Electronic Supplementary Information for

Copper-catalyzed direct borylation of alkyl, alkenyl and aryl halides with B(dan)

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General Remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer using residual chloroform or benzene (^{1}H, δ = 7.26 or 7.15), $CDCl_3$ or C_6D_6 (^{13}C, δ = 77.0 or 128.0) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint =quintet, sep = septet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and uncorrected. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (toluene as an eluent). Column chromatography was carried out using Merk Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene, THF and 1,4-dioxane were distilled from sodium/benzophenone ketyl. DMF was distilled from CaH_2. **1c**,[1] **1d**,[2] **1f**,[3] **2a**,[4] **2b**,[5] **2d**,[6] **2k**,[7] **2m**[7] and **2p**[8] are known compounds.

Cu-Catalyzed Borylation of Alkyl Halides: A General Procedure.

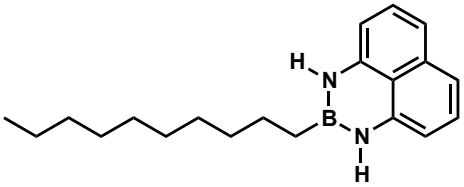
To a mixture of (SIMes)CuCl (15 μmol) and potassium *tert*-butoxide (1 M solution in THF, 0.36 mmol) were added an alkyl halide (0.30 mmol), (pin)B–B(dan) (0.36 mmol) and THF (1.0 mL), and the resulting mixture was stirred at -10 °C for 1 h. Then the mixture was diluted with diethyl ether before filtration through a Celite plug. The organic solution was washed with brine and dried over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product.

Cu-Catalyzed Borylation of Aryl or Alkenyl Halides: A General Procedure.

To a mixture of CuI (0.030 mmol), PCy (0.060 mmol) and potassium *tert*-butoxide (1 M solution in THF, 0.36 mmol) were added an aryl or alkenyl halide (0.30 mmol), (pin)B–B(dan) (0.60 mmol) and THF (1.0 mL), and the resulting mixture was stirred at room temperature for 1 h. Then the mixture was diluted with diethyl ether before filtration through a Celite plug. The organic solution was washed with brine and dried

over $MgSO_4$. Evaporation of the solvent followed by gel permeation chromatography (toluene as an eluent) gave the corresponding product. In ^{13}C NMR spectra, boron-bound carbons were not detected because of quadrupolar relaxation.

2-Decyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1a)



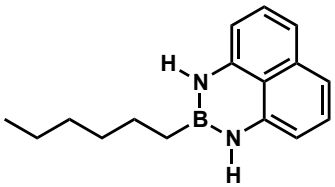
Colorless oil

^1H NMR ($CDCl_3$) δ 0.95 (t, *J* = 7.8 Hz, 2 H), 1.09 (t, *J* = 7.0 Hz, 3 H), 1.41-1.59 (m, 16 H), 5.68 (s, 2 H), 6.41 (dd, *J* = 7.3 Hz, 0.8 Hz, 2 H), 7.18 (dd, *J* = 8.3 Hz, 0.8 Hz, 2 H), 7.26 (dd, *J* = 7.8 Hz, 7.8 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 14.1, 15.0, 22.7, 24.7, 29.3, 29.5, 29.6, 29.7, 31.9, 32.5, 105.3, 117.2, 119.5, 127.4, 136.2, 141.1

HRMS Calcd for $C_{20}H_{30}BN_2$: $[M+H]^+$, 309.2497. Found: *m*/*z* 309.2503

2-Hexyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1b)



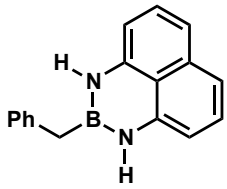
Colorless oil

^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.8 Hz, 2 H), 0.96 (t, *J* = 6.9 Hz, 3 H), 1.30-1.52 (m, 8 H), 5.61 (s, 2 H), 6.32 (d, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 7.14 (t, *J* = 7.7 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 14.1, 15.1, 22.6, 24.7, 31.7, 32.2, 105.3, 117.2, 119.5, 127.5, 136.2, 141.2

HRMS Calcd for $C_{16}H_{22}BN_2$: $[M+H]^+$, 253.1871. Found: *m*/*z* 253.1874

2-Benzyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1e)



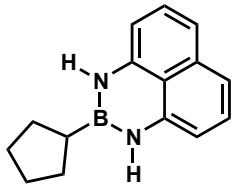
Colorless oil

^{1}H NMR ($CDCl_3$) δ 2.42 (s, 2 H), 5.50 (s, 2 H), 6.26 (dd, *J* = 7.2 Hz, 0.8 Hz, 2 H), 7.06 (d, *J* = 8.3 Hz, 2 H), 7.12 (dd, *J* = 7.7 Hz, 7.8 Hz, 2 H), 7.20 (d, *J* = 7.3 Hz, 2 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.4 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 24.0, 105.6, 117.5, 119.4, 125.1, 127.4, 128.7, 128.8, 136.2, 139.5, 140.8

HRMS Calcd for $C_{17}H_{16}BN_2$: $[M+H]^+$, 259.1401. Found: *m*/*z* 259.1405

2-Cyclopentyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1g)



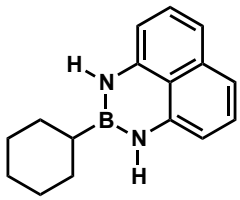
Colorless solid: mp 77-78 °C

^{1}H NMR ($CDCl_3$) δ 1.17-1.28 (m, 1 H), 1.34-1.46 (m, 2 H), 1.53-1.78 (m, 4 H), 1.80-1.96 (m, 2 H), 5.62 (s, 2 H), 6.32 (d, *J* = 7.4 Hz, 2 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 7.13 (dd, *J* = 8.2 Hz, 7.4 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 26.0, 26.5, 29.2, 105.4, 117.2, 119.5, 127.5, 136.3, 141.2

HRMS Calcd for $C_{15}H_{18}BN_2$: $[M+H]^+$, 237.1558. Found: *m*/*z* 237.1561

2-Cyclohexyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1h)



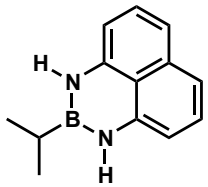
Colorless solid: mp 80-81 °C

^{1}H NMR ($CDCl_3$) δ 0.85-1.05 (m, 1 H), 1.17-1.42 (m, 5 H), 1.63-1.90 (m, 5 H), 5.60 (s, 2 H), 6.31 (d, *J* = 7.5 Hz, 2 H), 7.02 (d, *J* = 8.2 Hz, 2 H), 7.11 (dd, *J* = 7.8 Hz, 7.8 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 24.9, 26.7, 27.4, 28.8, 105.4, 117.2, 119.6, 127.5, 136.3, 141.2

HRMS Calcd for $C_{16}H_{20}BN_2$: $[M+H]^+$, 251.1715. Found: *m*/*z* 251.1717

2-Isopropyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1i)



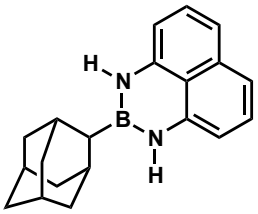
Colorless oil

^{1}H NMR ($CDCl_3$) δ 1.05-1.23 (m, 7 H), 5.62 (s, 2 H), 6.34 (d, *J* = 7.3 Hz, 2 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 7.14 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 13.4, 18.7, 105.4, 117.3, 119.5, 127.5, 136.2, 141.2

HRMS Calcd for $C_{13}H_{16}BN_2$: $[M+H]^+$, 211.1401. Found: *m*/*z* 211.1403

2-(Adamantan-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1j)



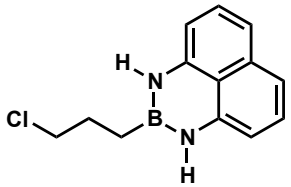
Colorless solid: 178-180 °C

^{1}H NMR ($CDCl_3$) δ 1.46 (s, 1 H), 1.69-2.09 (m, 14 H), 5.68 (s, 2 H), 6.32 (dd, *J* = 7.3 Hz, 0.8 Hz, 2 H), 7.02 (dd, *J* = 8.3 Hz, 0.8 Hz, 2 H), 7.12 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 28.0, 28.2, 29.4, 33.3, 35.7, 37.5, 39.4, 105.4, 117.2, 119.4, 127.5, 136.3, 141.1

HRMS Calcd for $C_{20}H_{24}BN_2$: $[M+H]^+$, 303.2027. Found: *m*/*z* 303.2033

2-(3-Chloropropyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1k)



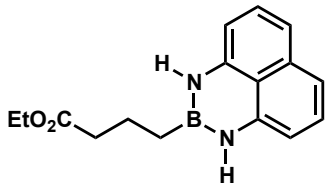
Colorless solid: mp 87-88 °C

^{1}H NMR ($CDCl_3$) δ 0.99 (t, *J* = 8.1 Hz, 2 H), 1.84-1.97 (m, 2 H), 3.58 (t, *J* = 6.7 Hz, 2 H), 5.61 (s, 2 H), 6.31 (d, *J* = 7.3 Hz, 2 H), 7.04 (d, *J* = 8.3 Hz, 2 H), 7.12 (t, *J* = 7.8 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 12.5, 28.1, 47.1, 105.6, 117.6, 119.5, 127.5, 136.2, 140.8

HRMS Calcd for $C_{13}H_{15}BClN_2$: $[M+H]^+$, 245.1011. Found: *m*/*z* 245.1013

Ethyl 4-(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)butanoate (1l)



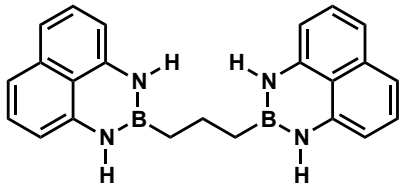
Colorless solid: 95-96 °C

^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 8.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 1.73-1.84 (m, 2 H), 2.37 (t, *J* = 7.3 Hz, 2 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 5.68 (s, 2 H), 6.30 (dd, *J* = 7.3 Hz, 0.9 Hz, 2 H), 7.01 (d, *J* = 8.3 Hz, 0.8 Hz, 2 H), 7.10 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 14.2, 14.5, 20.3, 36.6, 60.3, 105.5, 117.4, 119.5, 127.5, 136.2, 141.0, 173.7

HRMS Calcd for $C_{16}H_{20}BN_2O_2$: $[M+H]^+$, 283.1612. Found: *m*/*z* 283.1615

1,3-Bis(1*H*-naphtho[1,8-*de*][1,3,2]diazaborinin-2(3*H*)-yl)propane (1m)



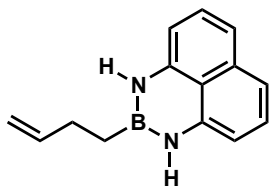
Colorless solid

^{1}H NMR ($CDCl_3$) δ 0.96 (t, *J* = 7.8 Hz, 4 H), 1.62 (quin, *J* = 7.8 Hz, 2 H), 5.63 (s, 4 H), 6.30 (d, *J* = 7.3 Hz, 4 H), 7.01 (d, *J* = 8.2 Hz, 4 H), 7.10 (dd, *J* = 8.2 Hz, 7.3 Hz, 4 H)

^{13}C NMR ($CDCl_3$) δ 18.0, 20.3, 105.4, 117.4, 119.5, 127.5, 136.3, 141.1

HRMS Calcd for $C_{23}H_{27}B_2N_4$: $[M+H]^+$, 377.2103. Found: *m*/*z* 377.2115

2-(But-3-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1n)



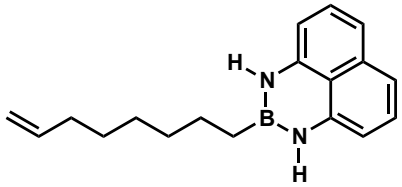
Colorless oil

^{1}H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.8 Hz, 2 H), 2.19-2.31 (m, 2 H), 5.05 (dq, *J* = 10.2 Hz, 1.7 Hz, 1 H), 5.14 (dq, *J* = 17.2 Hz, 1.7 Hz, 1 H), 5.66 (s, 2 H), 5.91-6.06 (m, 1 H), 6.32 (dd, *J* = 7.2 Hz, 1.0 Hz, 2 H), 7.06 (dd, *J* = 8.3 Hz, 0.7 Hz, 2 H), 7.15 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 13.6, 28.6, 105.4, 113.8, 117.3, 119.5, 127.5, 136.2, 140.5, 141.0

HRMS Calcd for $C_{14}H_{16}BN_2$: $[M+H]^+$, 223.1401. Found: *m*/*z* 223.1404

2-(Oct-7-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1o)



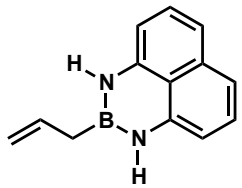
Colorless oil

^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.8 Hz, 2 H), 1.32-1.50 (m, 8 H), 2.10 (td, *J* = 7.3 Hz, 7.3 Hz, 2 H), 4.99 (d, *J* = 10.2 Hz, 1 H), 5.05 (d, *J* = 17.3 Hz, 1 H), 5.61 (s, 2 H), 5.81-5.95 (m, 1 H), 6.31 (d, *J* = 7.4 Hz, 2 H), 7.04 (d, *J* = 8.2 Hz, 2 H), 7.13 (dd, *J* = 7.8 Hz, 7.8 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 15.0, 24.7, 28.8, 29.0, 32.3, 33.8, 105.3, 114.2, 117.2, 119.5, 127.5, 136.2, 139.1, 141.2

HRMS Calcd for $C_{18}H_{24}BN_2$: $[M+H]^+$, 279.2027. Found: *m*/*z* 279.2034

2-Allyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1p)



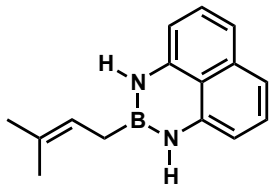
Colorless oil

^{1}H NMR ($CDCl_3$) δ 1.82 (d, *J* = 7.8 Hz, 2 H), 5.05-5.09 (m, 1 H), 5.10 (d, *J* = 1.0 Hz, 1 H), 5.63 (s, 2 H), 5.85-6.01 (m, 1 H), 6.31 (dd, *J* = 7.2 Hz, 0.7 Hz, 2 H), 7.04 (dd, *J* = 8.2 Hz, 0.8 Hz, 2 H), 7.12 (dd, *J* = 8.2 Hz, 7.2 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 21.4, 105.5, 115.5, 117.5, 119.5, 127.5, 135.1, 136.2, 140.9

HRMS Calcd for $C_{13}H_{14}BN_2$: $[M+H]^+$, 209.1247. Found: *m*/*z* 209.1246

2-(3-Methylbut-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1q)



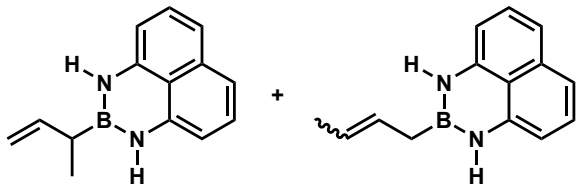
Colorless solid: mp 79-80 °C

^{1}H NMR ($CDCl_3$) δ 1.17 (s, 6 H), 5.62 (dd, *J* = 17.4 Hz, 1.4 Hz, 1 H), 5.07 (dd, *J* = 10.7 Hz, 1.4 Hz, 1 H), 5.62 (s, 2 H), 5.99 (dd, *J* = 17.4 Hz, 10.7 Hz, 1 H), 6.34 (d, *J* = 7.5 Hz, 2 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 7.12 (dd, *J* = 7.8 Hz, 7.8 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 23.9, 105.7, 110.7, 117.5, 119.4, 127.5, 136.2, 141.0, 147.2

HRMS Calcd for $C_{15}H_{18}BN_2$: $[M+H]^+$, 237.1557. Found: *m/z* 237.1560

Mixture of 2-(but-3-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1r) and 2-(but-2-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1'r)



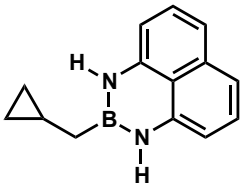
Green oil

^{1}H NMR ($CDCl_3$) δ 1.18 (dd, *J* = 7.3, 1.1 Hz, 3H, **1r**), 1.64 (d, *J* = 6.1 Hz, **1'r**), 1.78 (d, *J* = 7.1 Hz, **1'r**), 1.72 (d, *J* = 4.4 Hz, **1'r**), 1.96 (quint, *J* = 7.4 Hz, 1H, **1r**), 5.01-5.08 (m, 2H, **1r**), 5.44-5.64 (m, 2H, **1'r**), 5.61 (brs, 2H, **1r** + **1'r**), 5.88-5.99 (m, 1H, **1r**), 6.28-6.34 (m, 2H, **1r** + **1'r**), 6.97-7.04 (m, 2H, **1r** + **1'r**), 7.06-7.13 (m, 2H, **1r** + **1'r**)

^{13}C NMR ($CDCl_3$) δ 12.6, 14.8, 18.1, 105.5, 105.7, 112.6, 117.4, 117.5, 119.6, 124.4, 126.0, 126.1, 126.9, 127.5, 136.3, 141.0, 141.1, 141.9

HRMS Calcd for $C_{14}H_{16}N_2B$: $[M+H]^+$, 223.1401. Found: *m/z* 223.1405

2-(Cyclopropylmethyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1s)



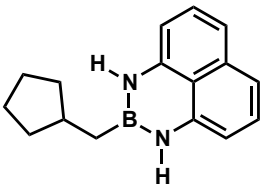
Colorless oil

^{1}H NMR (C_6D_6) δ 1.60 (m, 3 H), 1.76-2.10 (m, 4 H), 5.03 (s, 2 H), 5.95-6.01 (m, 2 H), 7.05-7.11 (m, 4 H)

^{13}C NMR (C_6D_6) δ 19.8, 21.7, 103.0, 115.0, 117.2, 134.1, 138.5

HRMS Calcd for $C_{14}H_{16}BN_2$: $[M+H]^+$, 223.1401. Found: *m*/*z* 223.1404

2-(Cyclopentylmethyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1t)



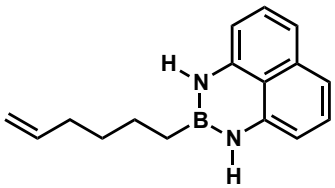
Colorless oil

^{1}H NMR ($CDCl_3$) δ 0.93 (d, *J* = 7.3 Hz, 2 H), 1.07-1.21 (m, 2 H), 1.50-1.76 (m, 4 H), 1.81-2.05 (m, 3 H), 5.62 (s, 2 H), 6.30 (dd, *J* = 7.3 Hz, 1.0 Hz, 2 H), 7.02 (dd, *J* = 8.3 Hz, 1.0 Hz, 2 H), 7.11 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 22.2, 25.1, 35.3, 36.7, 105.3, 117.2, 119.5, 127.5, 136.3, 141.2

HRMS Calcd for $C_{16}H_{20}BN_2$: $[M+H]^+$, 251.1714. Found: *m*/*z* 251.1717

2-(Hex-5-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1’t)



Colorless oil

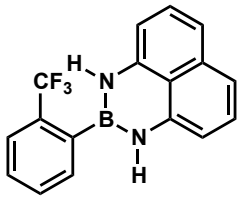
^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.6 Hz, 2 H), 1.41-1.51 (m, 4 H), 2.03-2.16 (m, 2 H), 4.97 (ddt, *J* = 10.1 Hz, 2.3 Hz, 1.1 Hz, 1 H), 5.03 (ddd, *J* = 17.0 Hz, 3.4 Hz, 1.5 Hz, 1 H), 5.61 (s, 2 H), 5.83 (ddt, *J* = 17.0 Hz, 10.1 Hz, 6.8 Hz, 1 H), 6.30 (dd, *J* = 7.3 Hz, 1.0 Hz, 2 H), 7.00 (dd, *J* = 8.3 Hz, 1.0 Hz, 2 H), 7.10 (dd, *J* = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 24.2, 31.6, 33.6, 105.4, 114.4, 117.3, 119.5, 127.5, 136.3, 138.9,

141.1

HRMS Calcd for $C_{16}H_{20}BN_2$: $[M+H]^+$, 251.1714. Found: *m*/*z* 251.1720

2-(2-(Trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2c)



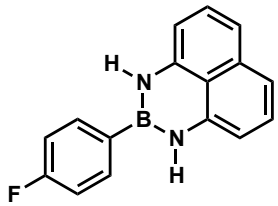
Colorless solid: mp 138-139 °C

^{1}H NMR ($CDCl_3$) δ5.85 (s, 2 H), 6.37 (dd, *J* = 7.2 Hz, 1.1 Hz, 2 H), 7.09 (dd, *J* = 8.3 Hz, 1.1 Hz, 2 H), 7.15 (dd, *J* = 8.3 Hz, 7.2 Hz, 2 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.65 (d, *J* = 7.2 Hz, 1 H), 7.73 (d, *J* = 7.2 Hz, 1 H)

