Solvent Dependent Access to *E* vs Z-allylic amines via Decarboxylative Vinylation of Amino Acids

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Supporting information

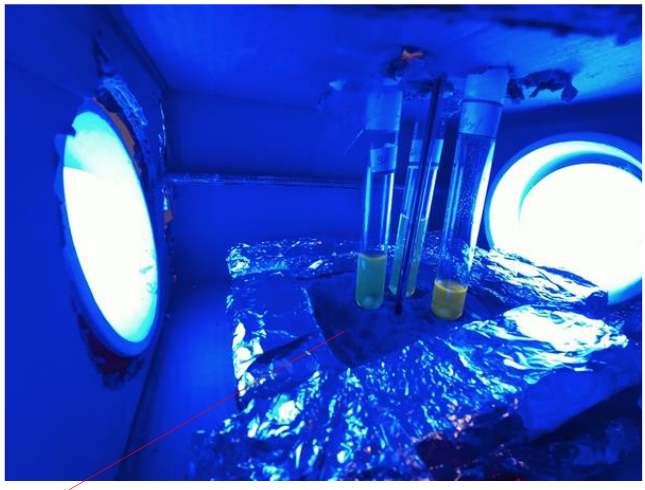
Table of Conents

General Information: Unless otherwise stated, reactions were performed under nitrogen using freshly purified solvents. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed with indicated solvents using silica gel. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 400, 500 MHz NMR instrument. Data for ^{1}H NMR are reported as follows: chemical shift (ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, ddd = doublet of doublets of doublets and m = multiplet), and coupling constant (Hz). Mass spectra were acquired on an Agilent technologies 1200 series LC/MS using indicated ionization methods. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. For all the known compounds copy of ^{1}H-NMR, ^{13}C NMR and the appropriate references are given.

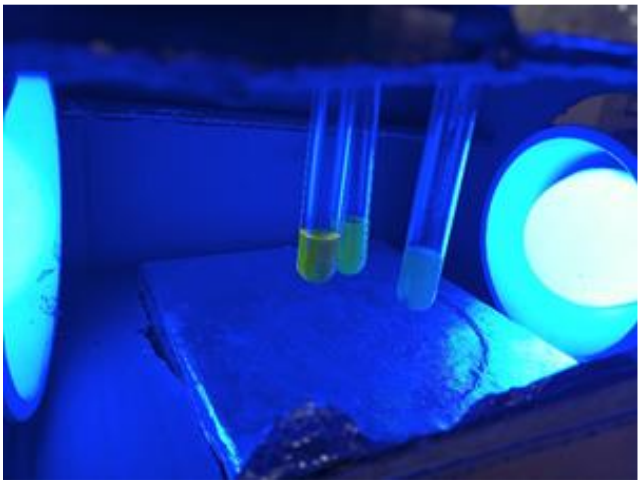
Materials: Chemicals were purchased from Aldrich, Alfa Aesar, Spectrochem, Avra, TCI and used without purification unless otherwise noted.

1. Experimental Set-up

Photo catalytic reactions were set up in a light bath which is described below. Blue LEDs (12W×2; model 12062, Empire LED company, India) were set up on the table lamp stand, which is fixed on a Cardboard Rectangle Corrugated Paper Box and then wrapped with aluminium foil. The reaction was set-up top of a magnetic stirrer. A lid which rest on the top was fashioned from cardboard and holes were made such that reaction tubes (18 x 150 mm, 27 ml borosilicate tube) were held firmly in the cardboard lid which was placed on the top of bath. To maintained the 50 ^{o}C (for *E*-isomer), we have used sand bath, which was connected with a temperature sensor and a thermometer to measure the accurate temperature. In case of *Z*-isomer, reactions were performed at room temperature.



Set-up for getting *E*-isomer



Set-up for getting *Z*-isomer

1. Decarboxylative Vinylation Procedure:

General procedure (A) for the decarboxylative (*E*) vinylation of N-Boc α amino acids:

To a dry 20 mL vial equipped with a stir bar was added 4CzIPN (2.3 mg, 0.003 mol,0.01 equiv.), the vinyl sulfone (0.30 mmol, 1.0 equiv.), Cs_2CO_3 (195mg, 0.60 mmol, 2 equiv.) and the *N*-Boc-α-amino acid (0.60 mmol, 2 equiv.). The vial was sealed and then DMA (5 ml) was added to the vial and the resulting mixture degassed by freeze-pump-thaw under nitrogen (three times). The vial was then placed in a photoreactor which was pre-set to 50 °C, and irradiated with 2 x Blue LED bulbs until complete consumption of the vinyl sulfone, as determined by TLC analysis (48–64h). The reaction mixture was diluted with H_2O and workup by using EtOAc and the organic residue concentrated *in vacuo*. Purification by flash column chromatography or preparative TLC afforded the (*E*)-vinylation product.

General procedure (B) for the decarboxylative (*Z*) vinylation of *N*-Boc α amino acids:

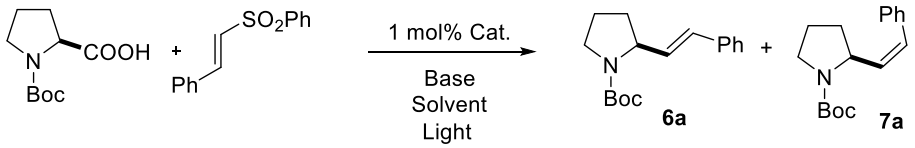
To a dry 20 mL vial equipped with a stir bar was added 4CzIPN (2.3 mg, 0.003 mol, 0.01 equiv.), the vinyl sulfone (0.30 mmol, 1.0 equiv.), Cs_2CO_3 (195mg, 0.60 mmol, 2 equiv.) and the *N*-Boc-α-amino acid (0.60 mmol, 2 equiv.). The vial was sealed and then 1,4-dioxane (4 ml) was added to the vial and the resulting mixture degassed by freeze-pump-thaw under nitrogen (three times). Then, the vial was placed in a photo reactor and irradiated with 2 x Blue LED bulbs for 48h. After the complete consumption, the reaction mixture was diluted with H_2O and workup by using EtOAc and the organic

residue concentrated *in vacuo*. Purification by flash column chromatography or preparative TLC afforded the (*Z*)-vinylation product.

General procedure (C) for the decarboxylative allylation of *N*-Boc α amino acids:

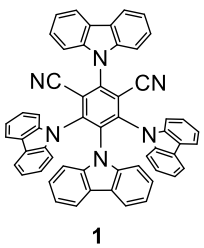
To a dry 20 mL vial equipped with a stir bar was added 4CzIPN (1 mol%), the allylic sulfone (0.23mmol, 1 equiv), Cs_2CO_3 (0.46 mmol, 2 equiv.) and the *N*-Boc-α-amino acid (2 equiv.). The vial was sealed and then DMF (0.05M) was added to the vial and the resulting mixture degassed by by freeze-pump-thaw under nitrogen (three times). The vial was then placed in photoreactor and irradiated with 2 x Blue LED. The reaction mixture was diluted with H_2O and workup by using EtOAc and the organic residue concentrated *in vacuo*. Purification by flash column chromatography or preparative TLC afforded the vinylation product. (for 1º amino acid, 4 equv of amino acid as well as 4 equv of base are used).

Table 2. Optimization Table for *Z*-selective vinylation



Entry	Solvent	Catalyst	Base	Light	dr (*Z*/*E*) Yield (%)[b]
1	Toluene	1	Cs_2CO_3	Blue	20: 80 (20)
2	Toluene	1	Cs_2CO_3	CFL[C]	33:67 (30)
3	Toluene	1	CsOAc	Blue	30:70 (20)
4	Toluene	1	K_2HPO_4	Blue	20:80 (15)
5	Toluene	1	NaOAc	Blue	0
6	Toluene	1	KOAc	Blue	65:35 (32)
7	Toluene	1	Na_2CO_3	Blue	30:70 (35)
8	Toluene	1	K_2CO_3	Blue	35:65 (20)
9	Toluene	1	DBU	Blue	55:45 (45)
10	Toluene	1	DABCO	Blue	0
11	Toluene	1	$NaHCO_3$	Blue	0
12	Toluene	1	K_3PO_4	Blue	0
13	Toluene	1	$(NH_4)HCO_3$	Blue	0
14	Toluene	2	K_2HPO_4	Blue	0
15	Toluene	2	Cs_2CO_3	Blue	0
16	Toluene	3	Cs_2CO_3	Blue	0
17	Toluene	1	DIPEA	Blue	0
18	Toluene : Chlorobenzene (1:1)	1	Cs_2CO_3	Blue	0
19	Hexane:ACN (2:1)	1	Cs_2CO_3	Blue	0
20	Toluene:DMF (4:1)	1	Cs_2CO_3	Blue	82:18 (50)
21	Toluene:DMF (9:1)	1	Cs_2CO_3	Blue	50:50 (40)
22	Ethyl acetate	1	Cs_2CO_3	Blue	53:47 (85)
23	Benzene	1	Cs_2CO_3	Blue	40:60 (20)
24[c]	Ethyl acetate/Benzene	1	Cs_2CO_3	Blue	10:90 (60)
25	DMSO	1	Cs_2CO_3	Blue	45:55 (70)
26	**1,4-dioxane**	**1**	**Cs_2CO_3**	**Blue**	**08:92 (79)**

[a]vinyl sulphone (1 equiv.), Boc-amino acid (2 equiv.), Cs_2CO_3 (2 equiv.)at RT, bIsolated Yield, solvent (2 ml), [c] single CFL bulb (PHILIPS, Tornado G 6E, 32W, 32 W cool daylight lamp (2150 lm, 67 Lm/W); [d] Ethyl acetate switch to benzene (We choose ethyl acetate for the formation of *E*-isomer majorly and then removed the solvent by roravap and benzene was added for the isomerization step)



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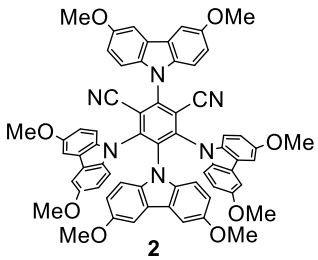

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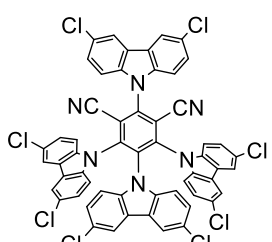

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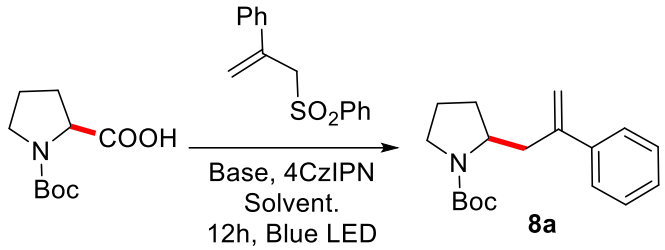
2. Optimization Table of decarboxylative allylation of *N*-Boc α amino acids:

Table 2. Optimization Table of homoallylic amine

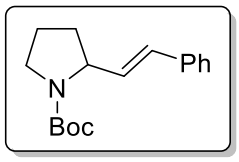


Entry	Solvent	Base	Yield)
1	Toluene	Cs_2CO_3	25
2	CH_3CN	Cs_2CO_3	15
3	MeOH	Cs_2CO_3	NA
4	DMF	Cs_2CO_3	63
5	DMA	Cs_2CO_3	58
6	DMF	Na_2CO_3	42
7	DMF	KOAc	31
8	DMF	K_2HPO_4	10
9	DMF	CsOAc	8
10	DMF	DBU	36

Boc-amino acid (2 equiv.), allylic sulfone (1 equiv.), Base (2 equiv.), RT, solvent (2 ml).

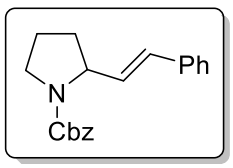
3. Experimental Data for Decarboxylative (*E*) Vinylation Products:

(*E*)-*tert*-butyl 2-styrylpyrrolidine-1-carboxylate (6a)[1]:[i]



Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 48 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (61 mg, 75%, 100:0 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.36-7.26 (m, 4H), 7.23-7.21 (m, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.10 (br. s, 1H), 4.39 (br. s, 1H), 3.46 (s, 2H), 2.09-2.00 (m, 1H), 1.92-1.77 (m, 3H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 154.77, 137.20, 130.86, 129.53, 128.59, 127.34, 126.38, 79.25, 59.05, 46.38, 32.65, 28.60, 23.20.

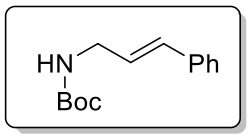
(*E*)-benzyl 2-styrylpyrrolidine-1-carboxylate (6b)[1]:



Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Cbz-Pro-OH (149 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and ACN (5.0 mL) instead of DMA. After 48 h, the reaction solvent was evaporated in reduce pressure. The crude mixture was diluted using DCM and purification was done by preparative TLC using 9:1 hexane:EtOAc

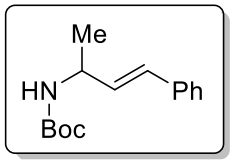
provided the title compound (87 mg, 95%, 98:02 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.35-7.23 (m, 10H), 6.36 (rotamer A, 0.6H, d, *J* = 15.6 Hz), 6.48 (rotamer B, 0.4H, d, *J* = 15.2 Hz), 6.12 (br. s, 1H), 5.21-5.05 (br. m, 2H), 4.60-4.53 (m, 1H), 3.54 (br. s, 2H), 2.10-2.00 (m, 1H), 1.93-1.81 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 155.14, 136.86, 130.25, 129.89, 128.48, 128.38, 127.86, 127.40, 126.43, 66.74, 58.96, 46.84, 46.46, 32.65, 31.67, 23.73, 23.00.

(*E*)-*tert*-butyl cinnamylcarbamate(6c)[2]:



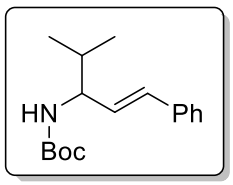
Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Gly-OH (105 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 16:1 hexane:EtOAc provided the title compound (62 mg, 89%, 97:03 *E*:*Z*) as a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.37-7.29 (m, 4H), 7.25-7.23 (m, 1H), 6.51 (d, *J* = 16 Hz, 1H), 6.19 (dt, *J* = 15.8, 6.1 Hz, 1H), 4.65 (br. s, 1H), 3.91 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) 155.78, 136.74, 131.51, 128.77, 128.58, 127.61, 126.38, 79.51, 42.76, 28.44.

(*E*)-*tert*-butyl 4-phenylbut-3-en-2-ylcarbamate (6d)[3]:



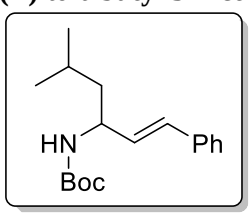
Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Ala-OH (113 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 52 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 16:1 hexane:EtOAc provided the title compound (55 mg, 75%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.37-7.26 (m, 4H), 7.24-7.20 (m, 1H), 6.49 (d, *J* = 16 Hz, 1H), 6.15 (dd, *J* = 16, 5.2 Hz, 1H), 4.55 (br. s, 1H), 4.39 (br. s, 1H), 1.46 (s, 9H), 1.31 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 155.14, 136.85, 131.74, 129.84, 129.18, 128.52, 127.47, 126.36, 79.40, 47.92, 28.43, 21.13.

(*E*)-*tert*-butyl 4-methyl-1-phenylpent-1-en-3-ylcarbamate (6e)[1]:



Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (72 mg, 87%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 16 Hz, 1H), 6.00 (dd, *J* = 16, 6.4 Hz, 1H), 4.59 (br. s, 1H), 4.14 (br. s, 1H), 1.86-1.85 (m, 1H), 1.46 (s, 9H), 0.95 (dd, *J* = 4.4 Hz, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 155.50, 137.08, 130.72, 129.12, 128.51, 127.40, 126.36, 79.35, 57.80, 32.83, 28.43, 18.79, 18.31.

(*E*)-*tert*-butyl 5-methyl-1-phenylhex-1-en-3-ylcarbamate (6f)[4]:

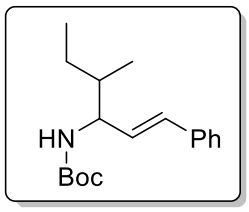


Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1 equiv.), Boc-Leu-OH (138 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 ml). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general

procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (75 mg, 87%, 92:08 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.51 (d, *J* =16 Hz, 1H), 6.00 (dd, *J* = 16, 6.4 Hz, 1H), 4.50 (br. s, 1H), 4.31 (br. s, 1H), 1.73-1.67 (m, 1H), 1.46 (s, 9H), 1.42-1.40 (m, 2H), 0.95 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 155.29, 137.00, 131.09, 129.76, 128.51, 127.41, 126.37, 79.31, 50.85, 44.88, 28.44, 28.39, 28.02, 25.14, 24.93, 24.80, 22.65, 22.54.

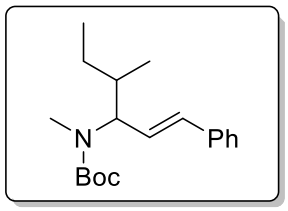
(*E*)-*tert*-butyl 4-methyl-1-phenylhex-1-en-3-ylcarbamate (6g):

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-IIe-OH (138 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (73 mg, 85%, 96:04 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.36 (d, *J* = 8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.50 (dd, *J* = 15.6, 5.6 Hz, 1H), 6.07 (dt, *J* = 15.6, 10.4 Hz, 1H), 4.61 (br. s, 1H), 4.27 (br. s, 1H), 1.74-1.62 (m, 1H), 1.46 (s, 9H), 1.26-1.12 (m, 2H), 0.96-0.90 (m, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 155.58, 137.06, 130.85, 130.25, 128.51, 127.40, 127.26, 126.36, 126.34, 79.30, 56.74, 56.22, 39.56, 39.49, 28.44, 25.55, 15.22, 14.68, 11.71, 11.68. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_2 + Na)^+$ 312.1934, found 312.1746.



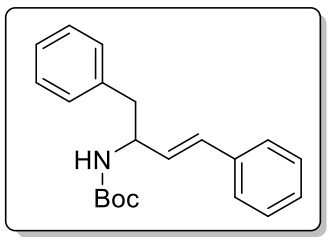
(*E*)-*tert*-butyl methyl(4-methyl-1-phenylhex-1-en-3-yl)carbamate (6h):

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), N-Boc-N-methyl-IIe-OH (147 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (85 mg, 95%, 100:0 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.51 (br. s, 1H), 6.18 (dd, *J* = 15.9, 8.0 Hz, 1H), 4.42-4.22 (m, 1H), 2.76 (s, 3H), 1.72-1.70 (m, 1H), 1.48 (s, 9H), 1.46-1.05 (m, 2H), 0.93-0.88 (m, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 156.08, 156.01, 137.12, 132.69, 128.54, 127.54, 127.51, 126.35, 79.35, 63.09, 61.96, 35.82, 28.55, 26.30, 25.41, 16.34, 11.01. HRMS (ESI) m/z cal. for $(C_{19}H_{29}NO_2 + H)^+$ 304.2271, found 304.2270.



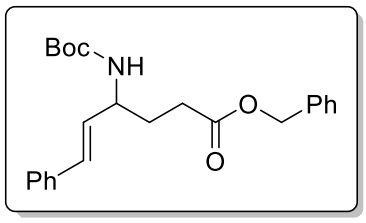
(*E*)-*tert*-butyl 1,4-diphenylbut-3-en-2-ylcarbamate (6i)[1]:

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1 equiv.), Boc-Phe-OH (159 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (88 mg, 91%, 97:03 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.31-7.21 (m, 10H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 5.0 Hz, 1H), 4.58 (br. s, 2H), 2.93 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 155.27, 137.48, 136.94, 130.32, 129.87, 129.71, 128.63, 128.50, 127.62, 126.63, 126.50, 79.62, 53.43, 42.07, 28.48.



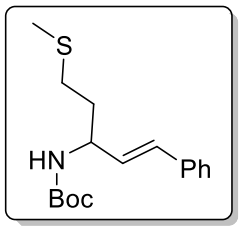
(*E*)-benzyl 4-(tert-butoxycarbonyl)-6-phenylhex-5-enoate (6j):

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1 equiv.), Boc-Glu(benzyl ester) -OH (202 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (82 mg, 70%, 100:0 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.35-7.21 (m, 10H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.00 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.10 (s, 2H), 4.62 (br. s, 1H), 4.29 (br. s, 1H), 2.47 (t, *J* = 8 Hz, 1H), 2.02-1.88 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 173.06, 155.27, 136.58, 135.87, 130.75, 129.56, 128.56, 128.24, 127.66, 126.44, 79.58, 66.43, 52.22, 30.91, 30.38, 28.40. HRMS (ESI) m/z cal. for $(C_{24}H_{29}NO_4 + Na)^+$ 418.2097, found 418.1662.



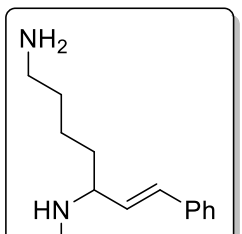
(*E*)-*tert*-butyl 5-(methylthio)-1-phenylpent-1-en-3-ylcarbamate (6k)[1]:

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Met-OH (149 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (55 mg, 60%, 97:03 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.37-7.29 (m, 4H), 7.23 (t, *J* = 8 Hz, 1H), 6.53 (d, *J* = 16 Hz, 1H), 6.06 (dd, *J* = 16, 6.4 Hz, 1H), 4.64 (br. s, 1H), 4.38 (br. s, 1H), 2.56 (t, *J* = 8 Hz, 2H), 2.12 (s, 3H), 1.89-1.88 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 155.28, 136.67, 130.68, 129.69, 128.58, 127.66, 126.43, 79.61, 52.04, 35.06, 30.58, 28.43, 15.63.



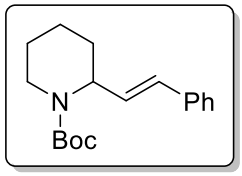
(*E*)-*tert*-butyl 7-amino-1-phenylhept-1-en-3-ylcarbamate (6l):

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Lys-OH (147 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (72 mg, 79%, 96:04 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.35-7.27 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 16 Hz, 1H), 6.06 (dd, *J* = 16, 6.4 Hz, 1H), 4.59 (br. s, 1H), 4.24 (br. s, 1H), 3.15 (d, *J* = 5.6 Hz, 2H), 1.45 (s, 9H), 1.42-1.40 (m, 8H). ^{13}C NMR (126 MHz, CDCl3) δ 156.08, 155.43, 136.85, 130.55, 130.11, 128.53, 127.50, 126.40, 79.07, 52.34, 40.30, 35.23, 29.86, 28.45, 23.01. HRMS (ESI) m/z cal. for $(C_{18}H_{28}N_2O_2 + Na)^+$ 327.2051, found 327.2074.



(*E*)-*tert*-butyl 2-styrylpiperidine-1-carboxylate (6m)[1]:

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Pipecolic acid (137 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (77 mg, 87%, 90:10



E:*Z*) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl3) δ (*E*-isomer) 7.39-7.32 (m, 4H), 7.28-7.23 (m, 1H), 6.41 (d, *J* = 16 Hz, 1H), 6.20 (dd, *J* = 16, 5 Hz, 1H), 4.99 (br. s, 1H), 4.03 (d, *J* = 14 Hz, 1H), 2.93 (t, *J* = 8 Hz, 1H), 1.87-1.64 (m, 6H), 1.50 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ (*E*-isomer) 155.40, 137.11, 130.80, 128.78, 128.54, 127.36, 126.25, 79.44, 52.27, 39.92, 29.53, 28.49, 25.58, 19.71.

(*E*)-2-styryl-tetrahydrofuran (6n)[5]:

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), tetrahydro 2-furoic acid (69 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (48 mg, 92%, 96:04 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 7.39-7.29 (m, 4H), 7.25-7.20 (m, 1H), 6.58 (d, *J* = 16 Hz, 1H), 6.21 (ddd, *J* = 15.9, 6.6, 1.1 Hz, 1H), 4.47 (q, *J* = 8 Hz, 1H), 3.96 (q, *J* = 8 Hz, 1H), 3.87-3.81 (m, 1H), 2.15-2.09 (m, 1H), 2.01-1.91 (m, 2H), 1.76-1.67 (m, 1H). ^{13}C NMR (126 MHz, CDCl3) δ (*E*-isomer) 136.92, 130.58, 130.42, 128.49, 127.47, 126.46, 79.64, 68.15, 32.39, 25.90.

(*E*)-*tert*-butyl 1-hydroxy-4-phenylbut-3-en-2-ylcarbamate (6o)[6]:

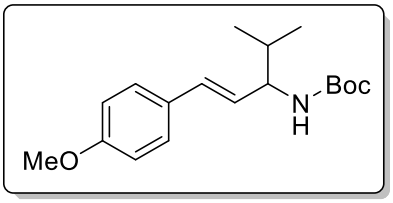
Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1 equiv.), Boc-Ser-OH (123 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (70 mg, 89%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.38-7.24 (m, 5H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 6.1 Hz, 1H), 4.96 (br. s, 1H), 4.42 (br. s, 1H), 3.84-3.69 (m, 2H), 2.24 (br. s, 1H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 155.97, 136.41, 132.04, 128.61, 127.87, 126.65, 126.49, 80.00, 65.70, 54.64, 28.40.

(*E*)-*tert*-butyl 1-(1H-indol-3-yl)-4-phenylbut-3-en-2-ylcarbamate (6p)[1]:

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Trp-OH (182mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (98mg, 91%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 8.16 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.30-7.27 (m, 4H), 7.26-7.19 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 6.50 (d, *J* = 16 Hz, 1H), 6.19 (dd, *J* = 16, 6.4 Hz, 1H), 4.70 (br. s, 2H), 3.10 (br. s, 2H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 155.40, 136.95, 136.26, 129.90, 128.50, 127.41, 126.42, 122.88, 122.11, 122.06, 119.52, 119.14, 111.45, 111.12, 79.47, 52.78, 31.45, 28.41.

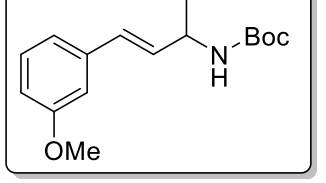
(*E*)-*tert*-butyl 1-(4-methoxyphenyl)-4-methylpent-1-en-3-ylcarbamate (6q):

Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-methoxy-benzene (82 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (64 mg, 70%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.29 (t, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 16 Hz, 1H), 5.93 (dd, *J* = 16, 6.4 Hz 1H), 4.58 (br. s, 1H), 4.09 (br. s, 1H), 3.80 (s, 3H), 1.84-1.80 (m, 1H), 1.45 (s, 9H), 0.95-0.92 (q, *J* = 4 Hz ,6H). ^{13}C NMR (126 MHz, CDCl3) δ 159.14, 139.53, 130.21, 129.85, 127.49, 125.81, 123.39, 120.31, 119.43, 113.97, 110.46, 79.30, 58.10, 55.29, 32.88, 28.44, 18.76, 18.33. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_3 + H)^+$ 306.1991, found 306.2061.



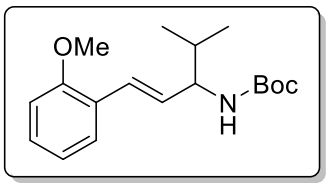
(*E*)-*tert*-butyl 1-(3-methoxyphenyl)-4-methylpent-1-en-3-ylcarbamate (6r):

Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-3-methoxy-benzene (82 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (82 mg, 90%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.21 (q, *J* = 8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.90-6.89 (m, 1H), 6.77 (dd, *J* = 8, 2.4 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.00 (q, *J* = 16, 6.4 Hz, 1H), 4.61 (br. s, 1H), 4.13 (br. s, 1H), 3.81 (s, 3H), 1.88-1.83 (m, 1H), 1.46 (s, 9H), 0.96-0.93 (q, *J* = 4.4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 159.79, 155.52, 138.48, 130.59, 129.48, 119.01, 112.99, 111.80, 79.32, 57.59, 55.22, 32.81, 28.43, 18.82, 18.30. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_3 + H)^+$ 306.1991, found 306.2070.



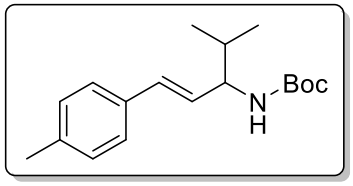
(*E*)-*tert*-butyl 1-(2-methoxyphenyl)-4-methylpent-1-en-3-ylcarbamate (6s):

Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-2-methoxy-benzene (82 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs$_2$CO3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (84 mg, 92%, 96:04 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.40 (br. s, 1H), 7.19 (br. s, 1H), 6.90-6.70 (m, 3H), 6.08 (br. s, 1H), 4.63 (br. s, 1H), 4.14 (br. s, 1H), 3.84 (s, 3H), 1.86-1.84 (m, 1H), 1.46 (s, 9H), 0.94 (br. s, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 156.81, 155.69, 129.67, 128.50, 126.89, 126.26, 125.60, 120.68, 111.06, 79.22, 58.15, 55.54, 32.99, 28.53, 18.88, 18.42. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_3 + H)^+$ 306.1991, found 306.2067.



(*E*)-*tert*-butyl 4-methyl-1-p-tolylpent-1-en-3-ylcarbamate (6t):

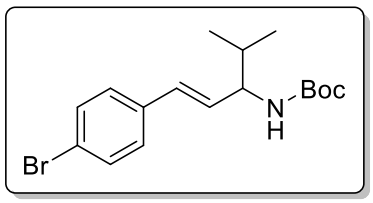
Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-methyl-benzene



(77 mg, 0.30 mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (65 mg, 75%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.25 (br. s, 2H), 7.10 (br. s, 2H), 6.46 (d, *J* = 16 Hz, 1H), 6.00 (br. s, 1H), 4.58 (br. s, 1H), 4.10 (br. s, 1H), 3.74 (br. s, 1H), 2.32 (s, 3H), 1.85 (br. s, 1H), 1.45 (s, 9H), 0.93 (br. s, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 155.59, 137.32, 134.22, 130.58, 129.20, 128.01, 126.25, 79.28, 57.86, 32.86, 28.43, 21.14, 18.77, 18.31. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_2 + H)^+$ 290.2042, found 290.2113.

(*E*)-*tert*-butyl 1-(4-bromophenyl)-4-methylpent-1-en-3-ylcarbamate (6u):

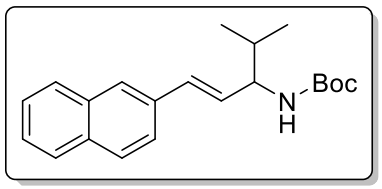
Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-bromo-benzene



(97 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (84 mg, 80%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 7.40 (d, *J* = 8 Hz, 2H), 7.25-7.20 (m, 2H), 6.42 (d, *J* = 16 Hz, 1H), 6.04 (dd, *J* = 16, 6.8 Hz, 1H), 4.60 (br. s, 1H), 4.10 (br. s, 1H), 1.85-1.82 (m, 1H), 1.44 (s, 9H), 0.94-0.91 (t, *J* = 4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 155.63, 136.08, 131.73, 130.20, 129.67, 128.01, 121.25, 79.54, 57.92, 32.87, 28.54, 18.95, 18.40. HRMS (ESI) m/z cal. for $(C_{17}H_{24}BrNO_2 + H)^+$ 354.0990, found 354.1074.

(*E*)-*tert*-butyl 4-methyl-1-(naphthalen-2-yl)pent-1-en-3-ylcarbamate (6v):

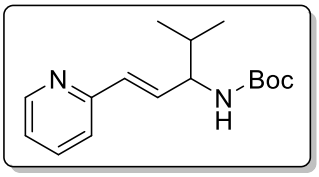
Prepared following the general procedure A, using (*E*)-2-(2-Benzenesulfonyl-vinyl)-naphthalene (88



mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (78 mg, 80%, 75:25 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 7.84-7.76 (m, 3H), 7.72 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.47-7.40 (m, 2H), 6.66 (m, 1.25H), 6.21 (dd, *J* = 16, 6.4 Hz, 1H), 4.65 (br. s, 1H), 4.20 (br. s, 1H), 1.92–1.79 (m, 1H), 1.47 (s, 9H), 0.98 (dd, *J* = 6.8, 4.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl3) δ (*E*-isomer) 155.60, 134.47, 133.64, 132.94, 130.85, 128.11, 127.92, 127.63, 126.22, 126.14, 125.75, 123.66, 79.38, 57.93, 32.89, 28.45, 18.85, 18.34. HRMS (ESI) m/z cal. for $(C_{21}H_{27}NO_2 + H)^+$ 326.2042, found 326.2163.

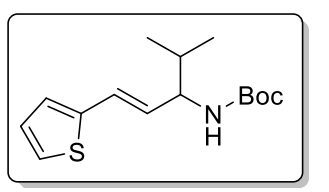
(*E*)-*tert*-butyl 4-methyl-1-(pyridin-2-yl)pent-1-en-3-ylcarbamate (6w):

Prepared following the general procedure A, using (*E*)-2-(2-Benzenesulfonyl-vinyl)-pyridine (73 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (78 mg, 95%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ 8.51 (d, *J* = 4.4 Hz, 2H), 7.22 (d, *J* = 6 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.67 (br. s, 1H), 4.16 (br. s, 1H), 1.92-1.84 (m, 1H), 1.45 (s, 9H), 0.96-0.93 (dd, *J* = 6.6, 5.8 Hz, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 155.50, 150.02, 144.38, 134.46, 128.32, 120.96, 79.60, 67.96, 57.65, 32.62, 28.39, 18.90, 18.23. HRMS (ESI) m/z cal. for $(C_{16}H_{24}N_2O_2 + H)^+$ 277.1838, found 277.1920.



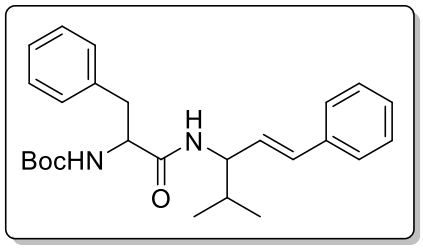
(*E*)-*tert*-butyl 4-methyl-1-(thiophen-2-yl)pent-1-en-3-ylcarbamate (6x):

Prepared following the general procedure A, using (*E*)-2-(2-Benzenesulfonyl-vinyl)-thiophene (75 mg, 0.30 mmol, 1 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (75 mg, 89%, 90:10 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 7.32 (s, 1H), 6.36-6.35 (m, 1H), 6.32 (d, *J* = 12.8 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 6.04 (dd, *J* = 15.8, 6.5 Hz, 1H), 4.57 (br. s, 1H), 4.11 (br. s, 1H), 1.86-1.82 (m, 1H), 1.45 (s, 9H), 0.94 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, CDCl3) δ (*E*-isomer) 155.51, 152.59, 141.69, 127.88, 119.20, 111.21, 107.55, 79.31, 57.56, 32.78, 28.41, 18.73, 18.25. HRMS (ESI) m/z cal. for $(C_{15}H_{23}NO_2S + H)^+$ 282.1449, found 282.1548.



(*E*)-*tert*-butyl 1-(4-methyl-1-phenylpent-1-en-3-ylamino)-1-oxo-3-phenylpropan-2-ylcarbamate (6y):

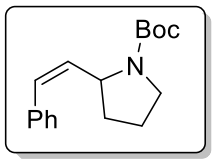
Prepared following the general procedure A, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-methoxy-benzene (82 mg, 0.30 mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane:EtOAc provided the title compound (64 mg, 70%, 100:0 *E*:*Z*, *dr* 1:1) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl3) δ (*E*-isomer) 7.35-7.22 (m, 10H), 6.42 (d, *J* = 15.9 Hz, 0.53H), 6.31 (d, *J* = 15.5 Hz, 0.37H), 5.99 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.90-5.76 (m, 1H), 5.13 (br. s, 0.43H), 5.04 (br. s, 0.54H), 4.42-4.27 (m, 2H), 3.18-2.97 (m, 3H), 1.82-1.71 (m, 1H), 1.67 (s, 1H), 1.42 (d, *J* = 5.4 Hz, 9H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ (*E*-isomer) 171.07, 170.50, 170.48, 155.50, 136.83, 131.33, 129.40, 129.31, 128.77, 128.71, 128.50, 128.48, 127.98, 127.53, 126.99, 126.94, 126.42, 126.40, 80.26, 56.42, 52.47, 46.83, 38.62, 38.20, 32.53, 32.45, 28.29, 19.95, 18.75, 18.61, 18.19. HRMS (ESI) m/z cal. for $(C_{26}H_{34}N_2O_3 + Na)^+$ 445.2569, found 445.2130.



4. Experimental Data for Decarboxylative (*Z*) Vinylation Products:

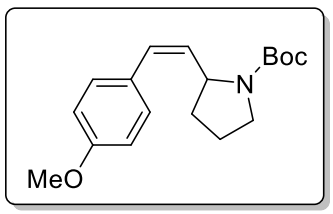
(*Z*)-*tert*-butyl 2-styrylpyrrolidine-1-carboxylate (7a)[7]:

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (53 mg, 65%, 08:92 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.34-7.25 (m, 5H), 6.41 (d, *J* = 11.6 Hz, 1H), 5.61 (br. s, 1H), 4.73 (br. s, 1H), 3.46 (br. s, 2H), 2.21 (br. s, 1H), 1.95-1.83 (m, 3H), 1.29 (s, 9H). ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.10 (br. s, 1H), 4.40 (br. s, 1H), 3.65 (br. s, 1H), 1.43 (s, 9H); the remaining signals could not be determined. ^{13}C NMR (101 MHz, CDCl3) δ (*Z*-isomer) 154.67, 137.03, 134.96, 128.81, 128.11, 126.74, 79.15, 55.00, 46.56, 33.89, 28.51, 28.48, 23.89.



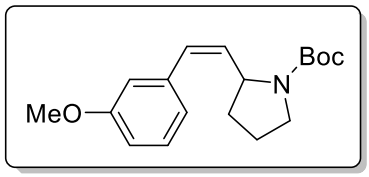
(Z)-tert-butyl 2-(4-methoxystyryl)pyrrolidine-1-carboxylate (7b)[7]:

Prepared following the general procedure B, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-methoxy-benzene (82 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (70 mg, 77%, 03:97 *E*:*Z*) as a colorless solid. ^{1}H NMR (500 MHz, CDCl3) δ (*Z*-isomer) 7.27-7.20 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 11.6 Hz, 1H), 5.95 (br. s, 1H), 5.52 (br. s, 1H), 4.73 (br. s, 1H), 3.81 (s, 3H), 3.45 (br. s, 2H), 2.19 (br. s, 1H), 1.97-1.90 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 158.43, 133.51, 130.03, 129.72, 127.36, 113.58, 79.11, 55.24, 46.25, 33.73, 28.45, 23.97.



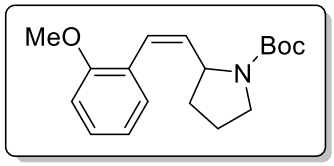
(Z)-tert-butyl 2-(3-methoxystyryl)pyrrolidine-1-carboxylate (7c):

Prepared following the general procedure B, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-3-methoxy-benzene (82 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane: EtOAc provided the title compound (66 mg, 73%, 01:99 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.23 (d, *J* = 7.9 Hz, 1H), 6.79-6.77 (m, 3H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.61 (br. s, 1H), 4.72 (br. s, 1H), 3.81 (s, 3H), 3.45 (br. s, 2H), 2.20-2.18 (m, 1H), 1.92-1.79 (m, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 159.40, 154.66, 138.41, 135.26, 129.07, 127.80, 121.40, 114.56, 112.14, 79.16, 55.19, 46.55, 33.94, 28.46, 23.96. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_3 + H)^+$ 306.1991, found 306.1893.



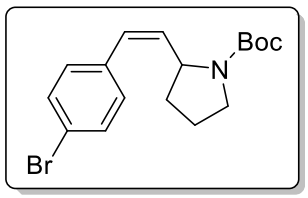
(Z)-tert-butyl 2-(2-methoxystyryl)pyrrolidine-1-carboxylate (7d):

Prepared following the general procedure B, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-2-methoxy-benzene (82 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (68 mg, 75%, 02:98 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.26-7.21 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 11.7 Hz, 1H), 5.62 (br. s, 1H), 4.64 (br. s, 1H), 3.80 (s, 3H), 3.44 (br. s, 2H), 2.18 (br. s, 1H), 1.92-1.81 (m, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ (*Z*-isomer) 156.99, 154.75, 134.13, 130.12, 128.28, 125.88, 123.54, 119.87, 110.22, 79.12, 55.07, 46.47, 33.95, 28.28, 23.79. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_3 + H)^+$ 306.1991, found 306.1909.



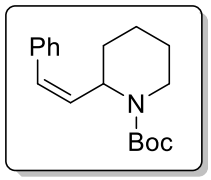
(Z)-tert-butyl 2-(4-bromostyryl)pyrrolidine-1-carboxylate (7e)[8]:

Prepared following the general procedure B, using (*E*)-1-(2-Benzenesulfonyl-vinyl)-4-bromo-benzene (97 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane: EtOAc provided the title compound (68 mg, 65%, 08:92 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.44 (d, *J* = 8.4 Hz, 2H), 7.24-7.04 (m, 2H), 6.32 (d, *J* = 11.7 Hz, 1H), 5.64 (t, *J* = 8 Hz, 1H), 4.65 (br. s, 1H), 3.44 (br. s, 2H), 2.17 (br. s, 1H), 1.97-1.79 (m, 3H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 154.58, 135.91, 135.78, 131.28, 130.42, 120.70, 79.26, 54.88, 46.61, 33.81, 28.46, 23.83.



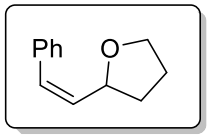
(Z)-tert-butyl 2-styrylpiperidine-1-carboxylate (7f)[7]:

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Pipecolic acid (137 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (67 mg, 81%, 08:92 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.34-7.27 (m, 4H), 7.24-7.20 (m, 1H), 6.48 (d, *J* = 11.9 Hz, 1H), 5.97 (dd, *J* = 11.9, 9.4 Hz, 16H), 5.30-5.28 (m, 1H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.00-2.93 (m, 1H), 1.77-1.72 (m, 2H), 1.66-1.62 (m, 4H), 1.24 (s, 9H). ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.41 (d, *J* = 16 Hz, 1H), 6.20 (dd, *J* = 16, 5 Hz, 1H), 1.46 (s, 9H); the remaining signals could not be determined. ^{13}C NMR (101 MHz, CDCl3) δ (*Z*-isomer) 155.14, 136.94, 129.55, 129.36, 128.68, 128.24, 126.93, 79.25, 48.74, 39.39, 30.48, 28.38, 28.19, 28.09, 25.47, 19.82.



(*Z*)-2-styryl-tetrahydrofuran (7g)[7]:

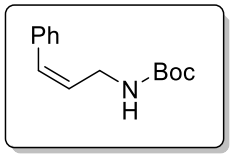
Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), tetrahydro 2-furoic acid (69 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane: EtOAc provided the title compound (36 mg, 70%, 18:82 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.39-7.22 (m, 5H), 6.58 (d, *J* = 11.6 Hz, 1H), 5.71 (dd, *J* = 11.6, 9.0



Hz, 1H), 4.66 (dd, *J* = 8 Hz, 1H), 3.96 (dd, *J* = 7.7 Hz, 1H), 3.82-3.76 (m, 1H), 2.18-2.11 (m, 1H), 2.06-1.90 (m, 2H), 1.74-1.65 (m, 1H). ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.58 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.6 Hz, 1H), 4.49 (d, *J* = 6.8 Hz, 1H), 4.21 (d, *J* = 6.3 Hz, 1H), 3.84 (d, *J* = 6.4 Hz, 1H); the remaining signals could not be determined. ^{13}C NMR (101 MHz, CDCl3) δ (*Z*-isomer) 136.72, 132.87, 131.49, 128.84, 128.16, 127.11, 79.67, 75.07, 68.18, 68.08 32.93, 26.39.

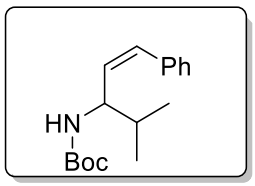
(*Z*)-*tert*-butyl cinnamylcarbamate(7h):

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Gly-OH (105 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 16:1 hexane: EtOAc provided the title compound (56 mg, 80%, 0:100 *E*:*Z*) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl3) δ (*Z*-isomer) 7.36 (t, *J* = 8 Hz, 2H), 7.28-7.23 (m, 3H), 6.57 (d, *J* = 11.5 Hz, 1H), 5.70 (dt, *J* = 12, 6.5 Hz, 1H), 4.61 (br. s, 1H), 4.06 (s, 2H), 1.47 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 155.27, 136.46, 131.16, 128.88, 128.74, 128.29, 127.17, 79.46, 39.03, 28.40. HRMS (ESI) m/z cal. for $(C_{14}H_{19}NO_2 + NH_4)^+$ 251.1754, found 251.1824.



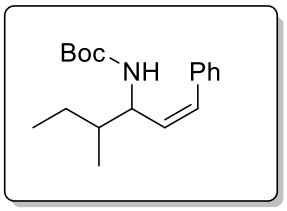
(*Z*)-*tert*-butyl 4-methyl-1-phenylpent-1-en-3-ylcarbamate (7i):

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 14:1 hexane: EtOAc provided the title compound (64 mg, 78%, 10:90 *E*:*Z*) as a colorless liquid. ^{1}H NMR (500 MHz, CDCl3) δ (*Z*-isomer) 7.39-9.34 (m, 5H), 6.55 (d, *J* =12 Hz, 1H), 5.51 (dd, *J* =12, 9.5 Hz, 1H), 4.52 (br. s, 2H), 1.79-1.75 (m, 1H), 1.49 (s, 9H), 0.91 (dd, *J* = 6.5 Hz, 6H), and the remains peaks for the *E*-isomer. ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 155.28, 136.79, 130.75, 128.74, 128.30, 127.01, 126.36, 79.15, 55.15, 53.47, 33.50, 32.84, 28.39, 19.95, 18.32, 18.19, and the remains peaks for the *E*-isomer. HRMS (ESI) m/z cal. for $(C_{17}H_{25}NO_2 + H)^+$ 276.1958, found 276.2025.



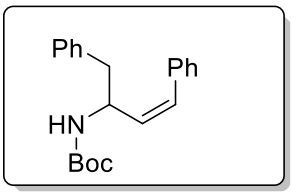
(*Z*)-*tert*-butyl 4-methyl-1-phenylhex-1-en-3-ylcarbamate (7j):

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-IIe-OH (138 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 14:1 hexane: EtOAc provided the title compound (65 mg, 76%, 10:90 *E*:*Z*) as a colorless solid. ^{1}H NMR (500 MHz, CDCl3) δ (*Z*-isomer) 7.36-7.17 (m, 5H), 6.54-6.48 (m, 1H), 5.52-5.46 (m, 1H), 4.57 (br. s, 2H), 1.54-1.50 (m, 1H), 1.43 (br. s, 9H), 1.08-0.77 (m, 8H), and the remains peaks for the *E*-isomer. ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 155.25, 136.81, 130.29, 128.72, 128.50, 128.29, 127.00, 126.35, 79.09, 52.13, 42.29, 28.41, 26.02, 14.16, 11.58. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_2 + Na)^+$ 312.1934, found 312.1913.



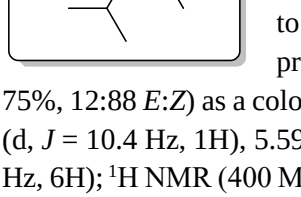
(*Z*)-*tert*-butyl 1,4-diphenylbut-3-en-2-ylcarbamate (7k):

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), Boc-Phe-OH (159 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2.00 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 14:1 hexane: EtOAc provided the title compound (74 mg, 77%, 10:90 *E*:*Z*) as a colorless solid. ^{1}H NMR (500 MHz, CDCl3) δ (*Z*-isomer) 7.35-7.17 (m, 10H), 6.51 (d, *J* = 12 Hz, 1H), 5.54 (t, *J* = 11 Hz, 1H), 4.88 (br. s, 1H), 4.52 (br. s, 1H), 2.96-2.81 (m, 2H), 1.45 (s, 9H), and the remains peaks for the *E*-isomer. ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 154.91, 137.37, 136.48, 129.72, 129.60, 128.79, 128.58, 128.28, 127.13, 126.43, 79.39, 49.78, 41.97, 28.42, 28.38, 38.35, and the remains peaks for the *E*-isomer. HRMS (ESI) m/z cal. for $(C_{21}H_{25}NO_2 + H)^+$ 324.1958, found 324.1942.



(*Z*)-*tert*-butyl methyl(4-methyl-1-phenylpent-1-en-3-yl)carbamate (7l):

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), N-Boc-N-methyl-Val-OH (138 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane: EtOAc provided the title compound (65 mg, 75%, 12:88 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.30-7.25 (m, 5H), 6.49 (d, *J* = 10.4 Hz, 1H), 5.59 (br. s, 1H), 4.68-4.52 (m, 1H), 2.80 (br. s, 3H), 1.40 (s, 9H), 0.85 (d, *J* = 6.4 Hz, 6H); ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.50 (d, *J* =16Hz, 1H), 6.00 (dd, *J* = 16, 6.4Hz, 1H), 4.28 (br. s, 1H), 3.00 (br. s, 3H), 1.90 (br. s, 1H), 1.45 (s, 9H), 0.95 (d, *J* = 6.4 Hz, 6H); the remaining signals could not be determined. ^{13}C NMR (101 MHz, CDCl3) δ (*Z*-isomer) 155.61, 136.95, 132.73, 129.90, 128.80, 128.55, 128.20, 127.04, 126.34, 79.43, 58.60, 31.44, 28.44, 19.66, 19.17. HRMS (ESI) m/z cal. for $(C_{18}H_{27}NO_2 + H)^+$ 290.2042, found 290.2119.

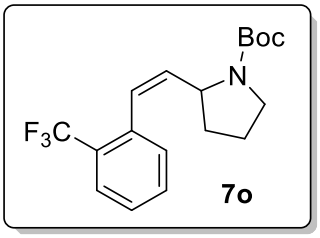


(*Z*)-*tert*-butyl cinnamyl(methyl)carbamate (7m)[7]:

Prepared following the general procedure B, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30 mmol, 1.00 equiv.), N-Boc-N-methyl-Gly-OH (113 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 48h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (52 mg, 70%, 10:90 *E*:*Z*) as a colorless solid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.36-7.20 (m, 5H), 6.59 (d, *J* = 12 Hz, 1H), 5.63 (dt, J = 12.4, 6.4 Hz, 1H), 4.12 (br. s, 2H), 2.77 (s, 3H), 1.43 (s, 9H); ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.46 (d, *J* = 18.0 Hz, 1H), 6.16 (dd, 1H), 3.98 (s, 2H), 2.86 (s, 3H), 1.47 (s, 9H); the remaining signals could not be determined. ^{13}C NMR (126 MHz, CDCl3) δ (*Z*-isomer) 155.75, 136.65, 131.29, 128.79, 128.56, 128.23, 127.55, 127.04, 126.35, 79.50, 46.80, 33.72, 28.42.

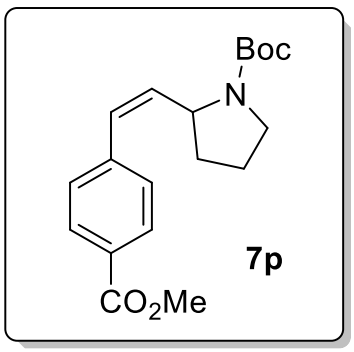
tert-butyl (Z)-2-(2-(trifluoromethyl)styryl)pyrrolidine-1-carboxylate (7o):

Prepared following the general procedure B, using (*E*)-1-(2-(phenylsulfonyl)vinyl)-2-(trifluoromethyl)benzene (90 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 56h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 9:1 hexane:EtOAc provided the title compound (66 mg, 71%, 0:100 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 7.67-7.52 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.63 (d, *J* = 11.6 Hz, 1H), 5.80-5.75 (m, 1H), 4.62 (m, 1H), 3.44 (br. s, 1H), 1.93-1.87 (m, 1H), 1.78-1.75 (m, 2H), 1.29 (s, 9H). ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.10 (br. s, 1H), 4.40 (br. s, 1H), 3.65 (br. s, 1H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 154.67, 136.61, 131.60, 128.67, 128.44, 126.97, 125.87, 125.44, 123.26, 79.50, 54.85, 46.79, 29.80, 28.60, 23.88. HRMS (ESI) m/z cal. for $(C_{18}H_{22}F_3NNaO_2 + Na)^+$ 364.1495, found 364.1373.



tert-butyl (Z)-2-(4-(methoxycarbonyl)styryl)pyrrolidine-1-carboxylate (7p):

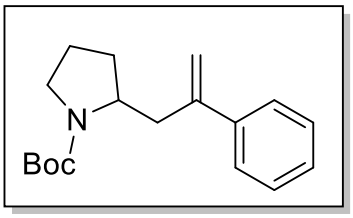
Prepared following the general procedure B, using methyl (*E*)-4-(2-(phenylsulfonyl)vinyl)benzoate (90 mg, 0.30 mmol, 1.00 equiv.), Boc-Pro-OH (129 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and 1,4-dioxane (4.0 ml). After 56h, the reaction mixture was subjected to the workup protocol outlined in the general procedure B. Purification by preparative TLC using 6:1 hexane:EtOAc provided the title compound (59 mg, 60%, 33:77 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*Z*-isomer) 8.00-7.98 (m, 2H), 7.40-7.32 (m, 2H), 6.42 (d, *J* = 12 Hz, 1H), 5.71 (m, 1H), 4.68 (m, 1H), 3.89 (s, 3H), 3.45 (br. s, 2H), 2.21-1.82 (m, 4H), 1.26 (s, 9H). ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 6.10 (br. s, 1H), 4.40 (br. s, 1H), 3.65 (br. s, 1H), 1.43 (s, 9H); the remains peak for the *E*-isomer. ^{13}C NMR (126 MHz, CDCl3) δ 154.59, 139.26, 137.02, 129.49, 128.75, 79.32, 54.98, 52.03, 46.65, 31.91, 29.68, 28.45, 22.66. HRMS (ESI) m/z cal. for $(C_{18}H_{22}F_3NNaO_2 + Na)^+$ 364.1495, found 364.1373.



5. Experimental Data for Decarboxylative allylation Products:

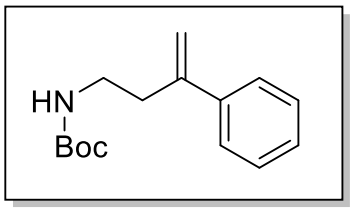
tert-butyl 2-(3-phenylprop-1-en-2-yl)pyrrolidine-1-carboxylate (8a)[9]:

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8a** in 63% yield (42 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.54-7.46 (m, 2H), 7.33-7.25 (m, 3H), 5.35 (s, 1H), 5.06 (s, 1H), 3.94-3.79 (m, 1H), 3.36-3.17 (m, 3H), 2.32-2.23 (m, 1H), 1.78-1.71 (m, 4H), 1.52-1.46 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 154.63, 145.86, 140.34, 128.42, 127.69, 126.30, 115.01, 114.58, 79.53, 55.97, 55.75, 46.77, 46.38, 40.01, 38.99, 28.79, 23.59, 22.67; HRMS (ESI): m/z calculated for $[C_{18}H_{25}NO_2 + H]^+$: 288.1958, found: 288.1956.



