1	1.0572	0.666	4.451
2	46.688	2806.9	30.1	1.5547	0.917	95.549



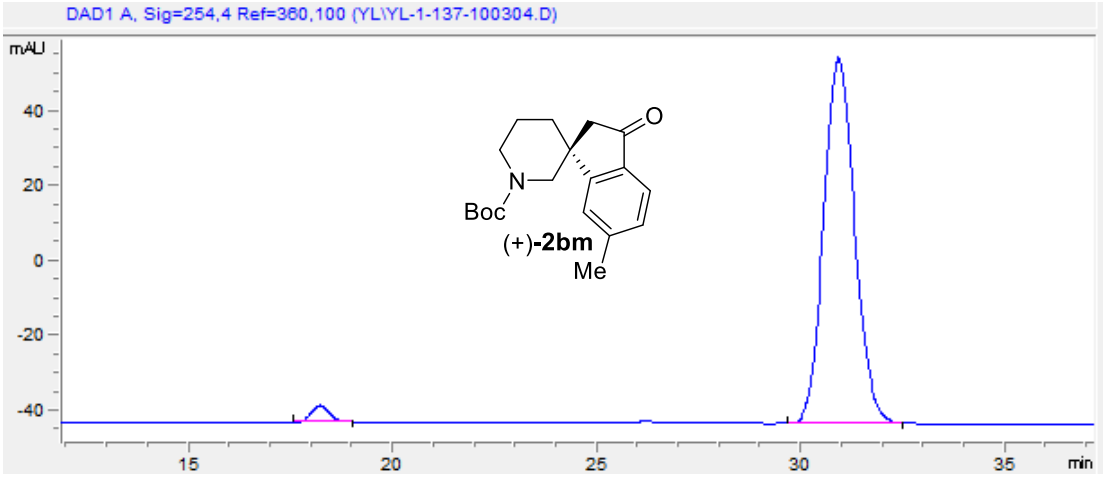
1	23.951	719.7	18.7	0.6423	0.903	50.056
2	37.429	718.1	11.7	1.0249	0.947	49.944



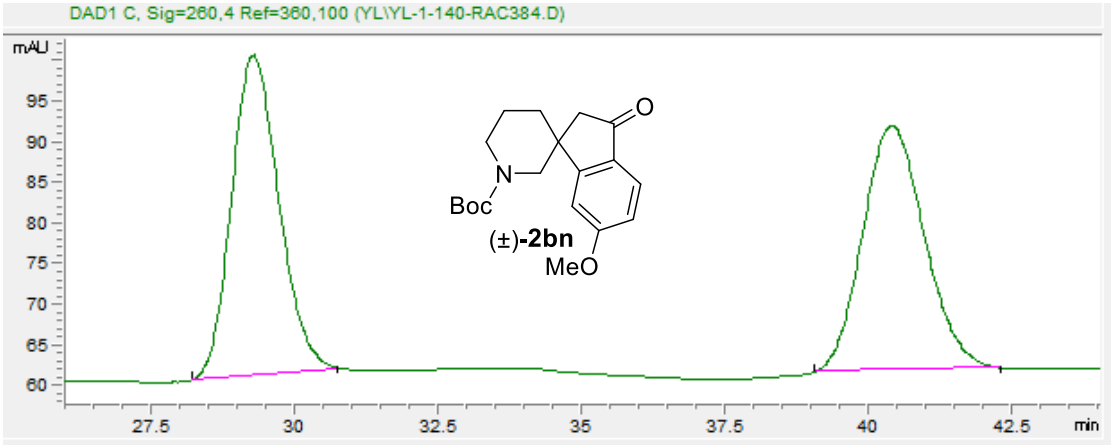
1	24.396	232	5.5	0.7002	0.903	4.893
2	38.254	4508.8	70.5	1.0653	1.252	95.107



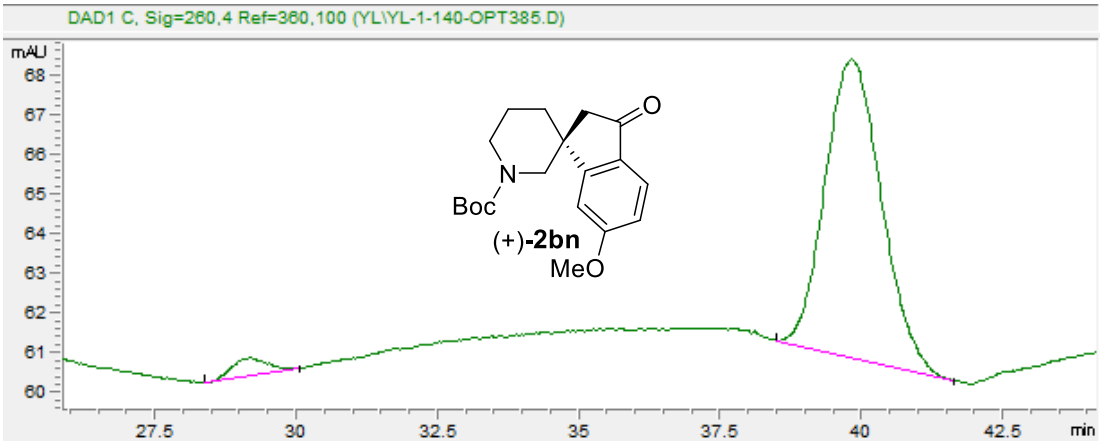
1	18.2	843.9	26.9	0.5222	0.862	48.265
2	30.946	904.6	16.2	0.933	0.835	51.735



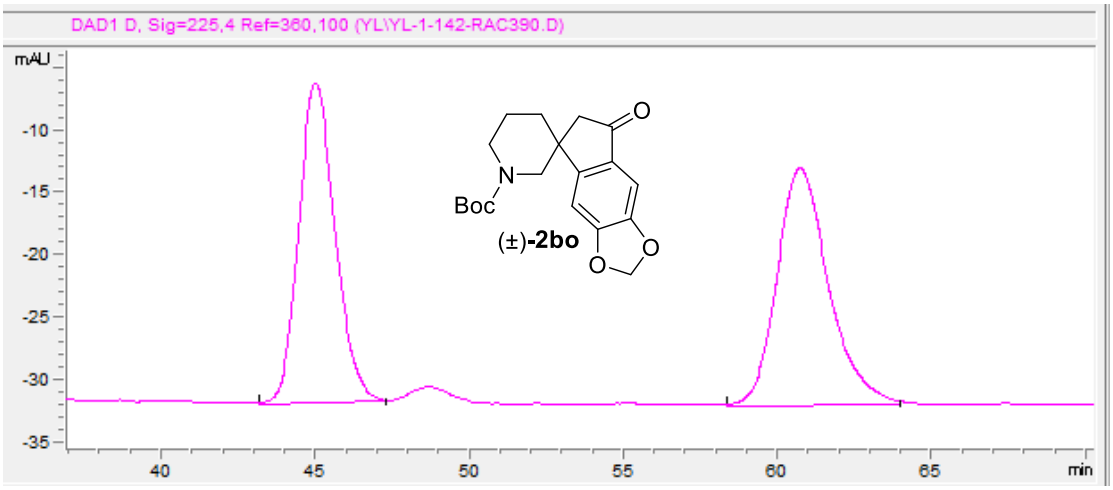
1	18.199	171.2	4.8	0.5969	0.741	3.146
2	30.905	5270.3	98.2	0.8944	0.879	96.854



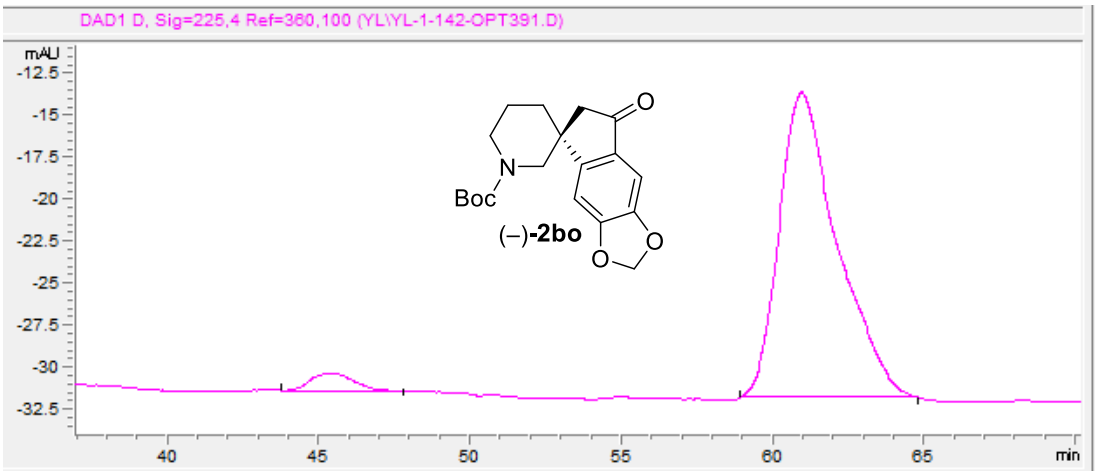
1	29.257	2265.8	39.5	0.8672	0.816	50.062
2	40.384	2260.1	30.2	1.05	0.834	49.938



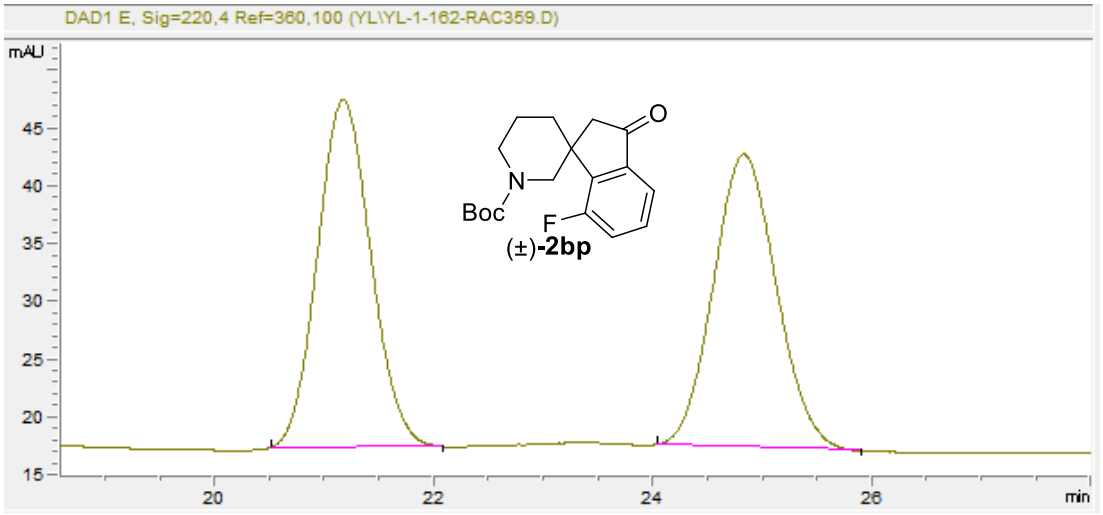
1	29.149	22.5	4.9E-1	0.7674	0.935	4.126
2	39.816	523.7	7.5	1.1608	0.843	95.874



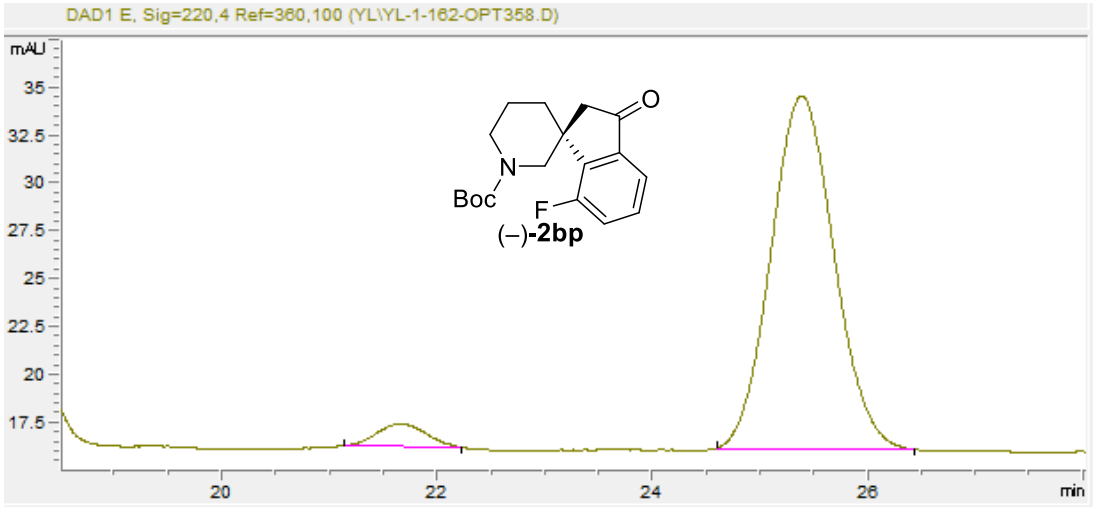
1	44.98	2018.2	25.2	1.0779	0.806	50.829
2	60.708	1952.3	18.1	1.311	0.778	49.197



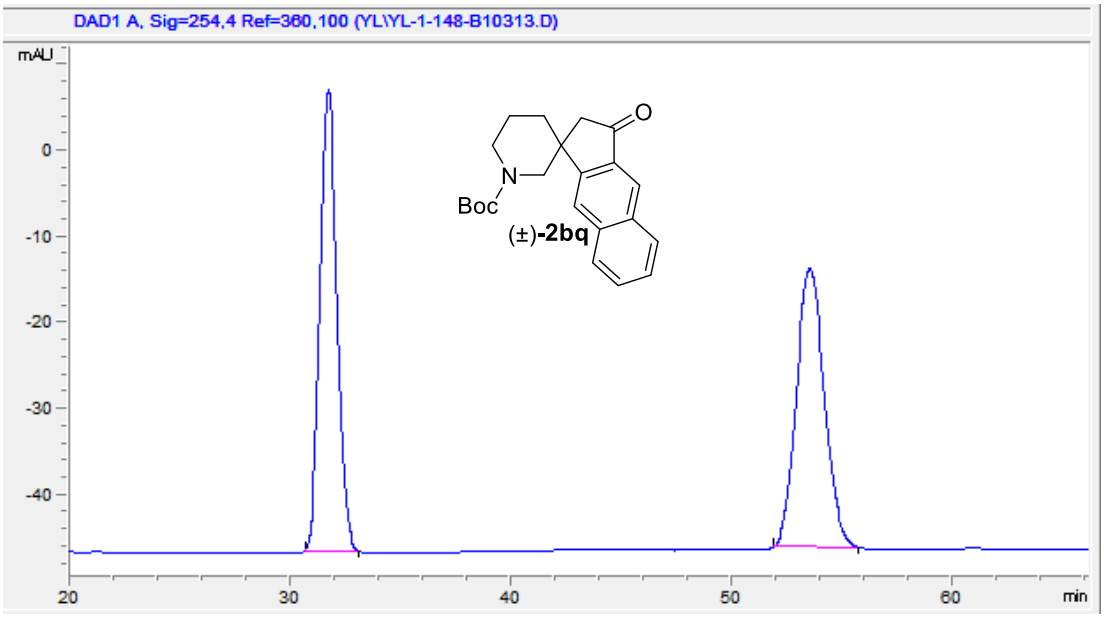
1	45.298	112.4	1.1	1.7557	0.73	4.407
2	60.916	2438.7	18.2	2.2305	0.598	95.593



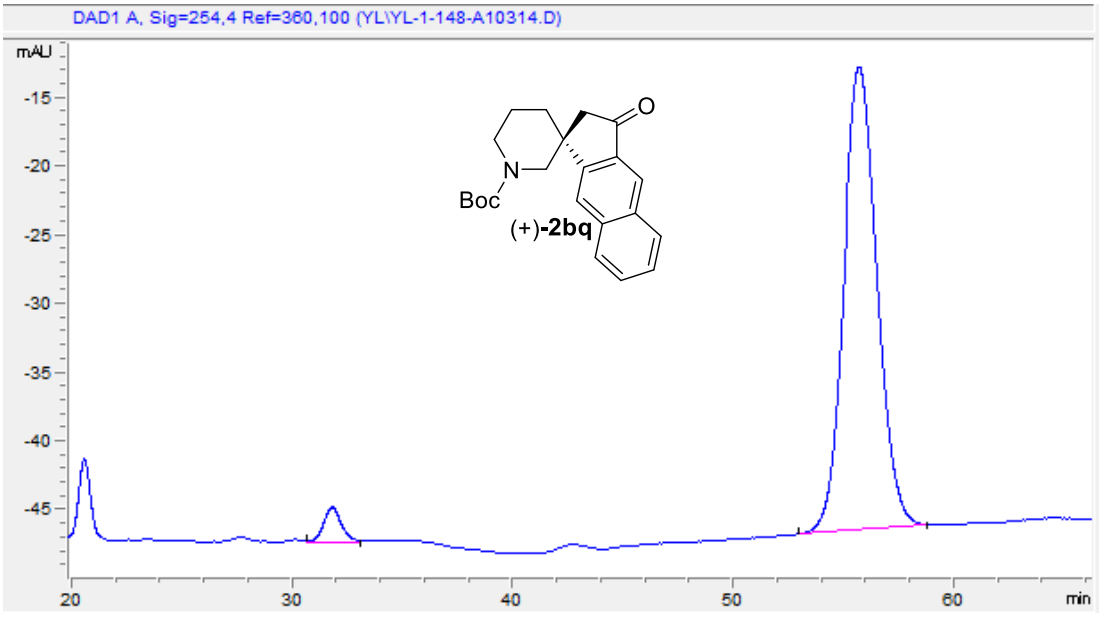
1	21.169	1027.1	30.2	0.5328	0.897	50.169
2	24.825	1020.1	25.4	0.6205	0.9	49.831



