Electronic Supplementary Information

Synthesis of Rotacatenanes by the Combination of Cu-Mediated Threading Reaction and Template Method: The Dual Role of One Ligand

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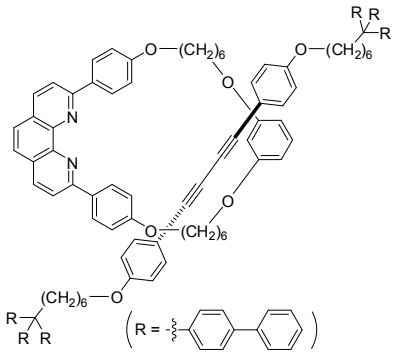
General Experimental.

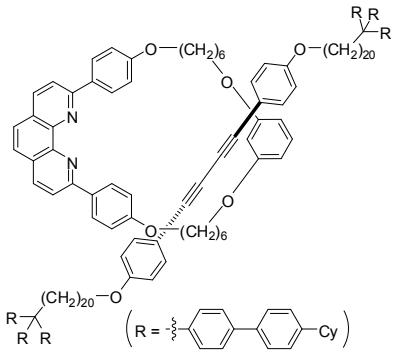
Commercially available reagents were used without further purification unless otherwise noted. NMR spectra were recorded using a JEOL JNM EX-300L FT NMR SYSTEM (300 MHz), a JEOL JNM LA 500 FT NMR SYSEM (500 MHz), on a Bruker Avance DPX-300 (300 MHz). Chemical shifts were reported in delta units (δ) relative to chloroform-*d* (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet) or m (multiplet). Coupling constants, *J*, are reported in Hz. IR spectra were recorded on a HORIBA FT-710 (FT-IR). Elemental analyses were measured by a YANACO CHN-recorder MT-6. High-resolution mass spectra (HR-MS) were measured by Varian 910-MS (ESI), JEOL JMS-700 (FAB-MS), Bruker Daltonics autoflex speed in Dithranol (20 mg/mL in $CHCl_3$) as a matrix (MALDI-TOF 1)) or Bruker ultrafleXtreame in α-cyano-4-hydroxycinnamic acid (10 mg/mL in MeOH) as a matrix (MALDI-TOF 2)). A JSI LC-918 was used for GPC separation. Thin layer chromatography (TLC) was performed on a Merck silica gel 60F-254 plate. Column chromatography was performed using Kanto Chemical silica gel 60N (spherical, neutral 63-210 m). Preparative thin layer chromatography (TLC) was performed using a Merck silica gel 60 plate.

Synthesis of [2]Rotaxanes 3a-d.



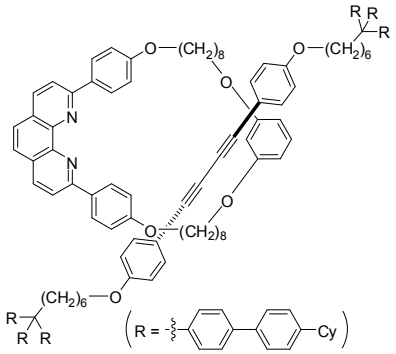
[2]Rotaxane 3a. A representative procedure (procedure A).

A mixture of **2a** (34 mg, 0.05 mmol), macrocyclic phenanthroline-CuI complex **1a** (17 mg, 0.02 mmol), K_2CO_3 (10 mg, 0.075 mmol) and I_2 (6.3 mg, 0.025 mmol) in dry xylene (1.0 mL) under Ar atmosphere was stirred at 130 °C for 48 h. The solution was cooled to room temperature and CH_2Cl_2 (1.5 mL), CH_3CN (3.5 mL) and aqueous ammonia (30% solution, 1.7 mL) was added.[(1)] After stirring at room temperature for overnight, the solution was extracted with CH_2Cl_2, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane-CH_2Cl_2 (3/1 (v/v)) and GPC using $CHCl_3$ to afford **3a** (29 mg, 0.014 mmol, 72%) as a colorless amorphous. The analytical data were identical with those reported in the reference.[(2)]



[2]Rotaxane 3b.

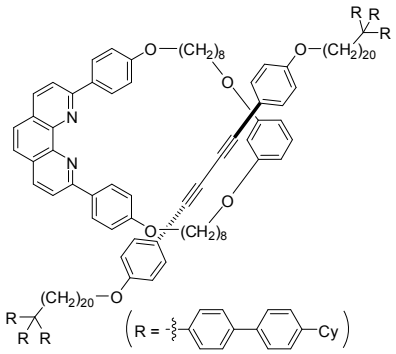
Procedure A was generally followed to synthesize **3b** from **2b** (56 mg, 0.05 mmol) and **1a** (17 mg, 0.02 mmol). The product was purified by silica gel column chromatography using hexane-CH_2Cl_2 (1/1 (v/v)) and GPC using $CHCl_3$ to afford **3b** (44 mg, 0.015 mmol, 76%) as a yellow amorphous. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 4H), 8.21 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.70 (s, 2H), 7.52-7.45 (m, 24H), 7.41 (d, *J* = 8.5 Hz, 4H), 7.36-7.30 (m, 12H), 7.26-7.20 (m, 12H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 4H), 6.75 (d, *J* = 8.5 Hz, 4H), 6.57 (s, 1H), 6.47 (dd, *J* = 8.5 Hz, 2.5 Hz, 2H), 4.00-3.91 (m, 8H), 3.83 (t, *J* = 6.0 Hz, 4H), 2.66-2.44 (m, 10H), 1.97-1.09 (m, 148H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 160.4, 159.8, 156.2, 150.0, 146.4, 146.0, 138.3, 138.2, 136.6, 134.0, 132.0, 129.7, 129.6, 128.9, 127.4, 127.1, 126.8, 126.2, 125.5, 119.0, 114.7, 114.7, 113.5, 107.0, 101.1, 81.5, 73.2, 68.1, 68.0, 67.7, 56.0, 44.2, 40.5, 34.4, 30.5, 29.7, 29.7, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 29.1, 26.9, 26.1, 26.0, 25.9, 25.9, 25.7; IR(KBr) 3433, 3024, 2924, 2854, 2137, 1905, 1597, 1496, 1288, 1250, 1173, 1003, 810, 733, 532 cm^{-1}; HR-MS (MALDI-TOF 2)) Calcd for $C_{208}H_{245}N_2O_6$ ($[M+H]^+$): 2866.8922. Found: 2866.9247.



[2]Rotaxane 3c.

Procedure A was generally followed to synthesize **3c** from **2c** (46 mg, 0.05 mmol) and **1b** (18 mg, 0.02 mmol). The product was purified by silica gel column chromatography using hexane-CH_2Cl_2 (1/1 (v/v)) and GPC using $CHCl_3$ to afford **3c** (14 mg, 5.5 μmol, 27%) as a yellow amorphous. The

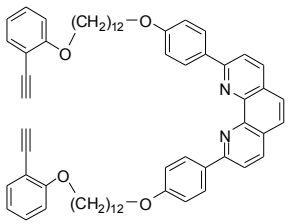
analytical data were identical with those reported in the reference.[3]



[2]Rotaxane 3d.

Procedure A was generally followed to synthesize **3d** from **2b** (56 mg, 0.05 mmol) and **1b** (18 mg, 0.02 mmol). The product was purified by silica gel column chromatography using hexane-CH_2Cl_2 (1/1 (v/v)) and GPC using $CHCl_3$ to afford **3d** (19 mg, 6.5 μmol, 32%) as a yellow amorphous. ^{1}H NMR (500MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 4H), 8.20 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 12H), 7.47 (d, *J* = 8.5 Hz, 12H), 7.39 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.5 Hz, 12H), 7.23 (d, *J* = 7.5 Hz, 12H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 9 Hz, 4H), 6.75 (d, *J* = 8.5 Hz, 4H), 6.48 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.5, 2.4 Hz, 2H), 3.97 (t, *J* = 6.7 Hz, 4H), 3.91 (t, *J* = 6.2 Hz, 4H), 3.84 (t, *J* = 6.7 Hz, 4H), 2.44-2.64 (m, 10H), 1.64-1.94 (m, 42H), 1.06-1.50 (m, 114H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.4, 159.8, 156.2, 147.0, 146.4, 138.3, 138.2, 136.6, 134.0, 131.9, 129.7, 129.6, 128.9, 127.4, 127.1, 126.8, 126.2, 125.5, 119.1, 114.6, 114.6, 113.6, 106.9, 100.8, 81.4, 73.1, 68.1, 68.0, 67.8, 56.0, 44.2, 40.5, 34.4, 30.5, 29.8, 29.8, 29.6, 29.6, 29.4, 29.3, 29.1, 26.9, 26.2, 26.0, 25.9, 25.8, 25.8; IR (KBr) 3024, 2924, 2846, 1597, 1496, 1466, 1288, 1250, 1173, 1003, 810, 532 cm^{-1}; HR-MS (MALDI-TOF 1)) Calcd for $C_{212}H_{253}N_2O_6$ ($[M+H]^+$): 2922.9548. Found: 2922.9626.

Preparation of Diyne 6.

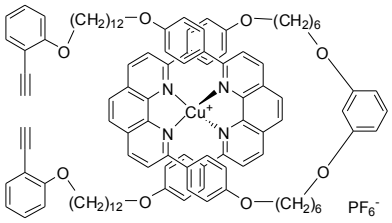


A mixture of 2,9-bis(*p*-phenol)-1,10-phenanthroline HCl salt (0.16 g, 0.39 mmol), [2-(12-bromo-dodecyloxy)phenylethynyl]trimethylsilane[4] (0.51 g, 1.2 mmol) and K_2CO_3 (0.82 g,

5.9 mmol) was dissolved in DMSO (4.6 mL), and the solution was heated to 70 °C. After 4 h, DMSO was removed *in vacuo*. Water was added to the yellow residue and aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography using hexane-CH_2Cl_2 (1/2(v/v)) to afford **6** (0.29 g, 0.31 mmol, 80%) as a colorless solid.

m.p. 106.0-108.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 9.0 Hz, 4H), 8.23 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 2H), 7.29-7.22 (m, 2H), 7.08 (d, *J* = 9.0 Hz, 4H), 6.90-6.82 (m, 4H), 4.10-3.90 (m, 8H), 3.24 (s, 2H), 1.90-1.75 (m, 8H), 1.55-1.20 (m, 32H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 160.1, 156.2, 145.9, 136.5, 133.9, 131.8, 130.0, 128.8, 127.3, 125.4, 120.1, 119.1, 114.6, 111.9, 111.6, 80.9, 80.1, 68.6, 68.0, 29.5, 29.4, 29.3, 29.2, 29.2, 28.9, 25.9, 25.8; IR (KBr) 3433, 3294, 3062, 3039, 2924, 2854, 2561, 2106, 1597, 1574, 1489, 1450, 1396, 1288, 1250, 1173, 1111, 1041, 1018, 833, 795, 748, 640, 602, 579, 509 cm^{-1}; Anal. Calcd for $C_{64}H_{72}N_2O_4$: C, 82.36; H, 7.78; N, 3.00. Found: C, 82.34; H, 7.79; N, 2.97.

Synthesis of [2]Catenanes 8a and 8b.

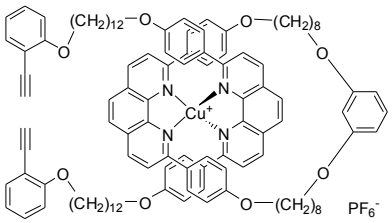


Tetrahedral Cu(I) complex 7a. A representative procedure (procedure B).

To a solution of $[Cu(CH_3CN)_4]PF_6$ (15 mg, 0.039 mmol) in dry CH_3CN (3.1 mL) was added **4a** (25 mg, 0.039 mmol) in dry CH_2Cl_2 (3.1 mL) at room temperature. The color of the mixture immediately turned yellow. After stirring for 30 min at room temperature, a solution of **6** (36 mg, 0.039 mmol) in dry CH_2Cl_2 (3.1 mL) was added to the reaction mixture, producing a color change to dark purple. The resulting mixture was stirred for 1 h. The solvents were removed *in vacuo*. The residue was purified by silica gel column choromatography using CH_2Cl_2 to afford the product **7a** (58 mg, 0.033 mmol, 84%) as a purple amorphous.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.81-7.69 (m, 8H), 7.26-7.24 (m, 8H), 7.12-7.08 (m, 5H), 6.70-6.67 (m, 4H), 6.66 (s, 1H), 6.46 (d, *J* = 8.2 Hz, 2H), 5.85-5.80 (m, 8H), 3.97 (t, *J* = 5.8 Hz, 4H), 3.85 (t, *J* = 6.4 Hz, 4H), 3.36 (t, *J* = 6.4 Hz, 4H), 3.29 (t, *J* = 6.4 Hz, 4H), 3.07 (s, 2H), 1.76-1.71 (m, 4H), 1.68-1.62 (m, 4H), 1.47-1.39 (m, 12H), 1.34-1.26 (m, 8H), 1.20-1.08 (m, 28H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 160.2, 159.8, 159.7, 156.4, 143.3, 136.9, 136.8, 134.0, 131.0, 130.8, 130.3, 130.1, 129.2, 127.8, 125.9, 124.3, 120.2, 112.9,

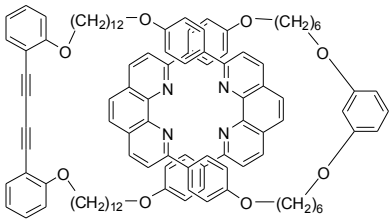
112.8, 112.0, 111.6, 106.8, 101.8, 80.9, 80.2, 68.7, 67.9, 67.8, 67.6, 29.6, 29.6, 29.0, 29.0, 28.9, 28.5, 26.0, 25.9, 25.7, 25.3; IR(KBr) 3310, 2932, 2861, 1734, 1602, 1587, 1489, 1250, 1175, 1151, 1017, 838 cm^{-1}; HR-MS (ESI): Calcd. For $C_{106}H_{114}N_4O_8Cu$ ($[M\text{-}PF_6]^+$): 1633.7927. Found: 1633.7927.



Tetrahedral Cu(I) complex 7b.

Procedure B was generally followed to synthesize **7b** from $[Cu(CH_3CN)_4]PF_6$ **5** (19 mg, 0.05 mmol), **4b** (35 mg, 0.05 mmol) and **6** (47 mg, 0.05 mmol). The product was purified by silica gel column chromatography using CH_2Cl_2 to afford **7b** (84 mg, 0.046 mmol, 91%) as a purple amorphous.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.5 Hz, 2H), 8.37 (d, *J* = 8.5 Hz, 2H), 7.92 (s, 2H), 7.88 (s, 2H), 7.84-7.79 (m, 4H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.40-7.34 (m, 8H), 7.29-7.21 (m, 2H), 7.18 (t, *J* = 8.5 Hz, 1H), 6.89-6.81 (m, 4H), 6.63 (s, 1H), 6.54 (dd, *J* = 8.5 Hz, 2.5 Hz, 2H), 6.04-5.96 (m, 8H), 4.06 (t, *J* = 6.0 Hz, 4H), 4.02 (t, *J* = 6.8 Hz, 4H), 3.54 (t, *J* = 6.0 Hz, 4H), 3.48 (t, *J* = 6.0 Hz, 4H), 3.23 (s, 2H), 1.91-1.77 (m, 8H), 1.68-1.22 (m, 56H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.3, 159.8, 159.8, 156.5, 156.5, 143.8, 143.5, 136.9, 136.8, 134.0, 131.0, 130.8, 130.1, 129.9, 129.2, 129.2, 127.8, 127.7, 125.9, 125.9, 124.4, 124.3, 120.2, 113.0, 112.9, 112.1, 111.7, 107.0, 101.5, 80.9, 80.2, 68.8, 68.0, 67.9, 67.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 29.1, 29.0, 28.9, 26.0, 26.0, 25.9, 25.8; IR(KBr) 3433, 3278, 3070, 2931, 2854, 2106, 1604, 1489, 1389, 1358, 1281, 1250, 1180, 1111, 1026, 849, 756, 648, 555 cm^{-1}; HR-MS (ESI) Calcd for $C_{110}H_{122}N_4O_8Cu$ ($[M\text{-}PF_6]^+$): 1689.85468. Found: 1689.85532.

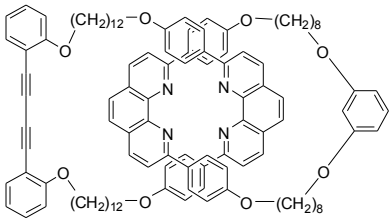


Catenane 8a. A representative procedure (procedure C).

A mixture of tetrahedral Cu(I) complex **7a** (14 mg, 7.9 μmol), CuCl (78 mg, 0.79 mmol) and $CuCl_2$ (13 mg, 0.094 mmol) in dry DMF (16 mL) was stirred at room temperature.[5] After 72 h, the solvent

was removed *in vacuo*. Water was added to the residue and aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over $MgSO_4$ and concentrated. The residue was purified by short silica gel chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) and the residue was added CH_3CN (2 mL), CH_2Cl_2 (2 mL), H_2O (2 mL) and KCN (23 mg). the solution was stirred at room temperature for overnight. Water was added to the solution and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) to afford the product **8a** (5.6 mg, 3.6 μmol, 45%) as a pale yellow amorphous.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45-8.40 (m, 8H), 8.20 (d, *J* = 8.5 Hz, 2H), 8.19 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 2H), 7.68 (s, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.21-7.12 (m, 3H), 7.05 (d, *J* = 8.7 Hz, 4H), 6.98 (d, *J* = 8.7 Hz, 4H), 6.85-6.76 (m, 4H), 6.70 (s, 1H), 6.50 (d, *J* = 8.1 Hz, 2H), 3.99 (t, *J* = 6.2 Hz, 4H), 3.94-3.85 (m, 12H), 1.82-1.68 (m, 18H), 1.53-1.19 (m, 38H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.5, 160.5, 160.3, 156.3, 156.2, 146.0, 136.7, 134.5, 132.0, 131.8, 130.4, 129.8, 129.0, 127.4, 125.5, 120.3, 119.2, 114.8, 114.7, 111.9, 111.6, 107.0, 101.2, 78.9, 78.7, 68.8, 68.1, 67.9, 67.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 28.9, 26.0, 25.9, 25.8, 25.7; IR(KBr) 2925, 2852, 1587, 1488, 1281, 1250, 1174, 1020, 837, 749, 416 cm^{-1}; HR-MS (FAB); Calcd. For $C_{106}H_{113}N_4O_{10}$ ($[M + H]^+$): 1569.8558. Found: 1569.8560.



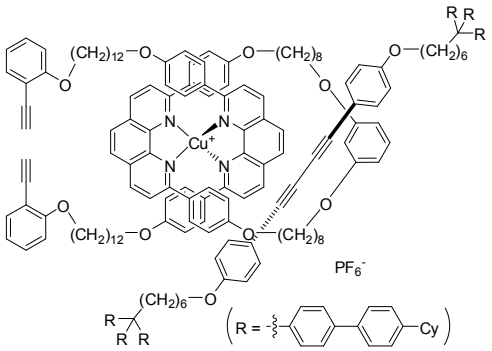
Catenane 8b.