^{13}C NMR ($CDCl_3$) δ 106.1, 118.0, 119.8, 124.7 (q, $J_{C–F}$ = 273.3 Hz), 125.3 (q, $J_{C–F}$ = 4.8 Hz), 127.6, 129.2, 131.2, 132.8 (q, $J_{C–F}$ = 31.0 Hz), 133.4, 136.3, 140.8

HRMS Calcd for $C_{17}H_{12}BF_3N_2$: $[M+H]^+$, 313.1118. Found: *m*/*z* 313.1126

2-(4-Fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2e)



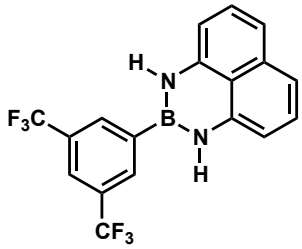
Colorless oil

^{1}H NMR ($CDCl_3$) δ 5.97 (s, 2 H), 6.42 (*J* = 7.2 Hz, 0.7 Hz, 2 H), 7.07 (dd, *J* = 8.4, 0.7 Hz, 2 H), 7.10-7.22 (m, 4 H), 7.62 (dd, *J* = 8.5, 6.0 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 106.0, 115.3 (d, $J_{C–F}$ = 20.3 Hz), 117.9, 119.7, 127.6, 133.4 (d, $J_{C–F}$ = 8.0 Hz), 136.3, 140.9, 164.3 (d, $J_{C–F}$ = 249.9 Hz)

HRMS Calcd for $C_{16}H_{13}BFN_2$: $[M+H]^+$, 263.1150. Found: *m*/*z* 263.1156

2-(3,5-Bis(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2f)



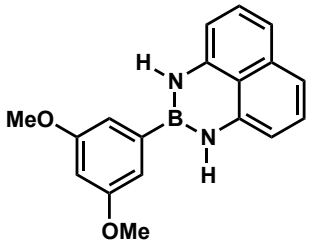
Colorless solid: 178-180 °C

^{1}H NMR ($CDCl_3$) δ 6.02 (s, 2 H), 6.47 (d, J = 7.2 Hz, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.17 (dd, J = 8.1 Hz, 7.2 Hz, 2 H), 7.97 (s, 1 H), 8.06 (s, 2 H)

^{13}C NMR ($CDCl_3$) δ 106.6, 118.6, 119.9, 123.4 (q, $J_{C\text{-}F}$ = 274.5 Hz), 123.8, 127.6, 131.3 (q, $J_{C\text{-}F}$ = 32.8 Hz), 131.4, 136.2, 140.1

HRMS Calcd for $C_{18}H_{12}BF_6N_2$: $[M+H]^+$, 381.0992. Found: *m*/*z* 381.0993

2-(3,5-Dimethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2g)



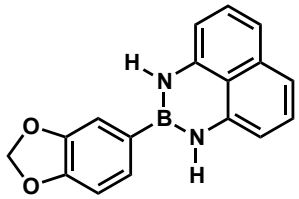
Colorless solid: mp 173-174 °C

^{1}H NMR ($CDCl_3$) δ 3.86 (s, 6 H), 5.99 (s, 2 H), 6.41 (dd, J = 7.3 Hz, 0.9 Hz, 2 H), 6.57 (t, J = 2.2 Hz, 1 H), 6.76 (d, J = 2.2 Hz, 2 H), 7.06 (dd, J = 8.3 Hz, 0.9 Hz, 2 H), 7.15 (dd, J = 8.3 Hz, 7.3 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ 55.4, 101.9, 106.0, 109.0, 117.8, 119.8, 127.6, 136.3, 140.9, 160.8

HRMS Calcd for $C_{18}H_{12}BN_2O_2$: $[M+H]^+$, 305.1456. Found: *m*/*z* 305.1458

2-(Benzo[*d*][1,3]dioxol-5-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2h)



Colorless solid: mp 138-139 °C

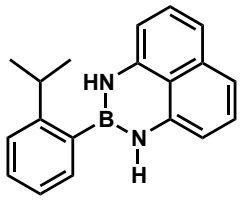
^{1}H NMR ($CDCl_3$) δ 5.95 (s, 2 H), 6.00 (s, 2 H), 6.40 (dd, J = 7.3 Hz, 1.0 Hz, 2 H), 6.91

(d, J = 7.7 Hz, 1 H), 7.04-7.10 (m, 3 H), 7.14 (t, J = 7.6 Hz, 3 H)

^{13}C NMR ($CDCl_3$) δ 100.9, 105.9, 108.7, 110.9, 117.7, 119.6, 125.7, 127.6, 136.3, 141.0, 147.8, 149.3

HRMS Calcd for $C_{17}H_{13}BN_2O_2$: $[M+H]^+$, 289.1143. Found: *m*/*z* 289.1149

2-(2-Isopropylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2i)



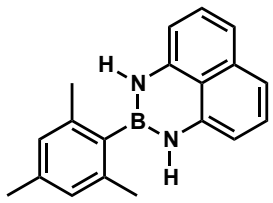
Colorless solid: mp 100-101 °C

^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 6.7 Hz, 6 H), 3.24 (sept, J = 6.7 Hz, 1 H), 5.83 (s, 2 H), 6.37 (d, J = 7.2 Hz, 2 H), 7.08-7.14 (m, 2 H), 7.18 (dd, J = 8.2 Hz, 7.3 Hz, 2 H), 7.26 (t, J = 7.0 Hz, 1 H), 7.36-7.49 (m, 3 H)

^{13}C NMR ($CDCl_3$) δ 24.8, 33.7, 105.9, 117.8, 119.7, 124.8, 125.4, 127.6, 129.4, 132.9, 136.3, 141.0, 151.9

HRMS Calcd for $C_{19}H_{20}BN_2$: $[M+H]^+$, 287.1714. Found: *m*/*z* 287.1719

2-Mesityl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2j)



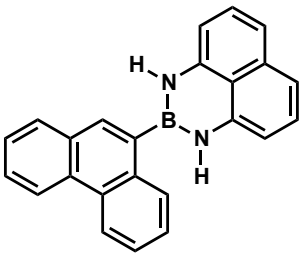
Colorless solid: 68-70 °C

^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.40 (s, 6 H), 5.77 (s, 2 H), 6.34 (dd, J = 7.2 Hz, 0.8 Hz, 2 H), 6.90 (s, 2 H), 7.09 (dd, J = 8.2 Hz, 0.8 Hz, 2 H), 7.16 (dd, J = 8.2 Hz, 7.2 Hz, 2 H)

^{13}C NMR ($CDCl_3$) δ21.2, 22.2, 105.8, 117.7, 127.2, 127.6, 128.2, 129.0, 136.3, 138.5, 140.6, 141.1

HRMS Calcd for $C_{19}H_{20}BN_2$: $[M+H]^+$, 287.1714. Found: *m*/*z* 287.1720

2-(Phenanthren-9-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2l)



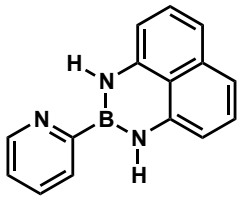
Colorless solid: 185-186 °C

^{1}H NMR ($CDCl_3$) δ 5.00 (s, 2 H), 5.67 (dd, *J* = 6.8 Hz, 1.6 Hz, 2 H), 6.75-6.89 (m, 5 H), 7.03-7.11 (m, 1 H), 7.13-7.22 (m, 3 H), 7.41-7.49 (m, 1 H), 7.71 (dd, J = 8.0 Hz, 1.2 Hz, 1 H), 8.18-8.37 (m, 2 H)

^{13}C NMR ($CDCl_3$) δ 106.0, 118.0, 119.9, 122.5, 123.2, 126.5, 126.7, 127.2, 127.6, 128.6, 128.7, 130.0, 130.7, 131.2, 132.3, 133.6, 136.4, 141.0

HRMS Calcd for $C_{24}H_{18}BN_2$: $[M+H]^+$, 345.1558. Found: *m*/*z* 345.1563

2-(Pyridin-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2n)



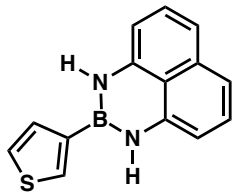
Yellow solid: mp 168-169 °C

^{1}H NMR (C_6D_6) δ 6.14 (dd, *J* = 6.0 Hz, 2.3 Hz, 2 H), 6.44 (s, 2 H), 6.74 (ddd, *J* = 7.7 Hz, 4.8 Hz, 1.2 Hz, 1 H), 6.83 (ddd, *J* = 7.7 Hz, 1.2 Hz, 1.2 Hz, 1 H), 7.02-7.12 (m, 5 H), 8.63 (ddd, *J* = 4.7 Hz, 1.6 Hz, 1.2 Hz, 1 H)

^{13}C NMR (C_6D_6) δ 106.6, 118.4, 121.1, 124.1, 126.8, 127.9, 134.3, 137.2, 141.5, 150.1

HRMS Calcd for $C_{15}H_{13}BN_3$: $[M+H]^+$, 246.1201. Found: *m*/*z* 246.1197

2-(Thiophen-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2o)



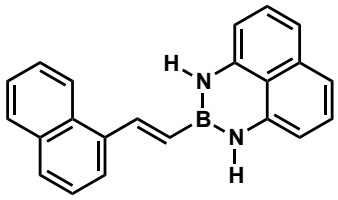
Purple oil

^{1}H NMR ($CDCl_3$) δ 5.96 (brs, 2H), 6.40 (d, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.14 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.32-7.35 (m, 1H), 7.42-7.48 (m, 1H), 7.68-7.71 (m, 1H)

^{13}C NMR ($CDCl_3$) δ 106.0, 117.8, 119.7, 126.3, 127.6, 129.7, 131.37, 136.3, 140.9

HRMS Calcd for $C_{14}H_{12}N_2BS$: $[M+H]^+$, 251.0809. Found: *m/z* 251.0813

(*E*)-2-(2-(Naphthalen-1-yl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2q)



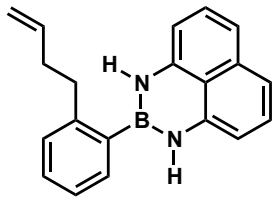
Colorless solid: mp 110-114 °C

^{1}H NMR ($CDCl_3$) δ 5.93 (s, 2 H), 6.40 (d, *J* = 18.3 Hz, 1 H), 6.41 (dd, *J* = 7.3 Hz, 0.7 Hz, 2 H), 7.06 (dd, *J* = 8.2 Hz, 0.7 Hz, 2 H), 7.15 (dd, *J* =8.3 Hz, 0.7 Hz, 2 H), 7.48-7.61 (m, 3 H), 7.74 (d, *J* = 7.2 Hz, 1 H), 7.85 (d, *J* = 8.2 Hz, 1 H), 7.89 (d, *J* = 8.2 Hz, 1 H), 7.95 (d, *J* = 18.2 Hz, 1 H), 8.24 (d, *J* = 8.3 Hz, 1 H)

^{13}C NMR ($CDCl_3$) δ 105.9, 117.7, 119.9, 123.5, 124.1, 125.6, 125.9, 126.3, 127.6, 128.7, 128.8, 131.0, 133.7, 135.6, 136.4, 140.7, 141.1

HRMS Calcd for $C_{22}H_{28}BN_2$: $[M+H]^+$, 320.1481. Found: *m*/*z* 320.1479

2-(2-(But-3-en-1-yl)phenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (2r)



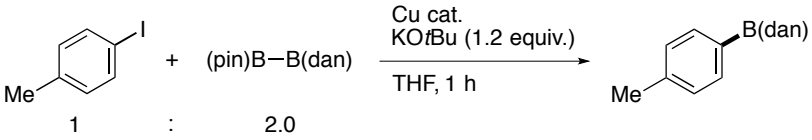
Colorless oil

^{1}H NMR ($CDCl_3$) δ 2.46 (dt, *J* = 7.8 Hz, 7.2 Hz, 2 H), 2.90 (t, *J* = 7.8 Hz, 2 H), 5.04 (d, *J* = 10.4 Hz, 1 H), 5.10 (d, *J* = 17.2 Hz, 1 H), 5.79 (m, 3 H), 6.36 (d, *J* = 7.1 Hz, 2 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 7.17 (dd, *J* = 8.3 Hz, 7.2 Hz, 2 H), 7.24-7.32 (m, 2 H), 7.39 (td, *J* = 7.5 Hz, 1.4 Hz, 1 H), 7.48 (dd, *J* = 7.3 Hz, 1.4 Hz, 1 H)

^{13}C NMR ($CDCl_3$) δ 35.5, 36.4, 105.8, 115.4, 117.8, 119.7, 125.5, 127.6, 128.7, 129.3, 132.3, 136.3, 138.0, 141.0, 144.6

HRMS Calcd for $C_{20}H_{20}BN_2$: $[M+H]^+$, 299.1714. Found: *m*/*z* 299.1721

Table S1. Optimization of the reaction conditions for an aryl halide



Cu cat. (mol %)	Temp. (°C)	Yield (%)
CuI (10), PCy_3 (20)	rt	74
CuI (5), PCy_3 (10)	rt	67
CuI (5), PCy_3 (15)	rt	52
CuI (5), PCy_3 (5)	rt	49
CuI (5), PCy_3 (10)	0	49
(SIMes)CuCl (20)[a]	60	50
(SIMes)CuCl (5)[a]	60	40
$(PPh_3)_3$CuCl (5)	50	29

[a]KO*t*Bu: 2.0 equiv.

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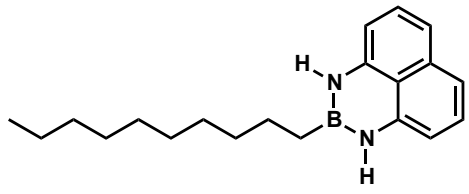
^{1}H and ^{13}C NMR Spectra of Products



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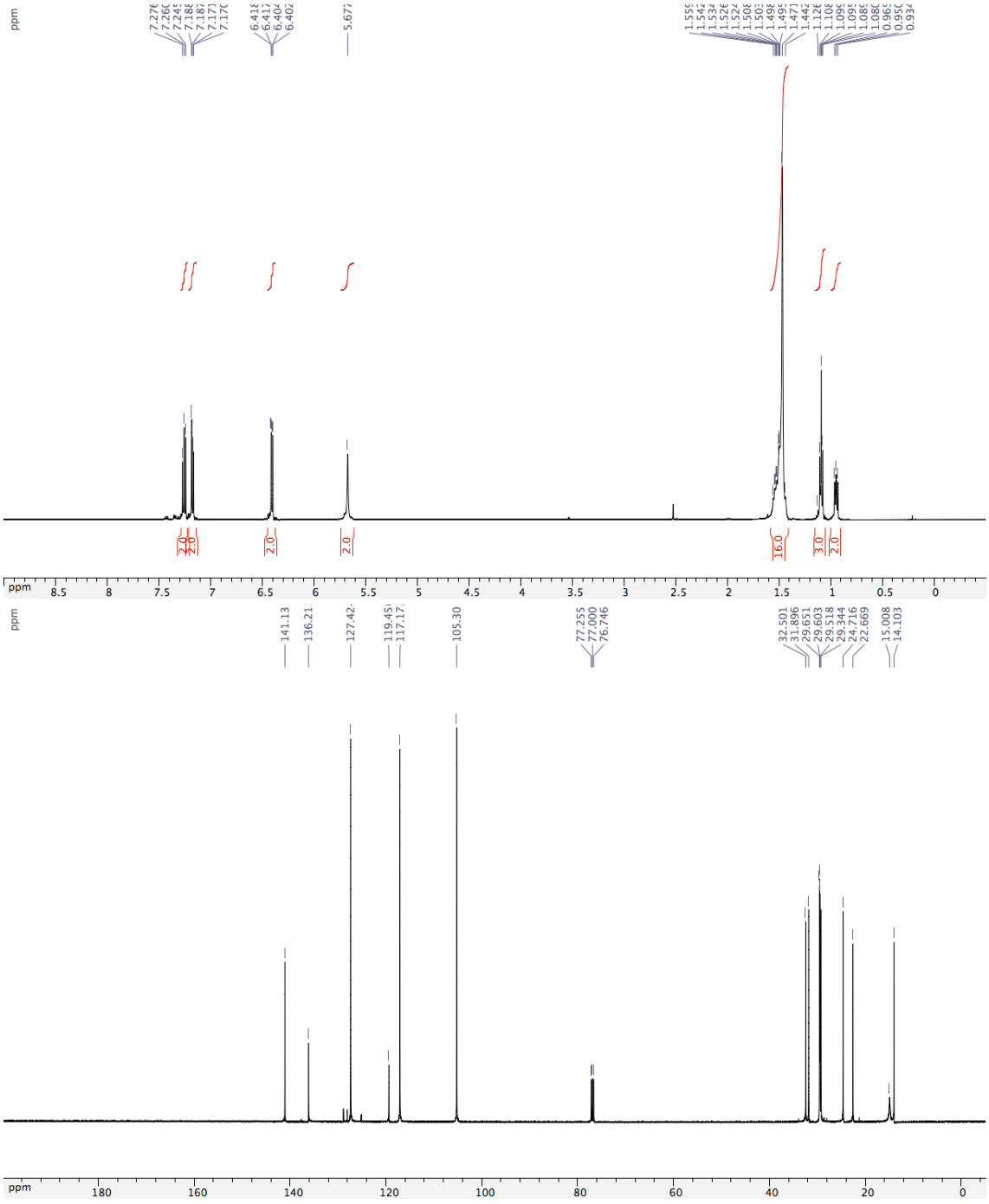

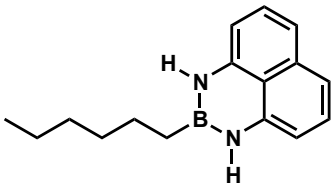

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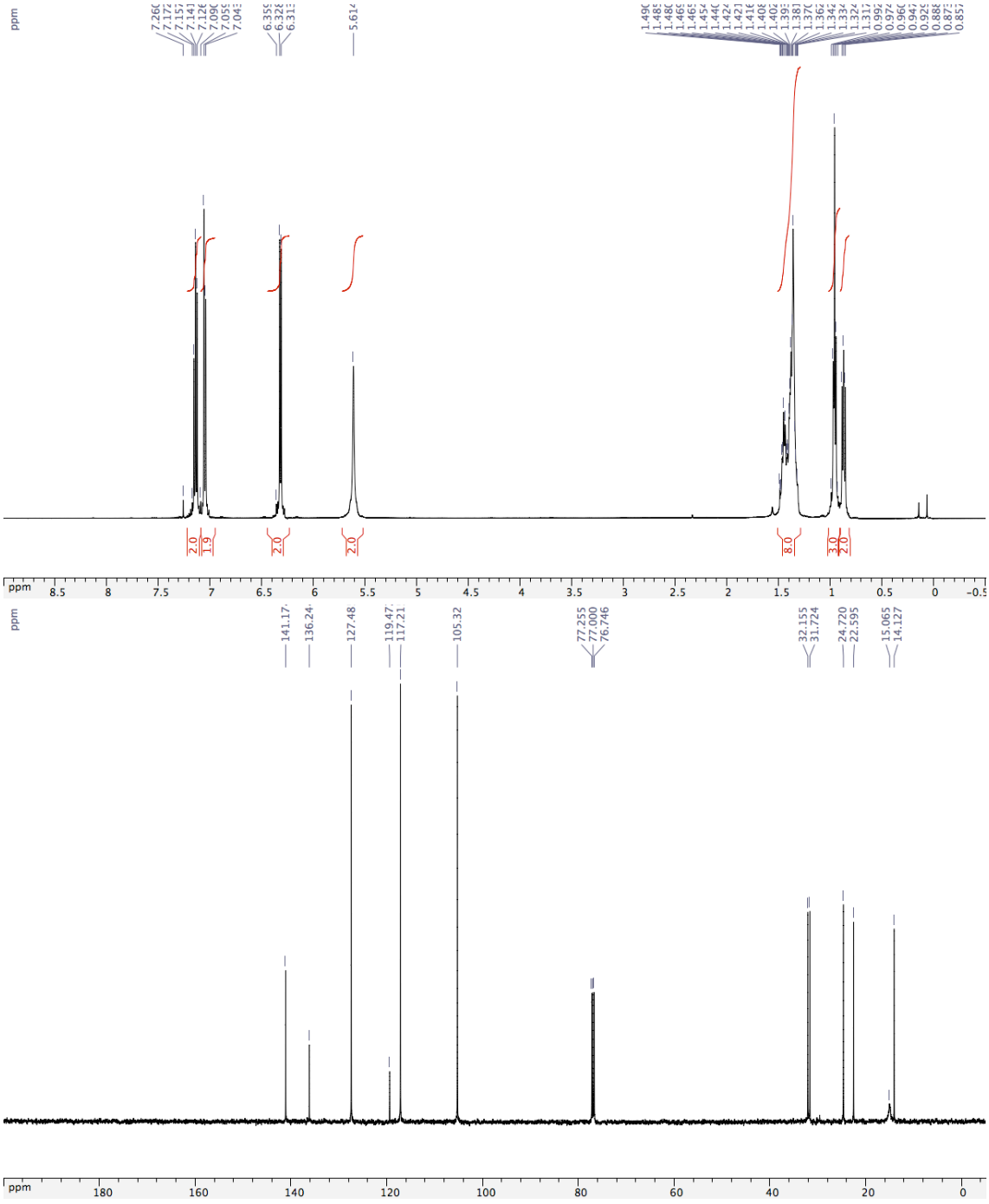

