Supporting Information

Aerobic oxidative homocoupling of aryl amines using heterogeneous rhodium catalysts

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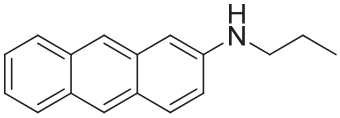
General Procedures

^{1}H NMR, ^{13}C NMR were measured in $CDCl_3$ solution using JEOL JNM-AL-400 spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz) and JNM-ECA-600 spectrometer (^{1}H NMR at 600 MHz, ^{13}C NMR at 150 MHz) as the referenced standard (^{1}H NMR at 0.00 ppm (TMS), ^{13}C NMR at 77.0 ppm ($CDCl_3$)). Chemical sifts are reported in ppm. Peak multiplicities are used the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broadend. IR spectra were recorded on JAS.CO FT/IR-410 and Shimadzu FT/IR-8300 spectrometers. Mass spectra and high resolution mass spectra were obtained on a JMS-K9, JEOL JMS-700 and Shimadzu LCMS-2010EV mass spectrometers. Elemental analyses were performed with YANACO 026 CHN analyzer. Melting points were measured with a Yanaco MP-500D apparatus and Büchi 535 melting point apparatus and are uncorrected. ESR spectra were recorded using a JEOL JES-FA200 spectrometer. Thin-layer chromatography (TLC) was performed on precoated plates (0.25 mm, silica gel Merck $60F_{245}$). Column

chromatography was performed on silica gel (Kanto Chemical Co., Inc.). Preparative HPLC was performed on a system utilizing a HITACHI L-6250 Intelligent Pump with a gradient solvent system of hexane and ethyl acetate and UV detector L-7400 at 254 nm, and also a system utilizing a JAS.CO PU-2087 Intelligent Pump with Dynamic Mixer MX-2080-32 and UV detector UV-2075 and RI detector RI-2031. The recycling preparative HPLC was performed with LC-908, which was consisted of UV detector UV-310B and RI detector RI-5. All reactions were performed under an air atmosphere unless otherwise noted, and dry dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Inc., and other solvents were distilled. Unless otherwise noted, reagents were obtained from chemical sources and without further purification.

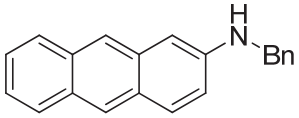
_N_-Propyl-2-anthracenylamine



To a solution of 2-aminoanthrathene (193 mg, 1.0 mmol) in 1,2-dichloroethane (2.6 ml) were added propionaldehyde (64 mg, 1.1 mmol) and $NaBH(OAc)_3$ (297 mg, 1.4 mmol) at room temperature, and the mixture was stirred for 6 hour. Then propionaldehyde (29 mg, 0.50 mmol) was added and stirred at room temperature for 1 hour. After addition of H_2O, the resulting mixture was extracted with $CHCl_3$ and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 5%) to afford 144 mg (76%) of the title compound as yellow solids.

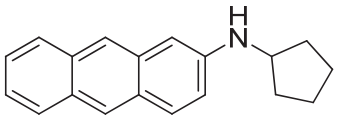
Mp. 78 ˚C (dec.). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.07 (t, J = 7.2 Hz, 3H), 1.71-1.80 (m, 2H), 3.24 (t, J = 7.2 Hz, 2H), 3.91 (brs, 1H), 6.84 (s, 1H), 6.89 (d, J = 8.8 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.89 (t, J = 9.2 Hz, 2H) , 8.12 (s, 1H), 8.23 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.7 (q), 22.4 (t), 45.6 (t), 101.0 (d), 120.3 (d), 122.3 (d), 123.4 (d), 125.2 (d), 126.0 (d), 127.3 (d), 127.3 (s), 128.2 (d), 129.2 (d), 129.3 (s), 132.4 (s), 133.7 (s), 145.1 (s). IR (KBr): 3406, 1634 cm^{-1}. MS (EI) *m/z* 235 (M^+, 100%), 206 (M^+-C_2H_5). HRMS (EI) *m/z* calcd for $C_{17}H_{17}N$ (M^+): 235.1361, found: 235.1358.

_N_-Benzyl-2-anthracenylamine



To a solution of 2-aminoanthrathene (772 mg, 4.0 mmol) in 1,2-dichloroethane (20 ml) were added benzaldehyde (510 mg, 5.6 mmol) and $NaBH(OAc)_3$ (1.19 g, 5.6 mmol) at room temperature, and the mixture was stirred for 3 days. After addition of H_2O, the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by recrystallization from toluene to afford 690 mg (61%) of the title compound as yellow solids.
Mp. 137-139 ˚C (toluene). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.48 (s, 2H), 6.90 (brs, 1H), 6.96 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.29-7.34 (m, 2H), 7.36-7.40 (m, 3H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H) , 8.24 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 48.3 (t), 101.7 (d), 120.1 (d), 122.7 (d), 123.6 (d), 125.3 (d), 126.1 (d), 127.37 (d), 127.39 (d), 127.5 (s), 127.7 (d), 128.2 (d), 128.7 (d), 129.4 (d), 129.5 (s), 132.5 (s), 133.5 (s), 138.9 (s), 144.8 (s). IR (KBr): 3424, 1636, 1506 cm^{-1}. MS (EI) *m/z* 283 (M^+, 100%), 192 (M^+-Bn), 91 (Bn). HRMS (EI) *m/z* calcd for $C_{21}H_{17}N$ (M^+): 283.1361, found: 283.1361.

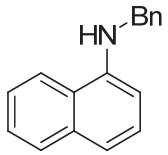
***N*-Cyclopentyl-2-anthracenylamine**



To a solution of 2-aminoanthrathene (386 mg, 2.0 mmol) in 1,2-dichloroethane (10 ml) were added cyclopentanone (320 mg, 3.8 mmol), $NaBH(OAc)_3$ (509 mg, 2.4 mmol), and AcOH (0.11 ml, 2.0 mmol) at room temperature, and the mixture was stirred for 22 hour. After addition of 3N NaOH (aq), the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 2%) to afford 275 mg (53%) of the title compound as yellow powder.
Mp. 108-110 ˚C (benzene). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.45-1.85 (m, 6H), 2.05-2.20 (m, 2H), 3.80-4.02 (m, 2H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.86 (dd, *J* = 2.2, 8.6 Hz, 1H), 7.25-7.42 (m, 2H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 8.11 (s, 1H) , 8.21 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 24.2 (t), 33.5 (t), 54.6 (d), 101.9 (d), 120.6 (d),

122.4 (d), 123.4 (d), 125.2 (d), 126.0 (d), 127.31 (s), 127.34 (d), 128.2 (d), 129.2 (d), 129.4 (s), 132.5 (s), 133.7 (s), 144.6 (s). IR (KBr): 3401, 2949, 1630, 1485 cm^{-1}. MS (FAB) *m/z* 261 (M^+, 100%). HRMS (FAB) *m/z* calcd for $C_{19}H_{19}N$ (M^+): 261.1517, found: 261.1516.

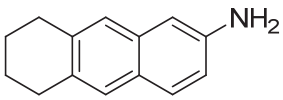
N-Benzyl-1-naphthylamine[1]



To a solution of 1-aminonaphthalene (1.44 g, 10 mmol) in 1,2-dichloroethane (50 ml) were added benzaldehyde (1.49 g, 14 mmol) and $NaBH(OAc)_3$ (2.97 g, 14 mmol) at room temperature, and the mixture was stirred for 34 hour. After addition of H_2O, the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 3%) to afford 2.0 g (88%) of the title compound as colorless needles.

Mp. 58-60 ˚C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.50 (s, 2H), 4.69 (br, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.29-7.48 (m, 8H), 7.77-7.83 (m, 2H). MS (EI) *m/z* 233 (M^+), 91 (Bn, 100%).

1,2,3,4-Tetrahydroanthracen-6-amine



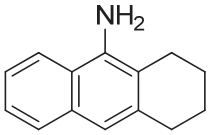
To a solution of 2-aminoanthracene (250 mg, 1.3 mmol) in EtOH (13 ml) was added 5% Rh/ Al_2O_3 (259 mg, 0.13 mmol) and the mixture was stirred at room temperature under H_2 (1 atm) for 22 hour. The reaction mixture was filtered through a pad of celite and concentrated to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1/9) to afford 109 mg (43%) of the title compound as brown needles.

Mp. 149-150 ˚C (MeCN, lit.[2] 154 ˚C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.81-1.86 (m, 4H),

[1] Cano, R.; Yus, M.; Ramón, D. J. *Tetrahedron* **2011**, *67*, 8079-8085.
[2] v. Braun, J.; Bayer, O. *Liebigs Ann. Chem.* **1929**, *472*, 90-121.

2.82-2.95 (m, 4H), 3.72 (brs, 2H), 6.84 (dd, J = 2.0, 8.4 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 7.29 (s, 1H), 7.39 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.4 (t), 23.5 (t), 29.4 (t), 29.8 (t), 107.8 (d), 117.6 (d), 124.5 (d), 126.4 (d), 126.8 (s), 128.2 (d), 132.5 (s), 133.4 (s), 136.5 (s), 143.2 (s). IR (KBr): 3398, 3329, 2924, 1635 cm^{-1}. MS (EI) *m/z* 197 (M^+, 100%). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10, found: C, 84.83; H, 7.69; N, 7.10.

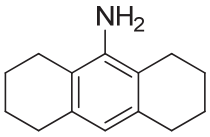
1,2,3,4-Tetrahydroanthracen-9-amine



To a solution of 9-nitroanthracene (1.12 g, 5 mmol) in EtOH (50 ml) was added 10% Pd/C (266 mg, 0.25 mmol) and stirred at rt under H_2 (1 atm) for 20 hour. The resulting mixture was filtered through a pad of celite and concentrated to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 1/4) to afford 722 mg (73%) of the title compound as colorless needles.

Mp. 99-101 ˚C (EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.79-1.85 (m, 2H), 1.92-2.00 (m, 2H), 2.67 (t, J = 6.3 Hz, 2H), 2.93 (t, J = 6.3 Hz, 2H), 4.12 (brs, 2H), 7.08 (s, 1H), 7.33-7.36 (brs, 2H), 7.65-7.75 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 22.9 (t), 23.4 (t), 24.7 (t), 30.8 (t), 116.7 (s), 117.5 (d), 120.0 (d), 121.6 (s), 123.8 (d), 124.9 (d), 127.7 (d), 132.4 (s), 136.6 (s), 138.6 (s). IR (KBr): 3339, 2931, 1630, 1506, 1397 cm^{-1}. MS (EI) *m/z* 197 (M^+, 100%). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10, found: C, 85.09; H, 7.66; N, 7.06.

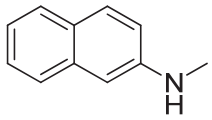
1,2,3,4,5,6,7,8-Octahydroanthracen-9-amine



To a solution of 9-nitroanthracene (446 mg, 2 mmol) in EtOH (13 ml) was added 5% Rh/Al_2O_3 (411 mg, 0.2 mmol, 0.1 eq) and stirred at rt under H_2 (1 atm) for 18 hour. Then 5% Rh/Al_2O_3 (411 mg, 0.2 mmol, 0.1 eq) was added and stirred at rt under H_2 (1 atm) for 48 hour. The resulting mixture was filtered through a pad of celite and concentrated to give a crude product, which was purified by recrystallization from MeOH to afford 213 mg (53%) of the title compound as colorless needles.

Mp. 83-84 ˚C (MeOH; lit.[3] 84.5-85 ˚C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.70-1.76 (m, 4H), 1.83-1.89 (m, 4H), 2.44 (t, *J* = 6.4 Hz, 4H), 2.69 (t, *J* = 6.4 Hz, 4H), 3.54 (brs, 2H), 6.36 (s, 1H). Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96, found: C, 83.19; H, 9.40; N, 6.90.

***N*-Methyl-2-naphthylamine**[4]



To a solution of 2-bromonaphthalene (1.0 g, 5.0 mmol) in toluene (20 ml) were added $Pd(P\mathit{t}Bu_3)_2$ (102 mg, 0.20 mmol) and LHMDS (7.5 ml, 7.5 mmol, 1 M in THF) at room temperature, and the mixture was stirred at room temperature for 10 hour. After addition of 1N HCl (aq), the resulting mixture was stirred at room temperature for 1 min and then basified with 3N NaOH (aq). The mixture was extracted with EtOAc and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was used to the next reaction without further purification.

The crude product was dissolved in ethanol (10 ml) and treated with benzotriazole (600 mg, 5.0 mmol) and formaldehyde (0.5ml, 6.5 mmol, 37% aqueous). The reaction mixture was stirred at room temperature for 3 hour. The precipitated solid was collected by filtration, washed with ethanol, and dried to give 980 mg (71%, 2 steps) of N-(benzotriazol-1-ylmethyl)-2-naphthylamine.

To a solution of the benzotriazole derivative (980 mg, 3.6 mmol) in THF (15 ml) was added $NaBH_4$ (380 mg, 10.0 mmol) at room temperature and the mixture was stirred at room temperature for 10 hour. After addition of H_2O, the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 10%) to afford 492 mg (87%) of the title compound as pale brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.94 (s, 3H), 3.87 (br, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.87 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.14-7.22 (m, 1H), 7.31-7.39 (m, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H) , 7.67 (d, *J* = 8.4 Hz, 1H) , 8.23 (s, 1H). MS (EI) *m/z* 157 (M^+, 100%).

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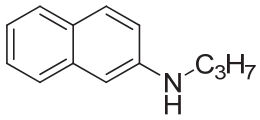
[3] Dewar, M. J. S.; Michl, J. *Tetrahedron* **1970**, *26*, 375-384.

[4] (a) Tang, Q.; Zhang, C.; Luo, M. *J. Am. Chem. Soc.* **2008**, *130*, 5840-5841. (b) Katritzky, A. R.; Black, M.; Fan, W.-Q. *J. Org. Chem.* **1991**, *56*, 5045-5048

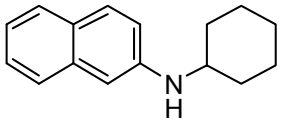
***N*-Propyl-2-naphthylamine**[5]



To a solution of 2-bromonaphthalene (621 mg, 3.0 mmol) in toluene (30 ml) were added propylamine (0.74 ml, 9.0 mmol), NaO*t*Bu (865 mg, 9.0 mmol), and $Pd(P\mathit{t}Bu_3)_2$ (77 mg, 0.15 mmol) at room temperature, and the mixture was refluxed for 9 hour. After addition of H_2O, the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 10/ 90) to afford 442 mg (80%) of the title compound as a pale brown oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 1.04 (t, *J* = 7.2 Hz, 3H), 1.71 (sext, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 3.81 (br, 1H), 6.80 (d, J = 1.8 Hz, 1H), 6.86 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H). MS (EI) *m/z* 185 (M^+), 156 (100%). HRMS (EI) *m/z* calcd for $C_{13}H_{15}N$ (M^+): 185.1204, found: 185.1199.

***N*-Cyclohexyl-2-naphthylamine**[6]



To a solution of 2-bromonaphthalene (828 mg, 4.0 mmol) in toluene (20 ml) were added cyclohexylamine (1.4 ml, 12.0 mmol), NaO*t*Bu (1.2 g, 12.0 mmol), and $Pd(P\mathit{t}Bu_3)_2$ (77 mg, 0.15 mmol) at room temperature, and the mixture was refluxed for 3 hour. After addition of H_2O, the resulting mixture was extracted with EtOAc and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (AcOEt/ hexane = 5/ 95) to afford 873 mg (97%) of the title compound as colorless solids.

Mp. 67-68 ˚C (hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.16-1.31 (m, 3H), 1.34-1.48 (m, 2H), 1.62-1.71 (m, 1H), 1.74-1.82 (m, 2H), 2.10-2.16 (m, 2H), 3.34-3.43 (m, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.87 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.14-7.20 (m, 1H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.61 (d, *J* = 5.2 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 1H). MS (EI) *m/z* 225 (M^+), 182 (100%).

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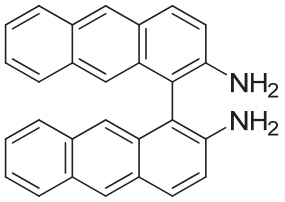
[5] Xu, H.; Wolf, C. *Chem. Commun.* **2009**, 1715-1717.

[6] Kwit, M.; Gawronski, J. *Tetrahedron* **2003**, *59*, 9323-9331.

General Procedure for the rhodium catalyzed oxidative coupling of aryl amines:

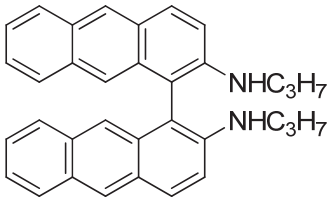
1,1'-Bianthracen-2,2'-diamine (2a) [7]



To a solution of 2-aminoanthracene (50 mg, 0.26 mmol) in TFA (2.6 ml) was added 5% Rh/ C (11 mg, 0.0052 mmol) and stirred at rt under air for 2 h. 3M NaOH was added and the resulting mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, evaporated to afford the crude, which was purified by silica gel column chromagtography ($CHCl_3$) to yield 50 mg (quant.) of **2a** as brown amorphous.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.23-7.31 (m, 6H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 9.6 Hz, 2H), 8.41 (s, 2H). MS (FAB) *m/z* 384 (M^+, 100%). HRMS (FAB) *m/z* calcd for $C_{28}H_{20}N_2$ (M^+): 384.1626. found: 384.1624.

***N,N'*-Dipropyl-1,1'-bianthracen-2,2'-diamine (2b)**



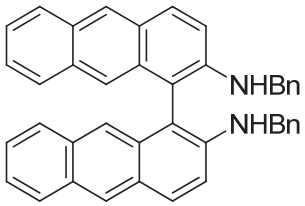
The title compound was prepared according to General Procedure using aryl amine (50 mg, 0.21 mmol) to yield 37 mg (72%) of **2b** as a yellow oil after silica gel column chromatography ($CHCl_3$/ hexane = 30%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.70 (t, *J* = 7.2 Hz, 6H), 1.32-1.45 (m, 4H), 3.15 (t, *J* = 7.2 Hz, 4H), 3.88 (brs, 2H), 7.17-7.26 (m, 4H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 8.39 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 11.2 (q), 23.6 (t), 45.7 (t), 109.3 (s), 116.1 (d), 120.8 (d), 123.5 (d), 124.9 (d), 126.6 (d), 127.7 (s), 127.9 (d), 129.2 (s), 130.0 (d), 132.2 (s), 132.5 (s), 143.9 (s). IR (KBr): 3400, 1616 cm^{-1}. MS (FAB) *m/z* 468 (M^+). HRMS(FAB) *m/z* calcd for $C_{34}H_{32}N_2$ (M^+): 468.2565.

[7] Vyskočil, Š.; Smrčina, M.; Lorenc, M.; Tišlerová, I.; Brooks, R. D.; Kulagowski, J. J.; Langer, V.; Farrugia, L. J.; Kočovský, P. *J. Org. Chem*. **2001**, *66*, 1359-1365.

found: 468.2566.

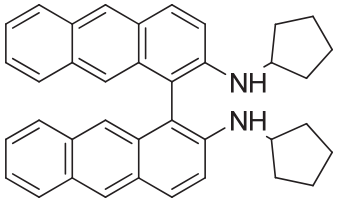
***N,N'*-Dibenzyl-1,1'-bianthracen-2,2'-diamine (2c)**



The title compound was prepared according to General Procedure using aryl amine (52 mg, 0.18 mmol) to yield 45 mg (90%) of **2c** as a yellow solids after silica gel column chromatography (EtOAc/ hexane = 10%).

Mp. 150-151 ˚C (benzene). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.38-4.52 (m, 6H), 7.14-7.20 (m, 10H), 7.22-7.30 (m, 4H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H), 8.39 (s, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 47.5 (t), 109.5 (s), 116.0 (d), 121.0 (d), 123.7 (d), 125.1 (d), 126.7 (d), 126.8 (d), 126.9 (d), 127.8 (s), 127.9 (d), 128.0 (d), 128.5 (d), 129.5 (s), 130.2 (d), 132.0 (s), 132.7 (s), 139.9 (s), 143.6 (s). IR (KBr): 3408, 1616, 1483 cm^{-1}. MS (FAB) *m/z* 564 (M^+). HRMS(FAB) *m/z* calcd for $C_{42}H_{32}N_2$ (M^+): 564.2565. found: 564.2560.

***N,N'*-Dicyclopentyl-1,1'-bianthracen-2,2'-diamine (2d)**

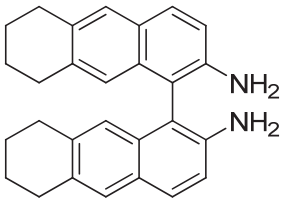


The title compound was prepared according to General Procedure using aryl amine (50 mg, 0.19 mmol) to yield 43 mg (87%) of **2d** as a yellow plate after silica gel column chromatography (AcOEt/ hexane = 3%).

Mp. 148 ˚C (dec.) (toluene). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.10-1.45 (m, 12H), 1.80-1.95 (m, 4H), 3.71 (d, *J* = 6.8 Hz, 2H), 4.02 (dt, *J* = 5.6, 6.8 Hz, 2H), 7.16-7.27 (m, 4H), 7.46 (d, *J* = 9.2 Hz, 2H), 7.48 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 8.11 (d, *J* = 9.2 Hz, 2H), 8.39 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.5 (t), 23.6 (t), 33.7 (t), 33.8 (t), 55.0 (d), 109.8 (s), 117.0 (d), 120.9 (d), 123.5 (d), 124.9 (d), 126.6 (d), 127.7 (s), 127.9 (d), 128.0 (d), 129.3 (s), 129.9 (d), 132.2 (s), 132.6 (s), 143.9 (s). IR (KBr): 3397, 2955, 1616, 1483, 1341 cm^{-1}. MS

(FAB) *m/z* 520 (M^+). HRMS(FAB) *m/z* calcd for $C_{38}H_{36}N_2$ (M^+): 564.2878. found: 520.2885.

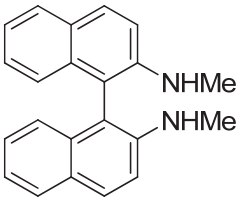
5,5',6,6',7,7',8,8'-Octahydro-1,1'-bianthracen-2,2'-diamine (2e)



The title compound was prepared according to General Procedure using aryl amine (50 mg, 0.25 mmol) to yield 44 mg (89%) of **2e** as brown solids after silica gel column chromatography (AcOEt/ hexane = 20%).

Mp. 120 ˚C (dec.). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.69-1.82 (m, 8H), 2.61-2.71 (m, 4H), 2.90 (t, *J* = 6.8 Hz, 4H), 3.54 (brs, 4H), 6.82 (s, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.50 (s, 2H), 7.67 (d, *J* = 8.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.3 (t), 23.4 (t), 29.4 (t), 29.8 (t), 112.2 (s), 117.7 (d), 122.8 (d), 127.0 (d), 127.2 (s), 128.3 (d), 132.1 (s), 132.4 (s), 137.0 (s), 141.8 (s). IR (KBr): 3456, 3373, 2928, 1626, 1613, 1501 cm^{-1}. MS (EI) *m/z* 392 (M^+, 100%). HRMS (EI) *m/z* calcd for $C_{28}H_{28}N_2$ (M^+): 392.2252. found: 392.2247.