Procedure C was generally followed to synthesize **8b** from tetrahedral Cu(I) complex **7b** (19 mg, 0.010 mmol). The product was purified by silica gel column chromatography using CH_2Cl_2-AcOEt (50/1 (v/v)) to afford **8b** (8.3 mg, 5.1 μmol, 51%) as a pale yellow solid.

m.p. 87.0-88.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47-8.39 (m, 8H), 8.23-8.15 (m, 4H), 8.07-7.98 (m, 4H), 7.68 (s, 2H), 7.66 (s, 2H), 7.45 (d, *J* = 6.0 Hz, 2H), 7.26-7.18 (m, 2H), 7.14 (t, *J* = 8.5 Hz, 1H), 7.06-6.96 (m, 8H), 6.84 (t, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 6.48 (dd, *J* = 8.5 Hz, 2.5 Hz, 2H), 3.98-3.78 (m, 16H), 1.80-1.09 (m, 64H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 160.5, 160.5, 160.5, 156.2, 156.2, 146.1, 136.6, 136.6, 134.5, 131.8, 131.8, 130.4, 129.8, 128.9, 127.4, 127.4, 125.5, 120.3, 119.1, 119.0, 114.7, 114.7, 112.0, 111.7, 106.9, 101.0, 78.8, 78.1, 68.8, 68.0, 67.9, 67.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.3, 29.3, 29.3, 29.0, 25.9, 25.9, 25.8, 25.7; IR(KBr) 3433, 3062, 3039, 2924, 2854, 2214, 2144, 1936, 1898, 1720.19, 1597, 1489, 1396,

1281, 1250, 1173, 1119, 1026, 841, 795, 748, 517, 463 cm^{-1}; HR-MS (ESI) Calcd for $C_{110}H_{121}N_4O_8$ ($[M+H^+]$): 1625.91789. Found: 1625.91789.

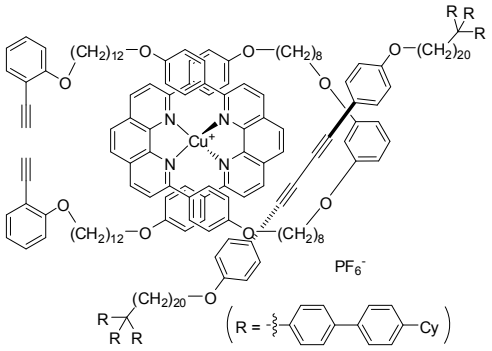
Synthesis of Rotacatenanes 10c and 10d.



Tetrahedral Cu(I)-complex 9c. A representative procedure (procedure D).

To a solution of $[Cu(CH_3CN)_4]PF_6$ **5** (2.4 mg, 6.4 μmol) in dry CH_3CN (1.0 mL) was added **3c** (16 mg, 6.4 μmol) in dry CH_2Cl_2 (2.0 mL) at room temperature. The color of the mixture immediately turned yellow. After stirring for 3 h at room temperature, a solution of **6** (6.0 mg, 6.4 μmol) in dry CH_2Cl_2 (2.0 mL) was added to the reaction mixture, producing a color change to dark red. The resulting mixture was stirred for 1 h. The solvents were removed *in vacuo*. The residue was purified by silica gel column choromatography using CH_2Cl_2-AcOEt (50/1 (v/v)) to afford **9c** (19 mg, 5.2 μmol, 83%) as a dark red amorphous.

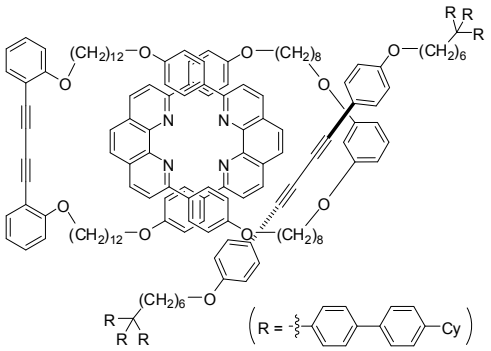
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.88 (s, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.67-7.62 (m, 4H), 7.51-7.45 (m, 24H), 7.42 (dd, *J* = 7.5 Hz, 2.5 Hz, 2H), 7.37-7.18 (m, 34H), 7.15-7.09 (m, 5H), 6.88-6.81 (m, 4H), 6.67 (t, *J* = 2.5 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 4 H), 6.49 (dd, *J* = 7.5 Hz , 2.5 Hz. 2H), 6.03 (d, *J* = 8.5 Hz, 4H), 5.99 (d, *J* = 10 Hz, 4H), 4.00 (t, *J* = 6.8 Hz, 4H), 3.97 (t, *J* = 6.8 Hz, 4H), 3.72 (t, *J* = 6.8 Hz, 4H), 3.54 (t, *J* = 6.0 Hz, 4H), 3.48 (t, *J* = 6.8 Hz, 4H), 3.22 (s, 2H), 2.64-2.44 (m, 10H), 1.93-1.11 (m, 140H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.2, 159.8, 159.7, 159.6, 156.5, 156.4, 147.1, 146.2, 143.5, 143.4, 138.4, 138.1, 137.0, 136.8, 134.0, 133.8, 131.2, 131.0, 130.1, 129.7, 129.5, 129.0, 128.9, 127.8, 127.6, 127.2, 126.7, 126.2, 126.0, 125.8, 124.5, 124.3, 120.2, 114.6, 113.2, 113.0, 113.0, 112.0, 111.6, 107.1, 101.3, 81.8, 80.9, 80.2, 73.5, 68.7, 68.0, 68.0, 67.9, 67.7, 56.0, 44.2, 40.4, 34.4, 30.2, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 29.1, 29.1, 26.9, 26.1, 26.1, 25.9, 25.7; IR(KBr) 3433, 3309, 3024, 2924, 2854, 2137, 2106, 1905, 1604, 1496, 1250, 1173, 1011, 841, 756, 555 cm^{-1}; HR-MS (MALDI-TOF 2)) Calcd for $C_{248}H_{268}N_4O_{10}Cu$ ($[M-PF_6]^+$): 3525.9954. Found: 3525.9887.



Tetrahedral Cu(I)-complex 9d.

Procedure D was generally followed to synthesize **9d** from $[Cu(CH_3CN)_4]PF_6$ **5** (2.6 mg, 6.9 μmol), **3d** (20 mg, 6.9 μmol) and **6** (6.3 mg, 6.9 μmol). The product was purified by silica gel column chromatography using CH_2Cl_2-AcOEt (50/1 (v/v)) to afford **9d** (25 mg, 6.1 μmol, 88%) as a dark red amorphous.

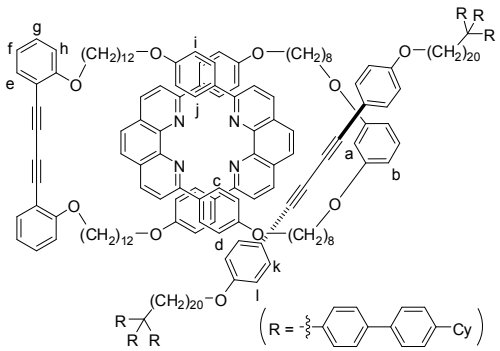
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 7.90 (s, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.74-7.65 (m, 4H), 7.53-7.44 (m, 24H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.37-7.20 (m, 34H), 7.19-7.12 (m, 5H), 6.89-6.81 (m, 4H), 6.67 (s, 1H), 6.65 (d, *J* = 8.5 Hz, 4H), 6.51 (dd, *J* = 9.0 Hz, 2.5 Hz, 2H), 6.05 (d, *J* = 8.5 Hz, 4H), 6.01 (d, *J* = 8.5 Hz, 4H), 4.07-3.95 (m, 8H), 3.79 (t, *J* = 6.0 Hz, 4H), 3.56 (t, *J* = 6.0 Hz, 4H), 3.51 (t, *J* = 6.8 Hz, 4H), 3.23 (s, 2H), 2.65-2.44 (m, 10H), 1.96-1.08 (m, 196H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.2, 159.9, 159.7, 159.6, 156.5, 156.4, 147.0, 146.4, 143.5, 143.4, 138.4, 138.2, 137.0, 136.8, 134.0, 133.8, 131.2, 131.0, 130.1, 129.7, 129.6, 129.0, 128.9, 127.8, 127.6, 127.1, 126.8, 126.2, 126.0, 125.9, 124.5, 124.4, 120.2, 114.6, 113.2, 113.0, 113.0, 112.0, 111.6, 107.1, 101.4, 81.8, 80.9, 80.2, 73.5, 68.7, 68.1, 68.0, 67.9, 67.7, 56.0, 44.1, 40.5, 34.4, 30.5, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.1, 29.1, 26.9, 26.2, 26.1, 26.1, 26.0, 25.9, 25.7; IR(KBr) 3433, 3024, 2924, 2854, 2137, 2106, 1905, 1604, 1496, 1281, 1250, 1173, 1003, 841, 748, 555 cm^{-1}; HR-MS (MALDI-TOF 2)) Calcd for $C_{276}H_{324}N_4O_{10}Cu$ ($[M\text{-}PF_6]^+$): 3917.4258. Found: 3917.4660.



Rotacatenane 10c. A representative procedure (procedure E).

A mixture of the Cu(I)-complex **9c** (20 mg, 5.3 μmol), CuCl (52 mg, 0.53 mmol) and $CuCl_2$ (8.6 mg, 0.064 mmol) in dry DMF (10 mL) was stirred at room temperature.[5] After 72 h, the solvent was removed *in vacuo*. Water was added to the residue and aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over $MgSO_4$ and concentrated. The residue was purified by short silica gel chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) and the residue was added CH_3CN (2.0 mL), CH_2Cl_2 (2.0 mL), H_2O (2.0 mL) and KCN (23 mg). the solution was stirred at room temperature for overnight. Water was added to the solution and aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) and preparative thin layer chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) to afford the rotacatenane **26a** (7.4 mg, 2.1 μmol, 40%) as a yellow amorphous.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39-8.34 (m, 8H), 8.15 (d, *J* = 8.5 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.64 (s, 2H), 7.61 (s, 2H), 7.50-7.42 (m, 24H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.31-7.26 (m, 16H), 7.25-7.19 (m, 12H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 1H), 7.04-6.99 (m, 8H), 6.76 (t, *J* = 7.5 Hz, 2H), 6.73-6.69 (m, 3H), 6.61 (d, 10.0 Hz, 4H), 6.45 (dd, *J* = 7.5 Hz, 2.5 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 4H), 3.94-3.88 (m, 8H), 3.86 (t, *J* = 6.8 Hz, 4H), 3.66 (t, *J* = 6.8 Hz, 4H), 2.55-2.44 (m, 10H), 1.96-1.00 (m, 140H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 160.6, 160.5, 160.4, 159.6, 156.6, 156.2, 147.0, 146.3, 146.0, 138.4, 138.1, 136.5, 136.5, 134.5, 134.0, 131.9, 131.7, 130.3, 129.5, 129.0, 128.9, 127.5, 127.3, 127.2, 126.8, 126.2, 125.5, 125.4, 120.2, 119.4, 119.0, 114.7, 114.7, 114.5, 113.6, 111.9, 111.6, 107.2, 101.1, 81.8, 79.0, 78.2, 73.7, 68.7, 68.1, 68.0, 68.0, 67.9, 55.9, 44.2, 40.4, 34.4, 30.2, 29.9, 29.9, 29.8, 29.7, 29.5, 29.5, 29.4, 29.4, 29.2, 28.9, 26.9, 26.2, 26.1, 26.1, 25.9, 25.8, 25.7; IR(KBr) 3433, 3032, 2924, 2854, 2206, 2144, 1905, 1728, 1597, 1496, 1281, 1250, 1173, 1011, 833, 818, 748, 532 cm^{-1}; HR-MS (MALDI-TOF 2)) Calcd for $C_{248}H_{267}N_4O_{10}$ ($[M+H]^+$): 3461.0502. Found: 3461.0447.

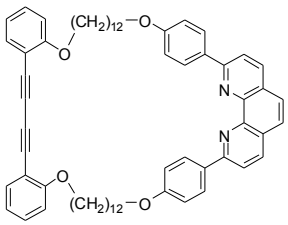


Rotacatenane 10d.

Procedure E was generally followed to synthesize **10d** from **9d** (23 mg, 5.6 μmol). The product was purified by silica gel column chromatography using CH_2Cl_2-AcOEt (50/1 (v/v)) and preparative thin layer chromatography using CH_2Cl_2-AcOEt (50/1(v/v)) to afford **10d** (6.3 mg, 1.6 μmol, 29%) as a yellow amorphous.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43-8.34 (m, 8H), 8.20-8.14 (m, 4H), 8.04-7.97 (m, 4H), 7.69-7.65 (m, 4H), 7.51-7.45 (m, 24H), 7.42 (d, *J* = 10.0 Hz, 2H), 7.36-7.30 (m, 16H), 7.26-7.20 (m, 12H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.07-7.02 (m, 8H), 6.78 (t, *J* = 7.5 Hz, 2H), 6.76-6.71 (m, 3H), 6.65 (d, *J* = 8.5 Hz, 4H), 6.46 (dd, *J* = 8.5 Hz, 2.5 Hz, 2H), 4.01 (t, *J* = 6.8 Hz, 4H), 3.98-3.91 (m, 8H), 3.88 (t, *J* = 7.5 Hz, 4H), 3.73 (t, *J* = 6.0 Hz, 4H), 2.63-2.44 (m, 10H), 1.93-1.07 (m, 196H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 160.6, 160.5, 160.4, 159.7, 156.6, 156.3, 147.0, 146.4, 146.3, 146.0, 138.4, 138.2, 136.5, 134.6, 134.0, 132.0, 131.8, 130.3, 129.6, 129.5, 129.0, 128.9, 127.5, 127.4, 127.1, 126.8, 126.2, 125.5, 125.4, 120.2, 119.4, 119.1, 114.7, 114.5, 113.6, 111.9, 111.6, 107.2, 101.1, 81.7, 79.0, 78.2, 73.6, 68.7, 68.1, 68.1, 68.0, 56.0, 44.2, 40.5, 34.4, 30.5, 30.0, 29.9, 29.7, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.4, 29.1, 28.9, 26.9, 26.2, 26.1, 26.0, 25.8, 25.7; IR(KBr) 3433, 3032, 2924, 2854, 2206, 2144, 1905, 1728, 1604, 1496, 1396, 1281, 1250, 1173, 1111, 1026, 1011, 833, 818, 748, 532 cm^{-1}; HR-MS (MALDI-TOF 2)) Calcd for $C_{276}H_{323}N_4O_{10}$ ([M+H]$^+$): 3853.4884. Found: 3853.5077.

Synthesis of Ring Compound 11.

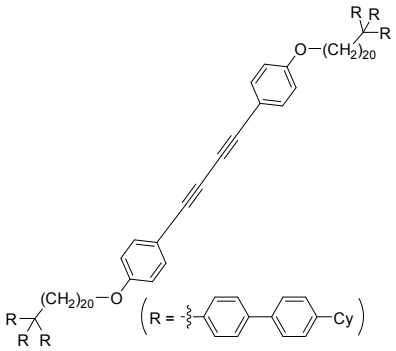


A mixture of **6** (40 mg, 0.042 mmol), CuCl (0.42 g, 4.2 mmol) and $CuCl_2$ (70 mg, 0.52 mmol) in

dry pyridine (74 mL) was stirred at room temperature[5] over 2 h. The color of the mixture changed from green to brown. The solution was stirred for 74 h and the solvent was removed *in vacuo*. Water was added to the dark green residue and aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using $CHCl_3$ to afford **11** (33 mg, 0.035 mmol, 85%) as a colorless solid.

m.p. 186.0-188.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.5 Hz, 4H), 8.24 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.72 (s, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.27-7.24 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 4H), 6.88-6.83 (m, 4H), 4.06-4.0 (m, 8H), 1.87-1.77 (m, 8H), 1.57-1.23 (m, 32H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 160.5, 156.3, 146.0, 136.7, 134.3, 132.0, 130.3, 128.9, 127.5, 125.5, 120.3, 119.2, 114.8, 112.1, 111.9, 78.5, 78.0, 68.9, 68.1, 29.7, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.0, 26.0, 25.9; IR(KBr) 3433, 3070, 3039, 2924, 2854, 2206, 2144, 1597, 1489, 1450, 1396, 1281, 1250, 1173, 1119, 1041, 1026, 841, 795, 748, 571, 517 cm^{-1}; HR FAB-MS Calcd. For $C_{64}H_{71}N_2O_4$ ($[M+H]^+$). 931.5408. Found: 931.5411.

Synthesis of Compound 12 (Dimer of 2b).[6]



A solution of **2b** (42 mg, 0.038 mmol), piperidine (4.0 µl, 0.04 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.0 mg, 5.0 µmol) in CH_2Cl_2 (0.1 mL) was stirred for 18 h. Water was added to the solution and aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using hex-CH_2Cl_2 (5/1 (v/v)) to afford **12** (37 mg, 0.017 mmol, 86%) as a colorless amorphous.

^{1}H NMR (500MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 12H), 7.49 (d, *J* = 8.1 Hz, 12H), 7.42 (d, *J* = 8.7 Hz, 4H), 7.35 (d, *J* = 8.1 Hz, 12H), 7.24 (d, *J* = 8.1 Hz, 12H), 6.81 (d, *J* = 9.0 Hz, 4H), 3.93 (t, *J* = 6.6 Hz, 4H), 2.45-2.73 (m, 10H), 1.70-2.02 (m, 34H), 1.10-1.52 (m, 98H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 146.9, 146.4, 138.3, 138.1, 133.9, 129.5, 127.1, 126.7, 126.2, 114.6, 113.7, 81.3, 73.1, 68.0, 556.0, 44.2, 40.5, 34.4, 30.5, 29.7, 29.6, 29.6, 29.5, 29.4, 29.1, 26.9, 26.1, 26.0, 25.7; IR

(KBr) 3024, 2924, 2846, 1604, 1496, 1466, 1450, 1250, 810, 532 cm^{-1}; Anal. Calcd for $C_{166}H_{202}O_2$: C, 89.43; H, 9.13. Found: C, 89.25; H, 9.32.

