Electronic Supplementary Material (ESI) for ChemComm.

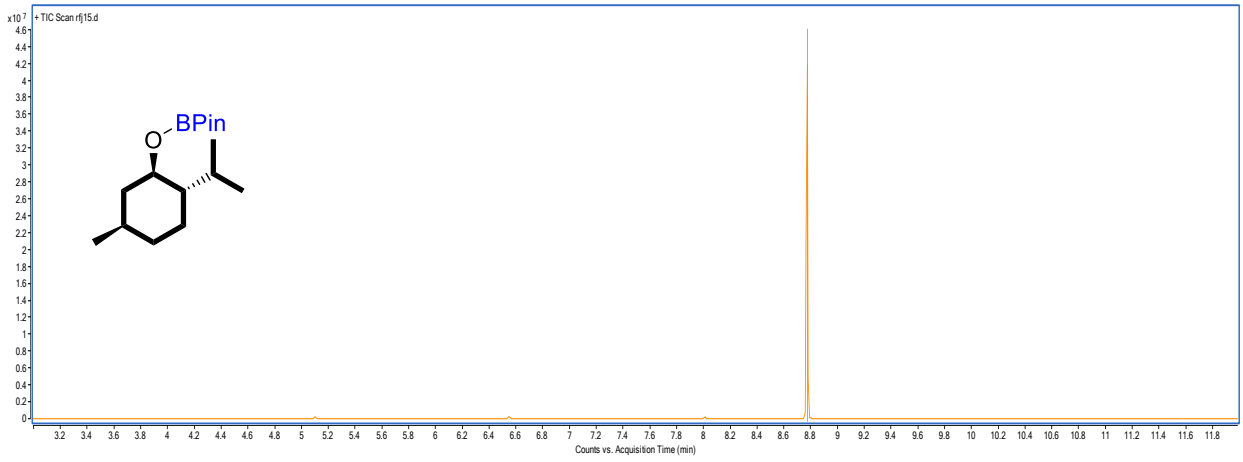
Catalyst-Free Dehydrocoupling of Amines, Alcohols, and Thiols with Pinacol Borane and 9-Borabicyclononane (9-BBN)

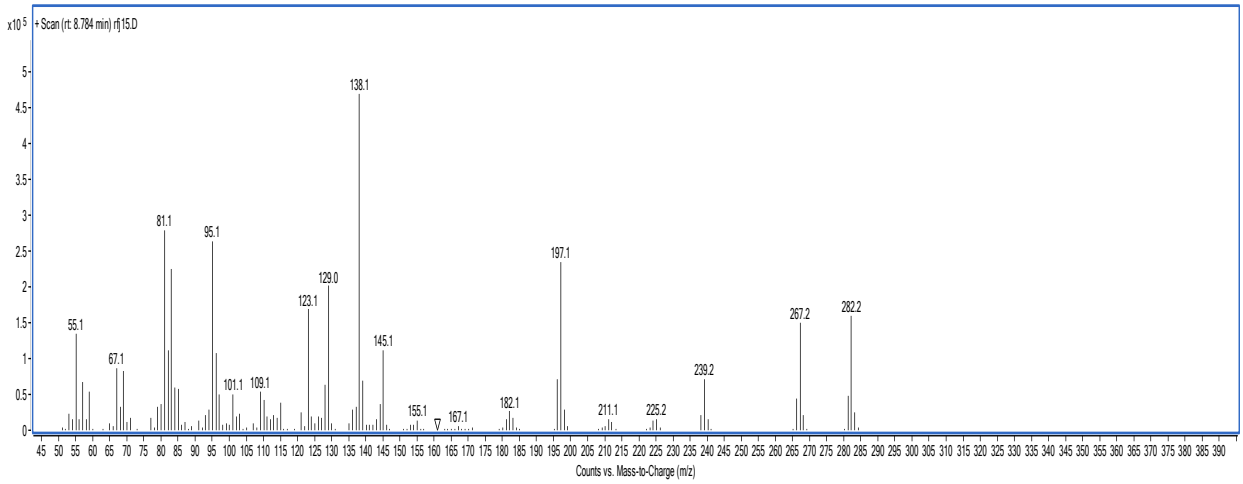
Erik A. Romero, Jesse L. Peltier, Rodolphe Jazzar, Guy Bertrand*

UCSD-CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

A. General Considerations

All reactions were performed under an atmosphere of argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, or CaH_2. **Reagents of analytical grade were obtained from commercial suppliers and used without drying, degassing, or purification** of any kind. New glassware and new stir bars were used to mitigate trace metal involvement. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were obtained using either a Bruker Avance 300 MHz, a Varian INOVA 500 MHz spectrometer or JOEL 500 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sept = septet, m = multiplet, br = broad signal. NB: We were unable to obtain HRMS data analysis using the facility available at UCSD; Hence all substrates were submitted either low-resolution ESI (Micromass Quattro Ultima Triple Quadrupole MS) or to GCMS analysis (Agilent GCMS: 7820A). Corresponding LRMS are reported as obtained. Regarding the GCMS analysis, please find an example hereafter of a typical GC trace and MS spectra (here **2v**).





B. Kinetics for Concentration Dependence

All the kinetic measurements were performed in a J-Young NMR tube at room temperature on a Bruker 300 MHz NMR machine using the multi_zgvd command. Conversions were measured following the growth of the characteristic signals for **1a** with respect to the depleting signals for the starting aniline. In each kinetic run, 0.4 mmol (0.036 mL) of aniline and 0.4 mmol (0.058 mL) of PinBH were used in combination with CD_3CN (x mL used to attain concentrations listed below).

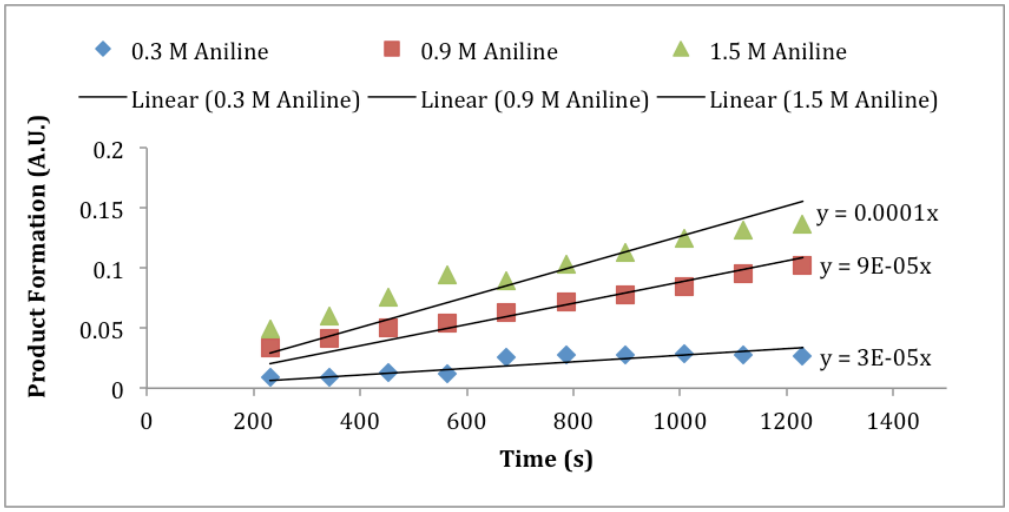


Fig. S1. Concentration dependence plot of the aniline dehydrocoupling reaction with pinacol borane in acetonitrile.

C. Time dependant dehydrocoupling of Allyl Amine and Pinacol borane

This experiment was performed in a J-Young NMR tube at room temperature on a Bruker 300 MHz NMR machine. The growth of the characteristic signals for **1g** were followed with respect to the depleting signals for the starting allyl amine. Typically 0.08 mmol (0.006 mL) of allyl amine and 0.08 mmol (0.012 mL) of PinBH were used in combination with CD_3CN.

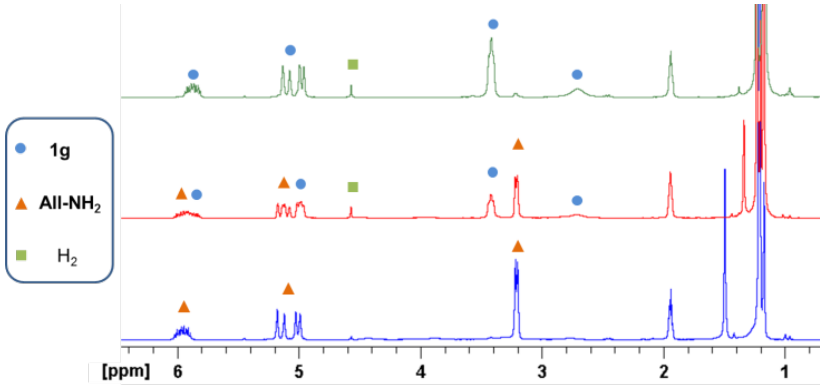


Fig. S2. ^1H NMR spectra of allylamine and pinacol borane in acetonitrile at t_0 (bottom), 12 h (middle), and 24 h (top).

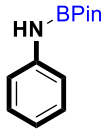
D. General Procedures for Formation of Dehydrocoupling Products

Protocol 1: Under an argon atmosphere, CD_3CN (if amine/alcohol/thiol is solid at RT to achieve 3 M solution), and the amine (0.8 mmol) were added to a 1 dram vial equipped with a magnetic stir bar. Then, pinacol borane (0.116 mL, 0.8 mmol) was added to the reaction mixture and the reaction was left stirring at room temperature until the reaction was complete. Evaporation of the volatiles under vacuum afforded the corresponding product.

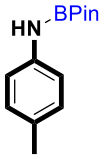
Protocol 2: Under an argon atmosphere, C_6D_6 (0.5 mL) and 9-BBN (97.6 mg, 0.4 mmol) were added to a 1 dram vial equipped with a magnetic stir bar. Then, the amine or alcohol (0.8 mmol) was added to the reaction mixture, and the reaction was left stirring at room temperature until the reaction was complete. Evaporation of the volatiles under vacuum afforded the corresponding product.

Protocol 3: Under an argon atmosphere, CD_3CN (to achieve 3 M solution), the aniline or phenol (0.8 mmol), pinacol borane (0.8 mmol), and 1 mol % Et_3N were added to a J-Young NMR tube. The reaction was sealed and heated to 120°C until the reaction was complete. Evaporation of the volatiles under vacuum afforded the corresponding product.

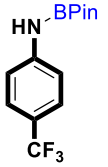
E. Compounds 1a-1s



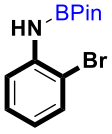
1a: **Protocol 1.** White solid (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.34 (s, 12H), 4.67 (s, br, 1H), 6.88 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.22 (d, J = 7.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.7, 82.9, 117.7, 120.2, 129.1, 143.4 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.9 ppm. GCMS (m/z : Calc : 219.1; Exp : 219.2).



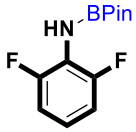
1b: Protocol 1. White solid (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.36 (s, 12H), 2.34 (s, 3H), 4.67 (s, br, 1H), 7.05 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 20.5, 24.6, 82.7, 117.6, 129.1, 129.5, 140.8 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.8 ppm. GCMS (m/z : Calc : 233.2; Exp : 233.2).



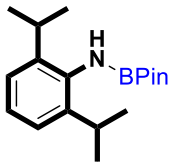
1c: **Protocol 1.** Colorless oil (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.32 (s, 12H), 4.85 (s, br, 1H), 7.15 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.7, 83.4, 114.3, 117.4, 122.3, 126.4, 146.8 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 24.0 ppm. ^{19}F NMR ($CDCl_3$, 283 MHz) δ = -61.5 ppm. GCMS (m/z : Calc : 287.1; Exp : 287.1).



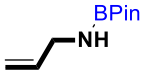
1d: **Protocol 1.** White solid (92% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.37 (s, 12H), 5.37 (s, br, 1H), 6.75 (m, 1H), 7.23 (m, 1H), 7.48 (dt, br, J = 1.4 Hz, 7.9 Hz, 1H), 7.71 (dt, br, J = 1.5 Hz, 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz)) δ = 24.8, 83.2, 112.5, 118.7, 121.1, 128.4, 132.3, 141.4 ppm. ^{11}B NMR ($CDCl_3$, 160 MHz) δ = 23.2 ppm. ESI-MS (M+K) (m/z : Calc : 336.0; Exp : 336.2).



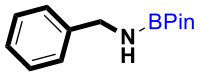
1e: **Protocol 1.** Colorless oil (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.26 (s, 12H), 4.35 (s, 1H), 6.80-6.82 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.4, 83.2, 111.3 (m), 120.0 (t, J_{C-F} = 15.9 Hz), 121.9 (t, J_{C-F} = 9.52 Hz), 156.0 (dd, J_{C-F} = 5.6 Hz, 246.4 Hz) ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.9 ppm. ^{19}F NMR ($CDCl_3$, 283 MHz) δ = -122.9 ppm. GCMS (m/z : Calc : 255.1; Exp : 255.2).



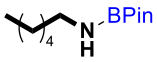
1f: **Protocol 3.** White solid (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.23 (d, J = 6.8 Hz, 12H), 1.27 (s, 12H), 3.39 (m, 2H), 3.78 (s, br, 1H), 7.14 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 23.7, 24.8, 28.4, 82.7, 123.1, 125.7, 135.5, 145.3 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 24.2 ppm. ESI-MS (m/z : Calc : 304.3; Exp : 304.3).



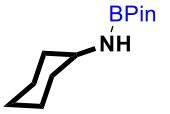
1g: Protocol 1. Deliquescent solid (96% yield). ^{1}H NMR (CD_3CN, 300 MHz) δ = 1.17 (s,12H), 2.71 (s, br, 1H), 3.42 (m, br, 2H), 4.98 (dd, J = 1.7 Hz, 10.4 Hz, 1H), 5.10 (dd, J = 1.9 Hz, 17.2 Hz, 1H), 5.87 (m, 1H) ppm. ^{13}C NMR (CD_3CN, 75 MHz)) δ = 24.9, 44.1, 82.7, 113.2, 140.5 ppm. ^{11}B NMR (CD_3CN, 96 MHz) δ = 24.6 ppm. ESI-MS (m/z : Calc : 184.1; Exp : 184.1).



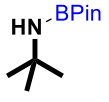
1h: Protocol 1. Deliquescent solid (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.22 (s, 12H), 2.52 (s, br, 1H), 4.08 (d, J = 7.9 Hz, 2H), 7.25 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.6, 45.2, 82.2, 116.5, 126.7, 128.3, 142.3 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 24.5 ppm. GCMS (m/z : Calc : 233.2; Exp : 233.2).



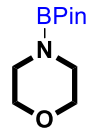
1i: **Protocol 1.** Deliquescent solid (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.85 (t, J = 7.3 Hz, 3H), 1.19 (s, 12H), 1.22-1.41 (m, 8H) 2.13 (s, br, 1H), 2.84 (q, J = 6.6 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 14.1, 22.7, 24.6, 26.3, 31.7, 33.6, 41.1, 81.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 24.3 ppm. GCMS (m/z : Calc : 227.2; Exp : 227.2).



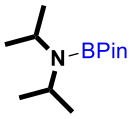
1j: **Protocol 1.** White Solid (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.85-1.05 (m, 4H), 1.12 (s, 12H), 1.30-1.64 (m, 4H), 1.74 (dd (br), J = 3.0 Hz, 12.6 Hz, 2H), 2.09 (s, br, 1H), 2.81 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.6, 25.3, 25.8, 37.2, 49.5, 81.8 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 24.6 ppm. GCMS (m/z : Calc : 225.2; Exp : 225.2).



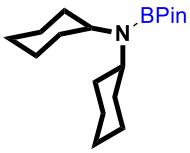
1k: **Protocol 1.** Deliquescent solid (95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.15 (s, 9H), 1.17 (s, 12H), 2.37 (s, br, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.6, 32.2, 47.8, 81.4 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.7 ppm. ESI-MS (m/z : Calc : 200.2; Exp : 200.2).



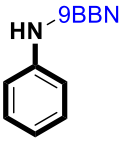
1l: **Protocol 1.** White solid (93% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.20 (s, 12H), 3.06 (t, J = 4.3 Hz, 4H), 3.55 (t, J = 4.6 Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.7, 44.6, 68.5, 82.3 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.4 ppm. GC/ESI-MS could not be obtained.



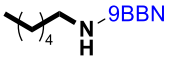
1m: **Protocol 1.** White solid (90% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ =1.09 (d, J = x.x Hz, 12H), 1.18 (s, 12H), 3.34 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz)) δ = 23.3, 24.6, 44.6, 81.0 ppm. ^{11}B NMR ($CDCl_3$, 160 MHz) δ = 24.2 ppm. GCMS (m/z : Calc : 227.2; Exp : 227.1).



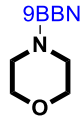
1n: Protocol 1. White solid (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.07 (m, 2H), 1.16 (s, 12H), 1.26 (m, 5H), 1.52 (m, 9H), 1.70 (m, 4H), 2.80 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 24.6, 25.9, 26.7, 33.8, 54.1, 80.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 23.9 ppm. GCMS (m/z : Calc : 307.3; Exp : 307.4).



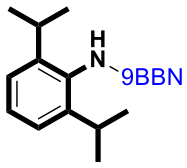
1o[Error! Bookmark not defined.]: **Protocol 2.** Deliquescent solid (97% yield). ^{1}H MR ($CDCl_3$, 300 MHz) δ = 1.07 (s, br, 2H), 1.40 (m, 4H), 1.79 (m, 8H), 6.05 (s, br, 1H), 7.00 (d, J = 8.1 Hz, 3H), 7.24 (t, J = 8.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.5, 33.0, 33.8, 122.4, 122.9, 129.0, 143.7 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 51.2 ppm. GC/ESI-MS could not be obtained.



1p: **Protocol 2.** Deliquescent solid (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.91 (s, br, 3H), 1.31 (s, 8H), 1.61-1.90 (m, 14H), 3.03 (q, J = 6.8 Hz, 2H), 3.92 (s, br, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 14.1, 22.8, 23.8, 26.5, 31.8, 33.1, 33.7, 33.9, 42.6 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 48.5 ppm. GC/ESI-MS could not be obtained.

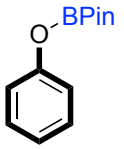


1q: Protocol 2. White solid (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.20-1.99 (m, br, 14H), 3.32 (t, J = 4.4 Hz, 2H), 3.60 (t, J = 4.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 23.5, 33.4, 47.6, 69.5 ppm, C[B] could not be detected. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 47.3 ppm. GC/ESI-MS (m/z : Calc : 208.2; Exp : 208.1).

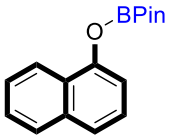


1r: **Protocol 2.** Deliquescent solid (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.29 (d, J = 6.6 Hz, 12H), 1.50 (m, br, 2H), 1.74 (m, 4H) 1.97 (m, br, 8H), 3.50 (m, 2H), 5.31 (s, br, 1H), 7.24 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz)) δ = 22.6, 23.5, 28.0, 33.0, 33.8, 123.0, 125.9, 137.2, 145.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 50.5 ppm. GC/ESI-MS could not be obtained.

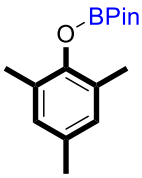
F. Compounds 2a-w



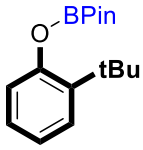
2a: Protocol 1. White solid 0.169 g (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.35 (s, 12H), 7.05-7.13 (m, 3H), 7.28-7.33 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 25.3, 84.5, 116.4, 122.1, 133.0, 153.3 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.8 ppm. GCMS (m/z : Calc : 220.13 ; Exp : 220.1).



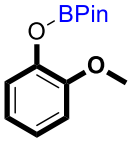
2b: Protocol 1. White solid 0.211 g (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.38 (s, 12 H), 7.31 (d, *J* = 9 Hz, 1H), 7.40-7.42 (m, 1H), 7.45-7.52 (m, 2H), 7.61 (d, *J* = 9 Hz, 1H), 7.85 (m, 1H), 8.22-8.23 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.8, 83.8, 114.1, 122.2, 123.2, 125.7, 125.9, 126.4, 126.9, 127.8, 134.8, 149.4 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.2 ppm. GCMS (m/z : Calc : 270.14 ; Exp : 270.2).



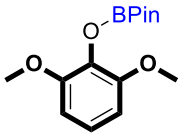
2c: Protocol 1. Colorless oil 0.203 g (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.40 (s, 12H), 2.31 (s, 6H), 2.34 (s, 3H), 6.92 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.4, 20.7, 24.5, 83.4, 127.9, 129.0, 132.4, 148.4 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.6 ppm. GCMS (m/z : Calc : 262.2 ; Exp : 262.2).



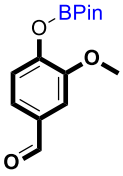
2d: Protocol 1. Colorless oil 0.214 g (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39 (s, 12H), 1.48 (s, 9H), 7.08-7.11 (m, 2H), 7.19-7.22 (m, 1H), 7.38 (d, *J* = 9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.7, 29.7, 30.1, 34.7, 83.6, 121.5, 123.3, 126.8, 127.0, 139.8, 152.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.9 ppm. GCMS (m/z : Calc : 276.2 ; Exp : 276.2).



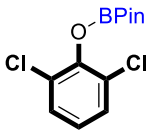
2e: Protocol 1. Colorless oil 10.98 g (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.34 (s, 12H), 3.85 (s, 3H), 6.87-6.94 (m, 2H), 7.03-7.11 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.5, 55.5, 83.4, 112.1, 120.4, 120.8, 123.8, 143.0, 150.1 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.0 ppm. GCMS (m/z : Calc : 250.1 ; Exp : 250.1).



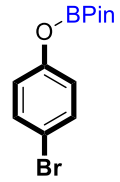
2f: Protocol 1. Colorless oil 0.221 g (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.31 (s, 12H), 3.84 (s, 6H), 6.59 (d, *J* = 6 Hz, 2H), 6.96 (t, *J* = 9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.6, 56.2, 83.5, 105.3, 122.9, 151.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.1 ppm. GCMS (m/z : Calc : 280.1 ; Exp : 280.1).



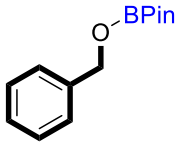
2g: Protocol 1. Colorless oil 0.211 g (95% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ = 1.01 (s, 12H), 3.29 (s, 3H), 6.41 (d, J = 9Hz, 1H), 7.29 (d, J= 0Hz, 1H), 7.47 (s, 1H), 9.49 (s, 1H) ppm. ^{13}C NMR (C_6D_6, 125 MHz) δ = 24.6, 55.6, 83.8, 111.7, 121.0, 127.3, 130.5, 144.0, 155.7, 190.7 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.0 ppm. GCMS (m/z : Calc : 278.1 ; Exp : 278.1).



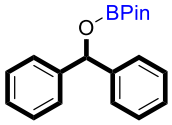
2h: Protocol 1. White solid 0.228 g (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.33 (s, 12H), 6.99 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 9 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.6, 84.5, 124.6, 17.3, 128.6, 146.8 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.6 ppm. GCMS (m/z : Calc : 289.0 ; Exp : 289.0).



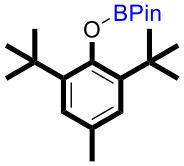
2i: Protocol 1. White solid 0.234 g (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.34 (s, 12H), 7.00 (d, *J* = 9 Hz, 2H), 7.39 (d, *J* = 6 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.7, 83.9, 115.8, 121.5, 132.4, 152.7 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.7 ppm. GCMS (m/z : Calc : 299.0 ; Exp : 299.0).



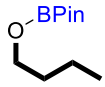
2j: Protocol 1. Colorless oil 0.178 g (95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.31 (s, 12H), 4.99 (s, 2H), 7.40 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.7, 66.7, 83.0, 126.8, 127.4, 128.3, 139.3 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.5 ppm. GCMS (m/z : Calc : 234.1 ; Exp : 234.1).



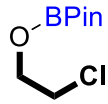
2k: Protocol 1. White solid 0.243 g (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.28 (s, 12H), 6.29 (s, 1H), 7.30-7.49 (m, 10H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.6, 83.1, 126.6, 127.4, 128.3, 143.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.5 ppm. GCMS (m/z : Calc : 310.2 ; Exp : 310.2).



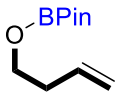
2l: Protocol 3. White solid 0.270 g (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.29 (s, 12H), 1.42 (s, 18H), 2.29 (s, 3H), 7.04 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.6, 25.4, 31.8, 35.3, 83.7, 126.5, 131.7, 140.7, 149.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.4 ppm. GCMS (m/z : Calc : 346.3 ; Exp : 346.3).



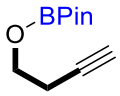
2m: Protocol 1. Colorless oil 0.150 g (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.87 (t, *J* = 7.5 Hz , 3H), 1.21 (s, 12H), 1.29-1.34 (m, 2H), 1.37-1.53 (m, 2H), 3.80 (t, *J* = 6 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 13.7, 18.8, 24.6, 33.6, 64.6, 82.6 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.0 ppm. GCMS (m/z : Calc : 200.2 ; Exp : 200.2).



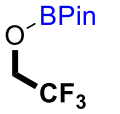
2n: Protocol 1. Colorless oil 0.163 g (99% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.24 (s, 12H), 3.58 (t, *J* = 4.5 Hz, 2H), 4.05 (t, *J* = 4.5 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = ppm. GCMS (m/z : Calc : 206.1 ; Exp : 206.1)



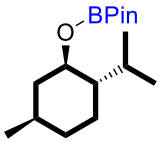
2o: Protocol 1. Colorless oil 0.155 g (98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.22 (s, 12H), 2.29-2.31 (m, 2H), 3.86 (m, 2H), 4.99-5.09 (m, 2H), 5.77-5.79 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.6, 36.0, 64.1, 82.7, 116.9, 134.7 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.0 ppm. GCMS (m/z : 182.1 Calc : ; Exp : 182.1).



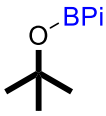
2p: Protocol 1. Colorless oil 0.150 g (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.22, (s, 12H), 1.94 (s, 1H), 2.42 (m, 2H), 3.91 (t, J = 7.5 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.6, 24.6, 63.0, 69.7, 80.6, 83.0 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.1 ppm. GCMS (m/z : Calc : 196.1 ; Exp : 196.1).



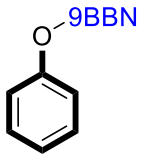
2q: Protocol 1. Colorless oil 0.173 g (95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.28 (s, 12H), 4.18 (q, $J_{H\text{-}F}$ = 8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.6, 62.8 (q, $J_{C\text{-}F}$ = 35 Hz), 84.0, 123.8 (q, $J_{C\text{-}F}$ = 272.5 Hz) ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.4 ppm. ^{19}F ($CDCl_3$, 96 MHz) δ = 76.57 ppm. GCMS (m/z : Calc : 226.1 ; Exp : 226.1).



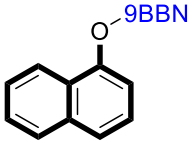
2r: Protocol 1. White solid 0.216 g (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.75-1.08 (m, 12H), 1.22 (s, 12H), 1.43-1.64 (1.88-2.03 (m, 2H), 3.80 (q, J = 5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 1.61, 21.1, 22.3, 23.0, 24.5, 24.7, 25.9, 31.5, 34.6, 43.8, 48.9, 74.3, 82.4 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 22.0 ppm. GCMS (m/z : Calc : 282.2 ; Exp : 282.2).



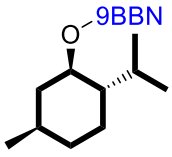
2s: Protocol 1. Colorless oil 0.153 g (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.17 (s, 12H), 1.28 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 24.5, 29.9, 73.8, 81.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 21.2 ppm. GCMS (m/z : Calc : 200.1 ; Exp : 200.1).



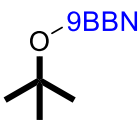
2t: Protocol 1. Colorless oil 0.152 g (96% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.34 (m, 2H), 1.48-1.52 (m, 2H), 1.94 (m, br, 10H), 7.01 (d, J = 6 Hz, 2H), 7.17 (t, J = 6 Hz, 1H), 7.35 (t, J = 9 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.3, 24.6, 33.6, 120.4, 123.6, 129.5, 155.7 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 58.7 ppm. GCMS (m/z : Calc : 198.2 ; Exp : 198.2).



2u: Protocol 1. White solid 0.186 g (94% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.36 (m, br, 2H), 1.54 (m, br, 2H), 1.97 (m, br, 12H), 7.06 (d, br, J = 6 Hz, 1H), 7.48-7.69 (m, 4H), 7.93 (d, br, 1H), 8.13 (d, br, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.4, 24.8, 33.8, 115.1, 121.9, 123.6, 125.9, 126.0, 126.5, 127.1, 128.0, 134.9, 151.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 59.4 ppm. GCMS (m/z : Calc : 248.2 ; Exp : 248.2).

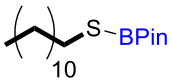


2v: Protocol 1. White solid 0.201 g (97% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.76-1.11 (m, 11H), 1.15-1.43 (m, 7H), 1.69-2.08 (m, 14H), 3.96 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 16.1, 21.0, 22.3, 23.4, 24.5, 25.9, 31.7, 33.3, 33.6, 34.6, 44.9, 48.6, 75.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 55.9 ppm. GCMS (m/z : Calc : 248.2 ; Exp : 248.2).

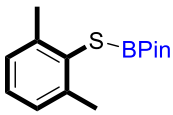


2w: Protocol 1. Colorless oil 0.134 g (95% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.32 (m, br, 3H), 1.42 (s, 9H), 1.82-1.88 (m, br, 11H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.2, 26.4, 31.2, 33.3, 74.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 55.6 ppm. GCMS (m/z : Calc : 178.1 ; Exp : 178.1).