1	21.662	41.7	1.3	0.5514	0.986	5.214
2	25.379	757.8	18.5	0.6241	0.908	94.786

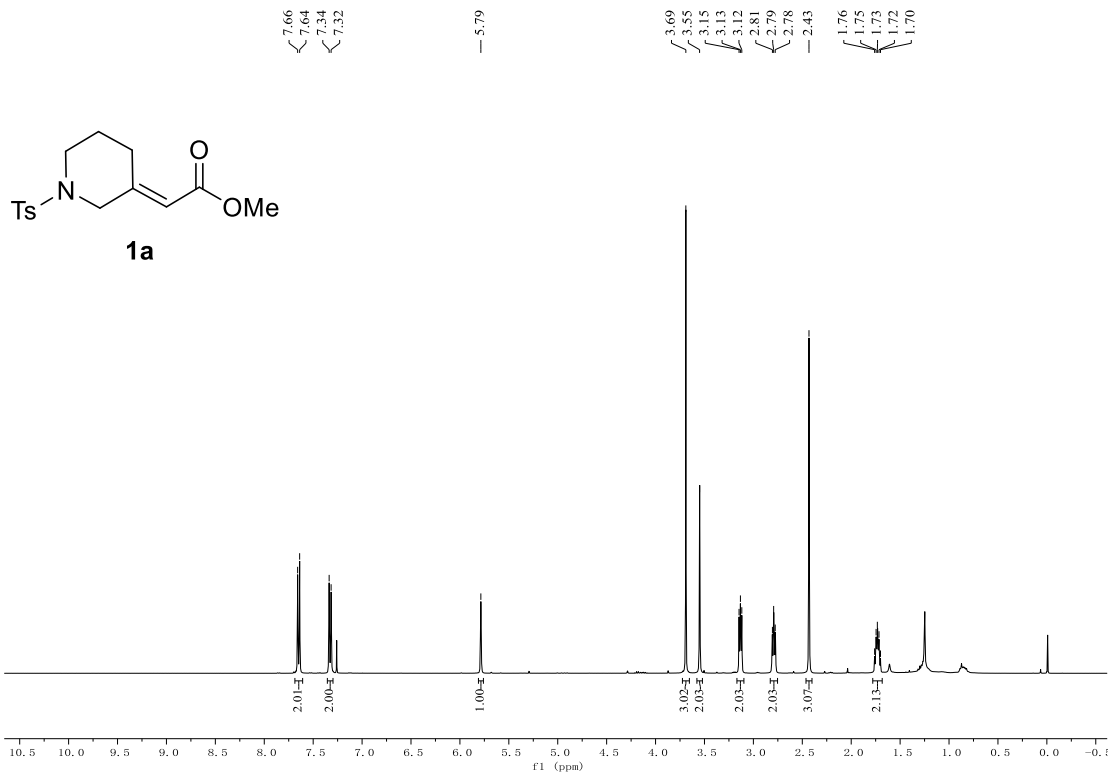


1	31.68	2928.5	53.9	0.9054	0.902	50.164
2	53.493	2909.3	32.6	1.488	0.892	49.836



1	31.771	192.2	2.9	1.1187	1.036	4.861
2	55.702	3761	34.1	1.8385	0.91	95.139

NMR Spectra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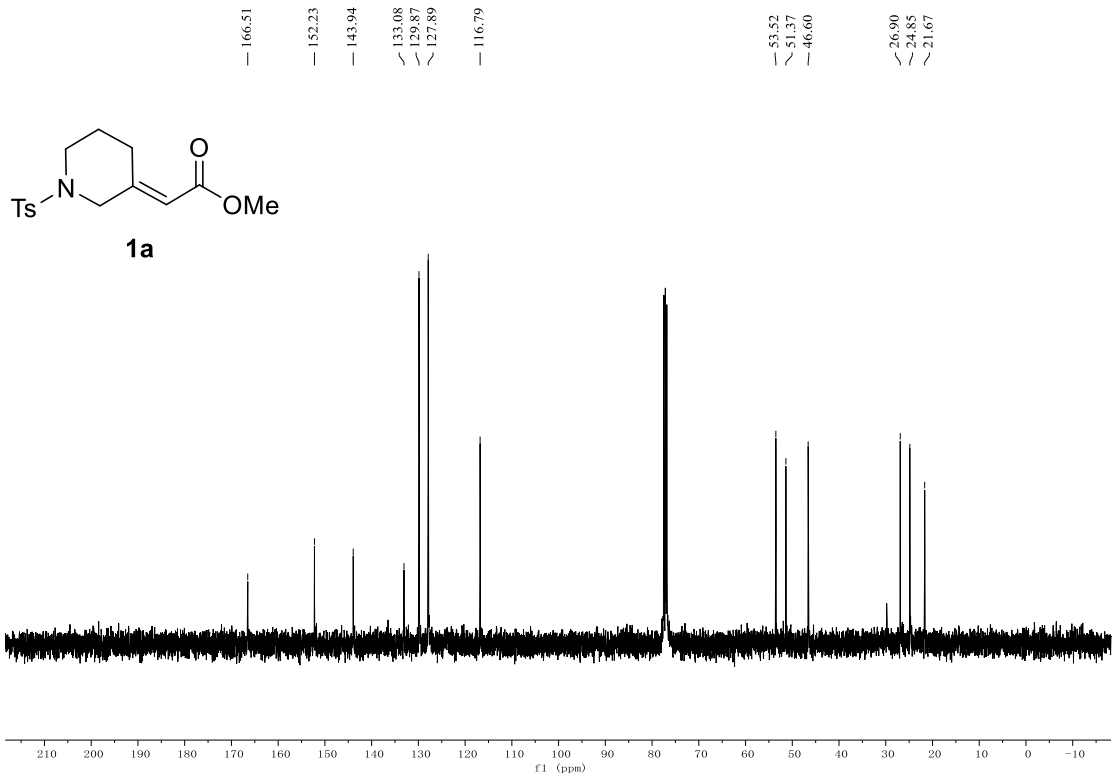
7.64
7.34
7.32
5.79
3.69
3.55
3.15
3.13
3.12
2.81
2.79
2.78
2.43
1.76
1.75
1.73
1.72
1.70
O
N
Ts
OMe
1a
2.01
2.00
1.00
3.02
2.03
2.03
2.03
3.07
2.13
f1 (ppm)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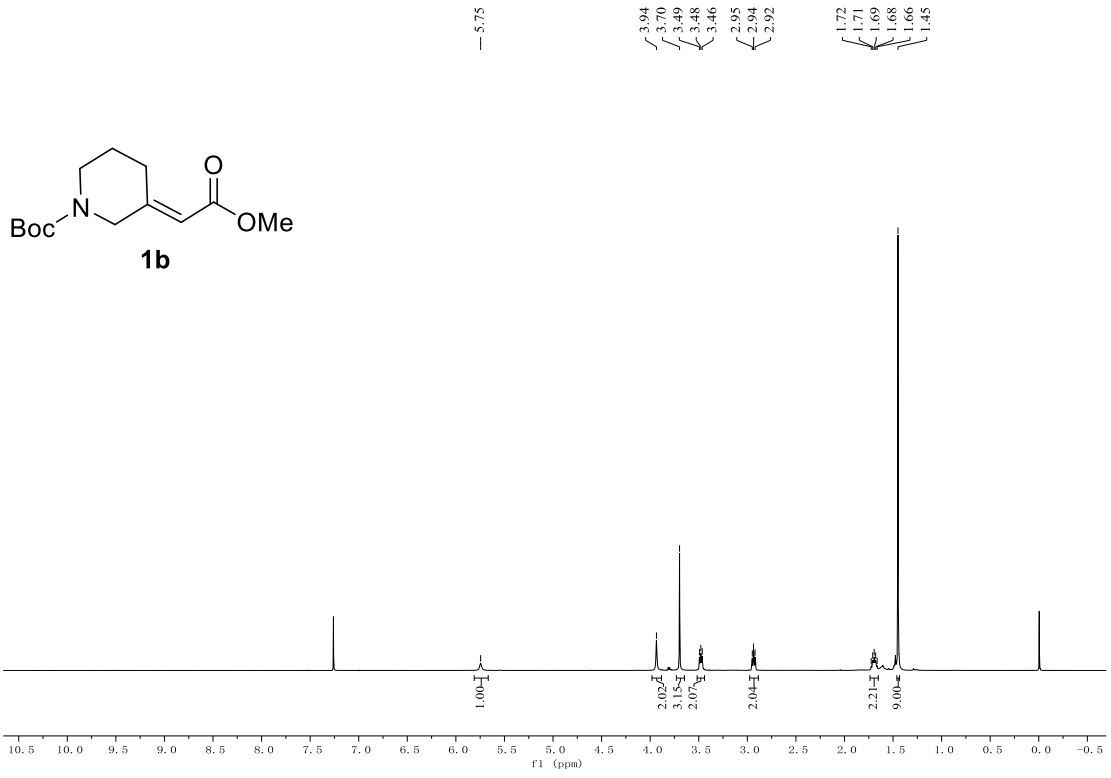
152.23
143.94
133.08
129.87
127.89
116.79
53.52
51.37
46.60
26.90
24.85
21.67
O
N
Ts
OMe
1a
f1 (ppm)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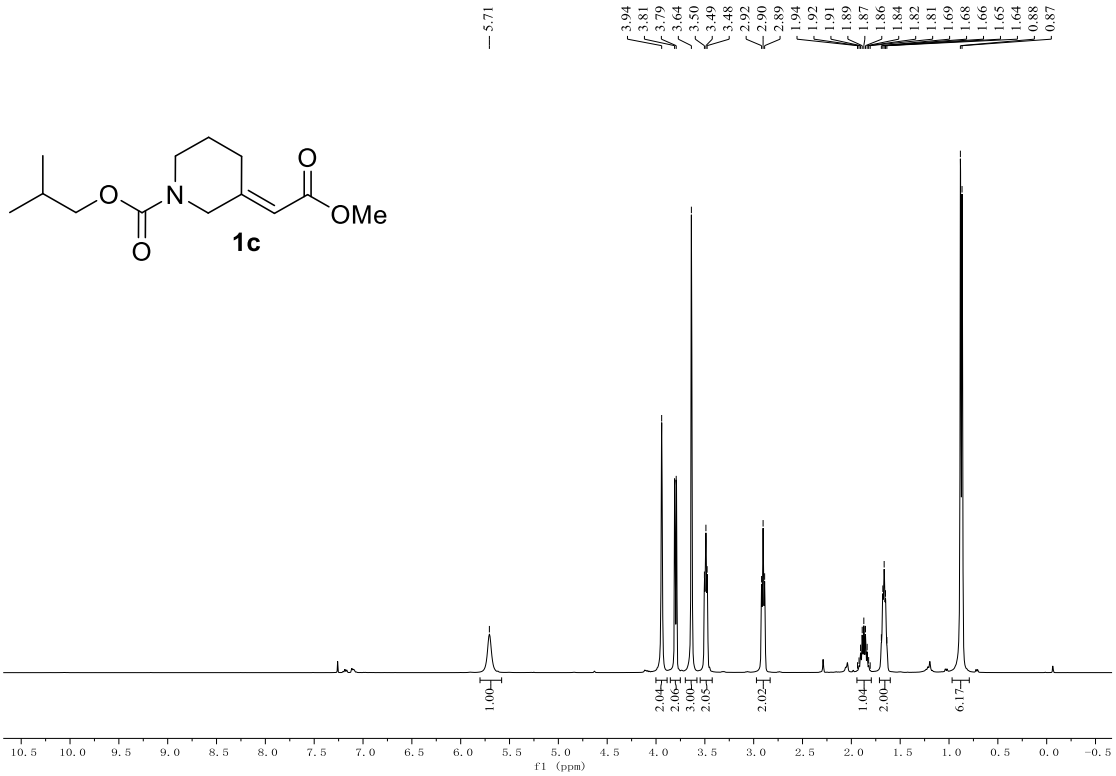
3.94
3.70
3.49
3.48
3.46
2.95
2.94
2.92
1.72
1.71
1.69
1.68
1.66
1.45
Boc
N
O
OMe
1b
1.00
2.02
3.15
2.07
2.04
2.21
9.00
f1 (ppm)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3.48
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2.90
2.89
1.94
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1.91
1.89
1.87
1.86
1.84
1.82
1.81
1.69
1.68
1.66
1.65
1.64
0.88
0.87
O
N
O
O
OMe
1c
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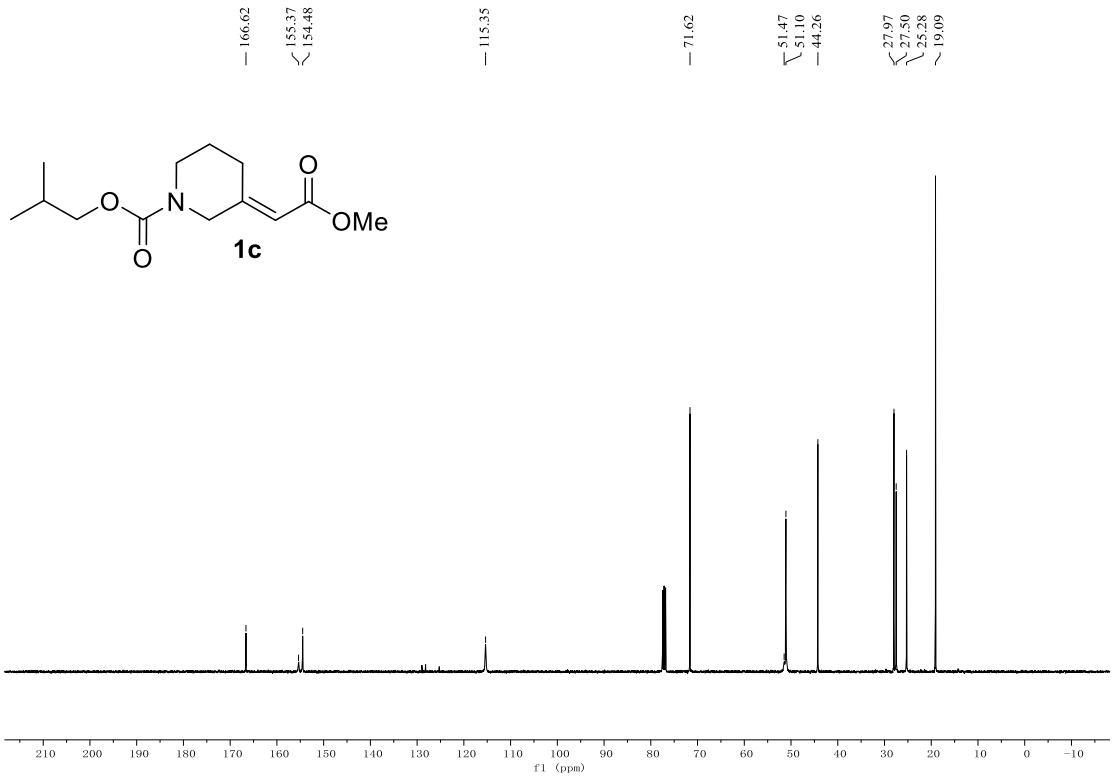
2.04
2.06
3.00
2.05
2.02
1.04
2.00
6.17
f1 (ppm)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51.10
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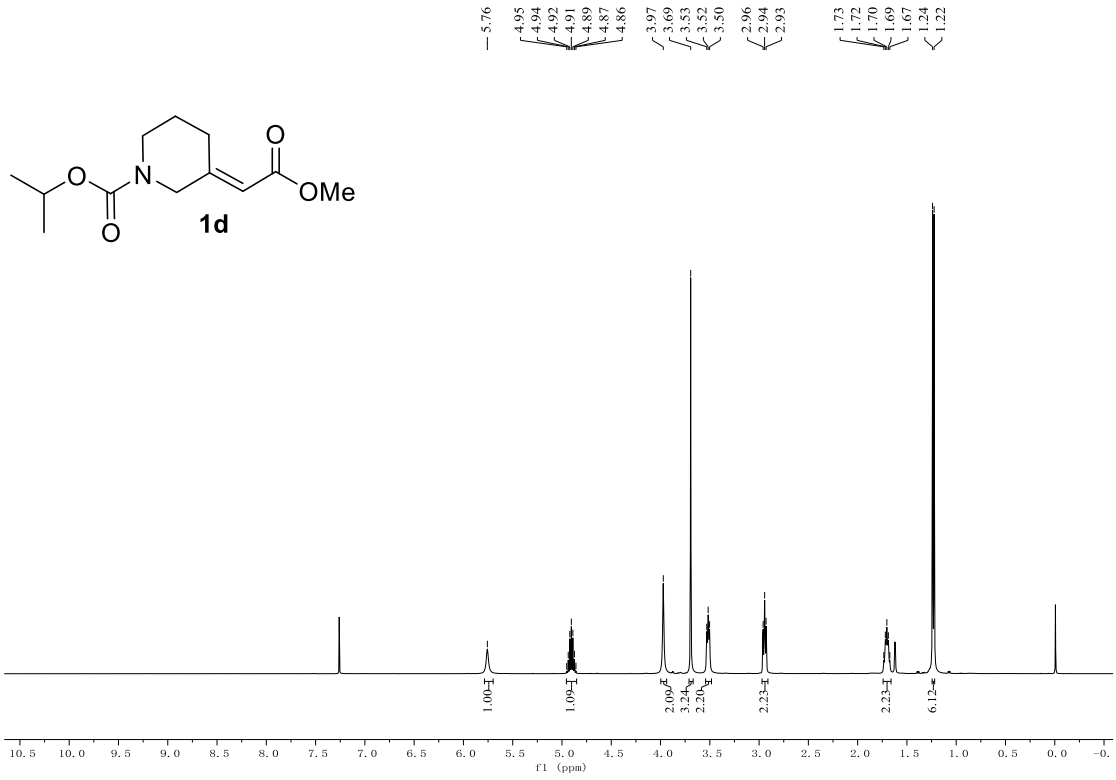
27.50
25.28
19.09
O
N
O
O
OMe
1c
f1 (ppm)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4.91
4.89
4.87
4.86
3.97
3.69
3.53
3.52
3.50
2.96
2.94
2.93
1.73
1.72
1.70
1.69
1.67
1.24
1.22
O
N
O
O
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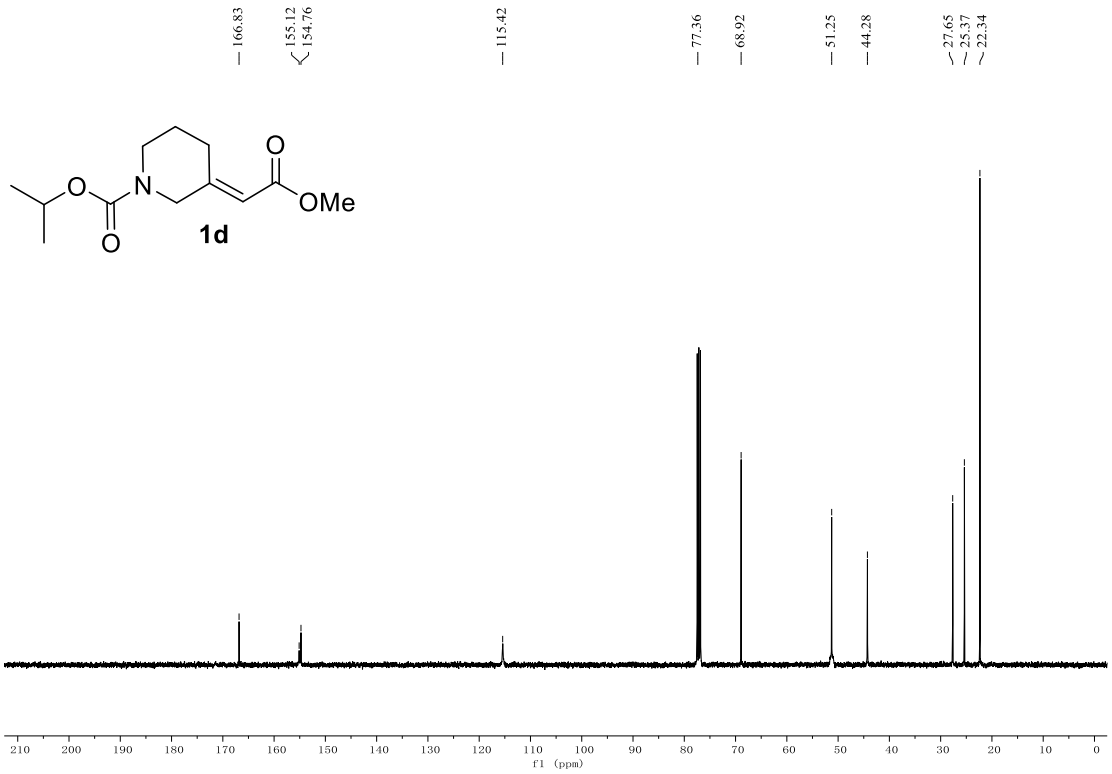
1d
1.00
1.09
2.09
3.24
2.20
2.23
2.23
6.12
f1 (ppm)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68.92
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44.28
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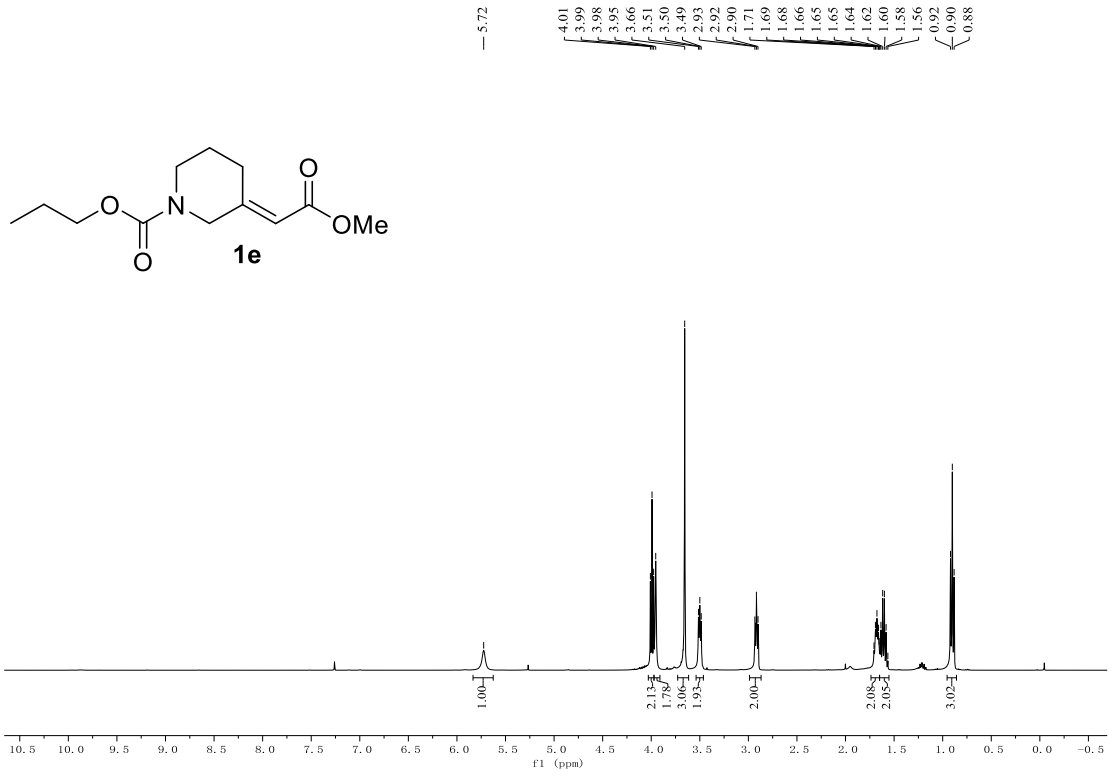
25.37
22.34
O
N
O
O
OMe
1d
f1 (ppm)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3.50
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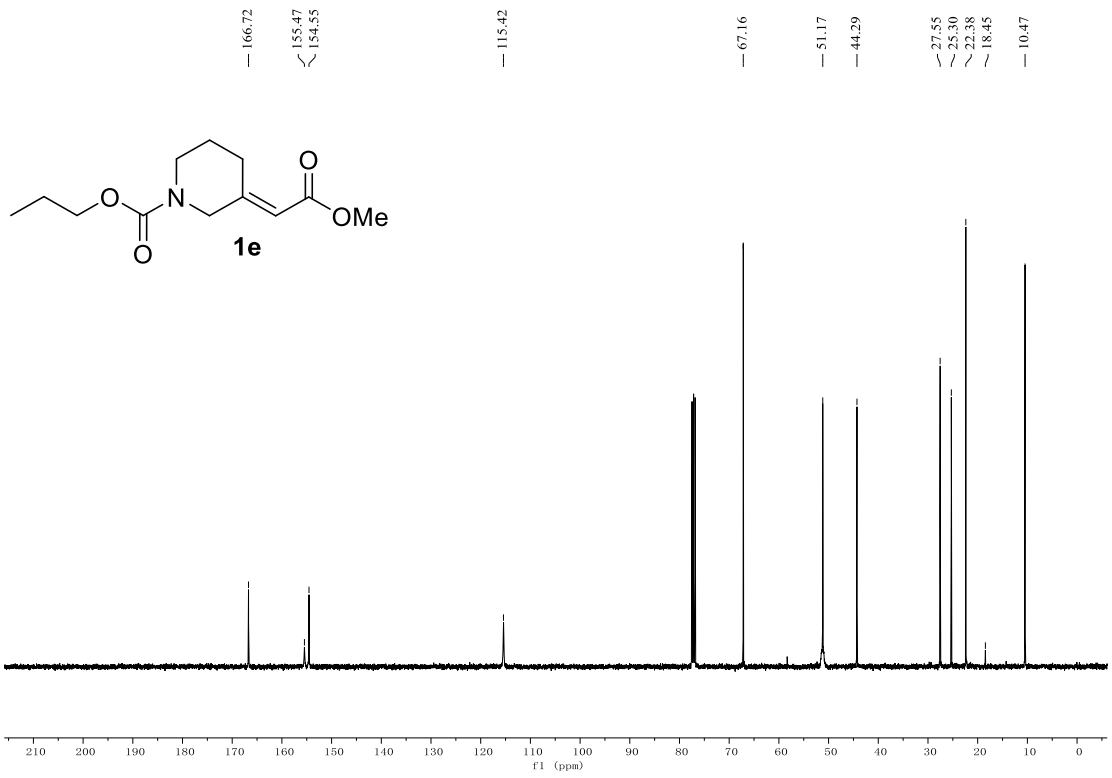
2.92
2.90
1.71
1.69
1.68
1.66
1.65
1.65
1.64
1.62
1.60
1.58
1.56
0.92
0.90
0.88
O
N
O
O
OMe
1e
1.00
2.13
1.78
3.06
1.93
2.00
2.08
2.05
3.02
f1 (ppm)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154.55
115.42
67.16
51.17
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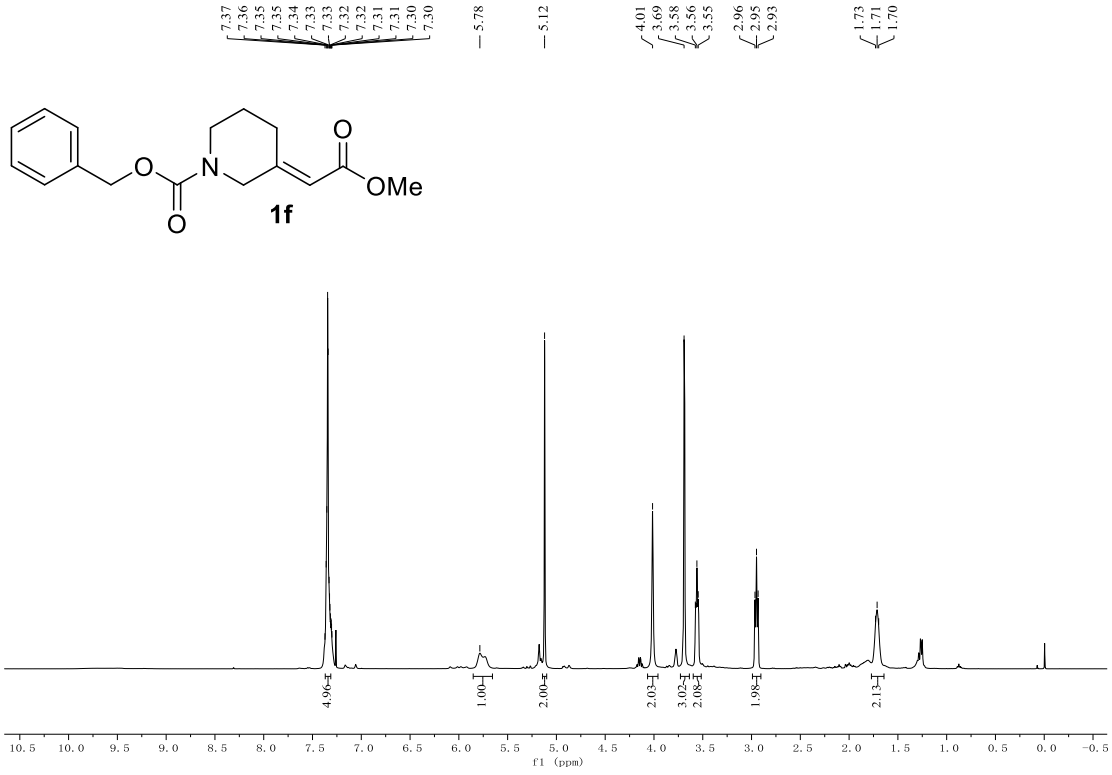
22.38
18.45
10.47
O
O
N
O
OMe
O
1e
f1 (ppm)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7.33
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7.32
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7.31
7.31
7.30
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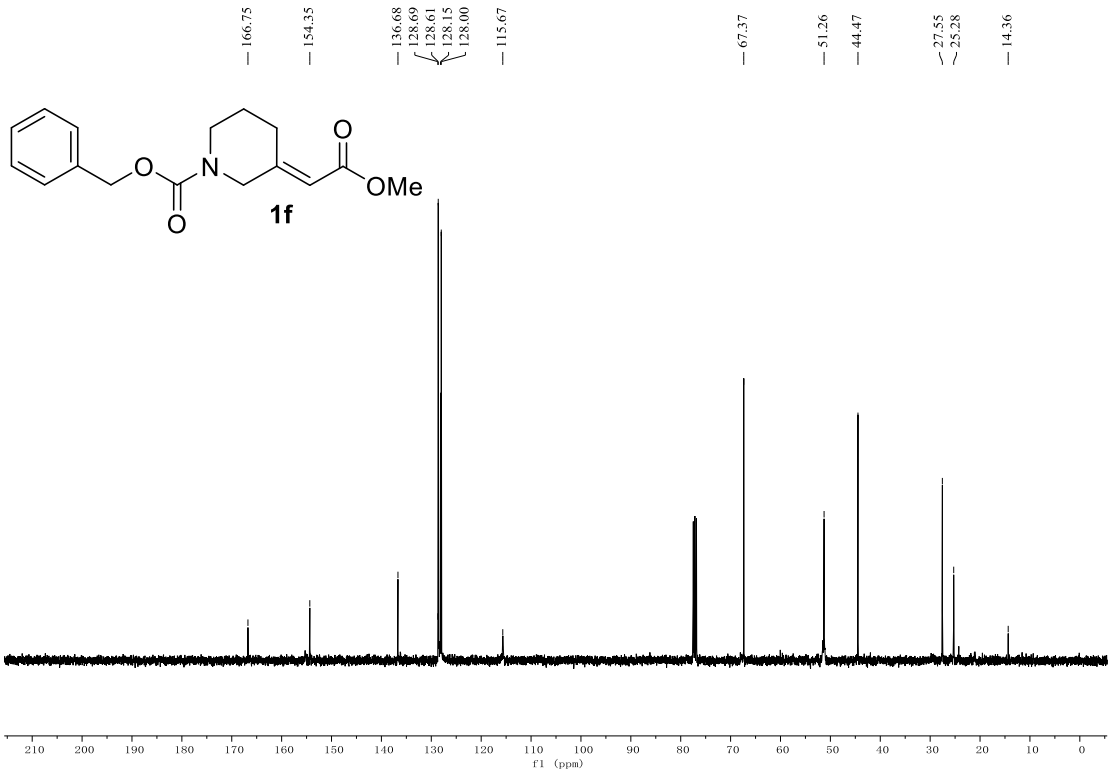
3.69
3.58
3.56
3.55
2.96
2.95
2.93
1.73
1.71
1.70
O
O
N
O
OMe
O
1f
4.96
1.00
2.00
2.03
3.02
2.08
1.98
2.13
f1 (ppm)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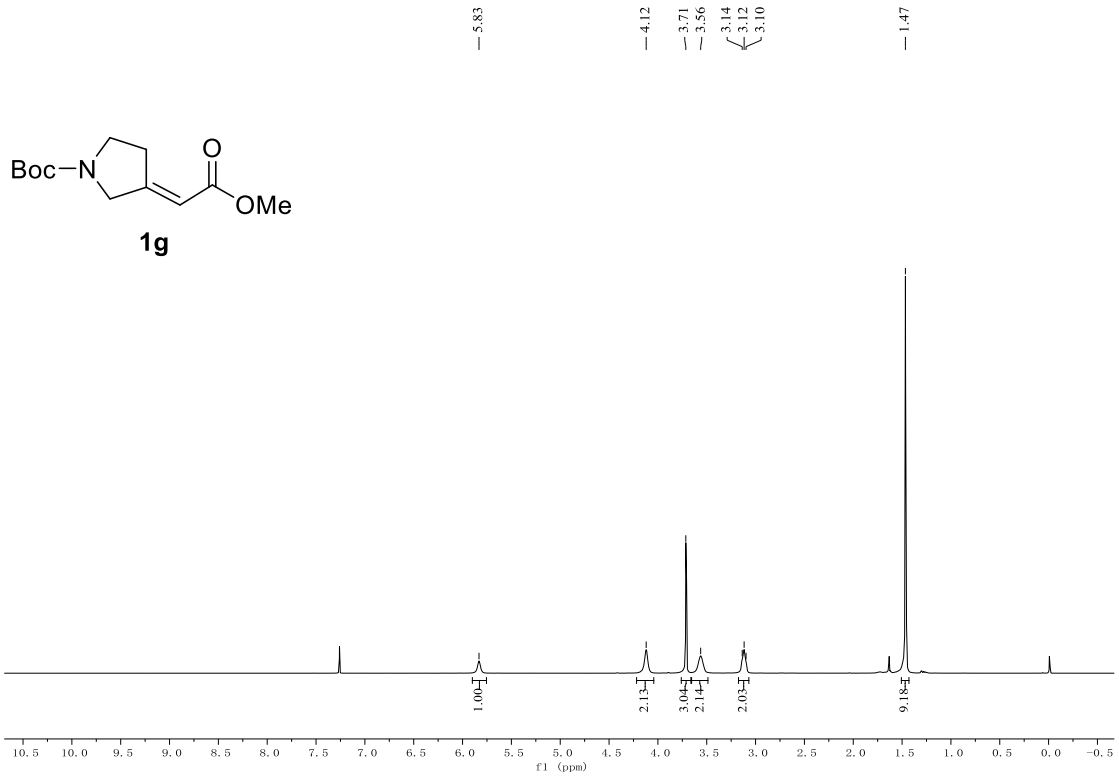
27.55
25.28
14.36
O
N
O
O
OMe
1f
f1 (ppm)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4.12
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3.56
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O
OMe
1g
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2.13
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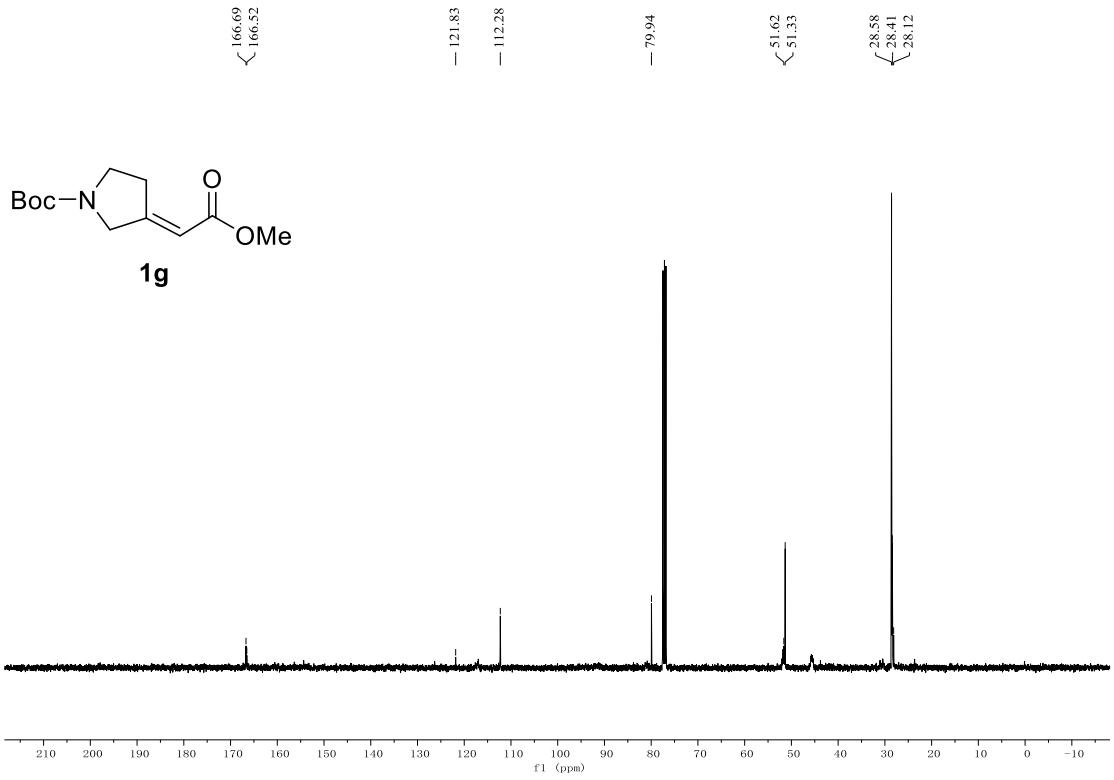
2.14
2.03
9.18
f1 (ppm)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28.41
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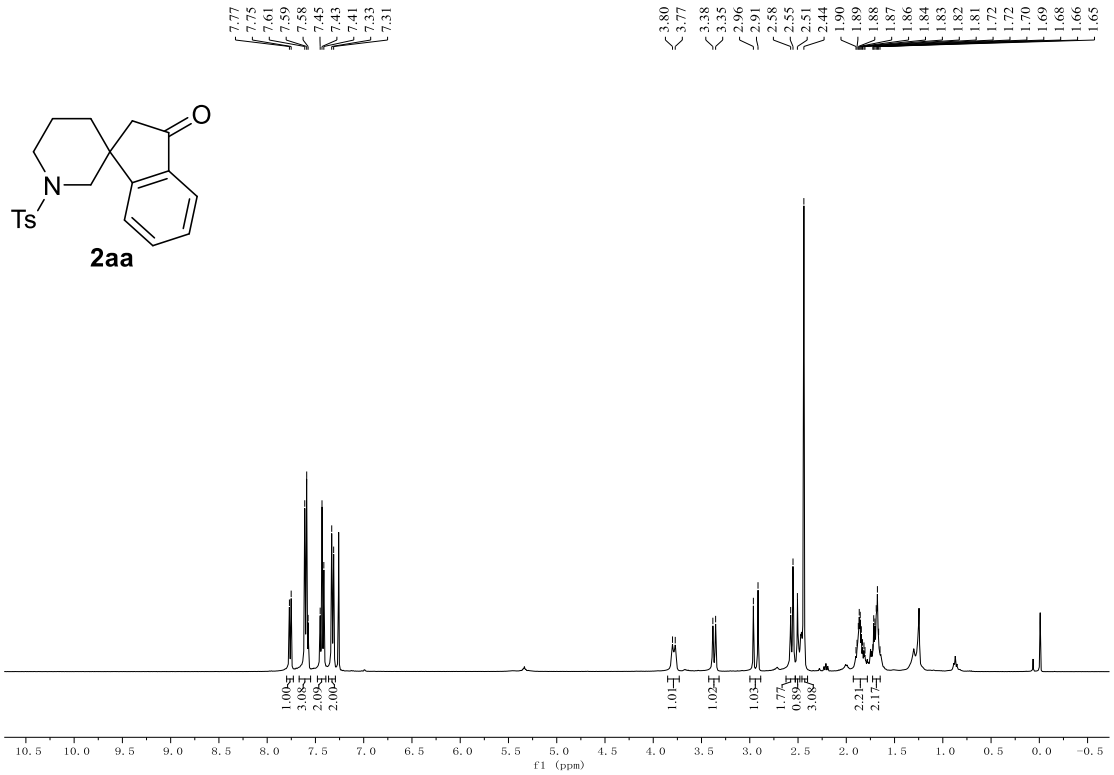