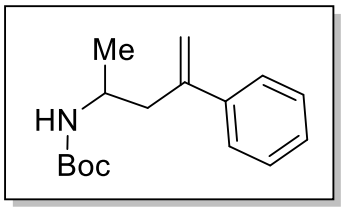
tert-butyl (2-benzylallyl)carbamate (8b)[10]:

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8b** in 73% yield (42 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.25 (m, 5H), 5.37-5.36 (m, 1H), 5.11-5.10 (m, 1H), 4.55 (br. s, 1H), 3.25-3.23 (m, 2H), 2.71-2.68 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 155.99, 145.65, 140.57, 128.59, 127.80, 126.23, 114.27, 79.30, 39.34, 35.75, 28.57.



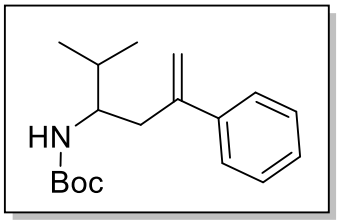
tert-butyl (3-benzylbut-3-en-2-yl)carbamate (8c):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8c** in 68% yield (41 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.25(m, 5H), 5.33-5.32 (m, 1H), 5.09-5.08 (m, 1H), 4.32 (br. s, 1H), 3.72 (br. s, 1H), 2.84-2.78 (m, 1H), 2.52-2.46 (m, 1H), 1.41 (s, 9H), 1.08-1.05 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.34, 145.64, 140.55, 128.54, 127.68, 126.39, 115.20, 79.62, 46.96, 41.51, 27.20, 20.73. HRMS (ESI): m/z calculated for $[C_{16}H_{23}NO_2 + Na]^+$: 284.1621, found: 284.1638.



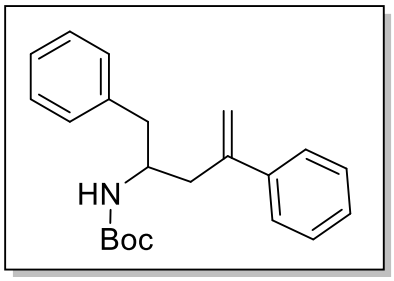
tert-butyl (2-benzyl-4-methylpent-1-en-3-yl)carbamate (8d):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8d** in 66% yield (45 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.40-7.25 (m, 5H), 5.29-5.28 (m, 1H), 5.09 (s, 1H), 4.28-4.08 (m, 1H), 3.72-3.56 (m, 1H), 2.75-2.40 (m, 2H), 1.49-1.25 (m, 9H), 0.88-0.77 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 155.71, 146.17, 141.08, 128.46, 127.59, 126.44, 114.92, 78.85, 53.59, 50.98, 39.06, 38.43, 37.83, 37.06, 29.84, 28.53, 26.51, 25.03, 17.80, 13.88, 7.21. HRMS (ESI): m/z calculated for $[C_{18}H_{27}NO_2 + H]^+$: 290.2115, found: 290.2068.



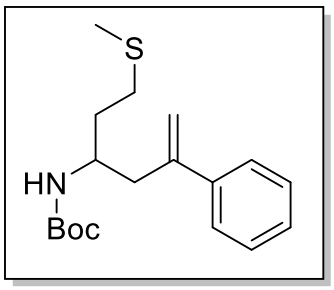
tert-butyl (3-benzyl-1-phenylbut-3-en-2-yl)carbamate (8e):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8e** in 61% yield (48 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31-7.11 (m, 10H), 5.33 (s, 1H), 5.11 (s, 1H), 4.32 (br. s, 1H), 3.86 (br. s, 1H), 2.78-2.61 (m, 4H), 1.44-1.25 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 155.37, 145.67, 140.28, 138.43, 129.62, 128.53, 128.46, 127.71, 126.45, 126.41, 120.45, 119.56, 115.36, 80.14, 50.76, 40.78, 40.23, 28.48. HRMS (ESI): m/z calculated for $[C_{22}H_{27}NO_2 + H]^+$ 338.2115, found: 338.2125.



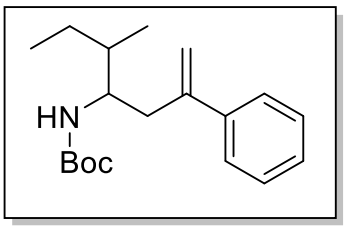
tert-butyl (2-benzyl-5-(methylthio)pent-1-en-3-yl)carbamate (8f):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8f** in 70% yield (52 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41-7.24 (m, 5H), 5.33-5.31 (m, 1H), 5.10-5.08 (m, 1H), 4.32 (br. s, 1H), 3.71 (br. s, 1H), 2.73-2.63 (m, 2H), 2.53-2.51 (m, 2H), 2.49-2.41 (m, 3H), 2.11-2.00 (m, 1H), 1.78-1.58 (m, 1H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.50, 145.42, 140.94, 128.59, 127.77, 126.39, 115.51, 79.22, 49.26, 41.23, 34.45, 30.81, 28.51, 15.62. HRMS (ESI): m/z calculated for $[C_{18}H_{27}NO_2S + H]^+$ 322.1835, found: 322.1818.



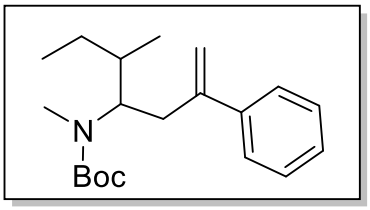
tert-butyl (2-benzyl-4-methylhex-1-en-3-yl)carbamate (8g):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8g** in 71% yield (50 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.57-6.42 (m, 5H), 4.46-4.45 (m, 1H), 4.27-4.26 (m, 1H), 3.43 (d, *J* = 9.2 Hz, 1H), 2.89-2.78 (m, 1H), 1.92-1.57 (m, 2H), 0.67-0.43 (m, 11H), 0.06-0.01 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 155.31, 146.19, 128.80, 128.47, 127.60, 126.45, 126.28, 114.95, 114.80, 78.85, 59.44, 53.60, 52.35, 39.08, 38.44, 37.83, 37.51, 28.53, 28.17, 26.51, 25.04, 16.68, 15.31, 13.89, 11.99, 11.85, 11.67. HRMS (ESI): m/z calculated for $C_{19}H_{29}NO_2$ + H]$^+$: 304.2271, found: 304.2273.



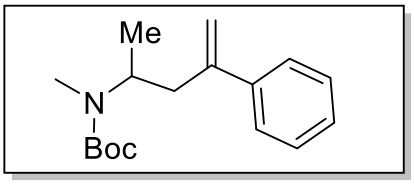
tert-butyl (2-benzyl-4-methylhex-1-en-3-yl)(methyl)carbamate (8h):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8h** in 76% yield (56 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38-7.24 (m, 5H), 5.30-5.21 (m, 1H), 5.06-5.03 (m, 1H), 2.98-2.86 (m, 1H), 2.62-2.50 (m, 4H), 1.54-1.44 (m, 5H), 1.37-1.12 (m, 6H), 0.97-0.75 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 156.2, 146.8, 146.7, 145.9, 145.6, 141.6, 140.6, 140.5, 128.4, 128.3, 128.2, 127.4, 126.2, 126.1, 114.7, 114.3, 114.3, 78.9, 78.8, 57.9, 57.2, 37.1, 36.3, 36.0, 35.8, 35.8, 28.5, 28.4, 28.0, 26.3, 26.2, 25.6, 25.5, 16.3, 15.5, 11.1, 10.9, 10.6. HRMS (ESI): m/z calculated for $[C_{20}H_{31}NO_2 + H]^+$ 318.2428, found: 318.2424.



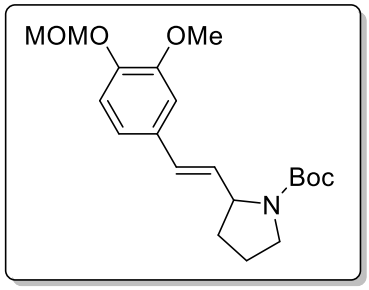
tert-butyl (3-benzylbut-3-en-2-yl)(methyl)carbamate (8i):

Synthesized using general procedure C and the crude residue was purified by column chromatography using neutral alumina to give the product **8i** in 82% yield (52 mg) as a pale yellow semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41-7.25 (m, 5H), 5.31 (s, 1H), 5.06 (s, 1H), 4.33-4.17 (m, 1H), 2.70-2.53 (m, 5H), 2.70-2.53 (m, 9H), 1.42-1.06 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 155.6, 145.3, 140.4, 128.4, 127.5, 126.2, 114.6, 79.2, 49.4, 40.3, 39.8, 28.4, 18.0. HRMS (ESI): m/z calculated for $[C_{17}H_{25}NO_2 + H]^+$ 276.1958, found: 276.1955.



(E)-tert-butyl 2-(3-methoxy-4-(methoxymethoxy)styryl)pyrrolidine-1-carboxylate (9)[1]:

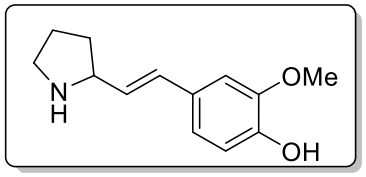
Prepared following the general procedure A, using (*E*) 4-(2-(phenylsulfonyl)vinyl)-2-methoxy-phenol



(87 mg, 0.30 mmol, 1.00 equiv.), Boc-Phe-OH (159 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO3 (195 mg, 0.60 mmol, 2.00 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane: EtOAc provided the title compound (87 mg, 91%, 100:0 *E*:*Z*) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 7.07 (d, *J* = 8.2 Hz, 1H), 6.90–6.85 (m, 2H), 6.32 (d, *J* = 14.0 Hz, 1H), 5.97 (br. s, 1H), 5.21 (s, 2H), 4.37 (br. s, 1H), 3.89 (s, 3H), 3.48 (s, 3H), 3.45 (br. s, 2H), 2.10-2.00 (m, 1H), 1.91-1.76 (m, 3H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 154.67, 149.85, 146.01, 131.90, 129.43, 129.09, 119.31, 116.52, 109.47, 95.58, 79.17, 58.92, 56.15, 55.88, 46.32, 31.91, 31.62, 28.52, 23.10, 22.66.

(*E*)-2-methoxy-4-(2-(pyrrolidin-2-yl)vinyl)phenol (10):

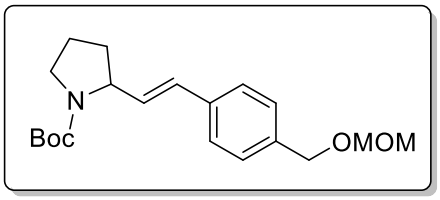
To a vial containing tert-butyl (*E*)-2-(3-methoxy-4-(methoxymethoxy)styryl)pyrrolidine-1- carboxylate



(9) (98 mg, 0.27 mmol) at 0 °C was added trifluoroacetic acid (2.08 mL, 27.0 mmol, 100 equiv.). The mixture was stirred at 0 °C for 2 h before being diluted with MeOH (10 mL) and the mixture concentrated in vacuo. The residue was diluted with MeOH (10 mL) and sat. aq. NaHCO3 was added to basify the mixture to pH ≥7 before removal of the MeOH and water under reduced pressure. Purification by flash column chromatography (100:8:1, DCM: MeOH: NH_3) yielded the title compound (45 mg, 76%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 6.83-6.72 (m, 3H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.11–6.06 (q, *J* = 8 Hz, 1H), 5.93 (br. s, 2H), 4.00 (dd, *J* = 15.7, 8.1 Hz, 1H), 3.81 (s, 3H), 3.27-3.21 (m, 1H), 3.17-3.13 (m, 1H), 2.16-2.10 (m, 1H), 2.05-1.99 (m, 2H), 1.85-1.79 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (*E*-isomer) 147.08, 146.42, 134.42, 128.21, 122.84, 120.63, 114.76, 108.84, 61.80, 55.87, 44.74, 31.66, 24.26. HRMS (ESI) m/z cal. for $(C_{13}H_{17}NO_2 + H)^+$ 220.1259, found 220.1346.

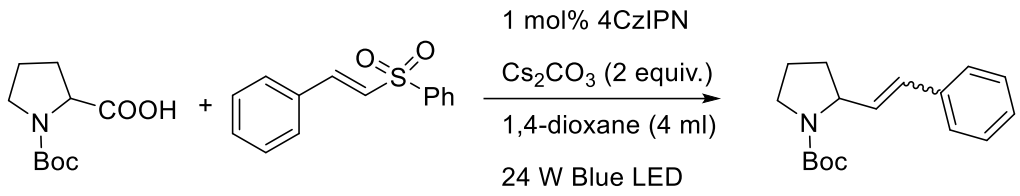
(*E*)-*tert*-butyl 2-(4-((methoxymethoxy)methyl)styryl)pyrrolidine-1-carboxylate (11):

Prepared following the general procedure A, using (*E*)-(2-(phenylsulfonyl)vinyl)benzene (73 mg, 0.30

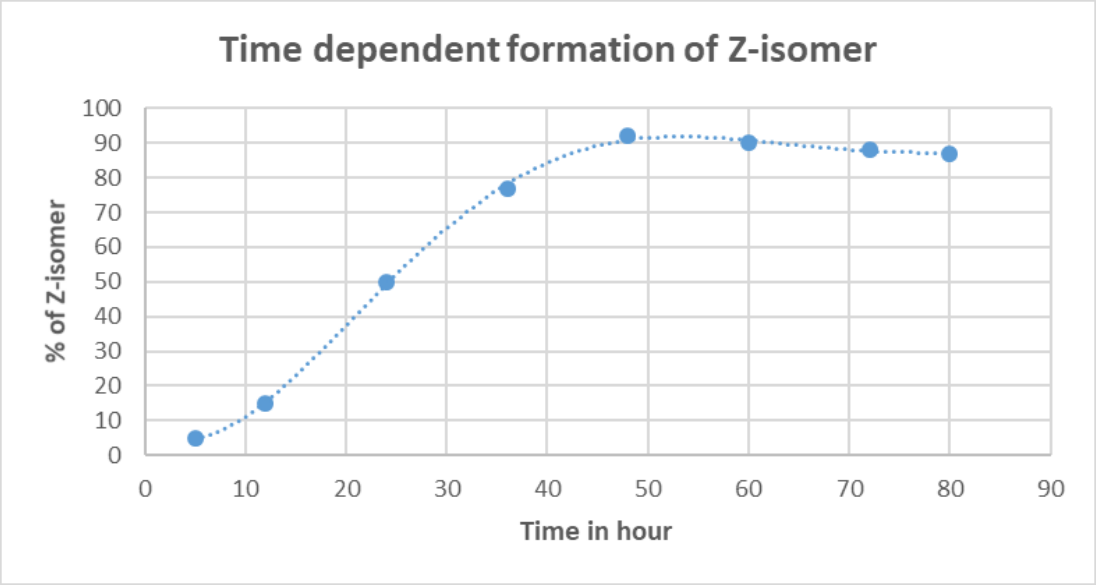


mmol, 1.00 equiv.), Boc-Val-OH (130 mg, 0.60 mmol, 2 equiv.), 4CzIPN (2.3 mg, 0.003 mmol, 0.01 equiv.), Cs_2CO_3 (195 mg, 0.60 mmol, 2 equiv.) and DMA (5.0 mL). After 50 h, the reaction mixture was subjected to the workup protocol outlined in the general procedure A. Purification by preparative TLC using 14:1 hexane: EtOAc provided the title compound (72 mg, 87%, 95:05 *E*:*Z*) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl3) δ (*E*-isomer) 7.32-7.30 (m, 4H), 6.38 (d, *J* = 14.1 Hz, 1H), 6.08 (br. s, 1H), 4.70 (s, 2H), 4.57 (s, 2H), 4.37 (br. s, 1H), 3.45 (br. s, 2H), 3.41 (s, 3H), 2.08 (br. s, 1H), 1.95-1.76 (m, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ (*E*-isomer) 154.67, 136.86, 136.60, 135.18, 130.84, 129.13, 128.16, 127.75, 126.34, 95.63, 79.19, 68.92, 59.02, 55.35, 46.31, 32.60, 28.49, 23.11. HRMS (ESI) m/z cal. for $(C_{20}H_{29}NO_4 + H)^+$ 348.2169, found 348.2168.

Photostationary state:



For the photostationary state, we have performed the above reaction and plotted the data from crude reaction mixture in the following time gap 5 h, 10 h, 24 h, 36 h, 48 h, 60 h, 72 h and 80 h. The diastereomeric ratios were determined from the ^{1}H-NMR of the crude reaction mixture. After 5 h the ratio was (*E*/*Z*) 95:5, at 10 h the ratio was 85:15, at 24 h the ratio was 50:50, at 36 h the ratio was 33:77, at 48 h the ratio was 08:92, at 60 h the ratio was 10:90, at 72 h the ratio was 12:88.

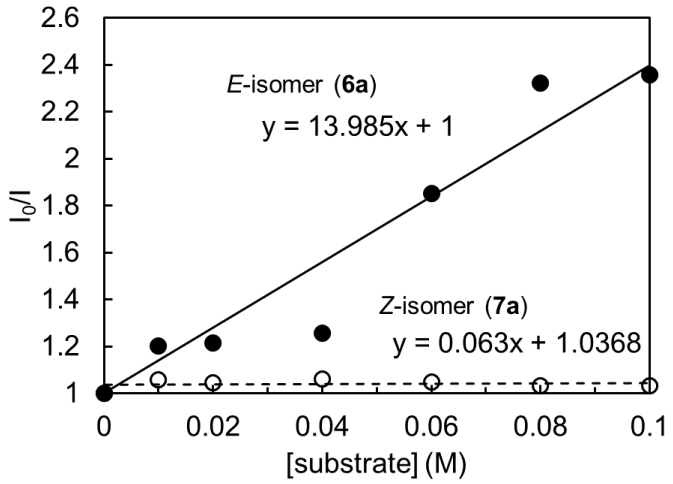


6. Stern Volmer Plot:

Emission intensities were recorded on spectrofluorometer (RF-6000, SHIMADZU.CO). All the samples of 4CzIPN were excited at 365 nm and the emission intensities were observed at 510 nm. In this experiment, the appropriate amount of the quencher (**6a** or **7a**) were added in 10-5M 1,4-dioxane solution of 4CzIPN. All the data were recorded after degassing all the samples with a stream of argon for 15 min.

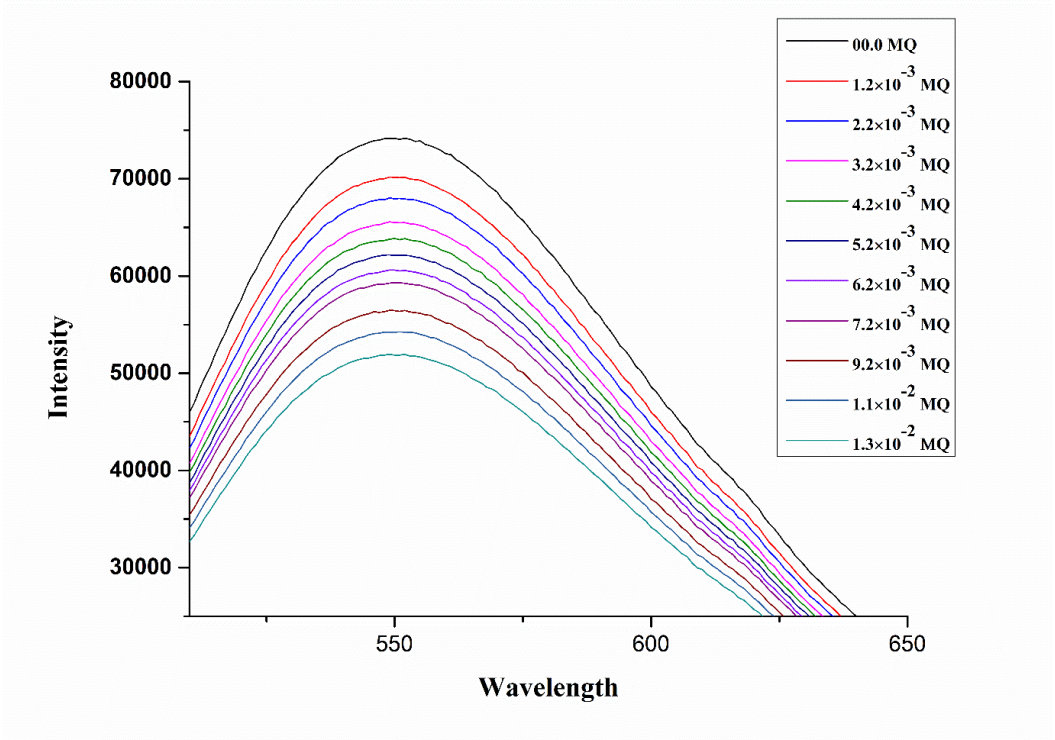
Figure 1. Stern-Volmer Plot of 4CzIPN emission quenching with **6a** (*E*-isomer) and **7a** (*Z*-isomer) in 1,4-dioxane, [4CzIPN] = 1.0×10^{-5} M, λ_{ex} = 365 nm, λ_{em} = 510 nm.

E-7a			*Z*-7a		
Conc. (mM)	I	I_0/I	Conc. (mM)	I	I_0/I
0	233482.886	1	0	233482.886	1
1	280809.866	1.2027	1	216801.510	1.0769
2	283705.054	1.2151	2	223453.502	1.0448
4	293114.415	1.2554	4	220201.389	1.0603
6	432457.001	1.8522	6	222800.824	1.04794
8	542147.261	2.3222	8	225880.799	1.0336
10	550132.375	2.3562	10	225894.352	1.03359

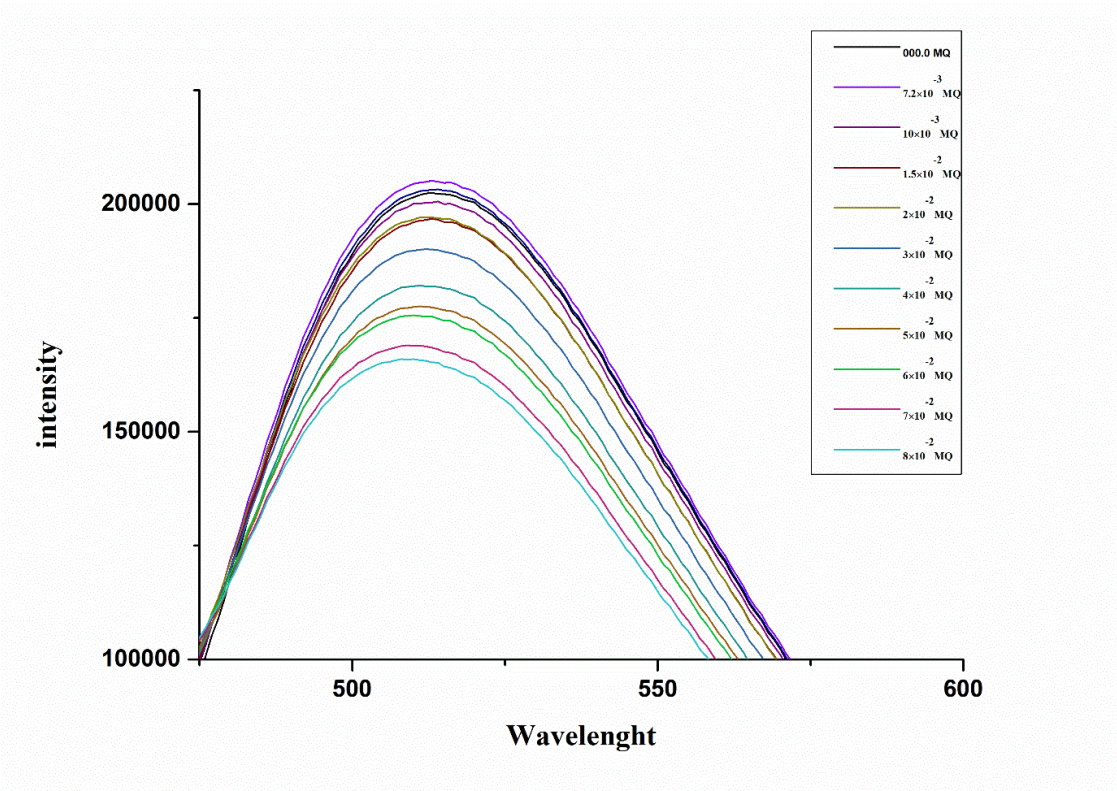


7. Fluorescence quenching of excited 4CzIPN* with *N*-Boc Proline carboxylate:

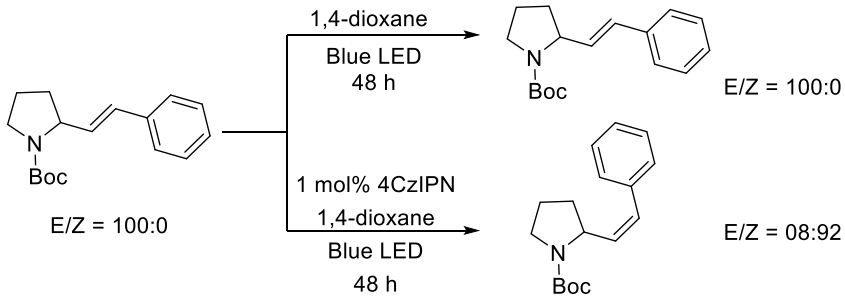
Figure 2: Fluorescence quenching of excited 4CzIPN* with *N* Boc Proline carboxylate anion (0.5 M) in DMF (excitation wavelength: 365 nm).



Fluorescence quenching of excited 4CzIPN* with *N* Boc Proline carboxylate anion (0.5 M) in 1,4-Dioxane (excitation wavelength: 365 nm).

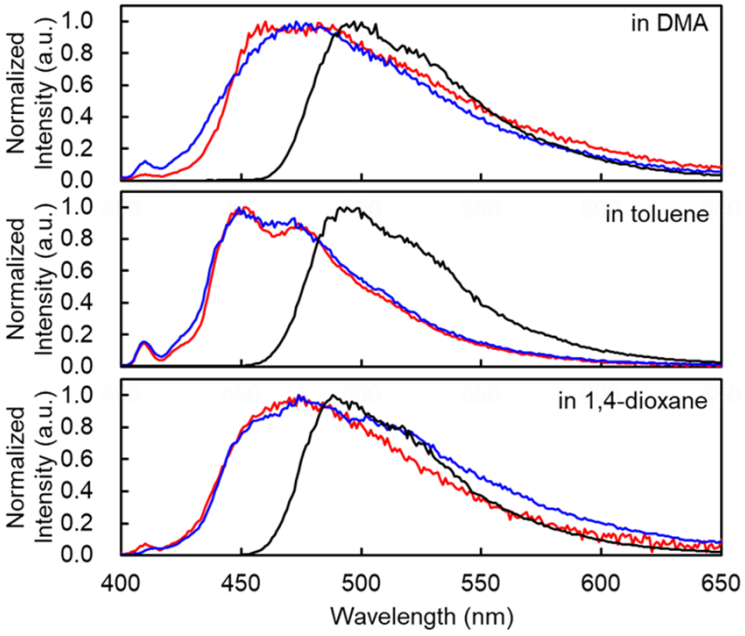


8. Control experiment for E to Z isomerization

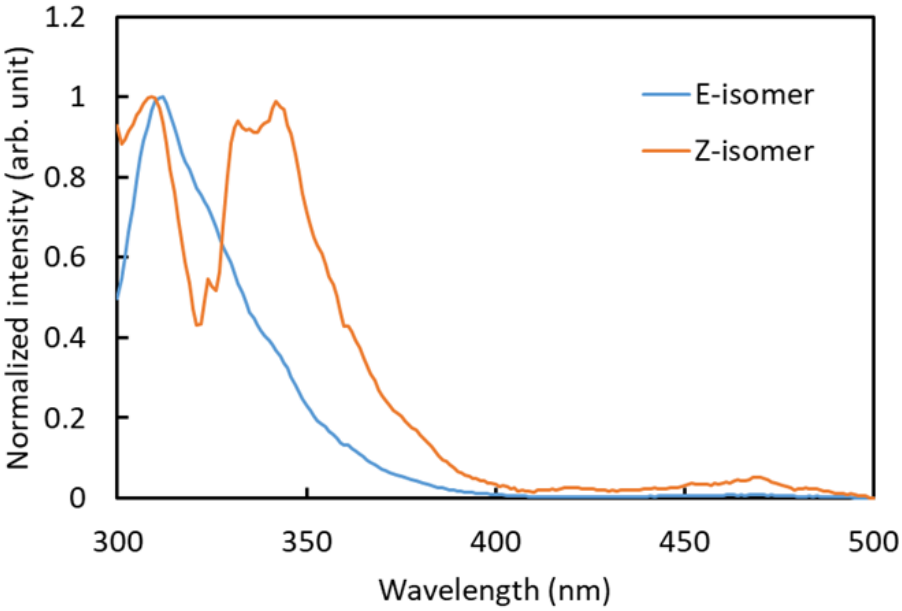


We have done two experiment, where the pure *E*-isomer was subjected to isomerization under the irradiation of blue light with and without the catalyst. We found that after 48 hours in the presence of catalyst Z-isomer (E/Z = 08:92) was formed as a major product, whereas without catalyst no isomerisation was observed.

9. Phosphorescence spectra of **6a** (*E*-isomer; red line), **7a** (*Z*-isomer; blue line), and 4CzIPN in DMA, toluene and 1,4-dioxane; λ_{ex} = 330 nm; [M] = 1.0 × 10^{-5} M.

