Electronic supplementary information

Content

Syntheses of preussin until 2002

Syntheses of preussin until 2002 as analyzed by B. Basler S. Brandes, A. Spiegel, T. Bach in *Top. Curr. Chem.* **2005**, 243, 1:

[1] Syntheses of (+)-preussin starting from carbohydrates: a) C. S. Pak, G. H. Lee, *J. Org. Chem.* **1991**, *56*, 1128. b) H. Yoda, H. Yamazaki, K. Takabe, *Tetrahedron: Asymmetry* **1996**, *7*, 373. c) P. de Armas, F. García-Tellado, J. J. Marrero-Tellado, J. Robles, *Tetrahedron Lett.* **1998**, *39*, 131.

[2] Syntheses of (+)-preussin starting from L-phenylalanin: a) P. L. McGrane, T. Livinghouse, *J. Am. Chem. Soc.* **1993**, *115*, 11485. b) M. Overhand, S. M. Hecht, *J. Org. Chem.* **1994**, *59*, 4721. c) W. Deng, L. E. Overman, *J. Am. Chem. Soc.* **1994**, *116*, 11241. d) C. Beier, E. Schaumann, *Synthesis* **1997**, 1296. e) G. Veeresa, A. Datta, *Tetrahedron* **1998**, *54*, 15673. f) K.-Y. Lee, Y.-H. Kim, C.-Y. Oh, W.-H. Ham, *Org. Lett.* **2000**, *2*, 4041. g) M. Okue, H. Watanabe, T. Kitahara, *Tetrahedron* **2001**, *57*, 4107. h) A. Krasinski, H. Gruza, J. Jurczak, *Heterocycles* **2001**, *54*, 581. I) M. Okue, H. Watanabe, K. Kasahara, M. Yoshida, S. Horinouchi, T. Kitahara, T. *Biosci. Biotechnol. Biochem.* **2002**, *66*, 1093.

[3] Synthesis to four diastereomers of preussin starting from *D*-phenylalanin: M. Shimazaki, F. Okazaki, F. Nakajima, T. Ishikawa, A. Ohta, *Heterocycles* **1993**, *36*, 1823-1836.

[4] Syntheses of (+)-preussin starting from *L*-asparaginic acid: a) I. Kadota, M. Kawada, S. Saya, Y. Yamamoto, *Tetrahedron Lett.* **1996**, *37*, 2109. b) I. Kadota, S. Saya, Y. Yamamoto, *Heterocycles* **1997**, *46*, 335.

[5] Syntheses of (+)-preussin starting from *L*-glutaminic acid: a) T. Bach, H. Brummerhop, *Angew. Chem.* **1998**, *110*, 3577; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3400. b) T. Bach, H. Brummerhop, K. Harms, *Chem. Eur. J.* **2000**, *6*, 3838.

[6] Syntheses of (+)-preussin starting from *L*-serin: J. J. Caldwell, D. Craig, S. P. East, *Synlett* **2001**, 1602.

[7] Asymmetric syntheses of (+)-preussin: a) R. Verma, S. K. Ghosh, *Chem. Commun.* **1997**, 1601. b) R. Verma, S. K. Ghosh, *J. Chem. Soc., Perkin Trans. 1* **1999**, 265. b) H.-Q. Dong, G.-Q Ling, *Chin. Chem. Lett.* **1997**, *8*, 693. c) H.-Q. Dong, G.-Q Ling, *Chin. Chem. Lett.* **1998**, *9*, 458.

[8] Auxilliary-based syntheses: a) A. Kanazawa, S. Gillet, P. Delair, A. E. Greene, *J. Org. Chem.* **1998**, *63*, 4660.

General Information

Reactions were generally performed under argon in flame-dried flasks and the components were added by syringe. Solvents were dried using standard procedures (abbreviations in the following text: DMSO = dimethylsulfoxide, THF = tetrahydrofuran). Reagents were purchased and used without further purification. Potassium *t*-butoxide was freshly sublimed in vacuo before use.

Products were purified by flash chromatography on neutral aluminum oxide (neutral, 6% water, activity III, Merck-Schuchardt or Fluka) or on silica gel (32-63 µm, Merck-Schuchardt or Fluka). HPLC was performed with nucleosil 50-5 columns (dimensions: analytical, 4x245 mm; preparative, 16x244 mm or 32x237 mm); detection by Knauer variable UV detector (λ = 255 nm) and Knauer refractometer. Unless otherwise stated, yields refer to analytically pure samples.

^{1}H NMR [$CHCl_3$ (δ = 7.26 ppm), TMS (δ = 0.00 ppm) as internal standard] and ^{13}C NMR spectra [$CDCl_3$ (δ = 77.0 ppm) as internal standard] were recorded with Bruker WH 270 and DRX 500 instruments in $CDCl_3$ solutions. Integrals are in accordance with assignments; coupling constants are given in Hz. Multiplicity of signals is indicated as follows: s (singlet), s_{br} (broad singlet), d (doublet), br d (broad doublet), dd (doublet of doublet), t (triplet), m (multiplet), m_c (centered multiplet). ^{1}H/^{13}C-correlated spectra (HSQC, HMBC) and ^{1}H/^{1}H-correlated spectra (COSY, NOESY) were recorded for assignments. Optical rotations $[\alpha]_D$ were measured with a Perkin Elmer 241 polarimeter in a 1 mL microcuvette at the temperature given. IR spectra were measured with Nicolet 5 SXC FTIR or Nicolet 205 FTIR spectrometers. MS analyses were performed with MAT 711, MAT 112 S and with HP 5890 II instruments. The elemental analyses were recorded with “Elemental-Analyzers” (Perkin-Elmer or Carlo Erba). Melting points were measured with a Reichert apparatus (Thermovar) or a Gallenkamp apparatus (MPD 350) and are uncorrected.

General procedure for the addition of lithiated alkoxyallenes to aldehydes or imines (GP1): For generation of the lithiated alkoxyallene, the corresponding alkoxyallene was dissolved in THF and *n*-butyllithium was added at -40 °C. After 30 min, the solution was cooled to -80 °C and the corresponding electrophile was added. The mixture was allowed to warm up to -30 °C and stirred for the time given in the individual experiments. After quenching with saturated aqueous $NaHCO_3$ solution (10 mL/), the organic phase was separated and the aqueous phase was extracted with diethyl ether (3 x 15 mL/mmol of alkoxyallene). The combined organic phases were dried (Na_2SO_4), filtered and evaporated in vacuo to provide the crude product that was used directly or purified as given in the individual experiment. The yields refer to the amount of electrophile used.

General procedure for silver nitrate-promoted cyclization (GP2): To a solution of the corresponding allenyl alcohol or amine in acetonitrile (5 mL/mmol) were added under a stream of argon via a funnel potassium carbonate and silver nitrate. The resulting mixture was stirred at room temperature under light exclusion for 12 h, then filtered and evaporated. The residue was dissolved in a small amount ethyl acetate and filtered through a pad of Celite (elution with ethyl acetate). After removal of the solvents in vacuo, the crude product was purified as indicated in the individual experiments.

***N*-(3-Methoxy-1-phenylpenta-3,4-dien-2-yl)-*p*-toluenesulfonamide (10):** According to **GP1**, methoxyallene **7**[1] (0.12 mL, 1.44 mmol), *n*-butyllithium (0.59 mL, 1.44 mmol of 2.44 M solution in hexanes) and **9** (0.308 g, 0.72 mmol) in THF (15 mL) provided after 2 h crude **10** (0.237 g) as light yellow solid (melting range 80-90 °C, decomposition). The product was not purified but directly used in the cyclization step. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.39 (s, 3 H, Tos-Me), 2.90, 2.96 (AB part of ABX system, J_{AB} = 13.8 Hz, J_{AX} = 7.4 Hz, J_{BX} = 6.3 Hz, 1 H each, 1-H), 3.12 (s, 3 H, OMe), 4.05–4.17 (m, 1 H, 2-H), 4.83 (d, *J* = 9.6 Hz, 1 H, NH), 5.03, 5.08 (AB system, J_{AB} = 7.4 Hz, 2 H, 5-H), 7.08 (d, *J* = 8.1 Hz, 2 H, Tos), 7.18–7.35 (m, 5 H, Ph), 7.65 ppm (d, *J* = 8.1 Hz, 2 H, Tos). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 21.4 (q, Tos-Me), 39.9 (t, C-1), 55.9, 56.2 (q, d, OMe, C-2), 91.8 (t, C-5), 126.5, 127.2, 128.1, 129.1, 129.5 (5 d, Ph, Tos), 130.9 (s, C-3), 136.6, 137.8, 143.0 ppm (3 s, Ph, Tos), 197.1 (s, C-4). IR (KBr): $\tilde{\nu}$ = 3260 (N-H), 3065–2830 (C-H), 1960 (C=C=C), 1325, 1160 cm^{-1} (Tos-N). MS (EI, 80 eV): *m/z* (%) = 343 (0.3) [M^+], 274 (2) [BnCHNHTos$^+$], 252 (36) [M^+ - Bn], 172 (49), 155 (24), 91 (100) [Bn^+].

2-Benzyl-3-methoxy-1-tosyl-2,5-dihydropyrrole (11): According to **GP2**, crude allenyl amine **10** (0.300 g, 0.88 mmol) in acetonitrile (10 mL) was treated with $AgNO_3$ (0.029 g, 0.17 mmol) and K_2CO_3 (0.243 g, 1.76 mmol) for 12 h to provide crude **11**. Purification by column chromatography (silica gel, hexanes/ethyl acetate 8:1) furnished **11** (0.180 g, 60%) as colorless crystals (m.p. 128 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.43 (s, 3 H, Tos-Me), 3.01, 3.31 (AB part of ABX system, J_{AB} = 13.4 Hz, J_{AX} = 2.6 Hz, J_{BX} = 4.4 Hz, 1 H each, PhCH_2), 3.50 (s, 3 H, OMe), 3.52 (dd, *J* = 12.5 Hz, *J* = 5.0 Hz, 1 H, 5-H) 3.81 (dd, *J* = 12.5 Hz, *J* = 1.7 Hz, 1 H, 5-H), 4.14 (s_{br}, 1 H, 4-H), 4.45–4.55 (m, 1 H, 2-H), 7.17–7.32 (m, 5 H, Ph), 7.32, 7.73 ppm (2 d, *J* = 8.1 Hz, 2 H each, Tos). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 21.5 (q, Tos-Me), 38.9 (t, Ph*C*H$_2$), 52.4 (t, C-5), 56.6 (q, OMe), 64.3 (d, C-2), 90.0 (d, C-4), 126.1, 127.3, 127.6, 129.7, 130.4 (5 d, Ph, Tos), 134.3, 136.2, 143.4 (3 s, Ph, Tos),154.4 ppm (s, C-3). IR (KBr): $\tilde{\nu}$ = 3030–

2860 (C-H), 1670 (C=C), 1335, 1165 cm^{-1} (Tos-N). $C_{19}H_{21}NO_3S$ (343.4): calcd. C 66.45, H 6.16, N 4.08; found C 6

Attempt to epimerize *trans*-14 into *cis*-14: *trans*-**14** (0.011 g, 0.02 mmol) was dissolved in dichloromethane (4 mL) and stirred with DBU (0.033 g, 0.2 mmol) for 2 h at room temperature. The proceeding of the reaction was followed by TLC. The mixture was filtered through a short pad of silica gel (elution with hexanes/ethyl acetate 4:1) and after evaporation of the solvents a yellow oil (0.007 g) was obtained, that was identified as a mixture of *cis*-**14** and compound **15** (ratio ca. 1:1).

Conversion of *cis*-14 into compound 15 and 16: *cis*-**14** (0.016 g, 0.04 mmol) was dissolved in dichloromethane (15 mL) and stirred with DBU (0.1 g, 0.66 mmol) for 5.5 h at room temperature. The proceeding of the reaction was followed by TLC. The mixture was filtered through a short pad of silica gel (elution with hexanes/ethyl acetate 3:1) and after evaporation of the solvents a yellow oil (0.005 g, ca. 48%) was obtained. ^{1}H NMR analysis showed that a mixture of **15** and **16** (ratio ca. 3:1, **16** as 1:1 mixture of *E*/*Z* isomers). ^{1}H NMR ($CDCl_3$, 270 MHz), signals of **15**: δ = 0.89 (t, *J* = 7.0 Hz, 3 H, Me), 0.90–1.50 (m, 16 H, CH_2), 2.05, 2.53 (AB part of ABX system, J_{AB} = 19.9 Hz, J_{AX} = 2.5 Hz, J_{BX} = 5.9 Hz, 1 H each, 4-H), 3.82 (s, 2 H, PhC*H*$_2$), 4.20–4.32 (m, 1 H, 5-H), 7.20–7.40 ppm (m, 5 H, Ph); characteristic signals of the *E*/*Z* isomers of **16**: (*E*/*Z* ca. 1:1): δ = 2.25, 2.72 (AB system of ABX system, J_{AB} = 18.4 Hz, J_{AX} = 5.9 Hz, J_{BX} = 6.6 Hz, 1 H each, 4-H), 4.98 (s, 1 H, NH), 5.10 (d, *J* = 4.1 Hz, 1 H, NH), 6.07 (s, 0.5 H, =CPh*H*), 6.60 ppm (d, *J* = 4.1 Hz, 0.5 H, =CPh*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz), signals of **15**: δ = 14.2 (q, Me), 22.6, 26.1, 29.3*, 29.5*, 31.9, 33.9, 36.3, 40.1 (8 t, CH_2, Ph*C*H_2, C-4), 65.3 (d, C-5), 126.7, 128.6, 128.8, 131.0 (3 d, s, Ph), 171.4 (s, C-2), 203.0 ppm (s, C-3); * signals with higher intensity; the signals of *E*/*Z*-**16** are too weak to be unambiguously identified in this mixture. MS (EI, 80 eV): *m/z* (%) = 299 (1) [M^+], 298 (14) [M^+ - H], 297 (38), 198 (36), 185 (57), 57 (89). 44(100).

2-Benzyl-3-methoxy-5-nonyl-2,5-dihydropyrrole (*cis*-17): A solution of sodium naphthalenide (0.63 mL of a 1 M solution in DME, prepared according to ref. 2) was added to a solution of *cis*-**14** (0.099 g, 0.21 mmol) in DME (10 mL) at -78 °C. After 1 h the mixture was quenched with water (5 mL) and concentrated in vacuo. The residue was taken up in saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried (Na_2SO_4), filtered and evaporated in vacuo to obtain the crude product (0.150 g) as yellow solid. Purification by column chromatography (alumina III, hexanes/ethyl acetate 10:1 + 1% of NEt_3) gave *cis*-**17** (0.050 g, 75%) as yellow oil. ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.81 (t, *J* = 6.3 Hz, 3 H, Me), 1.00–1.30 (m, 16 H, CH_2), 1.42 (s_{br}, 1 H, NH), 2.63, 2.93 (AB part of ABX system, J_{AB} = 14.0 Hz, J_{AX} = 7.4 Hz, J_{BX} = 3.7 Hz, 1 H each, PhC*H*$_2$), 3.58 (s, 3 H, OMe), 3.65–3.72, 3.95–4.05 (2 m, 1 H each, 2-H, 5-H), 4.46 (s, 1 H, 4-H), 7.08–7.25 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 14.1 (q, Me), 22.7, 26.1, 29.3, 29.6*, 29.7, 31.9, 38.8 (7 t, CH_2), 40.7 (t, Ph*C*H_2), 57.0 (q, OMe), 61.4, 63.0 (2 d, C-2, C-5), 97.2 (d, C-4), 126.1, 128.1, 129.6, 138.6 (3 d, s, Ph), 159.9 ppm (s, C-3); * signal with higher intensity. IR (film): $\tilde{\nu}$ = 3400 (N-H), 3060, 3025, 2925, 2855 (C-H), 1655 cm^{-1} (C=C). MS (FAB): *m/z* (%) = 316 (81) [M^+ + H], 284 (14) [M^+ - OMe], 224 (52) [M^+ - Bn], 188 (23) [$C_9H_{19}^+$], 91 (100) [Bn^+]. $C_{21}H_{33}NO$ (315.5): calcd. C 79.95, H 10.54, N 4.44; found C 79.34, H 10.51, N 4.08.