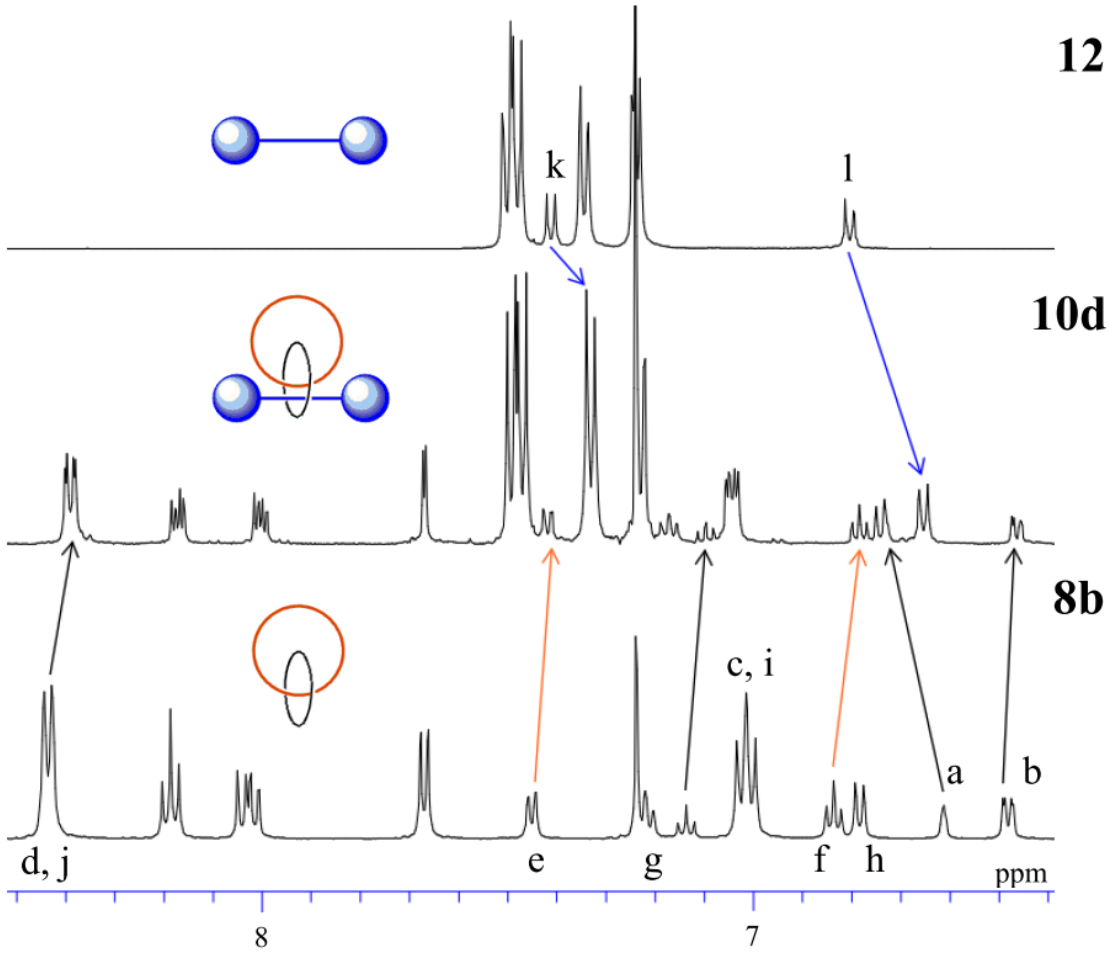


Figure S1. ^{1}H-NMR Spectra (500 MHz, $CDCl_3$) of a) **12**, b) Rotacatenane **10d** and c) [2]Catenane **8b**.

References

(1) J. D. Megiatto, D. I. Schuster, *Org. Lett.* **2011**, *13*, 1808-1811.

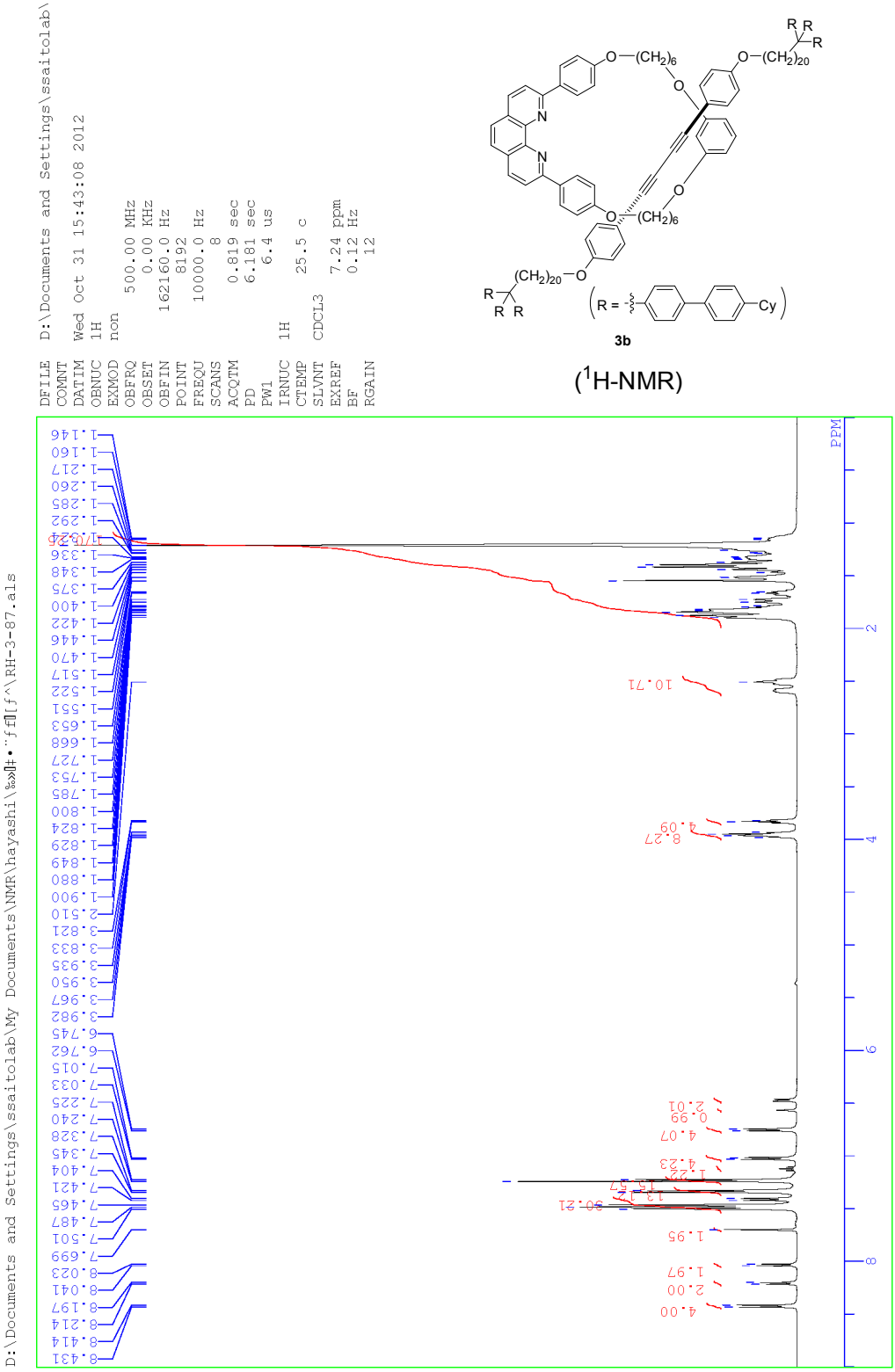
(2) S. Saito, E. Takahashi, K. Nakazono, *Org. Lett.* **2006**, *8*, 5133-5136.

(3) S. Saito, E. Takahashi, K. Wakatsuki, K. Inoue, T. Orikasa, K. Sakai, R. Yamasaki, Y. Mutoh, T. Kasama, *J. Org. Chem.* **2013**, *78*, 3553-3560.

(4) Y. Sato, R. Yamasaki, S. Saito, *Angew. Chem,* **2009**, *121*, 512-515; *Angew. Chem. Int. Ed.* **2009**, *48*, 504-507.

(5) S. Duda, A. Godt, *Eur. J. Org. Chem.* **2003**, 3412-3420.

(6) K. Balaraman, V. Kesavan, *Synthesis* **2010**, *20*, 3461-3466.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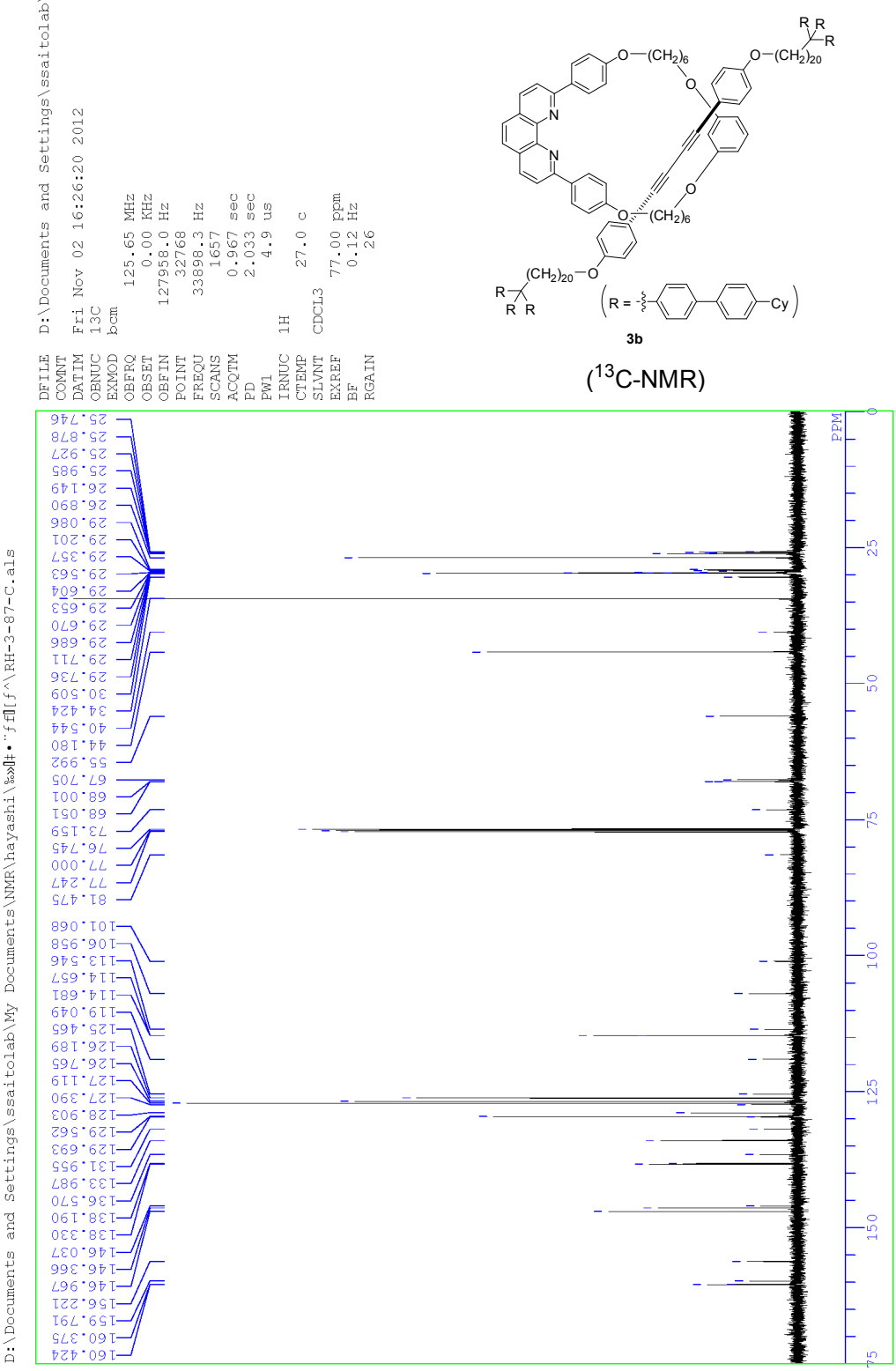
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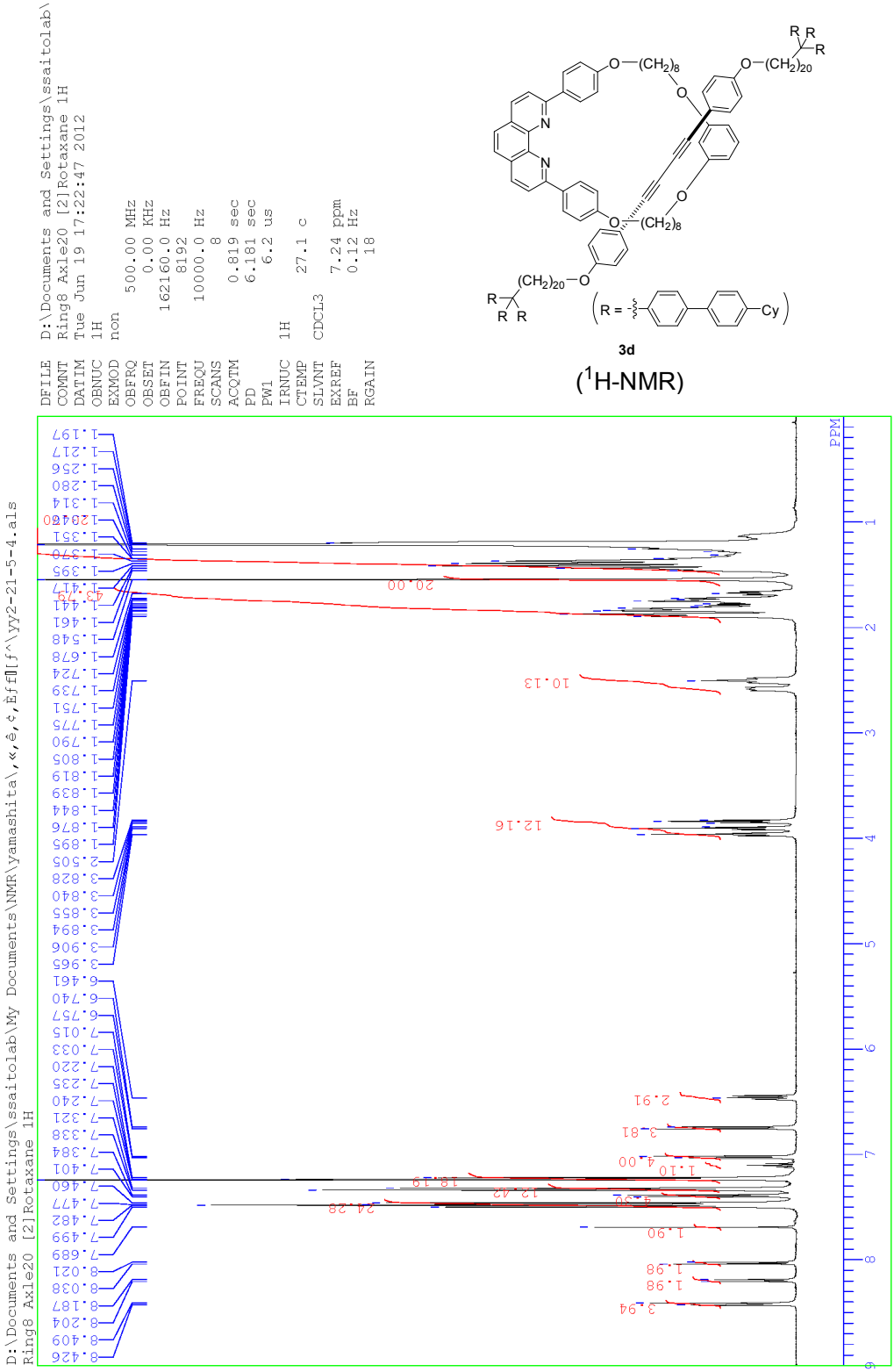
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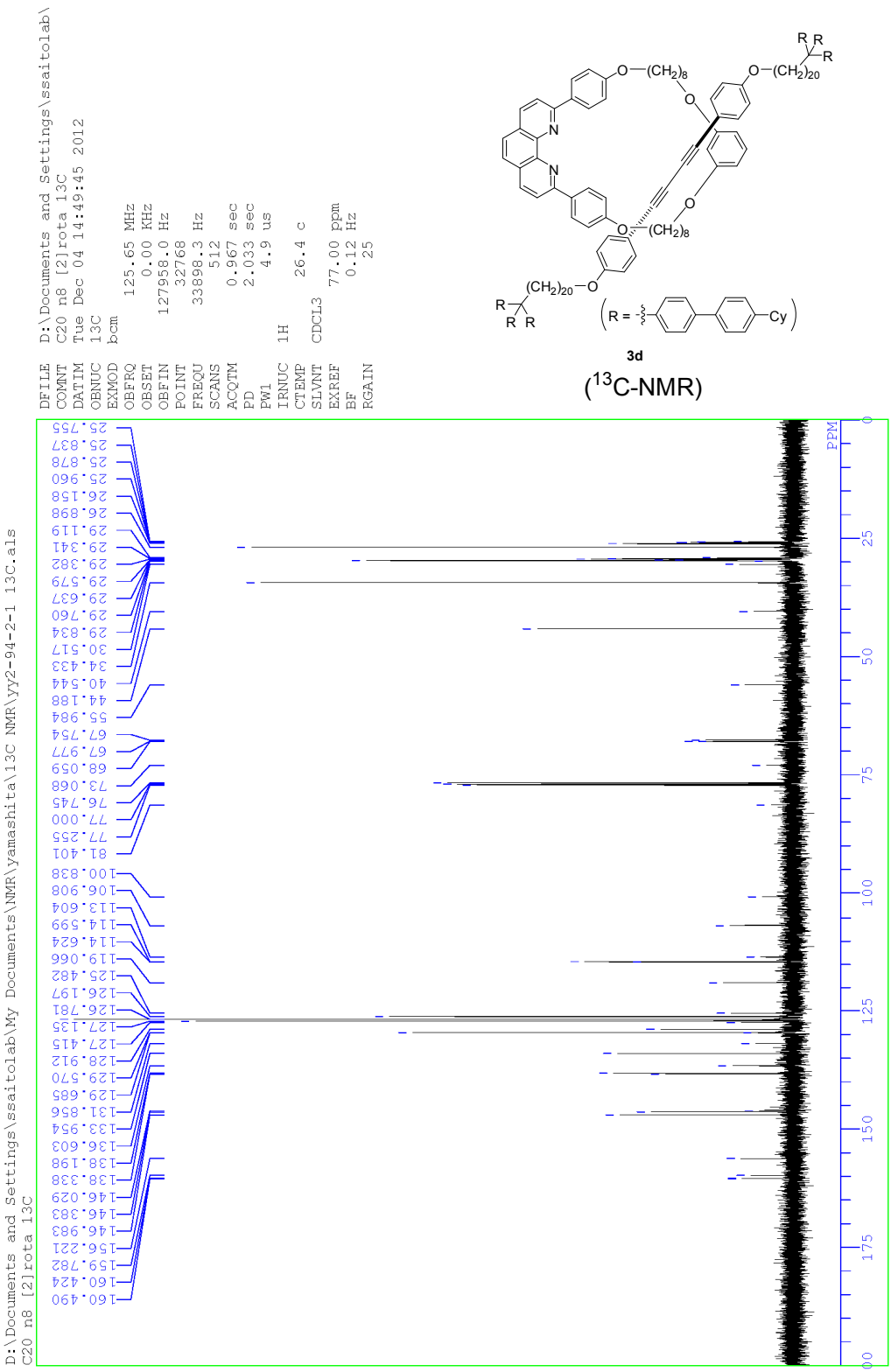
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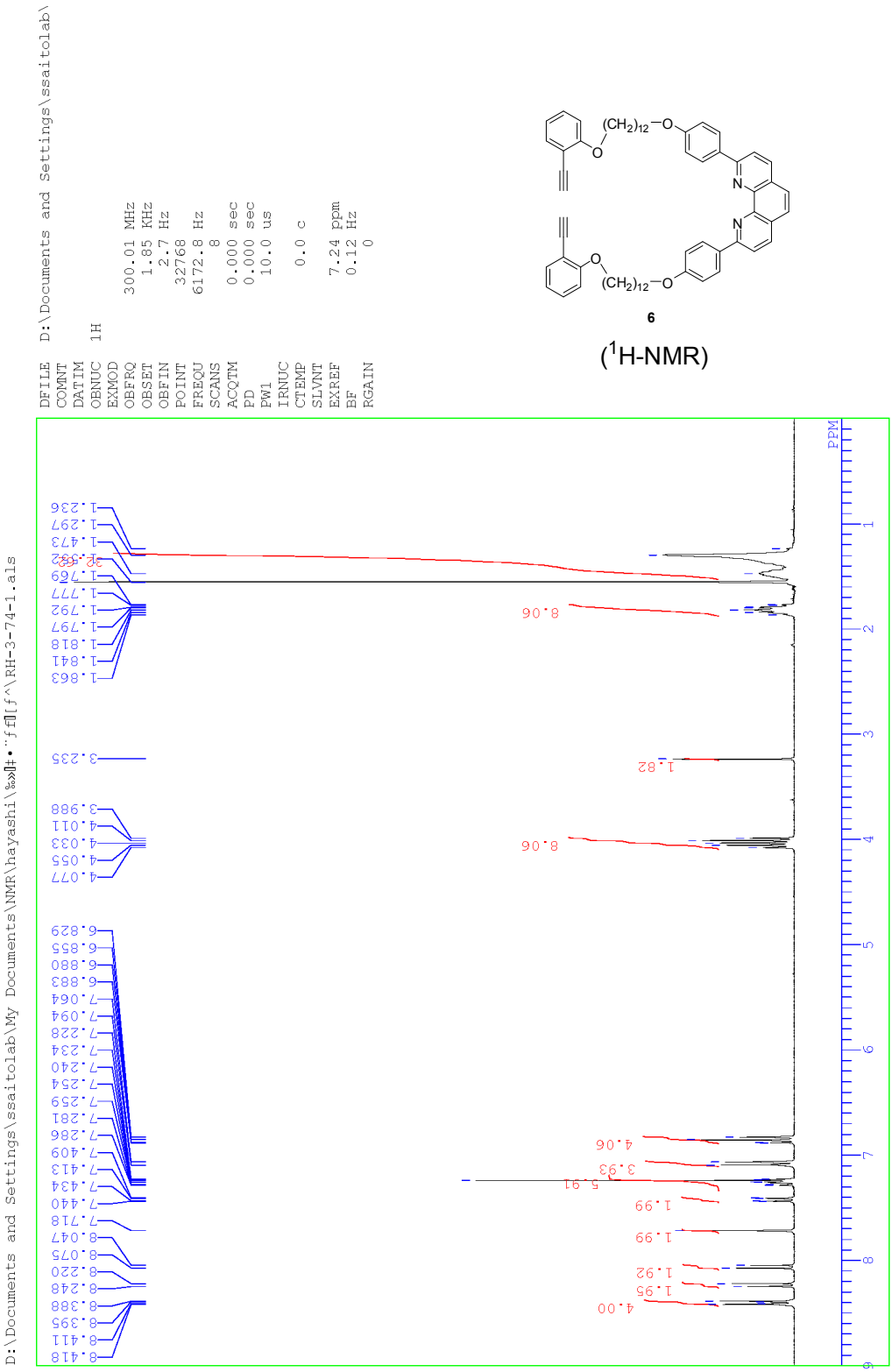
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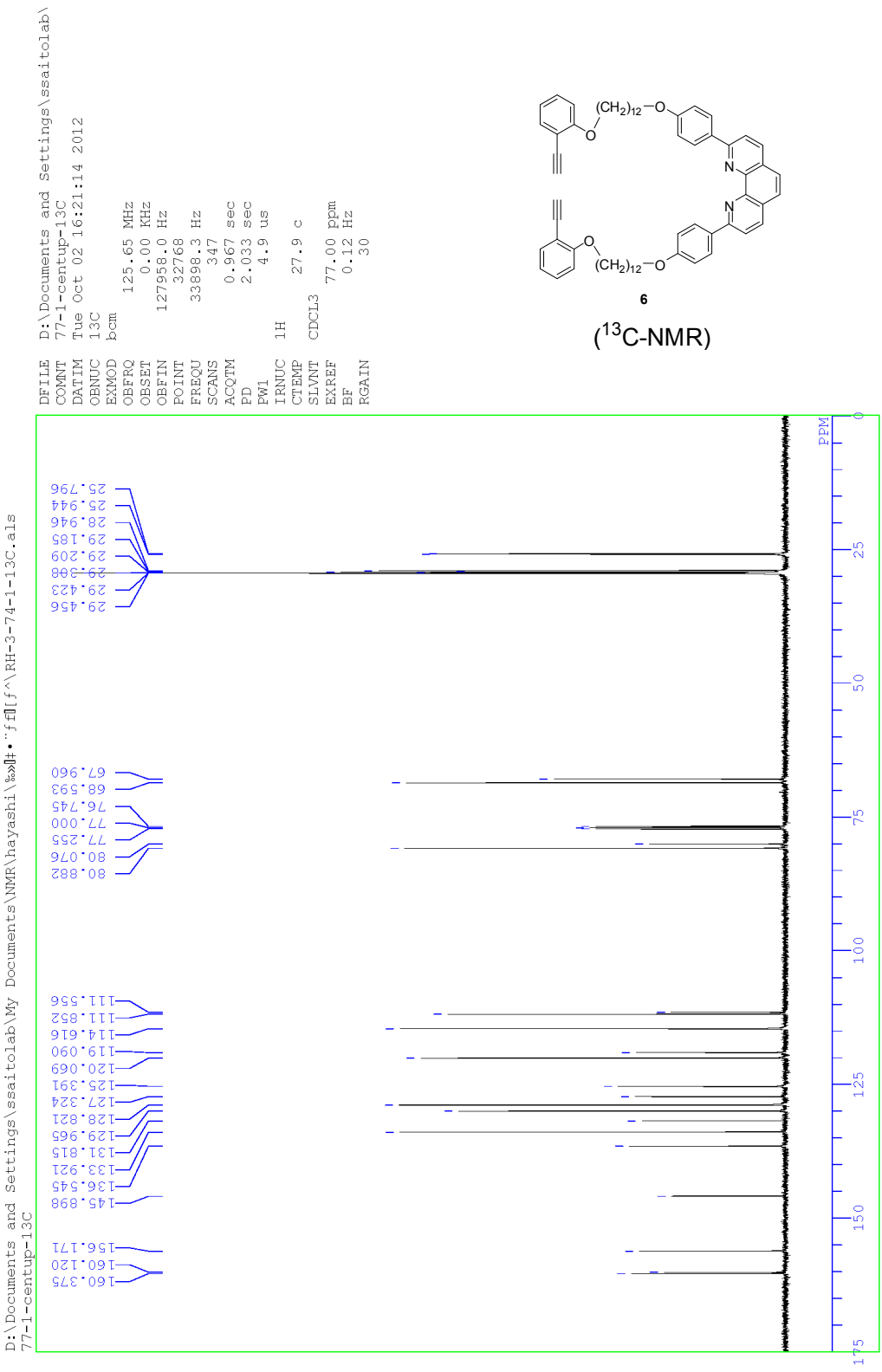
PPM

