Supporting Information

Synthesis of azepane derivatives by silyl-azaPrins cyclization of allylsilyl amines: influence of the catalyst in the outcome of the reaction

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1. General Procedures

Unless otherwise noted, experiments were carried out with dry solvents under nitrogen atmosphere. Solvents (tetrahydrofuran, methanol, acetonitrile and dichloromethane) were dried by standard methods (dichloromethane and acetonitrile were freshly distilled from CaH_2, tetrahydrofuran and methanol were dried with preactivated molecular sieves. Flash column chromatography was performed using Silica Gel 60 (230-400 mesh ASTM). Thin layer chromatography (TLC) was performed using aluminium backed plate, pre-coated with silica gel (0.20 mm, silica gel 60) with a fluorescent indicator (254 nm) from Macherey.
NMR spectra were recorded at nuclear magnetic resonance service of the Laboratory of Instrumental Techniques (L.T.I., www.laboratoriotecnicasinstrumentales.es) University of Valladolid at Varian 400 MHz (^{1}H, 399.85 MHz; ^{13}C, 100.61 MHz), Varian 500 MHz (1H, 500.12 MHz; 13C, 100.61 MHz) spectrometers at room temperature (25 ºC). Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual solvent peaks recorded, rounded to the nearest 0.01 for ^{1}H-NMR and 0.1 for ^{13}C-NMR (reference: $CDCl_3$ [^{1}H: 7.26, ^{13}C: 77.2]). Spin-spin coupling constants (J) in ^{1}H-NMR were given in Hz to the nearest 0.1 Hz, and peak multiplicity was indicated as follows s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). ^{13}C NMR were recordered with complete proton decoupling. Carbon types, structure assignments and attribution of peaks were determined from DEPT-NMR and two dimensional correlation experiments (HMQC, COSY and HMBC). Relative stereochemistry was assigned based on the 1D-NOE experiments. High-resolution mass spectra (HRMS) were measured at mass spectrometry service of the Laboratory of Instrumental Techniques, University of Valladolid, on a UPLC-MS system (UPLC: Waters ACQUITY H-class UPLC; MS: Bruker Maxis Impact) by electrospray ionization (ESI positive and negative). Compound **1** has been previously described.[1]

2. Experimental Section

General procedure for the synthesis of amine 2. A mixture of allylsilyl ketone **1** (1 mmol) and benzylamine (3 mmol, 0.33 ml) was added to a 25 ml vial and irradiated in a microwave system (110 ºC, 600 r.p.m.) for 15 min. After this time, the waterdrops at the top of the vial were removed and the obtained imine was used without further purification.
To a stirred solution of this allylsilyl imine (1 mmol) in dry methanol (10 mL) under inert atmosphere and at reflux temperature was added $NaBH_4$ (3 mmol, 115 mg) in small portions (caution!). The mixture was stirred for 22 h at this temperature. After that time, the mixture was allowed to cool down to room temperature and methanol was removed in vacuo. The residue was dissolved in dichoromethane (10 mL) and water (10 mL) and was extracted with dichoromethane and washed with brine. The combined organic layer was dried, concentrated to dryness and cromatographied on silica gel (dicholomethane/methanol, 95:5, v/v) to afford amine **2**.

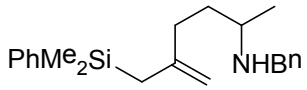
General procedure for Prins cyclization of allylsilyl amines under TMSOTf catalysis. To a stirred solution of the allylsilyl amine **2** (1 mmol) and the aldehyde (2.2 mmol) in dry dicholomethane (free of EtOH) (13 mL) under inert atmosphere at -78 °C was added dropwise TMSOTf (1.2 mmol). The mixture was stirred for 1 hour at -78 °C. Aqueous NaOH (2 M) was added and the mixture extracted with ether. The combined organic layer was dried, concentrated to dryness and cromatographied on silica gel (dicholomethane/methanol, 95:5/40:1, v/v) to afford compounds **3** and **4**.

[1] Pulido, F. J.; Barbero, A.; Castreño, P. *Eur. J. Org. Chem.* **2010**, 1307–1313.

General procedure for Prins cyclization of allylsilyl amines under $InCl_3$ catalysis. To a stirred suspension of $InCl_3$ (1 mmol, 23 mg) in dry acetonitrile (1 mL) under inert atmosphere and at reflux temperature was added dropwise the aldehyde (1 mmol) and a solution of the allylsilyl amine **2** (1 mmol) in acetonitrile (1 ml). The mixture was stirred for 18 h at this temperature. After that time, the mixture was allowed to cool to room temperature, and acetonitrile was removed in vacuo. The residue was dissolved in dicholomethane (10 mL) and was extracted with dicholomethane and washed with NaOH (1 M) and water. The combined organic layer was dried, concentrated to dryness and cromatographied on silica gel (hexanes/ethyl acetate, 50:1/30:1/20:1, v/v) to afford azepanes **7**.

3. Caracterization data for all compounds

***N*-Benzyl-5-(dimethylphenylsilylmethyl)hex-5-en-2-amine (2)**

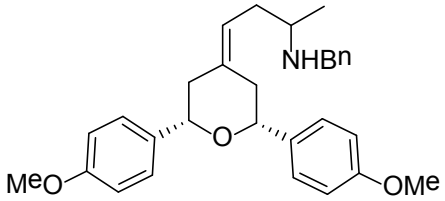


2

The product was isolated as a pale yellow oil (80% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.18, 95:5 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.39 – 7.31 (m, 8H), 4.62 (s, 1H), 4.54 (s, 1H), 3.84 (d, *J* = 13.1 Hz, 1H), 3.76 (d, *J* = 13.1 Hz, 1H), 2.70 – 2.61 (m, 1H), 1.87 – 1.82 (m, 2H), 1.77 (s, 2H), 1.71 – 1.61 (m, 1H), 1.51 – 1.42 (m, 1H), 1.06 (d, *J* = 6.3 Hz, 3H), 0.32 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6 (C), 139.1 (C), 133. 7 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 127.8 (CH), 127.4 (CH), 108.0 (CH_2), 52.3 (CH), 50.7 (CH_2), 34.4 (CH_2), 34.1 (CH_2), 26.1 (CH_2), 19.4 (CH_3), -2.9 (CH_3).
HRMS (ESI+) m/z calcd for $C_{22}H_{32}NSi$ ($[M+H]^+$): 338.2299, found 338.2300.

***N*-Benzyl-4-(*cis*-tetrahydro-2,6-di-(4-methoxyphenyl)pyran-4-ylidene)butan-2-amine (3a)**

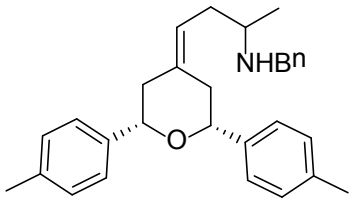


3a

The product was isolated as a viscous pale yellow oil (74% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.54, 10:1 DCM/MeOH). The doubling of some signals in ^{13}C indicates the presence of two epimers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 9H), 6.90 – 6.86 (m, 4H), 5.33 (t, *J* = 7.4 Hz, 1H), 4.45 – 4.41 (m, 1H), 4.37 – 4.31 (m, 1H), 3.89 (dd, *J* = 13.1 and 4.4 Hz, 1H), 3.82 – 3.77 (m, 1H), 3.80 (s, 6H), 2.83 – 2.74 (m, 2H), 2.40 – 2.28 (m, 3H), 2.24 – 2.16 (m, 2H), 2.08 (t, *J* = 12.7 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (C), 159.0 (C), 137.3 (C), 135.1 (C), 135.0 (C), 128.7 (CH), 128.5 (CH), 127.4 (CH), 127.3 (CH), 120.5 (CH), 113.8 (CH), 80.7 (CH), 80.0 (CH), 55.4 (CH_3), 55.3 (CH_3), 52.9 (CH), 51.3 (CH_2), 44.6 (CH_2), 37.4 (CH_2), 34.3 (CH_2), 20.0 (CH_3).
HRMS (ESI+) m/z calcd for $C_{30}H_{36}NO_3$ ($[M+H]^+$): 458.2690, found 458.2694.

***N*-Benzyl-4-(*cis*-tetrahydro-2,6-di-4-tolylpyran-4-ylidene)butan-2-amine (3b)**

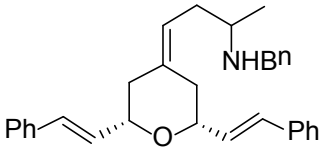


3b

The product was isolated as a viscous yellow oil (72% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.46, 10:1 DCM/MeOH). The doubling of some signals in ^{13}C indicates the presence of two epimers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 9H), 7.17 (d, *J* = 7.7 Hz, 4H), 5.36 (t, *J* = 7.5 Hz, 1H), 4.51 – 4.44 (m, 1H), 4.42 – 4.34 (m, 1H), 3.92 – 3.81 (m, 2H), 2.85 – 2.75 (m, 2H), 2.43 – 2.28 (m, 4H), 2.41 (s, 6H), 2.25 – 2.06 (m, 2H), 1.19 – 1.14 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9 (C), 139.8 (C), 137.2 (C), 137.1 (C), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.2 (CH), 125.9 (CH), 120.7 (CH), 80.8 (CH), 80.1 (CH), 52.9 (CH), 51.4 (CH_2), 44.7 (CH_2), 37.5 (CH_2), 34.4 (CH_2), 21.3 (CH_3), 20.1 (CH_3).
HRMS (ESI+) m/z calcd for $C_{30}H_{36}NO$ ($[M+H]^+$): 426.2791, found 426.2794.

***N*-Benzyl-4-(*cis*-tetrahydro-2,6-di-(*E*)-styrylpyran-4-ylidene)butan-2-amine (3c)**

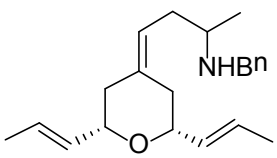


3c

The product was isolated as a viscous yellow oil (71% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.33, 95:5 DCM/MeOH). The doubling of some signals in ^{13}C indicates the presence of two epimers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.22 (m, 15H), 6.68 – 6.60 (m, 2H), 6.30 (dd, *J* = 16.0 and 6.2 Hz, 2H), 5.33 (t, *J* = 7.3 Hz, 1H), 4.11 – 4.03 (m, 1H), 4.03 – 3.93 (m, 1H), 3.90 (dd, *J* = 13.2 and 3.8 Hz, 1H), 3.79 (dd, *J* = 13.2 and 2.2 Hz, 1H), 2.84 – 2.73 (m, 1H), 2.73 – 2.66 (m, 1H), 2.36 – 2.13 (m, 5H), 2.02 – 1.93 (m, 1H), 1.16 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (C), 136.1 (C), 135.9 (C),131.0 (CH), 131.0 (CH), 129.9 (CH), 129.9 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.7 (CH), 127.1 (CH), 126.7 (CH), 126.7 (CH), 121.0 (CH), 79.3 (CH), 78.5 (CH), 52.9 (CH), 51.4 (CH_2), 42.4 (CH_2), 35.2 (CH_2), 34.4 (CH_2), 20.1 (CH_3).
HRMS (ESI+) m/z calcd for $C_{32}H_{36}NO$ ($[M+H]^+$): 450.2791, found 450.2797.

***N*-Benzyl-4-(*cis*-tetrahydro-2,6-di((*E*)-prop-1-enyl)pyran-4-ylidene)butan-2-amine (3d)**

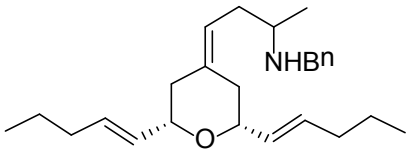


3d

The product was isolated as a pale yellow oil (68% yield) using flash chromatography 40:1 DCM/MeOH (Rf = 0.25, 5:1 DCM/MeOH). The doubling of some signals in ^{13}C indicates the presence of two epimers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 5.75 – 5.62 (m, 2H), 5.57 – 5.47 (m, 2H), 5.19 (t, *J* = 7.2 Hz, 1H), 3.92 – 3.60 (m, 4H), 2.78 – 2.74 (m, 1H), 2.49 (d, *J* = 13.6 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.18 – 2.07 (m, 4H), 1.82 – 1.78 (m, 1H), 1.69 (d, *J* = 6.2 Hz, 6H), 1.15 (d, *J* = 6.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1 (C), 137.1 (C), 131.9 (CH), 128.7 (CH), 128.7 (CH), 128.6 (CH), 119.8 (CH), 79.2 (CH), 78.4 (CH), 52.8 (CH), 50.8 (CH_2), 42.3 (CH_2), 35.1 (CH_2), 33.8 (CH_2), 19.4 (CH_3), 18.0 (CH_3), 17.9 (CH_3).
HRMS (ESI+) m/z calcd for $C_{22}H_{32}NO$ ($[M+H]^+$): 326.2478, found 326.2481.

***N*-Benzyl-4-(*cis*-tetrahydro-2,6-di((*E*)-pent-1-enyl)pyran-4-ylidene)butan-2-amine (3e)**

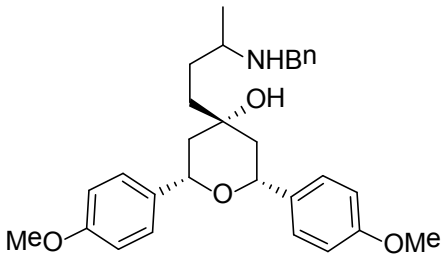


3e

The product was isolated as a viscous yellow oil (65% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.23, 5:1 DCM/MeOH). The doubling of some signals in ^{13}C indicates the presence of two epimers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 5.73 – 5.61 (m, 2H), 5.53 – 5.48 (m, 2H), 5.19 (t, *J* = 7.1 Hz, 1H), 3.91 – 3.62 (m, 4H), 2.78 – 2.74 (m, 1H), 2.49 (d, *J* = 14.0 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.19 – 1.95 (m, 8H), 1.83 – 1.77 (m, 1H), 1.43 – 1.39 (m, 4H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.92 – 0.87 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1 (C), 137.0 (C), 132.5 (CH), 130.8 (CH), 128.7 (CH), 128.6 (CH), 119.9 (CH_2), 79.3 (CH), 78.5 (CH), 52.7 (CH), 50.9 (CH_2), 42.5 (CH_2), 35.3 (CH_2), 34.6 (CH_2), 33.9 (CH_2), 22.3 (CH_2), 19.5 (CH_3), 13.9 (CH_3), 13.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{26}H_{40}NO$ ($[M+H]^+$): 382.3104, found 382.3103.

(2S*,4s*,6R*)-4-(3-Benzylaminobutyl)-tetrahydro-2,6-bis(4-methoxyphenyl)pyran-4-ol (4a)

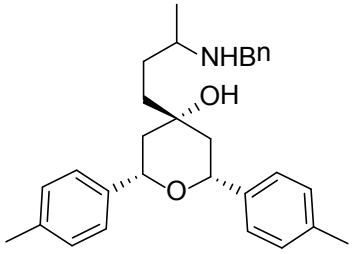


4a

The product was isolated as a viscous pale yellow oil (7% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.32, 10:1 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 10H), 6.88 – 6.82 (m, 4H), 4.51 – 4.45 (m, 2H), 3.90 (d, *J* = 12.9 Hz, 1H), 3.80 – 3.78 (m, 1H), 3.77 (s, 6H), 2.91 – 2.87 (m, 1H), 2.20 – 2.09 (m, 1H), 1.99 – 1.73 (m, 8H), 1.28 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (C), 159.0 (C), 134.8 (C), 129.1 (CH), 128.9 (CH), 128.1 (CH), 127.5 (CH), 127.5 (CH), 113.8 (CH), 77.0 (CH), 69.8 (C), 55.4 (CH_3), 55.3 (CH_3), 53.1 (CH), 50.4 (CH_2), 46.6 (CH_2), 45.6 (CH_2), 33.4 (CH_2), 29.8 (CH_2), 19.3 (CH_3).
HRMS (ESI+) m/z calcd for $C_{30}H_{38}NO_4$ ($[M+H]^+$): 476.2795, found 476.2795.

(2S*,4s*,6R*)-4-(3-Benzylaminobutyl)-tetrahydro-2,6-di-4-tolylpyran-4-ol (4b)

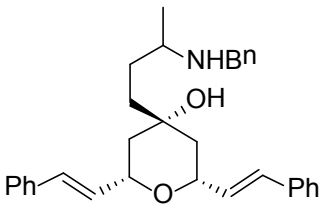


4b

The product was isolated as a viscous yellow oil (5% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.22, 5:1 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 9H), 7.14 – 7.11 (m, 4H), 4.50 (t, *J* = 10.8 Hz, 2H), 3.91 (d, *J* = 12.9 Hz, 1H), 3.79 (d, *J* = 12.9 Hz, 1H), 2.93 – 2.86 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.20 – 2.13 (m, 1H), 2.01 – 1.69 (m, 9H), 1.29 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7 (C), 137.1 (C), 136.7 (C), 129.1 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 126.1 (CH), 77.0 (CH), 69.8 (C), 53.1 (CH), 50.5 (CH_2), 46.6 (CH_2), 45.7 (CH_2), 33.3 (CH_2), 29.9 (CH_2), 21.3 (CH_3), 19.4 (CH_3).
HRMS (ESI+) m/z calcd for $C_{30}H_{38}NO_2$ ($[M+H]^+$): 444.2897, found 444.2901.

(2S*,4s*,6R*)-4-(3-Benzylaminobutyl)-tetrahydro-2,6-di-(*E*)-styrylpyran-4-ol (4c)

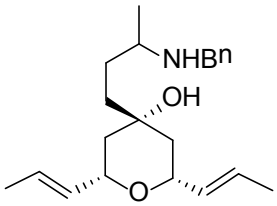


4c

The product was isolated as a viscous yellow white oil (7% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.21, 95:5 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 15H), 6.63 (dd, *J* = 16.0 and 4.4 Hz, 2H), 6.25 (ddd, *J* = 16.0, 6.2 and 3.2 Hz, 2H), 4.17 – 4.08 (m, 2H), 3.90 (d, *J* = 12.8 Hz, 1H), 3.80 (d, *J* = 12.8 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.10 – 2.01 (m, 1H), 1.87 (t, *J* = 13.1 Hz, 2H), 1.82 – 1.59 (m, 6H), 1.26 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9 (C), 136.8 (C), 130.9 (CH), 130.0 (CH), 128.9 (CH), 128.6 (CH), 127.9 (CH), 127.7 (CH), 126.7 (CH), 75.6 (CH), 75.5 (CH), 69.2 (C), 53.1 (CH), 50.8 (CH_2), 44.6 (CH_2), 43.8 (CH_2), 33.5 (CH_2), 30.1 (CH_2), 19.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{32}H_{38}NO_2$ ($[M+H]^+$): 468.2897, found 468.2898.

(2S*,4s*,6R*)-4-(3-Benzylaminobutyl)-tetrahydro-2,6-di((*E*)-prop-1-enyl)pyran-4-ol (4d)

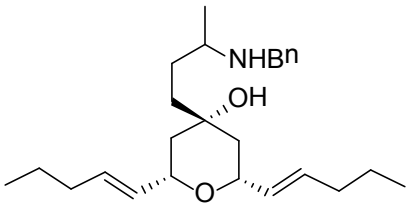


4d

The product was isolated as a yellow oil (8% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.40, 10:1 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 5H), 5.72 – 5.62 (m, 2H), 5.47 (ddd, *J* = 15.4, 4.8 and 1.8 Hz, 2H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.84 – 3.74 (m, 3H), 2.92 – 2.80 (m, 1H), 1.97 – 1.84 (m, 1H), 1.83 – 1.55 (m, 11H), 1.53 – 1.40 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2 (C), 131.9 (CH), 129.4 (CH), 129.0 (CH), 128.4 (CH), 127.7 (CH), 75.3 (CH), 75.2 (CH), 69.6 (C), 53.0 (CH), 49.8 (CH_2), 44.5 (CH_2), 43.2 (CH_2), 33.2 (CH_2), 29.1 (CH_2), 18.7 (CH_3), 17.9 (CH_3), 17.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{22}H_{34}NO_2$ ($[M+H]^+$): 344.2584, found 344.2579.

(2S*,4s*,6R*)-4-(3-Benzylaminobutyl)-tetrahydro-2,6-di((*E*)-pent-1-enyl)pyran-4-ol (4e)

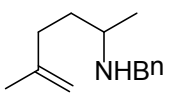


4e

The product was isolated as a viscous yellow oil (7% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.13, 95:5 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.25 (m, 5H), 5.71 – 5.60 (m, 2H), 5.51 – 5.41 (m, 2H), 3.93 (d, *J* = 13.0 Hz, 1H), 3.87 – 3.75 (m, 3H), 2.90 – 2.77 (m, 1H), 2.06 – 1.89 (m, 5H), 1.81 – 1.61 (m, 5H), 1.54 – 1.34 (m, 6H), 1.26 (d, *J* = 6.1 Hz, 3H), 0.91 – 0.83 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2 (C), 132.4 (CH), 130.8 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 75.4 (CH), 75.3 (CH), 69.5 (C), 53.0 (CH), 50.2 (CH_2), 44.8 (CH_2), 43.5 (CH_2), 34.5 (CH_2), 33.3 (CH_2), 29.4 (CH_2), 22.3 (CH_2), 19.0 (CH_3), 13.9 (CH_3).
HRMS (ESI+) m/z calcd for $C_{26}H_{42}NO_2$ ($[M+H]^+$): 400.3210, found 400.3211.

***N*-Benzyl-5-methylhex-5-en-2-amine (5)**

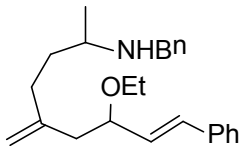


5

The product was isolated as a pale yellow oil (71% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.13, 95:5 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 4.68 (s, 1H), 4.66 (s, 1H), 3.85 (d, *J* = 13.0 Hz, 1H), 3.76 (d, *J* = 13.0 Hz, 1H), 3.19 (s, br, 1H), 2.80 – 2.66 (m, 1H), 2.11 – 1.96 (m, 2H), 1.71 – 1.62 (m, 1H), 1.70 (s, 3H), 1.55 – 1.48 (m, 1H), 1.13 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7 (C), 139.4 (C), 128.6 (CH), 128.6 (CH), 127.3 (CH), 110.1 (CH_2), 52.4 (CH), 51.0 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 22.6 (CH_3), 19.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{14}H_{22}N$ ($[M+H]^+$): 204.1747, found 204.1751.

(*E*)-*N*-Benzyl-7-ethoxy-5-methylene-9-phenylnon-8-en-2-amine (6c)

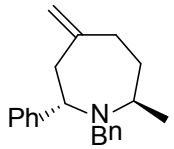


6c

The product (mixture of diastereoisomers) was isolated as a viscous yellow oil (66% yield) using flash chromatography 95:5 DCM/MeOH (Rf = 0.38, 10:1 DCM/MeOH).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 10H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9 and 7.7 Hz, 1H), 4.83 (s, 2H), 4.01 – 3.95 (m, 1H), 3.86 (d, *J* = 13.0 Hz, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 3.65 – 3.59 (m, 1H), 3.43 – 3.37 (m, 1H), 2.81 – 2.70 (m, 1H), 2.46 (dd, *J* = 14.3 and 7.1 Hz, 1H), 2.28 (dd, *J* = 14.3 and 6.2 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.78 – 1.67 (m, 1H), 1.60 – 1.50 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9 (C), 139.6 (C), 136.8 (C), 131.7 (CH), 130.6 (CH), 128.6 (CH), 128.5 (CH), 127.7 (CH), 127.2 (CH), 126.5 (CH), 111.9 (CH_2), 79.6 (CH), 63.9 (CH_2), 52.4 (CH), 51.0 (CH_2), 42.6 (CH_2), 34.4 (CH_2), 32.9 (CH_2), 19.8 (CH_3), 15.5 (CH_3).
HRMS (ESI+) m/z calcd for $C_{25}H_{34}NO$ ($[M+H]^+$): 364.2635, found 364.2637.

***Trans*-1-Benzyl-7-methyl-4-methylene-2-phenylazepane (7a)**

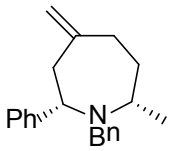


***Trans*-7a**

Flash chromatography (30:1 hexane/EtOAc) gave the azepanes as a mixture (80% yield) (Rf = 0.46, 20:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.34 – 7.16 (m, 8H), 4.87 (s, 1H), 4.86 (s, 1H), 4.12 (dd, *J* = 9.7 and 4.6 Hz, 1H), 3.71 (s, 2H), 3.21 – 3.11 (m, 1H), 2.89 (dd, *J* = 14.3 and 4.6 Hz, 1H), 2.77 (dd, *J* = 14.3 and 9.7 Hz, 1H), 2.48 – 2.31 (m, 2H), 1.93 – 1.86 (m, 1H), 1.67 – 1.59 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2 (C), 145.5 (C), 141.4 (C), 128.5 (CH), 128.1 (CH), 127.6 (CH), 126.5 (CH), 126.3 (CH), 112.2 (CH_2), 59.2 (CH), 52.3 (CH_2), 51.2 (CH), 40.8 (CH_2), 33.7 (CH_2), 32.6 (CH_2), 18.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{21}H_{26}N$ ($[M+H]^+$): 292.2060, found 292.2059.

***Cis*-1-Benzyl-7-methyl-4-methylene-2-phenylazepane (7a)**

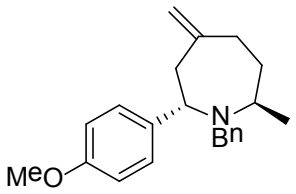


***Cis*-7a**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7a**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 2H), 3.34 – 3.26 (m, 1H), 3.02 (dd, *J* = 14.7 and 11.4 Hz, 1H), 2.65 (dd, *J* = 14.7 and 2.6 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8 (C), 145.3 (C), 142.8 (C), 128.1(CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 126.6 (CH), 126.1 (CH), 112.2 (CH_2), 67.5 (CH), 59.7 (CH), 50.8 (CH_2), 41.1 (CH_2), 34.3 (CH_2), 32.4 (CH_2), 23.5 (CH_3).

***Trans*-1-Benzyl-2-(4-methoxyphenyl)-7-methyl-4-methyleneazepane (7b)**

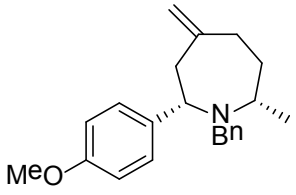


***Trans*-7b**

Flash chromatography (30:1 hexane/EtOAc) gave the *trans*-azepane as a pure compound (75% yield of the mixture of isomers) (Rf = 0.50, 15:1 hexane/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.28 – 7.12 (m, 5H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.85 (s, 1H), 4.83 (s, 1H), 4.08 (dd, *J* = 9.7 and 4.6 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 2H), 3.17 – 3.06 (m, 1H), 2.85 (dd, *J* = 14.6 and 4.6 Hz, 1H), 2.74 (dd, *J* = 14.6 and 9.7 Hz, 1H), 2.50 – 2.39 (m, 1H), 2.39 – 2.26 (m, 1H), 1.91 – 1.85 (m, 1H), 1.63 – 1.56 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (C), 149.4 (C), 141.5 (C), 137.6 (C), 128.7 (CH), 128.5 (CH), 128.1 (CH), 126.5 (CH), 113.4 (CH), 112.1 (CH_2), 58.2 (CH), 55.4 (CH_3), 52.1 (CH_2), 51.1 (CH), 40.7 (CH_2), 33.5 (CH_2), 32.7 (CH_2), 18.8 (CH_3).
HRMS (ESI+) m/z calcd for $C_{22}H_{28}NO$ ($[M+H]^+$): 322.2165, found 322.2170.

***Cis*-1-Benzyl-2-(4-methoxyphenyl)-7-methyl-4-methyleneazepane (7b)**

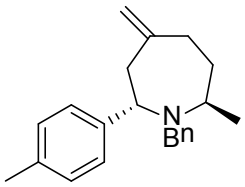


***Cis*-7b**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7b**

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.64 (s, 2H), 3.33 – 3.24 (m, 1H), 2.96 (dd, *J* = 14.6 and 11.5 Hz, 1H), 2.65 – 2.60 (m, 1H), 1.77 – 1.72 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, CDCl3) δ 129.0 (CH), 128.1 (CH), 127.7 (CH), 126.0 (CH), 113.4 (CH), 66.8 (CH), 59.7 (CH), 41.4 (CH_2), 34.4 (CH_2), 23.6 (CH_3).

***Trans*-1-Benzyl-7-methyl-4-methylene-2-p-tolylazepane (7c)**

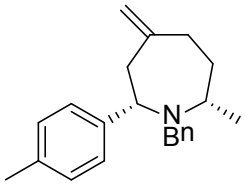


***Trans*-7c**

Flash chromatography (30:1 hexane/EtOAc) gave the azepanes as a mixture (82% yield) (Rf = 0.43, 20:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.33 – 7.23 (m, 4H), 7.21 – 7.12 (m, 3H), 4.89 (s, 1H), 4.88 (s, 1H), 4.12 (dd, *J* = 9.8 and 4.6 Hz, 1H), 3.73 (s, 2H), 3.20 – 3.14 (m, 1H), 2.90 (dd, *J* = 14.5 and 4.6 Hz, 1H), 2.78 (dd, *J* = 14.5 and 9.8 Hz, 1H), 2.50 – 2.43 (m, 1H), 2.40 – 2.33 (m, 1H), 2.36 (s, 3H), 1.95 – 1.88 (m, 1H), 1.68 – 1.60 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (C), 142.5 (C), 141.5 (C), 135.8 (C), 128.8 (CH), 128.5 (CH), 128.1 (CH), 127.5 (CH), 126.5 (CH), 112.1 (CH_2), 58.8 (CH), 52.2 (CH_2), 51.1 (CH), 40.8 (CH_2), 33.6 (CH_2), 32.6 (CH_2), 21.1 (CH_3), 18.7 (CH_3).
HRMS (ESI+) m/z calcd for $C_{22}H_{28}N$ ($[M+H]^+$): 306.2216, found 306.2220.

***Cis*-1-Benzyl-7-methyl-4-methylene-2-p-tolylazepane (7c)**

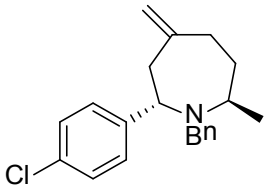


***Cis*-7c**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7c**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 2H), 3.36 – 3.26 (m, 1H), 3.01 (dd, *J* = 14.3 and 11.4 Hz, 1H), 2.65 (dd, *J* = 14.3 and 2.9 Hz, 1H), 1.82 – 1.75 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (C), 142.9 (C), 128.7 (CH), 128.0 (CH), 127.8 (CH), 126.0 (CH), 67.2 (CH), 59.5 (CH), 50.9 (CH_2), 41.3 (CH_2), 34.3 (CH_2), 32.2 (CH_2), 23.6 (CH_3).

***Trans*-1-Benzyl-2-(4-chlorophenyl)-7-methyl-4-methyleneazepane (7d)**

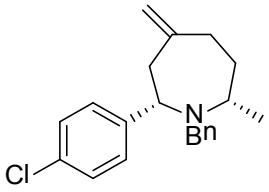


***Trans*-7d**

Flash chromatography (30:1 hexane/EtOAc) gave the azepanes as a mixture (79% yield) (Rf = 0.45, 20:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.12 (m, 7H), 4.87 (s, 1H), 4.83 (s, 1H), 4.06 (dd, *J* = 9.6 and 4.8 Hz, 1H), 3.68 (s, 2H), 3.19 – 3.08 (m, 1H), 2.85 (dd, *J* = 14.5 and 4.8 Hz, 1H), 2.68 (dd, *J* = 14.5 and 9.6 Hz, 1H), 2.42 (ddd, *J* = 12.8, 8.4 and 4.2 Hz, 1H), 2.36 – 2.28 (m, 1H), 1.89 – 1.81 (m, 1H), 1.67 – 1.58 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6 (C), 144.1 (C), 141.0 (C), 131.9 (C), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.7 (CH), 112.5 (CH_2), 58.9 (CH), 52.3 (CH_2), 51.2 (CH), 40.7 (CH_2), 33.8 (CH_2), 32.5 (CH_2), 19.0 (CH_3).
HRMS (ESI+) m/z calcd for $C_{21}H_{25}ClN$ ($[M+H]^+$): 326.1670, found 326.1673.

***Cis*-1-Benzyl-2-(4-chlorophenyl)-7-methyl-4-methyleneazepane (7d)**

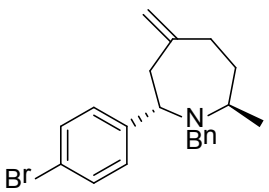


***Cis*-7d**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7d**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 – 3.24 (m, 1H), 2.96 (dd, *J* = 14.7 and11.4 Hz, 1H), 2.62-2.58 (m, 1H), 1.77 – 1.71 (m, 1H), 1.05 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 129.2 (CH), 128.0 (CH), 127.8 (CH), 126.2 (CH), 66.5 (CH), 59.8 (CH), 50.8 (CH_2), 40.8 (CH_2), 34.3 (CH_2), 32.6 (CH_2), 23.4 (CH_3).

