Supporting Information

Direct Hiyama Cross-Coupling of Enaminones With Triethoxy(aryl)silanes and Dimethylphenylsilanol

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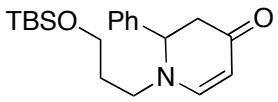
Materials and Methods

Palladium (II) acetate and other chemicals and solvents were commercially available. Flash column chromatography was carried out on silica gel. TLC was conducted on silica gel 250 micron, F254 plates. ^{1}H NMR spectra were recorded at 400 MHz. Chemical shifts are reported in ppm with the solvent as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded at 100 MHz NMR with complete proton decoupling. Chemical shifts are reported in ppm with the solvent as internal standard ($CDCl_3$: 77.2 ppm).

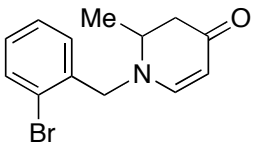
The starting enaminones were prepared using the method reported by Comins.[1] Compound **1f** was prepared according to our previous report.[2] Enaminones **1a**,[2,3] **1b**,[4] **1c**,[2,3] **1f**,[4] **1h**,[1] and 2,3-dihydropyridin-4(1*H*)-one[5] are known compounds and enaminone **1g** is commercially available.

Experimental Procedures



1d

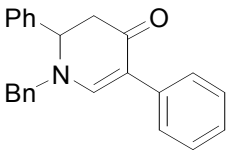
1-(3-(*tert*-Butyldimethylsilyloxy)propyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (1d). Into a solution of 2-phenyl-2,3-dihydropyridin-4(1*H*)-one[3] (450.0 mg, 2.60 mmol) in THF (25 mL) at –78 ºC was added a 1.6 M solution of ^{n}BuLi in hexane (2.0 mL, 3.20 mmol) dropwise under a N_2 atmosphere. After 15 min, (3-bromopropoxy)-*t*ert-butyldimethylsilane (1.2 mL, 5.18 mmol) was dropwise added into the reaction. The reaction was stirred for another 30 min at –78 ºC and then warmed up to room temperature over a course of 24 h. After the solvent was removed under reduced pressure, water (15 mL) was added and then the mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with saturated NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Further purification was carried out by flash column chromatography (60% EtOAc/hexane) to produce 285.0 mg (32%) of **2** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 7.17 (d, *J* = 7.6 Hz, 1H), 5.00 (d, *J* = 7.6 Hz, 1H), 4.60 (t, *J* = 7.4 Hz, 1H), 3.58 (t, *J* = 5.5 Hz, 2H), 3.34–3.22 (m, 1H), 3.20–3.08 (m, 1H), 2.85 (dd, *J* = 16.4, 7.0 Hz, 1H), 2.66 (dd, *J* = 16.4, 7.9 Hz, 1H), 1.71–1.60 (m, 2H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 154.6, 138.9, 129.1, 128.4, 127.0, 98.2, 61.1, 59.3, 50.2, 43.9, 31.5, 26.0, 18.3, -5.3; HRMS (ESI+) calcd for $[M+H]^+$ $C_{20}H_{32}NO_2Si$ 346.2202, found 346.2185.



1e

1-(2-Bromobenzyl)-2-methyl-2,3-dihydropyridin-4(1*H*)-one (1e). 1-(2-Bromobenzyl)pyridin-4(1*H*)-one (1500.0 mg, 5.68 mmol) in dry CH_2Cl_2 (20 mL) was treated with TMSOTf (2.4 mL, 13.26 mmol) at room temperature under a N_2 atmosphere. After the reaction was stirred for 1 h, 2,6-lutidine (1.5 mL, 12.88 mmol) was added, followed by the slow addition of a 3 M solution of methylmagnesium bromide in diethyl ether (4.0 mL, 12.00 mmol) using a syringe pump. The reaction was stirred for another 2 hours and then quenched with saturated NH_4Cl (10 mL). The mixture was extracted with CH_2Cl_2 (10 mL × 4). The combined organic layers were washed with saturated NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Further purification was carried out by flash column chromatography (99% EtOAc with 1% Et_3N) to produce 72.9 mg (5%) of **1e** as a yellow wax. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.39–7.29 (m, 2H), 7.21 (td, *J* = 7.6, 2.0 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 4.97 (d, *J* = 7.5 Hz, 1H), 4.51 (d, *J* = 15.6 Hz, 1H), 4.39 (d, *J* = 15.6 Hz, 1H), 3.69–3.56 (m, 1H), 2.77 (dd, *J* = 16.3, 6.7 Hz, 1H), 2.21 (dd, *J* = 16.3, 3.7 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 152.5, 135.6, 133.6, 130.0, 129.5, 128.1, 123.8, 97.8, 57.1, 52.4, 42.5, 15.0; HRMS (ESI+) calcd for $[M+H]^+$ $C_{13}H_{15}NOBr$ 280.0337, found 280.0335.

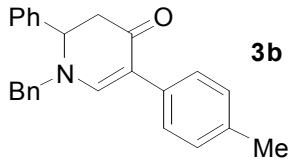
General Procedures for the Palladium (II)-Catalyzed Oxidative Hiyama Coupling of Enaminones. All reactions were run at the 0.2 mmol (enaminone) scale. The suspension of the enaminone (0.2 mmol) and palladium acetate (12 mg, 0.050 mmol) in a mixture of *tert*-butyl alcohol and acetic acid (4:1, 1 mL) were stirred at 65 °C for 15 min. The suspension of the corresponding siloxane (0.5 mmol) and cupric fluoride (252 mg, 0.5 mmol) in a mixture of *tert*-butyl alcohol and acetic acid (4:1, 1 mL) were stirred at room temperature for 30 min. The two suspensions then were mixed and allowed to stir at 65 °C for another 3 h. The reaction mixture was cooled to room temperature, filtered though a silica gel pad, and washed with ethyl acetate. The volatiles were removed *in vacuo*. The crude product was purified by silica gel flash chromatography (hexanes/ethyl acetate) to afford the corresponding title compound.



3a

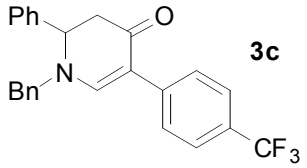
***N*-Benzyl-2,5-diphenyl-2,3-dihydropyridin-4(1*H*)-one (3a). Method A**, refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 56 mg (82%) of the title compound was obtained as an oil. **Method B**, refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with dimethylphenylsilanol (76 mg, 0.50 mmol) and 54 mg (80%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.44 (d, *J* = 8.2

Hz, 2H), 7.35 (m, 13H), 4.57 (t, *J* = 7.4 Hz, 1H), 4.43 (d, *J* = 15.1 Hz, 1H), 4.17 (d, *J* = 14.8 Hz, 1H), 2.97 (dd, *J* = 16.3 Hz, 7.0 Hz, 1H), 2.83 (dd, *J* = 16.1 Hz, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 153.3, 138.4, 136.1, 135.9, 129.1 (2C), 129.0 (2C), 128.5(2C), 128.3, 128.2 (2C), 127.8 (2C), 127.7 (2C), 127.1, 125.8, 111.3, 60.8, 57.7, 44.3; HRMS (ESI) calcd for $C_{24}H_{22}NO$ $[M+1]^+$ 340.1701, found 340.1685.



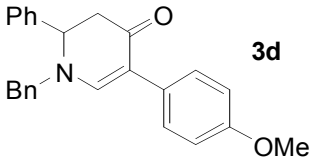
3b

***N*-Benzyl-2-phenyl-5-(4'-tolyl)-2,3-dihydropyridin-4(1*H*)-one (3b).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(4-tolyl)silane (127 mg, 0.500 mmol) and 60 mg (85%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.28 (m, 11H), 7.12 (m, 3H), 4.48 (t, 7.6 Hz, 1H), 4.34 (d, *J* = 15.1 Hz, 1H), 4.12 (d, *J* = 15.1 Hz, 1H), 2.91 (dd, *J* = 16.2 Hz, 6.9 Hz, 1H), 2.75 (dd, *J* = 16.3 Hz, 8.0 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 153.0, 138.5, 135.9, 135.4, 133.0, 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.4, 128.3 (2C), 127.8 (2C), 127.7 (2C), 127.1, 111.4, 60.9, 57.6, 44.3, 21.1; HRMS (ESI) calcd for $C_{25}H_{24}NO$ $[M+1]^+$ 354.1858, found 354.1872.



3c

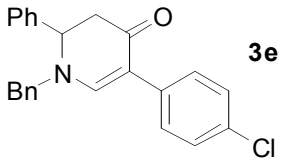
***N*-Benzyl-2-phenyl-5-(4'-(trifluoromethyl)phenyl)-2,3-dihydropyridin-4(1*H*)-one (3c).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(4-(trifluoromethyl)phenyl)silane (154 mg, 0.500 mmol) and 59 mg (73%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.56 (m, 4H), 7.36 (m, 6H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.59 (t, *J* = 7.2 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 4.25 (d, *J* = 15.1 Hz, 1H), 3.02 (dd, *J* = 16.3 Hz, 7.2 Hz, 1H), 2.83 (dd, *J* = 16.3 Hz, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 153.4, 139.7, 138.0, 135.4, 129.2 (2C), 129.1 (2C), 128.6 (2C), 128.5, 127.8 (2C), 127.4 (2C), 126.9 (2C), 125.1, 125.1, 125.0, 109.7, 0.6, 57.9, 44.0; HRMS (ESI) calcd for $C_{25}H_{21}F_3NO$ $[M+1]^+$ 408.1575, found 408.1558.



3d

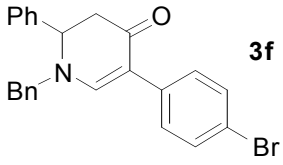
***N*-Benzyl-5-(4'-methoxyphenyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (3d).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(4-methoxyphenyl)silane (135 mg, 0.500 mmol) and 37 mg (50%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.35 (m, 7H), 7.27 (m, 3H), 7.16 (d, *J* =

7.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.55 (t, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 15.1 Hz, 1H), 4.19 (d, *J* = 15.1 Hz, 1H), 3.80 (s, 3H), 2.98 (dd, *J* = 16.3 Hz, 6.9 Hz, 1H), 2.83 (dd, *J* = 16.3 Hz, 8.2 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 157.9, 152.8, 138.5, 135.9, 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.5, 128.4, 128.3, 127.7 (2C), 127.1 (2C), 113.7 (2C), 111.2, 60.9, 57.5, 55.3, 44.3; HRMS (EI) calcd for $C_{25}H_{24}NO_2$ $[M+1]^+$ 370.1807, found 370.1788.



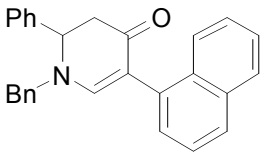
3e

***N*-Benzyl-5-(4'-chlorophenyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (3e).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(4-chlorophenyl)silane (137 mg, 0.500 mmol) and 49 mg (65%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.36 (m, 8H), 7.27 (m, 4H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 7.3 Hz, 1H), 4.44 (d, *J* = 15.1 Hz, 1H), 4.22 (d, *J* = 15.1 Hz, 1H), 2.99 (dd, *J* = 16.3 Hz, 7.1 Hz, 1H), 2.81 (dd, *J* = 16.3 Hz, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 153.1, 138.2, 135.6, 134.5, 131.3 (2C), 129.2 (2C), 129.1 (2C), 128.8, 128.5, 128.4, 128.3 (2C), 127.7 (2C), 127.0 (2C), 110.1, 60.7, 57.8, 44.1; HRMS (ESI) calcd for $C_{24}H_{21}ClNO$ $[M+1]^+$ 374.1312, found 374.1337.



3f

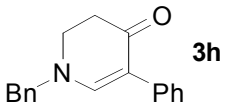
***N*-Benzyl-5-(4'-bromophenyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (3f).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with triethoxy(4-bromophenyl)silane (159 mg, 0.500 mmol) and 51 mg (61%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (dd, *J* = 6.5 Hz, 1.9 Hz, 2H), 7.35 (m, 8H), 7.25 (dd, *J* = 7.4 Hz, 2.0 Hz, 2H), 7.16 (dd, *J* = 7.7 Hz, 2.0 Hz, 2H), 4.56 (t, *J* = 7.3 Hz, 1H), 4.44 (d, *J* = 15.1 Hz, 1H), 4.22 (d, *J* = 15.1 Hz, 1H), 2.99 (dd, *J* = 16.3 Hz, 7.0 Hz, 1H), 2.81 (dd, *J* = 16.3 Hz, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 153.0, 138.1, 135.6, 134.9, 131.2 (2C), 129.1 (2C), 129.1 (2C), 129.0, 128.5, 128.4 (2C), 127.7 (2C), 127.0 (2C), 119.3, 110.0, 60.7, 57.7, 44.1; HRMS (ESI) calcd for $C_{24}H_{21}BrNO$ $[M+1]^+$ 418.0807, found 418. 0782.



3g

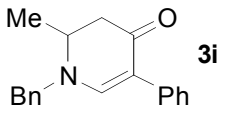
***N*-Benzyl-5-(1'-naphthyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (3g).** Refer to the general procedure. *N*-Benzyl-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (53 mg, 0.20 mmol) was reacted with trimethoxy(1-naphthyl)silane (124 mg, 0.500 mmol) and 34 mg (43%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 3H), 7.34 (m, 13H), 7.16 (d, *J* = 7.6 Hz,

2H), 4.68 (t, *J* = 7.5 Hz, 1H), 4.37 (d, *J* = 14.8 Hz, 1H), 4.20 (d, *J* = 15.1 Hz, 1H), 3.08 (dd, *J* = 16.4 Hz, 7.1 Hz, 1H), 2.94 (dd, *J* = 16.3 Hz, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 135.9, 134.1, 133.9, 129.2 (2C), 129.1 (2C), 129.0, 128.5, 128.4, 128.3 (2C), 127.9, 127.8, 127.7(2C), 127.2, 127.1, 126.2, 125.8, 125.7, 125.6, 125.5 (2C), 61.0, 57.6, 44.2; HRMS (ESI) calcd for $C_{28}H_{24}NO$ $[M+1]^+$ 390.1858, found 390.1872.



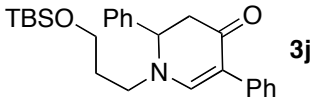
3h

***N*-Benzyl-5-phenyl-2,3-dihydropyridin-4(1*H*)-one (3h).** Refer to the general procedure. *N*-Benzyl-2,3-dihydropyridin-4(1*H*)-one (37 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 33 mg (62%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 4H), 7.32 (m, 5H), 7.17 (t, *J* = 7.3 Hz, 2H), 4.43 (s, 2H), 3.44 (t, *J* = 7.7 Hz, 2H), 2.60 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 153.2, 136.3 (2C), 135.7, 129.1 (2C), 128.4 (2C), 128.2, 127.8, 127.7 (2C), 125.7, 111.2, 60.2, 46.8, 36.3; HRMS (ESI) calcd for $C_{18}H_{18}NO$ $[M+1]^+$ 264.1388, found 264.1370.



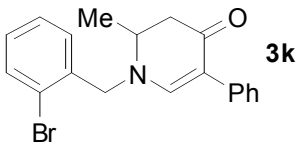
3i

***N*-Benzyl-2-methyl-5-phenyl-2,3-dihydropyridin-4(1*H*)-one (3i).** Refer to the general procedure. *N*-Benzyl-2-methyl-2,3-dihydropyridin-4(1*H*)-one (40 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 45 mg (81%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4H), 7.25 (m, 6H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.37 (dd, *J* = 25.8 Hz, 15.3 Hz, 2H), 3.55 (m, 1H), 2.76 (dd, *J* = 16.1 Hz, 6.5 Hz, 1H), 2.28 (dd, *J* = 16.0 Hz, 4.8 Hz, 1H), 1.18 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 150.6, 135.3, 128.0 (2C), 127.3, 127.1 (2C), 126.5, 126.4 (2C), 126.3 (2C), 124.5, 108.8, 56.5, 50.9, 42.1, 14.3; HRMS (ESI) calcd for $C_{19}H_{20}NO$ $[M+1]^+$ 278.1545, found 278.1561.



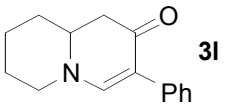
3j

***N*-(3'-((*tert*-Butyldimethylsilyl)oxy)propyl)-2,5-diphenyl-2,3-dihydropyridin-4(1*H*)-one (3j).** Refer to the general procedure. *N*-(3'-((*tert*-Butyldimethylsilyl)oxy)propyl)-2-phenyl-2,3-dihydropyridin-4(1*H*)-one (69 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 63 mg (75%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.31 (m, 7H), 7.15 (dd, *J* = 13.4 Hz, 7.4 Hz, 1H), 4.67 (t, *J* = 7.4 Hz, 1H), 3.63 (t, *J* = 5.5 Hz, 2H), 3.38 (m, 1H), 3.24 (m, 1H), 3.02 (dd, *J* = 16.2 Hz, 6.9 Hz, 1H), 2.82 (dd, *J* = 16.2 Hz, 7.8 Hz, 1H), 1.71 (m, 2H), 0.84 (s, 9H), -0.01 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 153.7, 138.6, 136.2, 129.1(2C), 128.3, 128.2 (2C), 127.5(2C), 126.9 (2C), 125.6, 110.7, 61.2, 59.2, 50.5, 44.3, 31.5, 25.8 (3C), 18.2, -5.4 (2C); HRMS (ESI) calcd for $C_{26}H_{36}NO_2Si$ $[M+1]^+$ 422.2515, found 422.2501.



3k

***N*-(2'-Bromobenzyl)-2-methyl-5-phenyl-2,3-dihydropyridin-4(1*H*)-one (3k).** Refer to the general procedure. *N*-(2'-Bromo)benzyl-2-methyl-2,3-dihydropyridin-4(1*H*)-one (56 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 48 mg (68%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.38 (m, 4H), 7.31 (m, 4H), 7.20 (m, 1H), 4.53 (dd, *J* = 37.6 Hz, 15.5 Hz, 2H), 3.66 (m, 1H), 2.91 (dd, *J* = 16.1 Hz, 6.6 Hz, 1H), 2.37 (dd, *J* = 16.0 Hz, 3.8 Hz, 1H), 1.27 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 151.6, 136.2, 135.3, 133.6, 130.0, 129.6, 128.2 (2C), 128.0, 127.6 (2C), 125.6, 123.9, 110.2, 57.5, 52.5, 43.0, 15.3; HRMS (ESI) calcd for $C_{19}H_{19}BrNO$ $[M+1]^+$ 356.0650, found 356.0636.

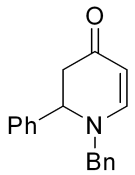


3l

3-Phenyl-7,8,9,9a-tetrahydro-1*H*-quinolizin-2(6*H*)-one (3l). Refer to the general procedure. 7,8,9,9a-Tetrahydro-1*H*-quinolizin-2(6*H*)-one (30 mg, 0.20 mmol) was reacted with triethoxy(phenyl)silane (120 mg, 0.500 mmol) and 33 mg (72%) of the title compound was obtained as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.05 (s, 1H), 6.85 (m, 3H), 3.41 (m, 1H), 3.36 (m, 1H), 3.01 (dt, *J* = 2.6, 6.3 Hz, 1H), 2.58 (m, 1H), 2.51 (m, 1H), 1.80 (m, 3H), 1.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 156.5, 152.9, 128.9 (2C), 128.1, 127.7 (2C), 105.4, 54.9, 51.7, 41.4, 29.8, 23.8, 20.8; HRMS (ESI) cal'd for $C_{15}H_{18}NO$ $[M+1]^+$ 228.1388, found 228.1400.