***N,N'*-Dimethyl-1,1'-binaphthalen-4,4'-diamine (2f)[8]**

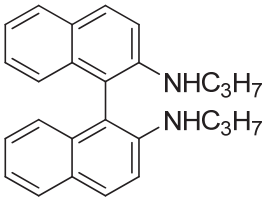


The title compound was prepared according to General Procedure using aryl amine (105 mg, 0.67 mmol) to yield 78 mg (75%) of **2f** as a colorless prism after silica gel column chromatography (Et_2O/ hexane = 10 to 50%).

Mp. 130-132 ˚C (Et_2O).^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.82 (s, 6H), 3.67 (br, 2H), 6.96 (d, *J* = 7.6 Hz, 2H), 7.12-7.21 (m, 4H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H). MS (EI) *m/z* 313 (M^++H), 312 (M^+), 170 (100%).

[8] Shi, M.; Wang, C.-J. *Tetrahedron: Asymmetry* **2002**, *13*, 2161-2166.

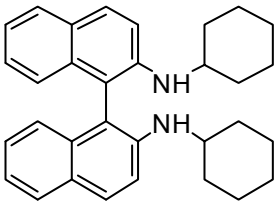
***N,N'*-Dipropyl-1,1'-binaphthalen-4,4'-diamine (2g)**



The title compound was prepared according to General Procedure using aryl amine (139 mg, 0.75 mmol) to yield 114 mg (83%) of **2g** as pale brown oil after silica gel column chromatography (hexane).

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.74 (t, *J* = 7.6 Hz, 6H), 1.36-1.46 (m, 4H), 3.12 (t, *J* = 7.2 Hz, 4H), 3.71 (br, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.10-7.20 (m, 4H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 11.2 (q), 22.9 (t), 45.8 (t), 111.9 (s), 114.1 (d), 121.7 (d), 123.8 (d), 126.6 (d), 127.5 (s), 128.0 (d), 129.5 (d), 133.9 (s), 144.7 (s). IR (neat): 3406, 1597, 1483 cm^{-1}. MS (EI) *m/z* 368 (M^+, 100%), 339 (M^+-Et). HRMS (EI) *m/z* calcd for $C_{26}H_{28}N_2$ (M^+): 368.2252. found: 368.2258.

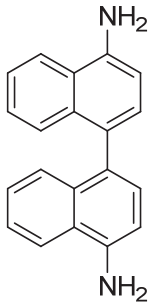
***N,N'*-Dicyclohexyl-1,1'-binaphthalen-4,4'-diamine (2h)**



The title compound was prepared according to General Procedure using aryl amine (108 mg, 0.48 mmol) to yield 86 mg (77%) of **2h** as pale brown powder after silica gel column chromatography (AcOEt/ hexane = 3%).

Mp 117-118 ˚C. (CH_2Cl_2-hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.72-1.06 (m, 6H), 1.16-1.33 (m, 4H), 1.48-1.62 (m, 6H), 1.78-1.94 (m, 4H), 3.30-3.70 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.06-7.19 (m, 4H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 24.9 (t), 25.0 (t), 25.6 (t), 33.6 (t), 33.7 (t), 51.9 (d), 112.3 (s), 114.9 (d), 121.7 (d), 124.0 (d), 126.4 (d), 127.5 (s), 127.9 (d), 129.3 (d), 134.1 (s), 143.9 (s). IR (KBr): 3399, 2922, 1618, 1597, 1512 cm^{-1}. MS (EI) *m/z* 448 (M^+, 100%). HRMS (EI) *m/z* calcd for $C_{32}H_{36}N_2$ (M^+): 448.2878. found: 448.2896.

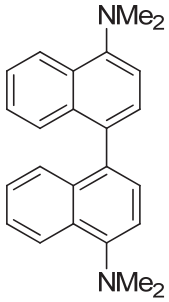
1,1'-Binaphthalen-4,4'-diamine (2i)[9]



The title compound was prepared according to General Procedure using aryl amine (50 mg, 0.28 mmol) to yield 33 mg (66%) of **2i** as pale brown solids after silica gel column chromatography ($CHCl_3$).

Mp. 162-163 ˚C (EtOAc-Hex). ^{1}H-NMR (600 MHz, DMSO-*d6*) δ: 5.75 (brs, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.13-7.21 (m, 4H), 7.30-7.34 (m, 2H), 8.12 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR (150 MHz, DMSO-*d6*) δ: 107.2 (d), 122.5 (d), 122.7 (s), 123.4 (d), 125.2 (d), 126.2 (s), 126.3 (d), 128.8 (d), 133.6 (s), 144.0 (s). MS (EI) *m/z* 284 (M^+, 100%), 267 (M^+-NH_3).

***N,N,N',N'*-Tetramethyl-1,1'-binaphthalen-4,4'-diamine (2j)** [9]



The title compound was prepared according to General Procedure using aryl amine (86 mg, 0.50 mmol) to yield 72 mg (84%) of **2j** as colorless solids after silica gel column chromatography (AcOEt/ hexane = 10%).

Mp. 117-120 ˚C (EtOAc-Hex). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.98 (s, 12H), 6.16 (d, *J* = 7.2 Hz, 2H), 7.23-7.28 (m, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.43-7.48 (m, 2H), 8.33 (d, *J* = 8.0 Hz, 2H). MS (EI) *m/z* 341 (M^++H, 100%), 340 (M^+), 325 (M^+-CH_3).

***N,N'*-Dibenzyl-1,1'-Binaphthalen-4,4'-diamine (2k)** [9]

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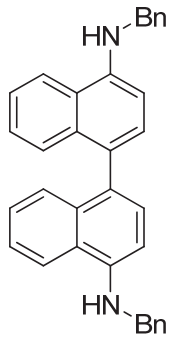
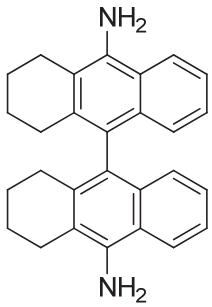
[9] Li, Z.-L.; Huang, J.-H.; Yang, L.-M. *Org. Lett.* **2011**, *13*, 4950-4953.



The title compound was prepared according to General Procedure using aryl amine (238 mg, 1.0 mmol) to yield 184 mg (79%) of **2k** as pale brown amorphous after silica gel column chromatography (Et_2O/ hexane = 20%).

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.55 (s, 4H), 4.76 (br, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.30-7.35 (m, 4H), 7.37-7.42 (m, 6H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 2H).

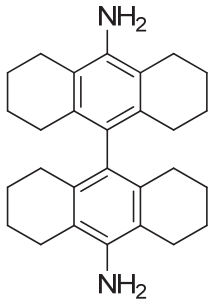
1,1',2,2',3,3',4,4'-Octahydro-9,9'-bianthracen-10,10'-diamine (2l)



The title compound was prepared according to General Procedure using aryl amine (51 mg, 0.25 mmol) to yield 54 mg (quant) of **2l** as colorless solids after silica gel column chromatography (AcOEt/ hexane = 20%).

Mp. 165 ˚C (dec). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.52-1.69 (m, 4H), 1.81-1.95 (m, 4H), 2.16-2.35 (m, 4H), 2.70-2.85 (m, 4H), 4.19 (s, 4H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.0 (t), 23.1 (t), 25.5 (t), 28.6 (t), 117.0 (s), 120.0 (d), 121.8 (s), 123.7 (d), 124.9 (d), 126.2 (s), 126.2 (d), 131.8 (s), 135.3 (s), 137.8 (s). IR (KBr) 3379, 3466 cm^{-1} (NH_2). HRMS (MALDI) *m/z* calcd for $C_{28}H_{27}N_2$ (M-H): 391.2180. found: 391.2174.

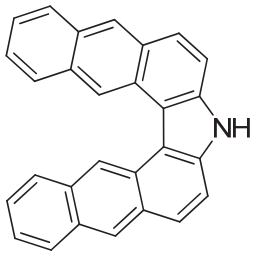
1,1',2,2',3,3',4,4',5,5',6,6',7,7',8,8'-Hexadecahydro-9,9'-bianthracen-10,10'-diamine (2m)



The title compound was prepared according to General Procedure using aryl amine (52 mg, 0.25 mmol) to yield 53 mg (quant) of **2m** as pink needles after silica gel column chromatography (AcOEt/ hexane = 20%).

Mp. 90 ˚C (dec.). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.56-1.62 (m, 8H), 1.76-1.81 (m, 8H), 2.05 (t, *J* = 6.4 Hz, 8H), 2.51 (d, *J* = 6.4 Hz, 8H), 3.54 (brs, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 23.1 (t), 23.1(t), 24.9 (t), 27.9 (t), 118.6 (s), 130.1 (s), 132.5 (s), 140.1 (d). IR (KBr): 3362, 2934, 1614 cm^{-1}. MS (EI) *m/z* 400 (M^+, 100%). HRMS (EI) *m/z* calcd for $C_{28}H_{36}N_2$ (M^+): 400.2878. found: 400.2879.

8*H*-Dinaphtho[*2,3-c:2',3'-g*]carbazole (3) [7]



To a solution of 2-aminoanthracene (50 mg, 0.26 mmol) in HFIP (2.6 ml) was added 5% Rh/ C (27 mg, 0.013 mmol) and stirred at rt under air for 6 h. 3M NaOH was added and the resulting mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, evaporated to afford the crude, which was purified by silica gel column chromagtography ($CHCl_3$/ hexane = 20%) to yield 36 mg (76%) of **3** as brown solid.

Mp. 222-226 ˚C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.52-7.61 (m, 4H), 7.64 (d, *J* = 9.6 Hz, 2H), 7.92-8.00 (m, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 8.60 (s, 2H), 8.94 (s, 1H), 9.97 (s, 2H). MS (FAB) *m/z* 367 (M^+). HRMS (FAB) *m/z* calcd for $C_{28}H_{17}N$ (M^+): 367.1361. found: 367.1359.

ESR experiment

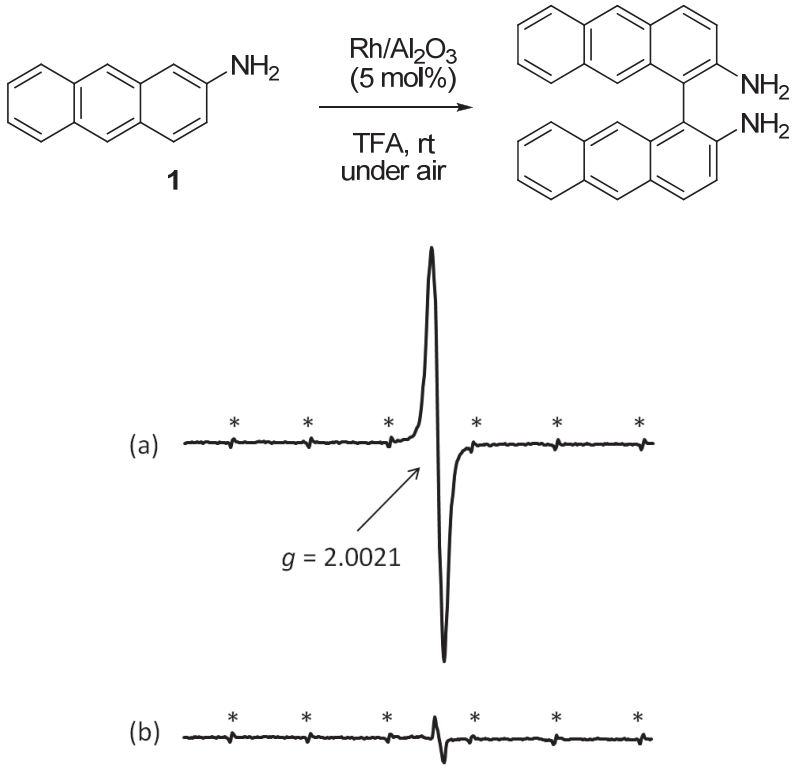
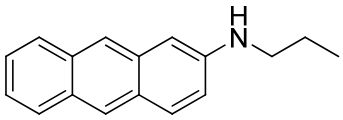
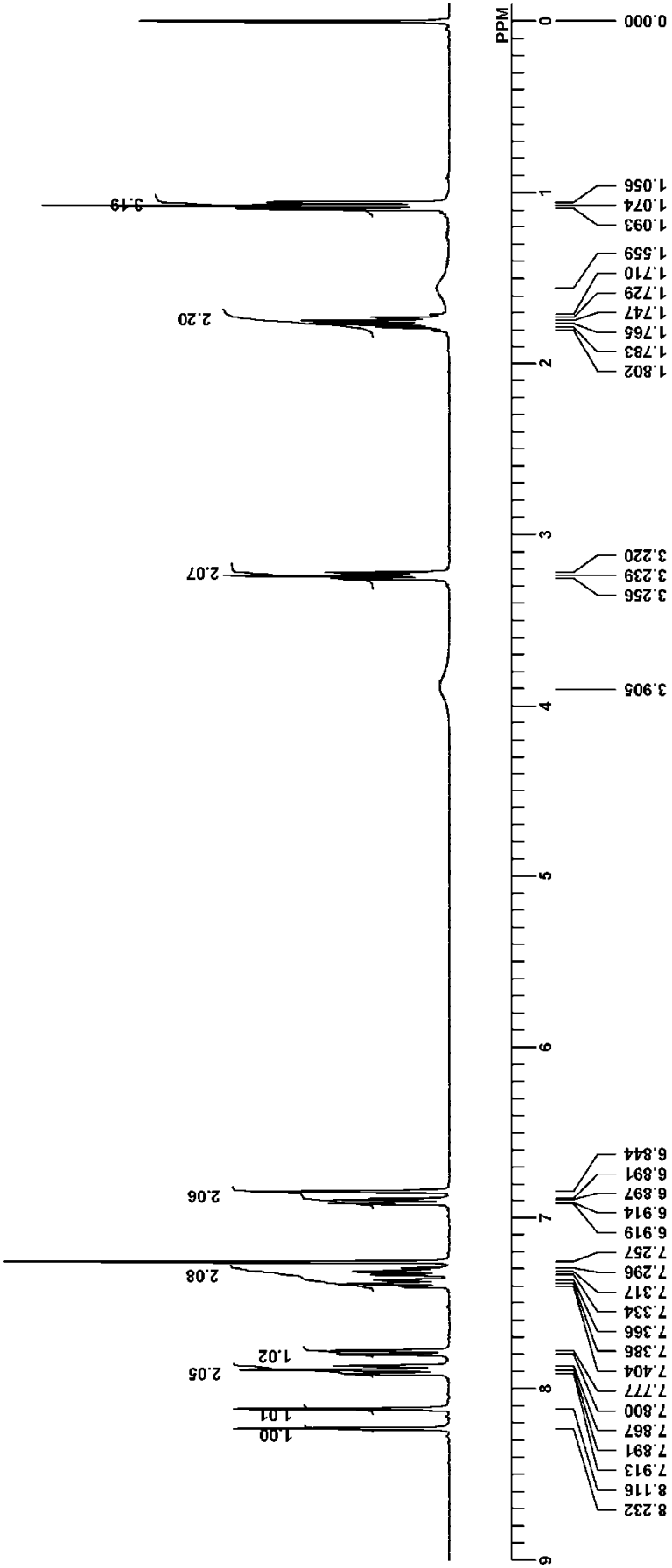


Figure S-1. (a) Rh/Al_2O_3 was treated with **1** in TFA under air and the spectrum was measured. (b) Rh/Al_2O_3 was suspended in TFA and the spectrum was measured. Astarisks were assigned to the signals of the Mn marker.




PPM
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1.093
1.559
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1.729
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1.783
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3.239
3.256
3.905
6.844
6.891
6.897
6.914
6.919
7.257
7.296
7.317
7.334
7.366
7.386
7.404
7.777
7.800
7.867
7.891
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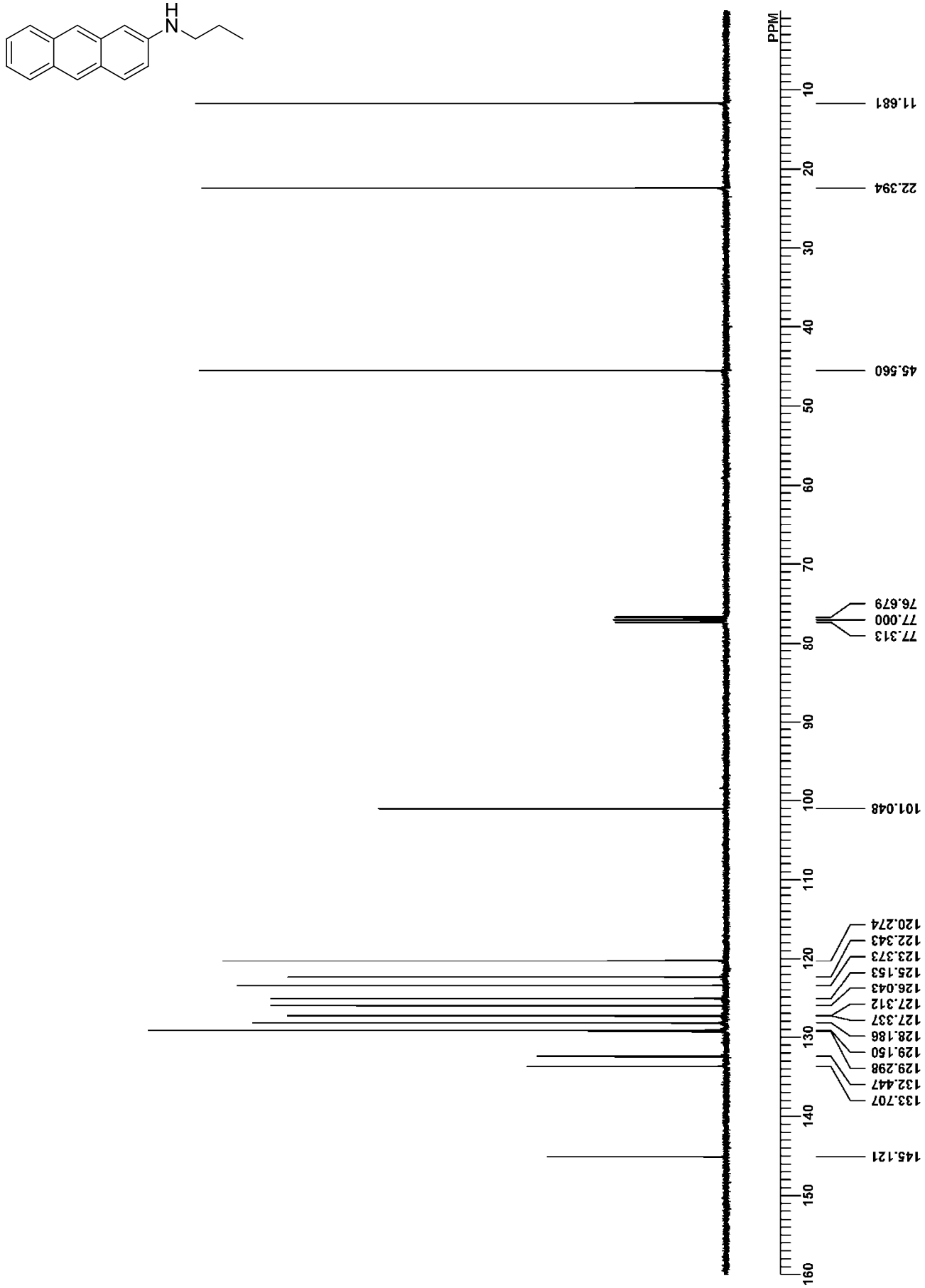
1.02
2.08
2.06
2.07
2.20
3.19


H
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45.560
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77.000
77.313
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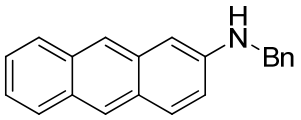
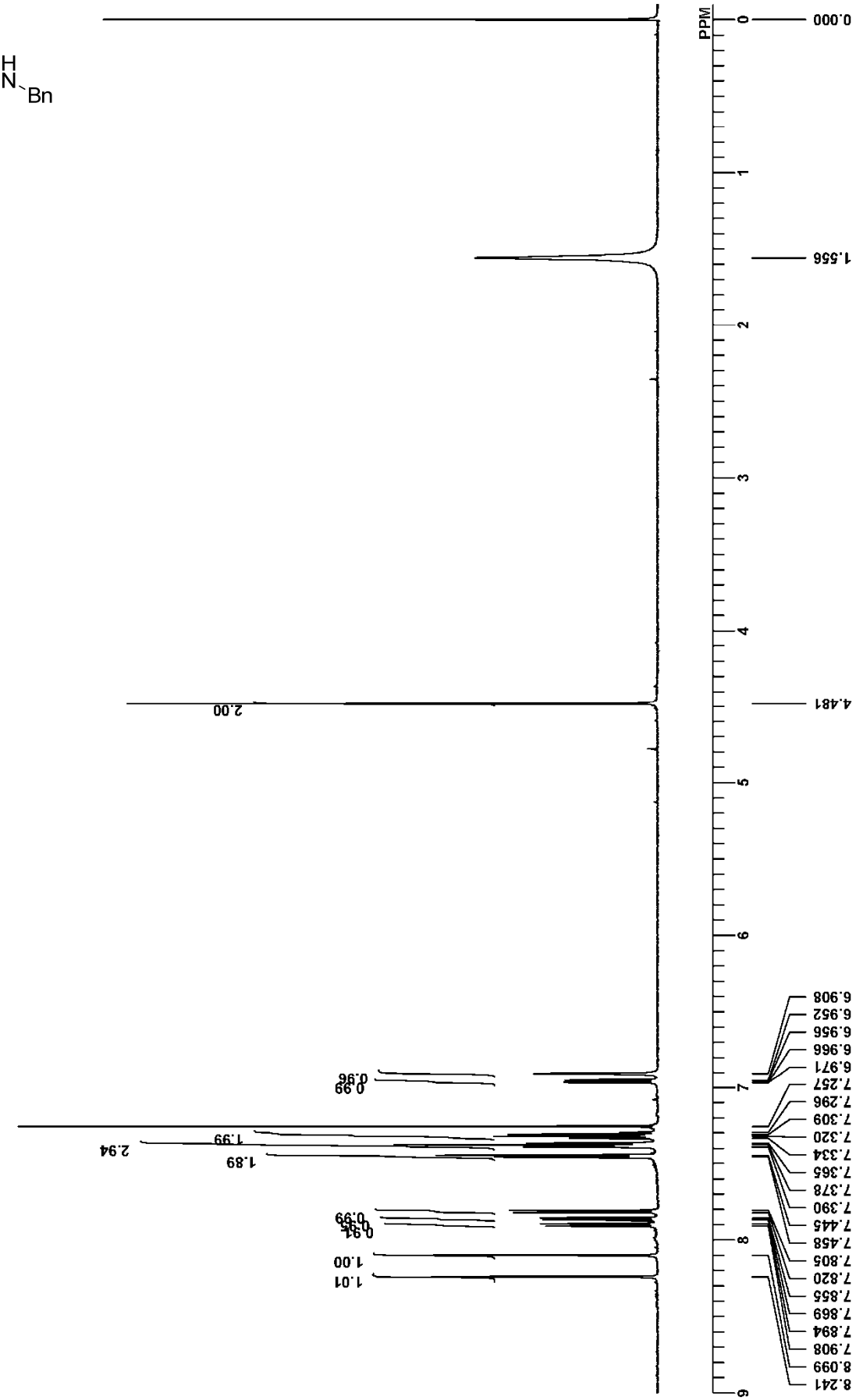