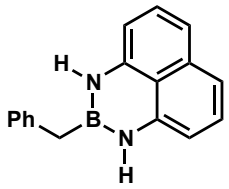
H
N
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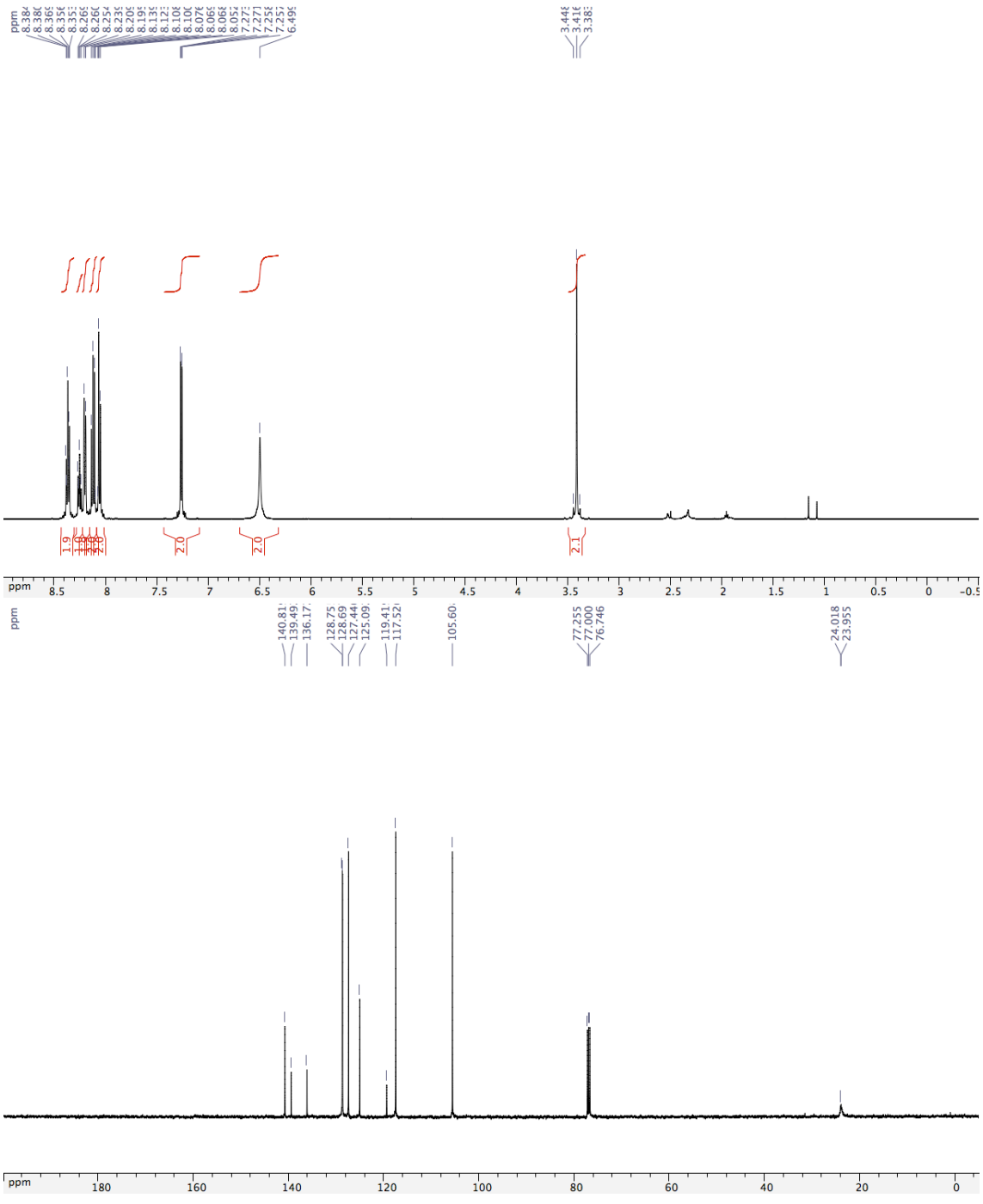
1e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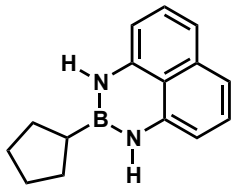
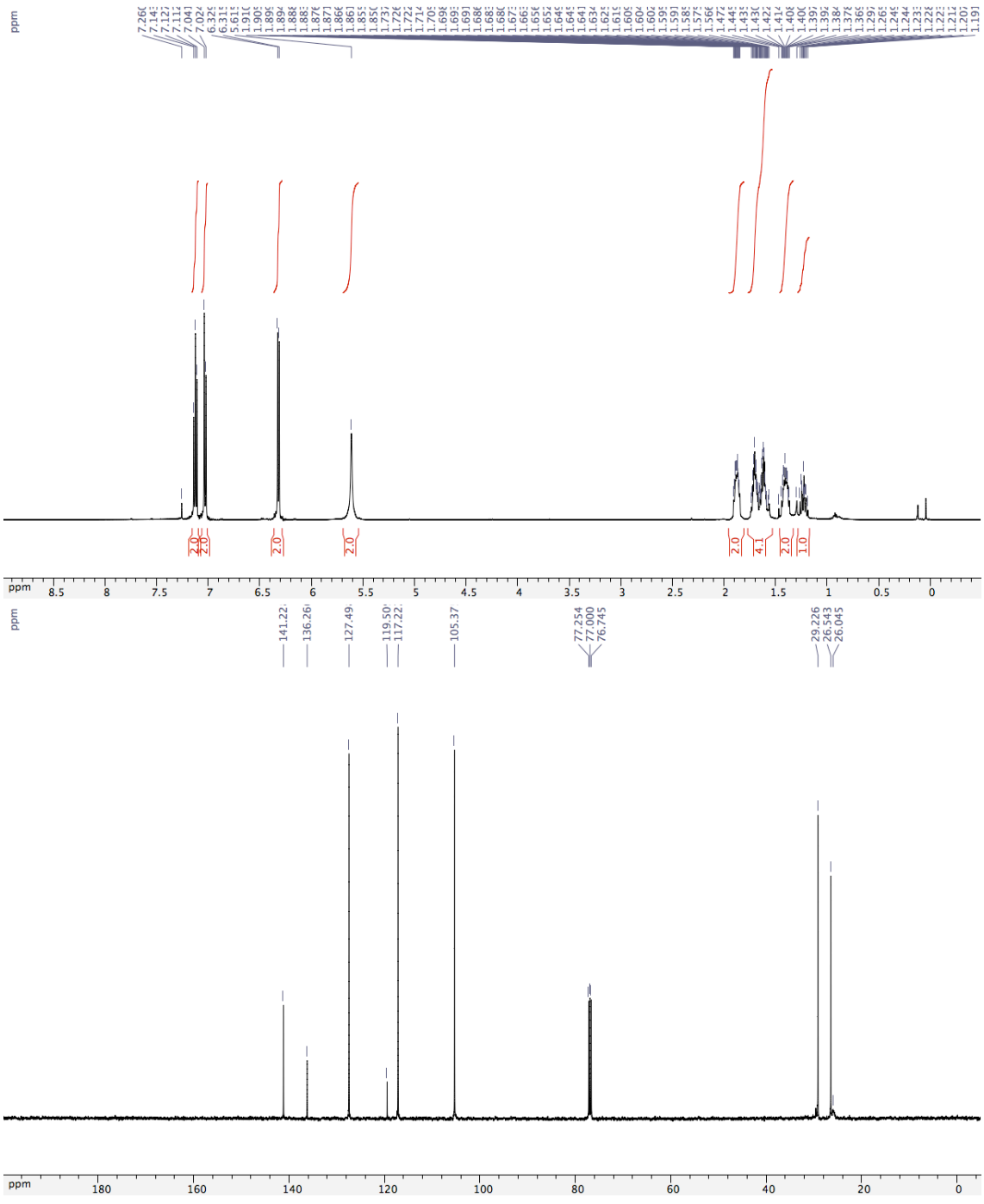
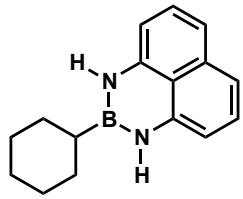
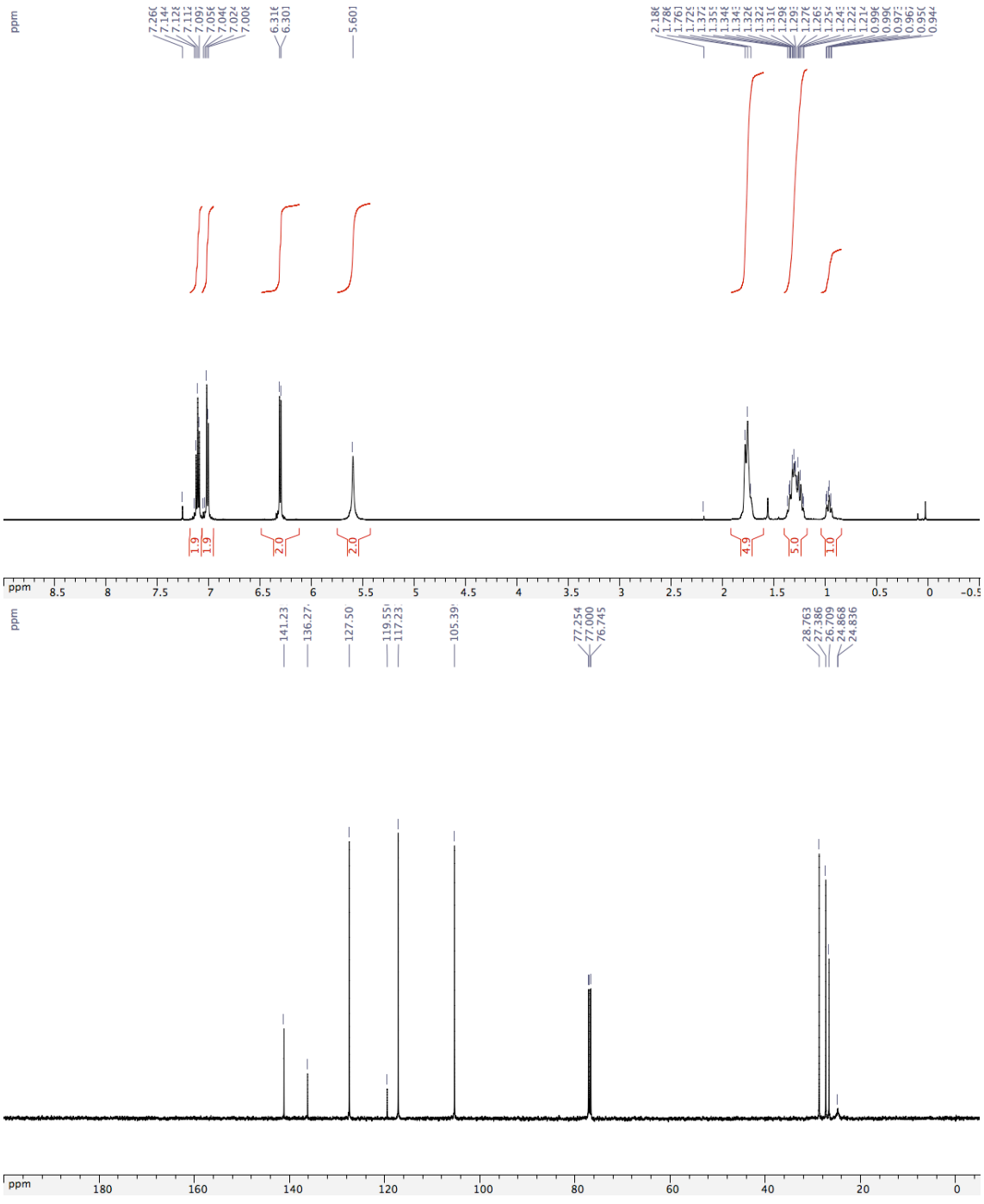


1g




H
N
B
N
H

1h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7.128
7.111
7.099
7.056
7.046
7.024
7.008
6.316
6.301
5.601
2.188
1.788
1.761
1.725
1.337
1.335
1.334
1.332
1.325
1.311
1.298
1.293
1.276
1.265
1.254
1.243
1.222
1.214
0.996
0.990
0.973
0.967
0.950
0.944
1.9
1.9
2.0
2.0
4.9
5.0
1.0
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
141.23
136.27
127.50
119.55
117.23
105.39
77.254
77.000
76.745
28.763
27.386
26.709
24.868
24.836
180
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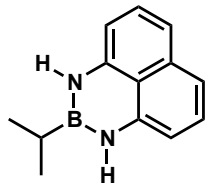
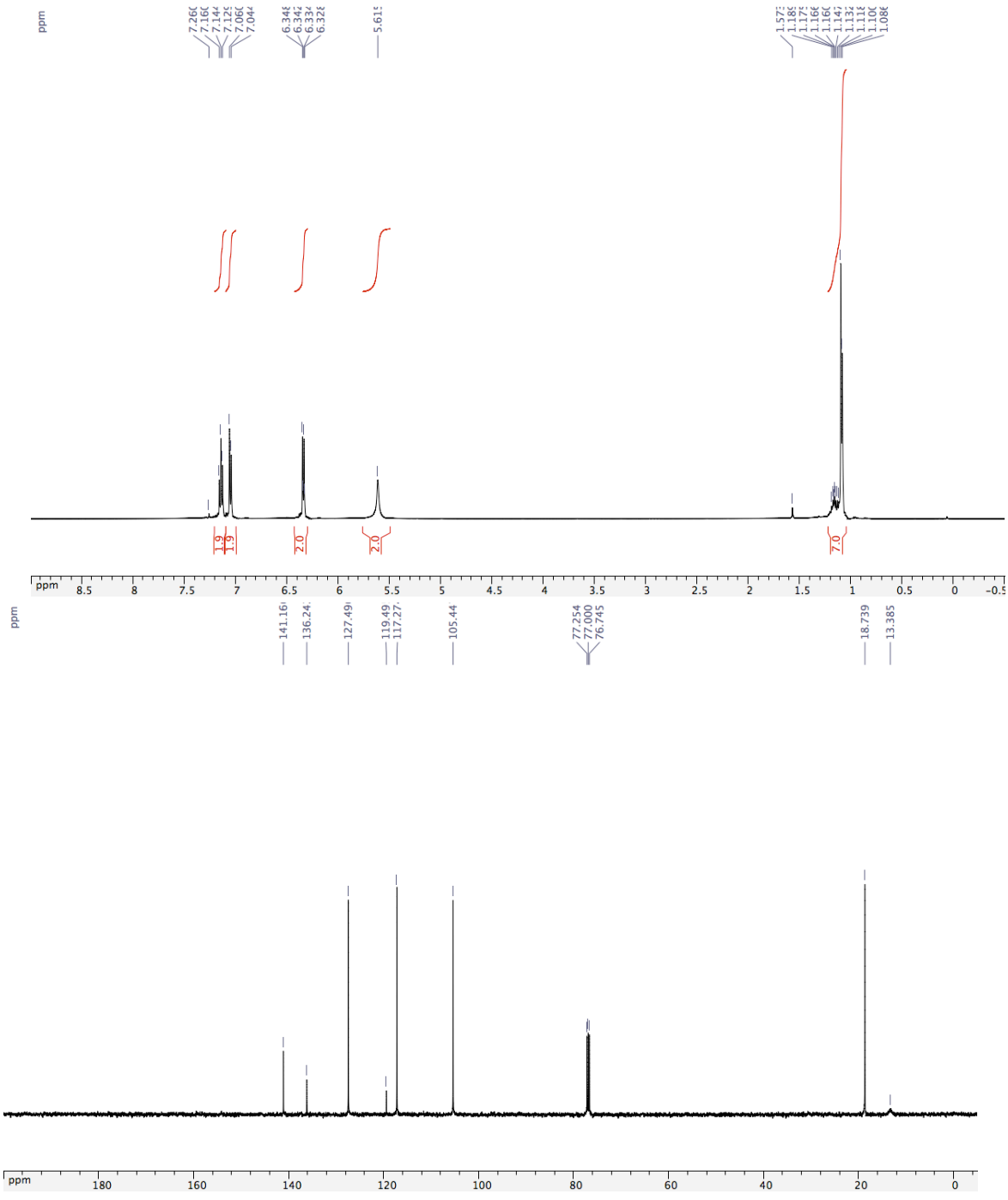
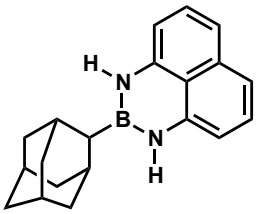
140
120
100
80
60
40
20
0