***Trans*-1-Benzyl-2-(4-bromophenyl)-7-methyl-4-methyleneazepane (7e)**

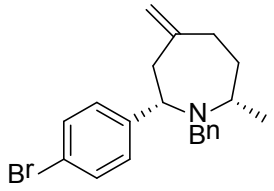


***Trans*-7e**

Flash chromatography (30:1 hexane/EtOAc) gave the azepanes as a mixture (78% yield) (Rf = 0.55, 30:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.20 (m, 9H), 4.88 (s, 1H), 4.84 (s, 1H), 4.04 (dt, *J* = 9.8 and 5.0 Hz, 1H), 3.69 – 3.67 (m, 2H), 3.20 – 3.06 (m, 1H), 2.85 (dt, *J* = 14.6 and 5.0 Hz, 1H), 2.67 (ddd, *J* = 14.6, 9.6 and 5.5 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.38 – 2.29 (m, 1H), 1.90 – 1.80 (m, 1H), 1.68 – 1.58 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6 (C), 144.7 (C), 141.1 (C), 140.0 (C), 131.2 (CH), 129.4 (CH), 128.5 (CH), 128.2 (CH), 126.7 (CH), 112.5 (CH_2), 59.3 (CH), 52.5 (CH_2), 51.3 (CH), 40.8 (CH_2), 33.9 (CH_2), 32.6 (CH_2), 19.0 (CH_3).
HRMS (ESI+) m/z calcd for $C_{21}H_{25}BrN$ ($[M+H]^+$): 370.1165, found 370.1169.

***Cis*-1-Benzyl-2-(4-bromophenyl)-7-methyl-4-methyleneazepane (7e)**

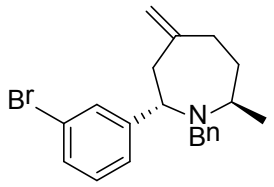


***Cis*-7e**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7e**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.32 – 3.24 (m, 1H), 2.96 (dt, *J* = 14.6 and 11.4 Hz, 1H), 2.65-2.60 (m, 1H), 1.78 – 1.72 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H).
).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (C), 144.3 (C), 142.2 (C), 131.0 (CH), 130.0 (CH), 128.0 (CH), 127.8 (CH), 126.2 (CH), 66.7 (CH), 59.8 (CH), 51.0 (CH_2), 40.7 (CH_2), 34.4 (CH_2), 23.5 (CH_3).

***Trans*-1-Benzyl-2-(3-bromophenyl)-7-methyl-4-methyleneazepane (7f)**



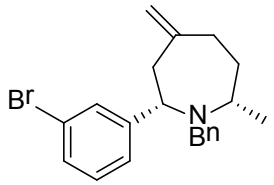
***Trans*-7f**

Flash chromatography (30:1 hexane/EtOAc) gave the azepanes as a mixture (76% yield) (Rf = 0.49, 30:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 1H), 7.43 – 7.16 (m, 8H), 4.91 (s, 1H), 4.88 (s, 1H), 4.09 (dd, *J* = 9.6 and 4.6 Hz, 1H), 3.72 (s, 2H), 3.26 – 3.11 (m, 1H), 2.89 (dd, *J* = 14.5 and 4.6 Hz, 1H), 2.71 (ddd, *J* = 14.5, 9.6 and 2.1 Hz, 1H), 2.49 – 2.43 (m, 1H), 2.39 – 2.30 (m, 1H), 1.93 – 1.84 (m, 1H), 1.73 – 1.62 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5 (C), 148.1 (C), 140.9 (C), 139.9 (C), 130.7 (CH), 129.7 (CH), 129.4 (CH), 128.5 (CH), 128.2 (CH), 126.7 (CH), 126.2 (CH), 112.6 (CH_2), 59.1 (CH), 52.4 (CH_2), 51.2 (CH), 40.7 (CH_2), 33.8 (CH_2), 32.4 (CH_2), 19.0 (CH_3).

HRMS (ESI+) m/z calcd for $C_{21}H_{25}BrN$ ($[M+H]^+$): 370.1165, found 370.1171.

***Cis*-1-Benzyl-2-(3-bromophenyl)-7-methyl-4-methyleneazepane (7f)**

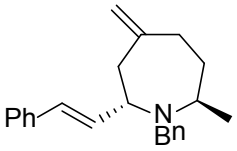


***Cis*-7f**

Minor isomer: distinguishable signals from a mixture of major ***trans*** and minor ***cis*-7f**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 – 3.26 (m, 1H), 3.03-2.95 (m, 1H), 1.82 – 1.72 (m, 1H), 1.11 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2 (C), 147.6 (C), 142.0 (C), 131.2 (CH), 129.6 (CH), 129.5 (CH), 128.0 (CH), 127.7 (CH), 126.4 (CH), 126.3 (CH), 66.6 (CH), 59.9 (CH), 50.6 (CH_2), 40.6 (CH_2), 34.3 (CH_2), 32.7 (CH_2), 23.4 (CH_3).

***Trans*-1-Benzyl-7-methyl-4-methylene-2-styrylazepane (7g)**

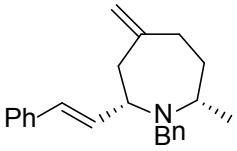


***Trans*-7g**

Chromatography (20:1 hexane/EtOAc) gave partial separation of both azepanes (80% yield of the mixture) (Rf = 0.56, 20:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 10H), 6.58 (d, *J* = 16.1 Hz, 1H), 6.28 (dd, *J* = 16.0 and 5.0 Hz, 1H), 4.88 (s, 2H), 3.92 (d, *J* = 14.5 Hz, 1H), 3.79 (d, *J* = 14.5 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.21 – 3.12 (m, 1H), 2.73 (dd, *J* = 14.4 and 5.0 Hz, 1H), 2.53 (dd, *J* = 14.4 and 8.9 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.37 – 2.30 (m, 1H), 1.85 – 1.77 (m, 1H), 1.68 – 1.60 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7 (C), 141.8 (C), 137.9 (C), 134.1 (CH), 129.2 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.1 (CH), 126.6 (CH), 126.3 (CH), 112.1 (CH_2), 56.6 (CH), 51.6 (CH_2), 51.2 (CH), 40.5 (CH_2), 33.9 (CH_2), 32.0 (CH_2), 20.5 (CH_3).
HRMS (ESI+) m/z calcd for $C_{23}H_{28}N$ ($[M+H]^+$): 318.2216, found 318.2217.

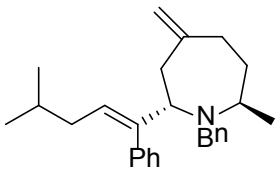
***Cis*-1-Benzyl-7-methyl-4-methylene-2-styrylazepane (7g)**



***Cis*-7g**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.12 (m, 10H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0 and 6.7 Hz, 1H), 4.84 (s, 2H), 3.76 (s, 2H), 3.75-3.72 (m, 1H), 3.18-3.13 (m, 1H), 2.69 (dd, *J* = 14.5 and 10.3 Hz, 1H), 2.59 (dd, *J* = 14.5 and 5.3 Hz, 1H), 2.41 – 2.35 (m, 2H), 1.75 – 1.66 (m, 2H), 1.06 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2 (C), 143.5 (C), 137.8 (C), 134.2 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 126.3 (CH), 126.2 (CH), 112.0 (CH_2), 64.3 (CH), 60.4 (CH), 49.2 (CH_2), 41.3 (CH_2), 34.5 (CH_2), 29.9 (CH_3).
HRMS (ESI+) m/z calcd for $C_{23}H_{28}N$ ($[M+H]^+$): 318.2216, found 318.2217.

***Trans*-1-Benzyl-7-methyl-2-((*E*)-4-methyl-1-phenylpent-1-enyl)-4-methyleneazepane (7h)**

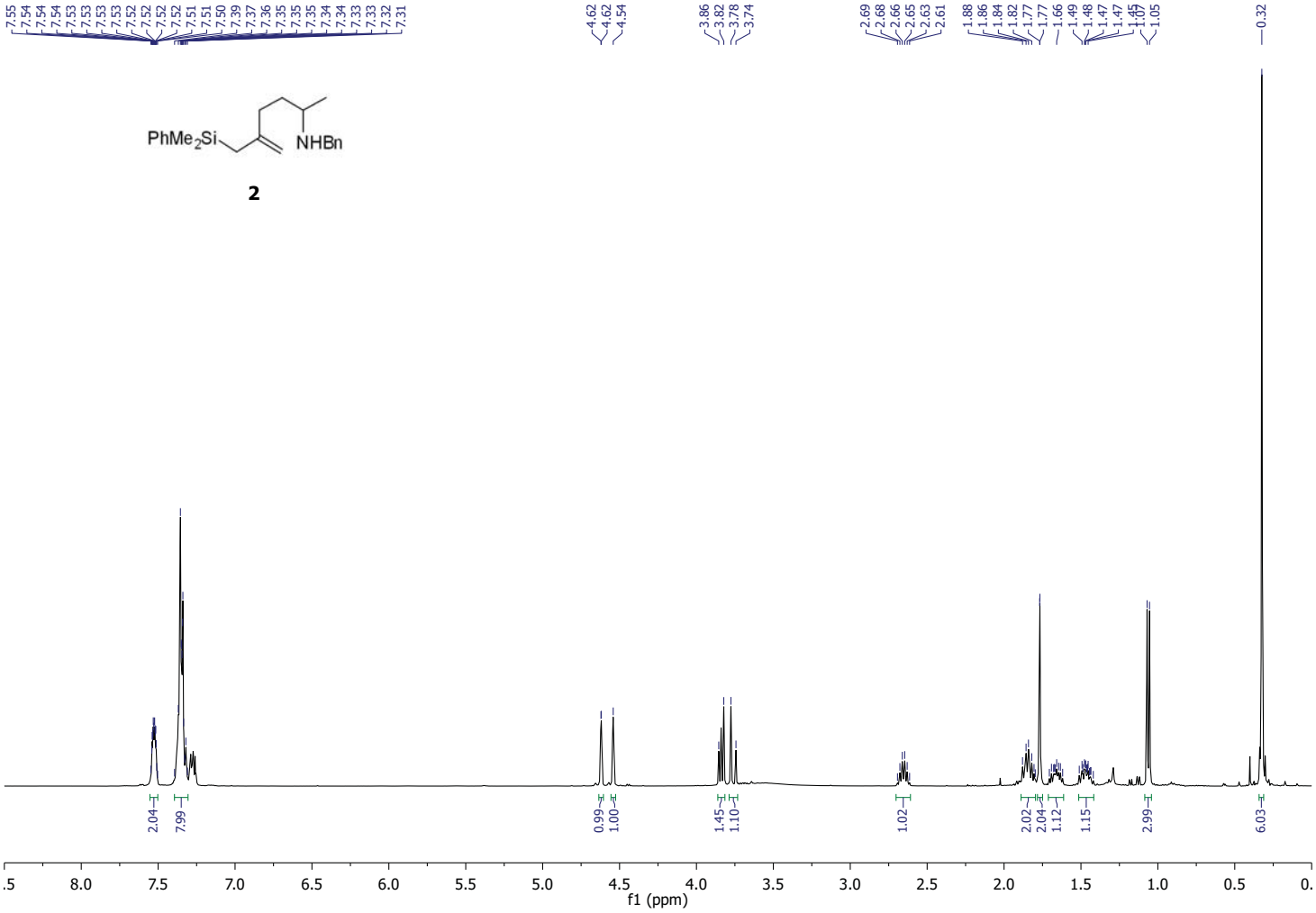


***Trans*-7h**

The product was isolated as a viscous brown oil (75% yield) using flash chromatography 50:1 hexane/EtOAc (Rf = 0.38, 30:1 hexane/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 8H), 7.00 – 6.95 (m, 2H), 5.68 (t, *J* = 7.4 Hz, 1H), 4.79 (s, 1H), 4.76 (s, 1H), 3.96 (d, *J* = 14.3 Hz, 1H), 3.74 (d, *J* = 14.3 Hz, 1H), 3.69 (dd, *J* = 10.1 and 5.7 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.54 – 2.42 (m, 2H), 2.40 – 2.35 (m, 1H), 2.21 – 2.14 (m, 1H), 1.77 – 1.50 (m, 5H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (C), 144.0 (C), 141.7 (C), 129.3 (CH), 128.7 (CH), 128.0 (CH), 127.7 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 111.7 (CH_2), 62.5 (CH), 52.1 (CH_2), 50.8 (CH), 40.0 (CH_2), 37.9 (CH_2), 35.2 (CH_2), 32.2 (CH_2), 29.1 (CH), 22.6 (CH_3), 22.5 (CH_3), 20.6 (CH_3).
HRMS (ESI+) m/z calcd for $C_{27}H_{36}N$ ($[M+H]^+$): 374.2842, found 374.2845.

4. Copies of NMR Spectra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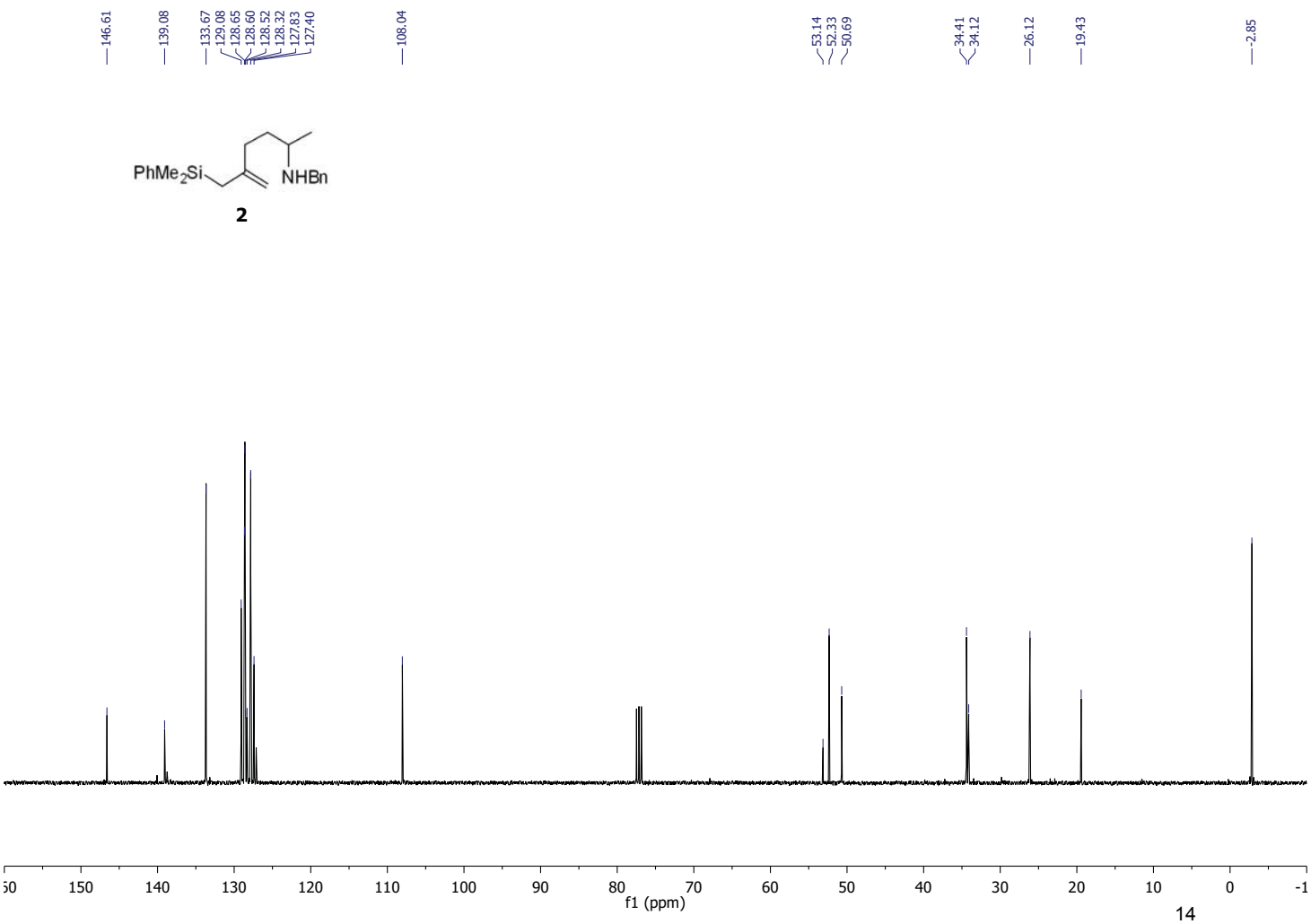
4.62 4.62 4.54
3.86 3.82 3.78 3.74
2.69 2.68 2.66 2.65 2.63 2.61
1.88 1.86 1.84 1.82 1.77 1.77 1.66 1.49 1.48 1.47 1.47 1.05 1.05
0.32
PhMe2Si
NHBn
2.04 7.99 0.99 1.00 1.45 1.10 1.02 2.02 2.04 1.12 1.15 2.99 6.03
f1 (ppm)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139.08
133.67
129.08
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128.60
128.52
128.32
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127.40
108.04
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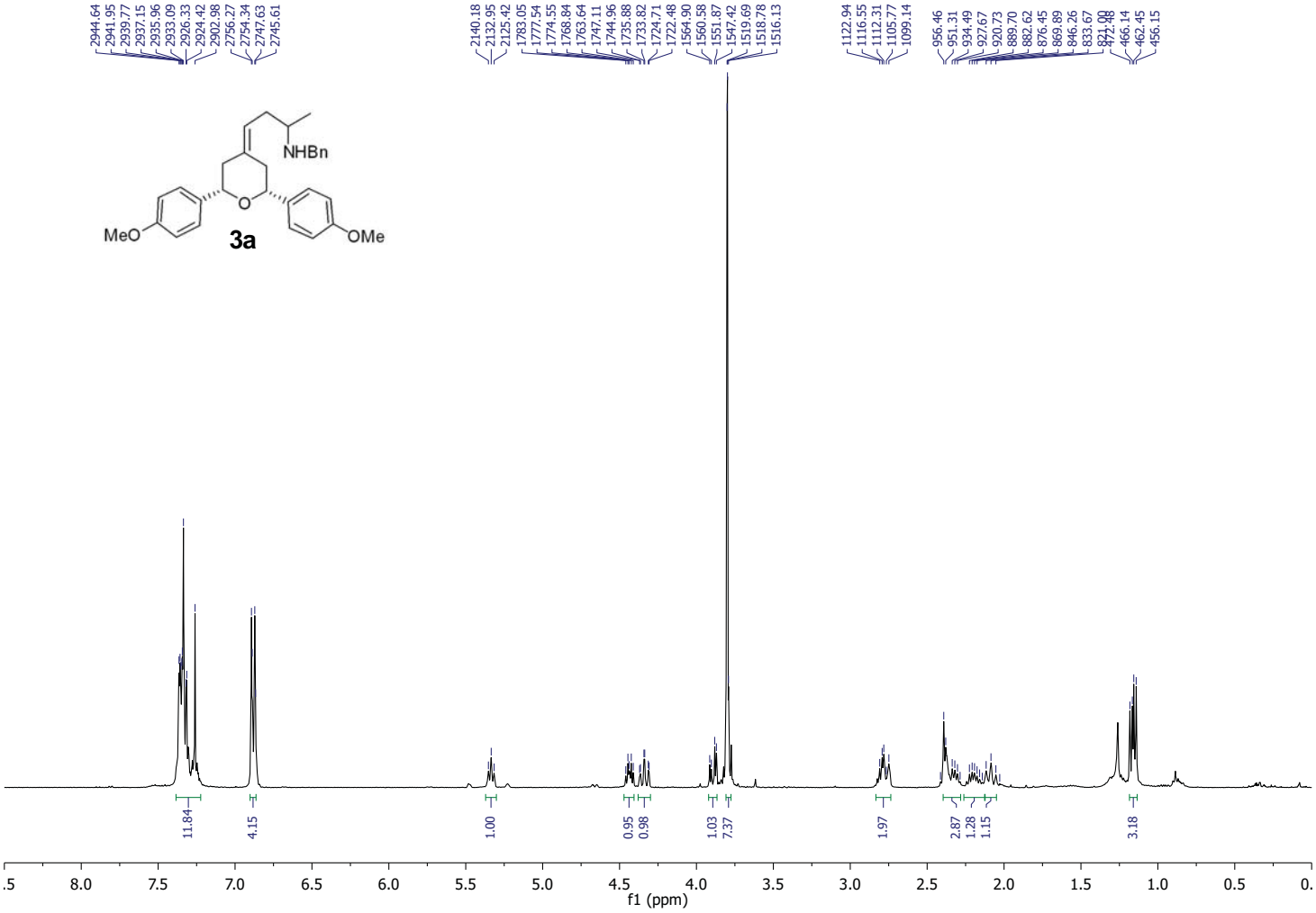
50.69
34.41
34.12
26.12
19.43
-2.85
PhMe2Si
NHBn
f1 (ppm)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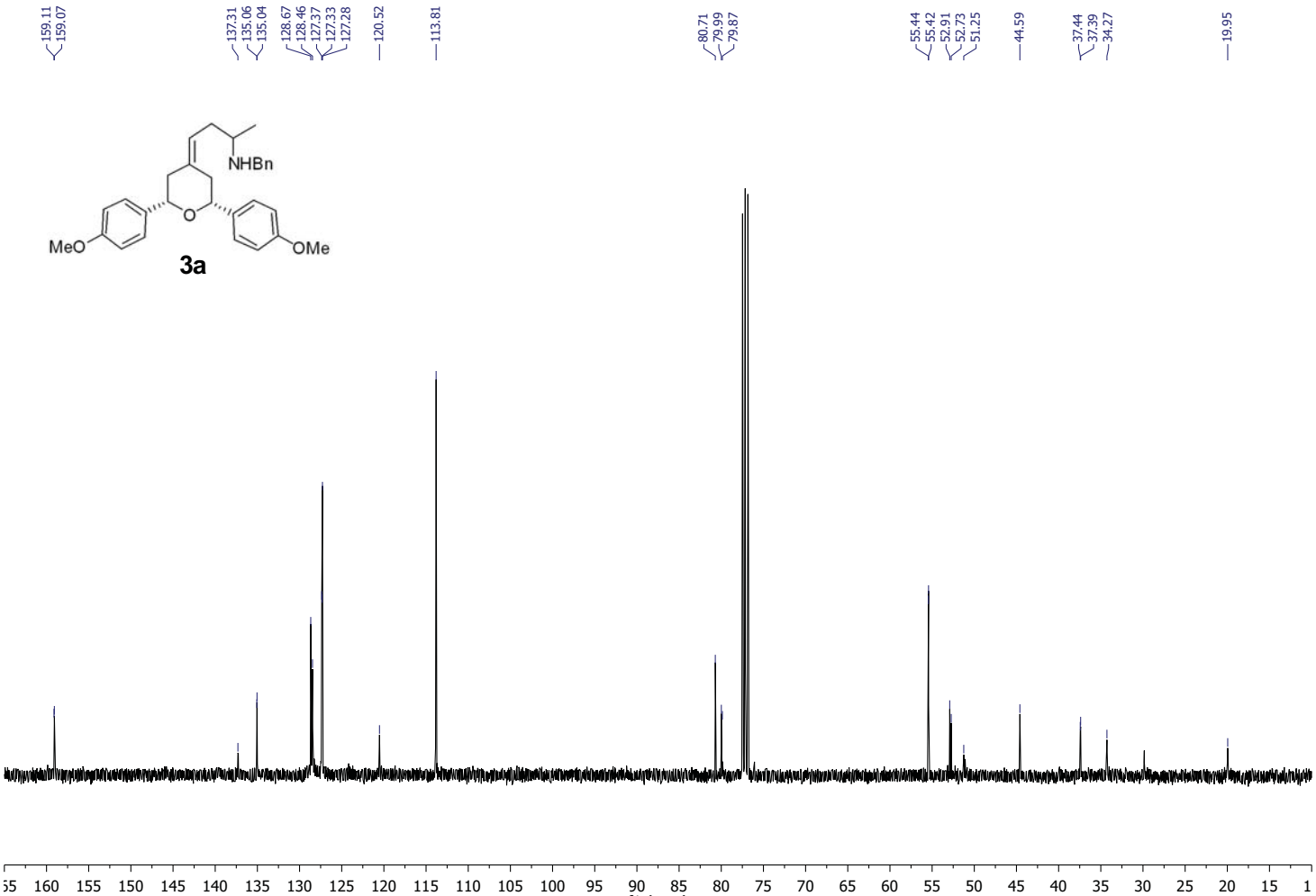
2939.77
2937.15
2935.96
2933.09
2926.33
2924.42
2902.98
2756.27
2754.34
2747.63
2745.61
2140.18
2132.95
2125.42
1783.05
1777.54
1774.55
1768.84
1763.64
1747.11
1744.96
1735.88
1733.82
1724.71
1722.48
1564.90
1560.58
1551.87
1547.42
1519.69
1518.78
1516.13
1122.94
1116.55
1112.31
1105.77
1099.14
956.46
951.31
934.49
927.67
920.73
889.70
882.62
876.45
869.89
846.26
833.67
821.00
472.48
466.14
462.45
456.15
NHBn
MeO
OMe
3a
11.84
4.15
1.00
0.95
0.98
1.03
7.37
1.97
2.87
1.28
1.15
3.18
f1 (ppm)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135.04
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128.46
127.37
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127.28
120.52
113.81
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79.99
79.87
55.44
55.42
52.91
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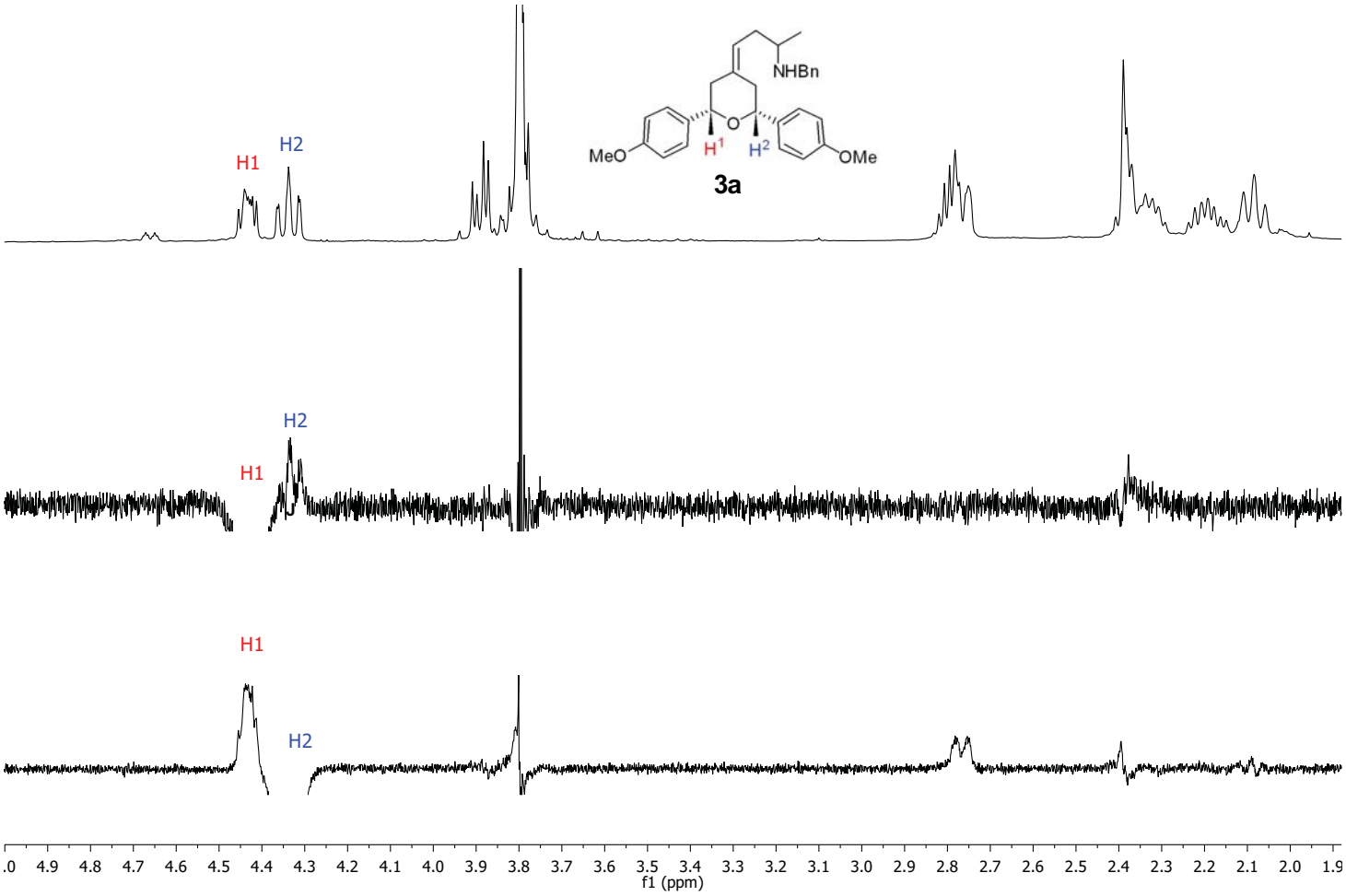
NHBn
MeO
OMe
3a
f1 (ppm)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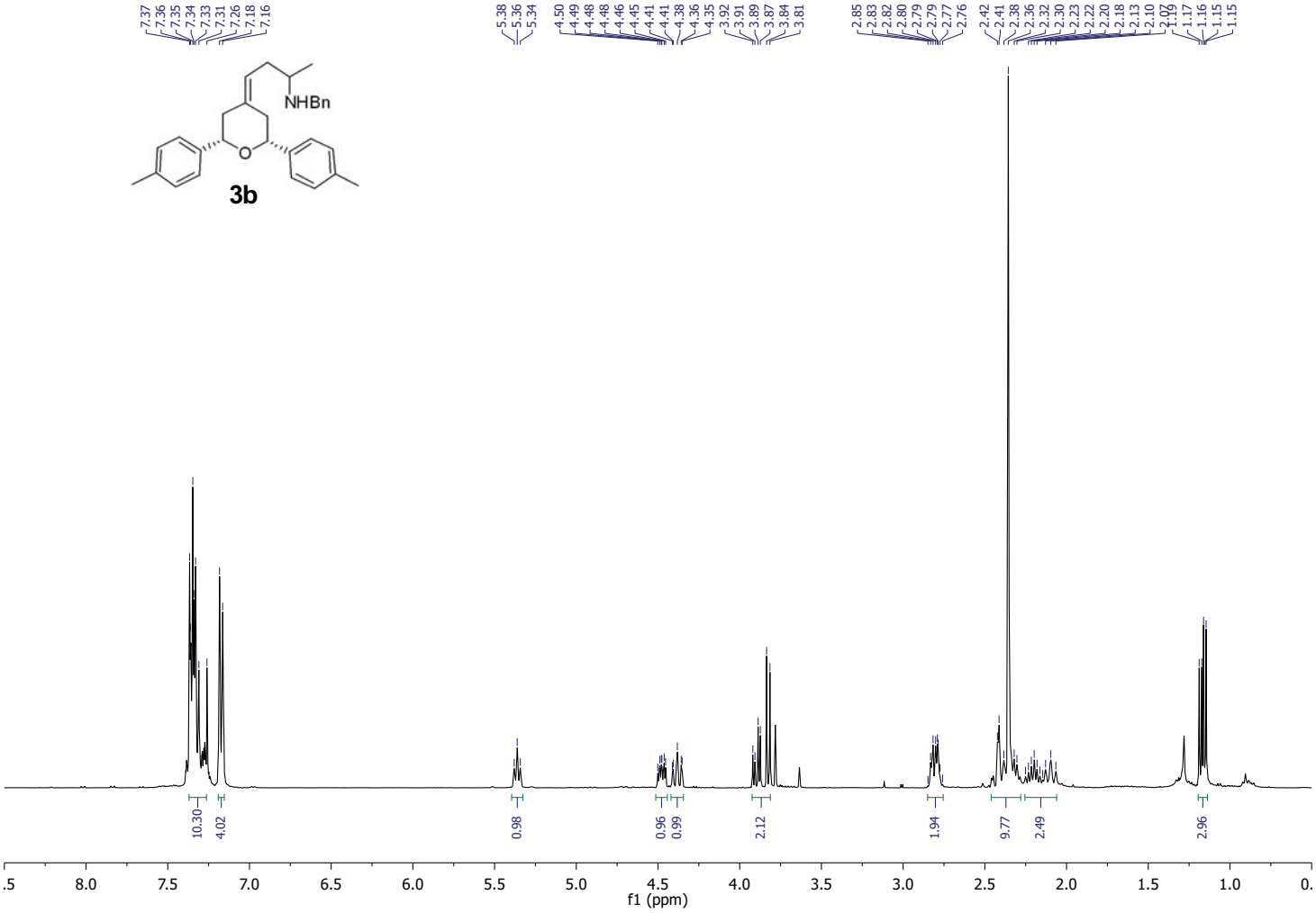
MeO
OMe
H1
H2
3a
H1
H2
H1
H2
f1 (ppm)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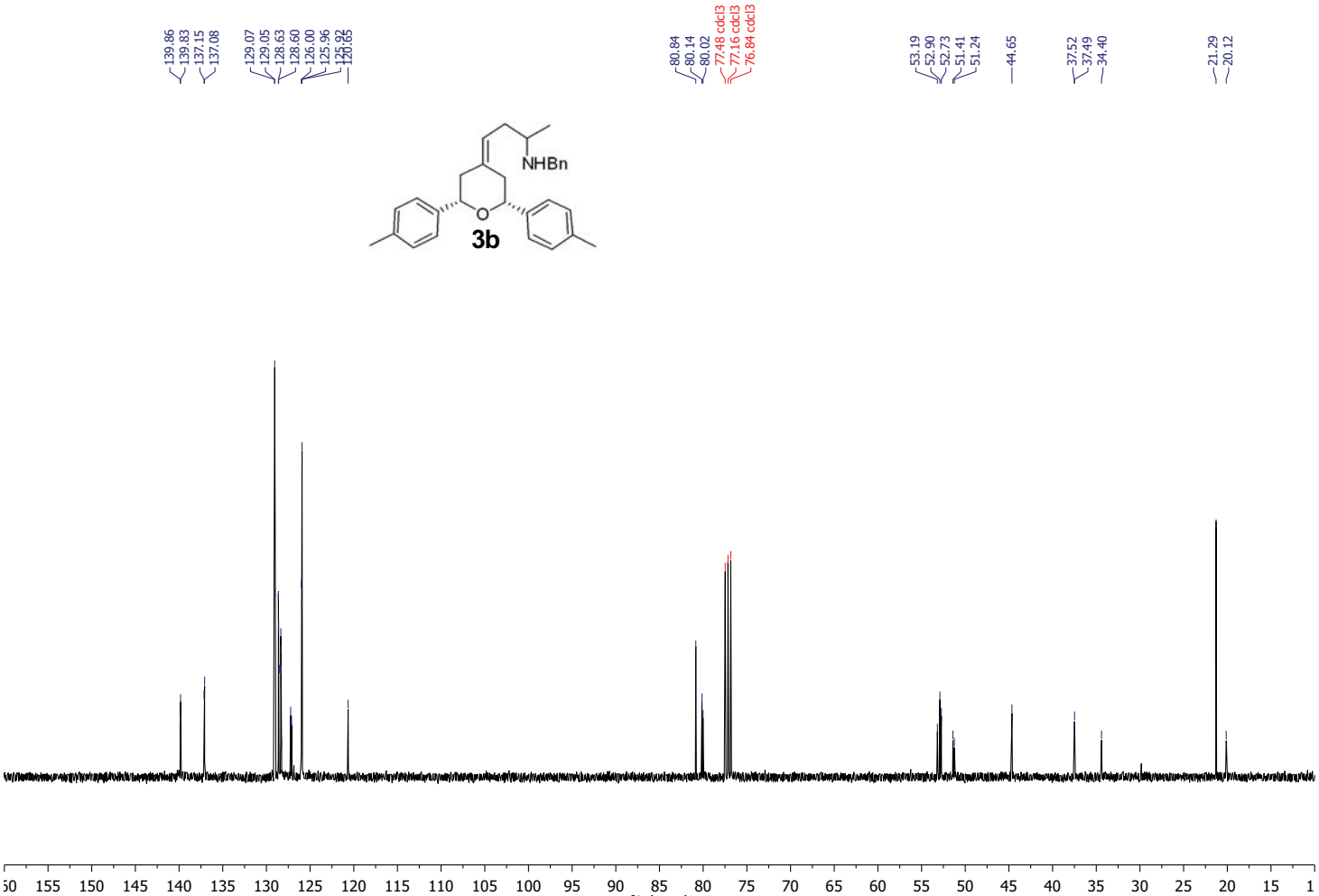
3b
f1 (ppm)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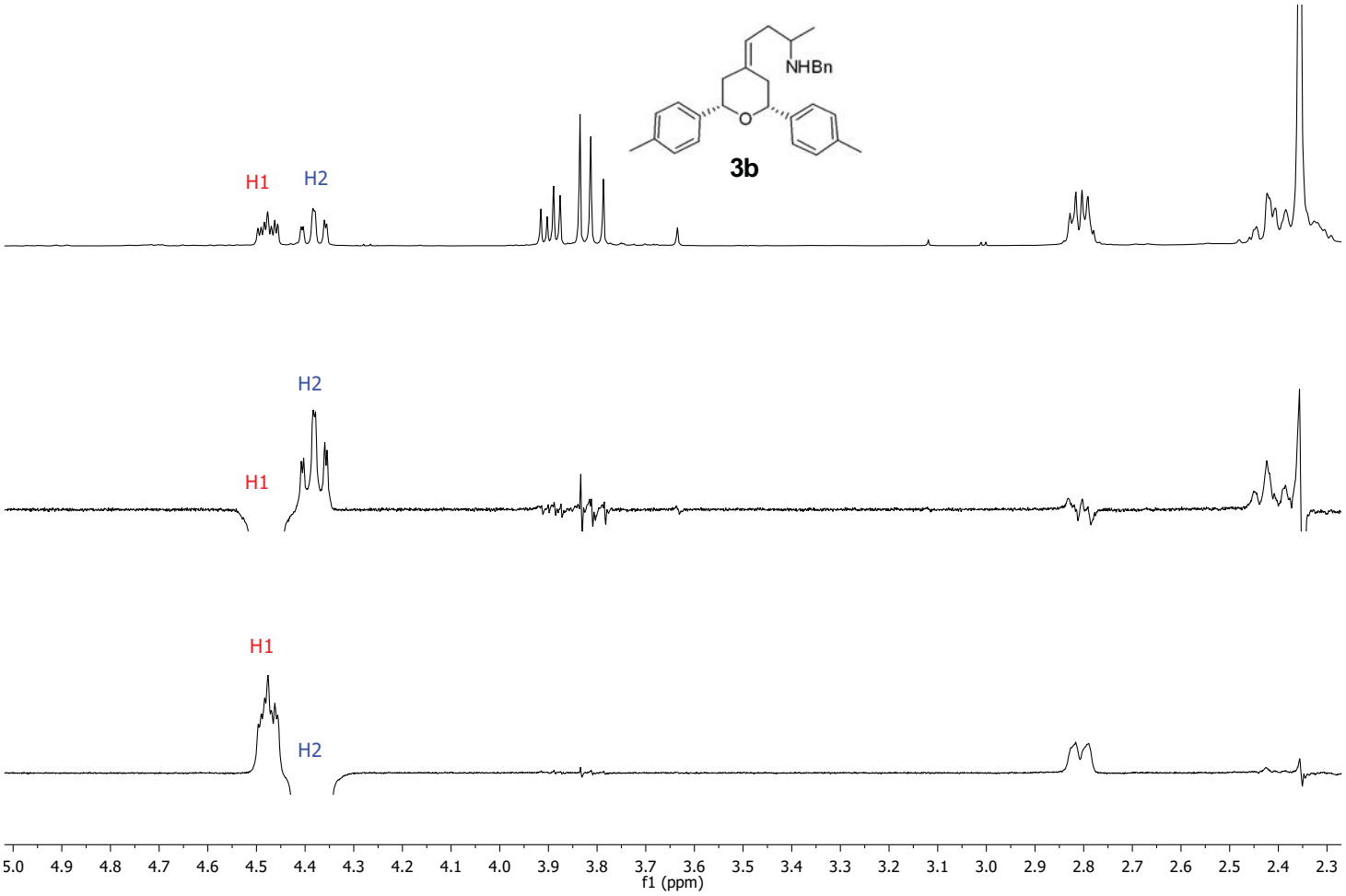
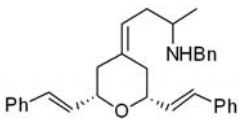
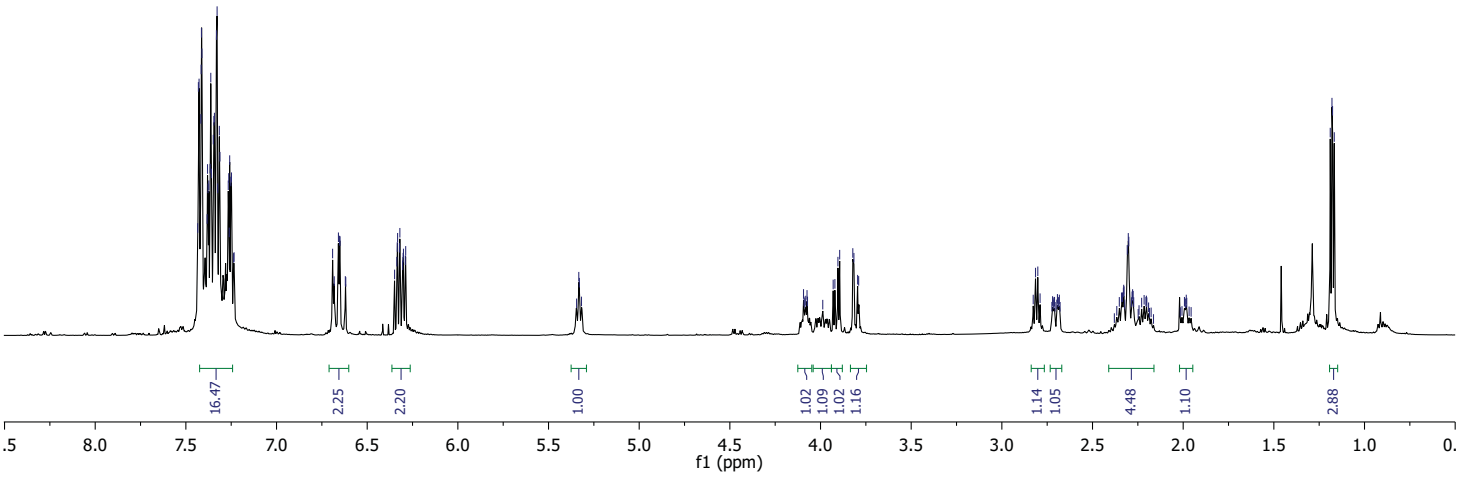
3b
f1 (ppm)


