Supporting Information

Aryl hydrazide beyond as surrogate of aryl hydrazine in the Fischer indolization: synthesis of *N*-Cbz-indoles, *N*-Cbz-carbazoles and *N,N'*-bis-Cbz-pyrrolo[2,3-*f*]indoles

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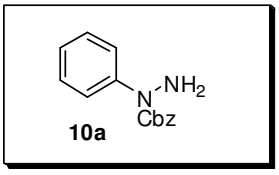
General methods. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz, with either TMS ($\delta = 0$) or residual $CHCl_3$ in the $CDCl_3$ solvent ($\delta = 7.24$) as internal standards. *J* values are reported in Hz. High resolution mass spectra were measured by using FAB method. Flash column chromatography was performed with Kieselgel 60 Art 9385 (230 – 400 mesh). All sovents used were purified according to standard procedures.

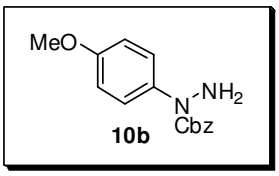
General procedure for aryl hydrazides 10a – 10l



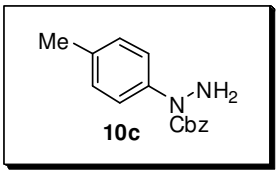
10a

Benzyl 1-phenylhydrazinecarboxylate (10a): To a sealed tube were charged iodobenzene (1.00 g, 4.90 mmol), CuI (0.09 g, 0.49 mmol), 1,10-phenanthroline (0.18 g, 0.98 mmol), Cs_2CO_3 (2.24 g, 6.86 mmol), benzyl carbazate (0.98 g, 5.88 mmol) and anhydrous DMF (5 mL) at rt. The reaction mixture was degassed, charged with Ar and heated to 80 ^{o}C. After 1 h, the reaction mixture was concentrated and purified by column chromatography (hexane/ether = 4/1) to afford **10a** (1.02 g, 86%

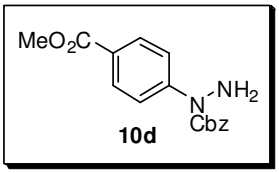
yield) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.35 – 7.31 (m, 7H), 7.18 – 7.14 (m, 1H), 5.23 (s, 2H), 4.53 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.5, 135.9, 128.4, 128.2, 128.1, 127.9, 125.0, 123.4, 67.8; HRMS Calcd for $C_{14}H_{14}NaN_2O_2$ ($M + Na^+$): 265.0947, found 265.0951.



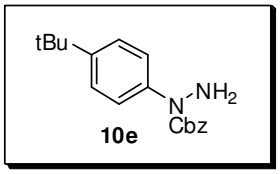
Benzyl 1-(4-methoxyphenyl)hydrazinecarboxylate (10b): yield 97%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, *J* = 2.8 Hz, 7H), 6.86 (dd, *J* = 7.2, 1.6 Hz, 2H), 5.21 (s, 2H), 4.53 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.3, 136.2, 135.8, 128.5, 128.2, 127.9, 125.6, 113.7, 67.9, 55.4; HRMS Calcd for $C_{15}H_{16}NaN_2O_3$ ($M + Na^+$): 295.1053, found 295.1050.



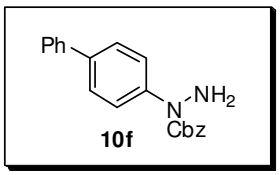
Benzyl 1-p-tolylhydrazinecarboxylate (10c): yield 99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 7H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.17 (s, 2H), 4.48 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 140.1, 136.1, 135.1, 129.0, 128.5, 128.1, 128.0, 123.7, 67.9, 20.9; HRMS Calcd for $C_{15}H_{16}NaN_2O_2$ ($M + Na^+$): 279.1104, found 279.1130.



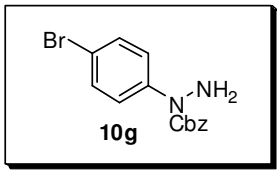
Benzyl 1-(4-(methoxycarbonyl)phenyl)hydrazine carboxylate (10d): yield 61%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.31 (m, 5H), 5.25 (s, 2H), 4.50 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 155.5, 146.7, 135.6, 130.0, 128.8, 128.6, 128.4, 125.9, 121.9, 68.6, 52.1; HRMS Calcd for $C_{16}H_{16}NaN_2O_4$ ($M + Na^+$): 323.1002, found 323.1009.



Benzyl 1-(4-tert-butylphenyl)hydrazinecarboxylate (10e): yield 99%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 9H), 5.23 (s, 2H), 4.52 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 148.2, 140.0, 136.2, 128.5, 128.2, 128.1, 125.3, 123.3, 68.0, 34.4, 31.4; HRMS Calcd for $C_{18}H_{22}NaN_2O_2$ ($M + Na^+$): 317.1260, found 317.1255.

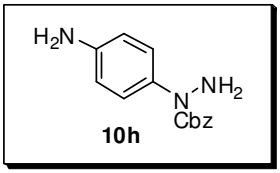


Benzyl 1-(biphenyl-4-yl)hydrazinecarboxylate (10f): yield 82%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.46 (d, *J* = 2.4 Hz, 6H), 7.45 – 7.23 (m, 8H), 5.23 (s, 2H), 4.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 141.9, 140.5, 138.0, 136.0, 128.8, 128.6, 128.4, 128.2, 127.3, 127.1, 127.0, 123.7, 68.3; HRMS Calcd for $C_{20}H_{18}NaN_2O_2$ ($M + Na^+$): 341.1260, found 341.1257.

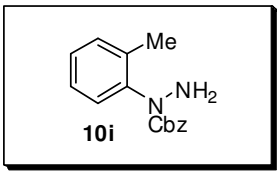


Benzyl 1-(4-bromophenyl)hydrazinecarboxylate (10g): yield 71%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 4H), 7.37 – 7.35 (m, 5H), 5.23 (s, 2H), 4.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 141.8, 135.8, 131.5, 128.8, 128.6, 128.4, 125.0, 118.2, 68.5; HRMS Calcd for $C_{14}H_{13}BrNaN_2O_2$

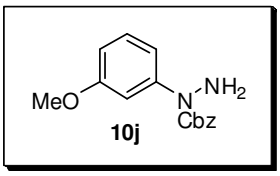
(M + Na^+): 343.0053, found 343.0048.



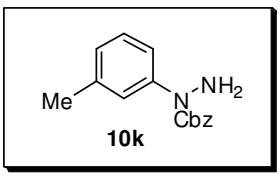
Benzyl 1-(4-aminophenyl)hydrazinecarboxylate (10h): yield ~80% unstable, decomposes on silica-gel. Both ^1H and ^{13}C NMR spectra contain small amount of inseparable impurities. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 7.14 (d, *J* = 6.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 5.19 (s, 2H), 4.01 (bs, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 144.7, 136.4, 133.8, 128.6, 128.4, 128.1, 127.9, 114.9, 67.8; HRMS Calcd for $C_{14}H_{13}BrNaN_2O_2$ (M + Na^+): 280.1046, found 280.1050.



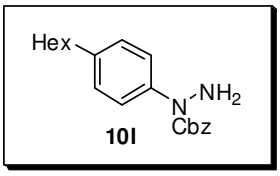
Benzyl 1-(biphenyl-4-yl)hydrazinecarboxylate (10f): yield 35%, ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 9H), 5.15 (s, 2H), 4.55 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 141.3, 136.4, 135.4, 131.0, 128.5, 128.1, 127.7, 127.5, 126.7, 67.9, 29.8, 17.8; HRMS Calcd for $C_{15}H_{16}NaN_2O_2$ (M + Na^+): 279.1104, found 279.1127.



Benzyl 1-(3-methoxyphenyl)hydrazinecarboxylate 1-m-tolyl-hydrazine carboxylate (10j): yield 98%, ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 9.6 Hz, 2H), 6.71 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.24 (s, 2H), 4.51 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.6, 143.7, 135.8, 128.8, 128.3, 128.0, 127.9, 115.5, 110.7, 109.1, 67.8, 55.0; HRMS Calcd for $C_{15}H_{16}NaN_2O_3$ (M + Na^+): 295.1053, found 295.1045.

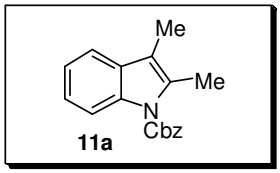


Benzyl 1-m-tolylhydrazinecarboxylate (10k): yield 92%, ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 7.28 – 7.17 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.23 (s, 2H), 4.52 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.5, 138.1, 136.0, 128.5, 128.4, 128.1, 127.9, 126.1, 124.3, 120.8, 67.9, 21.3; HRMS Calcd for $C_{15}H_{16}NaN_2O_2$ (M + Na^+): 279.1104, found 279.1129.



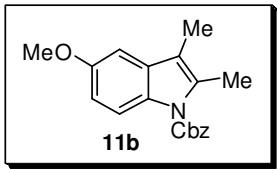
Benzyl 1-(4-hexylphenyl)hydrazinecarboxylate (10l): yield 89%, ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 7H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.22 (s, 2H), 4.52 (s, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 1.66-1.53 (m, 2H), 1.40-1.21 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 140.2, 139.9, 136.1, 128.4, 128.2, 128.0, 127.9, 123.5, 67.8, 35.3, 31.6, 31.3, 28.8, 22.5, 14.0; HRMS Calcd for $C_{20}H_{26}NaN_2O_2$ (M + Na^+): 349.1886, found 349.1891.

General procedure for *N*-Cbz-indoles 11a – 11l



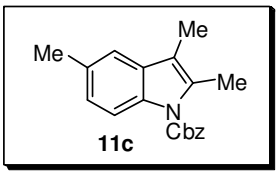
11a

Benzyl 2,3-dimethyl-1H-indole-1-carboxylate (11a): To a sealed tube charged with benzyl 1-phenylhydrazinecarboxylate **10a** (100 mg, 0.41 mmol), 2-butanone (61 mg, 0.82 mmol) in MeOH (2.0 mL) was added a drop of conc. H_2SO_4 (~70 mg) at rt. After 2 h under reflux, the reaction mixture was cooled to rt, concentrated and purified by column chromatography (hexane /EtOAc = 15/1) to afford **11a** (109 mg, 95%) as an oil. mp (°C) = 45 – 47, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.24 – 7.22 (m, 2H), 5.50 (s, 2H), 2.54 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100M Hz, $CDCl_3$) δ 151.3, 135.7, 135.4, 133.0, 131.1, 128.9, 128.7, 128.6, 123.7, 122.8, 118.1, 115.6, 114.7, 68.5, 13.9, 8.8; FT-IR (CH_2Cl_2) 3065, 3034, 2963, 1731, 1459, 1397, 1345, 1328, 1216, 1140 cm^{-1}; HRMS Calcd for $C_{18}H_{17}NaNO_2$ (M + Na^+): 302.1151, found 302.1159.



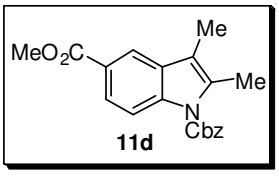
11b

Benzyl 5-methoxy-2,3-dimethyl-1H-indole-1-carboxylate (11b): mp (°C) = 74 – 76, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.36 (m, 3H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.82 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.44 (s, 2H), 3.86 (s, 3H), 2.52 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 152.1, 135.5, 133.8, 132.1, 130.2, 128.9, 128.7, 128.6, 116.4, 114.5, 111.5, 101.3, 68.4, 55.8, 14.0, 8.9; FT-IR (CH_2Cl_2) 3089, 3064, 3033, 2998, 2929, 1729, 1611, 1480, 1339, 1257, 1213, 1134 cm^{-1}; HRMS Calcd for $C_{19}H_{19}NaNO_3$ (M + Na^+): 332.1257, found 332.1261.



11c

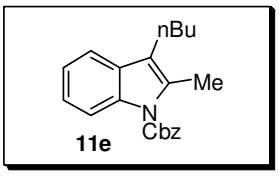
Benzyl 2,3,5-trimethyl-1H-indole-1-carboxylate (11c): mp (°C) = 35 – 37, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.20 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.45 (s, 2H), 2.52 (s, 3H), 2.44 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 135.5, 133.8, 132.9, 132.2, 131.3, 128.8, 128.6, 128.5, 124.9, 118.0, 115.2, 114.4, 68.3, 21.4, 13.8, 8.8; FT-IR (CH_2Cl_2) 3090, 3063, 3031, 2924, 2861, 1728, 1474, 1397, 1344, 1319, 1216 cm^{-1}; HRMS Calcd for $C_{19}H_{19}NaNO_2$ (M + Na^+): 316.1308, found 316.1315.



11d

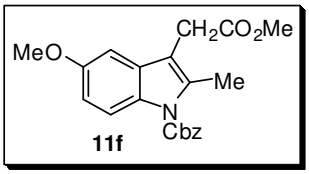
1-Benzyl 5-methyl 2,3-dimethyl-1H-indole-1,5-dicarboxylate (11d): mp (°C) = 121 – 123, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.35 (m, 3H), 5.46 (s, 2H), 3.94 (s, 3H), 2.52 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 151.9, 144.5, 138.5, 135.0, 134.3, 130.9, 128.9, 128.8, 125.1, 124.7, 120.2, 115.2, 115.1, 68.9, 52.1, 13.9, 8.8;

FT-IR (CH_2Cl_2) 3090, 3064, 3033, 2950, 2929, 2857, 1717, 1618, 1455, 1433, 1396, 1327, 1238 cm^{-1}; HRMS Calcd for $C_{20}H_{19}NaNO_4$ (M + Na^+): 360.1206, found 360.1214.



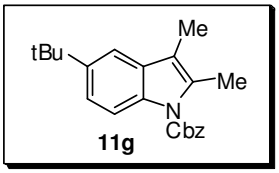
11e

Benzyl 3-butyl-2-methyl-1H-indole-1-carboxylate (11e): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.08 (m, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.22 – 7.20 (m, 2H), 5.46 (s, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.53 (s, 3H), 1.60 – 1.52 (m, 2H), 1.42 – 1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 135.8, 135.4, 132.9, 130.5, 128.8, 128.7, 128.6, 132.5, 122.7, 119.6, 118.1, 115.7, 68.5, 32.3, 23.8, 22.8, 14.1, 13.9; FT-IR (CH_2Cl_2) 3066, 3049, 3934, 2965, 2930, 2870, 1731, 1611, 1460, 1390, 1348, 1321, 1140 cm^{-1}; HRMS Calcd for $C_{21}H_{23}NaNO_2$ (M + Na^+): 344.1621, found 344.1628.



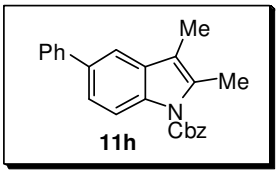
11f

Benzyl 5-methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indole-1-carboxylate (11f): mp (°C) = 96 – 98, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.35 (m, 3H), 6.93 (d, *J* = 2.6 Hz, 1H), 6.84 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.45 (s, 2H), 3.85 (s, 3H), 3.68 (s, 3H), 3.64 (s, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 156.2, 151.9, 136.0, 135.2, 130.7, 130.2, 128.9, 128.8, 128.7, 116.5, 112.1, 111.9, 101.3, 68.6, 55.8, 52.2, 30.2, 14.2; FT-IR (CH_2Cl_2) 3089, 3064, 3033, 2995, 2951, 2934, 1737, 1609, 1480, 1437, 1396, 1353, 1113 cm^{-1}; HRMS (M + Na^+) calcd for $C_{21}H_{21}NaNO_5$ 390.1312, found 390.1320.



11g

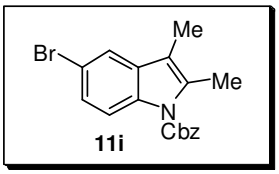
Benzyl 5-tert-butyl-2,3-dimethyl-1H-indole-1-carboxylate (11g): liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.34 (d, *J* = 8.8 Hz, 1H), 5.48 (s, 2H), 2.57 (s, 3H), 2.24 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 145.9, 135.5, 133.6, 133.0, 130.9, 128.8, 128.65, 128.56, 121.5, 115.1, 114.8, 114.2, 68.4, 34.7, 31.9, 13.8, 8.8; FT-IR (CH_2Cl_2) 3090, 3065, 3034, 2960, 2930, 1731, 1480, 1396, 1344, 1223, 1148 cm^{-1}; HRMS Calcd for $C_{22}H_{25}NaNO_2$ (M + Na^+): 358.1778, found 358.1785.



11h

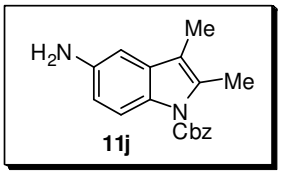
Benzyl 2,3-dimethyl-5-phenyl-1H-indole-1-carboxylate (11h): mp (°C) = 104 – 106, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.62 (s, 1H), 7.53 – 7.40 (m, 8H), 7.37 – 7.33 (m, 1H), 5.49 (s, 2H), 2.56 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 141.8, 136.1, 135.3, 135.0, 133.5, 131.6, 128.81, 128.76, 128.7, 128.6, 127.4, 126.8, 123.0, 116.4, 115.7, 114.8, 68.5, 13.9, 8.8; FT-IR

(CH_2Cl_2) 3061, 3032, 2962, 2927, 1730, 1466, 1396, 1302, 1219, 1139 cm^{-1}; HRMS Calcd for $C_{24}H_{21}NaNO_2$ ($M + Na^+$): 378.1465, found 378.1474.



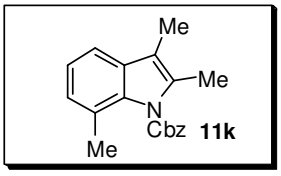
11i

Benzyl 5-bromo-2,3-dimethyl-1H-indole-1-carboxylate (11i): mp (°C) = 101 – 103, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.29 (dd, *J* = 8.8, 7.0 Hz, 1H), 5.45 (s, 2H), 2.51 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 135.1, 134.4, 134.3, 132.9, 128.92, 128.87, 128.7, 126.3, 120.8, 117.0, 116.2, 114.0, 68.8, 13.9, 8.8; FT-IR (CH_2Cl_2) 3065, 3033, 2962, 2928, 1733, 1459, 1396, 1324, 1214, 1144 cm^{-1}; HRMS Calcd for $C_{18}H_{16}BrNaNO_2$ ($M + Na^+$): 380.0257, found 380.0264.



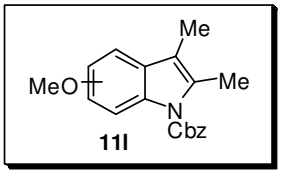
11j

Benzyl 5-amino-2,3-dimethyl-1H-indole-1-carboxylate (11j): mp (°C) = 85 – 87, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.35 (m, 3H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.60 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.43 (s, 2H), 3.48 (bs, 2H), 2.50 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 142.2, 135.6, 133.4, 132.2, 129.5, 128.8, 128.6, 128.5, 116.3, 114.2, 112.6, 103.6, 68.2, 13.9, 8.8; FT-IR (CH_2Cl_2) 3439, 3363, 3216, 3089, 3064, 3031, 2961, 2926, 1720, 1619, 1483, 1466, 1400, 1329, 1214, 1135 cm^{-1}; HRMS Calcd for $C_{18}H_{18}NaN_2O_2$ ($M + Na^+$): 317.1260, found 317.1264.



11k

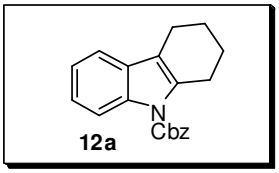
Benzyl 2,3,7-trimethyl-1H-indole-1-carboxylate (11k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.6 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 5.40 (s, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 135.3, 135.0, 133.0, 132.1, 128.9, 128.8, 126.6, 124.5, 122.8, 115.9, 115.9, 113.5, 69.0, 21.1, 13.1, 9.0; FT-IR (CH_2Cl_2) 3035, 2959, 2926, 1735, 1457, 1339, 1313, 1212, 1151 cm^{-1}; HRMS Calcd for $C_{19}H_{19}NaNO_2$ ($M + Na^+$): 316.1308, found 316.1312.



11l

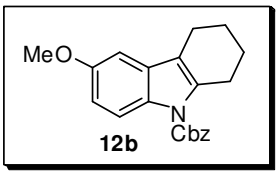
Mixture of benzyl 6-methoxy-2,3-dimethyl-1H-indole-1-carboxylate and benzyl 4-methoxy-1H-indole-1-carboxylate (11l): copy of ^{1}H NMR (400 MHz, $CDCl_3$) spectrum was attached.

General procedure for aryl hydrazides 12a – 12l



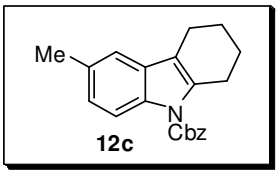
12a

Benzyl 3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12a): To a sealed tube charged with benzyl 1-phenylhydrazinecarboxylate (97 mg, 0.40 mmol), cyclohexanone (94 mg, 0.96 mmol) in MeOH (1.8 mL) was added a drop of conc. H_2SO_4 (~70 mg) at rt. After 4 h at 50 ^oC, the reaction mixture was cooled to rt, concentrated and purified by column chromatography (hexane /EtOAc = 16/1) to afford **12a** (106 mg, 86%) as an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.20 – 7.13 (m, 2H), 5.34 (s, 2H), 2.92 – 2.90 (m, 2H), 2.55 – 2.52 (m, 2H), 1.80 – 1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 135.7, 135.5, 135.4, 130.0, 128.7, 128.50, 128.46, 123.6, 122.7, 117.5, 117.2, 115.5, 68.2, 25.7, 23.5, 22.1, 21.0.



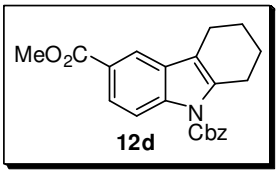
12b

Benzyl 6-methoxy-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12b): ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.33 – 7.24 (m, 3H), 6.78 – 6.76 (m, 2H), 5.31 (s, 2H), 3.75 (s, 3H), 2.87 (bs, 2H), 2.47 (bs, 2H), 1.76 – 1.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.6, 136.2, 135.4, 130.9, 130.1, 128.6, 128.4, 128.3, 117.0, 116.1, 111.2, 100.7, 68.0, 55.5, 25.6, 23.4, 22.0, 21.0.



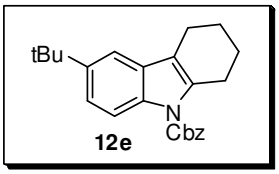
12c

Benzyl 6-methyl-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12c): ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.11 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.34 (s, 2H), 2.92 – 2.90 (m, 2H), 2.54 – 2.51 (m, 2H), 2.38 (s, 3H), 1.80 – 1.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 135.6, 135.5, 133.9, 132.1, 130.3, 128.7, 128.5, 128.4, 124.8, 117.6, 117.1, 115.2, 68.1, 25.7, 23.6, 22.2, 21.3, 21.1.



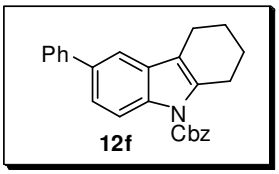
12d

9-Benzyl 6-methyl 3,4-dihydro-1H-carbazole-6,9(2H)-dicarboxylate (12e): ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 1H), 8.11 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.38 (m, 3H), 5.45 (s, 2H), 3.93 (s, 3H), 3.00 – 2.97 (m, 2H), 2.68 – 2.66 (m, 2H), 1.89 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 151.7, 138.6, 137.1, 135.1, 130.0, 128.9, 128.8, 128.7, 125.1, 124, 6, 119.8, 117.8, 115.2, 68.8, 52.1, 25.8, 23.5, 22.1, 21.0.

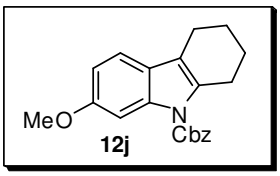


12e

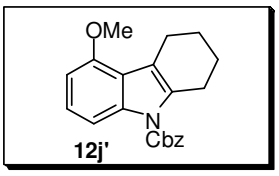
Benzyl 6-tert-butyl-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12e): ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.25 (m, 5H), 5.37 (s, 2H), 2.95 – 2.93 (m, 2H), 2.62 – 2.59 (m, 2H), 1.82 – 1.76 (m, 4H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 145.8, 135.7, 135.5, 133.7, 129.9, 128.7, 128.52, 128.45, 121.4, 117.5, 115.1, 113.8, 68.2, 34.6, 31.8, 25.7, 23.6, 22.3, 21.2.



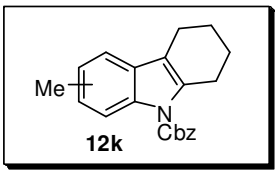
Benzyl 6-phenyl-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 1.5 Hz, 1H), 7.50 – 7.31 (m, 9H), 5.46 (s, 2H), 3.02 – 2.99 (m, 2H), 2.69 – 2.66 (m, 2H), 1.90 – 1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 141.8, 136.3, 136.0, 135.4, 135.2, 130.6, 128.73, 128.71, 128.6, 128.5, 127.3, 126.8, 123.0, 117.5, 116.0, 115.7, 68.3, 25.7, 23.5, 22.1, 21.0.



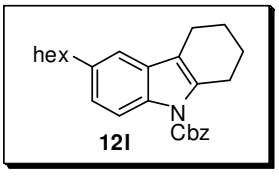
Benzyl 7-methoxy-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.37 (s, 2H), 3.73 (s, 3H), 2.94 – 2.91 (m, 2H), 2.56 – 2.53 (m, 2H), 1.82 – 1.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 152.0, 136.7, 135.4, 134.1, 128.8, 128.65, 128.59, 124.0, 117.9, 117.1, 111.4, 100.5, 68.4, 55.6, 25.7, 23.6, 22.2, 21.2.



Benzyl 5-methoxy-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12j'): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.12 – 7.08 (m, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.41 (s, 2H), 3.86 (s, 3H), 2.95 – 2.92 (m, 2H), 2.90 – 2.87 (m, 2H), 1.82 – 1.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 152.1, 137.2, 135.5, 133.8, 128.8, 128.7, 128.6, 124.2, 119.7, 117.4, 108.9, 103.9, 68.4, 55.5, 25.9, 23.8, 23.4, 22.7.

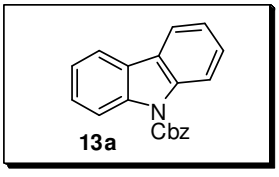


Mixture of benzyl 7-methyl- and **5-methyl-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12k)**: copy of ^{1}H NMR (400 MHz, $CDCl_3$) spectrum was attached.



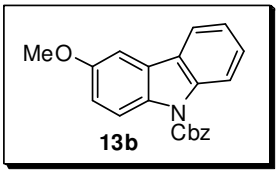
Benzyl 6-hexyl-3,4-dihydro-1H-carbazole-9(2H)-carboxylate (12l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.15 (s. 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 2H), 2.94 – 2.92 (m, 2H), 2.67 – 2.63 (m, 2H), 2.58 – 2.57 (m, 2H), 1.82 – 1.75 (m, 4H), 1.64 – 1.58 (m, 2H), 1.34 – 1.29 (m, 6H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 137.5, 135.7, 135.5, 134.1, 130.2, 128.7, 128.52, 128.47, 124.3, 117.2, 117.0, 115.3, 68.2, 36.0, 32.1, 31.9, 29.1, 25.8, 23.6, 22.7, 22.3, 21.2, 14.2.

General procedure for aryl hydrazides 13a – 13l



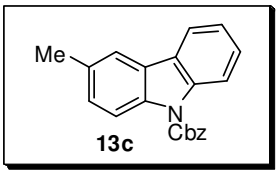
Benzyl 9H-carbazole-9-carboxylate (13a)[1]: To a sealed tube were charged **12a** (0.28 g, 0.90 mmol), DDQ (1.23 mg, 5.42 mmol) and anhydrous benzene

(4 mL) at rt. After 5 h at rt, the reaction mixture was concentrated and directly purified by column chromatography (CH_2Cl_2/MeOH = 50/1) to afford **13a** (0.24 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 – 7.24 (m, 7H), 5.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 138.2, 135.2, 128.8, 128.7, 128.6, 127.2, 125.9, 123.4, 119.6, 116.4, 68.6.



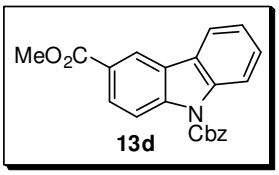
13b

Benzyl 3-methoxy-9H-carbazole-9-carboxylate (13b): mp (°C) = 61 – 63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.28 (m, 5H), 6.89 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.49 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.3, 139.6, 138.2, 135.2, 128.9, 128.9, 128.7, 126.1, 126.0, 123.5, 120.2, 119.4, 118.9, 116.3, 111.9, 100.9, 68.8, 55.5; FT-IR (CH_2Cl_2) 3429, 3062, 3034, 2954, 1737, 1489, 1454, 1391 cm^{-1}; HRMS Calcd for $C_{21}H_{17}NaNO_3$ (M + Na$^+$): 354.1101, found 354.1105.



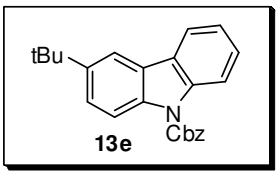
13c

Benzyl 3-methyl-9H-carbazole-9-carboxylate (13c): mp (°C) = 86 – 88. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.77 (s, 1H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.45 – 7.31 (m, 5H), 5.56 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 138.5, 136.3, 135.3, 132.9, 128.8, 128.7, 128.6, 128.4, 127.1, 126.05, 125.98, 123.3, 119.7, 119.5, 116.4, 116.0, 68.5, 21.3; FT-IR (CH_2Cl_2) 3434, 3063, 3033, 2954, 2919, 1726, 1488, 1450, 1389, 1385 cm^{-1}; HRMS Calcd for $C_{21}H_{17}NaNO_2$ (M + Na$^+$): 338.1151, found 338.1158.



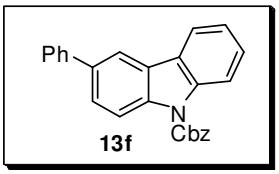
13d

9-Benzyl 3-methyl 9H-carbazole-3,9-dicarboxylate (13d)[2]: mp (°C) = 127 – 129, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.1 Hz, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 8.10 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.54 (*J* = 6.6 Hz, 2H), 7.53 – 7.34 (m, 5H), 5.55 (s, 2H), 3.96 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 167.2, 152.1, 141.2, 138.8, 135.0, 129.0, 128.8, 128.7, 128.0, 126.0, 125.5, 125.3, 123.9, 121.7, 120.6, 116.5, 116.1, 69.2, 52.3; HRMS Calcd for $C_{22}H_{17}NaNO_4$ (M + Na$^+$): 382.1050, found 382.1044.

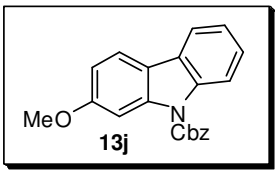


13e

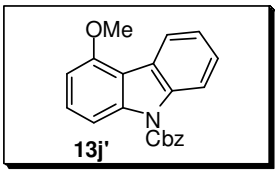
Benzyl 3-tert-butyl-9H-carbazole-9-carboxylate (13e): mp (°C) = 79 – 81. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.7 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.51 – 7.46 (m, 3H), 7.42 – 7.29 (m, 5H), 5.51 (s, 2H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.6, 138.6, 136.3, 135.4, 128.9, 128.7, 128.6, 127.1, 126.4, 125.8, 125.1, 123.3, 119.6, 116.4, 116.02, 115.96, 68.6, 34.8, 31.8; FT-IR (CH_2Cl_2) 3435, 3115, 3035, 2961, 2902, 1728, 1486, 1452, 1425, 1390, 1363 cm^{-1}; HRMS Calcd for $C_{24}H_{23}NaNO_2$ (M + Na$^+$): 380.1621, found 380.1625.



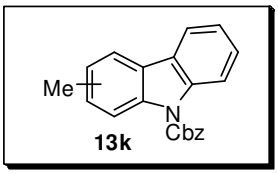
Benzyl 3-phenyl-9H-carbazole-9-carboxylate (13f): mp (°C) = 95 – 97. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 2H), 8.17 (d, *J* = 1.8 Hz, 1H), 8.02 (d, *J* = 7.3 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.50 – 7.35 (m, 8H), 5.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 141.0, 138.5, 137.4, 136.3, 135.2, 128.75, 128.72, 128.6, 128.5, 127.2, 127.0, 126.3, 126.2, 125.8, 123.2, 119.5, 117.7, 116.4, 116.3, 68.5; FT-IR (CH_2Cl_2) 3437, 3112, 3033, 2956, 1727, 1486, 1451, 1389 cm^{-1}; HRMS Calcd for $C_{26}H_{19}NaNO_2$ (M + Na^+): 400.1308, found 400.1315.



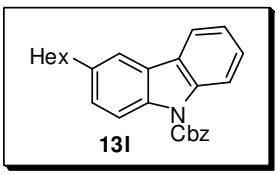
Benzyl 2-methoxy-9H-carbazole-9-carboxylate (13j): mp (°C) = 107 – 109. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.3, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.28 (5H), 6.89 (dd, *J* = 8.8, 1.8 Hz, 1H), 5.49 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 152.3, 139.6, 138.2, 135.2, 128.91, 128.85, 128.7, 126.1, 125.9, 123.5, 120,2, 119.4, 118.9, 116.3, 111.9, 100.9, 68.8, 55.5; FT-IR (CH_2Cl_2) 3430, 3064, 3034, 2956, 2834, 1725, 1623, 1501, 1461, 1438, 1352, 1339 cm^{-1}; HRMS Calcd for $C_{21}H_{17}NaNO_3$ (M^+): 354.1101, found 354.1104.



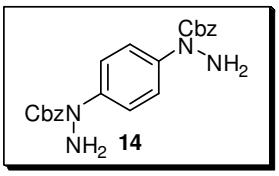
Benzyl 4-methoxy-9H-carbazole-9-carboxylate (13j'): mp (°C) = 119 – 121. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.27 (m, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.0, 2H), 7.45 – 7.33 (m, 6H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.56 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 152.5, 139.6, 137.6, 135.3, 128.9, 128.8, 128.7, 127.9, 126.3, 125.4, 123.5, 123.1, 115.8, 115.1, 109.0, 104.7, 68.8, 55.6; FT-IR (CH_2Cl_2) 3438, 3054, 3034, 2958, 2933, 2837, 1722, 1617, 1591, 1501, 1481, 1387, 1320 cm^{-1}; HRMS Calcd for $C_{21}H_{17}NaNO_3$ (M^+): 354.1101, found 354.1104.



Mixture of benzyl 2-methyl-9H-carbazole-9-carboxylate and benzyl 4-methyl-9H-carbazole-9-carboxylate (13k): copy of ^{1}H NMR (400 MHz, $CDCl_3$) spectrum was attached. FT-IR (CH_2Cl_2) 3434, 3054, 3033, 2954, 2923, 1727, 1499 cm^{-1}.

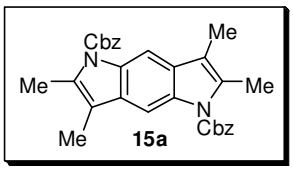


Benzyl 3-hexyl-9H-carbazole-9-carboxylate (13l): mp (°C) = 61 – 63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.75 (s, 1H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.23 (m, 5H), 5.54 (s, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.64 (m, 2H), 1.38 – 1.25 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 138.6, 138.3, 136.6, 135.4, 128.9, 128.8, 128.6, 128.0, 127.2, 126.2, 126.1, 123.4, 119.7, 119.2, 116.5, 116.2, 68.7, 35.9, 32.0, 31.9, 29.1, 22.8, 14.3; FT-IR (CH_2Cl_2) 3436, 3064, 3033, 2955, 2927, 2854, 1729, 1487, 1451, 1390, 1348 cm^{-1}; HRMS Calcd for $C_{26}H_{27}NaNO_2$ (M + Na^+): 408.1934, found 408.1941.