Reaction of (-)-preussin with Mosher´s chloride:

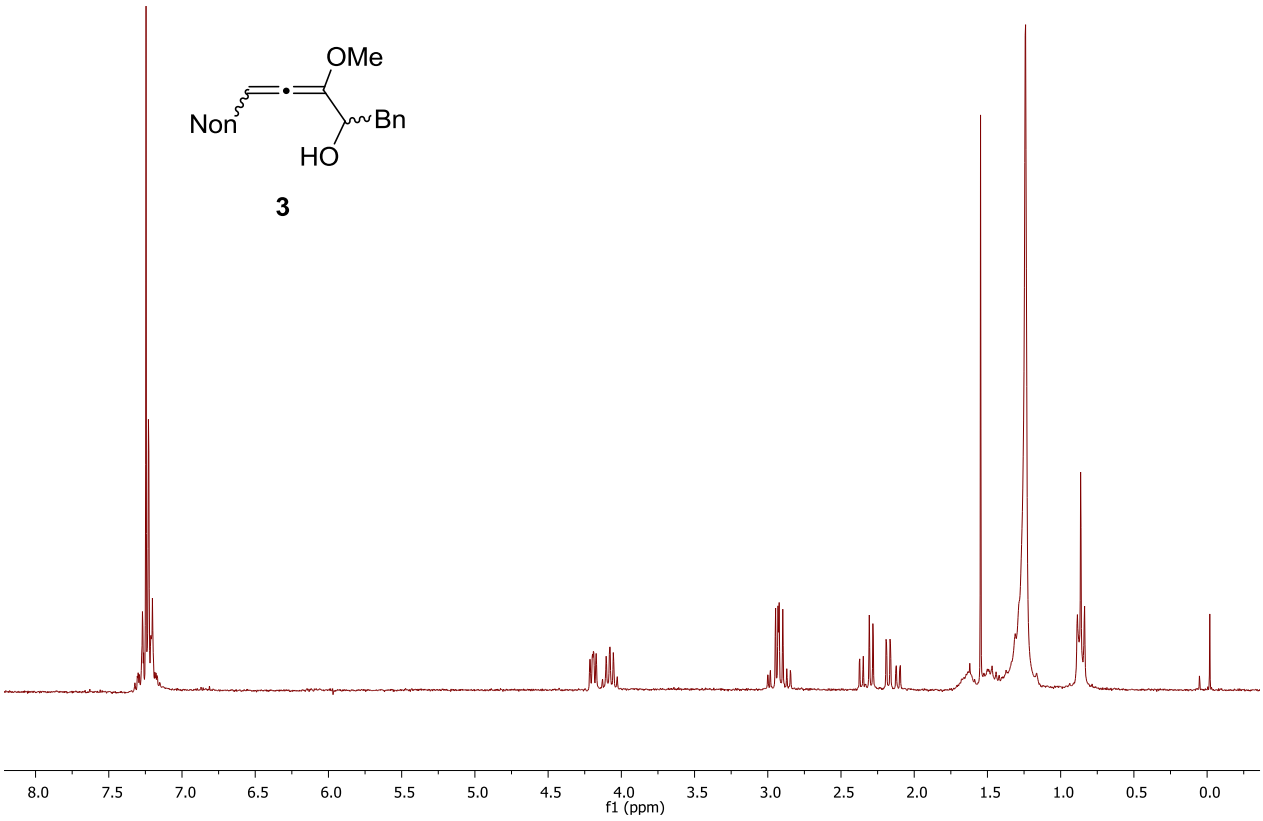
To a solution of (-)-preussin (8.3 mg, 26 μmol) in a 1:1 mixture of dichloromethane and pyridine (1 mL) Mosher's chloride (14 mg, 54 μmol) was added dropwise. After 3 d of stirring dichloromethane was added (5 mL) and the solution was extracted with aqueous 2 M HCl (2 x 5 mL), with saturated aqueous $NaHCO_3$ solution (2 x 5 mL) and water (5 mL). The organic phase was dried (Na_2SO_4), filtered and evaporated in vacuo to give the crude product (10 mg) as orange oil. ^{1}H NMR spectroscopy indicated a conversion of ca. 30% and analytical HPLC showed that the formed Mosher´s ester product is diastereomerically pure. Purification by HPLC (hexanes/ethyl acetate 95:5) provided pure product (4 mg, 28 %). ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.89 (t, *J* = 6.8 Hz, 3 H, Me), 1.15–1.40 (m, 14 H, CH_2), 1.46 (ddd, *J* = 14.6 Hz, *J* = 7.8 Hz, *J* = 2.4 Hz, 1 H, 4-H), 1.65–1.75, 2.10–2.20 (2 m, 1 H each, CH_2), 2.28 (s, 3 H, NMe), 2.40–2.55, 2.67–2.80 (2 m, 5 H, $PhCH_2$, 2-H, 4-H, 5-H), 3.61 (s, 3 H, OMe), 6.87–6.93, 7.09–7.14, 7.40–7.45, 7.57–7.63 ppm (4 m, 2 H, 3 H, 3 H, 2 H, Ar).

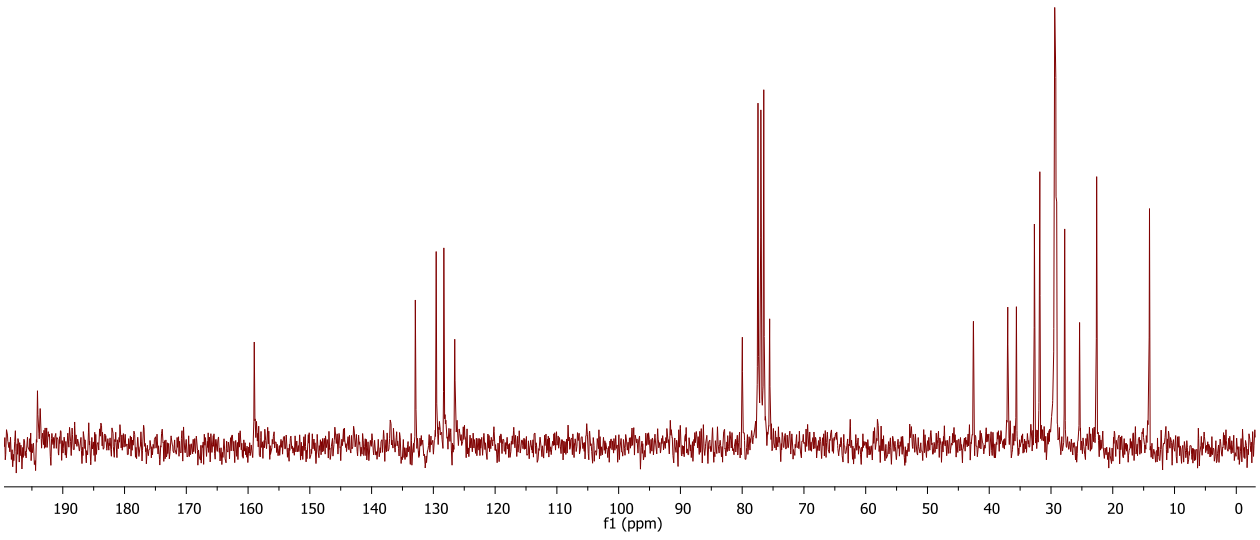
References

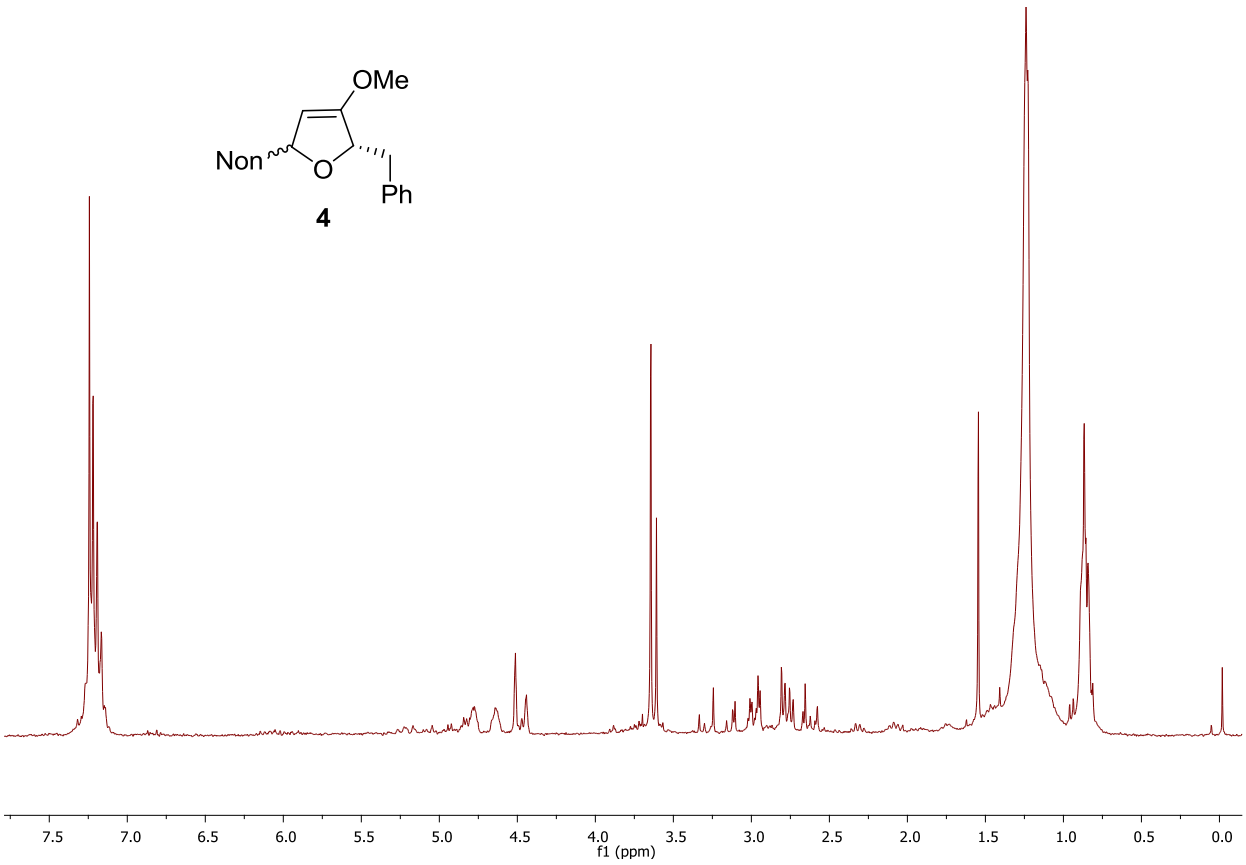
[1] a) S. Hoff, L. Brandsma, J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916. b) F. J. Weiberth, S. S. Hall, *J. Org. Chem.* **1985**, *50*, 5308.

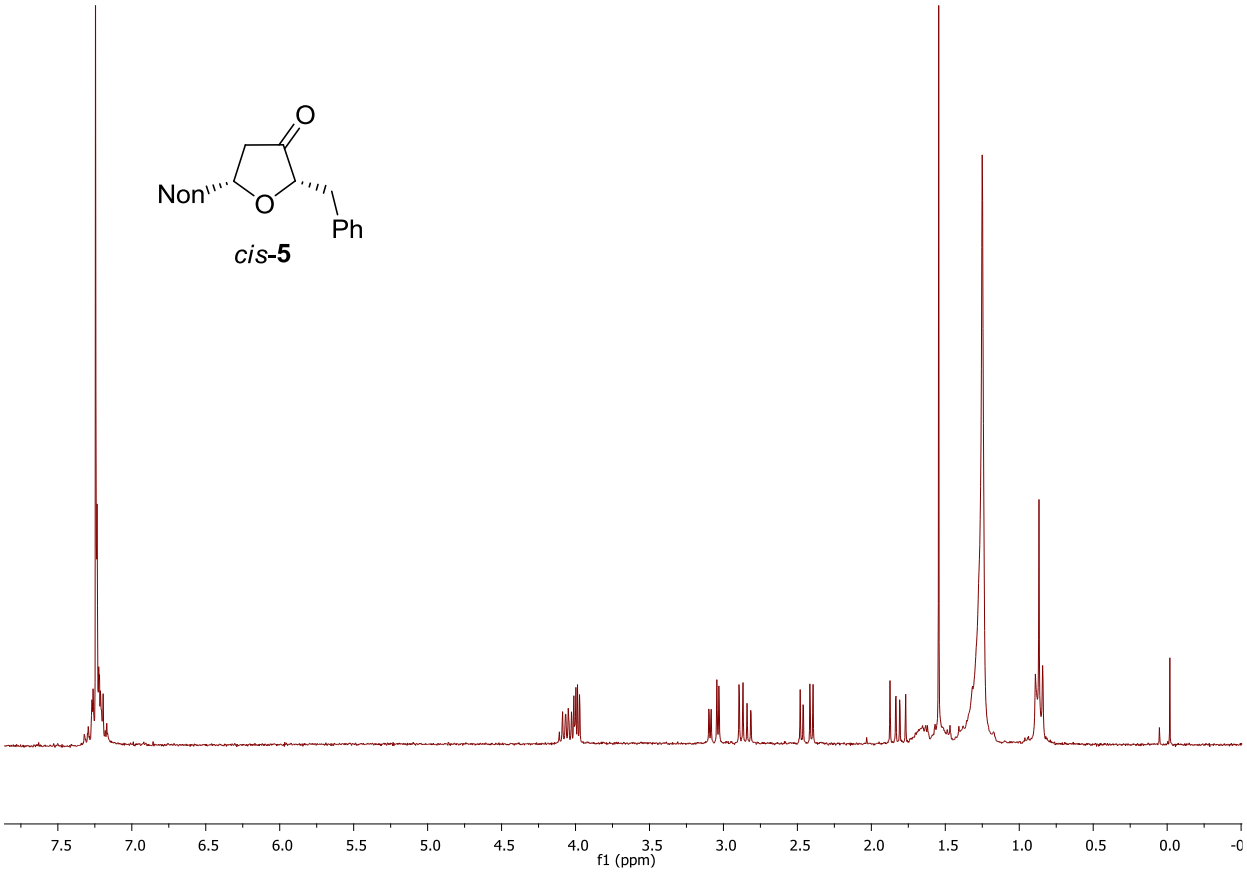
[2] A. B. Smith, T. A. Rano, N. Chida, A. G. Sulikowski, J. L. Wood, *J. Am. Chem. Soc.* **1992**, *114*, 8008.

