Supplementary information

A masked diboron in Cu-catalysed borylation reaction: Highly regioselective formal hydroboration of alkynes for synthesis of branched alkenylborons

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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; ^{11}B, x MHz) spectrometer using residual chloroform, benzene, DMSO (^{1}H, δ = 7.26, 7.15, 2.54) or $CDCl_3$, C_6D_6, DMSO-d_6 (^{13}C, δ = 77.0, 128.0, 40.5) as an internal standard, and boron trifluoride diethyl etherate (^{11}B, δ = 0) as an external standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, 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 Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Toluene and THF were distilled from sodium/benzophenone ketyl. DMSO and triethylamine were distilled from CaH_2. (SIPr)CuCl was synthesized according to a literature procedure.[1]

Synthesis of (pin)B–B(dan)

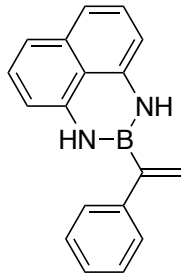
A toluene (10 mL) solution of (pin)B–B(pin) (20 mmol) and 1,8-diaminonaphthalene (20 mmol) was stirred at 100 °C for 42 h, and then the solvent was removed in vacuo at room temperature before the residue was washed with hexane (30 mL x 3). Bulb-to-bulb distillation (2 mmHg, 230 °C) of the resulting solid affords (pin)B–B(dan) as colorless solid (80% yield).

Cu-catalysed hydroboration of alkynes.

A Schlenk tube equipped with a magnetic stirring bar was charged with (SIPr)CuCl (6.0 μmol), KO*t*Bu (1.0 M solution in THF, 18.0 μmol), MeOH (0.9 mmol) and THF (1.0 mL) before the mixture was stirred at room temperature for 10 min. To the mixture was added (pin)B–B(dan) (0.36 mmol) and an alkyne (0.30 mmol), and the resulting mixture was stirred at 50 °C for 3 h. The mixture was diluted with ethyl acetate and filtered

through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$, and evaporated. Purification of the residue by silica gel-column chromatography (hexane/ethyl acetate as an eluent) gave the product.

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



Colorless liquid

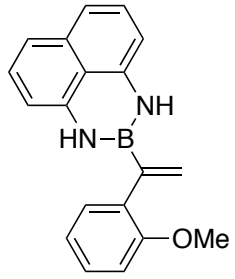
^{1}H NMR (C_6D_6) δ 5.34 (s, 2H), 5.36 (s, 1H), 5.74 (s, 1H), 5.82 (d, *J* = 7.1 Hz, 2H), 7.00-7.25 (m, 8H), 7.27-7.33 (m, 2H)

^{13}C NMR (C_6D_6) δ 106.4, 118.3, 120.5, 124.5, 127.6, 127.8, 129.0, 136.9, 141.2, 142.6

^{11}B NMR ($CDCl_3$) δ 28.9

HRMS Calcd for $C_{18}H_{15}N_2B$: M^+, 270.13283. Found: m/z 271.13245

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



Colorless solid: mp 92-94 °C

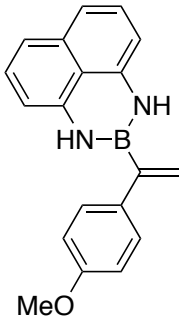
^{1}H NMR (C_6D_6) δ 3.17 (s, 3H), 5.41 (s, 2H), 5.44 (d. *J* = 2.9 Hz, 1H), 5.70 (d, *J* = 2.9 Hz, 1H), 5.79 (dd, *J* = 7.0, 1.5 Hz, 2H), 6.51 (d, *J* = 8.2 Hz, 1H), 6.91 (td, *J* = 1.0, 7.4 Hz, 1H), 6.97-7.06 (m, 4H), 7.11 (dt, *J* = 1.5, 8.0Hz, 1H), 7.28 (dd, *J* = 7.4, 1.6 Hz, 1H)

^{13}C NMR (C_6D_6) δ 55.3, 106.1, 111.4, 117.9, 120.4, 121.5, 124, 7, 127.8, 129.1, 129.4, 132.8, 137.1, 141.7, 157.1

^{11}B NMR ($CDCl_3$) δ 29.1

HRMS Calcd for $C_{19}H_{17}ON_2B$: M^+, 300.14339. Found: m/z 300.14327

2-(1-(4-Methoxyphenyl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1c)



Colorless solid: mp 120-123 °C

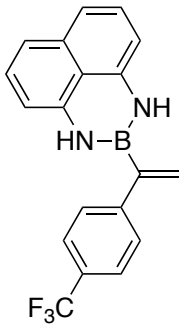
^{1}H NMR (C_6D_6) δ 3.32 (s, 3H), 5.32 (d, *J* = 2.2 Hz, 1H), 5.39 (s, 2H), 5.72 (d, *J* = 2.2 Hz, 1H), 5.85 (dd, *J* = 7.1, 1.1 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.99-7.08 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 2H)

^{13}C NMR (C_6D_6) δ 54.8, 106.4, 114.4, 118.3, 120.6, 122.7, 127.8, 128.9, 134,8, 137.0, 141.3, 159.7

^{11}B NMR ($CDCl_3$) δ 29.1

HRMS Calcd for $C_{19}H_{17}ON_2B$: M^+, 300.14339. Found: m/z 300.14285

2-(1-(4-(Trifluoromethyl)phenyl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diaza borinine (1d)



Colorless oil

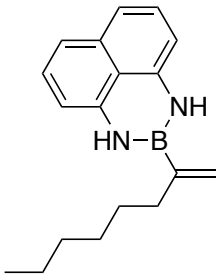
^{1}H NMR (C_6D_6) δ 5.16 (s, 2H), 5.28 (d, *J* = 2.0 Hz, 1H), 5.55 (d, *J* = 1.9 Hz, 1H), 5.85 (dd, *J* = 7.2, 1.1 Hz, 2H), 6.97-7.09 (m, 6H), 7.36 (d, *J* = 8.1 Hz, 2H)

^{13}C NMR (C_6D_6) δ 106.6, 118.6, 120.5, 125.0 (q, J_{C-F} = 270.8 Hz), 125.8 (q, J_{C-F} = 3.3 Hz) , 126.2, 129.5 (q, J_{C-F} = 32.2 Hz), 136.9, 140.9, 146.0

^{11}B NMR ($CDCl_3$) δ 29.0

HRMS Calcd for $C_{19}H_{14}N_2BF_3$: M^+, 338.12021. Found: m/z 338.11987

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



Colorless oil

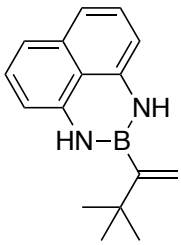
^{1}H NMR (C_6D_6) δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.16-1.42 (m, 8H), 1.98 (t, *J* = 7.6 H), 5.24 (d, *J* = 2.5 Hz, 1H), 5.33 (s, 2H), 5.40 (d, *J* = 2.4 Hz, 1H), 5.97 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.01-7.11 (m, 4H)

^{13}C NMR (C_6D_6) δ 14.4, 23.1, 29.48, 29.51, 32.1, 35.8, 106.3, 118.2, 120.5, 122.9, 137.0, 141.3

^{11}B NMR ($CDCl_3$) δ 28.5

HRMS Calcd for $C_{18}H_{23}N_2B$: M^+, 278.19543. Found: m/z 278.19539

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



Colorless solid: mp 54-56 °C

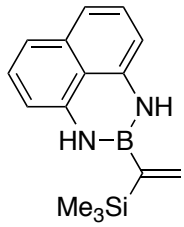
^{1}H NMR (C_6D_6) δ 1.02 (s, 3H), 5.08 (d, J = 2.1 Hz, 1H), 5.22 (s, 2H), 5.34 (d, *J* = 2.0 Hz, 1H), 5.92 (dd, *J* = 6.9, 1.3 Hz, 2H), 7.00-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 30.3, 35.8, 106.3, 117.8, 118.2, 120.4, 136.9, 141.3

^{11}B NMR ($CDCl_3$) δ 30.1

HRMS Calcd for $C_{16}H_{19}N_2B$: M^+, 250.16413. Found: m/z 250.16338

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



Colorless solid: mp 68-70 °C

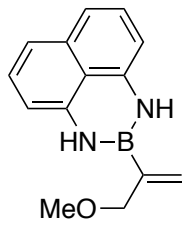
^{1}H NMR (C_6D_6) δ 0.08 (s, 9H), 5.21 (s, 2H), 5.92-5.99 (m, 3H), 6.05 (d, *J* = 5.0 Hz, 1H), 7.00-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ -0.88, 106.3, 118.2, 120.3, 127.8, 137.0, 137.2, 141.4

^{11}B NMR ($CDCl_3$) δ 30.1

HRMS Calcd for $C_{15}H_{19}N_2BSi$: M^+, 266.14106. Found: m/z 266.14052

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



Colorless solid: 88-90 °C

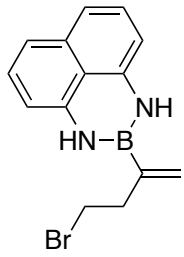
^{1}H NMR (C_6D_6) δ 3.01 (s, 3H), 3.81 (s, 2H), 5.20 (d, *J* = 2.5 Hz, 1H), 5.40 (s, 1H), 5.88 (s, 2H), 6.04 (dd, *J* = 6.7, 1.7 Hz, 2H), 7.02-7.10 (m, 4H)

^{13}C NMR (C_6D_6) δ 57.2, 77.6, 106.4, 118.2, 120.8, 125.9, 137.1, 141.4

^{11}B NMR ($CDCl_3$) δ 27.9

HRMS Calcd for $C_{14}H_{16}ON_2B$: $[M+H]^+$, 239.13557. Found: m/z 239.13472

2-(4-Bromobut-1-en-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (1i)



Colorless solid: mp 54-56 °C

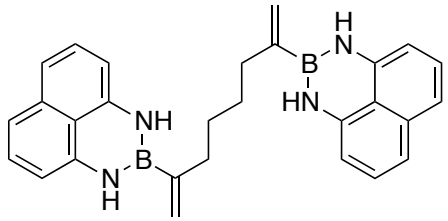
^{1}H NMR (C_6D_6) δ 2.23 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 5.05-5.30 (m, 5H), 5.94 (dd, *J* = 6.7, 1,8 Hz, 2H), 6.99-7.12 (m, 4H)

^{13}C NMR (C_6D_6) δ 32.0, 38.5, 106.5, 118.4, 120.5, 125.5, 127.8, 136.9, 141.0

^{11}B NMR ($CDCl_3$) δ 28.2

HRMS Calcd for $C_{14}H_{14}N_2BBr$: M^+, 300.04334. Found: m/z 300.04257

2,2'-(Octa-1,7-diene-2,7-diyl)bis(2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine) (1j)



Colorless solid: mp 174-176 °C

^{1}H NMR (C_6D_6) δ 1.14-1.51 (m, 4H), 1.99 (t, *J* = 6.2 Hz, 4H), 5.23 (d, *J* = 2.6 Hz, 2H), 5.33 (s, 4H), 5.40 (s, 2H), 5.97 (dd, *J* = 6.9, 1.3 Hz, 4H), 7.00-7.12 (m, 8H)

^{13}C NMR (C_6D_6) δ 29.1, 35.7, 106.4, 118.3, 120.5, 123.1, 137.0, 141.2

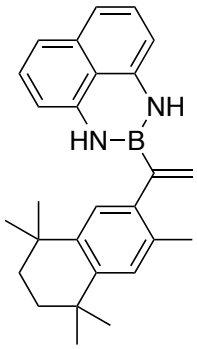
^{11}B NMR ($CDCl_3$) δ 28.8

HRMS Calcd for $C_{28}H_{29}N_4B_2$: $[M+H]^+$, 443.25783. Found: m/z 443.25764

Synthesis of 2-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (1k).