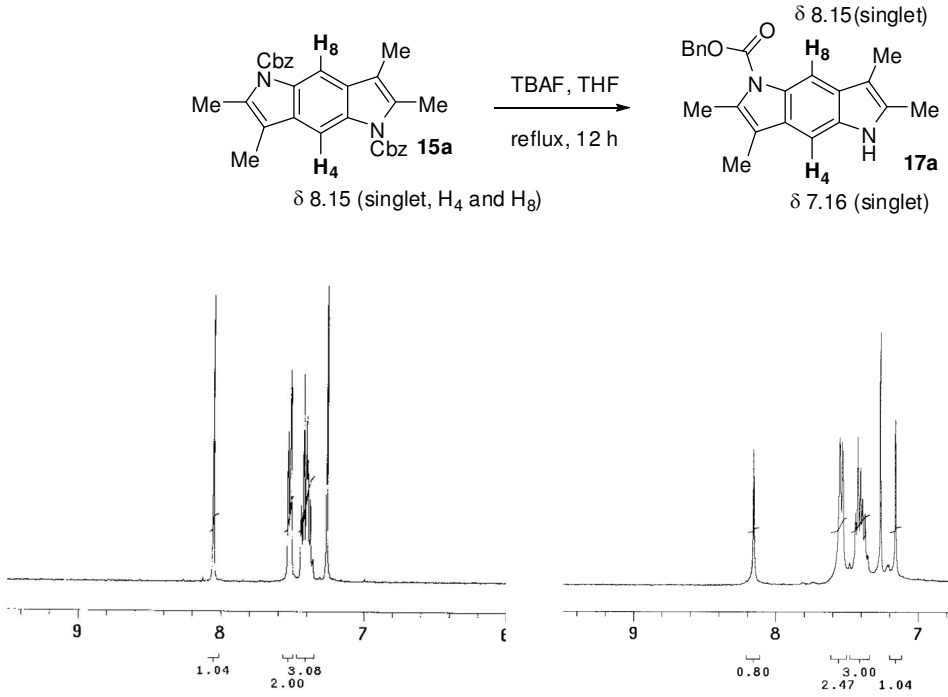


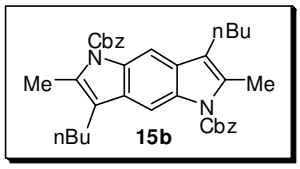
Benzyl 1,1'-(1,4-phenylene)bis(hydrazinecarboxylate) (14): To a sealed tube were charged 1,4-diiodobenzene (2.00 g, 6.1 mmol), benzyl carbazate (2.42 g, 14.6 mmol, 2.4 equiv), copper iodide (0.160 g, 0.84 mmol, 0.14 equiv), 1,10-phenanthroline (0.24 g, 1.33 mmol, 0.22 equiv) and cesium carbonate (4.80 g, 14.6 mmol, 2.4 equiv) in 10 mL of DMF. The mixture was degassed at -78 ^{o}C, charged with Ar gas and heated at 100 ^{o}C for 2 h. After completion of reaction, the reaction mixture was diluted with EtOAc (100 mL) and saturated NH_4Cl (100 mL). The organic layer was separated and the aqueous solution was extracted with EtOAc (50 mL X 3). The combined organic solution was dried over Na_2SO_4, concentrated and purified by flash silica gel column chromatography (hexane/EtOAc = 3/1 to 1/1, v/v) to give **14** as tan solids (1.7 g, 70% yield). mp (°C) = 111 – 113, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (bs, 4H), 7.36 – 7.35 (m, 10H), 5.23 (s, 4H), 4.51 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 139.7, 136.0, 128.7, 128.4, 128.2, 123.5, 68.3; FT-IR (CH_2Cl_2) 3344, 3292, 3220, 3088, 3063, 3032, 2954, 2894, 1698, 1624, 1507, 1386, 1322, 1308, 1272, 1153, 1056 cm^{-1}; HRMS Calcd for $C_{22}H_{22}NaN_4O_4$ (M + Na^+): 429.1533, found 429.1537.

General procedure for pyrrolo[2,3-f]indole-1,5-dicarboxylate 15a – 15g.

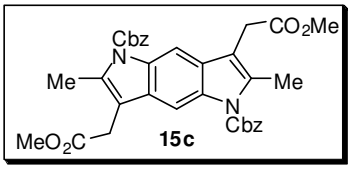


Dibenzyl 2,3,6,7-tetramethylpyrrolo[2,3-f]indole-1,5-dicarboxylate (15a): To a carousel tube were charged **14** (101 mg, 0.25 mmol), 2-butanone (180 mg, 2.5 mmol, 10 equiv) and 3 mL of methanolic H_2SO_4 solution (0.4 M). The mixture was heated under reflux for 12 h. Upon completion, the reaction mixture was diluted with dichloromethane and washed with water two times. The separated organic solution was dried over Na_2SO_4, concentrated and purified by flash silica gel column chromatography (100% CH_2Cl_2) to give a mixture of **15a** and **16a** (114 mg, 95%). **15a**: mp (°C) = 197 – 199, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.52 (d, *J* = 7.0, 4H), 7.44 – 7.38 (m, 6H), 5.46 (s, 4H), 2.53 (s, 6H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 135.5, 132.8, 132.6, 128.93, 128.88, 128.73, 128.69, 115.3, 104.5, 68.5, 14.2, 9.0; FT-IR (CH_2Cl_2) 3059, 3033, 2979, 2963, 2926, 1728, 1409, 1296, 1221, 1119 cm^{-1}; HRMS Calcd for $C_{30}H_{28}NaN_2O_4$ (M + Na^+): 503.1941, found 503.1944. To confirm the linearity of the structure (vs angular compound **15b**), **15a** was subjected to TBAF mediated unmasking conditions[3] to afford mono-*N*-Cbz-pyrrolo[2,3-*f*]indole **17a**. Its ^{1}H NMR clearly shows two distinctive singlets at 8.15 and 7.16 ppm.



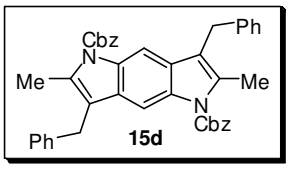


Dibenzyl 3,7-dibutyl-2,6-dimethylpyrrolo[2,3-f]indole-1,5-dicarboxylate (15b): mp (°C) = 143 – 145, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.52 (d, *J* = 7.0 Hz, 4H), 7.44 – 7.39 (m, 6H), 5.46 (s, 4H), 2.58 (t, *J* = 7.3 Hz, 4H), 2.53 (s, 6H), 1.47 (quintet, *J* = 7.3 Hz, 4H), 1.31 – 1.22 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 135.4, 132.82, 132.78, 129.0, 128.8, 128.2 120.2, 104.7, 68.6, 32.2, 23.8, 22.6, 14.21, 14.20; FT-IR (CH_2Cl_2) 3043, 2954, 2928, 1732, 1403, 1286, 1207, 1219, 1094 cm^{-1}; HRMS Calcd for $C_{36}H_{40}NaN_2O_4$ (M + Na^+): 587.2880, found 587.2888.

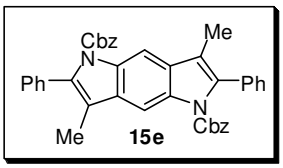


Dibenzyl 3,7-bis(2-methoxy-2-oxoethyl)-2,6-dimethyl-pyrrolo-[2,3-f]-indole-1,5-dicarboxylate (15d): mp (°C) = 211 – 213, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.53 (d, *J* = 6.8 Hz, 4H), 7.44 – 7.39 (m, 6H), 5.47 (s, 4H), 3.62 (s, 10H), 2.58 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 152.2, 135.4, 135.3, 132.9, 128.91, 128.86, 128.7, 127.9, 112.6, 104.7, 68.8, 52.2, 30.1, 14.4; FT-IR (CH_2Cl_2) 3065, 2991,

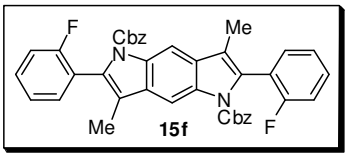
2951, 1737, 1722, 1497, 1451, 1404, 1326, 1293, 1225, 1110 cm^{-1}; HRMS Calcd for $C_{34}H_{32}NaN_2O_8$ (M + Na^+): 619.2051, found 619.2057.



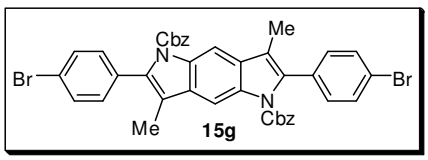
Dibenzyl 3,7-dibenzyl-2,6-dimethylpyrrolo[2,3-f]indole-1,5-dicarboxylate (15d): mp (°C) = 195 – 197, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.46 (d, *J* = 2.4 Hz, 2H), 7.44 (d, *J* = 2.4 Hz, 2H), 7.35 – 7.34 (m, 6H), 7.20 – 7.10 (m, 6H), 7.05 (d, *J* = 7.0 Hz, 4H), 5.41 (s, 4H), 3.94 (s, 4H), 2.57 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 140.3, 135.3, 134.2, 132.8, 128.9, 128.8, 128.5, 128.2, 128.1, 128.0. 126.0, 118.4, 105.0, 68.6, 30.0, 14.4; FT-IR (CH_2Cl_2) 3081, 3060, 2954, 2926, 1722, 1711, 1610, 1493, 1448, 1403, 1311, 1212, 1193 cm^{-1}; HRMS Calcd for $C_{42}H_{36}NaN_2O_4$ (M + Na^+): 655.2570, found 655.2567.



Dibenzyl 3,7-dimethyl-2,6-diphenylpyrrolo[2,3-f]indole-1,5-dicarboxylate (15e): mp (°C) = 220 – 221, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.37 – 7.33 (m, 8H), 7.27 – 7.25 (m, 8H), 7.06 – 7.04 (m, 4H), 5.17 (s, 4H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 136.0, 135.0, 134.0, 133.7, 130.0, 129.7, 128.54, 128.46, 128.40, 127.9, 127.6, 118.2, 105.3, 68.5, 9.6; FT-IR (CH_2Cl_2) 3057, 3026, 1714, 1405, 1301, 1204, 1025 cm^{-1}; HRMS Calcd for $C_{40}H_{32}NaN_2O_4$ (M + Na^+): 627.2254, found 627.2265.

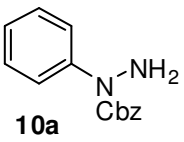


Dibenzyl 3,7-bis(2-fluorophenyl)-2,6-dimethylpyrrolo-[2,3-f]-indole-1,5-dicarboxylate (15f): mp (°C) = 250 – 251, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.35 – 7.28 (m, 10H), 7.18 – 7.13 (m, 6H), 7.00 – 6.96 (m, 2H), 5.21 (d, *J* = 1.8 Hz, 4H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, *J* = 246.4 Hz), 151.7, 134.8, 133.6, 131.8, 129.9 (d, *J* = 9.2 Hz), 129.6, 128.6, 128.54, 128.46, 123.6 (d, *J* = 3.1 Hz), 122.1, 121.9, 119.4, 115.3 (d, *J* = 22.1 Hz), 105.5, 68.6, 9.6; FT-IR (CH_2Cl_2) 3066, 3028, 2958, 2918, 1717, 1591, 1487, 1438, 1407, 1305, 1206 cm^{-1}; HRMS Calcd for $C_{40}H_{30}F_2NaN_2O_4$ (M + Na^+): 663.2066, found 663.2073.

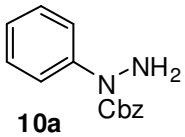


Dibenzyl 3,7-bis(4-bromophenyl)-2,6-dimethylpyrrolo-[2,3-f]indole-1,5-dicarboxylate (15g): mp (°C) = 278 – 279, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.45 (d, *J* = 8.9 Hz, 4H), 7.33 – 7.31 (m, 6H), 7.18 (d, *J* = 8.1 Hz, 4H), 7.08 – 7.06 (m, 4H), 5.17 (s, 4H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 134.8, 134.5, 133.2, 132.9, 131.6, 131.1, 129.7, 128.7, 128.6, 122.0, 118.7, 105.4, 68.8, 9.6; FT-IR (CH_2Cl_2) 3032, 2925, 2855, 1708, 1401, 1305, 1197 cm^{-1}; HRMS Calcd for $C_{40}H_{30}Br_2NaN_2O_4$ (M + Na^+): 783.0465, found 783.0464.

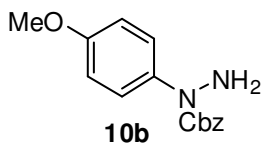
1) A. Kuwahara, K. Nakano, K. Nozaki, *J. Org. Chem*. **2005**, *70*, 413.
2) T. G. Back, A. Pandyra, J. E. Wulff, *J. Org. Chem*. **2003**, *68*, 3299.
3) U. Jacquemard, V. Bénéteau, M. Lefoix, S. Routier, J.-Y. Mérour, G. Coudert, *Tetrahedron* **2004**, *60*, 10039.



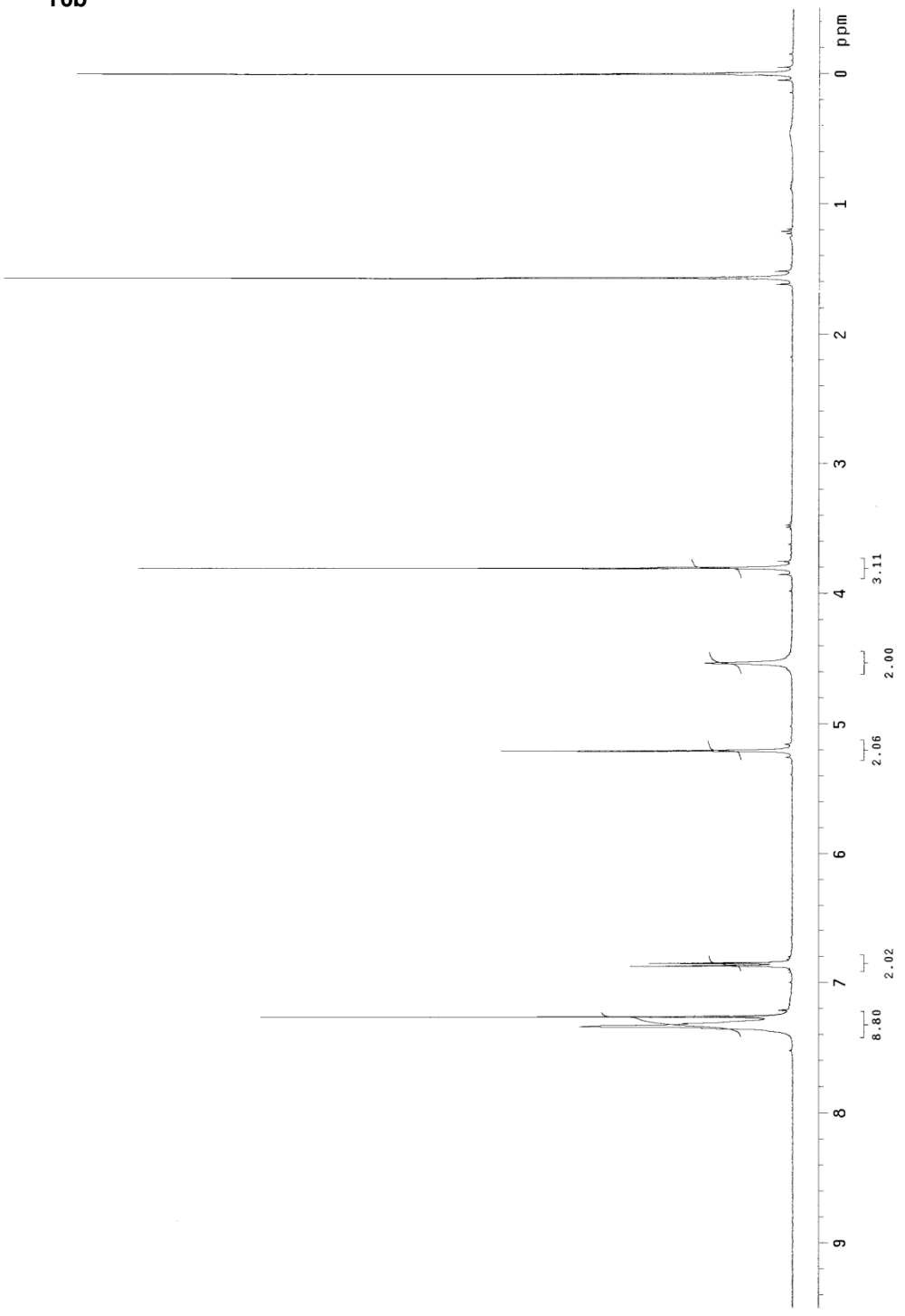
10a

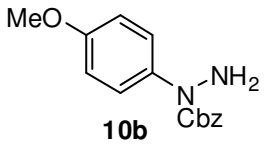


10a

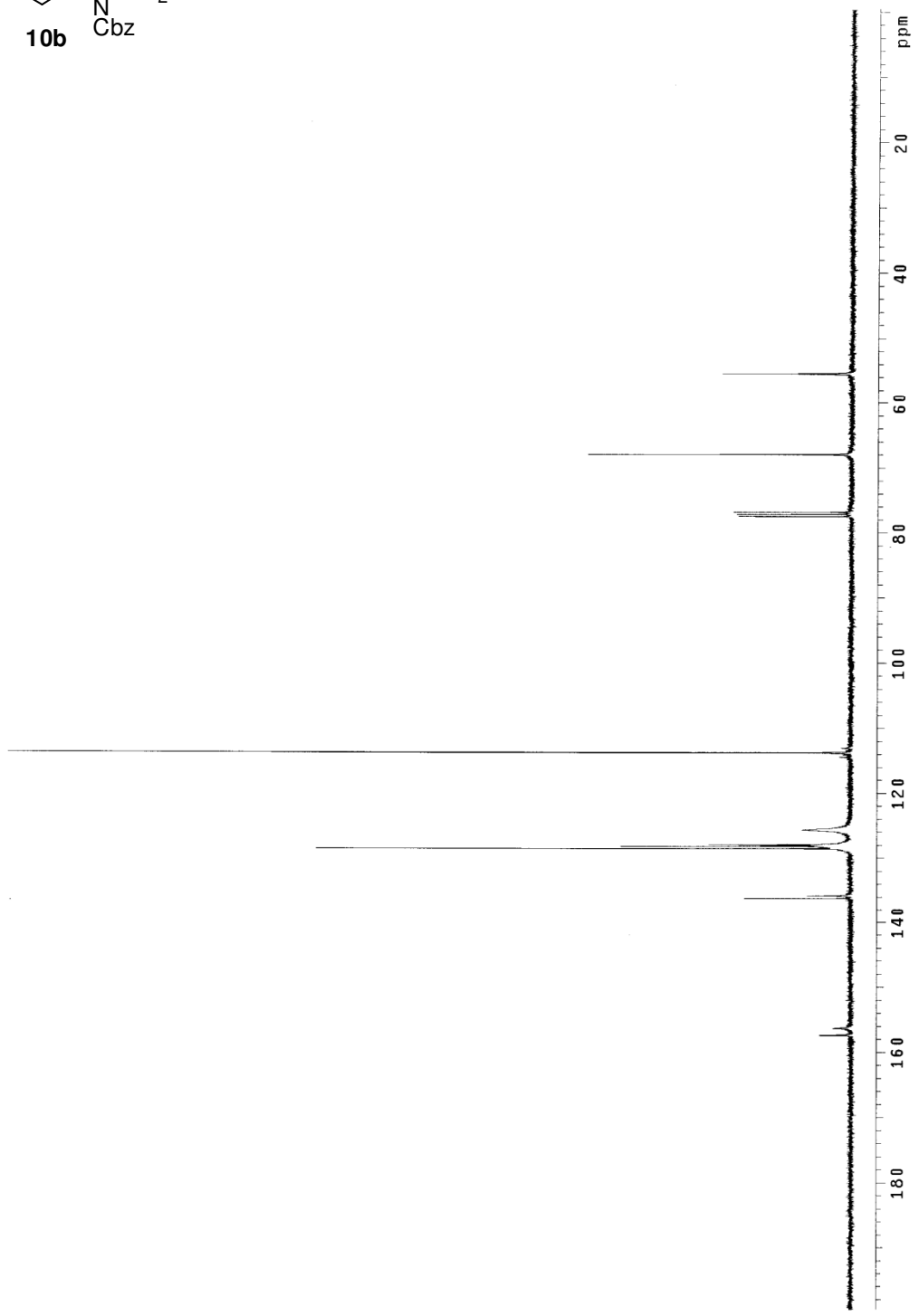


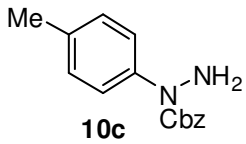
10b





10b





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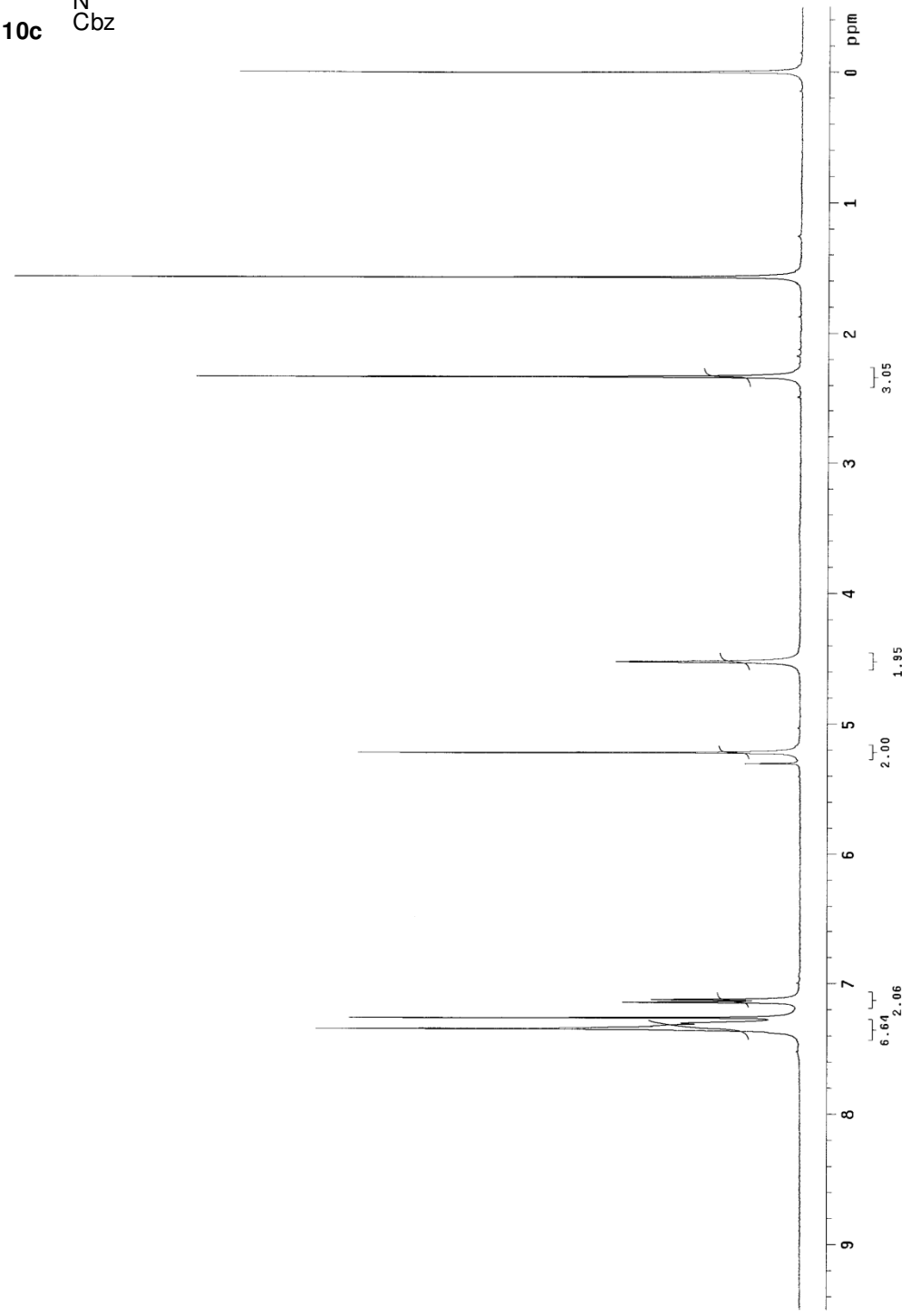

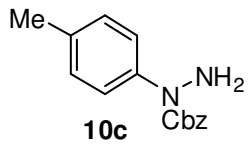

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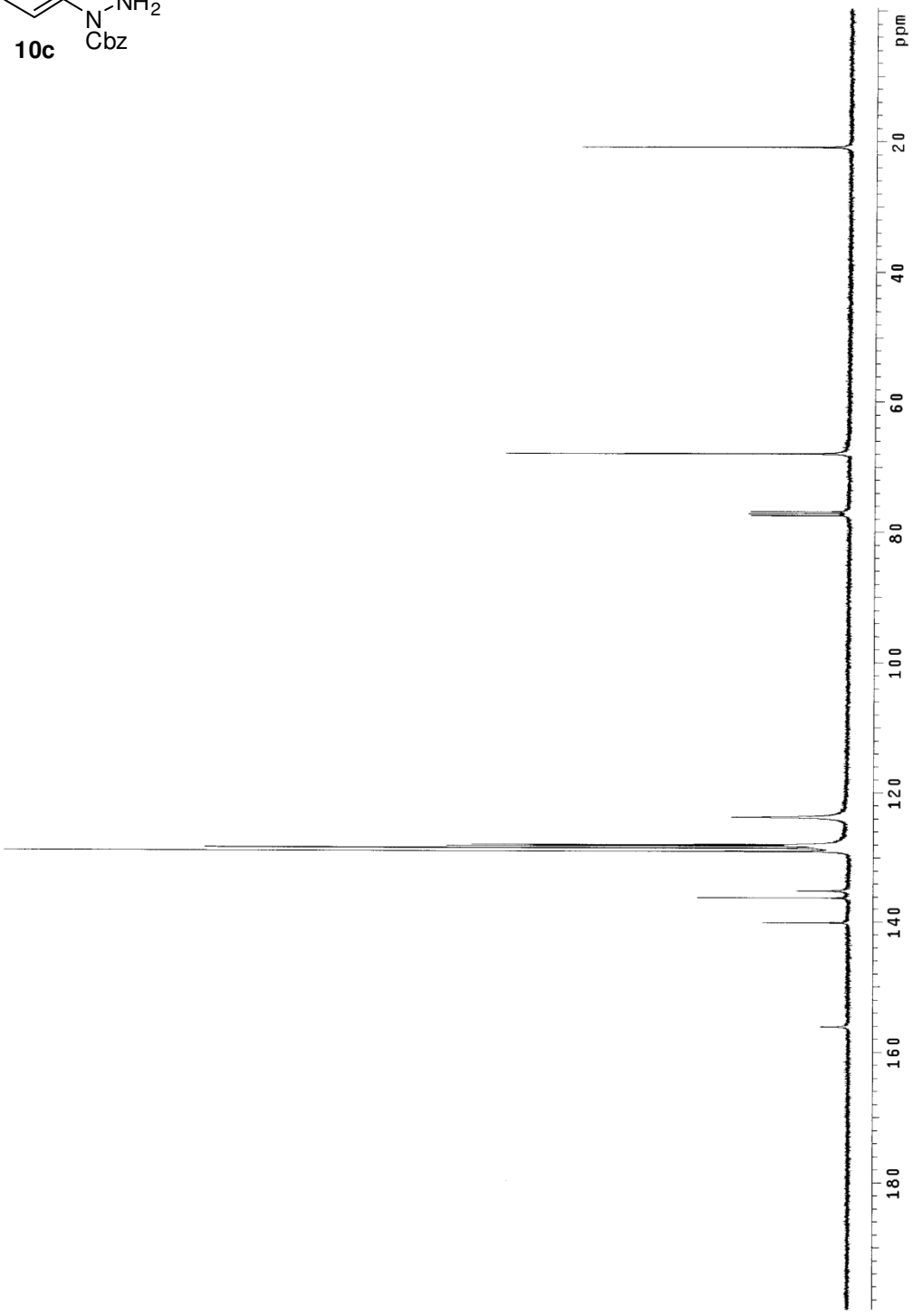

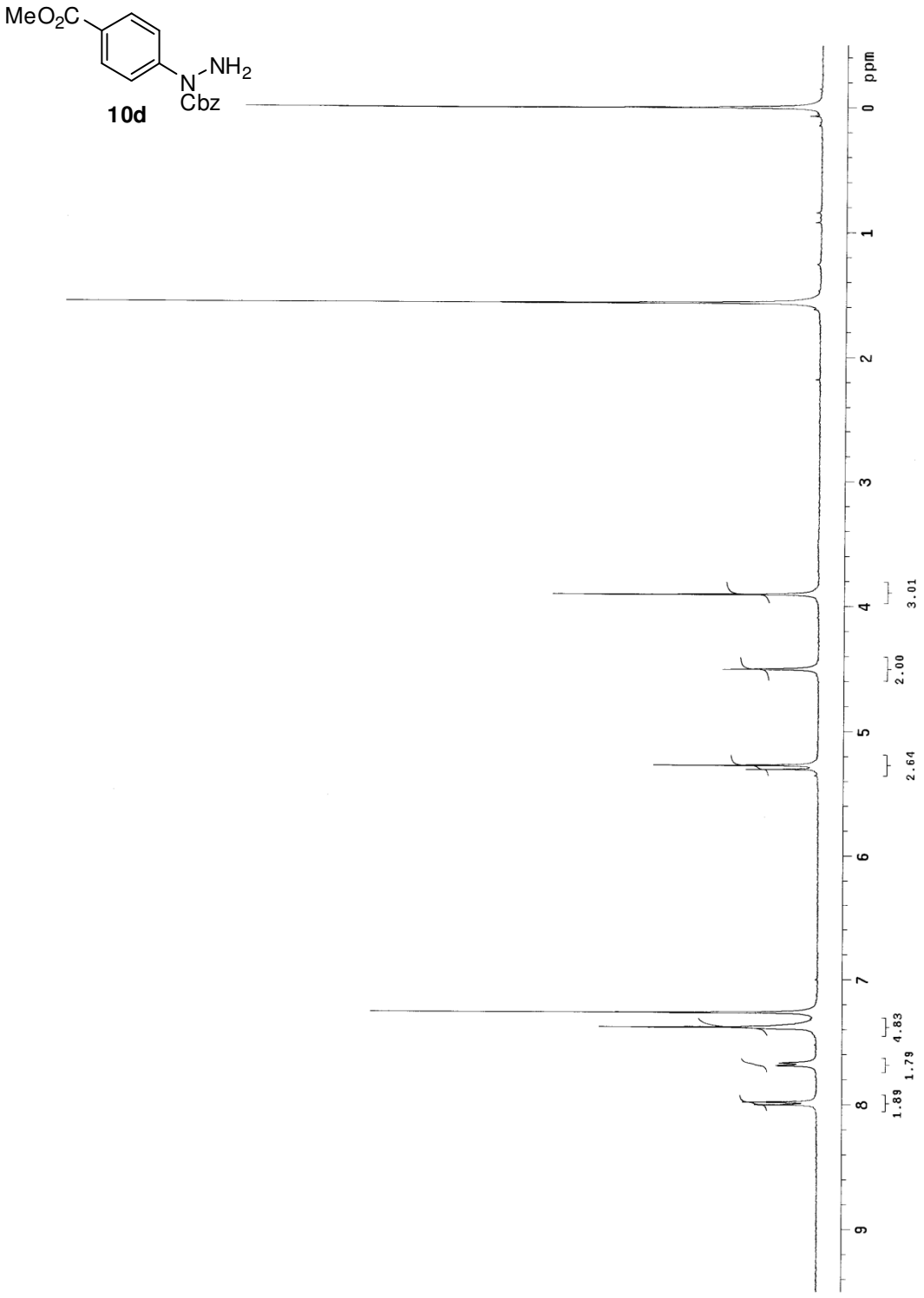
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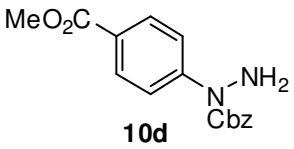