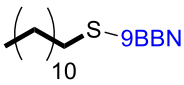
G. Compounds 3a-d



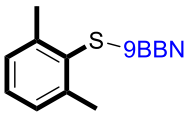
3a: Protocol 3. Colorless oil (95% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ = 0.93 (t, J = 5 Hz, 3H), 1.02 (s, 12H), 1.17-1.39 (m, 19H), 1.41 (quint, J = 5 Hz, 19H), 2.22 (q, 5 Hz, 2 H) ppm. ^{13}C NMR (C_6D_6, 125 MHz) δ = 14.9, 23.7, 25.5, 29.3, 30.1, 30.4, 30.6, 30.7, 35.0, 83.7. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 33.5 ppm. GCMS (m/z : Calc : 328.3 ; Exp : 328.3).



3b: Protocol 3. Colorless oil (95% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ = 1.32 (s, 12 H), 2.53 (s, 6H), 7.16 (m, 3H) ppm. ^{13}C NMR (C_6D_6, 125 MHz)δ = 22.9, 24.5, 85.1, 127.5, 127.9, 142.2 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 32.4 ppm. GCMS (m/z : Calc : 264.1 ; Exp : 264.1).



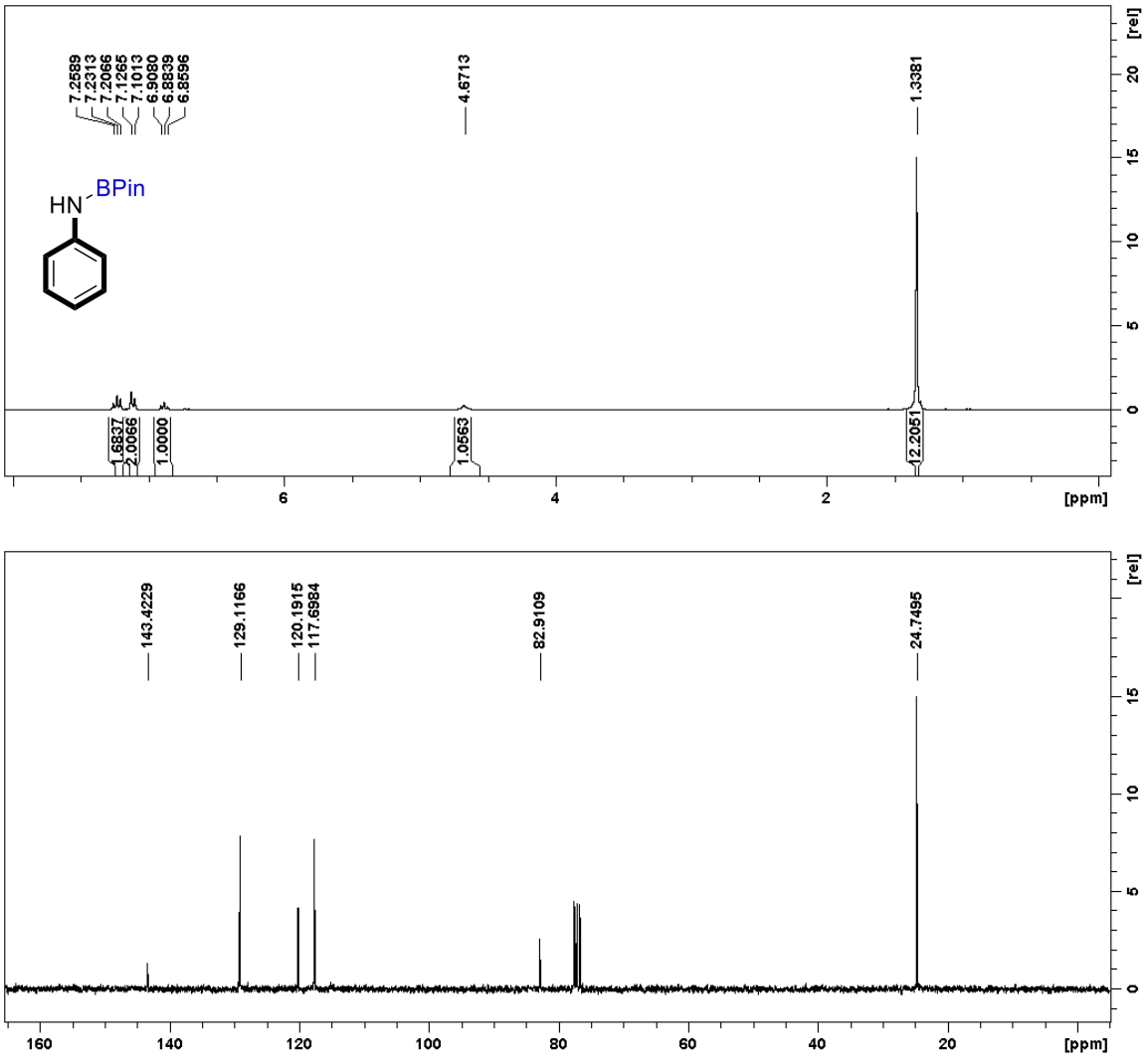
3c: Protocol 3. Colorless oil (95% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ = 0.88 (bt, J = 5 Hz, 3H), 1.26 (s, 16H), 1.38 (m, 4H), 1.58 (m, 3H), 1.74 (m, 4H), 1.80-1.95 (m, 7H) ppm. ^{13}C NMR (C_6D_6, 125 MHz) δ = 14.3, 22.9, 23.3, 26.6, 28.7, 28.9, 29.4, 29.6, 29.7, 29.8, 29.8, 29.9, 32.1, 32.6, 33.5, 33.9 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 77.7 ppm. GCMS (m/z : Calc : 322.3 ; Exp : 322.3).



3d: Protocol 3. White solid (95% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.39 (m, 2H), 1.62 (m, 2H), 1.70 (m, 2H) 1.89-1.94 (m, 8H), 2.41 (s, 6H), 7.13 (s, 3H) ppm. ^{13}C NMR (C_6D_6, 125 MHz) δ = 22.9, 23.1, 27.4, 29.7, 33.5, 34.0, 127.5, 128.0, 132.4, 141.1 ppm. ^{11}B NMR ($CDCl_3$, 96 MHz) δ = 77.7 ppm. GCMS (m/z : Calc : 258.2 ; Exp : 258.2).

H. Spectra

1a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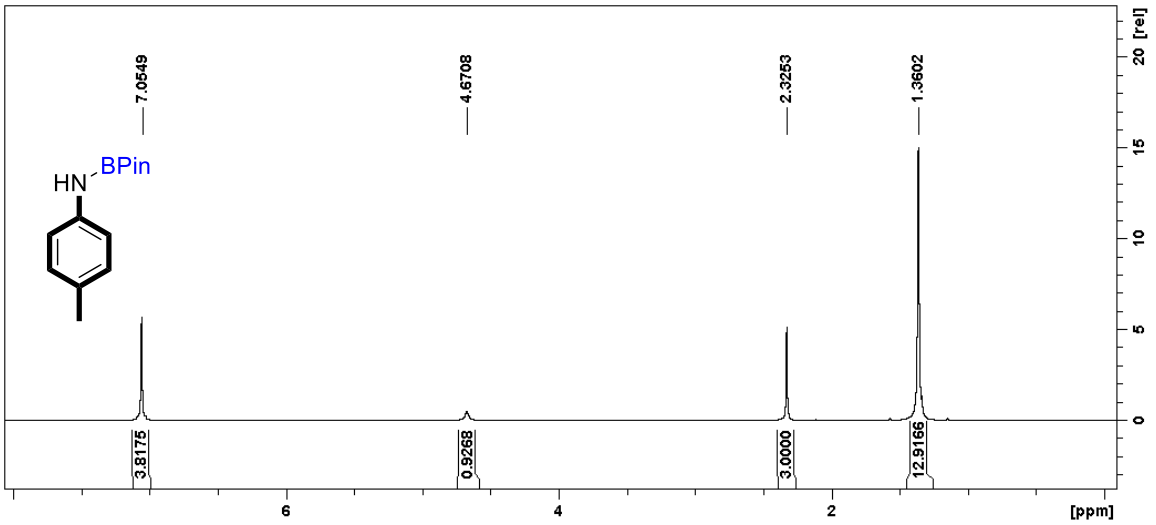
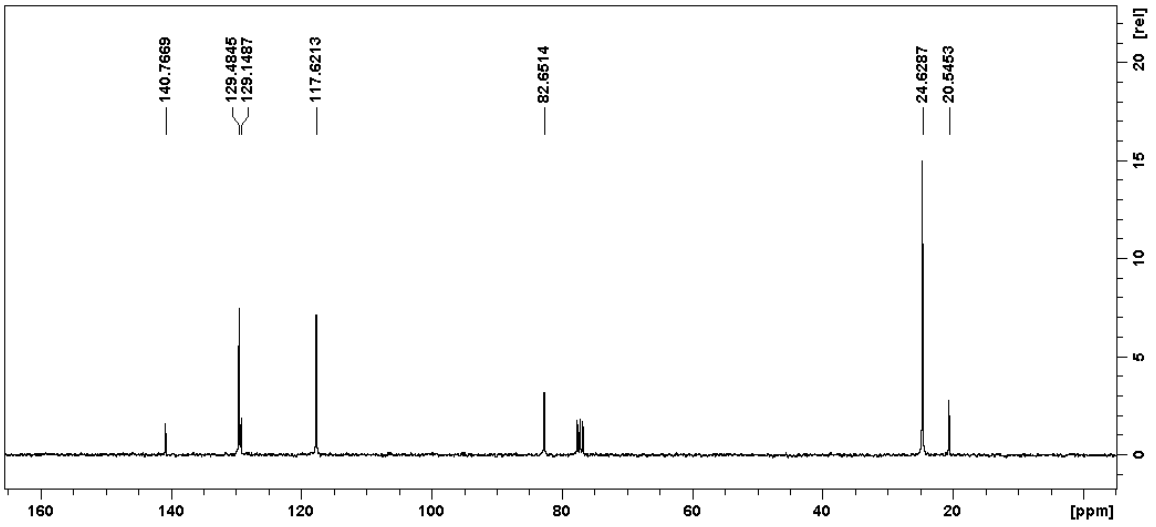
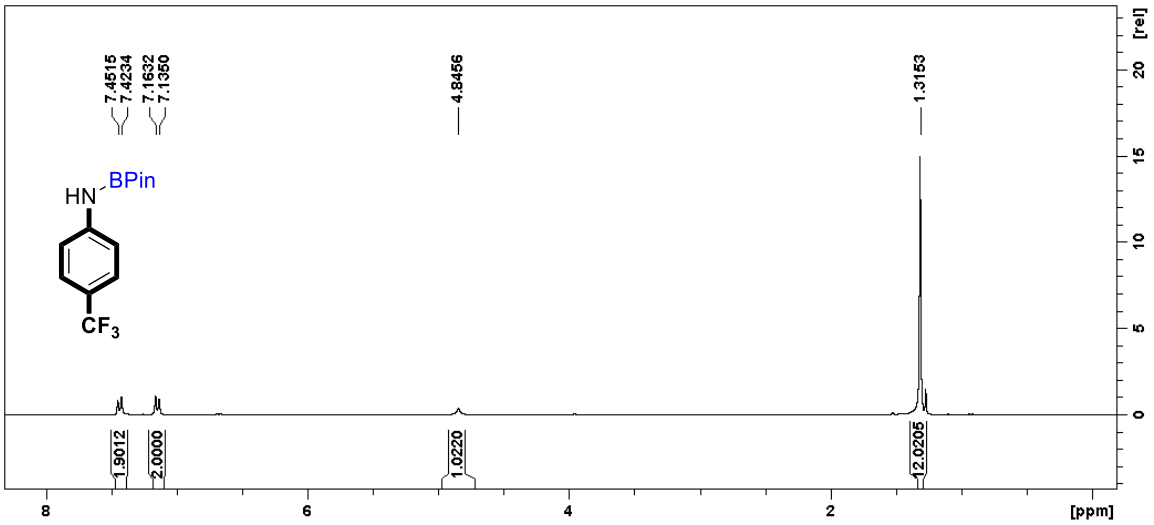
7.2313
7.2066
7.1265
7.1013
6.9080
6.8839
6.8596
4.6713
1.3381
HN
BPin
1.6837
2.0066
1.0000
1.0563
12.2051
[rel]
[ppm]
143.4229
129.1166
120.1915
117.6984
82.9109
24.7495

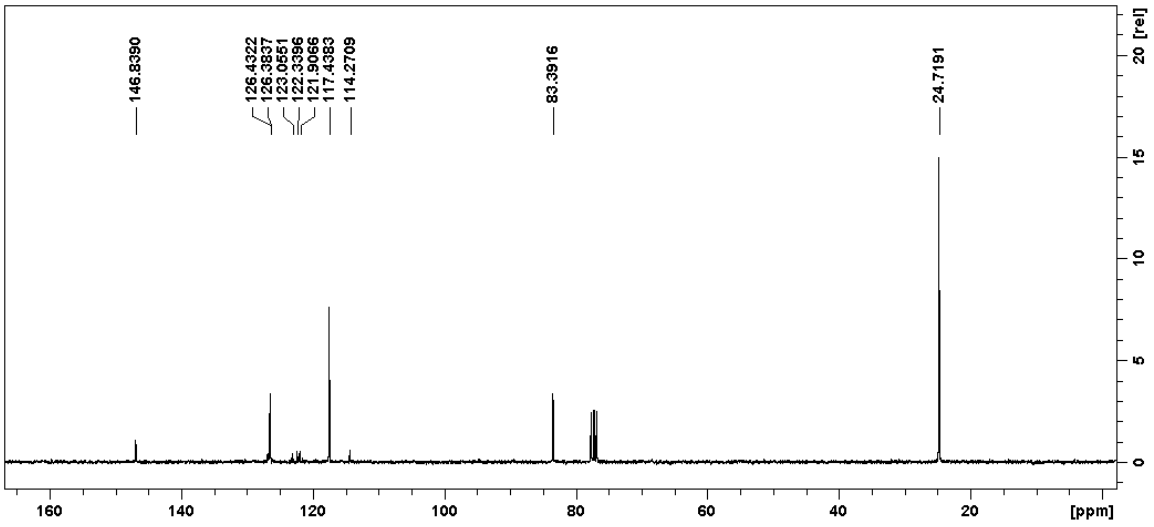
1b


7.0549
4.6708
2.3253
1.3602
HN
BPin
3.8175
0.9268
3.0000
12.9166
6
4
2
[ppm]
[rel]

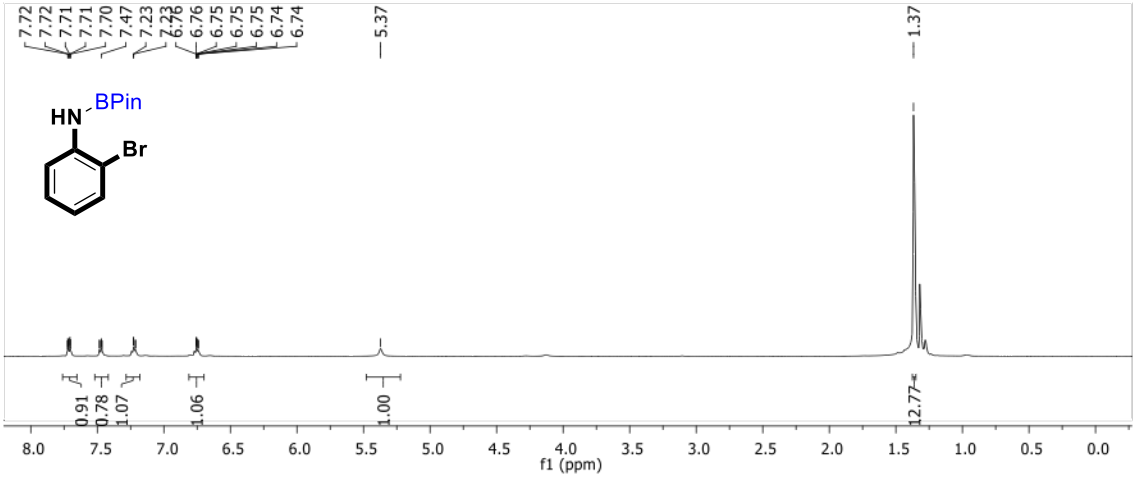

140.7669
129.4845
129.1487
117.6213
82.6514
24.6287
20.5453
160
140
120
100
80
60
40
20
[ppm]
[rel]

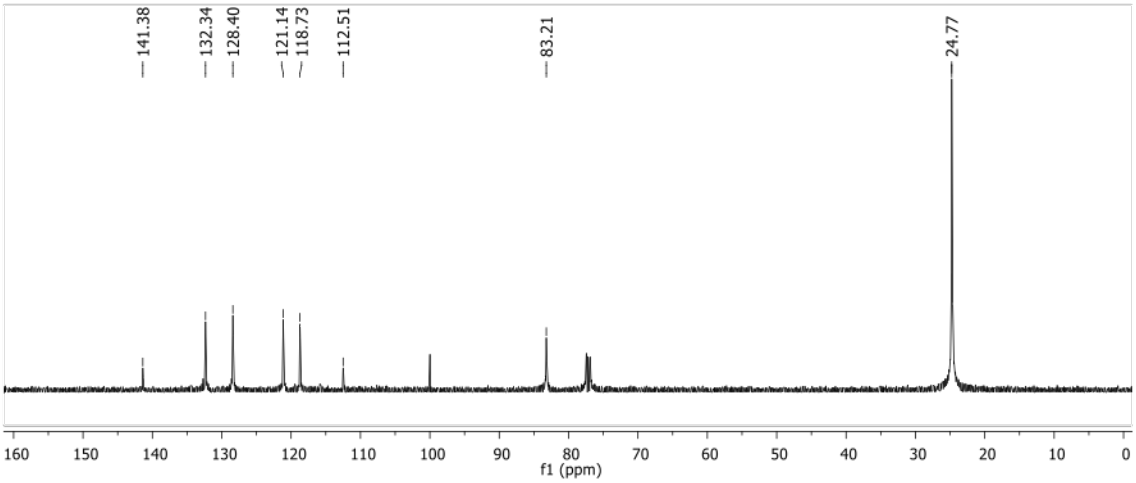
1c


7.4515
7.4234
7.1632
7.1350
4.8456
1.3153
HN
BPin
CF3
1.9012
2.0000
1.0220
12.0205
[rel]
[ppm]

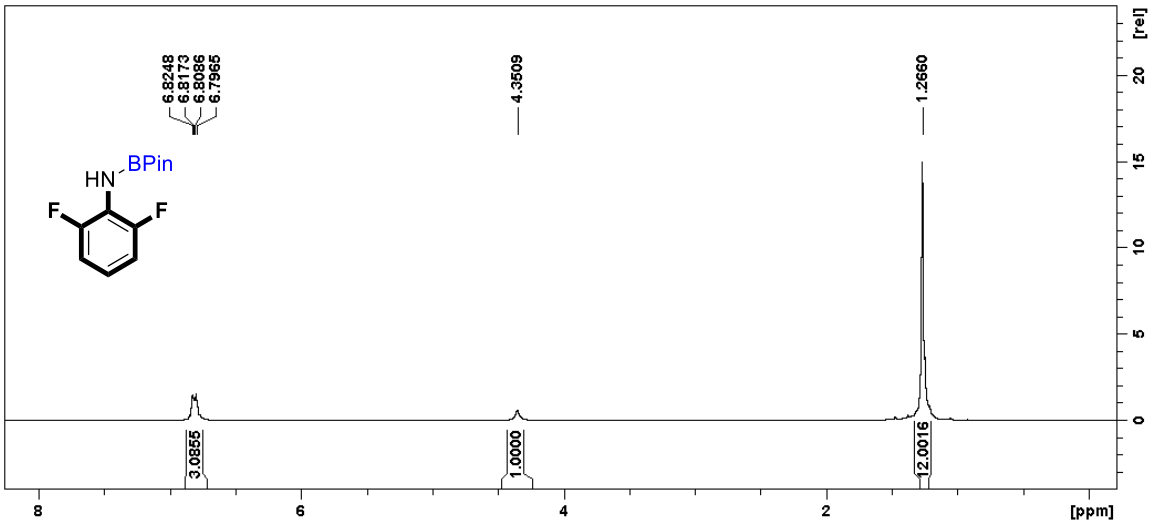

146.8390
126.4322
126.3837
123.0551
122.3396
121.9066
117.4383
114.2709
83.3916
24.7191
[rel]
[ppm]

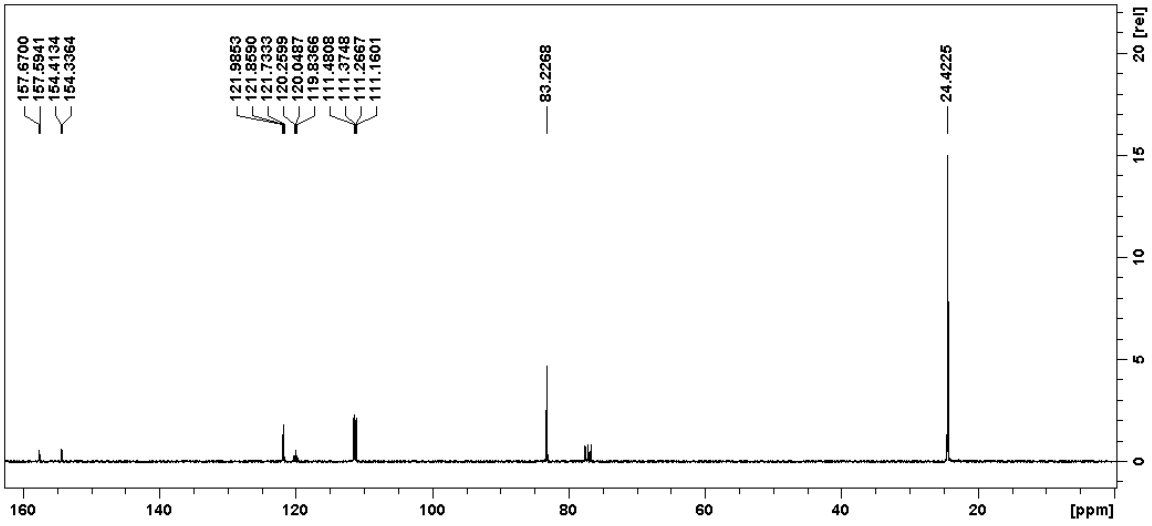
1d


7.72
7.72
7.71
7.71
7.70
7.47
7.23
7.23
6.76
6.76
6.75
6.75
6.75
6.74
6.74
5.37
1.37
HN
BPin
Br
0.91
0.78
1.07
1.06
1.00
12.77
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)

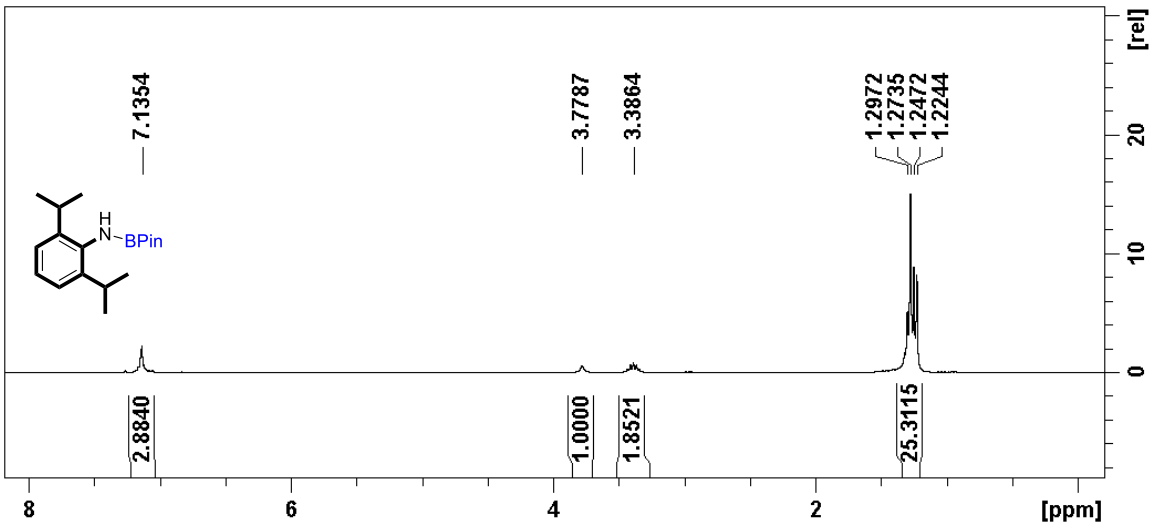

141.38
132.34
128.40
121.14
118.73
112.51
83.21
24.77
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

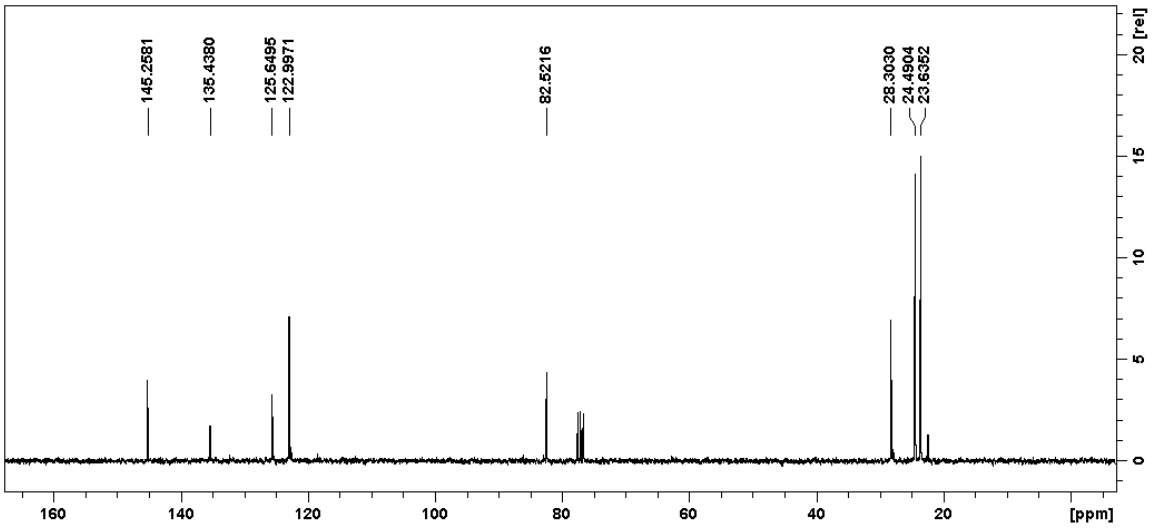
1e


6.8248
6.8173
6.8086
6.7965
4.3509
1.2660
HN
BPin
F
F
3.0855
1.0000
12.0016
[rel]
[ppm]

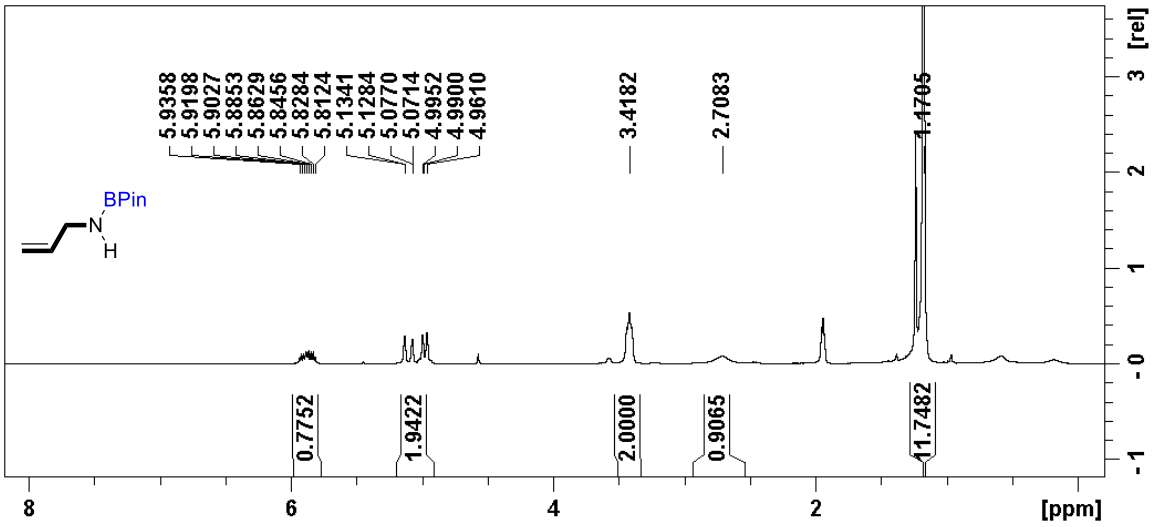

157.6700
157.5941
154.4134
154.3364
121.9853
121.8590
121.7333
120.2599
120.0487
119.8366
111.4808
111.3748
111.2667
111.1601
83.2268
24.4225
[rel]
[ppm]

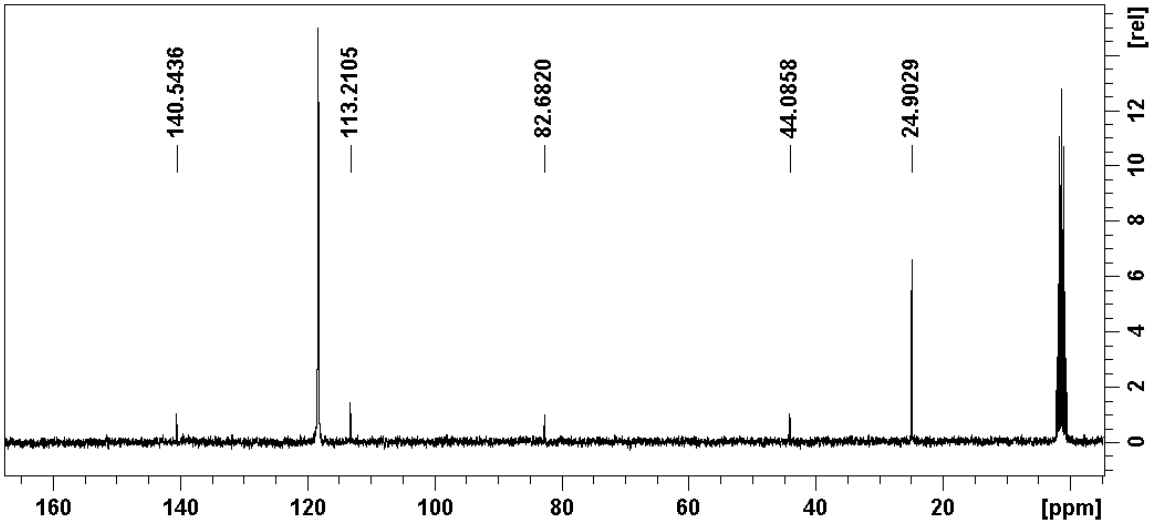
1f


7.1354
3.7787
3.3864
1.2972
1.2735
1.2472
1.2244
H
N
BPin
2.8840
1.0000
1.8521
25.3115
8
6
4
2
[ppm]
[rel]
0
10
20