A Schlenk tube equipped with a magnetic stirring bar was charged with (SIPr)CuCl (4.4 μmol), KO*t*Bu (1.0 M solution in THF, 13.3 μmol), MeOH (13.3 mmol) and THF (15.0 mL) before the mixture was stirred at room temperature for 10 min. To the mixture was added (pin)B–B(dan) (4.42 mmol) and an alkyne (4.42 mmol), and the resulting mixture

was stirred at 50 °C for 20 h. The mixture was diluted with ethyl acetate and filtered through a Celite plug, and the organic solution was washed with brine, dried over $MgSO_4$ and evaporated. Silica gel-column chromatography (hexane/ethyl acetate = 10:1 as an eluent) of the residue gave **1k**.



Isolated in 97% yield as a colorless solid. mp 68-69 °C

^{1}H NMR (C_6D_6) δ 1.28 (s, 6H), 1.32 (s, 6H), 1.61 (s, 4H), 2.23 (s, 3H), 5.38 (s, 2H), 5.47 (d, *J* = 3.0 Hz, 1H), 5.56-5.61 (m, 3H), 6.87-7.13 (m, 6H), 6.93-7.03 (m, 4H), 7.20, 7.27

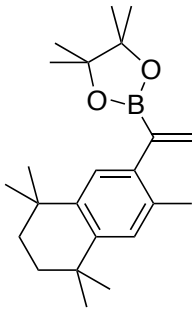
^{13}C NMR ($CDCl_3$) δ 20.3, 32.0, 32.1, 34.1, 35.48, 35.53, 106.4, 118.2, 120.5, 126.3, 127.0, 127.7, 128.4, 132.8, 136.9, 140.7, 141.2, 142.9, 144.2

^{11}B NMR ($CDCl_3$) δ 28.7

HRMS Calcd for $C_{27}H_{31}N_2B$: M^+, 394.25803. Found: m/z 394.25812.

Synthesis of 4,4,5,5-tetramethyl-2-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl) vinyl)-1,3,2-dioxaborolane (2)

A Schlenk tube equipped with a magnetic stirring bar was charged with **1k** (4.1 mmol), 2M H_2SO_4aq (8.2 mmol), pinacol (12.3 mmol) and THF (15.0 mL) before the mixture was stirred at 50 °C for 6 h. Then the mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$ and evaporated. Silica gel-column chromatography (hexane/ethyl acetate = 10:1 as an eluent) of the residue afforded **2**.



Isolated in 92% yield as a colorless solid. mp 118-120 °C

^{1}H NMR ($CDCl_3$) δ 1.29 (s, 12H), 1.33 (s, 12H), 1.68 (s, 4H), 2.27 (s, 3H), 5.84 (d, *J* = 3.7 Hz, 1H), 6,15 (d, *J* = 3.6 Hz, 1H), 7.06 (s, 1H), 7.07 (s, 1H)

^{13}C NMR ($CDCl_3$) δ 20.1, 24.8, 31.87, 31.9, 33.8, 33.9, 35.3, 83.6, 105.8, 117.6, 126.7, 127.7, 131.8, 132.7, 139.4, 142.0, 143.2

^{11}B NMR ($CDCl_3$) δ 30.1

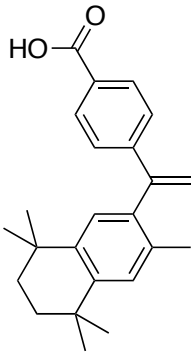
HRMS Calcd for $C_{23}H_{35}O_2B$: M^+, 354.27301. Found: m/z 354.27338.

Synthesis of ethyl 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoate (3)

A Schlenk tube equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$ (10 μmol), [1,1'-biphenyl]-2-yldicyclohexylphosphine (20 μmol), K_3PO_4 (0.60 mmol) and THF (1.0 mL). After the mixture was stirred at room temperature for 10 min, **2** (0.20 mmol) and ethy 4-bromobenzoate (0.22 mmol) was added. The resulting mixture was stirred at 60 °C for 24 h before the mixture was diluted with ethyl acetate and filtered through a Celite plug. The organic solution was washed with brine, dried over $MgSO_4$ and evaporated. Gel permeation chromatography (toluene as an eluent) of the residue gave **3**[2].

Synthesis of 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoic acid (bexarotene, 4)

A MeOH solution (2 mL) of **3** (0.179 mmol) and 5N KOHaq (0.72 mmol) was stirred at reflux temperature for 6 h before the mixture was acidified with 1N HCl and extracted with ethyl acetate. After the organic extract was washed with water, the solvent was removed in vacuo to give **4**.



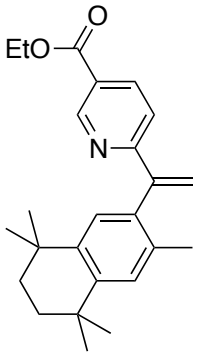
Isolated in 75% yield as a colorless solid.

^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6H), 1.31 (s, 6H), 1.71 (s, 4H), 1.95 (s, 3H), 5.36 (s, 1H), 5.84 (s, 1H), 7.09 (s, 1H), 7.14 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H)

^{13}C NMR ($CDCl_3$) δ 19.9, 31.88, 31.93, 33.9, 34.0, 35.2, 35.2, 117.2, 126.7, 128.1, 130.3, 132.7, 137.9, 142.3, 144.4, 146.5, 149.1, 171.6

Synthesis of ethyl 6-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)nicotinate (5)

A Schlenk tube equipped with a magnetic stirring bar was charged with (dppf)$PdCl_2$•CH_2Cl_2 (10 μmol), $[(PPh_3)CuCl]_4$ (10 μmol), K_3PO_4 (0.60 mmol) and DMF (1.0 mL). After the mixture was stirred at room temperature for 10 min, **2** (0.20 mmol) and ethyl 6-chloronicotinate (0.30 mmol) was added. The mixture was stirred at 80 °C for 24 h before the mixture was diluted with ethyl acetate and filtered through a Celite plug. After the organic solution was washed with brine, dried over $MgSO_4$ and evaporated, the residue was purified by silica gel-column chromatography (hexane/ethyl acetate/NEt_3 = 60:7:1 as an eluent) to give **5**.



Isolated in 78% as a colorless solid. mp 105-106 °C

^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6H), 1.31 (s, 6H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.70 (s, 4H),

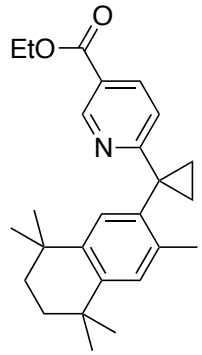
1.99 (s, 3H), 4.40 (q, J = 7.1 Hz, 2H), 5.51 (d, J = 2.1 Hz, 1H), 6.53 (d, J = 2.1 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 7.12 (s, 1H), 7.15 (s, 1H), 8.15 (dd, J = 8.3, 2.3 Hz, 1H), 9.23 (d, J = 2.1 Hz, 1H)

^{13}C NMR ($CDCl_3$) δ 14.3, 19.8, 24.8, 31.88, 31.91, 33.9, 34.0, 35.16, 35.18, 61.2, 120.9, 121.1, 124.5, 128.1, 132.8, 136.9, 137.6, 142.5, 144.5, 148.1, 150.6, 161.1, 165.4

HRMS Calcd for $C_{25}H_{32}O_2N$: $[M+H]^+$, 378.24330. Found: m/z 378.24292.

Synthesis of ethyl 6-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)cyclopropyl)nicotinate (6)

A suspension of trimethylsulfoxonium iodide (0.60 mmol) in DMSO (4 mL) was treated with KO*t*Bu (0.45 mmol) at room temperature for 1 h. Then **5** (0.30 mmol) was added to the ylide solution at room temperature and stirred for 1 h before the reaction solution was diluted with ethyl acetate and filtered through a Celite plug. Then the organic solution was washed with brine, dried over $MgSO_4$ and evaporated. Silica gel-column chromatography (hexane/ethyl acetate/NEt_3 = 60:7:1 as an eluent) of the residue provided **6**.



Isolated in 80% yield as a colorless solid. mp 140-142 °C

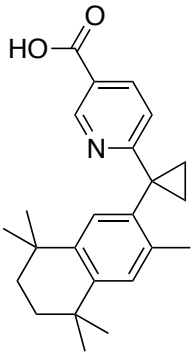
^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6H), 1.32 (s, 6H), 1.32-1.40 (m, 5H), 1.70 (s, 4H), 1.84 (d, J = 3.4 Hz, 2H), 2.13 (s, 3H), 4.37 (d, J = 7.1 Hz, 2H), 6.75 (dd, J = 8.3, 0.7 Hz, 1H), 7.13 (s, 1H), 7.29 (s, 1H), 7.99 (dd, J = 8.3, 2.2 Hz, 1H), 9.11 (dd, J = 2.3, 0.8 Hz, 1H)

^{13}C NMR ($CDCl_3$) δ 14.3, 19.3, 20.1, 24.7, 30.3, 31.87, 31.94, 33.92, 33.95, 35.14, 35.15, 60.9, 120.6, 122.4, 128.3, 129.2, 135.8, 136.5, 137.2, 142.6, 143.8, 150.4, 165.6, 169.1

HRMS Calcd for $C_{26}H_{34}O_2N$: $[M+H]^+$, 392.25895. Found: m/z 392.25831.