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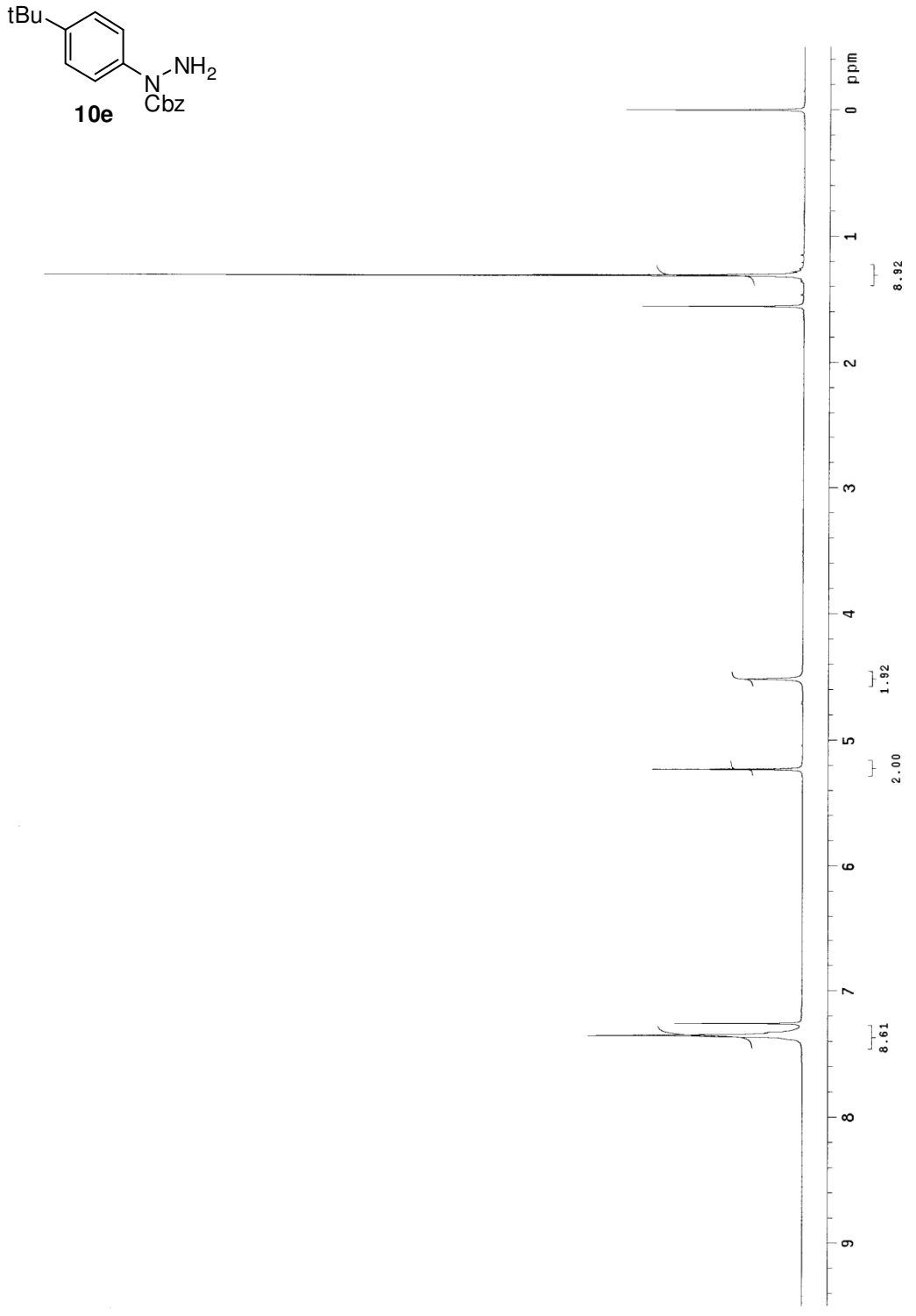
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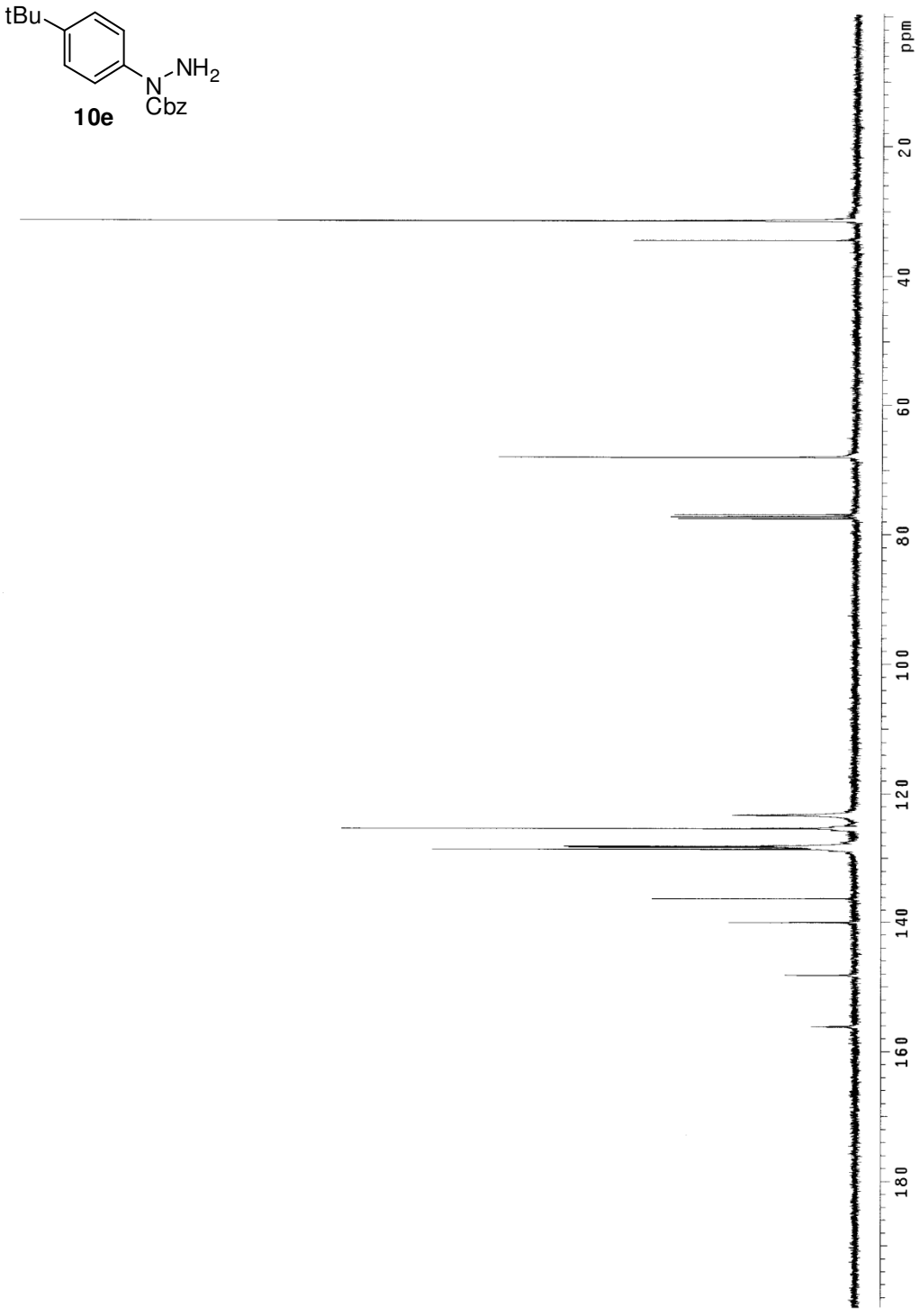
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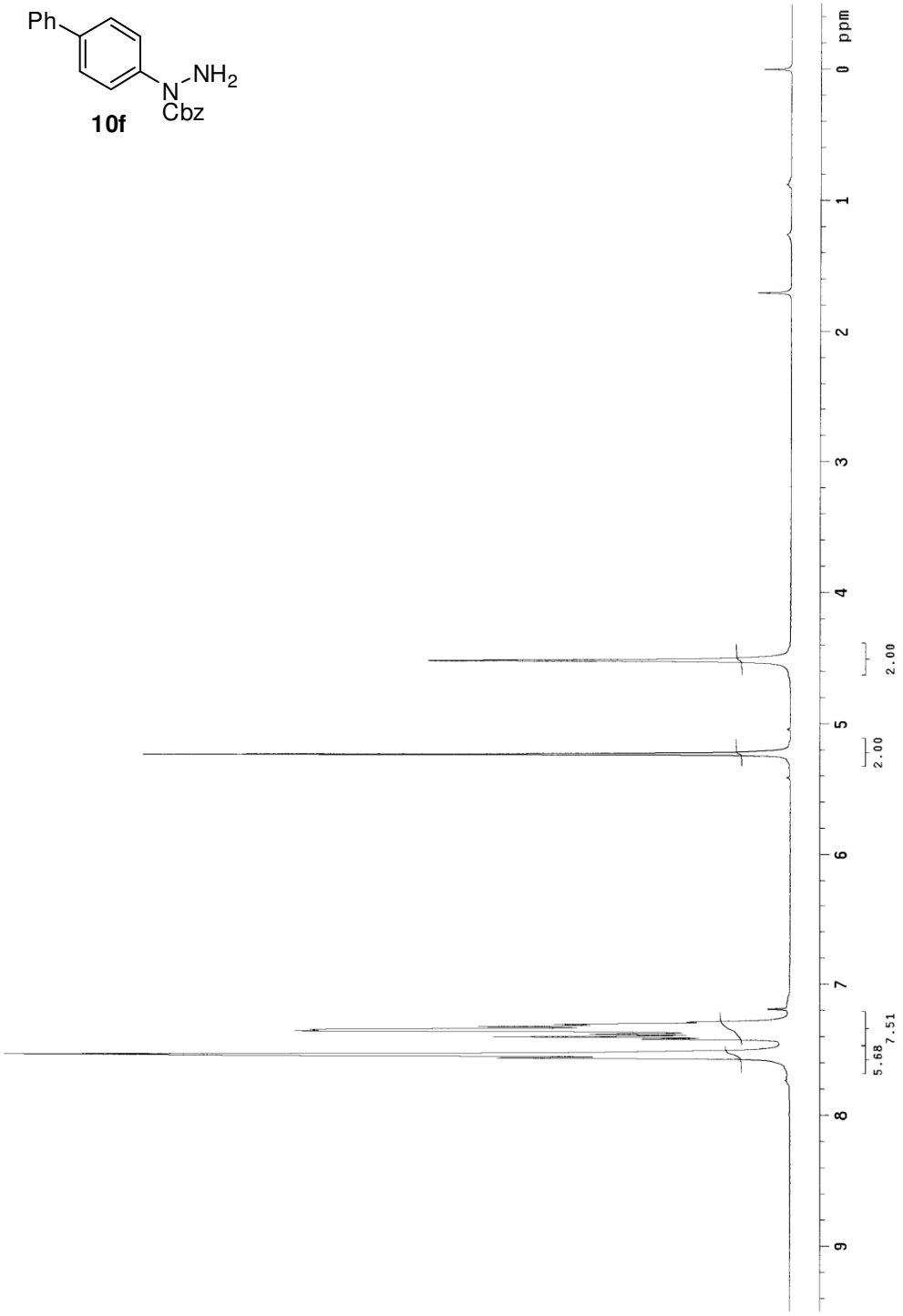
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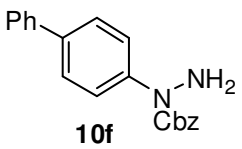

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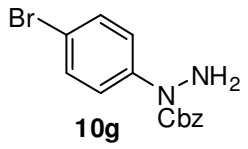

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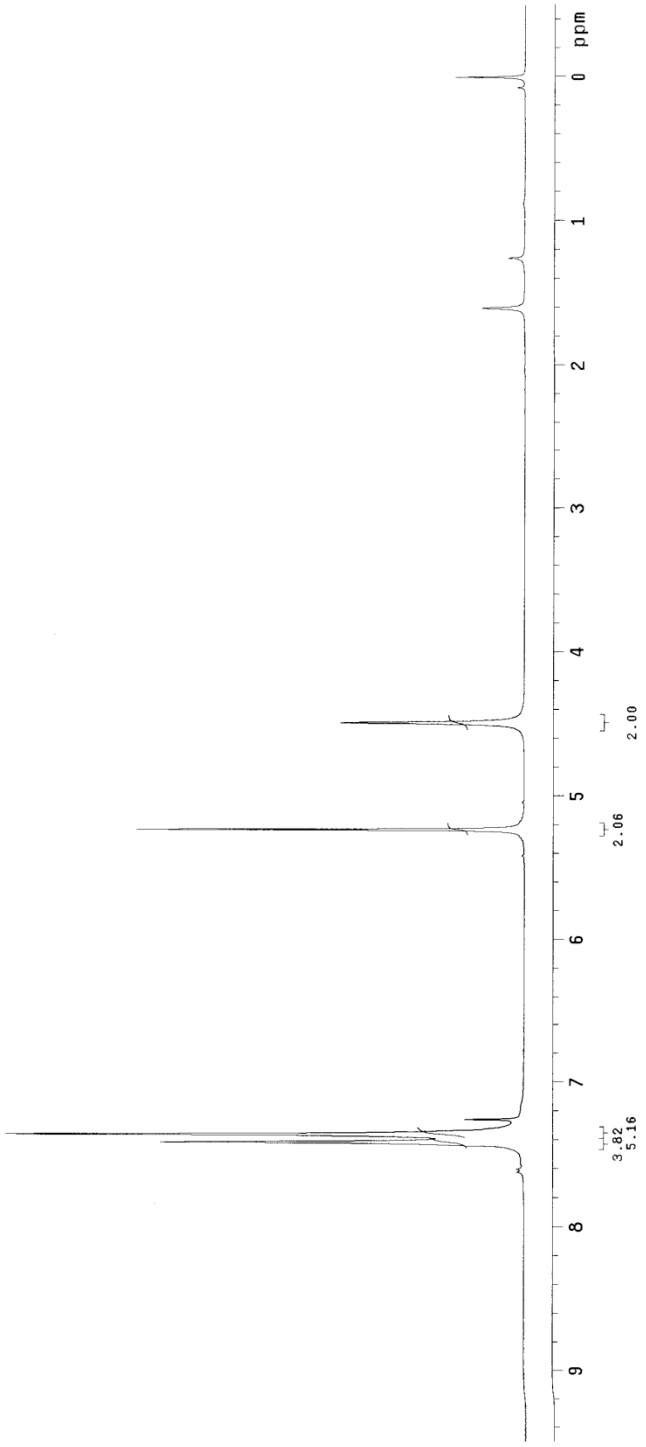

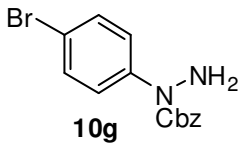

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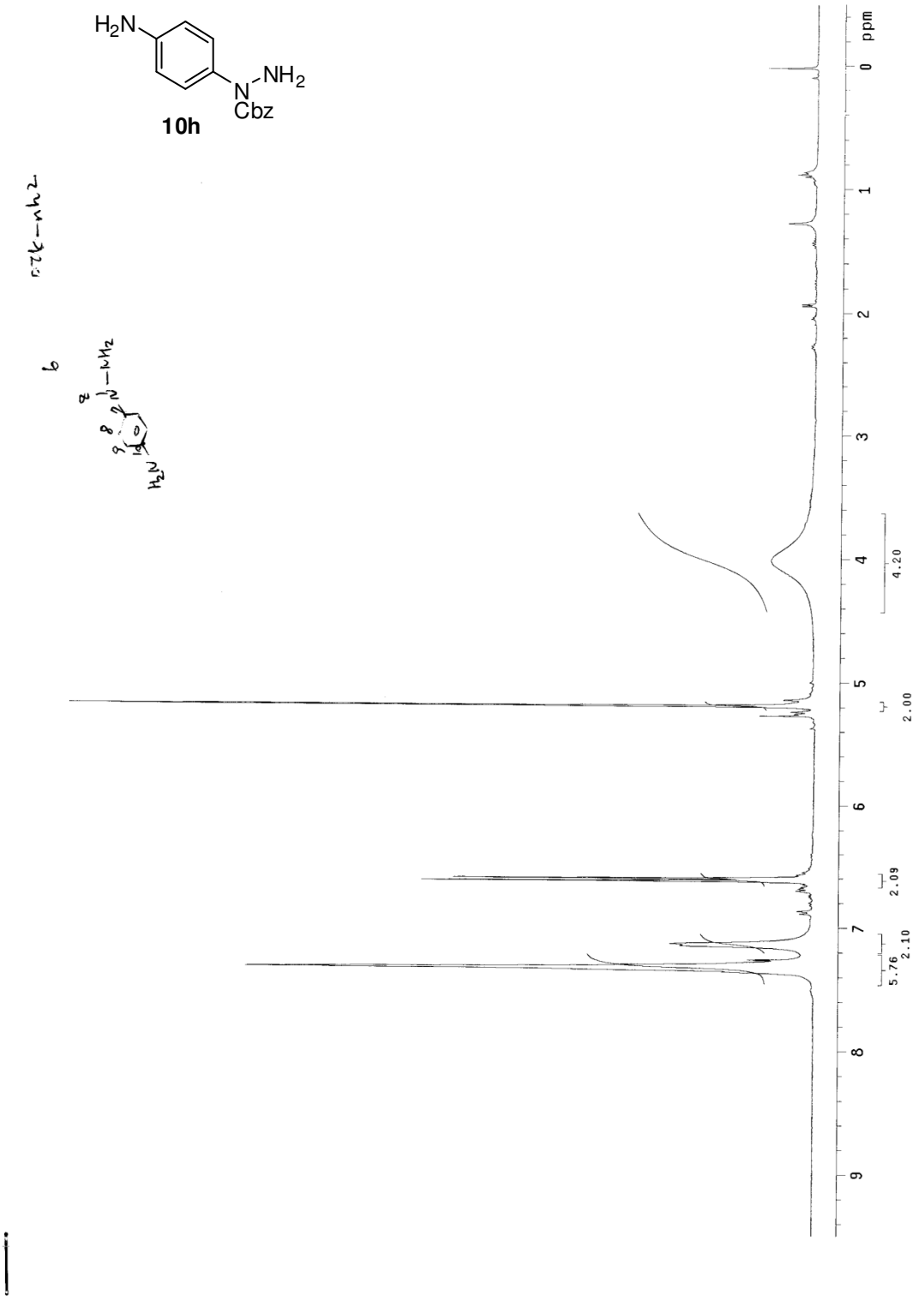
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Cbz
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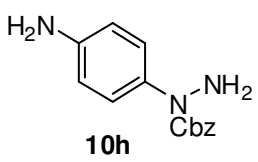
2.10



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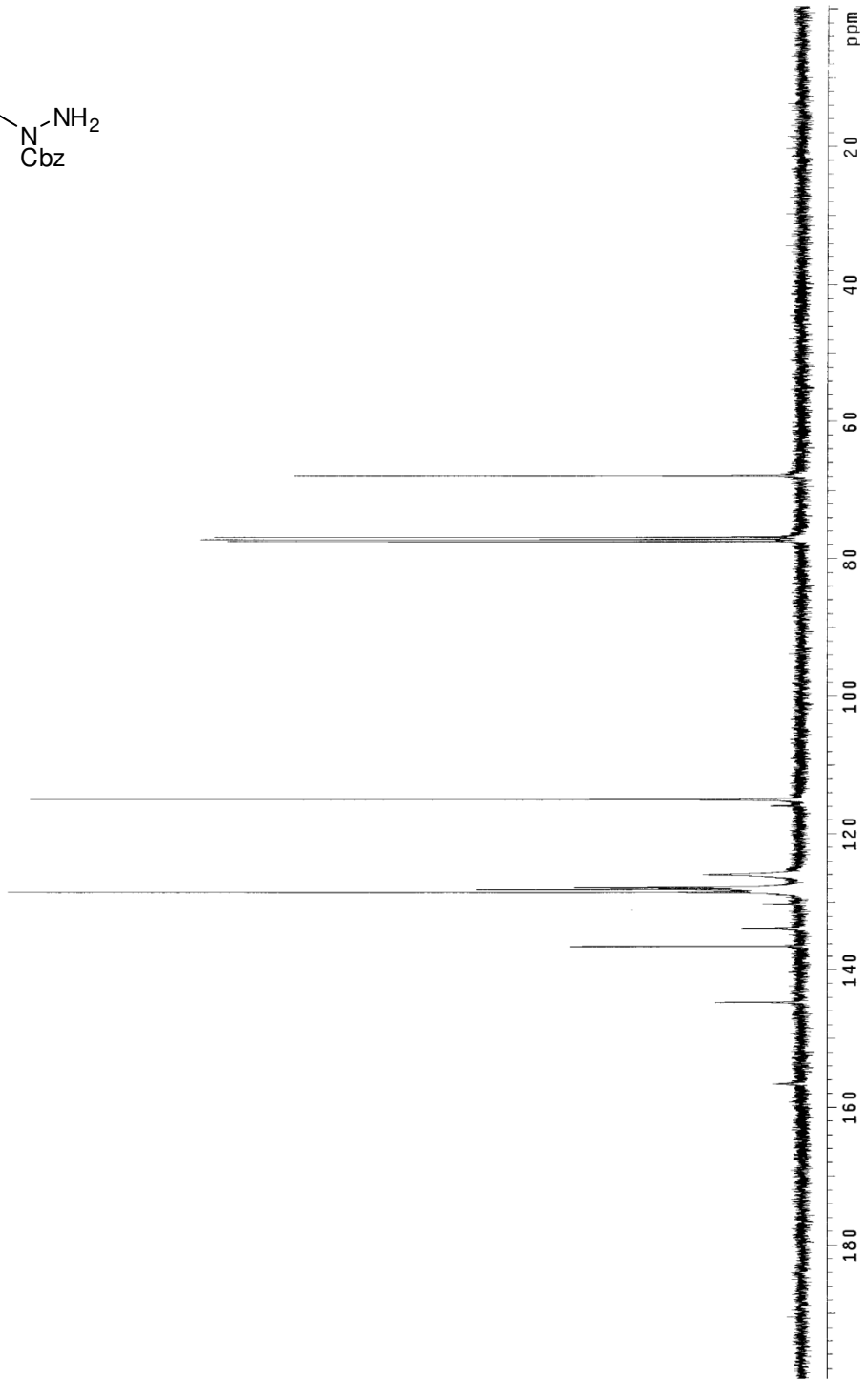

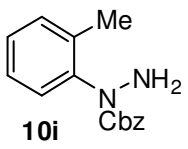

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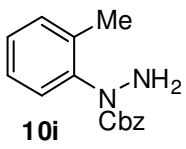

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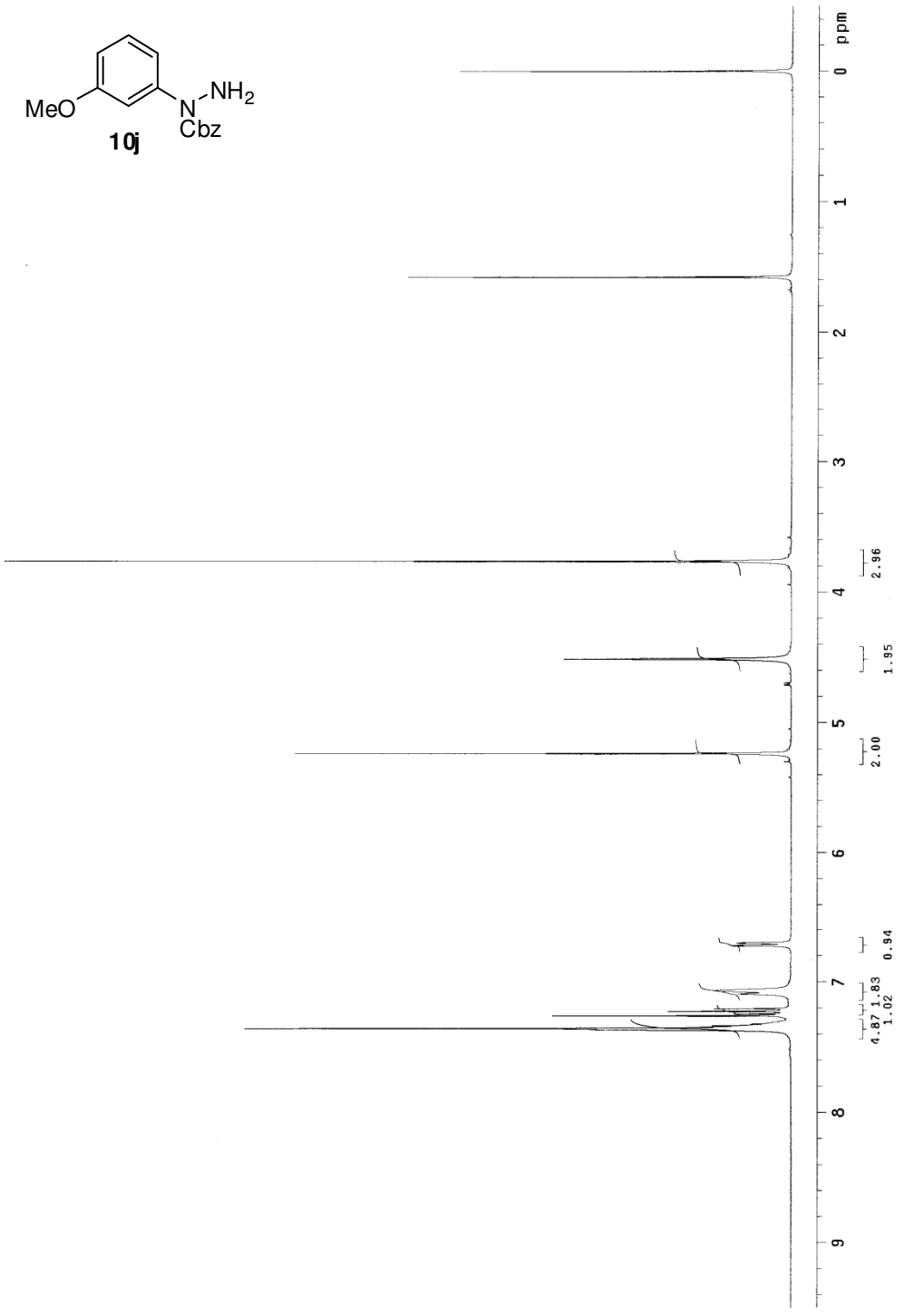
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Cbz
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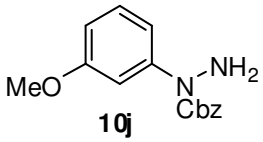
1.02



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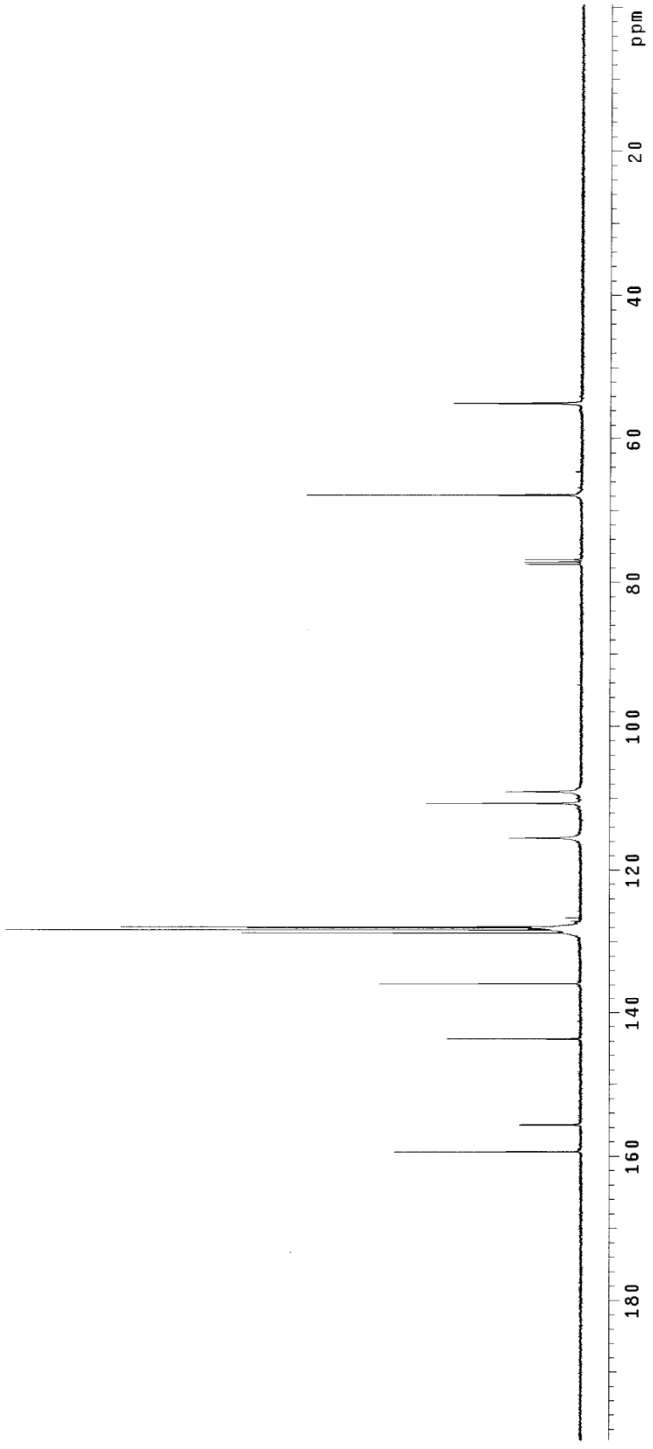

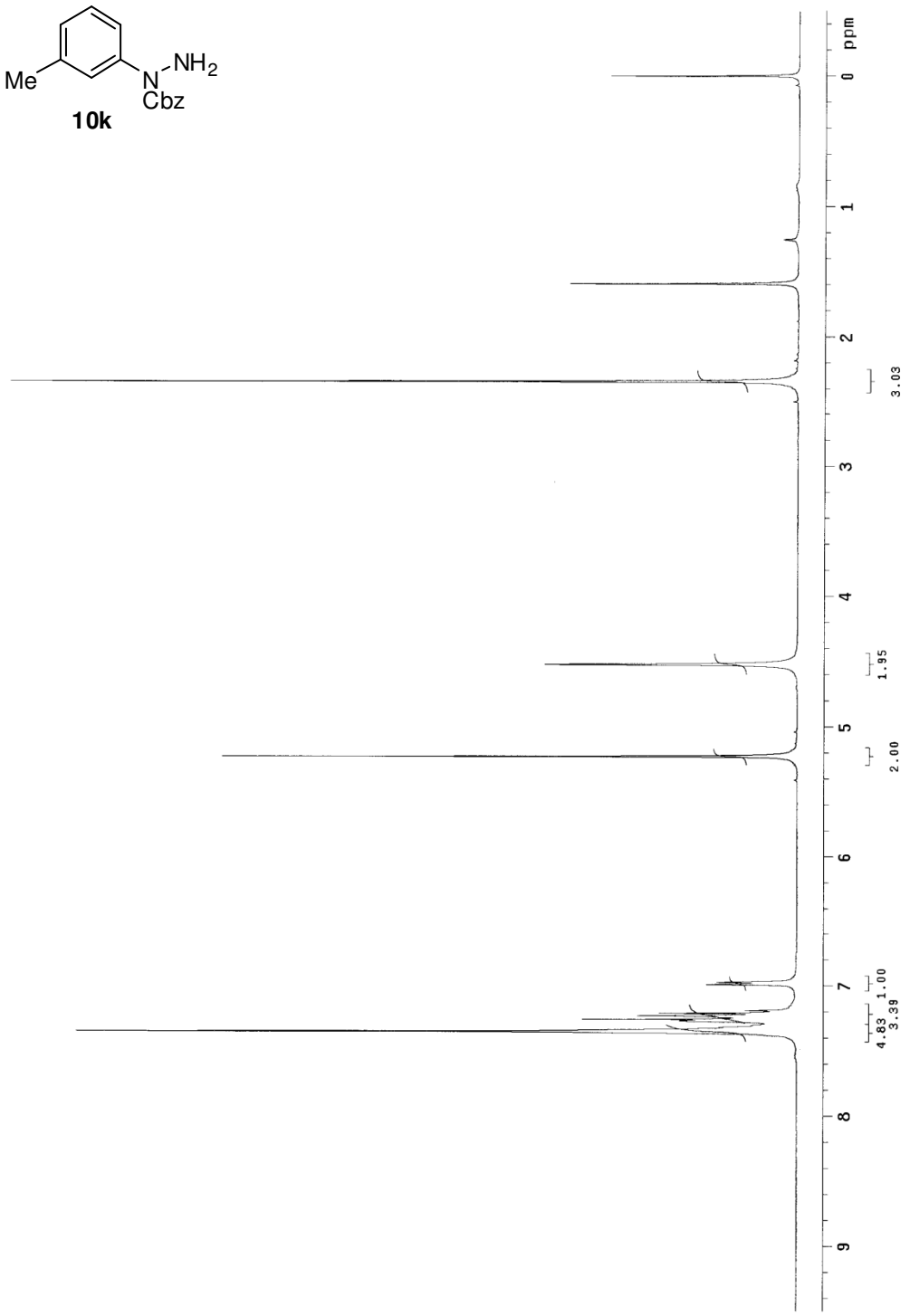
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Cbz
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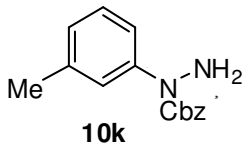

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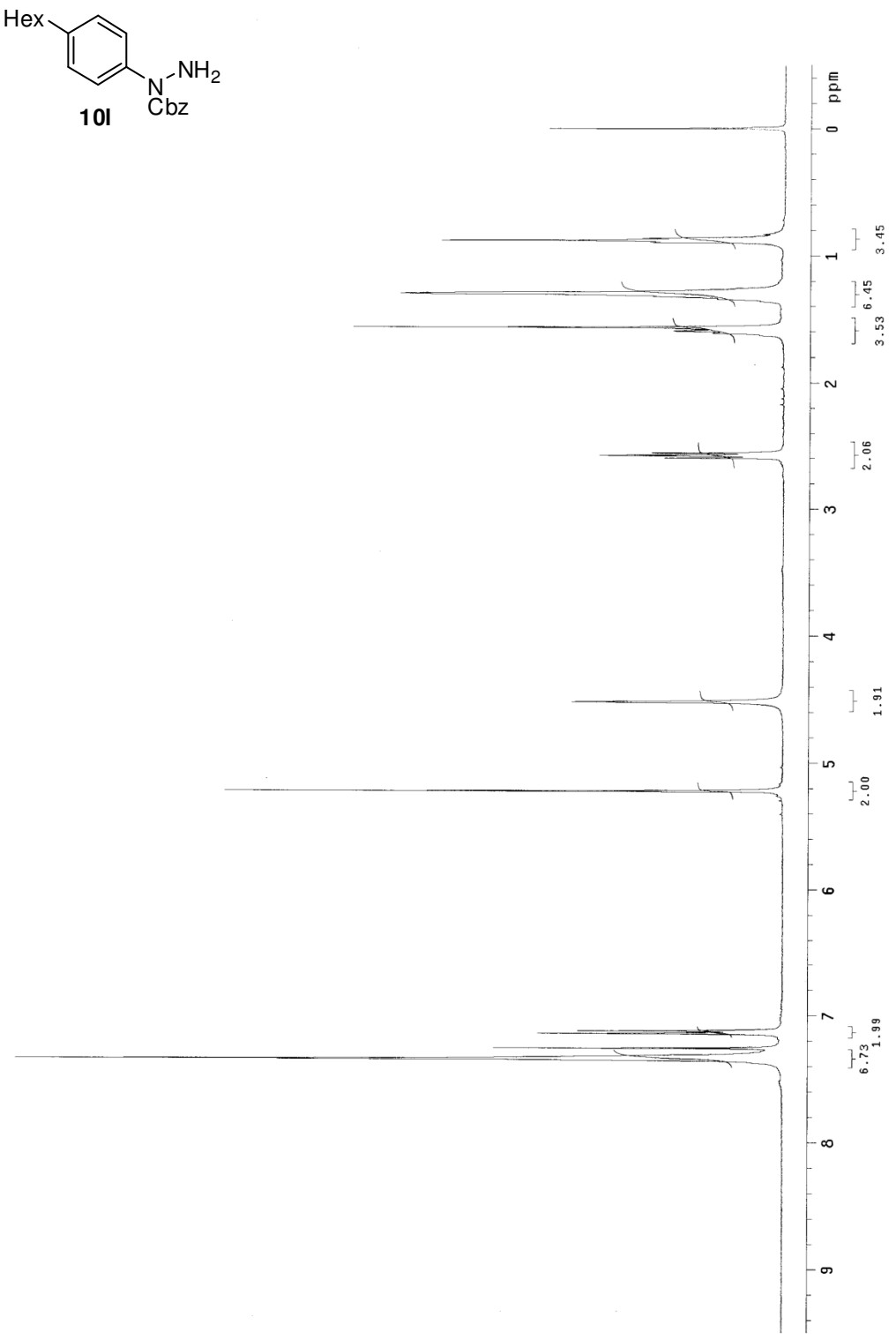
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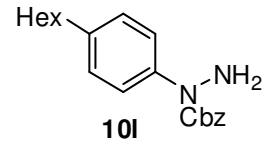
1.99