References:

(1) Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* **1986**, *27*, 4549-4552.
(2) Klegraf, E.; Follmann, M.; Schollmeyer, D.; Kunz, H. *Eur. J. Org. Chem.* **2004**, 3346-3360.
(3) Turunen, B. J.; Georg, G. I. *J. Am. Chem. Soc.* **2006**, *128*, 8702-8703.
(4) Guerry, P.; Neier, R. *Synthesis* **1984**, 485-488.
(5) Jones, T. N.; McClure, C. K. *Synlett* **2009**, 1289-1290.



1a

lb3209-Jul10 1 1 C:\Bruker\TOPSPIN leibi

Ph N-Bn enaminone

[*1e6]

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400

200

0

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4.9879 4.9689

4.4079 4.3892 4.3704 4.2617 4.2240 4.0278 3.9900

2.7595 2.7418 2.7183 2.7006 2.5952 2.5753 2.5540 2.5342

6.8285 1.9848 2.0182

0.9360

0.9675 0.9917 1.0101

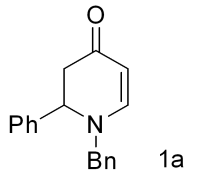
0.9989 1.0000

6

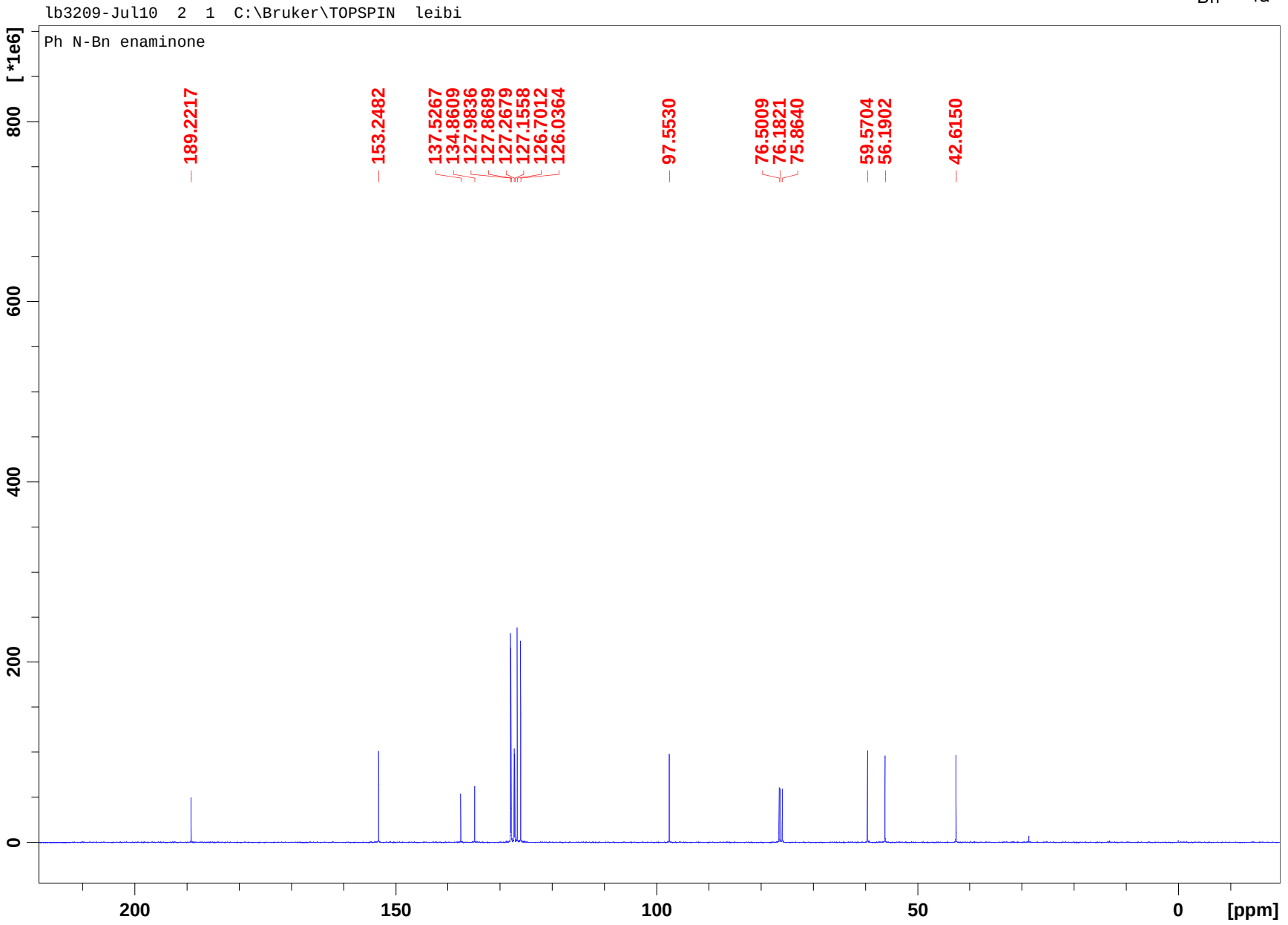
4

2

[ppm]


O
Ph
N
Bn

1a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126.7012
126.0364
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50
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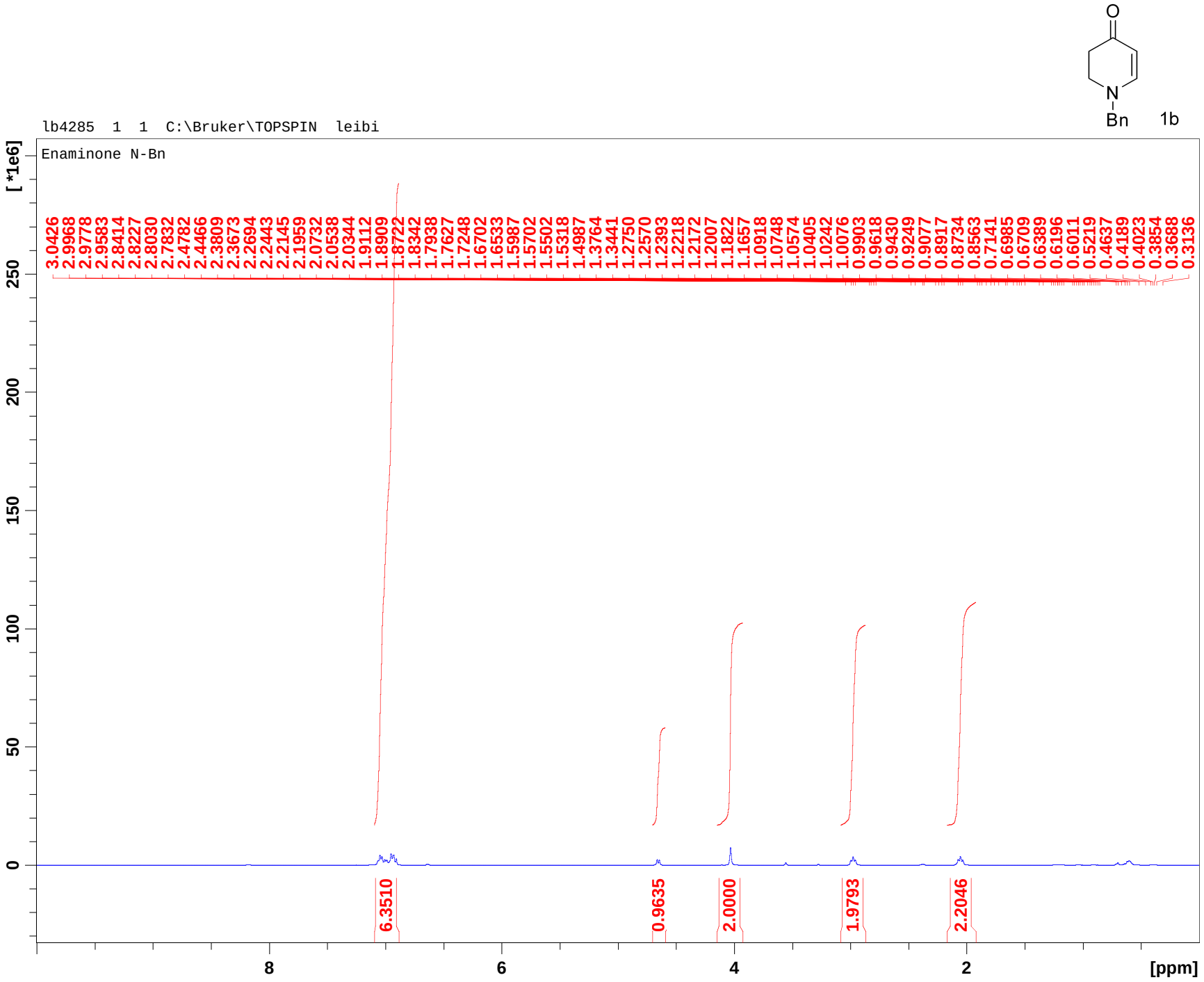
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N
Bn
1b
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2.8227
2.8030
2.7832
2.4782
2.4466
2.3809
2.3673
2.2694
2.2443
2.2145
2.1959
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2.0538
2.0344
1.9112
1.8909
1.8722
1.8342
1.7938
1.7627
1.7248
1.6702
1.6533
1.5987
1.5702
1.5502
1.5318
1.4987
1.3764
1.3441
1.2750
1.2570
1.2393
1.2218
1.2172
1.2007
1.1822
1.1657
1.0918
1.0748
1.0574
1.0405
1.0242
1.0076
0.9903
0.9618
0.9430
0.9249
0.9077
0.8917
0.8734
0.8563
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0.6389
0.6196
0.6011
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0.4023
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2.2046
8
6
4
2
[ppm]


lb4285 2 1 C:\Bruker\TOPSPIN leibi
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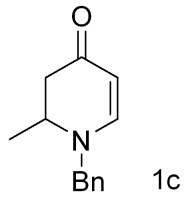
N
Bn
1b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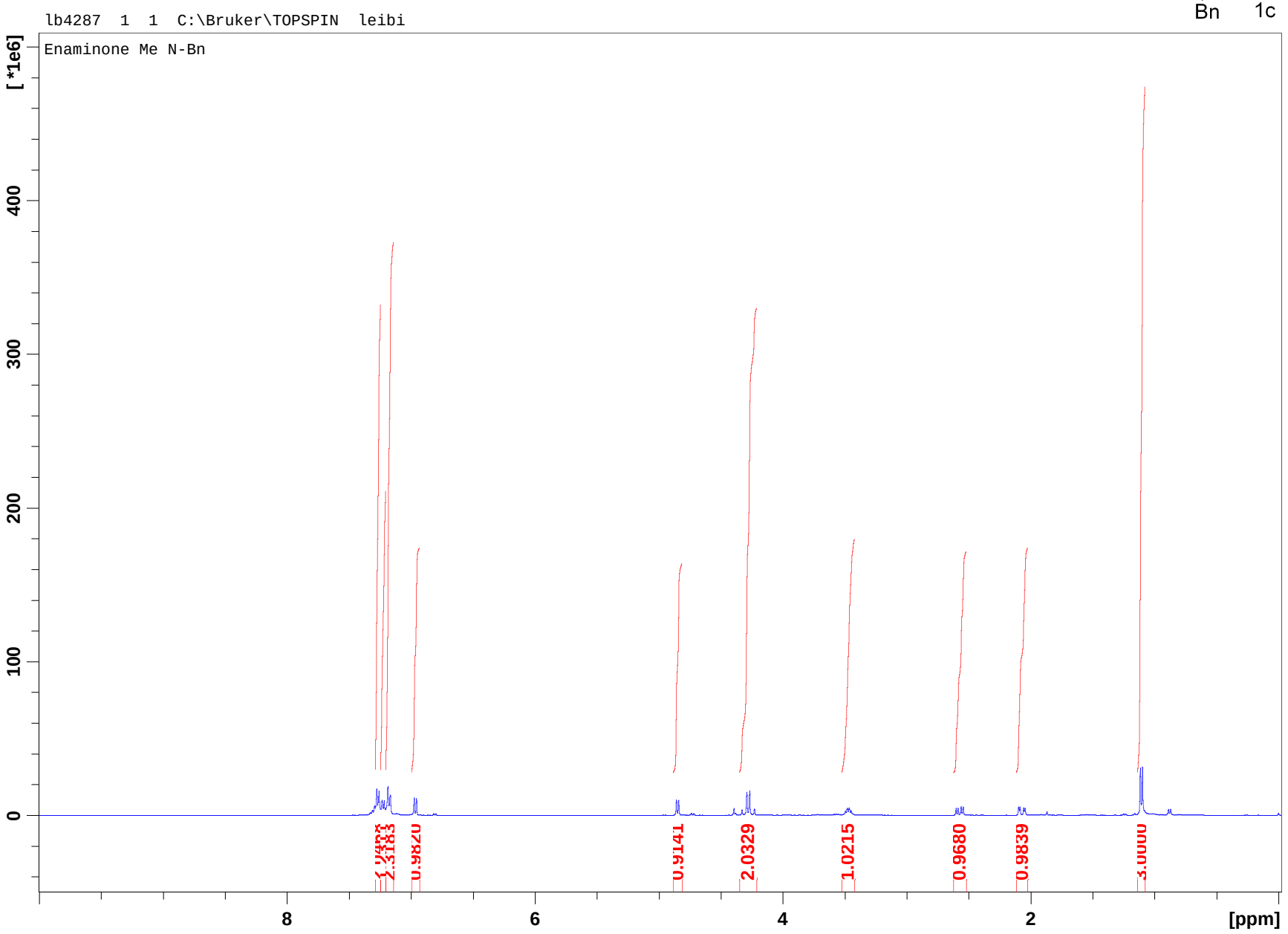
Bn