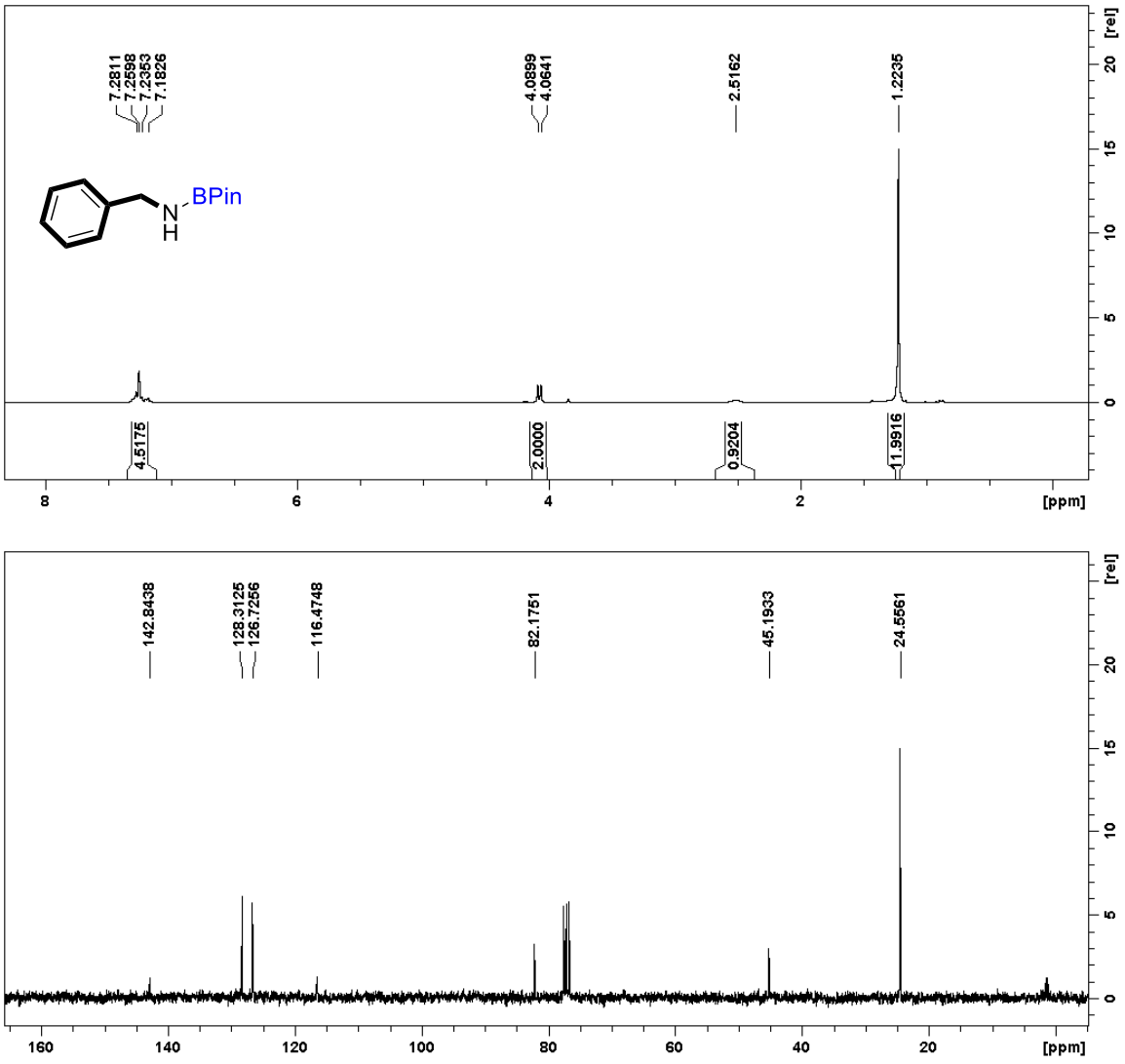

145.2581
135.4380
125.6495
122.9971
82.5216
28.3030
24.4904
23.6352
160
140
120
100
80
60
40
20
[ppm]
0
5
10
15
20 [rel]

1g

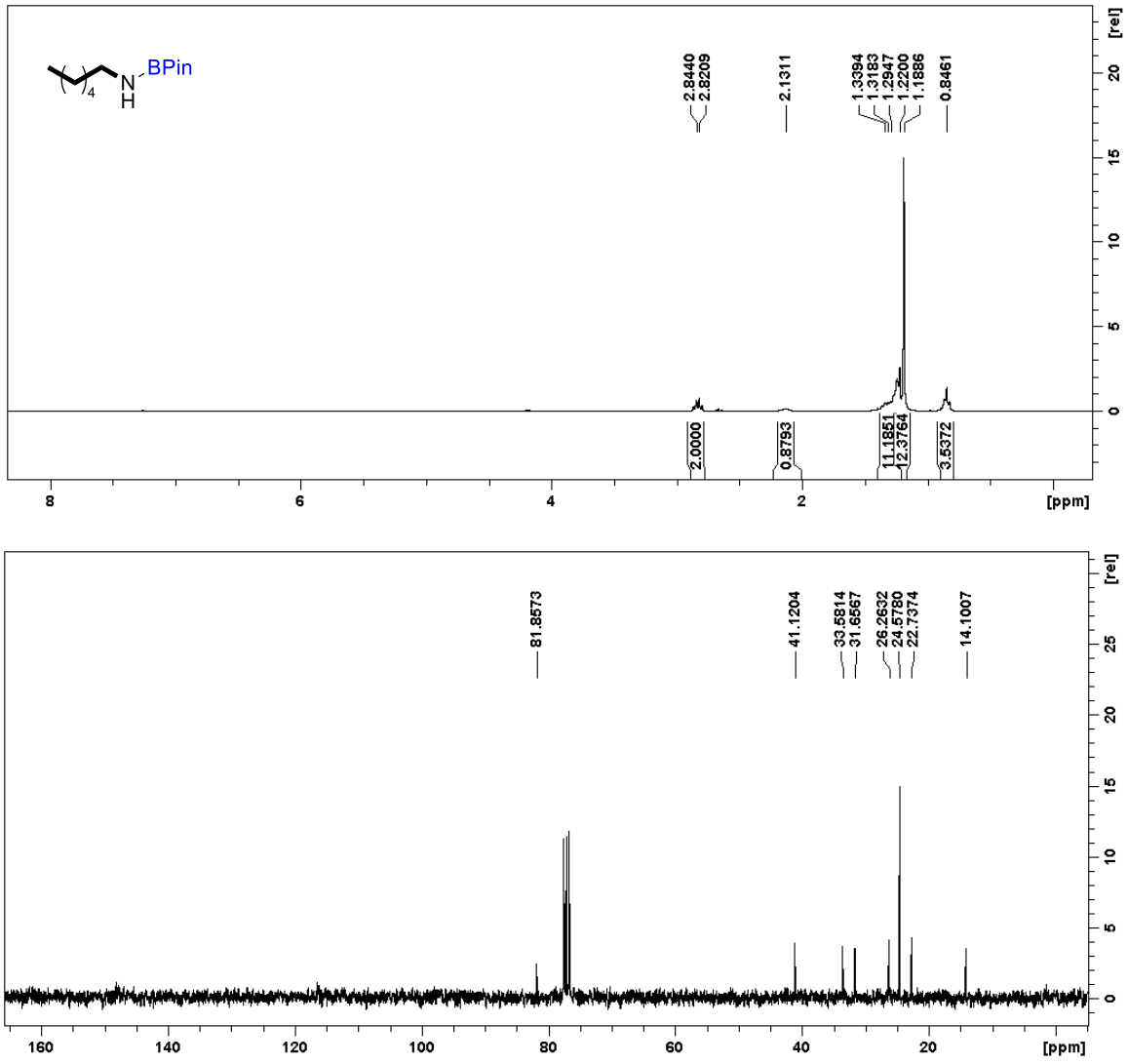

5.9358
5.9198
5.9027
5.8853
5.8629
5.8456
5.8284
5.8124
5.1341
5.1284
5.0770
5.0714
4.9952
4.9900
4.9610
3.4182
2.7083
1.4705
BPin
N
H
0.7752
1.9422
2.0000
0.9065
11.7482
[rel]
[ppm]


140.5436
113.2105
82.6820
44.0858
24.9029
[rel]
[ppm]

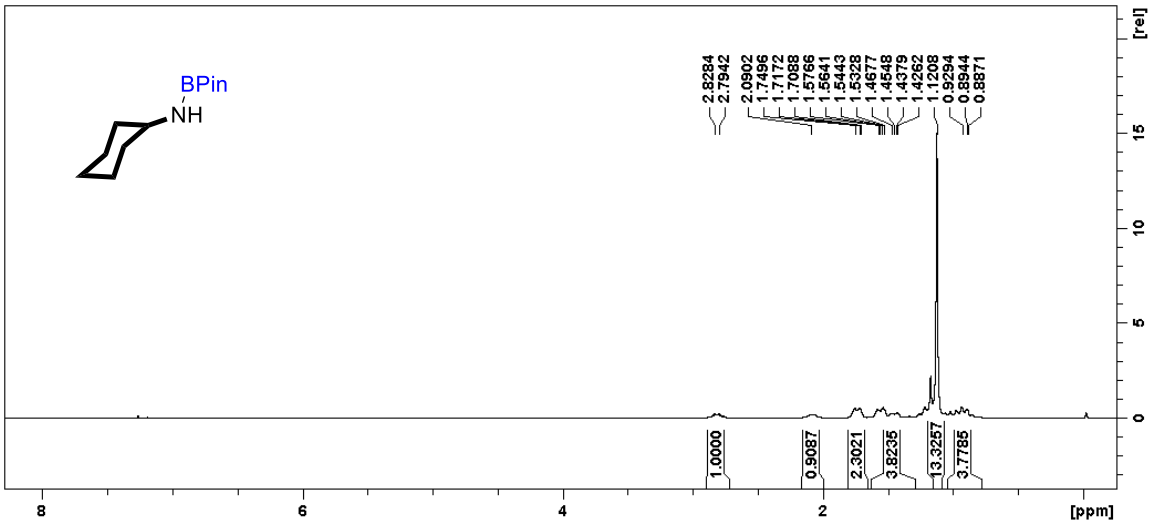
1h

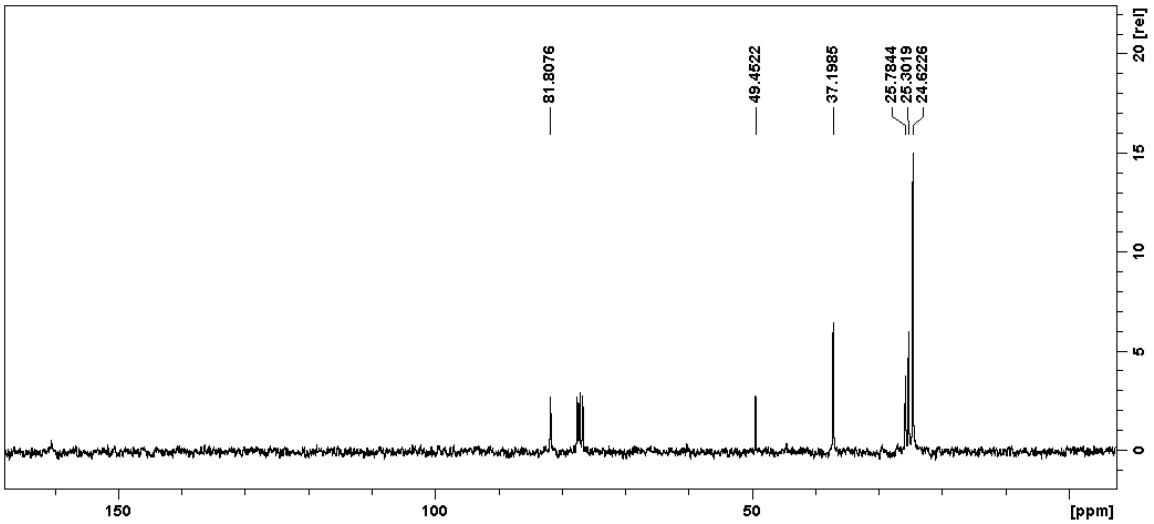

7.2811
7.2598
7.2353
7.1826
4.0899
4.0641
2.5162
1.2235
BPin
N
H
4.5175
2.0000
0.9204
11.9916
8
6
4
2
[ppm]
[rel]
142.8438
128.3125
126.7256
116.4748
82.1751
45.1933
24.5561
160
140
120
100
80
60
40
20
[ppm]
[rel]

1i

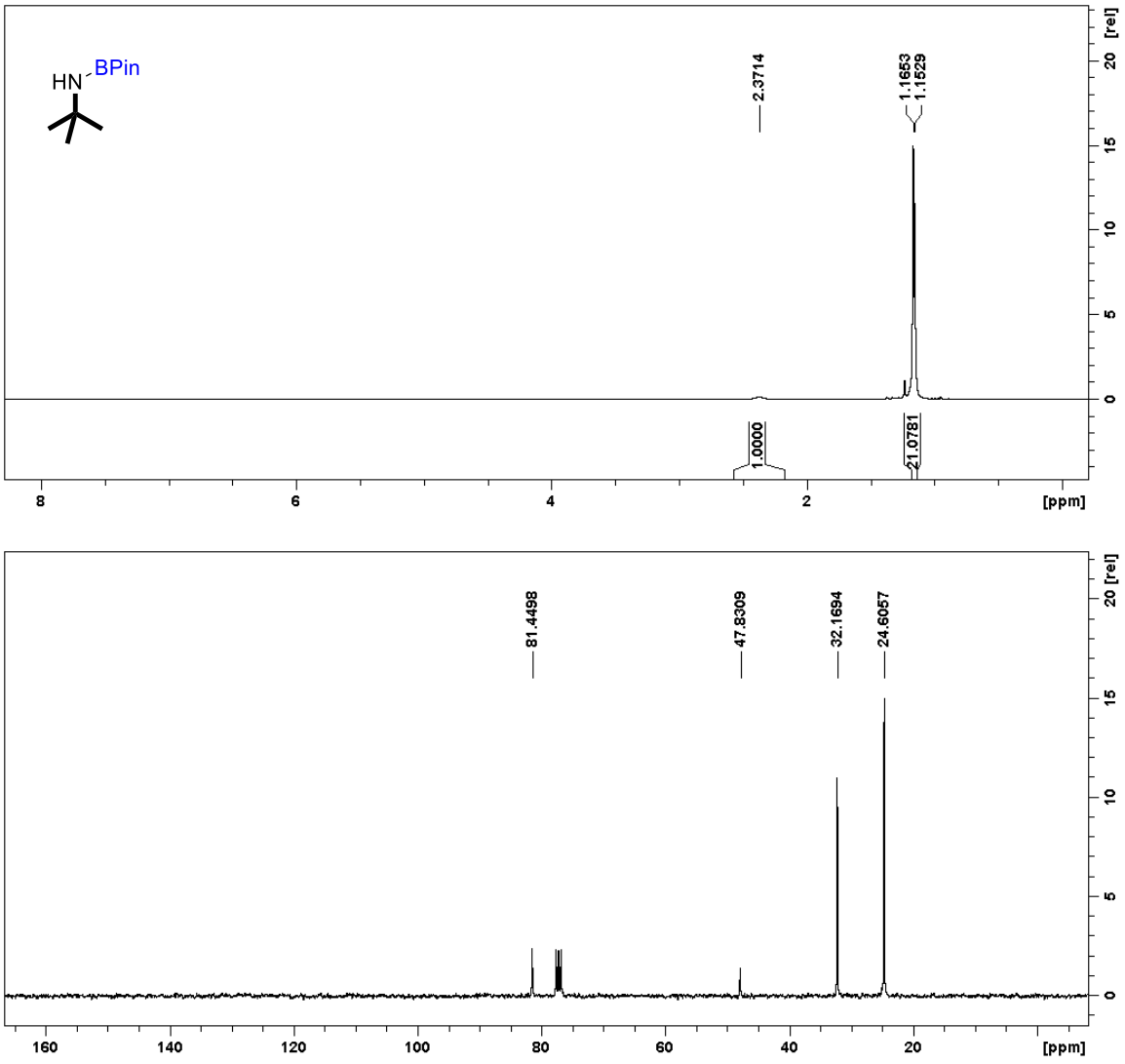

BPin
N
H
4
2.8440
2.8209
2.1311
1.3394
1.3183
1.2947
1.2200
1.1886
0.8461
2.0000
0.8793
11.1851
12.3764
3.5372
[rel]
[ppm]
81.8573
41.1204
33.5814
31.6567
26.2632
24.5780
22.7374
14.1007

1j

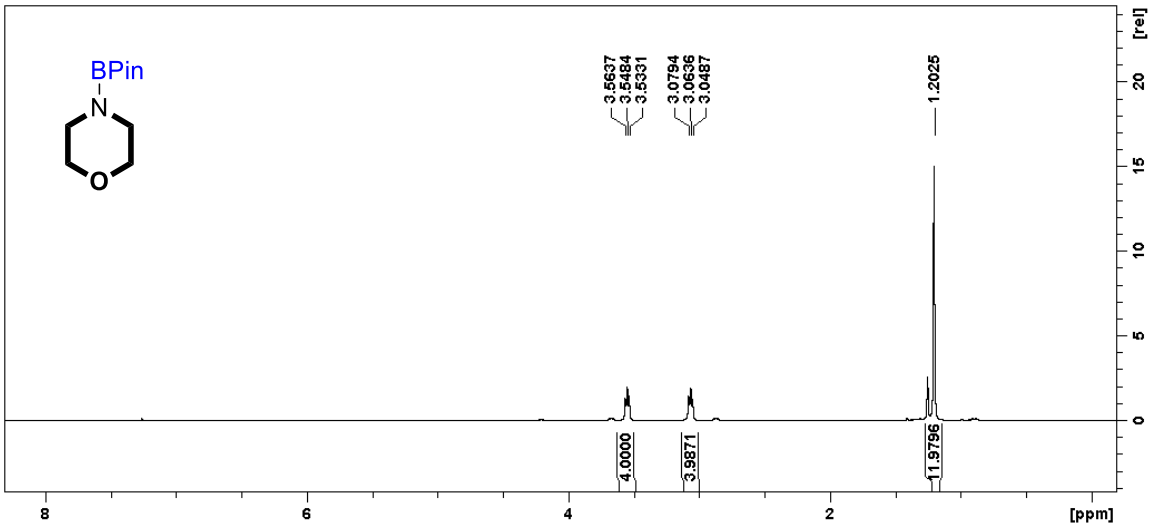

BPin
NH
2.8284
2.7942
2.0902
1.7496
1.7172
1.7088
1.5766
1.5641
1.5443
1.5328
1.4677
1.4548
1.4379
1.4262
1.1208
0.9294
0.8944
0.8871
1.0000
0.9087
2.3021
3.8236
13.3257
3.7785
[rel]
[ppm]

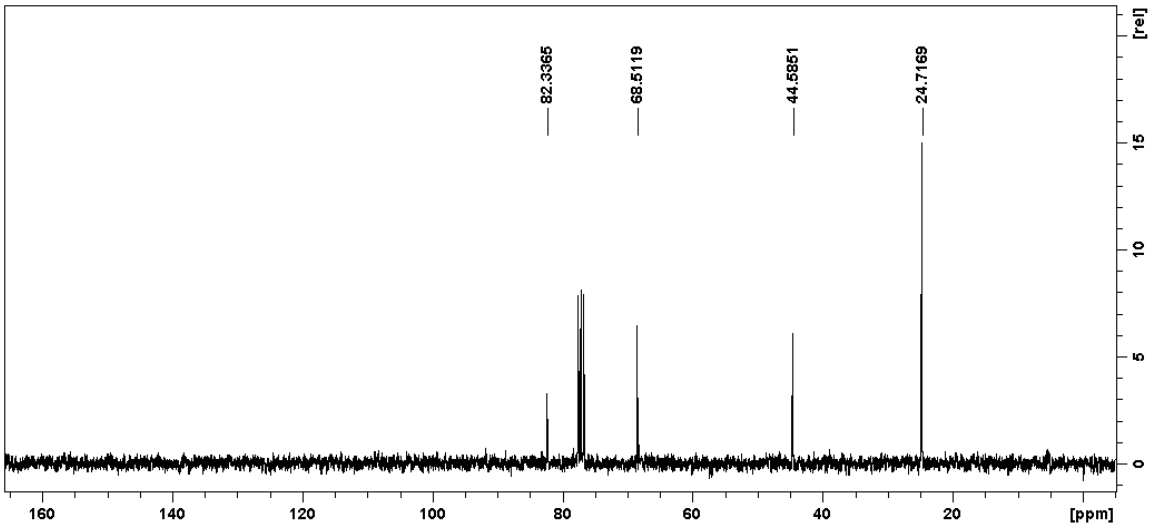

81.8076
49.4522
37.1985
25.7844
25.3019
24.6226
[rel]
[ppm]

1k

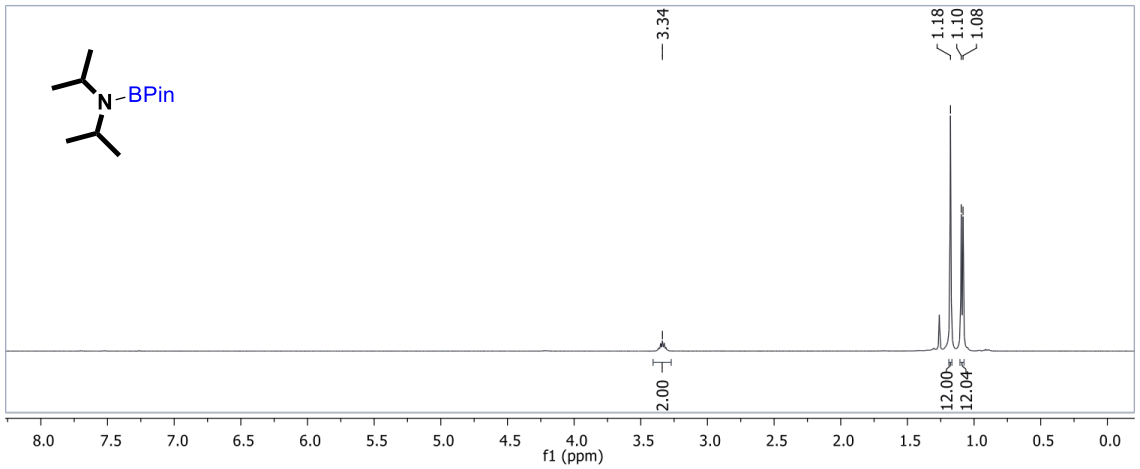

HN
BPin
2.3714
1.1653
1.1529
1.0000
21.0781
[rel]
[ppm]
81.4498
47.8309
32.1694
24.6057

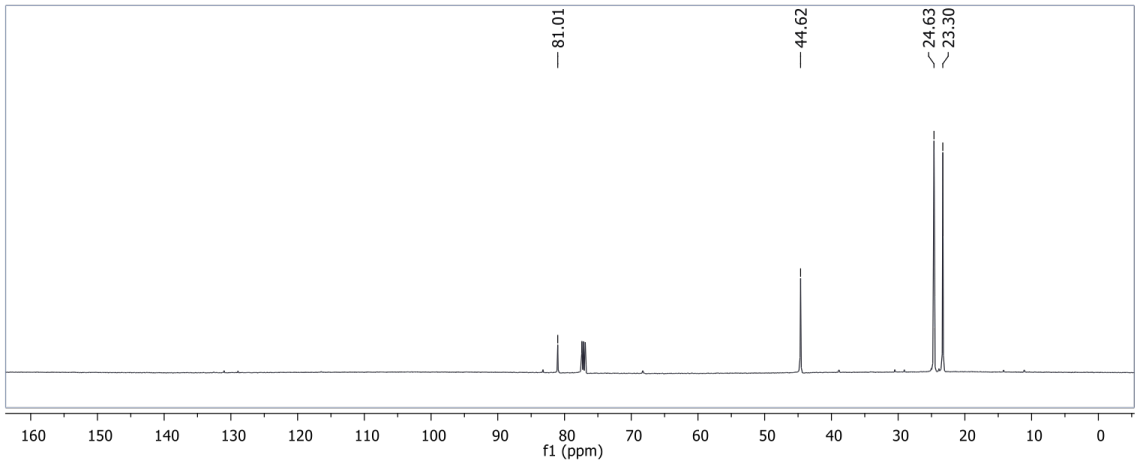
1l


BPin
N
O
3.5637
3.5484
3.5331
3.0794
3.0636
3.0487
1.2025
4.0000
3.9871
11.9796
8
6
4
2
[ppm]
[rel]

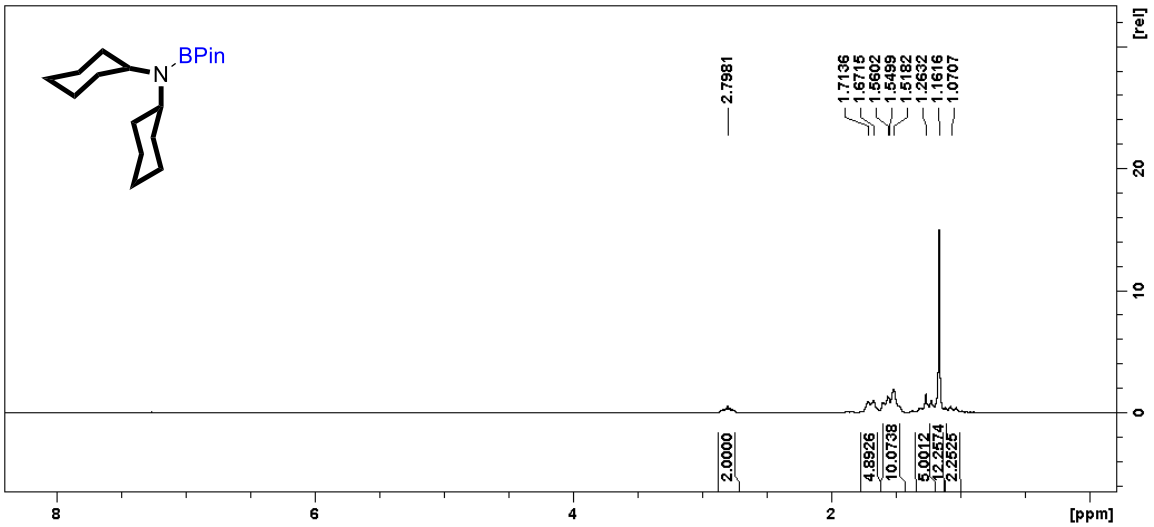

82.3365
68.5119
44.5851
24.7169
160
140
120
100
80
60
40
20
[ppm]
[rel]

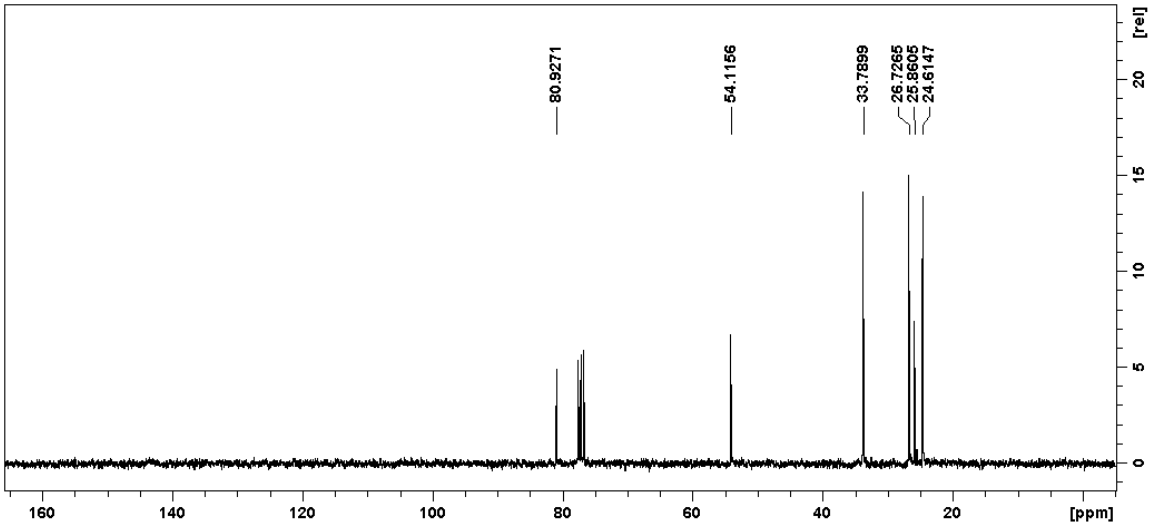
1m


N–BPin
3.34
1.18
1.10
1.08
2.00
12.00
12.04
f1 (ppm)

