Pd(II)-Catalyzed Enantioselective γ-C(sp^3)–H Functionalizations of Free Cyclopropylmethylamines

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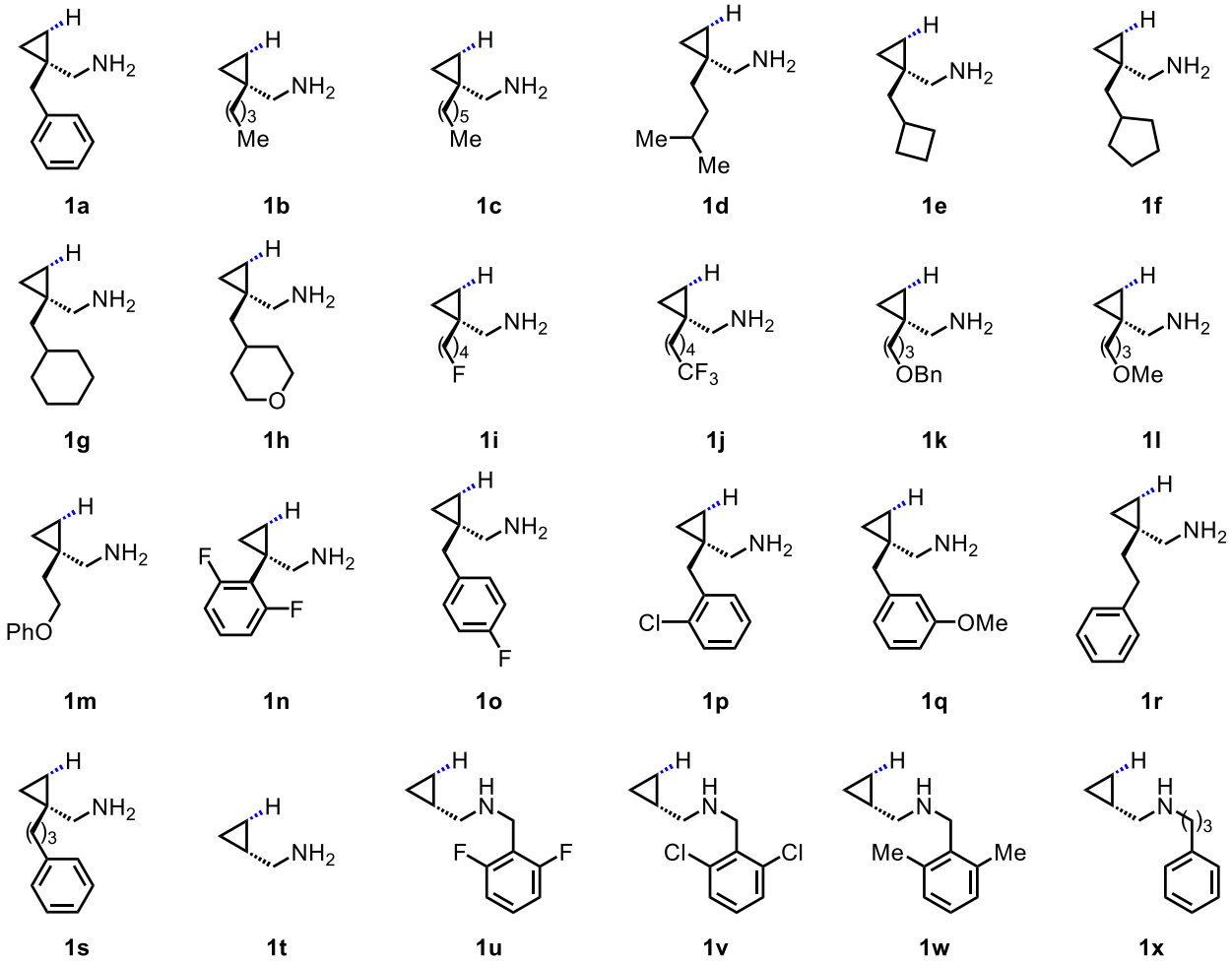
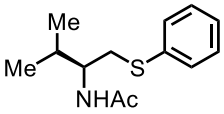
General Information: HFIP was obtained from Oakwood. $Pd(OAc)_2$, $Pd(TFA)_2$, and Ag_2O were obtained from Strem. Ag_2CO_3, NaOAc, and $Mo(CO)_6$ were purchased from Sigma-Aldrich. Pentafluorostyrene was purchased from Combi-Blocks. Free aliphatic primary and secondary amines were obtained from the commercial sources or synthesized following literature procedures. Other reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with short-wave UV light or $KMnO_4$ and heat as developing agents. ^1H NMR spectra were recorded on Bruker DRX-600 instrument. Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for TMS. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-600 and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of $CDCl_3$. Column chromatography was performed using E. Merck silica (60, particle size 0.043–0.063 mm), and pTLC was performed on Merck silica plates (60F-254). High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Enantiomeric ratios (er) were determined on the Agilent Technologies supercritical fluid chromatography (SFC) system using commercially available chiral columns.

Preparation of aliphatic primary and secondary amines

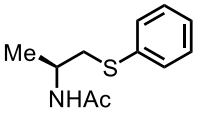


Aliphatic primary and secondary amines were obtained from the commercial sources or synthesized following literature procedures[1–3].

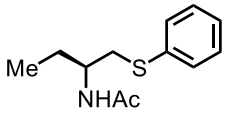
General procedure of the preparation of thioether ligands



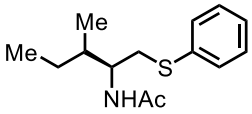
L6



L8



L9



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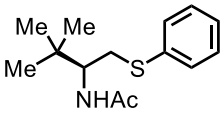
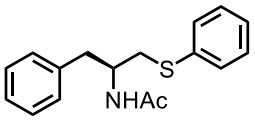
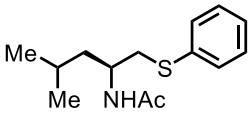


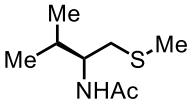
L11



L12

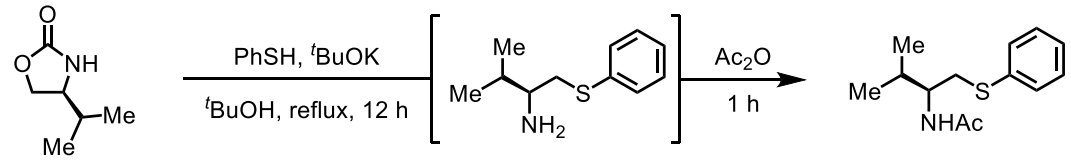


L13



L14

Thioether ligands (**L6** and **L8** to **L14**) were synthesized following literature procedure[4] with slight modification:

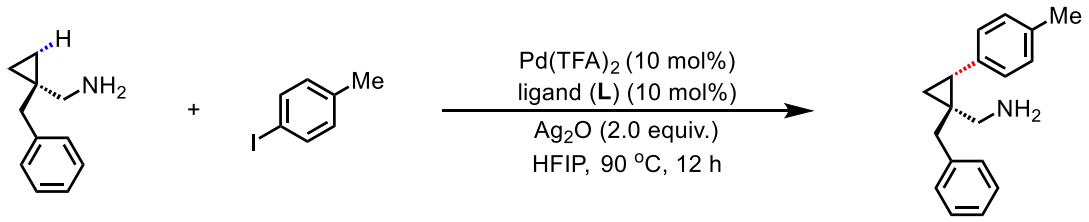


Evans' oxazolidinone chiral auxiliary

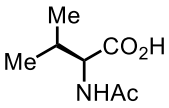
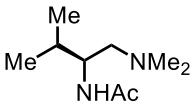
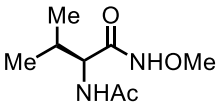
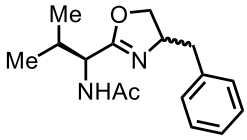
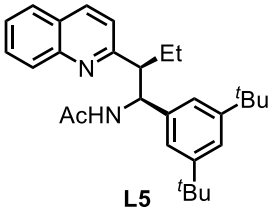
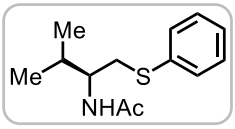
L6

To the *t*-BuOH (10.0 mL) solution of thiophenol (15.0 mmol, 1.54 mL) was added *t*-BuOK (11.0 mmol, 1.23 g) and the mixture was stirred at rt for 10 min. Then Evans oxazolidone chiral auxiliary (10.0 mmol, 1.29 g) was added to the solution and the mixture was stirred under reflux for 12 h. After being allowed to cool to room temperature, Ac_2O (15.0 mmol, 1.42 mL) was added to the solution and the mixture was stirred at rt for 1 h. The mixture was then concentrated *in vacuo*, diluted with EA, and washed with saturated NH_4Cl and $NaHCO_3$. The organic layer was dried over MgSO4, concentrated *in vacuo* and then purified by recrystallization in EA to yield thioether ligand **L6** (2.18 g, 92% yield). The NMR data matches the reported data[5].

Table S1. Ligand investigation for γ-C(sp^3)–H arylation[a,b]

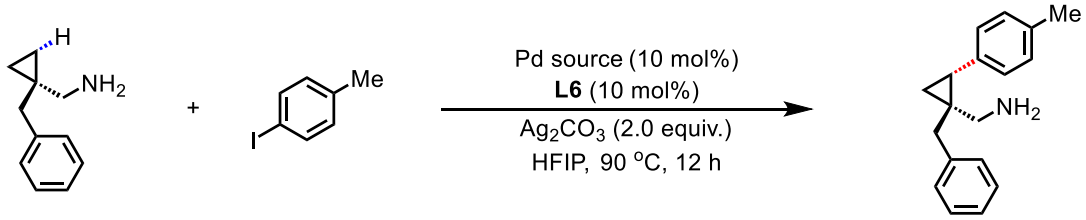


1a **2a** **3a**

w/o **L**			
6%	**L1** 41%, 85:15 er	**L2** 37%, 37:63 er	**L3** 37% yield, 47:53 er
			
***trans*-L4**, 35%, 74:26 er ***cis*-L4**, 39%, 43:57 er	**L5** 39%, 45:55 er	**L6** 68%, 97.5:2.5 er	

[a]Conditions: **1a** (0.1 mmol), Pd(TFA)$_2$ (10 mol%), ligand (**L**) (10 mol%), 4-iodotoluene **2a** (2.0 equiv.), Ag_2O (2.0 equiv.), HFIP (0.2 mL), 90 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns.

Table S2. Pd source investigation for γ-C(sp^3)–H arylation[a,b]

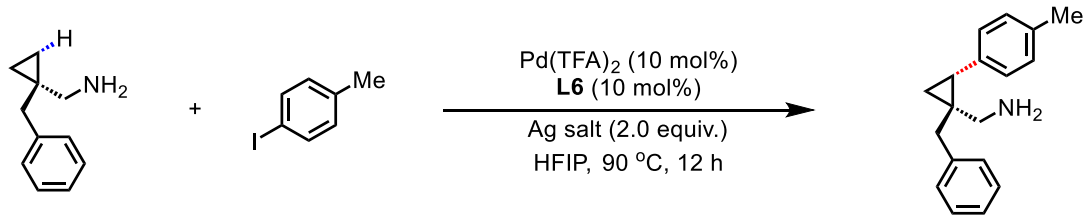


1a **2a** **3a**

entry	Pd source	yield (%)	er	entry	Pd source	yield (%)	er
1	w/o	0	n.d.	7	$[Pd(allyl)Cl]_2$	47	88:12
2	$Pd(OAc)_2$	54	89:11	8	$PdCl_2$	0	n.d.
3	$Pd(OPiv)_2$	50	77:23	9	PdI_2	46	88.5:11.5
4	$Pd(TFA)_2$	56	93:7	10	$Pd(CH_3CN)_4(BF_4)_2$	48	89:11
5	$Pd(CH_3CN)_2Cl_2$	44	90.5:9.5	11	$Pd_2(dba)_3$	39	87.5:12.5
6	$Pd(PhCN)_2Cl_2$	44	90:10				

[a]Conditions: **1a** (0.1 mmol), Pd source (10 mol%), **L6** (10 mol%), 4-iodotoluene **2a** (2.0 equiv.), Ag_2CO_3 (2.0 equiv.), HFIP (0.3 mL), 90 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns.

Table S3. Ag salt investigation for γ-C(sp^3)–H arylation[a,b]

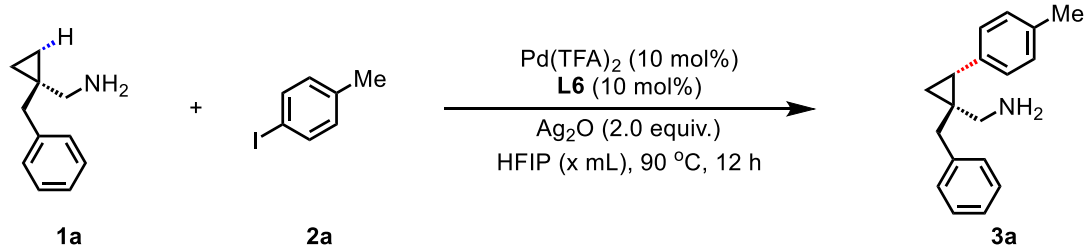


1a **2a** **3a**

entry	Ag salt	yield (%)	er	entry	Ag salt	yield (%)	er
1	w/o	0	n.d.	5	Ag_2O	58	95:5
2	Ag_2CO_3	56	93:7	6	AgO	53	90:10
3	AgOAc	47	47.5:52.5	7	Ag_3PO_4	0	n.d.
4	AgTFA	0	n.d.				

[a]Conditions: **1a** (0.1 mmol), $Pd(TFA)_2$ (10 mol%), **L6** (10 mol%), 4-iodotoluene **2a** (2.0 equiv.), Ag salt (2.0 equiv.), HFIP (0.3 mL), 90 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns.

Table S4. Concentration investigation for γ-C(sp^3)–H arylation[a,b]

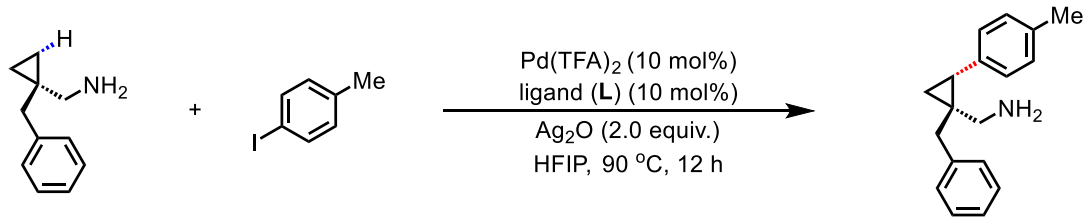


1a **2a** **3a**

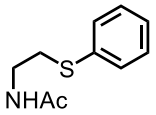
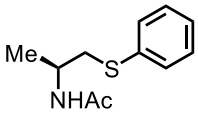
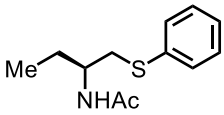
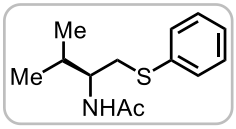
entry	x mL	yield (%)	er
1	1.0	46	80:20
2	0.5	55	85:15
3	0.3	58	95:5
4	0.2	68	97.5:2.5

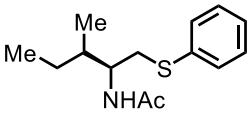
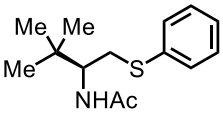
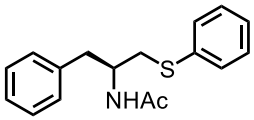
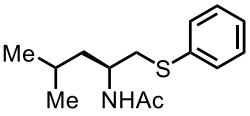
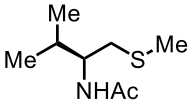
[a]Conditions: **1a** (0.1 mmol), $Pd(TFA)_2$ (10 mol%), **L6** (10 mol%), 4-iodotoluene **2a** (2.0 equiv.), Ag_2O (2.0 equiv.), HFIP (x mL), 90 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns.

Table S5. Thioether ligand investigation for γ-C(sp^3)–H arylation[a,b]



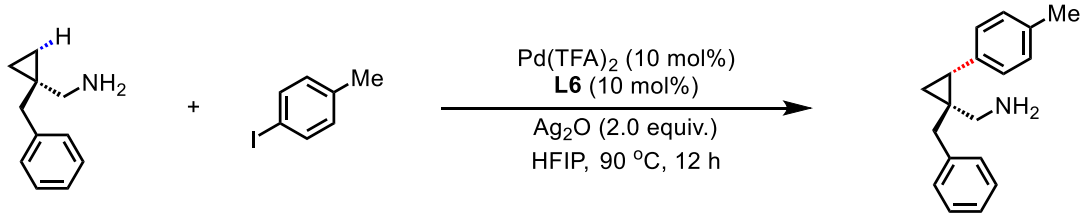
1a **2a** **3a**

w/o **L**				
	L7	**L8**	**L9**	**L6**
6%	57%	55%, 82.5:17.5 er	56%, 87.5:12.5 er	68%, 97.5:2.5 er

				
L10	**L11**	**L12**	**L13**	**L14**
69%, 97:3 er	51%, 89.5:10.5 er	51%, 87.5:12.5 er	62%, 89.5:10.5 er	43%, 97.5:2.5 er

[a]Conditions: **1a** (0.1 mmol), Pd(TFA)$_2$ (10 mol%), ligand (**L**) (10 mol%), 4-iodotoluene **2a** (2.0 equiv.), Ag_2O (2.0 equiv.), HFIP (0.2 mL), 90 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns.

Table S6. Aryl iodide loading investigation for γ-C(sp^3)–H arylation[a,b]

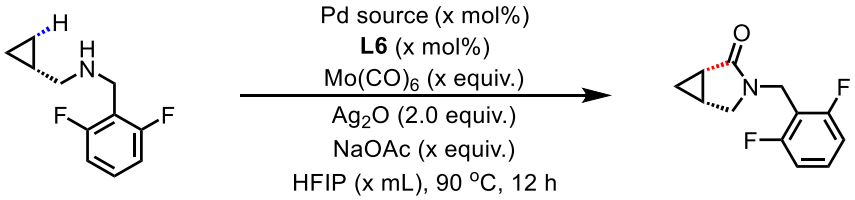


1a **2a** **3a**

entry	**2a** (x equiv.)	yield (%)	er
1	2.0	68	97.5:2.5
2	3.0	73(68[c])	97.5:2.5
3	4.0	75	97:3

[a]Conditions: **1a** (0.1 mmol), $Pd(TFA)_2$ (10 mol%), **L6** (10 mol%), 4-iodotoluene **2a** (x equiv.), Ag_2O (2.0 equiv.), HFIP (0.2 mL), 90 °C, 12 h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns. [c]Isolated yield of the corresponding Boc-protected amine.

Table S7. Optimization of conditions for γ-C(sp^3)–H carbonylation[a,b]

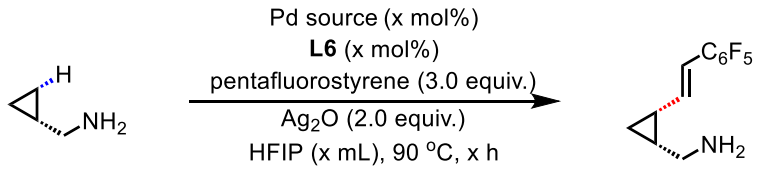


1u **5b**

entry	Pd source/**L6** (x mol%)	$Mo(CO)_6$ (x equiv.)	NaOAc (x equiv.)	HFIP (x mL)	yield (%)	er
1	$Pd(TFA)_2$/**L6** (10 mol%)	0.5	w/o	0.2	13	93.5:6.5
2	$Pd(OAc)_2$/**L6** (10 mol%)	0.5	w/o	0.2	15	93.5:6.5
3	$Pd(OAc)_2$/**L6** (10 mol%)	0.5	1.0	0.2	38	91.5:8.5
4	$Pd(OAc)_2$/**L6** (10 mol%)	0.3	1.0	0.2	40	93:7
5	$Pd(OAc)_2$/**L6** (10 mol%)	0.3	1.0	0.1	38	94.5:5.5
6	$Pd(OAc)_2$/**L6** (15 mol%)	0.3	1.0	0.1	43(45[c])	95:5

[a]Conditions: **1u** (0.1 mmol), Pd source (x mol%), **L6** (x mol%), $Mo(CO)_6$ (x equiv.), Ag_2O (2.0 equiv.), NaOAc (x equiv,), HFIP (x mL), 90 °C, 12 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns. [c]Isolated yield.

Table S8. Optimization of conditions for γ-C(sp^3)–H olefination[a,b]

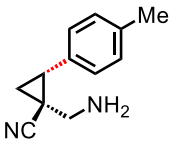


1i **5b**

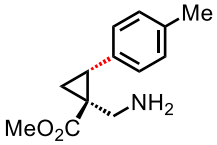
entry	Pd source/**L6** (x mol%)	HFIP (x mL)	time (x h)	yield (%)	er
1	$Pd(TFA)_2$/**L6** (10 mol%)	0.2	12	14	91:9
2	$Pd(OAc)_2$/**L6** (10 mol%)	0.2	12	22	90:10
3	$Pd(OAc)_2$/**L6** (10 mol%)	0.1	12	28	95.5:4.5
4	$Pd(OAc)_2$/**L6** (15 mol%)	0.1	12	36	95:5
5	$Pd(OAc)_2$/**L6** (15 mol%)	0.1	6	41(39[c])	95.5:4.5

[a]Conditions: **1i** (0.1 mmol), Pd source (x mol%), **L6** (x mol%), Ag_2O (2.0 equiv.), HFIP (x mL), 90 °C, x h. [b]The yields were determined by ^1H NMR analysis of the crude product using CH_2Br_2 as the internal standard. The er values were determined on the SFC system using commercially available chiral columns. [c]Isolated yield of the corresponding Boc-protected amine.

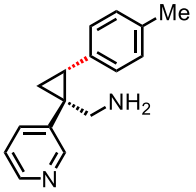
Table S9. Selected other substrates for γ-C(sp^3)–H arylation



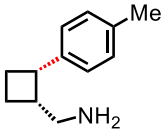
<5%, er n.d.



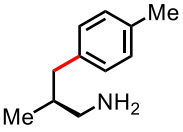
<5%, er n.d.



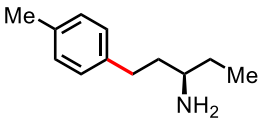
<5%, er n.d.



<5%, er n.d.

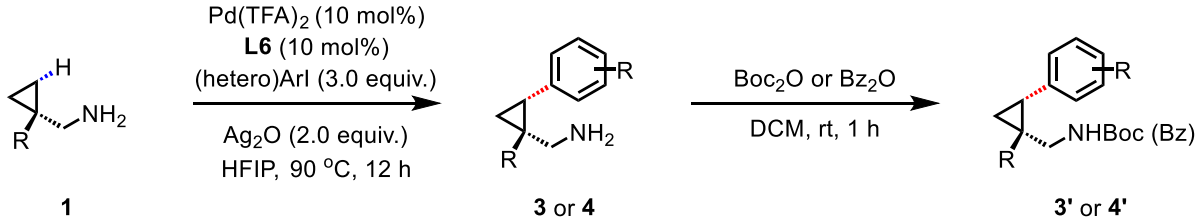


70% yield (3:1 mono:di), 75:25 er



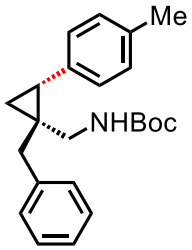
60% yield (6:1 mono:di), 80:20 er

General procedure for γ-C(sp^3)–H arylation



General Procedure A: In the culture tube, $Pd(TFA)_2$ (10 mol%, 3.3 mg), ligand **L6** (10 mol%, 2.4 mg), (hetero)aryl iodide (3.0 equiv.), Ag_2O (2.0 equiv., 46.3 mg), and free aliphatic amine **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (0.2 mL) were added. The reaction mixture was stirred at rt for 3 min, and then heated to 90 °C for 12 h (150 rpm). After being allowed to cool to room temperature, the mixture was diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. The resulting mixture was dissolved in DCM (1.0 mL) and treated with Boc_2O (2.0 equiv., 46 μL) (HFIP residue can catalyze Boc protection of free amines[6]) or Bz_2O (2.0 equiv., 45.2 mg). After being stirred at rt for 1 h, the crude mixture was concentrated *in vacuo* and purified by pTLC (hexane/EA or toluene/EA) to afford the corresponding Boc- or Bz-protected amine.

Substrate scope for γ-C(sp^3)–H arylation



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3a')**

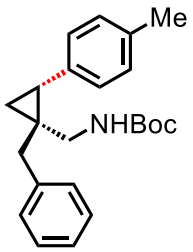
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 24.0 mg, 68% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 5.50 min (minor) and 5.91 min (major).

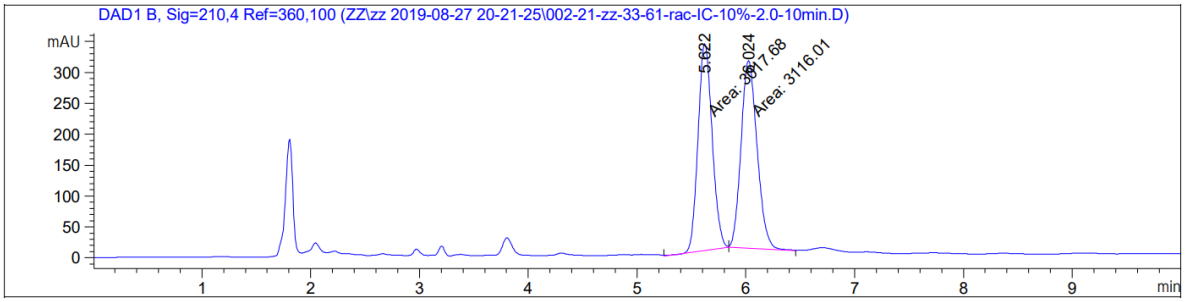
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 2H), 4.25 (br s, 1H), 2.92 – 2.80 (m, 2H), 2.80 – 2.70 (m, 2H), 2.29 (s, 3H), 2.15 (dd, *J* = 8.3, 6.3 Hz, 1H), 1.40 (s, 9H), 1.06 – 1.01 (m, 1H), 0.98 – 0.90 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.94, 139.35, 135.82, 135.20, 129.68, 129.18, 128.68, 128.50, 126.52, 79.08, 42.85, 41.77, 29.85, 28.54, 27.68, 21.13, 14.67.

HRMS (ESI-TOF) Calcd for $C_{18}H_{22}N$ [M-Boc]: 252.1752; found: 252.1753.

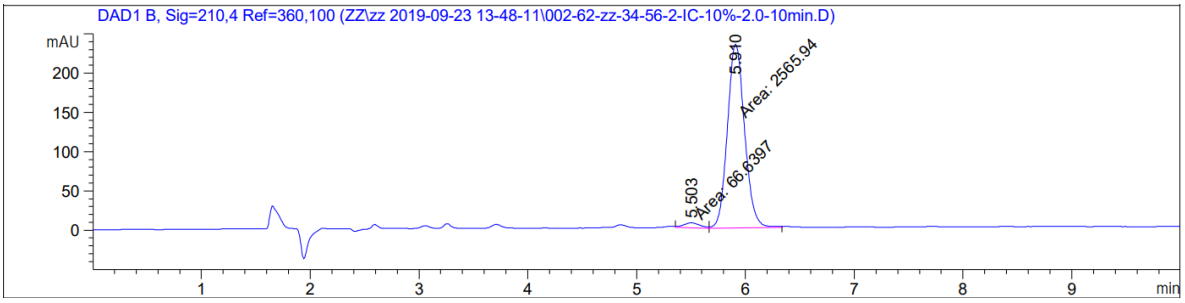
The absolute stereochemistry was assigned by analogy to compound **3t'**.



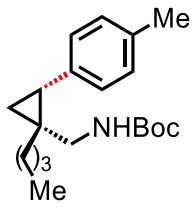


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.622	MM	0.1502	3017.67651	334.90594	49.1984
2	6.024	MM	0.1712	3116.01196	303.34796	50.8016
Totals :				6133.68848	638.25391	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.503	MM	0.1748	66.63972	6.35382	2.5313
2	5.910	MM	0.1829	2565.94434	233.83130	97.4687
Totals :				2632.58405	240.18512	



***tert*-Butyl (((1*R*,2*R*)-1-butyl-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3b')**

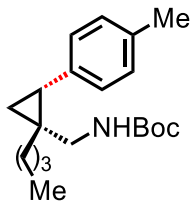
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 20.0 mg, 63% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 2.54 min (minor) and 2.80 min (major).

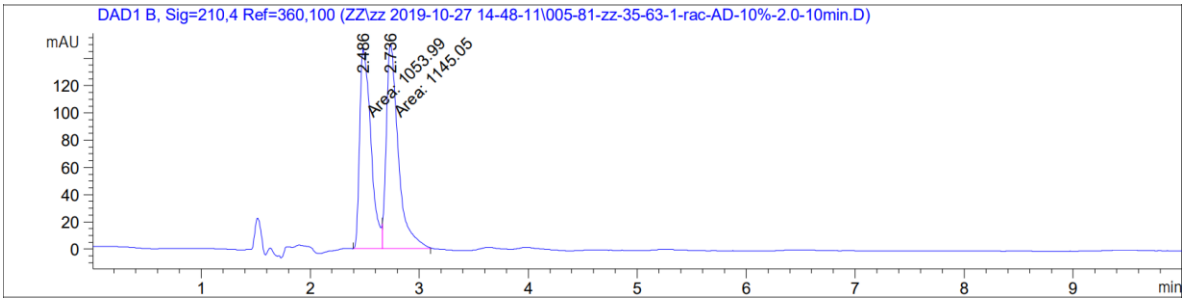
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 4H), 4.22 (br s, 1H), 2.89 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.81 (dd, *J* = 14.1, 5.2 Hz, 1H), 2.31 (s, 3H), 1.96 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.52 – 1.43 (m, 4H), 1.39 (s, 9H), 1.35 – 1.31 (m, 2H), 0.99 – 0.90 (m, 4H), 0.77 (dd, *J* = 8.4, 5.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.02, 135.67, 135.63, 129.15, 128.69, 78.98, 42.41, 36.18, 28.93, 28.53, 28.26, 27.58, 23.15, 21.13, 15.58, 14.23.

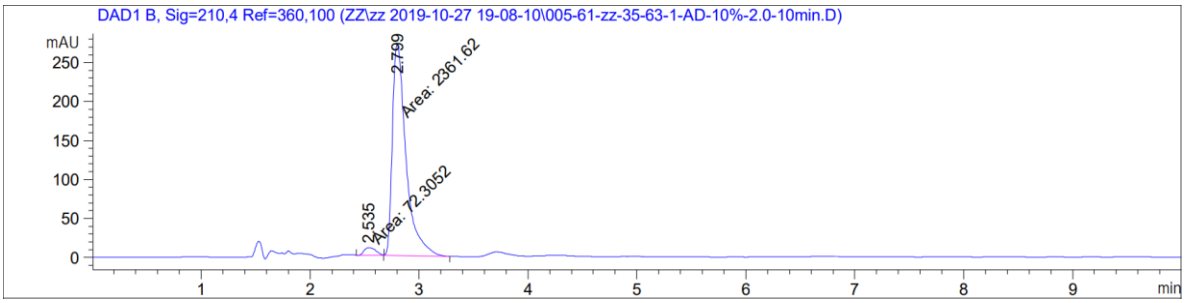
HRMS (ESI-TOF) Calcd for $C_{15}H_{24}N$ [M-Boc]: 218.1909; found: 218.1913.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

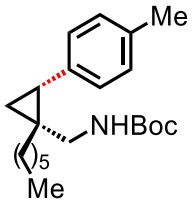




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.486	MF	0.1191	1053.99414	147.45099	47.9296
2	2.736	FM	0.1266	1145.05188	150.70715	52.0704
Totals :				2199.04602	298.15814	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.535	MM	0.1239	72.30518	9.72252	2.9707
2	2.799	MM	0.1449	2361.62134	271.59396	97.0293
Totals :				2433.92651	281.31648	



***tert*-Butyl (((1*R*,2*R*)-1-hexyl-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3c')**

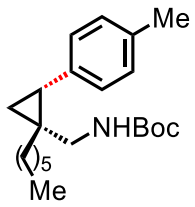
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 23.0 mg, 67% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (3% IPA/CO_2, 2.0 mL/min) with retention time 9.27 min (minor) and 10.13 min (major).

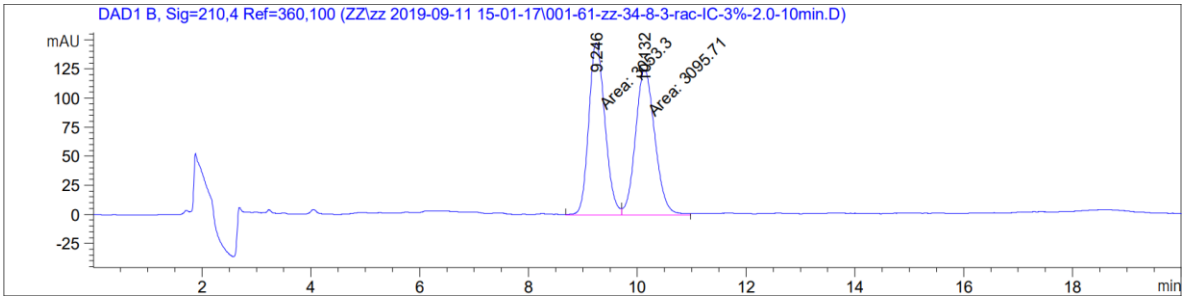
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 – 7.00 (s, 4H), 4.22 (br s, 1H), 2.89 (dd, *J* = 14.4, 6.5 Hz, 1H), 2.80 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.30 (s, 3H), 1.96 (t, *J* = 7.3 Hz, 1H), 1.51 – 1.44 (m, 3H), 1.39 (s, 9H), 1.36 – 1.24 (m, 7H), 1.00 – 0.92 (m, 1H), 0.89 (t, *J* = 6.6 Hz, 3H), 0.82 – 0.70 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.00, 135.66, 135.62, 129.14, 128.68, 78.97, 42.39, 36.48, 31.96, 29.77, 28.52, 28.25, 27.57, 26.68, 22.84, 21.13, 15.57, 14.26.

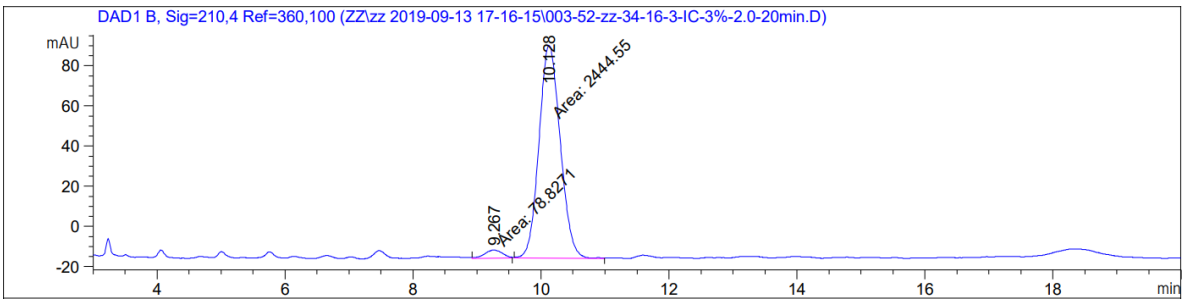
HRMS (ESI-TOF) Calcd for $C_{17}H_{28}N$ [M-Boc]: 246.2222; found: 246.2225.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

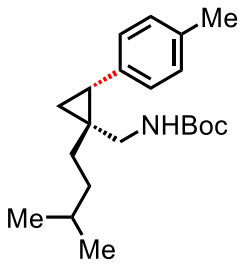




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.246	MF	0.3445	3053.29663	147.73560	49.6551
2	10.132	FM	0.4140	3095.70801	124.61242	50.3449
Totals :				6149.00464	272.34801	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.267	MM	0.3245	78.82707	4.04836	3.1239
2	10.128	MM	0.3842	2444.54810	106.03723	96.8761
Totals :				2523.37517	110.08560	



***tert*-Butyl (((1*R*,2*R*)-1-isopentyl-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3d')**

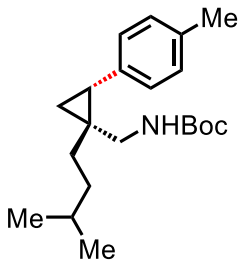
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 18.0 mg, 54% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 2.37 min (minor) and 2.54 min (major).

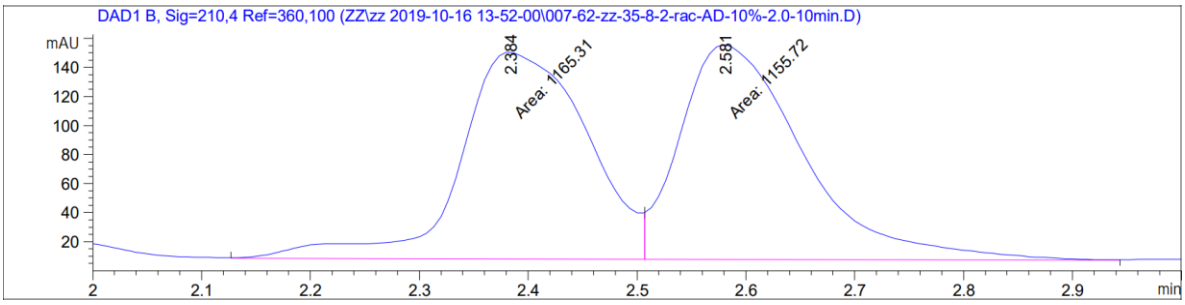
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 4H), 4.20 (br s, 1H), 2.90 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.80 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.31 (s, 3H), 1.95 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.48 – 1.43 (m, 2H), 1.39 (s, 9H), 1.36 – 1.27 (m, 2H), 0.94 (t, *J* = 5.6 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 6H), 0.76 (dd, *J* = 8.3, 5.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.98, 135.68, 135.63, 129.15, 128.69, 78.97, 42.34, 35.74, 34.16, 28.53, 28.46, 28.33, 27.74, 22.82, 22.73, 21.14, 15.59.

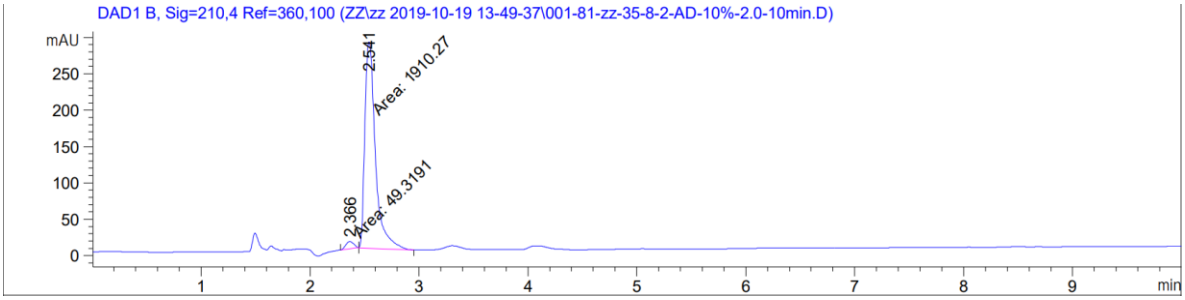
HRMS (ESI-TOF) Calcd for $C_{16}H_{26}N$ [M-Boc]: 232.2065; found: 232.2066.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

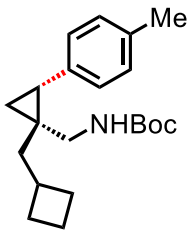




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.384	MF	0.1365	1165.30933	142.28049	50.2066
2	2.581	FM	0.1304	1155.71887	147.69949	49.7934
Totals :				2321.02820	289.97998	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.366	MM	0.0841	49.31909	9.77089	2.5168
2	2.541	MM	0.1119	1910.26697	284.41635	97.4832
Totals :				1959.58606	294.18724	



***tert*-Butyl (((1*R*,2*R*)-1-(cyclobutylmethyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3e')**

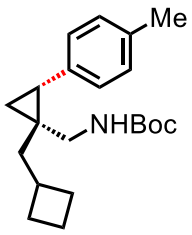
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (toluene/EA) afforded the title compound (colorless oil, 20.0 mg, 61% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 3.04 min (minor) and 3.33 min (major).

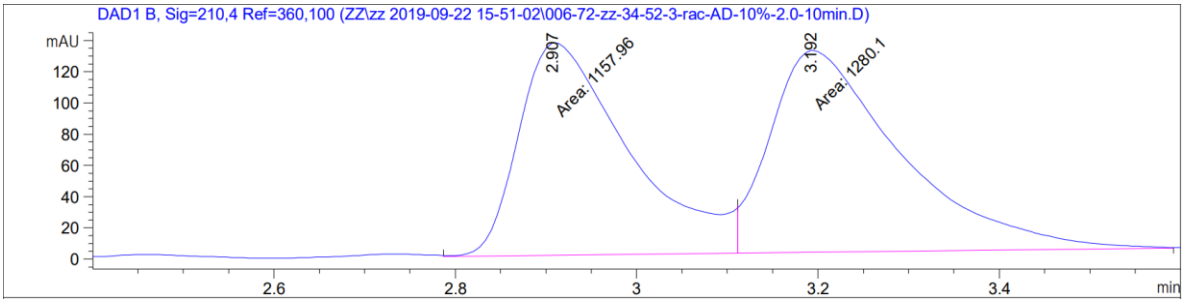
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (s, 4H), 4.23 (br s, 1H), 2.85 – 2.75 (m, 2H), 2.57 (dt, *J* = 16.6, 7.8 Hz, 1H), 2.30 (s, 3H), 2.19 – 2.06 (m, 2H), 2.03 – 1.95 (m, 1H), 1.95 – 1.85 (m, 1H), 1.84 – 1.73 (m, 2H), 1.73 – 1.63 (m, 2H), 1.40 (s, 10H), 0.91 (t, *J* = 5.3 Hz, 1H), 0.75 (dd, *J* = 8.3, 5.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.99, 135.69, 135.58, 129.13, 128.73, 79.00, 43.39, 42.93, 34.28, 29.64, 29.56, 28.54, 27.59, 26.33, 21.14, 19.25, 14.92.

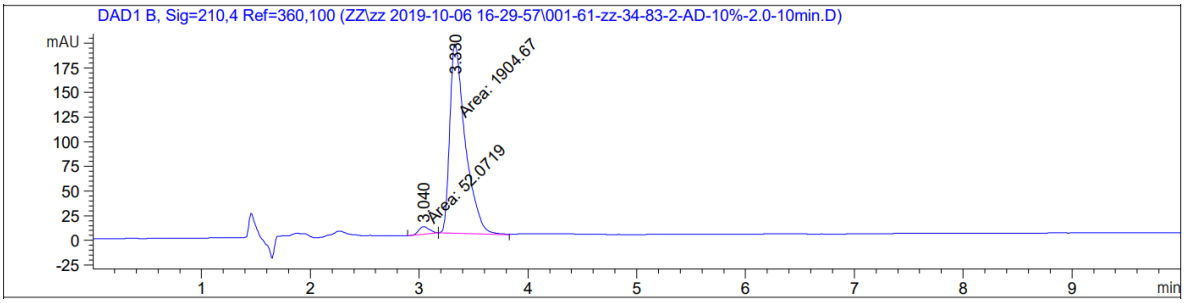
HRMS (ESI-TOF) Calcd for $C_{16}H_{24}N$ [M-Boc]: 230.1909; found: 230.1910.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

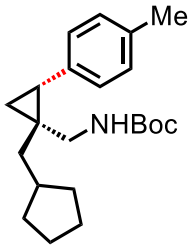




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.907	MF	0.1416	1157.96472	136.31445	47.4952
2	3.192	FM	0.1649	1280.10205	129.40999	52.5048
Totals :				2438.06677	265.72444	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.040	MM	0.1123	52.07194	7.72780	2.6612
2	3.330	MM	0.1654	1904.66663	191.91554	97.3388
Totals :				1956.73857	199.64334	



***tert*-Butyl (((1*R*,2*R*)-1-(cyclopentylmethyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3f')**

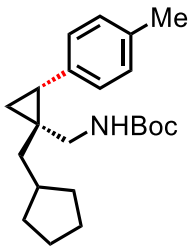
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 19.0 mg, 55% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (7% IPA/CO_2, 2.0 mL/min) with retention time 3.89 min (minor) and 4.37 min (major).

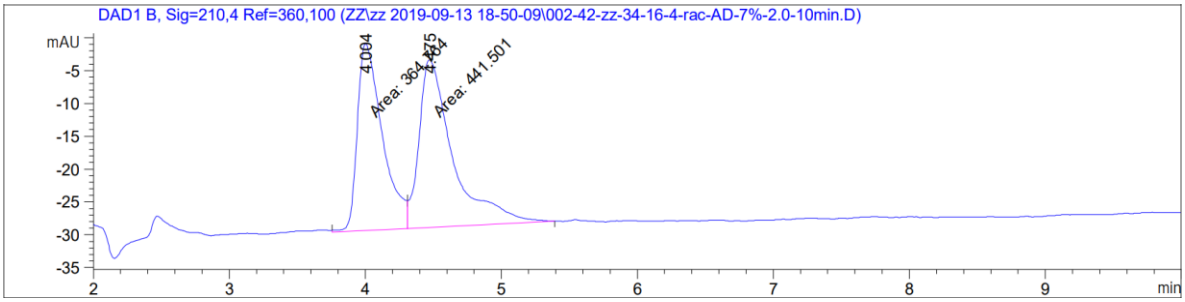
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (s, 4H), 4.23 (br s, 1H), 2.98 – 2.89 (m, 1H), 2.89 – 2.80 (m, 1H), 2.31 (s, 3H), 2.10 – 2.02 (m, 1H), 2.02 – 1.95 (m, 1H), 1.95 – 1.86 (m, 1H), 1.86 – 1.80 (m, 1H), 1.67 – 1.60 (m, 2H), 1.59 – 1.51 (m, 3H), 1.39 (s, 9H), 1.24 – 1.15 (m, 1H), 1.15 – 1.07 (m, 1H), 0.96 (t, *J* = 5.6 Hz, 1H), 0.90 – 0.81 (m, 1H), 0.77 (dd, *J* = 8.2, 5.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.99, 135.69, 135.63, 129.14, 128.67, 79.01, 42.52, 38.22, 33.56, 33.40, 29.85, 28.52, 28.30, 26.94, 25.12, 21.14, 15.51 (1 carbon signal was not assigned due to overlaps).

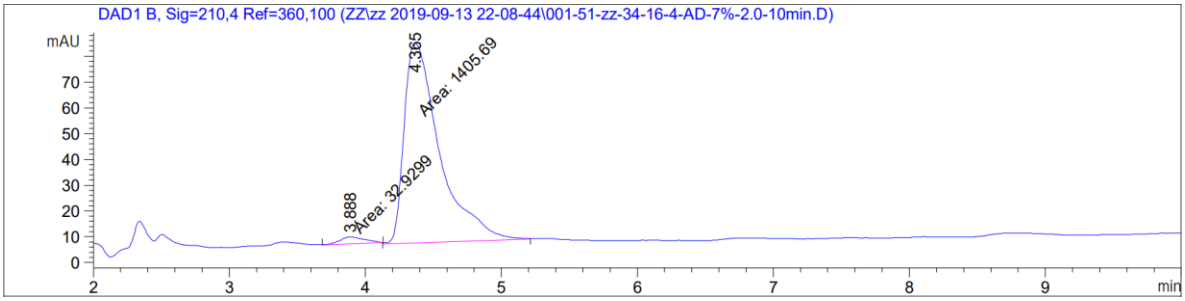
HRMS (ESI-TOF) Calcd for $C_{17}H_{26}N$ [M-Boc]: 244.2065; found: 244.2065.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

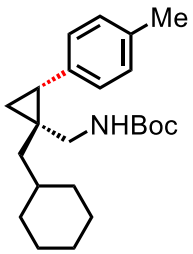




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.004	MF	0.2137	364.76437	28.45213	45.2412
2	4.475	FM	0.2880	441.50079	25.54582	54.7588
Totals :				806.26517	53.99795	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.888	MM	0.2052	32.92994	2.67472	2.2890
2	4.365	MM	0.3021	1405.69324	77.56008	97.7110
Totals :				1438.62318	80.23480	



***tert*-Butyl (((1*R*,2*R*)-1-(cyclohexylmethyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3g')**

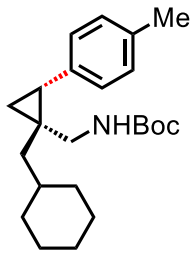
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 25.0 mg, 70% yield, 98:2 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (7% IPA/CO_2, 2.0 mL/min) with retention time 4.19 min (minor) and 4.70 min (major).

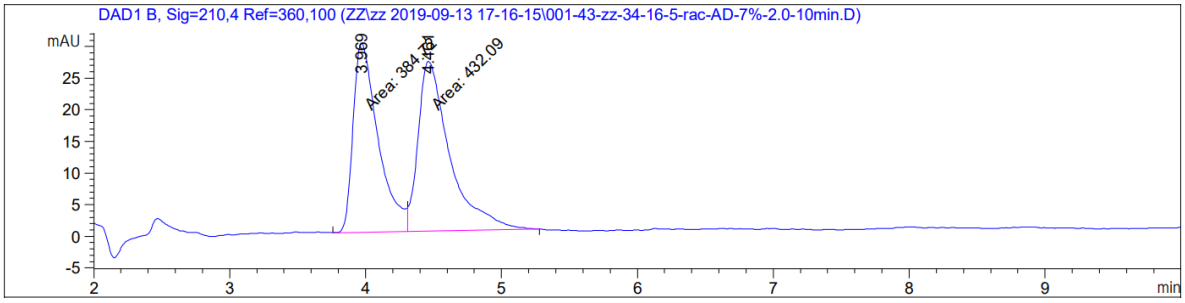
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (s, 4H), 4.21 (br s, 1H), 3.01 (dd, *J* = 14.3, 6.9 Hz, 1H), 2.78 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.31 (s, 3H), 1.98 – 1.89 (m, 1H), 1.89 – 1.75 (m, 2H), 1.75 – 1.63 (m, 3H), 1.63 – 1.58 (m, 1H), 1.39 (s, 9H), 1.33 – 1.21 (m, 4H), 1.20 – 1.11 (m, 1H), 0.98 (t, *J* = 5.6 Hz, 1H), 0.96 – 0.85 (m, 2H), 0.75 (dd, *J* = 8.1, 5.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.94, 135.66, 135.60, 129.15, 128.58, 78.98, 44.42, 42.19, 35.52, 34.11, 34.07, 28.52, 28.39, 26.77, 26.42, 25.78, 21.12, 15.70 (1 carbon signal was not assigned due to overlaps).

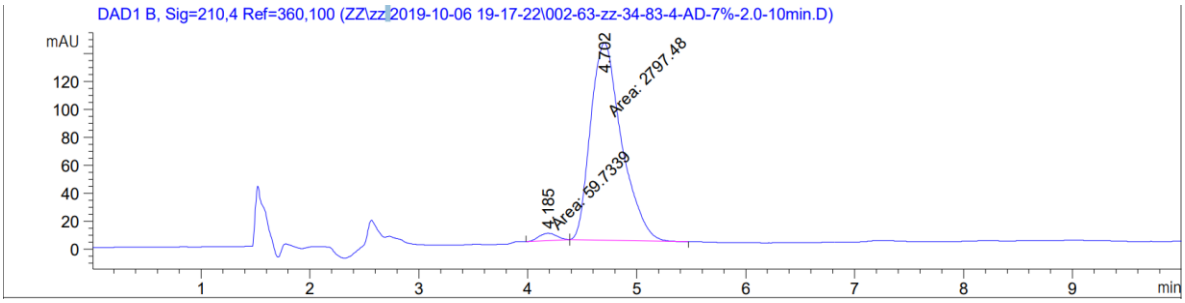
HRMS (ESI-TOF) Calcd for $C_{18}H_{28}N$ [M-Boc]: 258.2222; found: 258.2226.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

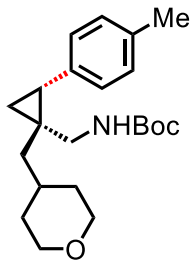




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.969	MF	0.2145	384.71997	29.89201	47.1003
2	4.461	FM	0.2686	432.09021	26.81486	52.8997
Totals :				816.81018	56.70687	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.185	MM	0.1899	59.73391	5.24326	2.0906
2	4.702	MM	0.3302	2797.47827	141.22035	97.9094
Totals :				2857.21218	146.46362	



***tert*-Butyl (((1*R*,2*R*)-1-((tetrahydro-2*H*-pyran-4-yl)methyl)-2-(*p*-tolyl)cyclopropyl)methyl) carbamate (3h')**

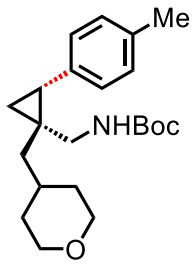
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 21.0 mg, 58% yield, 98.5:1.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 9.44 min (major) and 11.63 min (minor).

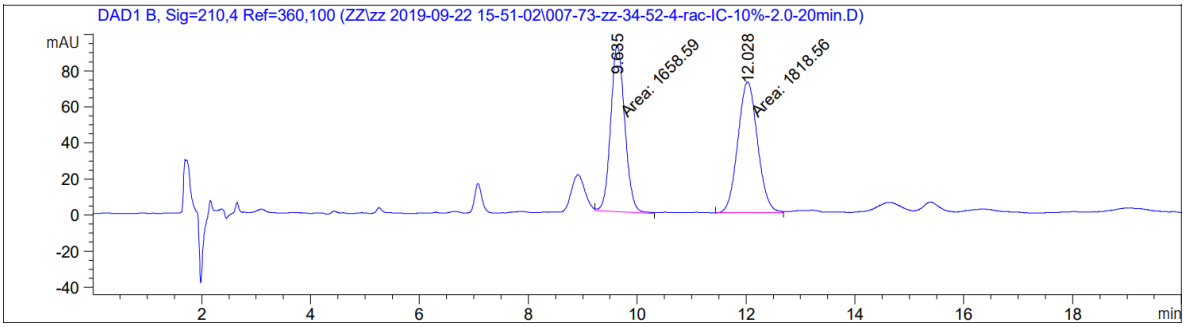
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 4.18 (br s, 1H), 4.00 – 3.92 (m, 2H), 3.47 – 3.39 (m, 2H), 3.09 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.75 (dd, *J* = 14.3, 4.9 Hz, 1H), 2.31 (s, 3H), 1.98 – 1.88 (m, 2H), 1.76 – 1.66 (m, 2H), 1.39 (s, 9H), 1.38 – 1.31 (m, 2H), 1.31 – 1.24 (m, 2H), 0.99 (t, *J* = 5.6 Hz, 1H), 0.79 (dd, *J* = 8.5, 5.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.95, 135.88, 135.28, 129.25, 128.53, 79.12, 68.19, 68.15, 43.89, 41.98, 33.93, 33.59, 32.92, 28.51, 25.59, 21.13, 15.56, 13.76.

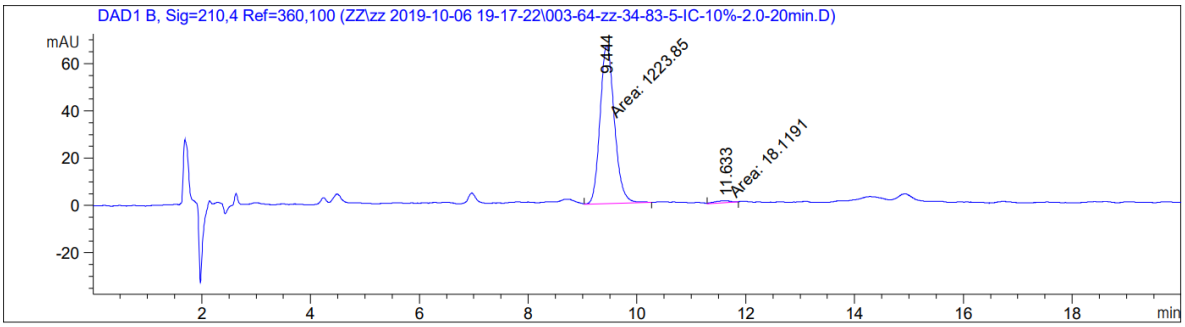
HRMS (ESI-TOF) Calcd for $C_{17}H_{26}NO$ [M-Boc]: 260.2014; found: 260.2020.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

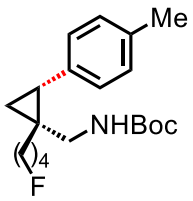




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.635	MM	0.2994	1658.59436	92.32034	47.6997
2	12.028	MM	0.4178	1818.56433	72.54531	52.3003
Totals :				3477.15869	164.86565	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.444	MM	0.3046	1223.84570	66.95682	98.5411
2	11.633	MM	0.2804	18.11912	7.69049e-1	1.4589
Totals :				1241.96482	67.72587	



***tert*-Butyl (((1*R*,2*R*)-1-(4-fluorobutyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3i')**

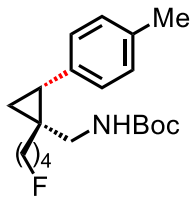
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 22.0 mg, 66% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (5% IPA/CO_2, 2.0 mL/min) with retention time 6.92 min (major) and 8.81 min (minor).

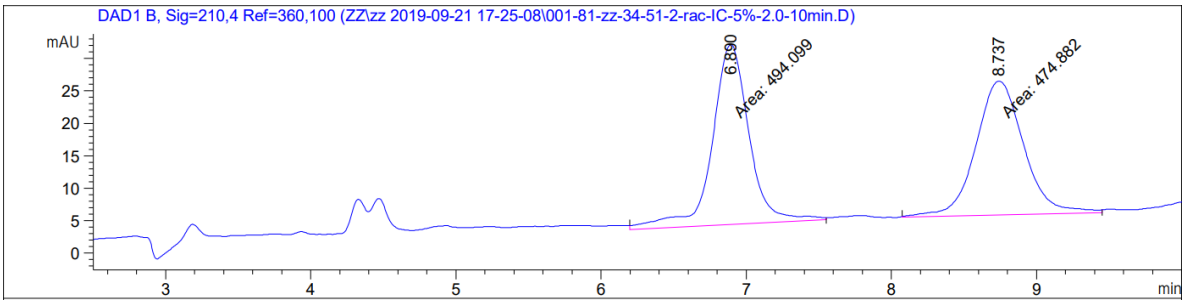
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.47 (dt, *J* = 47.3, 6.2 Hz, 2H), 4.21 (br s, 1H), 2.94 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.78 (dd, *J* = 14.3, 5.3 Hz, 1H), 2.31 (s, 3H), 1.98 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.79 – 1.67 (m, 2H), 1.66 – 1.60 (m, 2H), 1.53 – 1.46 (m, 1H), 1.42 – 1.36 (m, 10H), 0.97 (t, *J* = 5.6 Hz, 1H), 0.79 (dd, *J* = 8.5, 5.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.04, 135.81, 135.36, 129.20, 128.67, 84.29 (d, *J* = 164.1 Hz), 79.09, 42.24, 36.10, 30.79 (d, *J* = 19.4 Hz), 28.51, 28.26, 22.52 (d, *J* = 6.2 Hz), 21.13, 18.72, 15.49.

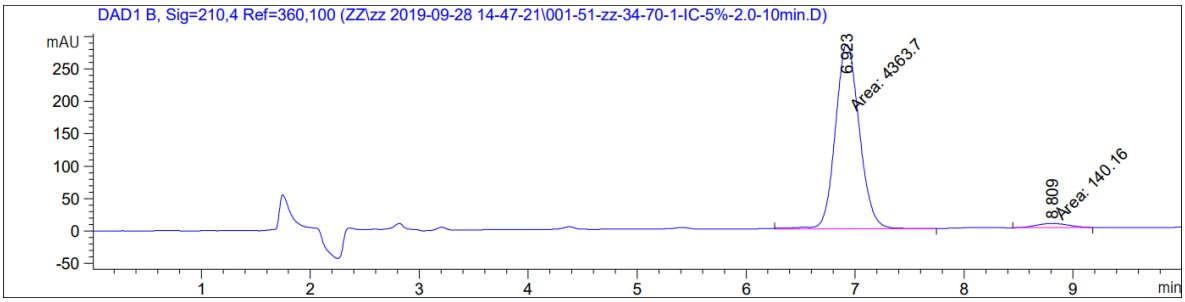
HRMS (ESI-TOF) Calcd for $C_{15}H_{23}FN$ [M-Boc]: 236.1815; found: 236.1818.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

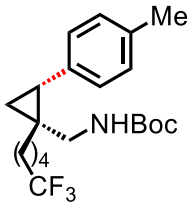




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.890	MM	0.2962	494.09866	27.80464	50.9916
2	8.737	MM	0.3829	474.88190	20.66815	49.0084
Totals :				968.98056	48.47279	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.923	MM	0.2551	4363.70313	285.05414	96.8880
2	8.809	MM	0.3553	140.16045	6.57462	3.1120
Totals :				4503.86357	291.62876	



***tert*-Butyl (((1*R*,2*R*)-2-(*p*-tolyl)-1-(5,5,5-trifluoropentyl)cyclopropyl)methyl)carbamate (3j')**

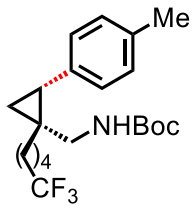
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 25.0 mg, 65% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak OD column (3% IPA/CO_2, 2.0 mL/min) with retention time 4.04 min (minor) and 4.72 min (major).

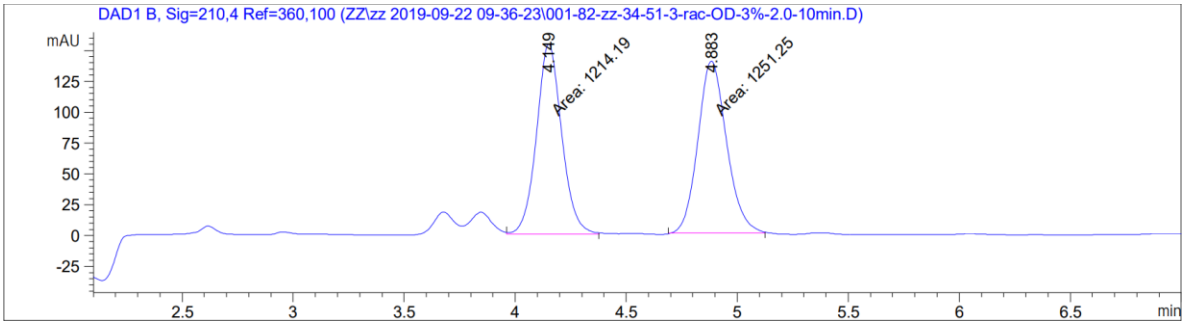
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.20 (br s, 1H), 2.95 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.76 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.31 (s, 3H), 2.16 – 2.05 (m, 2H), 1.96 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.65 – 1.54 (m, 5H), 1.42 – 1.34 (m, 10H), 0.96 (t, *J* = 5.6 Hz, 1H), 0.78 (dd, *J* = 8.5, 5.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.06, 135.88, 135.27, 129.23, 128.64, 127.38 (q, *J* = 276.3 Hz), 79.15, 42.10, 35.98, 33.83 (q, *J* = 28.6 Hz), 28.49, 28.33, 27.53, 25.84, 22.18 (q, *J* = 3.0 Hz), 21.13, 15.42.

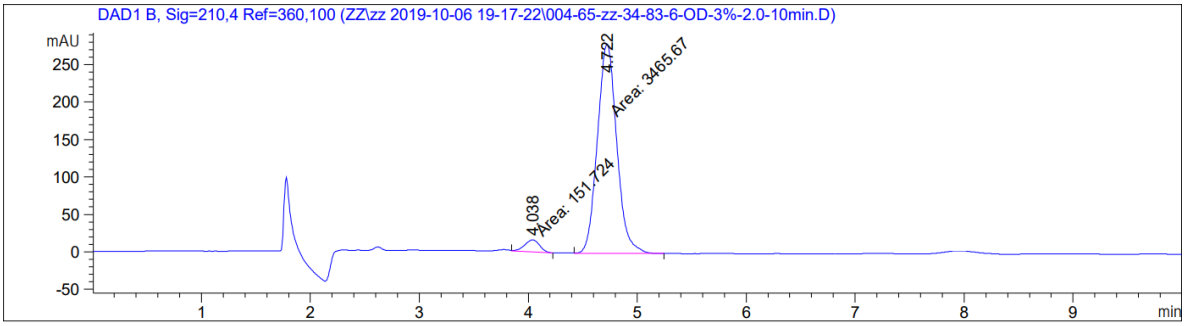
HRMS (ESI-TOF) Calcd for $C_{16}H_{23}F_3N$ [M-Boc]: 286.1783; found: 286.1785.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

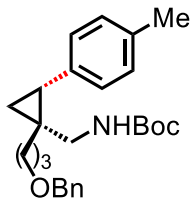




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.149	MM	0.1309	1214.18713	154.60463	49.2484
2	4.883	MM	0.1493	1251.24866	139.66620	50.7516
Totals :				2465.43579	294.27083	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.038	MM	0.1569	151.72357	16.12165	4.1943
2	4.722	MM	0.2066	3465.66724	279.58203	95.8057
Totals :				3617.39081	295.70368	



***tert*-Butyl (((1*R*,2*R*)-1-(3-(benzyloxy)propyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3k')**

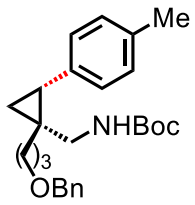
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 19.5 mg, 48% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak OD column (20% IPA/CO_2, 2.0 mL/min) with retention time 3.77 min (minor) and 4.27 min (major).

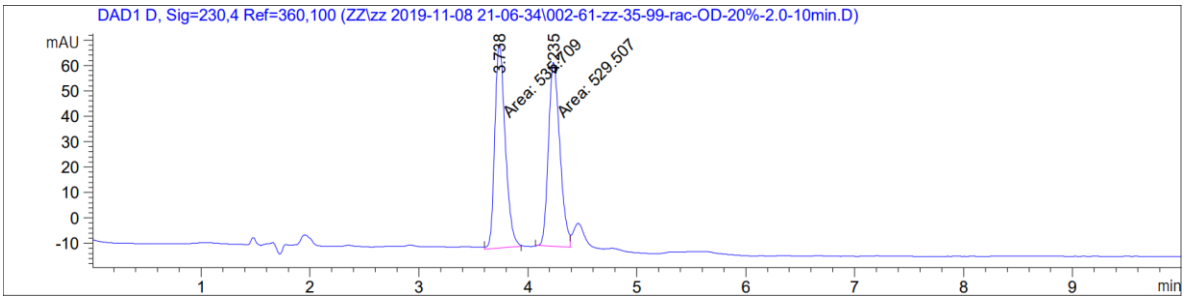
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.31 – 7.26 (m, 1H), 7.06 (s, 4H), 4.52 (s, 2H), 4.26 (br s, 1H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.91 (dd, *J* = 14.6, 6.7 Hz, 1H), 2.80 (dd, *J* = 14.6, 4.6 Hz, 1H), 2.30 (s, 3H), 1.98 (t, *J* = 7.4 Hz, 1H), 1.90 – 1.72 (m, 3H), 1.49 – 1.41 (m, 1H), 1.38 (s, 9H), 1.00 – 0.91 (m, 1H), 0.84 – 0.73 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.04, 138.75, 135.74, 135.43, 129.17, 128.69, 128.50, 127.80, 127.65, 79.04, 72.97, 70.49, 42.32, 32.93, 28.52, 28.24, 27.28, 27.00, 21.13, 15.59.

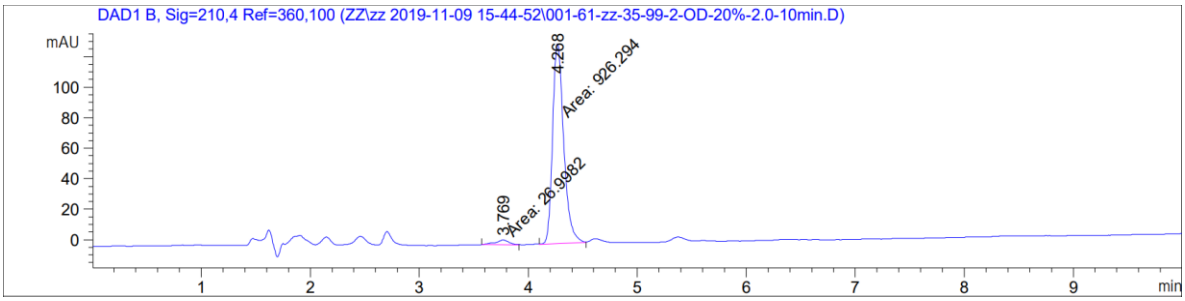
HRMS (ESI-TOF) Calcd for $C_{21}H_{28}NO$ [M-Boc]: 310.2171; found: 310.2171.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

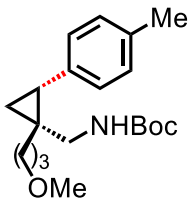




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.738	MM	0.1112	535.70868	80.30118	50.2911
2	4.235	MF	0.1218	529.50677	72.45930	49.7089
Totals :				1065.21545	152.76048	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.769	MM	0.1432	26.99818	3.14201	2.8321
2	4.268	MM	0.1176	926.29449	131.32811	97.1679
Totals :				953.29268	134.47012	



***tert*-Butyl (((1*R*,2*R*)-1-(3-methoxypropyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3l')**

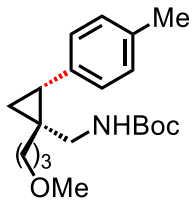
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 18.0 mg, 54% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 3.88 min (minor) and 4.53 min (major).

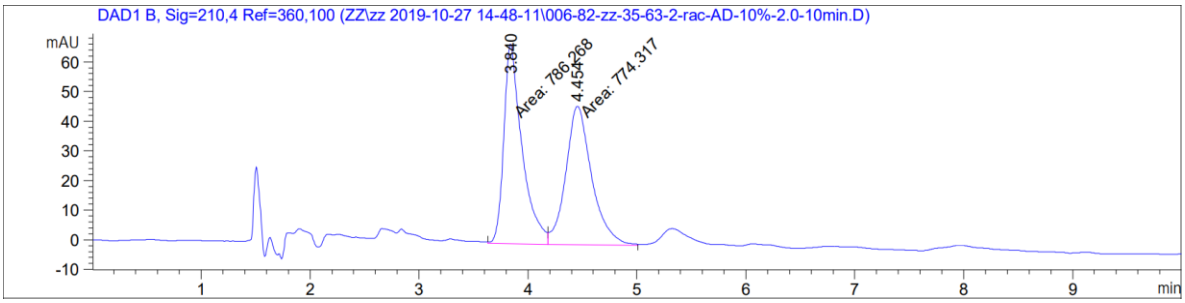
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 4H), 4.26 (br s, 1H), 3.42 (t, *J* = 6.3 Hz, 2H), 3.34 (s, 3H), 2.92 (dd, *J* = 15.1, 6.2 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.31 (s, 3H), 1.99 (dd, *J* = 8.5, 6.1 Hz, 1H), 1.85 – 1.71 (m, 2H), 1.72 – 1.62 (m, 1H), 1.56 – 1.49 (m, 1H), 1.39 (s, 9H), 0.97 (t, *J* = 5.7 Hz, 1H), 0.80 (dd, *J* = 8.5, 5.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.05, 135.76, 135.43, 129.18, 128.69, 79.04, 72.85, 58.62, 42.28, 32.87, 28.51, 28.27, 26.84, 21.13, 15.57, 10.64.