N
O
OMe
1g
f1 (ppm)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3.35
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1.88
1.87
1.86
1.84
1.83
1.82
1.81
1.72
1.72
1.70
1.69
1.68
1.66
1.65
O
N
Ts
2aa
1.00
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1.02
1.03
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3.08
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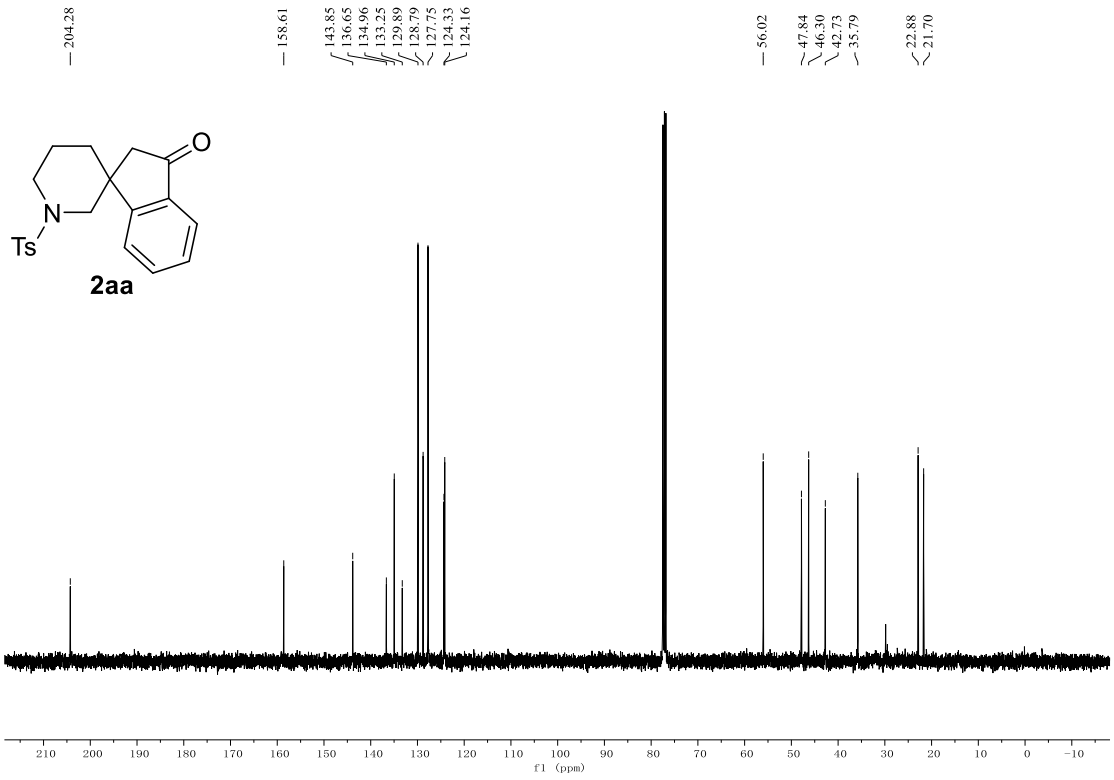
2.17
f1 (ppm)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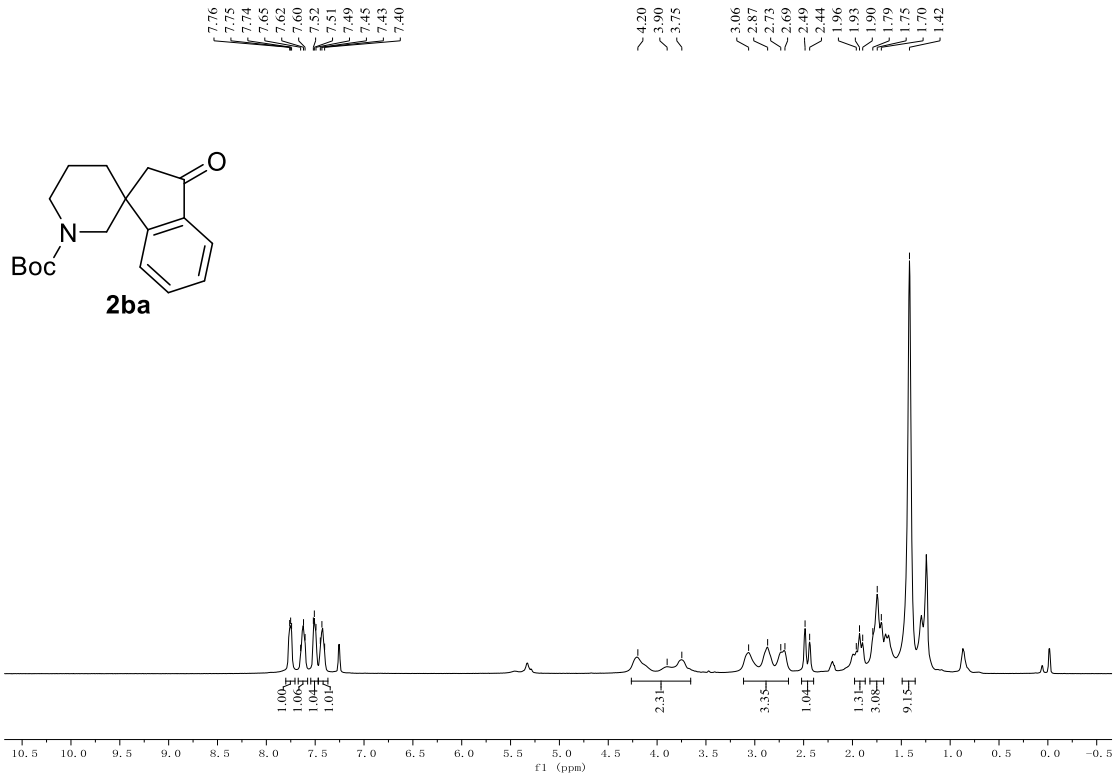
46.30
42.73
35.79
22.88
21.70
O
N
Ts
2aa
f1 (ppm)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7.43
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2.87
2.73
2.69
2.49
2.44
1.96
1.93
1.90
1.79
1.75
1.70
1.42
O
N
Boc
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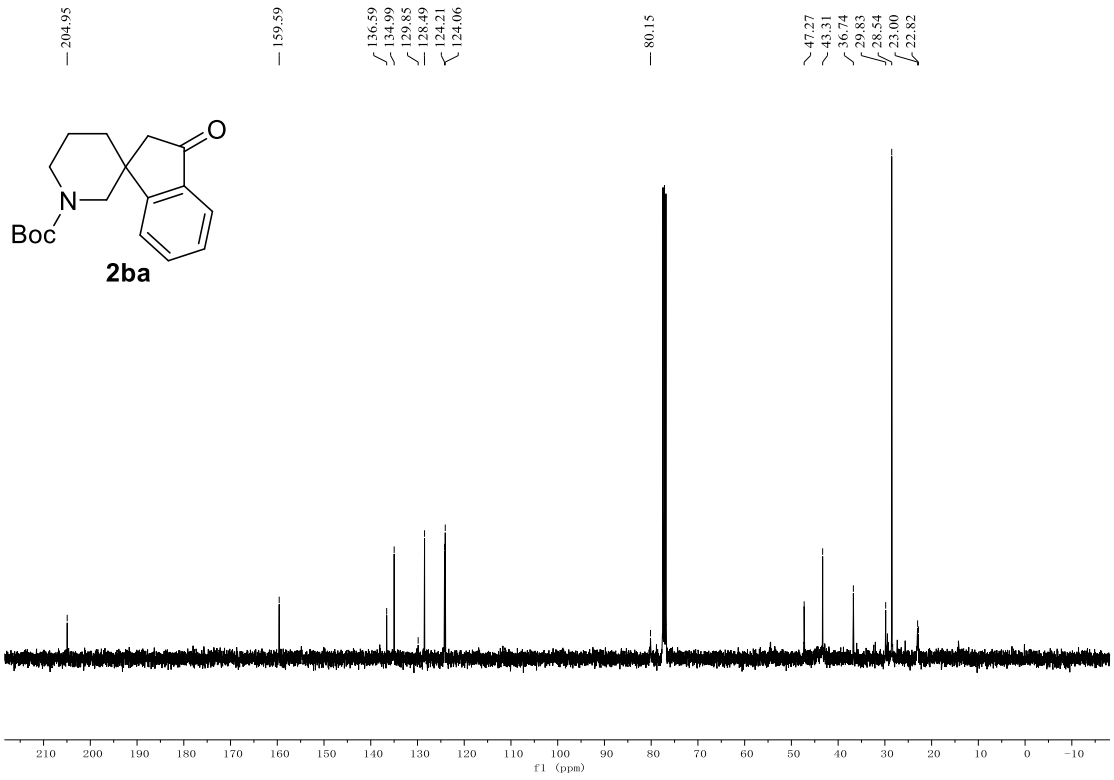
1.01
2.31
3.35
1.04
1.31
3.08
9.15
f1 (ppm)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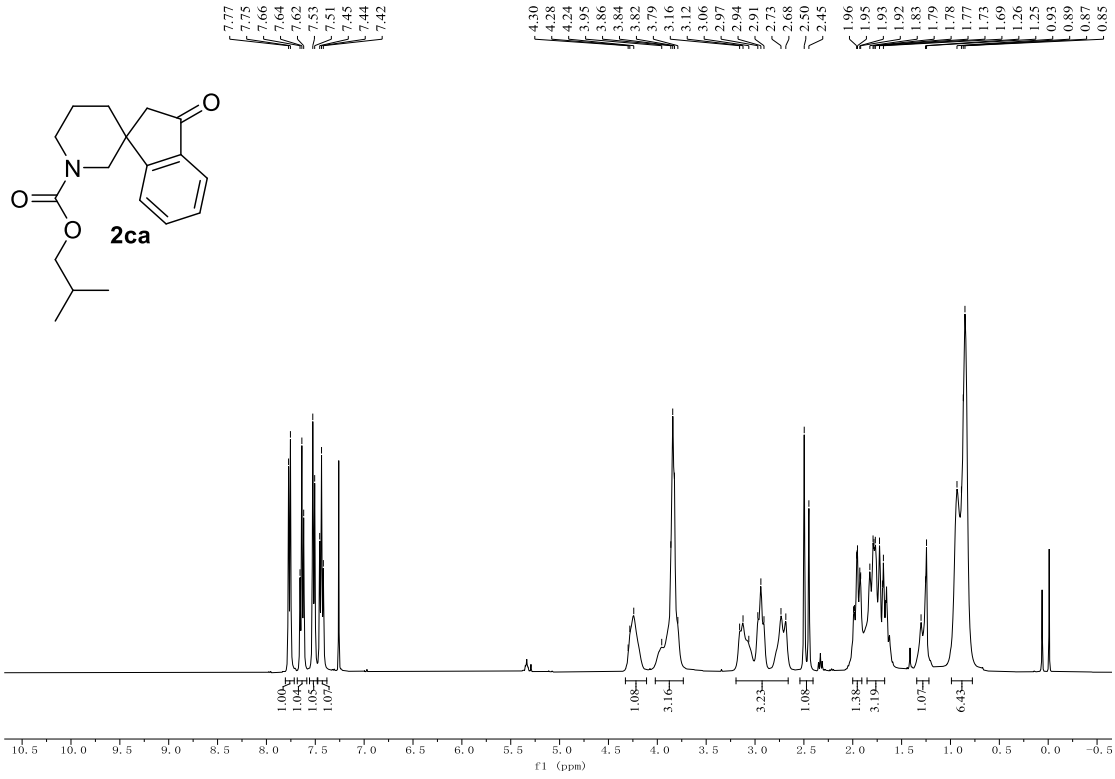
22.82
O
N
Boc
2ba
f1 (ppm)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7.42
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0.85
O
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O
O
2ca
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1.08
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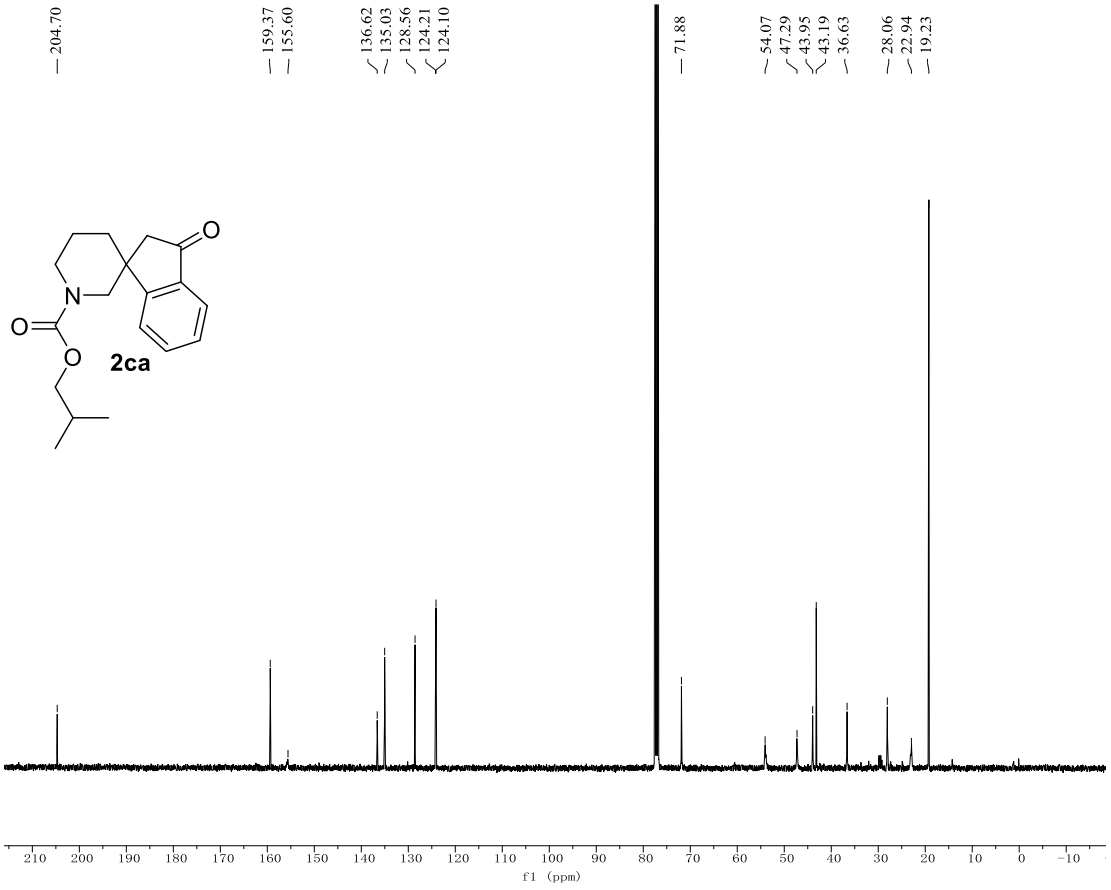
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43.19
36.63
28.06
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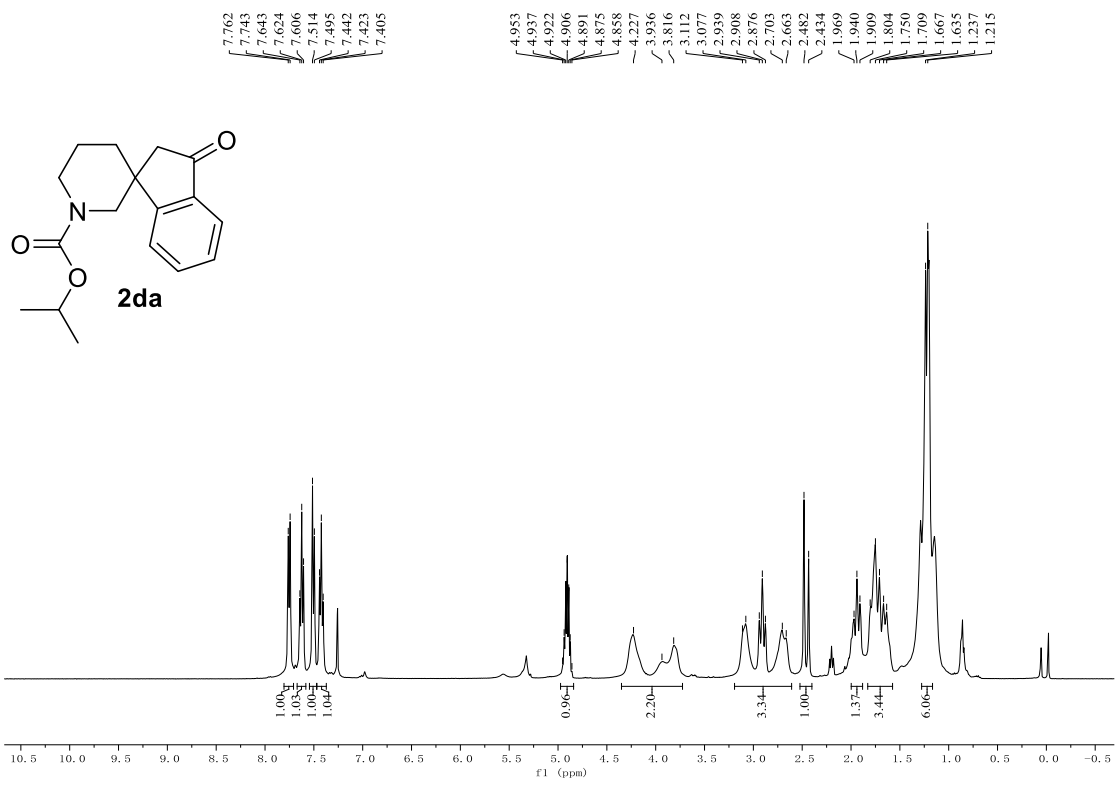
f1 (ppm)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4.906
4.891
4.875
4.858
4.227
3.936
3.816
3.112
3.077
2.939
2.908
2.876
2.703
2.663
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2.434
1.969
1.940
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1.750
1.709
1.667
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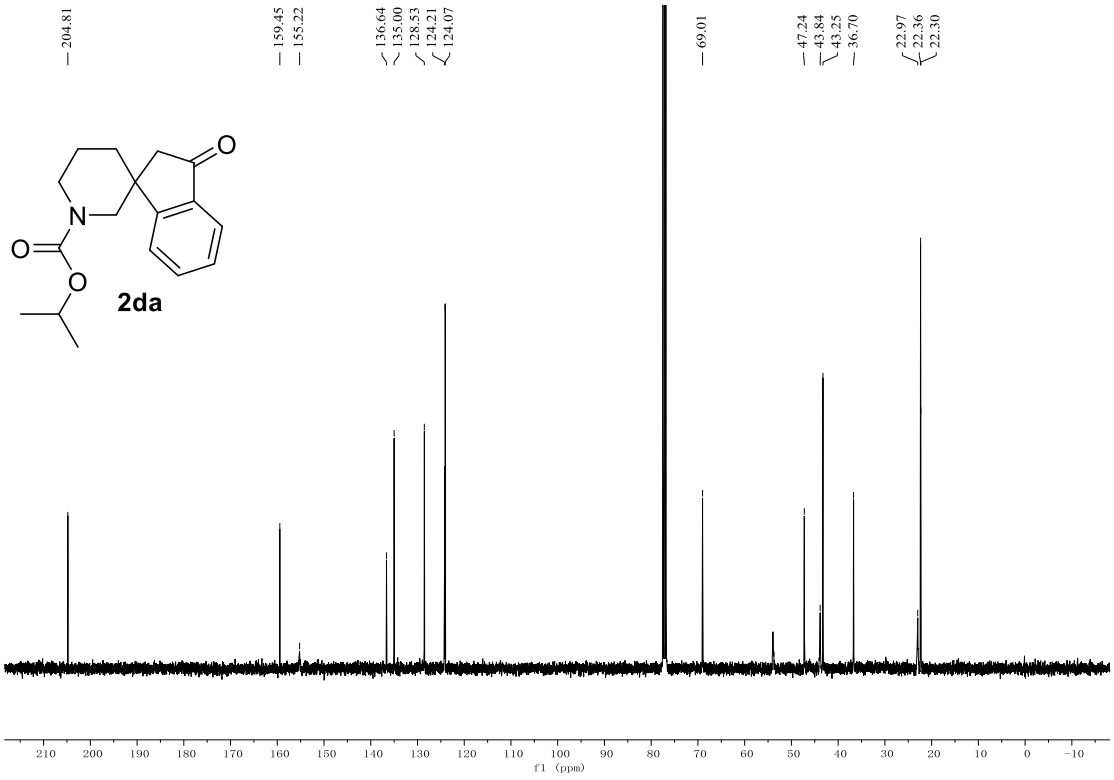
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22.36
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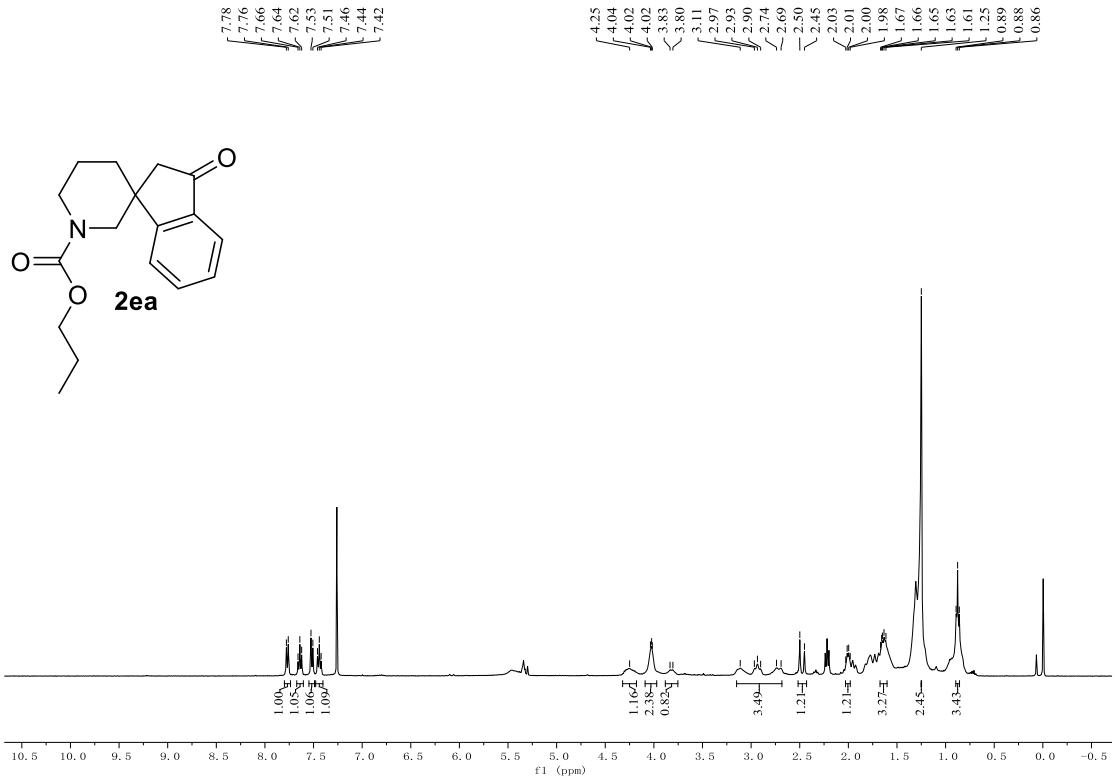
O
O
2da
f1 (ppm)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3.80
3.11
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2.90
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2.69
2.50
2.45
2.03
2.01
2.00
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1.61
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0.86
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O
O
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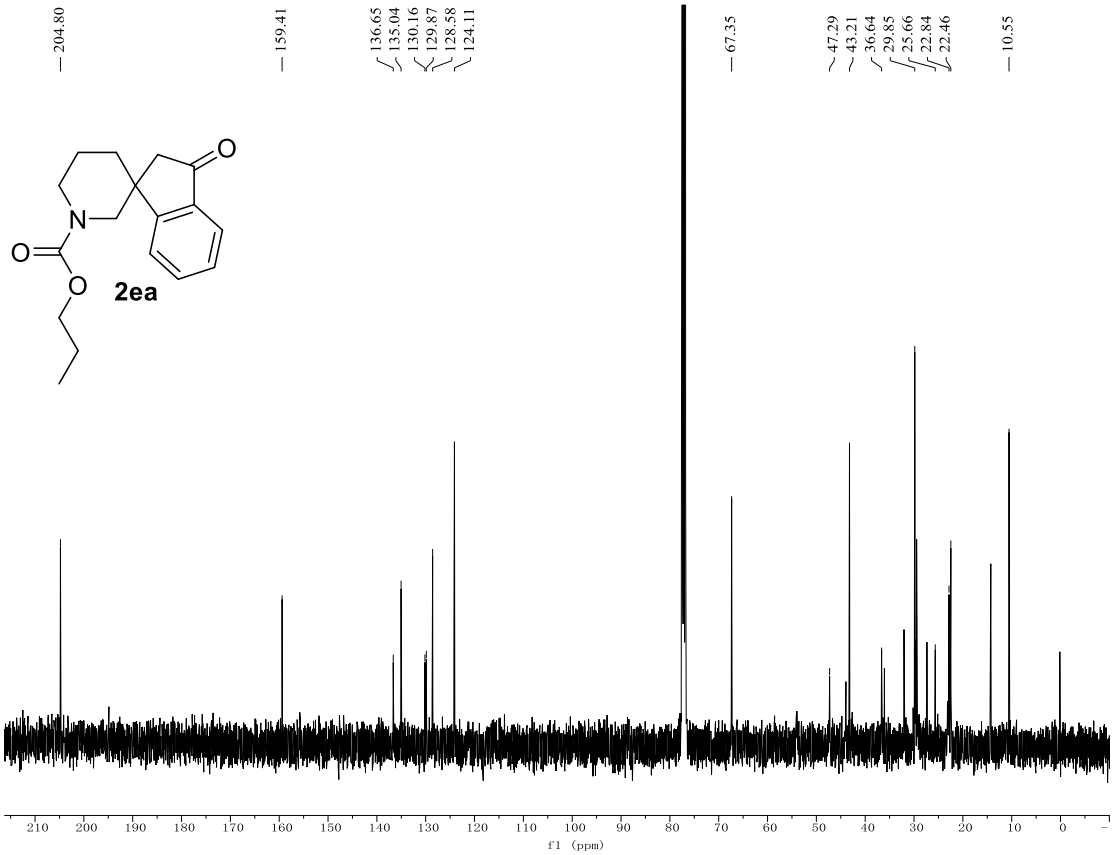
f1 (ppm)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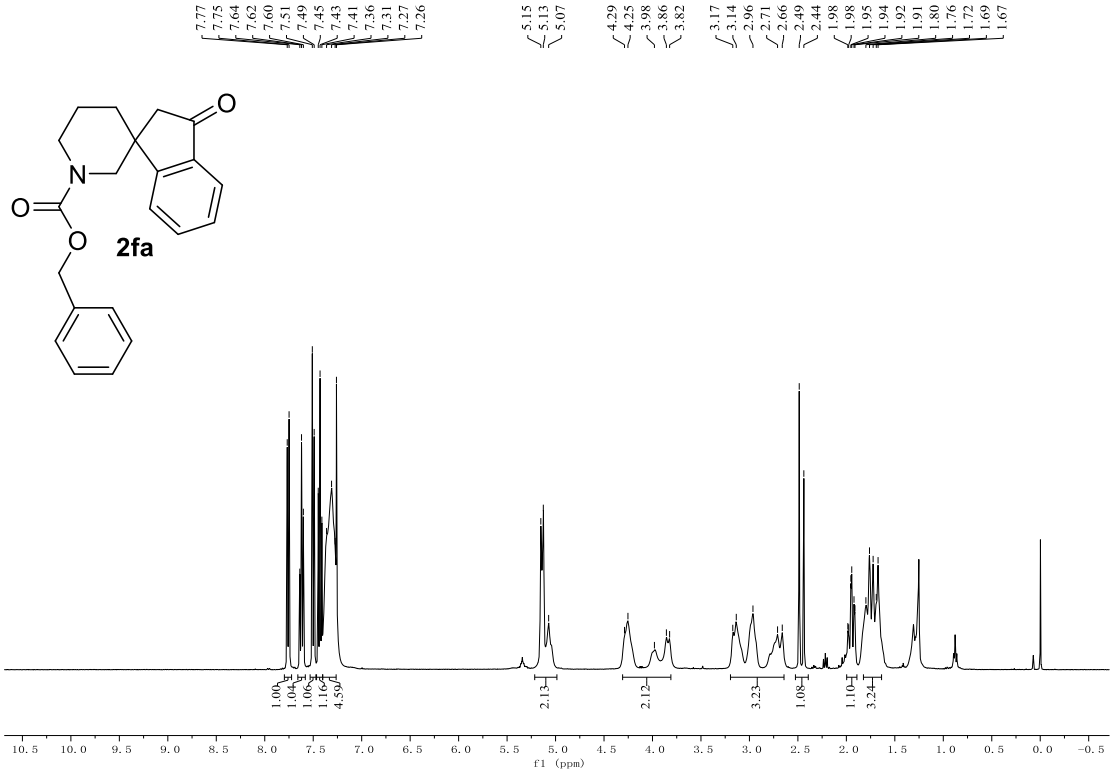
f1 (ppm)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5.15
5.13
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4.25
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3.86
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3.17
3.14
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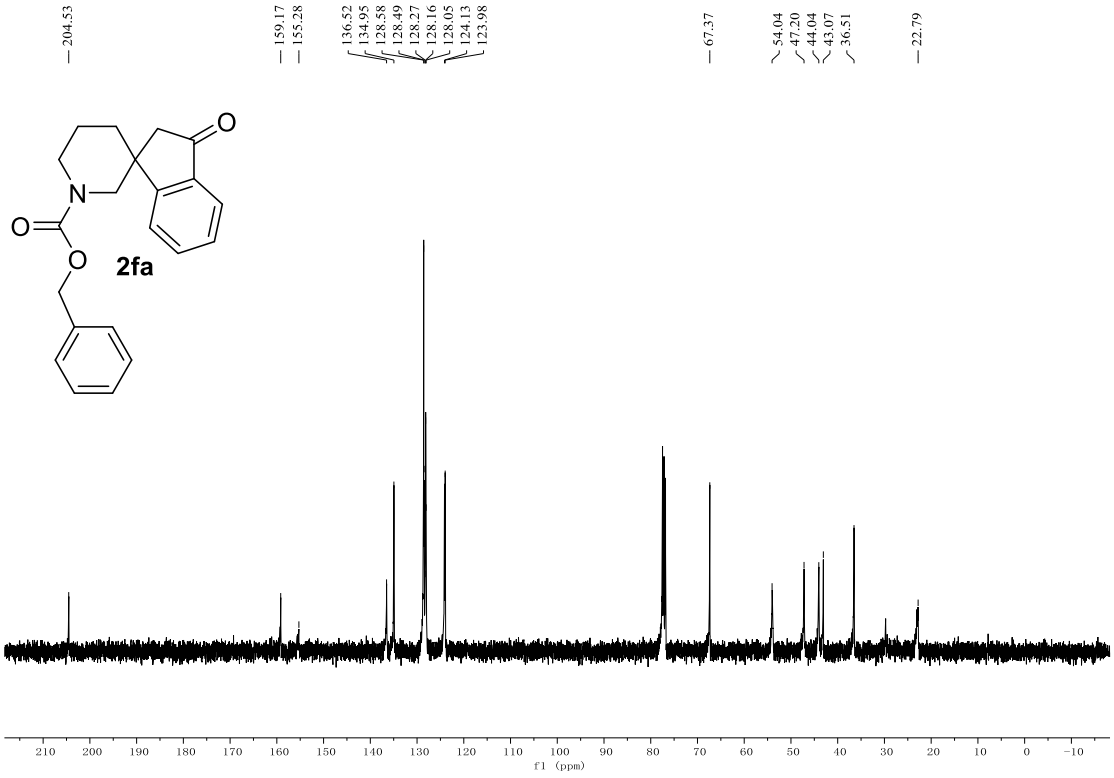
f1 (ppm)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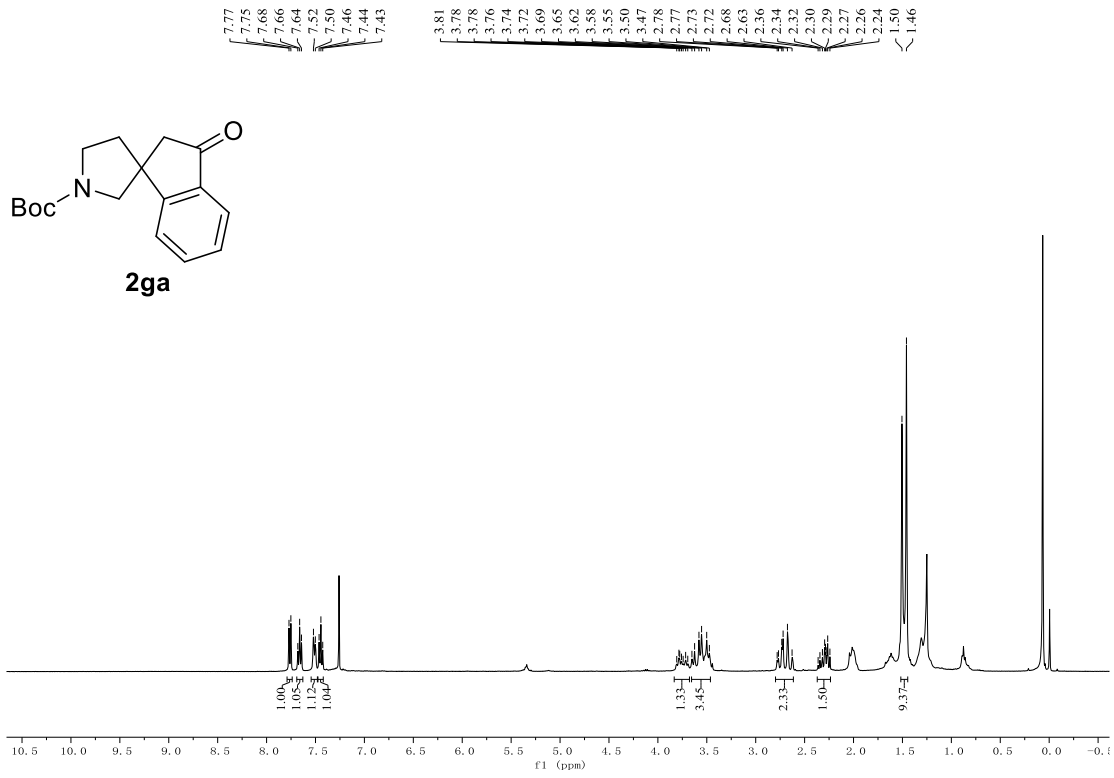
f1 (ppm)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3.78
3.76
3.74
3.72
3.69
3.65
3.62
3.58
3.55
3.50
3.47
2.78
2.77
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2.36
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2.29
2.27
2.26
2.24
1.50
1.46
O
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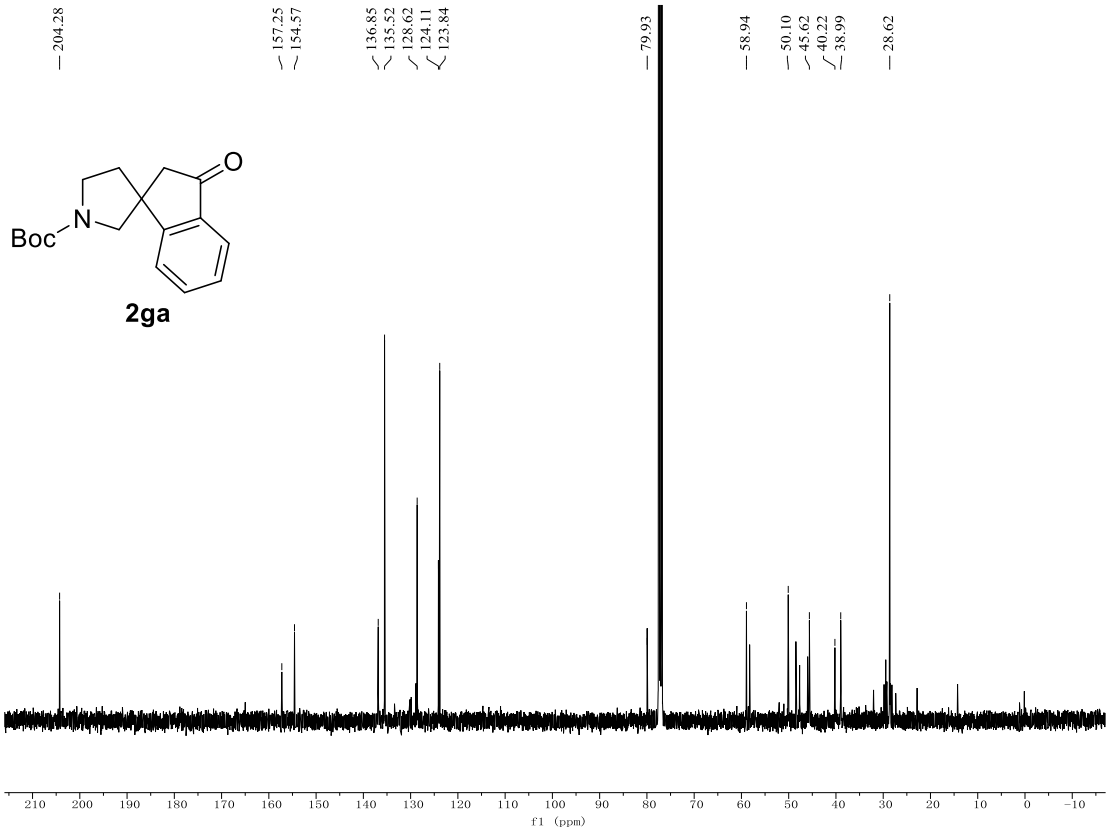
2.33
1.50
9.37
f1 (ppm)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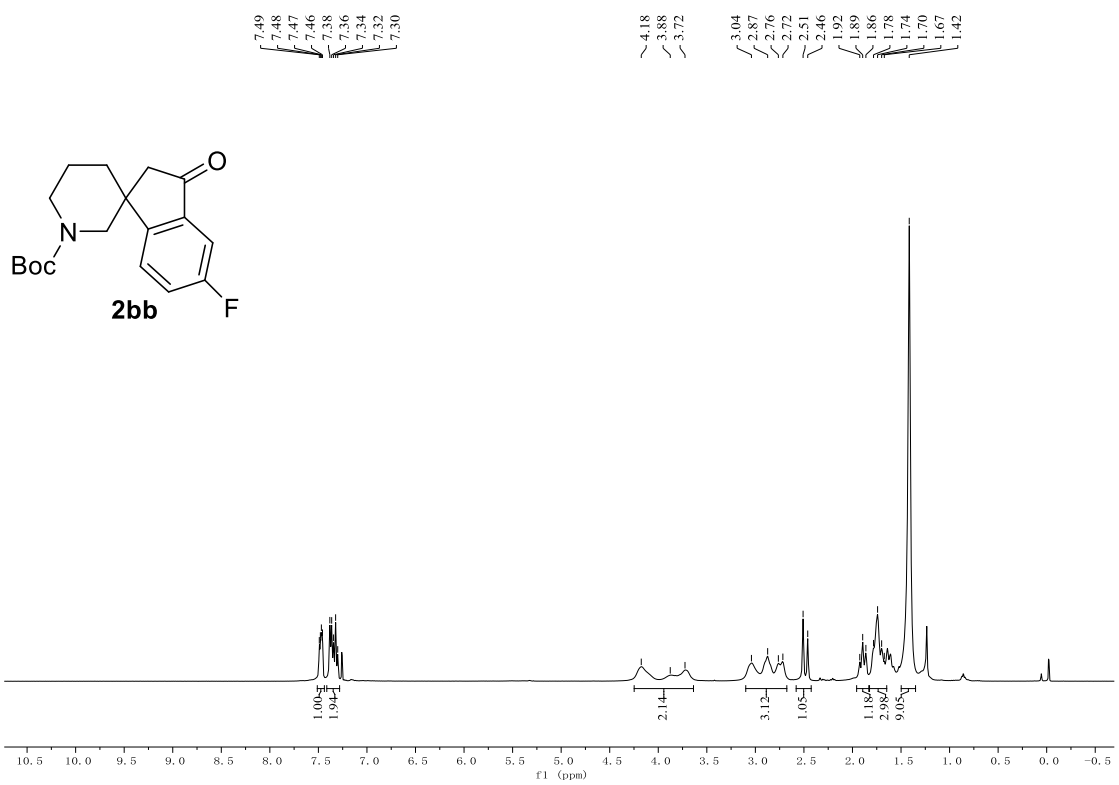
O
N
Boc
f1 (ppm)