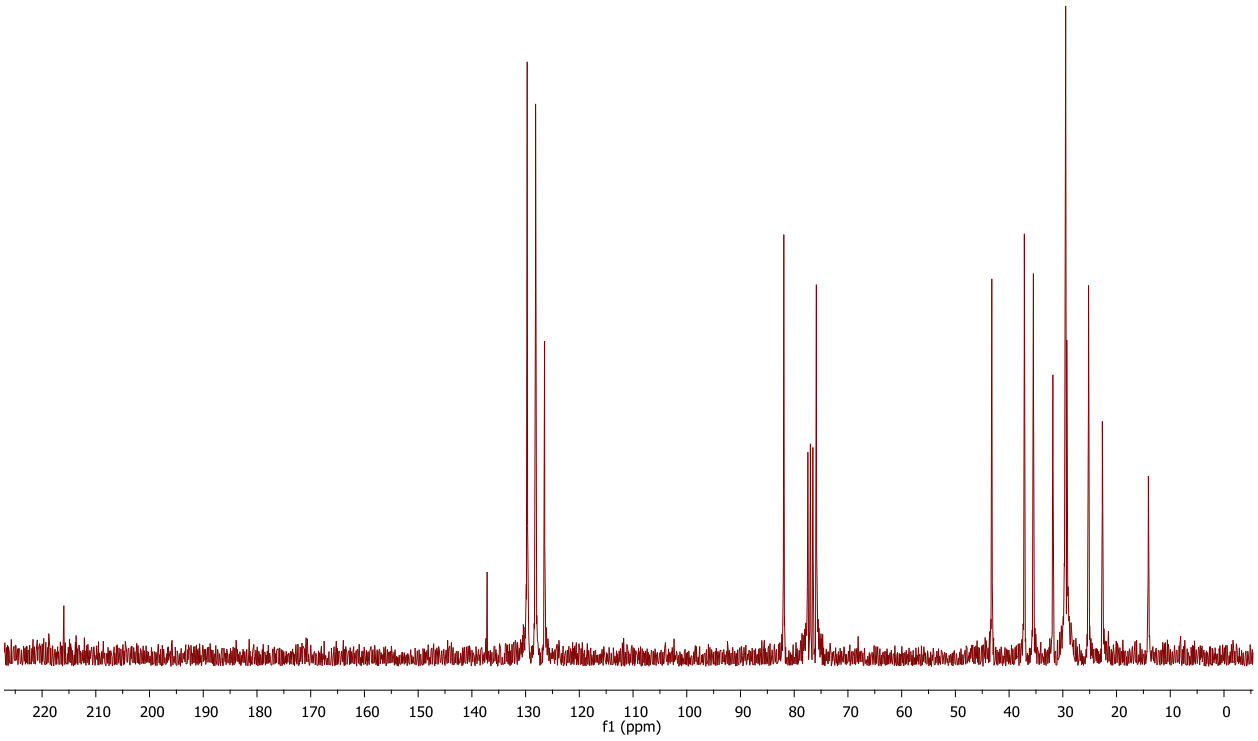
Copies of NMR spectra

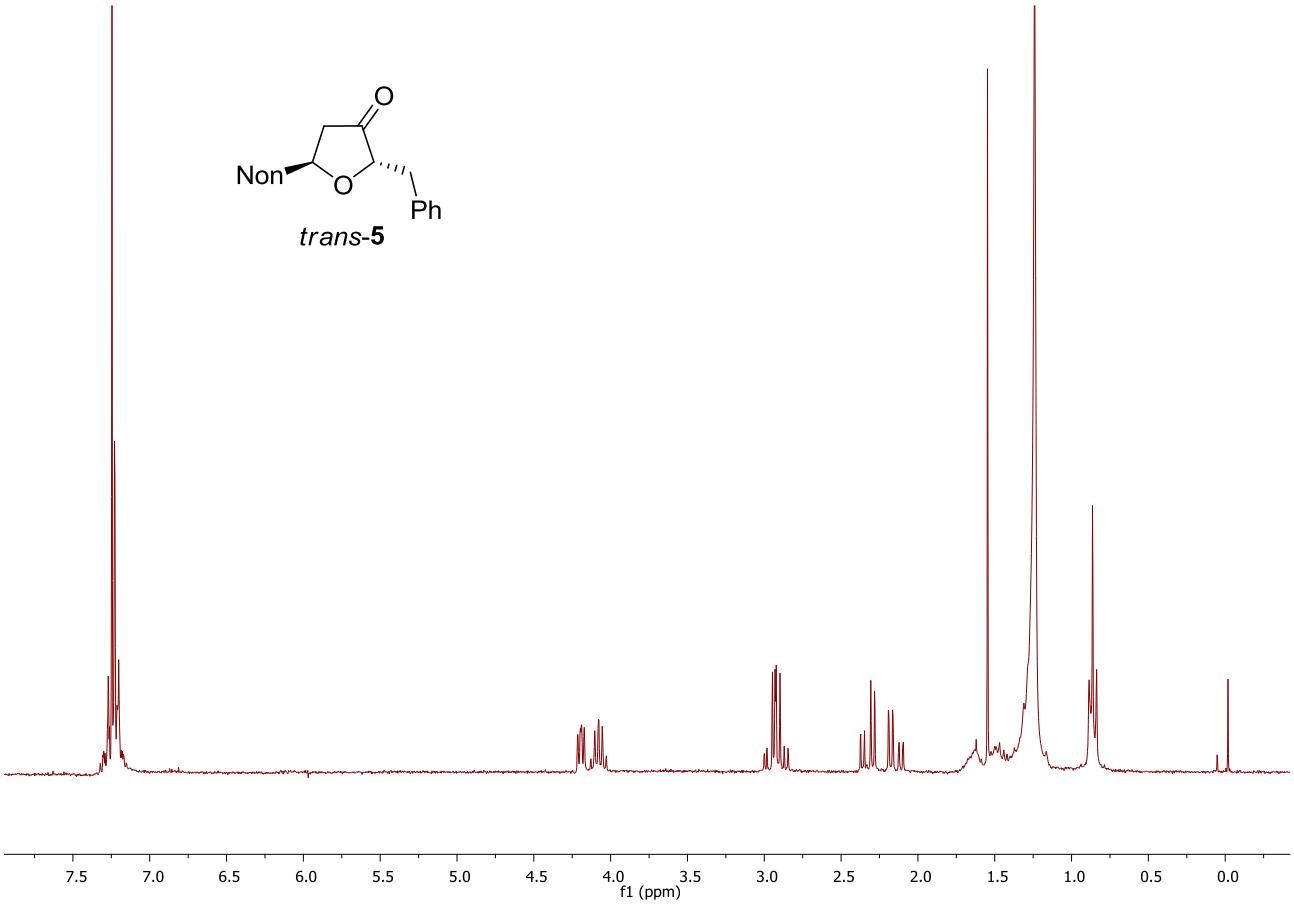




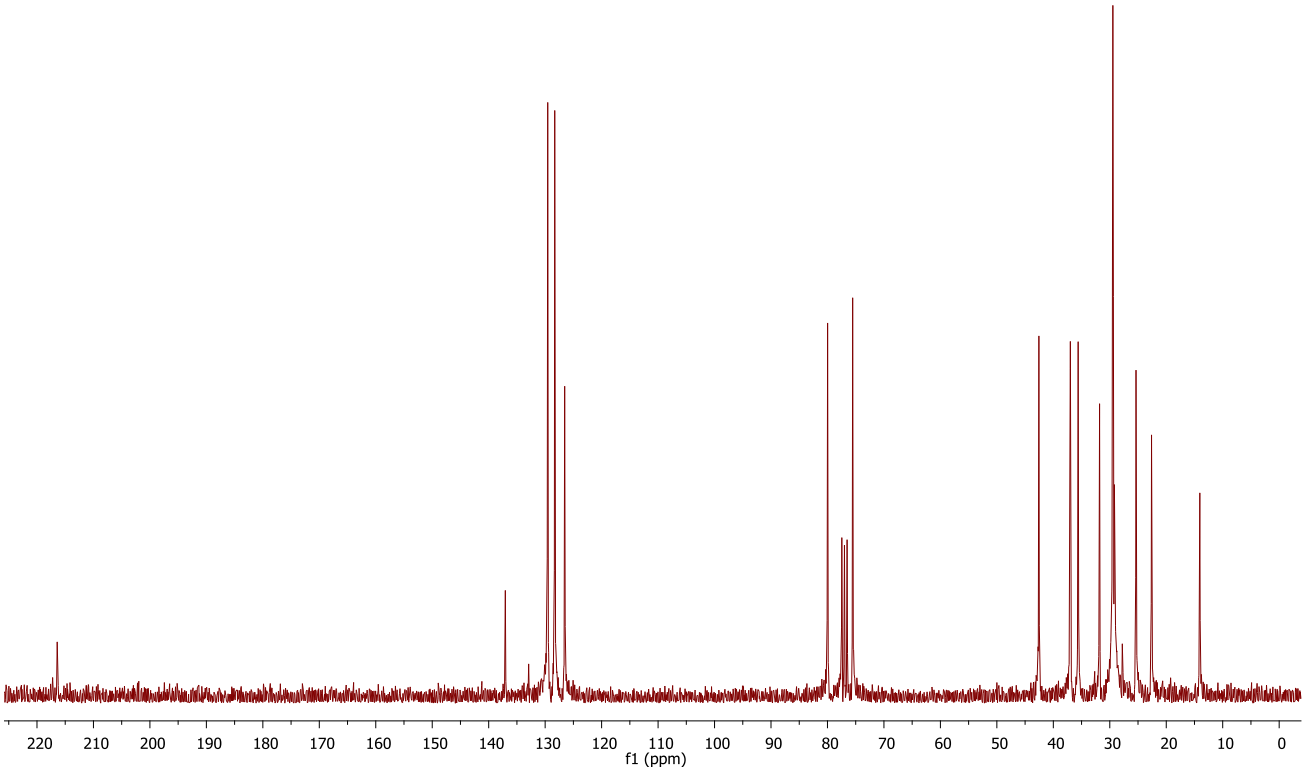

OMe
Non
O
Ph
4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

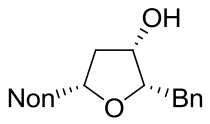

O
Non
O
Ph
cis-5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Non
O
Ph
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

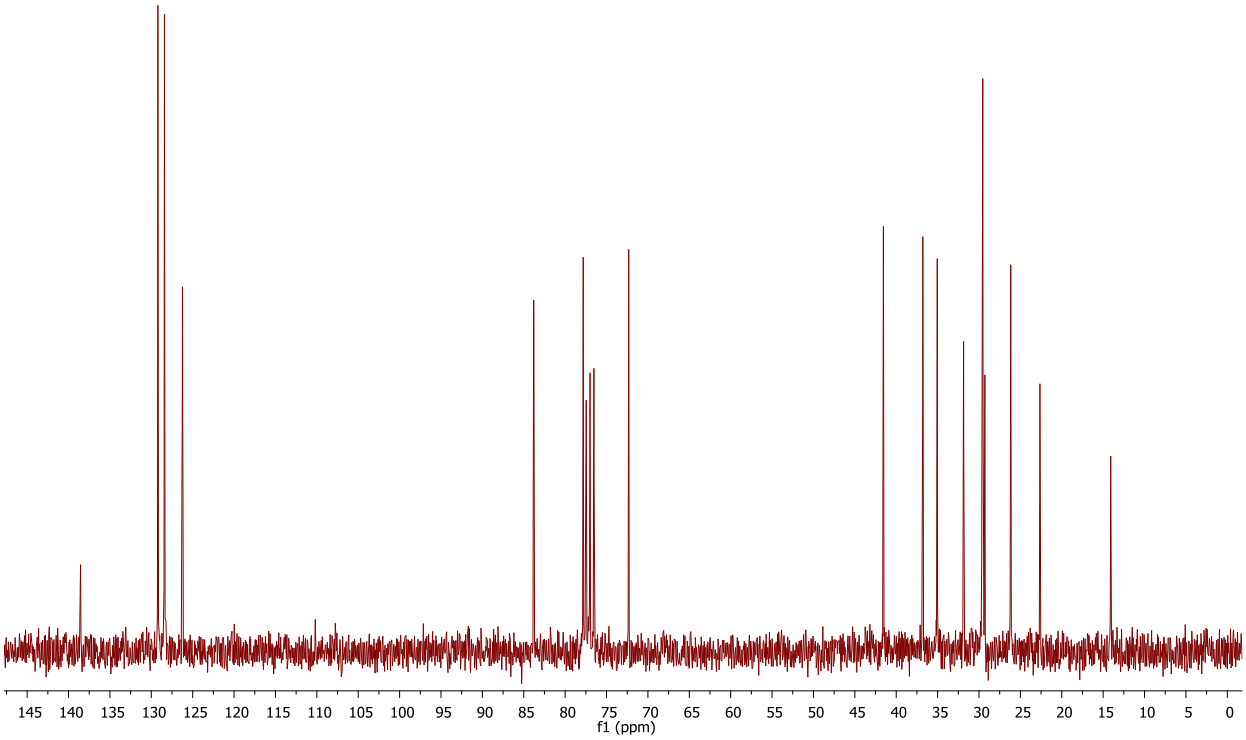
trans-**5**

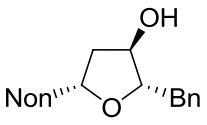

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Non
O
Bn

all-*cis*-**6**

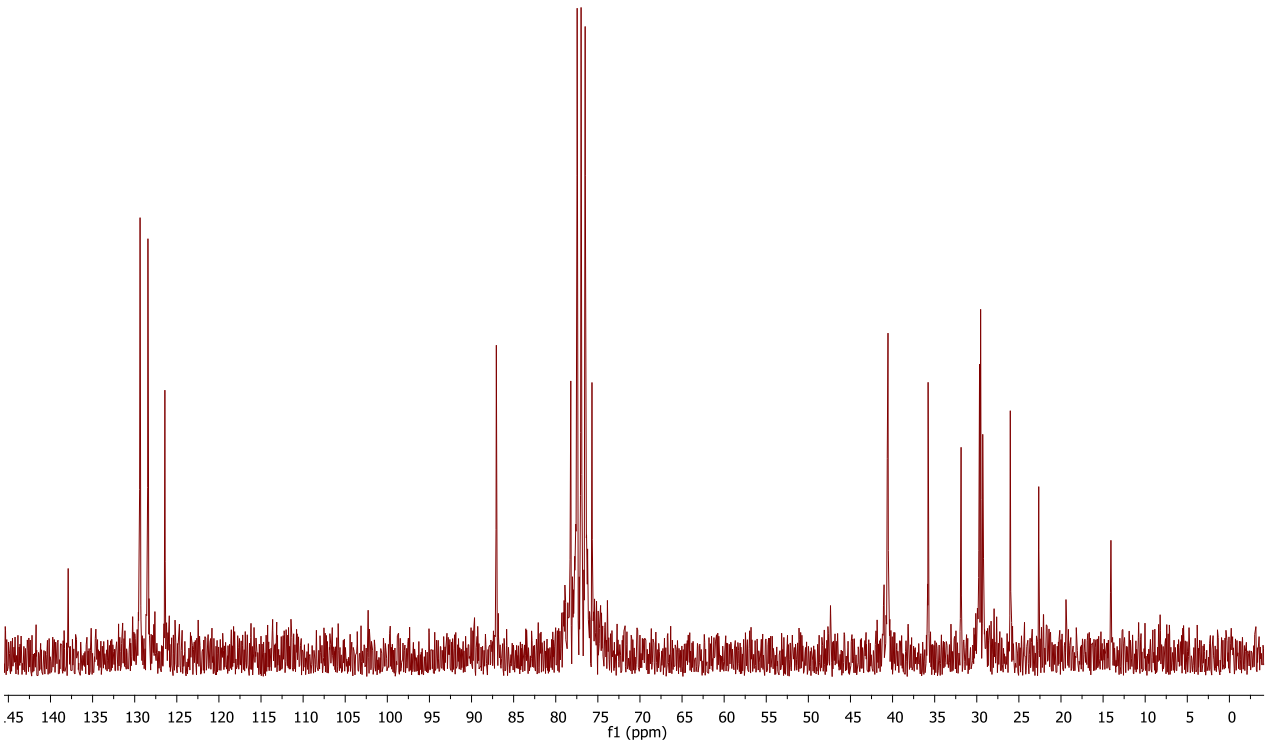
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

