Supporting information for

Condensation of 2-Methylindole with Acetophenones: an Unexpected Formation of 2-Arylanilines

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Table of Contents

Experimental.....S3
^{1}H NMR spectrum for **9**.....S16
^{13}C NMR spectrum for **9**.....S17
^{13}C NMR spectrum for **9** in $CDCl_3$.....S18
^{1}H NMR spectrum for **13a** in $CDCl_3$.....S19
^{13}C NMR spectrum for **13a** at 340K.....S20
^{1}H NMR spectrum for **13b**.....S21
^{13}C NMR spectrum for **13b**.....S22
^{1}H NMR spectrum for **13c**.....S23
^{13}C NMR spectrum for **13c**.....S24
^{1}H NMR spectrum for **13d**.....S25
^{13}C NMR spectrum for **13d** at 330K.....S26
^{1}H NMR spectrum for **13e**.....S27
^{13}C NMR spectrum for **13e**.....S28
^{1}H NMR spectrum for **13f** in $CDCl_3$.....S29
^{13}C NMR spectrum for **13f** in $CDCl_3$.....S30
^{1}H NMR spectrum for **13f** in DMSO.....S31
^{13}C NMR spectrum for **13f** in DMSO.....S32
^{1}H NMR spectrum for **13h**.....S33
^{13}C NMR spectrum for **13h** at 330K.....S34

^{1}H NMR spectrum for **13i**.....S35
^{13}C NMR spectrum for **13i** at 340K.....S36
^{1}H NMR spectrum for **13j**.....S37
^{13}C NMR spectrum for **13j**.....S38
^{1}H NMR spectrum for **13k**.....S39
^{13}C NMR spectrum for **13k** at 320K.....S40
^{1}H NMR spectrum for **13l**.....S41
^{13}C NMR spectrum for **13l** at 330K.....S42
^{1}H NMR spectrum for **13m**.....S43
^{13}C NMR spectrum for **13m**.....S44
^{1}H NMR spectrum for **14**.....S45
^{13}C NMR spectrum for **14**.....S46
^{1}H NMR spectrum for **13o** at rt.....S47
^{1}H NMR spectrum for **13o** at 370K.....S48
^{13}C NMR spectrum for **13o** at rt.....S49
^{1}H NMR spectrum for **13r**.....S50
^{13}C NMR spectrum for **13r** at 320K.....S51
^{1}H NMR spectrum for **13s** at rt.....S52
^{1}H NMR spectrum for **13s** at 375K.....S53
^{13}C NMR spectrum for **13s** at rt.....S54
^{1}H NMR spectrum for **13t** at rt.....S55
^{1}H NMR spectrum for **13t** at 350K.....S56
^{13}C NMR spectrum for **13t** at 345K.....S57
COSY spectrum for **13m**.....S58
HSQC spectrum for **13m**.....S59
HMBC spectrum for **13m**.....S60
HMBC region expansions for **13m**.....S61
NOE spectra for **13m**.....S62
COSY spectrum for **14**.....S63
HSQC spectrum for **14**.....S64
HMBC spectrum for **14**.....S65
HMBC region expansions for **14**.....S66
NOE spectra for **14**.....S67

Experimental

General information

Melting points were measured with a Mel-Temp apparatus, and were not corrected or calibrated. R_f values were obtained using SiO_2 in 1:5 EtOAc:hexanes. Infrared spectra were collected on a Thermo Fisher Scientific™ Nicolet TM iS™ 5 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AV-500 Bruker Avance III 500, Bruker HD-500 Avance III HD, Bruker AM-400 Avance III HD, or AX-400 Bruker Avance III HD spectrometers at ambient or specified temperature and are referenced to the solvent. Mass spectra were recorded on a Bruker Biotof II instrument using poly(ethylene glycol) as an internal calibrant. 2'-iodo, 3'-iodo, and 4'-iodo,[14] 2'-bromo, and 2'-chloroacetophenones[15] were prepared from the corresponding aminoacetophenones according to the reported procedures, purified by flash chromatography, and dried before use. Other acetophenones, reagents, and solvents were used as purchased.

General procedure for condensation of 2-methylindole with acetophenones

Concentrated aqueous HCl (1.5 ml) was added to a solution of 2-methylindole (0.263 g, 2.00 mmol, 1 eq) and acetophenone (0.725 g, 6.00 mmol, 3 eq) in MeOH (10 ml) under nitrogen atmosphere. The reaction mixtures were heated at reflux for the specified number of days (3 days in the case of unsubstituted acetophenone). Additional portions of methanol were added to bring the reaction mixture to the initial volumes if significant evaporation was observed. Upon completion, the reaction mixture was cooled, quenched with saturated sodium bicarbonate solution (30 ml), and extracted with DCM (3x60 ml/mmol). The combined DCM extracts were dried over anhydrous Na_2SO_4, and concentrated.

In the cases of 2'-, 3'-, and 4'-methoxyacetophenones (products **13f**, **13m**, and **13t**), the crude reaction mixture could be subjected directly to chromatography on silica gel in EtOAc-hexanes (1:9, with gradient to 1:4) to isolate the products. In other cases the starting acetophenone had very similar chromatographic mobility to the product, making direct separation difficult. Thus, the following operation was performed to reduce the acetophenone to a more polar alcohol:

The crude reaction mixture was dissolved in MeOH (10 ml), $NaBH_4$ (0.228 g, 6.00 mmol, 3 eq), was added, and the mixture was stirred at rt for 1 hour. After evaporation, the reaction mixture was partitioned between saturated aqueous sodium bicarbonate (20 ml) and EtOAc (80 ml/mmol). The layers were separated, and the aqueous layer was washed with EtOAc (2x20 ml), and the combined ethyl acetate layers were dried and concentrated. The crude product was purified by chromatography on silica gel, eluting with DCM-hexanes (3:7) to remove most byproducts, followed by gradient to DCM-EtOAc-hexanes (30:6:64) to elute the aniline product. If additional purification was necessary, crystallization, or chromatography in EtOAc-hexanes (7:93) was performed.

Note: many aniline products exhibited peak broadening in ^{1}H and ^{13}C NMR. The degree of this broadening depended on the structure, solvent, and concentration. Where specified, the spectra were obtained at elevated temperatures to reduce the broadening. In the cases of **13o** and **13s**, separate signals were observed for rotamers at rt. Merging of the peaks was observed at higher temperatures, but sufficiently sharp peaks were not observed at the highest temperature permitted by the variable temperature setup used.

2-(2-methyl-4,6-diphenylphenyl)aniline (**9**), obtained by general procedure from 2-methylindole and acetophenone as yellow oil; 486 mg (72%); R_f = 0.34 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3471, 3380, 3057, 3028, 1614, 1496, 1467, 1297, 1266, 1156, 881, 749; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 – 7.10 (m, 3H), 6.92 (td, *J* = 7.5, 1.6 Hz, 1H), 6.67 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.42 (td, *J* = 7.5, 1.2 Hz, 1H), 4.59 (br s, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.5 (C), 142.5 (C), 141.6 (C), 139.9 (C), 139.1 (C), 138.0 (C), 136.4 (C), 130.1 (CH), 128.9 (CH), 127.7 (CH), 127.5 (CH), 127.41 (CH), 127.37 (CH), 126.7 (CH), 126.4 (CH), 126.0 (CH), 124.3 (C), 116.2 (CH), 114.3 (CH), 20.0 (CH3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0 (C), 143.0 (C), 141.7 (C), 140.9 (C), 140.6 (C), 138.5 (C), 136.0 (C), 131.1 (CH), 129.3 (CH), 128.9 (CH), 128.24 (CH), 128.19 (CH), 127.7 (CH), 127.5 (CH), 127.3 (CH), 127.0 (CH), 126.7 (CH), 125.8 (C), 118.3 (CH), 115.0 (CH), 20.7 (CH3); HRMS (EI) $[M+H]^+$ calcd for $C_{25}H_{22}N$: 336.1747, found 336.1740; Anal. calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.28; H, 6.46; N, 4.16. Note: fewer than expected signals in ^{13}C NMR in DMSO-d_6 due to overlap of two phenyl CH signals (at 128.9). They are resolved in $CDCl_3$.

2-methyl-3-(1-phenylvinyl)indole (**10**), isolated from the reaction mixture in condensation of 2-methylindole and acetophenone performed by general procedure, with a modification: in ethanol at rt for 3 days. Obtained as a yellow oil, 93 mg (20%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.43-7.38 (m, 2H), 7.32 – 7.27 (m, 4H), 7.22 (d, *J* = 8.0, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 5.74 (d, *J* = 1.7 Hz, 1H), 5.34 (d, *J* = 1.7 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 142.0, 135.3, 133.3, 128.6, 128.3, 127.6, 127.4, 121.3, 119.7, 115.0, 114.1, 110.3, 127.5, 12.9; The spectroscopic properties for the compound match those previously reported in the literature.[4b,16]

2-methyl-3-(1-phenylethyl)indole (**11**), isolated from the reaction mixture in condensation of 2-methylindole and acetophenone when the reaction was performed at reflux in in ethanol for 1 day. Obtained as a yellow oil, 50 mg (10%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (br s, 1H), 7.42 (d, *J* = 7.7 Hz , 1H), 7.38 – 7.34 (m, 2H), 7.29 – 7.23 (m, 3H), 7.17 (t, *J* = 7.7 Hz , 1H), 7.09 (t, t, *J* = 7.7 Hz , 1H), 7.00 (t, t, *J* = 7.7 Hz , 1H), 4.44 (q, *J* = 7.3 Hz, 1H), 2.34 (s, 3H), 1.79 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 135.3, 130.7, 128.5, 128.2, 127.5, 125.7, 120.9, 119.4, 119.1, 116.1, 110.4, 35.6, 20.7, 12.4; The spectroscopic properties for the compound match those previously previously reported in the literature.[17]

2-Methyl-2-(2-oxo-2-phenylethyl)indolin-3-one (**12**), isolated from the reaction mixture in condensation of 2-methylindole and acetophenone when the reaction was performed in ethanol at rt for 11 days in air atmosphere. Obtained as a yellow oil, 20 mg (4%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.50 – 7.42 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 7.3 Hz, 1H), 5.71 (br s, 1H), 3.64 (d, *J* = 17.6 Hz, 1H), 2.92 (d, *J* = 17.6 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 198.6, 159.9, 137.7, 137.0, 133.8, 128.9, 128.2, 125.2, 119.0, 118.7, 112.4, 64.7, 44.0, 22.0; The spectroscopic properties for the compound match those previously reported in the literature.[18]

2-(2-methyl-4,6-di(4-chlorophenyl)phenyl)aniline (**13a**), obtained by general procedure from 2-methylindole (187 mg) and 4'-chloroacetophenone (661 mg) as white solid; 447 mg (77%); mp 150-151 °C; R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3473, 3383, 3052, 3029, 2923, 1614, 1494, 1465,1297, 1265, 1091, 1014, 824, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 1.5 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.15 (s, 4H), 7.06 (td, *J* = 7.6, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.71 – 6.62 (m, 2H), 3.52 (br s, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6,

340K): δ 145.1 (C), 141.0 (C), 140.0 (C), 138.3 (C), 137.9 (C), 137.6 (C), 136.4 (C), 132.1 (C), 131.1 (C), 130.4 (CH), 129.7 (CH), 128.5 (CH), 128.1 (CH), 127.6 (CH), 127.3 (CH), 127.0 (CH), 125.4 (CH), 123.6 (C), 116.0 (CH), 114.2 (CH), 19.5 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}Cl_2N$: 404.0967, found 404.0962; Anal. calcd for $C_{25}H_{19}Cl_2N$: C, 74.26; H, 4.74; N, 3.46; Cl, 17.54. Found: C, 73.99; H, 4.99; N, 3.30; Cl, 17.37.

2-(2-methyl-4,6-di(4-bromophenyl)phenyl)aniline (**13b**), obtained by general procedure from 2-methylindole (191 mg) and 4'-broromacetophenone (870 mg) as yellowish solid; 395 mg (55%); mp 170-171 °C; R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3471, 3381, 3048, 2921, 1613, 1491, 1465, 1297, 1264, 1074, 1010, 820, 749; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.73 (d, J = 8.5 Hz, 2H), 7.69 – 7.62 (m, 3H), 7.48 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.94 (td, J = 7.6, 1.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.57 (dd, J = 7.6, 1.6 Hz, 1H), 6.43 (td, J = 7.6, 1.0 Hz, 1H), 4.58 (br s, 2H), 2.13 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6): δ 145.6 (C), 141.3 (C), 140.7 (C), 138.9 (C), 138.3 (C), 137.9 (C), 136.8 (C), 131.8 (CH), 131.1 (CH), 130.3 (CH), 130.0 (CH), 128.8 (CH), 127.9 (CH), 127.6 (CH), 125.7 (CH), 123.7 (C), 121.0 (C), 120.0 (C), 116.1 (CH), 114.3 (CH), 20.0 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}Br_2N$: 491.9957, found 491.9956; Anal. calcd for $C_{25}H_{19}Br_2N$: C, 60.88; H, 3.88; N, 2.84; Br, 32.40. Found: C, 60.58; H, 4.12; N, 2.77; Br, 32.11.

2-(2-methyl-4,6-di(4-iodophenyl)phenyl)aniline (**13c**), obtained by general procedure from 2-methylindole (80 mg) and 4'-iodoacetophenone (450 mg) as yellowish solid; 206 mg (58%); mp 179-182 °C; R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3469, 3378, 3044, 3023, 2923, 1612, 1486, 1464, 1270, 1264, 1003, 817, 749; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.82 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.93 (td, J = 7.5, 1.6 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.57 (dd, J = 7.5, 1.6 Hz, 1H), 6.43 (t, J = 7.5, 1H), 4.57 (br s, 2H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.6 (C), 141.5 (C), 141.1 (C), 139.2 (C), 138.3 (C), 138.0 (C), 137.6 (CH), 136.70 (C), 136.2 (CH), 131.2 (CH), 130.0 (CH), 128.9 (CH), 127.9 (CH), 127.4 (CH), 125.5 (C), 123.7 (CH), 116.1 (CH), 114.3 (CH), 93.9 (C), 92.9 (C), 20.0 (CH3); HRMS (ESI) $[M+H]^+$ calcd for

$C_{25}H_{20}I_2N$: 587.9680, found 587.9706; Anal. calcd for $C_{25}H_{19}I_2N$: C, 51.13; H, 3.26; N, 2.39; I, 43.22. Found: C, 51.18; H, 3.30; N, 2.48; I, 43.22.

2-(2-methyl-4,6-di(4-fluorophenyl)phenyl)aniline (**13d**), obtained by general procedure from 2-methylindole (171 mg) and 4'-fluoroacetophenone (540 mg) as white solid; 385 mg (79%); mp 123-124 ºC; R_f = 0.31 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3474, 3383, 3045, 2924, 1607, 1511, 1468, 1297, 1264, 1223, 1158, 810, 750; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.83 – 7.78 (m, 2H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.33-7.25 (m, 4H), 6.99 (t, *J* = 8.5 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.43 (t, *J* = 7.5 Hz, 1H), 4.62 (br s, 2H), 2.12 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 330K): δ 161.7 (d, *J* = 245 Hz, C), 160.8 (d, *J* = 245 Hz, C), 145.2 (C), 141.2 (C), 137.9 (C), 137.8 (C), 137.6 (d, *J* = 3 Hz, C), 136.2 (C), 136.1 (d, *J* = 3 Hz, C), 130.5 (d, *J* = 8 Hz, CH), 129.8 (CH), 128.4 (d, *J* = 8 Hz, CH), 127.5 (CH), 127.2 (CH), 125.6 (CH), 123.9 (C), 116.0 (CH), 115.3 (d, *J* = 21 Hz, CH), 114.2 (CH), 113.9 (d, *J* = 21 Hz, CH), 19.6 (CH3);^{19}F NMR (376 MHz, $CDCl_3$): δ -115.6, -116.6; HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}F_2N$: 372.1558, found 372.1559; Anal. calcd for $C_{25}H_{19}F_2N$: C, 80.84; H, 5.16; N, 3.77; F, 10.23. Found: C, 80.55; H, 5.43; N, 3.84; F, 10.24. Note: the ^{13}C NMR spectrum was obtained at 330K to reduce peak broadening.

2-(2-methyl-4,6-di(4-methylphenyl)phenyl)aniline (**13e**), obtained by general procedure from 2-methylindole (188 mg) and 4'-methylacetophenone (577 mg) as yellow oil; 367 mg (70%); R_f = 0.35 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3471, 3379, 3023, 2919, 1613, 1515, 1497, 1468, 1451, 1296, 1265, 1003, 815, 748; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.92 (td, *J* = 7.5, 1.6 Hz, 1H), 6.65 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.42 (td, *J* = 7.5, 1.2 Hz, 1H), 4.51 (s, 2H), 2.35 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6): δ 145.6 (C), 142.3 (C), 139.0 (C), 138.7 (C), 137.9 (C), 137.1 (C), 136.7 (C), 136.0 (C), 135.3 (C), 130.1 (CH), 129.5 (CH), 128.8 (CH), 128.1 (CH), 127.7 (CH), 126.9 (CH), 126.5 (CH), 125.8 (CH), 124.5 (C), 116.2 (CH), 114.2 (CH),

20.7 (CH3), 20.6 (CH3), 20.1 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}N$: 364.2060, found 364.2070; Anal. calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85. Found: C, 89.15; H, 7.05; N, 3.88.

2-(2-methyl-4,6-di(4-methoxyphenyl)phenyl)aniline (**13f**), obtained by general procedure from 2-methylindole (184 mg) and 4'-methoxyacetophenone (632 mg) as yellow oil; 296 mg (53%); R_f = 0.15 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3468, 3376, 3033, 3000, 2956, 2933, 2836, 1610, 1508, 1459, 1290, 1242, 1179, 1033, 829, *737*; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.48-7.52 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.07 (td, *J* = 7.7, 1.6 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.87 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.72 – 6.54 (m, 2H), 3.88 (s, 3H), 3.76 (s, 3H), 3.35 (br s, 2H), 2.22 (s, 3H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.92 (td, *J* = 7.5, 1.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.65 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.43 (td, *J* = 7.5, 1.2 Hz, 1H), 4.49 (s, 2H), 3.80 (s, 3H), 3.67 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4 (C), 158.4 (C), 144.0 (C), 142.4 (C), 140.2 (C), 138.3 (C), 135.3 (C), 134.2 (C), 133.4 (C), 131.1 (CH), 130.3 (CH), 128.2 (CH), 128.1 (CH), 127.4 (CH), 126.5 (CH), 126.0 (C), 118.4 (CH), 115.1 (CH), 114.4 (CH), 113.2 (CH), 55.5 (CH3), 55.2 (CH3), 20.7 (CH3); ^{13}C NMR (101 MHz, DMSO-d_6): δ 158.9 (C), 157.9 (C), 145.6 (C), 142.0 (C), 138.8 (C), 137.9 (C), 135.6 (C), 134.0 (C), 132.4 (C), 130.2 (CH), 130.1 (CH), 127.8 (CH), 127.7 (CH), 126.6 (CH), 125.6 (CH), 124.7 (C), 116.3 (CH), 114.4 (CH), 114.3 (CH), 113.0 (CH), 55.2 (CH3), 54.9 (CH3), 20.2 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}NO_2$: 396.1958, found 396.1960; Anal. calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.85; H, 6.44; N, 3.65.

2-(2-methyl-4,6-di(3-chlorophenyl)phenyl)aniline (**13h**), obtained by general procedure from 2-methylindole (164 mg) and 3'-chloroacetophenone (580 mg) as yellow oil; 280 mg (55%); R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3473, 3383, 3061, 3024, 2978, 2921, 1615, 1594, 1557, 1499, 1463, 1296, 1265, 1081, 1003, 872, 785, 739, ; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.86 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* =

2.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.27 – 7.14 (m, 3H), 7.02 – 6.89 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.46 (t, *J* = 8.0 Hz, 1H), 4.75 (s, 2H), 2.14 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 330K): δ 144.8 (C), 143.2 (C), 141.7 (C), 140.9 (C), 138.0 (C), 137.5 (C), 136.7 (C), 133.5 (C), 132.0 (C), 130.4 (CH), 129.8 (CH), 128.8 (CH), 128.5 (CH), 127.72 (CH), 127.71 (CH), 127.4 (CH), 127.0 (CH), 126.2 (CH), 126.1 (CH), 125.7 (CH), 125.2 (CH), 123.7 (C), 116.3 (CH), 114.4 (CH), 19.6 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}Cl_2N$: 404.0967, found 404.0964; Anal. calcd for $C_{25}H_{19}Cl_2N$: C, 74.26; H, 4.74; N, 3.46; Cl, 17.54. Found: C, 74.34; H, 4.89; N, 3.36; Cl, 17.35.

1,3,5-tri(3-chlorophenyl)benzene, isolated from the reaction mixture in condensation of 2-methylindole (164 mg) and 3'-chloroacetophenone (580 mg) according to the general procedure. Obtained as a white solid, 55 mg (11%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 3H), 7.67 (t, *J* = 1.7 Hz, 3H), 7.56 (dt, *J* = 7.5, 1.7 Hz, 3H), 7.42 (t, *J* = 7.5 Hz, 3H), 7.38 (dt, *J* = 7.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.5, 135.0, 130.3, 128.0, 127.6, 125.6; The spectroscopic properties for the compound match those previously reported in the literature.[20b]

2-(2-methyl-4,6-di(3-bromophenyl)phenyl)aniline (**13i**), obtained by general procedure from 2-methylindole (175 mg) and 3'-bromoacetophenone (797 mg) as yellow oil; 395 mg (60%); R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3472, 3381, 3059, 3024, 1614, 1591, 1557, 1462, 1296, 1264, 1071, 1003, 872, 749; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.96 (td, *J* = 7.5, 1.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.46 (t, *J* = 7.5 Hz, 1H), 4.75 (s, 2H), 2.14 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 340K): δ 144.7 (C), 143.4 (C), 141.9 (C), 140.8 (C), 138.0 (C), 137.4 (C), 136.7 (C), 131.3 (CH), 130.5 (CH), 129.9 (CH), 129.7 (CH), 129.04 (CH), 129.01 (CH), 128.9 (CH), 127.73 (CH), 127.65 (CH), 125.6 (CH), 125.5 (CH), 123.7 (C), 122.0 (C), 120.5 (C), 116.3 (CH), 114.4

(CH), 19.5 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}Br_2N$: 491.9957, found 491.9980; Anal. calcd for $C_{25}H_{19}Br_2N$: C, 60.88; H, 3.88; N, 2.84; Br, 32.40. Found: C, 61.04; H, 4.01; N, 2.93; Br, 32.66. Note: the ^{13}C NMR spectrum was obtained at 330K to reduce peak broadening. One less signal is observed in ^{13}C NMR than expected due to overlap of two aromatic CH signals (at 127.65). The signals are resolved at rt.

1,3,5-tri(3-bromophenyl)benzene, isolated from the reaction mixture in condensation of 2-methylindole (175 mg) and 3'-bromoacetophenone (797 mg) according to the general procedure. Obtained as a white solid, 123 mg (16%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (t, J = 1.7 Hz, 3H), 7.71 (s, 3H), 7.60 (d, J = 7.7 Hz, 3H), 7.54 (d, J = 7.7 Hz, 3H), 7.36 (t, J = 7.7 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 141.4, 131.0, 130.6, 130.5, 126.1, 125.7, 123.2. The spectroscopic properties for the compound match those previously reported in the literature.[20a]

2-(2-methyl-4,6-di(3-iodophenyl)phenyl)aniline (**13j**), obtained by general procedure from 2-methylindole (150 mg) and 3'-iodoacetophenone (844 mg) as yellow oil; 321 mg (48%) ; R_f = 0.32 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3470, 3379, 3054, 3027, 2973, 2919, 1613, 1586, 1553, 1499, 1460, 1297, 1264, 1061, 1003, 874, 749; ^1H NMR (400 MHz, DMSO-d_6): δ 8.12 (t, J = 1.8 Hz, 1H), 7.79 (dt, J = 8.0, 1.3 Hz, 1H), 7.74 (dt, J = 8.0, 1.3 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.53 – 7.45 (m, 2H), 7.32 – 7.23 (m, 2H), 6.97 (t, J = 8.0 Hz, 1H), 6.94 (td, J = 7.5, 1.6 Hz, 1H), 6.67 (dd, J = 7.5, 1.2 Hz, 1H), 6.57 (dd, J = 7.5, 1.6 Hz, 1H), 6.43 (td, J = 7.5, 1.2 Hz, 1H), 4.57 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.6 (C), 143.6 (C), 142.1 (C), 141.0 (C), 138.3 (C), 137.6 (C), 137.5 (CH), 137.0 (C), 136.1 (CH), 135.14 (CH), 135.09 (CH), 131.0 (CH), 129.9 (CH), 129.5 (CH), 128.4 (CH), 127.9 (CH), 127.9 (CH), 126.3 (CH), 125.9 (CH), 123.6 (C), 116.2 (CH), 114.3 (CH), 95.6 (C), 94.0 (C), 19.9 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}I_2N$: 587.9680, found 587.9685; Anal. calcd for $C_{25}H_{19}I_2N$: C, 51.13; H, 3.26; N, 2.39; I, 43.22. Found: C, 51.31; H, 3.16; N, 2.37; I, 42.96.

2-(2-methyl-4,6-di(3-fluorophenyl)phenyl)aniline (**13k**), obtained by general procedure from 2-methylindole (197 mg) and 3'-fluoroacetophenone (622 mg) as a white solid; 412 mg (74%); mp 109-110 ^{o}C; R_f = 0.31 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3474, 3384, 3062, 2922, 1612, 1490, 1467, 1297, 1266, 1197, 1171, 1158, 866, 748; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.70 (d, *J* = 2.0 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.51 (td, *J* = 8.0, 6.0 Hz, 1H), 7.21 (td, *J* = 8.0, 6.0 Hz, 2H), 7.15 – 7.07 (m, 2H), 7.01 – 6.90 (m, 2H), 6.69 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.43 (td, *J* = 7.5, 1.2 Hz, 1H), 4.61 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6, 320K): δ 162.6 (d, *J* = 244 Hz, C), 161.3 (d, *J* = 244 Hz, C), 145.4 (C), 143.7 (d, *J* = 8 Hz, C), 142.1 (d, *J* = 8 Hz, C), 141.1 (d, *J* = 2 Hz, C), 138.1 (C), 137.7 (d, *J* = 3 Hz, C), 136.9 (C), 130.5 (d, *J* = 9 Hz, CH), 129.8 (CH), 129.0 (d, *J* = 8 Hz, CH), 127.8 (CH), 127.7 (CH), 125.8 (CH), 125.0 (d, *J* = 3 Hz, CH), 123.7 (C), 122.6 (d, *J* = 3 Hz, CH), 116.1 (CH), 115.6 (d, *J* = 21 Hz, CH), 114.2 (CH), 113.9 (d, *J* = 21 Hz, CH), 113.3 (d, *J* = 22 Hz, CH), 113.0 (d, *J* = 22 Hz, CH), 19.7 (CH3); ^{19}F NMR (376 MHz, $CDCl_3$): δ -113.5, -114.7; HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}F_2N$: 372.1558, found 372.1576; Anal. calcd for $C_{25}H_{19}F_2N$: C, 80.84; H, 5.16; N, 3.77; F, 10.23. Found: C, 80.65; H, 5.48; N, 3.67; F, 10.02.

2-(2-methyl-4,6-di(3-methylphenyl)phenyl)aniline (**13l**), obtained by general procedure from 2-methylindole (158 mg) and 3'-methylacetophenone (490 mg) as yellow oil; 326 mg (74%); R_f = 0.35 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3471, 3380, 3026, 2922, 1612, 1500, 1452, 1295, 1265, 1003, 876, 786, 748;^{1}H NMR (400 MHz, DMSO-d_6): δ 7.60 (d, *J* = 2.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (s, 1H), 7.03 (s, 1H), 7.02 (s, 1H), 6.99 – 6.89 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 4.73 (s, 2H), 2.39 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 330K): δ 145.2 (C), 142.2 (C), 141.3 (C), 139.7 (C), 139.0 (C), 137.7 (C), 137.6 (C), 136.1 (C), 136.0 (C), 129.8 (CH), 129.4 (CH), 128.5 (CH), 127.7 (CH), 127.4 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.7 (CH), 125.8 (CH), 125.7 (CH), 124.3 (C), 123.5 (CH), 116.0 (CH), 114.0 (CH), 20.8 (CH3), 20.7 (CH3), 19.7 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}N$: 364.2060, found 364.2070; Anal. calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85. Found: C, 88.92; H, 7.09; N, 3.87.

2-(2-methyl-4,6-di(3-methoxyphenyl)phenyl)aniline (**13m**), obtained by general procedure from 2-methylindole (174 mg) and 3'-methoxyacetophenone (598 mg) as yellow oil; 218 mg (42%); R_f = 0.16 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3467, 3376, 3052, 3000, 2936, 1597, 1491, 1466, 1287, 1229, 1172, 1048, 866, 783, 750; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 2 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.85 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.72 – 6.65 (m, 2H), 6.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.43 (td, *J* = 7.5, 1.2 Hz, 1H), 4.57 (br s, 2H), 3.83 (s, 3H), 3.59 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 159.8 (C), 158.3 (C), 145.7 (C), 142.9 (C), 142.2 (C), 141.5 (C), 139.1 (C), 138.0 (C), 136.5 (C), 129.9 (CH), 128.5 (CH), 127.7 (CH), 127.5 (CH), 125.9 (CH), 124.5 (C), 121.2 (CH), 119.1 (CH), 116.2 (CH), 114.21 (CH), 114.22 (CH), 113.1 (CH), 112.6 (CH), 112.1 (CH), 55.1 (CH3), 54.6 (CH3), 20.0 (CH3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.1 (C), 158.9 (C), 144.0 (C), 143.0 (C), 142.7 (C), 142.4 (C), 140.5 (C), 138.5 (C), 136.1 (C), 131.0 (CH), 129.9 (CH), 128.7 (CH), 128.3 (CH), 128.3 (CH), 126.9 (CH), 125.8 (C), 121.7 (CH), 119.8 (CH), 118.4 (CH), 115.0 (CH), 114.5 (CH), 113.14 (CH), 113.10 (CH), 112.9 (CH), 55.5 (CH3), 55.2 (CH3), 20.7 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}NO_2$: 396.1958, found 396.1965; Anal. calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.77; H, 6.65; N, 3.54. Note: fewer than expected signals in ^{13}C NMR in DMSO-d_6 due to overlap of two aryl CH signals (at 129.9). They are resolved in $CDCl_3$.