Synthesis of 6-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)cyclopropyl)nicotinic acid (LG100268, 7)

A MeOH solution (2 mL) of **6** (0.137 mmol) and 5N NaOHaq (0.548 mmol) was stirred at reflux temperature for 12 h before the mixture was acidified with 1N HCl and extracted with ethyl acetate. After the organic extract was washed with water, the solvent was removed in vacuo to give **7**.



Isolated in 95% yield as a white solid.

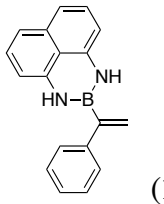
^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6H), 1.31 (s, 6H), 1.39 (d, *J* = 3.5 Hz, 2H), 1.70 (s, 4H), 1.86 (d, *J* = 3.5 Hz, 2H), 2.13 (s, 3H), 6.78 (d, *J* = 8.2 Hz, 1H), 7.12 (s, 1H), 7.27 (s, 1H), 8.03 (dd, *J* = 8.3, 2.2 Hz, 1H), 9.16 (d, *J* = 2.1 Hz, 1H)

^{13}C NMR ($CDCl_3$) δ 19.3, 20.5, 30.5, 31.9, 32.0, 33.95, 33.99, 35.1, 35.2, 120.9, 121.3, 128.4, 129.2, 135.8, 137.0, 137.2, 142.7, 143.9, 151.1, 170.3, 170.4

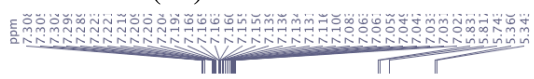
Reference

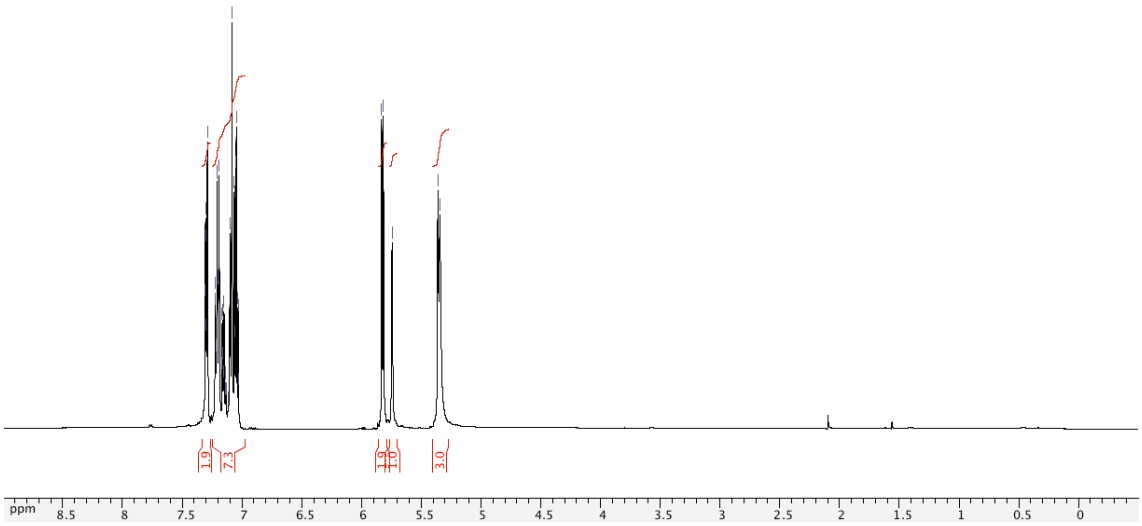
1. C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin and C. S. J. Cazin, *Dalton Trans*., 2010, **39**, 4489.

2. Y. Zou, L. Qin, X. Ren, Y. Lu, Y. Li and J. Zhou, *Chem. Eur. J*., 2013, **19**, 3504.


NH
HN–B

(**1a**)

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7.5
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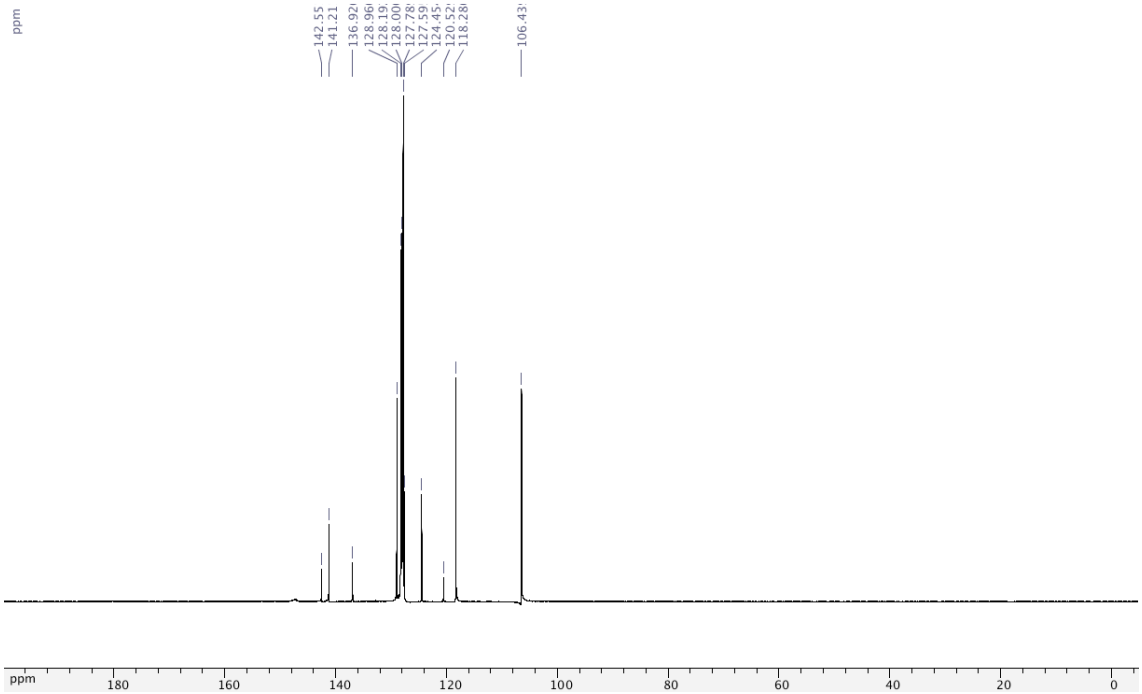
4
3.5
3
2.5
2
1.5
1
0.5
0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106.43
ppm
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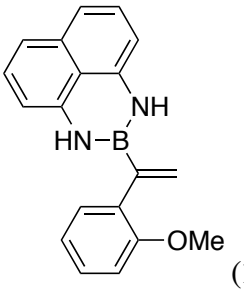
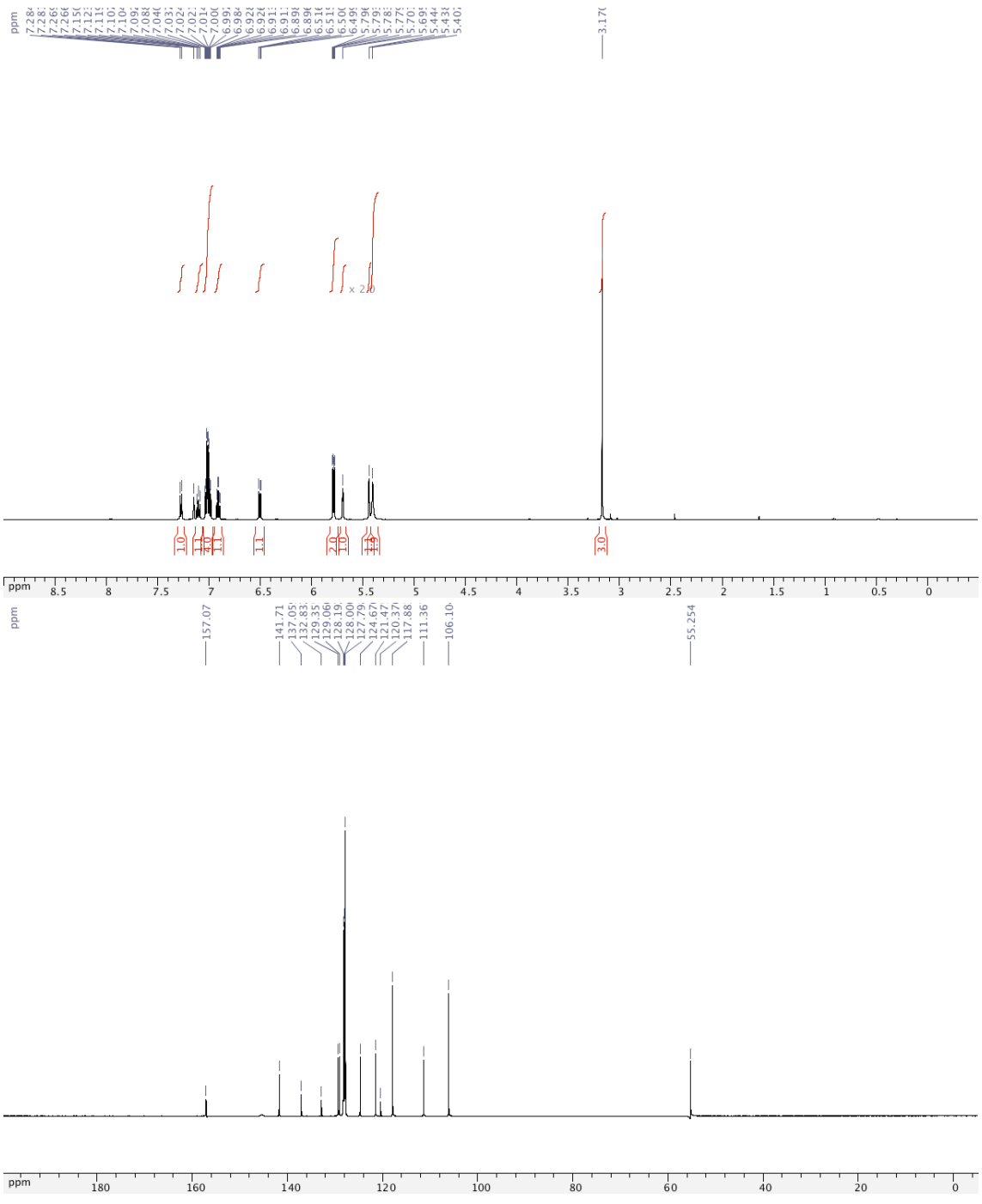
160
140
120
100
80
60
40
20
0