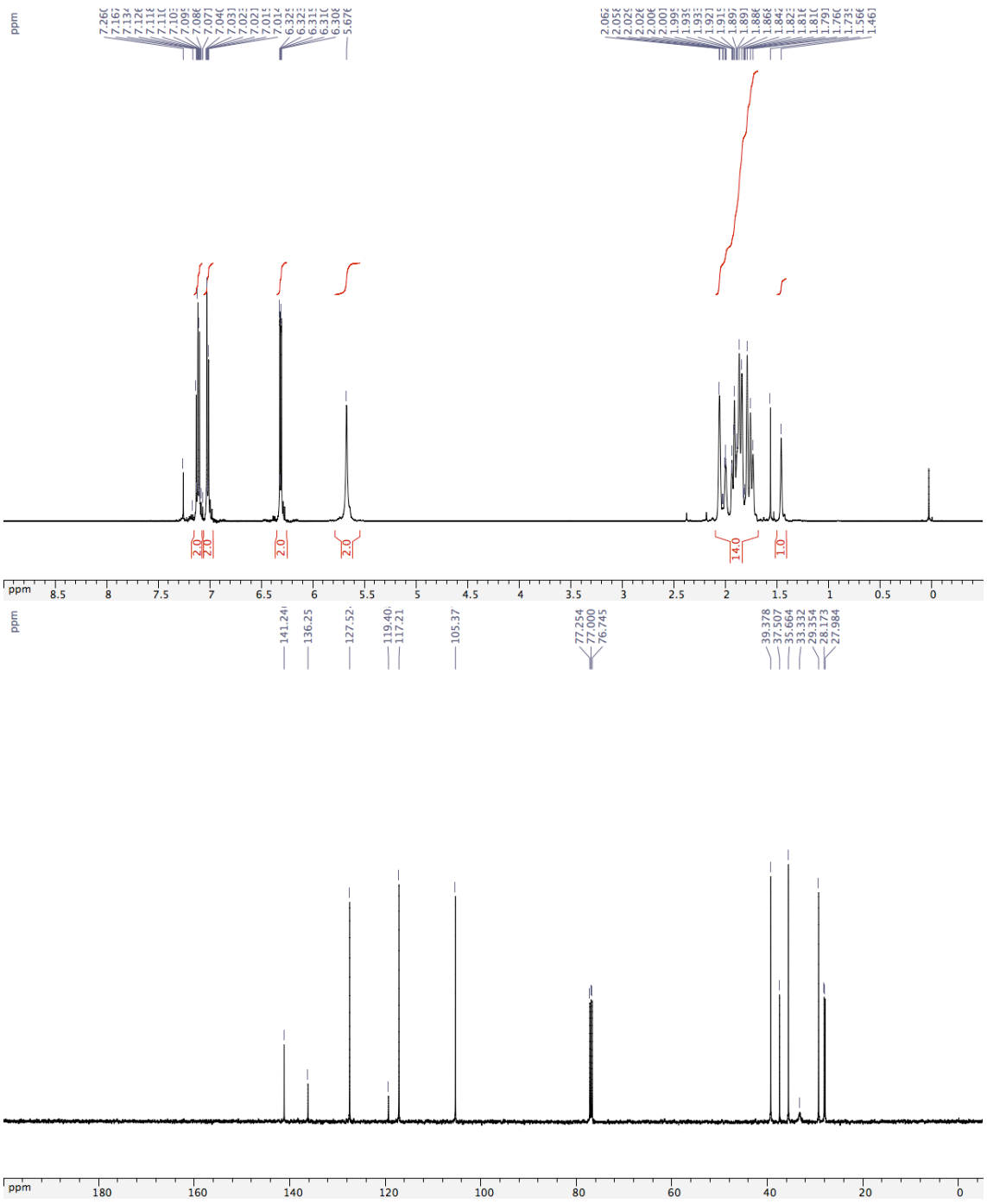


1i




H
N
B
N
H

1j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2.0
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2.0
2.0
14.0
1.0
141.24
136.25
127.52
119.40
117.21
105.37
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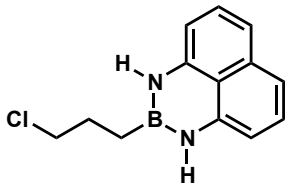
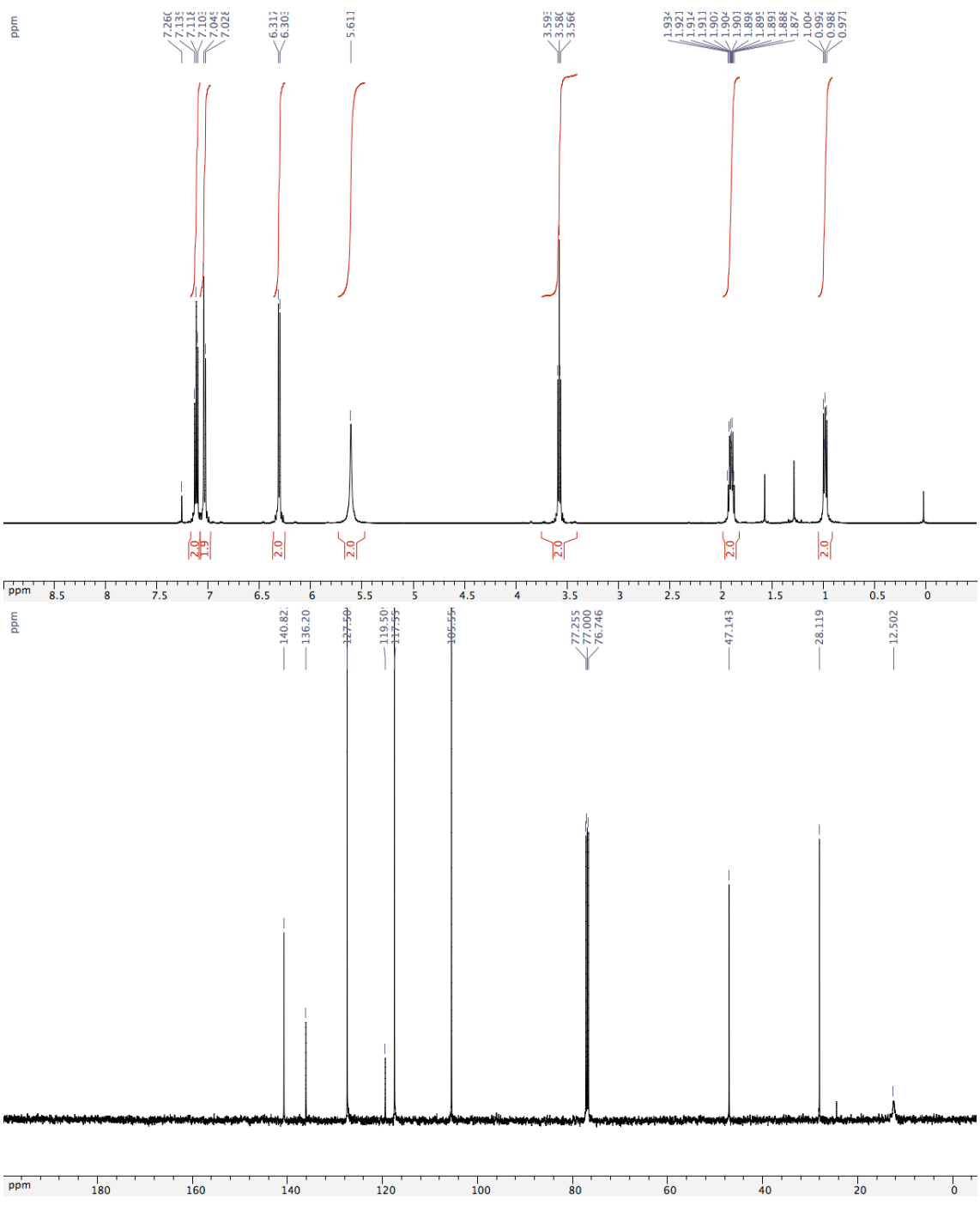
77.000
76.745
39.378
37.507
35.664
33.332
29.354
28.173
27.984


H
N
Cl
B
N
H

1k


ppm
7.266
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7.118
7.103
7.045
7.028
6.317
6.303
5.611
3.599
3.586
3.566
1.934
1.921
1.914
1.911
1.907
1.904
1.901
1.898
1.895
1.891
1.888
1.877
1.004
0.992
0.984
0.971
2.0
1.9
2.0
2.0
2.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
ppm
140.82
136.20
127.58
119.50
117.55
105.55
77.255
77.000
76.746
47.143
28.119
12.502
ppm
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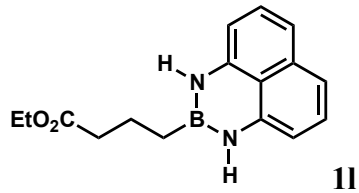
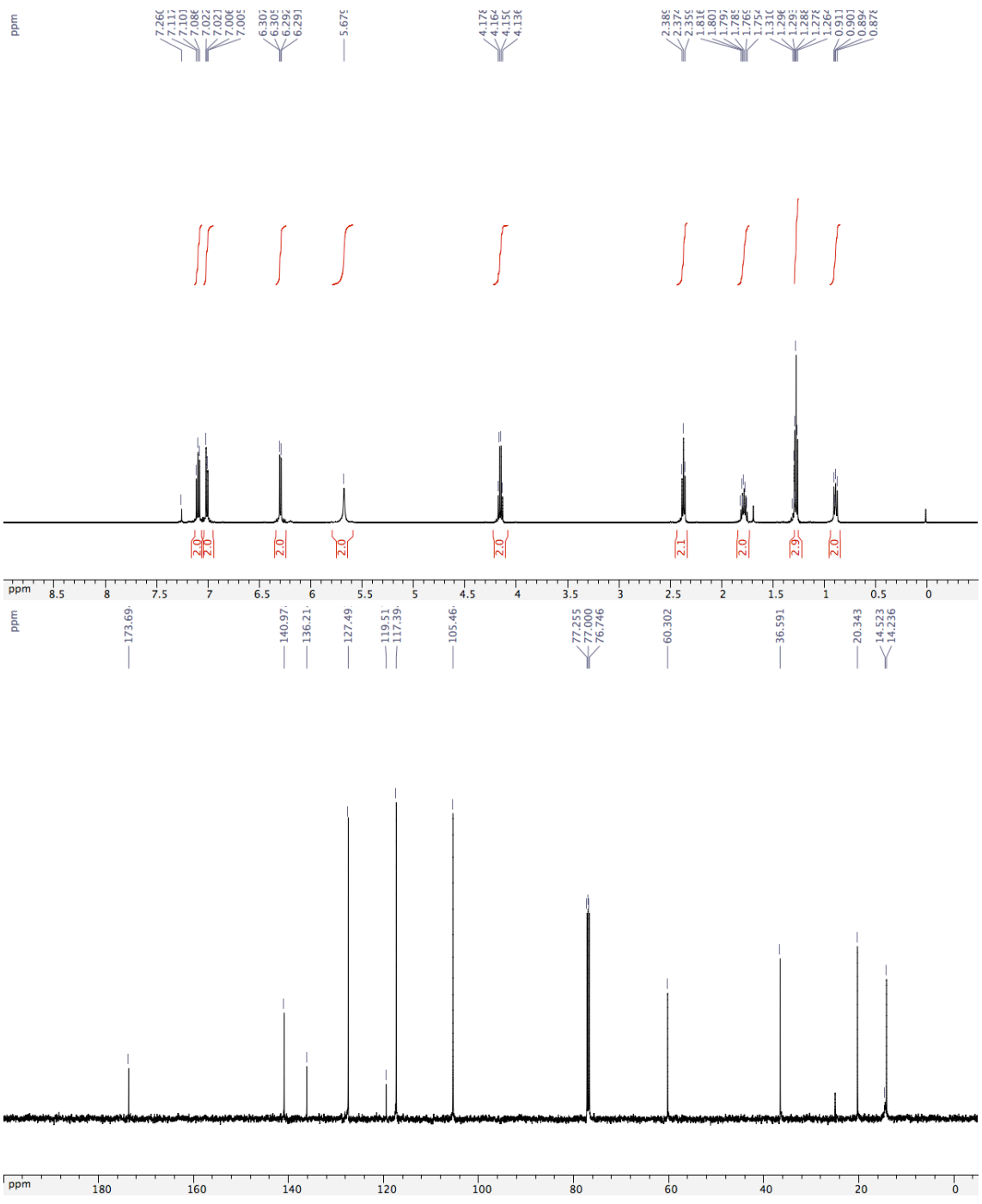
160
140
120
100
80
60
40
20
0


H
N
EtO2C
B
N
H

1l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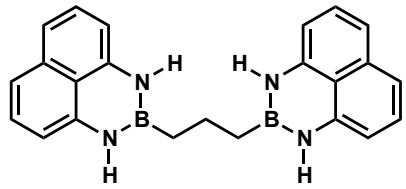
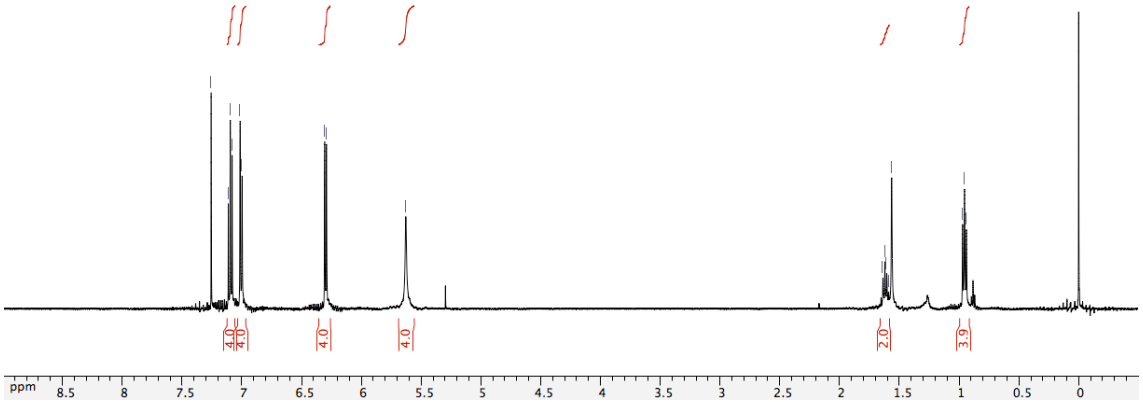
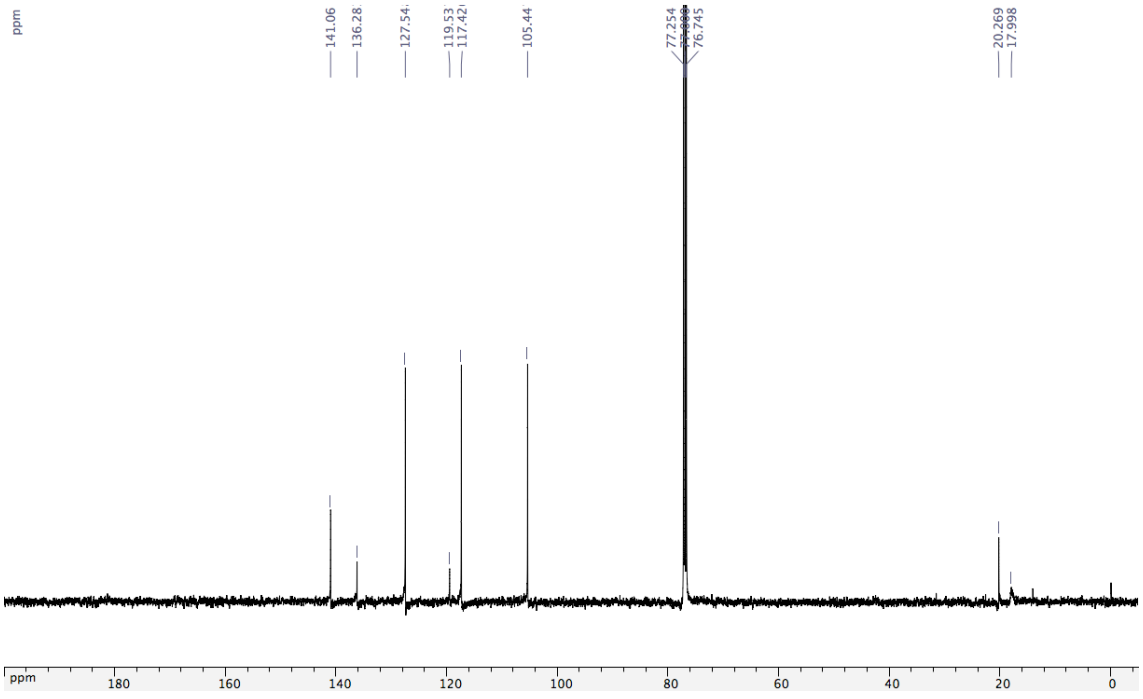
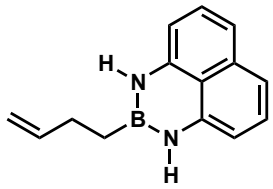
2.0
2.0
2.1
2.0
2.9
2.0
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
173.69
140.97
136.21
127.49
119.51
117.39
105.46
77.255
77.000
76.746
60.302
36.591
20.343
14.523
14.236
180
160
140
120
100
80
60
40
20
0



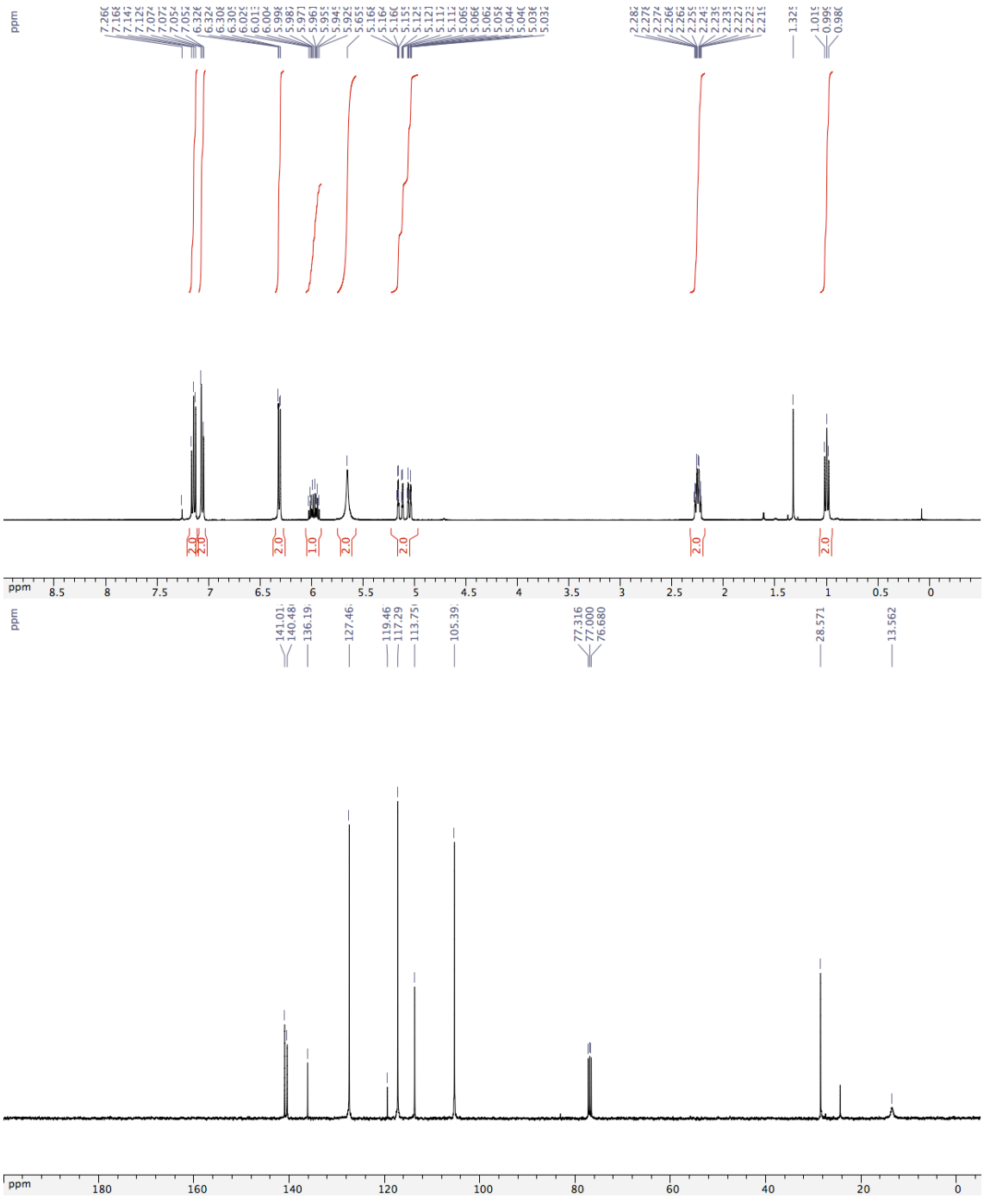
1m






H
N
B
N
H

1n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2.0
1.0
2.0
2.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
ppm
141.01
140.48
136.19
127.46
119.46
117.29
113.75
105.39
77.316
77.000
76.680
28.571
13.562
ppm
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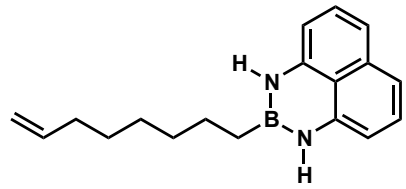
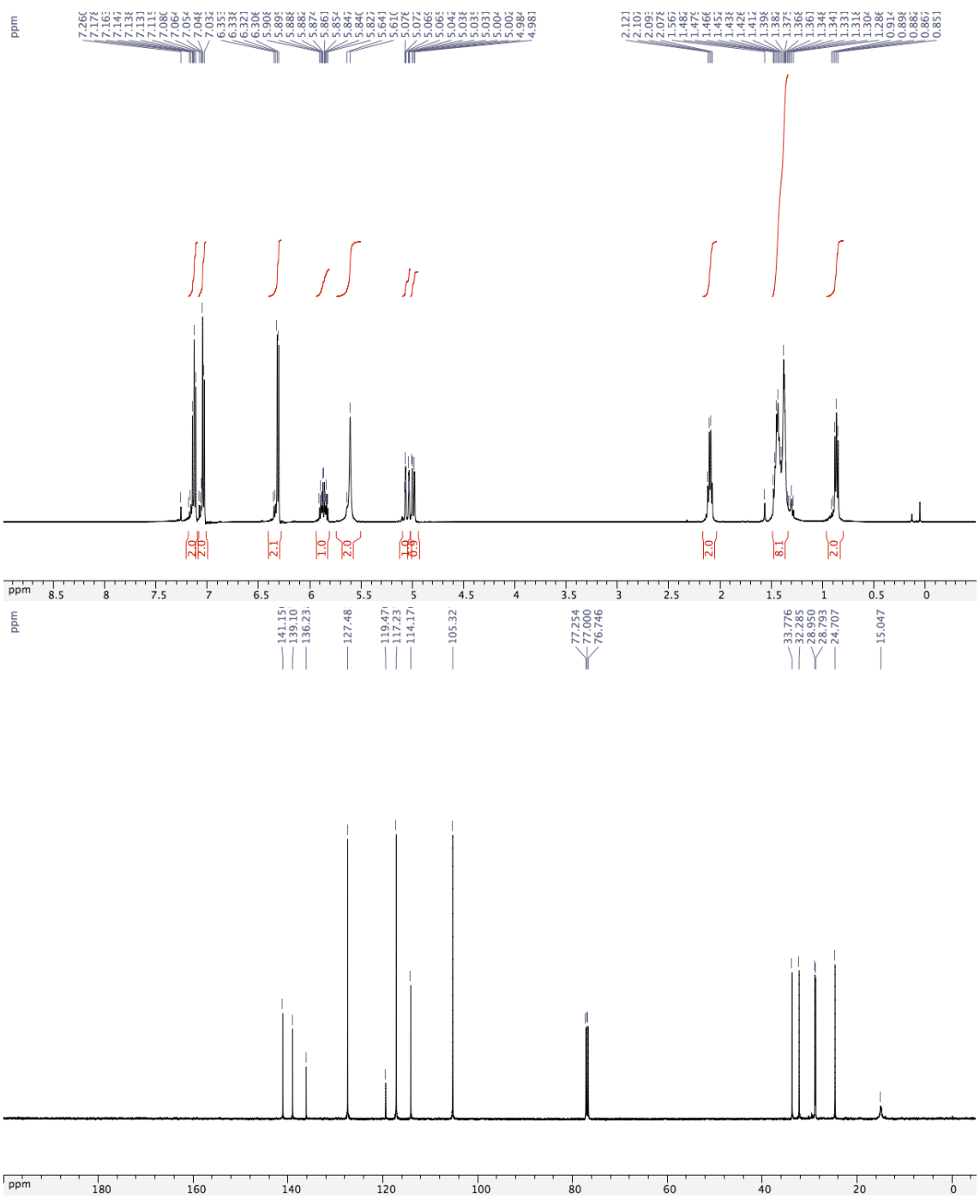
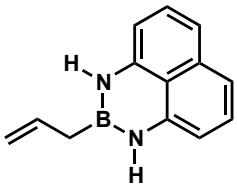
140
120
100
80
60
40
20
0