3-(5-methoxy-1-(3-methoxyphenyl)-1-methyl-1H-inden-3-yl)-2-methyl-1H-indole (**14**), isolated from the reaction mixture of condensation of 2-methylindole (174 mg) and 3'-methoxyacetophenone (598 mg), as yellow oil; 224 mg (43%); R_f = 0.11 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3403, 3053, 2962, 2936, 1604, 1582, 1460, 1431, 1290, 1266, 1242, 1041, 742;^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (br s, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.78 (t, *J* = 2.8 Hz, 1H), 6.76 (t, *J* = 2.8 Hz, 1H), 6.55 (s, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 2.51 (s, 3H), 1.89 (s, 3H);^{13}C NMR (126 MHz, $CDCl_3$): δ 159.7 (C), 159.1 (C), 146.2 (C), 145.9 (CH), 145.6 (C), 145.3 (C), 135.5 (C), 135.2 (C), 132.8 (C), 129.4 (CH), 128.4 (C), 123.3 (CH), 121.6 (CH), 119.81 (CH), 119.79 (CH), 118.8 (CH), 112.6 (CH), 111.5 (CH), 111.2 (CH), 110.4 (CH), 108.1 (C), 107.5 (CH), 55.6 (CH3), 55.5 (C), 55.2 (CH3), 23.6 (CH3), 13.0 (CH3); HRMS (ESI)

$[M+Na]^+$ calcd for $C_{27}H_{25}NO_2Na$: 418.1778, found 418.1769; Anal. calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.70; H, 6.59; N, 3.54.

2-(2-methyl-4,6-di(2-chlorophenyl)phenyl)aniline (**13o**), obtained by general procedure from 2-methylindole (180 mg) and 2'-chloroacetophenone (636 mg) as yellow oil; 55 mg (10%); R_f = 0.31 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3471, 3382, 3056, 2922, 1614, 1499, 1458, 1297, 1265, 1044, 1003, 888, 751;^{1}H NMR (400 MHz, DMSO-d_6, 370K): δ 7.55 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.50 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.34 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.25 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.16 (td, *J* = 7.5, 1.6 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.89 (td, *J* = 7.6, 1.6 Hz, 1H), 6.77 (br s, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 4.25 (s, 2H), 2.17 (s, 3H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.58 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.55 – 7.33 (m, 5H), 7.30 – 7.11 (m, 3.3H), 7.06 (td, *J* = 7.5, 1.2 Hz, 0.7H), 6.90 (d, *J* = 7.5 Hz, 0.6H), 6.86 (td, *J* = 7.5, 1.6 Hz, 0.7H), 6.68 – 6.58 (m, 1.4H), 6.55 (d, *J* = 7.5 Hz, 0.3H), 6.49 (t, *J* =7.5 Hz, 0.3H), 6.35 (td, *J* = 7.5, 1.2 Hz, 0.7H), 4.62 (s, 1.4H), 4.26 (s, 0.6H), 2.14 (s, 2.1H), 2.13 (s, 0.9H);^{13}C NMR (126 MHz, DMSO-d_6): δ 145.4 (C), 144.9 (C), 140.1 (C), 139.24 (C), 139.20 (C), 139.1 (C), 138.7 (C), 137.6 (C), 137.4 (C), 137.3 (C), 137.2 (C), 137.04 (C), 136.97 (C), 132.7 (CH), 132.08 (C), 132.06 (C), 131.6 (CH), 131.3 (C), 131.0 (CH), 130.7 (CH), 130.5 (CH), 130.2 (CH), 130.02 (CH), 129.99 (CH), 129.3 (CH), 129.2 (CH), 129.01 (CH), 128.96 (CH), 128.78 (CH), 128.75 (CH), 128.66 (CH), 128.57 (CH), 127.90 (CH), 127.86 (CH), 127.6 (CH), 126.2 (CH), 125.9 (CH), 124.0 (C), 122.9 (C), 116.1 (CH), 115.9 (CH), 114.6 (CH), 114.2 (CH), 20.2 (CH3), 19.7 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}Cl_2N$: 404.0967, found 404.0983; Anal. calcd for $C_{25}H_{19}Cl_2N$: C, 74.26; H, 4.74; N, 3.46; Cl, 17.54. Found: C, 74.39; H, 4.82; N, 3.60; Cl, 17.36. Notes: At rt, the number of signals in ^{13}C NMR was expected to double due to rotamers. 5 fewer signals than expected were observed in ^{13}C NMR due to overlap. Integration of the signals in the inverse-gated ^{13}C NMR spectrum indicated that the signal at 139.20 accounted for 3 signals, and the signals at 131.6, 131.3, 127.6 account for 2 signals each.

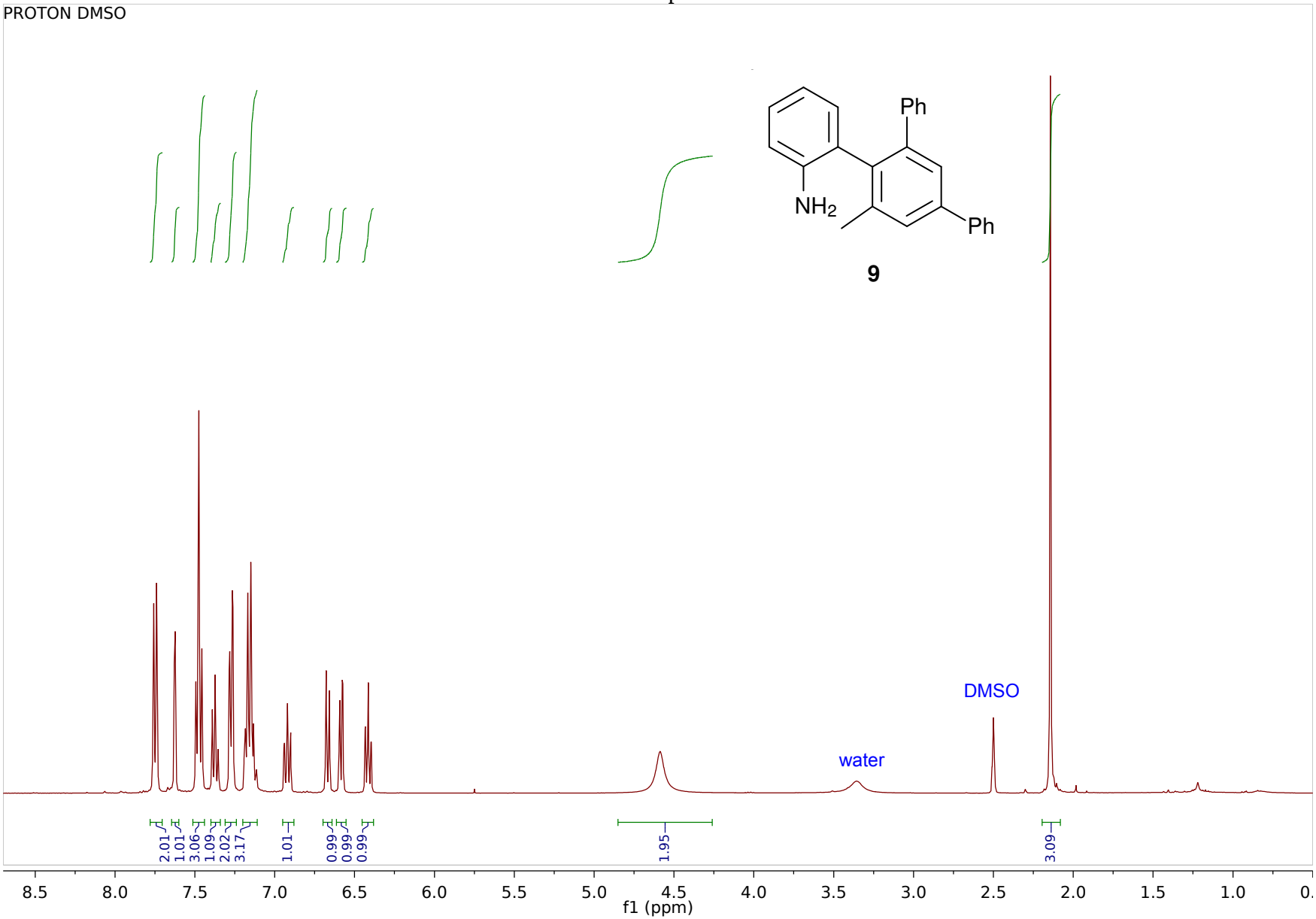
2-(2-methyl-4,6-di(2-fluorophenyl)phenyl)aniline (**13r**), obtained by general procedure from 2-methylindole (158 mg) and 2'-fluoroacetophenone (500 mg) as yellow oil; 270 mg (60%); R_f = 0.31 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3473, 3383, 3060, 2971, 2921, 1614, 1580, 1494, 1452, 1297, 1265, 1217, 1156, 831, 750;^{1}H NMR (400 MHz, DMSO-d_6): δ 7.62 (td, *J* = 8.0, 1.6 Hz, 1H), 7.57 (s, 1H), 7.48 – 7.38 (m, 1H), 7.36 (s, 1H), 7.35-7.28 (m, 2H), 7.28 – 7.14 (m, 2H), 7.05 (dd, *J* = 10.0, 8.0 Hz, 1H), 6.97 (td, *J* = 7.5, 1.2 Hz, 1H), 6.89 (td, *J* = 7.5, 1.6 Hz, 1H), 6.64 (dd, *J* = 10.0, 8.0 Hz, 2H), 6.42 (t, *J* = 7.5 Hz, 1H), 4.60 (s, 2H), 2.15 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 320K): δ 159.1 (d, *J* = 247 Hz, C), 158.8 (d, *J* = 244 Hz, C), 144.8 (C), 137.64 (C), 137.62 (C), 136.0 (C), 133.7 (C), 131.3 (d, *J* = 3 Hz, CH), 130.6 (d, *J* = 3 Hz, CH), 129.8 (d, *J* = 3 Hz, CH), 129.5 (CH), 129.4 (d, *J* = 8 Hz, CH), 128.8 (d, *J* = 8 Hz, CH), 128.5 (d, *J* = 16 Hz, C), 128.2 (br s, CH), 127.7 (CH), 127.5 (d, *J* = 13 Hz, C), 124.7 (d, *J* = 3 Hz, CH), 123.7 (C), 123.2 (d, *J* = 3 Hz, CH), 116.1 (CH), 115.9 (d, *J* = 22 Hz, CH), 114.7 (d, *J* = 22 Hz, CH), 114.4 (CH), 19.7 (CH3);^{19}F NMR (376 MHz, $CDCl_3$): δ -115.6, -118.3; HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{20}F_2N$: 372.1558, found 372.1566; Anal. calcd for $C_{25}H_{19}F_2N$: C, 80.84; H, 5.16; N, 3.77; F, 10.23. Found: C, 80.87; H, 5.27; N, 3.74; F, 10.12.

2-(2-methyl-4,6-di(2-methylphenyl)phenyl)aniline (**13s**), obtained by general procedure from 2-methylindole (155 mg) and 2'-methylacetophenone (470 mg) as yellow oil; 114 mg (27%); R_f = 0.35 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3473, 3381, 3057, 3019, 2953, 2923, 1613, 1500, 1490, 1453, 1296, 1266, 1046, 1003, 888, 755; ^{1}H NMR (400 MHz, DMSO-d_6, 375K): δ 7.34 – 7.22 (m, 5H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.88 (td, *J* = 7.5, 1.6 Hz, 1H), 6.70 (br s, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.42 (t, *J* = 7.5 Hz, 1H), 4.19 (s, 2H), 2.35 (s, 3H), 2.174 (s, 3H), 2.166 (s, 3H); ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.35 – 7.20 (m, 5H), 7.14 – 6.93 (m, 4.3H), 6.91 – 6.80 (m, 2H), 6.64 (dd, *J* = 8.0 Hz, 0.7H), 6.57 (d, *J* = 8.0 Hz, 0.3H), 6.54 (dd, *J* = 7.5, 1.6 Hz, 0.7H), 6.42 (t, *J* = 7.5 Hz, 0.3H), 6.33 (t, *J* = 7.5 Hz, 0.7H), 4.56 (s, 1.4H), 4.34 (s, 0.6H), 2.33 (s, 3H), 2.18 (s, 2.1H), 2.14 (s, 0.9H), 2.13 (s, 2.1H), 2.12 (s, 0.9H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 145.4 (C), 144.8 (C), 141.3 (C), 141.2 (C), 141.0 (C), 140.9 (C), 140.8 (C), 139.7 (C), 139.6 (C), 137.3 (C), 137.2 (C), 136.2 (C), 136.1 (C), 135.3 (C), 134.8 (C), 134.6 (C), 131.2 (CH), 130.9 (CH), 130.4 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 126.6 (CH), 126.4 (CH), 125.9 (CH), 124.70 (CH), 124.65 (C),

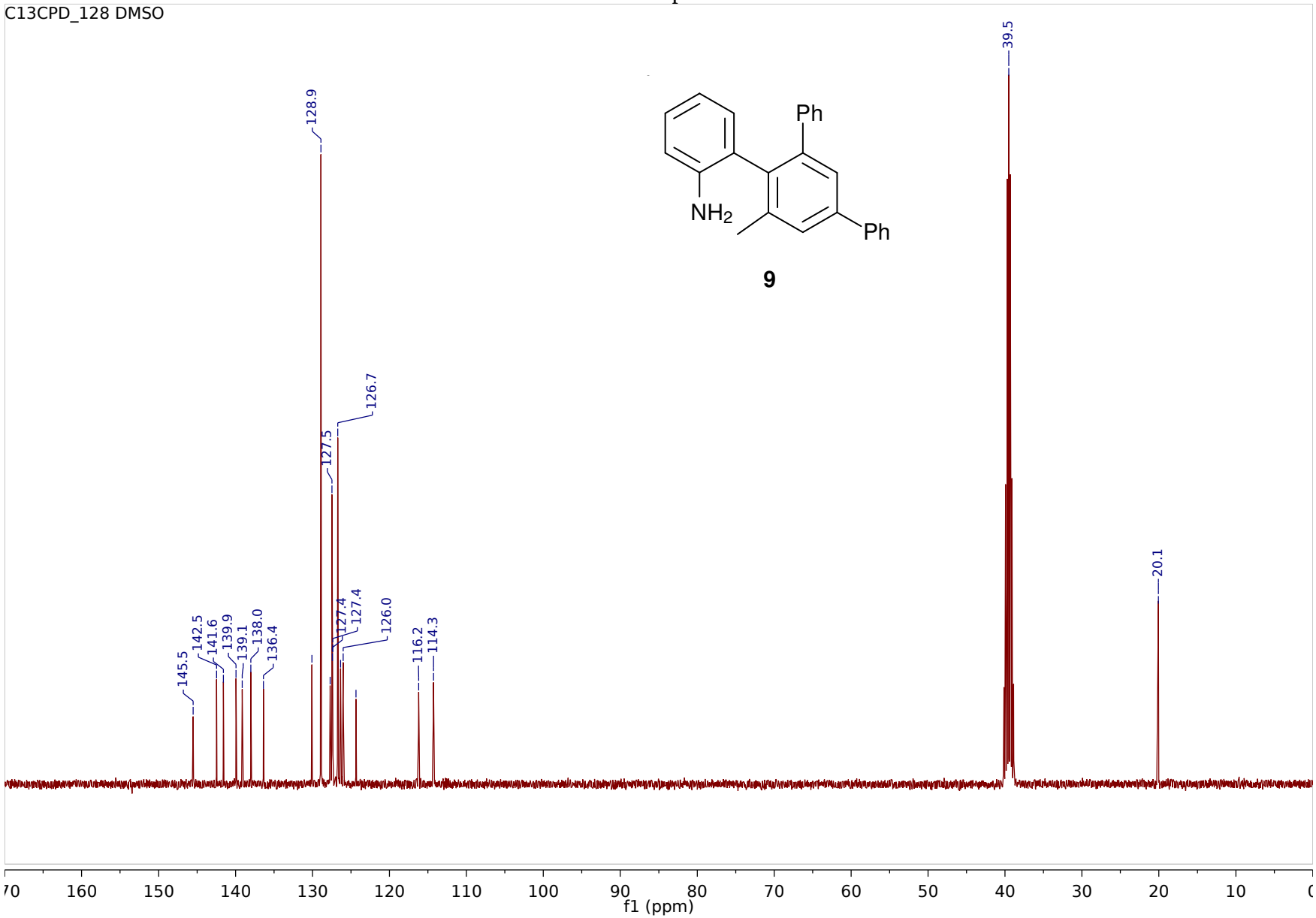
124.3 (CH), 123.4 (C), 116.0 (CH), 115.6 (CH), 114.3 (CH), 114.12 (CH), 20.31 (CH3), 20.29 (CH3), 20.1 (CH3), 20.0 (CH3), 19.9 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}N$: 364.2060, found 364.2075; Anal. calcd for $C_{27}H_{25}N$: C, 89.21; H, 6.93; N, 3.85. Found: C, 89.04; H, 6.92; N, 3.82. Notes: At rt, the number of signals in ^{13}C NMR was expected to double due to rotamers. 8 fewer signals than expected were observed in ^{13}C NMR at rt due to overlap. Integration of the signals in inverse-gated ^{13}C NMR spectrum indicated that signals at 141.2, 134.8, 130.4, 129.5, 129.4, 127.2, 125.9, and 20.29 account for 2 signals each.

2-(2-methyl-4,6-di(2-methoxyphenyl)phenyl)aniline (**13t**), obtained by general procedure from 2-methylindole (164 mg) and 2'-methoxyacetophenone (563 mg) as yellow oil; 298 mg (60%); R_f = 0.11 (EtOAc:Hexanes 1:5); IR (neat, cm^{-1}): 3463, 3375, 3056, 3024, 3000, 2924, 1613, 1494, 1463, 1244, 1026, 751;^1H NMR (400 MHz, DMSO-d_6, 350K): δ 7.42 (d, J = 2.0 Hz, 1H), 7.38 (dd, J = 7.5, 1.7 Hz, 1H), 7.33 (ddd, J = 8.0, 7.5, 1.7 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.15 – 7.00 (m, 4H), 6.90 – 6.80 (m, 2H), 6.74 (td, J = 7.5, 1.2 Hz, 1H), 6.68 (dd, J = 7.5, 1.6 Hz, 1H), 6.60 (dd, J = 8.0, 1.2 Hz, 1H), 6.40 (td, J = 7.5, 1.2 Hz, 1H), 4.20 (br s, 2H), 3.81 (s, 3H), 3.62 (s, 3H), 2.12 (s, 3H); ^1H NMR (500 MHz, DMSO-d_6): δ 7.41 (s, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.15 – 7.00 (m, 4H), 6.85 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.67 – 6.57 (m, 2H), 6.39 (t, J = 7.5 Hz, 1H), 4.56 (br s, 2H), 3.79 (s, 3H), 3.59 (br s, 3H), 2.09 (s, 3H);^{13}C NMR (101 MHz, DMSO-d_6, 345K): δ 156.1 (C), 155.9 (C), 144.8 (C), 138.2 (C), 136.3 (C), 136.2 (C), 135.9 (C), 130.42 (C), 130.37 (CH), 130.0 (CH), 129.5 (CH), 129.4 (C), 129.2 (CH), 128.7 (CH), 128.3 (CH), 127.6 (CH), 126.9 (CH), 124.6 (C), 120.5 (CH), 119.2 (CH), 115.6 (CH), 114.0 (CH), 111.8 (CH), 110.5 (CH), 55.3 (CH3), 54.7 (CH3), 19.5 (CH3); HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{26}NO_2$: 396.1958, found 396.1950; Anal. calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.74; H, 6.57; N, 3.60. Notes: The spectra were obtained at 350K and 345K to decrease peak broadening.

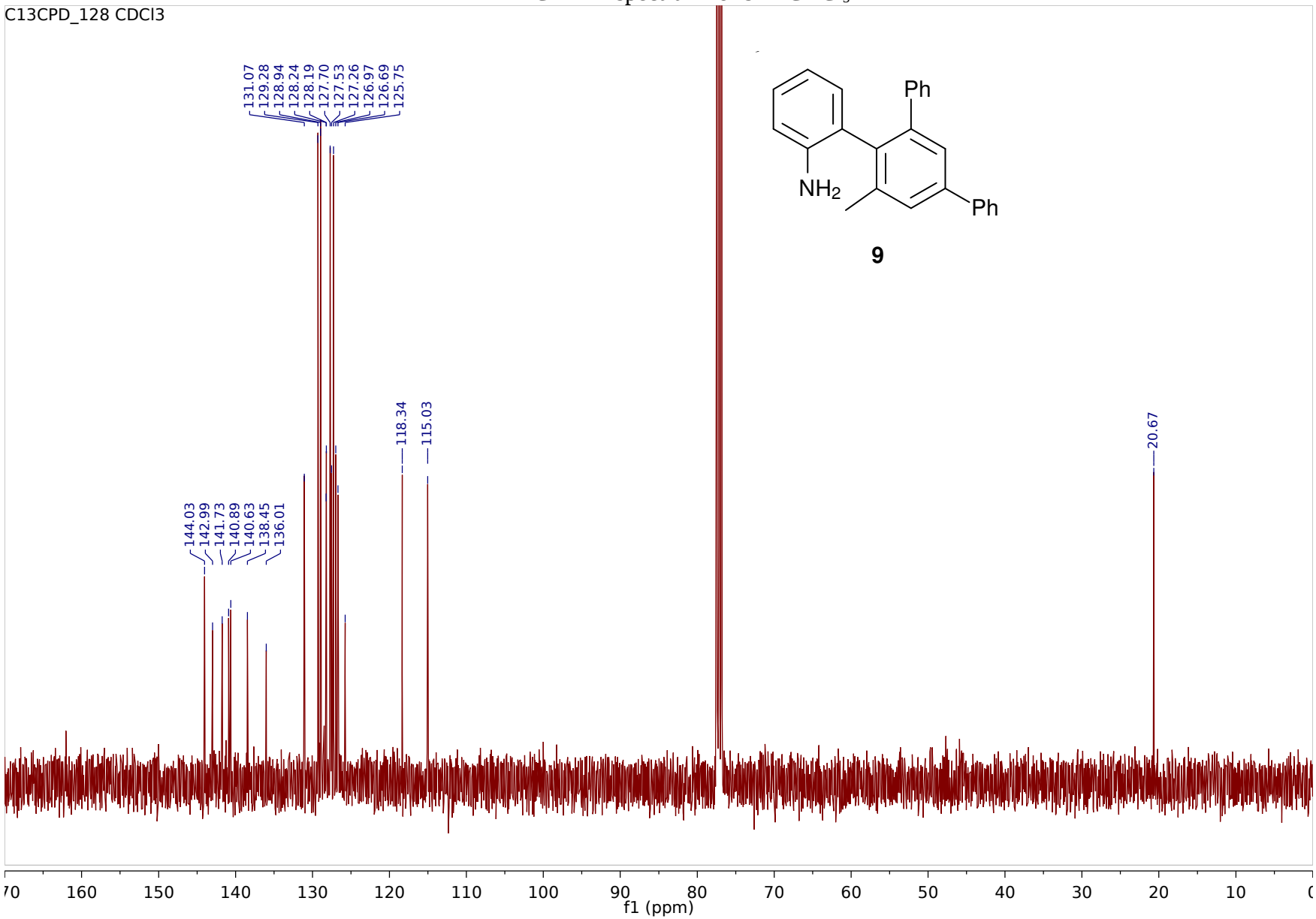
^{1}H NMR spectrum for **9**



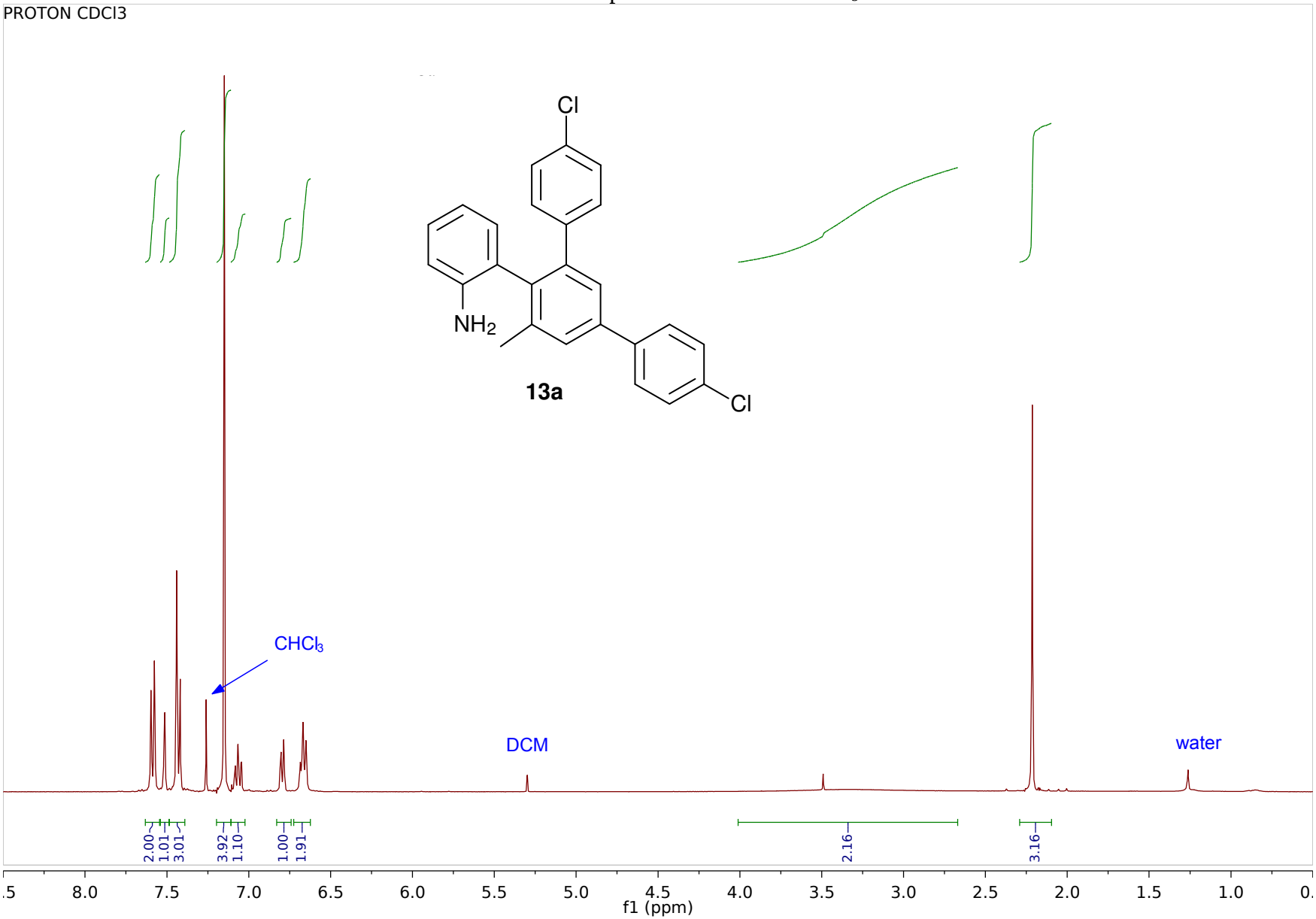
^{13}C NMR spectrum for **9**



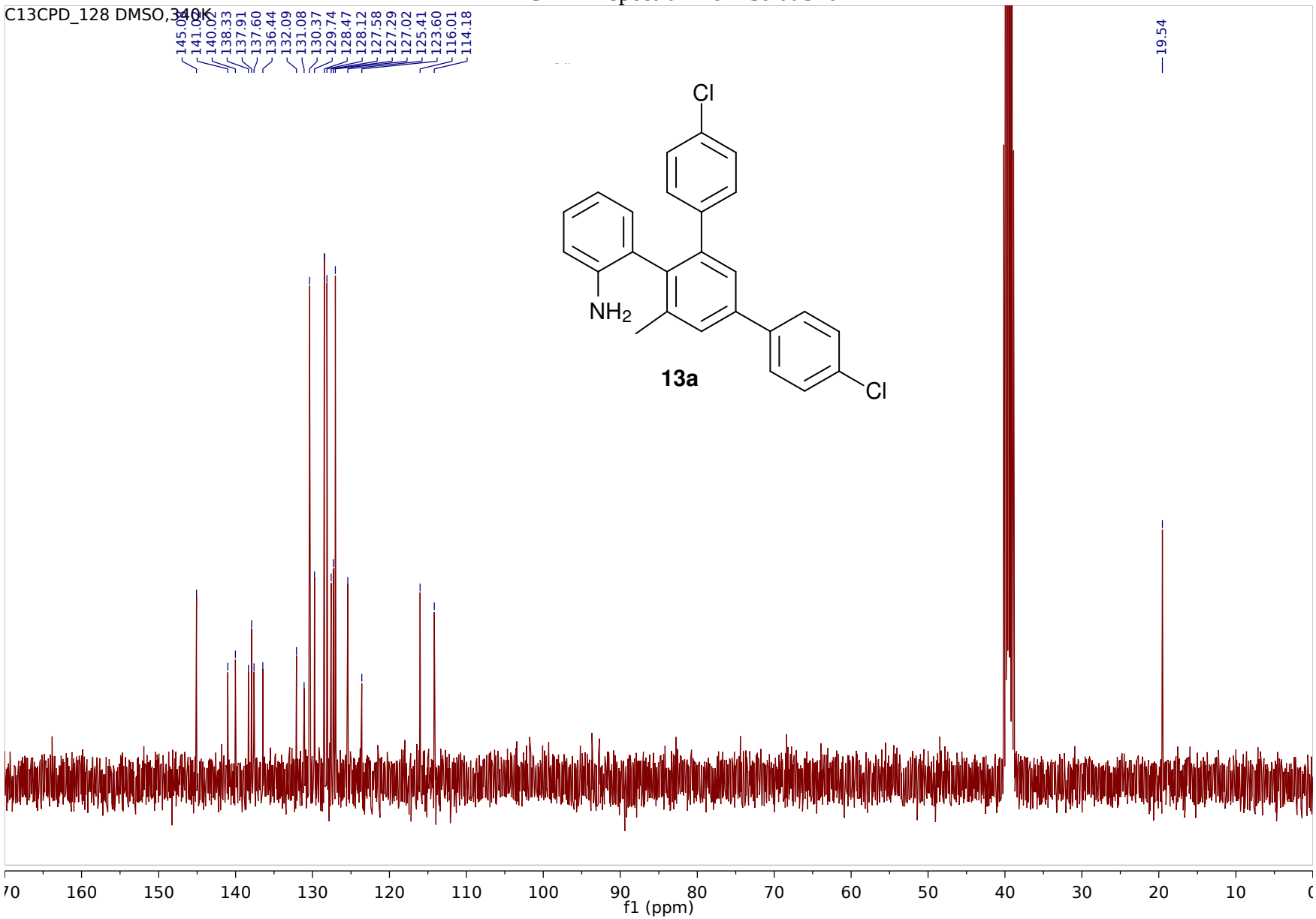
^{13}C NMR spectrum for **9** in $CDCl_3$