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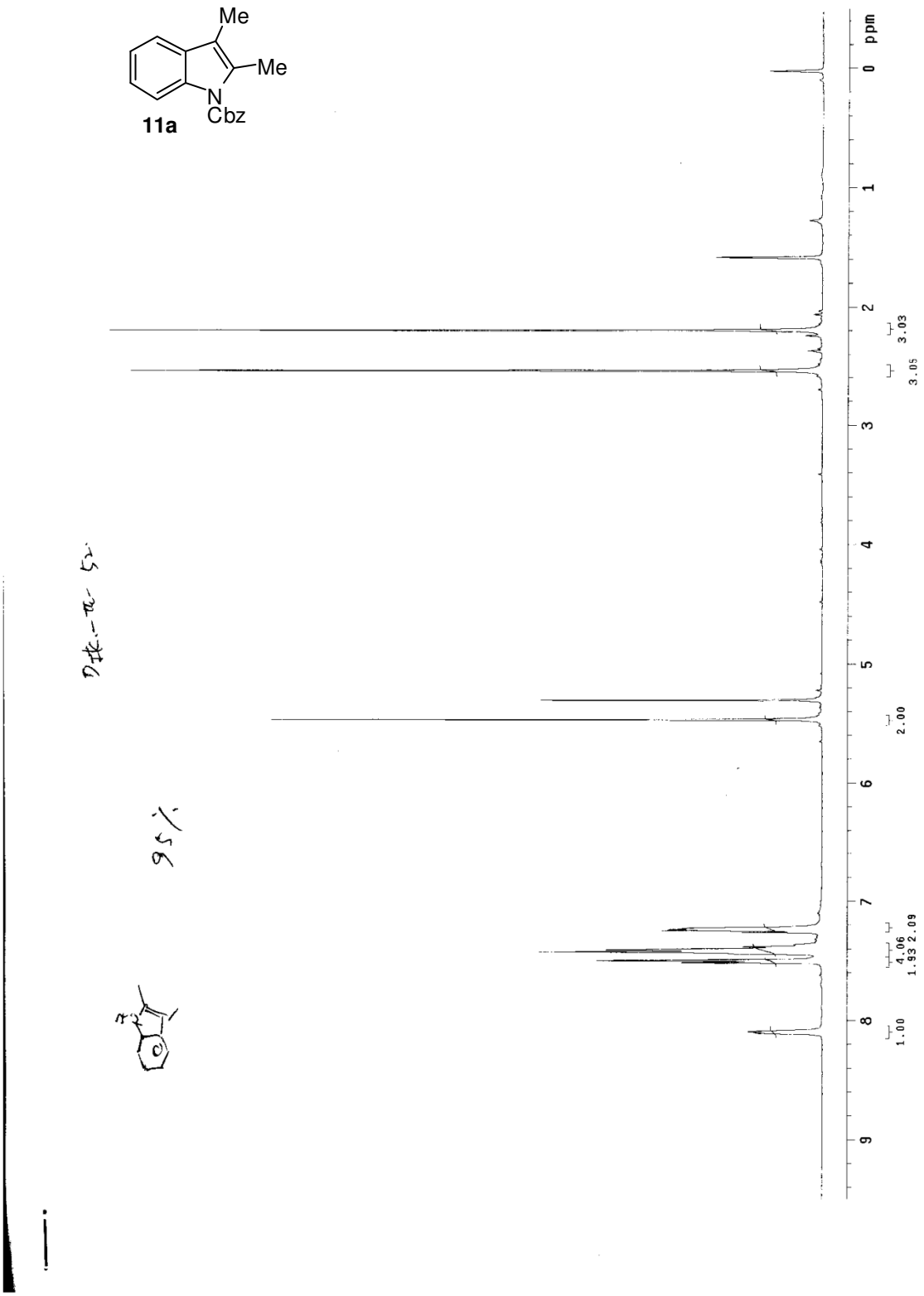
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Cbz
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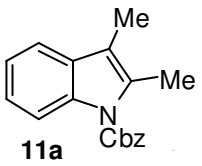
1.00



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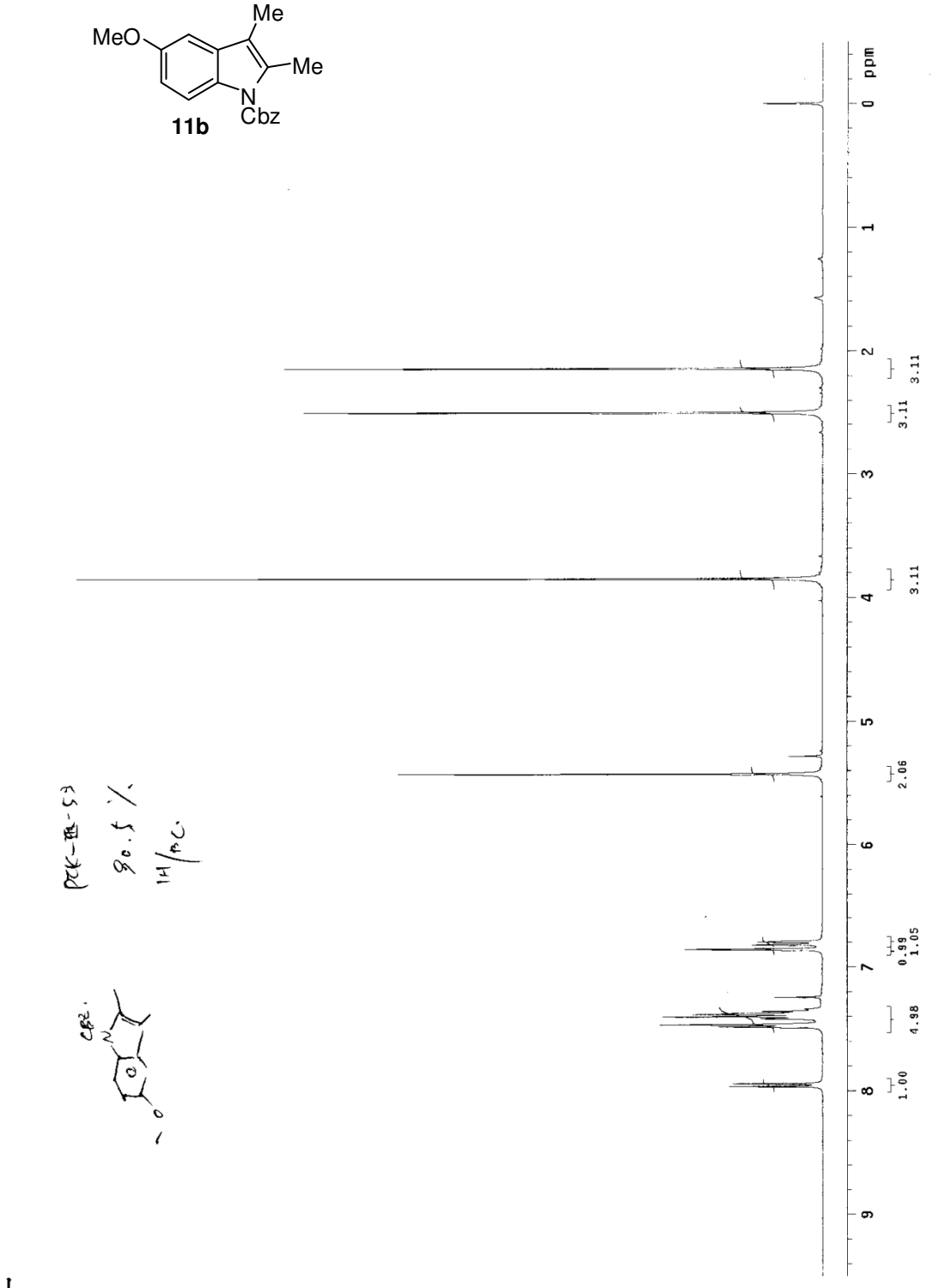
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Cbz
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ppm
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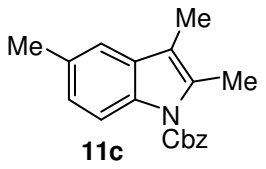
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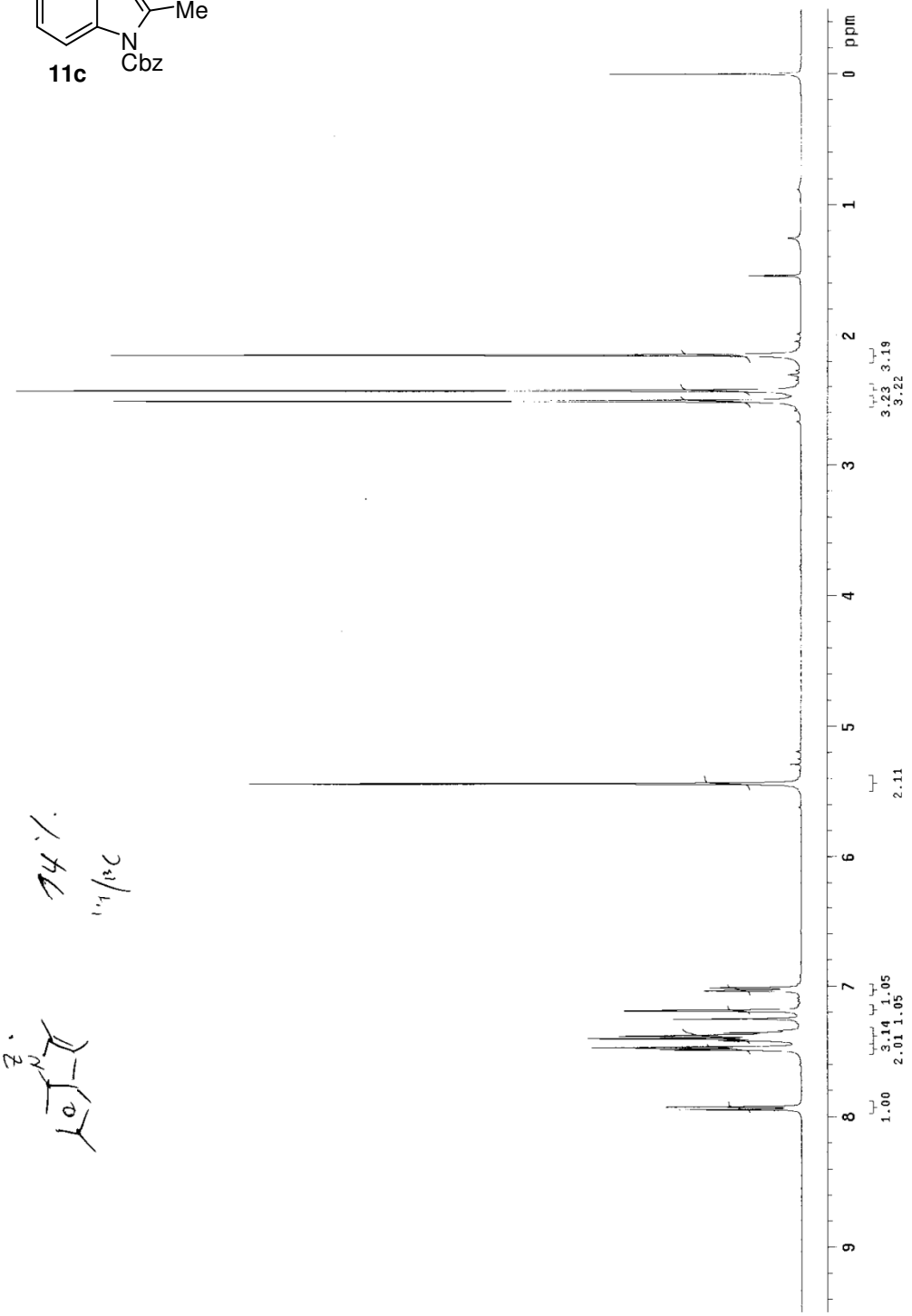
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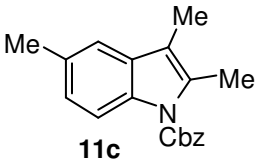

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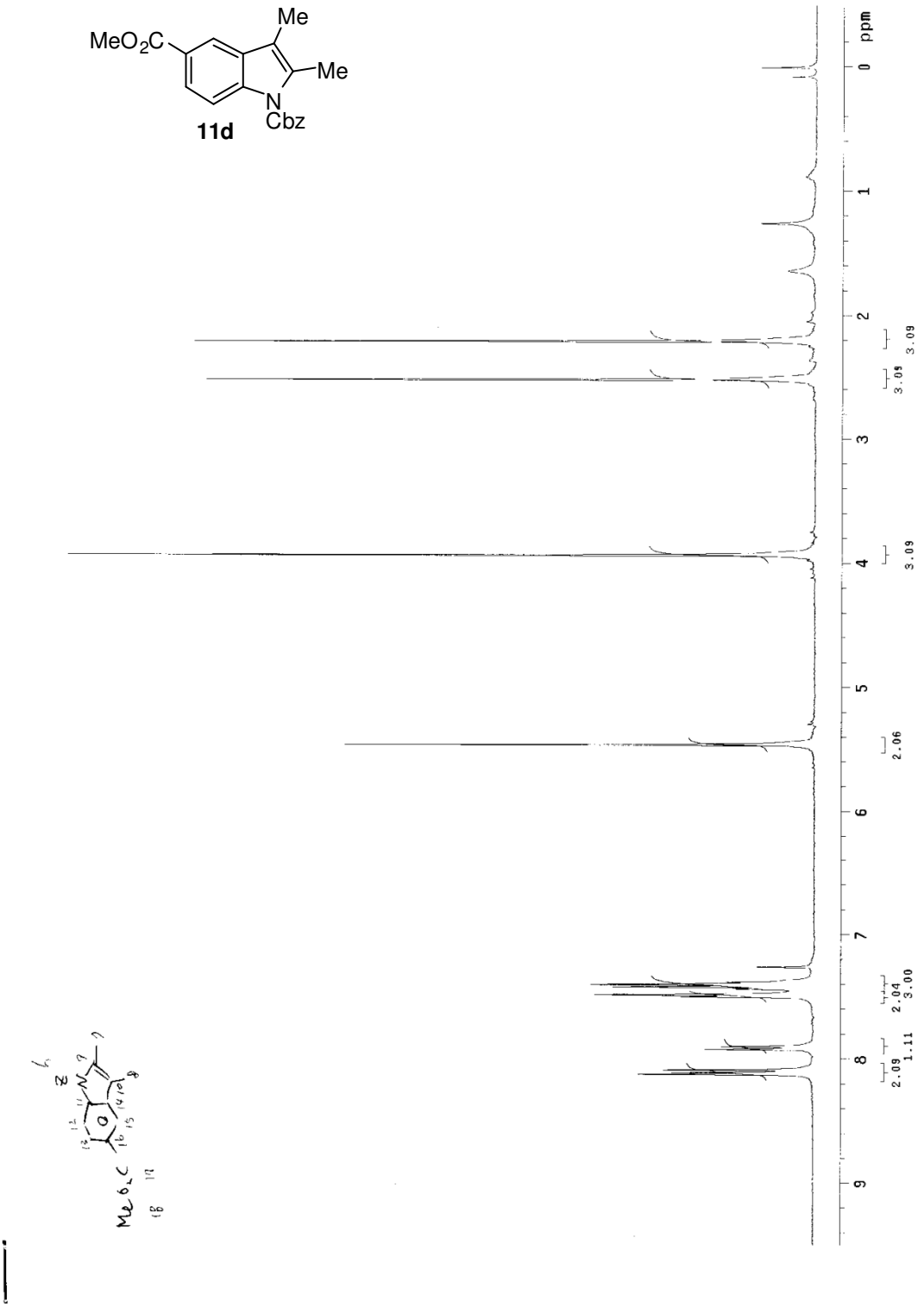
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Me
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Cbz
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ppm
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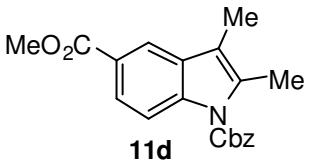

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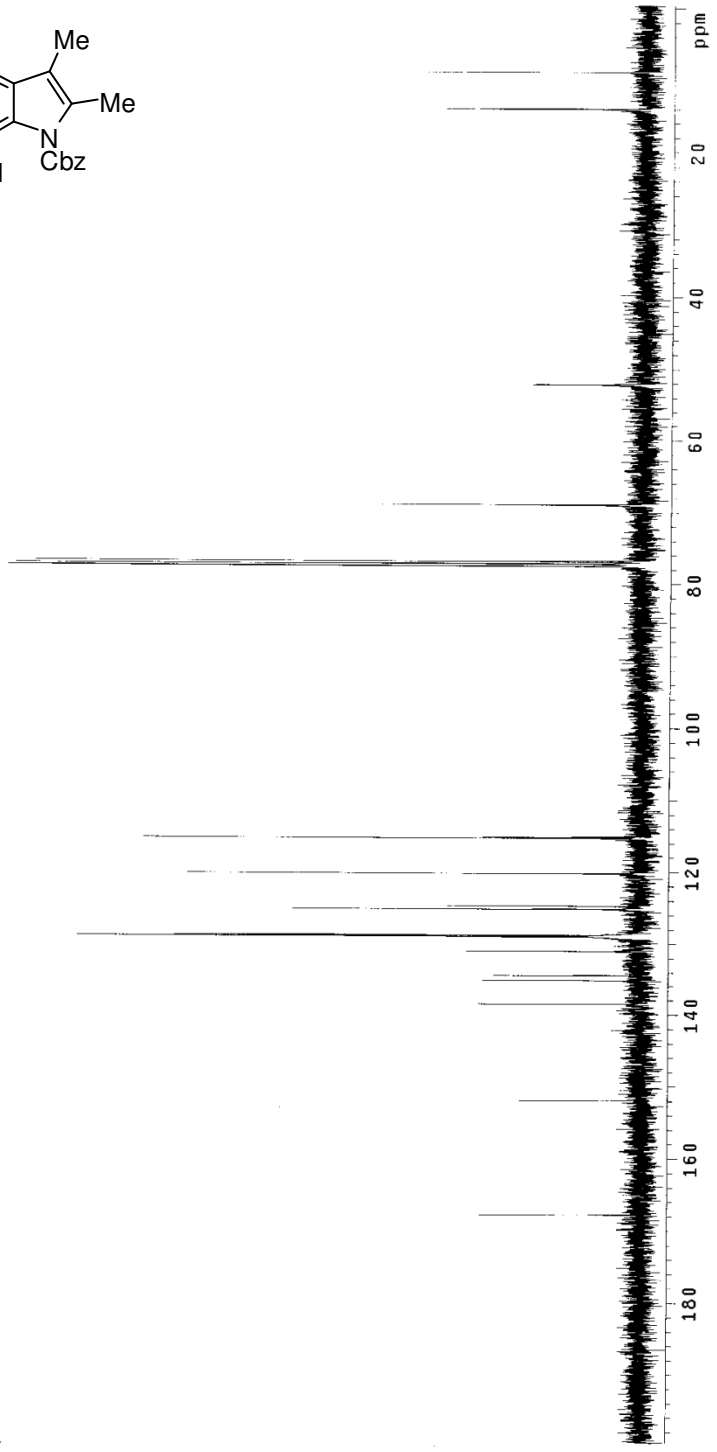

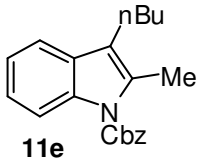
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Cbz

11e

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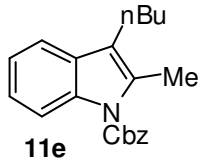

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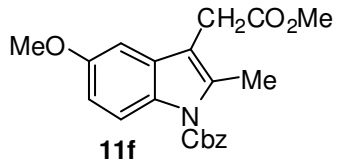
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Cbz

11f

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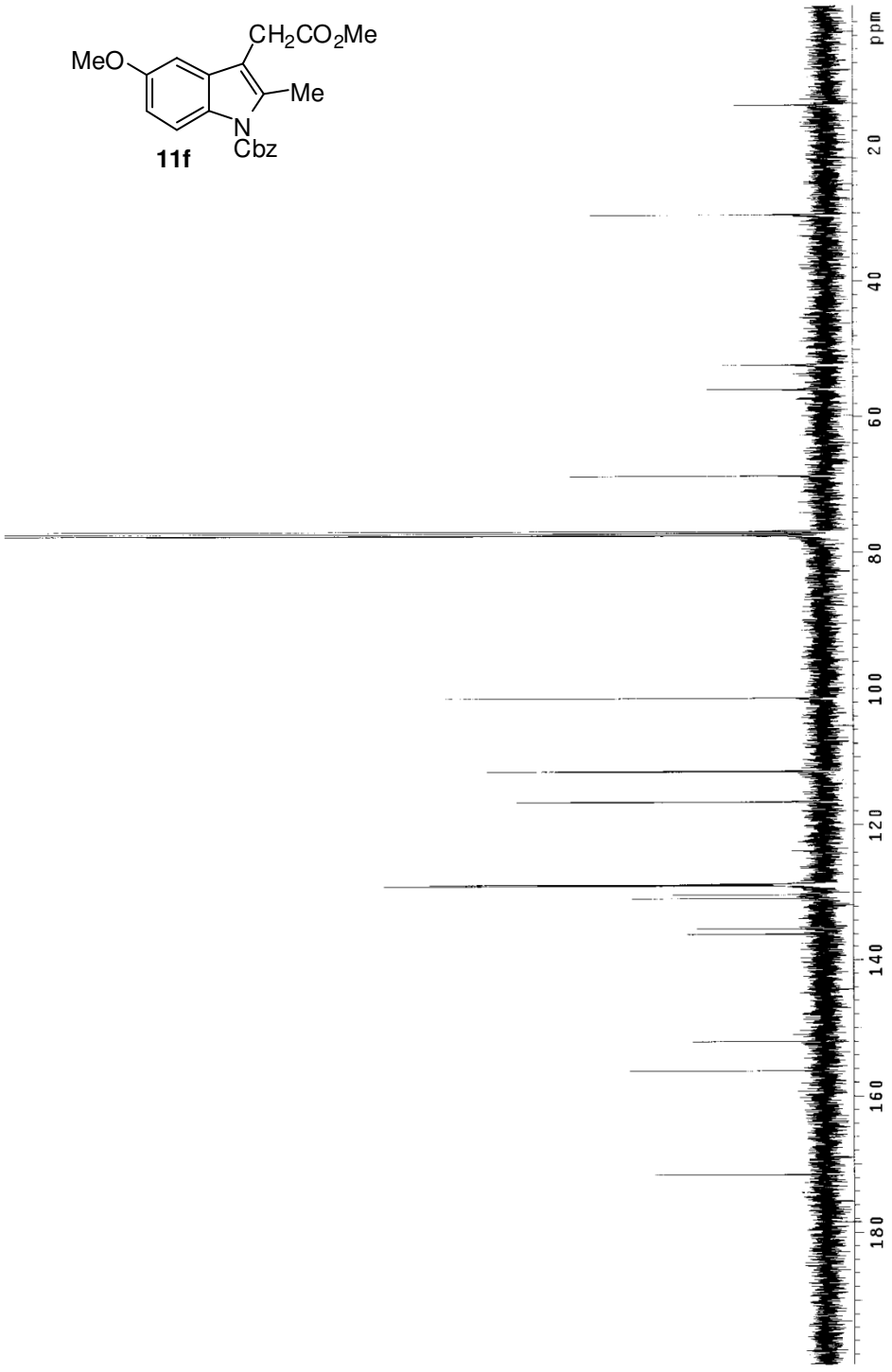
1.00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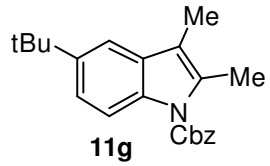

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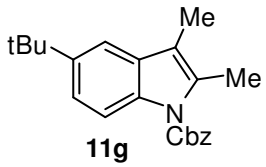

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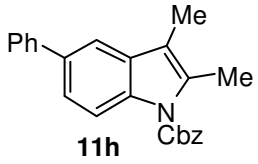

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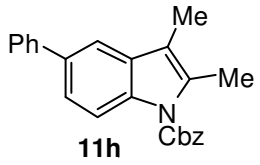
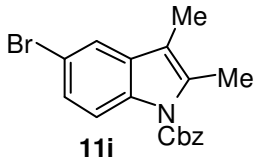
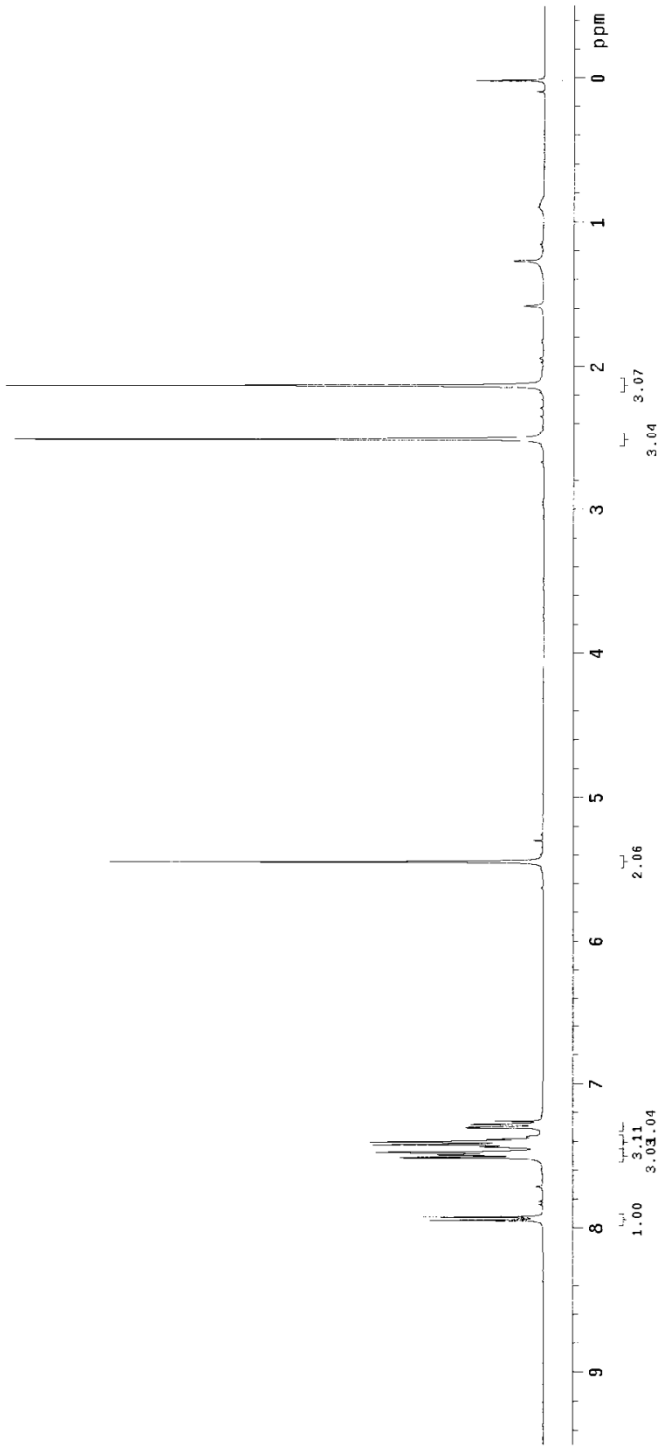
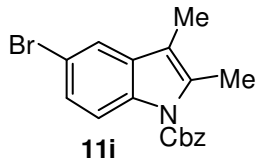


11h



11i





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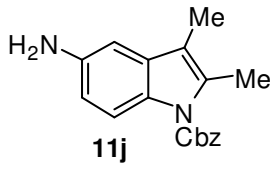
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Cbz

11j

ppm
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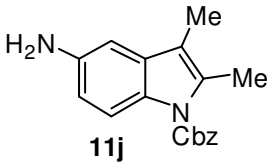

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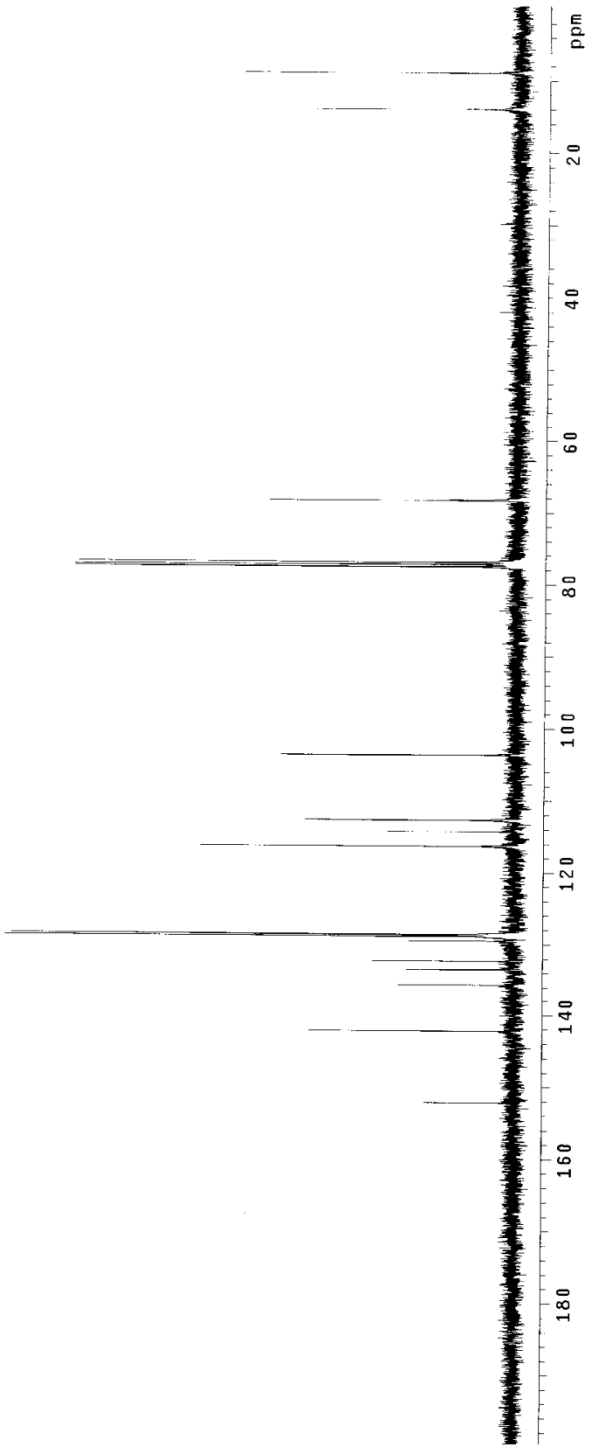

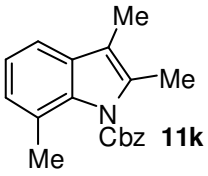

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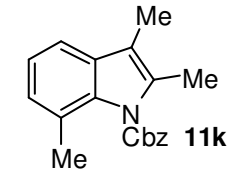

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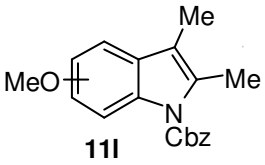
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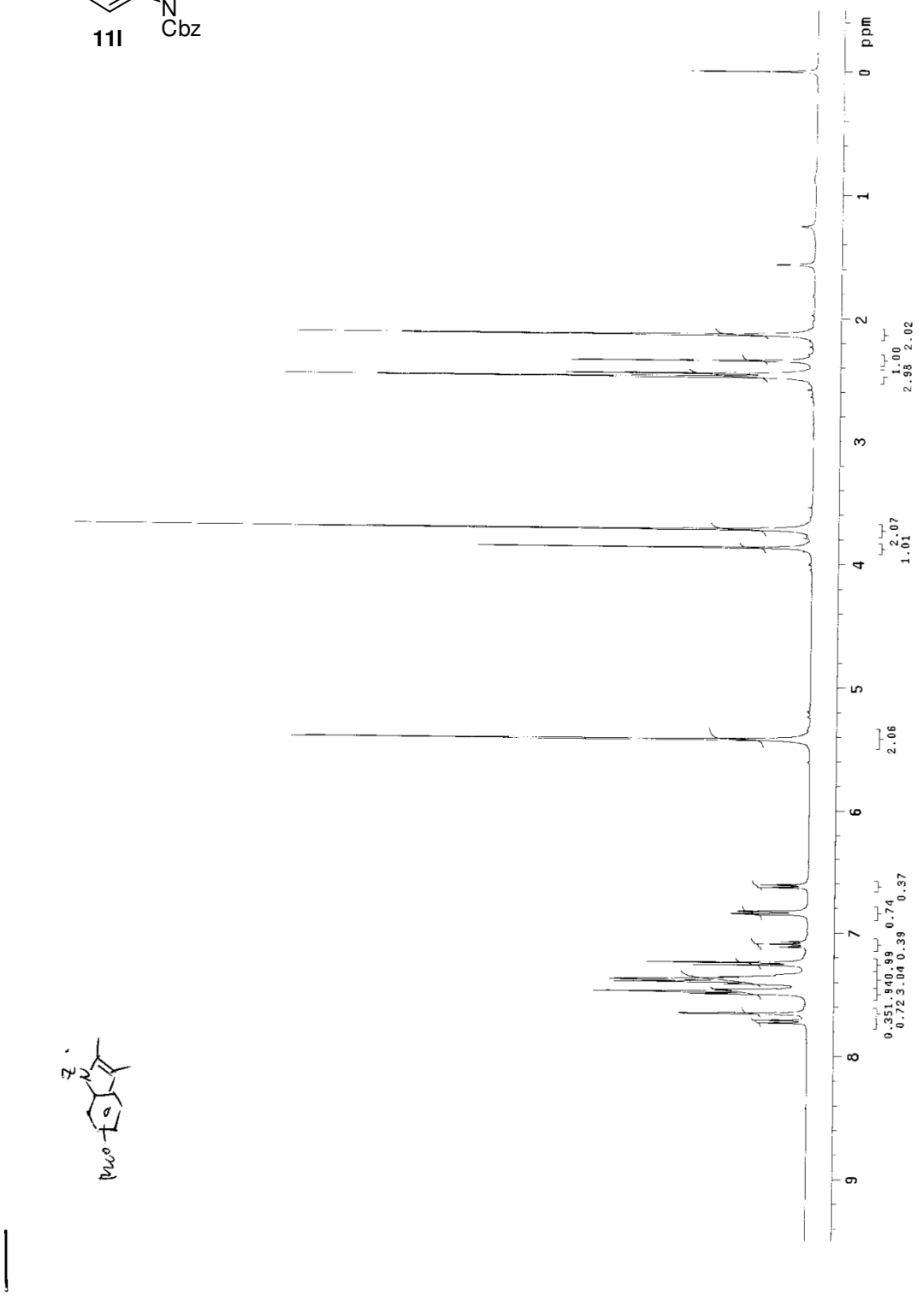
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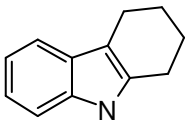

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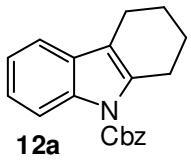

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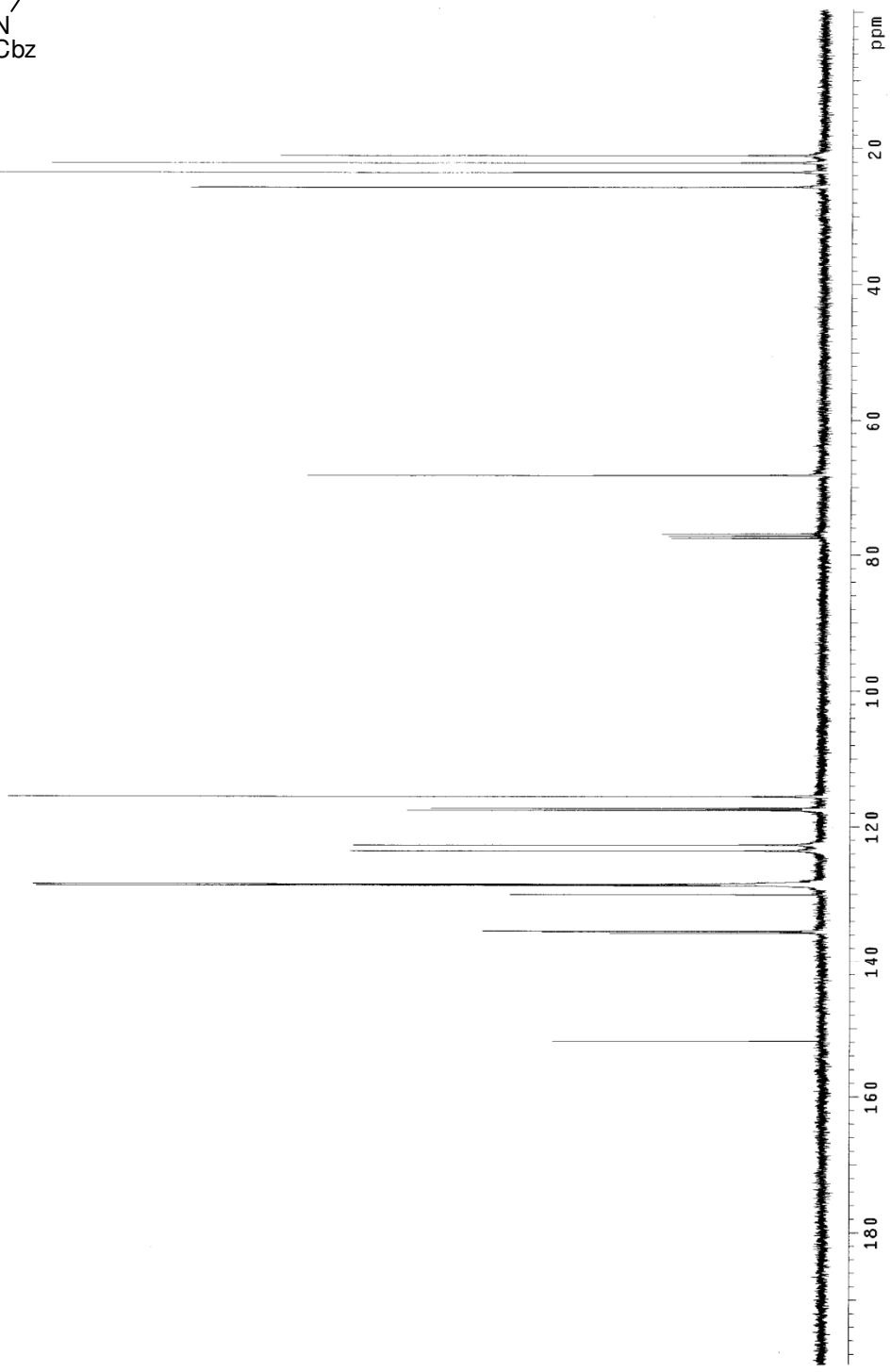