NHBn
O
3b
H1
H2
H2
H1
H1
H2
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3
f1 (ppm)


NHBn
Ph
Ph
O

3c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1.02
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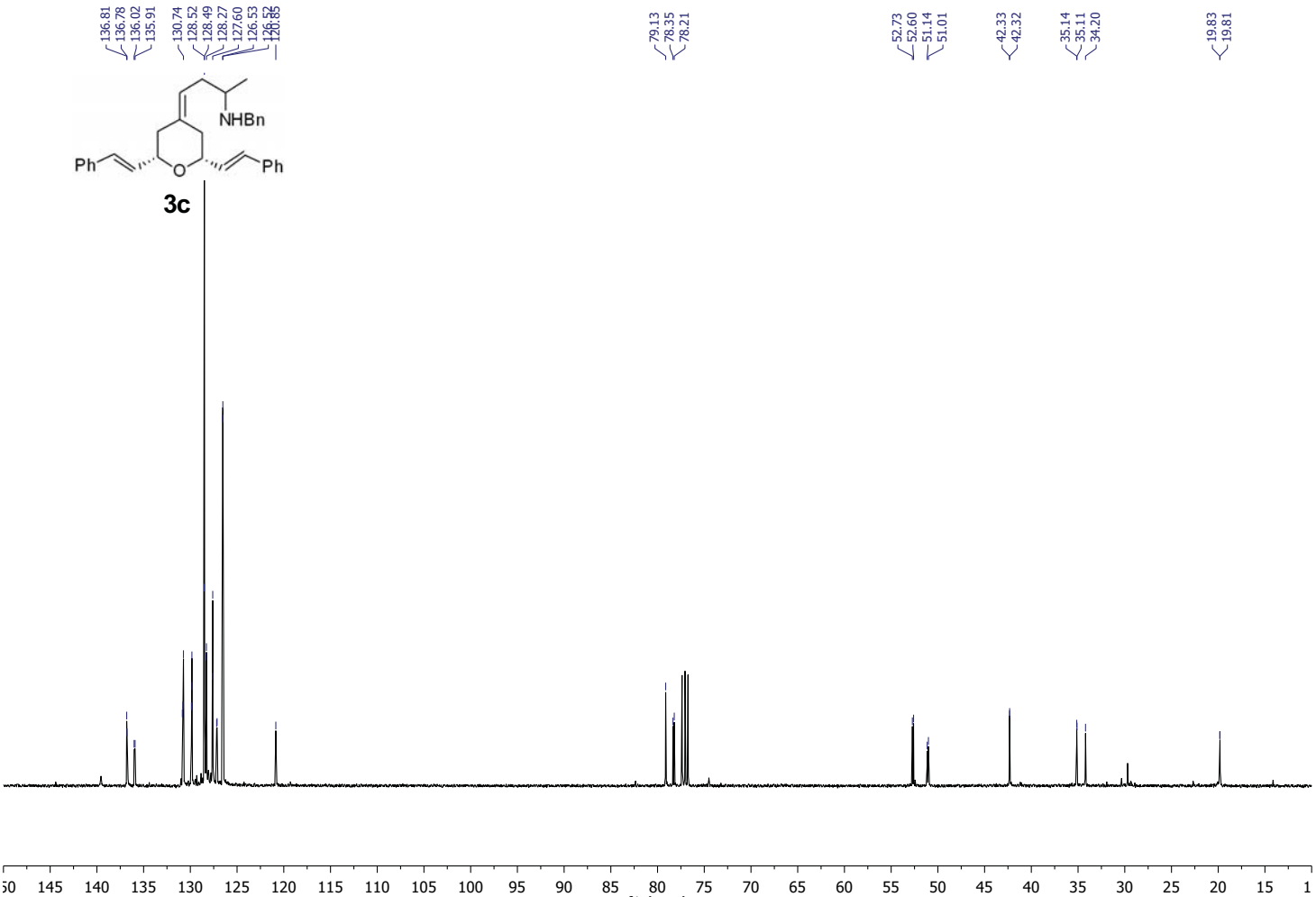
1.10
2.88
f1 (ppm)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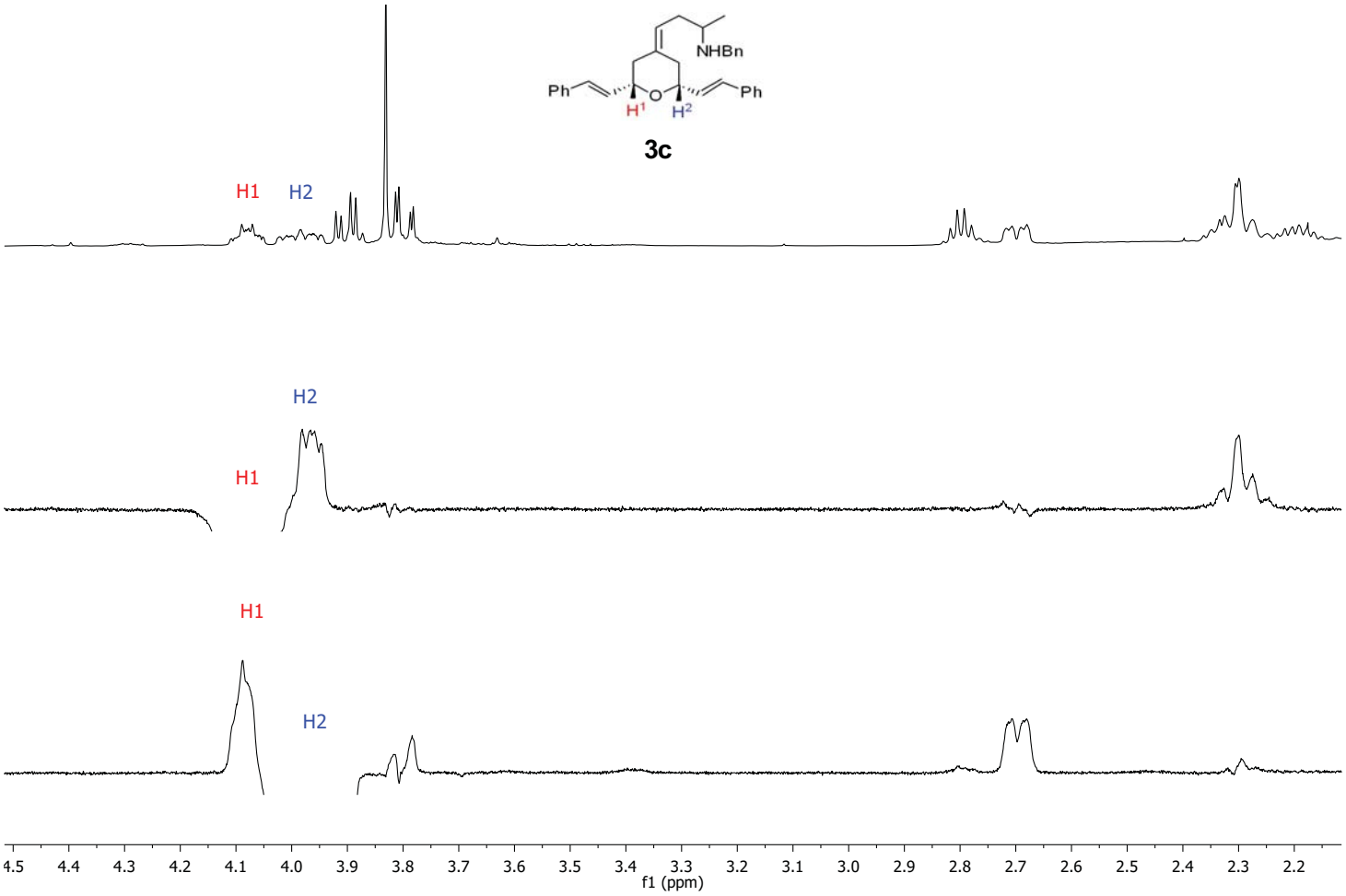
Ph
Ph
O
f1 (ppm)

3c


NHBn
Ph
Ph
O
H1
H2
3c
H1
H2
H2
H1
H1
H2
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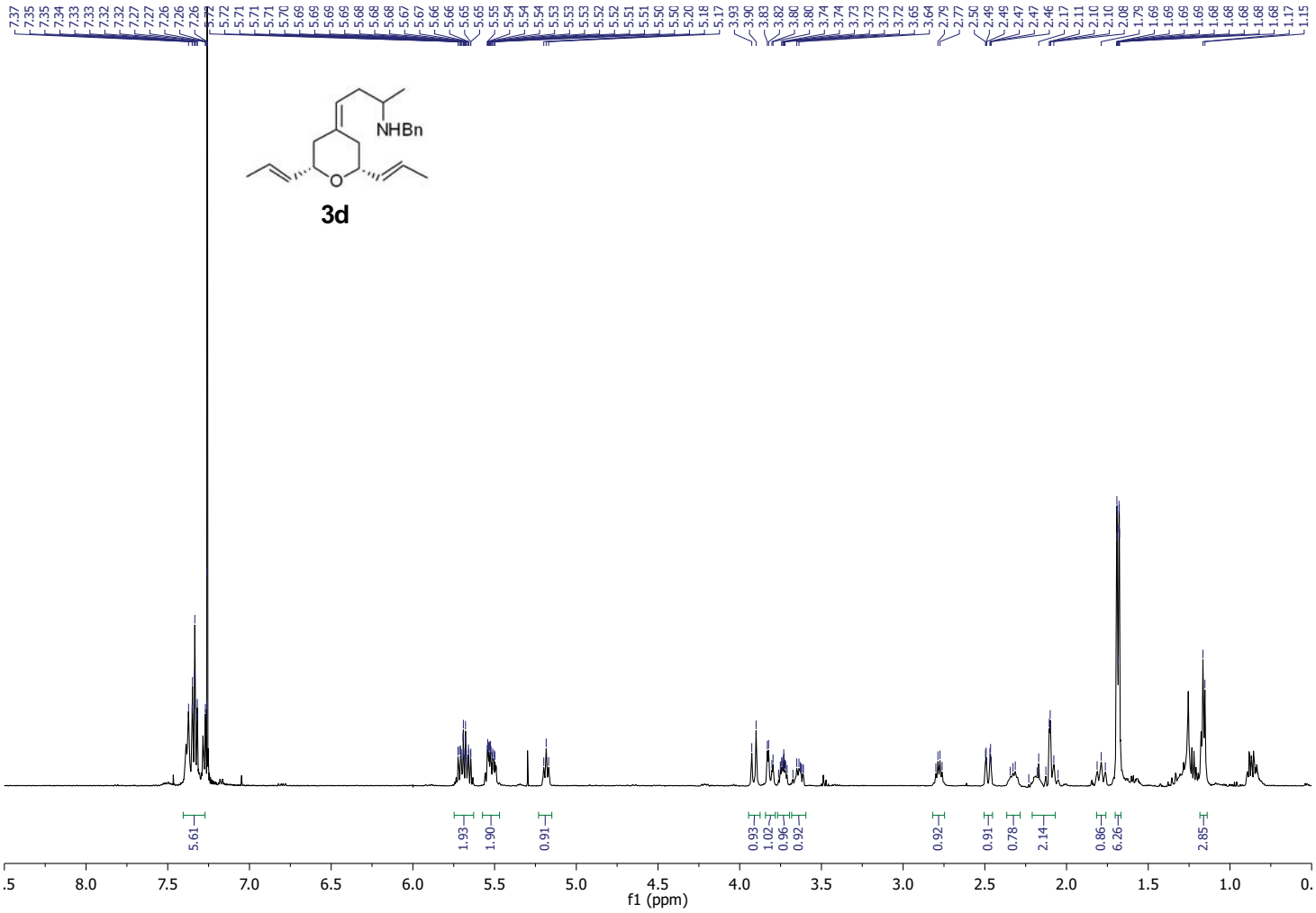
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
f1 (ppm)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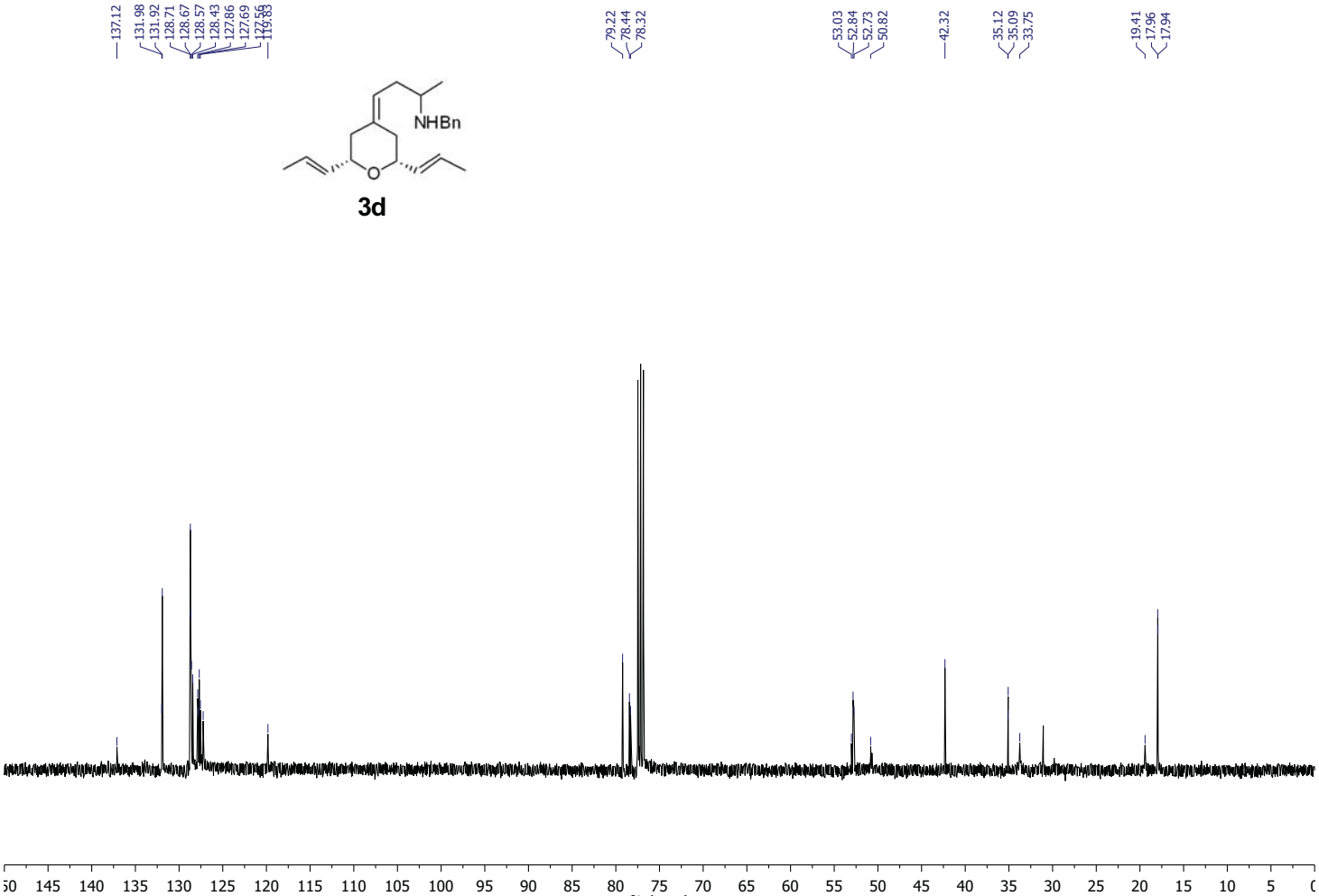
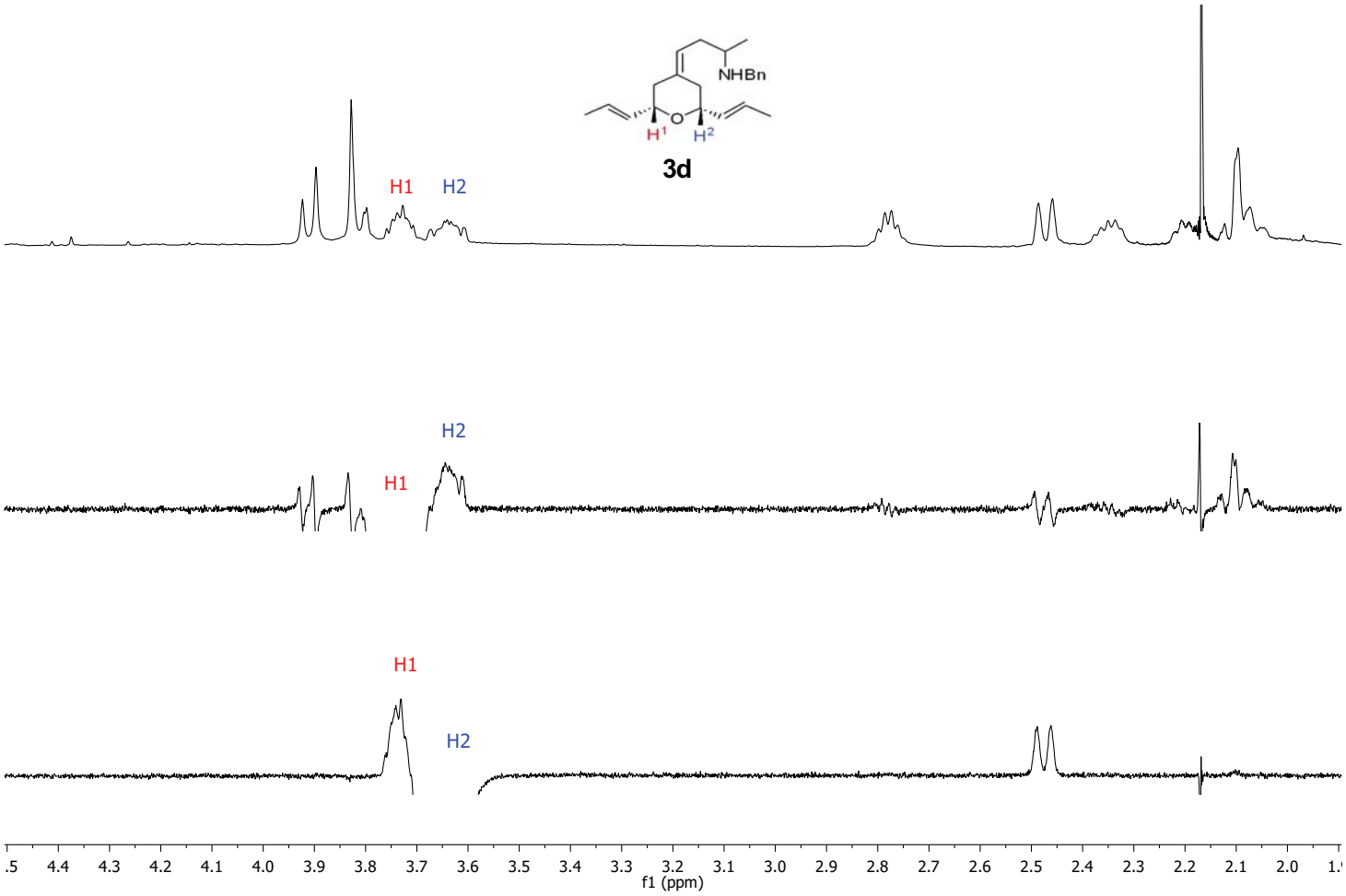
3d
f1 (ppm)