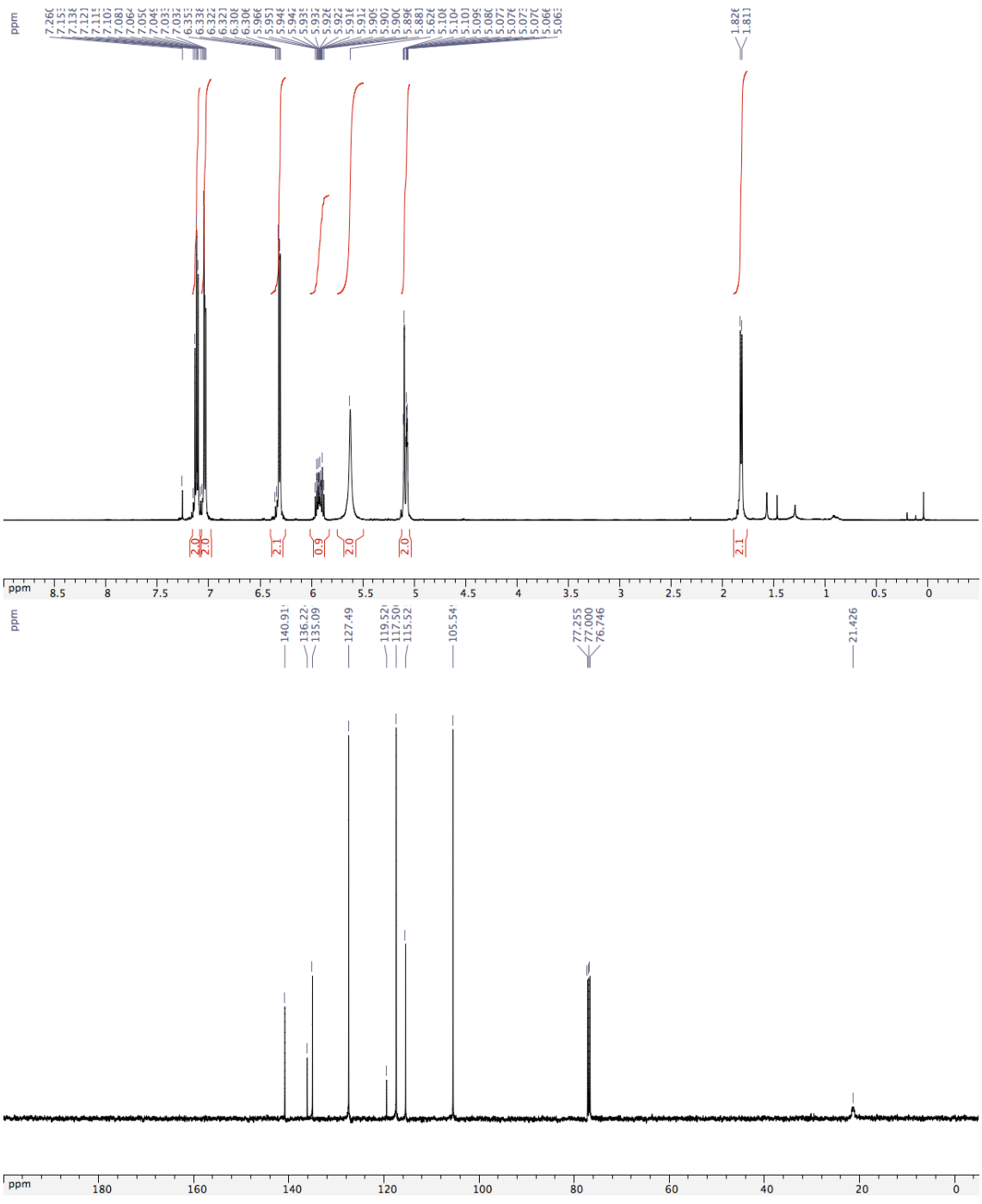


1o




H
N
B
N
H

1p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1.811
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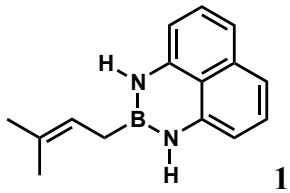
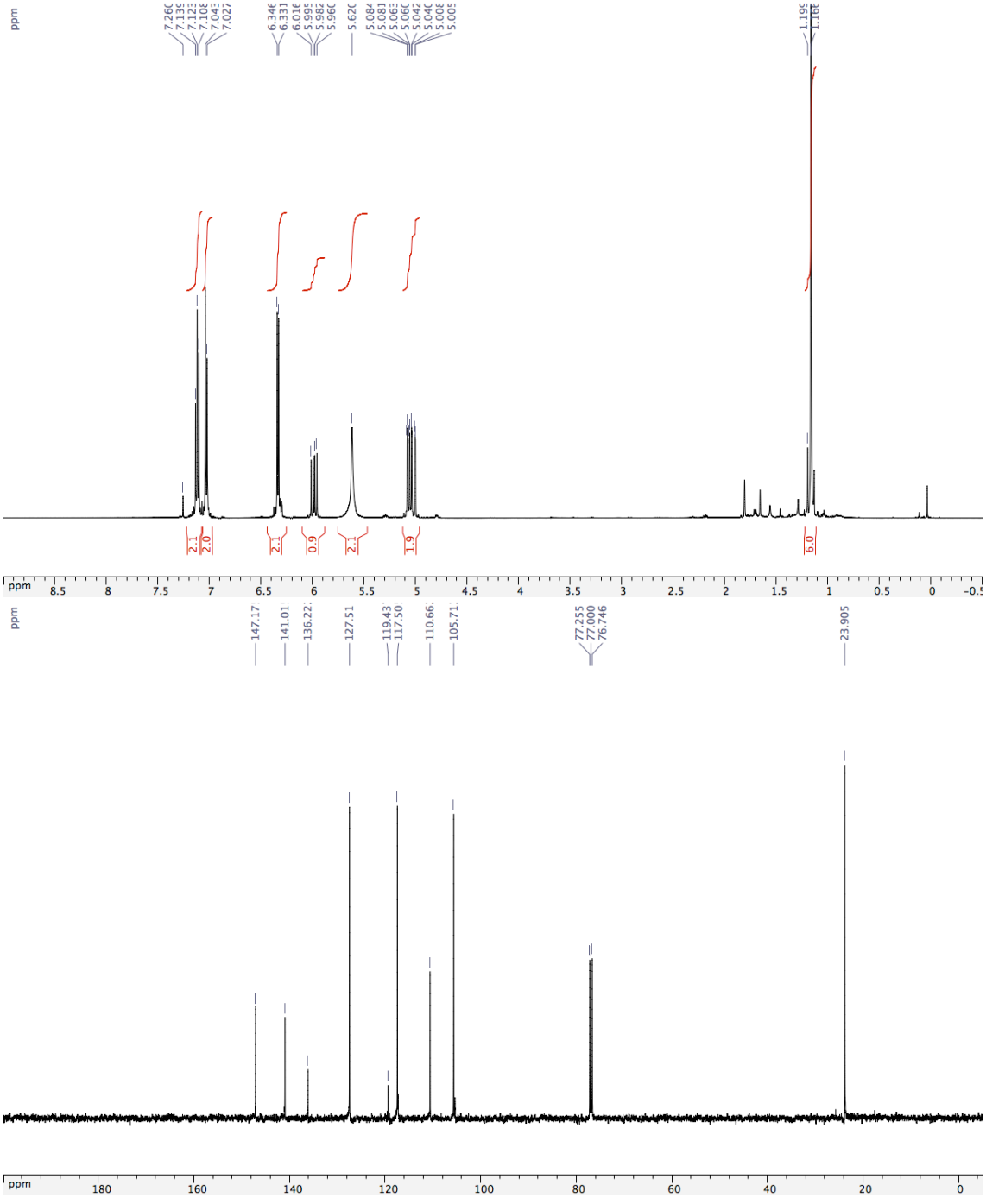
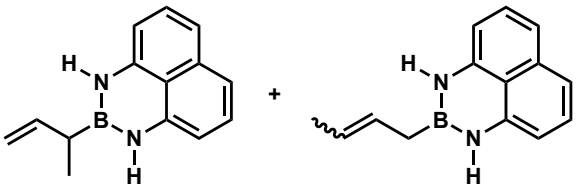
2.0
2.1
0.9
2.0
2.0
2.1
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
ppm
140.91
136.22
135.09
127.49
119.52
117.50
115.52
105.54
77.255
77.000
76.746
21.426
ppm
180
160
140
120
100
80
60
40
20
0