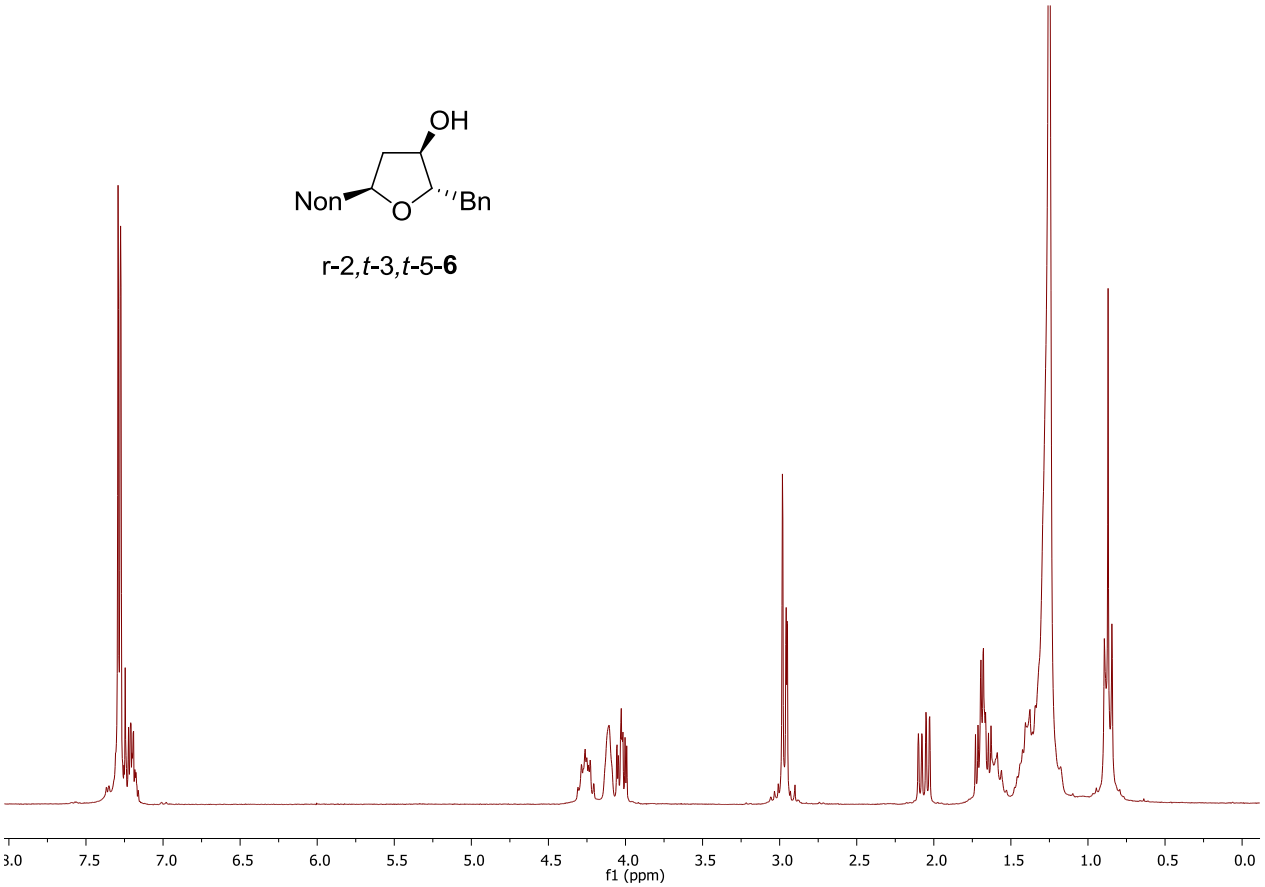

145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

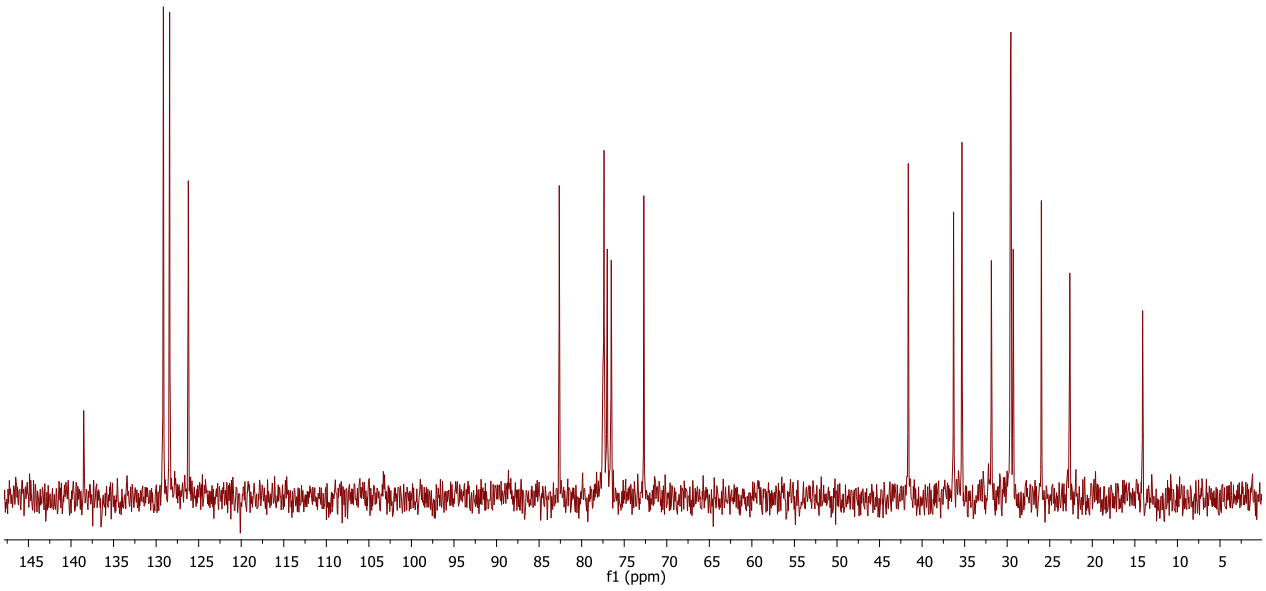

OH
Non
O
Bn

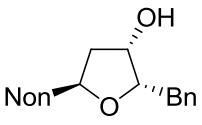
r-2,*t*-3,*c*-5-**6**

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

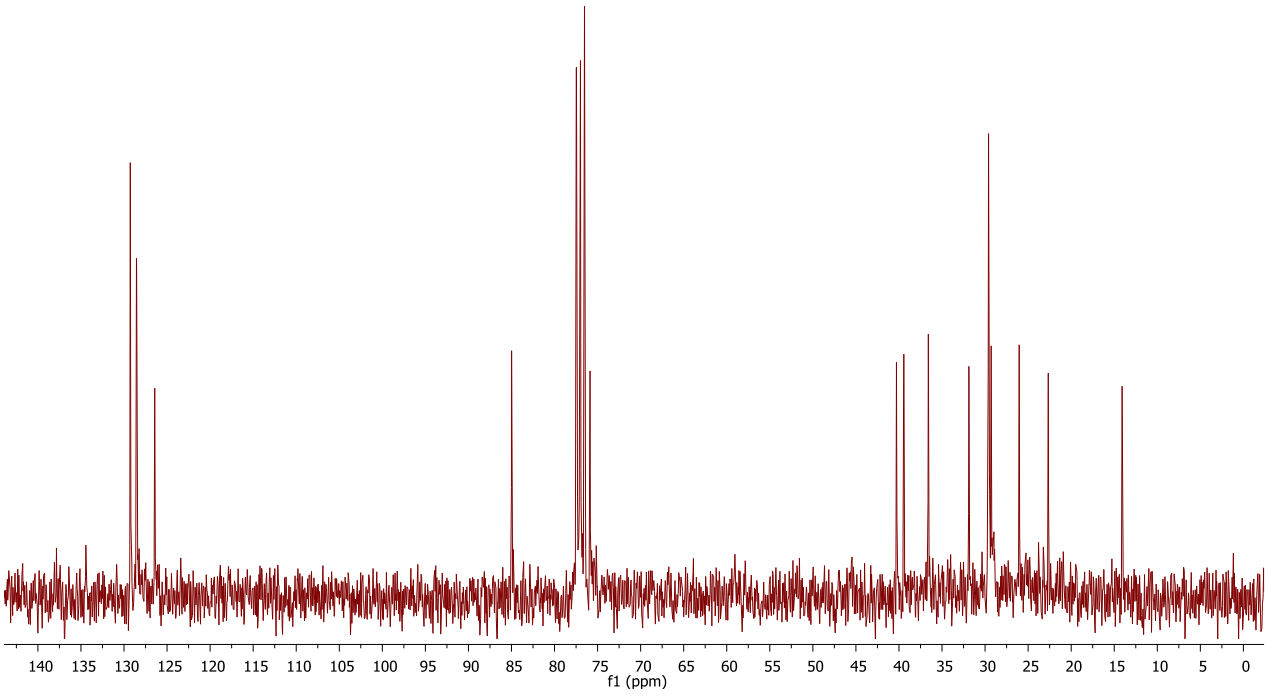

OH
Non
O
Bn
r-2,t-3,t-5-6
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

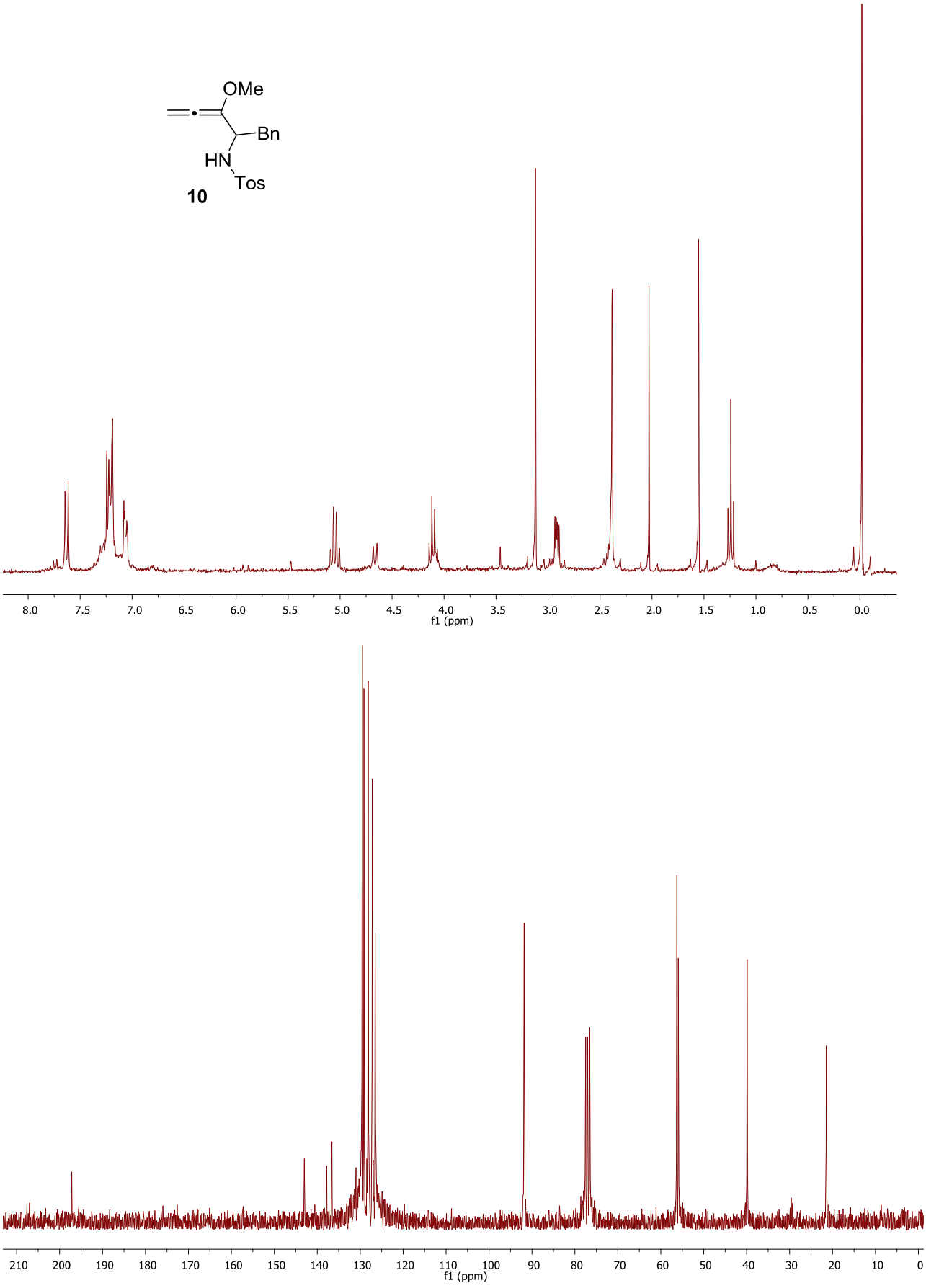

145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

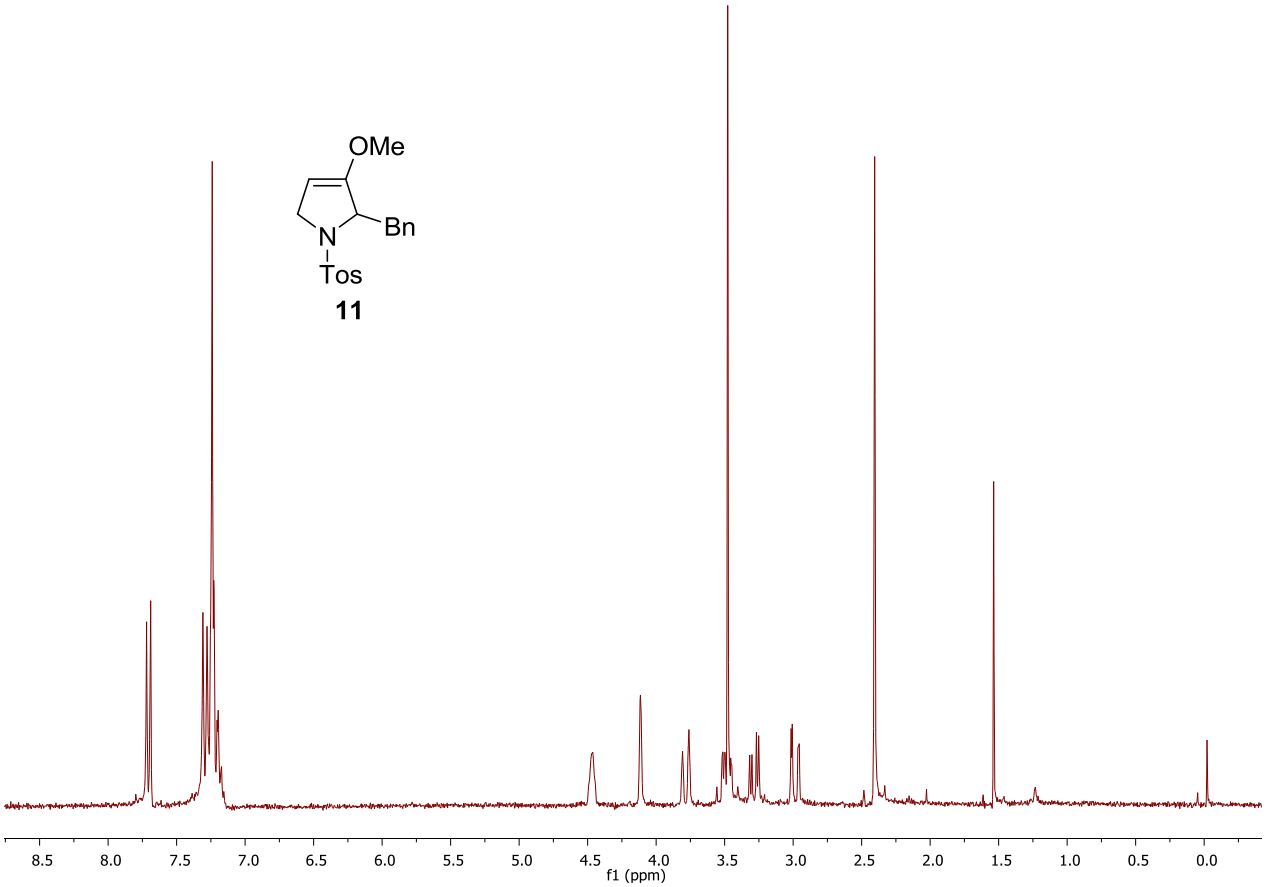

OH
Non
O
Bn

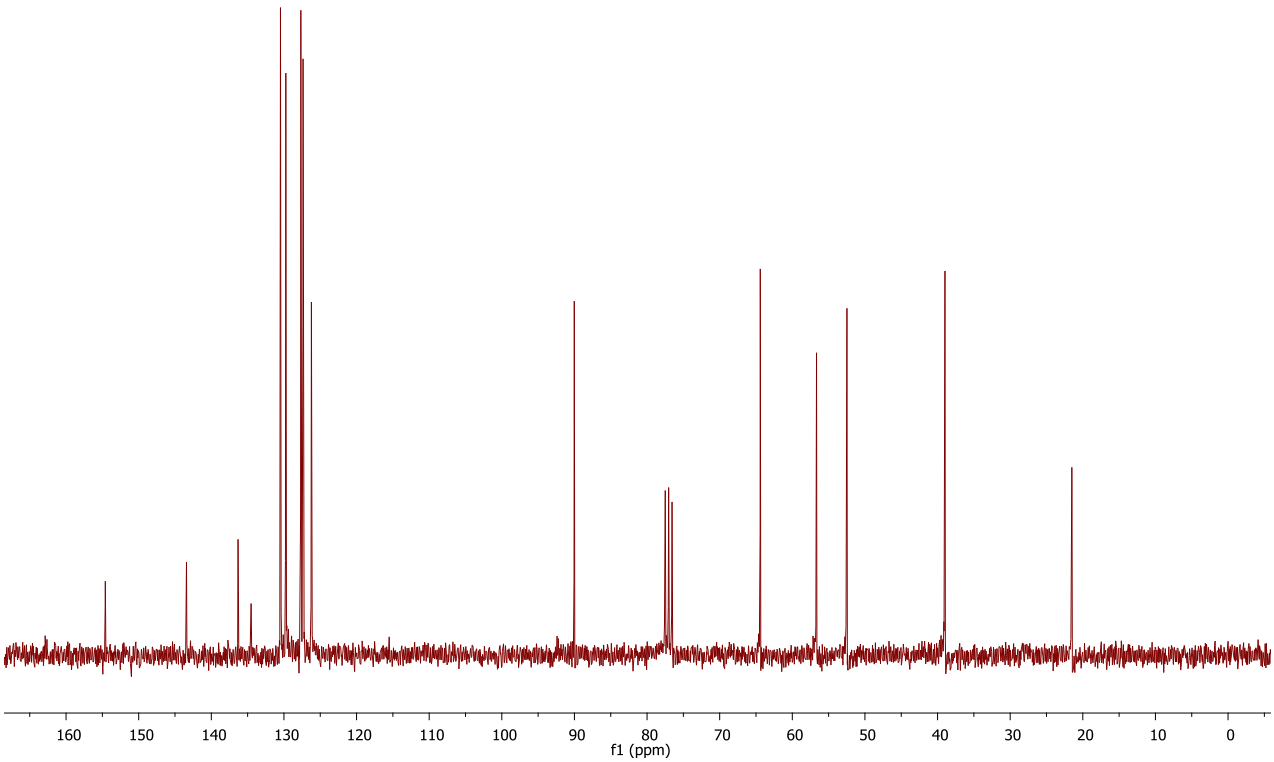
r-2,*c*-3,*t*-5-**6**

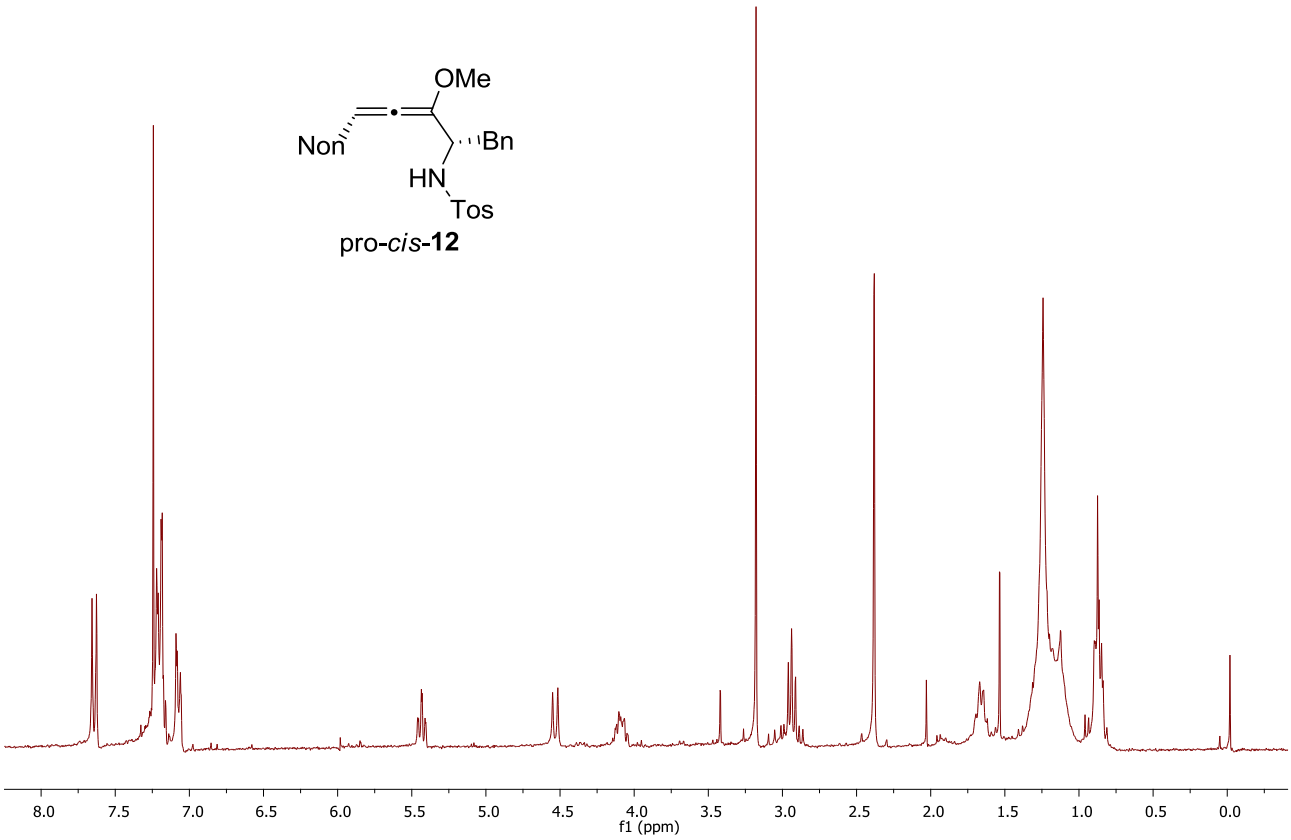
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