1c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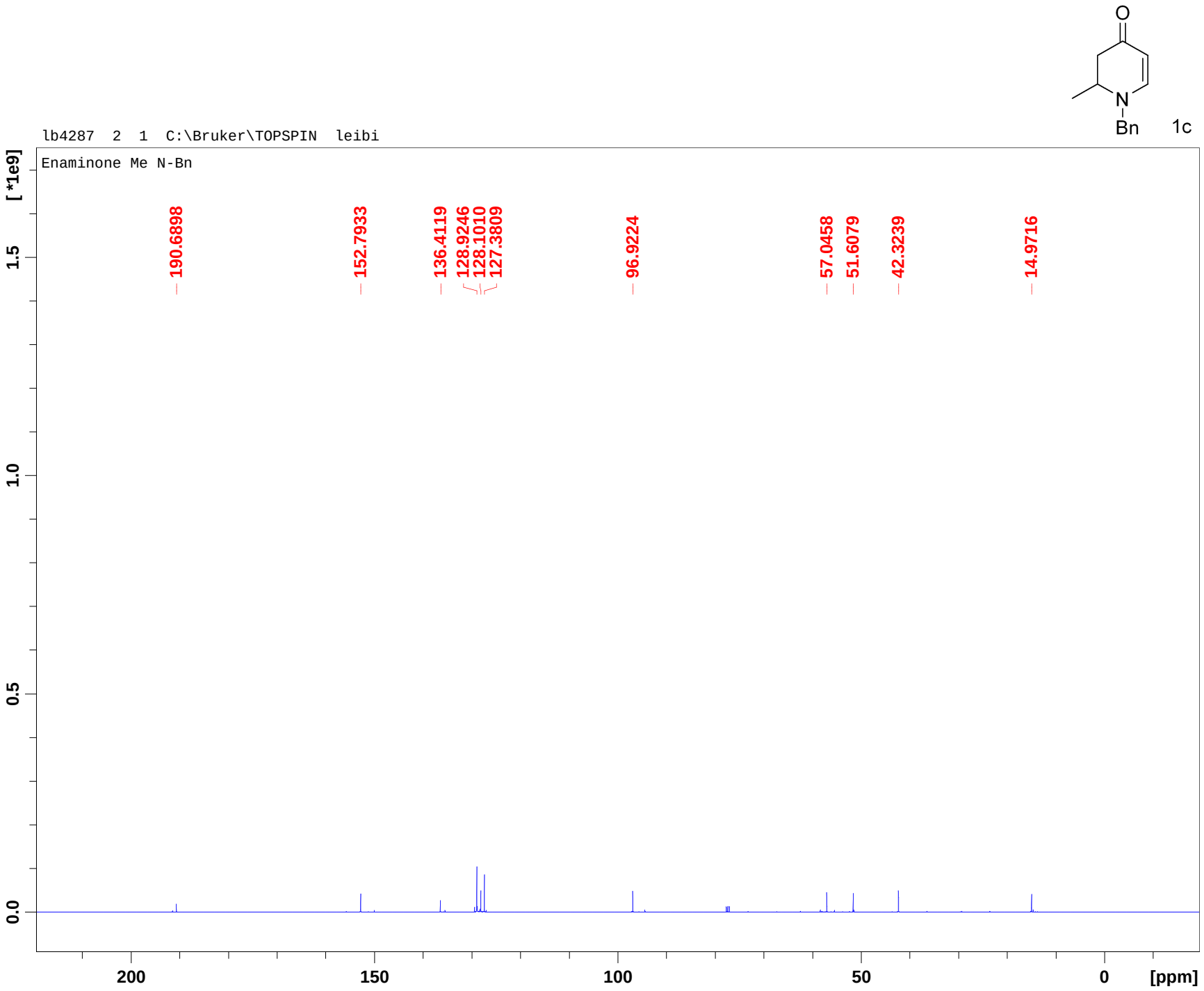
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N
Bn
1c
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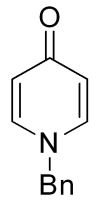
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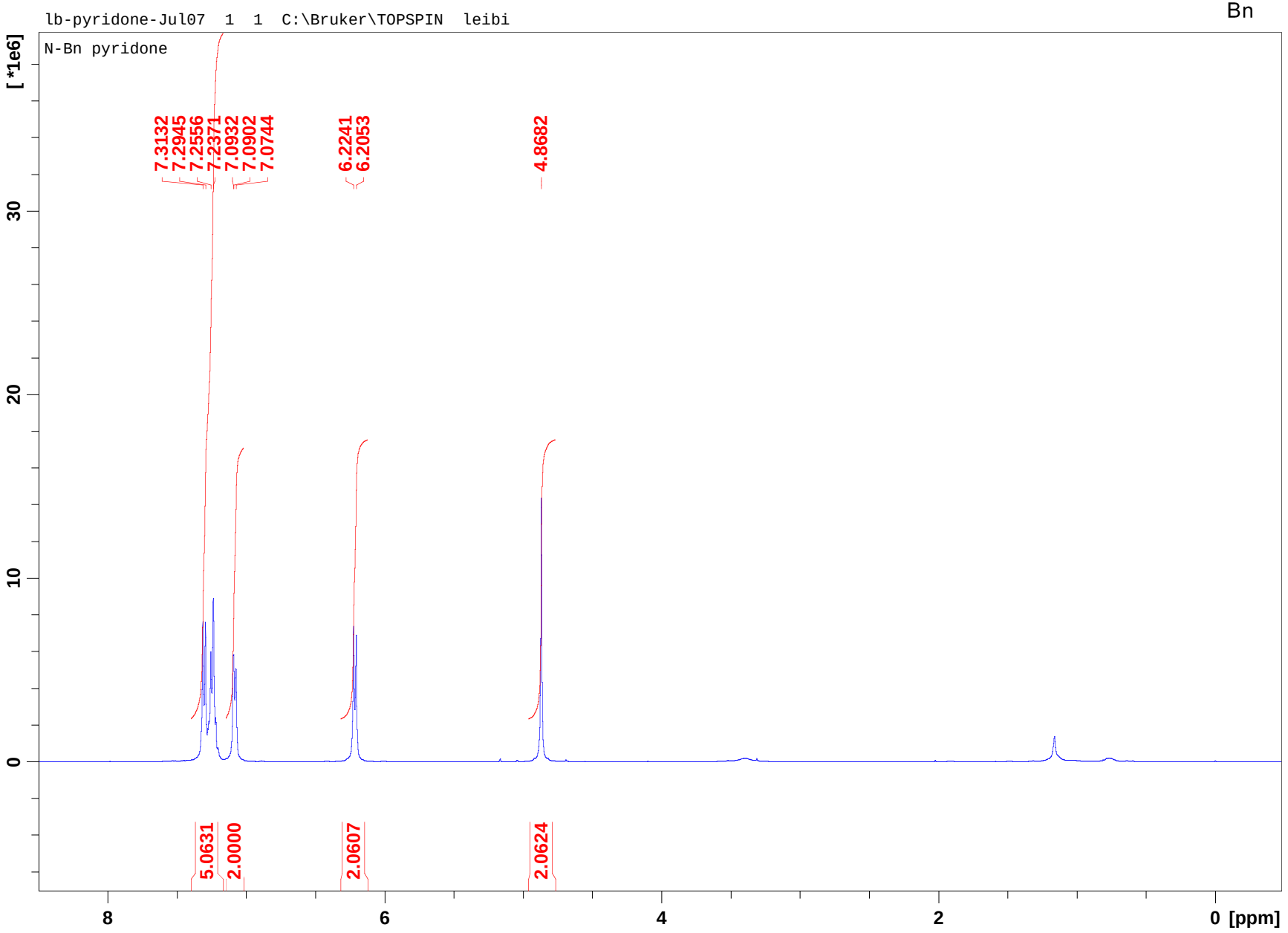
N
Bn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4.8682
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4
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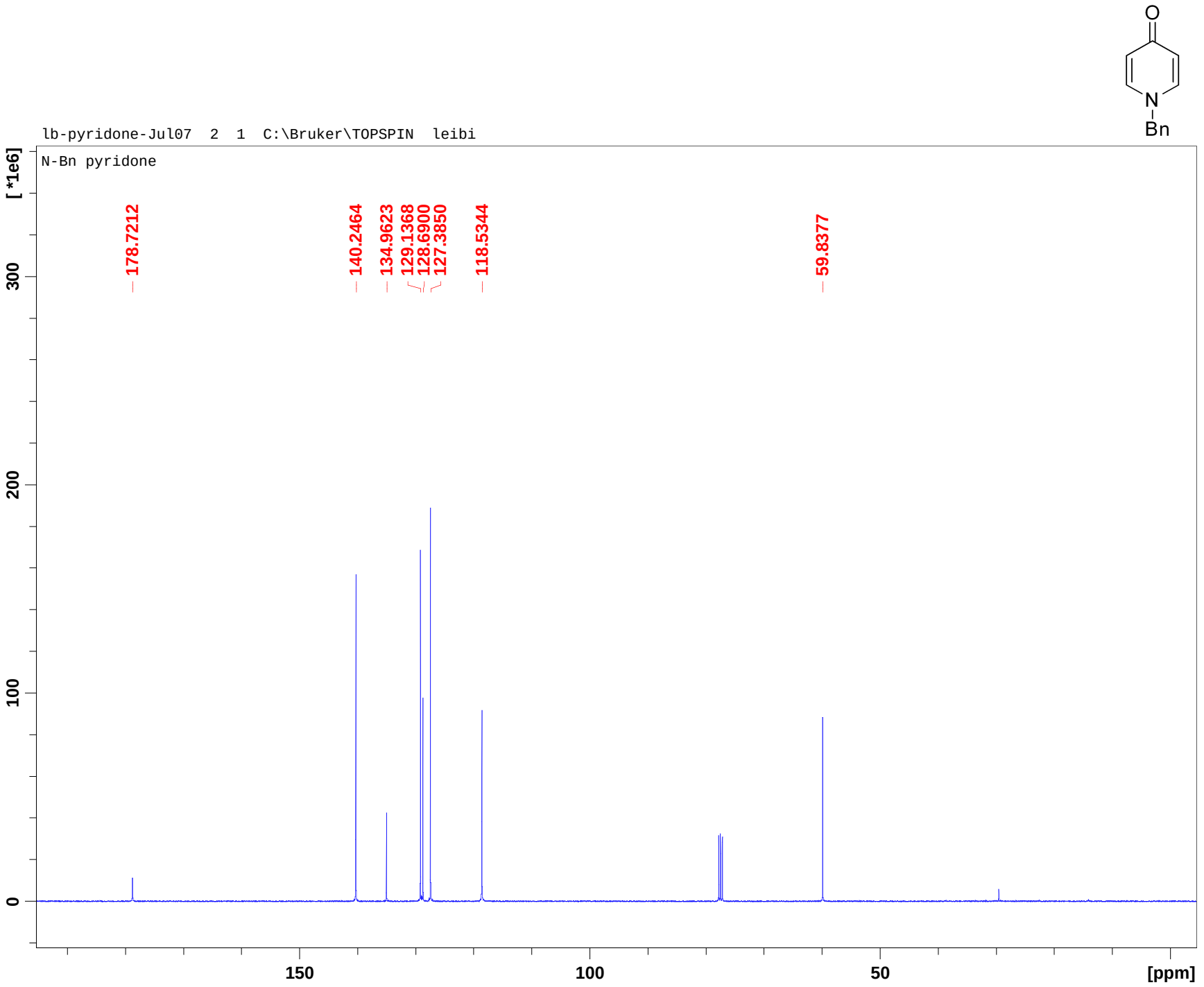
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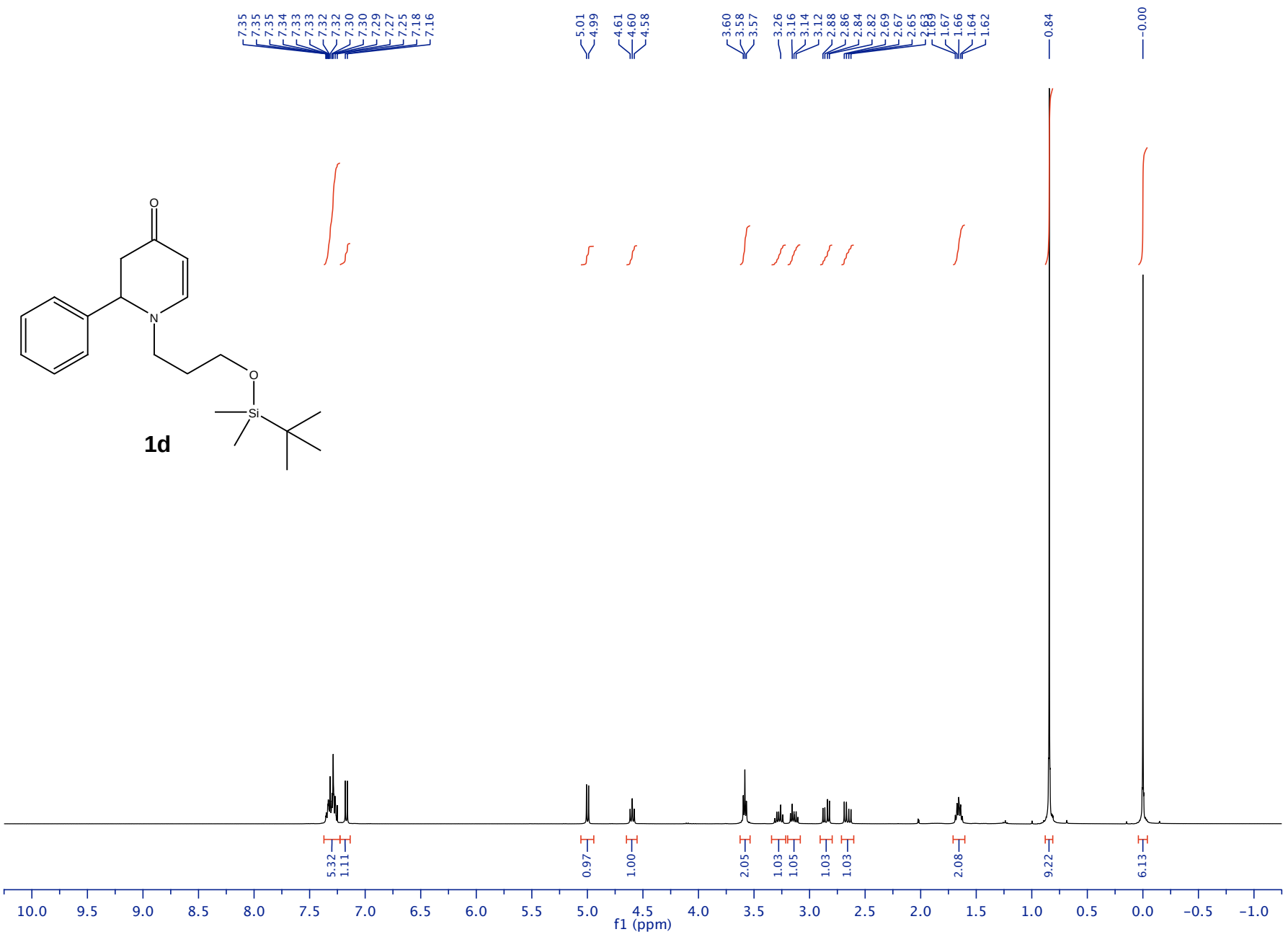
O
N
Bn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7.27
7.25
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7.16
5.01
4.99
4.61
4.60
4.58
3.60
3.58
3.57
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3.16
3.14
3.12
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2.84
2.82
2.69
2.67
2.65
1.67
1.66
1.64
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O
N
O
Si
1d
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0.97
1.00
2.05
1.03
1.05
1.03
1.03
2.08
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6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
4.0
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2.0
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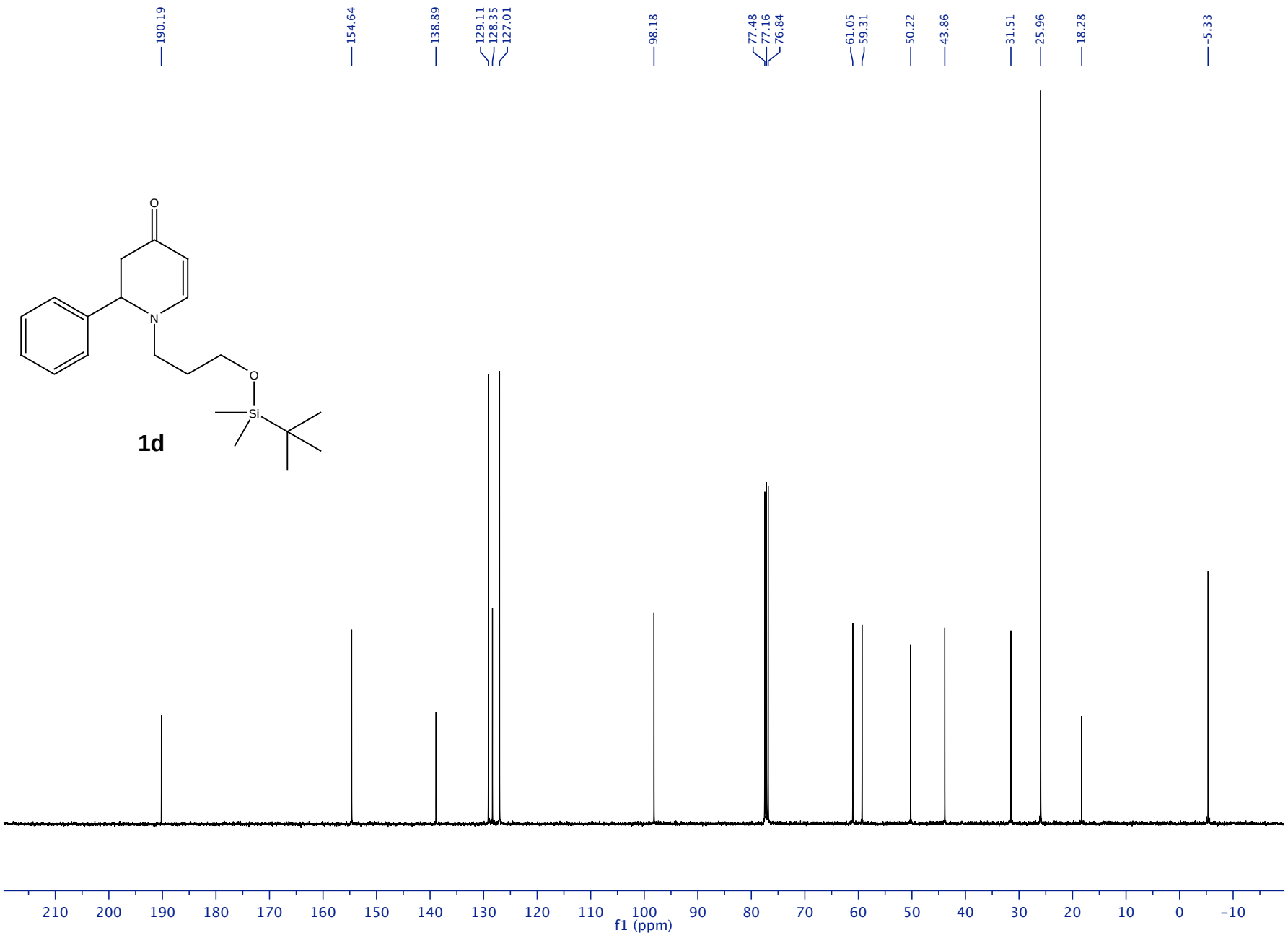
-1.0
f1 (ppm)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50.22
43.86
31.51
25.96
18.28
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N
O
Si
1d
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200
190
180
170
160
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140
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120
110
100
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80
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60
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40
30
20
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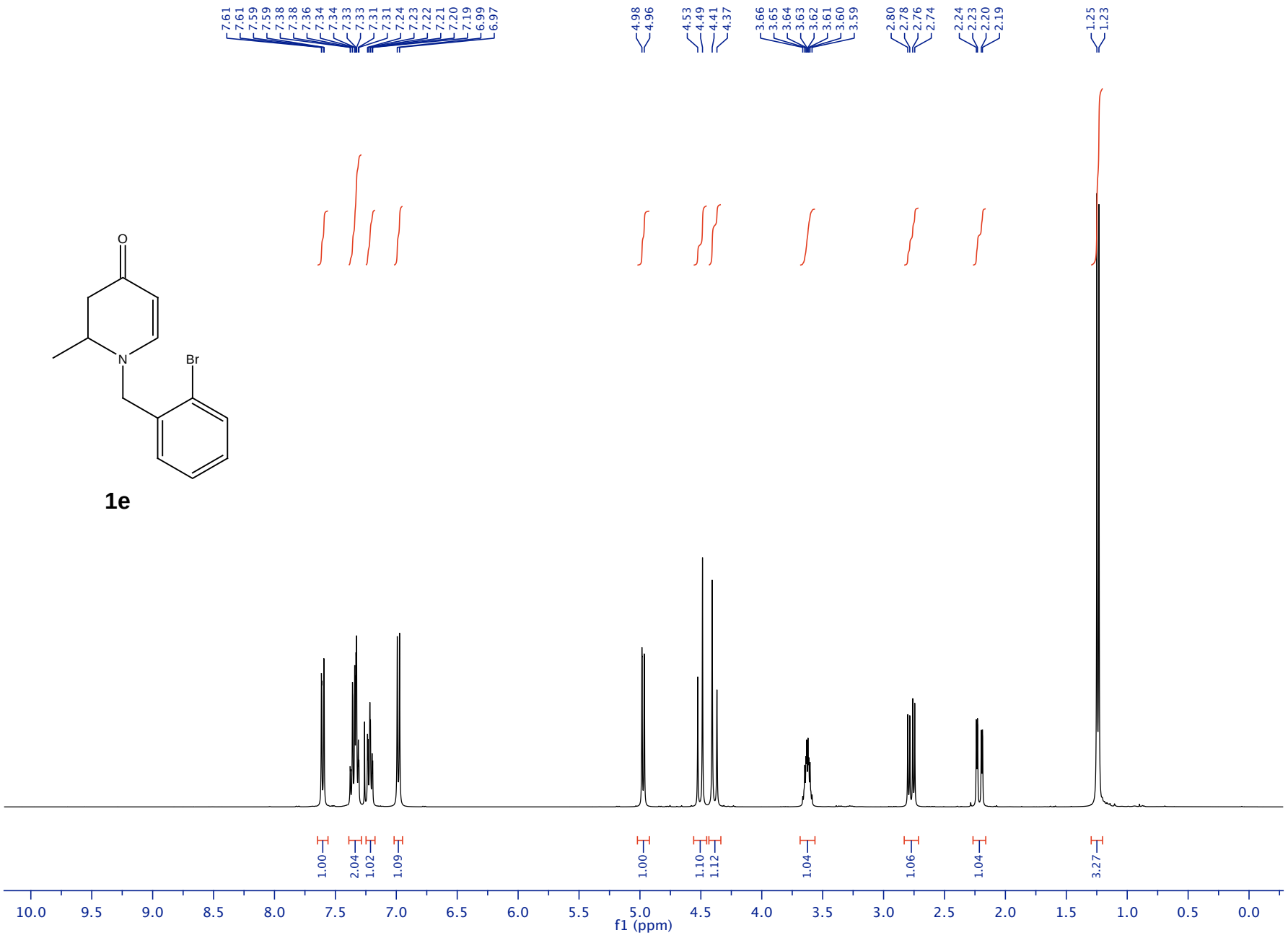
f1 (ppm)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7.22
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1.23
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1.00
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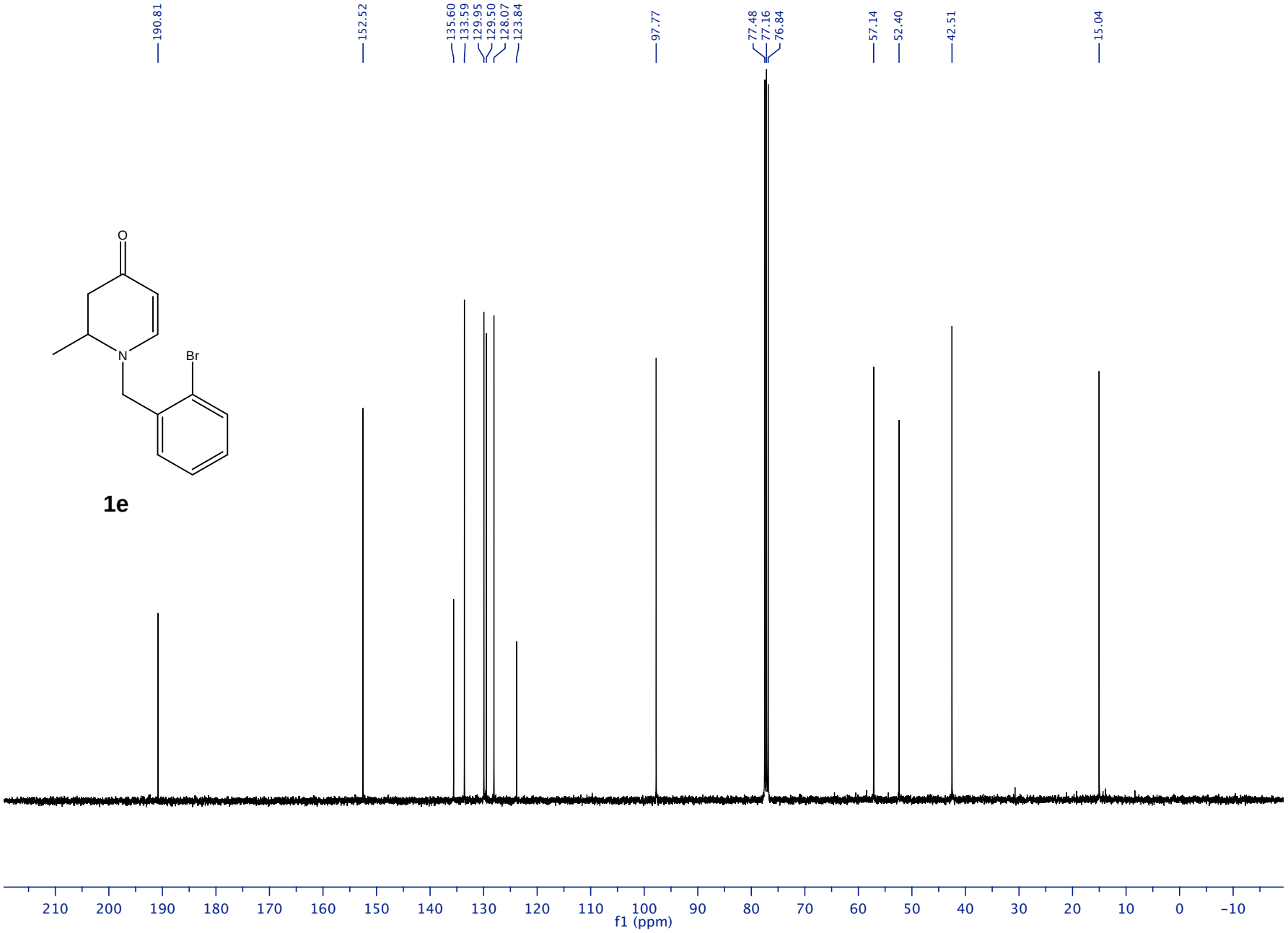
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52.40
42.51
15.04
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N
Br
1e
210
200
190
180
170
160
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120
110
100
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30
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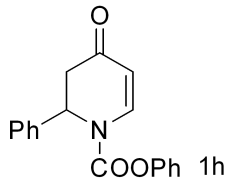
f1 (ppm)