H
N
Bn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0.94
1.00
1.01
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8.099
7.908
7.894
7.869
7.855
7.820
7.805
7.458
7.445
7.390
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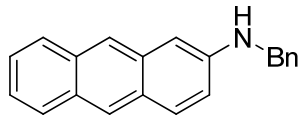
6.952
6.908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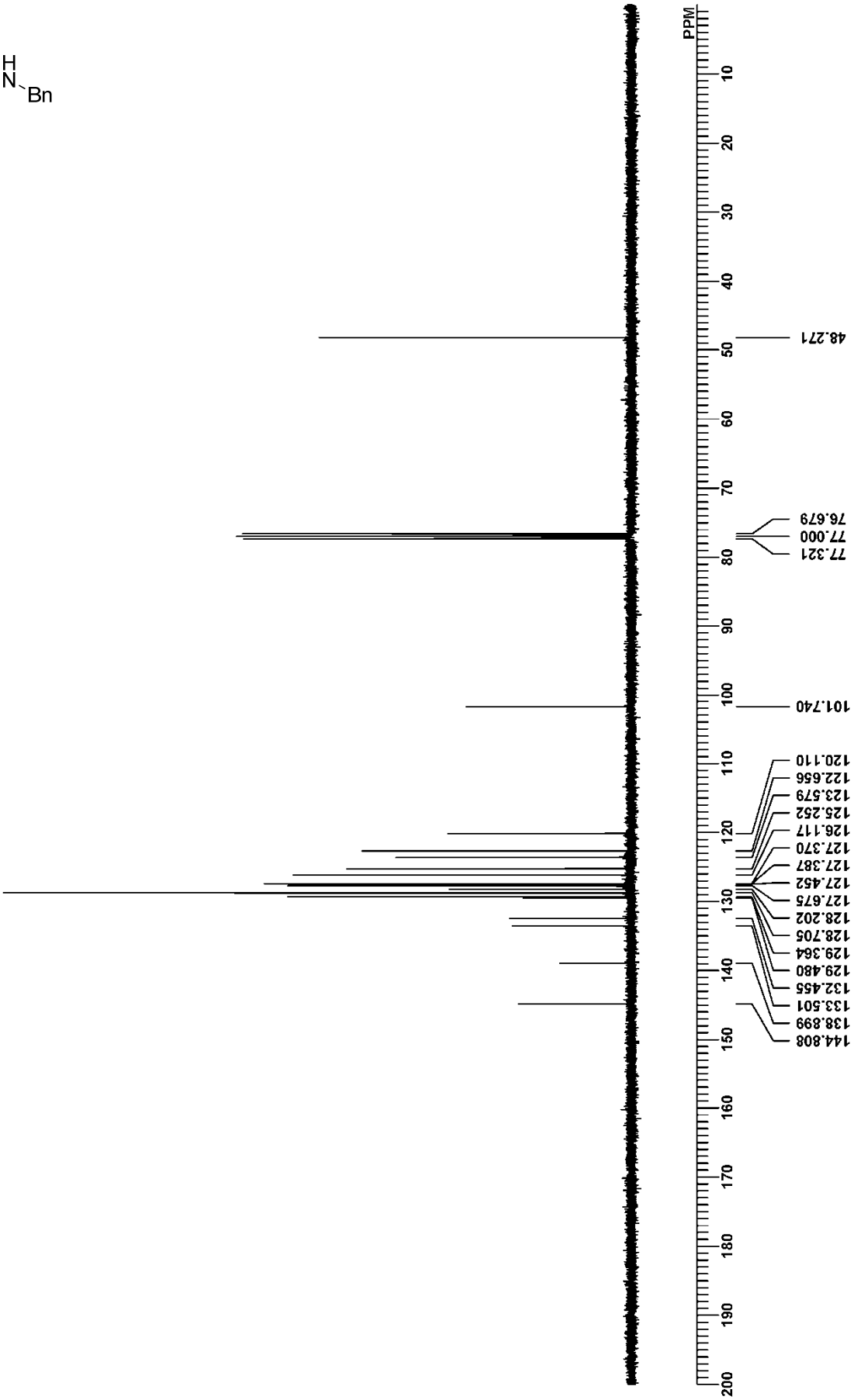
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190
200
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77.000
77.321
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123.579
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126.117
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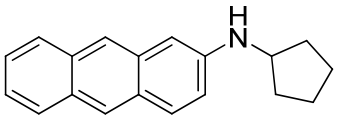
144.808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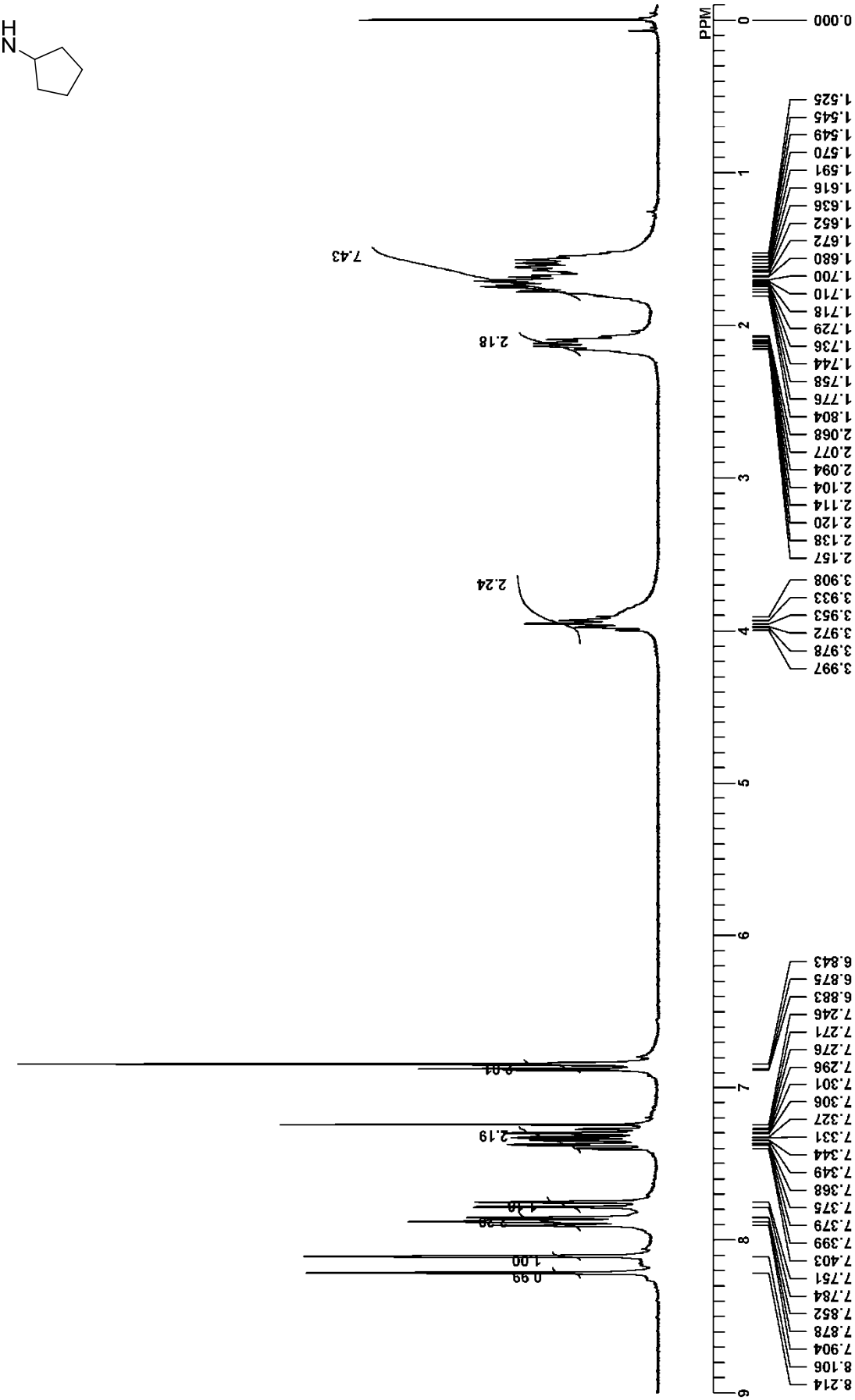
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1.710
1.718
1.729
1.736
1.744
1.758
1.776
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2.077
2.094
2.104
2.114
2.120
2.138
2.157
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3.933
3.953
3.972
3.978
3.997
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6.875
6.883
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7.271
7.276
7.296
7.301
7.306
7.327
7.331
7.344
7.349
7.368
7.375
7.379
7.399
7.403
7.751
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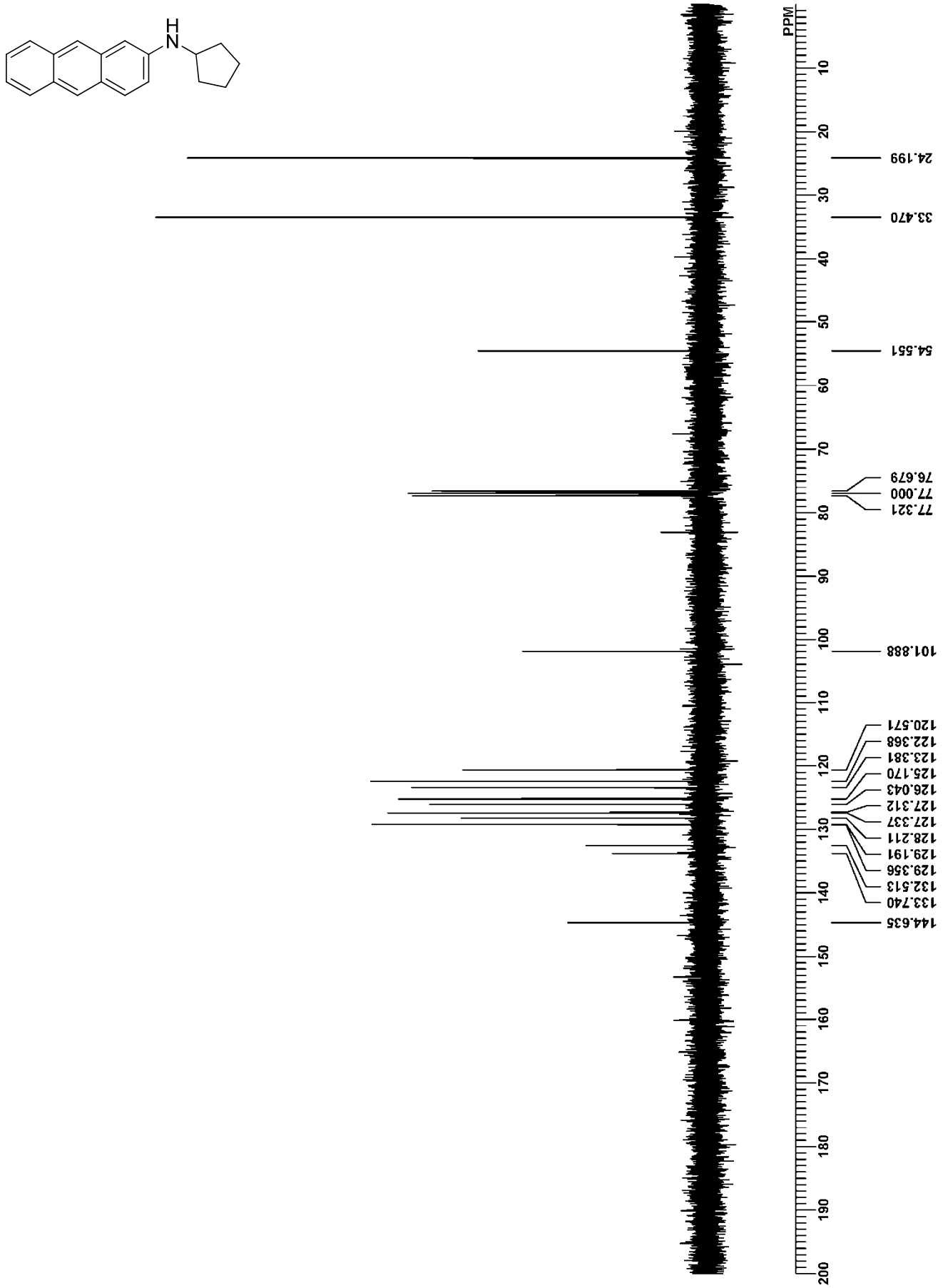
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180
190
200
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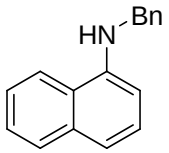
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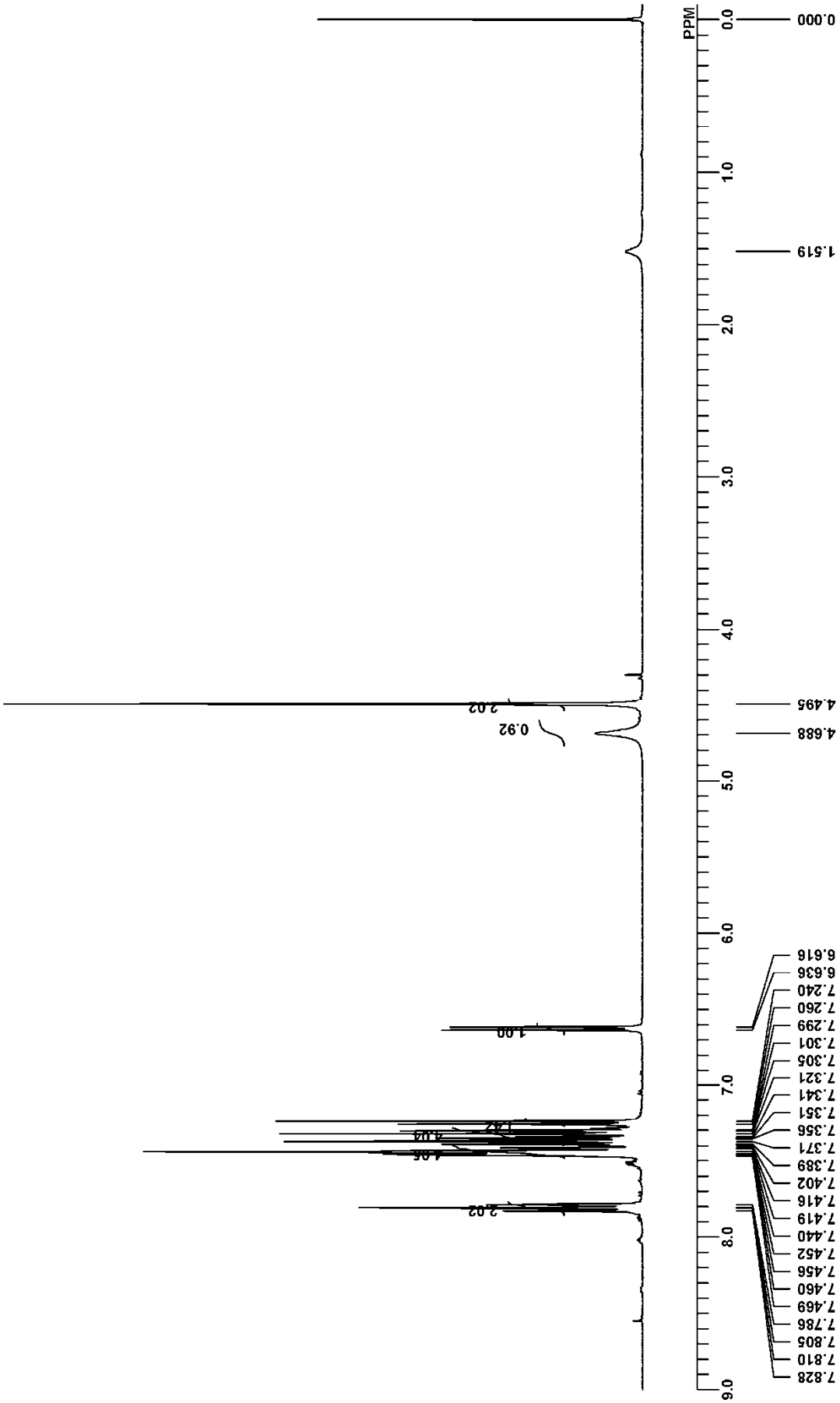
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7.351
7.356
7.371
7.389
7.402
7.416
7.419
7.440
7.452
7.456
7.460
7.469
7.786
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7.828
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4.04
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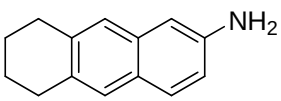
1.00
0.92
2.02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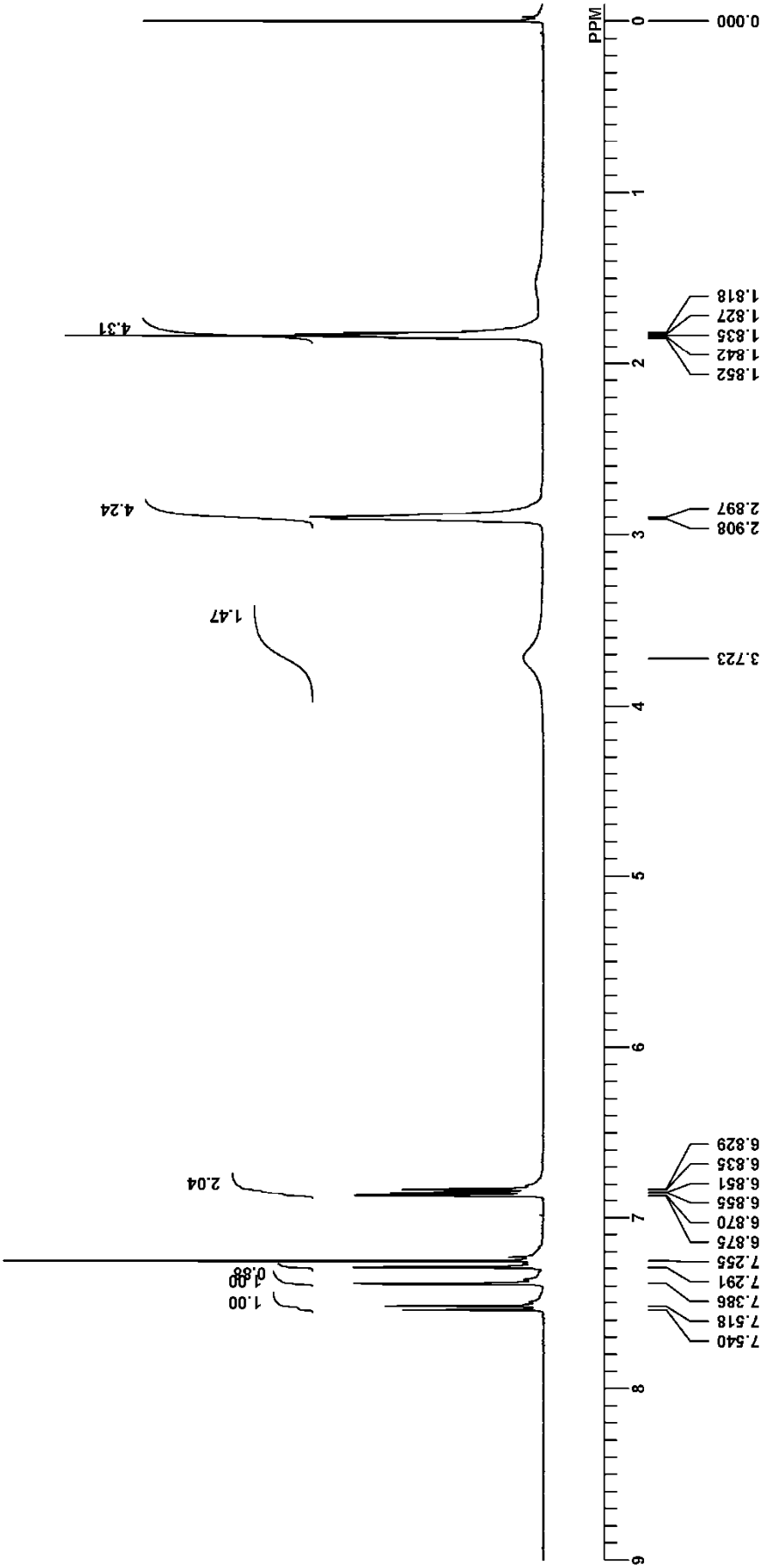
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7.518
7.386
7.291
7.255
6.875
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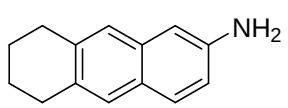
4.31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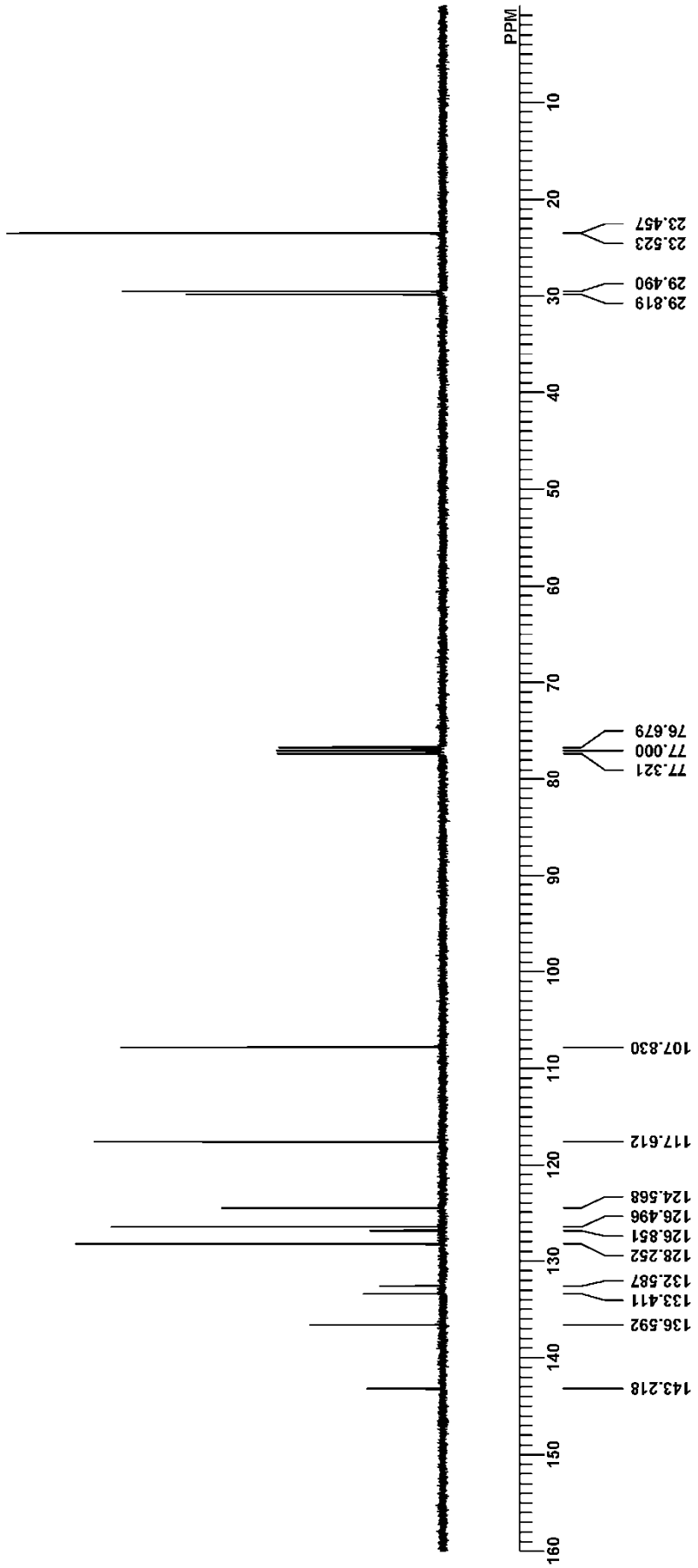
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140
150
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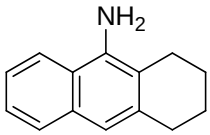
136.592
143.218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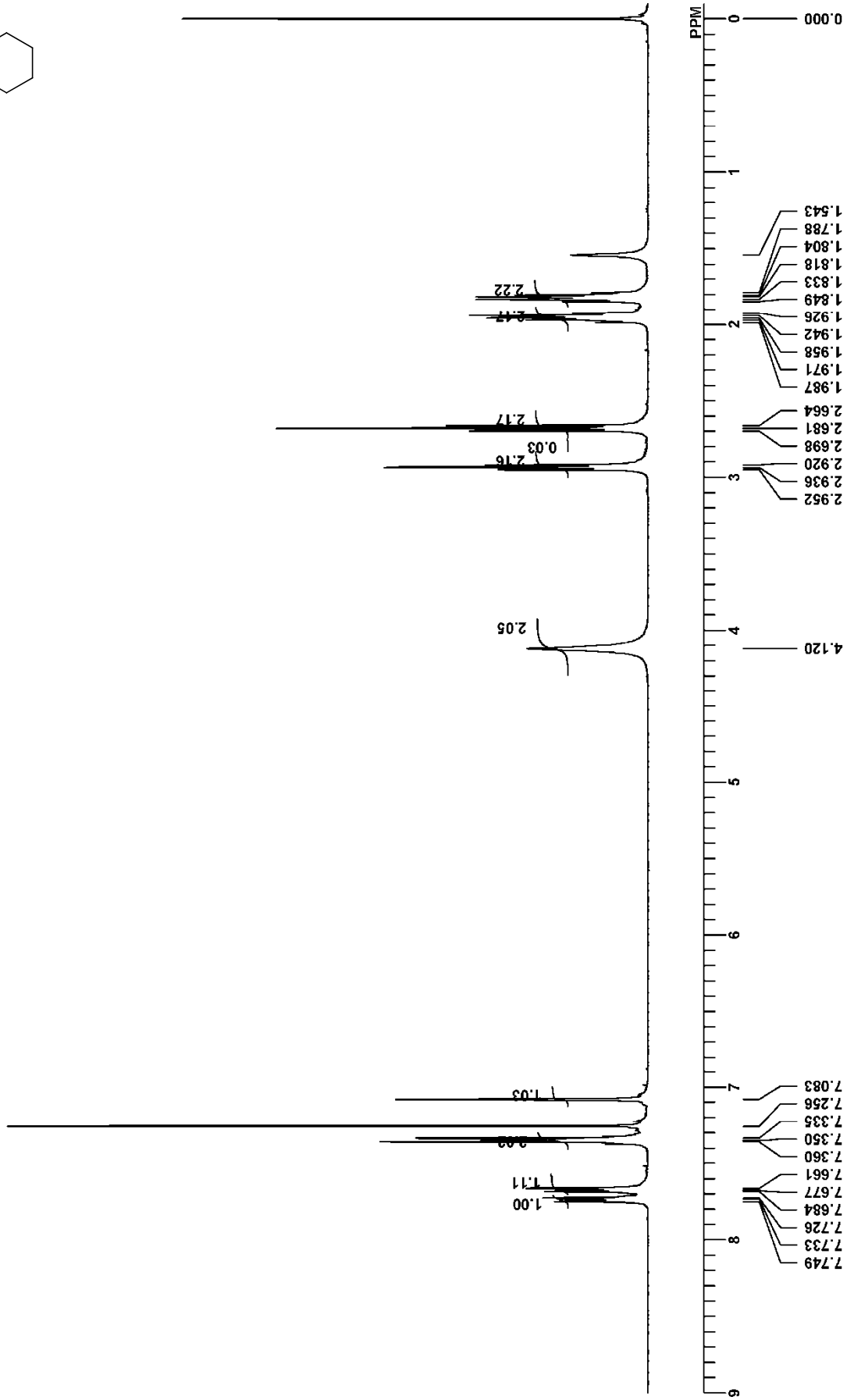
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1.971
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2.681
2.698
2.920
2.936
2.952
4.120
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7.256
7.335
7.350
7.360
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7.726
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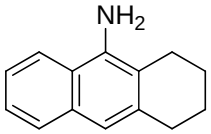
2.17
2.22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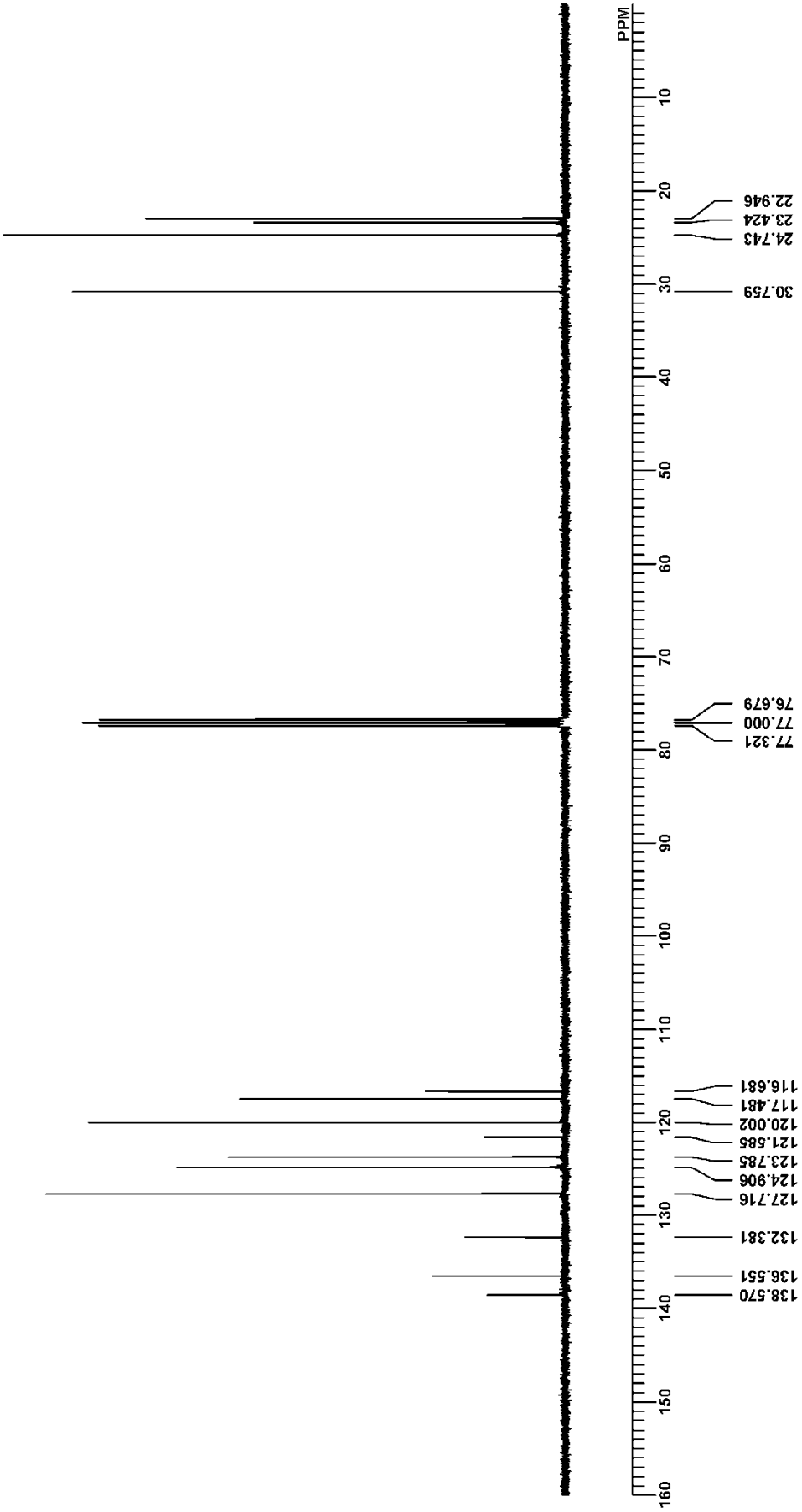
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30.759
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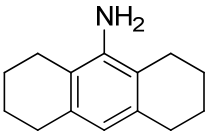
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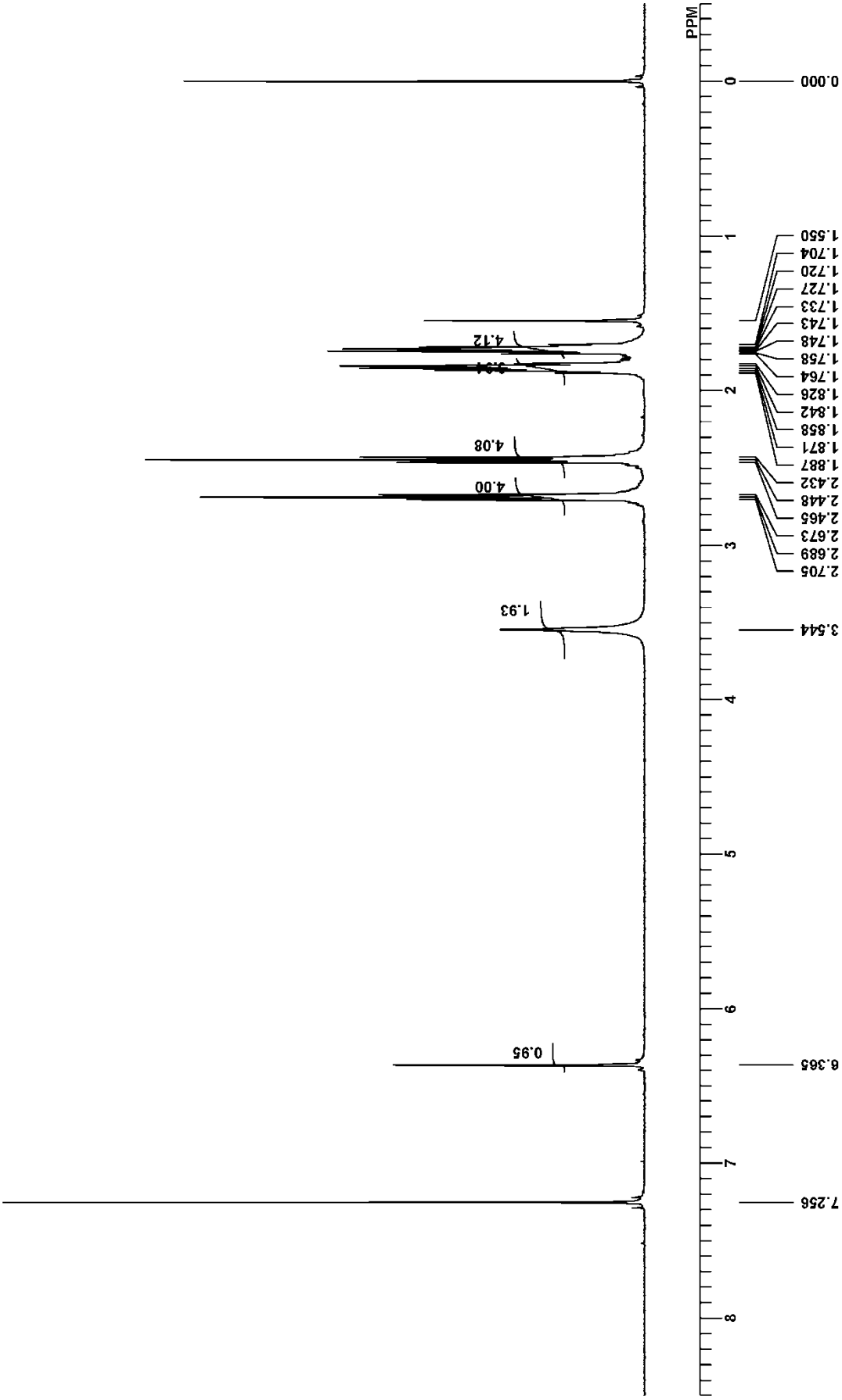
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1.842
1.858
1.871
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2.448
2.465
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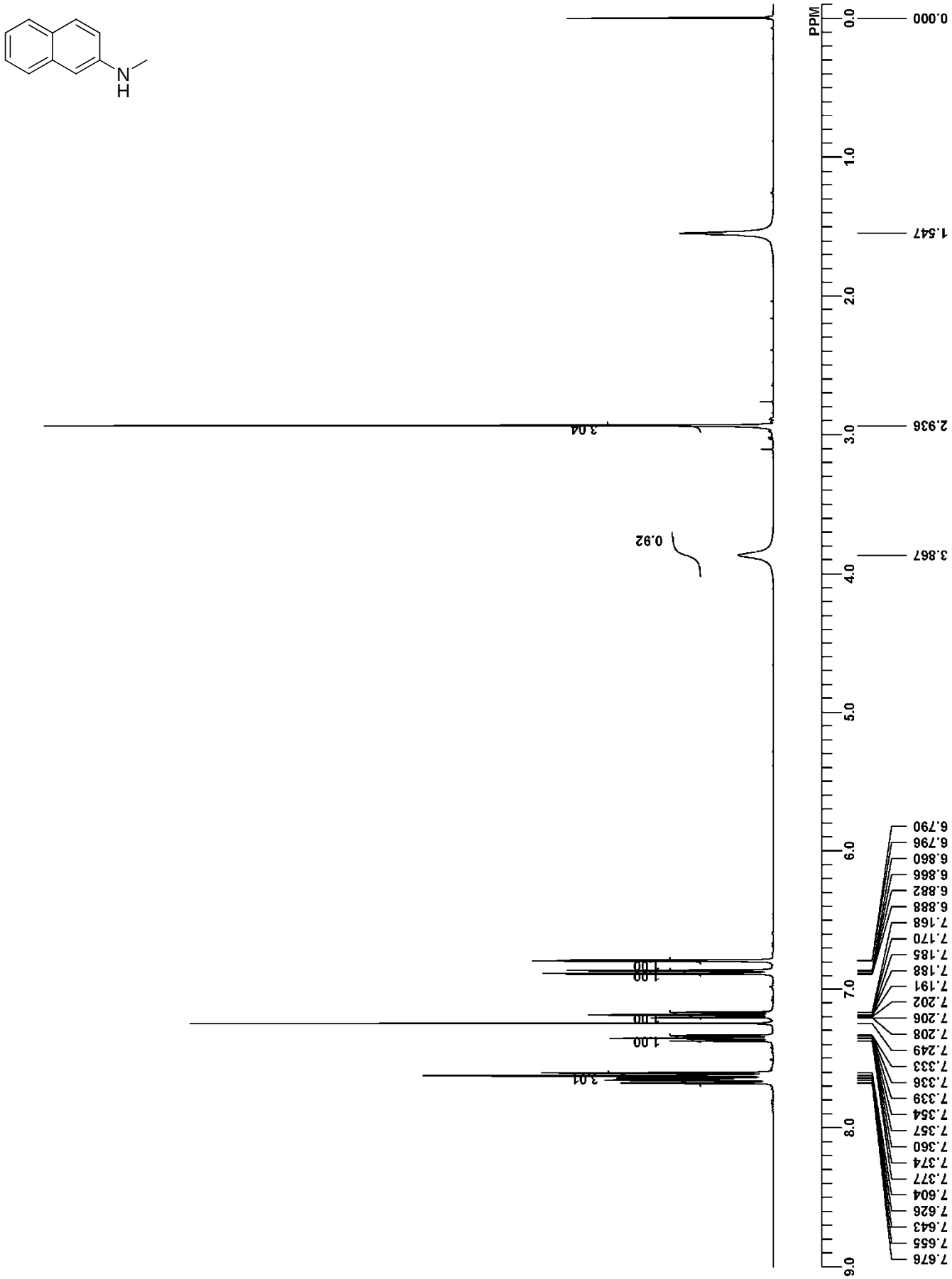
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1.00
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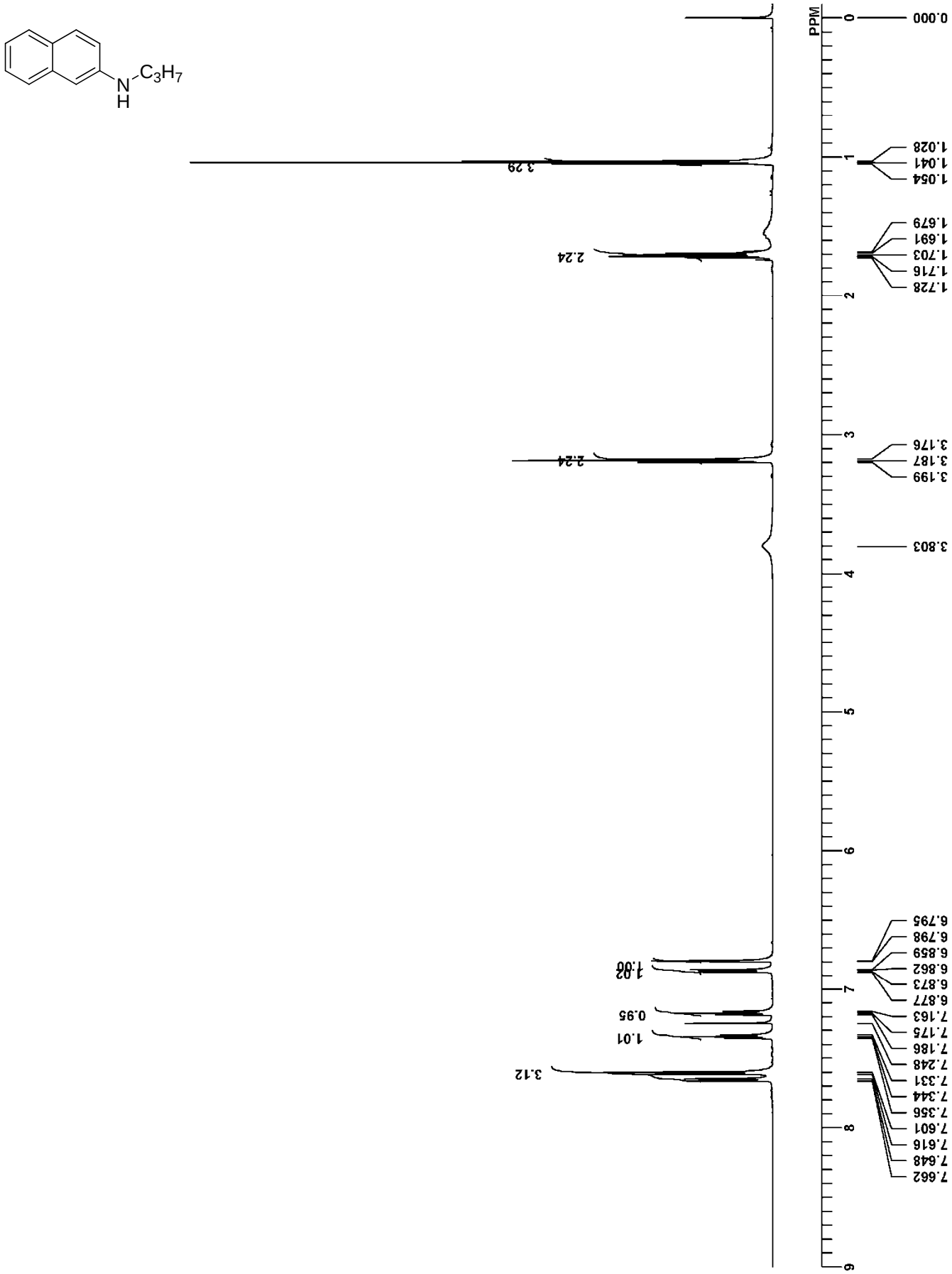
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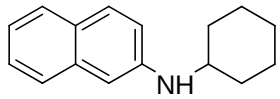
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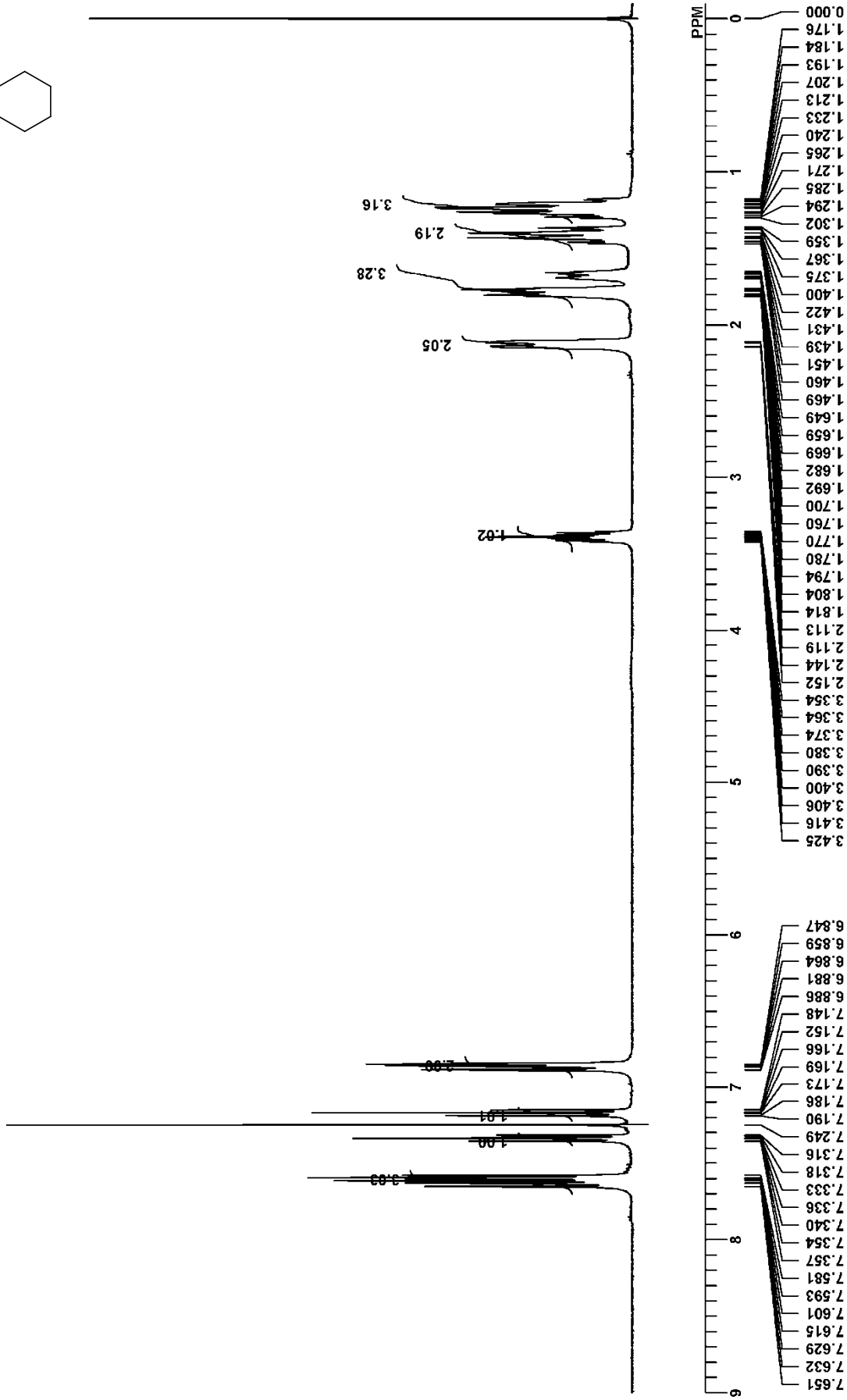
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1.367
1.375
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1.659
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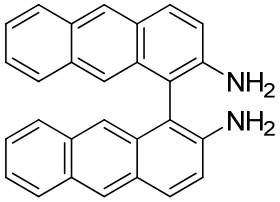
NH2
NH2