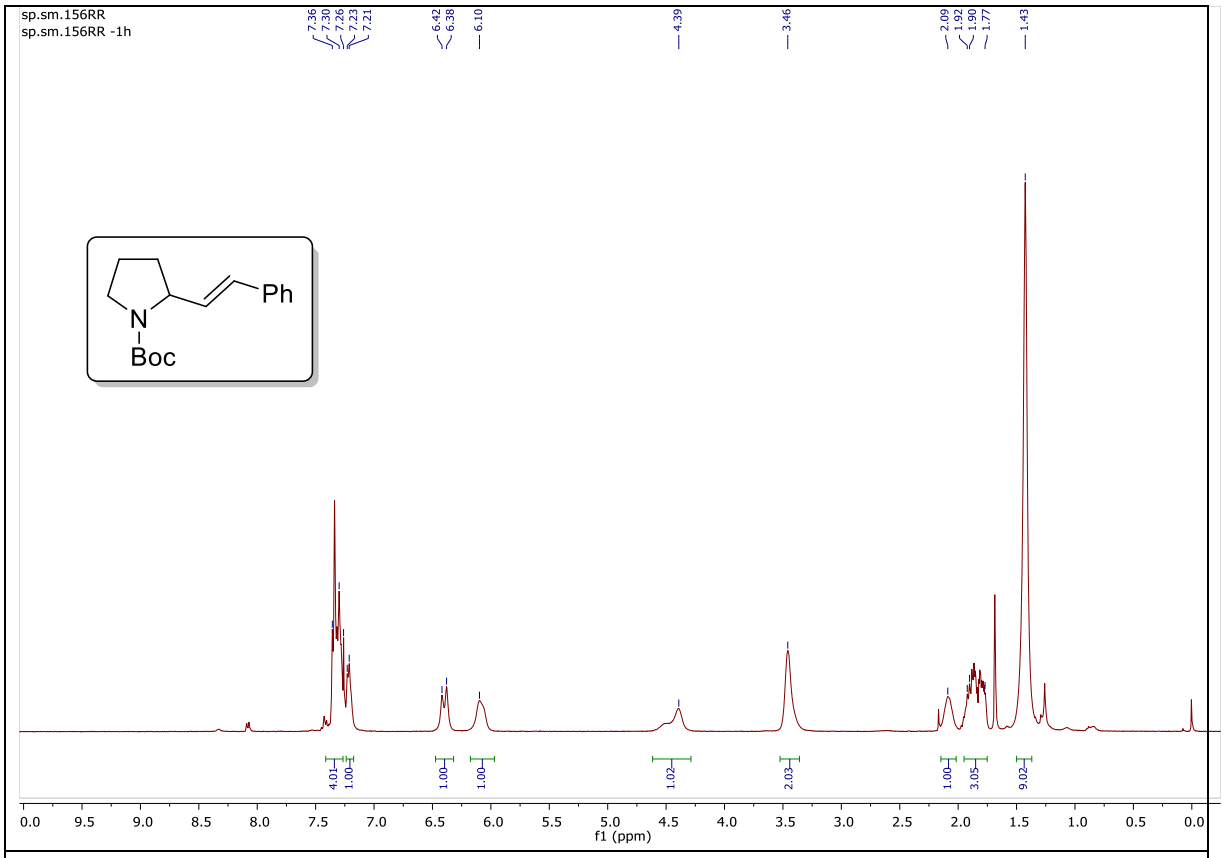


10. Normalized fluorescence spectra of 6a (E-isomer) and 7a (Z-isomer) in 1,4-dioxane; λex = 280 nm; [M] = 1.0 × 10-5 M.



11. Reference:

1. A. Nobel, D. W. C. Macmillan, *J. Am. Chem. Soc.*, **2014**, 136, 11602.
2. Y. Lei, R. Qiu, L. Zhang, C. Xu, Y. Pan, X. Qin, L. Xu, Y. Deng, *ChemCatChem Comm.*, **2015**, 7, 1275.
3. S. Akkarasamiyo, S. Sawadjoon, A. Orthaber, M. S. J. Samec, *Chem. Eur. J.*, **2018**, *24*, 3488.
4. Carrera, E. D. *Chem. Comm.*, **2017**, 53, 11185.
5. S. Paul, J. Guin, *Green Chem.*, **2017**, 19, 2530.
6. M. P. Sibi, D. Rutherford, P. A. Renhowe, B. Li, *J. Am. Chem. Soc.*, **1999**, 121, 7509.
7. M. M. Mastandrea, S. Cañellas, X. Caldentey, M. A. Pericas, *ACS Catal.*, **2020**, 10, 6402.
8. G. -L. Dai, S.-Z. Lai, Z. Luo, Z. –Y. Tang, *Org. Lett.*, **2019**, 21, 2269.
9. D. R. Heitz, K. Rizwan, G. A. Molander, *J. Org. Chem.*, **2016**, 81, 7308.
10. D. Karila, L. Leman, R. H. Dodd, *Org. Lett.*, **2011**, 13, 5830.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6.38
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2.09
1.92
1.90
1.77
1.43
Ph
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Boc
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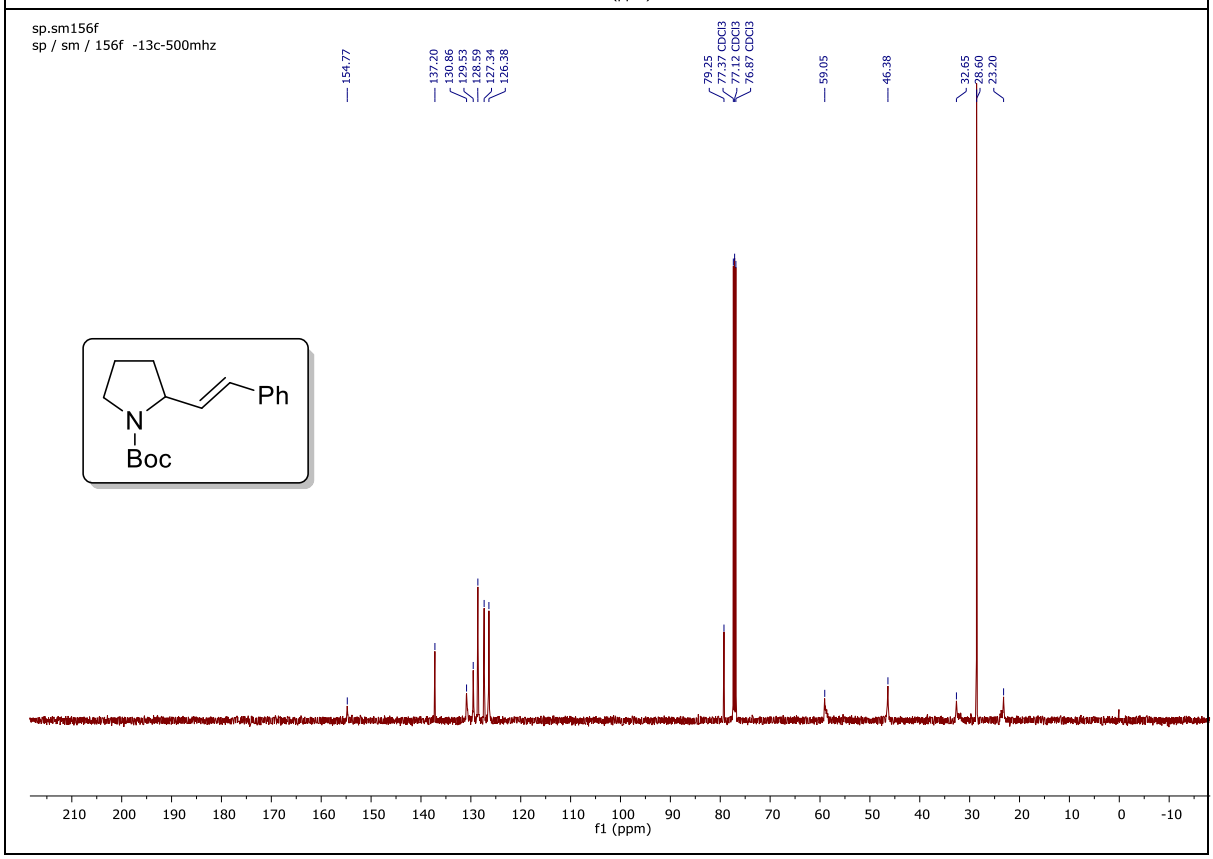
1.00
1.00
1.00
1.02
2.03
1.00
3.05
9.02
f1 (ppm)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76.87 CDCl3
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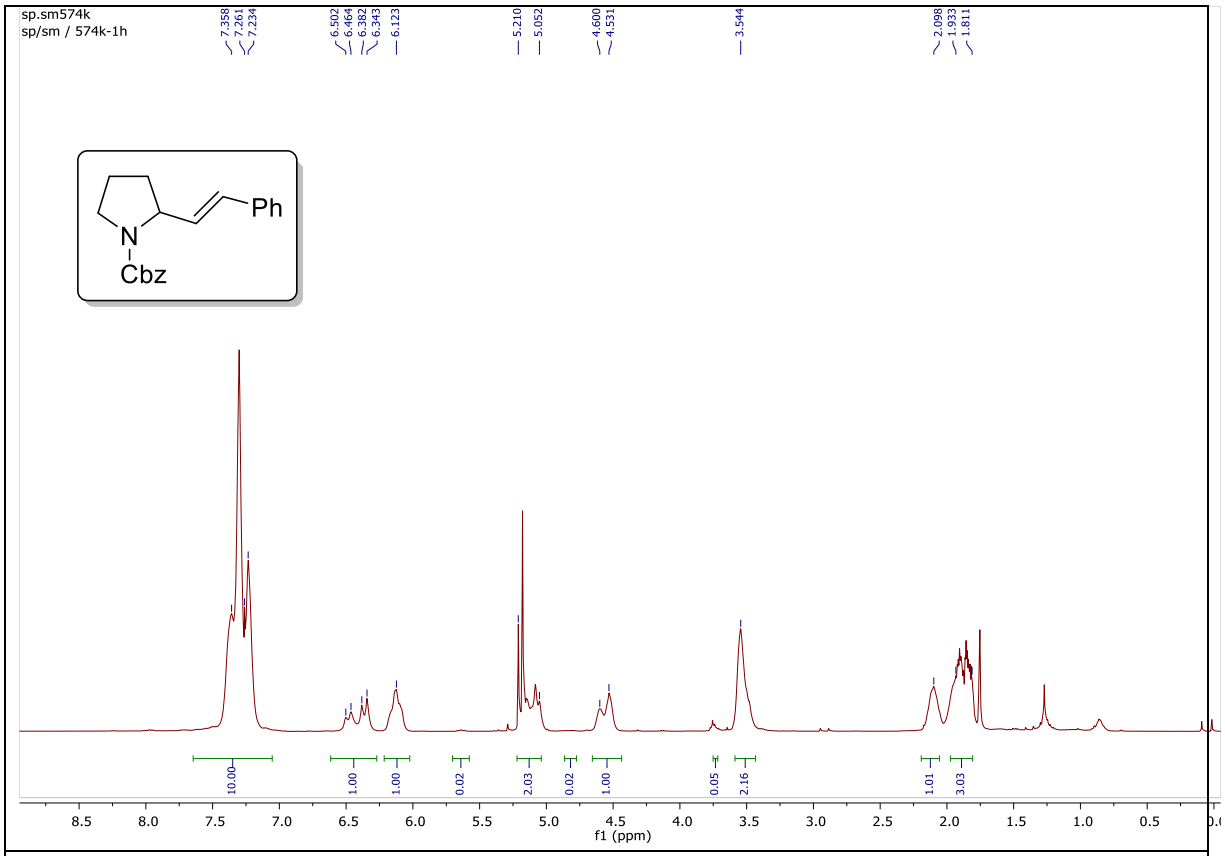
23.20
Ph
N
Boc
f1 (ppm)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0.05
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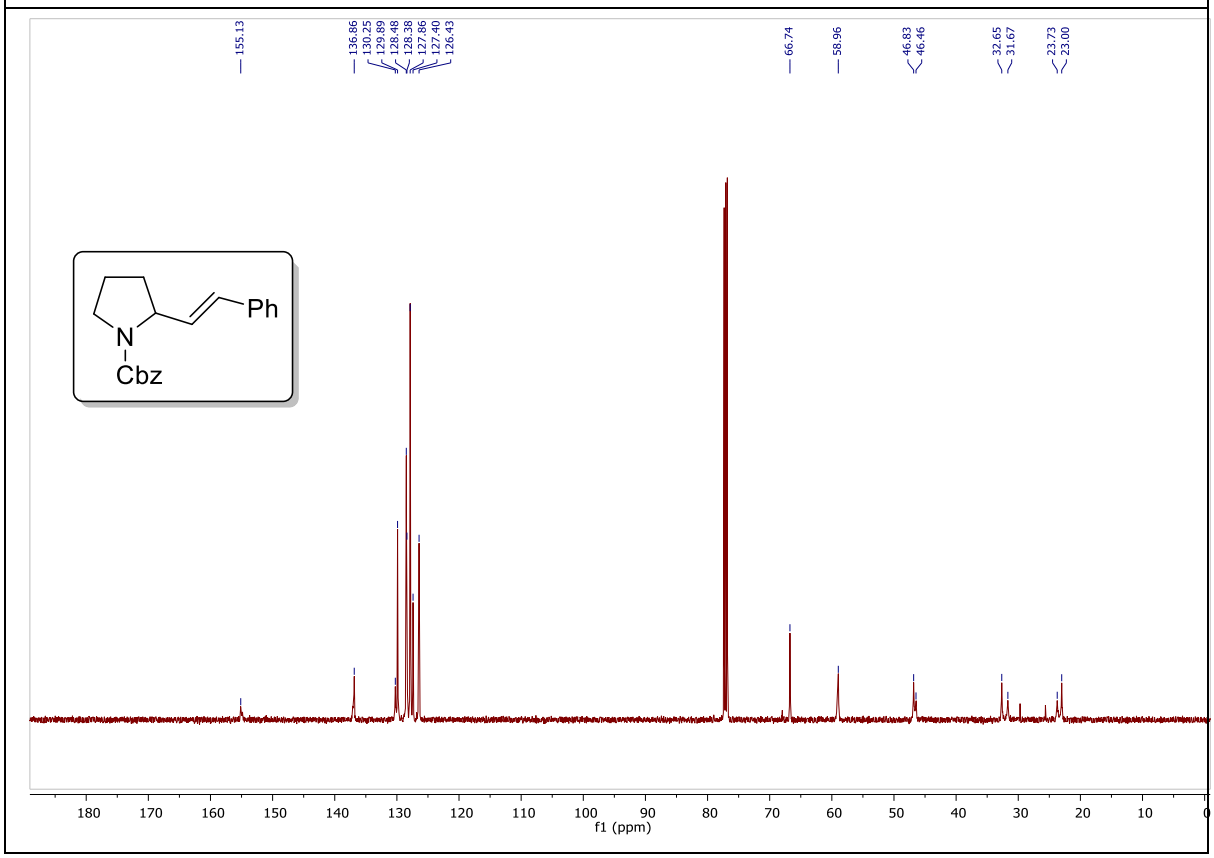
f1 (ppm)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Ph
N
Cbz
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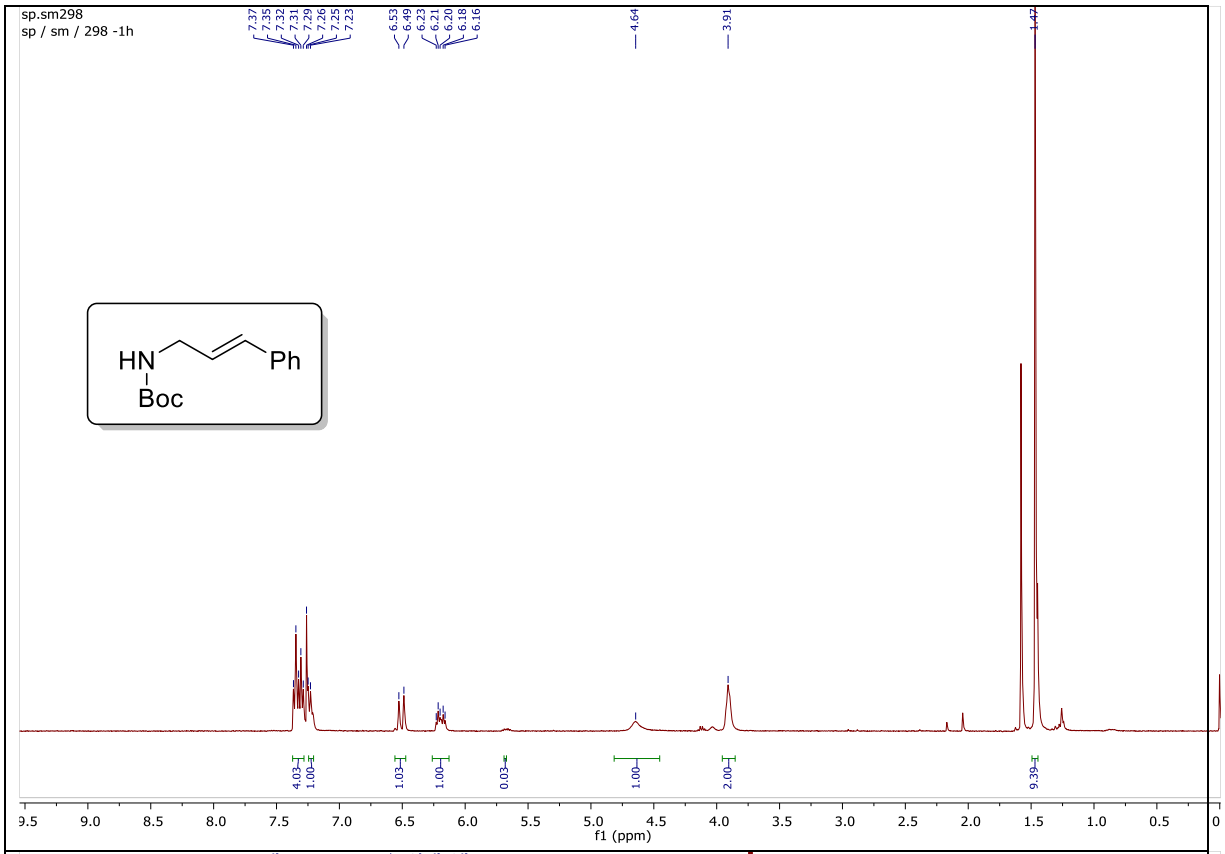
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Ph
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2.00
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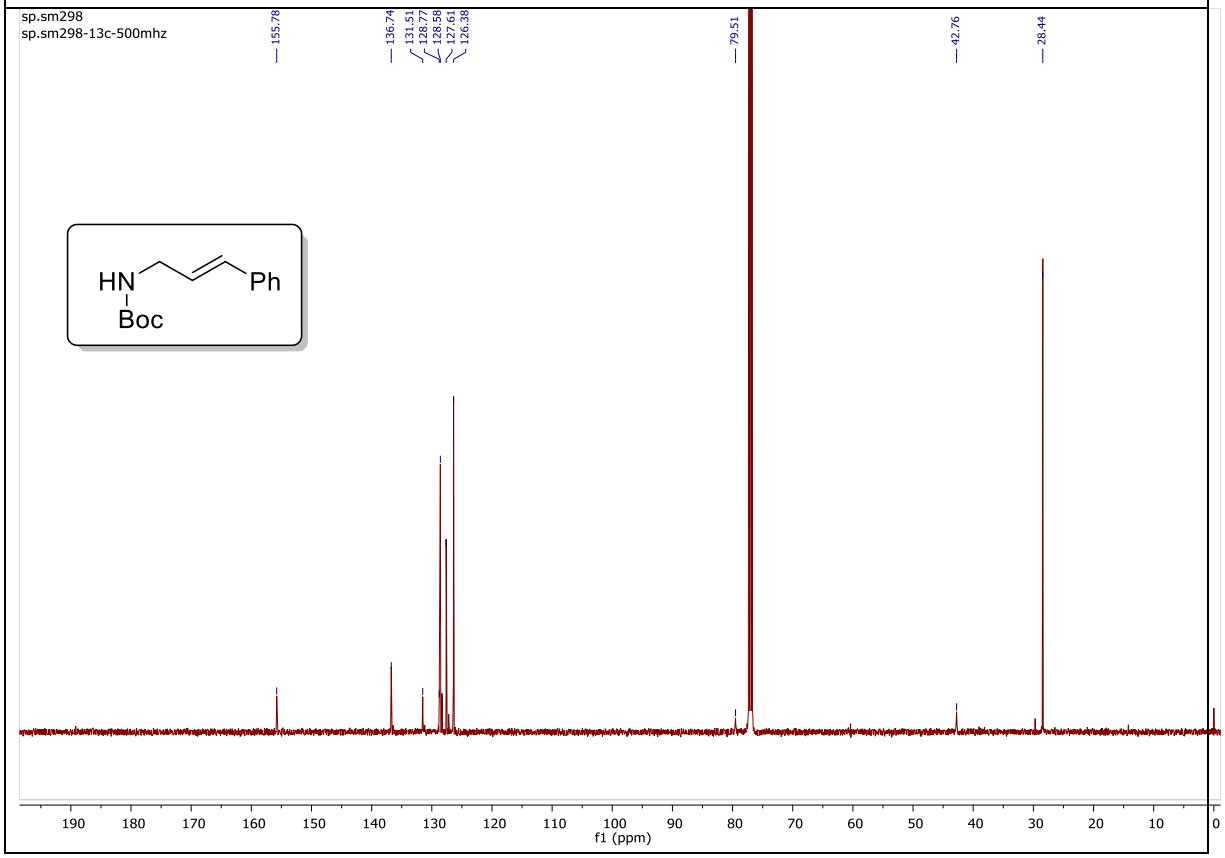
f1 (ppm)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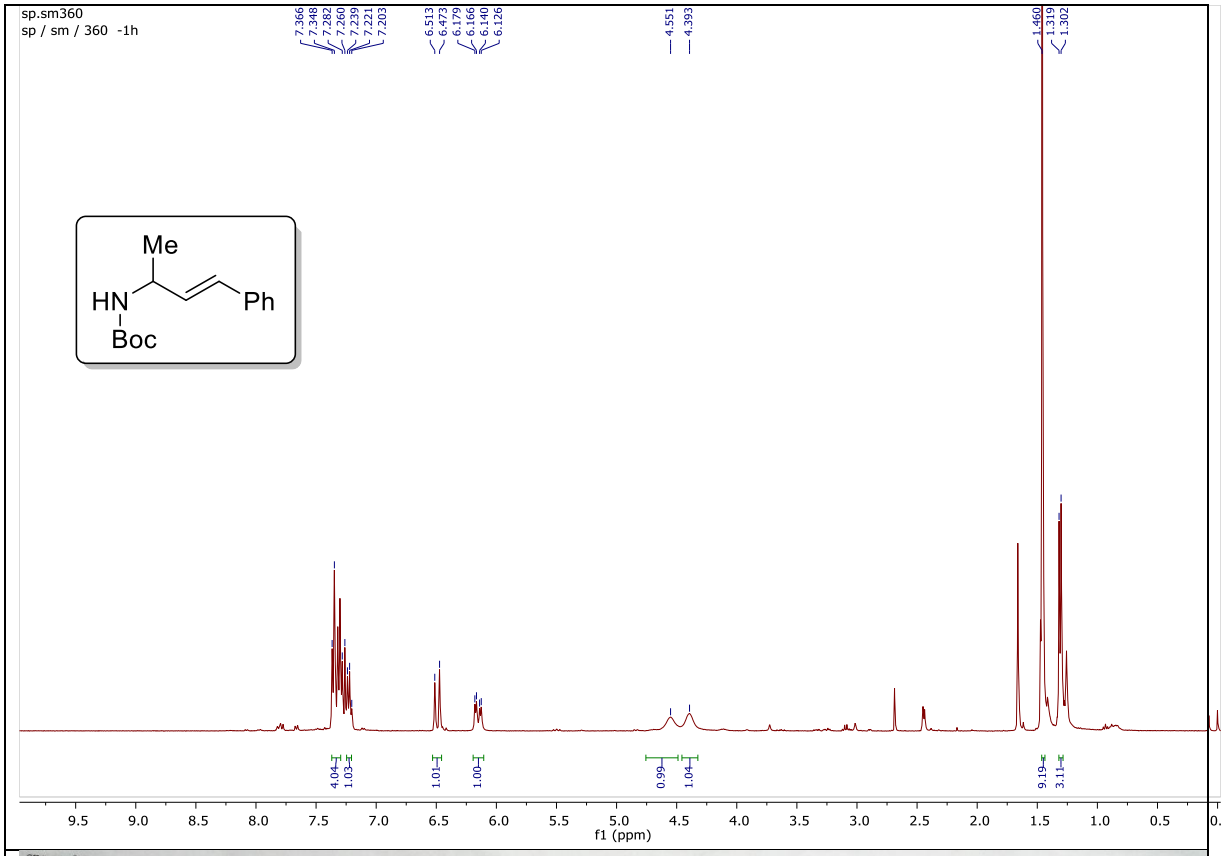
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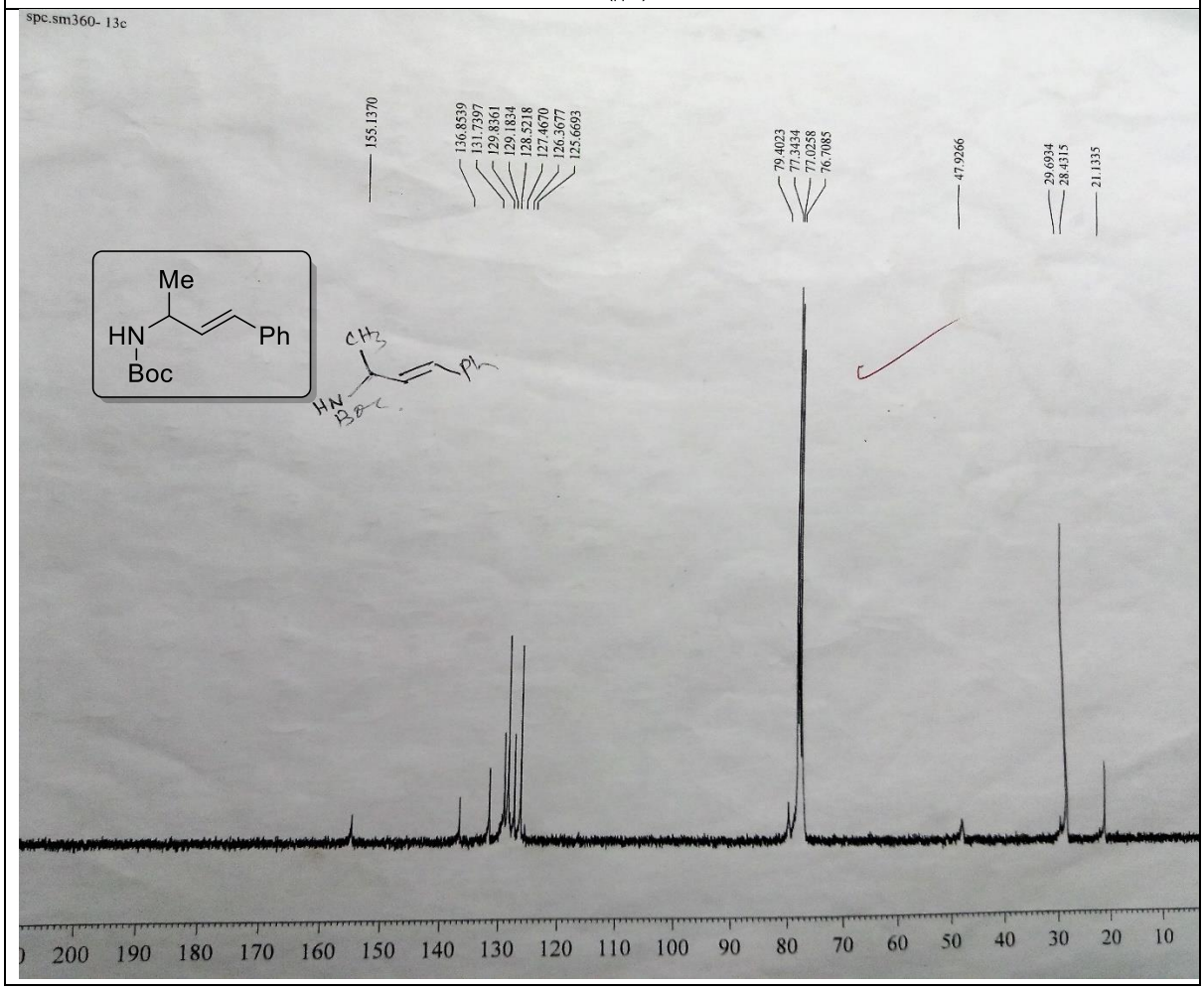
f1 (ppm)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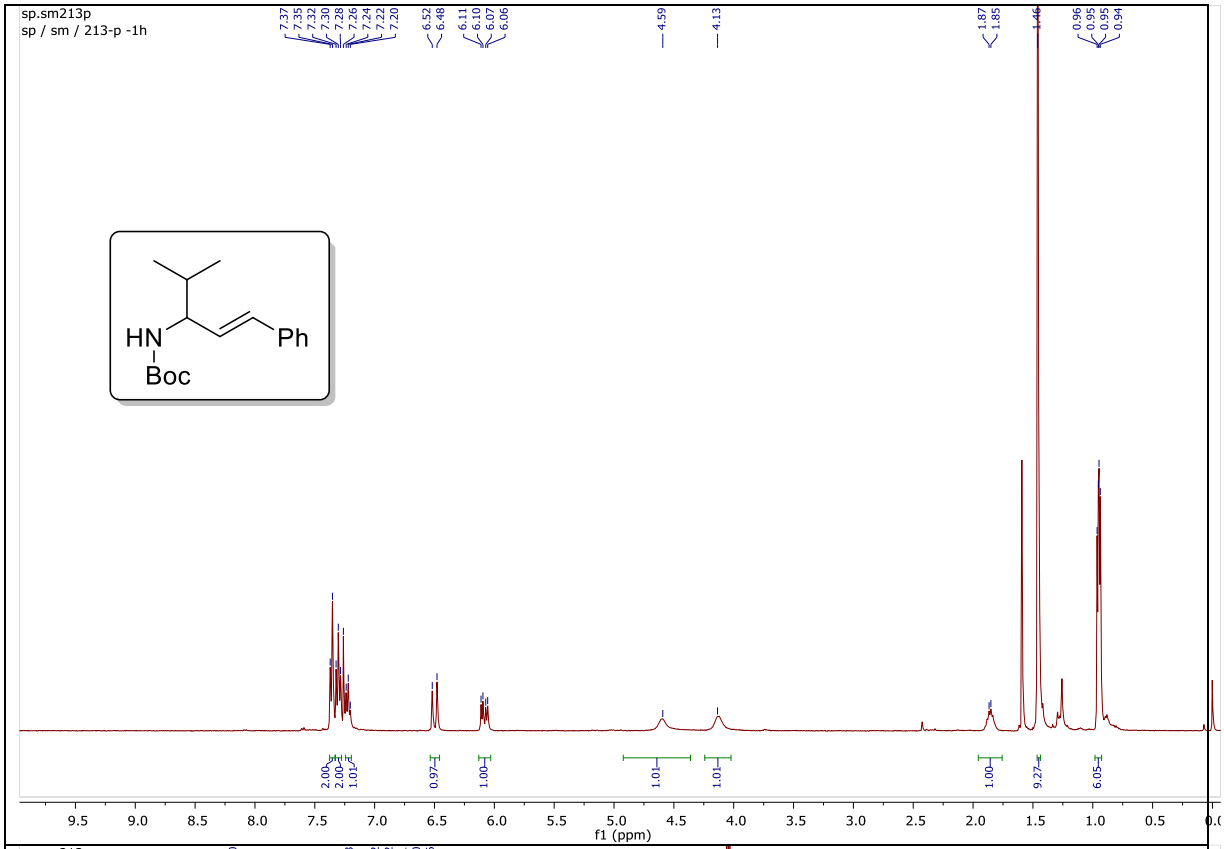
Boc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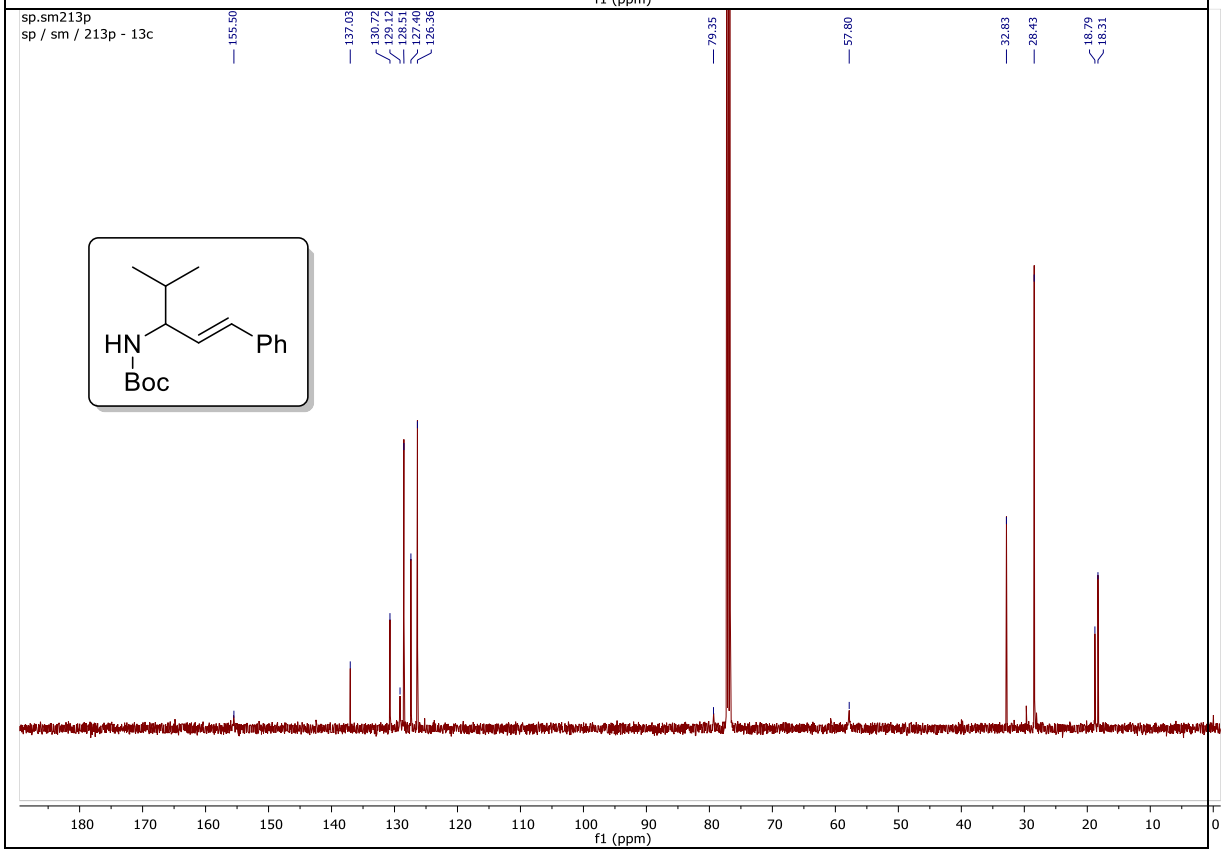
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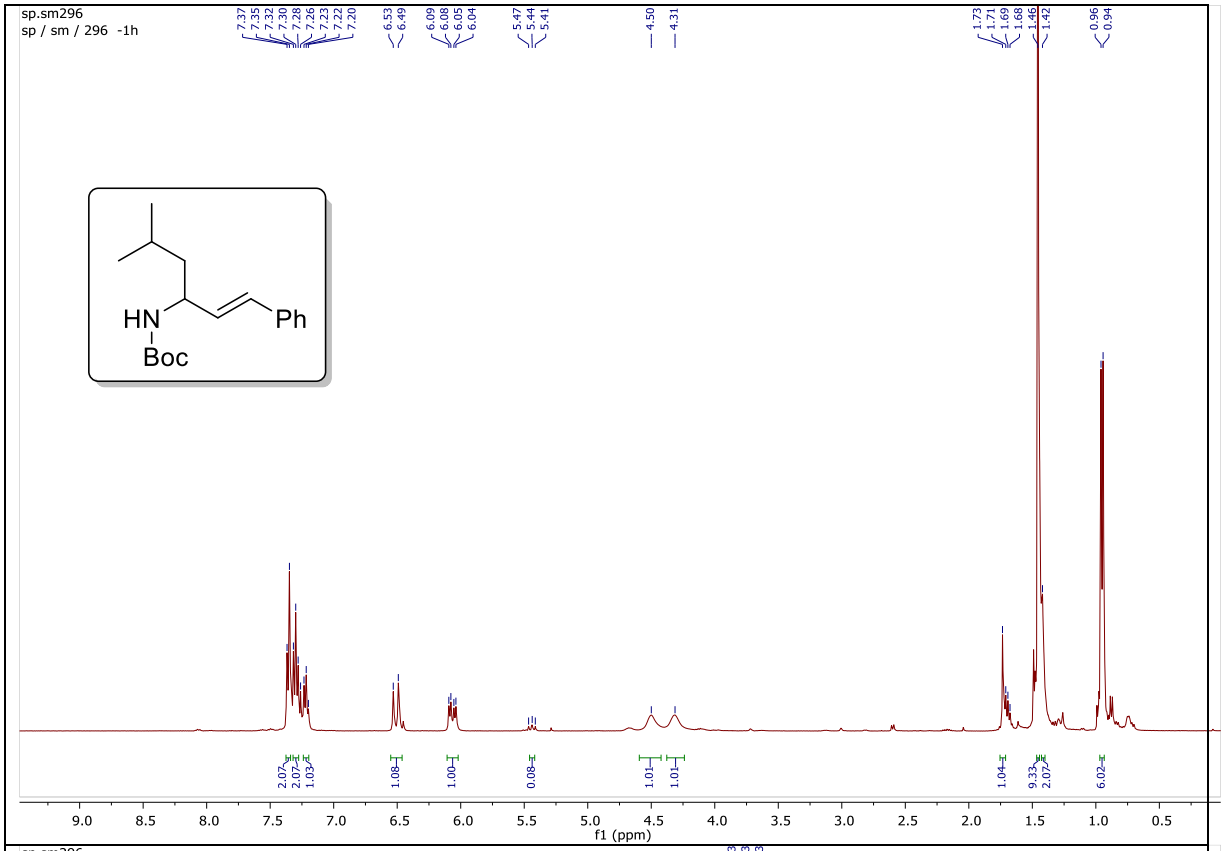
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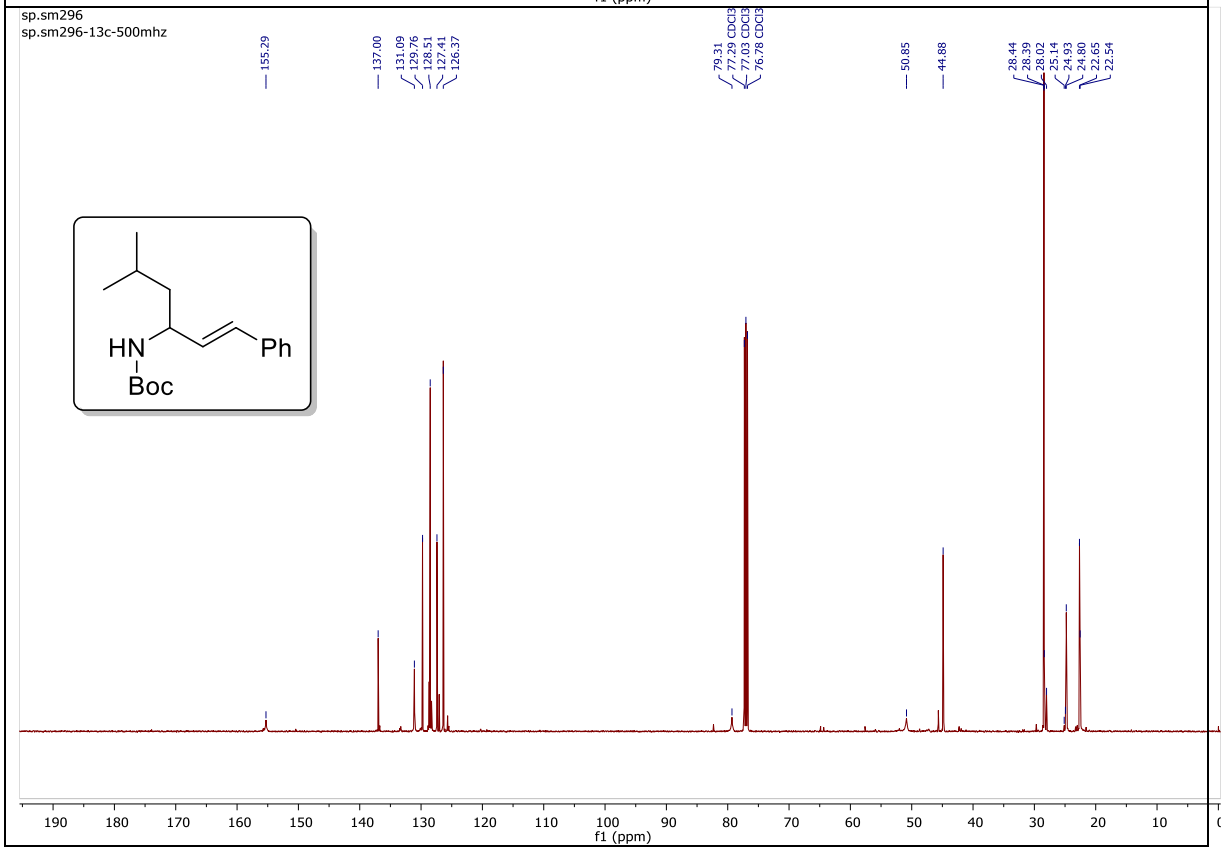
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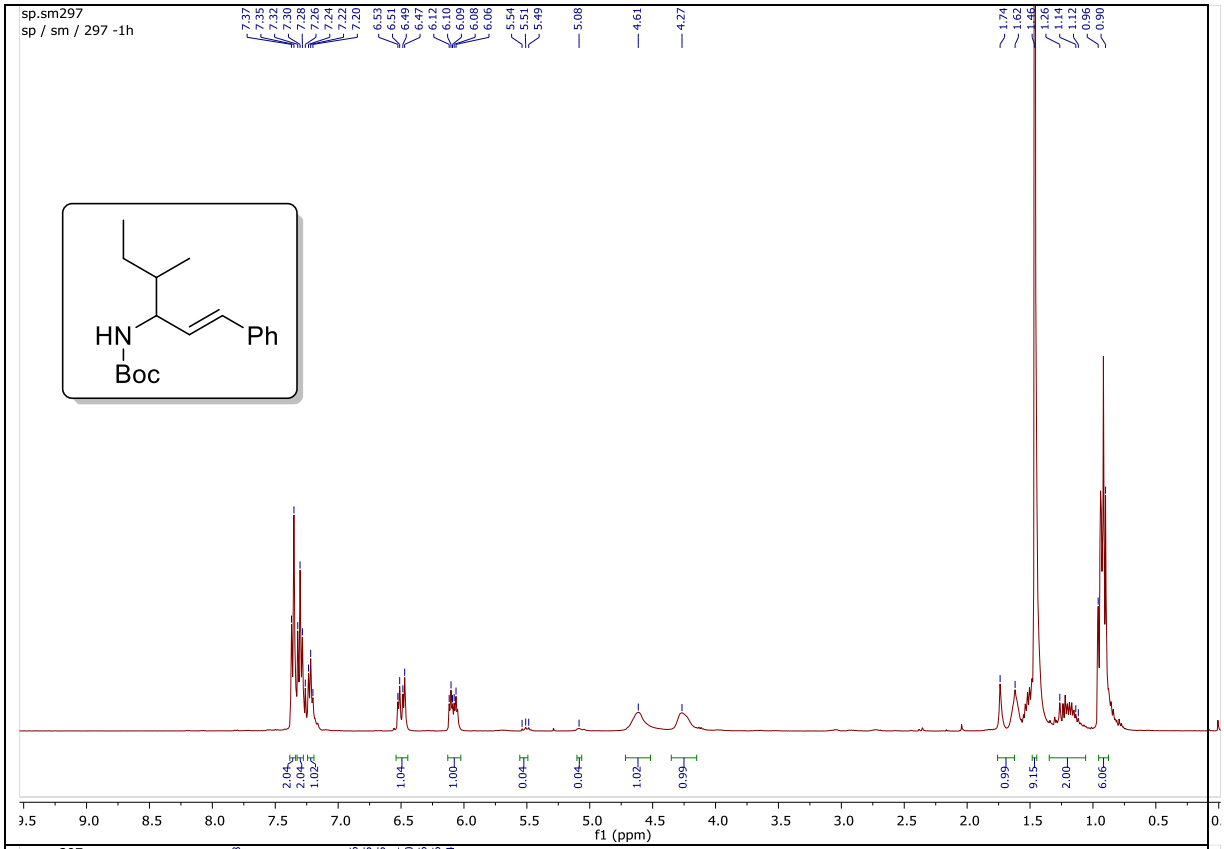
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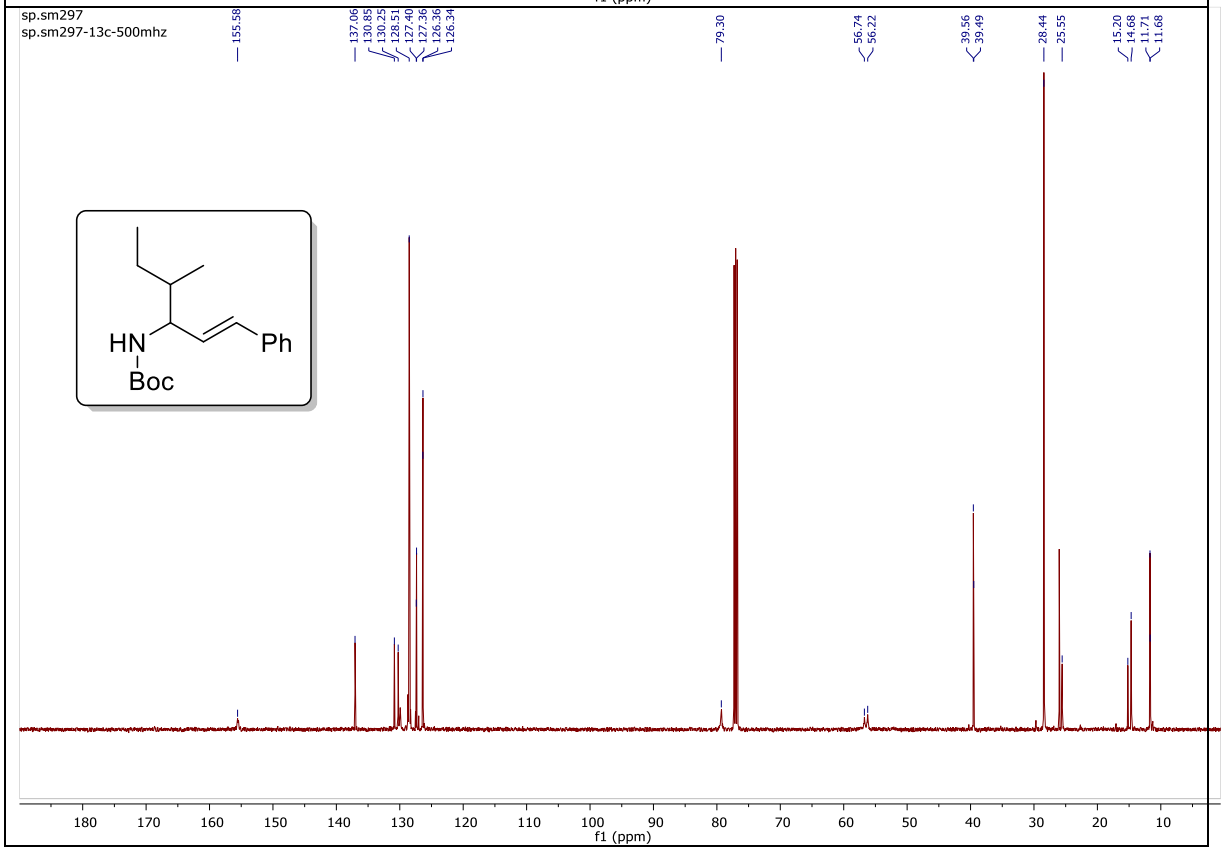
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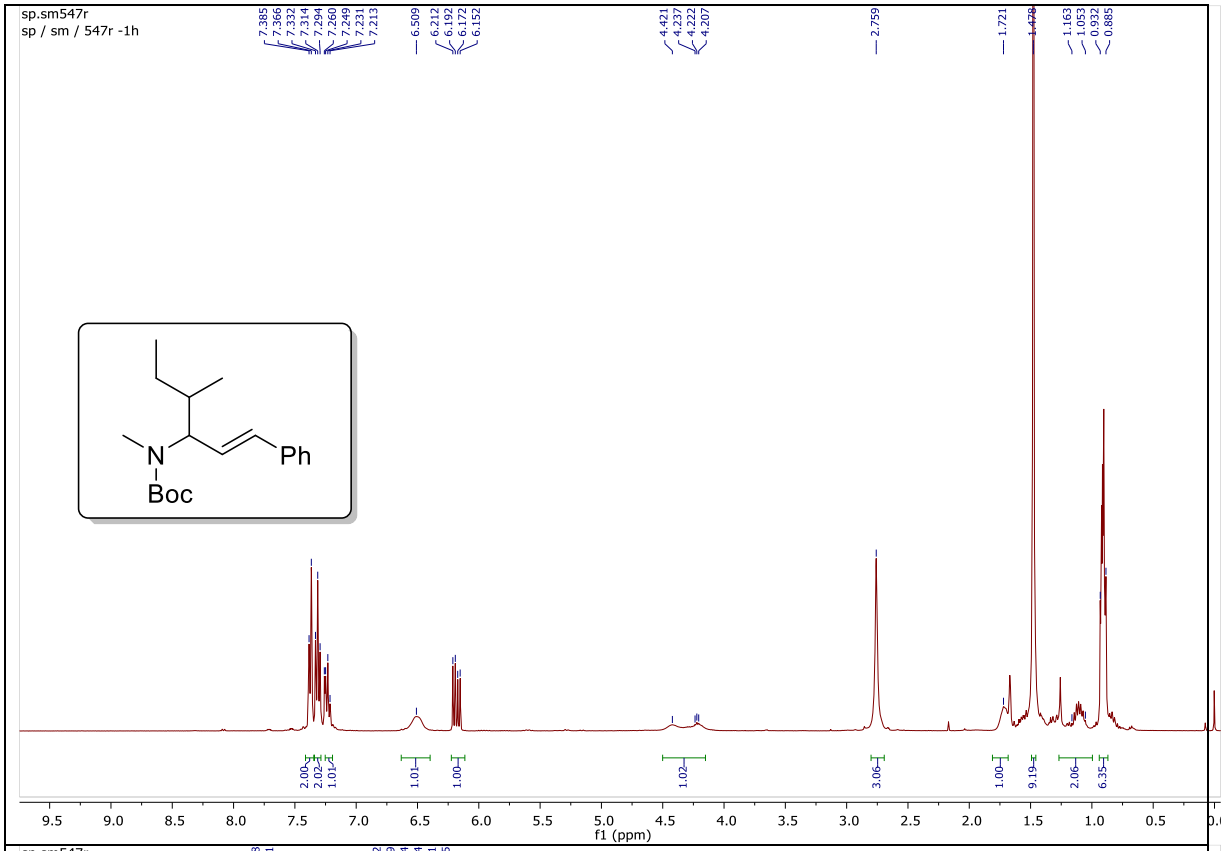
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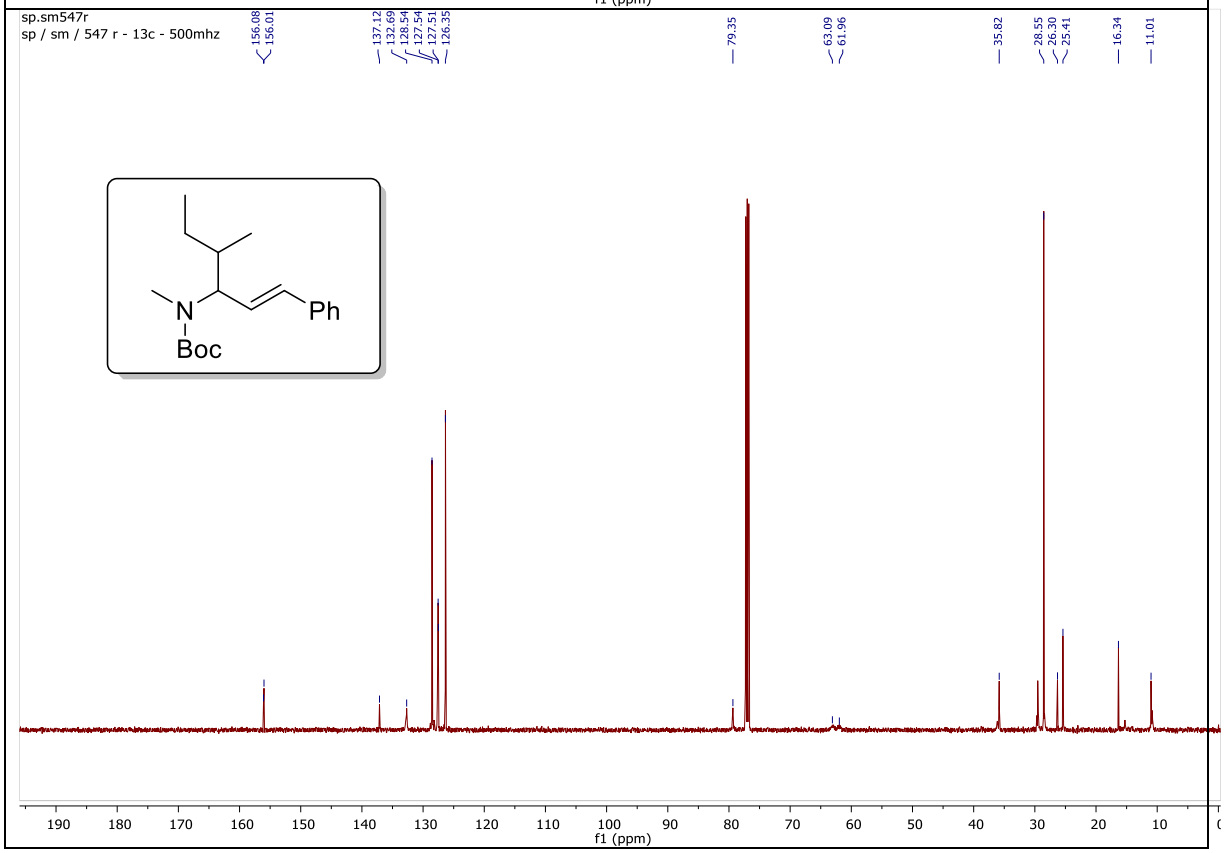
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Boc
Ph
f1 (ppm)


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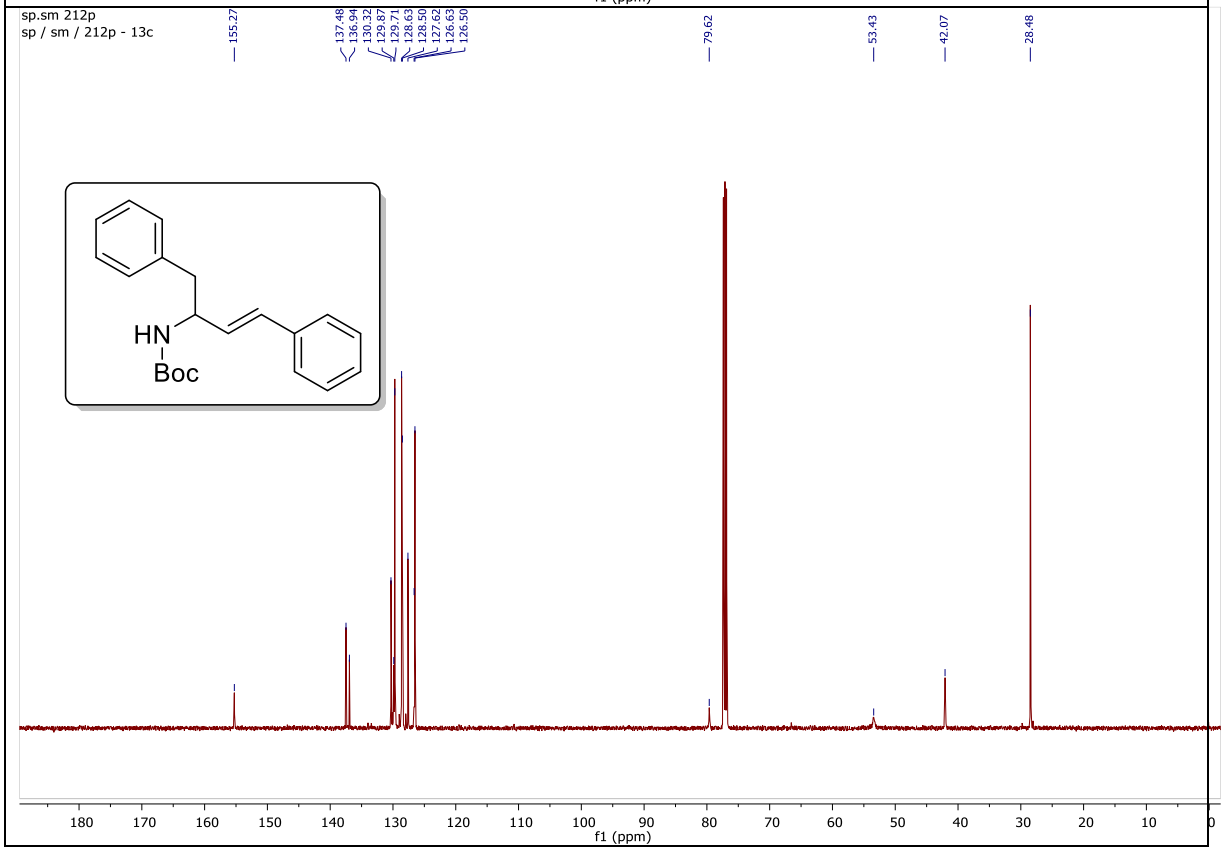
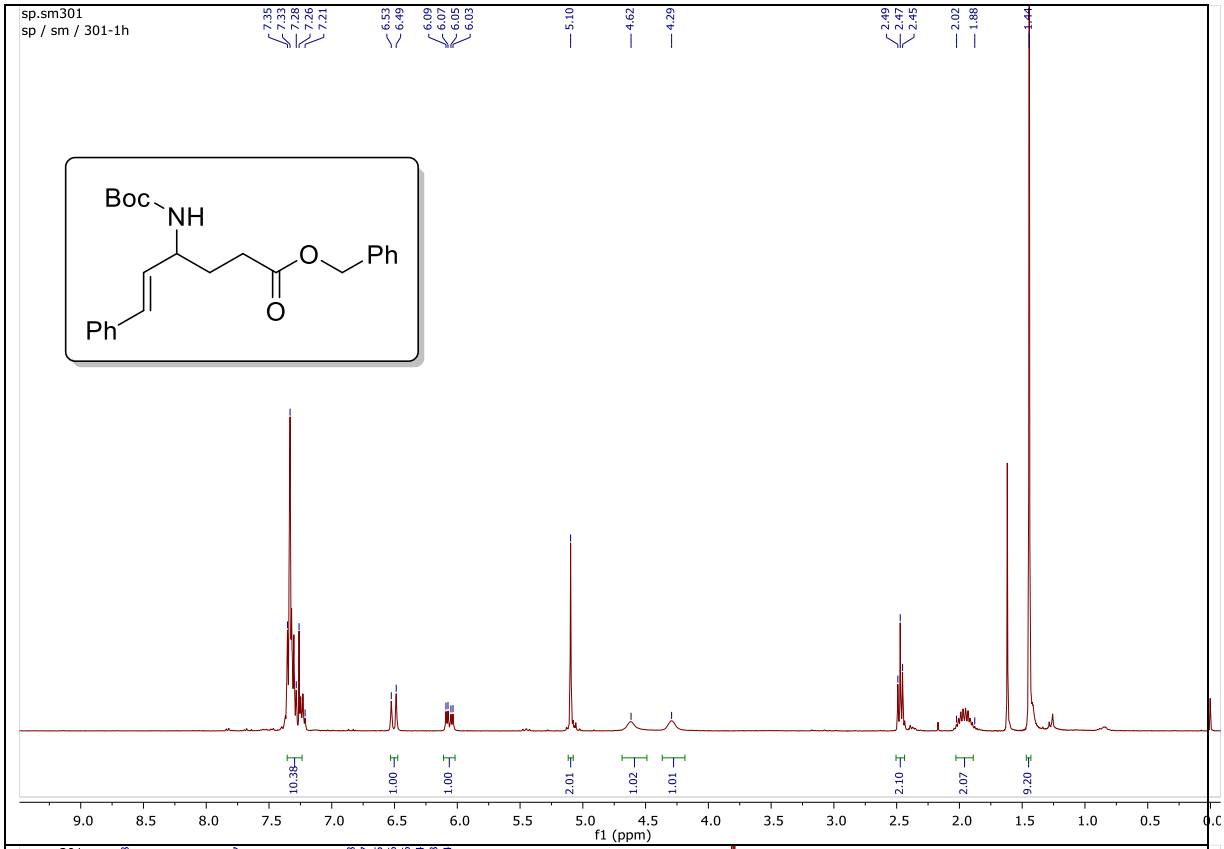
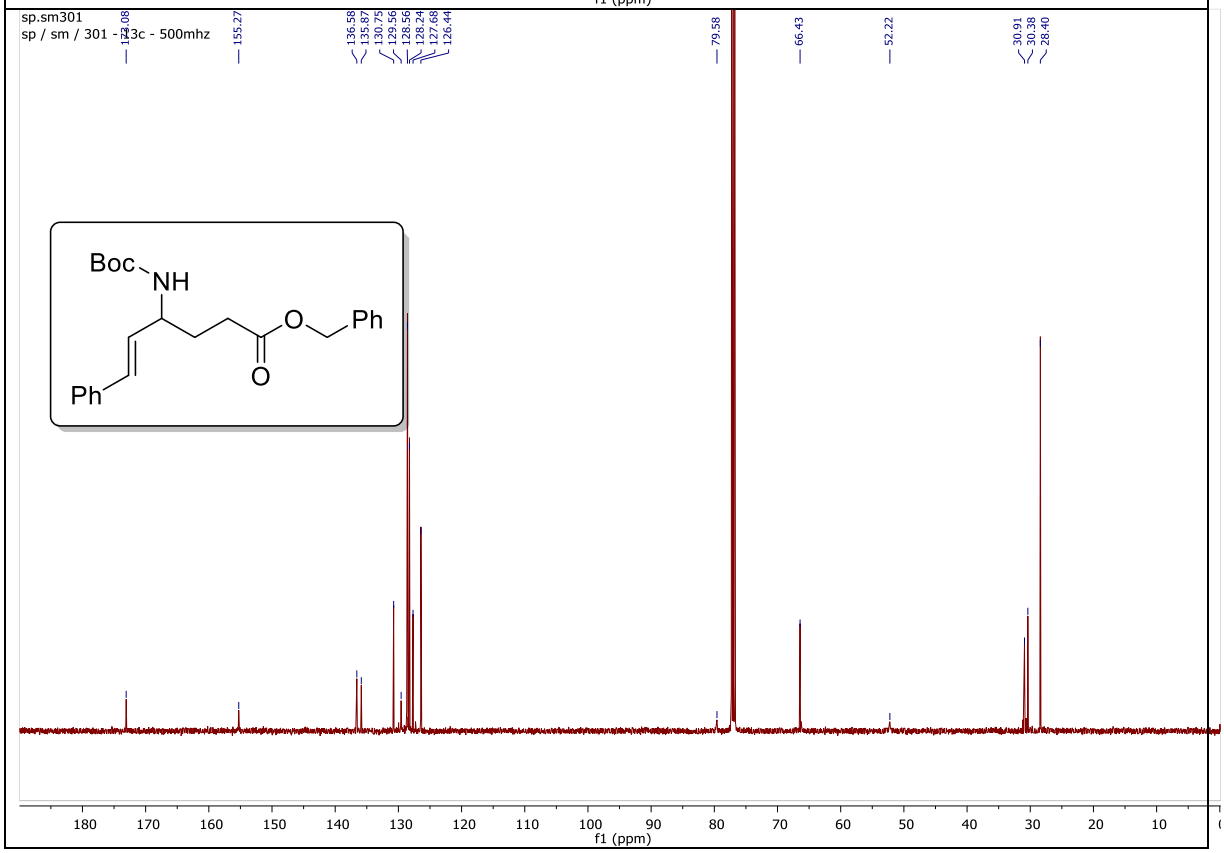
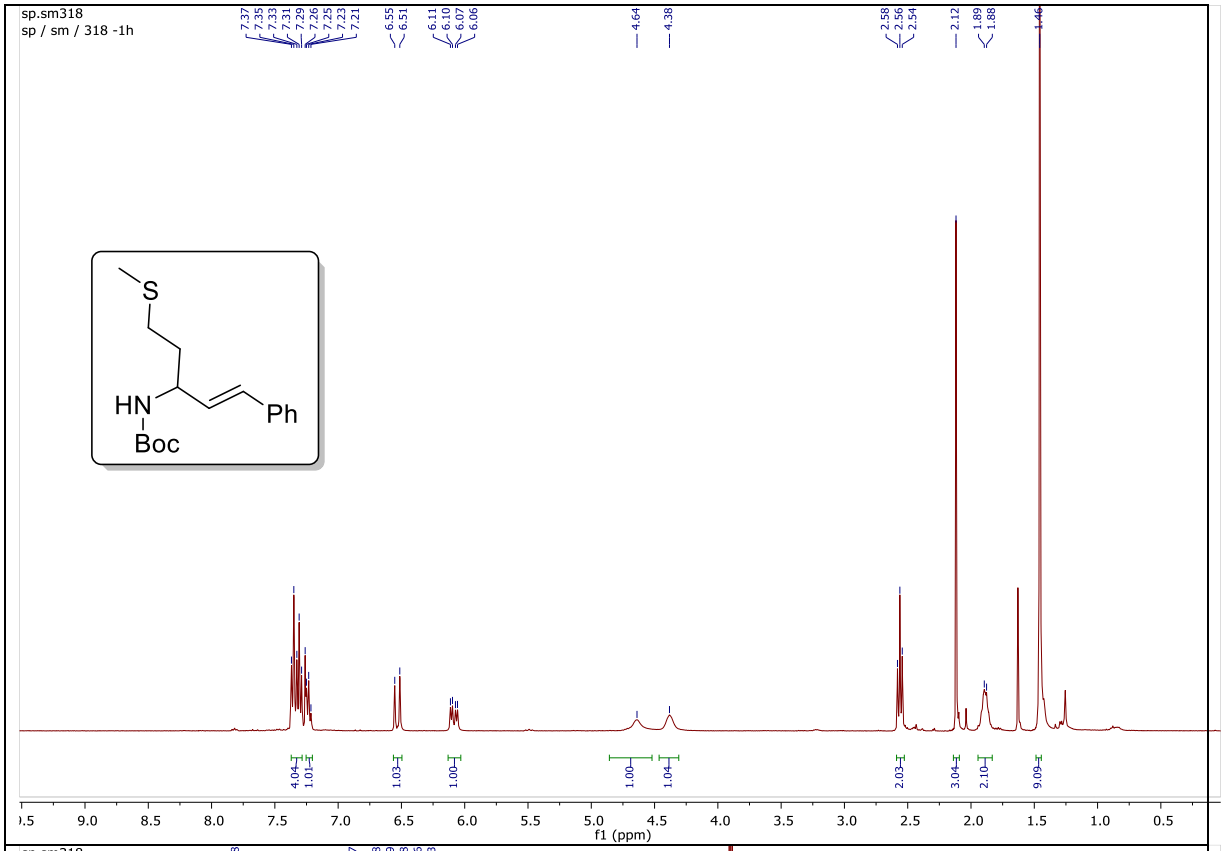
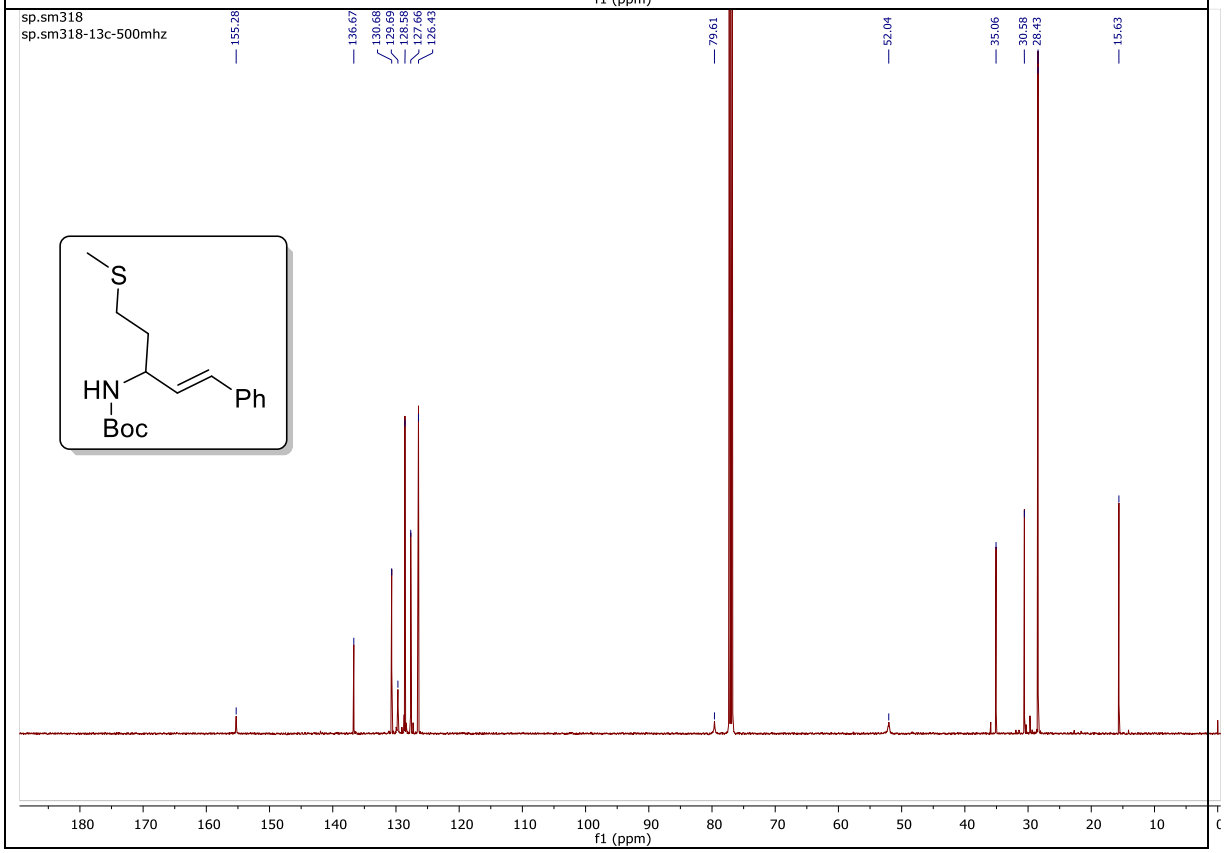
9.08
f1 (ppm)

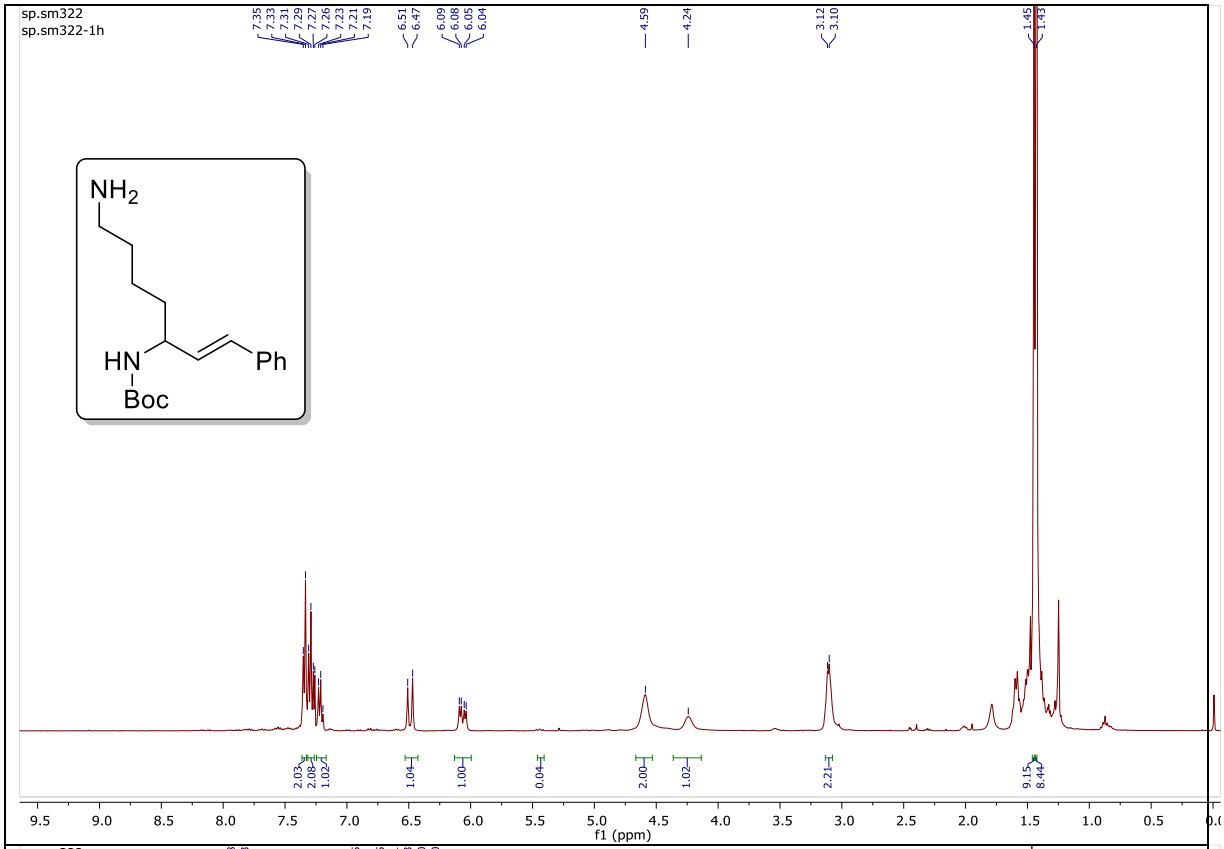

sp.sm 212p
sp / sm / 212p - 13c
155.27
137.48
136.94
130.32
129.87
129.71
128.63
128.50
127.62
126.63
126.50
79.62
53.43
42.07
28.48
HN
Boc
f1 (ppm)

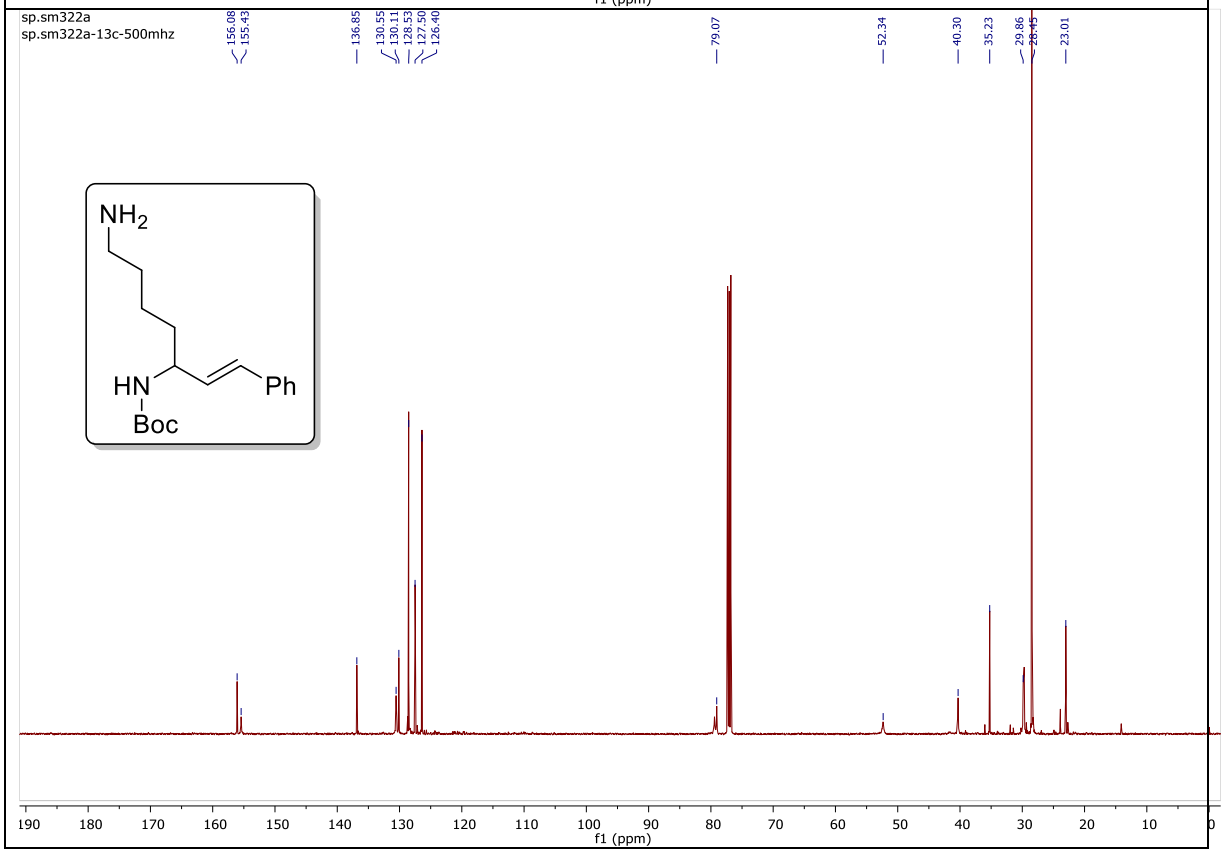

sp.sm301
sp / sm / 301-1h
Boc
NH
O
Ph
O
Ph
f1 (ppm)

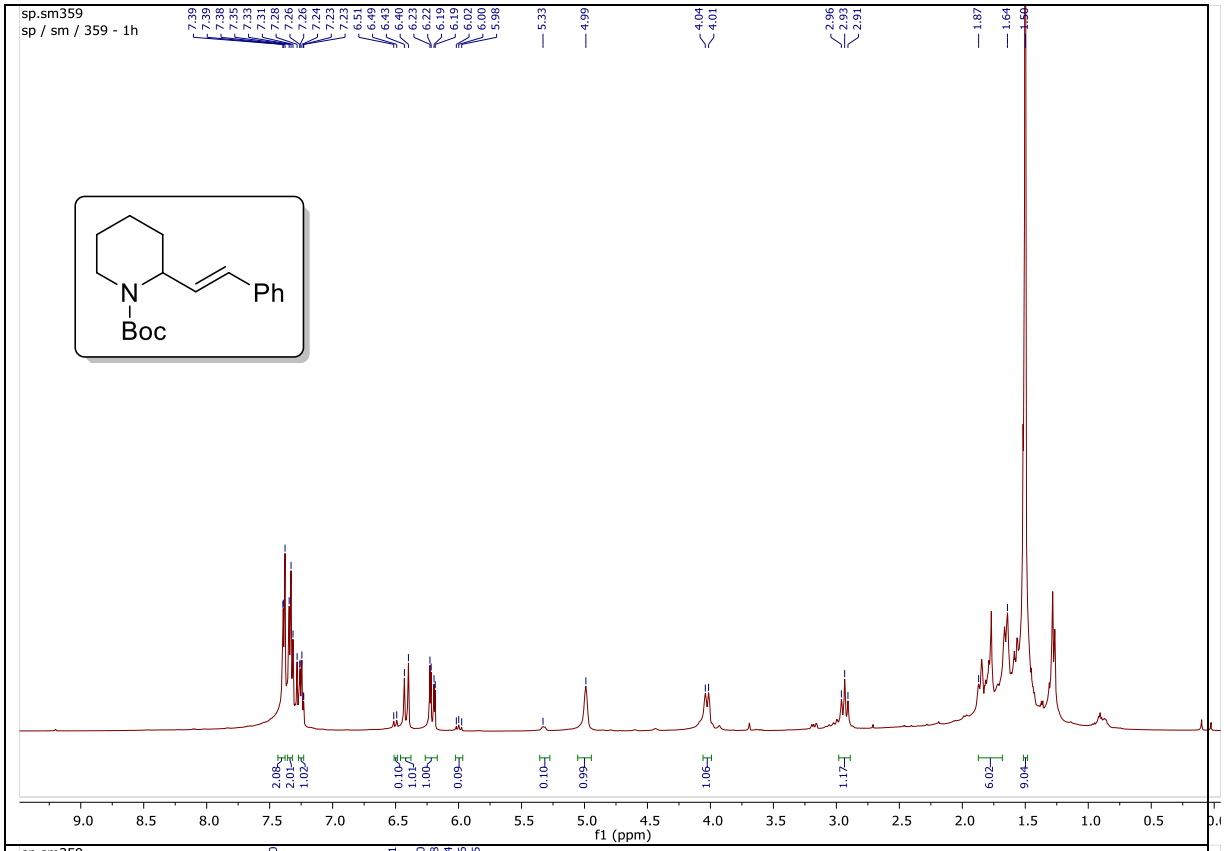

sp.sm301
sp / sm / 301 - 13c - 500mhz
Boc
NH
O
Ph
O
Ph
f1 (ppm)