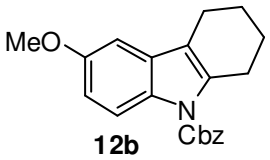

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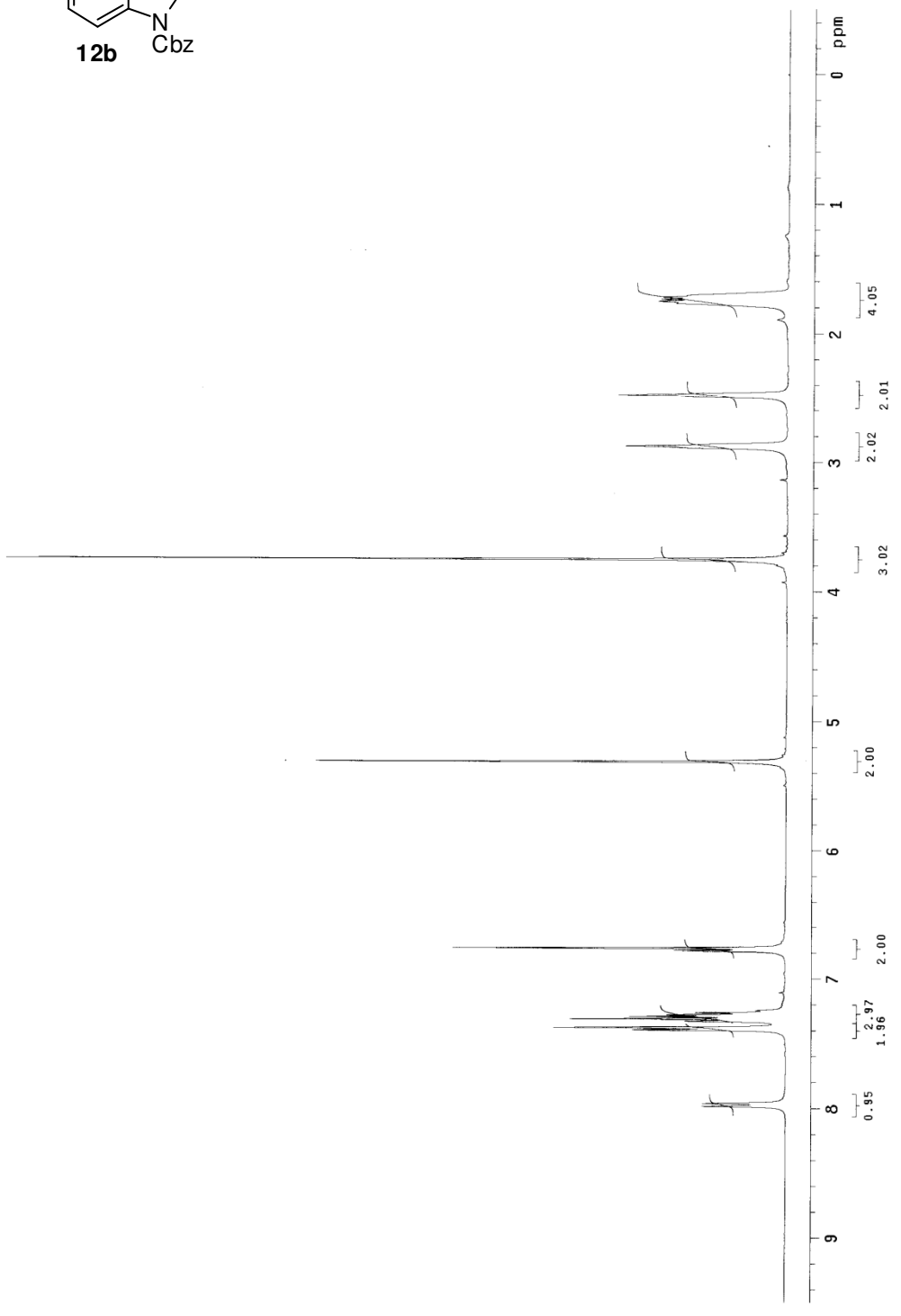

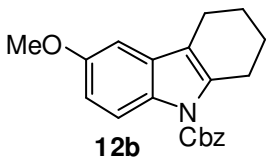

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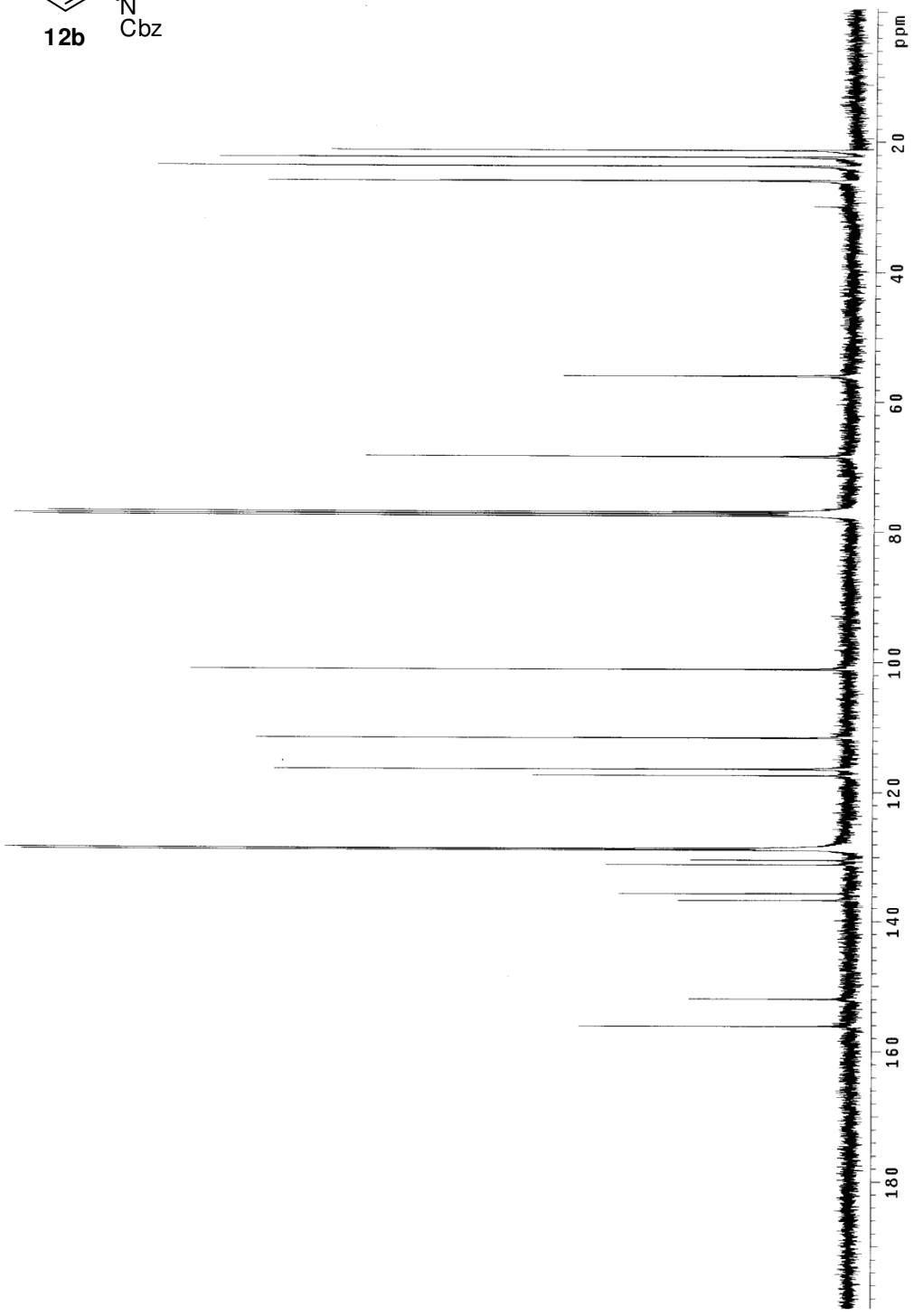

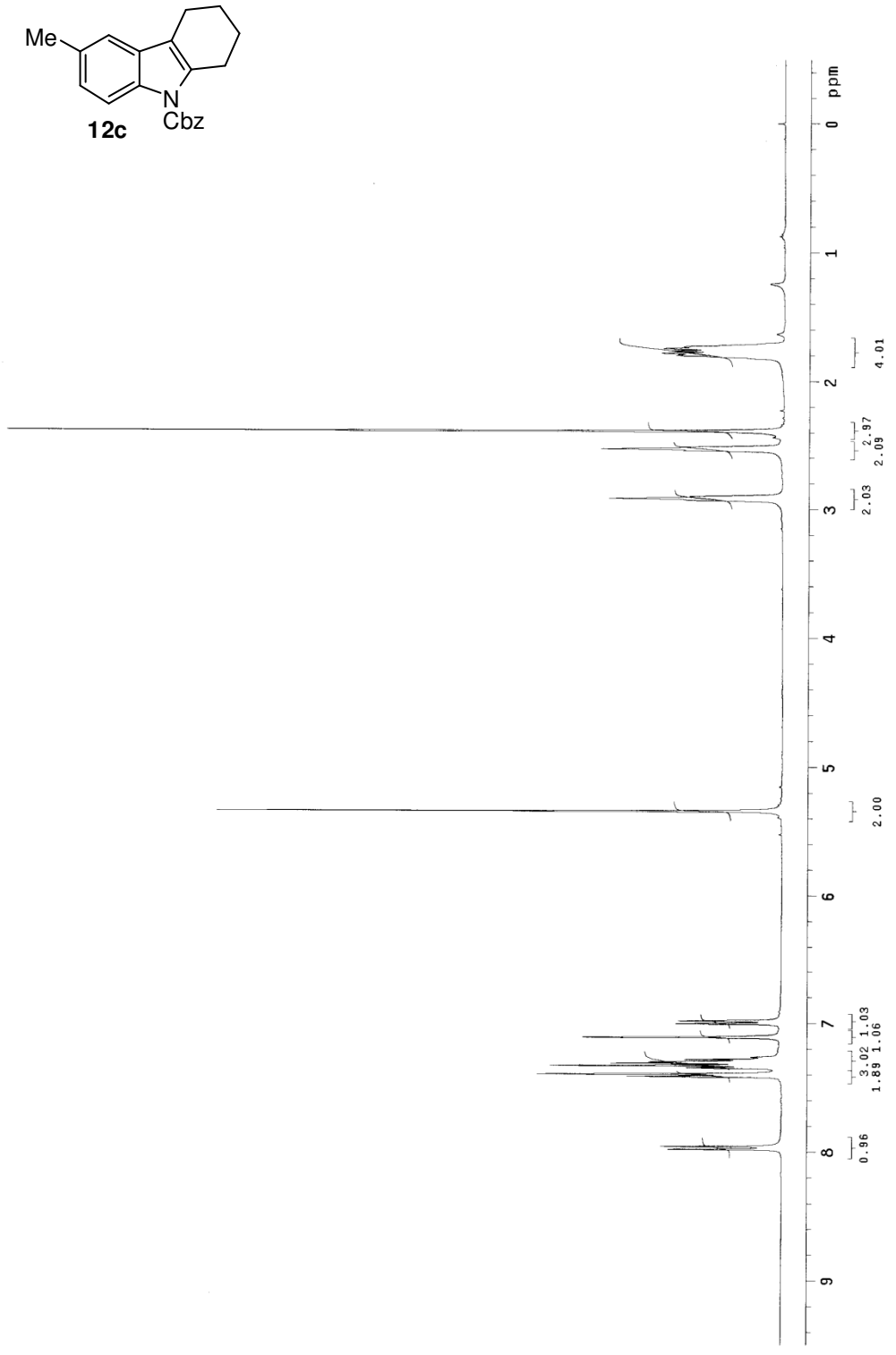
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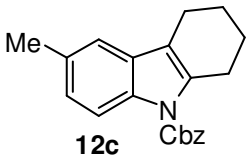

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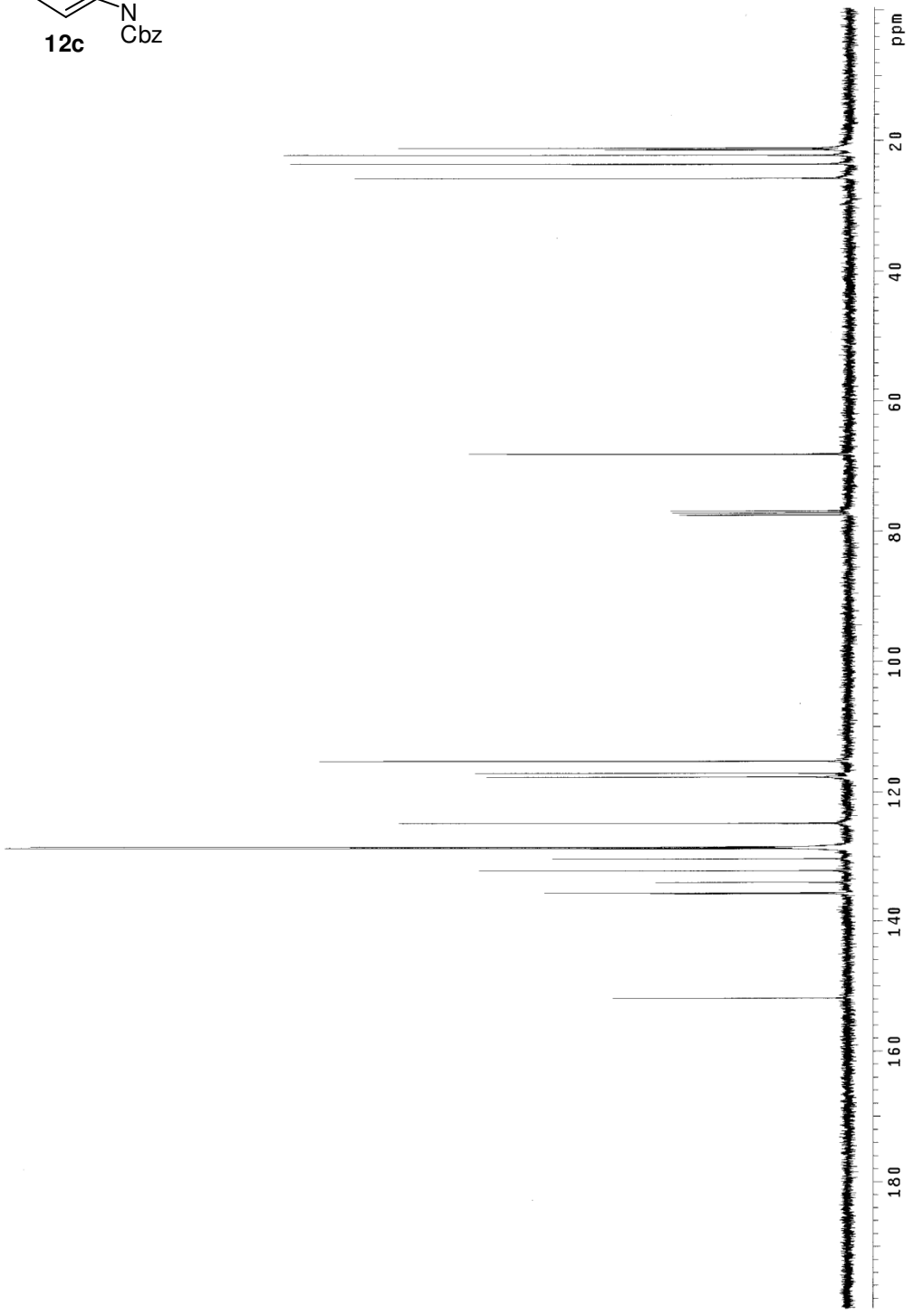

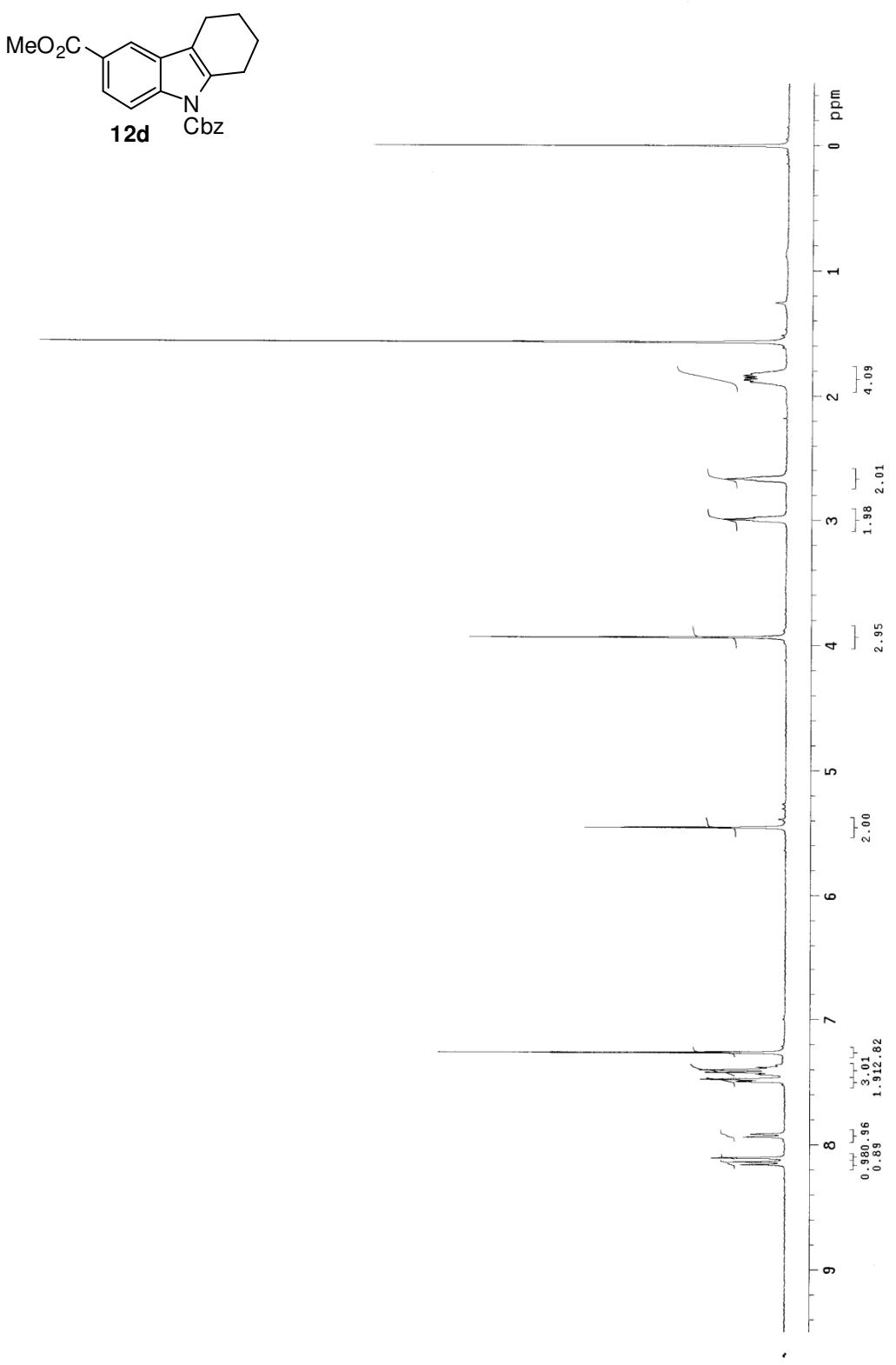
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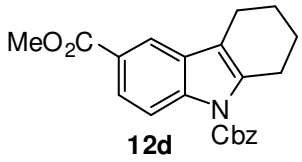

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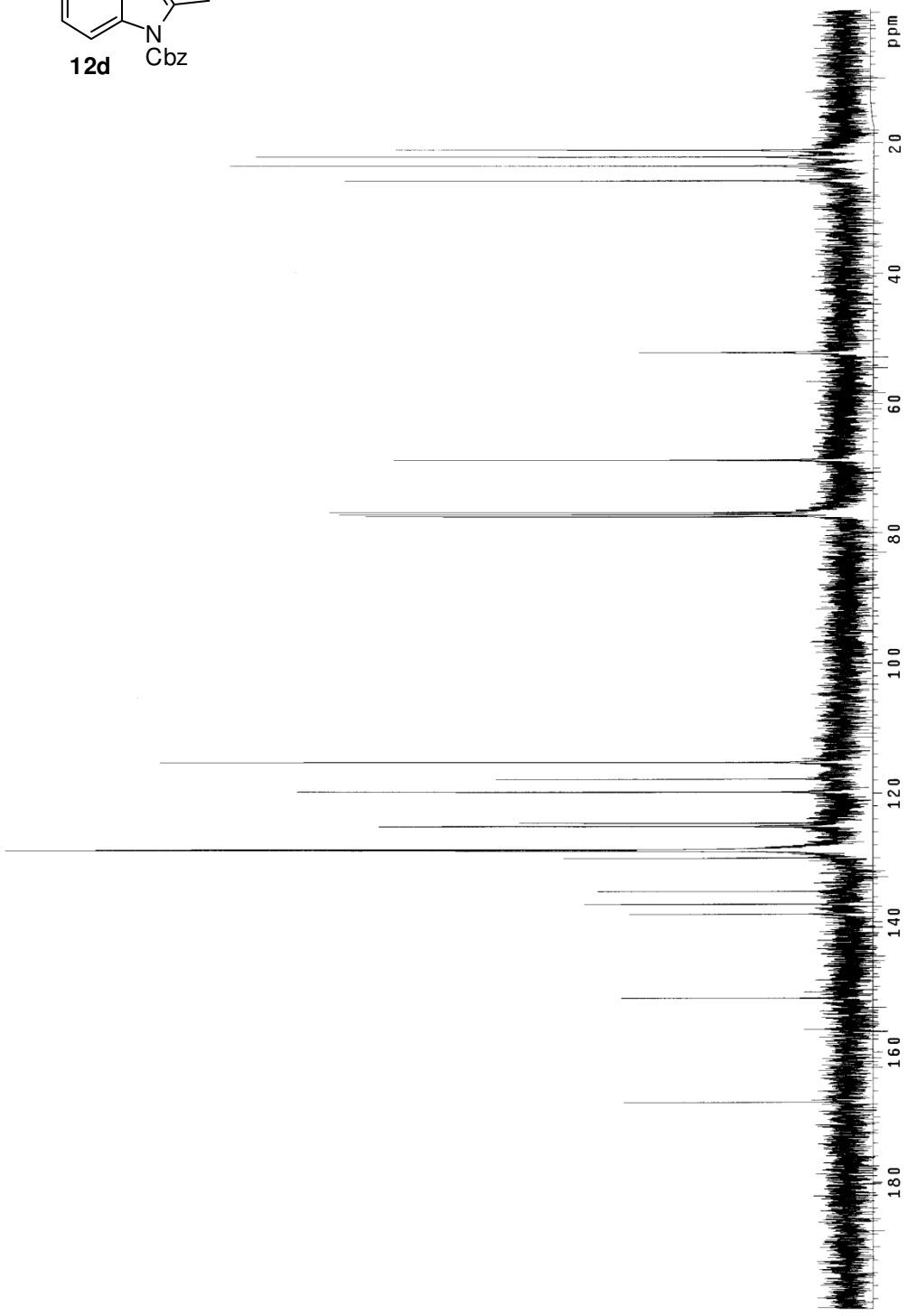

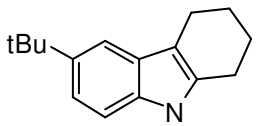

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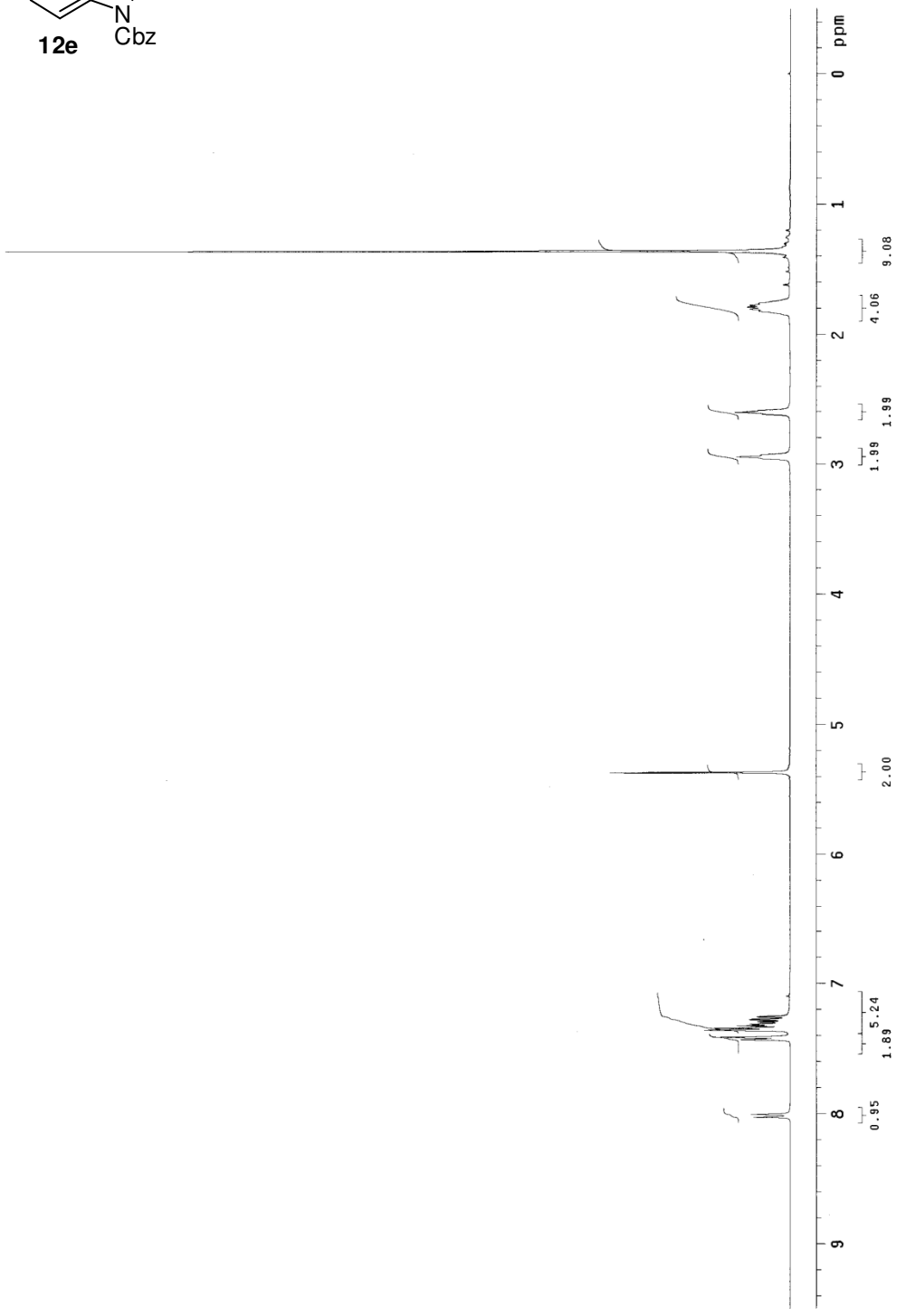

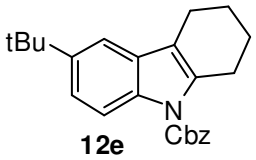

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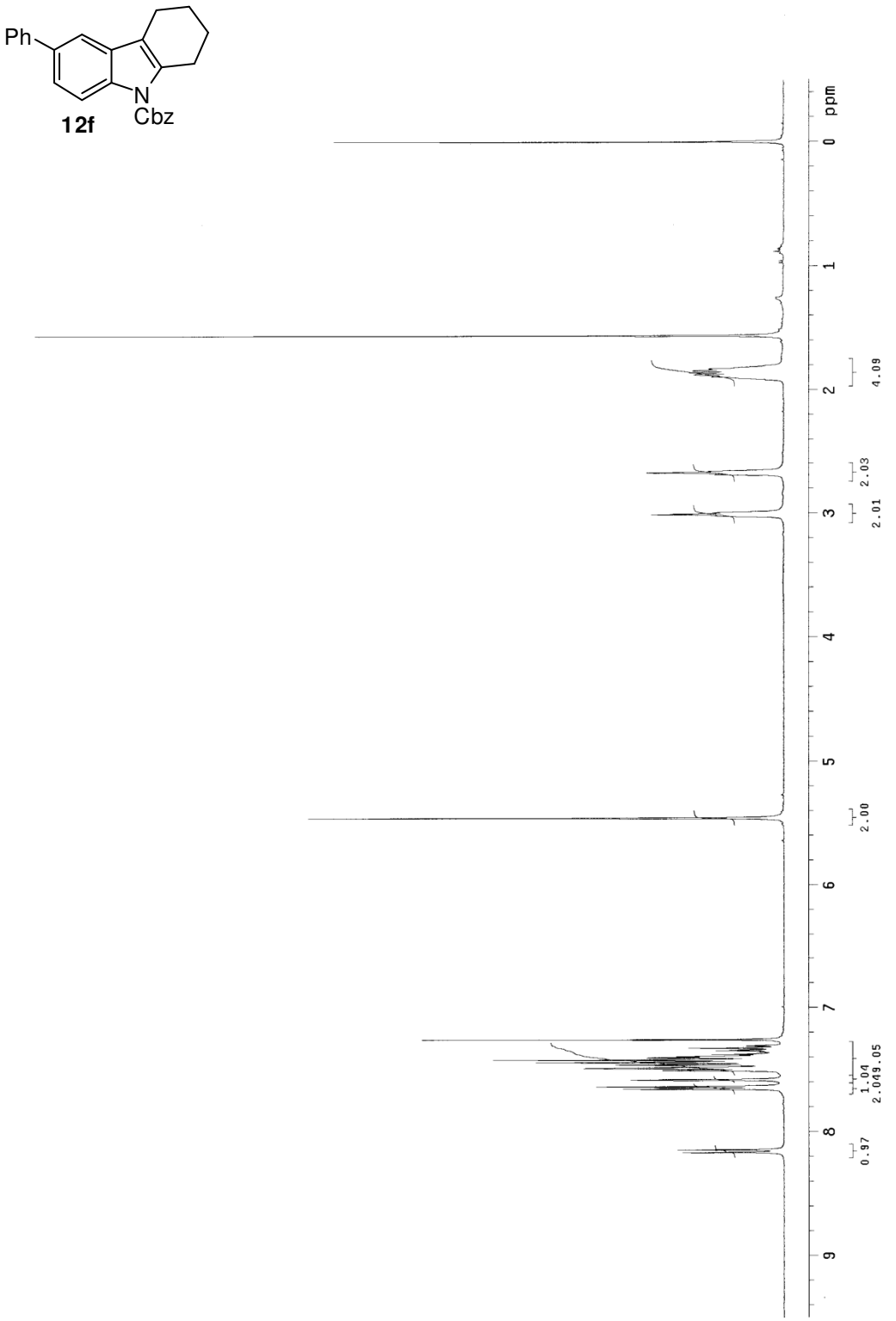
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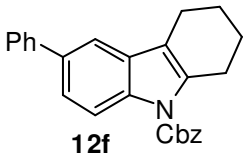

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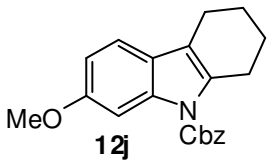
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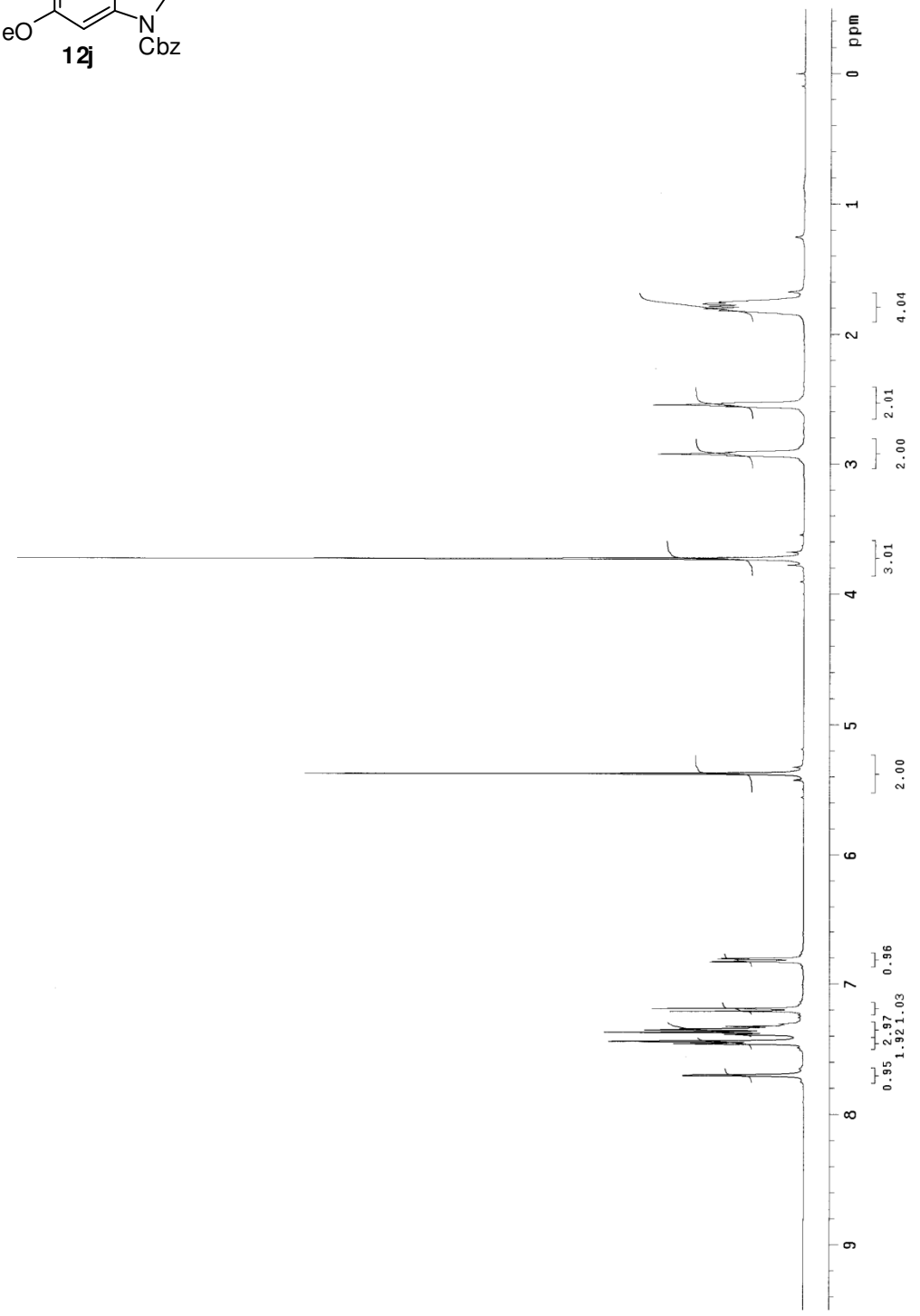
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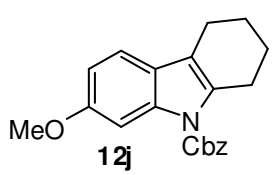