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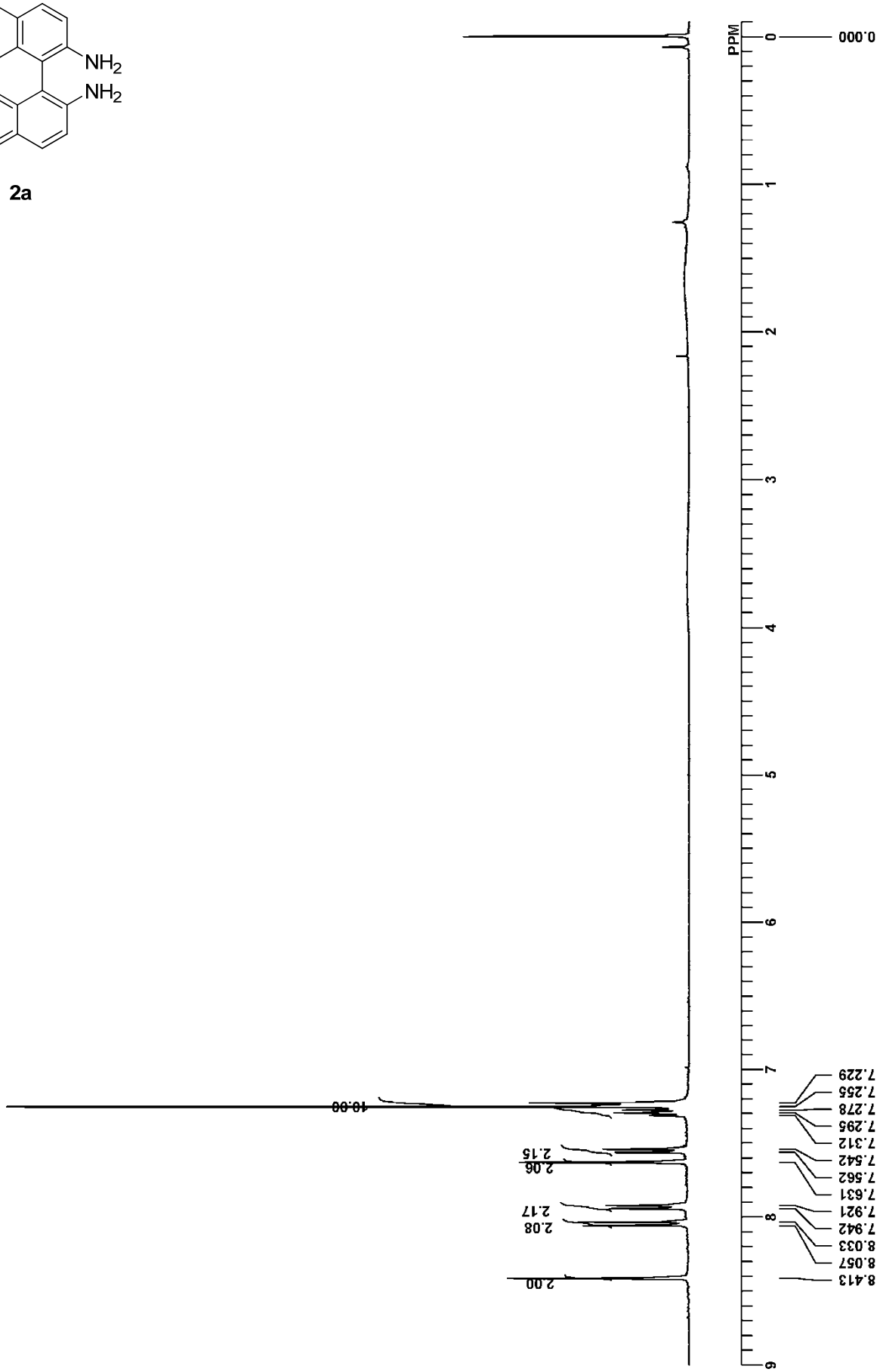
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7.278
7.255
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2.08
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2.15
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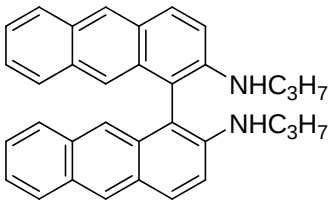
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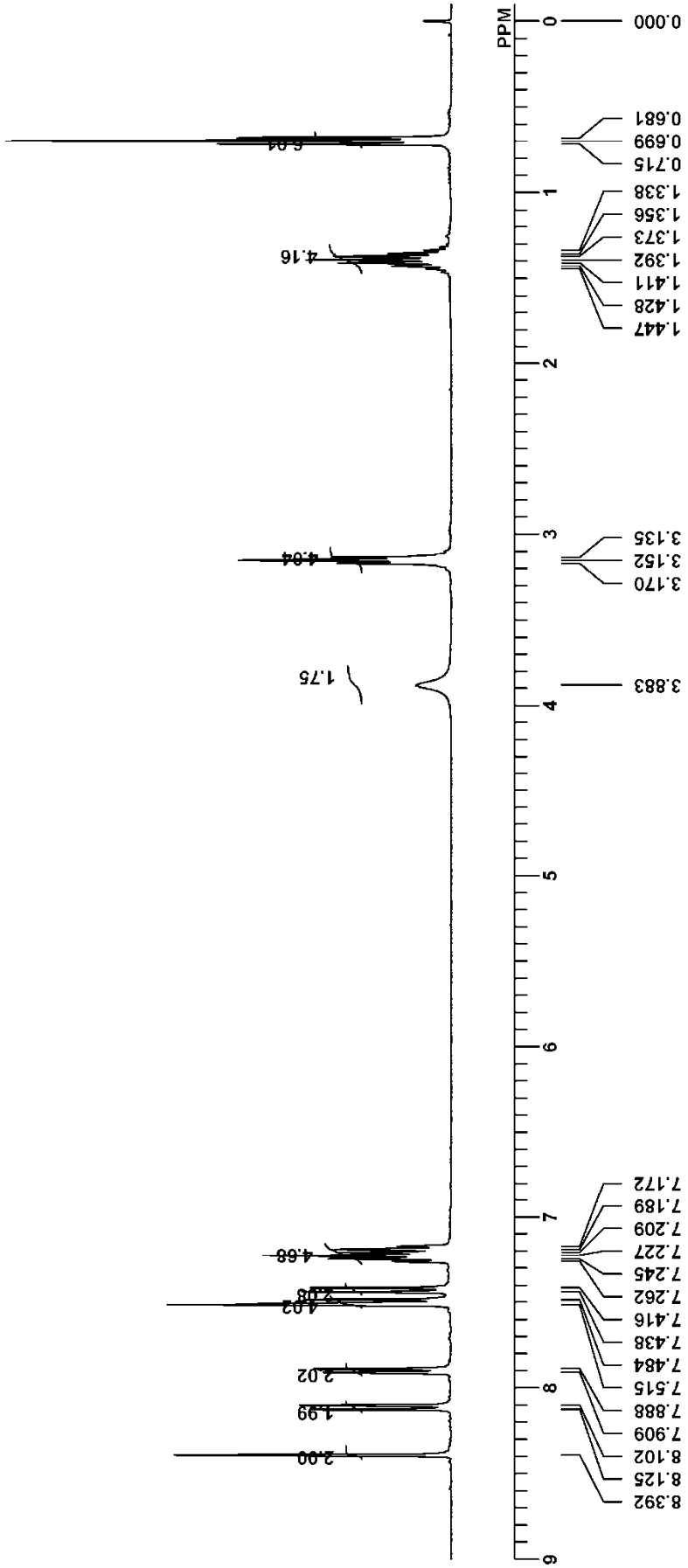
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3.152
3.170
3.883
7.172
7.189
7.209
7.227
7.245
7.262
7.416
7.438
7.484
7.515
7.888
7.909
8.102
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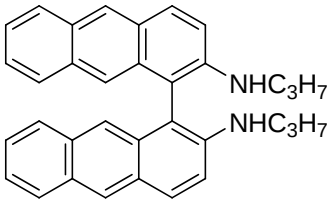
6.04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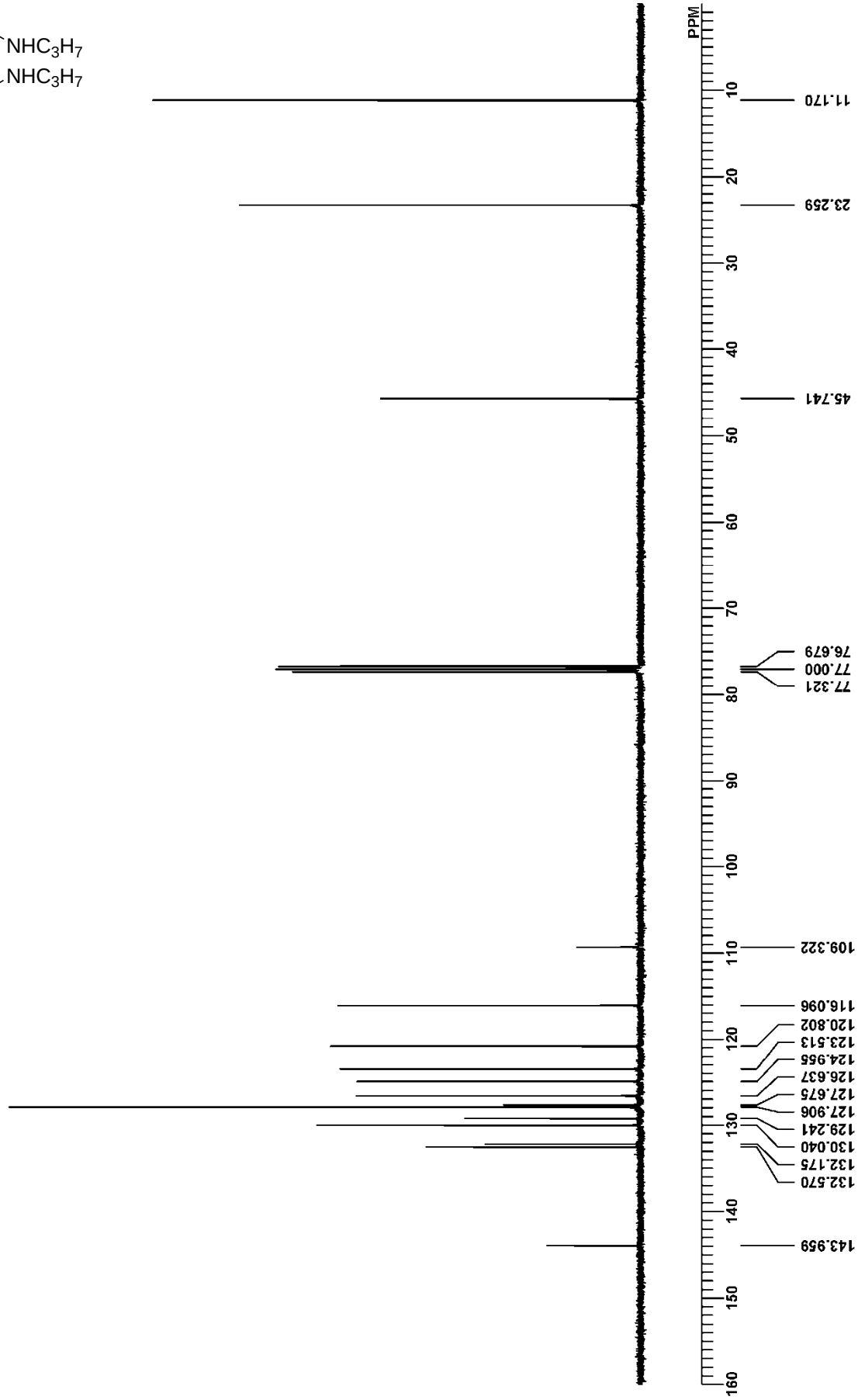
NHC3H7