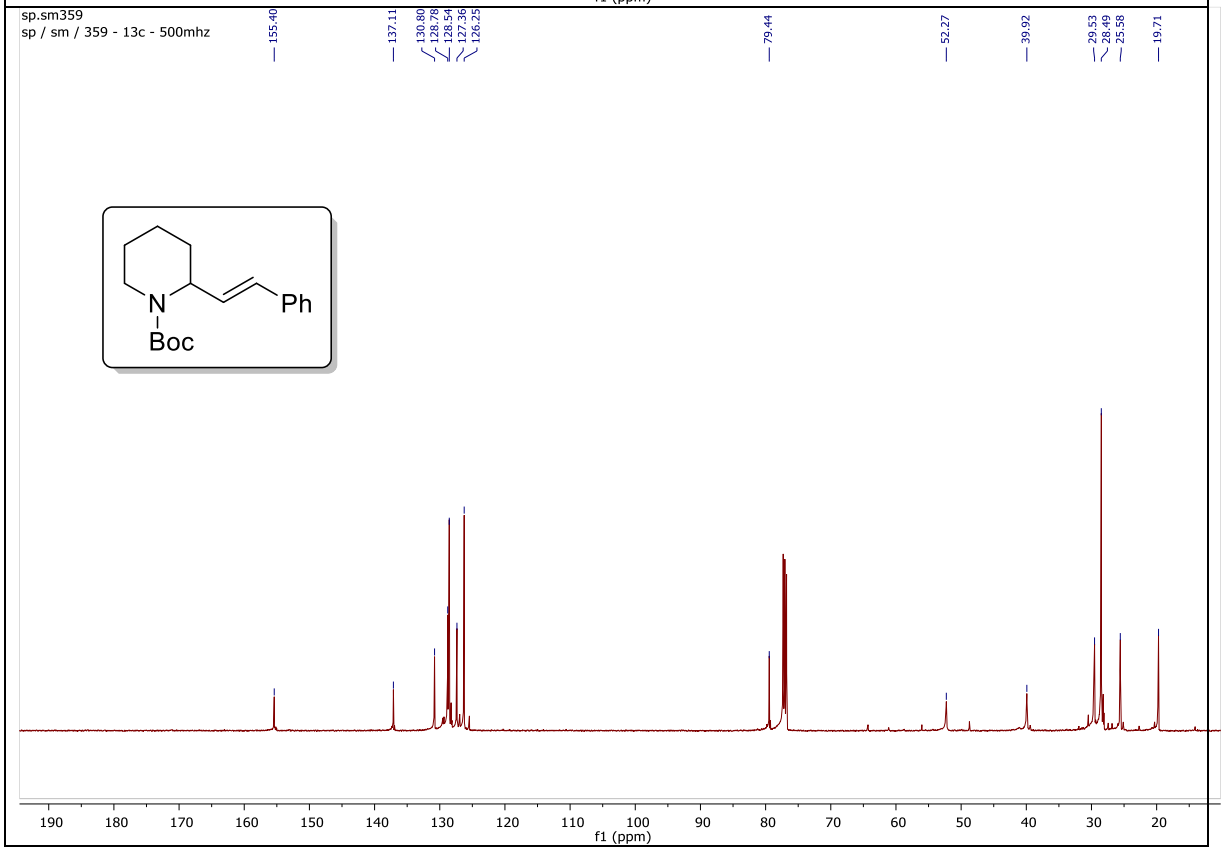

sp.sm318
sp / sm / 318 -1h
7.37
7.35
7.33
7.31
7.29
7.26
7.25
7.23
7.21
6.55
6.51
6.11
6.10
6.07
6.06
4.64
4.38
2.58
2.56
2.54
2.12
1.89
1.88
1.46
S
HN
Boc
Ph
4.04
1.01
1.03
1.00
1.00
1.04
2.03
3.04
2.10
9.09
f1 (ppm)

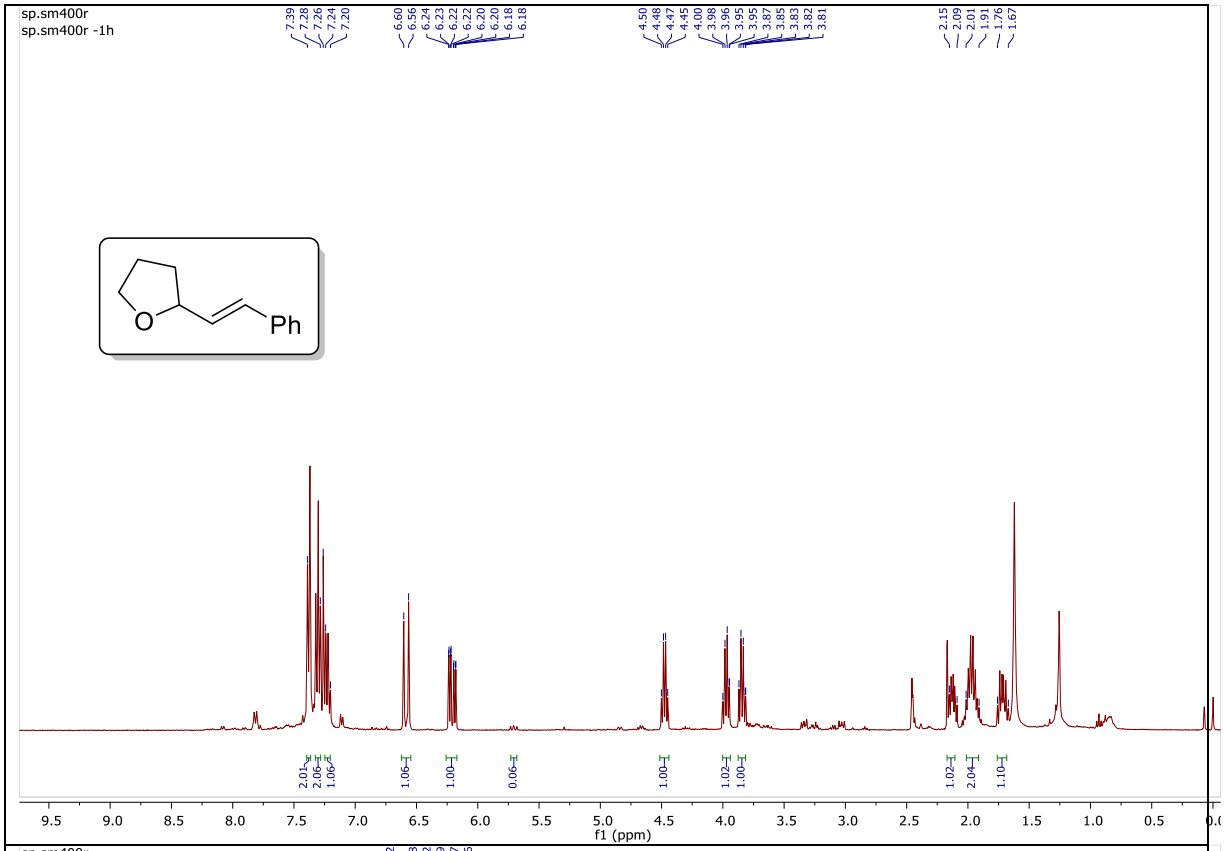

sp.sm318
sp.sm318-13c-500mhz
155.28
136.67
130.68
129.69
128.58
127.66
126.43
79.61
52.04
35.06
30.58
28.43
15.63
S
HN
Boc
Ph
f1 (ppm)

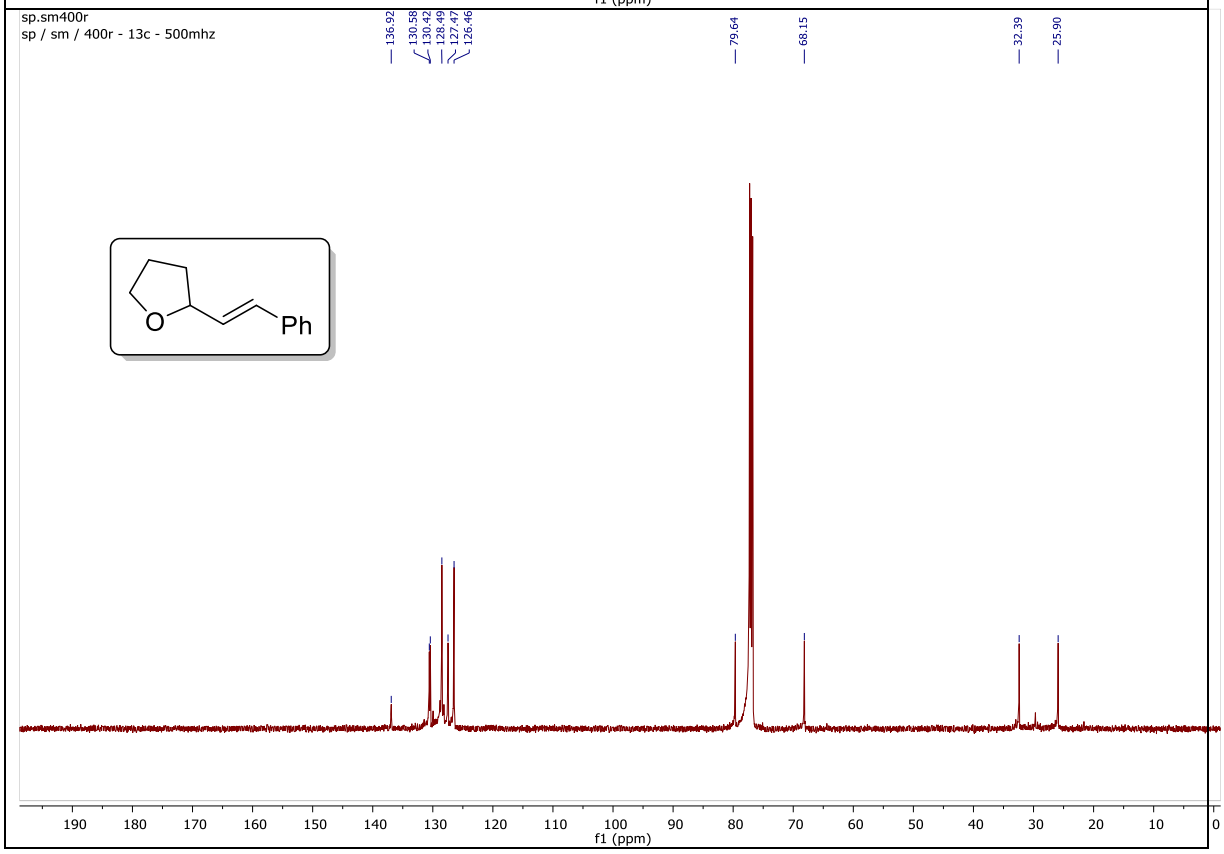

sp.sm322
sp.sm322-1h
NH2
HN
Boc
Ph
f1 (ppm)

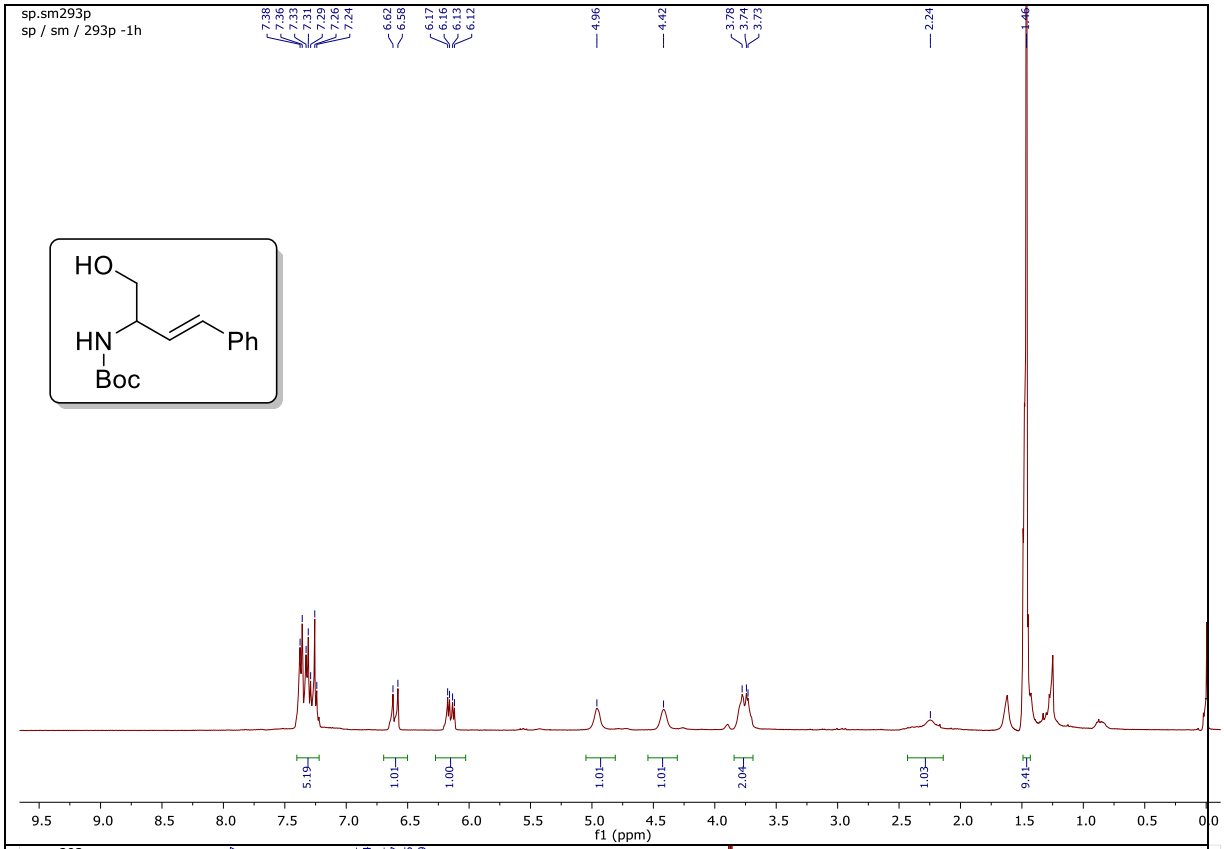

sp.sm322a
sp.sm322a-13c-500mhz
NH2
HN
Boc
Ph
f1 (ppm)

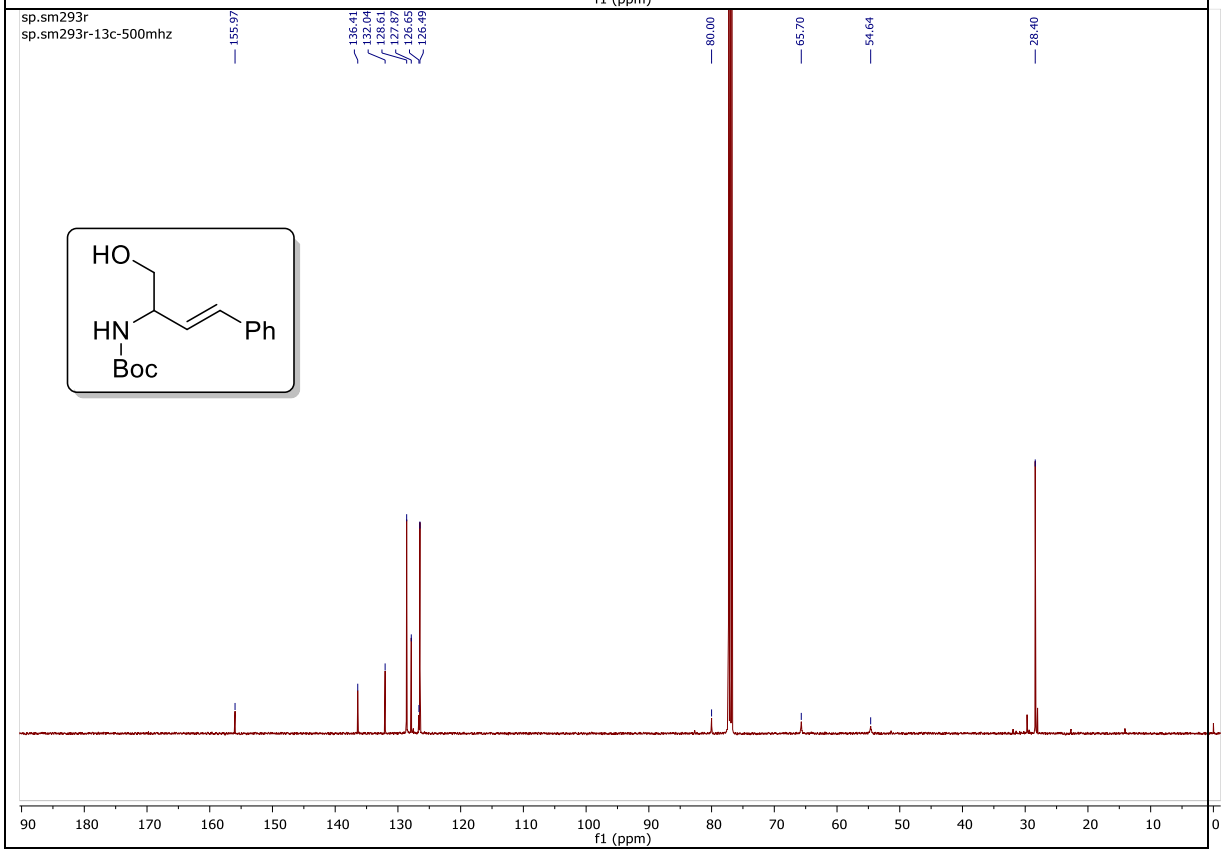

sp.sm359
sp / sm / 359 - 1h
N
Boc
Ph
f1 (ppm)

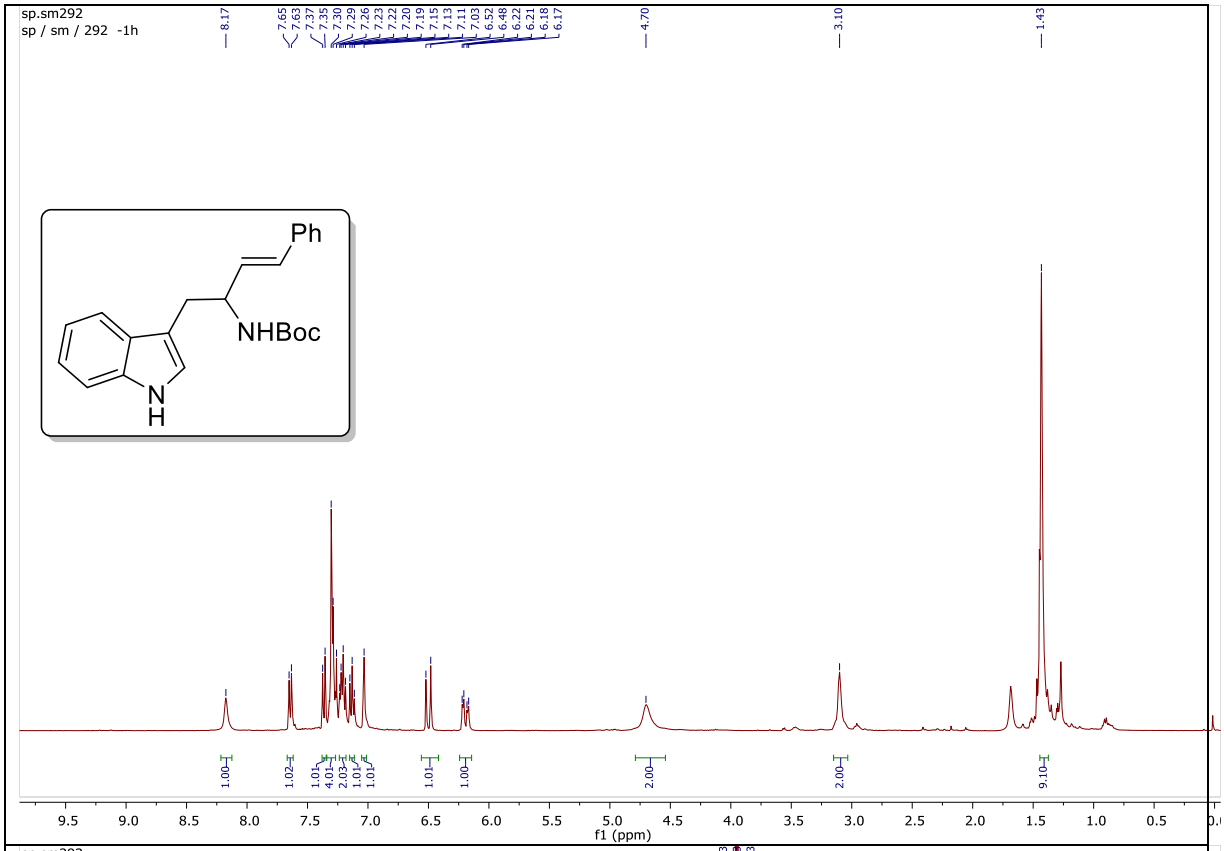

sp.sm359
sp / sm / 359 - 13c - 500mhz
N
Boc
Ph
f1 (ppm)

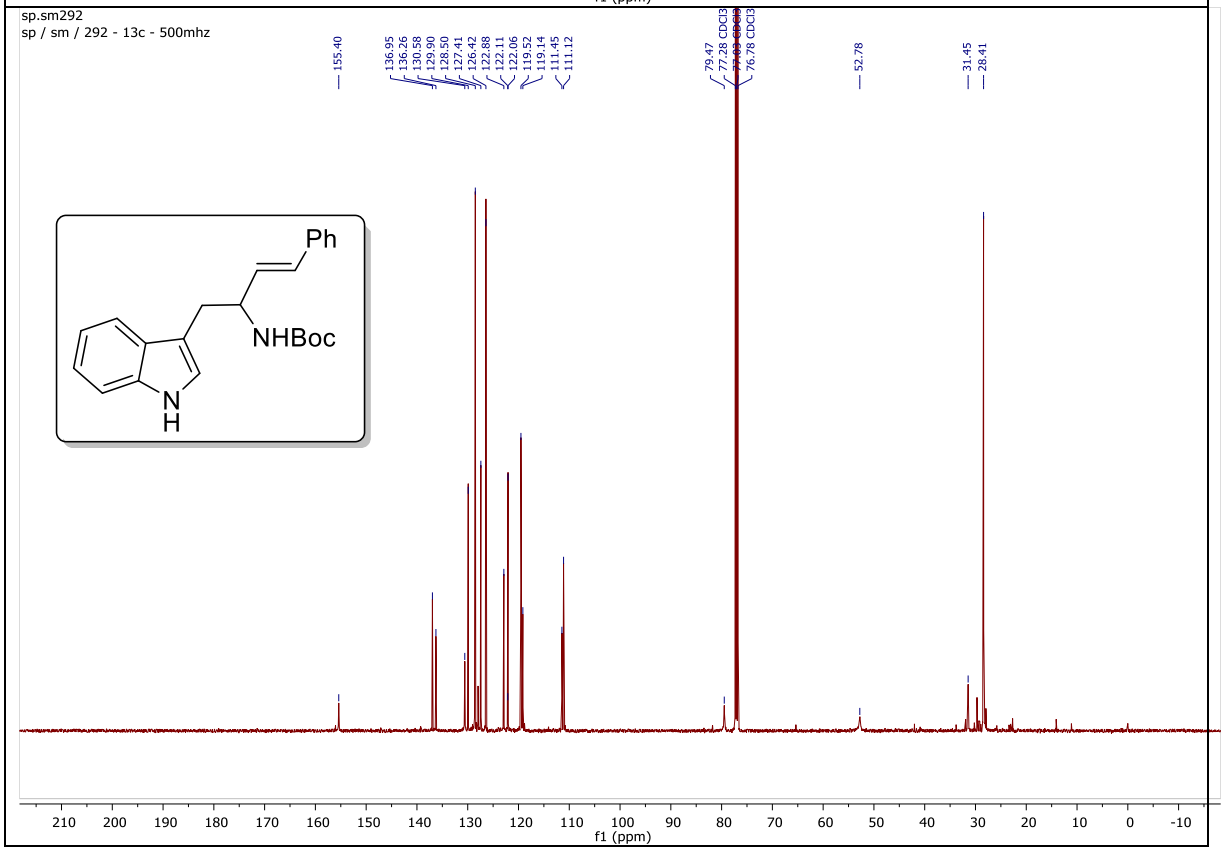

sp.sm400r
sp.sm400r -1h
7.39
7.28
7.26
7.24
7.20
6.60
6.56
6.24
6.23
6.22
6.22
6.20
6.20
6.18
6.18
4.50
4.48
4.47
4.45
4.00
3.98
3.96
3.95
3.95
3.87
3.85
3.83
3.82
3.81
2.15
2.09
2.01
1.91
1.76
1.67
O
Ph
2.01
2.06
1.06
1.06
1.00
0.06
1.00
1.02
1.00
1.02
2.04
1.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

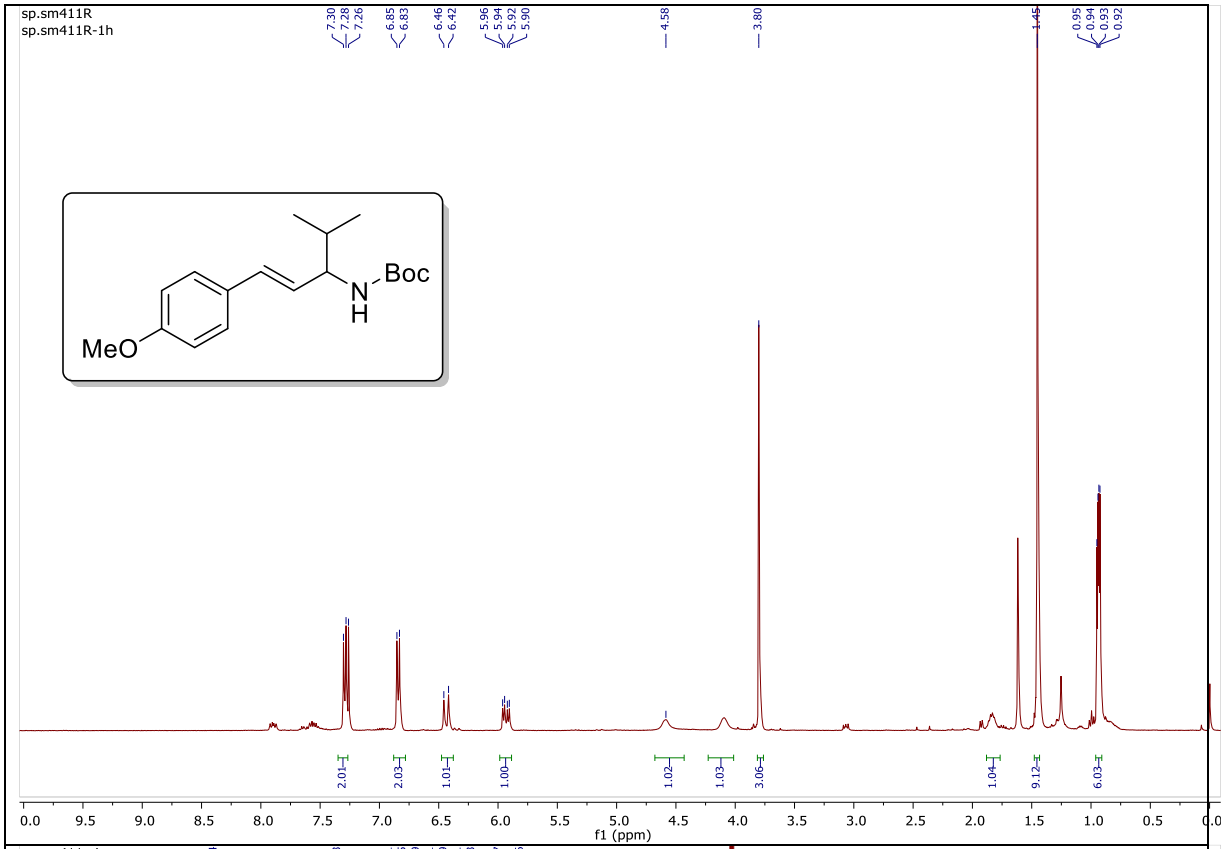

sp.sm400r
sp / sm / 400r - 13c - 500mhz
136.92
130.58
130.42
128.49
127.47
126.46
79.64
68.15
32.39
25.90
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

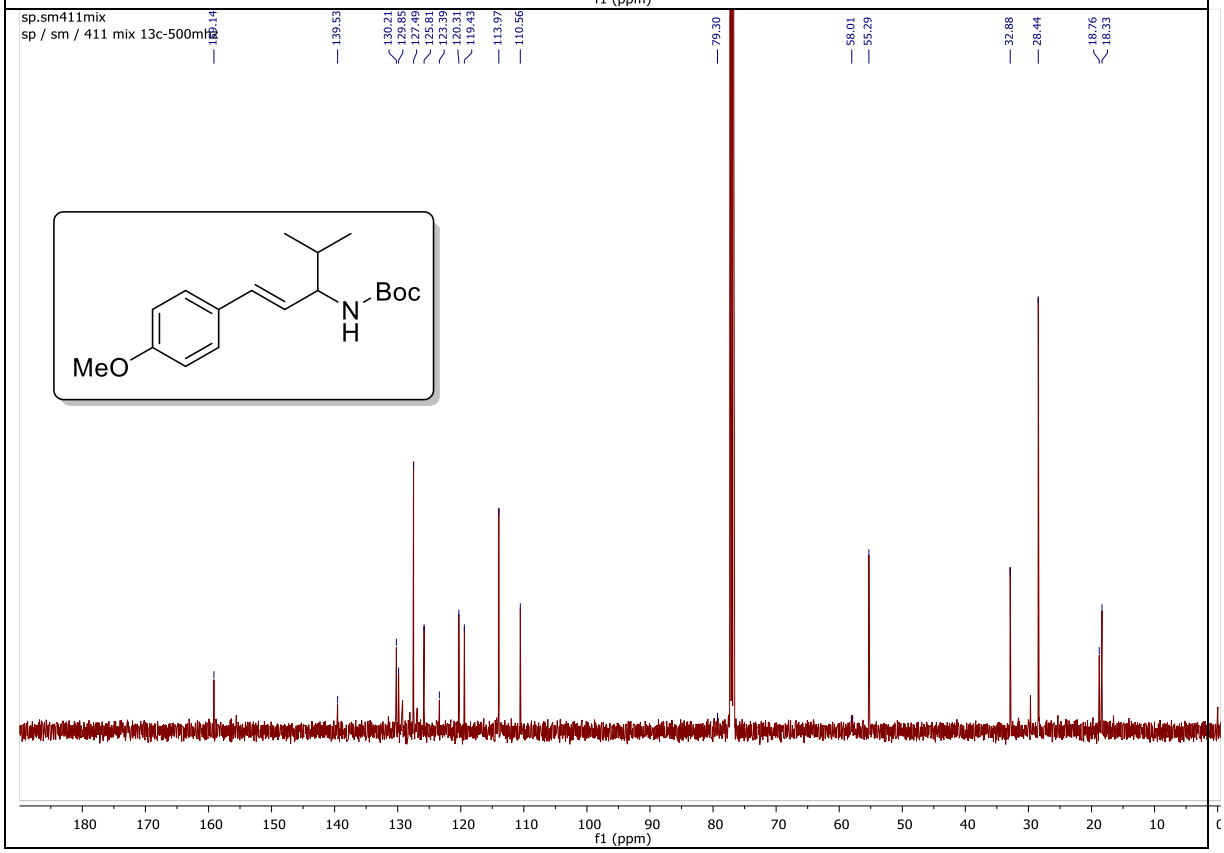

sp.sm293p
sp / sm / 293p -1h
7.38
7.36
7.33
7.31
7.29
7.26
7.24
6.62
6.58
6.17
6.16
6.13
6.12
4.96
4.42
3.78
3.74
3.73
2.24
1.46
HO
HN
Ph
Boc
5.19
1.01
1.00
1.01
1.01
2.04
1.03
9.41
f1 (ppm)

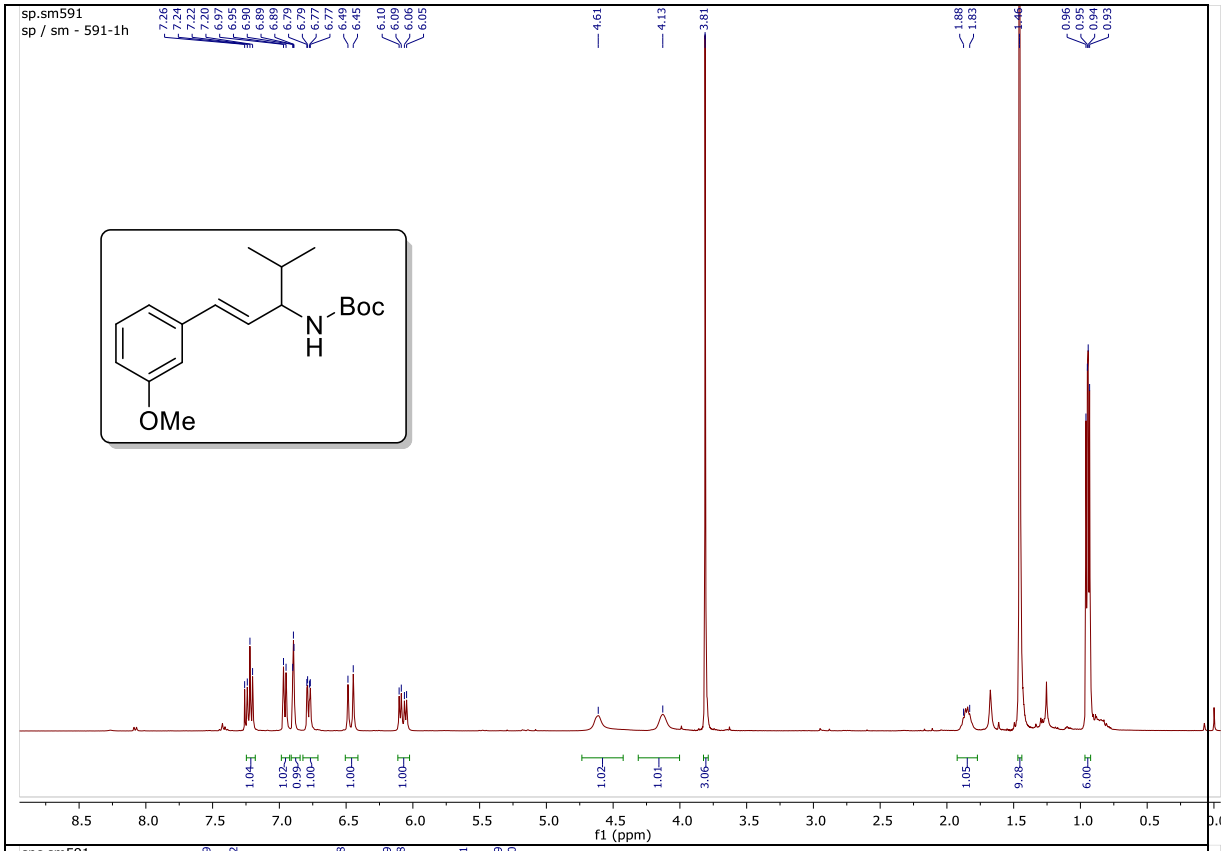

sp.sm293r
sp.sm293r-13c-500mhz
155.97
136.41
132.04
128.61
127.87
126.65
126.49
80.00
65.70
54.64
28.40
HO
HN
Ph
Boc
f1 (ppm)

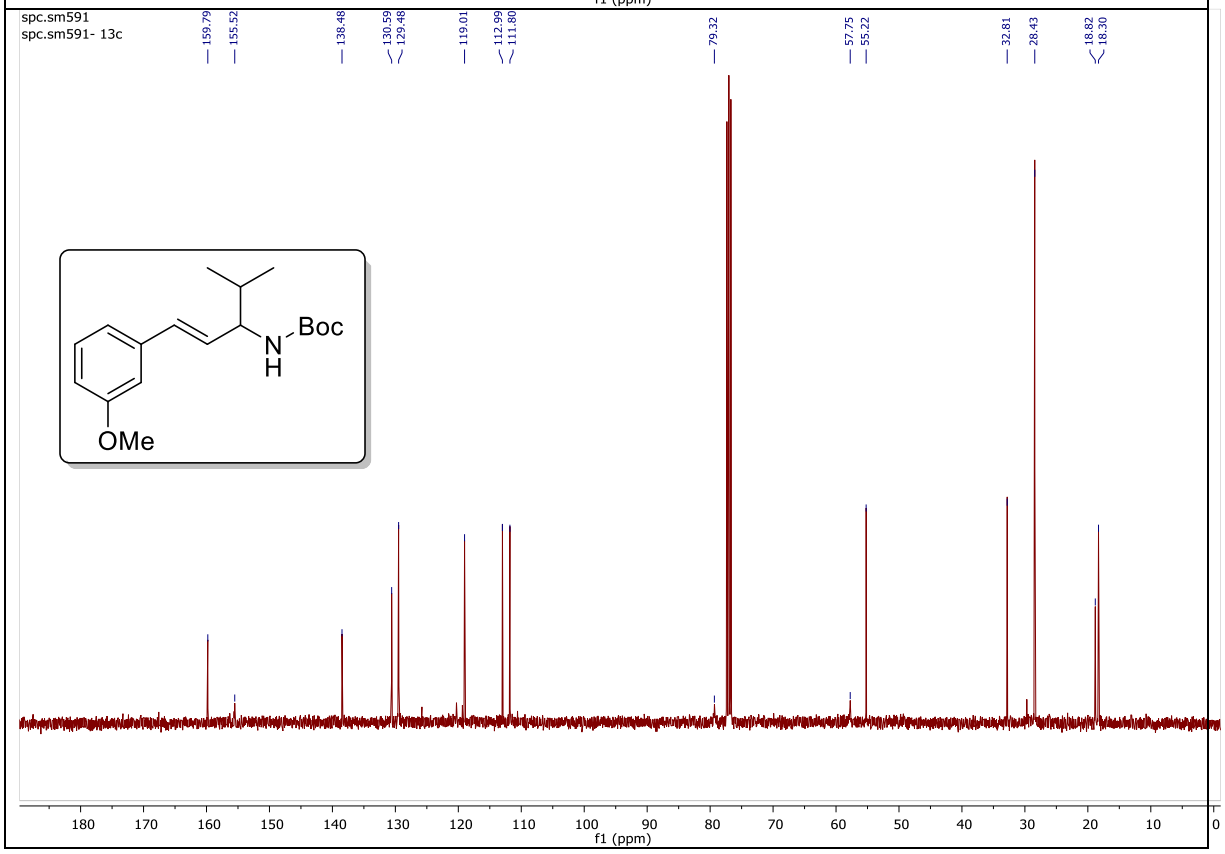

sp.sm292
sp / sm / 292 -1h
8.17
7.65
7.63
7.37
7.35
7.30
7.29
7.26
7.23
7.22
7.20
7.19
7.15
7.13
7.11
7.03
6.52
6.48
6.22
6.21
6.18
6.17
4.70
3.10
1.43
Ph
NHBoc
N
H
1.00
1.02
1.01
4.01
2.03
1.01
1.01
1.01
1.00
2.00
2.00
9.10
f1 (ppm)

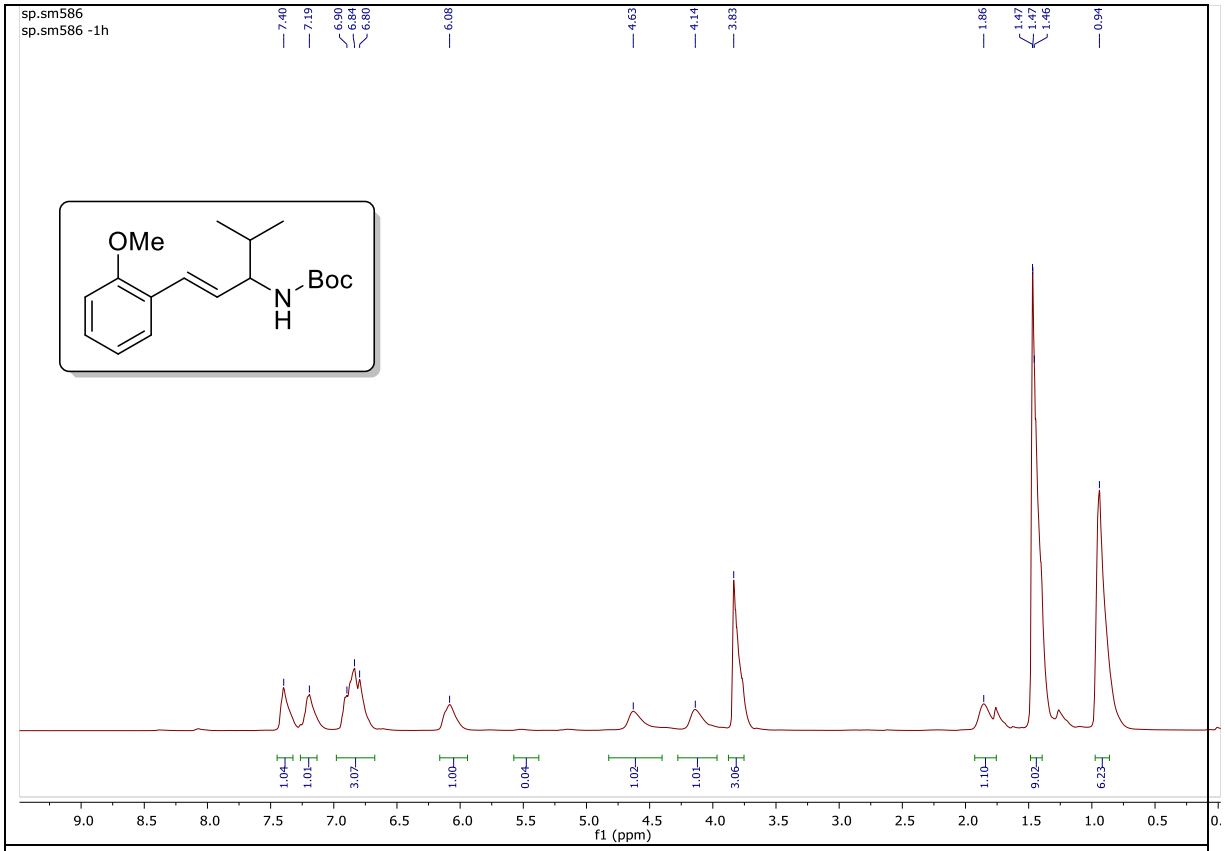

sp.sm292
sp / sm / 292 - 13c - 500mhz
155.40
136.95
136.26
130.58
129.90
128.50
127.41
126.42
122.88
122.11
122.06
119.52
119.14
111.45
111.12
79.47
77.28 CDCl3
76.78 CDCl3
52.78
31.45
28.41
Ph
NHBoc
N
H
f1 (ppm)

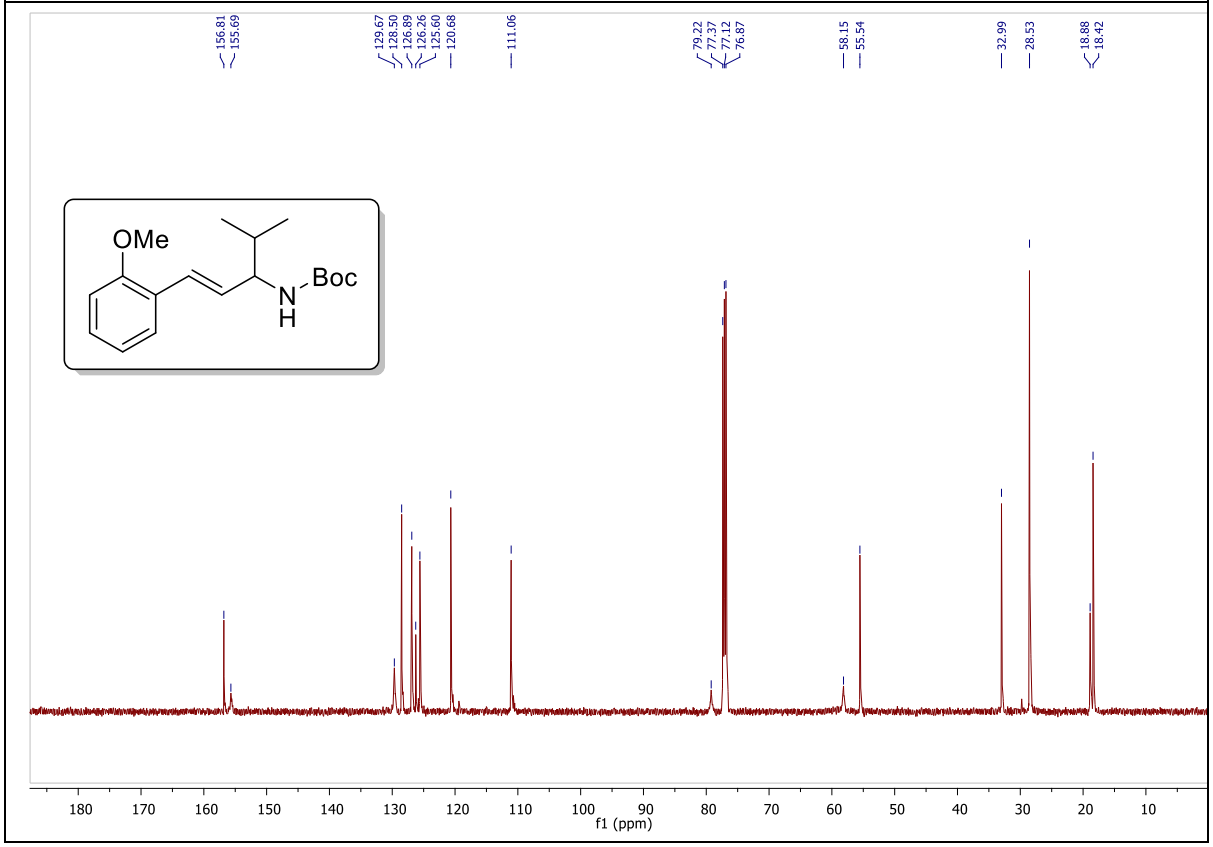

sp.sm411R
sp.sm411R-1h
Boc
N
H
MeO
f1 (ppm)

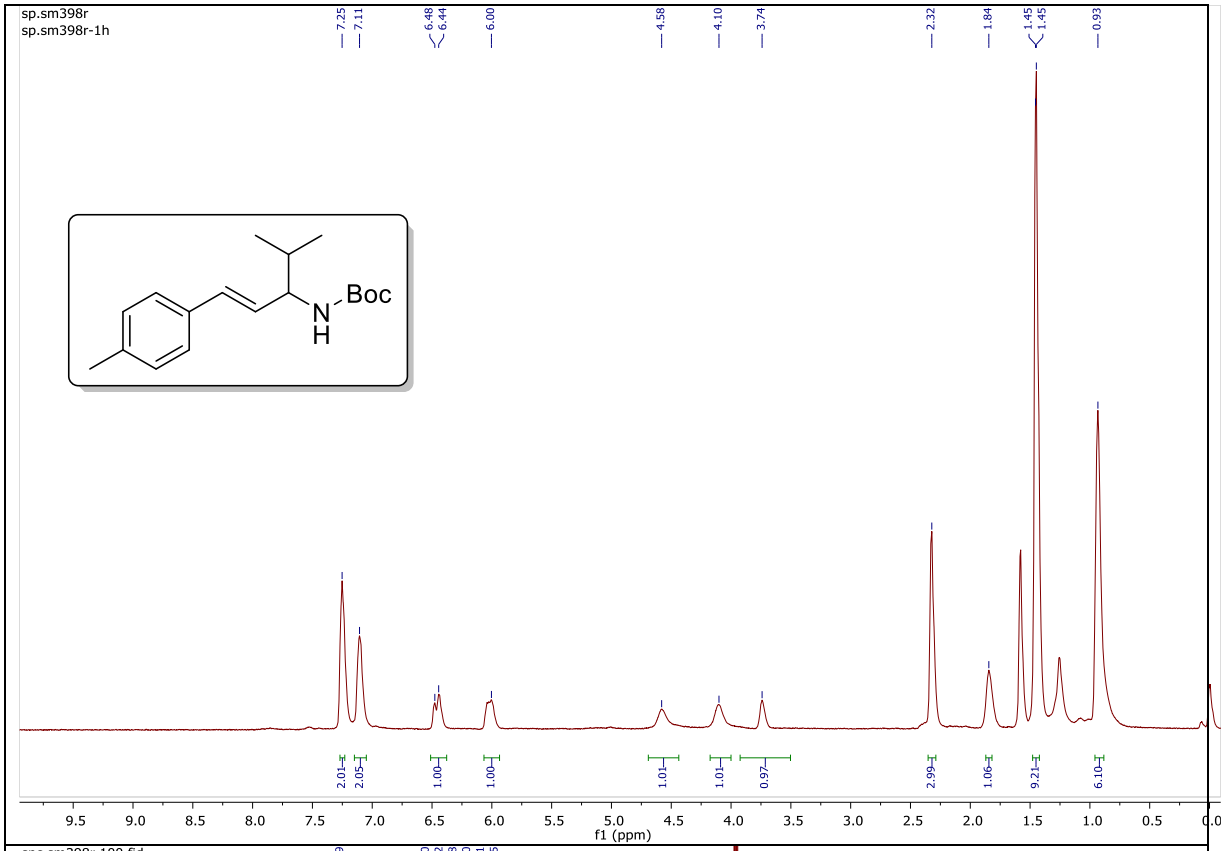

sp.sm411mix
sp / sm / 411 mix 13c-500mhz
Boc
N
H
MeO
f1 (ppm)

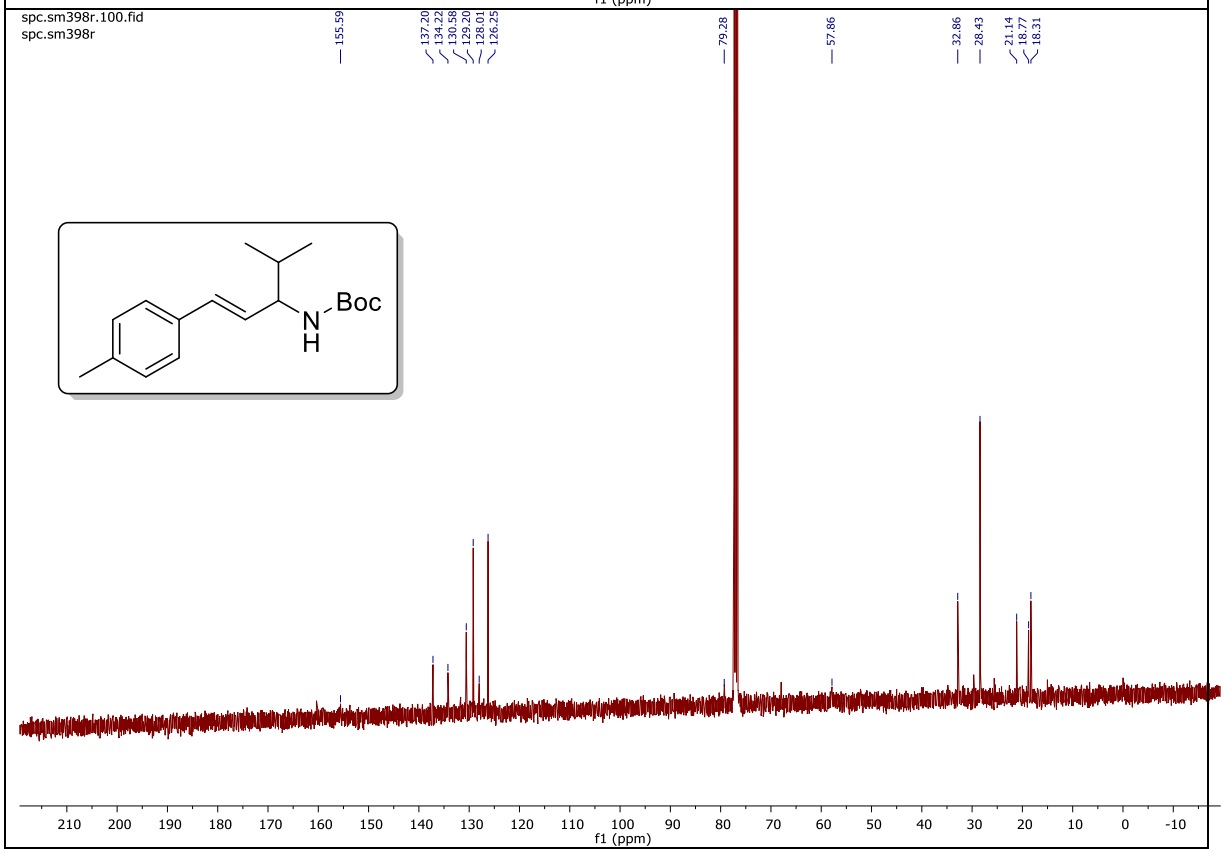

sp.sm591
sp / sm - 591-1h
7.26
7.24
7.22
7.20
6.97
6.95
6.90
6.89
6.79
6.77
6.77
6.49
6.45
6.10
6.09
6.06
6.05
4.61
4.13
3.81
1.88
1.83
1.46
0.96
0.95
0.94
0.93
Boc
N
H
OMe
1.04
1.02
0.99
1.00
1.00
1.00
1.02
1.01
3.06
1.05
9.28
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