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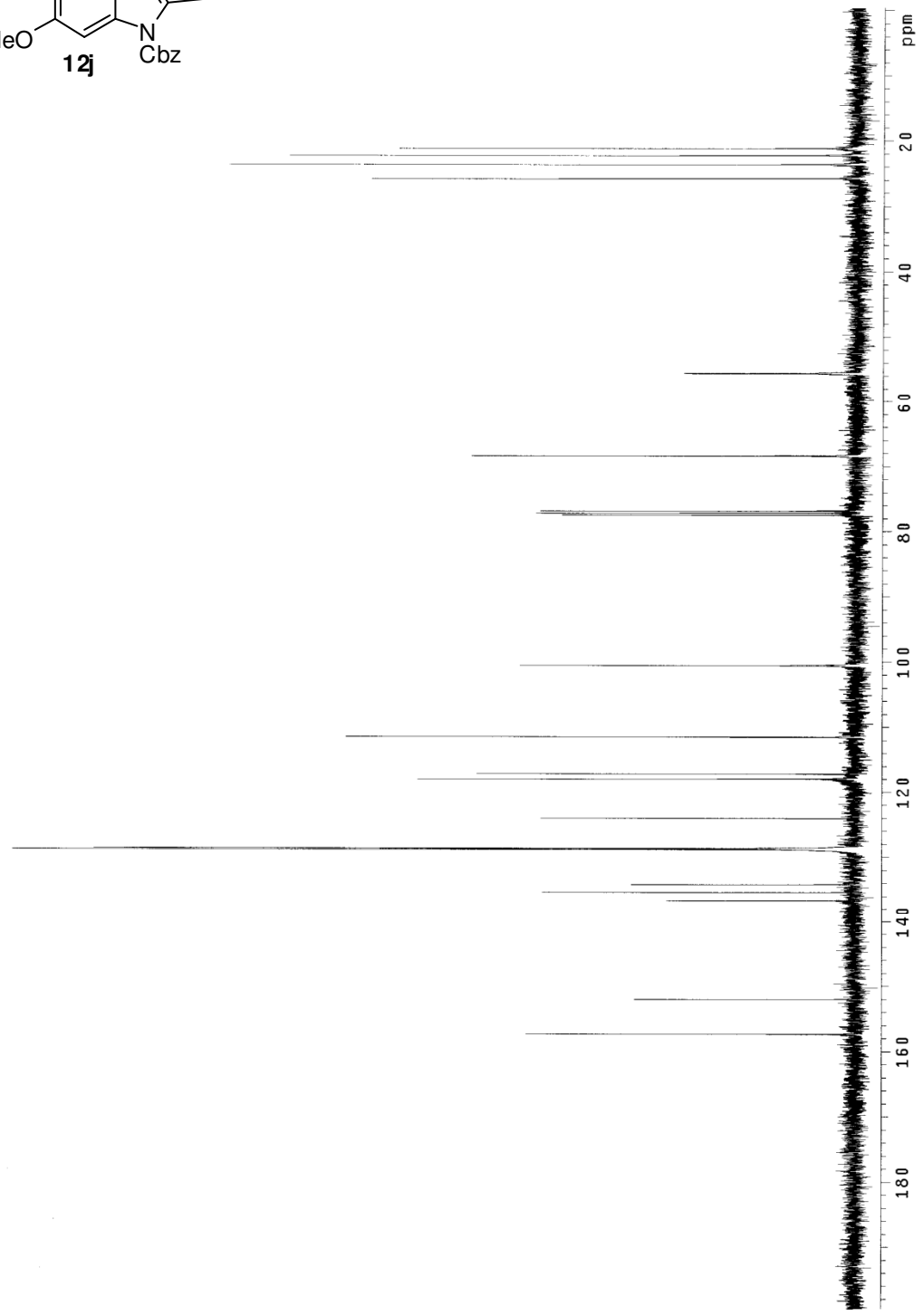

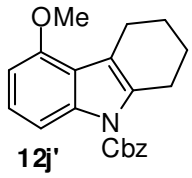

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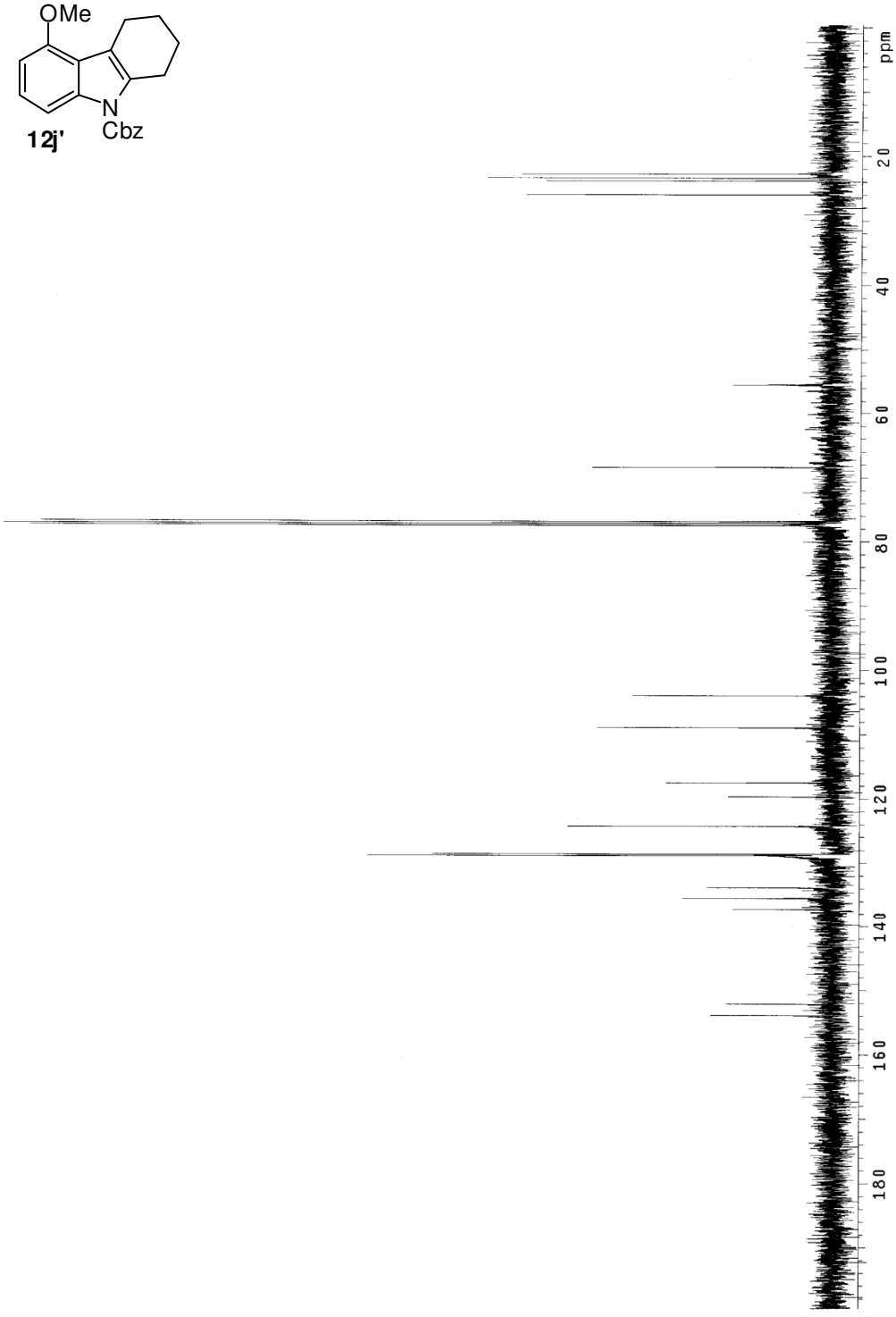
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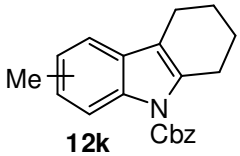
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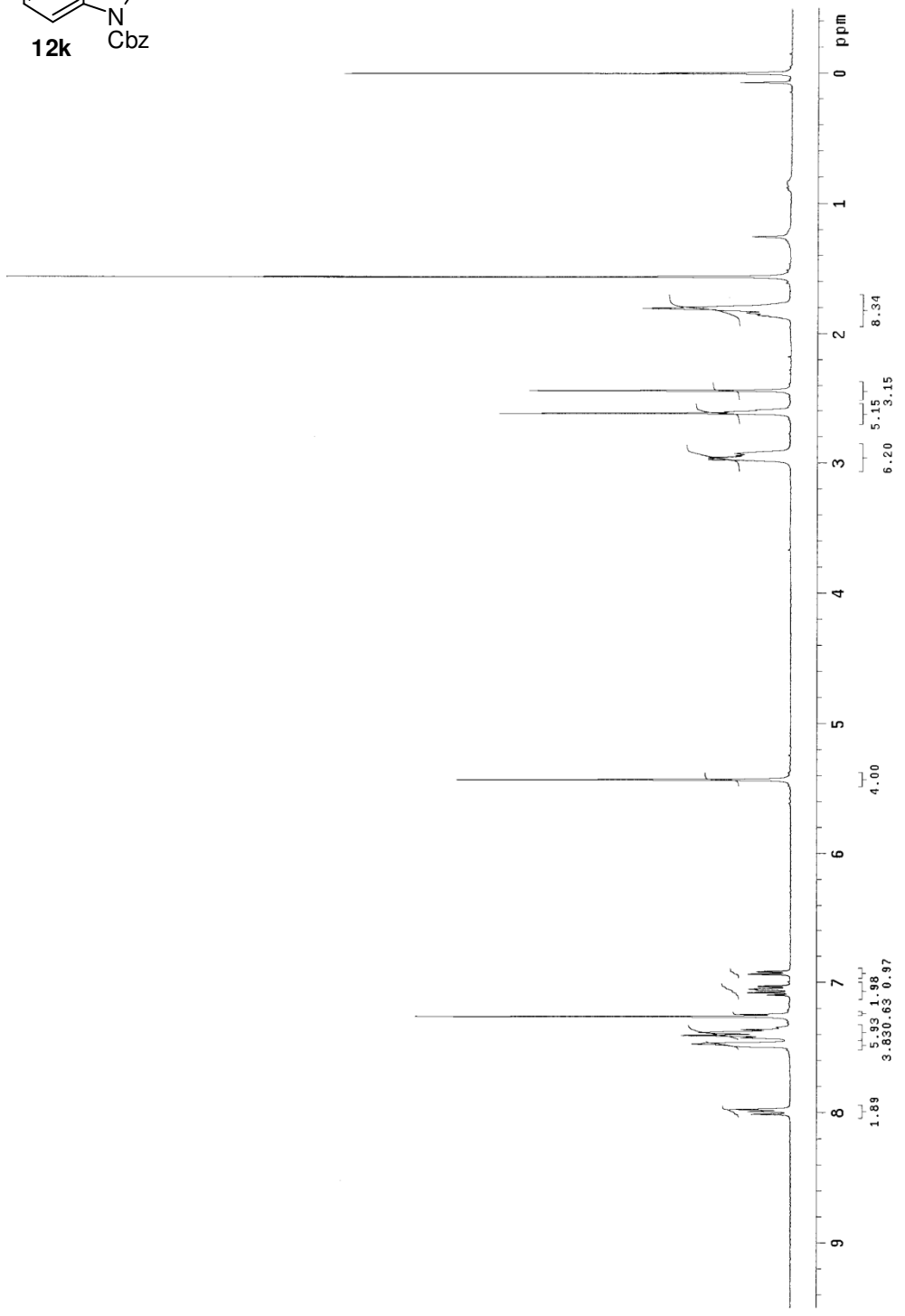
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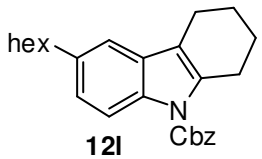
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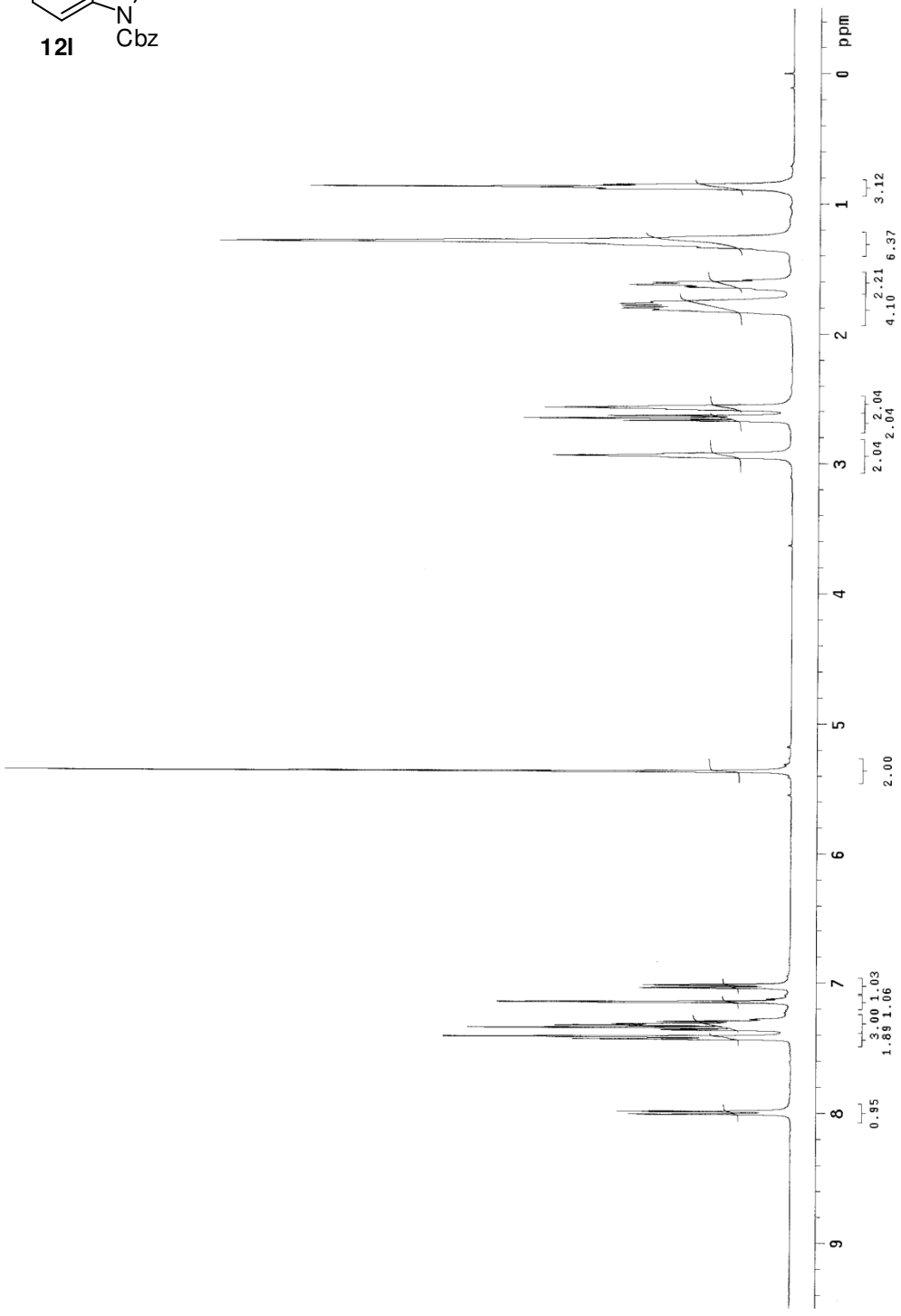
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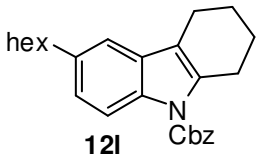

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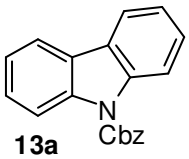

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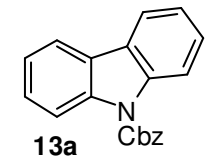

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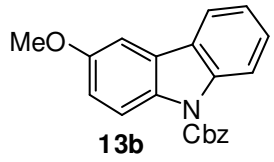

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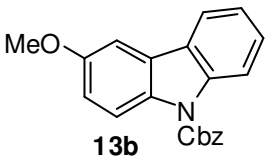

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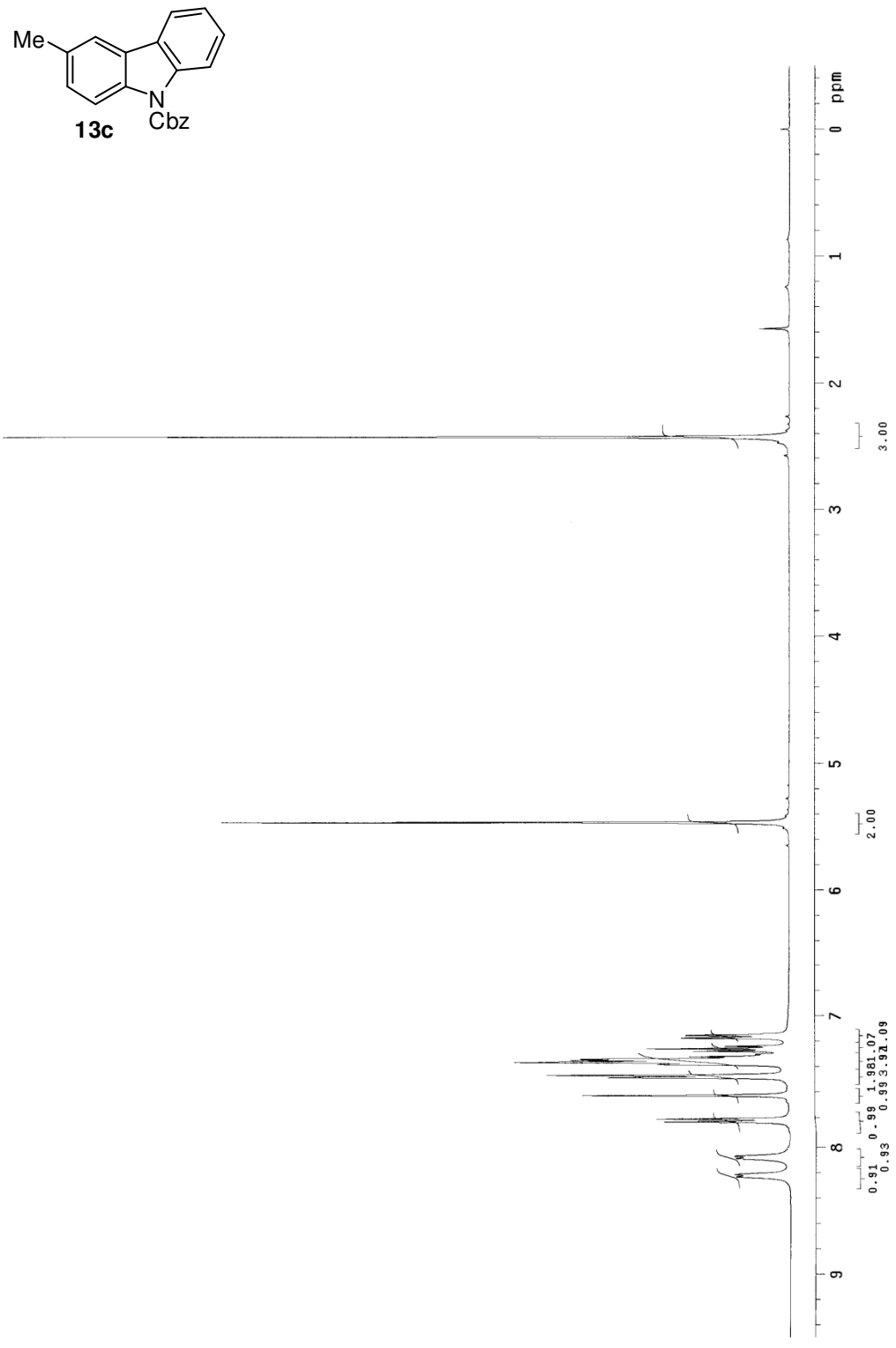
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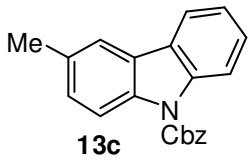

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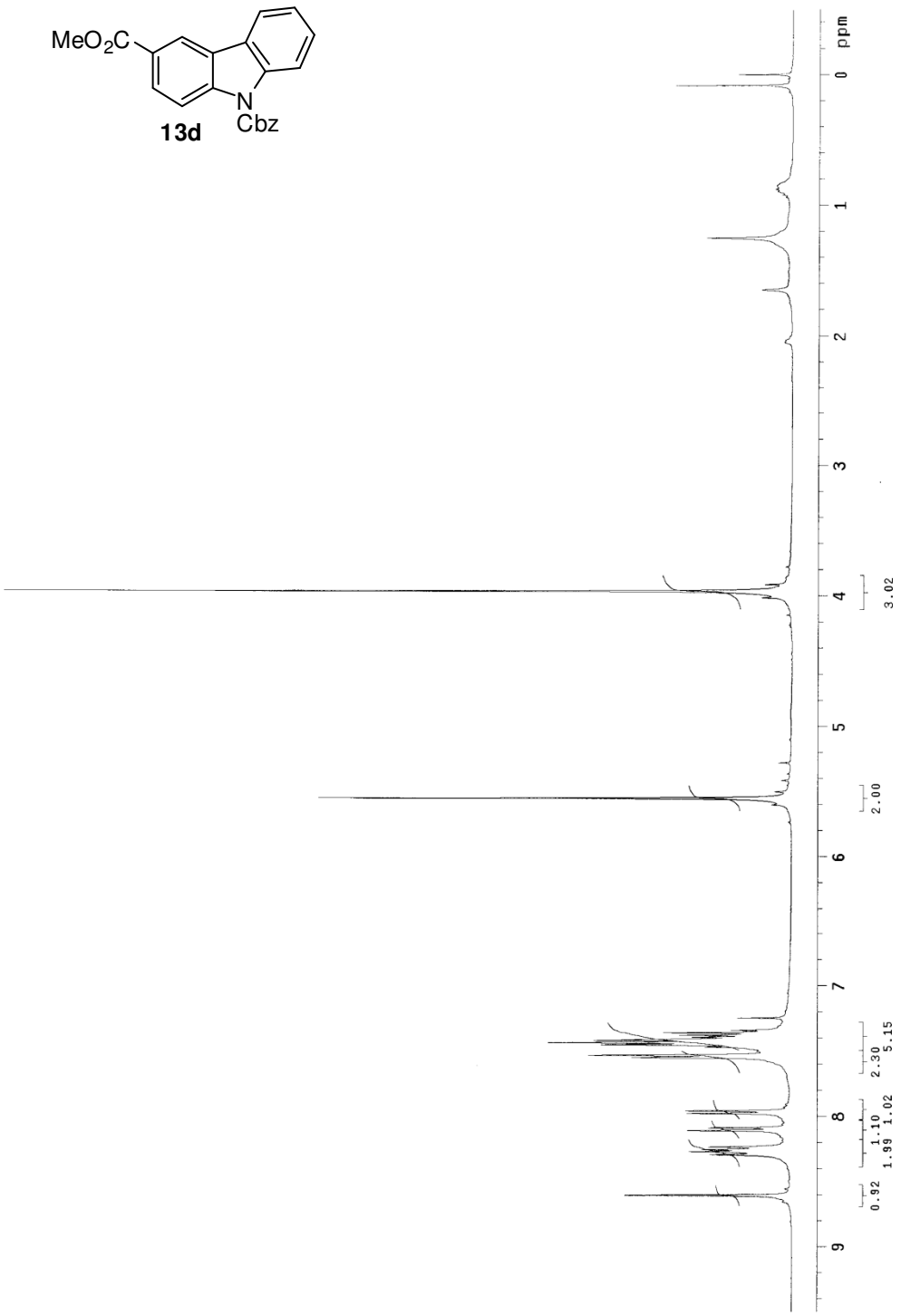
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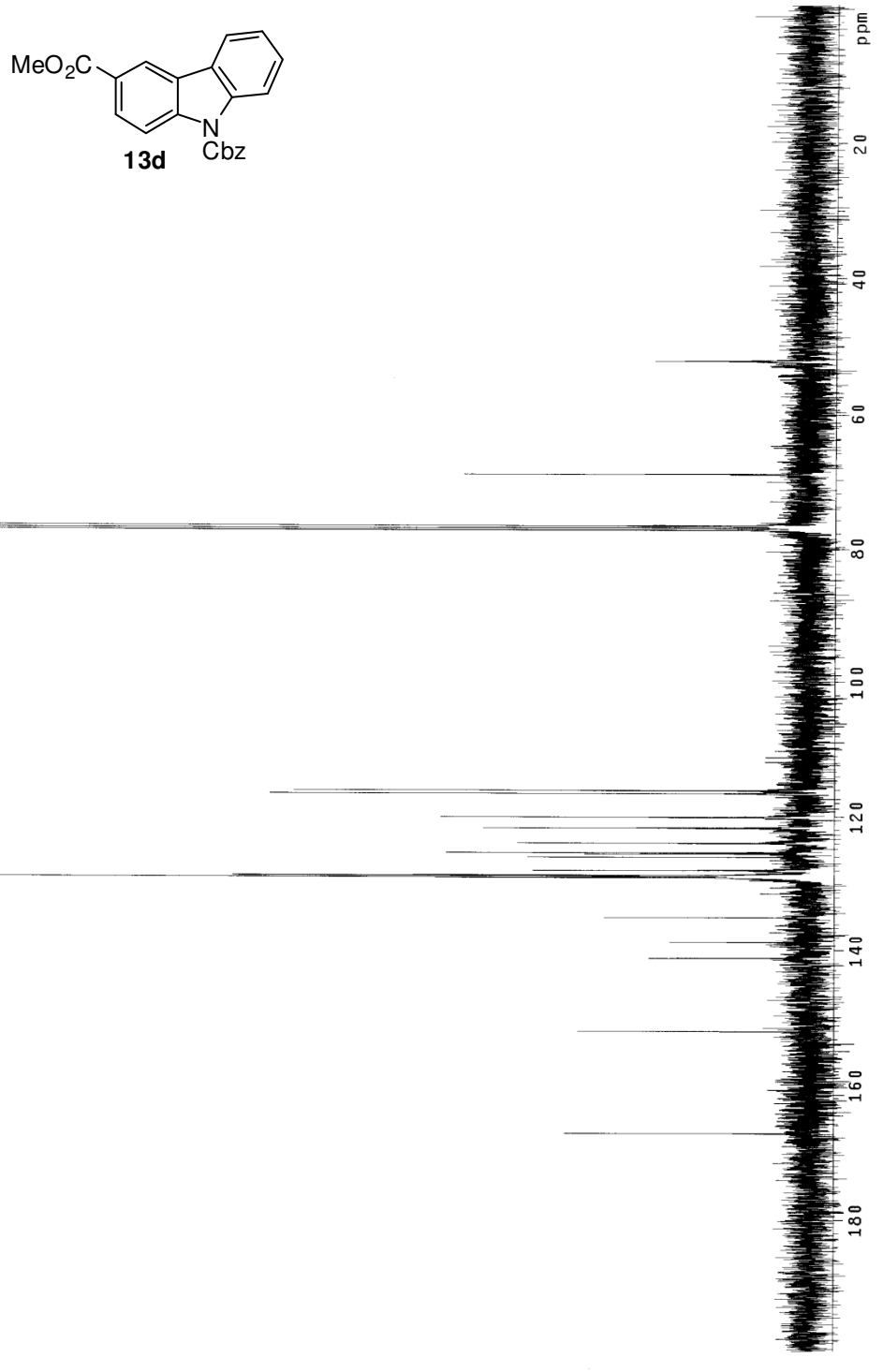
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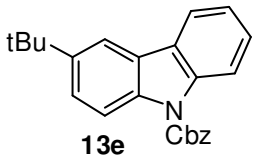

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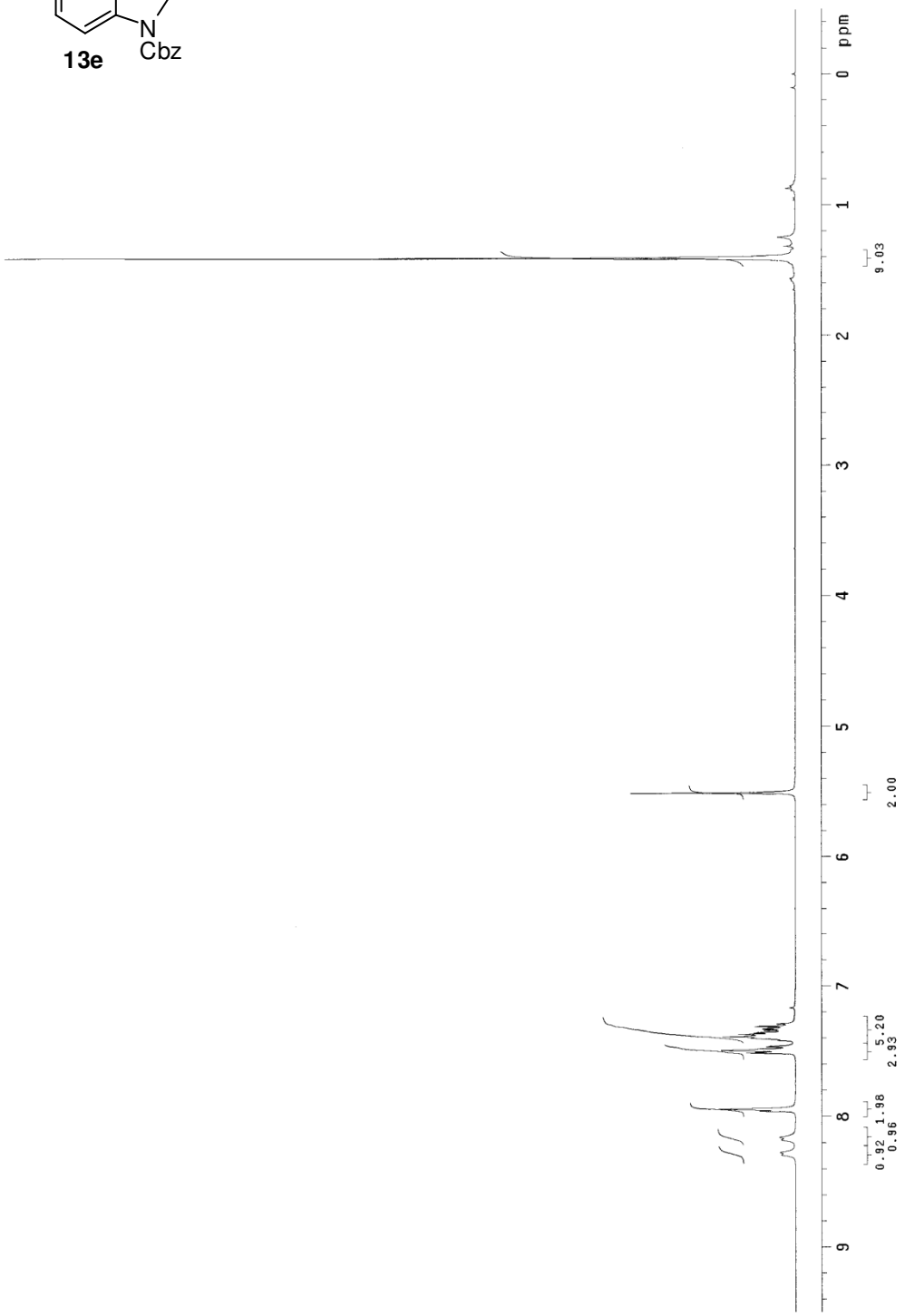

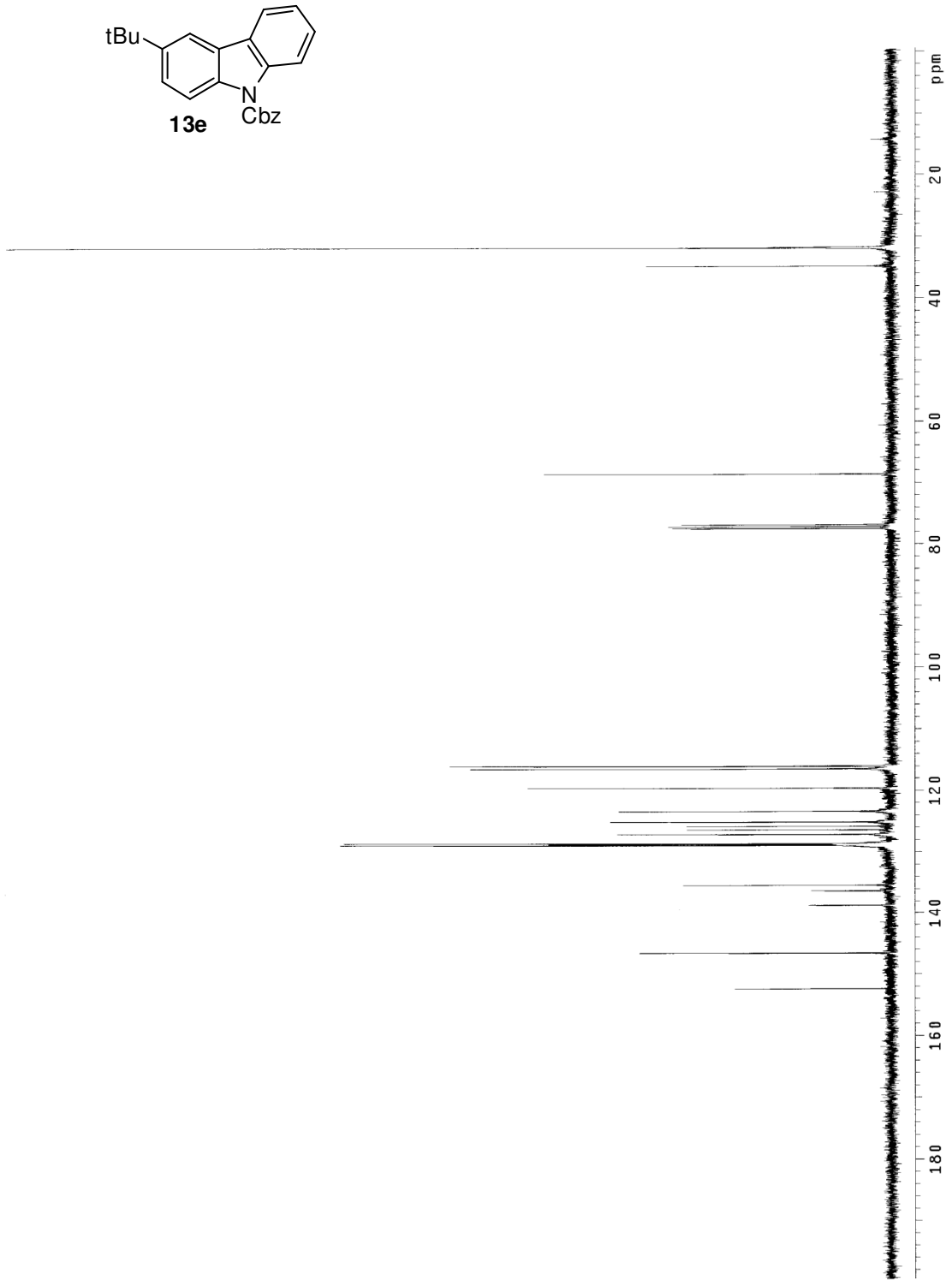
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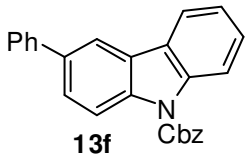