NH
HN−B
OMe

(**1b**)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2.0
1.0
1.1
3.0
ppm
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141.71
137.05
132.83
129.35
129.06
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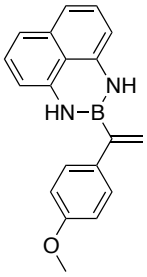
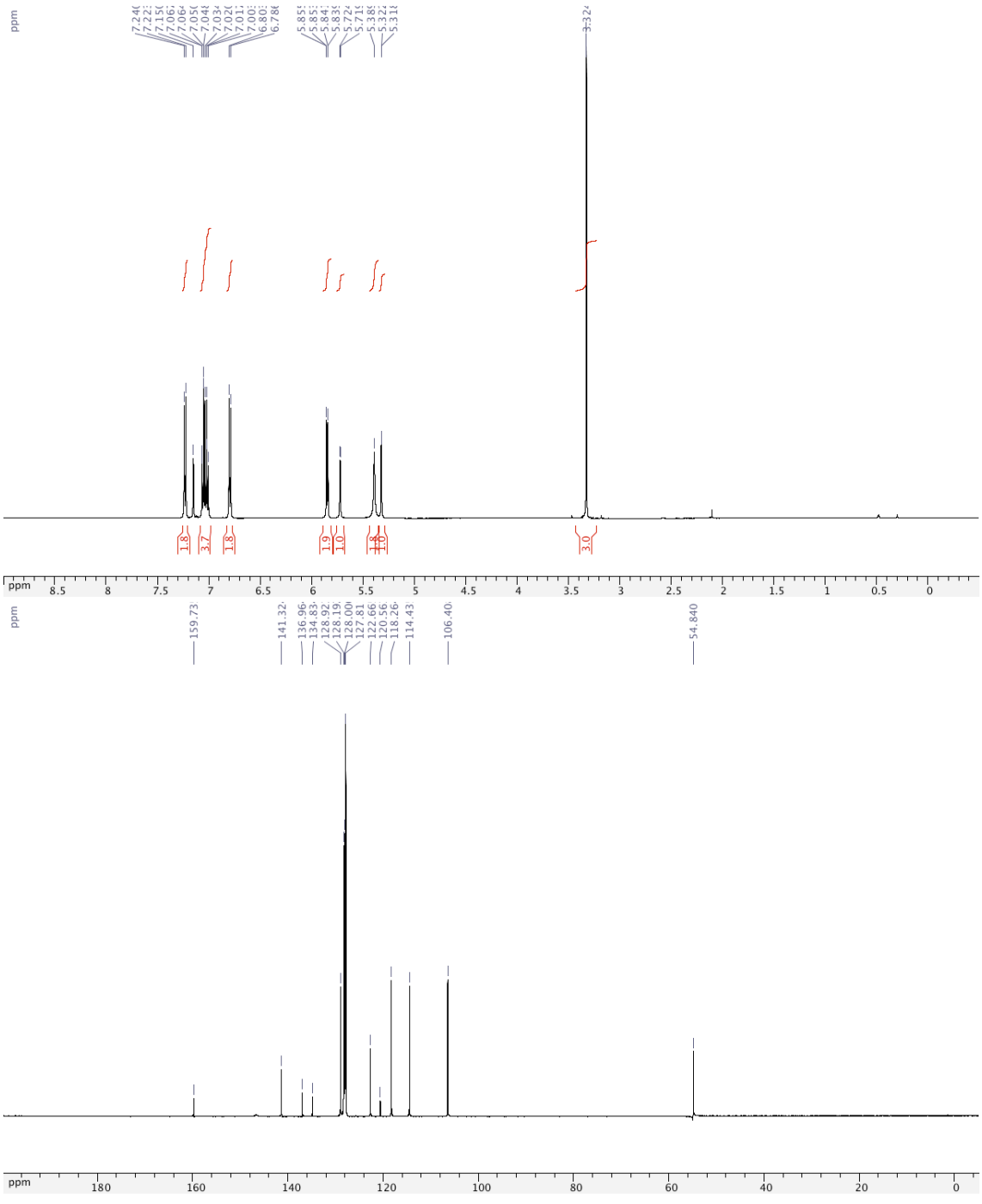
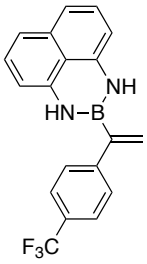
128.09
127.79
124.67
121.47
120.37
117.88
111.36
106.10
55.254
ppm

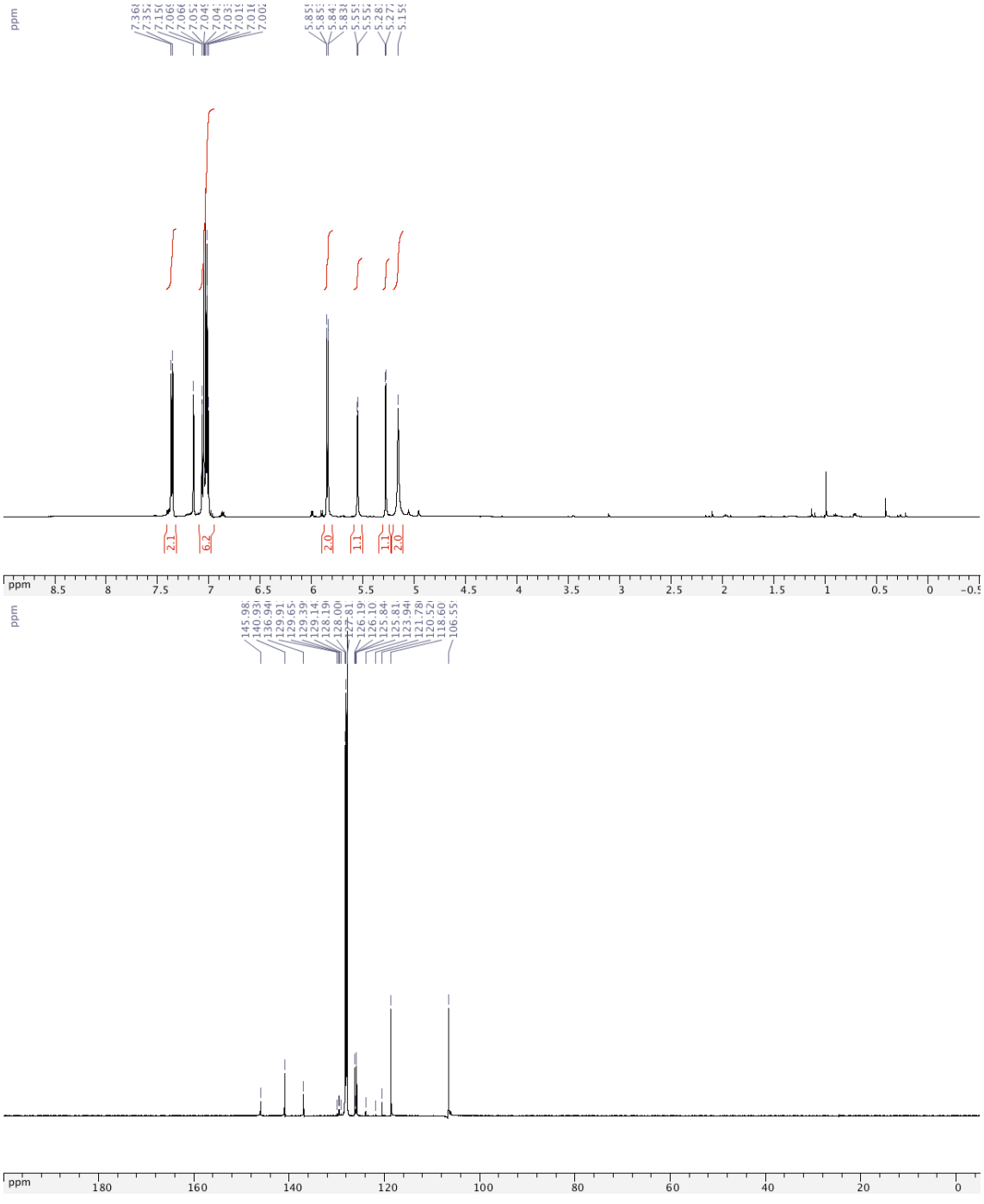


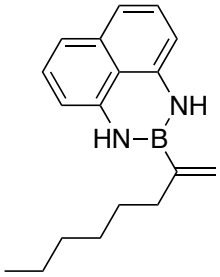
(1c)



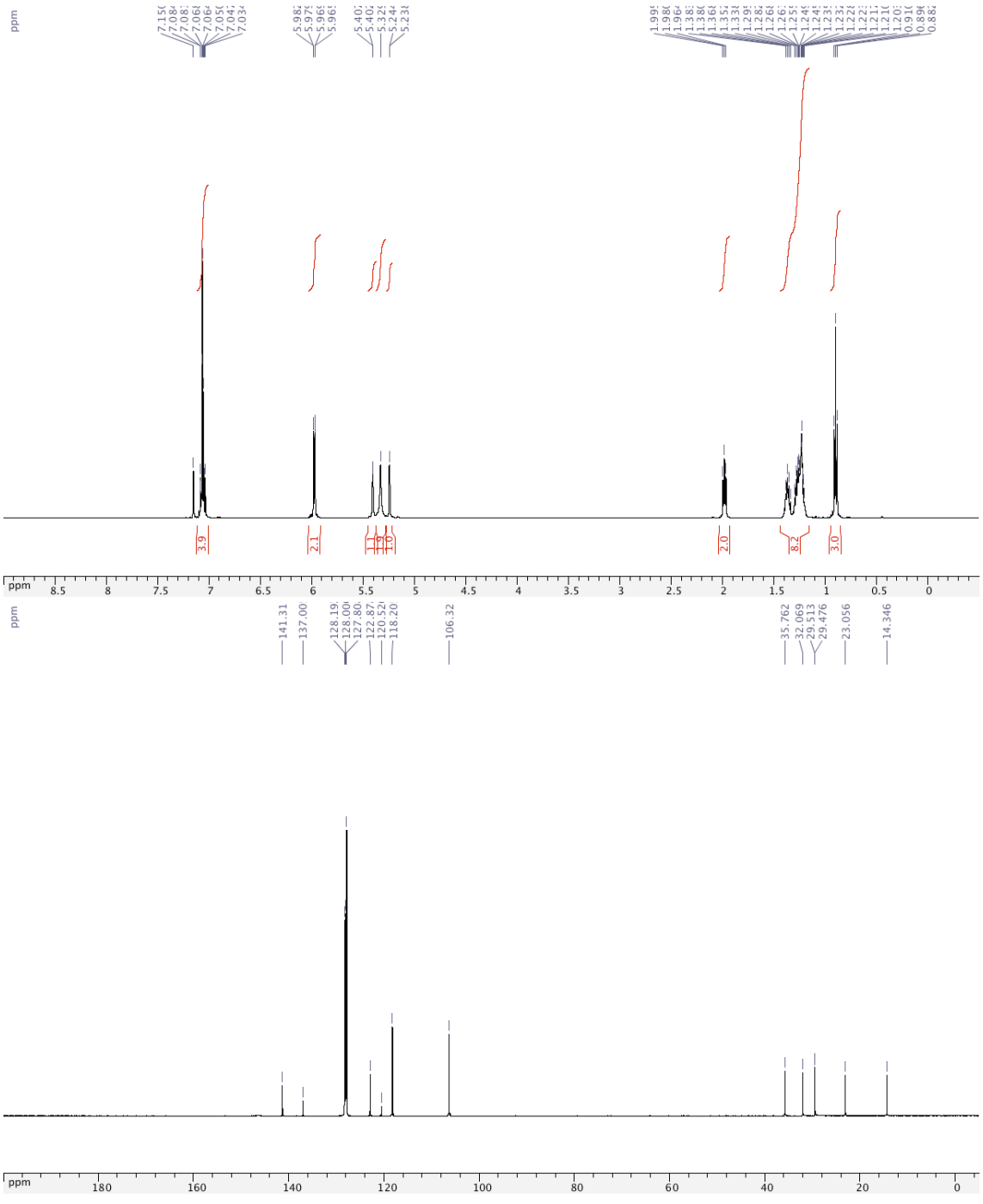


(**1d**)




