Vanadium-Catalyzed Regioselective Oxidative Coupling of 2-Hydroxycarbazoles

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Supporting Information

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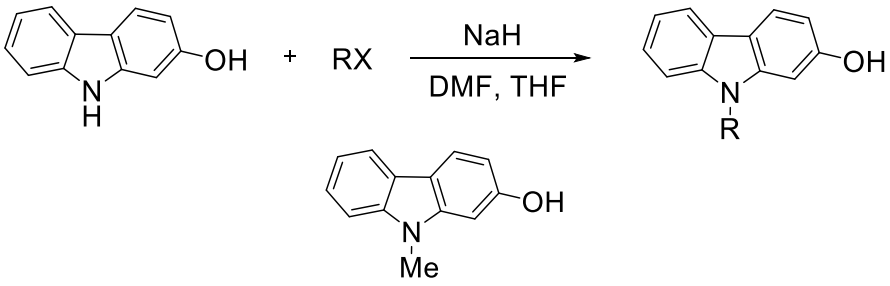
General Considerations.

Unless otherwise stated, all non-aqueous reactions were carried out under an atmosphere of dry argon in dry glassware. When necessary, solvents and reagents were dried prior to use. Tetrahydrofuran was distilled from Na/benzophenone prior to use. CH_2Cl_2 was distilled from CaH_2. Chloroform was distilled after drying over molecular sieves. Organometallic reagents were purchased from Aldrich. Analytical thin layer chromatography (TLC) was performed on Silicycle 250 μm silica-gel F-254 plates. High throughput experimentation was performed at the Penn/Merck High Throughput Experimentation Laboratory at the University of Pennsylvania. The screens were analyzed by HPLC with addition of an internal standard.

^{1}H NMR and ^{13}C NMR spectra were recorded on a AM-500 Fourier transform NMR spectrometer at 500 MHz and 125 MHz, respectively. Chemical shifts are reported relative to the solvent resonance peak δ 7.26 ($CDCl_3$), δ 2.50 (DMSO-*d*$_6$), δ 2.05 (acetone-*d*$_6$) for ^{1}H and δ 77.16 ($CDCl_3$), δ 39.52 (DMSO-*d*$_6$), δ 29.84 (acetone-*d*$_6$) for ^{13}C. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad singlet, m = multiplet), coupling constants, and number of protons. High resolution mass spectra were obtained using a VG autospec with an ionization mode of either ESI or CI. Infrared spectra are reported in cm^{-1}. Melting points were obtained and are uncorrected.

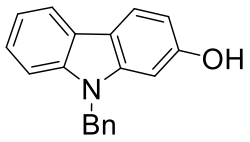
Preparation of Hydroxycarbazole Substrates

General Procedure A for the Synthesis of hydroxycarbazoles 1a and 1b



1a

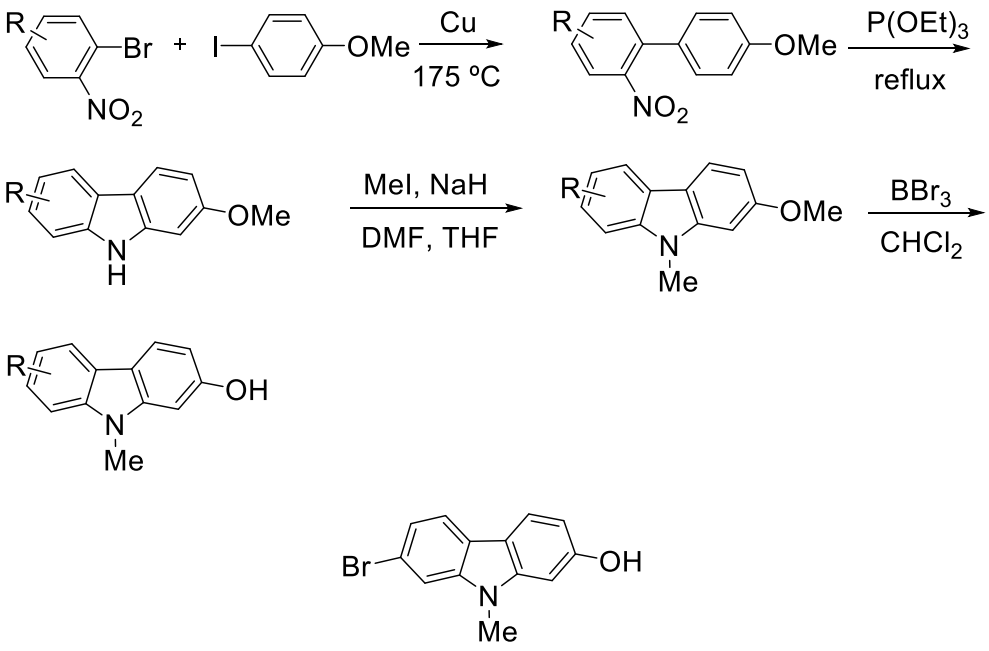
9-Methyl-2-hydroxycarbazole (1a) [Table 1]. A solution of 2-hydroxycarbazole (1.81 g, 9.88 mmol) and dry DMF (1.5 mL, 19.76 mmol) in dry THF (20 mL) was added dropwise to 95% NaH (0.59 g, 24.7 mmol) under a argon atmosphere and stirred at room temperature. After 10 min, CH_3I (0.68 mL, 10.87 mmol) was added and the stirring was continued for 2 h. The resulting mixture was cooled to 0 °C and quenched with water (2 mL). After concentration, the product was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (98:2) as the eluent. Compound **1a** (1.55 g) was obtained as a white solid in 80% yield. Spectral data matched those reported previously.[1]



1b

9-Benzyl-2-hydroxycarbazole (1b) [Table 2, entry 1]. Following the general procedure A, 2-hydroxycarbazole (916 mg, 5.0 mmol) and dry DMF (0.78 mL, 10.0 mmol) in dry THF (10 mL) was added dropwise to 95% NaH (300 mg, 12.5 mmol) under a argon atmosphere and stirred at room temperature. After 10 min, $PhCH_2Cl$ (0.63 mL, 5.5 mmol) was added and the stirring was continued at 50 °C for 5 h. After quenching, concentration and column chromatography with CH_2Cl_2/MeOH (98:2) product **1b** (1.06 g) was obtained as a white solid in 78% yield. Spectral data matched those reported previously.[1]

General Procedure B for the Synthesis of hydroxycarbazoles 1c-1l



1d

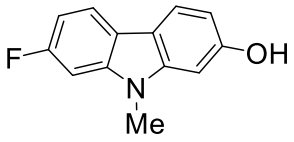
Following a modified procedure by Tidwell et al.,[2] copper powder (5.08 g, 80.0 mmol) was added over 40 min to a stirred molten mixture 2,5-dibromonitrobenzene (5.62 g, 20.0 mmol) and 4-iodoanisole (5.8 g, 24.8 mmol) and then maintained at 175 °C for another 3.5 h. The reaction mixture was extracted into hot toluene and filtered through Celite. The filtrate was washed with water, dried over $MgSO_4$, and concentrated. The resultant material was recrystallized from ethanol to give yellow needles in 62% yield. Spectral data matched those reported previously.[2]

A solution of 4-bromo-4'-methoxy-2-nitrobiphenyl (3.7 g, 12.0 mmol) in triethyl phosphite (10 mL, 62.4 mmol) was stirred at reflux under argon for 8.5 h. After the volatiles were removed under reduced pressure, the residue was suspended in ethanol with stirring. The solid was filtered off and washed with a little ice-ethanol. The product was obtained as a white solid in 72% yield. Spectral data matched those reported previously.[2]

A solution of 2-bromo-7-methoxycarbazole (2.38 g, 8.62 mmol) and dry DMF (0.8 mL, 10.34 mmol) in dry THF (10 mL) was added dropwise to 95% NaH (0.25 g, 10.34 mmol) under an argon atmosphere and stirred at room temperature. After 10 min, CH_3I (0.59 mL, 9.48 mmol) was added and the stirring was continued for 2 h. The resulting mixture was poured into ice-water. The precipitated product was collected by filtration and dried to give white powder in 93% yield. Spectral data matched those reported previously.[2]

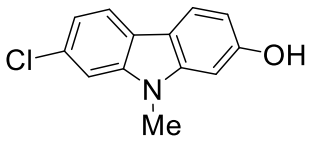
7-Bromo-9-methyl-2-hydroxycarbazol (1d) [Table 2, entry 4]. 2-Bromo-7-methoxy-9-methylcarbazole (508 mg, 1.75 mmol) in dry CH_2Cl_2 (25 mL) under argon was cooled to -40 °C. BBr_3 (0.51 mL, 5.25 mmol) was then added to the reaction mixture, which was

stirred overnight under argon, allowing gradual warming to room temperature. The reaction was quenched with ice-menthol (10 mL) and washed with water (10 mL), then extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, and dried over Na_2SO_4. After concentration, the material was purified by column chromatography on silica gel with Hexane/EtOAc (2:1). Product **1d** (435 mg) was obtained as white solid in 90% yield: mp 164-165 °C; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 9.67 (bs, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 157.2, 142.7, 141.5, 121.7, 121.3, 121.2, 120.5, 116.6, 114.1, 111.5, 109.0, 95.0, 29.0; IR (film) 3434, 1635, 1597, 1461, 1232, 1199, 949, 791 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_9NOBr$ $[M-H]^-$ *m/z* = 273.9868; found 273.9875.



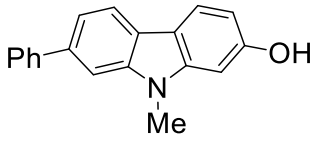
1c

7-Fluoro-9-methyl-2-hydroxycarbazol (1c) [Table 2, entry 2 and 3]. Following general procedure B, white solid, 40% yield over 4 steps; mp 195-196 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.01 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.94-6.90 (m, 1H), 6.82 (s, 1H), 6.74 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.88 (bs, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6 (d, *J* = 240 Hz), 154.6, 143.1 (d, *J* = 1.3 Hz), 142.0 (d, *J* = 11.3 Hz), 120.9, 120.3 (d, *J* = 10.0 Hz), 119.5, 116.8, 108.4, 107.0 (d, *J* = 23.8 Hz), 95.5 (d, *J* = 26.3 Hz), 95.2, 29.4; IR (film) 3419, 1639, 1606, 1586, 1467, 1205, 1103, 958, 794 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{10}NOF$ $[M]^+$ m/z = 215.0746; found 215.0750.



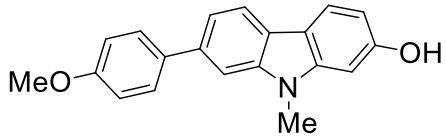
1e

7-Chloro-9-methyl-2-hydroxycarbazol (1e) [Table 2, entry 5 and 6]. Following general procedure B, white solid, 45% yield over 4 steps; mp 167-168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.86-7.84 (m, 2H), 7.31 (s, 1H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.80 (s, 1H), 6.74 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.97 (bs, 1H), 3.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 143.0, 141.9, 130.4, 121.7, 121.3, 120.3, 119.6, 116.5, 108.6, 108.5, 95.2, 29.3; IR (film) 3364, 1634, 1597, 1464, 1232, 1188, 1072, 949, 798 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{11}NOCl$ $[M+H]^+$ *m/z* = 232.0529; found 232.0523.



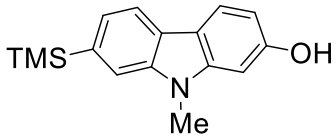
1f

7-Phenyl-9-methyl-2-hydroxycarbazol (1f) [Table 2, entry 7]. A mixture of 7-bromo-9-methyl-2-hydroxycarbazol **1d** (386 mg, 1.4 mmol), phenyl boronic acid (341 mg, 2.8 mmol), potassium carbonate (484 mg, 3.5 mmol), $Pd(PPh_3)Cl_2$ (5.0 mg, 7.0 μmol) were stirred in dioxane:H_2O (4:1 v:v, 6 mL, degassed with argon) and stirred at reflux overnight under argon. After cooling to room temperature, the reaction mixture was partitioned into diethyl ether and water. The aqueous mixture was extracted with diethyl ether and the combined extracts were dried over Na_2SO_4. After concentration, the material was purified by column chromatography on silica gel with hexane/EtOAc (3:1). Product **1f** (329 mg) was obtained as white solid in 86% yield: mp 194-195 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.75-7.73 (m, 2H), 7.54 (s, 1H), 7.51-7.46 (m, 3H), 7.40-7.37 (m, 1H), 6.82 (s, 1H), 6.76-6.74 (m, 1H), 5.02 (bs, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 143.2, 142.4, 141.9, 138.2, 128.9, 127.7, 127.1, 122.4, 121,4 119.8, 118.9, 116.9, 108.2, 107.0, 95.0, 29.3; IR (film) 3419, 1631, 1607, 1464, 1420, 1234, 950, 810, 764, 696 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{16}NO$ $[M+H]^+$ m/z = 274.1232; found 274.1232.



1g

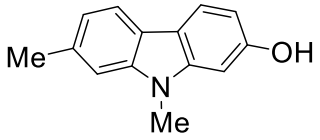
7-*p*-Methoxyphenyl-9-methyl-2-hydroxycarbazol (1g) [Table 2, entry 8]. Following the same procedure as for **1f**. White solid (305 mg), 85% yield; mp 216-218 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.57 (bs, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 2H), 7.71 (s, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.03 (d, J = 8.5 Hz, 2H), 6.88 (s, 1H), 6.70 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.6, 156.8, 142.9, 141.3, 136.0, 133.8, 128.0, 121.5, 120.9, 119.3, 117.4, 114.6, 114.3, 108.4, 106.3, 94.9, 55.2, 28.9; IR (film) 3434, 1637, 1521, 1465, 1237, 1183 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}NO_2$ $[M+H]^+$ m/z =304.1338; found 304.1345.



1h

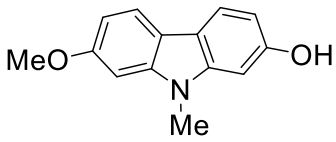
7-Trimethylsilyl-9-methyl-2-hydroxycarbazol (1h) [Table 2, entry 9 and 10]. Following a modified procedure by Node et al.,[3] 7-bromo-9-methyl-2-hydroxycarbazol **1d** (386 mg, 1.4 mmol) was dissolved in dry THF (10 mL) and the solution was cooled to –78 °C. *n*-BuLi (2.5 M in *n*-hexane, 1.25 mL, 3.08 mmol) was slowly added to the

solution over 15 min and the resulting mixture was stirred at the same temperature for 1.5 h. Trimethylsilylchloride (0.46 mL, 3.64 mmol) was then added slowly. The stirring was continued at –78 °C for 2 h and at room temperature for additional 12 h. The mixture was quenched with 1 N aq. HCl (6 mL) and stirred at rt for 1 h. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. After the volatiles were removed under reduced pressure, the product was purified by column chromatography on silica gel with hexane/EtOAc (3:1), product **1h** (332 mg) was obtained as white solid in 88% yield: mp 161-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.39 (d, J = 7.5 Hz, 1H), 6.81 (s, 1H), 6.74 (dd, J = 8.0, 2.0 Hz, 1H), 5.15 (bs, 1H), 3.77 (s, 3H), 0.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 142.7, 141.0, 136.2, 124.0, 123.7, 121.5, 119.0, 117.0, 112.9, 108.0, 94.9, 29.1, –0.6; IR (film) 3435, 1636, 1456, 1321, 1231, 1118 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}NOSi$ $[M+H]^+$ m/z = 270.1314; found 270.1311.



1i

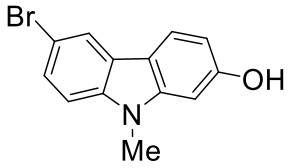
7-Methyl-9-methyl-2-hydroxycarbazol (1i) [Table 2, entry 11]. Following general procedure B, white solid, 38% yield over 4 steps; mp 181-183 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.15 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.79 (s, 1H), 6.71 (dd, J = 8.0, 2.0 Hz, 1H), 4.93 (bs, 1H), 3.72 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 142.6, 141.8, 134.7, 120.9, 120.8, 120.6, 119.2, 117.2, 108.7, 107.7, 95.0, 29.1, 22.3; IR (film) 3434, 1636, 1465, 1185, 1112, 813, 794 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{14}NO$ $[M+H]^+$ m/z = 212.1075; found 212.1065.



1j

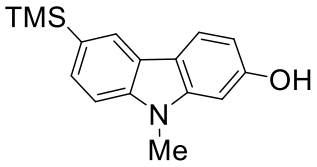
7-Methoxy-9-methyl-2-hydroxycarbazol (1j) [Table 2, entry 12]. Following a modified procedure by Maily et al.[4] A solution of 7-bromo-9-methyl-2-hydroxycarbazol **1d** (508 mg, 1.75 mmol) in dry THF (25 mL) under argon was cooled to -78 °C. *n*-BuLi (2.5 M, 0.84 mL, 2.1 mmol) was added dropwise and the reaction mixture was stirred with continued cooling for 10 minutes. Trimethyl borate (0.25 mL, 2.28 mmol) was added to the reaction mixture, which was stirred overnight under argon, allowing gradual warming to room temperature. The reaction mixture was acidified with 1 M aqueous HCl and extracted with diethyl ether. The combined extracts were concentrated, and the residue was dissolved in a mixture of THF (10 mL) and 1 M NaOH (20 mL). Hydrogen peroxide (2 mL, 30%) was added dropwise and the mixture was stirred for 15 minutes. The mixture was then acidified using 1M HCl and extracted with diethyl ether. The combined

organic extracts were washed with brine and dried over $MgSO_4$. After filtration and concentration, the crude product was purified by column chromatography on silica gel with hexane/EtOAc (3:1). The product **1j** (318 mg) was obtained as white solid in 80% yield: mp 167-169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.5, 2.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 6.84-6.82 (m, 2H), 6.78 (s, 1H), 6.71 (dd, J = 8.0, 2.0 Hz, 1H), 4.98 (bs, 1H), 3.93 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 153.9, 142.7, 142.6, 120.3, 120.2, 117.2, 117.0, 107.8, 107.2, 95.1, 93.3, 55.9, 29.2; IR (film) 3421, 1636, 1473, 1365, 1217, 1111, 1050, 957 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}NO_2$ $[M]^+$ m/z = 227.0946; found 227.0935.



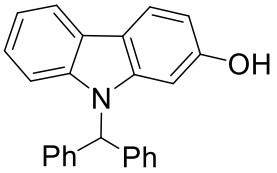
1k

6-Bromo-9-methyl-2-hydroxycarbazol (1k) [Table 2, entry 13]. Following general procedure B, white solid, 42% yield over 4 steps; mp 154-155 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.68 (bs, 1H), 8.18 (s, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.46-7.41 (m, 2H), 6.86 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.5, 142.8, 139.3, 126.0, 124.5, 121.6, 121.4, 113.7, 110.8, 110.6, 109.0, 94.9, 29.0; IR (film) 3420, 1637, 1466, 1277, 1199, 946 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_9NOBr$ $[M-H]^-$ m/z = 273.9868; found 273.9873.



1l

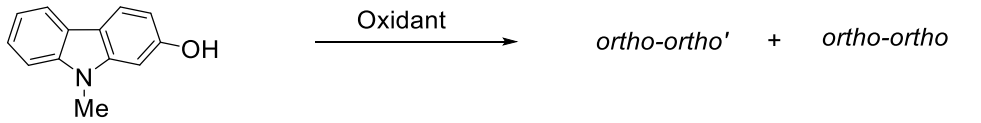
6-Trimethylsilyl-9-methyl-2-hydroxycarbazol (1l) [Table 2, entry 14]. Following the same procedure as for **1h**. White solid (353 mg), 86% yield; mp 128-130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.57 (dd, J = 8.0, 1.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 6.75 (dd, J = 8.0, 2.0 Hz, 1H), 5.00 (bs, 1H), 3.75 (s, 3H), 0.37 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.8, 142.6, 141.9, 129.6, 129.3, 124.7, 122.9, 121.3, 117.0, 108.1, 108.0, 95.0, 29.1, –0.4; IR (film) 3434, 2953, 1634, 1601, 1469, 1243, 1093, 946, 824 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{18}NOSi$ $[M-H]^-$ m/z = 268.1158; found 268.1168.



1m

9-Benzhydryl-2-hydroxycarbazole (1m) [Table 2]. Following the general procedure A, 2-hydroxycarbazole (92 mg, 0.5 mmol) and dry DMF (78 μL, 1.0 mmol) in dry THF (5 mL) was added dropwise to 95% NaH (30 mg, 1.25 mmol) under a argon atmosphere and stirred at room temperature. After 10 min, Ph_2CHCl (78 μL, 0.55 mmol) was added and the stirring was continued at 50 °C for 5 h. After quenching, concentration and column chromatography with CH_2Cl_2/MeOH (100:1) product **1m** (105 mg) was obtained as a white solid in 60% yield: mp 184-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.00 (m, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.94-7.30 (m, 6H), 7.26-7.17 (m, 6H), 7.08 (s, 1H), 7.03 (dd, *J* = 7.0, 2.0 Hz, 1H), 6.72 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.48 (d, *J* = 2.0 Hz, 1H), 4.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 142.4, 141.2, 139.0, 129.0, 128.7, 128.2, 124.7, 124.0, 121.3, 119.7, 119.6, 118.0, 110.8, 108.6, 97.6, 62.7; IR (film) 3352, 3029, 1631, 1600, 1449, 1342, 1167, 907, 698 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}NO$ $[M-H]^-$ *m/z* = 348.1388; found 348.1383.

Table S1. Oxidation of 2-Hydroxycarbazole with Conventional Oxidants



entry	oxidant	solvent	temp (°C)	*t* (h)	yield (%) *o-o'*	yield (%) *o-o*
1	$(t\text{-BuO})_2$	PhCl	135	8	32	29
2	$CuCl_2$/TMEDA/O_2	MeOH	rt	1	decompose	
3	$K_3Fe(CN)_6$	MeOH/H_2O	rt-70	24	8	6
4	MnO_2	DCE	80	16	20	18
5	Ag_2CO_3	MeCN	80	16	6	13
6	p-Chloroanil*	MeOH	70	18	<5	<5

*10% of tetramer was observed

Parallel Microscale Screening Results

HTE of 2-Hydroxycarbazole

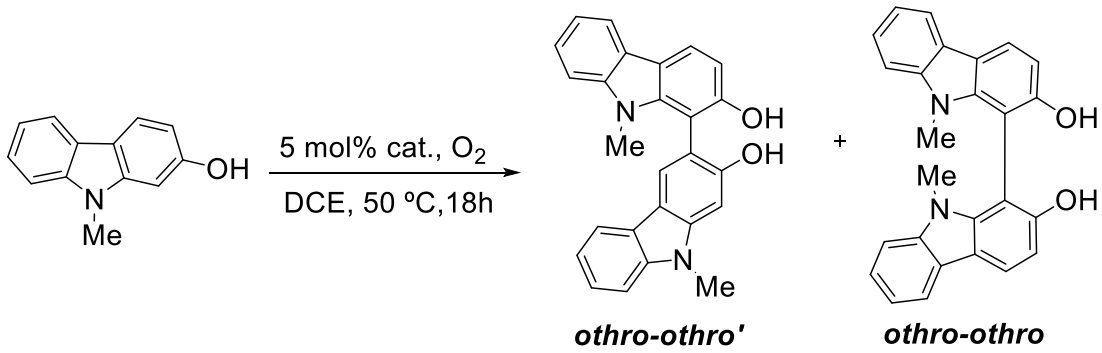
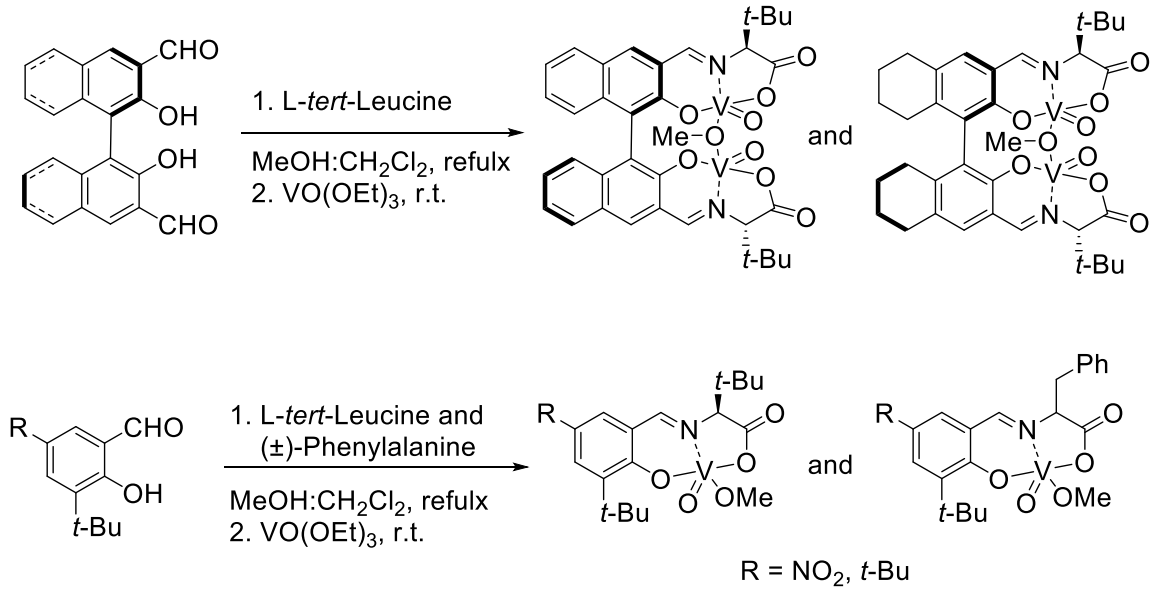


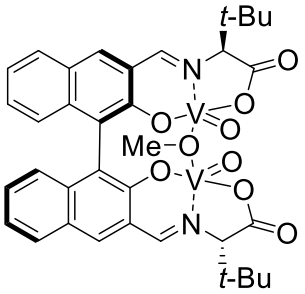
Table S2. Complete HTE Results of 2-Hydroxycarbazole

Catalyst	SM	*o-o'*	*o-o*	IS	*o-o'*/IS	*o-o*/IS
Co-Salen-Cy-*t*-Bu	37	12	95	325	0.04	0.29
Co-Salan-Cy-*t*-Bu	285	83	159	354	0.23	0.45
Cr-Salen-Cy-*t*-Bu	103	187	29	376	0.50	0.08
Cr-Salen-Ph-*t*-Bu	1372	112	12	369	0.30	0.03
Cr-Salen-Cy-NO_2	1697	0	0	377	0.00	0.00
Cr-Salan-Ph-*t*-Bu	1553	30	0	365	0.08	0.00
Cu-Salen-Ph-*t*-Bu	1832	0	0	405	0.00	0.00
Cu-Salan-Cy-t-Bu	1254	127	110	391	0.32	0.28
Cu-Salan-Ph-*t*-Bu	1472	88	73	387	0.23	0.19
Mn-Salen-Cy-*t*-Bu	1787	0	109	392	0.00	0.28
Mn-Salan-Cy-NO_2	918	169	191	384	0.44	0.50
V-Salen-H-*t*-Bu	1592	76	43	392	0.19	0.11
V-Salen-Ph-*t*-Bu	409	387	0	401	0.97	0.00
V-Salan-Ph-*t*-Bu	571	156	38	382	0.41	0.10
Ru-Salen-Cy-*t*-Bu	1350	128	104	388	0.33	0.27
Ru-Salen-Ph-*t*-Bu	820	168	170	389	0.43	0.44
Ru-Salan-Cy-*t*-Bu	453	137	187	393	0.35	0.47
Ru-Salan-Ph-*t*-Bu	987	180	132	392	0.46	0.34
Ru-Salan-Cy-NO_2	1104	129	86	364	0.35	0.24

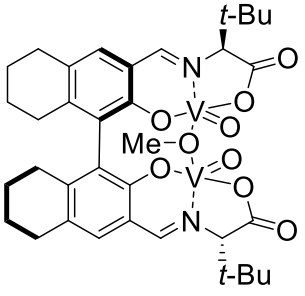
General Procedure for Vanadium Catalysts[5-7]



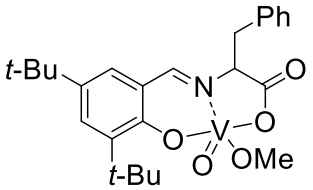
All glassware was flame dried. A mixture of L-*tert*-leucine or (±)-phenylalanine (0.34 mmol) and salicylaldehyde derivative (0.17 mmol or 0.34 mmol) in MeOH:CH_2Cl_2 (2 mL, 1:1) was heated to reflux and monitored by TLC. The reaction mixture was cooled to room temperature and $VO(OEt)_3$ (0.34 mmol) was added. After 3 h under air, solvent was removed under reduced pressure to afford the catalysts.



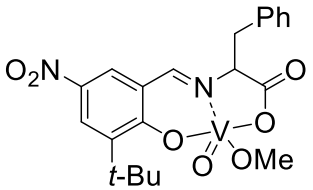
(S,R,S)-Vanadium catalyst V1. Dark green solid; HRMS (ESI) calcd for $C_{35}H_{35}N_2O_9V_2$ $[M]^+$ *m/z* = 729.1222; found 729.1253.



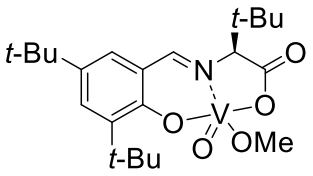
(S,R,S)-Vanadium catalyst V2. Dark green solid; HRMS (ESI) calcd for $C_{35}H_{43}N_2O_9V_2$ $[M]^+$ *m/z* = 737.1848; found 737.1843.



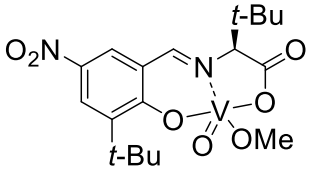
(±)-Vanadium catalyst V3. Dark Green solid; HRMS (ESI) calcd for $C_{25}H_{33}NO_5V$ $[M+H]^+$ *m/z* = 478.1798; found 478.1793.



(±)-Vanadium catalyst V4. Dark brown solid; HRMS (ESI) calcd for $C_{21}H_{24}N_2O_7V$ $[M+H]^+$ *m/z* = 467.1023; found 467.1028.

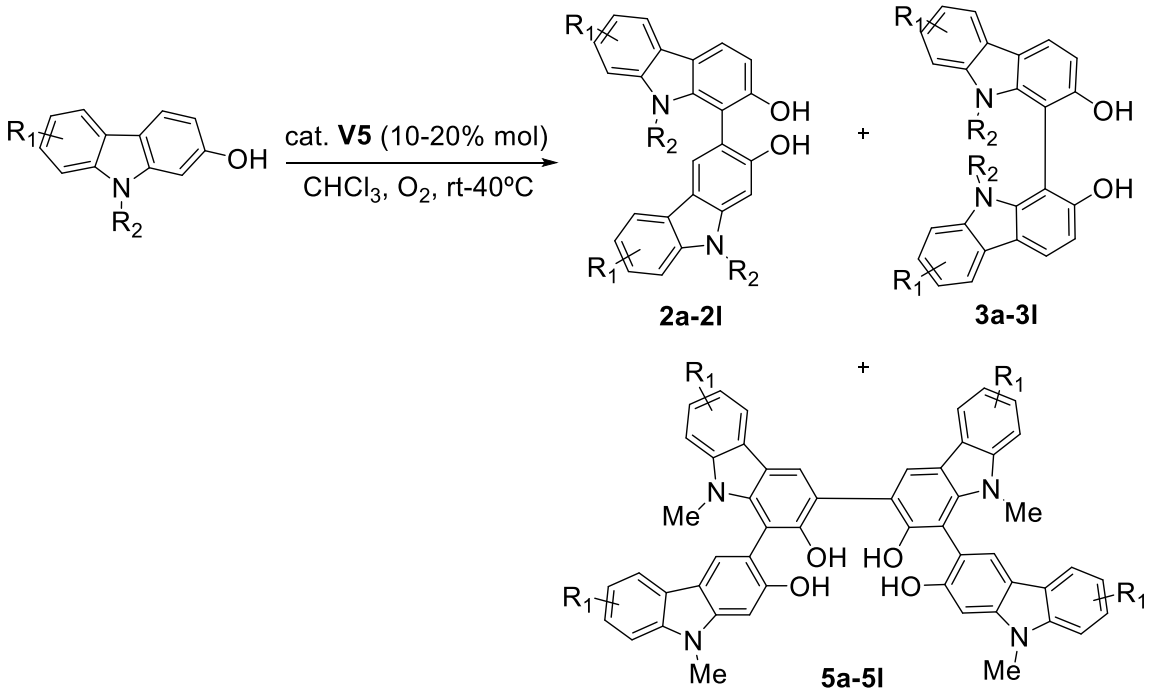


(S)-Vanadium catalyst V5. Dark Green solid; HRMS (ESI) calcd for $C_{22}H_{35}NO_5V$ $[M+H]^+$ *m/z* = 444.1955; found 444.1946.

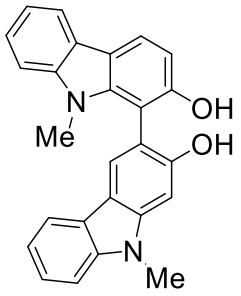


(S)-Vanadium catalyst V6. Dark Green solid; HRMS (ESI) calcd for $C_{18}H_{26}N_2O_7V$ $[M+H]^+$ *m/z* = 433.1180; found 433.1179.