NHBn
3d
f1 (ppm)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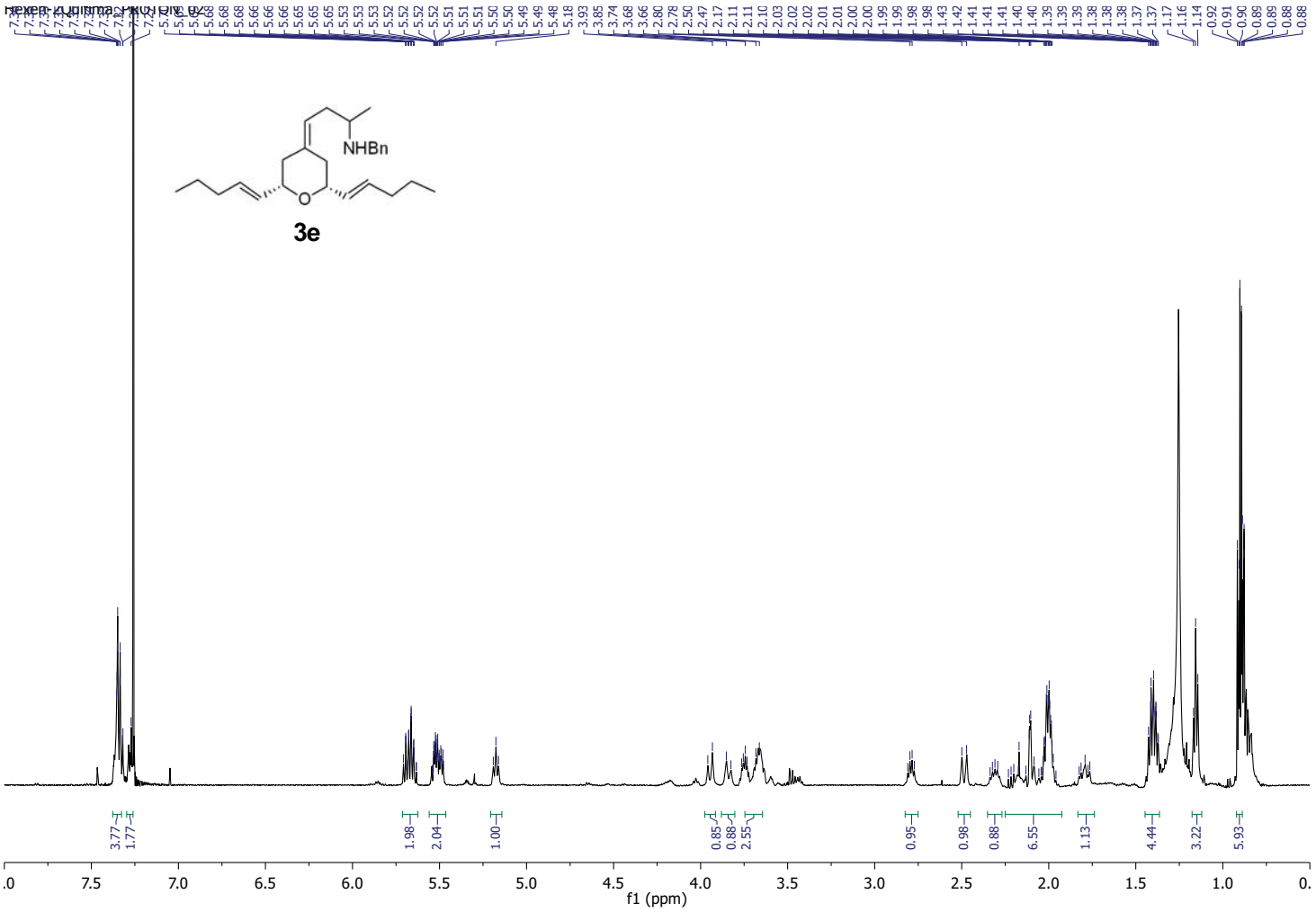
H1
H2
3d
H1
H2
H2
H1
f1 (ppm)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O
3e
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1.00
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0.88
6.55
1.13
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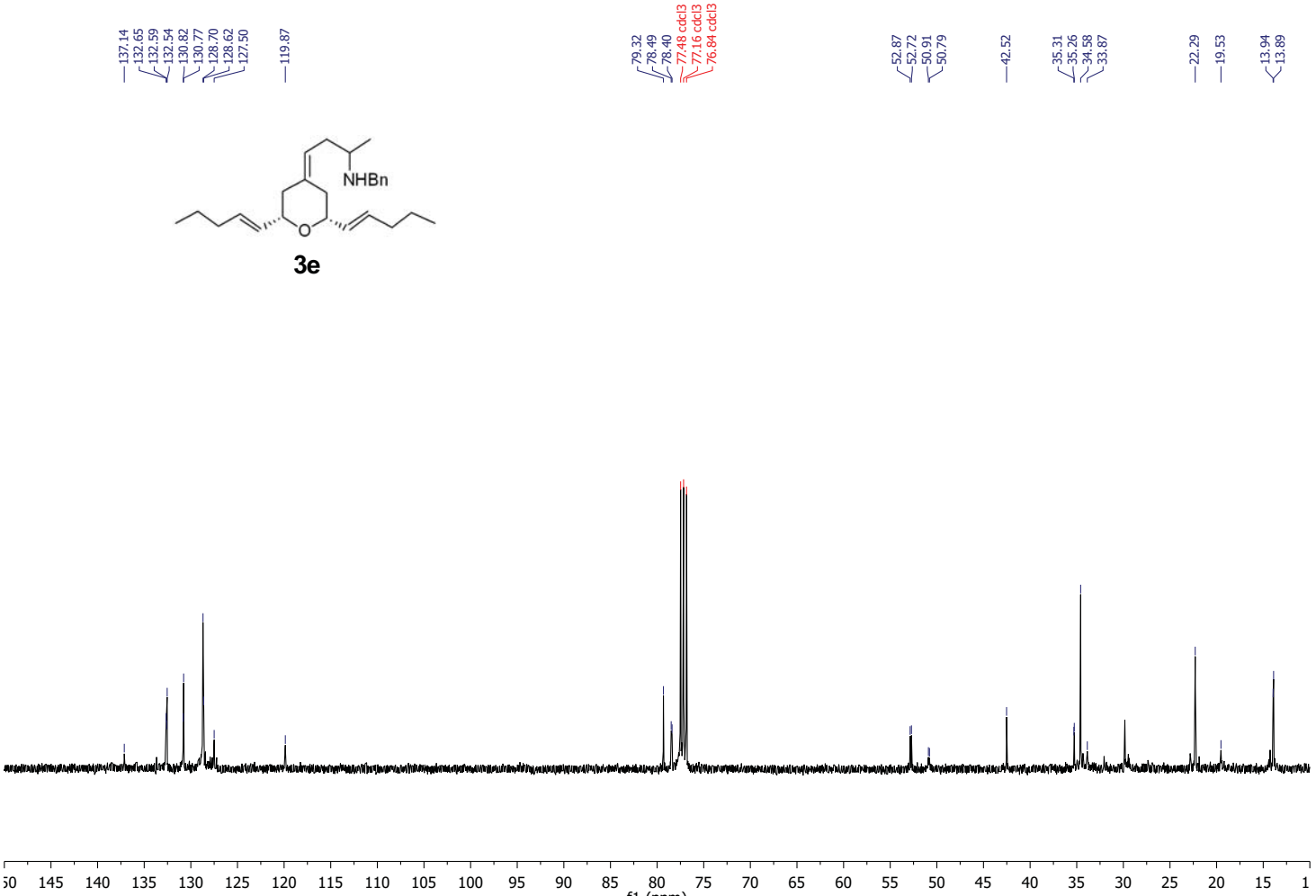
3.22
5.93
f1 (ppm)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78.40
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
52.87
52.72
50.91
50.79
42.52
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33.87
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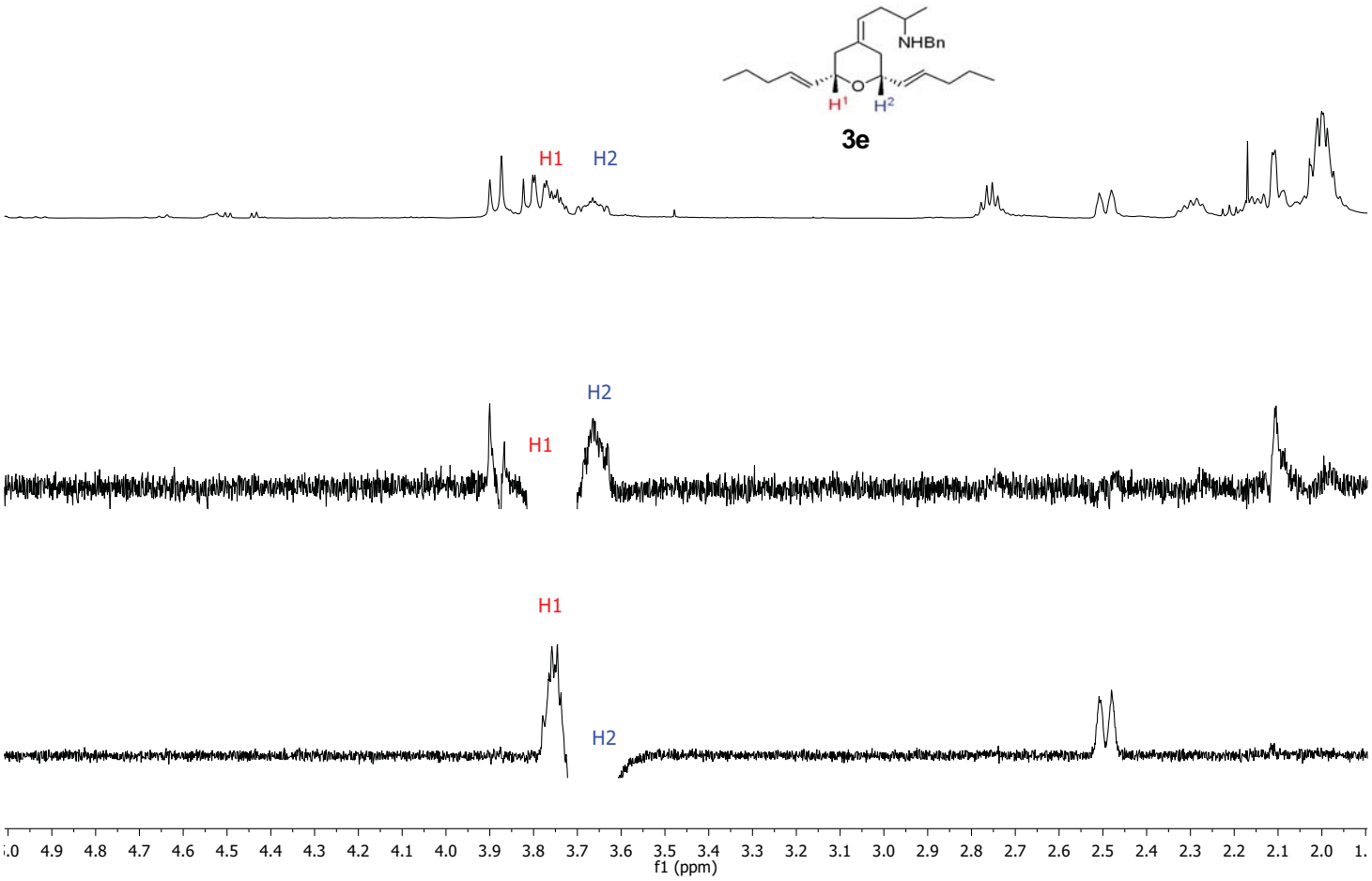
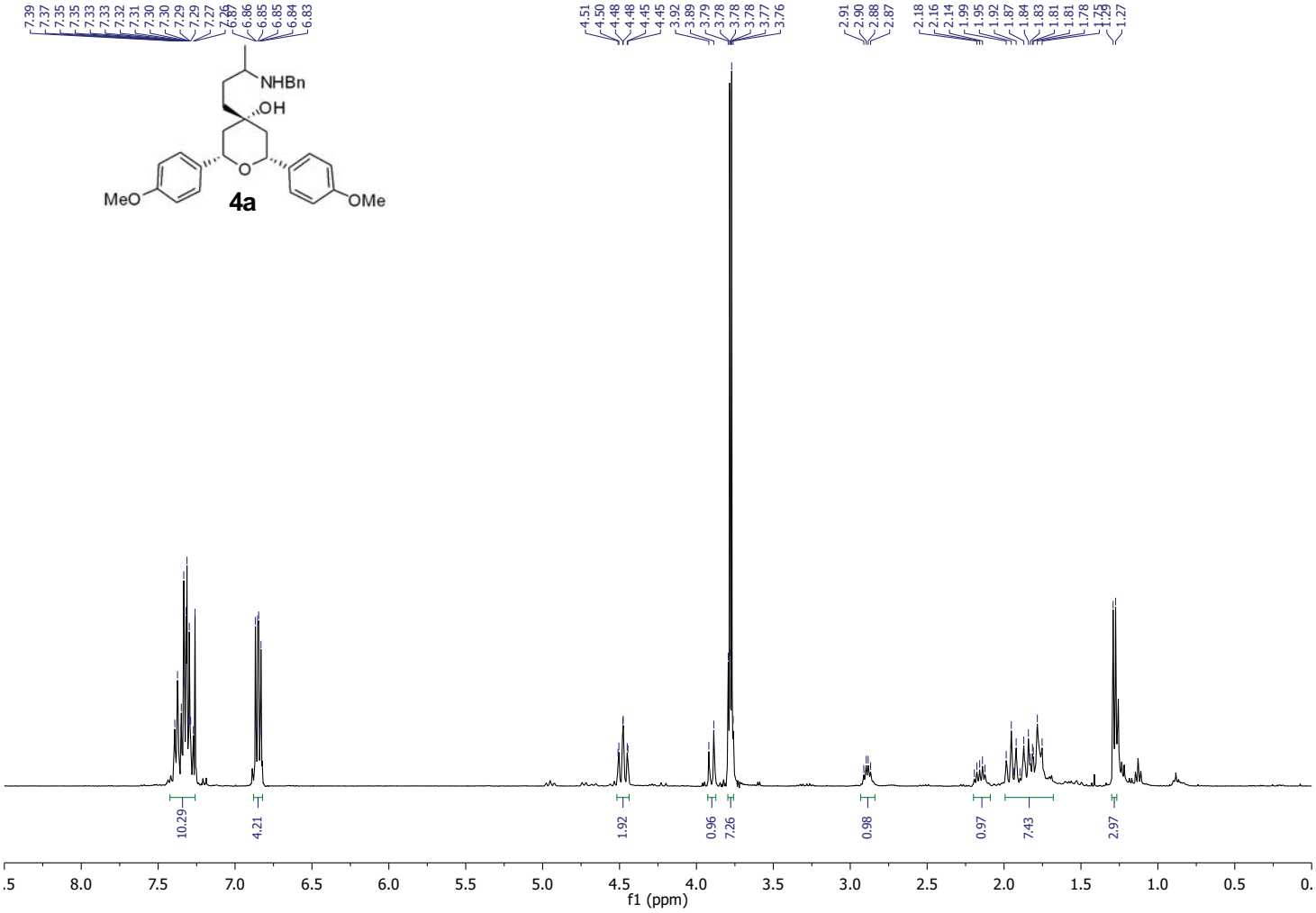
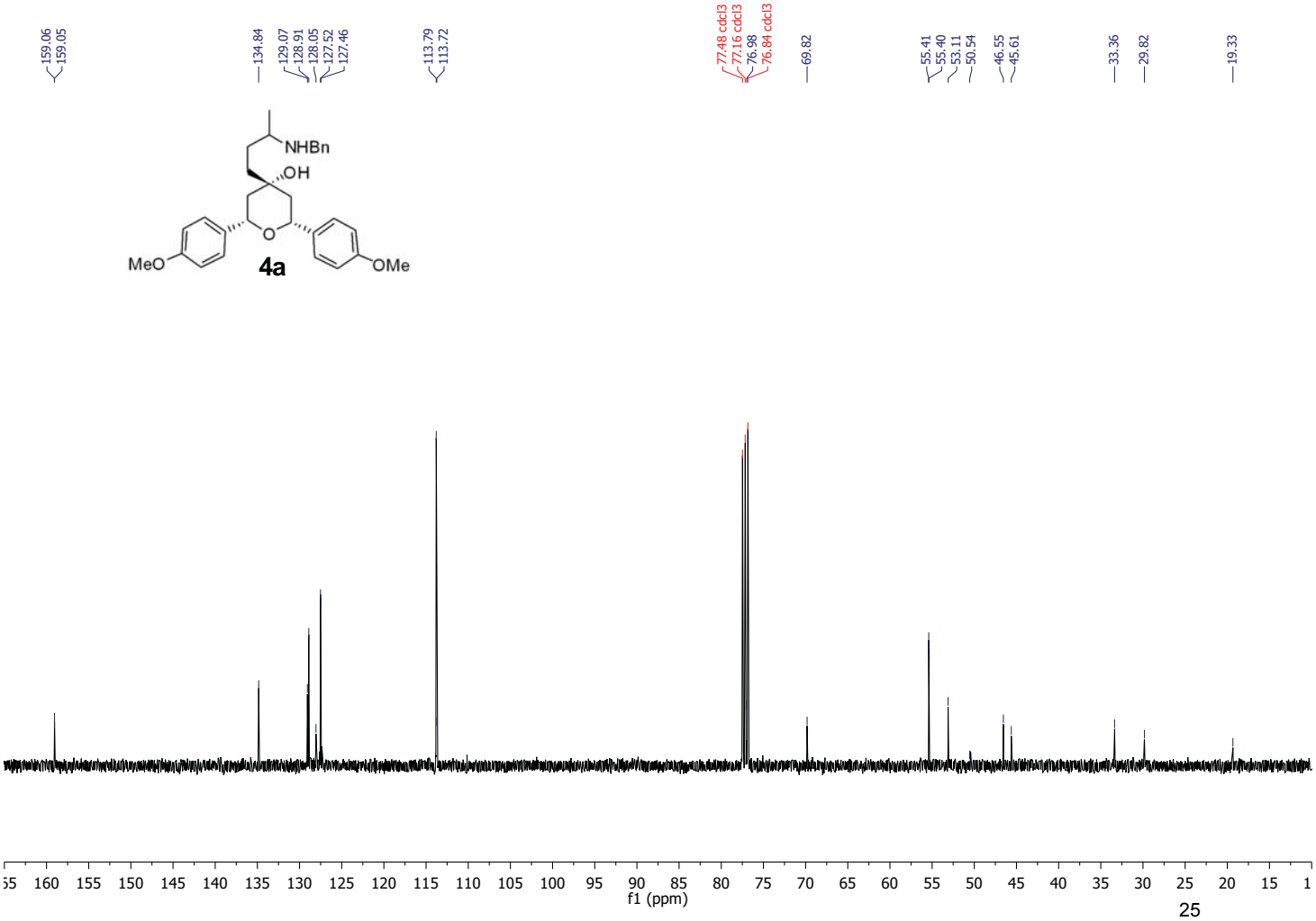
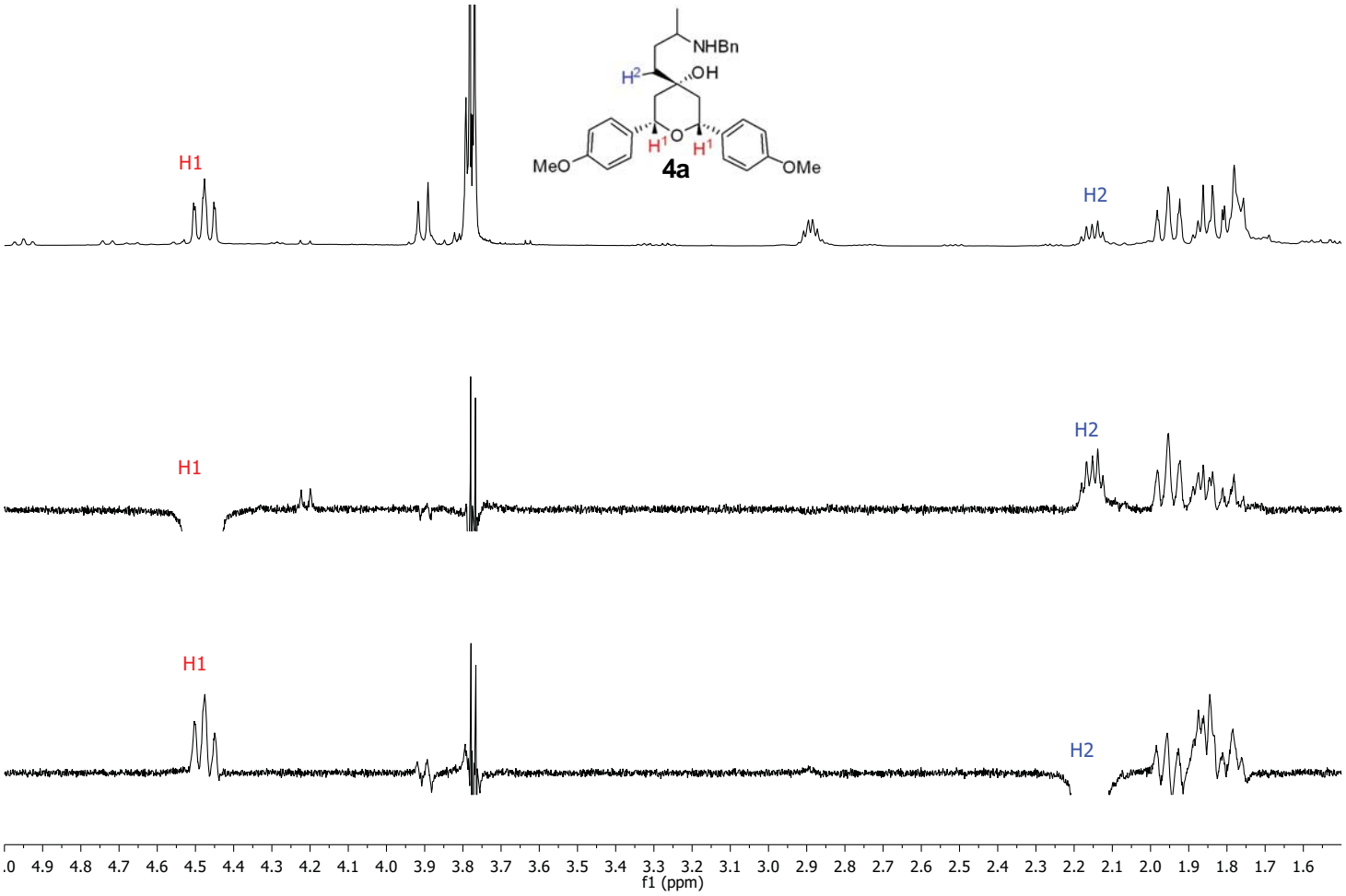
19.53
13.94
13.89
NHBn
O
3e
f1 (ppm)


NHBn
H1
H2
3e
H1
H2
H2
H1
H1
H2
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
f1 (ppm)


NHBn
OH
MeO
OMe
4a
f1 (ppm)


NHBn
OH
MeO
OMe
4a
f1 (ppm)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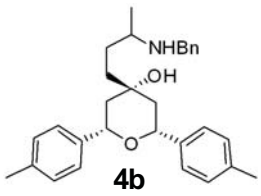
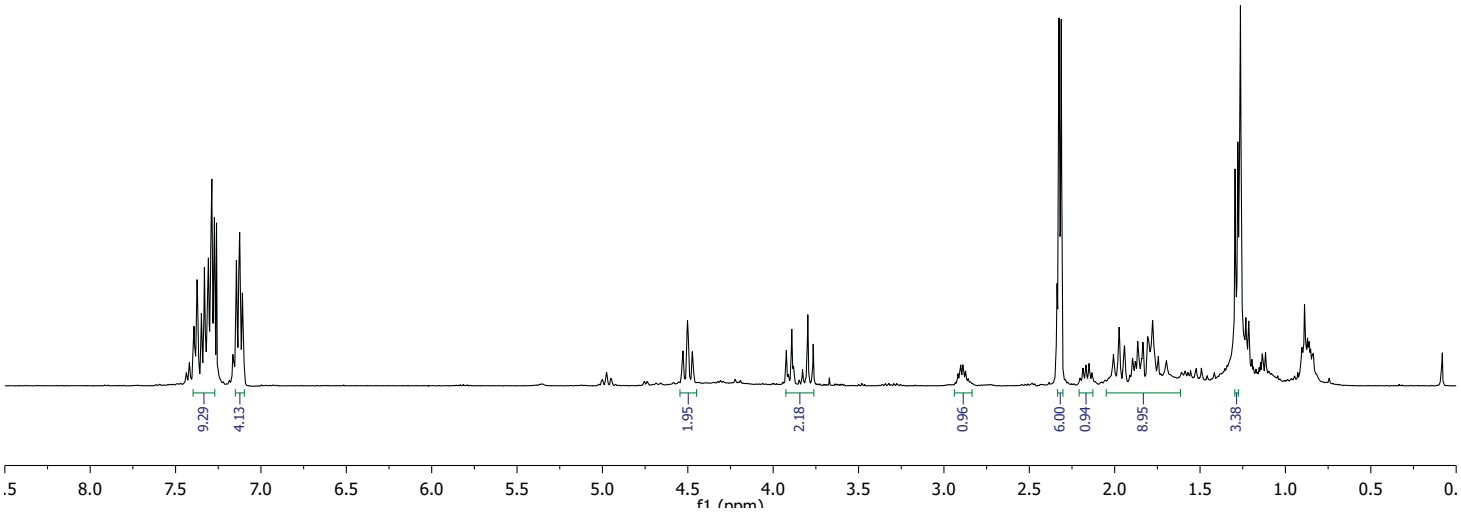
H2
OH
H1
H1
MeO
OMe
4a
H1
H2
H1
H2
H1
H2
.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)


NHBn
OH
O

4b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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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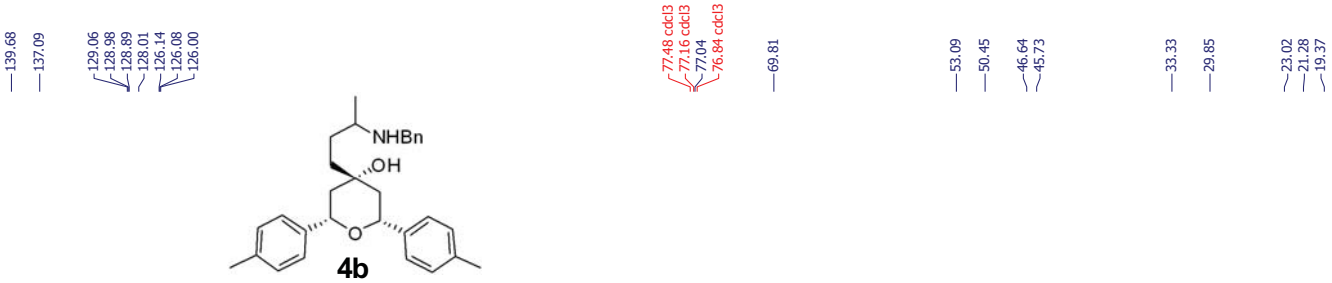
0.5
f1 (ppm)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69.81
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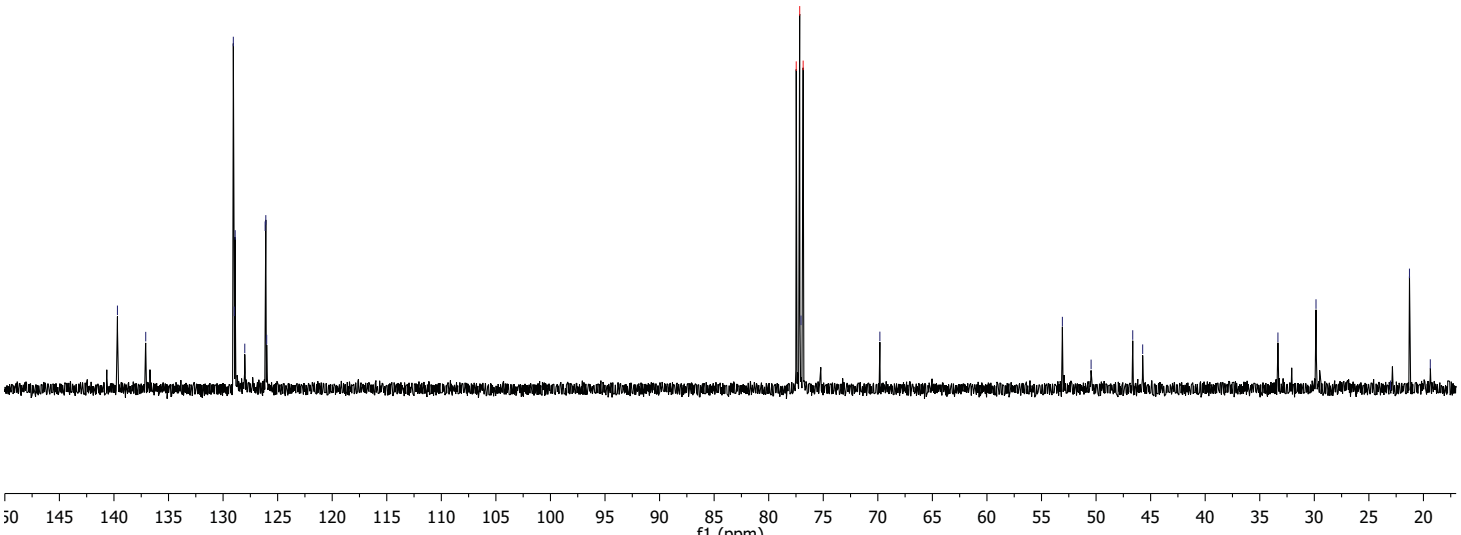
45.73
33.33
29.85
23.02
21.28
19.37

NHBn
OH
O

4b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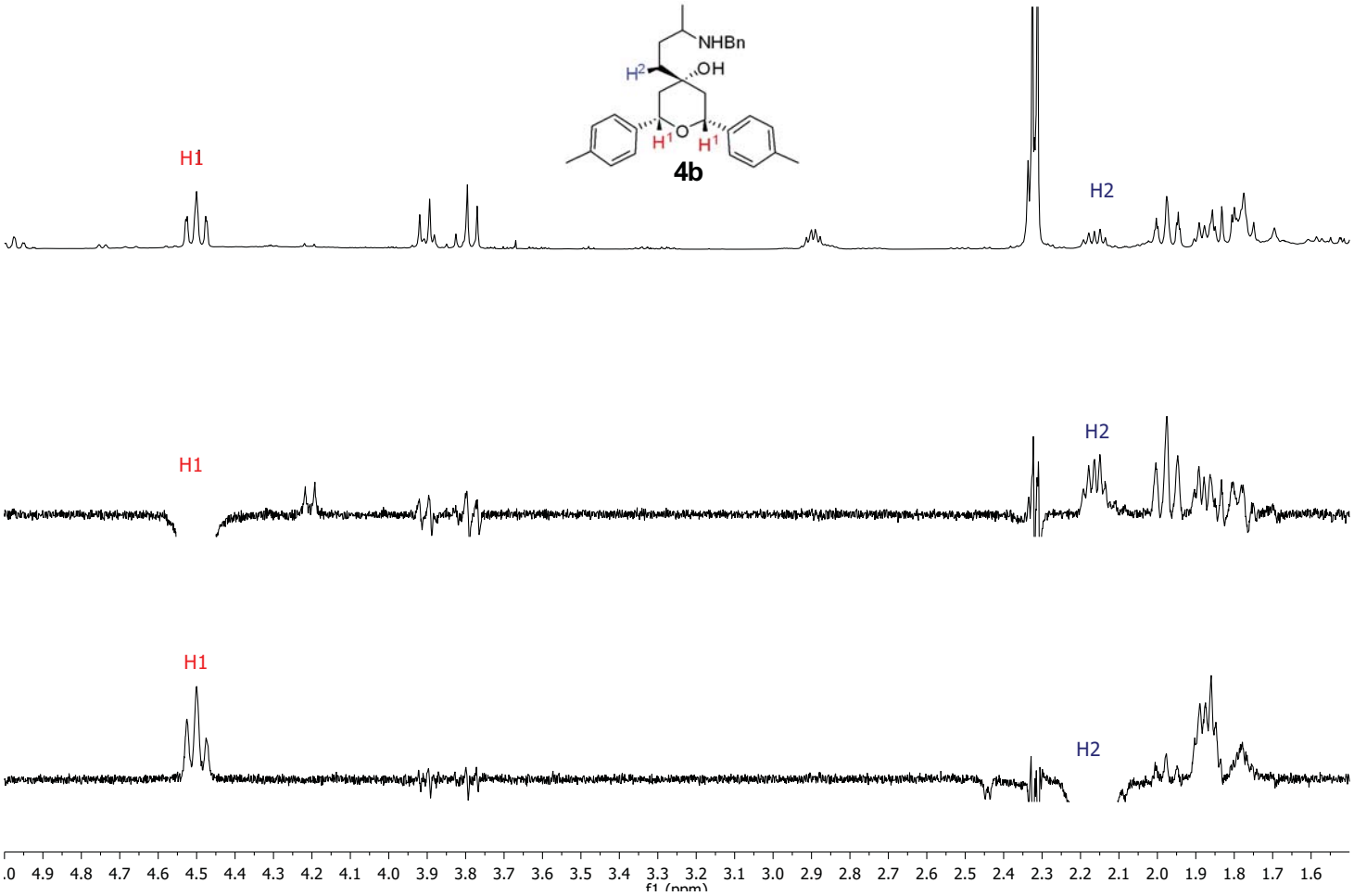
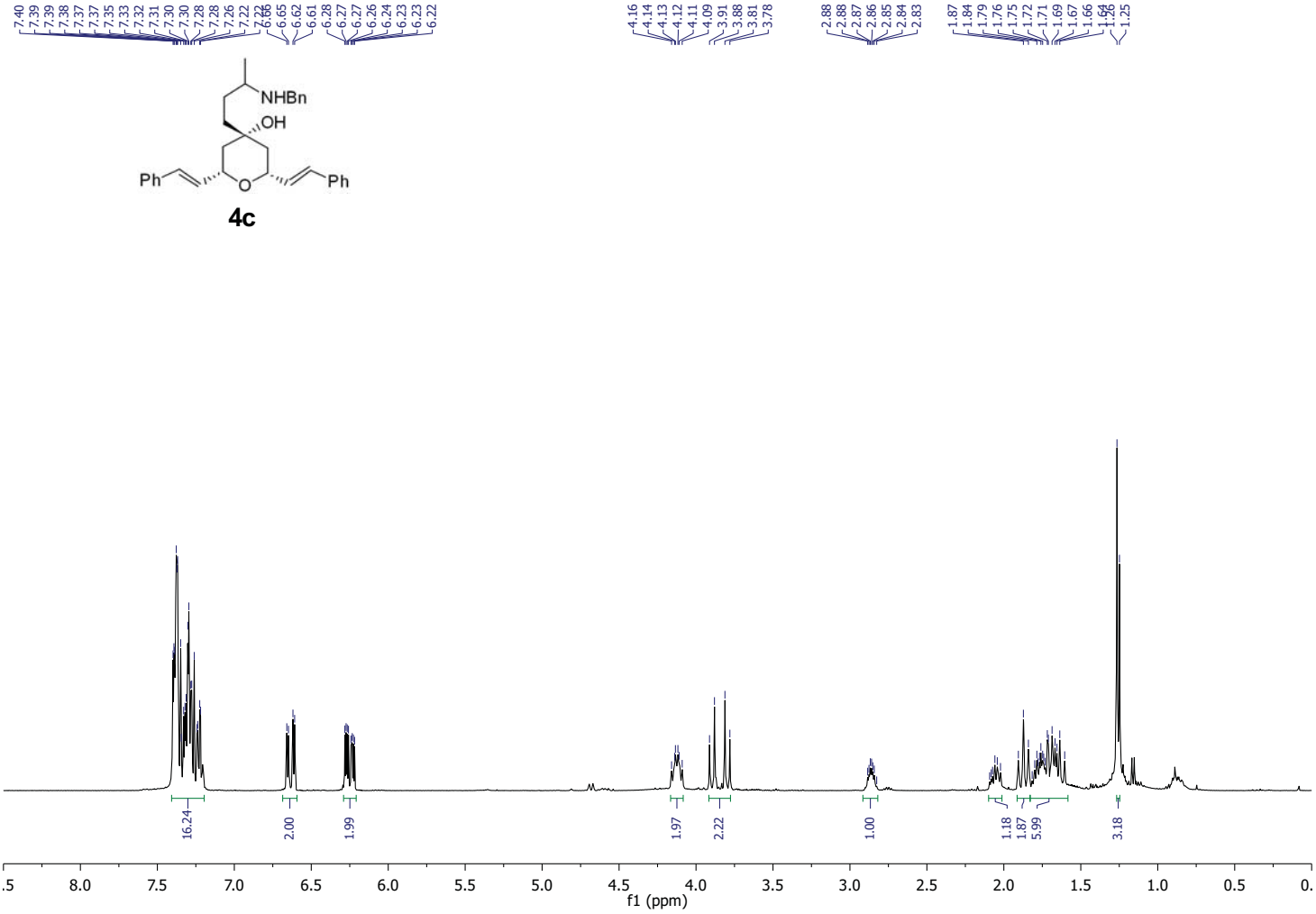
60
55
50
45
40
35
30
25
20
f1 (ppm)