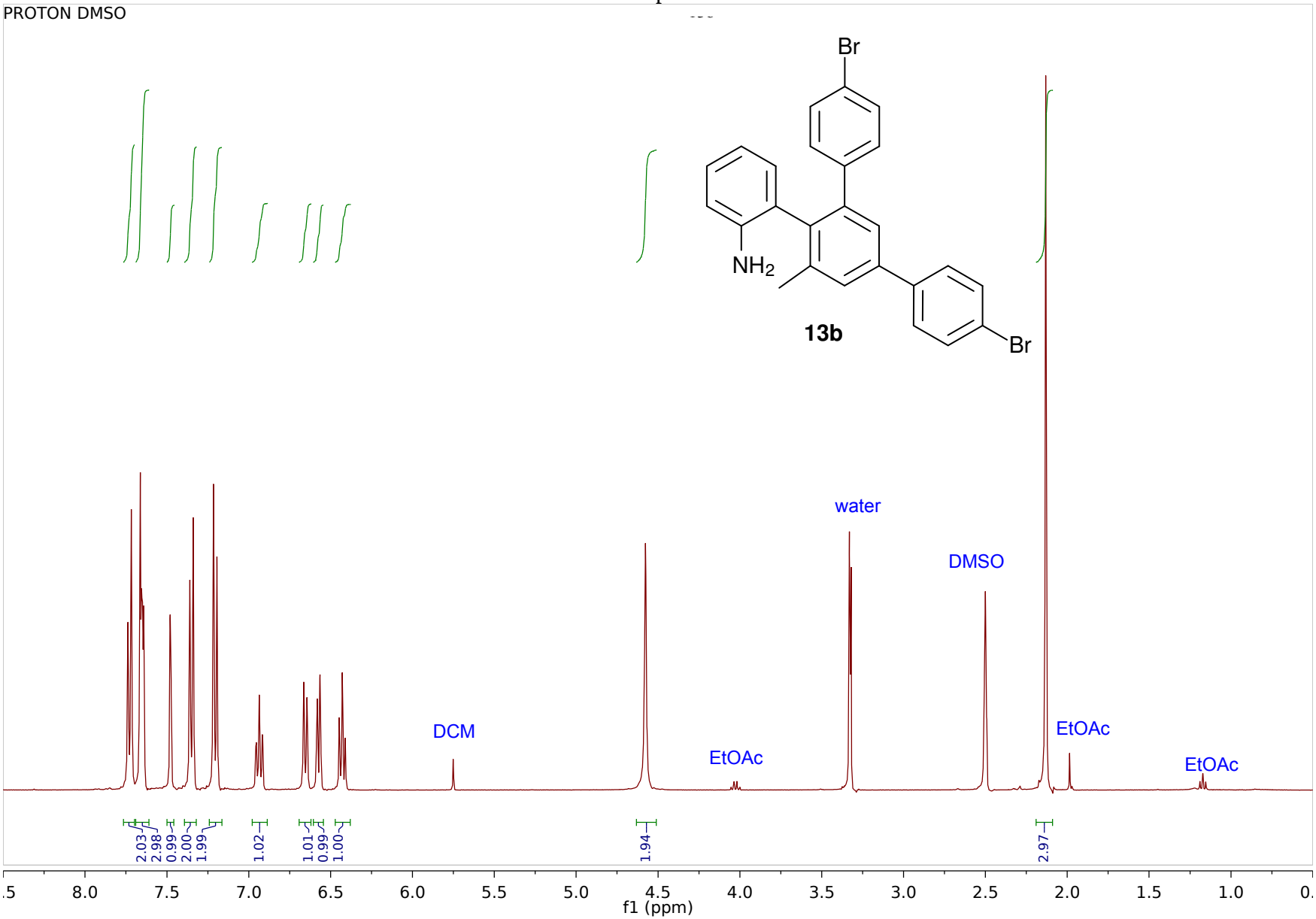
^{1}H NMR spectrum for **13a** in $CDCl_3$