General Procedure for Regioselective Oxidative Hydroxycarbazole Coupling (Table 1 and Table 2)



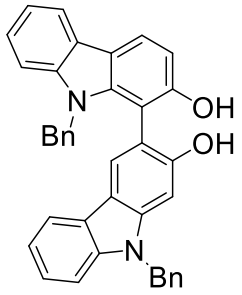
To a 5 mL microwave vial was added hydroxycabazole (0.1 mmol) and catalyst (0.01mmol). The vial was sealed with a septum and solvent (1 mL) was added. Oxygen was added *via* active purge. The septum was replaced with a crimping cap and the vessel was sealed and stirred for the indicated time at the indicated temperature. After the reaction mixture was filtered through a plug of silica and concentrated *in vacuo*, the resultant mixture was chromatographed on silica using ethyl acetate/hexane to afford the product.



2a

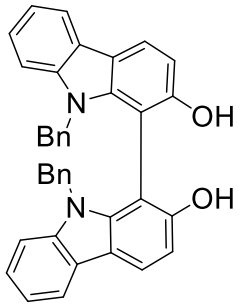
9,9'-Dimethyl-[1,3'-bicarbazole]-2,2'-diol (2a) [Table 1]. Following the general procedure, using catalyst **V5** (10 mol%) in chloroform at 40 °C for 2.5 d, the *ortho-ortho'* product was obtained as white solid (13.8 mg) in 70% yield: mp 154-156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 8.05 (s, 1H), 8.04 (d, J = 9.5 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.50-7.39 (m, 3H), 7.28-7.24 (m, 3H), 7.15 (s, 1H), 7.02 (d, J = 8.5 Hz, 1H), 5.26 (bs, 1H), 5.19 (bs, 1H), 3.88 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 154.1, 154.0, 143.7, 141.9, 141.6, 140.2, 125.4, 124.8, 123.8, 122.9, 122.7, 122.1, 119.8, 119.7, 119.6, 119.3, 117.8, 117.6, 110.0, 108.7, 108.6, 108.1, 103.4, 95.4, 30.8, 29.4; IR (film) 3421, 1636, 1593, 1466, 1442, 1257, 1206, 980, 746 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ *m/z* = 393.1603; found 393.1596; chiral HPLC (IA, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R = 31.54 and 44.16 min.



2b

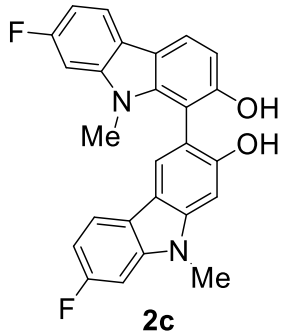
9,9'-dibenzyl-[1,3'-bicarbazole]-2,2'-diol (2b) [Table 2, entry 1]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 3 d, the *ortho-ortho'* product was obtained as white solid (15.3 mg) in 56% yield: mp 141-143 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.41-7.20 (m, 11H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.96-6.94 (m, 1H), 6.90 (s, 1H), 6.81-6.78 (m, 2H), 6.27 (d, *J* = 8.0 Hz, 2H), 5.52 (d, *J* = 16.5 Hz, 1H), 5.48 (d, *J* = 17.0 Hz, 1H), 5.08 (bs, 1H), 5.13 (d, *J* = 17.5 Hz, 1H), 4.93 (d, *J* = 17.5 Hz, 1H), 4.85 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 153.8, 143.1, 142.0, 141.2, 139.6, 137.4, 137.0, 129.0, 128.2, 127.9, 126.9, 126.7, 125.4, 125.3, 125.1, 124.1, 123.1, 123.0, 122.2, 120.1, 120.0, 119.8, 119.4, 118.3, 117.8, 109.6, 109.2, 108.6, 108.5, 103.9, 95.8, 43.7, 46.9; IR (film) 3434, 1635, 1452, 1325, 1265, 1172, 955 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{27}N_2O_2$ $[M-H]^-$ *m/z* = 543.2073; found 543.2099.



3b

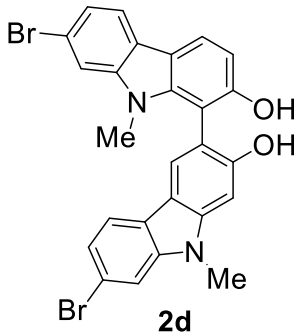
9,9'-Dibenzyl-[1,1'-bicarbazole]-2,2'-diol (3b) [Table 2, entry 1]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 3 d, the *ortho-ortho* product was obtained as white solid (2.2 mg) in 8% yield: mp 145-147 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.35-7.32 (m, 2H), 7.30-7.27 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.87-6.85 (m, 2H), 6.82-6.78 (m, 6H), 6.28 (d, *J* = 7.5 Hz, 4H), 4.76 (d, *J* = 17.5 Hz, 2H), 4.71 (bs, 2H), 4.56 (d, *J* = 17.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 142.0, 139.8, 137.2, 128.0, 126.8, 125.2, 125.1, 122.9, 122.8, 120.1, 119.3, 119.3, 109.4, 108.8, 99.3, 47.0; IR (film) 3422, 1637,

1452, 1415, 1344, 1182, 948 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{29}N_2O_2$ $[M+H]^+$ *m/z* = 545.2229; found 545.2225.



2c

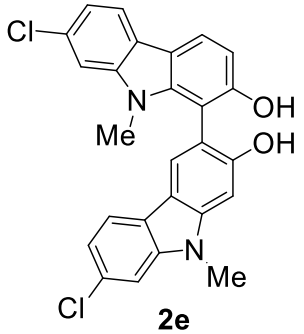
7,7'-Difluoro-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2c) [Table 2, entry 2 and 3]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 3 d, the *ortho-ortho'* product was obtained as white solid (13.3 mg) in 62% yield. Catalyst **V5** (10 mol%) at 40 °C for 2 d, the *ortho-ortho'* product was obtained (9.6 mg) in 45% yield (78% based on recovered starting material): mp 200-202 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.97 (s, 1H), 7.94-7.91 (m, 1H), 7.88-7.85 (m, 1H), 7.14 (s, 1H), 7.10 (dd, *J* = 10.0, 2.0 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.98-6.92 (m, 3H), 5.15 (bs, 2H), 3.84 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0 (d, *J* = 240 Hz), 161.7 (d, *J* = 240 Hz), 153.8, 153.6, 144.2 (d, *J* = 1.3 Hz), 142.6 (d, *J* = 11.3 Hz), 142.4 (d, *J* = 12.5 Hz), 140.6 (d, *J* = 1.3 Hz), 123.3, 121.8, 120.7 (d, *J* = 10 Hz), 120.1 (d, *J* = 10 Hz), 119.3, 119.1, 117.5, 117.3, 110.3, 108.6, 107.7 (d, *J* = 23.8 Hz), 107.6 (d, *J* = 23.8 Hz), 103.6, 96.0 (d, *J* = 27.5 Hz), 95.9 (d, *J* = 26.3 Hz), 95.7, 31.1, 29.7; IR (film) 3433, 1645, 1440, 1354, 1208, 1109, 985 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{19}N_2O_2F_2$ $[M+H]^+$ *m/z* = 429.1415; found 429.1423.



2d

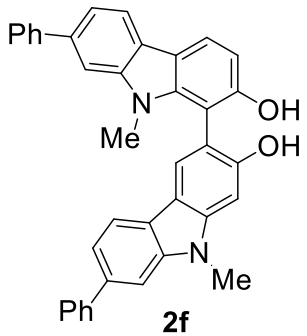
7,7'-Dibromo-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2d) [Table 2, entry 4]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 2 d, the *ortho-ortho'* product was obtained as white solid (11.1 mg) in 40% yield (73% based on recovered starting material): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.99 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.40 (s, 1H), 7.35-7.33 (m, 2H), 7.13 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.19 (bs, 2H), 3.85 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 154.3, 143.9, 142.7, 142.5, 140.3, 123.8, 122.9, 122.8, 122.3, 121.9, 121.7, 120.9, 120.4, 119.1, 118.4, 117.3, 117.1, 112.0 (2C), 110.4, 108.8, 103.5, 95.8, 31.0, 29.6; IR (film) 3435, 1636, 1589, 1438,

1365, 1235, 1205, 980, 798 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{19}N_2O_2Br_2$ $[M+H]^+$ *m/z* = 548.9790; found 548.9813.



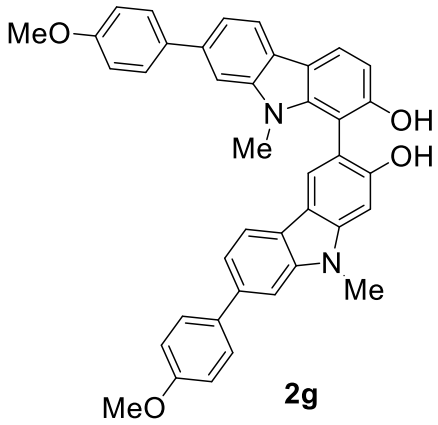
2e

7,7'-Dichloro-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2e) [Table 2, entry 5 and 6]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 3 d, the *ortho-ortho'* product was obtained as white solid (13.6 mg) in 59% yield. Catalyst **V5** (10 mol%) at 40 °C for 2 d, the *ortho-ortho'* product (9.2 mg) was obtained in 40% yield (75% based on recovered starting material): mp 262-264 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 1H), 7.99 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.24 (s, 1H), 7.21-7.19 (m, 2H), 7.13 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.19 (bs, 2H), 3.85 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 154.2, 144.0, 142.5, 142.2, 140.5, 131.3, 130.7, 123.7, 122.2, 121.5, 121.3, 120.6, 120.2, 120.1, 117.3, 117.1, 110.4, 109.0, 108.8, 103.5, 95.8, 31.0, 29.6; IR (film) 3419, 1634, 1592, 1440, 1347, 1237, 1205, 1075, 981, 799 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{19}N_2O_2Cl_2$ $[M+H]^+$ *m/z* = 461.0824; found 461.0812.



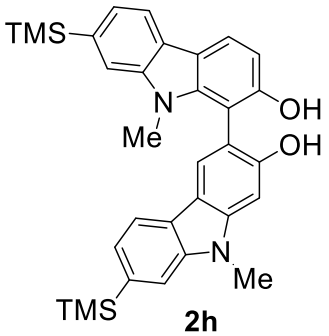
2f

7,7'-Diphenyl-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2f) [Table 2, entry 7]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 1 d, the *ortho-ortho'* product was obtained as white solid (11.7 mg) in 43% yield (79% based on recovered starting material): mp 184-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.07 (m, 2H), 8.07 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 7.0 Hz, 2H), 7.62 (s, 1H), 7.52-7.44 (m, 7H), 7.40-7.33 (m, 2H), 7.17 (s, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 5.26 (bs, 2H), 3.94 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 154.1, 144.3, 142.5, 142.4, 142.2, 142.1, 140.7, 139.1, 138.4, 129.0, 128.9, 127.7, 127.6, 127.3, 127.1, 123.8, 122.3, 122.2, 122.0, 120.1, 119.6, 119.5, 119.4, 117.7, 117.4, 110.2, 108.4, 107.4, 107.3, 103.5, 96.6, 30.8, 29.5; IR (film) 3435, 1639, 1445, 1350, 1261 cm^{-1}; HRMS (ESI) calcd for $C_{38}H_{29}N_2O_2$ $[M+H]^+$ *m/z* = 545.2229; found 545.2233.



2g

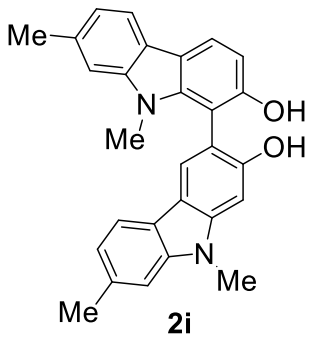
7,7'-Bis(*p*-methoxyphenyl)-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2g) [Table 2, entry 8]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 1.5 d, the *ortho-ortho'* product was obtained as white solid (11.8 mg) in 39% yield (79% based on recovered starting material): mp 181-183 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.68-7.66 (m, 2H), 7.63-7.61 (m, 2H), 7.56 (s, 1H), 7.46-7.44 (m, 2H), 7.39 (s, 1H), 7.16 (s, 1H), 7.05-7.03 (m, 3H), 7.00-6.99 (m, 2H), 5.28 (bs, 1H), 5.19 (bs, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 159.1, 154.1, 154.0, 144.2, 142.5, 142.3, 140.6, 138.7, 138.1, 134.9, 134.7, 128.7, 128.6, 123.7, 122.1, 121.8, 121.5, 120.0, 119.5, 119.2, 119.1, 117.7, 117.5, 114.4, 114.3, 110.1, 108.3, 106.9, 106.8, 103.5, 95.5, 55.6, 55.5, 30.8, 29.5; IR (film) 3433, 1640, 1519, 1440, 1350, 1241, 1178, 1038 cm^{-1}; HRMS (ESI) calcd for $C_{40}H_{33}N_2O_4$ $[M+H]^+$ *m/z* = 605.2440; found 605.2440.



2h

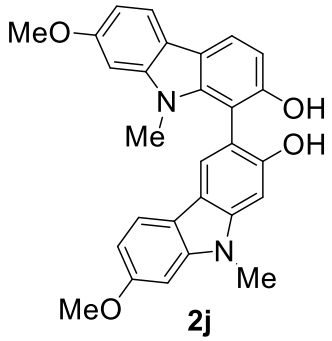
7,7'-Bis(trimethylsilyl)-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2h) [Table 2, entry 9 and 10]. Following the general procedure, using catalyst **V5** (10 mol%) in chloroform at 40 °C for 2 d, the *ortho-ortho'* product was obtained as white solid (20.7 mg) in 77% yield. Catalyst **V5** (10 mol%) in chloroform at 40 °C under nitrogen for 2 d, the *ortho-ortho'* product was obtained as white solid (12.9 mg) in 48% yield: mp 208-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 8.06 (s, 1H), 8.03 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.58 (s, 1H), 7.43-7.40 (m, 3H), 7.15 (s, 1H), 7.01 (d, J = 8.5 Hz, 1H), 5.29 (bs, 1H), 5.19 (bs, 1H), 3.92 (s, 3H), 3.27 (s, 3H), 0.40 (s, 9H), 0.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 154.2, 143.8, 141.6, 141.3, 140.3, 137.4, 136.5, 124.5, 124.4, 123.9, 123.6, 123.3, 122.3, 119.2, 118.7, 117.7, 117.5, 113.3, 113.2, 110.0, 108.1, 103.4, 95.4, 30.6, 29.4, -0.6 (2C); IR (film) 3436, 2953, 1636, 1591, 1443,

1346, 1258, 1246, 835, 753 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{37}N_2O_2Si_2$ $[M+H]^+$ *m/z* = 537.2394; found 537.2397.



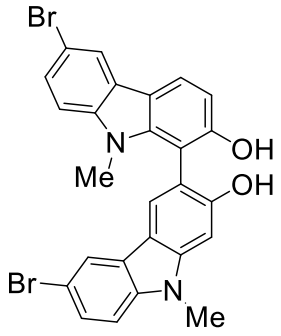
2i

7,7'-Dibromo-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2i) [Table 2, entry 11]. Following the general procedure, using catalyst **V5** (10 mol%) in chloroform at 40 °C for 2 d, the *ortho-ortho'* product was obtained as white solid (14.5 mg) in 69% yield: mp 228-230 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 5.23 (bs, 1H), 5.13 (bs, 1H), 3.84 (s, 3H), 3.23 (s, 3H), 2.59 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 153.6, 143.7, 142.3, 142.0, 140.2, 135.6, 134.9, 123.3, 121.7, 121.1, 120.7, 121.0, 120.4, 119.5, 119.0, 117.9, 117.7, 109.8, 109.0, 108.9, 107.9, 103.5, 95.4, 30.7, 29.4, 22.4, 22.3; IR (film) 3434, 2923, 1639, 1450, 1259, 1208, 979, 800 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}N_2O_2$ $[M+H]^+$ *m/z* = 421.1916; found 421.1924.



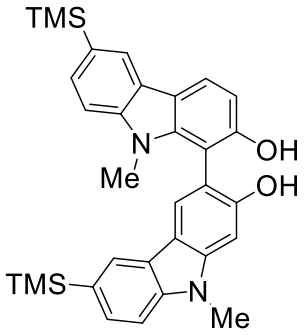
2j

7,7'-Dimethoxy-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2j) [Table 2, entry 12]. Following the general procedure, using catalyst **V5** (10 mol%) in chloroform at room temperature for 3 d, the *ortho-ortho'* product was obtained as white solid (11.5 mg) in 51% yield: mp 232-233 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.92 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.72 (s, 1H), 5.19 (bs, 1H), 5.12 (bs, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 158.5, 153.2, 153.0, 143.8, 143.2, 143.0, 140.2, 122.7, 121.1, 120.5, 120.0, 117.9, 117.7, 116.9, 116.6, 109.9, 108.0, 107.7, 107.6, 103.7, 95.5, 93.6, 93.5, 56.0, 55.9, 30.8, 29.5; IR (film) 3434, 1641, 1456, 1352, 1223, 1118, 1053 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}N_2O_4$ $[M+H]^+$ *m/z* = 453.1814; found 453.1813.



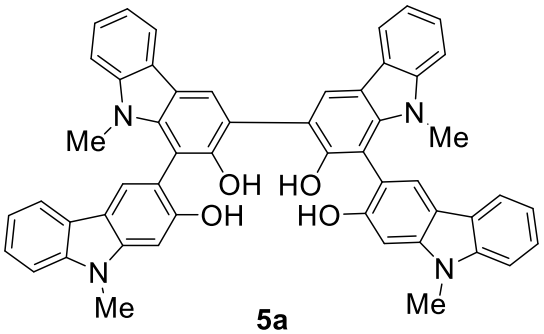
2k

6,6'-Dibromo-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2k) [Table 2, entry 13]. Following the general procedure, using catalyst **V5** (20 mol%) in chloroform at 40 °C for 2 d, the *ortho-ortho'* product was obtained as white solid (11.3 mg) in 41% yield (76% based on recovered starting material): mp 220-222 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.06 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.99 (s, 1H), 7.54 (dd, J = 8.5, 2.0 Hz, 1H), 7.46 (dd, J = 6.5, 2.0 Hz, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.14 (s, 1H), 7.13 (d, J = 7.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 5.21 (bs, 1H), 5.16 (bs, 1H), 3.86 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 154.5, 144.0, 140.6, 140.5, 140.3, 128.1, 127.5, 124.7, 124.5, 124.0, 122.6, 122.5, 122.1, 116.8, 116.6, 112.6, 112.5, 110.4, 110.2, 110.1, 108.8, 103.3, 95.7, 31.0, 29.6; IR (film) 3435, 1638, 1461, 1362, 1278, 1247, 1012, 974 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{19}N_2O_2Br_2$ $[M+H]^+$ m/z = 548.9813; found 548.9821.



2l

6,6'-Bis(trimethylsilyl)-9,9'-dimethyl-[1,3'-bicarbazole]-2,2'-diol (2l) [Table 2, entry 14]. Bollowing the general procedure, using catalyst **V5** (10 mol%) in chloroform at 40 °C for 2 d, the *ortho-ortho'* product was obtained as white solid (20.4 mg) in 76% yield: mp 200-202 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.15 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 8.11 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.5 Hz, 1H), 7.14 (s, 1H), 7.03 (d, J = 8.5 Hz, 1H), 5.24 (bs, 1H), 5.12 (bs, 1H), 3.88 (s, 3H), 3.26 (s, 3H), 0.37 (s, 9H), 0.33 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 154.0, 143.7, 142.5, 142.2, 140.2, 130.4, 130.2, 129.9, 129.7, 124.9, 124.4, 123.7, 122.8, 122.6, 122.1, 117.7, 117.5, 110.1, 108.4, 108.3, 108.2, 103.4, 95.4, 30.7, 29.4, –0.45, –0.53; IR (film) 3434, 2952, 1638, 1455, 1364, 1246, 1094, 980, 834 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{37}N_2O_2Si_2$ $[M+H]^+$ m/z = 537.2394; found 537.2395.



5a

9,9',9'',9'''-Tetramethyl-[3,1':3',3'':1'',3'''-quatercarbazole]-2,2',2'',2'''-tetraol (5a) [Table 1, entry 6]. Following the general procedure, using catalyst **V6** (10 mol%) in chloroform at room temperature 22 h, as a 1.3:1 mixture of diastereomers in the form of a light yellow solid (5.8 mg) in 30% yield: major diastereomer ^{1}H NMR (500 MHz, acetone-d_6) δ 8.16 (s, 2H), 8.15 (d, J = 8.0 Hz, 2H), 8.05 (s, 2H), 8.03 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.39-7.36 (m, 6H), 7.24-7.19 (m, 2H), 7.16-7.13 (m, 2H), 7.11 (s, 2H), 3.89 (s, 6H), 3.33 (s, 6H); minor diastereomer δ 8.16 (s, 2H), 8.13 (d, J = 7.5 Hz, 2H), 8.08 (s, 2H), 8.04 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.39-7.36 (m, 6H), 7.24-7.19 (m, 2H), 7.16-7.13 (m, 2H), 7.12 (s, 2H), 3.88 (s, 6H), 3.34 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.9, 155.8, 152.4, 152.2, 142.4, 142.3, 141.5, 141.4, 140.8, 140.1, 140.0, 124.3, 124.1, 122.7, 122.3, 122.1, 119.8, 119.5, 119.3, 119.1, 119.0, 118.8, 118.7, 116.2, 116.1, 114.8, 114.5, 109.2, 108.9, 108.6, 94.8, 30.5, 30.4, 29.1, 29.0; IR (film) 3496, 3050, 2934, 1636, 1603, 1578, 1482, 1454, 1403, 1321, 1254, 1205, 1115, 983, 967, 780, 743 cm^{-1}; HRMS (ESI) calcd for $C_{52}H_{37}N_4O_4$ $[M\text{-}H]^-$ m/z = 781.2815; found 781.2821.

Measurement of Atropisomerization Barrier for 2a. The two enantiomers of 2a were separated by CSP HPLC (IA, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R = 31.54 and 44.16 min. Isolated peaks were reinjected and analyzed after given time intervals at 18 °C (**Figure S1**). Conversion of the rate constant into ΔG_{atrop} and half lives was accomplished via equations S1 and S2.

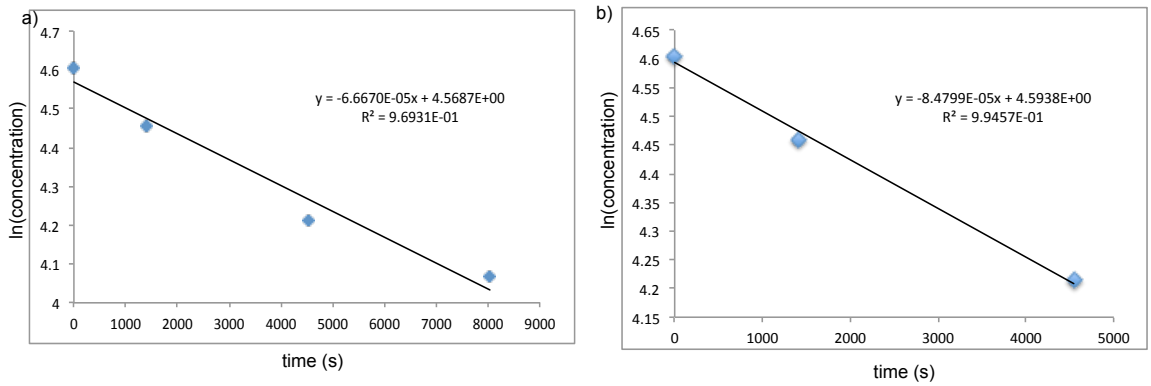
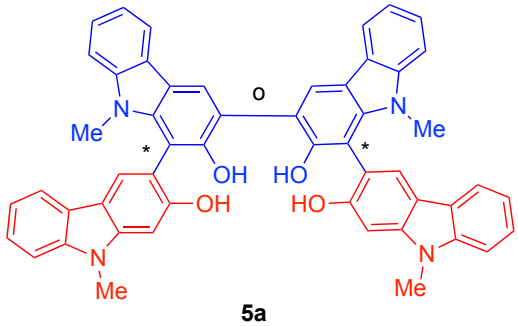


Figure S1. Plots of ln(concentration) vs time for atropisomerization of **2a**. a) all points ΔG_{atrop} = 22.6 kcal/mol, $t_{1/2}$ = 2.9 h. b) initial points (before back reaction becomes relevant) ΔG_{atrop} = 22.4 kcal/mol, $t_{1/2}$ = 2.3 h.

$$\Delta G^{\ddagger} = -RT\left(\ln\frac{(k^{*}h)}{T^{*}k_{B}}\right) \qquad \text{(S1)}$$

$$t_{1/2} = \ln 2/k \qquad \text{(S2)}$$

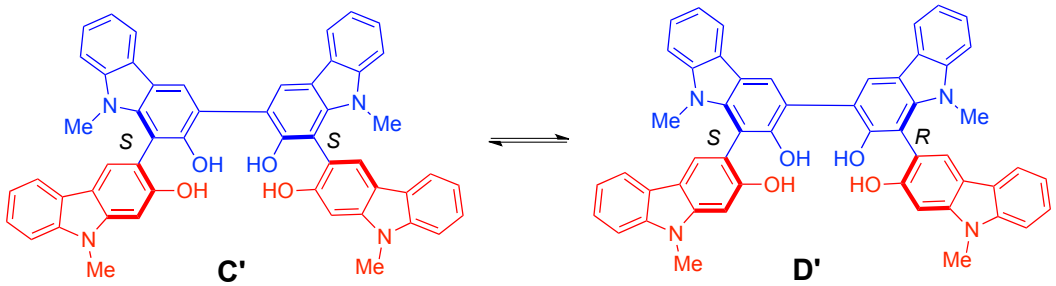
Calculations of Atropisomerization Barrier for 5a. In theory, compound **5a** can exist as three diastereomers arising from rotation about the axial chiral C-C bonds i.e., about the C-C (°) and C-C (*) bonds. In effort to gain insight into the stability of the stereoaxis of the potential diastereomers of the tetramer **5a**, energy scans were performed about the rotatable C-C bonds with Gaussian[8] using B3LYP/6-31G(d) in the gas phase.



5a

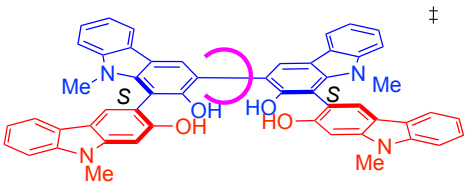
Calculations show no energetic preferences between the diasteromers about the central C-C-C(°) bond with the enthalpic and free energy differences being within 0.2 kcal/mol. Further, the computed barrier for the interconversion is extremely low and facile at room temperature i.e., 12-13 kcal/mol (**Figure S2**). This result implies at room temperature rotation about the middle C-C(°) bond is rapid.

Further energy scans about the rotatable C-C(*) bonds gave rise to larger barriers oning to the greater sterics arising from the N-Me and C-OH bonds. Calculations showed that the axial rotation in which the C-OH and N-Me bonds are passing through each other is high (ca. 55 kcal/mol). However, a much smaller barrier (22-23 kcal/mol) barrier was observed for the C-OH/C-OH passing each other (**Figure S3**). This result implies that the isomers **C'** and **D'** will equilibribrate slowly at room temperature with a half-life around one hour.

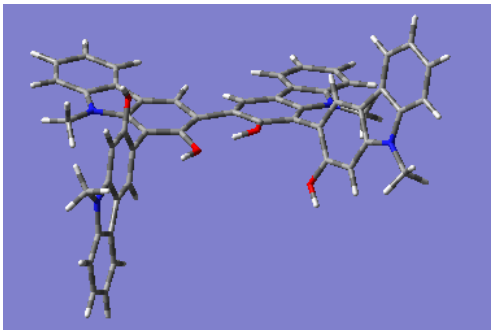


ΔH (0.0)
ΔG 0.0

(0.05)
-0.12



C'-D'-TS



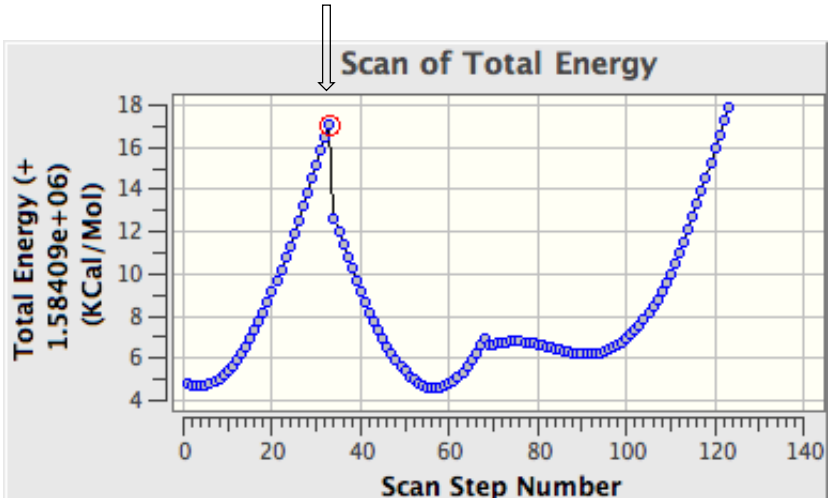
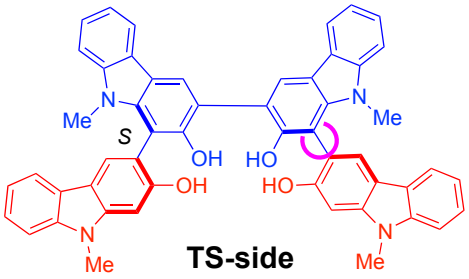
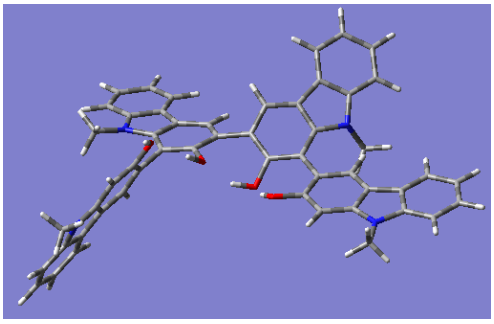


Figure S2: Scan of rotation about the middle bond of **5a**.



TS-side

$\Delta\Delta G^{\ddagger}$ **= 22-23 kcal/mol**



D'

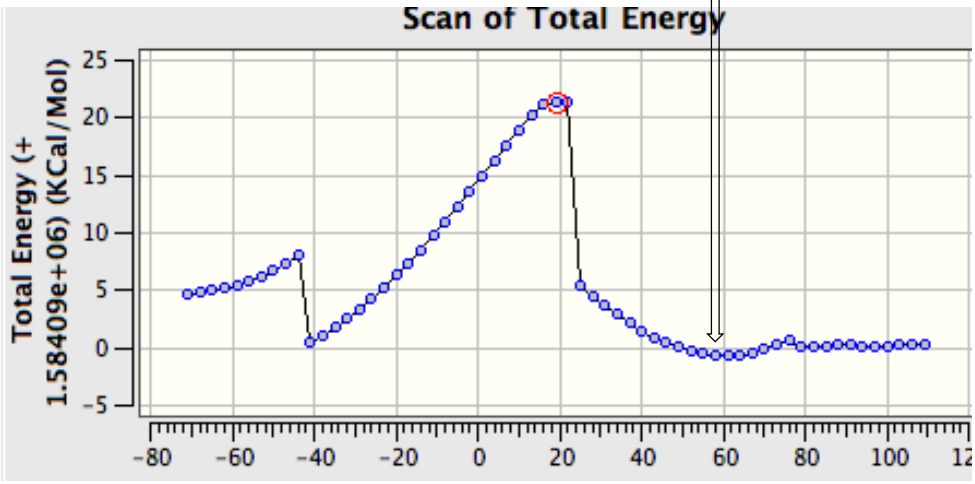


Figure S3: Scan of rotation about the side bond of **5a**.