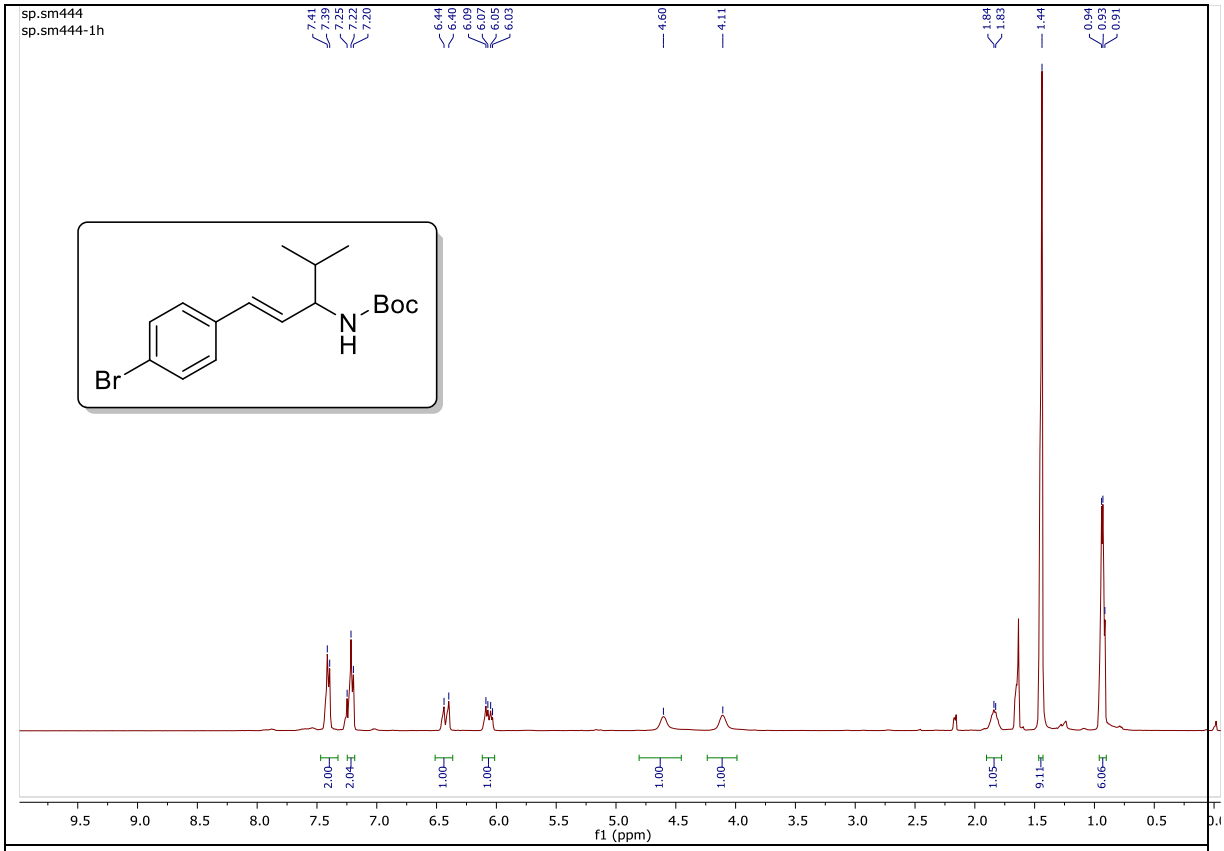

spc.sm591
spc.sm591- 13c
159.79
155.52
138.48
130.59
129.48
119.01
112.99
111.80
79.32
57.75
55.22
32.81
28.43
18.82
18.30
Boc
N
H
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

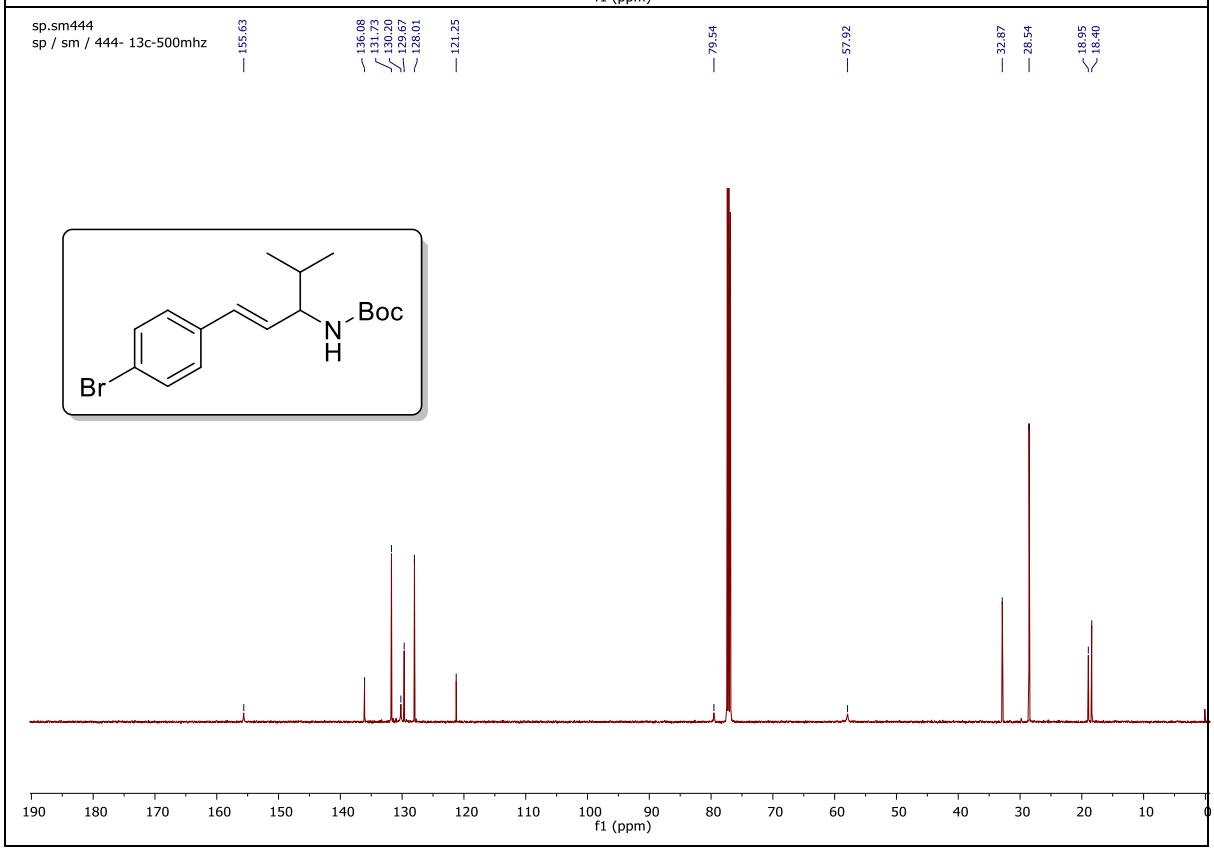

sp.sm586
sp.sm586 -1h
7.40
7.19
6.90
6.84
6.80
6.08
4.63
4.14
3.83
1.86
1.47
1.47
1.46
0.94
OMe
Boc
N
H
1.04
1.01
3.07
1.00
0.04
1.02
1.01
3.06
1.10
9.02
6.23
f1 (ppm)

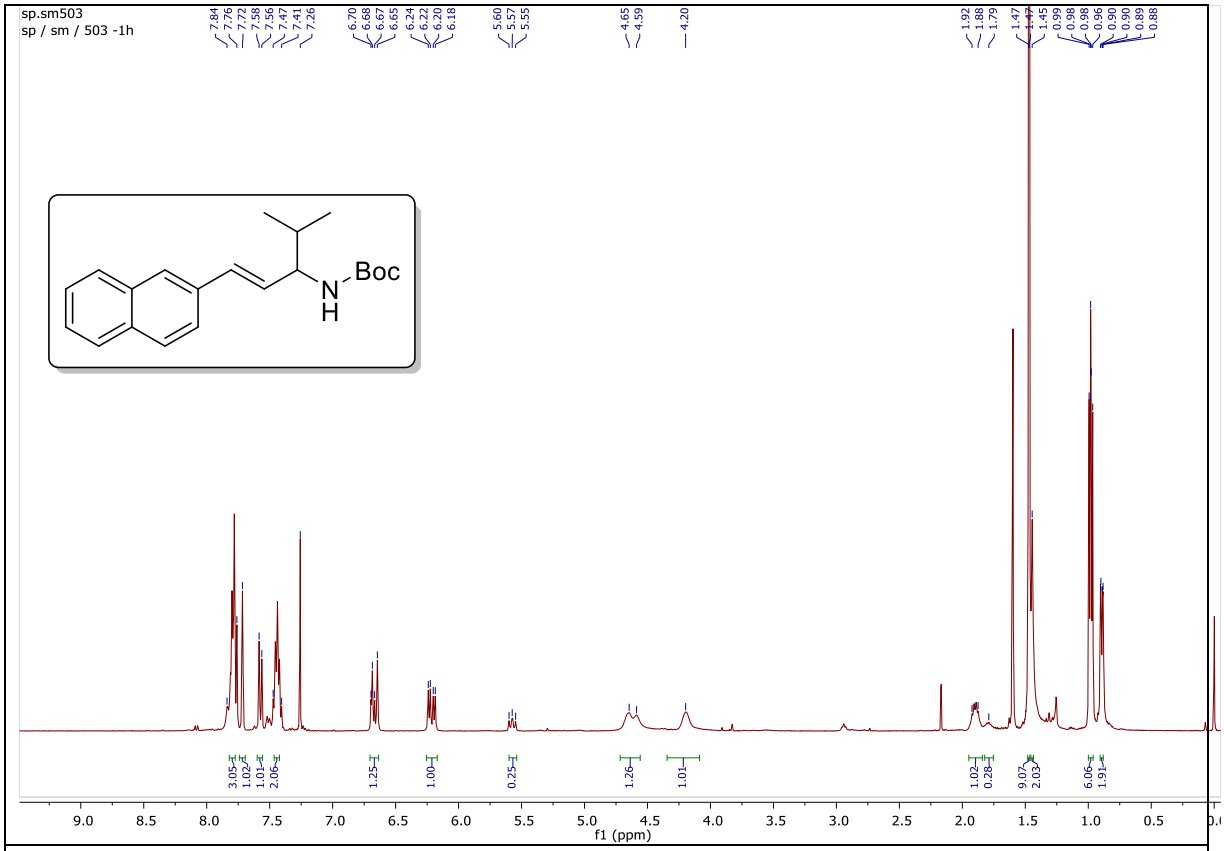

156.81
155.69
129.67
128.50
126.89
126.26
125.60
120.68
111.06
79.22
77.37
77.12
76.87
58.15
55.54
32.99
28.53
18.88
18.42
OMe
Boc
N
H
f1 (ppm)

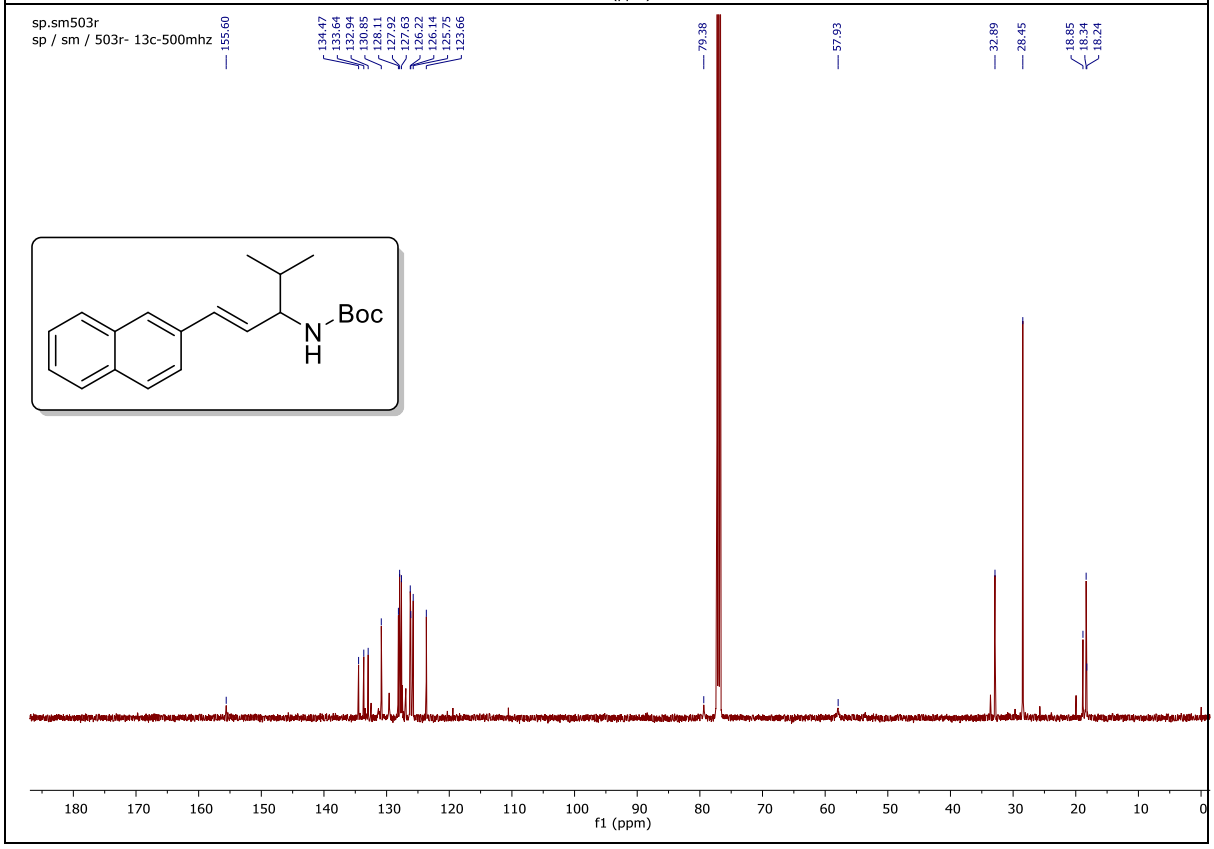

sp.sm398r
sp.sm398r-1h
7.25
7.11
6.48
6.44
6.00
4.58
4.10
3.74
2.32
1.84
1.45
1.45
0.93
Boc
N
H
2.01
2.05
1.00
1.00
1.01
1.01
0.97
2.99
1.06
9.21
6.10
f1 (ppm)

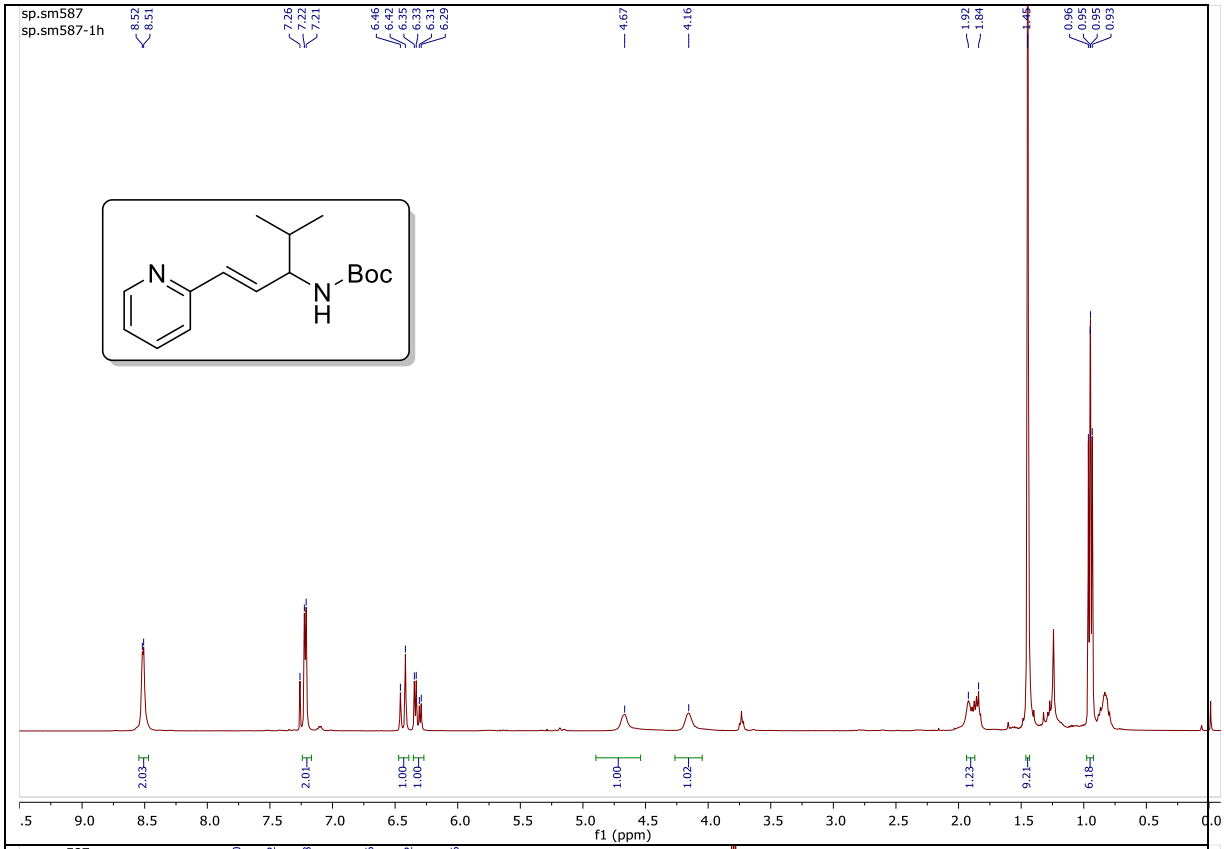

spc.sm398r.100.fid
spc.sm398r
155.59
137.20
134.22
130.58
129.20
128.01
126.25
79.28
57.86
32.86
28.43
21.14
18.77
18.31
Boc
N
H
f1 (ppm)

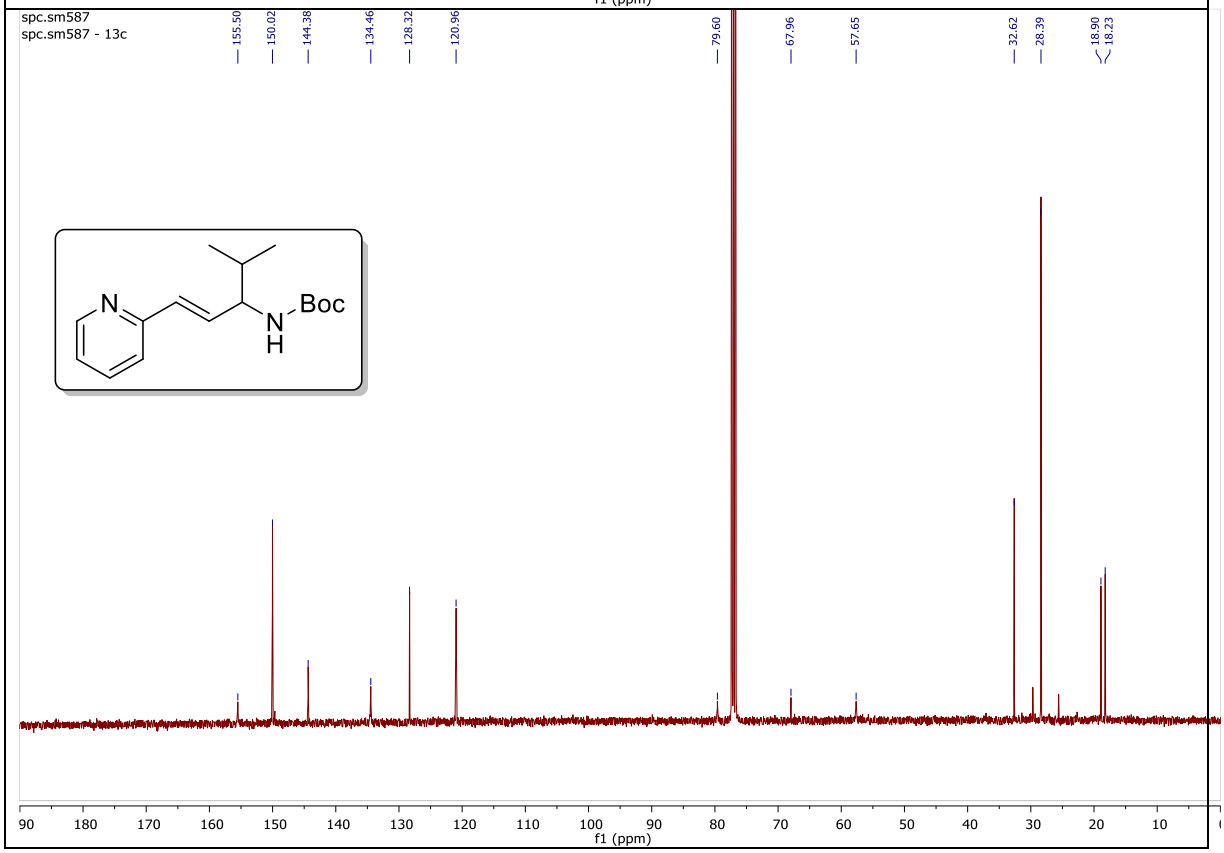

sp.sm444
sp.sm444-1h
7.41
7.39
7.25
7.22
7.20
6.44
6.40
6.09
6.07
6.05
6.03
4.60
4.11
1.84
1.83
1.44
0.94
0.93
0.91
Boc
N
H
Br
2.00
2.04
1.00
1.00
1.00
1.00
1.05
9.11
6.06
f1 (ppm)

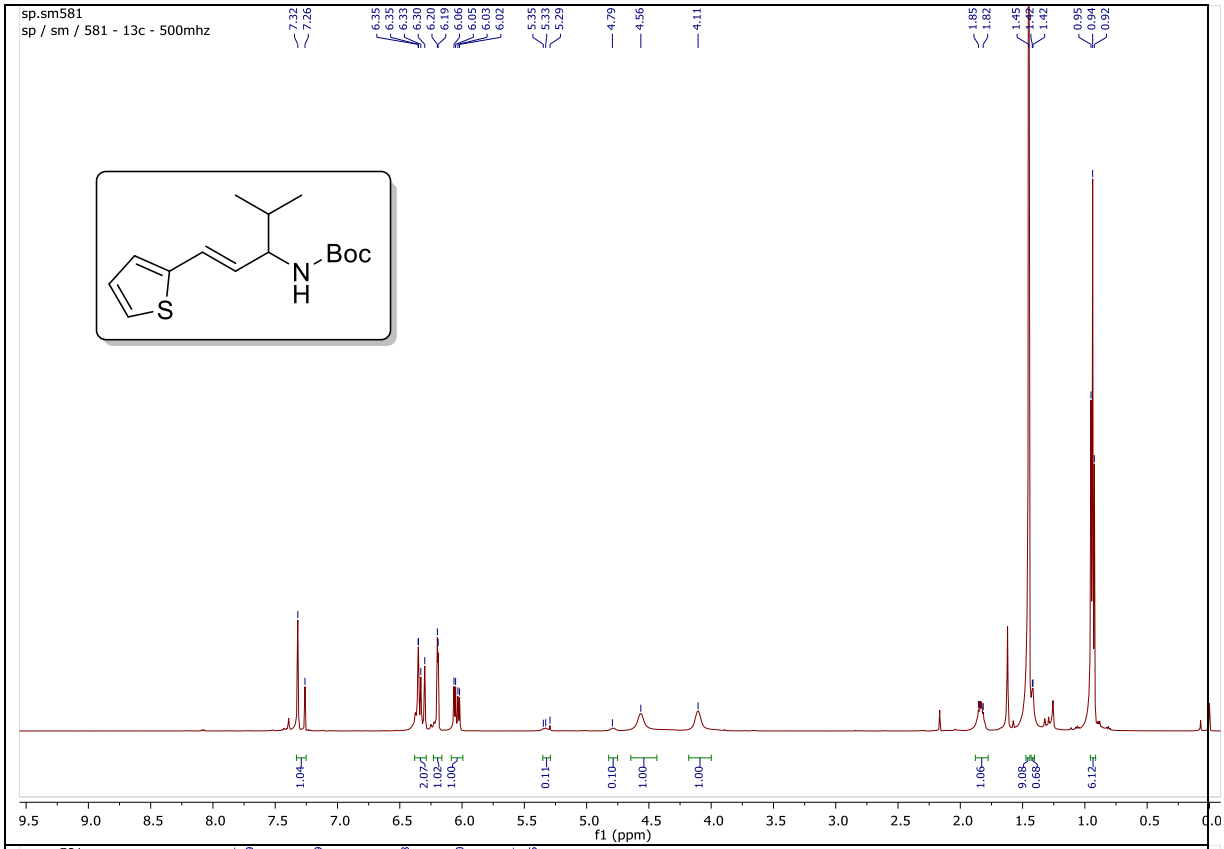

sp.sm444
sp / sm / 444- 13c-500mhz
155.63
136.08
131.73
130.20
129.67
128.01
121.25
79.54
57.92
32.87
28.54
18.95
18.40
Boc
N
H
Br
f1 (ppm)

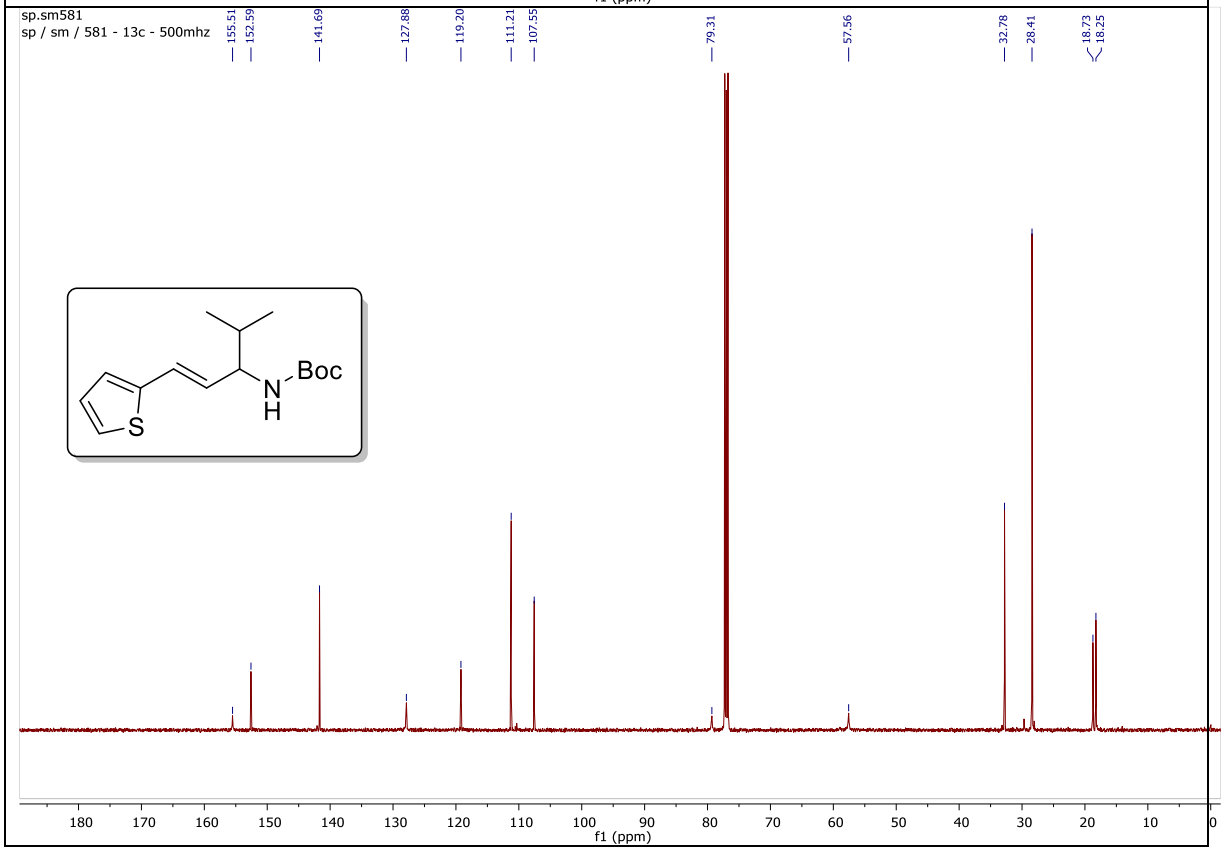

sp.sm503
sp / sm / 503 -1h
Boc
N
H
f1 (ppm)

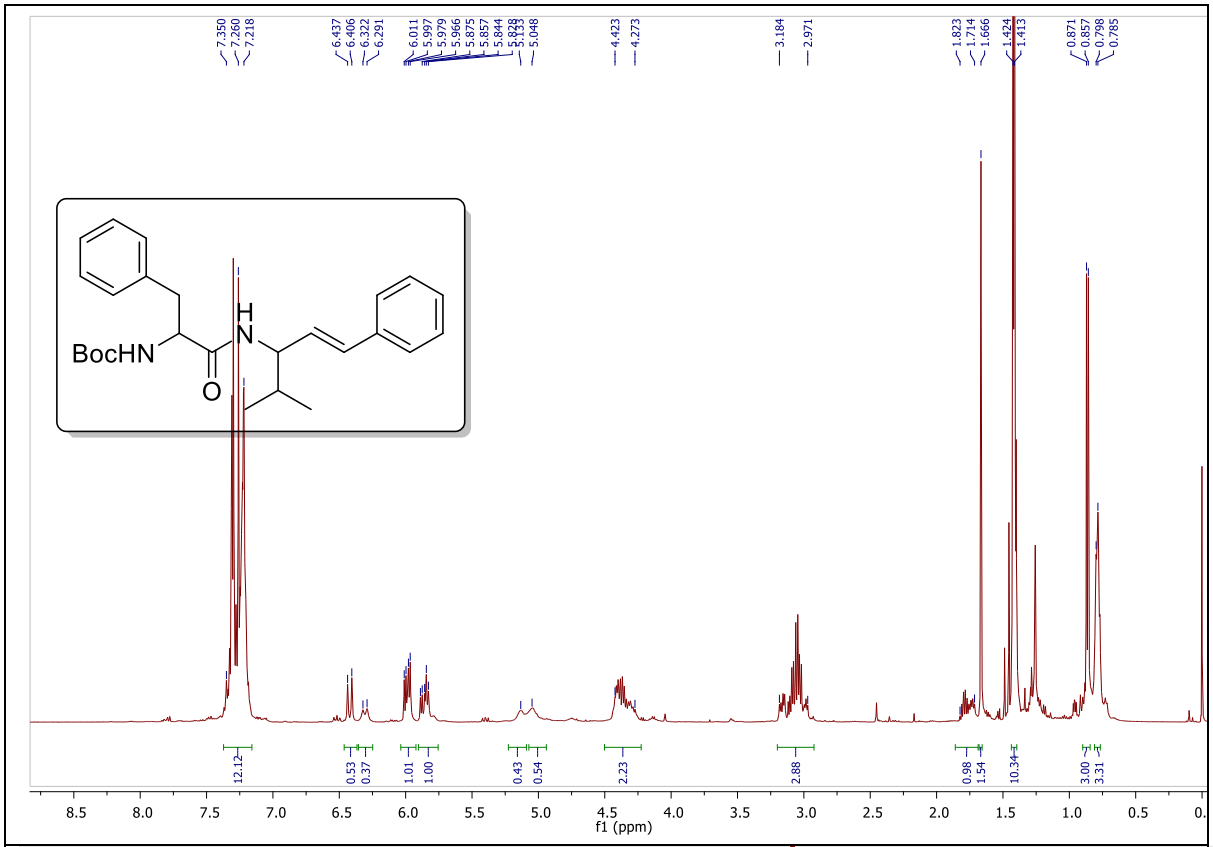

sp.sm503r
sp / sm / 503r- 13c-500mhz
Boc
N
H
f1 (ppm)

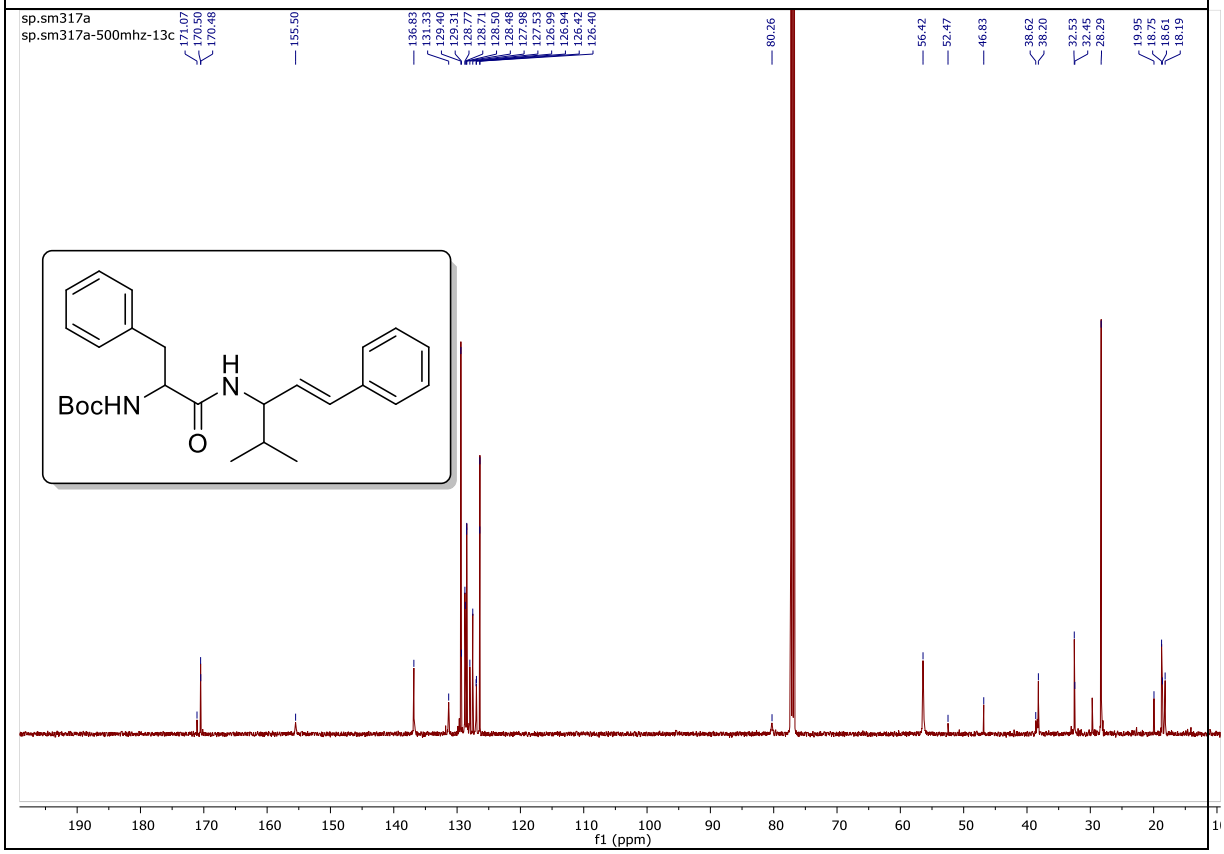

sp.sm587
sp.sm587-1h
8.52
8.51
7.26
7.22
7.21
6.46
6.42
6.35
6.33
6.31
6.29
4.67
4.16
1.92
1.84
1.45
0.96
0.95
0.95
0.93
N
N
H
Boc
2.03
2.01
1.00
1.00
1.00
1.02
1.23
9.21
6.18
f1 (ppm)

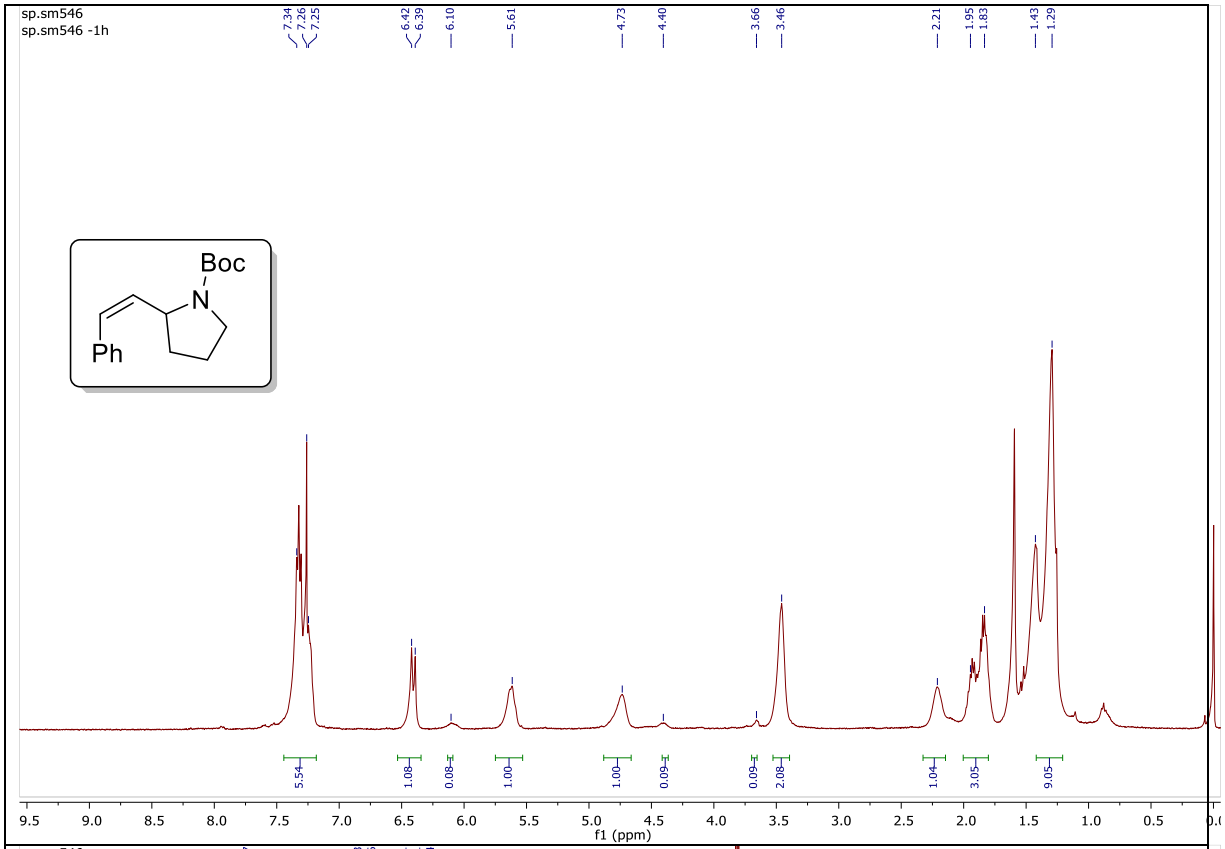

spc.sm587
spc.sm587 - 13c
155.50
150.02
144.38
134.46
128.32
120.96
79.60
67.96
57.65
32.62
28.39
18.90
18.23
N
N
H
Boc
f1 (ppm)

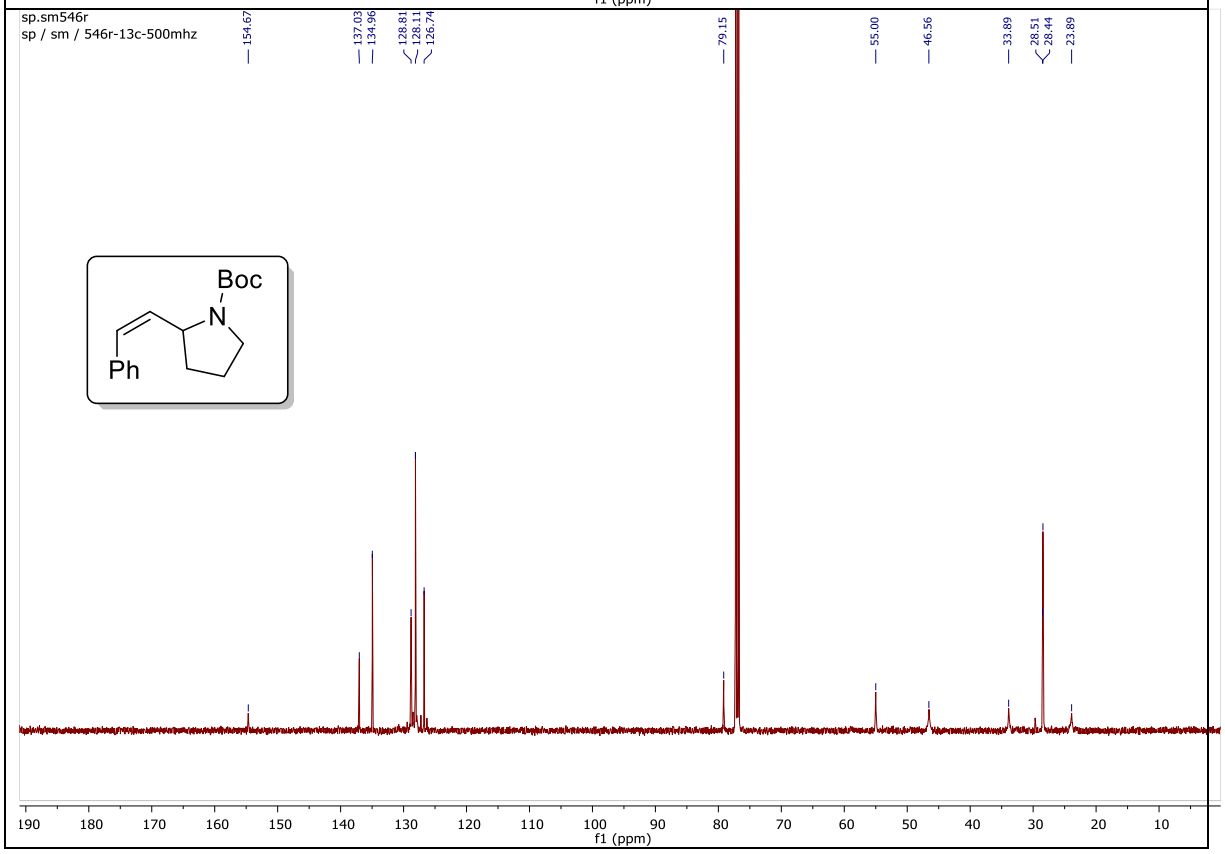

sp.sm581
sp / sm / 581 - 13c - 500mhz
Boc
N
H
S
f1 (ppm)

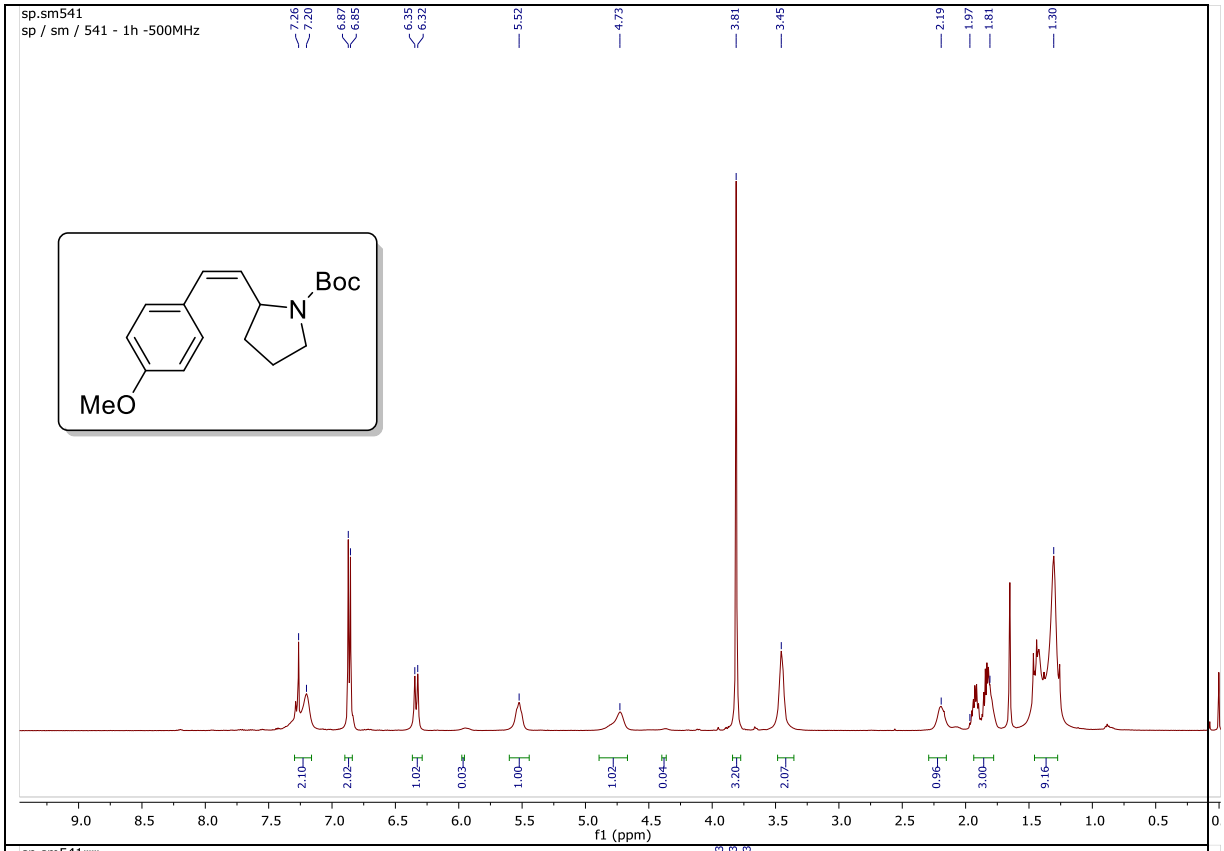

sp.sm581
sp / sm / 581 - 13c - 500mhz
Boc
N
H
S
f1 (ppm)

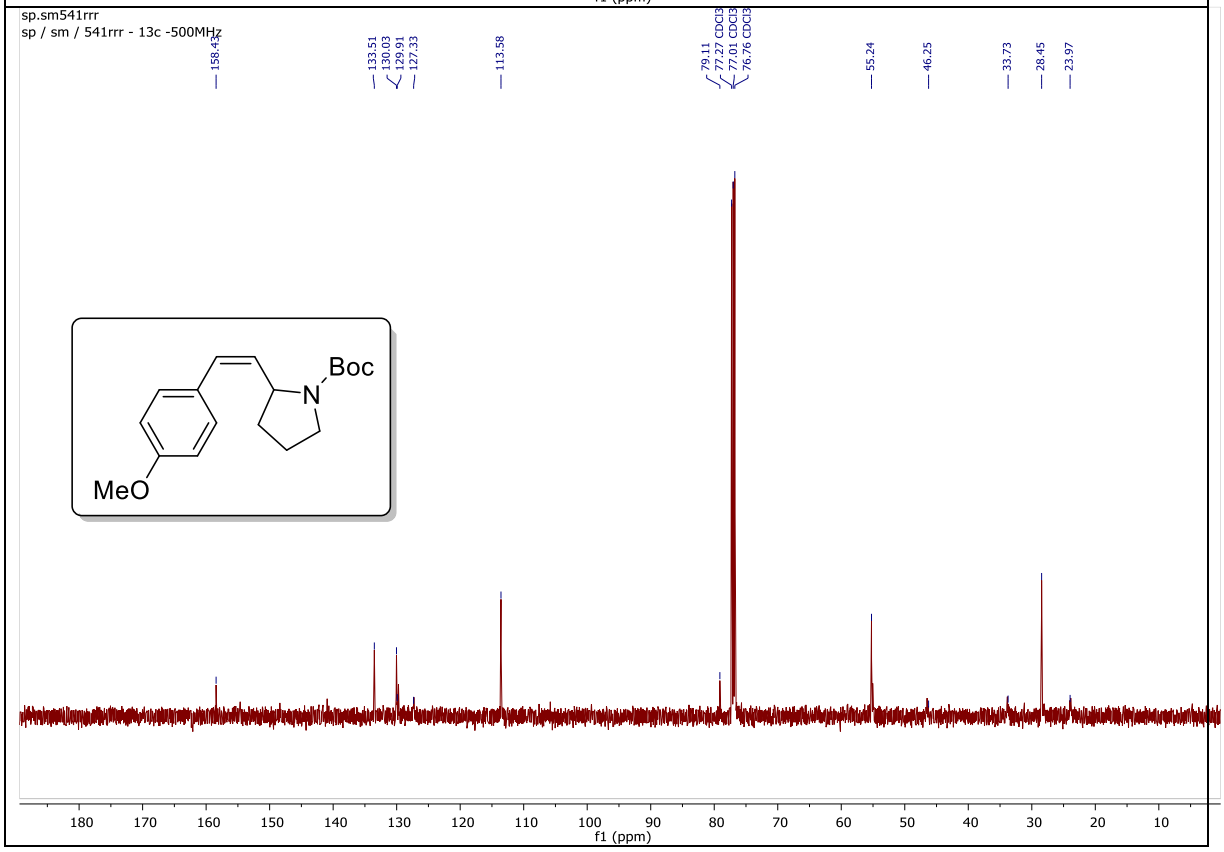

BocHN
H
N
O
f1 (ppm)

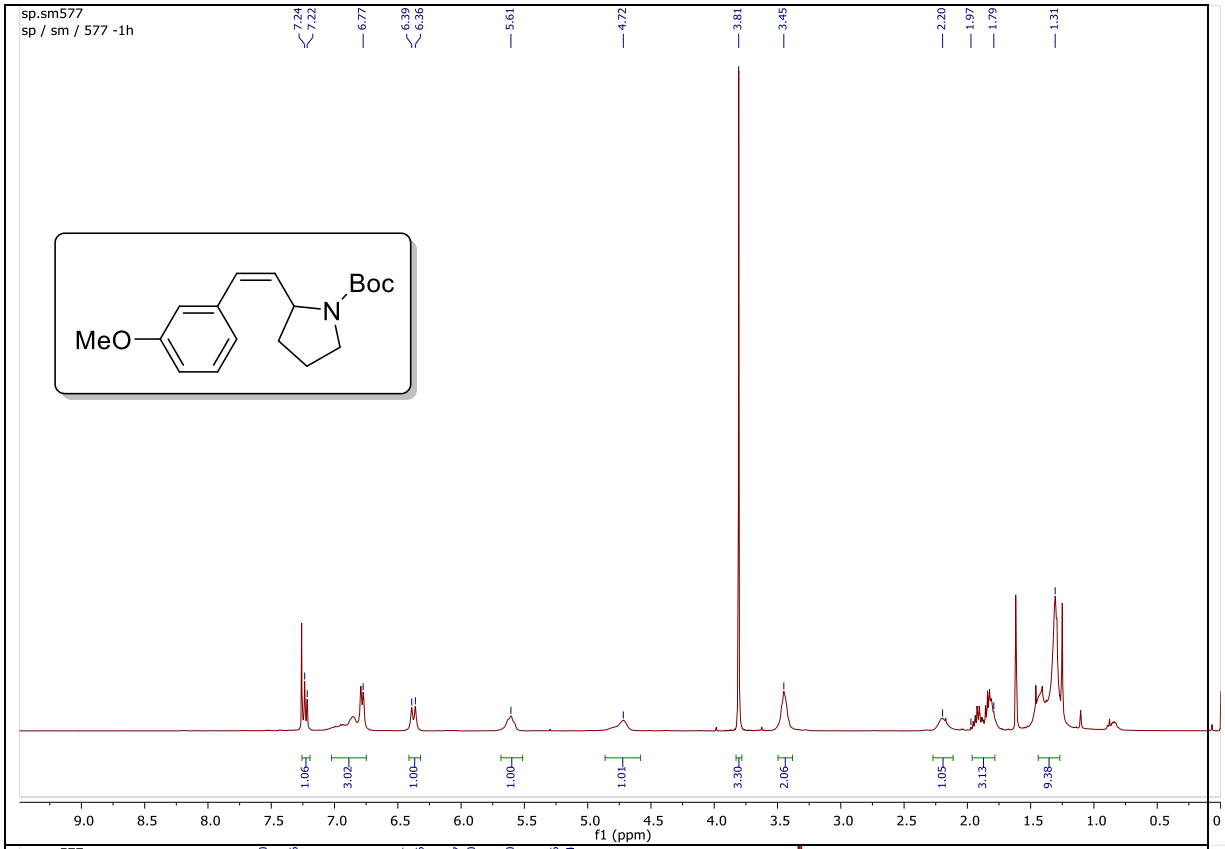

sp.sm317a
sp.sm317a-500mhz-13c
BocHN
H
N
O
f1 (ppm)

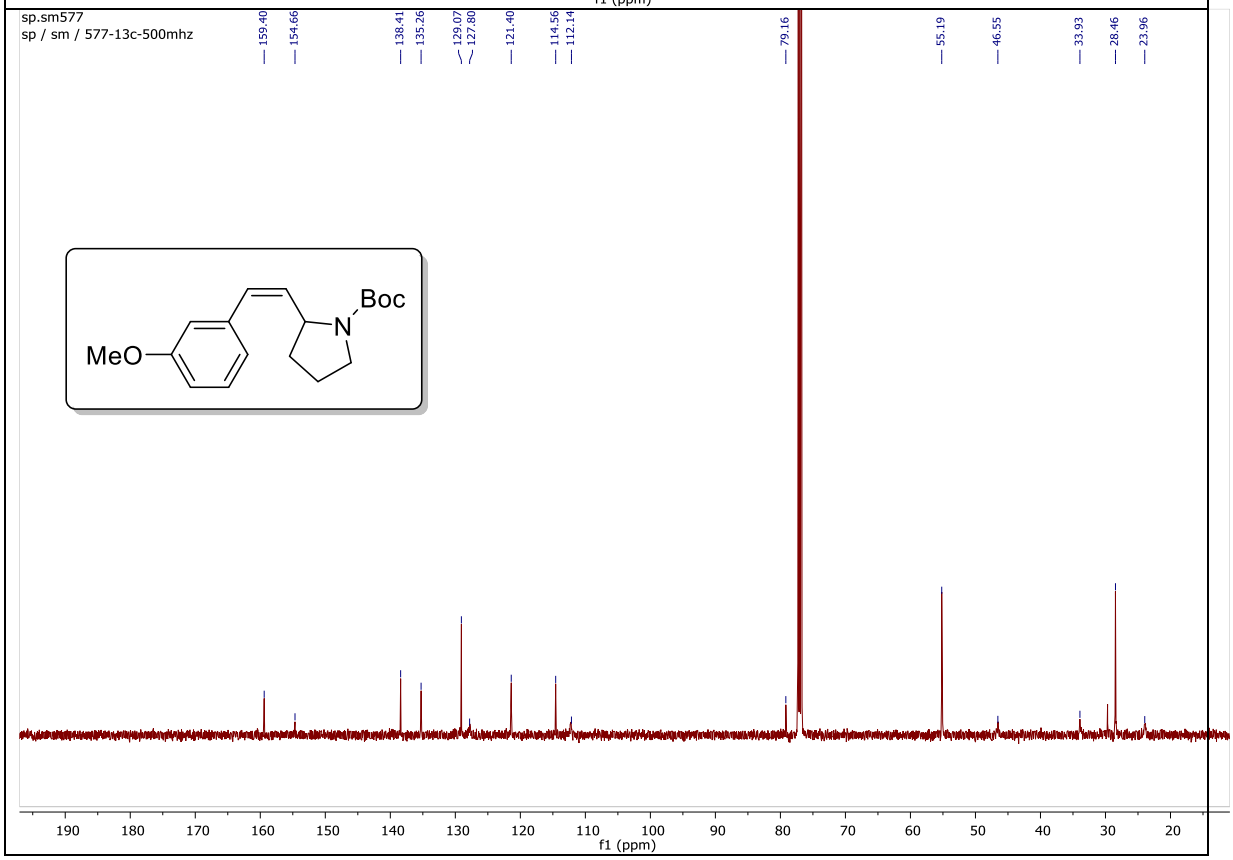

sp.sm546
sp.sm546 -1h
7.34
7.26
7.25
6.42
6.39
6.10
5.61
4.73
4.40
3.66
3.46
2.21
1.95
1.83
1.43
1.29
Boc
N
Ph
5.54
1.08
0.08
1.00
1.00
0.09
0.09
2.08
1.04
3.05
9.05
f1 (ppm)