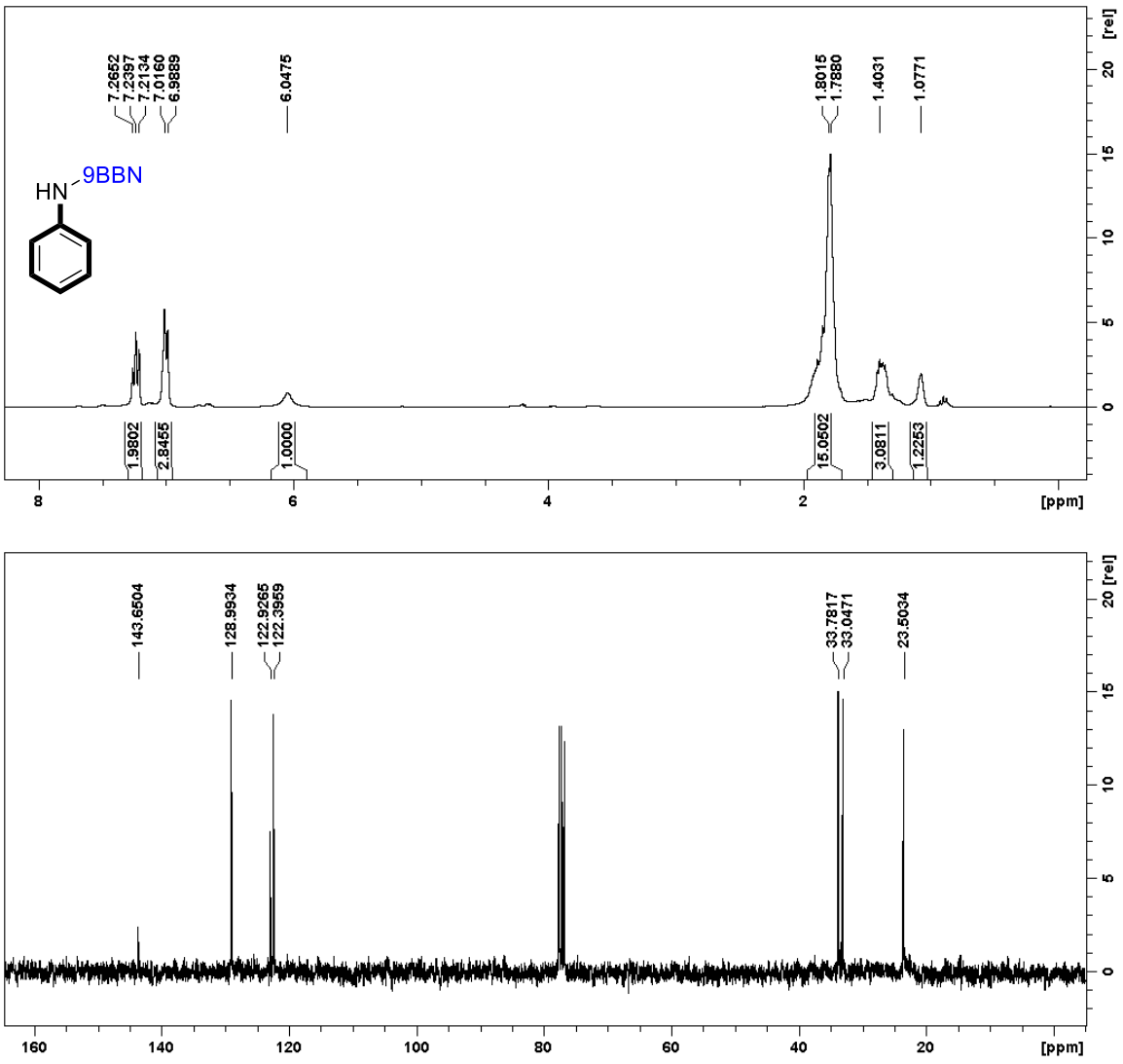

81.01
44.62
24.63
23.30
f1 (ppm)

1n

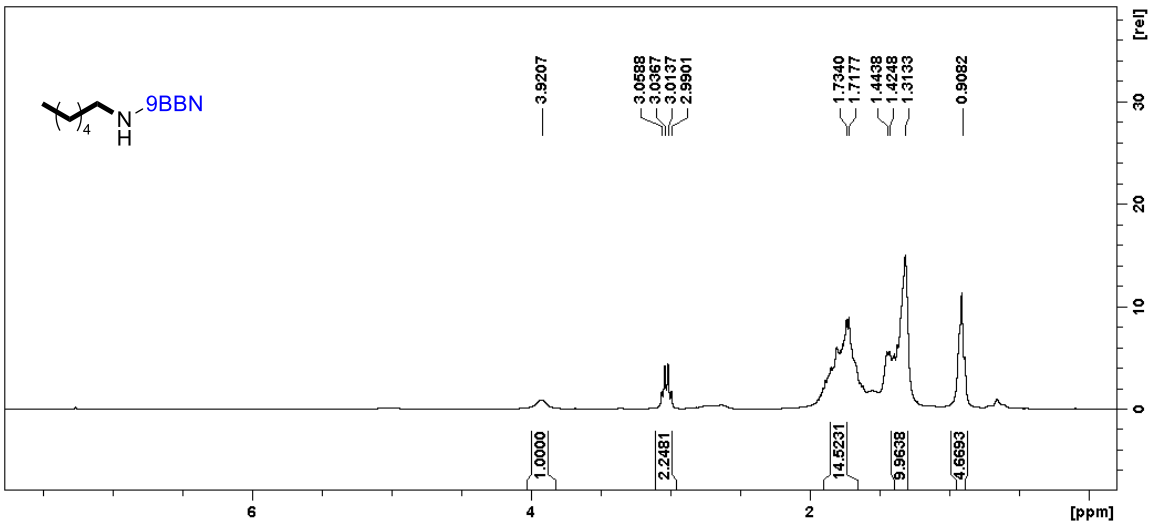

BPin
N
2.7981
1.7136
1.6715
1.5602
1.5499
1.5182
1.2632
1.1616
1.0707
2.0000
4.8926
10.0738
5.0012
12.2574
2.2525
8
6
4
2
[ppm]
[rel]
0
10
20

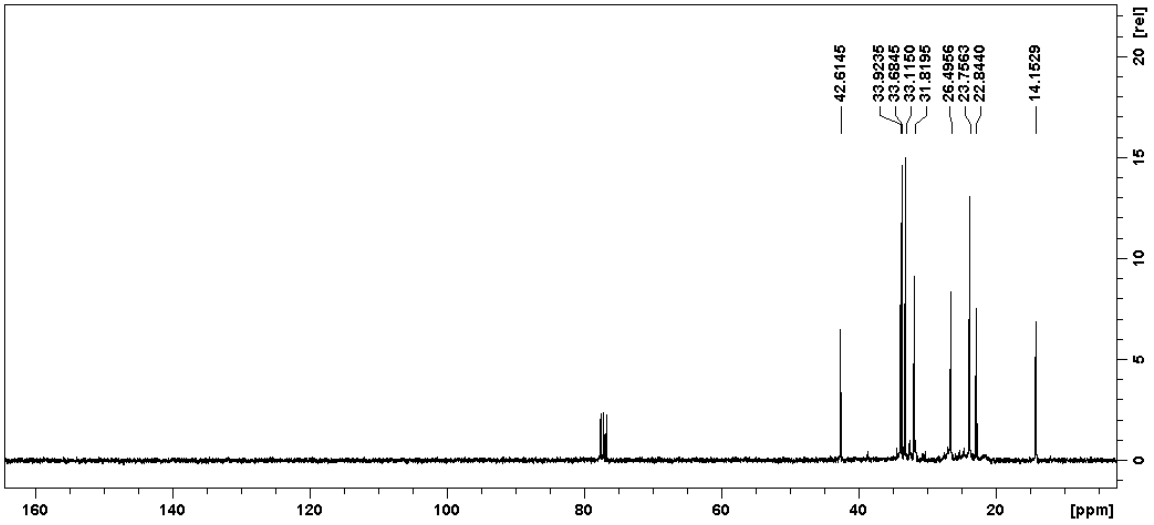

80.9271
54.1156
33.7899
26.7265
25.8805
24.6147
160
140
120
100
80
60
40
20
[ppm]
[rel]
0
5
10
15
20

1o

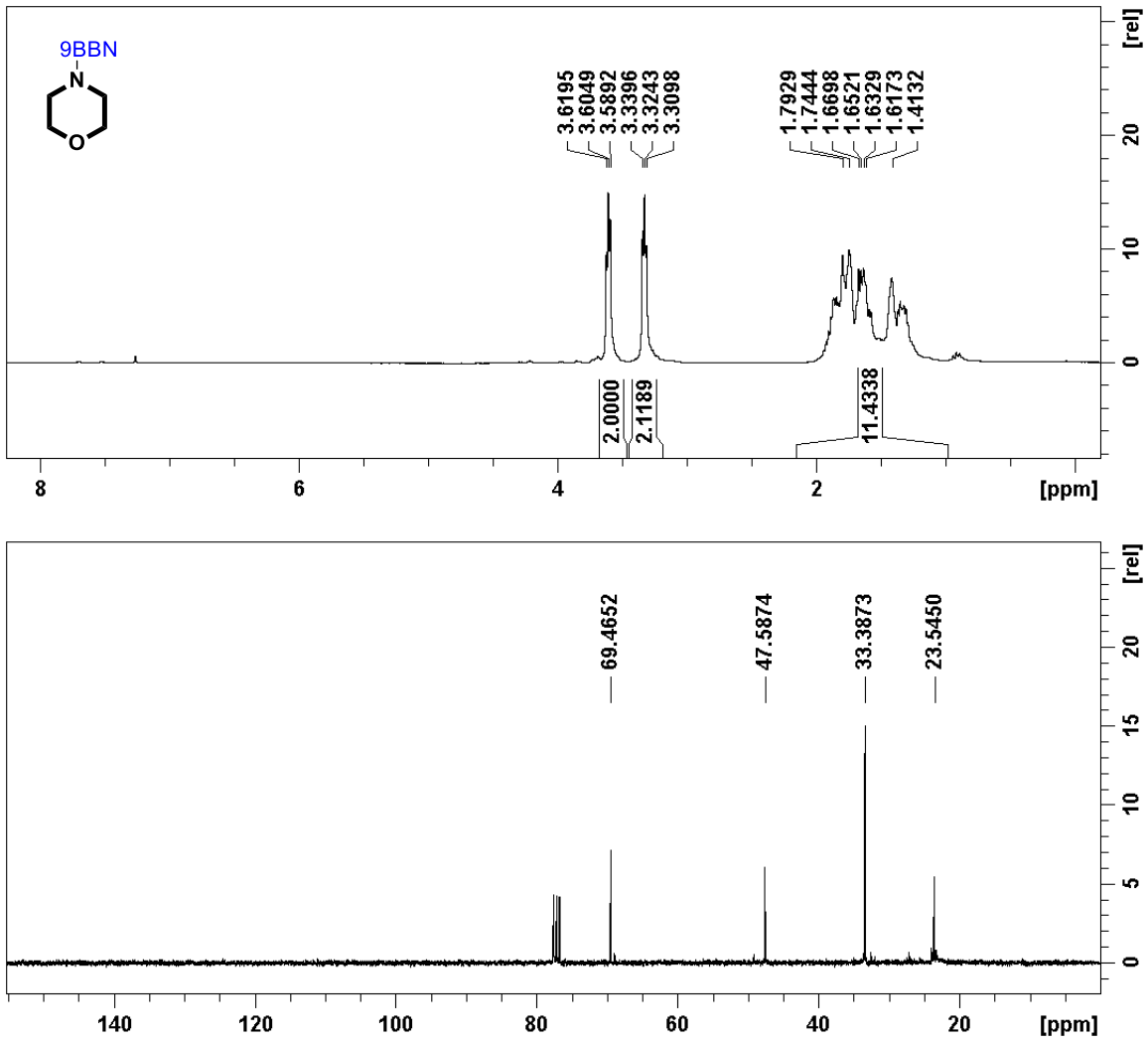

7.2652
7.2397
7.2134
7.0160
6.9889
6.0475
1.8015
1.7880
1.4031
1.0771
HN
9BBN
1.9802
2.8455
1.0000
15.0502
3.0811
1.2253
[rel]
[ppm]
143.6504
128.9934
122.9265
122.3959
33.7817
33.0471
23.5034

1p

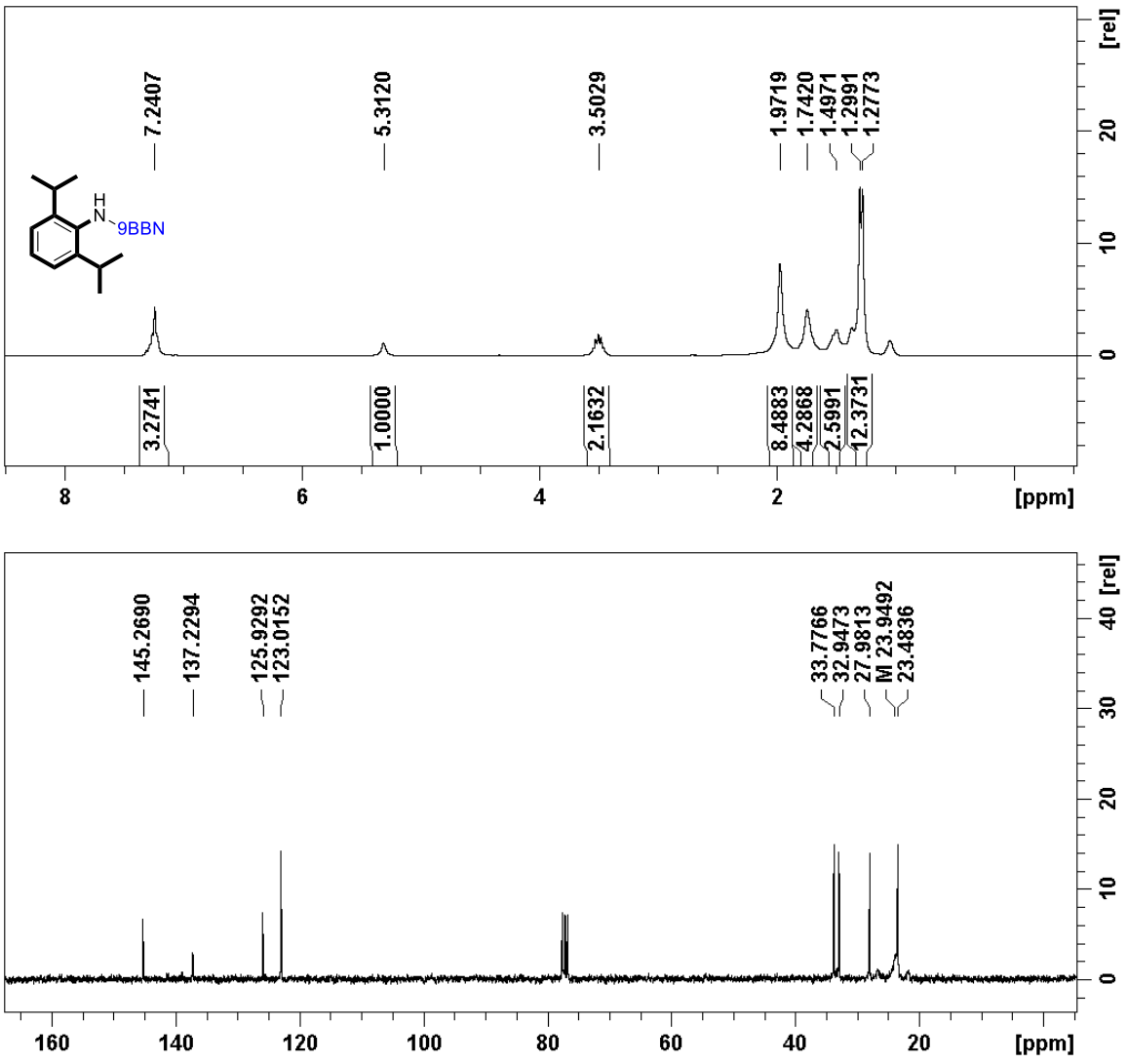

9BBN
N
H
3.9207
3.0588
3.0367
3.0137
2.9901
1.7340
1.7177
1.4438
1.4248
1.3133
0.9082
1.0000
2.2481
14.5231
9.9638
4.6693
6
4
2
[ppm]
[rel]


42.6145
33.9235
33.6845
33.1150
31.8195
26.4956
23.7563
22.8440
14.1529
160
140
120
100
80
60
40
20
[ppm]
[rel]

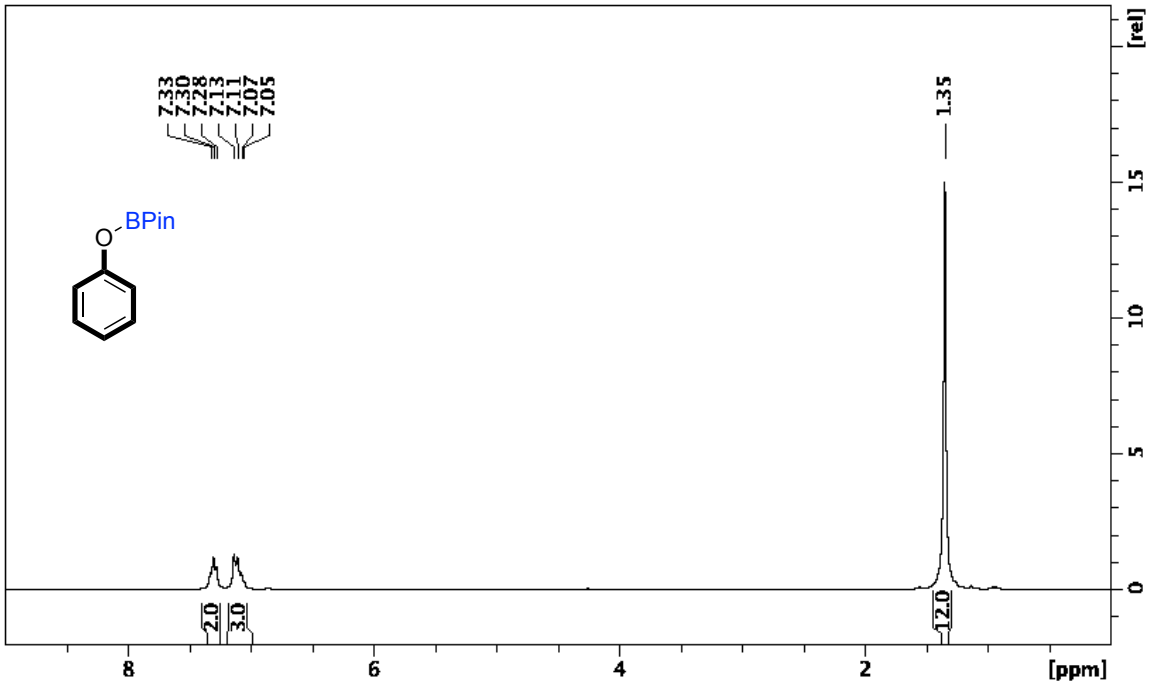
1q

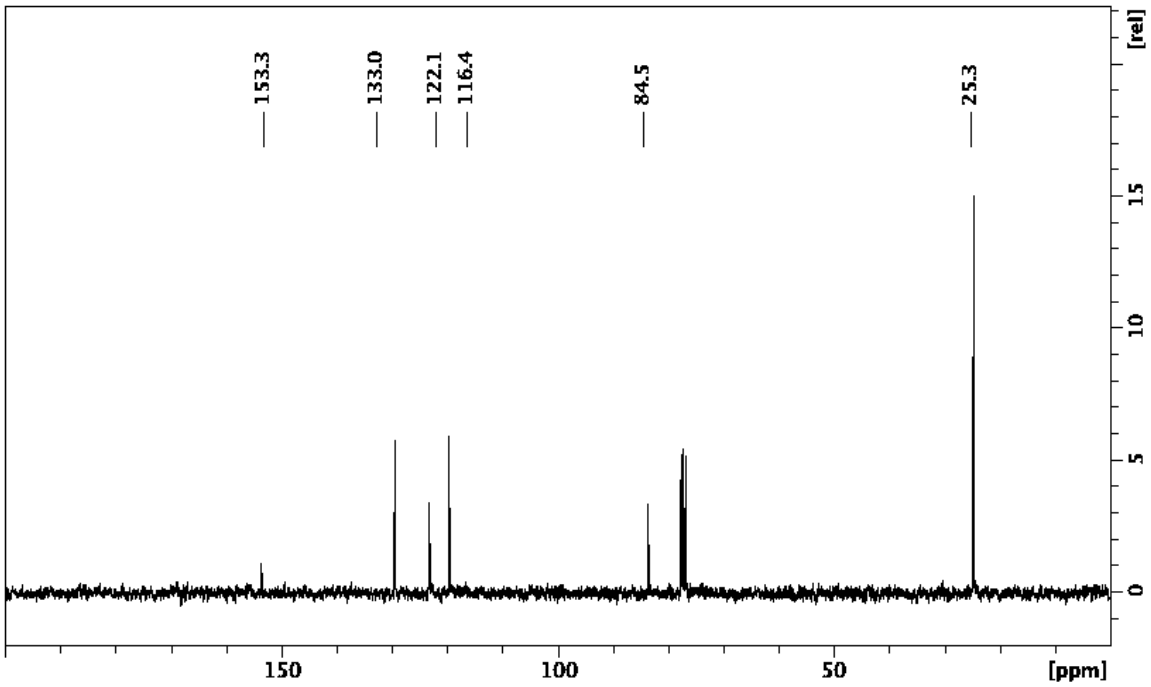

9BBN
N
O
3.6195
3.6049
3.5892
3.3396
3.3243
3.3098
1.7929
1.7444
1.6698
1.6521
1.6329
1.6173
1.4132
2.0000
2.1189
11.4338
[rel]
[ppm]
69.4652
47.5874
33.3873
23.5450
[rel]
[ppm]

1r

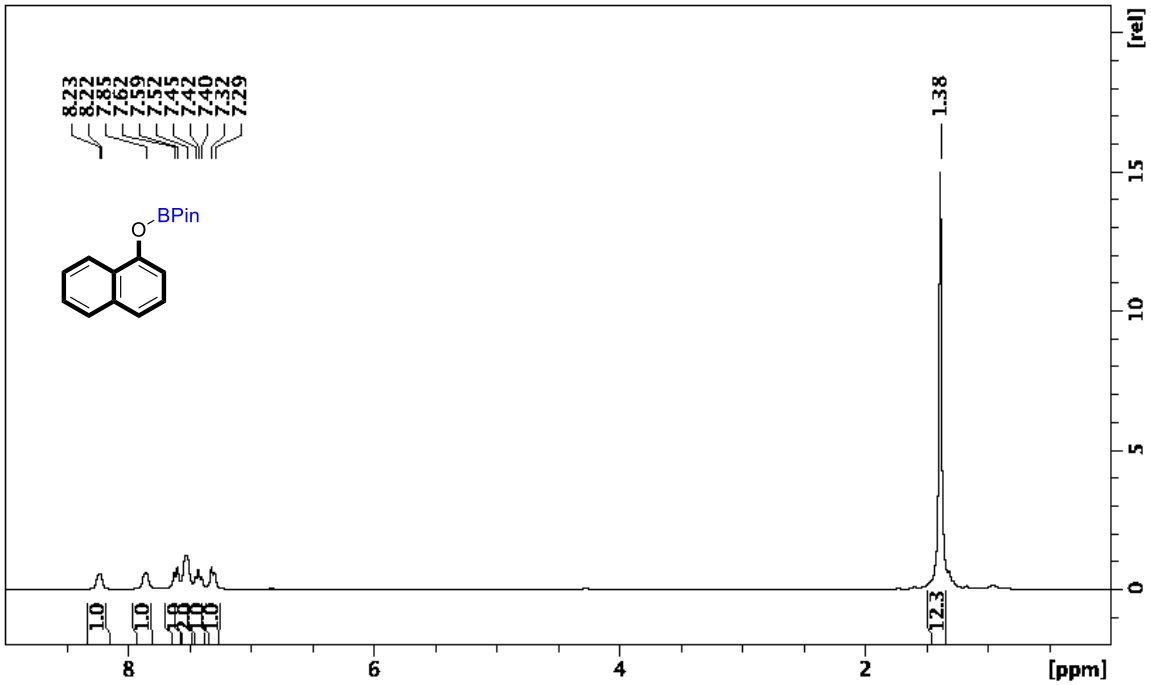

7.2407
5.3120
3.5029
1.9719
1.7420
1.4971
1.2991
1.2773
9BBN
3.2741
1.0000
2.1632
8.4883
4.2868
2.5991
12.3731
[rel]
[ppm]
145.2690
137.2294
125.9292
123.0152
33.7766
32.9473
27.9813
M 23.9492
23.4836
[rel]
[ppm]

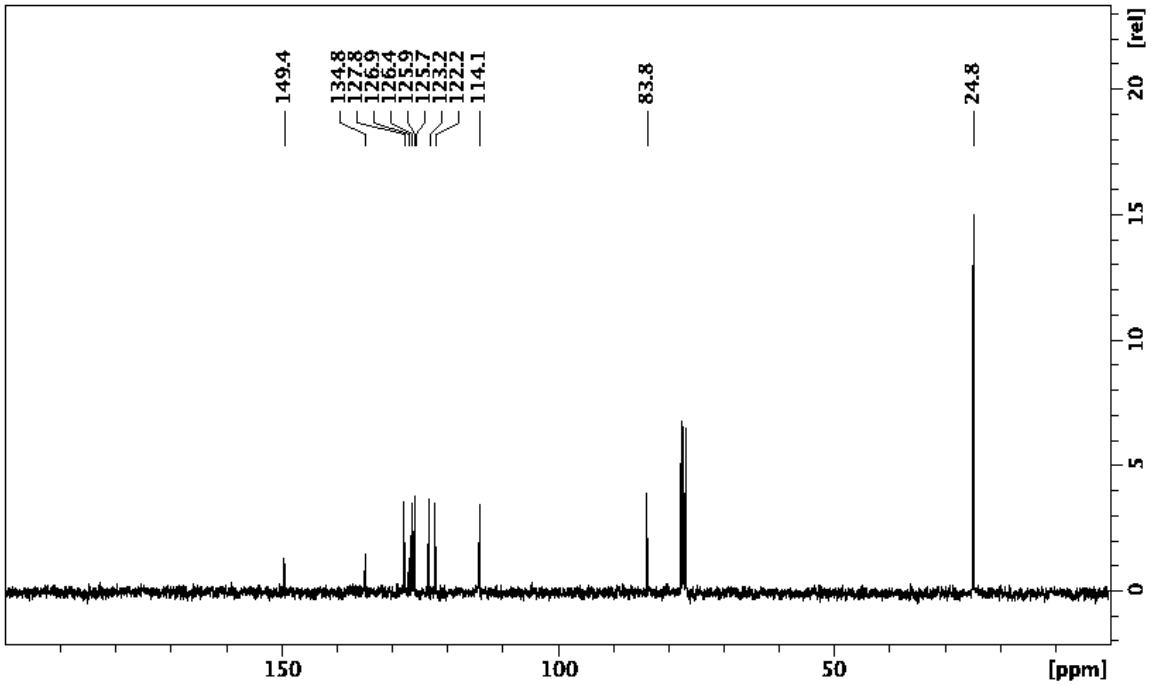
2a


7.33
7.30
7.28
7.13
7.11
7.07
7.05
1.35
BPin
O
2.0
3.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15

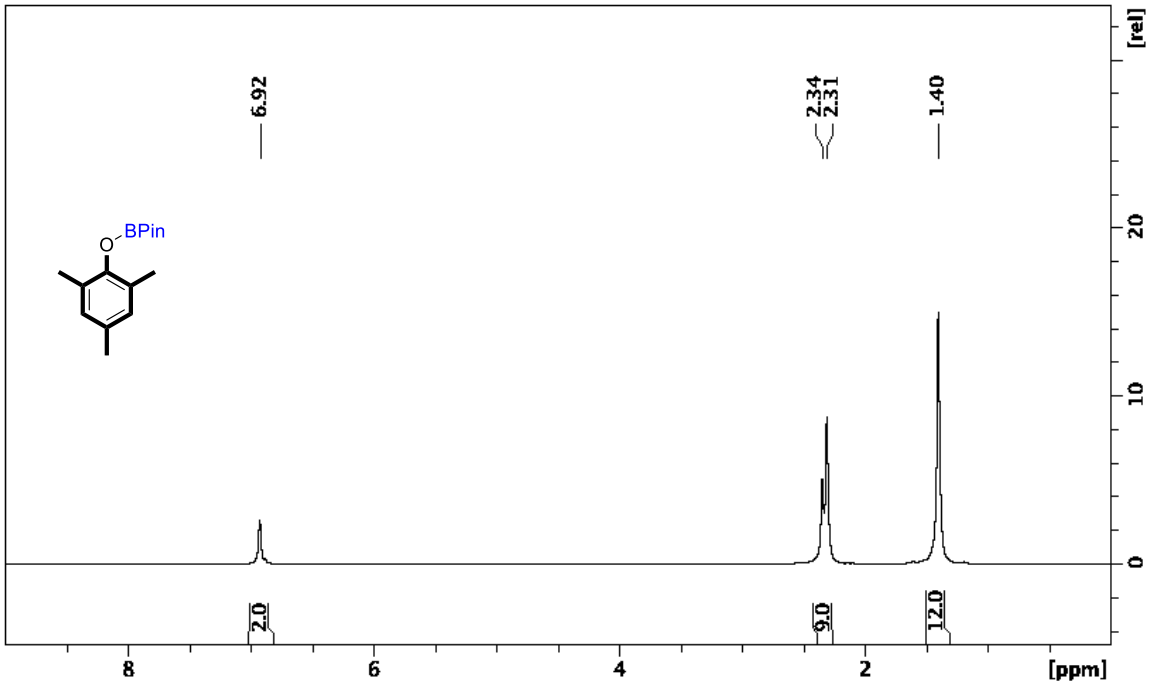

153.3
133.0
122.1
116.4
84.5
25.3
150
100
50
[ppm]
[rel]
0
5
10
15

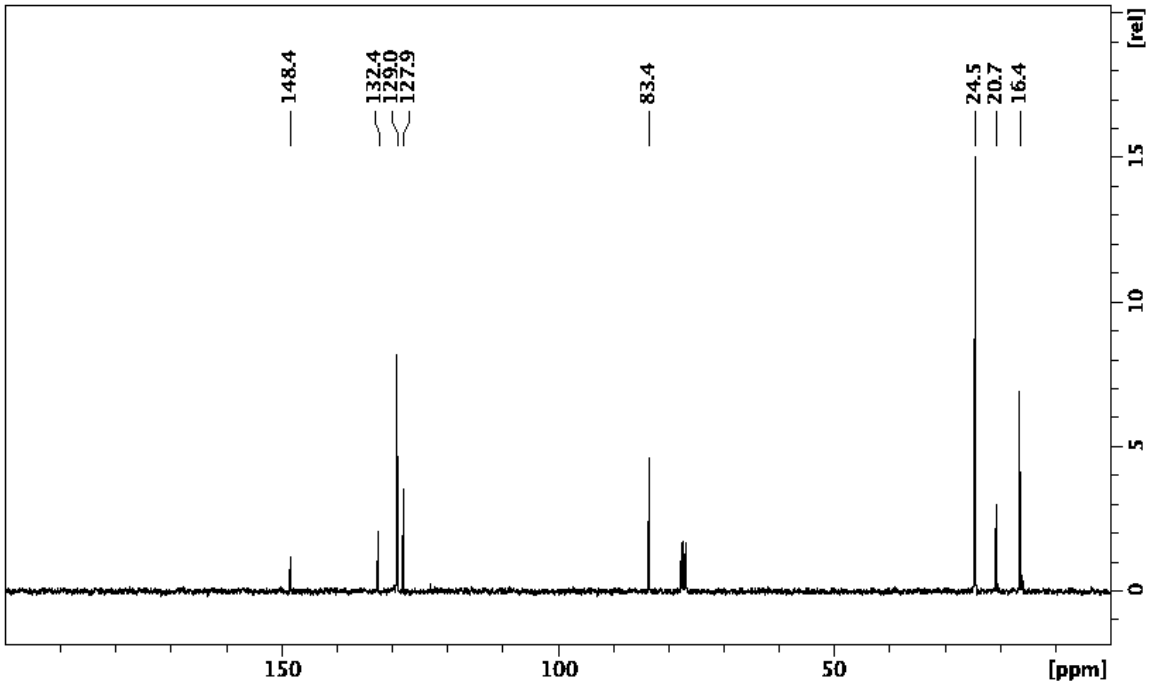
2b


8.23
8.22
7.85
7.62
7.59
7.52
7.45
7.42
7.40
7.32
7.29
1.38
BPin
O
1.0
1.0
2.8
2.8
1.0
12.3
8
6
4
2
[ppm]
[rel]
0
5
10
15