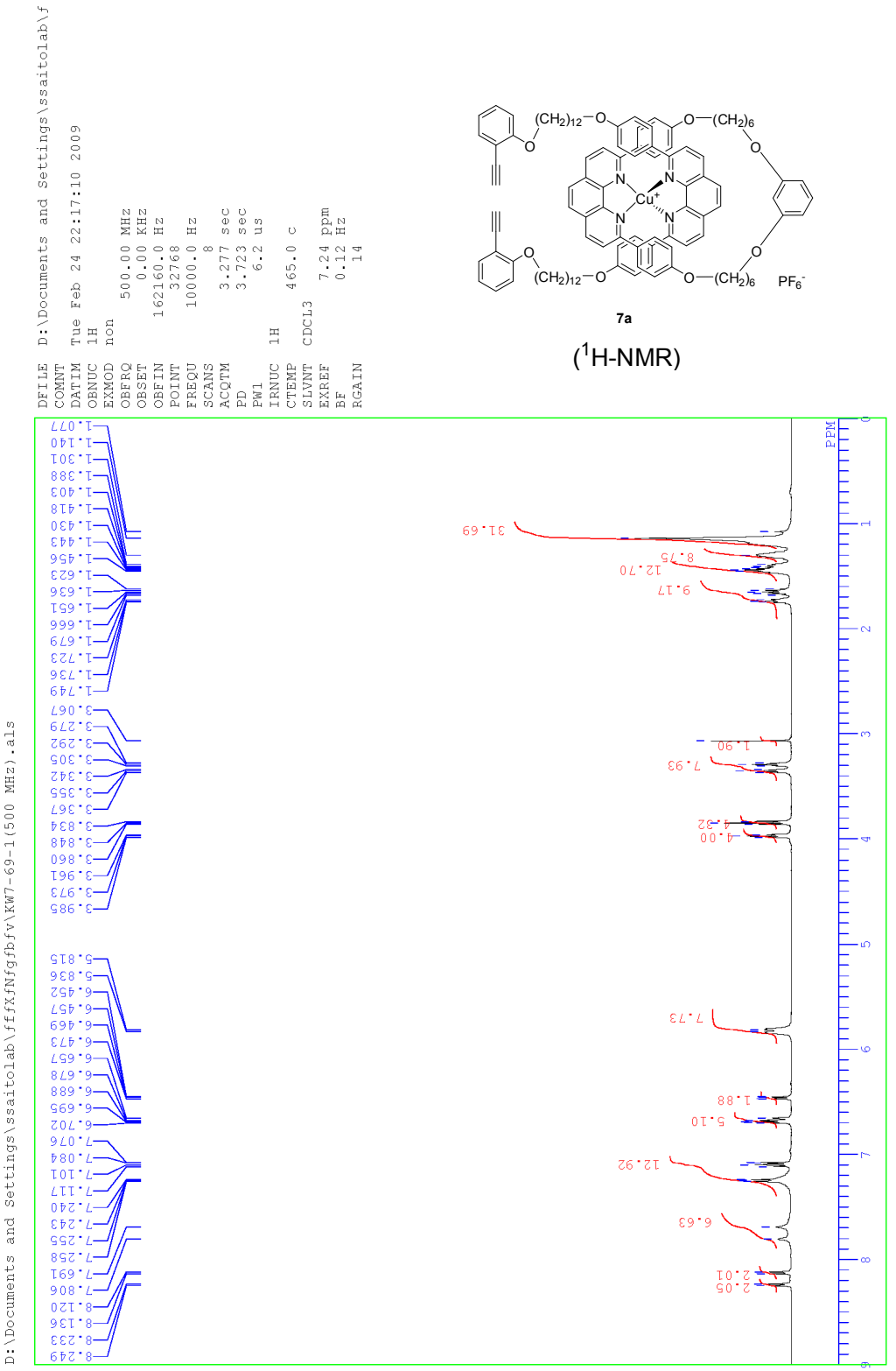
6

(^{1}H-NMR)


DFILE D:\Documents and Settings\ssaitolab\
COMNT 77-1-centup-13C
DATIM Tue Oct 02 16:21:14 2012
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 347
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30
25.796
25.944
28.946
29.185
29.209
29.308
29.423
29.456
67.960
68.593
76.745
77.000
77.255
80.076
80.882
111.556
111.852
114.616
119.090
120.069
125.391
127.324
128.821
129.965
131.815
133.921
136.545
145.898
156.171
160.120
160.375
PPM
0
25
50
75
100
125
150
175
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\‰»Ì•¨ƒfƒ[ƒ^\RH-3-74-1-13C.als
77-1-centup-13C

(CH2)12
O
N
6

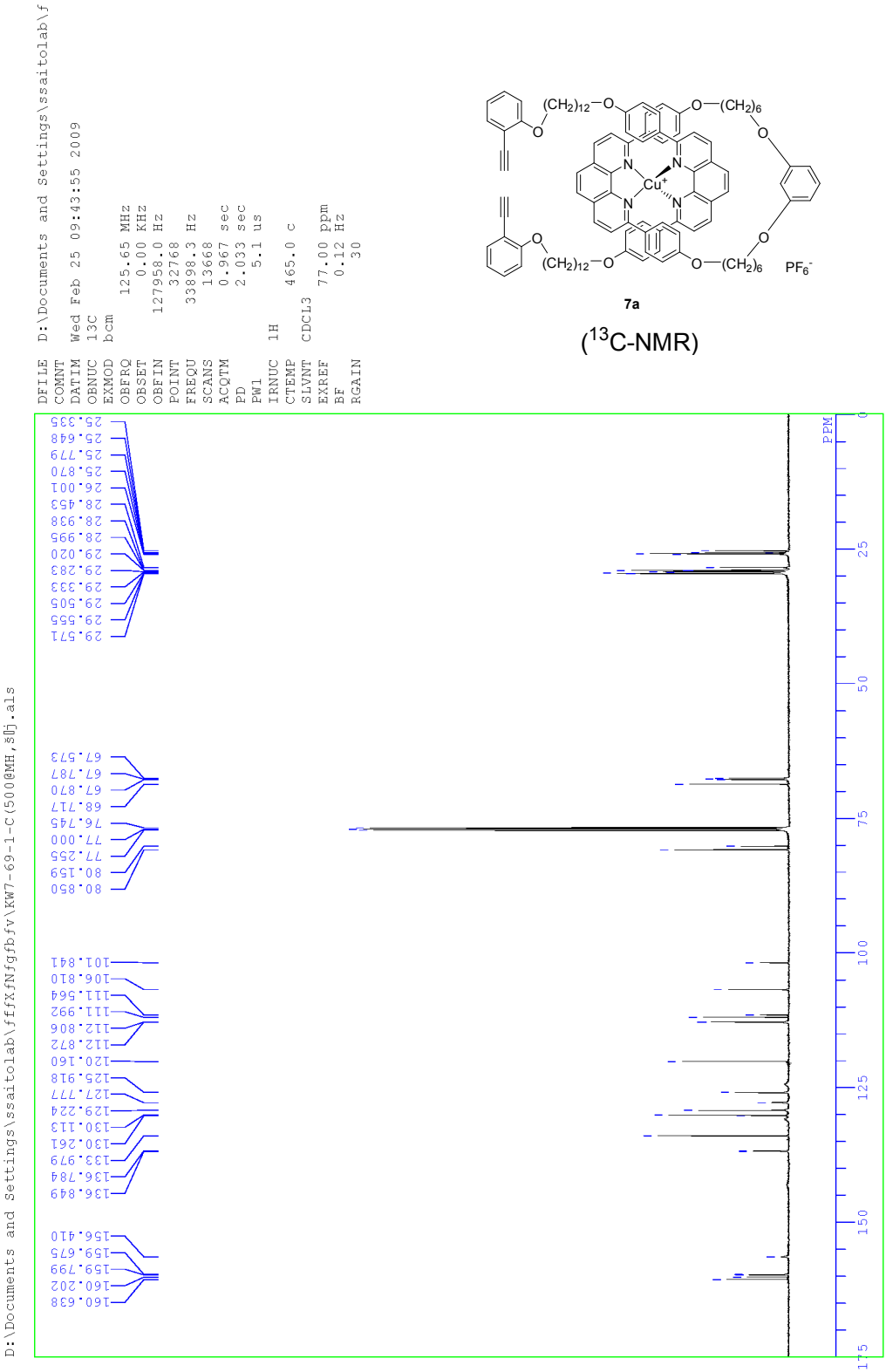
(^{13}C-NMR)

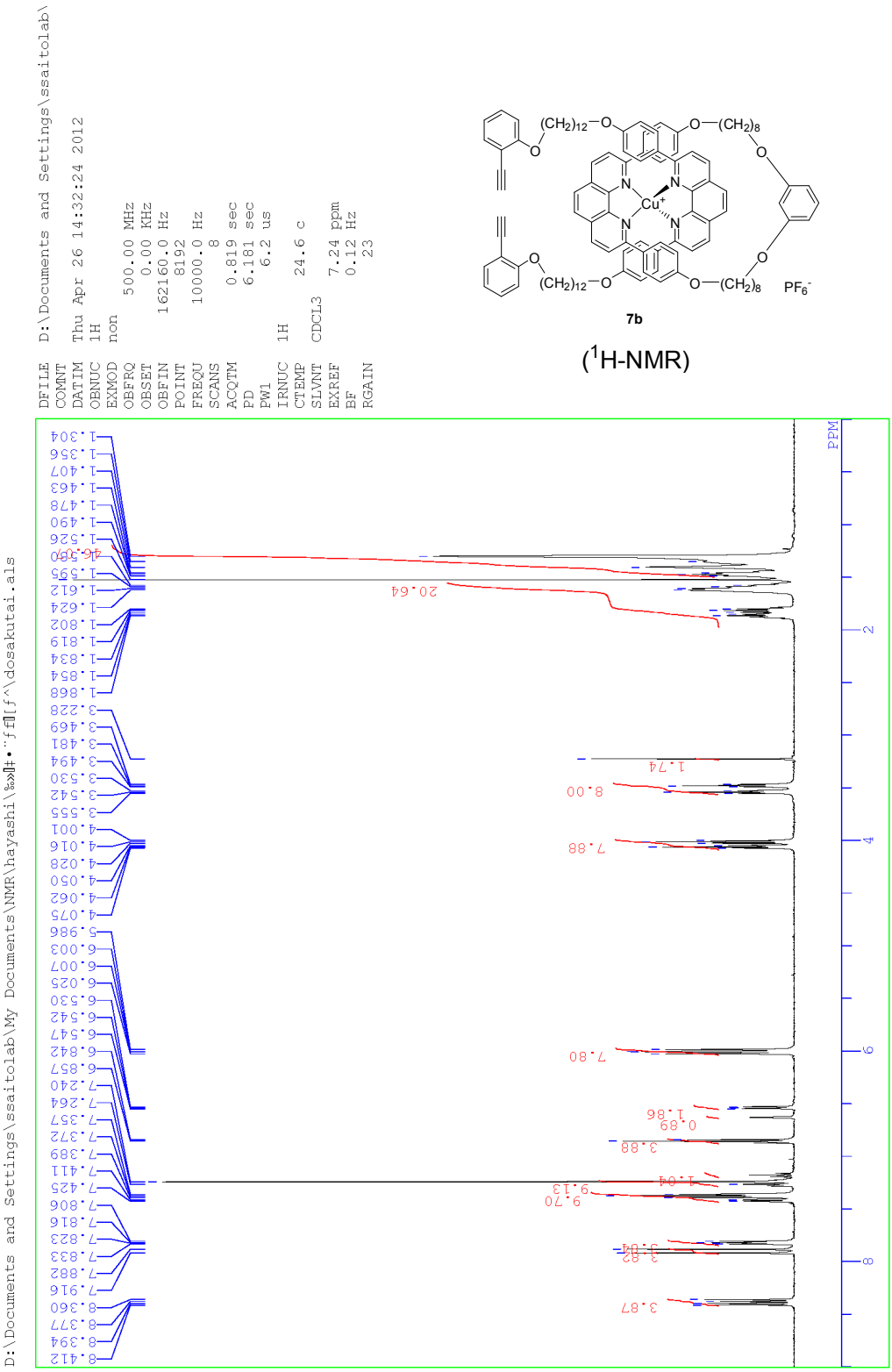

DFILE D:\Documents and Settings\ssaitolab\f
COMNT
DATIM Tue Feb 24 22:17:10 2009
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 8
ACQTM 3.277 sec
PD 3.723 sec
PW1 6.2 us
IRNUC 1H
CTEMP 465.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 14
D:\Documents and Settings\ssaitolab\ffXfNfgfbfv\KW7-69-1(500 MHz).als
PPM
31.69
12.70
8.75
9.17
1.90
7.93
4.32
4.00
7.73
1.88
5.10
12.92
6.63
2.05
2.01