1h

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COOPh Ph enaminone

[*1e6]

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200

100

0

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2.7192

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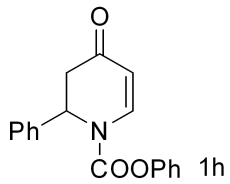
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Ph
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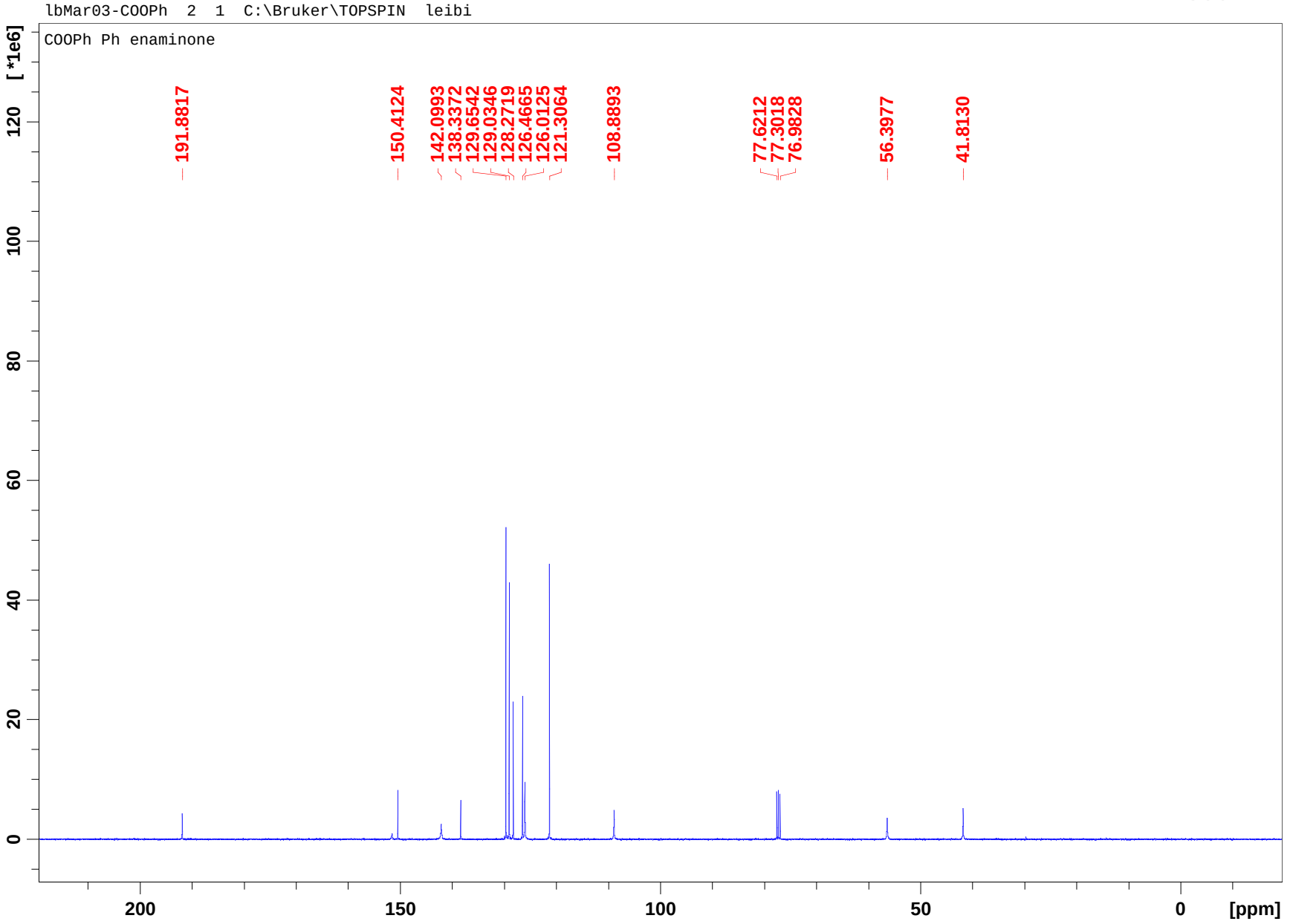
COOPh

1h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COOPh Ph enaminone
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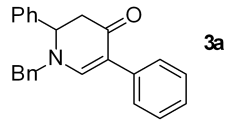
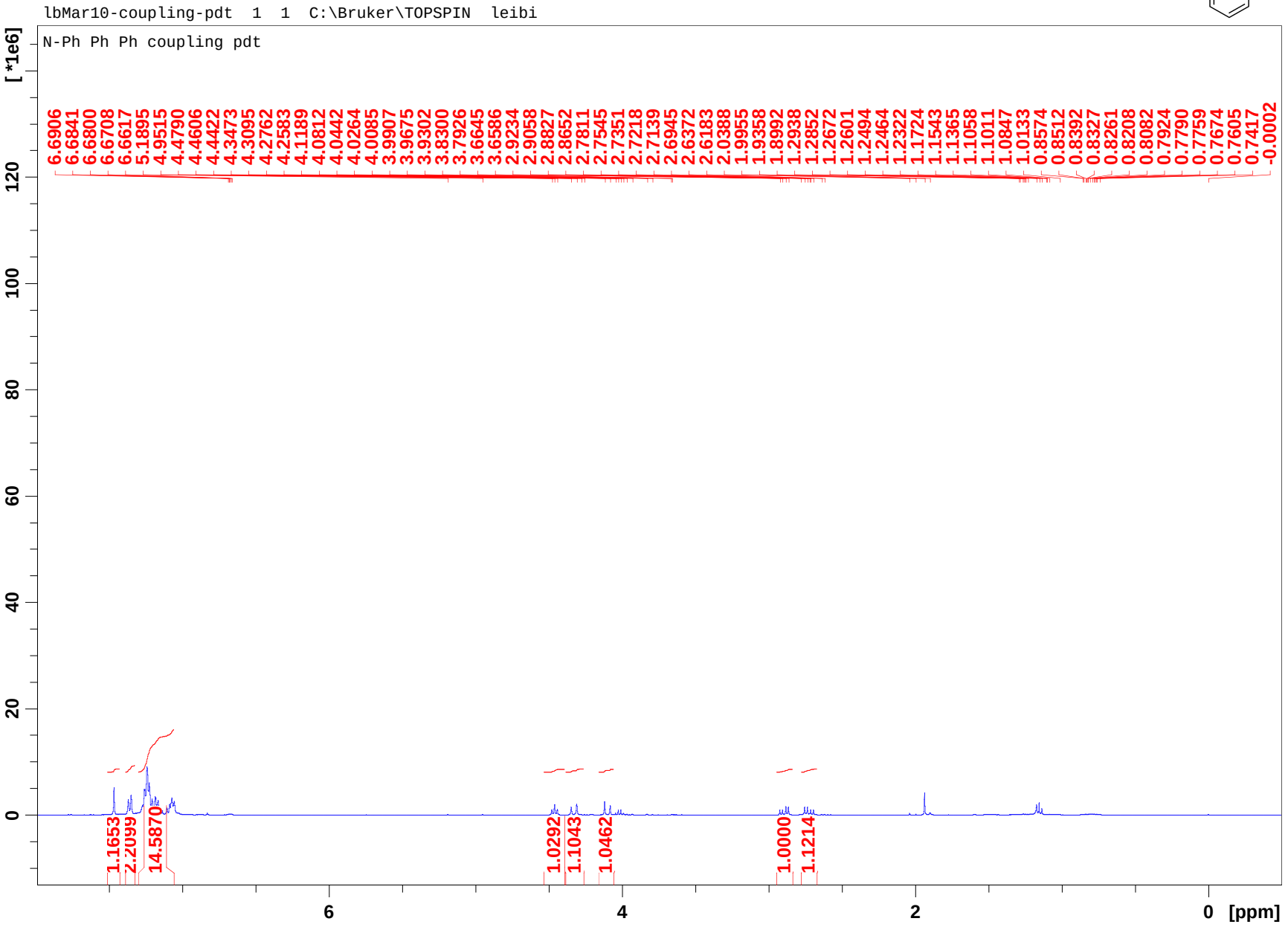