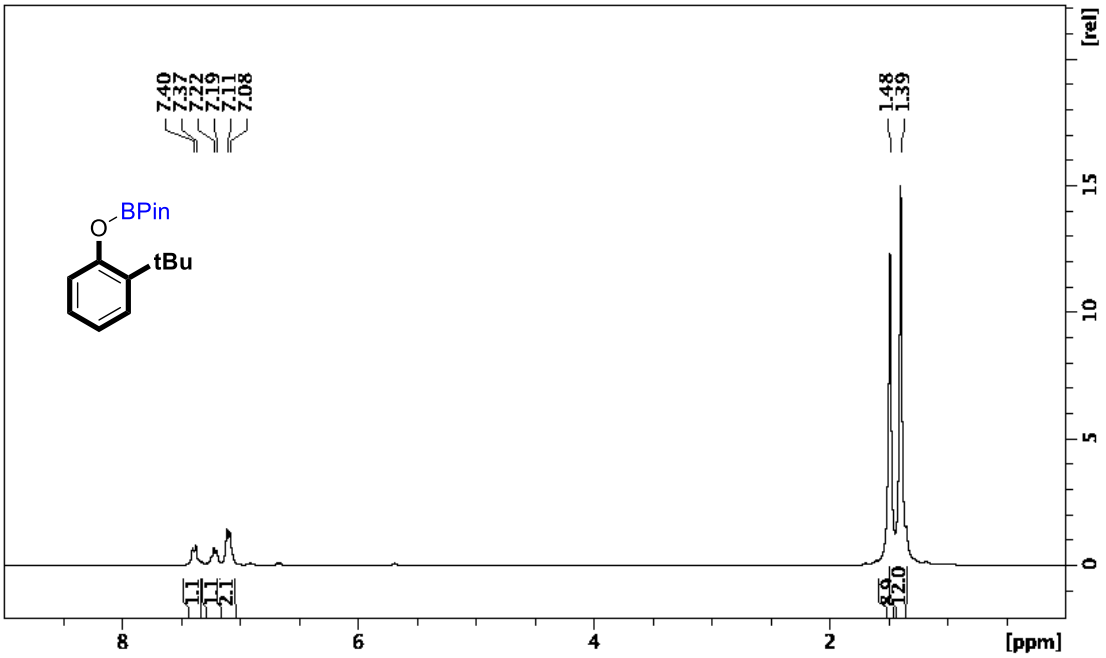

149.4
134.8
127.8
126.9
126.4
125.9
125.7
123.2
122.2
114.1
83.8
24.8
150
100
50
[ppm]
[rel]
0
5
10
15
20

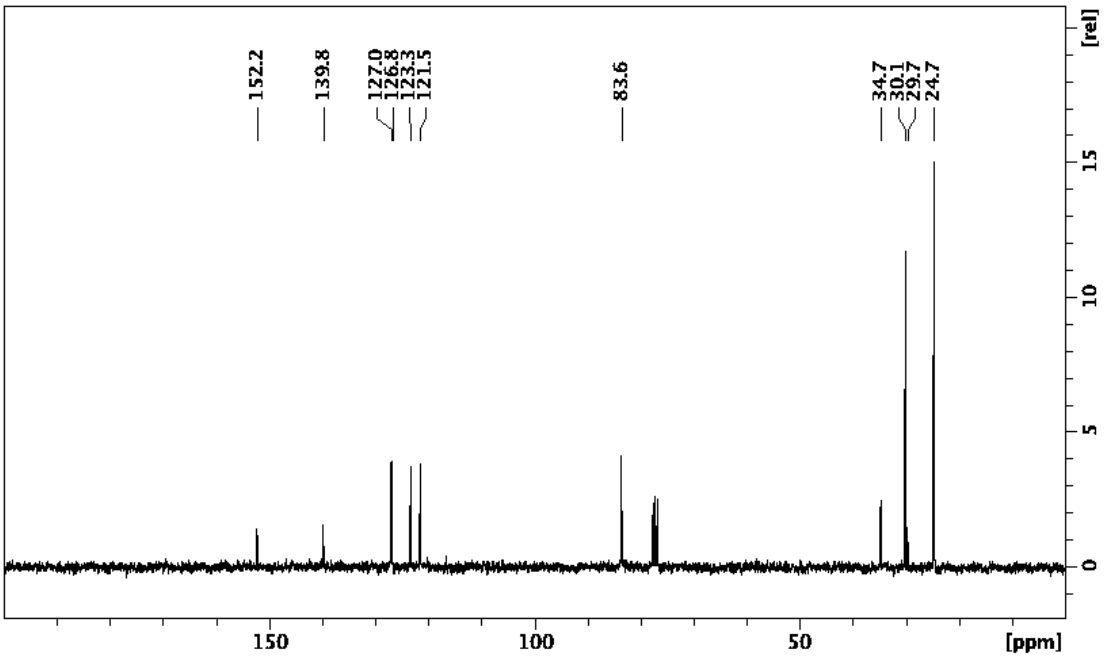
2c


6.92
2.34
2.31
1.40
BPin
O
2.0
9.0
12.0
8
6
4
2
[ppm]
[rel]
0
10
20

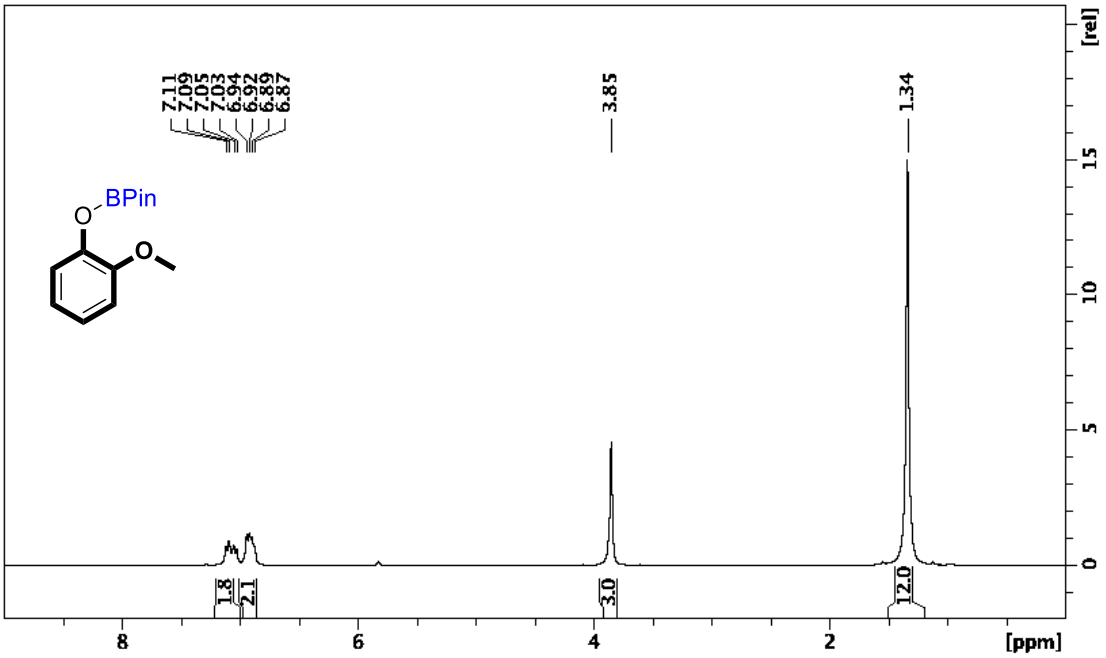

148.4
132.4
129.0
127.9
83.4
24.5
20.7
16.4
150
100
50
[ppm]
[rel]
0
5
10
15

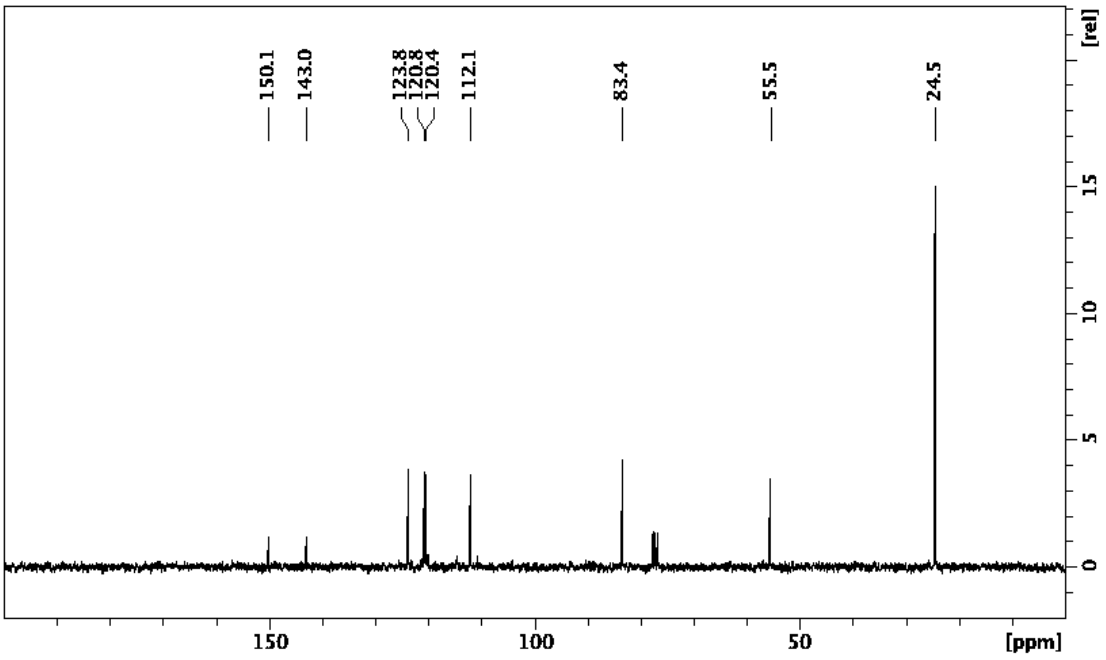
2d


7.40
7.37
7.22
7.19
7.11
7.08
1.48
1.39
BPin
O
tBu
1.1
1.1
2.1
6.6
12.0
[rel]
15
10
5
0
8
6
4
2
[ppm]

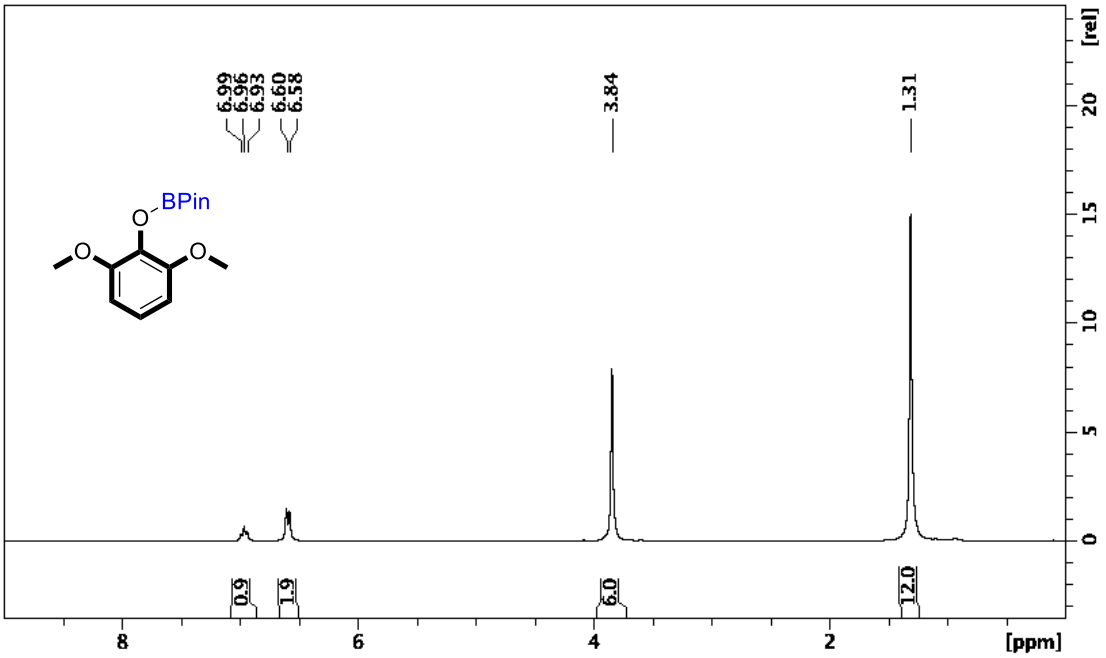

152.2
139.8
127.0
126.8
123.3
121.5
83.6
34.7
30.1
29.7
24.7
[rel]
15
10
5
0
150
100
50
[ppm]

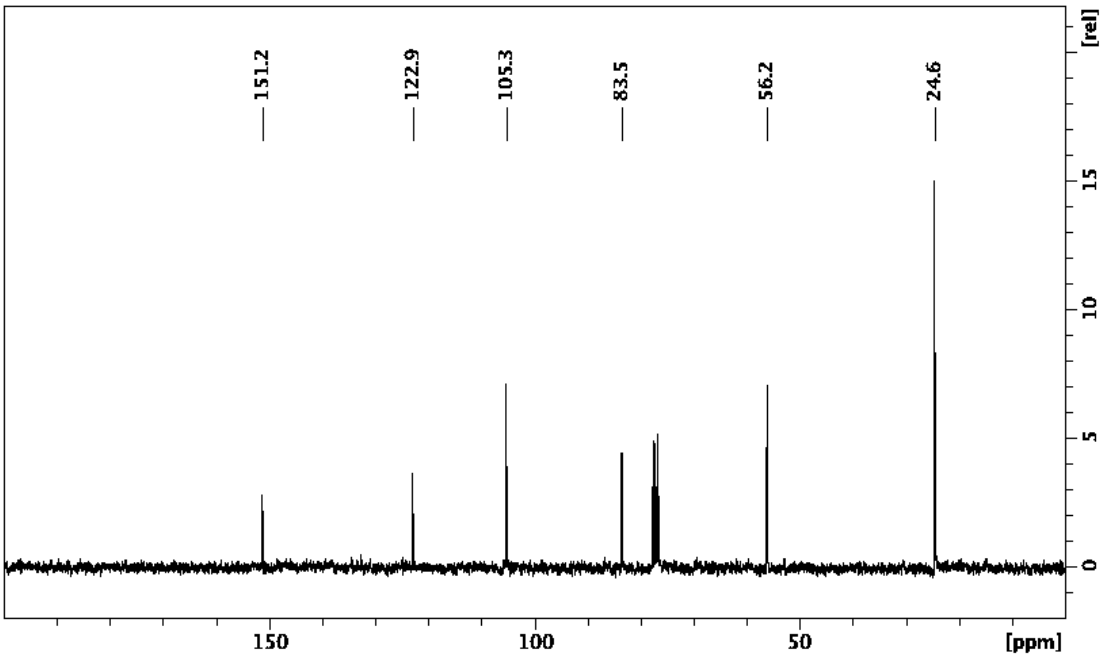
2e


7.11
7.09
7.05
7.03
6.94
6.92
6.89
6.87
3.85
1.34
BPin
O
O
1.8
2.1
3.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15

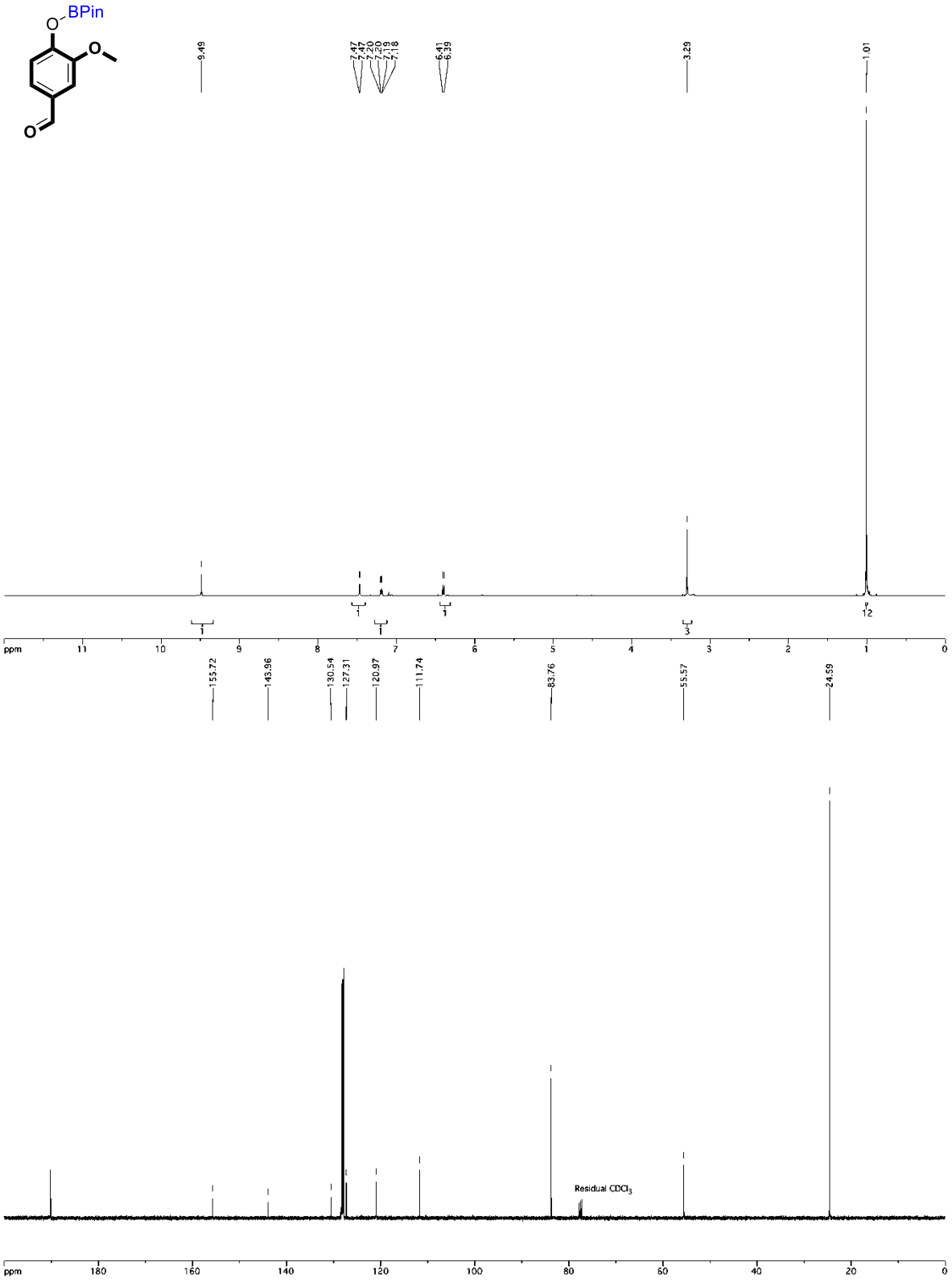

150.1
143.0
123.8
120.8
120.4
112.1
83.4
55.5
24.5
150
100
50
[ppm]
[rel]
0
5
10
15

2f

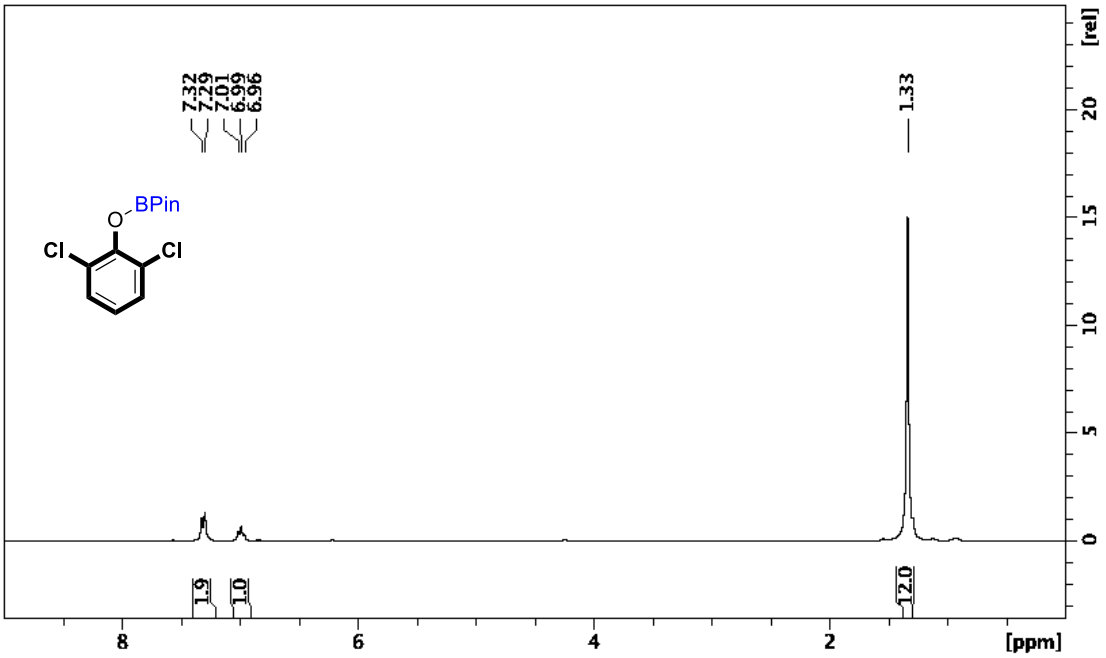

6.99
6.96
6.93
6.60
6.58
3.84
1.31
BPin
O
O
O
0.9
1.9
6.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

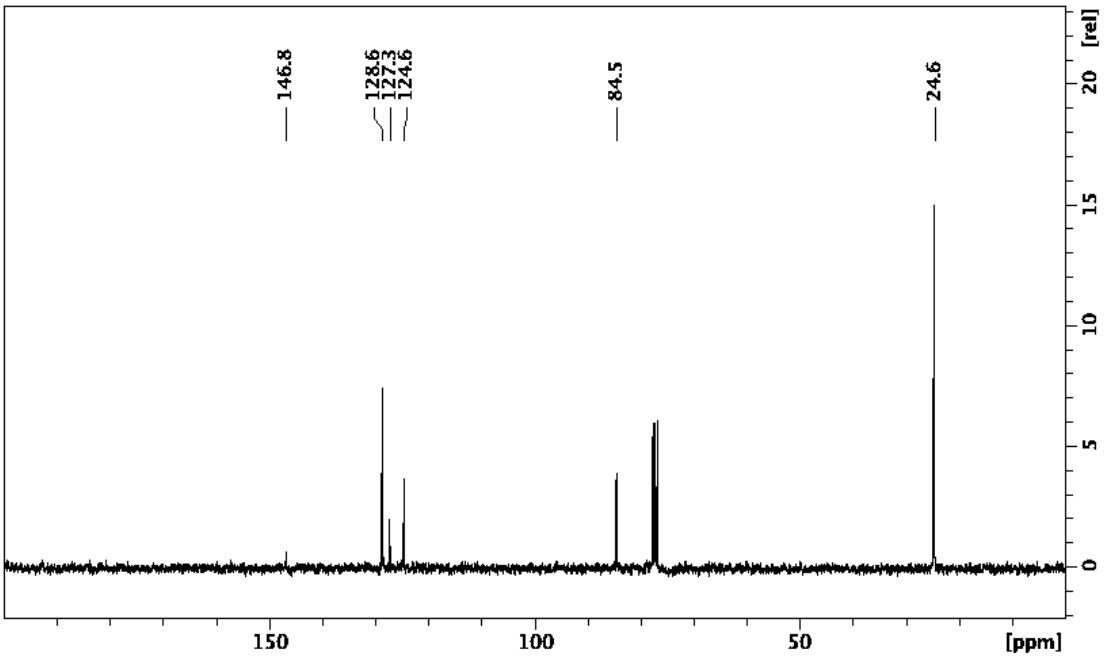

151.2
122.9
105.3
83.5
56.2
24.6
150
100
50
[ppm]
[rel]
0
5
10
15

2g

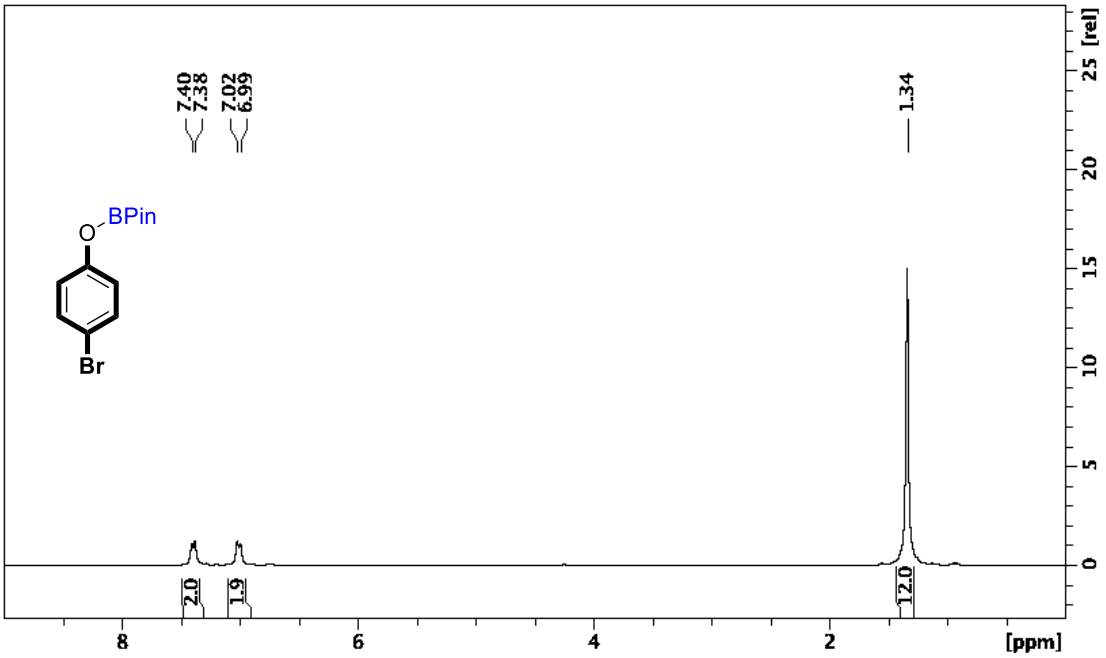

BPin
9.49
7.47
7.47
7.20
7.19
7.18
6.41
6.39
3.29
1.01
1
1
1
3
12
ppm
155.72
143.96
130.54
127.31
120.97
111.74
83.76
55.57
24.59
Residual CDCl3
ppm