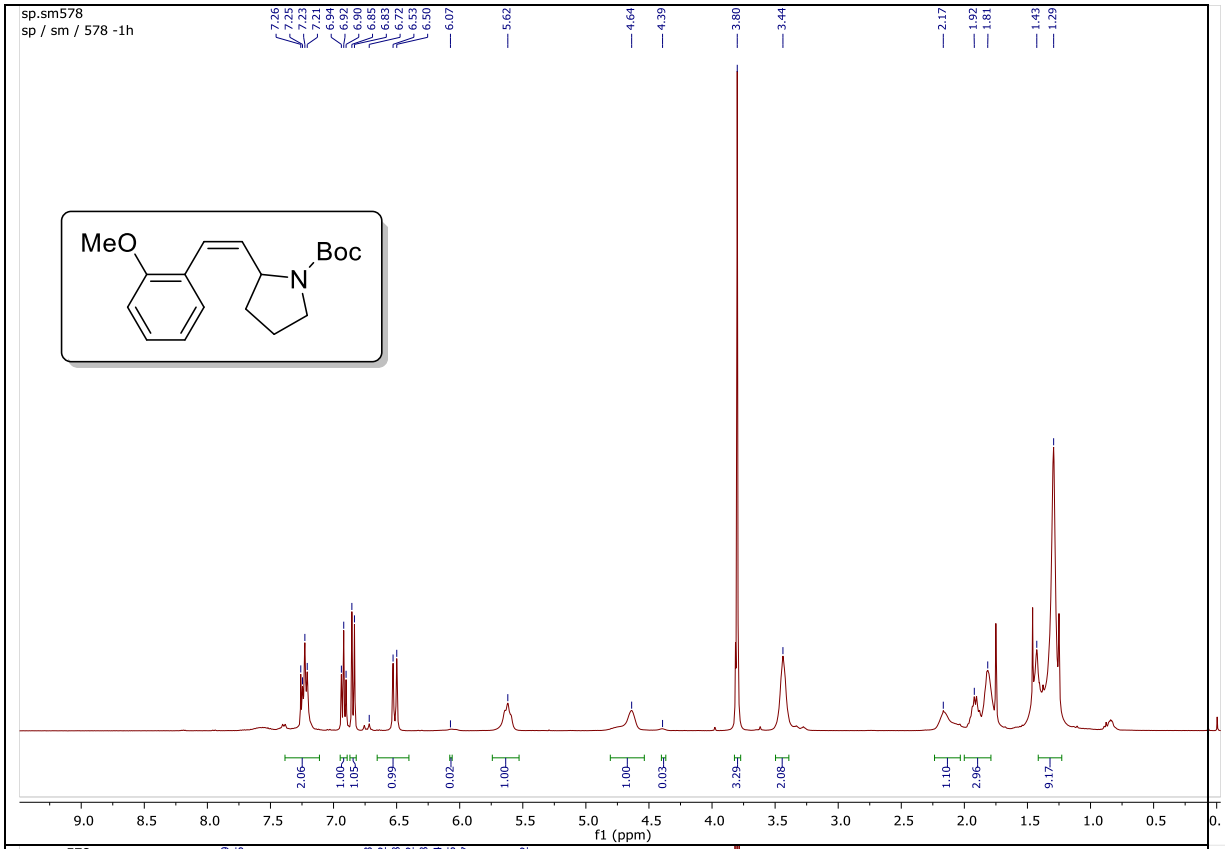

sp.sm546r
sp / sm / 546r-13c-500mhz
154.67
137.03
134.96
128.81
128.11
126.74
79.15
55.00
46.56
33.89
28.51
28.44
23.89
Boc
N
Ph
f1 (ppm)

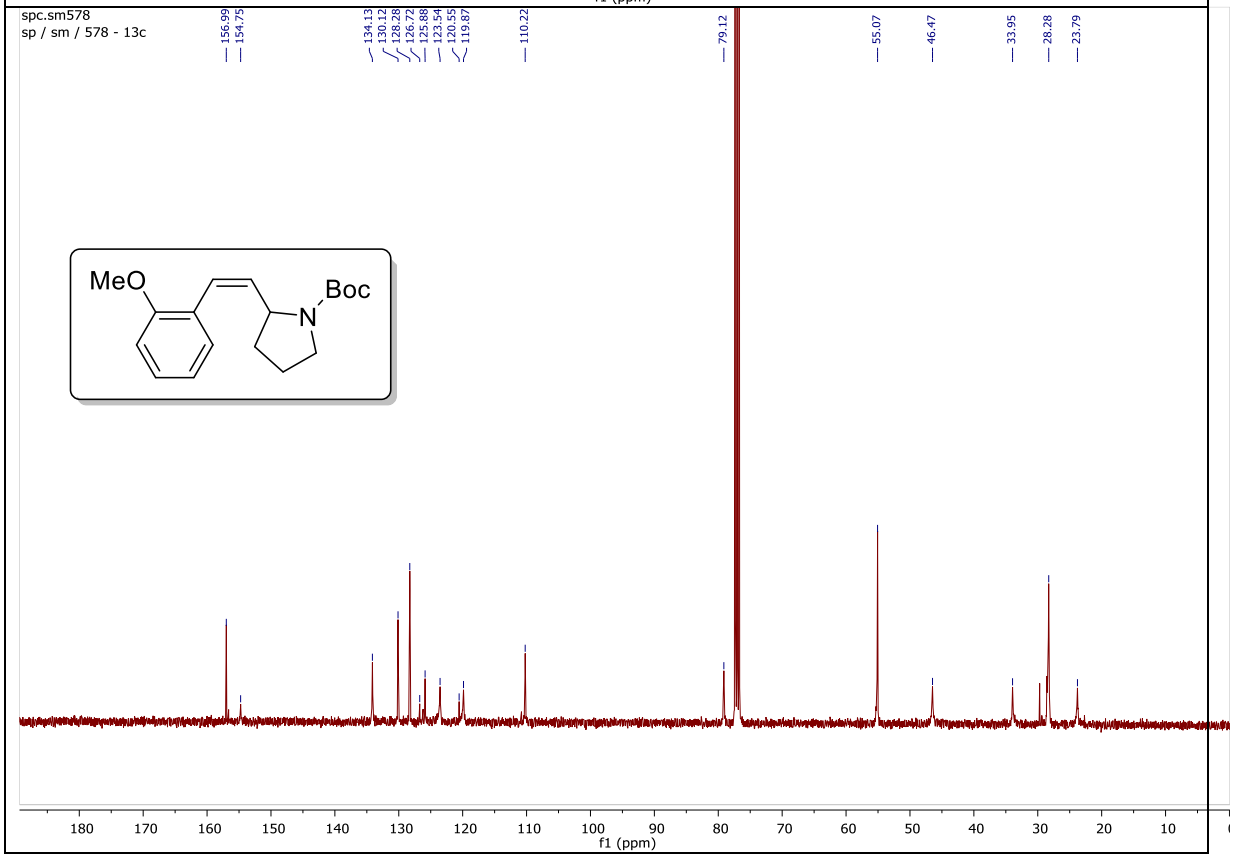

sp.sm541
sp / sm / 541 - 1h -500MHz
7.26
7.20
6.87
6.85
6.35
6.32
5.52
4.73
3.81
3.45
2.19
1.97
1.81
1.30
Boc
N
MeO
2.10
2.02
1.02
0.03
1.00
1.02
0.04
3.20
2.07
0.96
3.00
9.16
f1 (ppm)

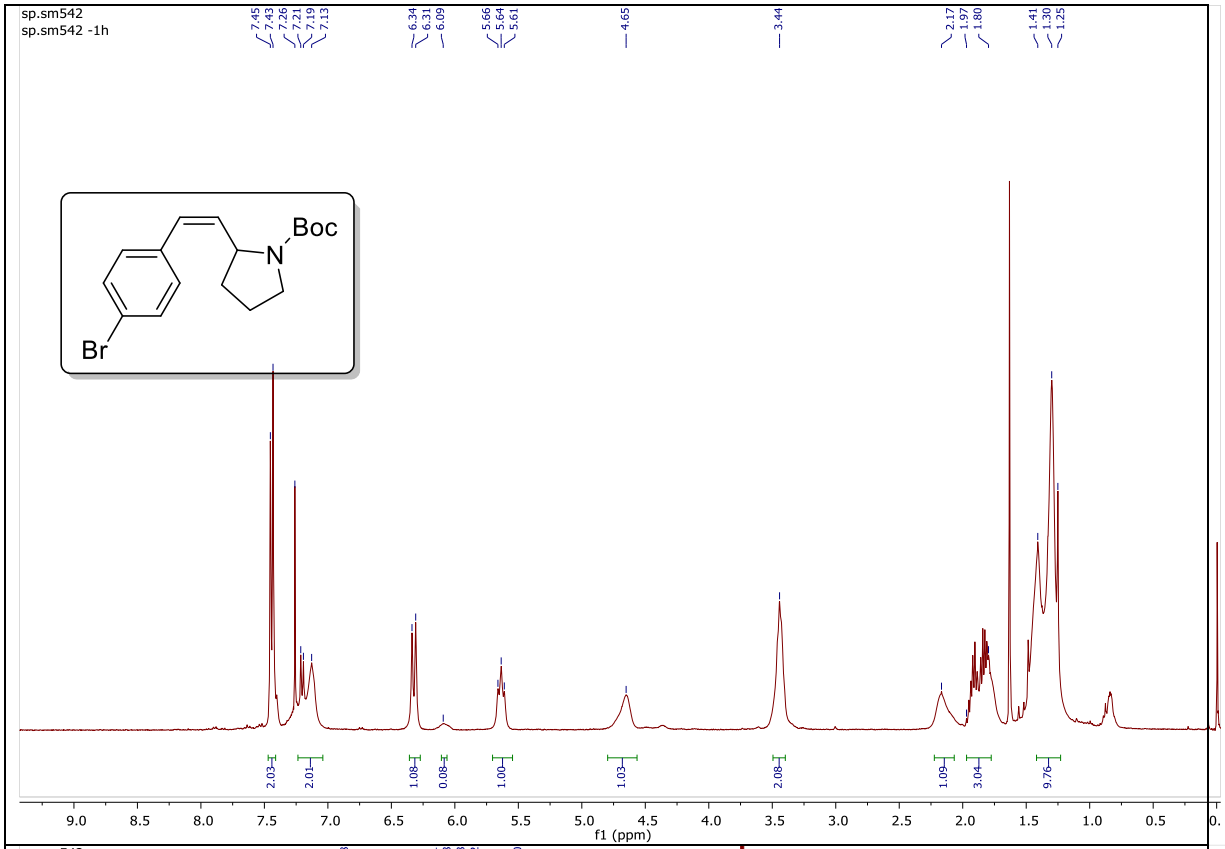

sp.sm541rrr
sp / sm / 541rrr - 13c -500MHz
158.43
133.51
130.03
120.91
127.33
113.58
79.11
77.27 CDCl3
77.01 CDCl3
76.76 CDCl3
55.24
46.25
33.73
28.45
23.97
Boc
N
MeO
f1 (ppm)

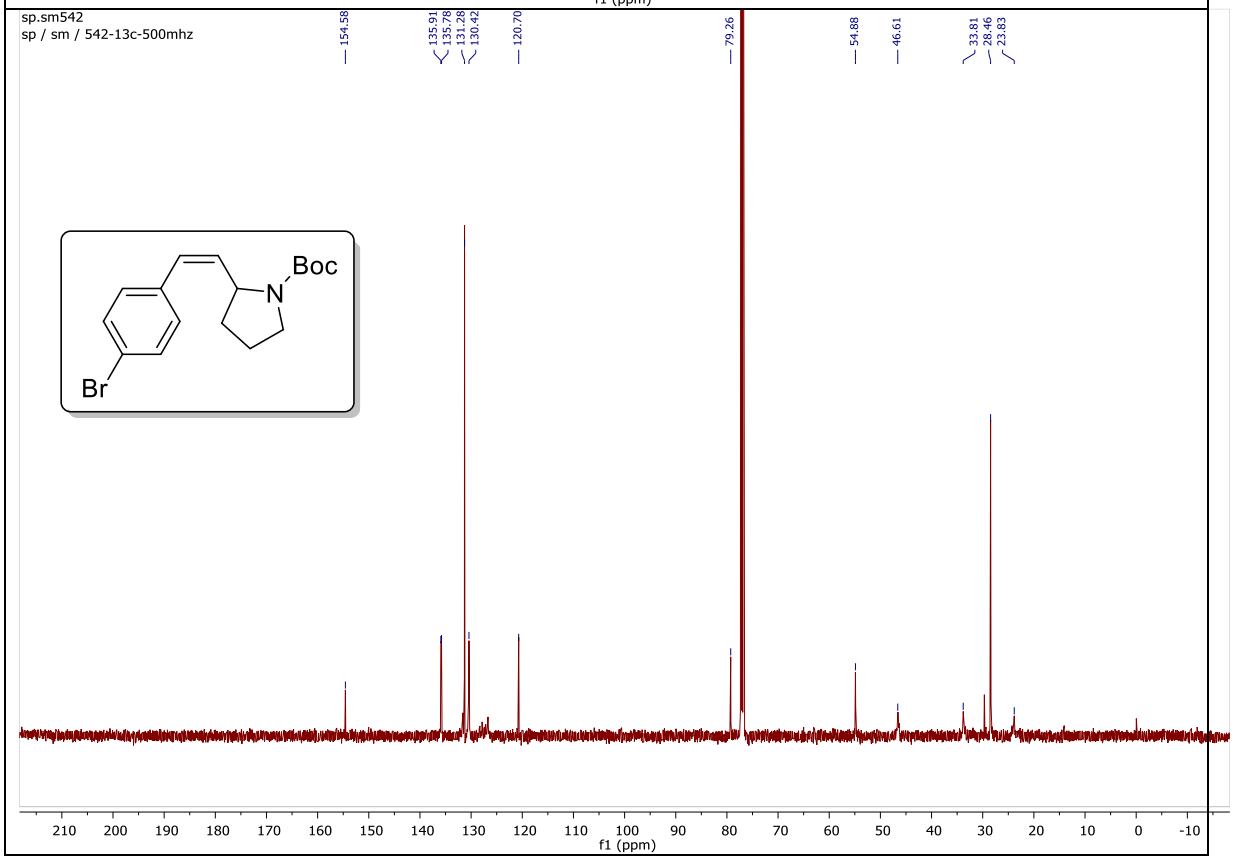

sp.sm577
sp / sm / 577 -1h
7.24
7.22
6.77
6.39
6.36
5.61
4.72
3.81
3.45
2.20
1.97
1.79
1.31
Boc
N
MeO
1.06
3.02
1.00
1.00
1.01
3.30
2.06
1.05
3.13
9.38
f1 (ppm)

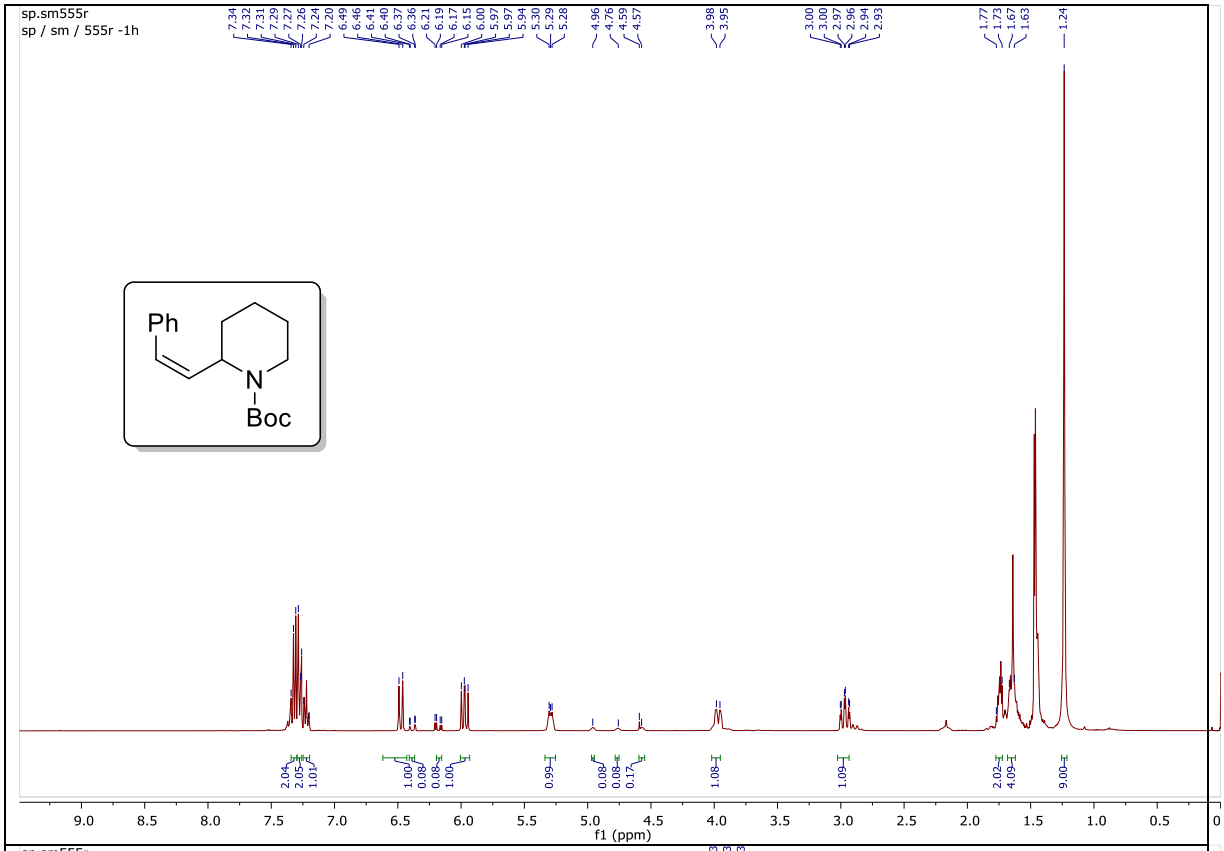

sp.sm577
sp / sm / 577-13c-500mhz
159.40
154.66
138.41
135.26
129.07
127.80
121.40
114.56
112.14
79.16
55.19
46.55
33.93
28.46
23.96
Boc
N
MeO
f1 (ppm)

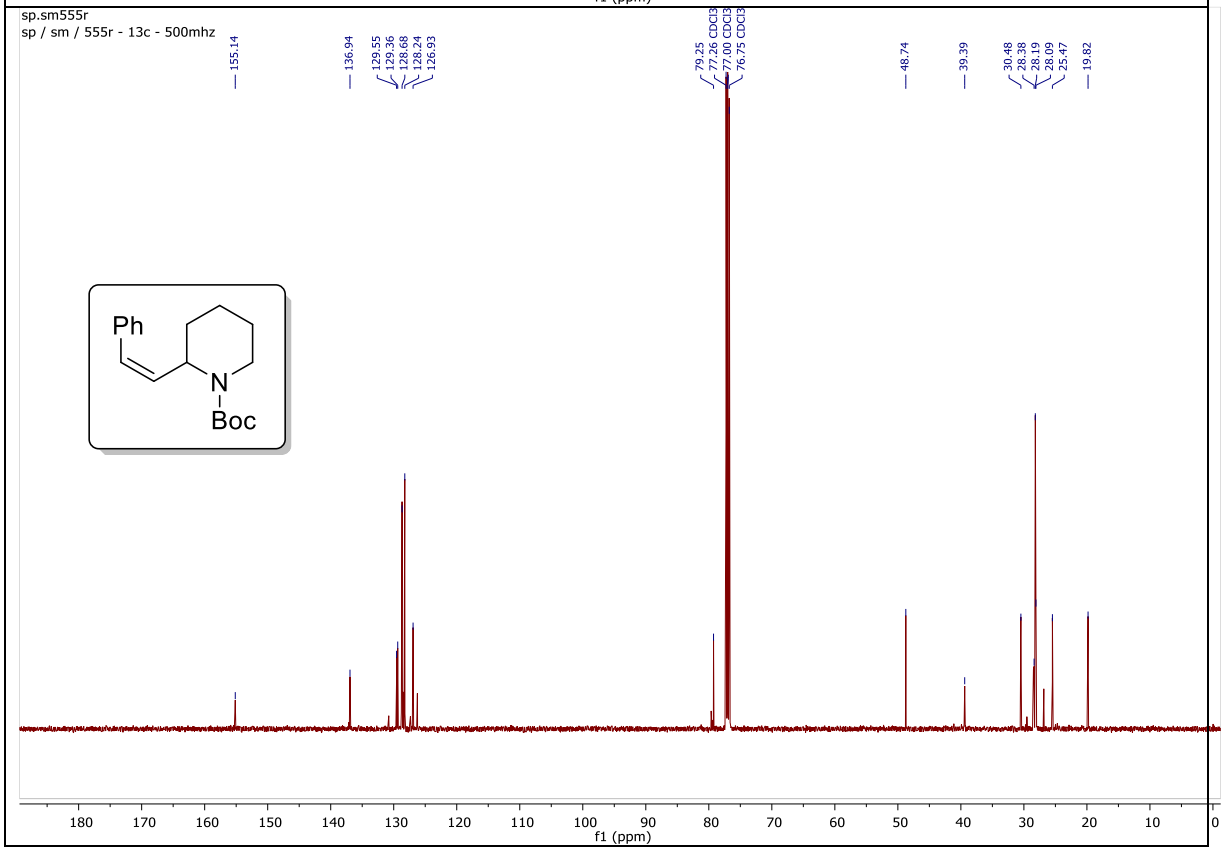

sp.sm578
sp / sm / 578 -1h
MeO
Boc
N
f1 (ppm)

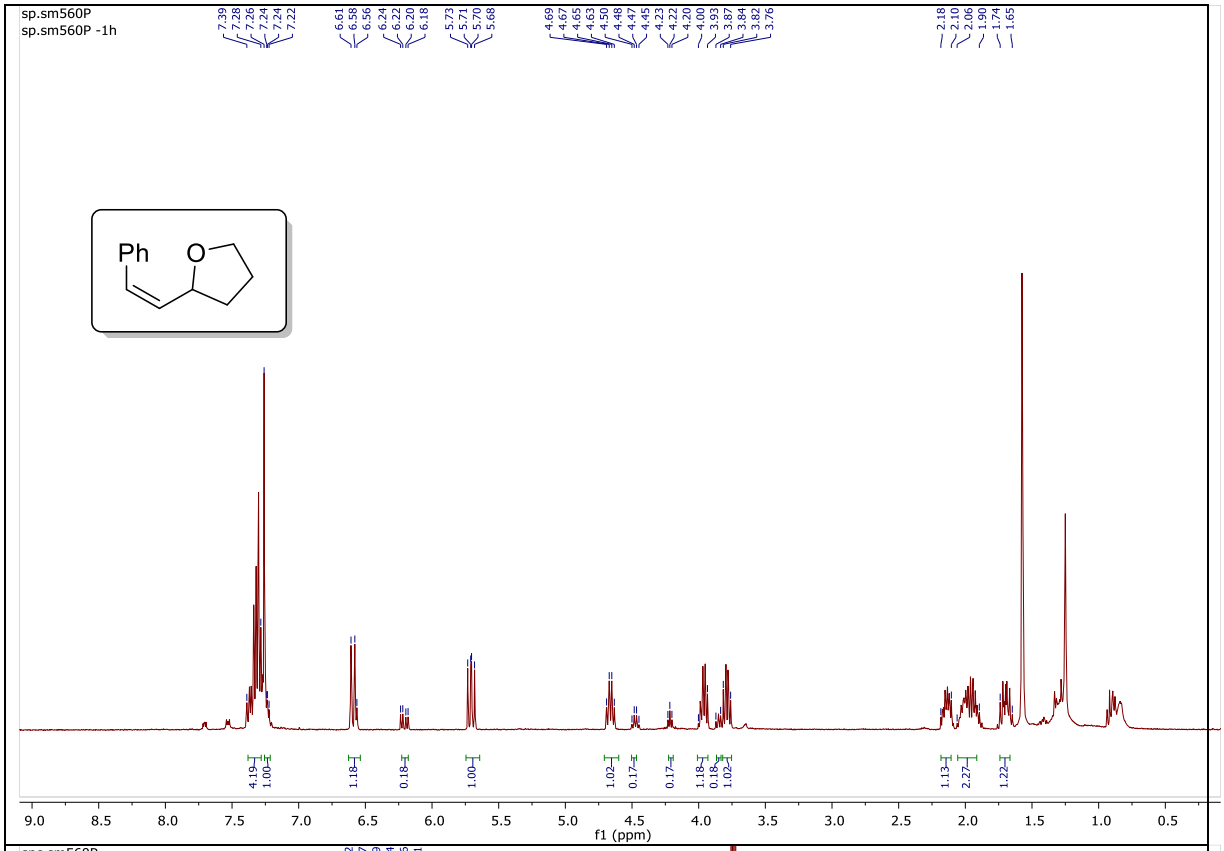

spc.sm578
sp / sm / 578 - 13c
MeO
Boc
N
f1 (ppm)

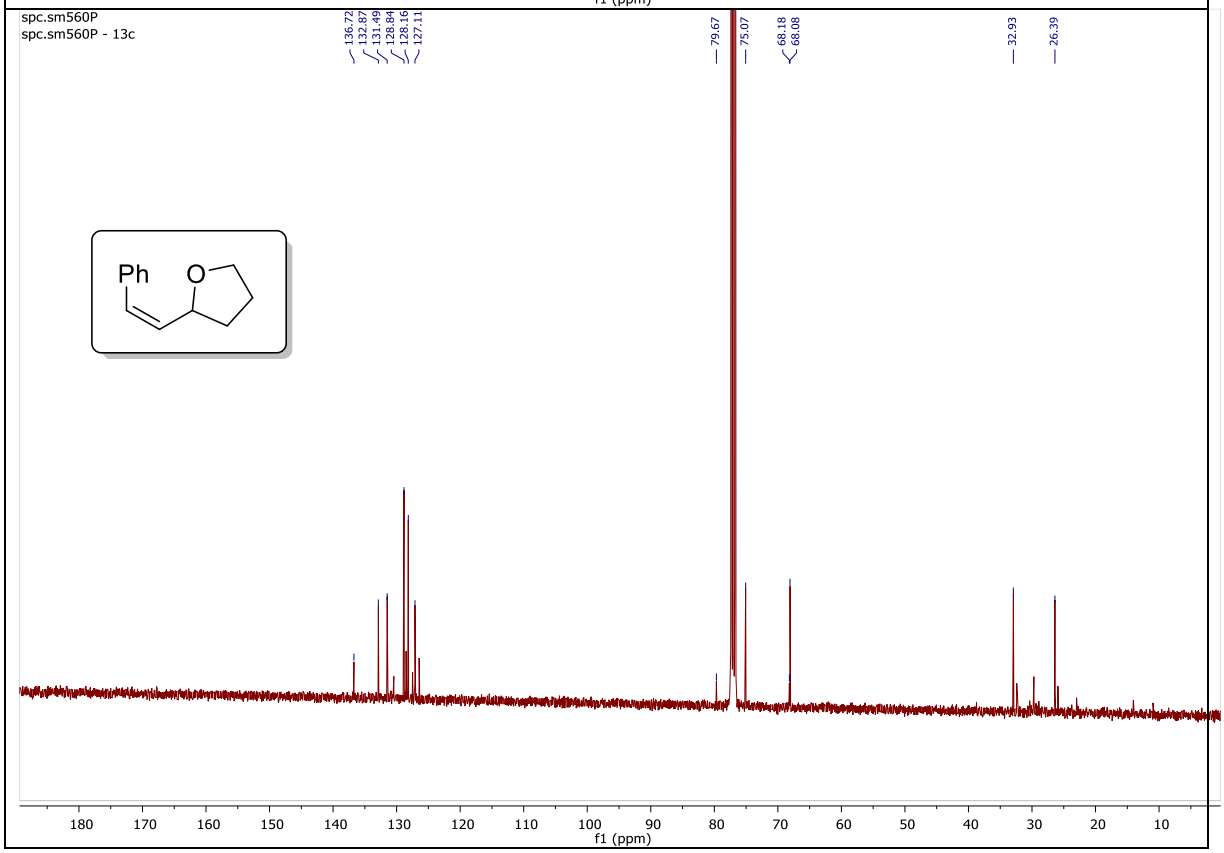

sp.sm542
sp.sm542 -1h
7.45
7.43
7.26
7.21
7.19
7.13
6.34
6.31
6.09
5.66
5.64
5.61
4.65
3.44
2.17
1.97
1.80
1.41
1.30
1.25
Boc
N
Br
2.03
2.01
1.08
0.08
1.00
1.03
2.08
1.09
3.04
9.76
f1 (ppm)

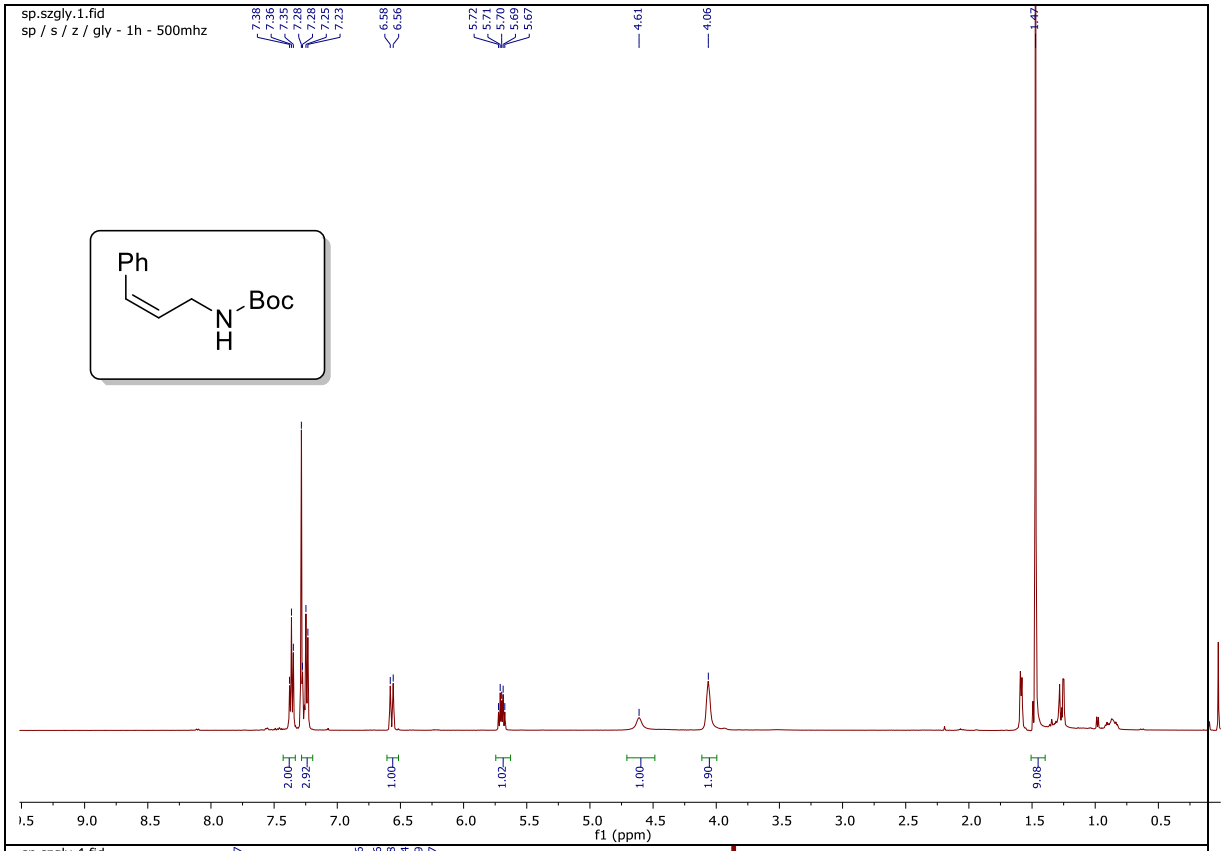

sp.sm542
sp / sm / 542-13c-500mhz
154.58
135.91
135.78
131.28
130.42
120.70
79.26
54.88
46.61
33.81
28.46
23.83
Boc
N
Br
f1 (ppm)

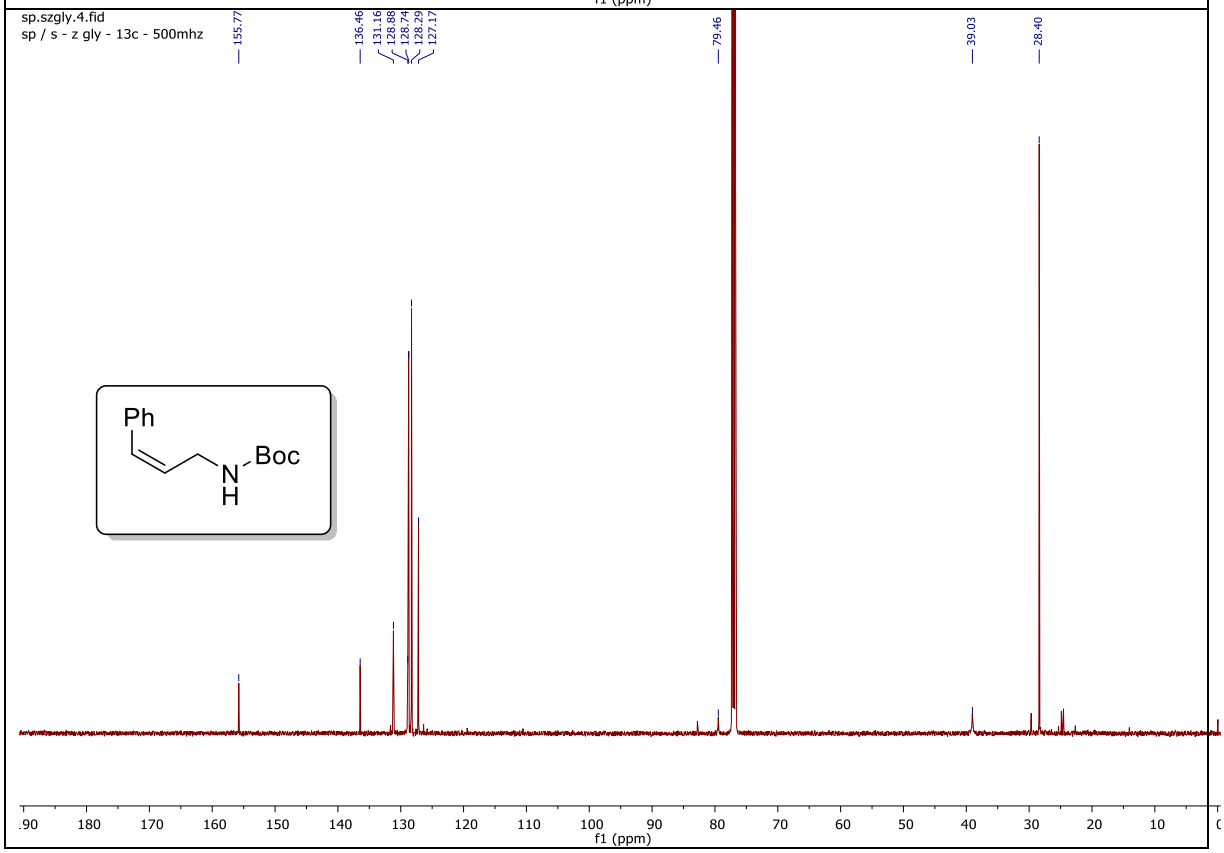

sp.sm555r
sp / sm / 555r -1h
Ph
N
Boc
f1 (ppm)

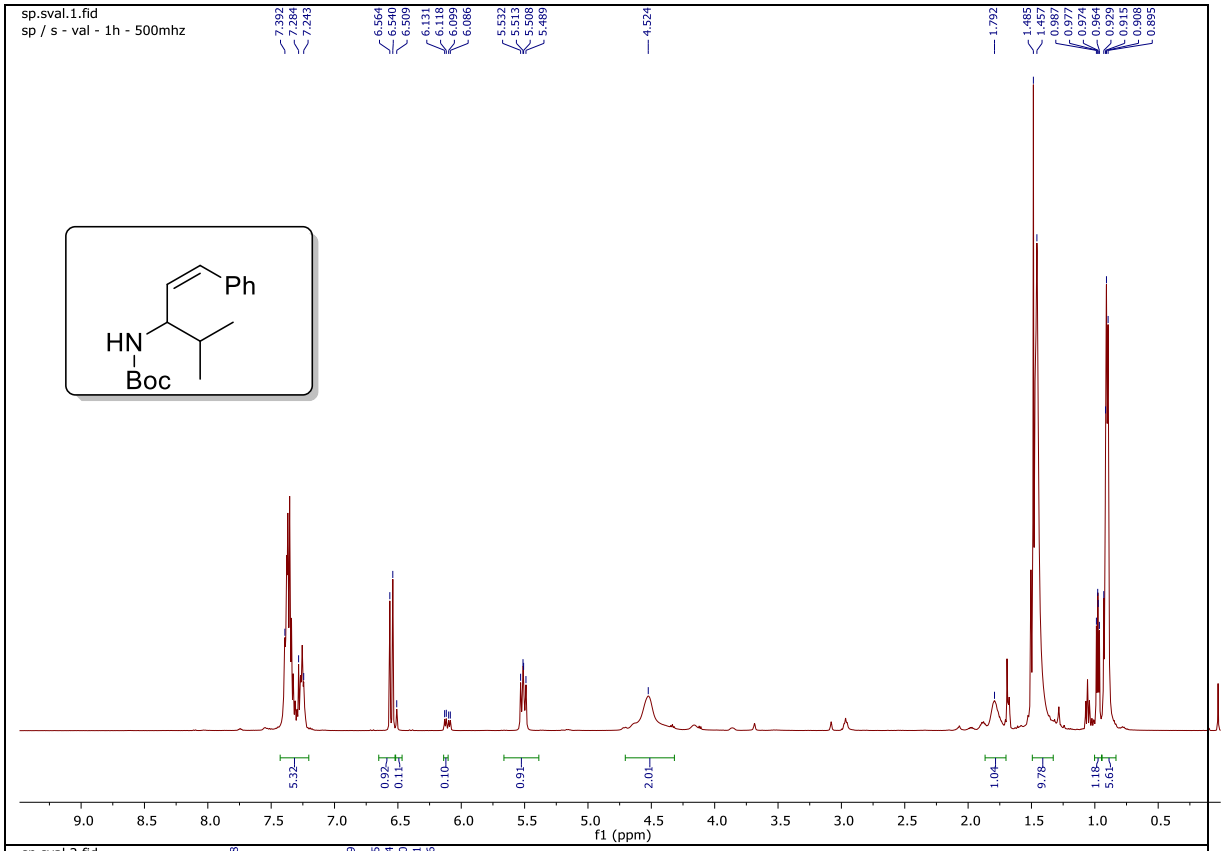

sp.sm555r
sp / sm / 555r - 13c - 500mhz
Ph
N
Boc
f1 (ppm)

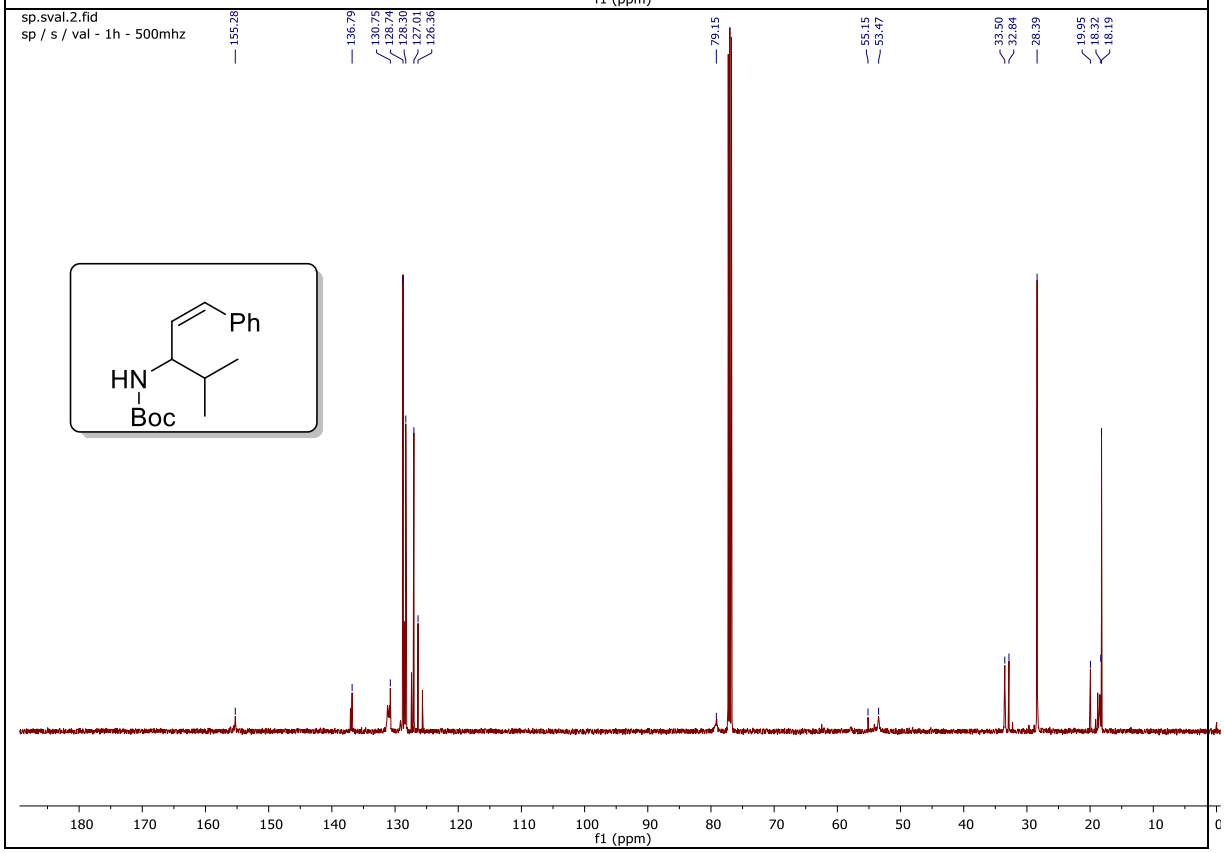

sp.sm560P
sp.sm560P -1h
7.39
7.28
7.26
7.24
7.24
7.22
6.61
6.58
6.56
6.24
6.22
6.20
6.18
5.73
5.71
5.70
5.68
4.69
4.67
4.65
4.63
4.50
4.48
4.47
4.45
4.23
4.22
4.20
4.00
3.93
3.87
3.84
3.82
3.76
2.18
2.10
2.06
1.90
1.74
1.65
Ph
O
4.19
1.00
1.18
0.18
1.00
1.02
0.17
0.17
1.18
0.18
1.02
1.13
2.27
1.22
f1 (ppm)

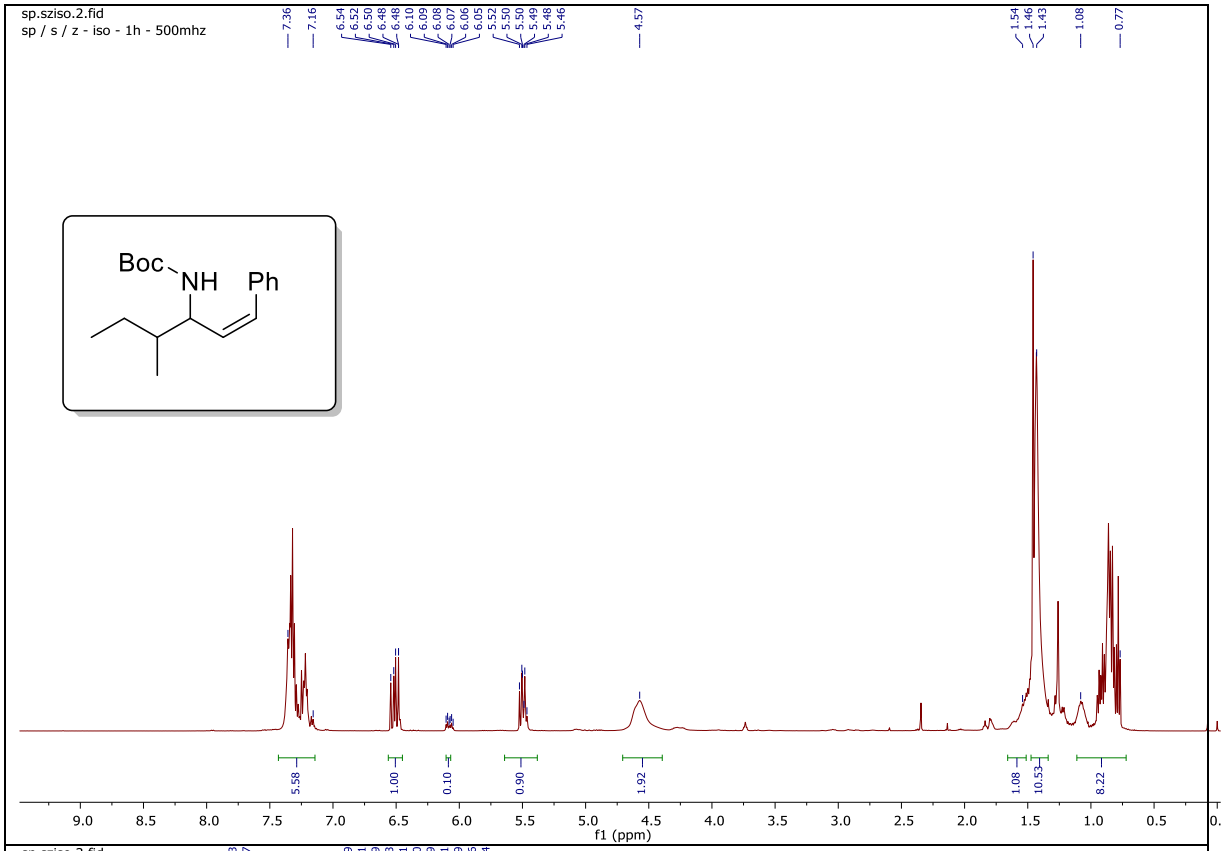

spc.sm560P
spc.sm560P - 13c
136.72
132.87
131.49
128.84
128.16
127.11
79.67
75.07
68.18
68.08
32.93
26.39
Ph
O
f1 (ppm)

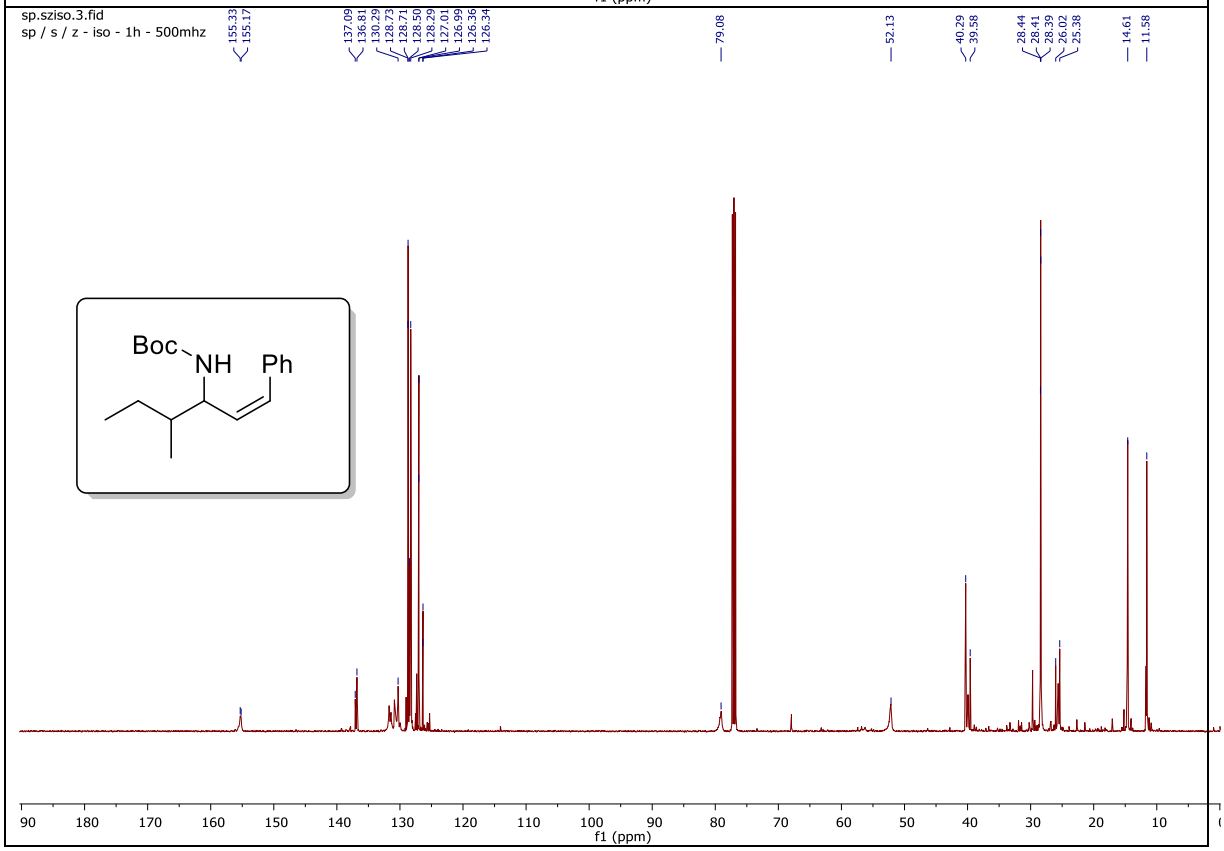

sp.szgly.1.fid
sp / s / z / gly - 1h - 500mhz
7.38
7.36
7.35
7.28
7.28
7.25
7.23
6.58
6.56
5.72
5.71
5.70
5.69
5.67
4.61
4.06
1.47
Ph
N
H
Boc
2.00
2.92
1.00
1.02
1.00
1.90
9.08
f1 (ppm)

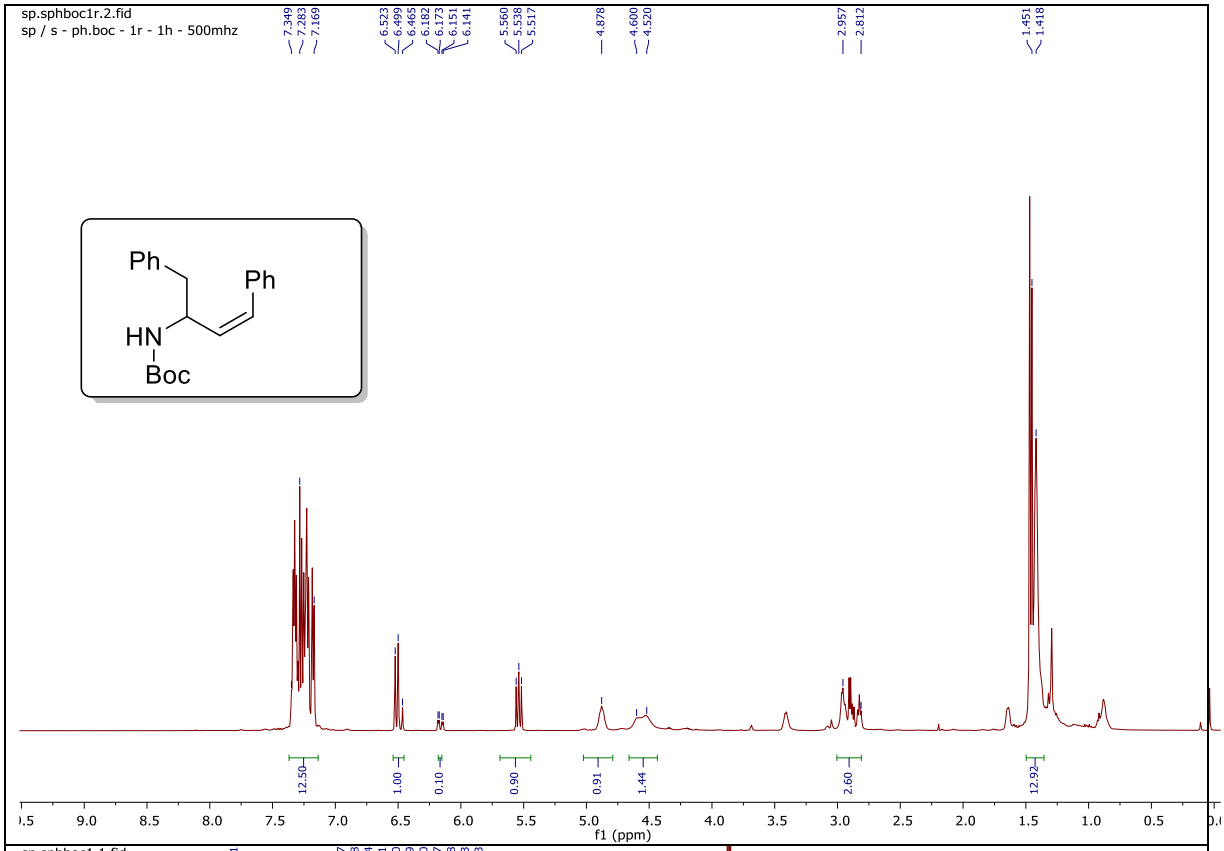

sp.szgly.4.fid
sp / s - z gly - 13c - 500mhz
155.77
136.46
131.16
128.88
128.74
128.29
127.17
79.46
39.03
28.40
Ph
N
H
Boc
f1 (ppm)

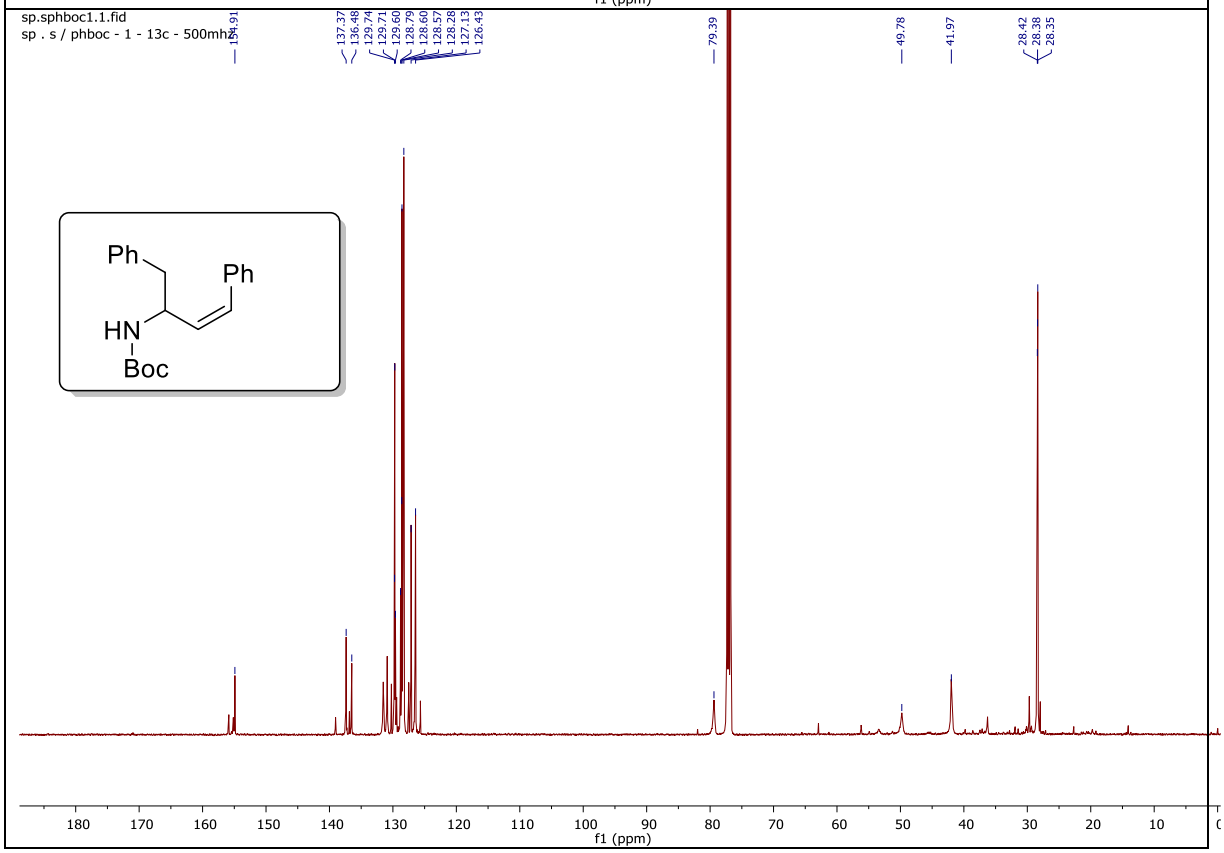

sp.sval.1.fid
sp / s - val - 1h - 500mhz
7.392
7.284
7.243
6.564
6.540
6.509
6.131
6.118
6.099
6.086
5.532
5.513
5.508
5.489
4.524
1.792
1.485
1.457
0.987
0.977
0.974
0.964
0.929
0.915
0.908
0.895
Ph
HN
Boc
5.32
0.92
0.11
0.10
0.91
2.01
1.04
9.78
1.18
5.61
f1 (ppm)