NHBn
H2
OH
H1
H1
4b
H1
H2
H1
H2
H1
H2
.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)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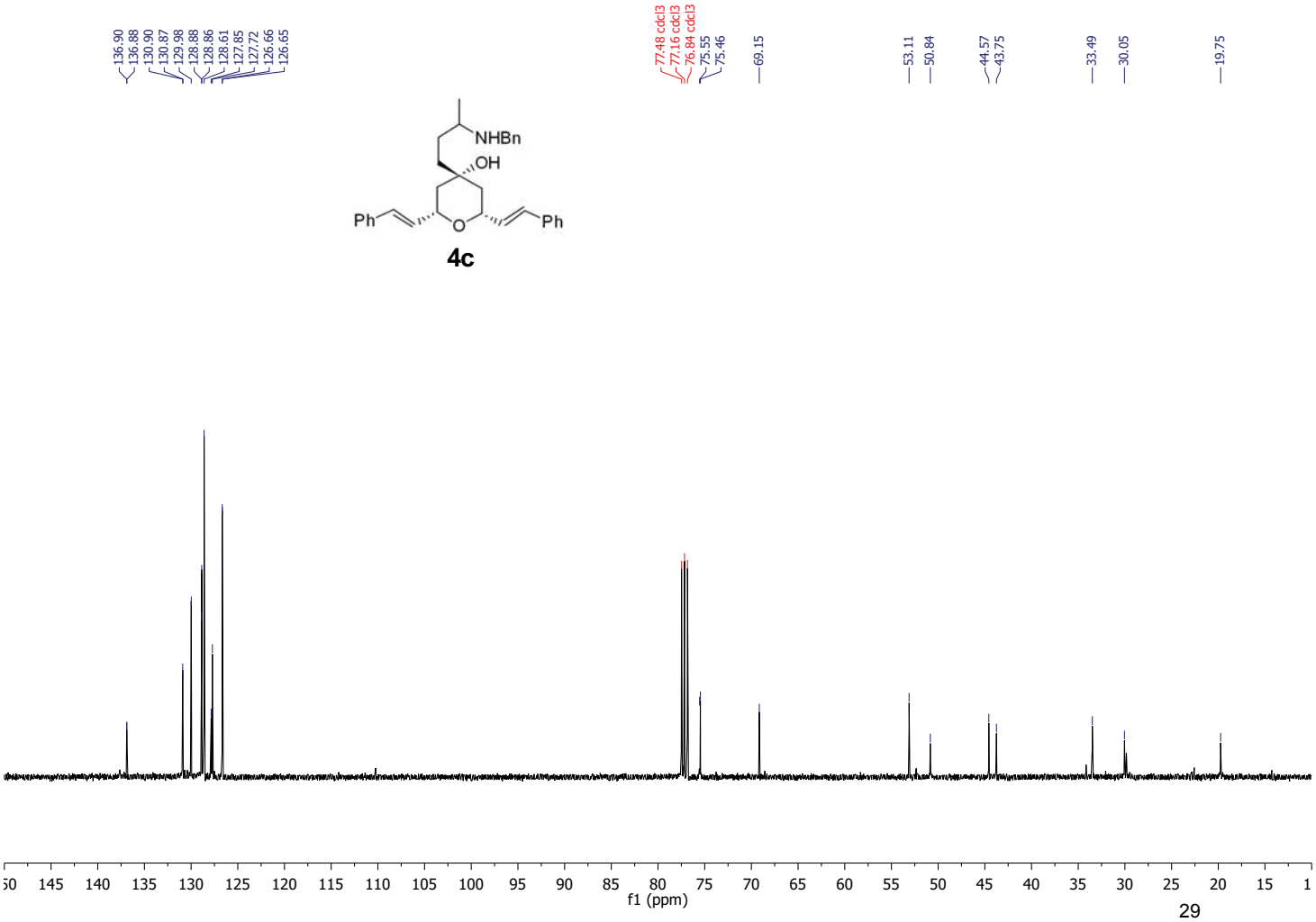
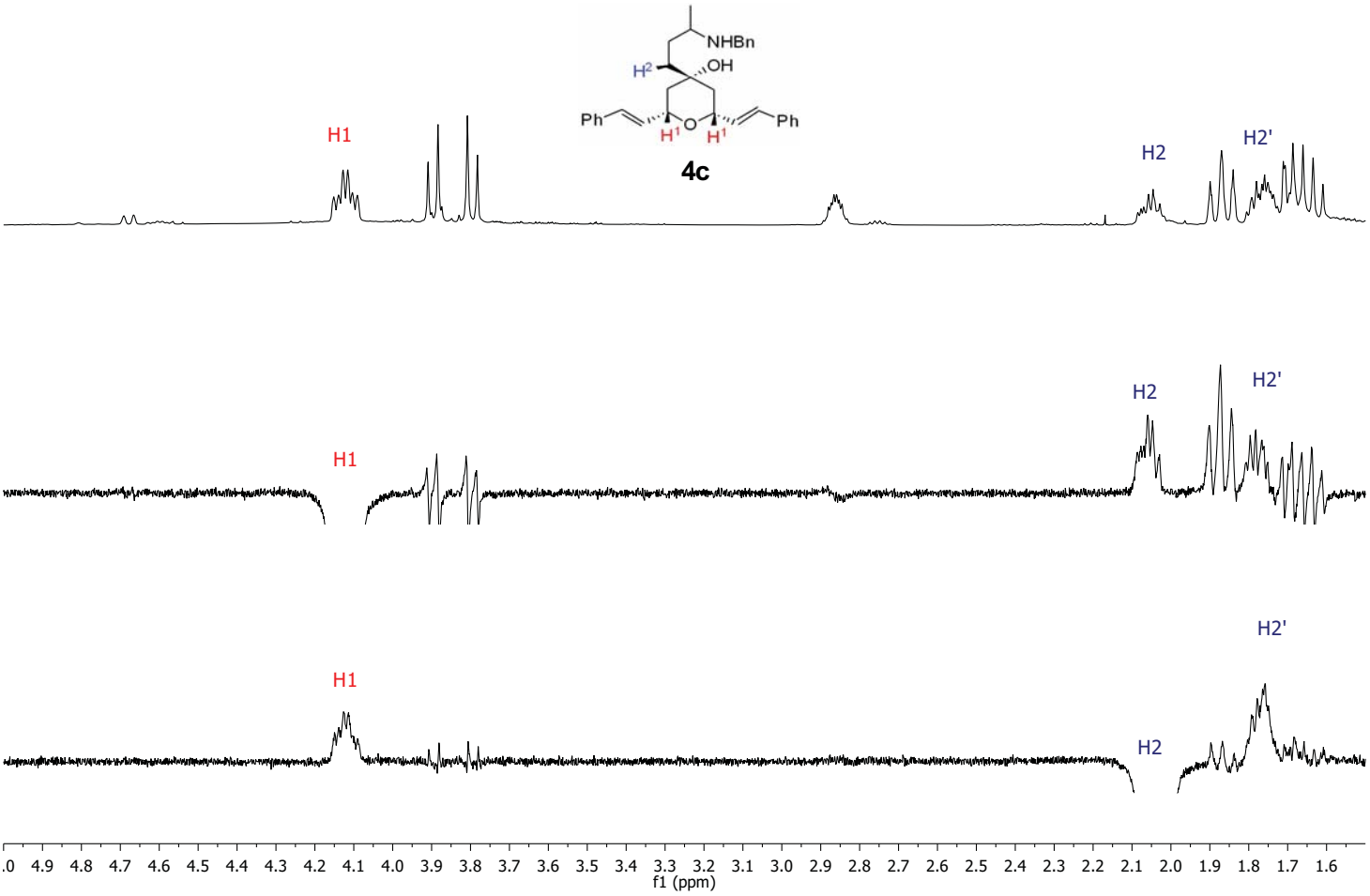
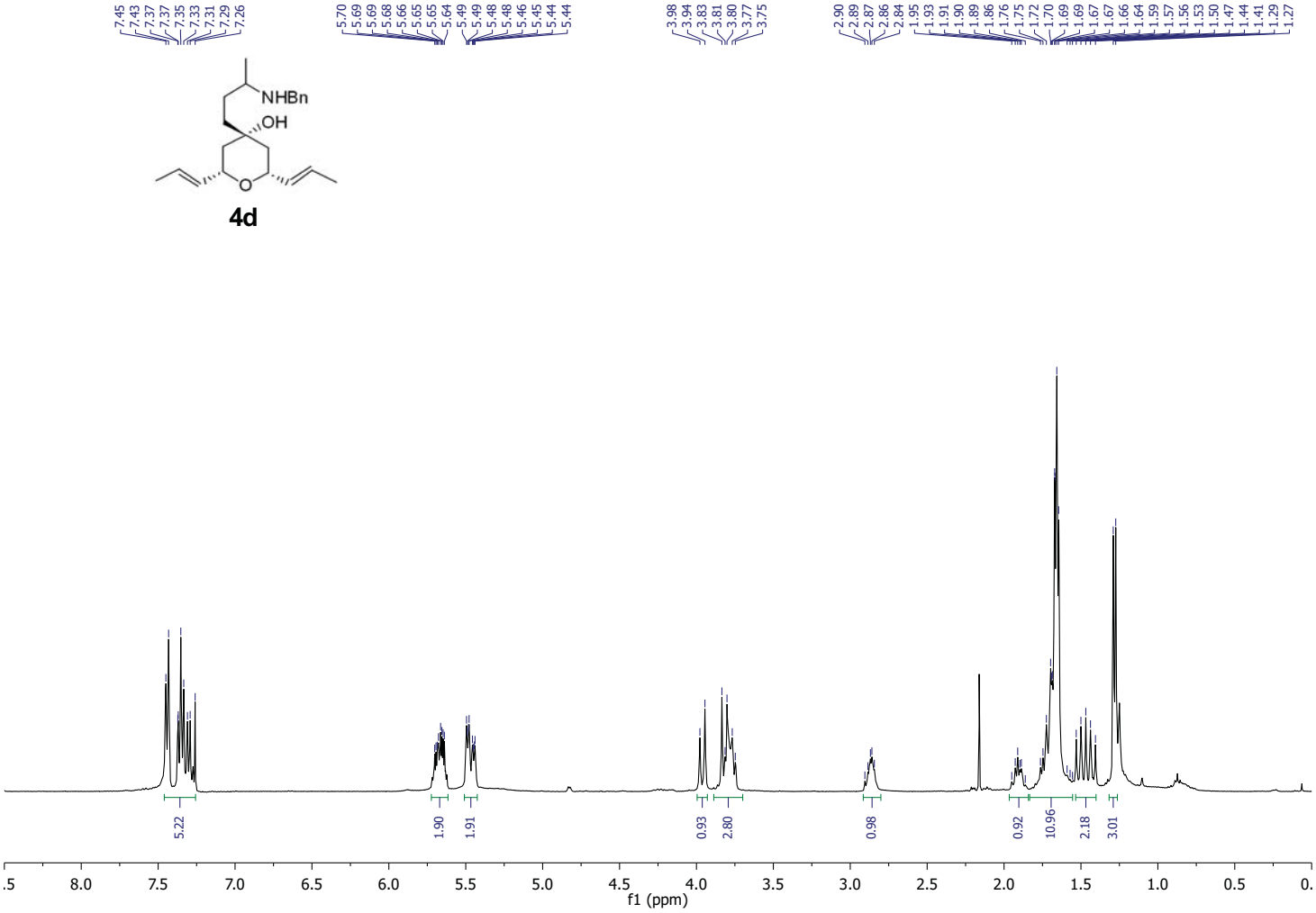
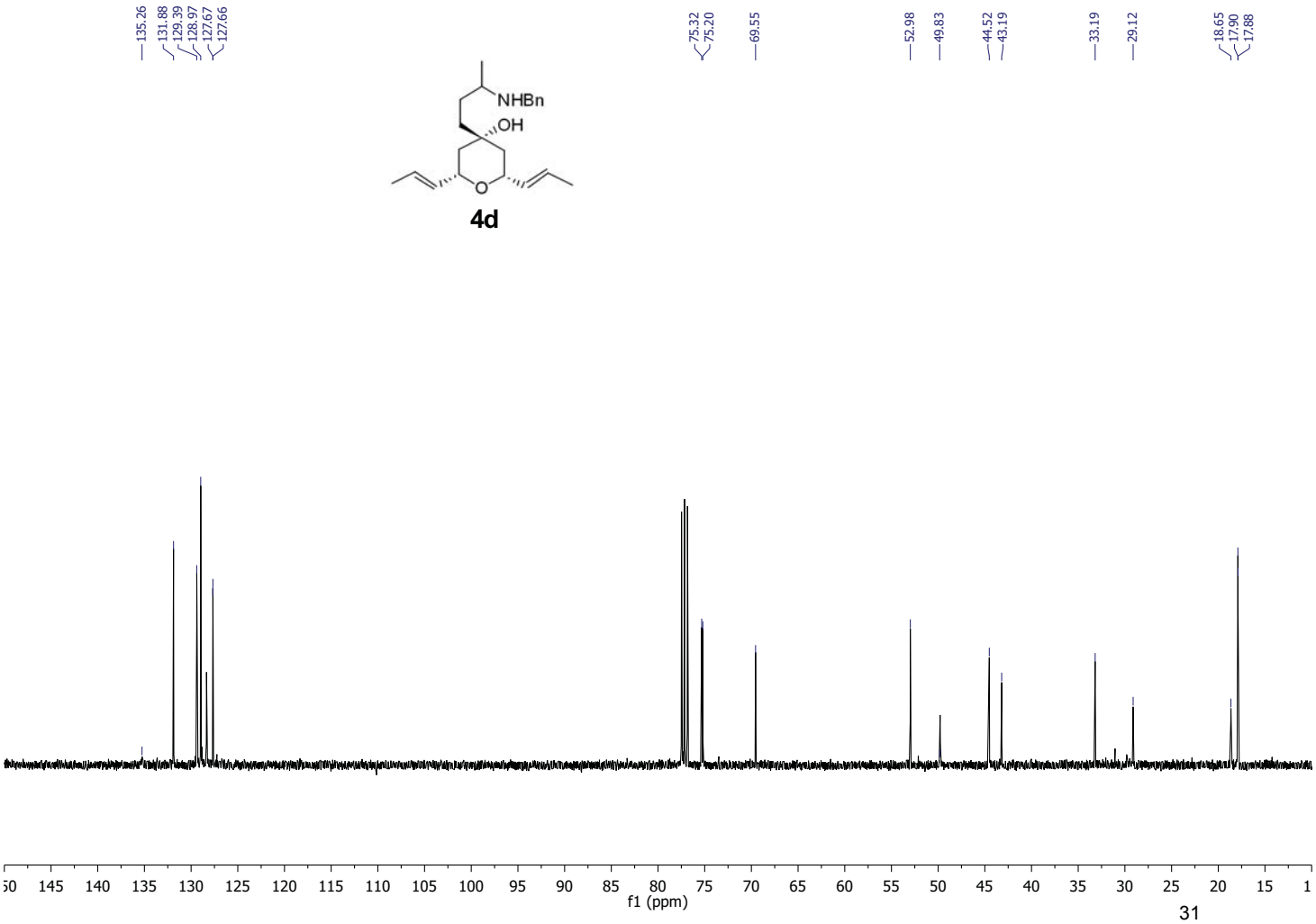
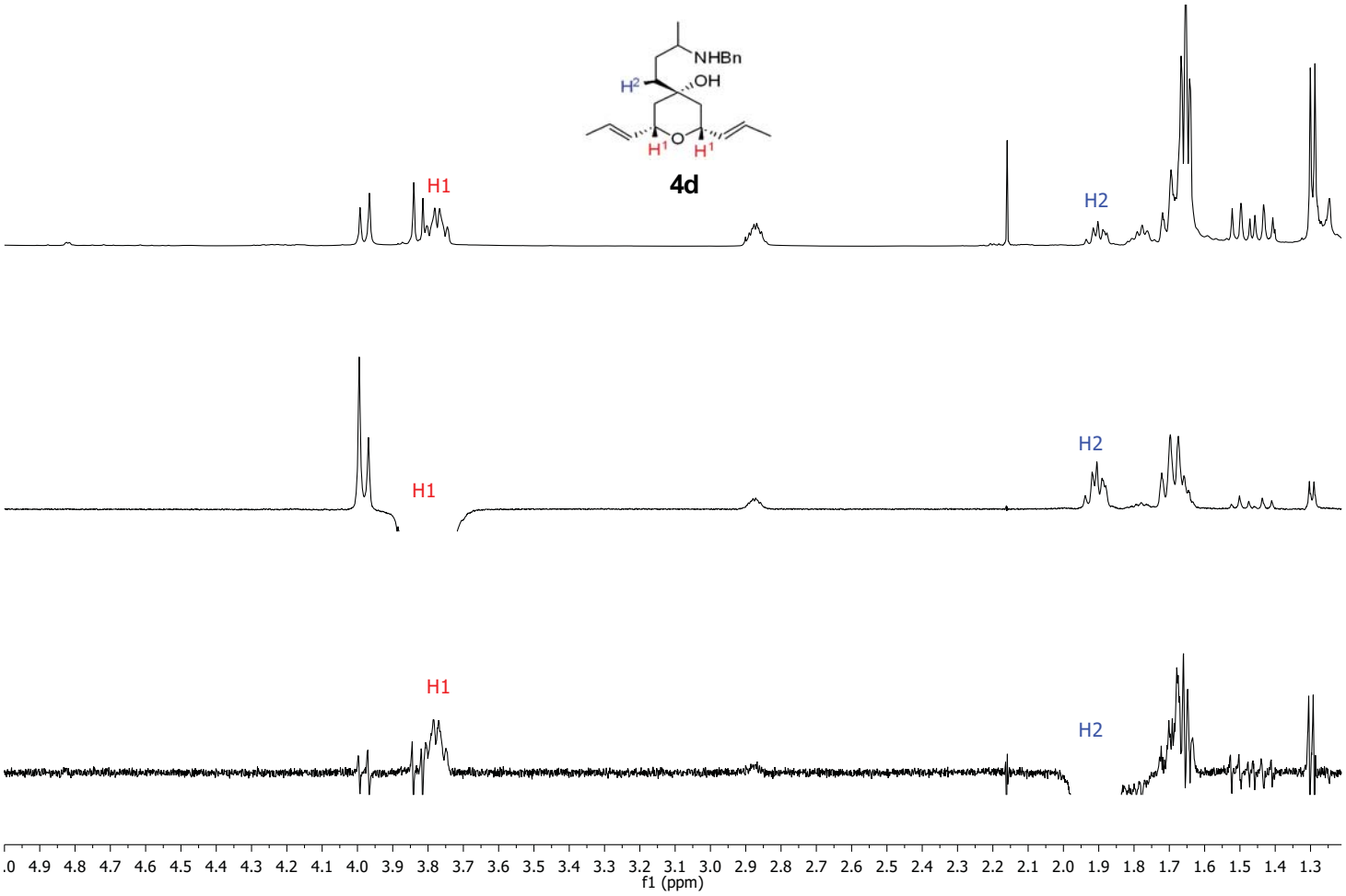
OH
Ph
Ph
O
4c
f1 (ppm)

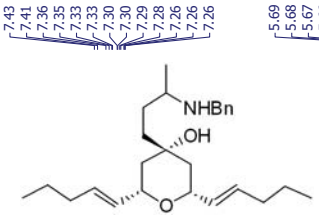

NHBn
OH
Ph
Ph
O
4c
f1 (ppm)


NHBn
OH
H2
Ph
Ph
H1
H1
4c
H1
H2
H2'
H2
H2'
H1
H2'
H1
H2
.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

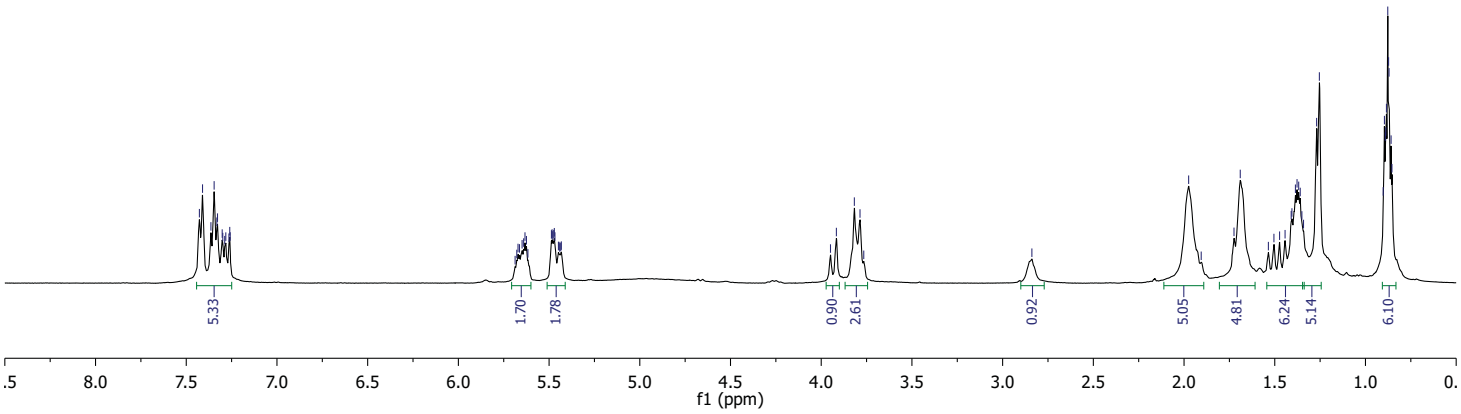

NHBn
OH
4d
f1 (ppm)

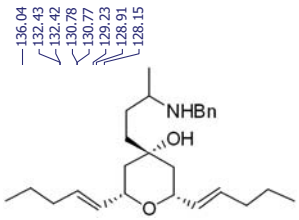

NHBn
OH
4d
f1 (ppm)


NHBn
OH
H2
H1
H1
4d
H1
H2
H1
H2
H1
H2
.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3
f1 (ppm)

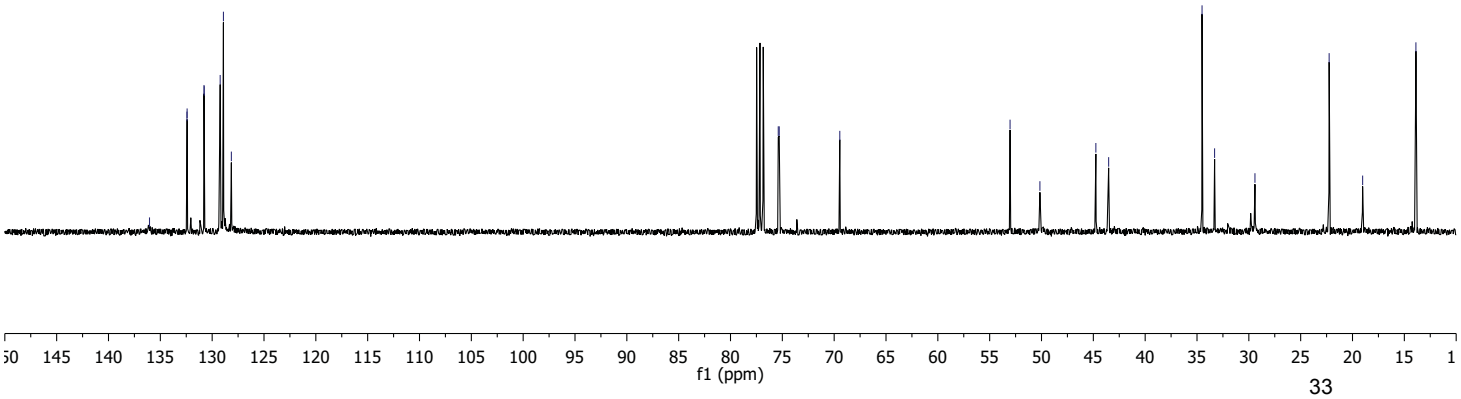

NHBn
OH
O

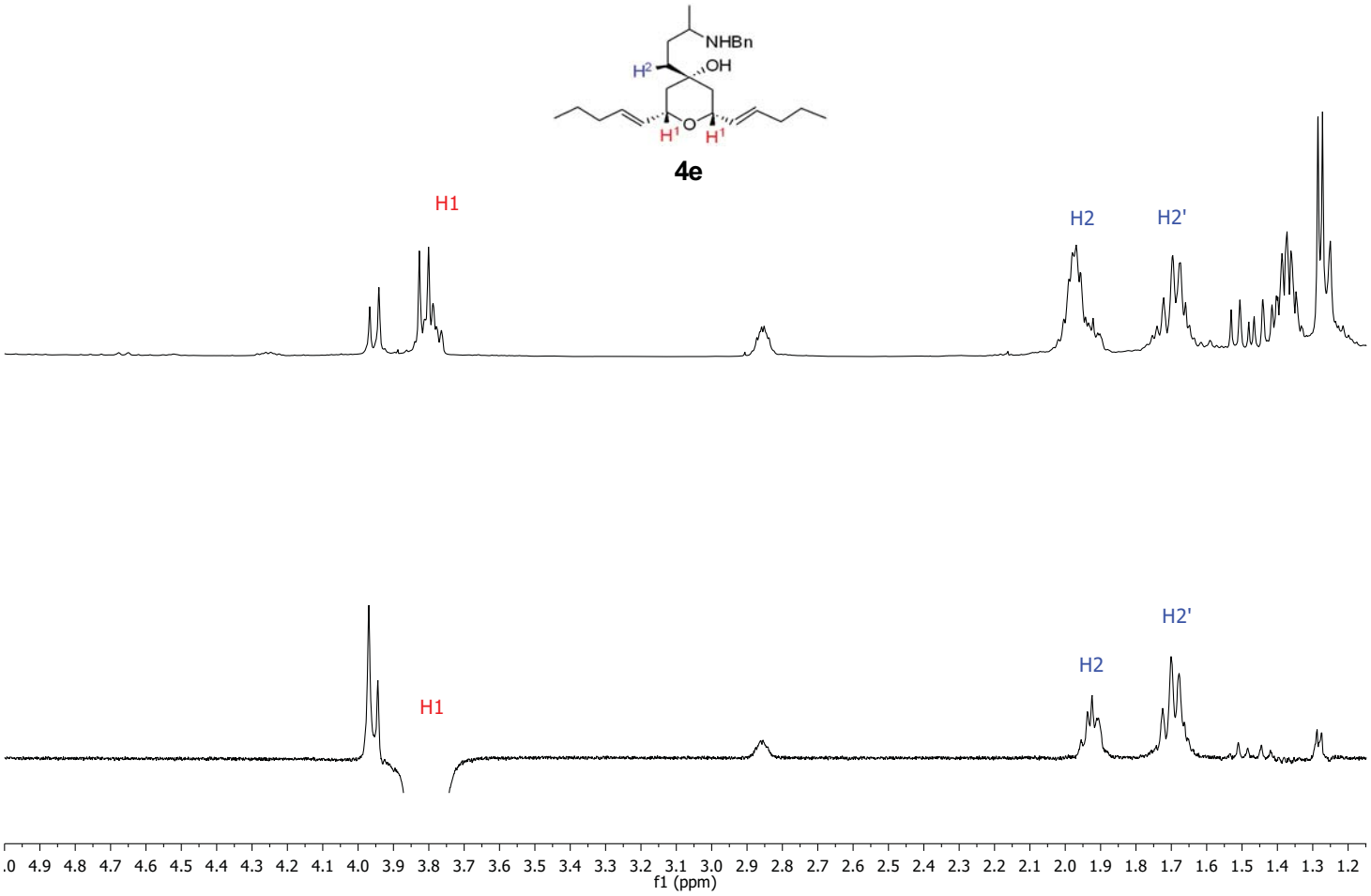
4e

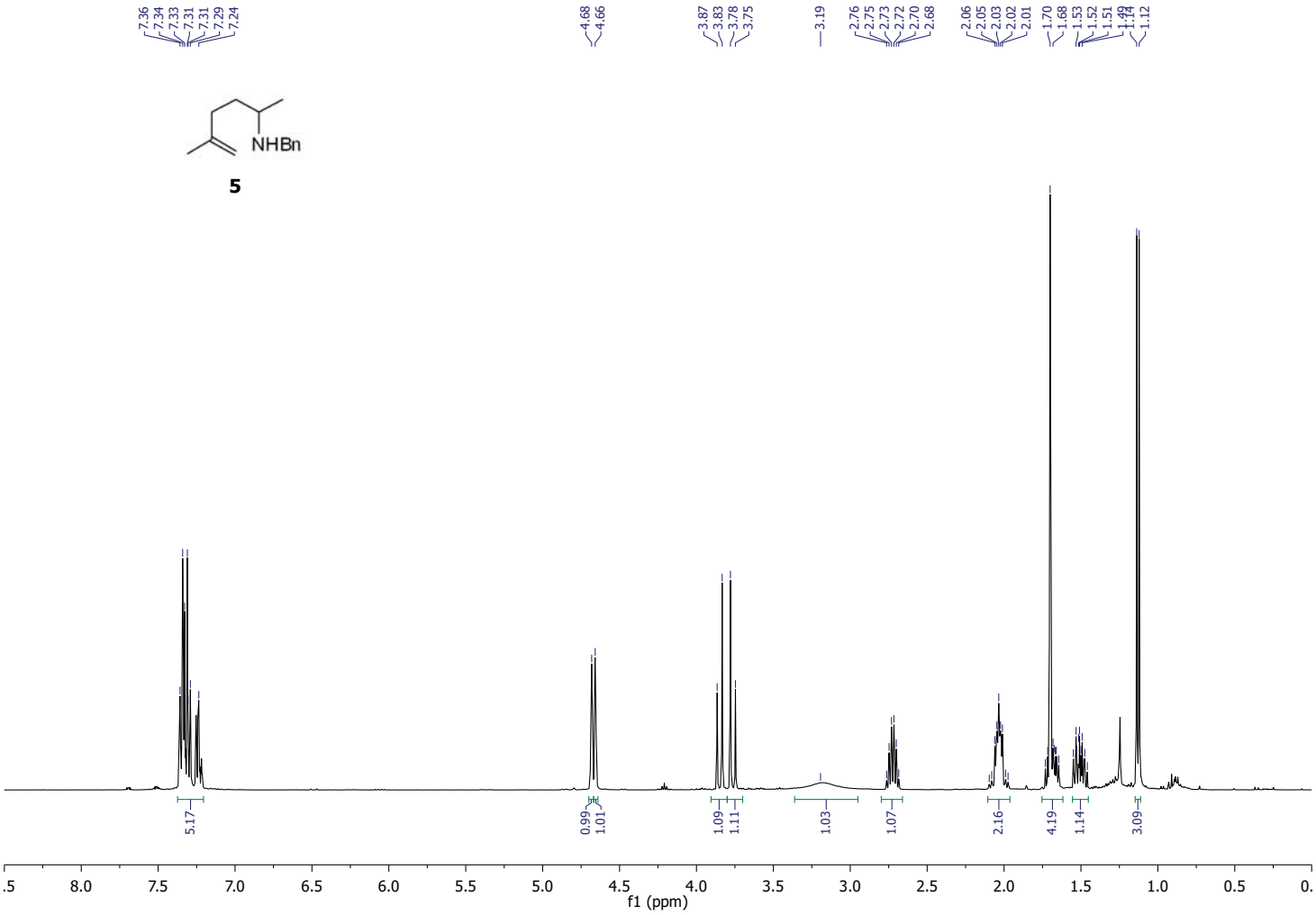

5.33
1.70
1.78
0.90
2.61
0.92
5.05
4.81
6.24
5.14
6.10
f1 (ppm)