Coordinates:

C’

C	-7.88461600	3.10609000	9.27121300
C	-6.79159900	3.78516900	9.83419400
C	-5.78972200	4.33608900	9.03591900
C	-5.91081200	4.19510500	7.65176000
C	-7.00505400	3.50495700	7.06679200
C	-7.99670200	2.96192100	7.89035900
H	-8.64844100	2.68835300	9.92062800
H	-6.72033700	3.88202600	10.91405600
H	-4.94527100	4.84963600	9.48563700
H	-8.84341800	2.43476800	7.45855900
C	-5.58714100	4.25177000	5.41866200
C	-5.09759700	4.46741200	4.12869400
C	-5.83442700	3.95728100	3.06167500
C	-7.03601000	3.22906500	3.22672200
C	-7.50361300	3.04875500	4.53638700
C	-6.79565000	3.53970300	5.63341400
H	-4.17493100	5.01365700	3.94753300
H	-8.43836900	2.51523200	4.68249100
N	-5.06994700	4.65652500	6.63790400
C	-3.82856900	5.37360300	6.83082100
H	-3.66956600	6.06666700	5.99951400
H	-3.88643400	5.96350400	7.74887900
H	-2.96501700	4.69844500	6.89915600
C	-10.35472600	-2.74478100	1.34076400
C	-9.47341500	-3.10308100	2.37395200
C	-8.60111300	-2.17275500	2.93851400
C	-8.62906000	-0.86705700	2.44070100
C	-9.51175800	-0.49112600	1.39820900
C	-10.37809800	-1.44161200	0.84867500
H	-11.02538500	-3.49113000	0.92438100
H	-9.47301200	-4.12350300	2.74784800
H	-7.93645400	-2.45997400	3.74774300
H	-11.06137300	-1.16688300	0.04916900
C	-8.25739800	1.33347200	2.04549400
C	-7.83207900	2.67917600	2.08755300
C	-8.34292000	3.52008700	1.07639600
C	-9.32060900	3.12137200	0.13412600
C	-9.79084900	1.80587200	0.21018500
C	-9.25979200	0.90886500	1.13428400
H	-10.57170800	1.48699400	-0.47373800
N	-7.86584700	0.23727900	2.82039000
C	-6.67952800	0.12497000	3.65146700

H	-6.28602400	-0.89180200	3.56589600
H	-5.91389400	0.81928200	3.30249600
H	-6.88287500	0.33859600	4.70741500
C	-9.01873900	12.83862100	-0.09884500
C	-10.08533800	13.69246400	0.22481200
C	-11.40582100	13.24285100	0.20119600
C	-11.63546900	11.91382200	-0.16056900
C	-10.56716000	11.03356400	-0.48331100
C	-9.25290500	11.51092000	-0.45206800
H	-8.00090600	13.21768800	-0.07054100
H	-9.88177600	14.72298500	0.50340500
H	-12.22085400	13.91102300	0.46377100
H	-8.42385500	10.85209300	-0.69772200
C	-12.56649700	9.91081500	-0.63642900
C	-13.44794500	8.84818000	-0.84719000
C	-12.90860000	7.61511500	-1.21943500
C	-11.51593300	7.42166400	-1.39288400
C	-10.66272300	8.50153800	-1.16259800
C	-11.16643100	9.75066600	-0.78810900
H	-14.52206100	8.95909500	-0.71679000
H	-9.59246300	8.35062500	-1.27230900
N	-12.84105900	11.22377800	-0.27809700
C	-14.15039900	11.75433300	0.02673700
H	-14.89873100	11.27993200	-0.61507400
H	-14.43259800	11.59163200	1.07602400
H	-14.16774200	12.82791300	-0.17833400
C	-10.77481300	2.86847500	-6.84592400
C	-11.43765200	3.98977000	-7.37050300
C	-11.74562200	5.09052400	-6.57106600
C	-11.36944400	5.04907200	-5.22506000
C	-10.70790000	3.91904300	-4.67989200
C	-10.40908800	2.82785900	-5.50201300
H	-10.54929900	2.02559400	-7.49347400
H	-11.72245100	4.00208700	-8.41939500
H	-12.27023100	5.94295700	-6.99179600
H	-9.89945900	1.95727400	-5.09634900
C	-11.03143600	5.50043600	-3.02833900
C	-10.96995100	6.07452600	-1.74418600
C	-10.35951300	5.31486400	-0.72526900
C	-9.83471100	4.00910400	-0.95109600
C	-9.90726700	3.48650500	-2.24539400
C	-10.49430600	4.20959300	-3.28038400
H	-9.49682600	2.49914100	-2.43934400
N	-11.53913600	6.00570100	-4.22669300
C	-12.19782500	7.27991200	-4.44466000
H	-11.70722200	8.06210100	-3.86570800

H	-12.12154400	7.53920800	-5.50307400
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D’

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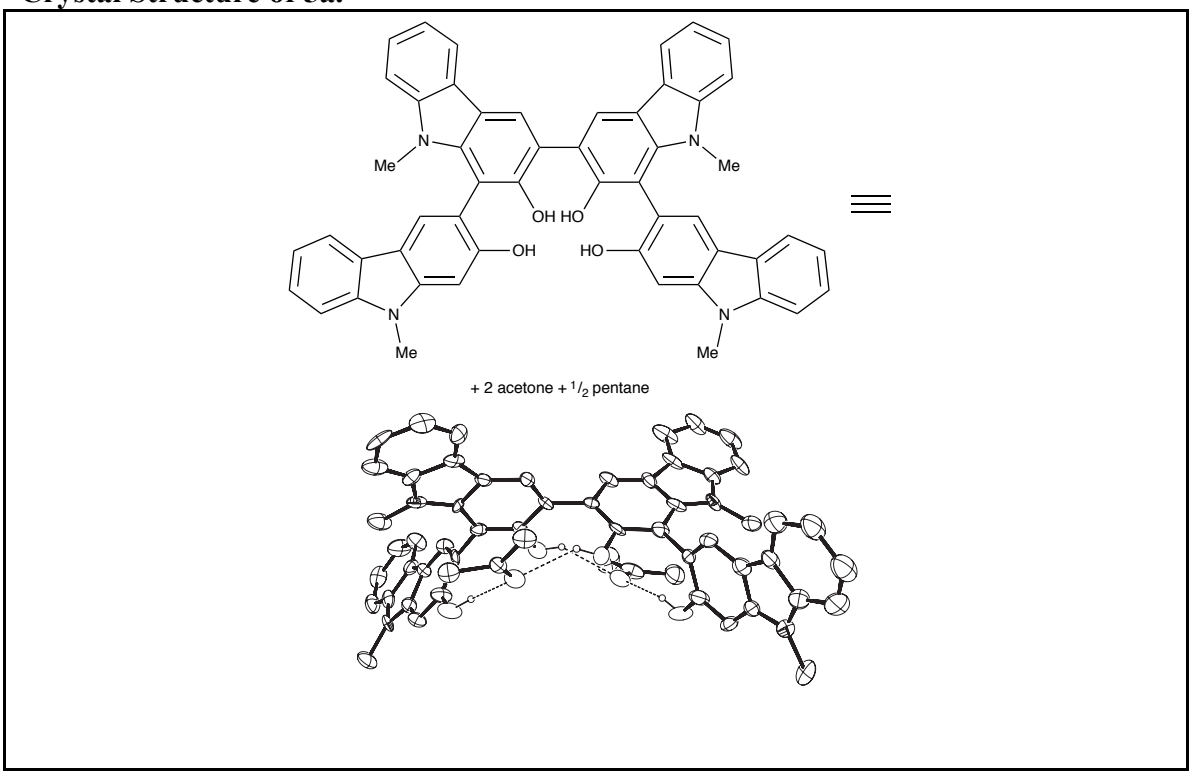
Crystal Structure of 5a.



Compound **5a**, $C_{121}H_{112}N_8O_{12}$, crystallizes in the monoclinic space group Cc (systematic absences hkl: h+k=odd) with a=16.1723(13)Å, b=24.7158(17)Å, c=24.1251(18)Å, β=90.474(3)°, V=9642.7(12)Å^3, Z=4, and d_{calc}=1.288 g/cm^3 . X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. A total of 2348 frames were collected with a crystal to detector distance of 37.4 mm, rotation widths of 0.5° and exposures of 30 seconds:

scan type	2θ	ω	ϕ	χ	frames
ϕ	-15.50	258.48	8.28	19.46	739
ϕ	-23.00	334.21	38.95	73.66	739
ϕ	-23.00	315.83	12.48	28.88	696

Rotation frames were integrated using SAINT[9], producing a listing of unaveraged F^2 and σ(F^2) values which were then passed to the SHELXTL[10] program package for further processing and structure solution. A total of 78535 reflections were measured over the ranges $1.50 \leq \theta \leq 25.55°$, $-19 \leq h \leq 19$, $-22 \leq k \leq 29$, $-29 \leq l \leq 29$ yielding 17225 unique reflections (Rint = 0.0476).

The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[11] (minimum and maximum transmission 0.6023, 0.7452).

The structure was solved by direct methods (SHELXS-97[12]). The asymmetric unit consists of two molecules of the title compound, each of which is hydrogen bonded to two acetone molecules, plus a molecule of pentane. Refinement was by full-matrix least squares based on F^2 using SHELXL-97. All reflections were used during refinement. The crystal forms a pseudo-merohedral twin in which the two components are related by a rotation of 180º about the a* axis. Refinement was performed using the twin matrix {1 0 0 0 -1 0 0 0 -1}. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0300P)^2 + 54.0191P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0732 and wR2=0.1639 for 15120 observed reflections for which $F > 4\sigma(F)$ and R1=0.0861 and wR2=0.1729 and GOF =1.053 for all 17225 unique, non-zero reflections and 1287 variables.[13] The maximum Δ/σ in the final cycle of least squares was 0.005 and the two most prominent peaks in the final difference Fourier were +0.370 and -0.379 e/Å^3. The twinning parameter refined to a value of 0.330(2).

Table S3 lists cell information, data collection parameters, and refinement data. **Figure S4** and **Figure S5** are ORTEP[14] representations of the molecule with 50% probability thermal ellipsoids displayed.

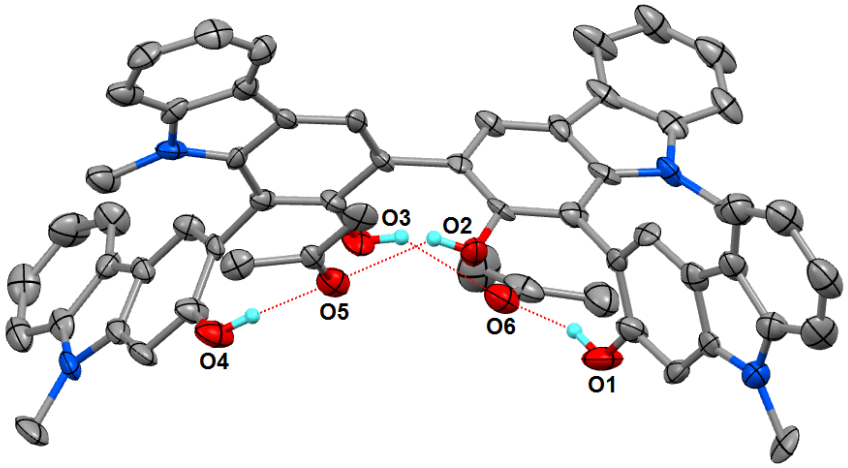


Figure S4. ORTEP drawing of molecule no. 1 of the asymmetric unit with 50% probability thermal ellipsoids.

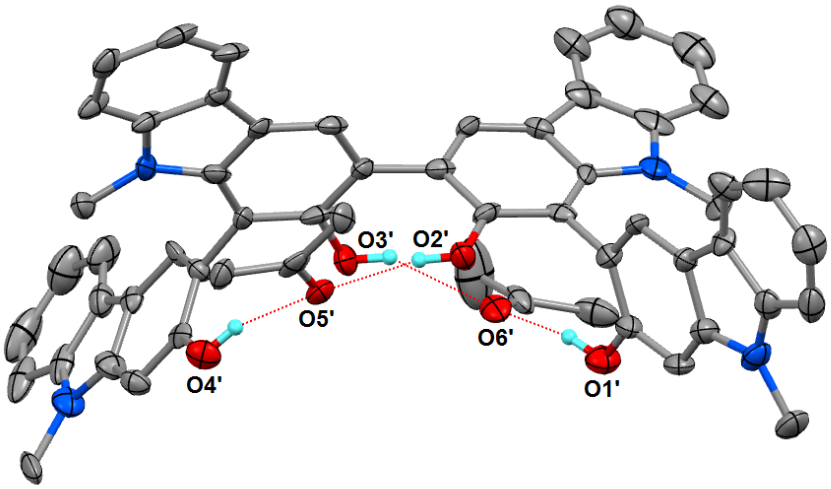
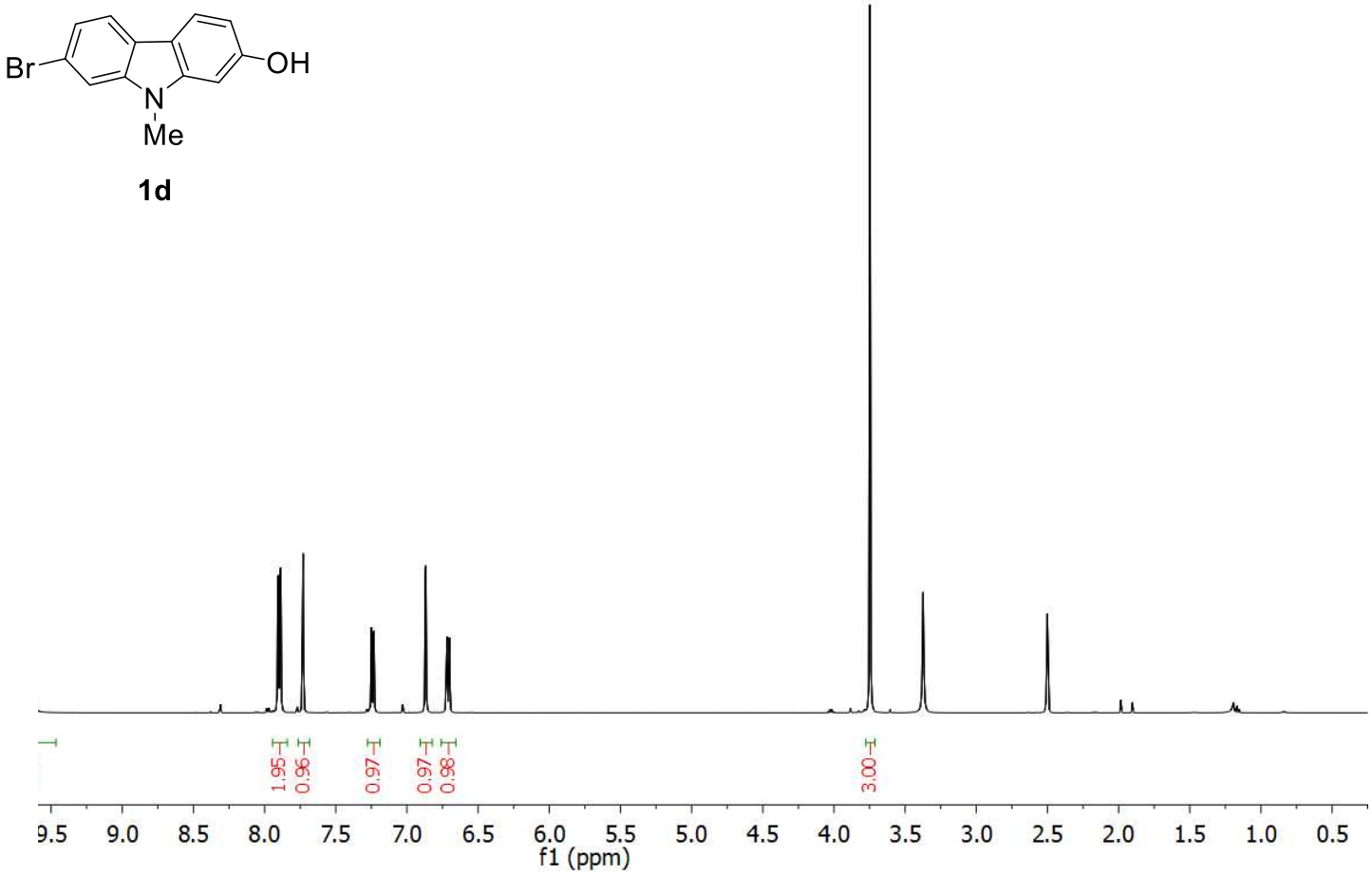


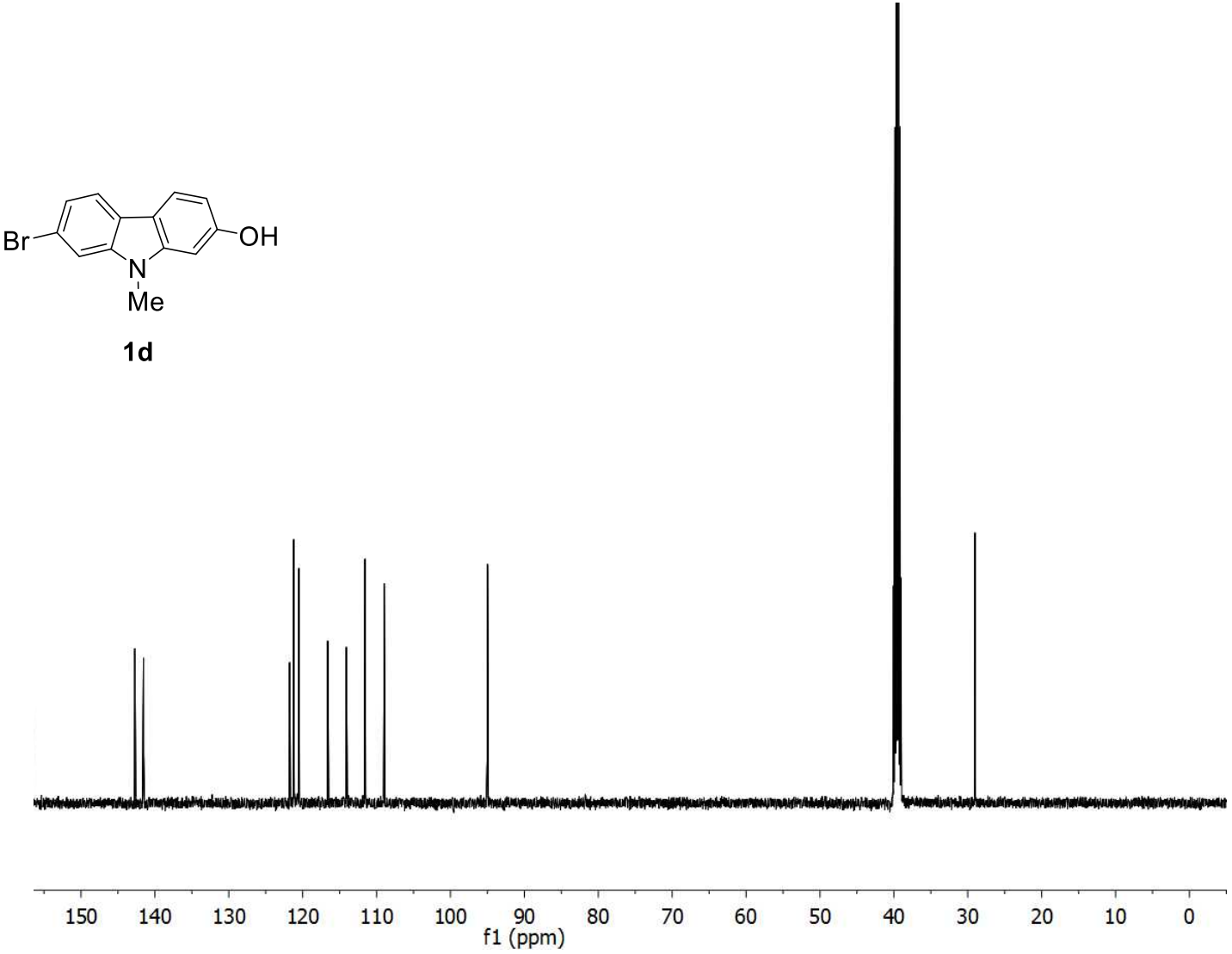
Figure S5. ORTEP drawing of molecule no. 2 of the asymmetric unit with 50% probability thermal ellipsoids.

Table S3. Summary of Structure Determination of Compound 5a

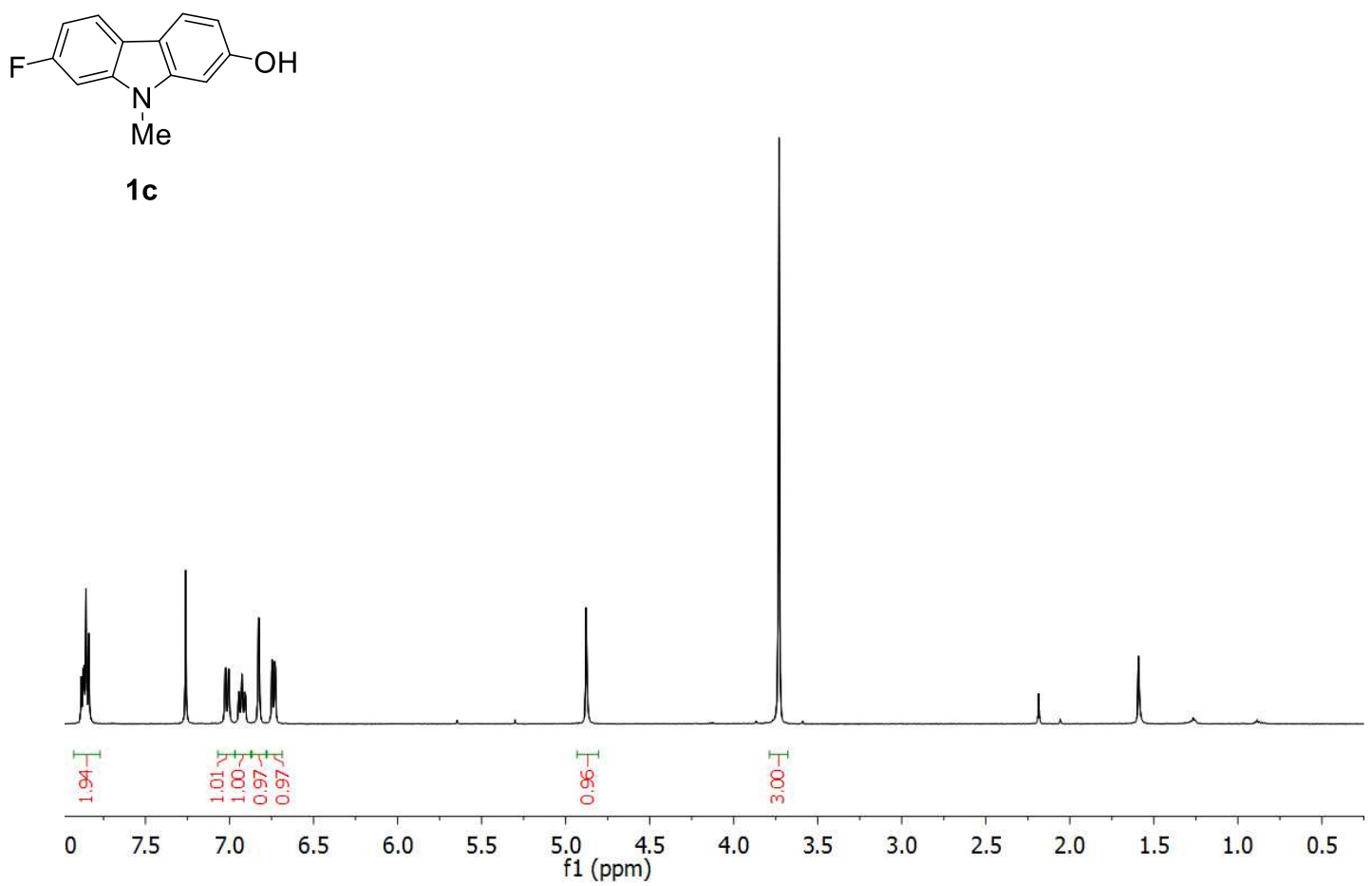
Empirical formula	$C_{121}H_{112}N_8O_{12}$
Formula weight	1870.19
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	Cc
Cell constants:	
a	16.1723(13) Å
b	24.7158(17) Å
c	24.1251(18) Å
β	90.474(3)°
Volume	9642.7(12) $Å^3$
Z	4
Density (calculated)	1.288 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	3960
Crystal size	0.35 x 0.25 x 0.08 mm^3
Theta range for data collection	1.50 to 25.55°
Index ranges	$-19 \le h \le 19$, $-22 \le k \le 29$, $-29 \le l \le 29$
Reflections collected	78535
Independent reflections	17225 [R(int) = 0.0476]
Completeness to theta = 25.55°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6023
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17225 / 33 / 1287
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0732, wR2 = 0.1639
R indices (all data)	R1 = 0.0861, wR2 = 0.1729
Absolute structure parameter	0.0(14)
Largest diff. peak and hole	0.370 and -0.379 $e.Å^{-3}$



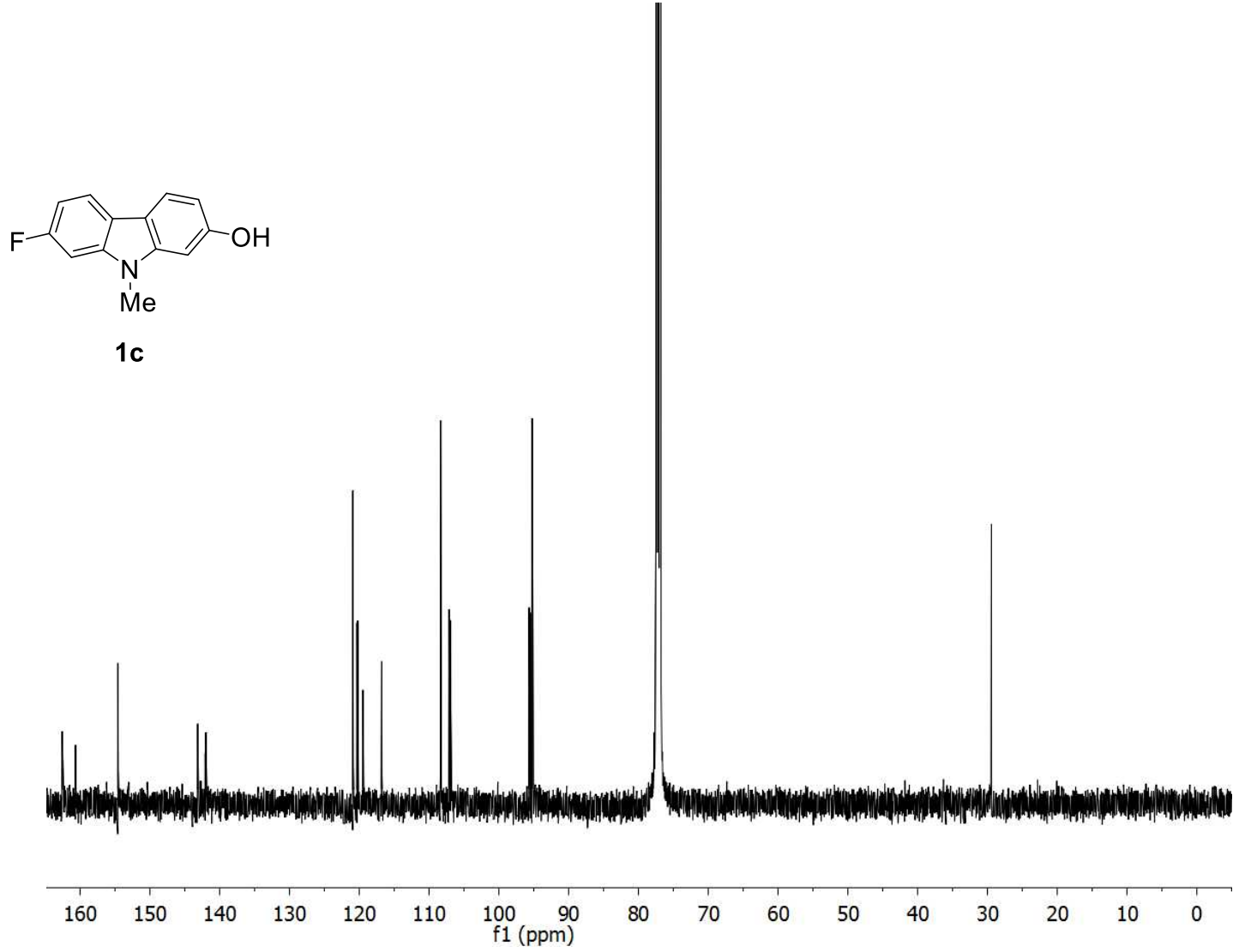
500 MHz ^{1}H NMR Spectrum of Compound **1d** in DMSO-d_6



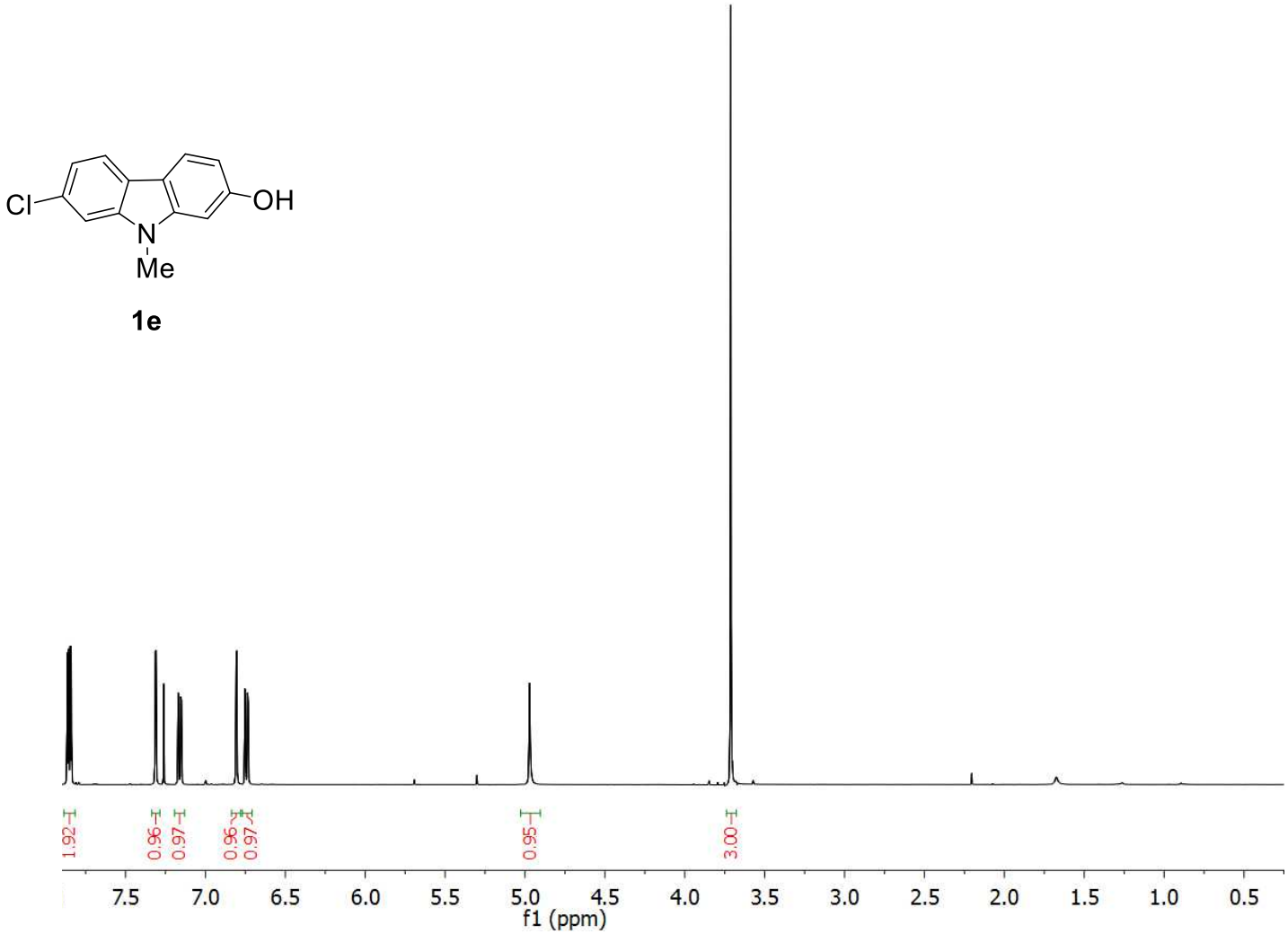
125 MHz ^{13}C NMR Spectrum of Compound **1d** in DMSO-d_6



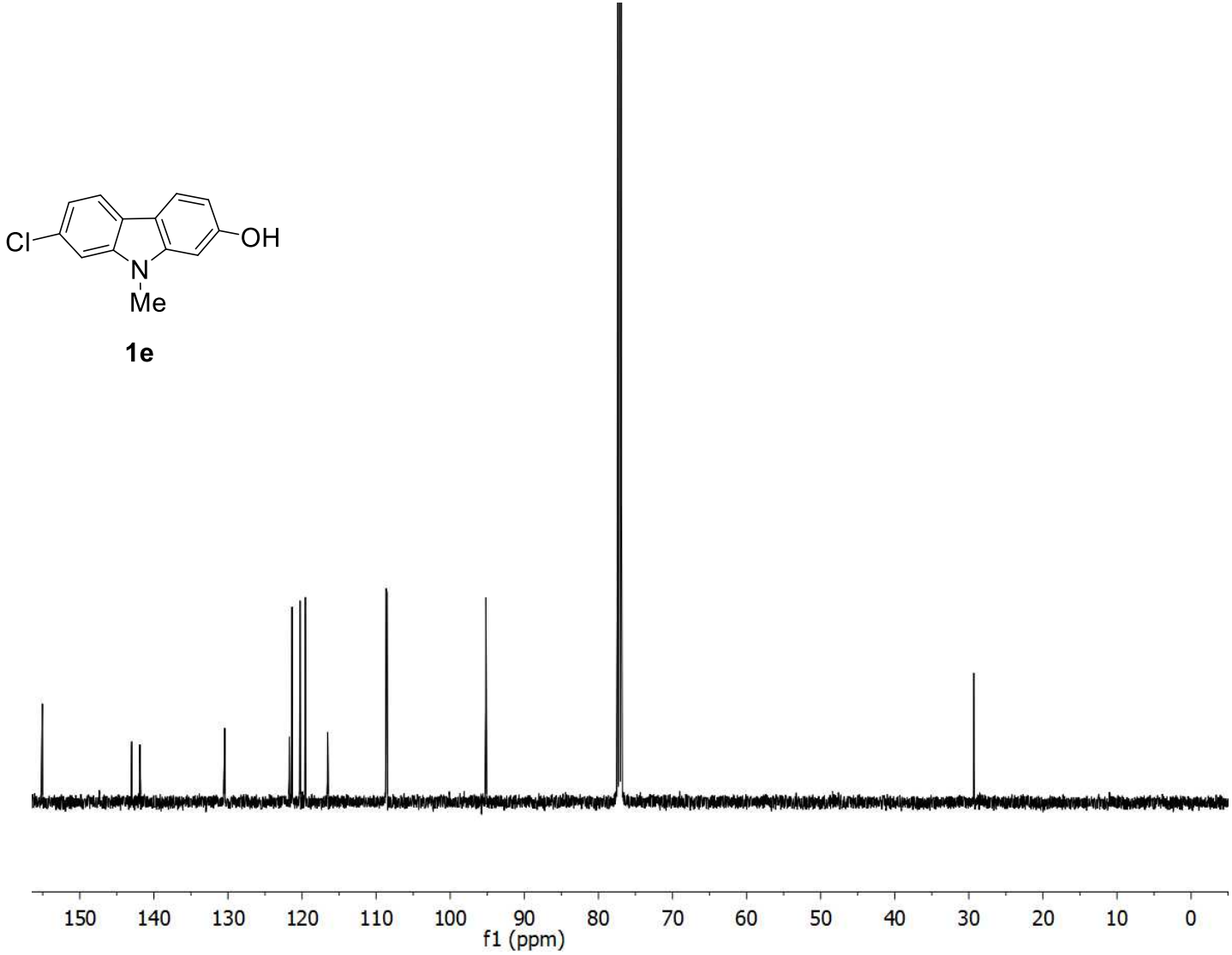
500 MHz ^{1}H NMR Spectrum of Compound **1c** in $CDCl_3$