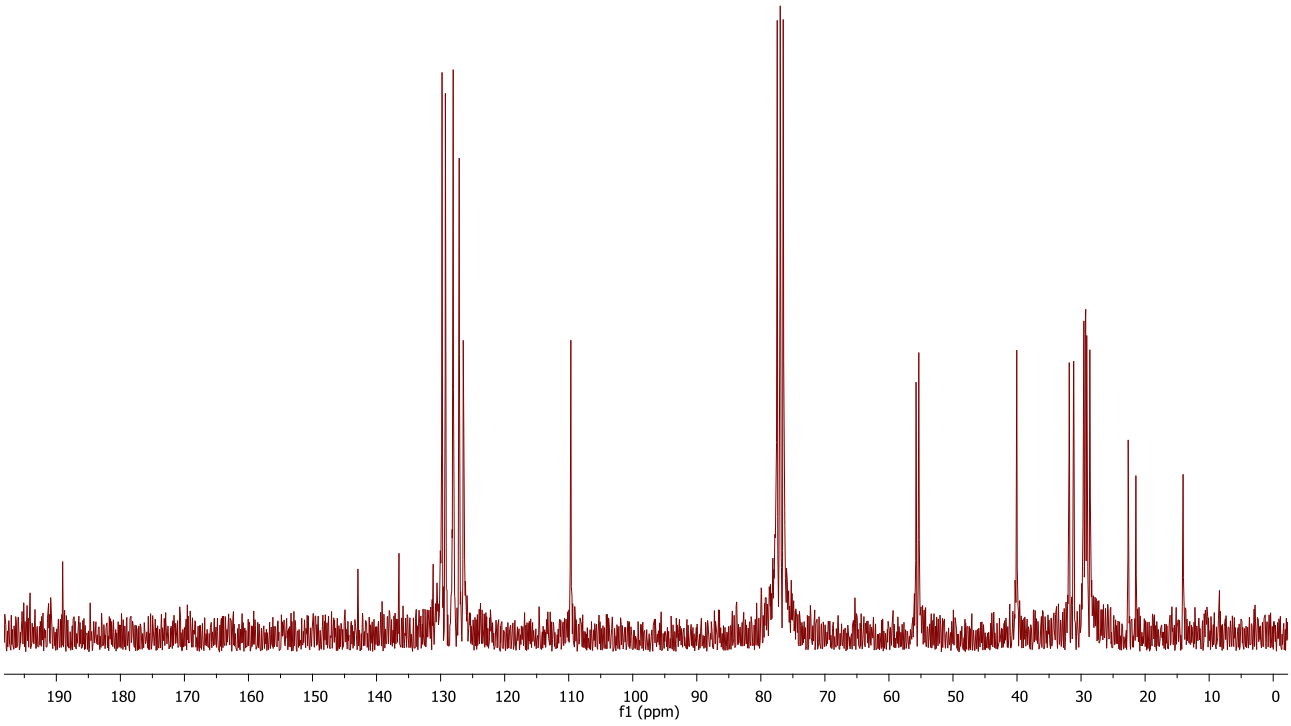

140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

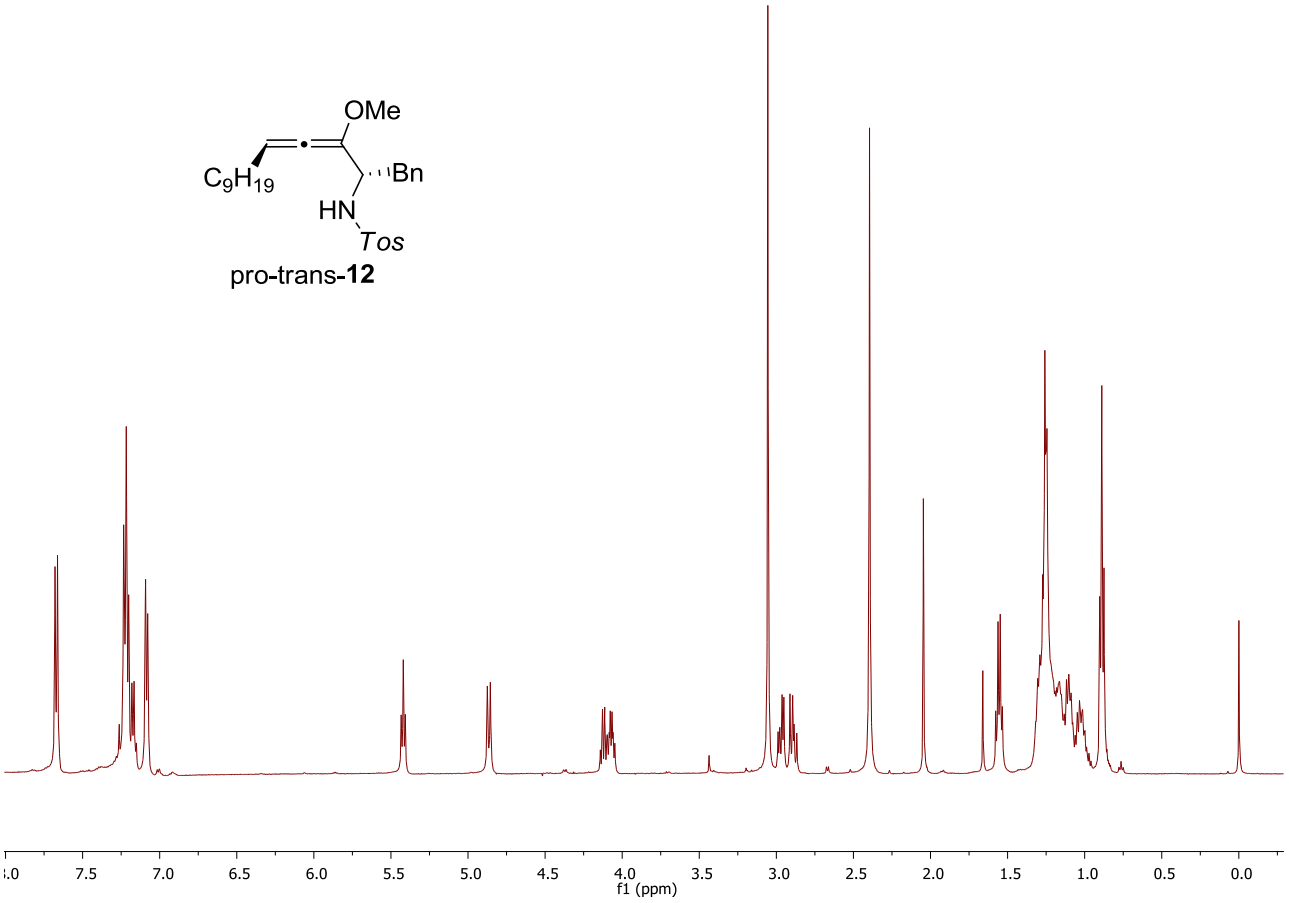

OMe
Bn
HN
Tos
10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

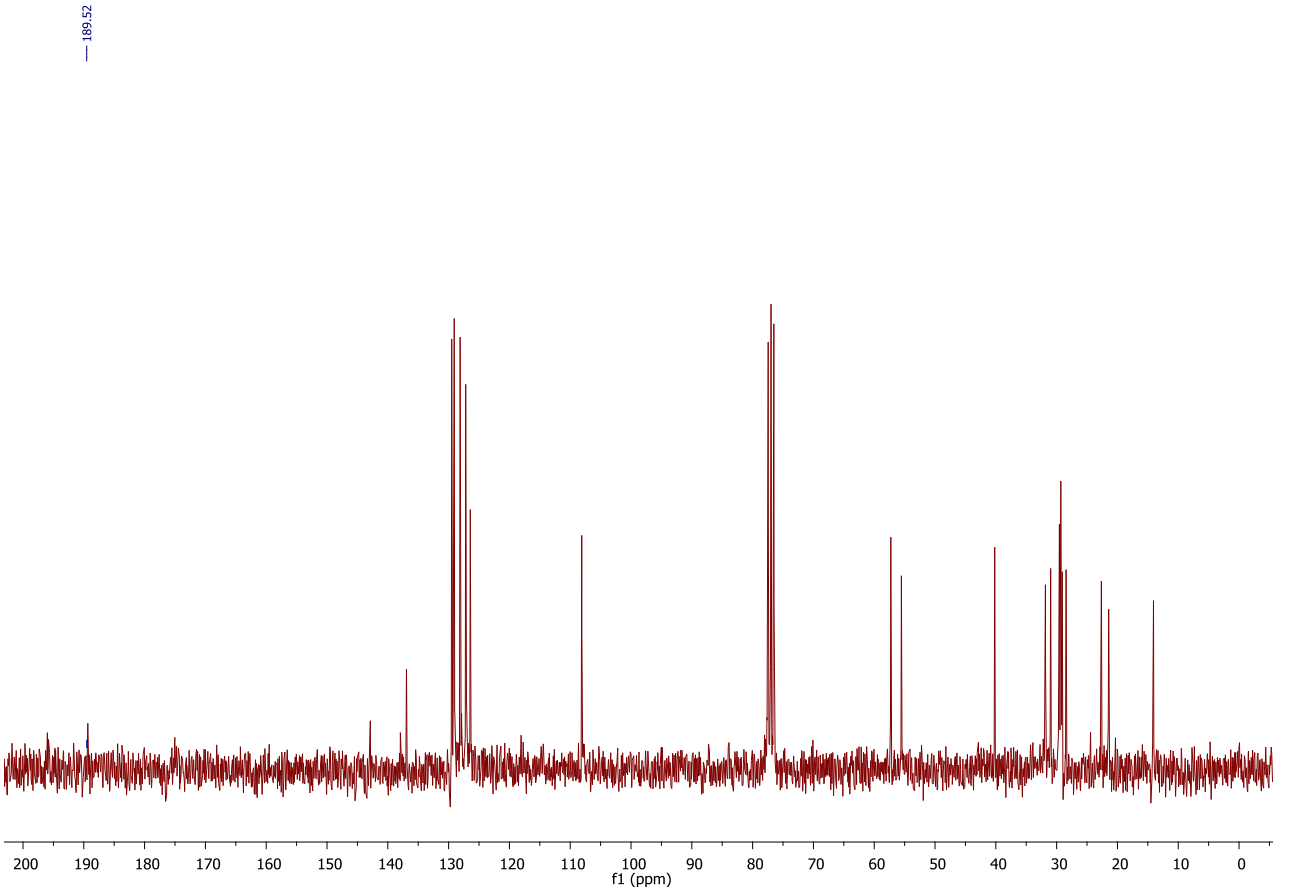

OMe
Bn
N
Tos
11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

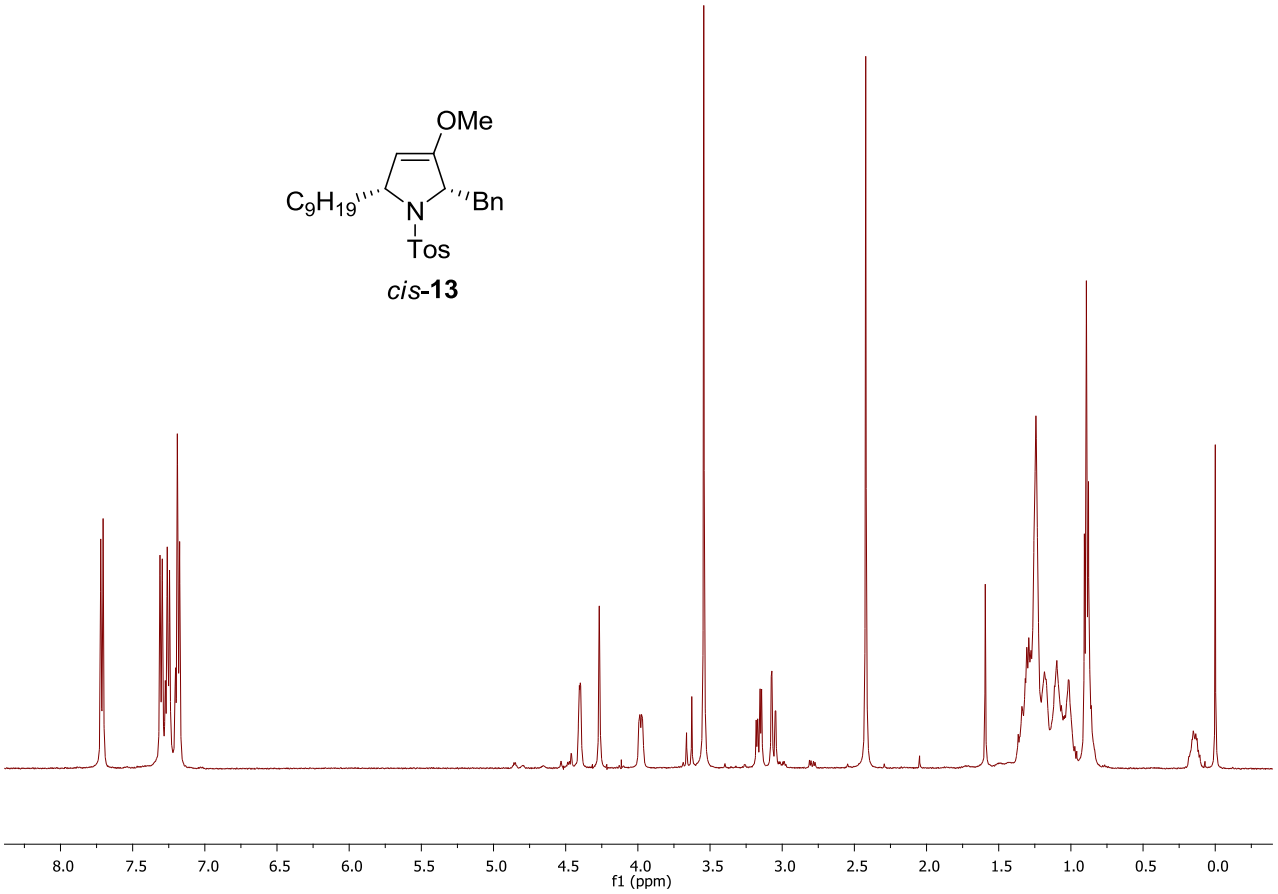

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

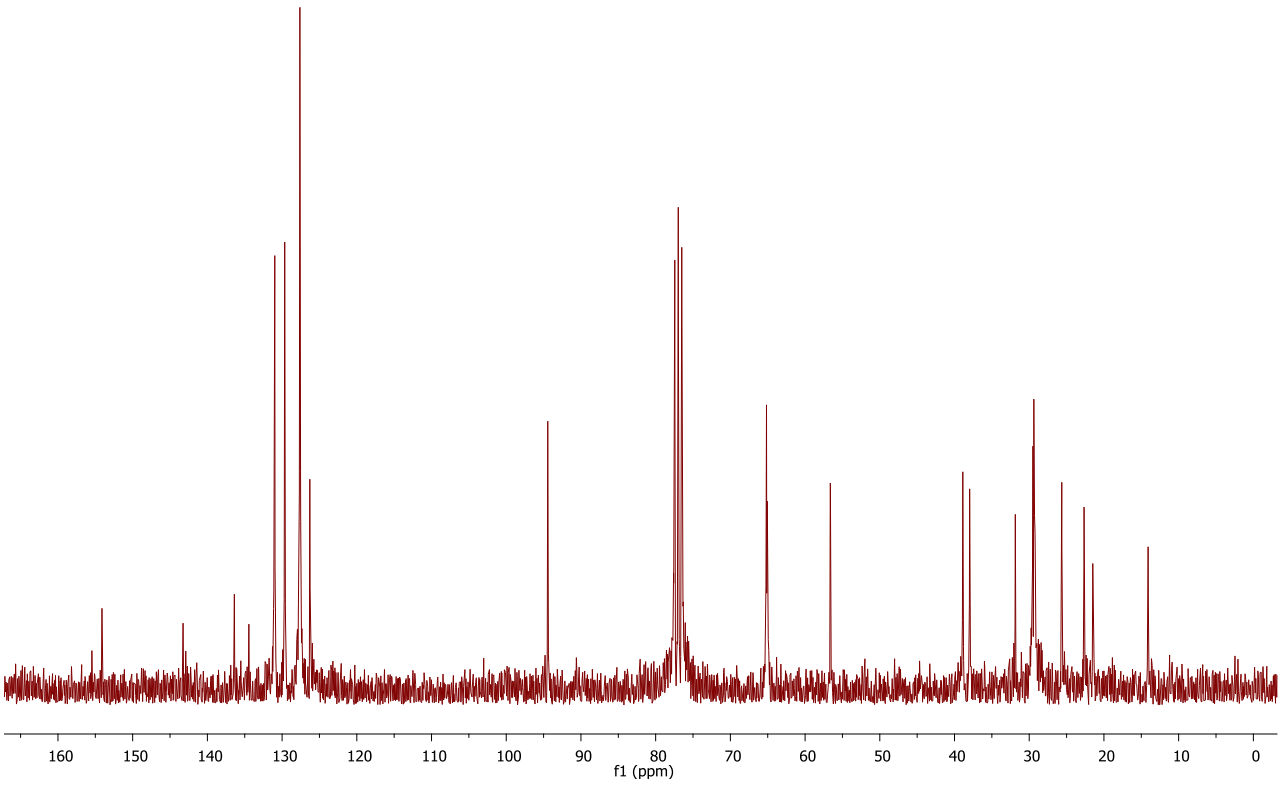

OMe
Non
Bn
HN
Tos
pro-*cis*-**12**
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