Ph
O
N
Bn

3a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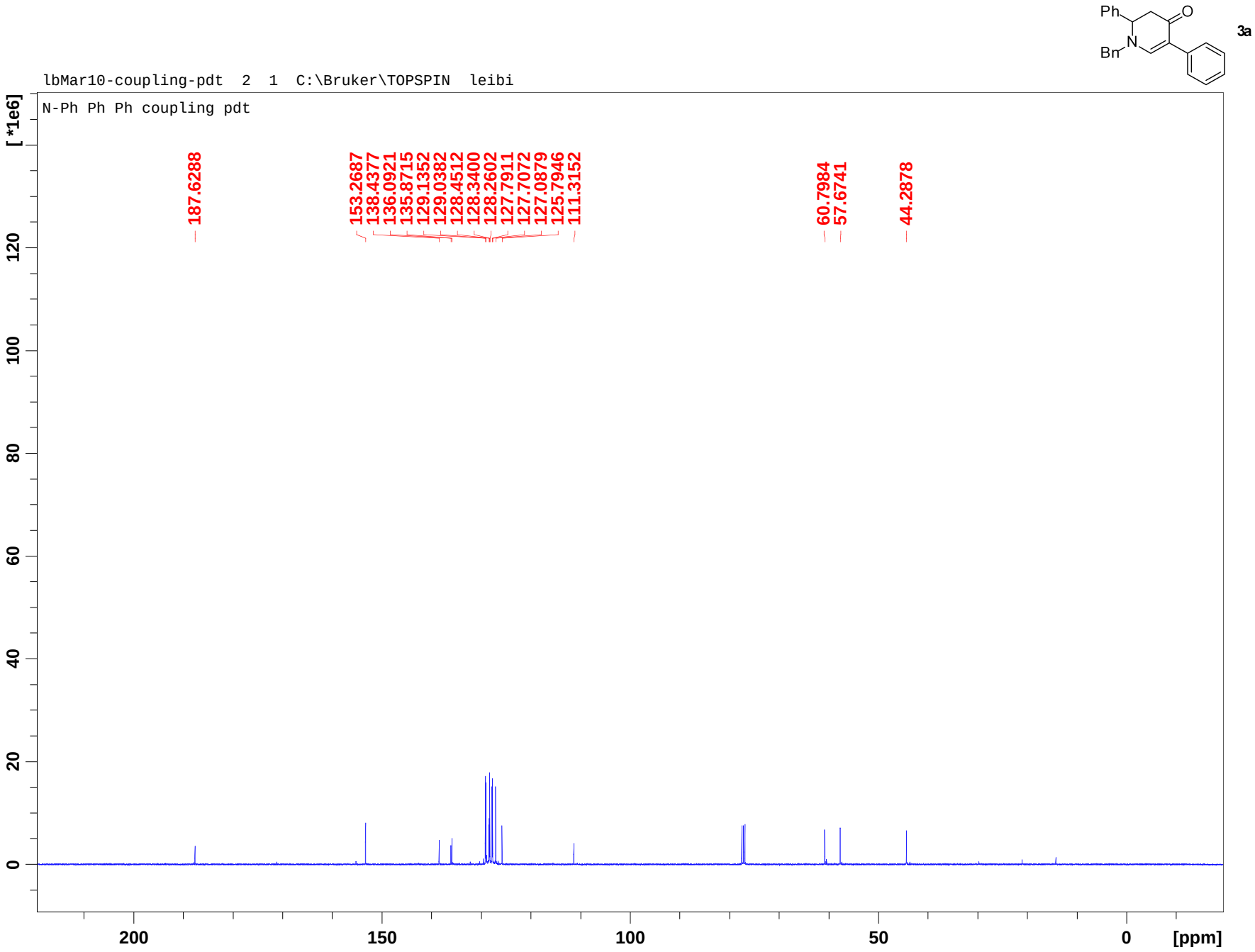
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O
N
Bn
3a
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N-Ph Ph Ph coupling pdt
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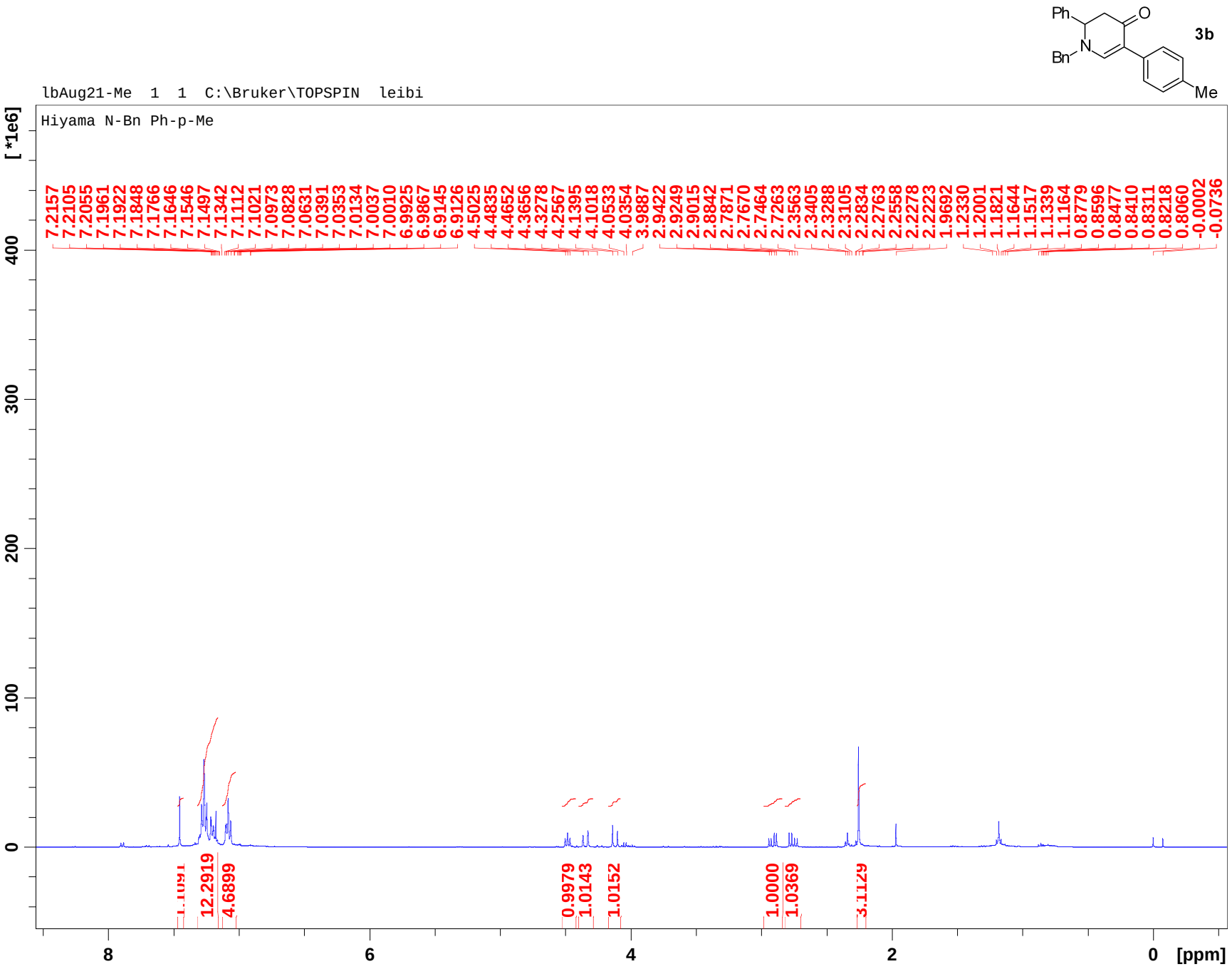
3b
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200
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7.1497
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7.1112
7.1021
7.0973
7.0828
7.0631
7.0391
7.0353
7.0134
7.0037
7.0010
6.9925
6.9867
6.9145
6.9126
4.5025
4.4835
4.4652
4.3656
4.3278
4.2567
4.1395
4.1018
4.0533
4.0354
3.9887
2.9422
2.9249
2.9015
2.8842
2.7871
2.7670
2.7464
2.7263
2.3563
2.3405
2.3288
2.3105
2.2834
2.2763
2.2558
2.2278
2.2223
1.9692
1.2330
1.2001
1.1821
1.1644
1.1517
1.1339
1.1164
0.8779
0.8596
0.8477
0.8410
0.8311
0.8218
0.8060
-0.0002
-0.0736
12.2919
4.6899
0.9979
1.0143
1.0152
1.0000
1.0369
8
6
4
2
0
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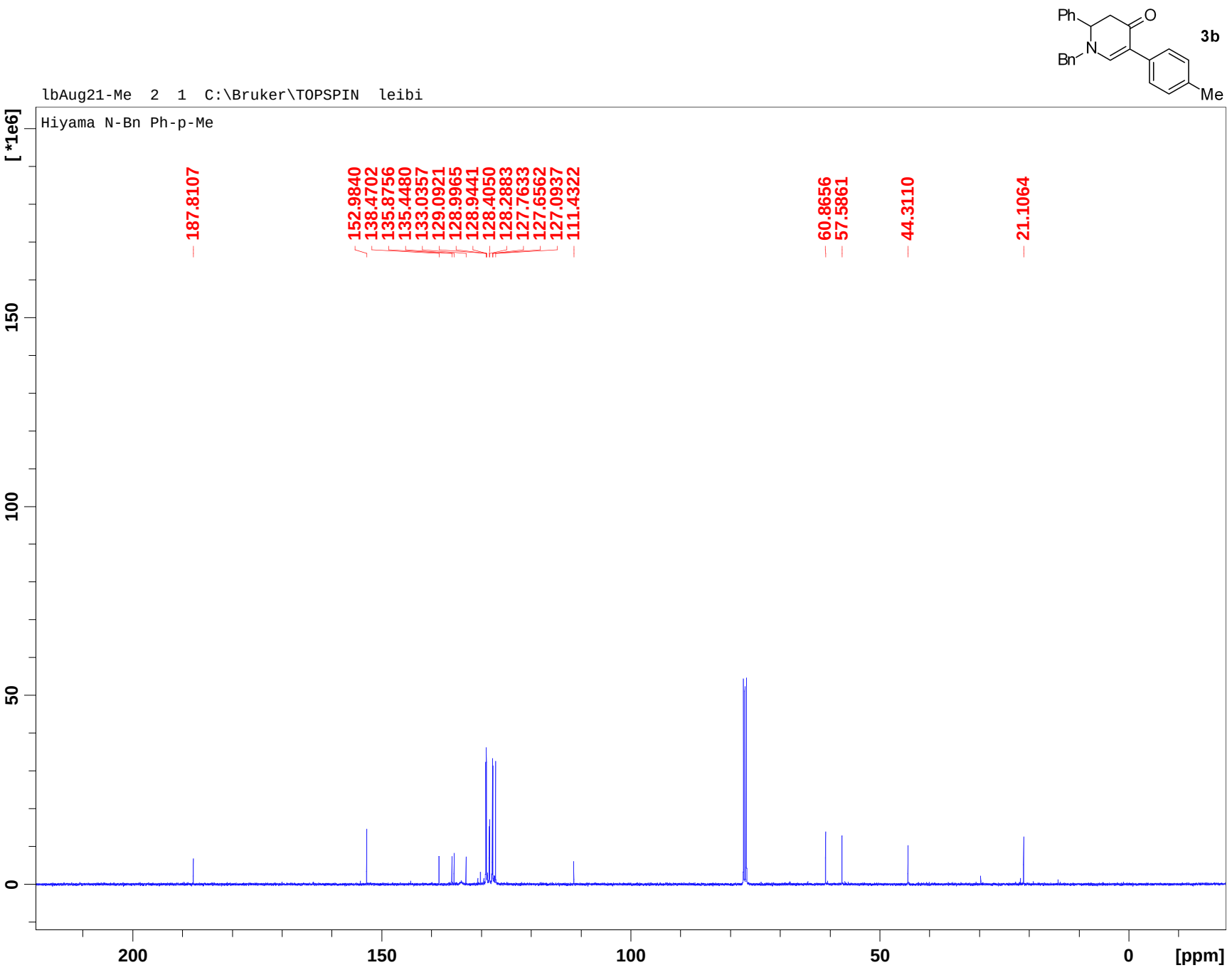
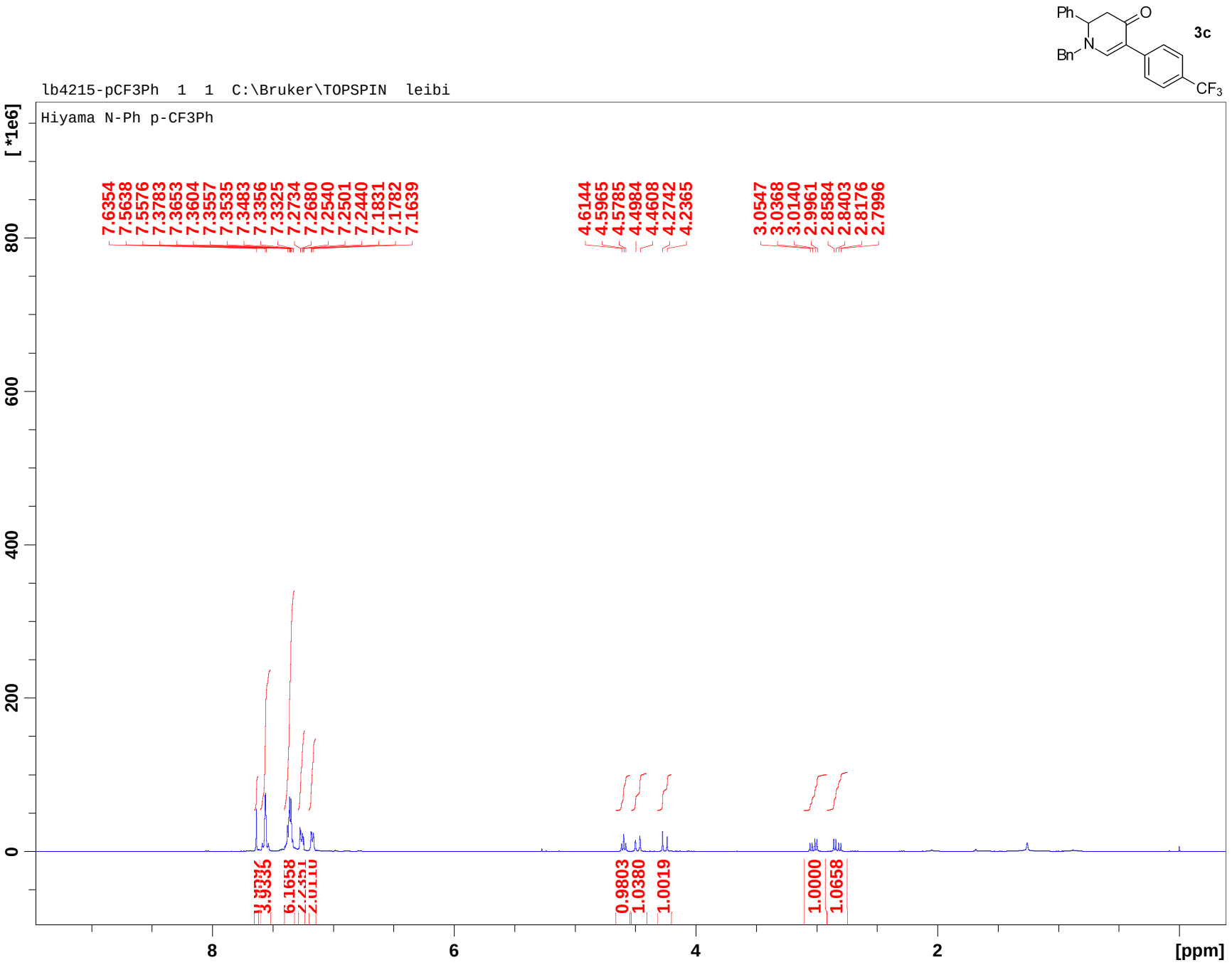
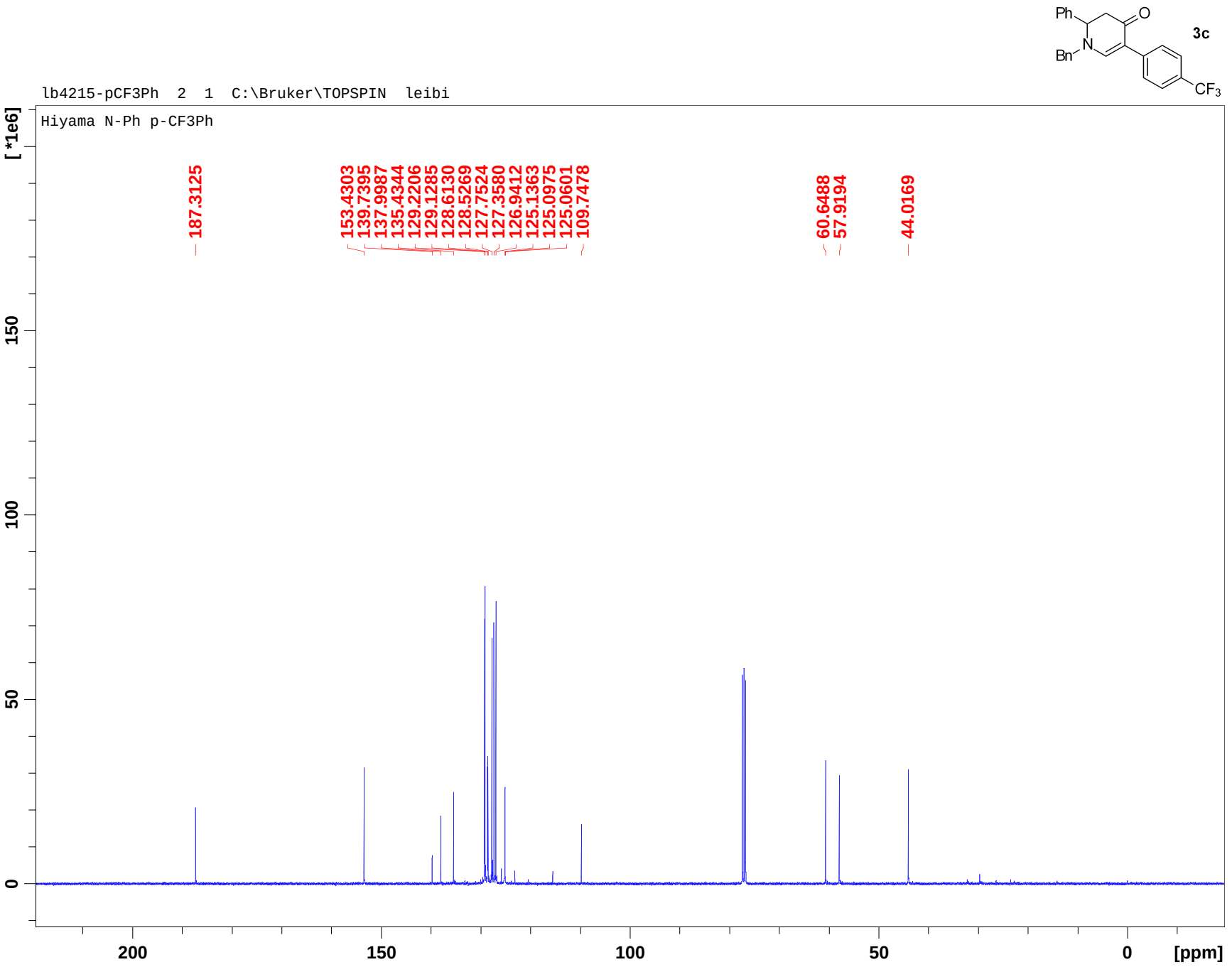
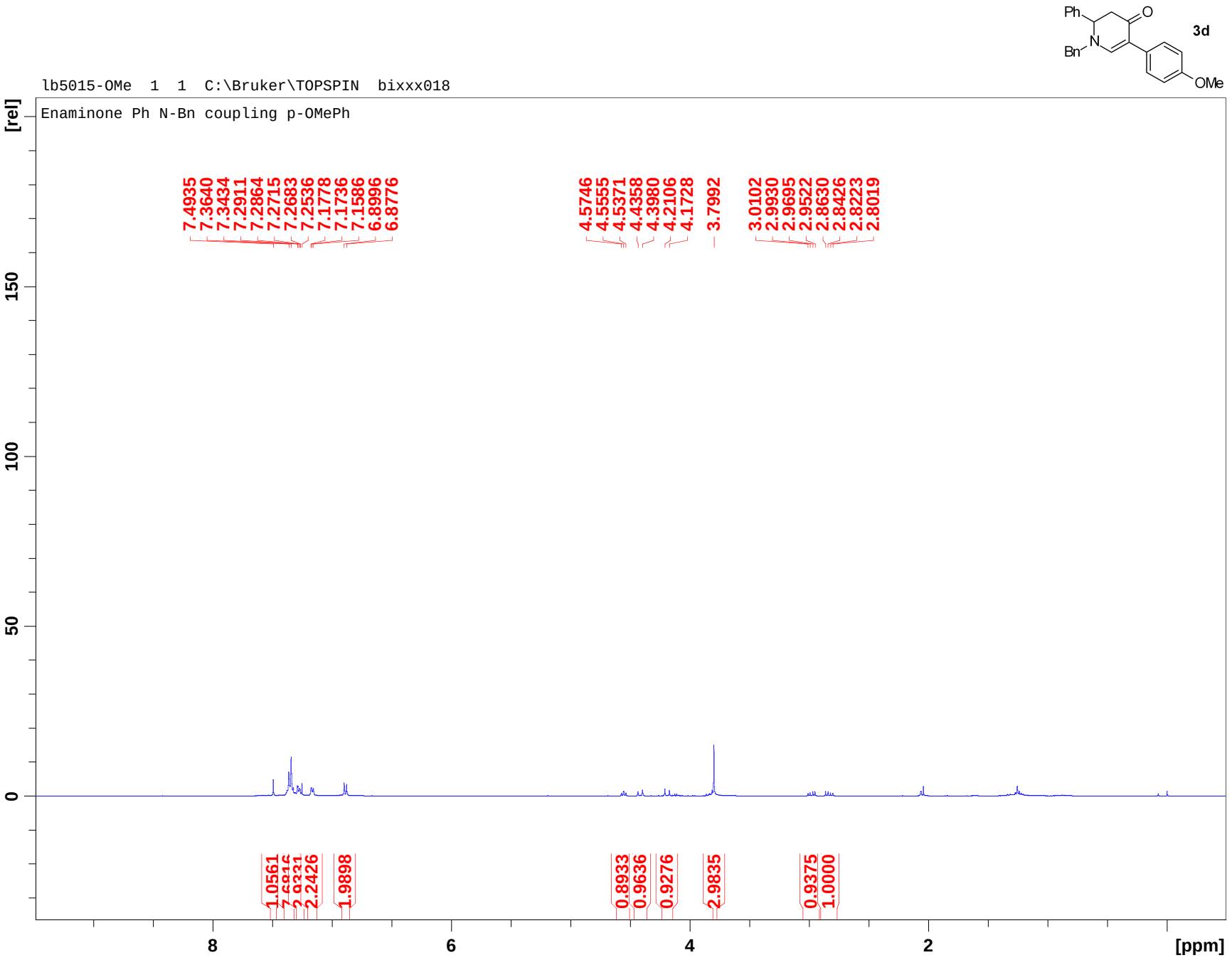
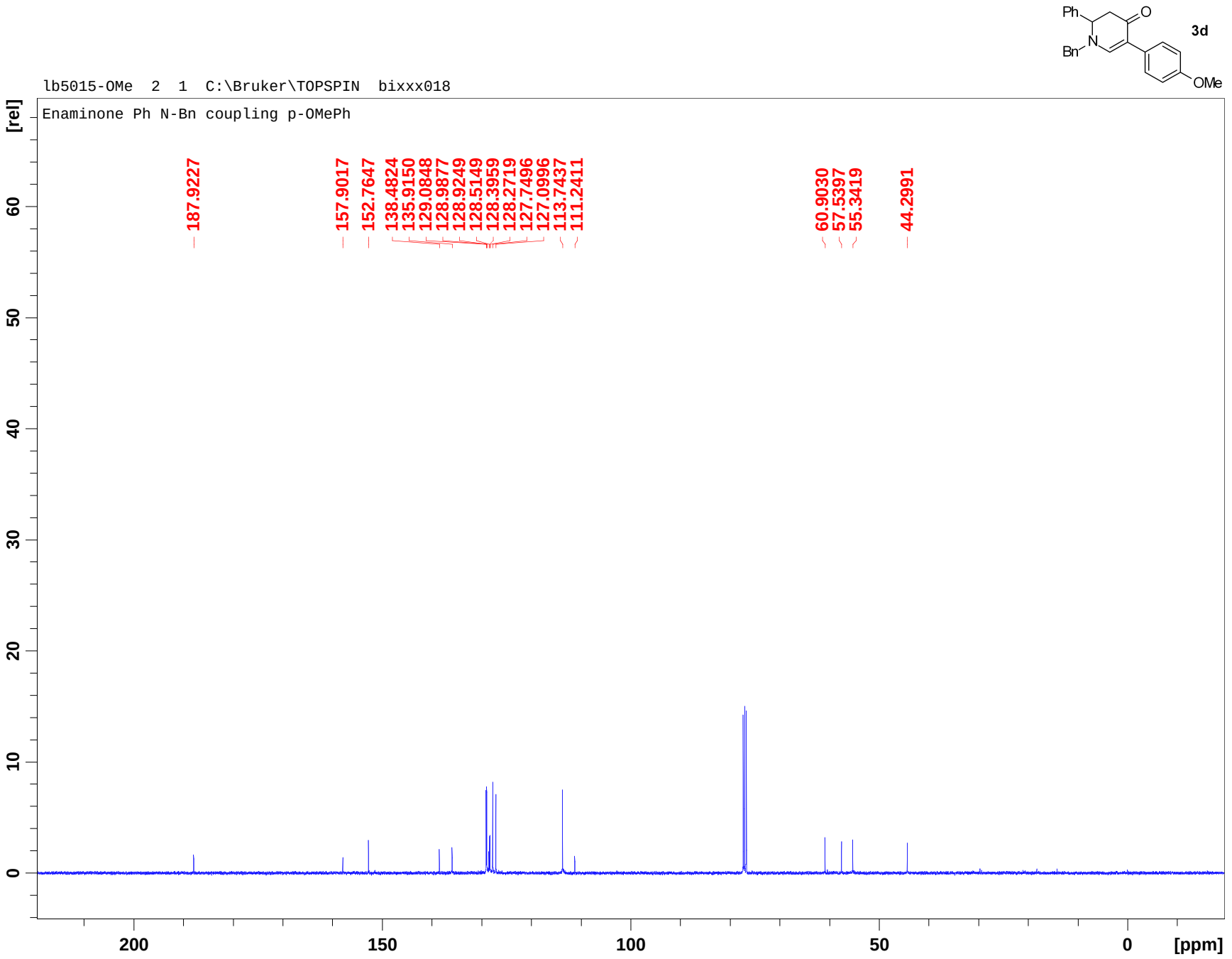
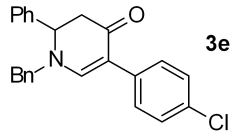

Ph
O
N
Bn
3b
Me
lbAug21-Me 2 1 C:\Bruker\TOPSPIN leibi
Hiyama N-Bn Ph-p-Me
[*1e6]
187.8107
152.9840
138.4702
135.8756
135.4480
133.0357
129.0921
128.9965
128.9441
128.4050
128.2883
127.7633
127.6562
127.0937
111.4322
60.8656
57.5861
44.3110
21.1064
150
100
50
0
200
150
100
50
0
[ppm]


Ph
O
N
Bn
3c
CF3
lb4215-pCF3Ph 1 1 C:\Bruker\TOPSPIN leibi
Hiyama N-Ph p-CF3Ph
[*1e6]
800
600
400
200
0
7.6354
7.5638
7.5576
7.3783
7.3653
7.3604
7.3557
7.3535
7.3483
7.3356
7.3325
7.2734
7.2680
7.2540
7.2501
7.2440
7.1831
7.1782
7.1639
4.6144
4.5965
4.5785
4.4984
4.4608
4.2742
4.2365
3.0547
3.0368
3.0140
2.9961
2.8584
2.8403
2.8176
2.7996
3.9335
6.1658
0.9803
1.0380
1.0019
1.0000
1.0658
8
6
4
2
[ppm]


Ph
O
N
Bn
3c
CF3
lb4215-pCF3Ph 2 1 C:\Bruker\TOPSPIN leibi
Hiyama N-Ph p-CF3Ph
[*1e6]
187.3125
153.4303
139.7395
137.9987
135.4344
129.2206
129.1285
128.6130
128.5269
127.7524
127.3580
126.9412
125.1363
125.0975
125.0601
109.7478
60.6488
57.9194
44.0169
150
100
50
0
200
150
100
50
0
[ppm]