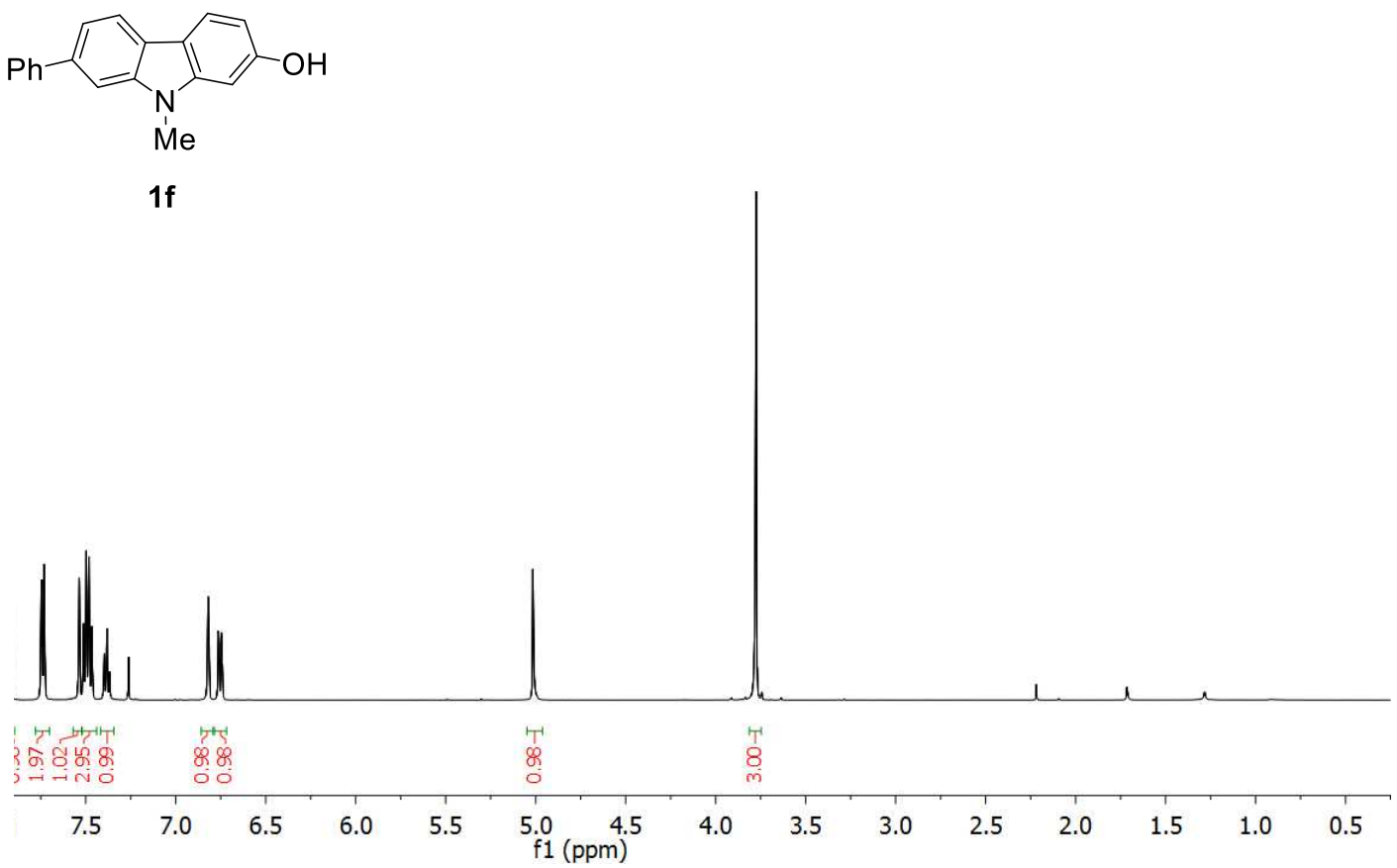
125 MHz ^{13}C NMR Spectrum of Compound **1c** in $CDCl_3$



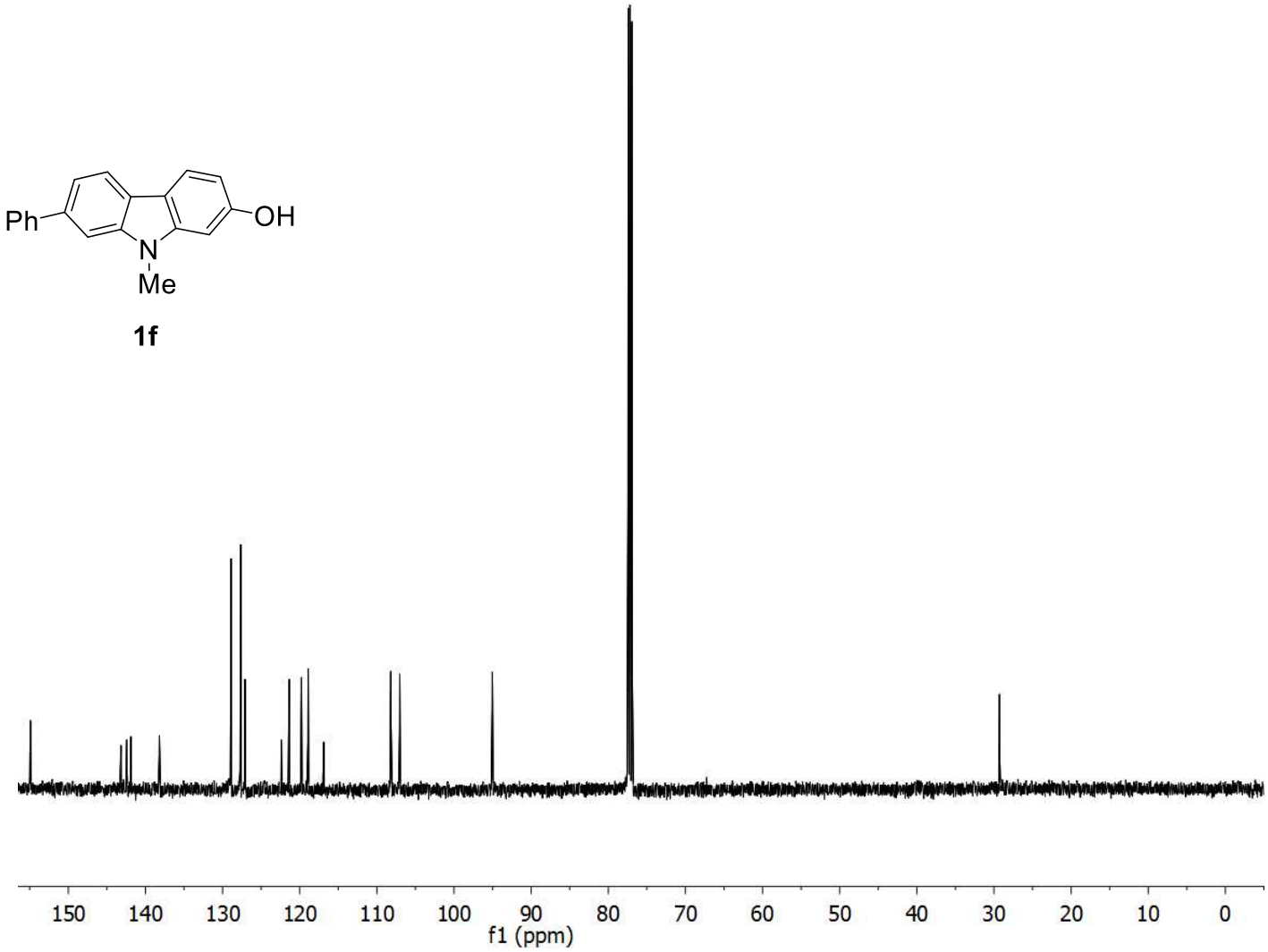
500 MHz ^{1}H NMR Spectrum of Compound **1e** in $CDCl_3$



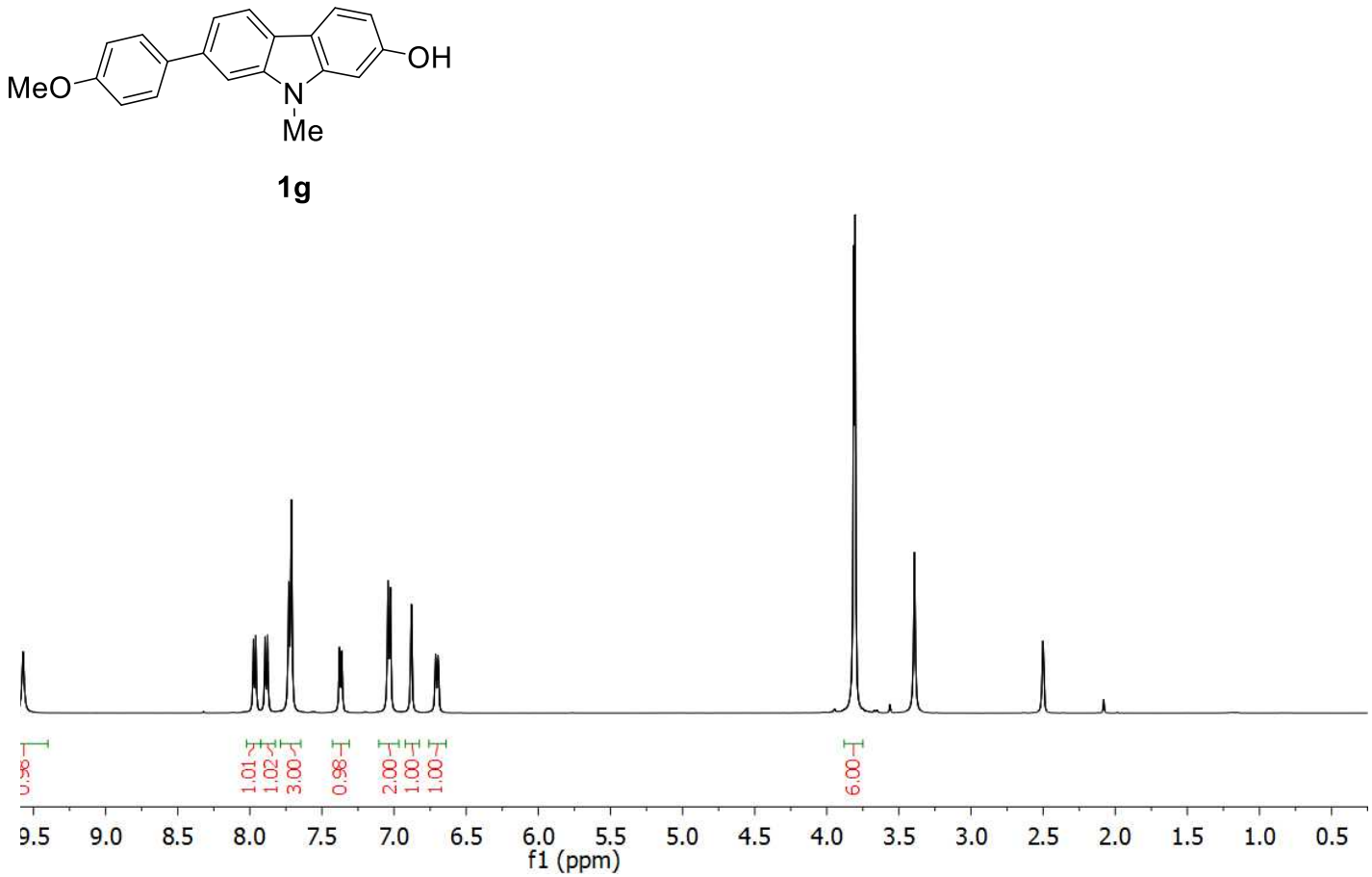
125 MHz ^{13}C NMR Spectrum of Compound **1e** in $CDCl_3$



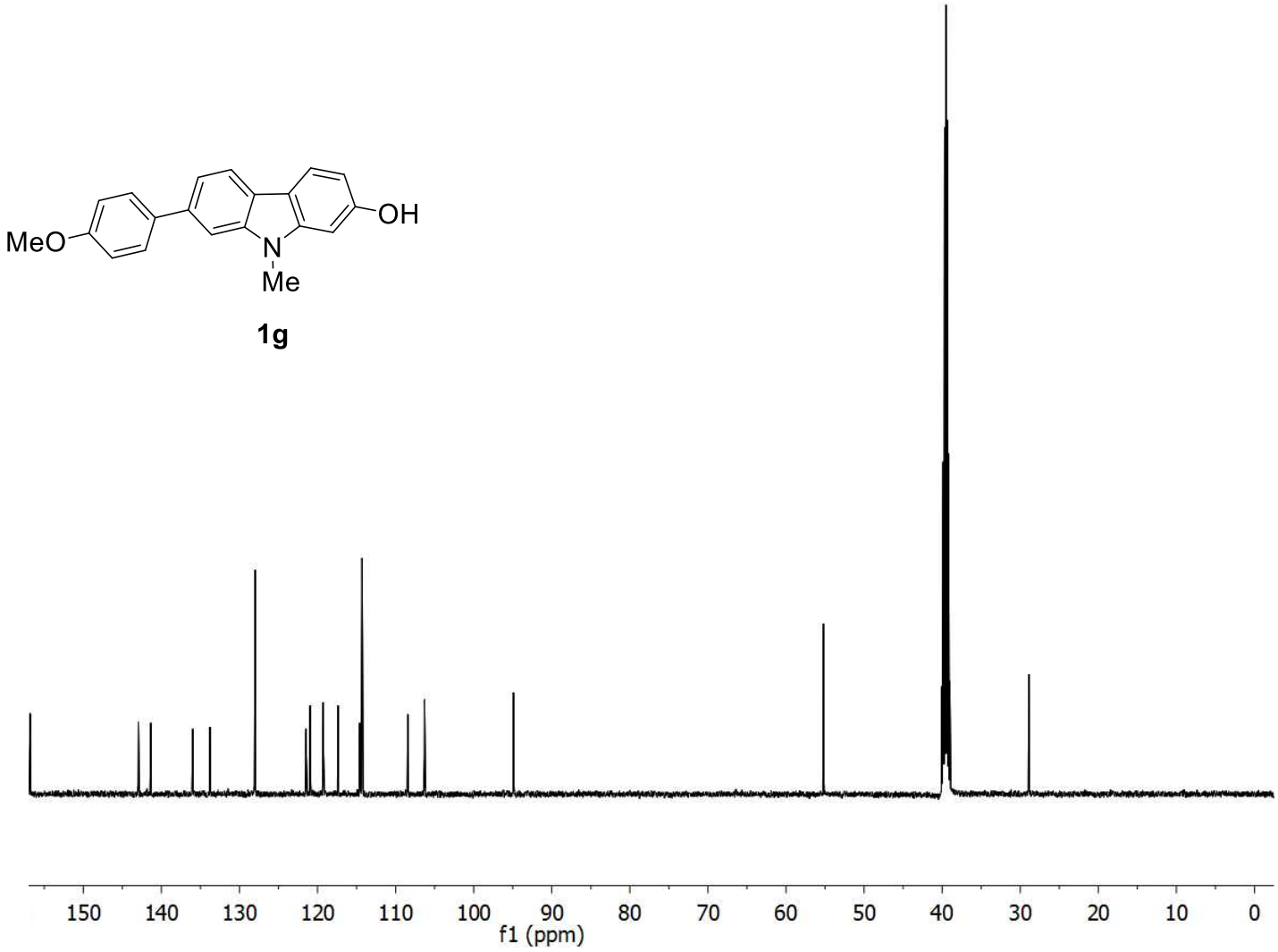
500 MHz ^{1}H NMR Spectrum of Compound **1f** in $CDCl_3$



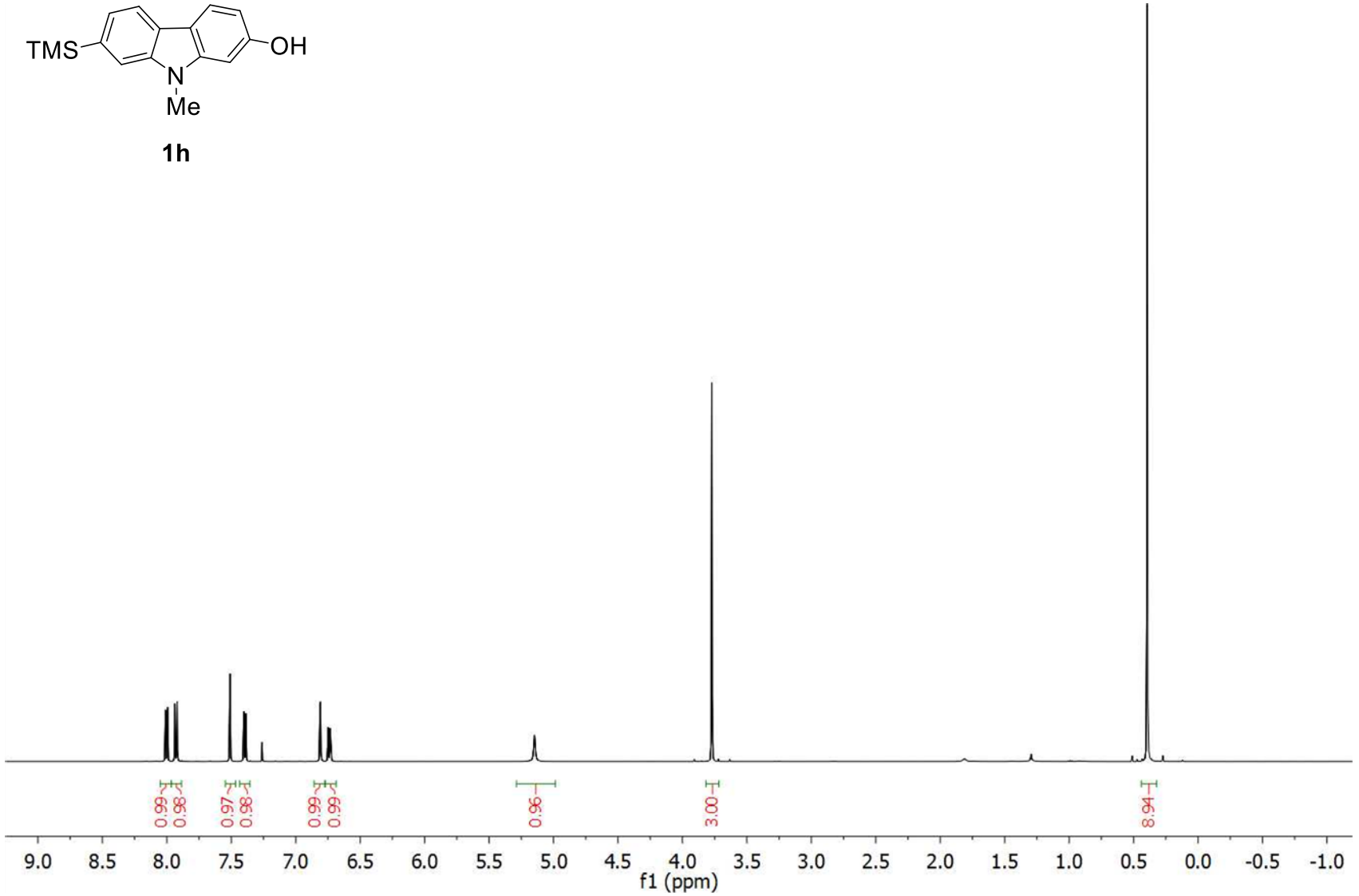
125 MHz ^{13}C NMR Spectrum of Compound **1f** in $CDCl_3$



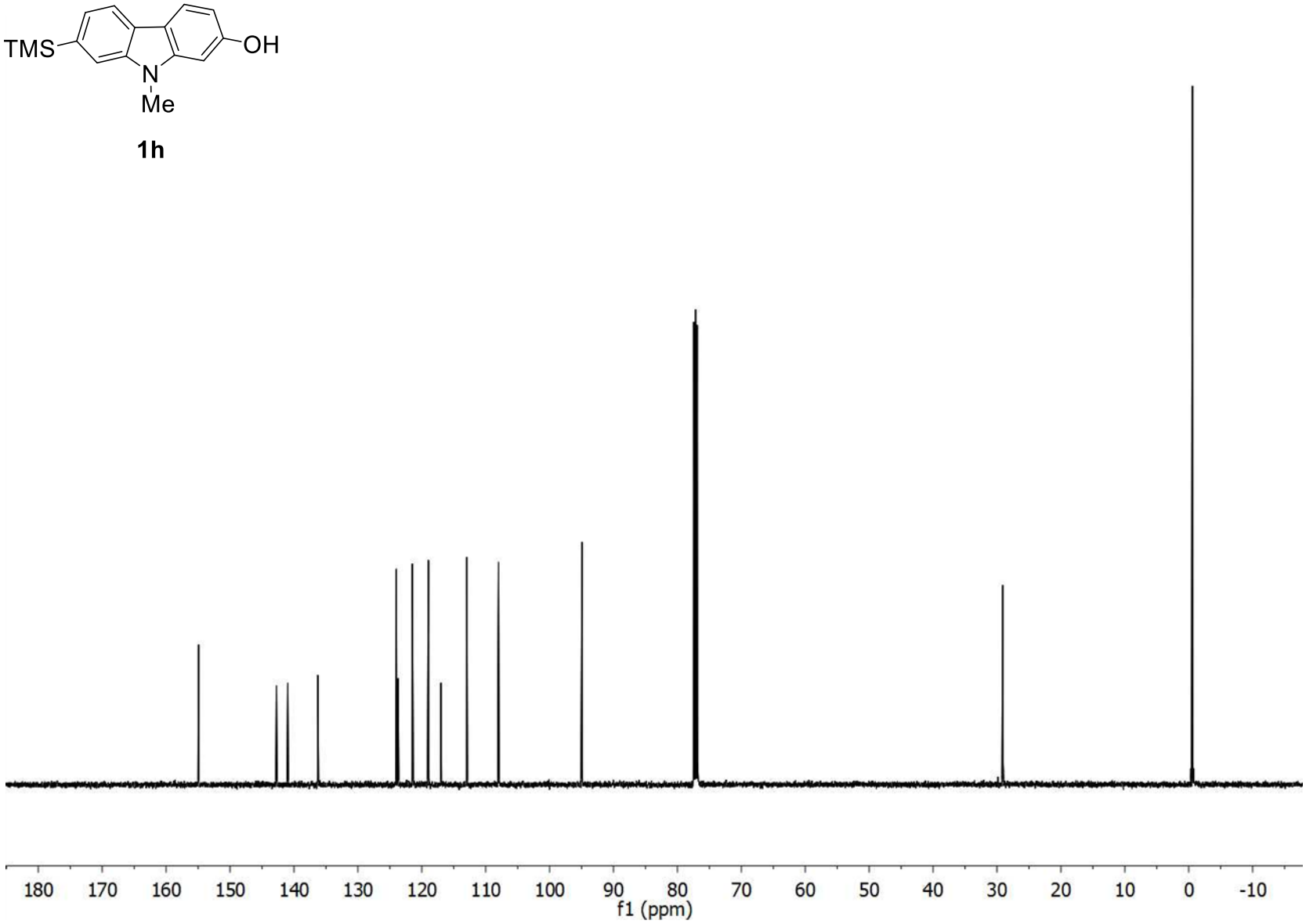
500 MHz ^{1}H NMR Spectrum of Compound **1g** in DMSO-d_6



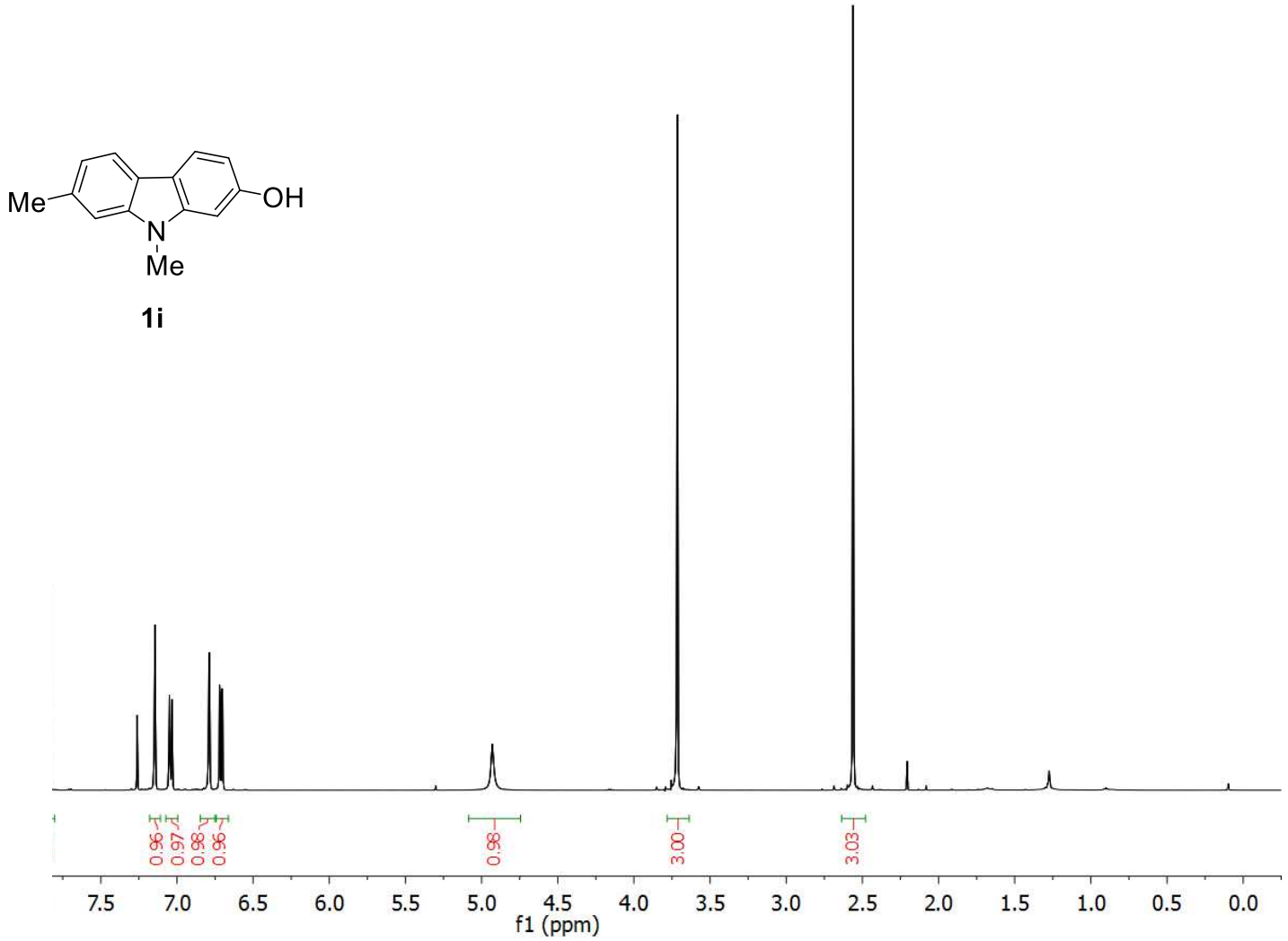
125 MHz ^{13}C NMR Spectrum of Compound **1g** in DMSO-d_6



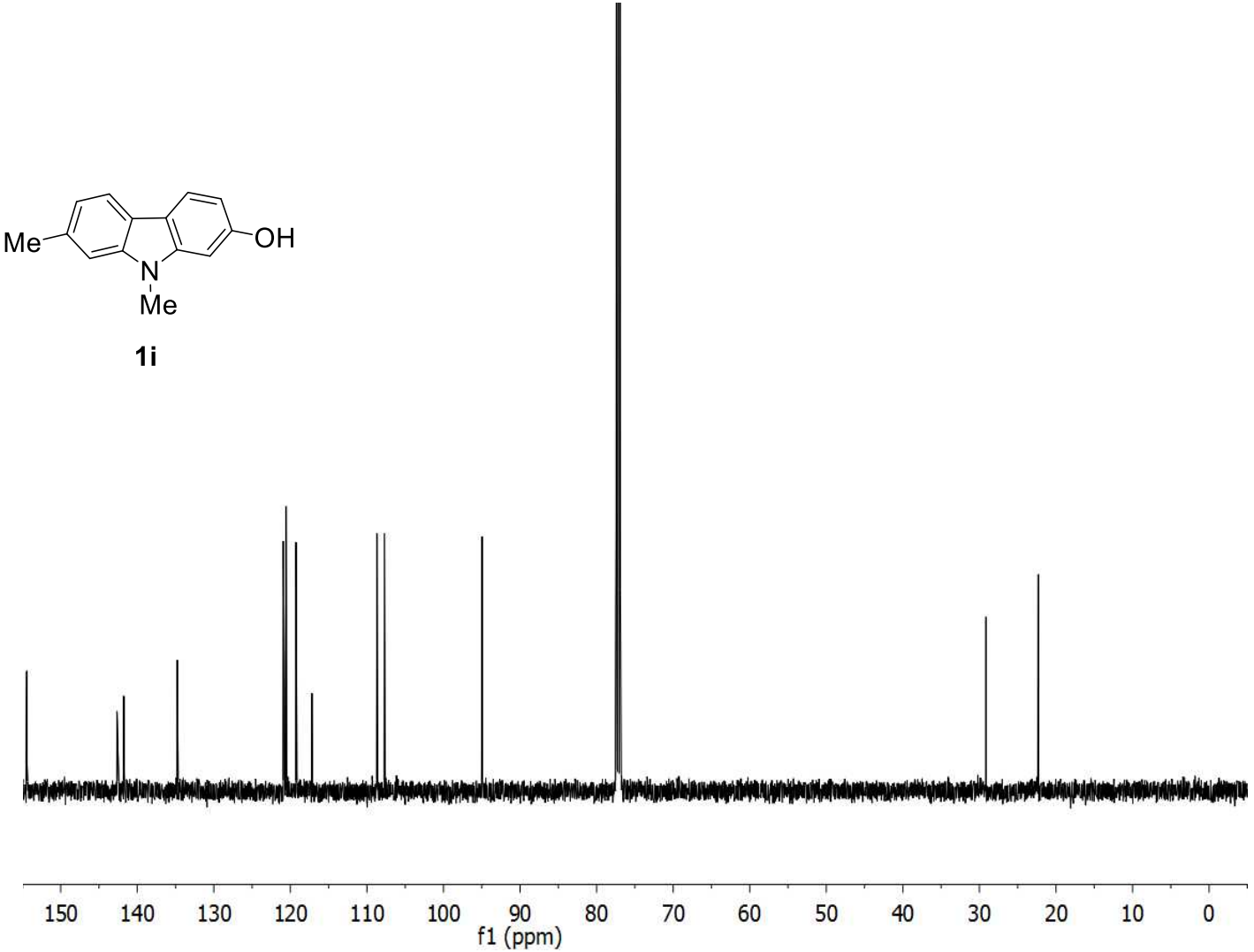
500 MHz ^{1}H NMR Spectrum of Compound **1h** in $CDCl_3$



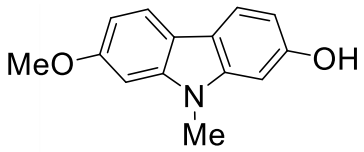
125 MHz ^{13}C NMR Spectrum of Compound **1h** in $CDCl_3$