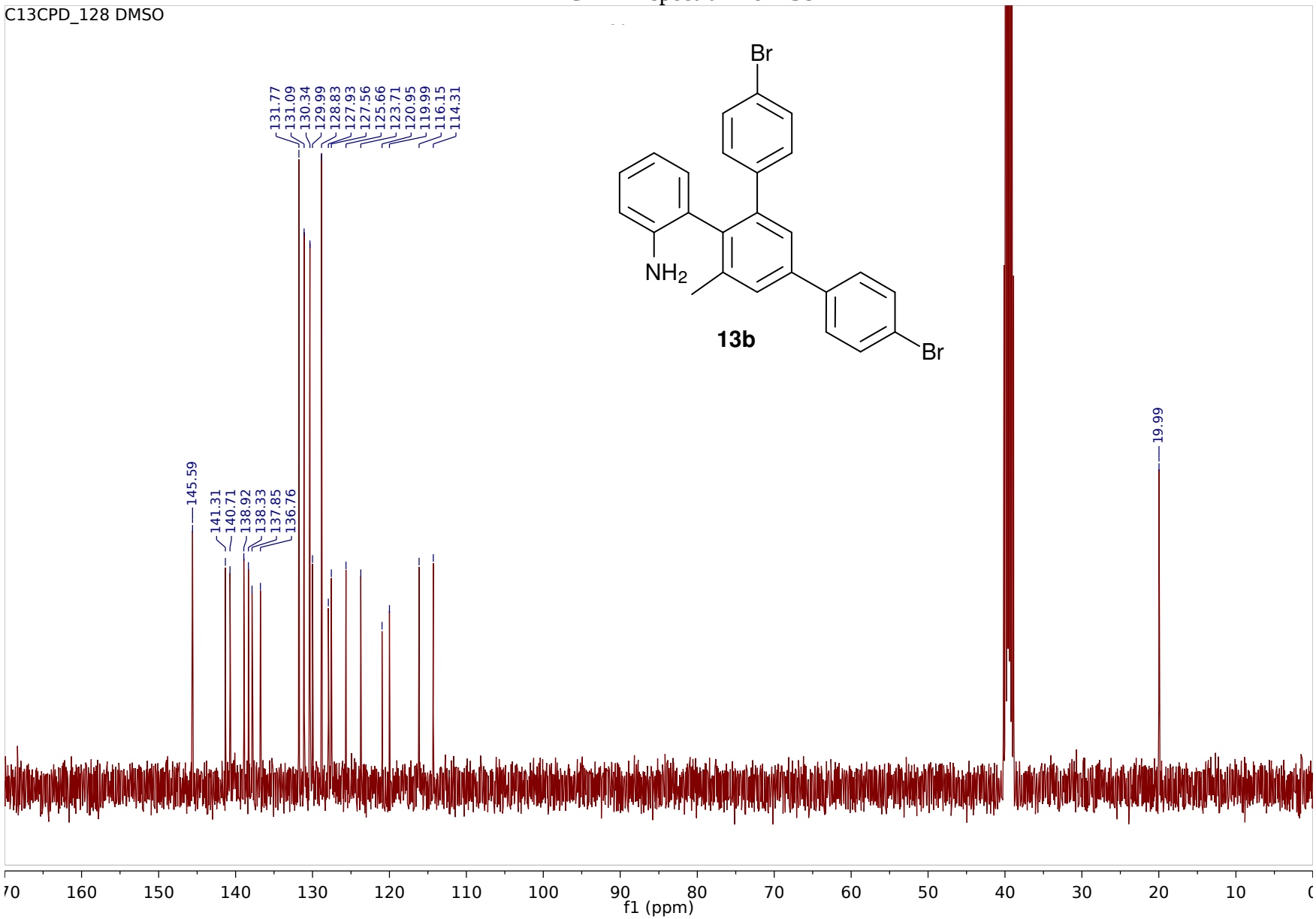
^{13}C NMR spectrum for **13a** at 340K



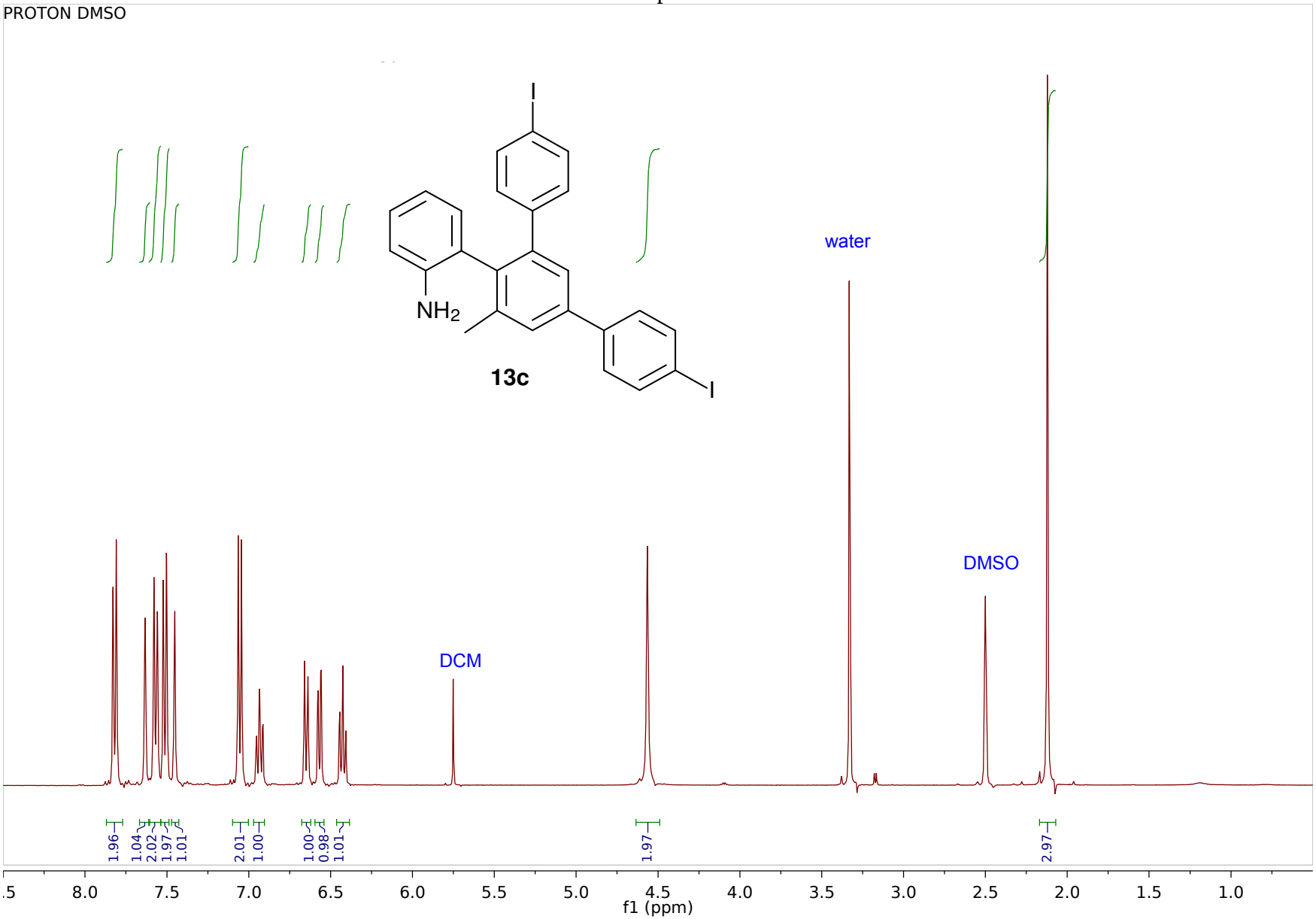
^{1}H NMR spectrum for **13b**



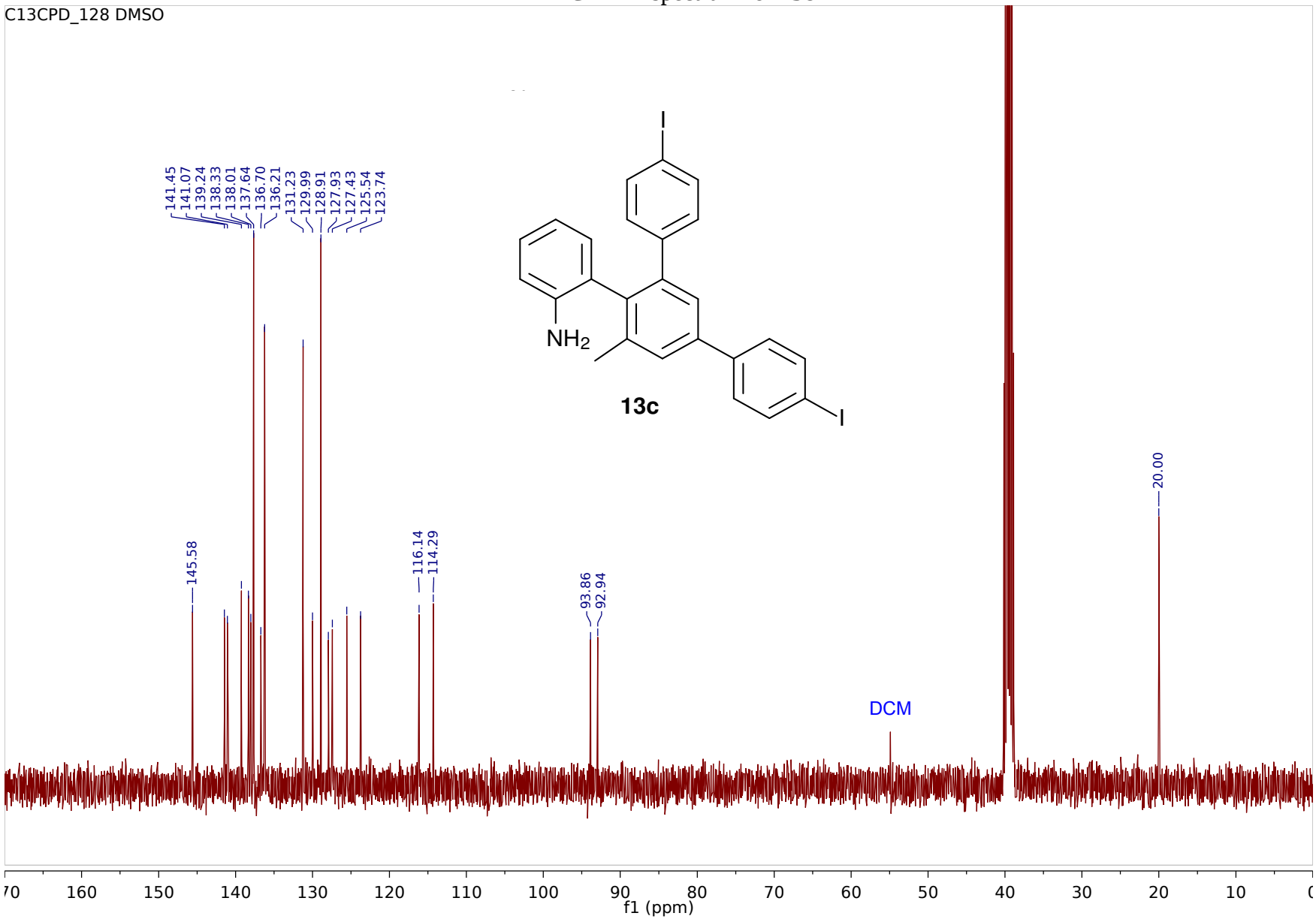
^{13}C NMR spectrum for **13b**



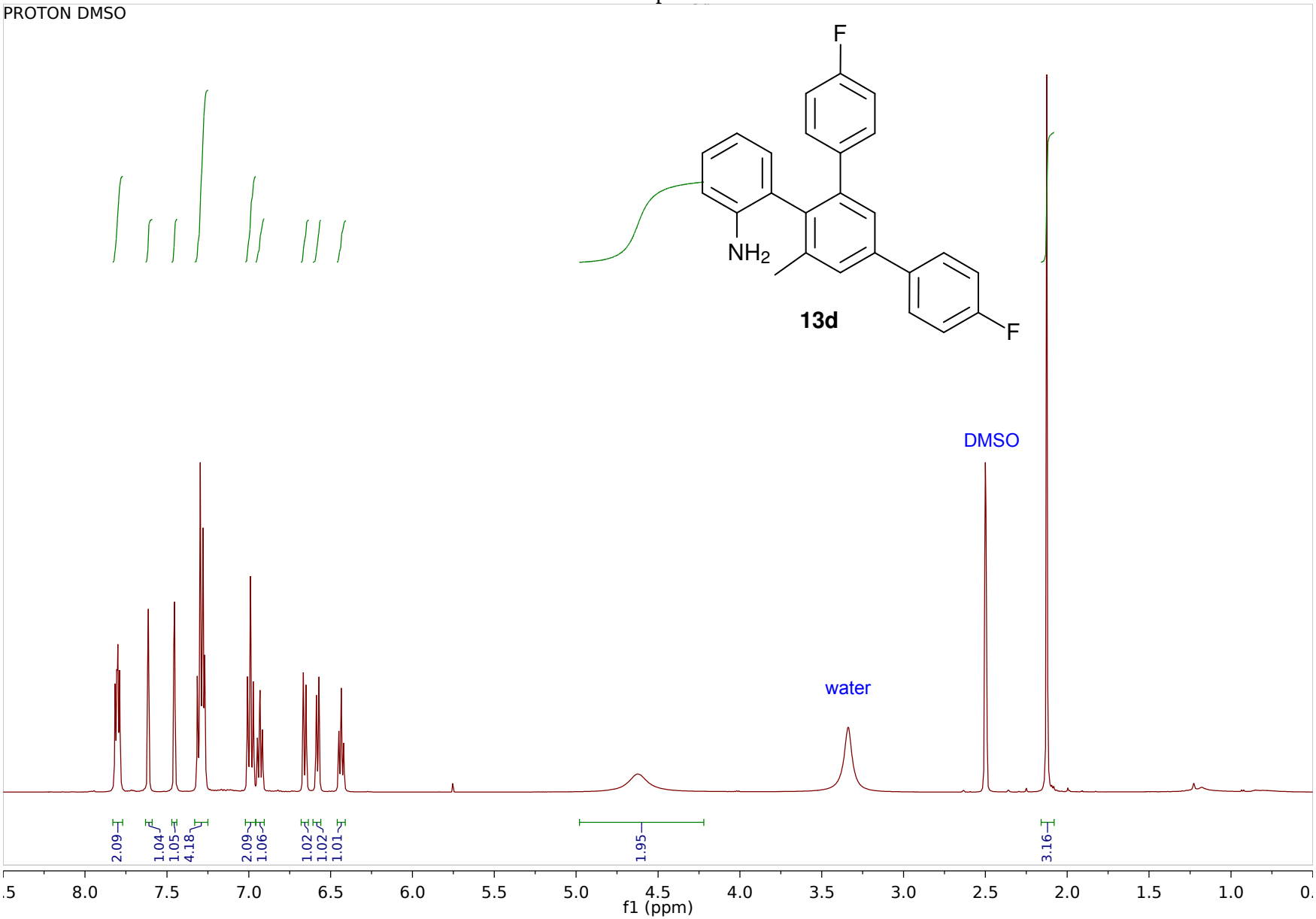
^{1}H NMR spectrum for **13c**



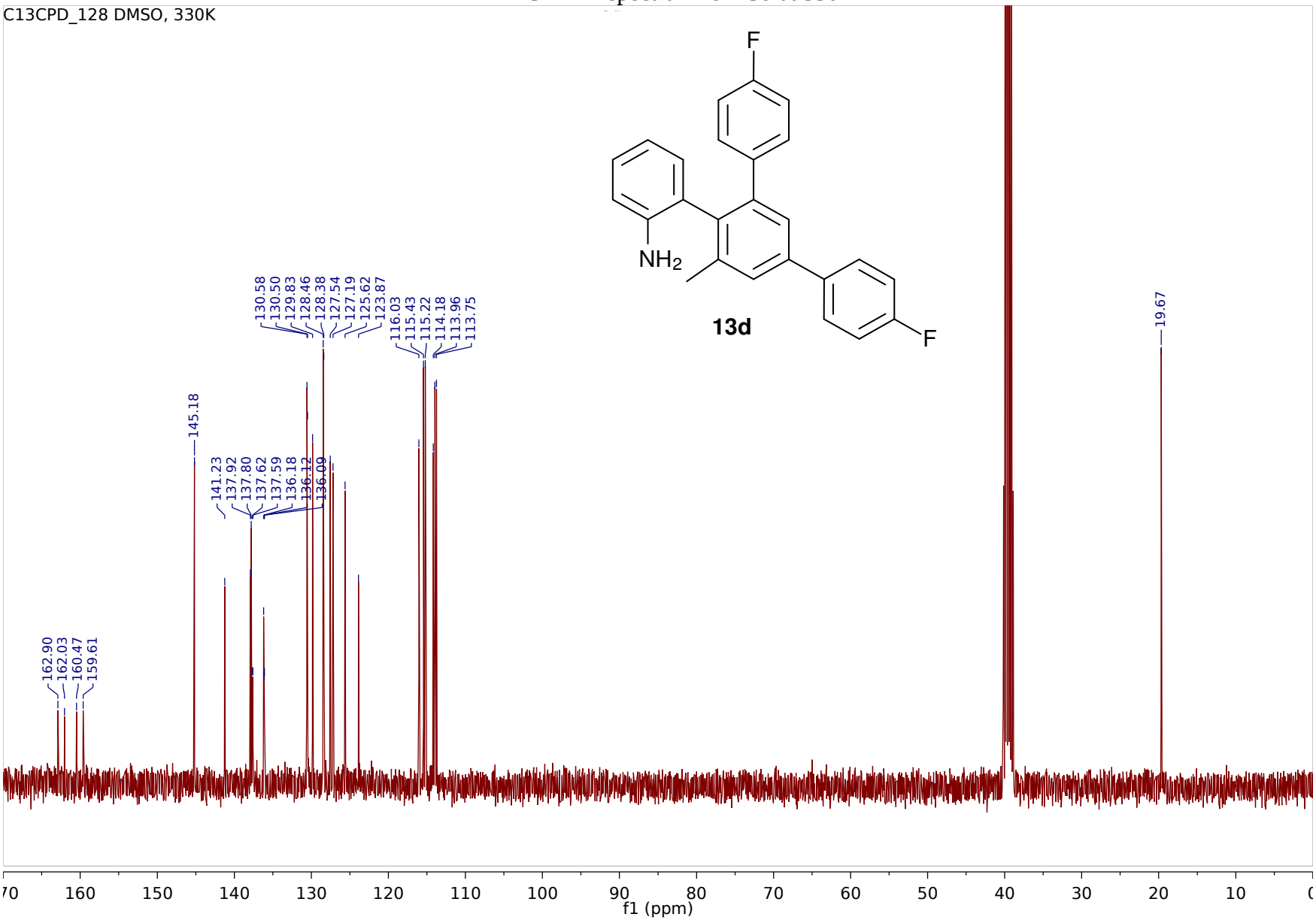
^{13}C NMR spectrum for **13c**



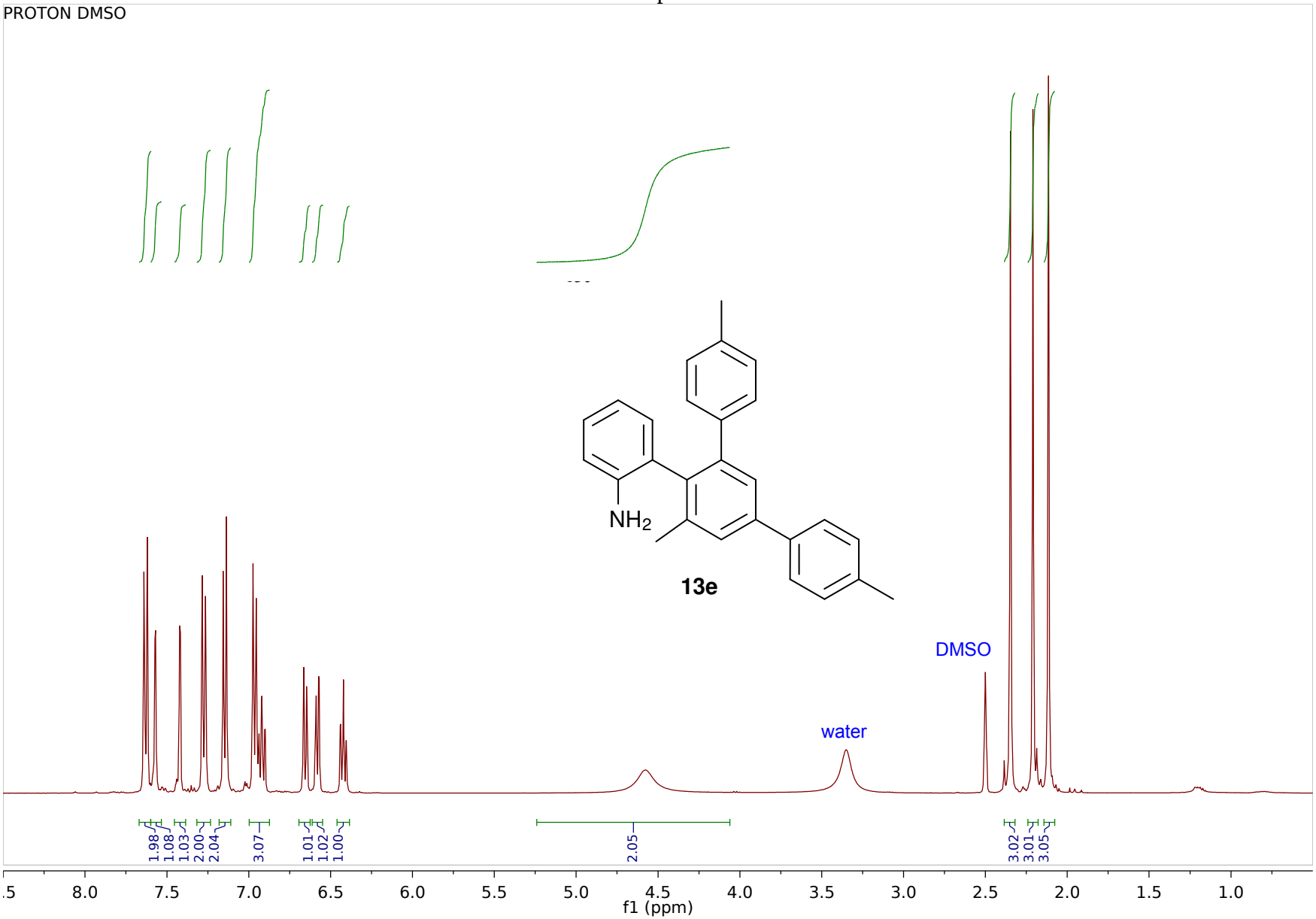
^{1}H NMR spectrum for **13d**



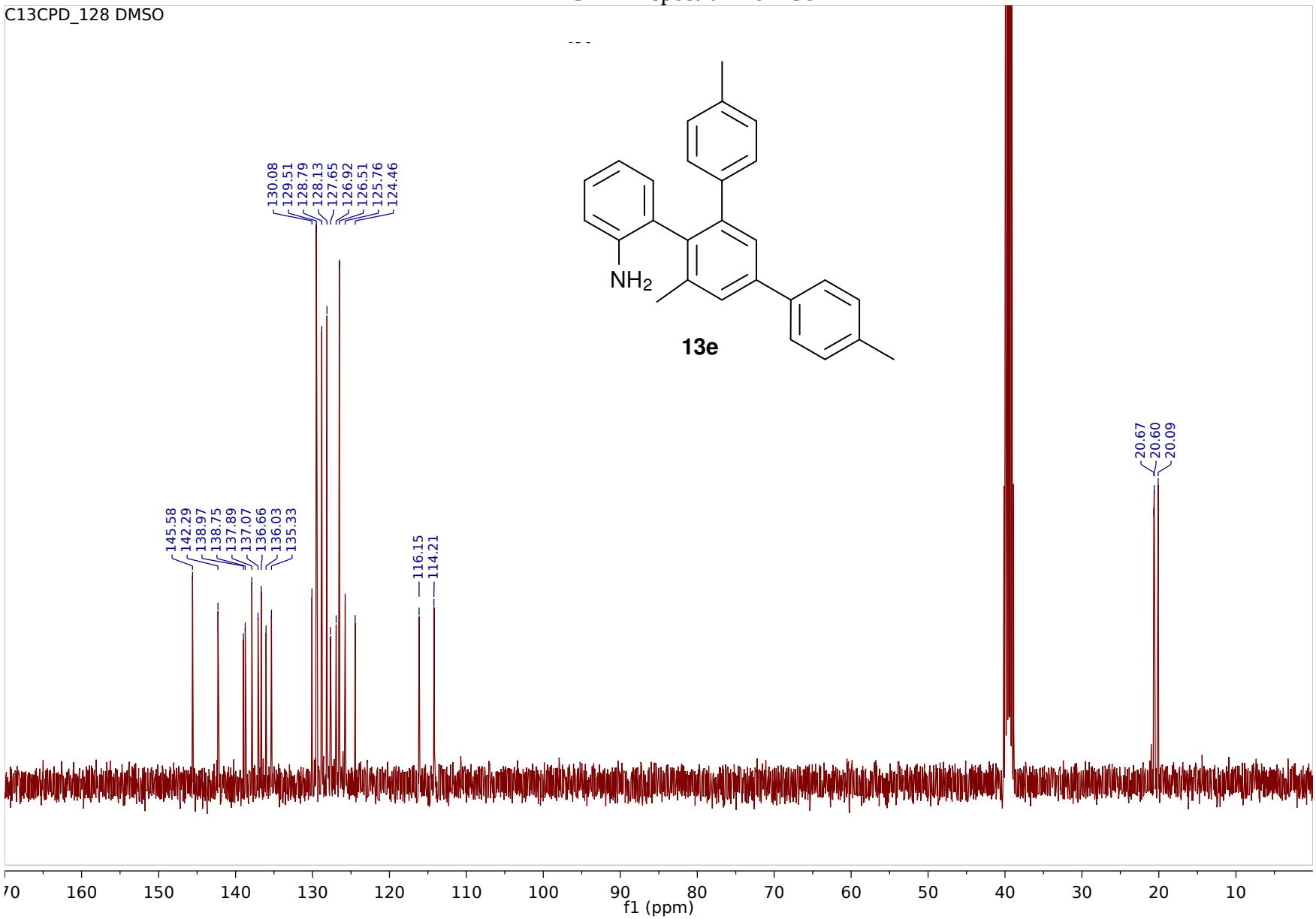
^{13}C NMR spectrum for **13d** at 330K



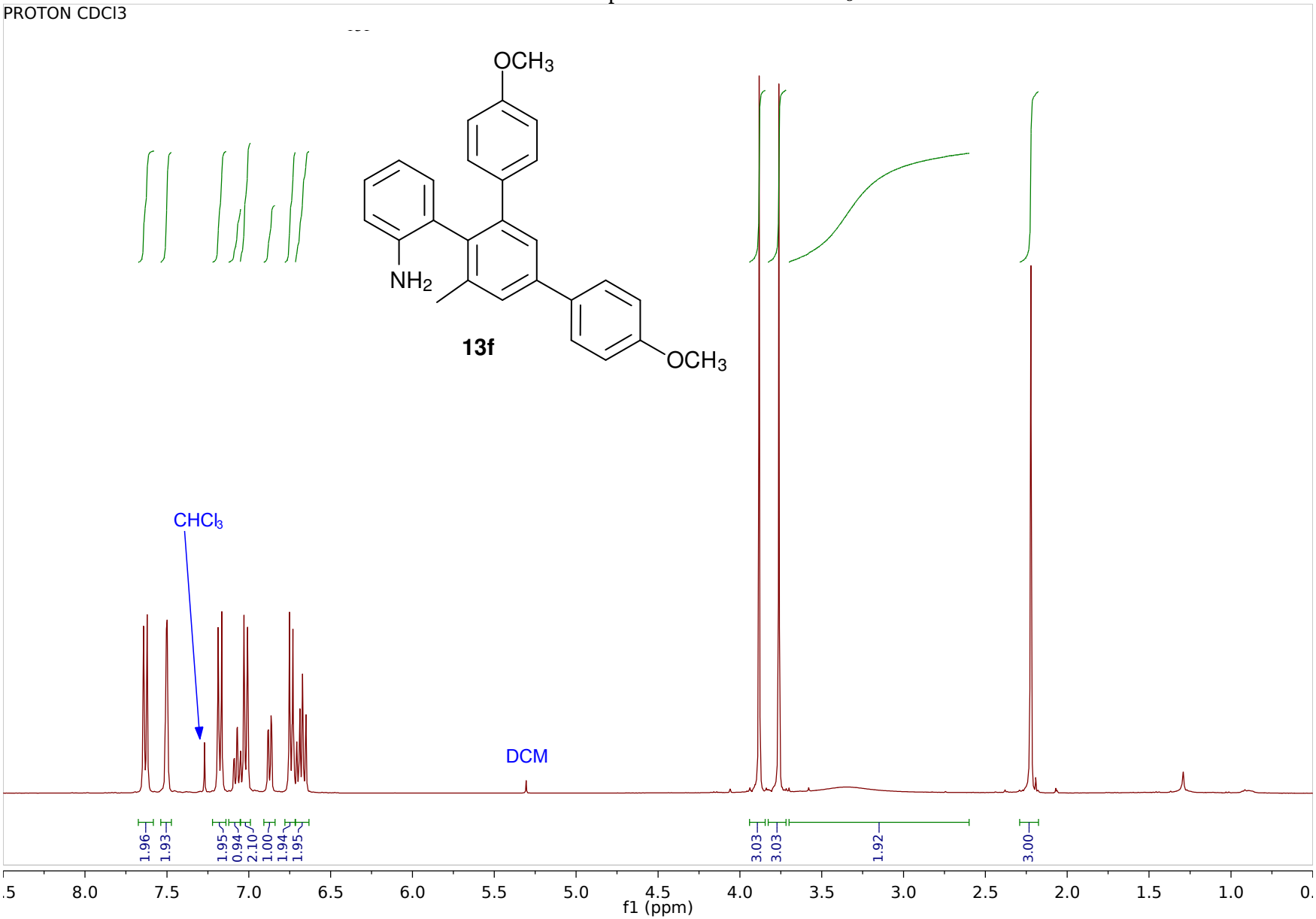
^{1}H NMR spectrum for **13e**



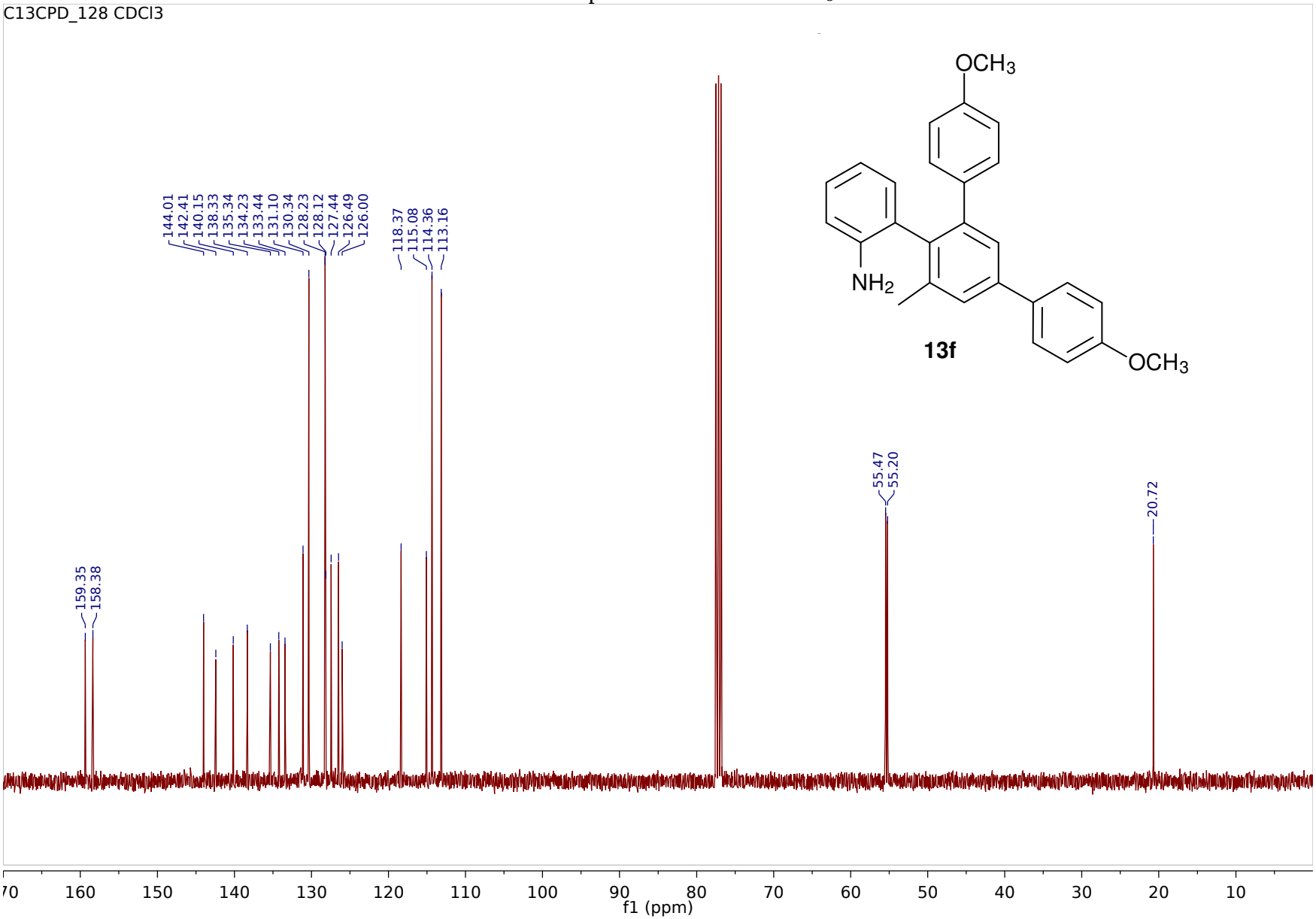
^{13}C NMR spectrum for **13e**



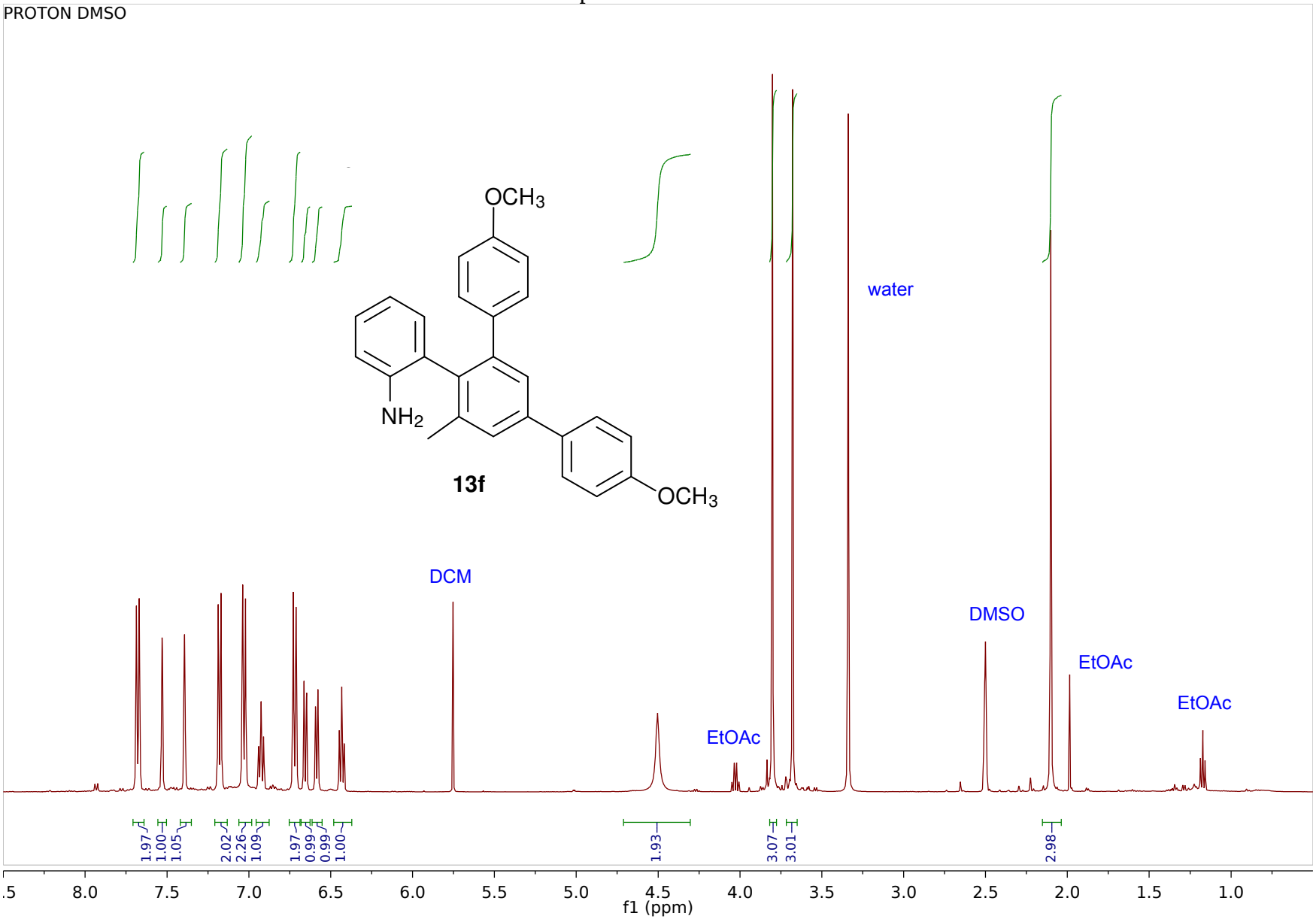
^{1}H NMR spectrum for **13f** in $CDCl_3$



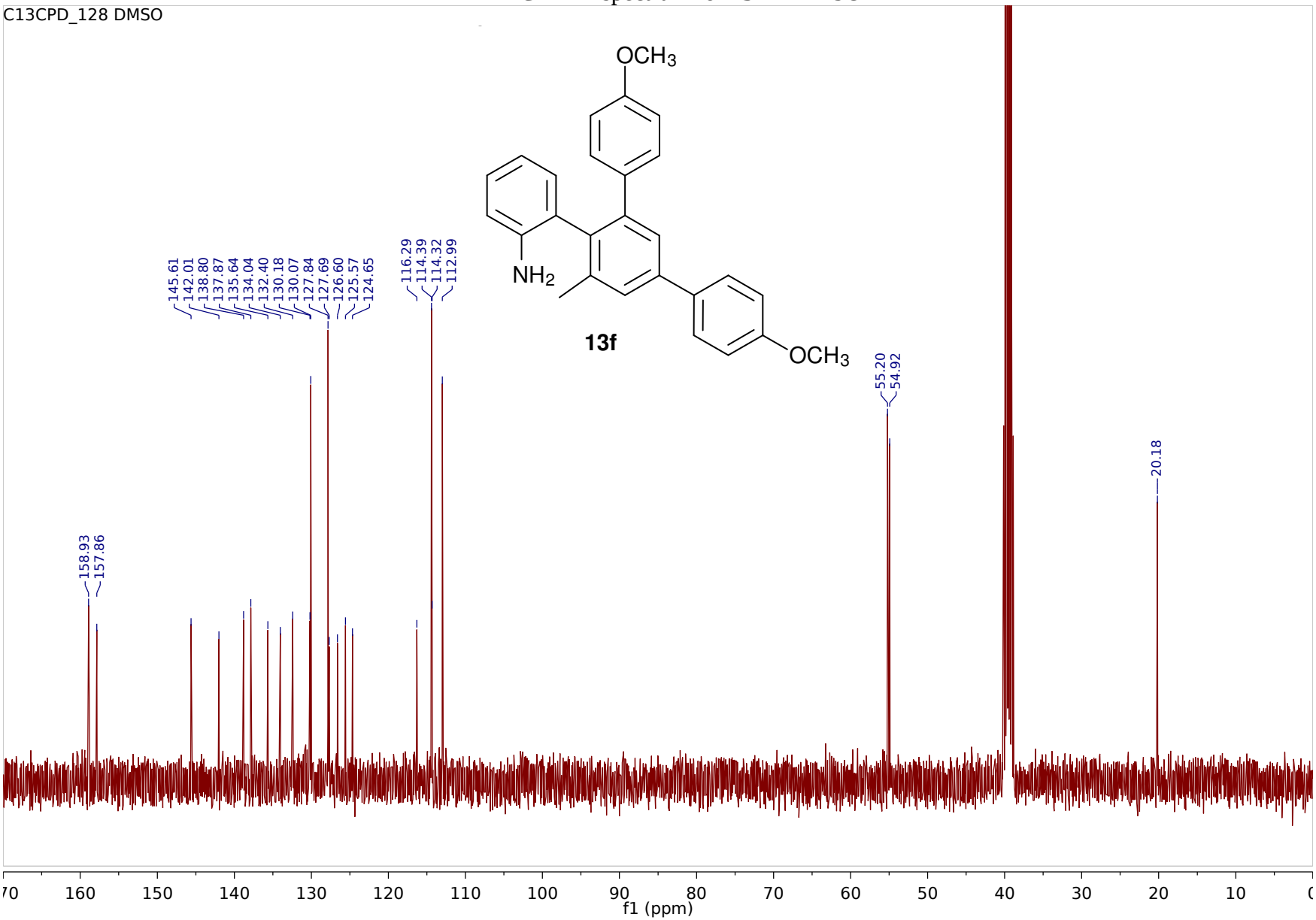
^{13}C NMR spectrum for **13f** in $CDCl_3$