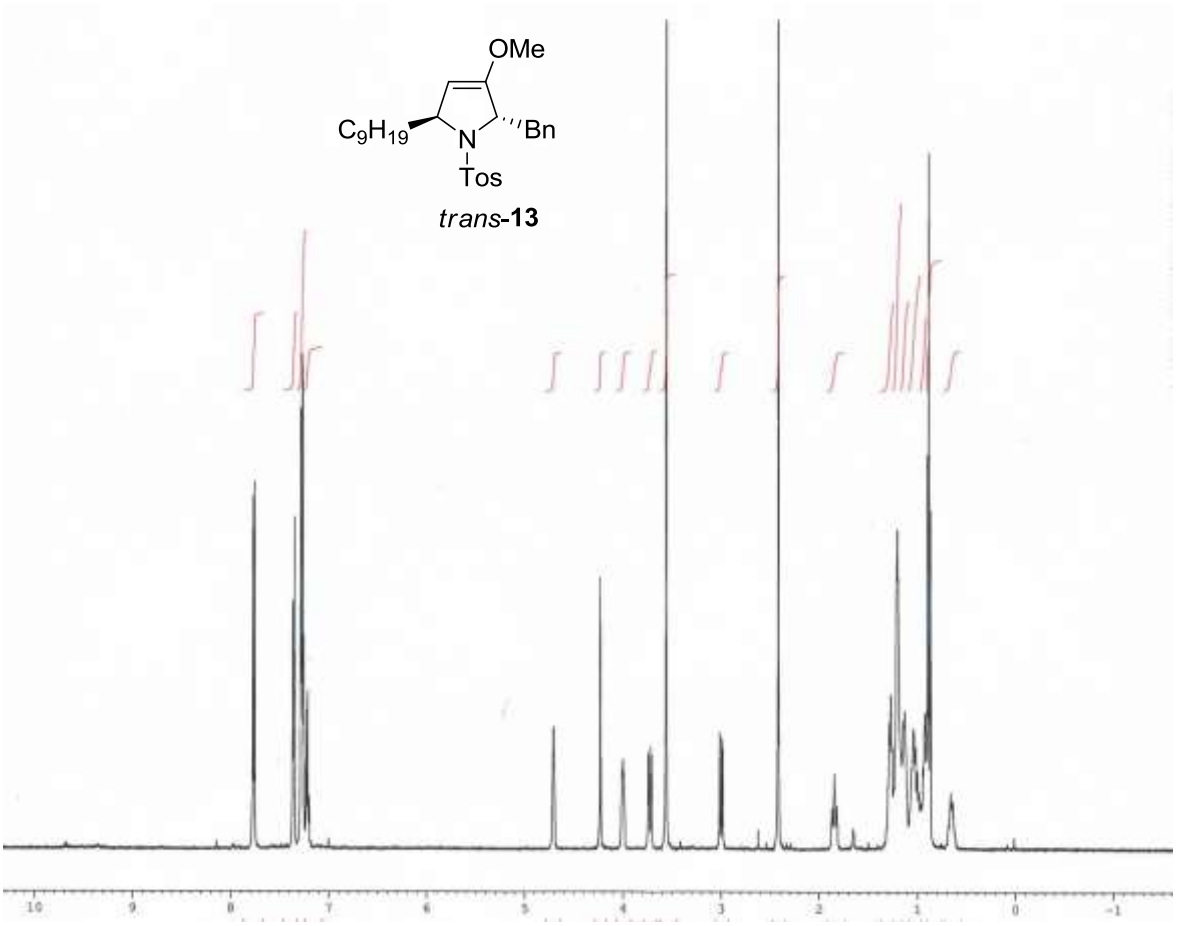

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

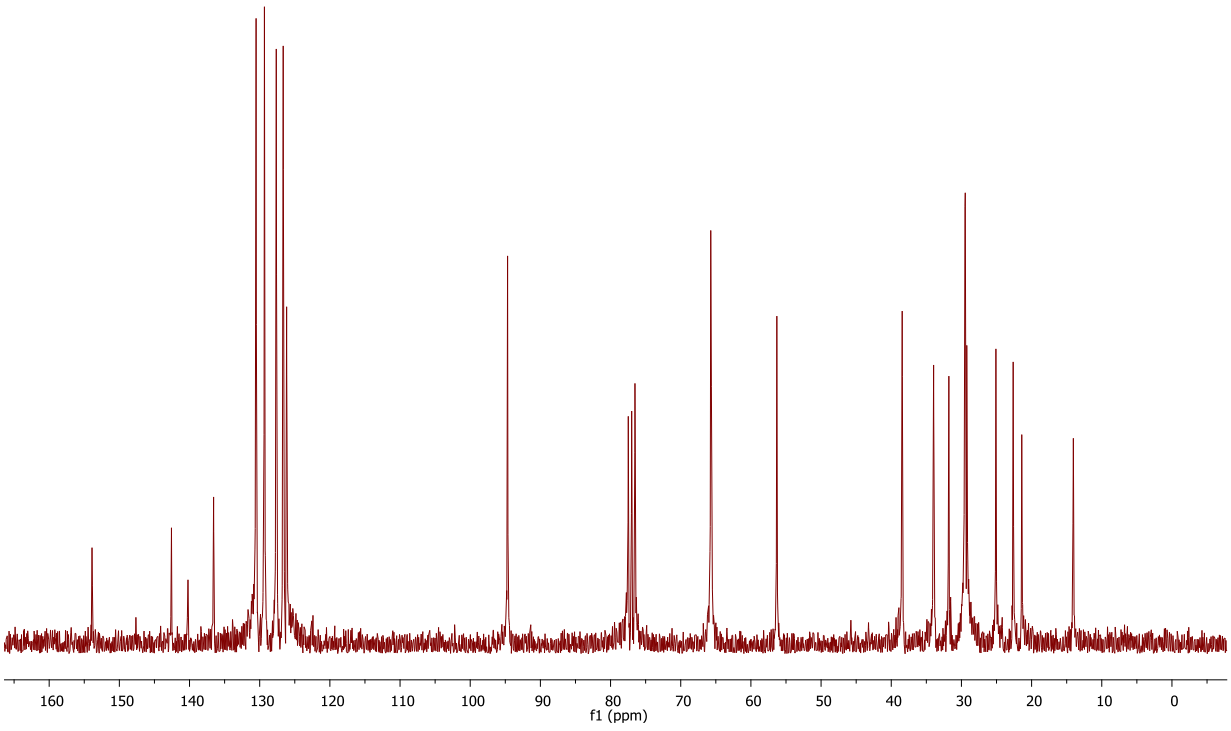

OMe
C9H19
Bn
HN
Tos
pro-trans-12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

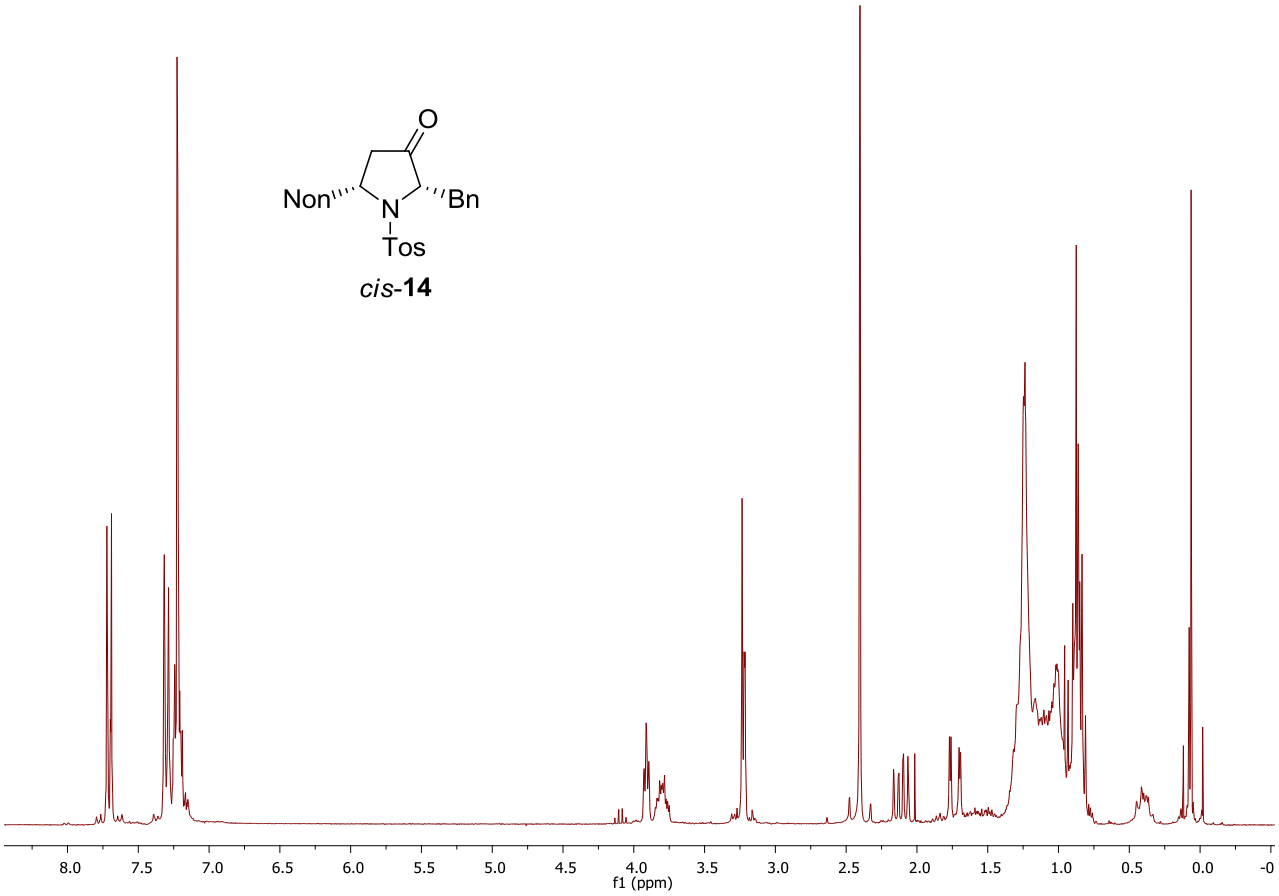

189.52
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
C9H19
Bn
N
Tos
cis-13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

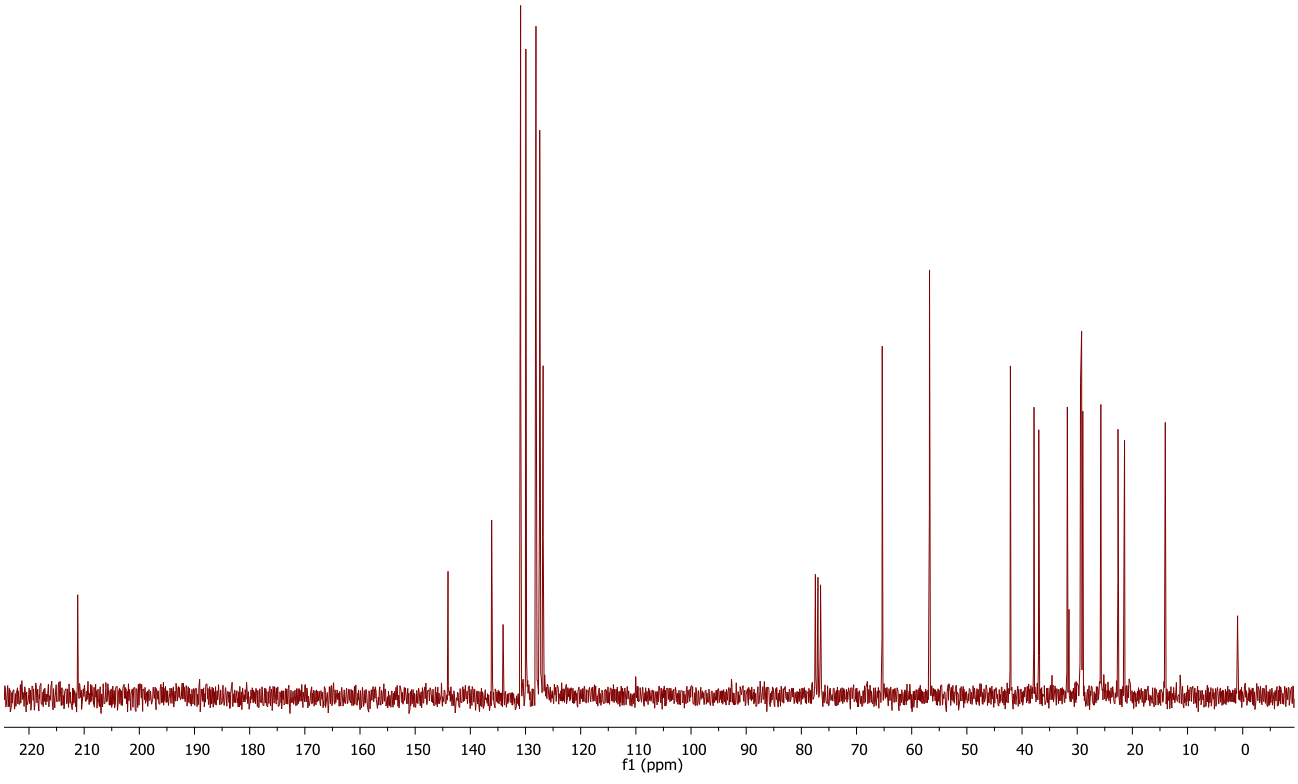

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

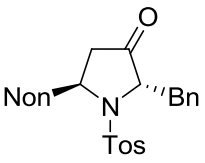

OMe
C9H19
Bn
N
Tos
trans-13


f1 (ppm)


O
Non
N
Bn
Tos
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

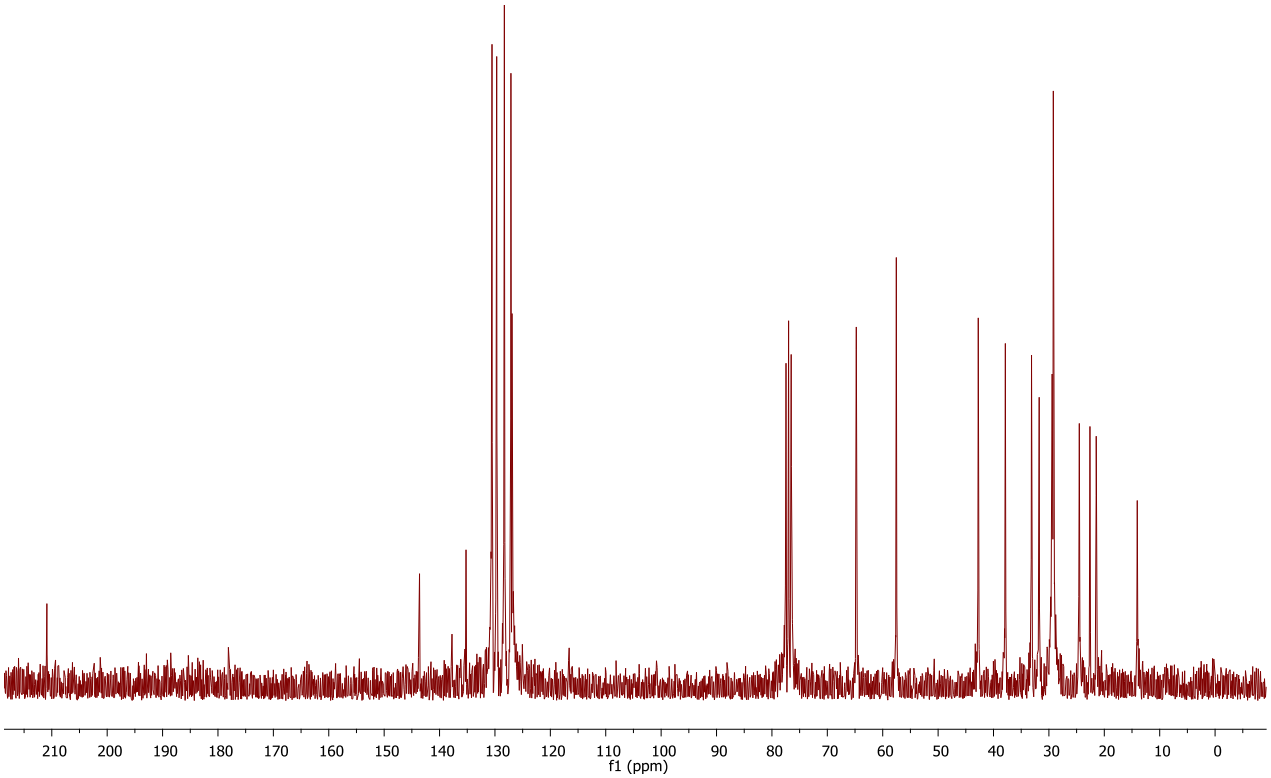
cis-**14**

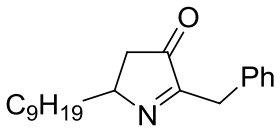

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
Non
N
Bn
Tos

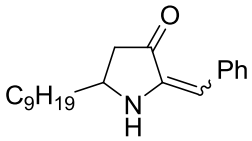
trans-**14**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