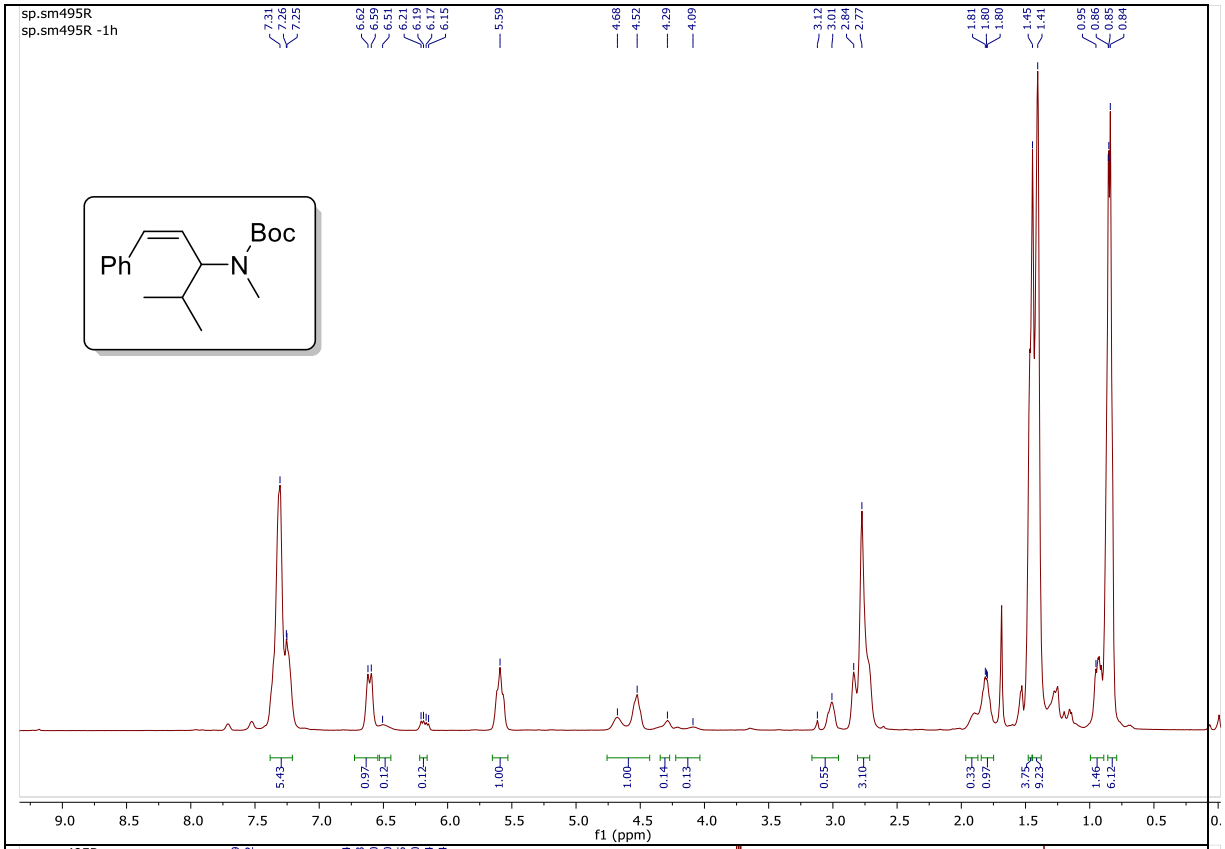

sp.sval.2.fid
sp / s / val - 1h - 500mhz
155.28
136.79
130.75
128.74
128.30
127.01
126.36
79.15
55.15
53.47
33.50
32.84
28.39
19.95
18.32
18.19
Ph
HN
Boc
f1 (ppm)

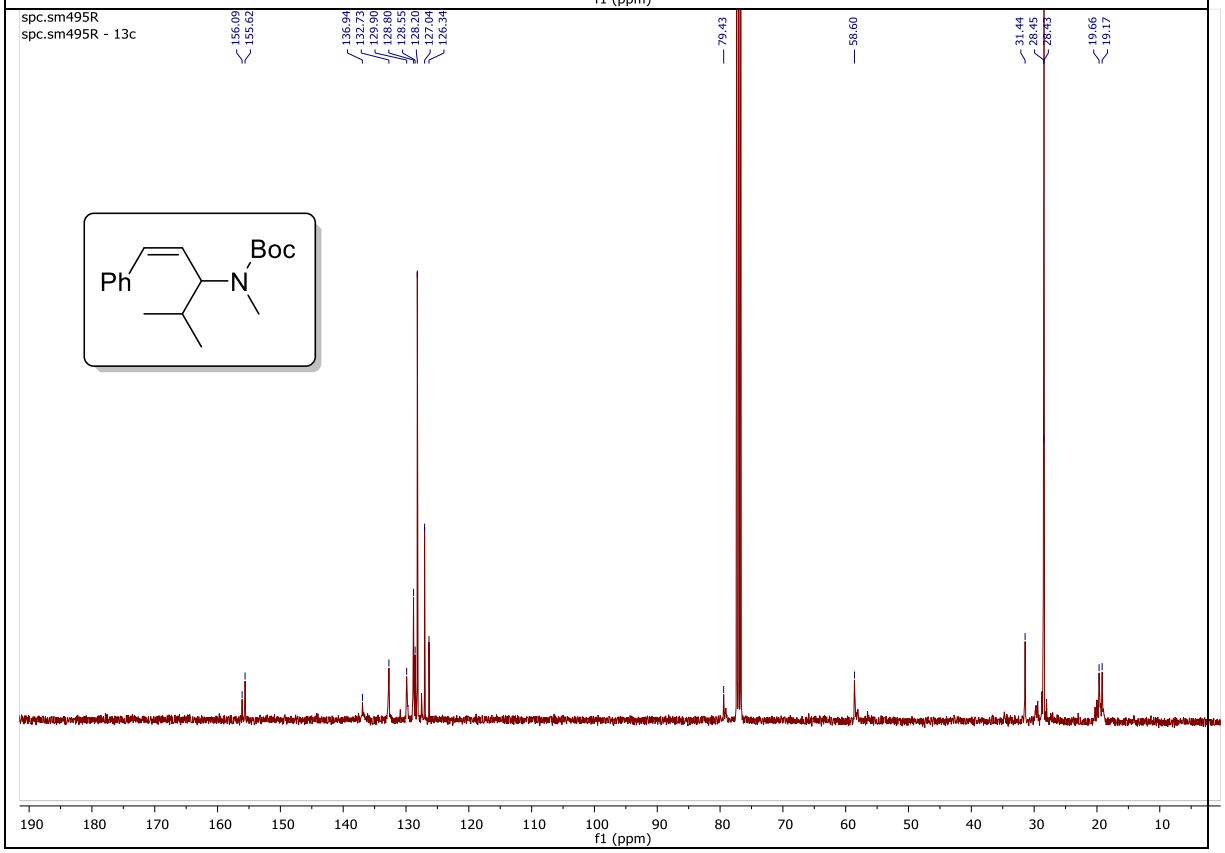

sp.sziso.2.fid
sp / s / z - iso - 1h - 500mhz
7.36
7.16
6.54
6.52
6.50
6.48
6.10
6.09
6.08
6.07
6.06
6.05
5.52
5.50
5.50
5.49
5.48
5.46
4.57
1.54
1.46
1.43
1.08
0.77
Boc
NH
Ph
5.58
1.00
0.10
0.90
1.92
1.08
10.53
8.22
f1 (ppm)

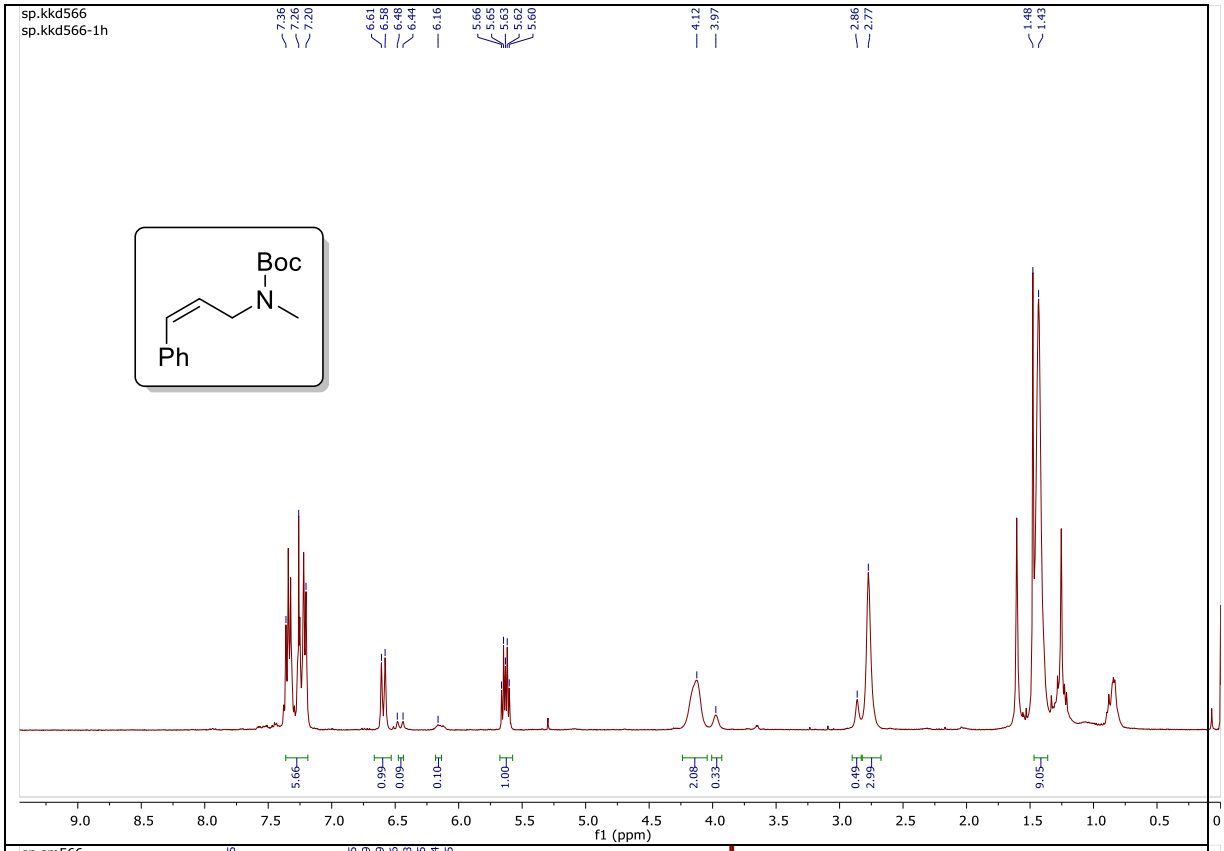

sp.sziso.3.fid
sp / s / z - iso - 1h - 500mhz
155.33
155.17
137.09
136.81
130.29
128.73
128.71
128.50
128.29
127.01
126.99
126.36
126.34
79.08
52.13
40.29
39.58
28.44
28.41
28.39
26.02
25.38
14.61
11.58
Boc
NH
Ph
f1 (ppm)

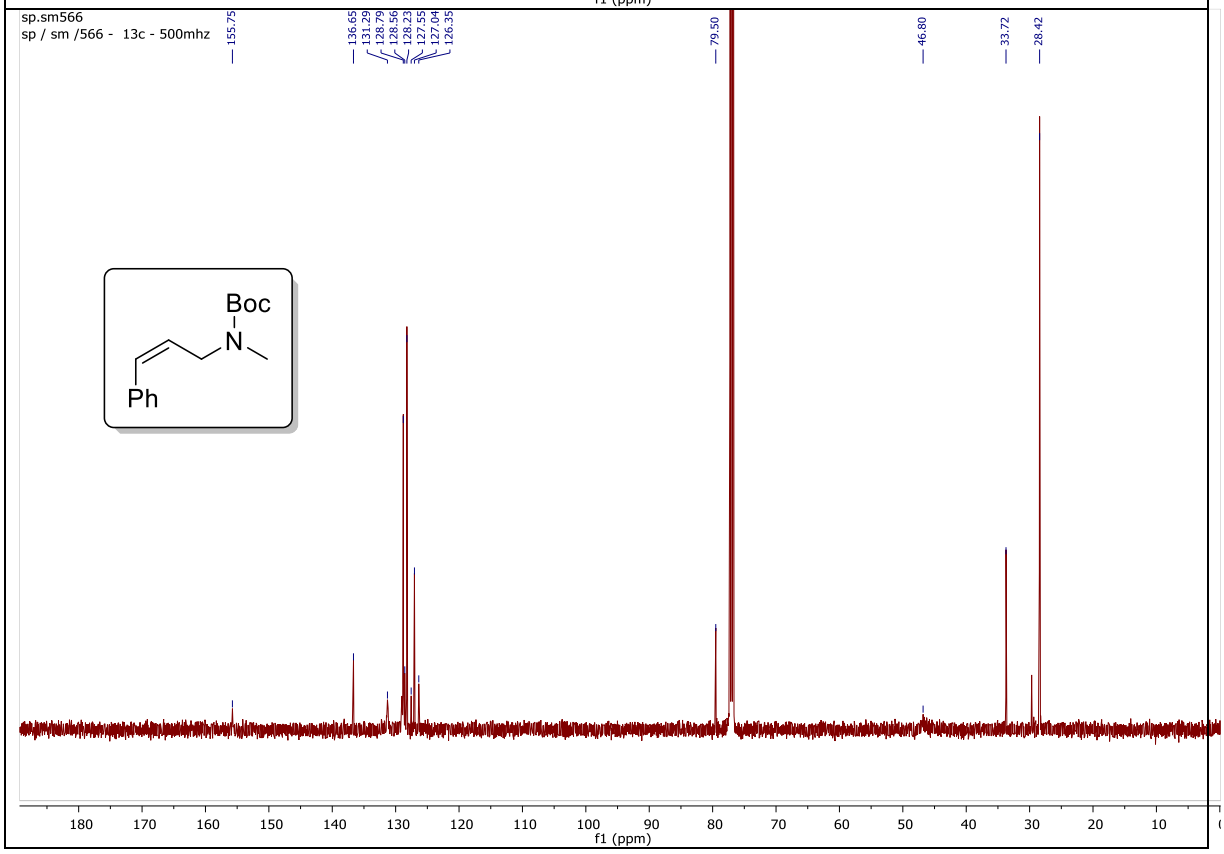

sp.sphboc1r.2.fid
sp / s - ph.boc - 1r - 1h - 500mhz
7.349
7.283
7.169
6.523
6.499
6.465
6.182
6.173
6.151
6.141
5.560
5.538
5.517
4.878
4.600
4.520
2.957
2.812
1.451
1.418
Ph
Ph
HN
Boc
12.50
1.00
0.10
0.90
0.91
1.44
2.60
12.92
f1 (ppm)

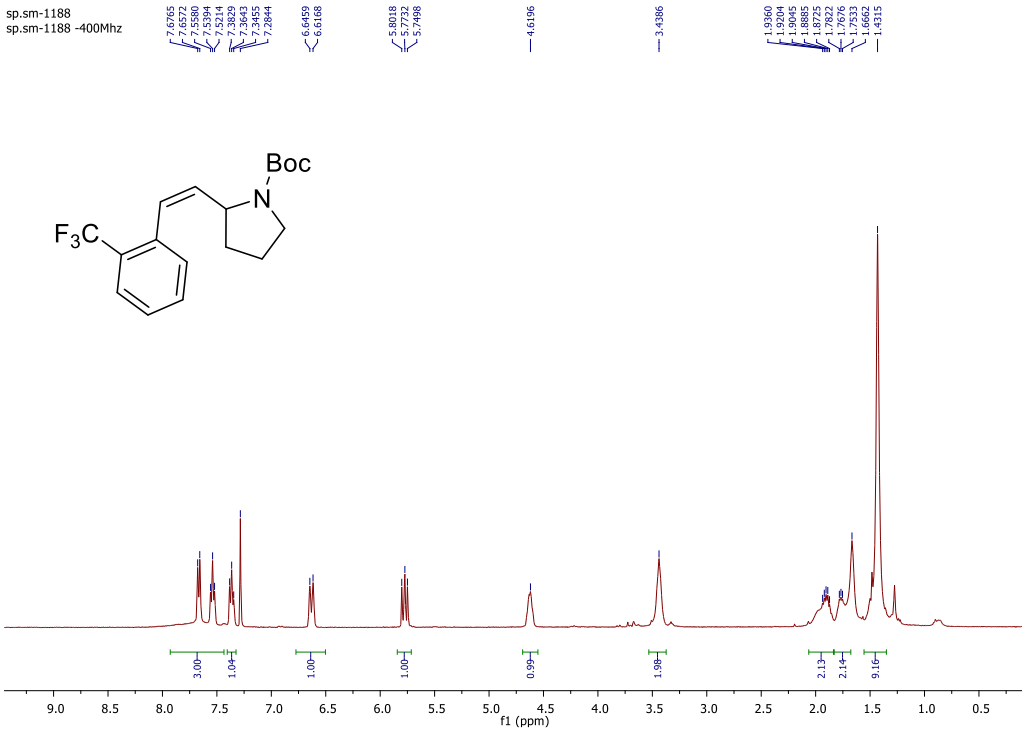

sp.sphboc1.1.fid
sp . s / phboc - 1 - 13c - 500mhz
154.91
137.37
136.48
129.74
129.71
129.60
128.79
128.60
128.57
128.28
127.13
126.43
79.39
49.78
41.97
28.42
28.38
28.35
Ph
Ph
HN
Boc
f1 (ppm)

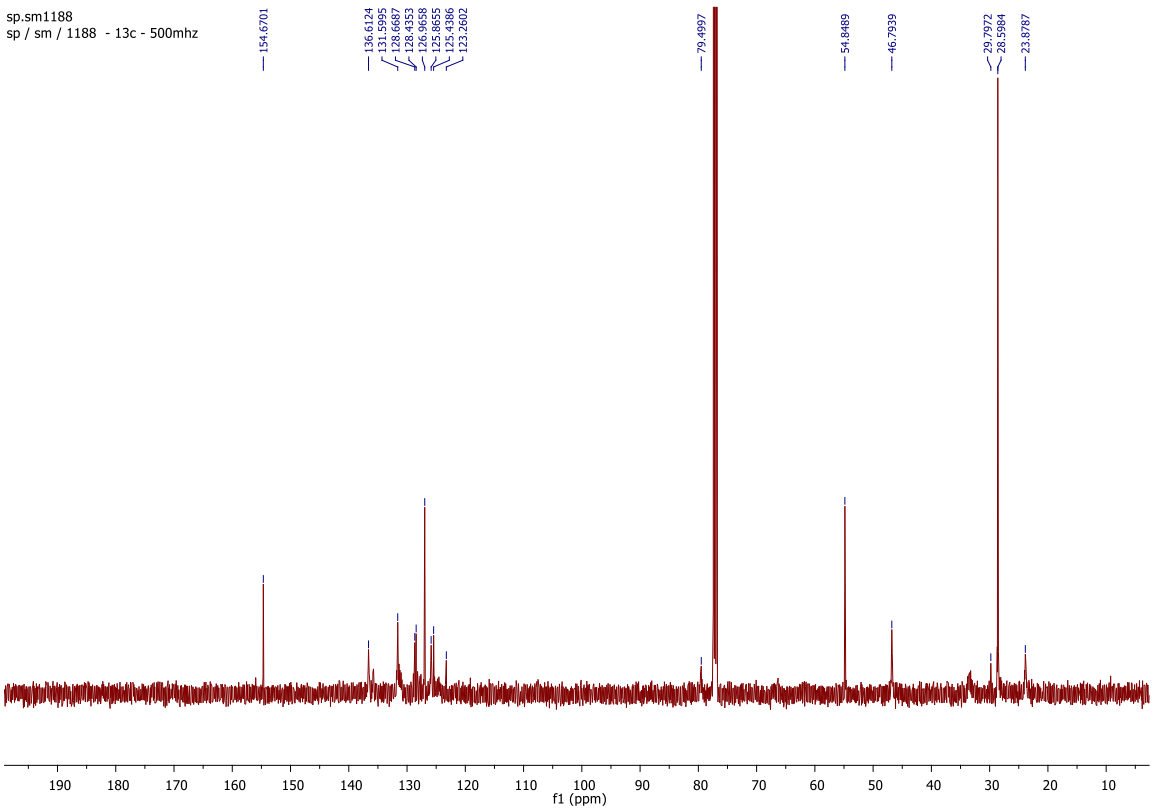

sp.sm495R
sp.sm495R -1h
Boc
Ph
N
f1 (ppm)

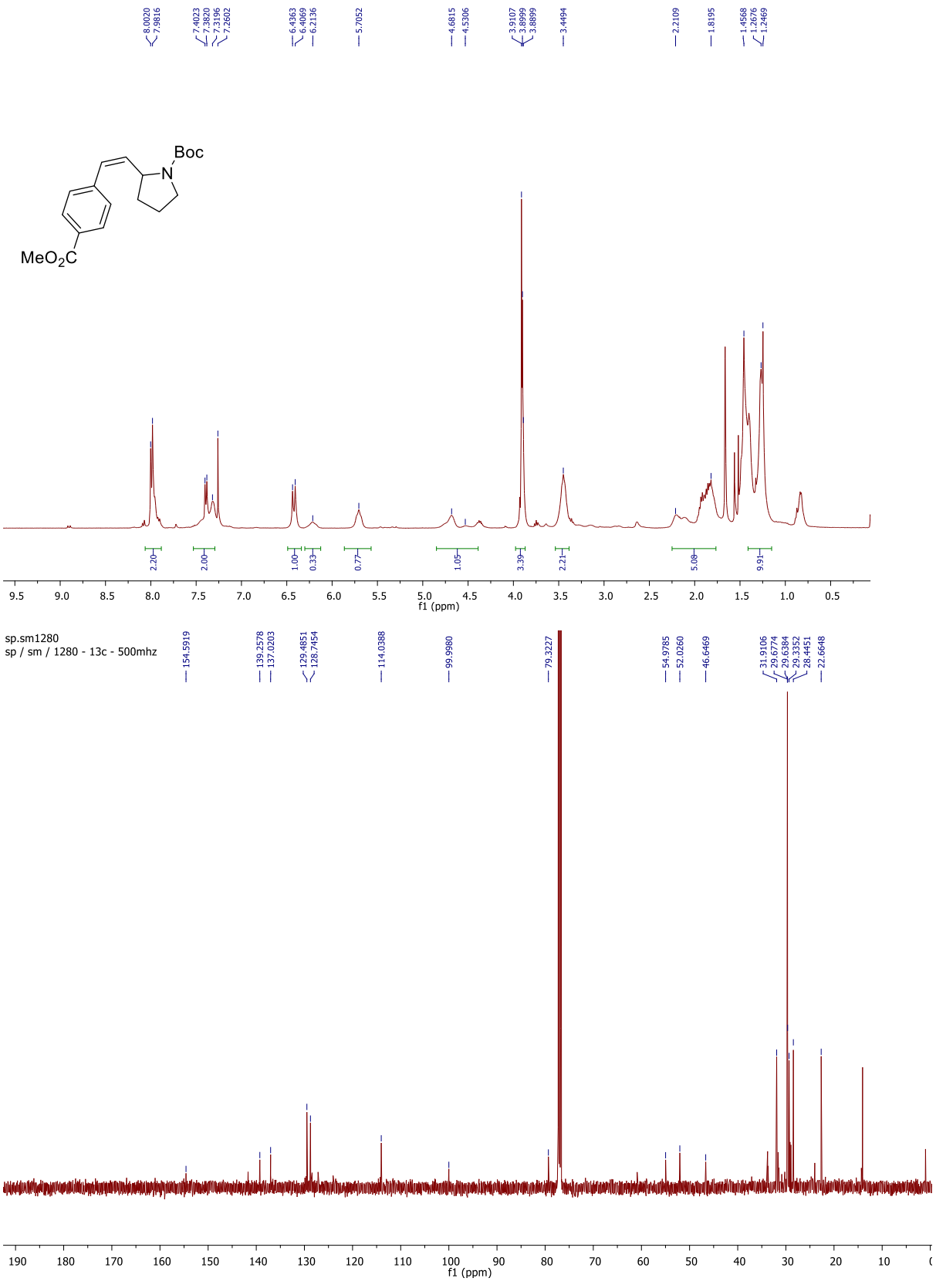

spc.sm495R
spc.sm495R - 13c
Boc
Ph
N
f1 (ppm)

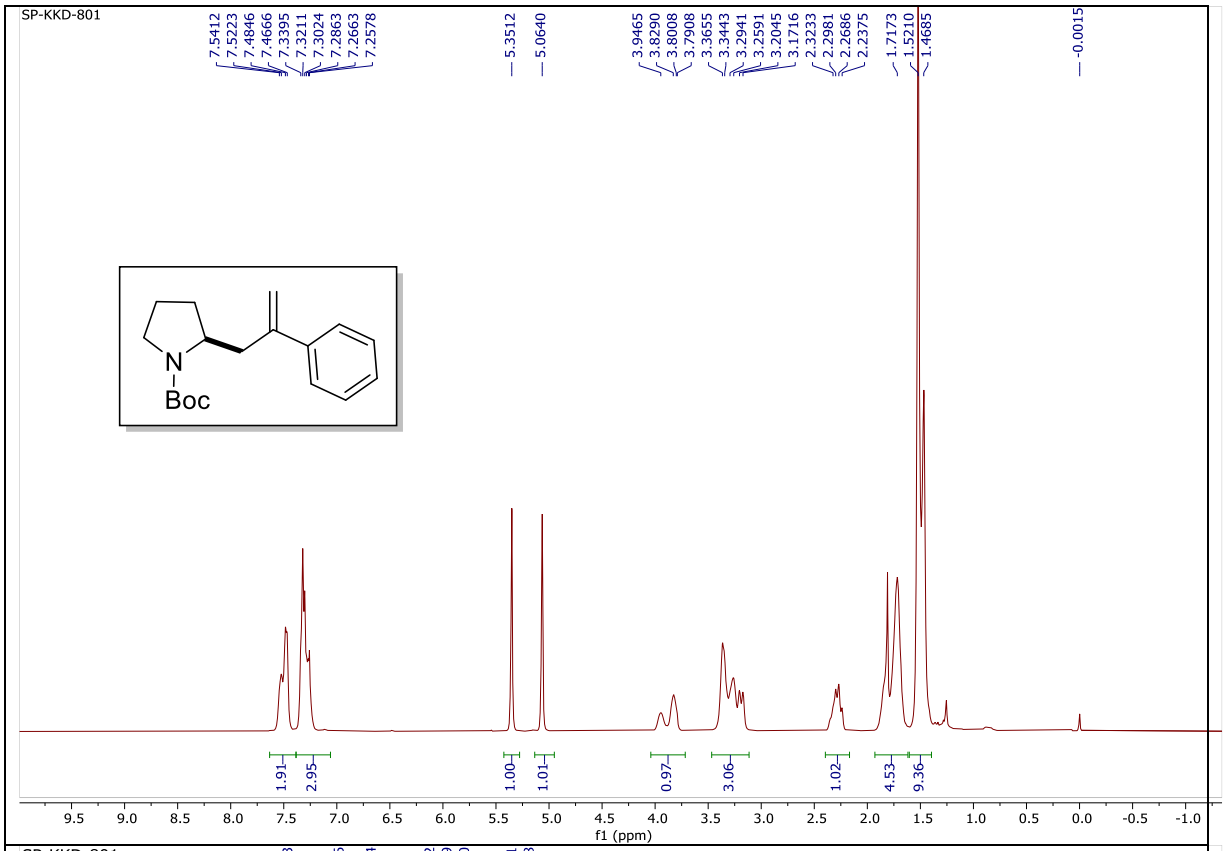

sp.kkd566
sp.kkd566-1h
7.36
7.26
7.20
6.61
6.58
6.48
6.44
6.16
5.66
5.65
5.63
5.62
5.60
4.12
3.97
2.86
2.77
1.48
1.43
Boc
N
Ph
5.66
0.99
0.09
0.10
1.00
2.08
0.33
0.49
2.99
9.05
f1 (ppm)

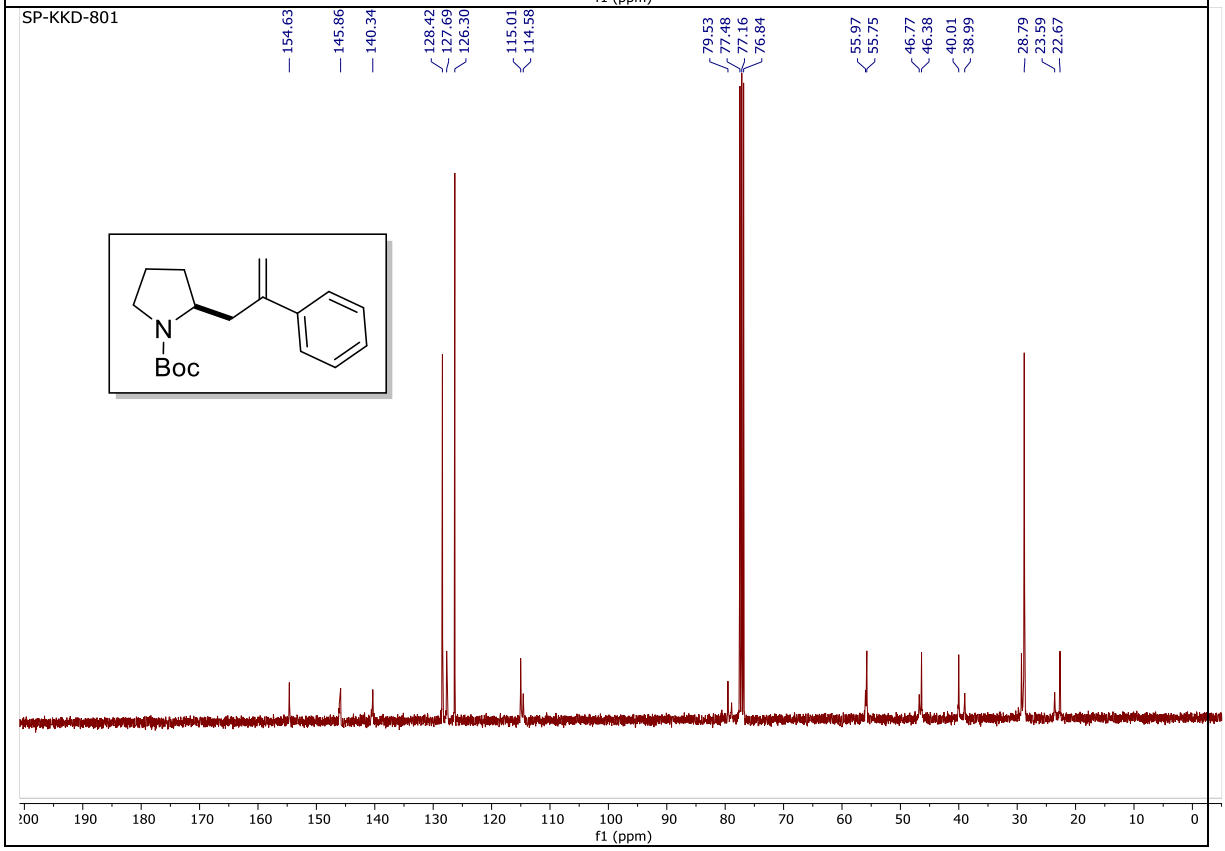

sp.sm566
sp / sm /566 - 13c - 500mhz
155.75
136.65
131.29
128.79
128.56
128.23
127.55
127.04
126.35
79.50
46.80
33.72
28.42
Boc
N
Ph
f1 (ppm)

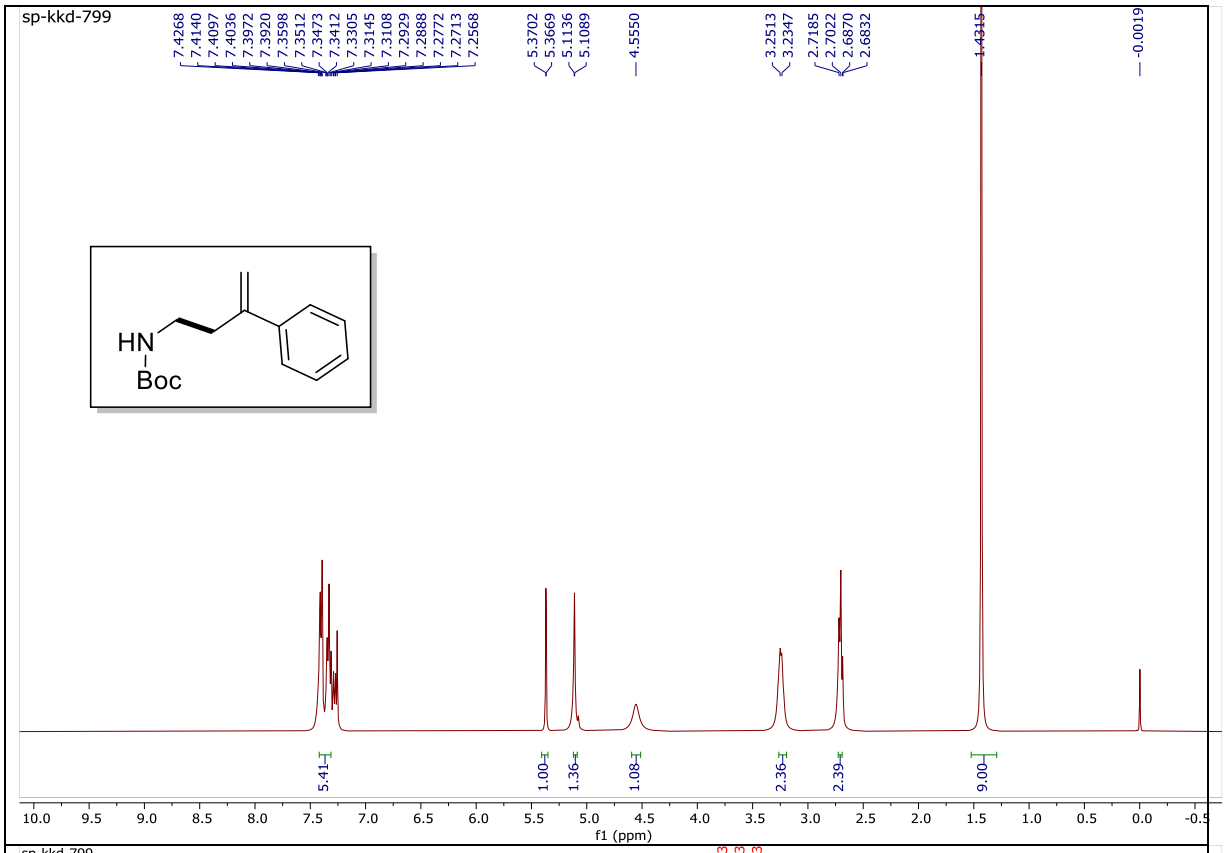

sp.sm-1188
sp.sm-1188 -400Mhz
7.6765
7.6572
7.5580
7.5394
7.5214
7.2898
7.3643
7.3455
7.2844
6.6459
6.6168
5.8018
5.7732
5.7498
4.6196
3.4386
1.9360
1.9204
1.8965
1.8885
1.8725
1.7822
1.7676
1.7533
1.6662
1.4315
Boc
N
F3C
3.00
1.04
1.00
1.00
0.99
1.98
2.13
2.14
9.16
f1 (ppm)

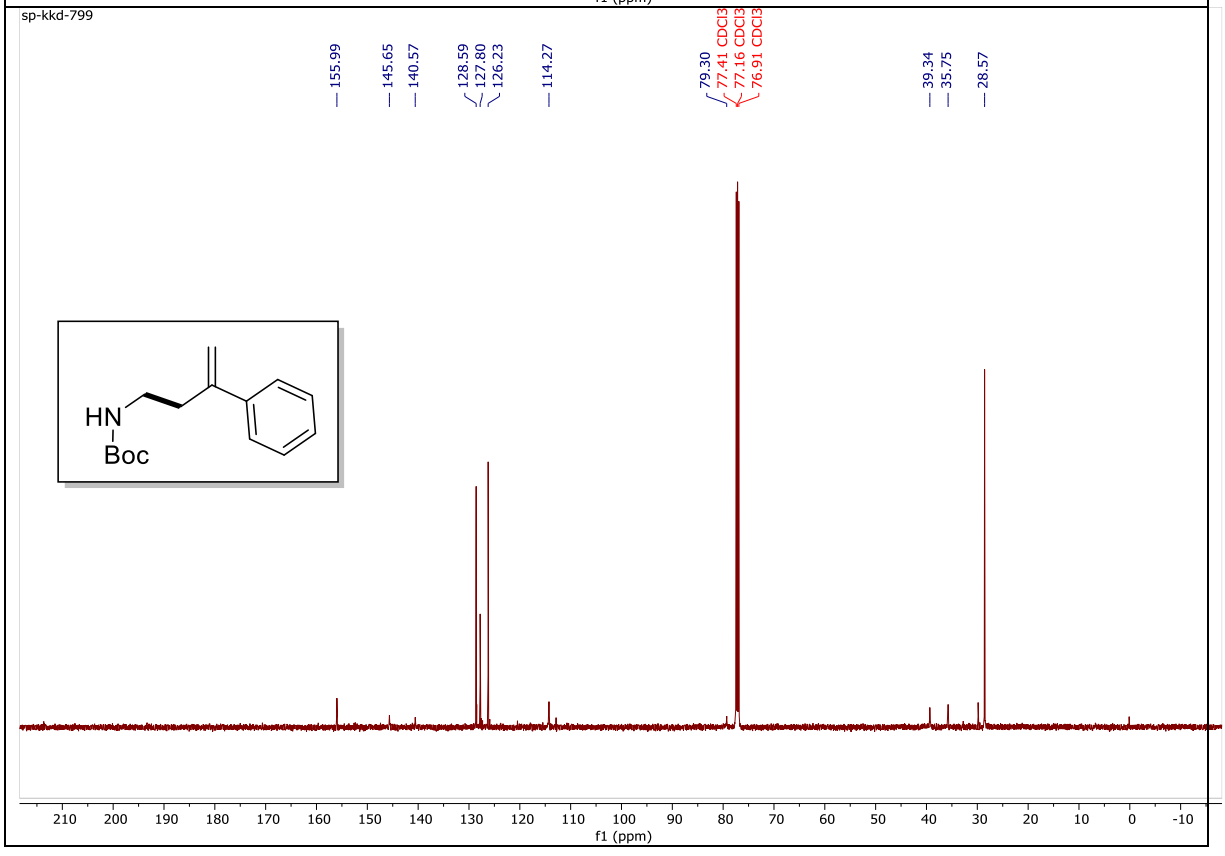

sp.sm1188
sp / sm / 1188 - 13c - 500mhz
154.6701
136.6124
131.5995
128.6687
128.4353
126.9658
125.8655
125.4386
123.2602
79.4997
54.8489
46.7939
29.7972
28.5984
23.8787
f1 (ppm)

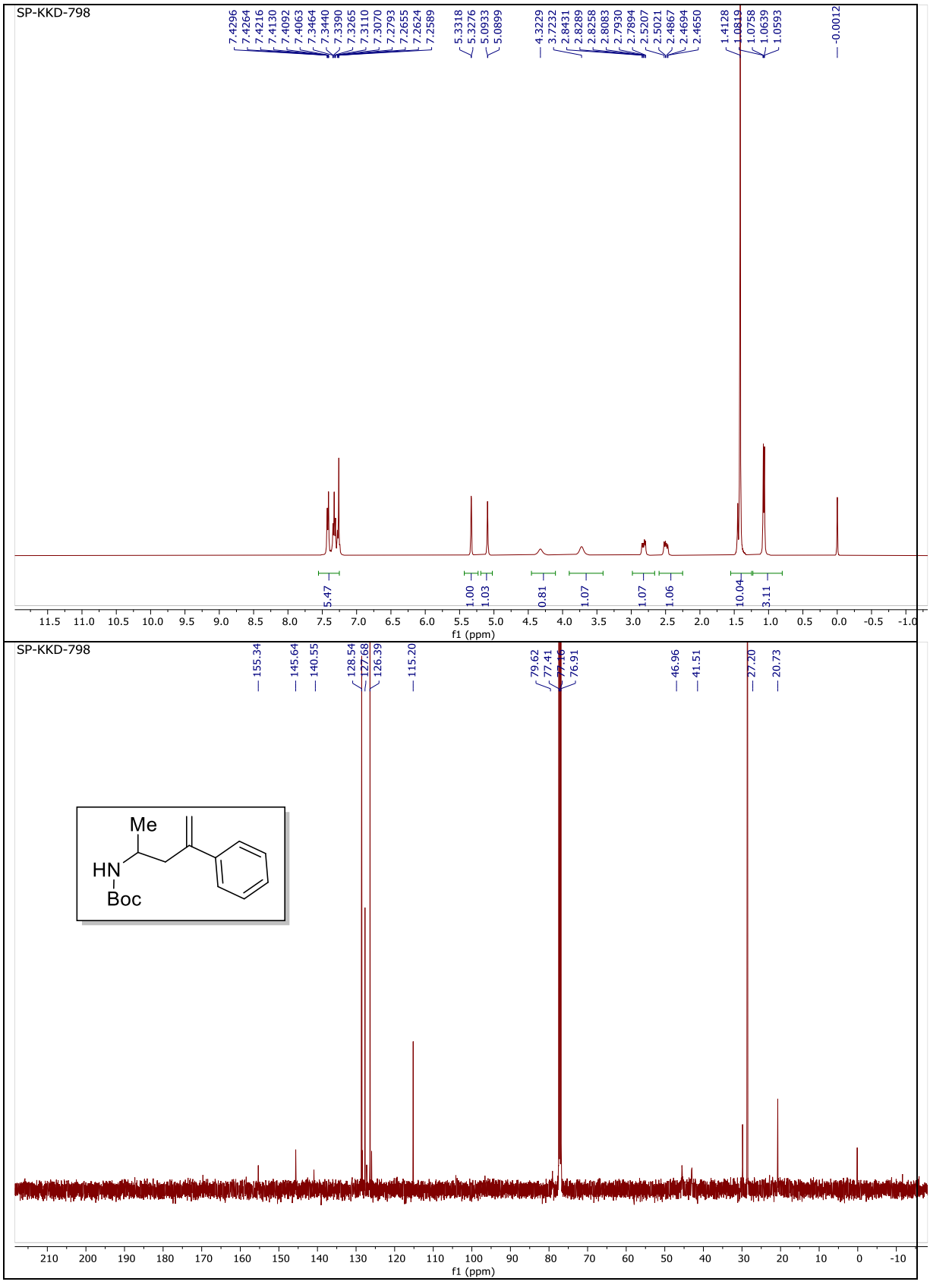

8.0020
7.9816
7.4023
7.3820
7.3196
7.2602
6.4363
6.4069
6.2136
5.7052
4.6815
4.5306
3.9107
3.8999
3.8899
3.4494
2.2109
1.8195
1.4568
1.2676
1.2469
Boc
N
MeO2C
2.20
2.00
1.00
0.33
0.77
1.05
3.39
2.21
5.08
9.91
f1 (ppm)
sp.sm1280
sp / sm / 1280 - 13c - 500mhz
154.5919
139.2578
137.0203
129.4851
128.7454
114.0388
99.9980
79.3227
54.9785
52.0260
46.6469
31.9106
29.6774
29.6384
29.3352
28.4451
22.6648
f1 (ppm)

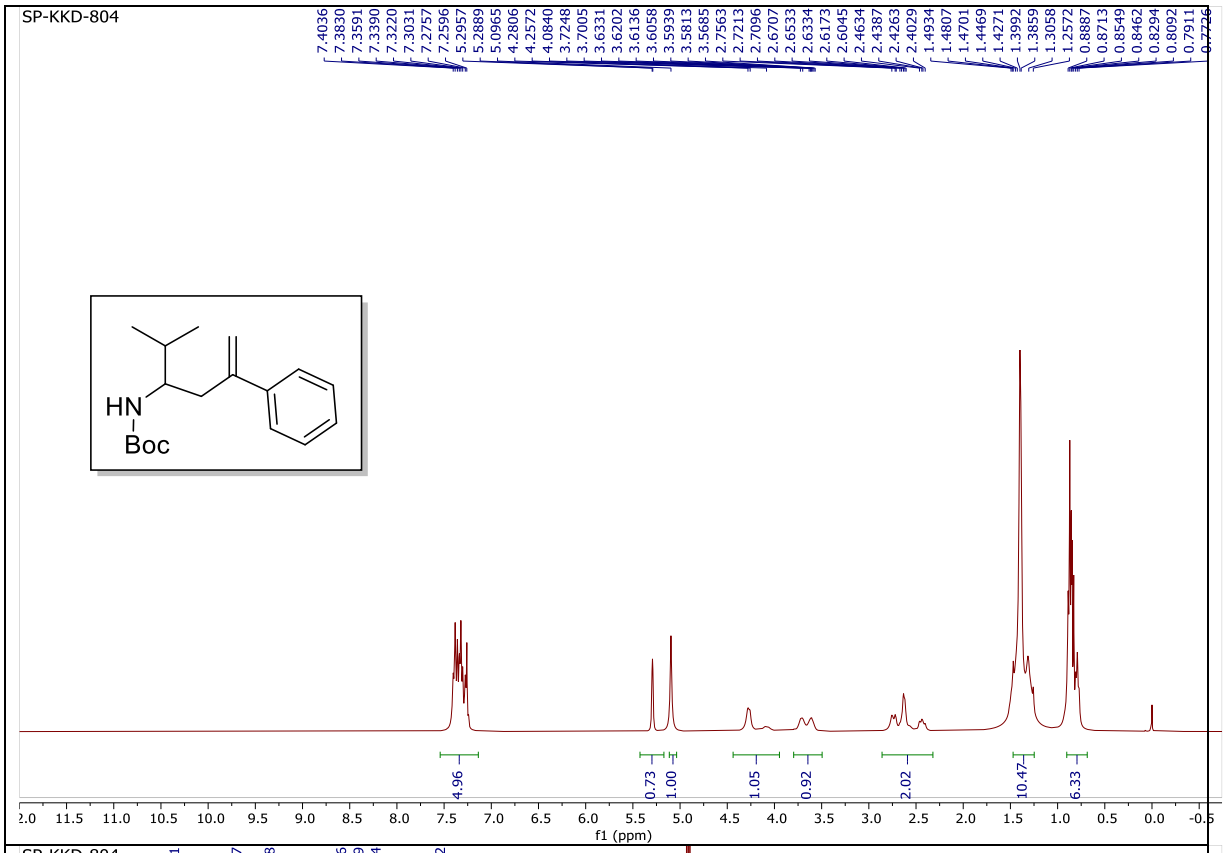

SP-KKD-801
7.5412
7.5223
7.4846
7.4666
7.3395
7.3211
7.3024
7.2863
7.2663
7.2578
5.3512
5.0640
3.9465
3.8290
3.8008
3.7908
3.3655
3.3443
3.2941
3.2591
3.2045
3.1716
2.3233
2.2981
2.2686
2.2375
1.7173
1.5210
1.4685
-0.0015
1.91
2.95
1.00
1.01
0.97
3.06
1.02
4.53
9.36
f1 (ppm)
N
Boc

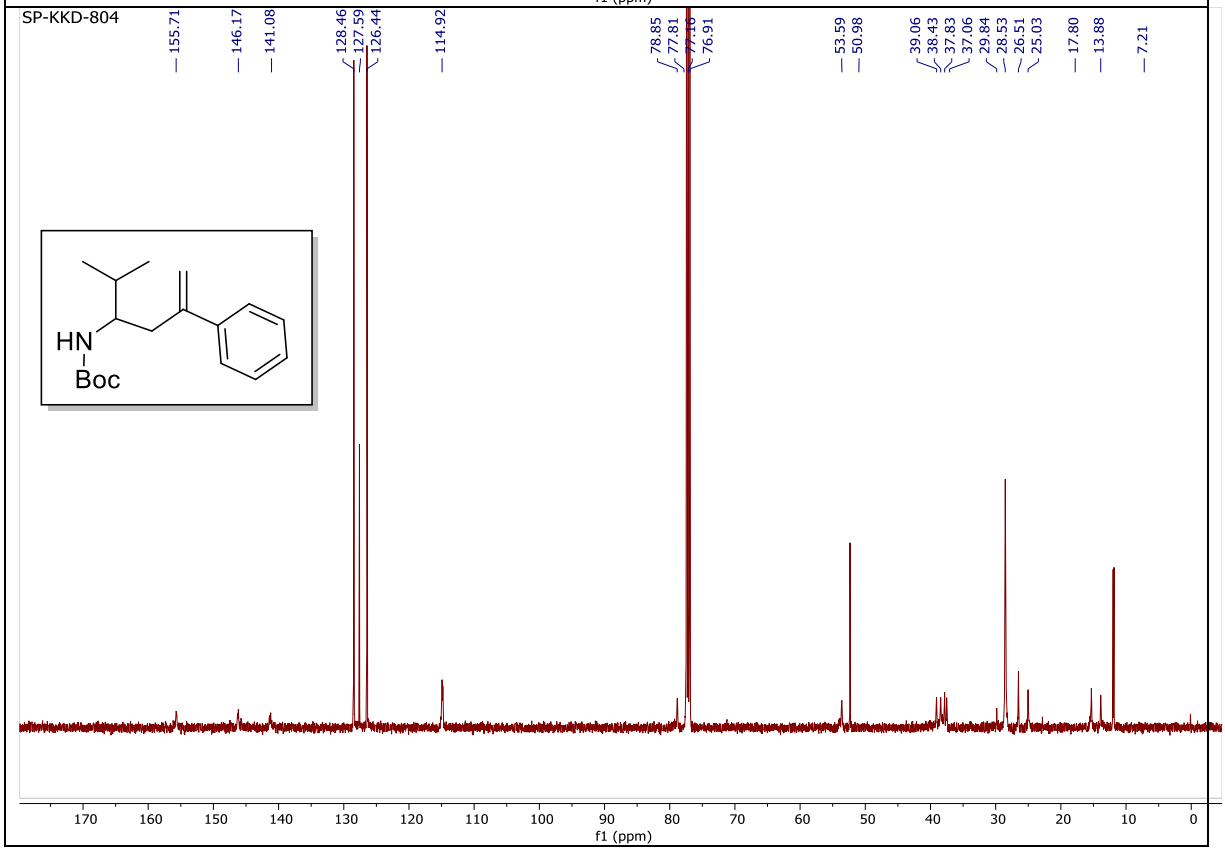

SP-KKD-801
154.63
145.86
140.34
128.42
127.69
126.30
115.01
114.58
79.53
77.48
77.16
76.84
55.97
55.75
46.77
46.38
40.01
38.99
28.79
23.59
22.67
f1 (ppm)
N
Boc

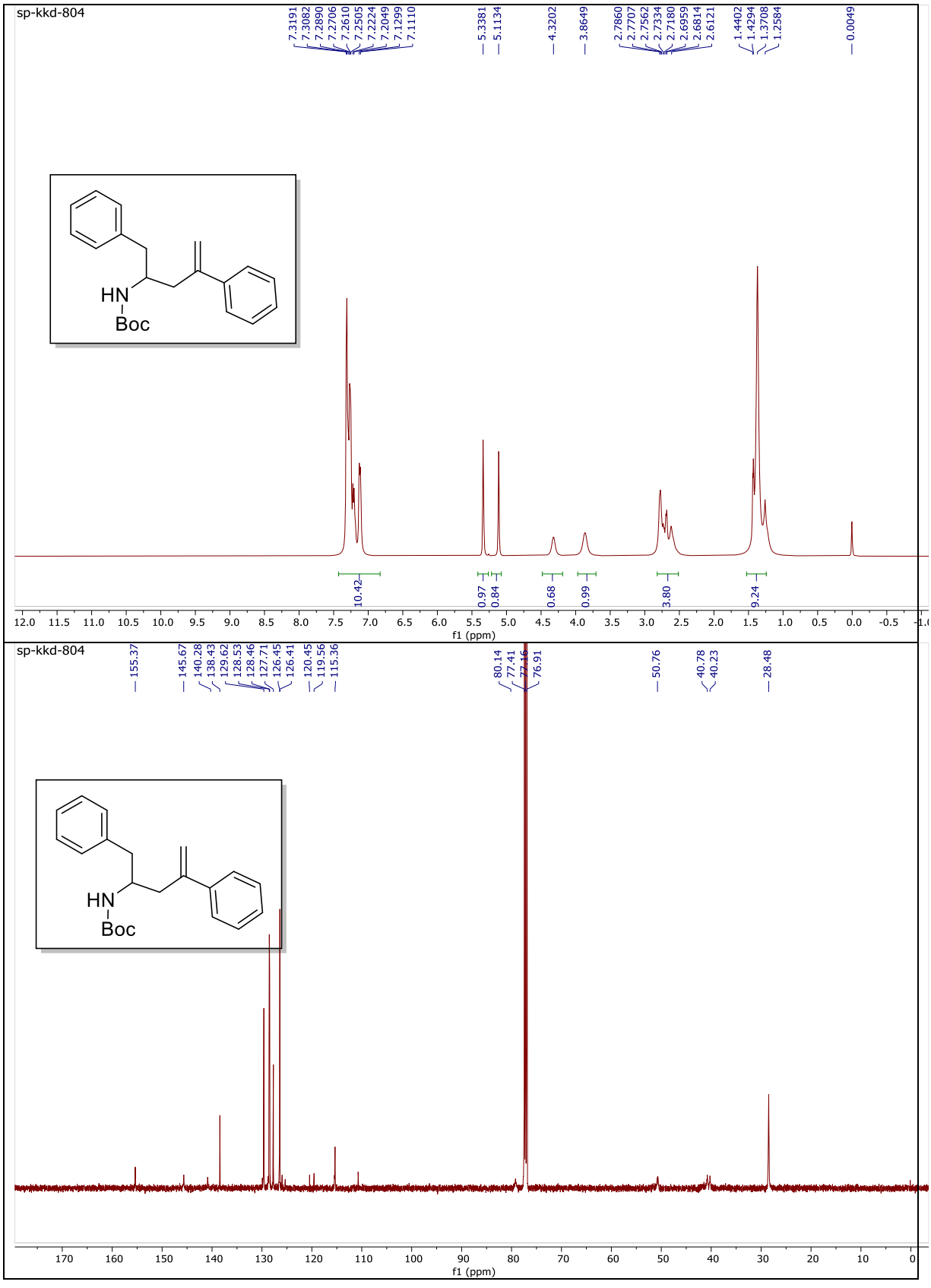

sp-kkd-799
7.4268
7.4140
7.4097
7.4036
7.3972
7.3920
7.3598
7.3512
7.3473
7.3412
7.3305
7.3145
7.3108
7.2929
7.2888
7.2772
7.2713
7.2568
5.3702
5.3669
5.1136
5.1089
4.5550
3.2513
3.2347
2.7185
2.7022
2.6870
2.6832
1.4315
-0.0019
HN
Boc
5.41
1.00
1.36
1.08
2.36
2.39
9.00
f1 (ppm)