(CH2)12—O
O—(CH2)6
Cu+
PF6-

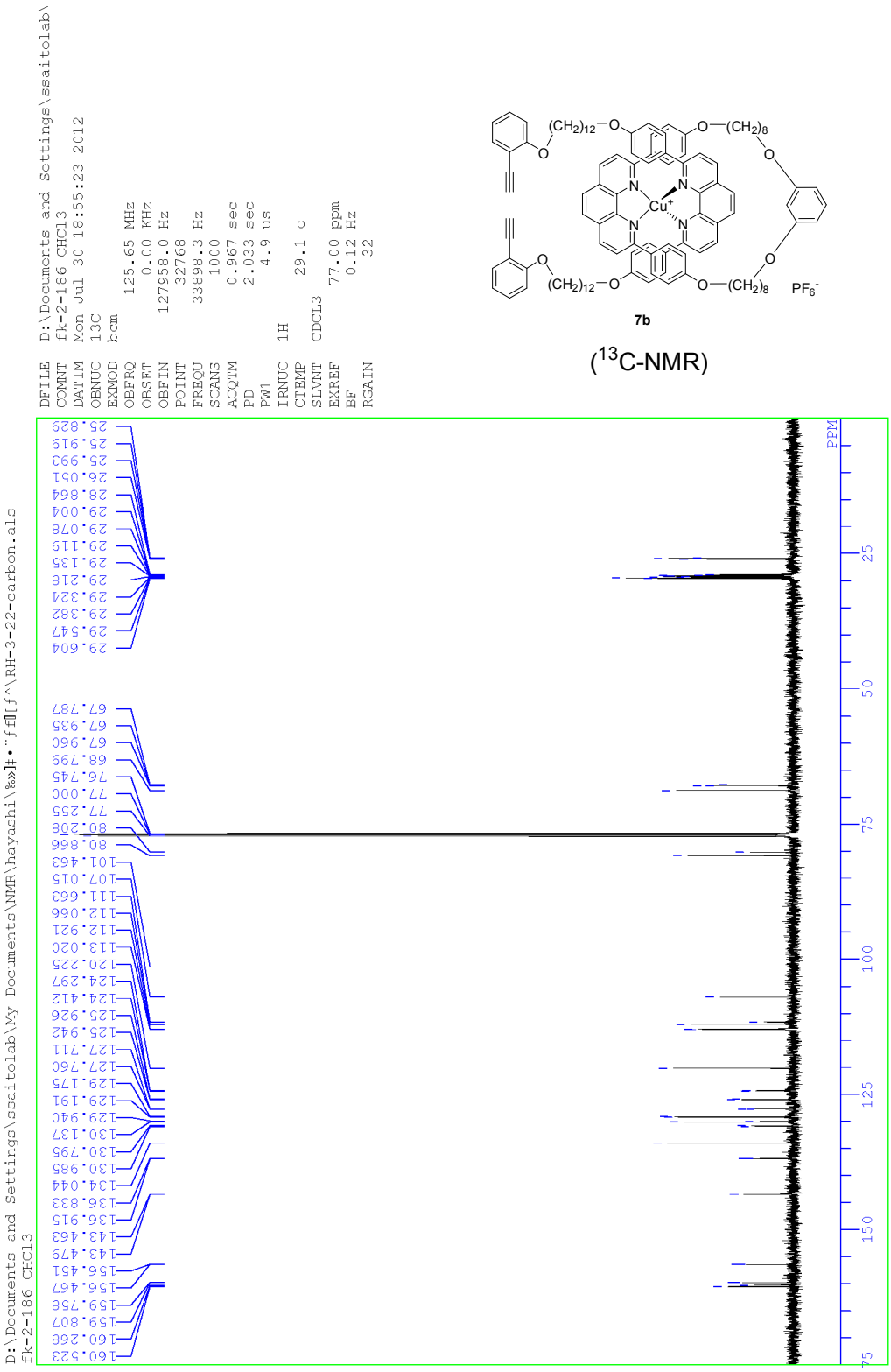
7a

(^{1}H-NMR)


D:\Documents and Settings\ssaitolab\f
DFILE
COMNT
DATIM Wed Feb 25 09:43:55 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 13668
ACQTM 0.967 sec
PD 2.033 sec
PW1 5.1 us
IRNUC 1H
CTEMP 465.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30
D:\Documents and Settings\ssaitolab\ffXfNfgfbfv\KW7-69-1-C(500@MH,šÛj.als
PPM
7a
(^{13}C-NMR)

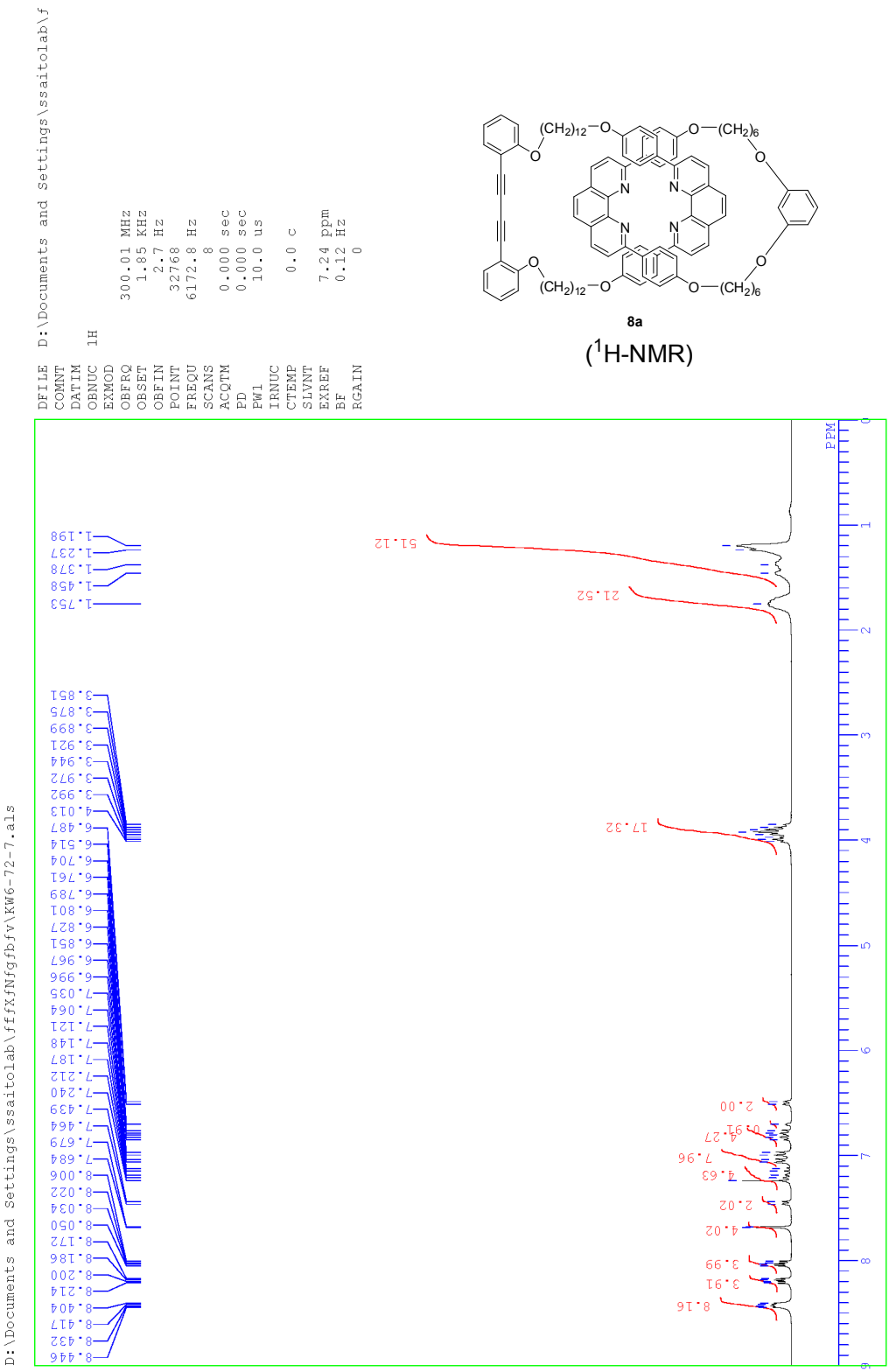

DFILE D:\Documents and Settings\ssaitolab\
COMNT
DATIM Thu Apr 26 14:32:24 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.2 us
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 23
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\‰»¶•¨ƒfl[f^\dosakutai.als
PPM
20.64
8.00
7.88
7.80
9.70
9.13
1.74
1.86
0.89
3.88
3.87
7b
PF6-

(^{1}H-NMR)


D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\%»¶•"ƒfl[f^\RH-3-22-carbon.als
fk-2-186 CHCl3
DFILE D:\Documents and Settings\ssaitolab\
COMNT fk-2-186 CHCl3
DATIM Mon Jul 30 18:55:23 2012
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 1000
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 29.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 32
PPM
25
50
75
100
125
150
175

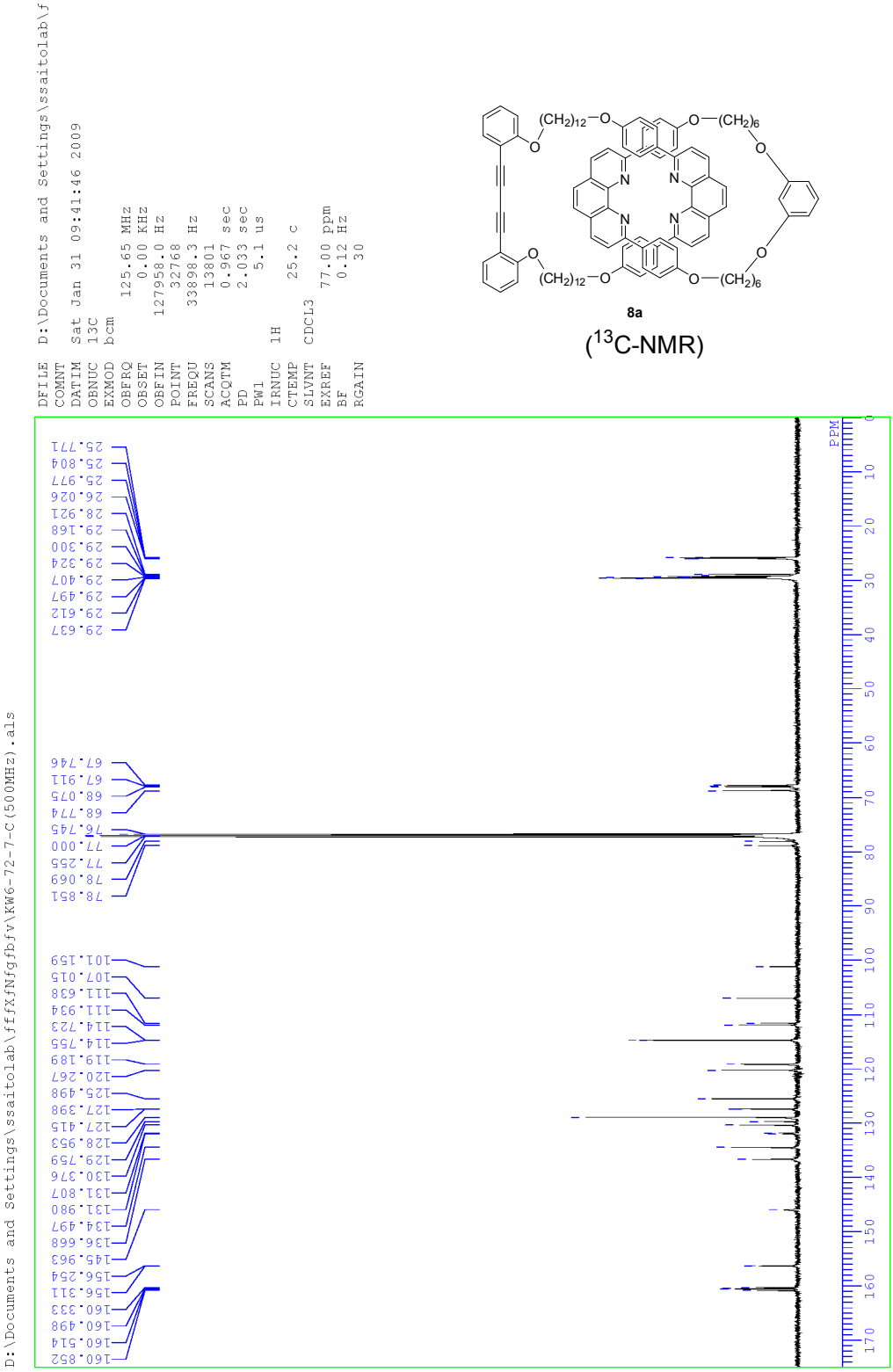
7b

(^{13}C-NMR)


D:\Documents and Settings\ssaitolab\f
DFILE
COMNT
DATIM
OBNUC 1H
EXMOD
OBFRQ 300.01 MHz
OBSET 1.85 KHz
OBFIN 2.7 Hz
POINT 32768
FREQU 6172.8 Hz
SCANS 8
ACQTM 0.000 sec
PD 0.000 sec
PW1 10.0 us
IRNUC
CTEMP 0.0 c
SLVNT
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 0
51.12
21.52
17.32
2.00
0.92
4.27
7.96
4.63
2.02
4.02
3.99
3.91
8.16
PPM
D:\Documents and Settings\ssaitolab\ffXfNfgfbfv\KW6-72-7.als

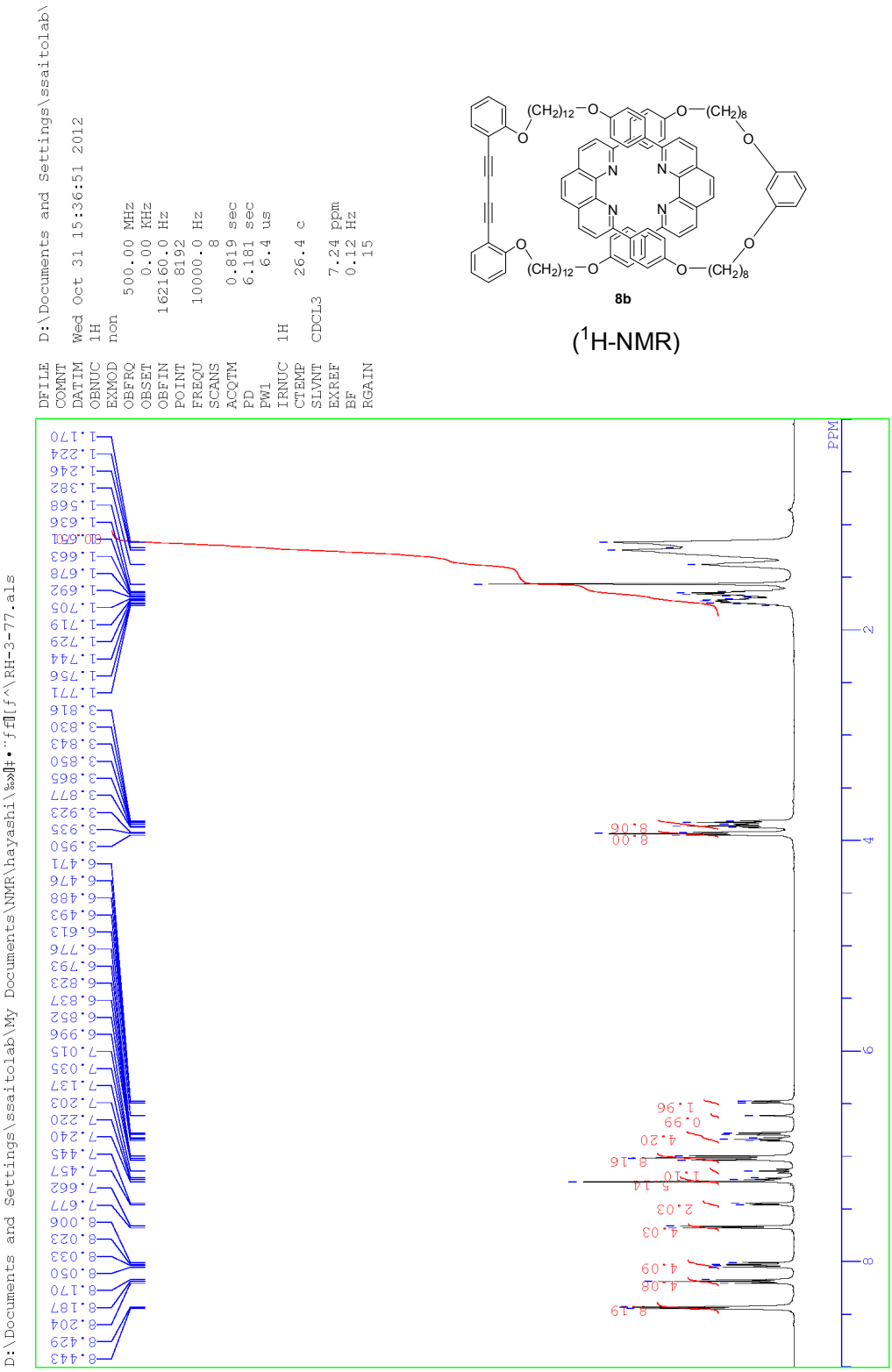
8a

(^{1}H-NMR)