NH
HN−B

(**1e**)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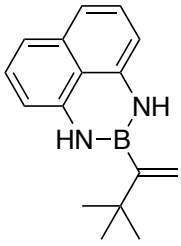
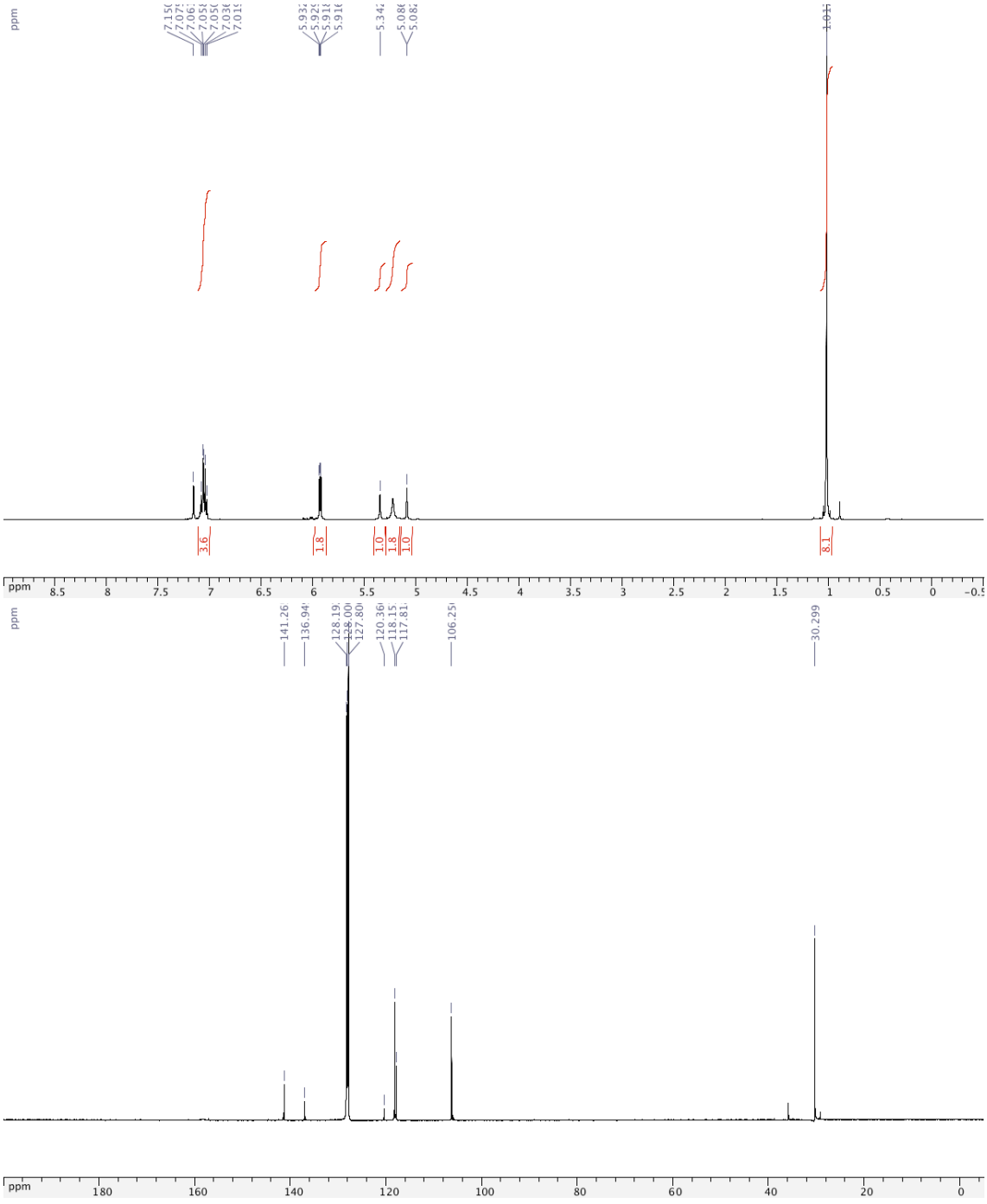
29.476
23.056
14.346


NH
HN−B

(**1f**)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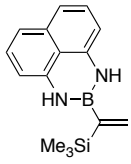
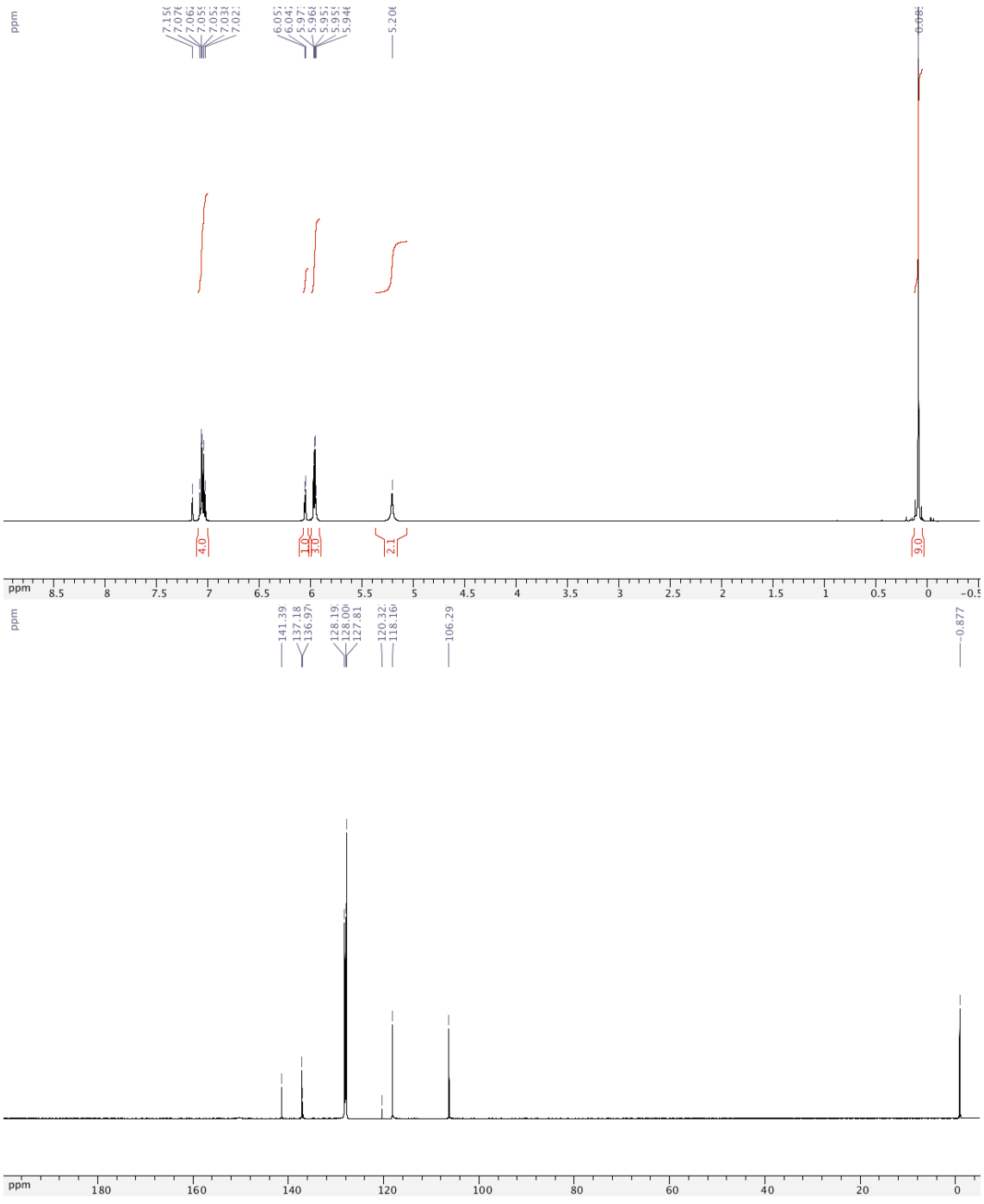
106.25
30.299
ppm