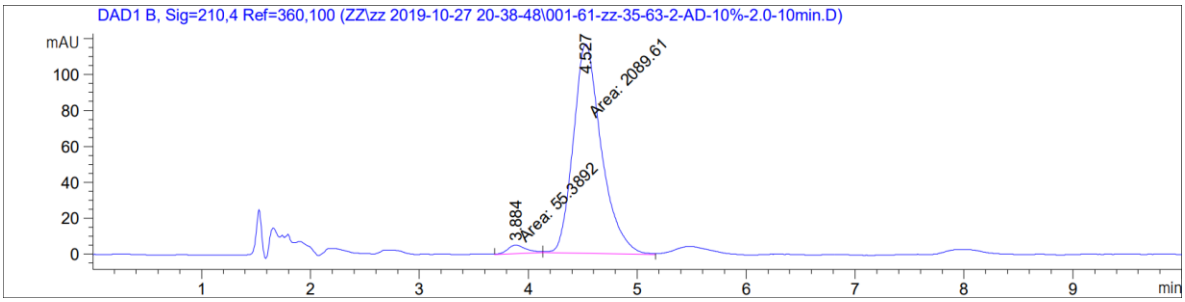
HRMS (ESI-TOF) Calcd for $C_{15}H_{24}NO$ [M-Boc]: 234.1858; found: 234.1863.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

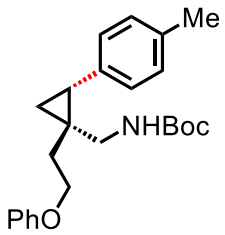




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.840	MF	0.1943	786.26825	67.44659	50.3829
2	4.454	FM	0.2764	774.31677	46.68417	49.6171
Totals :				1560.58502	114.13076	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.884	MM	0.1939	55.38919	4.76218	2.5822
2	4.527	MM	0.2989	2089.61230	116.50014	97.4178
Totals :				2145.00150	121.26232	



***tert*-Butyl (((1*S*,2*R*)-1-(2-phenoxyethyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3m')**

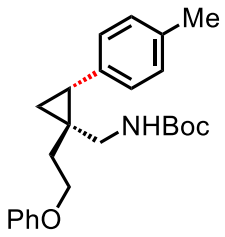
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 17.0 mg, 45% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (15% IPA/CO_2, 2.0 mL/min) with retention time 4.62 min (minor) and 5.10 min (major).

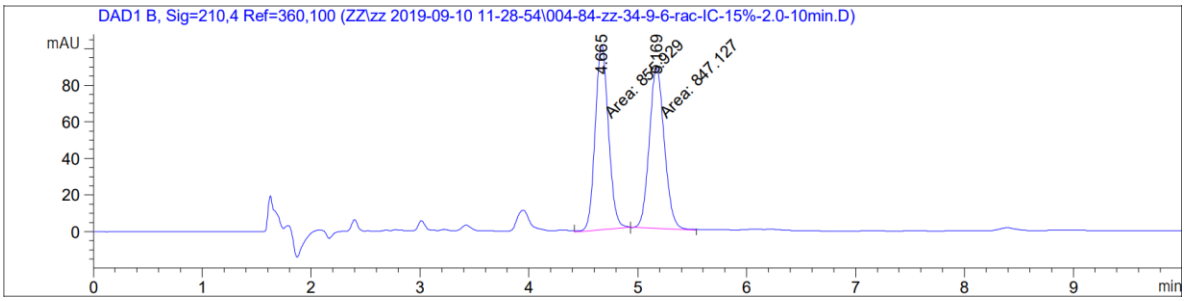
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.00 – 6.90 (m, 3H), 4.49 (br s, 1H), 4.27 – 4.20 (m, 1H), 4.20 – 4.12 (m, 1H), 2.93 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.87 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.31 (s, 3H), 2.18 – 2.12 (m, 1H), 2.07 – 2.00 (m, 1H), 1.89 – 1.81 (m, 1H), 1.39 (s, 9H), 1.04 (t, *J* = 5.7 Hz, 1H), 0.91 (dd, *J* = 8.5, 5.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.92, 135.92, 135.14, 129.61, 129.21, 128.82, 120.81, 114.67, 114.56, 79.12, 66.07, 42.98, 35.99, 28.53, 28.31, 27.57, 21.15, 15.47.

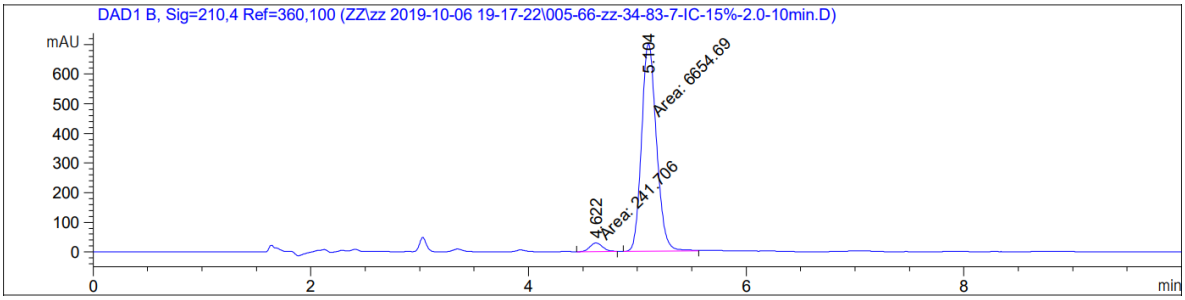
HRMS (ESI-TOF) Calcd for $C_{19}H_{24}NO$ [M-Boc]: 282.1858; found: 282.1864.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

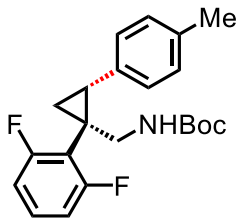




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.665	MM	0.1408	855.92877	101.32438	50.2584
2	5.169	MM	0.1614	847.12720	87.49296	49.7416
Totals :				1703.05597	188.81734	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.622	MM	0.1364	241.70641	29.53849	3.5048
2	5.104	MM	0.1582	6654.69189	701.03290	96.4952
Totals :				6896.39830	730.57139	



***tert*-Butyl (((1*R*,2*R*)-1-(2,6-difluorophenyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3n')**

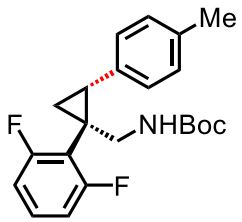
Following **General Procedurea A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 18.0 mg, 48% yield, 99:1 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 4.67 min (minor) and 5.40 min (major).

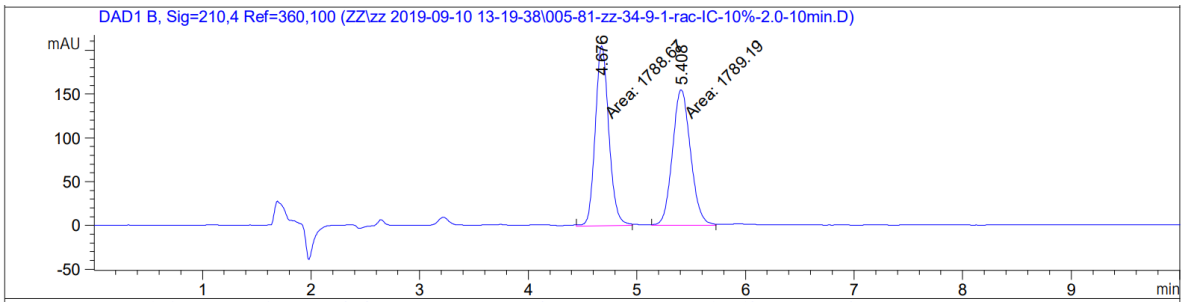
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.16 (m, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.89 (t, *J* = 8.3 Hz, 2H), 4.43 (br s, 1H), 3.17 (dd, *J* = 14.2, 7.2 Hz, 1H), 2.91 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.34 (s, 3H), 1.52 (t, *J* = 6.3 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.28 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.97 (dd, *J* = 248.4, 7.9 Hz), 155.82, 136.36, 134.26, 129.31, 129.04, 128.79 (t, *J* = 10.5 Hz), 119.48 (t, *J* = 17.3 Hz), 111.58 (dd, *J* = 25.9, 3.4 Hz), 78.96, 44.81, 28.38, 28.24, 22.66, 21.22, 15.65.

HRMS (ESI-TOF) Calcd for $C_{17}H_{18}F_2N$ [M-Boc]: 274.1407; found: 274.1407.

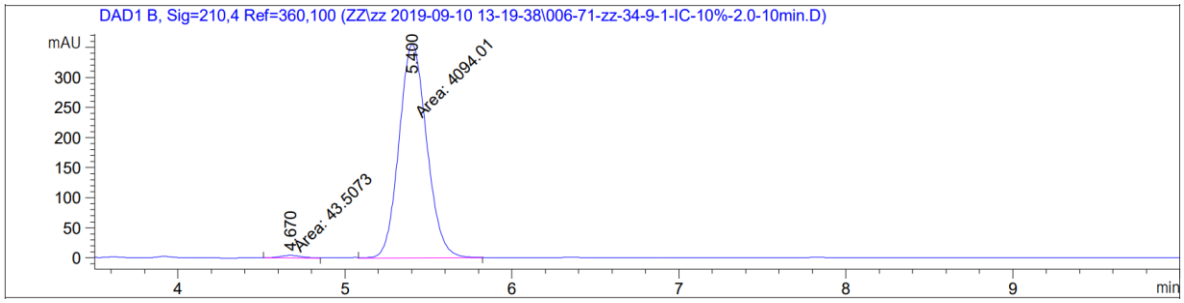
The absolute stereochemistry was assigned by analogy to compound **3t'**.





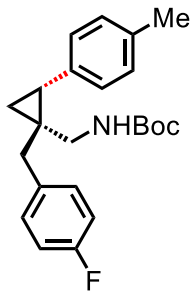
Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.676	MM	0.1450	1788.66638	205.55940	49.9927
2	5.408	MM	0.1927	1789.18604	154.74773	50.0073
Totals :				3577.85242	360.30713	



Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.670	MM	0.1632	43.50726	4.44184	1.0515
2	5.400	MM	0.1921	4094.01270	355.20718	98.9485
Totals :				4137.51995	359.64902	



***tert*-Butyl (((1*S*,2*R*)-1-(4-fluorobenzyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3o')**

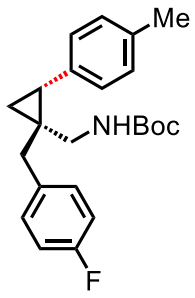
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 22.5 mg, 61% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak OJ column (5% IPA/CO_2, 2.0 mL/min) with retention time 4.30 min (minor) and 5.01 min (major).

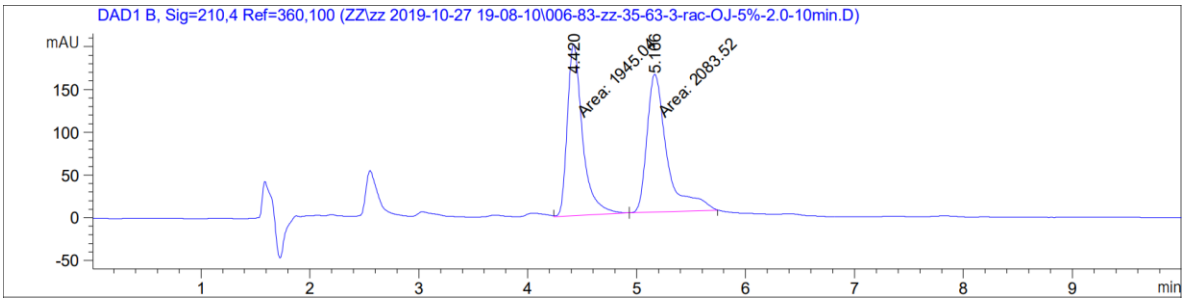
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 7.05 – 6.94 (m, 4H), 4.22 (br s, 1H), 2.88 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.83 – 2.68 (m, 3H), 2.30 (s, 3H), 2.13 (dd, *J* = 8.6, 6.0 Hz, 1H), 1.40 (s, 9H), 1.03 (t, *J* = 6.0 Hz, 1H), 0.97 – 0.90 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.21 (d, *J* = 244.1 Hz), 155.32, 135.35, 134.47, 134.45, 130.40 (d, *J* = 8.0 Hz), 128.64, 128.03, 114.67 (d, *J* = 21.2 Hz), 78.55, 42.02, 40.32, 33.88, 27.92, 27.07, 20.53, 14.10.

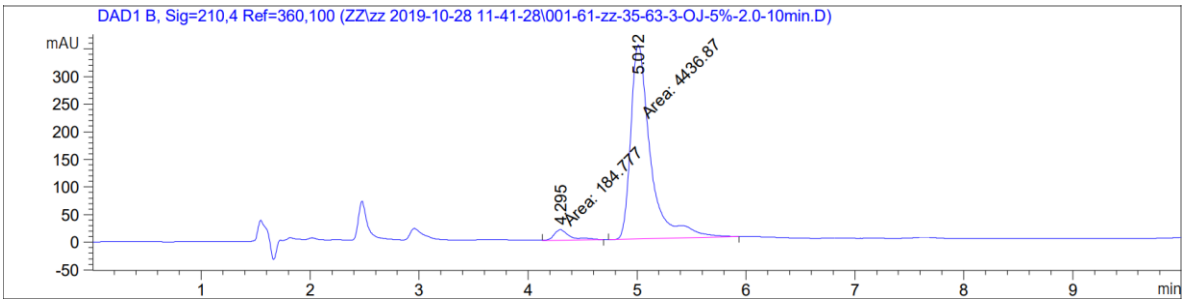
HRMS (ESI-TOF) Calcd for $C_{18}H_{21}FN$ [M-Boc]: 270.1658; found: 270.1659.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

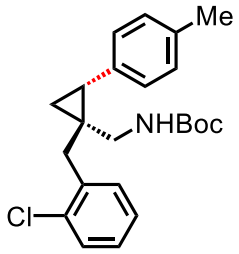




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.420	MM	0.1614	1945.04150	200.82118	48.2813
2	5.166	MM	0.2156	2083.52246	161.07678	51.7187
Totals :				4028.56396	361.89796	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.295	MM	0.1633	184.77670	18.85480	3.9981
2	5.012	MM	0.2102	4436.86963	351.77042	96.0019
Totals :				4621.64633	370.62522	



***tert*-Butyl (((1*S*,2*R*)-1-(2-chlorobenzyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3p')**

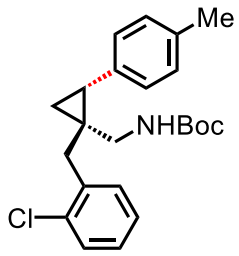
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 28.0 mg, 73% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 6.57 min (minor) and 8.17 min (major).

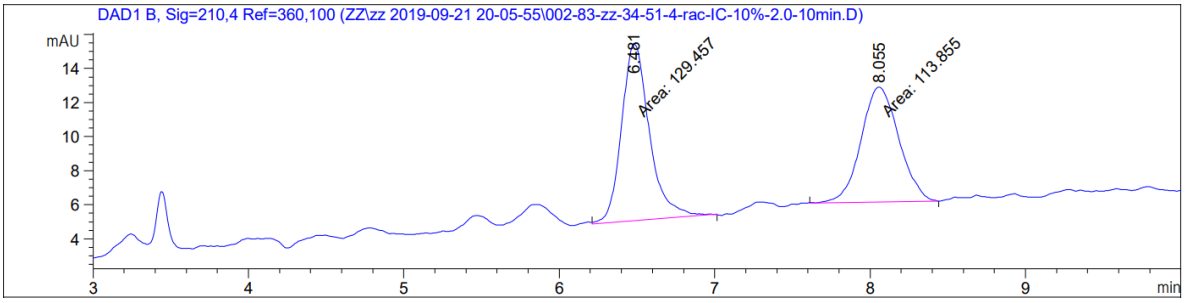
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.23 (td, *J* = 7.5, 1.2 Hz, 1H), 7.18 (td, *J* = 7.7, 1.5 Hz, 1H), 7.07 (s, 4H), 4.38 (br s, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 3.04 (dd, *J* = 14.3, 7.5 Hz, 1H), 2.91 (d, *J* = 13.5 Hz, 1H), 2.78 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.30 (s, 3H), 2.04 – 1.98 (m, 1H), 1.40 (s, 9H), 1.06 – 1.01 (m, 1H), 0.87 – 0.80 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.12, 136.66, 135.82, 135.16, 134.92, 131.81, 129.72, 129.19, 128.67, 128.01, 126.84, 79.11, 43.71, 37.45, 28.54, 27.27, 26.55, 21.14, 13.52.

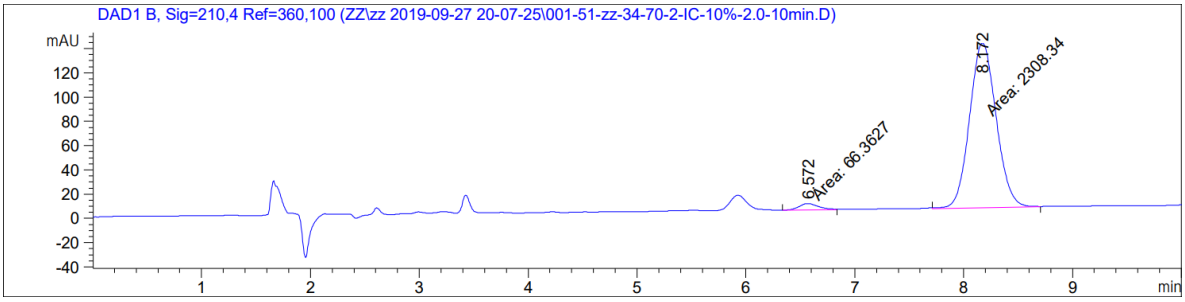
HRMS (ESI-TOF) Calcd for $C_{18}H_{21}ClN$ [M-Boc]: 286.1363; found: 286.1369.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

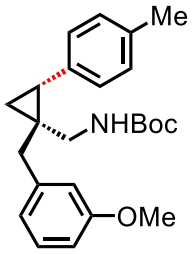




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.481	MM	0.2070	129.45726	10.42374	53.2062
2	8.055	MM	0.2814	113.85495	6.74379	46.7938
Totals :				243.31221	17.16753	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.572	MM	0.2090	66.36269	5.29160	2.7946
2	8.172	MM	0.2832	2308.33740	135.85718	97.2054
Totals :				2374.70009	141.14878	



***tert*-Butyl (((1*S*,2*R*)-1-(3-methoxybenzyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3q')**

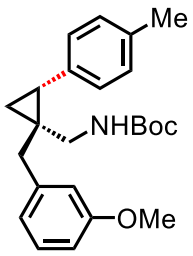
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 25.0 mg, 66% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (20% IPA/CO_2, 2.0 mL/min) with retention time 4.15 min (minor) and 4.68 min (major).

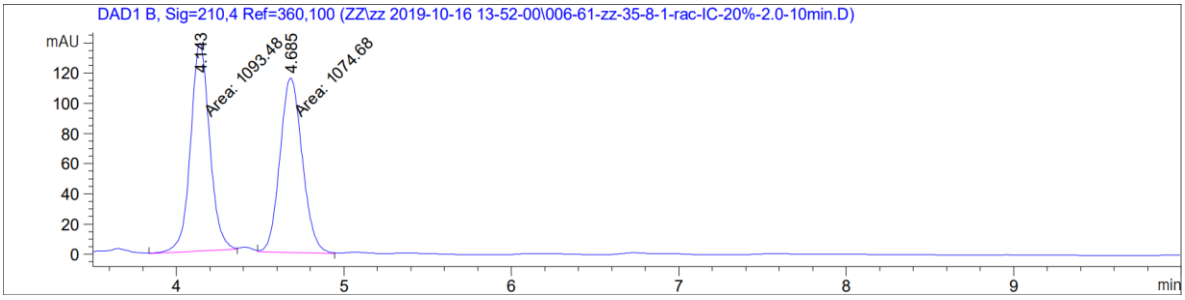
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.85 (s, 1H), 6.79 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 4.25 (br s, 1H), 3.82 (s, 3H), 2.90 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.85 – 2.60 (m, 3H), 2.29 (s, 3H), 2.19 – 2.11 (m, 1H), 1.39 (s, 9H), 1.05 (t, *J* = 5.7 Hz, 1H), 0.98 – 0.91 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.72, 155.93, 140.93, 135.83, 135.18, 129.42, 129.18, 128.68, 122.03, 115.31, 112.04, 79.05, 55.33, 42.79, 41.89, 28.51, 28.50, 27.82, 21.13, 14.73.

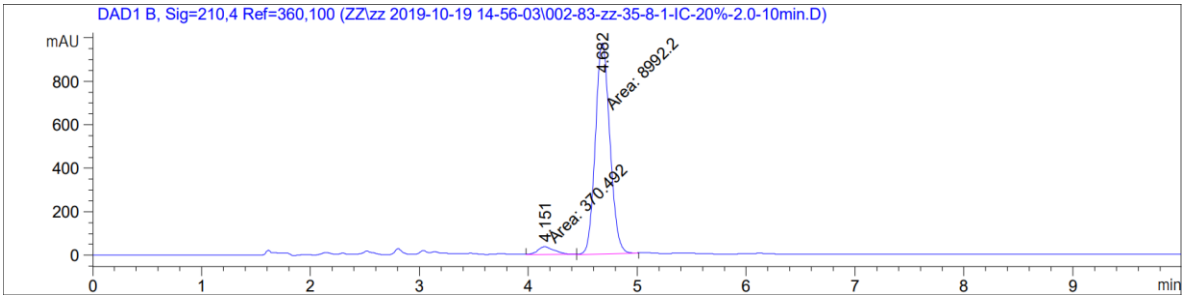
HRMS (ESI-TOF) Calcd for $C_{19}H_{24}NO$ [M-Boc]: 282.1858; found: 282.1864.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

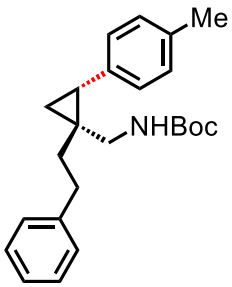




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.143	MM	0.1322	1093.48474	137.86510	50.4335
2	4.685	MM	0.1547	1074.68481	115.81234	49.5665
Totals :				2168.16956	253.67744	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.151	MM	0.1742	370.49158	35.45380	3.9571
2	4.682	MM	0.1544	8992.20215	970.43518	96.0429
Totals :				9362.69373	1005.88898	



***tert*-Butyl (((1*R*,2*R*)-1-phenethyl-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3r')**

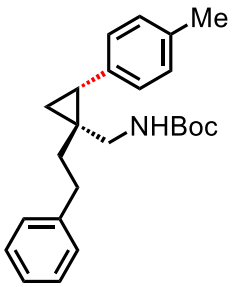
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 19.0 mg, 52% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (15% IPA/CO_2, 2.0 mL/min) with retention time 3.78 min (minor) and 4.54 min (major).

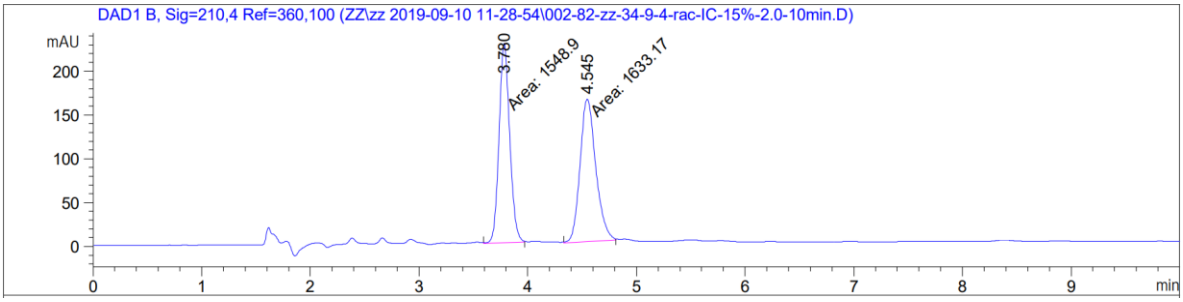
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 4.25 (br s, 1H), 3.05 (dd, *J* = 14.5, 6.9 Hz, 1H), 2.92 – 2.73 (m, 3H), 2.31 (s, 3H), 2.03 – 1.95 (m, 1H), 1.78 – 1.66 (m, 2H), 1.42 (s, 9H), 1.01 – 0.94 (m, 1H), 0.83 – 0.75 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.10, 142.64, 135.83, 135.32, 129.19, 128.70, 128.63, 128.47, 125.83, 79.14, 42.10, 38.92, 33.22, 28.55, 27.75, 27.57, 21.14, 15.54.

HRMS (ESI-TOF) Calcd for $C_{19}H_{24}N$ [M-Boc]: 266.1909; found: 266.1909.

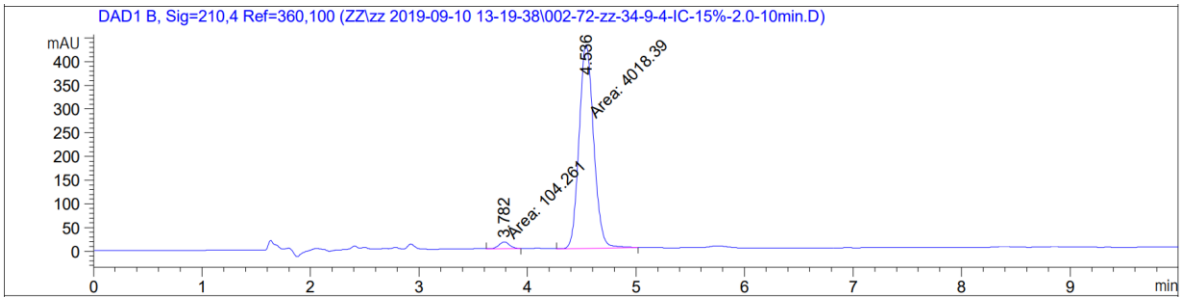
The absolute stereochemistry was assigned by analogy to compound **3t'**.



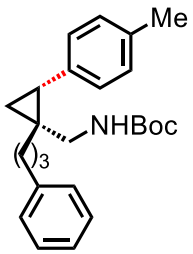


Signal 2: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.780	MM	0.1131	1548.90222	228.16875	48.6759
2	4.545	MM	0.1673	1633.17151	162.74539	51.3241
Totals :				3182.07373	390.91414	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.782	MM	0.1183	104.26067	14.68604	2.5290
2	4.536	MM	0.1559	4018.38794	429.61642	97.4710
Totals :				4122.64861	444.30246	



***tert*-Butyl (((1*R*,2*R*)-1-(3-phenylpropyl)-2-(*p*-tolyl)cyclopropyl)methyl)carbamate (3s')**

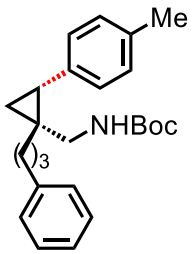
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 28.0 mg, 74% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (15% IPA/CO_2, 2.0 mL/min) with retention time 4.05 min (major) and 4.61 min (minor).

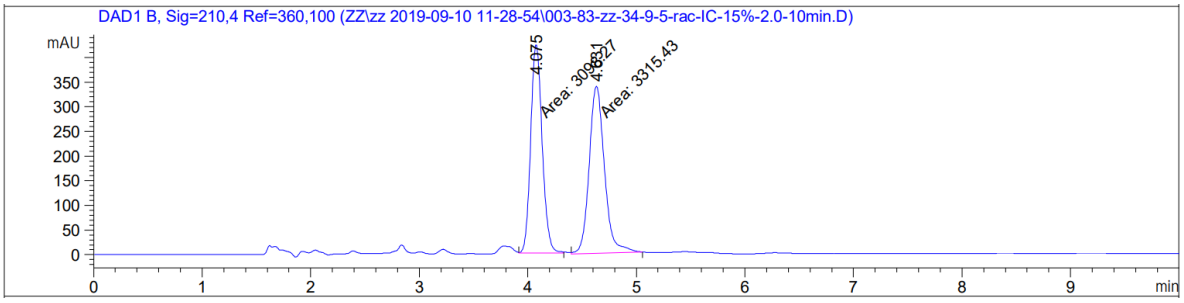
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.06 (s, 4H), 4.19 (br s, 1H), 2.92 (dd, *J* = 14.3, 6.5 Hz, 1H), 2.80 (dd, *J* = 14.3, 4.6 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 1.94 (dd, *J* = 8.3, 6.3 Hz, 1H), 1.91 – 1.76 (m, 2H), 1.54 – 1.47 (m, 1H), 1.46 – 1.40 (m, 1H), 1.39 (s, 9H), 0.95 (t, *J* = 5.6 Hz, 1H), 0.75 (dd, *J* = 8.3, 5.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.00, 142.54, 135.74, 135.44, 129.16, 128.68, 128.56, 128.44, 125.84, 79.03, 42.38, 36.32, 36.14, 28.53, 28.26, 27.48, 21.13, 15.55, 13.30.

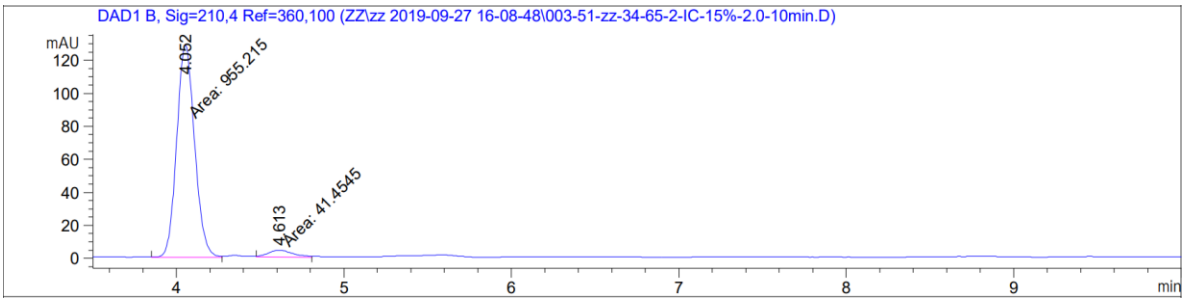
HRMS (ESI-TOF) Calcd for $C_{20}H_{26}N$ [M-Boc]: 280.2065; found: 280.2071.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

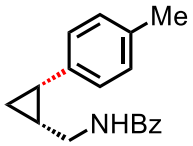




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.075	MM	0.1221	3098.27393	422.95941	48.3071
2	4.631	MM	0.1631	3315.43188	338.89459	51.6929
Totals :				6413.70581	761.85400	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.052	MM	0.1236	955.21539	128.82640	95.8407
2	4.613	MM	0.1698	41.45452	4.06780	4.1593
Totals :				996.66991	132.89420	

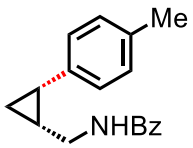


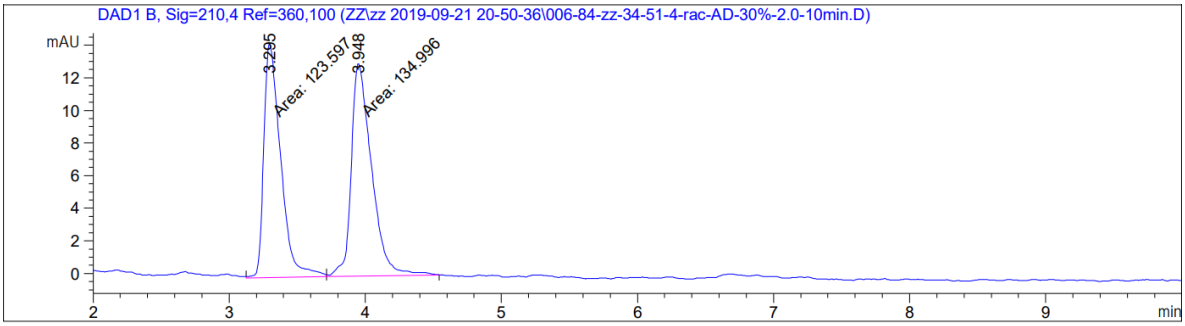
***N*-(((1*R*,2*S*)-2-(*p*-tolyl)cyclopropyl)methyl)benzamide (3t')**

Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 11.0 mg, 42% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (30% IPA/CO_2, 2.0 mL/min) with retention time 3.30 min (major) and 3.97 min (minor).

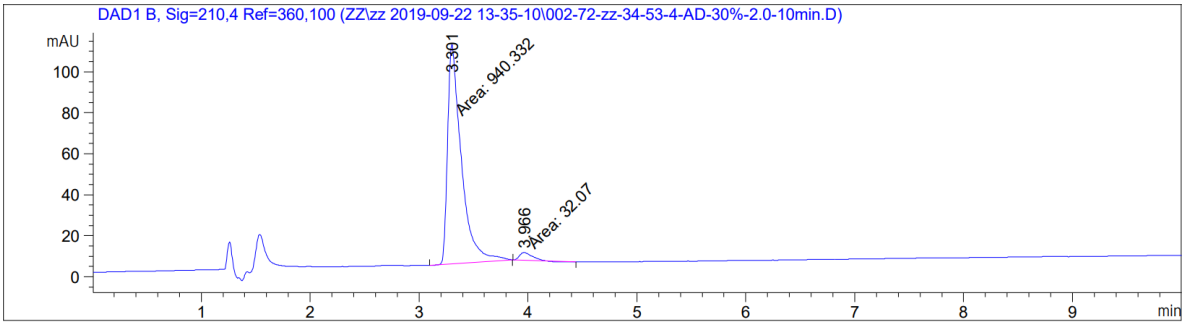
The NMR data matches the reported data[1].

The absolute stereochemistry was assigned by the reported compounds[1,7].



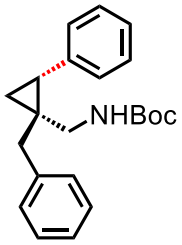


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.295	MM	0.1437	123.59656	14.33376	47.7958
2	3.948	MM	0.1724	134.99648	13.05299	52.2042
Totals :				258.59303	27.38675	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.301	MM	0.1462	940.33191	107.20582	96.7020
2	3.966	MM	0.1384	32.07000	3.86315	3.2980
Totals :				972.40191	111.06897	

Aryl and heteroaryl iodide scope for γ-C(sp^3)–H arylation



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-phenylcyclopropyl)methyl)carbamate (4b')**

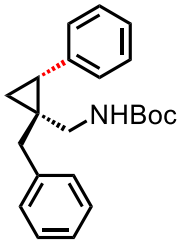
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 24.0 mg, 71% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 5.07 min (minor) and 5.49 min (major).

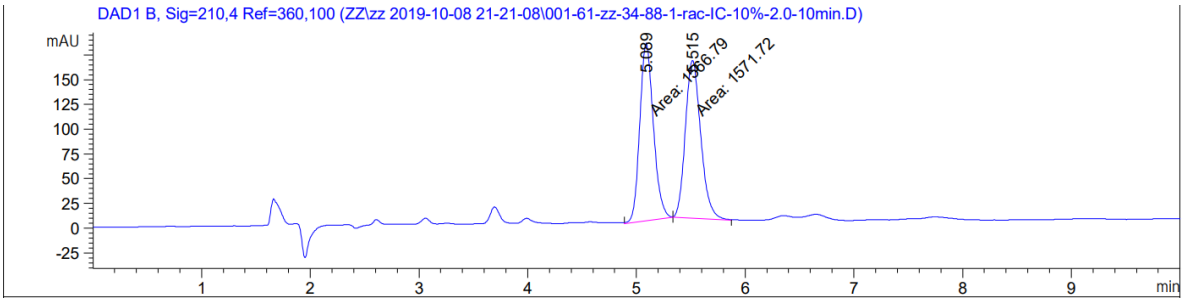
^{1}H NMR (600 MHz, CDCl3) δ 7.35 – 7.32 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.22 (m, 3H), 7.19 – 7.11 (m, 3H), 4.24 (br s, 1H), 2.87 (d, *J* = 16.3 Hz, 2H), 2.83 – 2.77 (m, 1H), 2.74 (d, *J* = 14.0 Hz, 1H), 2.20 (dd, *J* = 8.5, 6.1 Hz, 1H), 1.40 (s, 9H), 1.08 (t, *J* = 5.7 Hz, 1H), 0.99 – 0.93 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.94, 139.26, 138.35, 129.68, 128.81, 128.53, 128.47, 126.57, 126.33, 79.11, 42.85, 41.77, 28.74, 28.53, 28.01, 14.75.

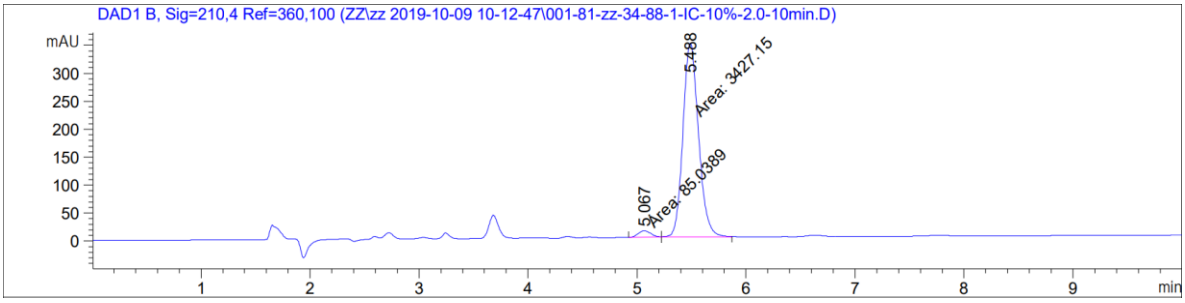
HRMS (ESI-TOF) Calcd for $C_{17}H_{20}N$ [M-Boc]: 238.1596; found: 238.1594.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

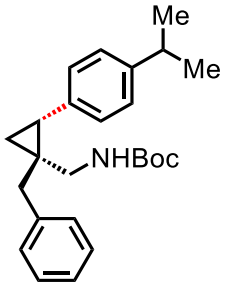




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.089	MM	0.1452	1566.79358	179.87347	49.9215
2	5.515	MM	0.1643	1571.71985	159.44844	50.0785
Totals :				3138.51343	339.32191	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.067	MM	0.1259	85.03890	11.25927	2.4213
2	5.488	MM	0.1649	3427.14990	346.43365	97.5787
Totals :				3512.18880	357.69293	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(4-isopropylphenyl)cyclopropyl)methyl)carbamate (4c')**

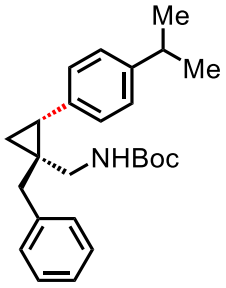
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 23.0 mg, 61% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 5.04 min (minor) and 5.42 min (major).

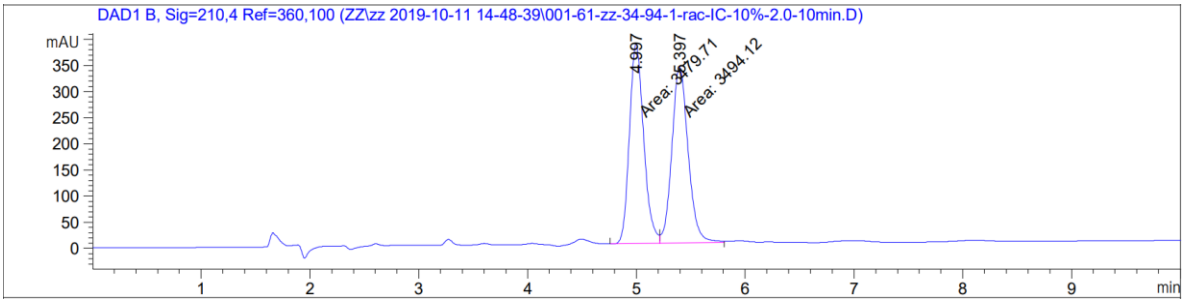
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.29 (br s, 1H), 2.95 – 2.79 (m, 4H), 2.73 (d, *J* = 14.4 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.43 (s, 9H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.08 (t, *J* = 5.7 Hz, 1H), 1.01 – 0.93 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.98, 146.88, 139.39, 135.56, 129.64, 128.75, 128.51, 126.53, 126.51, 79.05, 42.87, 41.86, 33.81, 28.54, 27.77, 24.14, 14.86 (1 carbon signal was not assigned due to overlaps).

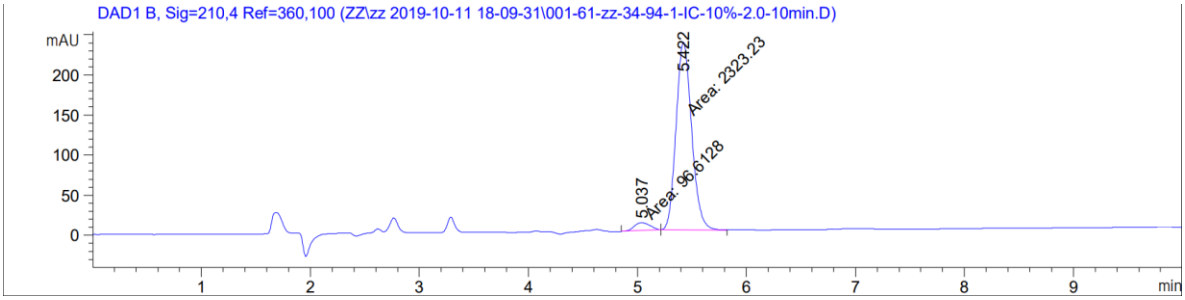
HRMS (ESI-TOF) Calcd for $C_{20}H_{26}N$ [M-Boc]: 280.2065; found: 280.2065.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

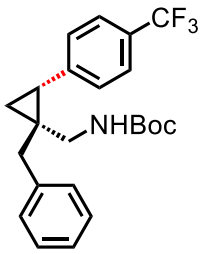




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.997	MF	0.1516	3479.70654	382.59589	49.8967
2	5.397	FM	0.1728	3494.11865	336.95877	50.1033
Totals :				6973.82520	719.55466	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.037	MM	0.1623	96.61280	9.91823	3.9925
2	5.422	MM	0.1653	2323.22974	234.27878	96.0075
Totals :				2419.84254	244.19701	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(4-(trifluoromethyl)phenyl)cyclopropyl)methyl)carbamate (4d')**

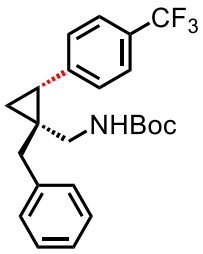
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 29.0 mg, 72% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (5% IPA/CO_2, 2.0 mL/min) with retention time 5.01 min (minor) and 5.91 min (major).

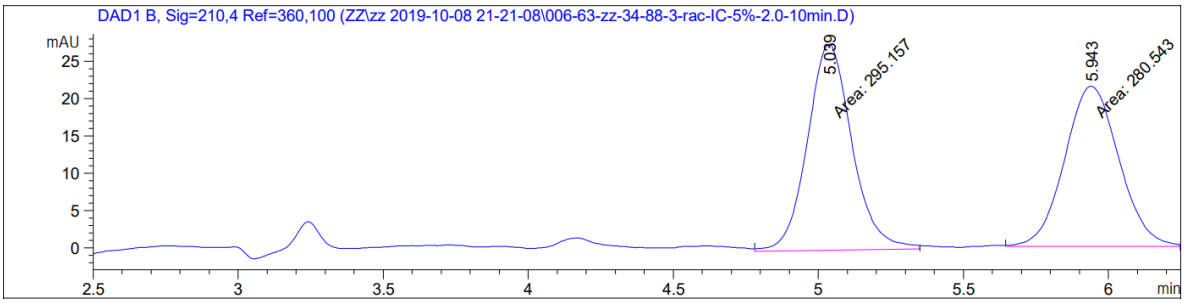
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.27 (br s, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.87 – 2.74 (m, 2H), 2.70 (d, *J* = 14.0 Hz, 1H), 2.28 – 2.18 (m, 1H), 1.40 (s, 9H), 1.17 (t, *J* = 5.3 Hz, 1H), 1.08 – 0.99 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.88, 142.69, 138.89, 129.59, 129.10, 128.66, 126.78, 125.35 (q, *J* = 4.0 Hz), 124.37 (q, *J* = 271.9 Hz), 79.34, 42.72, 41.76, 29.34, 28.49, 27.83, 15.32.

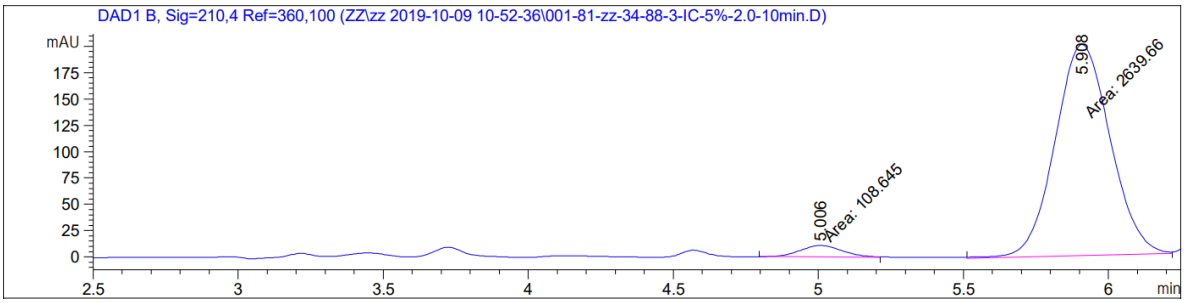
HRMS (ESI-TOF) Calcd for $C_{18}H_{19}F_3N$ [M-Boc]: 306.1470; found: 306.1476.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

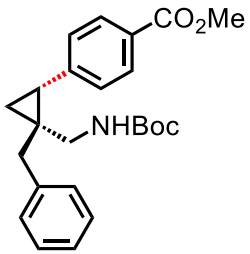




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.039	MM	0.1782	295.15726	27.60513	51.2693
2	5.943	MM	0.2174	280.54254	21.50617	48.7307
Totals :				575.69980	49.11129	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.006	MM	0.1675	108.64465	10.81055	3.9532
2	5.908	MM	0.2195	2639.65869	200.41650	96.0468
Totals :				2748.30334	211.22705	



Methyl 4-((1*R*,2*S*)-2-benzyl-2-(((tert-butoxycarbonyl)amino)methyl)cyclopropyl)benzoate (4e')

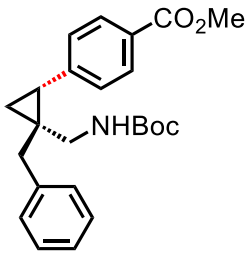
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 18.0 mg, 46% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (20% IPA/CO_2, 2.0 mL/min) with retention time 5.68 min (minor) and 6.42 min (major).

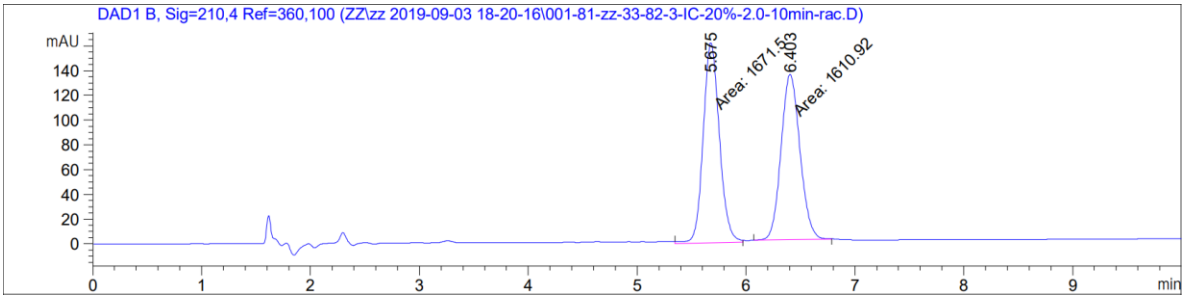
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 7.20 (d, *J* = 8.1 Hz, 2H), 4.22 (br s, 1H), 3.89 (s, 3H), 2.95 – 2.83 (m, 2H), 2.82 – 2.73 (m, 2H), 2.25 – 2.18 (m, 1H), 1.39 (s, 9H), 1.17 (t, *J* = 5.8 Hz, 1H), 1.07 – 0.99 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.09, 155.86, 144.11, 138.89, 129.75, 129.65, 128.73, 128.59, 128.21, 126.71, 79.27, 52.15, 42.69, 41.67, 29.65, 28.49, 28.05, 15.21.

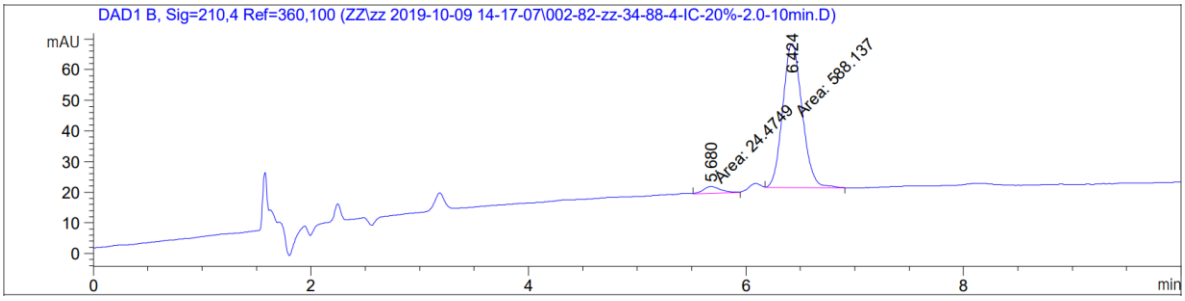
HRMS (ESI-TOF) Calcd for $C_{19}H_{22}NO_2$ [M-Boc]: 296.1651; found: 296.1651.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

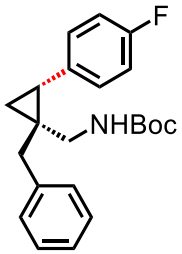




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.675	MM	0.1722	1671.50391	161.78822	50.9228
2	6.403	MM	0.2009	1610.92078	133.61922	49.0772
Totals :				3282.42468	295.40744	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.680	MM	0.1848	24.47491	2.20788	3.9952
2	6.424	MM	0.2081	588.13702	47.11264	96.0048
Totals :				612.61194	49.32052	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(4-fluorophenyl)cyclopropyl)methyl)carbamate (4f')**

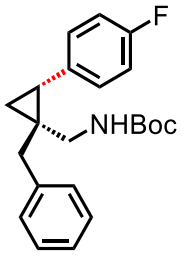
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (toluene/EA) afforded the title compound (colorless oil, 18.0 mg, 51% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 4.36 min (minor) and 4.79 min (major).

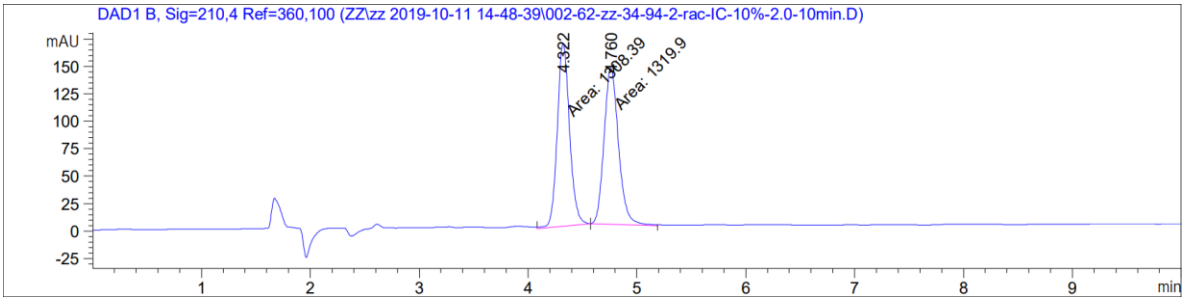
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 7.10 (dd, *J* = 8.0, 5.6 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 4.28 (br s, 1H), 2.92 (d, *J* = 14.2 Hz, 1H), 2.88 – 2.77 (m, 2H), 2.71 (d, *J* = 14.2 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.43 (s, 9H), 1.07 (t, *J* = 5.7 Hz, 1H), 1.03 – 0.95 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.58 (d, *J* = 244.9 Hz), 155.91, 139.18, 134.00, 130.27 (d, *J* = 7.8 Hz), 129.61, 128.59, 126.65, 115.28 (d, *J* = 21.5 Hz), 79.22, 42.86, 41.72, 28.58, 28.52, 27.25, 15.14.

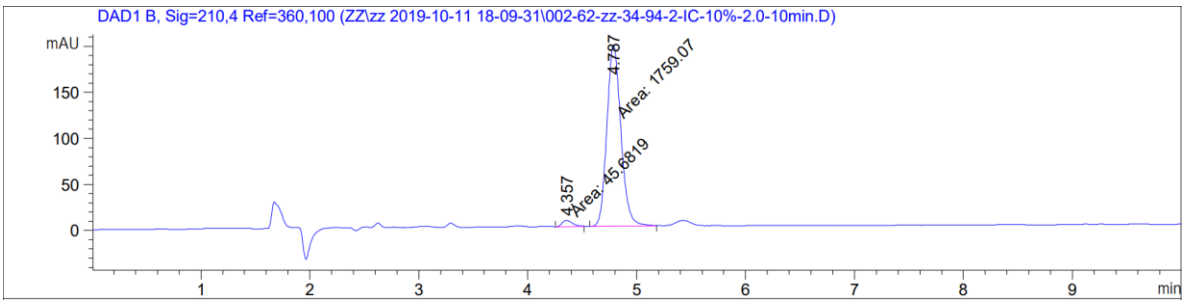
HRMS (ESI-TOF) Calcd for $C_{17}H_{19}FN$ [M-Boc]: 256.1502; found: 256.1503.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

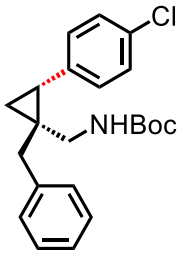




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.322	MM	0.1304	1308.38843	167.28415	49.7810
2	4.760	MM	0.1543	1319.90027	142.57883	50.2190
Totals :				2628.28870	309.86298	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.357	MM	0.1130	45.68194	6.73976	2.5312
2	4.787	MM	0.1490	1759.07227	196.77205	97.4688
Totals :				1804.75421	203.51181	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(4-chlorophenyl)cyclopropyl)methyl)carbamate (4g')**

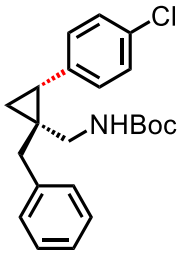
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (toluene/EA) afforded the title compound (colorless oil, 23.0 mg, 62% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 6.11 min (minor) and 6.76 min (major).

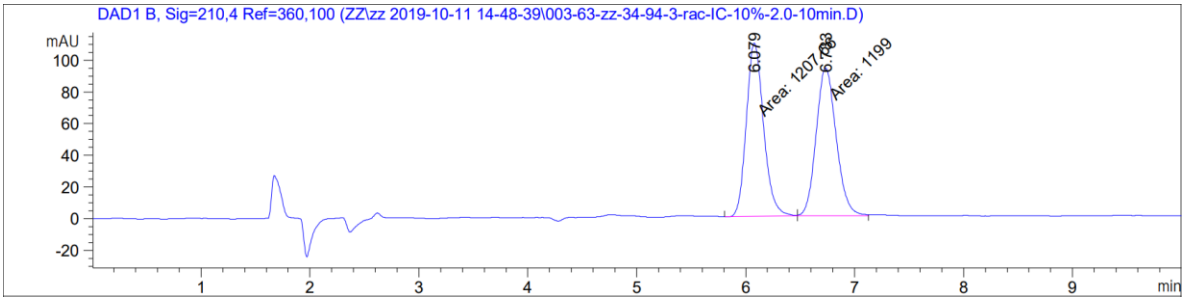
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 4.25 (br s, 1H), 2.89 (d, *J* = 14.1 Hz, 1H), 2.85 – 2.76 (m, 2H), 2.70 (d, *J* = 14.1 Hz, 1H), 2.20 – 2.10 (m, 1H), 1.40 (s, 9H), 1.06 (t, *J* = 5.7 Hz, 1H), 1.03 – 0.93 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.90, 139.05, 136.93, 132.09, 130.15, 129.61, 128.59, 128.57, 126.68, 79.26, 42.79, 41.69, 28.90, 28.52, 27.39, 15.08.

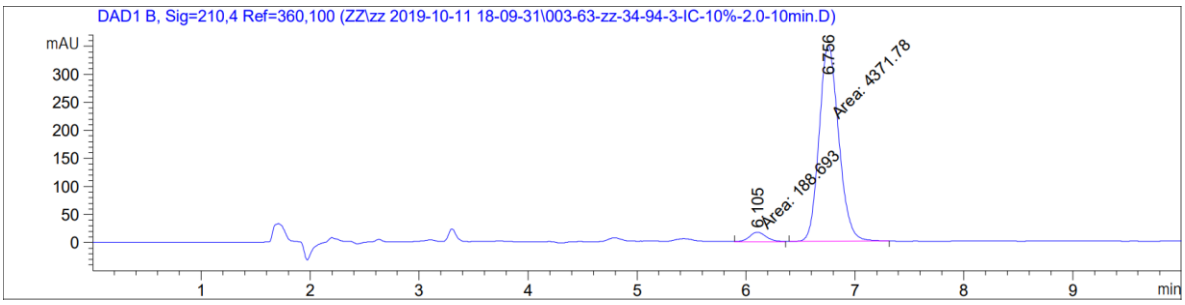
HRMS (ESI-TOF) Calcd for $C_{17}H_{19}ClN$ [M-Boc]: 272.1206; found: 272.1210.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

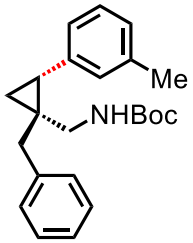




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.079	MM	0.1837	1207.66309	109.54874	50.1799
2	6.733	MM	0.2137	1199.00232	93.50866	49.8201
Totals :				2406.66541	203.05740	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.105	MM	0.1845	188.69276	17.04367	4.1376
2	6.756	MM	0.2082	4371.78076	350.02069	95.8624
Totals :				4560.47353	367.06436	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(*m*-tolyl)cyclopropyl)methyl)carbamate (4h')**

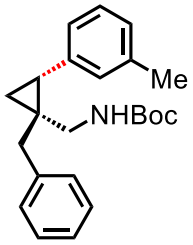
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 24.0 mg, 68% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 5.05 min (minor) and 5.47 min (major).

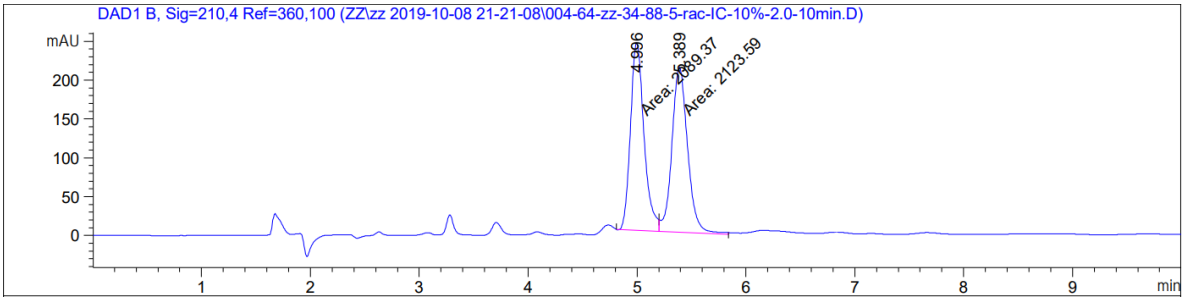
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.03 – 6.88 (m, 3H), 4.24 (br s, 1H), 2.96 – 2.70 (m, 4H), 2.30 (s, 3H), 2.17 – 2.10 (m, 1H), 1.40 (s, 9H), 1.05 (t, *J* = 5.3 Hz, 1H), 0.97 – 0.90 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.94, 139.28, 138.26, 137.99, 129.71, 129.57, 128.49, 128.36, 127.12, 126.53, 125.85, 79.06, 42.93, 41.72, 28.52, 27.87, 21.57, 14.64, 12.98.

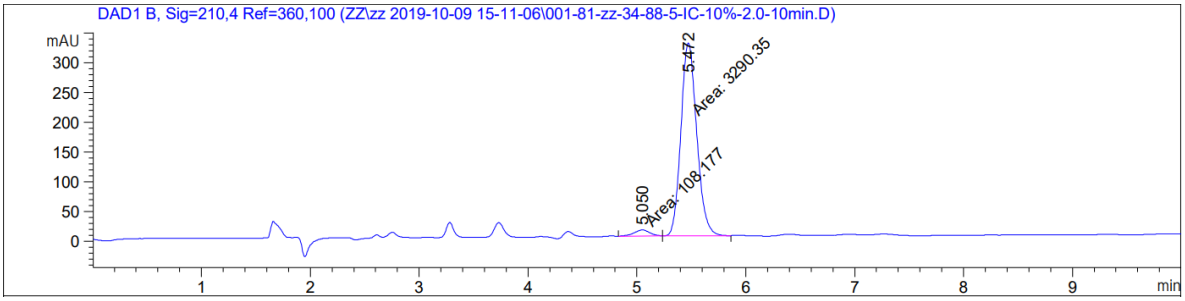
HRMS (ESI-TOF) Calcd for $C_{18}H_{22}N$ [M-Boc]: 252.1752; found: 252.1751.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

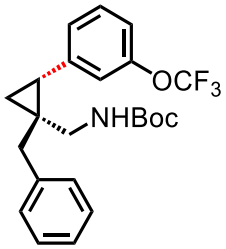




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.996	MF	0.1444	2089.36987	241.22739	49.5939
2	5.389	FM	0.1670	2123.58545	211.95427	50.4061
Totals :				4212.95532	453.18166	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.050	MM	0.1705	108.17698	10.57442	3.1831
2	5.472	MM	0.1688	3290.35205	324.93680	96.8169
Totals :				3398.52903	335.51122	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(3-(trifluoromethoxy)phenyl)cyclopropyl)methyl)carbamate (4i')**

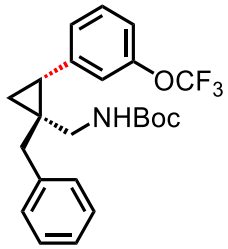
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (toluene/EA) afforded the title compound (colorless oil, 24.0 mg, 57% yield, 94.5:5.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (5% IPA/CO_2, 2.0 mL/min) with retention time 4.52 min (minor) and 5.09 min (major).

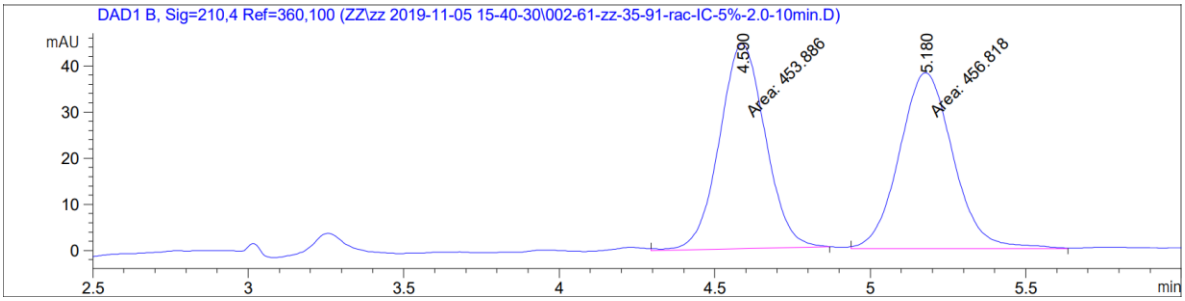
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.23 (m, 4H), 7.12 – 7.01 (m, 2H), 6.99 (s, 1H), 4.25 (br s, 1H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.86 – 2.78 (m, 2H), 2.73 (d, *J* = 14.1 Hz, 1H), 2.24 – 2.15 (m, 1H), 1.40 (s, 9H), 1.12 – 1.05 (m, 1H), 1.05 – 0.98 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.90, 149.40, 140.96, 138.92, 129.77, 129.62, 128.62, 127.08, 126.73, 121.52, 120.58 (q, *J* = 257.3 Hz), 118.79, 79.27, 42.86, 41.56, 29.07, 28.48, 27.60, 15.13.

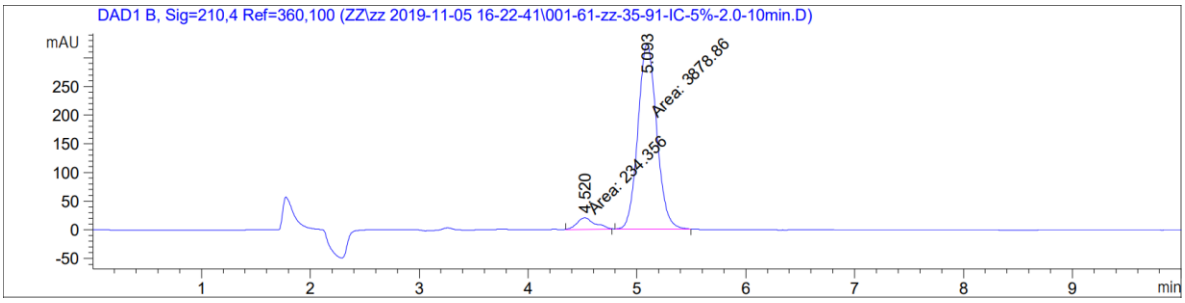
HRMS (ESI-TOF) Calcd for $C_{18}H_{19}F_3NO$ [M-Boc]: 322.1419; found: 322.1425.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

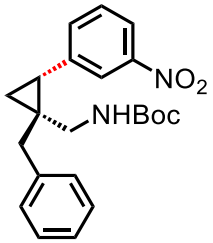




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.590	MM	0.1706	453.88605	44.34946	49.8390
2	5.180	MM	0.2000	456.81824	38.05876	50.1610
Totals :				910.70428	82.40822	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.520	MM	0.1930	234.35570	20.23736	5.6976
2	5.093	MM	0.1999	3878.86377	323.32617	94.3024
Totals :				4113.21947	343.56354	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(3-nitrophenyl)cyclopropyl)methyl)carbamate (4j')**

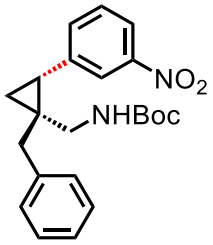
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 19.5 mg, 51% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak OD column (10% IPA/CO_2, 2.0 mL/min) with retention time 7.18 min (minor) and 7.74 min (major).

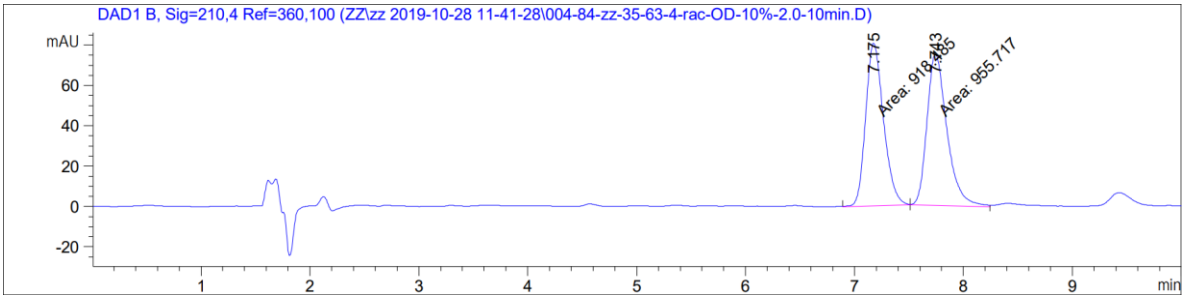
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.51 – 7.39 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 4.31 (br s, 1H), 2.96 (d, *J* = 14.1 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.81 – 2.65 (m, 2H), 2.26 (t, *J* = 7.5 Hz, 1H), 1.39 (s, 9H), 1.21 (t, *J* = 5.7 Hz, 1H), 1.14 – 1.05 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.80, 148.36, 140.75, 138.63, 134.99, 129.57, 129.32, 128.72, 126.89, 123.80, 121.48, 79.43, 42.80, 41.57, 29.34, 28.45, 27.46, 15.43.

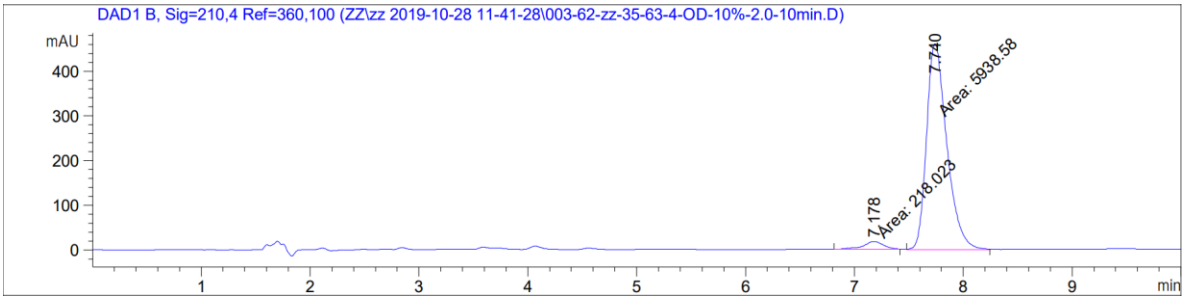
HRMS (ESI-TOF) Calcd for $C_{17}H_{19}N_2O_2$ [M-Boc]: 283.1447; found: 283.1446.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

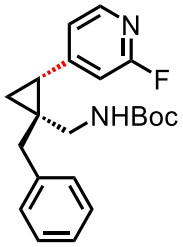




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.175	MM	0.1895	918.48474	80.76911	49.0067
2	7.743	MM	0.2125	955.71667	74.94640	50.9933
Totals :				1874.20142	155.71551	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.178	MM	0.2117	218.02339	17.16334	3.5413
2	7.740	MM	0.2147	5938.57666	461.10233	96.4587
Totals :				6156.60005	478.26567	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2-fluoropyridin-4-yl)cyclopropyl)methyl)carbamate (4k')**

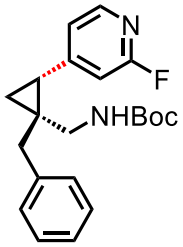
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 15.0 mg, 42% yield, 94.5:5.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 5.08 min (minor) and 5.78 min (major).