Ph
O
N
Bn
OMe
3d
lb5015-OMe 1 1 C:\Bruker\TOPSPIN bixxx018
Enaminone Ph N-Bn coupling p-OMePh
[rel]
150
100
50
0
7.4935
7.3640
7.3434
7.2911
7.2864
7.2715
7.2683
7.2536
7.1778
7.1736
7.1586
6.8996
6.8776
4.5746
4.5555
4.5371
4.4358
4.3980
4.2106
4.1728
3.7992
3.0102
2.9930
2.9695
2.9522
2.8630
2.8426
2.8223
2.8019
1.0561
2.2426
1.9898
0.8933
0.9636
0.9276
2.9835
0.9375
1.0000
8
6
4
2
[ppm]


3d
lb5015-OMe 2 1 C:\Bruker\TOPSPIN bixxx018
Enaminone Ph N-Bn coupling p-OMePh
[rel]
187.9227
157.9017
152.7647
138.4824
135.9150
129.0848
128.9877
128.9249
128.5149
128.3959
128.2719
127.7496
127.0996
113.7437
111.2411
60.9030
57.5397
55.3419
44.2991
[ppm]



3e

lb4221-pClPh 1 1 C:\Bruker\TOPSPIN leibi

Hiyama N-Bn p-ClPh

[*1e6]

7.5494 7.3901 7.3854 7.3686 7.3627 7.3585 7.3535 7.3497 7.3446 7.3402 7.2905 7.2863 7.2814 7.2694 7.2647 7.2496 7.2462 7.1737 7.1690 7.1545

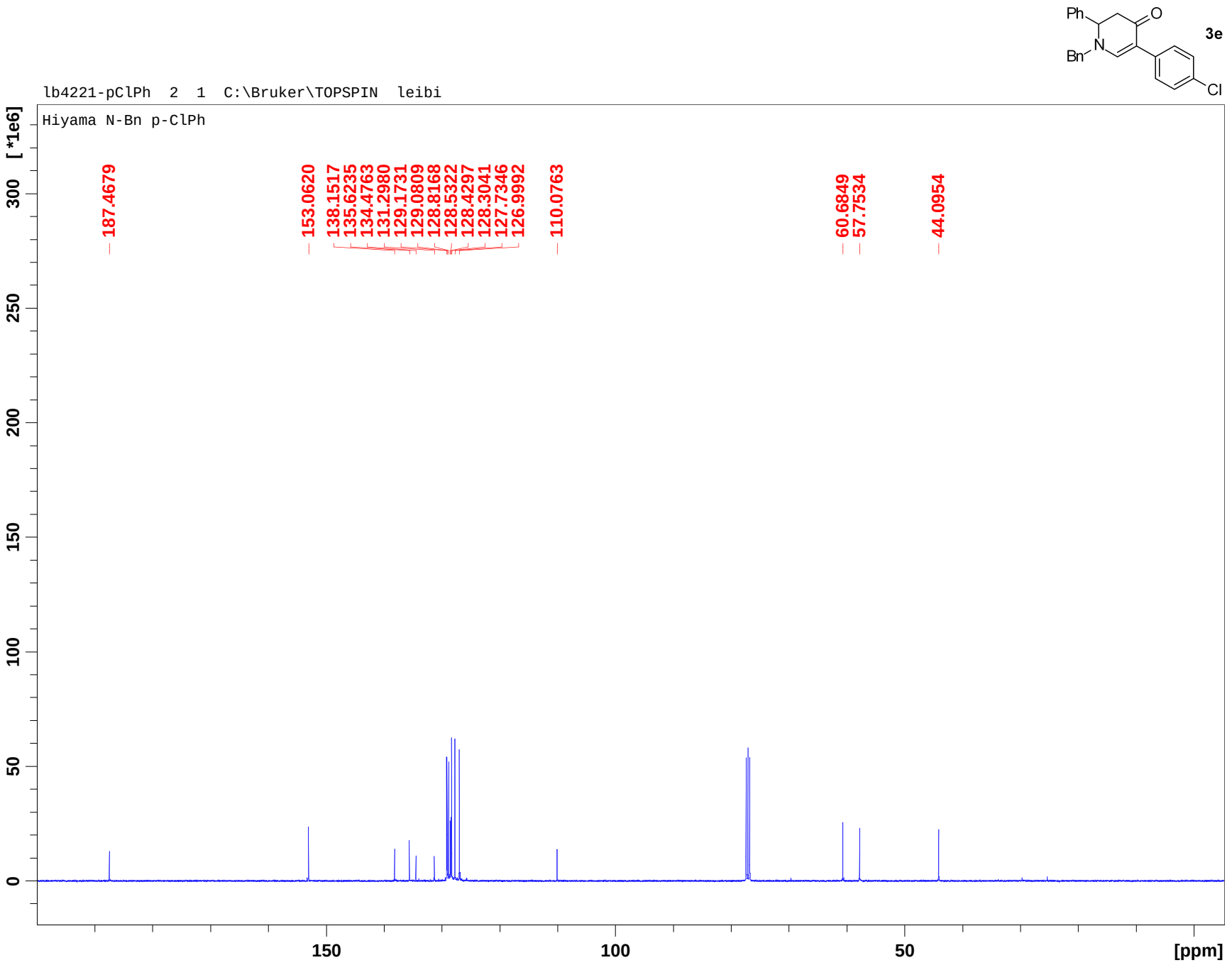
4.5849 4.5666 4.5484 4.4661 4.4283 4.2400 4.2023

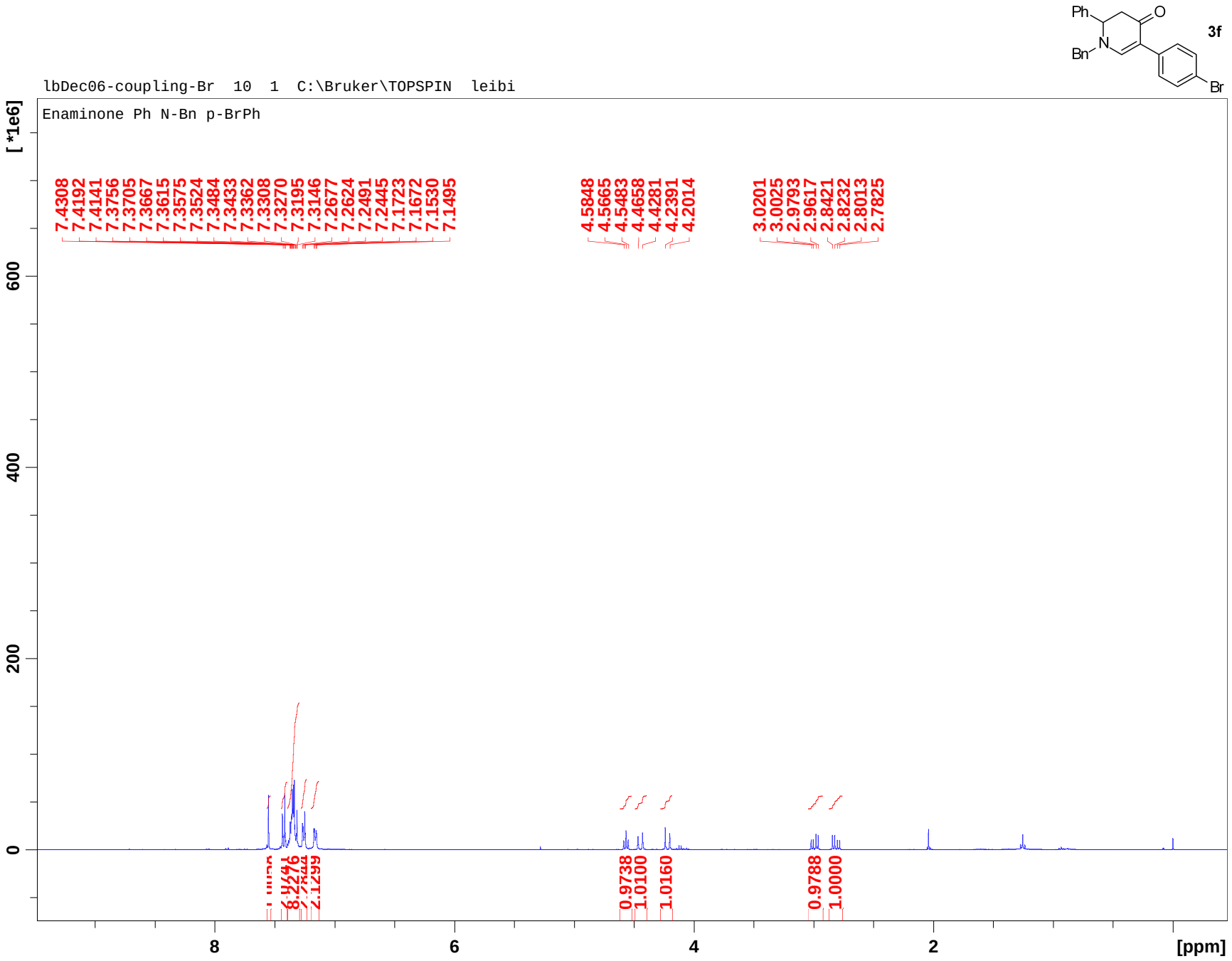
3.0194 3.0017 2.9786 2.9610 2.8425 2.8236 2.8017 2.7828

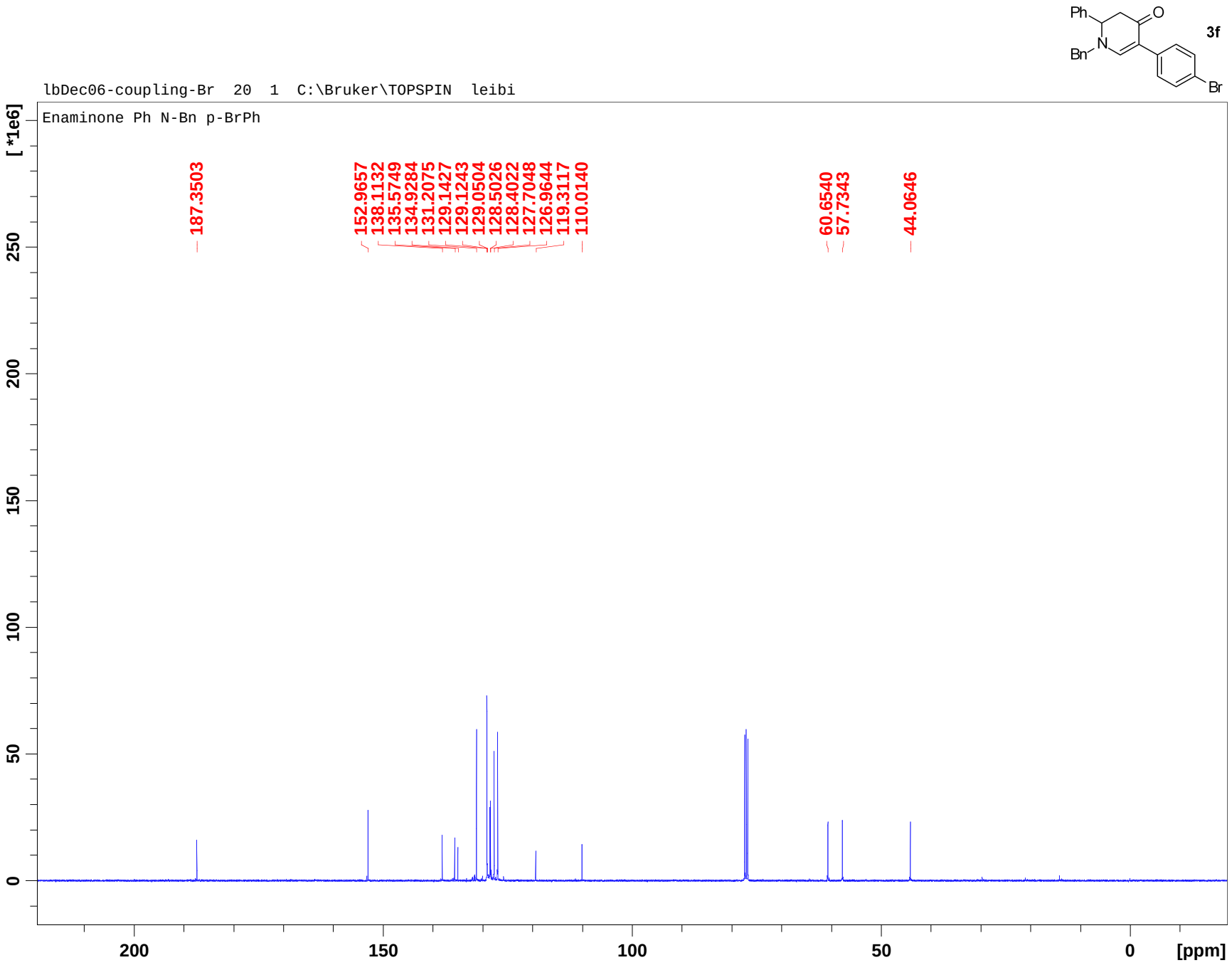
1.1056 7.8327 4.4490 2.0844 0.9802 0.9928 0.9619 1.0000 0.9999

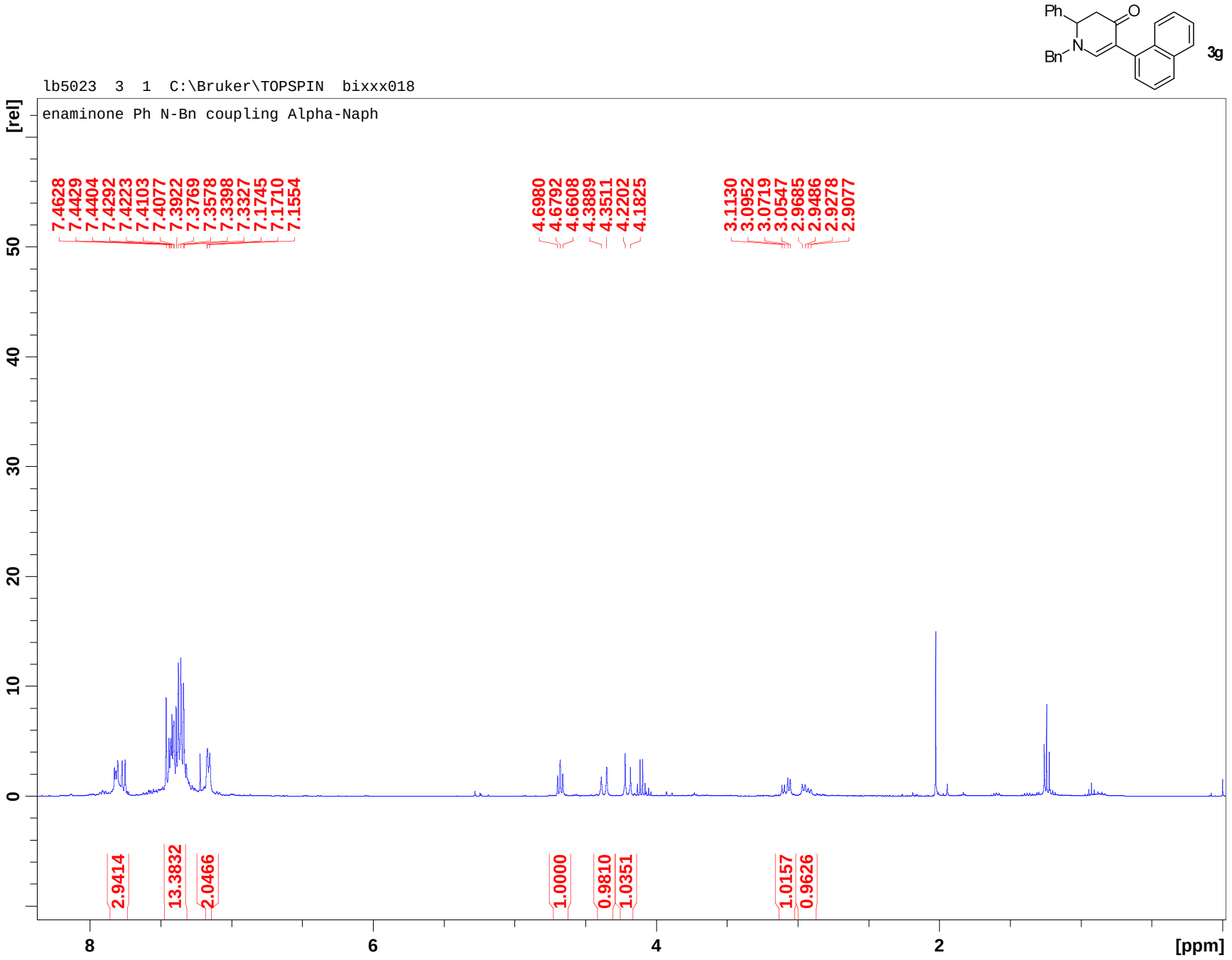
0 200 400 600

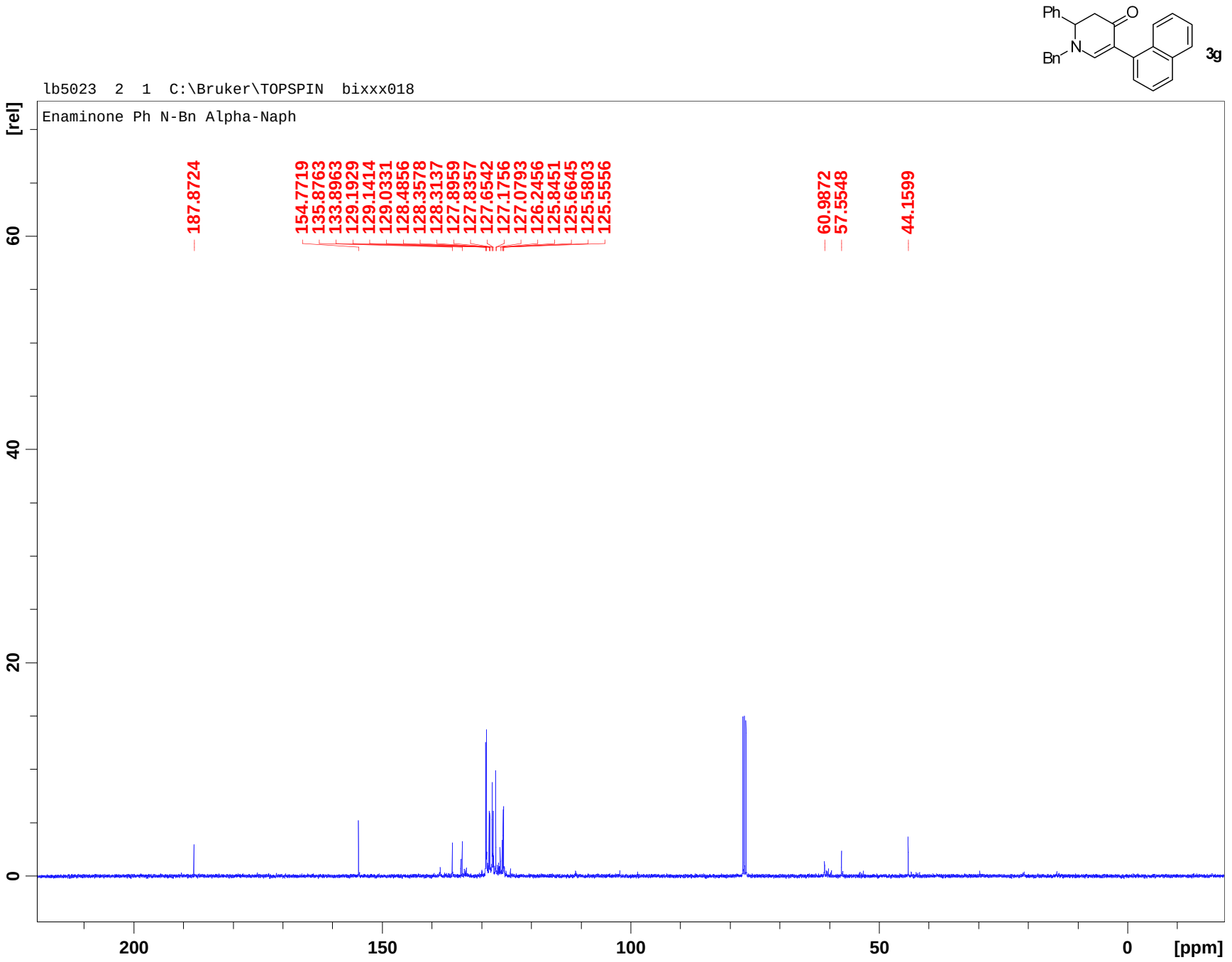
8 6 4 2 0 [ppm]