NH
HN–B
Me3Si

(**1g**)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2
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1
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0
4.0
1.0
3.0
2.1
9.0
141.39
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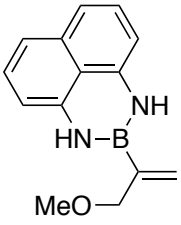
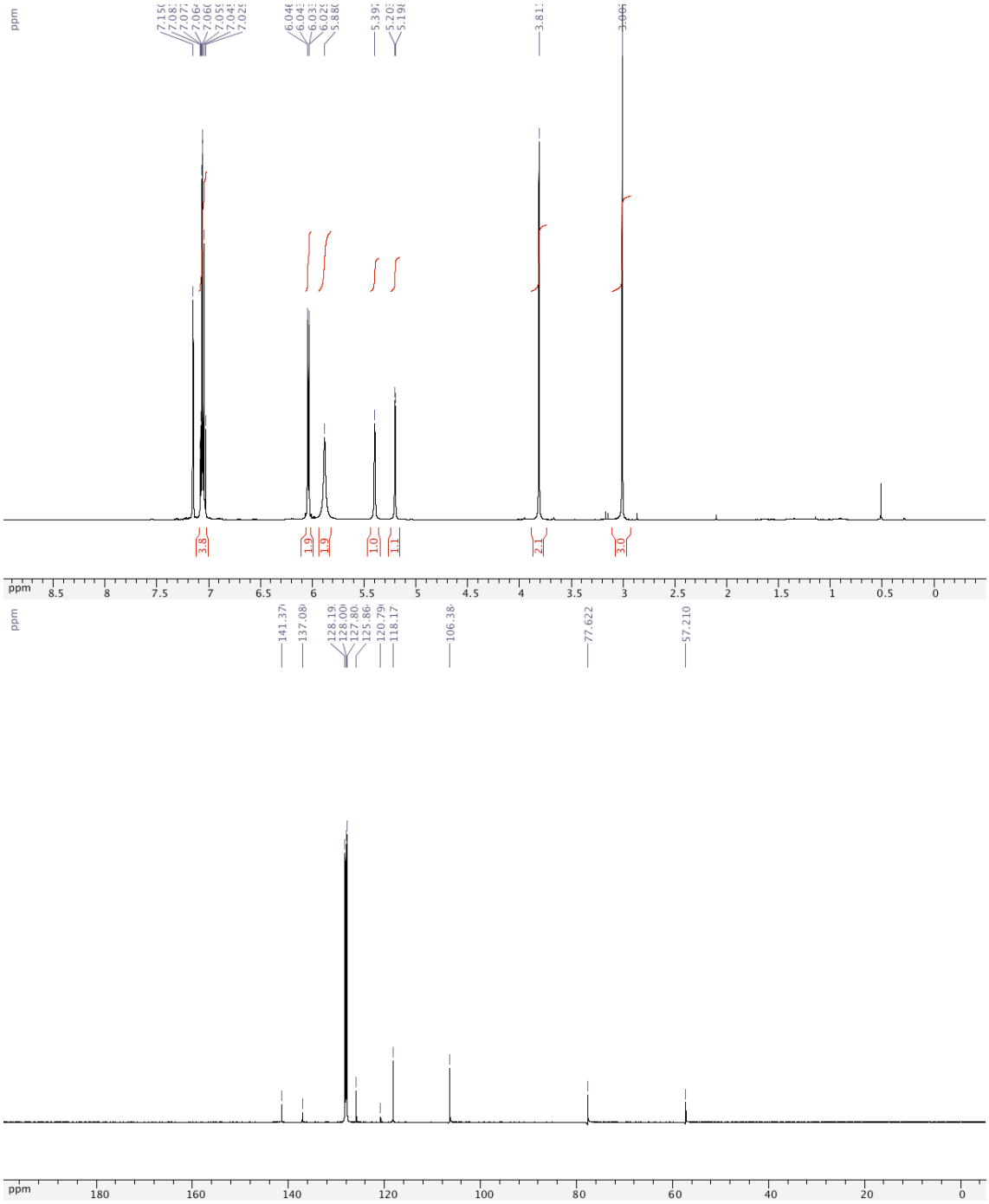
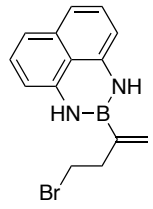
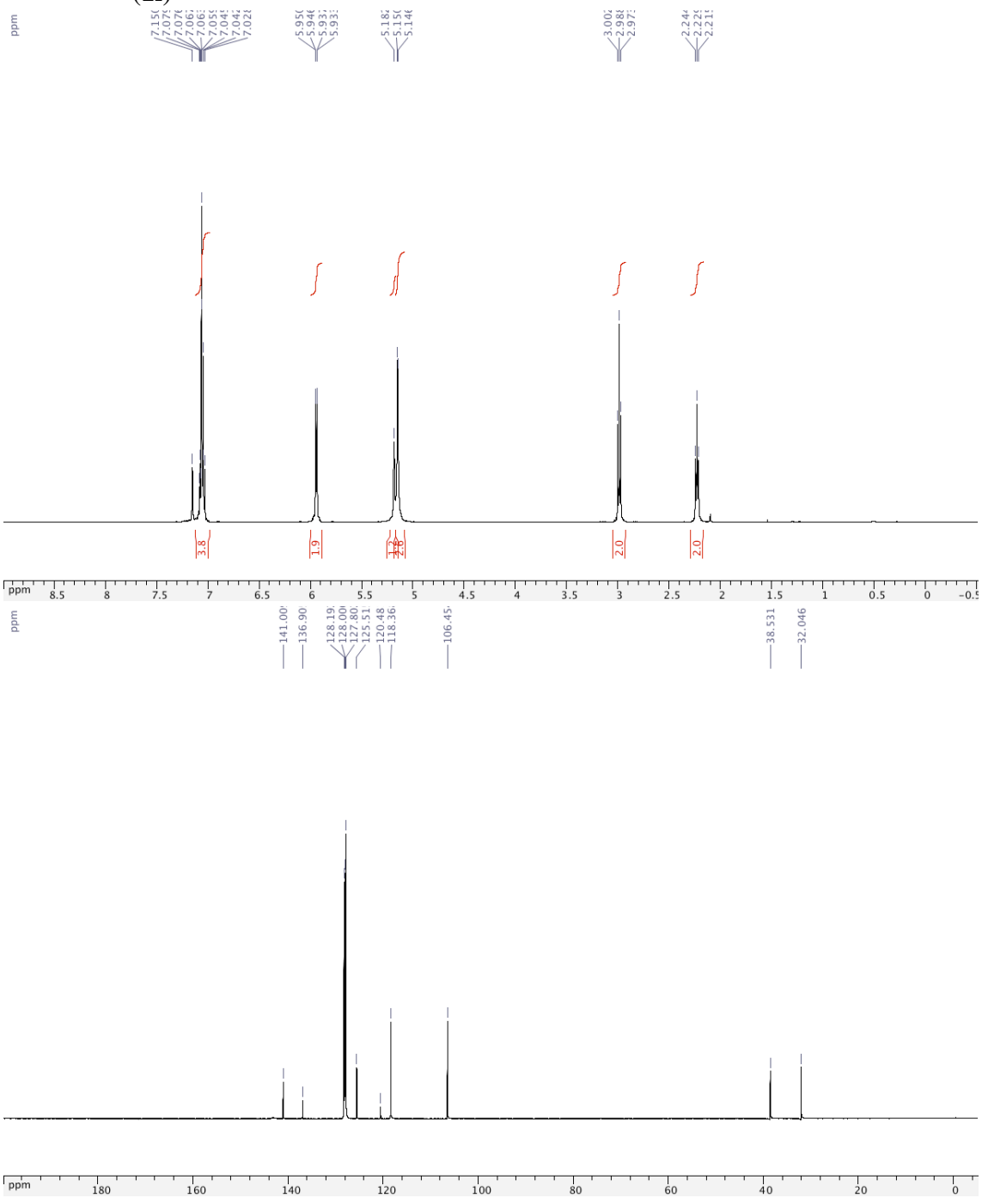


(**1h**)




NH
HN−B
Br

(1i)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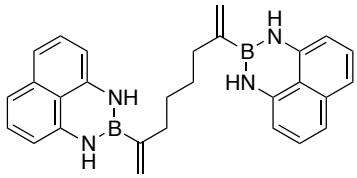
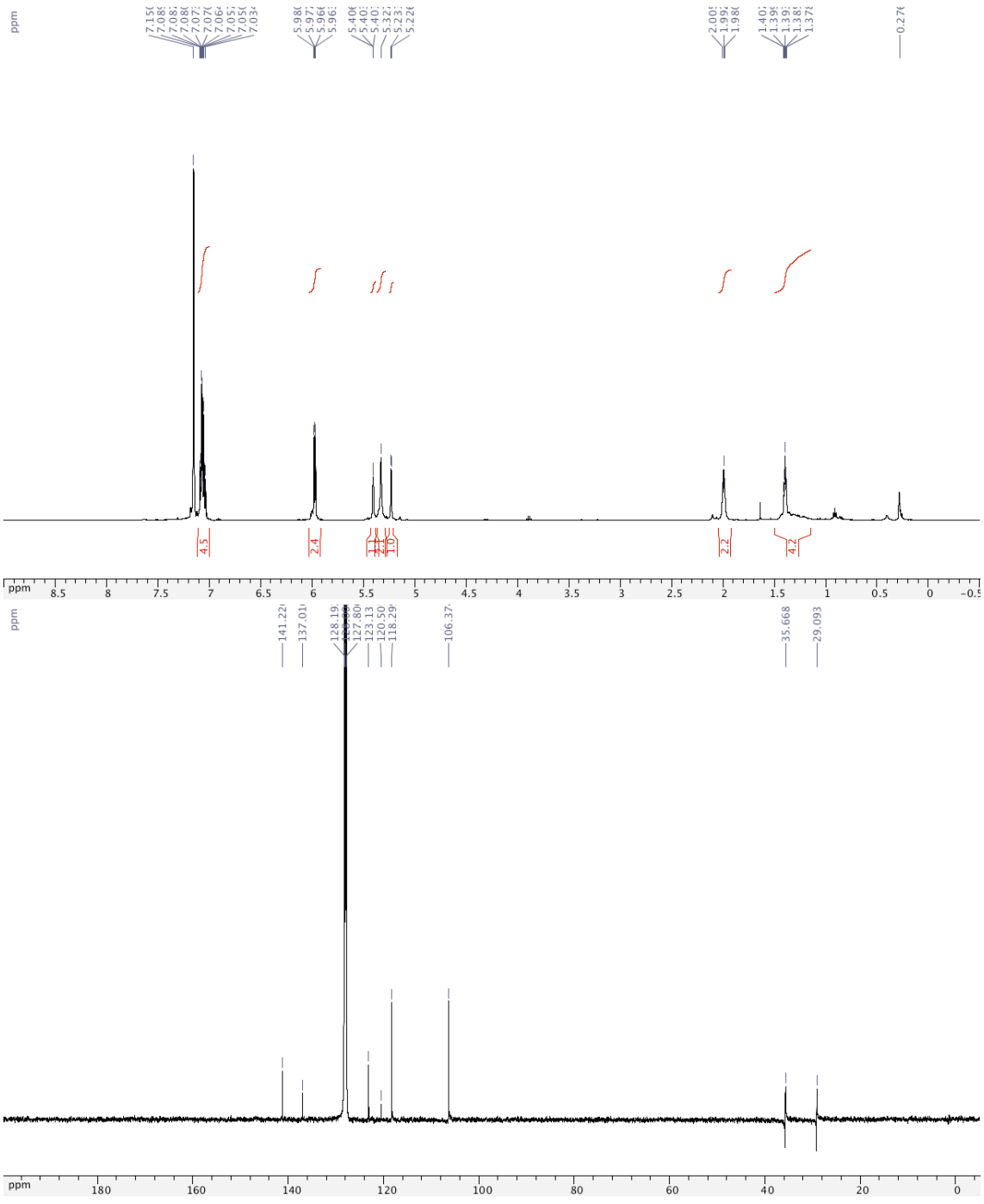