2ga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2.76
2.72
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2.46
1.92
1.89
1.86
1.78
1.74
1.70
1.67
1.42
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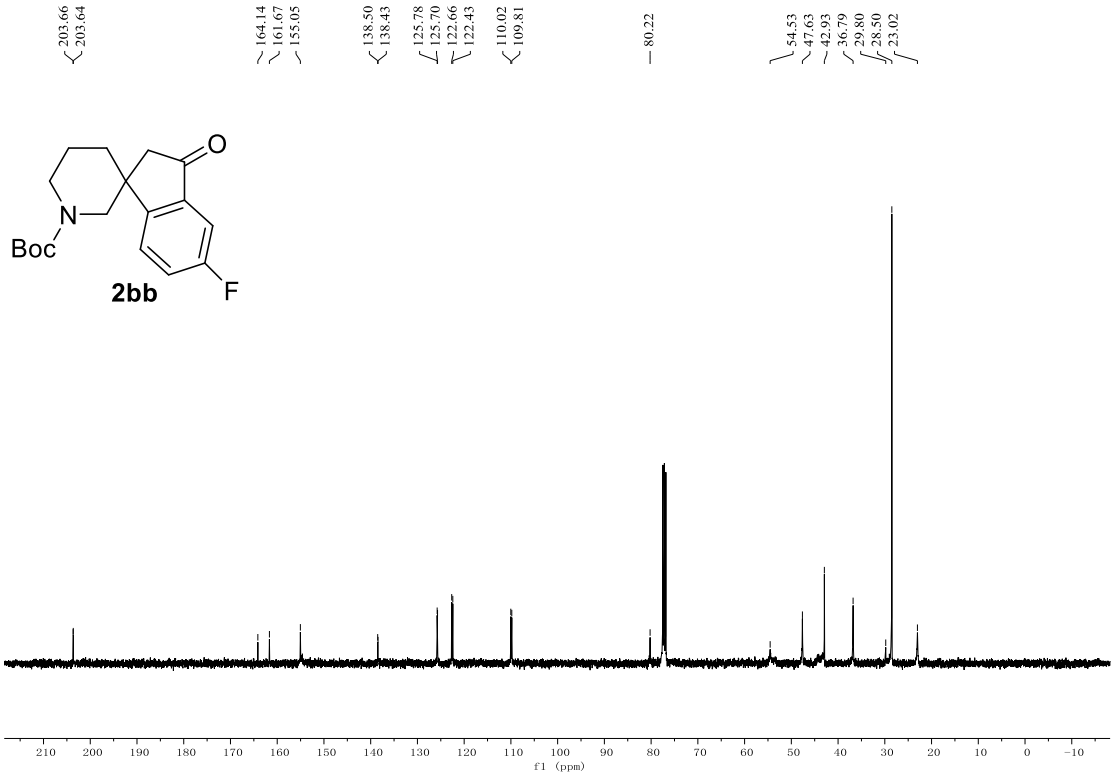
9.05
f1 (ppm)