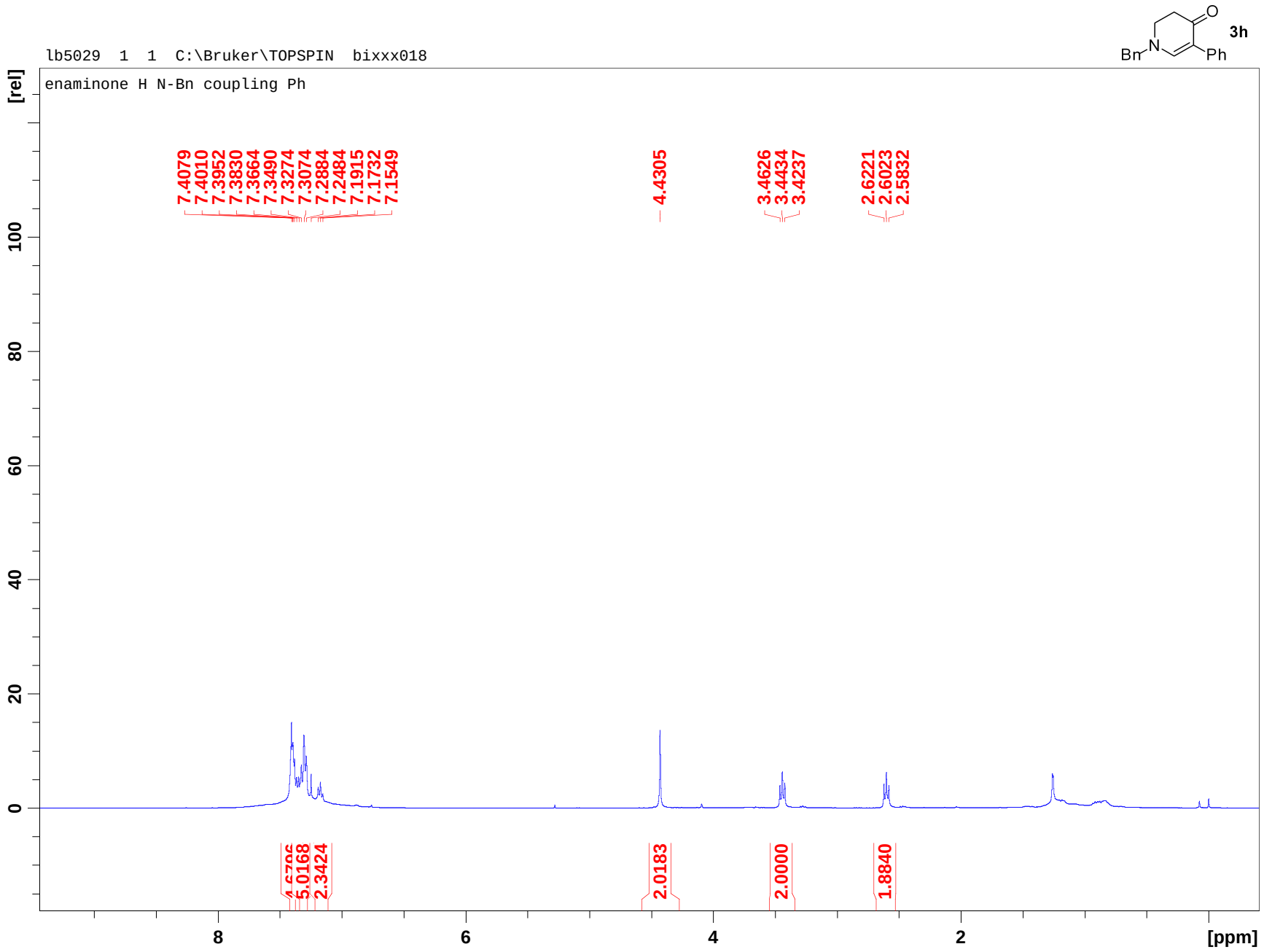

Ph
O
N
Bn
Cl
3e
lb4221-pClPh 2 1 C:\Bruker\TOPSPIN leibi
Hiyama N-Bn p-ClPh
187.4679
153.0620
138.1517
135.6235
134.4763
131.2980
129.1731
129.0809
128.8168
128.5322
128.4297
128.3041
127.7346
126.9992
110.0763
60.6849
57.7534
44.0954
[*1e6]
300
250
200
150
100
50
0
150
100
50
[ppm]

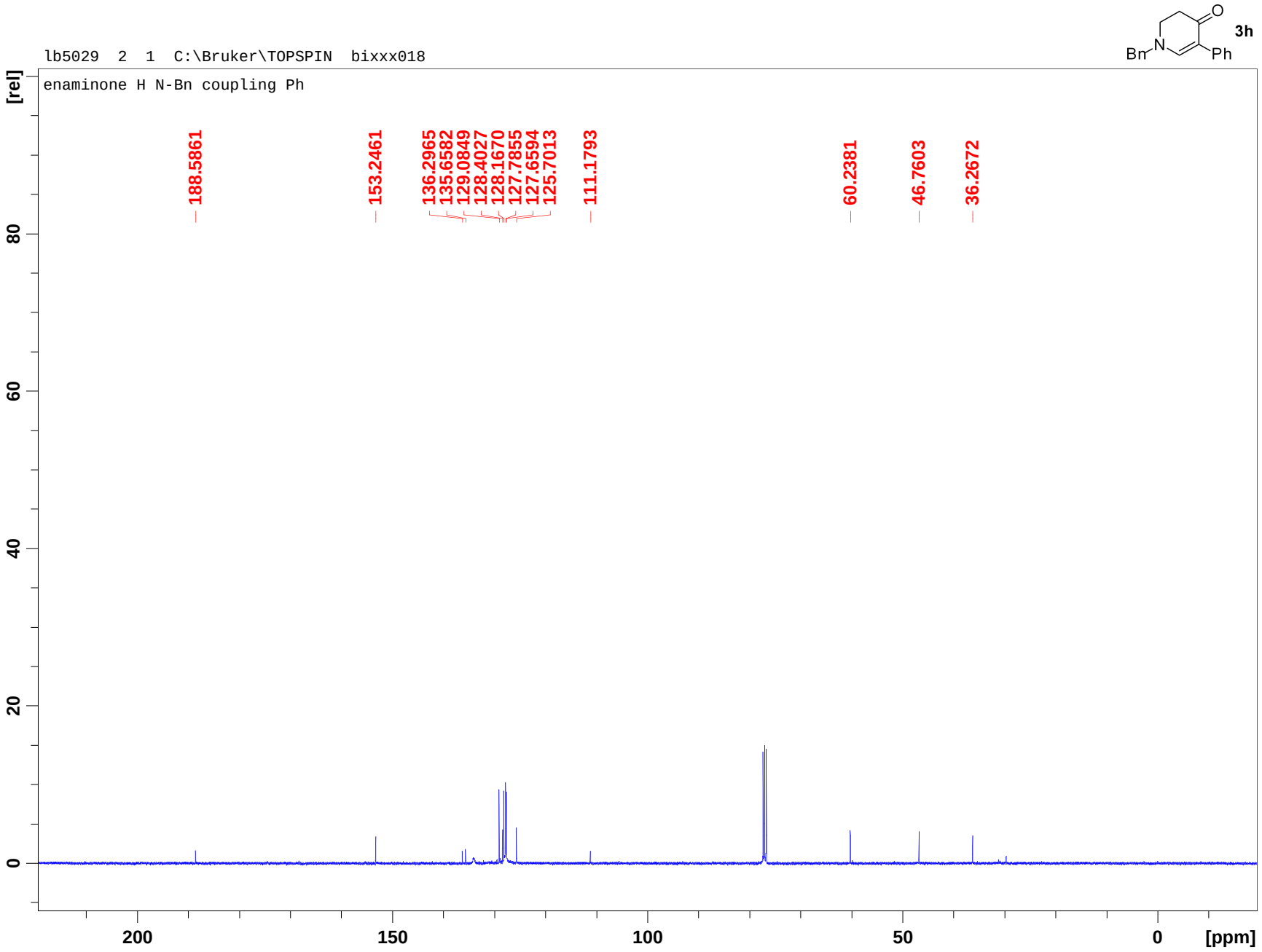

3f
lbDec06-coupling-Br 10 1 C:\Bruker\TOPSPIN leibi
Enaminone Ph N-Bn p-BrPh
[*1e6]
7.4308
7.4192
7.4141
7.3756
7.3705
7.3667
7.3615
7.3575
7.3524
7.3484
7.3433
7.3362
7.3308
7.3270
7.3195
7.3146
7.2677
7.2624
7.2491
7.2445
7.1723
7.1672
7.1530
7.1495
4.5848
4.5665
4.5483
4.4658
4.4281
4.2391
4.2014
3.0201
3.0025
2.9793
2.9617
2.8421
2.8232
2.8013
2.7825
0.9738
1.0100
1.0160
0.9788
1.0000
[ppm]

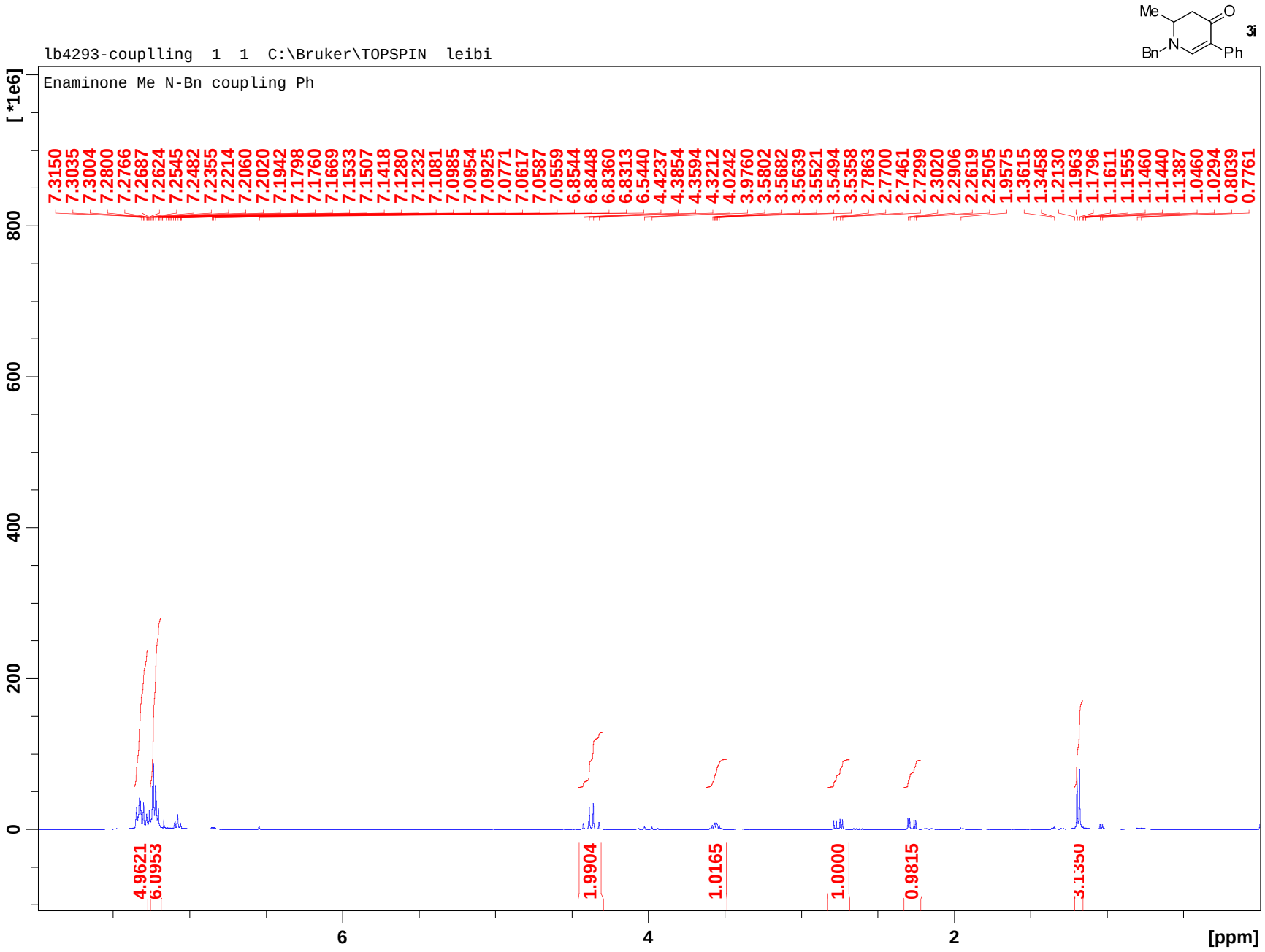

Ph
O
N
Bn
Br
3f
lbDec06-coupling-Br 20 1 C:\Bruker\TOPSPIN leibi
Enaminone Ph N-Bn p-BrPh
[*1e6]
187.3503
152.9657
138.1132
135.5749
134.9284
131.2075
129.1427
129.1243
129.0504
128.5026
128.4022
127.7048
126.9644
119.3117
110.0140
60.6540
57.7343
44.0646
250
200
150
100
50
0
200
150
100
50
0
[ppm]

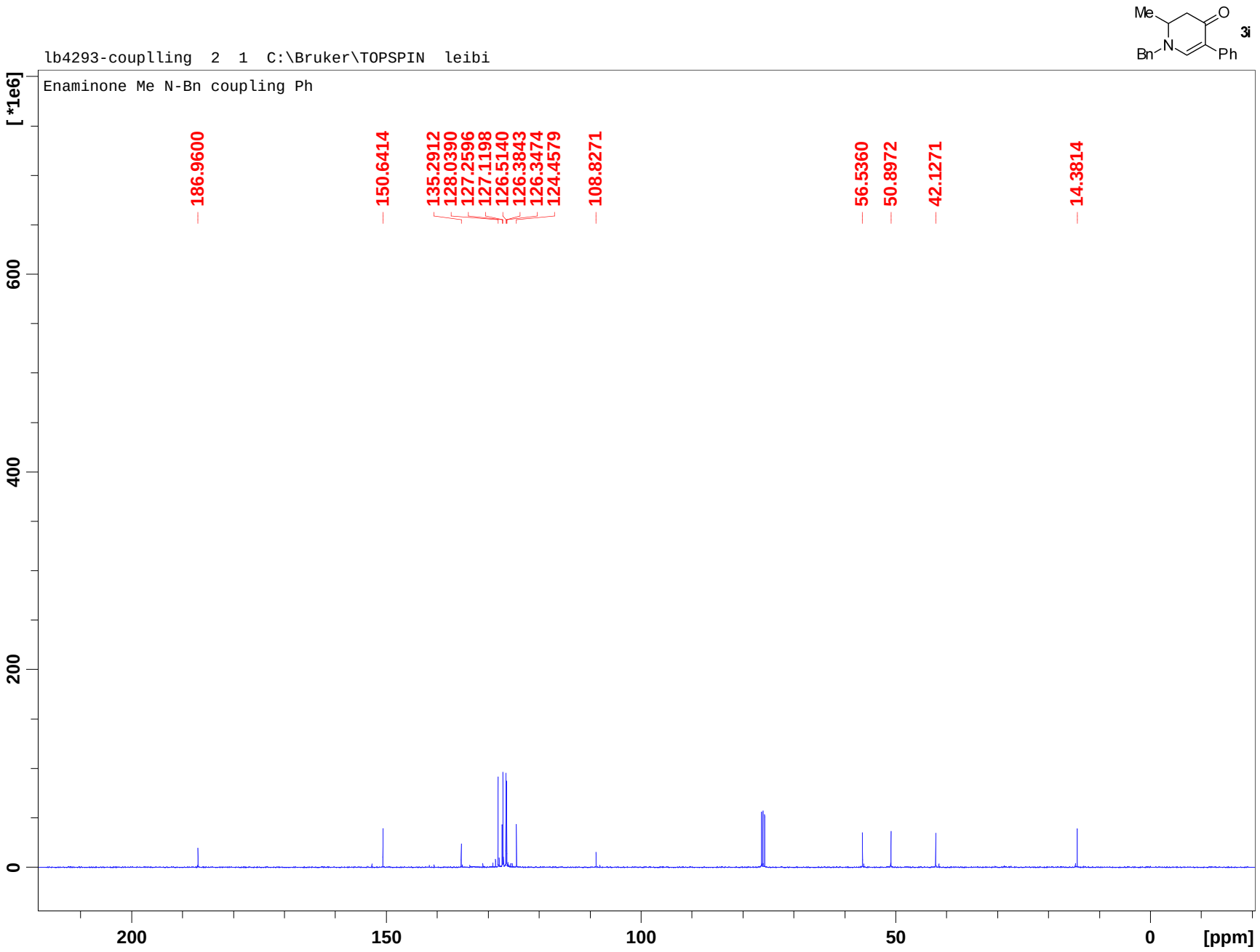

Ph
O
N
Bn
3g
lb5023 3 1 C:\Bruker\TOPSPIN bixxx018
enaminone Ph N-Bn coupling Alpha-Naph
[rel]
7.4628
7.4429
7.4404
7.4292
7.4223
7.4103
7.4077
7.3922
7.3769
7.3578
7.3398
7.3327
7.1745
7.1710
7.1554
4.6980
4.6792
4.6608
4.3889
4.3511
4.2202
4.1825
3.1130
3.0952
3.0719
3.0547
2.9685
2.9486
2.9278
2.9077
2.9414
13.3832
2.0466
1.0000
0.9810
1.0351
1.0157
0.9626
8
6
4
2
[ppm]