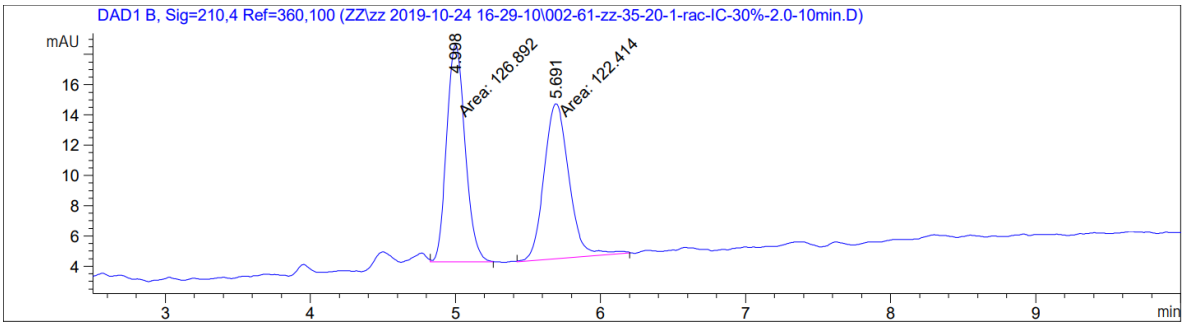
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.23 (m, 3H), 6.94 (d, *J* = 5.3 Hz, 1H), 6.68 (s, 1H), 4.28 (br s, 1H), 2.94 (d, *J* = 13.9 Hz, 1H), 2.91 – 2.80 (m, 2H), 2.73 (d, *J* = 13.9 Hz, 1H), 2.22 – 2.10 (m, 1H), 1.41 (s, 9H), 1.25 – 1.18 (m, 1H), 1.15 – 1.06 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.20 (d, *J* = 238.6 Hz), 155.83, 154.10 (d, *J* = 7.0 Hz), 147.45 (d, *J* = 15.8 Hz), 138.37, 129.55, 128.77, 126.98, 121.78, 109.36 (d, *J* = 37.1 Hz), 79.57, 42.40, 41.66, 30.53, 28.48, 27.25 (d, *J* = 3.2 Hz), 15.75.

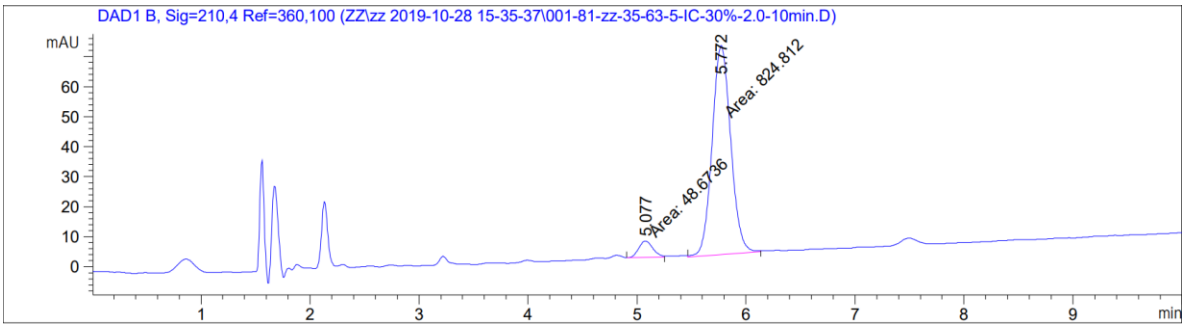
HRMS (ESI-TOF) Calcd for $C_{21}H_{26}FN_2O_2$ [M+H]: 357.1978; found: 357.1982.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

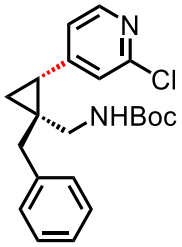




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.998	MM	0.1476	126.89172	14.33001	50.8980
2	5.691	MM	0.1990	122.41425	10.25482	49.1020
Totals :				249.30598	24.58482	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.077	MM	0.1482	48.67357	5.47288	5.5723
2	5.772	MM	0.1975	824.81219	69.59493	94.4277
Totals :				873.48577	75.06781	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2-chloropyridin-4-yl)cyclopropyl)methyl)carbamate (4l')**

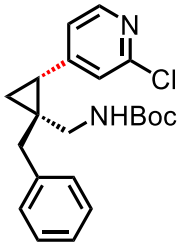
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 17.0 mg, 46% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 6.03 min (minor) and 6.45 min (major).

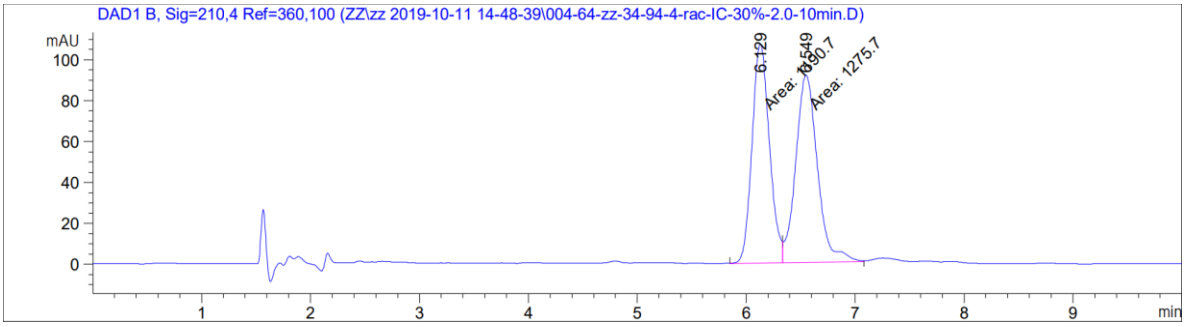
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 5.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.10 (s, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 4.27 (br s, 1H), 2.93 (d, *J* = 14.3 Hz, 1H), 2.90 – 2.79 (m, 2H), 2.74 (d, *J* = 14.3 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.41 (s, 9H), 1.24 – 1.19 (m, 1H), 1.08 (dd, *J* = 8.0, 5.7 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.82, 151.84, 151.55, 149.48, 138.31, 129.56, 128.77, 126.99, 124.38, 122.70, 79.59, 42.48, 41.61, 30.52, 28.49, 27.02, 15.60.

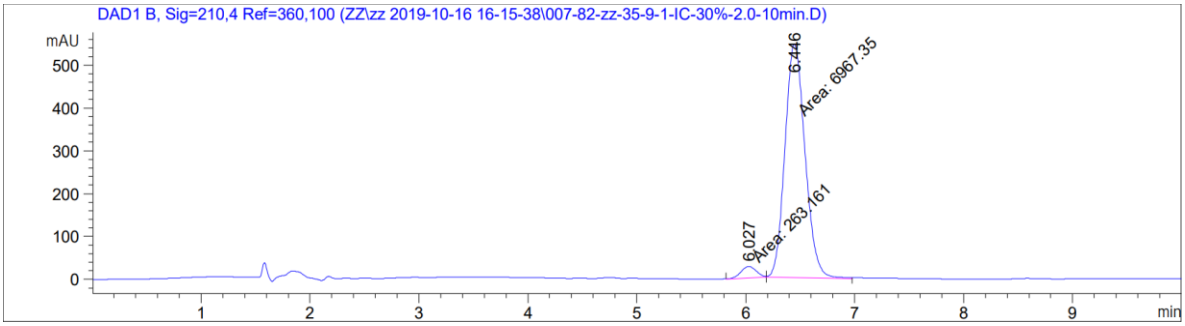
HRMS (ESI-TOF) Calcd for $C_{21}H_{26}ClN_2O_2$ [M+H]: 373.1683; found: 373.1683.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

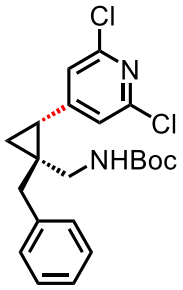




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.129	MF	0.1850	1190.70093	107.24229	48.2769
2	6.549	FM	0.2321	1275.69580	91.60175	51.7231
Totals :				2466.39673	198.84405	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.027	MM	0.1634	263.16058	26.84538	3.6396
2	6.446	MM	0.2130	6967.35352	545.22614	96.3604
Totals :				7230.51410	572.07152	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2,6-dichloropyridin-4-yl)cyclopropyl)methyl)carbamate (4m')**

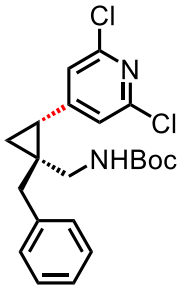
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 15.0 mg, 37% yield, 95.5:4.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 3.68 min (minor) and 4.18 min (major).

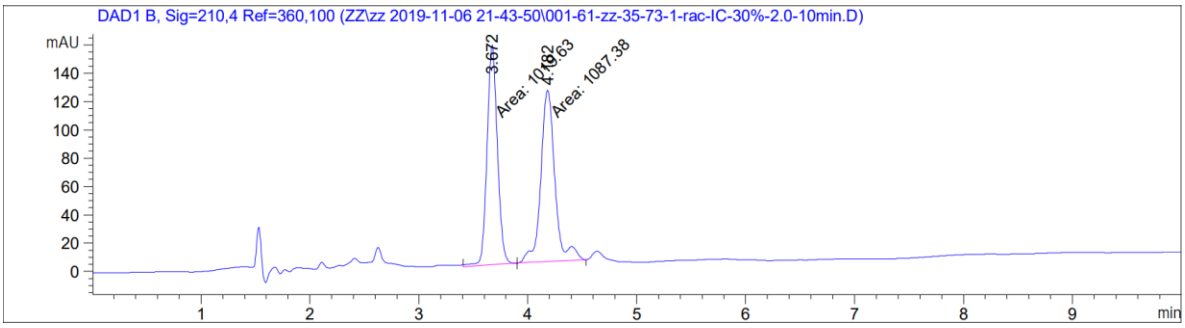
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.01 (s, 2H), 4.30 (br s, 1H), 2.98 – 2.88 (m, 2H), 2.88 – 2.79 (m, 1H), 2.74 (d, *J* = 14.1 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.42 (s, 9H), 1.23 – 1.18 (m, 1H), 1.13 – 1.08 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.76, 154.29, 150.66, 138.02, 129.55, 128.84, 127.11, 123.00, 79.72, 42.54, 41.47, 30.96, 28.48, 26.74, 15.91.

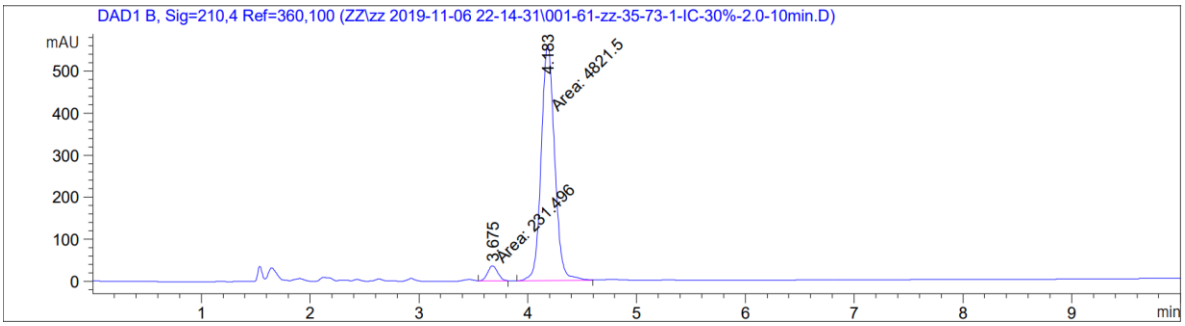
HRMS (ESI-TOF) Calcd for $C_{21}H_{25}Cl_2N_2O_2$ [M+H]: 407.1293; found: 407.1297.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

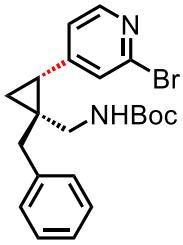




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.672	MM	0.1097	1019.62524	154.89294	48.3923
2	4.182	MM	0.1496	1087.37549	121.10316	51.6077
Totals :				2107.00073	275.99610	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.675	MM	0.1073	231.49638	35.95980	4.5814
2	4.183	MM	0.1433	4821.50049	560.74500	95.4186
Totals :				5052.99687	596.70480	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2-bromopyridin-4-yl)cyclopropyl)methyl)carbamate (4n')**

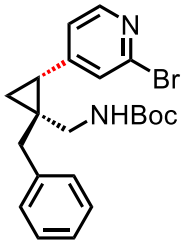
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 17.0 mg, 41% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 6.71 min (minor) and 7.14 min (major).

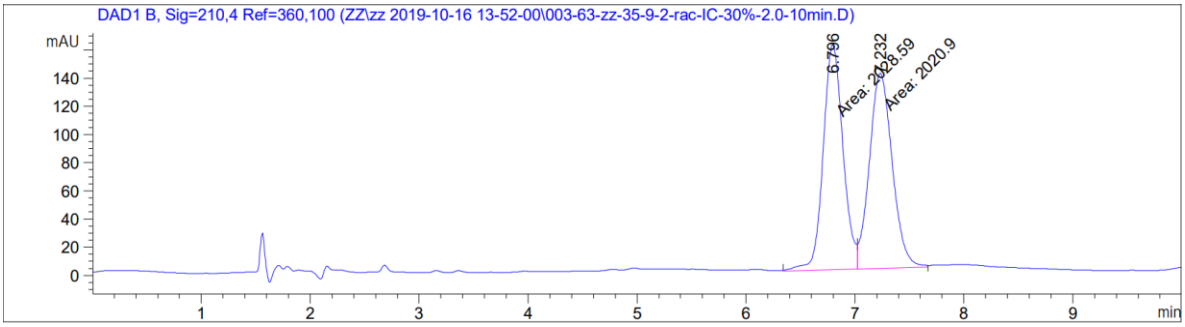
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30 – 7.23 (m, 4H), 6.99 (d, *J* = 4.6 Hz, 1H), 4.28 (br s, 1H), 2.92 (d, *J* = 14.2 Hz, 1H), 2.88 – 2.78 (m, 2H), 2.74 (d, *J* = 14.2 Hz, 1H), 2.08 (t, *J* = 7.0 Hz, 1H), 1.41 (s, 9H), 1.23 – 1.18 (m, 1H), 1.10 – 1.04 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.82, 151.31, 149.87, 142.59, 138.28, 129.56, 128.77, 128.19, 126.99, 123.05, 79.59, 42.49, 41.58, 30.54, 28.49, 26.90, 15.59.

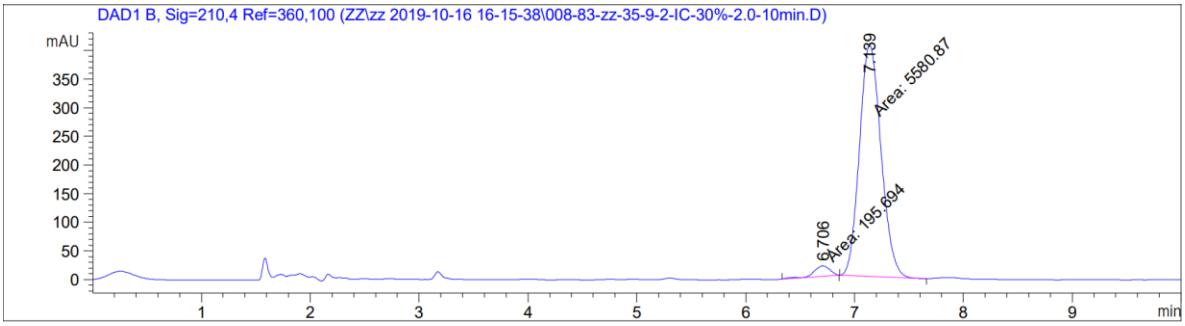
HRMS (ESI-TOF) Calcd for $C_{21}H_{26}BrN_2O_2$ [M+H]: 417.1178; found: 417.1171.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

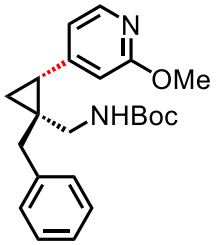




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.796	MF	0.2115	2028.59497	159.85562	50.0950
2	7.232	FM	0.2431	2020.90076	138.55829	49.9050
Totals :				4049.49573	298.41391	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.706	MM	0.1766	195.69365	18.46432	3.3877
2	7.139	MM	0.2296	5580.86768	405.10892	96.6123
Totals :				5776.56133	423.57323	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2-methoxypyridin-4-yl)cyclopropyl)methyl)carbamate (4o')**

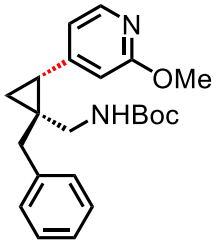
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 16.0 mg, 43% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak OD column (10% IPA/CO_2, 2.0 mL/min) with retention time 6.21 min (major) and 6.71 min (minor).

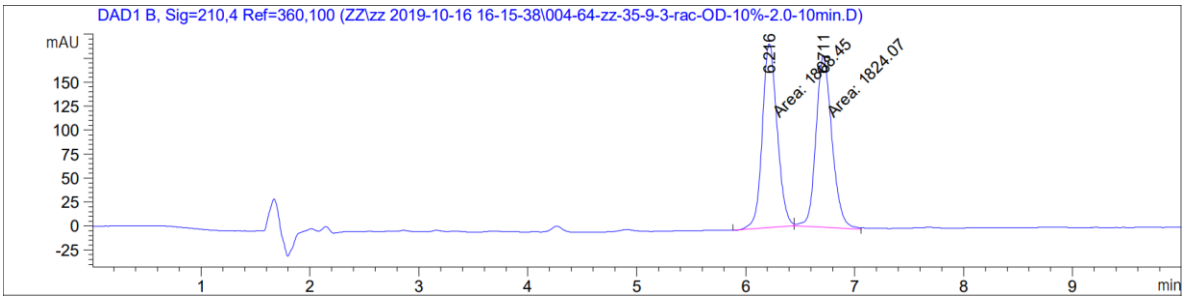
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H), 6.66 (d, *J* = 5.3 Hz, 1H), 6.49 (s, 1H), 4.24 (br s, 1H), 3.90 (s, 3H), 2.94 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.89 (d, *J* = 14.1 Hz, 1H), 2.85 – 2.78 (m, 1H), 2.74 (d, *J* = 14.1 Hz, 1H), 2.08 (t, *J* = 7.3 Hz, 1H), 1.40 (s, 9H), 1.13 (t, *J* = 5.9 Hz, 1H), 1.04 – 0.97 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.60, 155.87, 150.67, 146.71, 138.67, 129.64, 128.65, 126.79, 117.69, 110.47, 79.36, 53.48, 42.52, 41.61, 29.82, 28.50, 27.21, 15.07.

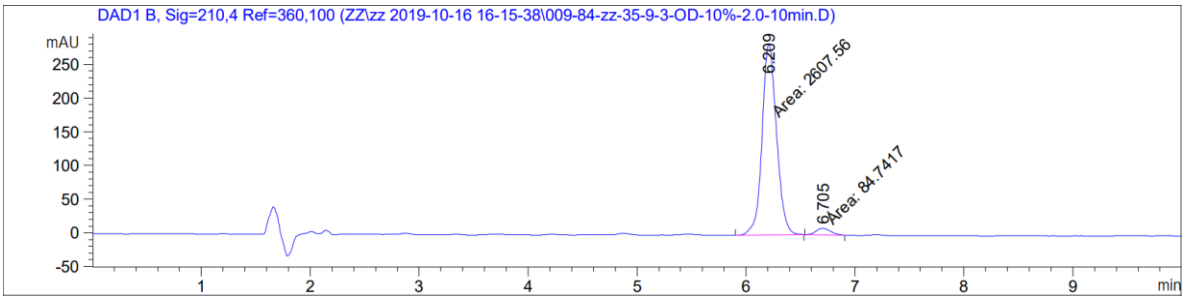
HRMS (ESI-TOF) Calcd for $C_{22}H_{29}N_2O_3$ [M+H]: 369.2178; found: 369.2172.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

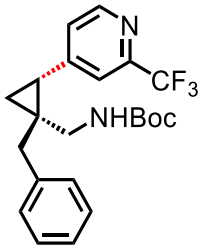




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.216	MM	0.1573	1808.44653	191.67393	49.7849
2	6.711	MM	0.1708	1824.07288	178.02965	50.2151
Totals :				3632.51941	369.70358	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.209	MM	0.1534	2607.56250	283.32437	96.8524
2	6.705	MM	0.1476	84.74171	9.57119	3.1476
Totals :				2692.30421	292.89556	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(2-(trifluoromethyl)pyridin-4-yl)cyclopropyl)methyl)carbamate (4p')**

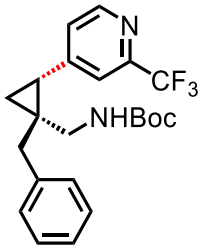
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 16.0 mg, 39% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 6.23 min (minor) and 7.44 min (major).

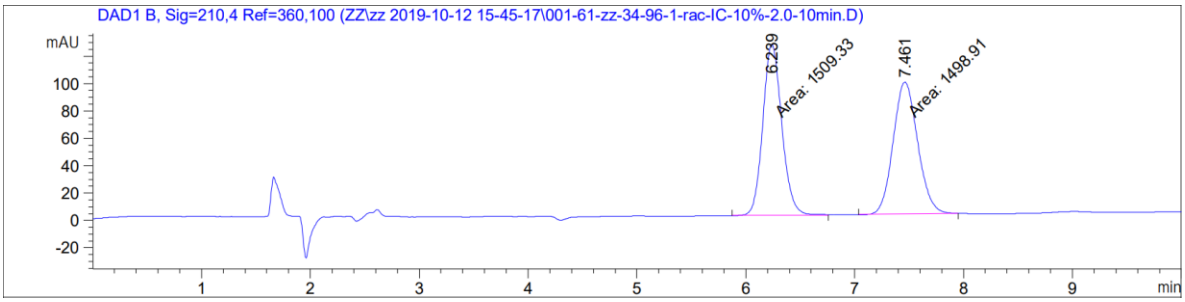
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.1 Hz, 1H), 7.45 (s, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.22 (d, *J* = 4.9 Hz, 1H), 4.27 (br s, 1H), 2.96 (d, *J* = 14.1 Hz, 1H), 2.92 – 2.85 (m, 1H), 2.85 – 2.78 (m, 1H), 2.76 (d, *J* = 14.1 Hz, 1H), 2.26 – 2.12 (m, 1H), 1.39 (s, 9H), 1.32 – 1.27 (m, 1H), 1.18 – 1.11 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.79, 150.23, 149.94, 148.29 (q, *J* = 33.9 Hz), 138.26, 129.53, 128.81, 127.06, 126.23, 121.69 (q, *J* = 274.4 Hz), 120.93, 79.62, 42.44, 41.71, 30.74, 28.45, 27.31, 15.80.

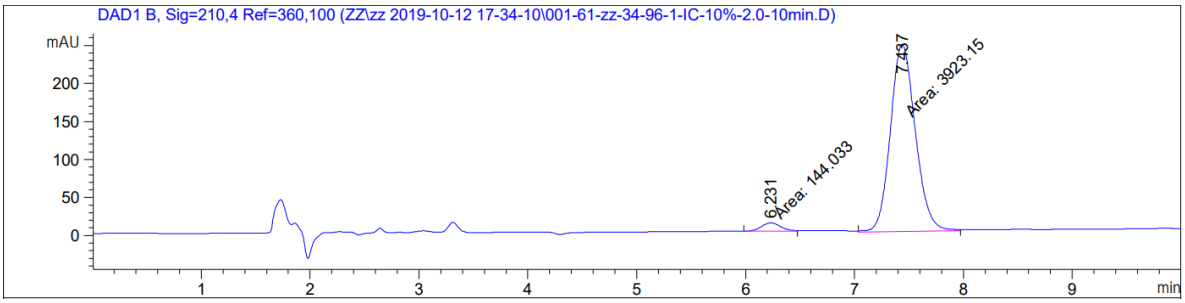
HRMS (ESI-TOF) Calcd for $C_{22}H_{26}F_3N_2O_2$ [M+H]: 407.1946; found: 407.1941.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

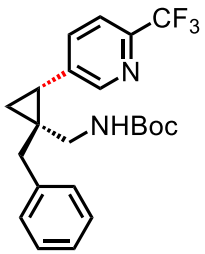




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.239	MM	0.2011	1509.33435	125.11450	50.1733
2	7.461	MM	0.2597	1498.90588	96.18461	49.8267
Totals :				3008.24023	221.29911	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.231	MM	0.2137	144.03255	11.23383	3.5413
2	7.437	MM	0.2651	3923.14771	246.62218	96.4587
Totals :				4067.18025	257.85601	



***tert*-Butyl (((1*S*,2*S*)-1-benzyl-2-(6-(trifluoromethyl)pyridin-3-yl)cyclopropyl)methyl)carbamate (4q')**

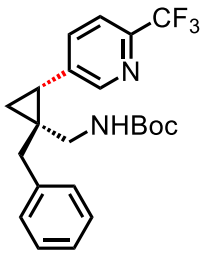
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 21.0 mg, 52% yield, 95.5:4.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (20% IPA/CO_2, 2.0 mL/min) with retention time 3.07 min (minor) and 6.06 min (major).

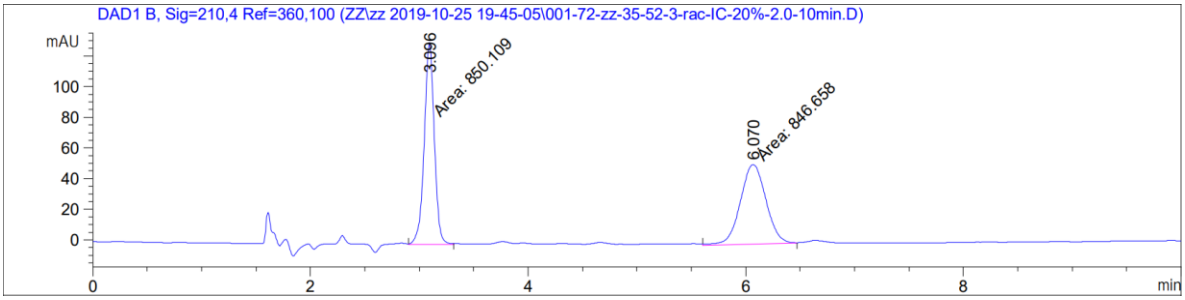
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.57 (s, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.22 (m, 3H), 4.34 (br s, 1H), 3.00 (d, *J* = 14.3 Hz, 1H), 2.86 (dd, *J* = 14.9, 4.8 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.24 (t, *J* = 7.5 Hz, 1H), 1.39 (s, 9H), 1.29 – 1.24 (m, 1H), 1.18 – 1.10 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.86, 155.82, 151.08, 146.11 (q, *J* = 35.4 Hz), 138.53, 136.81, 129.44, 128.83, 127.02, 121.79 (q, *J* = 274.1 Hz), 120.12, 79.58, 42.52, 41.80, 29.83, 28.47, 25.35, 15.54.

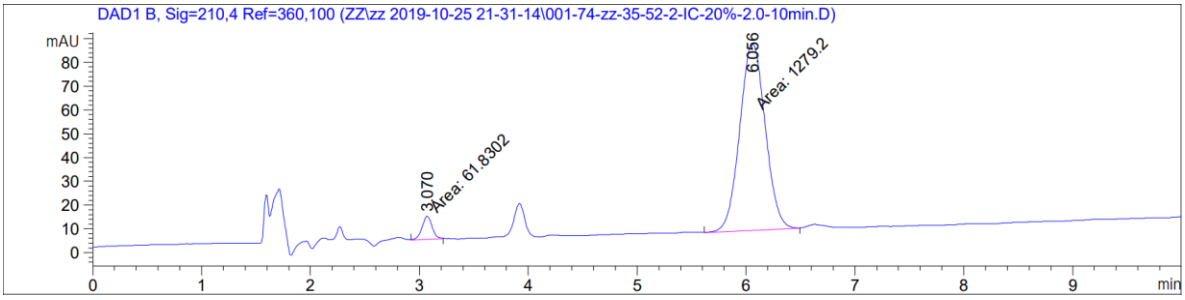
HRMS (ESI-TOF) Calcd for $C_{22}H_{26}F_3N_2O_2$ [M+H]: 407.1946; found: 407.1937.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

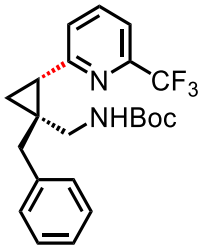




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.096	MM	0.1077	850.10938	131.57498	50.1017
2	6.070	MM	0.2719	846.65778	51.89341	49.8983
Totals :				1696.76715	183.46839	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.070	MM	0.1059	61.83019	9.73213	4.6107
2	6.056	MM	0.2704	1279.19604	78.84225	95.3893
Totals :				1341.02624	88.57438	



***tert*-Butyl (((1*S*,2*S*)-1-benzyl-2-(6-(trifluoromethyl)pyridin-2-yl)cyclopropyl)methyl)carbamate (4r')**

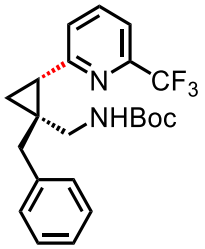
Following **General Procedure A** on 0.1 mmol scale by using $Pd(OAc)_2$ (15 mol%, 3.4 mg) and ligand **L6** (15 mol%, 3.6 mg). Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 25.0 mg, 62% yield, 97.5:2.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 3.72 min (major) and 4.07 min (minor).

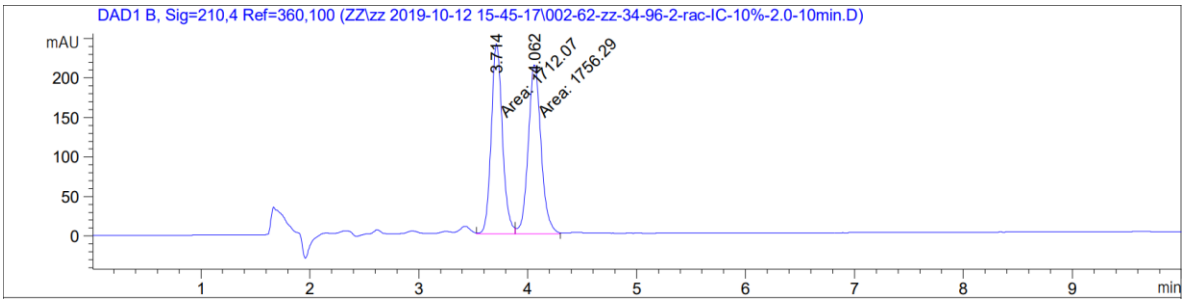
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.29 – 7.22 (m, 2H), 4.97 (br s, 1H), 3.39 (dd, *J* = 14.1, 7.4 Hz, 1H), 3.04 (d, *J* = 14.2 Hz, 1H), 2.81 (d, *J* = 14.2 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.30 – 2.21 (m, 1H), 1.44 (s, 9H), 1.37 – 1.32 (m, 1H), 1.21 – 1.14 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.60, 156.08, 147.55 (q, *J* = 34.3 Hz), 138.69, 137.63, 129.83, 128.51, 126.96, 126.62, 121.60 (q, *J* = 274.5 Hz), 117.77, 78.95, 42.18, 41.60, 30.93, 29.26, 28.50, 16.55.

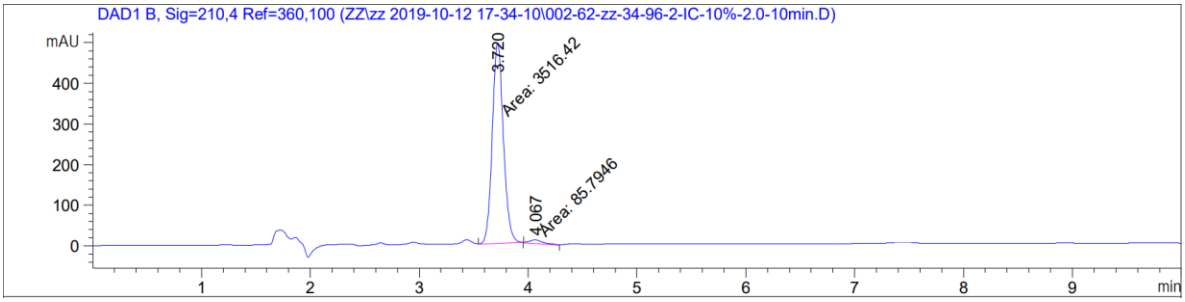
HRMS (ESI-TOF) Calcd for $C_{22}H_{26}F_3N_2O_2$ [M+H]: 407.1946; found: 407.1942.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

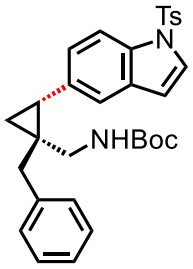




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.714	MF	0.1187	1712.06738	240.47415	49.3624
2	4.062	FM	0.1366	1756.29358	214.35849	50.6376
Totals :				3468.36096	454.83264	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.720	MM	0.1186	3516.42432	494.18491	97.6183
2	4.067	MM	0.1591	85.79463	8.98958	2.3817
Totals :				3602.21895	503.17449	



***tert*-Butyl (((1*S*,2*R*)-1-benzyl-2-(1-tosyl-1*H*-indol-5-yl)cyclopropyl)methyl)carbamate (4s')**

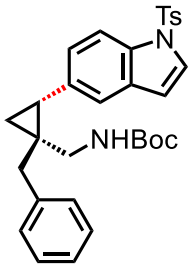
Following **General Procedure A** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 27.0 mg, 51% yield, 96.5:3.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 8.82 min (minor) and 9.30 min (major).

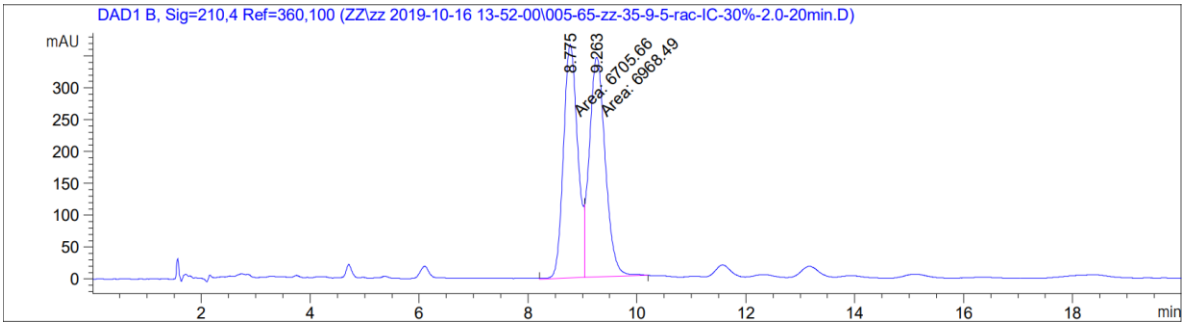
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 3.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.19 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 3.5 Hz, 1H), 4.24 (br s, 1H), 2.91 (d, *J* = 15.0 Hz, 1H), 2.86 – 2.77 (m, 1H), 2.76 – 2.63 (m, 2H), 2.33 (s, 3H), 2.25 (dd, *J* = 8.6, 6.0 Hz, 1H), 1.38 (s, 9H), 1.07 (t, *J* = 6.0 Hz, 1H), 1.00 – 0.94 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.93, 145.01, 139.28, 135.43, 133.56, 133.44, 131.04, 130.05, 129.65, 128.54, 126.92, 126.70, 126.59, 126.02, 121.08, 113.37, 108.98, 79.14, 42.98, 41.70, 28.58, 28.50, 27.85, 21.71, 15.08.

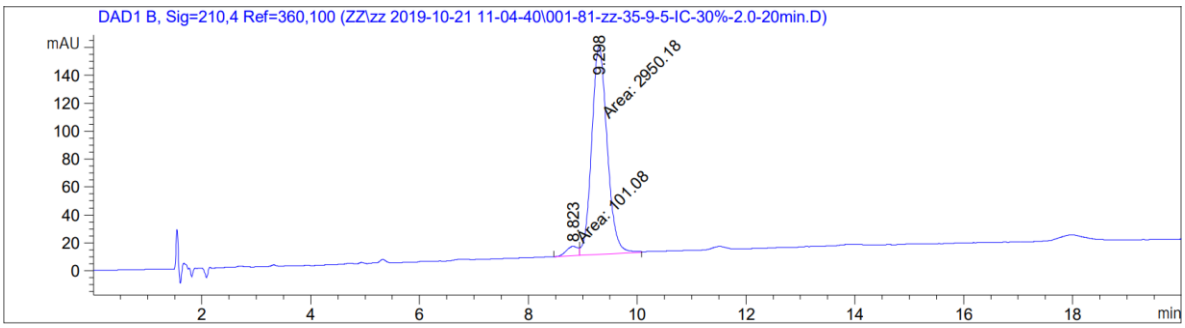
HRMS (ESI-TOF) Calcd for $C_{26}H_{27}N_2O_2S$ [M-Boc]: 431.1793; found: 431.1783.

The absolute stereochemistry was assigned by analogy to compound **3t'**.



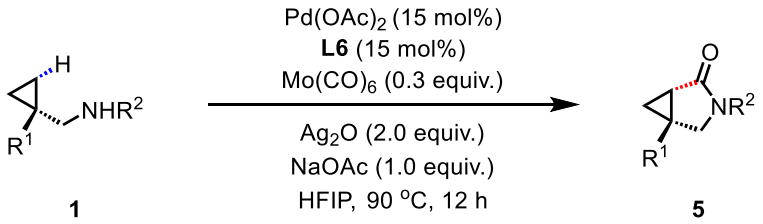


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.775	MF	0.3051	6705.65674	366.36597	49.0389
2	9.263	FM	0.3367	6968.49170	344.98260	50.9611
Totals :				1.36741e4	711.34857	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.823	MF	0.2490	101.08009	6.76690	3.3127
2	9.298	FM	0.3301	2950.18140	148.94737	96.6873
Totals :				3051.26149	155.71427	

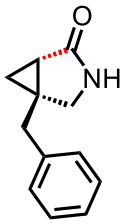
General procedure for γ-C(sp^3)–H carbonylation



1 **5**

General Procedure B: In the culture tube, $Pd(OAc)_2$ (15 mol%, 3.4 mg), ligand **L6** (15 mol%, 3.6 mg), $Mo(CO)_6$ (0.3 equiv., 7.9 mg), Ag_2O (2.0 equiv., 46.3 mg), NaOAc (1.0 equiv., 8.2 mg), and free aliphatic amine **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (0.1 mL) were added. The reaction mixture was stirred at rt for 3 min, and then heated to 90 ^oC for 12 h (150 rpm). After being allowed to cool to room temperature, the mixture was diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. The crude mixture was purified by pTLC (hexane/EA) to afford the corresponding γ-lactam product.

Substrate scope for γ-C(sp^3)–H carbonylation



(1*S*,5*S*)-5-Benzyl-3-azabicyclo[3.1.0]hexan-2-one (5a)

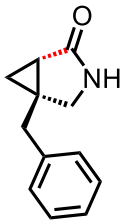
Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 8.5 mg, 45% yield, 89.5:10.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (20% IPA/CO_2, 2.0 mL/min) with retention time 3.78 min (minor) and 4.14 min (major).

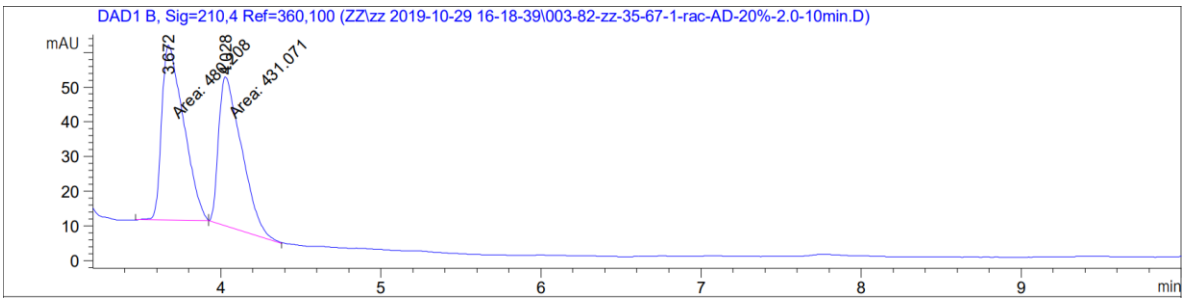
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.14 (m, 2H), 5.18 (br s, 1H), 3.33 (d, *J* = 9.9 Hz, 1H), 3.27 (d, *J* = 9.9 Hz, 1H), 3.00 (d, *J* = 14.6 Hz, 1H), 2.84 (d, *J* = 14.6 Hz, 1H), 1.79 – 1.71 (m, 1H), 1.19 (dd, *J* = 8.8, 4.6 Hz, 1H), 0.95 – 0.89 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 178.47, 138.13, 129.00, 128.77, 126.92, 47.61, 39.34, 27.82, 24.68, 18.38.

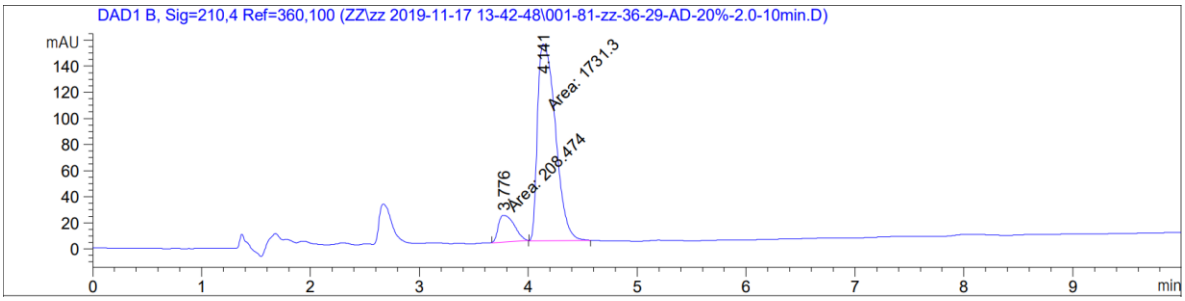
HRMS (ESI-TOF) Calcd for $C_{12}H_{14}NO$ [M+H]: 188.1075; found: 188.1078.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

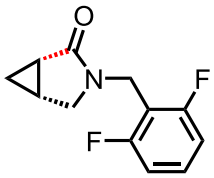




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.672	MM	0.1586	480.20758	50.45845	52.6960
2	4.028	MM	0.1673	431.07092	42.94436	47.3040
Totals :				911.27850	93.40281	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.776	MM	0.1696	208.47360	20.48741	10.7473
2	4.141	MM	0.1912	1731.30469	150.88240	89.2527
Totals :				1939.77829	171.36981	



(1*S*,5*R*)-3-(2,6-Difluorobenzyl)-3-azabicyclo[3.1.0]hexan-2-one (5b)

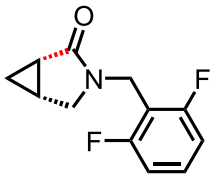
Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 10.0 mg, 45% yield, 95:5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 8.36 min (major) and 9.71 min (minor).

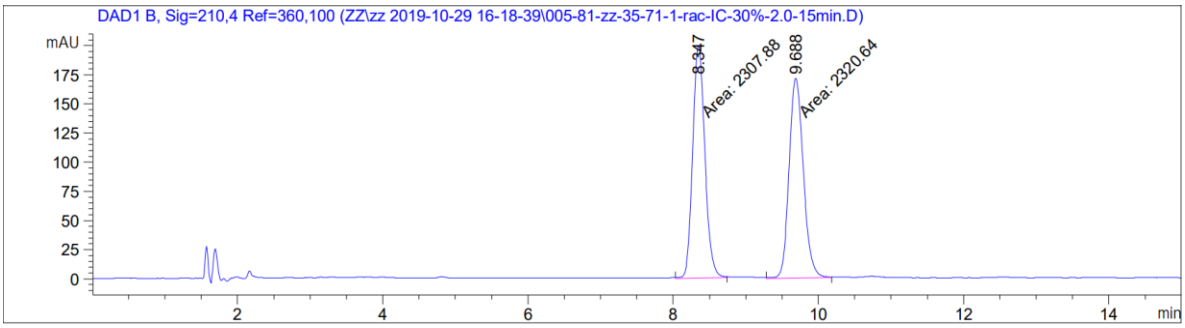
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 6.95 – 6.87 (m, 2H), 4.57 (d, *J* = 14.4 Hz, 1H), 4.45 (d, *J* = 14.4 Hz, 1H), 3.42 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.19 (d, *J* = 10.4 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.85 – 1.77 (m, 1H), 1.08 (td, *J* = 7.9, 4.7 Hz, 1H), 0.58 – 0.51 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.47, 161.82 (dd, *J* = 249.9, 7.8 Hz), 129.88 (t, *J* = 10.3 Hz), 112.26 (t, *J* = 19.4 Hz), 111.52 (dd, *J* = 20.9, 5.0 Hz), 48.45, 33.72 (t, *J* = 3.8 Hz), 20.12, 12.64, 11.78.

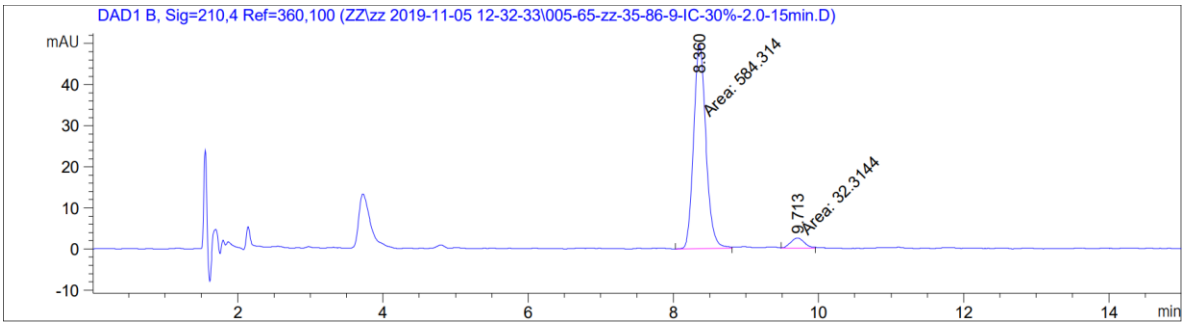
HRMS (ESI-TOF) Calcd for $C_{12}H_{12}F_2NO$ [M+H]: 224.0887; found: 224.0890.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

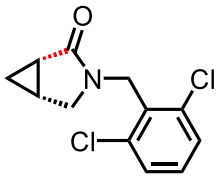




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.347	MM	0.1930	2307.88403	199.32324	49.8622
2	9.688	MM	0.2259	2320.64453	171.25166	50.1378
Totals :				4628.52856	370.57491	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.360	MM	0.1962	584.31390	49.63335	94.7595
2	9.713	MM	0.2186	32.31441	2.46343	5.2405
Totals :				616.62831	52.09679	



(1*S*,5*R*)-3-(2,6-Dichlorobenzyl)-3-azabicyclo[3.1.0]hexan-2-one (5c)

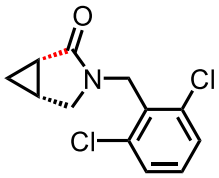
Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 11.0 mg, 43% yield, 97:3 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AS column (20% IPA/CO_2, 2.0 mL/min) with retention time 6.30 min (minor) and 7.25 min (major).

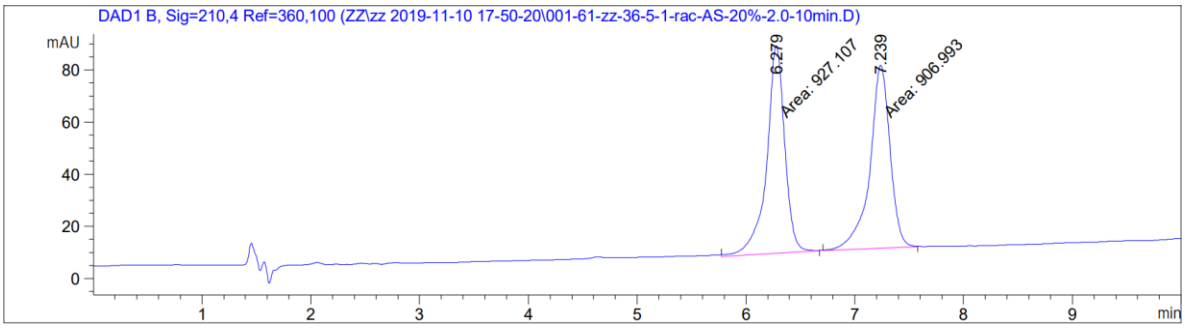
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 4.85 (d, *J* = 14.1 Hz, 1H), 4.56 (d, *J* = 14.1 Hz, 1H), 3.36 (dd, *J* = 10.2, 5.9 Hz, 1H), 2.98 (dd, *J* = 10.2, 1.7 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.82 – 1.70 (m, 1H), 1.04 (td, *J* = 8.0, 4.6 Hz, 1H), 0.60 – 0.51 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.36, 136.66, 131.78, 129.81, 128.62, 47.75, 41.33, 20.16, 12.61, 11.79.

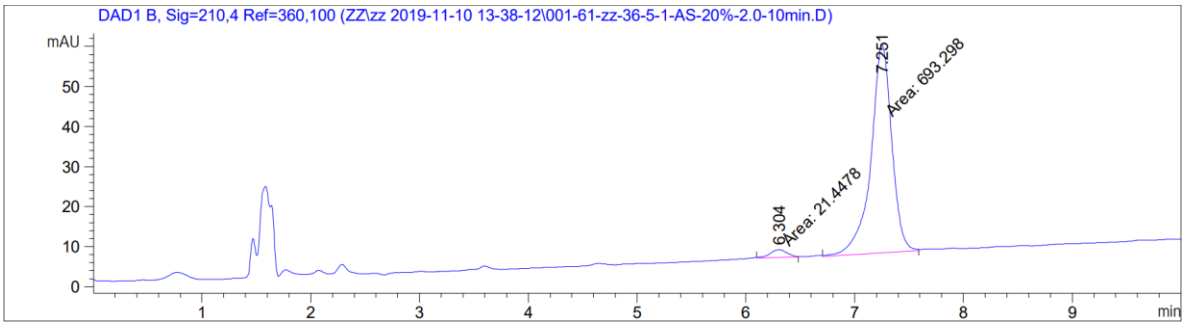
HRMS (ESI-TOF) Calcd for $C_{12}H_{12}Cl_2NO$ [M+H]: 256.0296; found: 256.0299.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

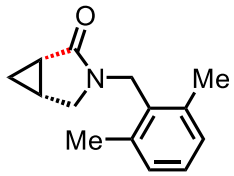




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.279	MM	0.1935	927.10669	79.84350	50.5483
2	7.239	MM	0.2150	906.99304	70.30294	49.4517
Totals :				1834.09973	150.14644	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.304	MM	0.1819	21.44777	1.96523	3.0008
2	7.251	MM	0.2223	693.29767	51.97482	96.9992
Totals :				714.74544	53.94005	



(1*S*,5*R*)-3-(2,6-Dimethylbenzyl)-3-azabicyclo[3.1.0]hexan-2-one (5d)

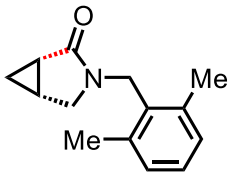
Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 13.5 mg, 63% yield, 95:5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 8.52 min (major) and 9.32 min (minor).

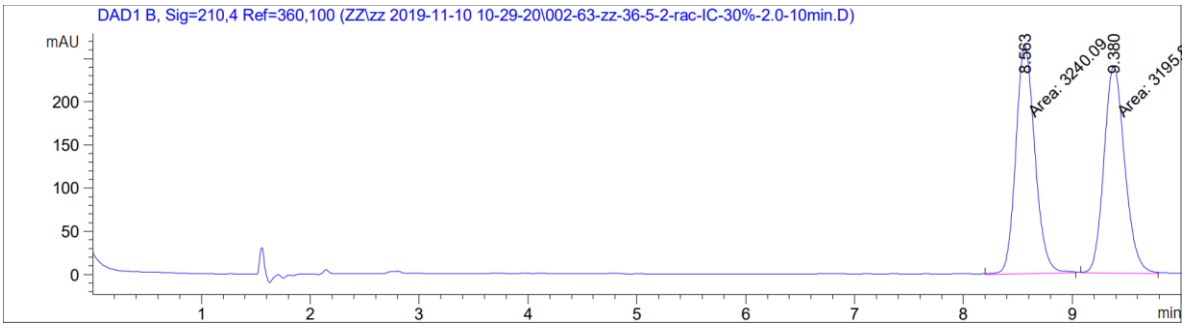
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 3.24 (dd, *J* = 10.3, 6.0 Hz, 1H), 2.94 (dd, *J* = 10.3, 1.8 Hz, 1H), 2.29 (s, 6H), 1.98 – 1.91 (m, 1H), 1.79 – 1.71 (m, 1H), 1.04 (td, *J* = 8.0, 4.8 Hz, 1H), 0.51 – 0.45 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.41, 137.81, 132.40, 128.57, 127.83, 47.85, 40.17, 20.39, 20.09, 12.77, 11.81.

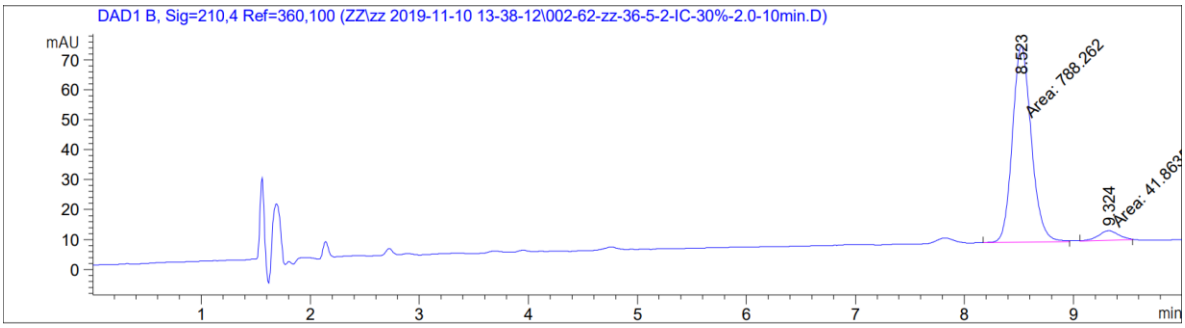
HRMS (ESI-TOF) Calcd for $C_{14}H_{18}NO$ [M+H]: 216.1388; found: 216.1392.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

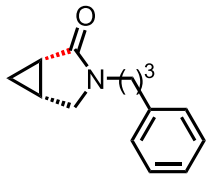




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.563	MM	0.2034	3240.09180	265.43857	50.3436
2	9.380	MM	0.2215	3195.86865	240.47191	49.6564
Totals :				6435.96045	505.91048	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.523	MM	0.2001	788.26239	65.64828	94.9570
2	9.324	MM	0.2182	41.86349	3.19696	5.0430
Totals :				830.12589	68.84524	



(1*S*,5*R*)-3-(3-Phenylpropyl)-3-azabicyclo[3.1.0]hexan-2-one (5e)

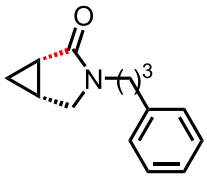
Following **General Procedure B** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 7.0 mg, 33% yield, 93:7 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (30% IPA/CO_2, 2.0 mL/min) with retention time 8.80 min (major) and 10.91 min (minor).

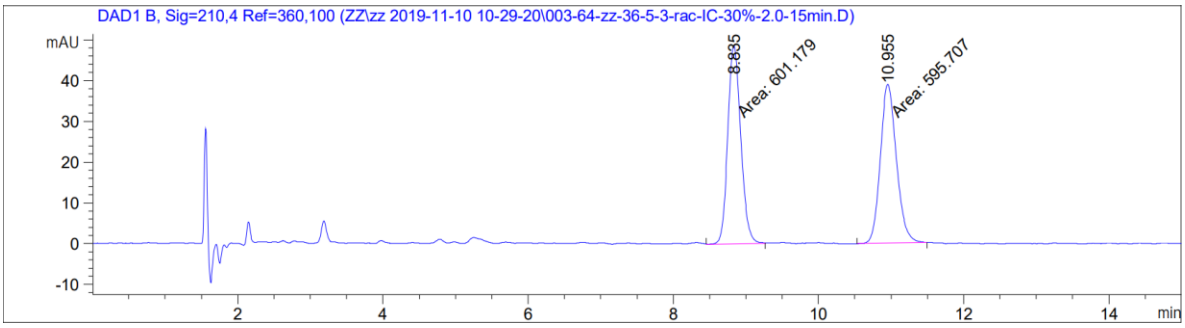
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.13 (m, 3H), 3.52 (dd, *J* = 10.2, 5.9 Hz, 1H), 3.33 – 3.24 (m, 2H), 3.24 – 3.16 (m, 1H), 2.61 (t, *J* = 7.9 Hz, 2H), 1.97 – 1.91 (m, 1H), 1.88 – 1.74 (m, 3H), 1.11 (td, *J* = 8.0, 4.7 Hz, 1H), 0.59 – 0.52 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.15, 141.62, 128.57, 128.45, 126.11, 49.26, 41.99, 33.28, 29.44, 20.60, 12.83, 11.90.

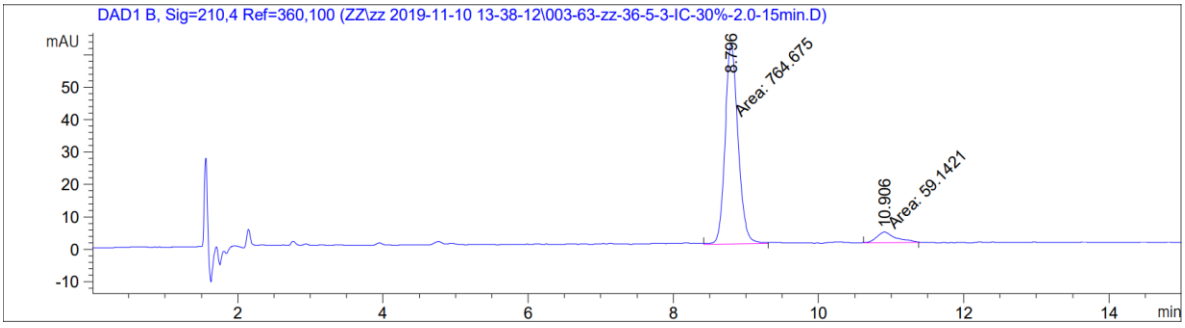
HRMS (ESI-TOF) Calcd for $C_{14}H_{18}NO$ [M+H]: 216.1388; found: 216.1393.

The absolute stereochemistry was assigned by analogy to compound **3t'**.



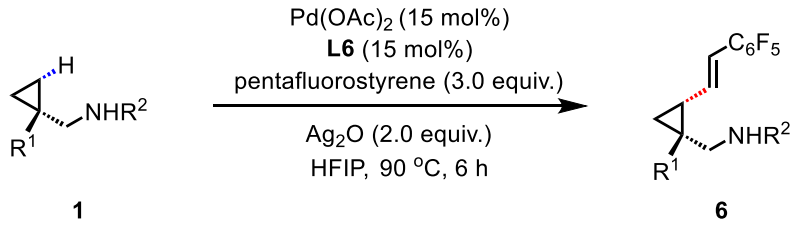


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.835	MM	0.2059	601.17883	48.66322	50.2286
2	10.955	MM	0.2553	595.70728	38.89220	49.7714
Totals :				1196.88611	87.55542	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.796	MM	0.2070	764.67456	61.57568	92.8210
2	10.906	MM	0.3034	59.14210	3.24893	7.1790
Totals :				823.81666	64.82461	

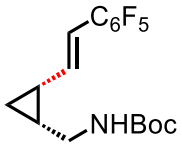
General procedure for γ-C(sp^3)–H olefination



1 **6**

General Procedure C: In the culture tube, $Pd(OAc)_2$ (15 mol%, 3.4 mg), ligand **L6** (15 mol%, 3.6 mg), pentafluorostyrene (3.0 equiv.,), Ag_2O (2.0 equiv., 46.3 mg), and free aliphatic amine **1** (0.1 mmol) in order were weighed in air and placed with a magnetic stir bar. Then HFIP (0.1 mL) were added. The reaction mixture was stirred at rt for 3 min, and then heated to 90 °C for 6 h (150 rpm). After being allowed to cool to room temperature, the mixture was diluted with DCM, filtered through a Celite plug, and concentrated *in vacuo*. When using secondary amine as substrate, the resulting mixture was purified by pTLC (hexane/EA) to afford the corresponding γ-olefination product. When using primary amine as substrate, the resulting mixture was dissolved in DCM (1.0 mL) and treated with Boc_2O (2.0 equiv., 46 μL) (HFIP residue can catalyze Boc protection of free amines[6]). After being stirred at rt for 1 h, the crude mixture was concentrated *in vacuo* and purified by pTLC (hexane/EA or toluene/EA) to afford the corresponding Boc-protected amine.

Substrate scope for γ-C(sp^3)–H olefination



***tert*-Butyl (((1*R*,2*R*)-2-((*E*)-2-(perfluorophenyl)vinyl)cyclopropyl)methyl)carbamate (6a')**

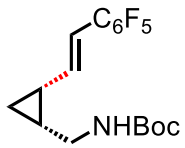
Following **General Procedure C** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 14.0 mg, 39% yield, 95.5:4.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak IC column (10% IPA/CO_2, 2.0 mL/min) with retention time 3.82 min (minor) and 5.73 min (major).

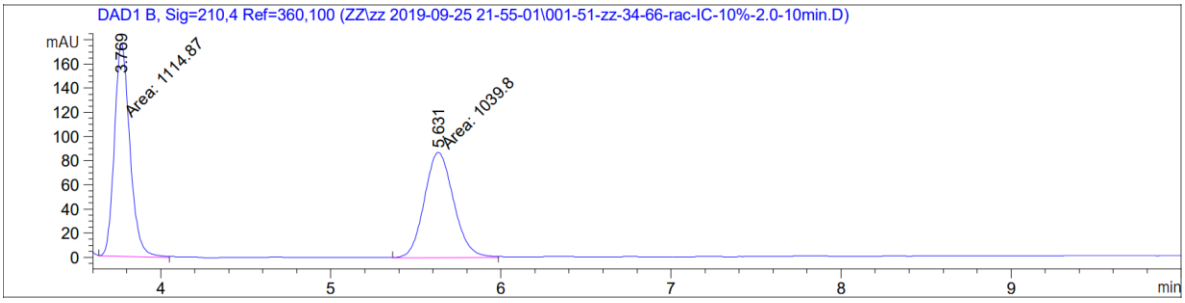
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.42 (d, *J* = 16.2 Hz, 1H), 6.27 (dd, *J* = 16.2, 9.2 Hz, 1H), 4.58 (br s, 1H), 3.50 – 3.38 (m, 1H), 3.06 – 2.95 (m, 1H), 1.81 – 1.71 (m, 1H), 1.43 (s, 10H), 1.13 (td, *J* = 8.2, 5.2 Hz, 1H), 0.66 – 0.59 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.83, 139.61, 114.56, 79.50, 41.10, 28.52, 20.62, 20.24, 13.04.

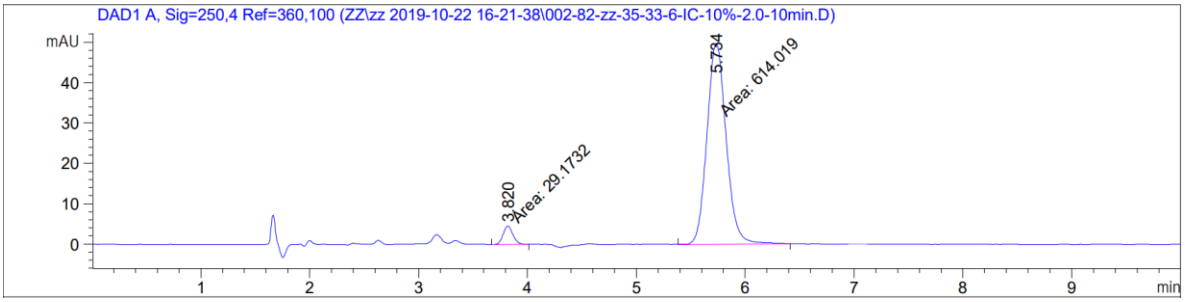
HRMS (ESI-TOF) Calcd for $C_{12}H_{11}F_5N$ [M-Boc]: 264.0812; found: 264.0814.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

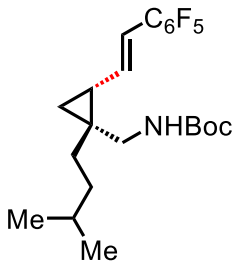




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.769	MM	0.1052	1114.87048	176.70636	51.7421
2	5.631	MM	0.1990	1039.79846	87.10205	48.2579
Totals :				2154.66895	263.80841	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.820	MM	0.1065	29.17324	4.56623	4.5357
2	5.734	MM	0.2054	614.01947	49.83403	95.4643
Totals :				643.19271	54.40025	



***tert*-Butyl (((1*R*,2*R*)-1-isopentyl-2-((*E*)-2-(perfluorophenyl)vinyl)cyclopropyl)methyl)carbamate (6b')**

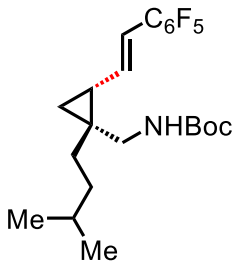
Following **General Procedure C** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 15.0 mg, 33% yield, 94:6 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (3% IPA/CO_2, 2.0 mL/min) with retention time 2.69 min (minor) and 2.91 min (major).

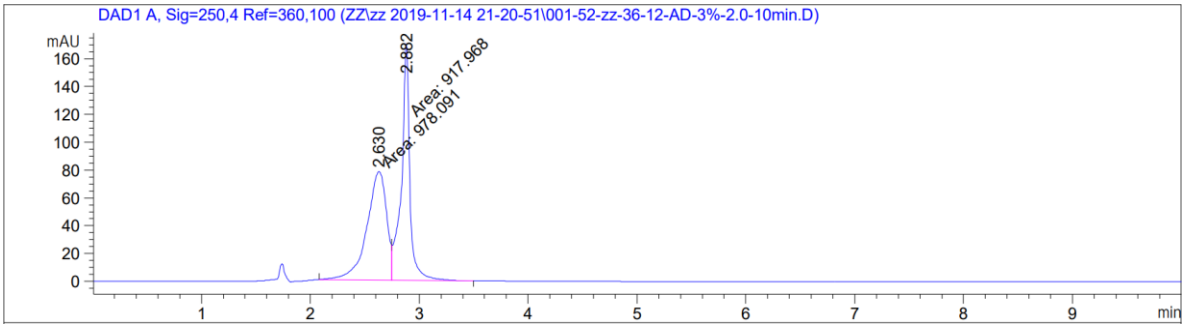
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.42 (d, *J* = 16.1 Hz, 1H), 6.37 – 6.21 (m, 1H), 4.47 (br s, 1H), 3.60 – 3.42 (m, 1H), 3.07 – 2.89 (m, 1H), 1.63 – 1.53 (m, 4H), 1.45 (s, 9H), 1.40 – 1.32 (m, 1H), 1.26 – 1.17 (m, 1H), 1.00 – 0.94 (m, 1H), 0.91 (d, *J* = 6.2 Hz, 6H), 0.79 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.93, 140.15, 114.27, 79.39, 42.90, 35.28, 34.00, 29.75, 28.50, 28.36, 27.58, 22.78, 22.62, 20.27.

HRMS (ESI-TOF) Calcd for $C_{17}H_{21}F_5N$ [M-Boc]: 334.1594; found: 334.1595.

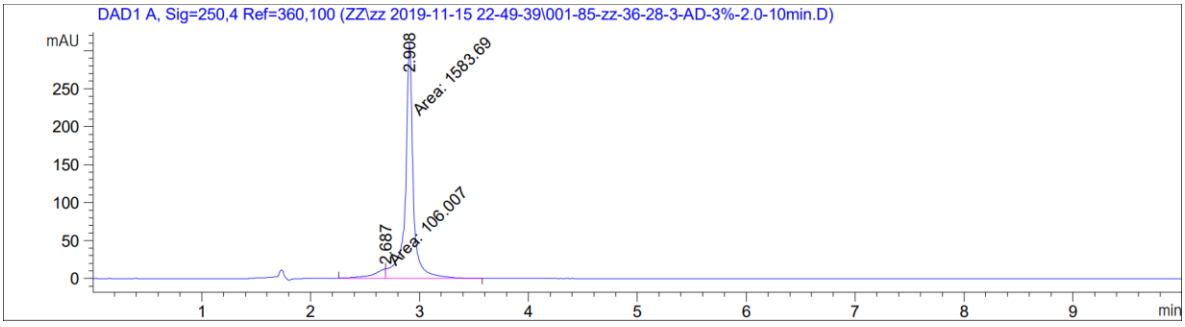
The absolute stereochemistry was assigned by analogy to compound **3t'**.





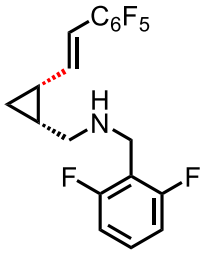
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.630	MF	0.2093	978.09076	77.89690	51.5855
2	2.882	FM	0.0898	917.96844	170.30934	48.4145

Totals : 1896.05920 248.20624



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.687	MF	0.1383	106.00673	12.77074	6.2737
2	2.908	FM	0.0851	1583.69434	310.12543	93.7263

Totals : 1689.70107 322.89617



***N*-(2,6-Difluorobenzyl)-1-((1*R*,2*R*)-2-((*E*)-2-(perfluorophenyl)vinyl)cyclopropyl)methanamine (6c)**

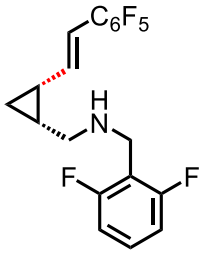
Following **General Procedure C** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 20.0 mg, 51% yield, 96:4 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 2.41 min (major) and 3.06 min (minor).

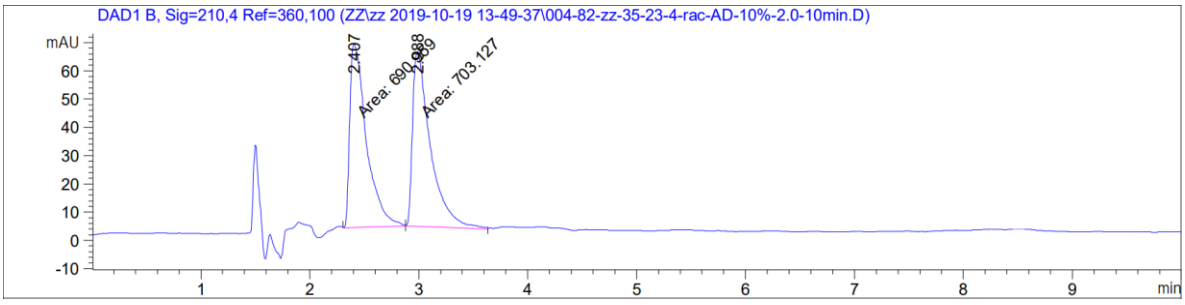
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 1H), 6.80 (t, *J* = 7.7 Hz, 2H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.15 (dd, *J* = 16.2, 9.5 Hz, 1H), 3.92 (d, *J* = 13.1 Hz, 1H), 3.85 (d, *J* = 13.1 Hz, 1H), 2.86 (dd, *J* = 12.2, 5.9 Hz, 1H), 2.50 – 2.44 (m, 1H), 1.76 – 1.67 (m, 1H), 1.47 – 1.41 (m, 1H), 1.11 (td, *J* = 8.2, 5.0 Hz, 1H), 0.59 – 0.53 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.81 (dd, *J* = 247.3, 8.6 Hz), 140.00, 128.91 (t, *J* = 10.3 Hz), 115.84 (t, *J* = 20.6 Hz), 114.12, 111.23 (dd, *J* = 20.9, 5.4 Hz), 49.10, 40.70, 20.59, 20.45, 13.28.