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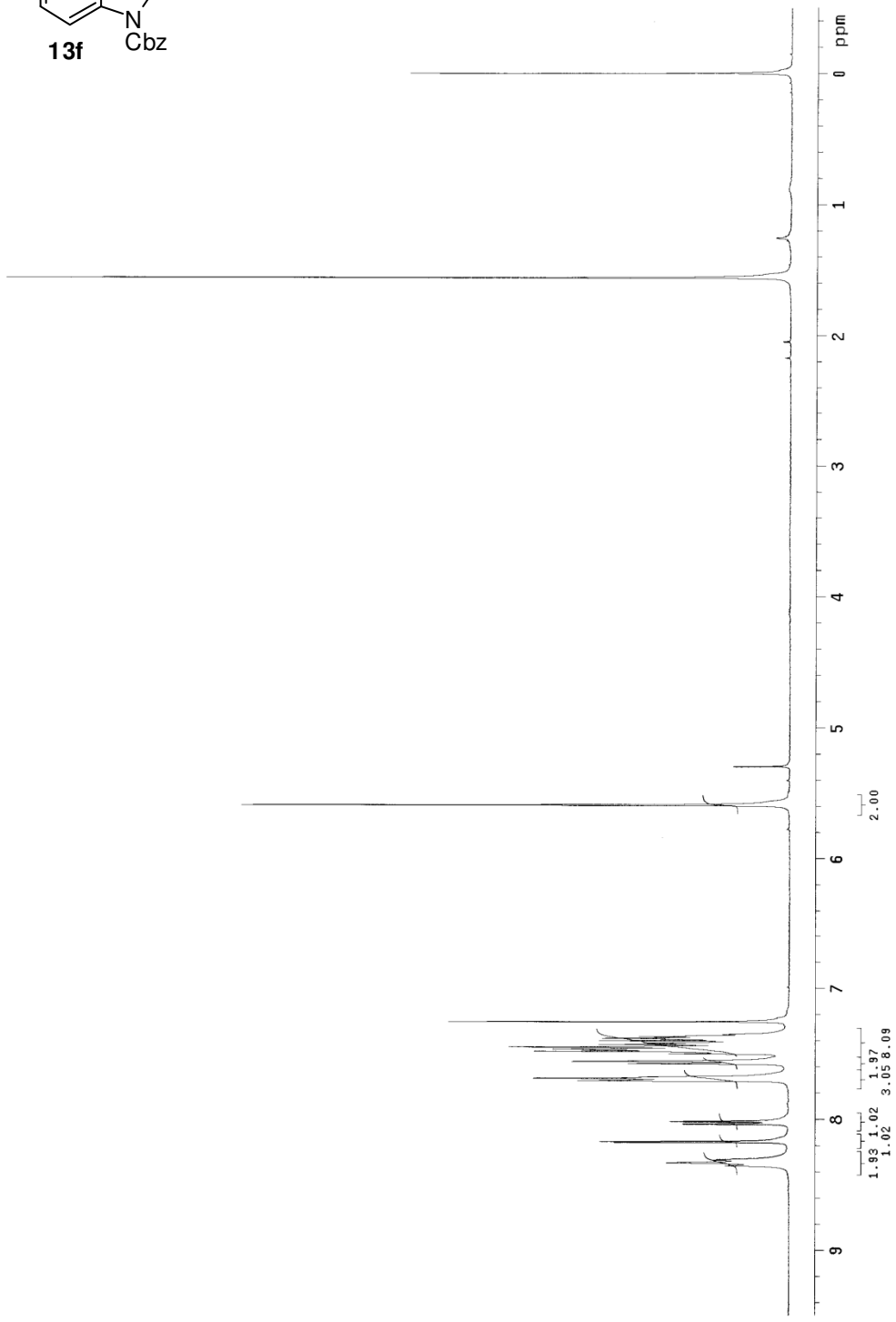

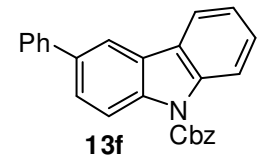

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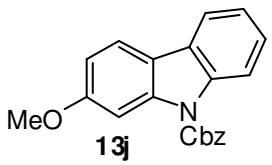

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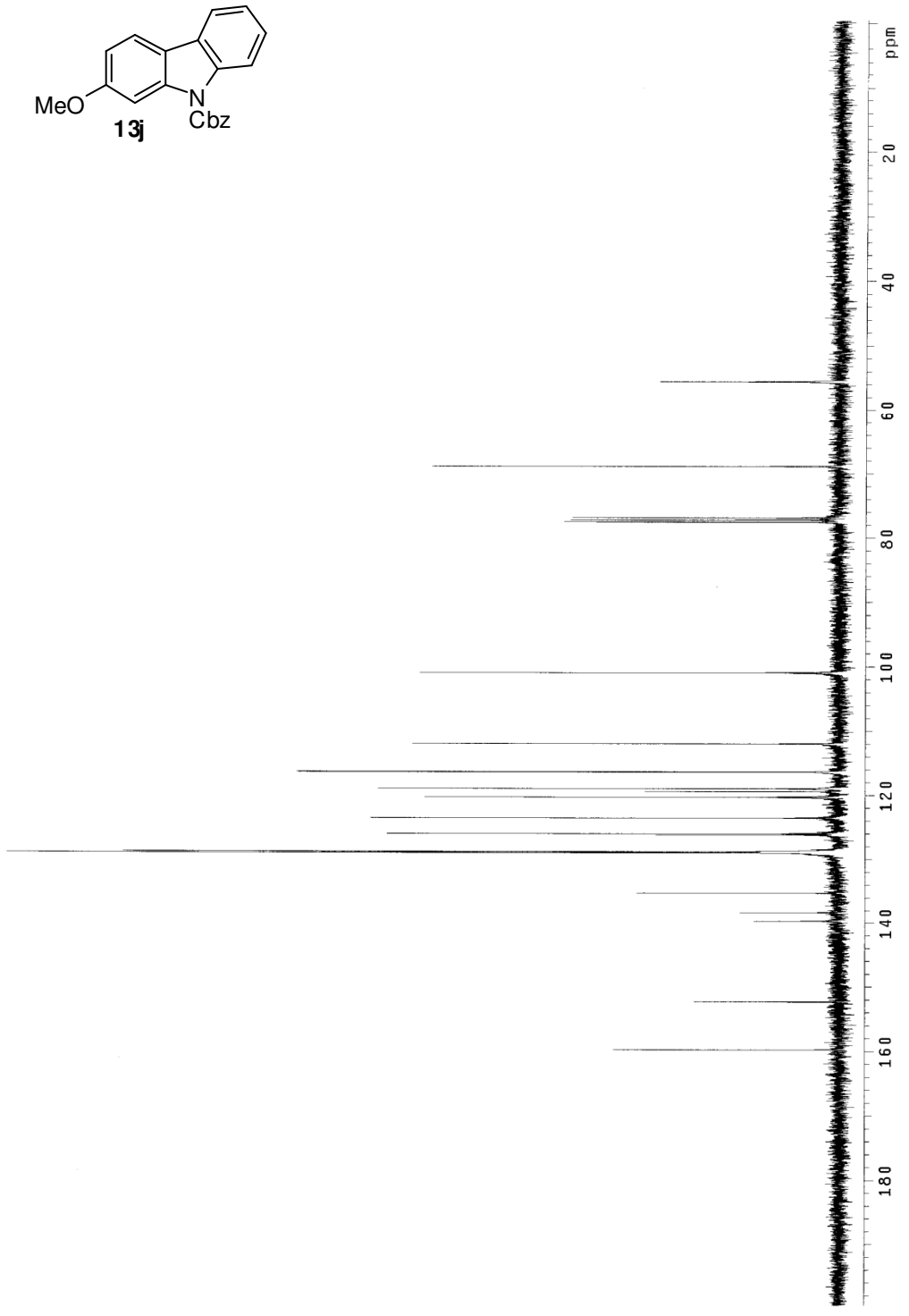
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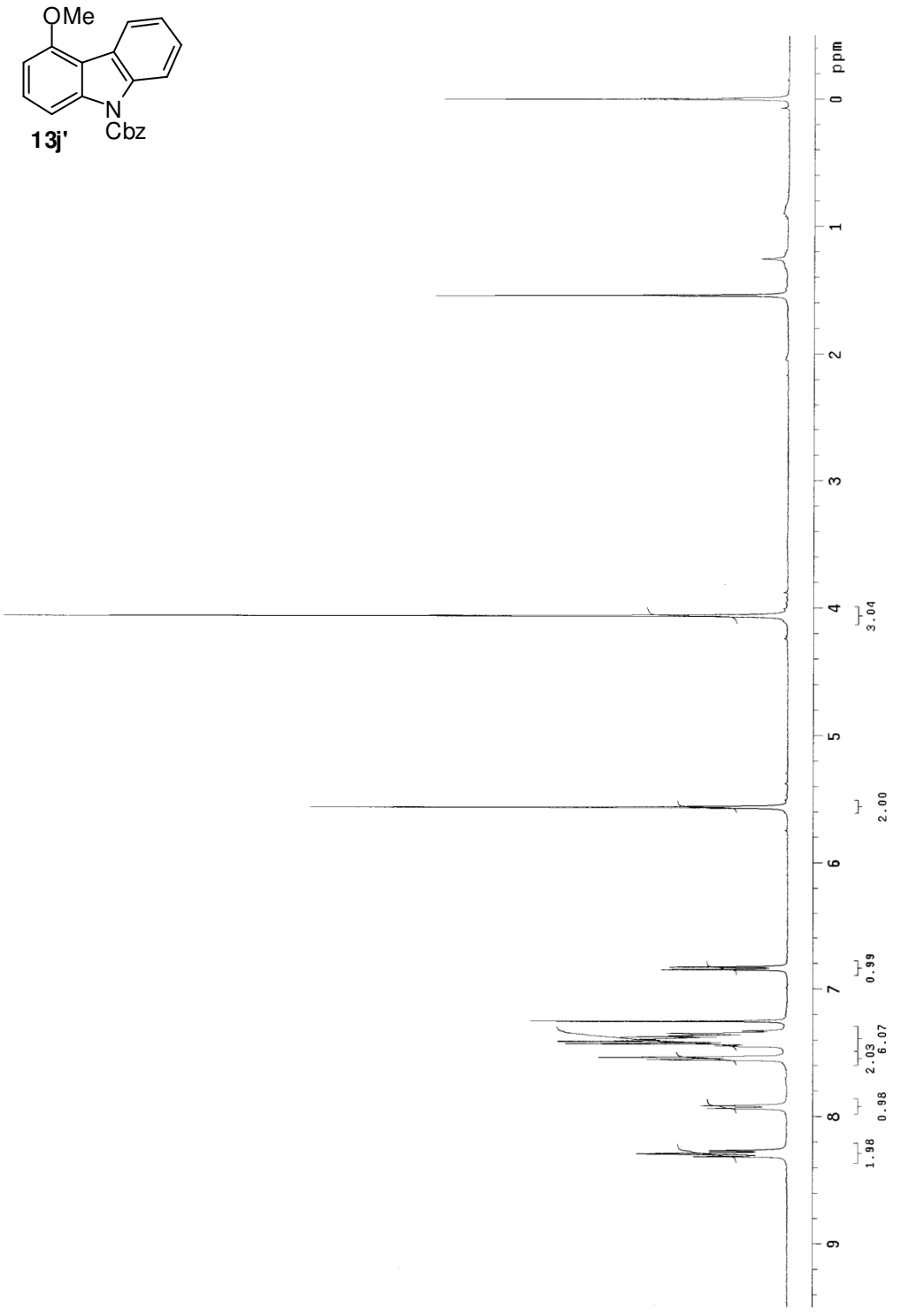
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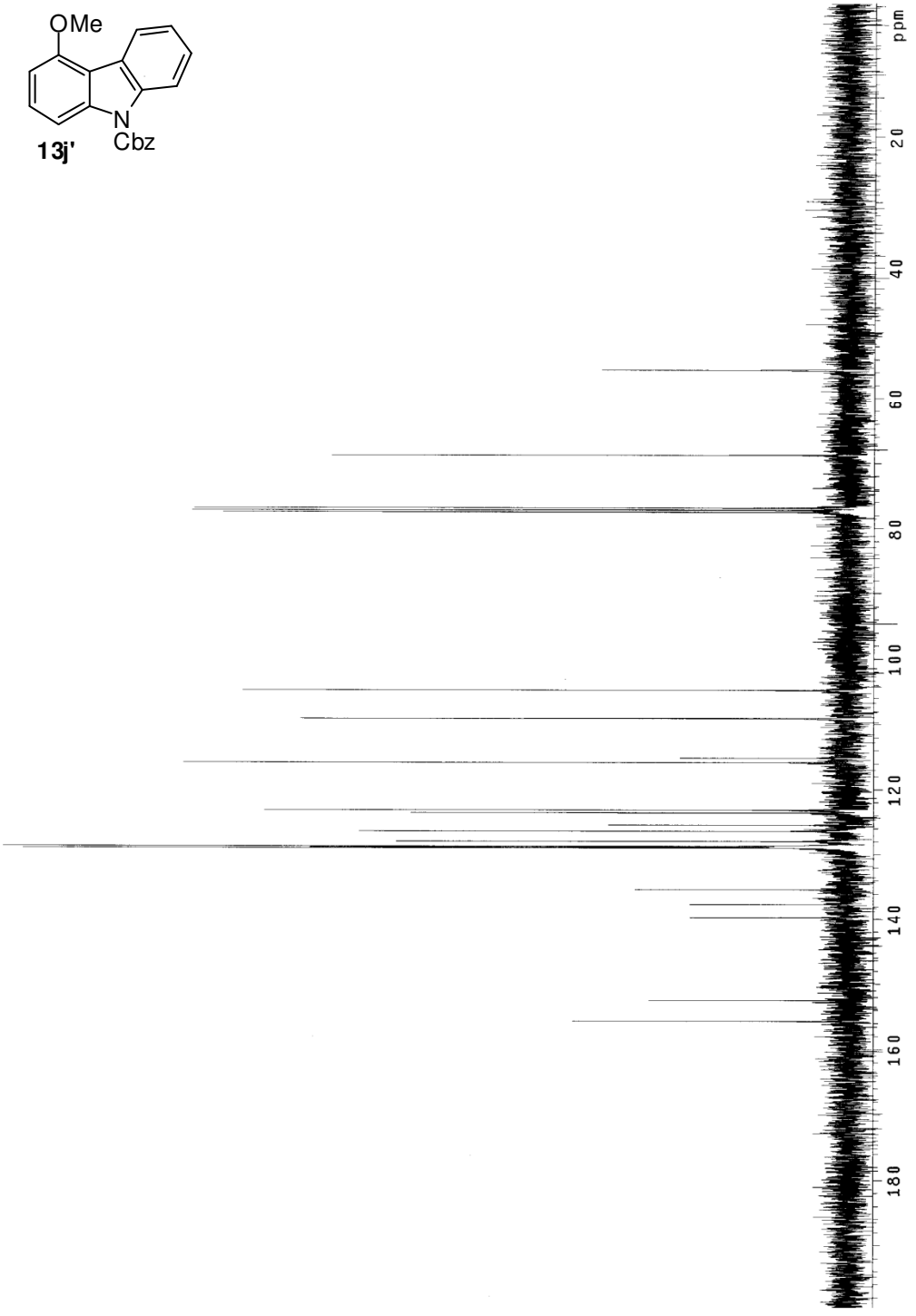
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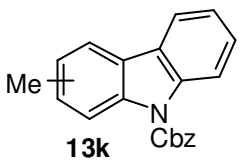

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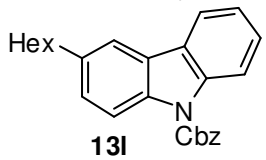
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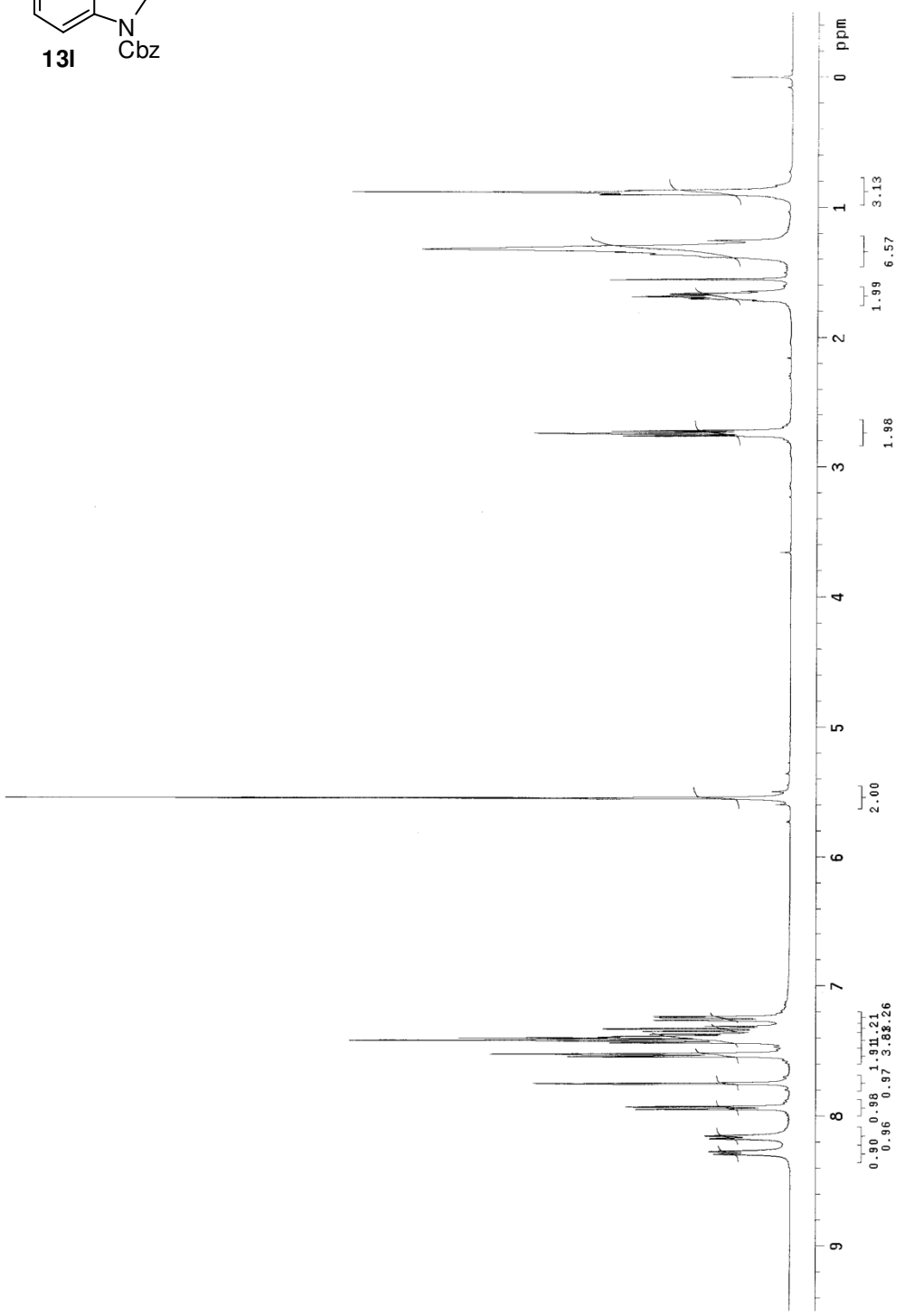
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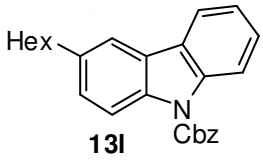

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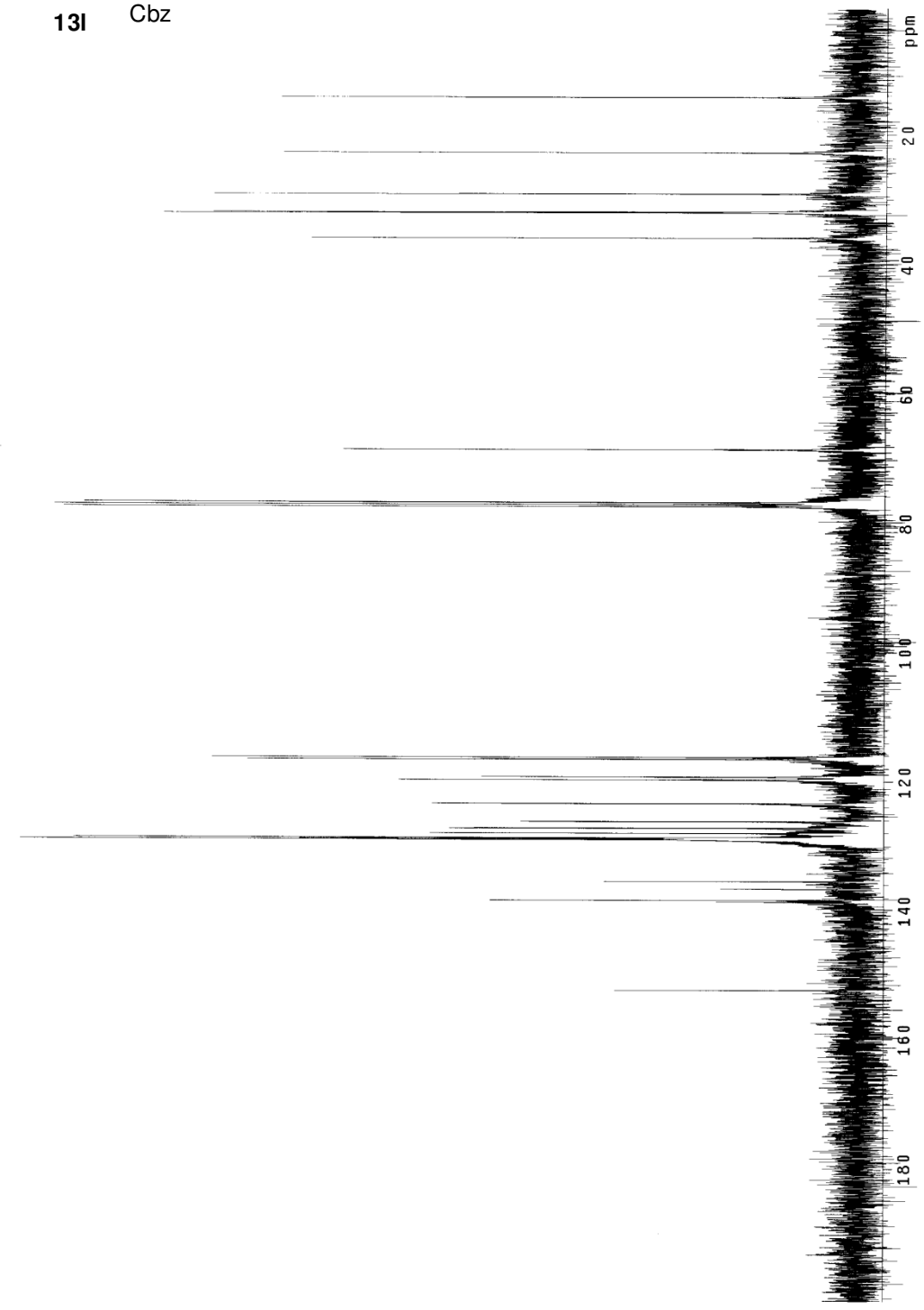

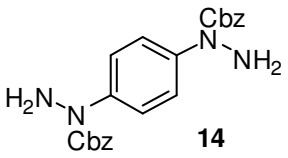

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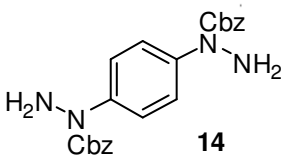

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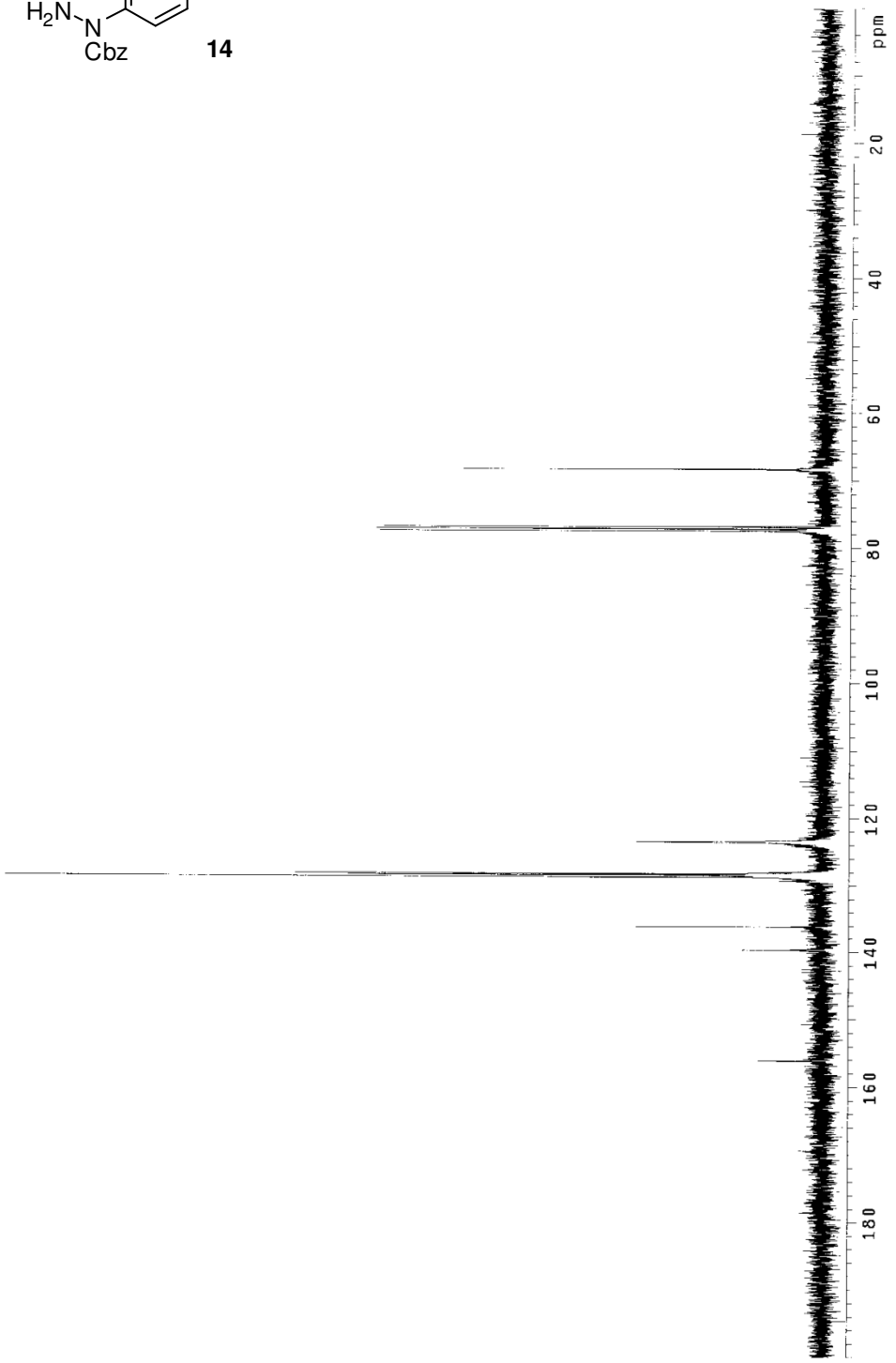

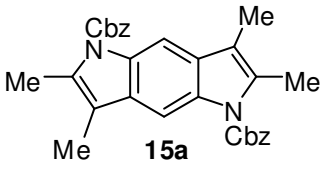

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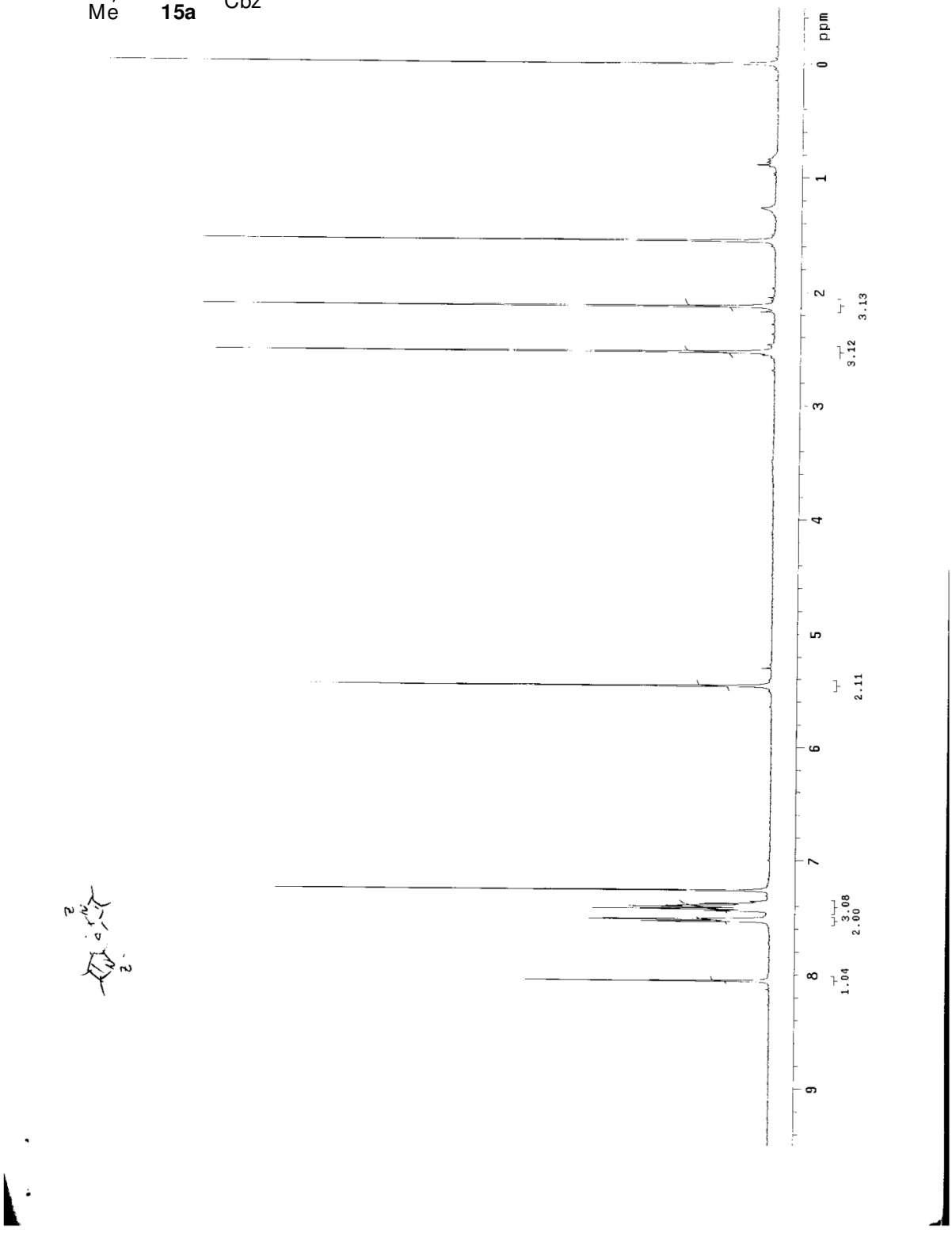

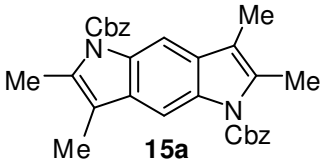

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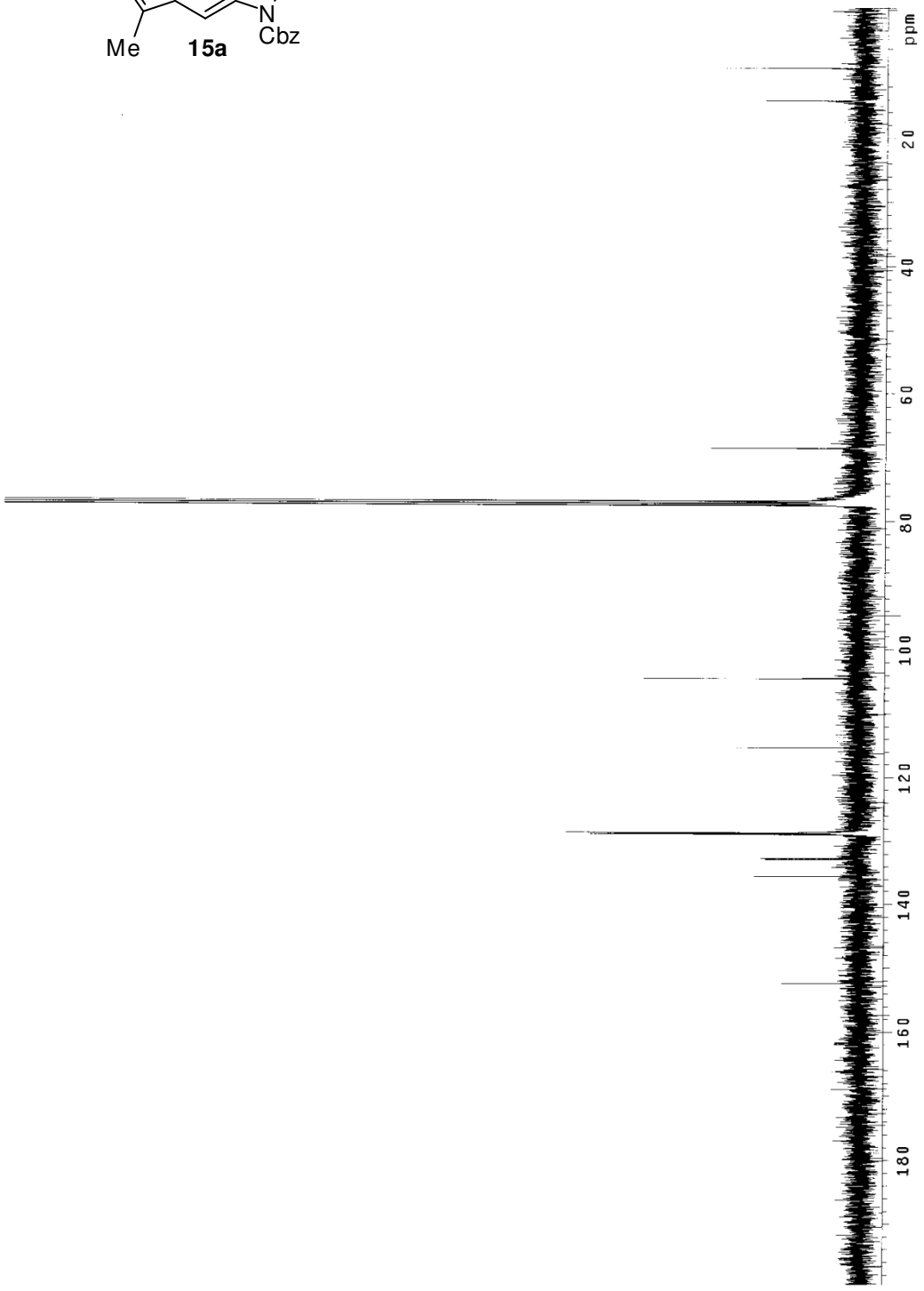