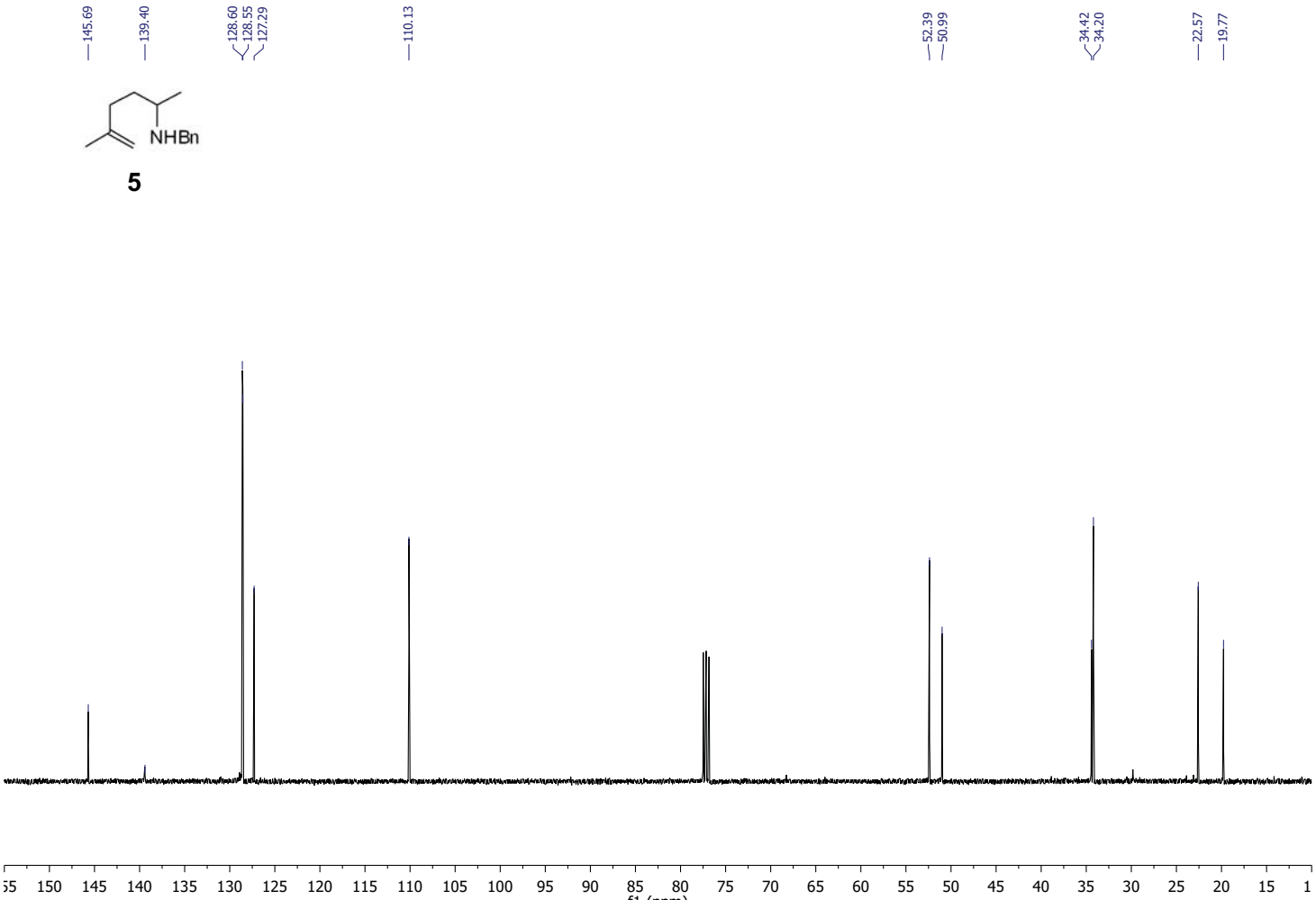

NHBn
OH
O

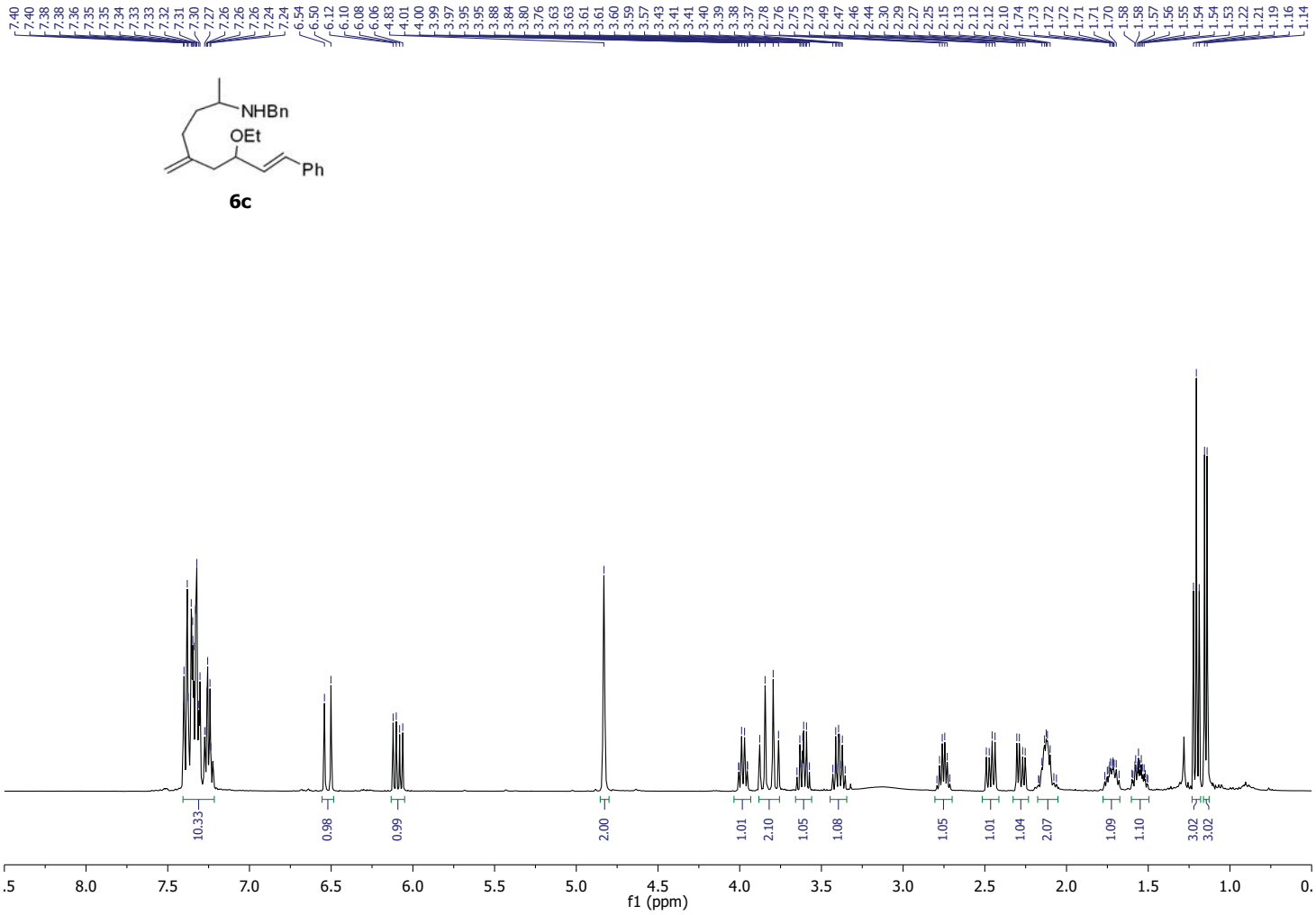
4e

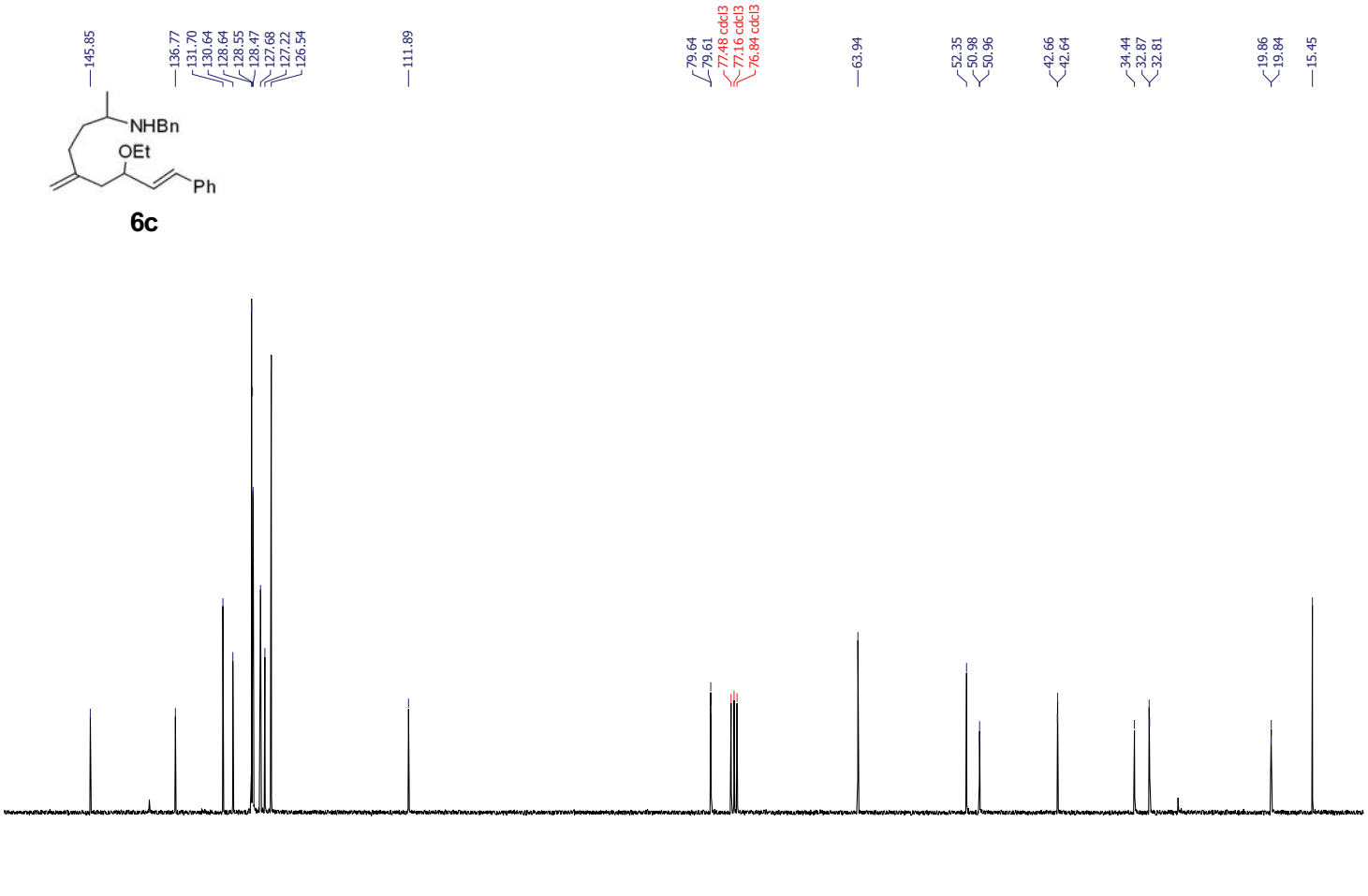

f1 (ppm)

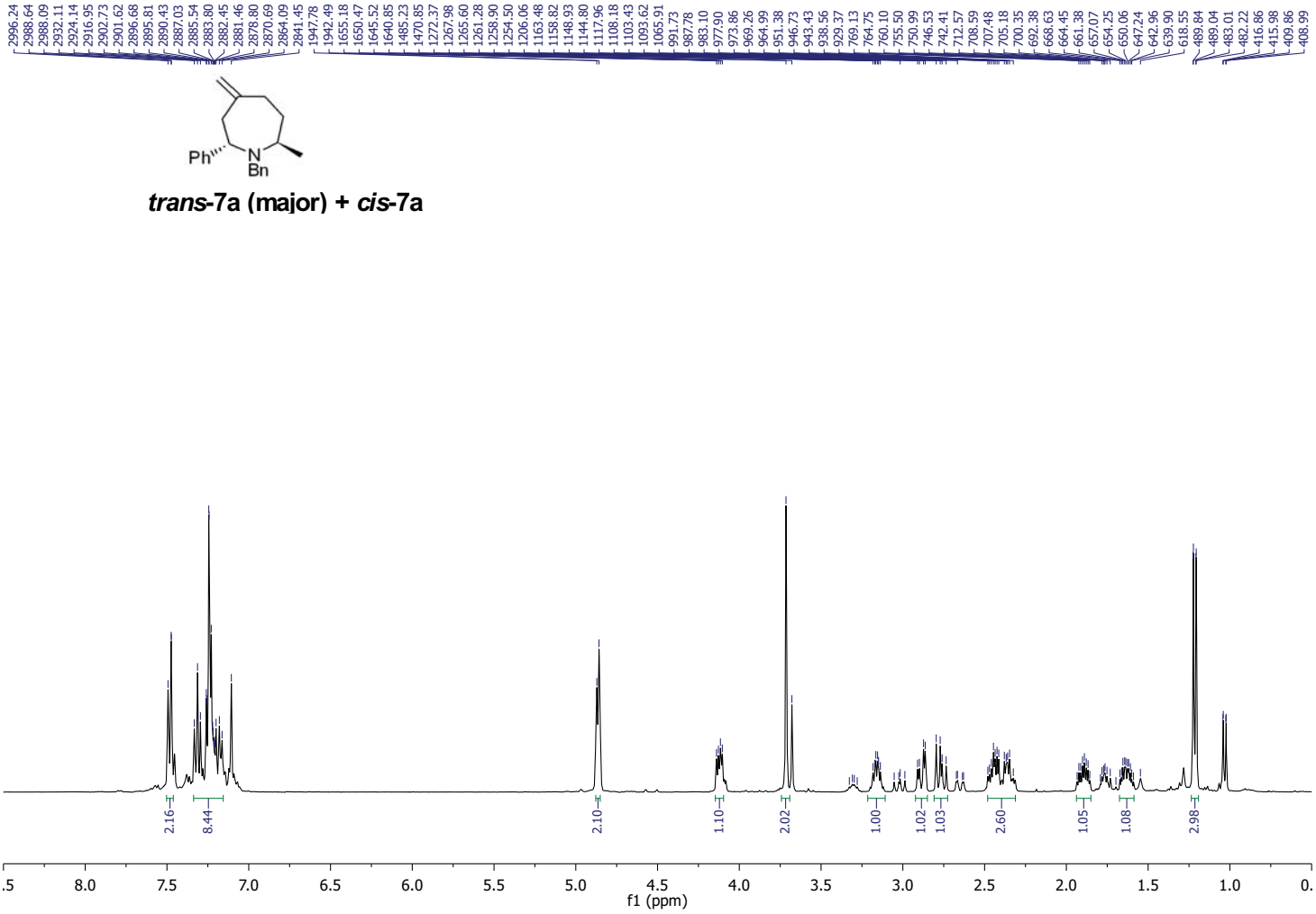

NHBn
OH
H2
H1
H1
4e
H1
H2
H2'
H2'
H2
H1
.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
f1 (ppm)


7.36
7.34
7.33
7.31
7.31
7.29
7.24
4.68
4.66
3.87
3.83
3.78
3.75
3.19
2.76
2.75
2.73
2.72
2.70
2.68
2.06
2.05
2.03
2.02
2.01
1.70
1.68
1.53
1.52
1.51
1.49
1.14
1.12
NHBn
5
5.17
0.99
1.01
1.09
1.11
1.03
1.07
2.16
4.19
1.14
3.09
f1 (ppm)

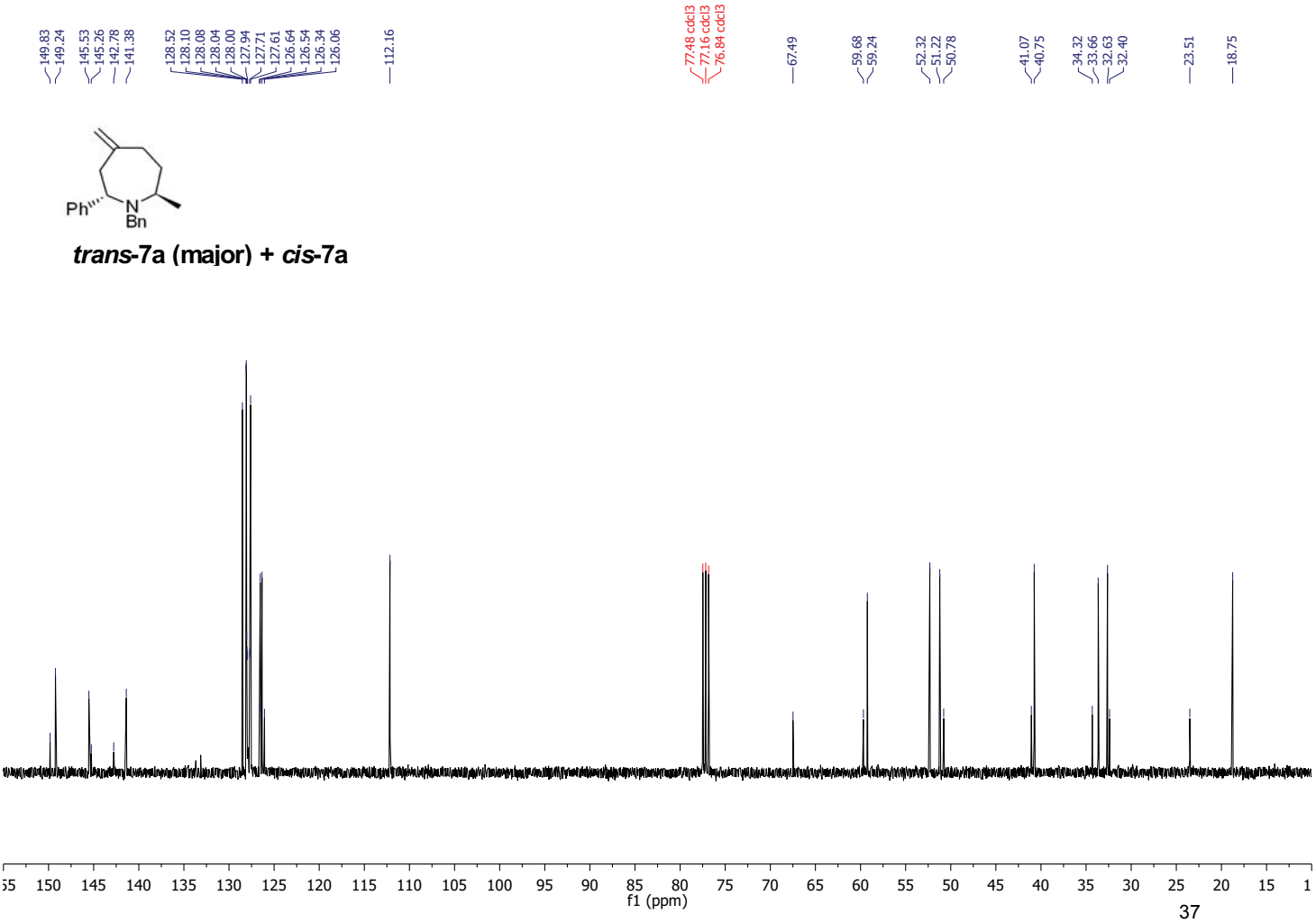

145.69
139.40
128.60
128.55
127.29
110.13
52.39
50.99
34.42
34.20
22.57
19.77
NHBn
5
f1 (ppm)


NHBn
OEt
Ph
6c
f1 (ppm)

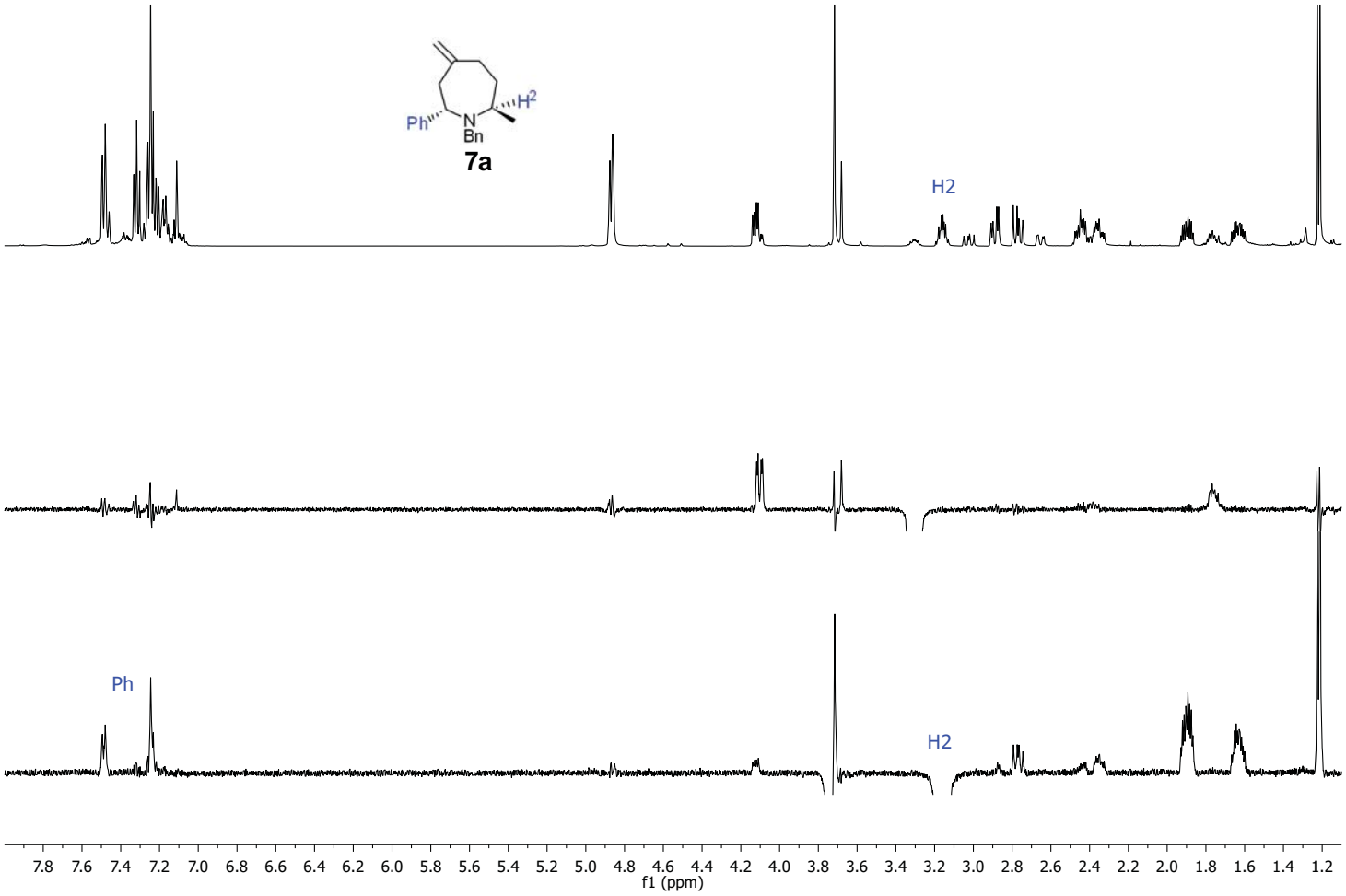

NHBn
OEt
Ph
6c
f1 (ppm)