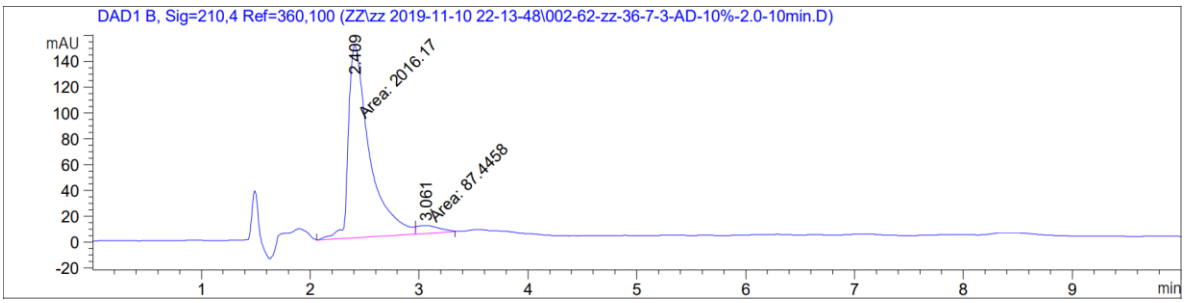
HRMS (ESI-TOF) Calcd for $C_{19}H_{15}F_7N$ [M+H]: 390.1093; found: 390.1092.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

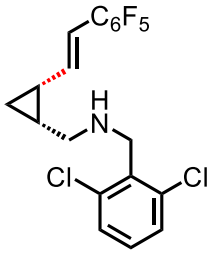




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.407	MM	0.1773	690.95886	64.95244	49.5636
2	2.988	MM	0.1892	703.12665	61.94228	50.4364
Totals :				1394.08551	126.89472	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.409	MF	0.2249	2016.17139	149.38541	95.8431
2	3.061	FM	0.2364	87.44581	6.16533	4.1569
Totals :				2103.61720	155.55073	



***N*-(2,6-Difluorobenzyl)-1-((1*R*,2*R*)-2-((*E*)-2-(perfluorophenyl)vinyl)cyclopropyl)methanamine (6d)**

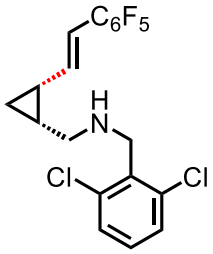
Following **General Procedure C** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 17.0 mg, 40% yield, 98.5:1.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (10% IPA/CO_2, 2.0 mL/min) with retention time 3.43 min (major) and 4.67 min (minor).

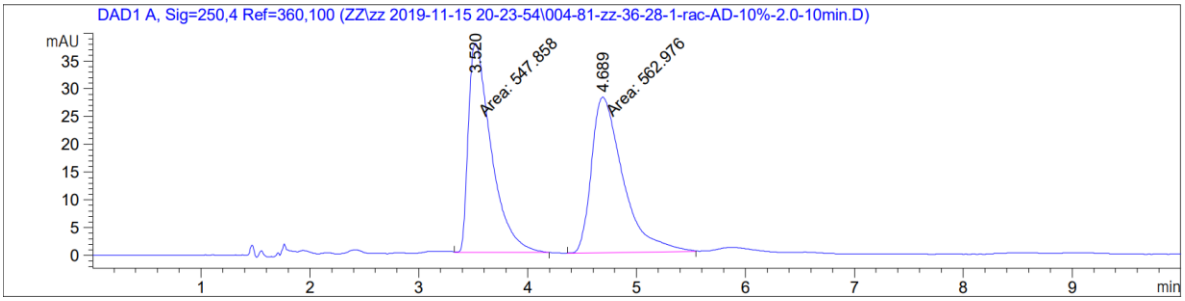
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 2H), 7.10 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.13 (dd, *J* = 16.2, 9.5 Hz, 1H), 4.08 (s, 2H), 2.97 (dd, *J* = 12.2, 5.6 Hz, 1H), 2.43 (dd, *J* = 12.2, 9.1 Hz, 1H), 1.76 – 1.66 (m, 1H), 1.51 – 1.43 (m, 1H), 1.12 (td, *J* = 8.2, 5.1 Hz, 1H), 0.60 – 0.51 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.95, 135.97, 135.62, 128.95, 128.41, 114.18, 48.99, 48.36, 20.76, 20.48, 13.29.

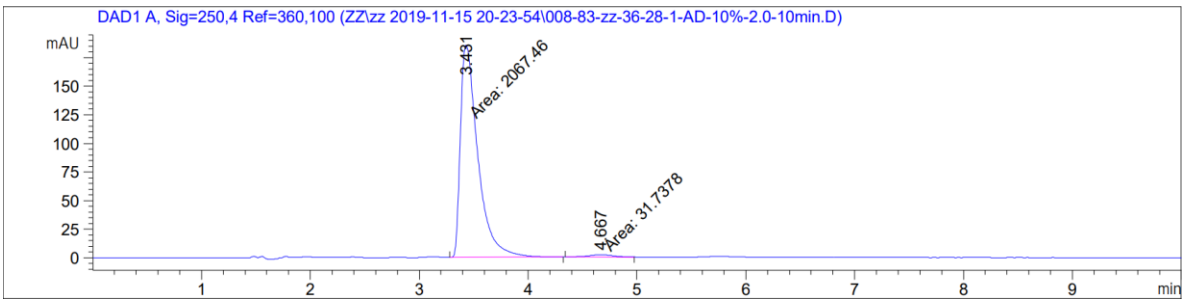
HRMS (ESI-TOF) Calcd for $C_{19}H_{15}F_5Cl_2N$ [M+H]: 422.0502; found: 422.0500.

The absolute stereochemistry was assigned by analogy to compound **3t'**.

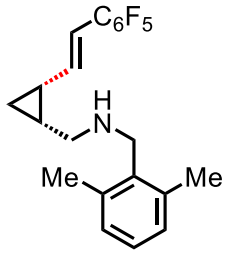




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.520	MM	0.2426	547.85809	37.63811	49.3195
2	4.689	MM	0.3349	562.97565	28.01604	50.6805
Totals :				1110.83374	65.65416	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.431	MM	0.1856	2067.46191	185.65993	98.4881
2	4.667	MM	0.2769	31.73776	1.91005	1.5119
Totals :				2099.19968	187.56998	



***N*-(2,6-Dimethylbenzyl)-1-((1*R*,2*R*)-2-((*E*)-2-(perfluorophenyl)vinyl)cyclopropyl)methanamine (6e)**

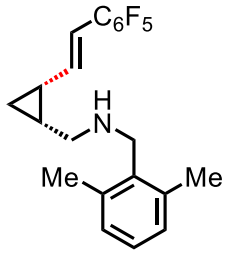
Following **General Procedure C** on 0.1 mmol scale. Purification by pTLC (hexane/EA) afforded the title compound (colorless oil, 11.5 mg, 30% yield, 98.5:1.5 er). The enantiomeric purity was determined by SFC analysis on a Chiralpak AD column (30% IPA/CO_2, 2.0 mL/min) with retention time 2.55 min (major) and 5.54 min (minor).

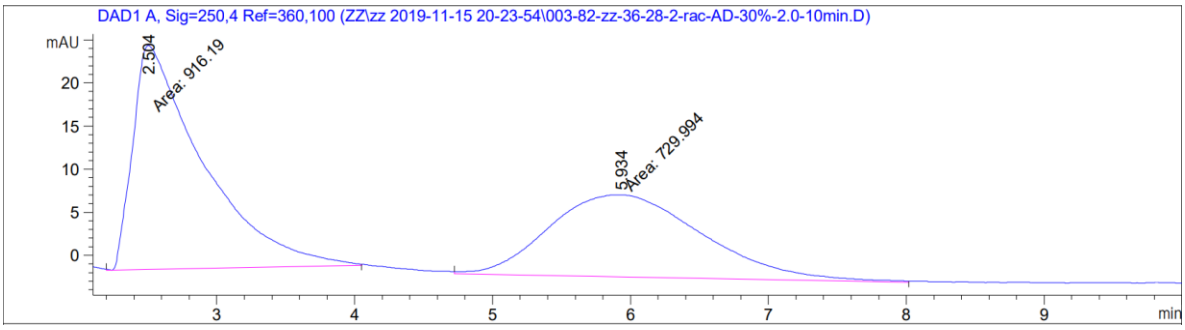
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 – 6.98 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.26 (dd, *J* = 16.1, 9.5 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 3.75 (d, *J* = 12.0 Hz, 1H), 2.97 (dd, *J* = 12.3, 5.9 Hz, 1H), 2.59 (dd, *J* = 12.3, 8.7 Hz, 1H), 2.32 (s, 6H), 1.78 – 1.69 (m, 1H), 1.52 – 1.45 (m, 1H), 1.14 (td, *J* = 8.2, 4.9 Hz, 1H), 0.64 – 0.57 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.40, 136.95, 136.54, 128.34, 127.11, 113.97, 50.22, 47.74, 20.82, 20.70, 19.53, 13.41.

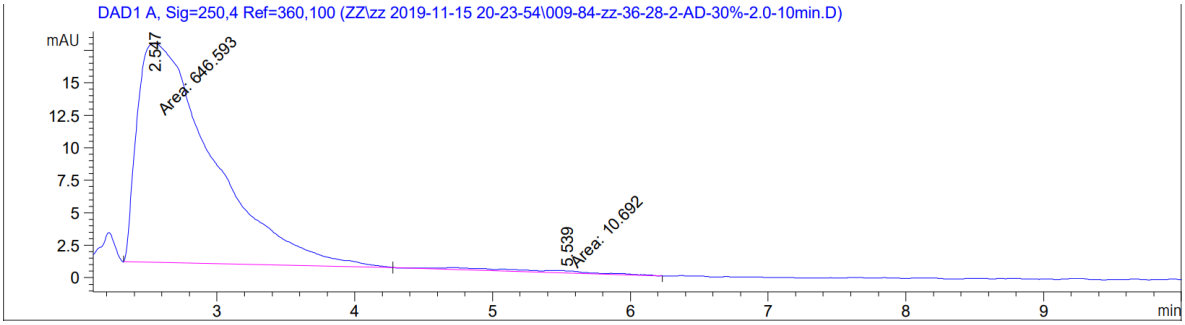
HRMS (ESI-TOF) Calcd for $C_{21}H_{21}F_5N$ [M+H]: 382.1594; found: 382.1593.

The absolute stereochemistry was assigned by analogy to compound **3t'**.





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.504	MM	0.5875	916.18994	25.99087	55.6554
2	5.934	MM	1.2806	729.99353	9.50046	44.3446
Totals :				1646.18347	35.49133	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.547	MM	0.6383	646.59314	16.88287	98.3733
2	5.539	MM	1.0567	10.69198	1.68634e-1	1.6267
Totals :				657.28512	17.05150	

Reference:

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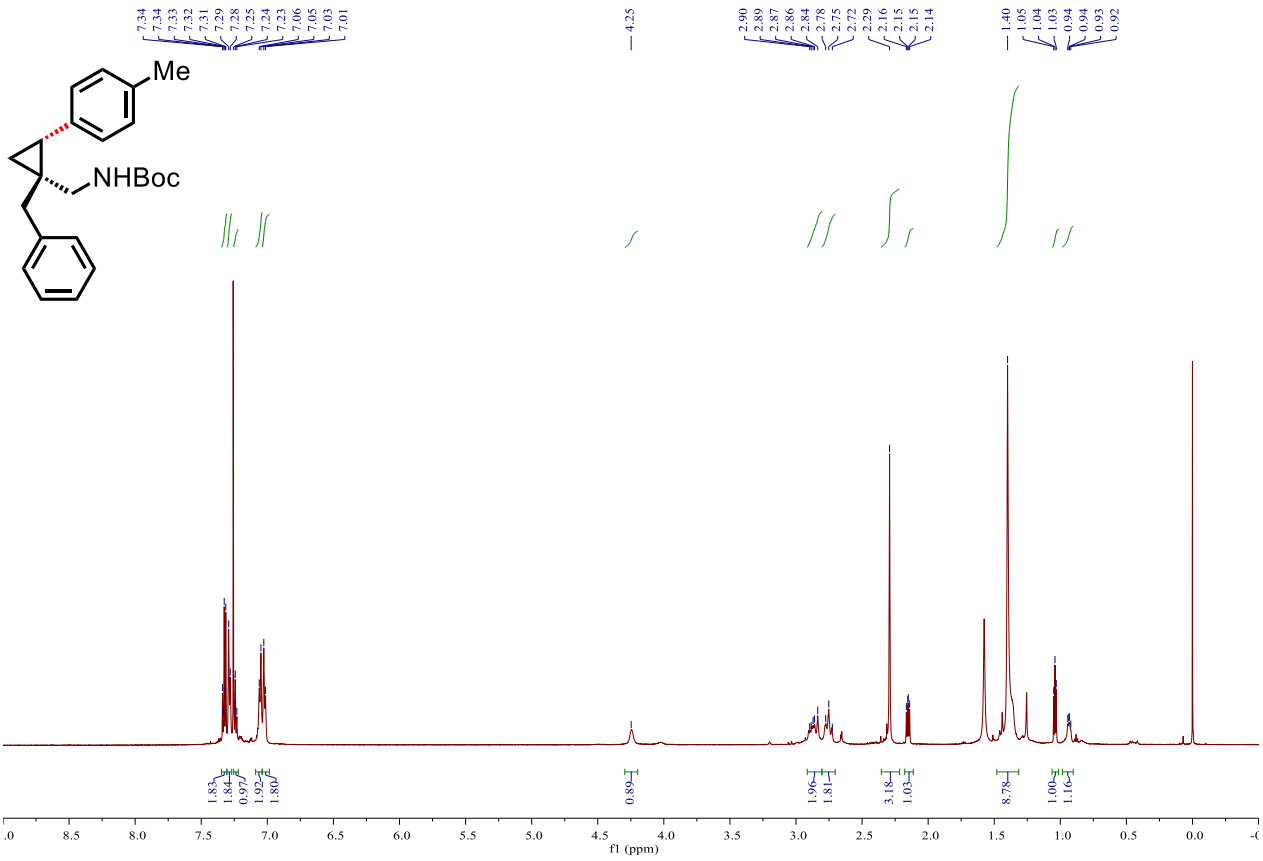
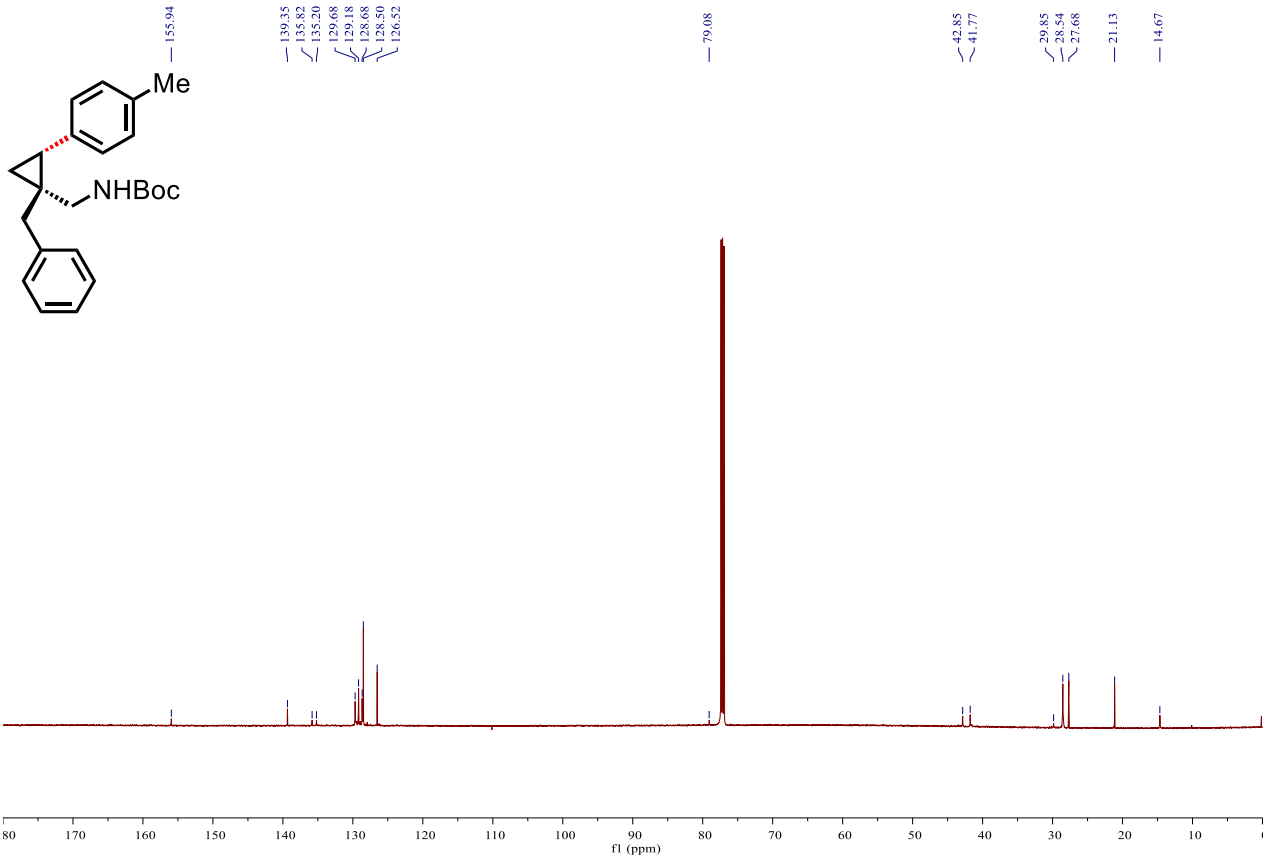
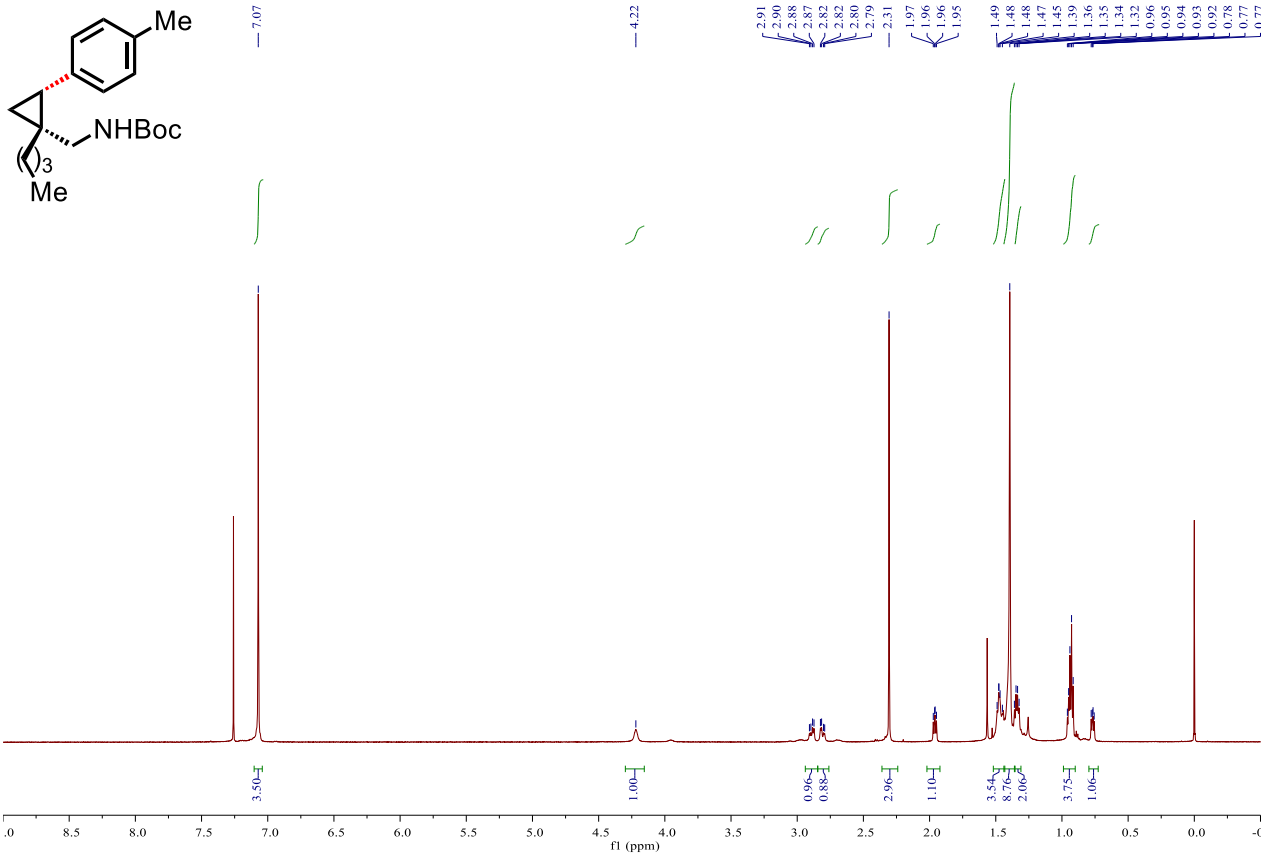
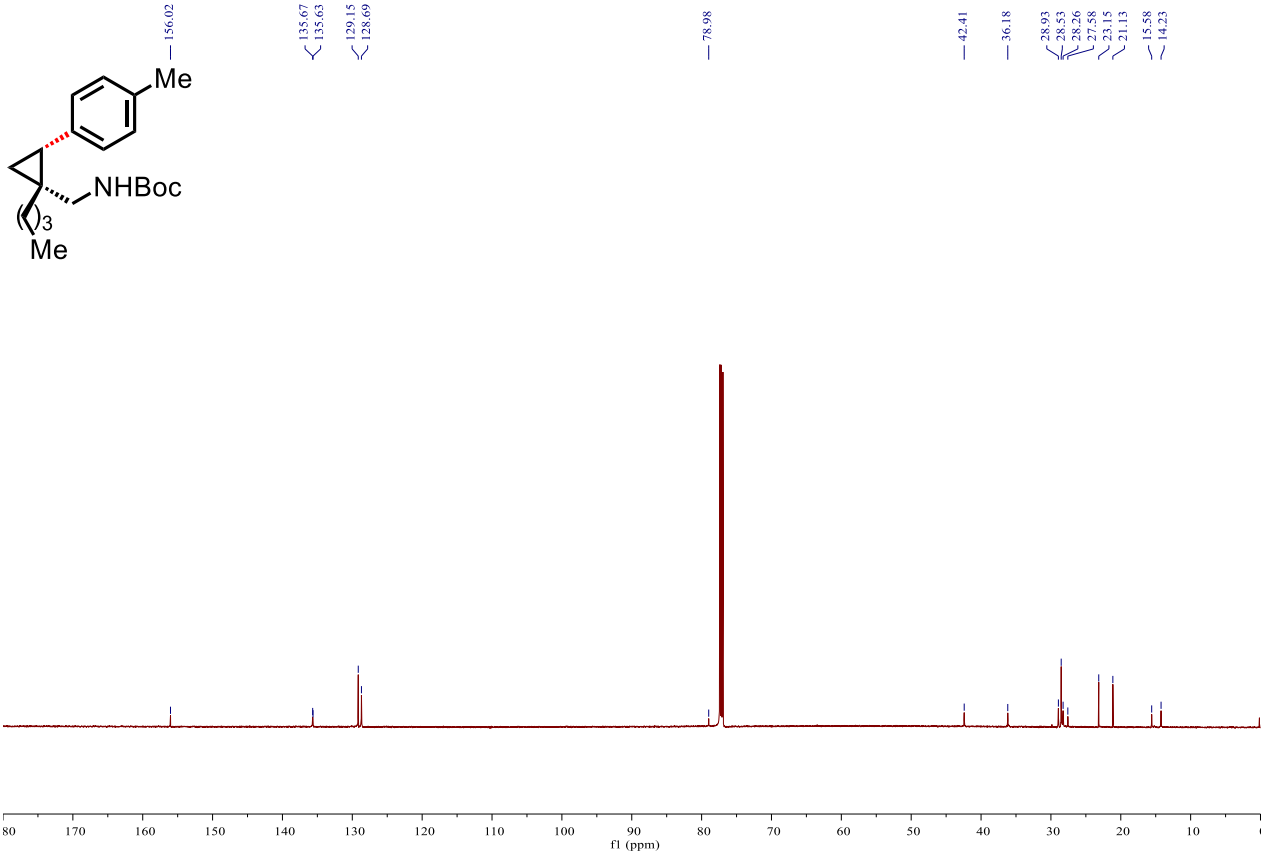
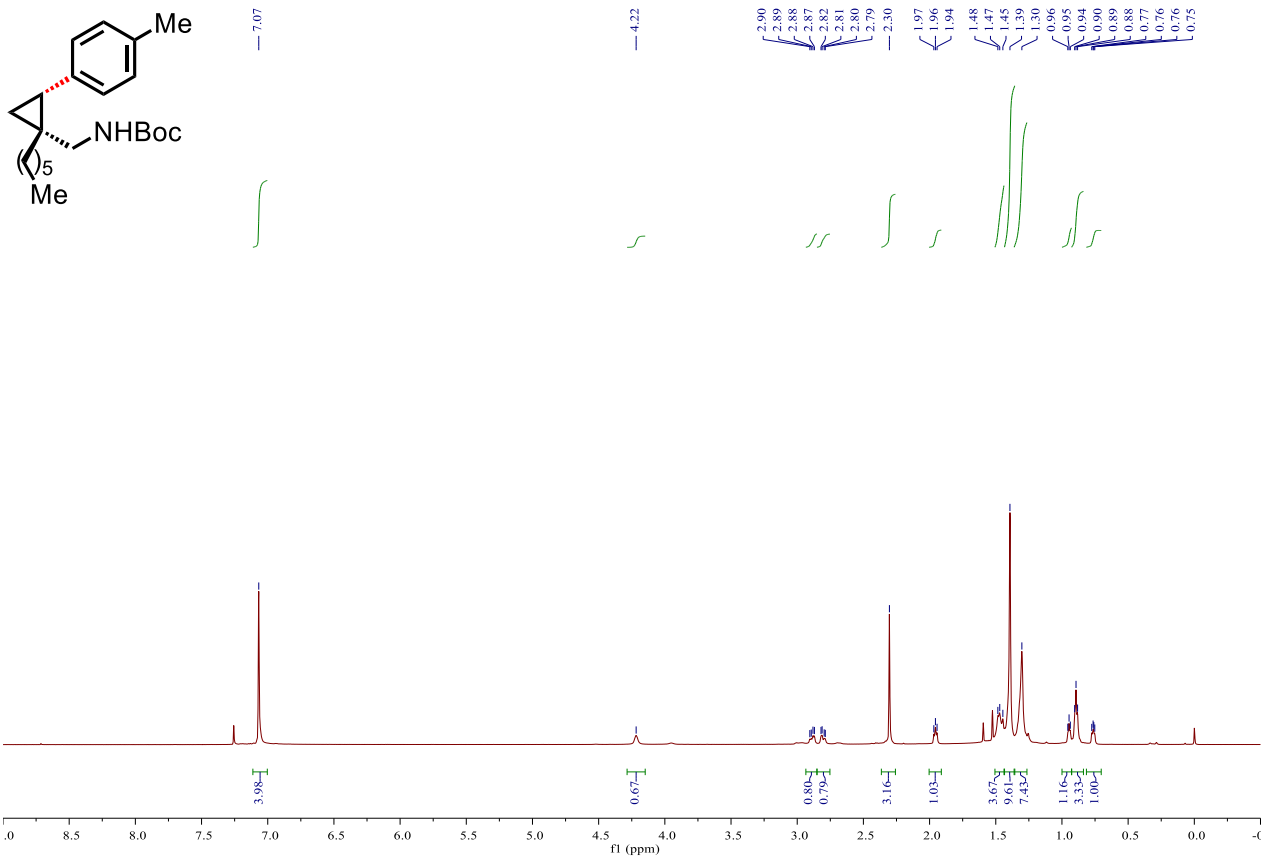
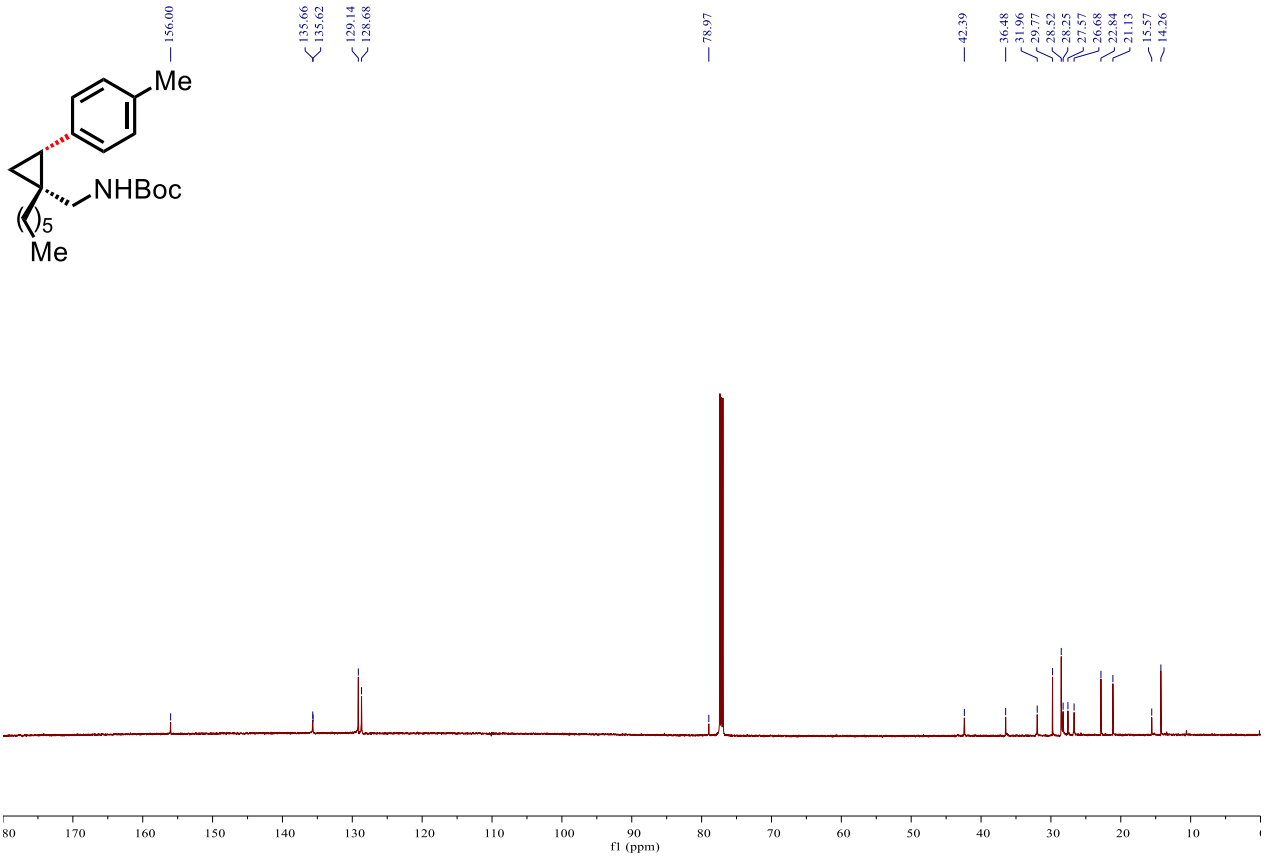

Me
NHBoc
f1 (ppm)


Me
NHBoc
f1 (ppm)


Me
NHBoc
3
Me
7.07
4.22
2.91
2.90
2.88
2.87
2.82
2.82
2.80
2.79
2.31
1.97
1.96
1.96
1.95
1.49
1.48
1.48
1.47
1.45
1.39
1.36
1.35
1.34
1.32
0.96
0.95
0.94
0.93
0.92
0.78
0.77
3.50
1.00
0.96
0.88
2.96
1.10
3.54
8.76
2.06
3.75
1.06
f1 (ppm)


Me
NHBoc
3
Me
156.02
135.67
135.63
129.15
128.69
78.98
42.41
36.18
28.93
28.53
28.26
27.58
23.15
21.13
15.58
14.23
f1 (ppm)


Me
NHBoc
5
Me
7.07
4.22
2.90
2.89
2.88
2.87
2.82
2.81
2.80
2.79
2.30
1.97
1.96
1.94
1.48
1.47
1.45
1.39
1.30
0.96
0.95
0.94
0.90
0.89
0.88
0.77
0.76
0.76
0.75
3.98
0.67
0.80
0.79
3.16
1.03
3.67
9.61
7.43
1.16
3.33
1.00
f1 (ppm)


Me
NHBoc
5
Me
156.00
135.66
135.62
129.14
128.68
78.97
42.39
36.48
31.96
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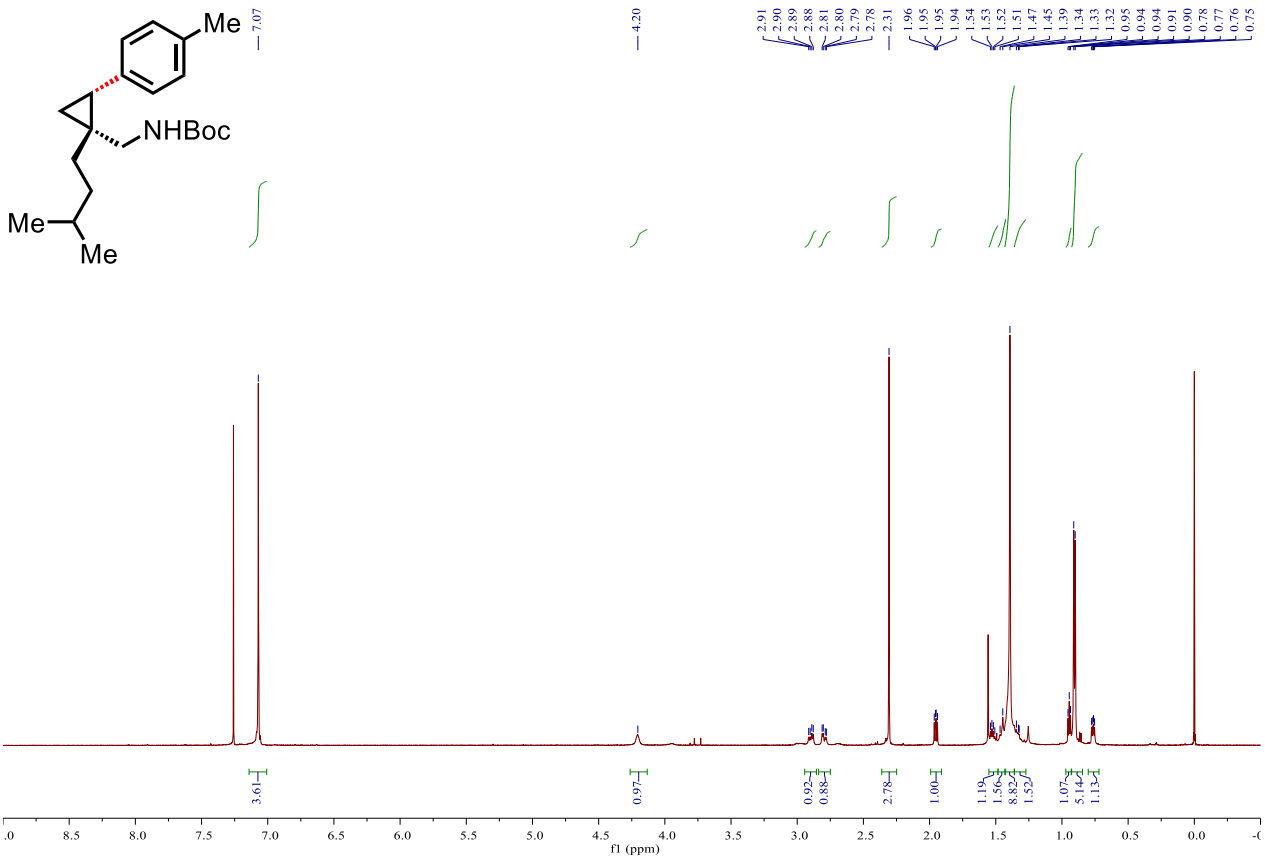
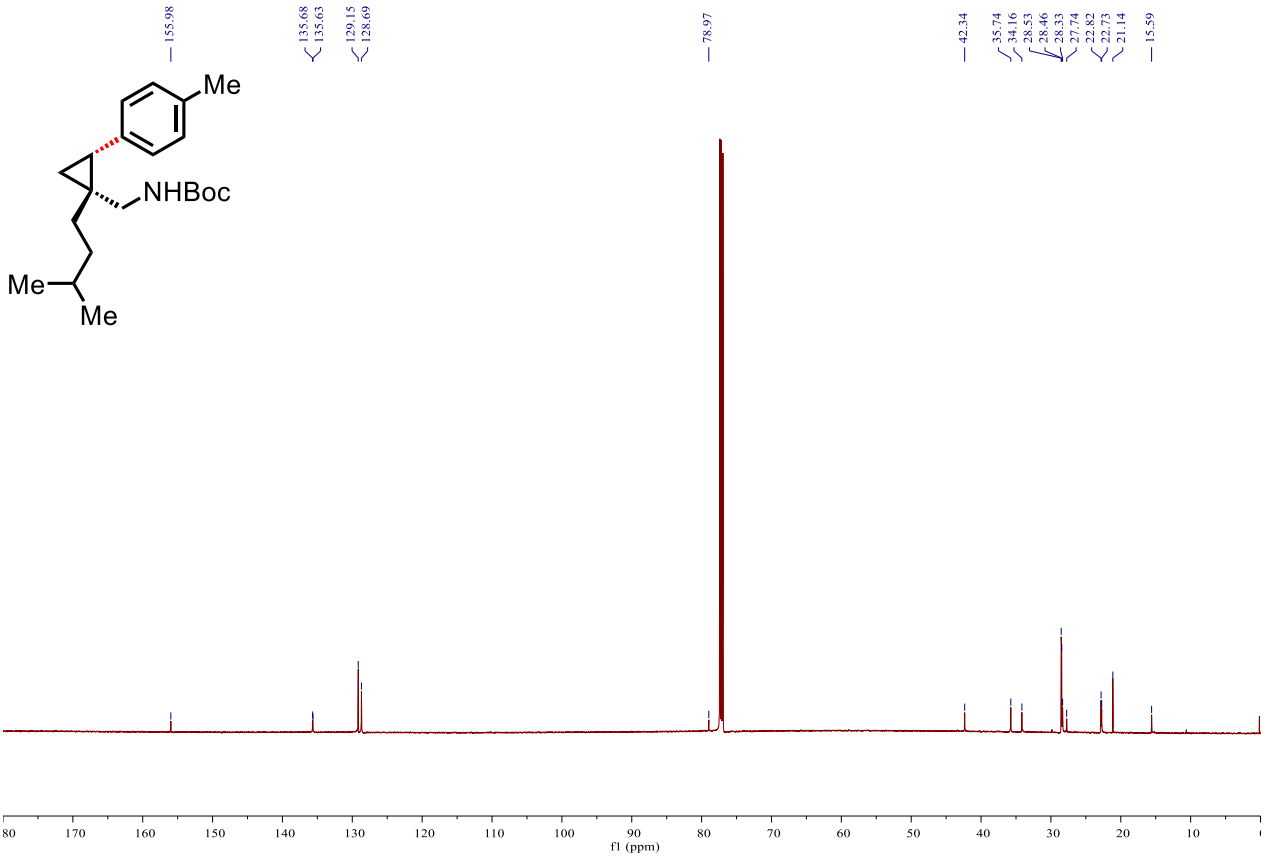
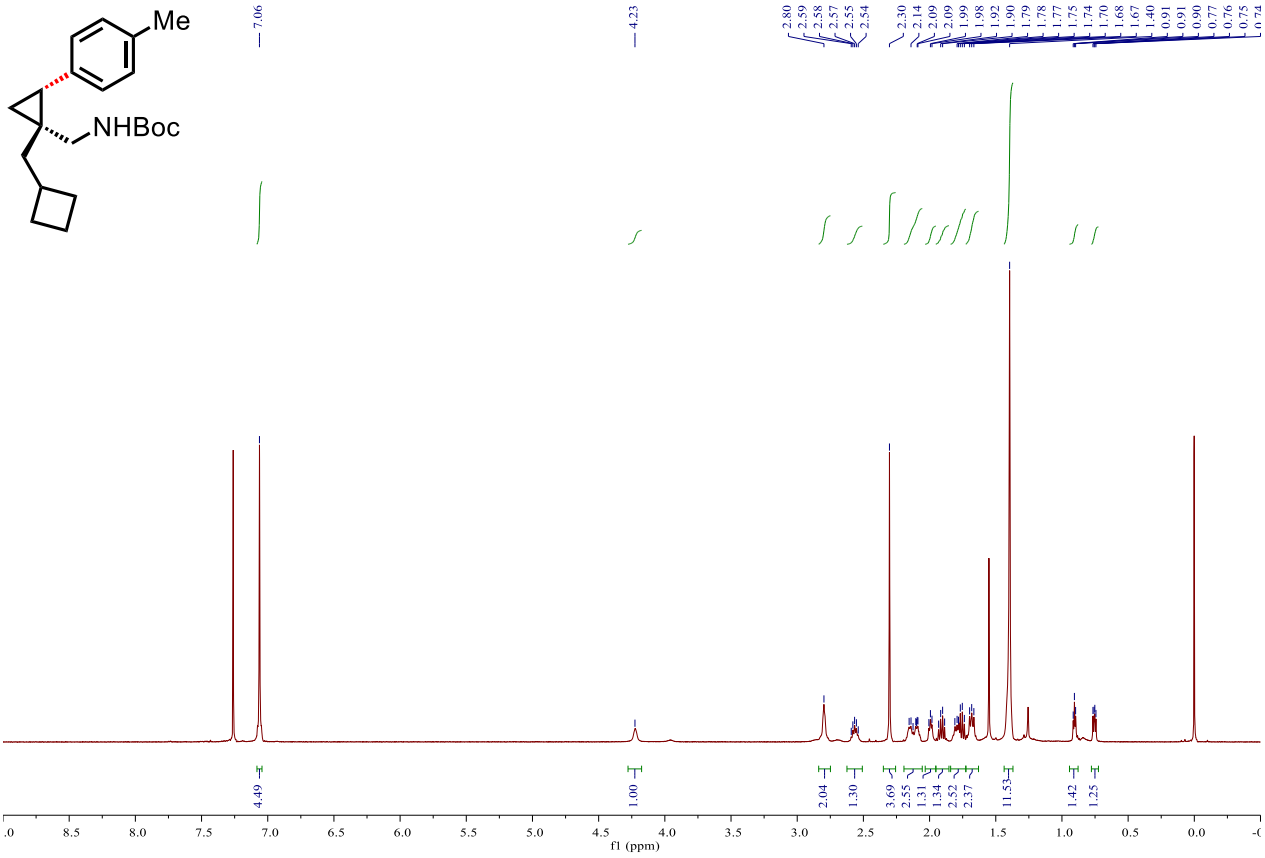
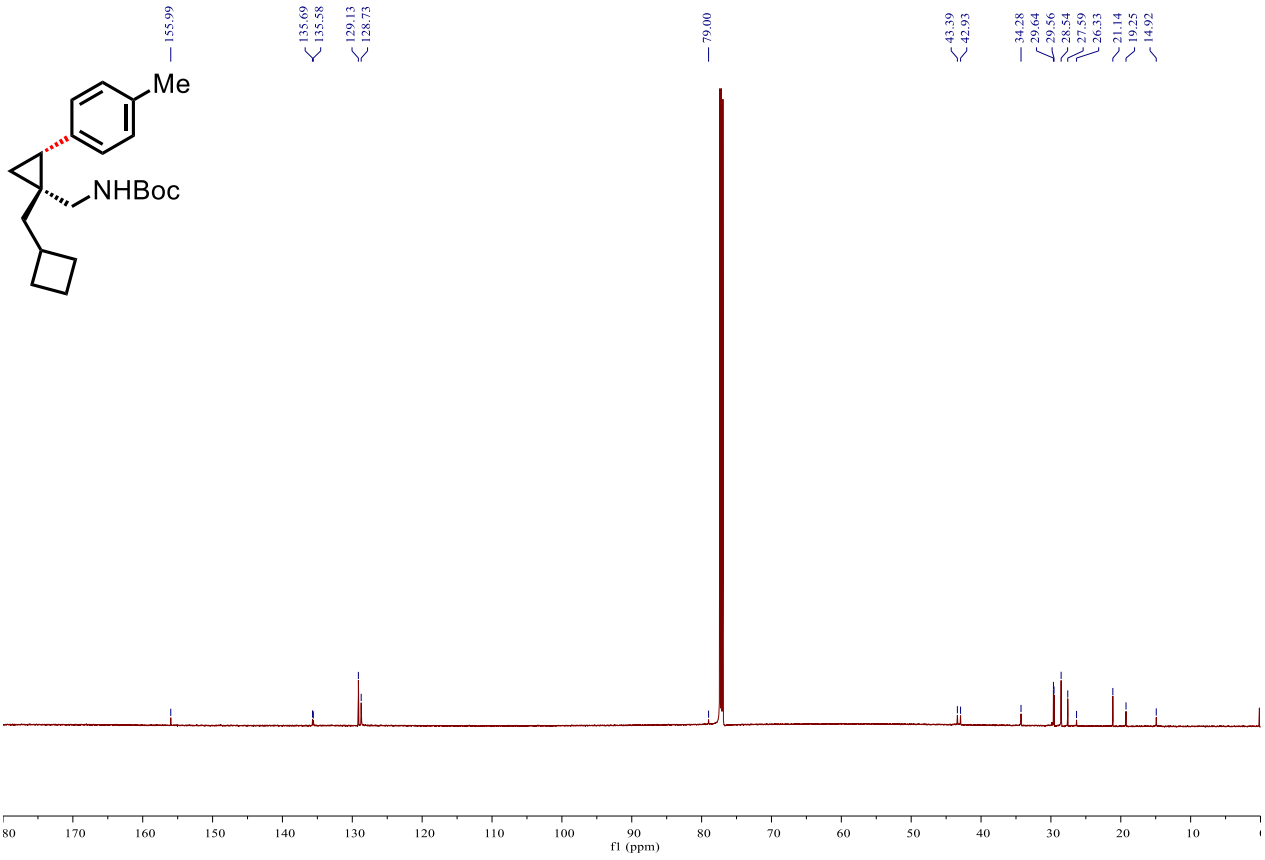
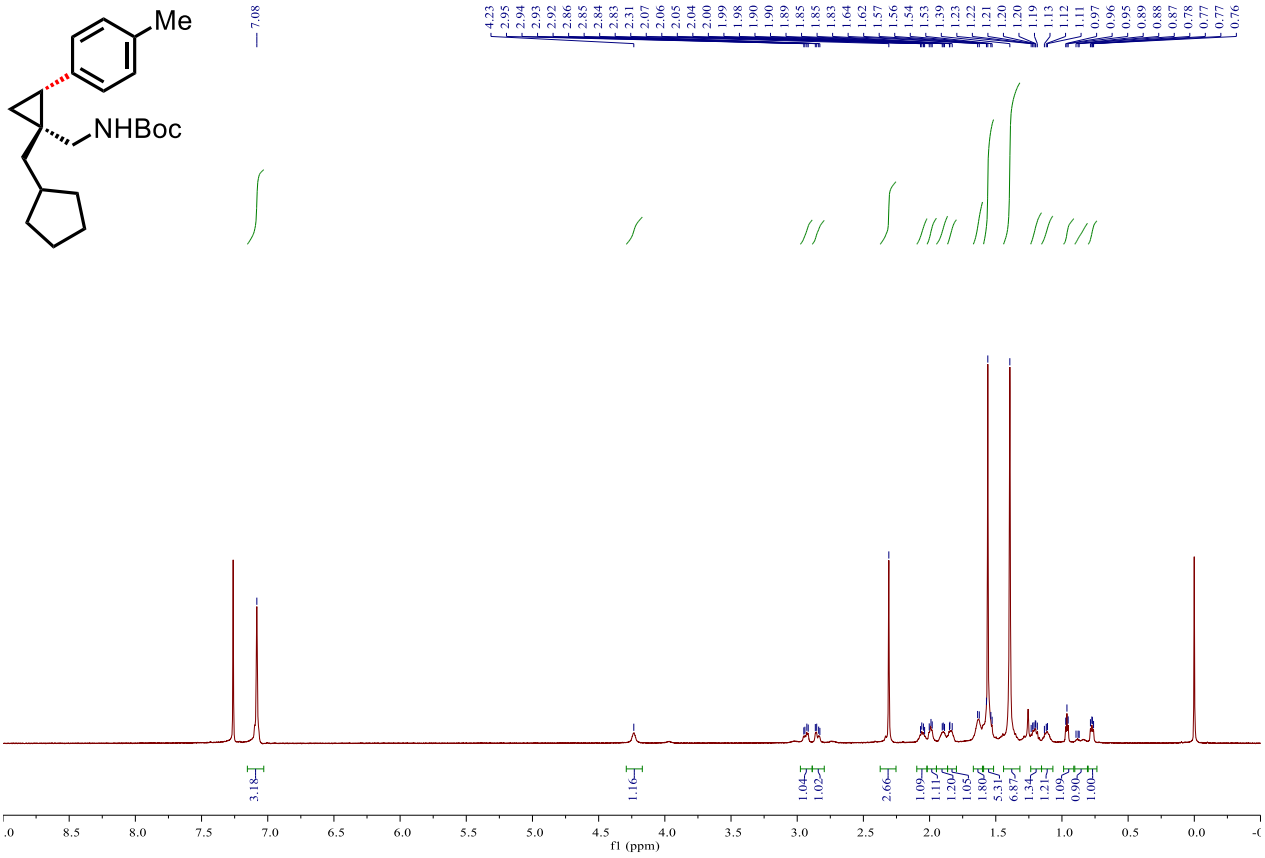
22.84
21.13
15.57
14.26
f1 (ppm)

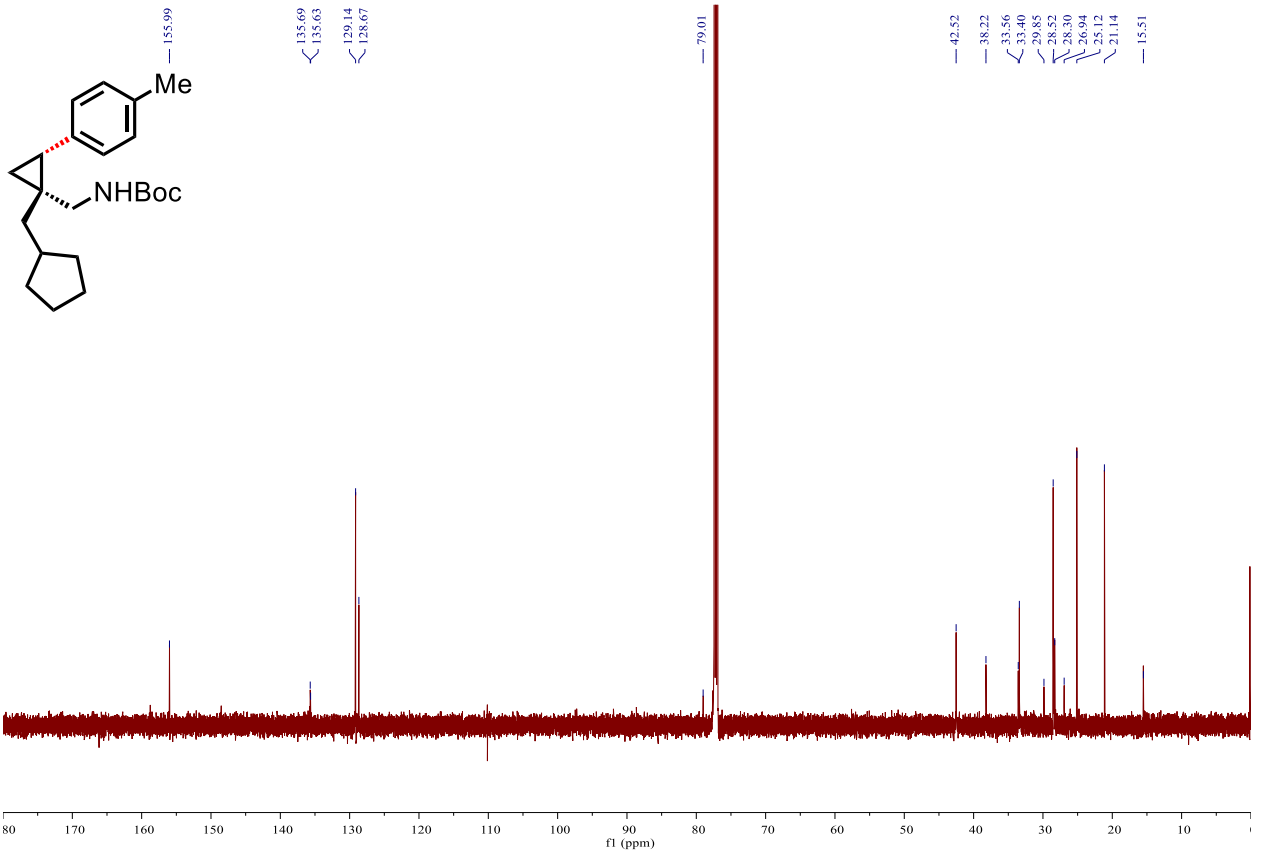

Me
NHBoc
Me
Me
7.07
4.20
2.91
2.90
2.89
2.88
2.81
2.80
2.79
2.78
2.31
1.96
1.95
1.95
1.94
1.54
1.53
1.52
1.51
1.47
1.45
1.39
1.34
1.33
1.32
0.95
0.94
0.94
0.91
0.90
0.78
0.77
0.76
0.75
3.61
0.97
0.92
0.88
2.78
1.00
1.19
1.56
8.82
1.52
1.07
5.14
1.13
f1 (ppm)

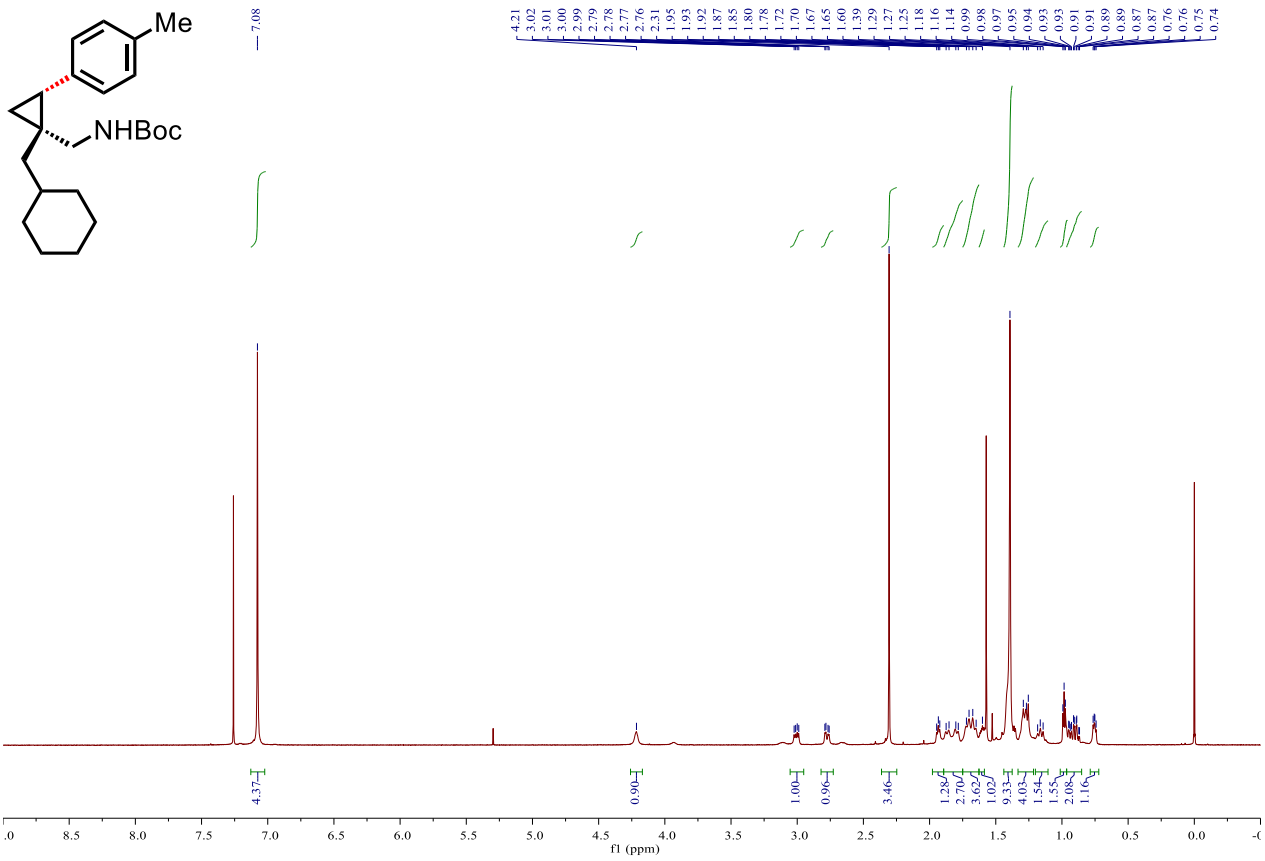

155.98
135.68
135.63
129.15
128.69
78.97
42.34
35.74
34.16
28.53
28.46
28.33
27.74
22.82
22.73
21.14
15.59
Me
NHBoc
Me
Me
f1 (ppm)

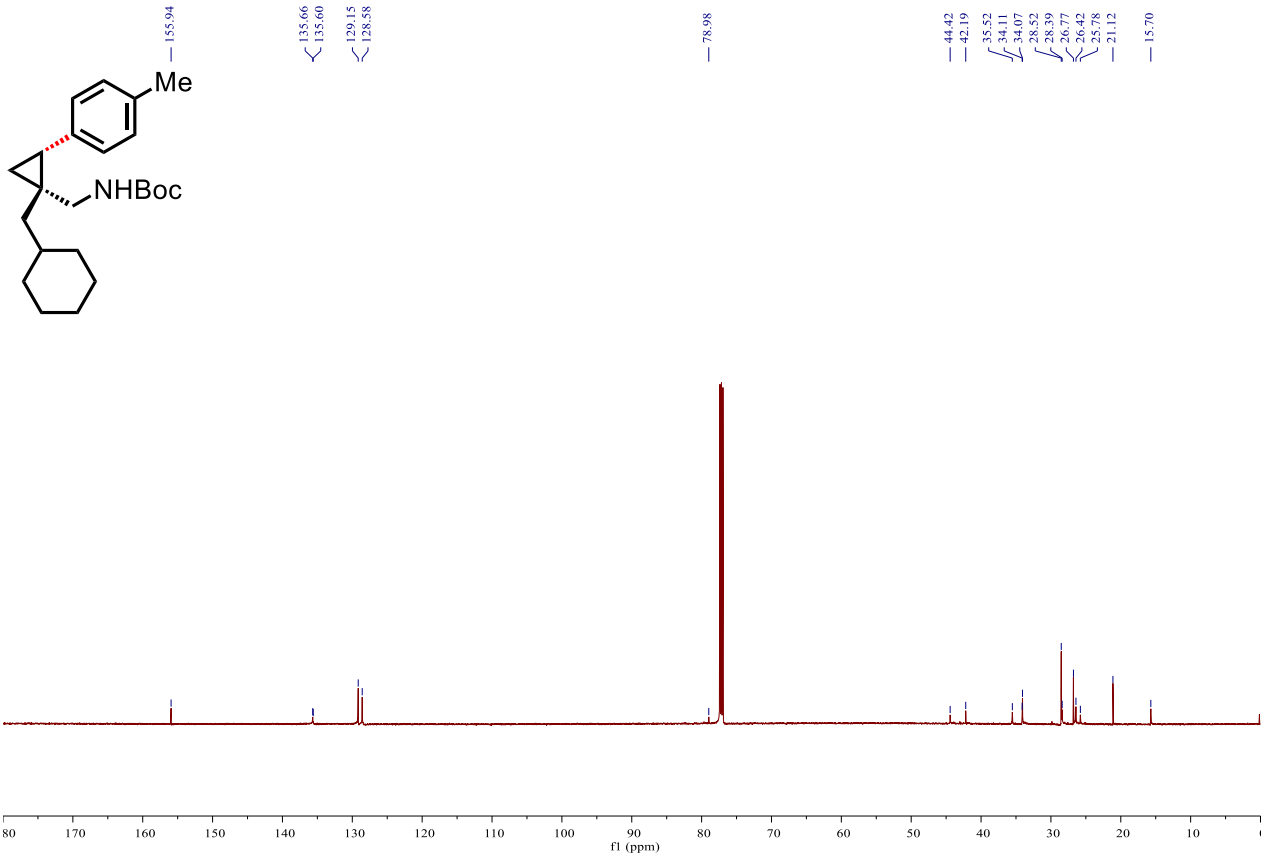

Me
NHBoc
7.06
4.23
2.80
2.59
2.58
2.57
2.55
2.54
2.30
2.14
2.09
2.09
1.99
1.98
1.92
1.90
1.79
1.78
1.77
1.75
1.74
1.70
1.68
1.67
1.40
0.91
0.91
0.90
0.77
0.76
0.75
0.74
4.49
1.00
2.04
1.30
3.69
2.55
1.31
1.34
2.52
2.37
11.53
1.42
1.25
f1 (ppm)

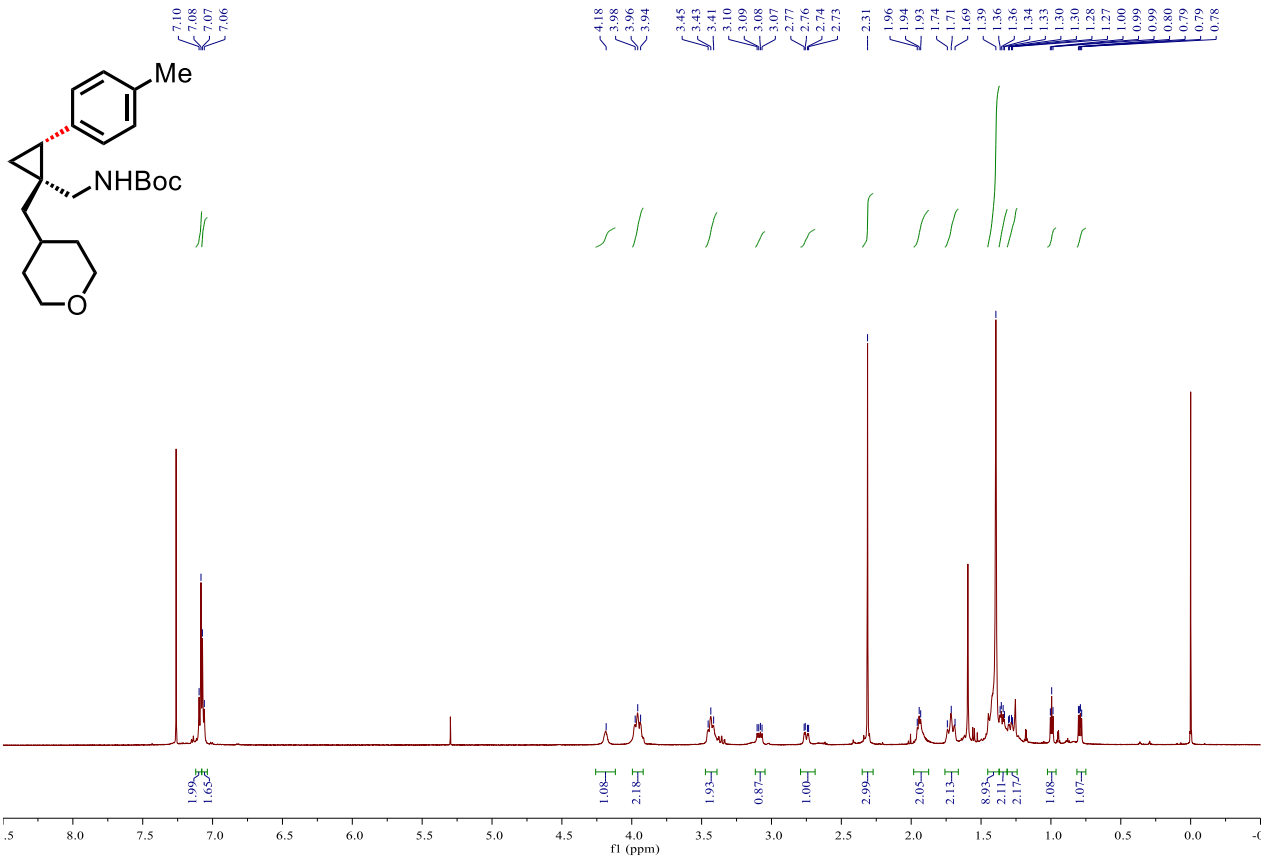

Me
NHBoc
155.99
135.69
135.58
129.13
128.73
79.00
43.39
42.93
34.28
29.64
29.56
28.54
27.59
26.33
21.14
19.25
14.92
f1 (ppm)

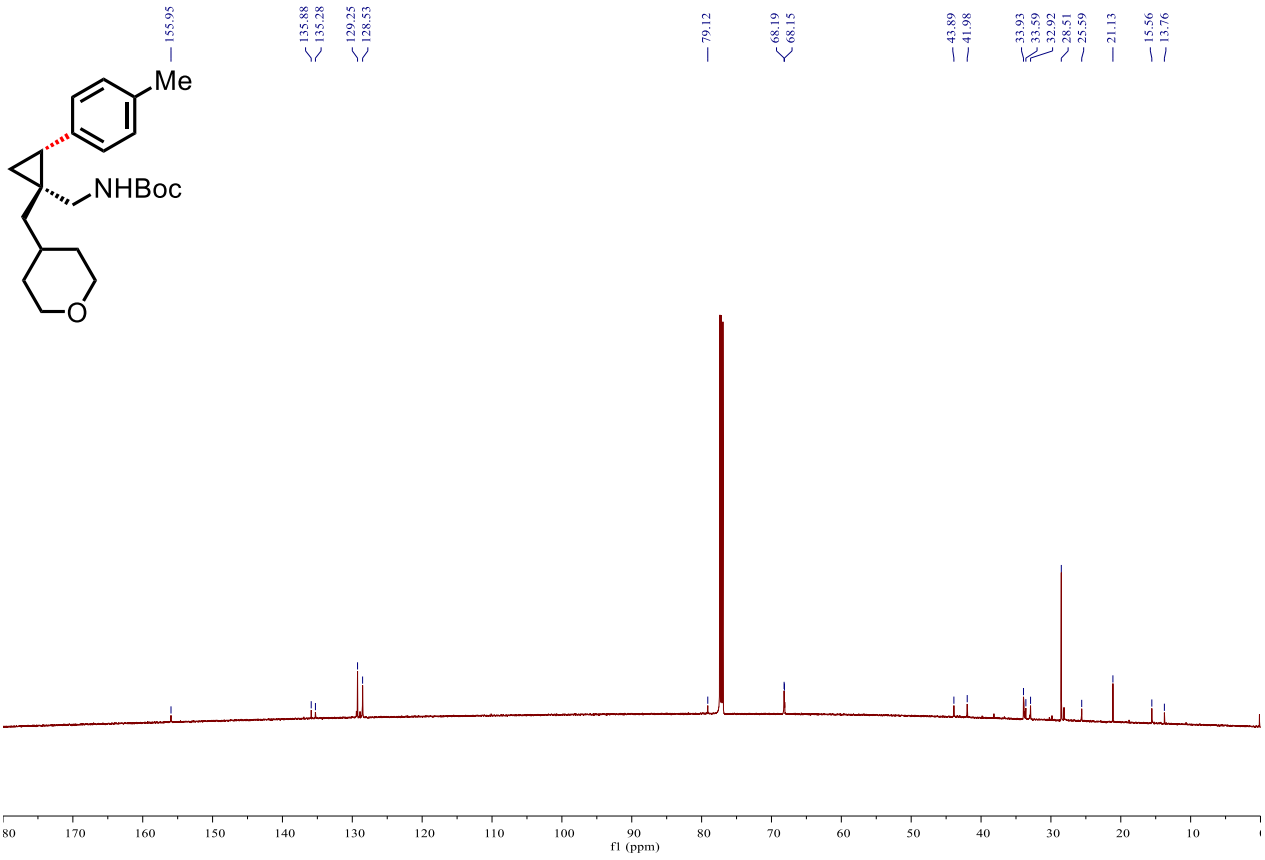

Me
NHBoc
7.08
4.23 2.95 2.94 2.93 2.92 2.86 2.85 2.84 2.83 2.31 2.07 2.06 2.05 2.04 2.00 1.99 1.98 1.90 1.90 1.89 1.85 1.85 1.83 1.64 1.62 1.57 1.56 1.54 1.53 1.39 1.23 1.22 1.21 1.20 1.19 1.13 1.12 1.11 0.97 0.96 0.95 0.89 0.88 0.87 0.78 0.77 0.77 0.76
3.18 1.16 1.04 1.02 2.66 1.09 1.11 1.20 1.05 1.80 5.31 6.87 1.34 1.21 1.09 0.90 1.00
f1 (ppm)

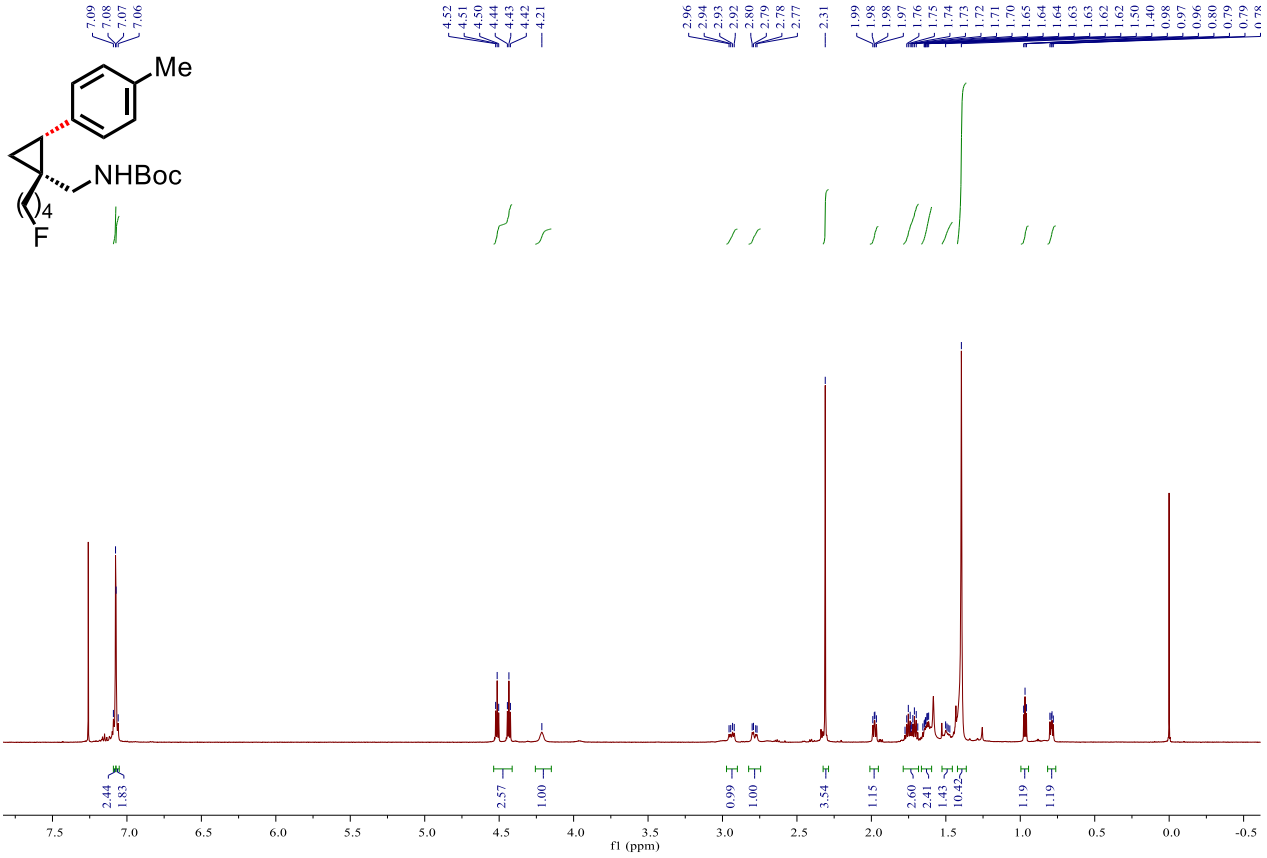

Me
NHBoc
155.99
135.69 135.63 129.14 128.67
79.01
42.52 38.22 33.56 33.40 29.85 28.52 28.30 26.94 25.12 21.14 15.51
f1 (ppm)