2b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127.906
129.241
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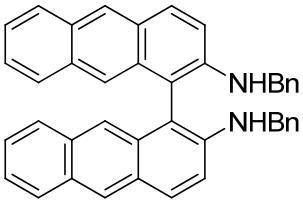
132.570
143.959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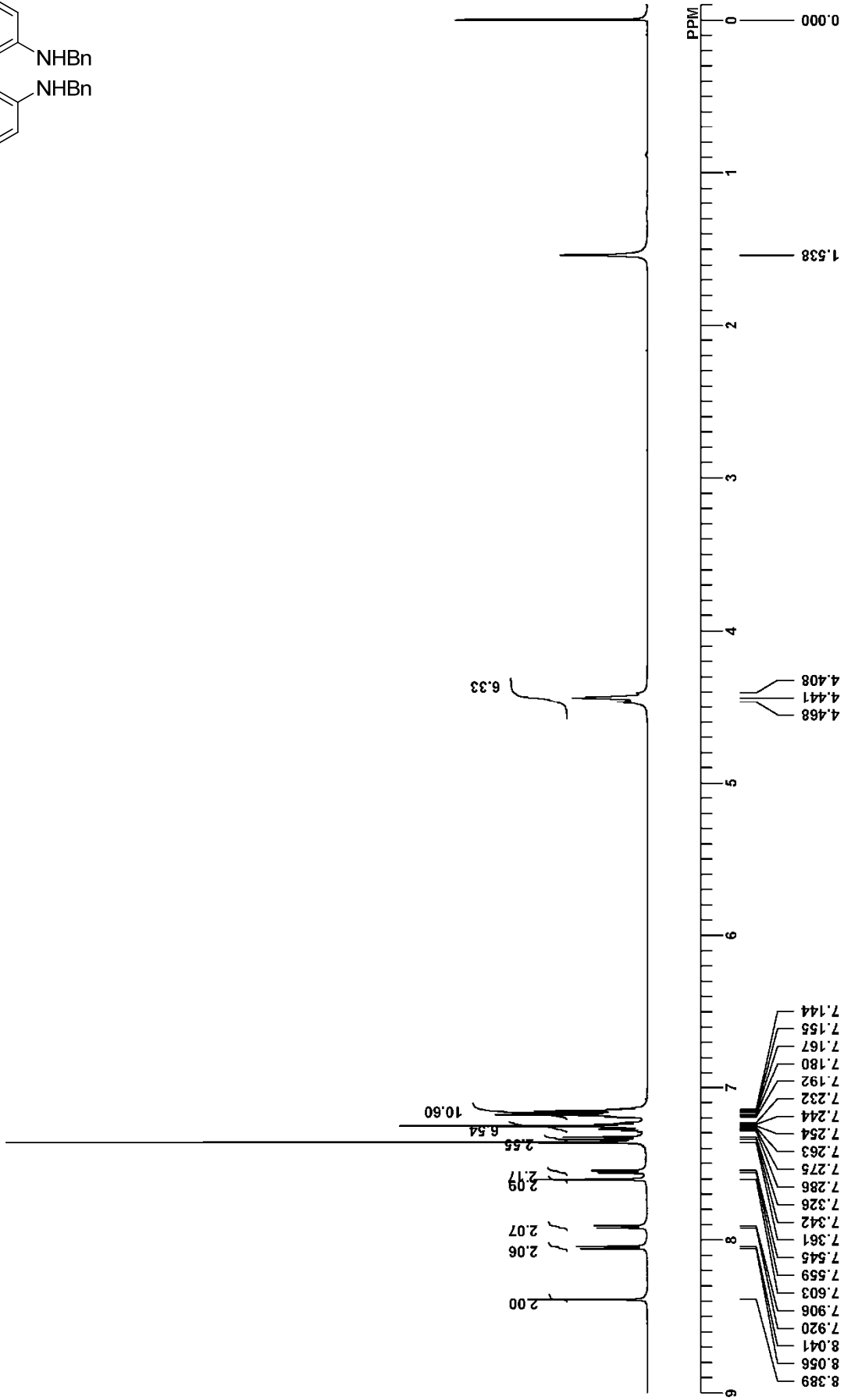
NHBn

2c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4.408
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8.041
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7.603
7.559
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7.286
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7.254
7.244
7.232
7.192
7.180
7.167
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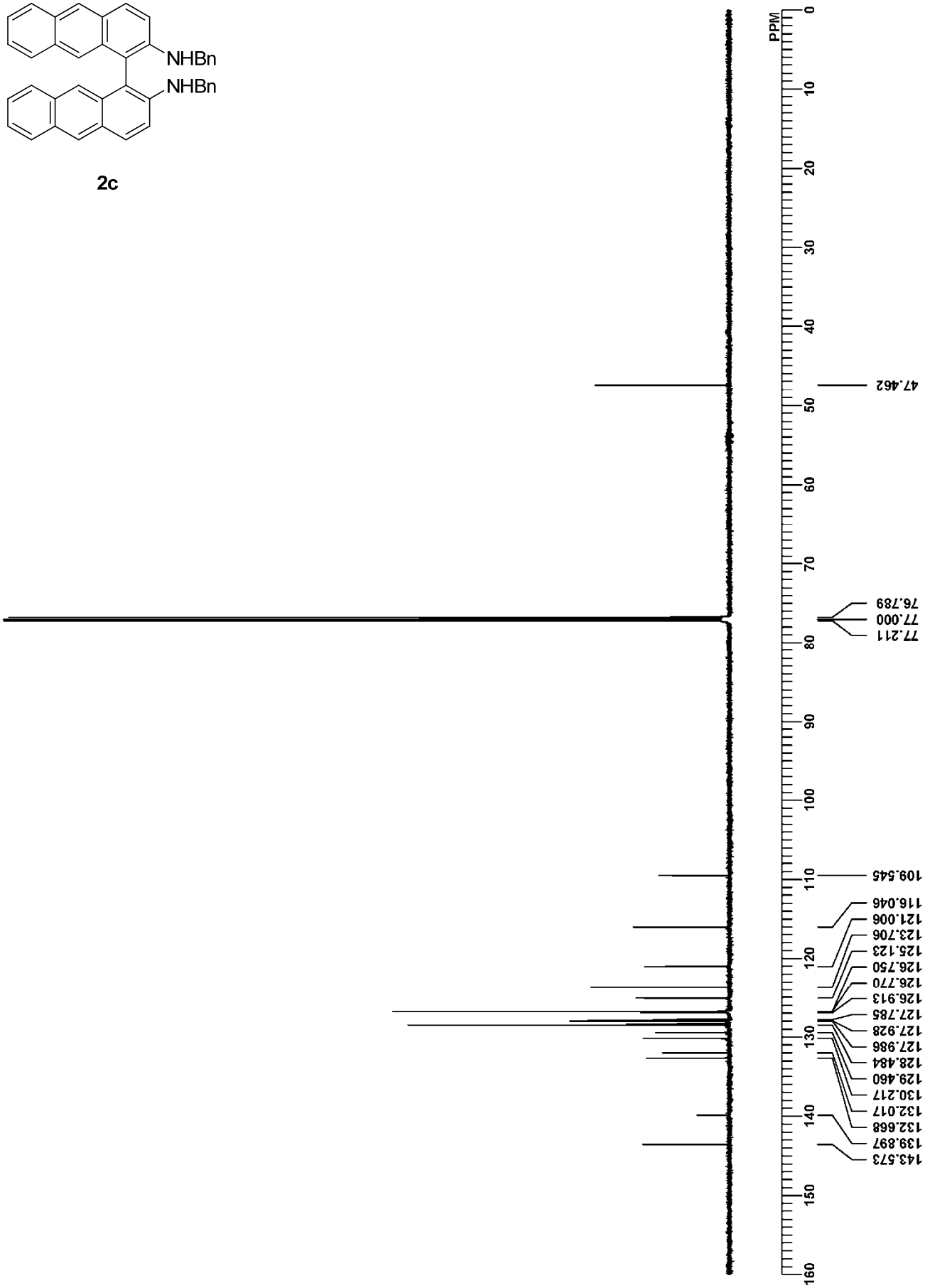
2.09
2.07
2.06
2.00

NHBn
NHBn

2c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77.000
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109.545
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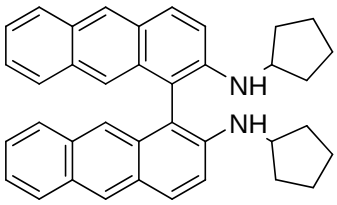
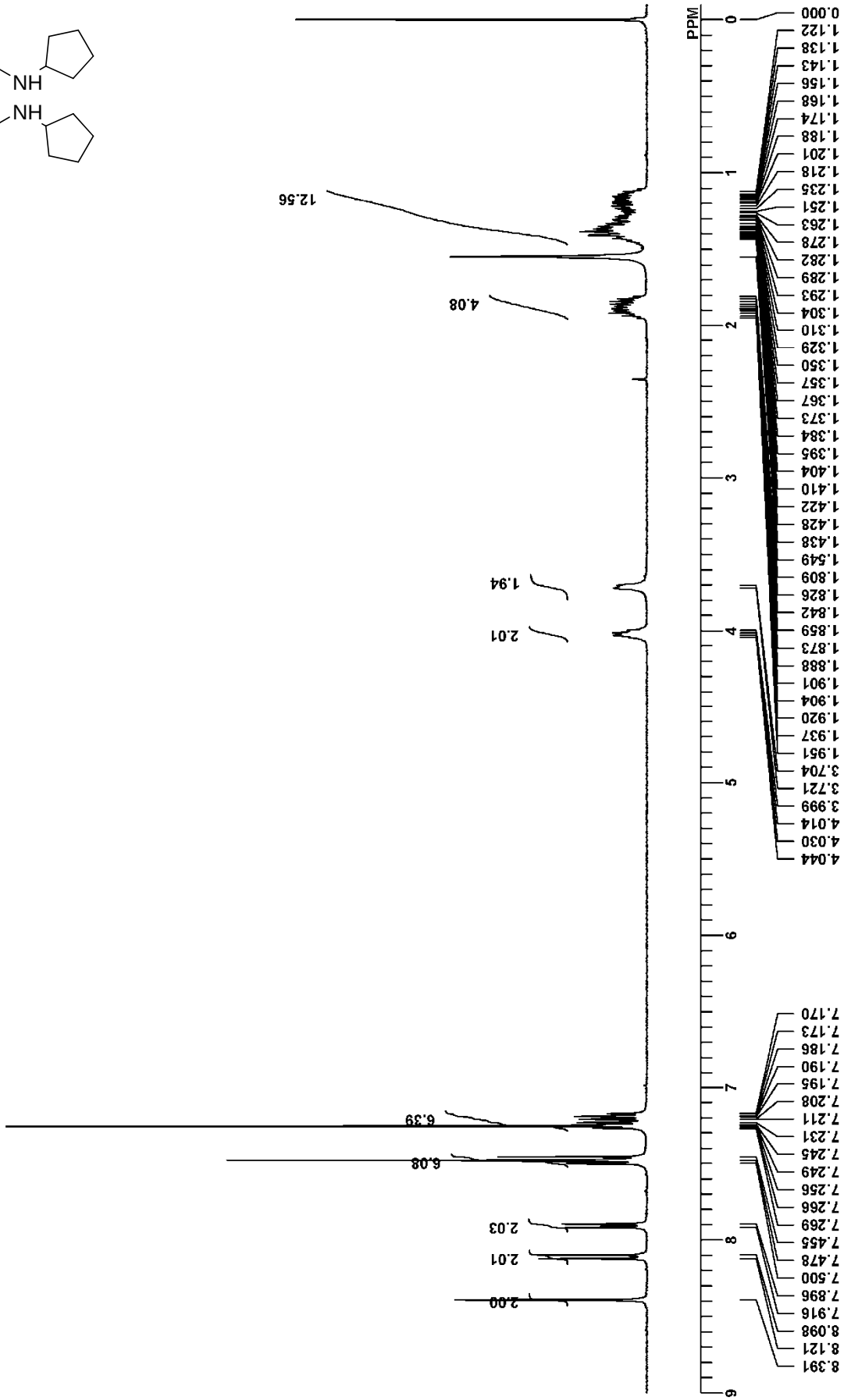