2bb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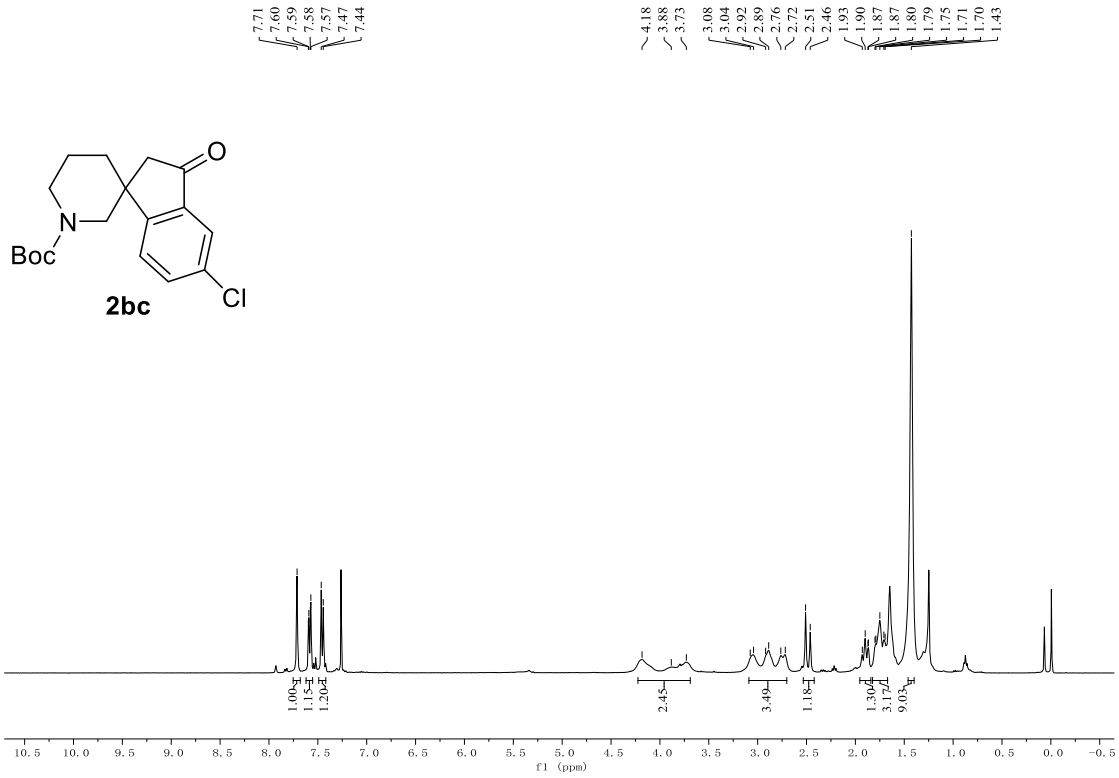
Boc
F
2bb
f1 (ppm)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2.72
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1.87
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1.79
1.75
1.71
1.70
1.43
O
N
Boc
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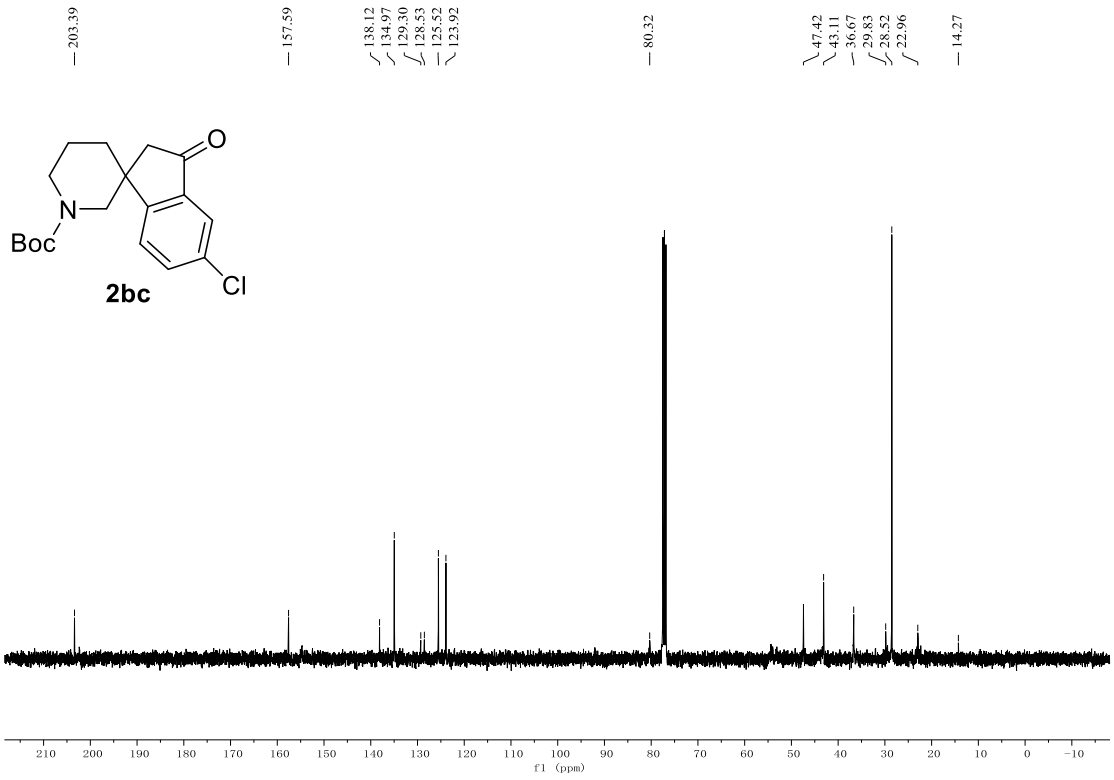
f1 (ppm)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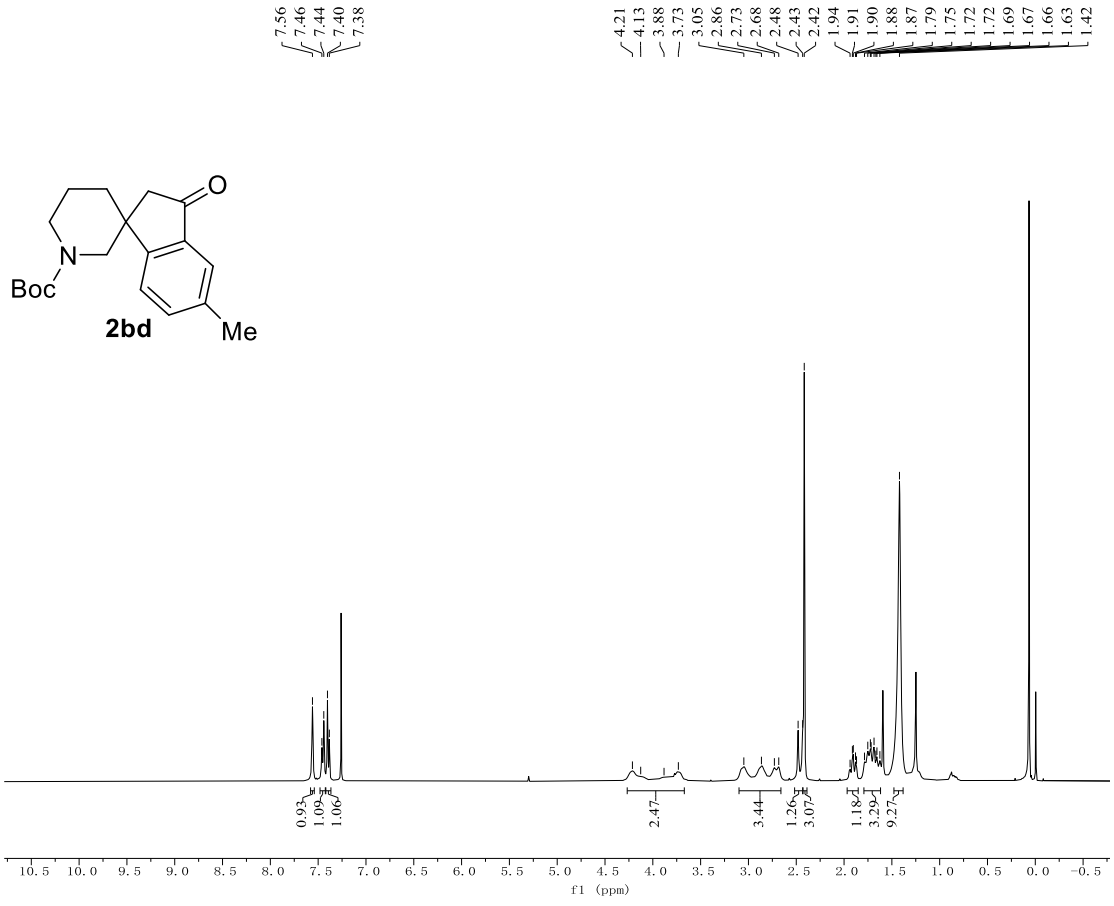
22.96
14.27
O
N
Boc
Cl
2bc
f1 (ppm)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2.43
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1.91
1.90
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1.42
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Boc
Me
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1.18
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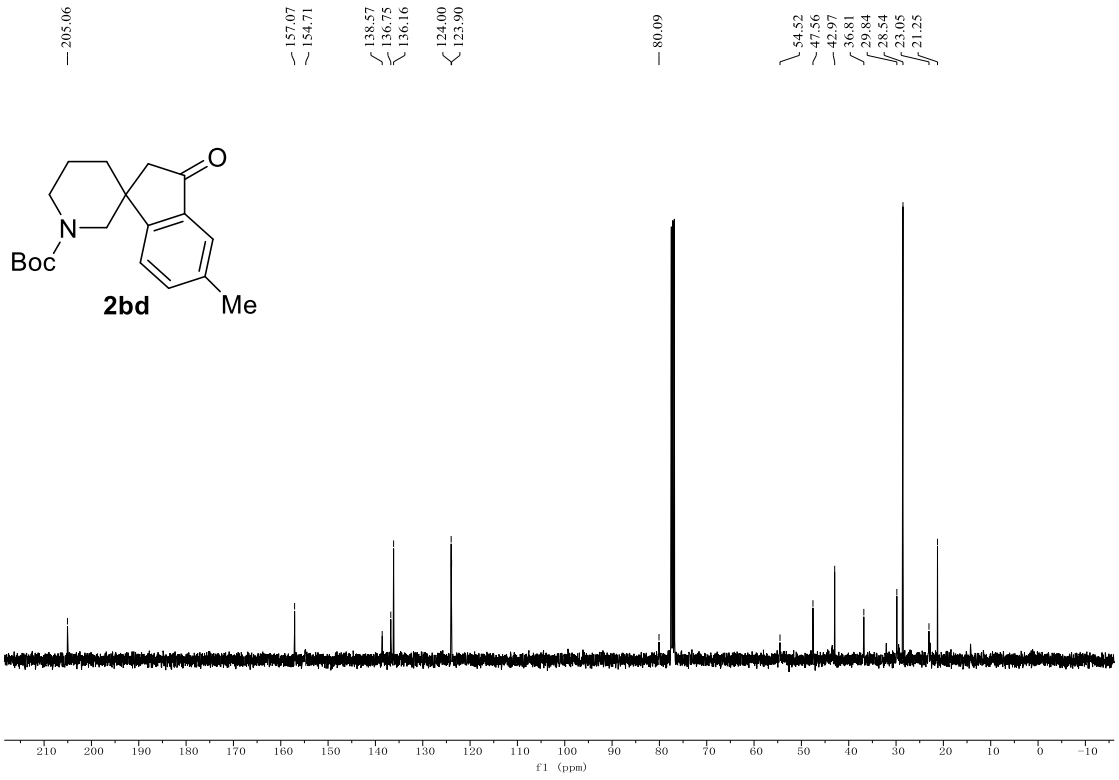
f1 (ppm)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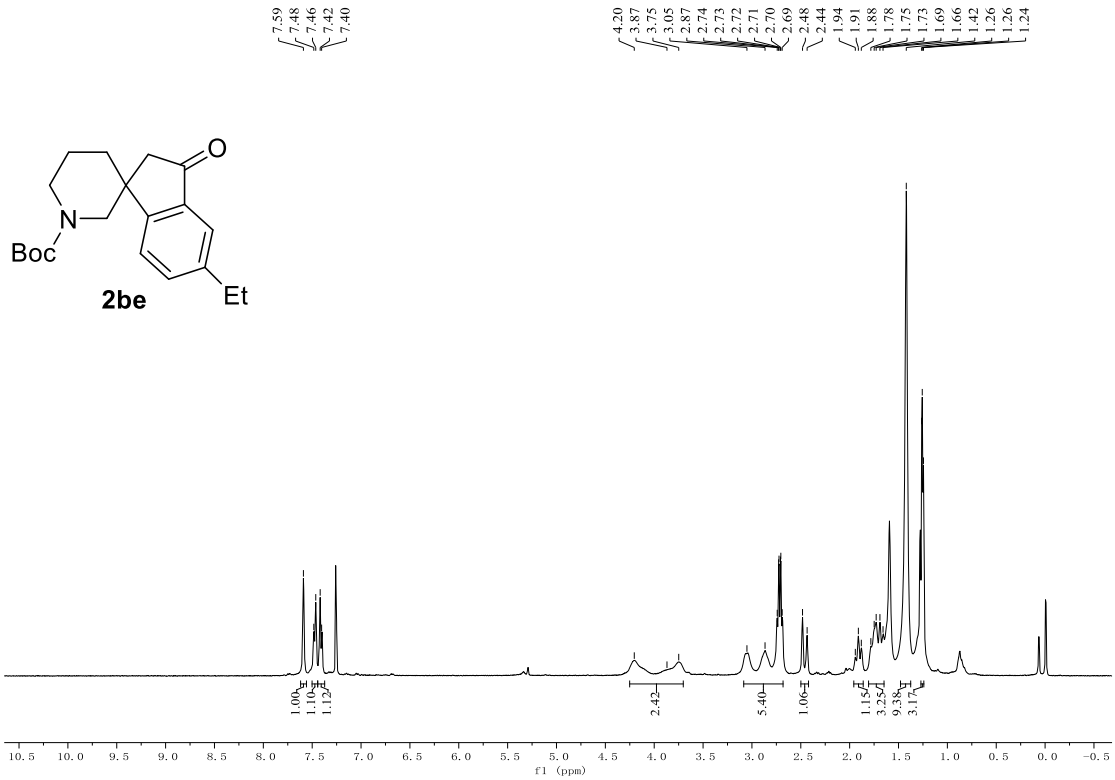
O
N
Boc
2bd
Me
f1 (ppm)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1.78
1.75
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1.66
1.42
1.26
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1.24
O
N
Boc
2be
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3.25
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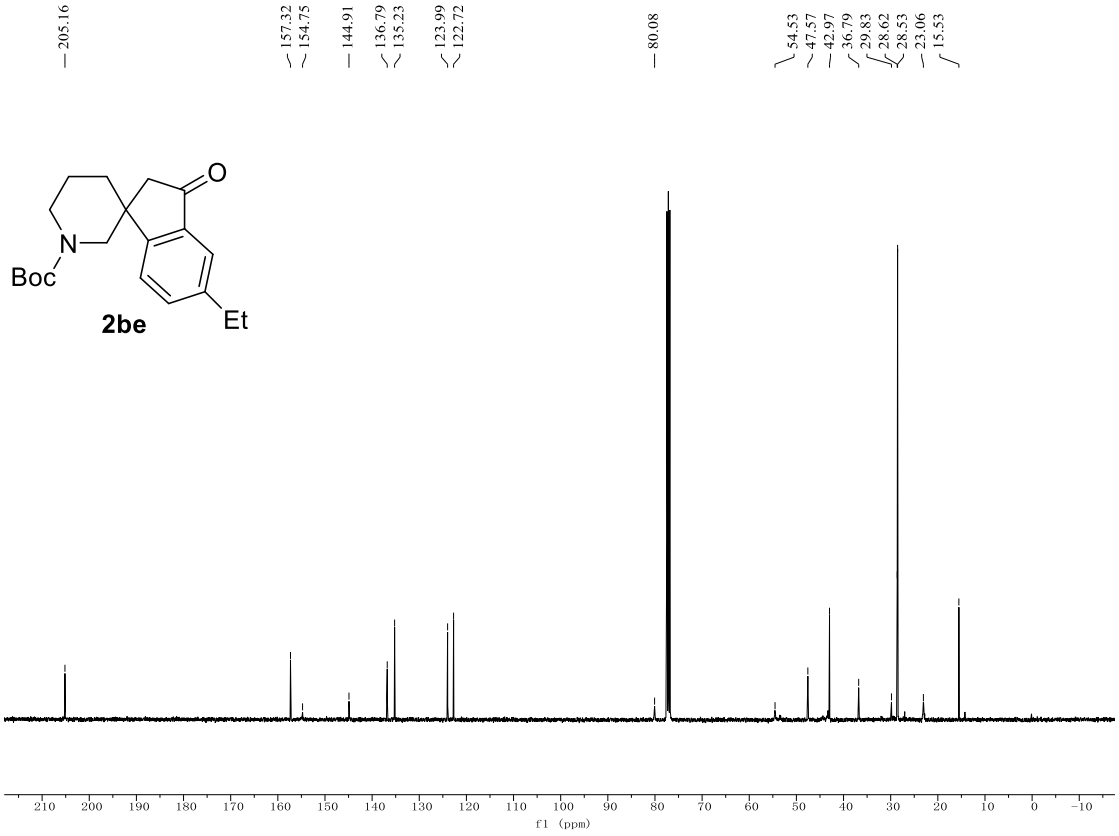
3.17
f1 (ppm)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O
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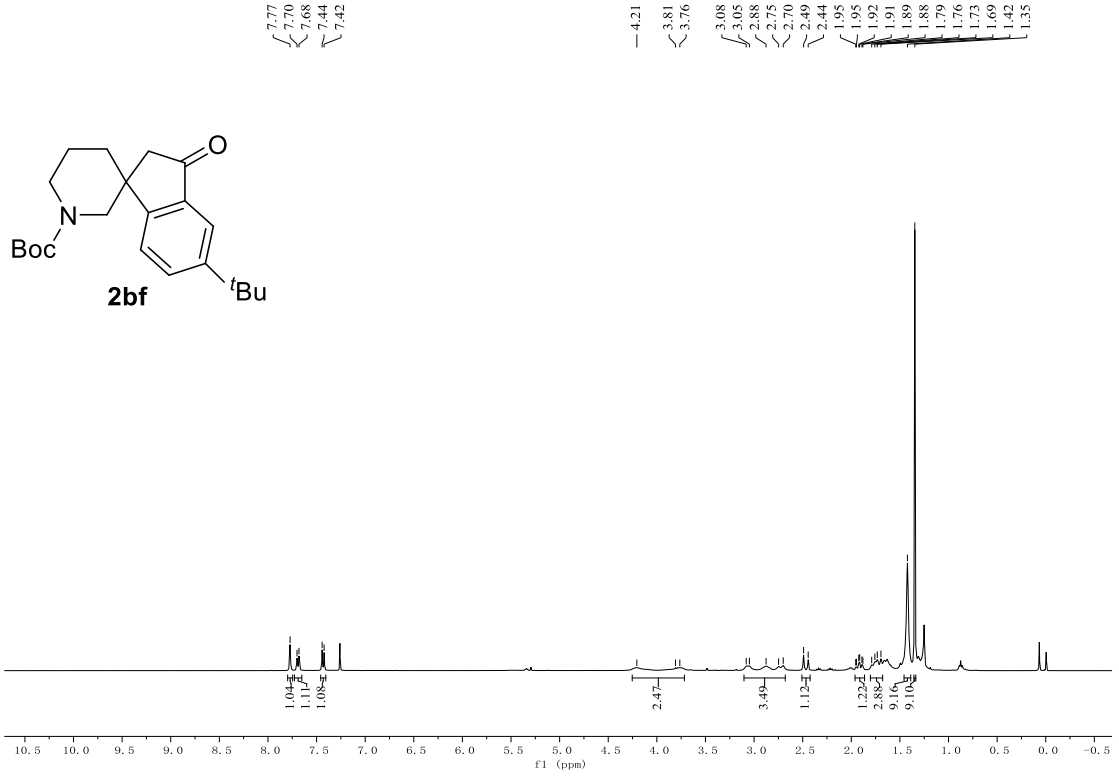
Boc
Et
2be
f1 (ppm)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1.95
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1.91
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1.73
1.69
1.42
1.35
1.04
1.17
1.08
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O
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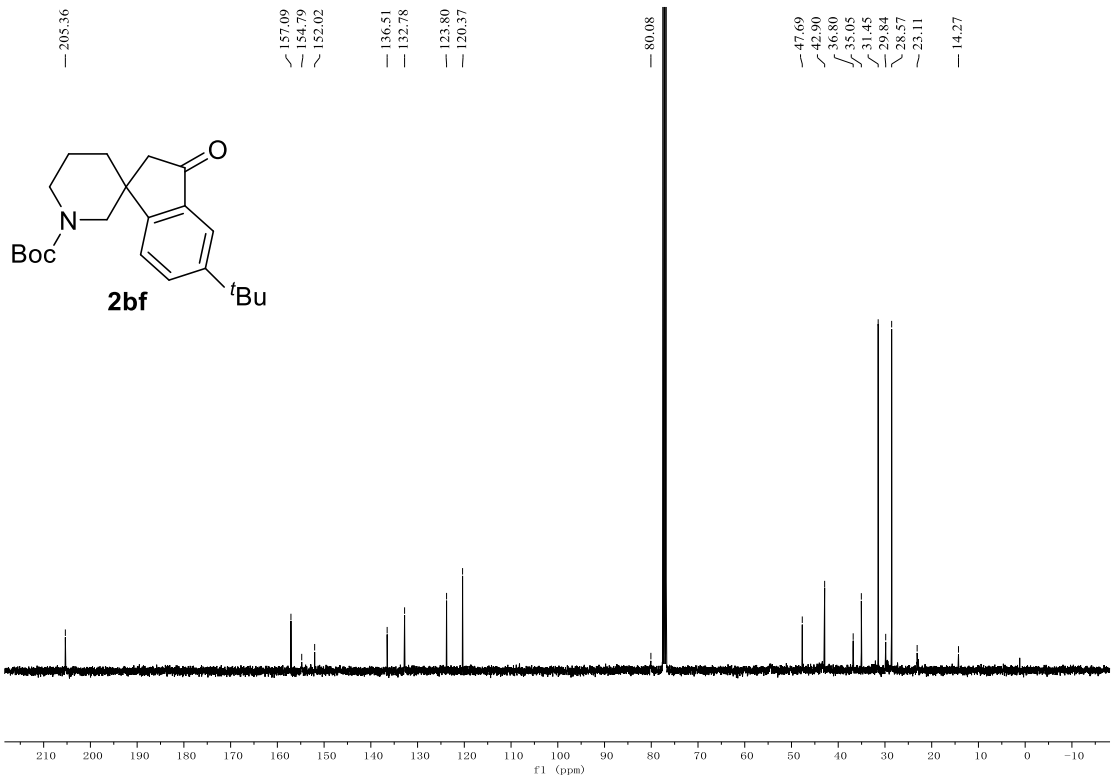
Boc
tBu
2bf
f1 (ppm)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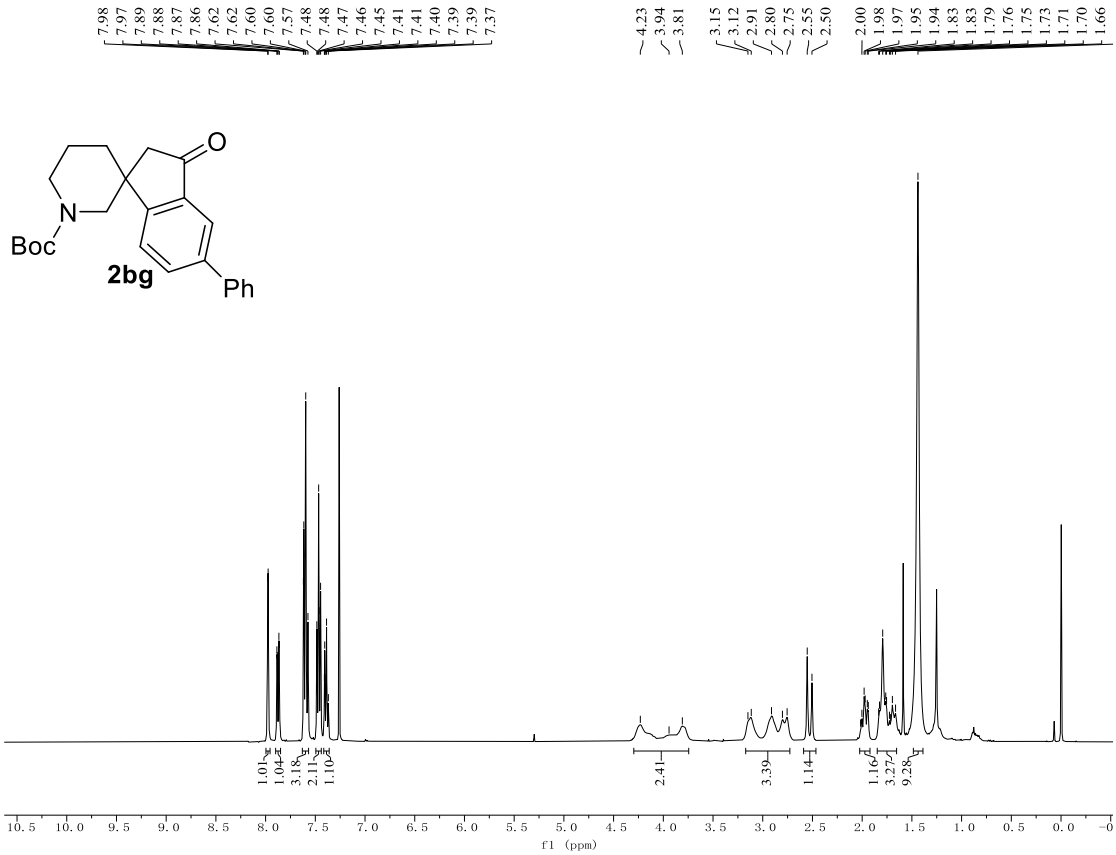
23.11
14.27
O
N
Boc
tBu
2bf
f1 (ppm)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7.37
4.23
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3.81
3.15
3.12
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1.95
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1.83
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1.66
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Boc
2bg
Ph
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3.39
1.14
1.16
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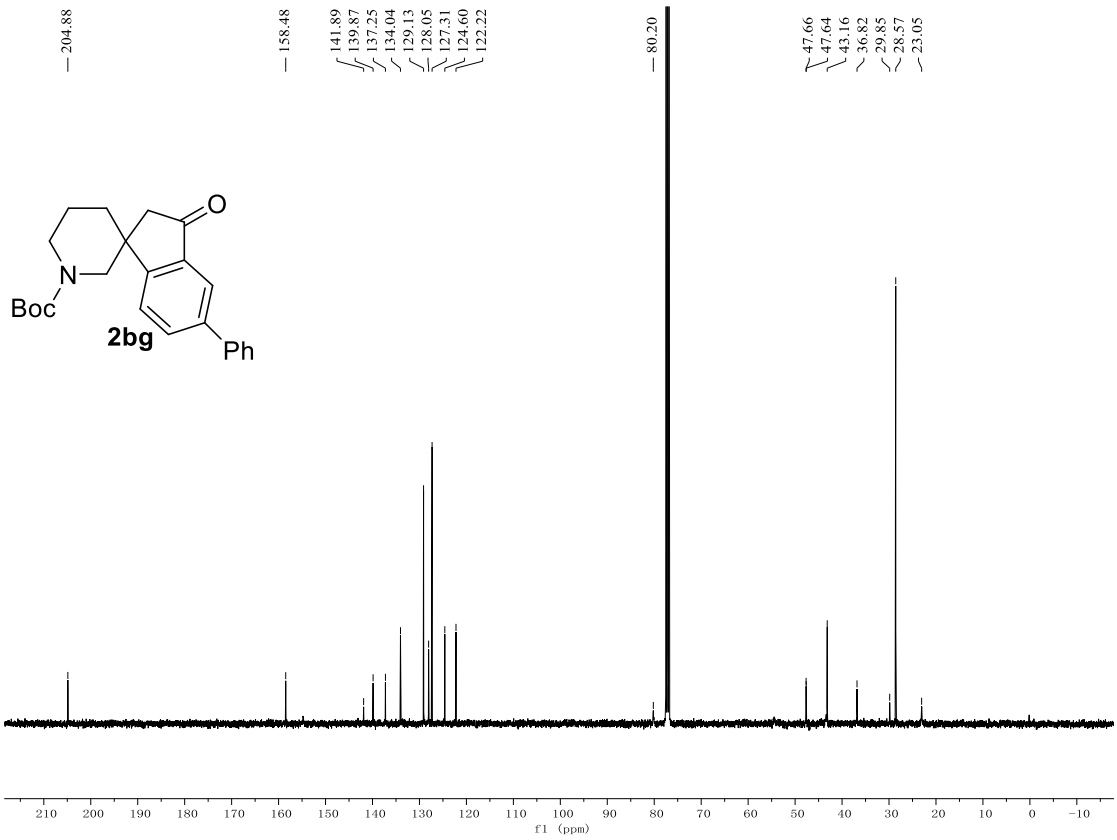
9.28
f1 (ppm)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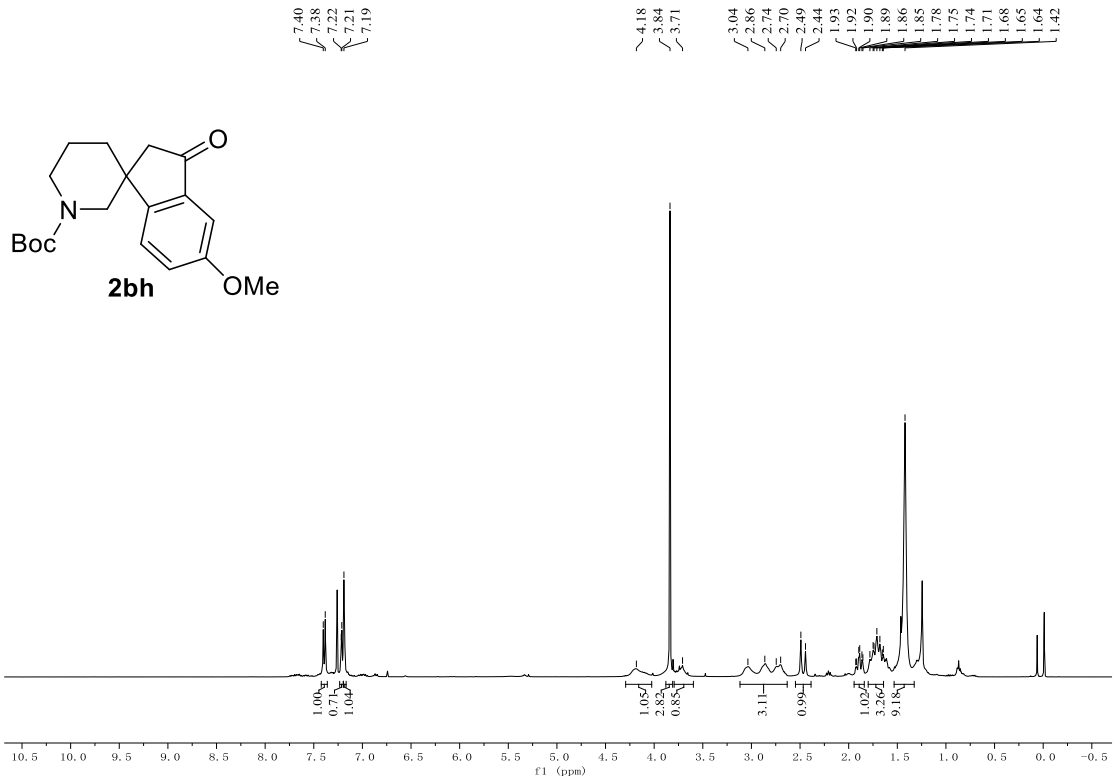
O
N
Boc
2bg
Ph
f1 (ppm)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1.92
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1.85
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1.65
1.64
1.42
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Boc
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OMe
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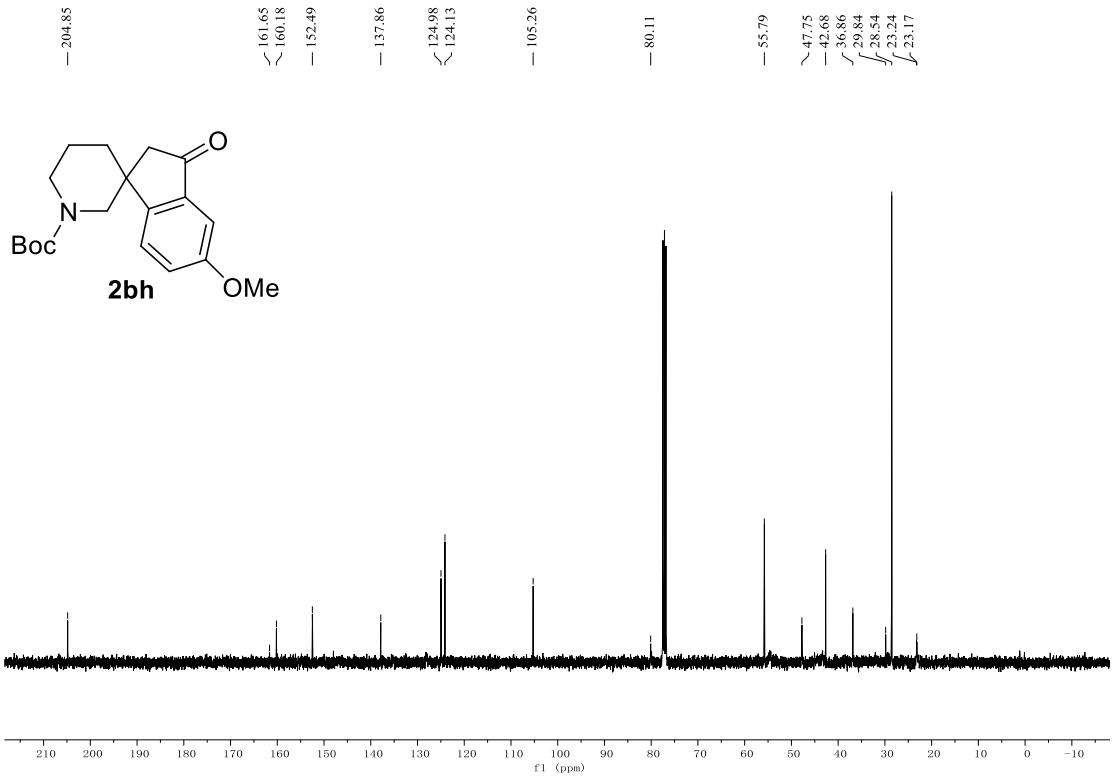
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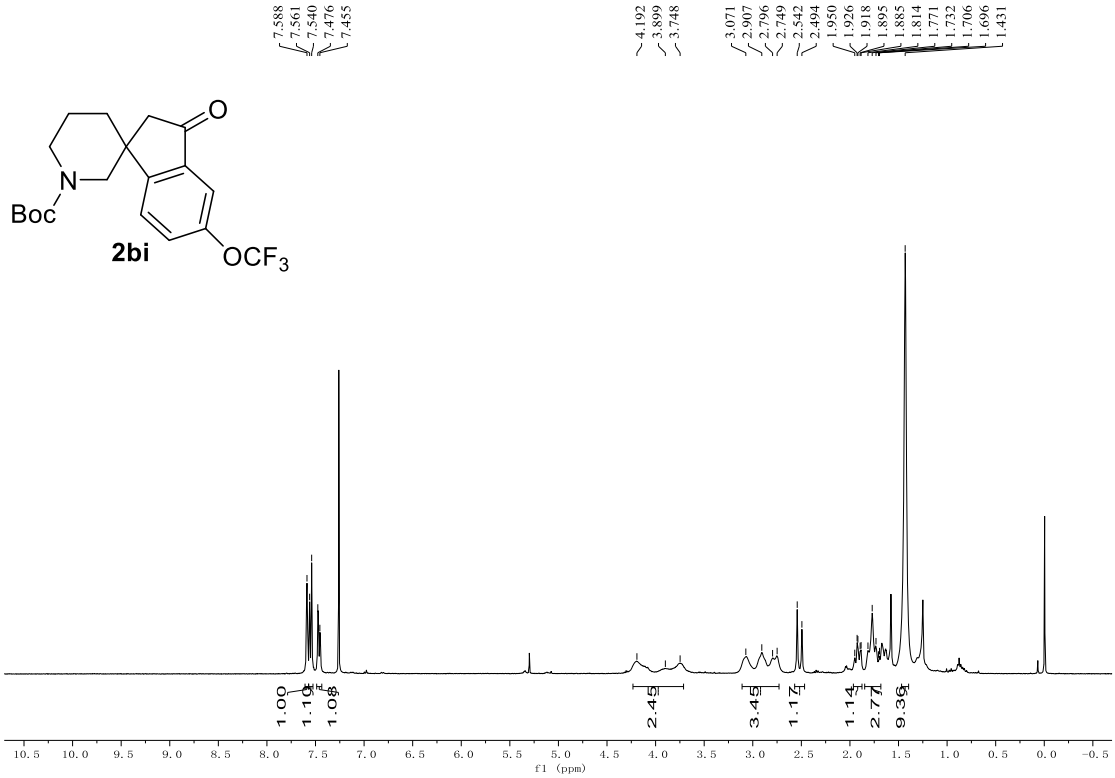
O
N
Boc
OMe
2bh
f1 (ppm)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1.895
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1.814
1.771
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1.706
1.696
1.431
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N
Boc
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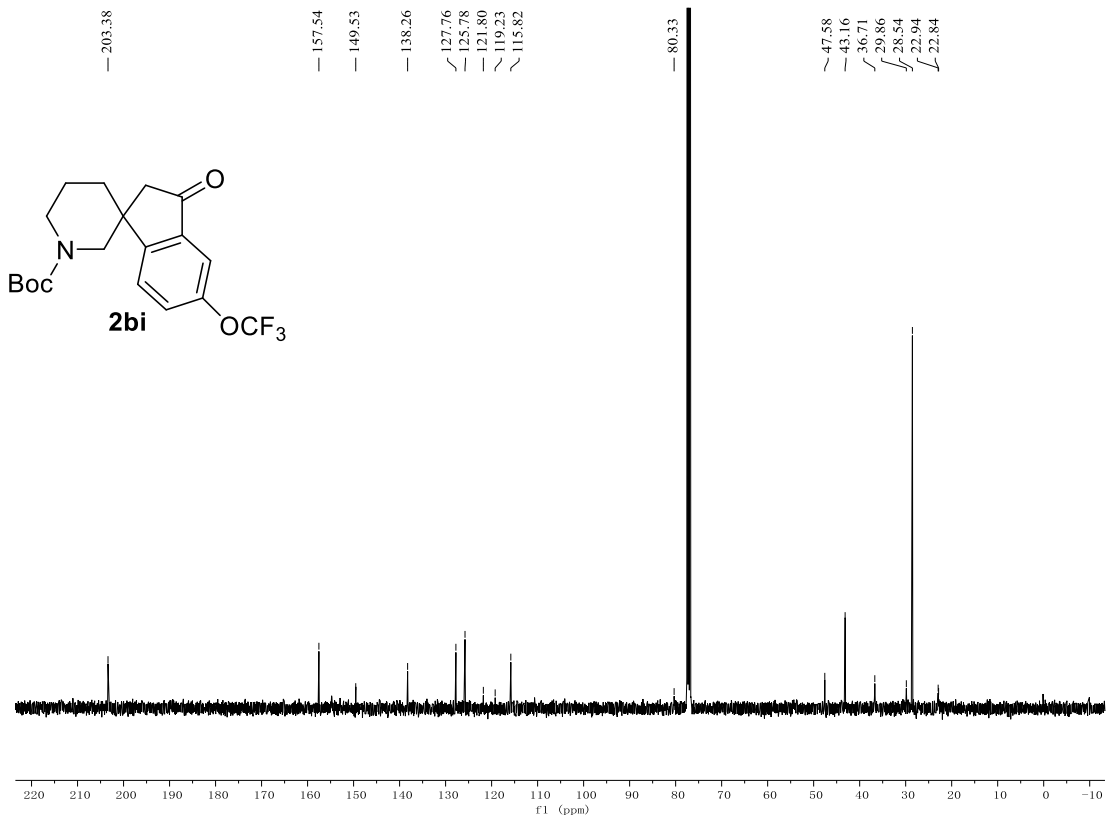
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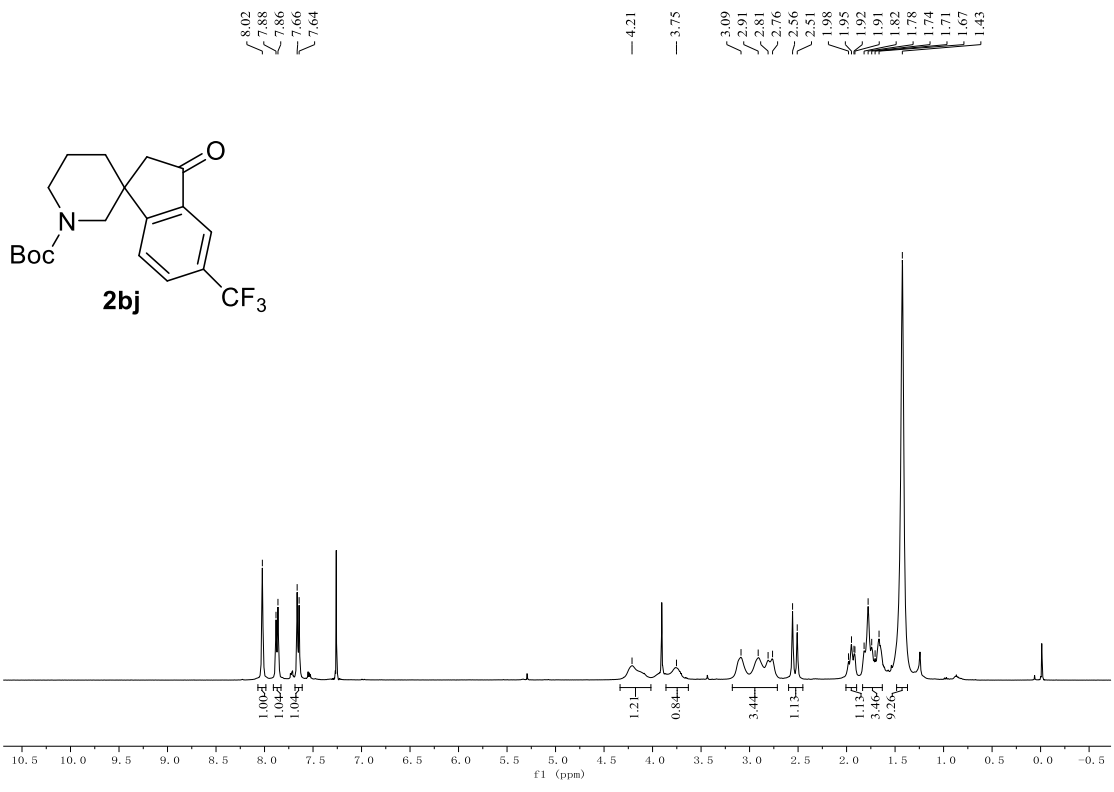
22.94
22.84
O
N
Boc
2bi
OCF3
f1 (ppm)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1.74
1.71
1.67
1.43
O
N
Boc
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1.13
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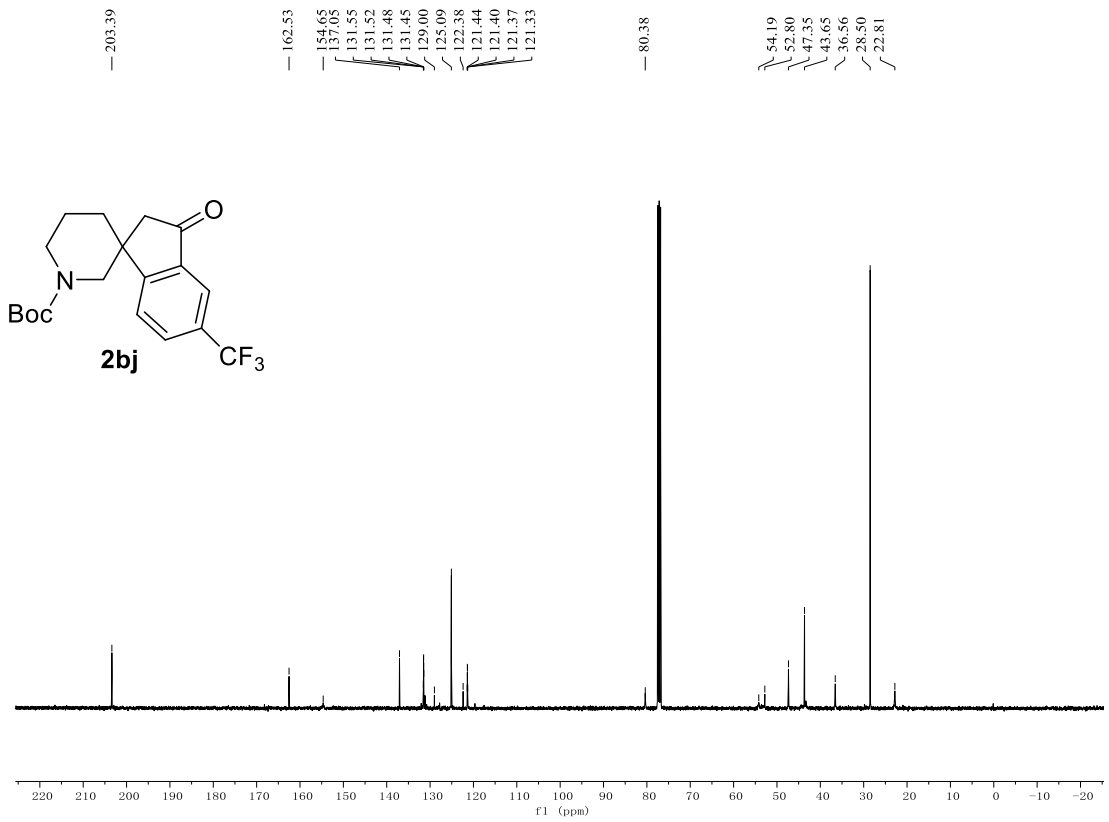
f1 (ppm)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CF3
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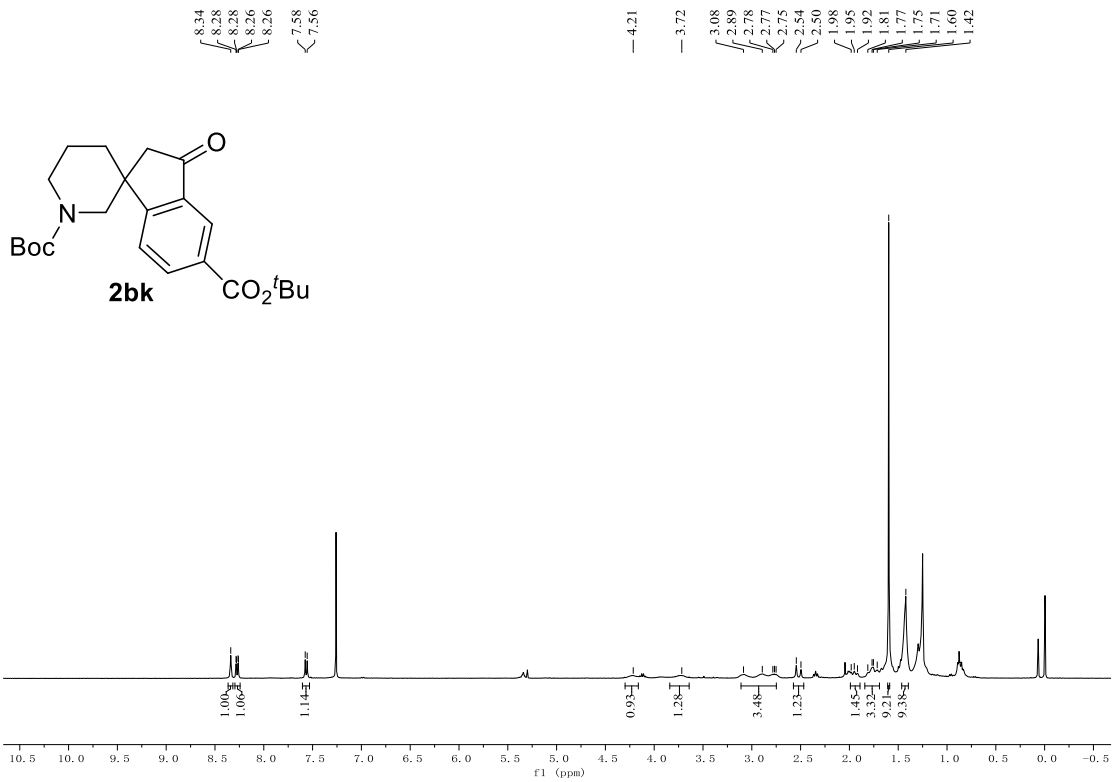
f1 (ppm)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1.92
1.81
1.77
1.75
1.71
1.60
1.42
O
N
Boc
CO2tBu
2bk
1.00
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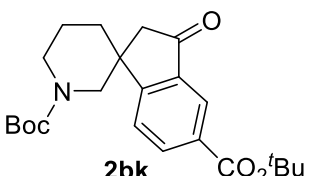
1.28
3.48
1.23
1.45
3.32
9.21
9.38
f1 (ppm)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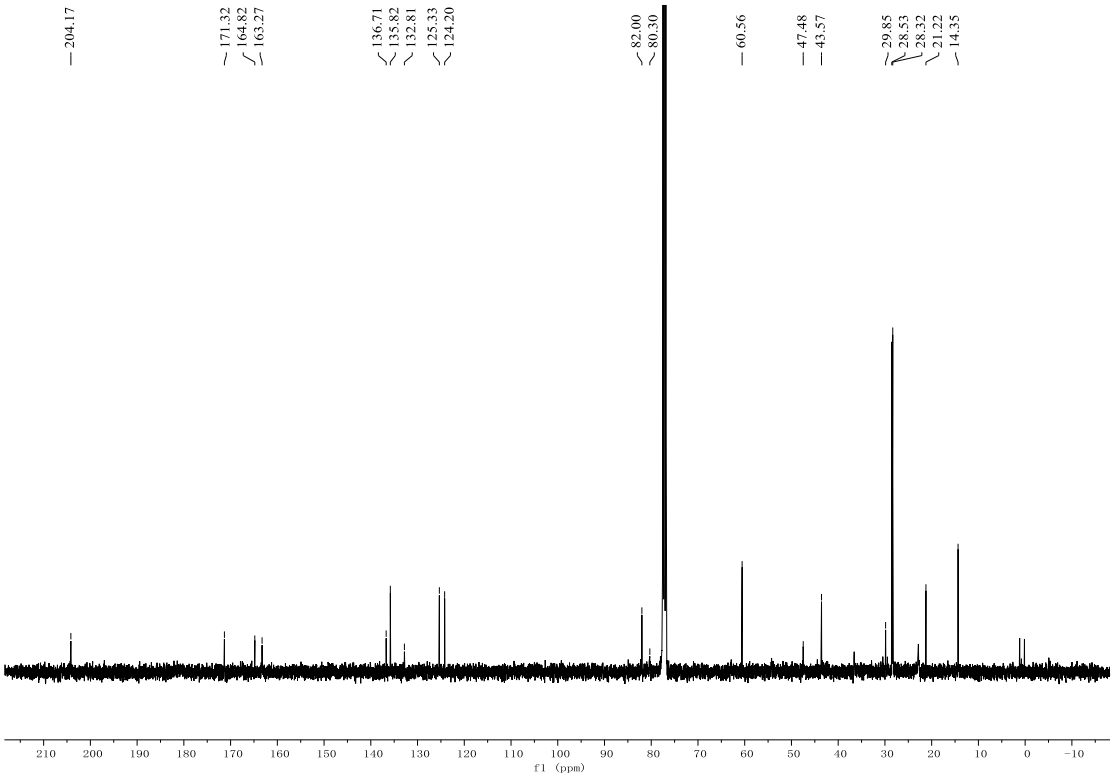
Boc
CO2tBu
2bk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171.32
164.82
163.27
136.71
135.82
132.81
125.33
124.20
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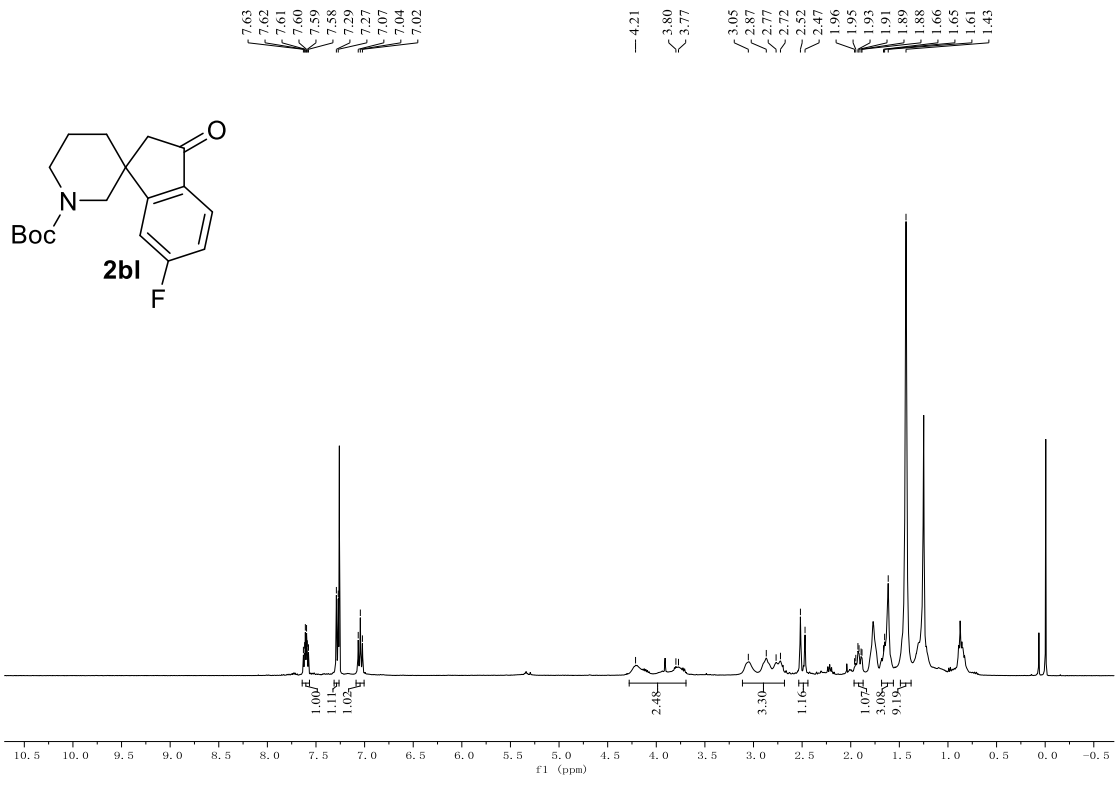
60.56
47.48
43.57
29.85
28.53
28.32
21.22
14.35
f1 (ppm)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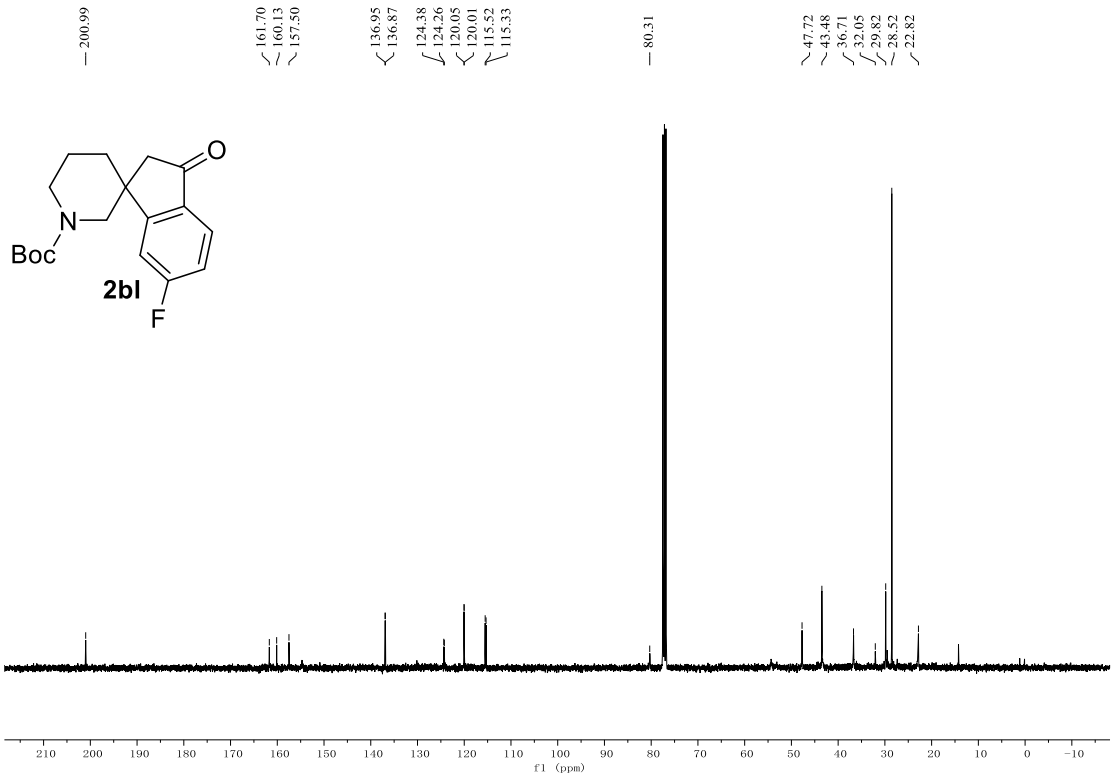
7.62
7.61
7.60
7.59
7.58
7.29
7.27
7.07
7.04
7.02
4.21
3.80
3.77
3.05
2.87
2.77
2.72
2.52
2.47
1.96
1.95
1.93
1.91
1.89
1.88
1.66
1.65
1.61
1.43
1.00
1.11
1.02
2.48
3.30
1.16
1.07
3.08
9.19
f1 (ppm)