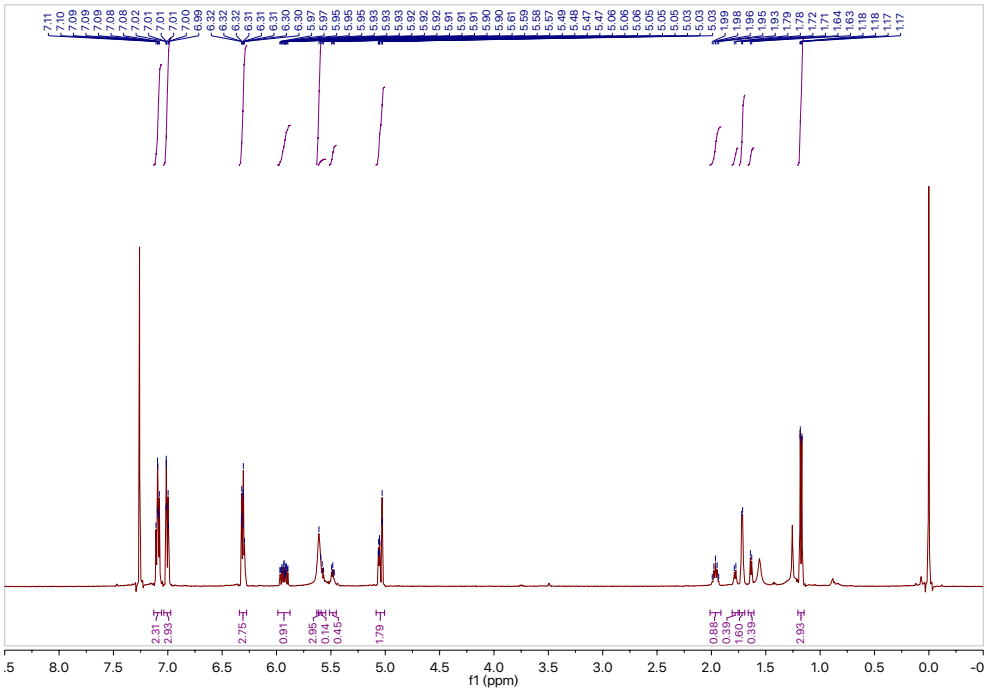


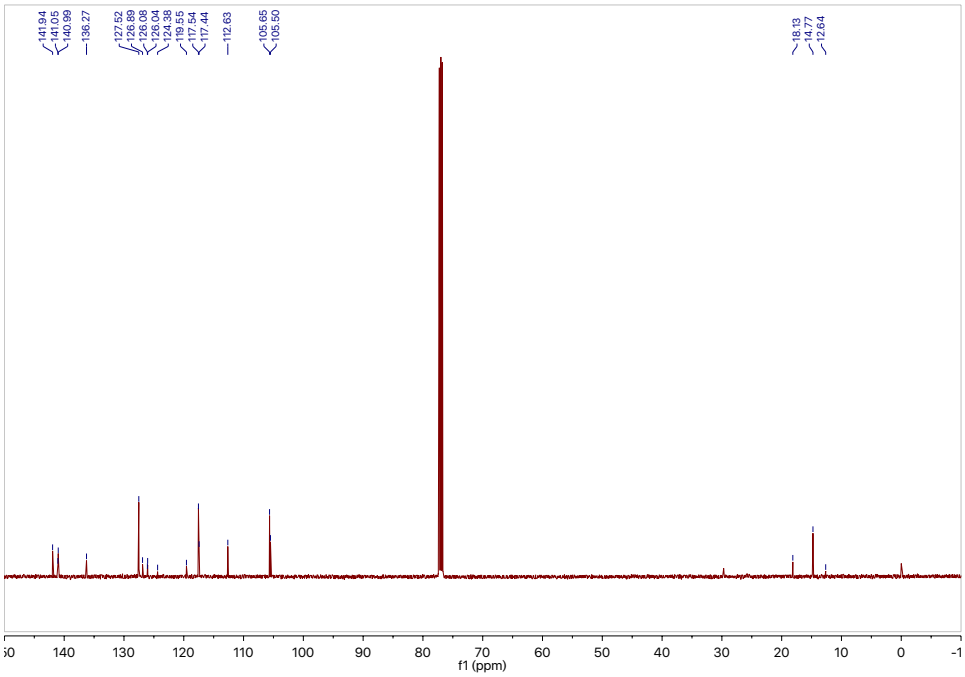
1q

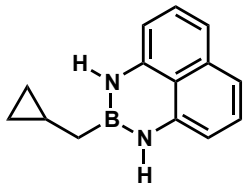




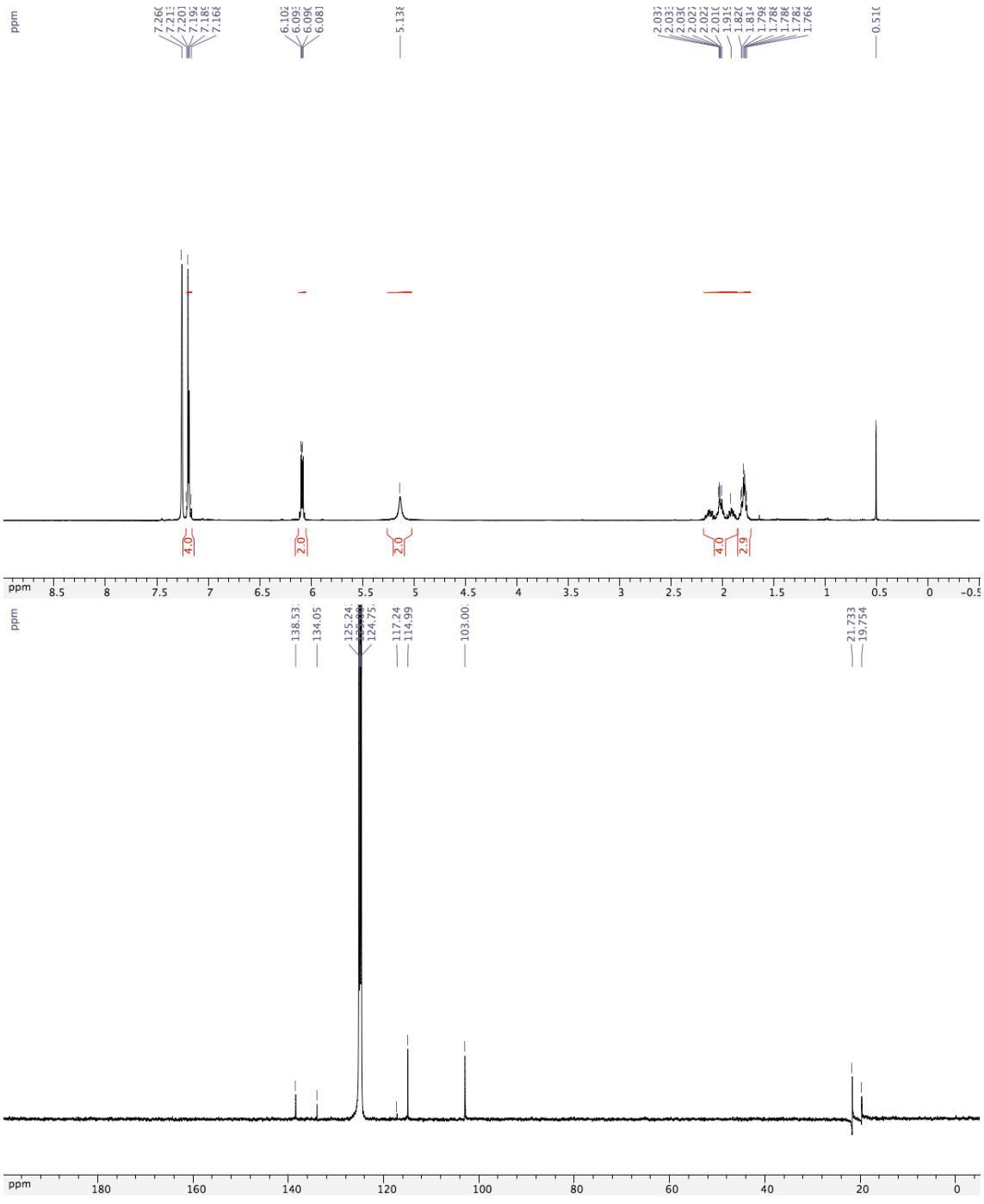
1r + 1'r

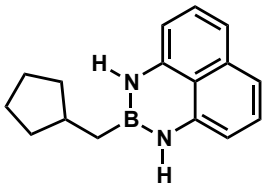




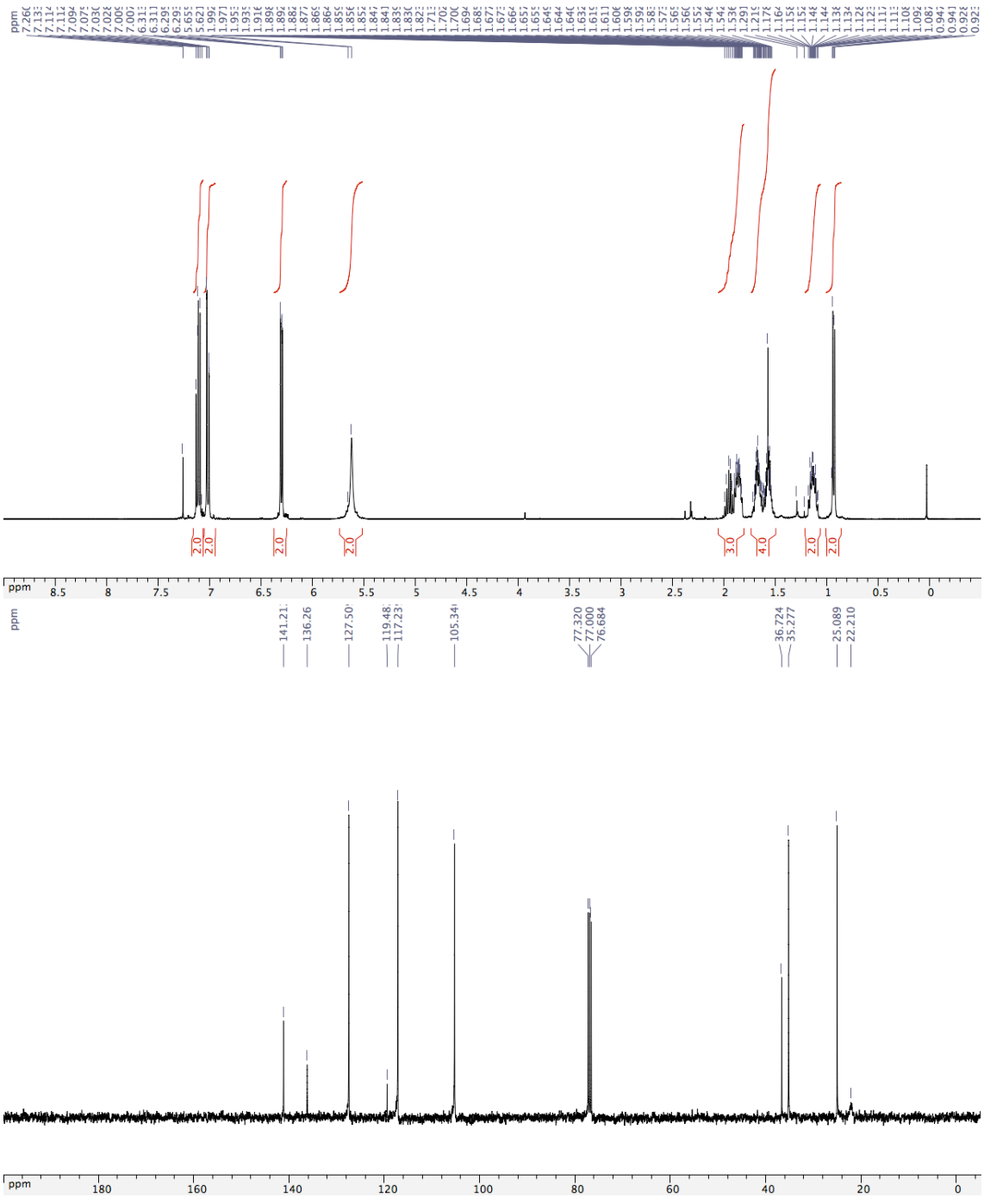


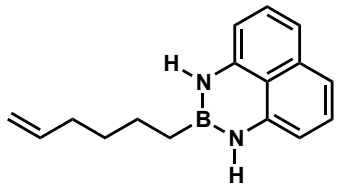
1s



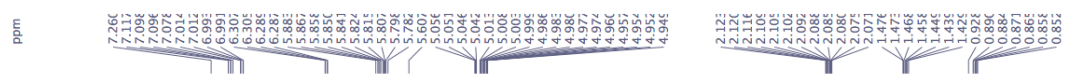

H
N
B
N
H

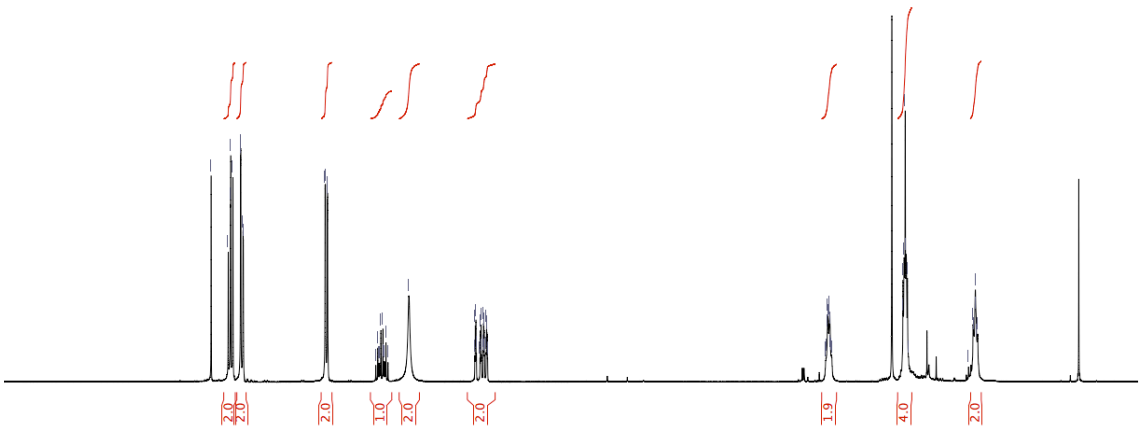
1t

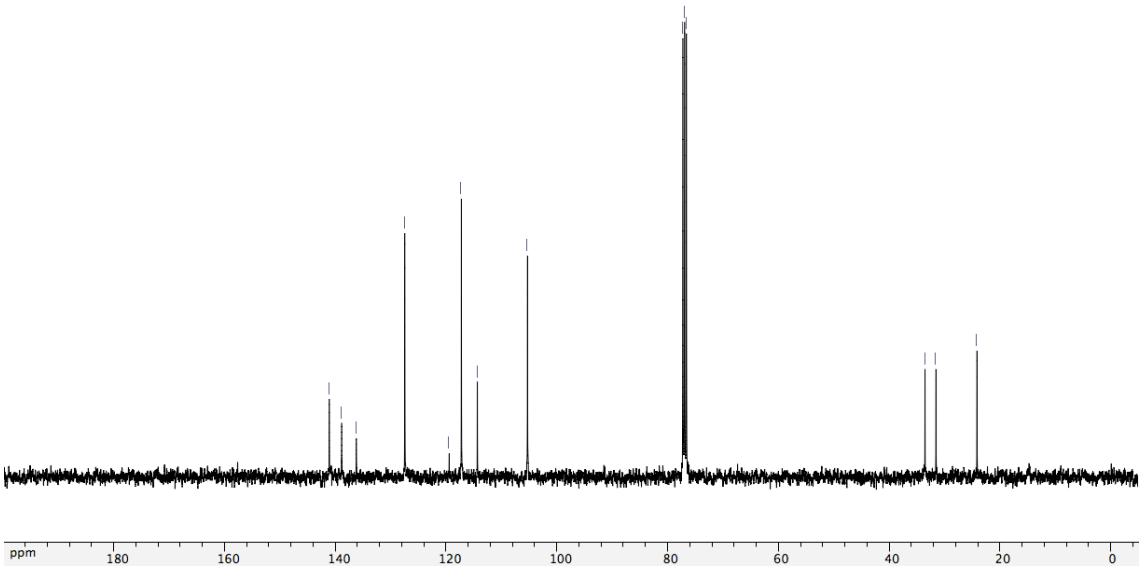

ppm
2.0
2.0
2.0
2.0
3.0
4.0
2.0
2.0
141.21
136.26
127.50
119.48
117.23
105.34
77.320
77.000
76.684
36.724
35.277
25.089
22.210

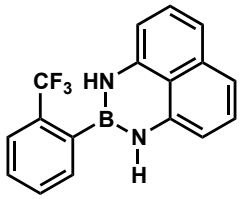


1't

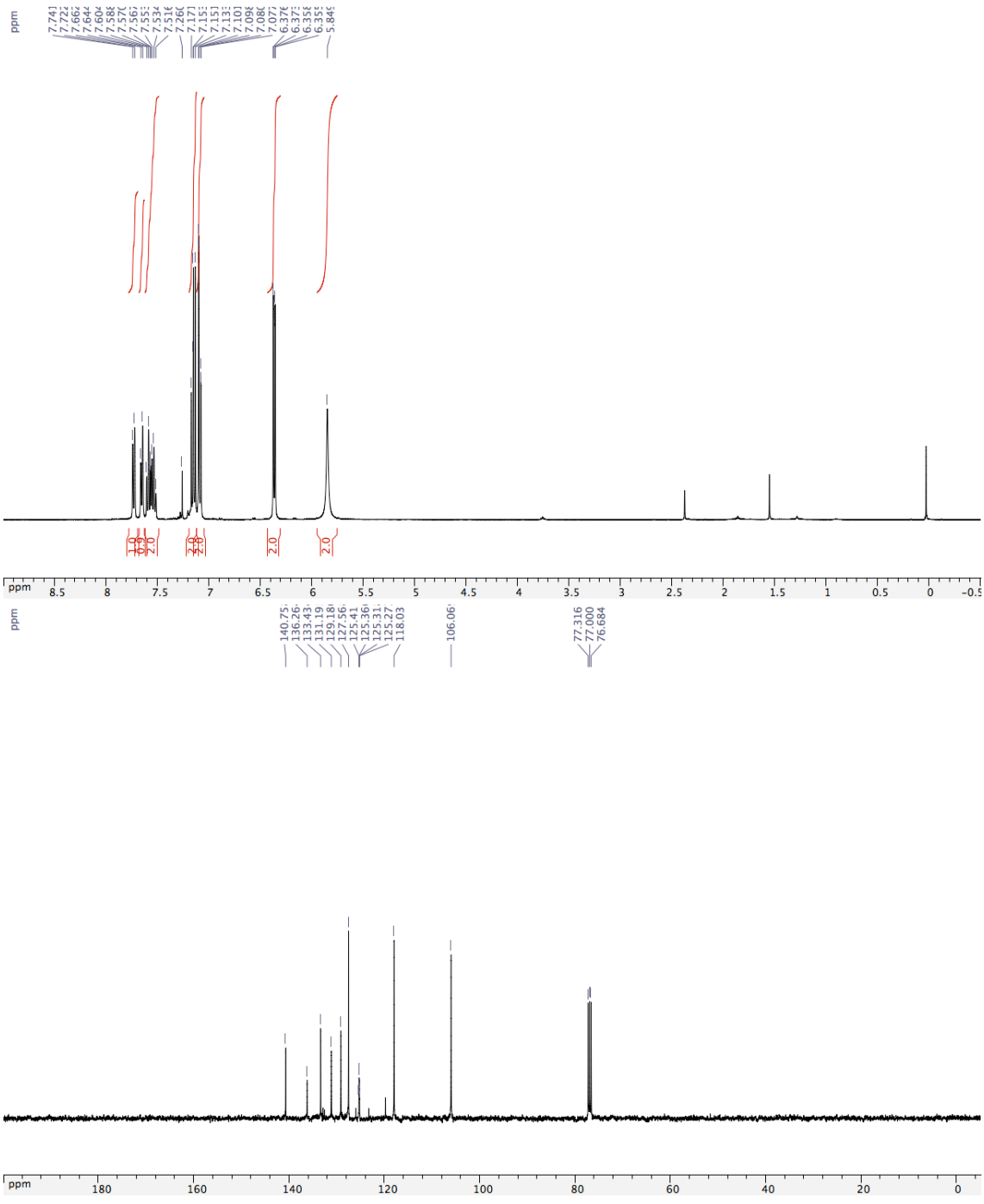







CF3
HN
B
N
H

2c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7.604
7.584
7.577
7.566
7.555
7.534
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7.171
7.155
7.151
7.133
7.101
7.098
7.086
7.077
6.376
6.373
6.358
6.355
5.845
1.0
0.9
2.0
2.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
ppm
140.75
136.26
133.43
131.19
129.18
127.56
125.41
125.36
125.31
125.27
118.03
106.06
77.316
77.000
76.684

ppm
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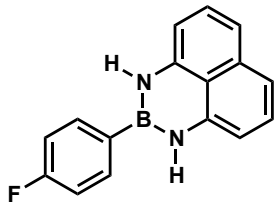
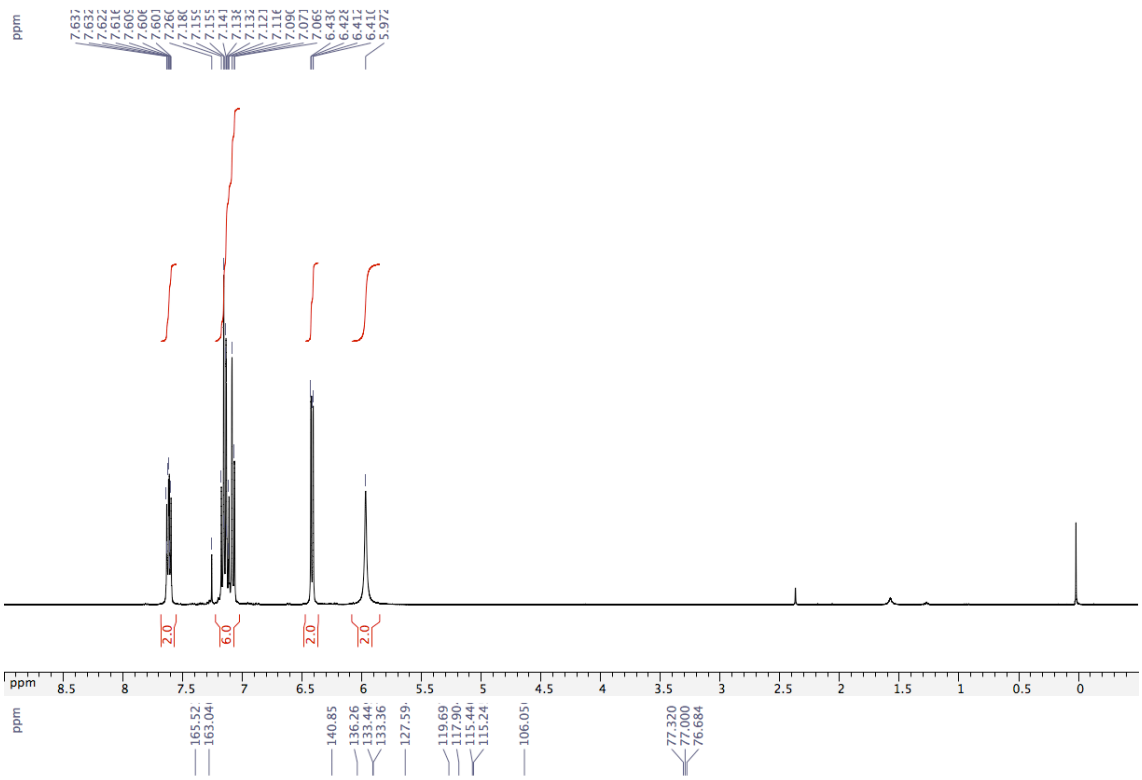
160
140
120
100
80
60
40
20
0


H
N
B
N
H
F

2e


ppm
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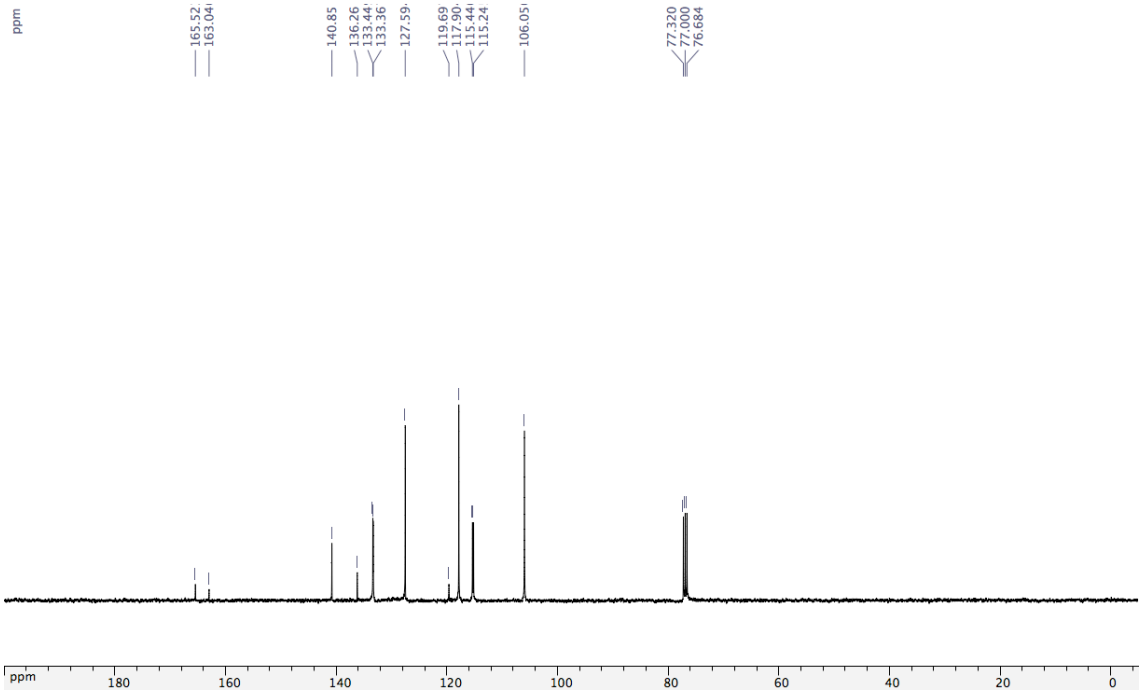
6.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0


ppm
165.52
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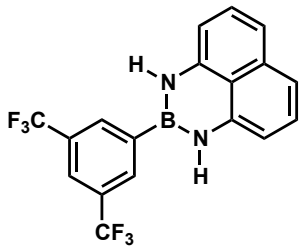
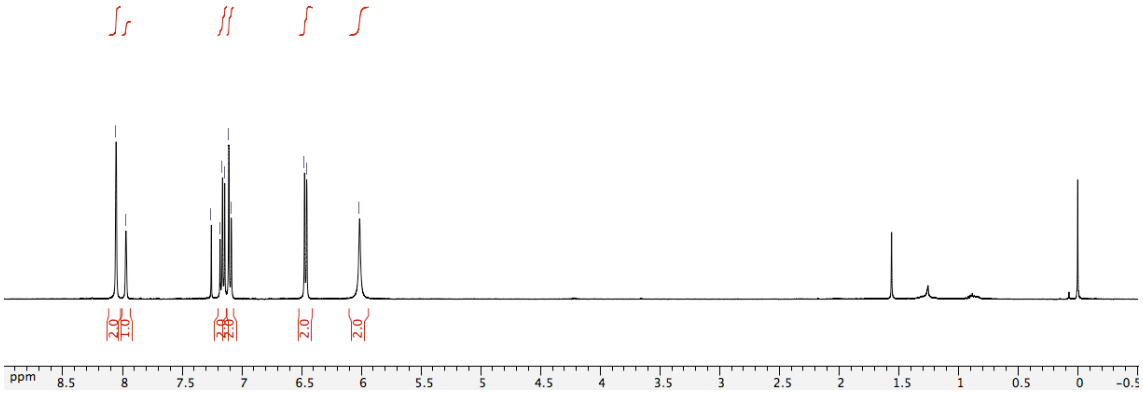
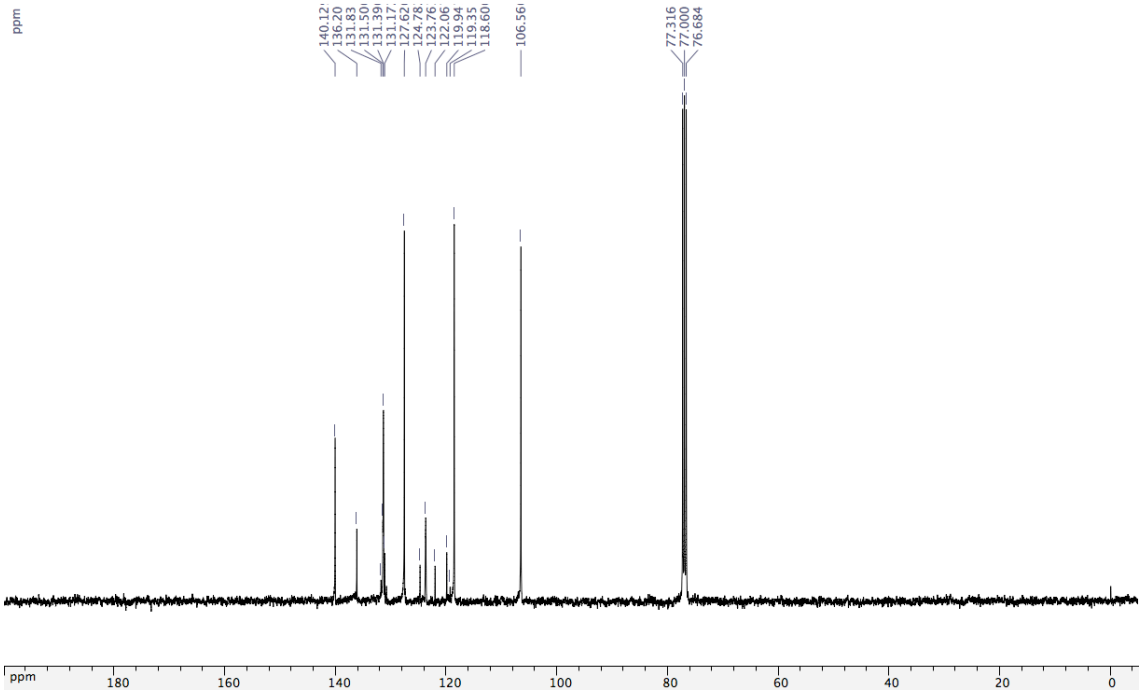
140.85
136.26
133.44
133.36
127.59
119.69
117.90
115.44
115.24
106.05
77.320
77.000
76.684
ppm
180
160
140
120
100
80
60
40
20
0