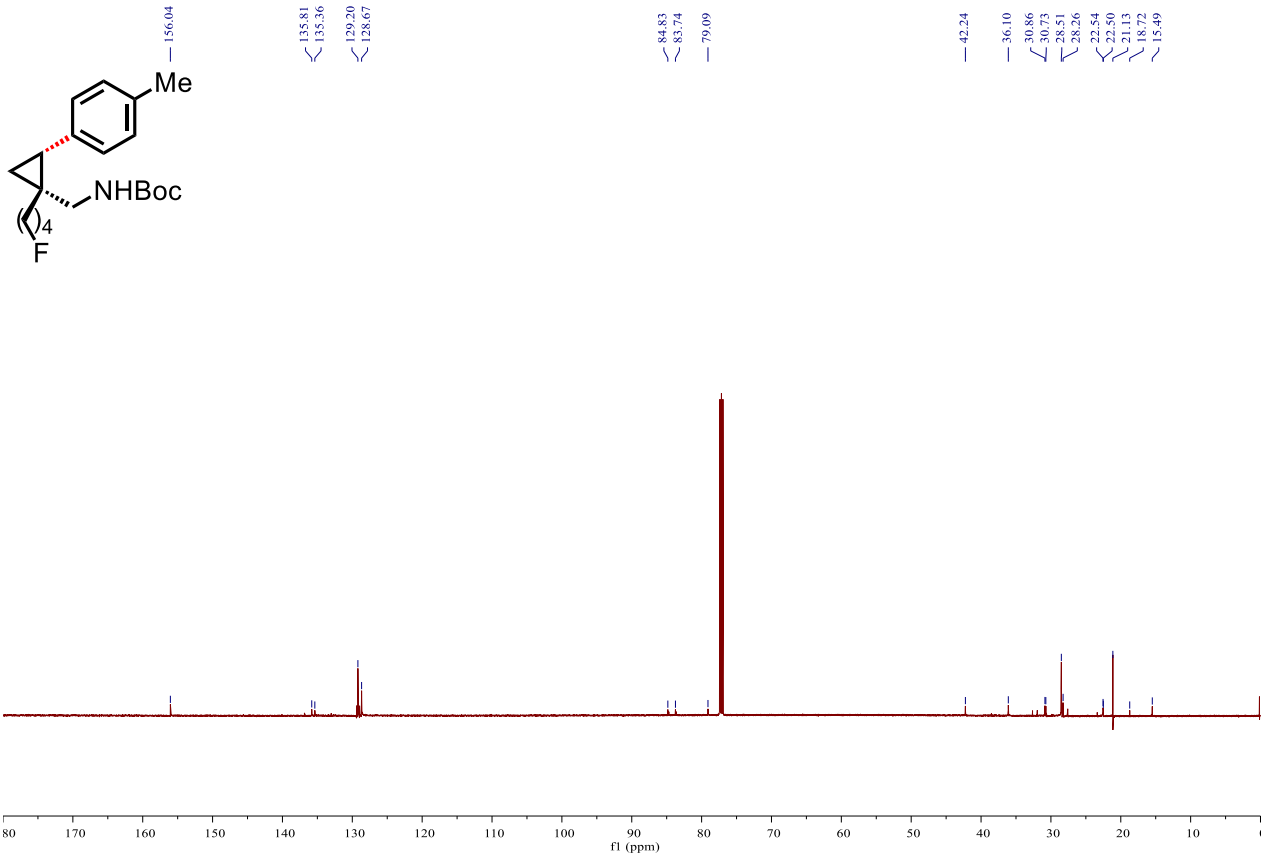

Me
NHBoc
f1 (ppm)

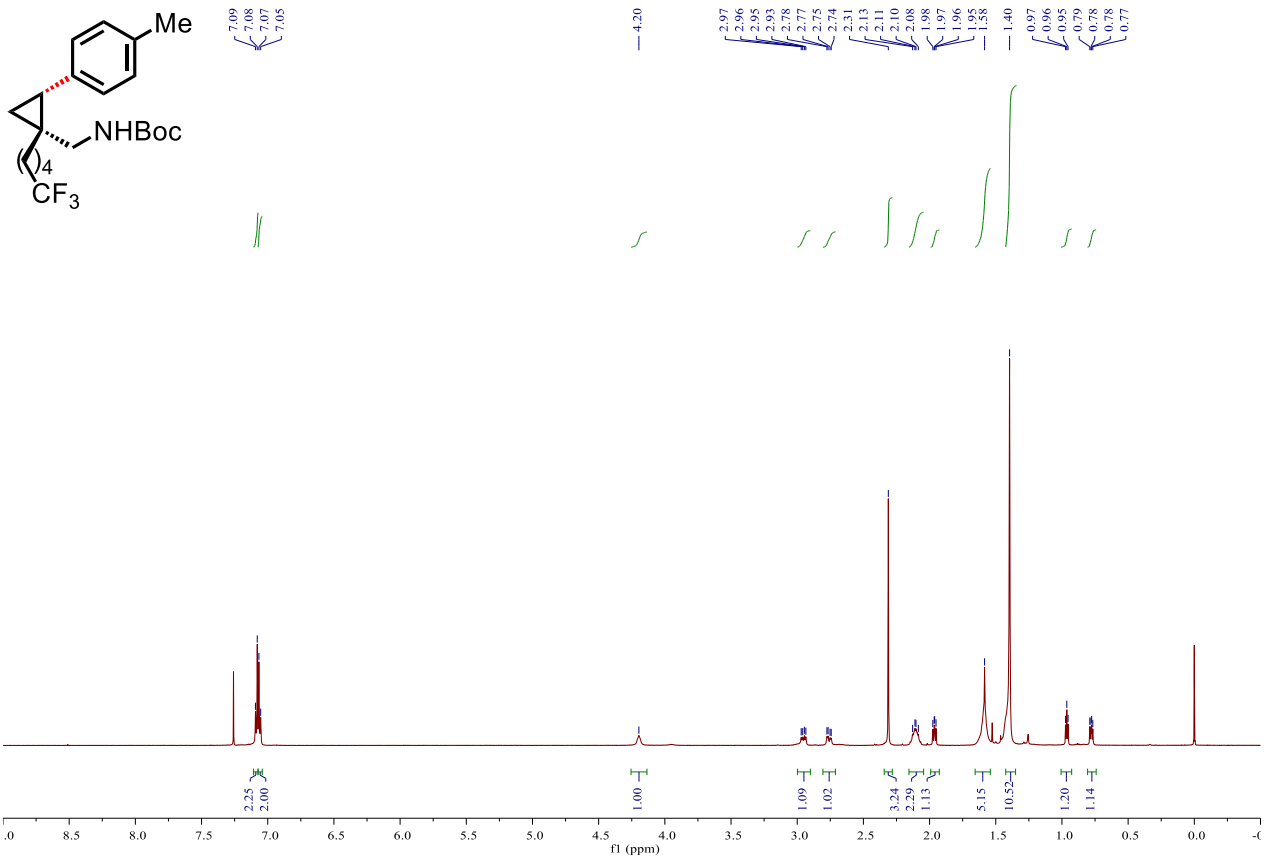

Me
NHBoc
f1 (ppm)

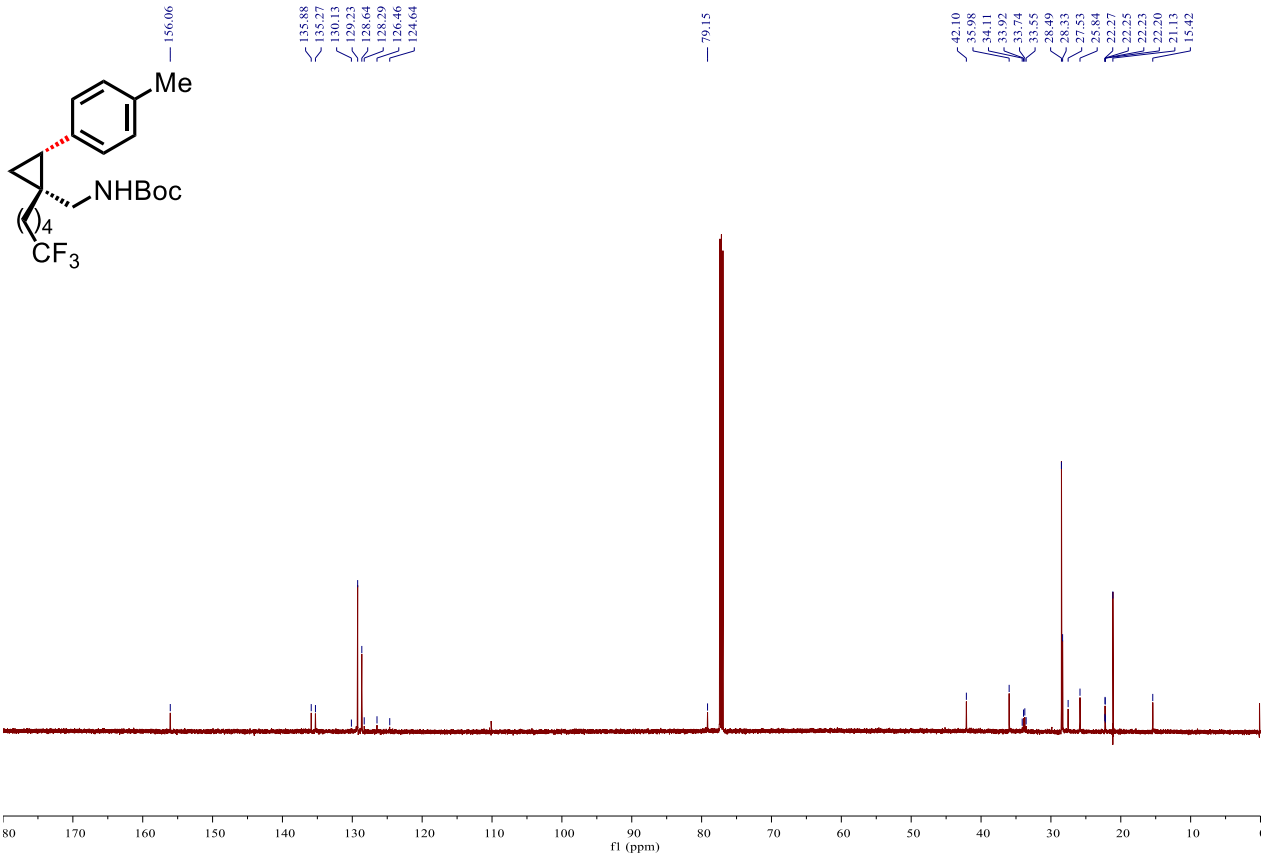

Me
NHBoc
O
f1 (ppm)

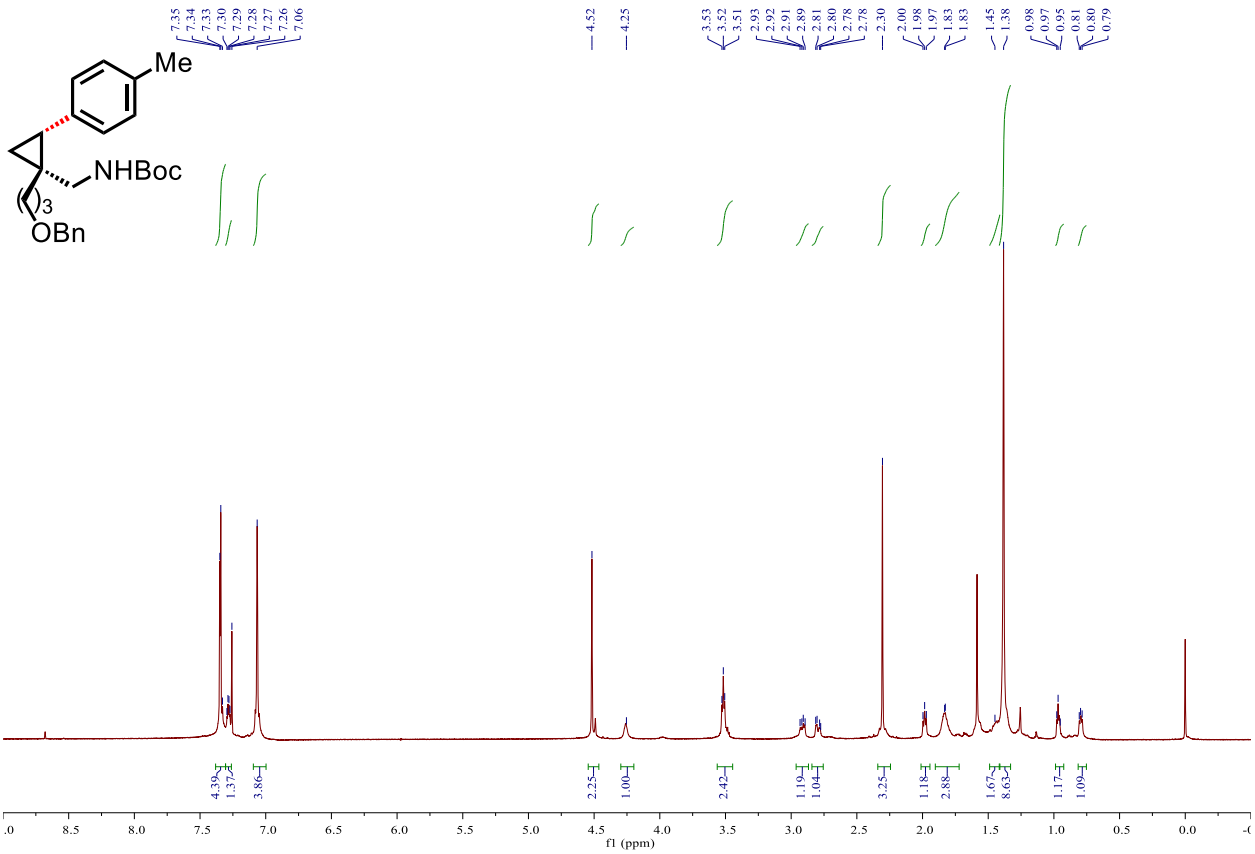

Me
NHBoc
O
f1 (ppm)

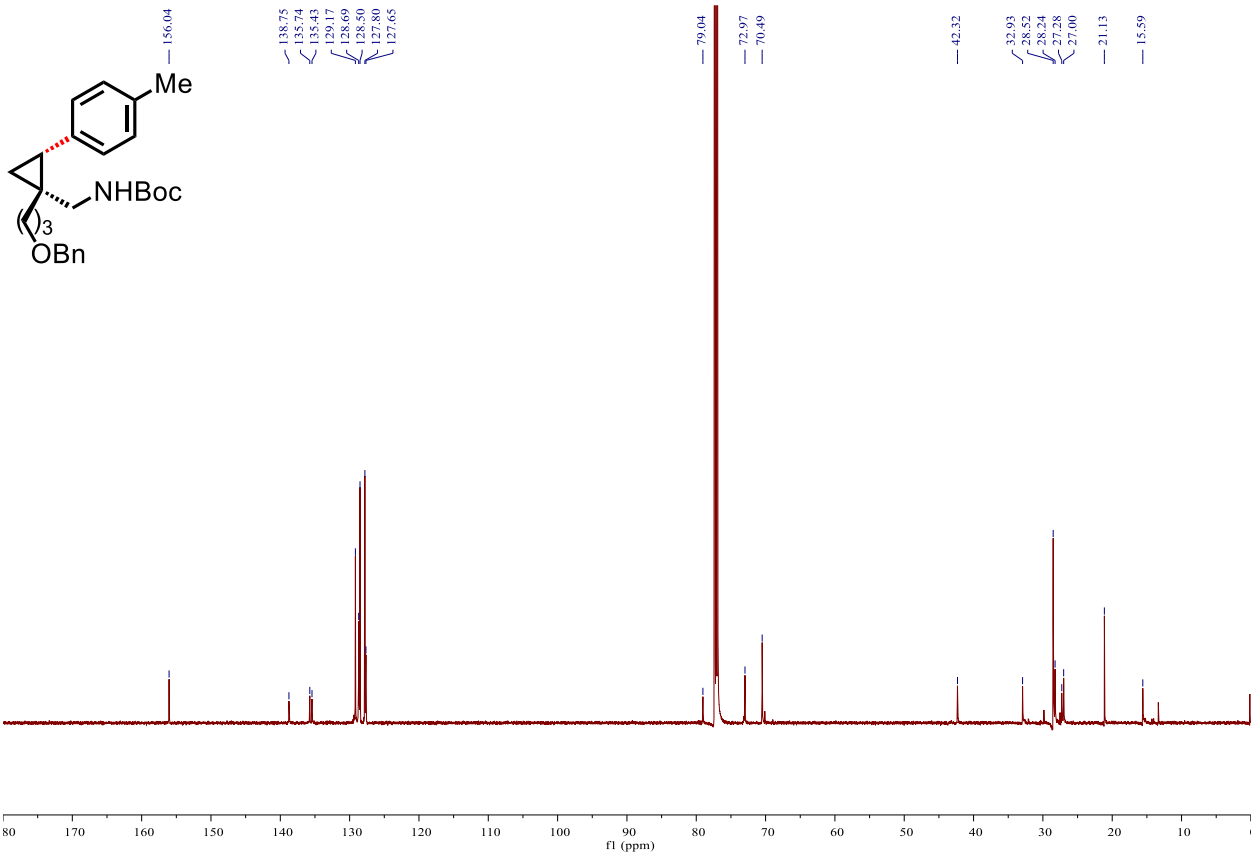

Me
NHBoc
4
F
f1 (ppm)

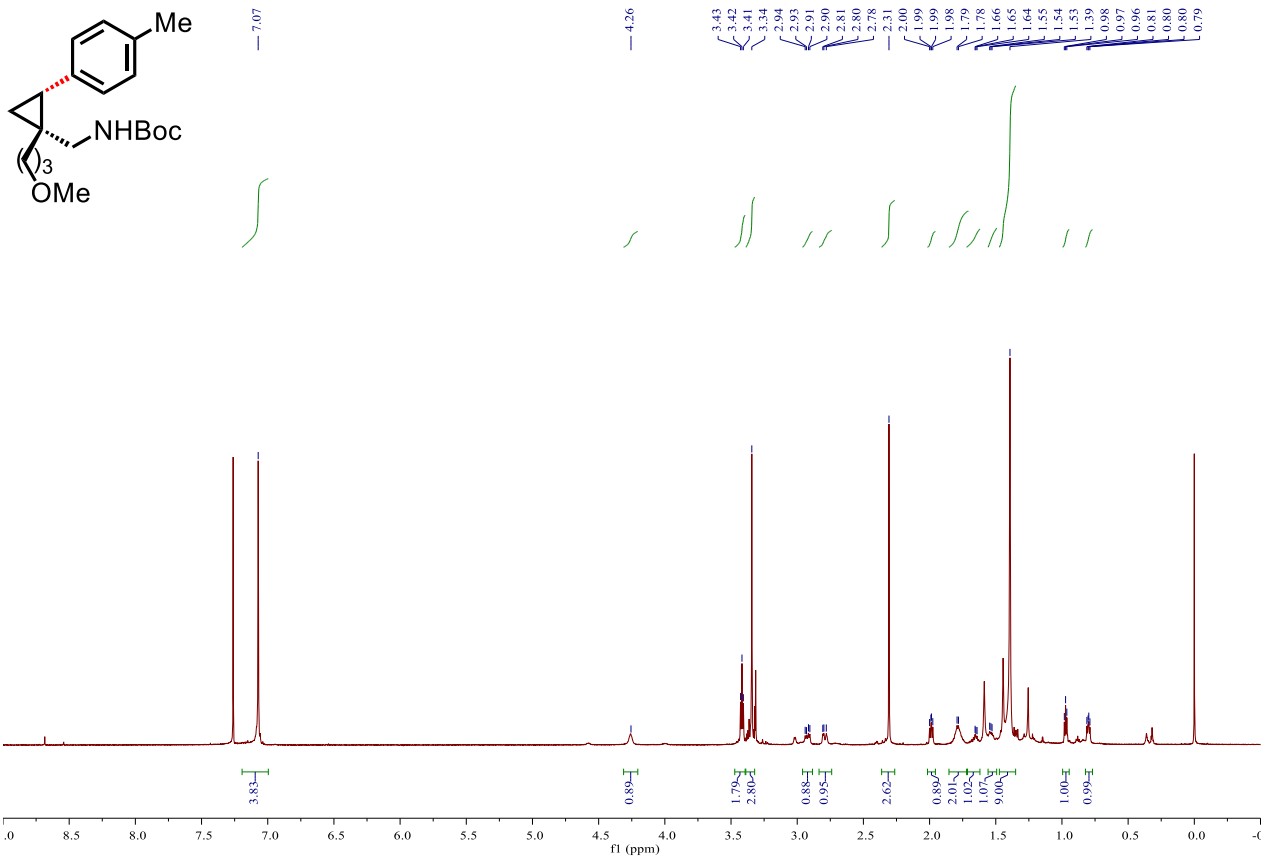

Me
NHBoc
4
F
f1 (ppm)

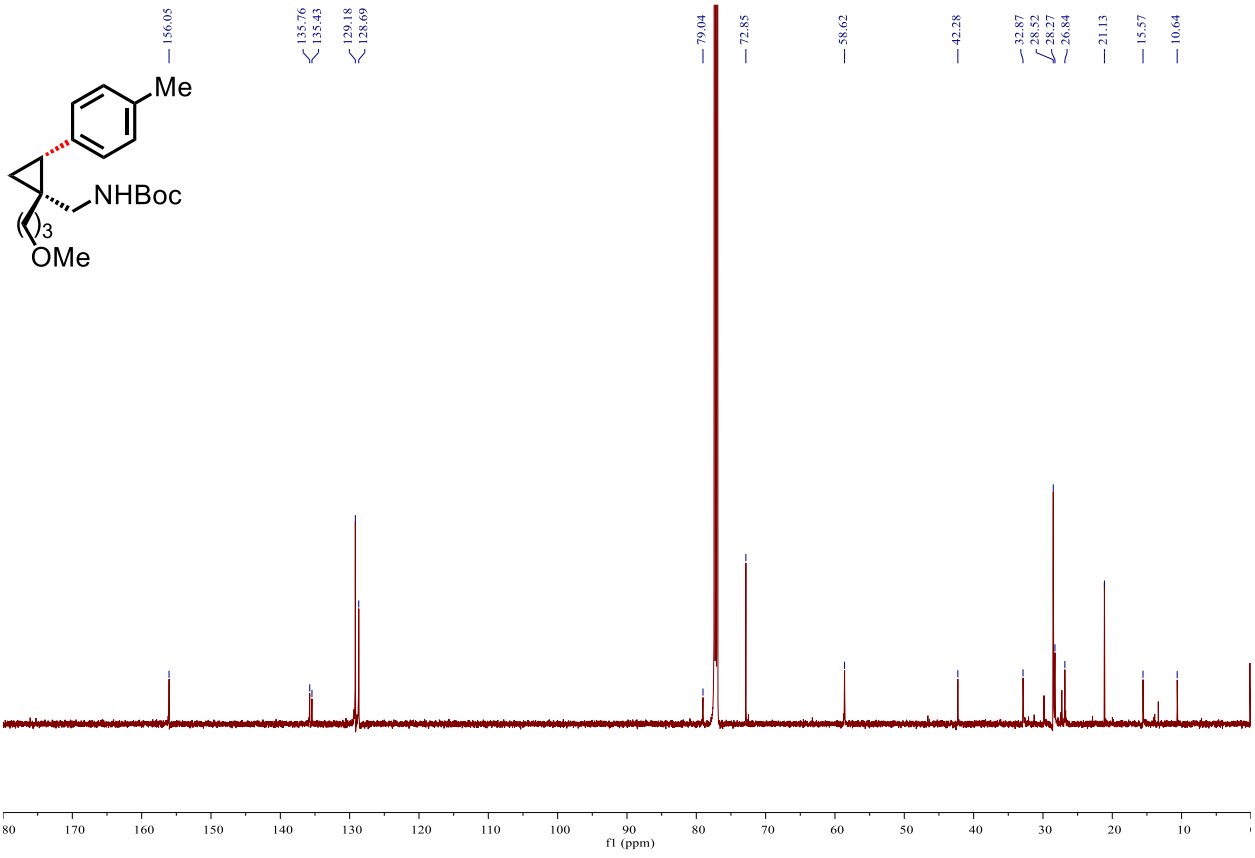

Me
NHBoc
4
CF3
7.09
7.08
7.07
7.05
4.20
2.97
2.96
2.95
2.93
2.78
2.77
2.75
2.74
2.31
2.13
2.11
2.10
2.08
1.98
1.97
1.96
1.95
1.58
1.40
0.97
0.96
0.95
0.79
0.78
0.78
0.77
2.25
2.00
1.00
1.09
1.02
3.24
2.29
1.13
5.15
10.52
1.20
1.14
f1 (ppm)

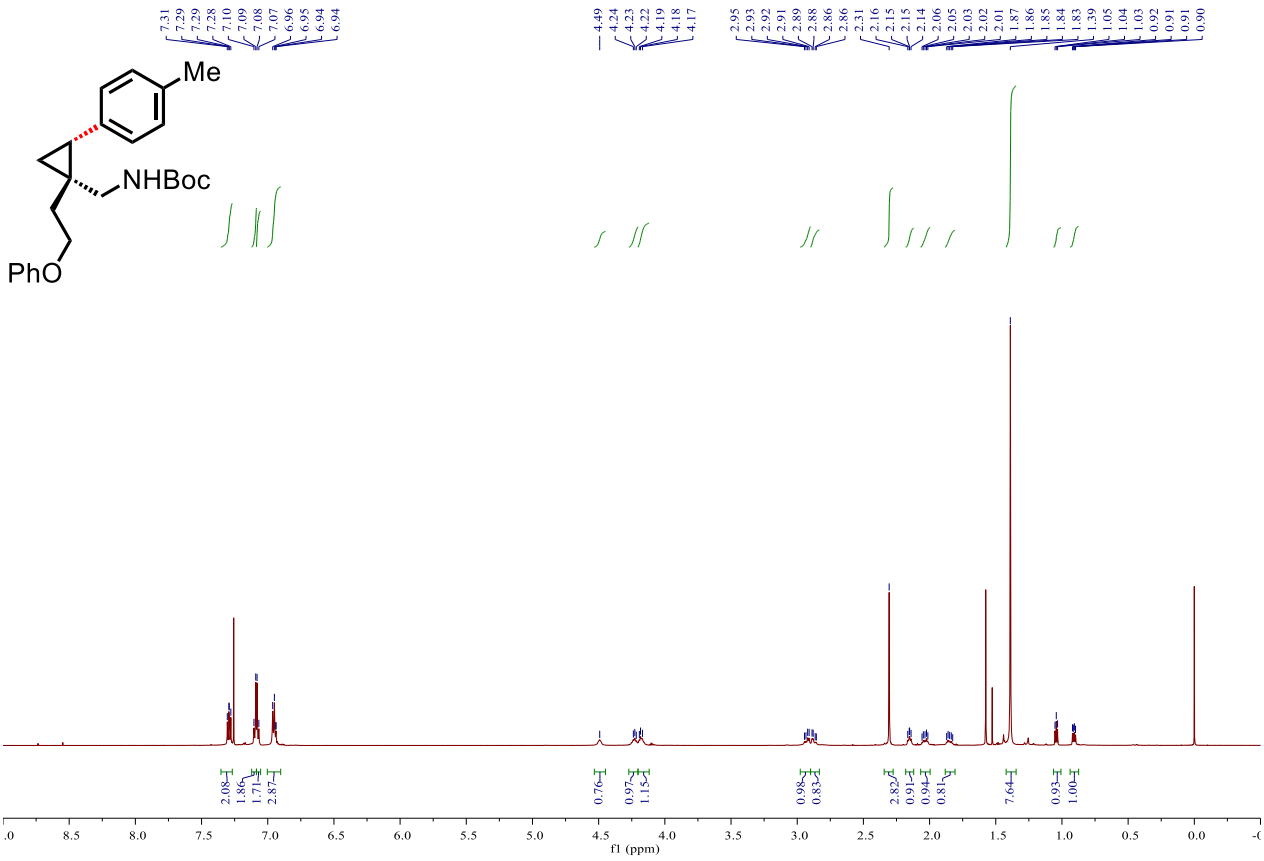

Me
NHBoc
4
CF3
156.06
135.88
135.27
130.13
129.23
128.64
128.29
126.46
124.64
79.15
42.10
35.98
34.11
33.92
33.74
33.55
28.49
28.33
27.53
25.84
22.27
22.25
22.23
22.20
21.13
15.42
f1 (ppm)

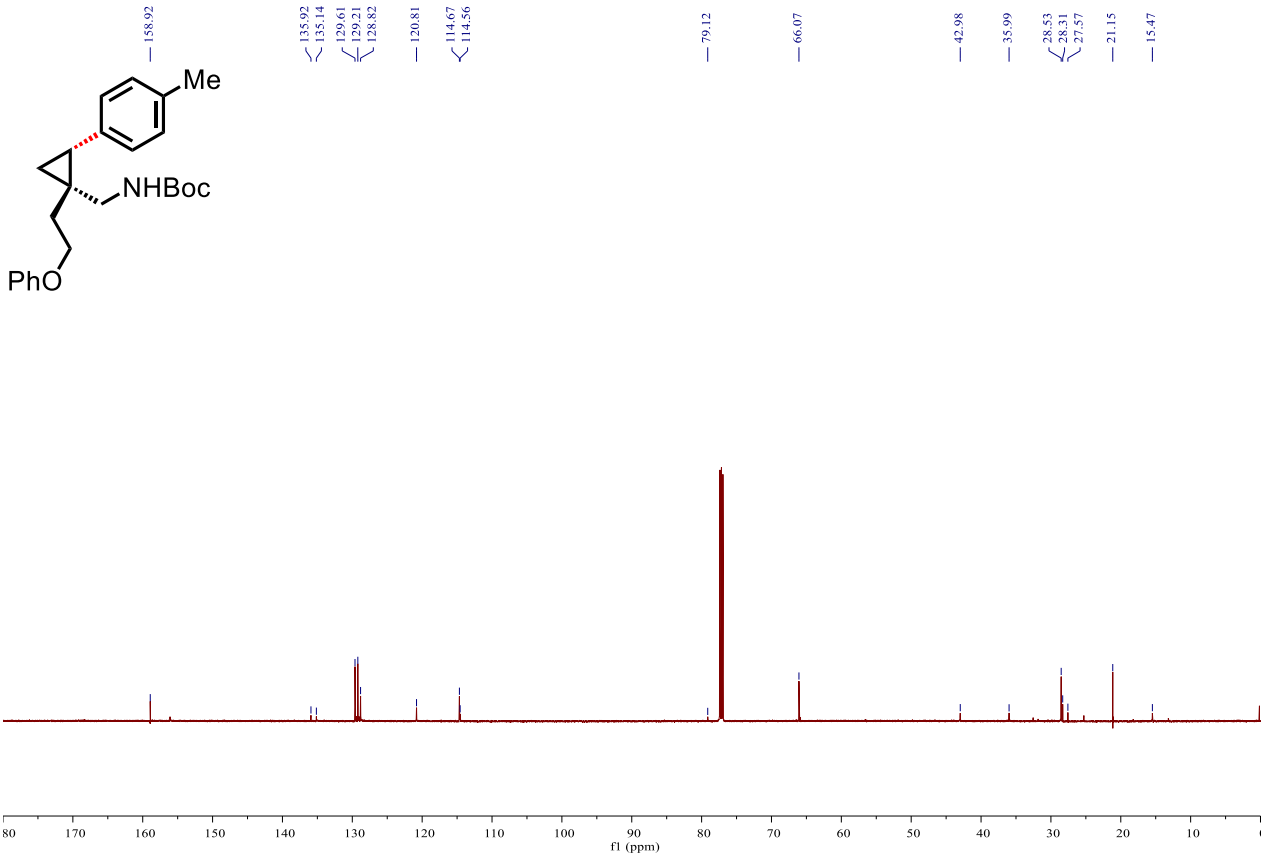

Me
NHBoc
3
OBn
7.35
7.34
7.33
7.30
7.29
7.28
7.27
7.26
7.06
4.52
4.25
3.53
3.52
3.51
2.93
2.92
2.91
2.89
2.81
2.80
2.78
2.78
2.30
2.00
1.98
1.97
1.83
1.83
1.45
1.38
0.98
0.97
0.95
0.81
0.80
0.79
4.39
1.37
3.86
2.25
1.00
2.42
1.19
1.04
3.25
1.18
2.88
1.67
8.63
1.17
1.09
f1 (ppm)

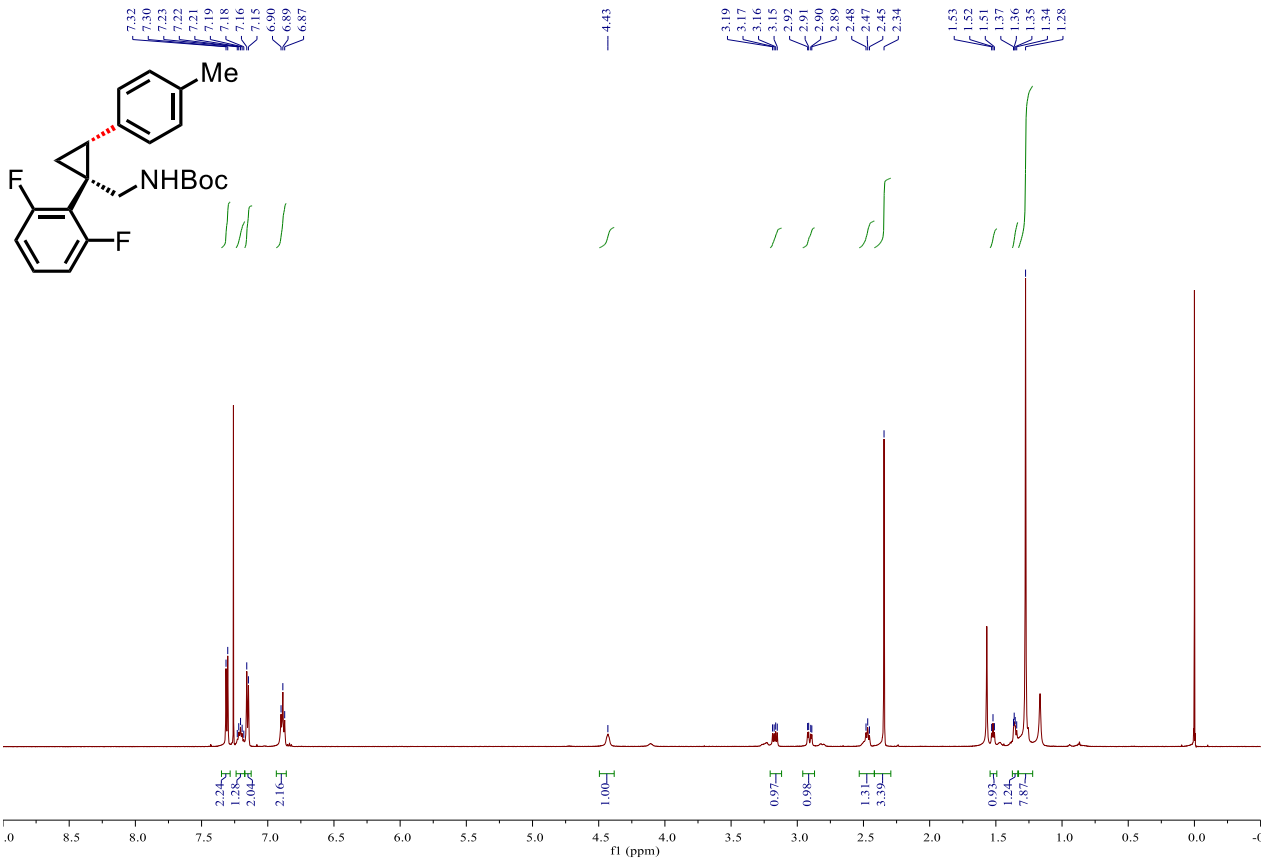

Me
NHBoc
3
OBn
156.04
138.75
135.74
135.43
129.17
128.69
128.50
127.80
127.65
79.04
72.97
70.49
42.32
32.93
28.52
28.24
27.28
27.00
21.13
15.59
f1 (ppm)

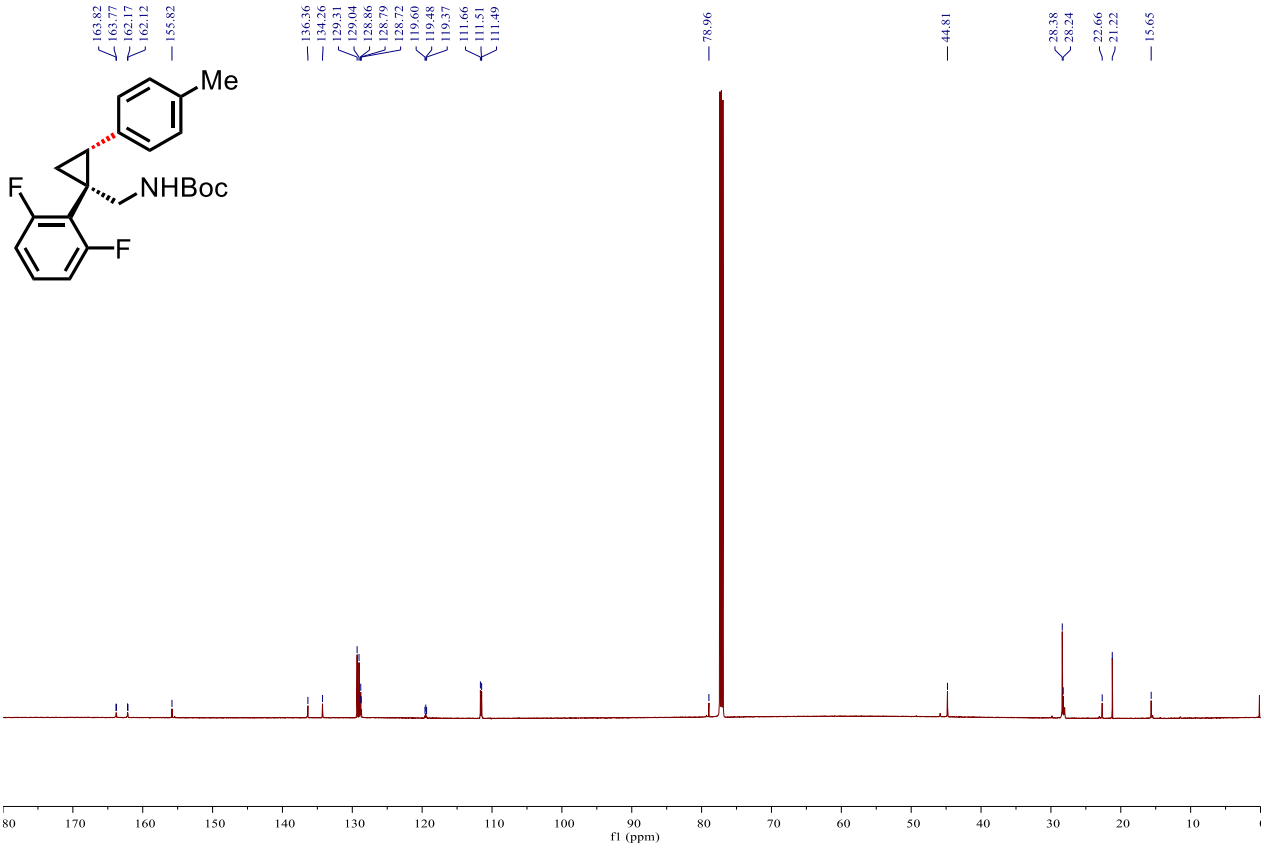

Me
NHBoc
3
OMe
f1 (ppm)

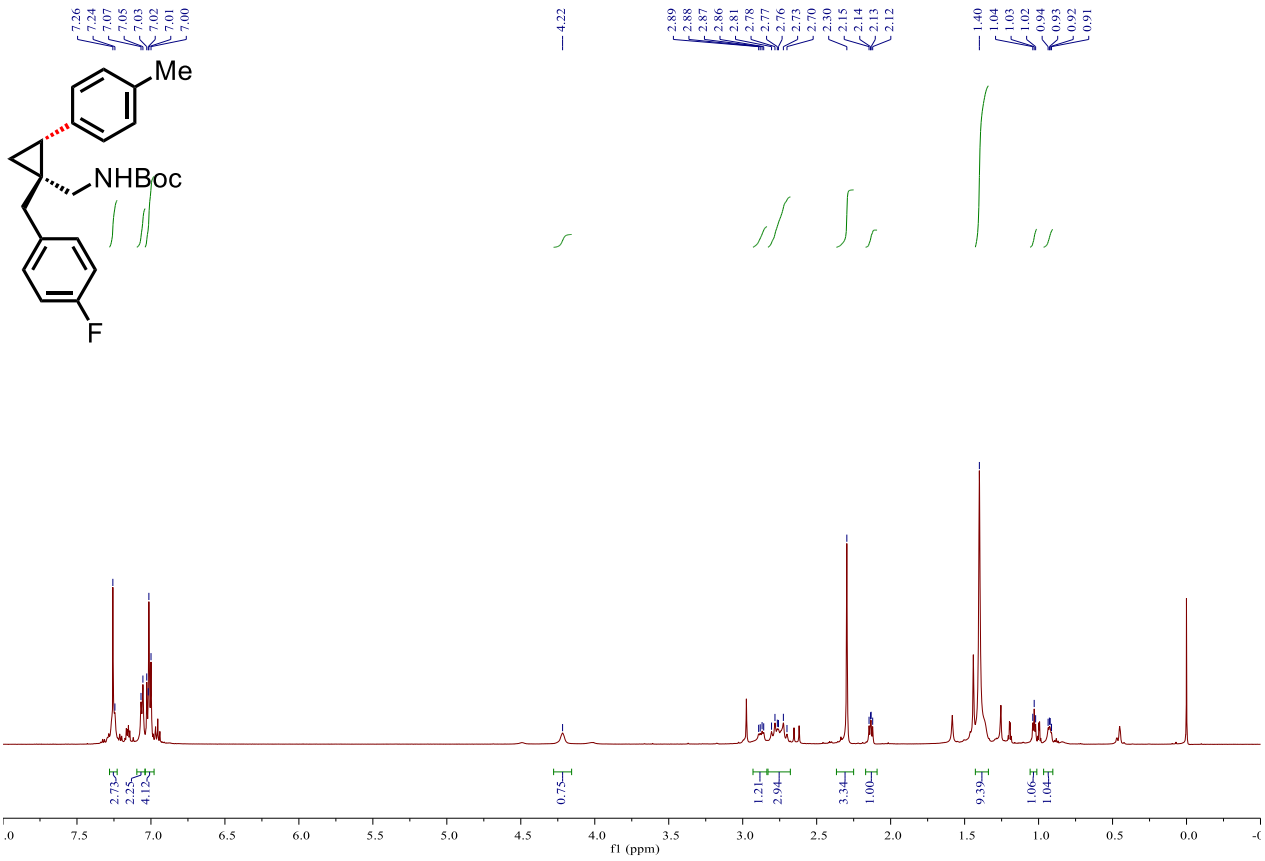

Me
NHBoc
3
OMe
f1 (ppm)

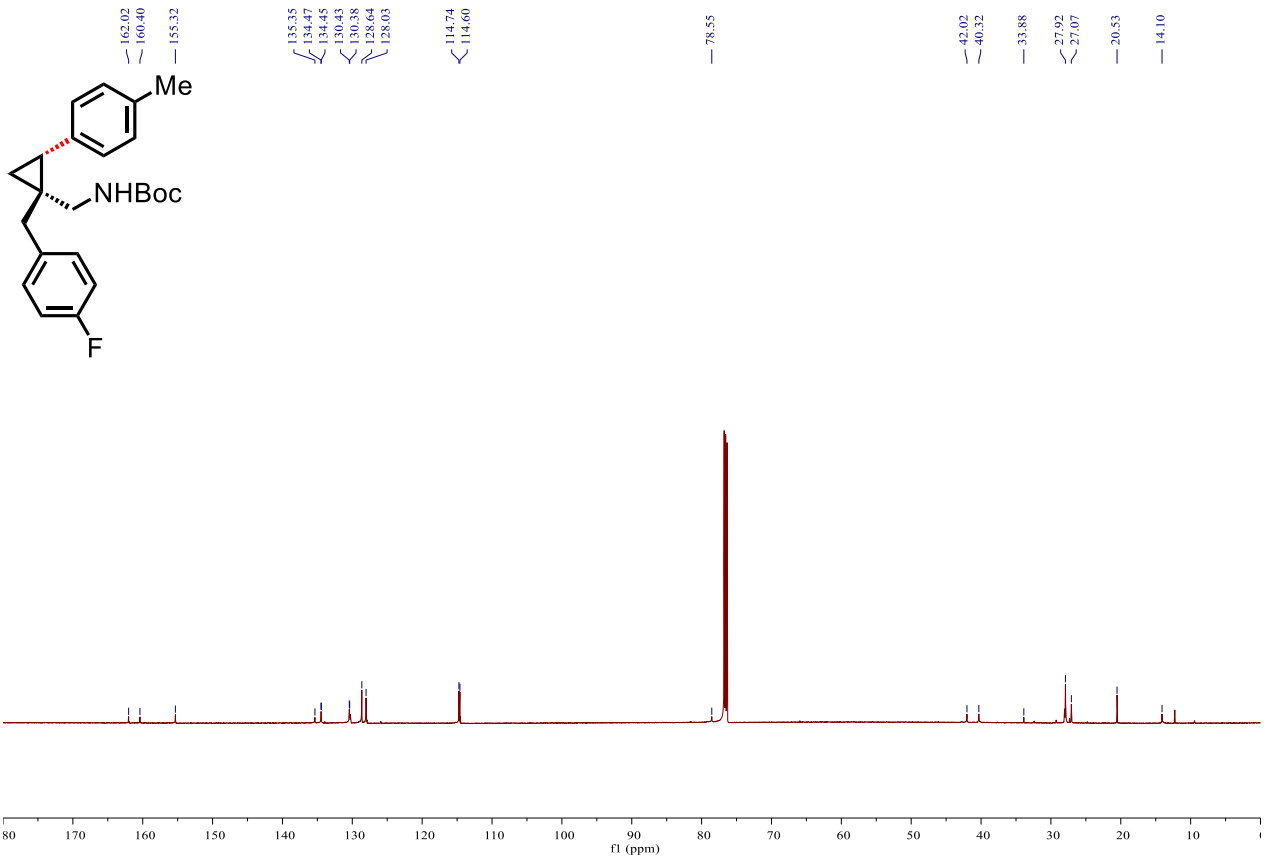

Me
NHBoc
PhO
f1 (ppm)

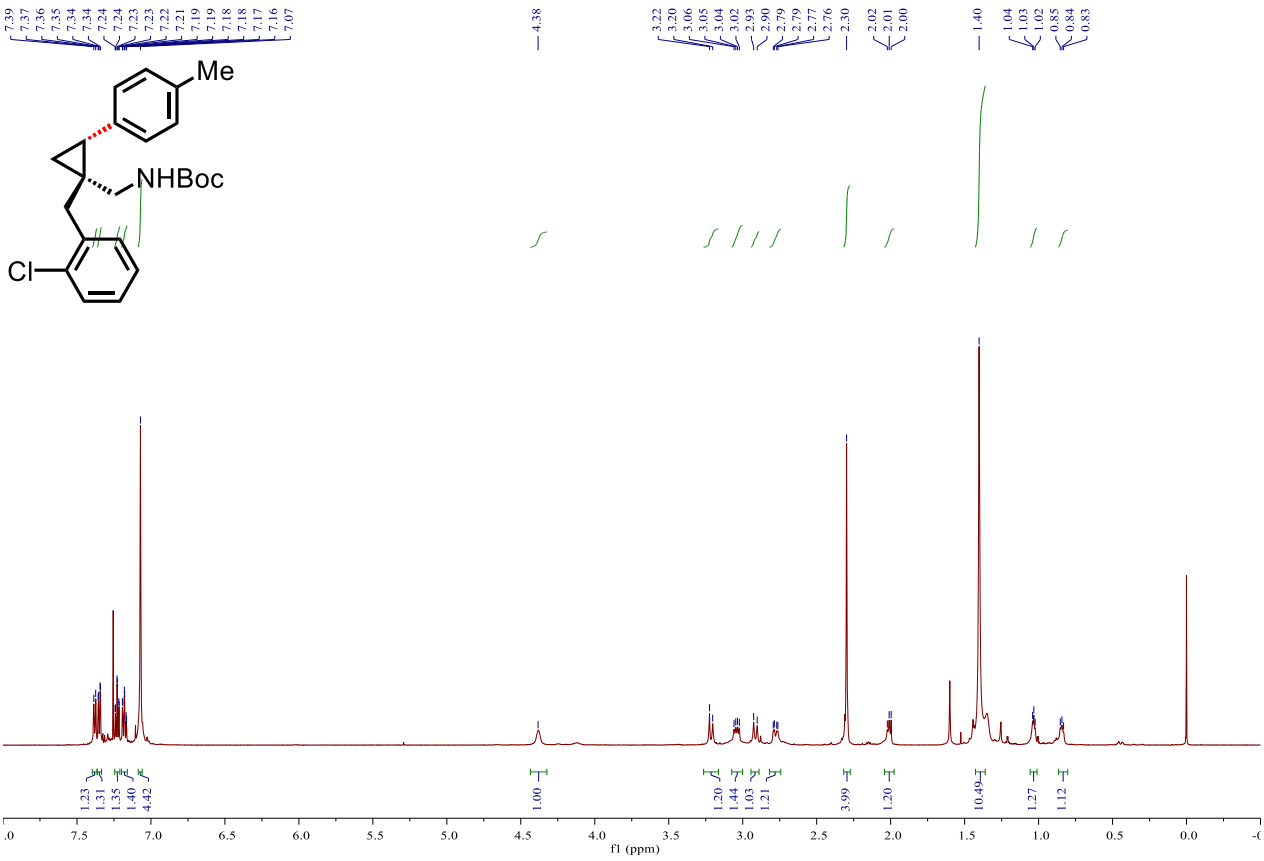

Me
NHBoc
PhO
f1 (ppm)

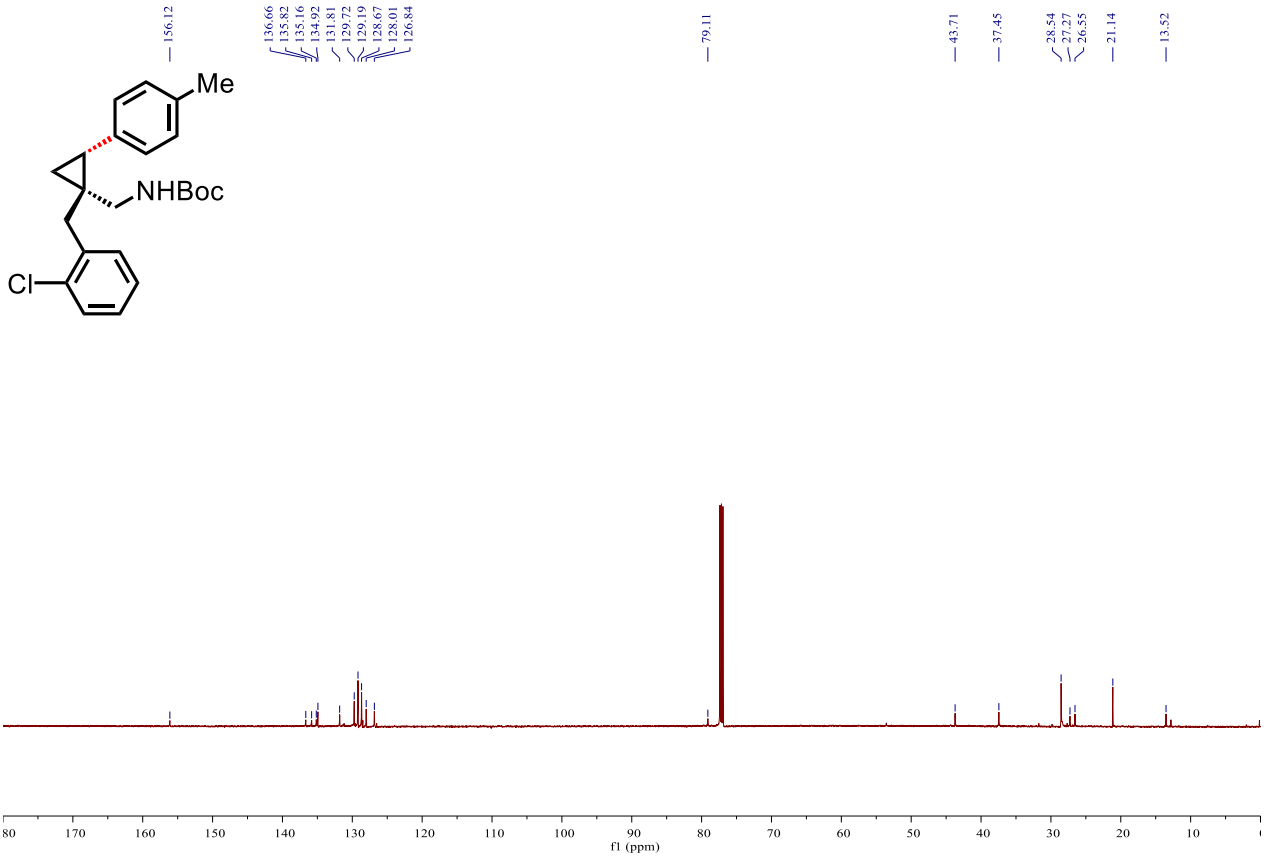

Me
F
NHBoc
F
f1 (ppm)

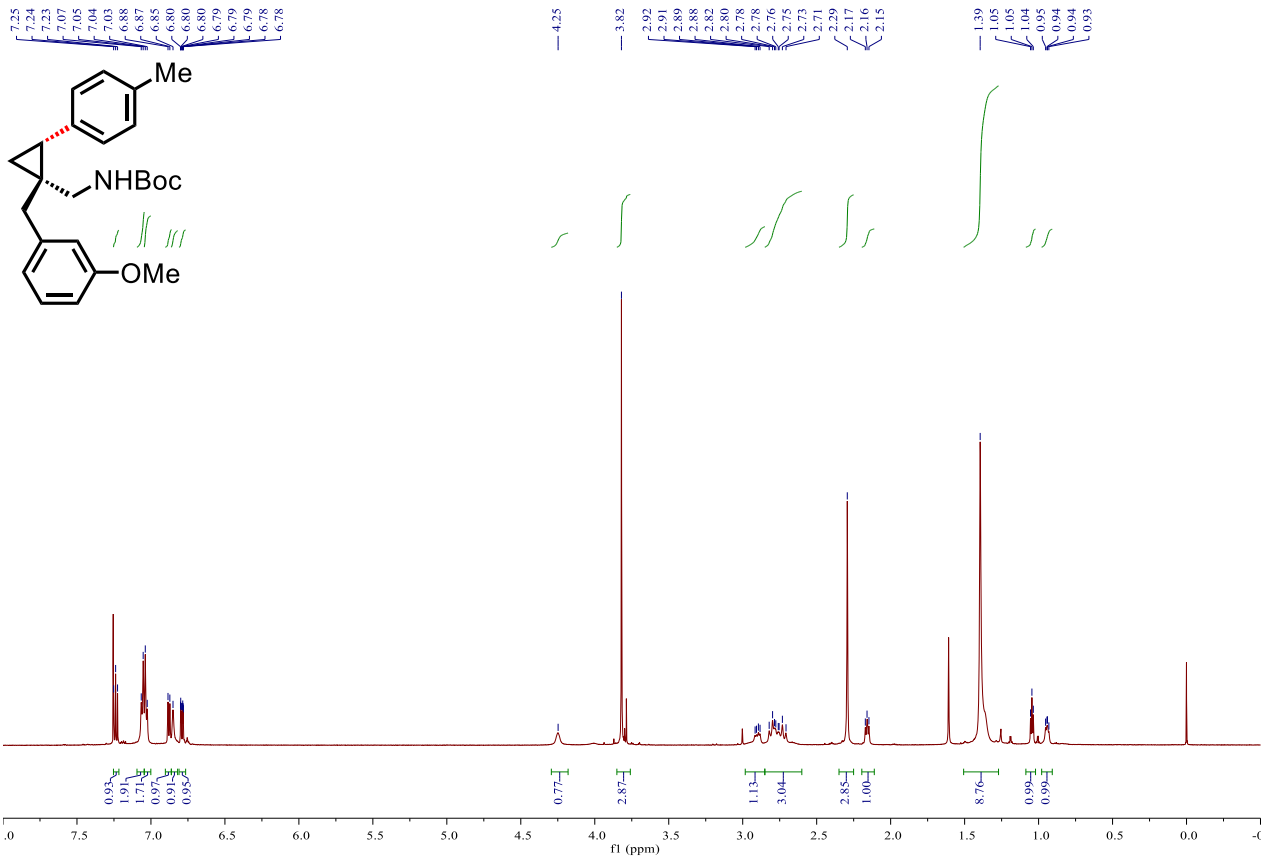

Me
F
NHBoc
F
f1 (ppm)

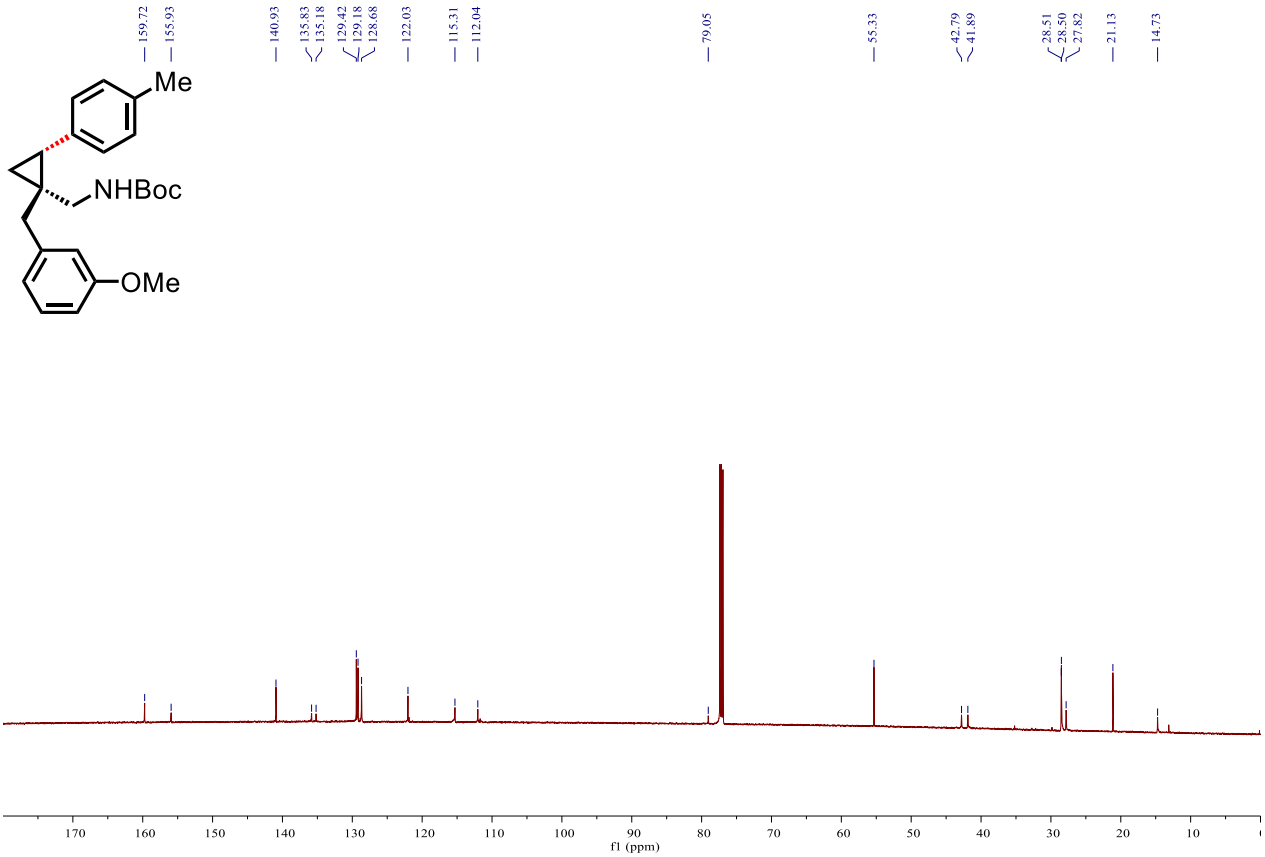

Me
NHBoc
F
f1 (ppm)

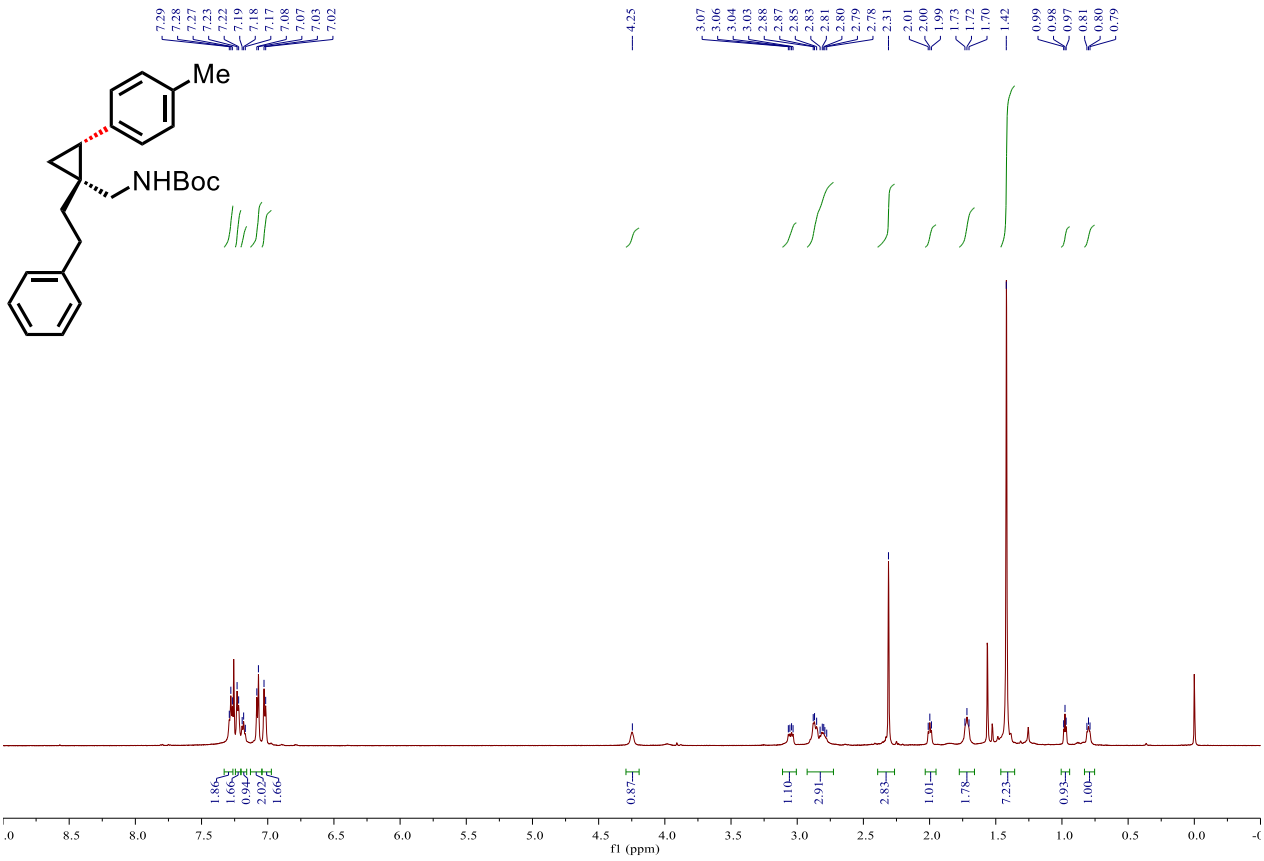

Me
NHBoc
F
f1 (ppm)

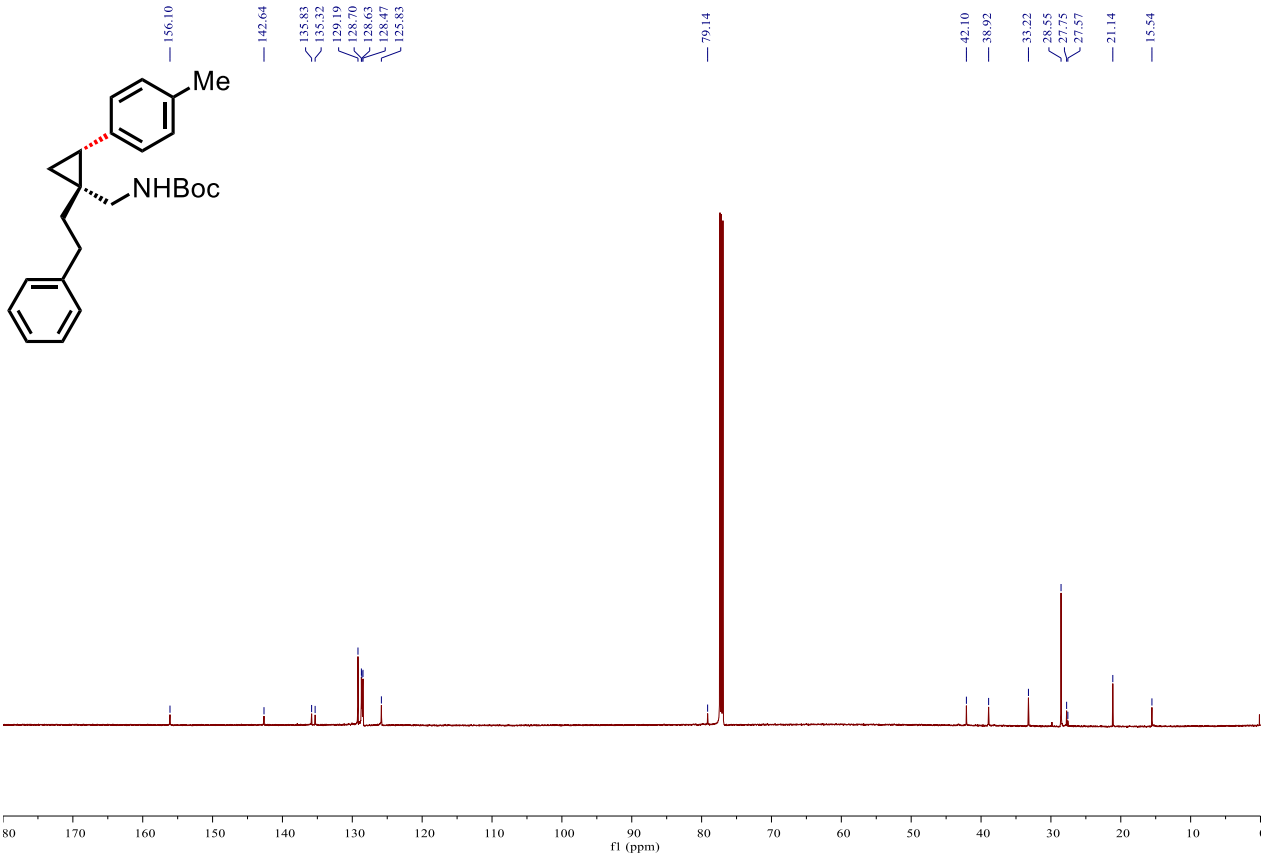

Me
NHBoc
Cl
f1 (ppm)

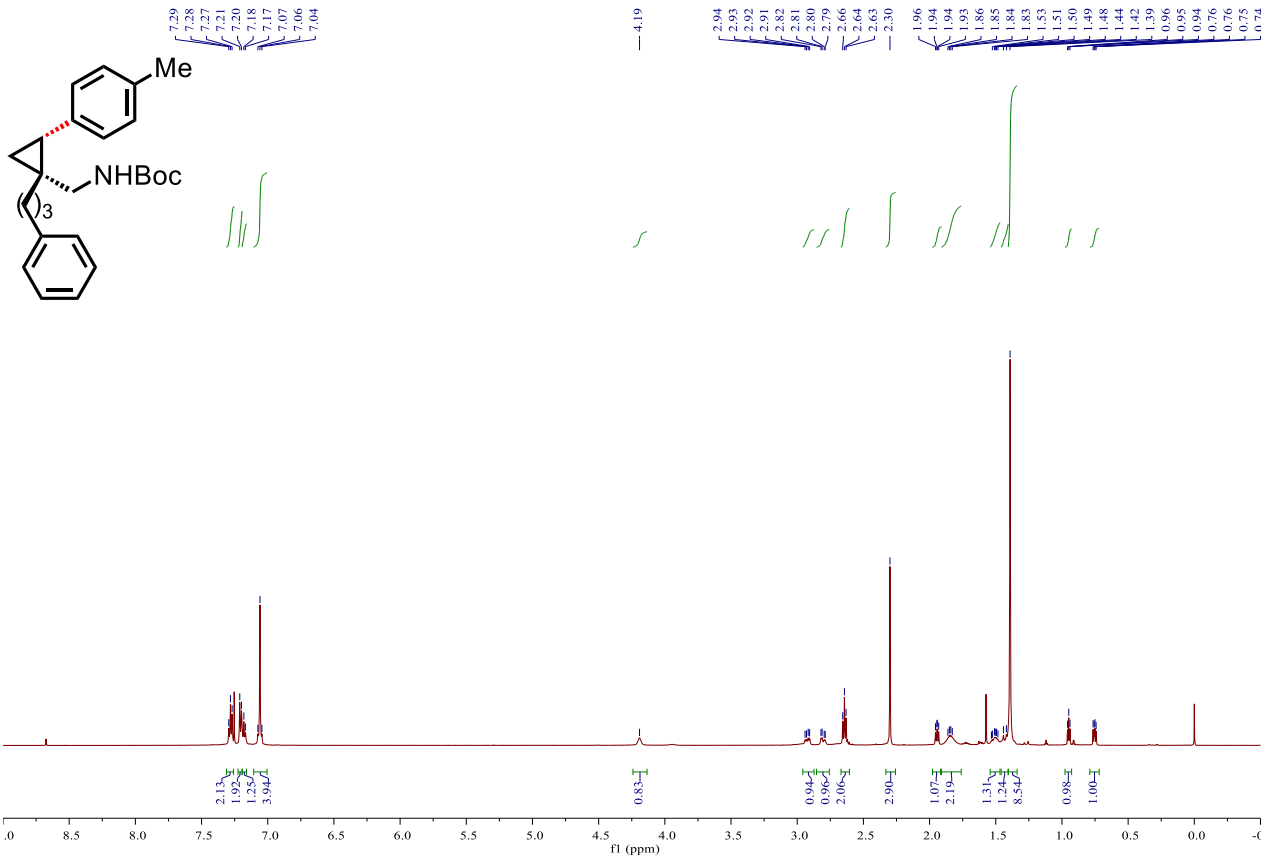

Me
NHBoc
Cl
f1 (ppm)