O
N
Boc
2bl
F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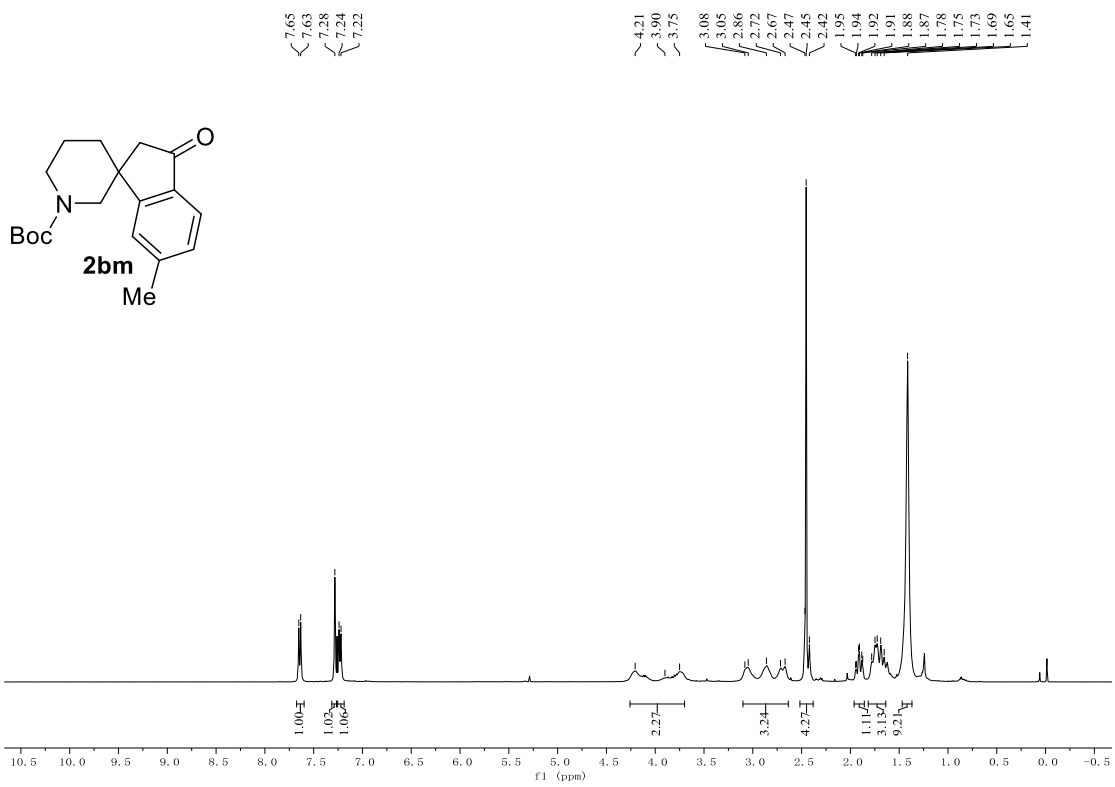
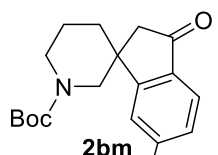
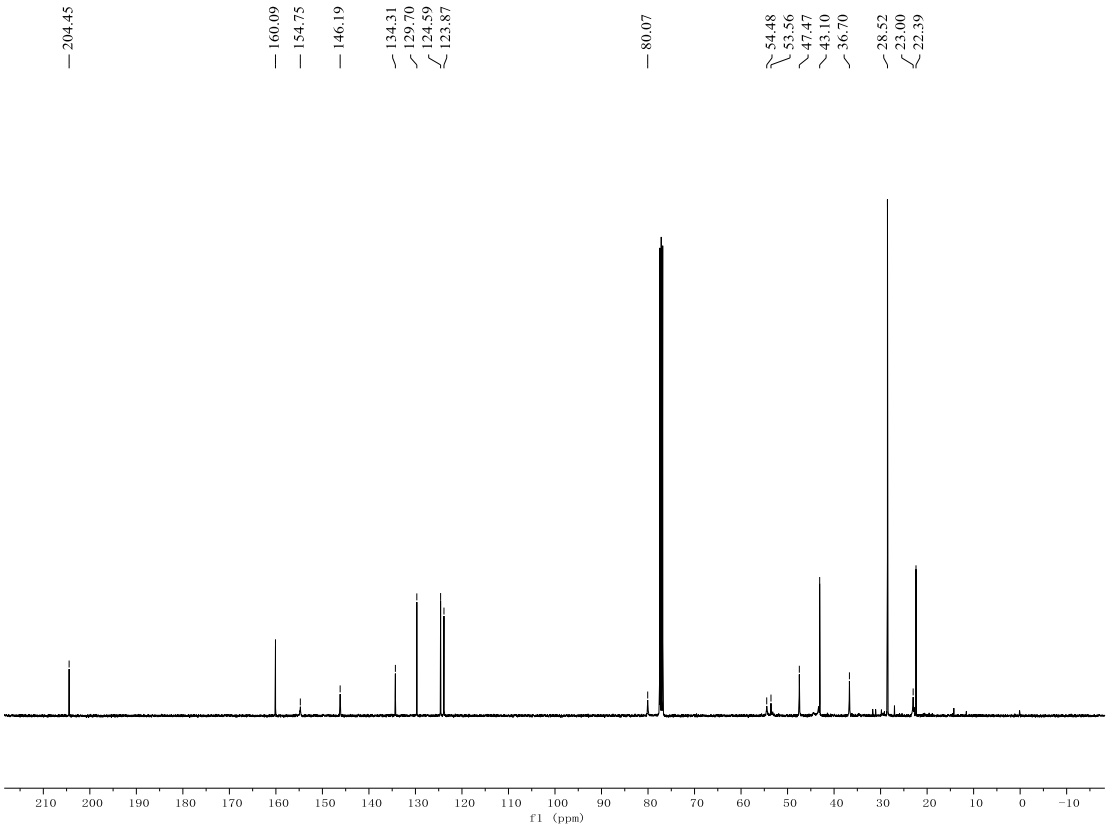
157.50
136.95
136.87
124.38
124.26
120.05
120.01
115.52
115.33
80.31
47.72
43.48
36.71
32.05
29.82
28.52
22.82
O
N
Boc
2bl
F
f1 (ppm)