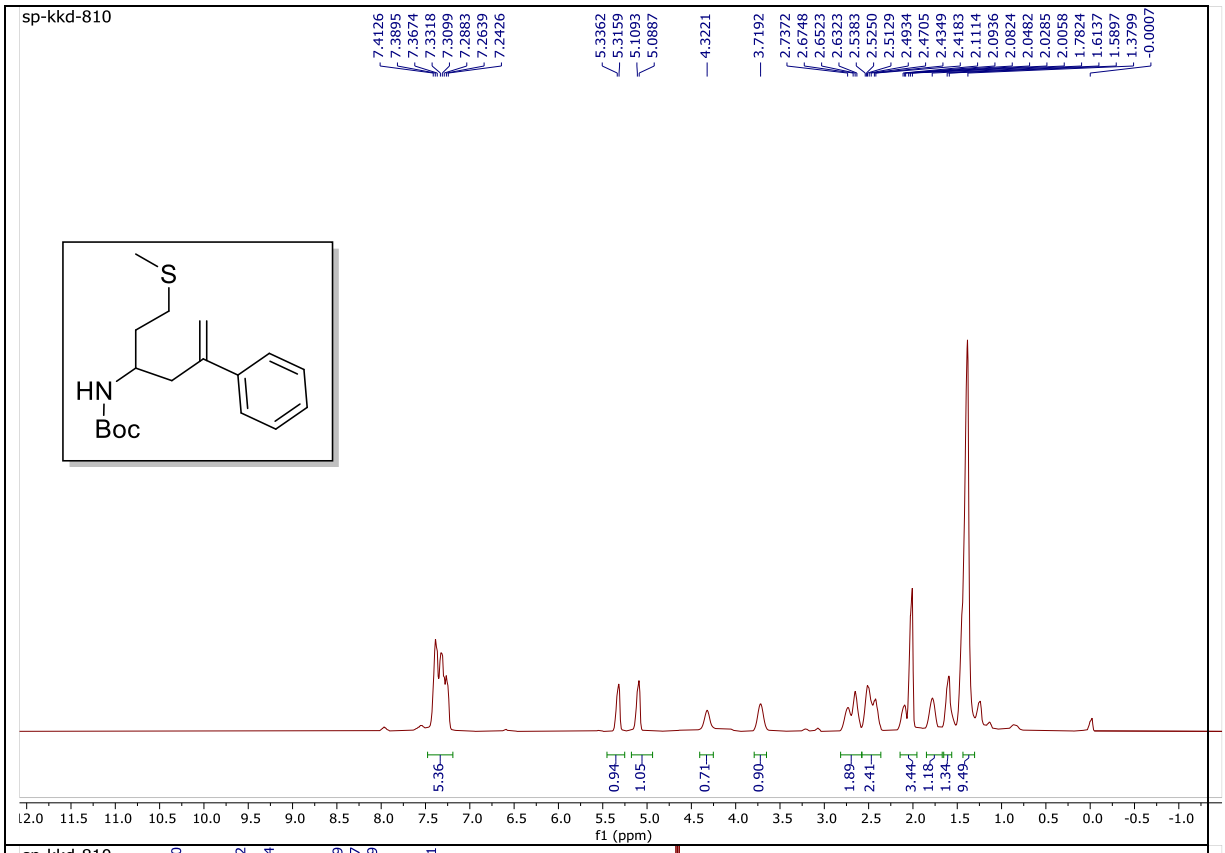

sp-kkd-799
155.99
145.65
140.57
128.59
127.80
126.23
114.27
79.30
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
39.34
35.75
28.57
HN
Boc
f1 (ppm)

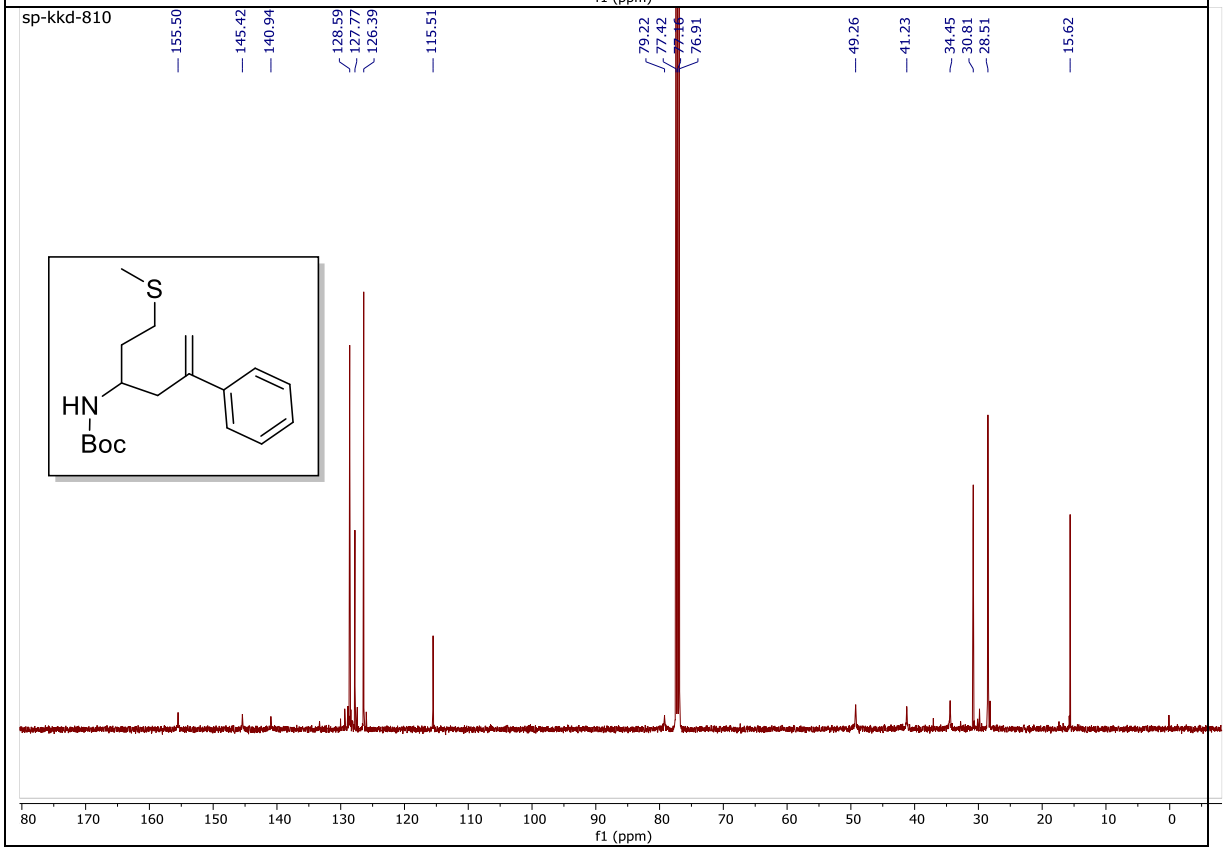

SP-KKD-798
7.4296
7.4264
7.4216
7.4130
7.4092
7.4063
7.3464
7.3440
7.3390
7.3265
7.3110
7.3070
7.2793
7.2655
7.2624
7.2589
5.3318
5.3276
5.0933
5.0899
4.3229
3.7232
2.8431
2.8289
2.8258
2.8083
2.7930
2.7894
2.5207
2.5021
2.4867
2.4694
2.4650
1.4128
1.0819
1.0758
1.0639
1.0593
-0.0012
5.47
1.00
1.03
0.81
1.07
1.07
1.06
10.04
3.11
f1 (ppm)
SP-KKD-798
155.34
145.64
140.55
128.54
127.68
126.39
115.20
79.62
77.41
77.16
76.91
46.96
41.51
27.20
20.73
Me
HN
Boc
f1 (ppm)

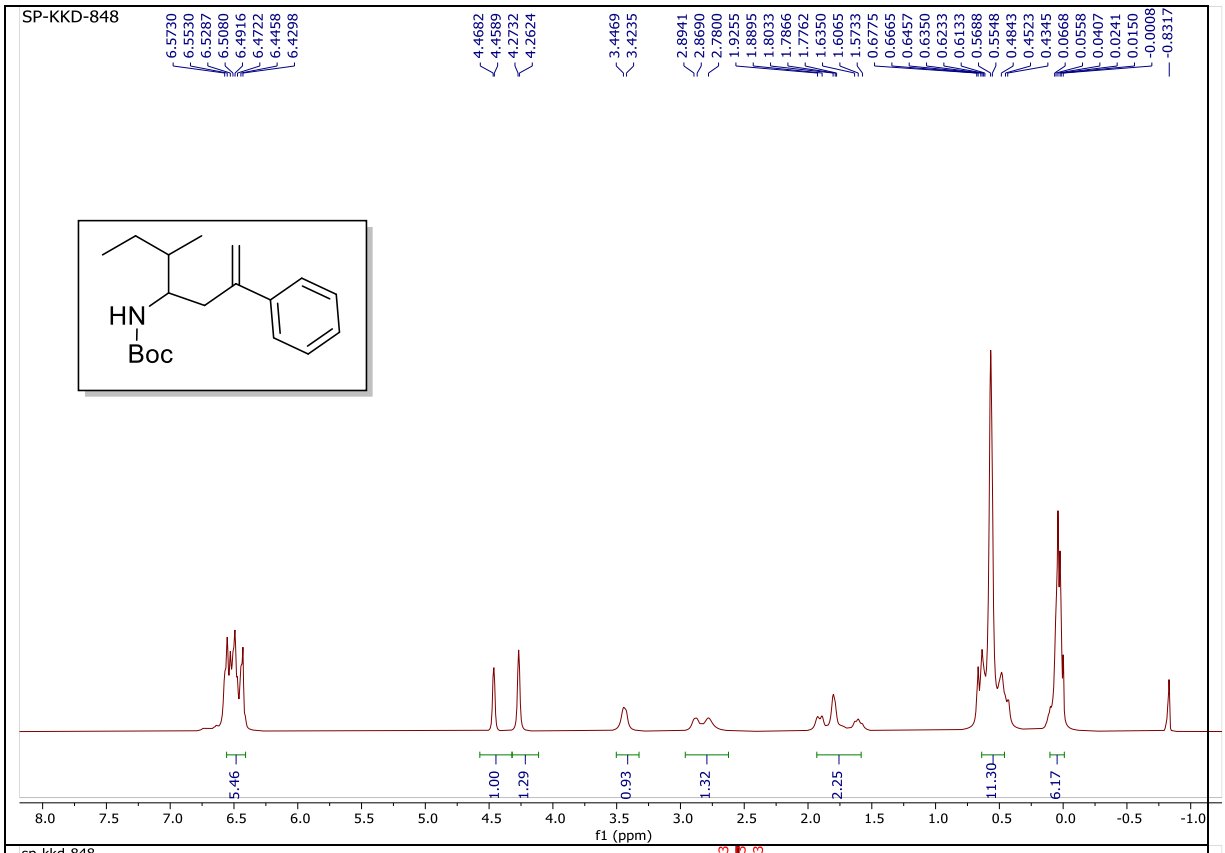

SP-KKD-804
HN
Boc
4.96
0.73
1.00
1.05
0.92
2.02
10.47
6.33
f1 (ppm)

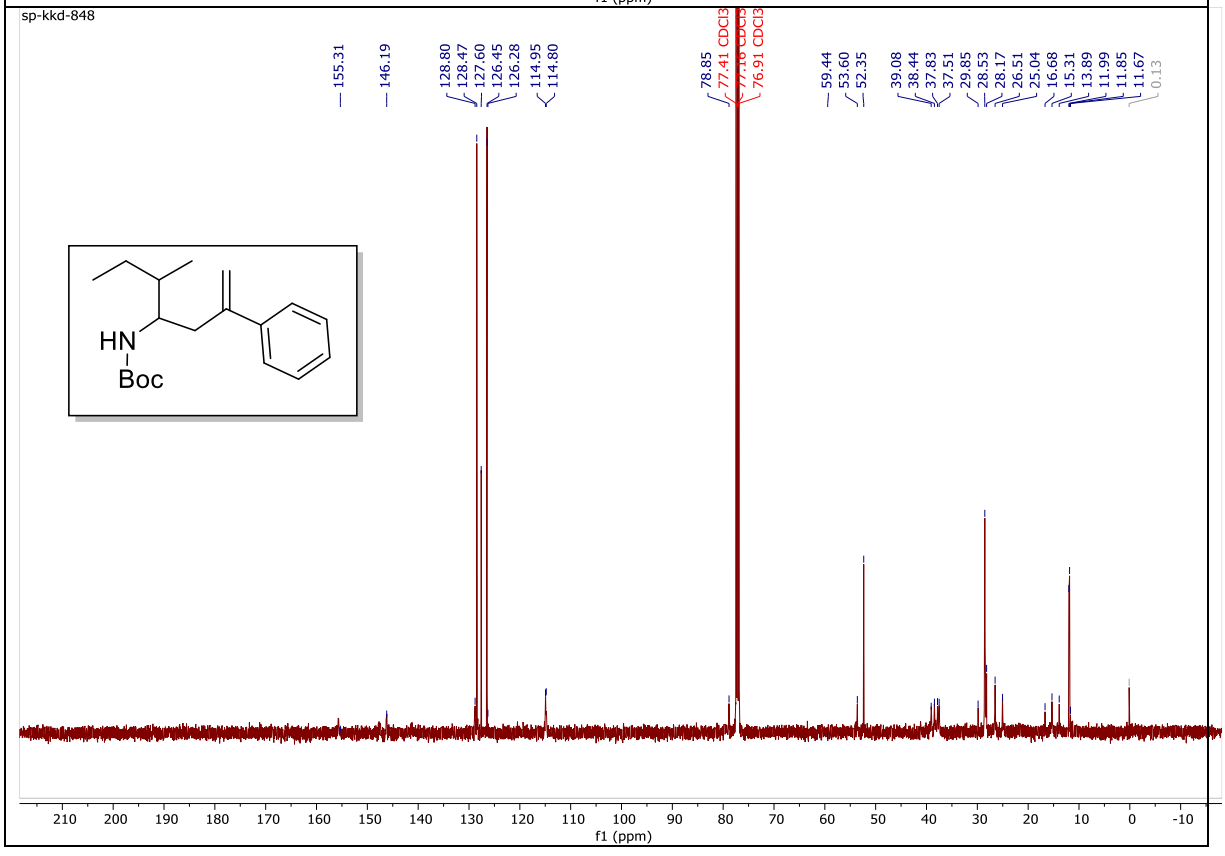

SP-KKD-804
155.71
146.17
141.08
128.46
127.59
126.44
114.92
78.85
77.81
77.16
76.91
53.59
50.98
39.06
38.43
37.83
37.06
29.84
28.53
26.51
25.03
17.80
13.88
7.21
HN
Boc
f1 (ppm)

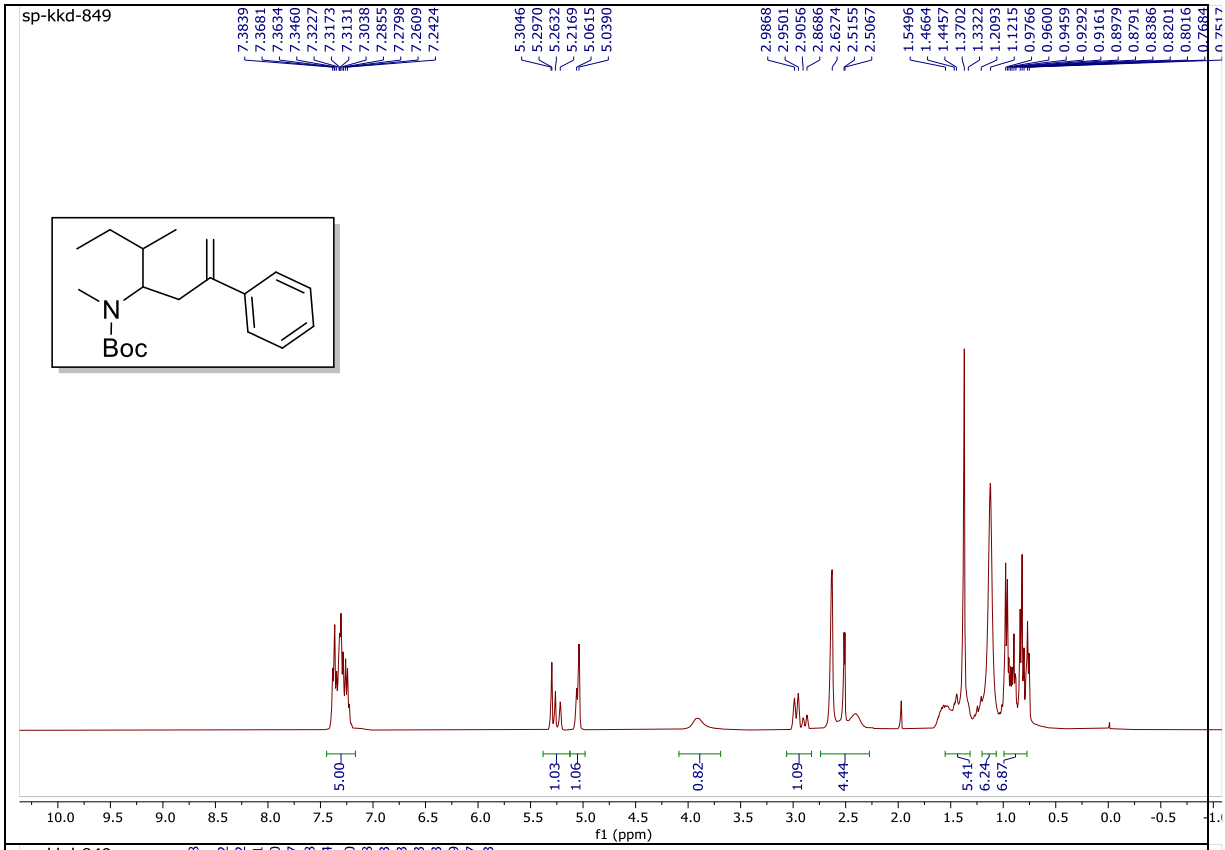

sp-kkd-804
7.3191
7.3082
7.2890
7.2706
7.2610
7.2505
7.2224
7.2049
7.1299
7.1110
5.3381
5.1134
4.3202
3.8649
2.7860
2.7707
2.7562
2.7334
2.7180
2.6959
2.6814
2.6121
1.4402
1.4294
1.3708
1.2584
0.0049
HN
Boc
10.42
0.97
0.84
0.68
0.99
3.80
9.24
f1 (ppm)
sp-kkd-804
155.37
145.67
140.28
138.43
129.62
128.53
128.46
127.71
126.45
126.41
120.45
119.56
115.36
80.14
77.41
77.16
76.91
50.76
40.78
40.23
28.48
HN
Boc
f1 (ppm)

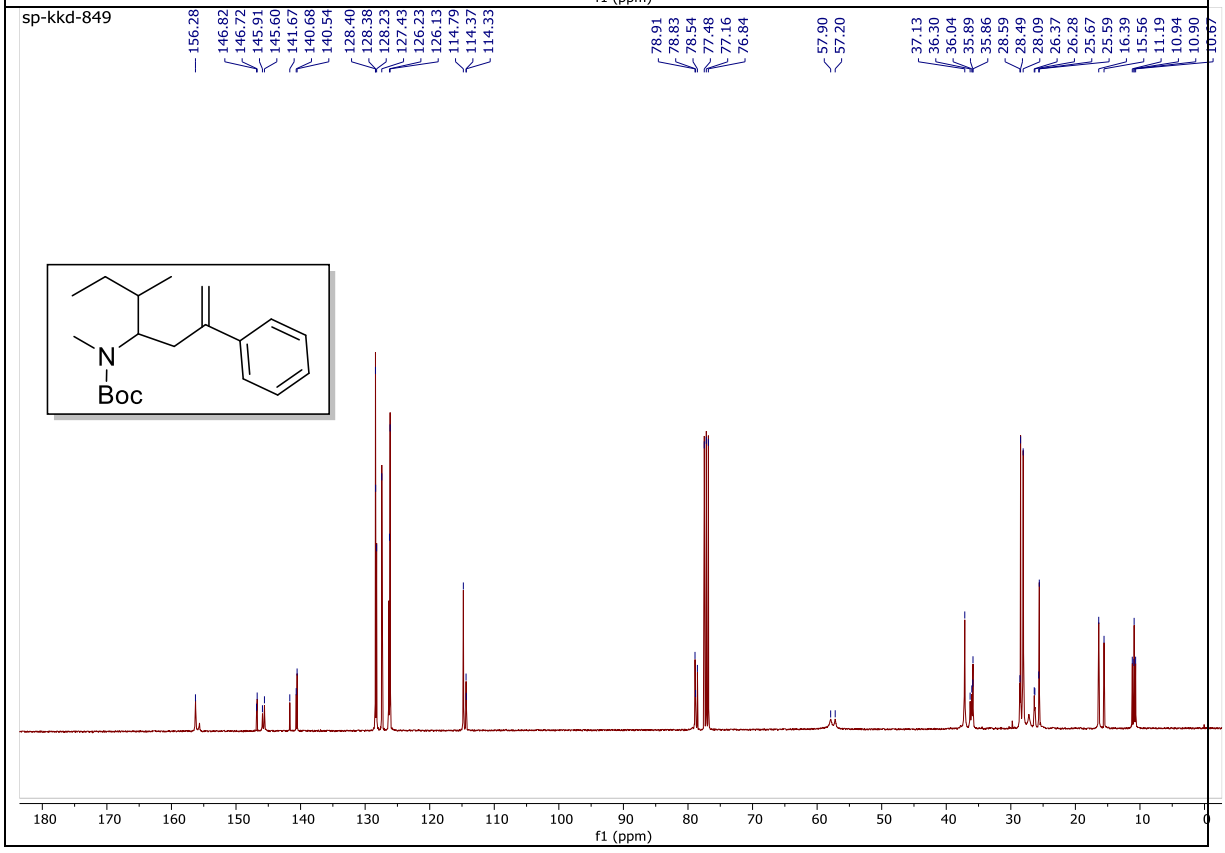

sp-kkd-810
7.4126
7.3895
7.3674
7.3318
7.3099
7.2883
7.2639
7.2426
5.3362
5.3159
5.1093
5.0887
4.3221
3.7192
2.7372
2.6748
2.6523
2.6323
2.5383
2.5250
2.5129
2.4934
2.4705
2.4349
2.4183
2.1114
2.0936
2.0824
2.0482
2.0285
2.0058
1.7824
1.6137
1.5897
1.3799
-0.0007
S
HN
Boc
5.36
0.94
1.05
0.71
0.90
1.89
2.41
3.44
1.18
1.34
9.49
f1 (ppm)

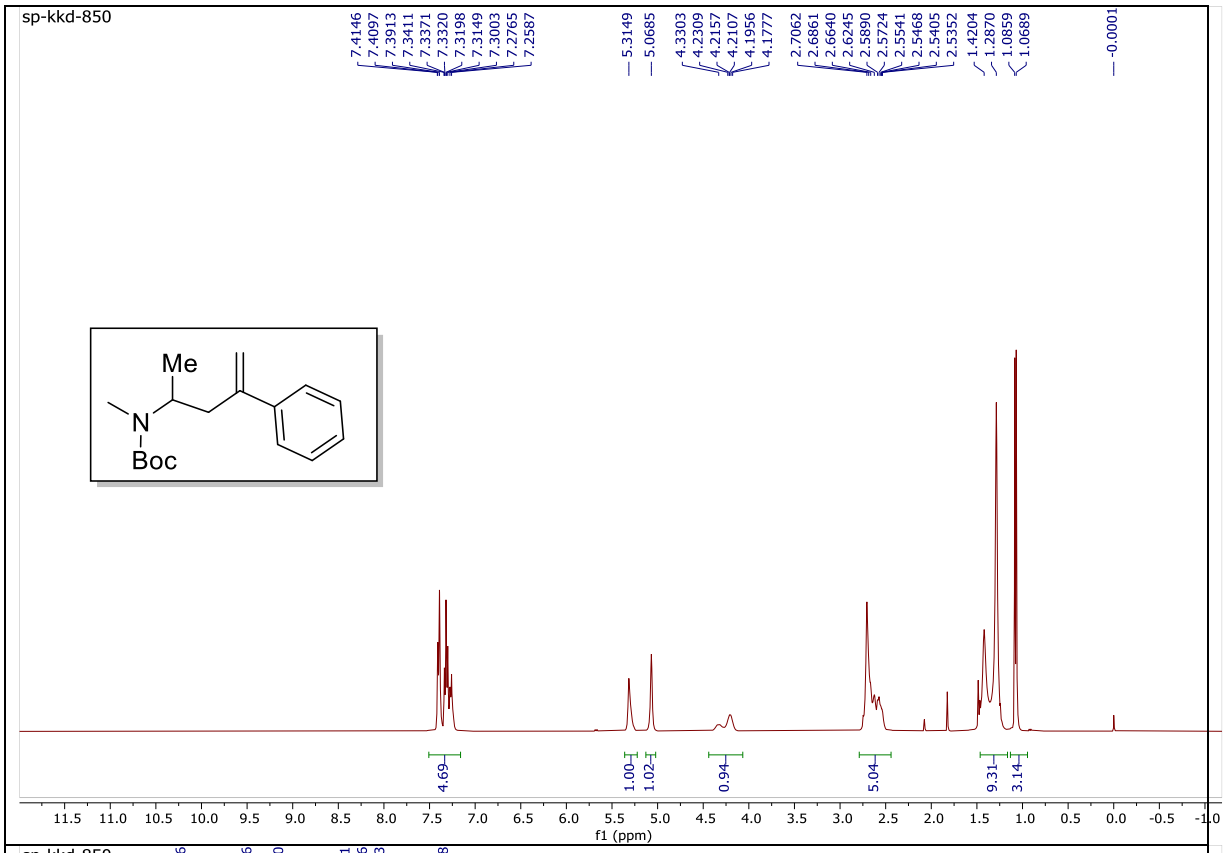

sp-kkd-810
155.50
145.42
140.94
128.59
127.77
126.39
115.51
79.22
77.42
77.16
76.91
49.26
41.23
34.45
30.81
28.51
15.62
S
HN
Boc
f1 (ppm)

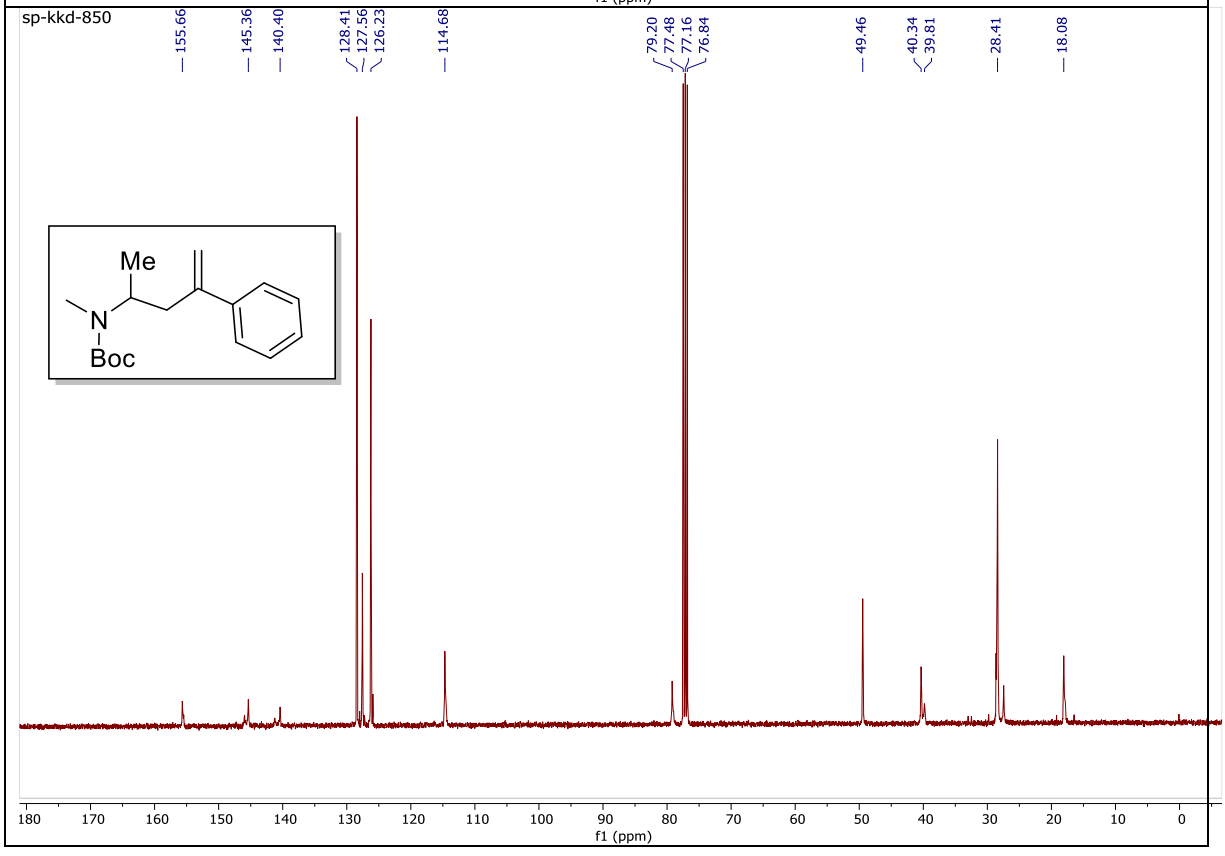

SP-KKD-848
6.5730
6.5530
6.5287
6.5080
6.4916
6.4722
6.4458
6.4298
4.4682
4.4589
4.2732
4.2624
3.4469
3.4235
2.8941
2.8690
2.7800
1.9255
1.8895
1.8033
1.7866
1.7762
1.6350
1.6065
1.5733
0.6775
0.6665
0.6457
0.6350
0.6233
0.6133
0.5688
0.5548
0.4843
0.4523
0.4345
0.0668
0.0558
0.0407
0.0241
0.0150
-0.0008
-0.8317
HN
Boc
5.46
1.00
1.29
0.93
1.32
2.25
11.30
6.17
f1 (ppm)

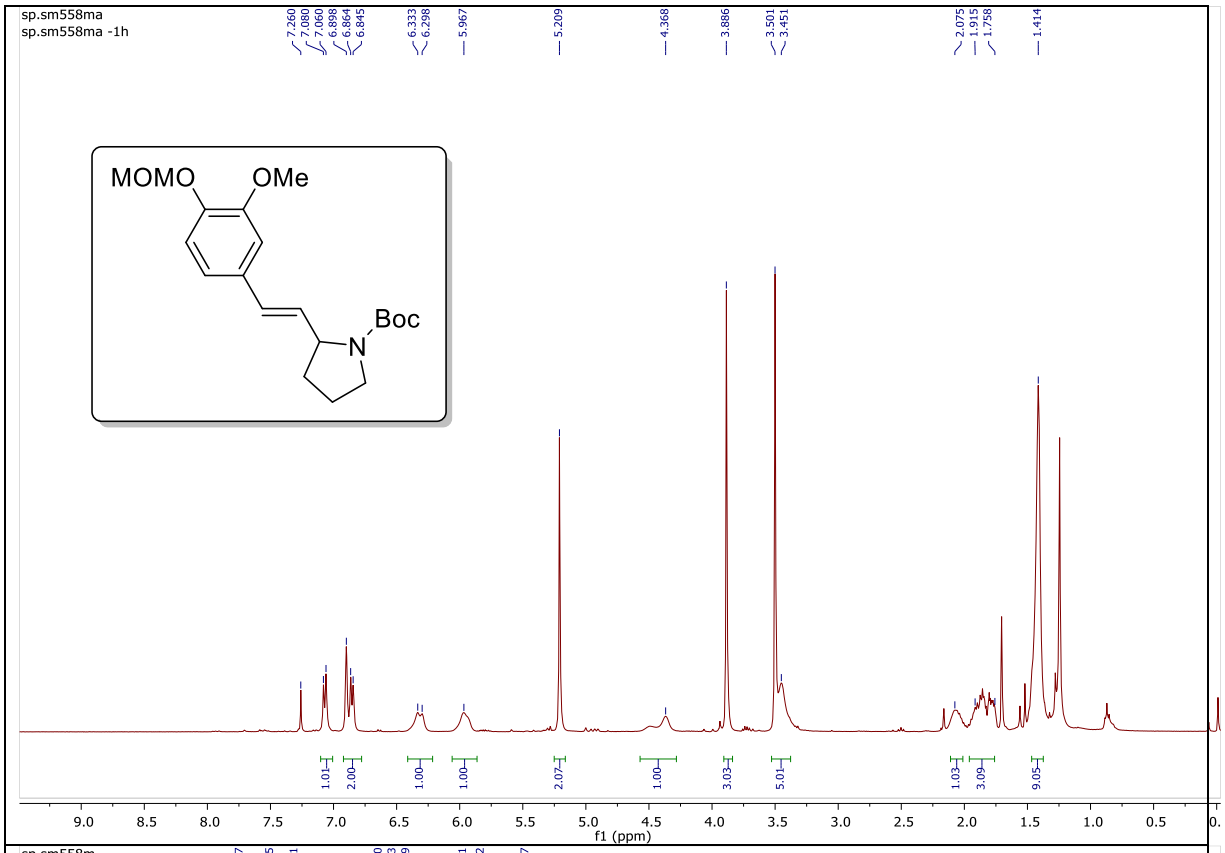

sp-kkd-848
155.31
146.19
128.80
128.47
127.60
126.45
126.28
114.95
114.80
78.85
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
59.44
53.60
52.35
39.08
38.44
37.83
37.51
29.85
28.53
28.17
26.51
25.04
16.68
15.31
13.89
11.99
11.85
11.67
0.13
HN
Boc
f1 (ppm)

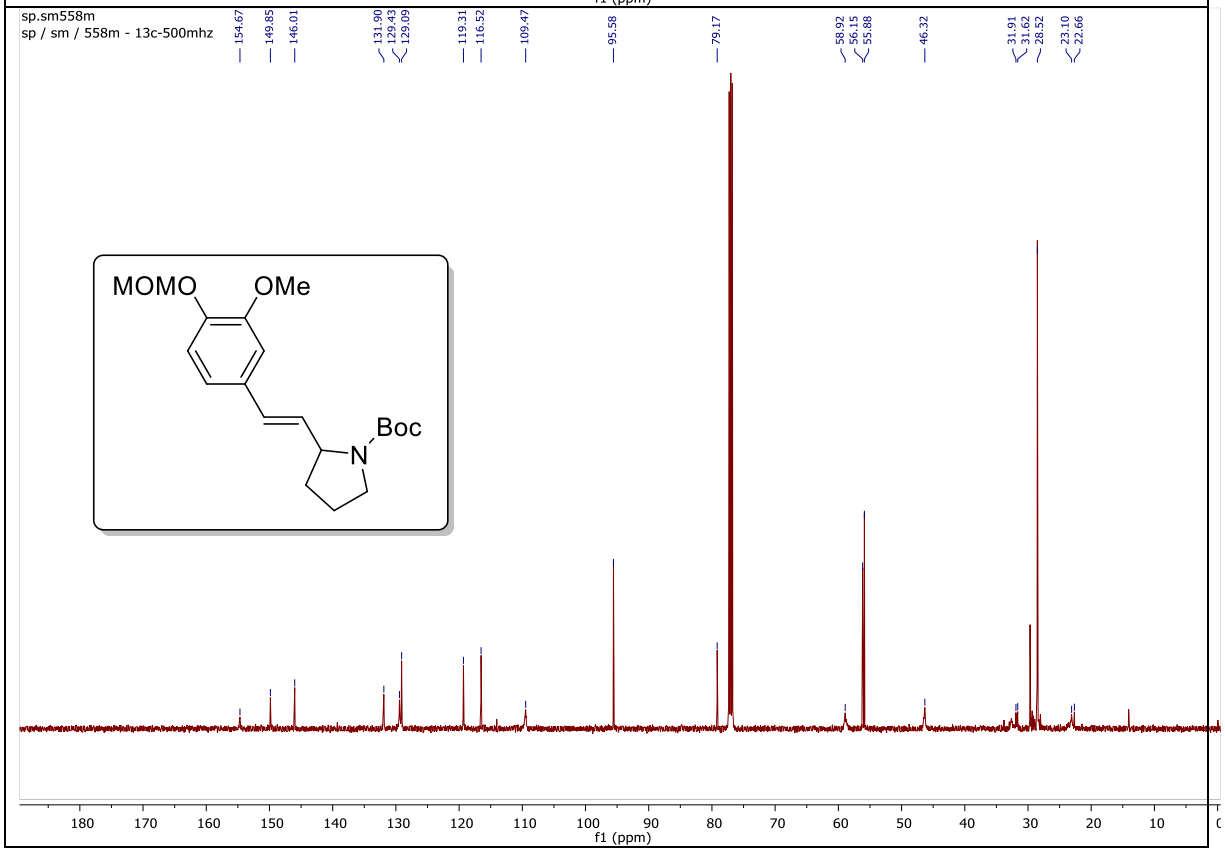

sp-kkd-849
7.3839
7.3681
7.3634
7.3460
7.3227
7.3173
7.3131
7.3038
7.2855
7.2798
7.2609
7.2424
5.3046
5.2970
5.2632
5.2169
5.0615
5.0390
2.9868
2.9501
2.9056
2.8686
2.6274
2.5155
2.5067
1.5496
1.4664
1.4457
1.3702
1.3322
1.2093
1.1215
0.9766
0.9600
0.9459
0.9292
0.9161
0.8979
0.8791
0.8386
0.8201
0.8016
0.7684
N
Boc
5.00
1.03
1.06
0.82
1.09
4.44
5.41
6.24
6.87
f1 (ppm)

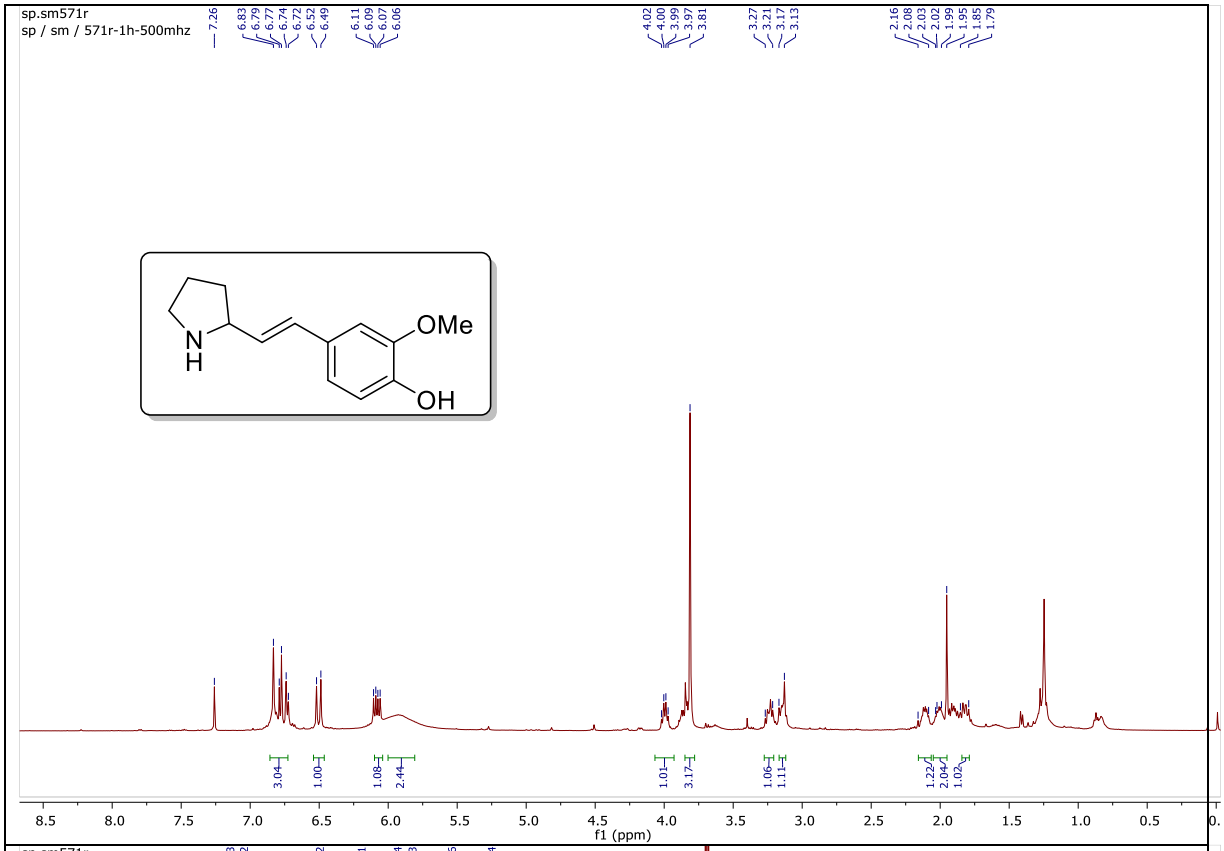

sp-kkd-849
156.28
146.82
146.72
145.91
145.60
141.67
140.68
140.54
128.40
128.38
128.23
127.43
126.23
126.13
114.79
114.37
114.33
78.91
78.83
78.54
77.48
77.16
76.84
57.90
57.20
37.13
36.30
36.04
35.89
35.86
28.59
28.49
28.09
26.37
26.28
25.67
25.59
16.39
15.56
11.19
10.94
10.90
10.67
N
Boc
f1 (ppm)

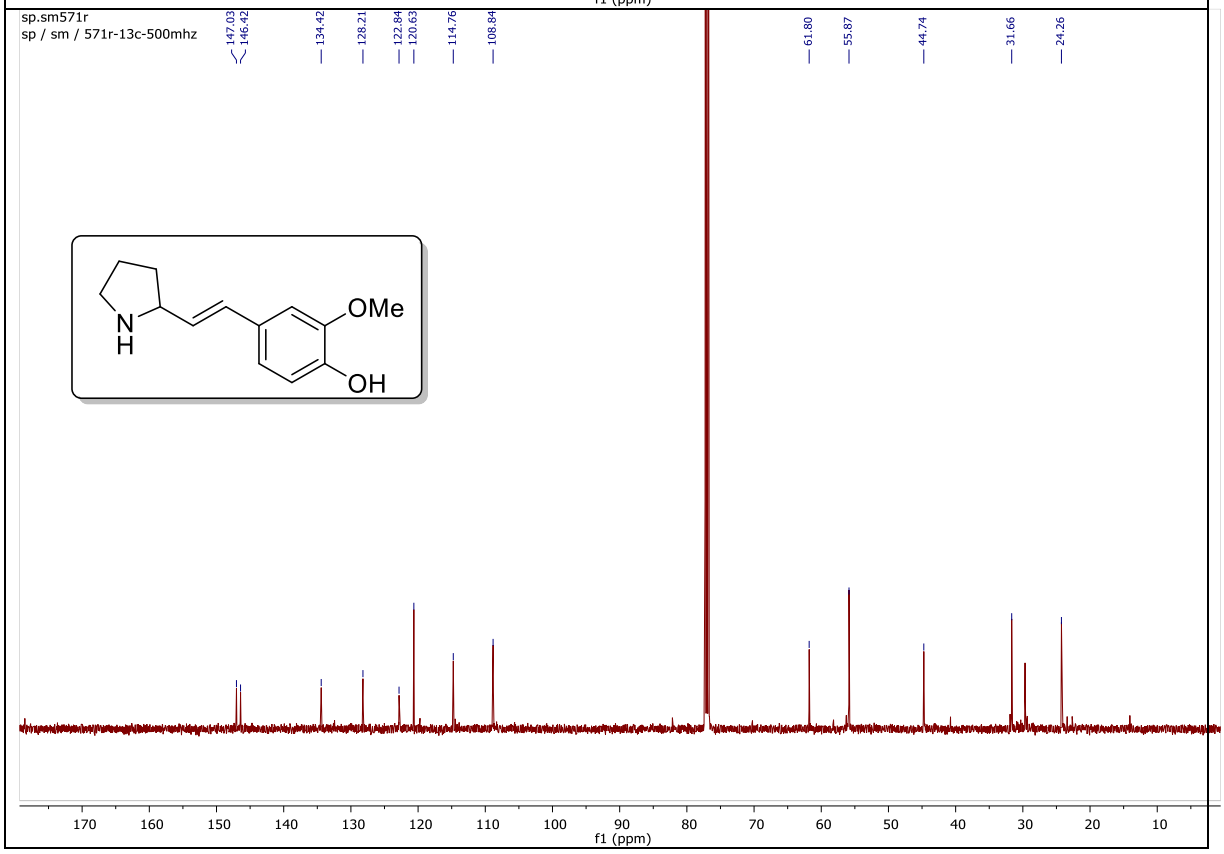

sp-kkd-850
7.4146
7.4097
7.3913
7.3411
7.3371
7.3320
7.3198
7.3149
7.3003
7.2765
7.2587
5.3149
5.0685
4.3303
4.2309
4.2157
4.2107
4.1956
4.1777
2.7062
2.6861
2.6640
2.6245
2.5890
2.5724
2.5541
2.5468
2.5405
2.5352
1.4204
1.2870
1.0859
1.0689
-0.0001
Me
N
Boc
4.69
1.00
1.02
0.94
5.04
9.31
3.14
f1 (ppm)

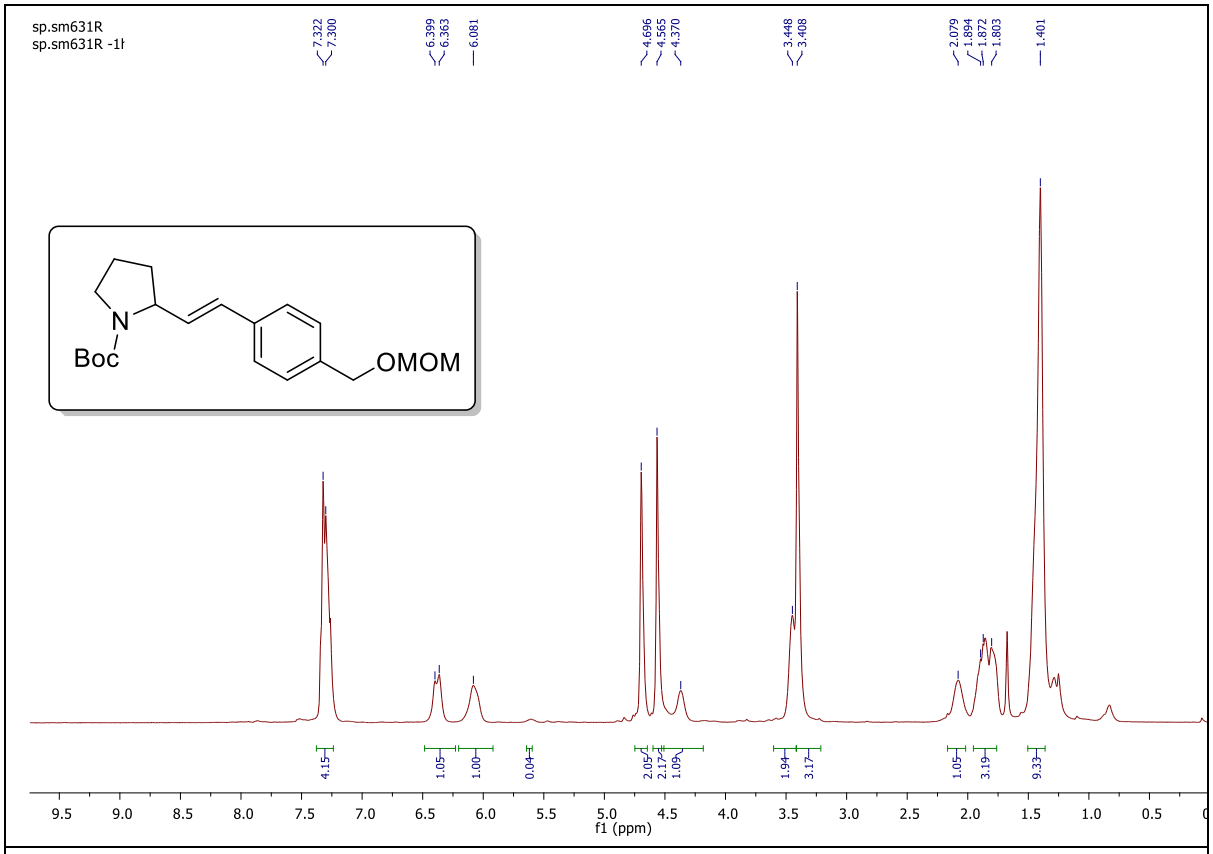

sp-kkd-850
155.66
145.36
140.40
128.41
127.56
126.23
114.68
79.20
77.48
77.16
76.84
49.46
40.34
39.81
28.41
18.08
Me
N
Boc
f1 (ppm)

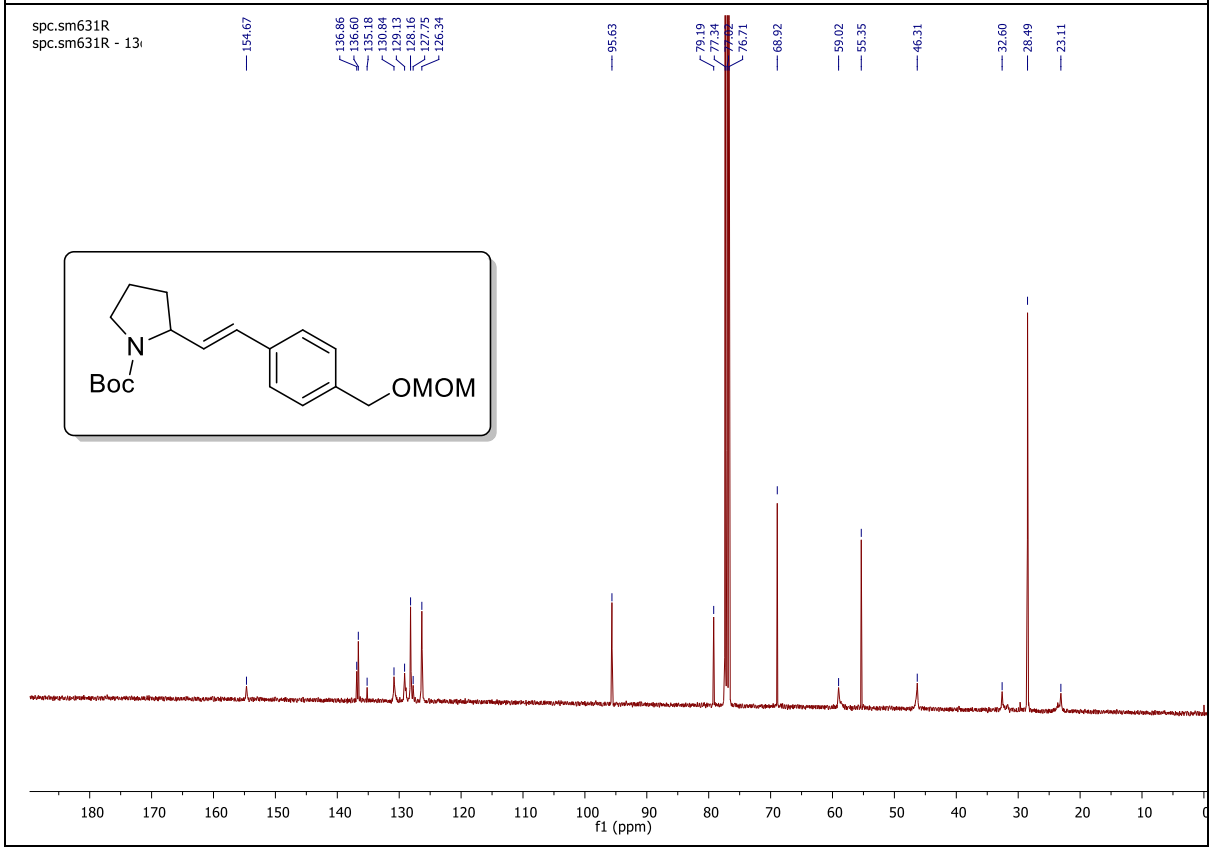

sp.sm558ma
sp.sm558ma -1h
MOMO
OMe
Boc
N
f1 (ppm)


sp.sm558m
sp / sm / 558m - 13c-500mhz
MOMO
OMe
Boc
N
f1 (ppm)


sp.sm571r
sp / sm / 571r-1h-500mhz
7.26
6.83
6.79
6.77
6.74
6.72
6.52
6.49
6.11
6.09
6.07
6.06
4.02
4.00
3.99
3.97
3.81
3.27
3.21
3.17
3.13
2.16
2.08
2.03
2.02
1.99
1.95
1.85
1.79
OMe
OH
3.04
1.00
1.08
2.44
1.01
3.17
1.06
1.11
1.22
2.04
1.02
f1 (ppm)


sp.sm571r
sp / sm / 571r-13c-500mhz
147.03
146.42
134.42
128.21
122.84
120.63
114.76
108.84
61.80
55.87
44.74
31.66
24.26
OMe
OH
f1 (ppm)


sp.sm631R
sp.sm631R -1ł
7.322
7.300
6.399
6.363
6.081
4.696
4.565
4.370
3.448
3.408
2.079
1.894
1.872
1.803
1.401
N
Boc
OMOM
4.15
1.05
1.00
0.04
2.05
2.17
1.09
1.94
3.17
1.05
3.19
9.33
f1 (ppm)


spc.sm631R
spc.sm631R - 13
154.67
136.86
136.60
135.18
130.84
129.13
128.16
127.75
126.34
95.63
79.19
77.34
76.71
68.92
59.02
55.35
46.31
32.60
28.49
23.11
N
Boc
OMOM
f1 (ppm)