NH
B
N
H
H
N
B
HN

(1j)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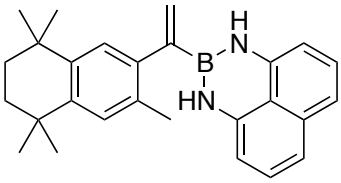
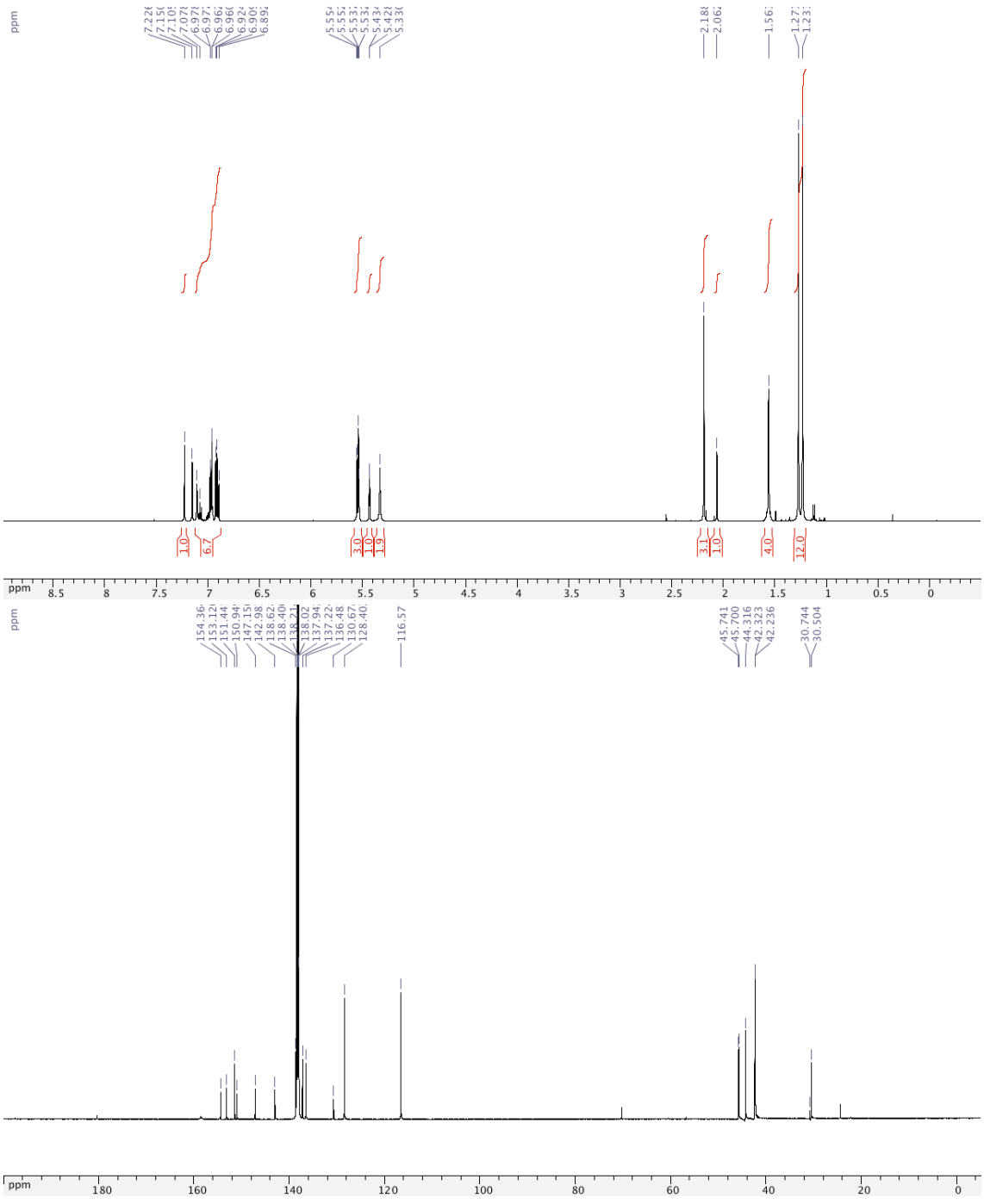
ppm


H
N
B
HN

(**1k**)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1.0
1.9
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1.0
4.0
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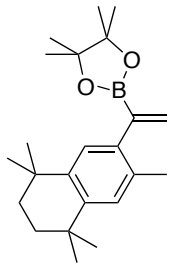
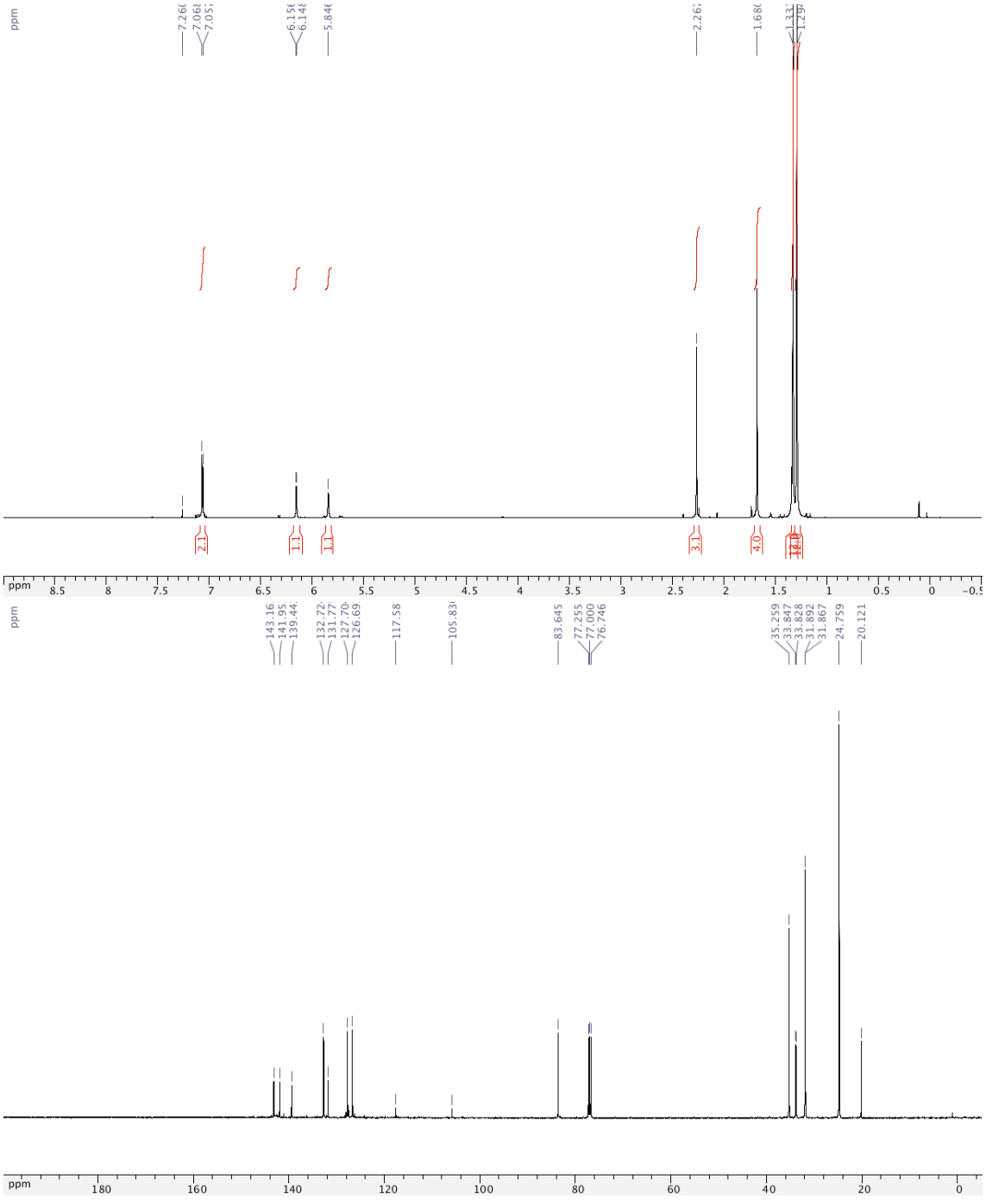
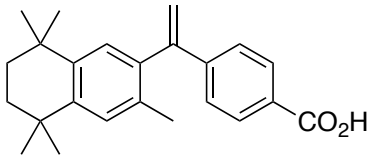
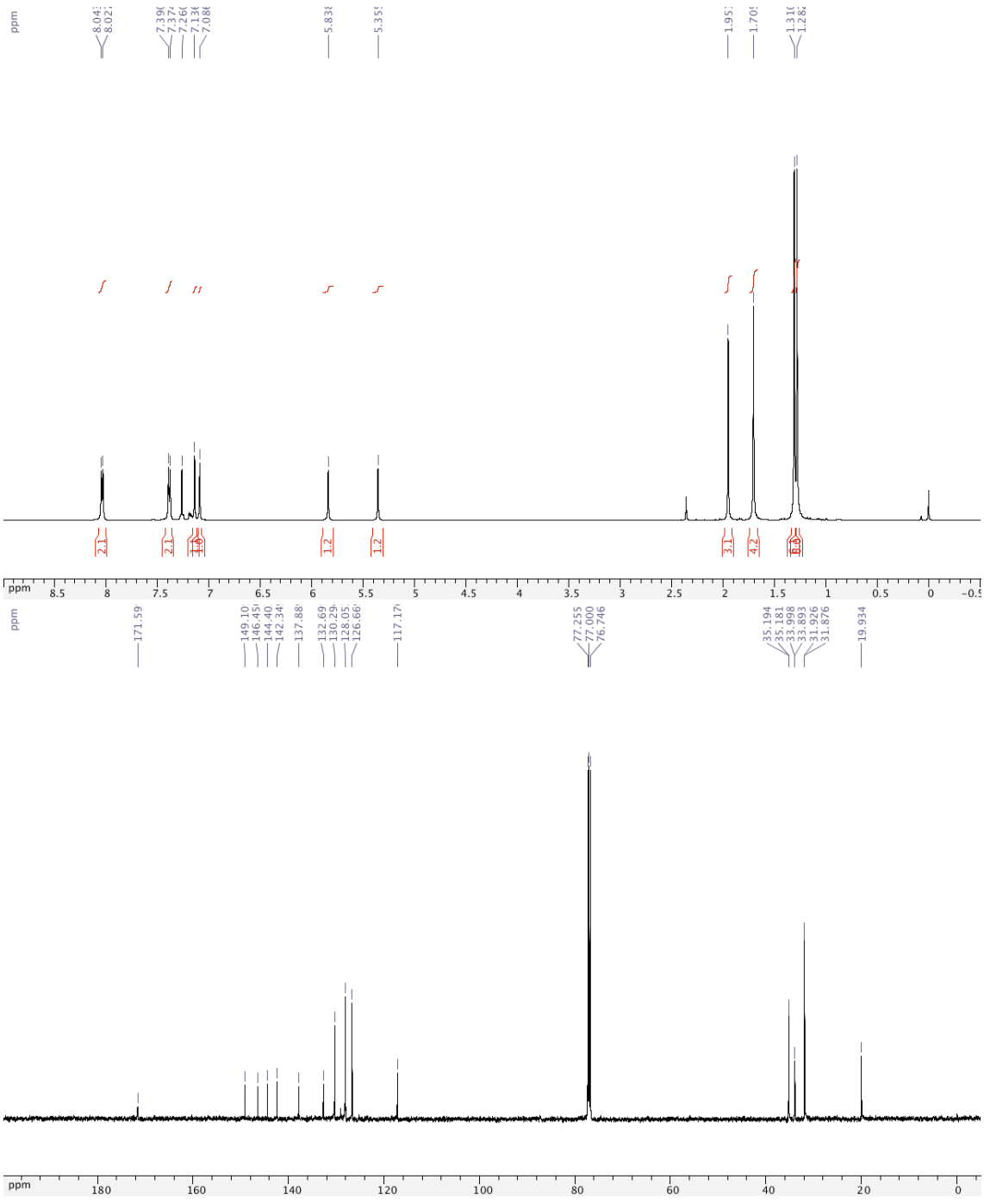