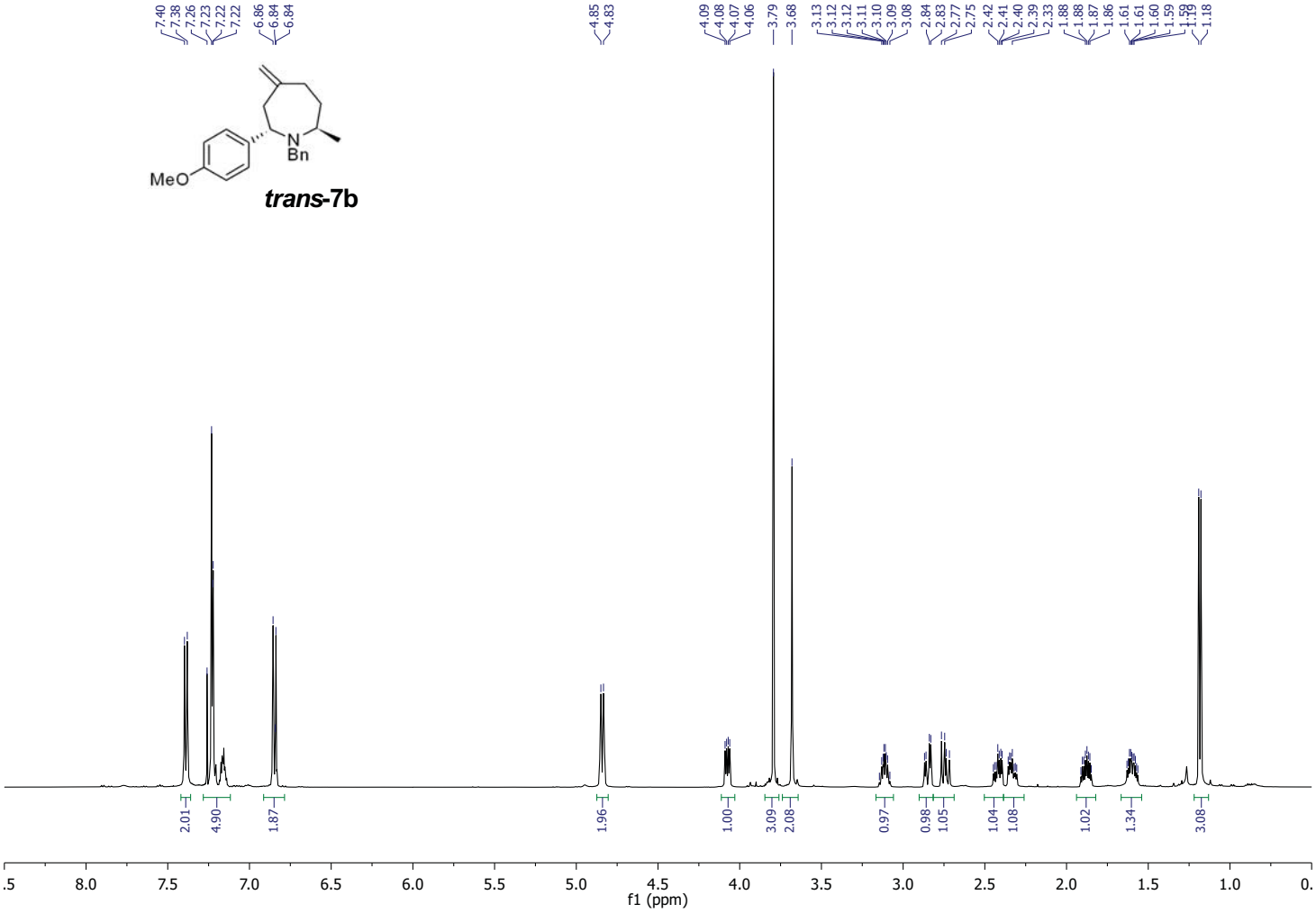


***trans*-7a (major) + *cis*-7a**

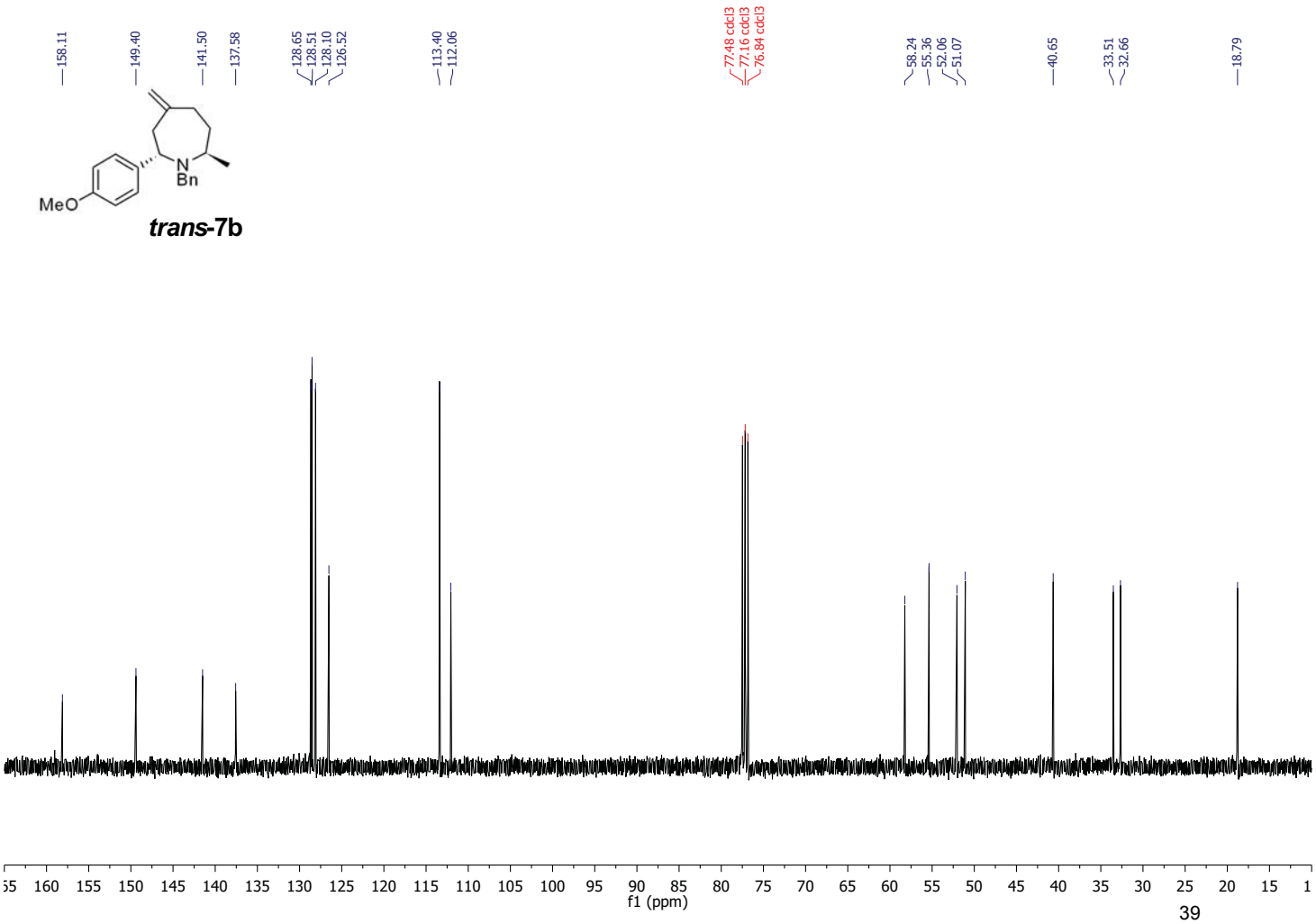


***trans*-7a (major) + *cis*-7a**

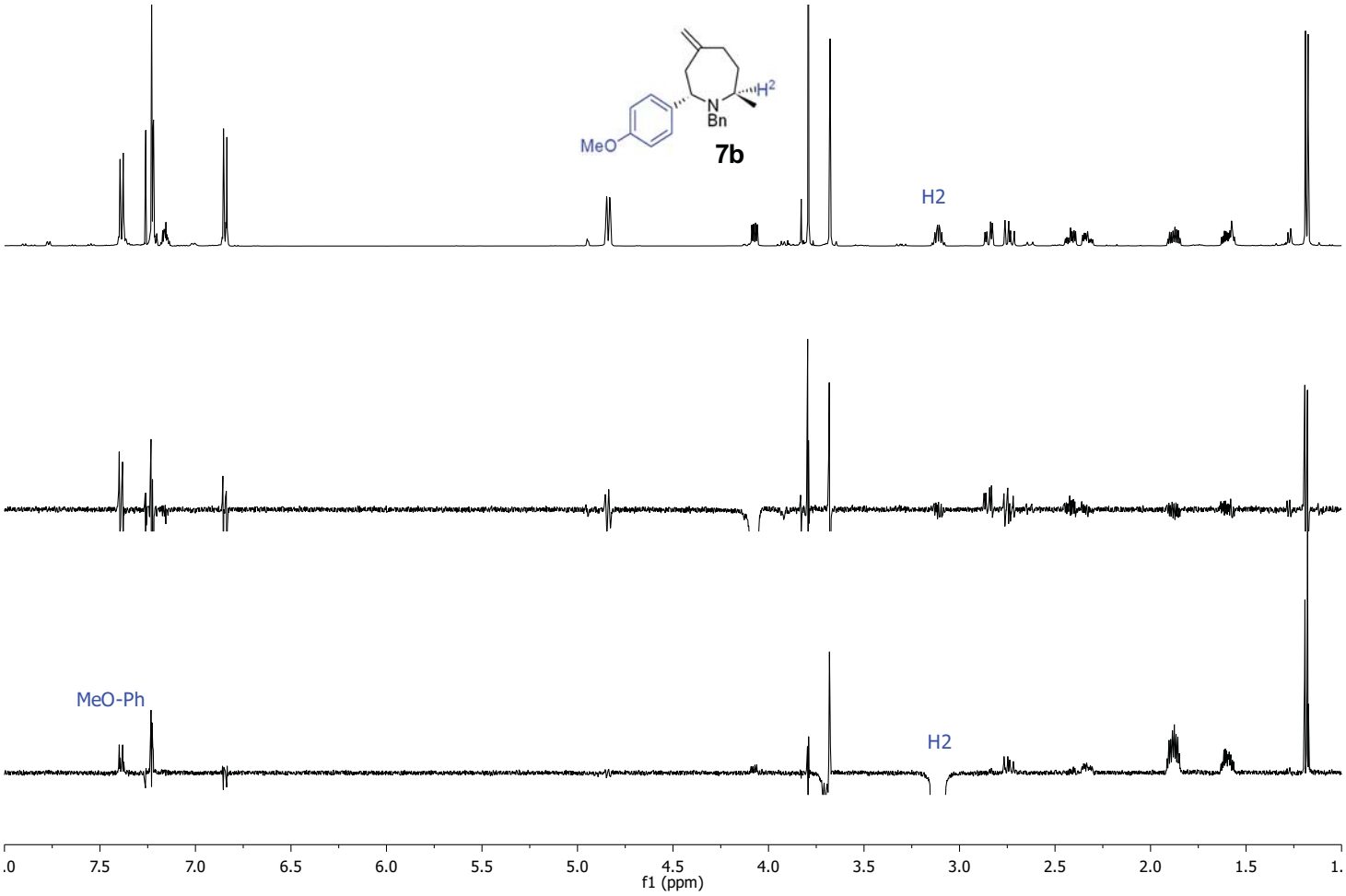

Ph
N
Bn
H2
7a
H2
Ph
H2
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

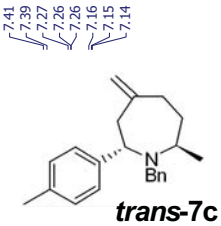


***trans*-7b**

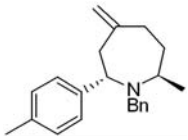


***trans*-7b**

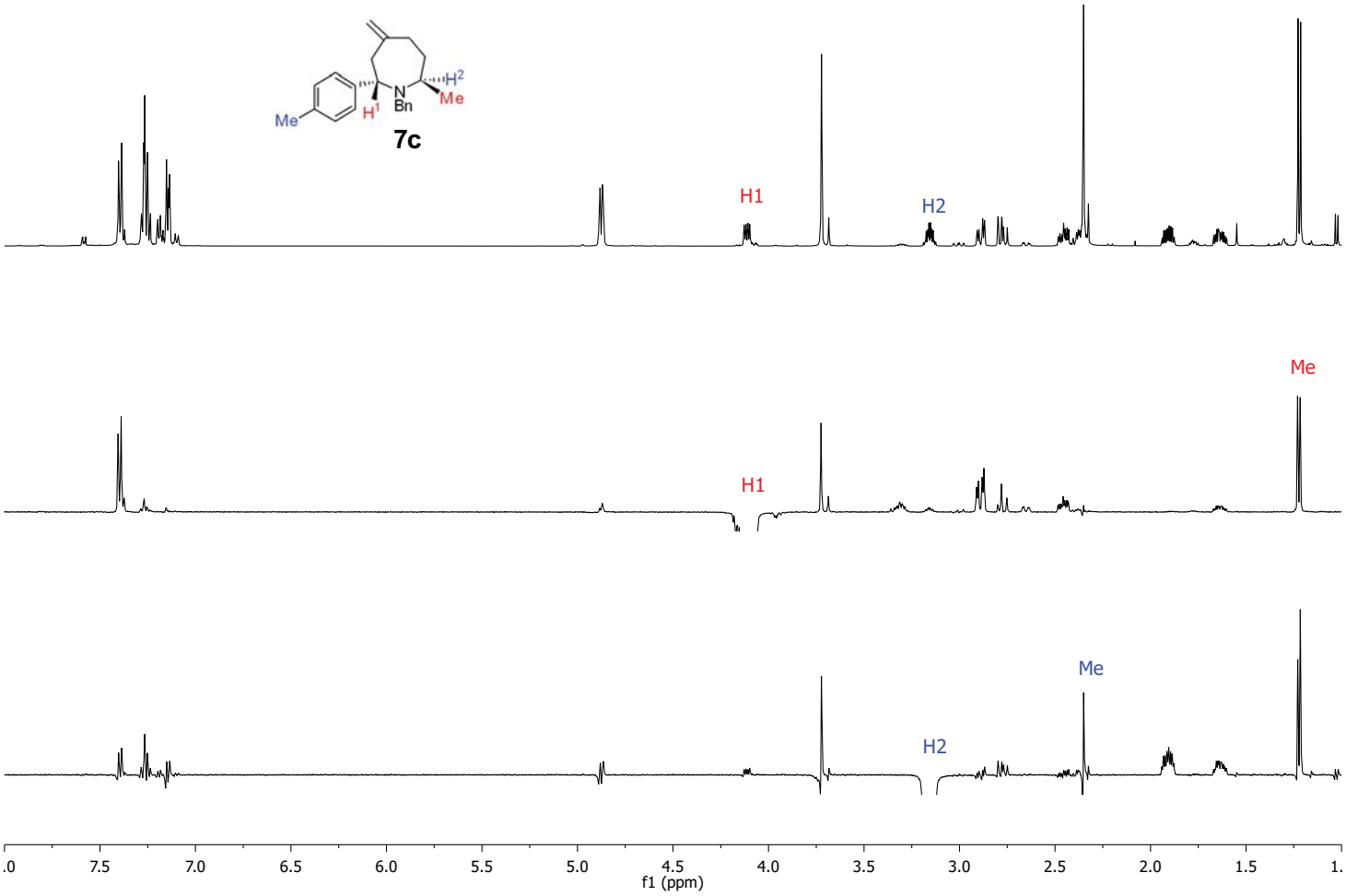

MeO
N
Bn
H2
7b
H2
MeO-Ph
H2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

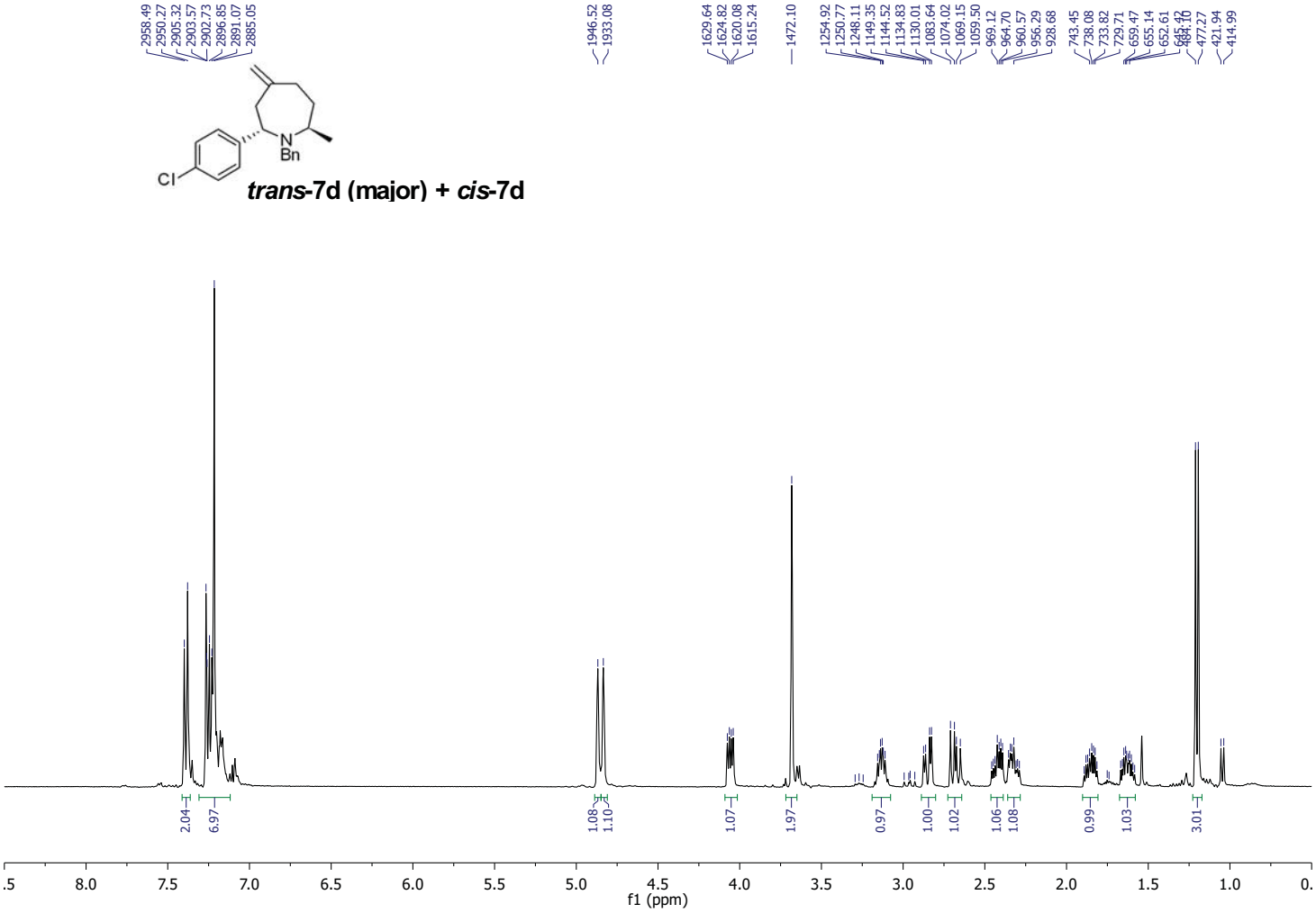


***trans*-7c (major) + *cis*-7c**

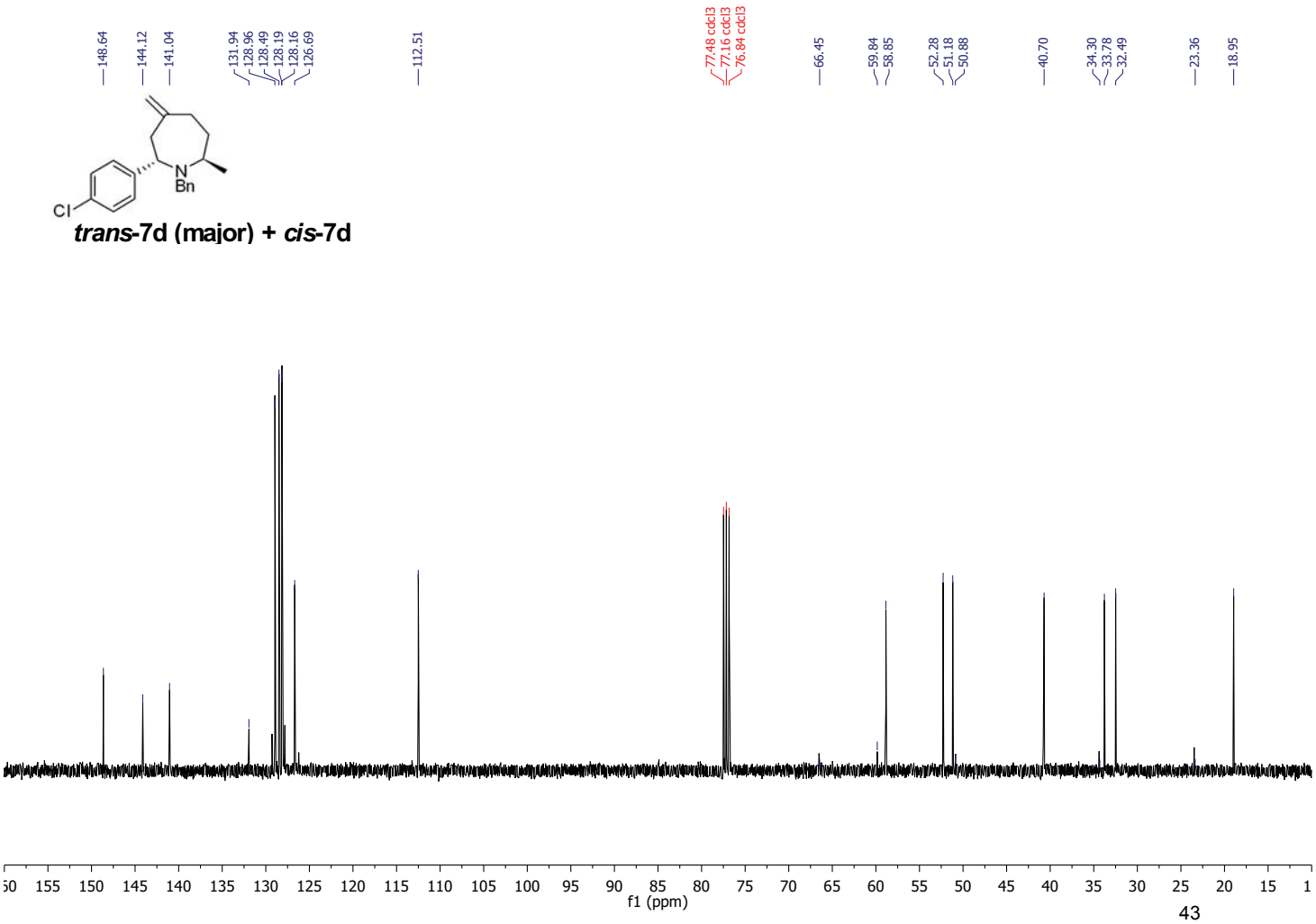


***trans*-7c (major) + *cis*-7c**

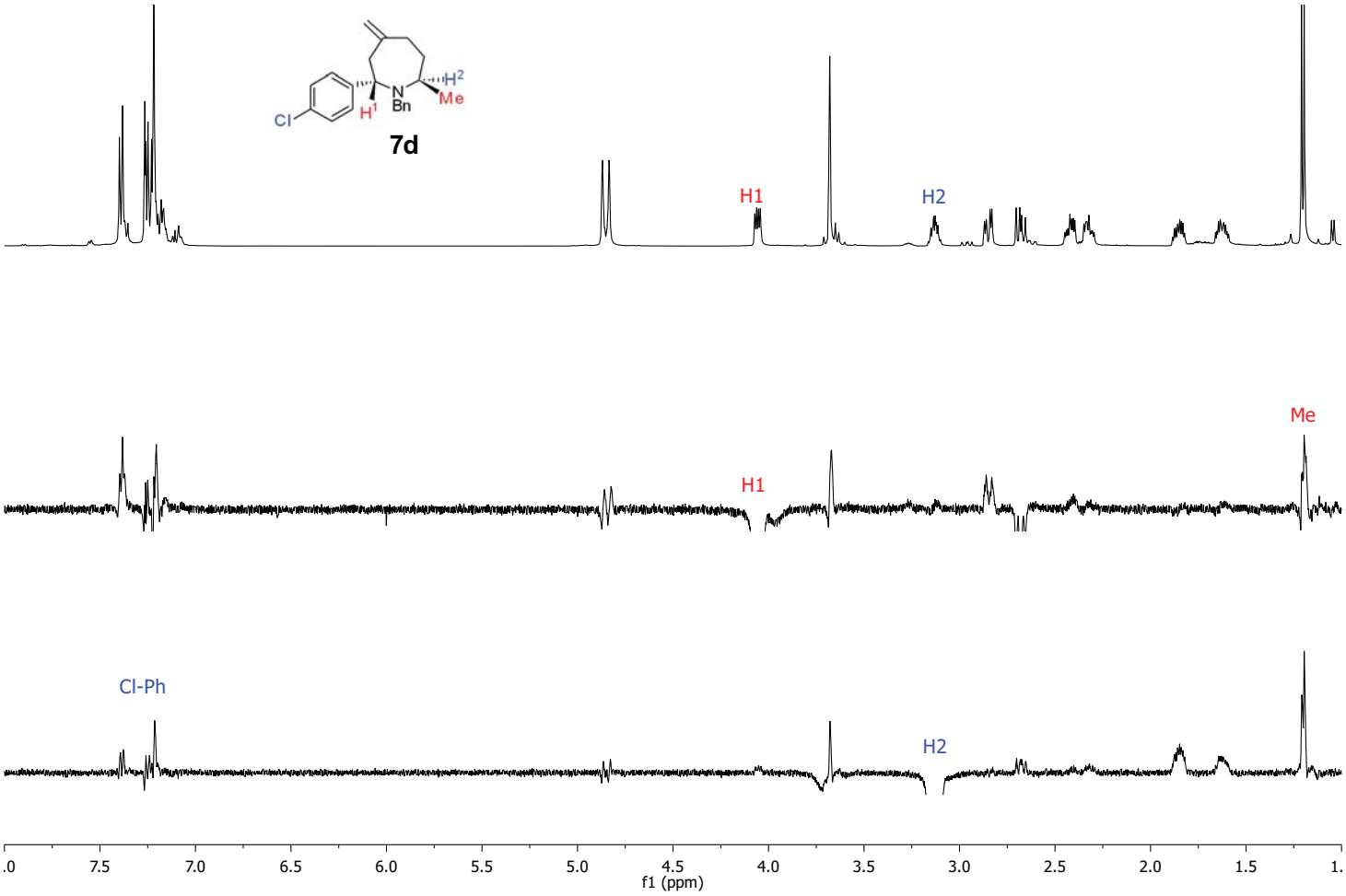

Me
H1
N
Bn
H2
Me
7c
H1
H2
Me
H1
H2
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

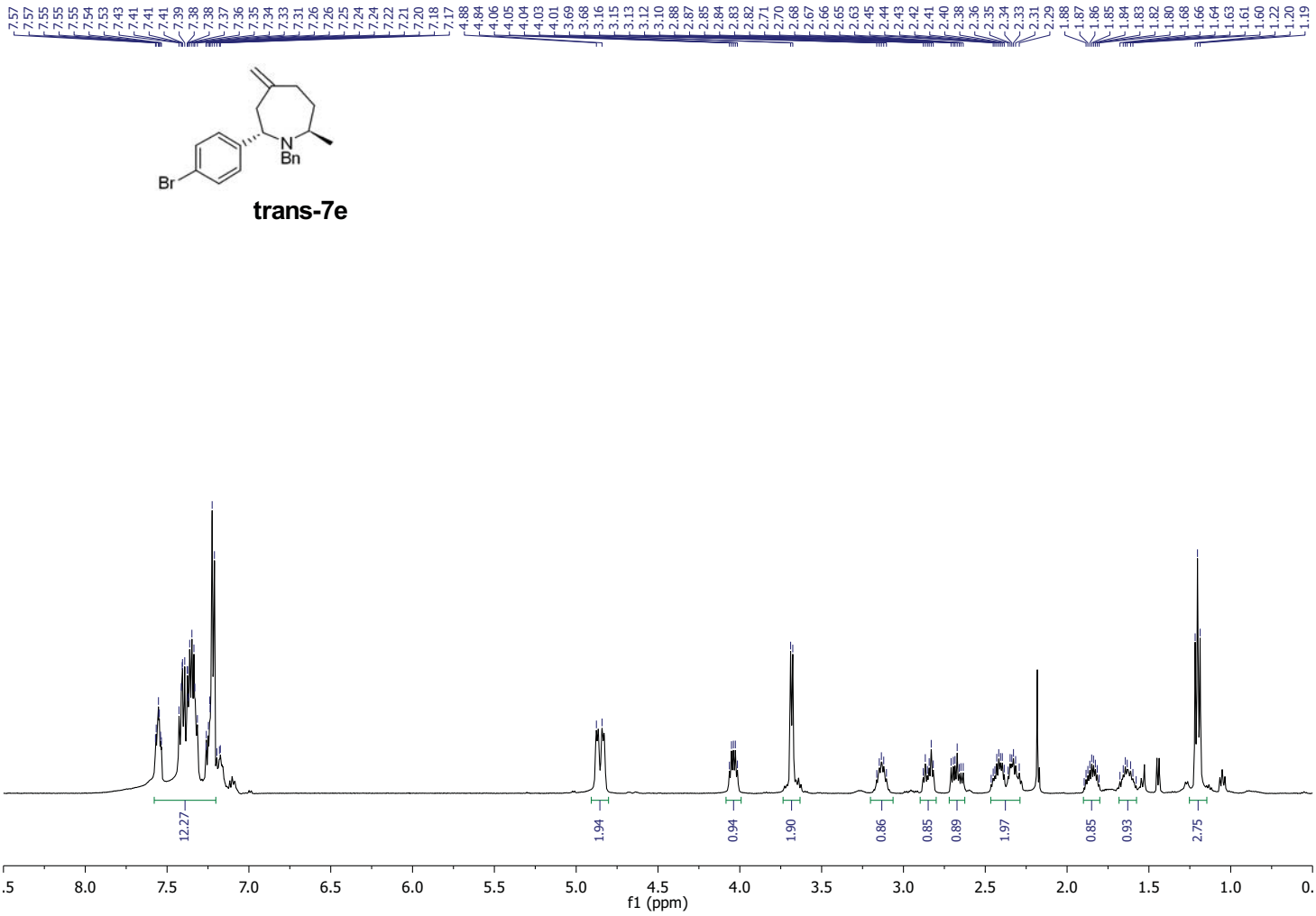


***trans*-7d (major) + *cis*-7d**

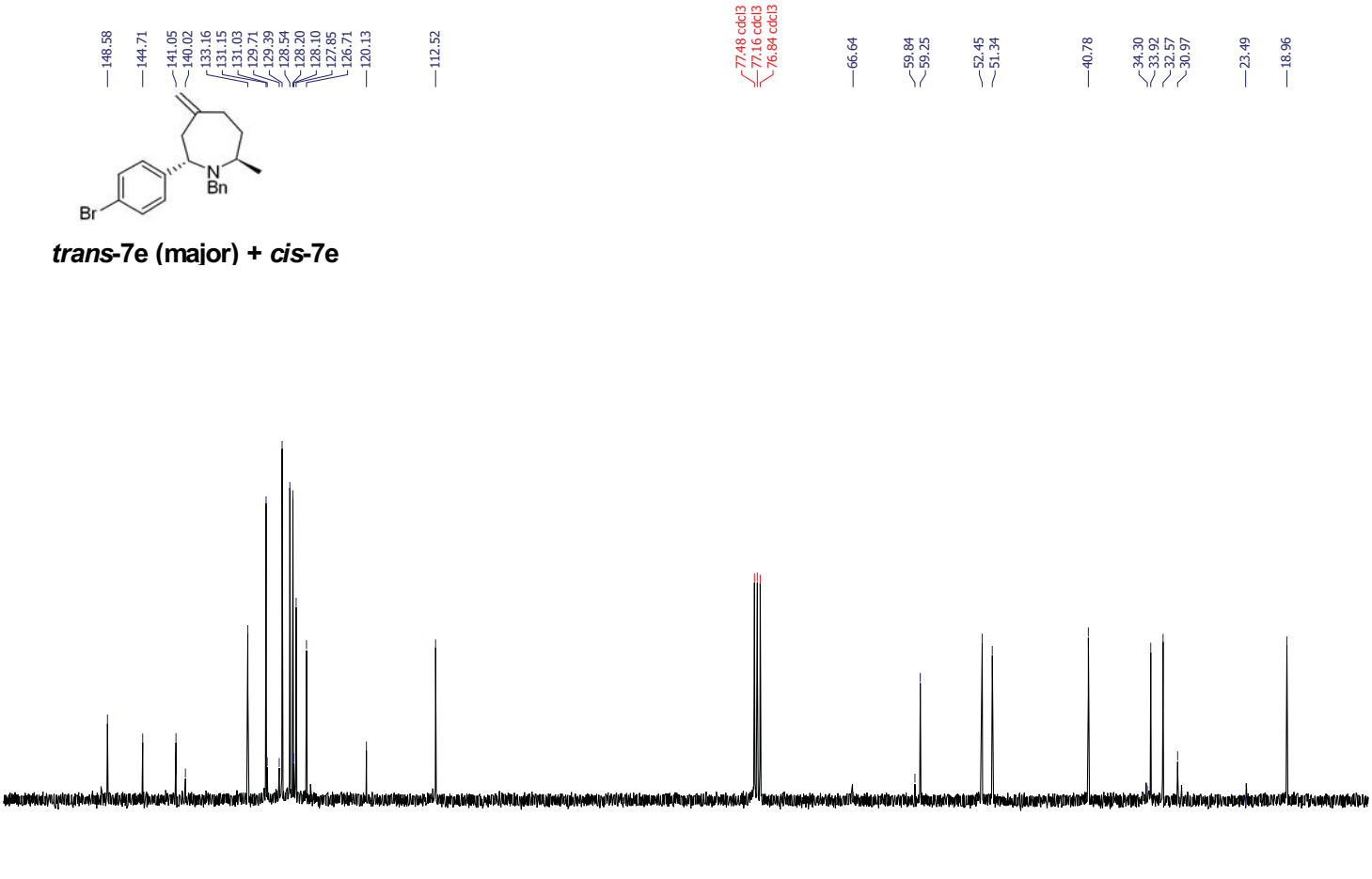


***trans*-7d (major) + *cis*-7d**

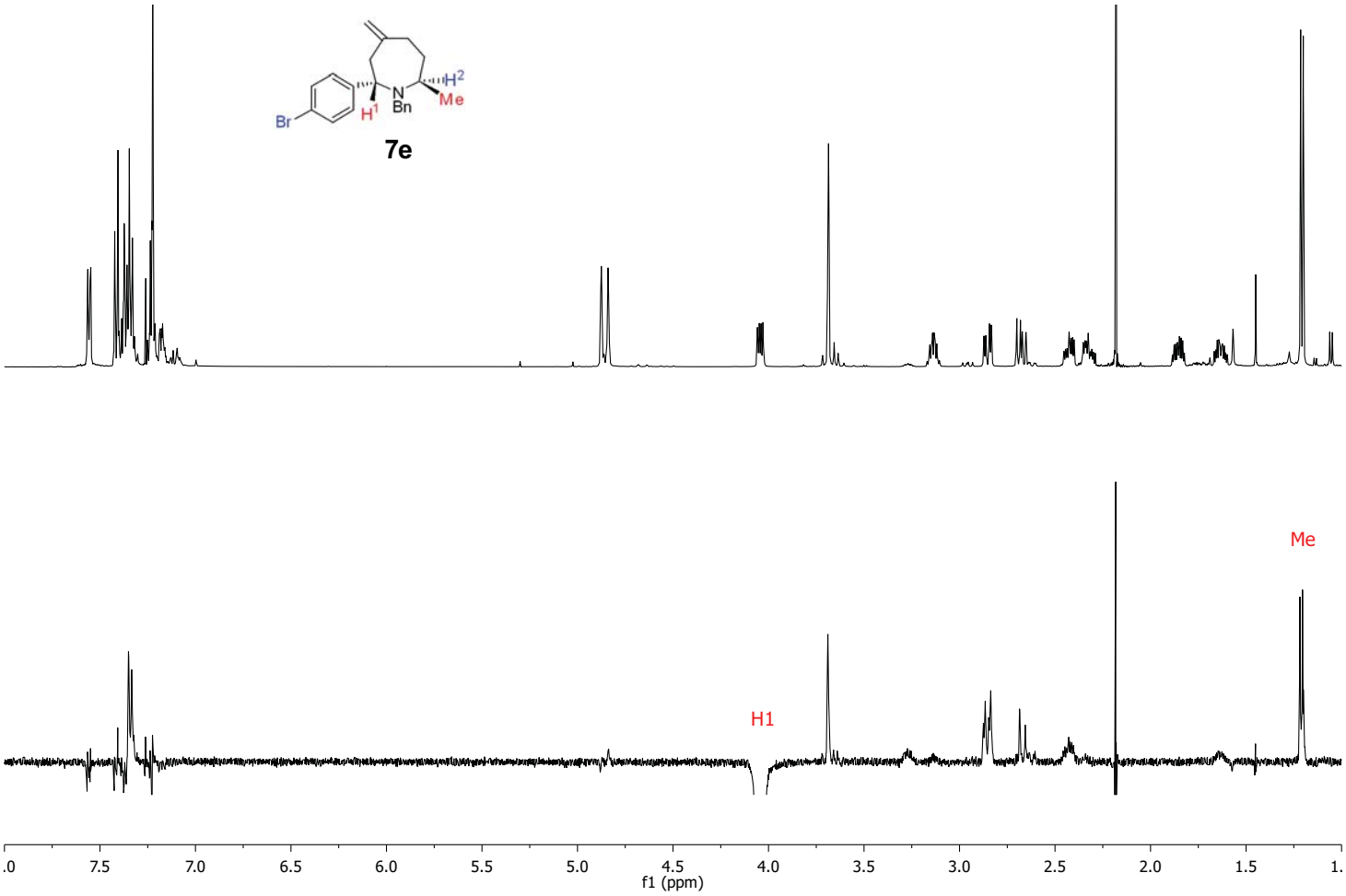

Cl
H1
N
Bn
H2
Me
7d
H1
H2
Me
H1
Cl-Ph
H2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