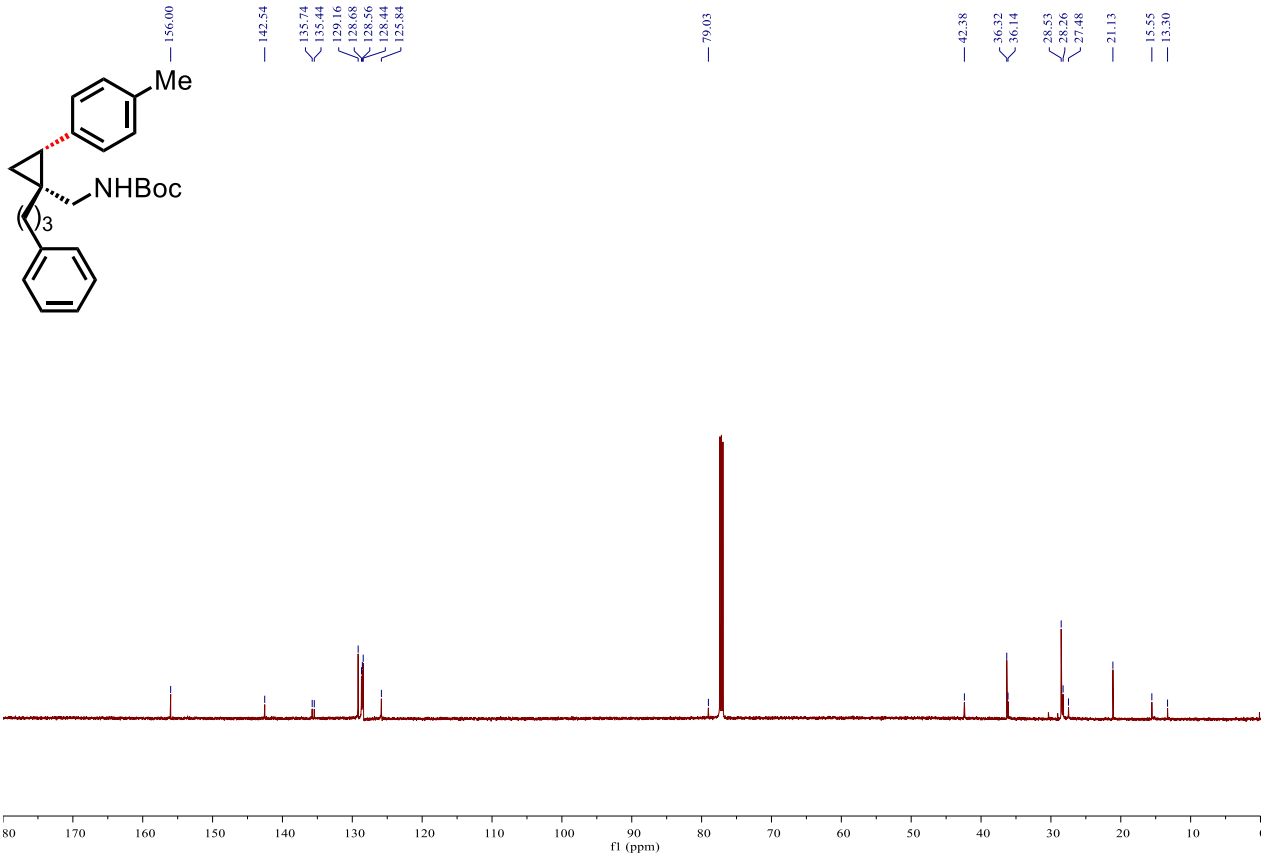

Me
NHBoc
OMe
f1 (ppm)

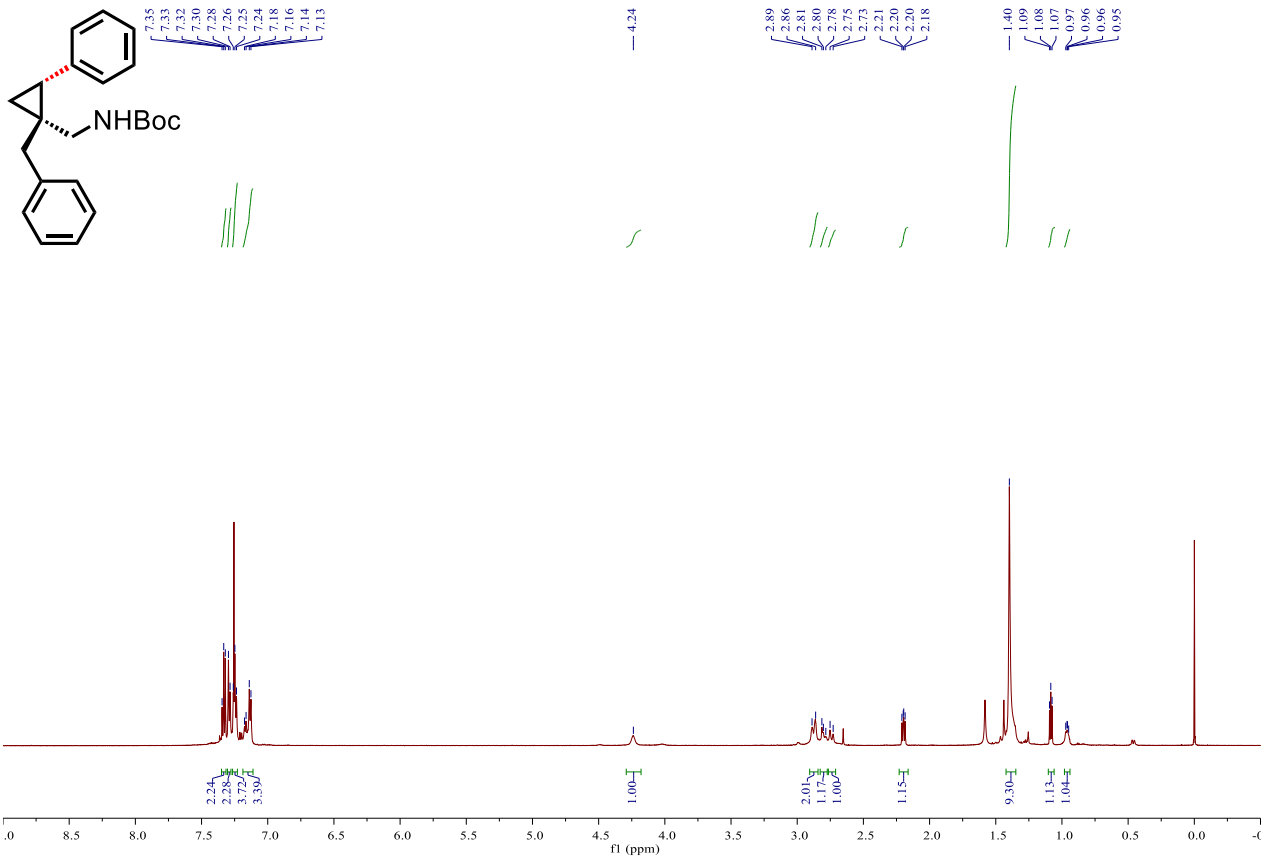

Me
NHBoc
OMe
f1 (ppm)

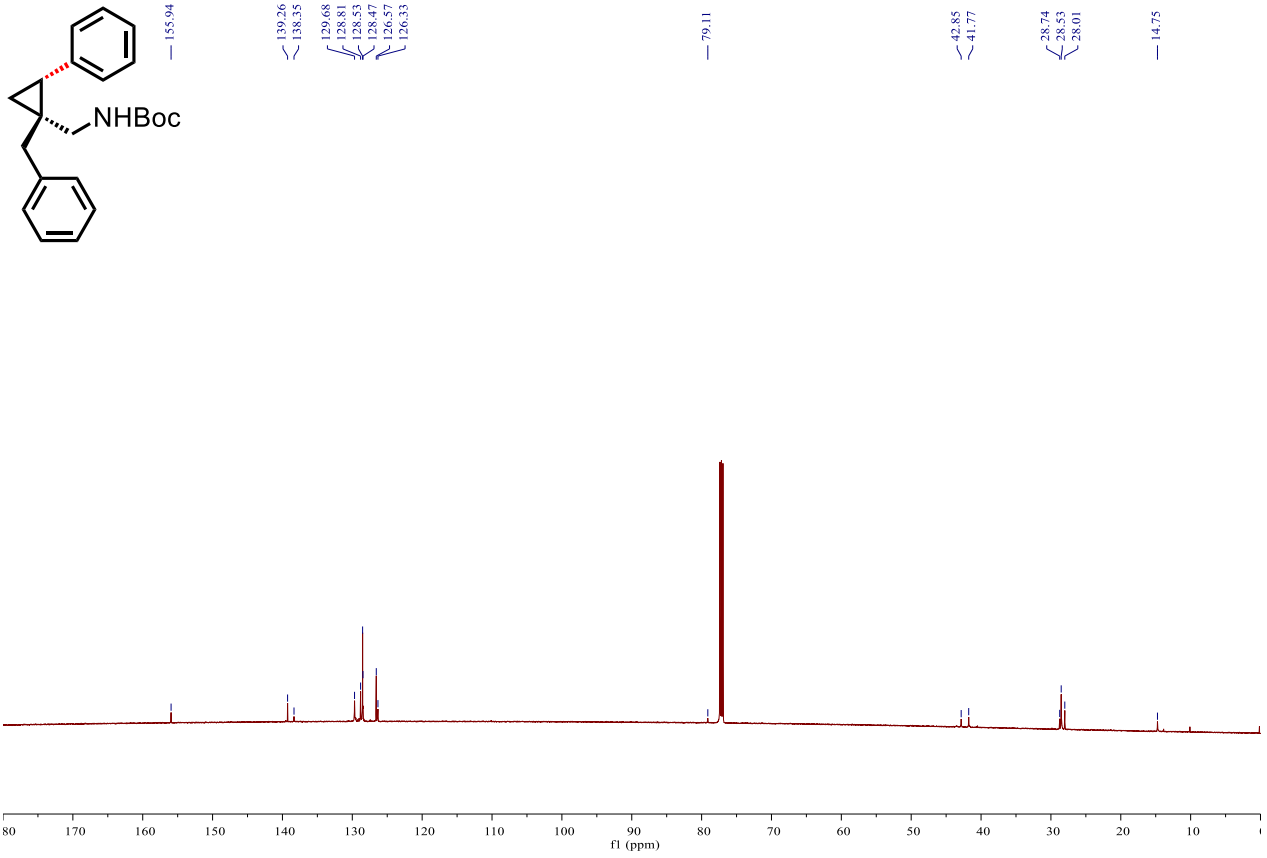

Me
NHBoc
f1 (ppm)

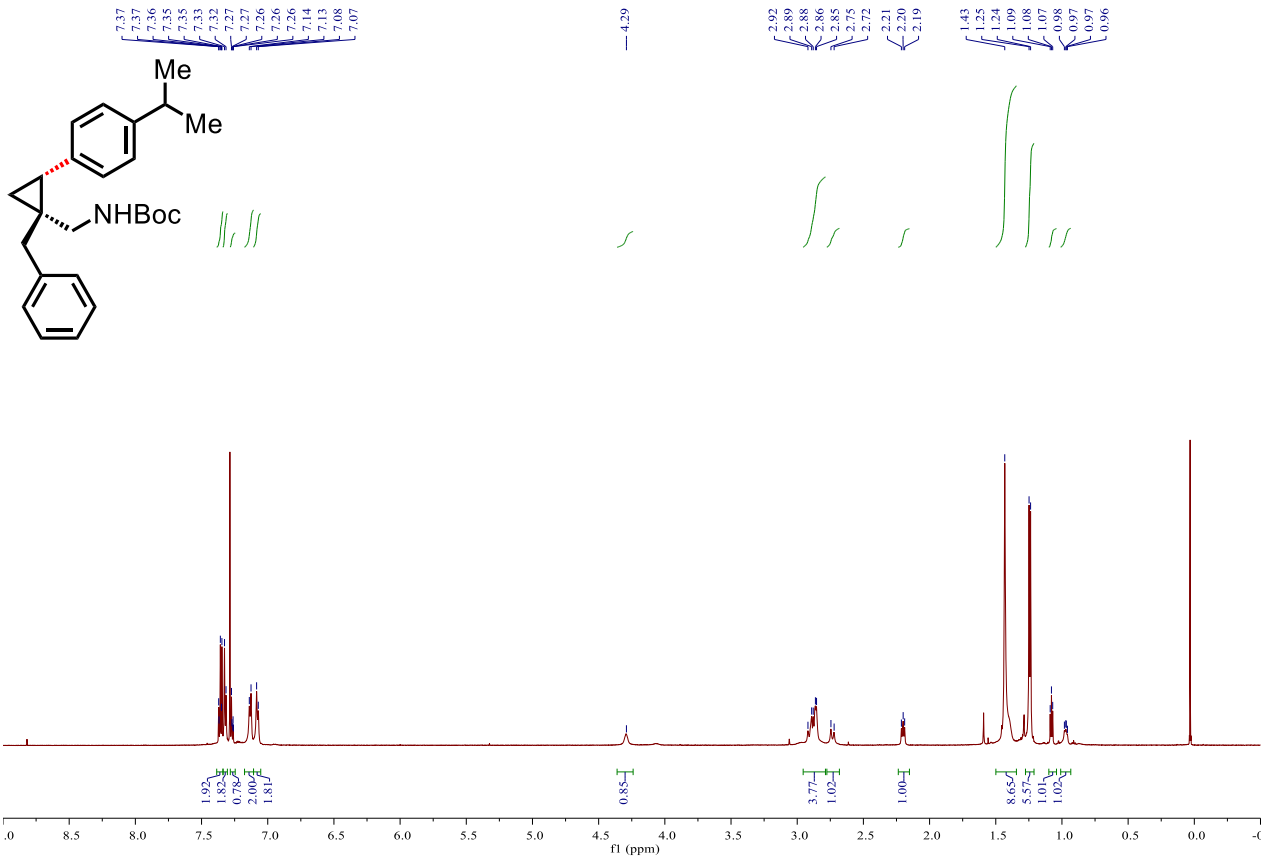

Me
NHBoc
f1 (ppm)

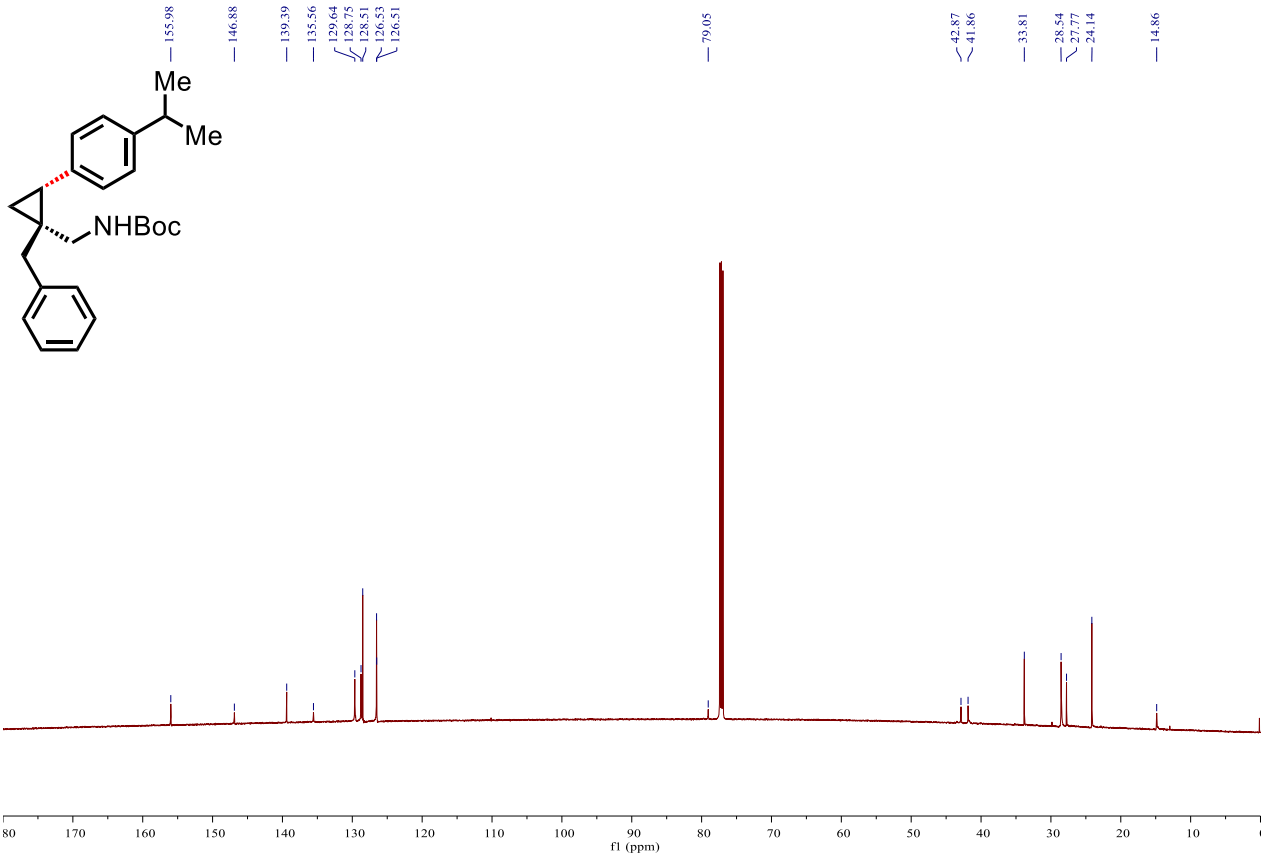

Me
NHBoc
3
f1 (ppm)

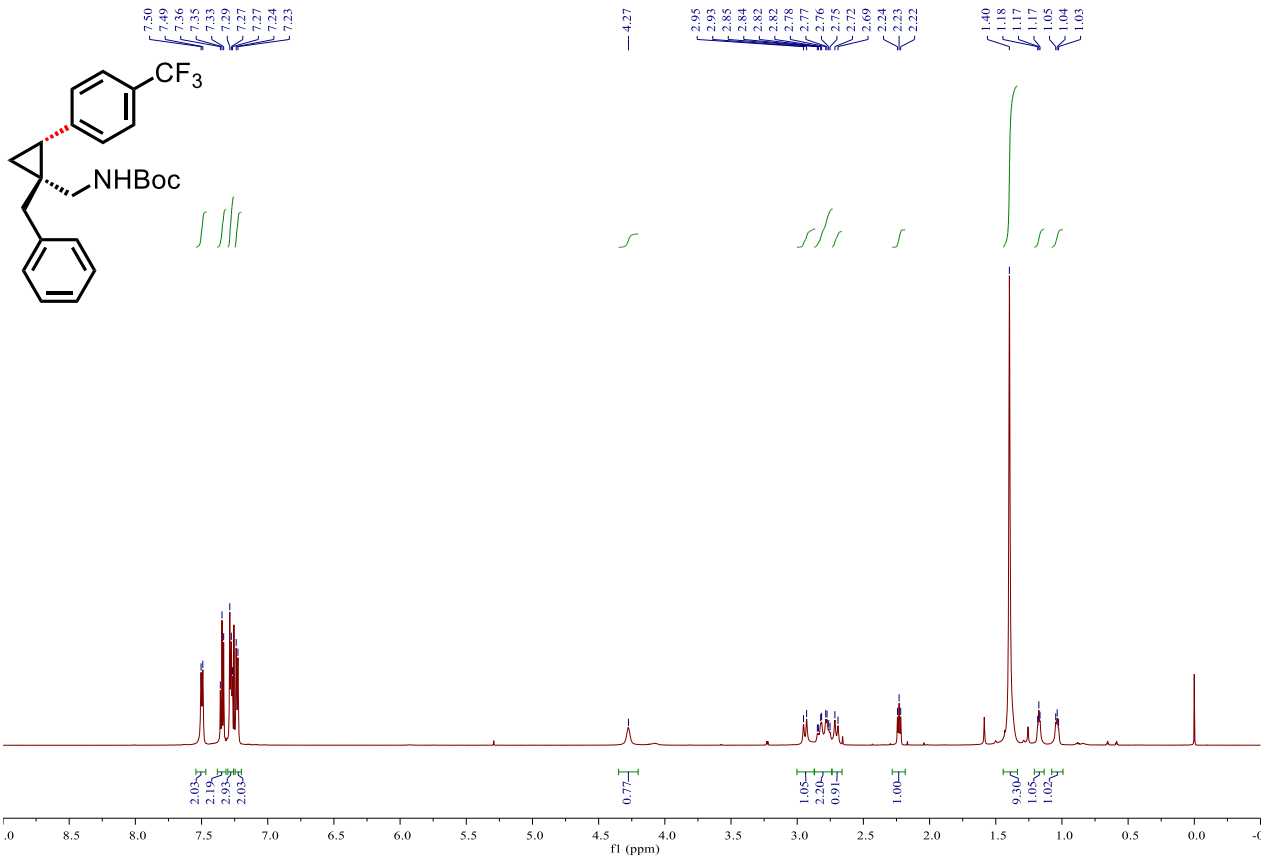

Me
NHBoc
3
f1 (ppm)

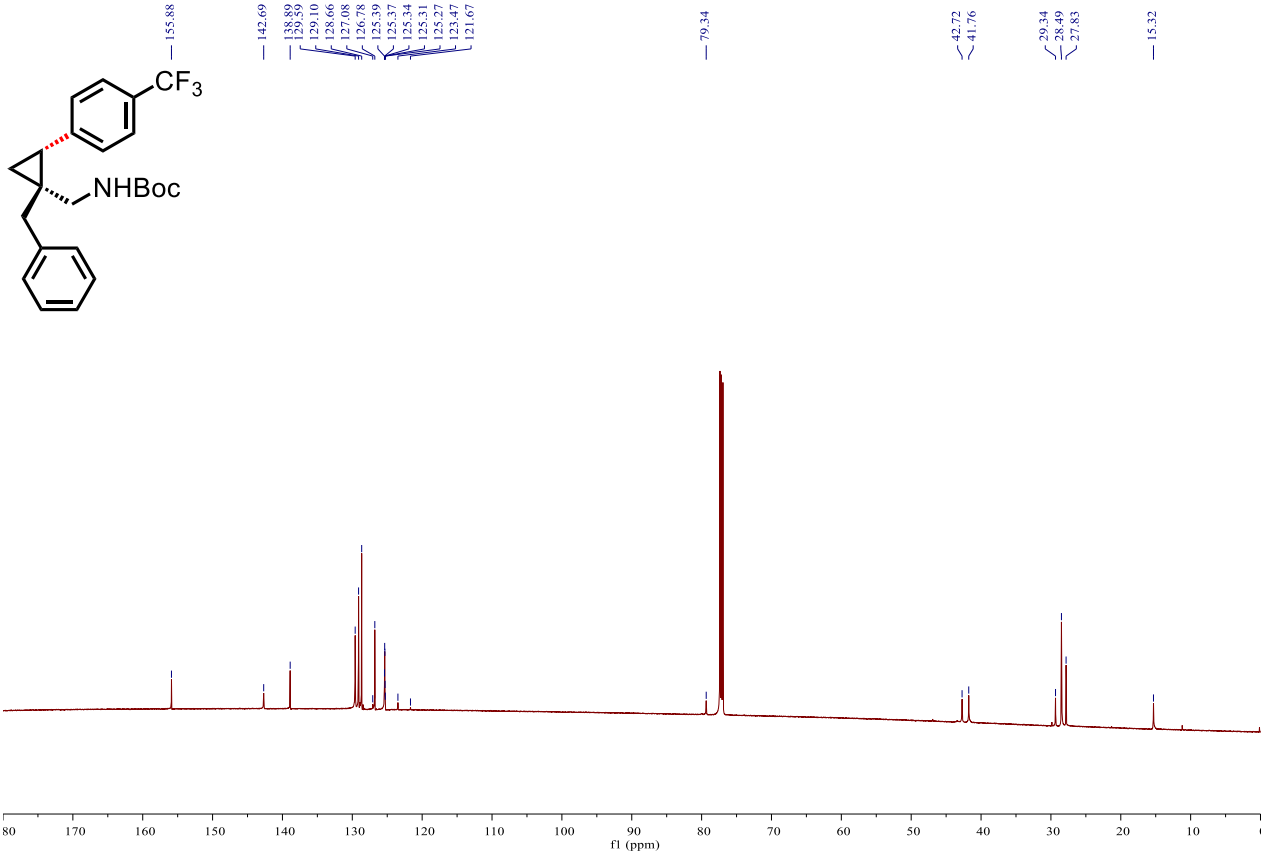

NHBoc
7.35
7.33
7.32
7.30
7.28
7.26
7.25
7.24
7.18
7.16
7.14
7.13
4.24
2.89
2.86
2.81
2.80
2.78
2.75
2.73
2.21
2.20
2.20
2.18
1.40
1.09
1.08
1.07
0.97
0.96
0.96
0.95
2.24
2.28
3.72
3.39
1.00
2.01
1.17
1.00
1.15
9.30
1.13
1.04
f1 (ppm)

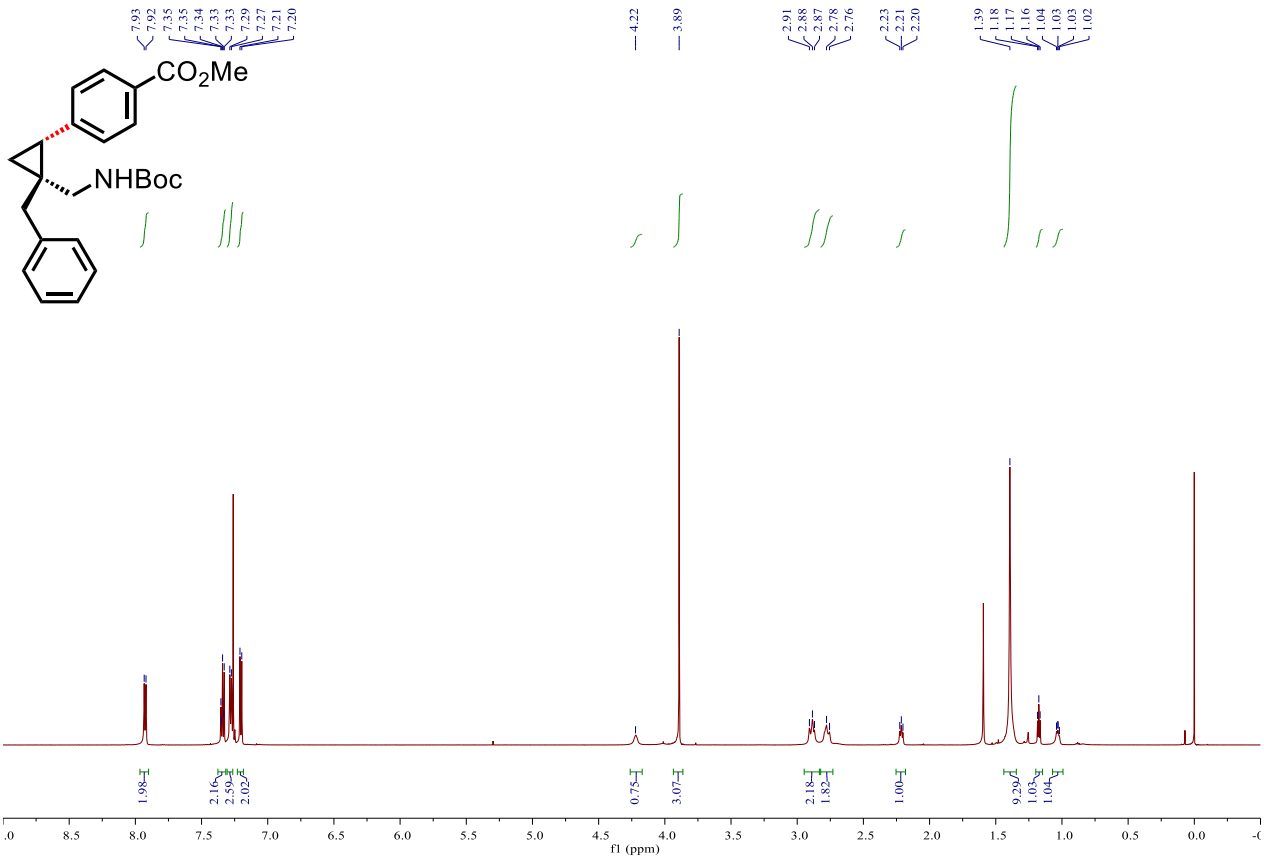

NHBoc
155.94
139.26
138.35
129.68
128.81
128.53
128.47
126.57
126.33
79.11
42.85
41.77
28.74
28.53
28.01
14.75
f1 (ppm)

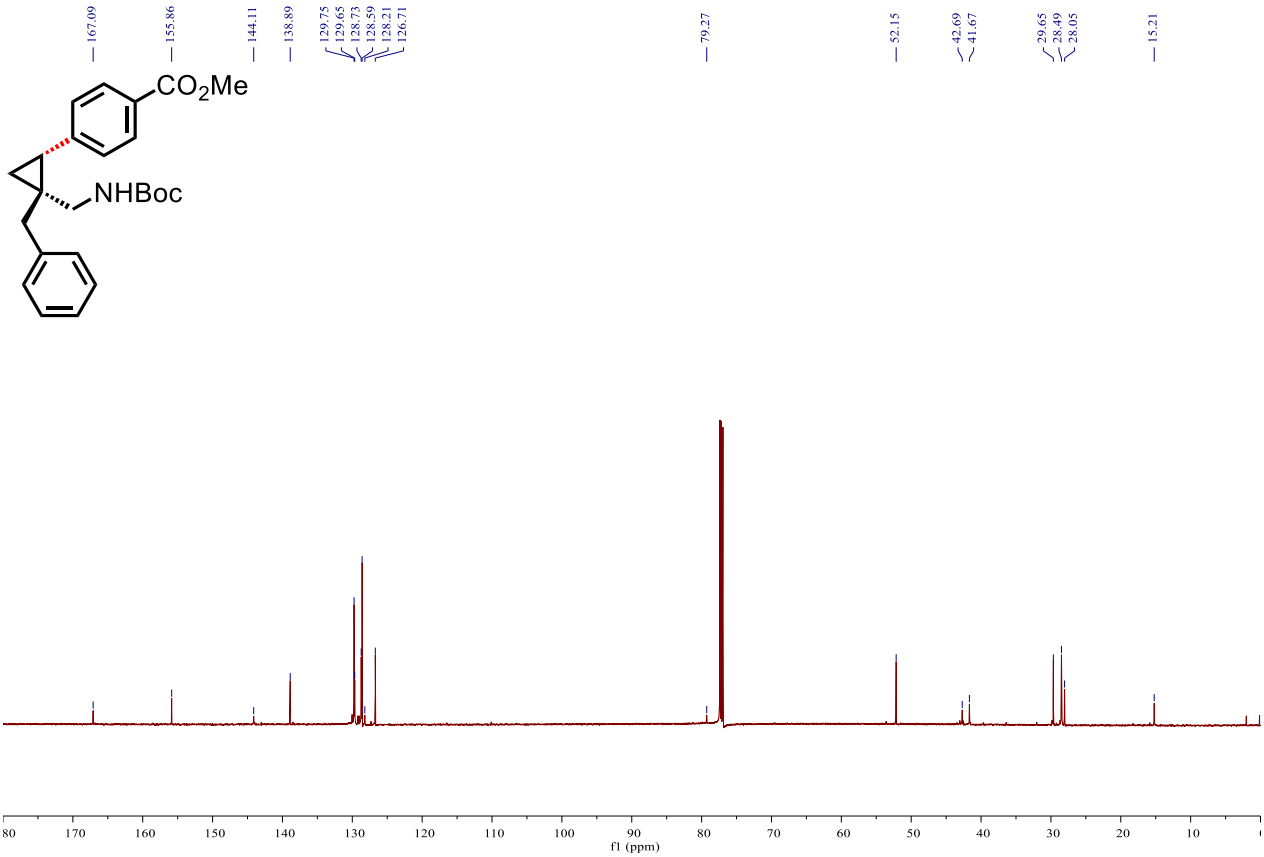

Me
Me
NHBoc
7.37
7.37
7.36
7.35
7.35
7.33
7.32
7.27
7.27
7.26
7.26
7.26
7.14
7.13
7.08
7.07
4.29
2.92
2.89
2.88
2.86
2.85
2.75
2.72
2.21
2.20
2.19
1.43
1.25
1.24
1.09
1.08
1.07
0.98
0.97
0.97
0.96
1.92
1.82
0.78
2.00
1.81
0.85
3.77
1.02
1.00
8.65
5.57
1.01
1.02
f1 (ppm)

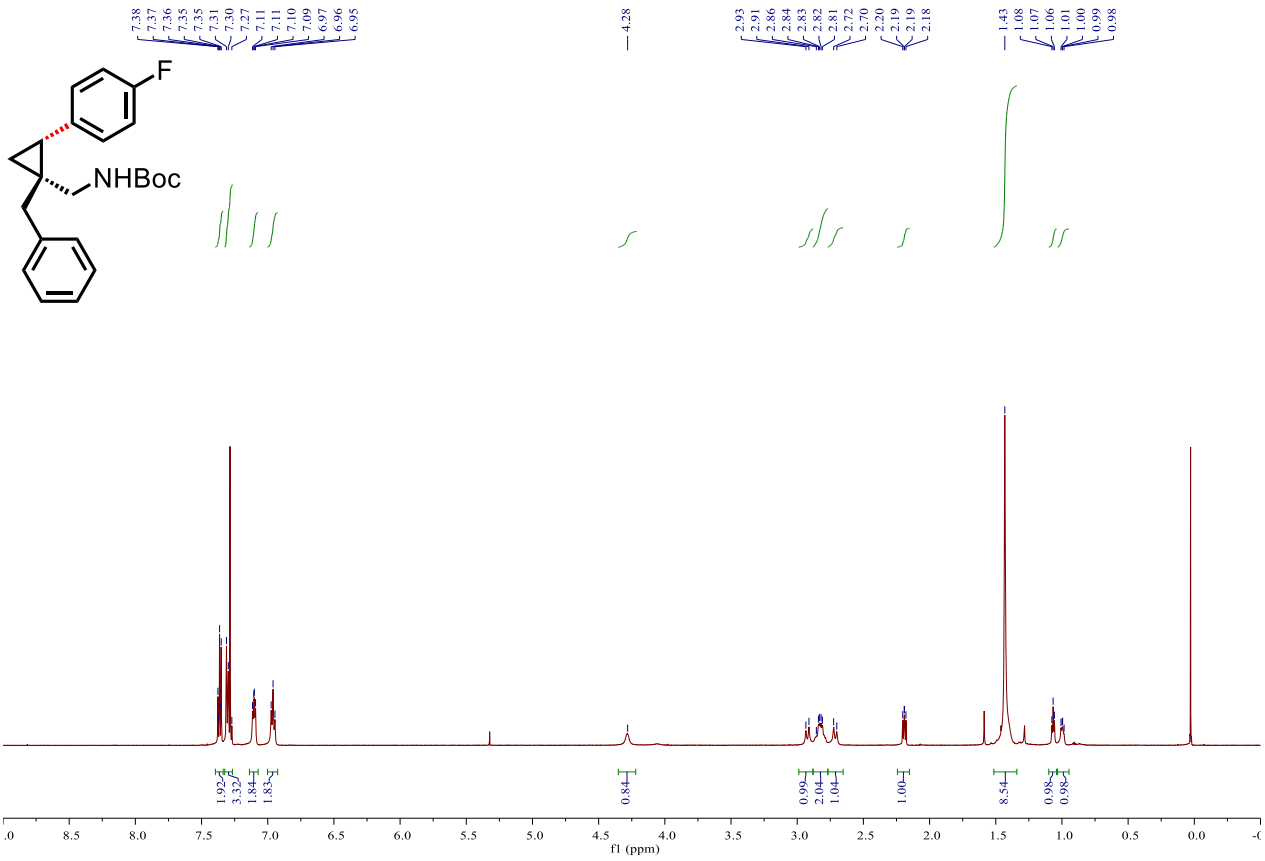

Me
Me
NHBoc
155.98
146.88
139.39
135.56
129.64
128.75
128.51
126.53
126.51
79.05
42.87
41.86
33.81
28.54
27.77
24.14
14.86
f1 (ppm)

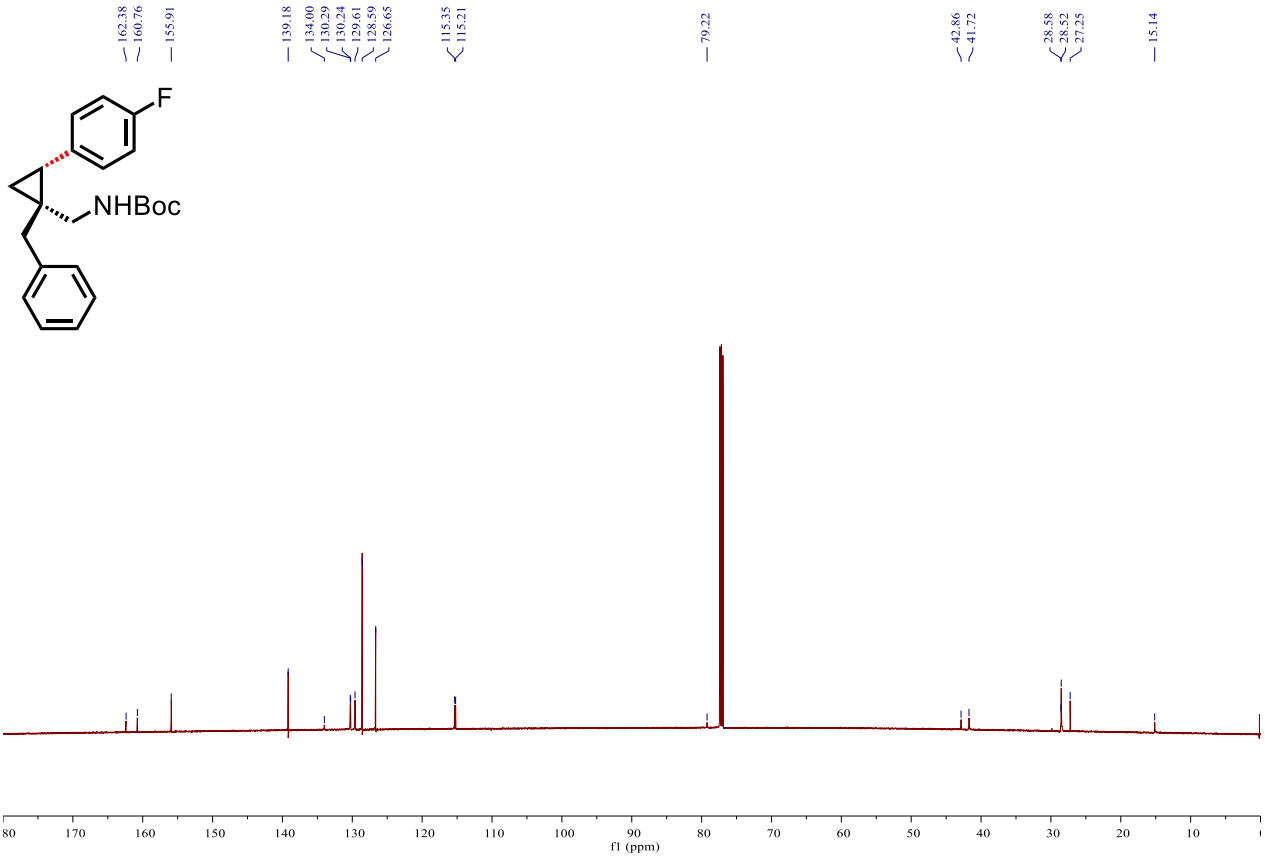

CF3
NHBoc
f1 (ppm)

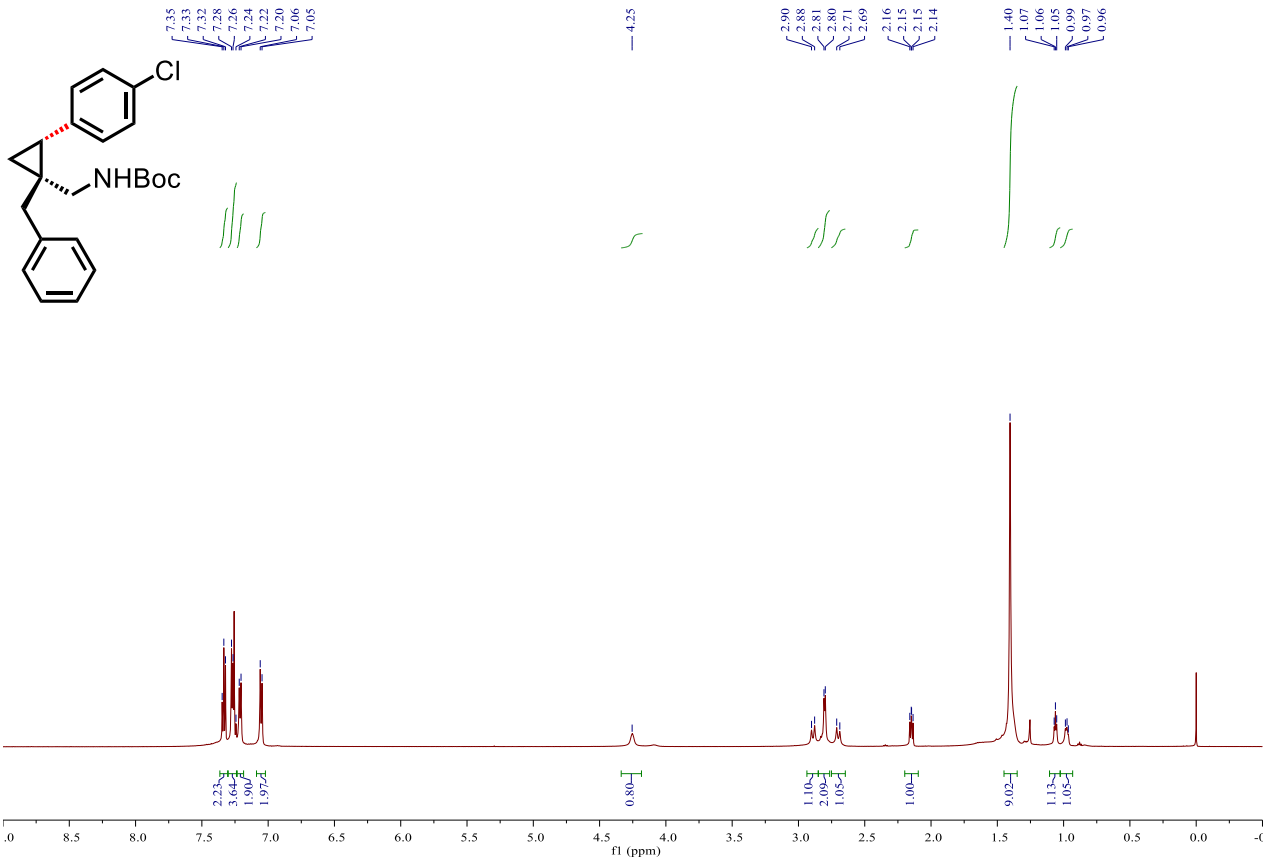

CF3
NHBoc
f1 (ppm)

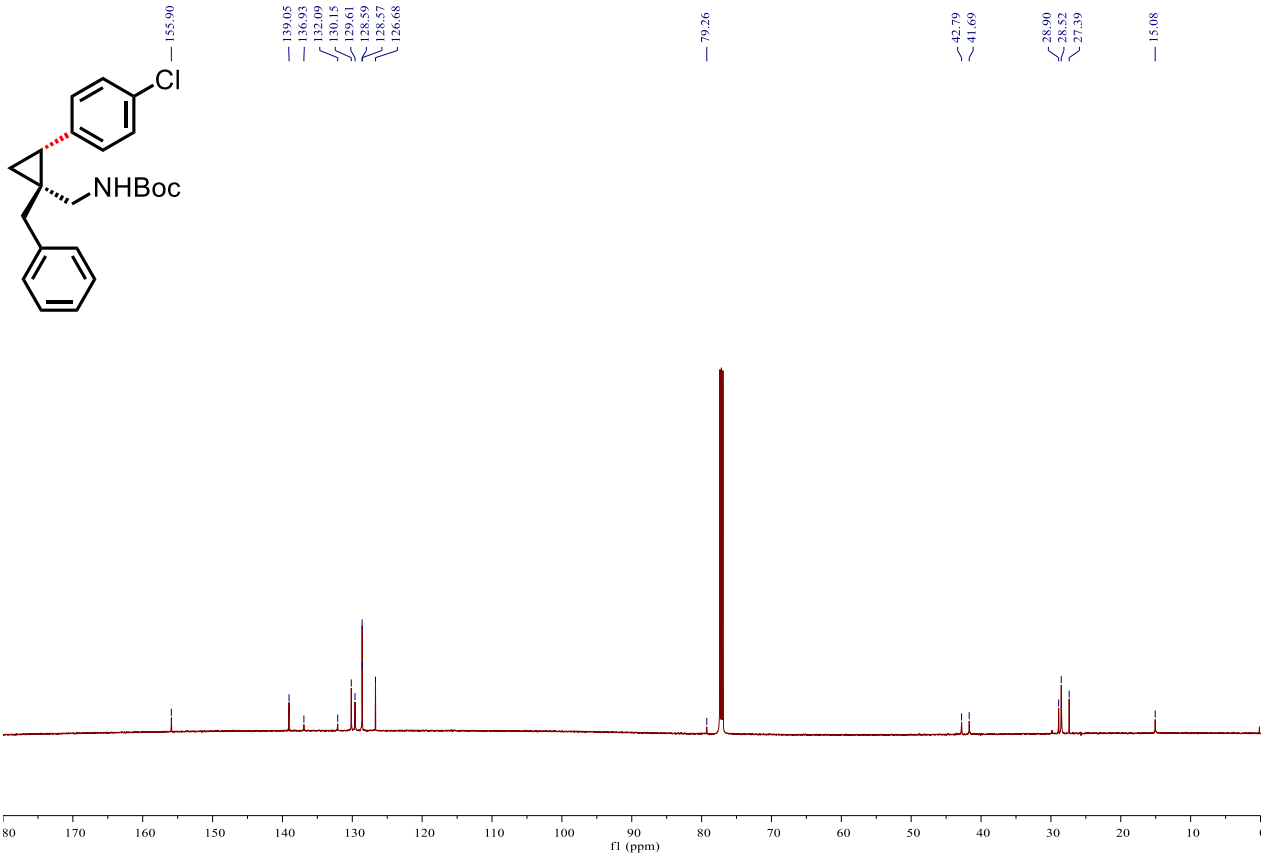

7.93
7.92
7.35
7.35
7.34
7.33
7.33
7.29
7.27
7.21
7.20
4.22
3.89
2.91
2.88
2.87
2.78
2.76
2.23
2.21
2.20
1.39
1.18
1.17
1.16
1.04
1.03
1.02
CO2Me
NHBoc
1.98
2.16
2.59
2.02
0.75
3.07
2.18
1.82
1.00
9.29
1.03
1.04
f1 (ppm)

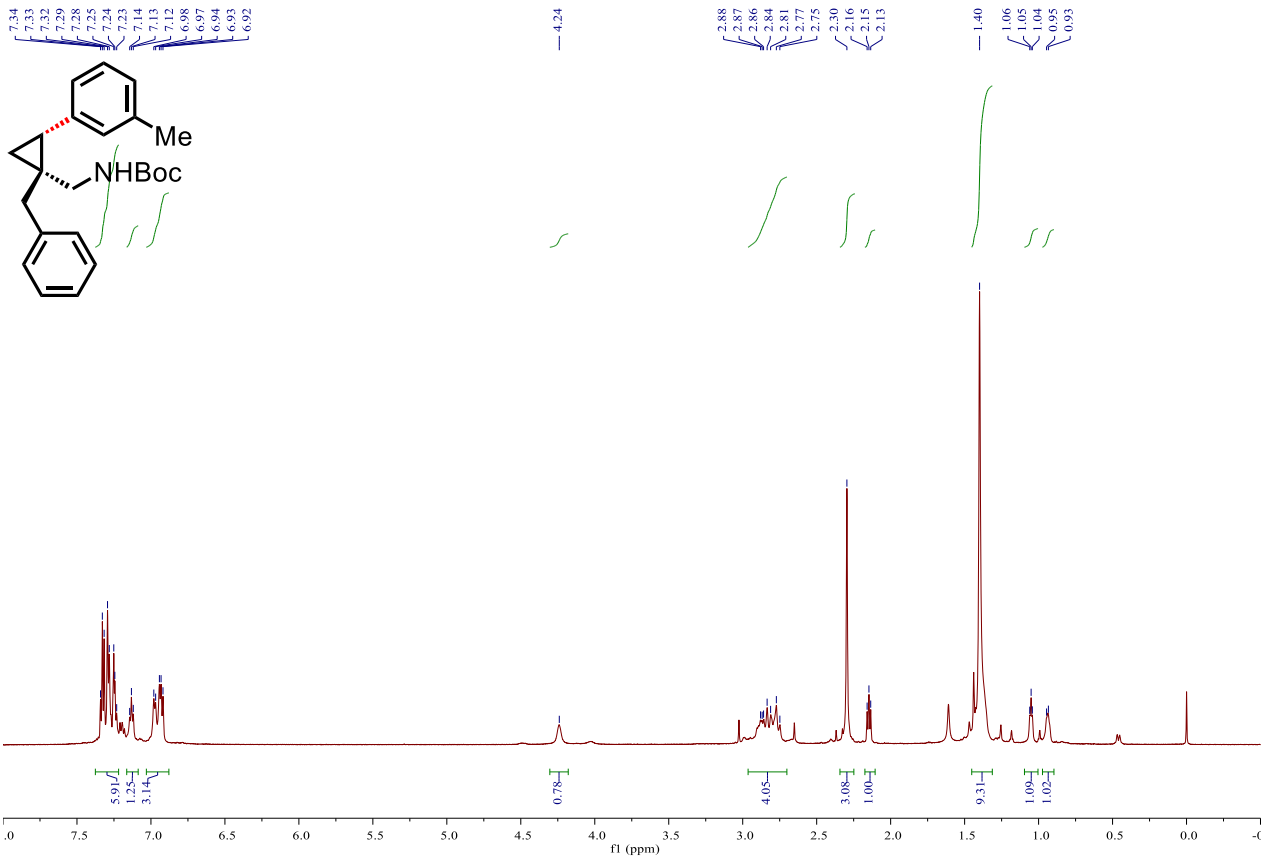

167.09
155.86
144.11
138.89
129.75
129.65
128.73
128.59
128.21
126.71
79.27
52.15
42.69
41.67
29.65
28.49
28.05
15.21
CO2Me
NHBoc
f1 (ppm)

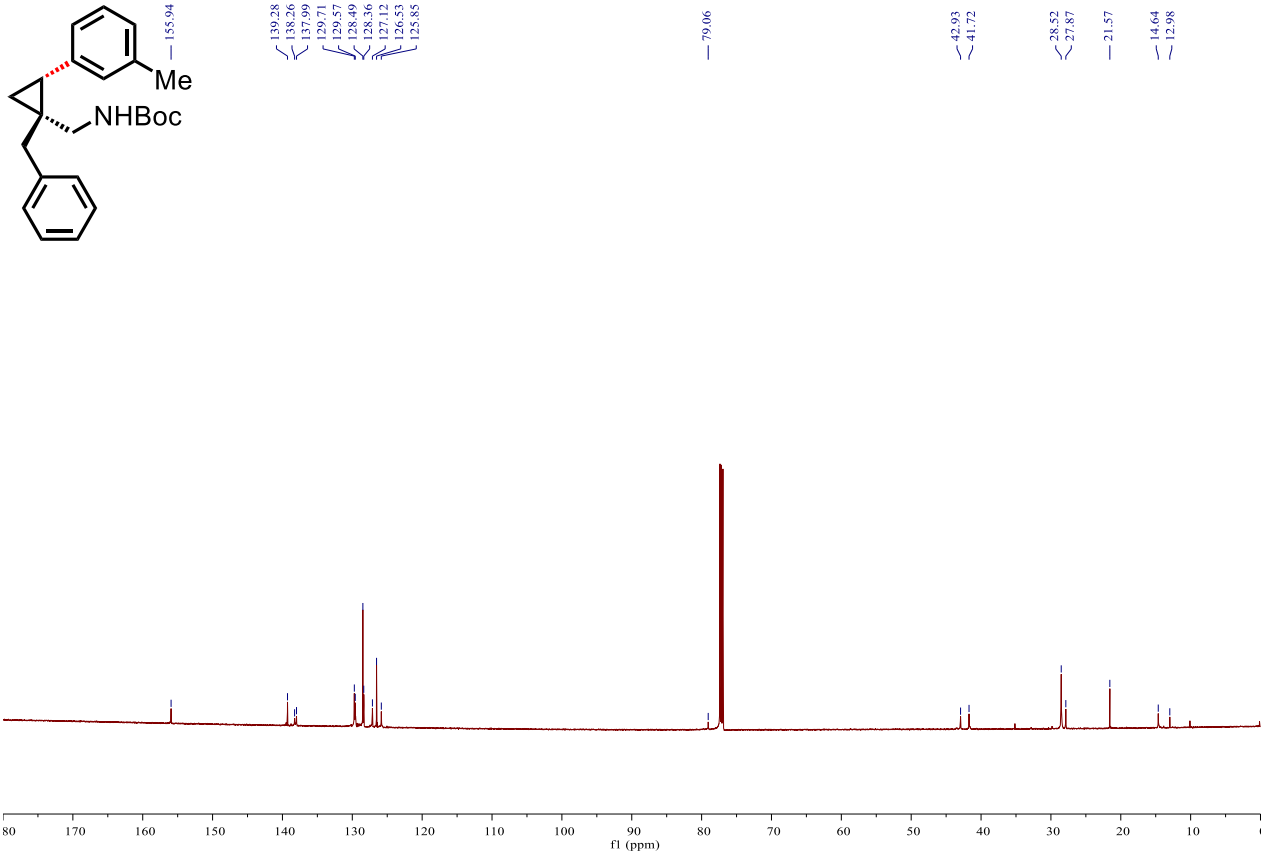

F
NHBoc
7.38
7.37
7.36
7.35
7.35
7.31
7.30
7.27
7.11
7.11
7.10
7.09
6.97
6.96
6.95
4.28
2.93
2.91
2.86
2.84
2.83
2.82
2.81
2.72
2.70
2.20
2.19
2.19
2.18
1.43
1.08
1.07
1.06
1.01
1.00
0.99
0.98
1.92
3.32
1.84
1.83
0.84
0.99
2.04
1.04
1.00
8.54
0.98
0.98
f1 (ppm)

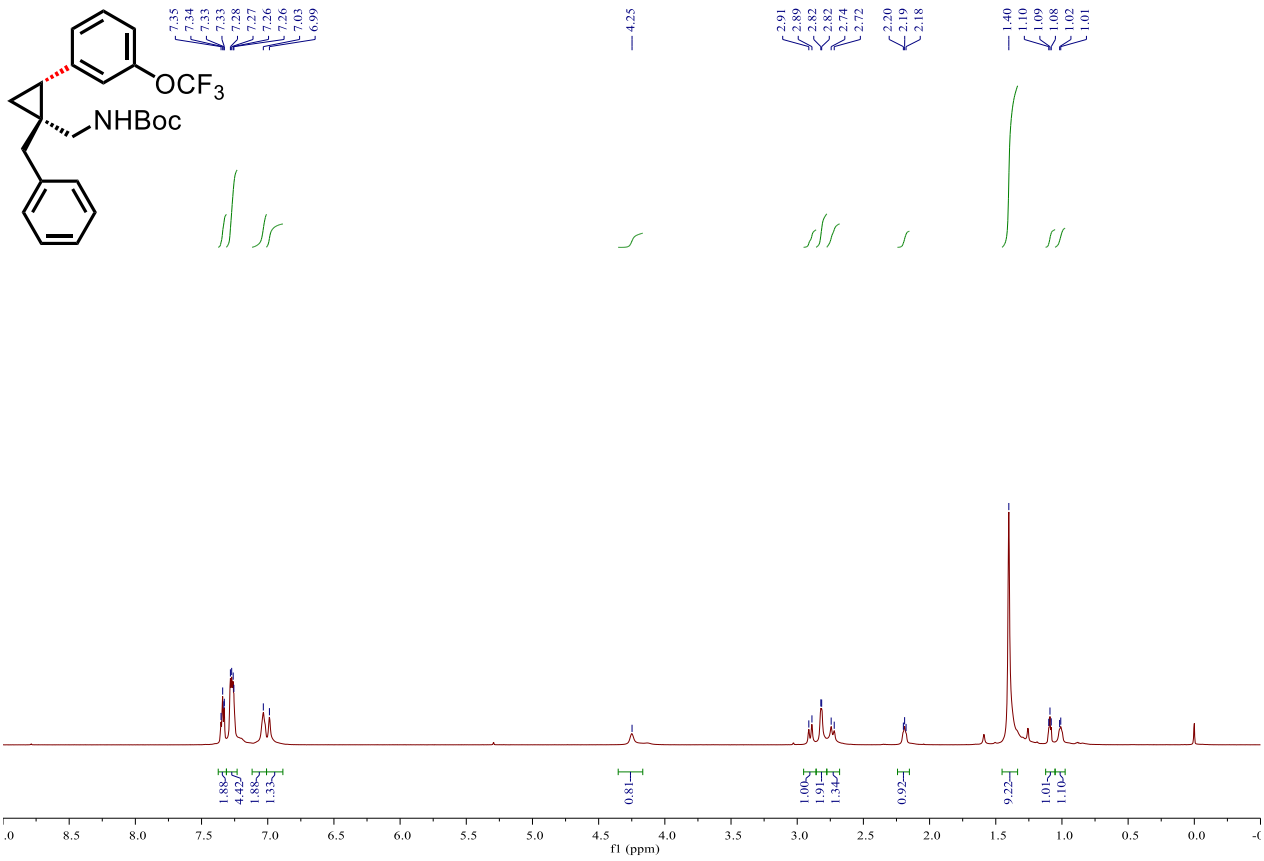

F
NHBoc
162.38
160.76
155.91
139.18
134.00
130.29
130.24
129.61
128.59
126.65
115.35
115.21
79.22
42.86
41.72
28.58
28.52
27.25
15.14
f1 (ppm)

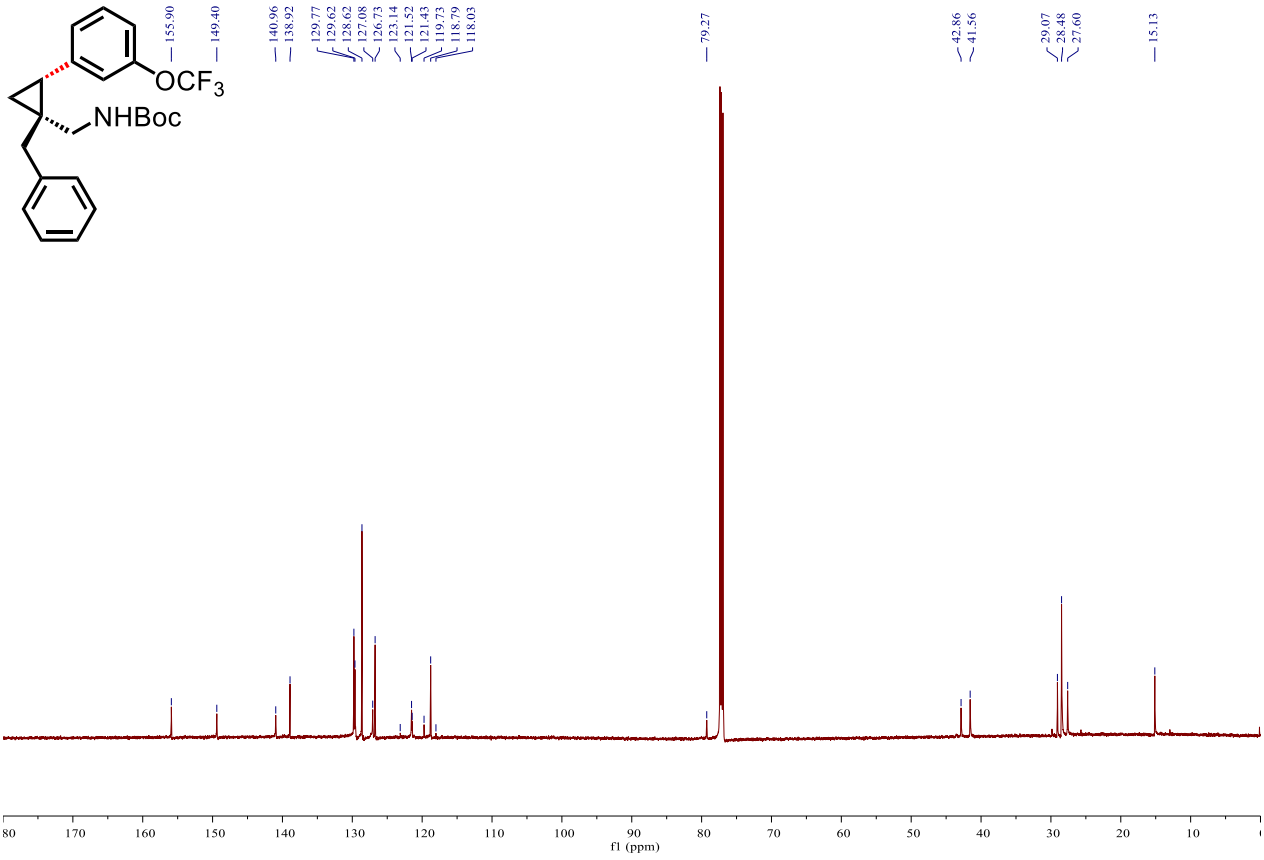

Cl
NHBoc
7.35
7.33
7.32
7.28
7.26
7.24
7.22
7.20
7.06
7.05
4.25
2.90
2.88
2.81
2.80
2.71
2.69
2.16
2.15
2.15
2.14
1.40
1.07
1.06
1.05
0.99
0.97
0.96
2.23
3.64
1.90
1.97
0.80
1.10
2.09
1.05
1.00
9.02
1.13
1.05
f1 (ppm)

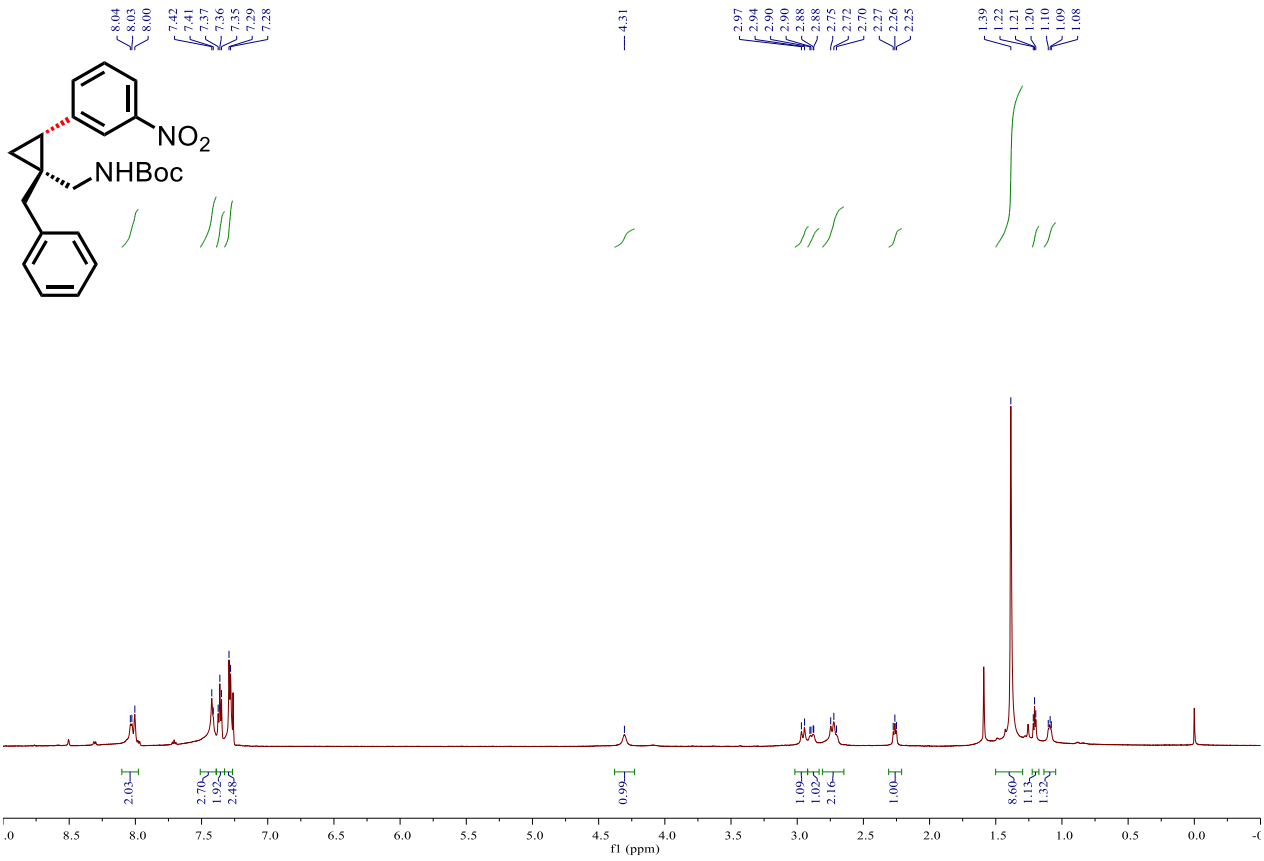

Cl
NHBoc
155.90
139.05
136.93
132.09
130.15
129.61
128.59
128.57
126.68
79.26
42.79
41.69
28.90
28.52
27.39
15.08
f1 (ppm)

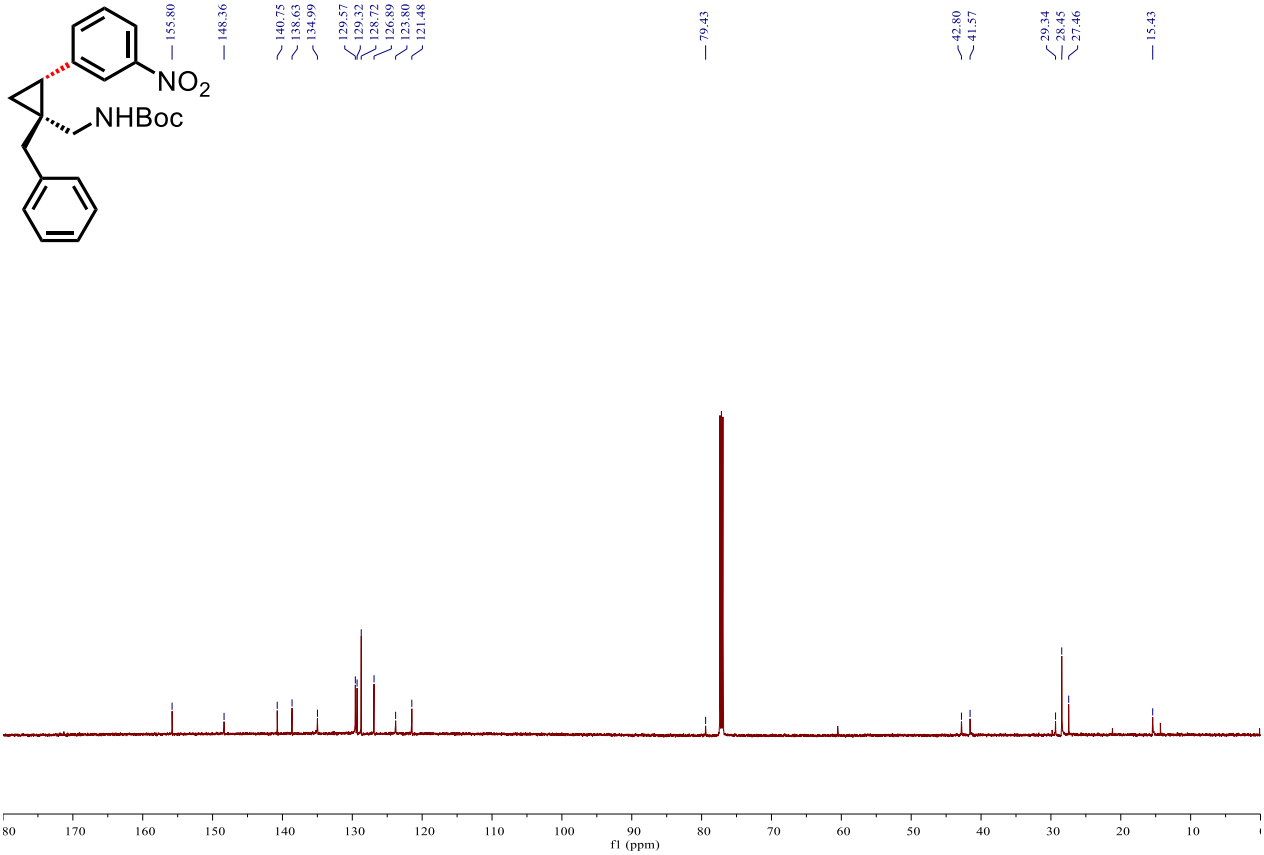

Me
NHBoc
f1 (ppm)