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

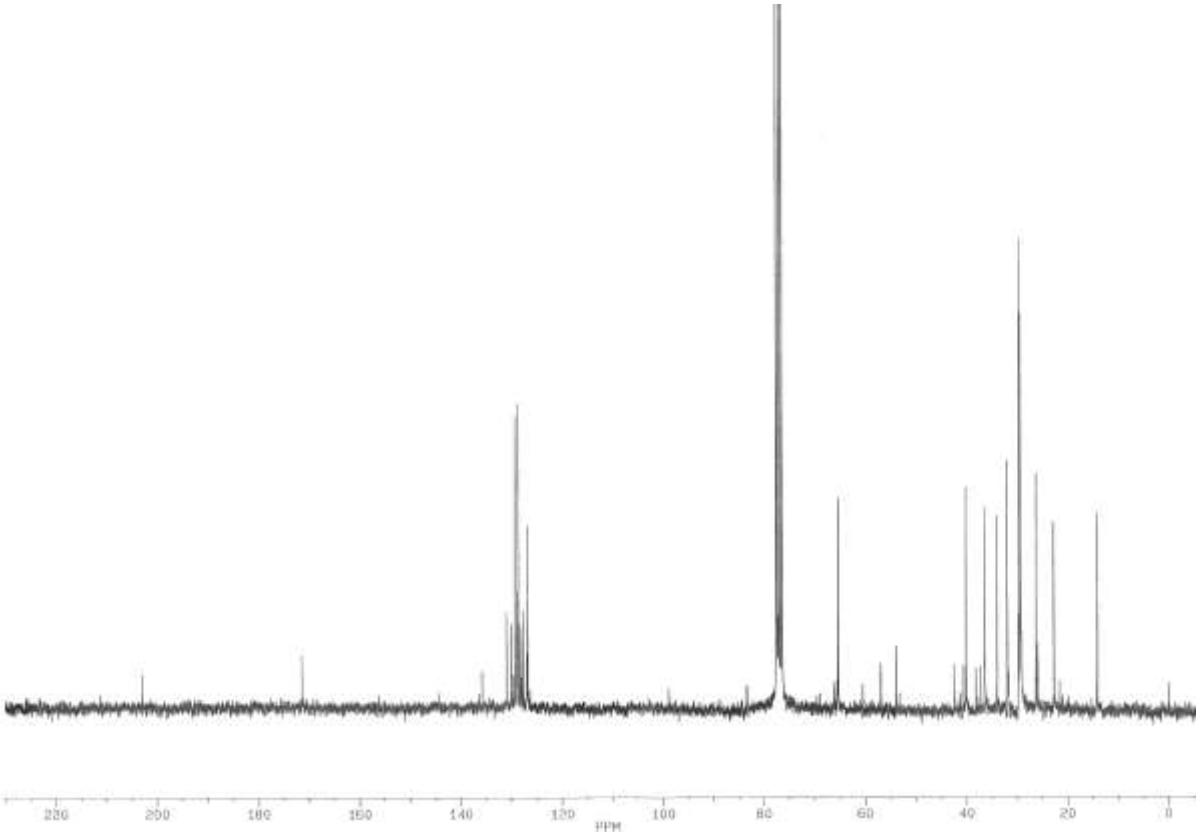

O
Ph
C_9H_{19}
N

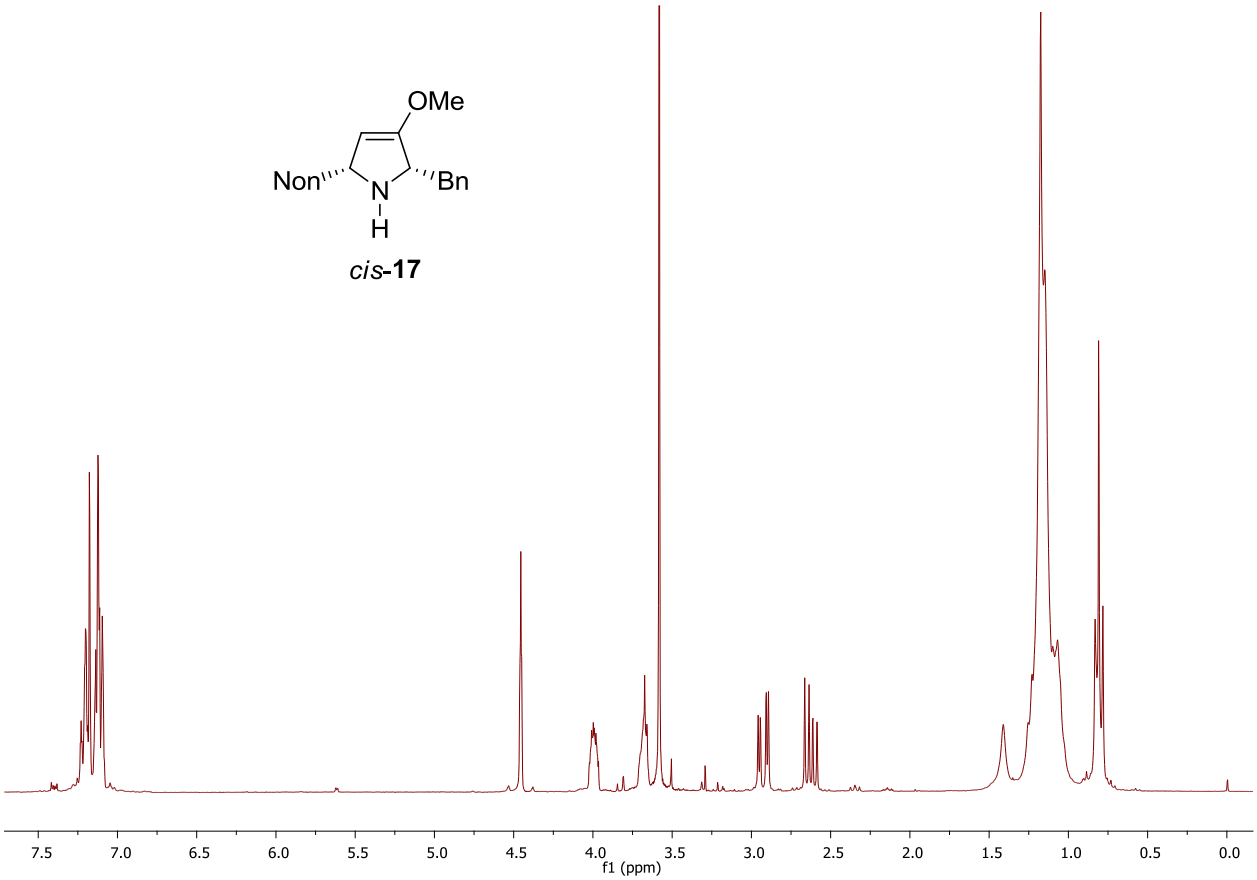
15


O
Ph
C_9H_{19}
N
H

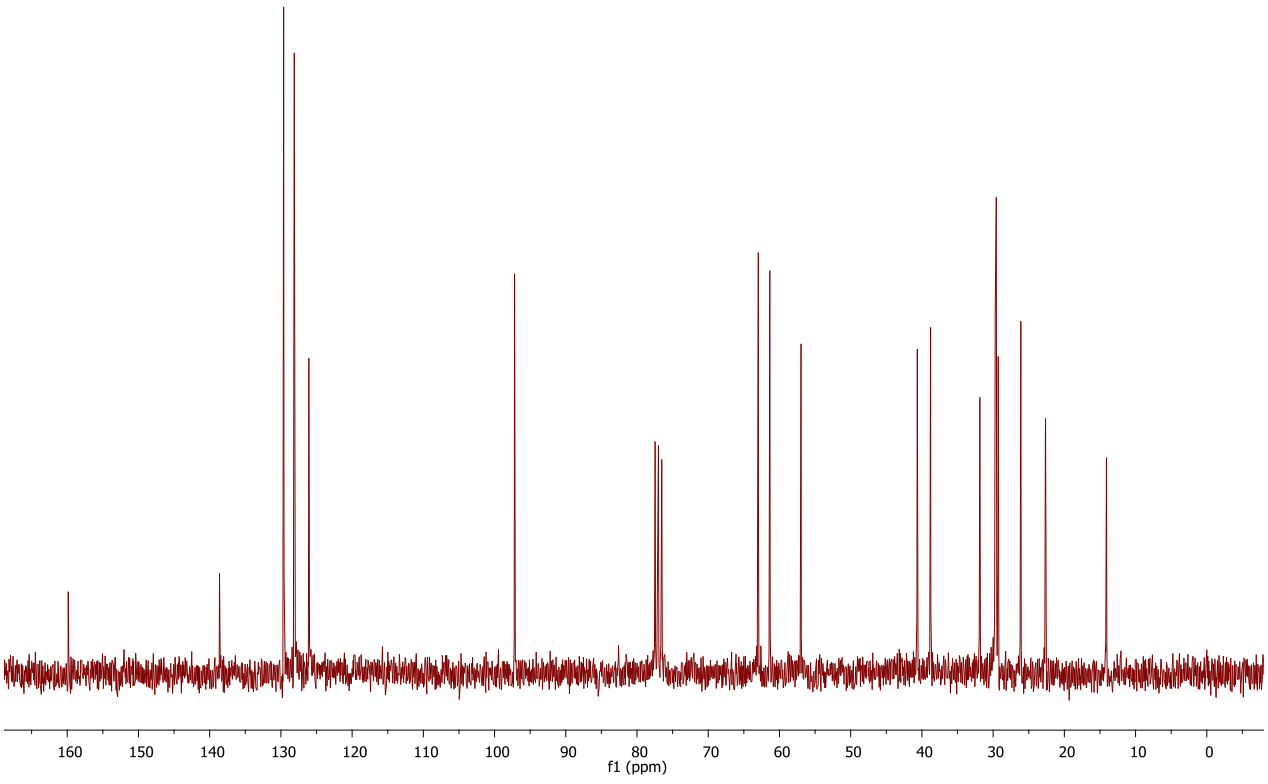
16

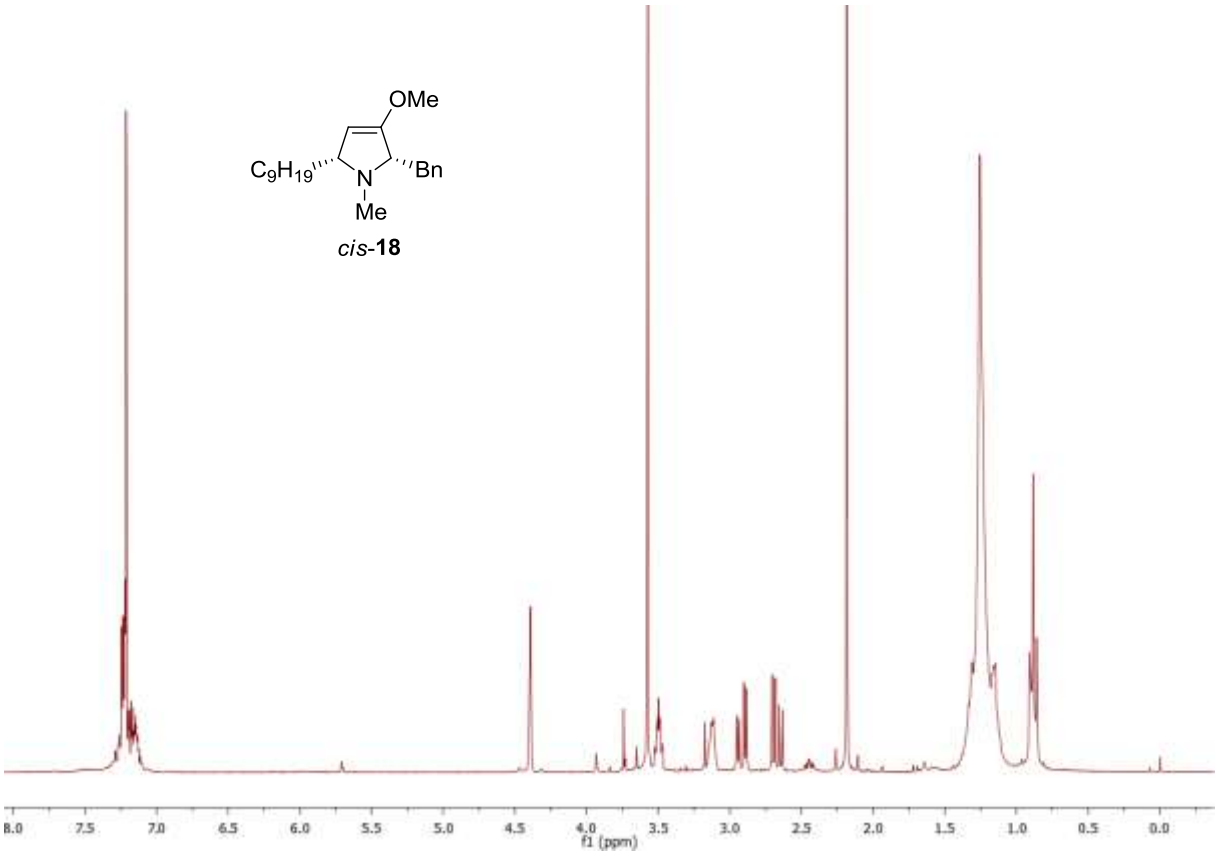
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