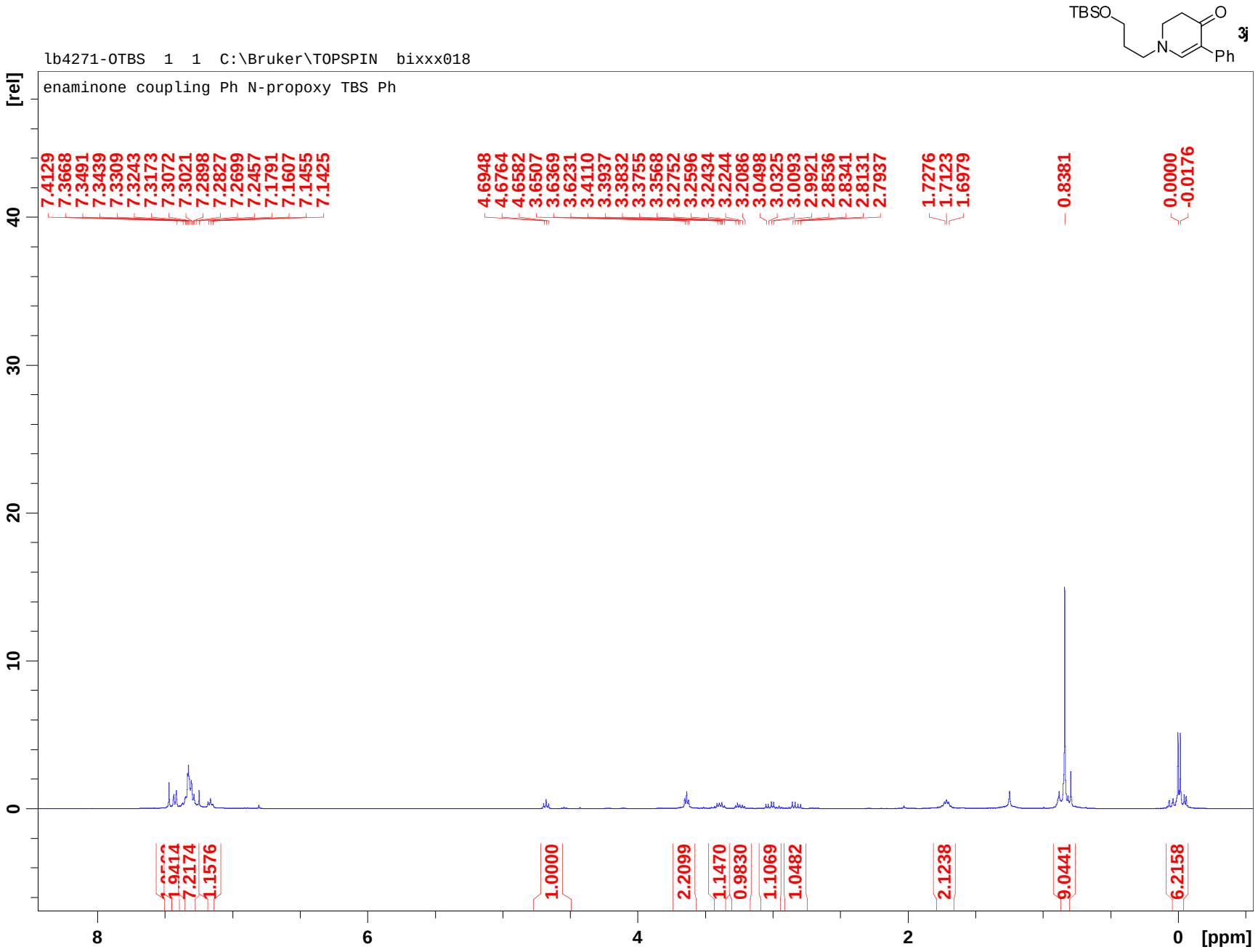

Ph
O
N
Bn
3g
lb5023 2 1 C:\Bruker\TOPSPIN bixxx018
Enaminone Ph N-Bn Alpha-Naph
[rel]
187.8724
154.7719
135.8763
133.8963
129.1929
129.1414
129.0331
128.4856
128.3578
128.3137
127.8959
127.8357
127.6542
127.1756
127.0793
126.2456
125.8451
125.6645
125.5803
125.5556
60.9872
57.5548
44.1599
60
40
20
0
200
150
100
50
0
[ppm]

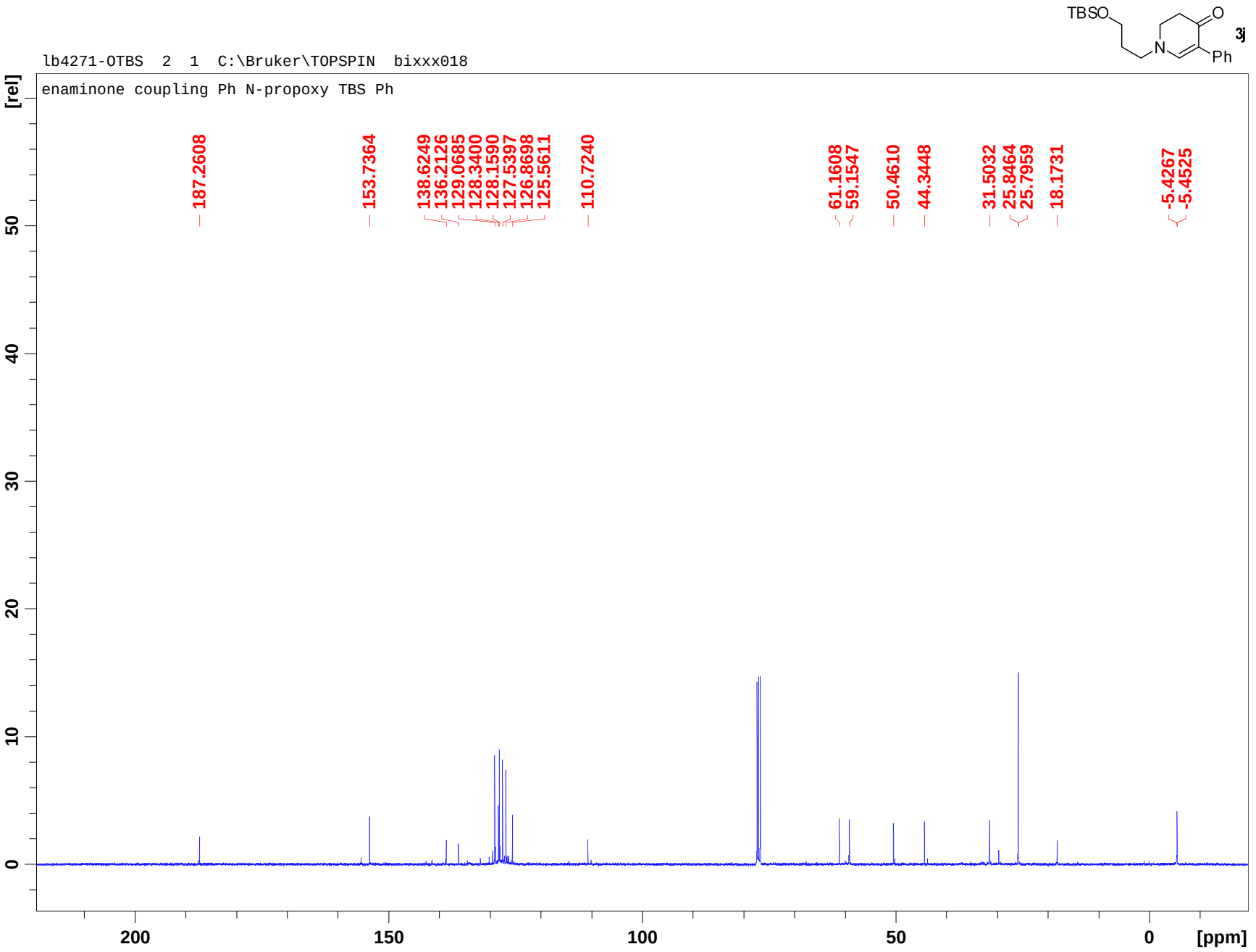

lb5029 1 1 C:\Bruker\TOPSPIN bixxx018
enaminone H N-Bn coupling Ph
3h
Bn
N
O
Ph
[rel]
100
80
60
40
20
0
7.4079
7.4010
7.3952
7.3830
7.3664
7.3490
7.3274
7.3074
7.2884
7.2484
7.1915
7.1732
7.1549
4.4305
3.4626
3.4434
3.4237
2.6221
2.6023
2.5832
5.0168
2.3424
2.0183
2.0000
1.8840
8
6
4
2
[ppm]

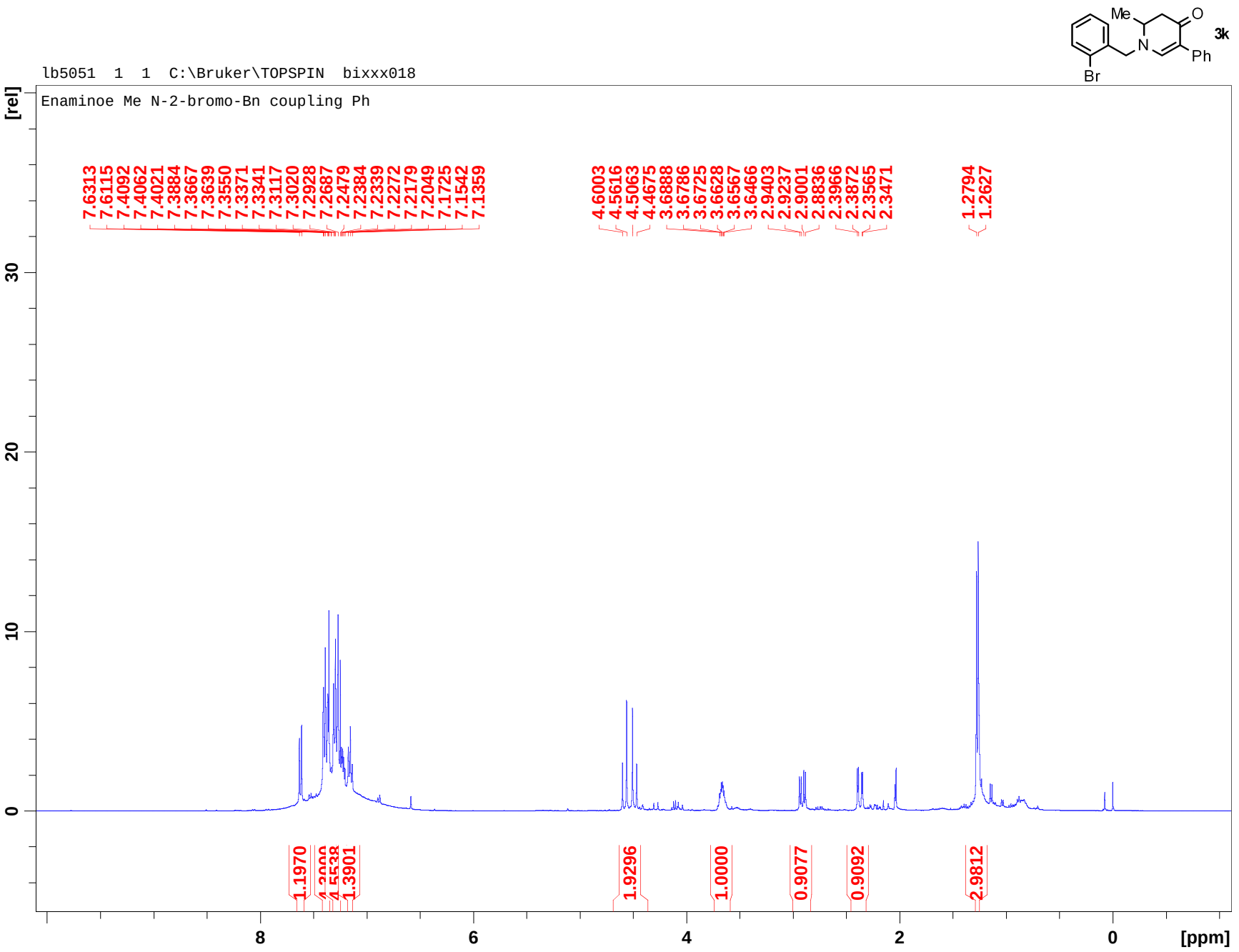

lb5029 2 1 C:\Bruker\TOPSPIN bixxx018
enaminone H N-Bn coupling Ph
3h
Bn
N
Ph
O
[rel]
188.5861
153.2461
136.2965
135.6582
129.0849
128.4027
128.1670
127.7855
127.6594
125.7013
111.1793
60.2381
46.7603
36.2672
0
20
40
60
80
200
150
100
50
0
[ppm]

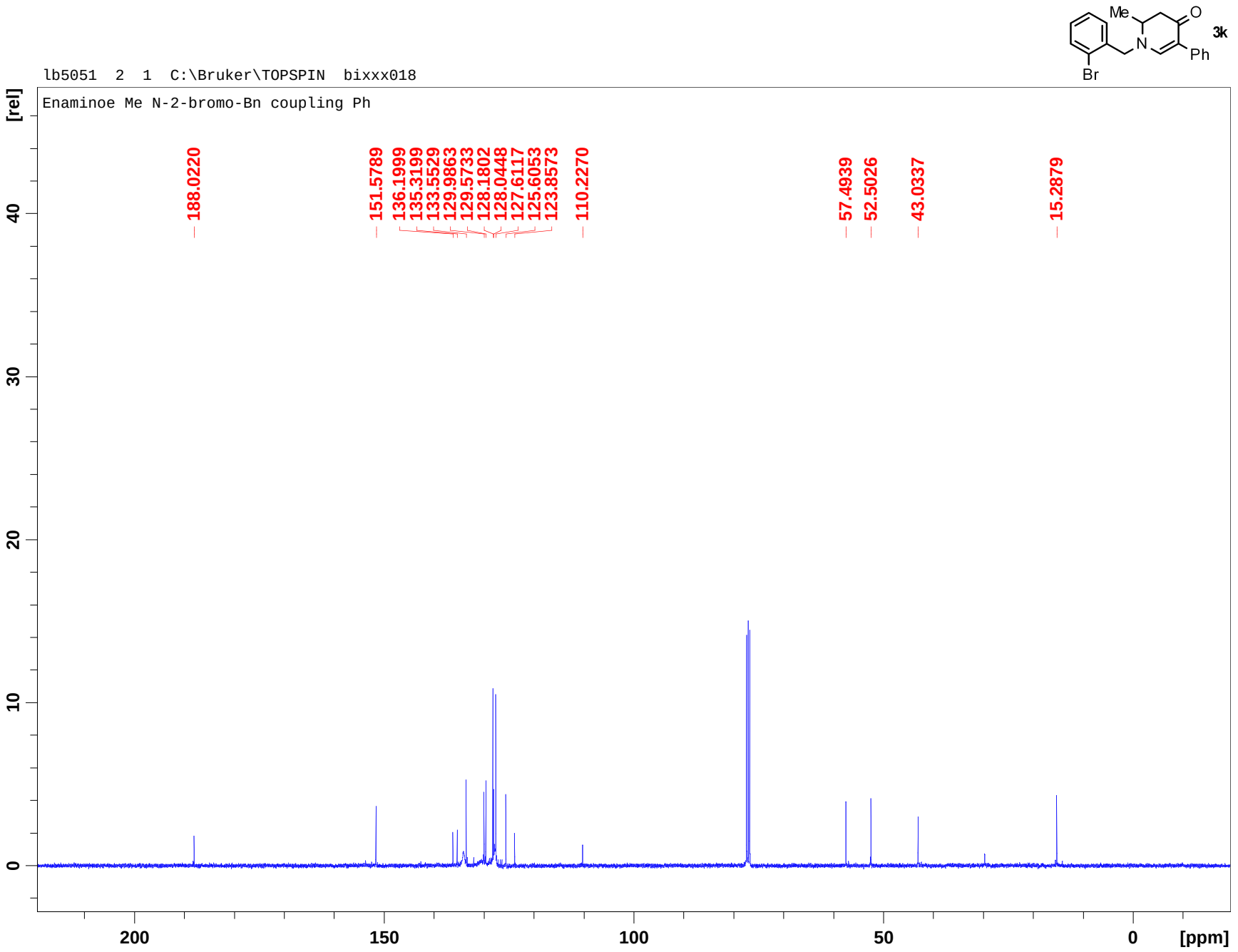

lb4293-couplling 1 1 C:\Bruker\TOPSPIN leibi
Enaminone Me N-Bn coupling Ph
Me
O
Bn
N
Ph
3i
[*1e6]
800
600
400
200
0
7.3150
7.3035
7.3004
7.2800
7.2766
7.2687
7.2624
7.2545
7.2482
7.2355
7.2214
7.2060
7.2020
7.1942
7.1798
7.1760
7.1669
7.1533
7.1507
7.1418
7.1280
7.1232
7.1081
7.0985
7.0954
7.0925
7.0771
7.0617
7.0587
7.0559
6.8544
6.8448
6.8360
6.8313
6.5440
4.4237
4.3854
4.3594
4.3212
4.0242
3.9760
3.5802
3.5682
3.5639
3.5521
3.5494
3.5358
2.7863
2.7700
2.7461
2.7299
2.3020
2.2906
2.2619
2.2505
1.9575
1.3615
1.3458
1.2130
1.1963
1.1796
1.1611
1.1555
1.1460
1.1440
1.1387
1.0460
1.0294
0.8039
0.7761
4.9621
6.0953
1.9904
1.0165
1.0000
0.9815
6
4
2
[ppm]


lb4293-couplling 2 1 C:\Bruker\TOPSPIN leibi
Enaminone Me N-Bn coupling Ph
[*1e6]
600
400
200
0
186.9600
150.6414
135.2912
128.0390
127.2596
127.1198
126.5140
126.3843
126.3474
124.4579
108.8271
56.5360
50.8972
42.1271
14.3814
200
150
100
50
0
[ppm]
Me
O
N
Bn
Ph
3i


TBSO
O
N
Ph
3j
lb4271-OTBS 1 1 C:\Bruker\TOPSPIN bixxx018
enaminone coupling Ph N-propoxy TBS Ph
[rel]
7.4129
7.3668
7.3491
7.3439
7.3309
7.3243
7.3173
7.3072
7.3021
7.2898
7.2827
7.2699
7.2457
7.1791
7.1607
7.1455
7.1425
4.6948
4.6764
4.6582
3.6507
3.6369
3.6231
3.4110
3.3937
3.3832
3.3755
3.3568
3.2752
3.2596
3.2434
3.2244
3.2086
3.0498
3.0325
3.0093
2.9921
2.8536
2.8341
2.8131
2.7937
1.7276
1.7123
1.6979
0.8381
0.0000
-0.0176
1.9414
7.2174
1.1576
1.0000
2.2099
1.1470
0.9830
1.1069
1.0482
2.1238
9.0441
6.2158
[ppm]


TBSO
O
N
Ph
3j
lb4271-OTBS 2 1 C:\Bruker\TOPSPIN bixxx018
enaminone coupling Ph N-propoxy TBS Ph
[rel]
187.2608
153.7364
138.6249
136.2126
129.0685
128.3400
128.1590
127.5397
126.8698
125.5611
110.7240
61.1608
59.1547
50.4610
44.3448
31.5032
25.8464
25.7959
18.1731
-5.4267
-5.4525
0
10
20
30
40
50
200
150
100
50
0
[ppm]


lb5051 1 1 C:\Bruker\TOPSPIN bixxx018
Enaminoe Me N-2-bromo-Bn coupling Ph
Me
O
N
Ph
Br
3k
[rel]
7.6313
7.6115
7.4092
7.4062
7.4021
7.3884
7.3667
7.3639
7.3550
7.3371
7.3341
7.3117
7.3020
7.2928
7.2687
7.2479
7.2384
7.2339
7.2272
7.2179
7.2049
7.1725
7.1542
7.1359
4.6003
4.5616
4.5063
4.4675
3.6888
3.6786
3.6725
3.6628
3.6567
3.6466
2.9403
2.9237
2.9001
2.8836
2.3966
2.3872
2.3565
2.3471
1.2794
1.2627
1.1970
1.9296
1.0000
0.9077
0.9092
2.9812
[ppm]


lb5051 2 1 C:\Bruker\TOPSPIN bixxx018
Enaminoe Me N-2-bromo-Bn coupling Ph
[rel]
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135.3199
133.5529
129.9863
129.5733
128.1802
128.0448
127.6117
125.6053
123.8573
110.2270
57.4939
52.5026
43.0337
15.2879
Me
O
N
Ph
Br
3k
0
10
20
30
40
200
150
100
50
0
[ppm]