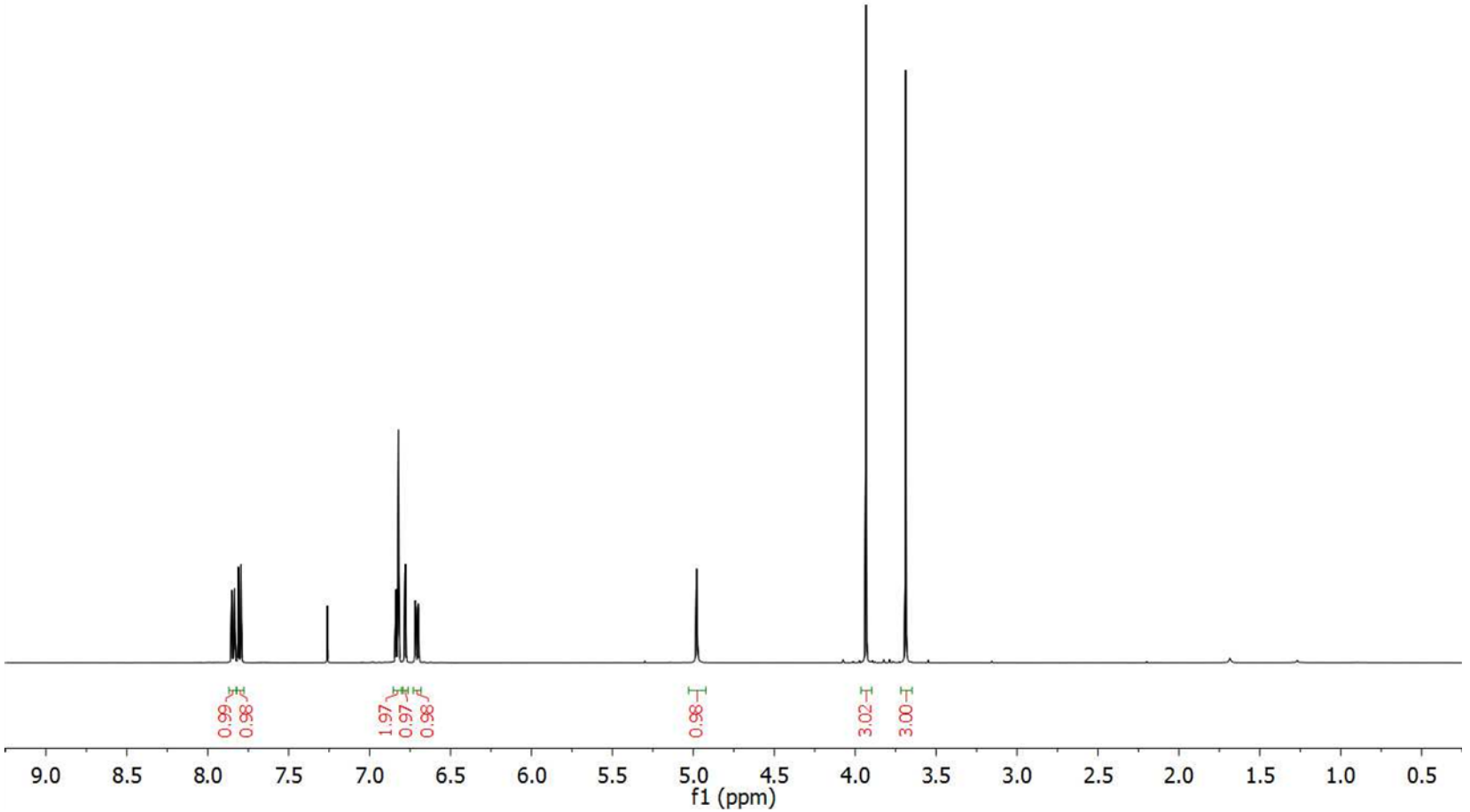
500 MHz ^{1}H NMR Spectrum of Compound **1i** in $CDCl_3$



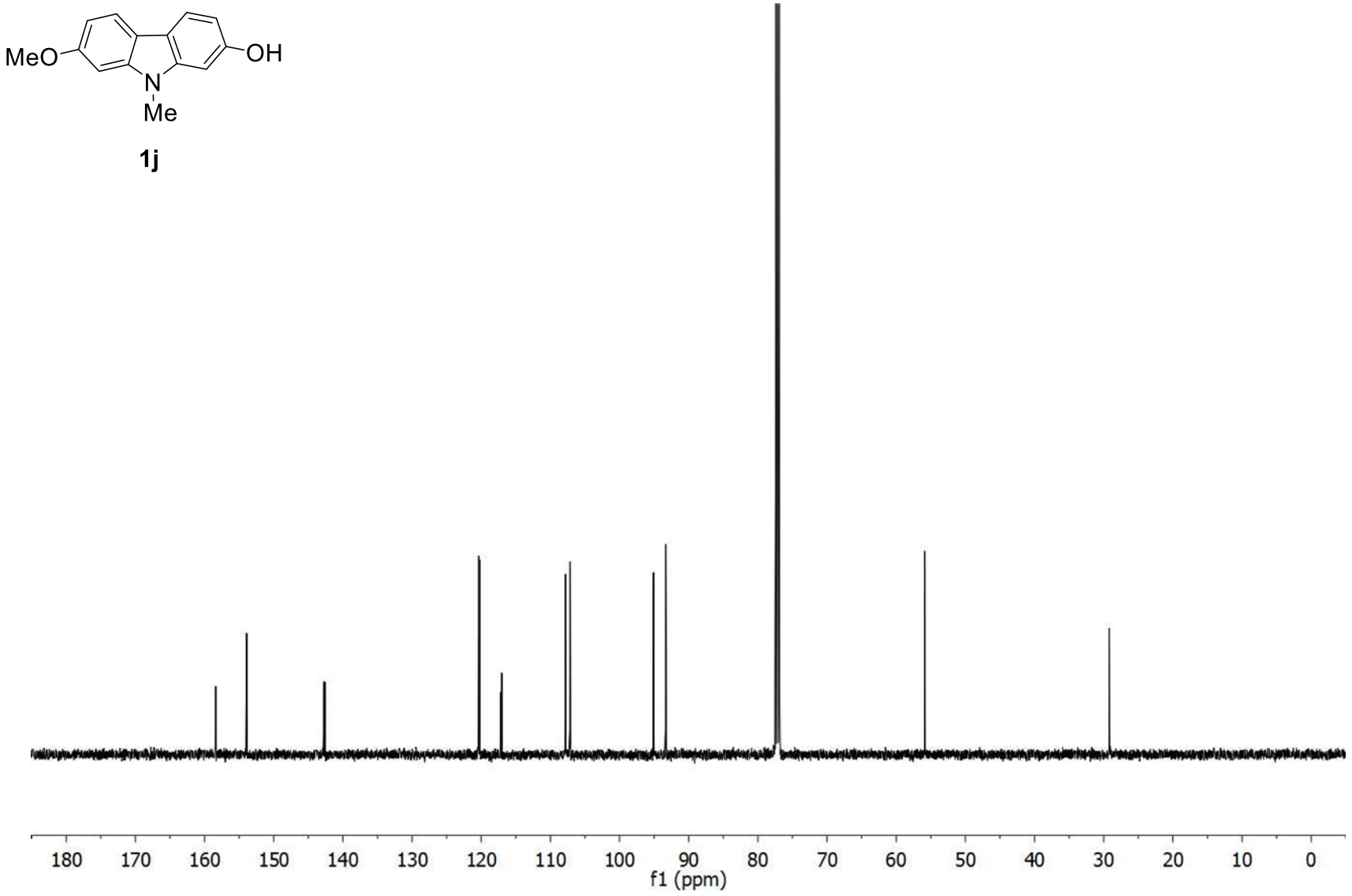
125 MHz ^{13}C NMR Spectrum of Compound **1i** in $CDCl_3$



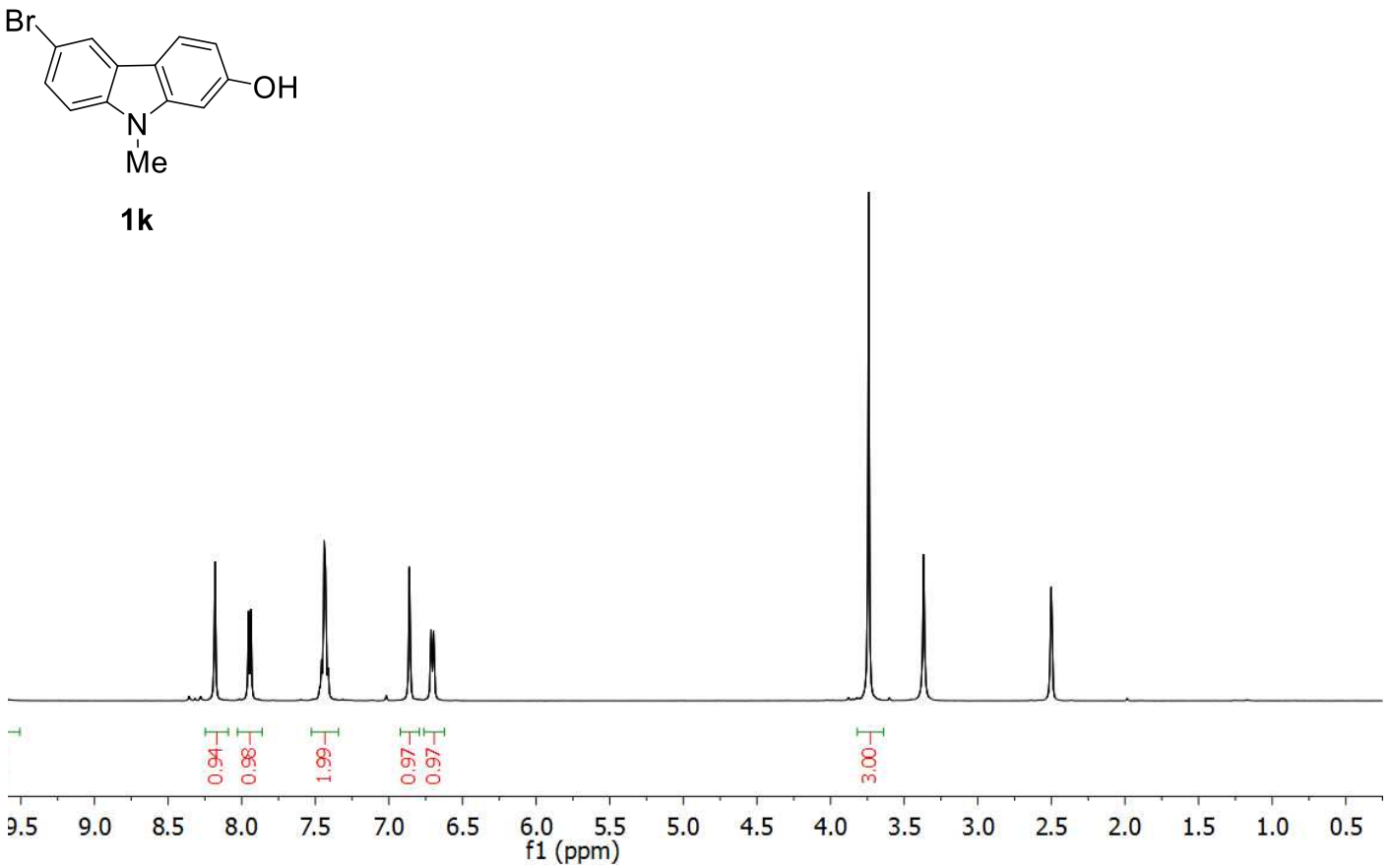
1j



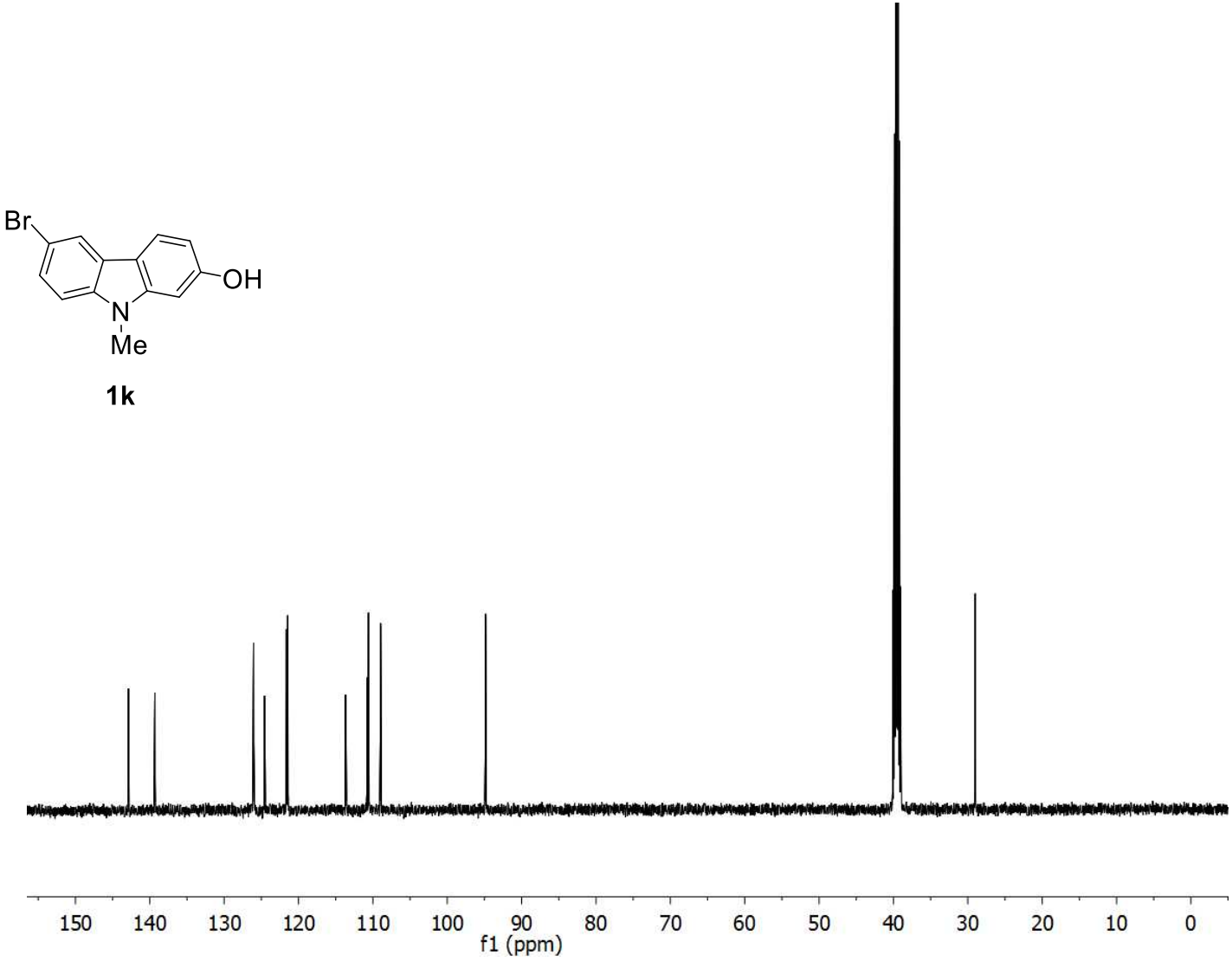
500 MHz ^{1}H NMR Spectrum of Compound **1j** in $CDCl_3$



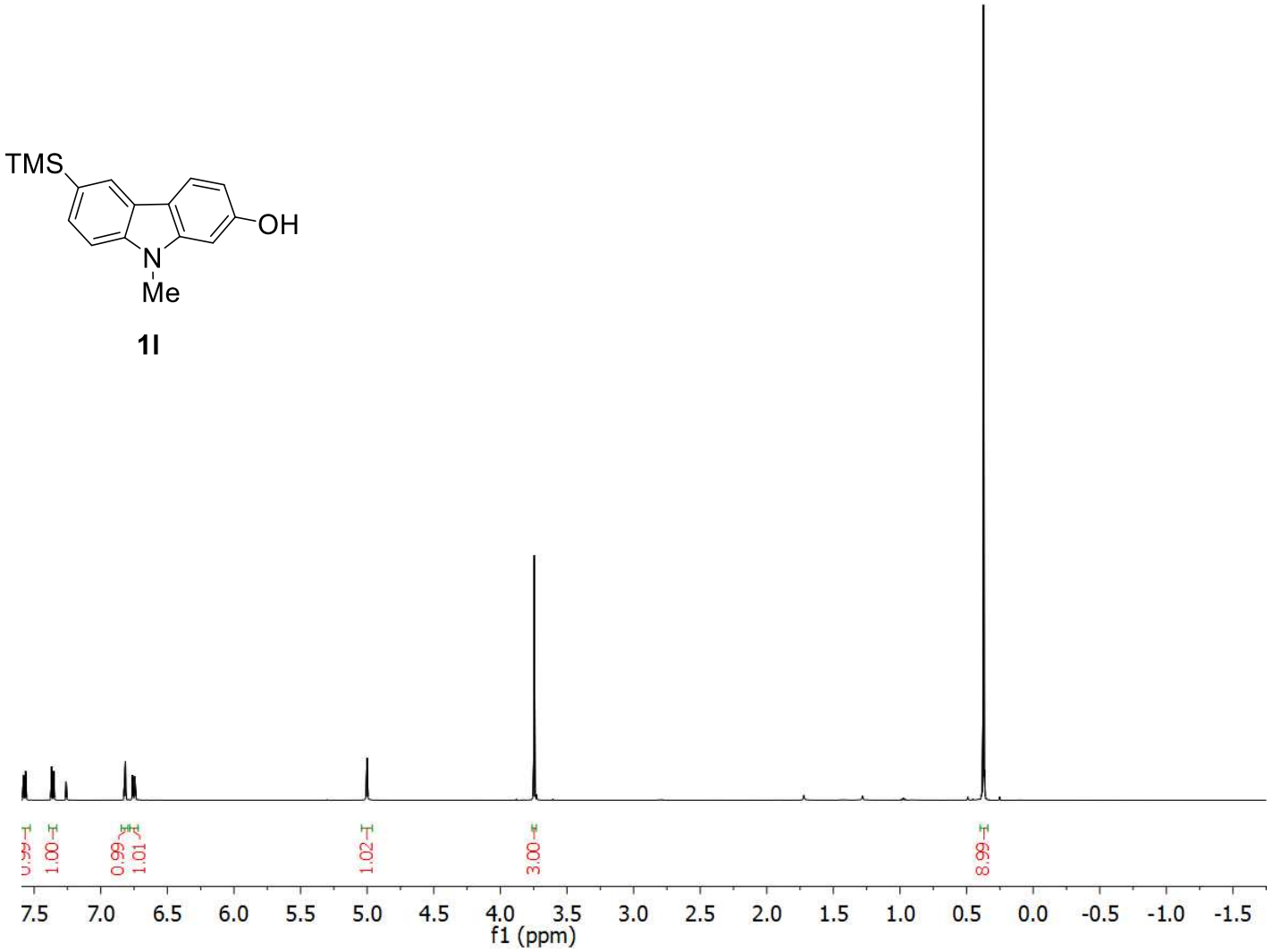
125 MHz ^{13}C NMR Spectrum of Compound **1j** in $CDCl_3$



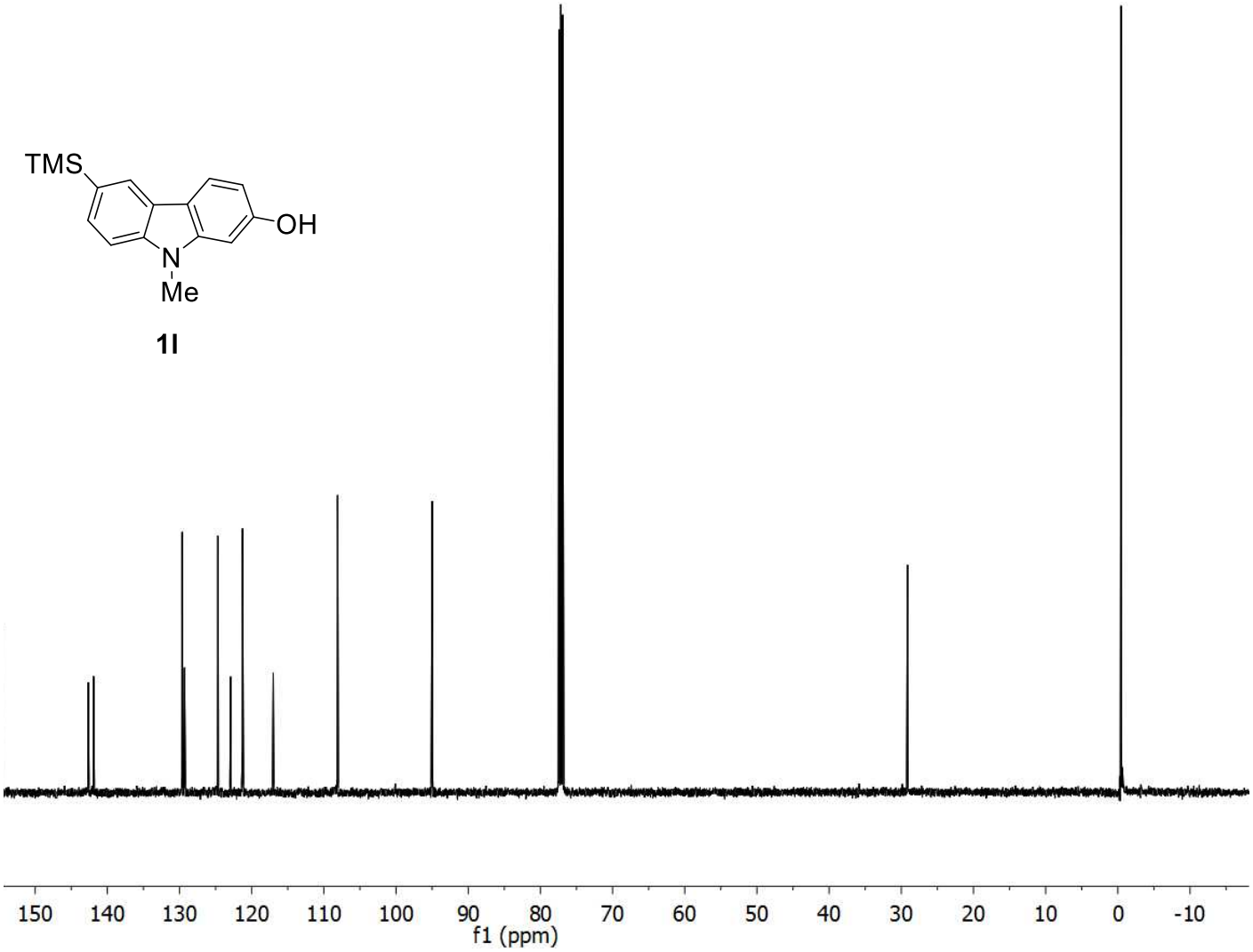
500 MHz ^{1}H NMR Spectrum of Compound **1k** in DMSO-d_6



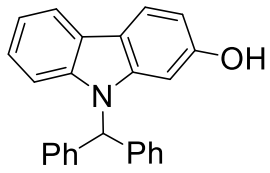
125 MHz ^{13}C NMR Spectrum of Compound **1k** in DMSO-d_6



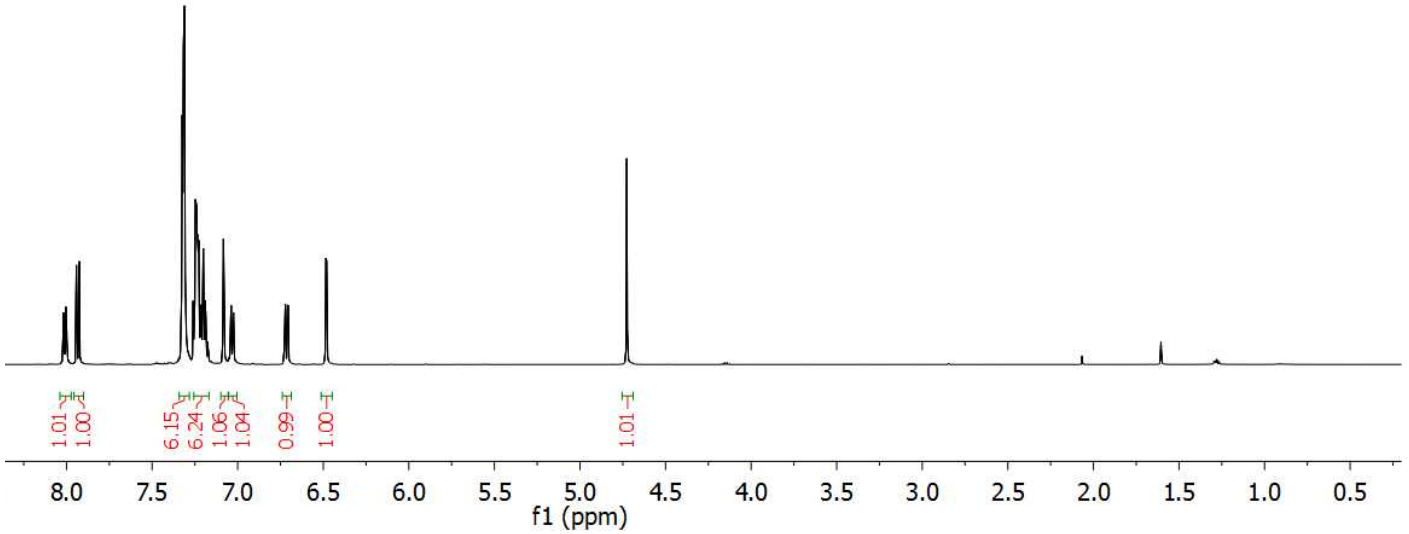
500 MHz ^{1}H NMR Spectrum of Compound **1l** in $CDCl_3$



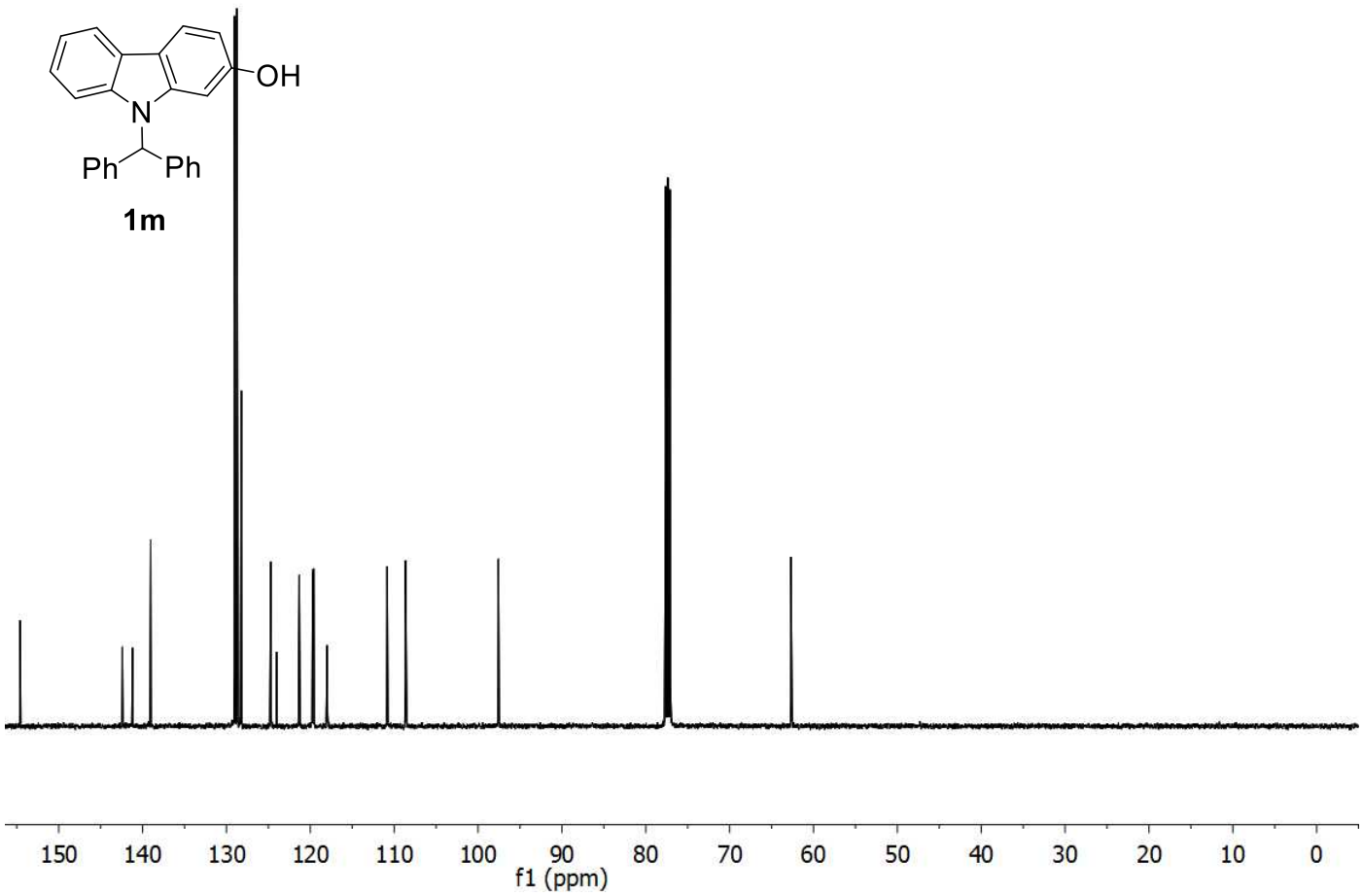
125 MHz ^{13}C NMR Spectrum of Compound **1l** in $CDCl_3$



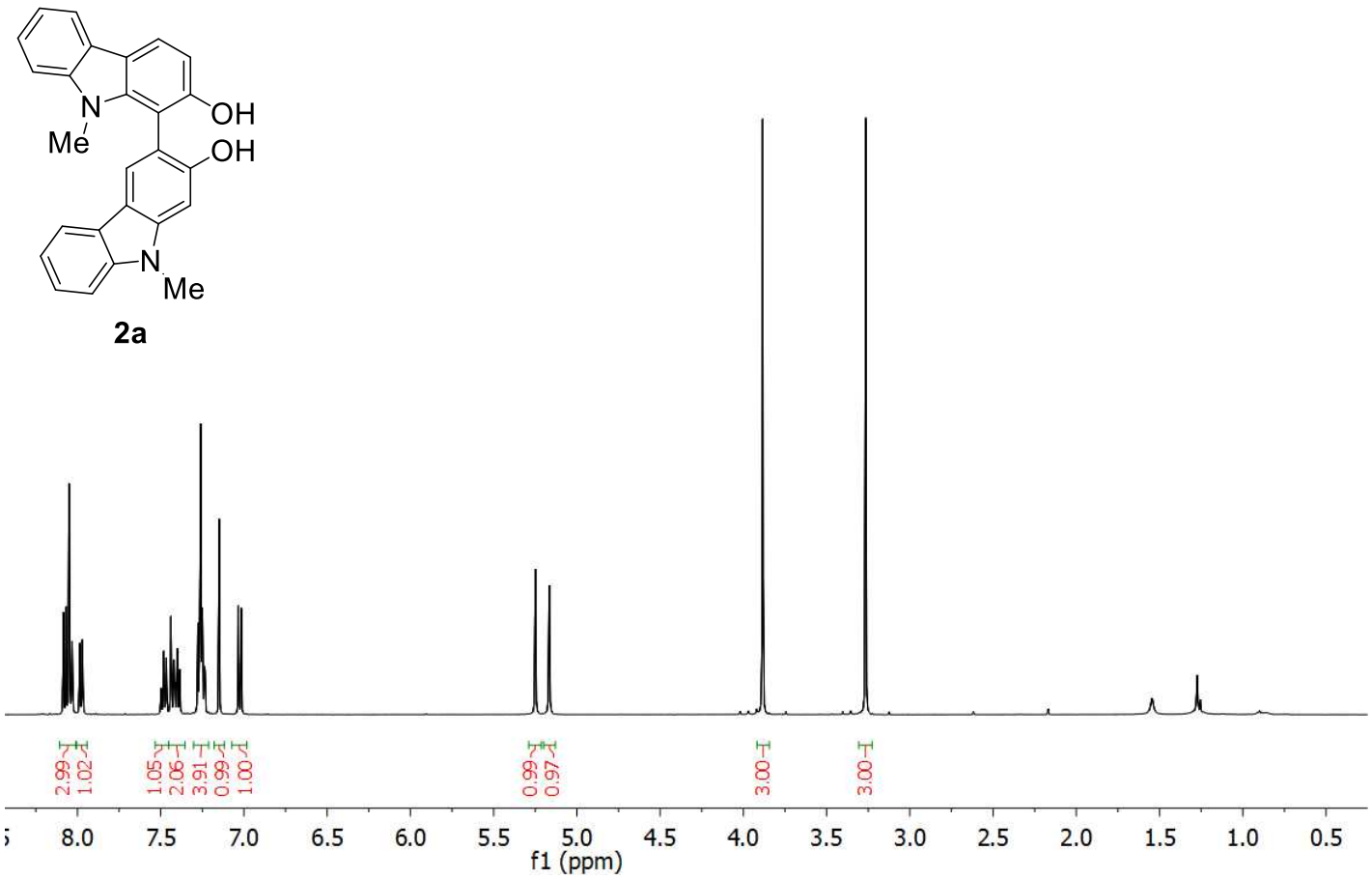
1m



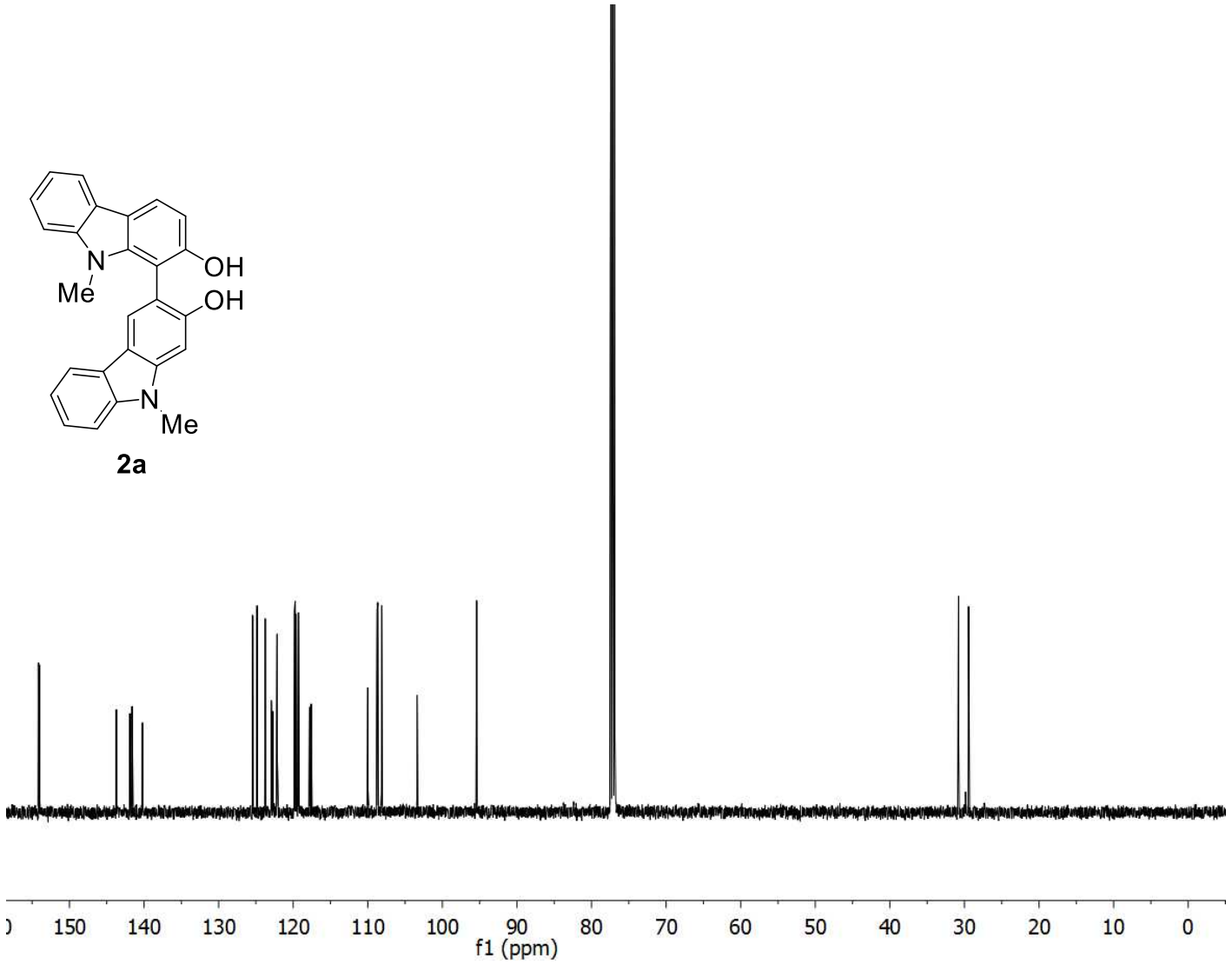
500 MHz ^{1}H NMR Spectrum of Compound **1m** in $CDCl_3$