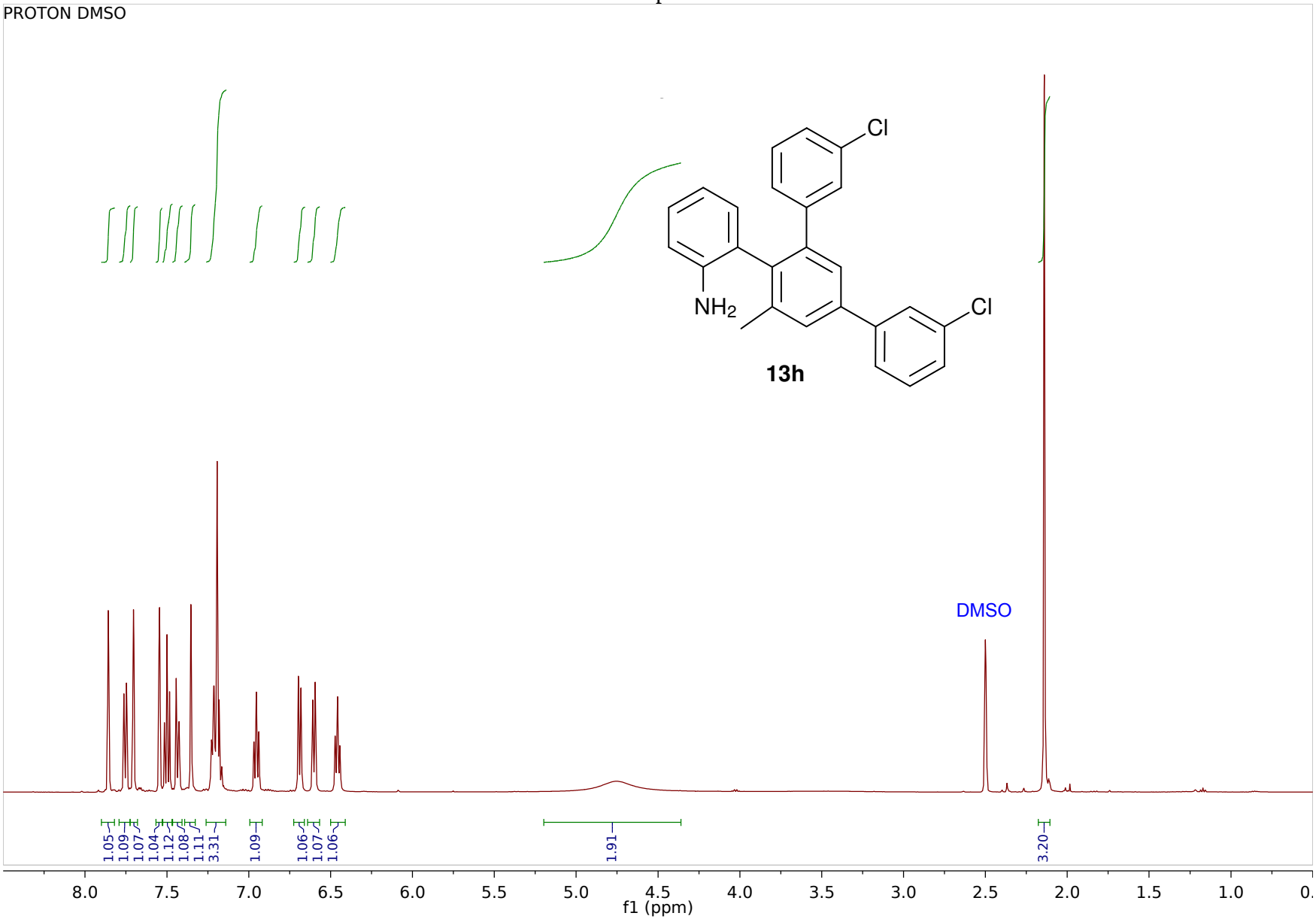
^{1}H NMR spectrum for **13f** in DMSO



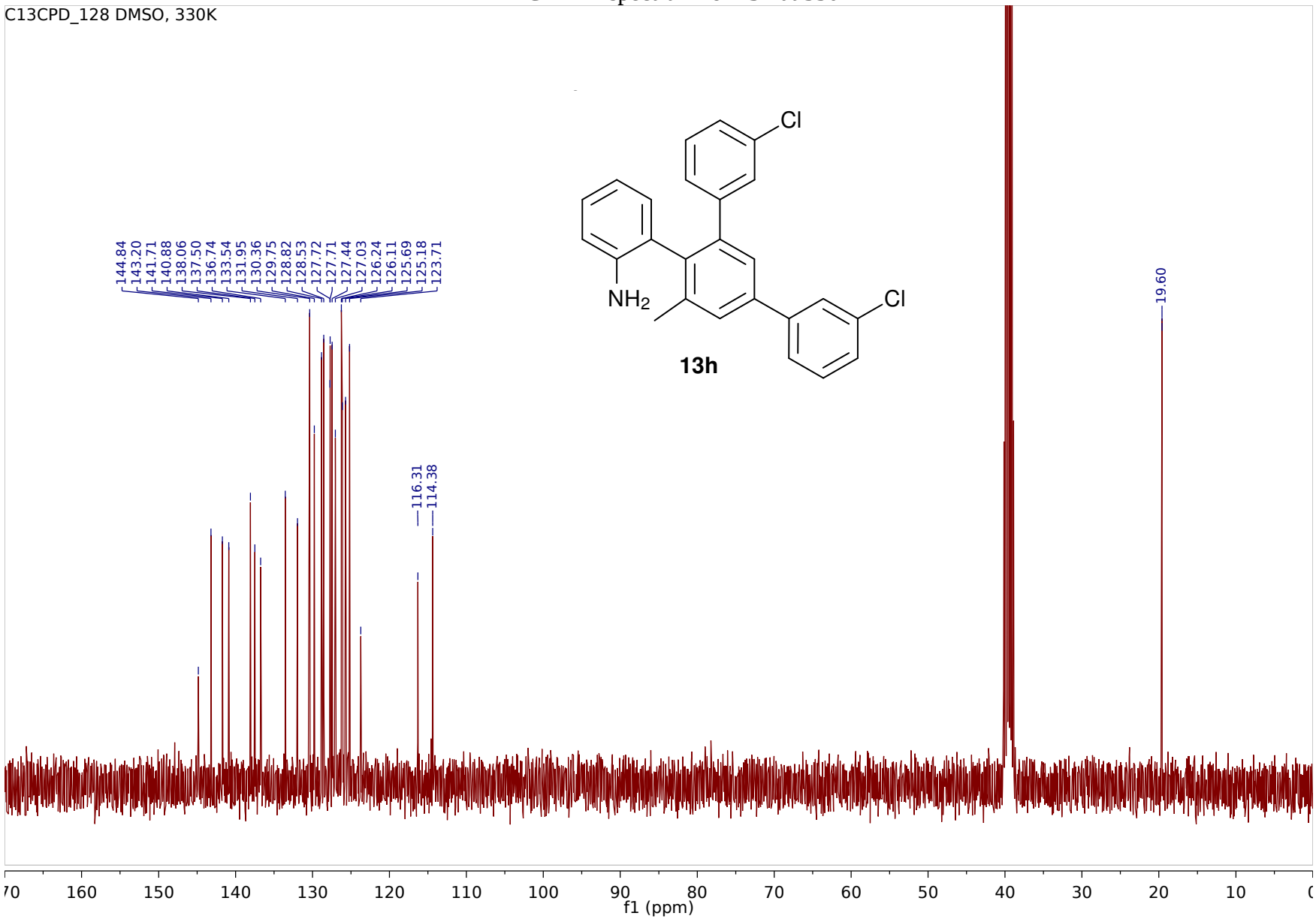
^{13}C NMR spectrum for **13f** in DMSO



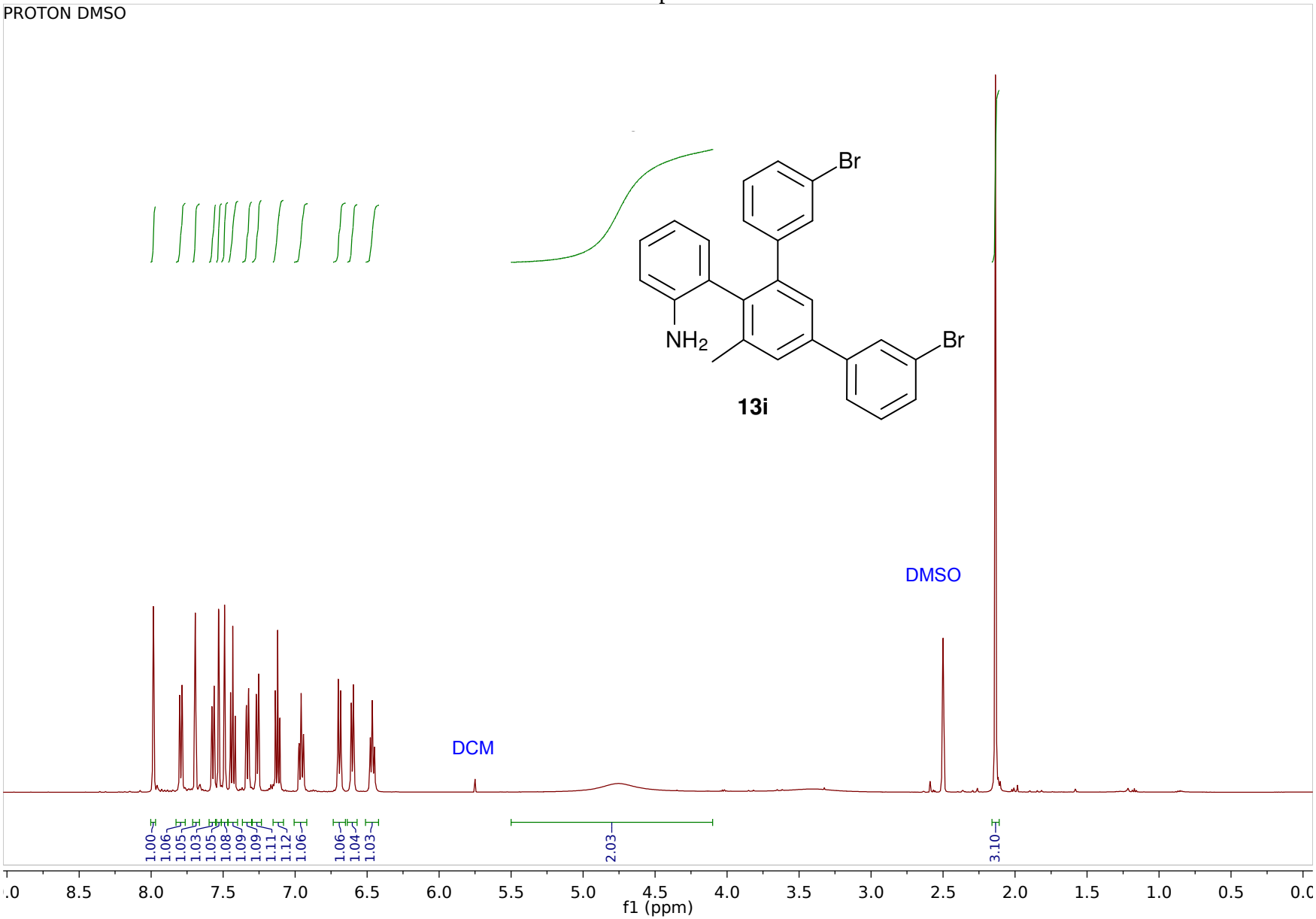
^{1}H NMR spectrum for **13h**



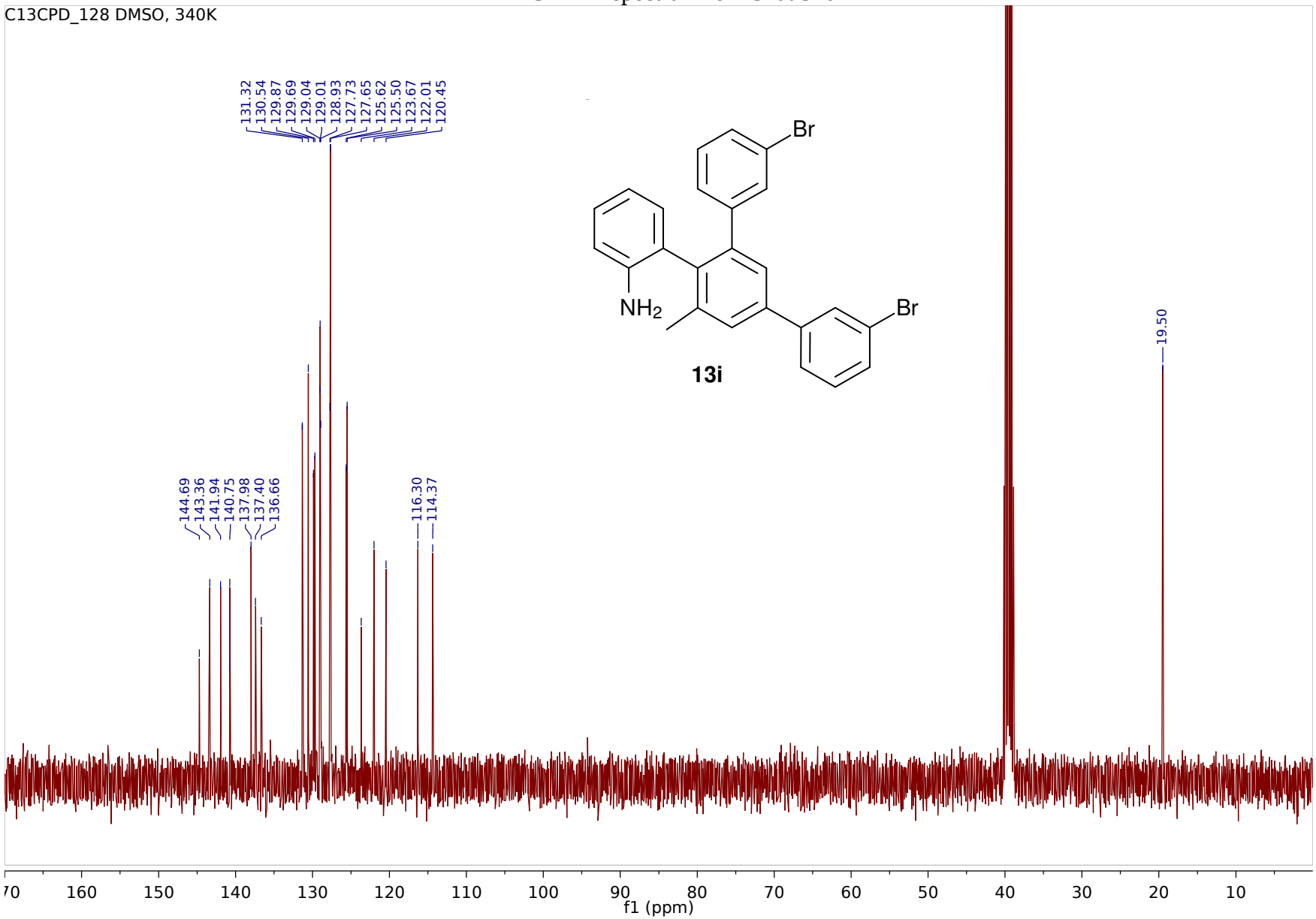
^{13}C NMR spectrum for **13h** at 330K



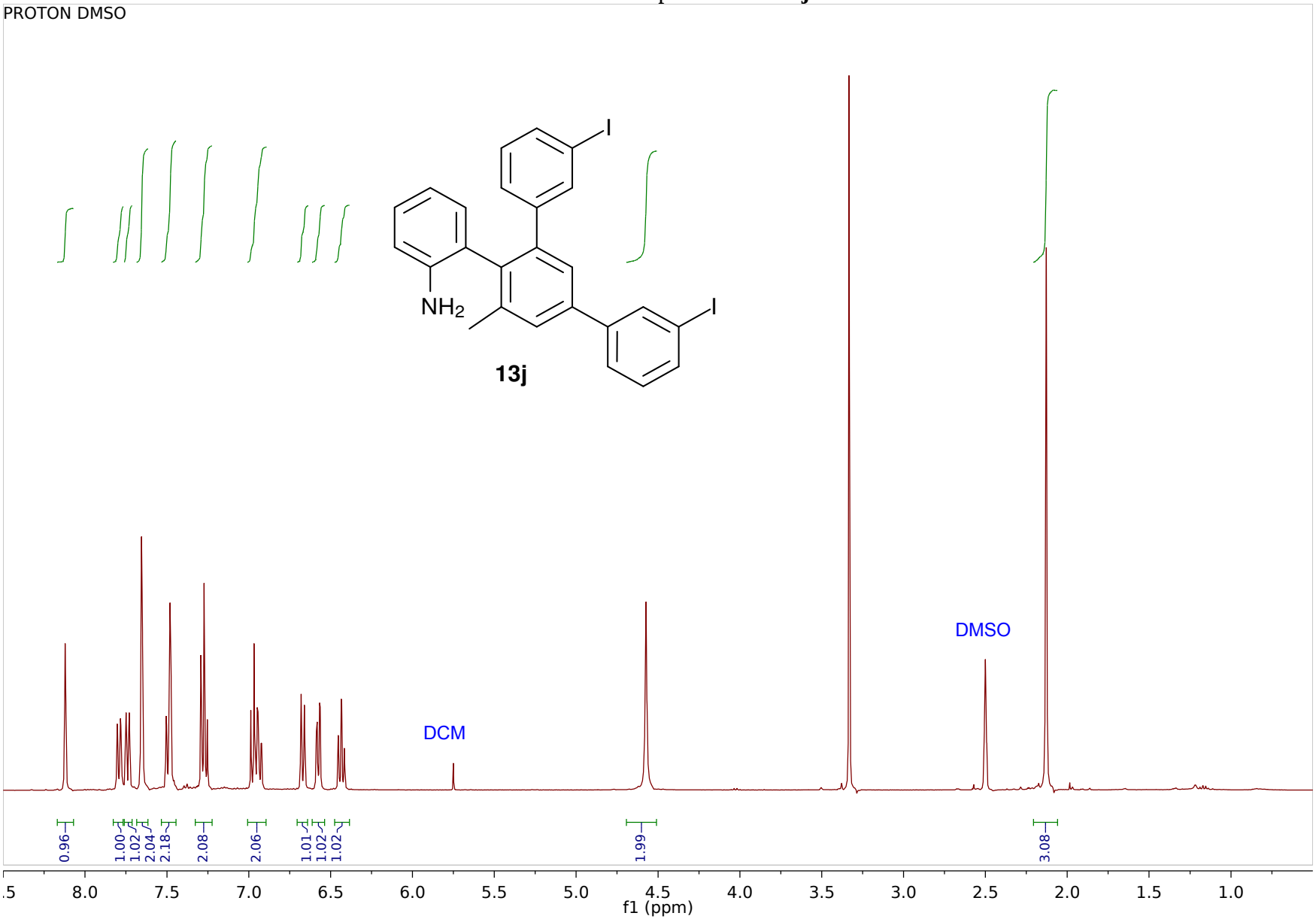
^{1}H NMR spectrum for **13i**



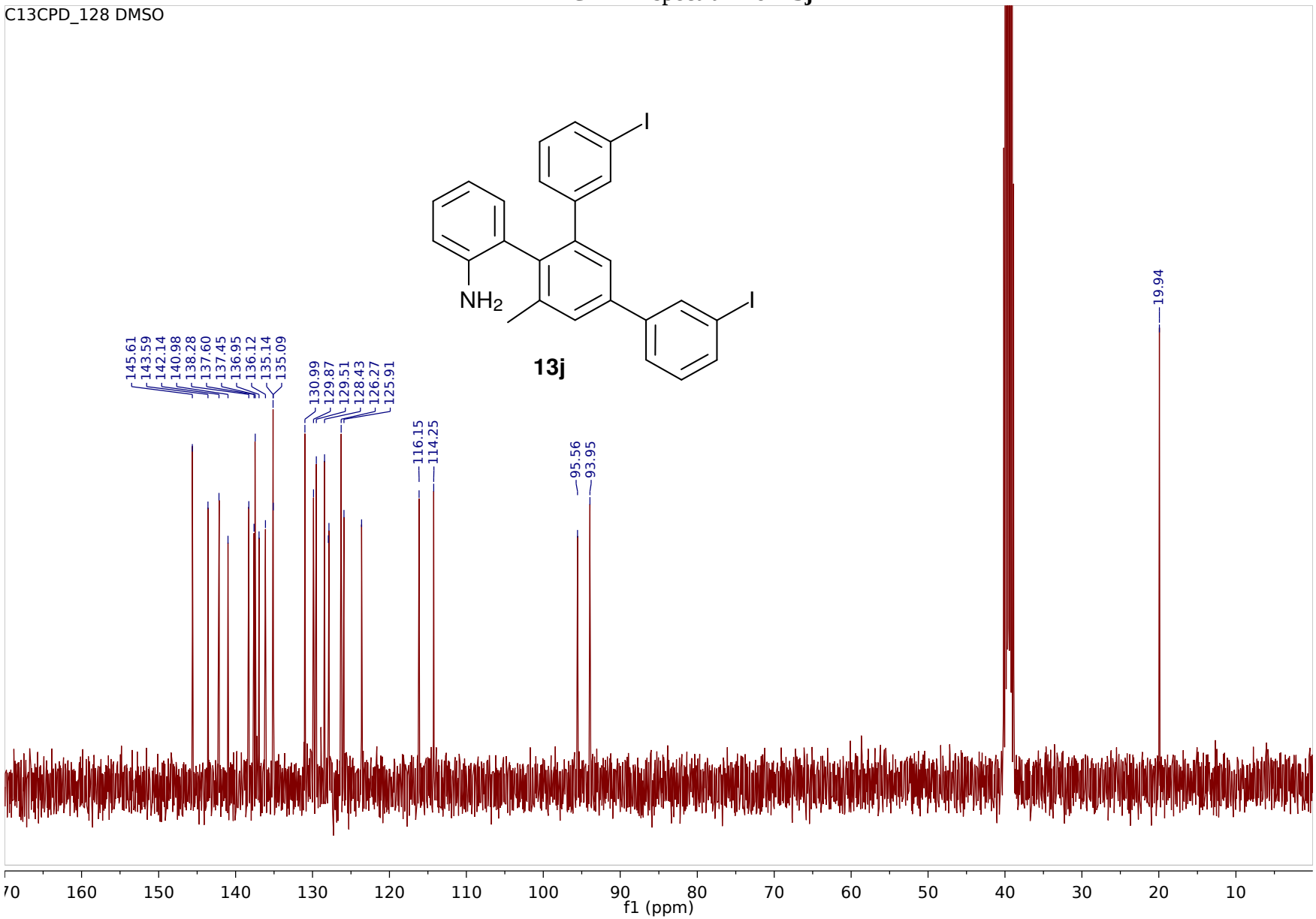
^{13}C NMR spectrum for **13i** at 340K



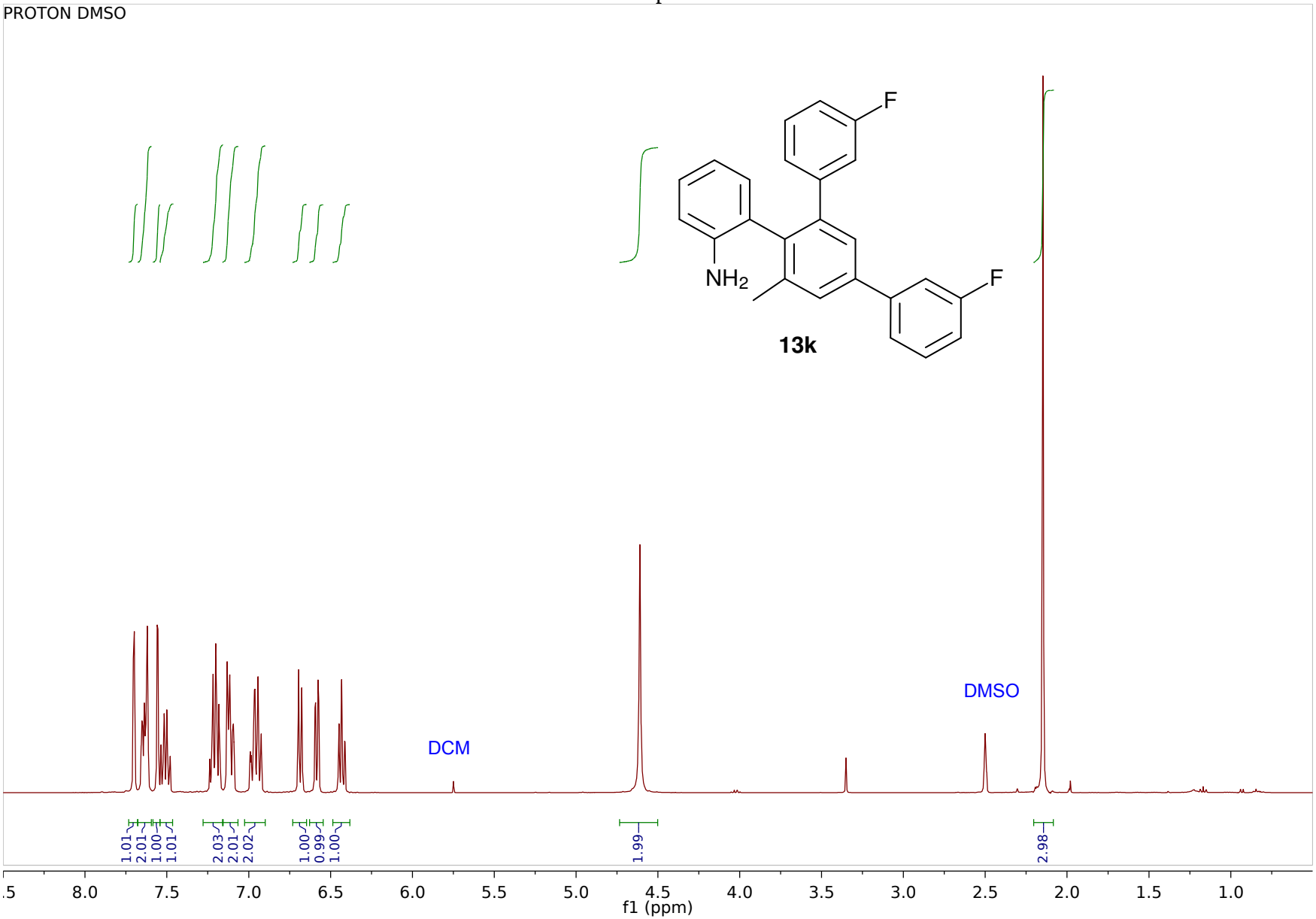
^{1}H NMR spectrum for **13j**



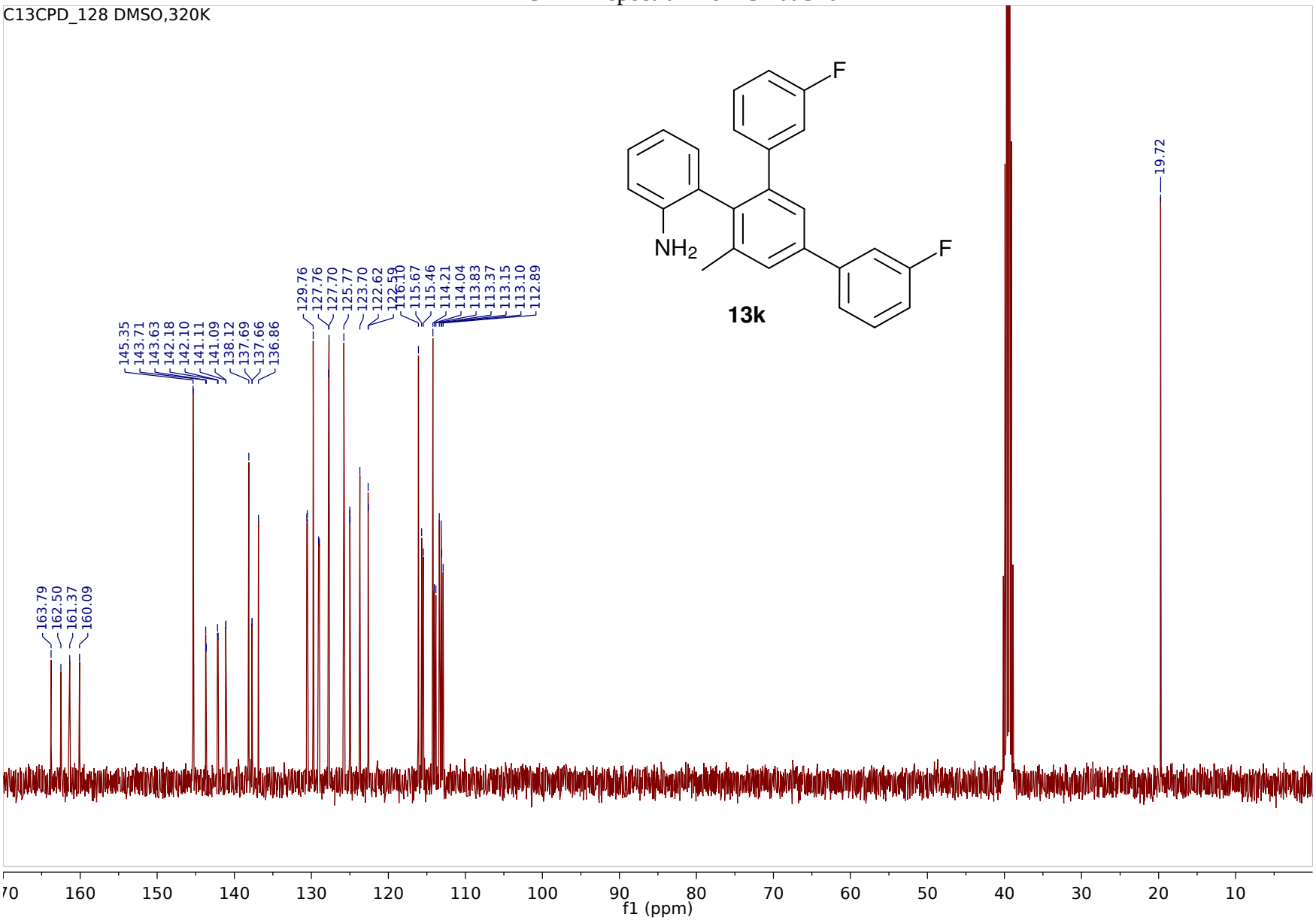
^{13}C NMR spectrum for **13j**



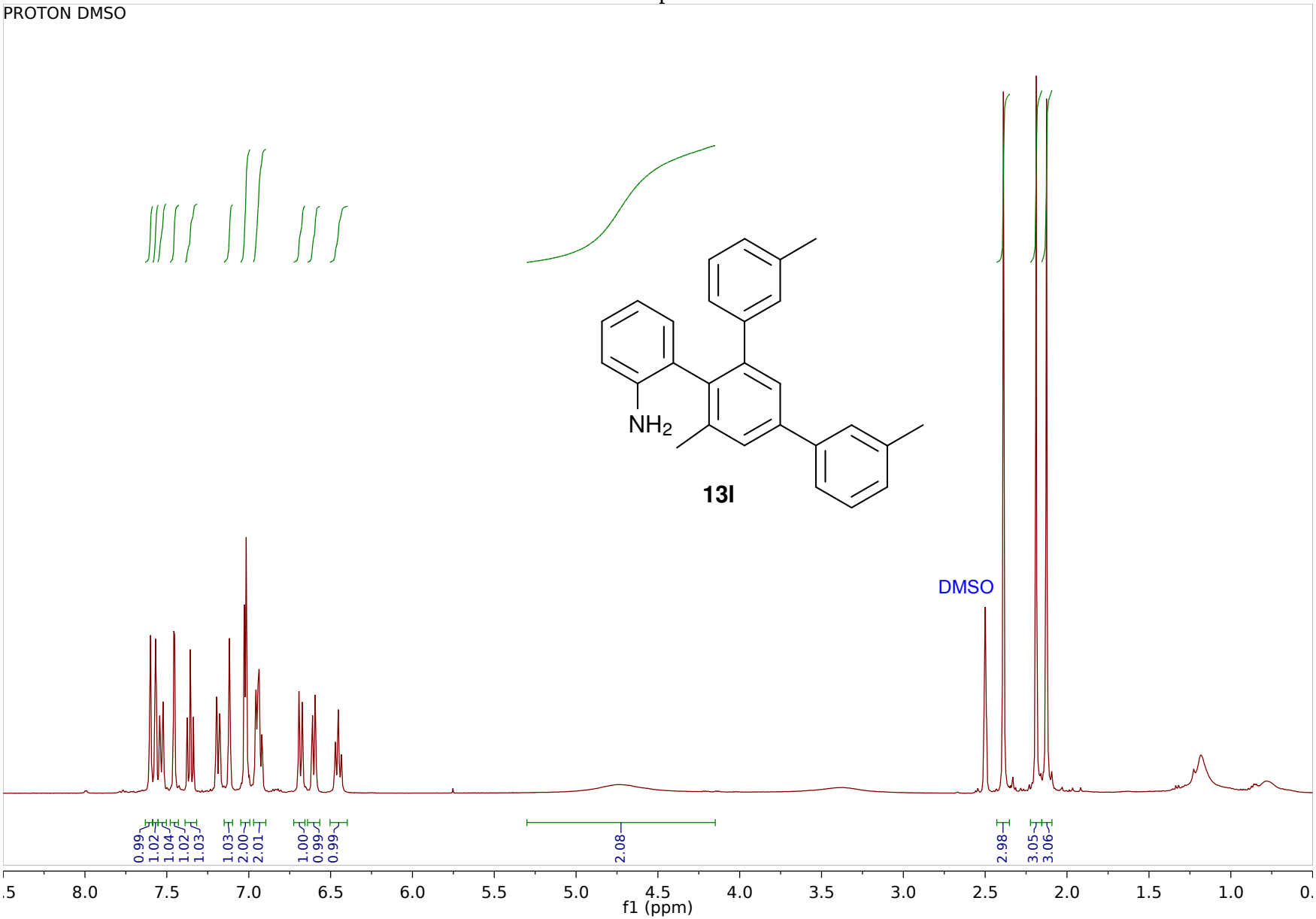
^{1}H NMR spectrum for **13k**



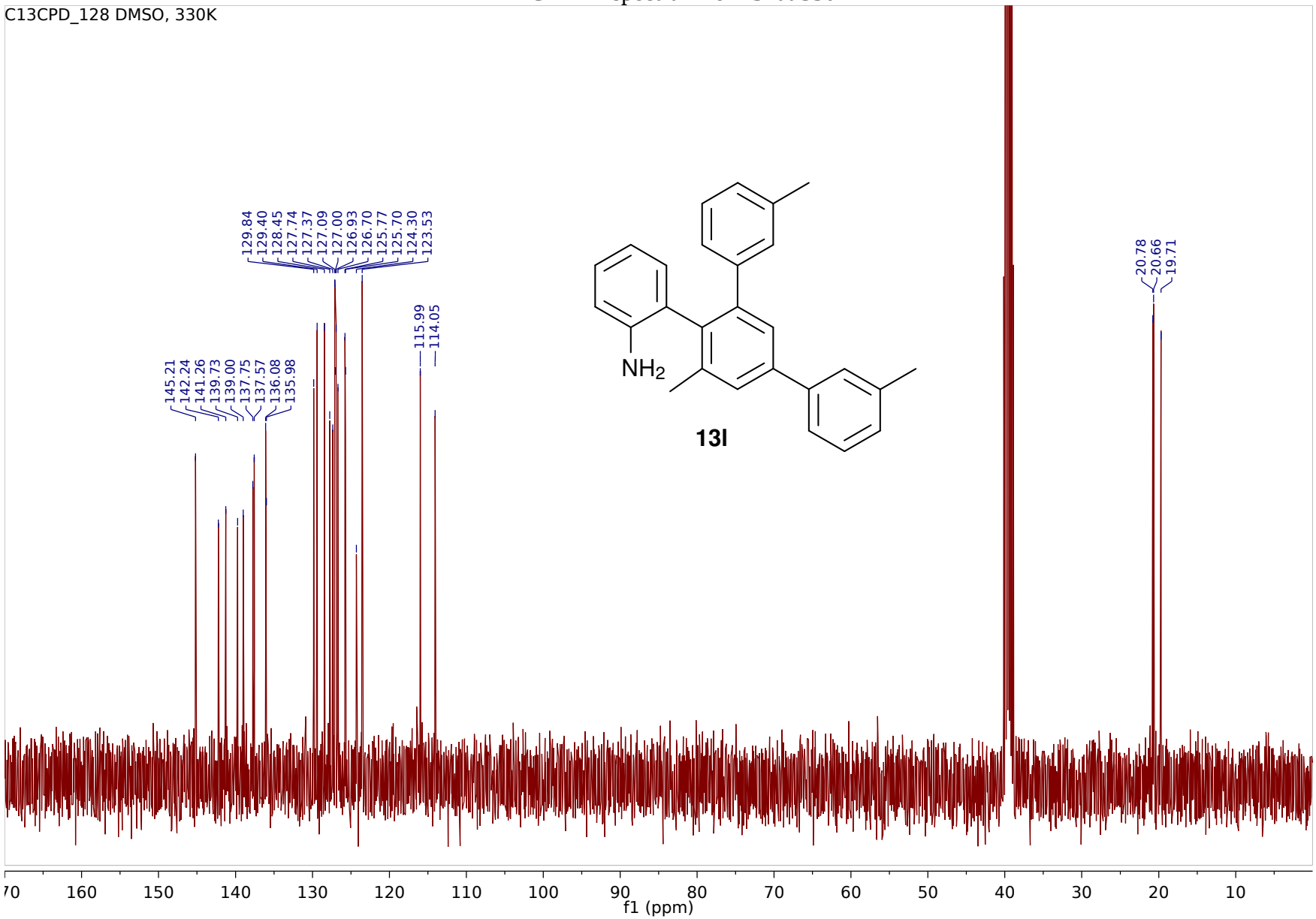
^{13}C NMR spectrum for **13k** at 320K



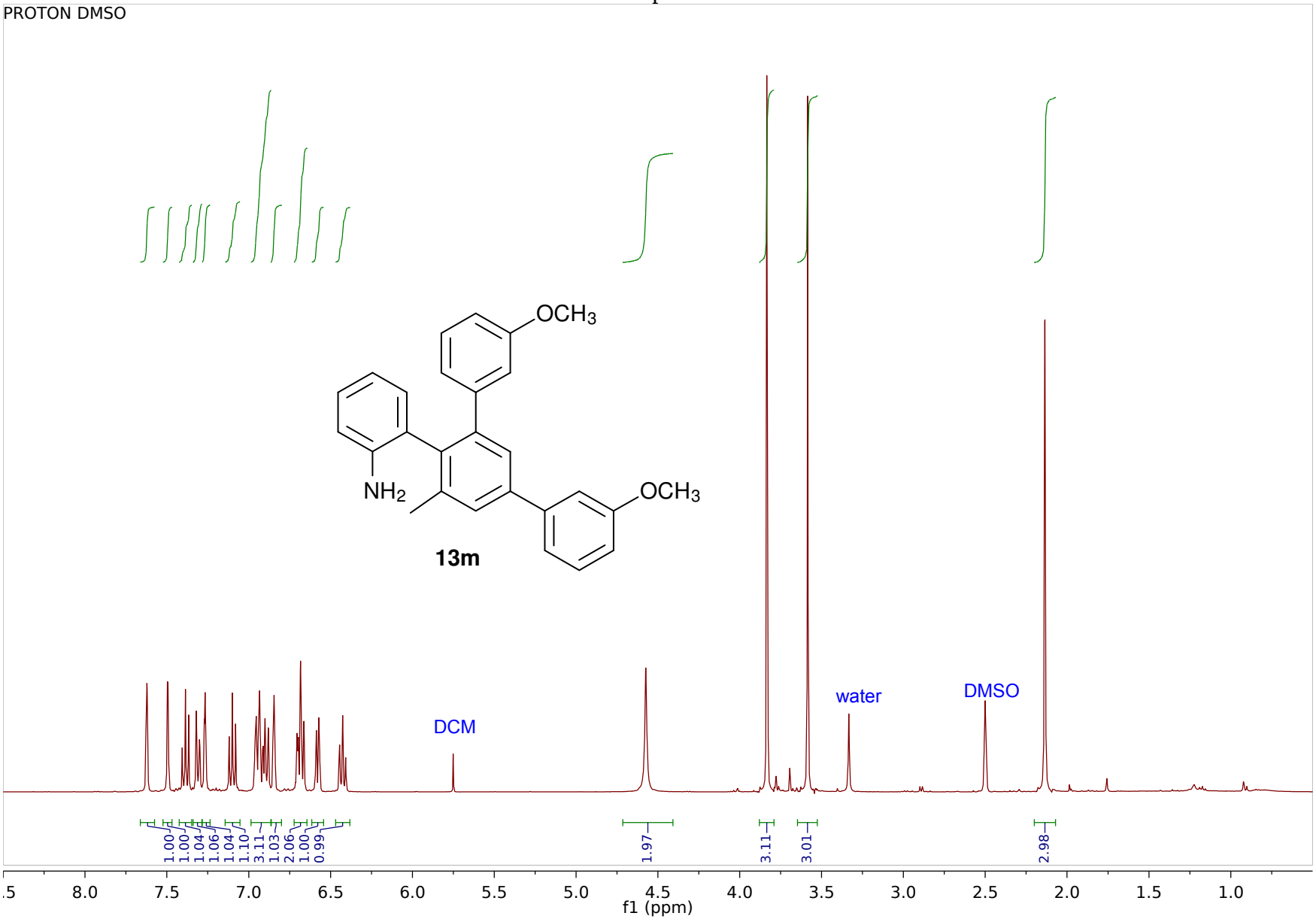