NH
NH

2d


PPM
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1.174
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1.201
1.218
1.235
1.251
1.263
1.278
1.282
1.289
1.293
1.304
1.310
1.329
1.350
1.357
1.367
1.373
1.384
1.395
1.404
1.410
1.422
1.428
1.438
1.549
1.809
1.826
1.842
1.859
1.873
1.888
1.901
1.904
1.920
1.937
1.951
3.704
3.721
3.999
4.014
4.030
4.044
7.170
7.173
7.186
7.190
7.195
7.208
7.211
7.231
7.245
7.249
7.256
7.266
7.269
7.455
7.478
7.500
7.896
7.916
8.098
8.121
8.391
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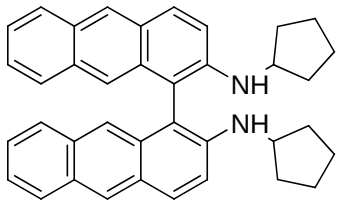
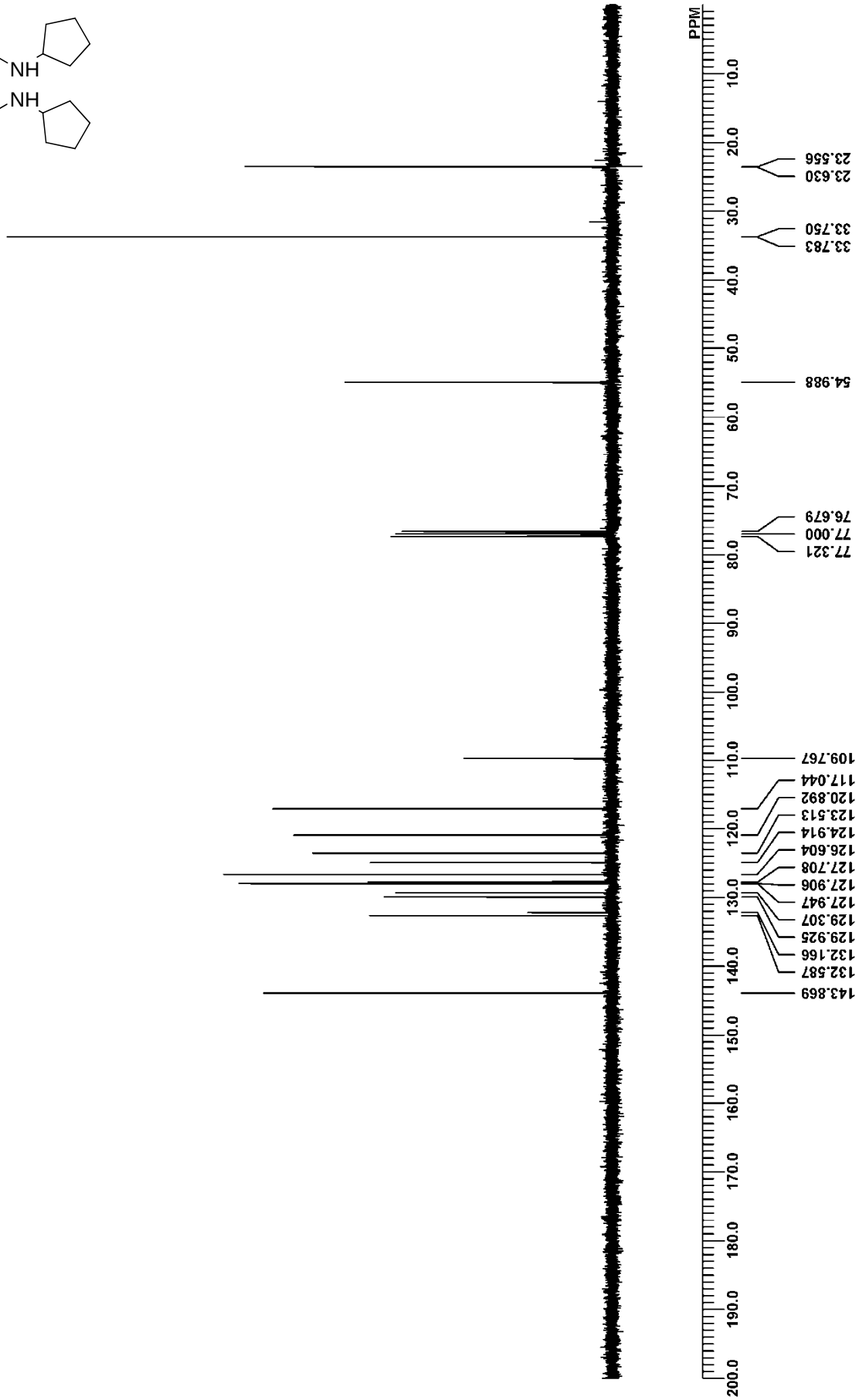
2.03
6.08
6.39
2.01
1.94
4.08
12.56


NH
NH

2d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50.0
60.0
70.0
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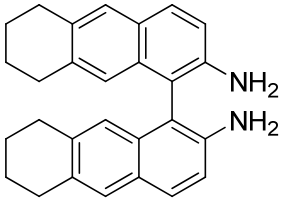
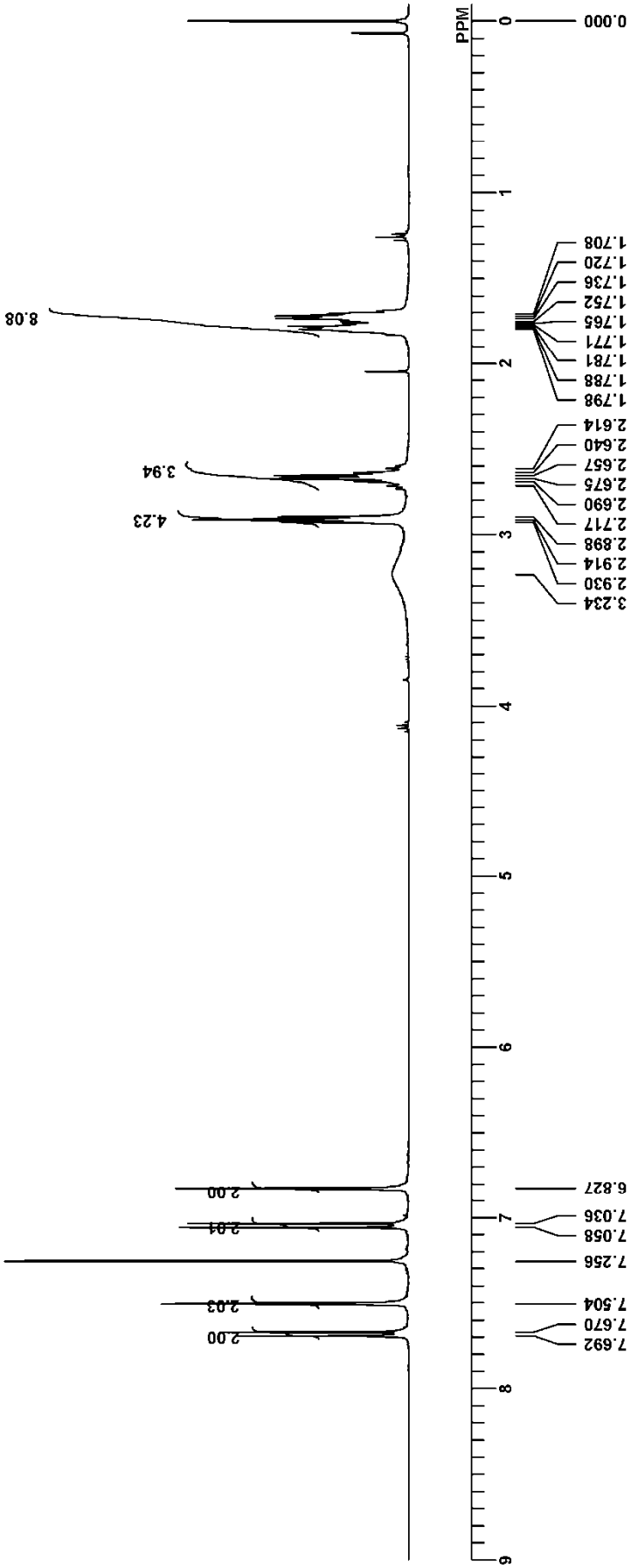
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
23.556
23.630
33.750
33.783
54.988
76.679
77.000
77.321
109.767
117.044
120.892
123.513
124.914
126.604
127.708
127.906
127.947
129.307
129.925
132.166
132.587
143.869


NH2
NH2

2e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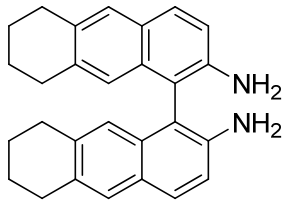
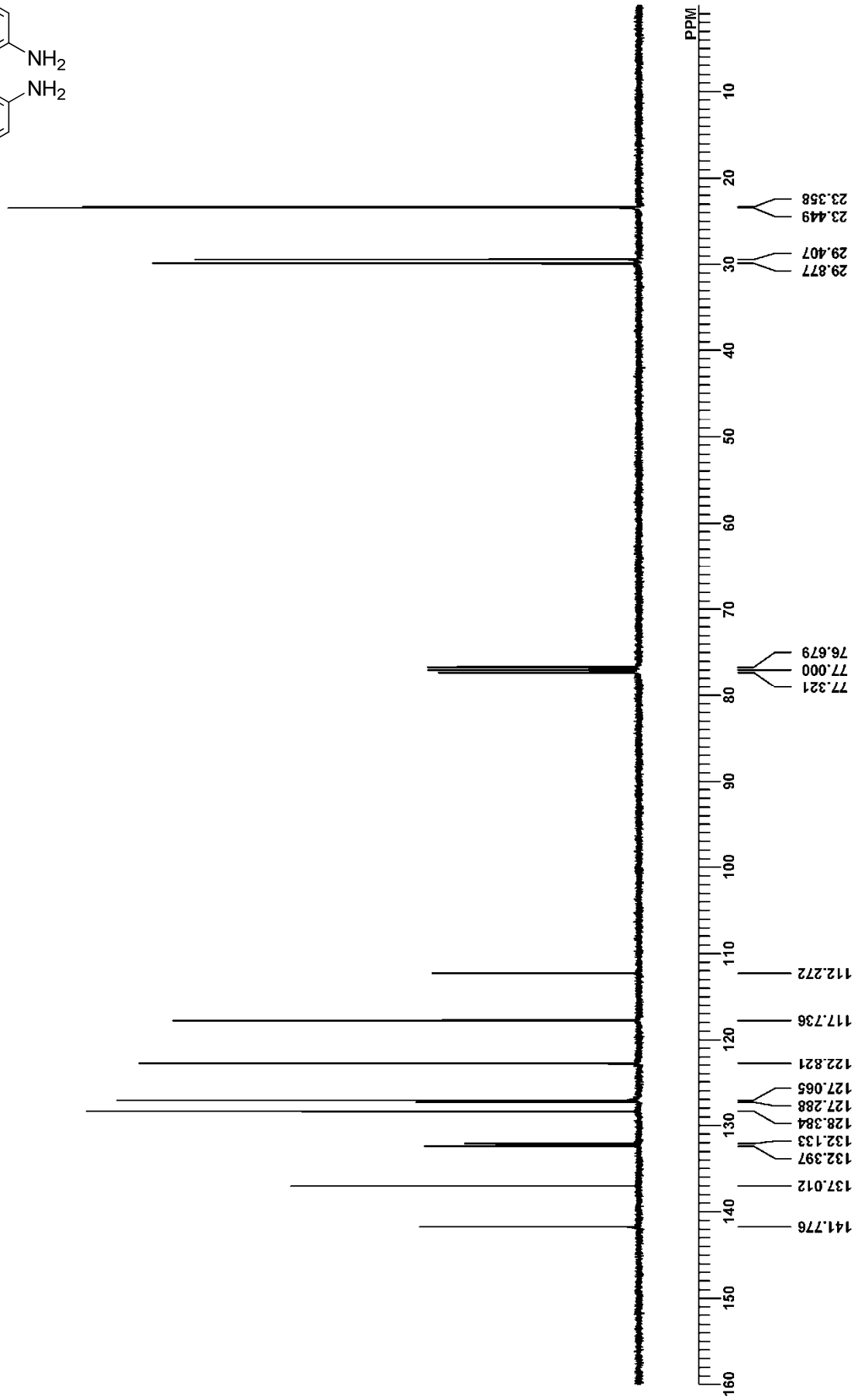
1.736
1.752
1.765
1.771
1.781
1.788
1.798
8.08
2.614
2.640
2.657
2.675
2.690
3.94
2.717
4.23
2.898
2.914
2.930
3.234
2.00
2.01
6.827
7.036
7.058
7.256
2.03
7.504
7.670
7.692
2.00


NH2
NH2

2e


PPM
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20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
23.358
23.449
29.407
29.877
76.679
77.000
77.321
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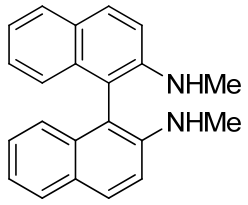
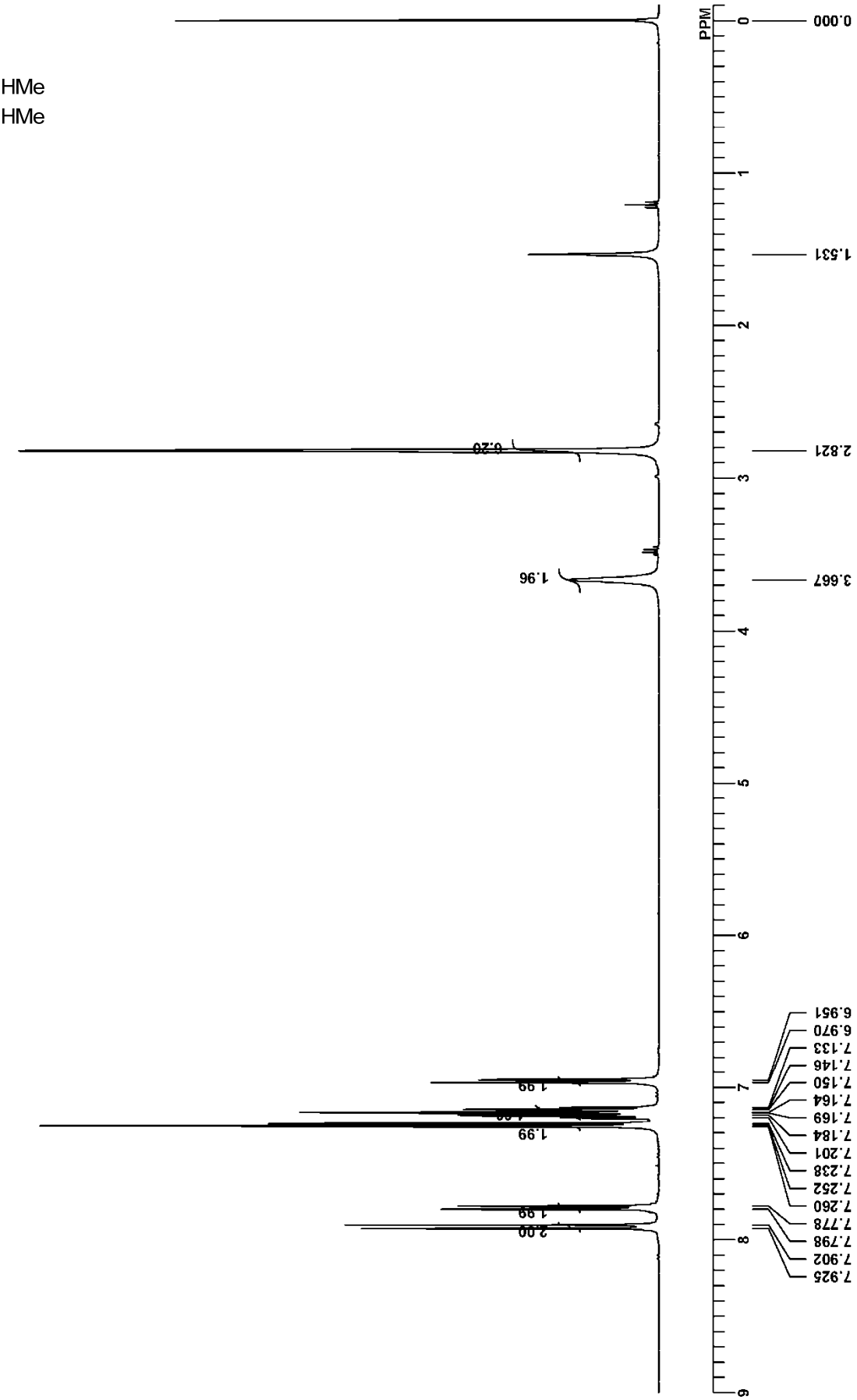
117.736
122.821
127.065
127.288
128.384
132.133
132.397
137.012
141.776


NHMe
NHMe

2f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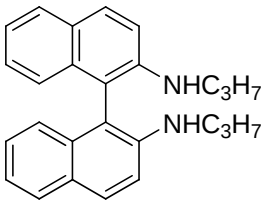
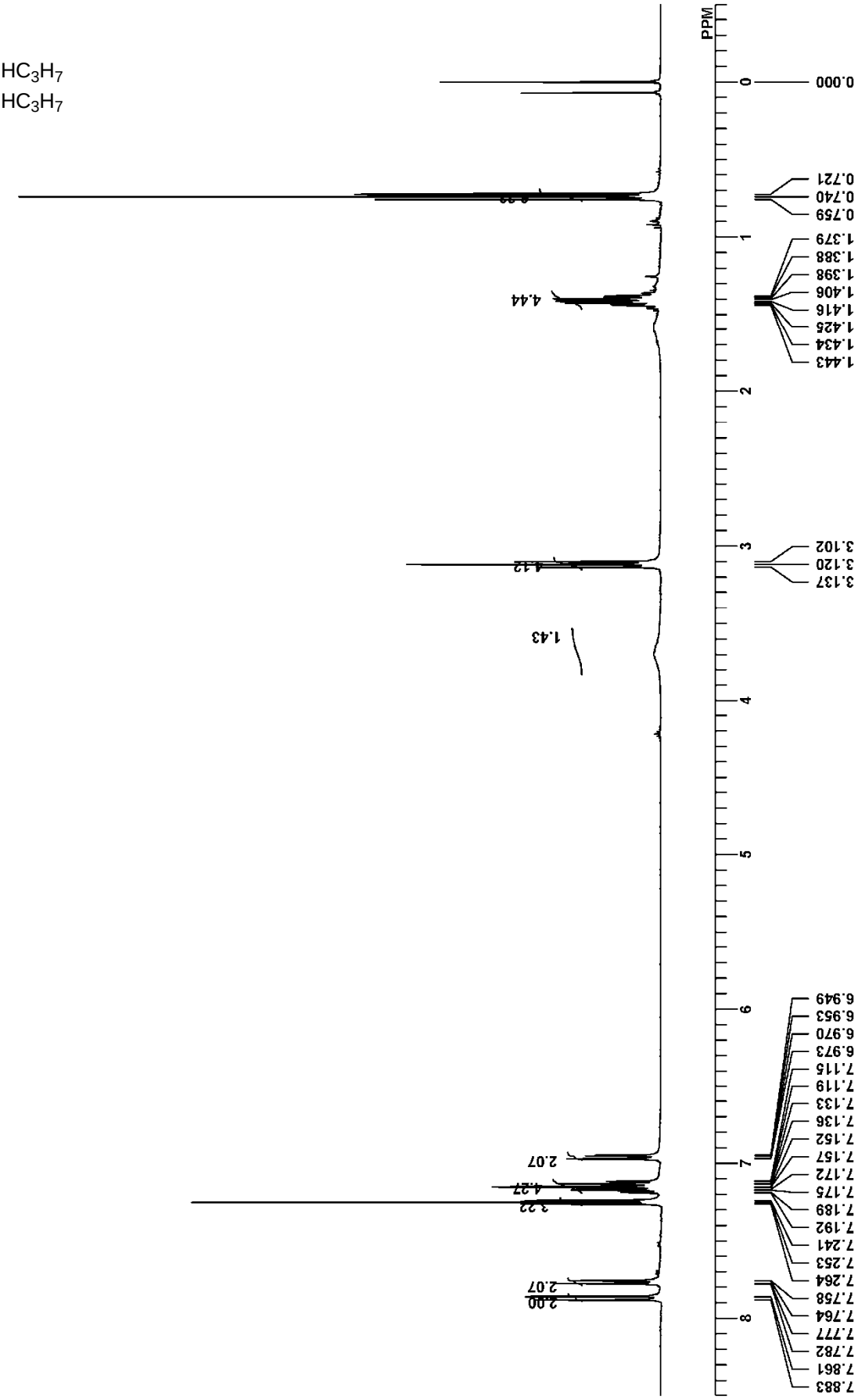
1.531
2.821
3.667
7.925
7.902
7.798
7.778
7.260
7.252
7.238
7.201
7.184
7.169
7.164
7.150
7.146
7.133
6.970
6.951
2.00
1.99
1.99
1.99
1.99
1.96
6.20


NHC3H7
NHC3H7

2g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0.759
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1.398
1.406
1.416
1.425
1.434
1.443
4.44
3.102
3.120
3.137
4.12
1.43
2.07
4.27
3.22
2.07
2.00
7.264
7.253
7.241
7.192
7.189
7.175
7.172
7.157
7.152
7.136
7.133
7.119
7.115
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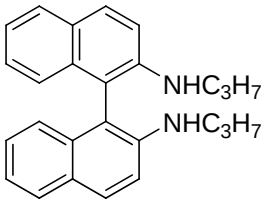
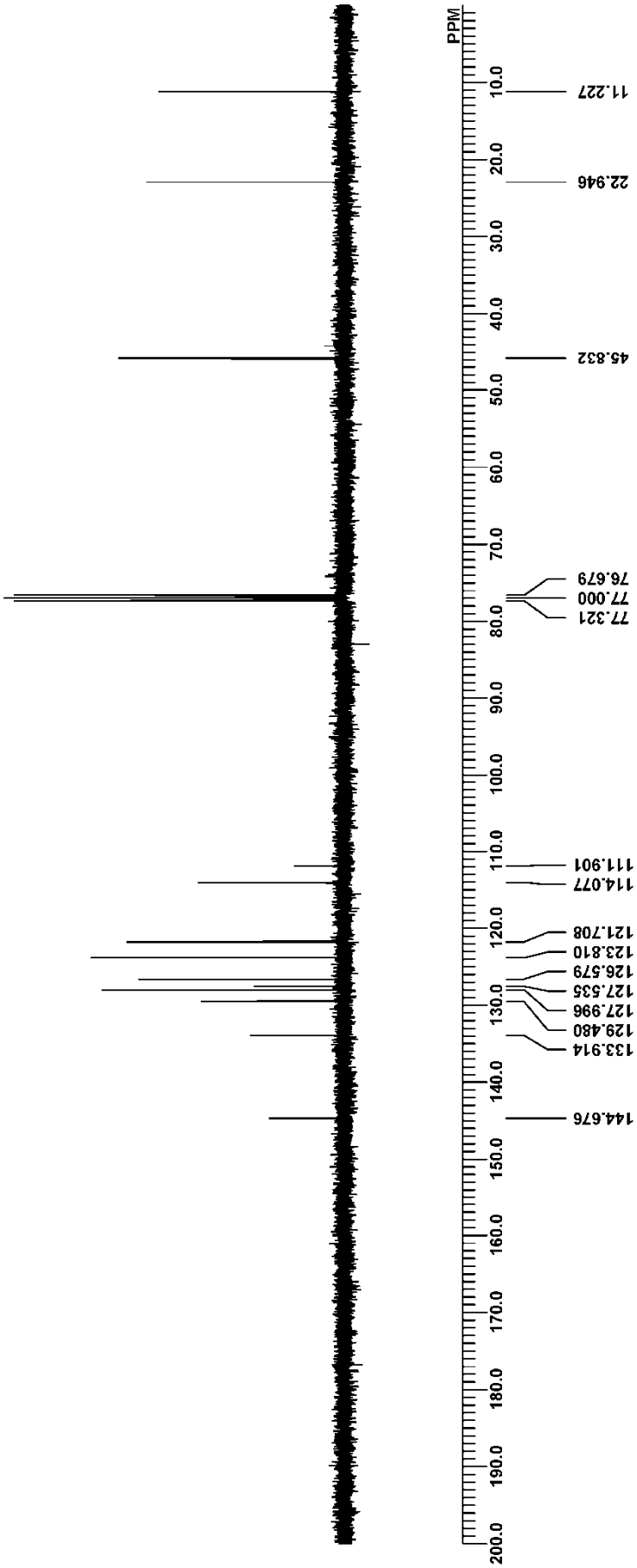
6.970
6.953
6.949
7.764
7.758
7.777
7.782
7.861
7.883