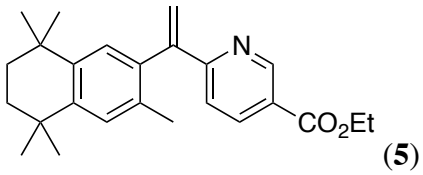
(**2**)



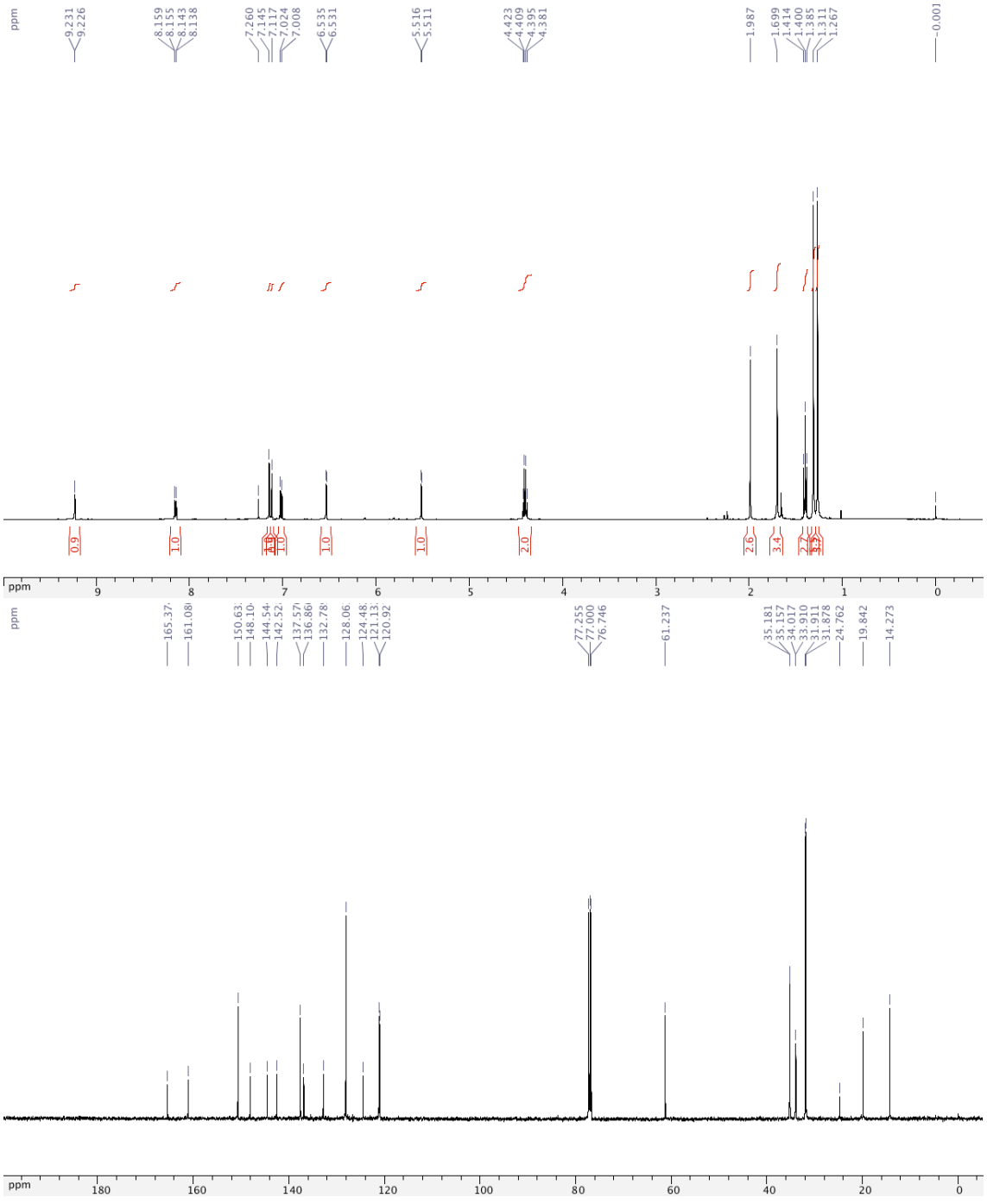


(**4**)




N
CO2Et

(**5**)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5.511
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4.409
4.395
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1.699
1.414
1.400
1.385
1.311
1.267
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1.0
1.0
2.0
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2.7
4.5
ppm
9
8
7
6
5
4
3
2
1
0
ppm
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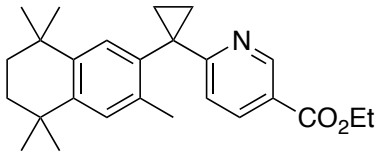
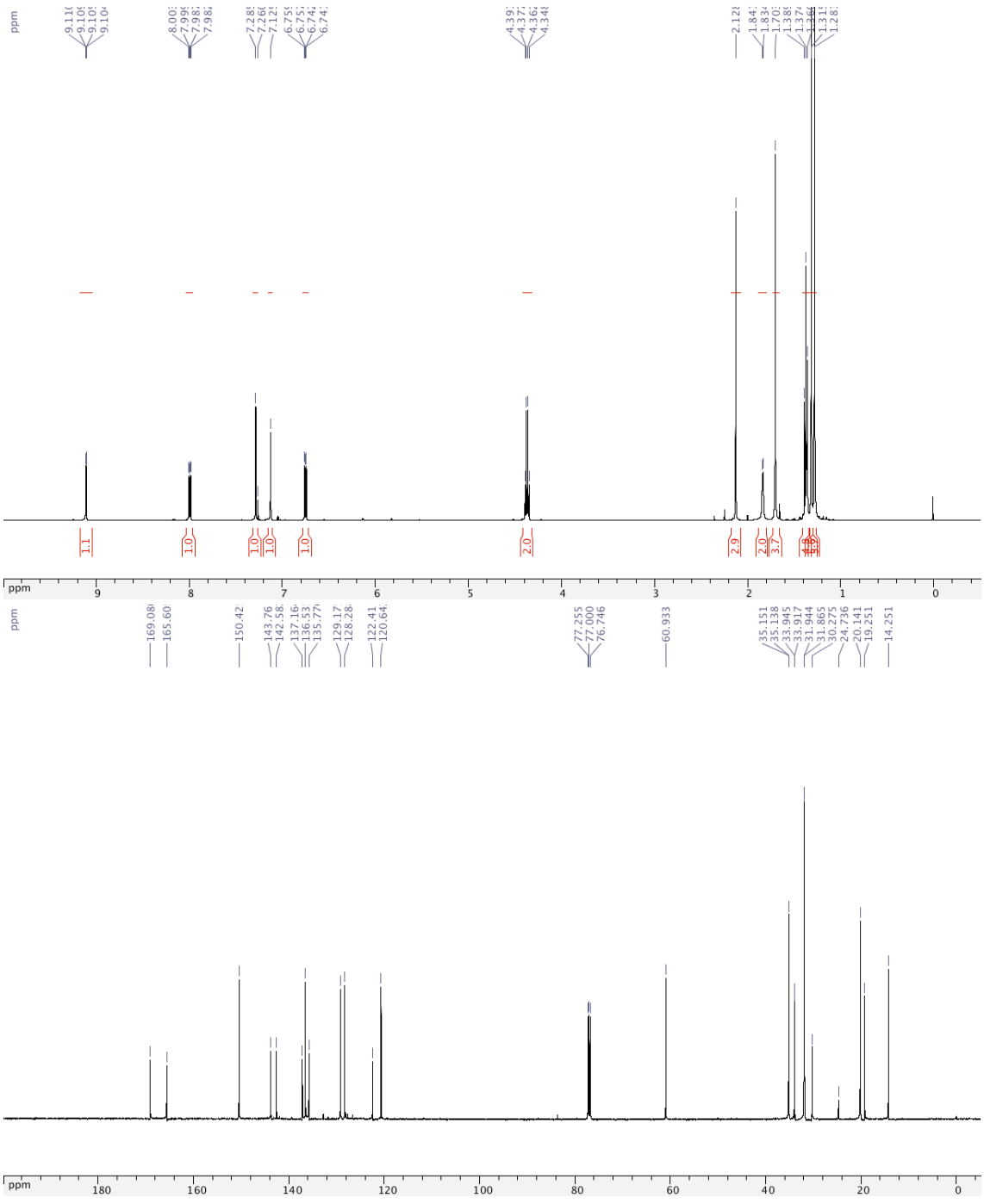
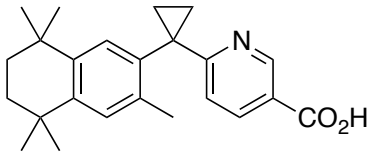


(**6**)





(**7**)