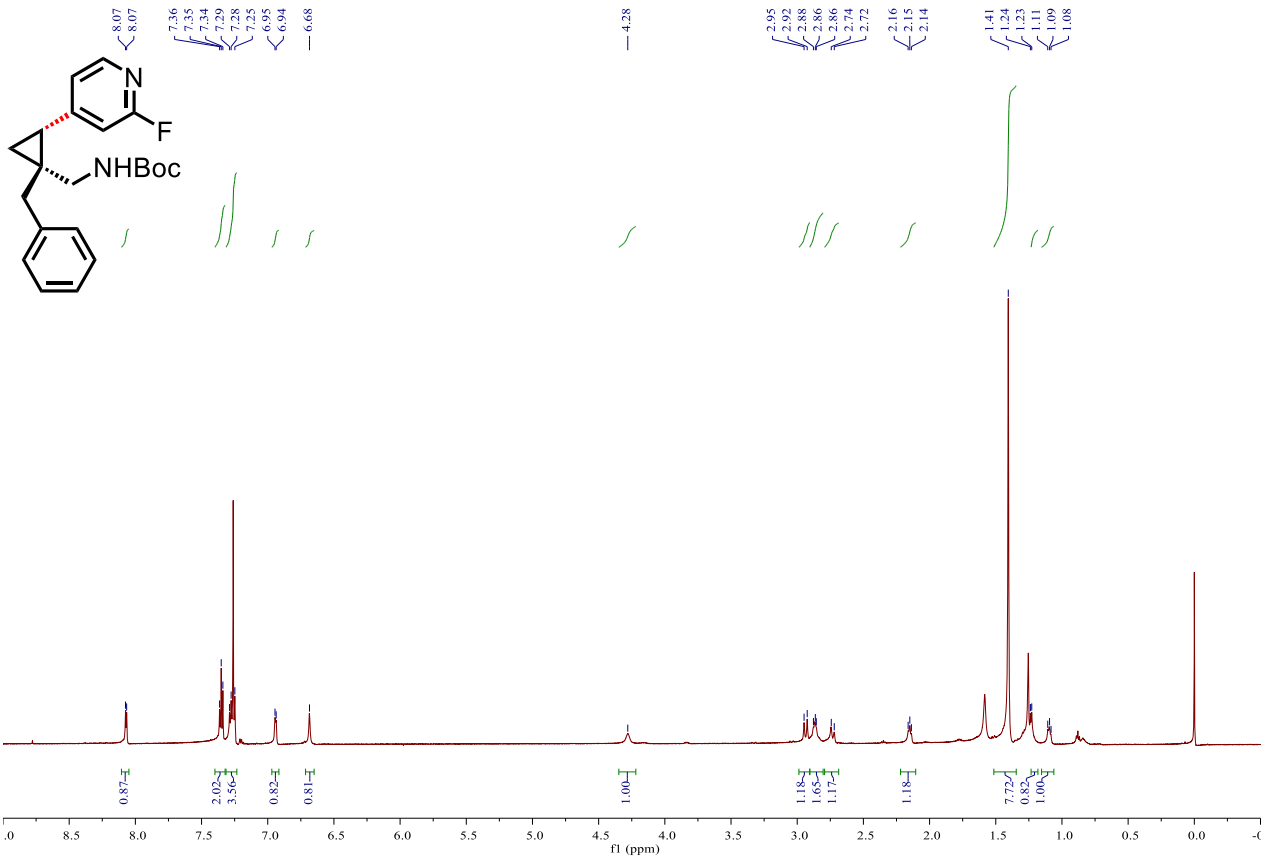

Me
NHBoc
f1 (ppm)

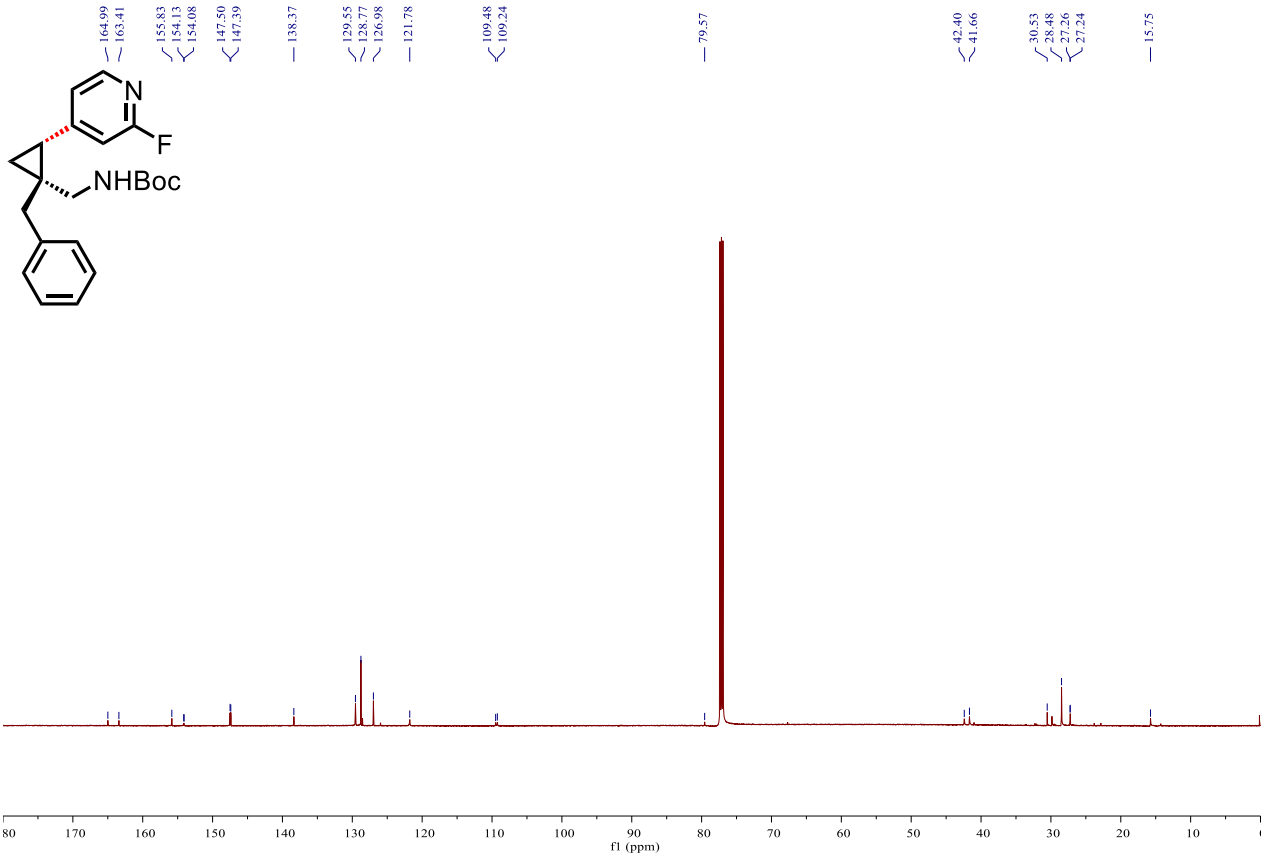

OCF3
NHBoc
7.35
7.34
7.33
7.33
7.28
7.27
7.26
7.26
7.03
6.99
4.25
2.91
2.89
2.82
2.82
2.74
2.72
2.20
2.19
2.18
1.40
1.10
1.09
1.08
1.02
1.01
1.88
4.42
1.88
1.33
0.81
1.00
1.91
1.34
0.92
9.22
1.01
1.10
f1 (ppm)

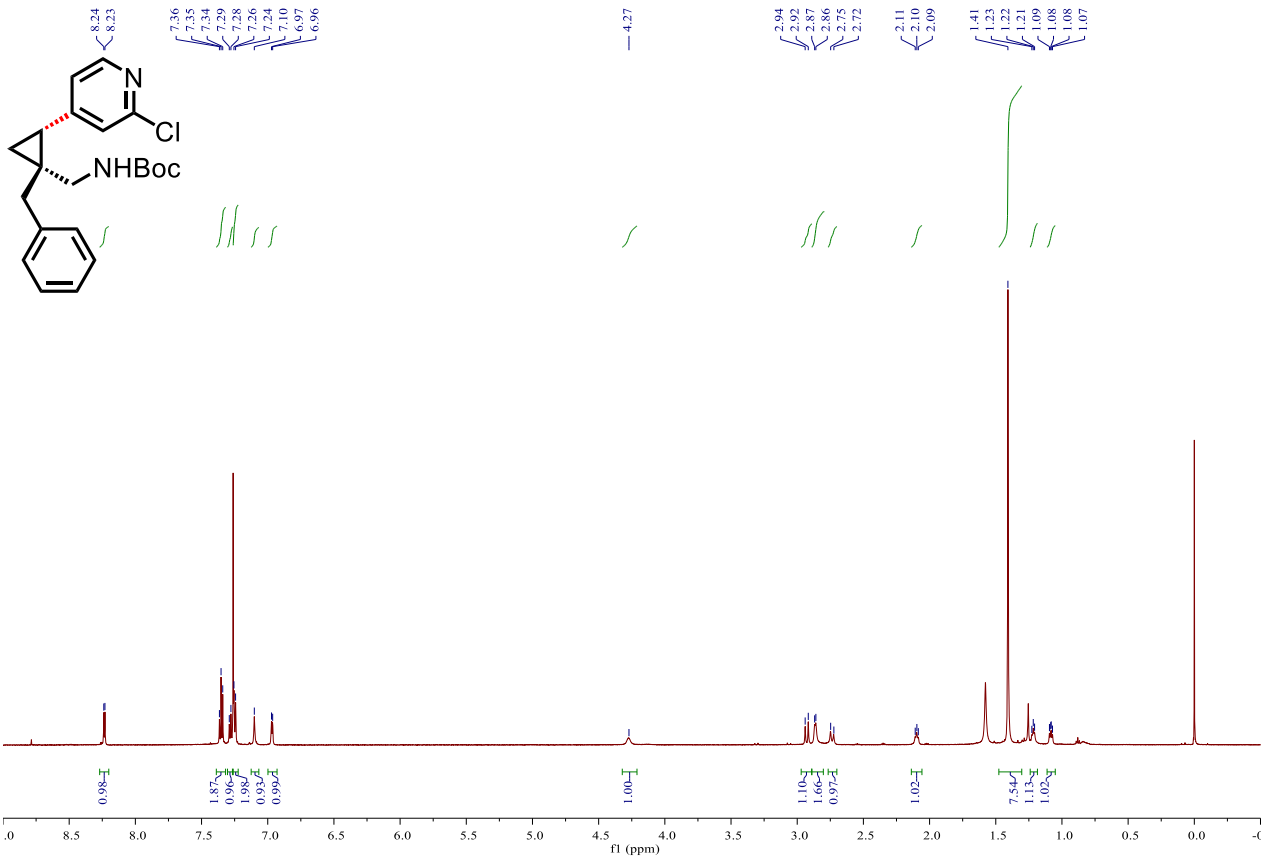

OCF3
NHBoc
155.90
149.40
140.96
138.92
129.77
129.62
128.62
127.08
126.73
123.14
121.52
121.43
119.73
118.79
118.03
79.27
42.86
41.56
29.07
28.48
27.60
15.13
f1 (ppm)

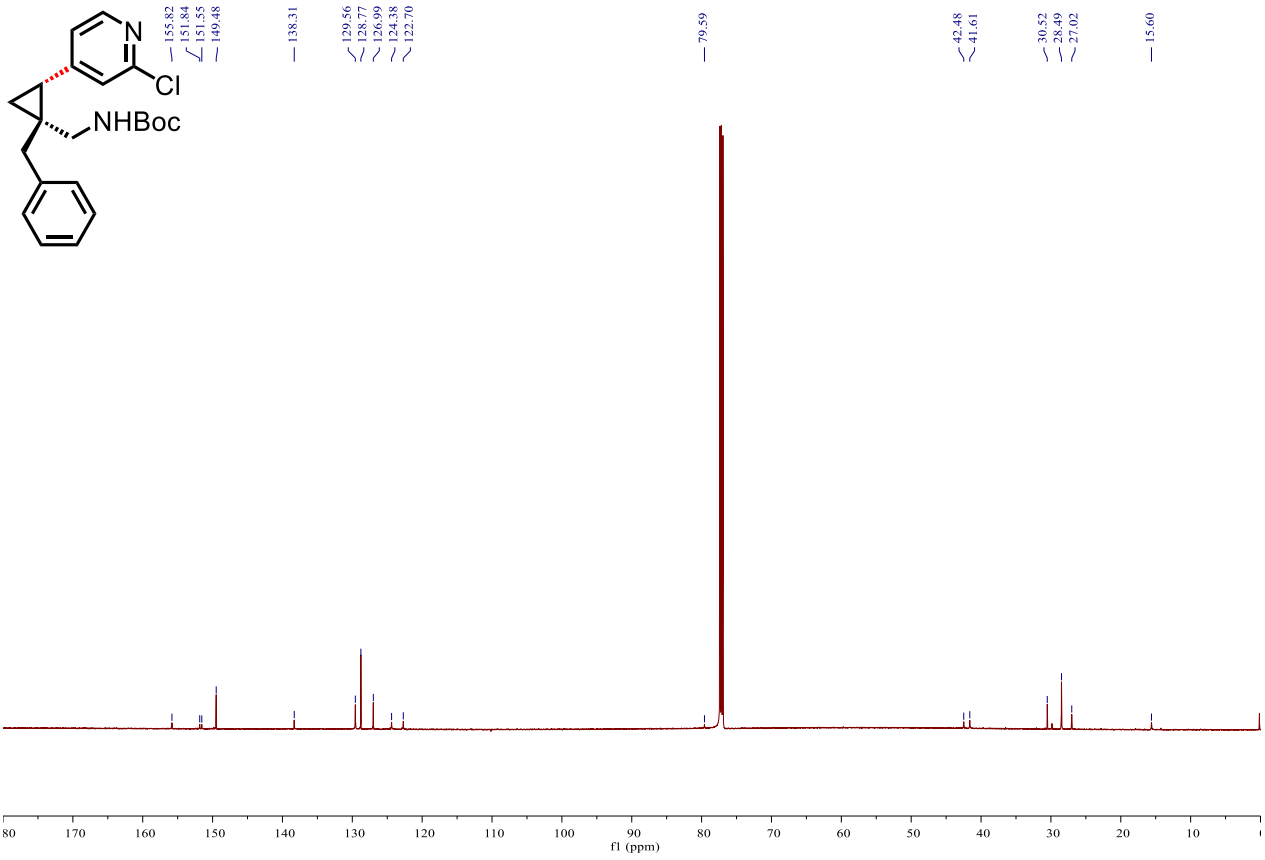

8.04
8.03
8.00
7.42
7.41
7.37
7.36
7.35
7.29
7.28
4.31
2.97
2.94
2.90
2.90
2.88
2.88
2.75
2.72
2.70
2.27
2.26
2.25
1.39
1.22
1.21
1.20
1.10
1.09
1.08
NO2
NHBoc
2.03
2.70
1.92
2.48
0.99
1.09
1.02
2.16
1.00
8.60
1.13
1.32
f1 (ppm)

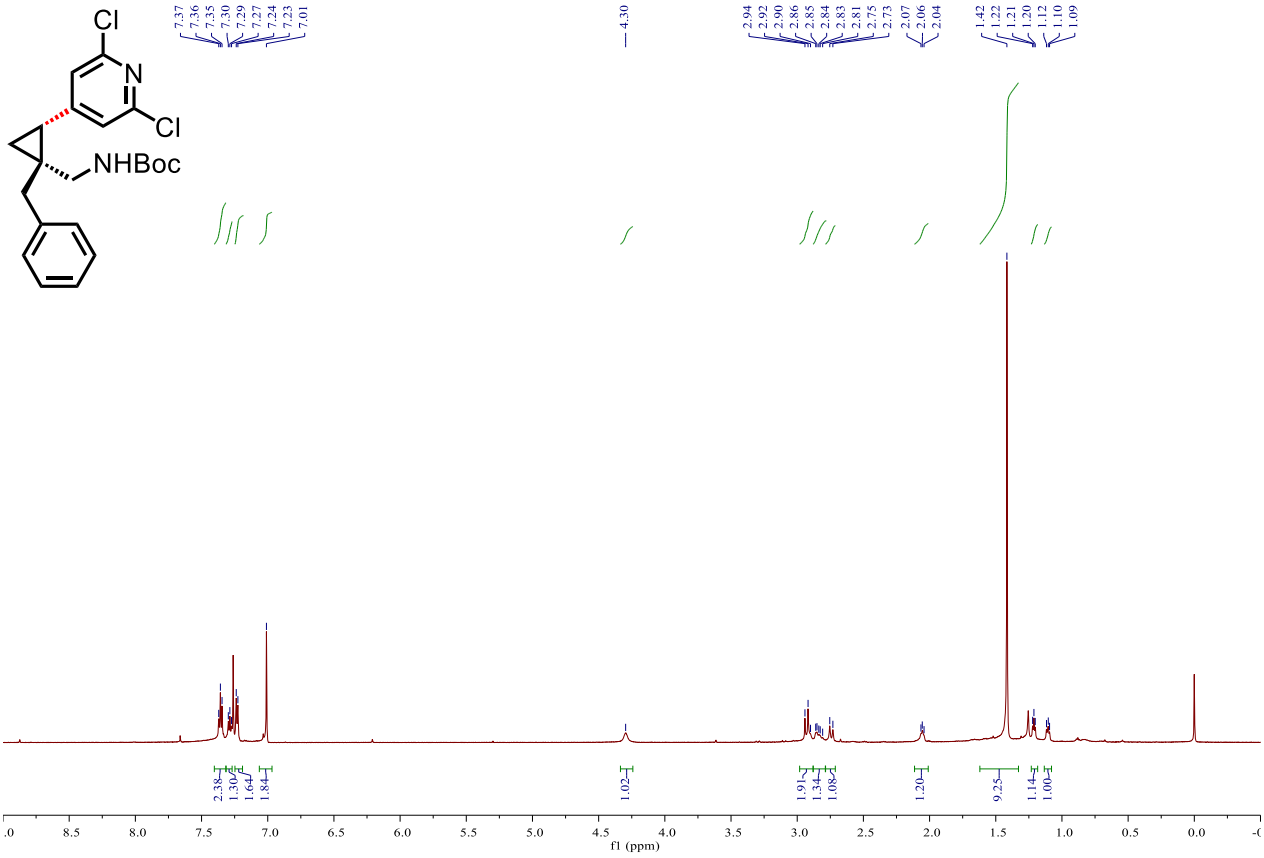

155.80
148.36
140.75
138.63
134.99
129.57
129.32
128.72
126.89
123.80
121.48
79.43
42.80
41.57
29.34
28.45
27.46
15.43
NO2
NHBoc
f1 (ppm)

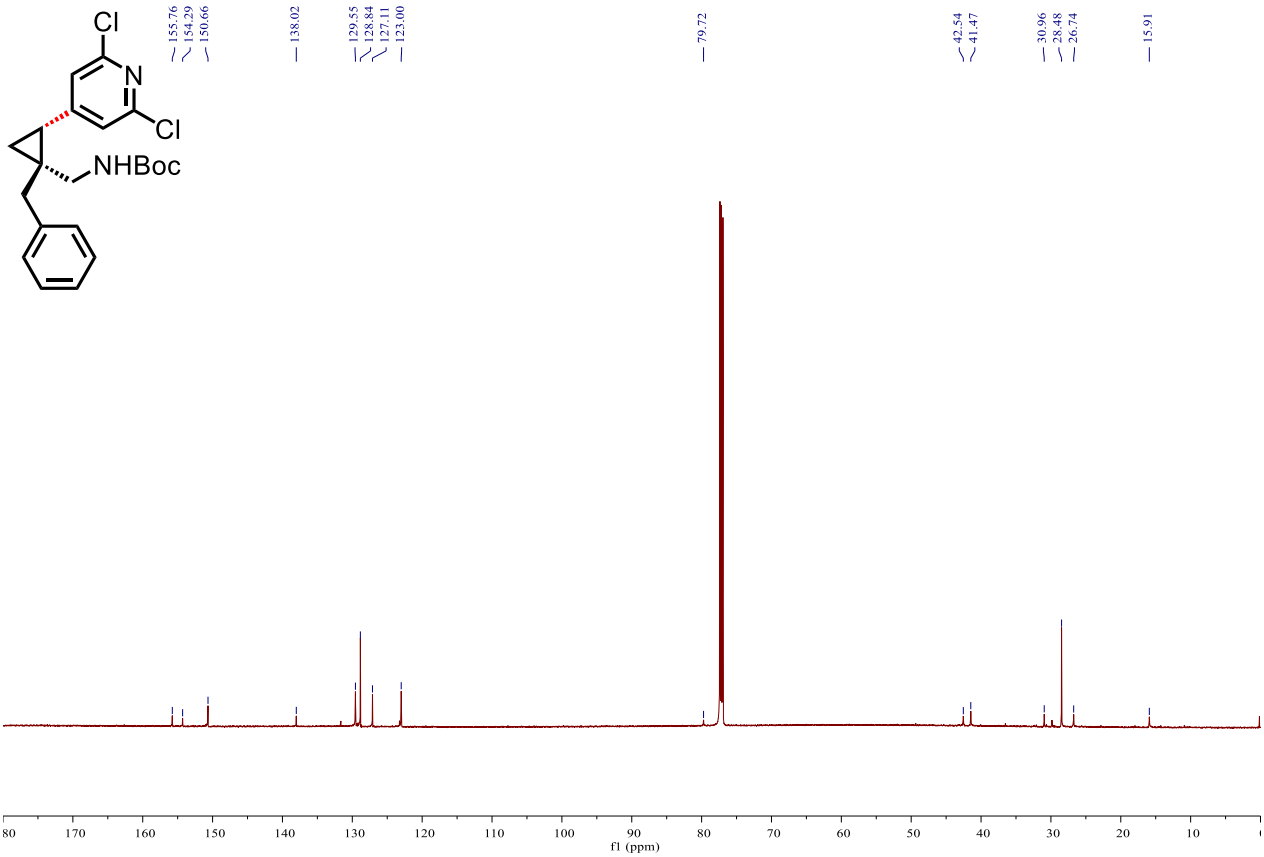

8.07
8.07
7.36
7.35
7.34
7.29
7.28
7.25
6.95
6.94
6.68
4.28
2.95
2.92
2.88
2.86
2.86
2.74
2.72
2.16
2.15
2.14
1.41
1.24
1.23
1.11
1.09
1.08
N
F
NHBoc
0.87
2.02
3.56
0.82
0.81
1.00
1.18
1.65
1.17
1.18
7.72
0.82
1.00
f1 (ppm)

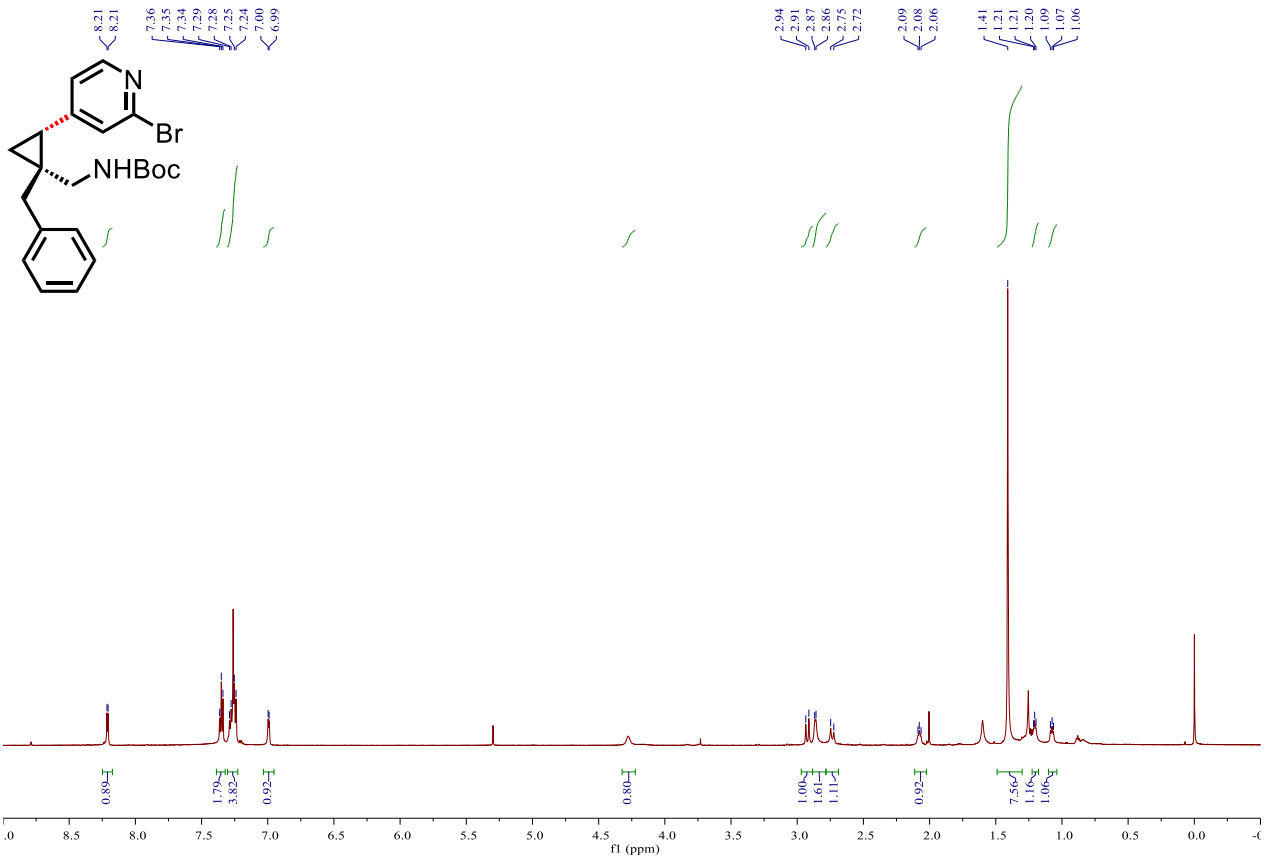

164.99
163.41
155.83
154.13
154.08
147.50
147.39
138.37
129.55
128.77
126.98
121.78
109.48
109.24
79.57
42.40
41.66
30.53
28.48
27.26
27.24
15.75
N
F
NHBoc
f1 (ppm)

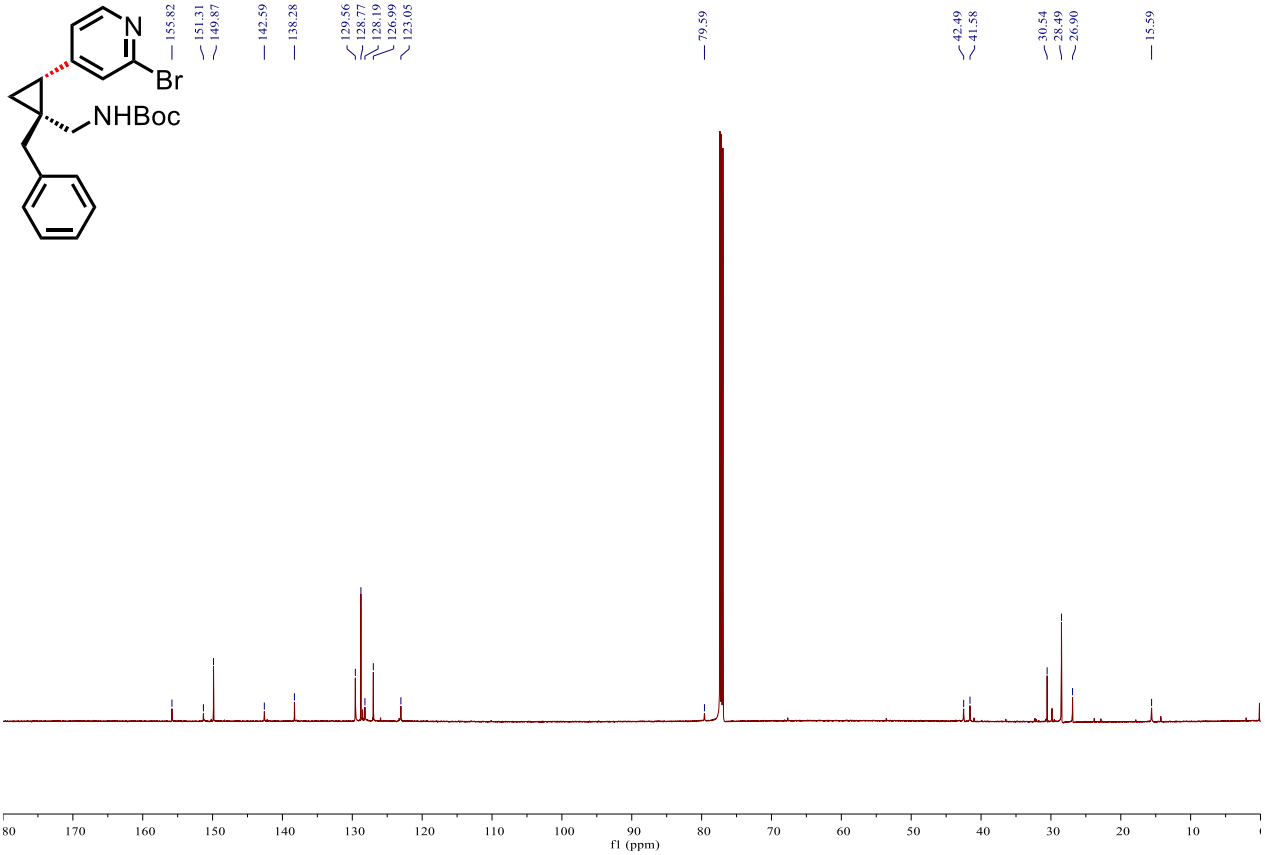

N
Cl
NHBoc
f1 (ppm)

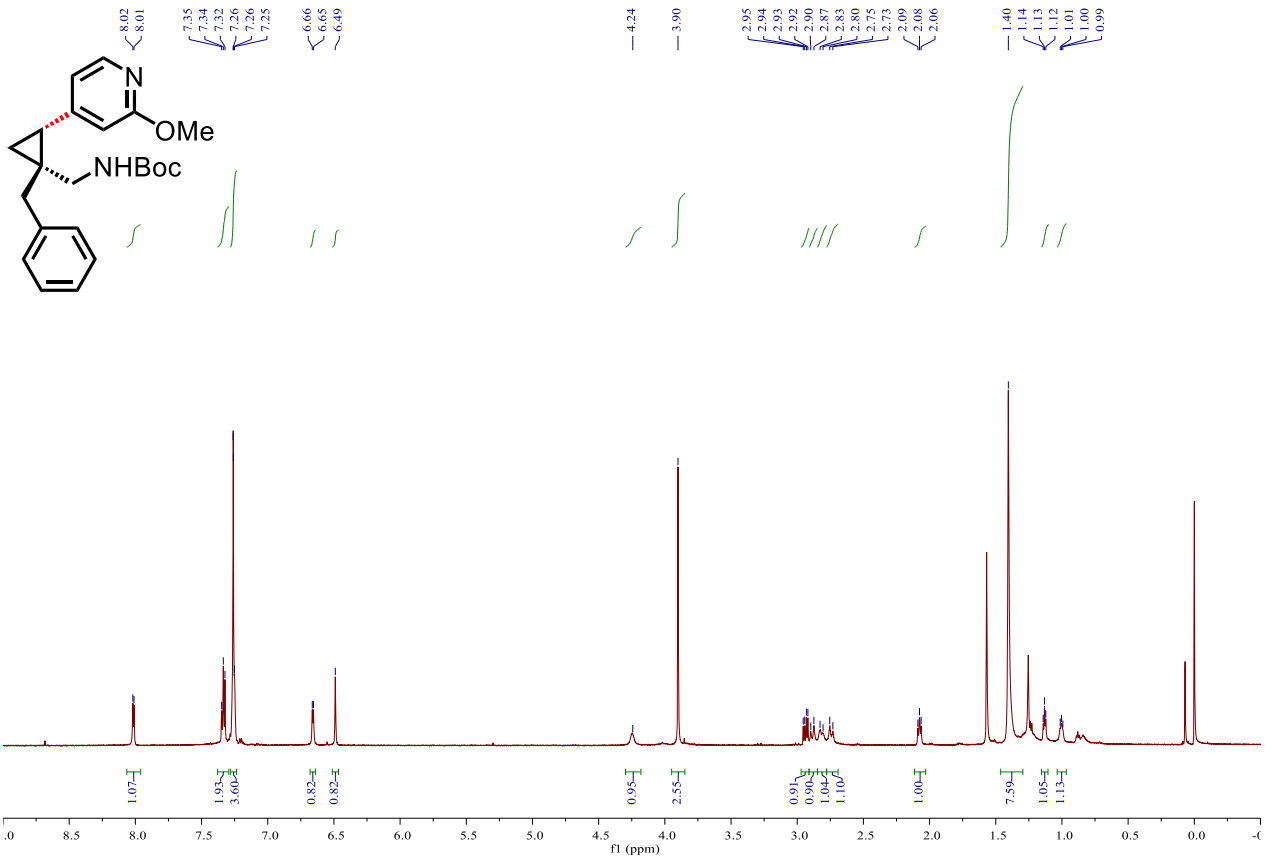

N
Cl
NHBoc
f1 (ppm)

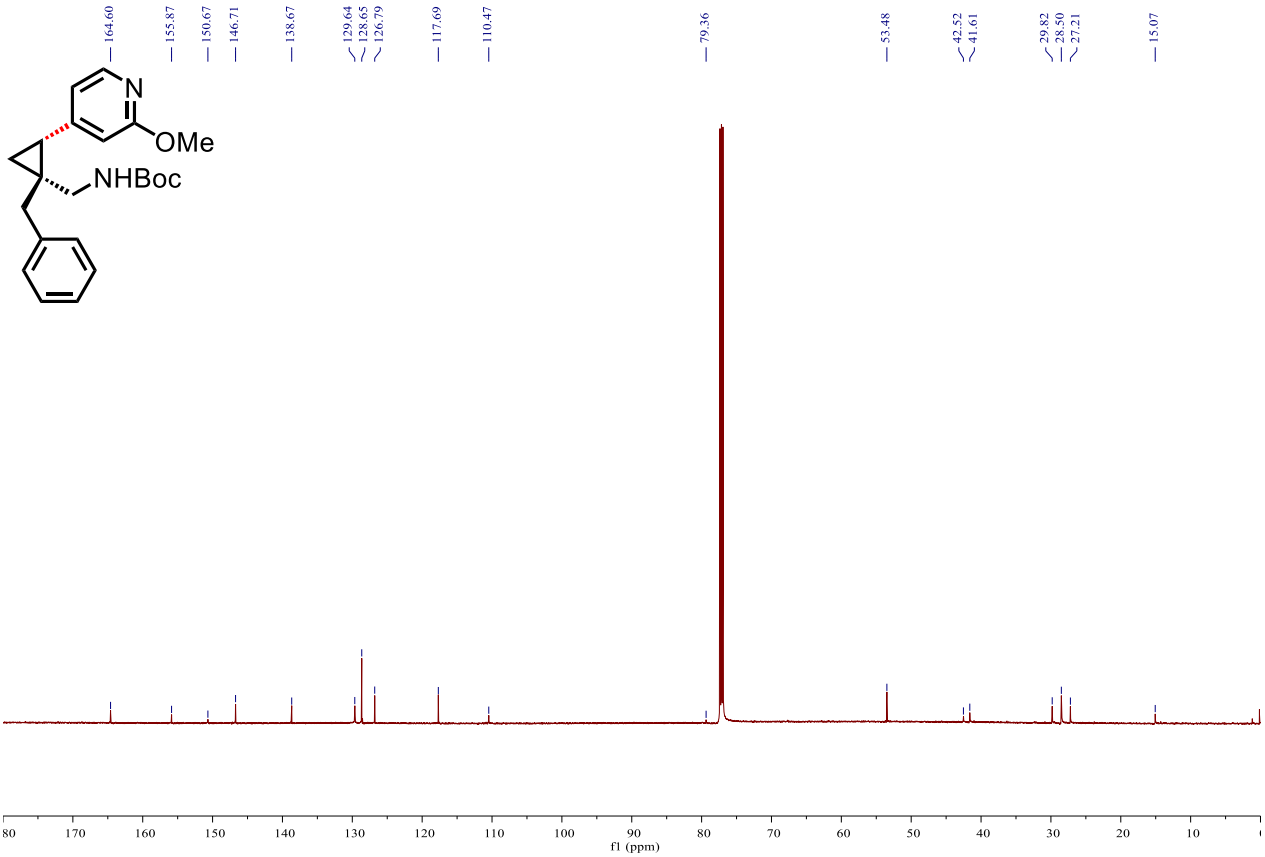

Cl
N
Cl
NHBoc
7.37
7.36
7.35
7.30
7.29
7.27
7.24
7.23
7.01
4.30
2.94
2.92
2.90
2.86
2.85
2.84
2.83
2.81
2.75
2.73
2.07
2.06
2.04
1.42
1.22
1.21
1.20
1.12
1.10
1.09
2.38
1.30
1.64
1.84
1.02
1.91
1.34
1.08
1.20
9.25
1.14
1.00
f1 (ppm)

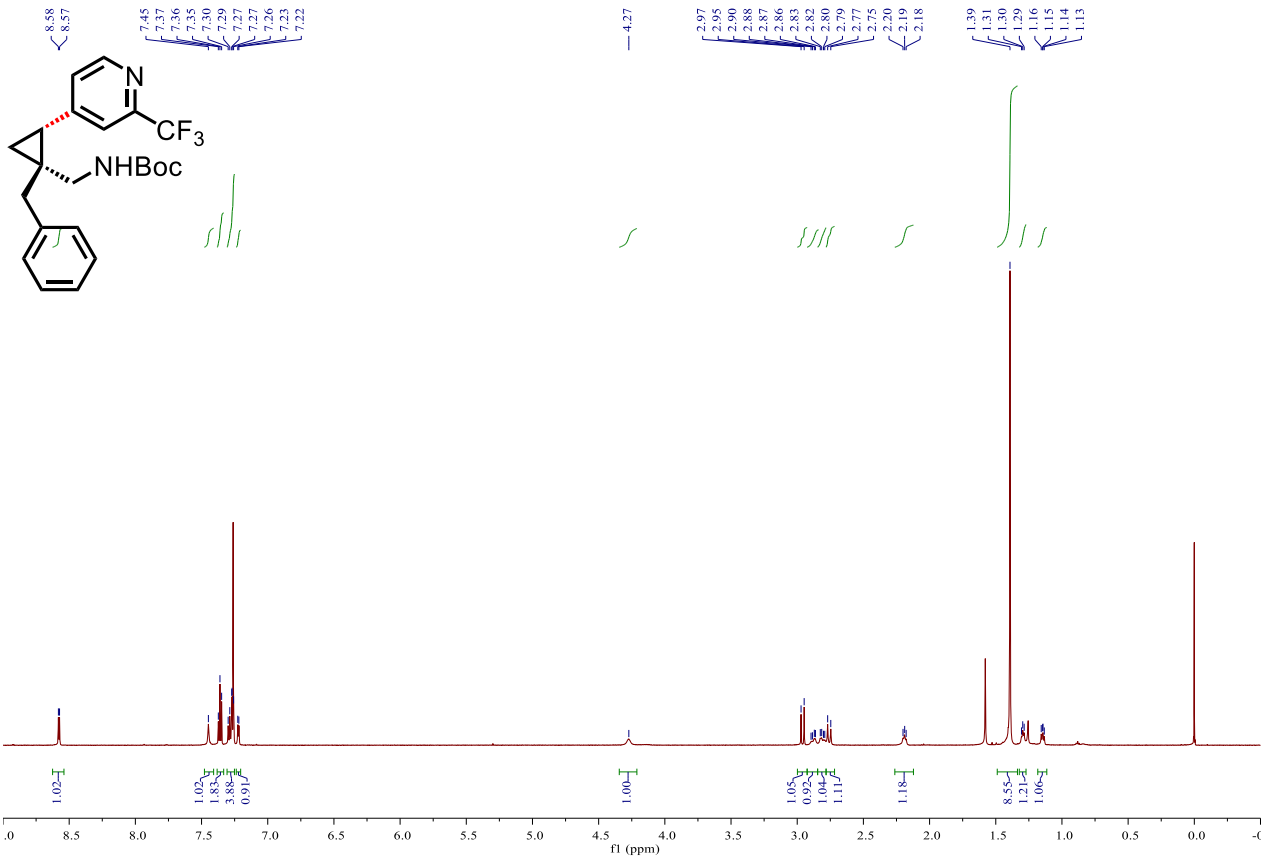

Cl
N
Cl
NHBoc
155.76
154.29
150.66
138.02
129.55
128.84
127.11
123.00
79.72
42.54
41.47
30.96
28.48
26.74
15.91
f1 (ppm)

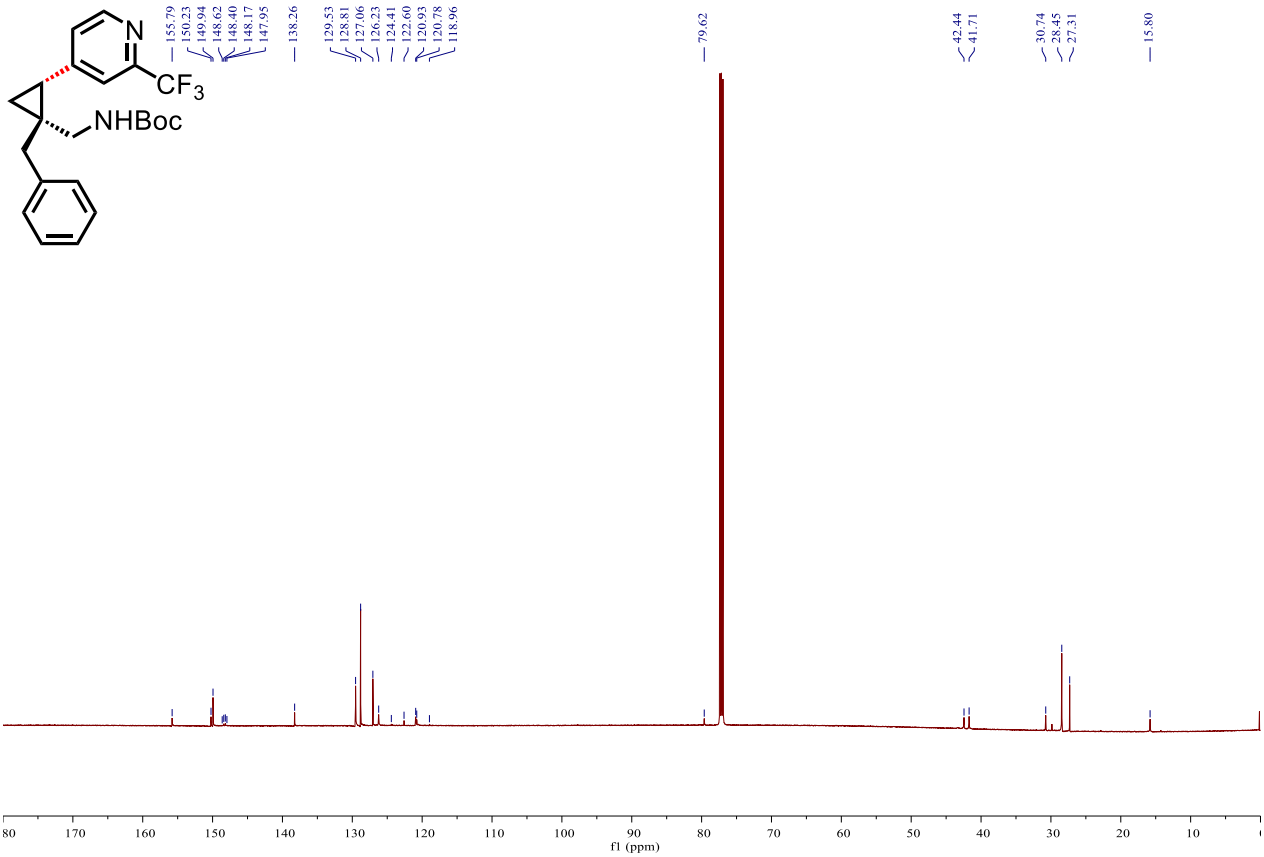

8.21
8.21
7.36
7.35
7.34
7.29
7.28
7.25
7.24
7.00
6.99
2.94
2.91
2.87
2.86
2.75
2.72
2.09
2.08
2.06
1.41
1.21
1.21
1.20
1.09
1.07
1.06
N
Br
NHBoc
0.89
1.79
3.82
0.92
0.80
1.00
1.61
1.11
0.92
7.56
1.16
1.06
f1 (ppm)


155.82
151.31
149.87
142.59
138.28
129.56
128.77
128.19
126.99
123.05
79.59
42.49
41.58
30.54
28.49
26.90
15.59
N
Br
NHBoc
f1 (ppm)


8.02
8.01
7.35
7.34
7.32
7.26
7.26
7.25
6.66
6.65
6.49
4.24
3.90
2.95
2.94
2.93
2.92
2.90
2.87
2.83
2.80
2.75
2.73
2.09
2.08
2.06
1.40
1.14
1.13
1.12
1.01
1.00
0.99
N
OMe
NHBoc
1.07
1.93
3.60
0.82
0.82
0.95
2.55
0.91
0.90
1.04
1.10
1.00
7.59
1.05
1.13
f1 (ppm)


164.60
155.87
150.67
146.71
138.67
129.64
128.65
126.79
117.69
110.47
79.36
53.48
42.52
41.61
29.82
28.50
27.21
15.07
N
OMe
NHBoc
f1 (ppm)


8.58
8.57
7.45
7.37
7.36
7.35
7.30
7.29
7.27
7.27
7.26
7.23
7.22
4.27
2.97
2.95
2.90
2.88
2.87
2.86
2.83
2.82
2.80
2.79
2.77
2.75
2.20
2.19
2.18
1.39
1.31
1.30
1.29
1.16
1.15
1.14
1.13
N
CF3
NHBoc
1.02
1.02
1.83
3.88
0.91
1.00
1.05
0.92
1.04
1.11
1.18
8.55
1.21
1.06
f1 (ppm)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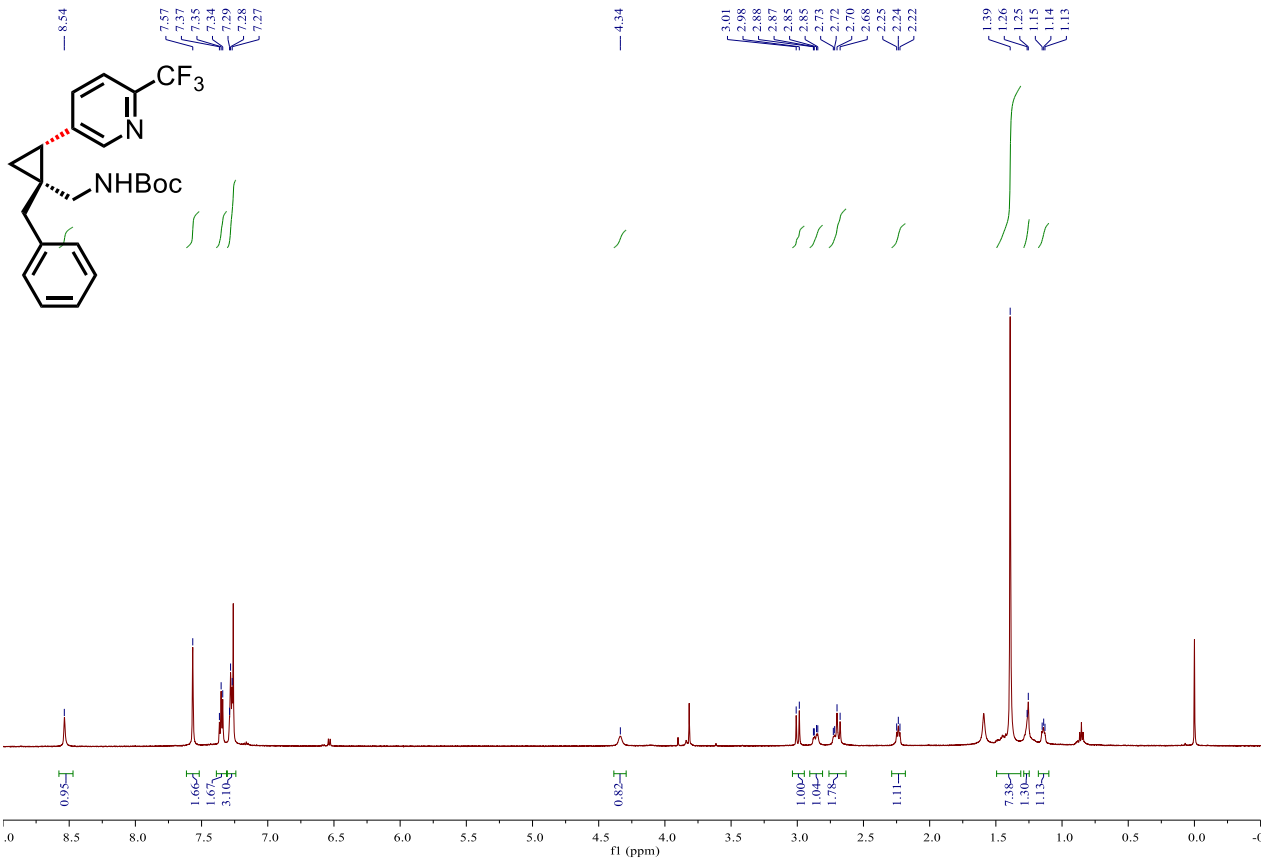
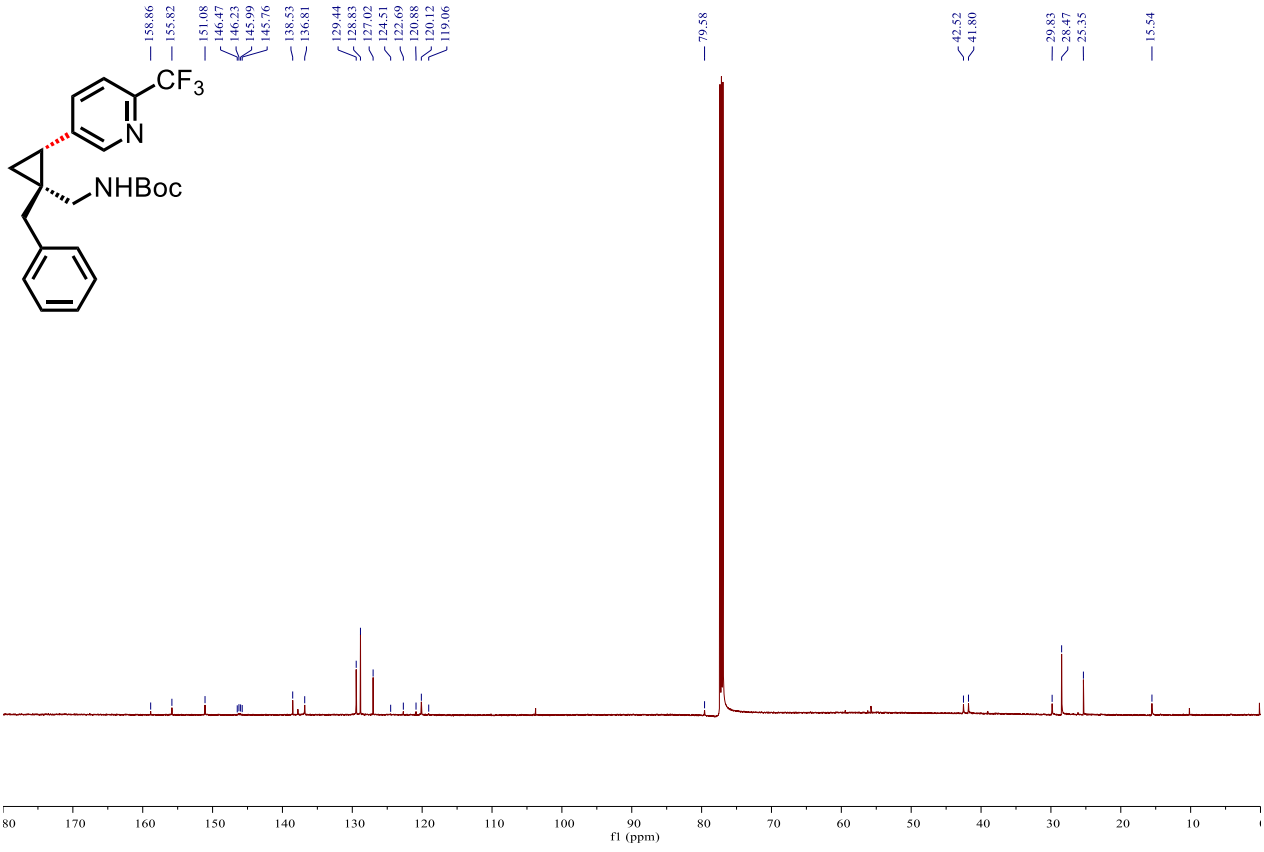
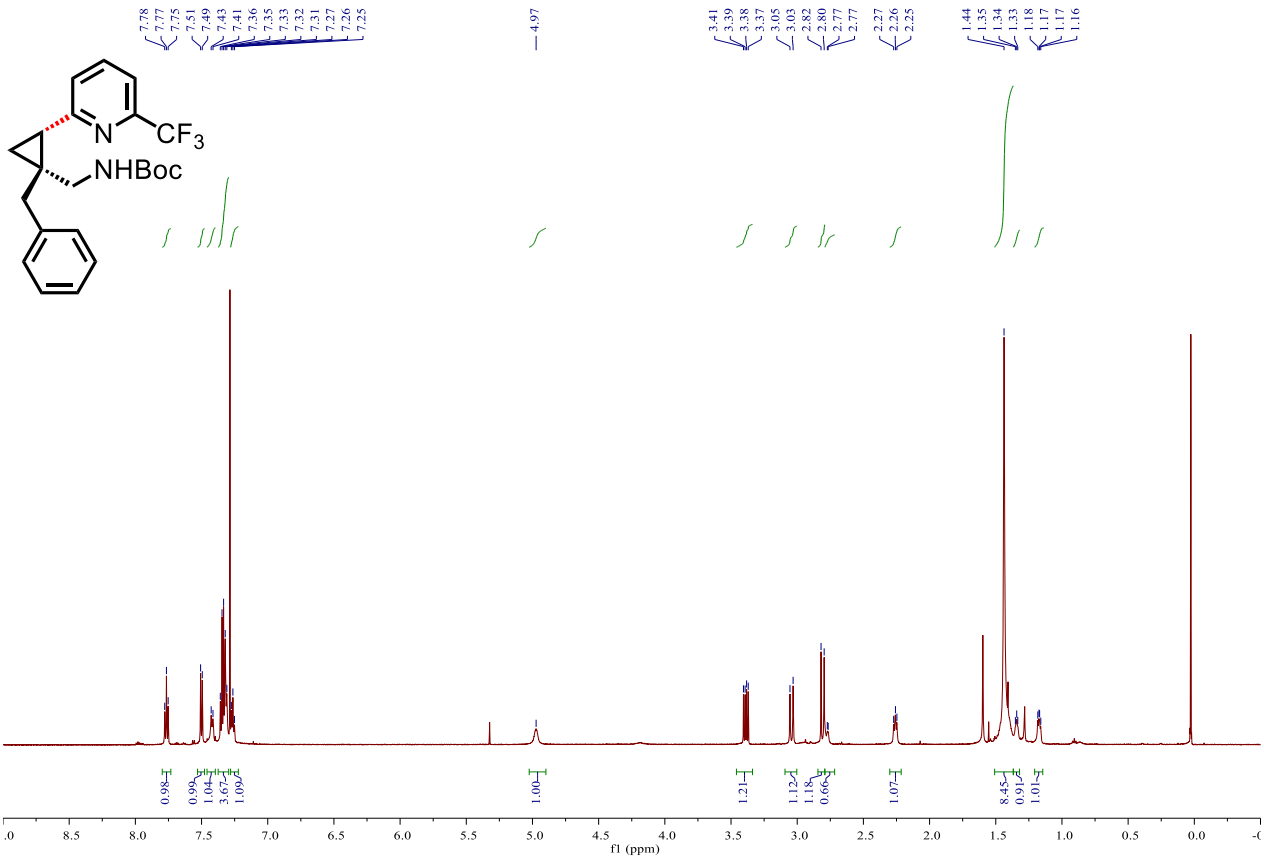
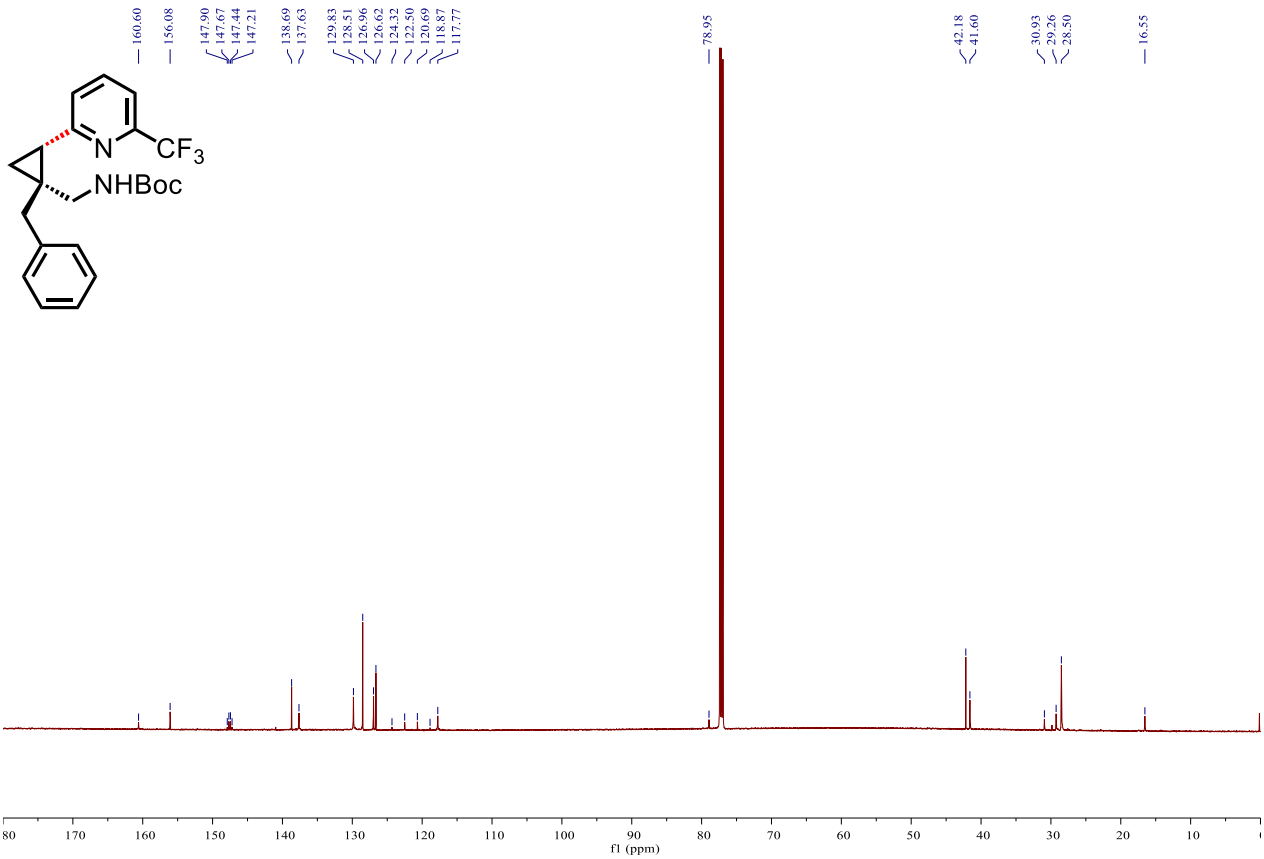
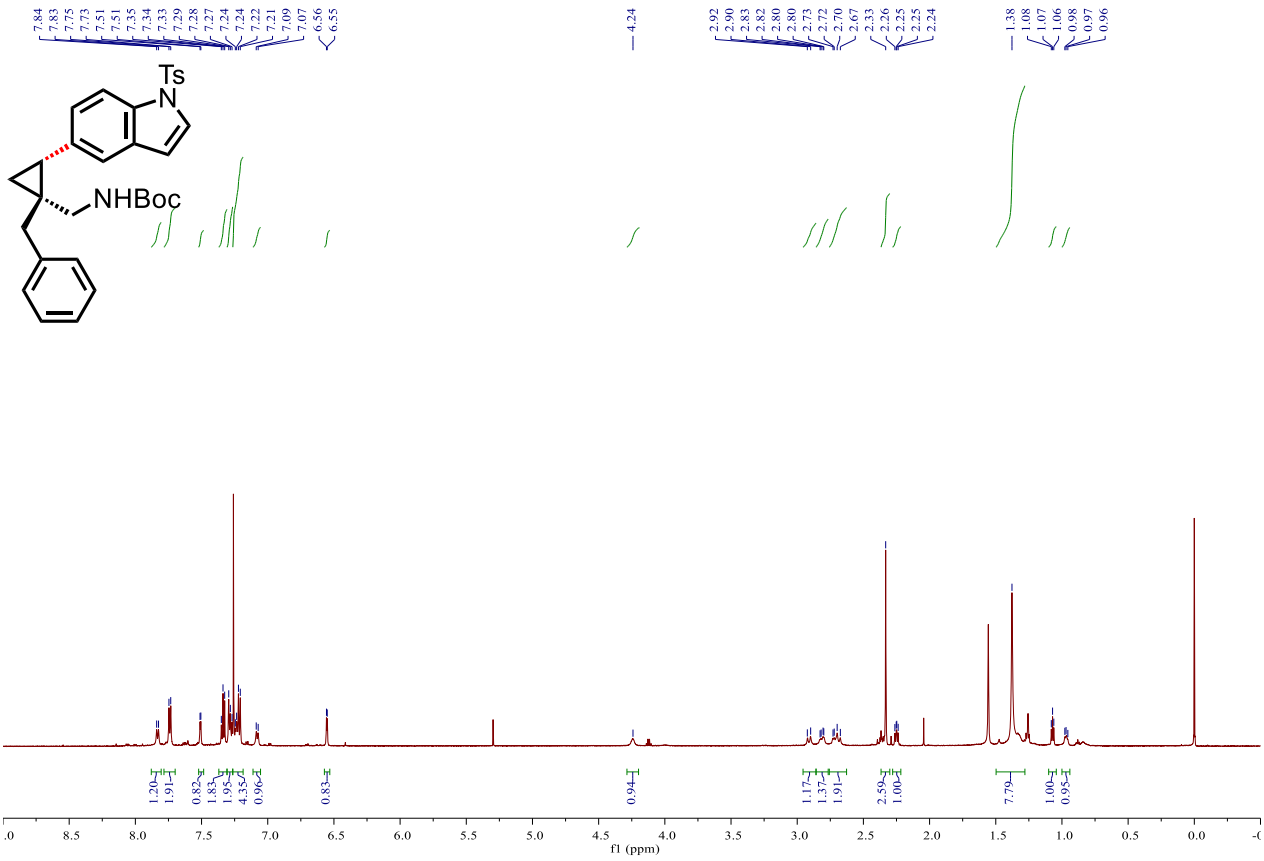
148.40
148.17
147.95
138.26
129.53
128.81
127.06
126.23
124.41
122.60
120.93
120.78
118.96
79.62
42.44
41.71
30.74
28.45
27.31
15.80
N
CF3
NHBoc
f1 (ppm)

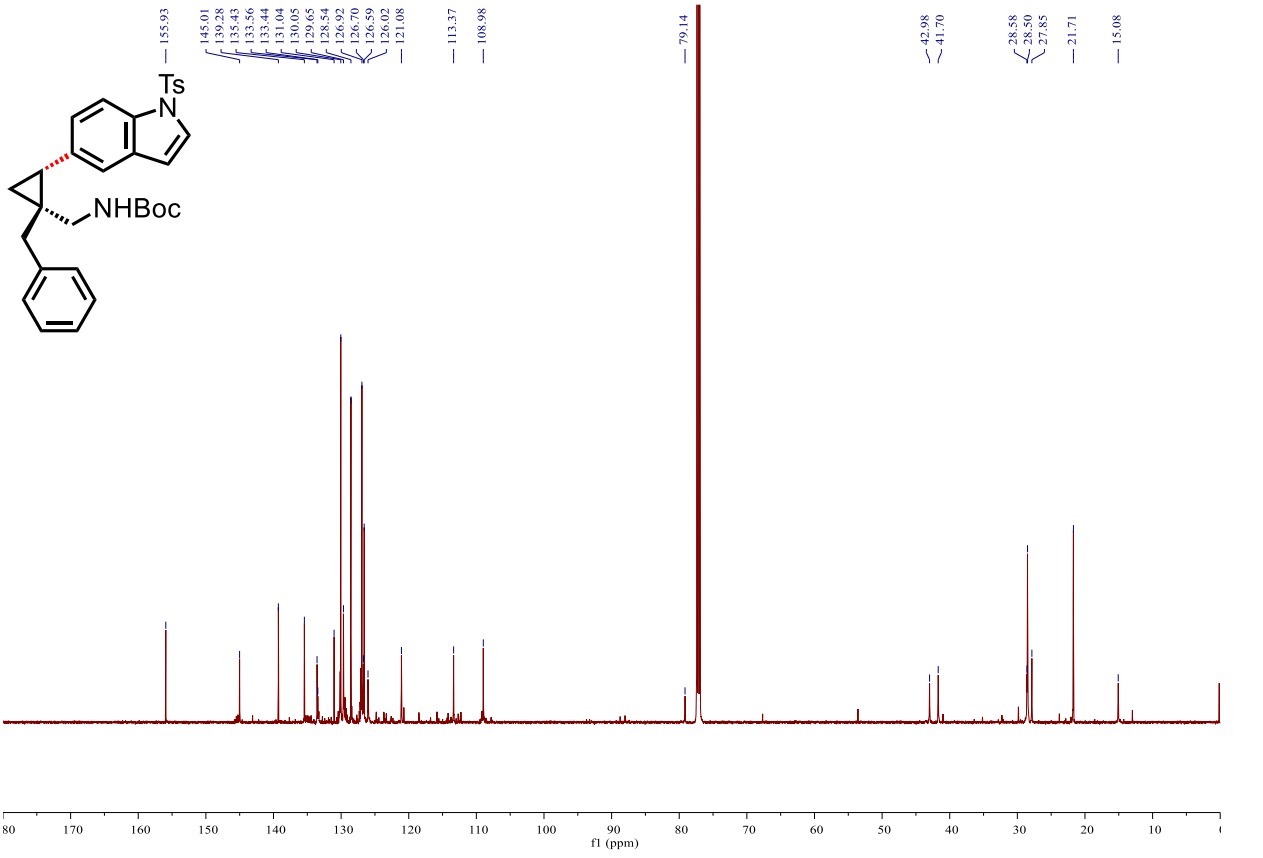

8.54
7.57
7.37
7.35
7.34
7.29
7.28
7.27
4.34
3.01
2.98
2.88
2.87
2.85
2.85
2.73
2.72
2.70
2.68
2.25
2.24
2.22
1.39
1.26
1.25
1.15
1.14
1.13
CF3
N
NHBoc
0.95
1.66
1.67
3.10
0.82
1.00
1.04
1.78
1.11
7.38
1.30
1.13
f1 (ppm)

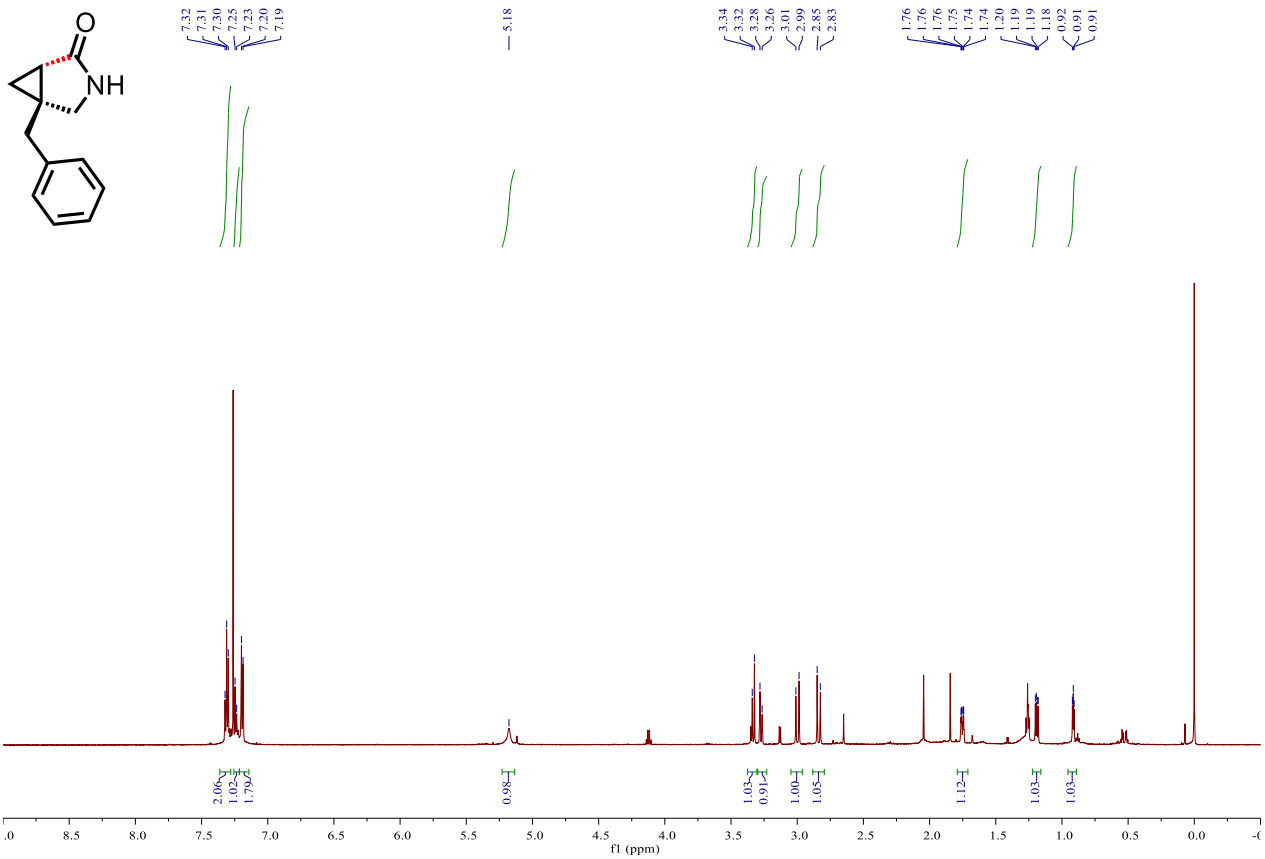

158.86
155.82
151.08
146.47
146.23
145.99
145.76
138.53
136.81
129.44
128.83
127.02
124.51
122.69
120.88
120.12
119.06
79.58
42.52
41.80
29.83
28.47
25.35
15.54
CF3
N
NHBoc
f1 (ppm)