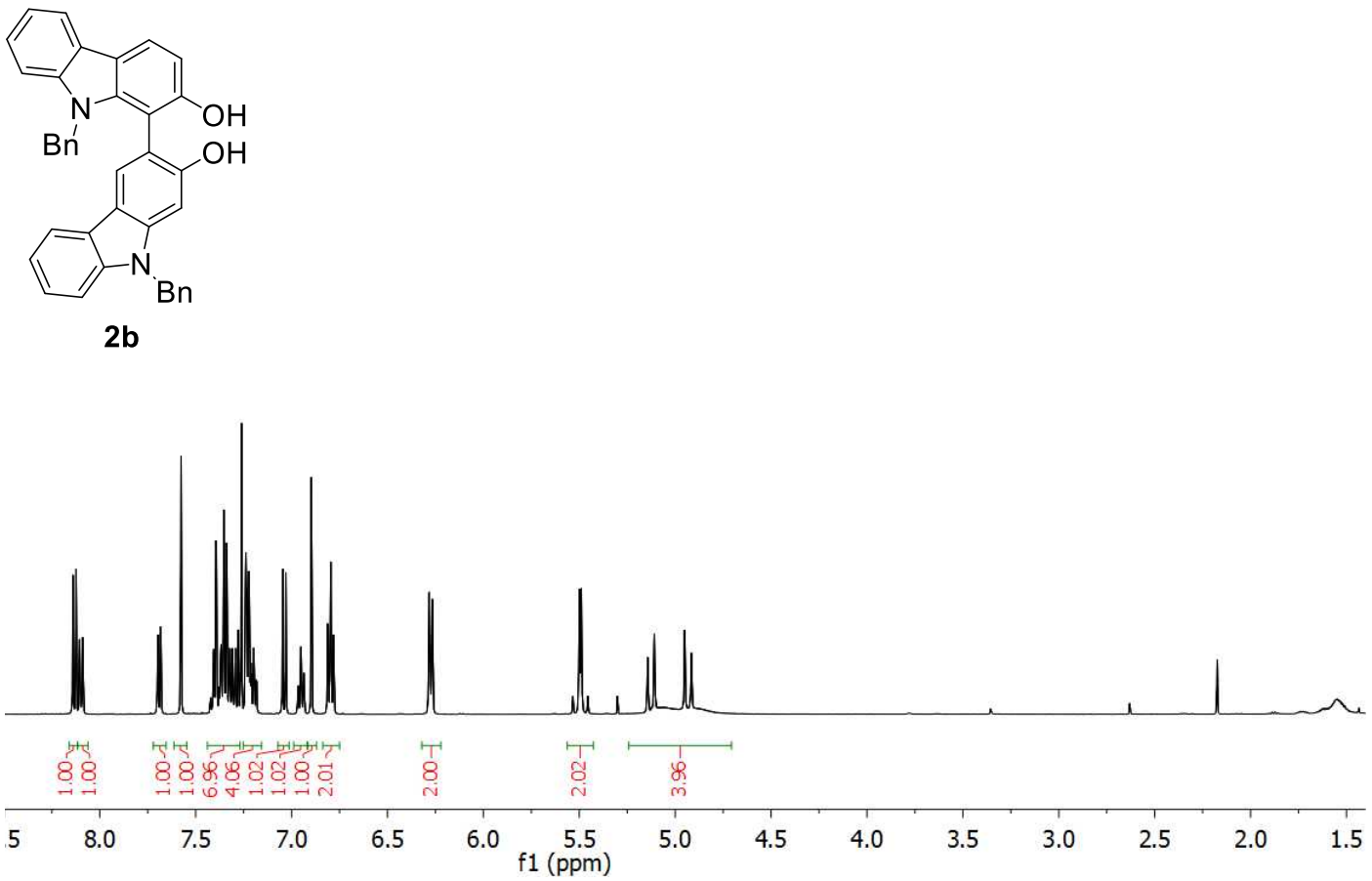
125 MHz ^{13}C NMR Spectrum of Compound **1m** in $CDCl_3$



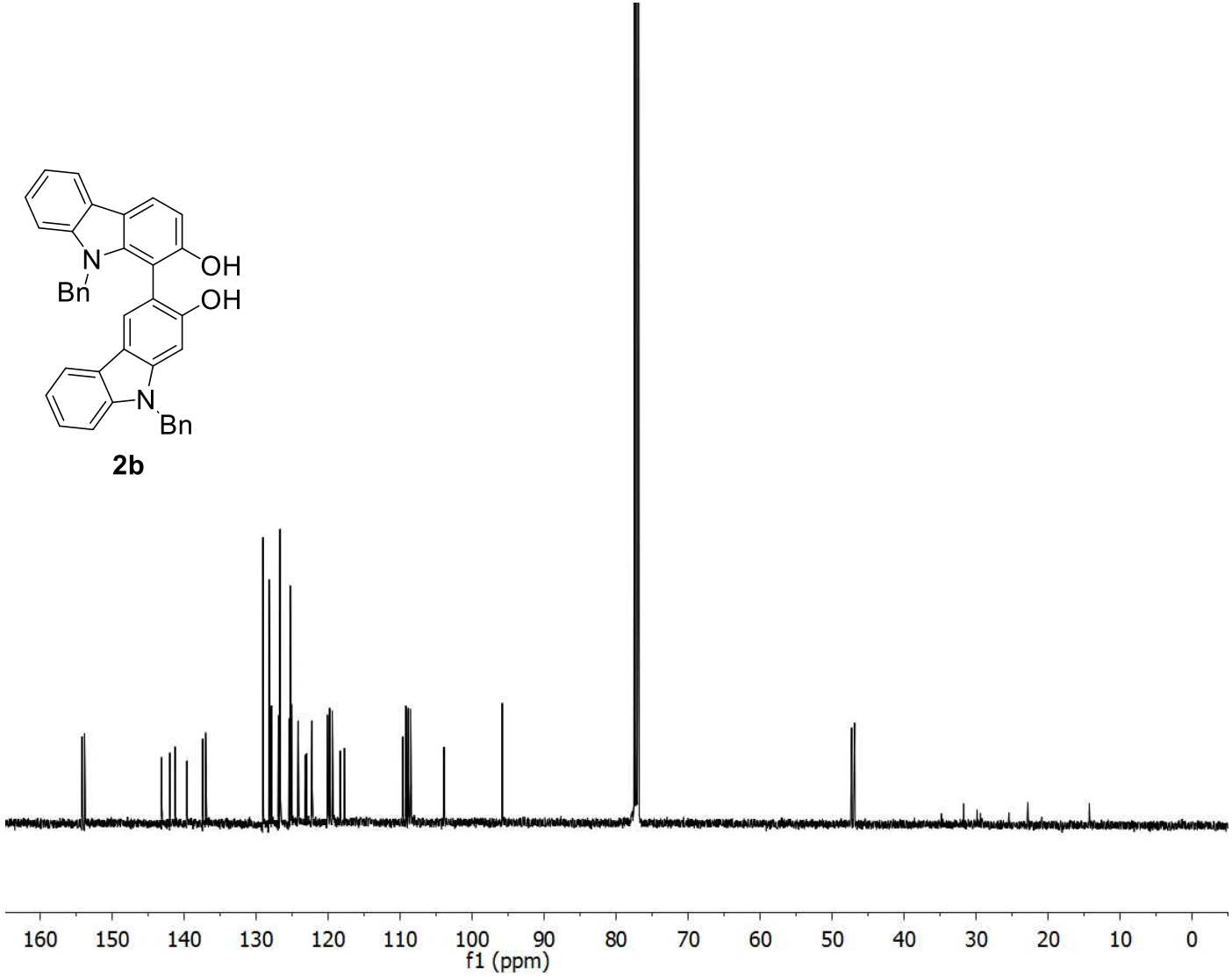
500 MHz ^{1}H NMR Spectrum of Compound **2a** in $CDCl_3$



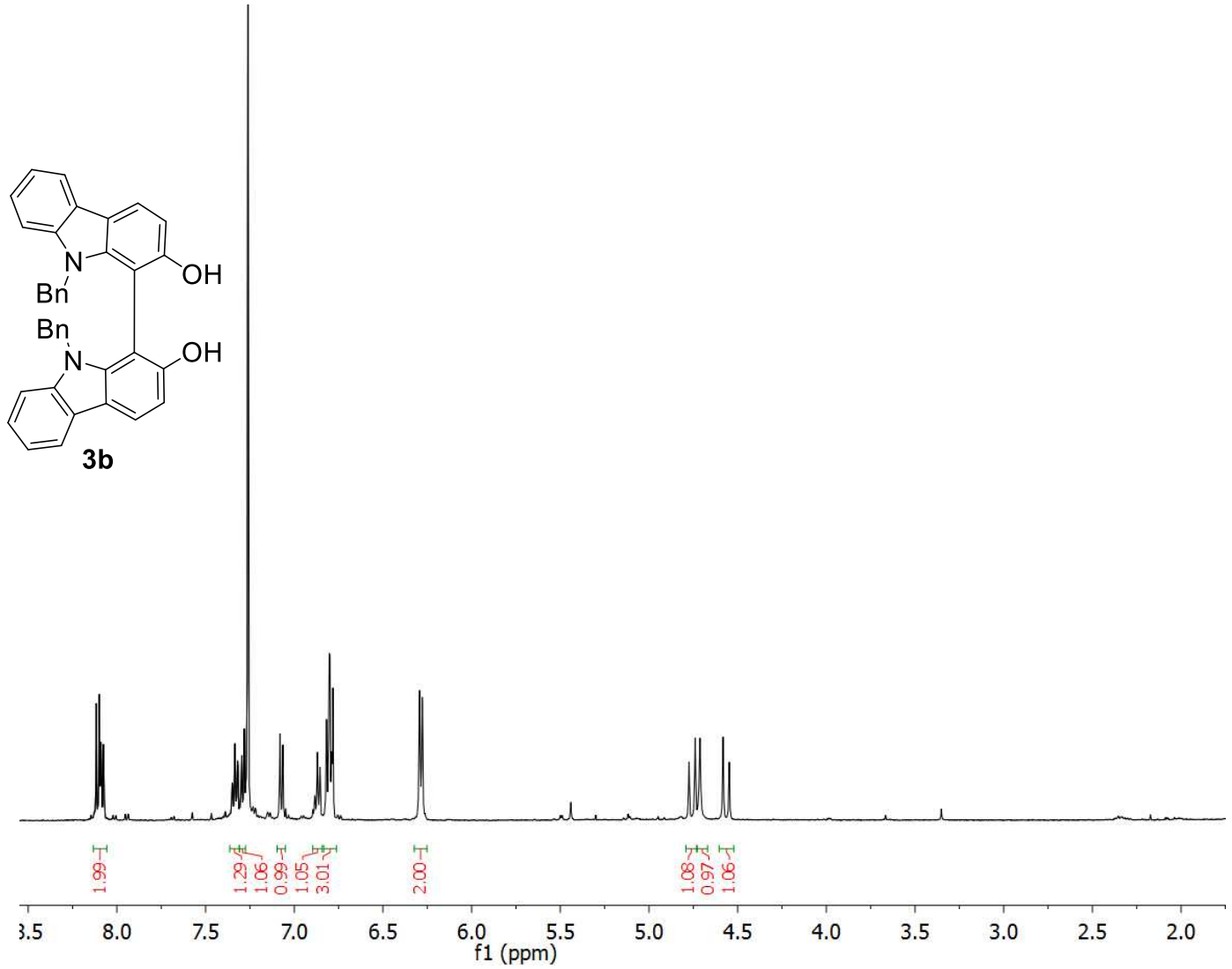
125 MHz ^{13}C NMR Spectrum of Compound **2a** in $CDCl_3$



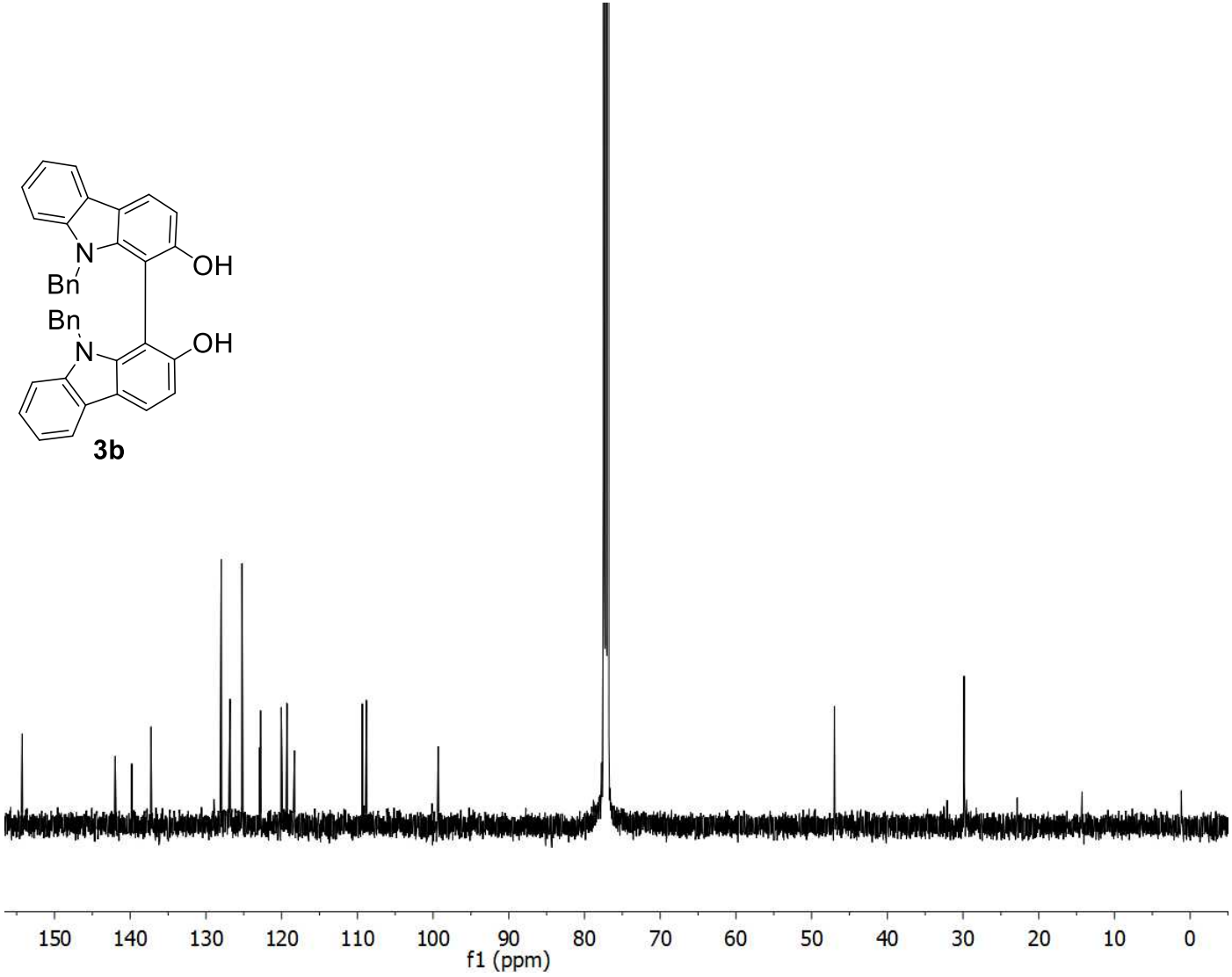
500 MHz ^{1}H NMR Spectrum of Compound **2b** in $CDCl_3$



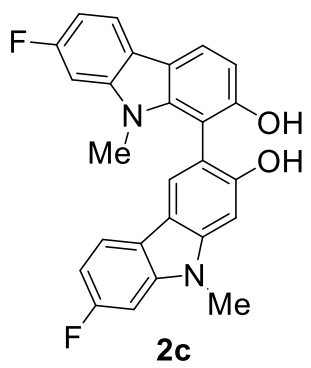
125 MHz ^{13}C NMR Spectrum of Compound **2b** in $CDCl_3$



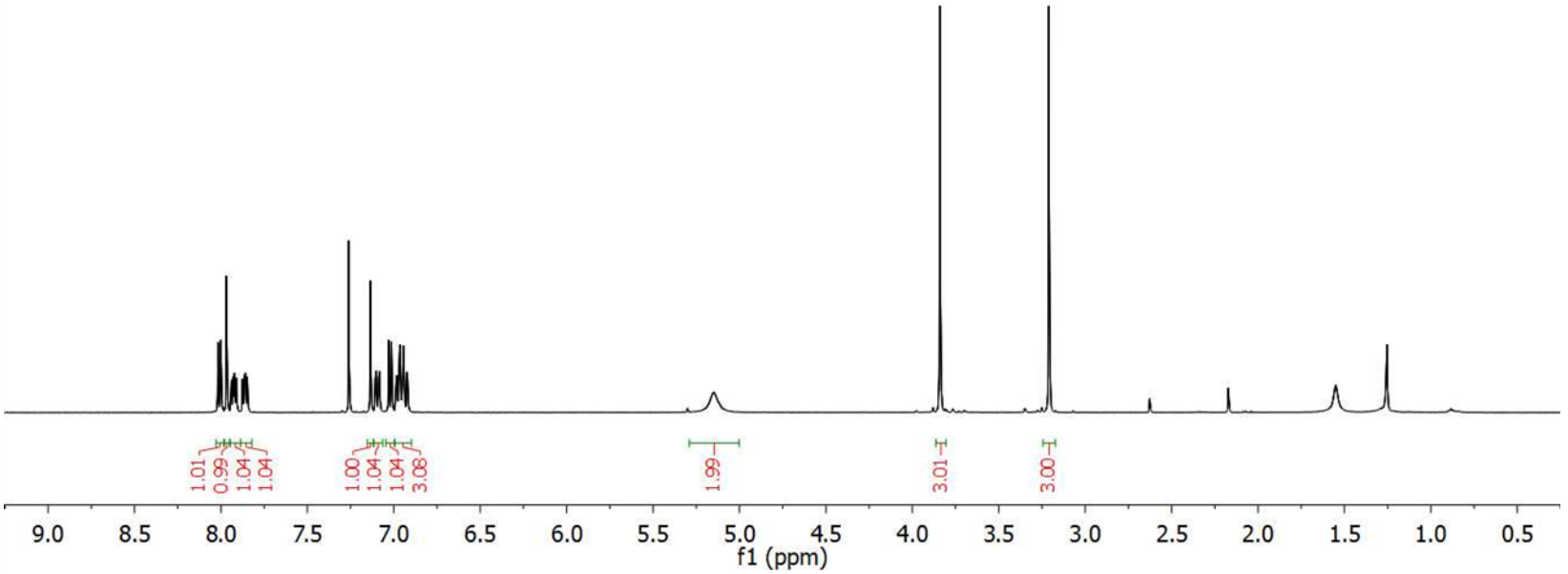
500 MHz ^{1}H NMR Spectrum of Compound **3b** in $CDCl_3$



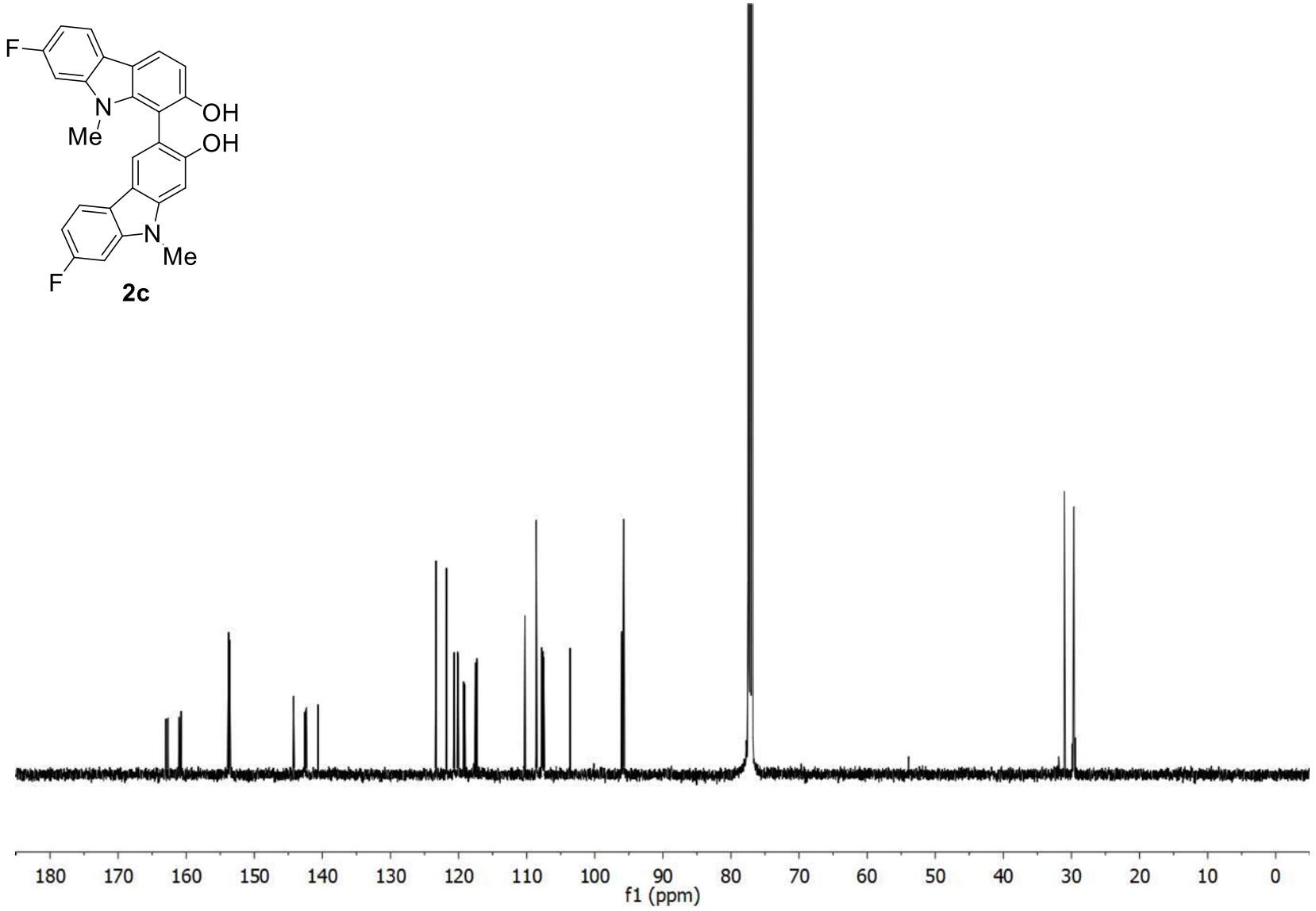
125 MHz ^{13}C NMR Spectrum of Compound **3b** in $CDCl_3$



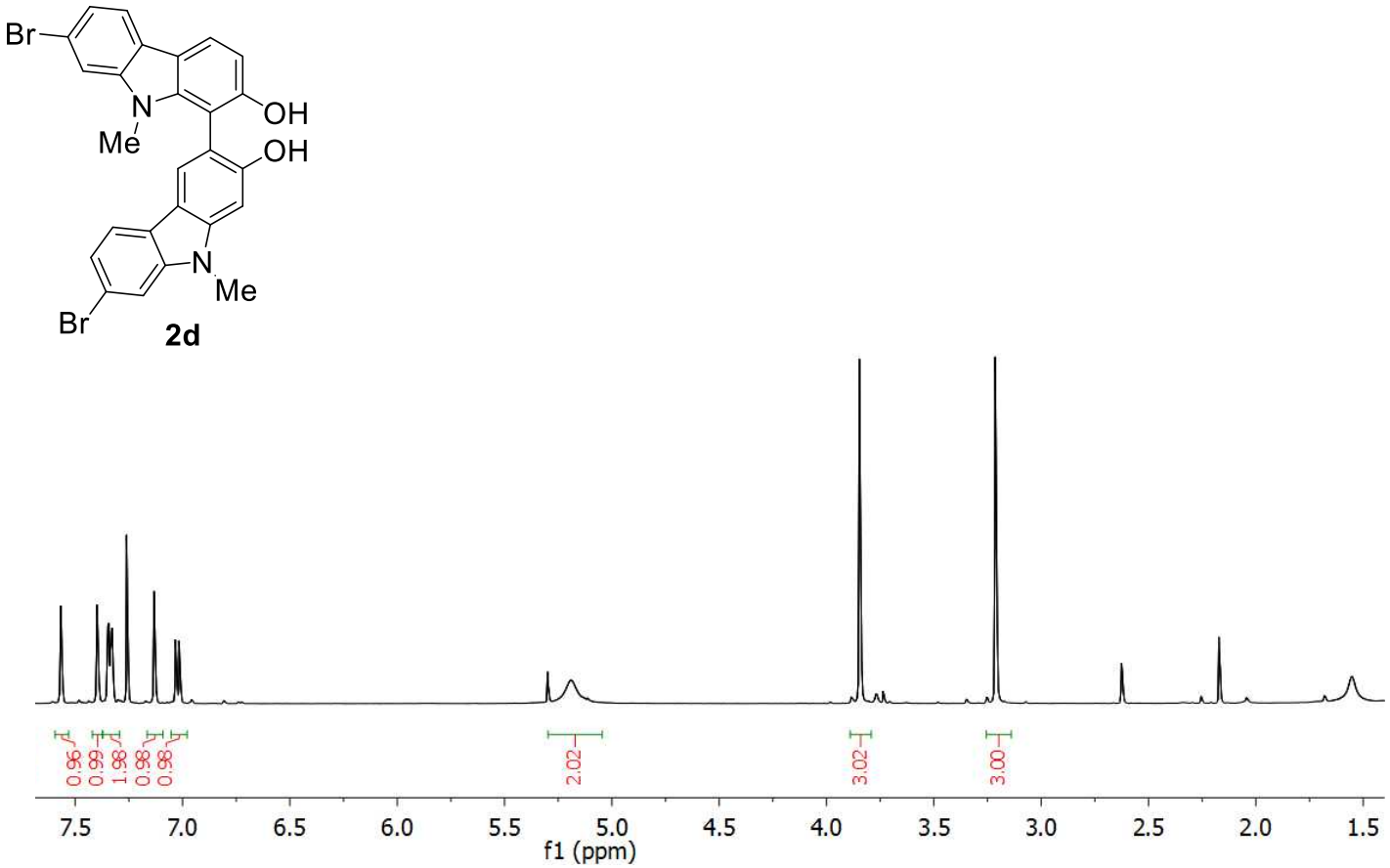
2c



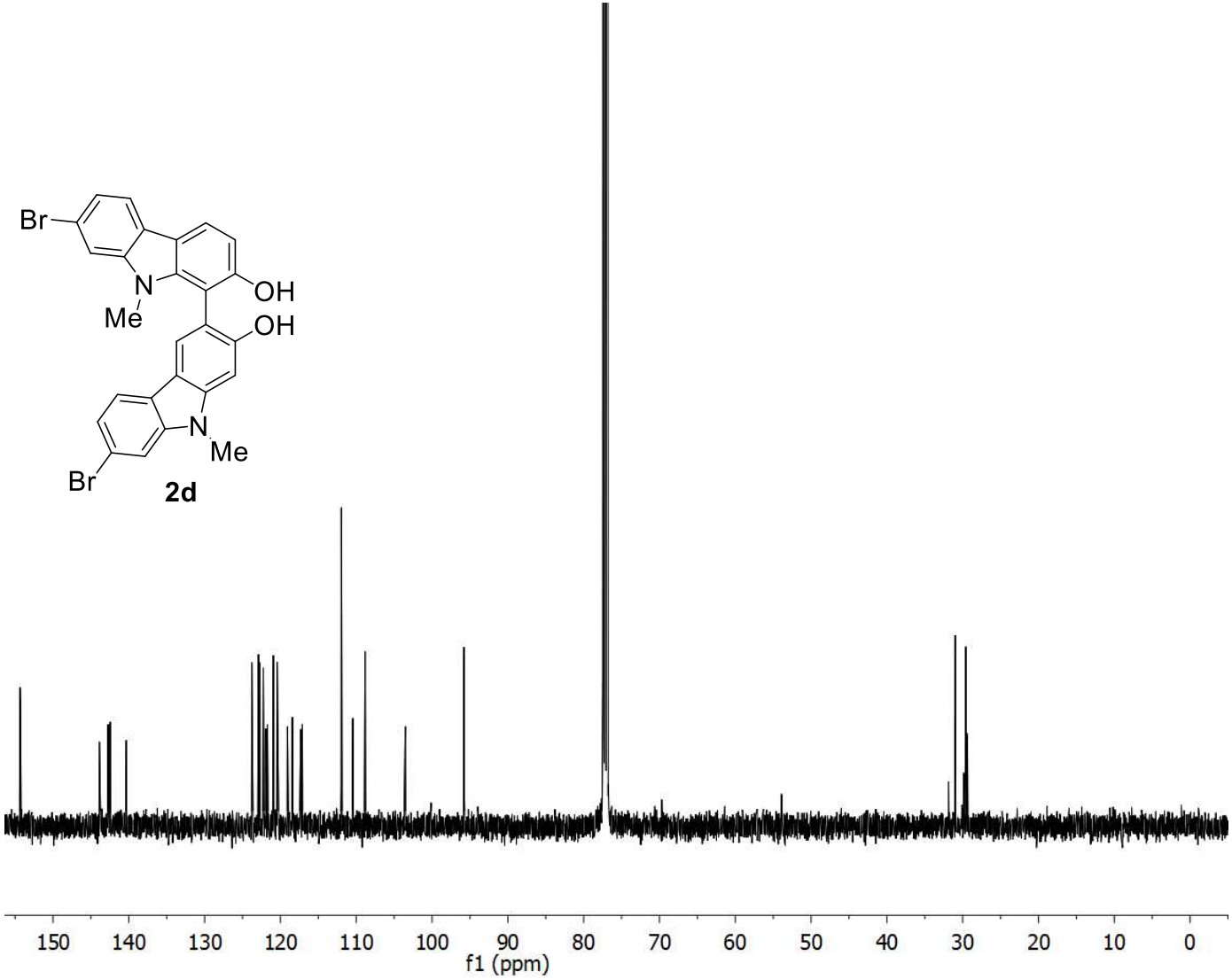
500 MHz ^{1}H NMR Spectrum of Compound **2c** in $CDCl_3$