7.65
7.63
7.28
7.24
7.22
4.21
3.90
3.75
3.08
3.05
2.86
2.72
2.67
2.47
2.45
2.42
1.95
1.94
1.92
1.91
1.88
1.87
1.78
1.75
1.73
1.69
1.65
1.41
O
N
Boc
2bm
Me
1.00
1.02
1.06
2.27
3.24
4.27
1.11
3.13
9.21
f1 (ppm)


O
N
Boc
2bm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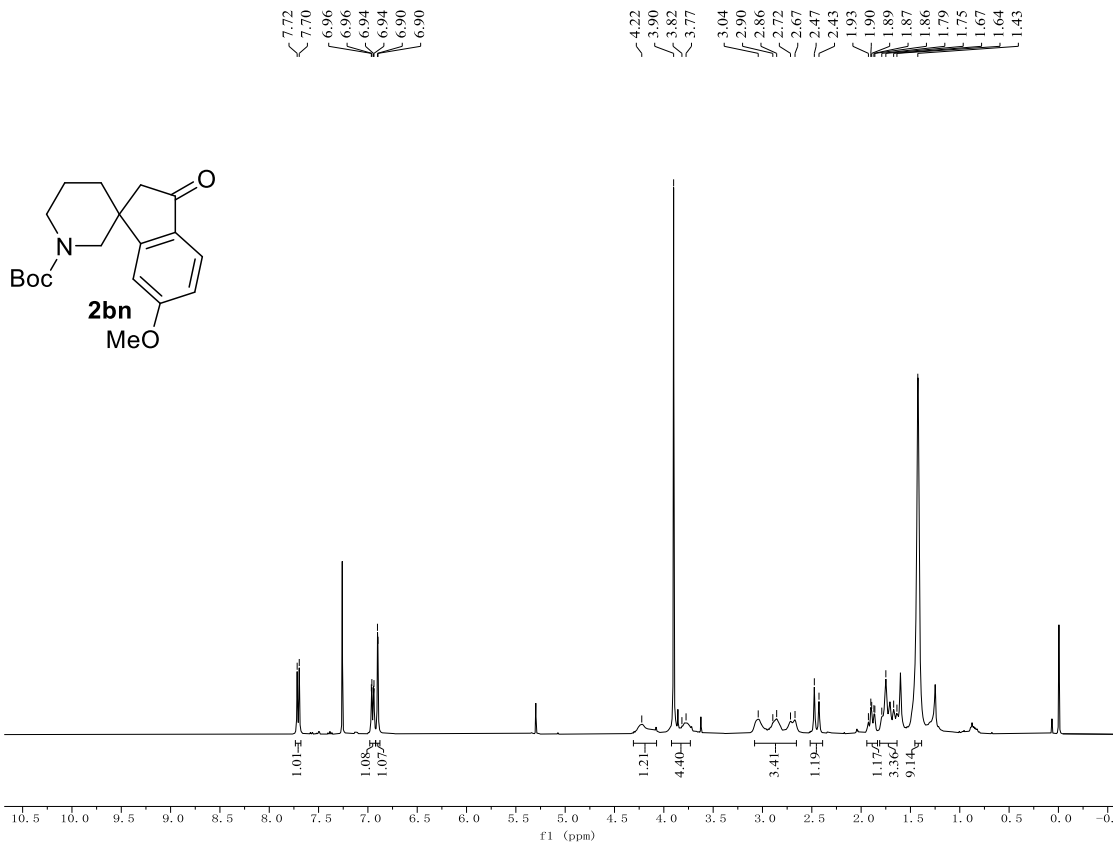
154.75
146.19
134.31
129.70
124.59
123.87
80.07
54.48
53.56
47.47
43.10
36.70
28.52
23.00
22.39
f1 (ppm)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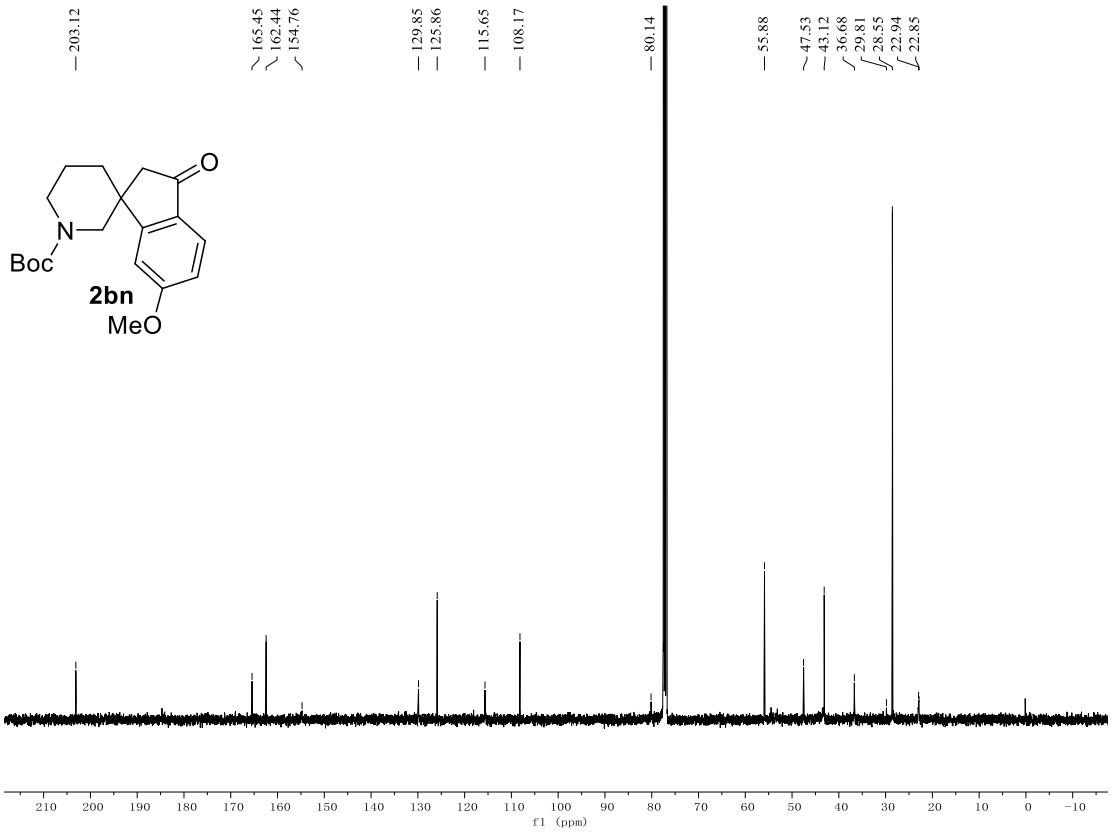
7.70
6.96
6.96
6.94
6.94
6.90
6.90
4.22
3.90
3.82
3.77
3.04
2.90
2.86
2.72
2.67
2.47
2.43
1.93
1.90
1.89
1.87
1.86
1.79
1.75
1.67
1.64
1.43
O
N
Boc
2bn
MeO
1.01
1.08
1.07
1.21
4.40
3.41
1.19
1.17
3.36
9.14
f1 (ppm)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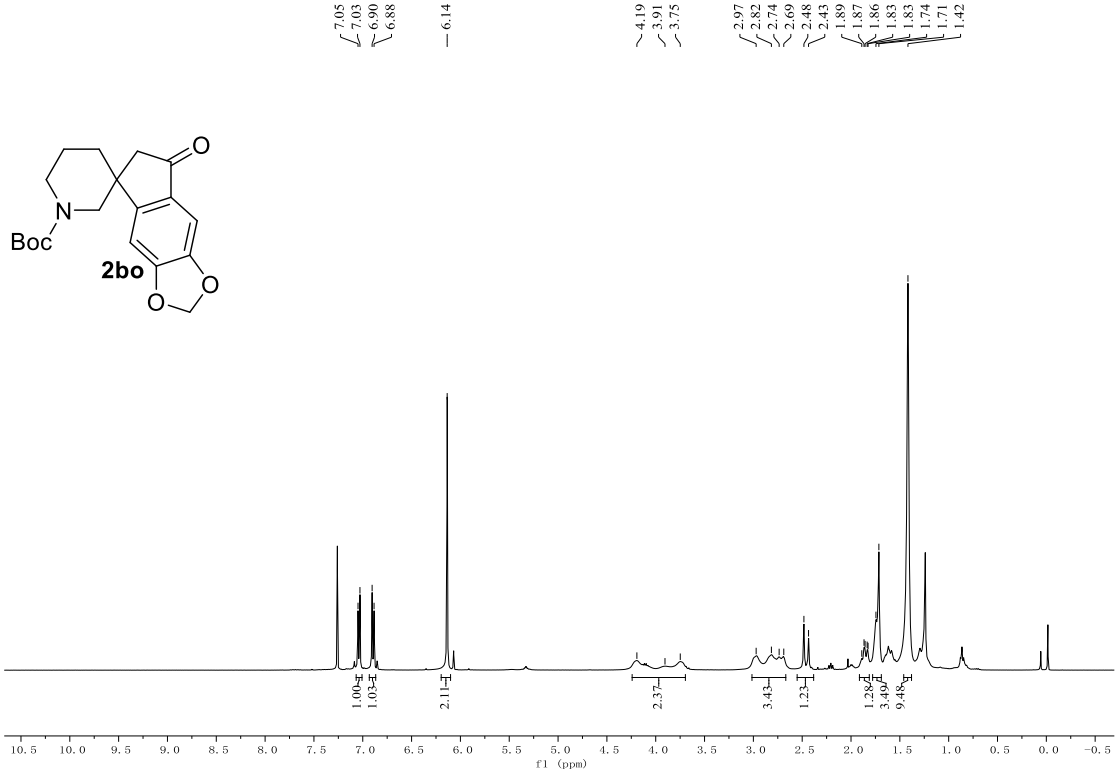
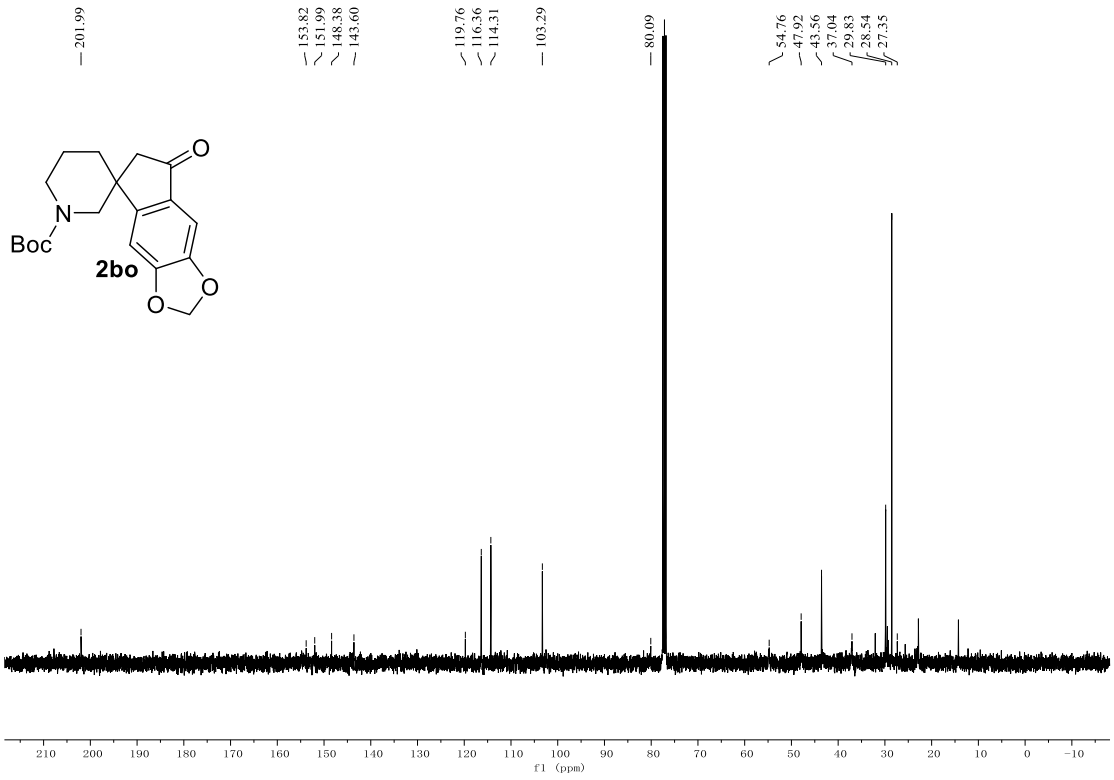
125.86
115.65
108.17
80.14
55.88
47.53
43.12
36.68
29.81
28.55
22.94
22.85
O
N
Boc
2bn
MeO
f1 (ppm)


7.05
7.03
6.90
6.88
6.14
4.19
3.91
3.75
2.97
2.82
2.74
2.69
2.48
2.43
1.89
1.87
1.86
1.83
1.83
1.74
1.71
1.42
O
N
Boc
2bo
O
O
1.00
1.03
2.11
2.37
3.43
1.23
1.28
3.49
9.48
f1 (ppm)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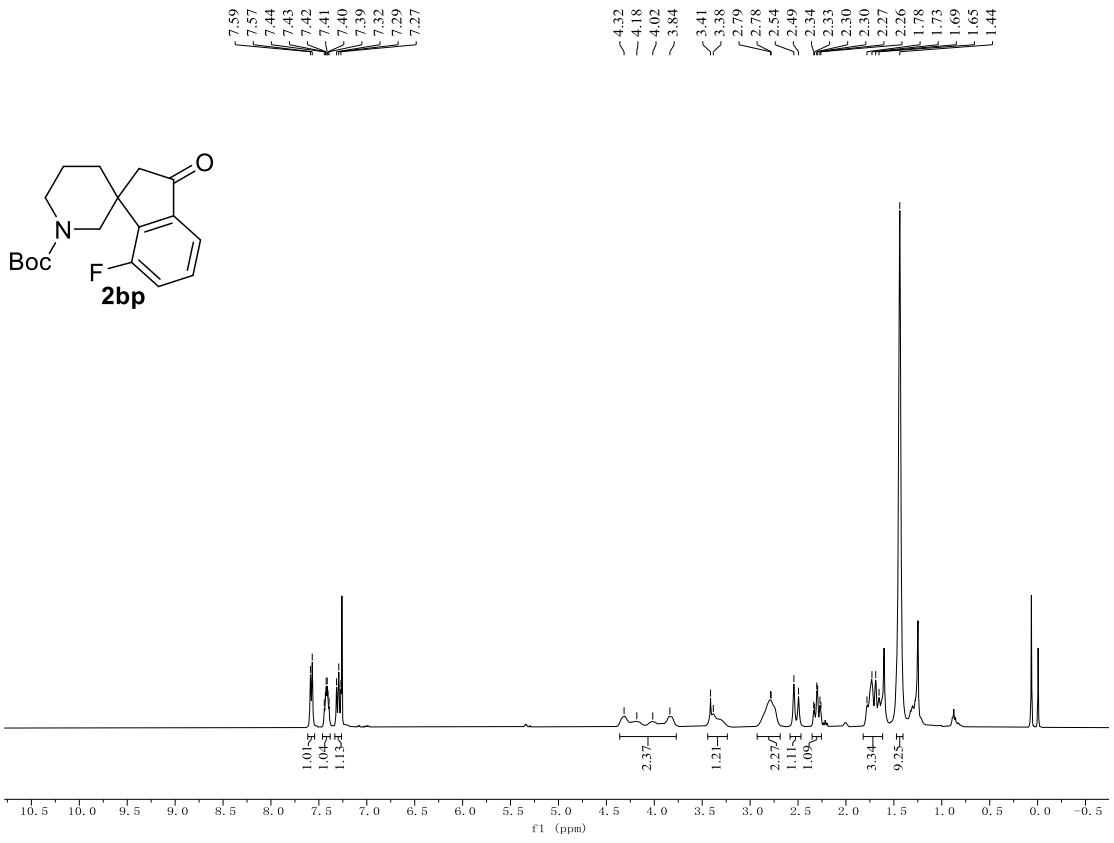
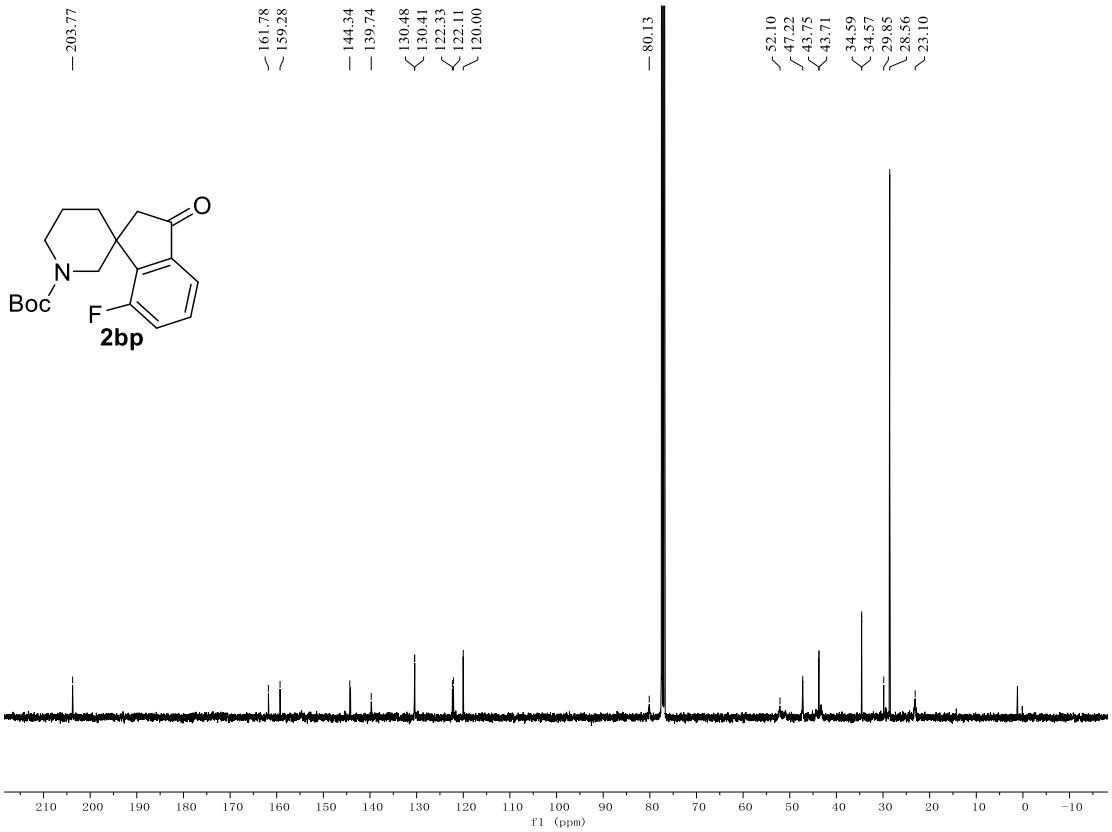
153.82
151.99
148.38
143.60
119.76
116.36
114.31
103.29
80.09
54.76
47.92
43.56
37.04
29.83
28.54
27.35
O
N
Boc
2bo
O
O
f1 (ppm)