H
N
B
N
H
F3C
CF3

2f


ppm
8.057
7.974
7.266
7.186
7.166
7.147
7.115
7.095
6.486
6.461
6.018


2.0
1.0
2.0
2.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5


ppm
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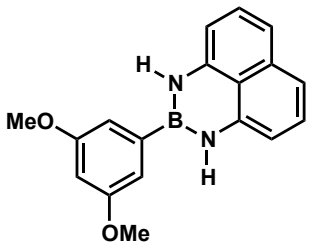
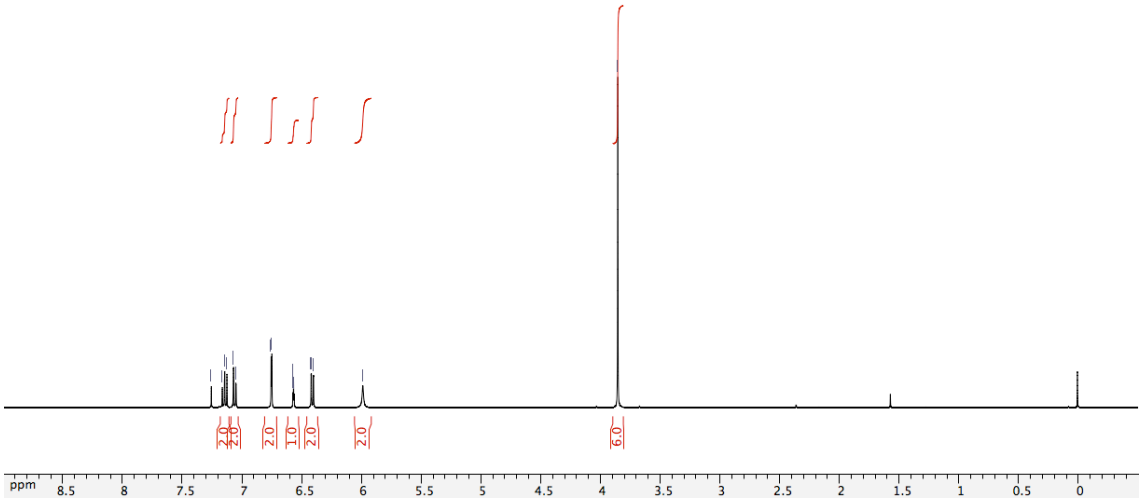
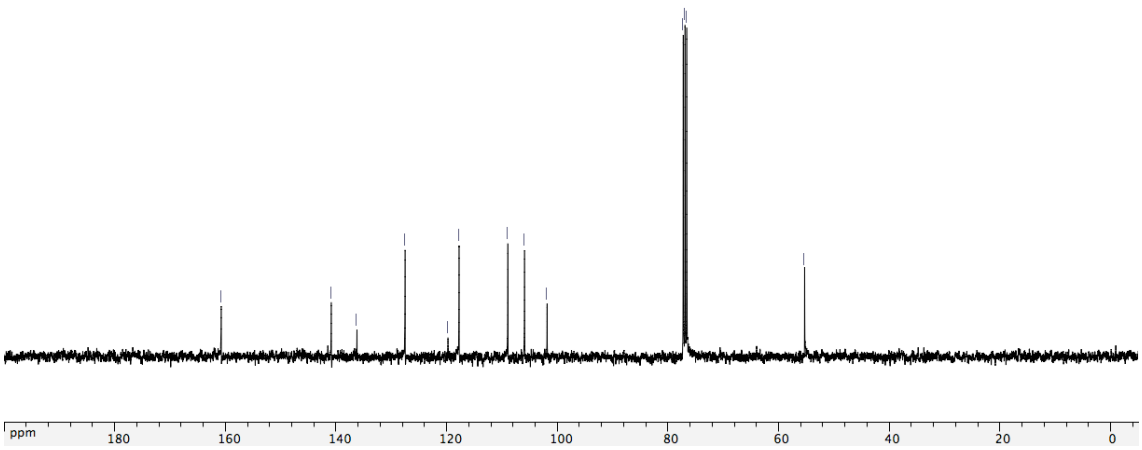
131.50
131.39
131.17
127.62
124.78
123.76
122.06
119.94
119.35
118.60
106.56
77.316
77.000
76.684
ppm
180
160
140
120
100
80
60
40
20
0

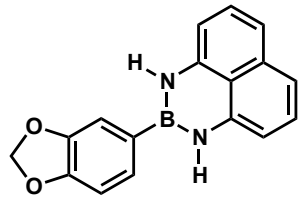

H
N
B
N
H
MeO
OMe

2g

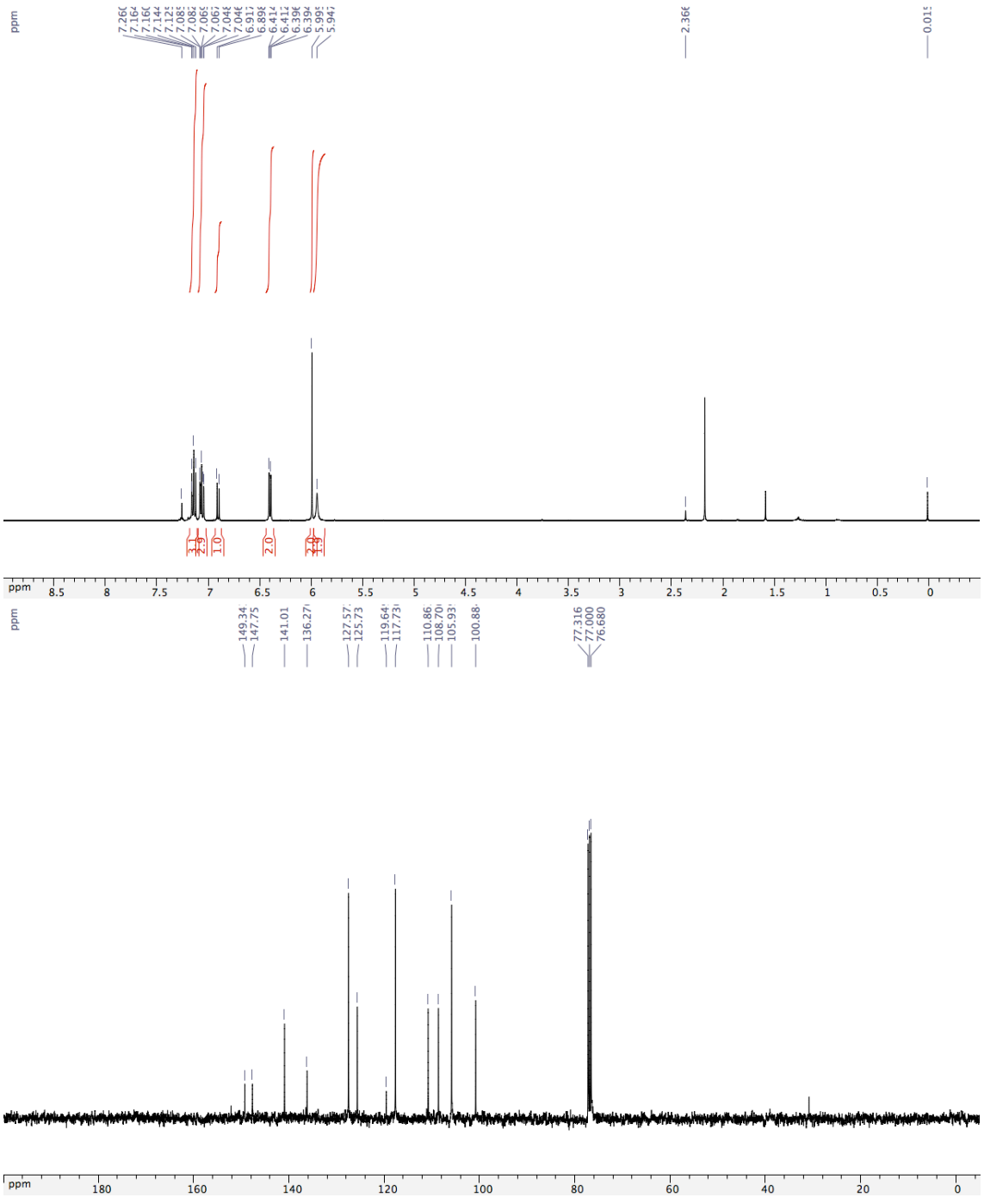

2.0
2.0
2.0
1.0
2.0
2.0
6.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

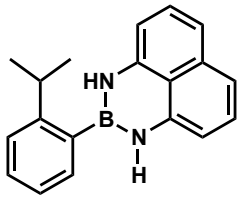

ppm
160.82
140.93
136.28
127.58
119.83
117.83
109.02
106.00
101.92
77.316
77.000
76.680
55.370


ppm
180
160
140
120
100
80
60
40
20
0

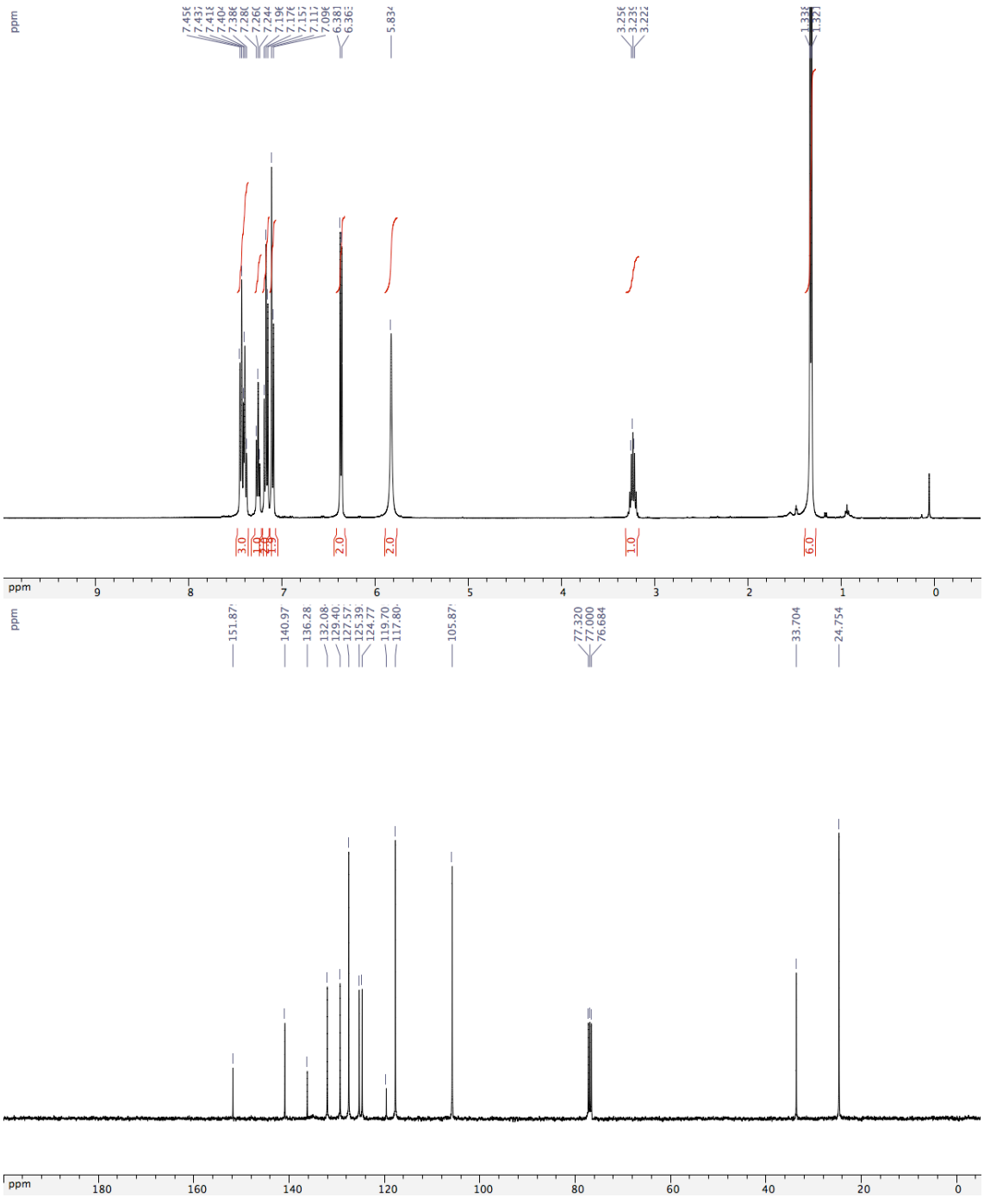

H
N
B
N
H
O
O

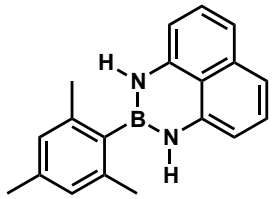
2h


ppm
2.366
0.015
3.1
2.9
1.0
2.0
2.0
1.9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
149.34
147.75
141.01
136.27
127.57
125.73
119.64
117.73
110.86
108.70
105.93
100.88
77.316
77.000
76.680
180
160
140
120
100
80
60
40
20
0

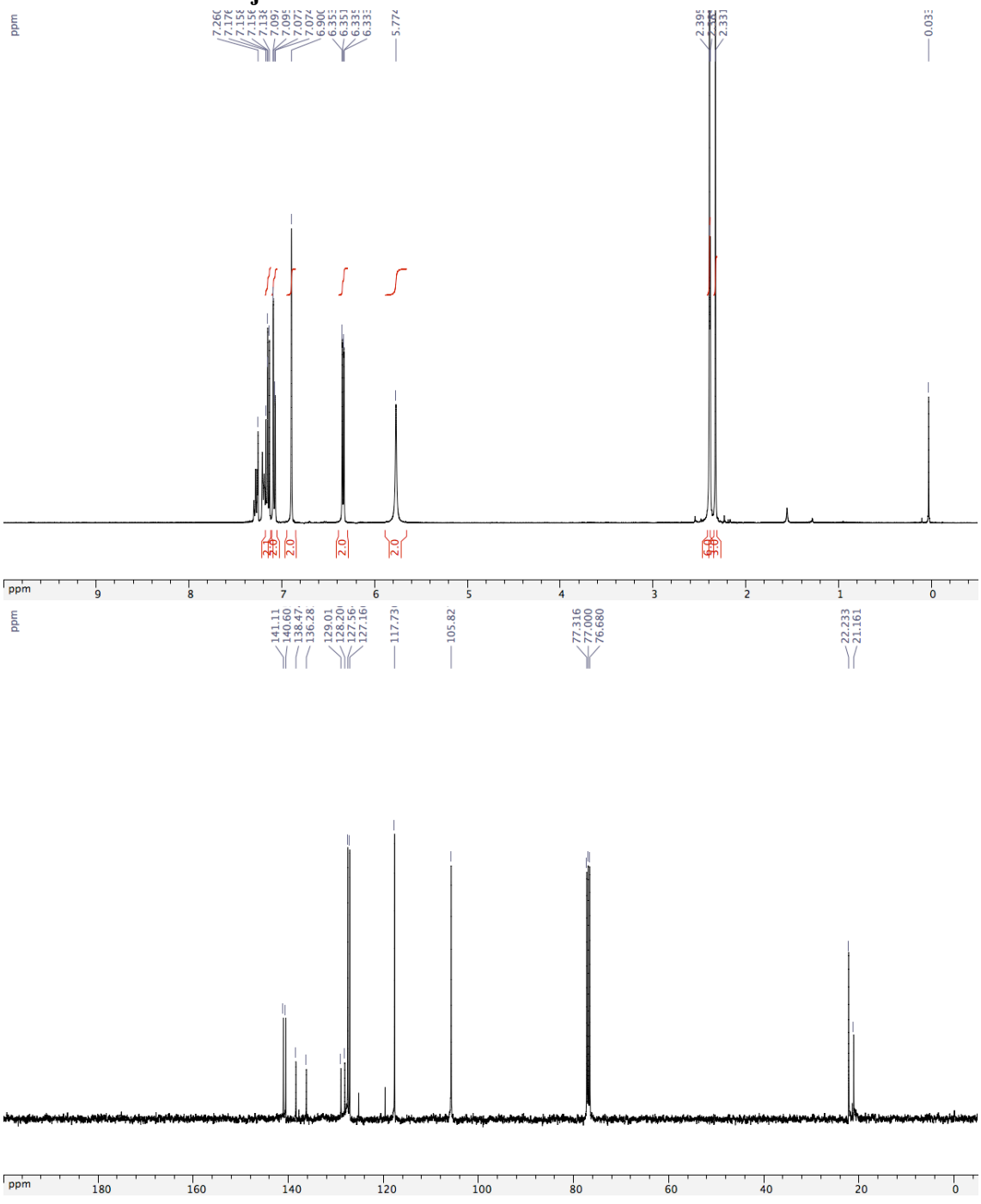

HN
B
N
H

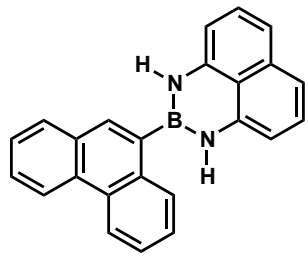
2i


ppm
3.0
2.0
2.0
1.0
6.0
ppm
151.87
140.97
136.28
132.08
129.40
127.57
125.39
124.77
119.70
117.80
105.87
77.320
77.000
76.684
33.704
24.754
ppm

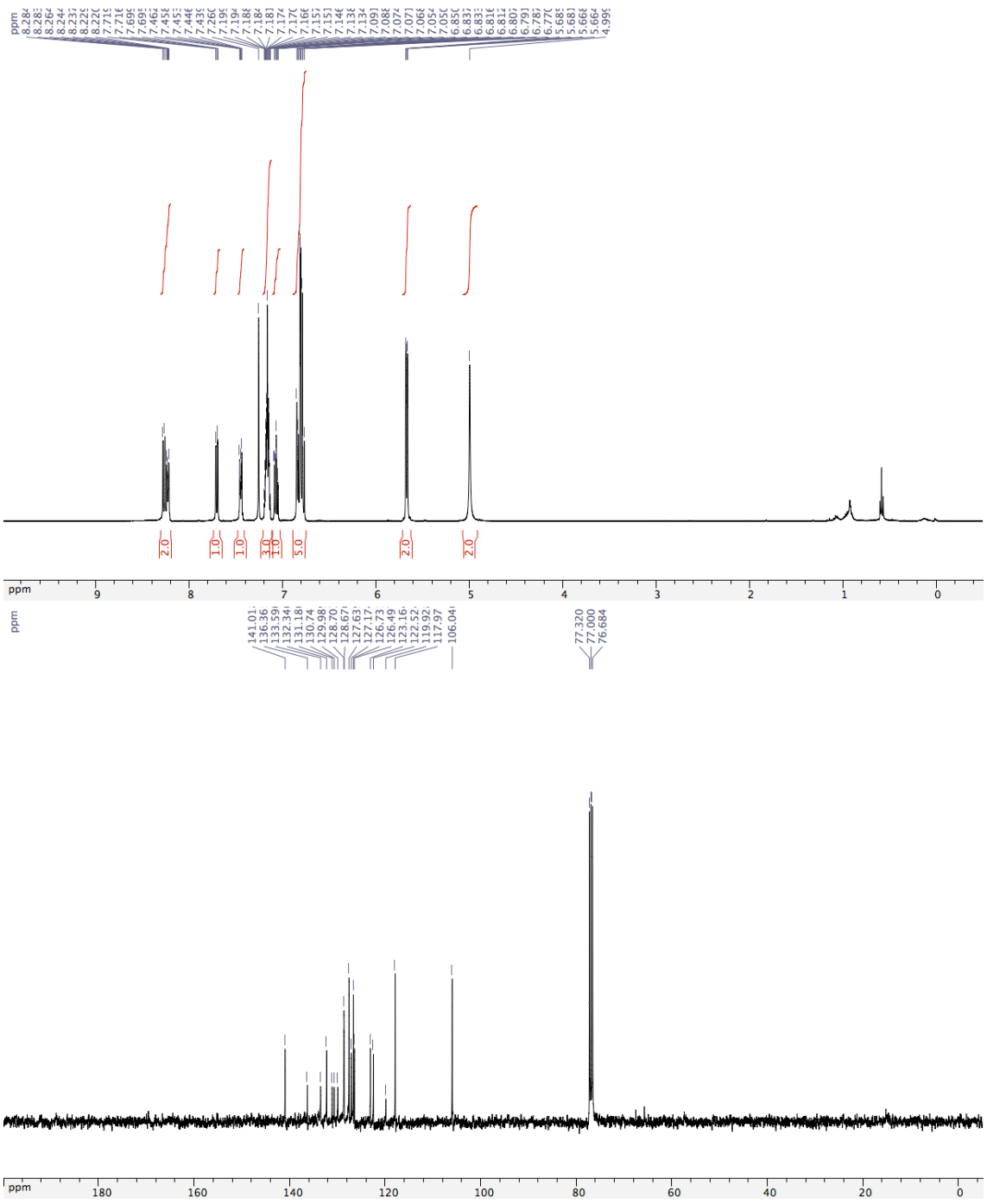

H
N
B
N
H

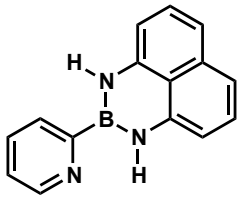
2j


ppm
9
8
7
6
5
4
3
2
1
0
2.0
2.0
2.0
2.0
6.0
3.0
141.11
140.60
138.47
136.28
129.01
128.20
127.56
127.16
117.73
105.82
77.316
77.000
76.680
22.233
21.161
ppm
180
160
140
120
100
80
60
40
20
0