D:\Documents and Settings\ssaitolab\f
DFILE
COMNT
DATIM Sat Jan 31 09:41:46 2009
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 1380l
ACQTM 0.967 sec
PD 2.033 sec
PW1 5.1 us
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 30
D:\Documents and Settings\ssaitolab\ffXfNfgfbfv\KW6-72-7-C(500MHz).als
PPM

8a

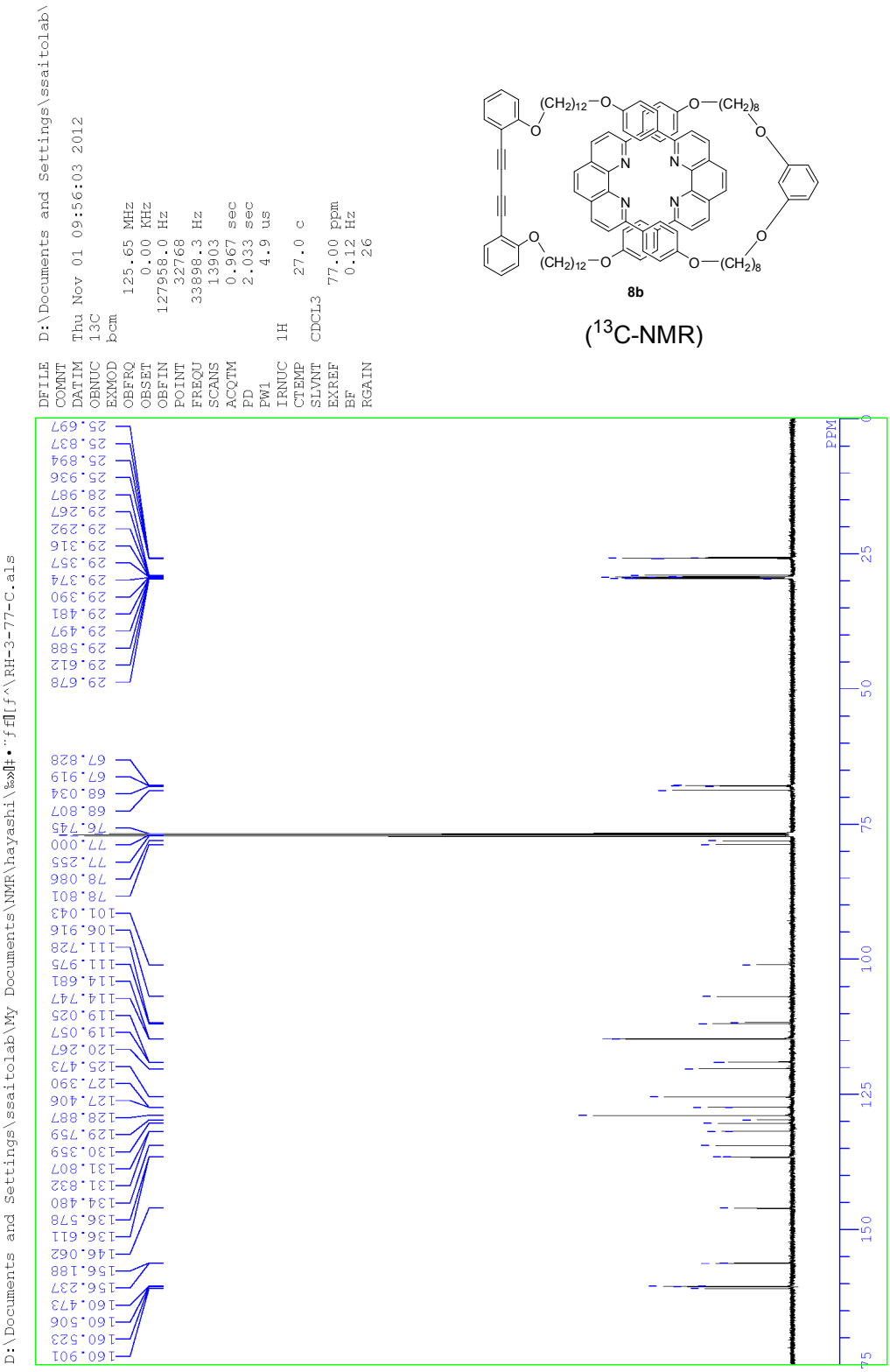
(^{13}C-NMR)


D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Wed Oct 31 15:36:51 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.4 us
IRNUC 1H
CTEMP 26.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 15
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\%»¶•¨ƒfÐ[ƒ^\RH-3-77.als
PPM
8.00
8.06
1.96
0.99
4.20
8.16
1.10
5.14
2.03
4.03
4.09
4.08
8.19

(CH2)12
O
(CH2)8
N

8b

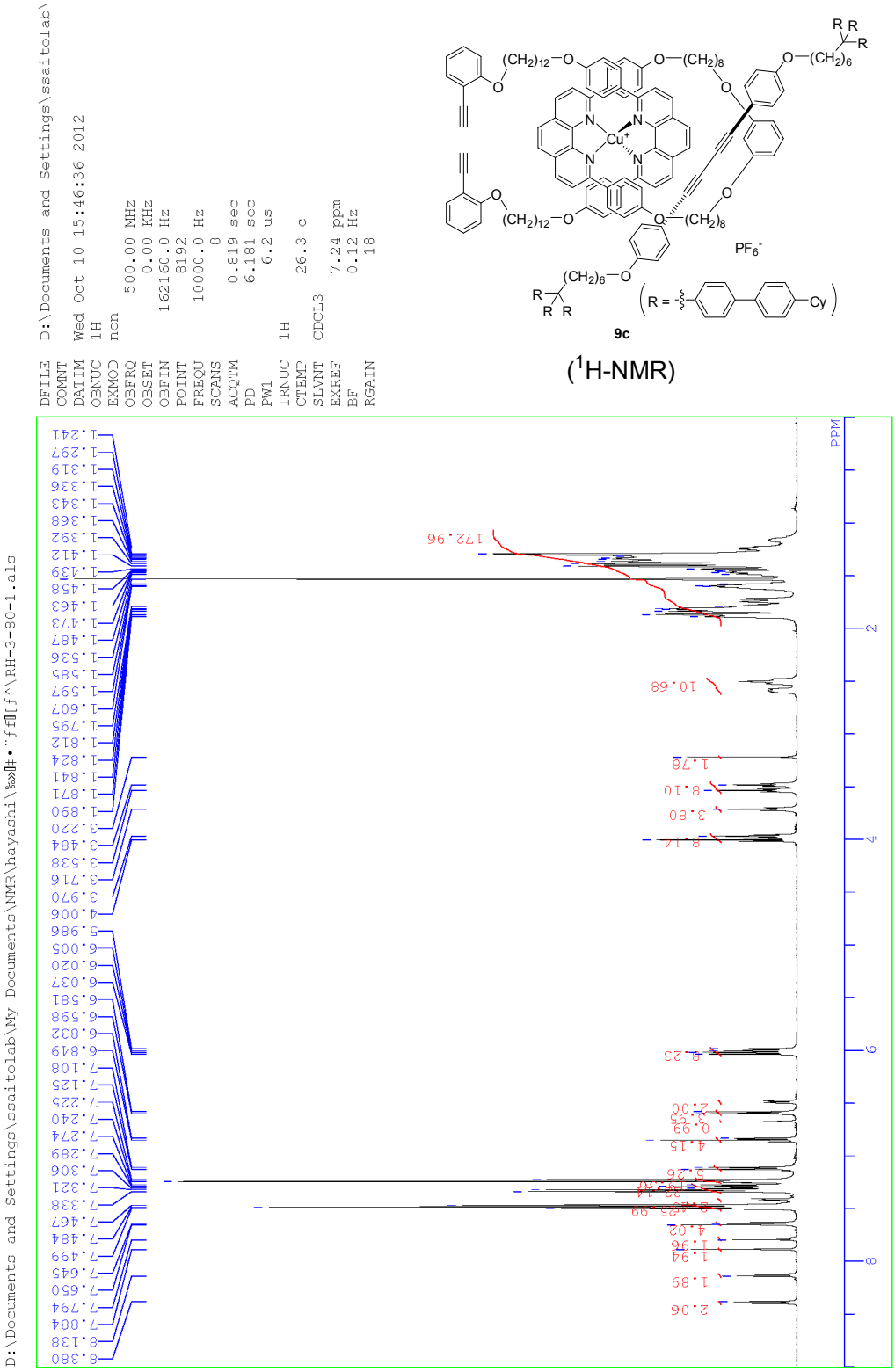
(^{1}H-NMR)

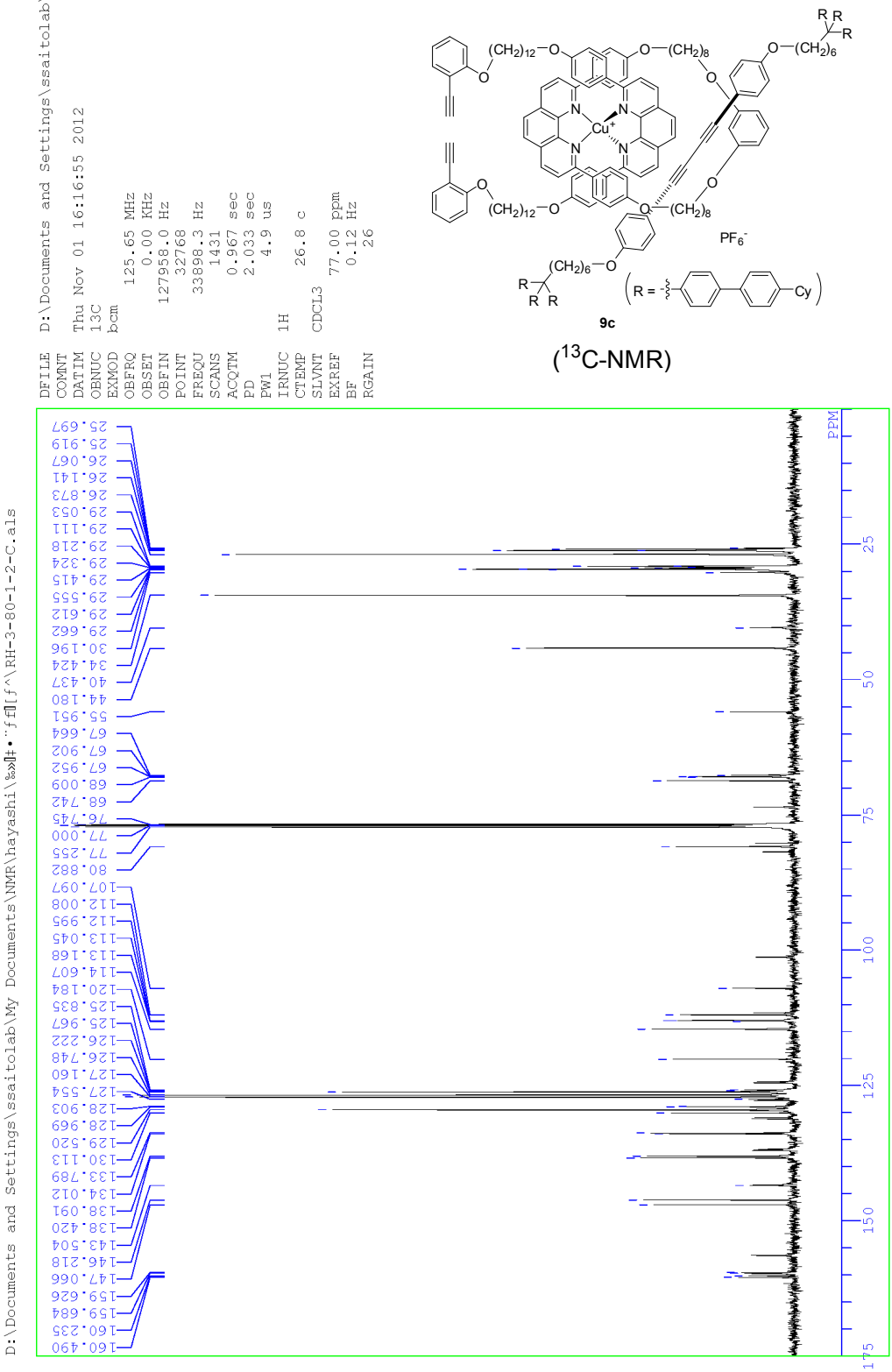

D:\Documents and Settings\ssaitolab\
Thu Nov 01 09:56:03 2012
13C
bcm
125.65 MHz
0.00 KHz
127958.0 Hz
32768
33898.3 Hz
13903
0.967 sec
2.033 sec
4.9 us
1H
27.0 c
CDCL3
77.00 ppm
0.12 Hz
26
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\%»¥•"ƒfl[ƒ^\RH-3-77-C.als
PPM

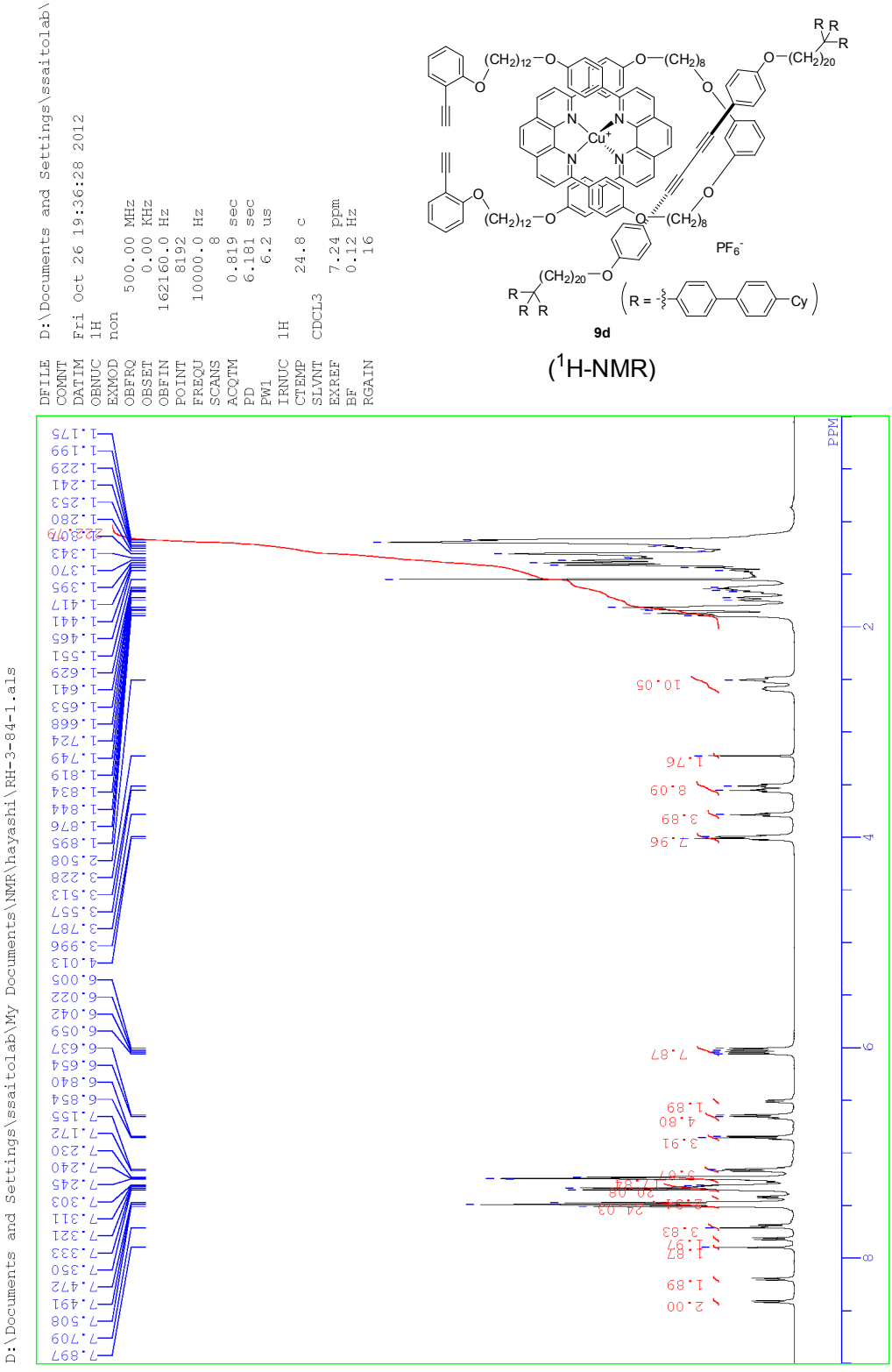
(CH2)12—O
O—(CH2)8
N
O
(CH2)12—O
O—(CH2)8