^{1}H NMR spectrum for **13l**



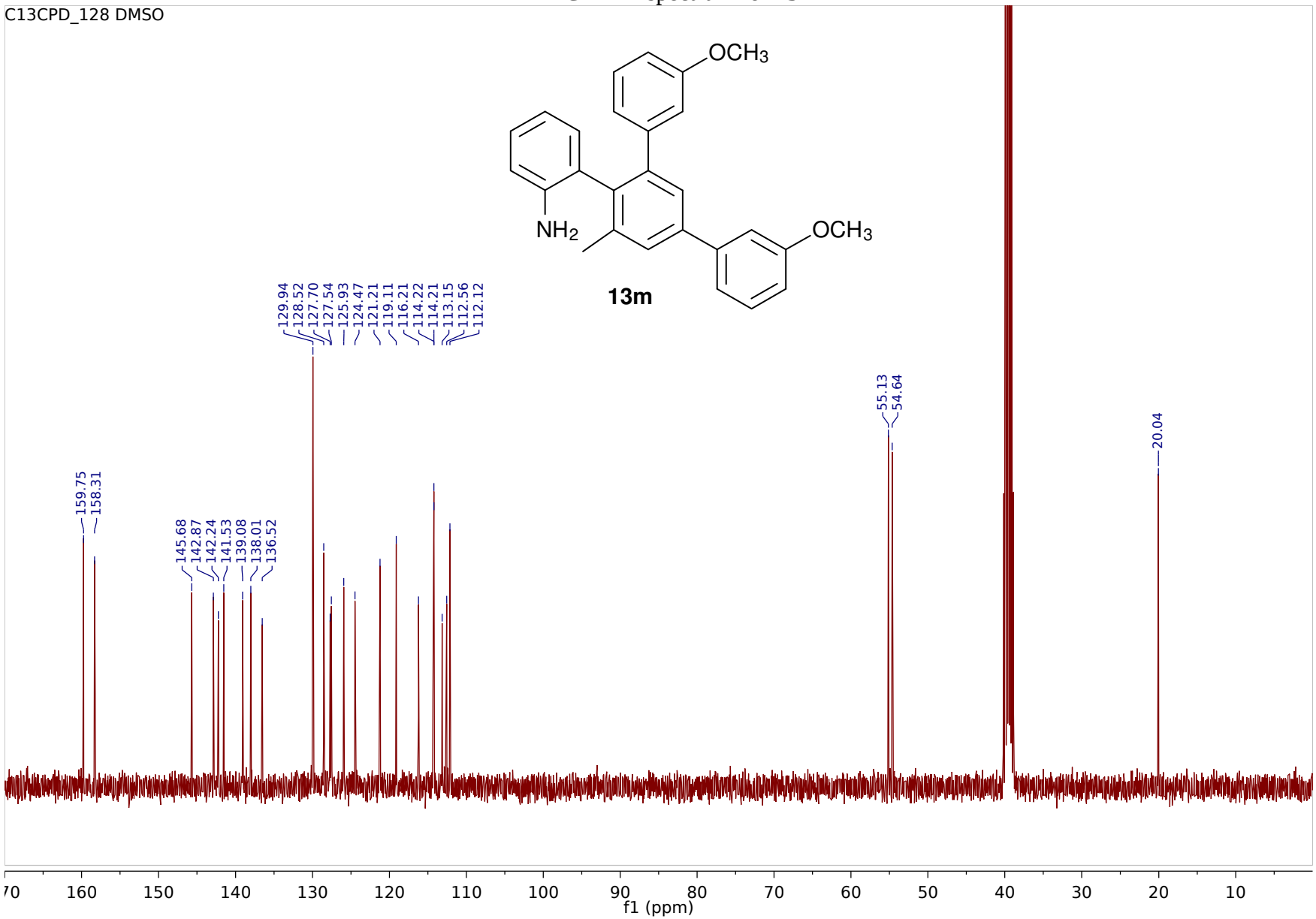
^{13}C NMR spectrum for **13l** at 330K



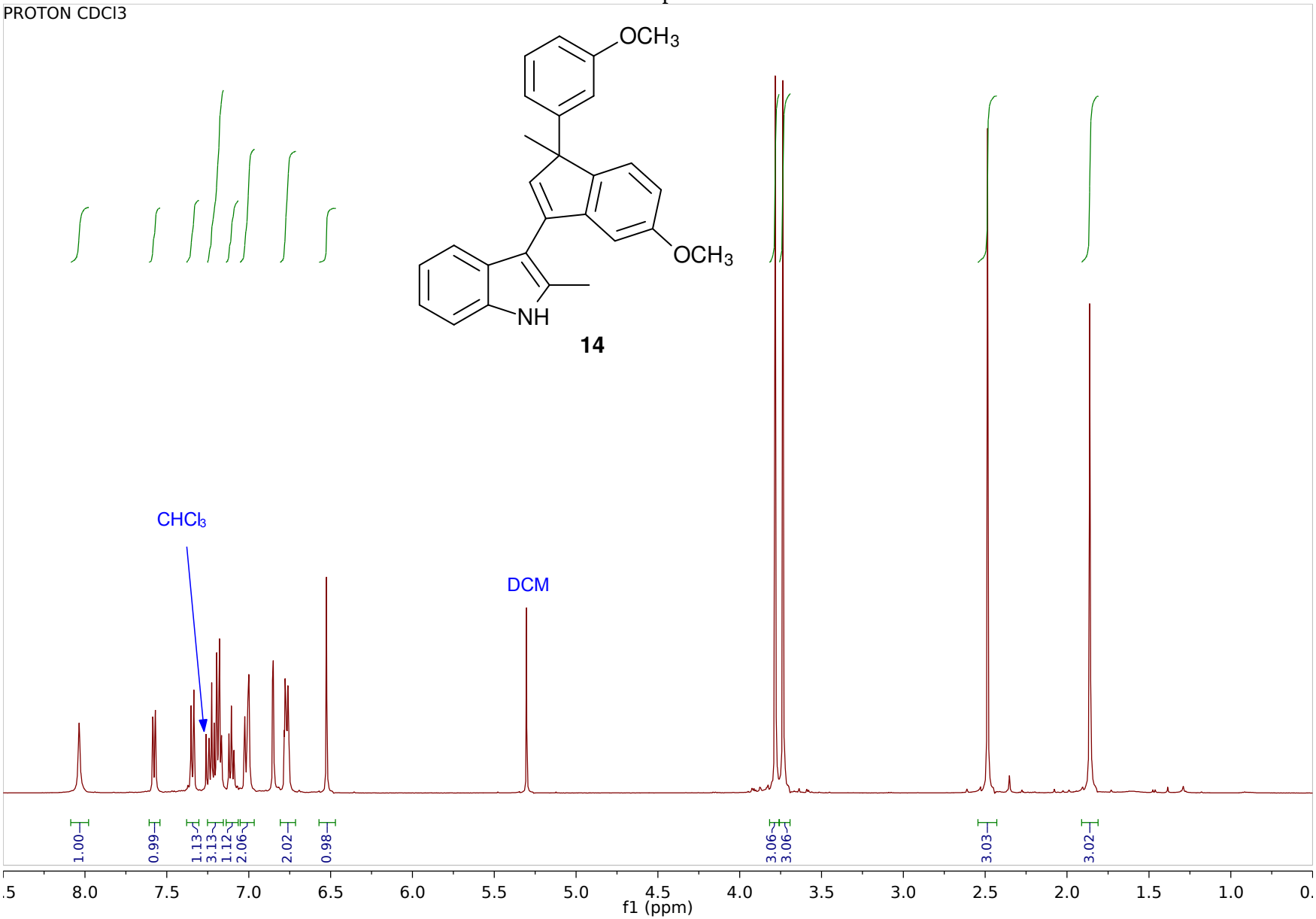
^{1}H NMR spectrum for **13m**



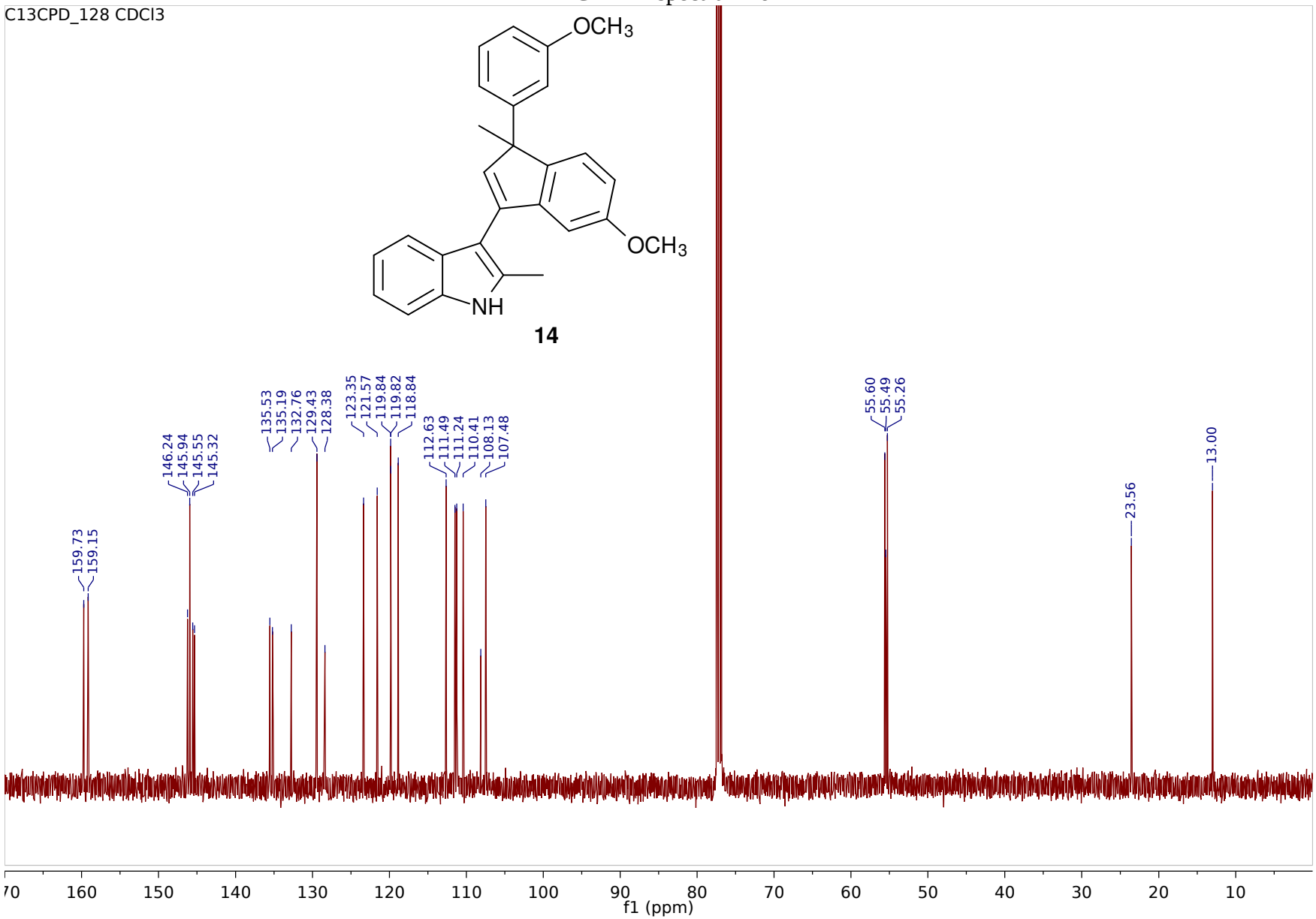
^{13}C NMR spectrum for **13m**



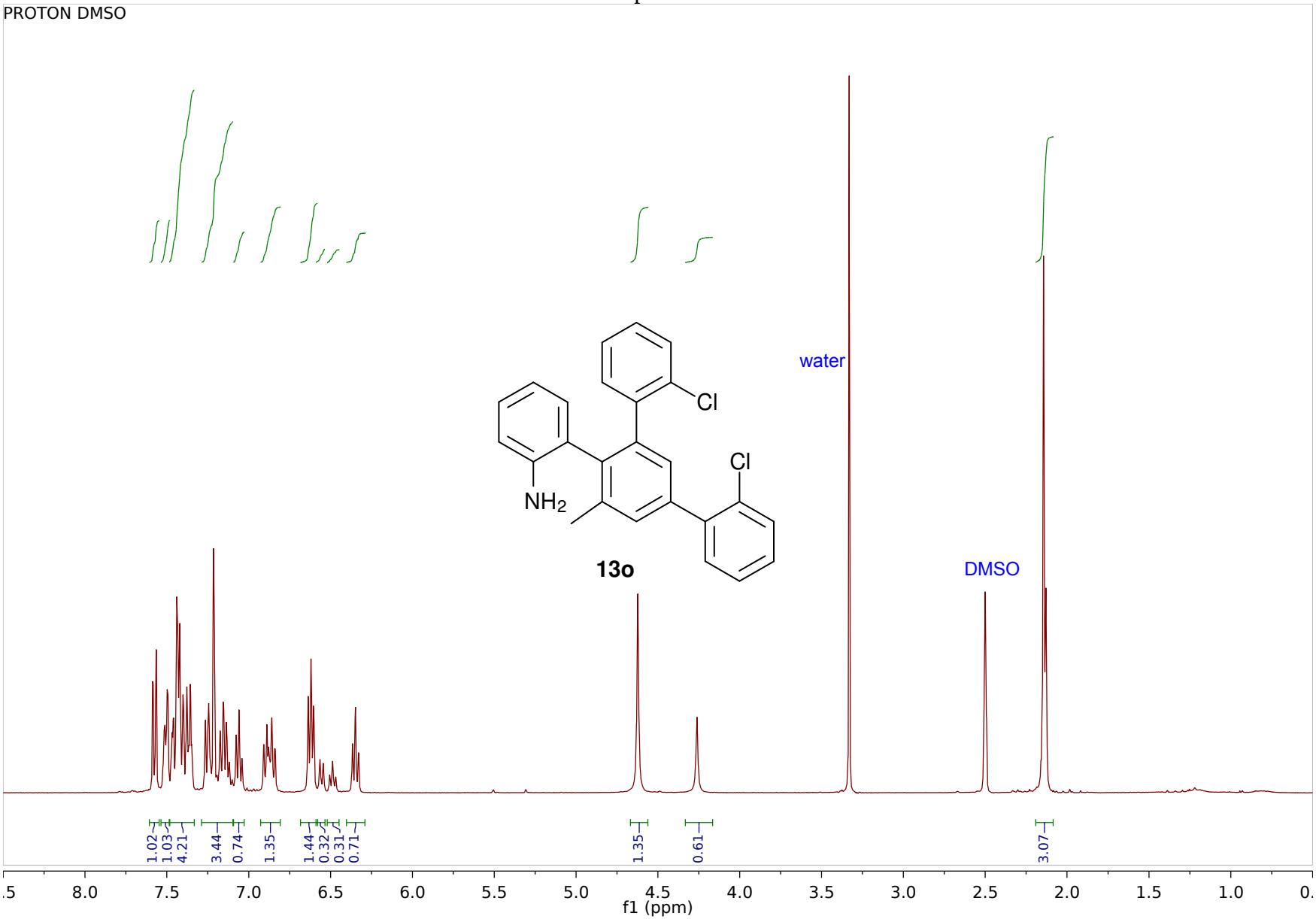
^{1}H NMR spectrum for **14**



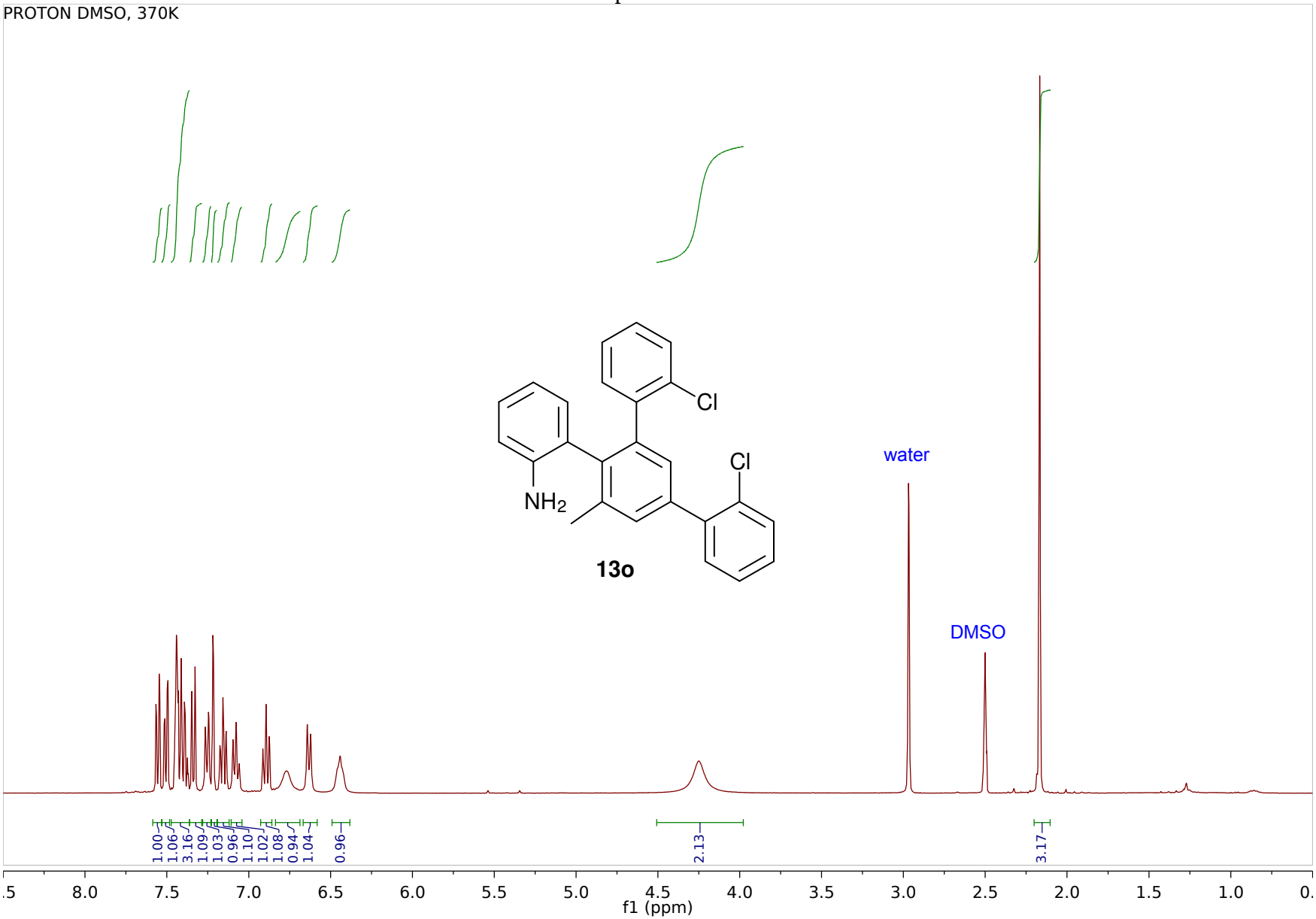
^{13}C NMR spectrum for **14**



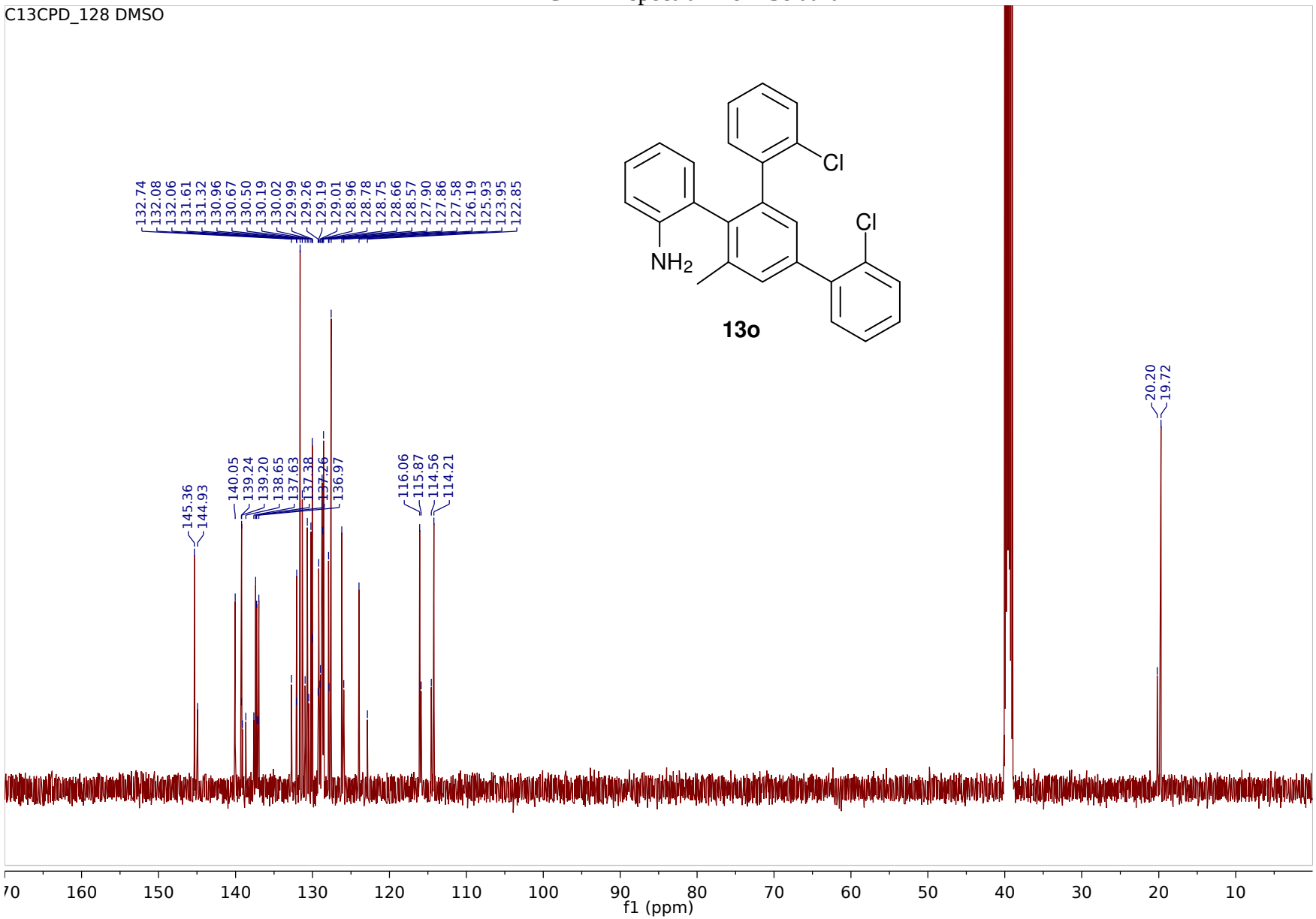
^{1}H NMR spectrum for **13o** at rt



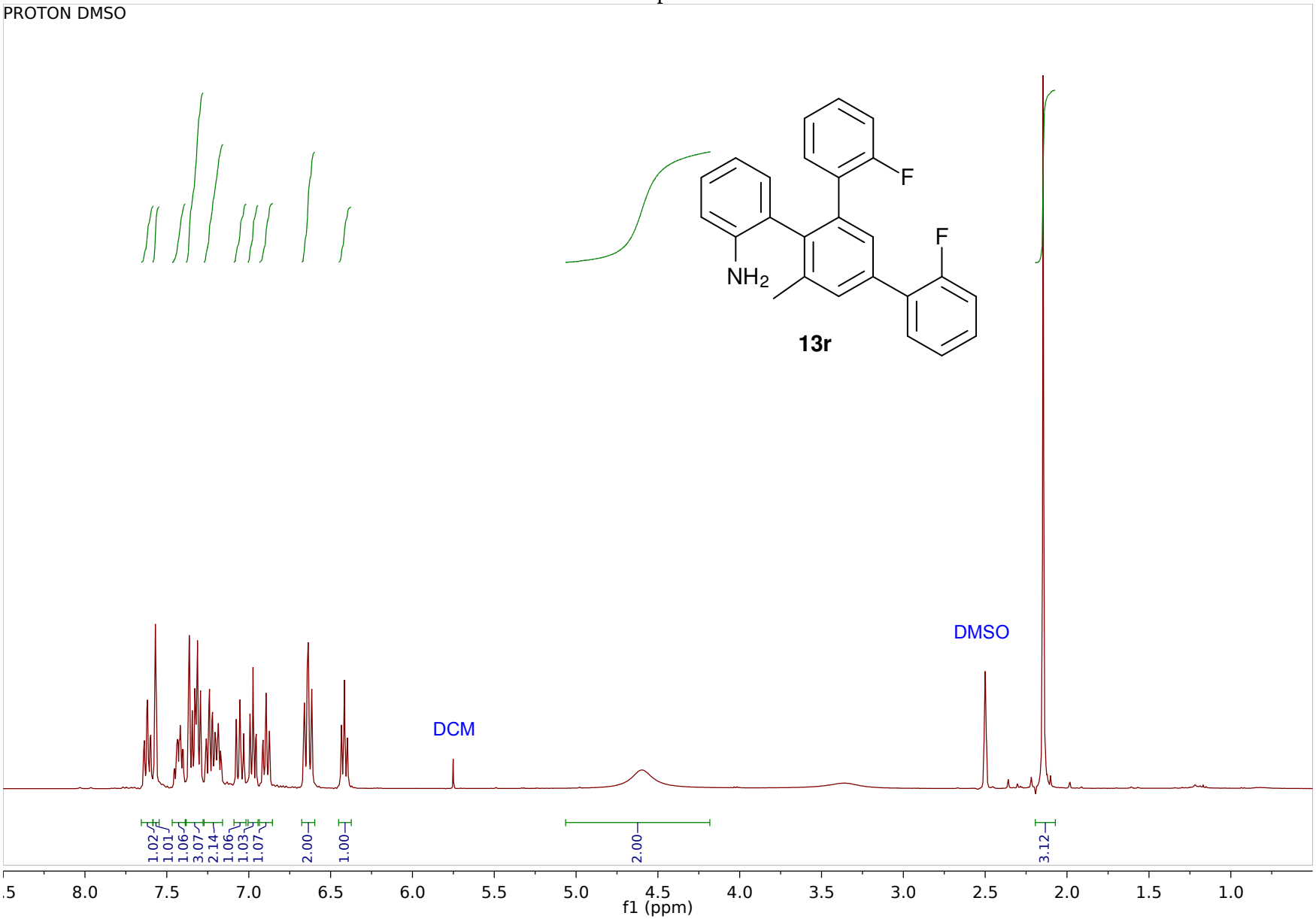
^{1}H NMR spectrum for **13o** at 370K



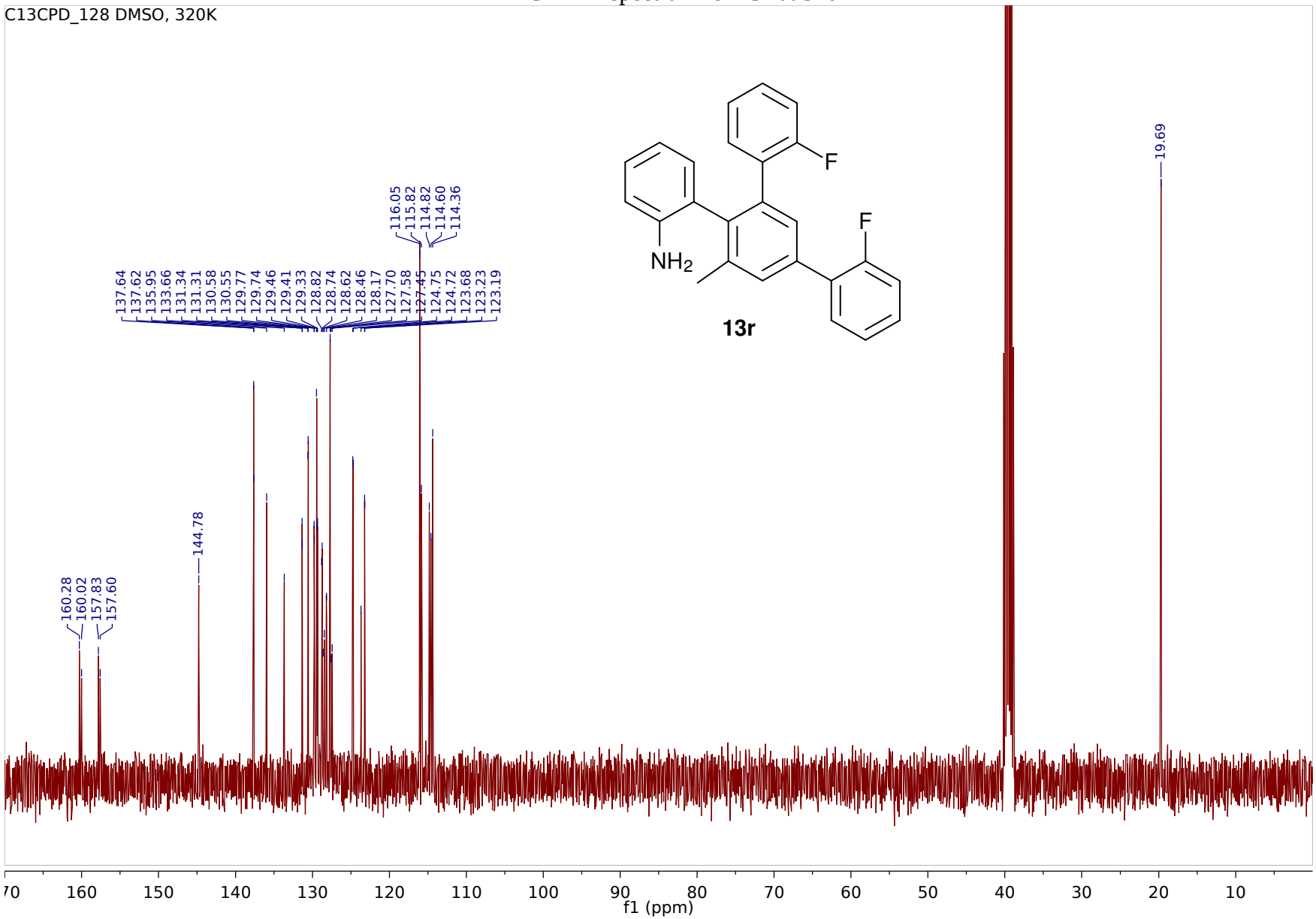
^{13}C NMR spectrum for **13o** at rt



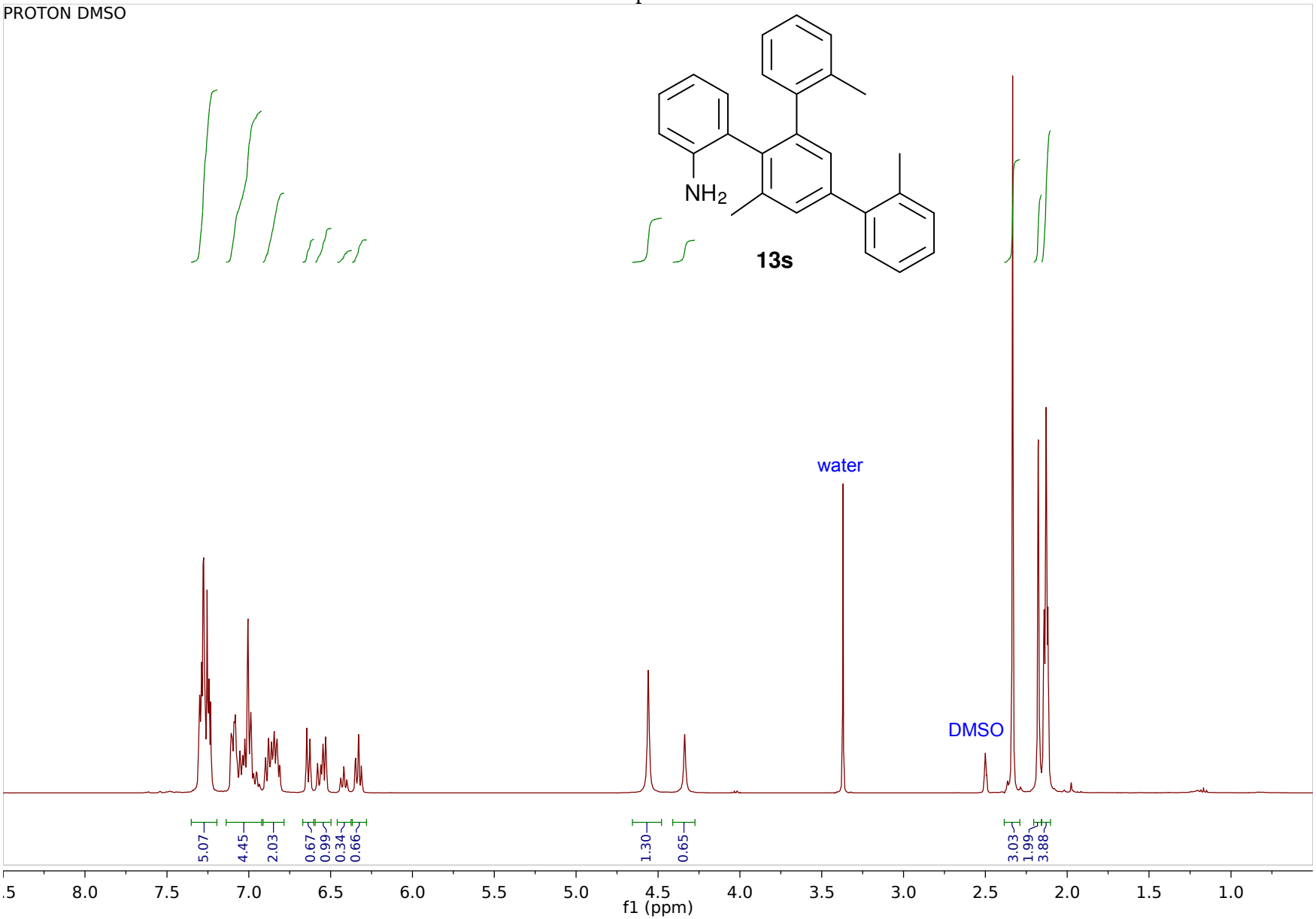
^{1}H NMR spectrum for **13r**



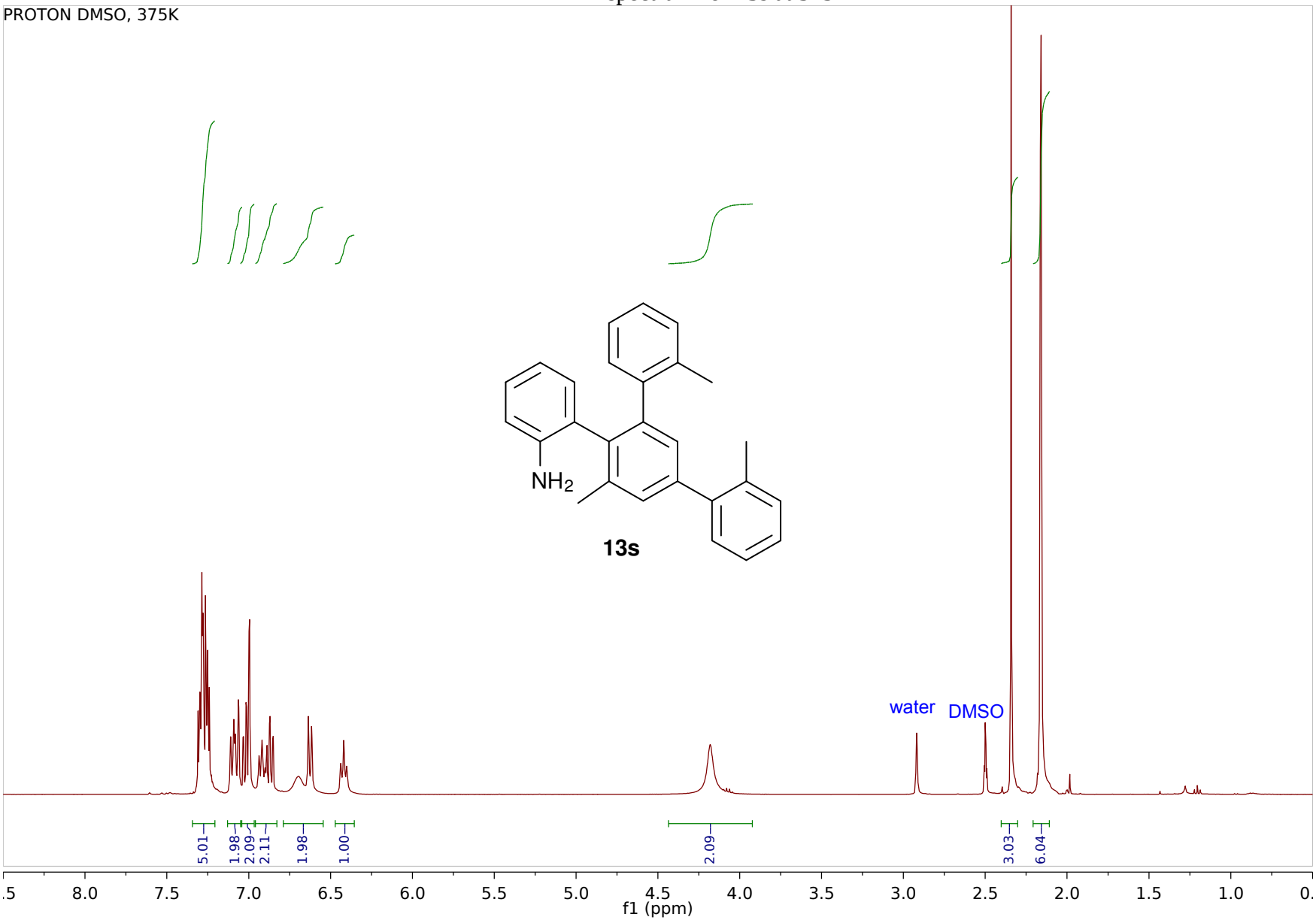
^{13}C NMR spectrum for **13r** at 320K



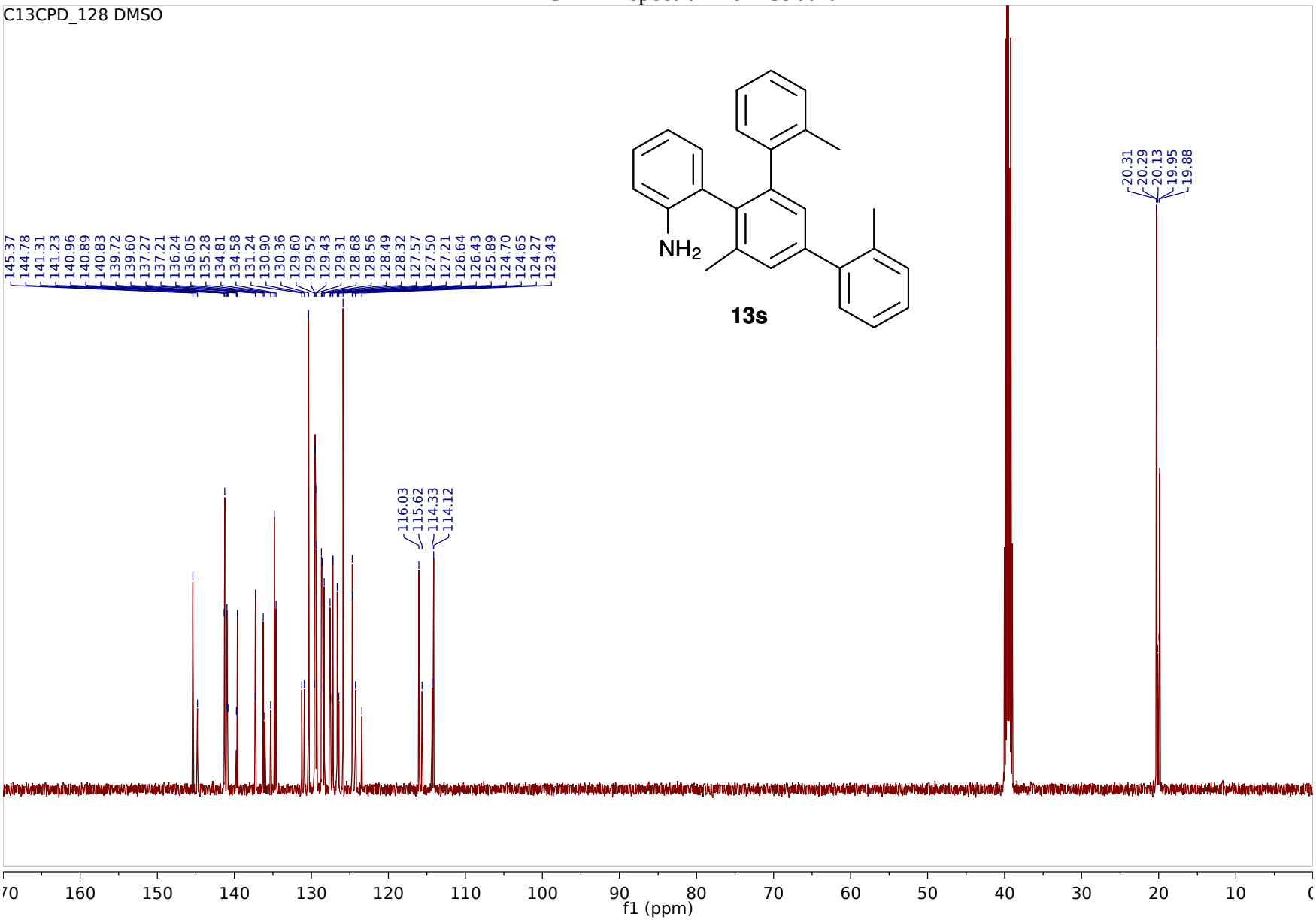