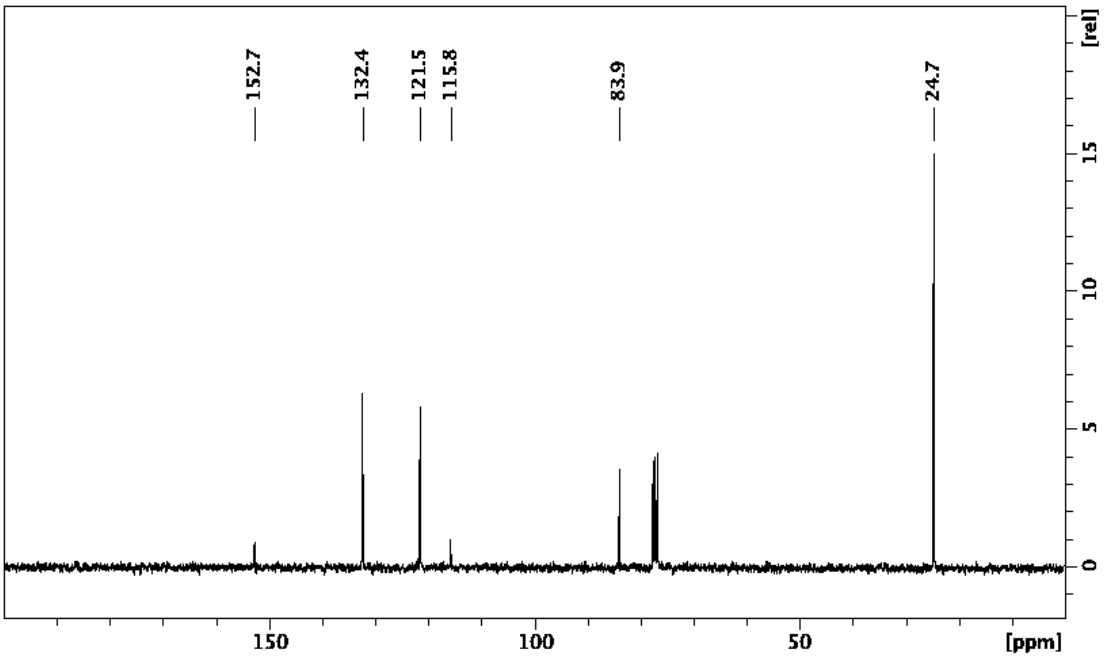
2h


7.32
7.29
7.01
6.99
6.96
1.33
BPin
O
Cl
Cl
1.9
1.0
12.0
[rel]
[ppm]

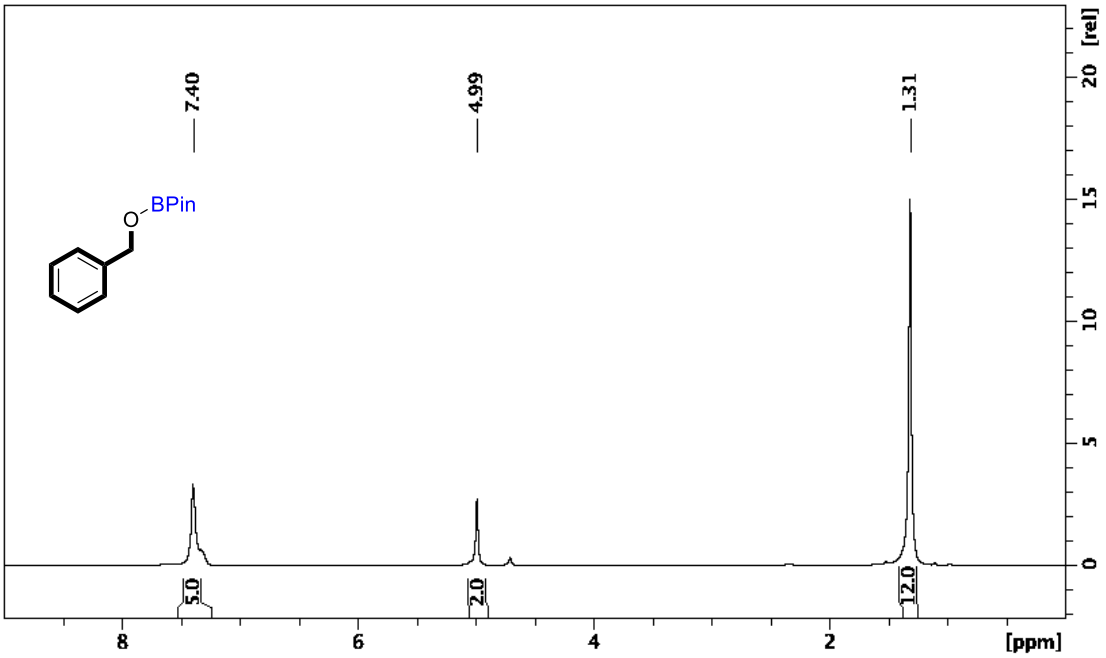

146.8
128.6
127.3
124.6
84.5
24.6
[rel]
[ppm]

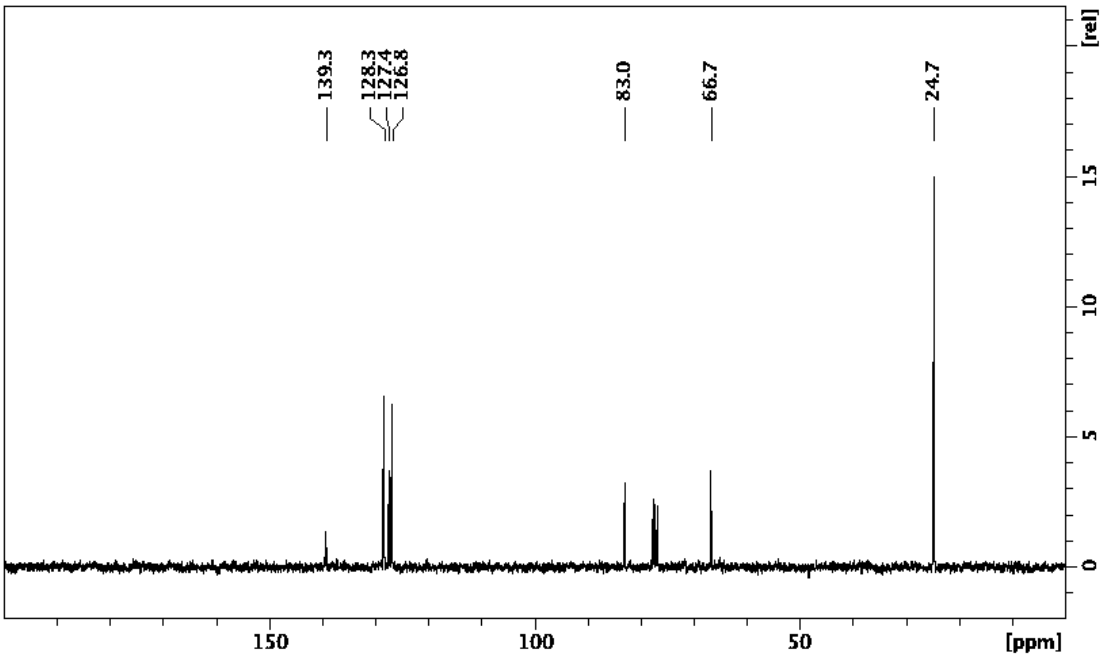
2i


7.40
7.38
7.02
6.99
1.34
BPin
O
Br
2.0
1.9
12.0
8
6
4
2
[ppm]
0
5
10
15
20
25
[rel]

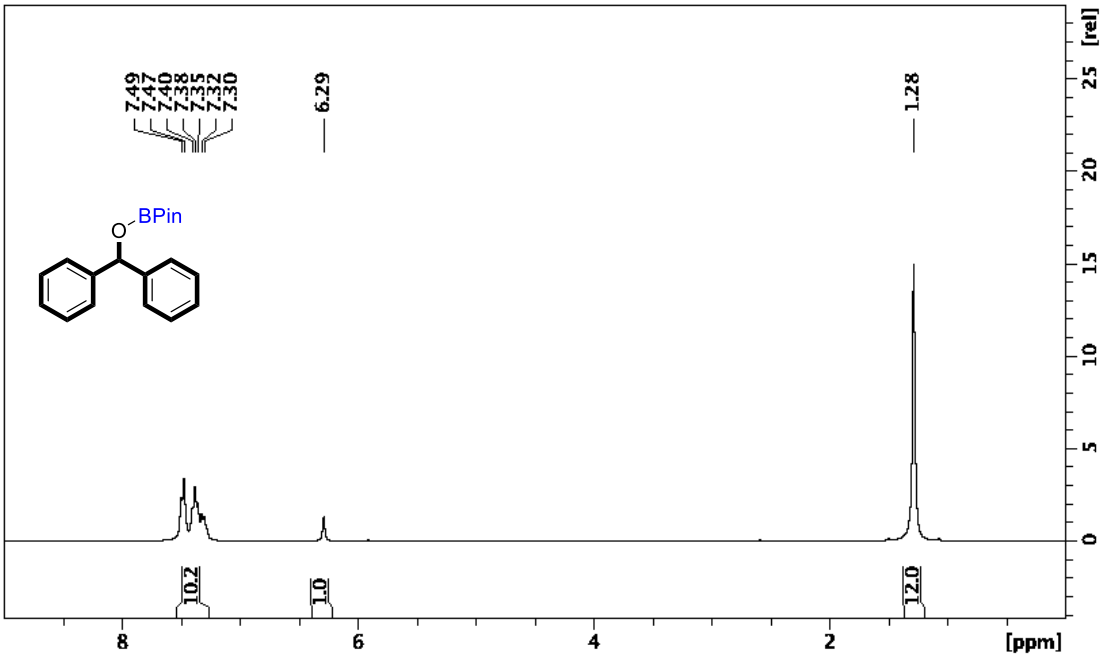

152.7
132.4
121.5
115.8
83.9
24.7
150
100
50
[ppm]
0
5
10
15
[rel]

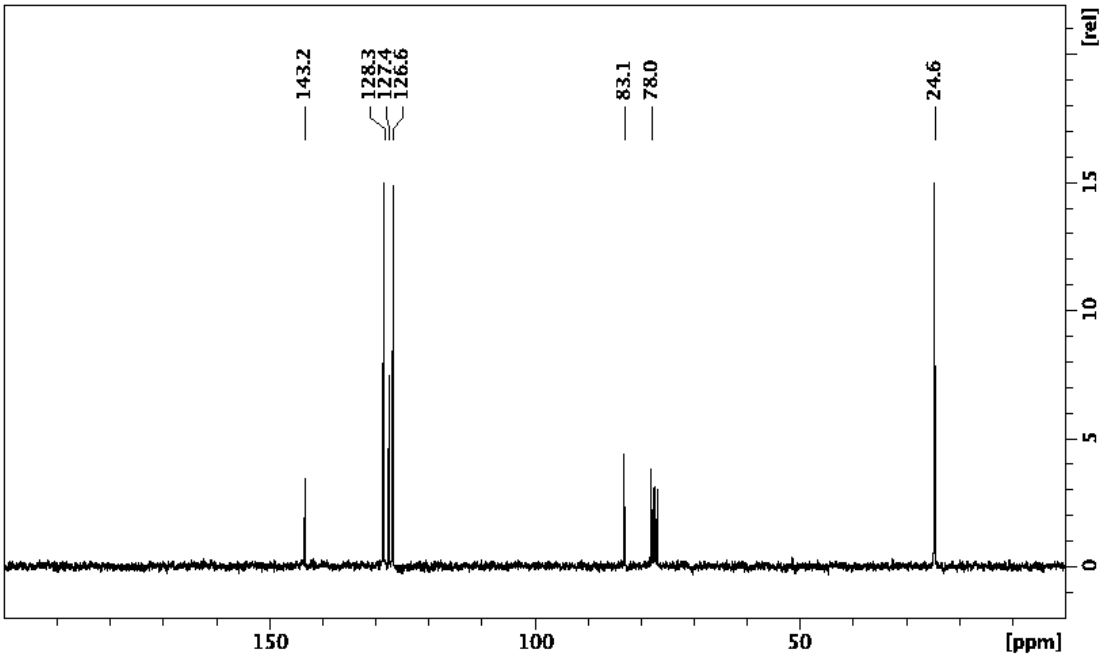
2j


7.40
4.99
1.31
BPin
O
5.0
2.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

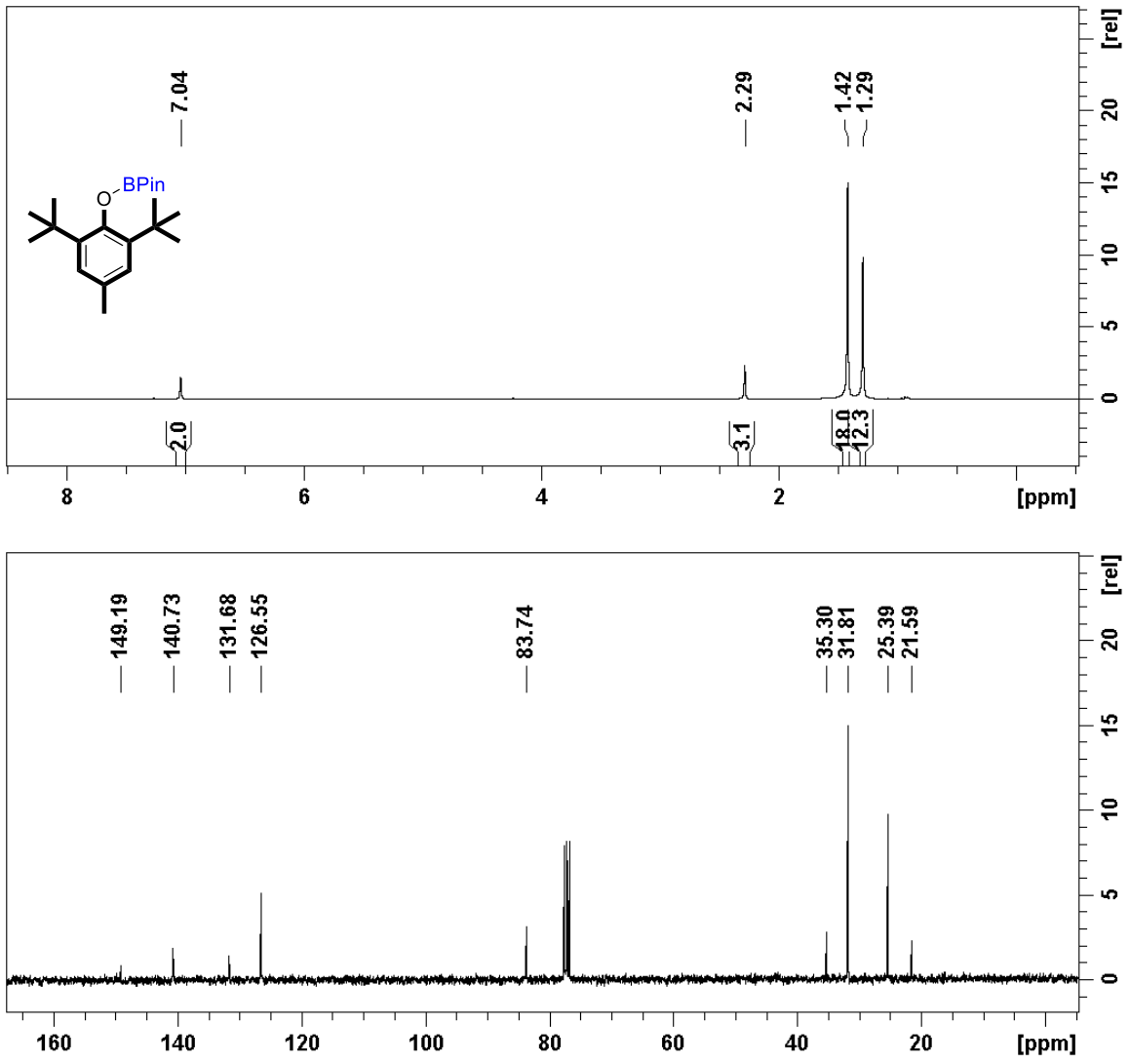

139.3
128.3
127.4
126.8
83.0
66.7
24.7
150
100
50
[ppm]
[rel]
0
5
10
15

2k

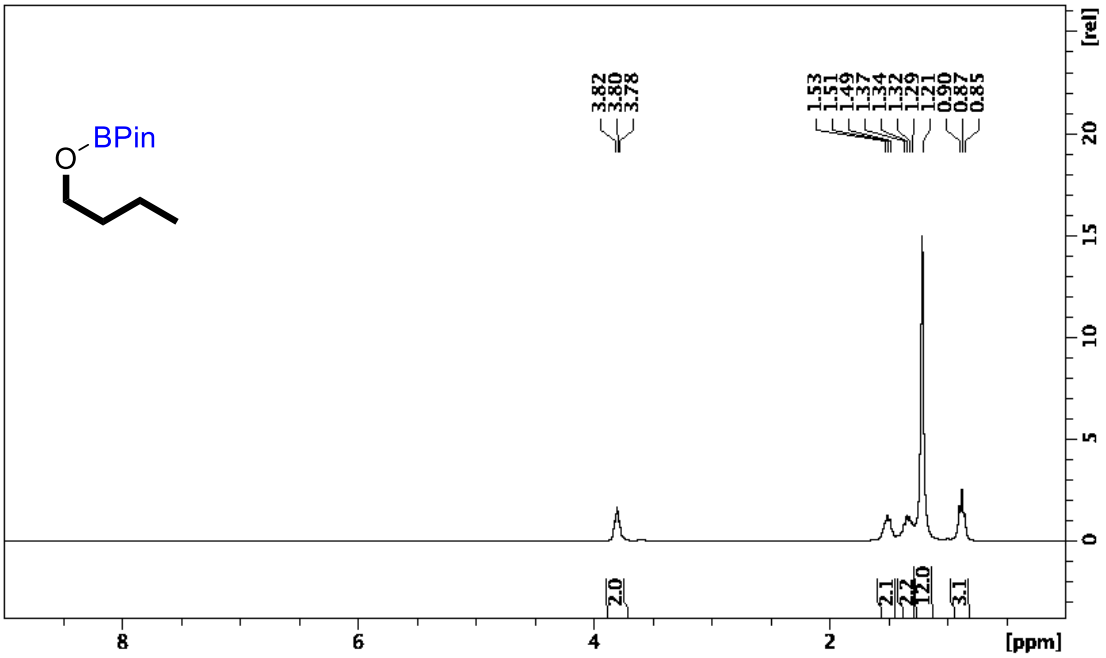

7.49
7.47
7.40
7.38
7.35
7.32
7.30
6.29
1.28
BPin
O
10.2
1.0
12.0
8
6
4
2
[ppm]
[rel]

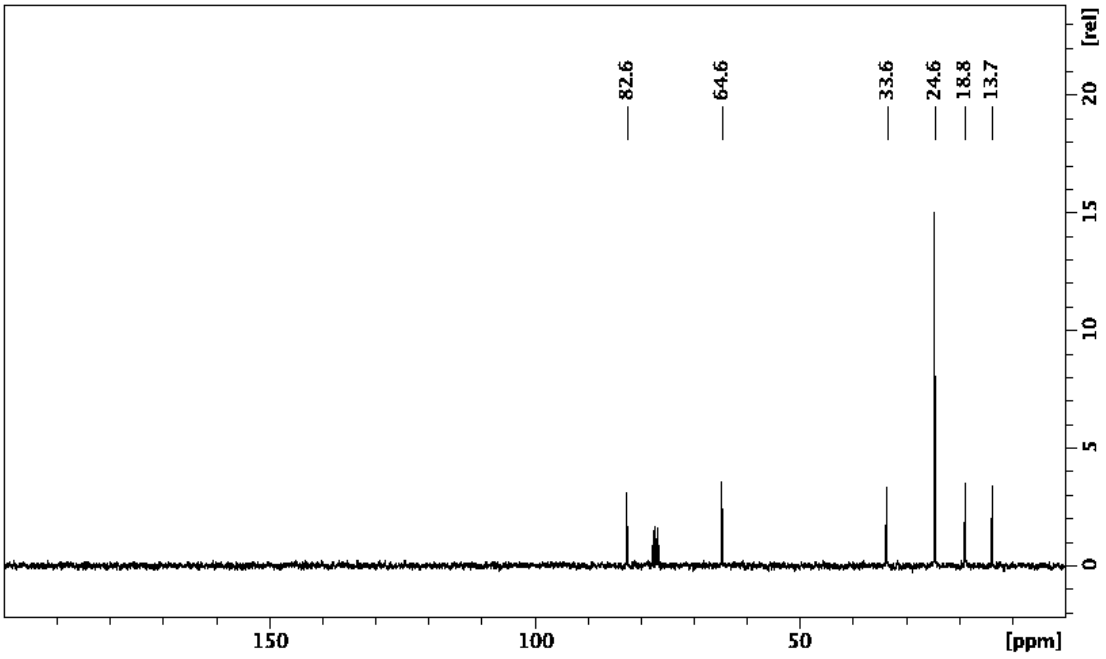

143.2
128.3
127.4
126.6
83.1
78.0
24.6
150
100
50
[ppm]
[rel]

2l

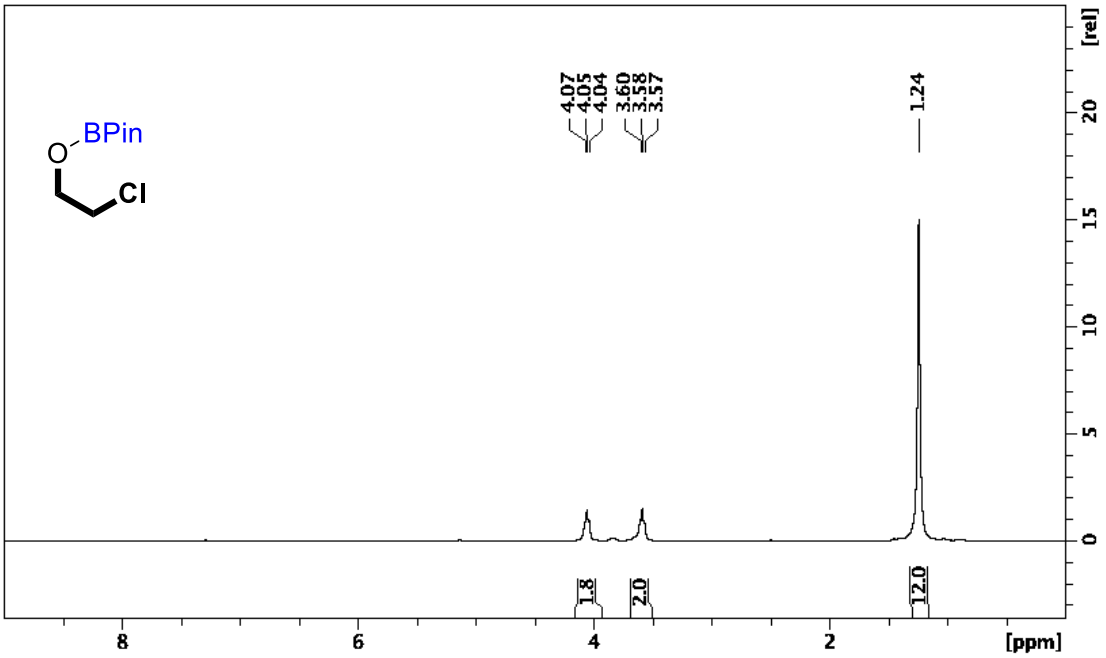

7.04
2.29
1.42
1.29
BPin
O
2.0
3.1
18.0
12.3
[rel]
[ppm]
149.19
140.73
131.68
126.55
83.74
35.30
31.81
25.39
21.59

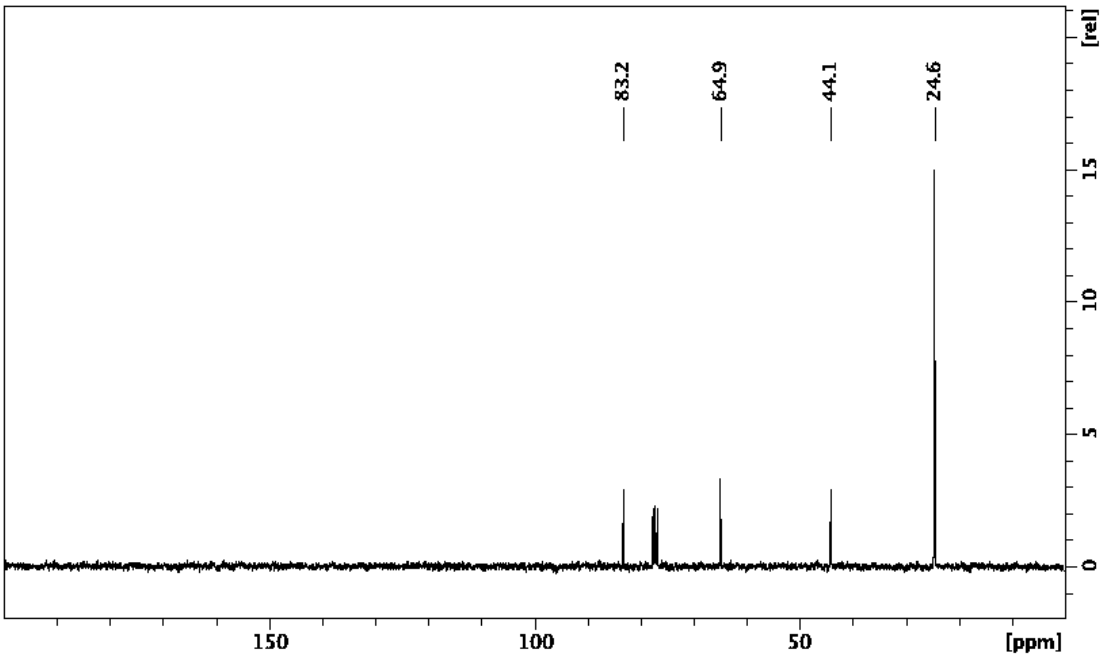
2m


BPin
O
3.82
3.80
3.78
1.53
1.51
1.49
1.37
1.34
1.32
1.29
1.21
0.90
0.87
0.85
2.0
2.1
2.2
12.0
3.1
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

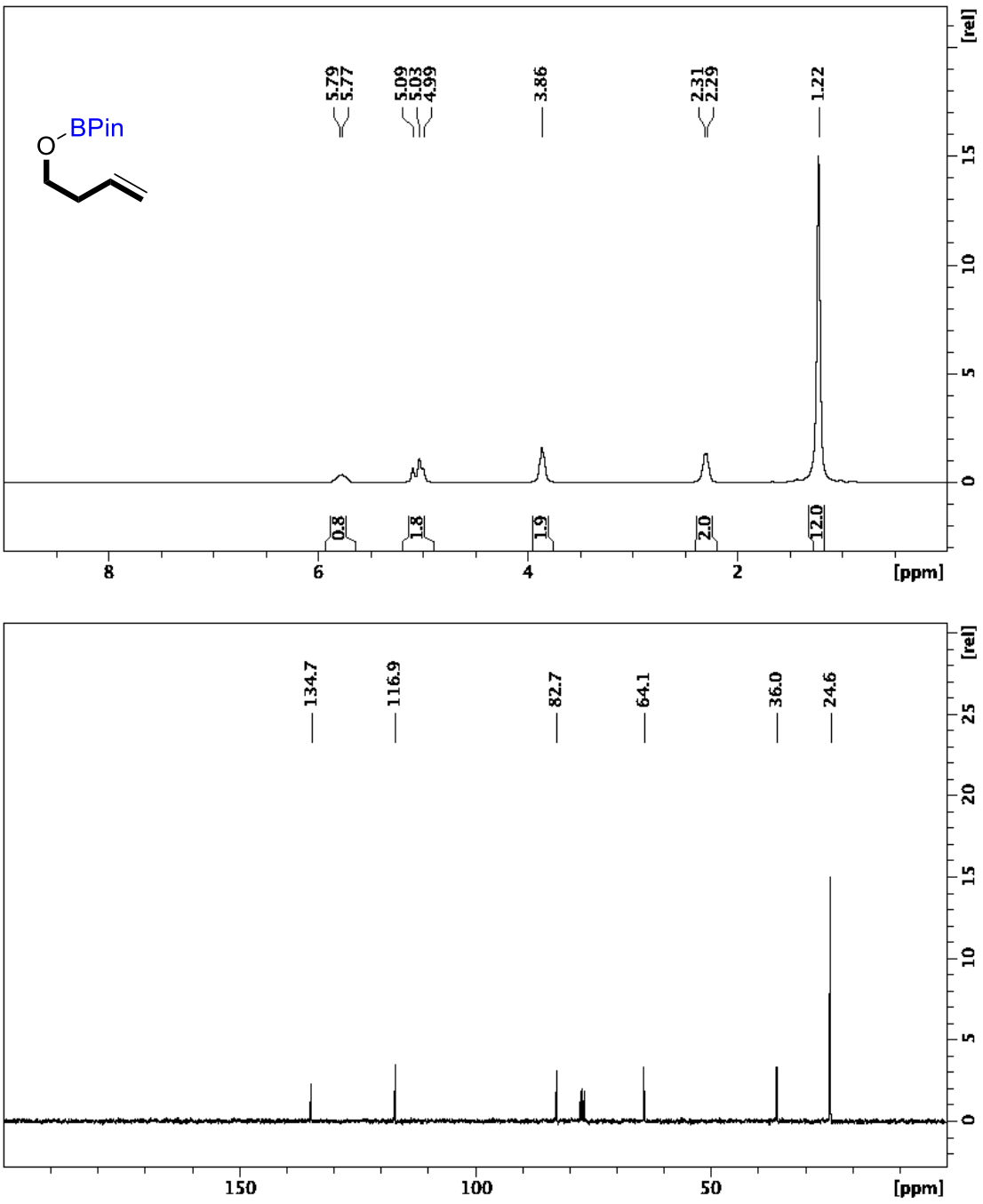

82.6
64.6
33.6
24.6
18.8
13.7
150
100
50
[ppm]
[rel]
0
5
10
15
20

2n

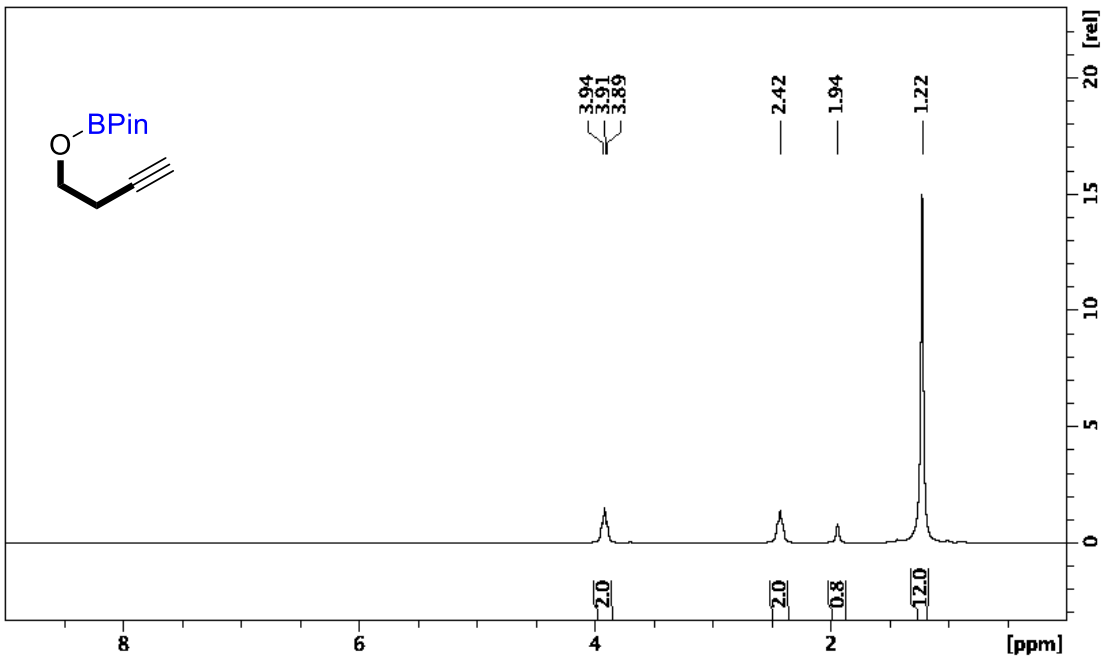

BPin
O
Cl
4.07
4.05
4.04
3.60
3.58
3.57
1.24
1.8
2.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