NHC3H7
NHC3H7

2g


PPM
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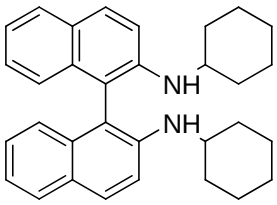
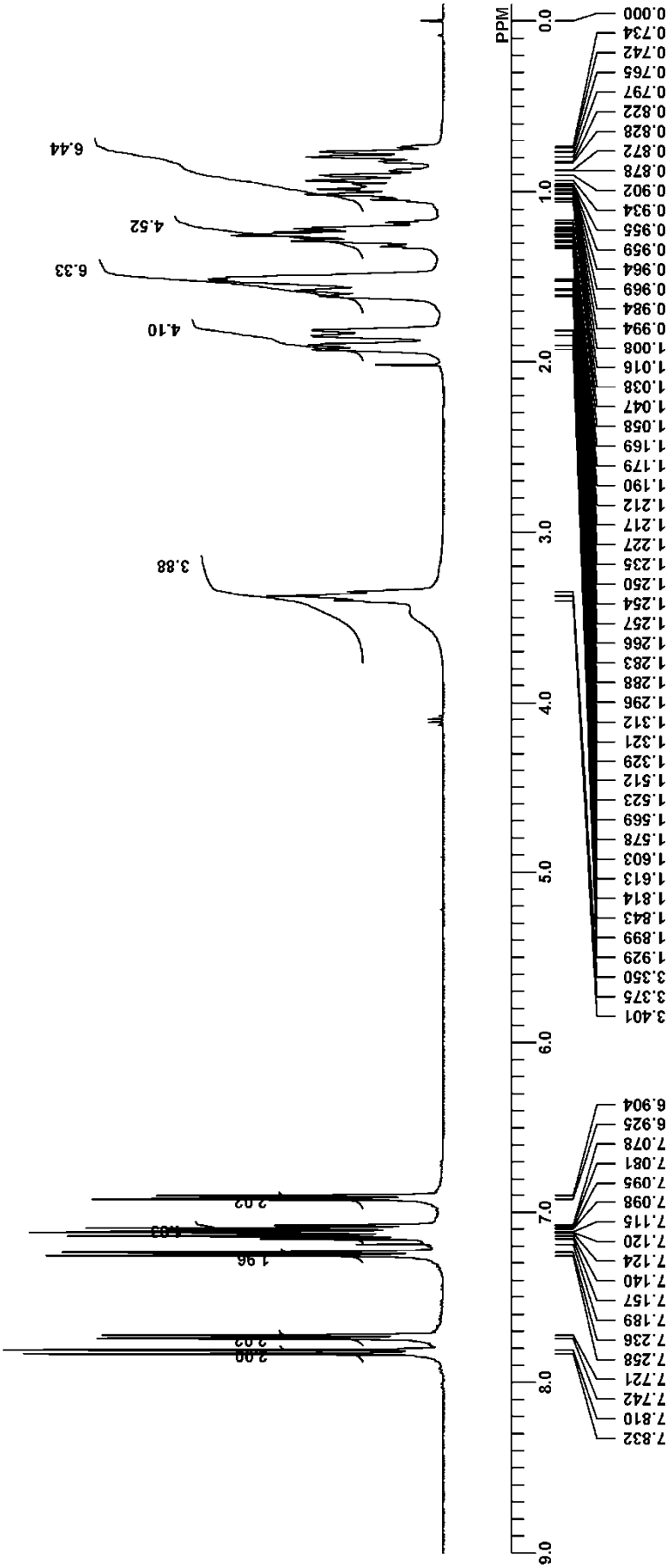
76.679
77.000
77.321
111.901
114.077
121.708
123.810
126.579
127.535
127.996
129.480
133.914
144.676


NH
NH

2h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5.0
6.0
7.0
8.0
9.0
0.000
0.734
0.742
0.765
0.797
0.822
0.828
0.872
0.878
0.902
0.934
0.955
0.959
0.964
0.969
0.984
0.994
1.008
1.016
1.038
1.047
1.058
1.169
1.179
1.190
1.212
1.217
1.227
1.235
1.250
1.254
1.257
1.266
1.283
1.288
1.296
1.312
1.321
1.329
1.512
1.523
1.569
1.578
1.603
1.613
1.814
1.843
1.899
1.929
3.350
3.375
3.401
6.904
6.925
7.078
7.081
7.095
7.098
7.115
7.120
7.124
7.140
7.157
7.189
7.236
7.258
7.721
7.742
7.810
7.832
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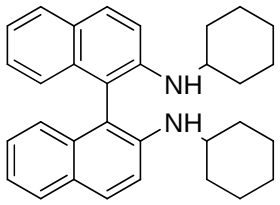
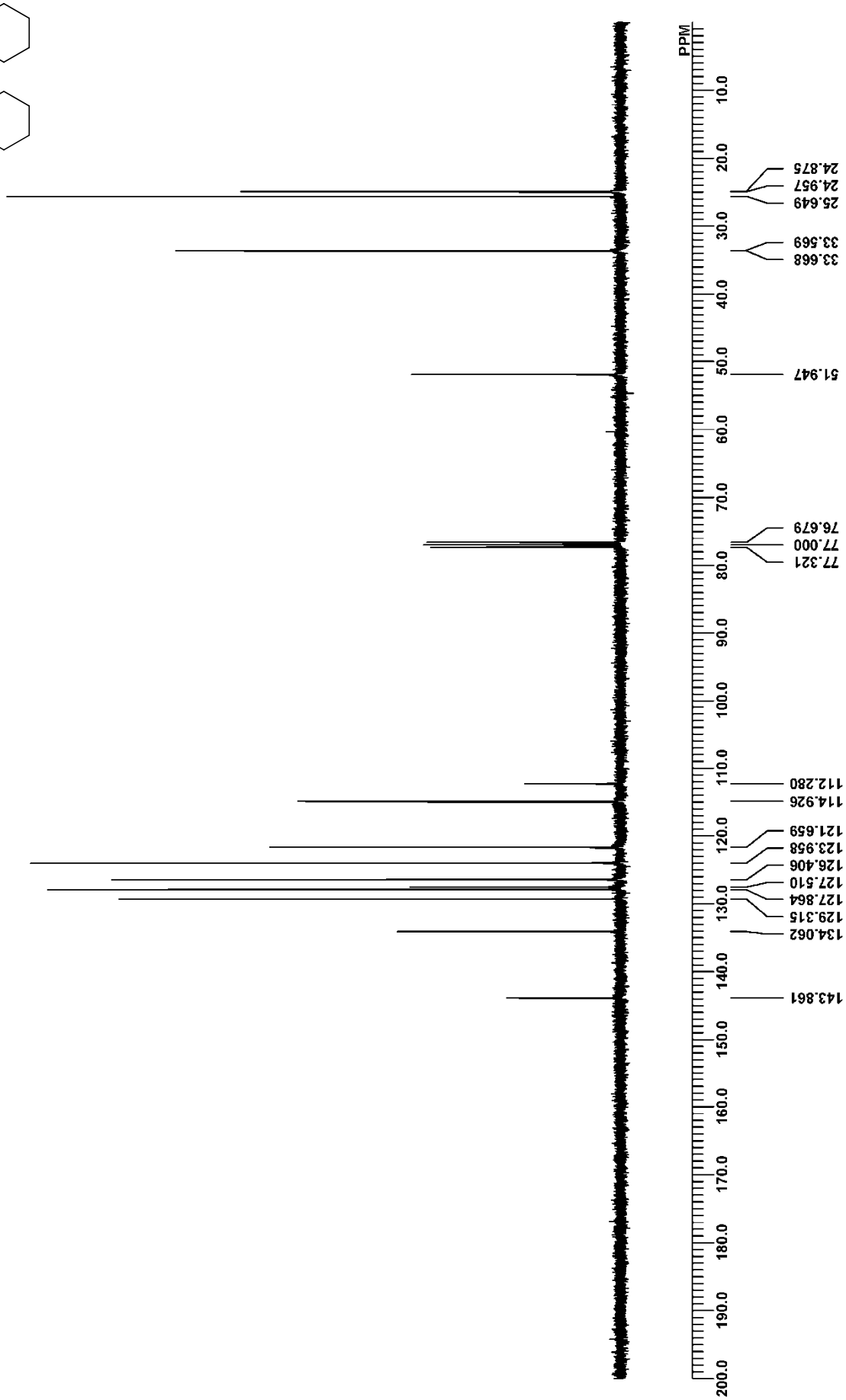
2.02
1.96
4.83
2.02
3.88
4.10
6.33
4.52
6.44


NH
NH

2h


PPM
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40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
24.875
24.957
25.649
33.569
33.668
51.947
76.679
77.000
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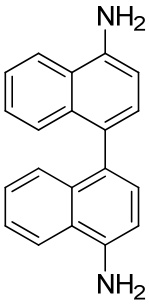
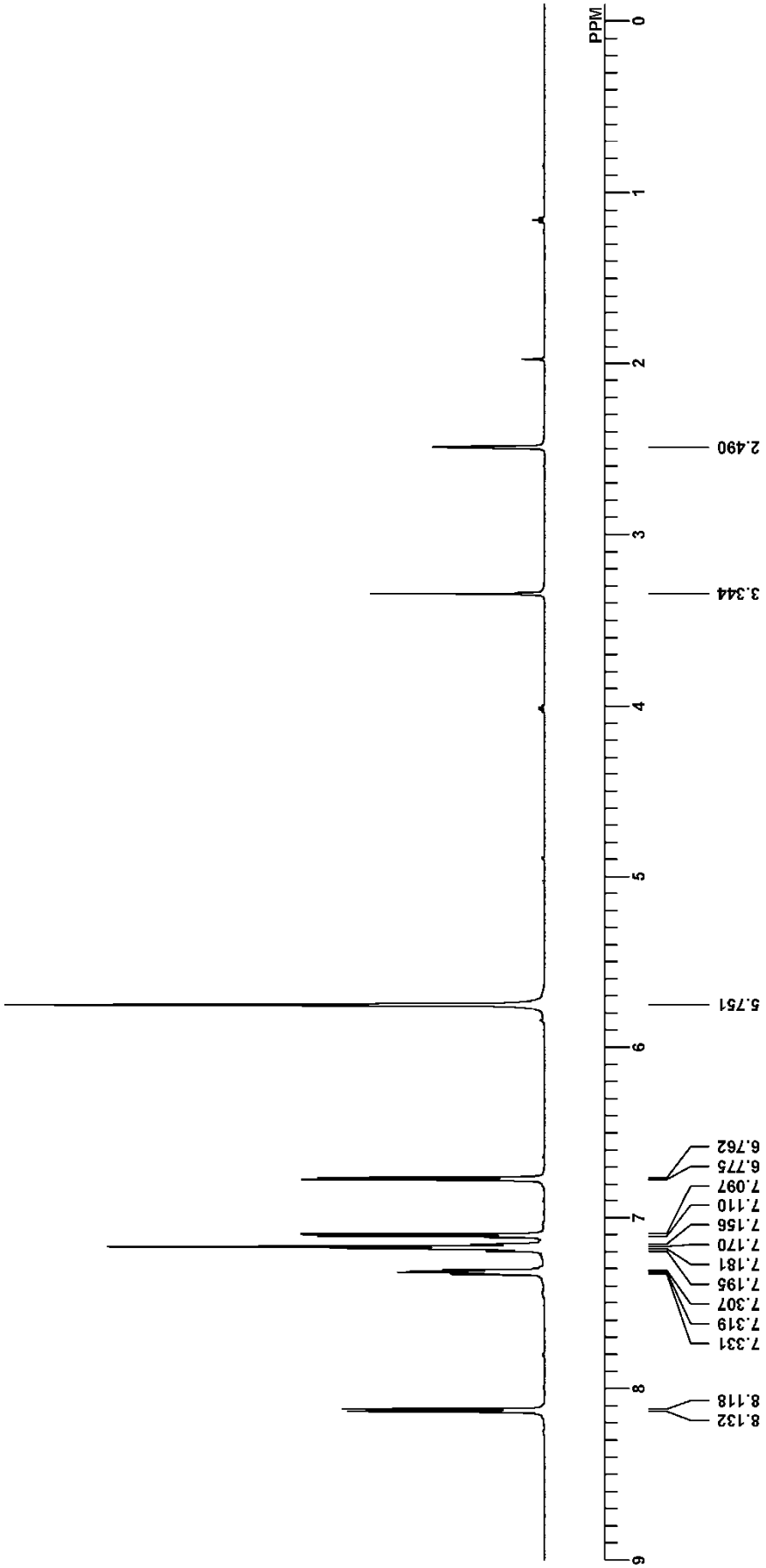
126.406
127.510
127.864
129.315
134.062
143.861



2i


PPM
0
1
2
3
4
5
6
7
8
9
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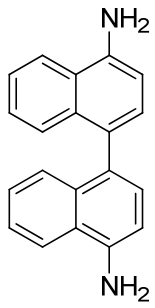
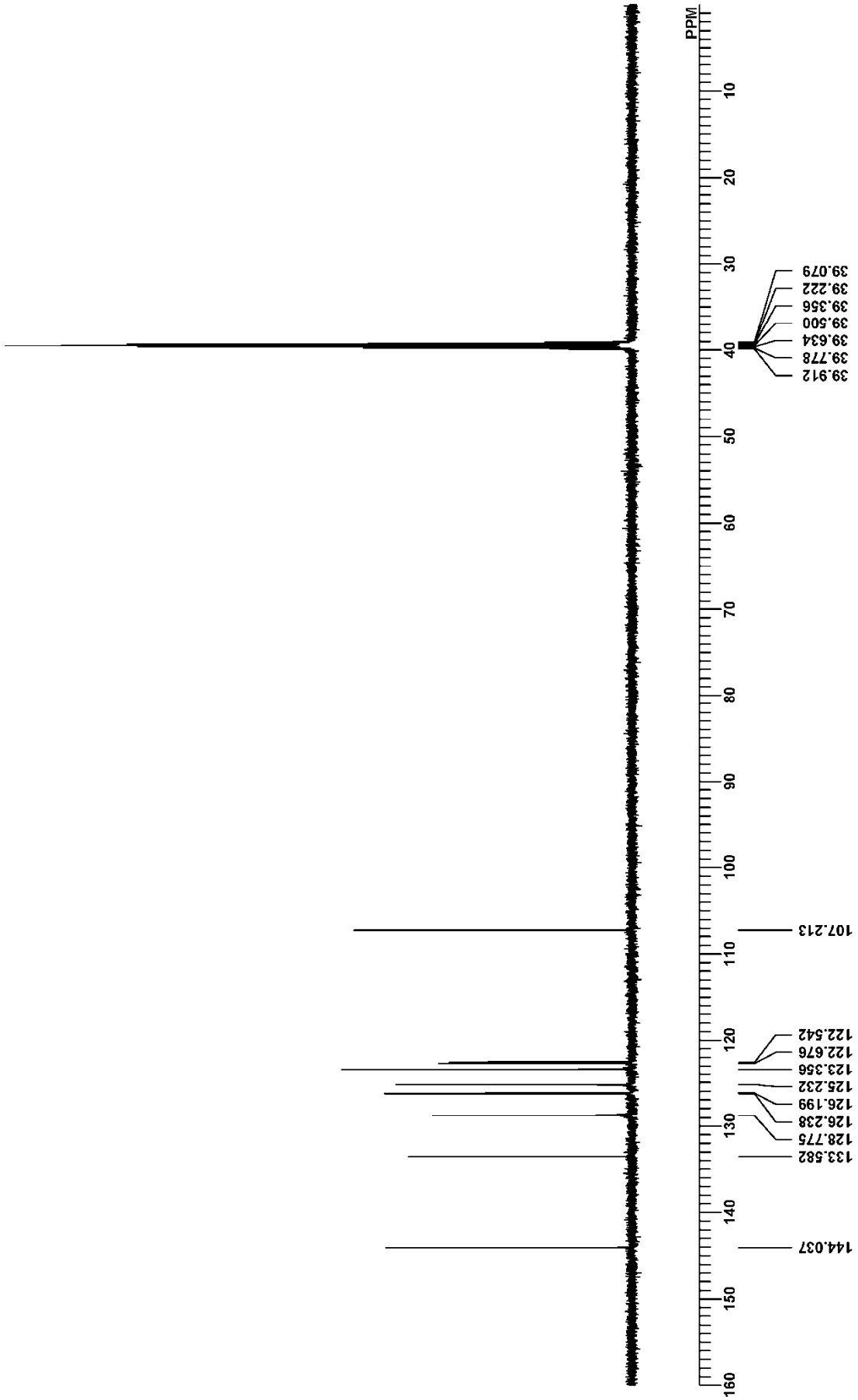
3.344
5.751
6.762
6.775
7.097
7.110
7.156
7.170
7.181
7.195
7.307
7.319
7.331
8.118
8.132


NH2
NH2

2i


PPM
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39.500
39.634
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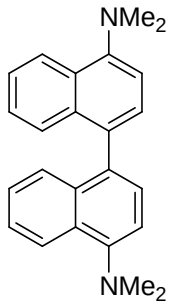
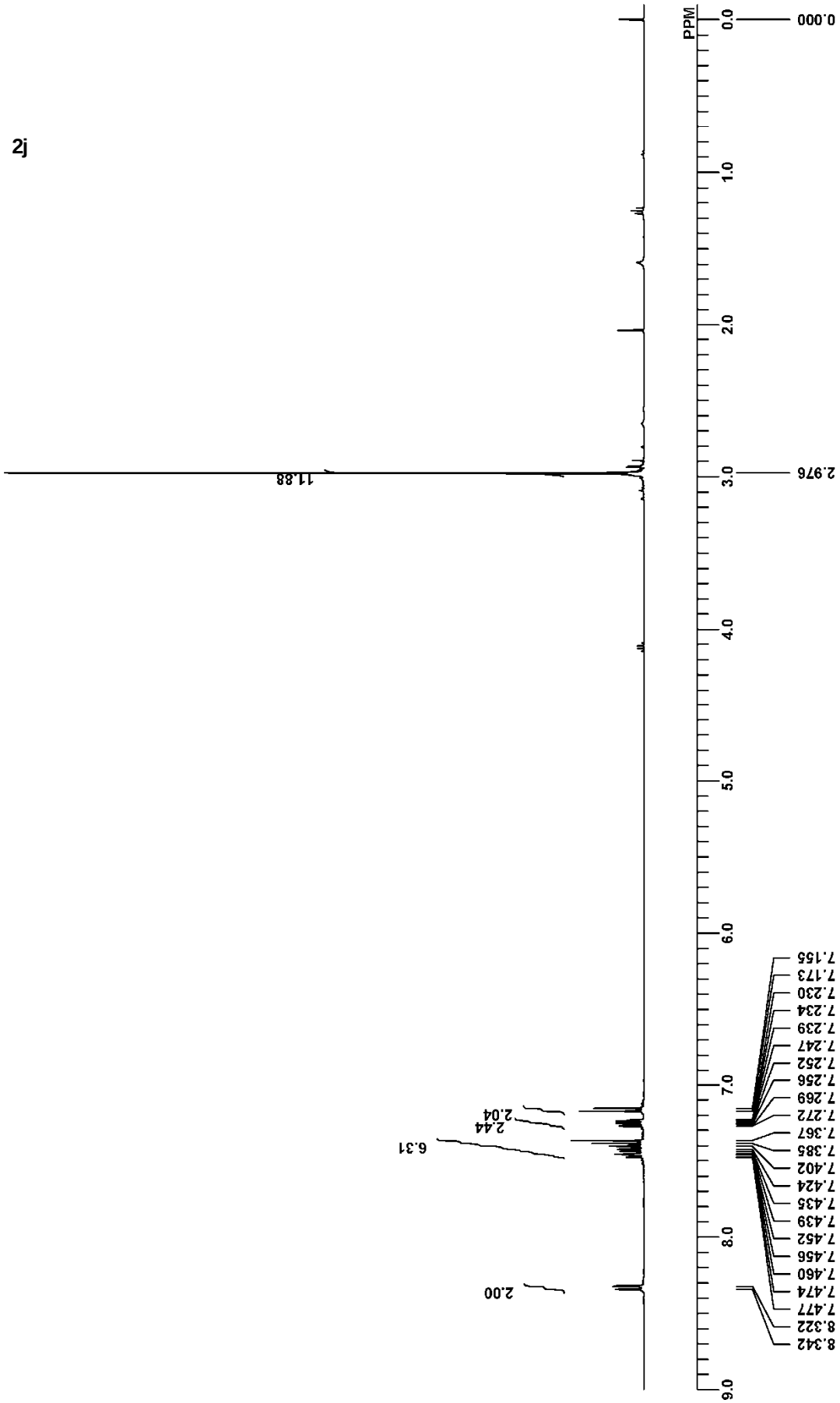
39.912
107.213
122.542
122.676
123.356
125.232
126.199
126.238
128.775
133.582
144.037