^{1}H NMR spectrum for **13s** at rt



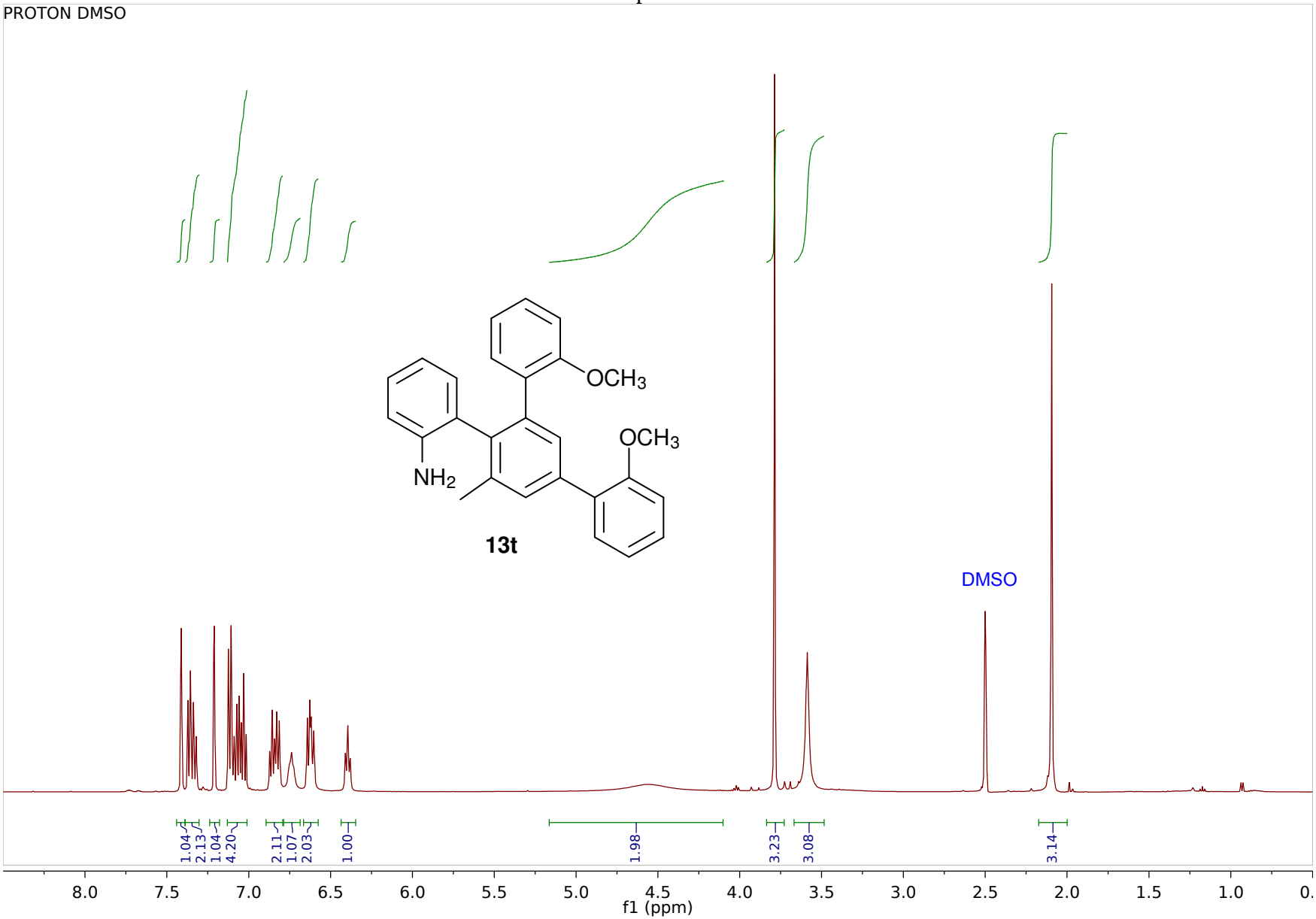
^{1}H NMR spectrum for **13s** at 375K



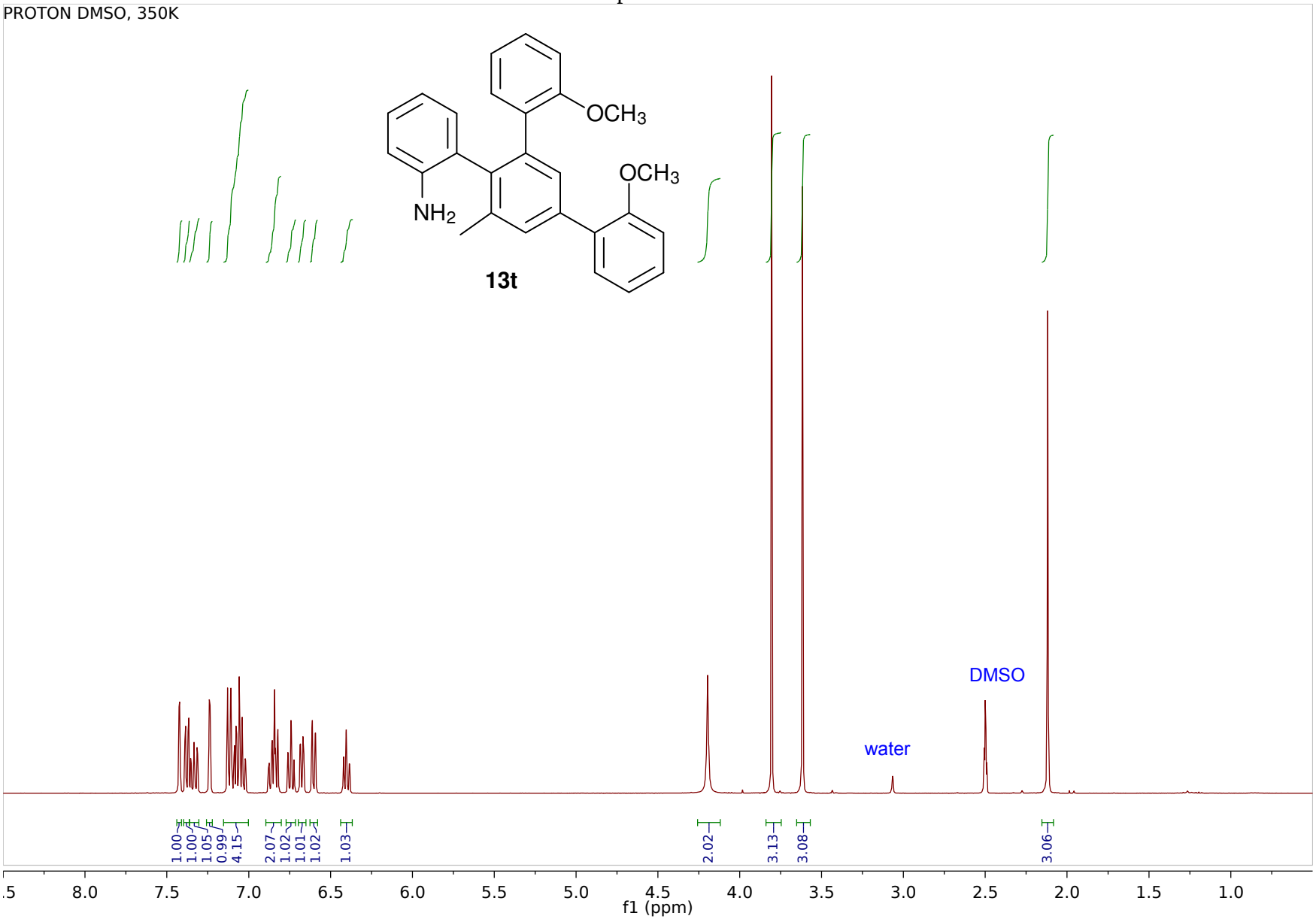
^{13}C NMR spectrum for **13s** at rt



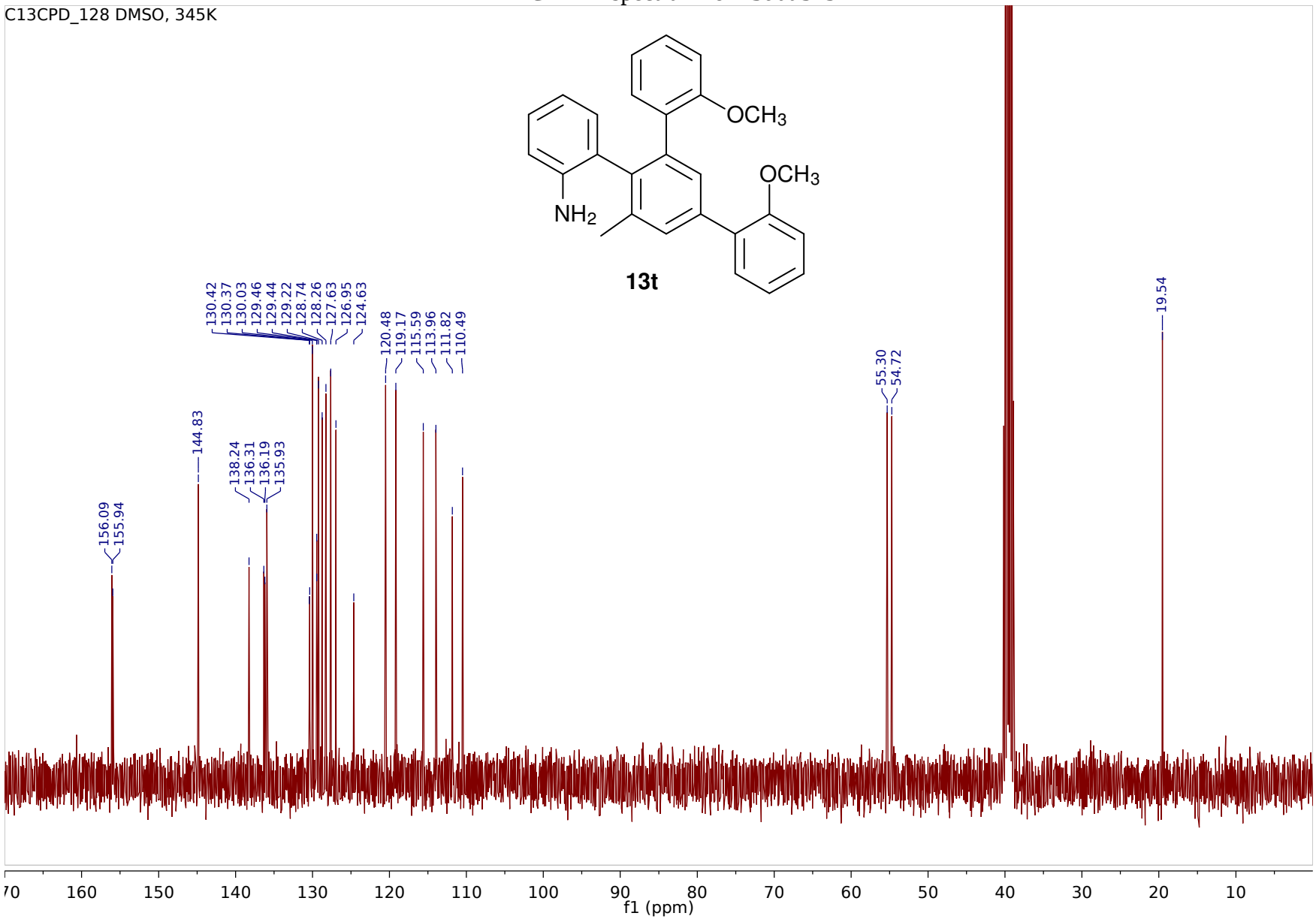
^{1}H NMR spectrum for **13t** at rt



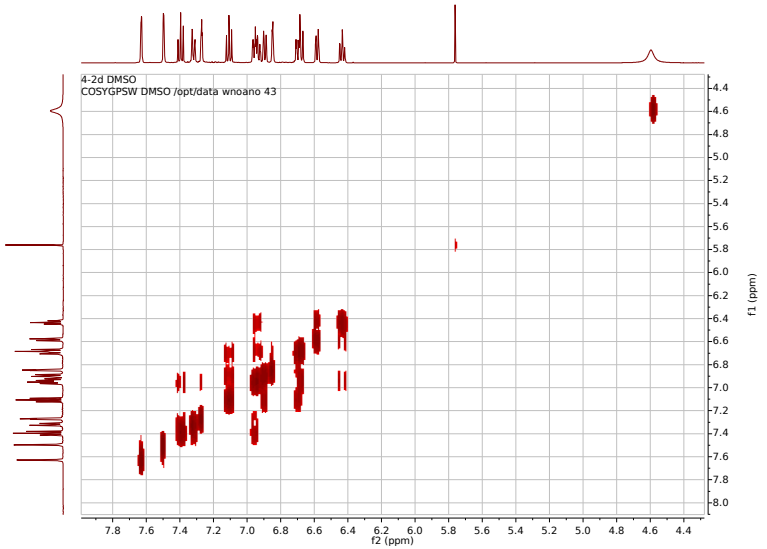
^{1}H NMR spectrum for **13t** at 350K

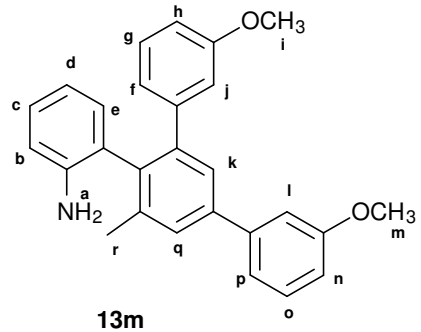


^{13}C NMR spectrum for **13t** at 345K

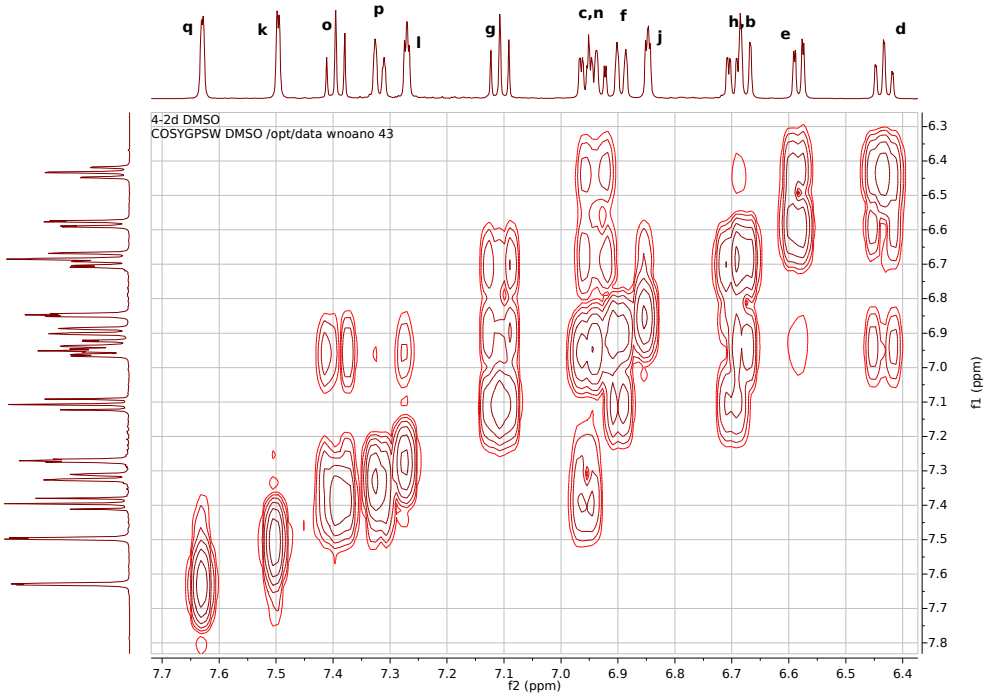


COSY spectrum for **13m**

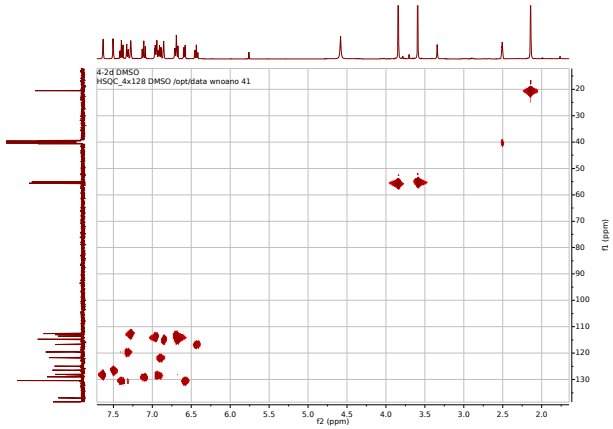


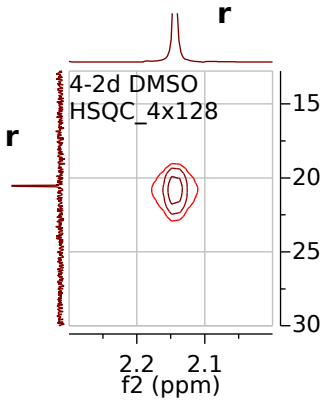


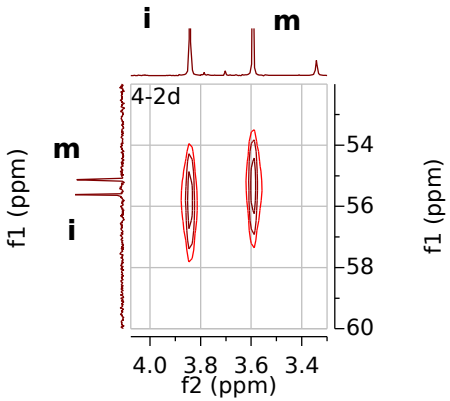
13m

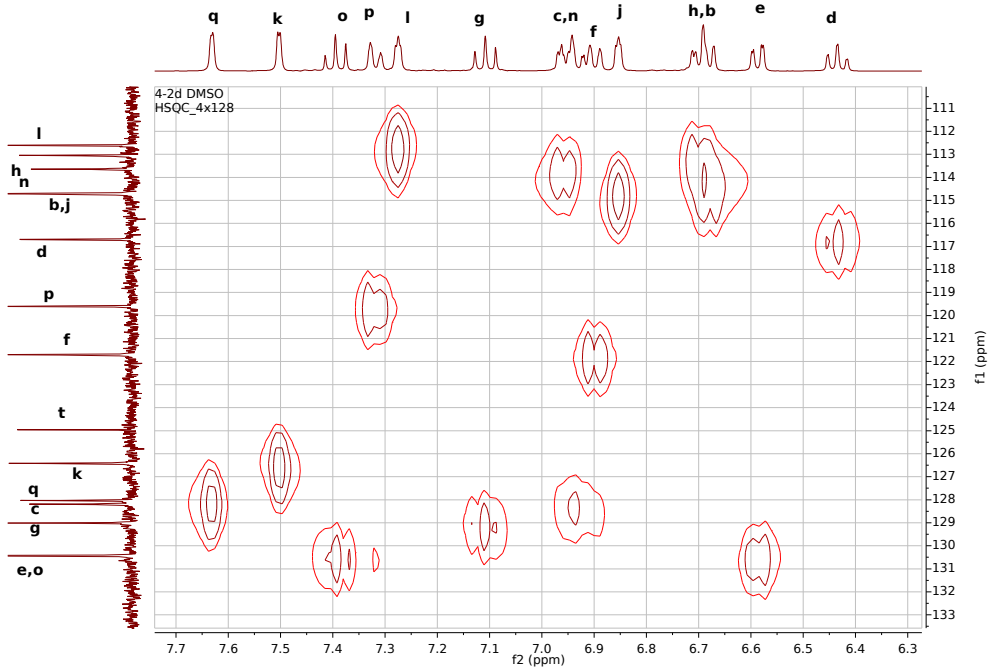


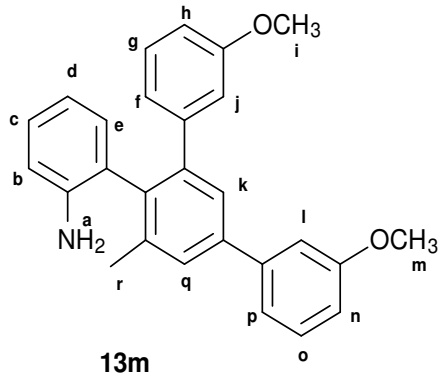
HSQC spectrum for **13m**





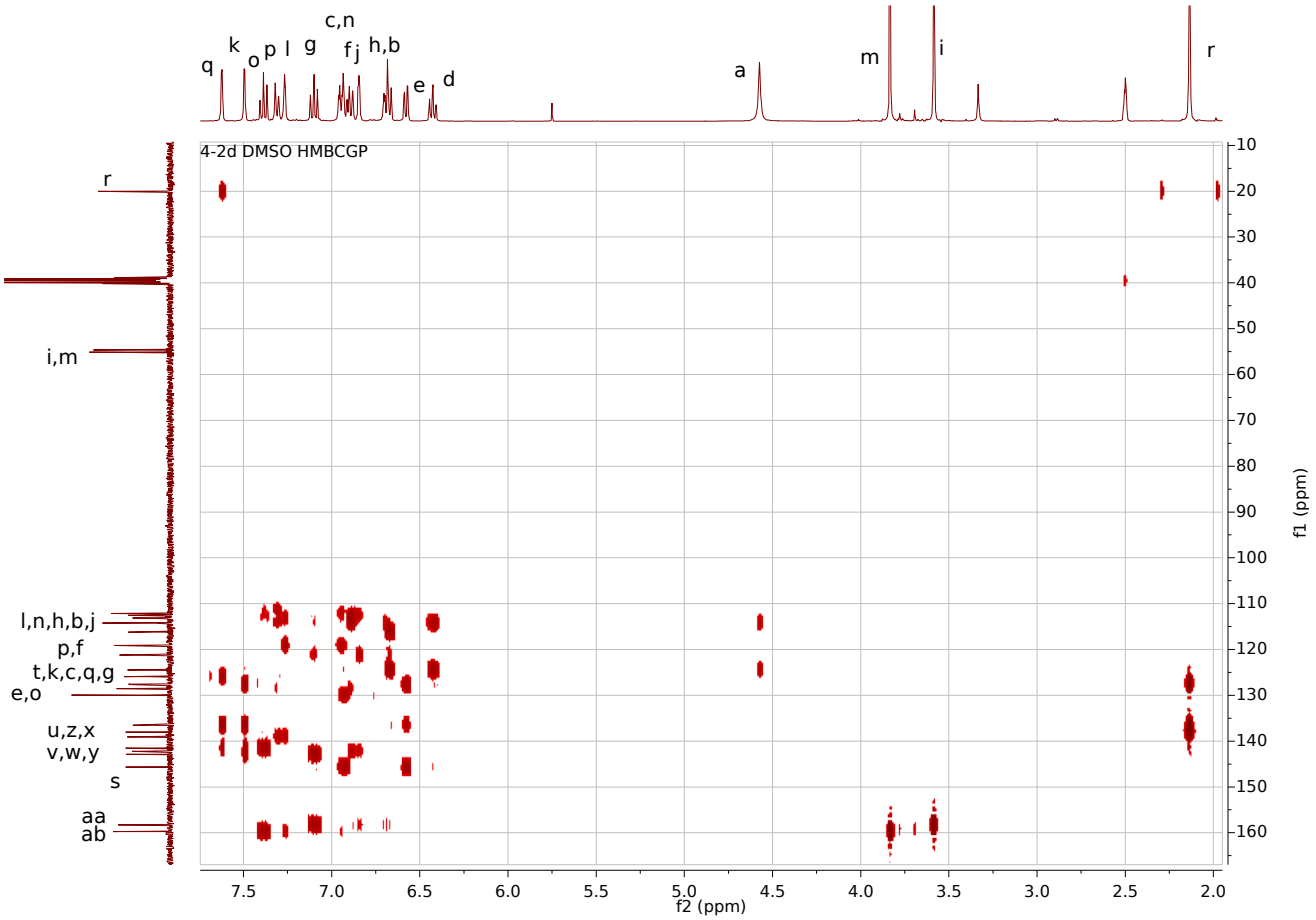