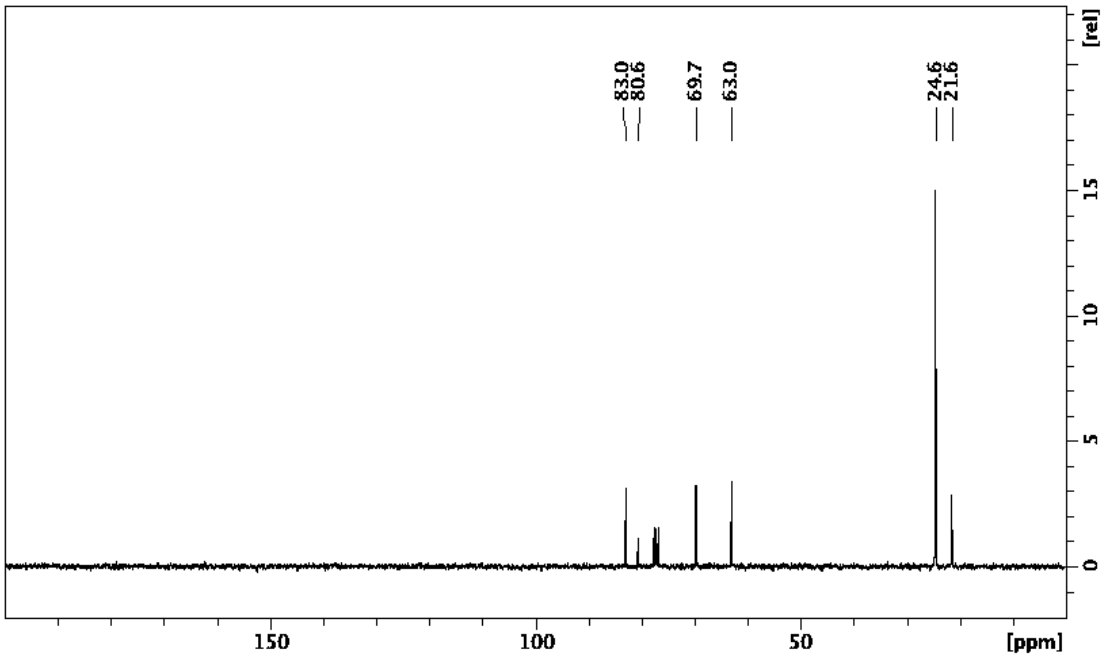

83.2
64.9
44.1
24.6
150
100
50
[ppm]
[rel]
0
5
10
15

2o

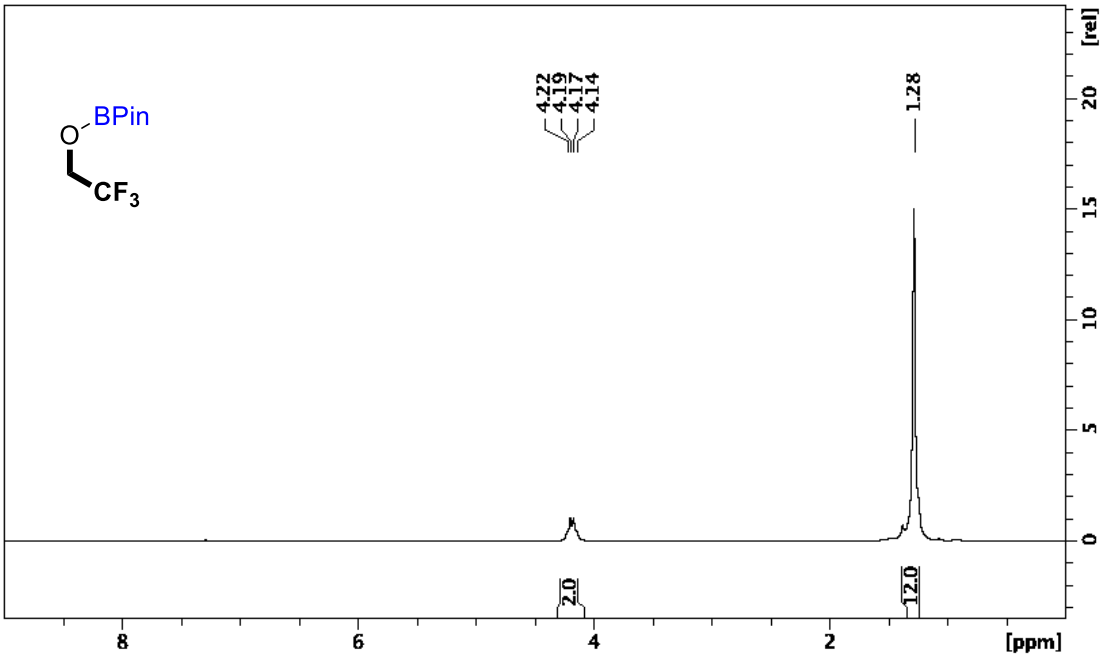

BPin
O
5.79
5.77
5.09
5.03
4.99
3.86
2.31
2.29
1.22
0.8
1.8
1.9
2.0
12.0
[rel]
[ppm]
134.7
116.9
82.7
64.1
36.0
24.6
[rel]
[ppm]

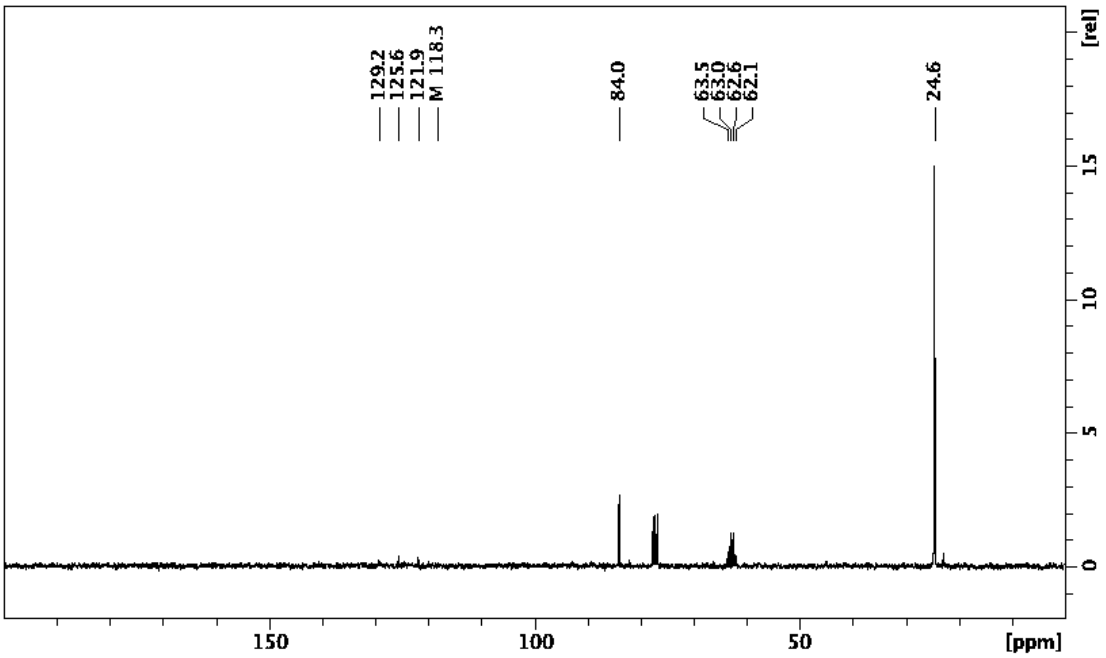
2p


BPin
O
3.94
3.91
3.89
2.42
1.94
1.22
2.0
2.0
0.8
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

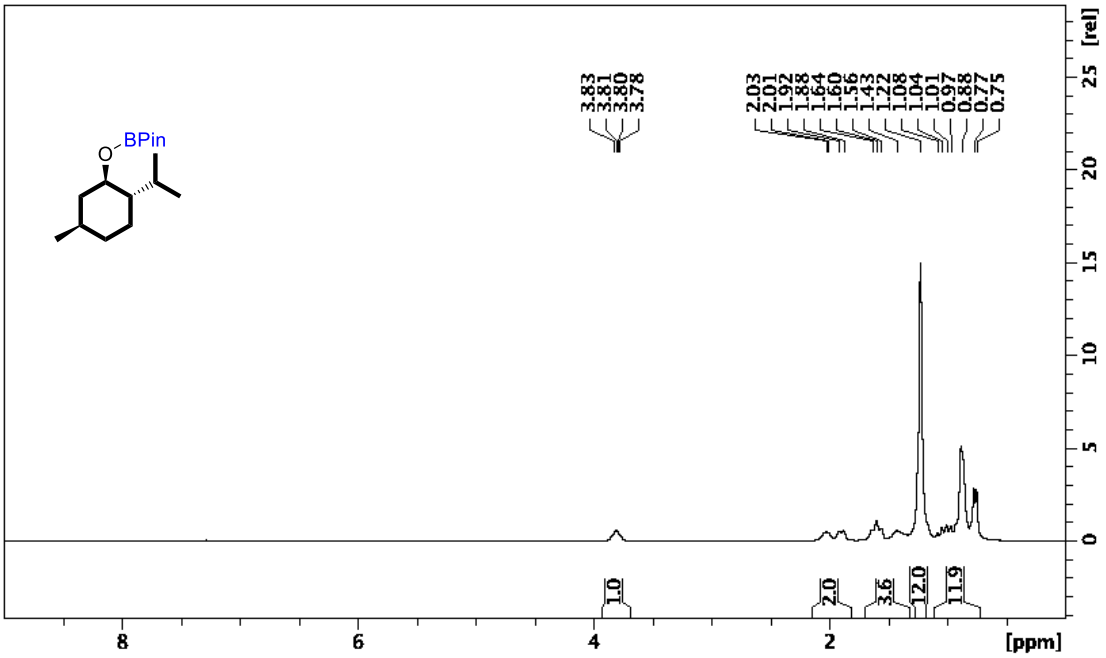

83.0
80.6
69.7
63.0
24.6
21.6
150
100
50
[ppm]
[rel]
0
5
10
15

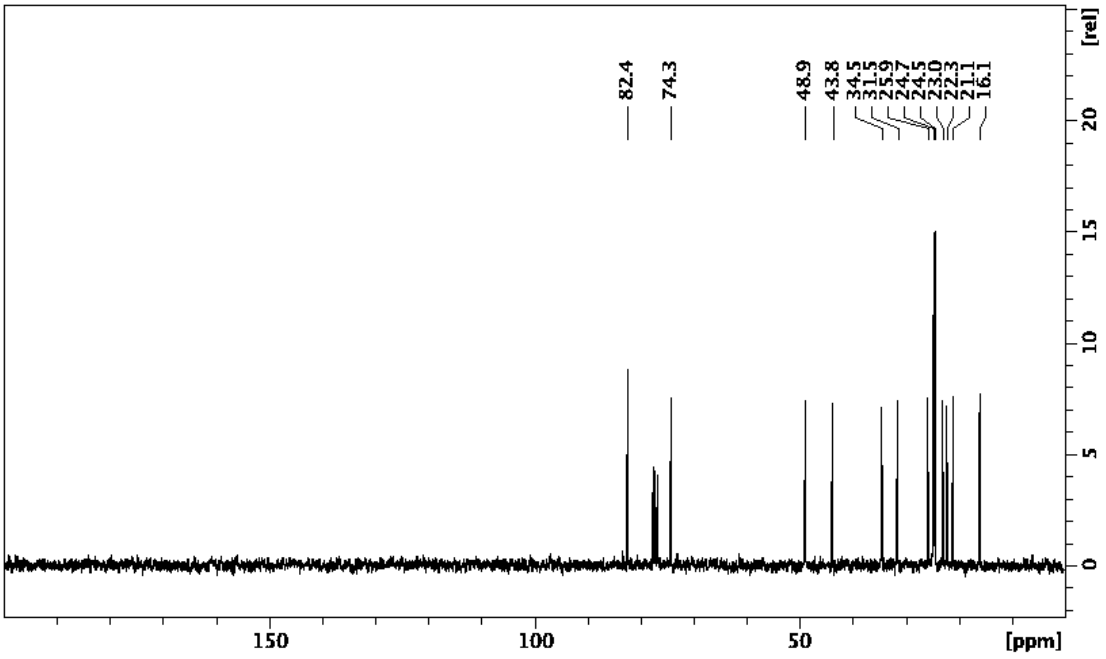
2q


BPin
O
CF3
4.22
4.19
4.17
4.14
1.28
2.0
12.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

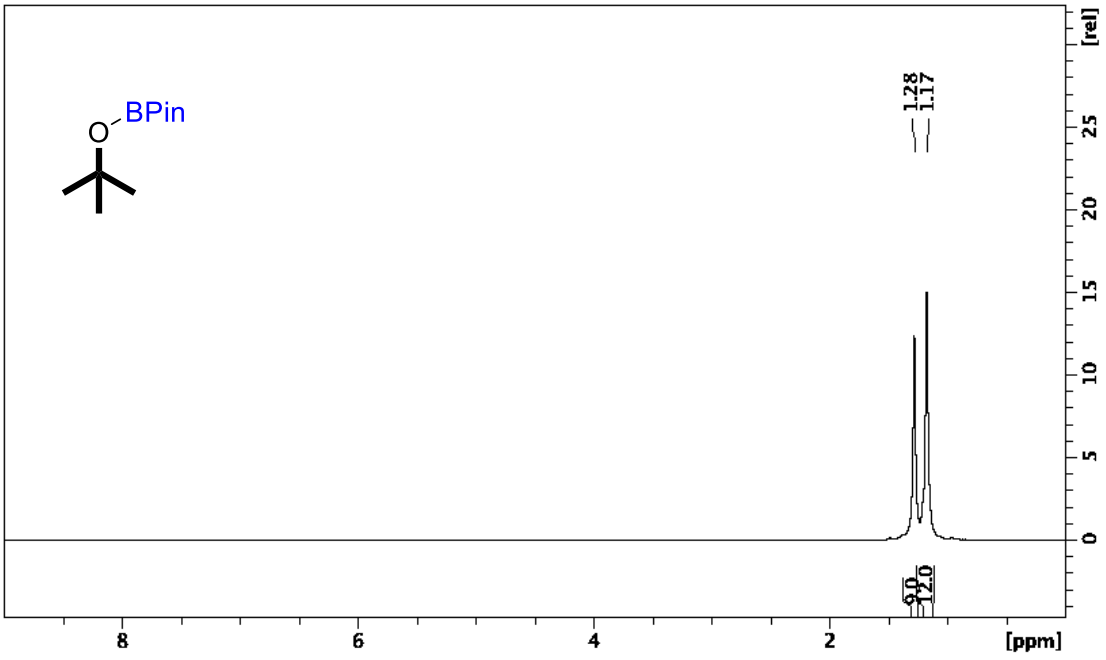

129.2
125.6
121.9
M 118.3
84.0
63.5
63.0
62.6
62.1
24.6
150
100
50
[ppm]
[rel]
0
5
10
15

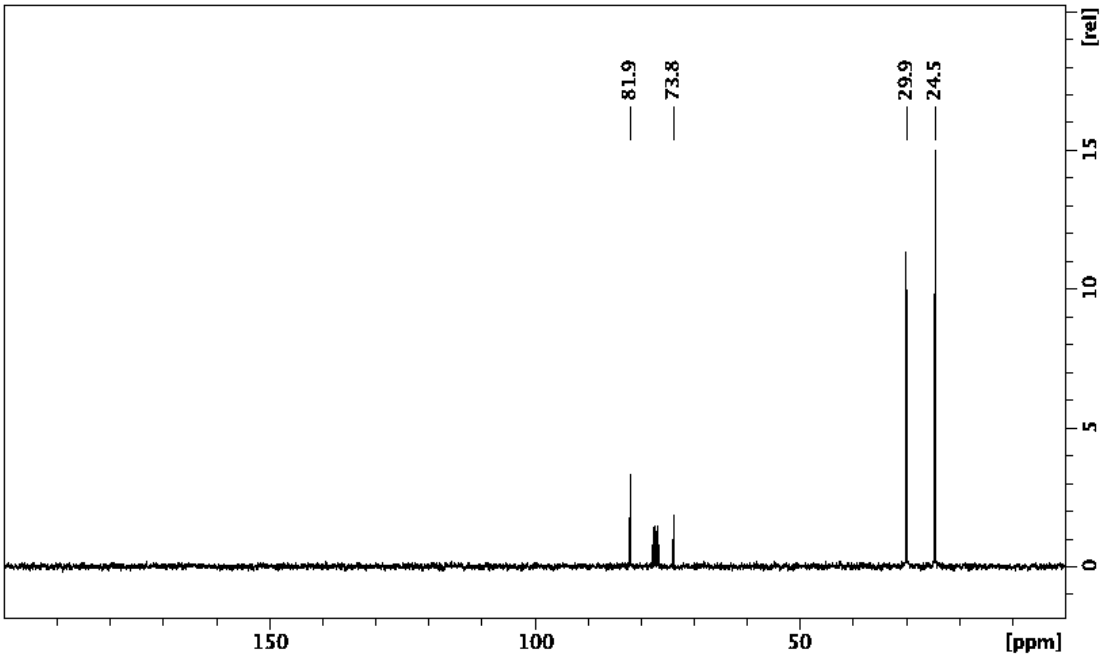
2r


BPin
O
3.83
3.81
3.80
3.78
2.03
2.01
1.92
1.88
1.64
1.60
1.56
1.43
1.22
1.08
1.04
1.01
0.97
0.88
0.77
0.75
1.0
2.0
3.6
12.0
11.9
8
6
4
2
[ppm]
[rel]

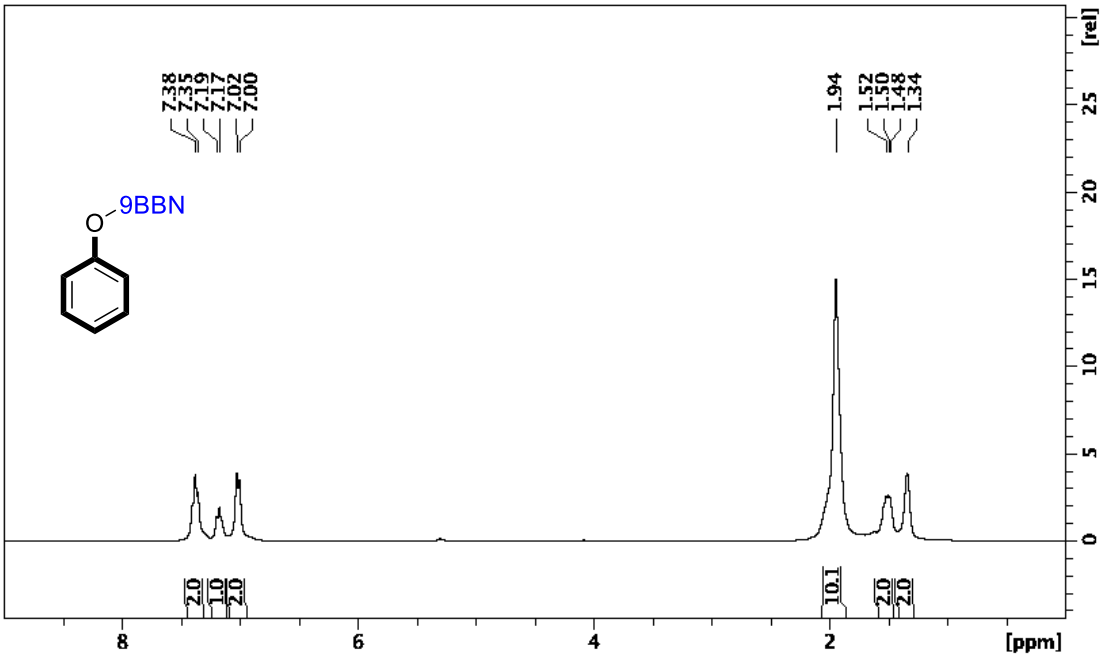

82.4
74.3
48.9
43.8
34.5
31.5
25.9
24.7
24.5
23.0
22.3
21.1
16.1
150
100
50
[ppm]
[rel]

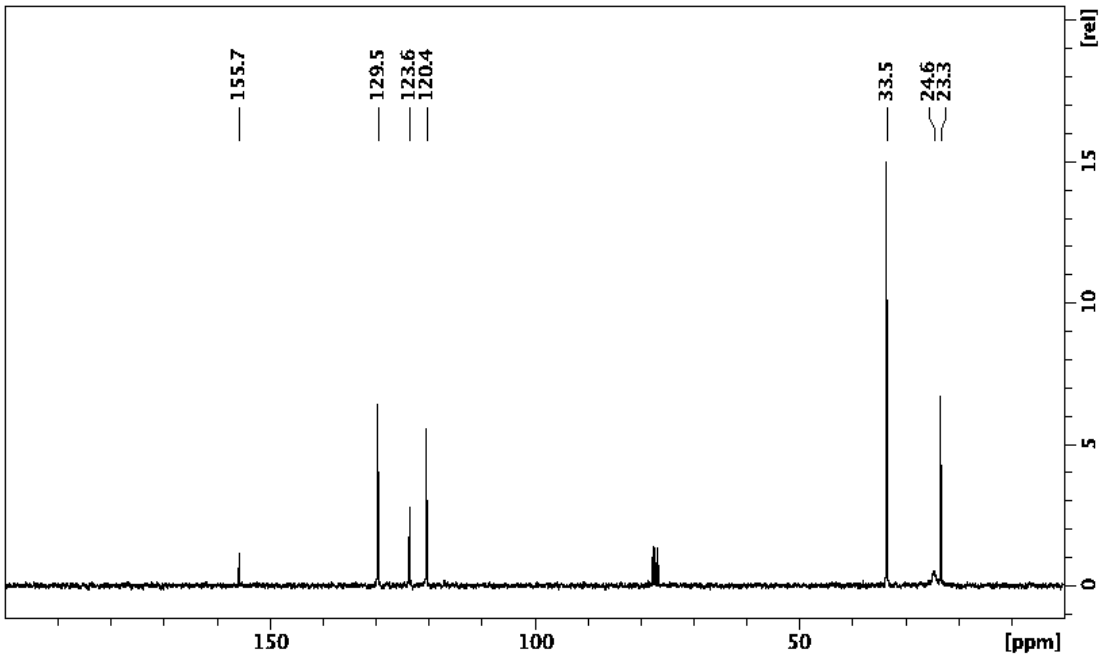
2s


BPin
O
1.28
1.17
9.0
12.0
[rel]
25
20
15
10
5
0
8
6
4
2
[ppm]

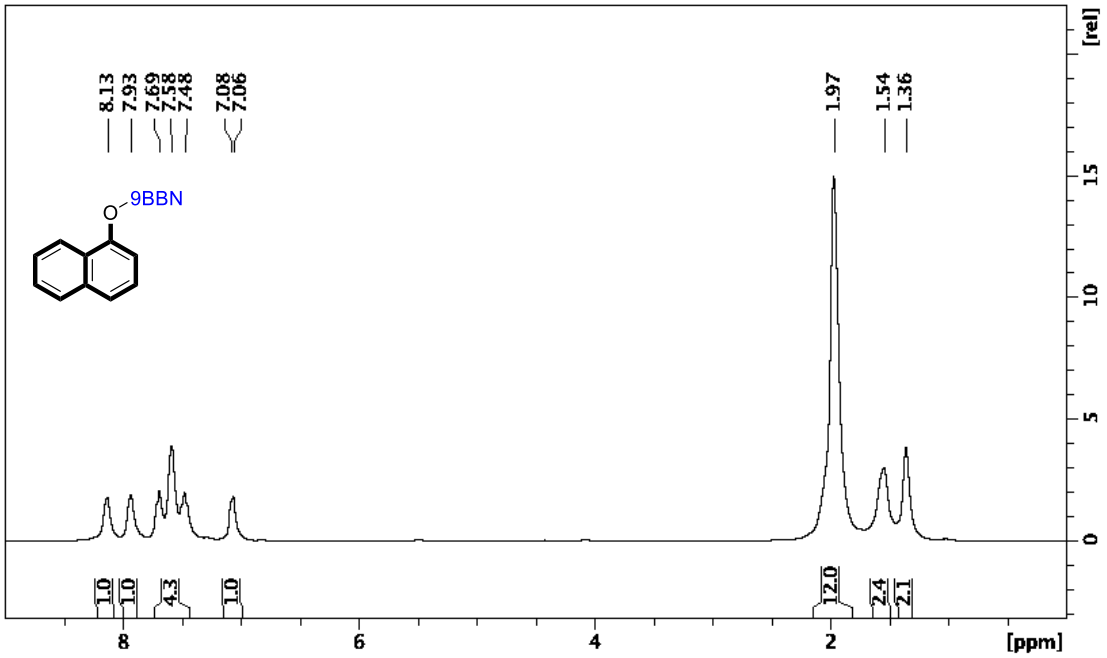

81.9
73.8
29.9
24.5
[rel]
15
10
5
0
150
100
50
[ppm]

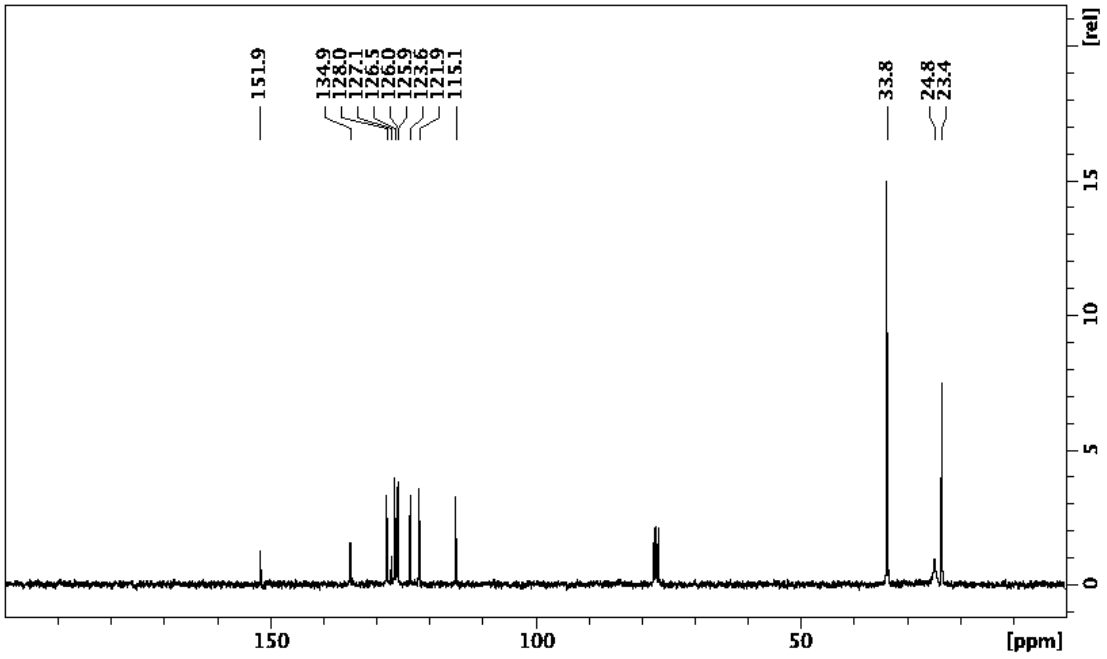
2t


7.38
7.35
7.19
7.17
7.02
7.00
1.94
1.52
1.50
1.48
1.34
9BBN
O
2.0
1.0
2.0
10.1
2.0
2.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20
25