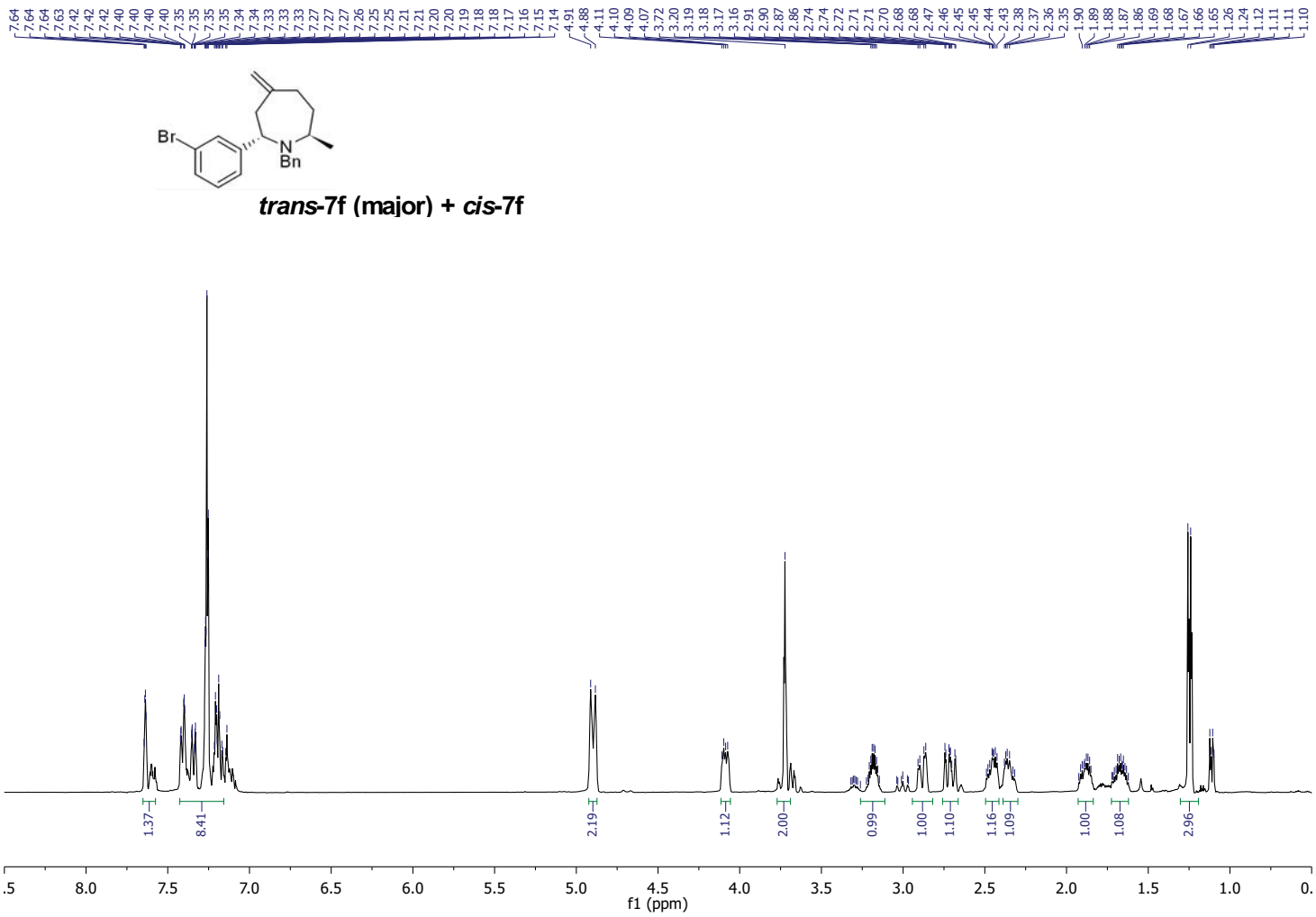


trans-7e

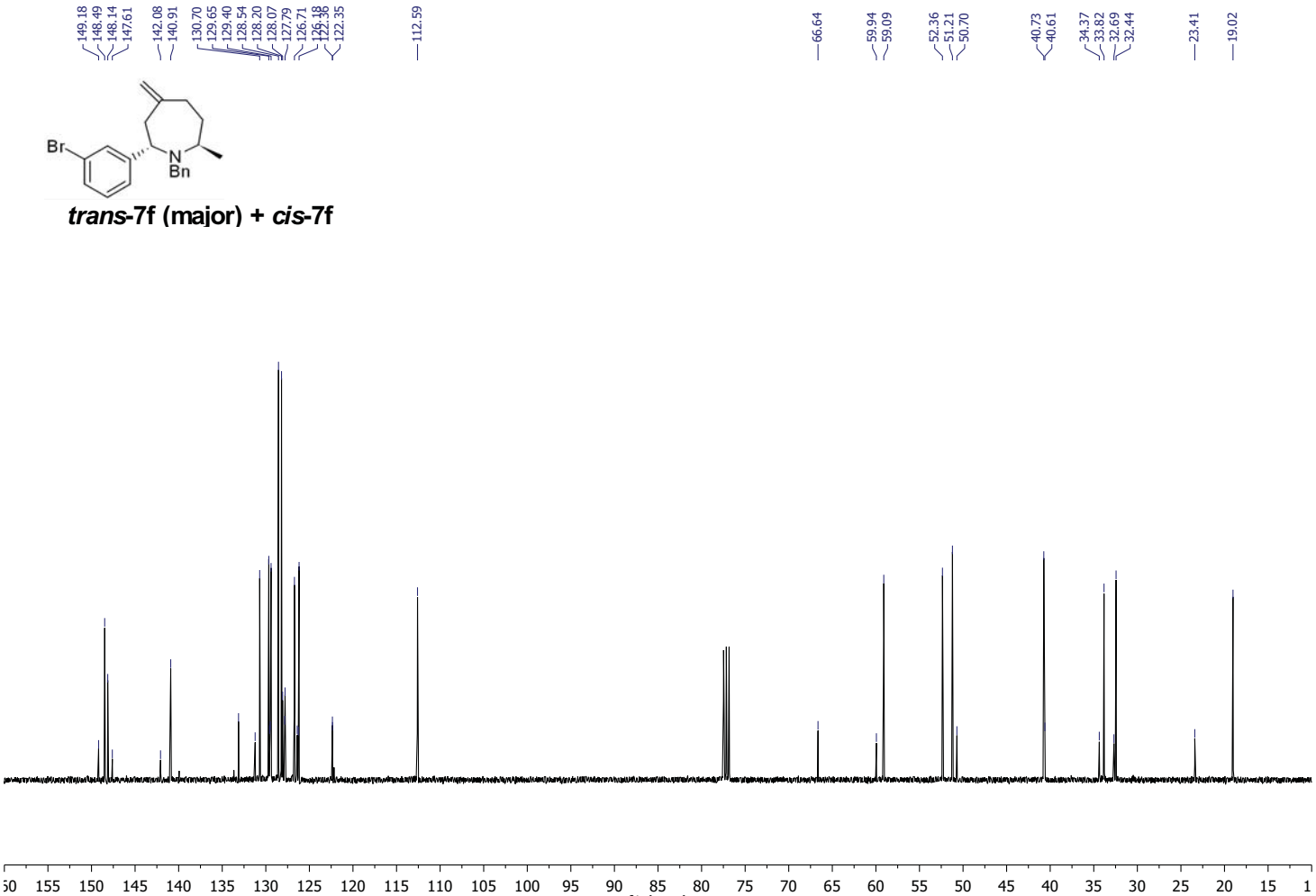


***trans*-7e (major) + *cis*-7e**

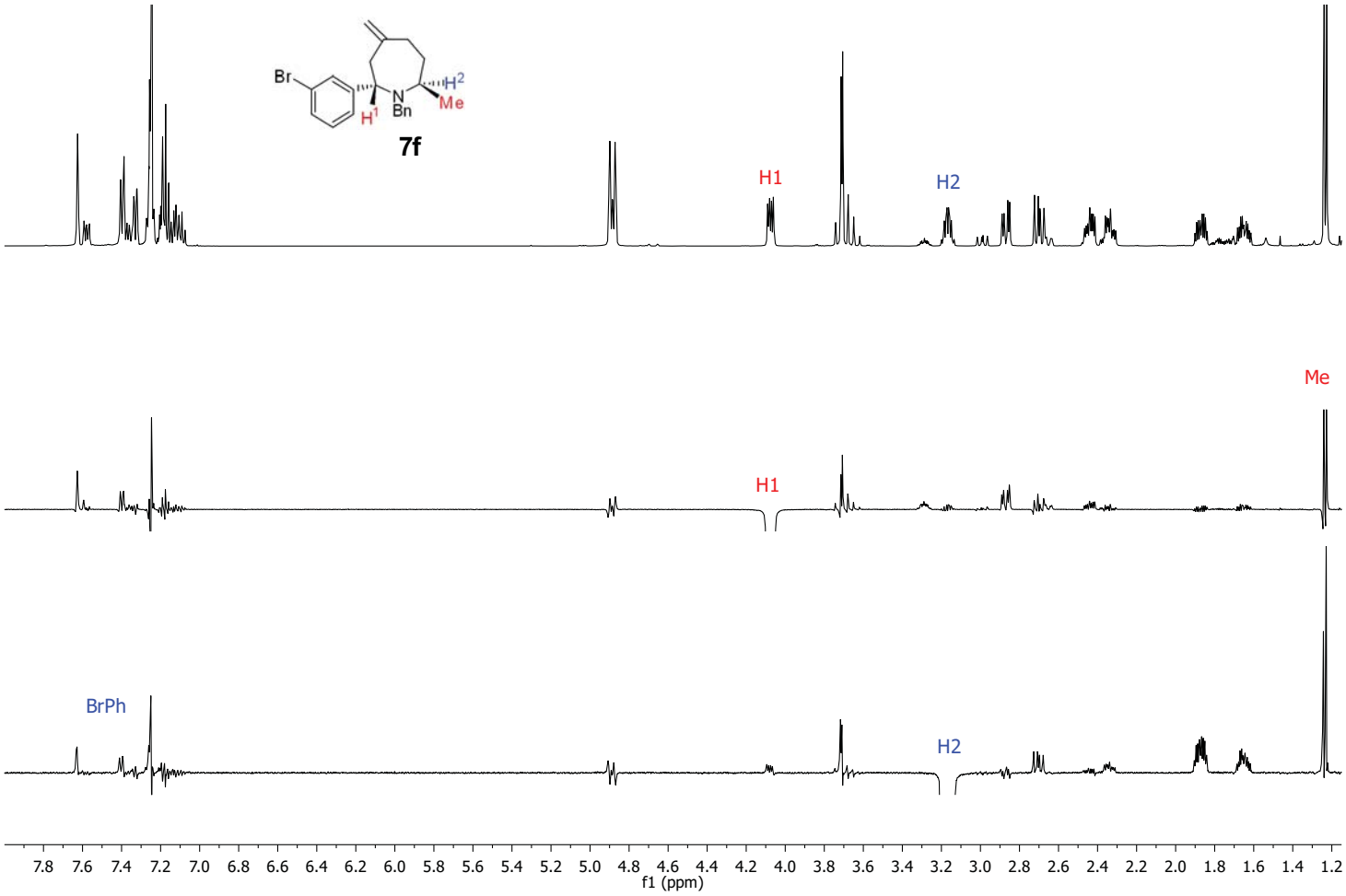

Br
H1
N
Bn
H2
Me
7e
H1
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

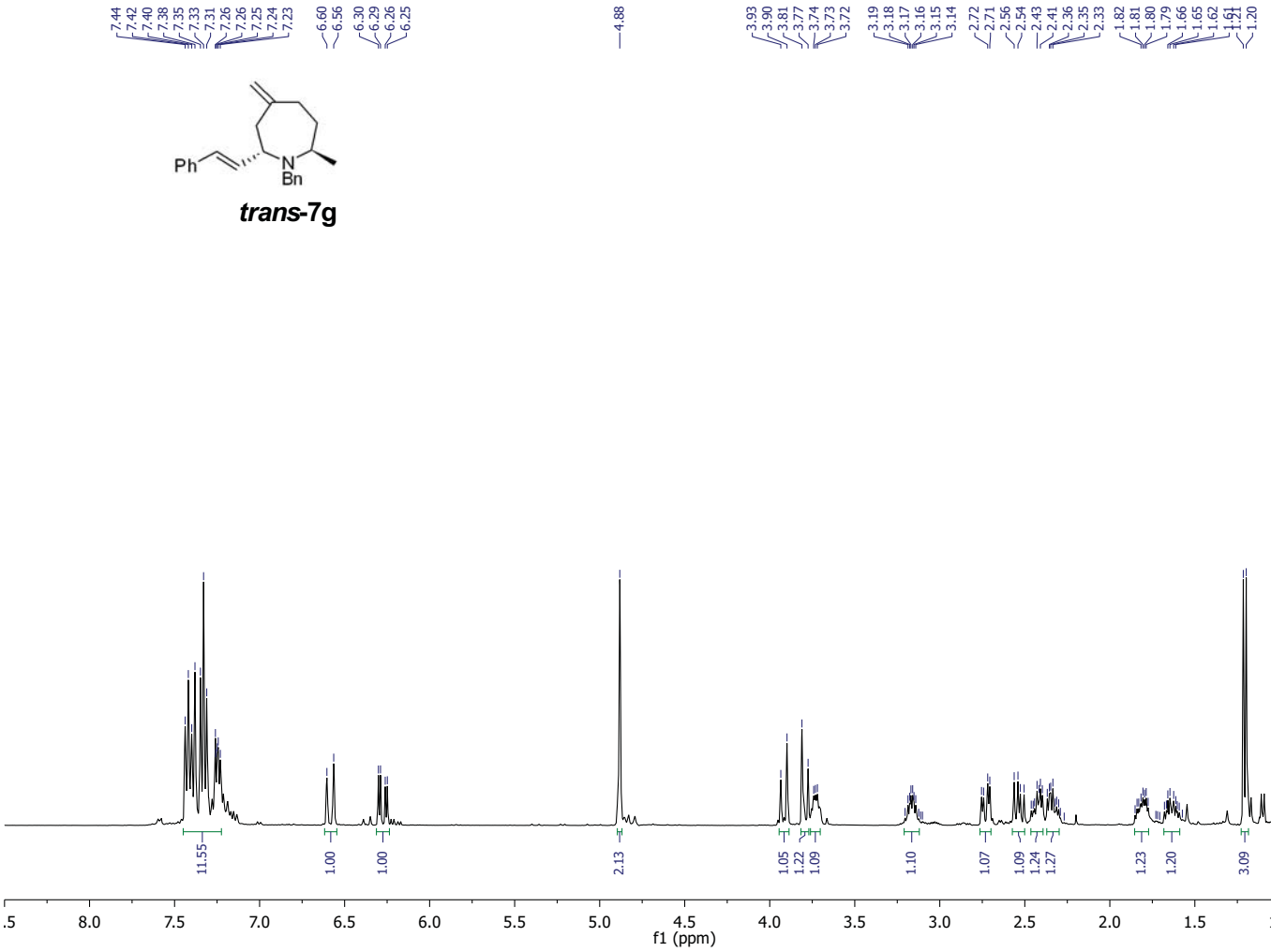


***trans*-7f (major) + *cis*-7f**

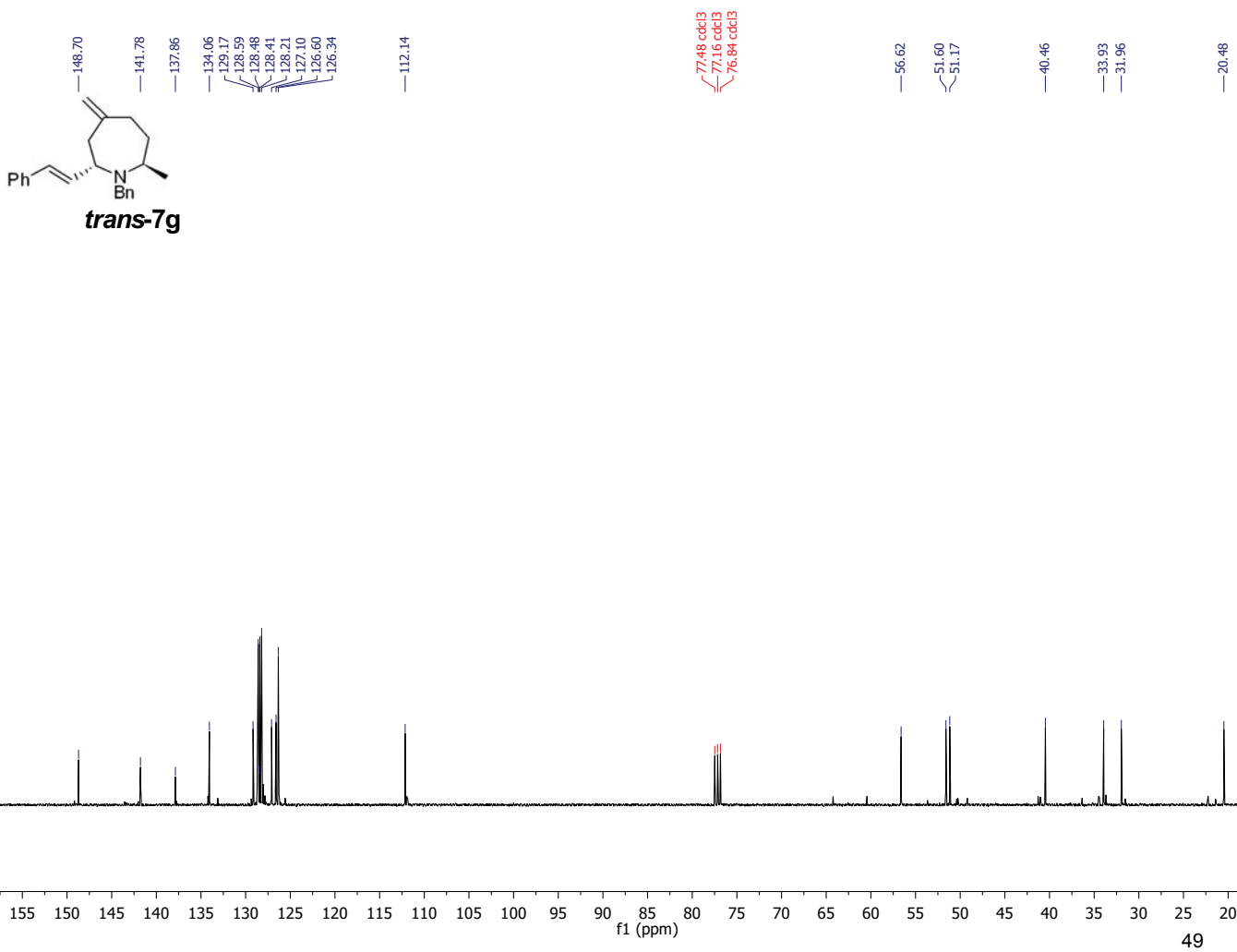


***trans*-7f (major) + *cis*-7f**

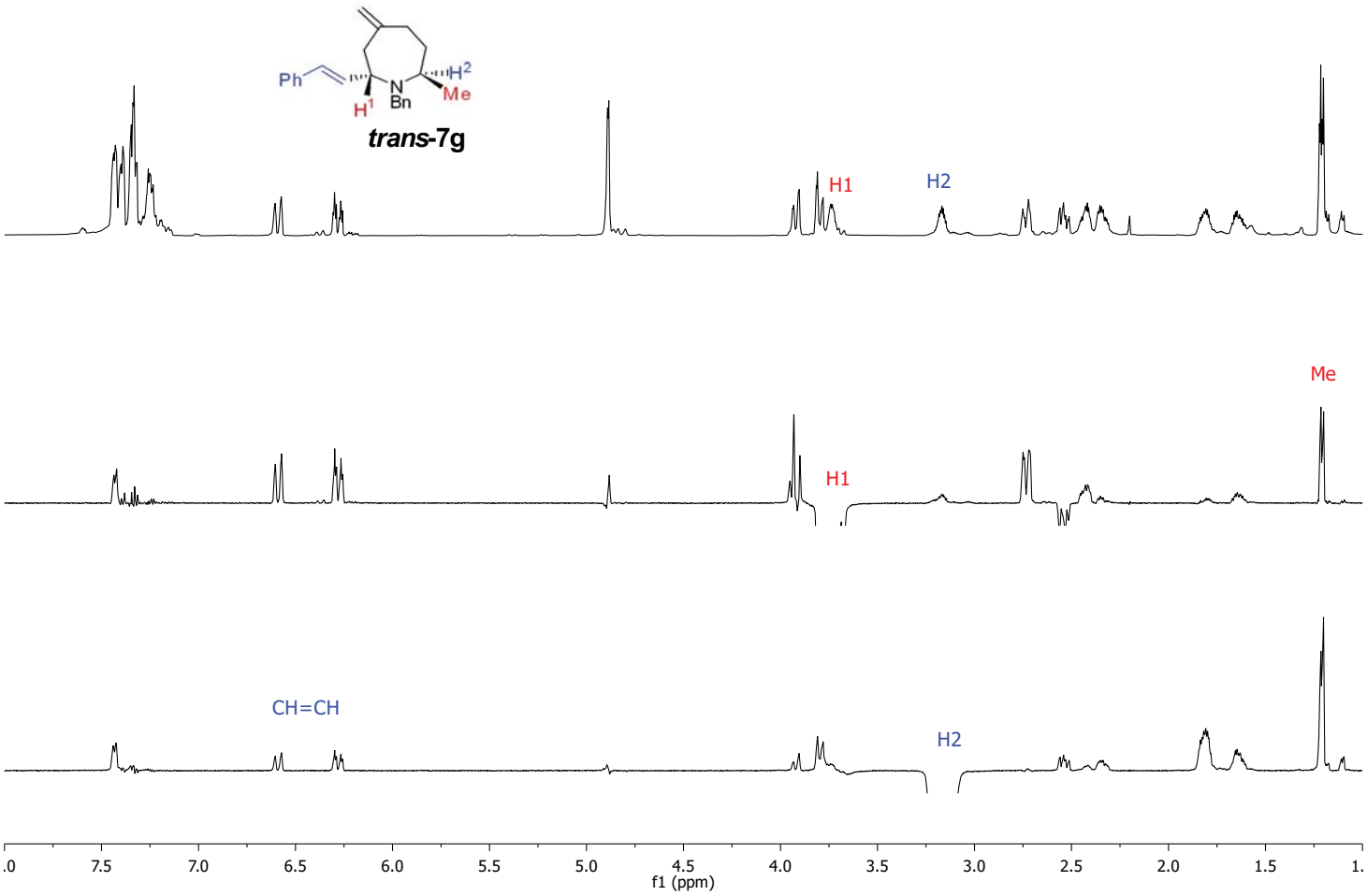

Br
H2
Me
H1
Bn
7f
H1
H2
Me
H1
BrPh
H2
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

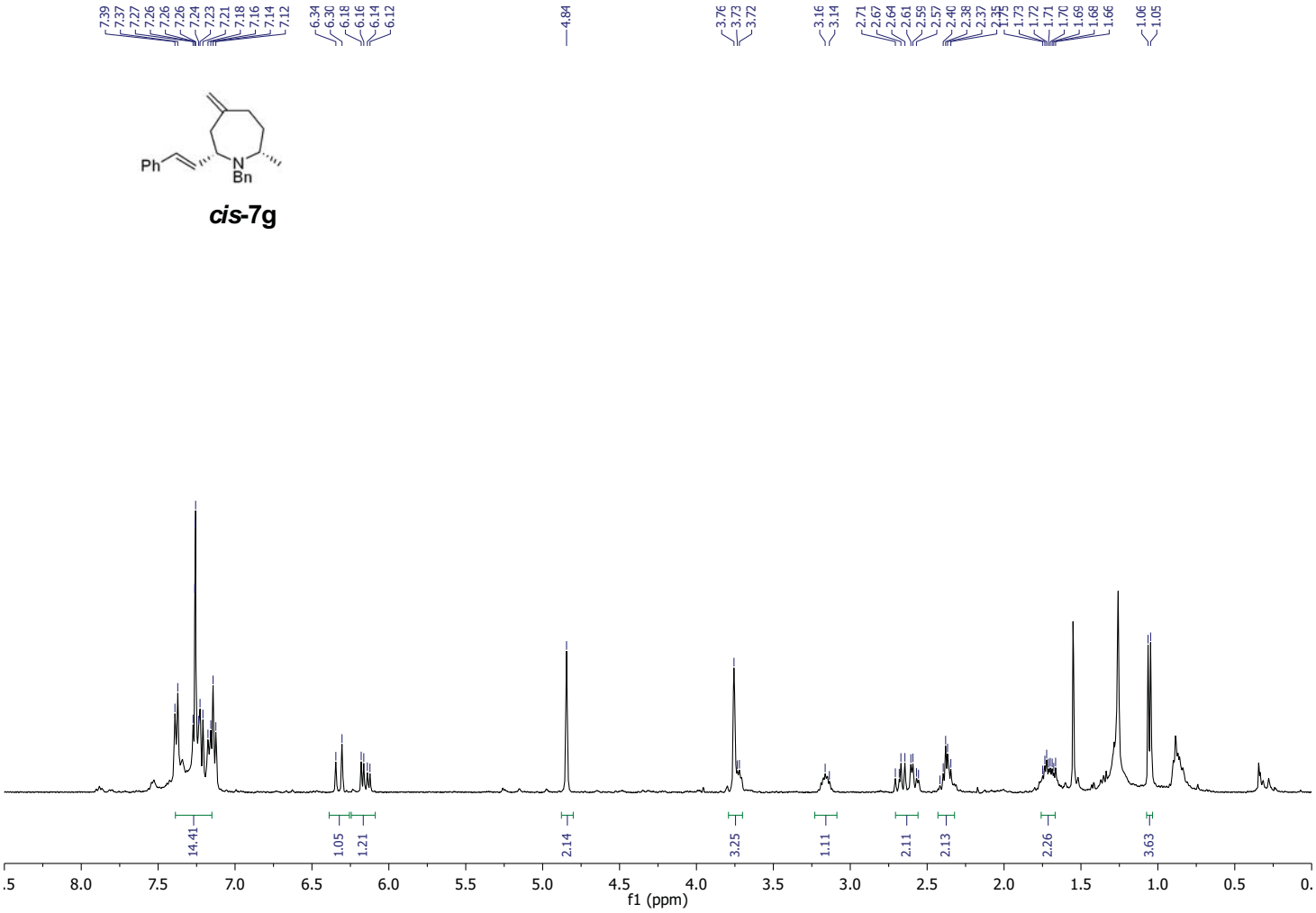


***trans*-7g**

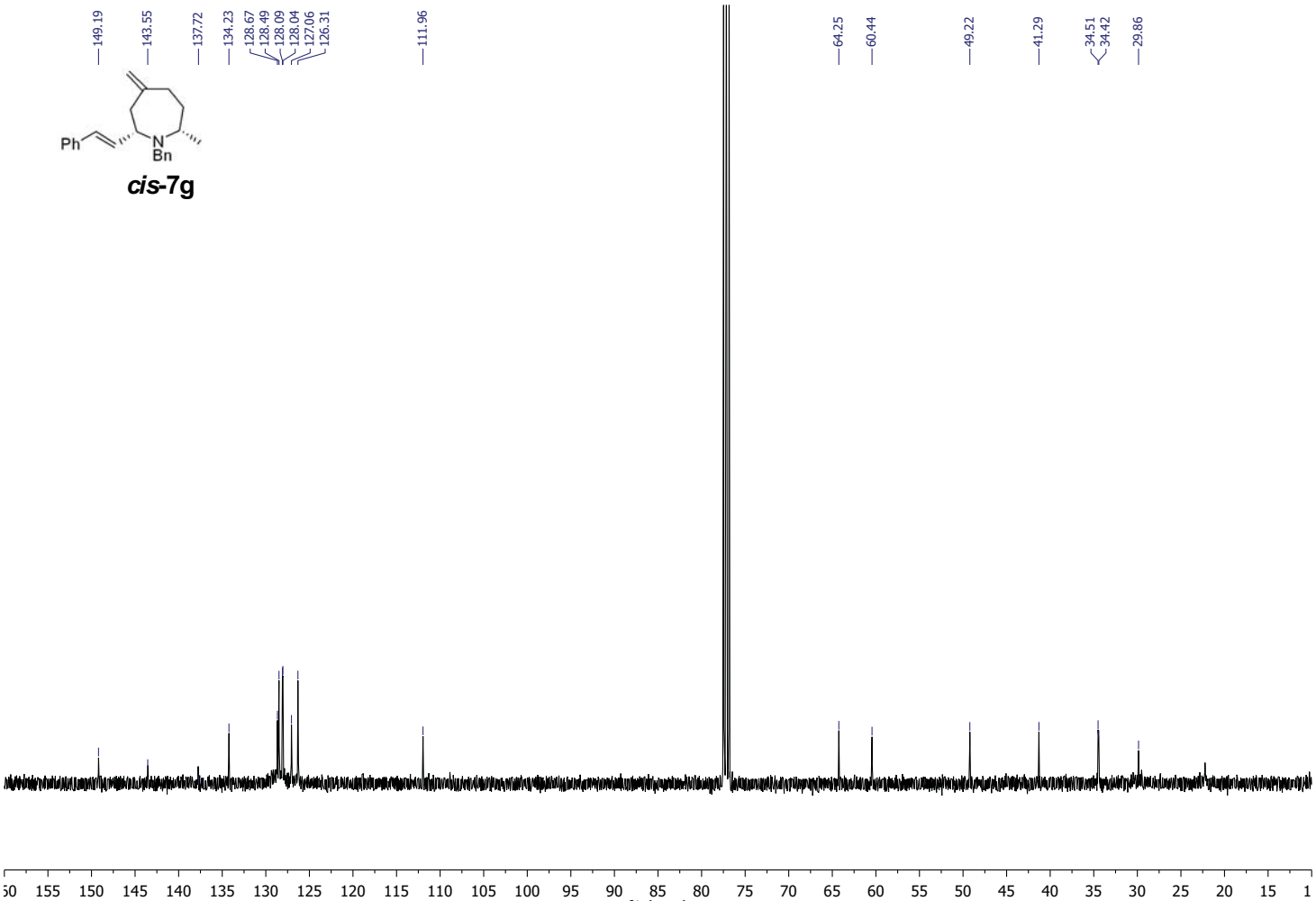


***trans*-7g**

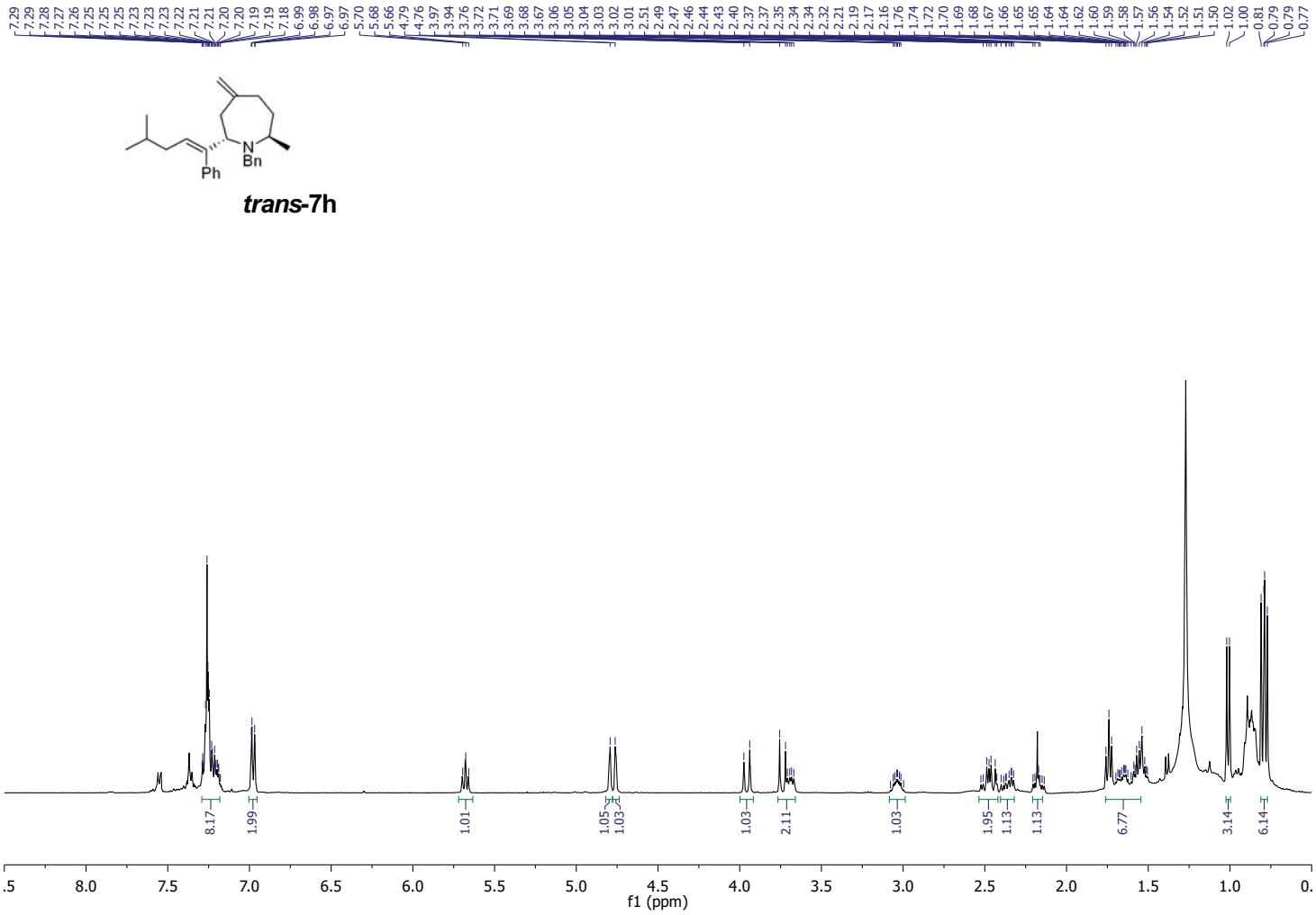

Ph
H2
H1
N
Bn
Me
trans-7g
H1
H2
Me
H1
CH=CH
H2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


7.39
7.37
7.27
7.26
7.26
7.26
7.24
7.23
7.21
7.18
7.16
7.14
7.12
6.34
6.30
6.18
6.16
6.14
6.12
4.84
3.76
3.73
3.72
3.16
3.14
2.71
2.67
2.64
2.61
2.59
2.57
2.40
2.38
2.37
1.73
1.72
1.71
1.70
1.69
1.68
1.66
1.06
1.05
Ph
N
Bn
14.41
1.05
1.21
2.14
3.25
1.11
2.11
2.13
2.26
3.63
f1 (ppm)

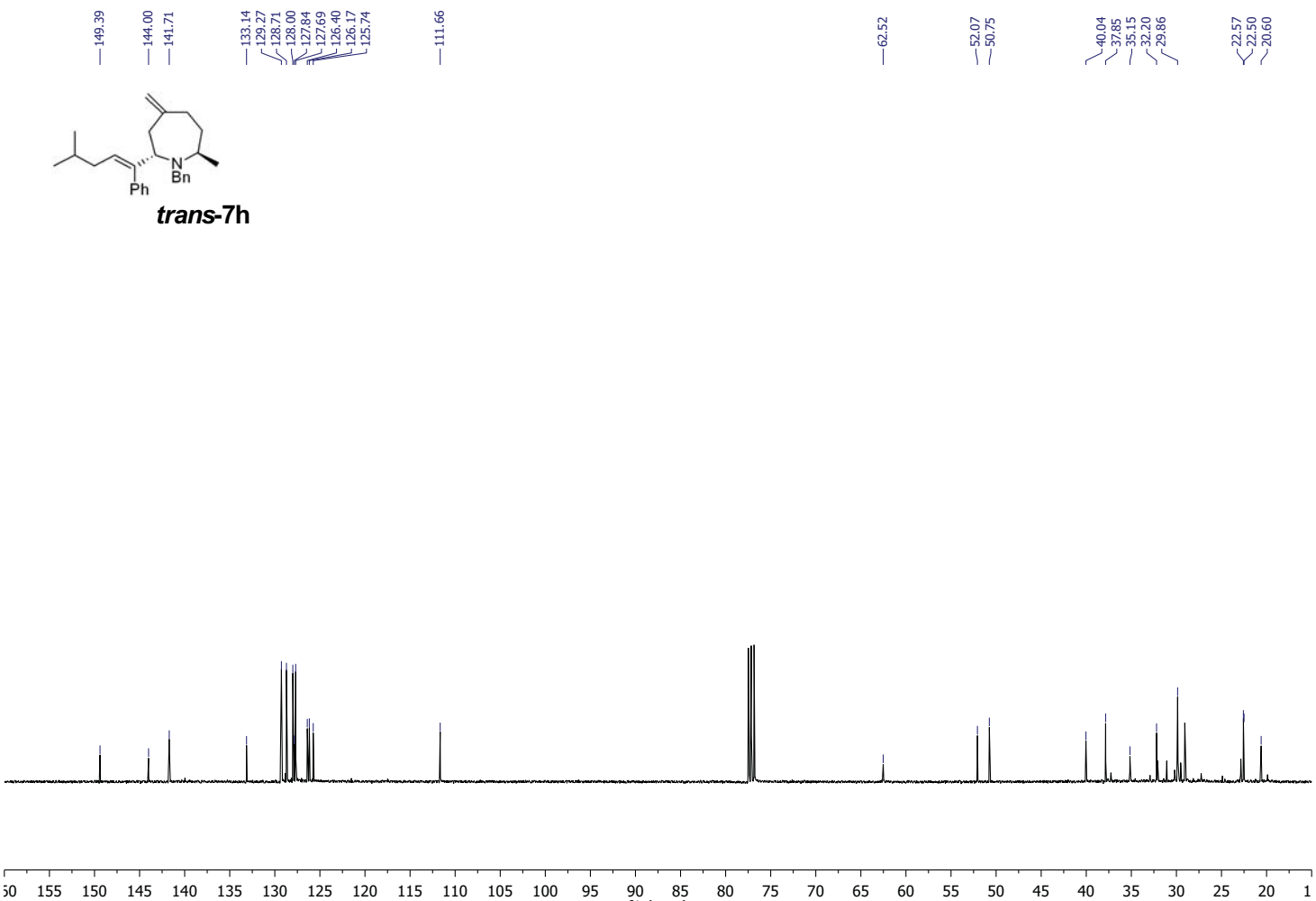
***cis*-7g**


149.19
143.55
137.72
134.23
128.67
128.49
128.09
128.04
127.06
126.31
111.96
64.25
60.44
49.22
41.29
34.51
34.42
29.86
Ph
N
Bn
f1 (ppm)

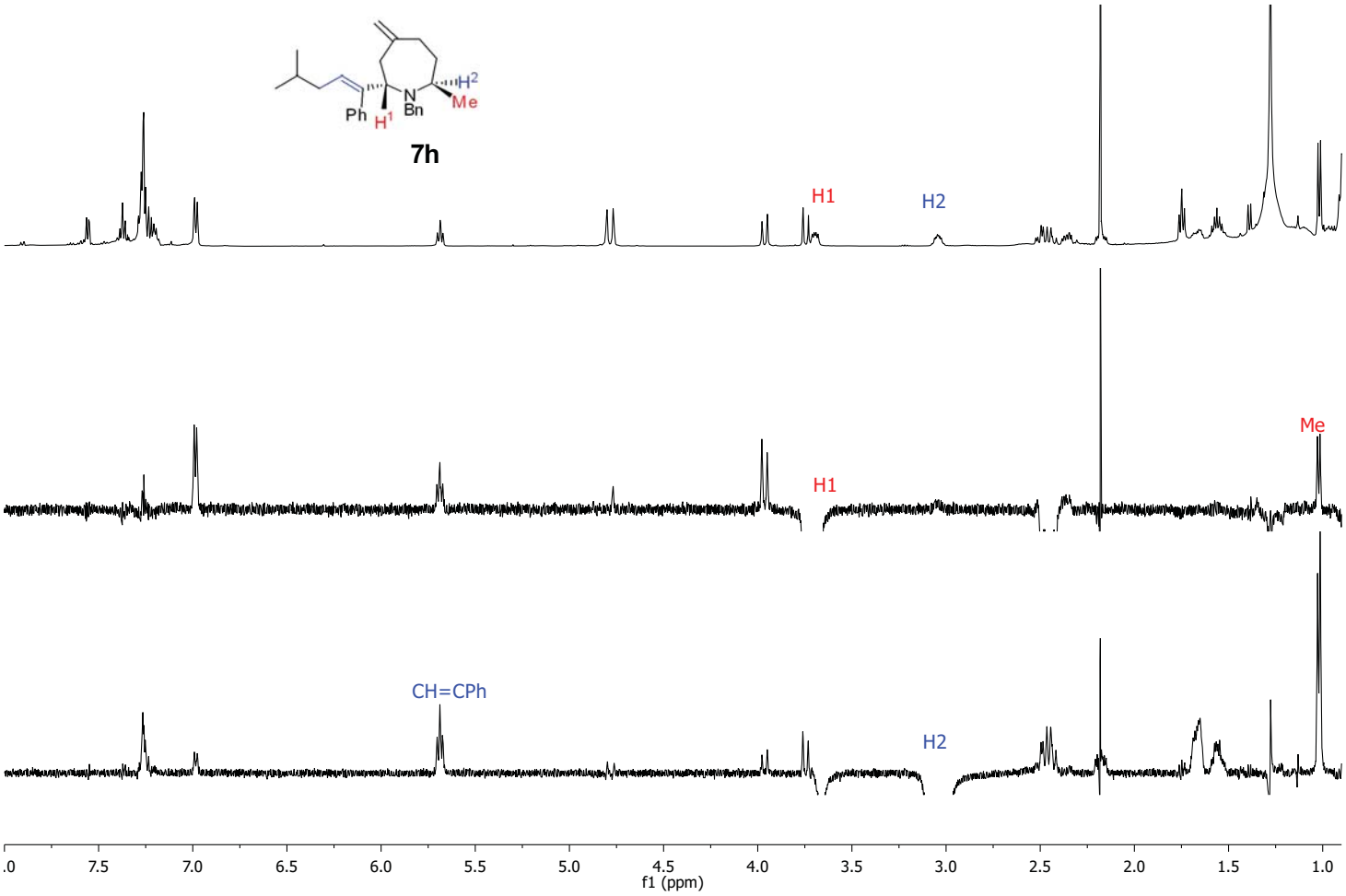
***cis*-7g**



***trans*-7h**



***trans*-7h**


H2
Me
Ph
H1
Bn
N
7h
H1
H2
Me
H1
CH=CPh
H2
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
f1 (ppm)