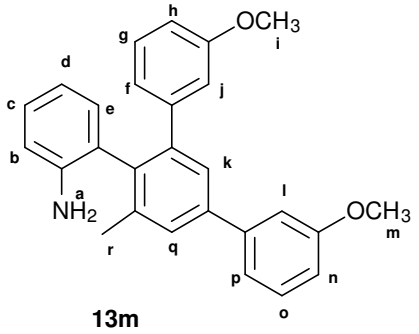




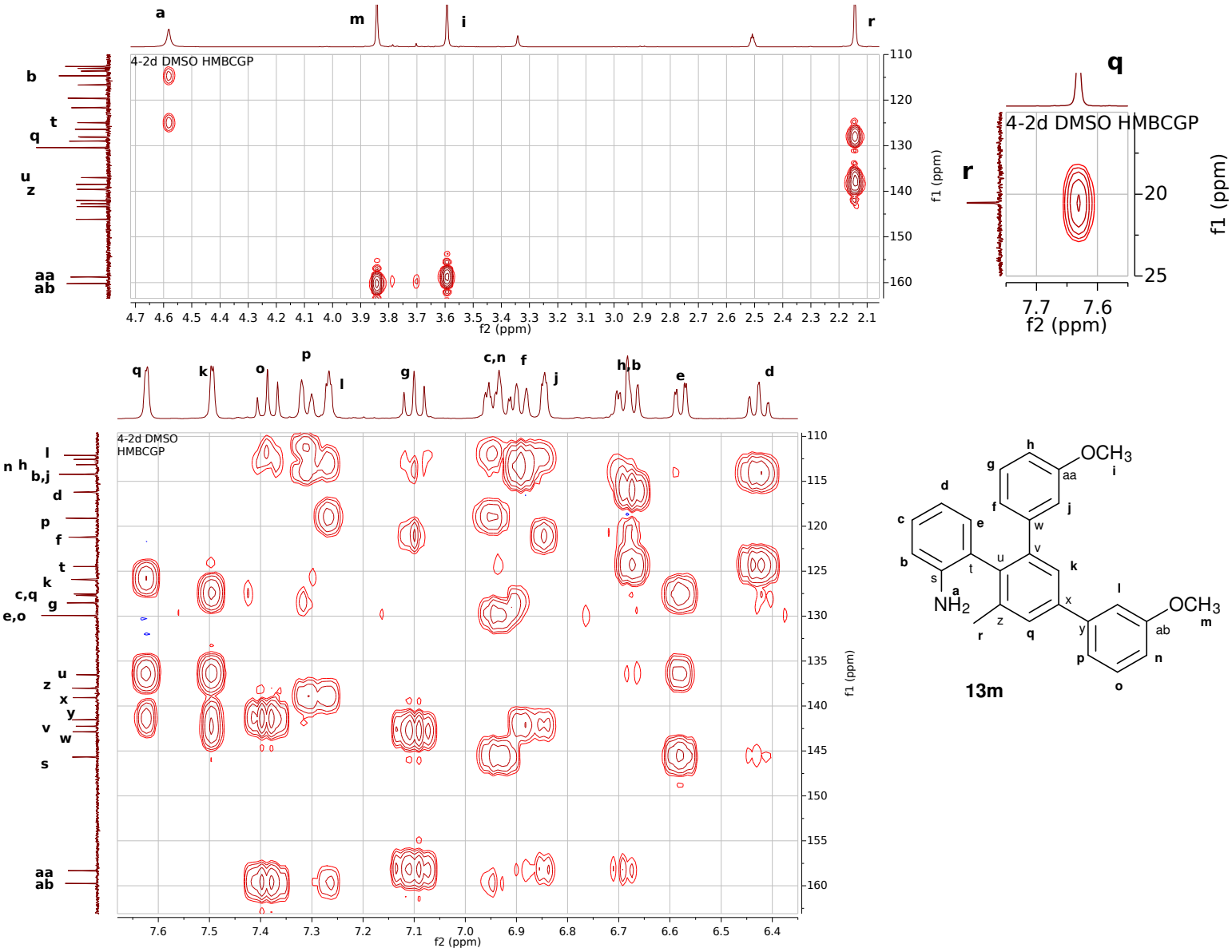
13m

HMBC spectrum for **13m**

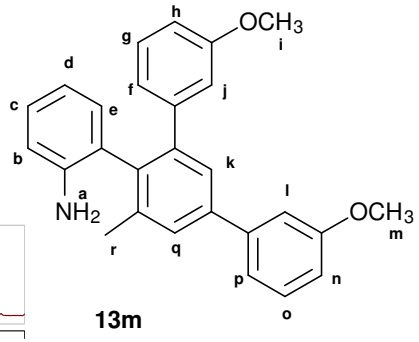


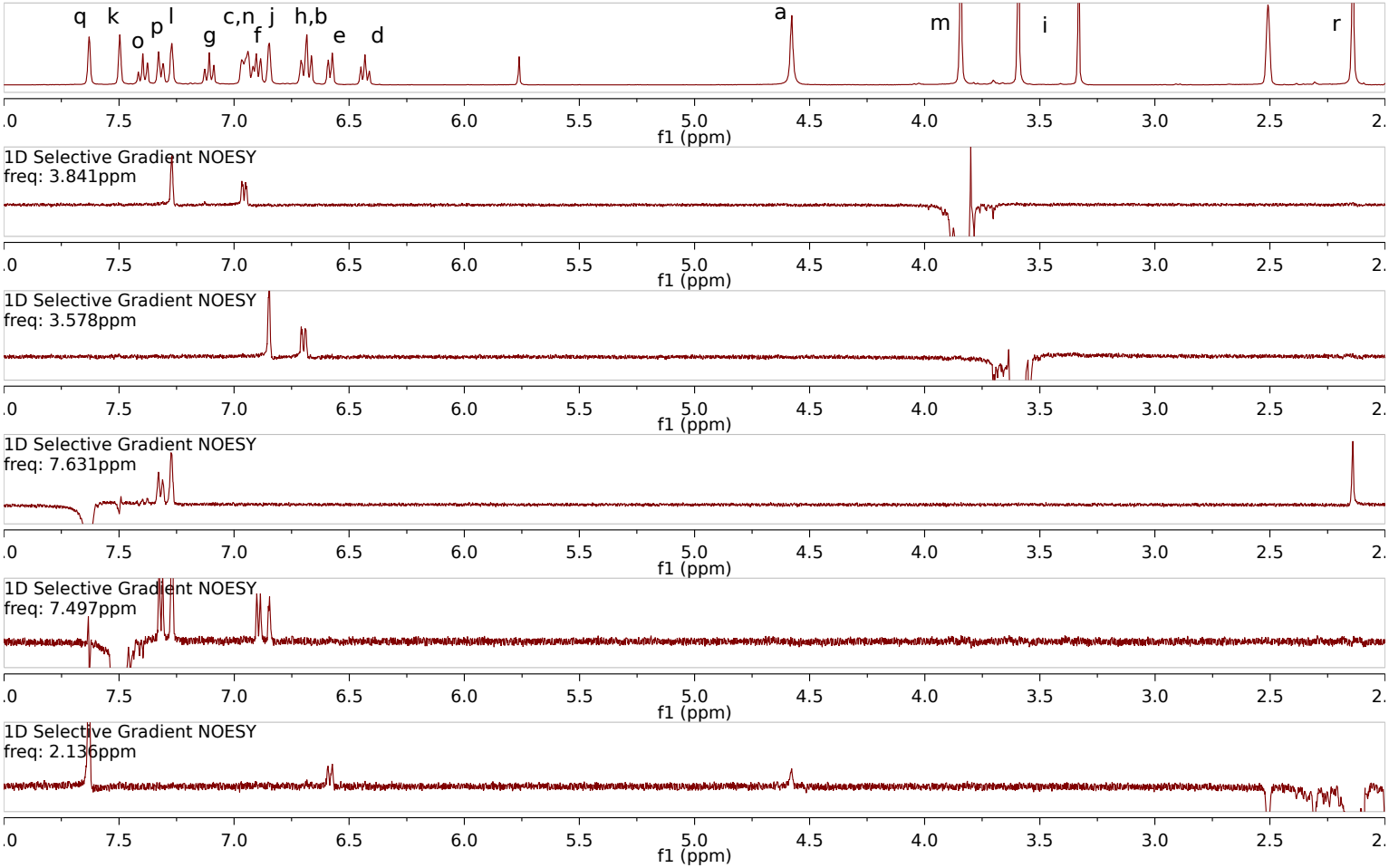


HMBC region expansions for **13m**

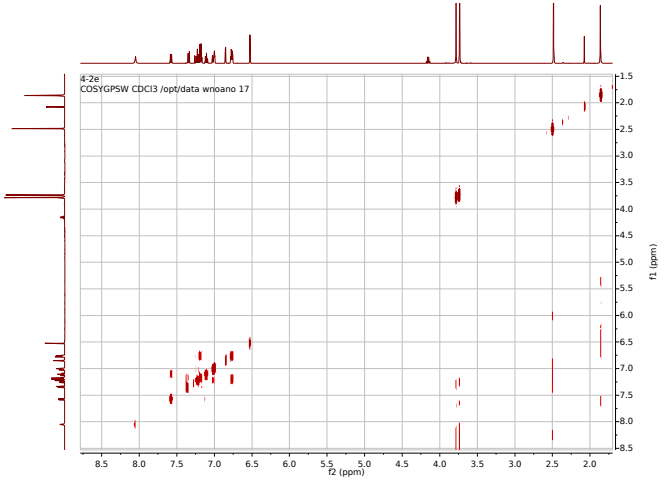


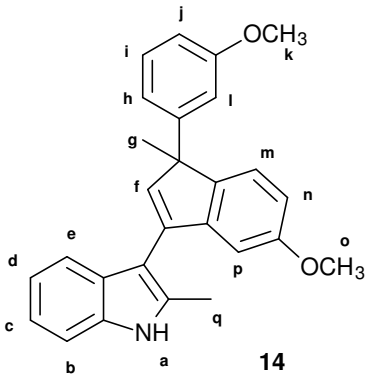
NOE spectra for **13m**

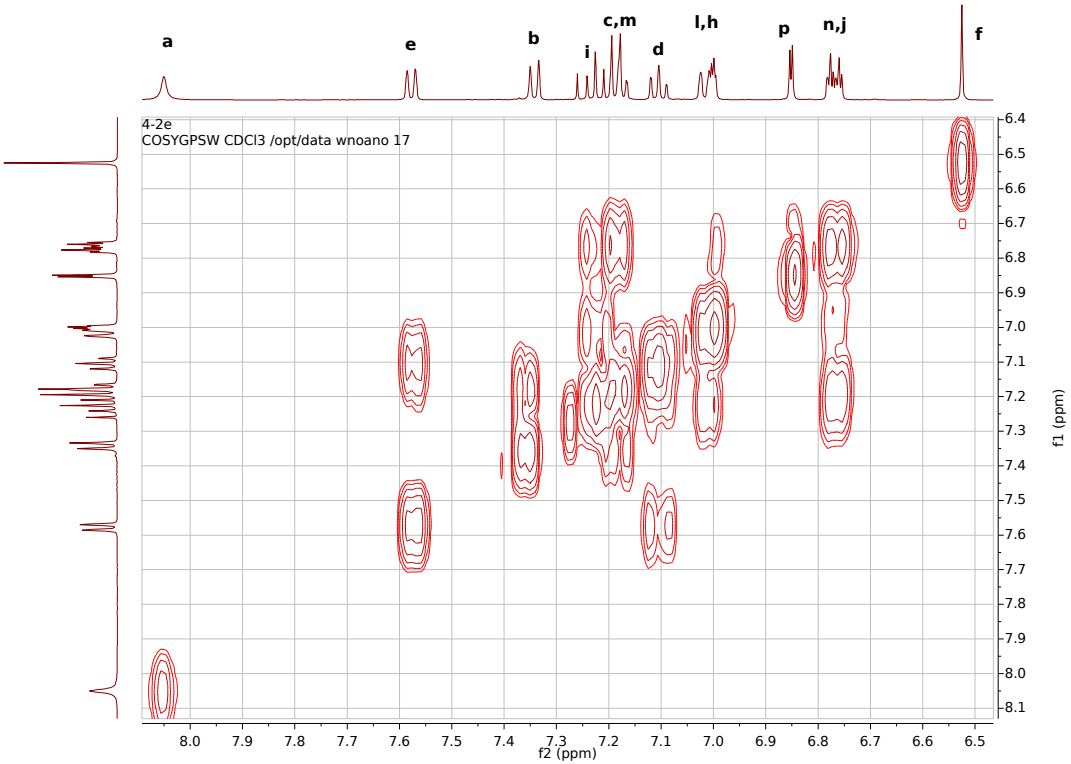




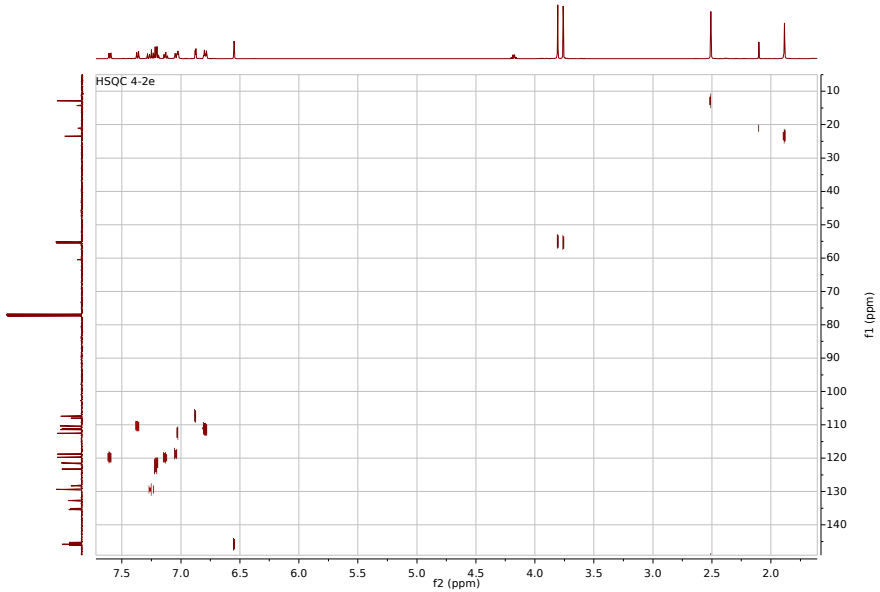
COSY spectrum for **14**

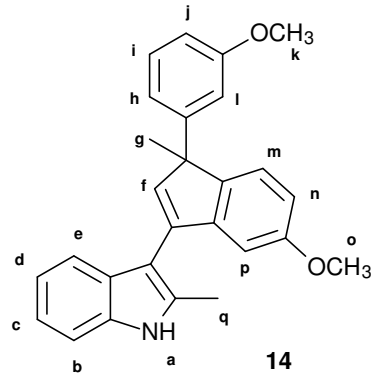




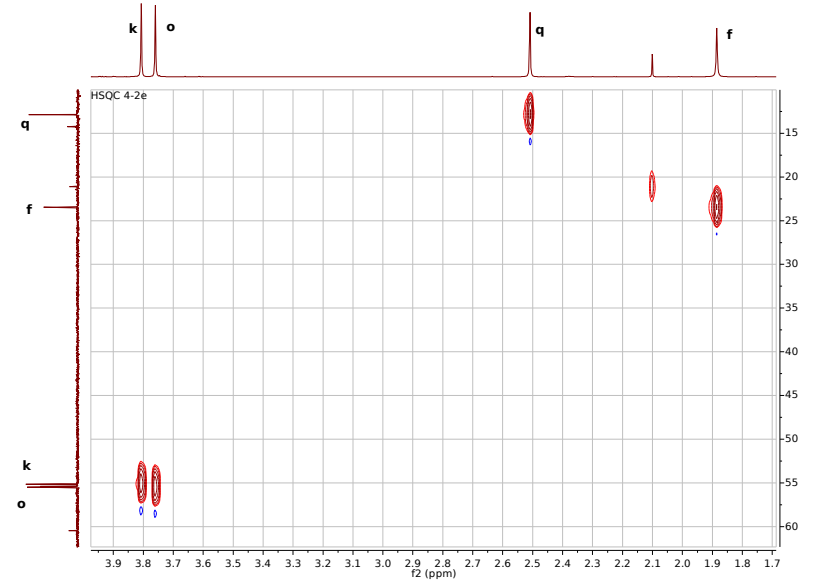


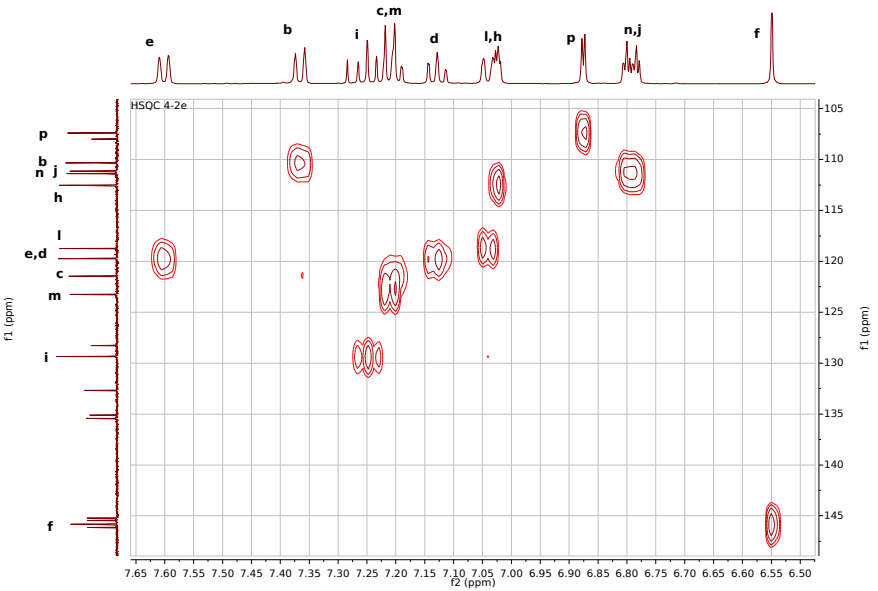
HSQC spectrum for **14**



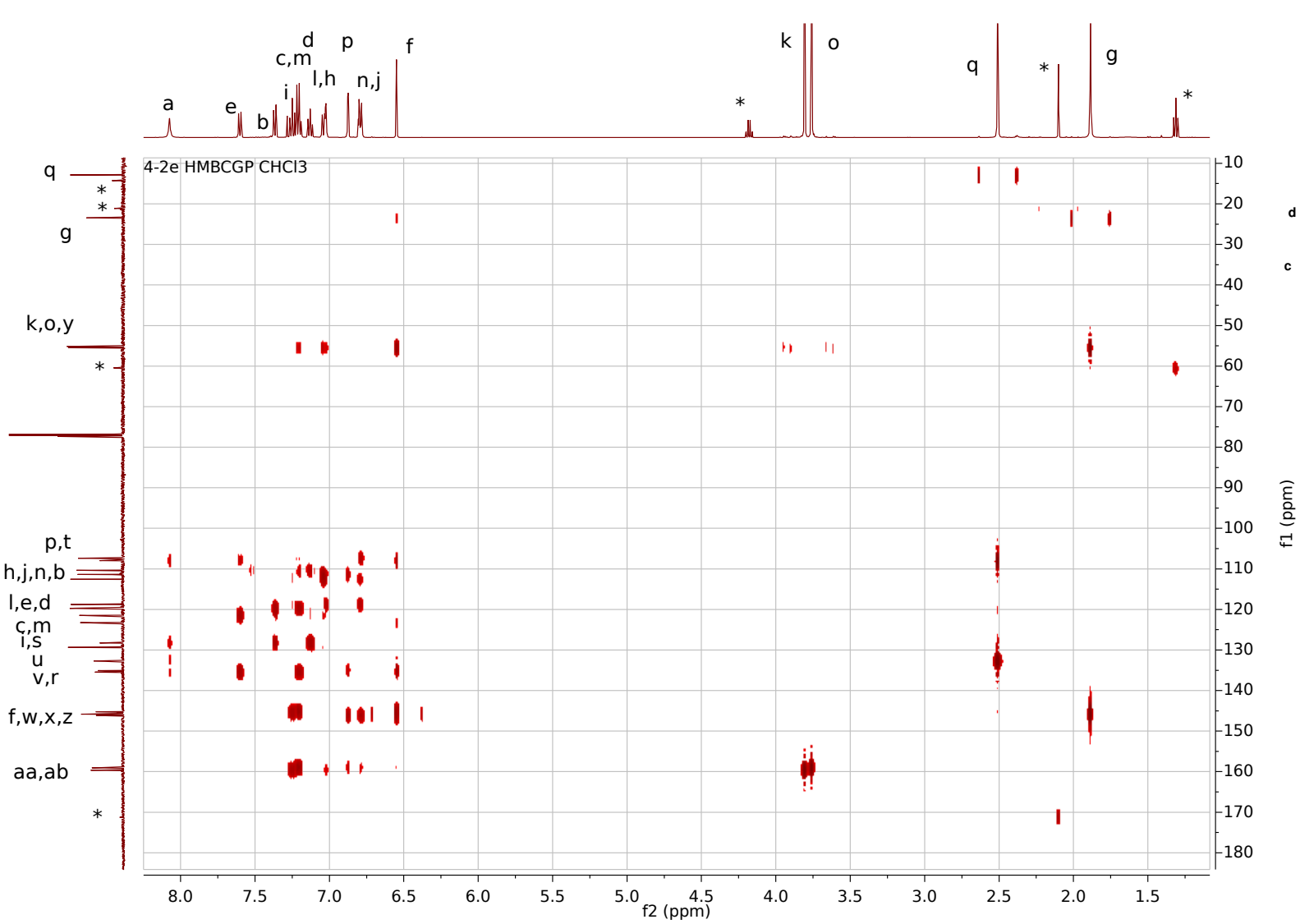


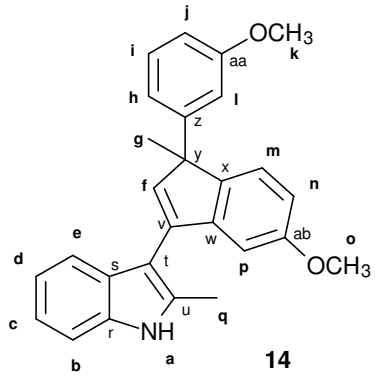
14





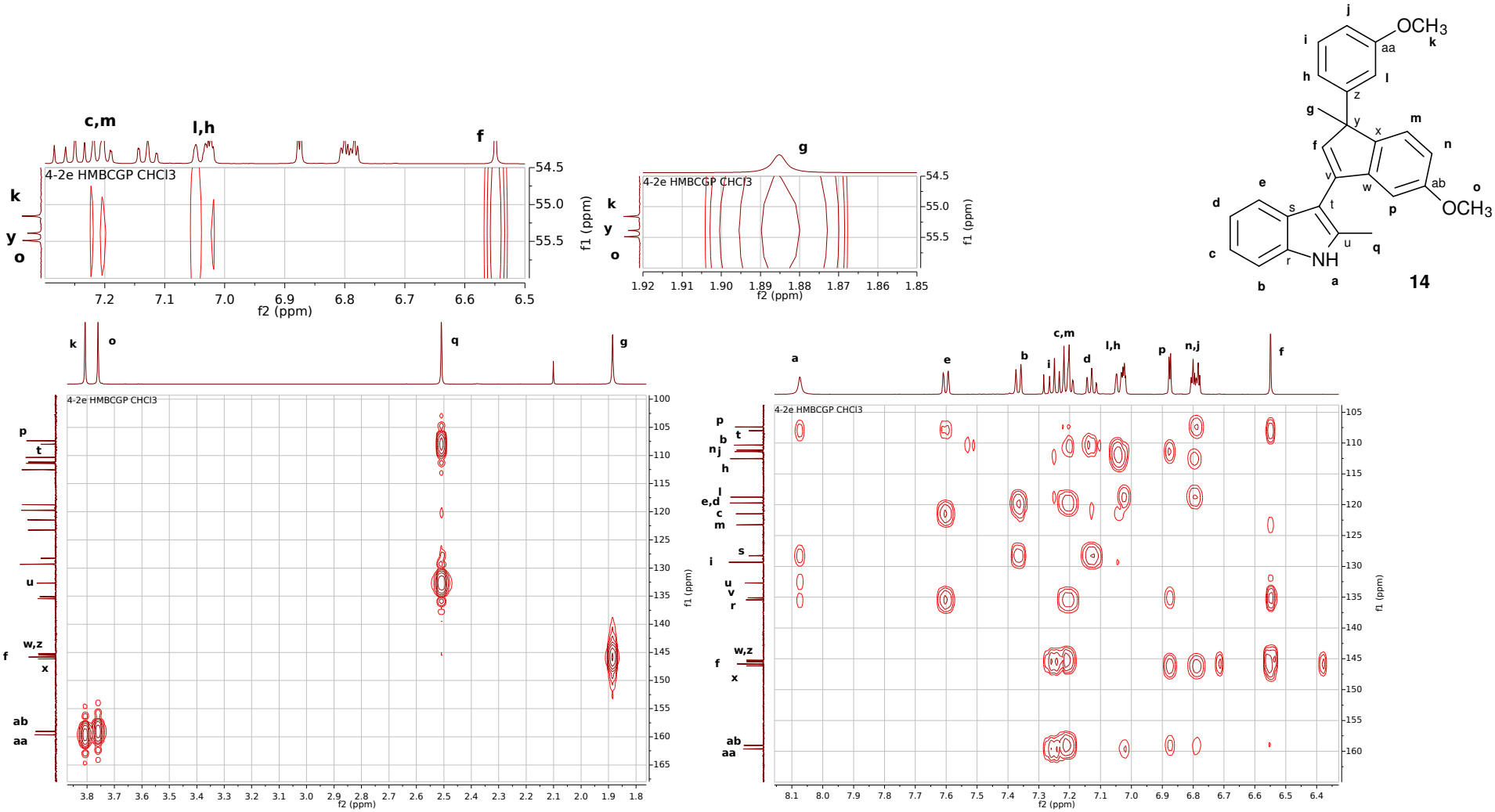
HMBC spectrum for **14**





* - ethyl acetate

HMBC region expansions for **14**



NOE spectra for **14**