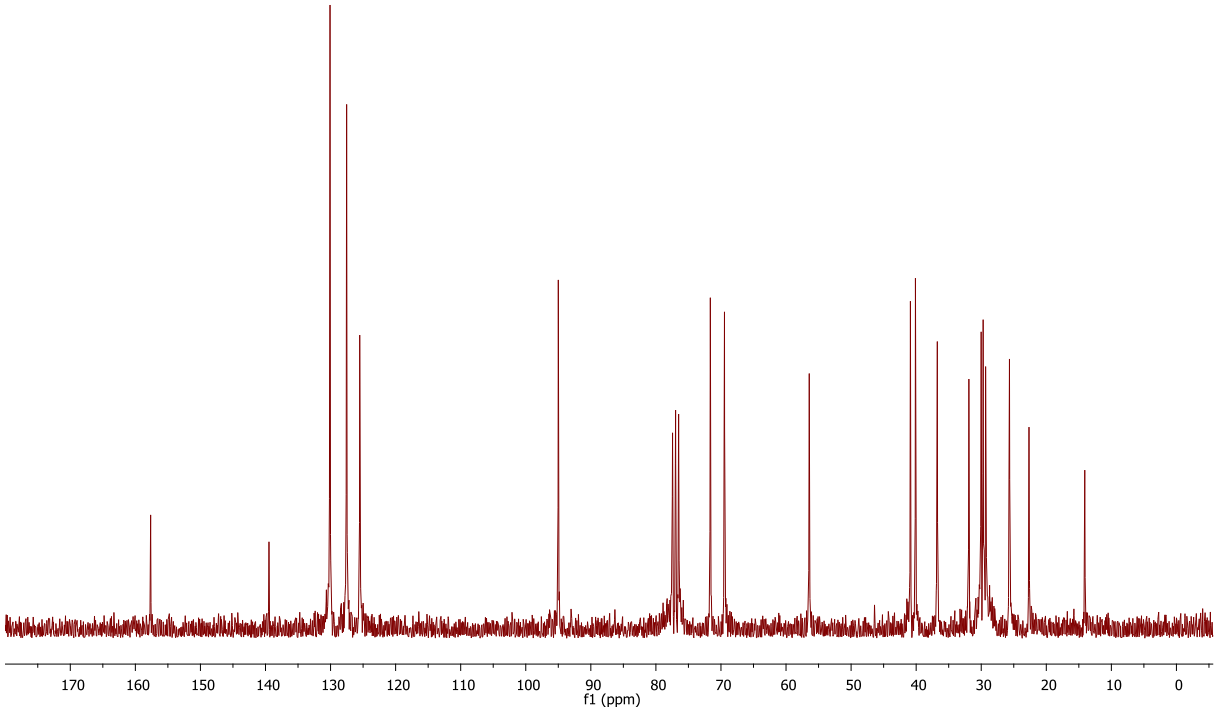

220
200
180
160
140
120
100
80
60
40
20
0
PPM

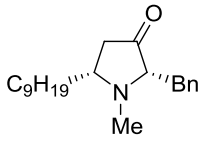

OMe
Non
Bn
N
H
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

cis-**17**


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

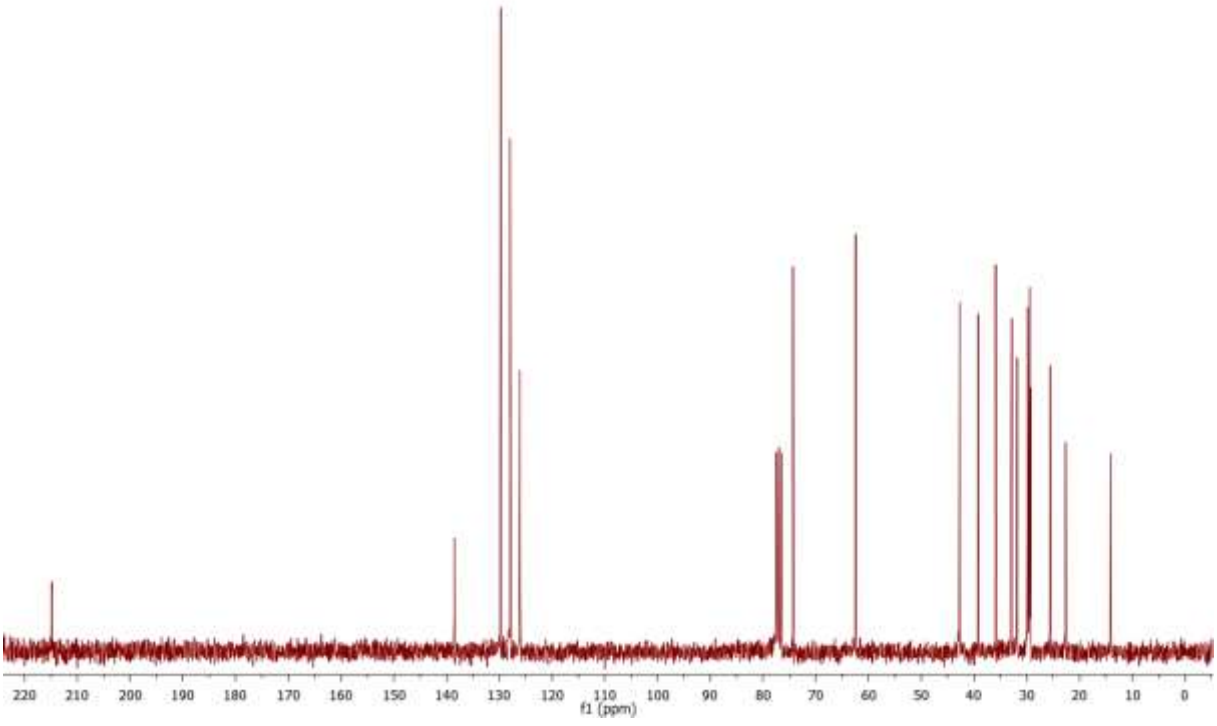

OMe
C9H19
Bn
N
Me
cis-18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

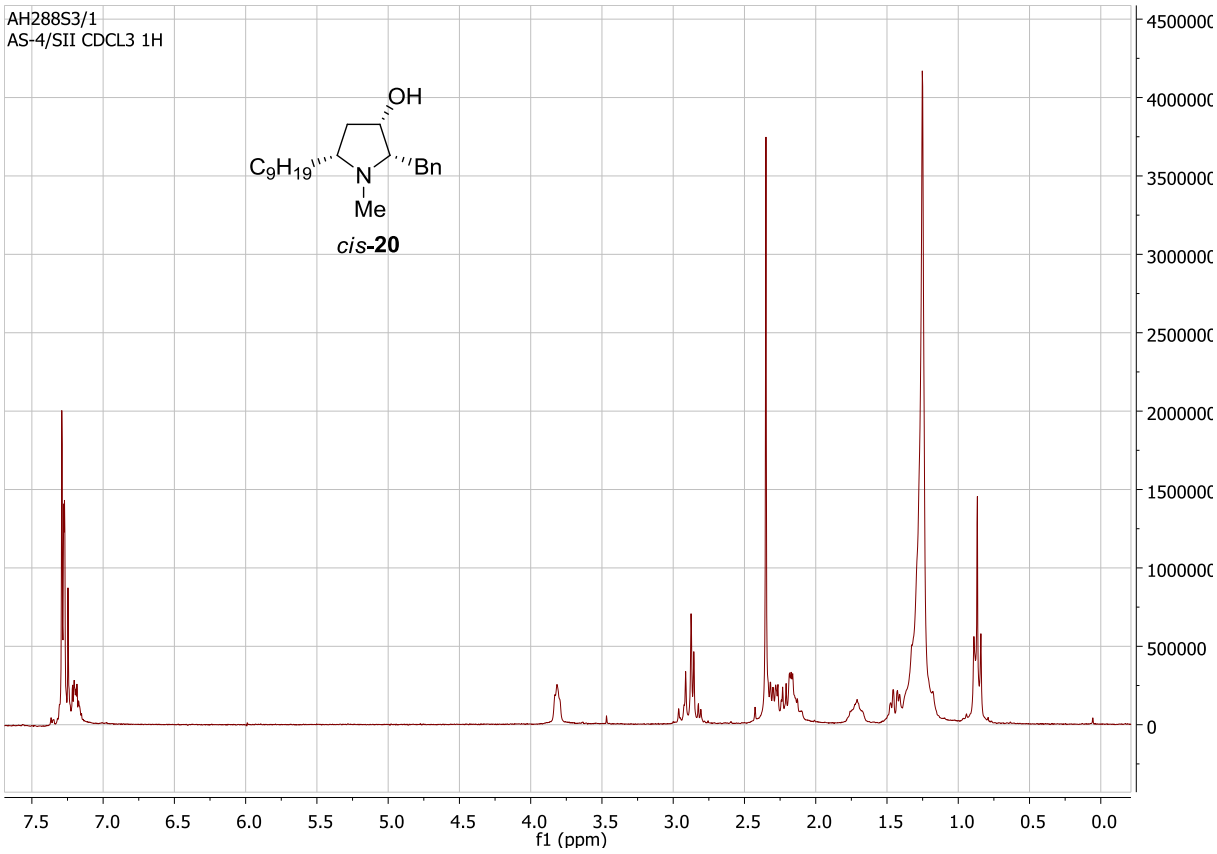

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

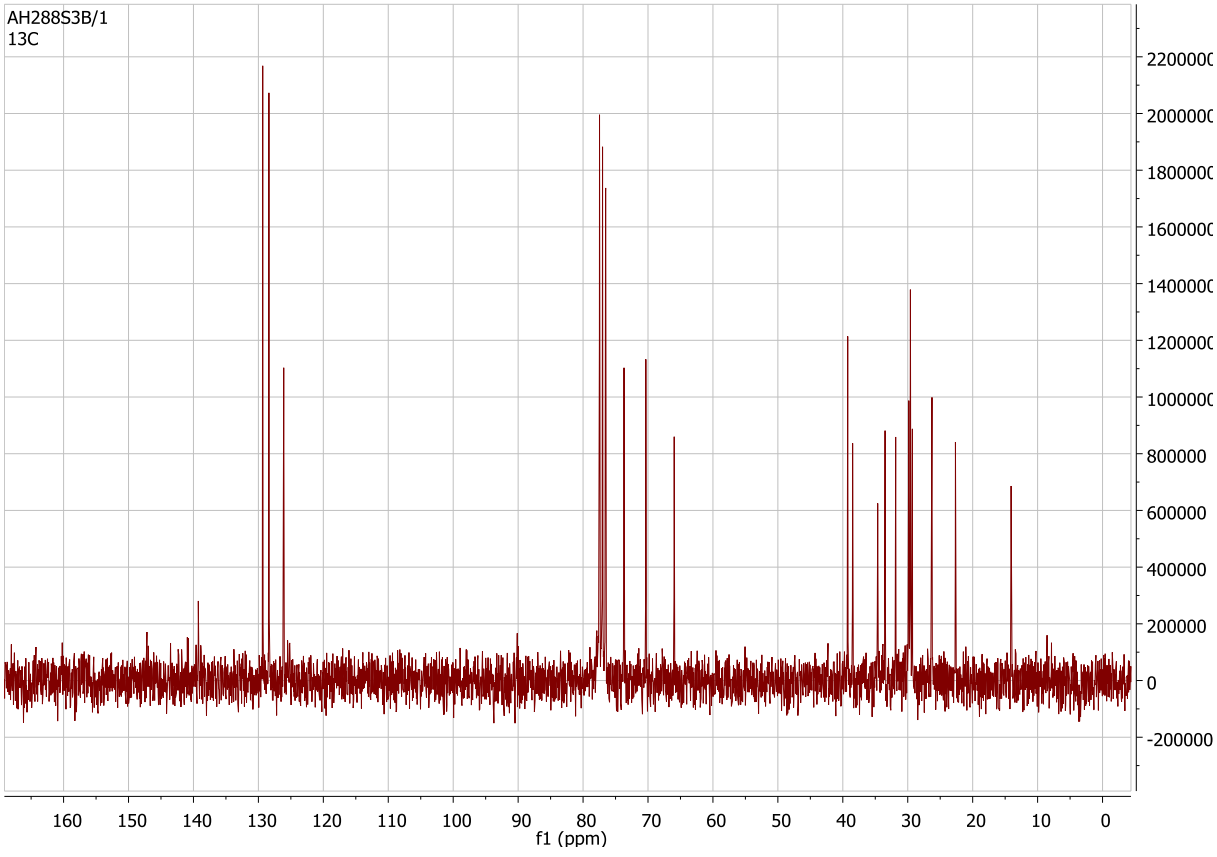

O
C9H19
N
Bn
Me

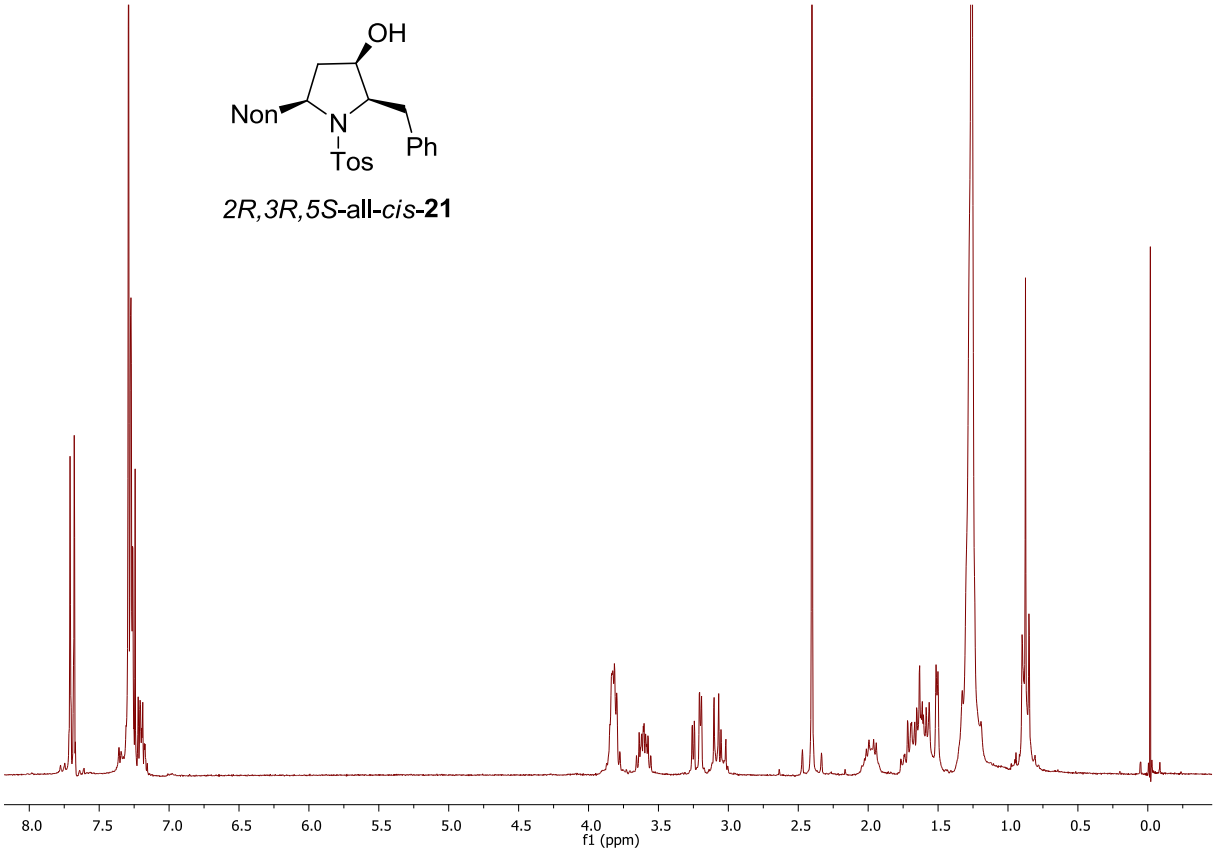
cis-**19**

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

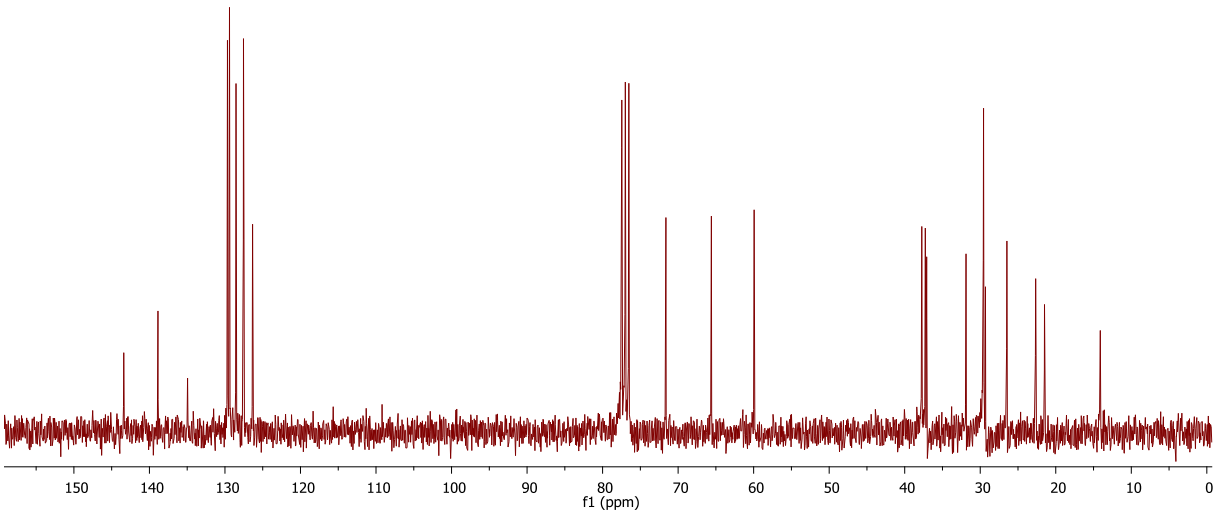

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

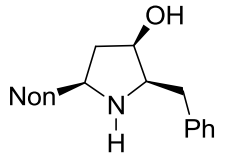

AH288S3/1
AS-4/SII CDCL3 1H
OH
C_9H_{19}
N
Bn
Me
cis-**20**
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


AH288S3B/1
13C
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

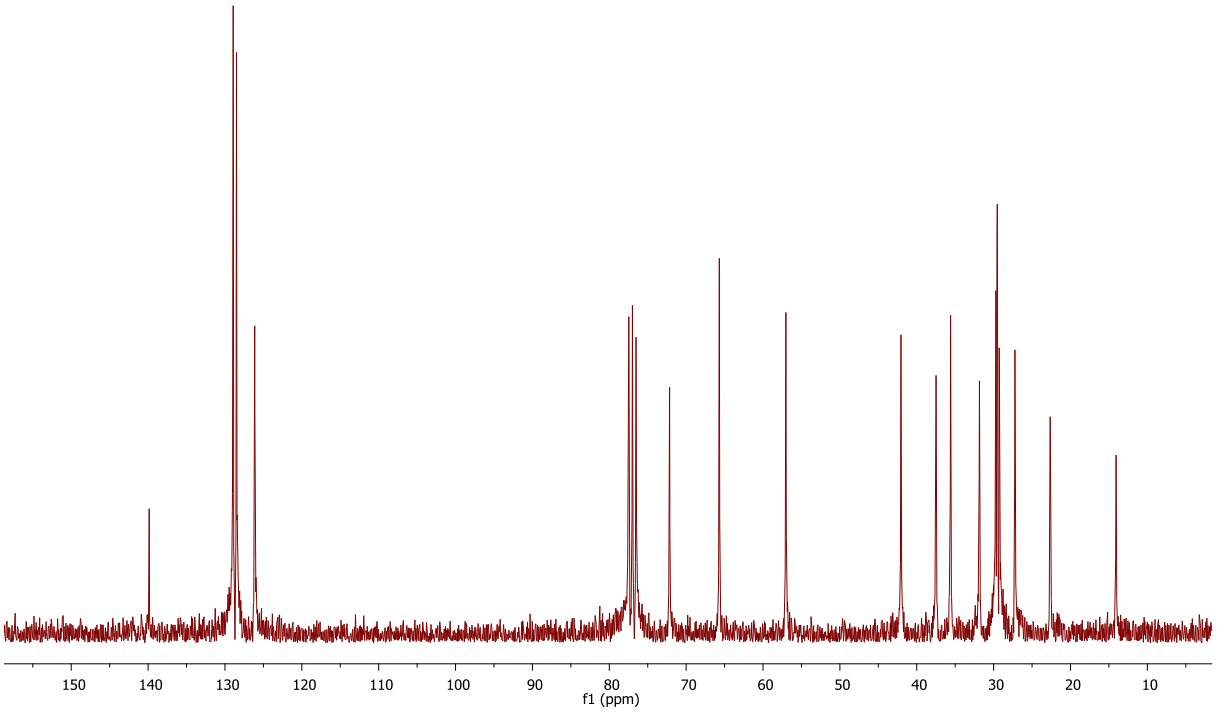


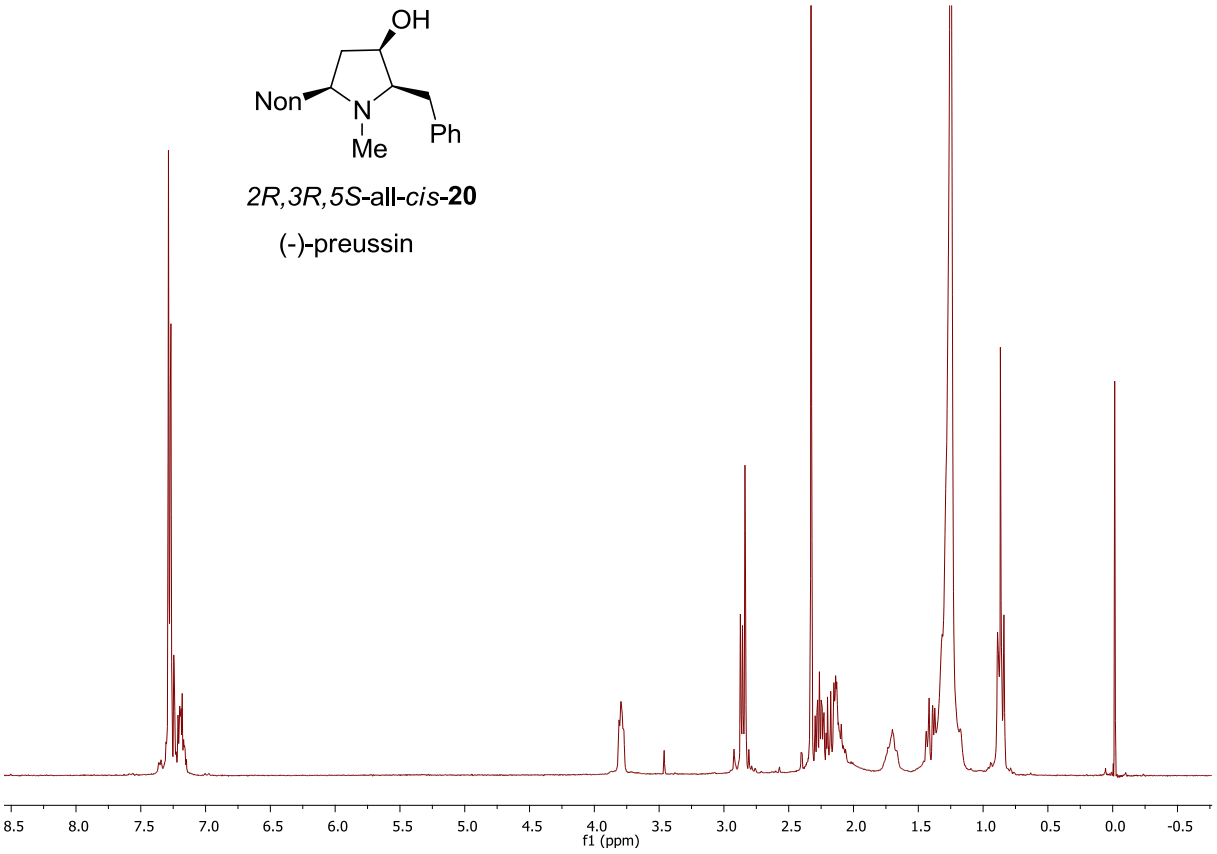
2R,3R,5S-all-*cis*-**21**





2R,3R,5S-all-*cis*-**22**





2R,3R,5S-all-*cis*-**20**

(-)-preussin