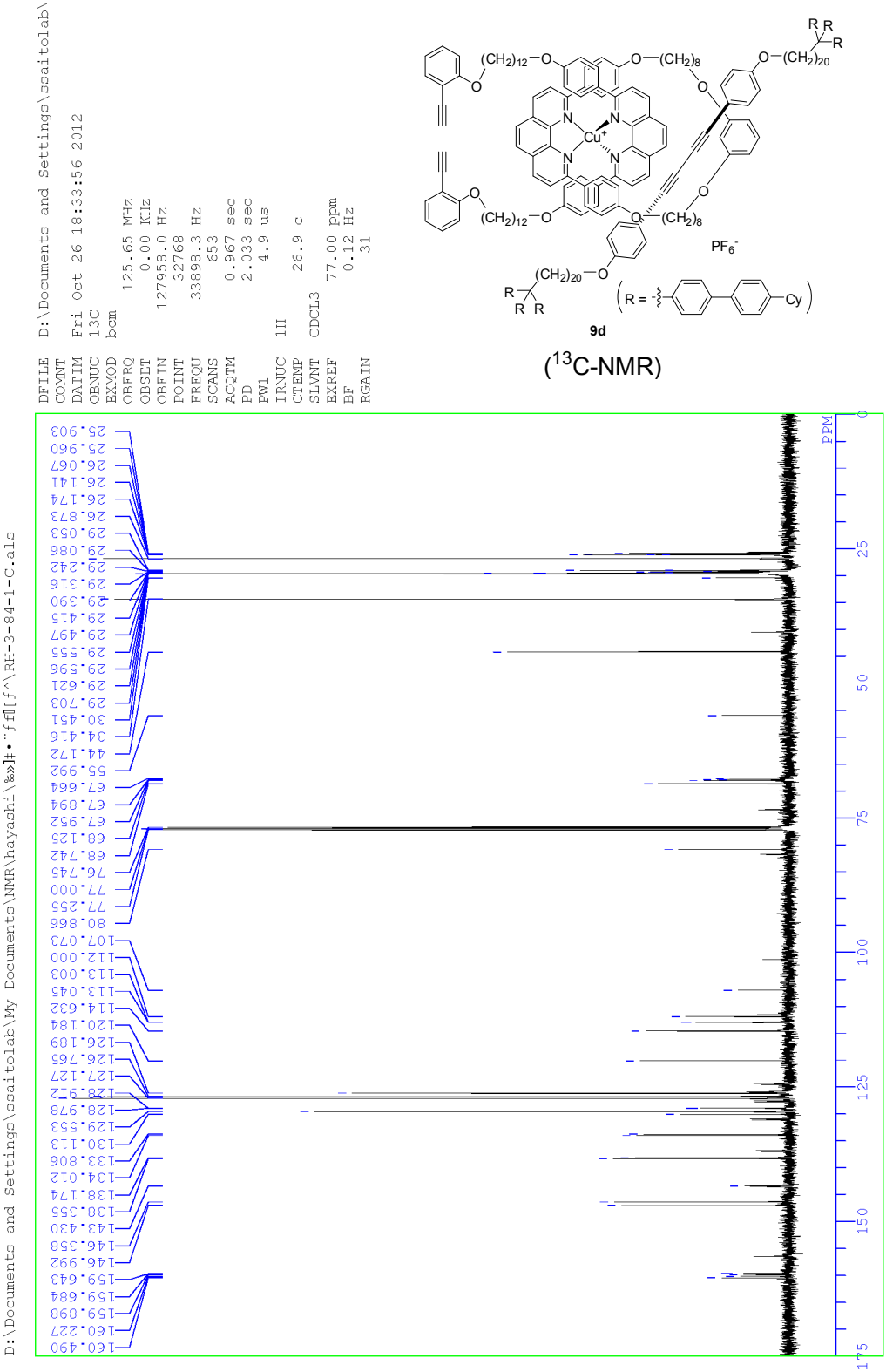
8b

(^{13}C-NMR)


DFILE D:\Documents and Settings\ssaitolab\
COMNT
DATIM Wed Oct 10 15:46:36 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.2 us
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 18
9c
(1H-NMR)
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\%»¶•¨ƒfl[f^\RH-3-80-1.als
PPM

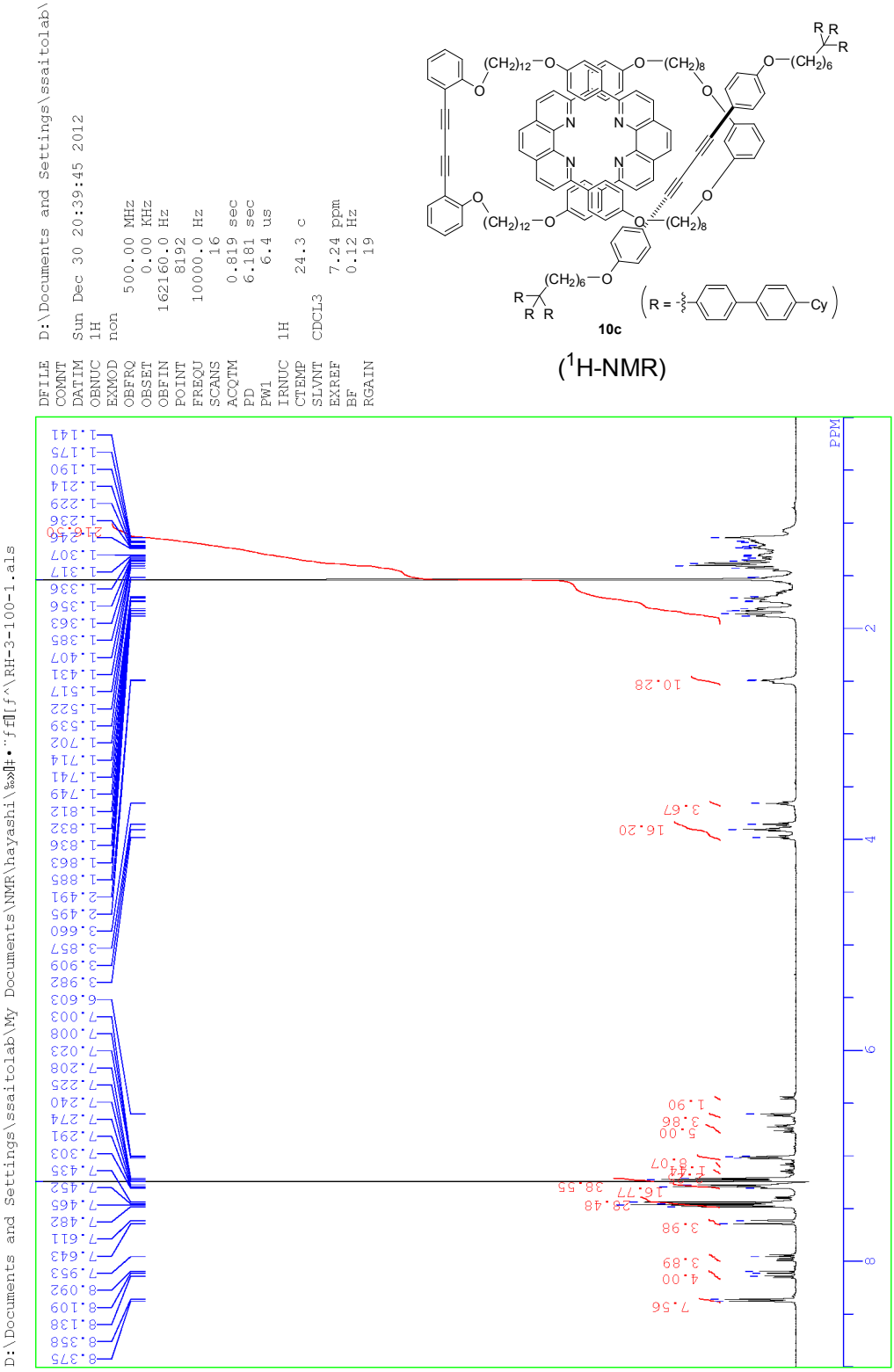

D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Thu Nov 01 16:16:55 2012
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 1431
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 26
PF6-
R = Cy
9c
(13C-NMR)
PPM
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\


D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Fri Oct 26 19:36:28 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.2 us
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 16
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\RH-3-84-1.als
PPM
9d
(1H-NMR)

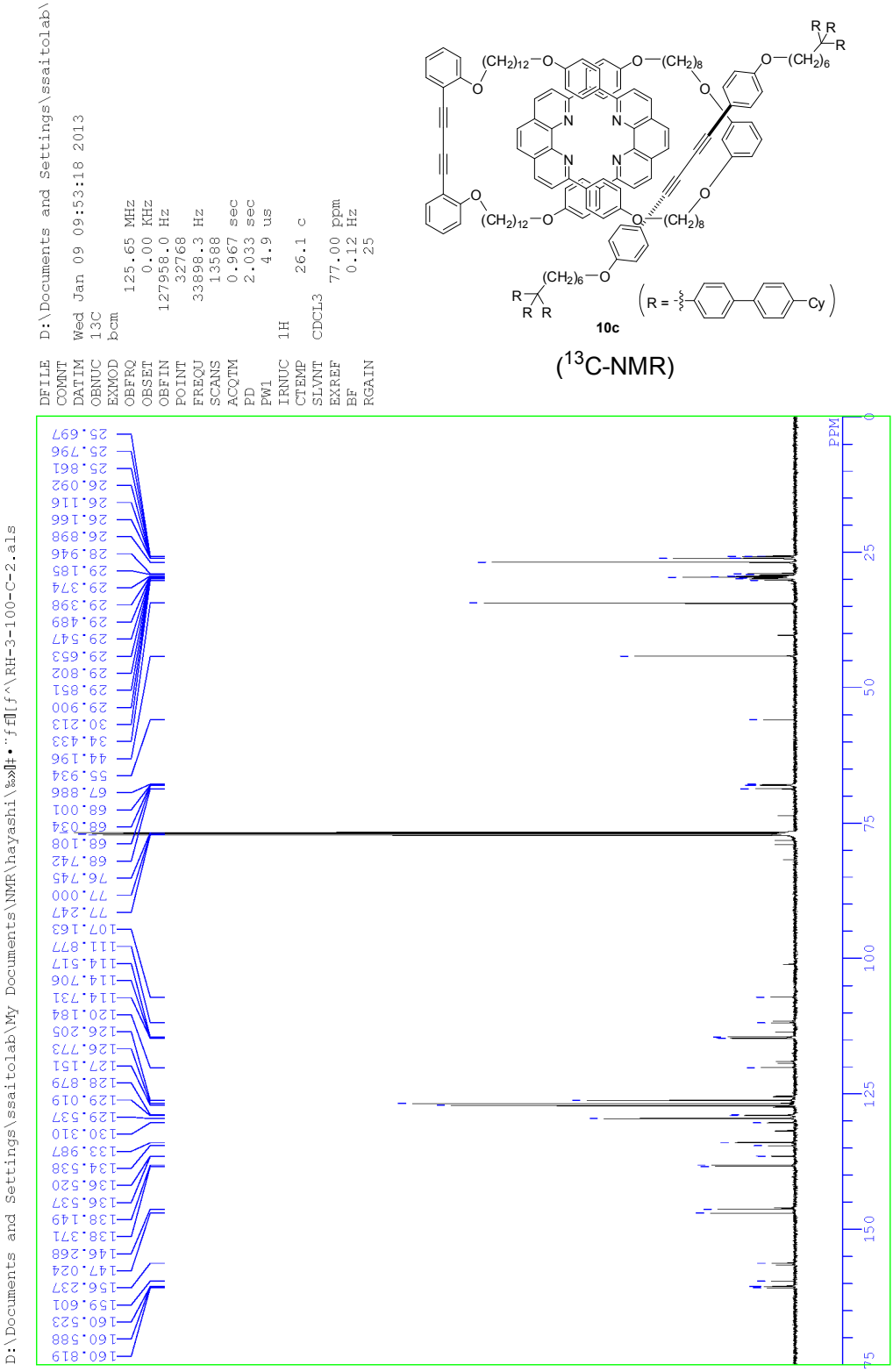

D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Fri Oct 26 18:33:56 2012
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 653
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
1H
IRNUC
CTEMP 26.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 31
PPM
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\

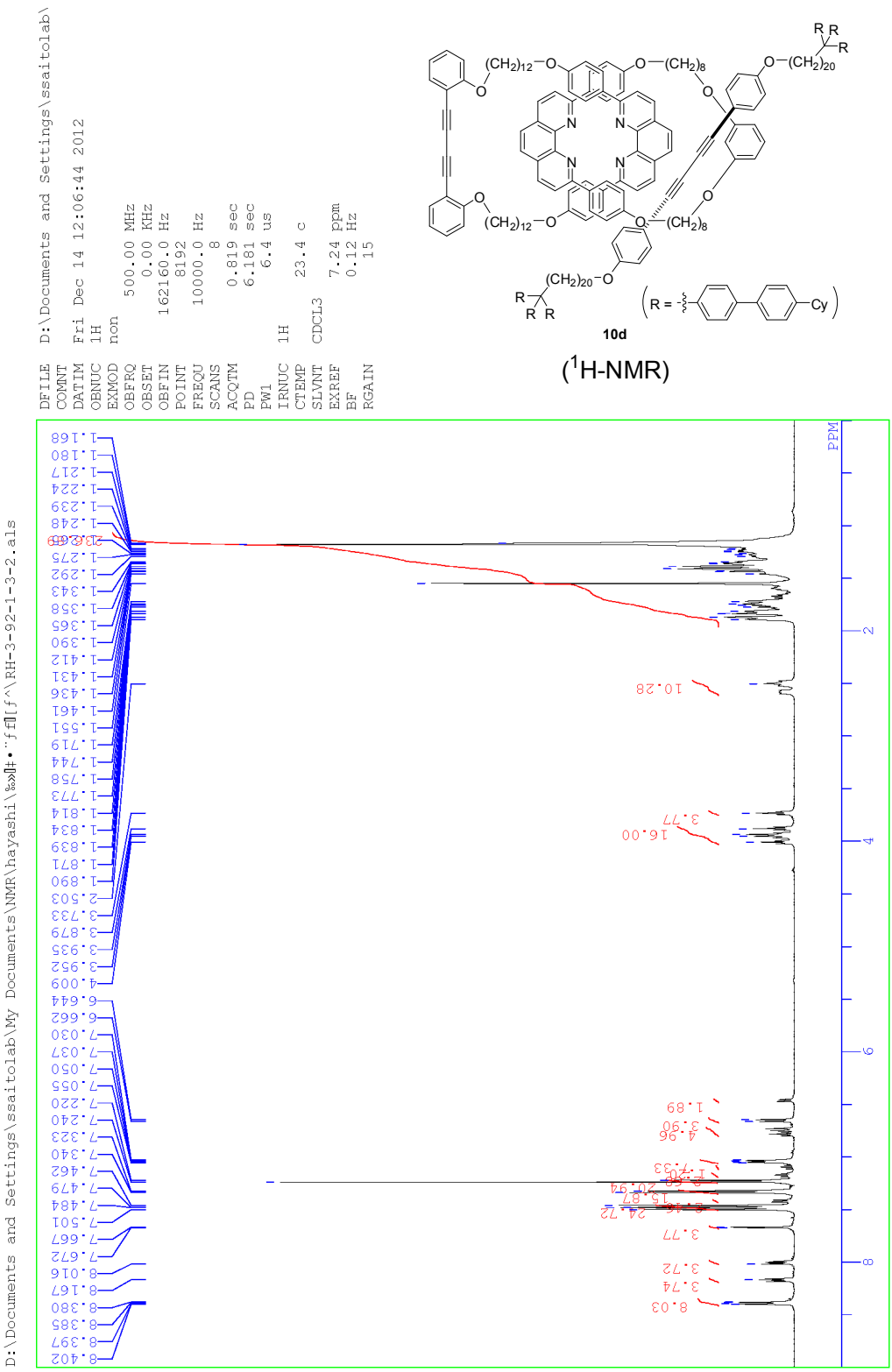
(CH2)12
(CH2)8
(CH2)20
Cu+
PF6-
R = Cy
9d

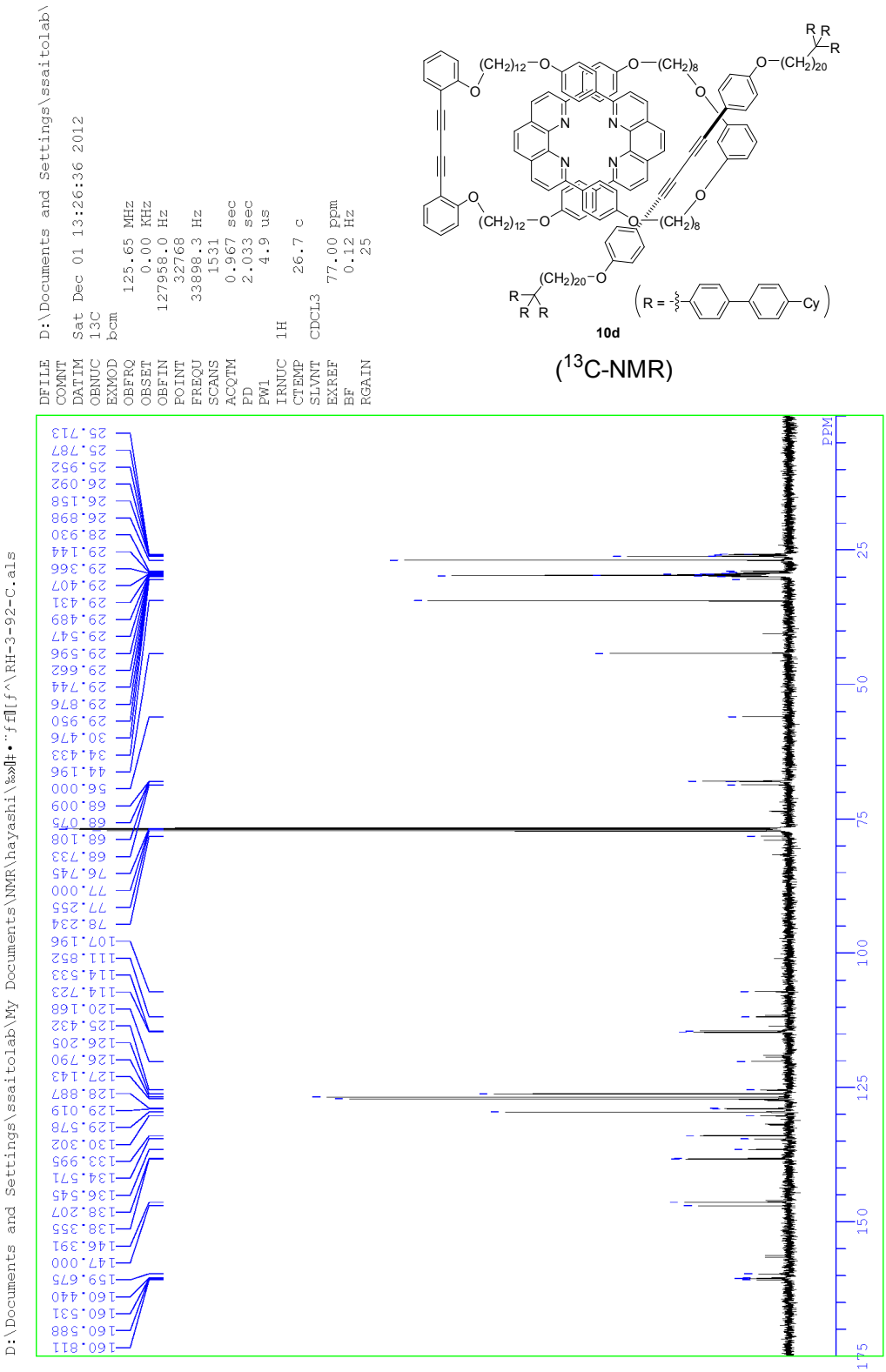
(^{13}C-NMR)


D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Sun Dec 30 20:39:45 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 16
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.4 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 19
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\‰»Ì•¨ƒfƒ[ƒ^\RH-3-100-1.als
PPM
10.28
3.67
16.20
1.90
3.86
5.00
8.07
16.77
38.55
28.48
3.98
3.89
4.00
7.56
10c
R = Cy

(^{1}H-NMR)