7.59
7.57
7.44
7.43
7.42
7.41
7.40
7.39
7.32
7.29
7.27
4.32
4.18
4.02
3.84
3.41
3.38
2.79
2.78
2.54
2.49
2.34
2.33
2.30
2.30
2.27
2.26
1.78
1.73
1.69
1.65
1.44
O
N
Boc
F
2bp
1.01
1.04
1.13
2.37
1.21
2.27
1.11
1.09
3.34
9.25
f1 (ppm)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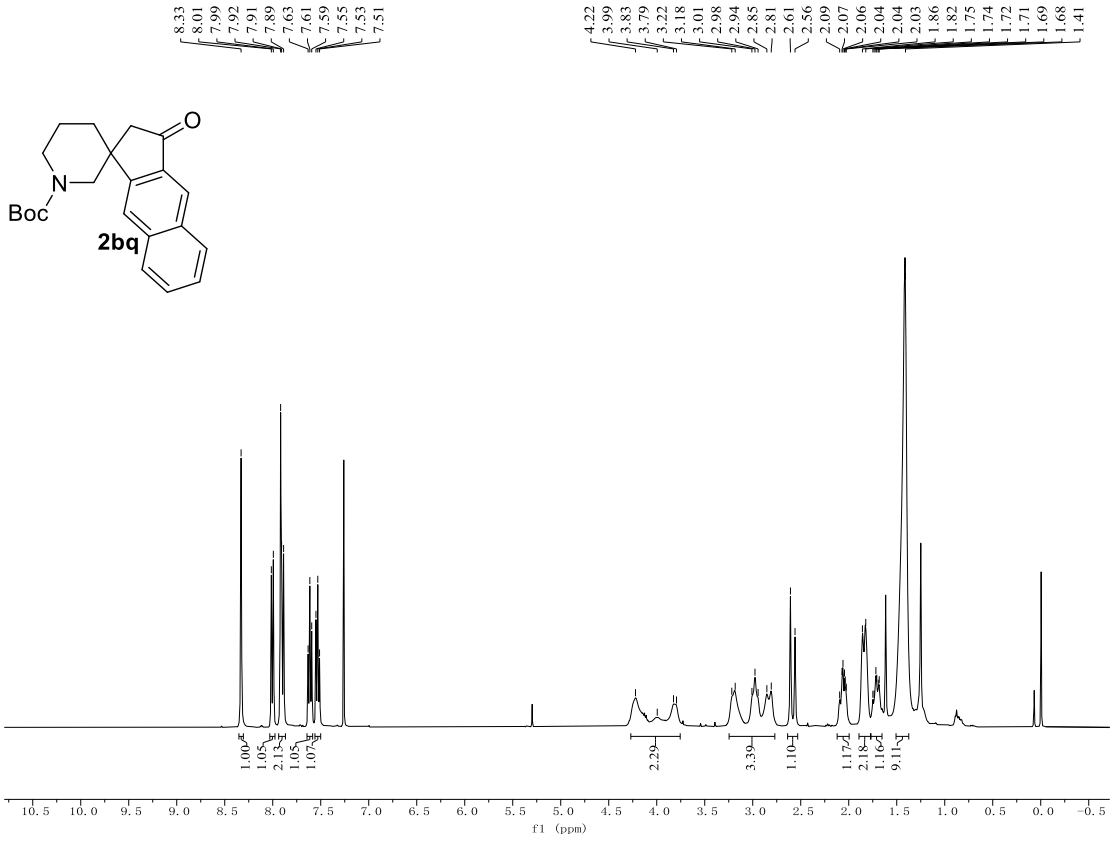
130.48
130.41
122.33
122.11
120.00
80.13
52.10
47.22
43.75
43.71
34.59
34.57
29.85
28.56
23.10
O
N
Boc
F
2bp
f1 (ppm)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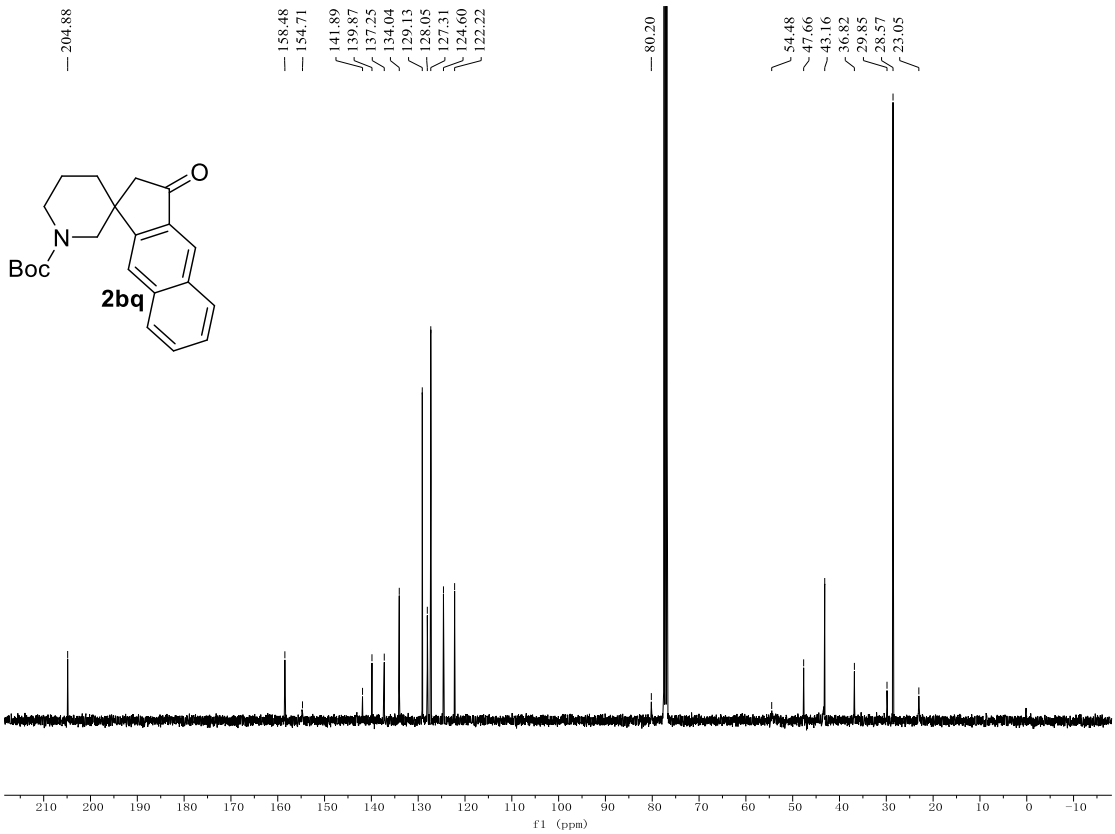
7.91
7.89
7.63
7.61
7.59
7.55
7.53
7.51
4.22
3.99
3.83
3.79
3.22
3.18
3.01
2.98
2.94
2.85
2.81
2.61
2.56
2.09
2.07
2.06
2.04
2.04
2.03
1.86
1.82
1.75
1.74
1.72
1.71
1.69
1.68
1.41
O
N
Boc
2bq
1.00
1.05
2.13
1.05
1.07
2.29
3.39
1.10
1.17
2.18
1.16
9.11
f1 (ppm)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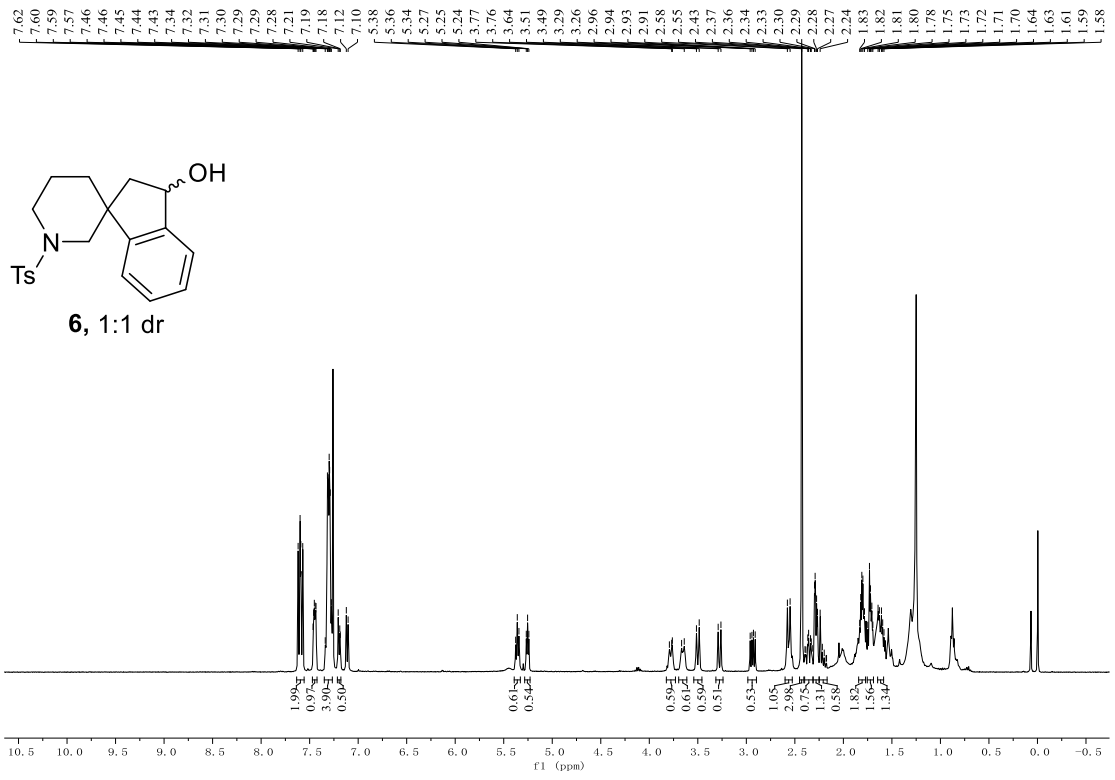
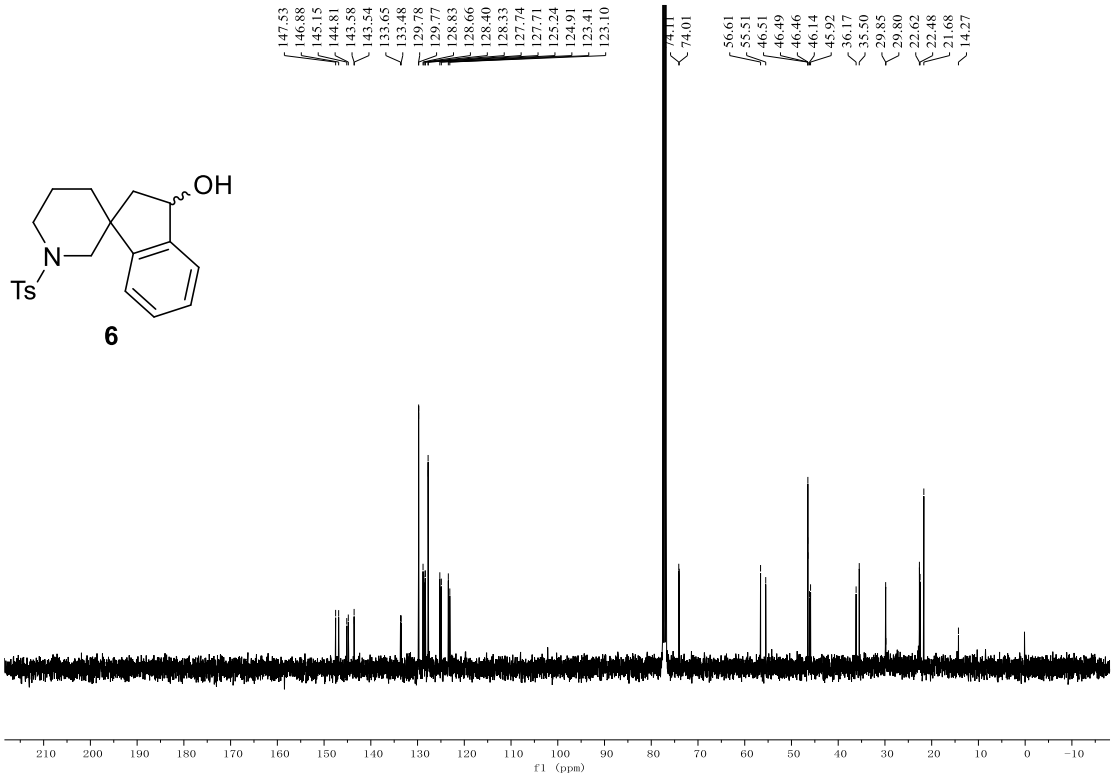
137.25
134.04
129.13
128.05
127.31
124.60
122.22
80.20
54.48
47.66
43.16
36.82
29.85
28.57
23.05
O
N
Boc
2bq
f1 (ppm)


OH
N
Ts
6, 1:1 dr
f1 (ppm)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145.15
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143.58
143.54
133.65
133.48
129.78
129.77
128.83
128.66
128.40
128.33
127.74
127.71
125.24
124.91
123.41
123.10
77.41
74.01
56.61
55.51
46.51
46.49
46.46
46.14
45.92
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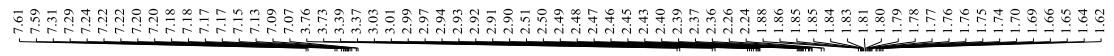
29.85
29.80
22.62
22.48
21.68
14.27
OH
N
Ts
6
f1 (ppm)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7.22
7.20
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7.18
7.18
7.17
7.17
7.15
7.13
7.09
7.07
3.76
3.73
3.39
3.37
3.03
3.01
2.99
2.97
2.94
2.93
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2.91
2.90
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.43
2.40
2.39
2.37
2.36
2.26
2.24
1.88
1.86
1.85
1.85
1.84
1.83
1.81
1.80
1.79
1.78
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1.70
1.69
1.66
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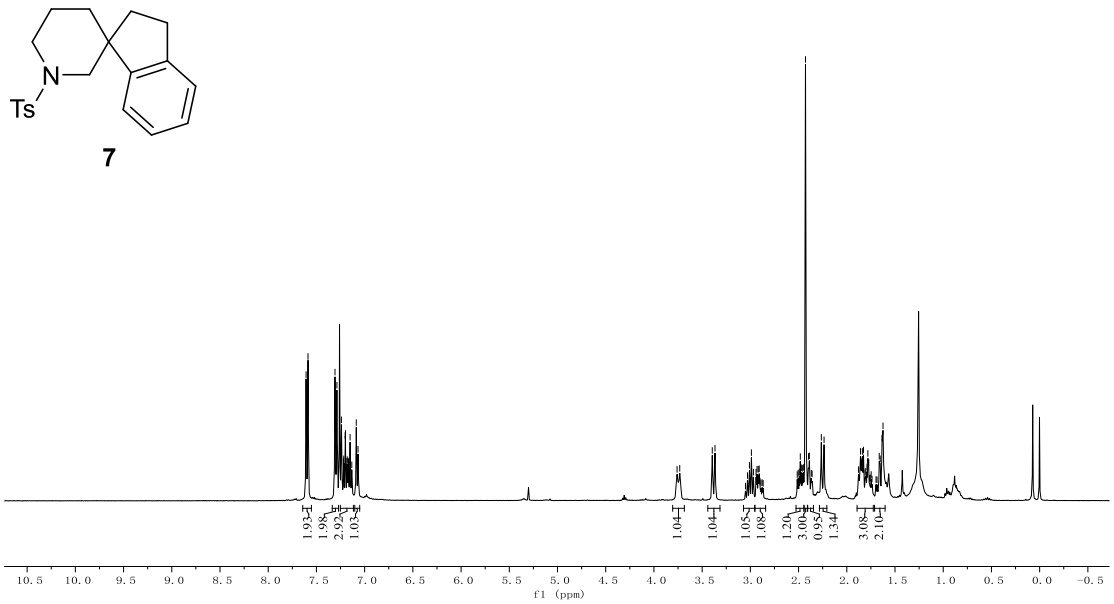
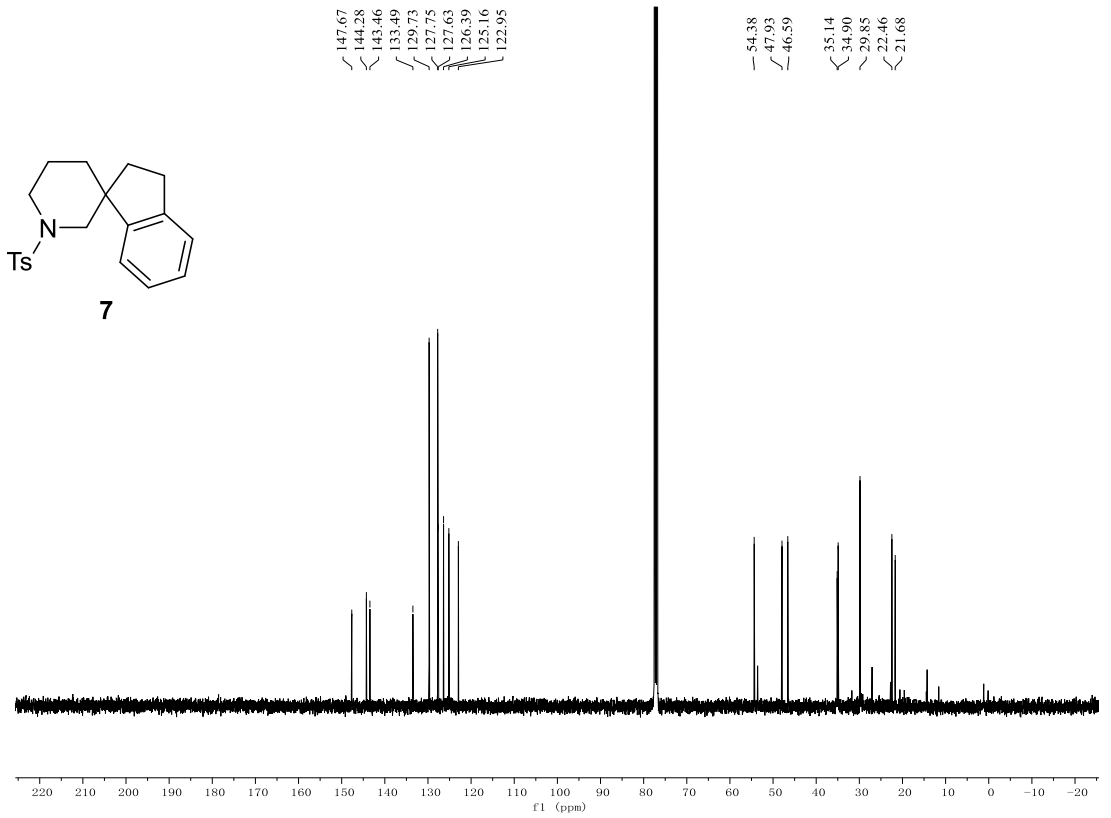
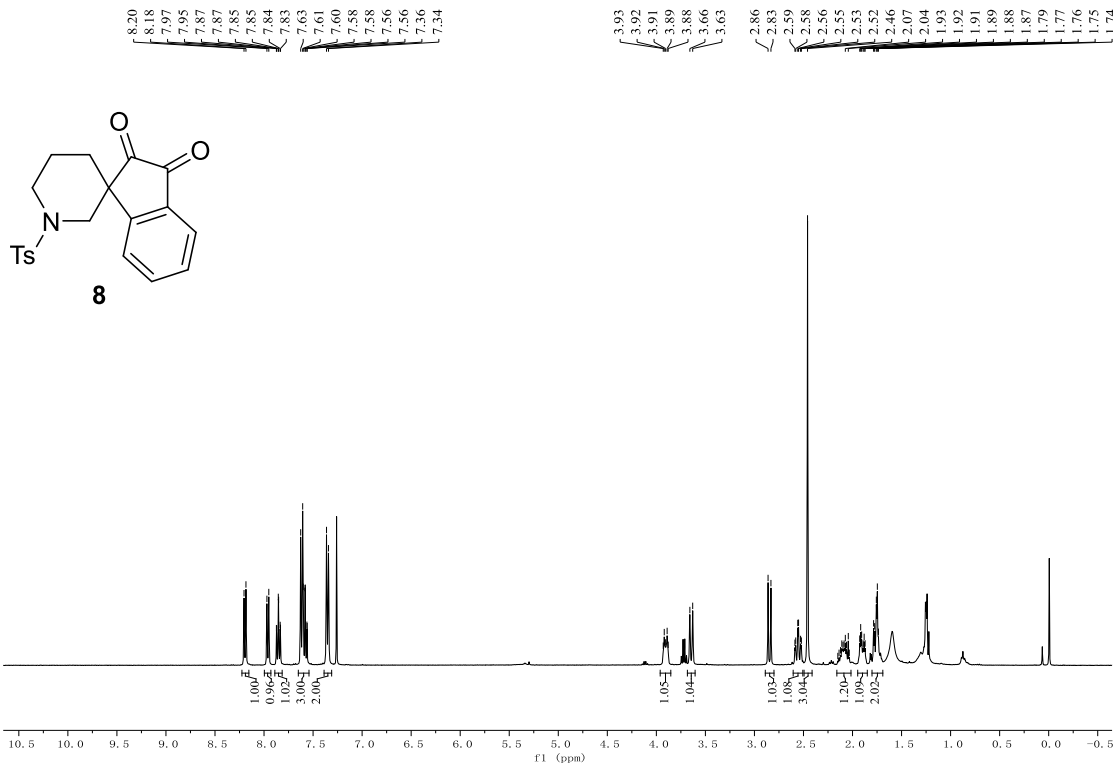
1.64
1.62


N
Ts
7
1.93
1.98
2.93
1.04
1.04
1.04
1.05
1.08
1.20
3.00
0.95
1.34
3.08
2.10
f1 (ppm)


147.67
144.28
143.46
133.49
129.73
127.75
127.63
126.39
125.16
122.95
54.38
47.93
46.59
35.14
34.90
29.85
22.46
21.68
N
Ts
f1 (ppm)

7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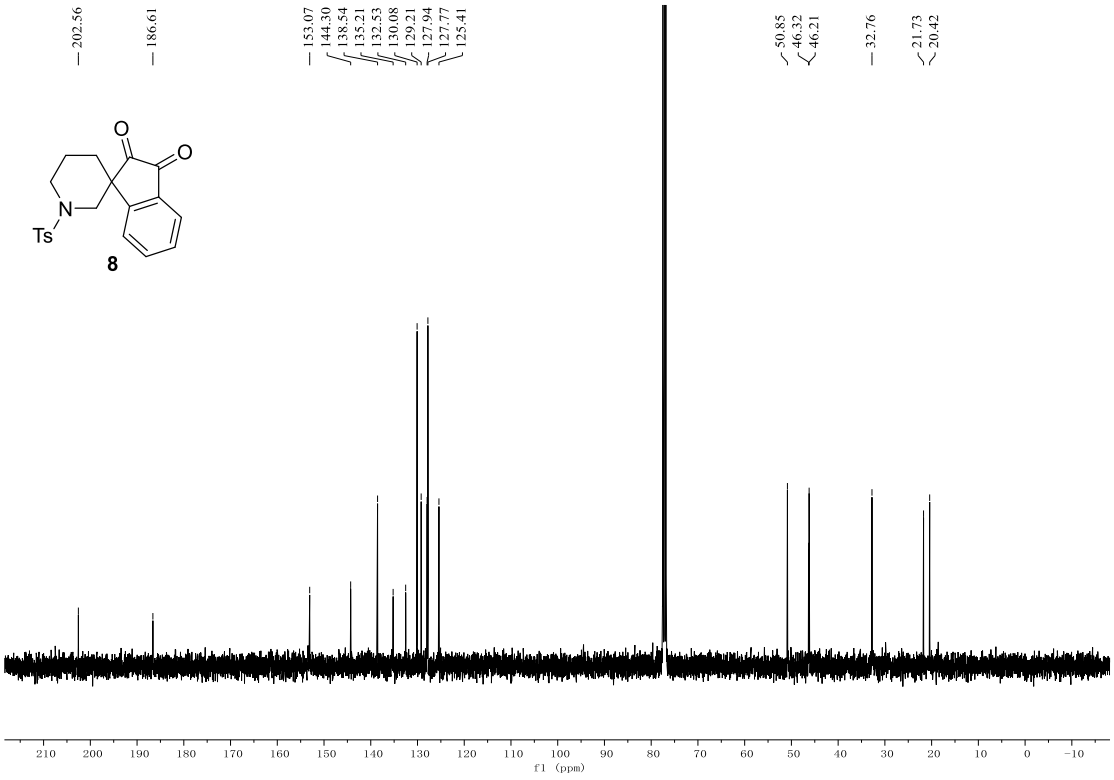
7.87
7.85
7.85
7.84
7.83
7.63
7.61
7.60
7.58
7.58
7.56
7.56
7.36
7.34
3.93
3.92
3.91
3.89
3.88
3.66
3.63
2.86
2.83
2.59
2.58
2.56
2.55
2.53
2.52
2.46
2.07
2.04
1.93
1.92
1.91
1.89
1.88
1.87
1.79
1.77
1.76
1.75
1.74
O
O
N
Ts
1.00
0.96
1.02
3.00
2.00
1.05
1.04
1.03
1.08
3.04
1.20
1.09
2.02
f1 (ppm)

8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144.30
138.54
135.21
132.53
130.08
129.21
127.94
127.77
125.41
50.85
46.32
46.21
32.76
21.73
20.42
O
O
N
Ts
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)