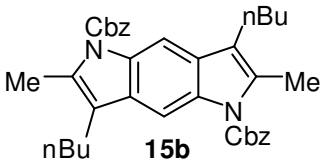
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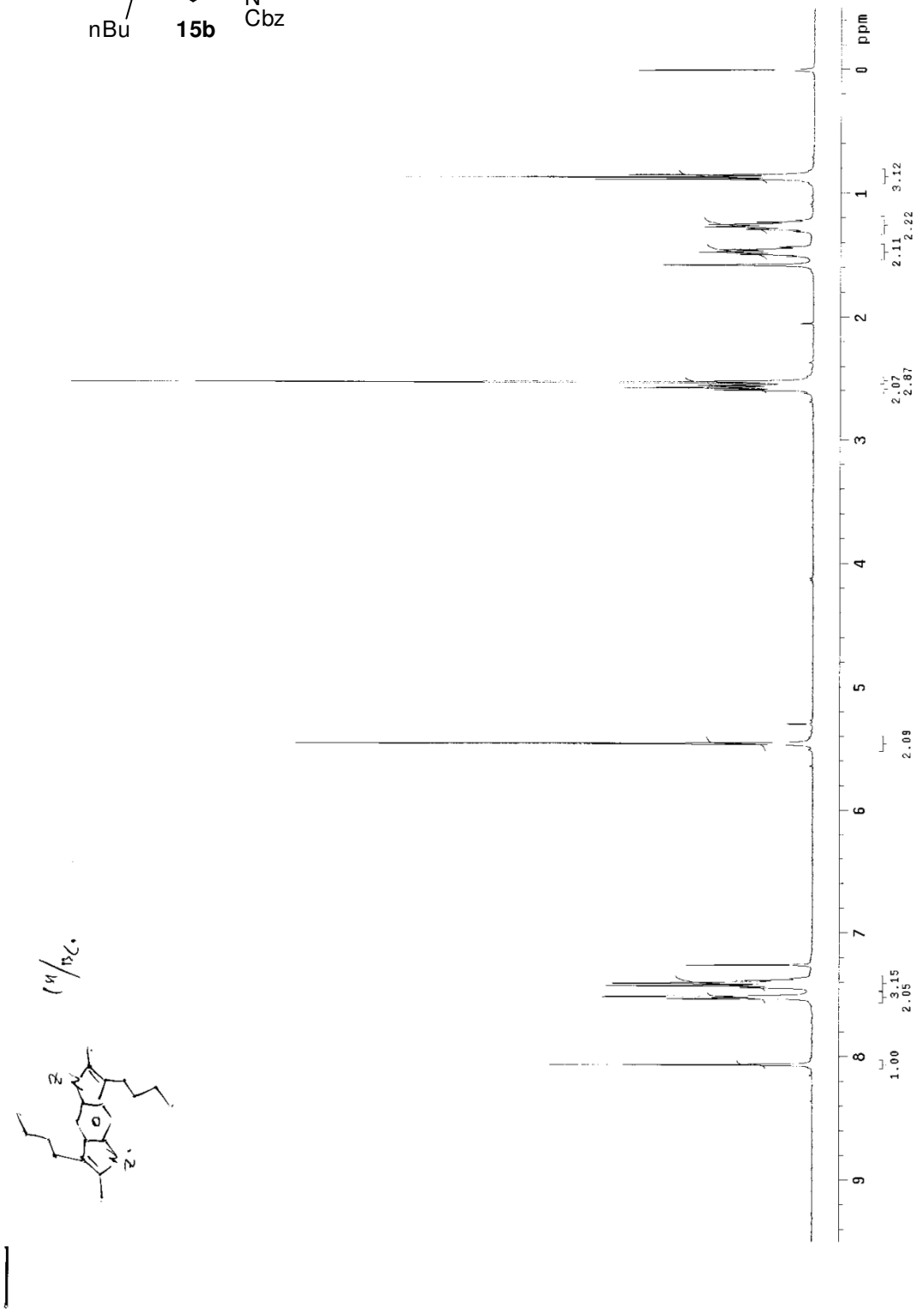
Cbz
nBu

15b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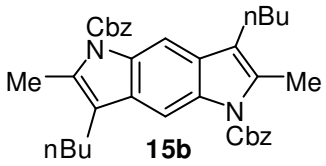
1.00



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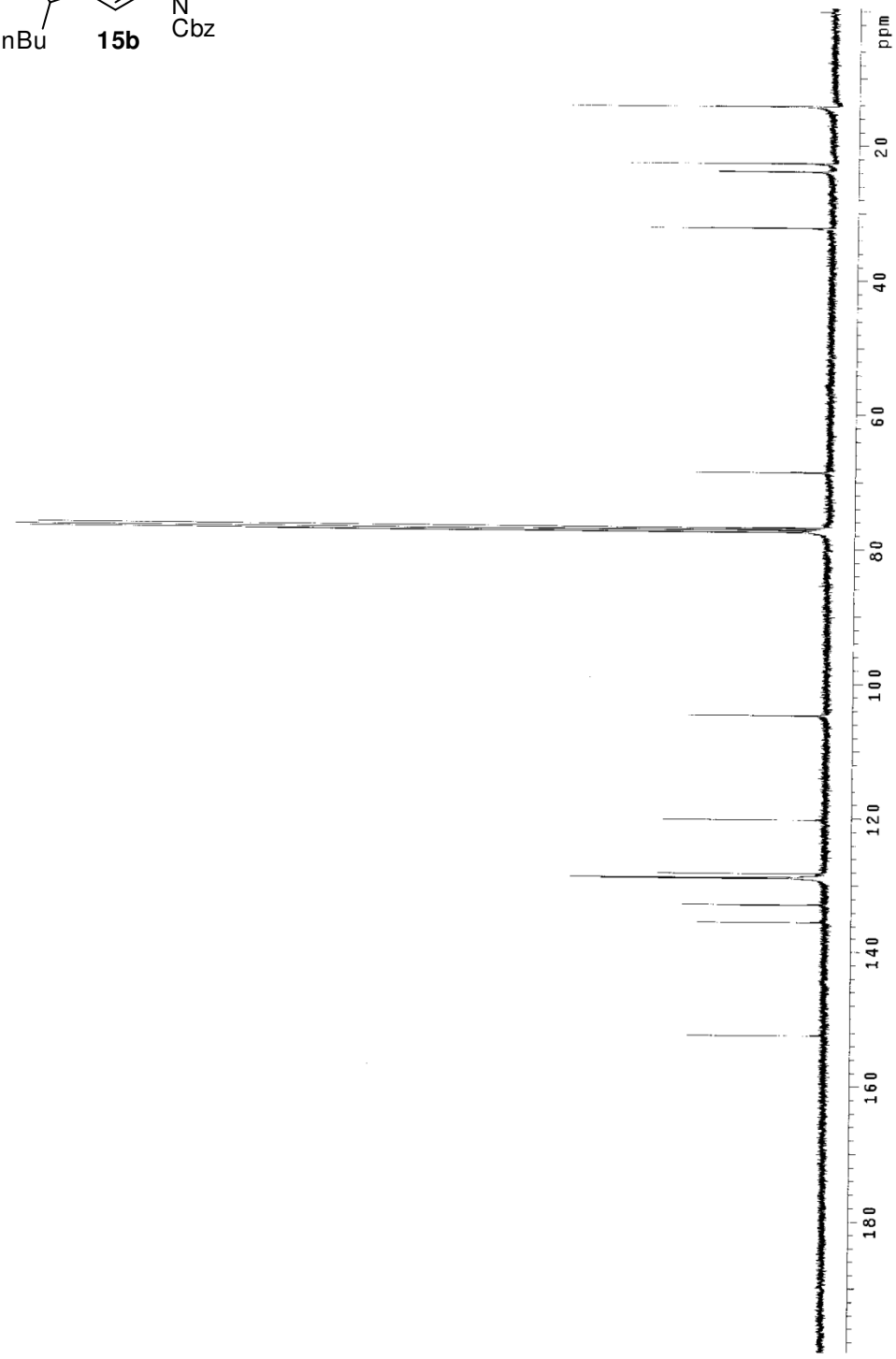

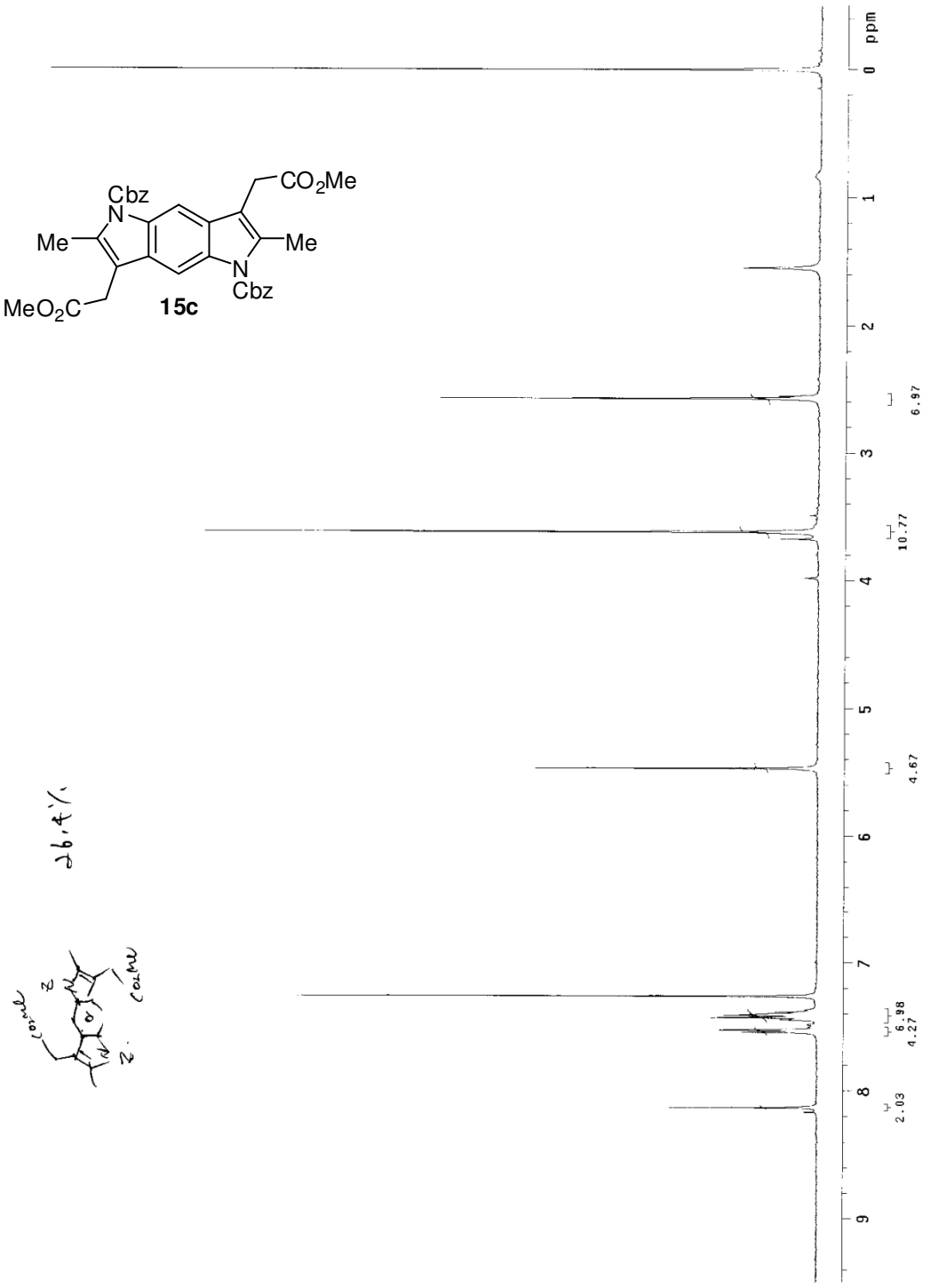
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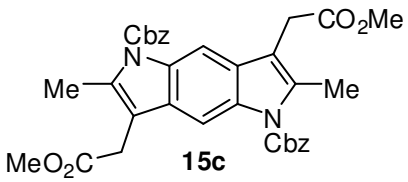

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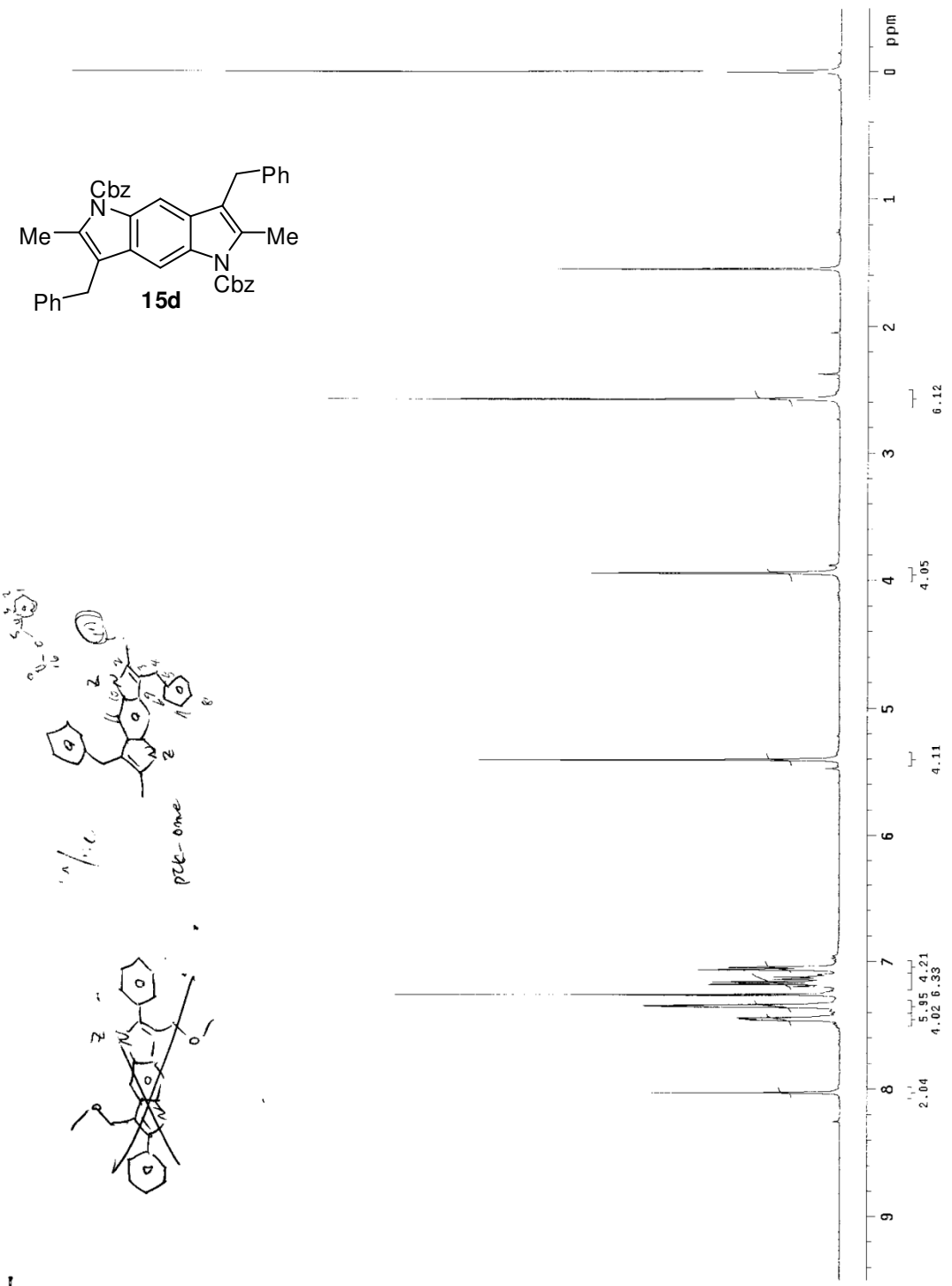
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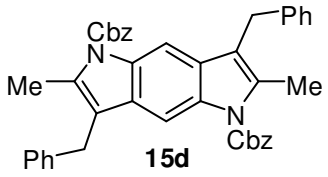

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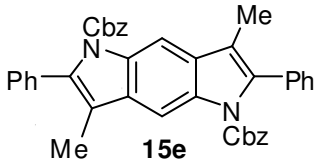
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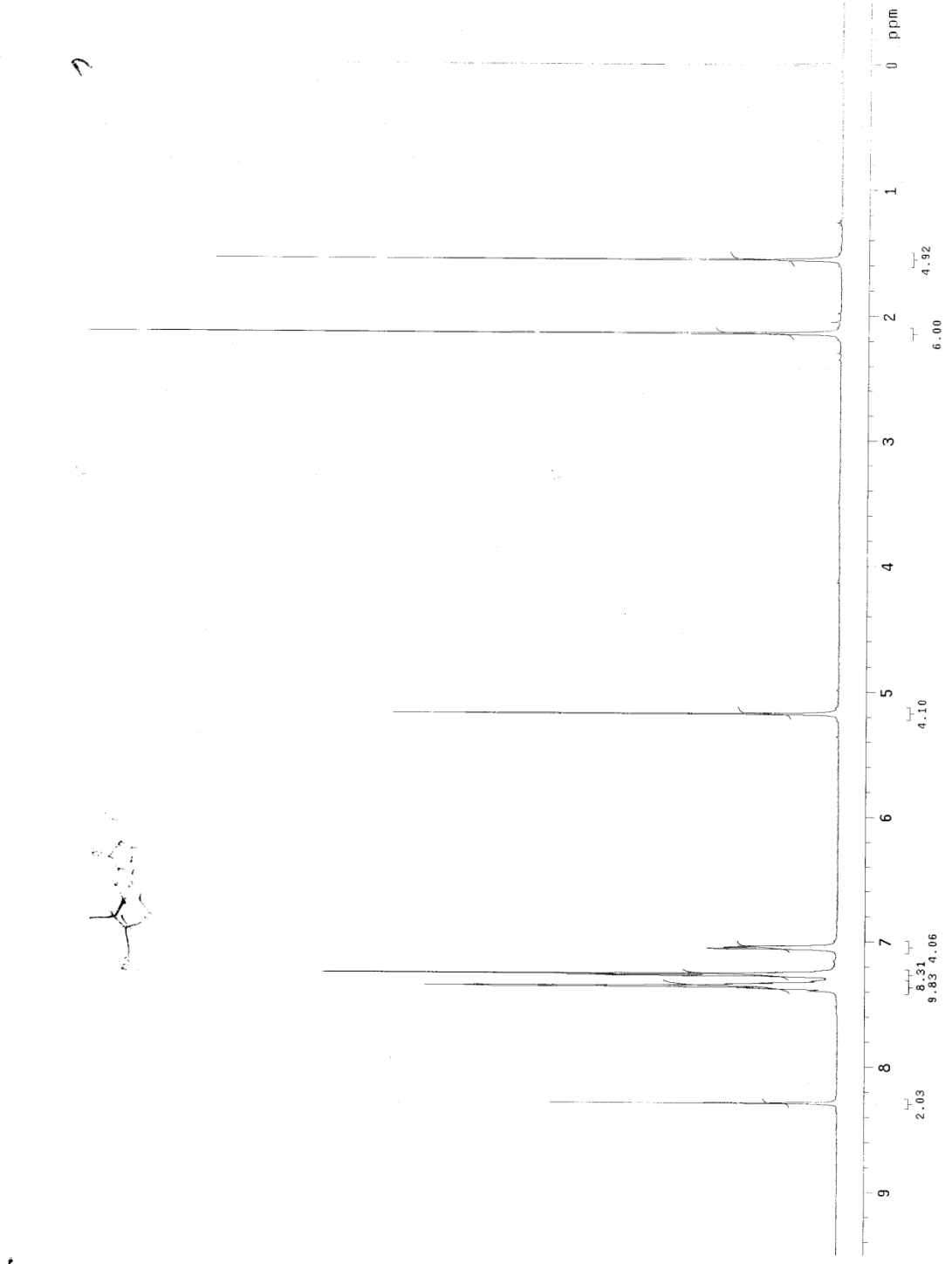
15e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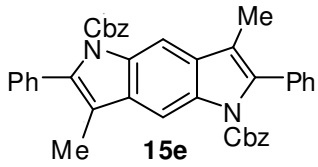

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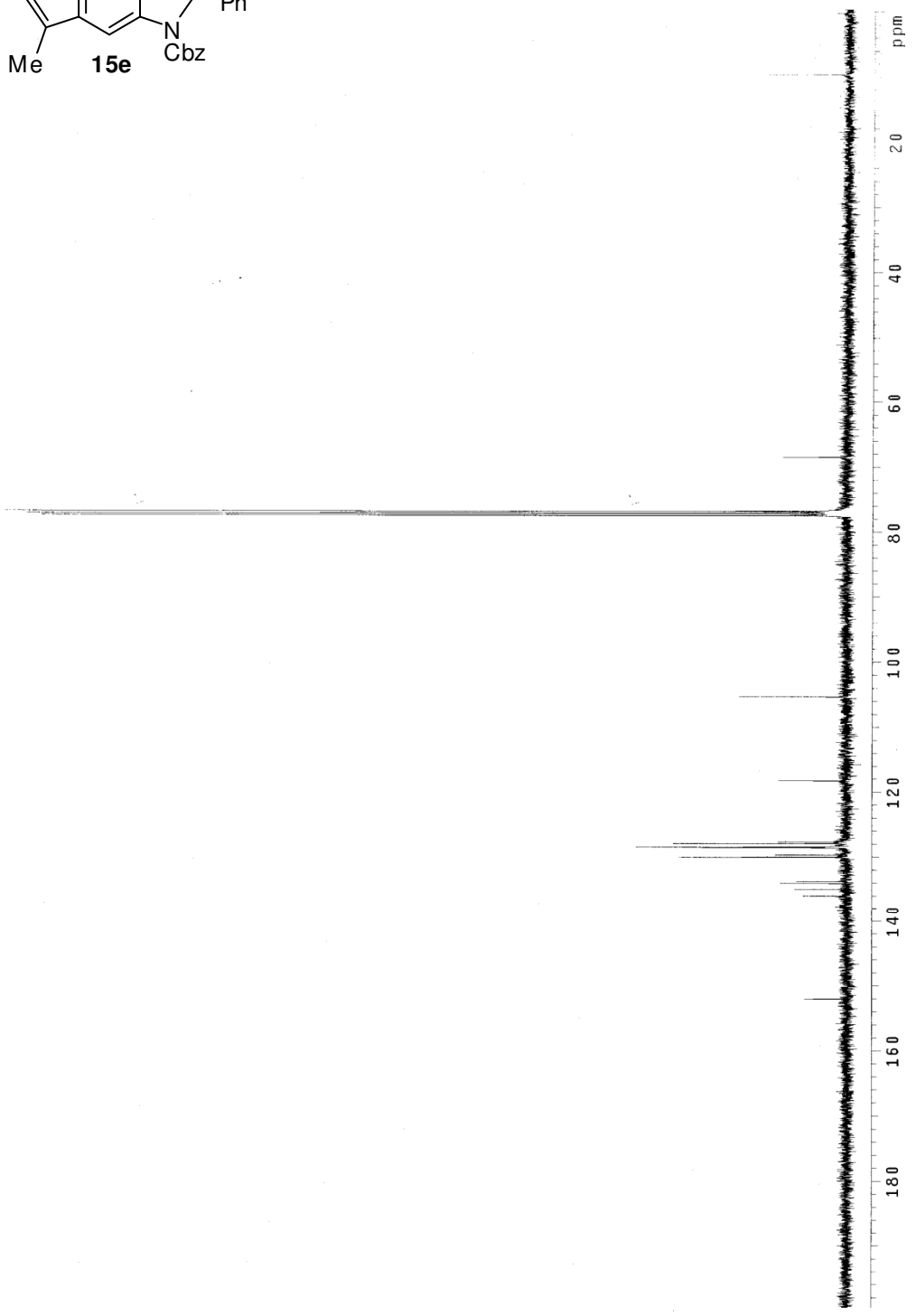

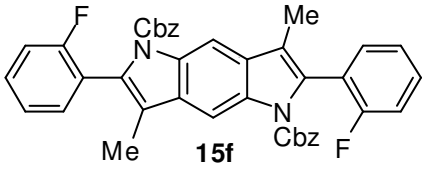

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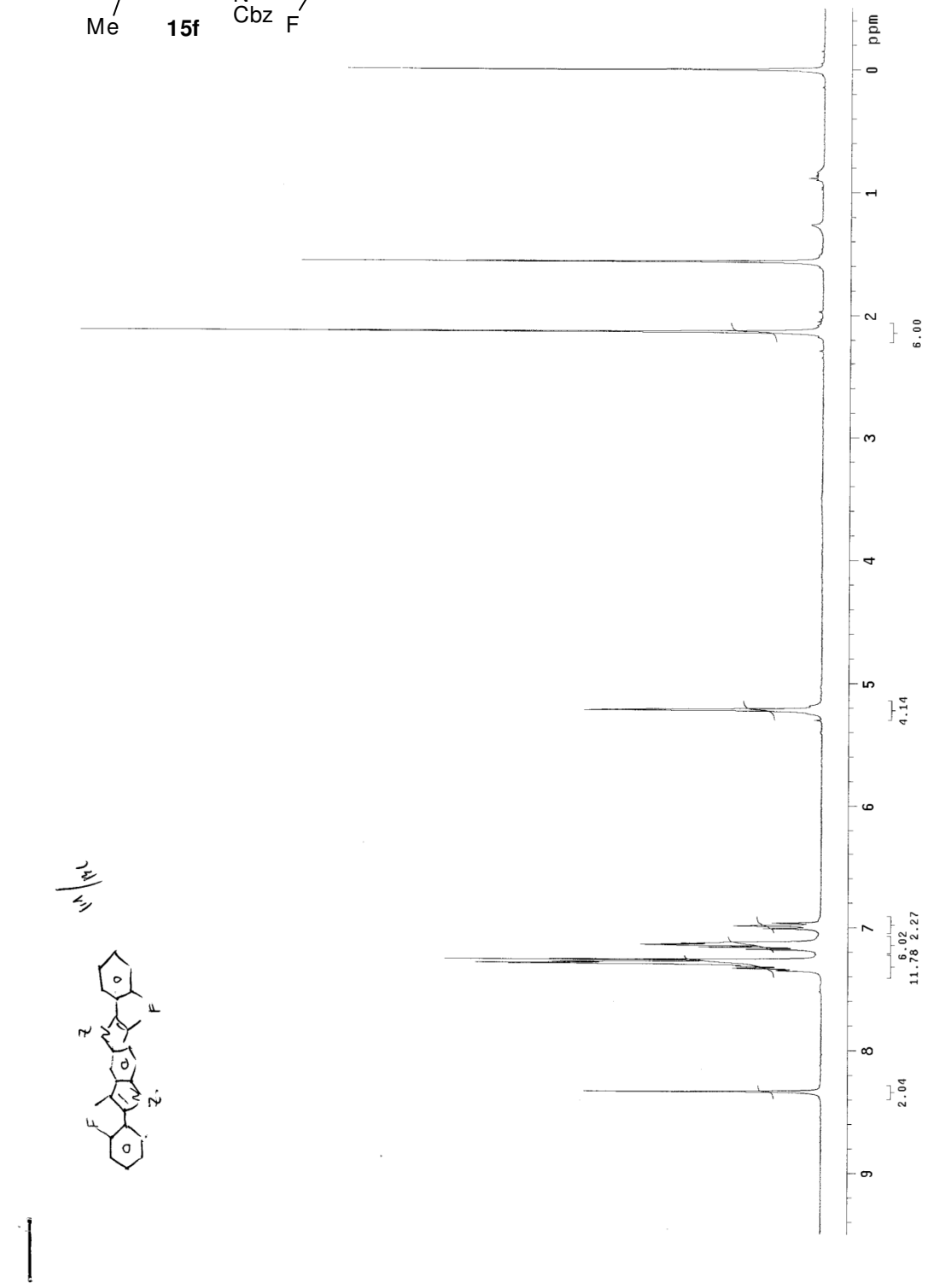

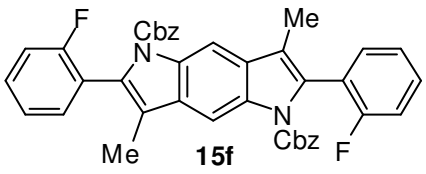

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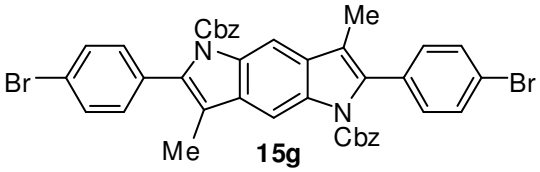

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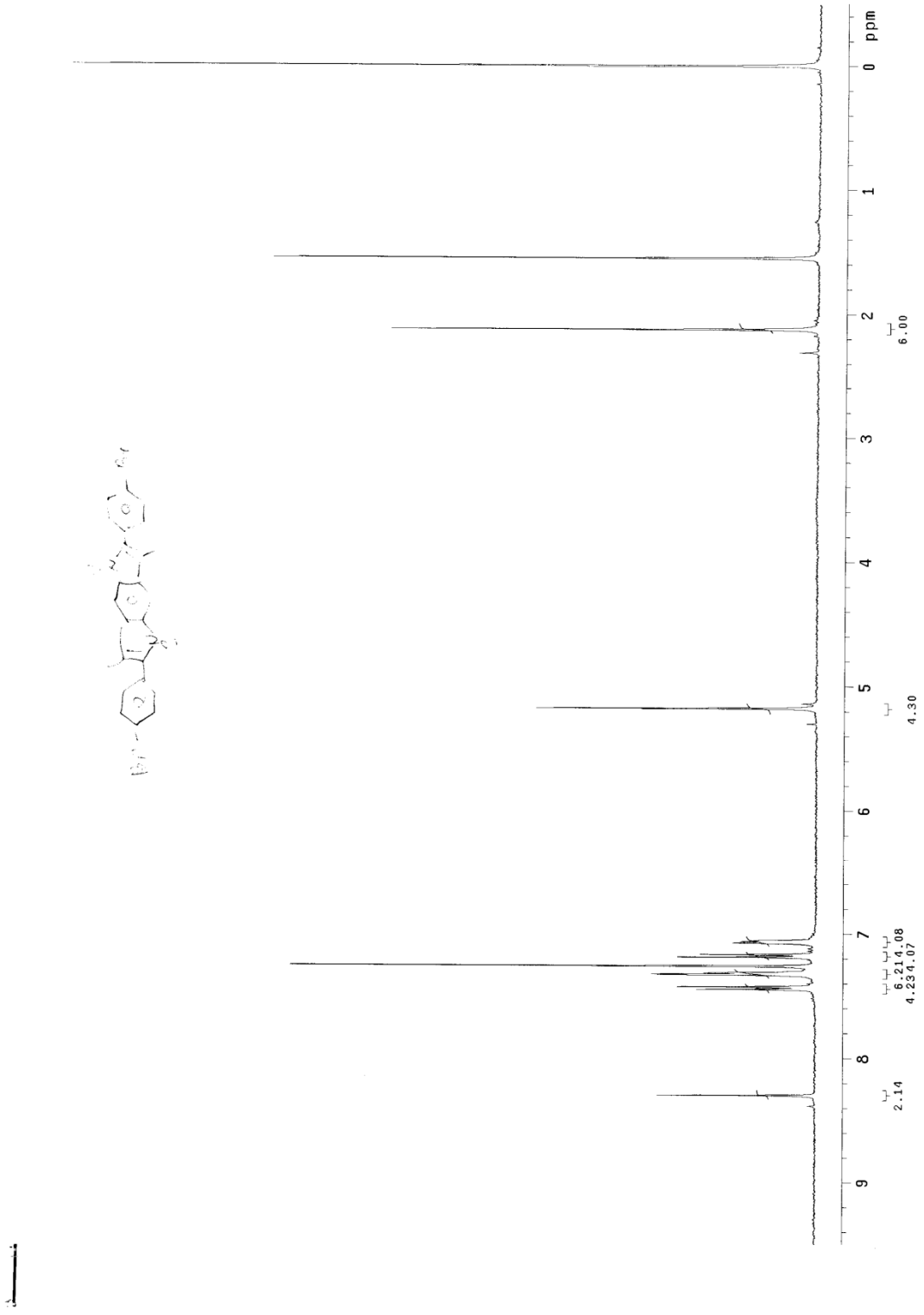

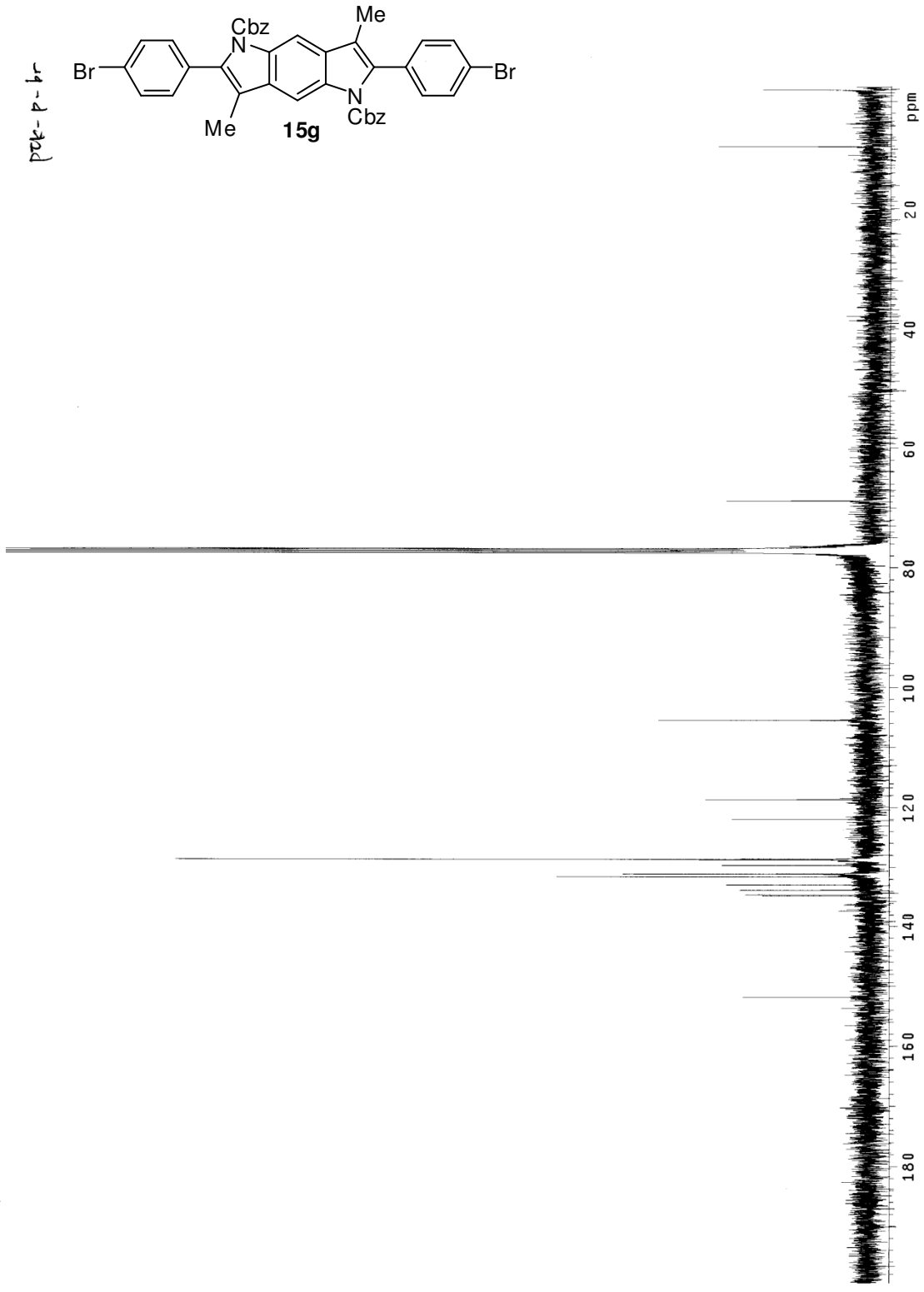
Cbz
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Cbz
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ppm
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