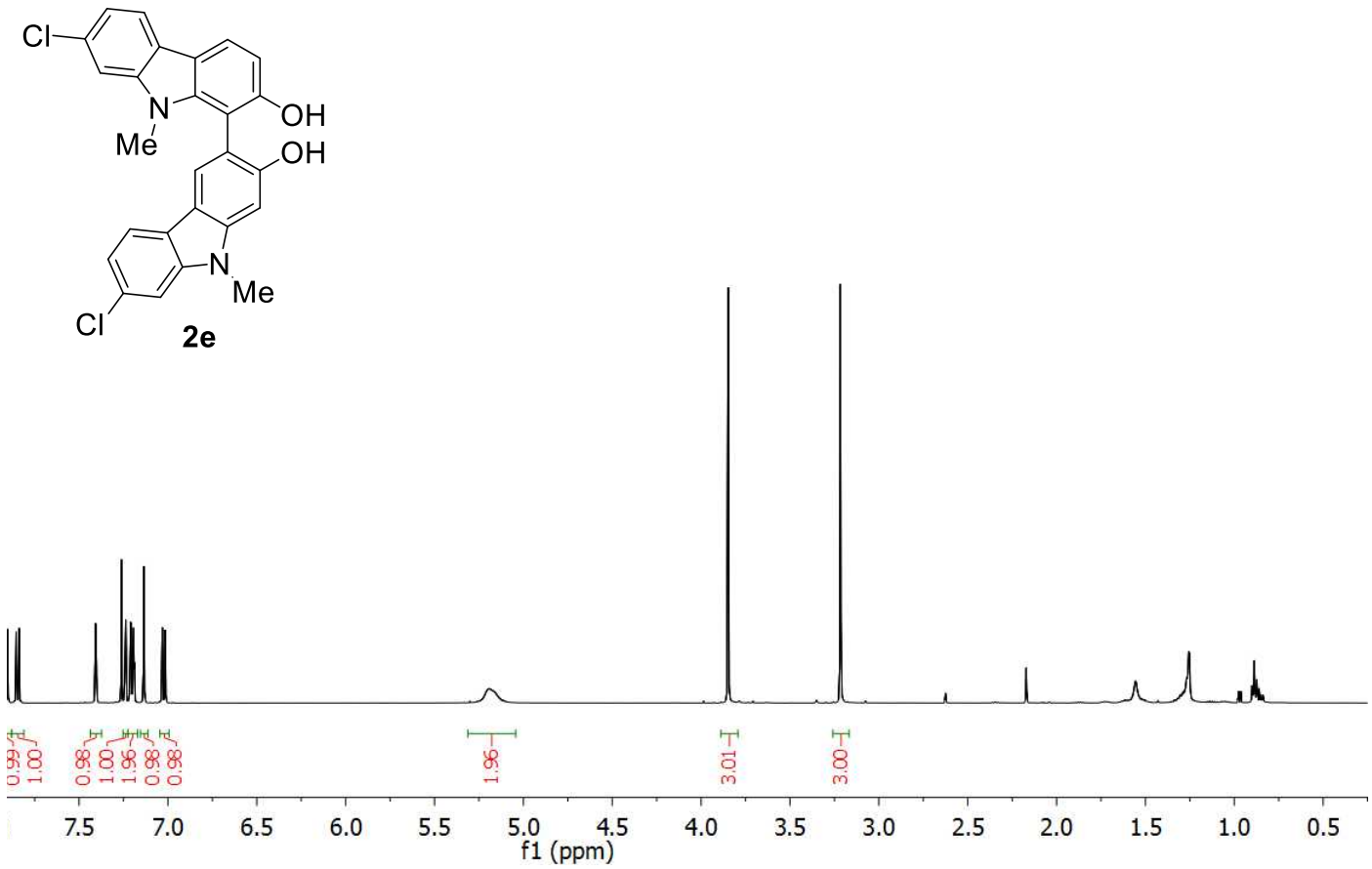
125 MHz ^{13}C NMR Spectrum of Compound **2c** in $CDCl_3$



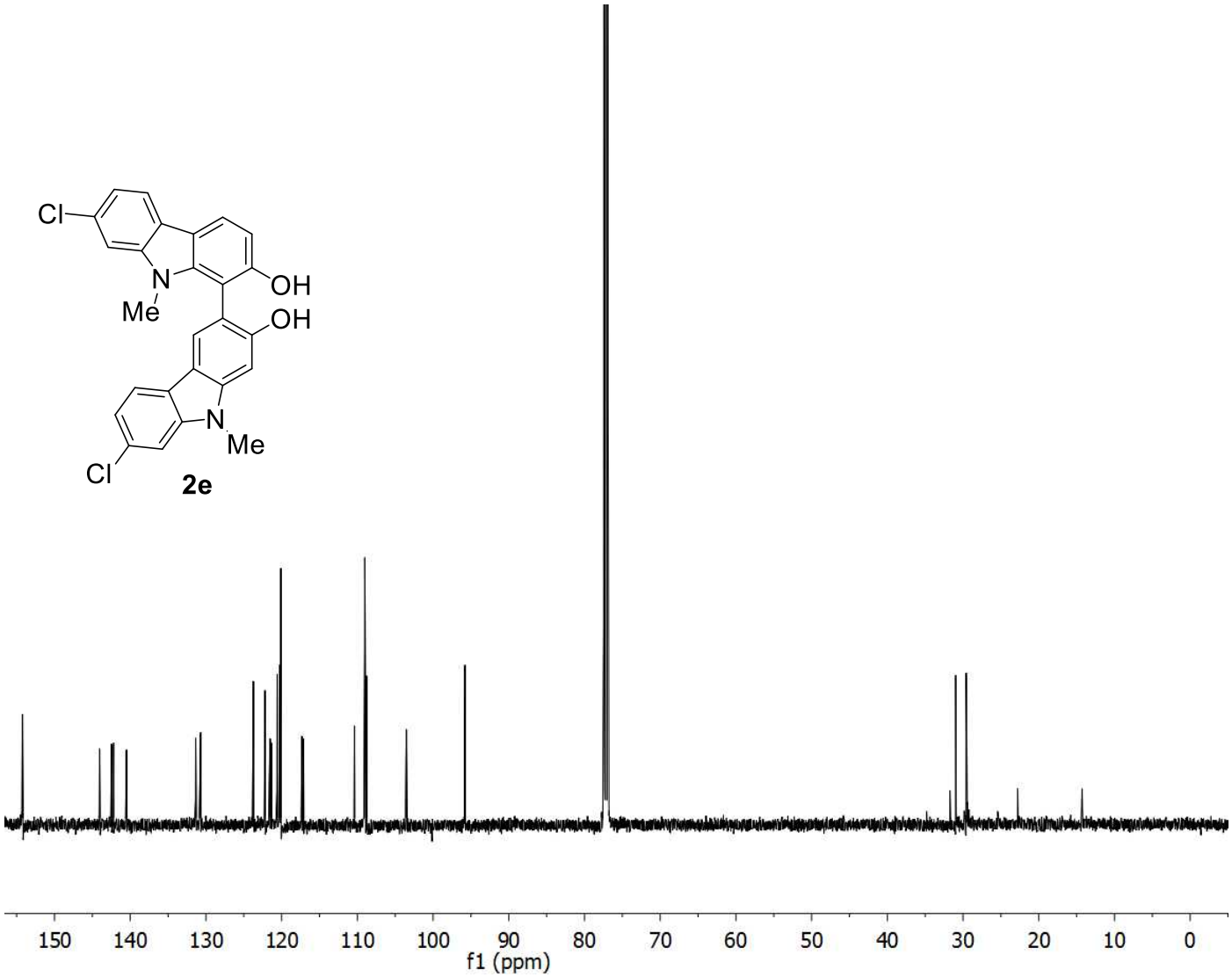
500 MHz ^{1}H NMR Spectrum of Compound **2d** in $CDCl_3$



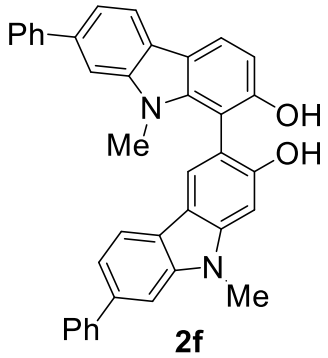
125 MHz ^{13}C NMR Spectrum of Compound **2d** in $CDCl_3$



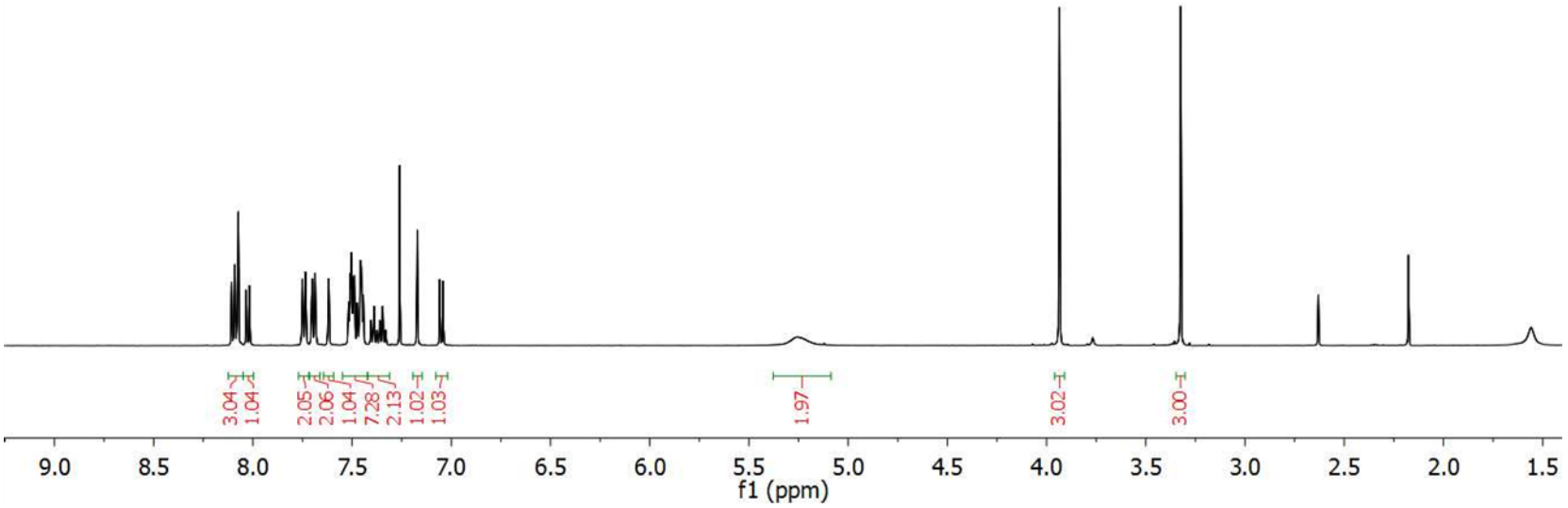
500 MHz ^{1}H NMR Spectrum of Compound **2e** in $CDCl_3$



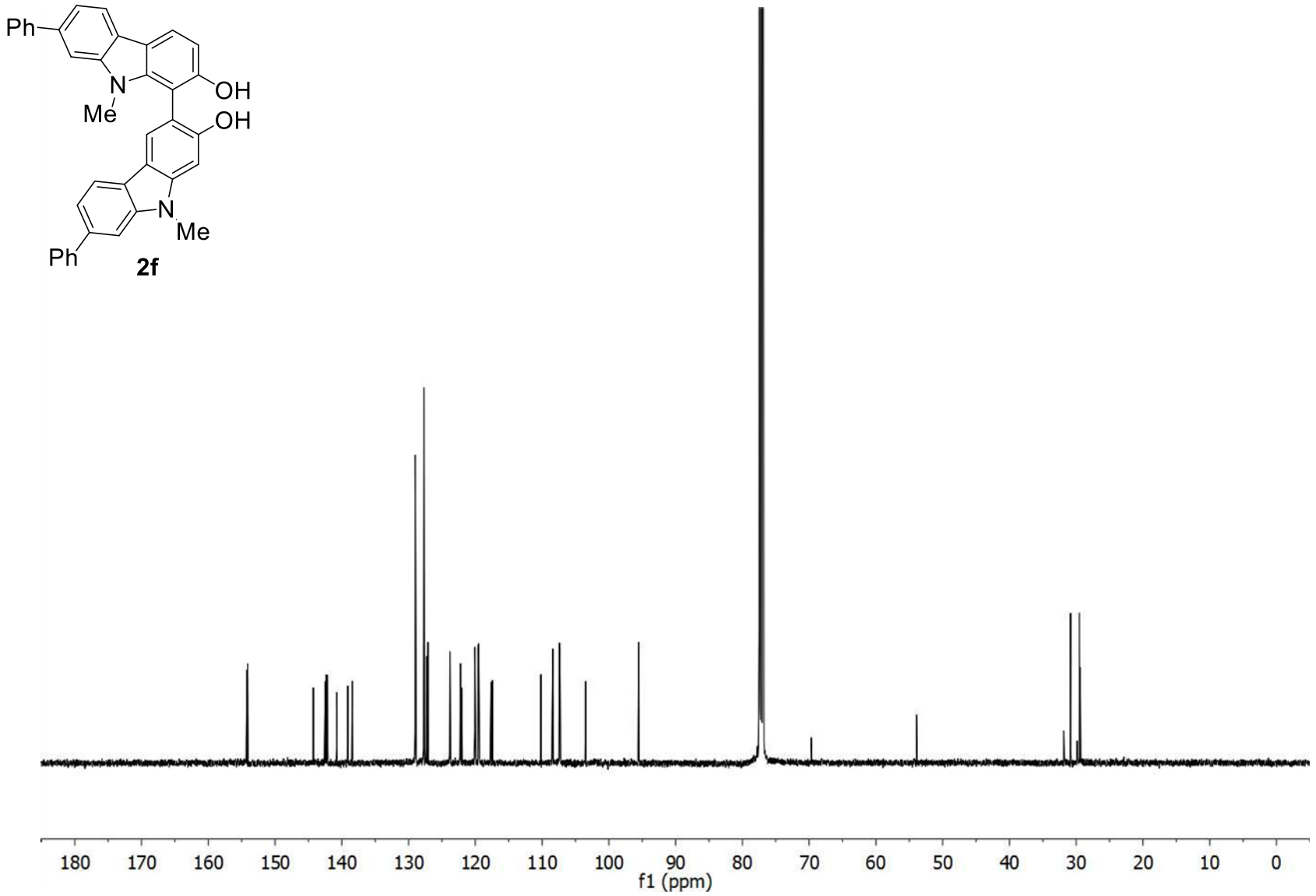
125 MHz ^{13}C NMR Spectrum of Compound **2e** in $CDCl_3$



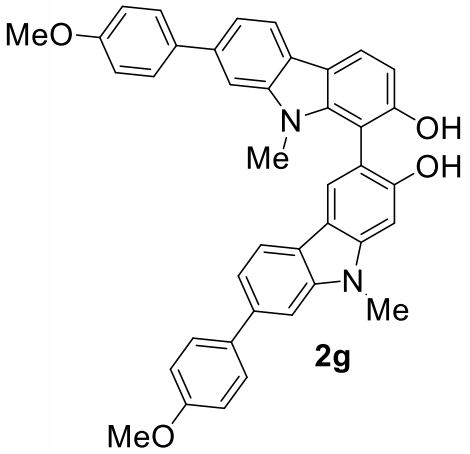
2f



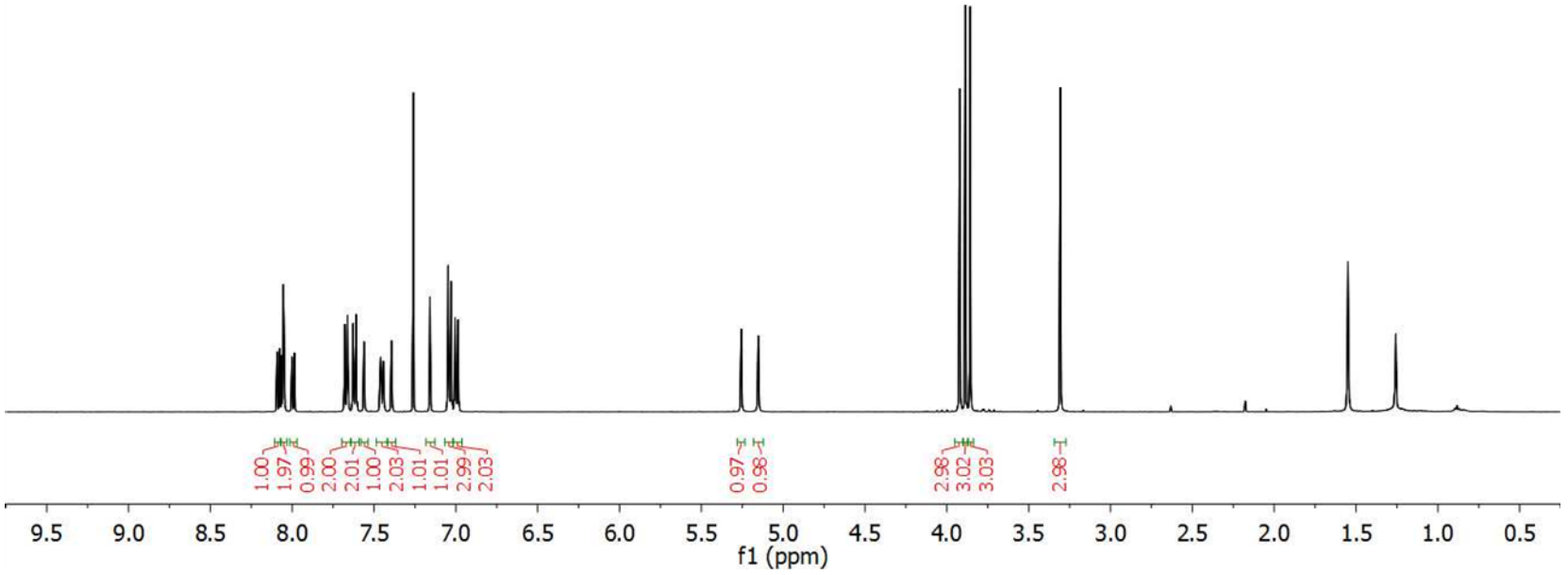
500 MHz ^{1}H NMR Spectrum of Compound **2f** in $CDCl_3$



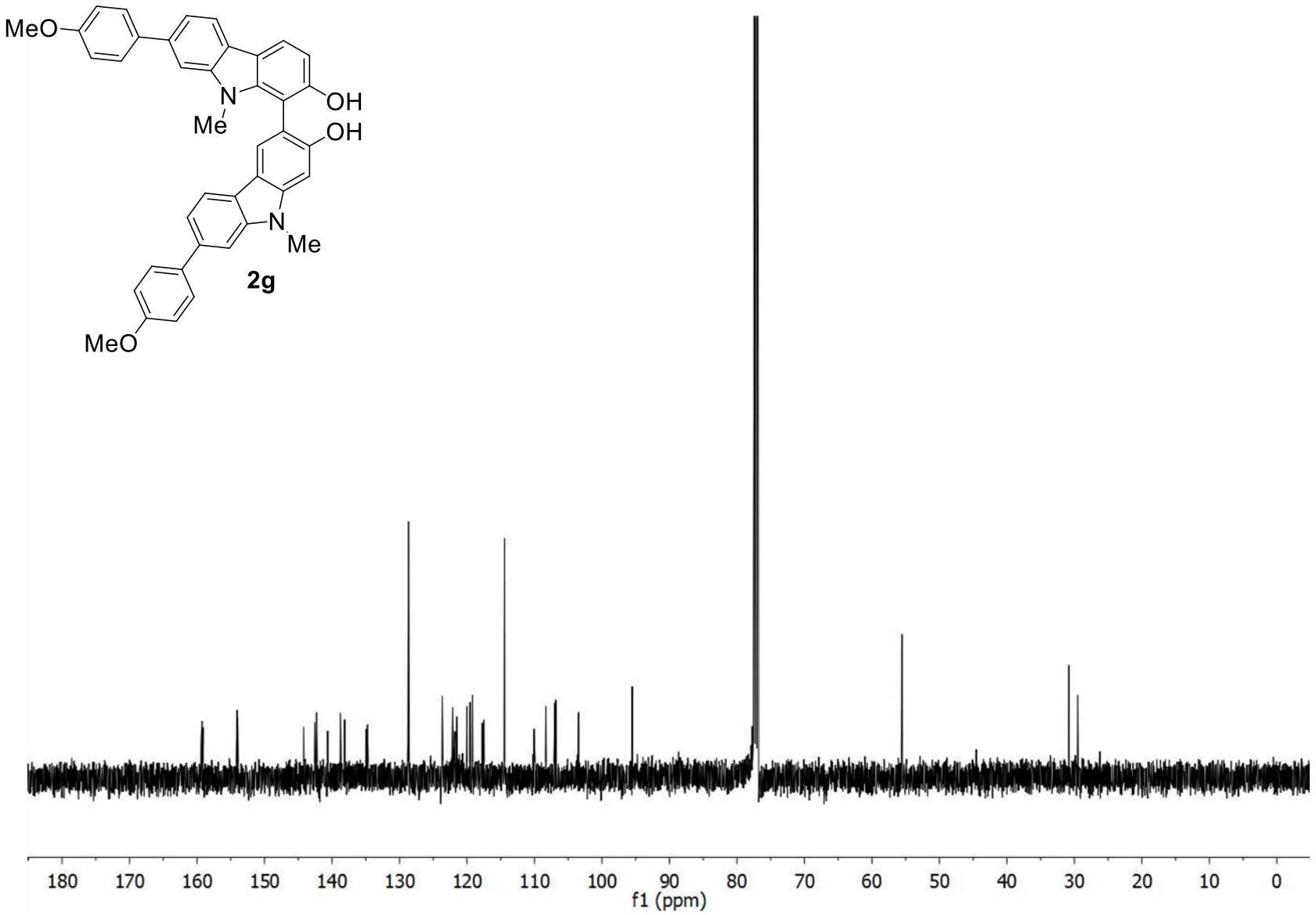
125 MHz ^{13}C NMR Spectrum of Compound **2f** in $CDCl_3$



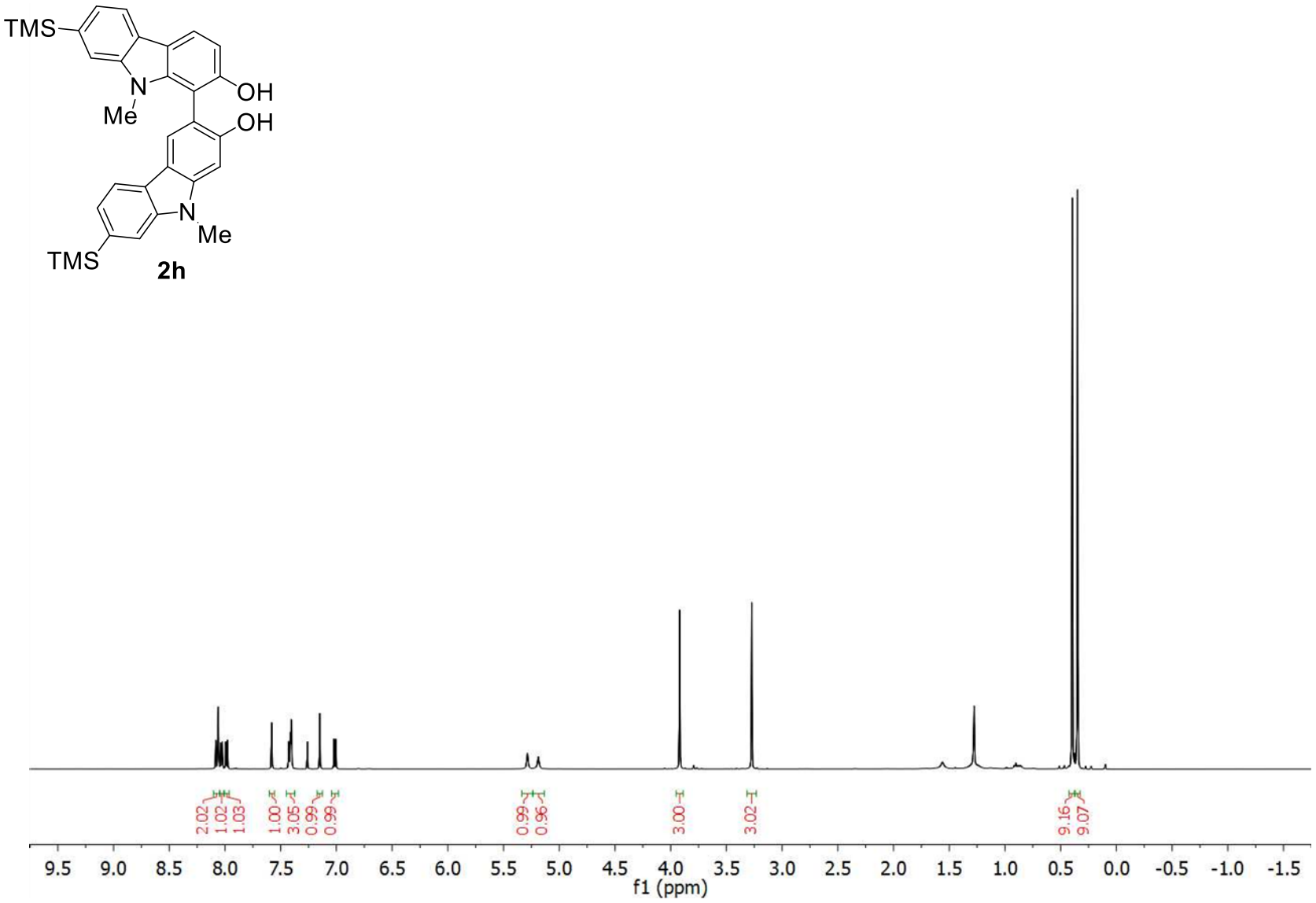
2g



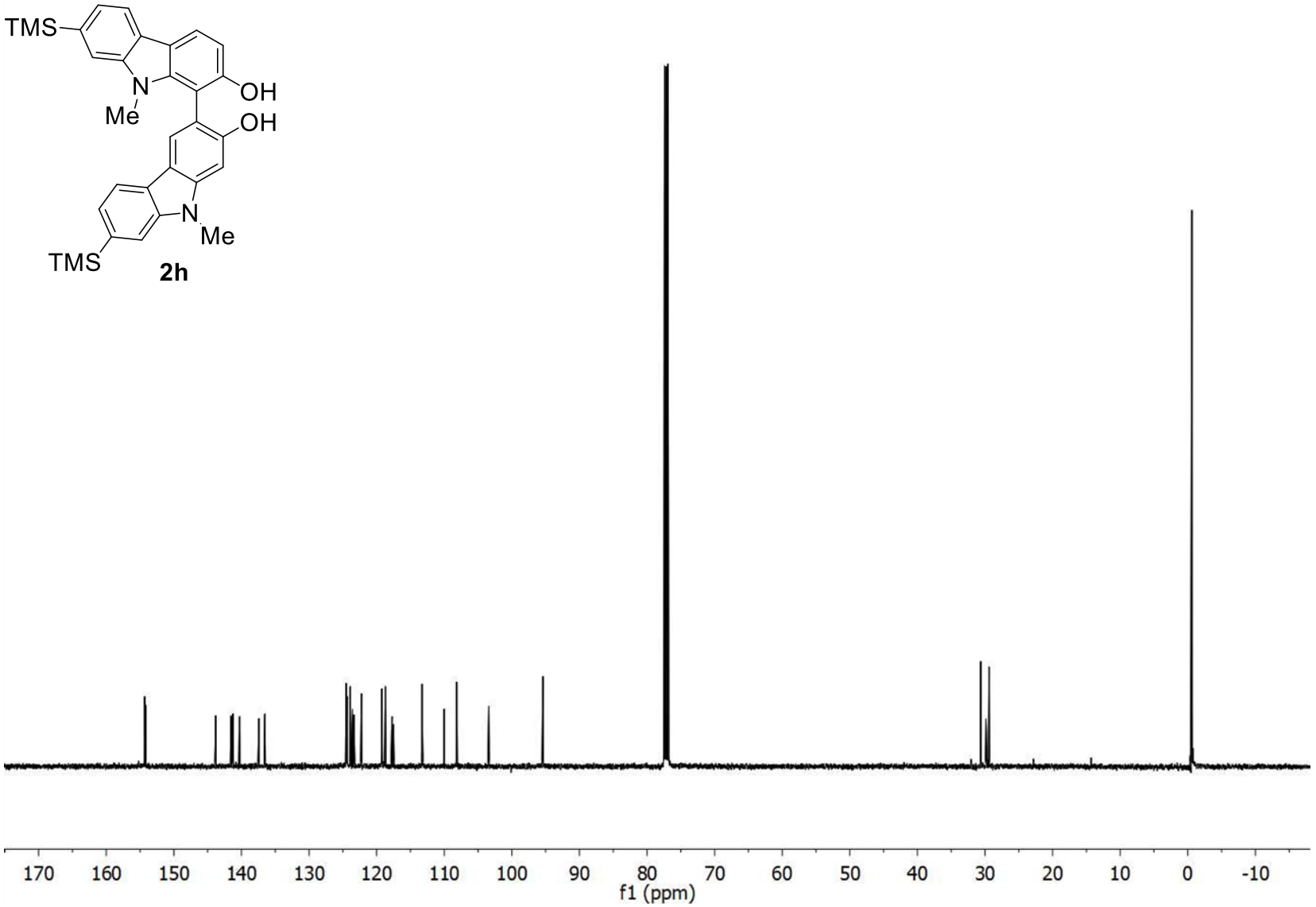
500 MHz ^{1}H NMR Spectrum of Compound **2g** in $CDCl_3$



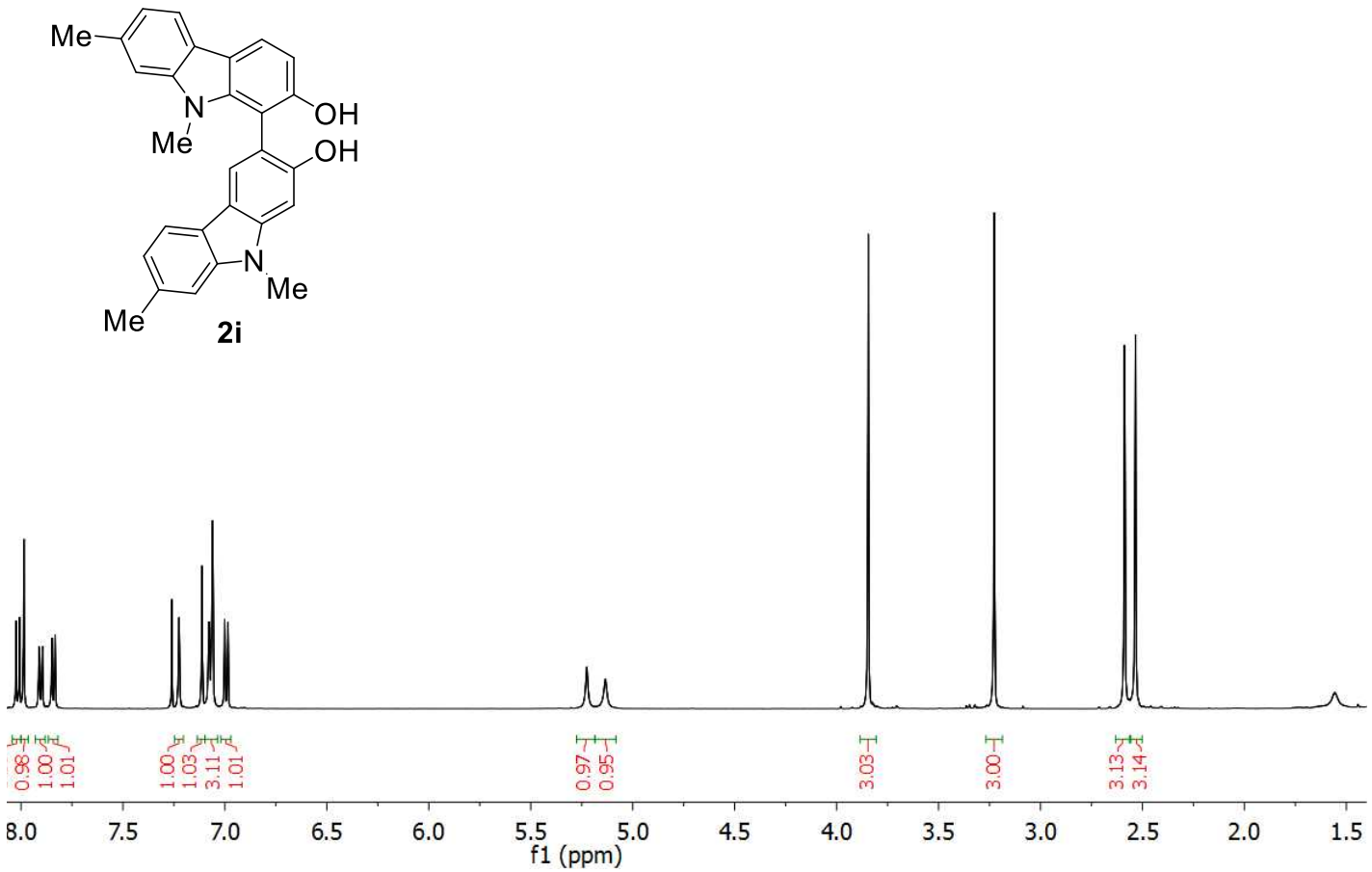
125 MHz ^{13}C NMR Spectrum of Compound **2g** in $CDCl_3$