NMe2
NMe2

2j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2.04
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8.322
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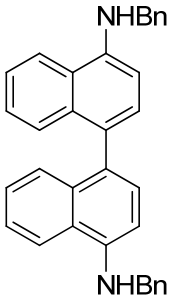
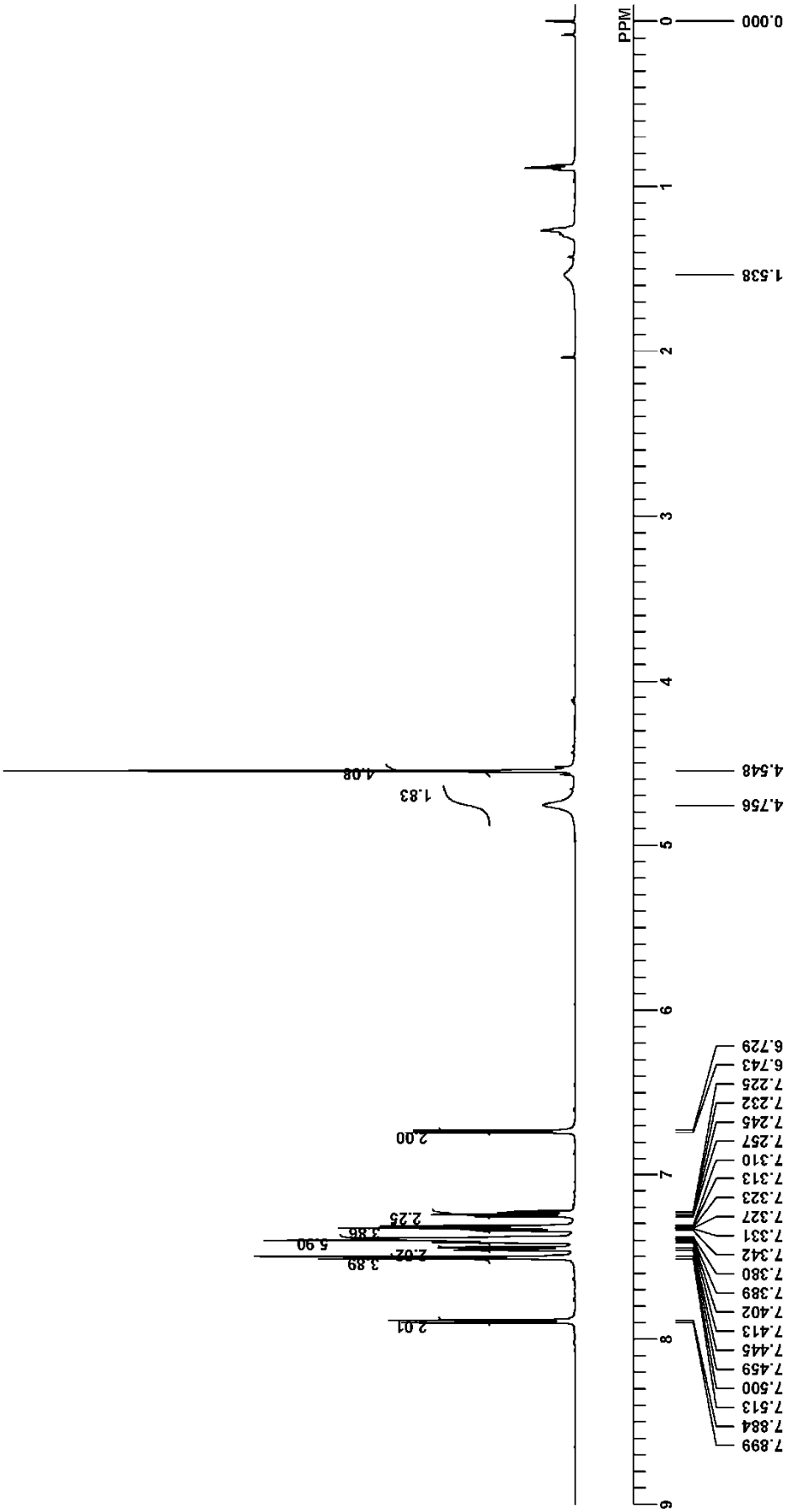
7.474
7.460
7.456
7.452
7.439
7.435
7.424
7.402
7.385
7.367
7.272
7.269
7.256
7.252
7.247
7.239
7.234
7.230
7.173
7.155


NHBn
NHBn

2k


PPM
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7.884
7.513
7.500
7.459
7.445
7.413
7.402
7.389
7.380
7.342
7.331
7.327
7.323
7.313
7.310
7.257
7.245
7.232
7.225
6.743
6.729
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2.02
5.90
3.86
2.25
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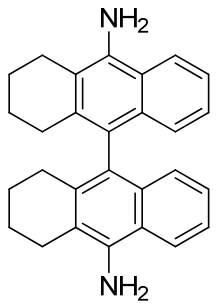
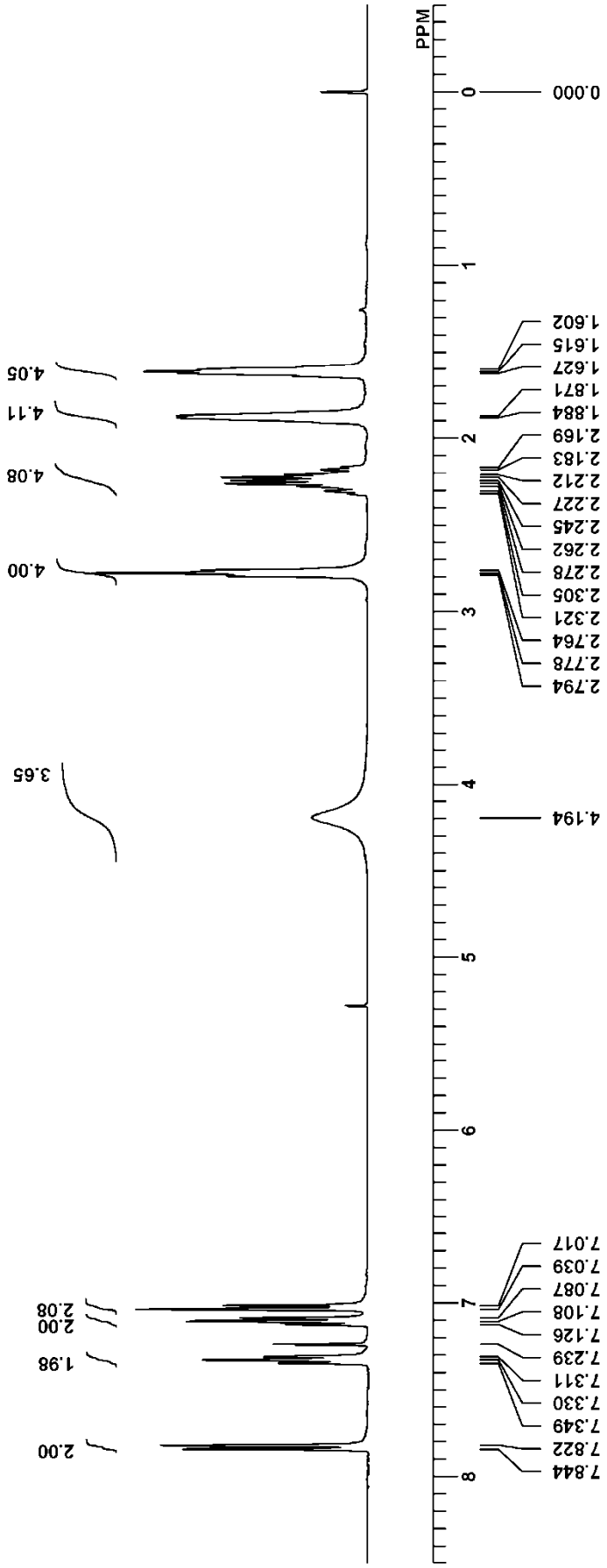
1.83
4.08



2l


PPM
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1.627
1.871
1.884
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2.183
2.212
2.227
2.245
2.262
2.278
2.305
2.321
2.764
2.778
2.794
4.194
7.017
7.039
7.087
7.108
7.126
7.239
7.311
7.330
7.349
7.822
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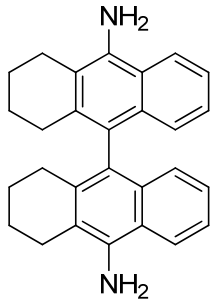
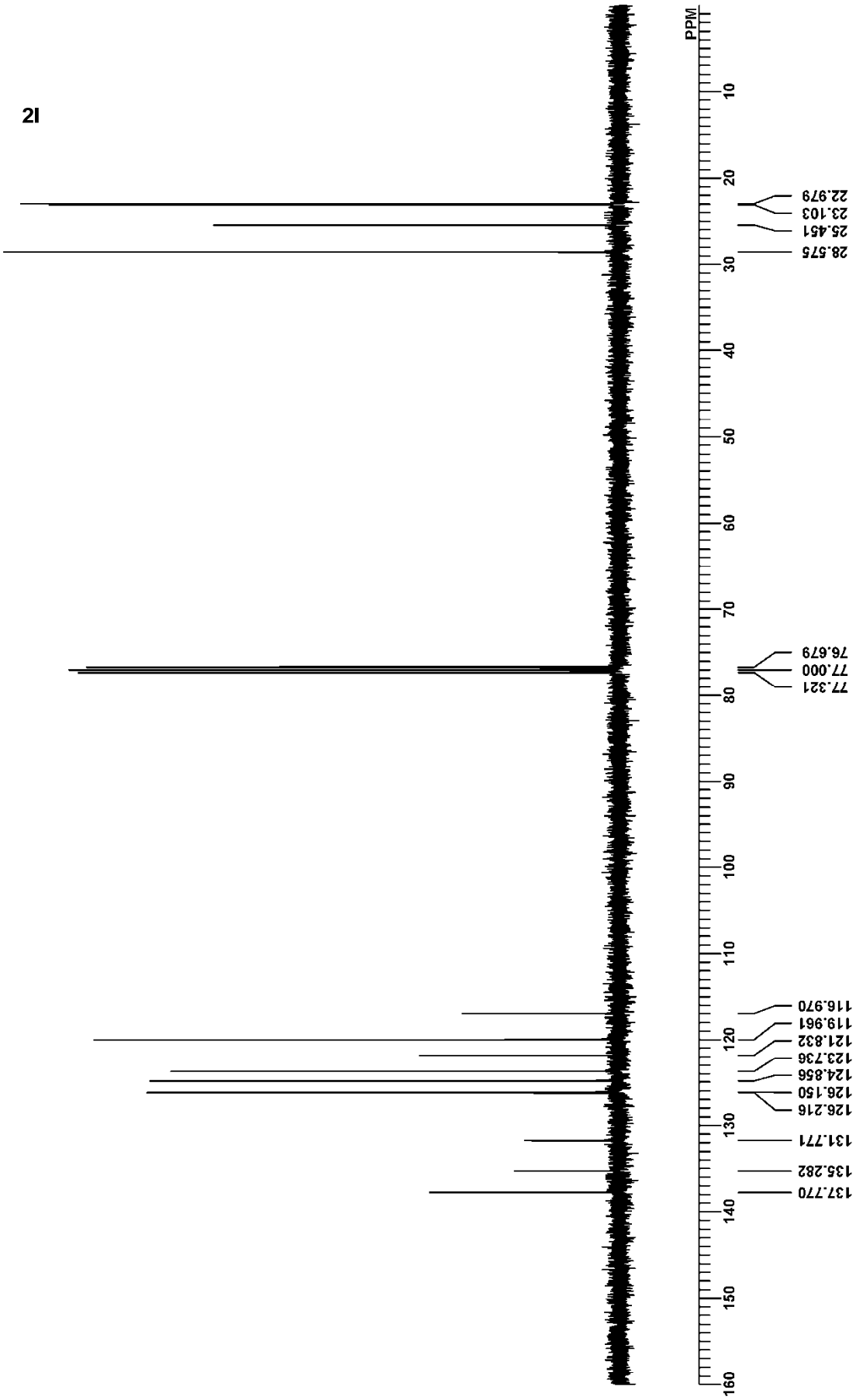
2.08
3.65
4.00
4.08
4.11
4.05


NH2
NH2

2l


PPM
10
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30
40
50
60
70
80
90
100
110
120
130
140
150
160
22.979
23.103
25.451
28.575
76.679
77.000
77.321
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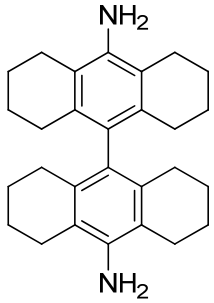
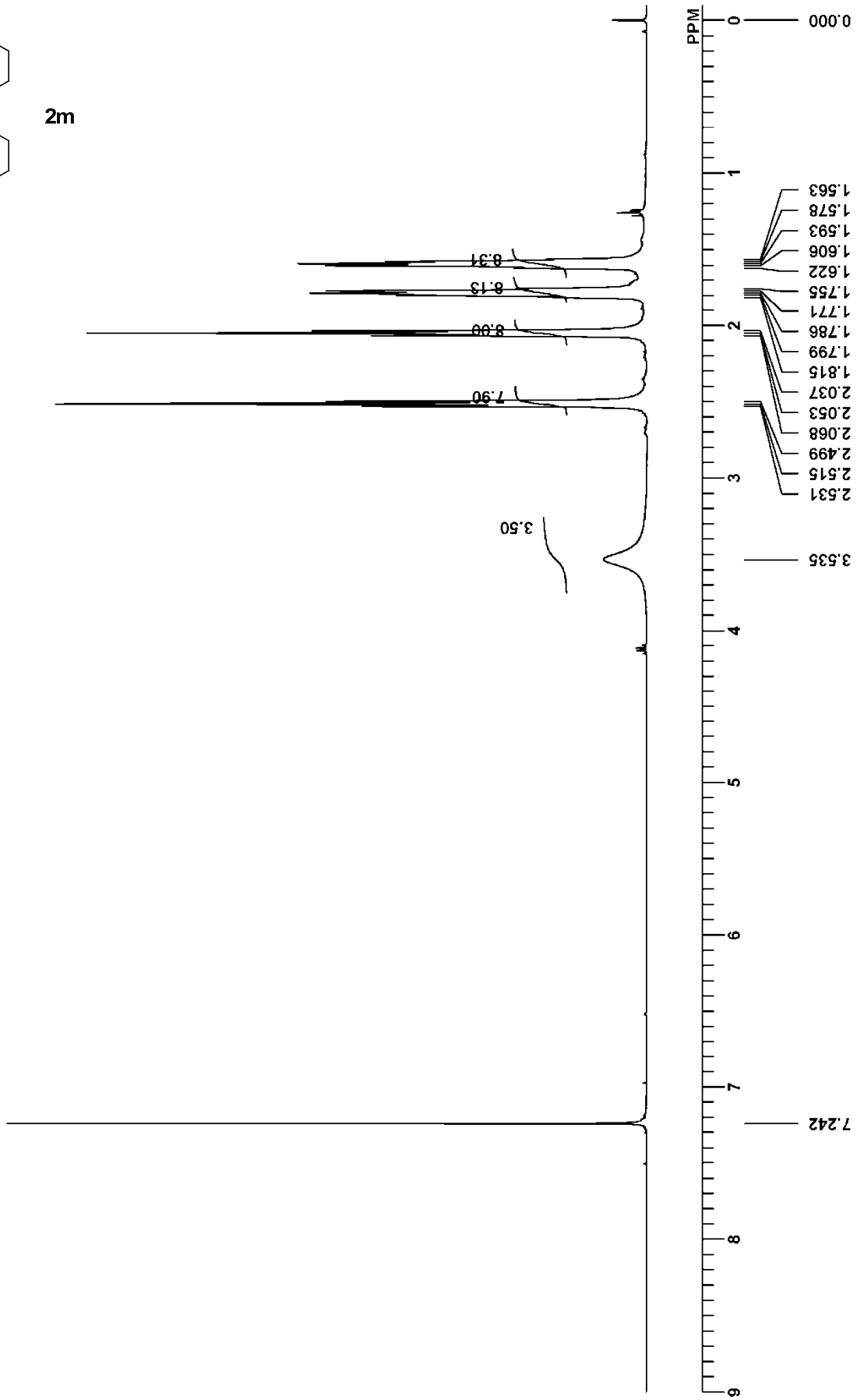
119.961
121.832
123.736
124.856
126.150
126.216
131.771
135.282
137.770


NH2
NH2

2m


PPM
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1.606
1.622
1.755
1.771
1.786
1.799
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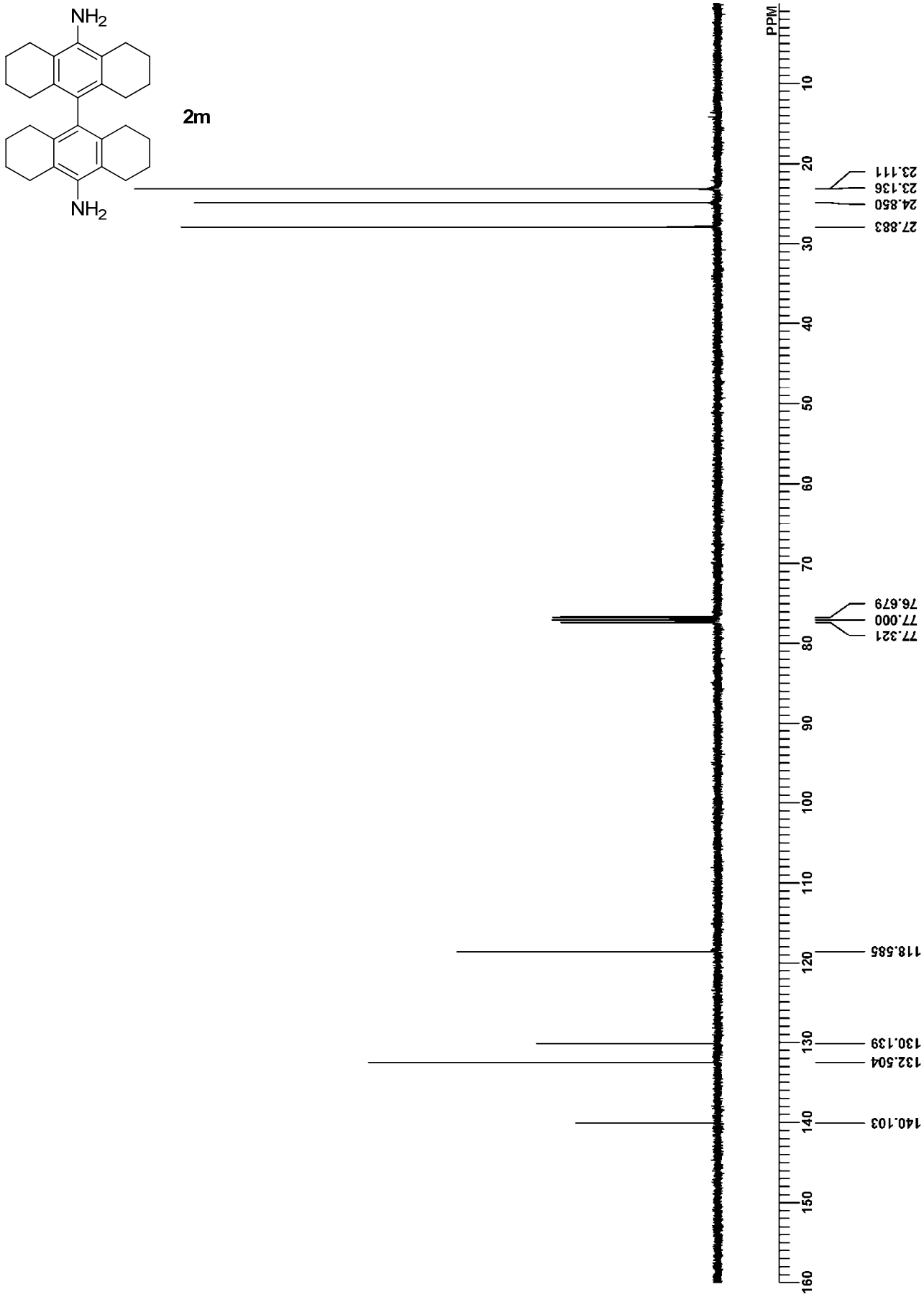
2.037
2.053
2.068
2.499
2.515
2.531
3.535
7.242
3.50
7.90
8.00
8.13
8.31


NH2
NH2
2m
PPM
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
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23.136
24.850
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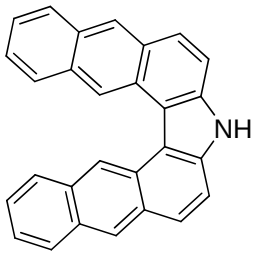
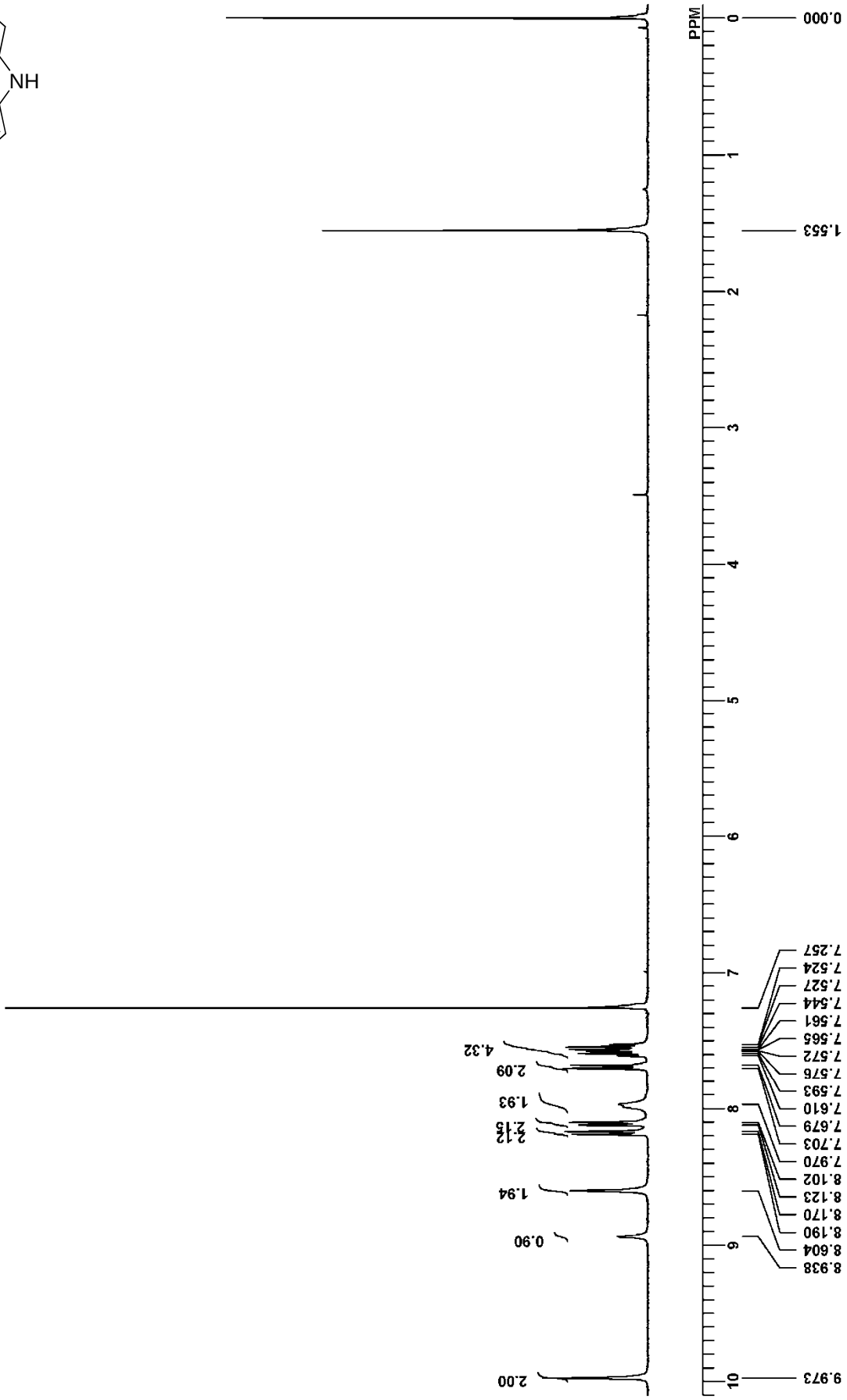
76.679
77.000
77.321
118.585
130.139
132.504
140.103


NH

3


PPM
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8.938
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7.970
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7.679
7.610
7.593
7.576
7.572
7.565
7.561
7.544
7.527
7.524
7.257
4.32
2.09
1.93
2.15
2.12
1.94
0.90
2.00