H
N
B
N
H

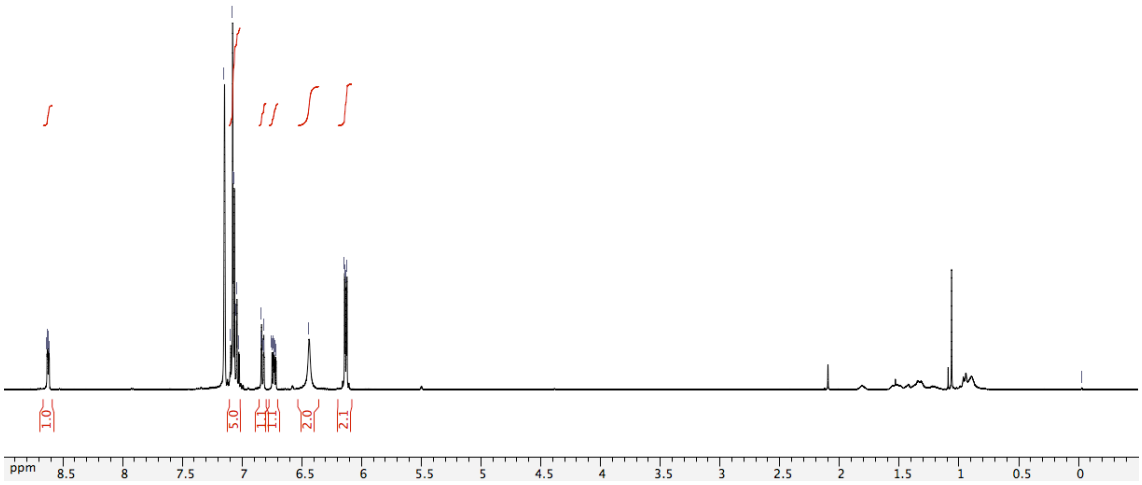
2l

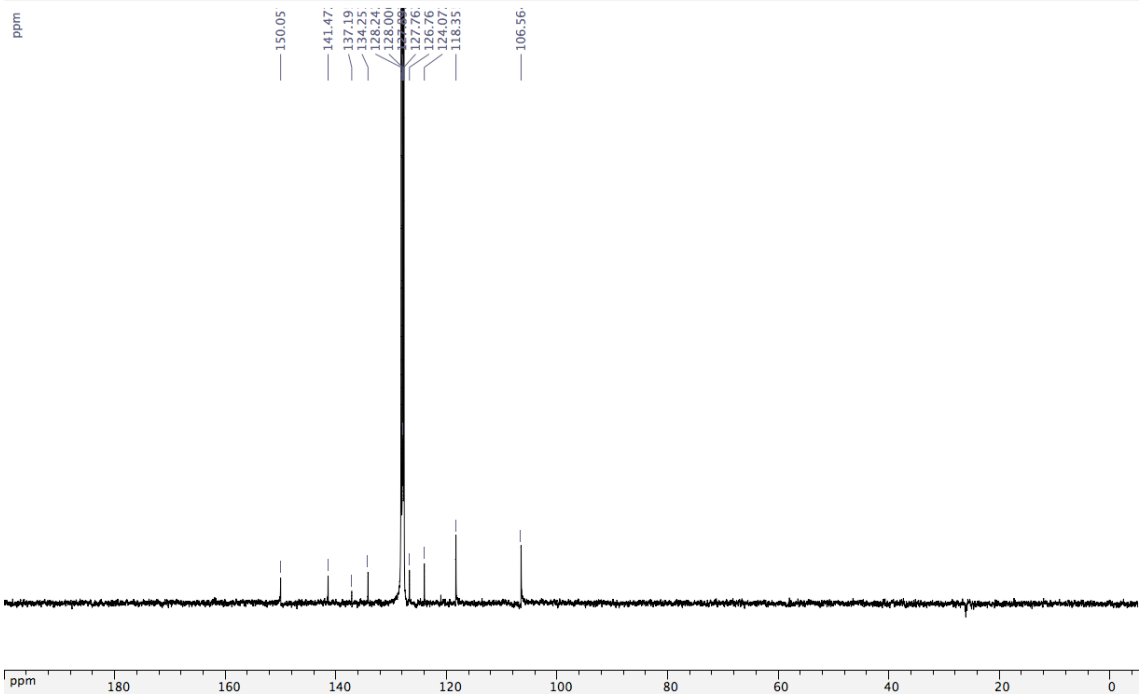

ppm
2.0
1.0
1.0
3.0
1.0
5.0
2.0
2.0
9
8
7
6
5
4
3
2
1
0
141.01
136.36
133.59
132.34
131.18
130.74
129.98
128.70
128.67
127.63
127.17
126.73
126.49
123.16
122.52
119.92
117.97
106.04
77.320
77.000
76.684
180
160
140
120
100
80
60
40
20
0

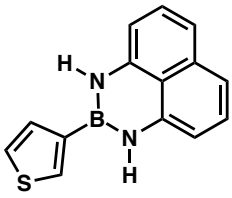

H
N
B
N
H
N

2n

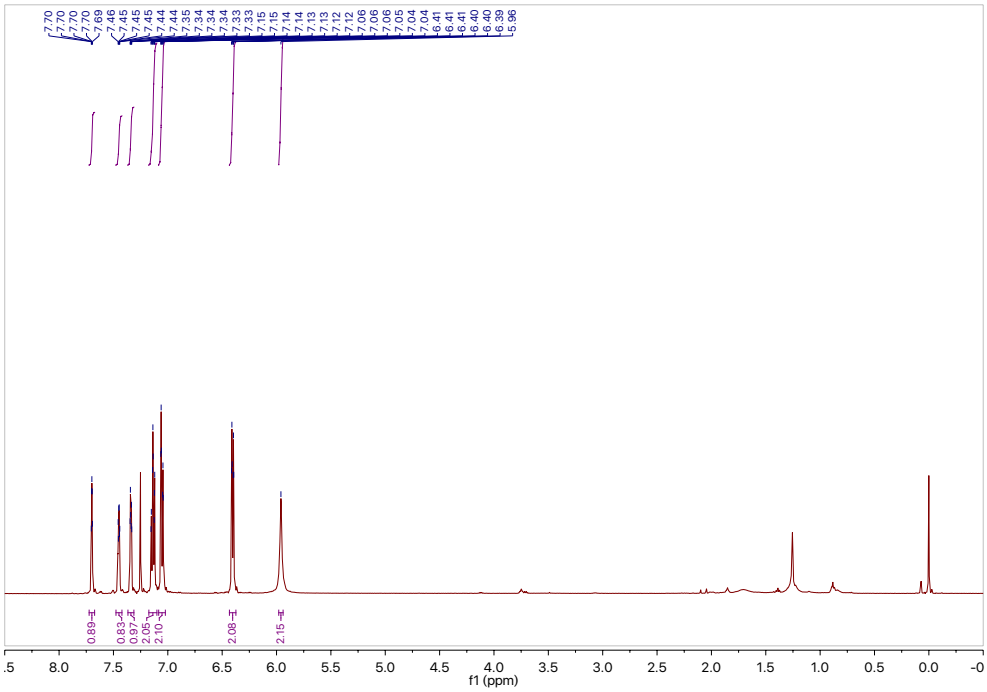

ppm
8.635
8.632
8.628
8.623
8.620
8.617
7.150
7.098
7.083
7.077
7.067
7.050
7.046
7.031
7.026
6.844
6.841
6.838
6.825
6.822
6.819
6.753
6.750
6.741
6.738
6.734
6.730
6.722
6.719
6.442
6.146
6.140
6.131
6.125

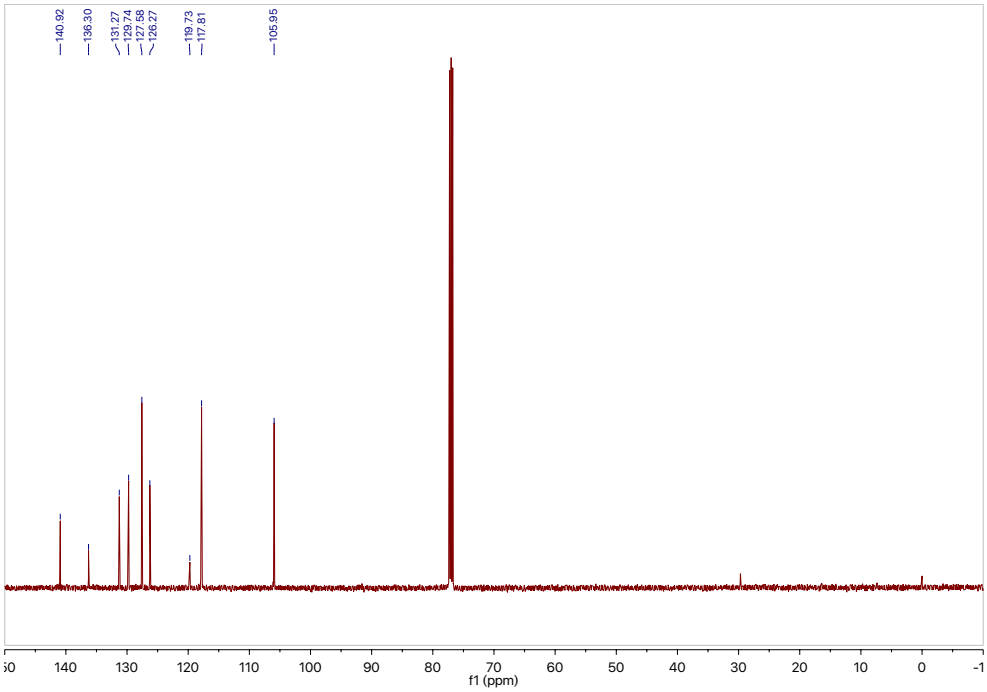

1.0
5.0
1.1
1.1
2.0
2.1
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

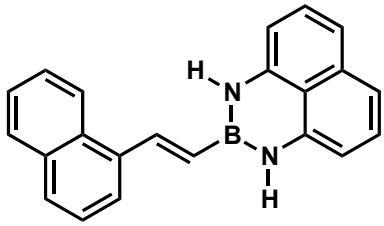

ppm
150.05
141.47
137.19
134.25
128.24
128.00
127.76
126.76
124.07
118.35
106.56
ppm
180
160
140
120
100
80
60
40
20
0



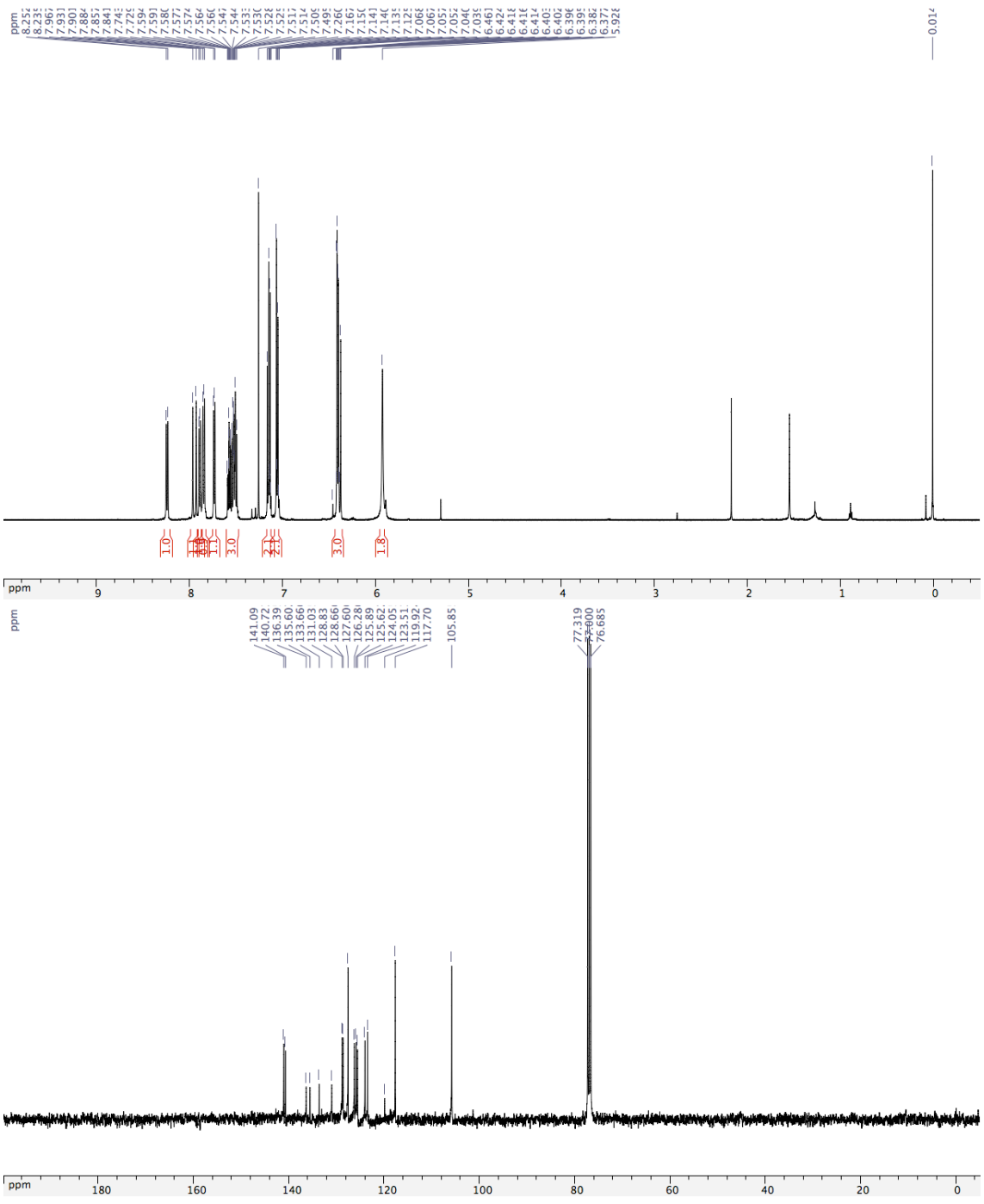
2o

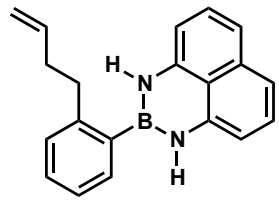

7.70
7.70
7.70
7.70
7.69
7.46
7.45
7.45
7.45
7.44
7.44
7.35
7.34
7.34
7.34
7.33
7.33
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.06
7.06
7.06
7.05
7.04
7.04
6.41
6.41
6.40
6.40
6.39
5.96
0.89
0.83
0.97
2.05
2.10
2.08
2.15
f1 (ppm)


140.92
136.30
131.27
129.74
127.68
126.27
119.73
117.81
105.95
f1 (ppm)

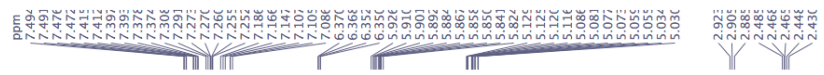

H
N
B
N
H

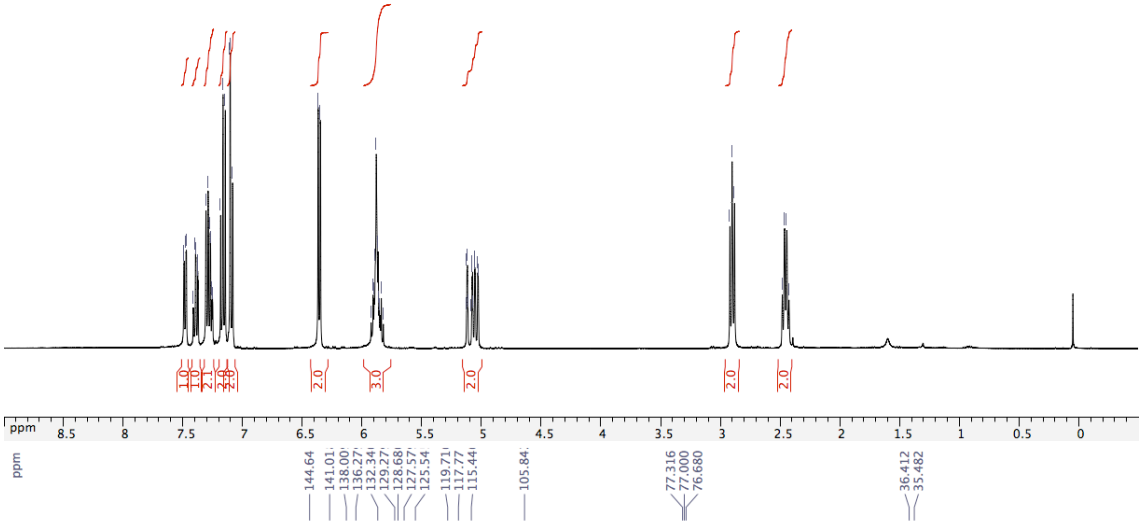
2q


ppm
9
8
7
6
5
4
3
2
1
0
1.0
3.0
2.1
3.0
1.8
ppm
180
160
140
120
100
80
60
40
20
0

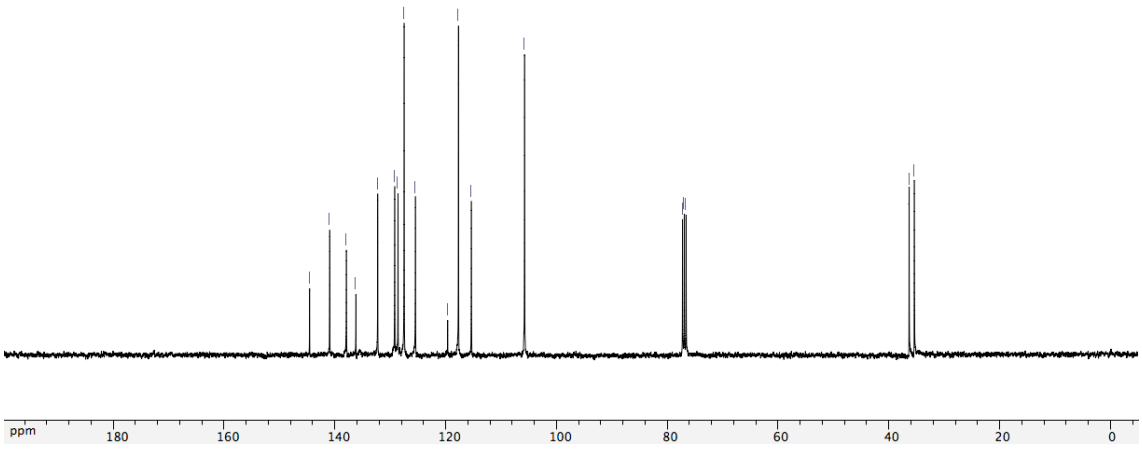

H
N
B
N
H

2r




1.0
1.0
2.1
2.6
2.8
2.0
3.0
2.0
2.0
2.0
ppm
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

ppm
144.64
141.01
138.00
136.27
132.34
129.27
128.68
127.57
125.54
119.71
117.77
115.44
105.84
77.316
77.000
76.680
36.412
35.482


ppm
180
160
140
120
100
80
60
40
20
0