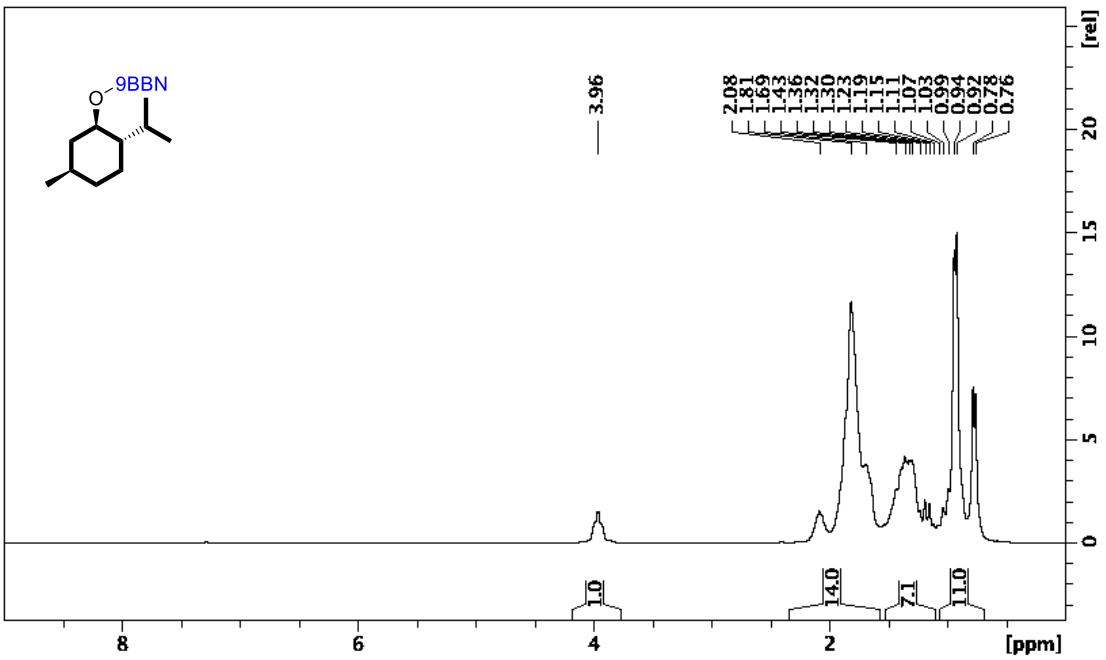

155.7
129.5
123.6
120.4
33.5
24.6
23.3
150
100
50
[ppm]
[rel]
0
5
10
15

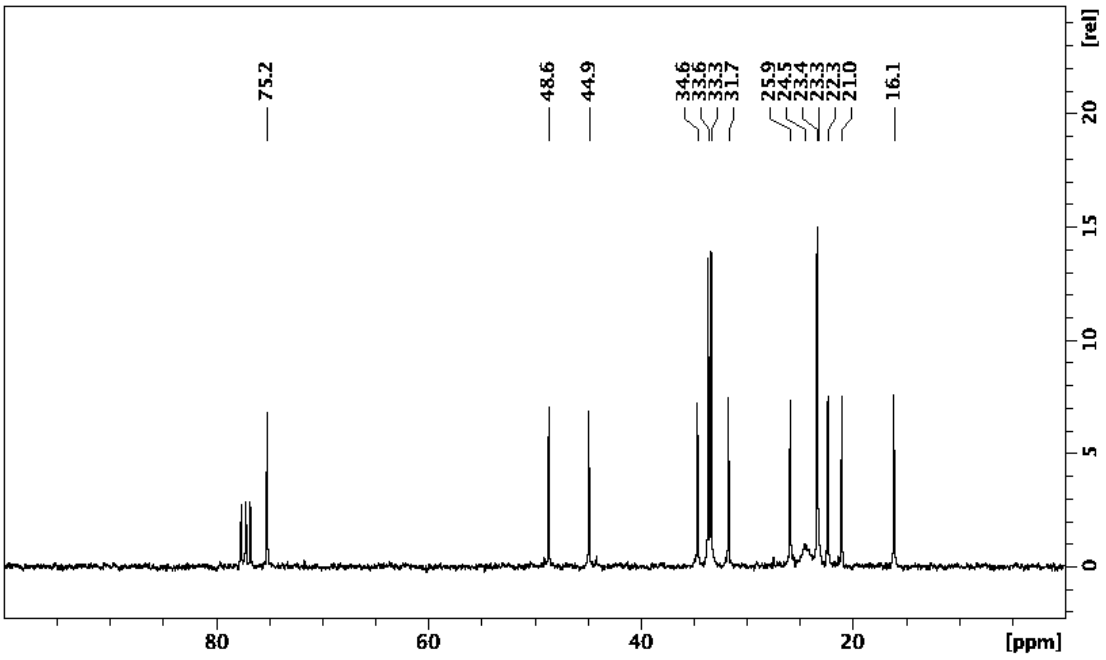
2u


8.13
7.93
7.69
7.58
7.48
7.08
7.06
1.97
1.54
1.36
9BBN
O
1.0
1.0
4.3
1.0
12.0
2.4
2.1
8
6
4
2
[ppm]
[rel]
0
5
10
15

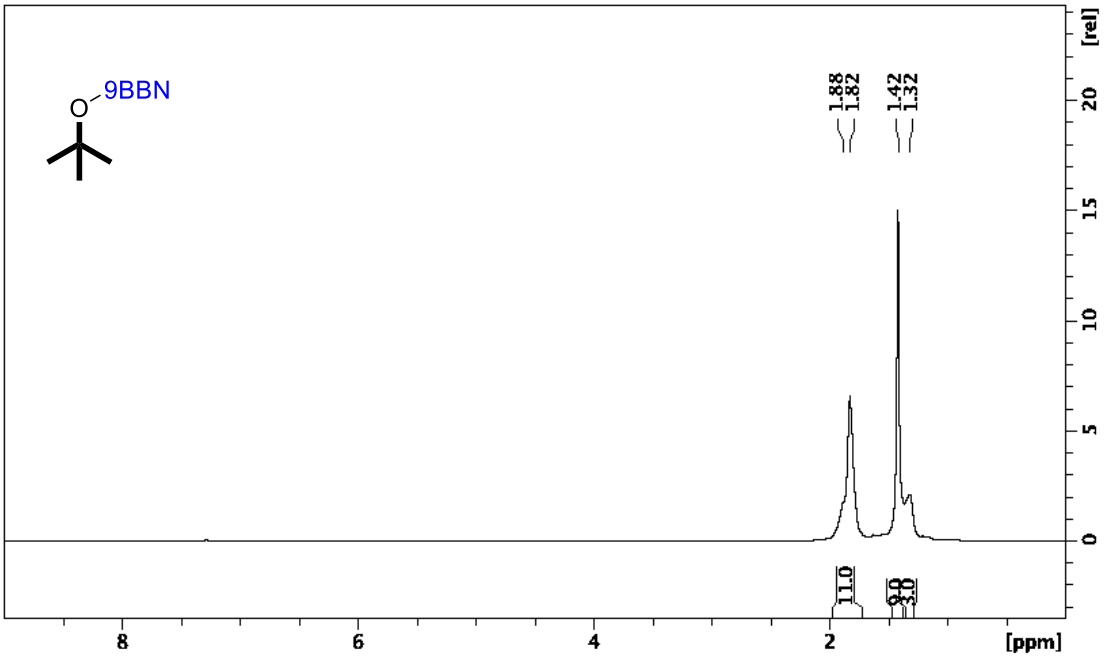

151.9
134.9
128.0
127.1
126.5
126.0
125.9
123.6
121.9
115.1
33.8
24.8
23.4
150
100
50
[ppm]
[rel]
0
5
10
15

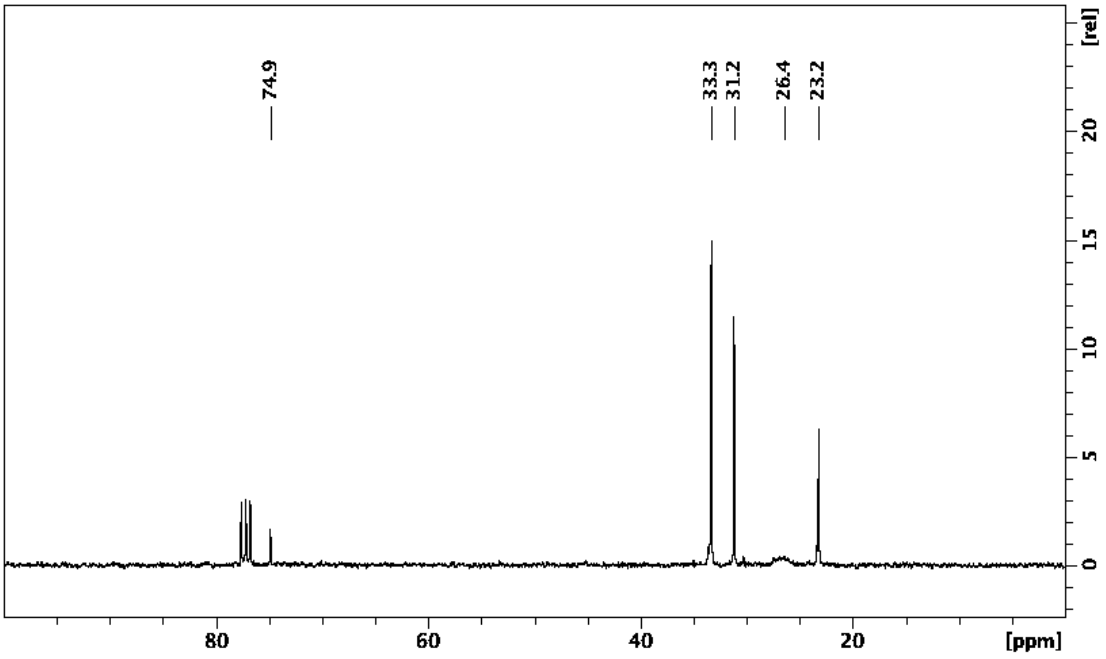
2v


9BBN
O
3.96
2.08
1.81
1.69
1.43
1.36
1.32
1.30
1.23
1.19
1.15
1.11
1.07
1.03
0.99
0.94
0.92
0.78
0.76
1.0
14.0
7.1
11.0
8
6
4
2
[ppm]
[rel]
0
5
10
15
20

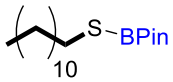

75.2
48.6
44.9
34.6
33.6
33.3
31.7
25.9
24.5
23.4
23.3
22.3
21.0
16.1
80
60
40
20
[ppm]
[rel]
0
5
10
15
20

2w

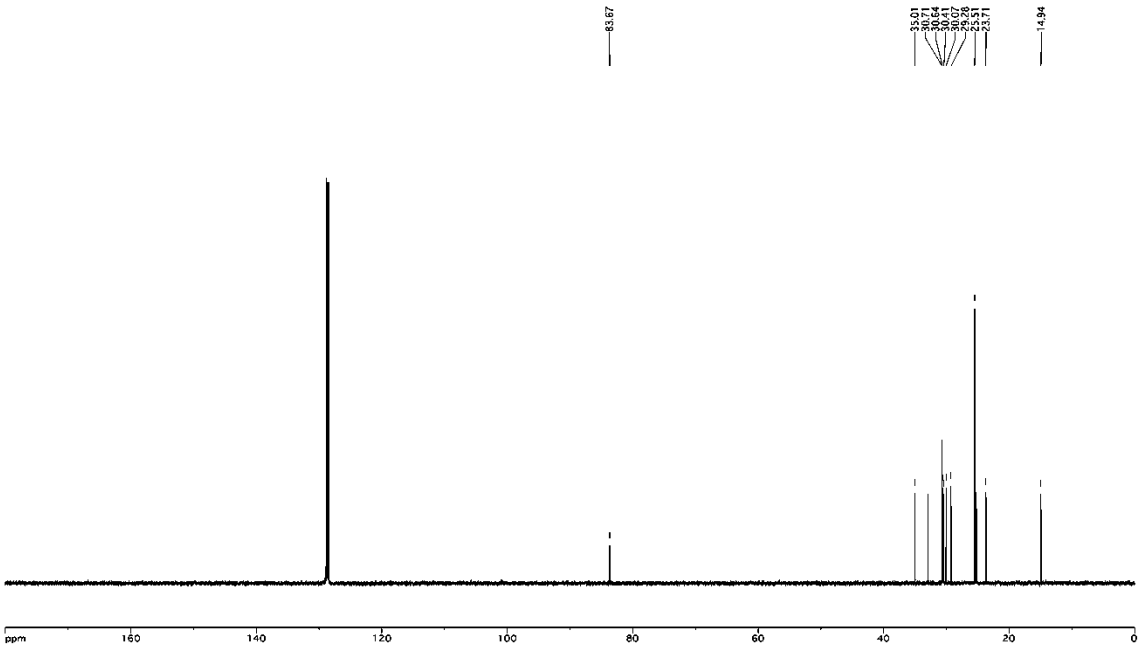




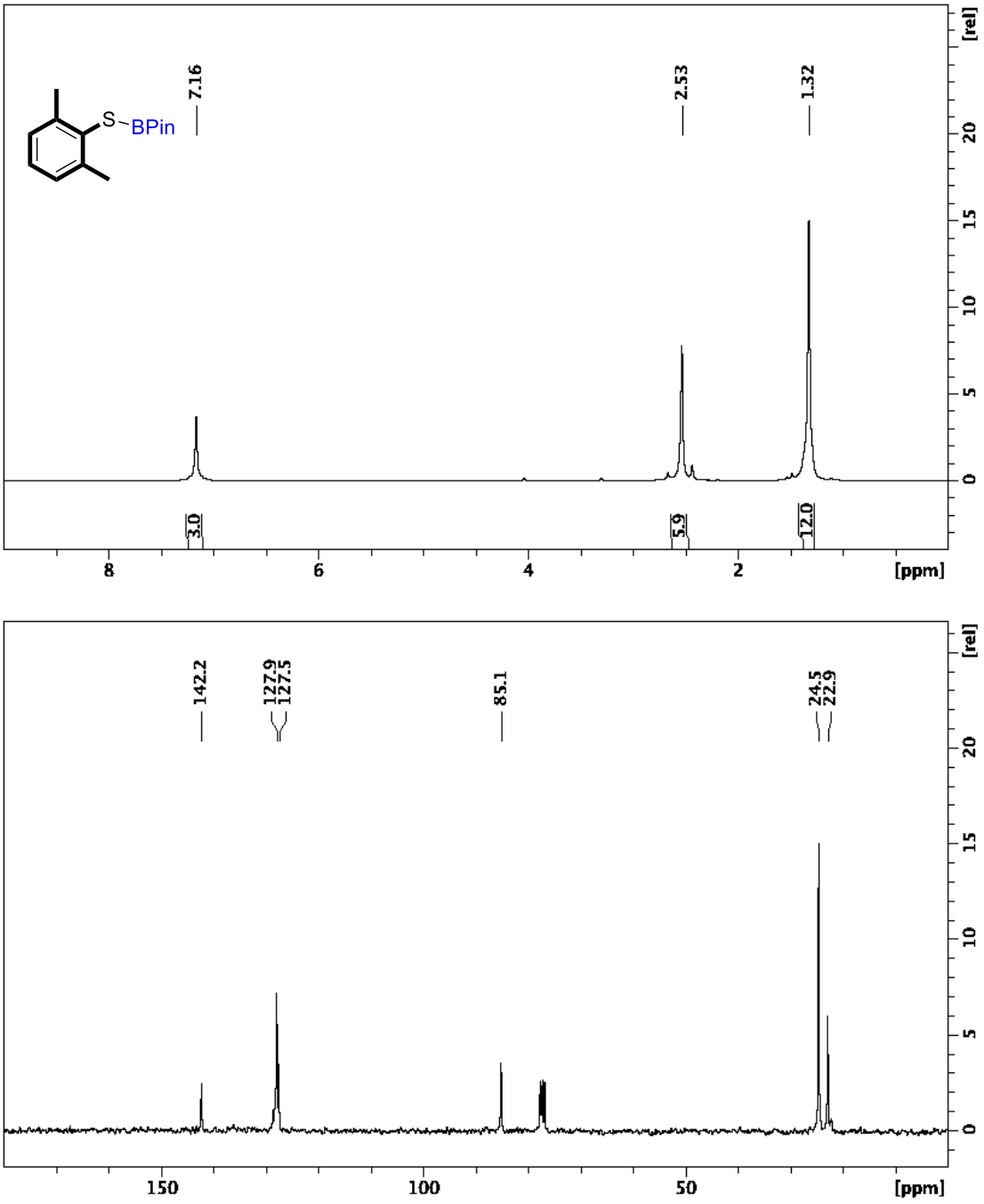
3a


S
BPin
10

2.25
2.23
2.22
2.20
1.42
1.41
1.40
1.39
1.37
1.33
1.17
1.02
0.94
0.93
0.92
2
19
12
3
ppm
7
6
5
4
3
2
1
0


83.67
35.01
30.71
30.64
30.41
30.07
29.97
29.28
25.51
23.71
14.94
ppm
160
140
120
100
80
60
40
20
0

3b


S
BPin
7.16
2.53
1.32
3.0
5.9
12.0
8
6
4
2
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127.9
127.5
85.1
24.5
22.9
150
100
50
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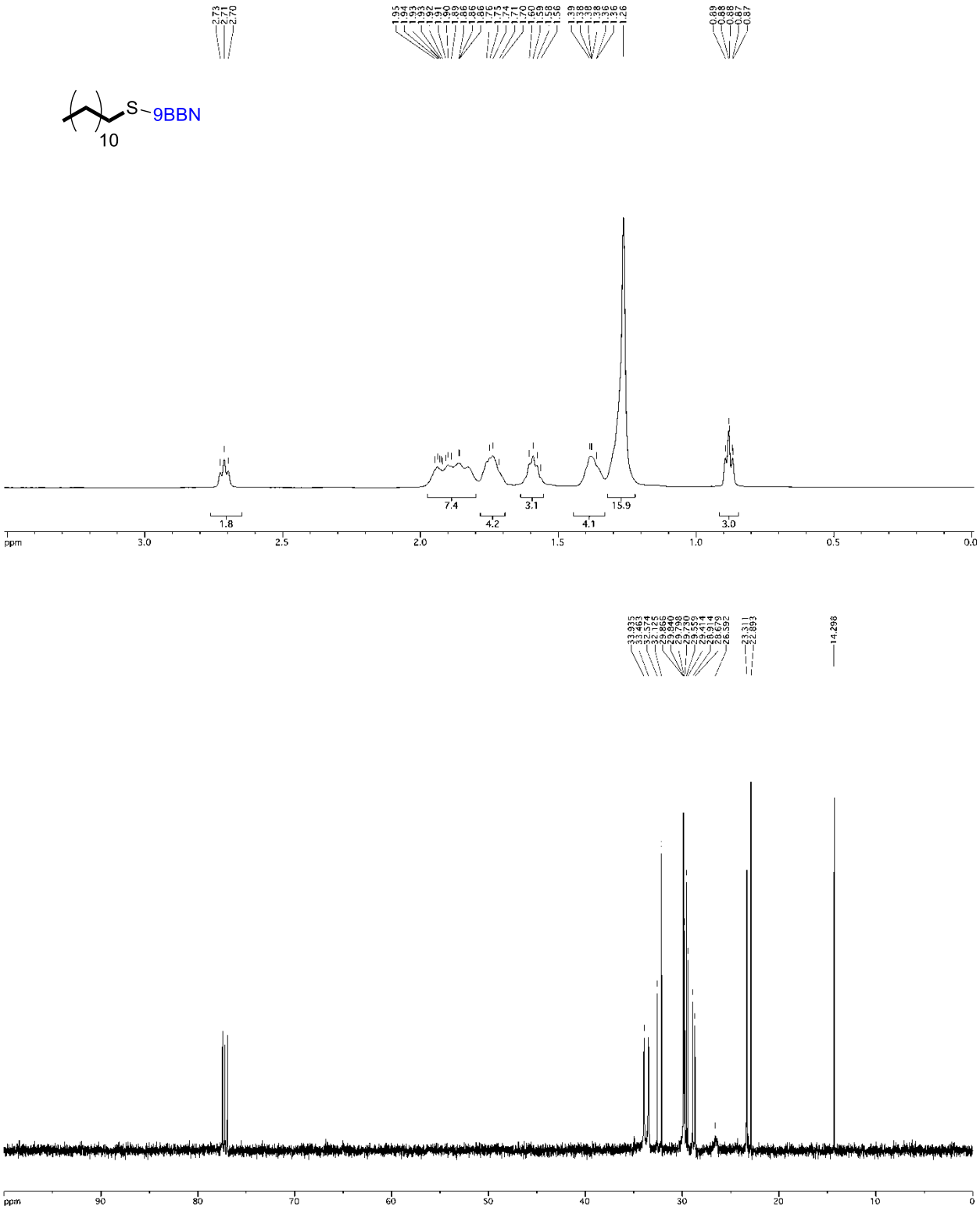
[rel]

3c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1.86
1.76
1.75
1.74
1.74
1.71
1.70
1.60
1.59
1.58
1.56
1.39
1.38
1.38
1.38
1.36
1.26
0.89
0.88
0.88
0.87
0.87
S
9BBN
10
7.4
3.1
15.9
1.8
4.2
4.1
3.0
ppm
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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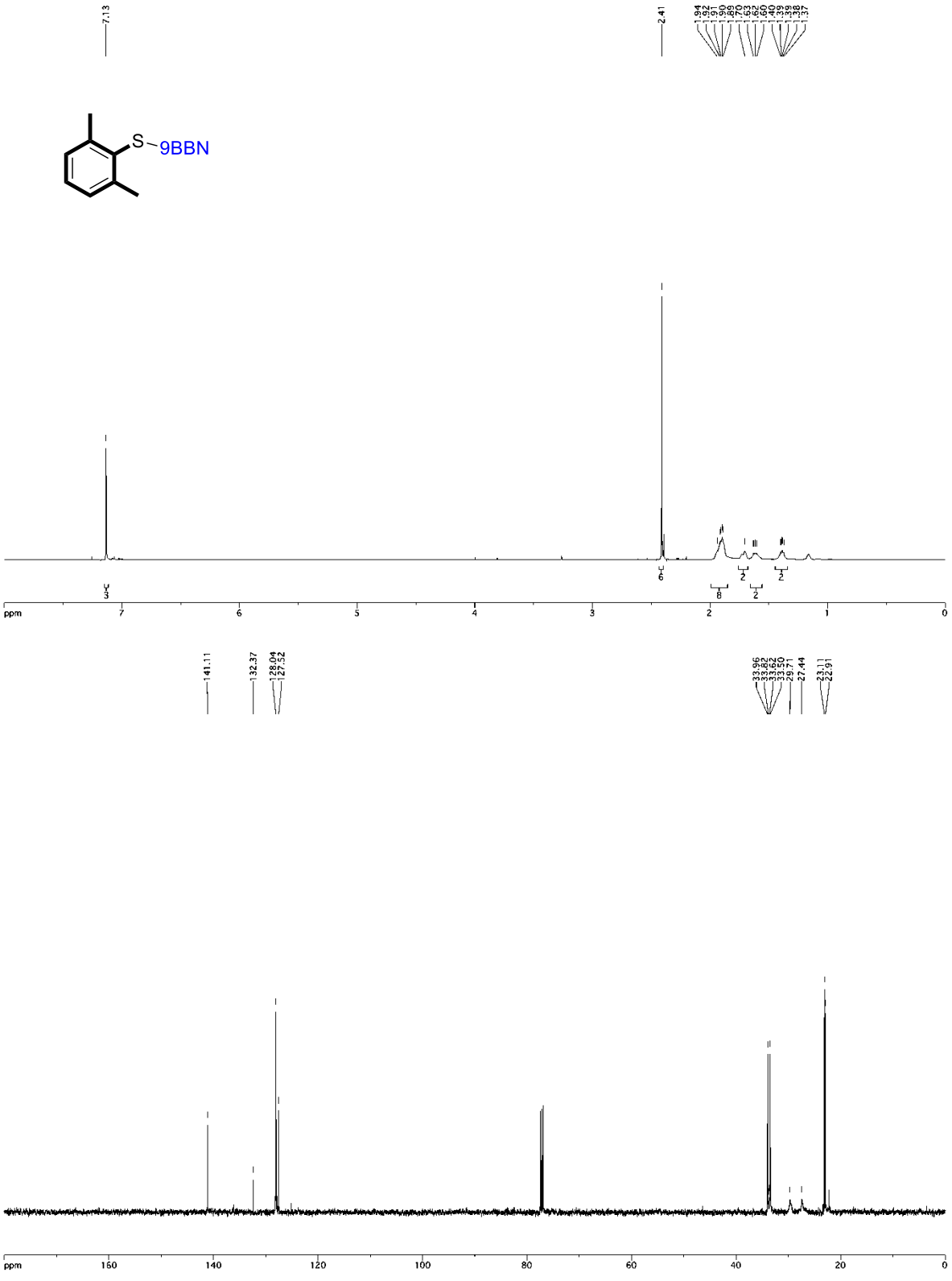
33.462
32.574
32.125
31.866
29.840
29.798
29.730
29.265
29.213
29.014
28.679
28.592
23.311
22.893
14.298
ppm
90
80
70
60
50
40
30
20
10
0

3d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1.92
1.91
1.90
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1.70
1.67
1.62
1.60
1.40
1.39
1.38
1.37
S
9BBN
ppm
141.11
132.37
128.04
127.52
33.96
33.82
33.62
33.50
29.71
27.44
23.11
22.91

I. X-ray

Crystal data and structure refinement for AllylNH2HBPin. CCDC 1489647

Identification code	AllylNH2HBPin
Empirical formula	$C_9H_{20}BNO_2$
Formula weight	185.07
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Iba2
a/Å	10.1195(6)
b/Å	29.385(2)
c/Å	7.4892(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2227.0(2)
Z	8
ρ_{calc}g/cm^3	1.104
μ/mm^{-1}	0.074
F(000)	816.0
Crystal size/mm^3	0.2 × 0.1 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.772 to 56.246
Index ranges	-13 ≤ h ≤ 13, -37 ≤ k ≤ 38, -9 ≤ l ≤ 9
Reflections collected	8760
Independent reflections	2442 [R_{int} = 0.0709, R_{sigma} = 0.0791]
Data/restraints/parameters	2442/1/130
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.0905
Final R indexes [all data]	R_1 = 0.0893, wR_2 = 0.1063
Largest diff. peak/hole / e Å^{-3}	0.19/-0.21
Flack parameter	0.5

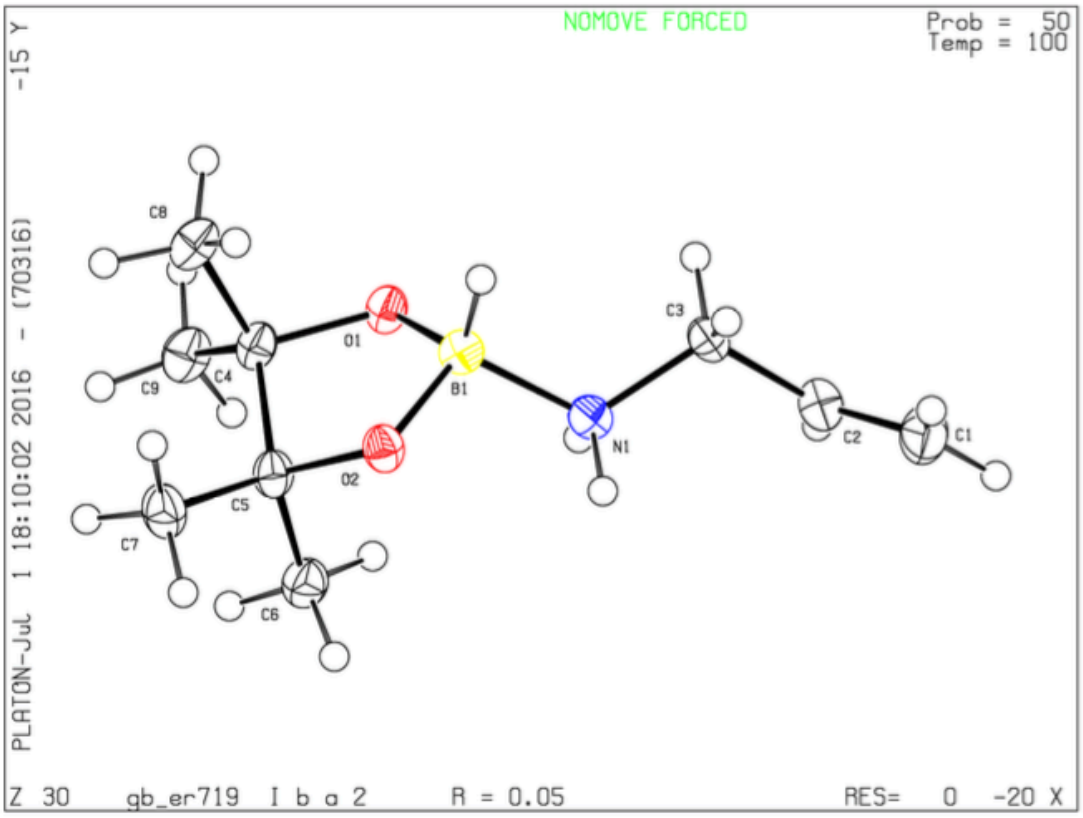

Table 1 Bond Lengths for AllylNH2HBPin.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C4	1.441(4)	C2	C3	1.492(4)
O1	B1	1.463(4)	C4	C5	1.552(4)
O2	C5	1.442(4)	C4	C8	1.531(4)
O2	B1	1.467(4)	C4	C9	1.524(4)
N1	C3	1.493(4)	C5	C6	1.528(4)
N1	B1	1.617(4)	C5	C7	1.512(4)
C1	C2	1.310(5)			

Table 2 Bond Angles for AllylNH2HBPin.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	O1	B1	106.9(2)	C9	C4	C8	109.5(3)
C5	O2	B1	108.6(2)	O2	C5	C4	101.7(2)
C3	N1	B1	116.3(2)	O2	C5	C6	108.4(3)
C1	C2	C3	123.9(3)	O2	C5	C7	108.7(3)
C2	C3	N1	112.1(3)	C6	C5	C4	112.1(3)
O1	C4	C5	102.0(2)	C7	C5	C4	115.2(3)
O1	C4	C8	108.7(2)	C7	C5	C6	110.2(3)
O1	C4	C9	108.7(3)	O1	B1	O2	105.6(3)
C8	C4	C5	112.4(3)	O1	B1	N1	108.4(3)
C9	C4	C5	115.0(2)	O2	B1	N1	109.2(2)