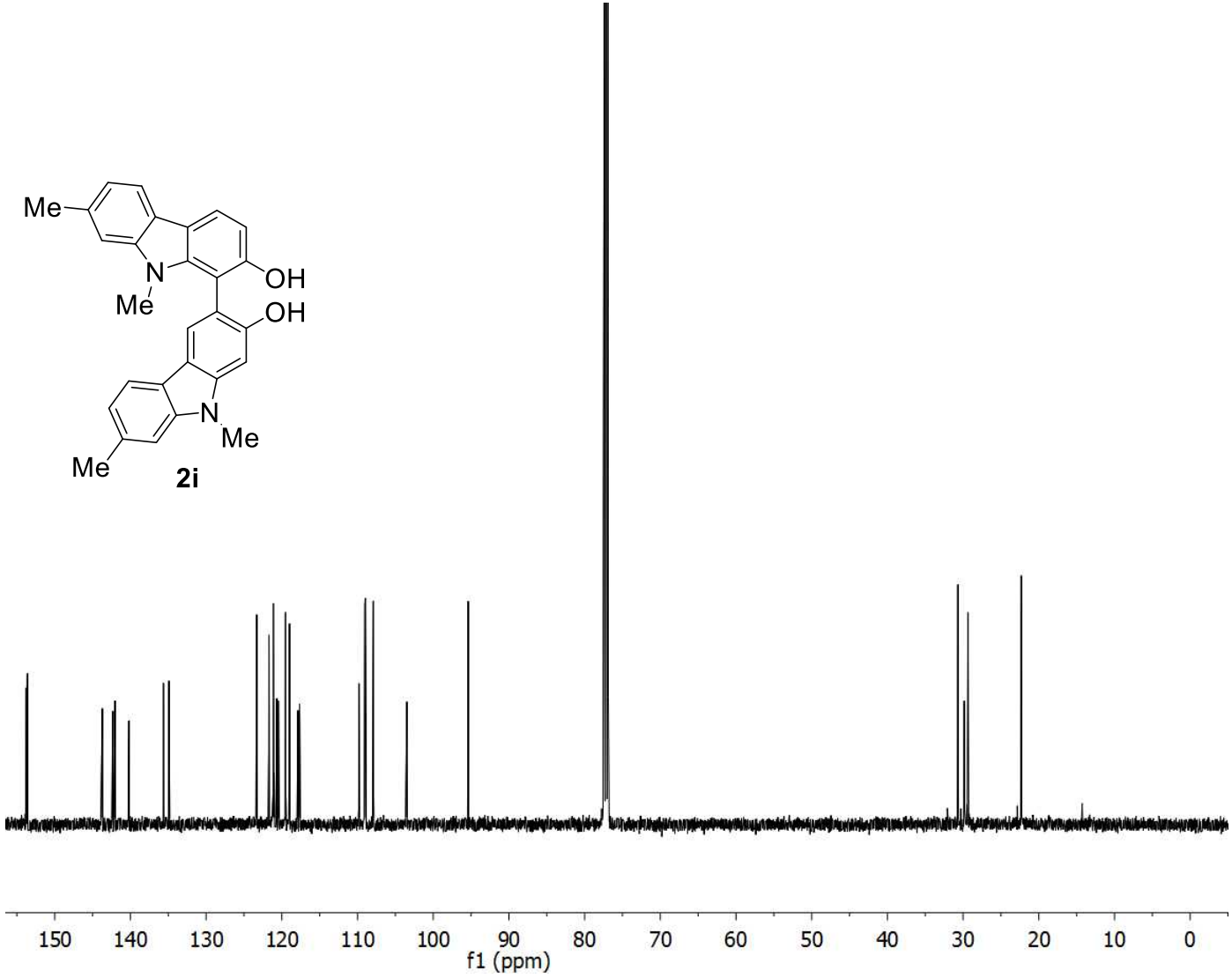
500 MHz ^{1}H NMR Spectrum of Compound **2h** in $CDCl_3$



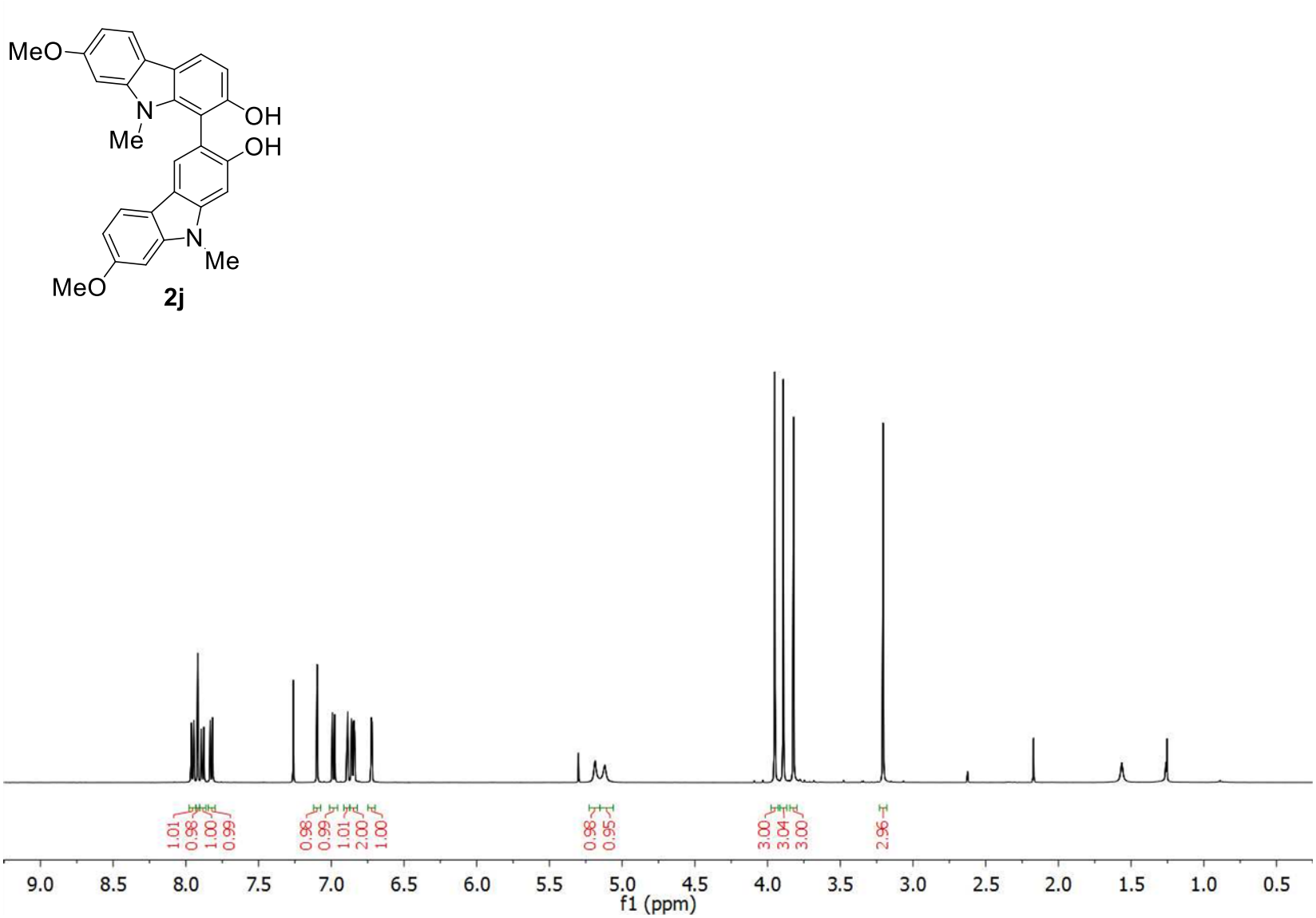
125 MHz ^{13}C NMR Spectrum of Compound **2h** in $CDCl_3$



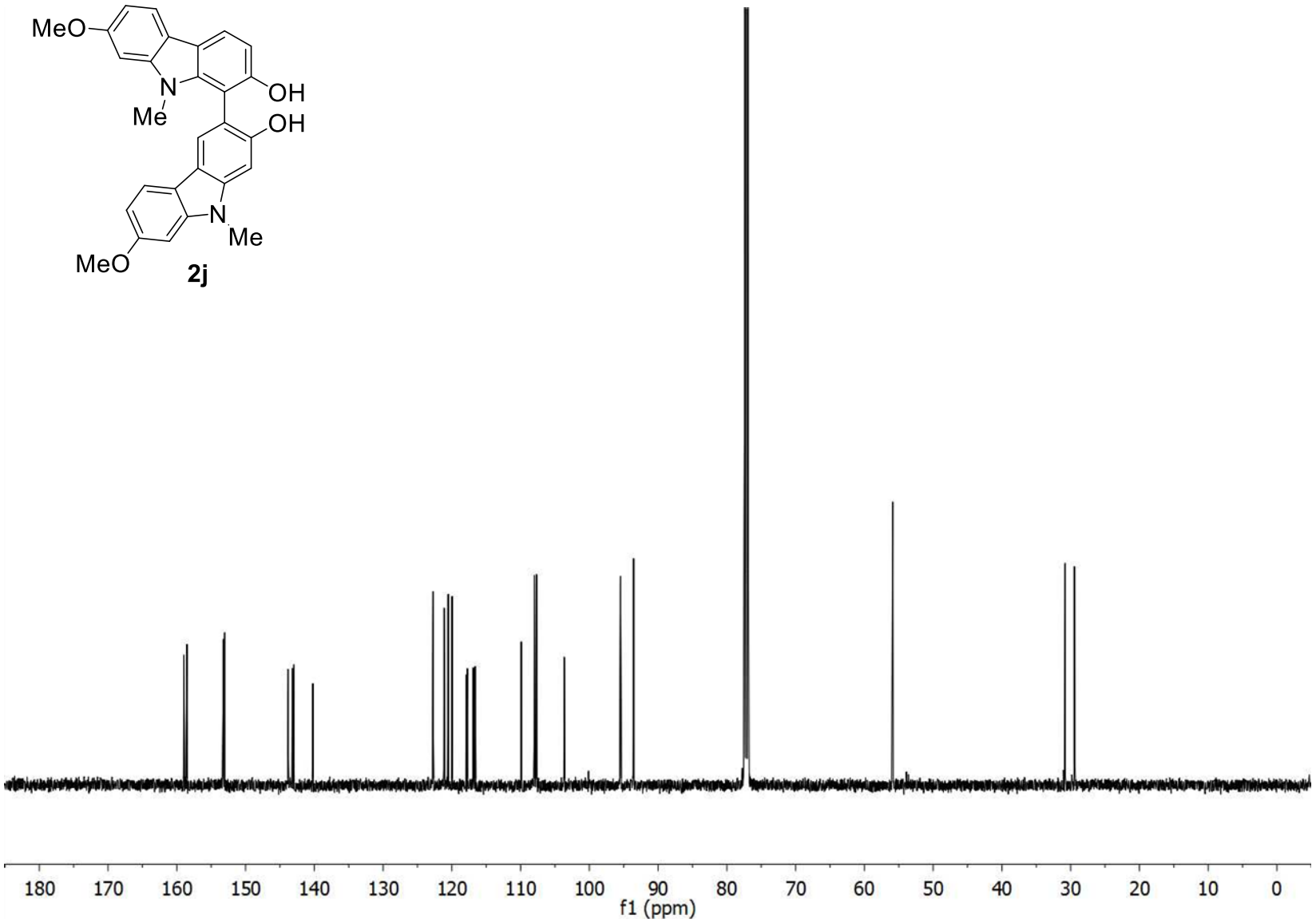
500 MHz ^{1}H NMR Spectrum of Compound **2i** in $CDCl_3$



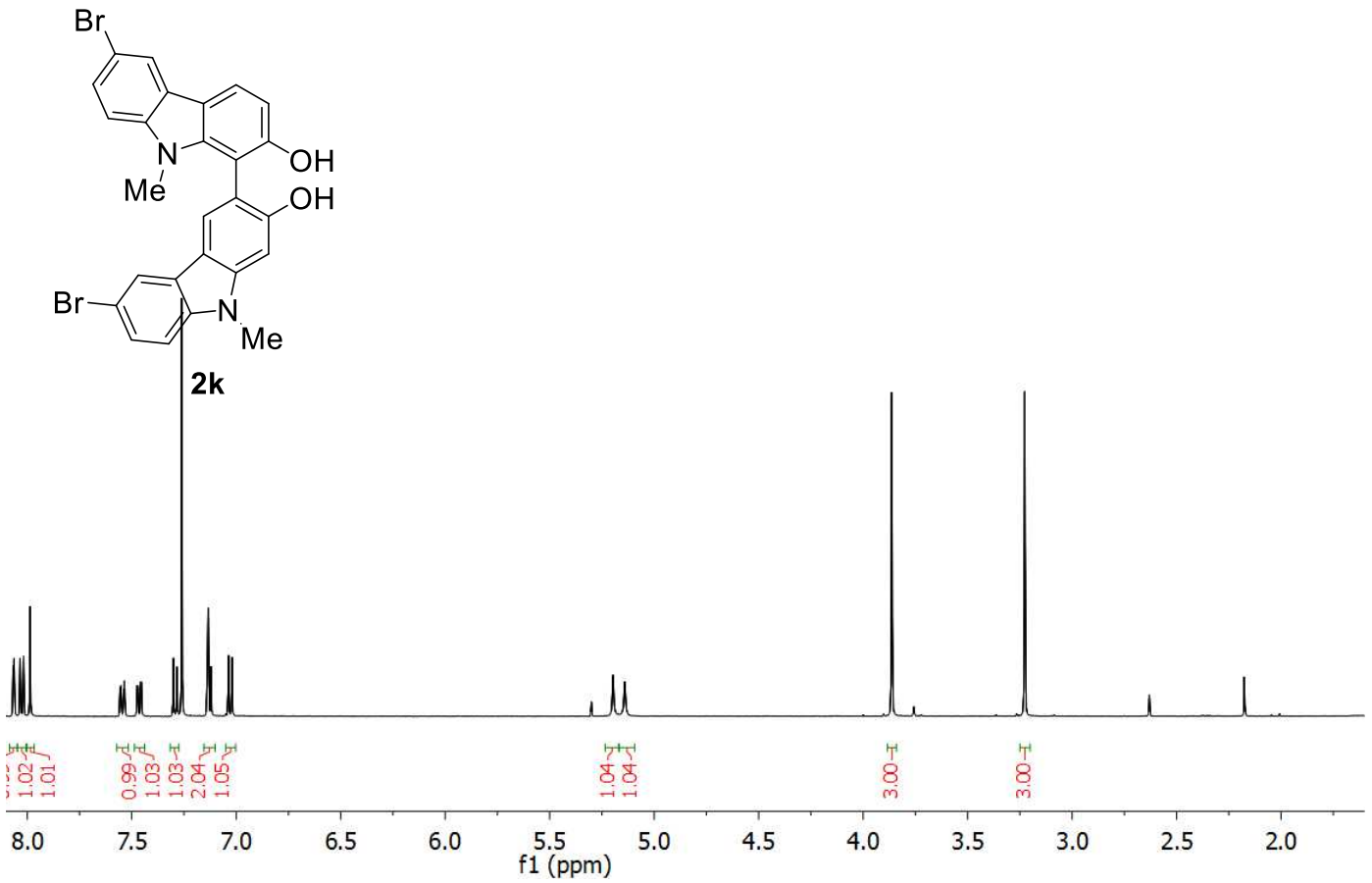
125 MHz ^{13}C NMR Spectrum of Compound **2i** in $CDCl_3$



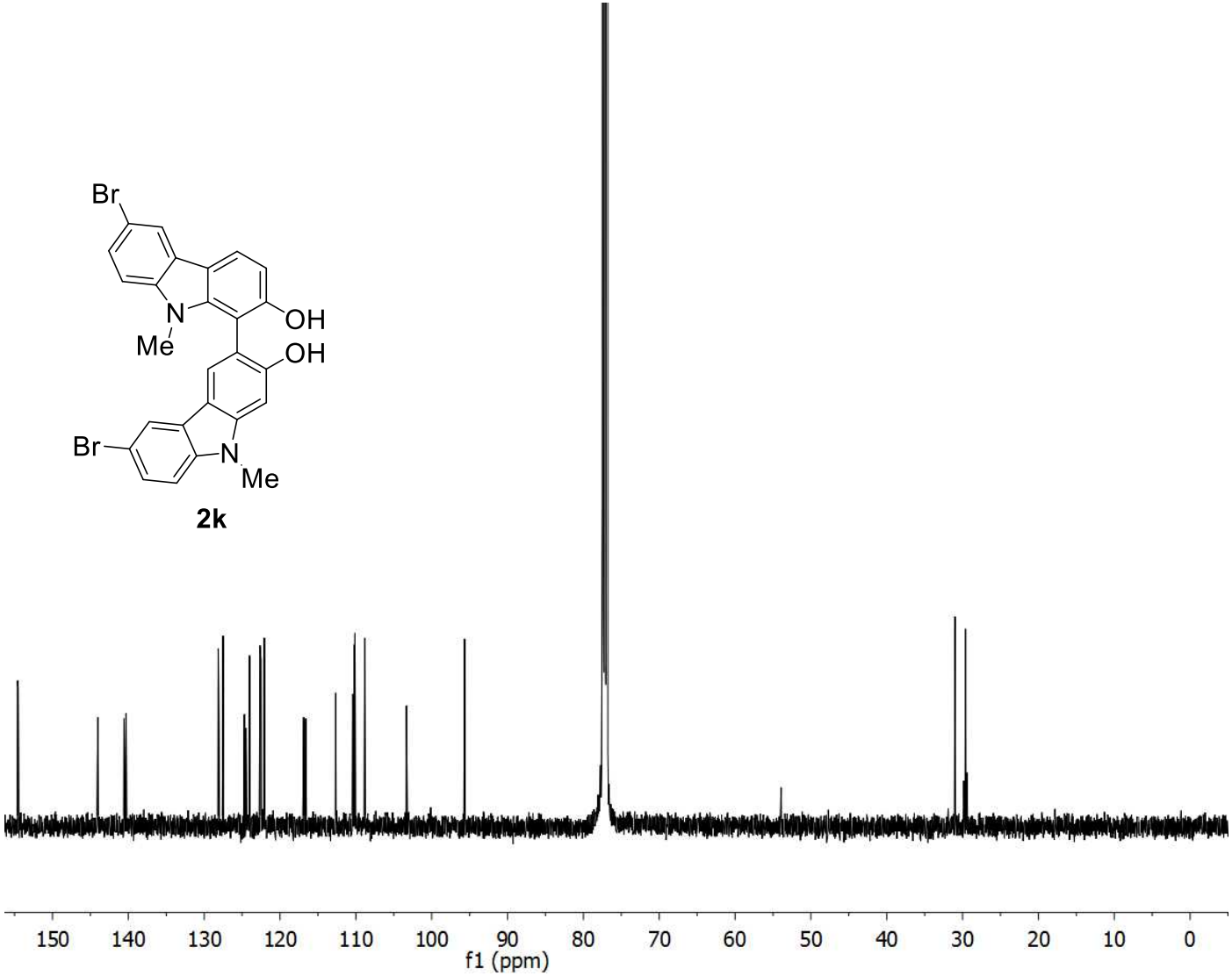
125 MHz ^{1}H NMR Spectrum of Compound **2j** in $CDCl_3$



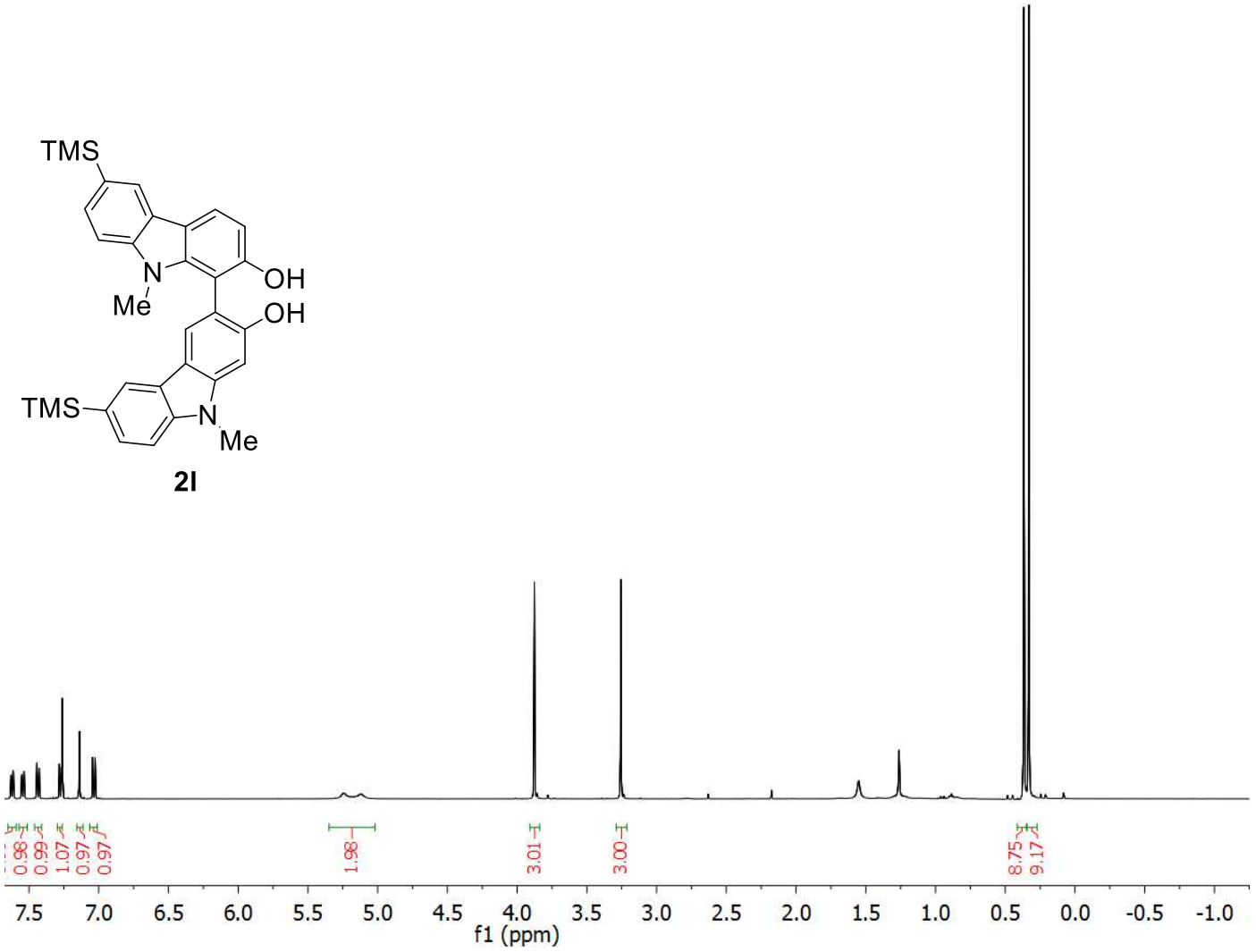
500 MHz ^{13}C NMR Spectrum of Compound **2j** n $CDCl_3$



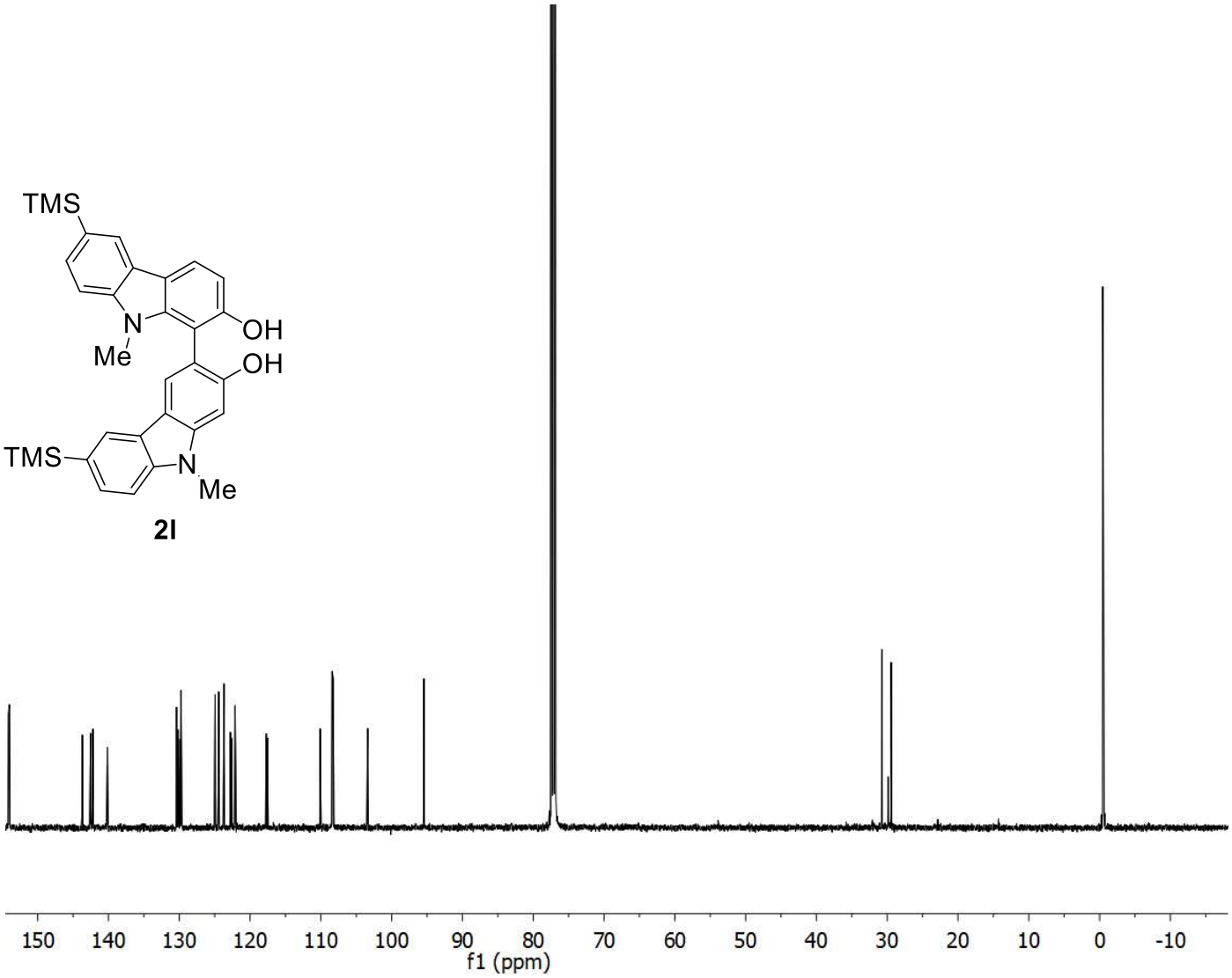
500 MHz ^{1}H NMR Spectrum of Compound **2k** in $CDCl_3$



125 MHz ^{13}C NMR Spectrum of Compound **2k** in $CDCl_3$



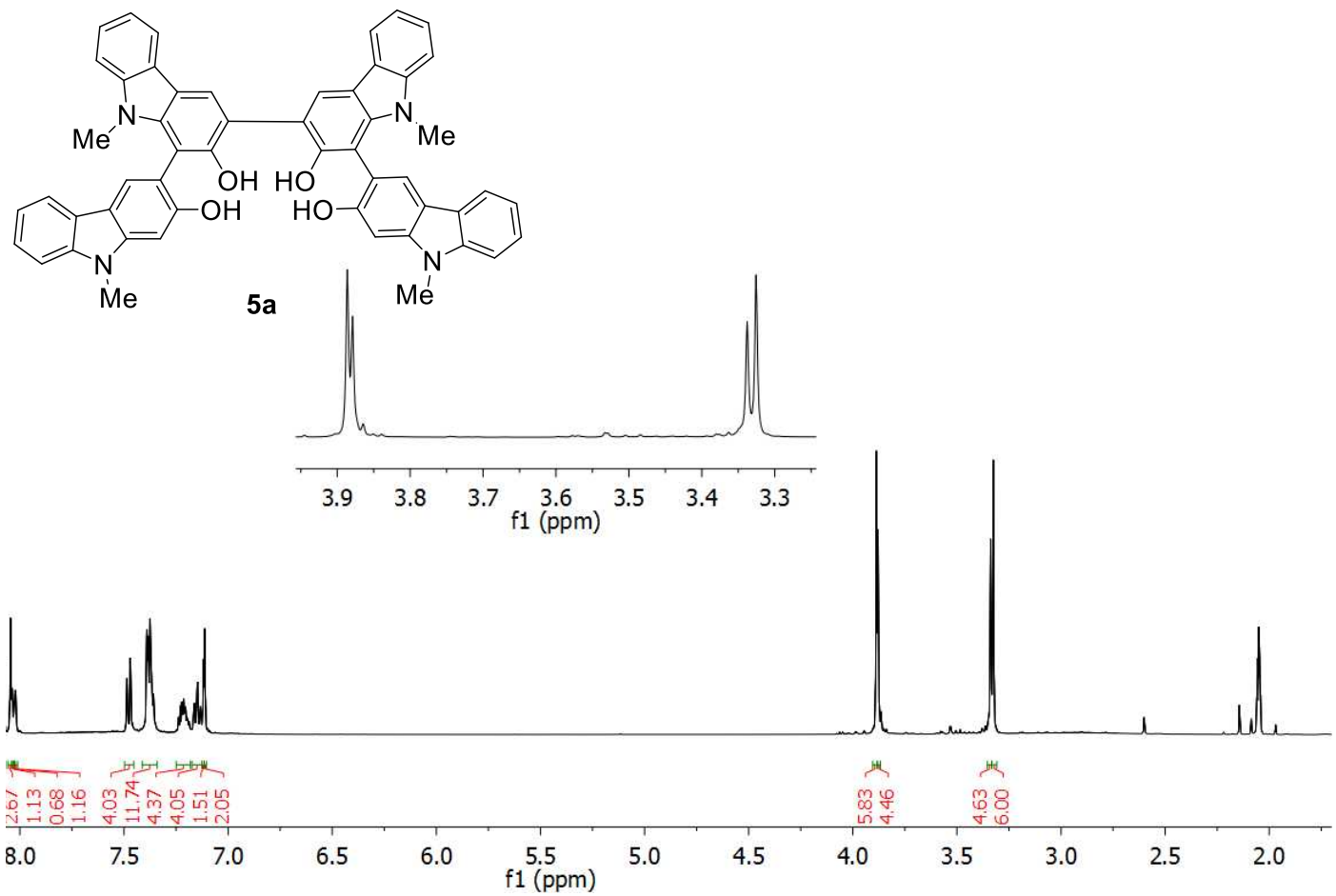
500 MHz ^{1}H NMR Spectrum of Compound **2l** in $CDCl_3$



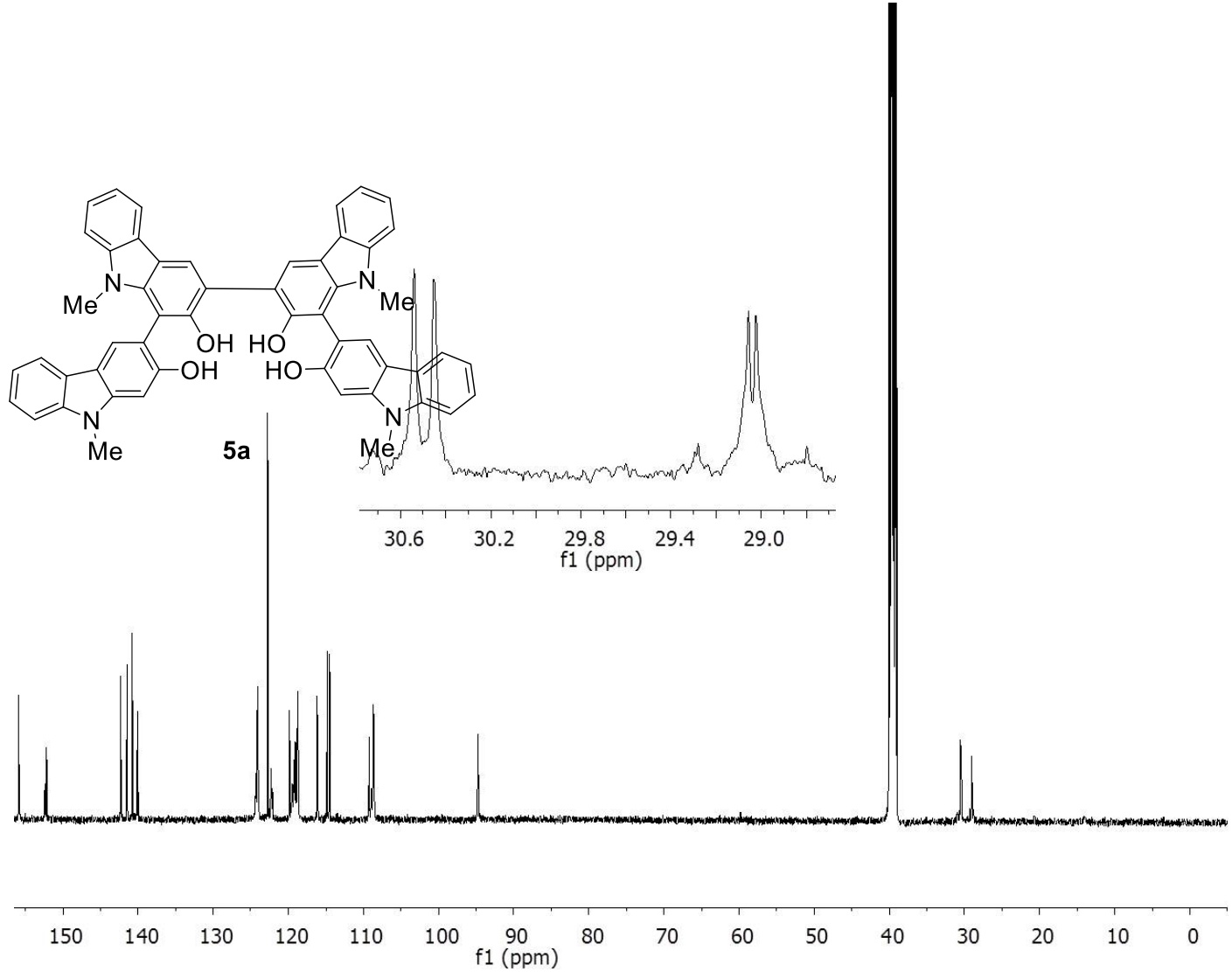
125 MHz ^{13}C NMR Spectrum of Compound **2l** in $CDCl_3$

500 MHz ^{1}H NMR Spectrum of Compound **2m** in $CDCl_3$

2m



500 MHz ^{1}H NMR Spectrum of Compound **5a** in acetone-d_6



125 MHz ^{13}C NMR Spectrum of Compound **5a** in DMSO-d_6

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$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$
where n = the number of reflections and p = the number of parameters refined.
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