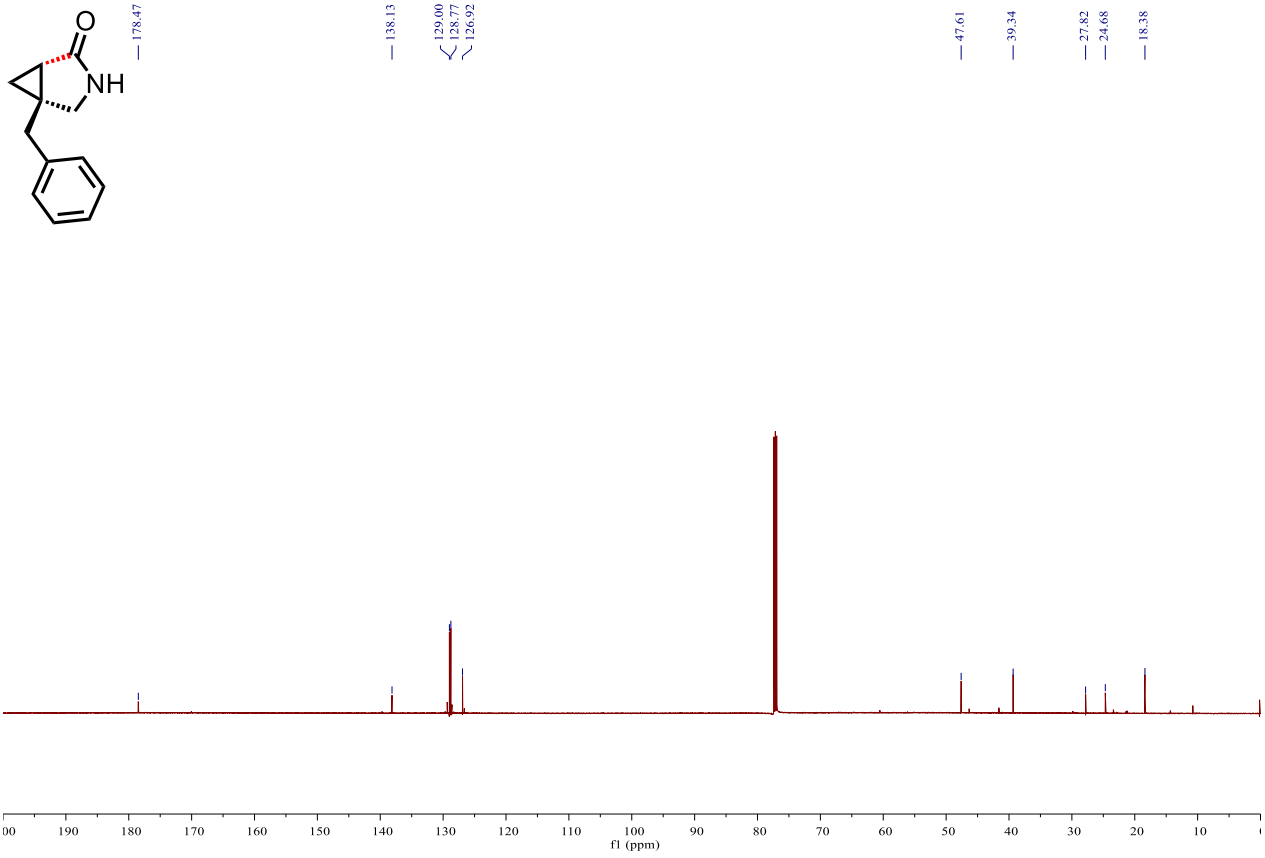

7.78
7.77
7.75
7.51
7.49
7.43
7.41
7.36
7.35
7.33
7.32
7.31
7.27
7.26
7.25
4.97
3.41
3.39
3.38
3.37
3.05
3.03
2.82
2.80
2.77
2.77
2.27
2.26
2.25
1.44
1.35
1.34
1.33
1.18
1.17
1.17
1.16
N
CF3
NHBoc
0.98
0.99
1.04
3.67
1.09
1.00
1.21
1.12
1.18
0.66
1.07
8.45
0.91
1.01
f1 (ppm)

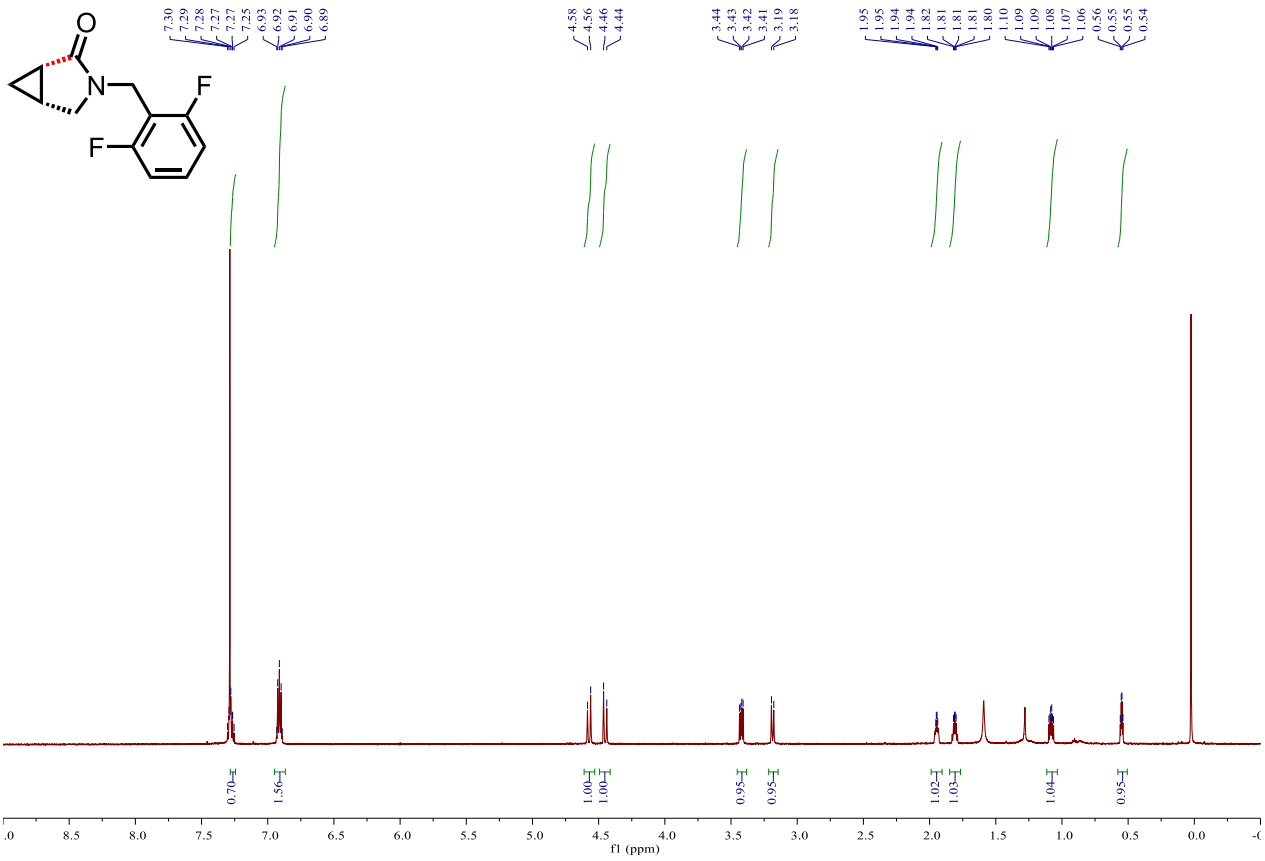

160.60
156.08
147.90
147.67
147.44
147.21
138.69
137.63
129.83
128.51
126.96
126.62
124.32
122.50
120.69
118.87
117.77
78.95
42.18
41.60
30.93
29.26
28.50
16.55
N
CF3
NHBoc
f1 (ppm)

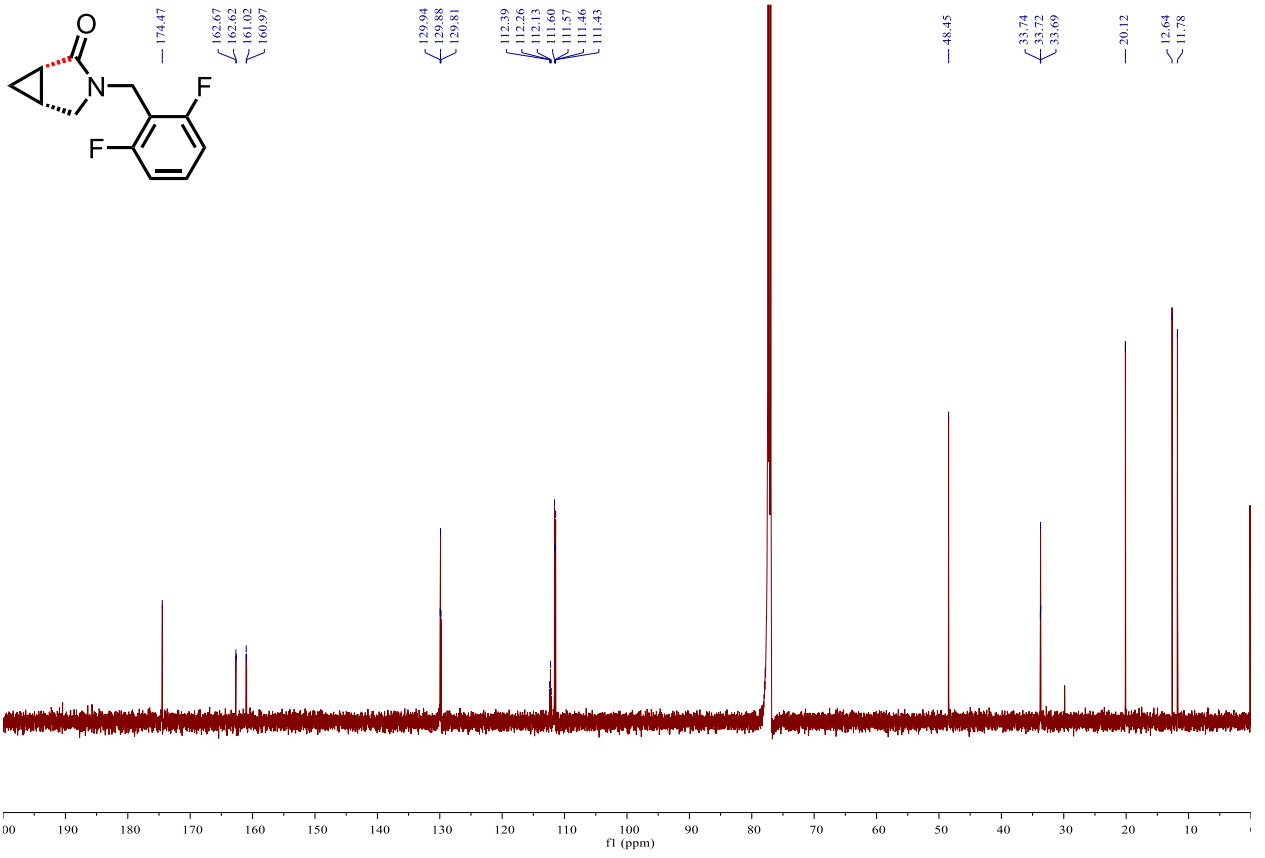

Ts
N
NHBoc
f1 (ppm)

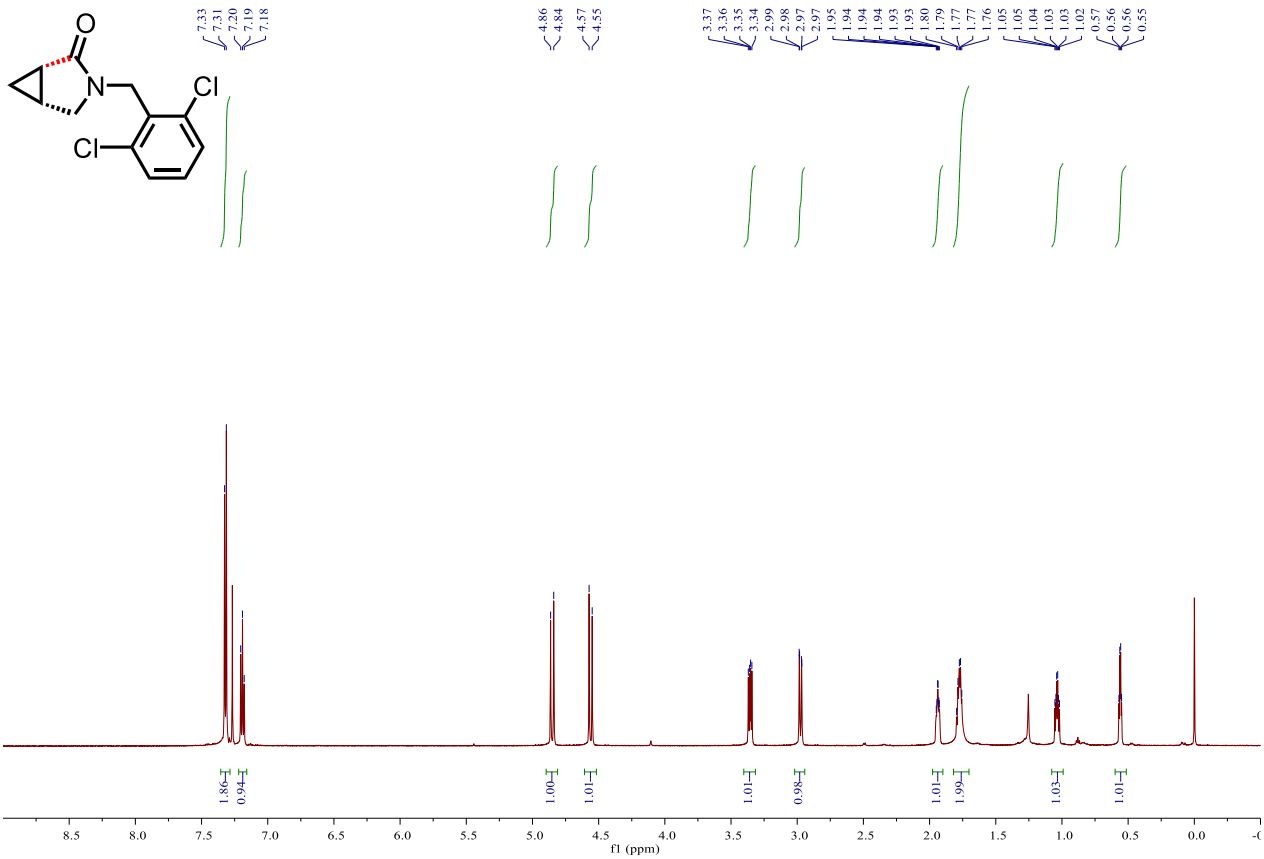

Ts
N
NHBoc
f1 (ppm)

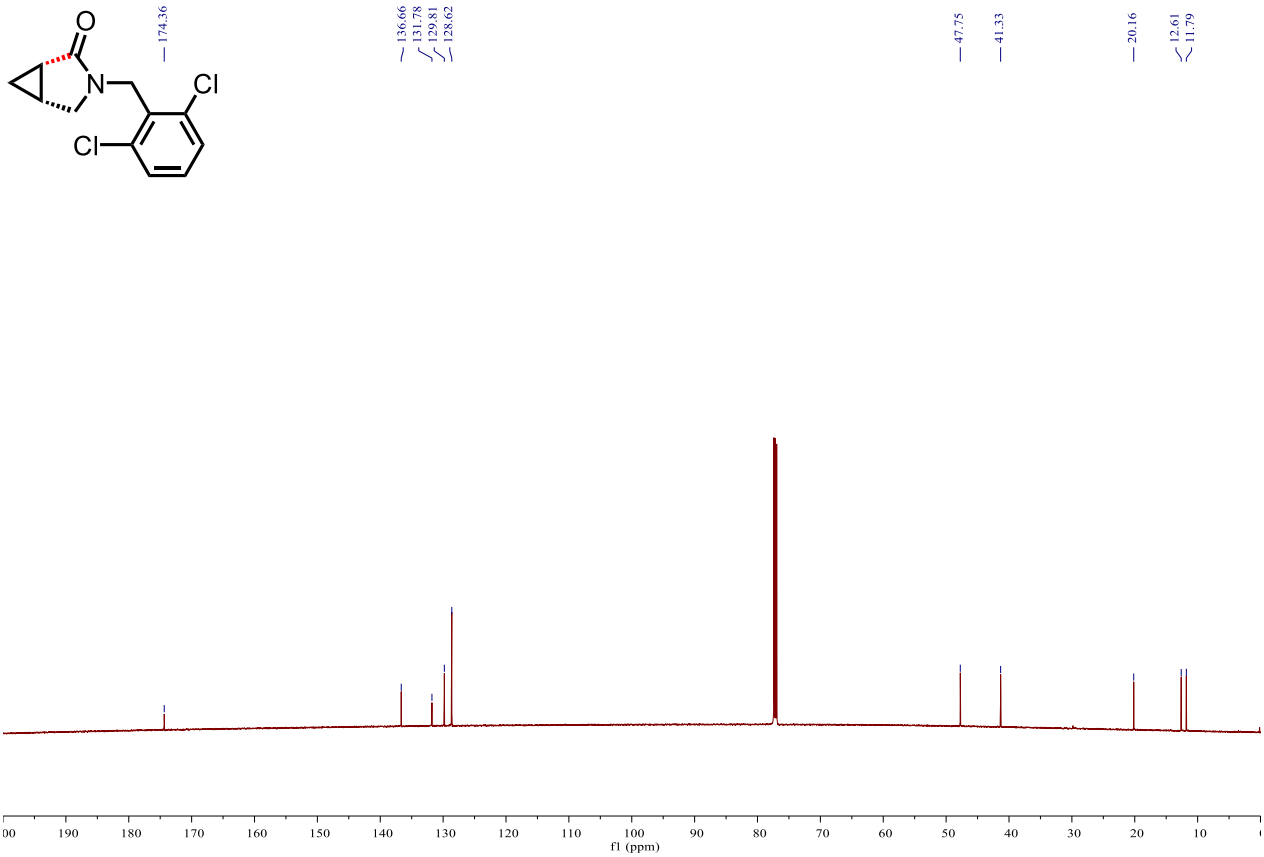

O
NH
7.32
7.31
7.30
7.25
7.23
7.20
7.19
5.18
3.34
3.32
3.28
3.26
3.01
2.99
2.85
2.83
1.76
1.76
1.76
1.75
1.74
1.74
1.20
1.19
1.19
1.18
0.92
0.91
0.91
2.06
1.02
1.79
0.98
1.03
0.91
1.00
1.05
1.12
1.03
1.03
f1 (ppm)

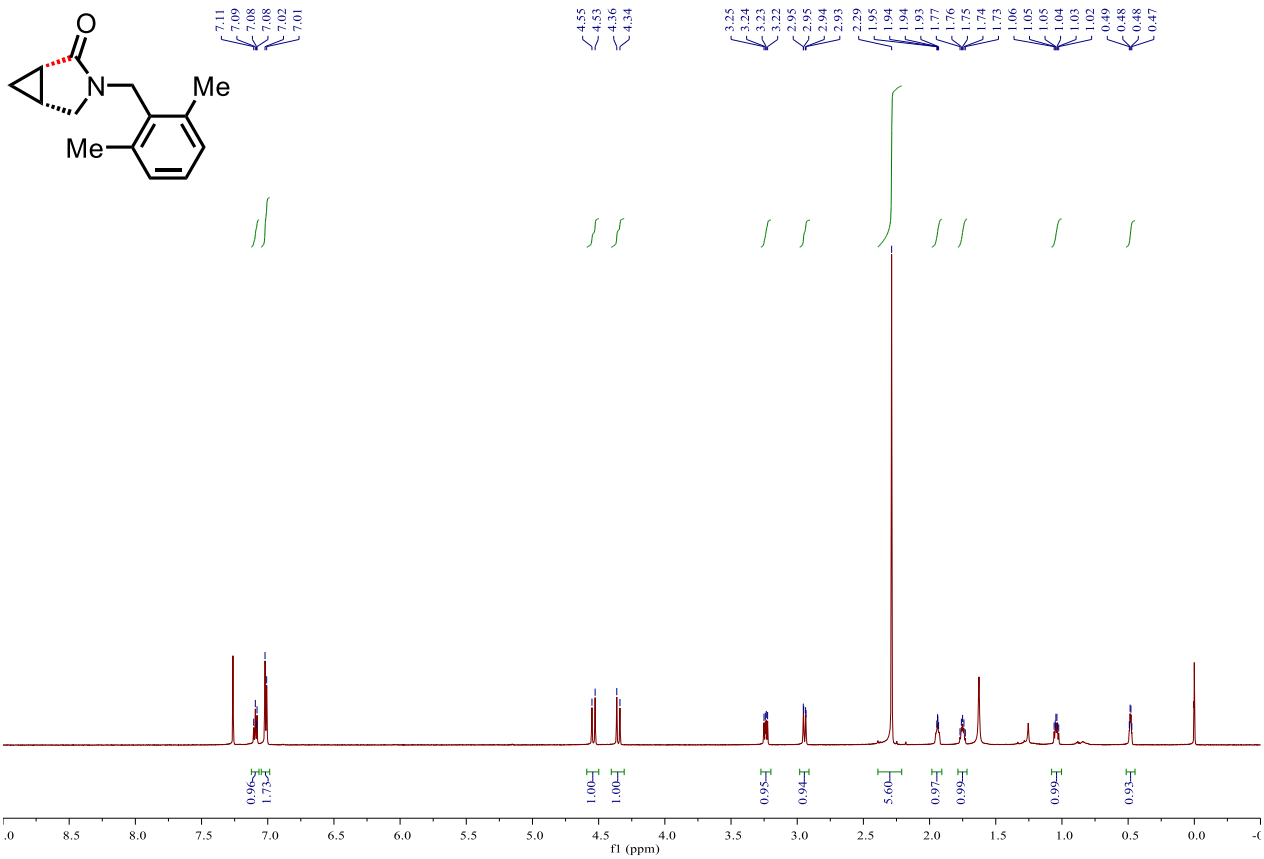

O
NH
178.47
138.13
129.00
128.77
126.92
47.61
39.34
27.82
24.68
18.38
f1 (ppm)

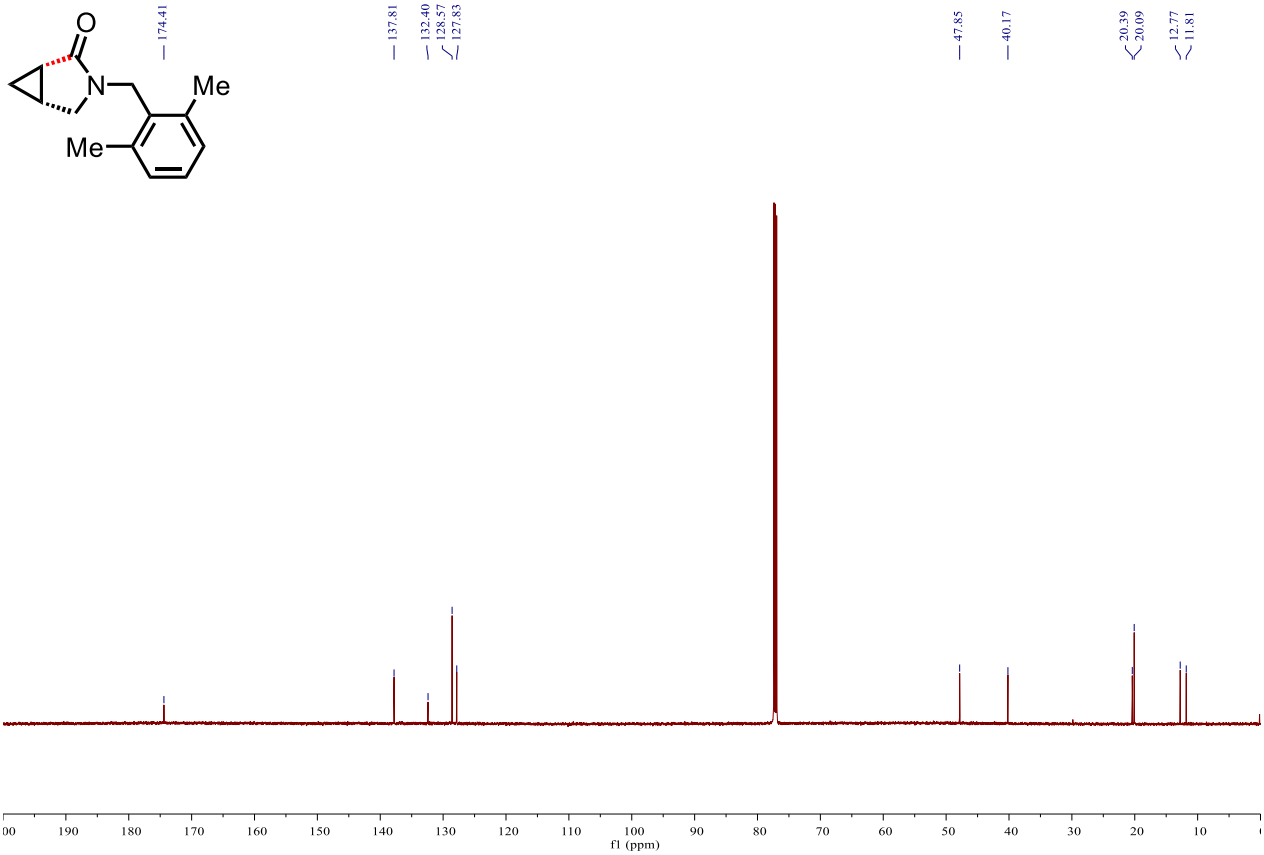

O
N
F
F
7.30
7.29
7.28
7.27
7.27
7.25
6.93
6.92
6.91
6.90
6.89
4.58
4.56
4.46
4.44
3.44
3.43
3.42
3.41
3.19
3.18
1.95
1.95
1.94
1.94
1.82
1.81
1.81
1.81
1.80
1.10
1.09
1.09
1.08
1.07
1.06
0.56
0.55
0.55
0.54
0.70
1.56
1.00
1.00
0.95
0.95
1.02
1.03
1.04
0.95
f1 (ppm)

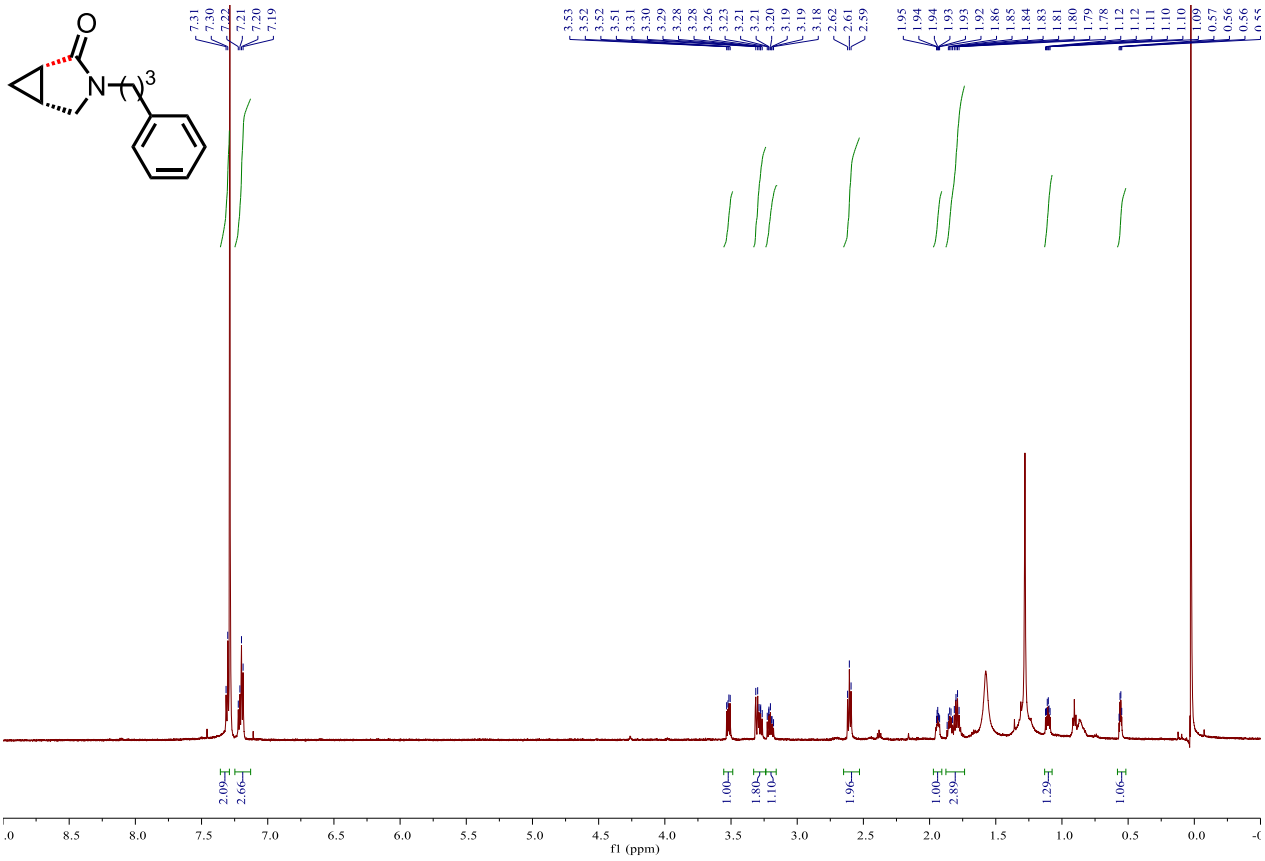

O
N
F
F
174.47
162.67
162.62
161.02
160.97
129.94
129.88
129.81
112.39
112.26
112.13
111.60
111.57
111.46
111.43
48.45
33.74
33.72
33.69
20.12
12.64
11.78
f1 (ppm)

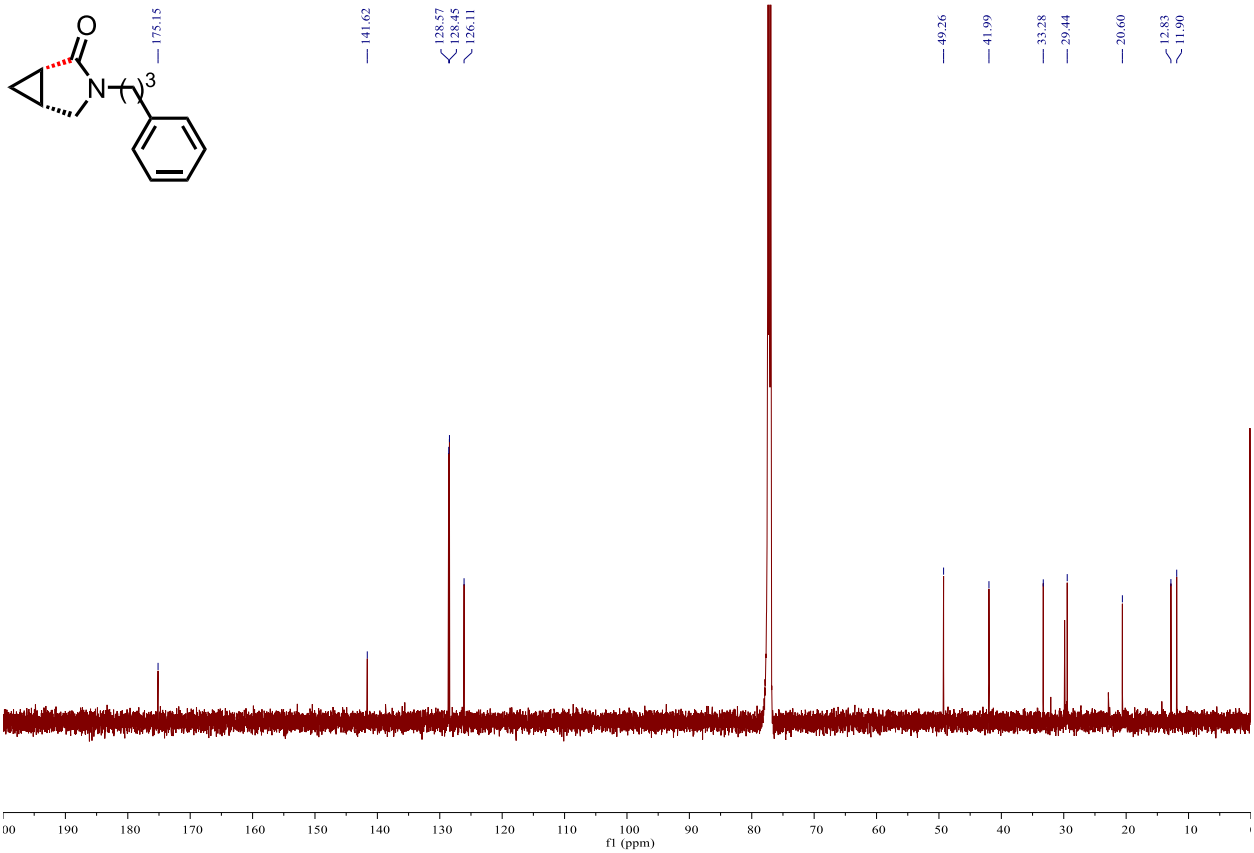

O
N
Cl
Cl
7.33
7.31
7.20
7.19
7.18
4.86
4.84
4.57
4.55
3.37
3.36
3.35
3.34
2.99
2.98
2.97
2.97
1.95
1.94
1.94
1.94
1.93
1.93
1.80
1.79
1.77
1.77
1.76
1.05
1.05
1.04
1.03
1.03
1.02
0.57
0.56
0.56
0.55
1.86
0.94
1.00
1.01
1.01
0.98
1.01
1.99
1.03
1.01
f1 (ppm)

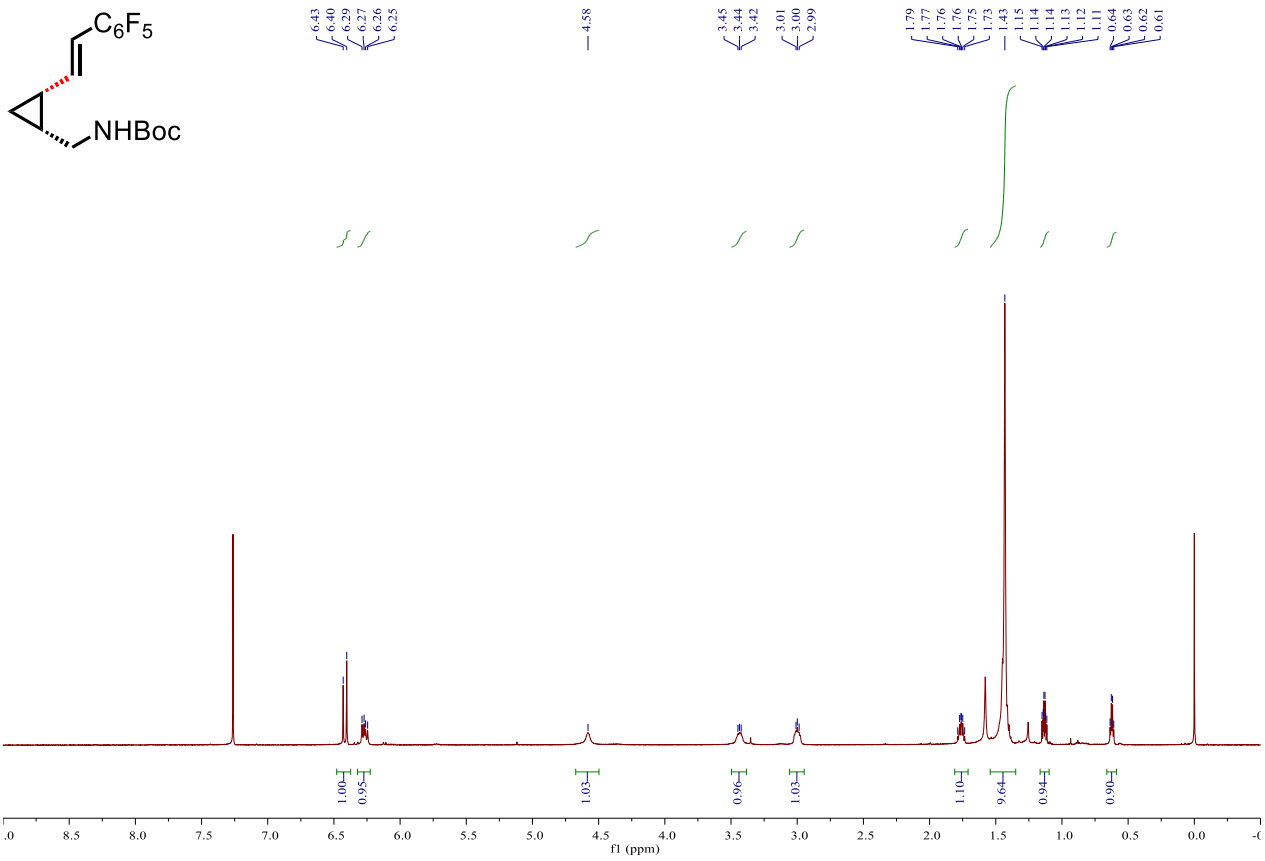

O
N
Cl
Cl
174.36
136.66
131.78
129.81
128.62
47.75
41.33
20.16
12.61
11.79
f1 (ppm)

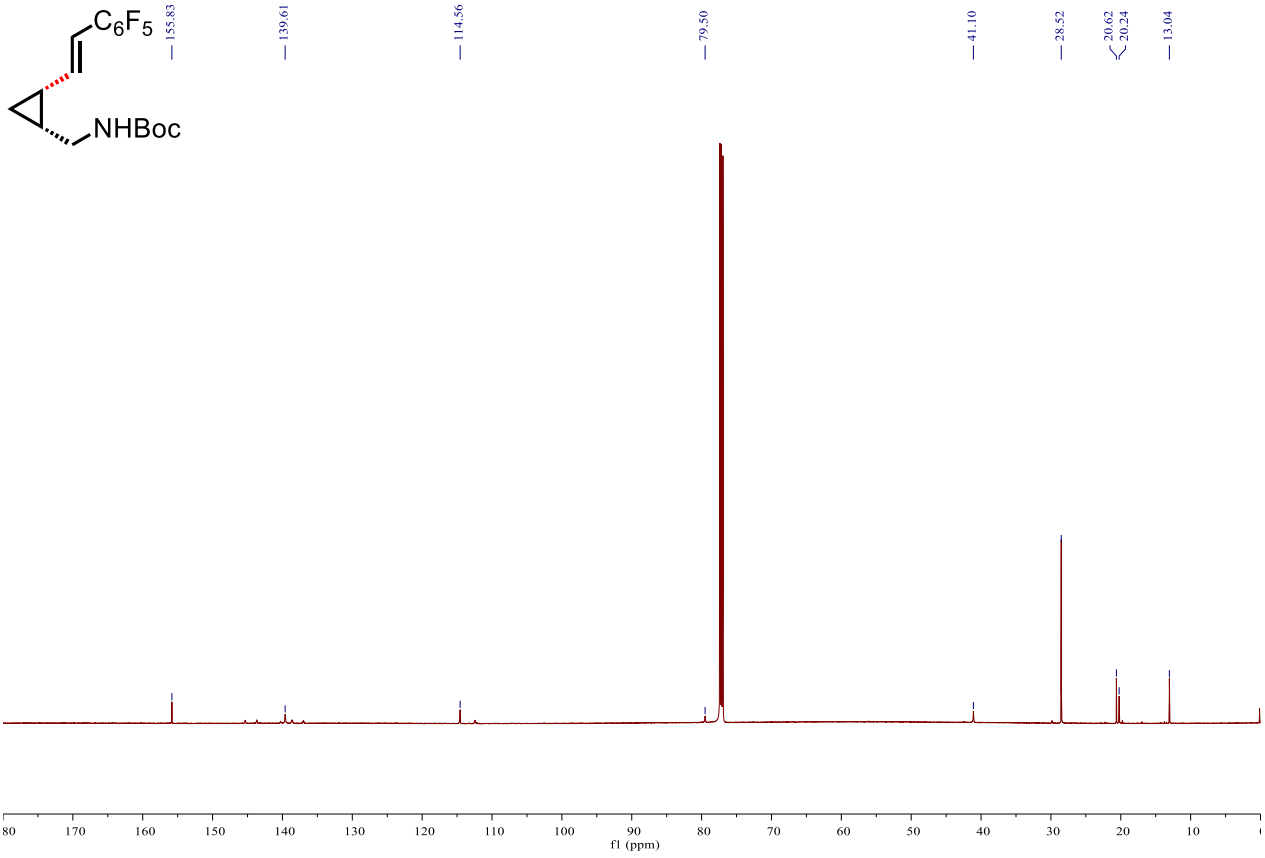

O
N
Me
Me
7.11
7.09
7.08
7.08
7.02
7.01
4.55
4.53
4.36
4.34
3.25
3.24
3.23
3.22
2.95
2.95
2.94
2.93
2.29
1.95
1.94
1.94
1.93
1.77
1.76
1.75
1.74
1.73
1.06
1.05
1.05
1.04
1.03
1.02
0.49
0.48
0.48
0.47
0.96
1.73
1.00
1.00
0.95
0.94
5.60
0.97
0.99
0.99
0.93
f1 (ppm)

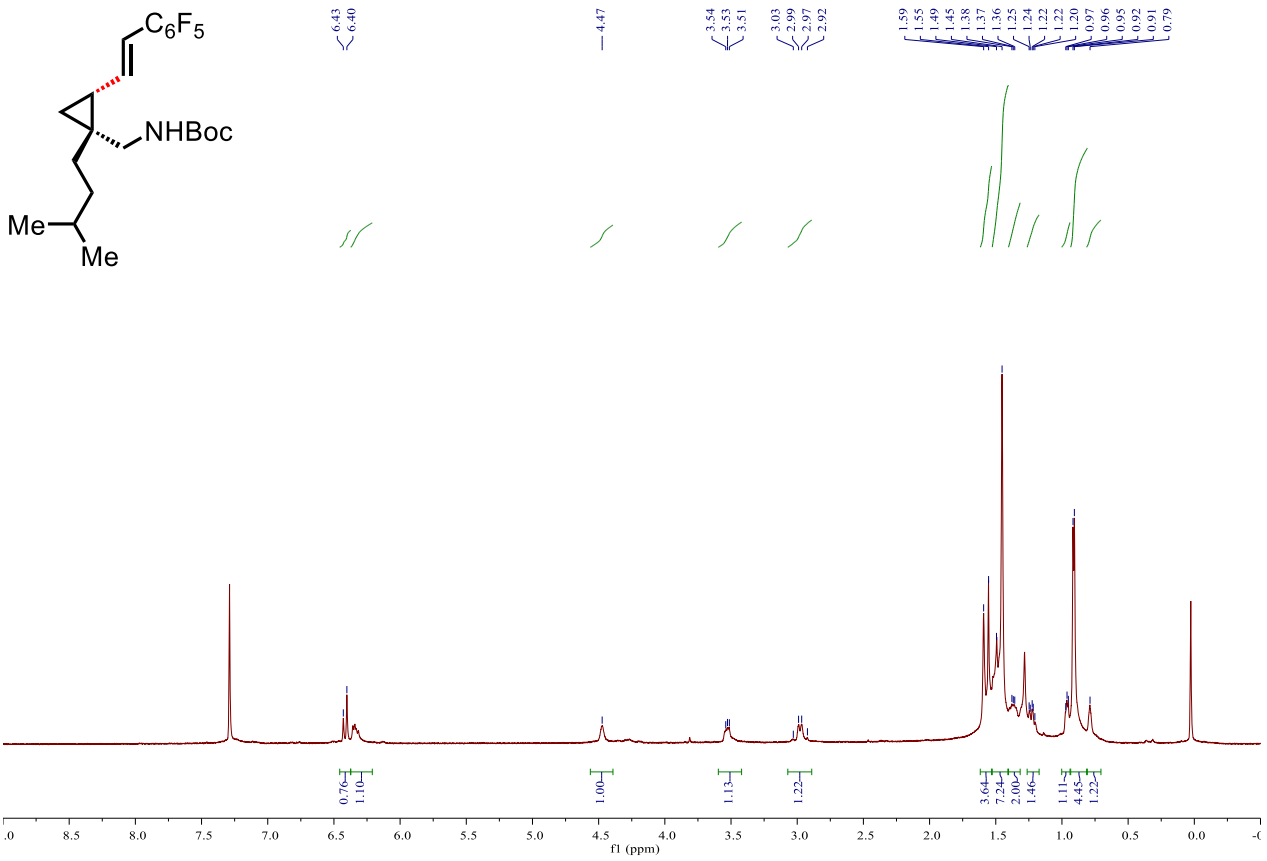

O
N
Me
Me
174.41
137.81
132.40
128.57
127.83
47.85
40.17
20.39
20.09
12.77
11.81
f1 (ppm)

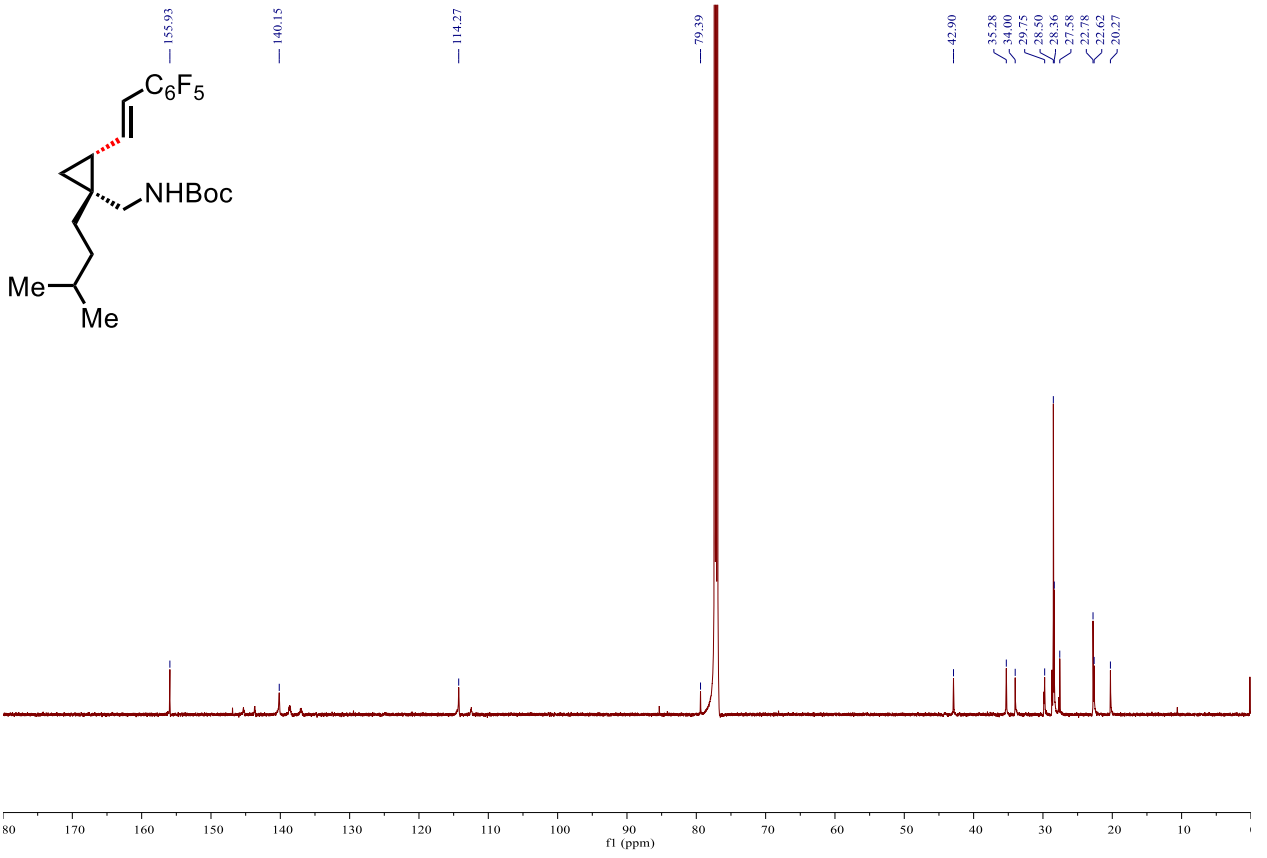

O
N
3
7.31
7.30
7.22
7.21
7.20
7.19
3.53
3.52
3.52
3.51
3.31
3.30
3.29
3.28
3.28
3.26
3.23
3.21
3.21
3.20
3.19
3.19
3.18
2.62
2.61
2.59
1.95
1.94
1.94
1.93
1.93
1.92
1.86
1.85
1.84
1.83
1.81
1.80
1.79
1.78
1.12
1.12
1.11
1.10
1.10
1.09
0.57
0.56
0.56
2.09
2.66
1.00
1.80
1.10
1.96
1.00
2.89
1.29
1.06
f1 (ppm)

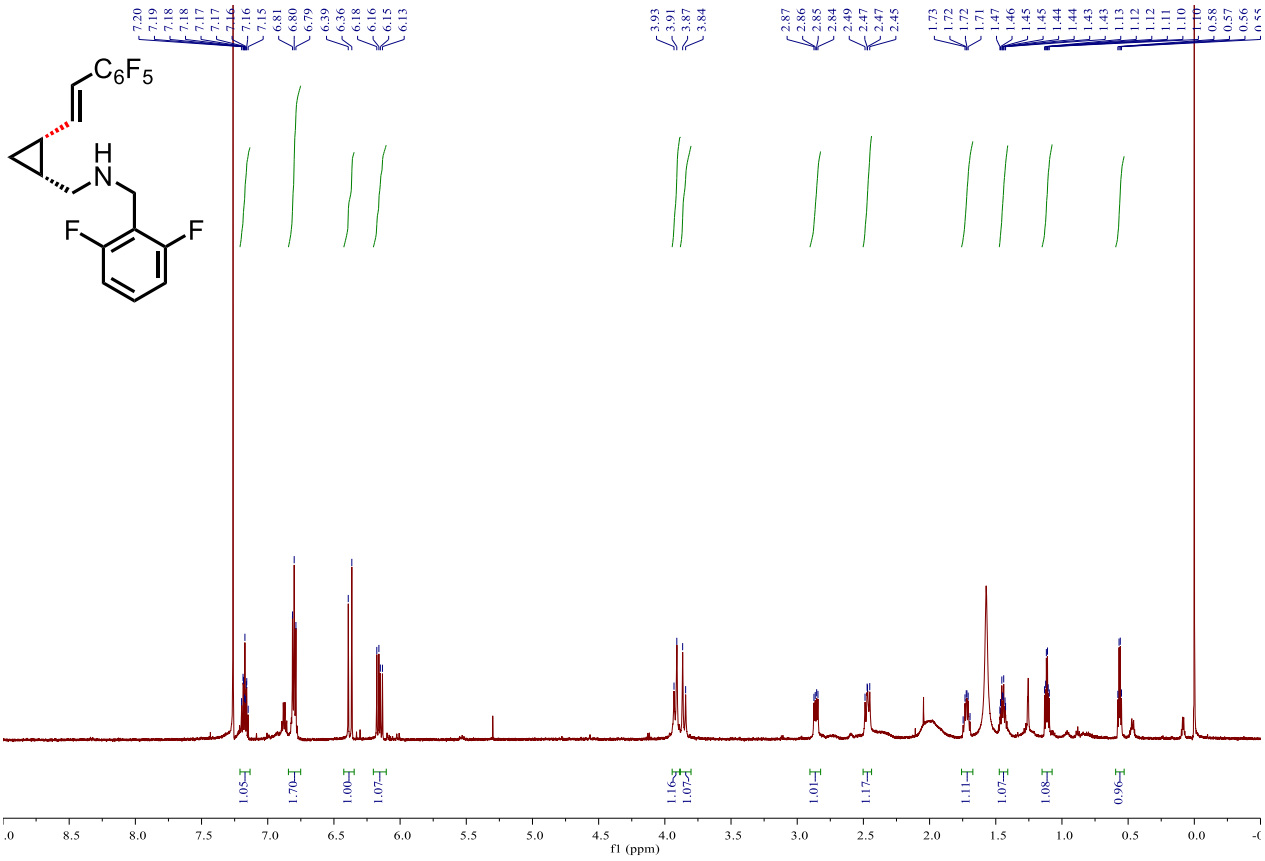

O
N
3
175.15
141.62
128.57
128.45
126.11
49.26
41.99
33.28
29.44
20.60
12.83
11.90
f1 (ppm)

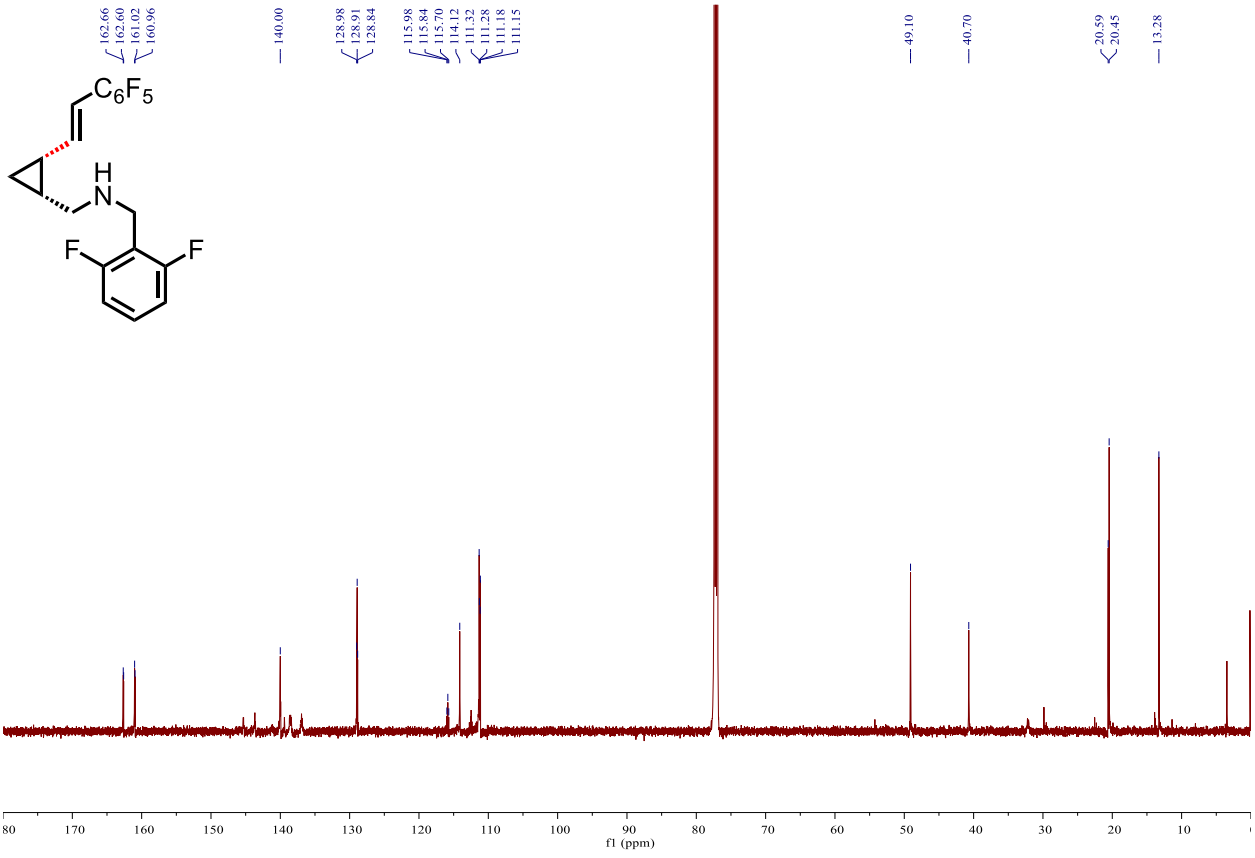

C6F5
NHBoc
6.43
6.40
6.29
6.27
6.26
6.25
4.58
3.45
3.44
3.42
3.01
3.00
2.99
1.79
1.77
1.76
1.76
1.75
1.73
1.43
1.15
1.14
1.14
1.13
1.12
1.11
0.64
0.63
0.62
0.61
1.00
0.95
1.03
0.96
1.03
1.10
9.64
0.94
0.90
f1 (ppm)

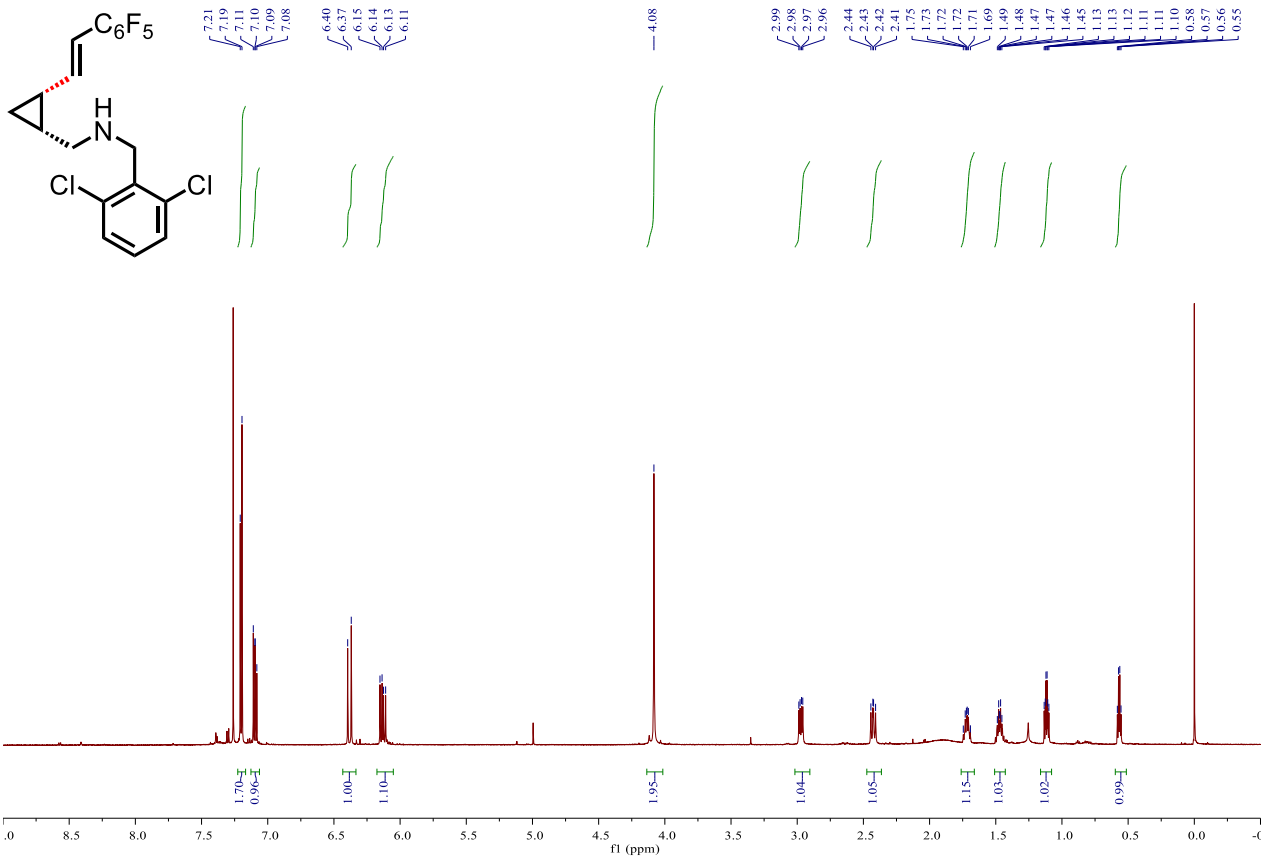

C6F5
NHBoc
155.83
139.61
114.56
79.50
41.10
28.52
20.62
20.24
13.04
f1 (ppm)

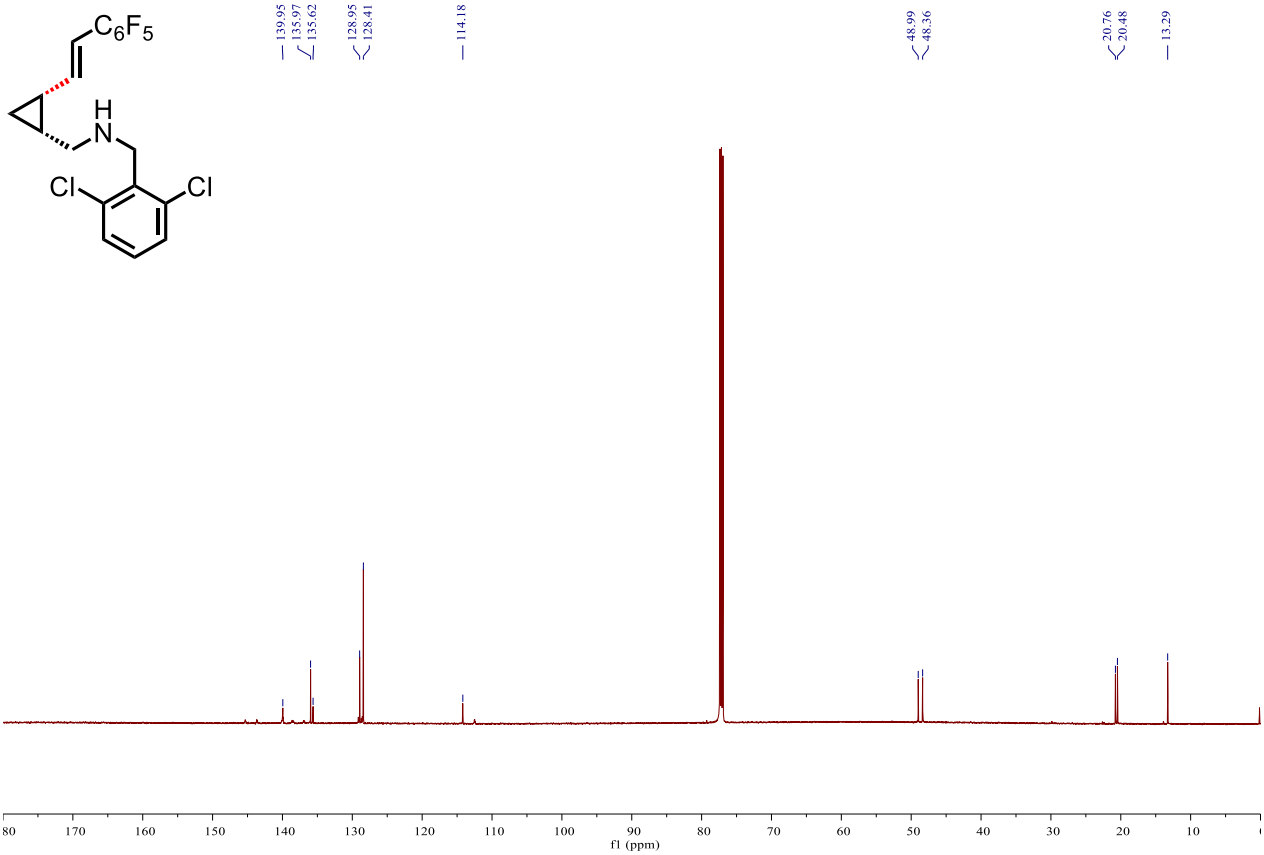

C6F5
NHBoc
Me
Me
6.43
6.40
4.47
3.54
3.53
3.51
3.03
2.99
2.97
2.92
1.59
1.55
1.49
1.45
1.38
1.37
1.36
1.25
1.24
1.22
1.22
1.20
0.97
0.96
0.95
0.92
0.91
0.79
0.76
1.10
1.00
1.13
1.22
3.64
7.24
2.00
1.46
1.11
4.45
1.22
f1 (ppm)

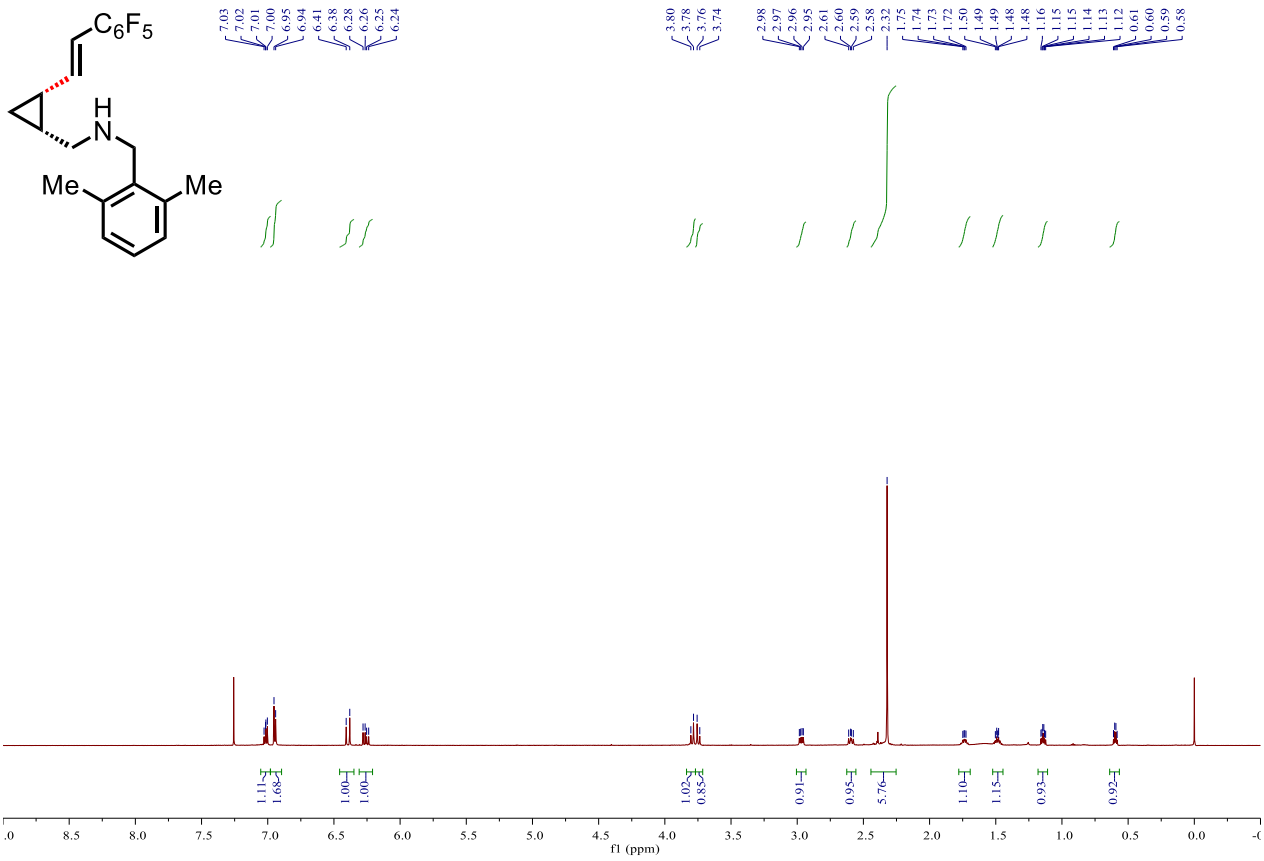

C6F5
NHBoc
Me
Me
155.93
140.15
114.27
79.39
42.90
35.28
34.00
29.75
28.50
28.36
27.58
22.78
22.62
20.27
f1 (ppm)

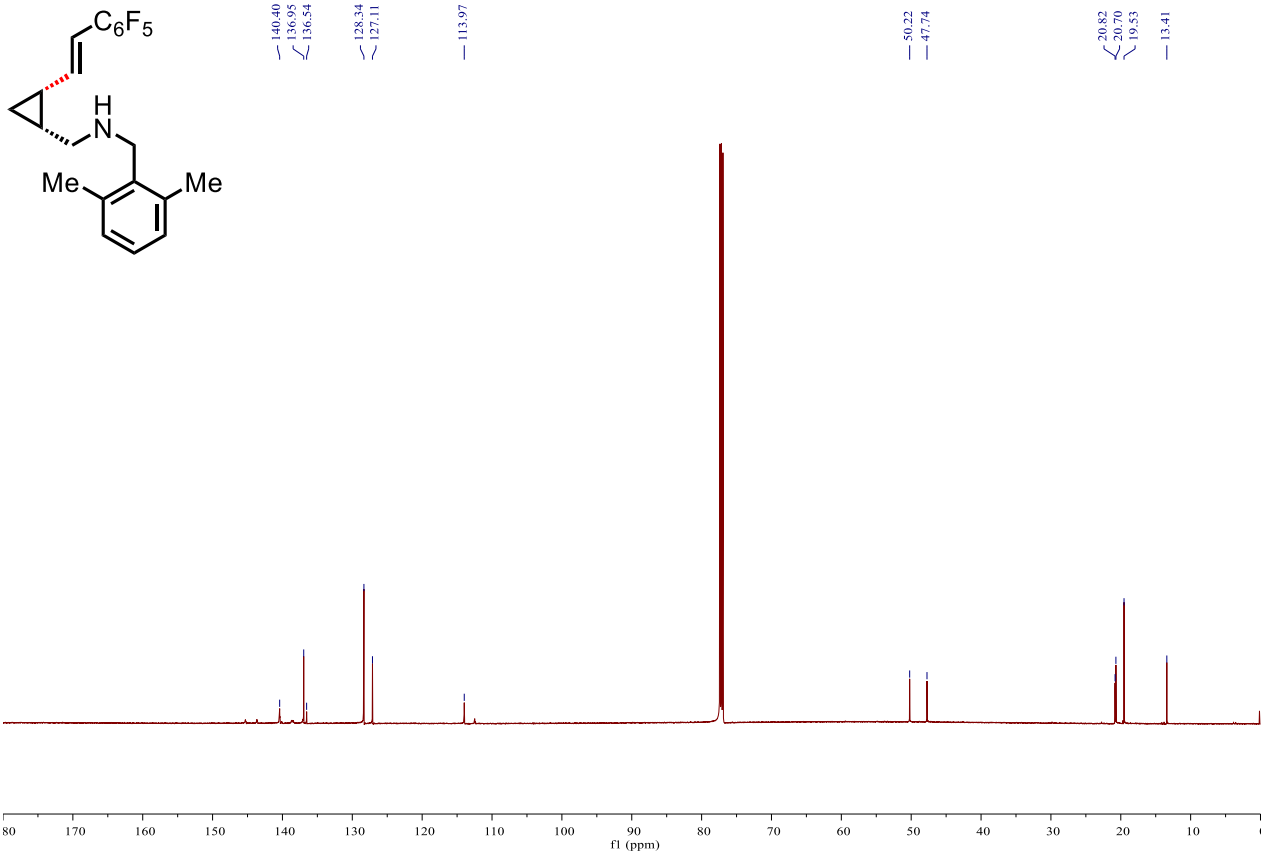

C6F5
H
N
F
F
f1 (ppm)


C6F5
H
N
F
F
f1 (ppm)


C6F5
H
N
Cl
Cl
7.21
7.19
7.11
7.10
7.09
7.08
6.40
6.37
6.15
6.14
6.13
6.11
4.08
2.99
2.98
2.97
2.96
2.44
2.43
2.42
2.41
1.75
1.73
1.72
1.72
1.71
1.69
1.49
1.48
1.47
1.47
1.46
1.45
1.13
1.13
1.12
1.11
1.11
1.10
0.58
0.57
0.56
0.55
1.70
0.96
1.00
1.10
1.95
1.04
1.05
1.15
1.03
1.02
0.99
f1 (ppm)


C6F5
H
N
Cl
Cl
139.95
135.97
135.62
128.95
128.41
114.18
48.99
48.36
20.76
20.48
13.29
f1 (ppm)


C6F5
H
N
Me
Me
7.03
7.02
7.01
7.00
6.95
6.94
6.41
6.38
6.28
6.26
6.25
6.24
3.80
3.78
3.76
3.74
2.98
2.97
2.96
2.95
2.61
2.60
2.59
2.58
2.32
1.75
1.74
1.73
1.72
1.50
1.49
1.49
1.48
1.48
1.16
1.15
1.15
1.14
1.13
1.12
0.61
0.60
0.59
0.58
1.11
1.68
1.00
1.00
1.02
0.85
0.91
0.95
5.76
1.10
1.15
0.93
0.92
f1 (ppm)


C6F5
H
N
Me
Me
140.40
136.95
136.54
128.34
127.11
113.97
50.22
47.74
20.82
20.70
19.53
13.41
f1 (ppm)