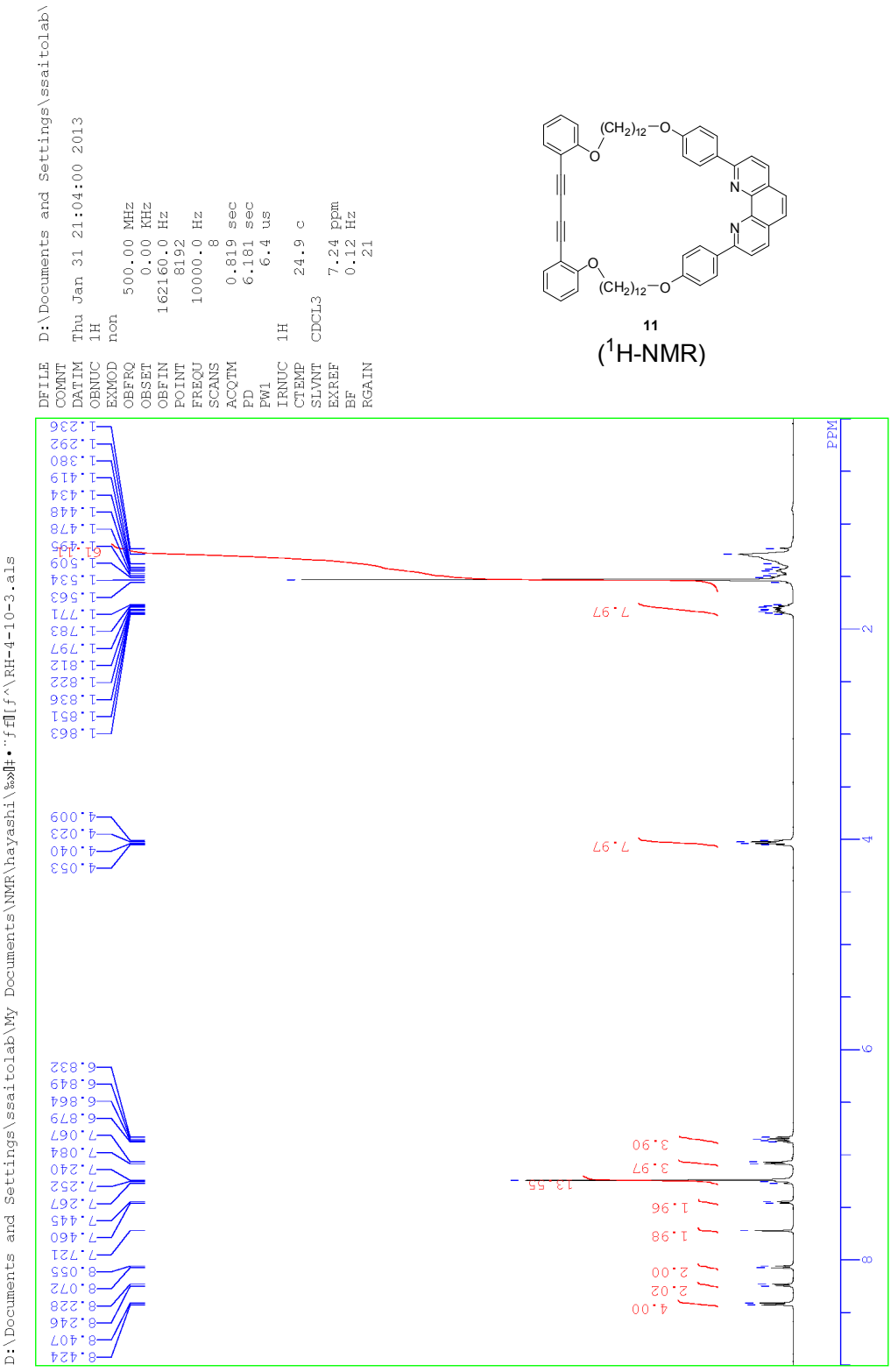

D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Wed Jan 09 09:53:18 2013
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 13588
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25
10c
(13C-NMR)
PPM
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\


D:\Documents and Settings\ssaitolab\
DFILE
COMNT
DATIM Fri Dec 14 12:06:44 2012
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.4 us
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 15
10d
(1H-NMR)
PPM
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\


DFILE D:\Documents and Settings\ssaitolab\
COMNT
DATIM Sat Dec 01 13:26:36 2012
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 1531
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25
PPM
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\‰»Ì•¨ƒfƒ[ƒ^\RH-3-92-C.als

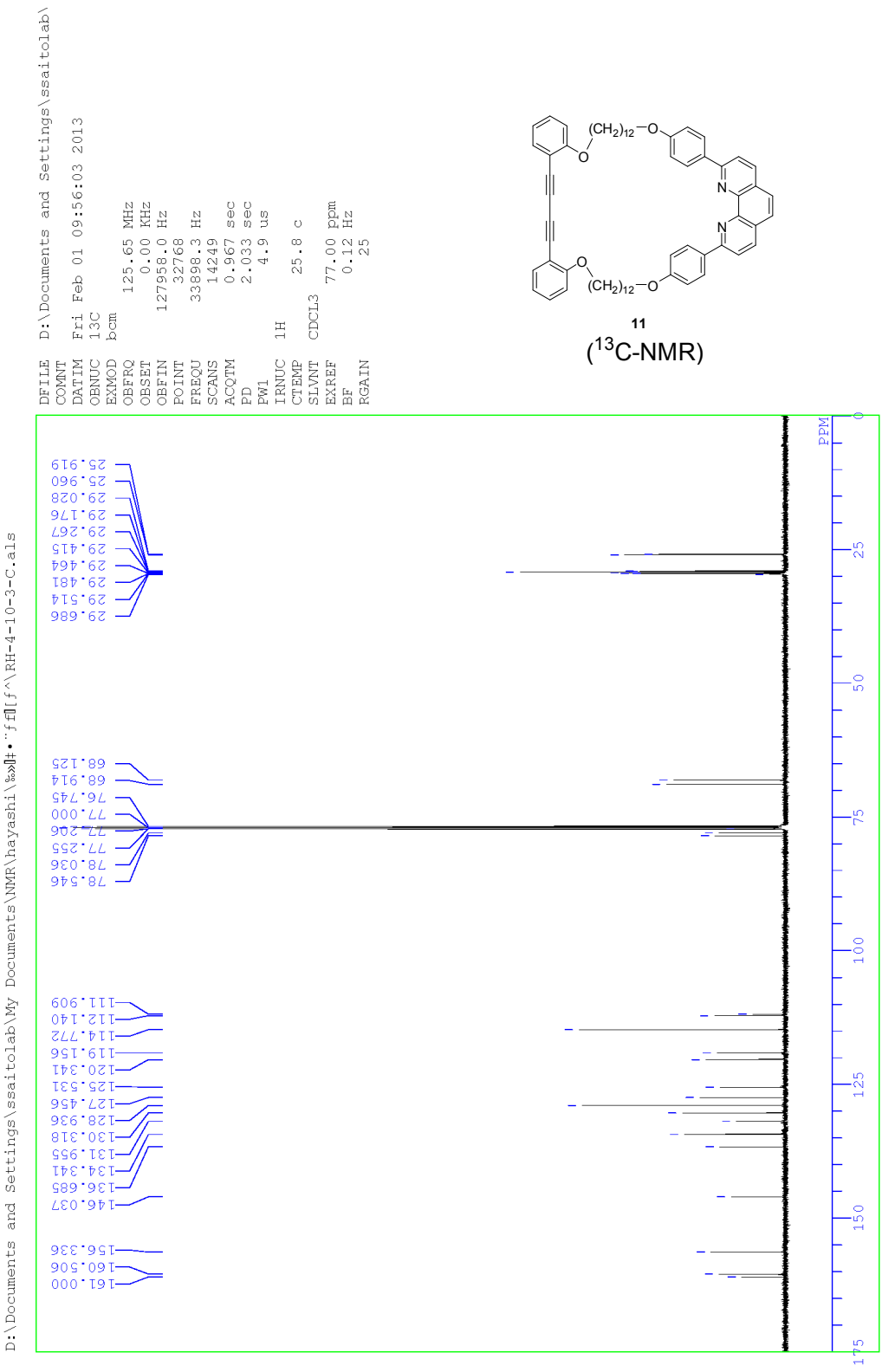
10d

(^{13}C-NMR)


DFILE D:\Documents and Settings\ssaitolab\
COMNT
DATIM Thu Jan 31 21:04:00 2013
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 8
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.4 us
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 21
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\%»¶•"ƒfÐ[ƒ^\RH-4-10-3.als
PPM
7.97
7.97
3.90
3.97
13.55
1.96
1.98
2.00
2.02
4.00

11

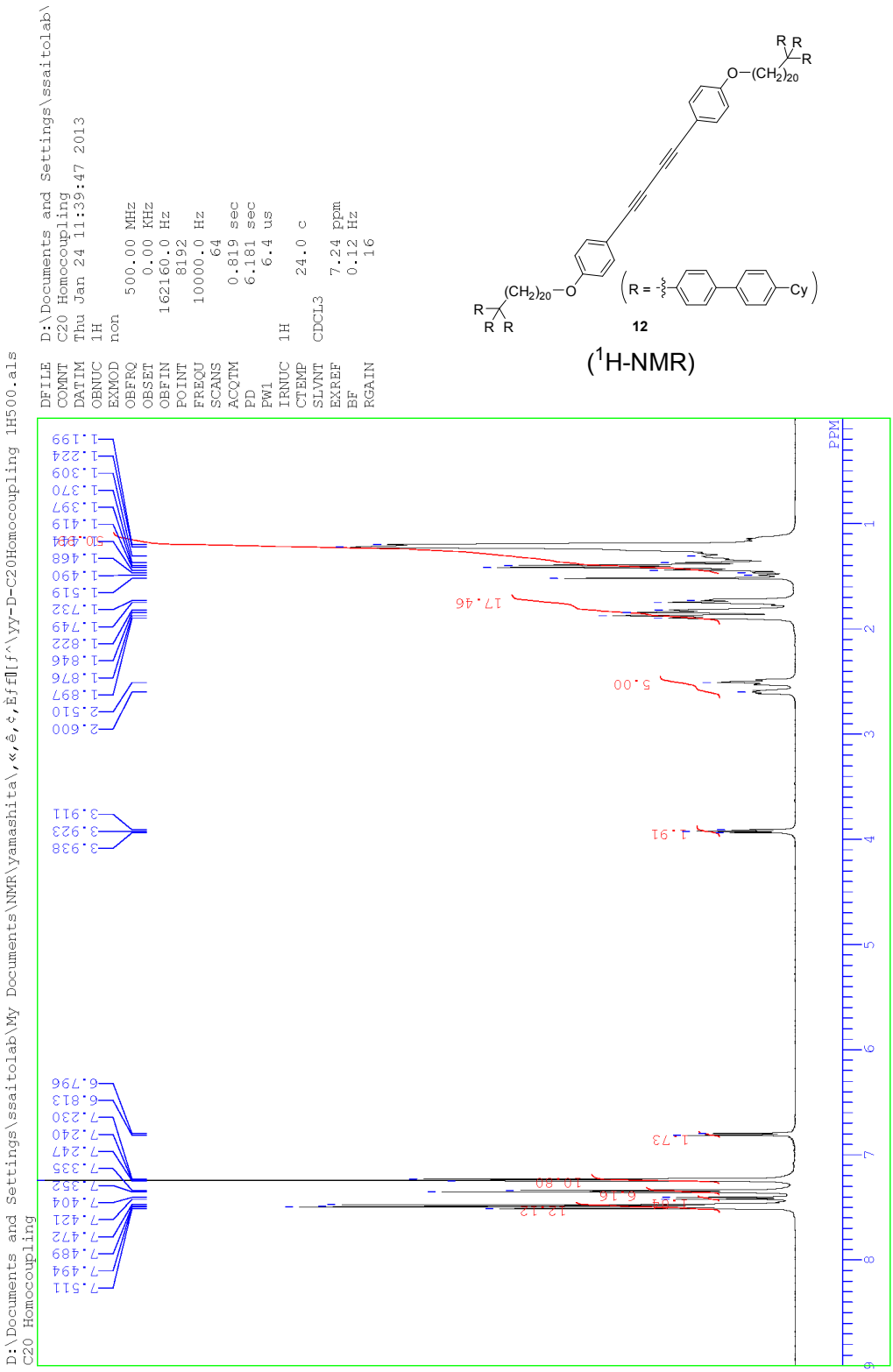
(^{1}H-NMR)

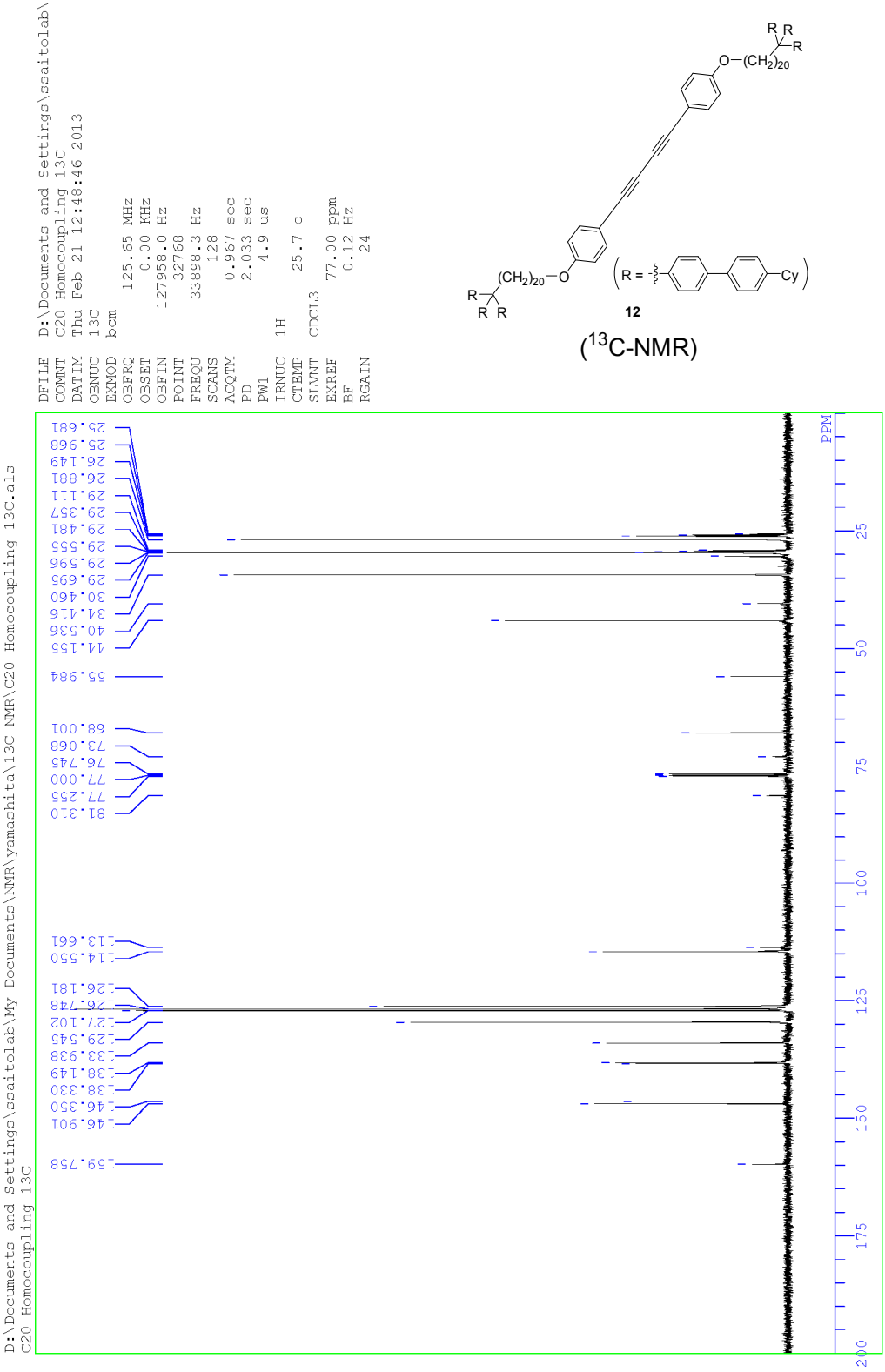

DFILE D:\Documents and Settings\ssaitolab\
COMNT
DATIM Fri Feb 01 09:56:03 2013
OBNUC 13C
EXMOD bcm
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 127958.0 Hz
POINT 32768
FREQU 33898.3 Hz
SCANS 14249
ACQTM 0.967 sec
PD 2.033 sec
PW1 4.9 us
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25
D:\Documents and Settings\ssaitolab\My Documents\NMR\hayashi\‰»Ħ•"ƒfÐ[ƒ^\RH-4-10-3-C.als
PPM
25.919
25.960
29.028
29.176
29.267
29.415
29.464
29.481
29.514
29.686
68.125
68.914
76.745
77.000
77.206
77.255
78.036
78.546
111.909
112.140
114.772
119.156
120.341
125.531
127.456
128.936
130.318
131.955
134.341
136.685
146.037
156.336
160.506
161.000

(CH2)12—O
O
N
N
O
(CH2)12—O

11

(^{13}C-NMR)


DFILE D:\Documents and Settings\ssaitolab\
COMNT C20 Homocoupling
DATIM Thu Jan 24 11:39:47 2013
OBNUC 1H
EXMOD non
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162160.0 Hz
POINT 8192
FREQU 10000.0 Hz
SCANS 64
ACQTM 0.819 sec
PD 6.181 sec
PW1 6.4 us
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 16
D:\Documents and Settings\ssaitolab\My Documents\NMR\yamashita\,«,ê,¢,ÈfflÍf^\yy-D-C20Homocoupling 1H500.als
C20 Homocoupling
PPM
17.46
5.00
1.91
1.73
10.80
6.16
12.12
O—(CH2)20
(CH2)20—O
R =
Cy
12
(1H-NMR)


D:\Documents and Settings\ssaitolab\
C20 Homocoupling 13C
Thu Feb 21 12:48:46 2013
13C
bcm
125.65 MHz
0.00 KHz
127958.0 Hz
32768
33898.3 Hz
128
0.967 sec
2.033 sec
4.9 us
1H
25.7 c
CDCL3
77.00 ppm
0.12 Hz
24
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
25.681
25.968
26.149
26.881
29.111
29.357
29.481
29.555
29.596
29.695
30.460
34.416
40.536
44.155
55.984
68.001
73.068
76.745
77.000
77.255
81.310
113.661
114.550
126.181
126.748
127.102
129.545
133.938
138.149
138.330
146.350
146.901
159.758
PPM
25
50
75
100
125
150
175
200
D:\Documents and Settings\ssaitolab\My Documents\NMR\yamashita\13C NMR\C20 Homocoupling 13C.als
C20 Homocoupling 13C

R R
R
O—(CH2)20
(CH2)20—O
R
R R
R = Cy

12

(^{13}C-NMR)